Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

A Synthesis of Multisubstituted Vinylsilanes *via* Ynolates: Stereoselective Formation of β-Silyl-β-Lactones Followed by Decarboxylation

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General Procedures.

^{1}H NMR, ^{13}C NMR and ^{29}Si NMR were measured in $CDCl_3$ solution using JEOL JNM-AL-400 spectrometer (^{1}H NMR at 400 MHz, ^{13}C NMR at 100 MHz, ^{29}Si NMR at 79.5 MHz) as the referenced standard [^{1}H NMR at 0.00 ppm (TMS), ^{13}C NMR at 77.0 ppm ($CDCl_3$), ^{29}Si NMR at 0.00 ppm (TMS)]. Chemical sifts are reported in ppm. Peak multiplicities are used the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; sept, septet; m, multiplet; br, broadend. IR spectra were recorded on JASCO FT/IR-410 spectrometers. Mass spectra and high resolution mass spectra were obtained on a JMS-AMSUN200, JMS-SX102A, and Waters LCT Premier mass spectrometers. Elemental analyses were performed with Yanaco MT-3 CHN-Corder. Melting points were measured with a Yanaco MP-500D apparatus and Büchi 535 melting point apparatus and are uncorrected. Thin-layer chromatography (TLC) was performed on precoated plates (0.25 mm, silica gel Merck $60F_{245}$). Columun chromatography was performed on a silica gel (Kanto Chemical Co., Inc.). All reactions were performed in oven-dried glassware under positive pressure of argon or nitrogen, unless otherwise noted. Solution of alkyllithium reagents were transferred by syringe and were introduced into reaction vessels through rubber.

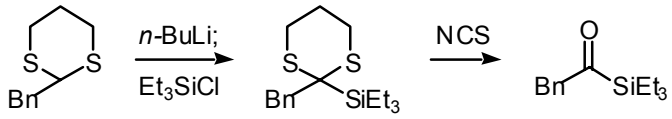
Materials.

α,α-Dibromo esters were synthesized according to the literature.[1)] Decarboxylation was performed using a silica gel (FUJI SILYSIA CHEMICAL BW-127ZH). Unless otherwise noted, reagents were obtained from commercial sources and without further purification. *tert*-Butyllithium and *n*-butyllithium, purchased from Kanto Chemical Co., Inc., were titrated with diphenylacetic acid. Tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl. Anhydrous dichloromethane (CH_2Cl_2) was purchased from Kanto Chemical Co., Inc. Hexamethylphosphoramide (HMPA) was distilled from calcium hydride and kept over 4 Å molecular sieves. Iodomethane was distilled from P_2O_5 and kept over copper.

[I] Synthesis of Acylsilanes

The following compounds have been described previously. Trimethyl(phenylacetyl)-silane (**2a**)[2] and 5-hexenoyltrimethylsilane (**2k**)[3] were prepared from silyl thioacetal according to the literatures.[4] Benzoyltrimethylsilane (**2h**)[5] and benzoyltriethylsilane (**2i**)[6] were prepared from 2-silyl-1,3-dithiane. Dimethylphenylpropenoylsilane (**2f**)[7] was prepared from silylated allenyl ether according to a literature procedure.

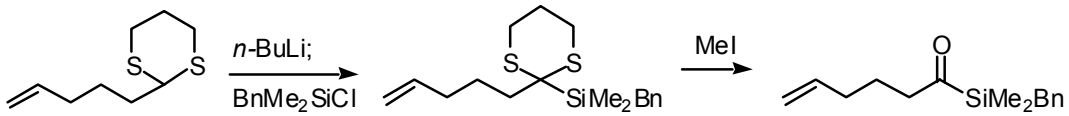
Triethyl(phenylacetyl)silane (2g)[8]



To a solution of 2-benzyl-1,3-dithiane[9] (2.1 g, 10 mmol) in THF (45 mL), cooled to -78 ˚C under argon, was added dropwise a solution of *n*-butyllithium (7.4 mL, 11 mmol, 1.48 M in hexane). After stirred for 2 hr at –20 ˚C, the reaction mixture was cooled to –78 ˚C and a solution of chlorotriethylsilane (2.0 mL, 12 mmol) in THF (5 mL) and HMPA (3.5 mL, 20 mmol) were added and then the reaction mixture was allowed to warm to room temperature. After 15 hr, water was added and the resulting mixture was extracted with ethyl acetate. The organic phase was washed with a saturated $NaHCO_3$ solution and brine, dried over $MgSO_4$, filtered and concentrated to afford a pale yellow oil, which was chromatographed over silica gel (5% ethyl acetate in hexane) to yield 3.15 g (97%) of 2-benzyl-2-triethylsilyl-1,3-dithiane as a pale yellow oil: ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.78 (q, *J* = 7.8 Hz, 6H), 1.04 (t, *J* = 7.8 Hz, 9H), 1.64-1.77 (m, 1H), 1.79-1.87 (m, 1H), 2.25 (ddd, *J* = 3.4, 4.4, 14.2 Hz, 2H), 2.49 (ddd, *J* = 2.9, 12.7, 14.2 Hz, 2H), 3.42 (s, 2H), 7.25-7.31 (m, 3H), 7.54-7.59 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 2.7 (t), 8.4 (q), 24.0 (t), 24.6 (t), 38.5 (s), 46.7 (t), 126.6 (d), 127.7 (d), 131.1 (d), 139.0 (s). IR (Neat): 1602, 1493 cm^{-1}. MS (EI) *m/z* 324 (M^+), 233 (100%). HRMS (EI) Calcd for $C_{17}H_{28}S_2Si$ (M^+): 324.1402, found: 324.1388.

To a solution of *N*-chlorosuccinimide (5.0 g, 37.0 mmol) and silver nitrate (7.1 g, 41.6 mmol) in MeCN-H_2O (4:1, 200 mL) was added a solution of 2-benzyl-2-triethylsilyl-1,3-dithiane (3.0 g, 9.2 mmol) in MeCN (40 mL). After stirred for 10 min at room temperature, a saturated Na_2SO_3 solution (50 mL), a saturated Na_2CO_3 solution (50 mL), brine (50 mL), hexane-CH_2Cl_2 (200 mL) were sequentially added at 1 min intervals. After stirred for 30 min, the resulting mixture was filtered through celite and the filtrate was extracted with hexane-CH_2Cl_2. The organic phase was washed with brine, dried over $MgSO_4$, filtered and concentrated to afford a yellow oil, which was chromatographed over silica gel (3% ethyl acetate in hexane) to yield 1.34 g (62%) of triethyl(phenylacetyl)silane as a yellow oil. Purification by Kügelrohr distillation (140-150 ˚C/ 1.5 mmHg) afforded a pale yellow oil: ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.67 (q, *J* = 7.8 Hz, 6H), 0.915 (t, *J* = 7.8 Hz, 9H), 3.83 (s, 2H), 7.09-7.14 (m, 2H), 7.21-7.33 (m, 3H). IR (Neat): 1649, 1635, 723, 700 cm^{-1}. MS (EI) *m/z* 234 (M^+), 206 (M^+-Et), 59 (100%).

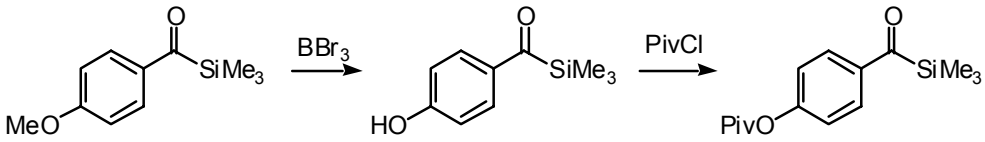
Benzyl(5-hexenoyl)dimethylsilane (2l)



To a solution of 2-(4'-pentenyl)-1,3-dithiane[10] (1.88 g, 10 mmol) in THF (45 mL), cooled to -40 ˚C under argon, was added dropwise a solution of *n*-butyllithium (4.3 mL, 11 mmol, 2.55 M in hexane). After stirred for 2 hr at –20 ˚C, a solution of chloro(benzyl)dimethylsilane (1.8 mL, 10 mmol) in THF (5 mL) was added and then the reaction mixture was allowed to warm to room temperature. After 5 hr, water was added and the resulting mixture was extracted with ethyl acetate. The organic phase was washed with a saturated $NaHCO_3$ solution and brine, dried over $MgSO_4$, filtered and concentrated to afford a yellow oil, which was chromatographed over silica gel (2% ethyl acetate in hexane) followed by Kügelrohr distillation (180-220 ˚C/ 1 mmHg) to yield 1.93 g (57%) of 2-(benzyldimethylsilyl)-2-(4'-pentenyl)-1,3-dithiane as a colorless oil: ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.10 (s, 6H), 1.57-1.67 (m, 2H), 1.91 (dtt, *J* = 3.4, 12.2, 12.2 Hz, 1H), 2.03-2.15 (m, 3H), 2.22-2.27 (m, 2H), 2.37 (s, 2H), 2.47 (ddd, *J* = 3.4, 4.2, 14.2 Hz, 2H), 3.05 (ddd, *J* = 2.7, 12.2, 14.2 Hz, 2H), 4.97-5.02 (m, 1H), 5.06 (ddt, *J* = 1.5, 2.0, 16.8 Hz, 1H), 5.83 (ddt, *J* = 6.6, 10.0, 16.8 Hz, 1H), 7.01-7.10 (m, 3H), 7.17-7.23 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: -4.6 (q), 23.1 (t), 23.5 (t), 25.1 (t), 27.0 (t), 34.1 (t), 37.0 (t), 38.8 (s), 115.0 (t), 124.1 (d), 128.1 (d), 128.5 (d), 138.3 (d), 139.2 (s). ^{29}Si-NMR (79.5 MHz, $CDCl_3$) δ: 7.02. IR (Neat): 1639, 1599, 824 cm^{-1}. MS (APCI) *m/z* 337 (M^++H). HRMS (APCI) Calcd for $C_{18}H_{29}S_2Si$ (M^++H): 337.1480, found: 337.1478.

To a solution of 2-(benzyldimethylsilyl)-2-(4'-pentenyl)-1,3-dithiane (337 mg, 1.0 mmol) and $NaHCO_3$ (840 mg, 10 mmol) in MeCN-H_2O (4:1, 10 mL) was added iodomethane (1.25 mL, 20 mmol). After stirred for 8 hr at 55 ˚C, water was added and the resulting mixture was extracted with ethyl acetate. The organic phase was washed with brine, dried over $MgSO_4$, filtered and concentrated to afford a yellow oil, which was chromatographed over silica gel (5% ethyl acetate in hexane) to yield 209 mg (85%) of **2l** as a pale yellow oil. Purification by Kügelrohr distillation (140-170 ˚C/ 0.5 mmHg) afforded a pale yellow oil: ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.18 (s, 6H), 1.52-1.61 (m, 2H), 1.94-2.02 (m, 2H), 2.25 (s, 2H), 2.48 (t, *J* = 7.3 Hz, 2H), 4.92-5.01 (m, 2H), 5.72 (ddt, *J* = 6.6, 10.0, 17.1 Hz, 1H), 6.96-7.00 (m, 2H), 7.05-7.11 (m, 1H). 7.18-7.24 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: -4.9 (q), 21.0 (t), 23.3 (t), 33.1 (t), 48.4 (t), 115.0 (t), 124.5 (d), 128.1 (d), 128.4 (d), 138.1 (d), 138.2 (s), 246.7 (s). ^{29}Si-NMR (79.5 MHz, $CDCl_3$) δ: -10.93. IR (Neat): 1642, 1600, 840 cm^{-1}. MS (APCI) *m/z* 269 (M^++Na), 247 (M^++H). HRMS (APCI) Calcd for $C_{15}H_{23}OSi$ (M^++H): 247.1518, found: 247.1507.

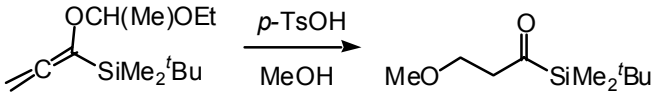
4-(Trimethylsilylcarbonyl)phenyl 2,2-dimethylpropionate (2j)



To a solution of 4-methoxybenzoyltrimethylsilane[11] (54 mg, 0.26 mmol) in CH_2Cl_2 (4 mL), cooled to 0 ˚C under argon, was added boron tribromide (0.25 mL, 2.6 mmol). After stirred for 1.5 hr at 0 ˚C, water was added and the resulting mixture was extracted with CH_2Cl_2 (×3). The organic phase was washed with a saturated $NaHCO_3$ solution and brine, dried over $MgSO_4$, filtered and concentrated to afford a yellow oil, which was chromatographed over silica gel (10% ethyl acetate in hexane) to yield 50 mg (98%) of 4-hydroxybenzoyltrimethylsilane as a yellow oil: ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.37 (s, 9H), 5.34-5.39 (brs, 1H), 6.88-6.91 (m, 2H), 7.78-7.82 (m, 2H).

To a solution of 4-hydroxybenzoyltrimethylsilane (49 mg, 0.25 mmol) in pyridine (1 mL) was added pivaloyl chloride (91 mg, 0.76 mmol) and DMAP (1.5 mg, 0.013 mmol). After stirred for 4.5 hr at room temperature, water was added and the resulting mixture was extracted with ethyl acetate. The organic phase was washed with 10% HCl, a saturated $NaHCO_3$ solution and brine, dried over $MgSO_4$, filtered and concentrated to afford a yellow oil, which was chromatographed over silica gel (5% ethyl acetate in hexane) to yield 97 mg (quant.) of 4-(trimethylsilylcarbonyl)phenyl 2,2-dimethylpropionate as a yellow oil. Purification by Kügelrohr distillation (140-160 ˚C/ 0.3 mmHg) afforded a yellow oil: ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.37 (s, 9H), 1.37 (s, 9H), 7.15-7.19 (m, 2H), 7.84-7.89 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: -1.3 (q), 27.1 (q), 39.2 (s),121.7 (d), 128.9 (d), 138.7 (s), 154.4 (s), 176.4 (s), 233.7 (s). ^{29}Si-NMR (79.5 MHz, $CDCl_3$) δ: -7.03. IR (Neat): 1810, 1756, 844 cm^{-1}. MS (EI) *m/z* 278 (M^+), 263 (M^+-Me), 57 (CMe_3, 100%). HRMS (EI) Calcd for $C_{15}H_{22}O_3Si$ (M^+): 278.1338, found: 278.1348.

***tert*-Butyldimethyl(3-methoxypropanoyl)silane (2m)**

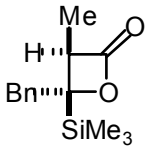


To a solution of 1-(*tert*-butyldimethylsilyl)-1-(1-ethoxyethoxy)-1,2-propadiene[12] (2.42 g, 10 mmol) in MeOH (35 mL) was added *p*-TsOH•H_2O (380 mg, 2.0 mmol). The resulting yellow reaction mixture was stirred at room temperature. After 1 hr, a saturated $NaHCO_3$ solution (50 mL) was added and the resulting mixture was extracted with ethyl acetate (×3). The organic phase was washed with brine, dried over $MgSO_4$, filtered and concentrated to afford a yellow oil, which was purified by Kügelrohr distillation (80-90 ˚C/ 2 mmHg) to yield 1.66 g (82%) of *tert*-butyldimethyl(3-methoxypropanoyl)silane as a pale yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.19 (s, 6H), 0.93 (s, 9H), 2.87 (t, J = 6.3 Hz, 2H), 3.31 (s, 3H), 3.61 (t, J = 6.3 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: -6.9 (q), 16.7 (s), 26.5 (q),49.7 (t), 58.8 (q), 66.5 (t), 245.6 (s). IR

(Neat): 1639, 1119 cm^{-1}. MS (APCI) *m/z* 203 (M^++H). HRMS (APCI) Calcd for $C_{10}H_{23}O_2Si$ (M^++H): 203.1467, found: 203.1460.

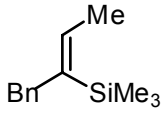
[II] Experimental Procedure for Scheme 2

4-Benzyl-3-methyl-4-trimethylsilyl-2-oxetanone (3a)



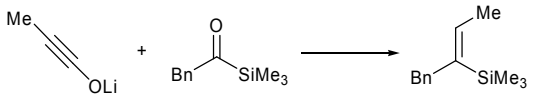
To a solution of ethyl 2,2-dibromopropionate (520 mg, 2.0 mmol) in THF (12 mL), cooled to –78 ˚C under argon, was added dropwise a solution of *tert*-butyllithium (5.9 mL, 8.0 mmol, 1.35 M in pentane). The yellow solution was stirred for 3 hr at –78 ˚C and allowed to warm to 0 ˚C. After 30 min, the resulting colorless reaction mixture was cooled to –78 ˚C and a solution of trimethyl(phenylacetyl)silane (**2a**, 308 mg, 1.6 mmol) in THF (2 mL) was added. After 2.5 hr at –78 ˚C, a saturated NH_4Cl solution (10 mL) was added and the resulting mixture was extracted with ethyl acetate (×3). The organic phase was washed with brine (30 mL), dried over $MgSO_4$, filtered and concentrated to afford a pale yellow solid, which was chromatographed over silica gel (5% ethyl acetate in hexane) to yield 362 mg (91%) of β-lactone **3a** as a white solid. Followed by recrystallization from hexane afforded colorless needles (mp 76.9-77.5 ˚C) of **3a**. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.17 (s, 9H), 1.32 (d, *J* = 7.8 Hz, 3H), 2.97 (d, *J* = 14.5 Hz, 1H), 3.28 (d, *J* = 14.5 Hz, 1H), 3.41 (q, *J* = 7.8 Hz, 1H), 7.18-7.22 (m, 2H), 7.25-7.35 (m, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: -2.5 (q), 10.8 (q), 41.8 (t), 50.8 (d), 80.0 (s), 127.2 (d), 128.4 (d), 130.1 (d), 134.5 (s), 172.0 (s). IR ($CHCl_3$): 1804, 1256, 845 cm^{-1}. MS (EI) *m/z* 248 (M^+), 221 (M^++1-CO), 74 (100%). Anal. Calcd for $C_{14}H_{20}O_2Si$: C, 67.70; H, 8.12, found: C, 67.52; H, 8.11.

(*Z*)-2-(Trimethylsilyl)-1-phenyl-2-butene (4a)



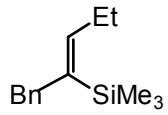
To a solution of β-lactone **3a** (30 mg, 0.12 mmol) in benzene (1 mL) was added 20 mg of silica gel. The reaction mixture was heated at reflux for 22 hr and then allowed to cool to room temperature. The resulting reaction was filtered and concentrated to afford a yellow oil, which was chromatographed over silica gel (5% ethyl acetate in hexane) to yield 22 mg (88%) of **4a** as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.04 (s, 9H), 1.83 (d, *J* = 7.1 Hz, 3H), 3.42 (s, 2H), 6.07 (q, *J* = 7.1 Hz, 1H), 7.11-7.18 (m, 3H), 7.22-7.28 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 0.2 (q), 17.8 (q), 44.6 (t), 125.6 (d), 127.9 (d), 128.8 (d), 138.7 (s), 139.1 (d), 141.5 (s). ^{29}Si-NMR (79.5 MHz, $CDCl_3$) δ: -6.83. IR (Neat): 1614, 1249, 838 cm^{-1}. MS (EI) *m/z* 204 (M^+), 189 (M^+-Me), 73 (TMS, 100%). HRMS (EI) Calcd for $C_{13}H_{20}Si$ (M^+): 204.1334, found: 204.1346.

[III] Representative Procedure for Synthesis of Vinylsilanes (Table 1, Entry 1)



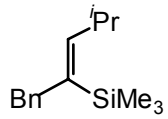
To a solution of ethyl 2,2-dibromopropionate (312 mg, 1.2 mmol) in THF (6 mL), cooled to –78 ˚C under argon, was added dropwise a solution of *tert*-butyllithium (3.53 mL, 4.8 mmol, 1.36 M in pentane). The yellow solution was stirred for 3 hr at –78 ˚C and allowed to warm to 0 ˚C. After 30 min, the resulting colorless reaction mixture was cooled to –78 ˚C and a solution of trimethyl(phenylacetyl)silane (**2a**, 192 mg, 1.0 mmol) in THF (2 mL) was added. After 0.5 hr at –78 ˚C, a saturated NH_4Cl solution (10 mL) was added and the resulting mixture was extracted with ethyl acetate (×3). The organic phase was washed with a saturated $NaHCO_3$ solution and brine, dried over $MgSO_4$, filtered and concentrated to afford 272 mg of **3a** (1809 cm^{-1}) as a pale yellow oil, which was used to the next reaction without further purification. To a solution of the crude β-lactone **3a** (272 mg) in benzene (10 mL) was added 105 mg of silica gel. The reaction mixture was heated at reflux for 21 hr and then allowed to cool to room temperature. After filtrated and concentrated, the resulting mixture was chromatographed over silica gel (2% ethyl acetate in hexane) to yield 147 mg (72%) of **4a**, which was isolated as a 98:2 mixture of inseparable stereoisomer.

(*Z*)-2-(Trimethylsilyl)-1-phenyl-2-pentene (4b, Table 1, Entry 2)



The crude β-lactone (298 mg; 1810 cm^{-1}) was obtained according to Representative Procedure, using 329 mg (1.2 mmol) of α,α-dibromoester, 3.53 mL (4.8 mmol) of *tert*-BuLi, 192 mg (1.0 mmol) of **2a**. The β-lactone (298 mg) was decarboxylated with 110 mg of silica gel in benzene for 28 hour to afford 161 mg (74%) of the title compound, which was isolated as a 95:5 mixture of inseparable stereoisomer. Data for major isomer: colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.02 (s, 9H), 1.02 (t, J = 7.5 Hz, 3H), 2.21 (dt, J = 7.5, 7.5 Hz, 2H), 3.42 (s, 2H), 5.98 (t, J = 7.5 Hz, 1H), 7.11-7.18 (m, 3H), 7.22-7.29 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 0.4 (q), 14.6 (q), 25.5 (t), 44.6 (t), 125.6 (d), 127.9 (d), 128.7 (d), 136.9 (s), 141.4 (s), 147.1 (d). ^{29}Si-NMR (79.5 MHz, $CDCl_3$) δ: -6.77. IR (Neat): 1611, 1248, 838 cm^{-1}. MS (EI) *m/z* 218 (M^+), 203 (M^+-Me), 73 (TMS, 100%). HRMS (EI) Calcd for $C_{14}H_{22}Si$ (M^+): 218.1491, found: 218.1478.

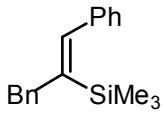
(*Z*)-4-Methyl-2-(trimethylsilyl)-1-phenyl-2-pentene (4c, Table 1, Entry 3)



The crude β-lactone (321 mg; 1811 cm^{-1}) was obtained according to Representative Procedure,

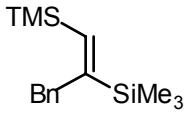
using 346 mg (1.2 mmol) of α,α-dibromoester, 3.53 mL (4.8 mmol) of *tert*-BuLi, 192 mg (1.0 mmol) of **2a**. The β-lactone was decarboxylated with 105 mg of silica gel in benzene for 22 hour and then refluxed in toluene for 6 hour to afford 140 mg (78%) of the title compound, which was isolated as a 94:6 mixture of inseparable stereoisomers. Data for major isomer: colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.01 (s, 9H), 1.01 (d, J = 6.8 Hz, 6H), 2.62 (dsept, J = 6.8, 10.8 Hz, 1H), 3.40 (brs, 2H), 5.79 (dt, J = 1.2, 10.8 Hz, 1H), 7.11-7.17 (m, 3H), 7.21-7.27 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 0.6 (q), 23.2 (q), 31.3 (d), 44.6 (t), 125.6 (d), 127.9 (d), 128.7 (d), 134.4 (s), 141.5 (s), 153.1 (d). ^{29}Si-NMR (79.5 MHz, $CDCl_3$) δ: -6.67. IR (Neat): 1612, 1248, 837 cm^{-1}. MS (EI) *m/z* 232 (M^+), 217 (M^+-Me), 73 (TMS, 100%). HRMS (EI) Calcd for $C_{15}H_{24}Si$ (M^+): 232.1647, found: 232.1632.

(*Z*)-2-(Trimethylsilyl)-1,3-diphenylpropene (4d, Table 1, Entry 4)



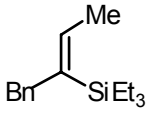
The crude β-lactone (785 mg; 1805 cm^{-1}) was obtained according to Representative Procedure, using 773 mg (2.4 mmol) of α,α-dibromoester, 6.76 mL (9.6 mmol) of *tert*-BuLi, 385 mg (2.0 mmol) of **2a**. The β-lactone (315 mg) was decarboxylated with 120 mg of silica gel in toluene for 4 hour to afford 128 mg (60%) of the title compound: colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: -0.16 (s, 9H), 3.61 (s, 2H), 7.15 (s, 1H), 7.16-7.32 (m, 10H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 0.5 (q), 45.1 (t), 125.9 (d), 126.8 (d), 127.7 (d), 128.1 (d), 128.5 (d), 129.1 (d), 140.4 (s), 140.7 (s), 143.1 (s), 143.9 (d). ^{29}Si-NMR (79.5 MHz, $CDCl_3$) δ: -5.73. IR (Neat): 1597, 1492, 1250, 838 cm^{-1}. MS (EI) *m/z* 266 (M^+), 73 (TMS, 100%). HRMS (EI) Calcd for $C_{18}H_{22}Si$ (M^+): 266.1491, found: 266.1497.

(*E*)-1,2-Bis(trimethylsilyl)-3-phenyl-1-propene (4f, Table 1, Entry 6)



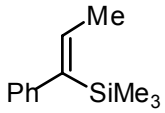
The 55:45 mixture of the crude β-lactone (375 mg; 1793 cm^{-1}) was obtained according to Representative Procedure, using 382 mg (1.2 mmol) of α,α-dibromoester, 3.38 mL (4.8 mmol) of *tert*-BuLi, 192 mg (1.0 mmol) of **2a**. The β-lactone (156 mg) was decarboxylated with 67 mg of silica gel in toluene for 10 hour to afford 50 mg (46%) of the title compound, which was isolated as a 81:19 mixture of inseparable stereoisomer. Data for major isomer: colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: -0.14 (s, 9H), 0.15 (s, 9H), 3.68 (s, 2H), 6.22 (s, 1H), 7.10-7.19 (m, 3H), 7.22-7.28 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: -0.8 (q), 0.6 (q), 42.3 (t), 125.9 (d), 128.0 (d), 129.0 (d), 140.1 (s), 143.4 (d), 162.6 (s). ^{29}Si-NMR (79.5 MHz, $CDCl_3$) δ: -4.42, -11.82. IR (Neat): 1601, 1494, 1248, 835 cm^{-1}. MS (EI) *m/z* 262 (M^+), 247 (M^+-Me), 73 (TMS, 100%). HRMS (EI) Calcd for $C_{15}H_{26}Si_2$ (M^+): 262.1573, found: 262.1563.

(*Z*)-2-(Triethylsilyl)-1-phenyl-2-butene (4g, Table 1, Entry 7)



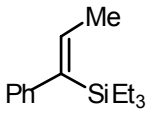
The crude β-lactone (320 mg; 1812 cm^{-1}) was obtained according to Representative Procedure, using 312 mg (1.2 mmol) of α,α-dibromoester, 3.53 mL (4.8 mmol) of *tert*-BuLi, 234 mg (1.0 mmol) of triethyl(phenylacetyl)silane. The β-lactone (320 mg) was decarboxylated with 108 mg of silica gel in benzene for 21 hour to afford 192 mg (78%) of the title compound, which was isolated as a 95:5 mixture of inseparable stereoisomers. Data for major isomer: colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.58 (q, *J* = 7.6 Hz, 6H), 0.87 (t, *J* = 7.6 Hz, 9H), 1.81 (d, *J* = 6.8 Hz, 3H), 3.38 (brs, 2H), 6.07 (dq, *J* = 0.8, 6.8 Hz, 1H), 7.10-7.18 (m, 3H), 7.20-7.28 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 4.3 (t), 7.6 (q), 17.7 (q), 44.7 (t), 125.6 (d), 127.9 (d), 129.0 (d), 136.3 (s), 139.4 (d), 141.4 (s). ^{29}Si-NMR (79.5 MHz, $CDCl_3$) δ: 1.06. IR (Neat): 1611, 1004, 732 cm^{-1}. MS (EI) *m/z* 246 (M^+), 217 (M^+-Et), 87 (100%). Anal. Calcd for $C_{16}H_{26}Si$: C, 77.97; H, 10.63, found: C, 77.70; H, 10.48.

(*Z*)-1-(Trimethylsilyl)-1-phenyl-1-propene[13] (4h, Table 1, Entry 8)



The crude β-lactone (286 mg; 1819 cm^{-1}) was obtained according to Representative Procedure, using 312 mg (1.2 mmol) of α,α-dibromoester, 3.53 mL (4.8 mmol) of *tert*-BuLi, 178 mg (1.0 mmol) of benzoyltrimethylsilane. After purified by column chromatography, the β-lactone was decarboxylated with 105 mg of silica gel in benzene for 2 hour to afford 118 mg (62%) of the title compound, which was isolated as a 92:8 mixture of inseparable stereoisomers. Data for major isomer: colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.15 (s, 9H), 1.91 (d, *J* = 7.2 Hz, 3H), 6.17 (q, *J* = 7.2 Hz, 1H), 6.97-7.01 (m, 2H), 7.11-7.18 (m, 1H), 7.21-7.26 (m, 2H). IR (Neat): 1606, 1250, 837 cm^{-1}. MS (EI) *m/z* 190 (M^+), 175 (M^+-Me), 73 (TMS, 100%).

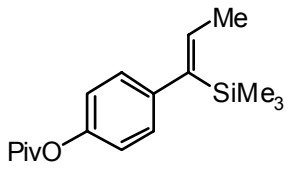
(*Z*)-1-(Triethylsilyl)-1-phenyl-1-propene[14] (4i, Table 1, Entry 9)



The crude β-lactone (299 mg; 1820 cm^{-1}) was obtained according to Representative Procedure, using 312 mg (1.2 mmol) of α,α-dibromoester, 3.53 mL (4.8 mmol) of *tert*-BuLi, 220 mg (1.0 mmol) of benzoyltriethylsilane. The β-lactone (299 mg) was decarboxylated with 60 mg of silica gel in benzene for 15 hour to afford 166 mg (71%) of the title compound, which was isolated as a 88:12 mixture of inseparable stereoisomer. Data for major isomer: colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.64 (q, *J* = 7.6 Hz, 6H), 0.90 (t, *J* = 7.6 Hz, 9H), 1.90 (d, *J* = 6.8 Hz, 3H), 6.21 (q, *J* = 6.8 Hz, 1H), 6.96-7.02 (m, 2H), 7.10-7.16 (m, 1H), 7.20-7.26 (m, 2H). IR

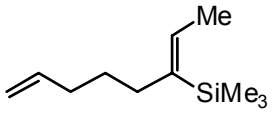
(Neat): 1605 cm^{-1}. MS (EI) *m/z* 232 (M^+), 203 (M^+-Et, 100%).

4-[(*Z*)-1-(Trimethylsilyl)propenyl]phenyl 2,2-dimethylpropionate (4j, Table 1, Entry 10)



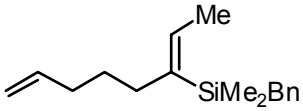
The crude β-lactone (176 mg; 1814, 1747 cm^{-1}) was obtained according to Representative Procedure, using 156 mg (0.60 mmol) of α,α-dibromoester, 1.68 mL (2.4 mmol) of *tert*-BuLi, 139 mg (0.50 mmol) of 4-(trimethylsilylcarbonyl)phenyl 2,2-dimethylpropionate. The β-lactone (176 mg) was decarboxylated with 50 mg of silica gel in benzene for 18 hour to afford 92 mg (64%) of the title compound, which was isolated as a 92:8 mixture of inseparable stereoisomer. Data for major isomer: colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.14 (s, 9H), 1.35 (s, 9H), 1.90 (d, *J* = 6.8 Hz, 3H), 6.18 (q, *J* = 6.8 Hz, 1H), 6.90-7.00 (m, 4H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 0.6 (q), 18.1 (q), 27.2 (q), 39.0 (s), 120.5 (d), 128.1 (d), 140.7 (d), 143.3 (s), 144.5 (s), 148.8 (s), 177.0 (s). ^{29}Si-NMR (79.5 MHz, $CDCl_3$) δ: -7.81. IR (Neat): 1752, 1602, 1119 cm^{-1}. MS (APCI) *m/z* 308 (M^++NH_4), 291 (M^++H). HRMS (APCI) Calcd for $C_{17}H_{27}O_2Si$ (M^++H): 291.1780, found: 291.1803. Anal. Calcd for $C_{17}H_{26}O_2Si$: C, 70.29; H, 9.02, found: C, 69.97; H, 9.06.

(*Z*)-3-(Trimethylsilyl)octa-2,7-diene (4k, Table 1, Entry 11)



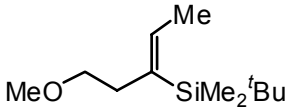
The crude β-lactone (1813 cm^{-1}) was obtained according to Representative Procedure, using 312 mg (1.2 mmol) of α,α-dibromoester, 3.53 mL (4.8 mmol) of *tert*-BuLi, 170 mg (1.0 mmol) of 5-hexenoyltrimethylsilane. The β-lactone was decarboxylated with 104 mg of silica gel in benzene for 17 hour to afford 131 mg (72%) of the title compound, which was isolated as a 94:6 mixture of inseparable stereoisomer. Data for major isomer: colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.16 (s, 9H), 1.37-1.46 (m, 2H), 1.75 (d, *J* = 6.8 Hz, 3H), 2.00-2.10 (m, 4H), 4.94 (ddt, *J* = 1.2, 1.2, 10.4 Hz, 1H), 5.00 (ddt, *J* = 1.2, 2.0, 17.2 Hz, 1H), 5.81 (ddt, *J* = 6.8, 10.4, 17.2 Hz, 1H), 6.05 (q, *J* = 6.8 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 0.3 (q), 17.8 (q), 30.2 (t), 33.7 (t), 38.0 (t), 114.3 (t), 136.7 (d), 138.9 (d), 140.0 (s). ^{29}Si-NMR (79.5 MHz, $CDCl_3$) δ: -7.77. IR (Neat): 1641, 1615, 1249, 838 cm^{-1}. MS (EI) *m/z* 167 (M^+-Me), 108 (100%). HRMS (EI) Calcd for $C_{10}H_{19}Si$ (M^+-Me): 167.1256, found: 167.1268.

(*Z*)-3-(Bnezyldimethylsilyl)octa-2,7-diene (4l, Table 1, Entry 12)



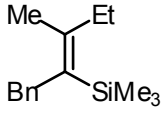
The crude β-lactone (329 mg; 1811 cm^{-1}) was obtained according to Representative Procedure, using 312 mg (1.2 mmol) of α,α-dibromoester, 3.38 mL (4.8 mmol) of *tert*-BuLi, 246 mg (1.0 mmol) of benzyl(5-hexenoyl)dimethylsilane. The β-lactone (329 mg) was decarboxylated with 130 mg of silica gel in toluene for 4 hour to afford 179 mg (69%) of the title compound, which was isolated as a 86:14 mixture of inseparable stereoisomer. Data for major isomer: colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.10 (s, 6H), 1.29 (quin, J = 7.8 Hz, 2H), 1.70 (d, J = 6.8 Hz, 3H), 1.94-2.01 (m, 4H), 2.21 (s, 2H), 4.92 (ddt, J = 2.2, 5.5, 10.0 Hz, 1H), 4.96 (ddt, J = 1.5, 2.2, 16.8 Hz, 1H), 5.78 (ddt, J = 6.8, 10.0, 16.8 Hz, 1H), 6.09 (q, J = 6.8 Hz, 1H), 6.96-7.08 (m, 3H), 7.14-7.22 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: -1.8 (q), 18.0 (q), 26.5 (t), 30.1 (t), 33.6 (t), 37.9 (t), 114.3 (t), 123.9 (d), 128.0 (d), 128.2 (d), 137.8 (d), 138.3 (s), 138.8 (d), 140.1 (s). ^{29}Si-NMR (79.5 MHz, $CDCl_3$) δ: -6.59. IR (Neat): 1601, 833 cm^{-1}. MS (EI) *m/z* 167 (M^+-Bn). Anal. Calcd for $C_{17}H_{26}Si$: C, 79.00; H, 10.14, found: C, 78.77; H, 10.07.

(*Z*)-3-(*tert*-Butyldimethylsilyl)-5-methoxy-2-pentene (4m, Table 1, Entry 13)



The crude β-lactone (286 mg; 1814 cm^{-1}) was obtained according to Representative Procedure, using 312 mg (1.2 mmol) of α,α-dibromoester, 3.53 mL (4.8 mmol) of *tert*-BuLi, 202 mg (1.0 mmol) of *tert*-butyldimethyl(3-methoxypropanoyl)silane. The β-lactone (286 mg) was decarboxylated with 122 mg of silica gel in benzene for 17 hour to afford 181 mg (84%) of the title compound, which was isolated as a 93:7 mixture of inseparable stereoisomer. Data for major isomer: colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.15 (s, 6H), 0.90 (s, 9H), 1.75 (d, J = 6.8 Hz, 3H), 2.27-2.33 (m, 2H), 3.30-3.36 (m, 2H), 3.33 (s, 3H), 6.20 (dt, J = 1.2, 6.8 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: -3.5 (q), 18.5 (s), 18.8 (q), 27.1 (q), 37.6 (t), 58.4 (q), 73.7 (t), 133.5 (d), 140.1 (s). ^{29}Si-NMR (79.5 MHz, $CDCl_3$) δ: 0.52. IR (Neat): 1614, 1251, 1118 cm^{-1}. MS (APCI) *m/z* 215 (M^++H). HRMS (APCI) Calcd for $C_{21}H_{27}OSi$ (M^++H): 215.1831, found: 215.1828.

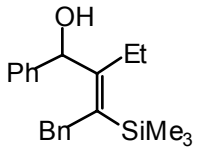
(*Z*)-3-Methyl-2-(trimethylsilyl)-1-phenyl-2-pentene (4o)



To a solution of ethyl 2,2-dibromobutanoate (164 mg, 0.60 mmol) in THF (3 mL), cooled to –78 ˚C under argon, was added dropwise a solution of *tert*-butyllithium (1.68 mL, 2.4 mmol, 1.43 M in pentane). The yellow solution was stirred for 3 hr at –78 ˚C and allowed to warm to

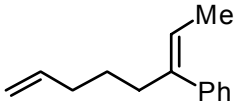
0 ˚C. After 30 min, the resulting colorless reaction mixture was cooled to –78 ˚C and a solution of trimethyl(phenylacetyl)silane (**2a**, 96 mg, 0.50 mmol) in THF (1 mL) was added. After 20 min at –78 ˚C, iodomethane (0.16 mL, 2.5 mmol) and HMPA (0.43 mL, 2.5 mmol) was added. After 17 hour at –78 ˚C, a saturated NH_4Cl solution (10 mL) was added and the resulting mixture was extracted with ethyl acetate (×3). The organic phase was washed with a saturated $NaHCO_3$ solution and brine, dried over $MgSO_4$, filtered and concentrated to afford the crude β-lactone (1807 cm^{-1}) as a yellow oil, which was decarboxylated with 100 mg of silica gel in toluene for 5 hour to afford 85 mg (70%) of **4o** as a colorless oil: ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.05 (s, 9H), 1.09 (t, *J* = 7.2 Hz, 3H), 1.72 (s, 3H), 2.29 (q, *J* = 7.2 Hz, 2H), 3.51 (s, 2H), 7.08-7.17 (m, 3H), 7.21-7.27 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 1.0 (q), 13.7 (q), 18.4 (q), 32.3 (t), 37.5 (t), 125.3 (d), 128.02 (d), 128.04 (d), 129.9 (s), 141.2 (s), 151.3 (s). ^{29}Si-NMR (79.5 MHz, $CDCl_3$) δ: -7.04. IR (Neat): 1604, 1248, 836 cm^{-1}. MS (EI) *m/z* 232 (M^+), 217 (M^+-Me), 73 (TMS, 100%). HRMS (EI) Calcd for $C_{15}H_{24}Si$ (M^+): 232.1647, found: 232.1644.

(*E*)-2-Ethyl-1,4-diphenyl-3-(trimethylsilyl)-2-buten-1-ol (4p)



To a solution of ethyl 2,2-dibromobutanoate (164 mg, 0.60 mmol) in THF (3 mL), cooled to –78 ˚C under argon, was added dropwise a solution of *tert*-butyllithium (1.68 mL, 2.4 mmol, 1.43 M in pentane). The yellow solution was stirred for 3 hr at –78 ˚C and allowed to warm to 0 ˚C. After 30 min, the resulting colorless reaction mixture was cooled to –78 ˚C and a solution of trimethyl(phenylacetyl)silane (**2a**, 96 mg, 0.50 mmol) in THF (1 mL) was added. After 20 min at –78 ˚C, a solution of benzaldehyde (186 mg, 1.75 mmol) in THF (1 mL) was added. After 17 hour at –78 ˚C, a saturated NH_4Cl solution (10 mL) was added and the resulting mixture was extracted with ethyl acetate (×3). The organic phase was washed with a saturated $NaHCO_3$ solution and brine, dried over $MgSO_4$, filtered and concentrated to afford the crude β-lactone (286 mg; 1798 cm^{-1}) as a white solid, which was used to the next reaction without further purification. The β-lactone (95 mg) was decarboxylated with 40 mg of silica gel in toluene for 8 hour to afford 39 mg (72%) of **4p**, which was isolated as a 93:7 mixture of inseparable stereoisomer. Data for major isomer: colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.12 (s, 9H), 0.95 (t, *J* = 7.2 Hz, 3H), 1.71 (d, *J* = 4.4 Hz, 1H), 2.20 (dq, *J* = 7.2, 14.6 Hz, 1H), 2.40 (dq, *J* = 7.2, 14.6 Hz, 1H), 3.67 (d, *J* = 17 Hz, 1H), 3.70 (d, *J* = 17 Hz, 1 H), 5.73 (d, *J* = 4.4 Hz, 1H), 7.15-7.35 (m, 10H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 1.0 (q), 16.1 (q), 26.2 (t), 36.7 (t), 73.0 (d), 125.8 (d), 126.8 (d), 128.06 (d), 128.09 (d), 128.3 (d), 134.9 (s), 141.0 (s), 142.7 (s), 155.2 (s). ^{29}Si-NMR (79.5 MHz, $CDCl_3$) δ: -5.55. IR (Neat): 3451, 1601, 1249, 838 cm^{-1}. MS (FAB) *m/z* 347 (M^++Na). HRMS (FAB) Calcd for $C_{21}H_{28}SiNa$ (M^++Na): 347.1807, found: 347.1808.

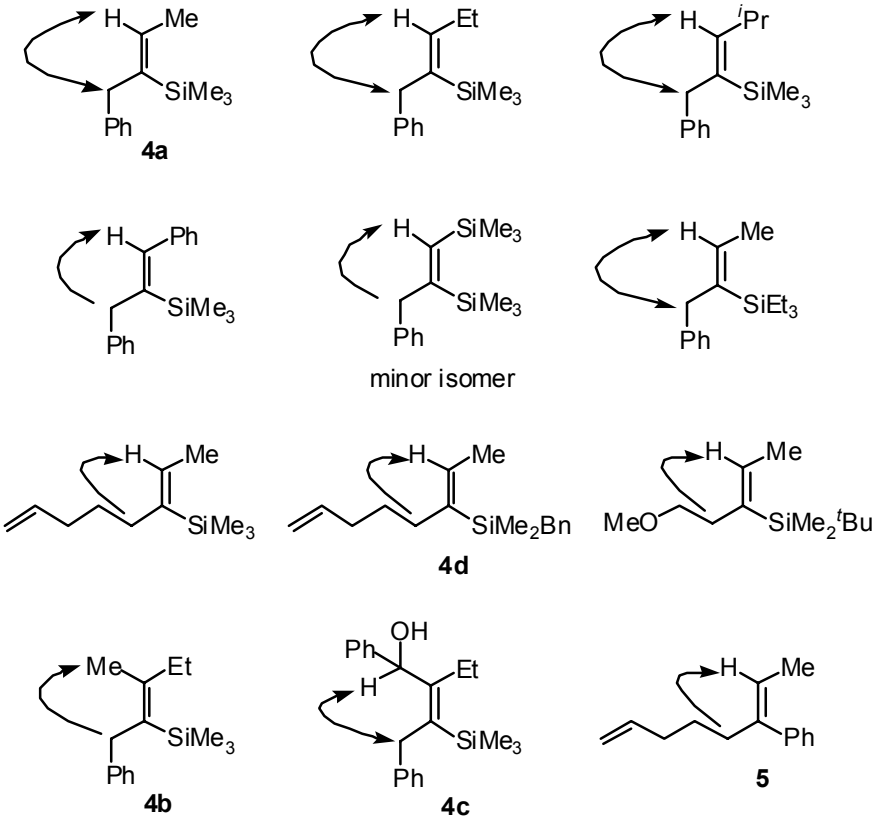
(*Z*)-3-Phenylocta-2,7-diene (5)



To a solution of (*Z*)-3-(bnezyldimethylsilyl)octa-2,7-diene (**4l**, 50 mg, 0.19 mmol) and iodobenzene (51 mg, 0.25 mmol) in THF (1 mL), cooled to 0 ˚C under argon, was added dropwise a solution of TBAF (0.39 mL, 0.39 mmol, 1.0 M in THF). After stirred for 10 min at 0 ˚C, $Pd_2(dba)_3$•$CHCl_3$ (5.0 mg, 0.0048 mmol) was added. After 8 hour at room temperature, the resulting mixture was diluted with Et_2O, filtered over celite and concentrated to afford a brown oil, which was chromatographed over silica gel (100% hexane) to yield 33 mg (57%, *Z* : *E* = 91 : 9) of **5** as a colorless oil. These isomers were separated by preparative HPLC (100% hexane): ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.39 (quin, *J* = 7.6 Hz, 2H), 1.55 (d, *J* = 6.8 Hz, 3H), 1.98-2.05 (m, 2H), 2.34 (t, *J* = 7.6 Hz, 2H), 4.87-5.00 (m, 2H), 5.54 (q, *J* = 6.8 Hz, 1H), 5.76 (ddt, *J* = 6.4, 10.0, 16.8 Hz, 1H), 7.12-7.35 (m, 5H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 14.7 (q), 27.5 (t), 33.3 (t), 38.6 (t), 114.3 (t), 121.2 (d), 126.2 (d), 127.9 (d), 128.4 (d), 138.7 (d), 141.0 (s), 141.4 (s). IR (Neat): 1640, 910 cm^{-1}. MS (EI) *m/z* 186 (M^+), 103 (100%). HRMS (EI) Calcd for $C_{14}H_{18}$ (M^+): 186.1409, found: 186.1397.

[IV] Determination of Stereochemistry

1) n.*O*.e. Experiment



[IV] References

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