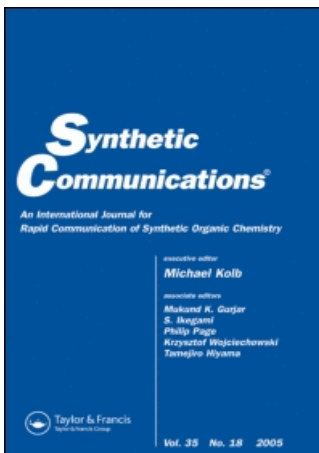


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Nora E. Restrepo-Sánchez^a, Fernando J. Gómez^a, Luz M. Jaramillo-Gómez^a,
Tomas Hudlioký^b

^a Departamento de Química, Universidad del Valle, Cali, Colombia
^b Chemistry Department, University of Florida, Gainesville, FL, USA

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**FREE RADICAL CYCLIZATIONS OF TRIENES WITH
TRIS(TRIMETHYLSILYL)SILANE**

Nora E. Restrepo-Sánchez,[§] Fernando J. Gómez,[§] Luz M. Jaramillo-Gómez,^{*§}
Tomas Hudlicky[†]

[§]Departamento de Química, Universidad del Valle, A.A. 25360, Cali, Colombia

[†]Chemistry Department, University of Florida, Gainesville, FL, 32611-7200, USA

Abstract: The intramolecular trapping of a stabilized intermediate allylic radical generated by the addition of tris(trimethylsilyl)silyl (silyl) radical to a conjugated system was performed. The observed low stereoselectivity suggests thermodynamic rather than kinetic control in this cyclization process.

Radical cyclizations usually consist of intramolecular addition of radicals centered on carbon or an atom other than carbon (e.g. N, O, S, etc.) to multiple bonds: C=C, C≡C, C=O and C≡N.¹ They are of great synthetic interest as they allow the formation of 5- and 6-membered rings with high regioselectivity and often very good stereoselectivity.² The types of radicals than can be generated in these cyclizations, range from the most reactive (and nucleophilic) aryl and vinyl radicals through alkyl radicals,³ to stable radicals such as allyl⁴ and benzyl.⁵ The

* To whom correspondence should be addressed. luzmaja@quimica.univalle.edu.co

known and efficient hydrosilylation ability of tris(trimethylsilyl)silane (TTMS) with alkenes and alkynes⁶ has been used for intramolecular addition of the corresponding generated alkyl⁷ or vinyl radicals⁸ to double bonds. To our knowledge there have been no reports of hydrosilylation of conjugated dienes with TTMS, although the related addition ($k = 1.4 \times 10^8$) of triethylsilyl radicals to *trans*-1,3-pentadiene has been reported.⁹ Similar addition to a triene system followed by cyclization with tri-*n*-butyltinhydride under sonochemical initiation, was published by Nakamura *et al.*¹⁰

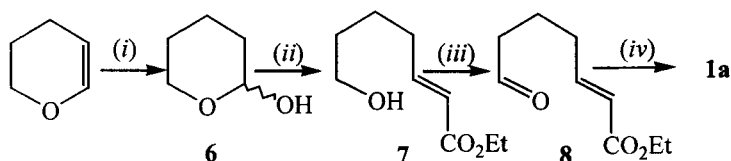
To assess the potential of tris(trimethylsilyl)silane in free radical cyclizations we decided to explore the free-radical-mediated silylation of conjugated dienes tethered to alkenes **1** and **2** (Scheme 1) to trigger one-electron cyclization of these triene precursors to carbocyclic systems of type **4** or **5**. Tris(trimethylsilyl)silyl radical is added to the conjugated diene moiety generating an intermediate allylic radical **3**, which must be trapped by the isolated double bond, in a typical 5-*exo* closure.

Scheme 1



The cyclization precursors ethyl and methyl 2,7,9-decatrien-1-oates (**1a**, **1b**) were prepared following two synthetic sequences. The first one was carried out in four steps from commercial 3,4-dihydro-2H-pyran (Scheme 2) to afford ethyl-2,7,9-decatrien-1-oate (**1a**) in a ratio (1.3:1) of stereoisomers *2E,7E* : *2E,7Z*.

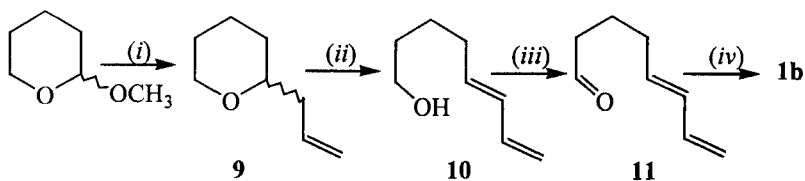
Scheme 2



(i) HCl (aq); r.t. (1.5 hs), then NaOH (aq), 85%; (ii) $\text{Ph}_3\text{P}=\text{CHCO}_2\text{Et}/\text{CHCl}_3$ r.t. 52%
 (iii) PCC/ $\text{CH}_2\text{Cl}_2/\text{SiO}_2$, 60%; (iv) $[\text{Ph}_3\text{P}=\text{CH}-\text{CH}=\text{CH}_2]^+\text{Br}^- / \text{PhLi} / \text{Et}_2\text{O}$, 15-22%

An alternative sequence started from commercial 5,6-dihydro-4-methyl-2-H-pyran and allyltrimethylsilane according to the procedure of Noyori *et al*¹¹ and afforded the known allylpyran **9**, which was opened with Schlosser base¹² to yield diene alcohol **10**. Swern oxidation¹³ of **10** followed by Wittig reaction led to the desired triene **1b** as the only isomer (*2E,7E*).

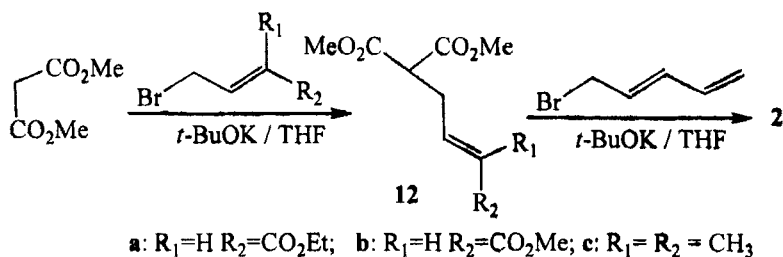
Scheme 3



(i) $(\text{Me})_3\text{SiCH}_2\text{CH}=\text{CH}_2/\text{TMSOTf}/\text{CH}_2\text{Cl}_2$ (-60°C), 86%; (ii) LDA/THF (-50°C), 65 %
 (iii) $(\text{COCl})_2$, DMSO, NEt_3 , CH_2Cl_2 , -78°C , 60%; (iv) $\text{Ph}_3\text{P}=\text{CHCO}_2\text{Me}$, CH_2Cl_2 , 47%

Trienes **2** derived from malonic dimethyl ester were obtained through two successive alkylations using *t*-BuOK / THF^{8b} at room temperature with ethyl or methyl 4-bromocrotonate, or 4-bromo-2-methylbut-2-ene as the first alkylating agent and 5-bromo-1,3-pentadiene¹⁴ as the second one for all of the compounds (Scheme 4).

Scheme 4



Free radical cyclization of the prepared trienes was carried out as follows: a stirred solution of the triene **1** or **2** (0.21 - 1.8 mmol), TTMS (1.2 - 1.3 eq) and AIBN (0.2 eq) in benzene or toluene was flushed with argon during 30 min. The reaction mixture was then heated at 75 - 100 °C during 2 - 5 h until no starting material was observed by TLC. The concentrated crude mixture was purified by flash column chromatography (30-42% yield). For the precursor **2b**, Et_3B / O_2 ¹⁵ was used as the initiator in order to run the cyclization reaction at room temperature and to avoid thermal decomposition of the labile starting material. This reaction mixture appeared cleaner and led to a better yield (46 %) of the cyclic product **5b**.

In all cases the isolated major product was identified as the expected cyclic product by $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$. Compounds **4b**, **5a**, **5b** were shown to consist of four isomers in ratios of 19:19:1.2:1, 9.4:9.3:1.2:1, 30:23:1.2:1, respectively (GC). Each cyclization would be expected to afford four stereoisomeric cyclic products because the geometric isomerism of the double bond and of the cyclopentane ring.

For the carbocycles **4a** and **5a**, high resolution MS showed the expected molecular weight 443.2634 (calc. 442.9372) and 559.2772 (calc. 559.0104) respectively. However by low resolution GC-MS we observed a mixture of four compounds, two major and two minor isomers, in an approximately 1:1 ratio with the same molecular weight. Similar results were obtained by low resolution GC - MS for the remaining cyclic products.

It is difficult to assign the identity of the expected stereoisomers *E-trans*, *E-cis*, *Z-trans* and *Z-cis* on a fully saturated ring of the type **4** or **5**. The vinyl protons of the double bond allylsilane appendage show complex multiplets, which do not allow the determination of the coupling constants of *cis* or *trans* double bond hydrogens. However the cyclic product **5c** showed clearly the more stable *E* configuration of the double bond.

It also has not been possible to establish the *cis* / *trans* ratio of the cyclopentane by NMR, although GC analysis suggests an approximately 1:1 ratio. The lack of stereoselectivity in this cyclization process can be attributed to the resonance stabilization of the intermediate allylic radical, which allows a reversible reaction leading to thermodynamic rather than kinetic control. It is known that

analogous 5-hexenyl radical cyclizations, under kinetic control, produce preferentially *cis*-disubstituted cyclopentanes.^{2,16}

It is worth mentioning that the five-membered rings produced exhibit an allylsilane functionality, which could be removed by reaction with a variety of electrophiles such as H⁺, aldehydes, ketones and acetals, among others.¹⁷ This reactivity would be advantageous for a second intramolecular cyclization generating bicyclic systems.

In addition, oxidative transformation could lead to bicyclic lactones in which the *cis*-fused system would be more favored and could be generated from the mixtures by isomerization. Synthetic utility of such transformations will be evaluated in future work from our research group.

EXPERIMENTAL

All of the ¹H-NMR and ¹³C-NMR spectra were recorded in a Gemini 300, in deuterated chloroform at 300 MHz and 75 MHz, respectively, unless otherwise indicated. The gas chromatograms were run on a HP 5890A Series II instrument, using a HP-5 (crosslinked 5% PH ME Silicone) column.

Ethyl 2,7,9-decatrien-1-oate (**1a**):¹⁸ In a flame-dried round bottom flask propyltriphenylphosphonium bromide [590.2 mg, 1.54 mmol] was placed followed by dry ether. To the stirred suspension phenyllithium [1.2 mL, 1.5 mmol] was added dropwise. The resulting orange-red solution was stirred at room temperature for 2.5 h, then aldehyde **8** [250.1 mg, 1.47 mmol] was added. After the mustard-colored slurry was stirred at room temperature for 2 h, it was filtered through silica gel, which was then washed with 120 mL of hexanes:EtOAc (2:1). The expected triene **1a** was isolated by

column chromatography (Hex : Et₂O, gradient 0 - 10%, +5%) as an *E/Z* mixture in a 22 % yield. ¹H NMR of the compound matched with that one previously reported by Takacs.¹⁸ $R_f = 0.35$, Hex : Et₂O (9:1). ¹H NMR: Data corresponding to the *E* isomer, δ 6.9 (dt, $J = 15.9, 6.9, 1H$), 6.2 (dt, $J = 16.8, 6.6, 1H$), 6.0 (m, 1H), 5.8 (dt, $J = 15.6, 1.5, 1H$), 5.6 (dt, $J = 15.3, 6.6, 1H$), 5.0 (overlapping d, $J = 15.3, 1H$), 4.9 (d, $J = 10.2, 1H$), 4.2 (q, 2H), 2.2 (q, 2H), 2.1 (q, 2H), 1.6 (q, 2H), 1.3 (t, 3H) ppm. Data corresponding to the *Z* isomer, δ 6.9 (dt, $J = 15.9, 6.9, 1H$), 6.5 (dtd, $J = 16.8, 10.2, 1.2, 1H$), 6.0 (m, 1H), 5.8 (dt, $J = 15.6, 1.5, 1H$), 5.4 (m, 1H), 5.1 (d, $J = 15.0, 1H$), 5.0 (overlapping d, $J = 12.6, 1H$), 4.2 (q, 2H), 2.2 (q, 2H), 2.1 (q, 2H), 1.6 (q, 2H), 1.3 (t, 3H) ppm.

Methyl 2,7,9-decatrien-1-oate (**1b**):¹⁹ To a stirred solution of (carbomethoxymethylene)triphenylphosphorane [600 mg, 4.8 mmol] in CH₂Cl₂ (3 mL), was added a solution of the aldehyde **11** in CH₂Cl₂ (1 mL). The reaction mixture was stirred for 18 h with monitoring by TLC. Upon completion of the reaction, hexanes was added (10 mL) and a precipitated solid (Ph₃PO) removed by gravity filtration. The decanted liquid was concentrated to afford an oily solid, which was purified by flash column chromatography (Hex : Et₂O, gradient 0 - 10%, +2%) to give triene **1b** in 47% yield as an *E/Z* mixture (ratio 19:1 determined by ¹H NMR). ¹H NMR of the compound matched with that one previously reported by Roush.¹⁹ $R_f = 0.57$, Hex : Et₂O (4:1). ¹H NMR: Data corresponding to the major isomer; δ 6.96 (dt, $J = 15.66, 7.15, 1H$), 6.30 (ddd, $J = 16.76, 10.44, 10.44, 1H$), 6.05 (dd, $J = 15.10, 10.43, 1H$), 5.81 (dt, $J = 15.65, 1.65, 1H$), 5.65 (dt, $J = 15.11, 7.40, 1H$), 5.1 (d, $J = 17.04, 1H$), 4.9 (d, $J = 10.16, 1H$), 3.6 (t, 2H), 2.1 (q, 2H), 1.9 (br.s., 1H), 1.4 - 1.7 (m, 4H) ppm.

General Procedure for the Synthesis of Trienes 2

Potassium *tert*-butoxide (1.0 eq) was placed in a flame-dried flask under argon followed by dry THF. The suspension was stirred for 0.5 h and the corresponding ester

12 (1.0 eq) was added. After 30 min 5-bromo-1,3-pentadiene (1.0 -1.3 eq) was added and the reaction mixture stirred at room temperature overnight. After aqueous work up and extraction (EtOAc), the dried crude product was purified by flash column chromatography to isolate the corresponding triene **2**.

1-Ethoxycarbonyl-4,4-bis(methoxycarbonyl)-1,6,8-nonatriene (**2a**): Yield; 52% of a 1*E*,6*E*:1*E*,6*Z* mixture in a ratio 4.8:1 determined by ¹H NMR. *R*_f = 0.3, Hex : EtOAc (17 : 3). ¹H NMR: δ 6.74 (ddd, *J* = 15.39, 7.69, 7.69, 1H), 6.24 (dt, *J* = 17.03, 10.17, 1H), 6.06 (dd, *J* = 14.84, 10.72, 1H), 5.82 (d, *J* = 15.66, 1H), 5.44 (ddd, *J* = 15.11, 7.7, 7.7, 1H), 5.13 (d, *J* = 16.48, 1H), 5.03 (d, *J* = 9.89, 1H), 4.15 (q, *J* = 7.14, 2H), 3.70 (s, 6H), 2.75 (dd, *J* = 7.70, 1.38, 2H), 2.65 (d, *J* = 7.69, 0.83, 2H), 1.25 (t, *J* = 7.14, 3H) ppm.

1,4,4-Tris(methoxycarbonyl)-1,6,8-nonatriene (**2b**). Yield; 58%. ¹H NMR: δ 6.70 (dt, *J* = 15.66, 7.69, 1H), 6.28 (dt, *J* = 16.74, 10.17, 1H), 6.10 (dd, *J* = 14.83, 10.71, 1H), 5.86 (dt, *J* = 15.38, 1.38, 1H), 5.48 (dt, *J* = 15.11, 7.41, 1H), 5.15 (d, *J* = 16.48, 1H), 5.05 (d, *J* = 9.34, 1H), 3.74 (s, 6H), 3.72 (s, 3H), 2.76 (dd, *J* = 7.69, 1.38, 2H), 2.68 (d, *J* = 7.42, 2H) ppm.

5,5-Bis(methoxycarbonyl)-2-methyl-2,7,9-decatriene (**2c**): Yield; 35%, obtained through flash column chromatography purification (Hex : EtOAc, gradient 0 - 5%, +1%). *R*_f = 0.4, Hex : EtOAc (97 : 3). ¹H NMR: δ 6.3 (dt, *J* = 16.8, 10.2, 1H), 6.0 (dd, *J* = 14.4, 10.2, 1H), 5.5 (dt, *J* = 15.0, 7.5, 1H), 5.1 (d, *J* = 16.8, 1H), 5.0 (d, *J* = 9.3, 1H), 4.9 (t, *J* = 7.8, 1H), 3.7 (s, 6H), 2.6 (complex absorption, 4H), 1.7 (s, 3H), 1.6 (s, 3H) ppm.

Cyclization Reactions

Ethyl 2-(2-(3-(trimethylsilyl)-1-propenyl)cyclopentyl) acetate (**4a**): In a flame-dried round bottom flask under argon atmosphere, triene **1a** [87.4 mg; 0.45 mmol] was added to a solution of AIBN [14.8 mg; 0.09 mmol] in toluene (4.5 mL), followed

immediately by addition of tris(trimethylsilylsilane) (TTMS) [149.9 mg; 0.58 mmol]. The resulting solution was degassed for 45 min and then stirred at 100°C. The reaction, monitored by thin-layer chromatography, was complete in 2.2 h. The reaction mixture was cooled to room temperature, and the solvent was removed under vacuum to yield a yellow oil. A compound whose ¹H NMR indicates the expected product **4a** was isolated by flash column chromatography (Hex : Et₂O, gradient 0 - 5%, +1%) in 45% yield. *R_f* = 0.59, Hex : Et₂O (9 : 1). ¹H NMR: δ 5.4 (m, 1H), 5.1 - 5.2 (m, 1H), 4.1 (q, 2H), 2.5 (dd, *J* = 15.3, 3.7, 1H), 2.4- 1.4 (complex absorption, 11H), 1.2 (t, 3H), 0.1 (s, *ca* 27H) ppm. ¹³C NMR: δ 173.5, 130.8, 130.4, 129.9, 129.5, 128.0, 60.0, 50.0, 45.9, 42.8, 40.2, 38.9, 36.2, 32.0, 31.8, 31.0, 30.7, 23.3, 23.0, 14.3, 13.1, 13.0 ppm. IR: 3055.5 (w), 2953.1 (s), 2895.7 (m), 1731.3 (s), 1446.1 (m), 1396.9 (m), 1374.2 (m), 1248.1 (s), 1184.4 (m), 1068.8 (s), 965.4 (w), 837.9(s), 740.2 (s), 688.5 (m), 622.6 (m) cm⁻¹. GC-MS: (CI) Four isomers *m/z* Obs. 443.2638 (M⁺+1), 443.2636 (M⁺+1), 443.2626 (M⁺+1), 443.2620 (M⁺+1). Calc. 442.9372.

Methyl 2-[2-[3-(trimethylsilyl)-1-propenyl]cyclopentyl] acetate (**4b**): Triene **1b** [320 mg; 1.8 mmol] was added to a solution of AIBN [58 mg; 0.4 mmol] in benzene (180 mL), followed immediately by addition of TTMS [564.2 mg; 2.4 mmol]. The resulting solution was degassed for 45 min and then stirred at 70 - 85 °C. The reaction, monitored by thin-layer chromatography, was complete in 4.5 h. The reaction was cooled to room temperature and the solvent removed under vacuum to yield a yellow oil. A compound was isolated by flash column chromatography (Hex : Et₂O, gradient 0 - 5%, +1%) in *ca* 25 %, the ¹H NMR of which suggests the expected product **4b** as well as impurities. This sample was purified by preparative TLC in order to obtain the pure compound, which based on the ¹H NMR seems to be mostly the *E* isomer. *R_f* = 0.54, Hex : Et₂O (9 : 1). ¹H NMR (CDCl₃, 500 MHz): δ 5.4 (ddd, *J* = 15.1, 9.34, 6.32, 1H), 5.12

(dd, $J = 14.5, 8.0, 1\text{H}$), 3.6 (s, 3H), 2.5 (dd, $J = 15.11, 4.12, 1\text{H}$), 2.0 (dd, $J = 14.83, 9.34, 1\text{H}$), 1.6 - 2.0 (complex absorption, 12H), 0.5 (br. s., *ca* 27 H) ppm. GC: 60°C $\xrightarrow{30\text{ deg/min}}$ 270°C (25 min) four isomers t_{R} (ratio): 27.019 (1.2) 28.500 (1.0) 29.694 (19) : 30.559 (19) min.

Dimethyl 3-(2-ethoxy-2-oxoethyl)-4-{3-trimethylsilyl)-1-propenyl}-1,1-cyclopentadecarboxylate (**5a**): Triene **2a** [170 mg; 0.55 mmol] was added to a solution of AIBN [18.0 mg; 0.11 mmol] in benzene (6 mL), followed immediately by addition of TTMS [182.6 mg; 0.71 mmol]. The resulting solution was degassed for 40 min and then stirred at $75 - 85^{\circ}\text{C}$. The reaction was monitored by thin-layer chromatography and was complete in 5 h. Flash column chromatography (Hex : EtOAc, gradient 0 - 10%, +5%) of the crude gave compound **5a** in 36 % yield. $R_{\text{f}} = 0.45$, Hex : EtOAc (17 : 3). $^1\text{H NMR}$: δ 5.4 (m, 1H), 5.1 (m, 1H), 4.1 (q, 2H), 3.7 (s, 6H), 2.75 - 1.8 (complex absorption, 8H), 1.7 - 1.6 (complex absorption, 2H), 1.2 (t, 3H) ppm. $^{13}\text{C NMR}$: δ 173.1, 132.0, 128.4, 126.2, 60.7, 59.2, 58.3, 52.0, 49.1, 45.3, 42.3, 40.9, 39.2, 38.7, 36.2, 14.1, 12.0 ppm. IR: 2950.8 (s), 2893.7 (m), 1736.7 (s), 1435.0 (m), 1395.5 (w), 1244.7 (s), 1196.1 (m), 1158.7 (m), 1109.1 (w), 1031.9 (w), 965.9 (w), 835.9 (s), 747.1 (w), 725.3 (w), 687.8 (m), 623.1 (m) cm^{-1} . GC-MS (FAB): Obs. 559.2772, calc. 559.0104. GC: 60°C $\xrightarrow{30\text{ deg/min}}$ 270°C (25 mm); t_{R} (ratio): 18.731 (1.0) : 19.413 (1.2) : 19.880 (9.4) 20.284 (9.3) min.

Dimethyl 3-(2-methoxy-2-oxoethyl)-4-{3-trimethylsilyl)-1-propenyl}-1,1-cyclopentadecarboxylate (**5b**): Triethyl borane [1.5 mL, 0.1 M in hexanes] was added to a solution of TTMS [174 mg, 0.68 mmol] and triene **2b** [200 mg, 0.68 mmol] in freshly distilled benzene (7 mL). The reaction mixture was stirred at room temperature overnight, then the reaction was quenched (H_2O). Although some starting material remaining. The aqueous phase was extracted with EtOAc (2 x 20 mL) and dried over MgSO_4 . The desired product **5b** was isolated by flash column chromatography (Hex :

EtOAc, gradient 0 - 8%, +4%) in 46% yield, and 4% of the starting material was recovered. $R_f = 0.3$, Hex : EtOAc (8 : 1) $^1\text{H NMR}$: δ 5.4 (m, 1 H), 5.1 (m, 1H), 3.7 (m, 1H), 3.6 (s, 3H), 2.74 - 2.26 (complex absorption, 4H), 2.2 - 1.8 (complex absorption, 4H), 1.7 - 1.6 (m, 2H), 0.12 (d, 27H) ppm. GC: 60°C $\xrightarrow{25\text{ deg/min}}$ 250°C (35 mm); t_R (ratio): 32.267 (1.0): 34.178 (1.2): 35.627 (30): 36.723 (23) min.

Dimethyl 3-isopropyl-4-(3-trimethylsilyl)-1-propenyl)-1,1-cyclopentadecarboxylate (**5c**): Triene **2c** [70 mg; 0.26 mmol] was added to a solution of AIBN [8.5 mg; 0.05 mmol] in toluene (3 mL), followed immediately by addition of TTMS [86.6 mg; 0.34 mmol]. The resulting solution was degassed for 40 min and then stirred at $90 - 100^\circ\text{C}$. The reaction monitored by thin-layer chromatography was complete in 3 h. After flash column chromatography (Hex : EtOAc, gradient 0 - 2.5%, + 0.3%) the cyclic compound **5c** was isolated in a 31% yield. $R_f = 0.52$, Hex : EtOAc (97 : 3) $^1\text{H NMR}$ (CDCl_3 , 500MHz): δ 5.4(m, 1H), 5.1 (d, $J = 15.5$, 8.5, 1H), 3.7 (s, 6H), 2.7 - 1.6 (complex absorption, ca 9H), 0.89 (d, $J = 6.5$, 3H), 0.79 (d, $J = 7.0$, 3 H), 0.15 (s, ca 27H) ppm. $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 173.27, 130.42, 58.67, 58.40, 57.99, 52.76, 52.68, 52.60, 51.14, 46.07, 41.12, 41.07, 40.09, 34.93, 29.69, 28.92, 27.99, 22.19, 17.10, 13.08, 13.02 ppm.

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