

Supporting Information

Palladium-Catalyzed Medium-Ring Formation for Construction of the Core Structure of *Laurencia* Oxacycles: Synthetic Study of Laurendecumallene B

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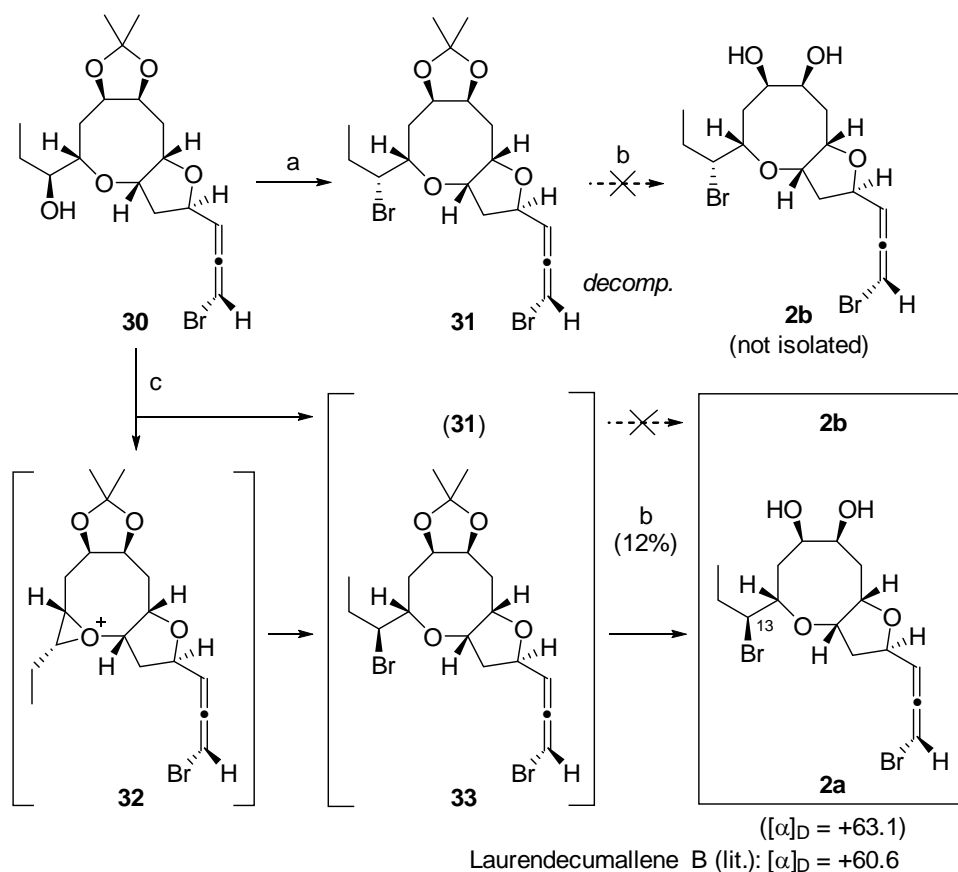
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Determination of the Relative Configuration of **28**

It is well established that the relative configurations of the propargylic position and the neighboring 2-position of the related tetrahydrofuran-substituted propargyl alcohol derivatives can be unambiguously predicted based on their ^1H NMR vicinal coupling constants; the *erythro* isomers generally show smaller vicinal coupling constants ($J = 2\text{--}4$ Hz) than the corresponding *threo* isomers ($J = 6\text{--}8$ Hz).^{1a} In this case, the corresponding trisylate **29** was assigned as the *erythro* isomer on the basis of the small coupling constant between the H_3 and H_4 protons ($J = 3.4$ Hz). The optical rotation value of the bromoallene **30** ($[\alpha]_{\text{D}} = +68.4$) supports the observed Felkin–Anh-type diastereoselectivity in the formation of **28** ($[\alpha]_{\text{D}} = -2.6$), which is in agreement with the results reported by Overman and Kim.¹

Toward Total Synthesis of Laurendecumallene **B** (Scheme S1)

It was important to note that the bromine atom should be introduced with both retention and inversion of the configuration at the C-13 position, because the stereochemistry at this position had not yet been elucidated. In other total syntheses of this class of haloethers, the introduction of the bromo substituent has typically been accomplished by direct $\text{S}_{\text{N}}2$ displacement of the corresponding alcohol with $\text{Oct}_3\text{P-CBr}_4$ in heated toluene, with inversion of the configuration.^{1b,2,3a} Treatment of alcohol **30** with $\text{Oct}_3\text{P-CBr}_4$ in heated toluene resulted in clean conversion to the corresponding bromide of the possible structure **31** (monitored by TLC). However, subsequent deprotection by AcOH at $80\text{--}90^\circ\text{C}$ for 75 min led to decomposition of the bromination product without isolation of **2b**. Analysis of the crude reaction mixture did not indicate the presence of laurendecumallene **B** or its isomer. This suggested that the possible isomer **2b** and/or its precursor **31** are unstable under the deprotection conditions. We next investigated other bromination conditions, based on Murai's report.^{3a} They reported that the bromination of related alcohols bearing the core structure of *Laurencia* oxacycles with dppe-Br_2 in the presence of 2,6-lutidine and tetrabutylammonium bromide (TBAB) affords a considerable amount of the retention product via an oxonium ion intermediate, depending on the substrate structure.³ We expected that application of the conditions using dppe to **30** would afford the corresponding bromide **31** as well as the retention product **33** (via the oxonium intermediate **32**). Exposure of **30** to the dppe -mediated bromination conditions, followed by cleavage of the acetonide with AcOH at $80\text{--}90^\circ\text{C}$ for 4 h, gave isomer **2a** (or **2b**) in 12% yield with a substantial amount of unidentified products. The inversion product **2b** and **31** might also be produced here, but they would be decomposed during the deprotection step using AcOH . In spite of our efforts for purification of **2a** (or **2b**) by repeated column chromatography and preparative TLC, it could not be isolated in a pure form. The ^1H NMR spectrum and optical rotation value ($[\alpha]_{\text{D}} = +63.1$; lit⁴: $[\alpha]_{\text{D}} = +60.6$) of **2a** (or **2b**) corresponded well with those of the natural product **2**. Unfortunately, we could not isolate the protected bromide **33** because of its instability.



Scheme S1. Toward Total synthesis of laurendecumallene B.

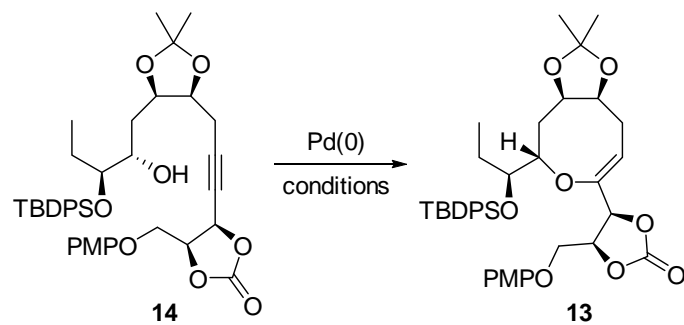
Reagents and conditions: (a) Oct₃P, CBr₄, toluene, rt to 70 °C; (b) AcOH/H₂O/THF (5:1:1), 80–90 °C; (c) dppe, Br₂, 2,6-lutidine, TBAB, CH₂Cl₂, rt.

Abbreviations: dppe = 1,4-bis(diphenylphosphino)ethane. TBAB = tetrabutylammonium bromide.

- (1) (a) Grese, T. A.; Hutchinson, K. D.; Overman, L. E. *J. Org. Chem.* **1993**, *58*, 2468–2477. (b) Jeong, W.; Kim, M. J.; Kim, H.; Kim, S.; Kim, D.; Shin, K. *J. Angew. Chem., Int. Ed.* **2010**, *49*, 752–756.
- (2) (a) Sasaki, M.; Oyamada, K.; Takeda, K. *J. Org. Chem.* **2010**, *75*, 3941–3943. (b) Kim, M. J.; Sohn, T.; Kim, D.; Paton, R. S. *J. Am. Chem. Soc.* **2012**, *134*, 20178–20188. (c) Kim, H.; Lee, H.; Lee, D.; Kim, S.; Kim, D. *J. Am. Chem. Soc.* **2007**, *129*, 2269–2274. (d) Kim, B.; Lee, M.; Kim, M. J.; Lee, H.; Kim, S.; Kim, D.; Koh, M.; Park, S. B.; Bum, S. B.; Shin, K. *J. Am. Chem. Soc.* **2008**, *130*, 16807–16811.
- (3) (a) Fujiwara, K.; Kobayashi, M.; Awakura, D.; Murai, A. *Synlett* **2000**, 1187–1189. See also, (b) Bratz, M.; Bullock, W. H.; Overman, L. E.; Takemoto, T. *J. Am. Chem. Soc.* **1995**, *117*, 5958–5966. (c) Fujiwara, K.; Tsunashima, M.; Awakura, D.; Murai, A. *Tetrahedron Lett.* **1995**, *36*, 8263–8266.
- (4) Ji, N. Y.; Li, X. M.; Li, K.; Wang, B. G. *J. Nat. Prod.* **2007**, *70*, 1499–1502.

Detailed Results of the Palladium-Catalyzed Cyclization

Table S1. Palladium-Catalyzed Cyclization of **14**.^a



entry	solvent	catalyst (mol %)	ligand (mol %)	H ₂ O (equiv)	yield (%) ^b
1	MeOH	Pd ₂ (dba) ₃ (30)	dppf (60)	0	0
2	DMF	Pd ₂ (dba) ₃ (30)	dppf (60)	0	14
3	DMF	Pd ₂ (dba) ₃ (30)	dppf (60)	3	40
4 ^c	DMF	Pd ₂ (dba) ₃ (20)	dppf (60)	10	9
5	DMF	Pd ₂ (dba) ₃ (30)	dppf (80)	2	44
6 ^d	DMF	Pd ₂ (dba) ₃ (30)	dppf (80)	2	58
7	DMSO	Pd ₂ (dba) ₃ (30)	dppf (80)	2	25
8	DMA	Pd ₂ (dba) ₃ (30)	dppf (80)	2	ND
9	acetone	Pd ₂ (dba) ₃ (30)	dppf (80)	2	ND
10	dioxane	Pd ₂ (dba) ₃ (30)	dppf (80)	2	ND
11	DMF	Pd ₂ (dba) ₃ (30)	dppb (80)	2	ND
12	DMF	Pd ₂ (dba) ₃ (30)	xantphos (0.8)	2	ND
13	DMF	[Ir(cod)Cl]₂ (30)	dppf (80)	2	ND
14	DMF	[Pd(allyl)Cl]₂ (30)	dppf (80)	2	ND

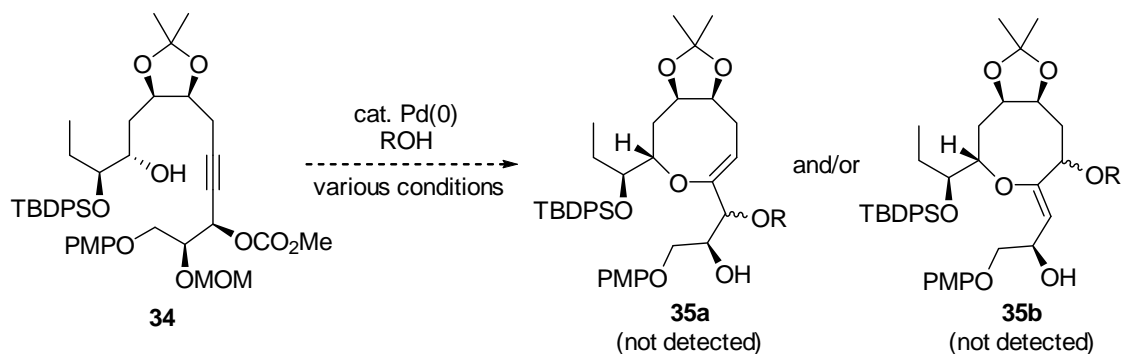
^a Unless otherwise noted, the reactions were carried out at 50 °C in 10 mg scale.

^b ND = not detected.

^c The reaction was carried out at 70 °C.

^d The reaction was carried out in a 100 mg scale.

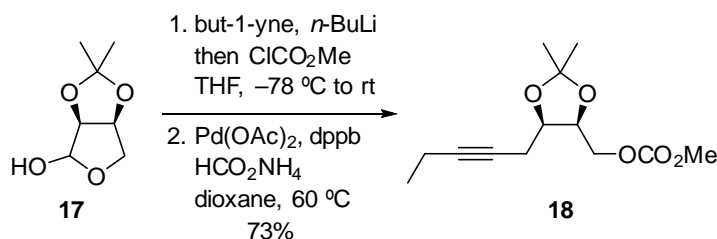
The palladium-catalyzed cyclization of the carbonate **34** was also investigated. In all cases examined, only slow decomposition of the starting material was observed, without detecting the desired cyclization products **35a/35b**.



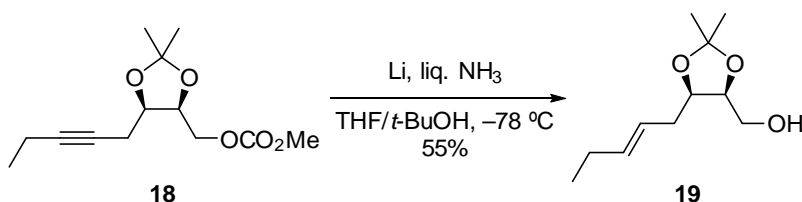
Scheme S2. Unsuccessful Palladium-Catalyzed Cyclization of Methyl Carbonate **34**.

Experimental Section

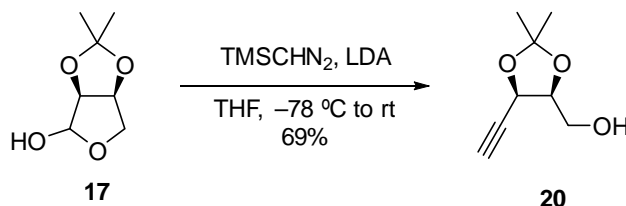
General Methods. All moisture-sensitive reactions were performed using syringe-septum cap techniques under an argon atmosphere and all glassware was dried in an oven for 2 h at 80 °C prior to use. Reactions at –78 °C employed a CO₂–MeOH bath. Melting points were measured by a hot stage melting point apparatus (uncorrected). ¹H NMR spectra were recorded at 500 or 400 MHz frequency, and chemical shifts are reported in δ (ppm) relative to TMS (in CDCl₃) as internal standard. ¹³C NMR spectra were recorded at 125 or 100 MHz frequency and referenced to the residual CHCl₃ signal. ¹H NMR spectra are tabulated as follows: chemical shift, multiplicity (b = broad, s = singlet, d = doublet, t = triplet, q = quartet, br s = broad singlet, m = multiplet), number of protons, and coupling constant(s).



[(4*S*,5*R*)-2,2-Dimethyl-5-(pent-2-yn-1-yl)-1,3-dioxolan-4-yl]methyl Methyl Carbonate (18**).** To a stirred mixture of but-1-yne (2.6 g, 48.1 mmol) in THF (40 mL) was added *n*-BuLi in *n*-hexane (1.65 M; 29 mL, 47.9 mmol) at –78 °C, and the mixture was stirred for 30 min at this temperature. To the mixture of the resulting acetylide was added dropwise a solution of **17** (2.5 g, 15.6 mmol) in THF (13 mL) at –78 °C, and the mixture was allowed to warm to room temperature. After stirring for 7 h at this temperature, ClCO₂Me was added dropwise at –78 °C and the mixture was allowed to warm to room temperature. The mixture was stirred for 20 min at this temperature and quenched by addition of saturated NH₄Cl. The whole was extracted with Et₂O, dried over MgSO₄. Concentration under reduced pressure followed by rapid filtration through a short pad of silica gel gave crude carbonate, which was used without further purification. To a stirred solution of the above carbonate in dioxane (32 mL) were added Pd(OAc)₂ (360 mg, 1.60 mmol), dppb (1.4 g, 3.29 mmol) and ammonium formate (3.0 g, 47.6 mmol) at room temperature under Ar, and the mixture was stirred for 1.5 h at 60 °C. H₂O was added to the mixture, and the whole was extracted Et₂O. The extract was washed with H₂O, and dried over MgSO₄. The filtrate was concentrated under reduced pressure to give an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (10:1) to give **18** as a colorless oil (2.9 g, 73% yield): [α]_D²⁵ –59.8 (*c* 1.42, CHCl₃); IR (neat): 2359 (C≡C), 1752 (C=O); ¹H NMR (500 MHz, CDCl₃) δ 1.12 (t, *J* = 6.9 Hz, 3H), 1.36 (s, 3H), 1.47 (s, 3H), 2.15 (qdd, *J* = 6.9, 2.3, 2.3 Hz, 2H), 2.38–2.42 (m, 1H), 2.50–2.54 (m, 1H), 3.80 (s, 3H), 4.25 (dd, *J* = 11.0, 6.9 Hz, 1H), 4.32 (ddd, *J* = 8.0, 5.5, 5.5 Hz, 1H), 4.38 (ddd, *J* = 6.9, 5.5, 4.0 Hz 1H), 4.45 (dd, *J* = 11.0, 4.0 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 12.3, 13.9, 20.3, 25.4, 27.8, 54.8, 66.3, 74.2, 75.1, 75.4, 84.2, 109.1, 155.6. *Anal.* Calcd for C₁₃H₂₀O₅: C, 60.92; H, 7.87. Found: C, 61.19; H, 8.02.



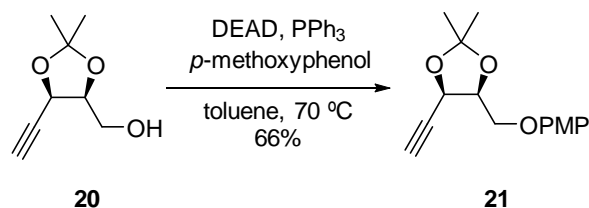
{(4*S*,5*R*)-2,2-Dimethyl-5-[(*E*)-pent-2-en-1-yl]-1,3-dioxolan-4-yl}methanol (19). Freshly cut pieces of lithium wire (380 mg, 54.2 mmol) were added in portions to liquid NH₃ (9 mL) at $-78\text{ }^\circ\text{C}$. After 10 min, a solution of **18** (695 mg, 2.71 mmol) in THF/*t*-BuOH (12 mL, 3:1) was added dropwise at $-78\text{ }^\circ\text{C}$, and the mixture was stirred at this temperature for 1 h. The reaction mixture was quenched by addition of solid NH₄Cl (2.9 g, 54.7 mmol), and the cooling bath was removed. After NH₃ has evaporated, the residue was diluted with H₂O and extracted with Et₂O. The extract was dried over MgSO₄, and the filtrate was concentrated under reduced pressure to give an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (10:1) to give **19** as a colorless oil (300 mg, 55% yield): $[\alpha]_{\text{D}}^{25} -9.6$ (*c* 1.52, CHCl₃); IR (neat): 3004 (C=C), 2962 (OH), 1752 (C=O); ¹H NMR (500 MHz, CDCl₃) δ 0.98 (t, *J* = 7.4 Hz, 3H), 1.37 (s, 3H), 1.48 (s, 3H), 1.86–1.90 (m, 1H), 1.99–2.07 (m, 2H), 2.18–2.25 (m, 1H), 2.33–2.40 (m, 1H), 3.61–3.68 (m, 2H), 4.17–4.21 (m, 2H), 5.40 (dtd, *J* = 15.5, 8.0, 1.1 Hz, 1H), 5.59 (dt, *J* = 15.5, 6.3 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 13.6, 25.5, 25.6, 28.2, 32.4, 61.7, 76.8, 77.8, 107.9, 123.7, 135.5. *Anal.* Calcd for C₁₁H₂₀O₃: C, 65.97; H, 10.07. Found: C 65.69; H, 9.86.



[(4*S*,5*R*)-5-Ethynyl-2,2-dimethyl-1,3-dioxolan-4-yl]methanol (20). By the procedure identical with that reported by Myers,⁵ the known hemiacetal **17**⁶ (14.5 g, 90.9 mmol) was converted into **20** (9.8 g, 69% yield). All spectral data were in agreement with those reported.

(5) Myers, A. G.; Goldberg, S. D. *Angew. Chem. Int. Ed.* **2000**, *39*, 2732–2735.

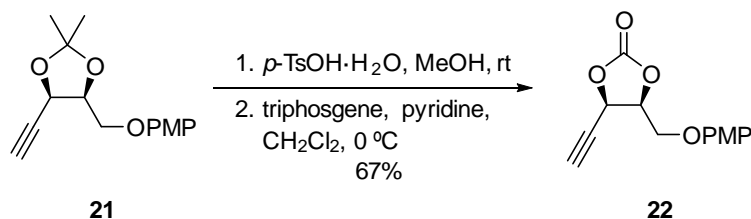
(6) Chapman, T. M.; Courtney, S.; Hay, P.; Davis, B. G. *Chem. Eur. J.* **2003**, *9*, 3397–3414.



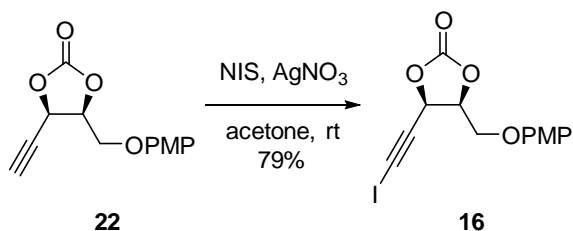
(4*R*,5*S*)-4-Ethynyl-5-[(4-methoxyphenoxy)methyl]-2,2-dimethyl-1,3-dioxolane (21).

To a stirred solution of **20** (87 mg, 0.557 mmol) in toluene (2.8 mL) were added PPh₃ (190 mg, 0.724 mmol), *p*-methoxyphenol (207 mg, 1.67 mmol) and DEAD in toluene (2.2 M; 329 μL , 0.724

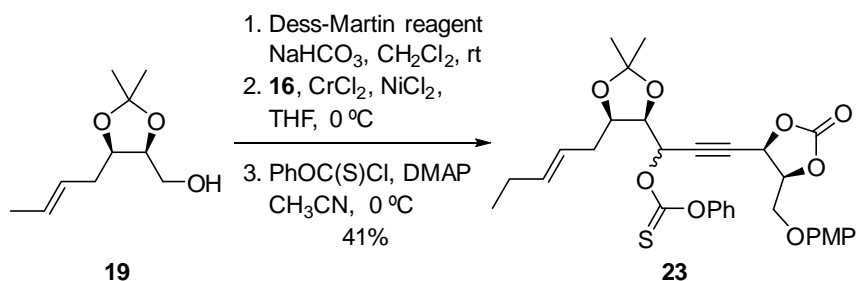
mmol) at 0 °C under argon, and the mixture was warmed to 70 °C. After stirring for 1 h at this temperature, the mixture was concentrated under reduced pressure, and diluted with Et₂O to give white precipitate, which was removed by filtration. The filtrate was concentrated under reduced pressure to give an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (10:1) to give **21** as colorless crystals (97 mg, 66% yield): mp 80 °C; [α]²⁵_D +16.3 (*c* 0.163, CHCl₃); IR (neat): 2358 (C≡C); ¹H NMR (500 MHz, CDCl₃) δ 1.41 (s, 3H), 1.58 (s, 3H), 2.52 (d, *J* = 2.3 Hz, 1H), 3.77 (s, 3H), 4.17–4.23 (m, 2H), 4.51 (dd, *J* = 12.0, 5.7 Hz, 1H), 4.94 (dd, *J* = 6.3, 2.3 Hz, 1H), 6.82–6.85 (m, 2H), 6.87–6.91 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 25.9, 27.7, 55.7, 67.6, 68.6, 75.8, 76.0, 77.1, 111.0, 114.6 (2C), 115.8 (2C), 152.7 (2C). *Anal.* Calcd for C₁₅H₁₈O₄: C, 68.68; H, 6.92. Found: C, 68.40; H, 6.92.



(4*R*,5*S*)-4-Ethynyl-5-[(4-methoxyphenoxy)methyl]-1,3-dioxolan-2-one (22). To a stirred solution of **21** (1.0 g, 3.81 mmol) in MeOH (38 mL) was added TsOH·H₂O (363 mg, 1.91 mmol) at room temperature, and the mixture was stirred for 17 h at this temperature. The mixture was quenched by addition of Et₃N (281 μ L, 3.81 mmol), and concentrated under reduced pressure to give an oily residue. Rapid filtration of the residue through a short pad of silica gel to give crude diol, which was used without further purification. To a stirred mixture of the above diol and pyridine (3.1 mL, 38.4 mmol) in CH₂Cl₂ (30 mL) was added dropwise triphosgene (1.1 g, 3.70 mmol) in CH₂Cl₂ (8 mL) at 0 °C, and stirred for 30 min at this temperature. The mixture was quenched by addition of 1N HCl at –78 °C, and the whole was extracted with CH₂Cl₂. The extract was dried over MgSO₄, and the filtrate was concentrated under reduced pressure to give an oily residue. The residue was purified by flash chromatography over silica gel with CHCl₃ to give **22** as a white solid (636 mg, 67% yield). Recrystallization from *n*-hexane–EtOAc gave pure **22** as colorless crystals: mp 125 °C; [α]²⁵_D –6.3 (*c* 0.22, CHCl₃); IR (neat): 2362 (C≡C), 1752 (C=O); ¹H NMR (500 MHz, CDCl₃) δ 2.75 (d, *J* = 2.3 Hz, 1H), 3.76 (s, 3H), 4.31–4.33 (m, 2H), 4.99–5.04 (m, 1H), 5.48 (dd, *J* = 8.0, 2.3 Hz, 1H), 6.81–6.91 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 55.7, 67.0, 68.1, 74.0, 75.6, 79.9, 114.7 (2C), 116.0 (2C), 151.8, 152.9, 154.8. *Anal.* Calcd for C₁₃H₁₂O₅: C, 62.90; H, 4.87. Found: C, 62.73; H, 4.76.

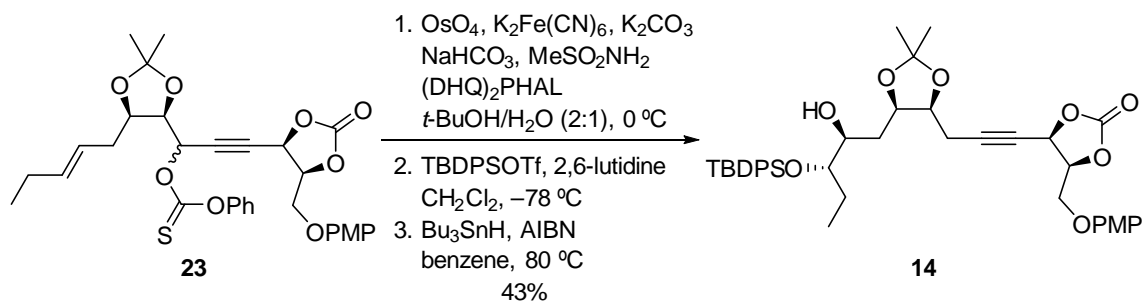


(4*R*,5*S*)-4-(Iodoethynyl)-5-[(4-methoxyphenoxy)methyl]-1,3-dioxolan-2-one (16). To the solution of **22** (630 mg, 2.54 mmol) in acetone (25 mL) were added NIS (686 mg, 3.05 mmol) and AgNO₃ (259 mg, 1.52 mmol) at room temperature, and the mixture was stirred at this temperature for 15 min. The mixture was diluted with Et₂O (25 mL) and quenched with saturated Na₂S₂O₃. Aqueous layer was separated and extracted with EtOAc, and the combined organic layer was concentrated under reduced pressure to give an oily residue. The residue was purified by flash chromatography over silica gel with CHCl₃ to give **16** as a white solid (746 mg, 79% yield), which was recrystallized from *n*-hexane–EtOAc to give colorless crystals: mp 125 °C; [α]_D²⁵ +16.2 (*c* 0.59, CHCl₃); IR (neat): 2359 (C≡C), 1811 (C=O); ¹H NMR (500 MHz, CDCl₃) δ 3.78 (s, 3H), 4.27–4.33 (m, 2H), 4.98 (dt, *J* = 7.4, 5.2 Hz, 1H), 5.59 (d, *J* = 7.4 Hz, 1H), 6.83–6.89 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 11.9, 55.8, 67.1, 69.5, 76.0, 84.5, 114.7 (2C), 116.4 (2C), 151.9, 152.8, 154.6. *Anal.* Calcd for C₁₃H₁₁IO₅: C, 41.73; H, 2.96. Found: C, 41.79; H, 2.94.



***O*-(1-((4*R*,5*R*)-2,2-Dimethyl-5-[(*E*)-pent-2-en-1-yl]-1,3-dioxolan-4-yl)-3-((4*R*,5*S*)-5-[(4-methoxyphenoxy)methyl]-2-oxo-1,3-dioxolan-4-yl)prop-2-yn-1-yl) *O*-Phenyl Carbothioate (23).** To a stirred solution of **19** (5.7 g, 28.3 mmol) in CH₂Cl₂ (280 mL) were added NaHCO₃ (7.1 g, 84.5 mmol) and Dess-Martin periodinane (18.0 g, 42.5 mmol) at room temperature, and the mixture was stirred for 15 min at this temperature, followed by quenching with saturated Na₂S₂O₃ at 0 °C. The whole was extracted with CH₂Cl₂ and the extract was dried over MgSO₄. The filtrate was concentrated under reduced pressure to give crude aldehyde as yellow oil, which was used without further purification. To a stirred solution of above aldehyde in THF (140 mL) were added **16**, CrCl₂ (13.9 g, 113 mmol) and NiCl₂ (184 mg, 1.42 mmol) at 0 °C under Ar, and the mixture was stirred for 1 h at this temperature and further 10 min at room temperature, followed by quenching with saturated NH₄Cl. The whole was extracted with Et₂O. The extract was dried over MgSO₄, and concentrated under reduced pressure to give an oily residue, which was purified by column chromatography over silica gel with *n*-hexane–EtOAc (2:1) to give crude propargyl alcohol. To the stirred mixture of above propargyl alcohol and DMAP (5.2 g, 42.6 mmol) in CH₃CN (35 mL) was added dropwise PhOC(S)Cl (5.9 mL, 42.6 mmol) in CH₃CN (35 mL) at 0 °C, and the mixture was stirred at this temperature for 10 min, followed by quenching with MeOH (3.5 mL, 86.4 mmol). Saturated NH₄Cl was added to the mixture and the whole was extracted with Et₂O. The extract was dried over MgSO₄, and concentrated under reduced pressure to give an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (4:1) to give **23** as a pale yellow amorphous (6.8 g, 41% yield): [α]_D²⁵ +3.4 (*c* 0.77, CHCl₃); IR (neat): 2963 (OH), 2362 (C≡C), 1814 (C=O), 1233 (C=S); ¹H NMR (500 MHz, CDCl₃) δ 0.97 (t, *J* = 7.4 Hz, 3H), 1.36 (s,

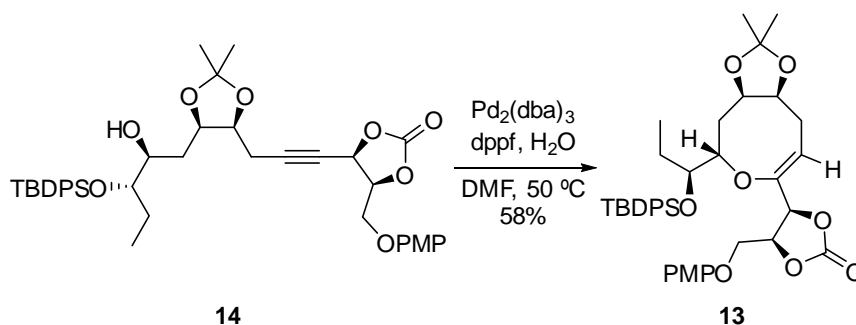
3H), 1.49 (s, 3H), 1.98–2.09 (m, 2H), 2.30–2.43 (m, 2H), 3.74 (s, 3H), 4.25–4.36 (m, 4H), 5.01–5.06 (m, 1H), 5.38–5.46 (m, 1H), 5.55–5.63 (m, 2H), 5.84 (dd, $J = 5.7, 1.7$ Hz, 1H), 6.78–6.90 (m, 4H), 7.04 (d, $J = 8.6$ Hz, 2H), 7.31 (dd, $J = 7.4, 7.4$ Hz, 1H), 7.41 (dd, $J = 7.4, 7.4$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 13.6, 25.1, 25.6, 27.4, 32.1, 55.7, 67.2, 68.1, 69.4, 72.3, 76.0, 76.1, 78.5, 85.9, 109.2, 114.7 (2C), 115.9 (2C), 121.7 (2C), 123.6, 126.9, 129.7 (2C), 135.7, 151.9, 152.9, 153.5, 154.7, 193.5; HRMS (FAB) calcd for $\text{C}_{31}\text{H}_{34}\text{NaO}_9\text{S}$ $[\text{M}+\text{Na}]^+$, 605.1821; found: 605.1825.



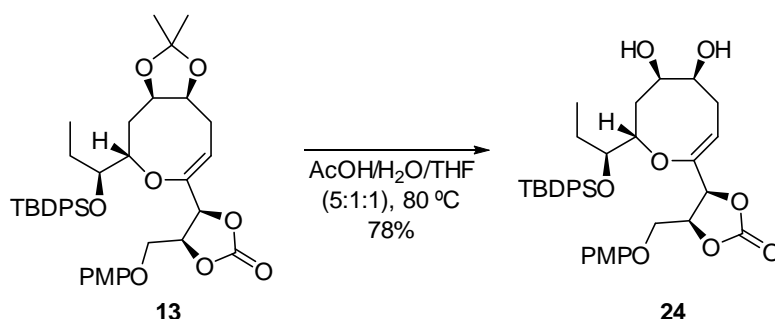
(4*R*,5*S*)-4-[3-((4*S*,5*R*)-5-((2*S*,3*S*)-3-[(*tert*-Butyldiphenylsilyl)oxy]-2-hydroxypentyl)-2,2-dimethyl-1,3-dioxolan-4-yl)prop-1-yn-1-yl]-5-[(4-methoxyphenoxy)methyl]-1,3-dioxolan-2-one (14).

To a stirred solution of **23** (6.1 g, 10.5 mmol) in $t\text{-BuOH}/\text{H}_2\text{O}$ (525 mL, 2:1) were added OsO_4 in $t\text{-BuOH}$ (2.5 w/v%, 2.1 mL, 0.207 mmol), $(\text{DHQ})_2\text{PHAL}$ (490 mg, 0.629 mmol), K_2CO_3 (4.3 g, 31.2 mmol), $\text{K}_2\text{Fe}(\text{CN})_6$ (10.3 g, 31.3 mmol), MeSO_2NH_2 (3.0 g, 31.6 mmol) and NaHCO_3 (2.6 g, 31.0 mmol) at $0\text{ }^\circ\text{C}$. The mixture was stirred at this temperature for 1.5 h, and the mixture was quenched by saturated $\text{Na}_2\text{S}_2\text{O}_3$. The whole was extracted with EtOAc , and dried over MgSO_4 . The filtrate was concentrated to give an oily residue, which was followed by rapid filtration through a short pad of silica gel to give unstable crude diol. This crude material was used without further purification. To the stirred mixture of the above diol in CH_2Cl_2 (30 mL) were added 2,6-lutidine (2.3 mL, 20.0 mmol) and TBDPSOTf (6.2 g, 16.0 mmol) in CH_2Cl_2 (10 mL) at $-78\text{ }^\circ\text{C}$, and the mixture was stirred for 3 h at this temperature. The mixture was quenched by addition of MeOH (648 μL , 16 mmol) and 1N HCl . The whole was extracted with CH_2Cl_2 , and dried over MgSO_4 . The filtrate was concentrated under reduced pressure to give an oily residue, which was followed by rapid filtration through a short pad of silica gel to give unstable silyl ether, which was used without further purification. To the stirred mixture of the above silyl ether in degassed benzene (29 mL), Bu_3SnH (4.7 mL, 17.4 mmol) and AIBN (48 mg, 0.293 mmol) were added at room temperature and warmed to $80\text{ }^\circ\text{C}$. After stirring for 40 min at this temperature, concentration under reduced pressure gave an oily residue, which was purified by flash chromatography over silica gel with $n\text{-hexane}-\text{EtOAc}$ (4:1) to give **14** as a pale yellow amorphous (3.2 g, 43% yield): $[\alpha]_D^{25} -24.6$ (c 0.35, CHCl_3); IR (neat): 2335 ($\text{C}\equiv\text{C}$), 1805 ($\text{C}=\text{O}$); ^1H NMR (500 MHz, CDCl_3) δ 0.78 (t, $J = 7.4$ Hz, 3H), 1.07 (s, 9H), 1.21 (s, 3H), 1.23–1.29 (m, 1H), 1.36 (s, 3H), 1.38–1.46 (m, 1H), 1.54–1.75 (m, 3H), 2.16–2.22 (m, 1H), 2.30 (ddd, $J = 16.6, 7.4, 1.7$ Hz, 1H), 2.78 (d, $J = 4.6$ Hz, 1H), 3.63–3.71 (m, 2H), 3.76 (s, 3H), 3.85–3.96 (m, 2H), 4.23–4.31 (m, 2H), 4.91–4.96 (m, 1H), 5.38 (ddd, $J = 7.4, 3.4, 1.7$ Hz, 1H), 6.79–6.85 (m, 2H), 6.85–6.90 (m, 2H), 7.35–7.46 (m, 6H), 7.65–7.69 (m, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ 10.0, 19.5, 21.2, 25.3, 25.5, 27.1 (3C), 28.1,

31.4, 55.6, 67.2, 68.6, 71.6, 75.7, 76.1, 76.3, 76.5, 77.2, 89.4, 108.6, 114.6 (2C), 115.9 (2C), 127.6 (4C), 129.9 (2C), 134.0 (2C), 135.9 (4C), 152.1, 153.3, 154.5; HRMS (ESI) calcd for $C_{40}H_{50}NaO_9Si$ $[M+Na]^+$, 725.3122; found: 725.3131.



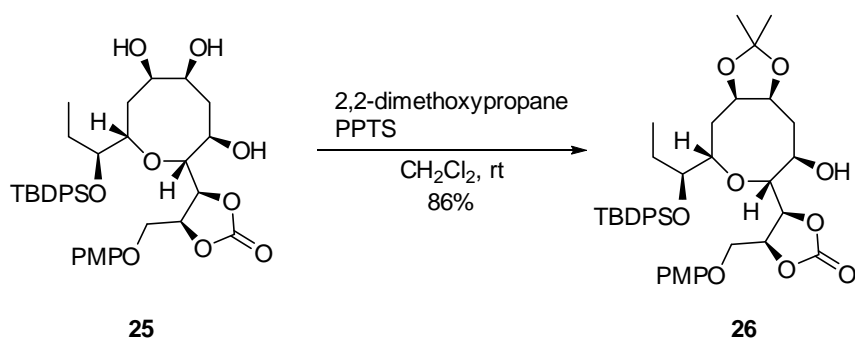
(4*S*,5*S*)-4-((3*aR*,5*S*,9*aS*,*Z*)-5-((*S*)-1-[(*tert*-Butyldiphenylsilyl)oxy]propyl)-2,2-dimethyl-4,5,9,9a-tetrahydro-3*aH*-[1,3]dioxolo[4,5-*d*]oxocin-7-yl)-5-[(4-methoxyphenoxy)methyl]-1,3-dioxolan-2-one (13). To a stirred mixture of **14** (103 mg, 0.147 mmol) in DMF (29 mL) were added H₂O (8 μ L, 0.444 mmol), Pd₂(dba)₃ (40 mg, 0.0437 mmol) and dppf (65 mg, 0.117 mmol) at room temperature under Ar. The mixture was stirred for 5 min at room temperature and further 30 min at 50 °C, followed by addition of H₂O. The whole was extracted with Et₂O, dried over MgSO₄. The extract was concentrated under reduced pressure to give an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (4:1) to give **13** as a pale yellow amorphous (61 mg, 58% yield): $[\alpha]^{25}_D$ –35.1 (*c* 0.12, CHCl₃); IR (neat): 2931 (C=C), 1814 (C=O); ¹H NMR (500 MHz, CDCl₃) δ 0.78 (t, *J* = 7.4 Hz, 3H), 1.07 (s, 9H), 1.19 (s, 3H), 1.37 (s, 3H), 1.45–1.53 (m, 1H), 1.56–1.66 (m, 1H), 1.98 (ddd, *J* = 15.5, 12.0, 6.3 Hz, 1H), 2.05 (ddd, *J* = 15.5, 8.6, 3.4 Hz, 1H), 2.16–2.27 (m, 2H), 3.74 (s, 3H), 3.79–3.84 (m, 1H), 3.84–3.89 (m, 1H), 4.05 (dd, *J* = 9.7, 5.2 Hz, 1H), 4.08–4.13 (m, 1H), 4.19 (dd, *J* = 9.7, 5.7 Hz, 1H), 4.21–4.26 (m, 1H), 4.91–4.99 (m, 3H), 6.71–6.76 (m, 2H), 6.77–6.82 (m, 2H), 7.34–7.45 (m, 6H), 7.65–7.70 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 10.8, 19.8, 25.1, 25.9, 27.2, 27.4 (3C), 28.6, 29.8, 55.9, 66.8, 75.2, 76.7 (2C), 76.8, 79.3, 79.6, 107.5, 109.3, 115.0 (2C), 115.6 (2C), 128.0 (4C), 130.0 (2C), 134.1, 134.3, 136.2 (4C), 150.0, 152.0, 153.8, 154.8; HRMS (ESI) calcd for $C_{40}H_{50}NaO_9Si$ $[M+Na]^+$, 725.3122; found: 725.3127.



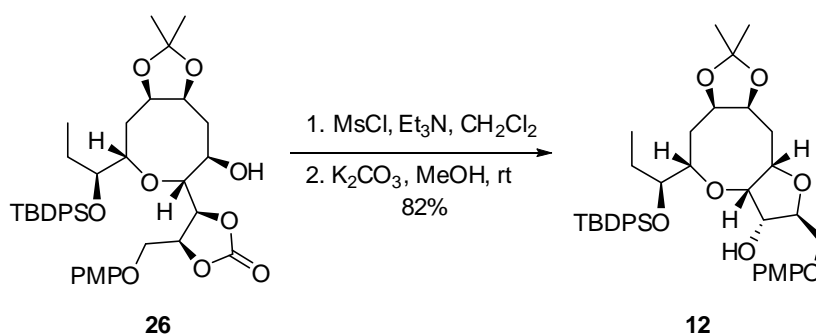
(4*S*,5*S*)-4-((2*S*,4*R*,5*S*,*Z*)-2-((*S*)-1-[(*tert*-Butyldiphenylsilyl)oxy]propyl)-4,5-dihydroxy-3,4,5,6-tetrahydro-2*H*-oxocin-8-yl)-5-[(4-methoxyphenoxy)methyl]-1,3-dioxolan-2-one (24). A mixed solvent of AcOH/THF/H₂O (24 mL, 5:1:1) was added to a flask containing **13** (840 mg, 1.19 mmol), and the mixture was stirred at 80 °C for 4 h. The mixture was concentrated under reduced pressure

to give an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (1:1) to give **24** as a colorless oil (611 mg, 78% yield): $[\alpha]_D^{25}$ –26.1 (*c* 0.93, CHCl₃); IR (neat): 3014 (C=C), 2861 (OH), 1808 (C=O); ¹H NMR (400 MHz, CDCl₃) δ 0.73 (t, *J* = 7.8 Hz, 3H), 1.07 (s, 9H), 1.41–1.54 (m, 1H), 1.57–1.72 (m, 1H), 1.95–2.06 (m, 3H), 2.47 (ddd, *J* = 16.4, 10.0, 5.0 Hz, 1H), 3.64 (ddd, *J* = 6.4, 6.4, 3.2 Hz, 1H), 3.70–3.76 (m, 1H), 3.74 (s, 3H), 3.84–3.90 (m, 1H), 4.15–4.20 (m, 1H), 4.21–4.26 (m, 1H), 4.34–4.40 (m, 1H), 4.87 (dd, *J* = 9.6, 5.0 Hz, 1H), 4.94–5.02 (m, 2H), 6.74–6.84 (m, 4H), 7.33–7.45 (m, 6H), 7.64–7.72 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 10.2, 19.4, 25.3, 27.0 (3C), 28.1, 32.8, 55.6, 66.4, 69.6, 72.4, 76.2, 76.6, 76.7, 79.1, 105.1, 114.8 (2C), 115.5 (2C), 127.6 (4C), 129.6 (2C), 133.7 (2C), 135.8 (4C), 148.0, 151.8, 153.7, 154.3; HRMS (ESI) calcd for C₃₇H₄₆NaO₉Si [M+Na]⁺, 685.2809; found: 685.2809.

(4*S*,5*S*)-4-((2*R*,3*R*,5*S*,6*R*,8*S*)-8-((*S*)-1-[(*tert*-Butyldiphenylsilyl)oxy]propyl)-3,5,6-trihydroxy-oxocan-2-yl)-5-[(4-methoxyphenoxy)methyl]-1,3-dioxolan-2-one (25). To a stirred solution of **24** (150 mg, 0.227 mmol) in THF (2.2 mL) was added dropwise BH₃·SMe₂ in THF (2.0 M, 550 μL, 2.2 mmol) at 0 °C and the mixture was allowed to warm to room temperature. After stirring for 2 h at this temperature, H₂O (2.2 mL) and NaBO₃ (347 mg, 2.27 mmol) were added to the mixture at 0 °C, and the mixture was allowed to warm to room temperature. The mixture was stirred at this temperature for 1 h, followed by quenching with saturated NH₄Cl. The whole was extracted with EtOAc. The extract was washed with H₂O and dried over MgSO₄. The filtrate was concentrated under reduced pressure to give an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (1:2) to give **25** as a colorless oil (80 mg, 49% yield): [α]_D²⁵ –29.1 (*c* 1.70, CHCl₃); IR (neat): 2938 (OH), 1805 (C=O); ¹H NMR (500 MHz, CDCl₃) δ 0.91 (t, *J* = 6.9 Hz, 3H), 1.06 (s, 9H), 1.36–1.46 (m, 1H), 1.46–1.54 (m, 1H), 1.67–1.73 (m, 2H), 1.90 (br s, 1H), 1.99 (ddd, *J* = 14.9, 6.3, 2.3 Hz, 1H), 2.07–2.16 (m, 1H), 2.25 (br s, 1H), 3.21 (br s, 1H), 3.56–3.63 (m, 1H), 3.71–3.78 (m, 2H), 3.76 (s, 3H), 3.78–3.86 (m, 2H), 3.94–4.01 (m, 1H), 4.10 (dd, *J* = 10.3, 5.2 Hz, 1H), 4.20 (dd, *J* = 10.3, 5.2 Hz, 1H), 4.69 (dd, *J* = 8.0, 4.0 Hz, 1H), 4.80–4.86 (m, 1H), 6.68–6.75 (m, 2H), 6.77–6.81 (m, 2H), 7.33–7.46 (m, 6H), 7.63–7.72 (m, 4H); ¹³C NMR (125 MHz, CD₃Cl) δ 10.8, 19.6, 24.1, 27.1 (3C), 32.9, 37.0, 55.7, 66.2, 70.2, 72.0, 72.1, 75.3, 77.1, 77.9, 78.5, 82.0, 114.8 (2C), 115.6 (2C), 127.7 (4C), 129.8 (2C), 133.8, 134.2, 136.1 (4C), 151.6, 153.7, 154.5; HRMS (FAB) calcd for C₃₇H₄₉O₁₀Si [M+H]⁺, 681.3090; found: 681.3098.

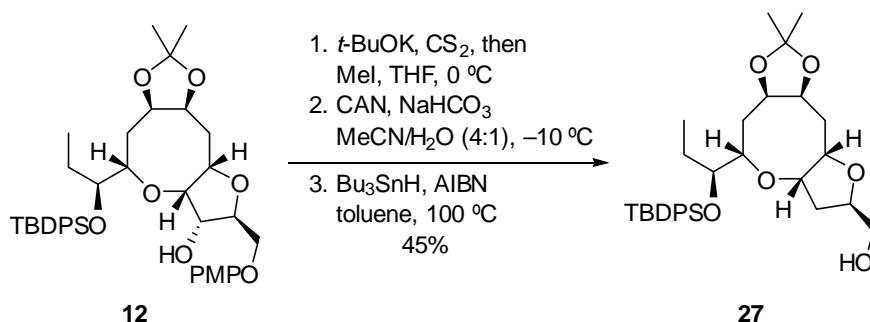


(4*S*,5*S*)-4-((3*aR*,5*S*,7*R*,8*R*,9*aS*)-5-((*S*)-1-[(*tert*-Butyldiphenylsilyl)oxy]propyl)-8-hydroxy-2,2-dimethylhexahydro-3*aH*-[1,3]dioxolo[4,5-*d*]oxocin-7-yl)-5-[(4-methoxyphenoxy)methyl]-1,3-dioxolan-2-one (26). To a stirred solution of **25** (159 mg, 0.233 mmol) in CH₂Cl₂ (2.3 mL) were added 2,2-dimethoxypropane (143 μL, 1.17 mmol) and PPTS (18 mg, 0.0717 mmol) at room temperature, and the mixture was stirred at room temperature for 11 h. The mixture was quenched by addition of diisopropylethylamine (24 μL, 0.138 mmol) and concentrated under reduced pressure to give an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (3:1) to give **26** as a colorless oil (144 mg, 86% yield): [α]_D²⁵ –21.7 (*c* 1.43, CHCl₃); IR (neat): 2933 (OH), 1806 (C=O); ¹H NMR (400 MHz, CDCl₃) δ 0.75 (t, *J* = 6.9 Hz, 3H), 1.07 (s, 9H), 1.26 (s, 3H), 1.41 (s, 3H), 1.42–1.48 (m, 1H), 1.50–1.58 (m, 1H), 1.88–1.99 (m, 3H), 2.05–2.16 (m, 1H), 3.63–3.75 (m, 7H), 4.14–4.24 (m, 2H), 4.23–4.33 (m, 2H), 4.87–4.95 (m, 2H), 6.73–6.80 (m, 4H), 7.34–7.45 (m, 6H), 7.67–7.74 (m, 4H); ¹³C NMR (100 MHz, CD₃Cl) δ 9.9, 19.5, 24.3 (2C), 25.7, 27.1 (3C), 27.4, 29.2, 55.7, 66.6, 68.8, 73.7, 75.4, 76.1, 77.2, 79.4, 79.7, 80.5, 106.5, 114.8 (2C), 115.4 (2C), 127.6 (4C), 129.7 (2C), 133.7, 133.8, 136.0 (4C), 151.7, 153.8, 154.5; HRMS (FAB) calcd for C₄₀H₅₃O₁₀Si [M+H]⁺, 721.3403; found: 721.3406.



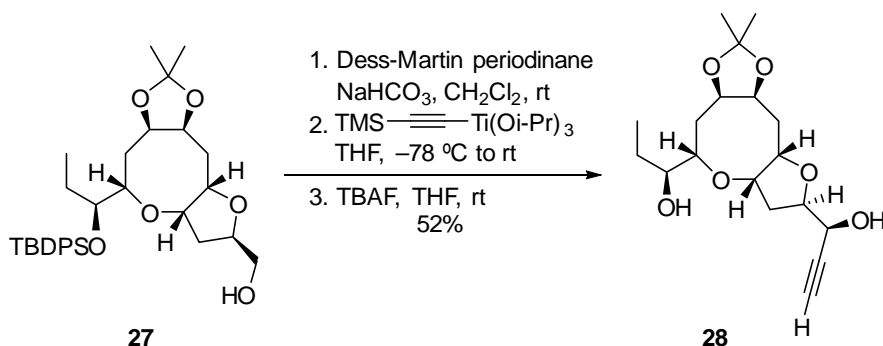
(3*aR*,5*S*,6*aS*,7*S*,8*S*,9*aS*,10*aS*)-5-((*S*)-1-[(*tert*-Butyldiphenylsilyl)oxy]propyl)-8-[(4-methoxyphenoxy)methyl]-2,2-dimethyloctahydro-3*aH*-[1,3]dioxolo[4,5-*e*]furo[3,2-*b*]oxocin-7-ol (12). To a stirred solution of **26** (140 mg, 0.194 mmol) in CH₂Cl₂ (4 mL) were added Et₃N (81 μL, 0.584 mmol) and MsCl (30 μL, 0.386 mmol) at room temperature. After stirring for 10 min at this temperature, the mixture was quenched by addition of saturated NH₄Cl. The whole was extracted with CH₂Cl₂, and the extract was dried over MgSO₄. The filtrate was concentrated under reduced pressure to give crude mesylate, which was used without further purification. To a stirred mixture of above mesylate in MeOH (4.0 mL) was added K₂CO₃ (82 mg, 0.594 mmol) at room temperature. After stirring for 30 min at this temperature, the mixture was quenched by addition of saturated

NH₄Cl. The whole was extracted with CH₂Cl₂, and the extract was dried over MgSO₄. The filtrate was concentrated under reduced pressure to give an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (3:1) to give **12** as a colorless oil (108 mg, 82% yield): [α]_D²⁵ –29.8 (*c* 1.03, CHCl₃); IR (neat), 2934 (OH); ¹H NMR (500 MHz, CDCl₃) δ 0.77 (t, *J* = 7.4 Hz, 3H), 1.09 (s, 9H), 1.28 (s, 3H), 1.32–1.39 (m, 2H) 1.38 (s, 3H), 1.99–2.14 (m, 4H), 2.91 (d, *J* = 9.7 Hz, 1H), 3.64–3.71 (m, 2H), 3.75 (s, 3H), 3.83–3.87 (m, 1H), 3.95 (dd, *J* = 10.3, 4.6 Hz, 1H), 4.04–4.10 (m, 1H), 4.12 (dd, *J* = 10.3, 2.3 Hz, 1H), 4.17–4.20 (m, 1H), 4.20–4.26 (m, 1H), 4.26–4.32 (m, 1H), 4.61–4.68 (m, 1H) 6.77–6.83 (m, 2H), 6.84–6.89 (m, 2H), 7.35–7.46 (m, 6H), 7.70 (d, *J* = 7.4 Hz, 2H), 7.76 (d, *J* = 7.4 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 7.9, 19.3, 25.3, 25.6, 27.2 (3C), 28.1, 29.2, 32.5, 55.6, 69.1, 73.3 (2C), 73.9, 74.7, 77.1, 80.1, 80.5, 82.1, 106.2, 114.5 (2C), 115.8 (2C), 127.7 (4C), 129.8 (2C), 133.7, 134.3, 135.6 (2C), 135.9 (2C), 153.1, 153.9; HRMS (FAB) calcd for C₃₉H₅₃O₈Si [M+H]⁺, 677.3504; found: 677.3510.

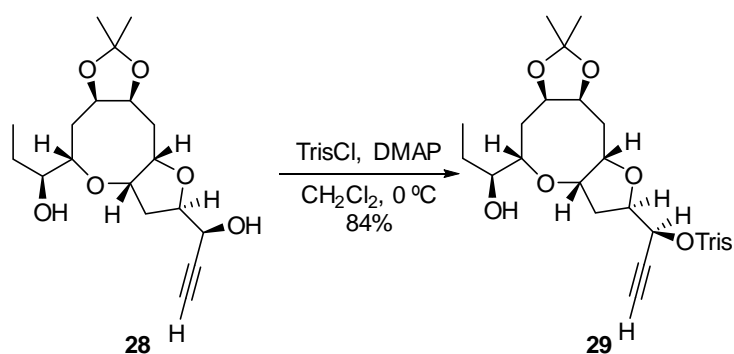


(3*aR*,5*S*,6*aS*,8*R*,9*aS*,10*aS*)-5-[(*S*)-1-[(*tert*-Butyldiphenylsilyl)oxy]propyl-2,2-dimethyloctahydro-3*aH*-[1,3]dioxolo[4,5-*e*]furo[3,2-*b*]oxocin-8-yl)methanol (**27**). To a stirred solution of **12** (35.0 mg, 0.0518 mmol) in THF (1.7 mL) were added CS₂ (15.6 μ L, 0.259 mmol) and *t*-BuOK (29.0 mg, 0.259 mmol) at –78 °C. After stirring for 10 min at room temperature, MeI (16.1 μ L, 0.256 mmol) was added to the solution. After stirring for 10 min at this temperature, the mixture was quenched by addition of saturated NH₄Cl. The whole was extracted with Et₂O, and the extract was dried over MgSO₄. The filtrate was concentrated under reduced pressure to give crude xanthate, which was used without further purification. To a stirred solution of the above crude xanthate in CH₃CN/H₂O (2.1 mL, 4:1) were added NaHCO₃ (11.0 mg, 0.131 mmol) and CAN (34.0 mg, 0.0620 mmol) at –10 °C. After stirring for 15 min at this temperature, the mixture was quenched by addition of saturated Na₂S₂O₃. The whole was extracted with EtOAc, and the extract was dried over MgSO₄. The filtrate was concentrated under reduced pressure to give crude alcohol, which was used without further purification. To the stirred mixture of above alcohol in toluene (300 μ L), Bu₃SnH (69 μ L, 0.256 mmol) and AIBN (0.4 mg, 0.00244 mmol) were added at room temperature and, and the mixture was allowed to warm to 100 °C. After stirring for 15 min at 100 °C, concentration under reduced pressure gave an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (2:1) to give **27** as a colorless oil (12.9 mg, 45% yield): [α]_D²⁵ –24.6 (*c* 1.29, CHCl₃); IR (neat): 2932 (OH); ¹H NMR (500 MHz, CDCl₃) δ 0.92 (t, *J* = 7.4 Hz, 3H), 1.06 (s, 9H), 1.27 (s, 3H), 1.38 (s, 3H), 1.39–1.51 (m, 2H), 1.64–1.74 (m, 2H), 1.81 (br s, 1H), 1.92–2.08 (m, 4H), 3.37 (dd, *J* = 11.5, 5.7 Hz, 1H), 3.50–3.55 (m, 1H), 3.63 (dd, *J* = 11.5, 3.4 Hz, 1H), 3.69–3.72

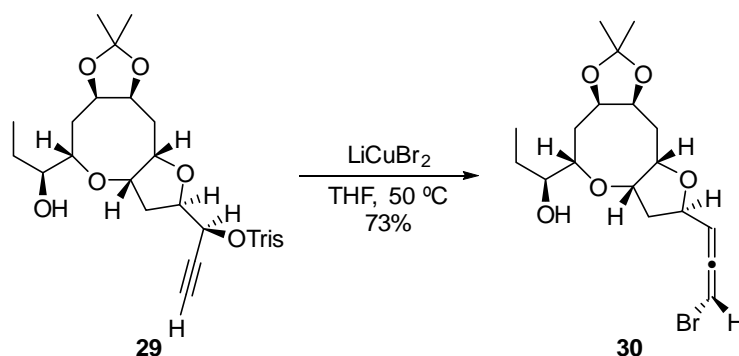
(m, 1H), 3.83–3.88 (m, 1H), 3.94–3.97 (m, 1H), 4.09–4.15 (m, 1H), 4.20 (ddd, $J = 5.2, 5.2, 5.2$ Hz, 1H), 4.53–4.58 (m, 1H), 7.33–7.45 (m, 6H), 7.01–7.75 (m, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ 8.5, 25.5, 26.8, 27.0 (3C), 27.8, 28.1, 29.6 (2C), 36.1, 73.7, 74.3, 77.3, 79.2, 80.8, 81.3, 81.4, 82.4, 106.0, 127.4 (4C), 129.5 (2C), 134.4 (2C), 136.0 (4C); HRMS (ESI) calcd for $\text{C}_{32}\text{H}_{46}\text{NaO}_6\text{Si}$ $[\text{M}+\text{Na}]^+$, 577.2961; found: 577.2959.



(S)-1-((3aR,5S,6aS,8R,9aS,10aS)-5-((S)-1-Hydroxypropyl)-2,2-dimethyloctahydro-3aH-[1,3]-dioxolo[4,5-e]furo[3,2-b]oxocin-8-yl)prop-2-yn-1-ol (28). To a stirred solution of **27** (16.5 mg, 0.0297 mmol) and NaHCO_3 (10.0 mg, 0.119 mmol) in CH_2Cl_2 (1.0 mL) was added Dess-Martin periodinane (25.0 mg, 0.0589 mmol) at room temperature. After stirring for 40 min at this temperature, the mixture was quenched by addition of saturated $\text{Na}_2\text{S}_2\text{O}_3$. The whole was extracted with CH_2Cl_2 , dried over MgSO_4 . The filtrate was concentrated under reduced pressure to give crude aldehyde, which was used without further purification. To a stirred solution of trimethylsilyl-acetylene (42 μL , 0.296 mmol) in Et_2O (1.5 mL) was added $n\text{-BuLi}$ in $n\text{-hexane}$ (1.65 M; 135 μL , 0.222 mmol) at -78°C , and the mixture was stirred for 5 min at room temperature. To the mixture of the resulting acetylide was added dropwise $\text{Ti}(\text{O}-i\text{-Pr})_3\text{Cl}$ (1.0 M in THF, 210 μL , 0.210 mmol) at -78°C . After 30 min at -78°C , the above crude aldehyde in Et_2O (1.5 mL) was added dropwise to this reagent and the mixture was allowed to warm to room temperature. After stirring for 10 min at this temperature, The mixture was filtered through a short pad of silica gel to give crude propargyl alcohol, which was used without further purification. To a above propargyl alcohol, TBAF (1.0 M in THF, 500 μL , 0.50 mmol) was added at room temperature and the mixture was warmed to 50°C . The mixture was stirred at this temperature for 5 h, which was directly purified by flash chromatography over silica gel with EtOAc to give **28** as a colorless oil (5.3 mg, 52% yield): $[\alpha]_D^{25} -2.6$ (c 0.29, CHCl_3); IR (neat): 2935 (OH), 2338 ($\text{C}\equiv\text{C}$); ^1H NMR (500 MHz, CDCl_3) δ 1.02 (t, $J = 6.9$ Hz, 3H), 1.31 (s, 3H), 1.40 (s, 3H), 1.40–1.48 (m, 1H), 1.59–1.68 (m, 1H), 1.98–2.16 (m, 5H), 2.23–2.31 (m, 1H), 2.40 (d, $J = 2.3$ Hz, 1H), 2.42 (d, $J = 2.3$ Hz, 1H), 2.44–2.49 (m, 1H), 3.36–3.42 (m, 1H), 3.51–3.58 (m, 1H), 3.92–3.97 (m, 1H), 4.13–4.18 (m, 1H), 4.25–4.35 (m, 2H), 4.45–4.50 (m, 1H), 4.54–4.63 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 9.7, 25.6, 26.0, 28.2, 30.1, 32.2, 35.8, 64.3, 73.1 (2C), 73.7, 74.3, 79.2, 80.8, 81.3, 81.4, 82.4, 106.4; HRMS (FAB) calcd for $\text{C}_{18}\text{H}_{28}\text{NaO}_6$ $[\text{M}+\text{Na}]^+$, 363.1784; found: 363.1783.



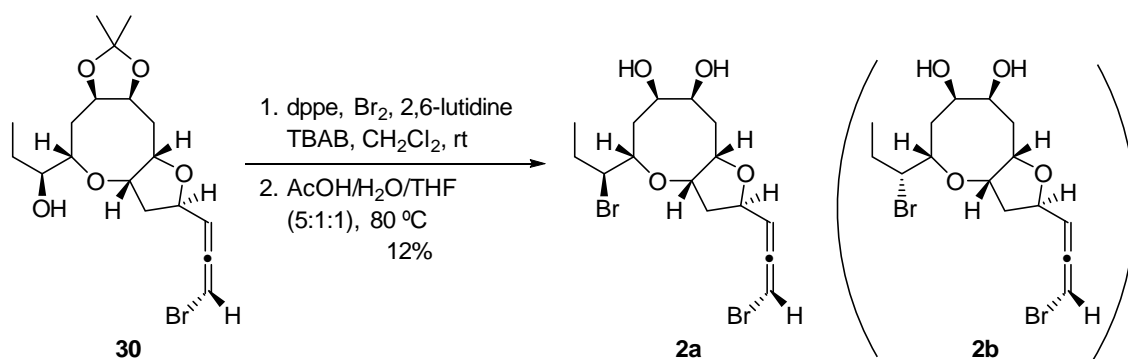
(S)-1-((3a*R*,5*S*,6a*S*,8*R*,9a*S*,10a*S*)-5-((*S*)-1-hydroxypropyl)-2,2-dimethyloctahydro-3a*H*-[1,3]-dioxolo[4,5-*e*]furo[3,2-*b*]oxocin-8-yl)prop-2-yn-1-yl 2,4,6-triisopropylbenzenesulfonate (29). To a stirred solution of **28** (15.0 mg, 0.0441 mmol) in CH₂Cl₂ (1.5 mL) were added DMAP (54.0 mg, 0.443 mmol) and TrisCl (67.0 mg, 0.221 mmol) at –30 °C, and the mixture was warmed to –20 °C. After stirring for 2 h at this temperature, the mixture was quenched by addition of MeOH. The mixture was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (2:1) to give **29** as a colorless oil (22.6 mg, 84% yield): [α]_D²⁵ +1.55 (*c* 2.26, CHCl₃); IR (neat): 2361 (C=C=C), 1349 (OSO₂); ¹H NMR (400 MHz, CDCl₃) δ 1.01 (t, *J* = 7.0 Hz, 3H), 1.19–1.49 (m, 26H), 1.57–1.68 (m, 1H), 1.93–2.07 (m, 4H), 2.07–2.15 (m, 1H), 2.17–2.25 (m, 1H), 2.27 (d, *J* = 2.3 Hz, 1H), 2.41 (d, 2.3 Hz, 1H), 2.85–2.97 (m, 1H), 3.32–3.43 (m, 1H), 3.47–3.58 (m, 1H), 3.84–3.99 (m, 1H), 4.00–4.08 (m, 1H), 4.09–4.18 (m, 1H), 4.26 (ddd, *J* = 9.8, 4.6, 4.6 Hz, 1H), 4.40 (ddd, *J* = 9.8, 6.4, 3.5 Hz, 1H), 4.51–4.59 (ddd, *J* = 9.8, 5.8, 2.3 Hz, 1H), 5.25 (dd, *J* = 3.5, 2.3 Hz, 1H), 7.16 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 9.65, 23.5 (4C), 24.6, 24.8, 25.7, 25.9, 28.2, 29.7, 30.1, 31.9, 34.2, 36.7 (2C), 71.2, 73.0 (2C), 73.6, 76.6, 77.2, 77.9, 80.6, 81.4, 81.8, 106.1, 123.7 (2C), 130.7, 150.7, 153.8 (2C); HRMS (ESI) calcd for C₃₃H₅₀NaO₈S [M+Na]⁺, 629.3124; found: 629.3123.



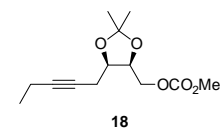
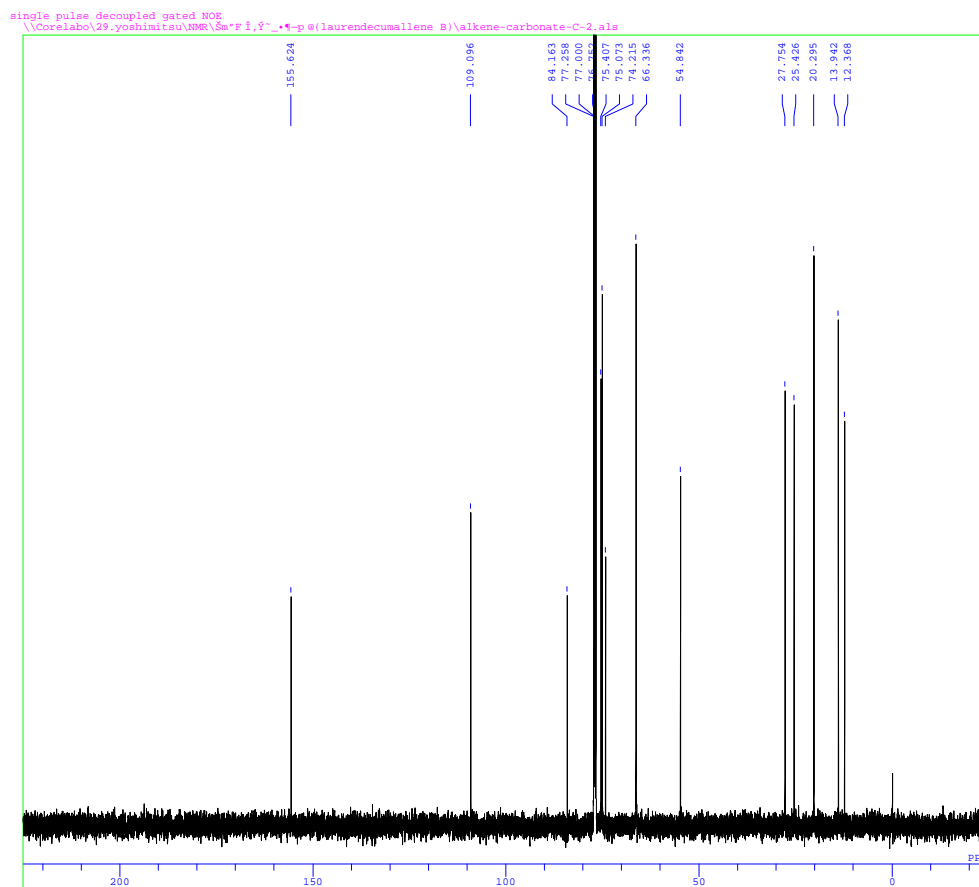
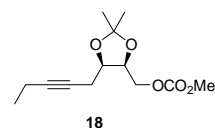
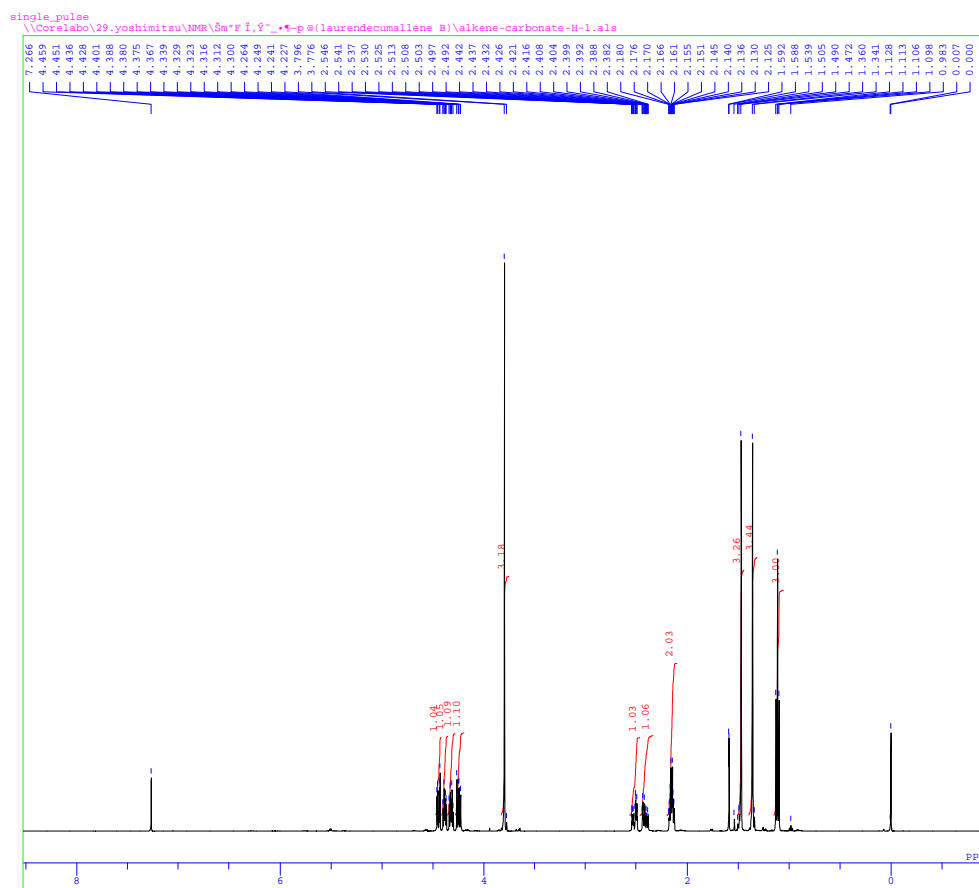
(S)-1-((3a*R*,5*S*,6a*S*,8*R*,9a*S*,10a*S*)-8-[(*S*)-3-Bromoprop-1,2-dien-1-yl]-2,2-dimethyloctahydro-3a*H*-[1,3]dioxolo[4,5-*e*]furo[3,2-*b*]oxocin-5-yl)propan-1-ol (30).

A mixture of CuBr (53.3 mg, 0.373 mmol) and LiBr (32.5 mg, 0.373 mmol) was dissolved in THF (1.8 mL) at room temperature under argon and stirred for 30 min at this temperature. To this mixture was added a solution of **29** (22.6 mg, 0.0372 mmol) in THF (1.8 mL) at room temperature. The mixture was allowed to warm to 50 °C and stirred at this temperature for 2 h, which was quenched by addition of saturated NH₄Cl. The whole was extracted with EtOAc, and the extract was dried over MgSO₄. The filtrate was concentrated under reduced pressure to give an oily residue,

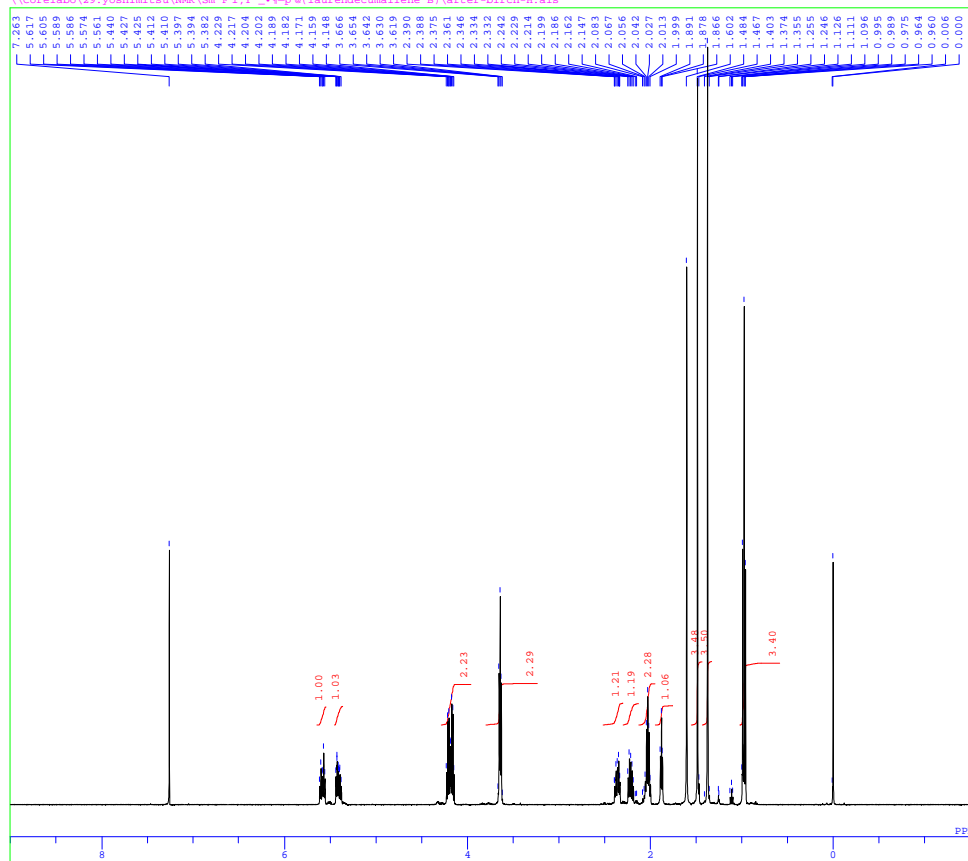
which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (2:1) to give **30** as a colorless oil (10.9 mg, 73% yield) with small amount of impurity: $[\alpha]^{25}_{\text{D}} +68.4$ (*c* 0.11, CHCl₃); IR (neat): 2931 (OH), 2355 (C=C=C); ¹H NMR (500 MHz, CDCl₃) δ 1.01 (t, *J* = 6.9 Hz, 3H), 1.32 (s, 3H), 1.40 (s, 3H), 1.40–1.50 (m, 1H), 1.57–1.69 (m, 1H), 1.94–2.16 (m, 5H), 2.15–2.24 (m, 1H), 3.34–3.43 (m, 1H), 3.49–3.57 (m, 1H), 3.89–3.99 (m, 1H), 3.99–4.06 (m, 1H), 4.26–4.34 (m, 1H), 4.52–4.63 (m, 1H), 4.73–4.81 (m, 1H), 5.48 (dd, *J* = 5.5, 5.5 Hz, 1H), 6.06 (dd, *J* = 5.5, 1.8 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 9.7, 25.6, 26.0, 28.1, 29.7, 30.3, 41.1, 73.1 (2C), 73.7, 74.0, 79.1, 81.4 (2C), 82.2, 102.3, 106.1, 201.2; HRMS (ESI) calcd for C₁₈H₂₇BrNaO₅ [M+Na]⁺, 425.0940; found: 425.0933.



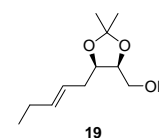
(2*R*,3*aS*,5*S*,7*R*,8*S*,9*aS*)-2-[(*S*)-3-Bromopropa-1,2-dien-1-yl]-5-[1-bromopropyl]octahydro-2*H*-furo[3,2-*b*]oxocine-7,8-diol (2*a*/2*b*) (Possible Isomers of Laurendecumallene B; not Completely Characterized). To the solution of Br₂ (3.6 mg, 0.0225 mmol) in CH₂Cl₂ (300 μ L) was added dppe (4.5 mg, 0.0113 mmol) at room temperature. After stirring for 10 min at this temperature, a mixture of **30** (2.3 mg, 0.00571 mmol), TBAB (18.4 mg, 0.0568 mmol) and 2,6-lutidine (2.6 μ L, 0.0261 mmol) in THF (200 μ L) was added to this reagent at room temperature. The mixture was stirred at this temperature for 18 h, which was filtered through a short pad of silica gel to give crude bromide, which was used without further purification. A mixed solvent of AcOH/THF/H₂O (560 μ L, 5:1:1) was added to a flask containing the above bromide and the mixture was stirred at 80 °C for 4 h. The mixture was concentrated under reduced pressure to give an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (1:1) to give crude **2a** (or **2b**) containing some impurities as a colorless oil (0.3 mg, 12% yield); $[\alpha]^{25}_{\text{D}} +63.1$, (*c* 0.03, CHCl₃), [lit $[\alpha]^{18}_{\text{D}} +60.6$ (*c* 0.33, CHCl₃)]⁴; IR (neat): 2941 (OH); ¹H NMR (500 MHz, CDCl₃) δ 1.07 (t, *J* = 7.3 Hz, 3H), 1.73–1.81 (m, 1H), 1.94–2.14 (m, 5H), 2.15–2.23 (m, 1H), 2.36–2.45 (m, 1H), 3.79–3.85 (m, 1H), 3.85–3.90 (m, 1H), 4.08–4.13 (m, 1H), 4.15–4.24 (m, 2H), 4.29–4.34 (m, 1H), 4.72–4.80 (m, 1H), 5.42–5.48 (m, 1H), 6.06 (dd, *J* = 5.5, 1.8 Hz, 1H); HRMS (ESI) calcd for C₁₅H₂₂Br₂NaO₄ [M+Na]⁺, 448.9762; found: 448.9762.



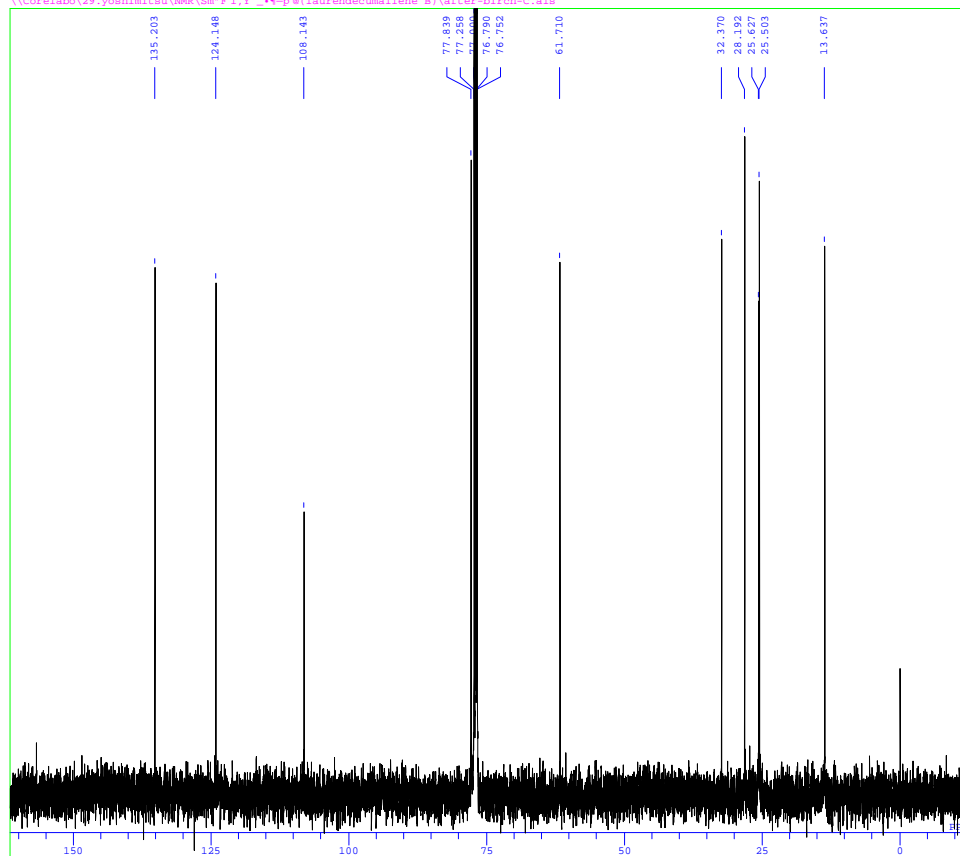
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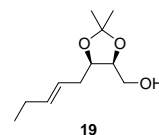
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 CTEMP 25.9 c
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 RGAIN 46



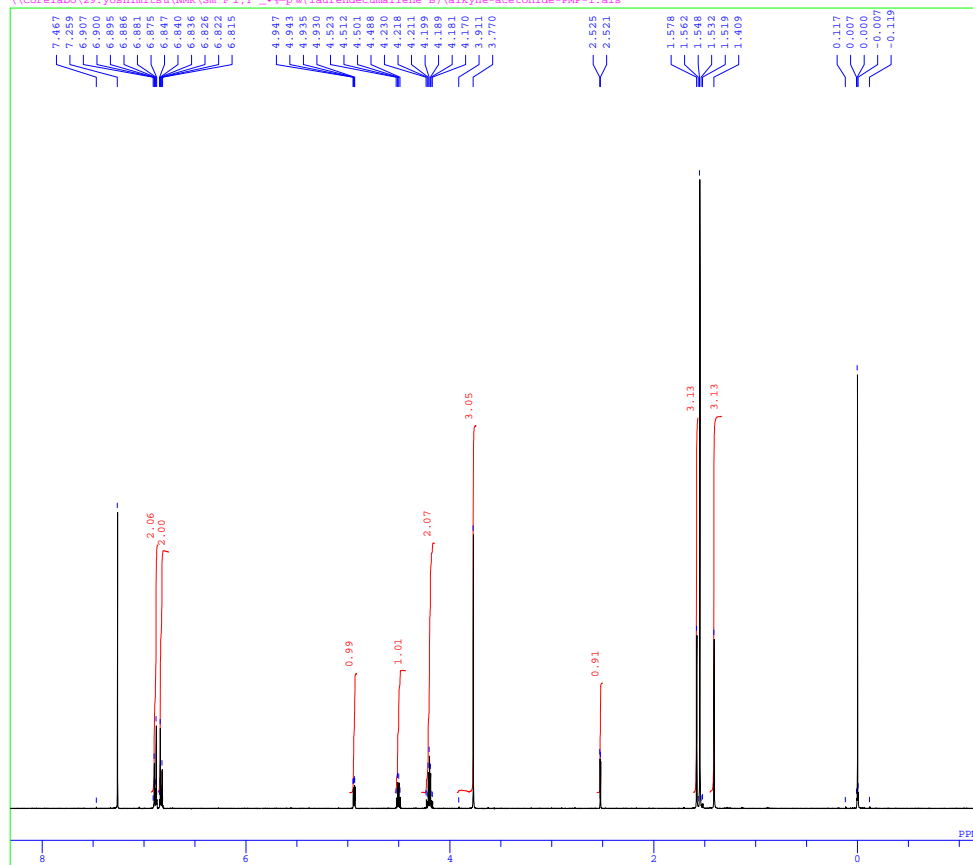
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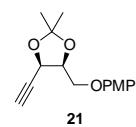
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 EXREF 77.00 ppm
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 RGAIN 54



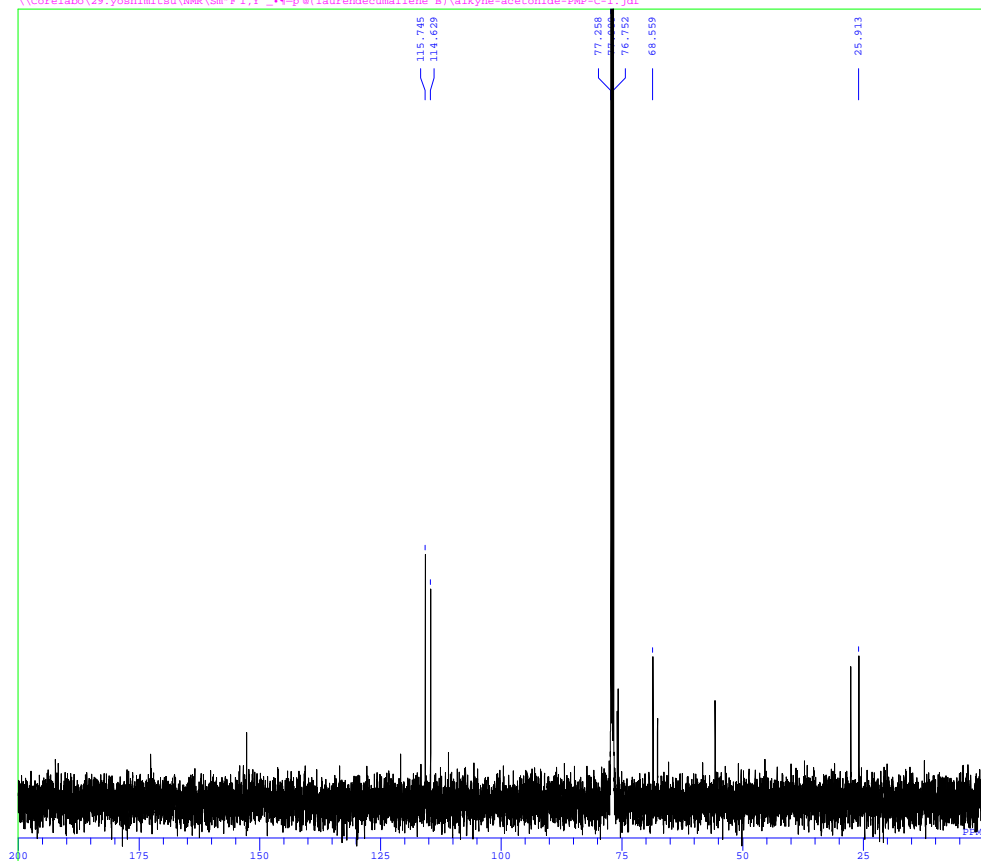
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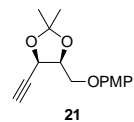
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RGAIN 52



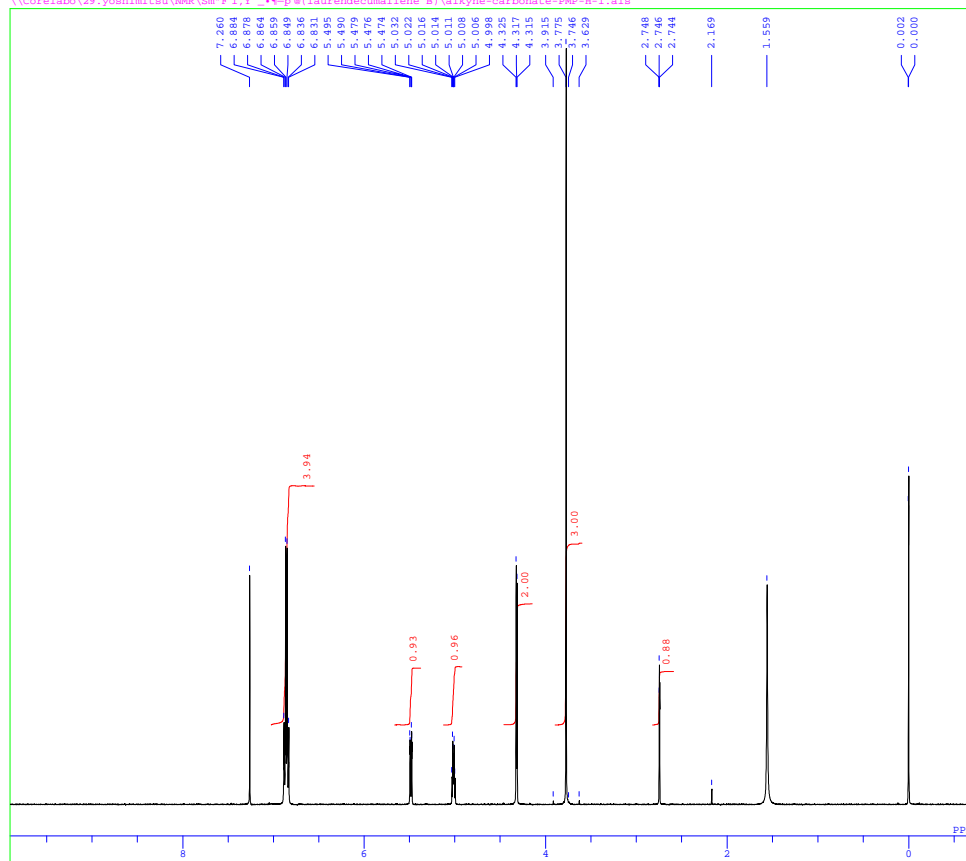
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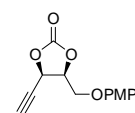
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BF 1.20 Hz
RGAIN 54



single_pulse
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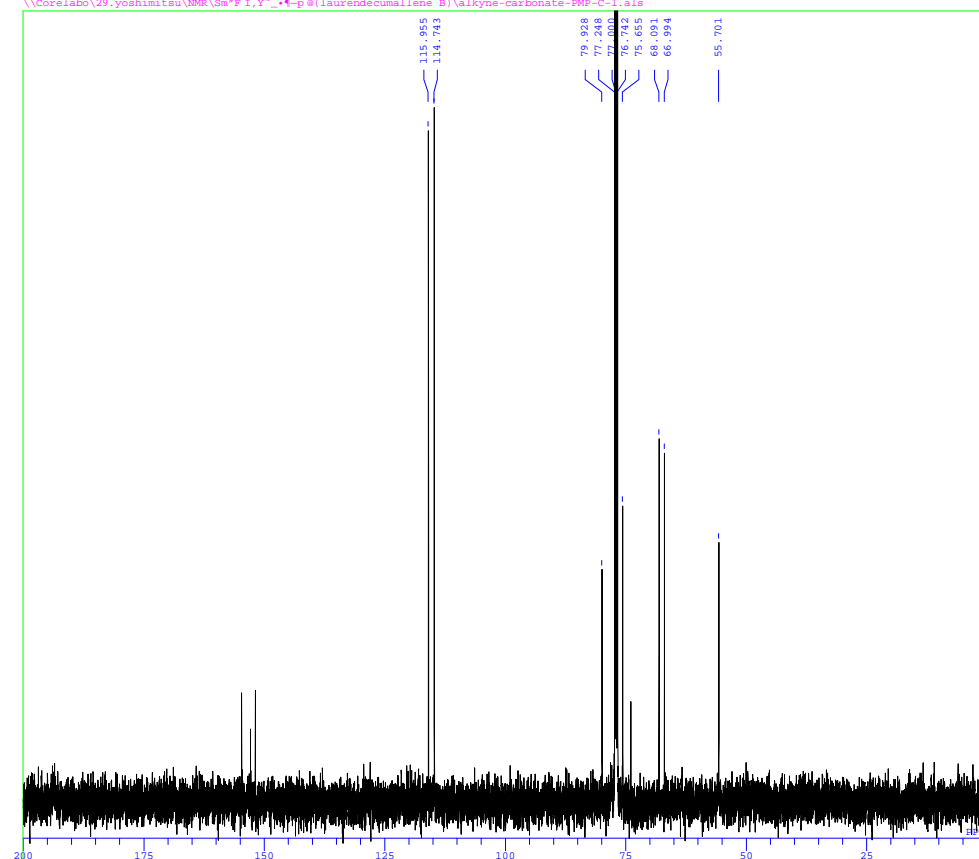


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 RF 0.12 Hz
 RGAIN 50

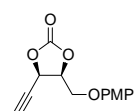


22

single_pulse decoupled gated NOE
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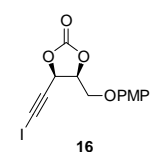
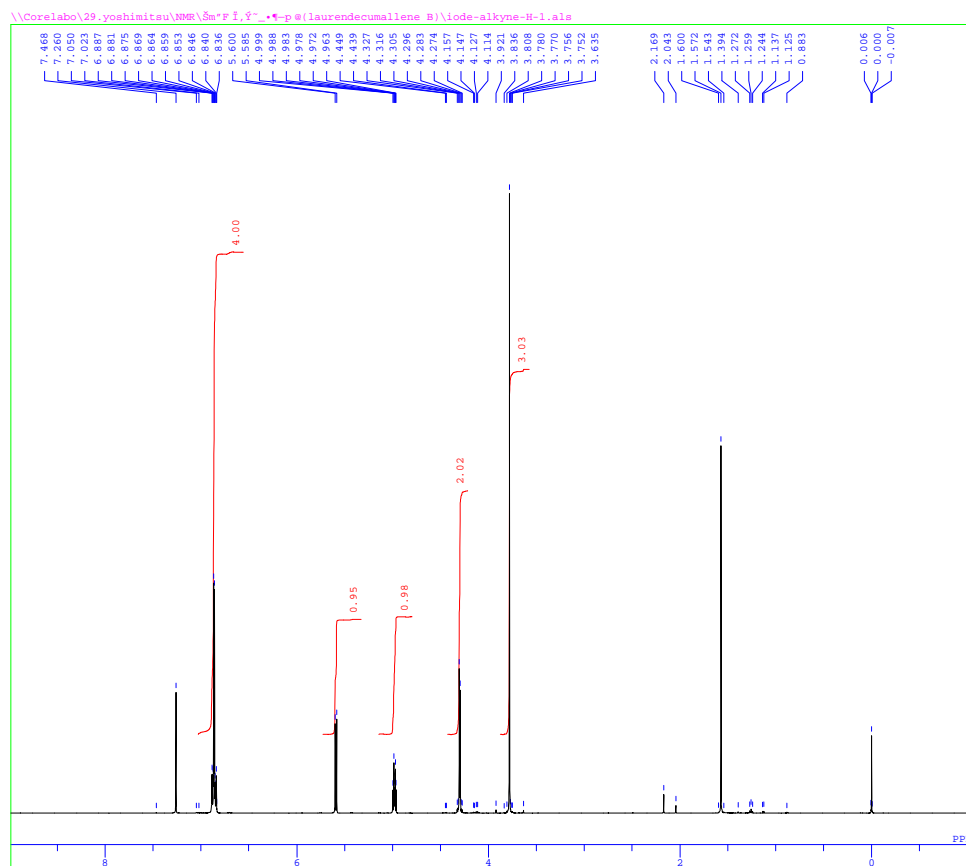


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 EXREF 77.00 ppm
 RF 1.20 Hz
 RGAIN 54

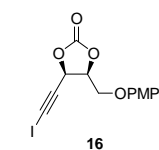
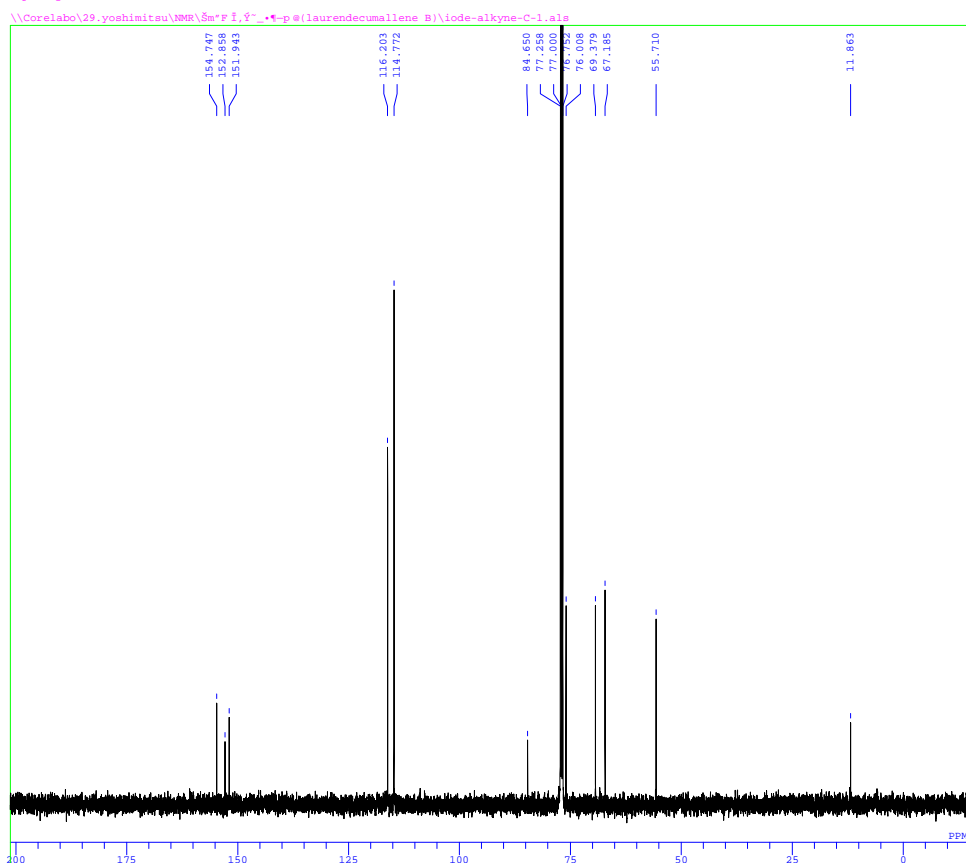


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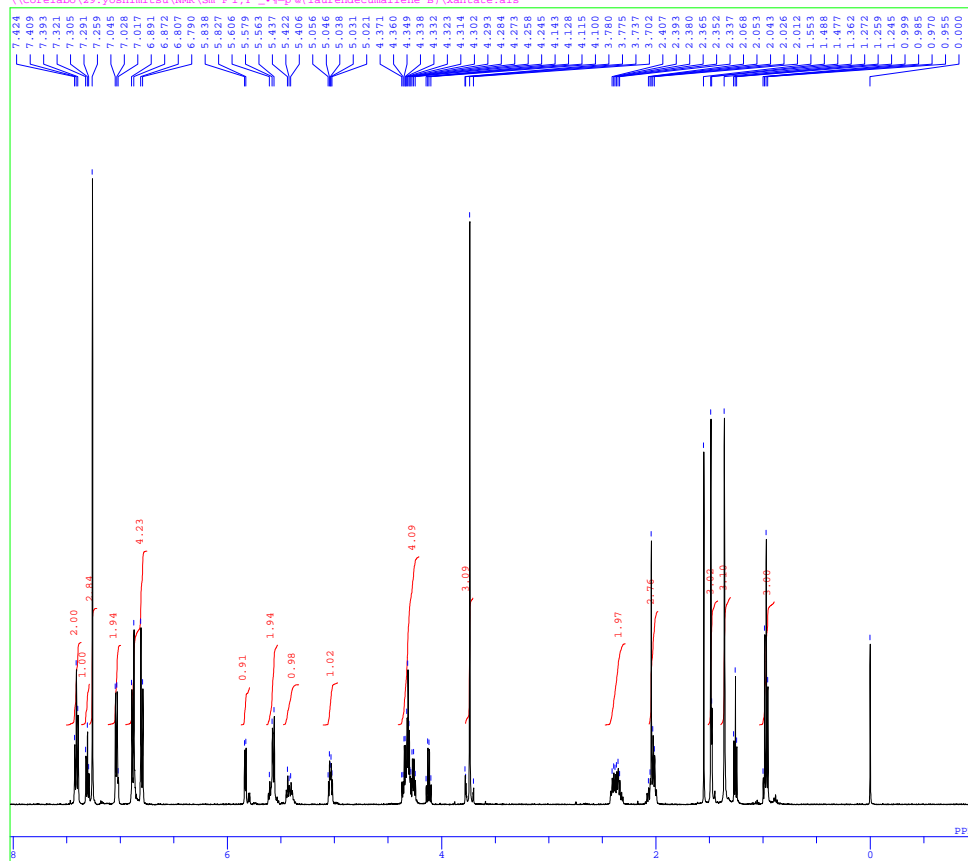
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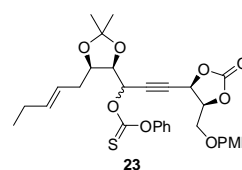
single pulse decoupled gated NOE



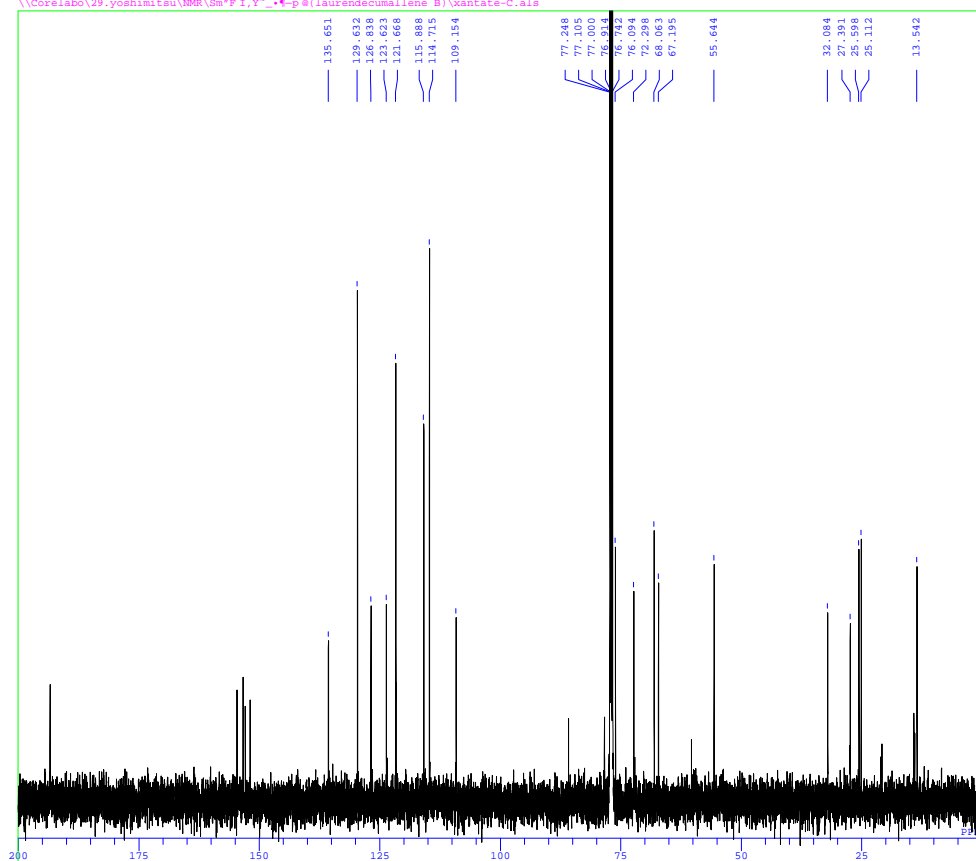
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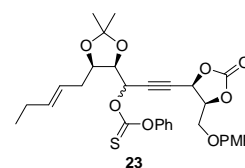
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 POINT 13107
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 RGAIN 46



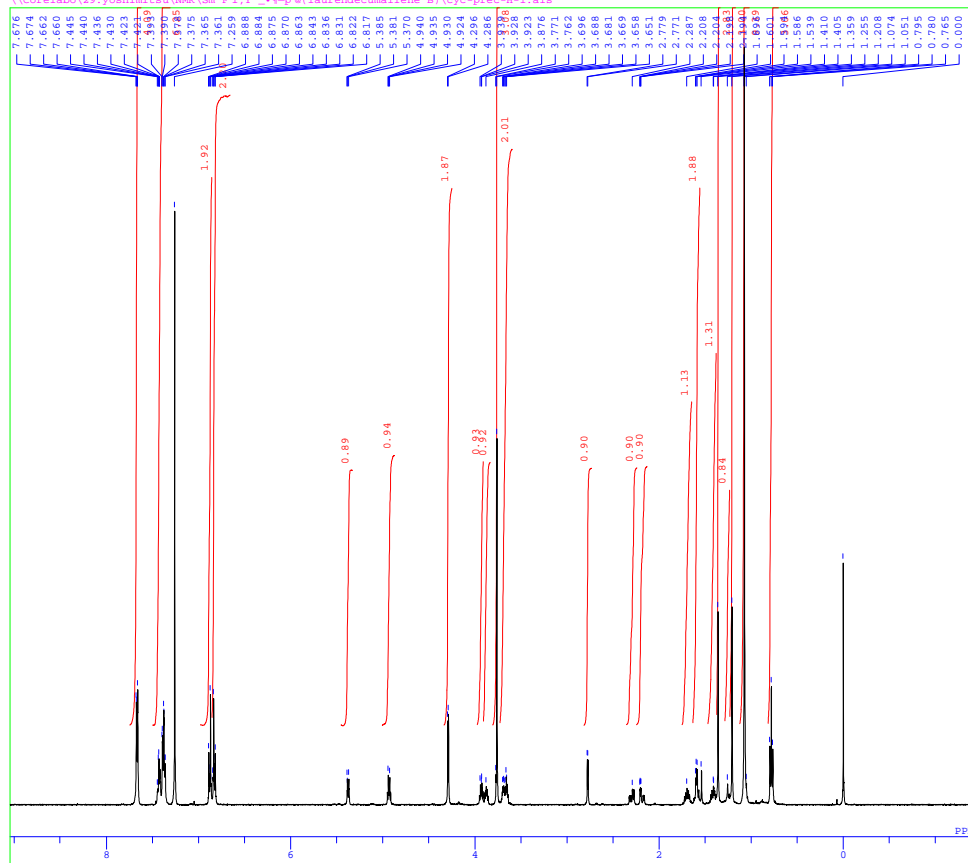
single_pulse decoupled gated NOE
 \Corelab\29.yoshimitsu\NMR\8m*F1.f*-.*-p@laurendecumallene B\kxntate-C.als



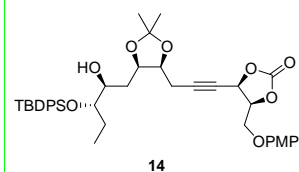
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 RGAIN 52



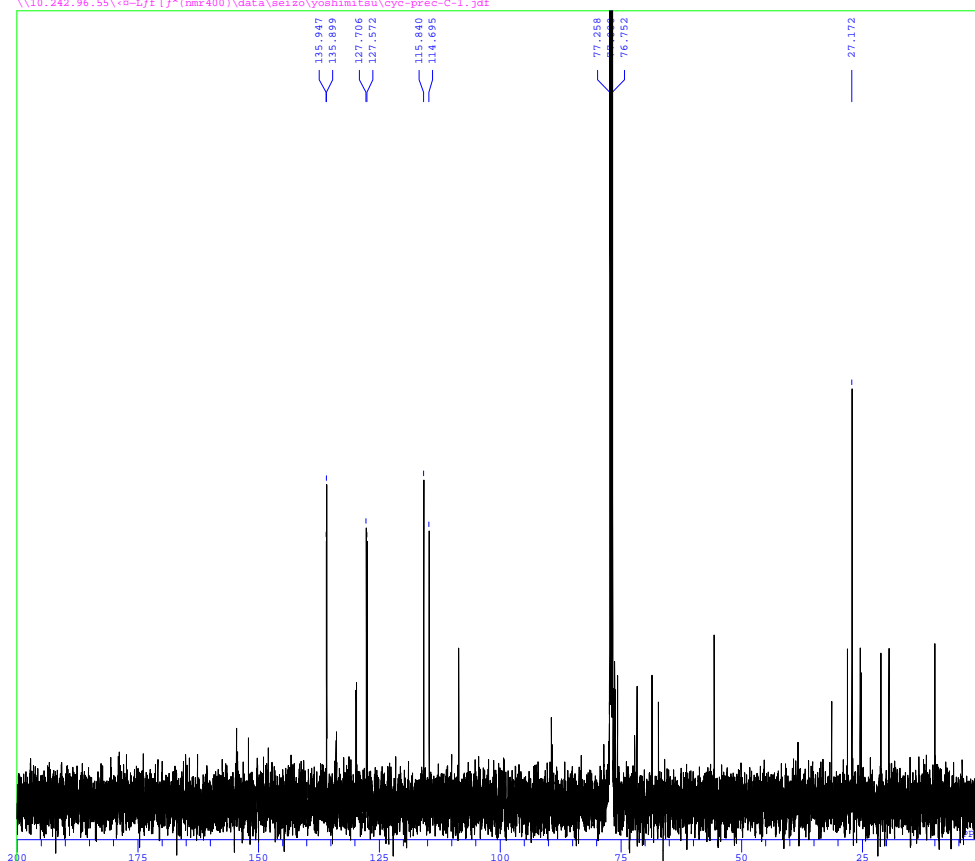
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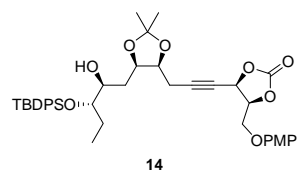
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POINT 13107
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SCANS 8
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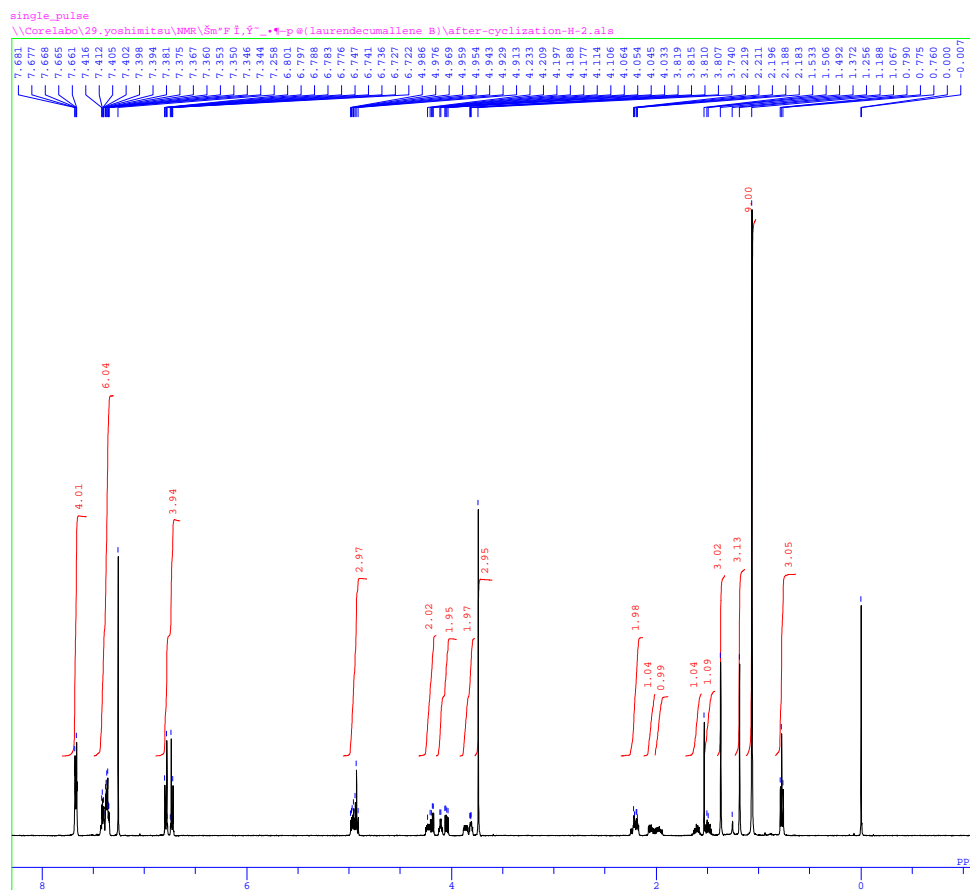


single_pulse decoupled gated NOE
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OBPIN 4.21 Hz
POINT 32768
FREQU 39308.18 Hz
SCANS 1000
AQTM 0.8336 sec
PD 2.0000 sec
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IRNUC 1H
CTEMP 26.0 c
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XREF 77.00 ppm
BF 1.20 Hz
RGAIN 54

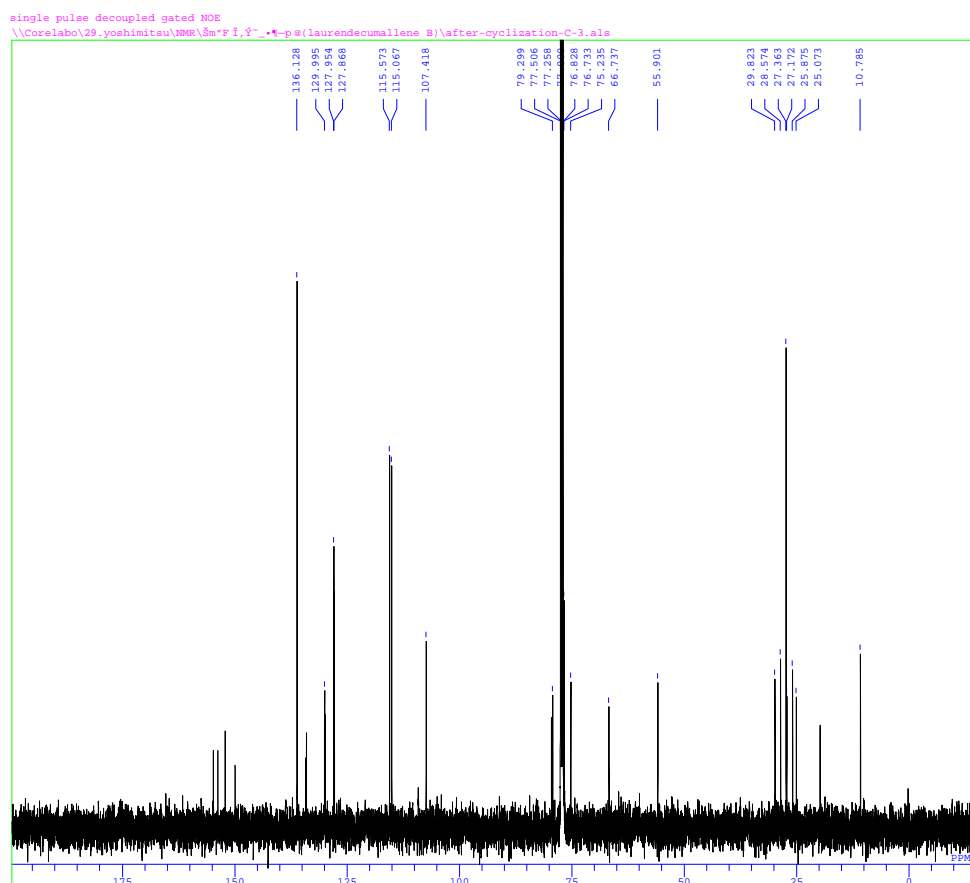
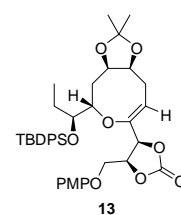




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DATIM 2012-12-18 19:47:11
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
AQTM 1.7459 sec
PD 5.0000 sec
FW 6.50 usec
IRNUC 1H
CTEMP 27.1 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 50

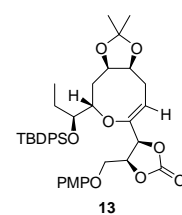
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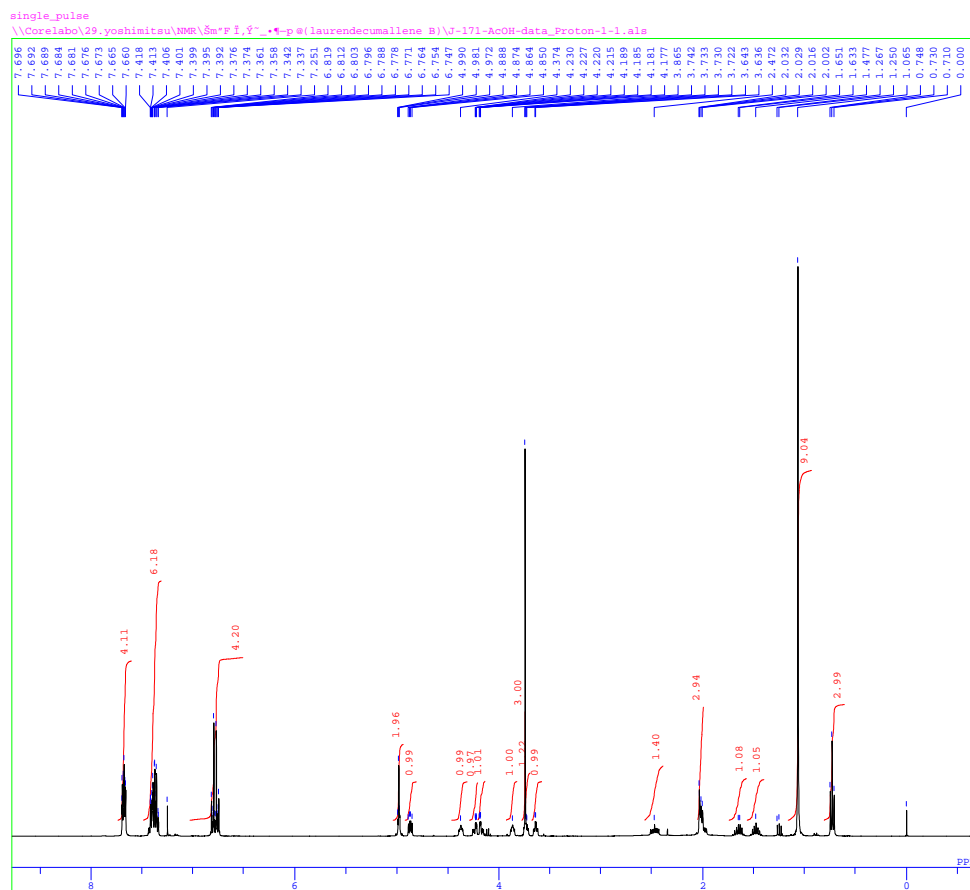


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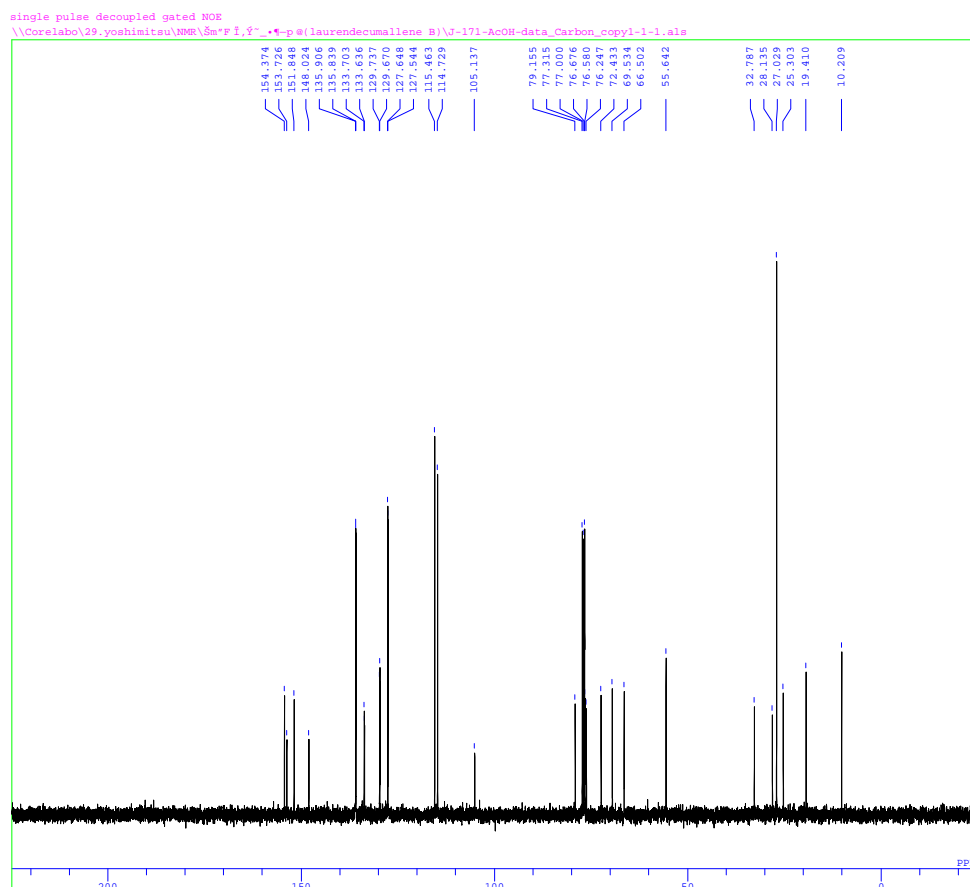
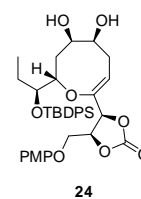
DFFILE after-cyclization-C-3.
COMNT single pulse decoupled
DATIM 2012-12-18 20:44:26
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 1200
AQTM 0.8336 sec
PD 2.0000 sec
FW 3.73 usec
IRNUC 1H
CTEMP 27.6 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 54

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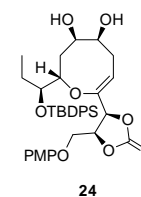


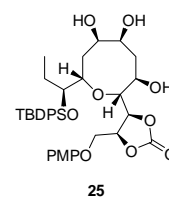
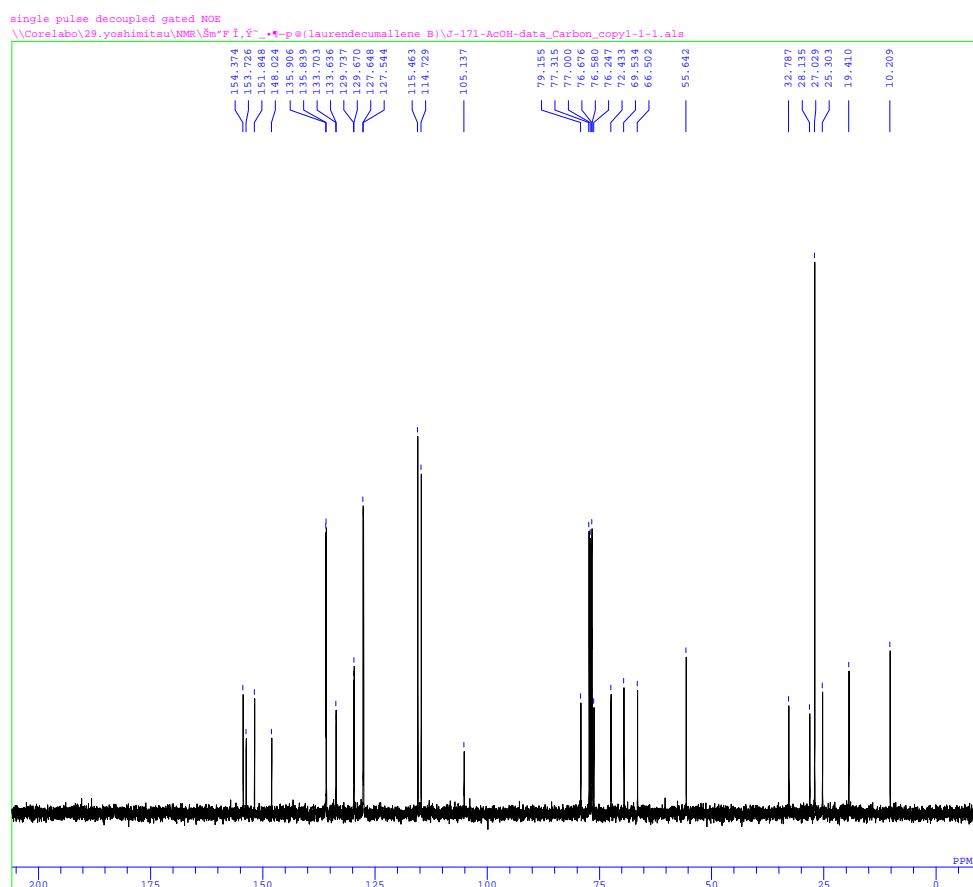
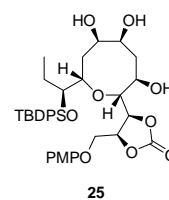
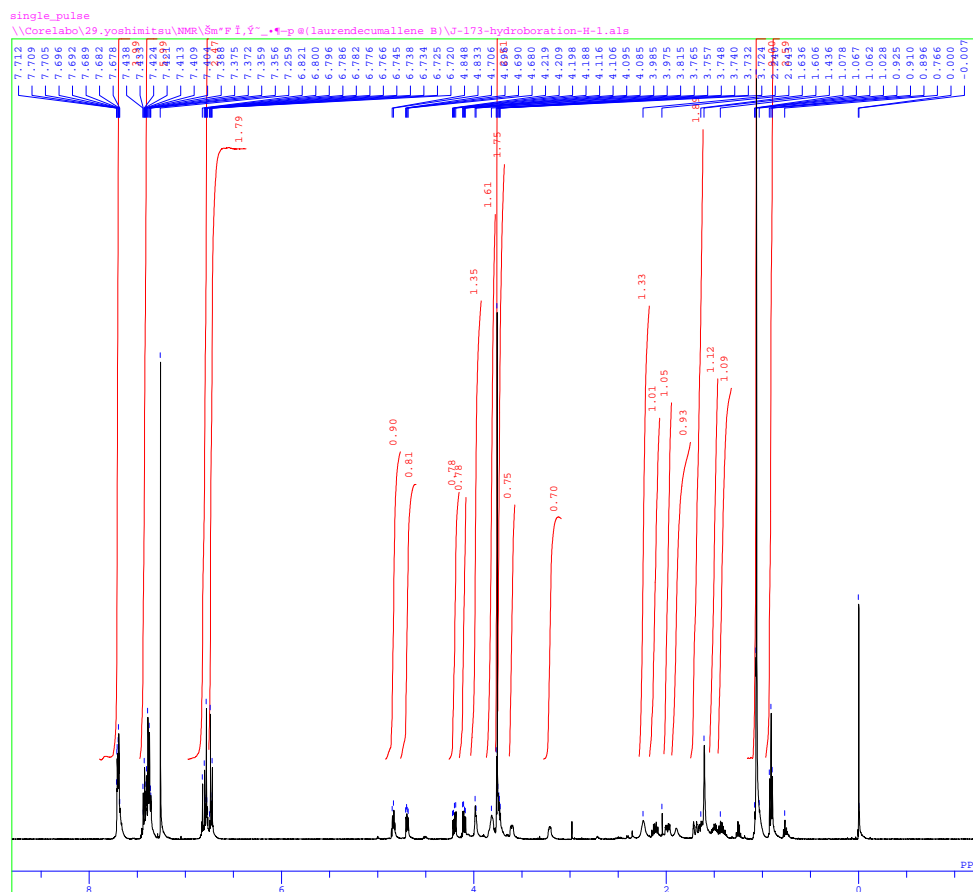


DFILE J-171-AcOH-data_Proton-
COMNT single_pulse
DATIM 2012-10-16 11:09:59
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 4
ACQTM 2.1837 sec
PD 5.0000 sec
PWL 4.65 usec
IRNUC 1H
CTEMP 24.1 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 24

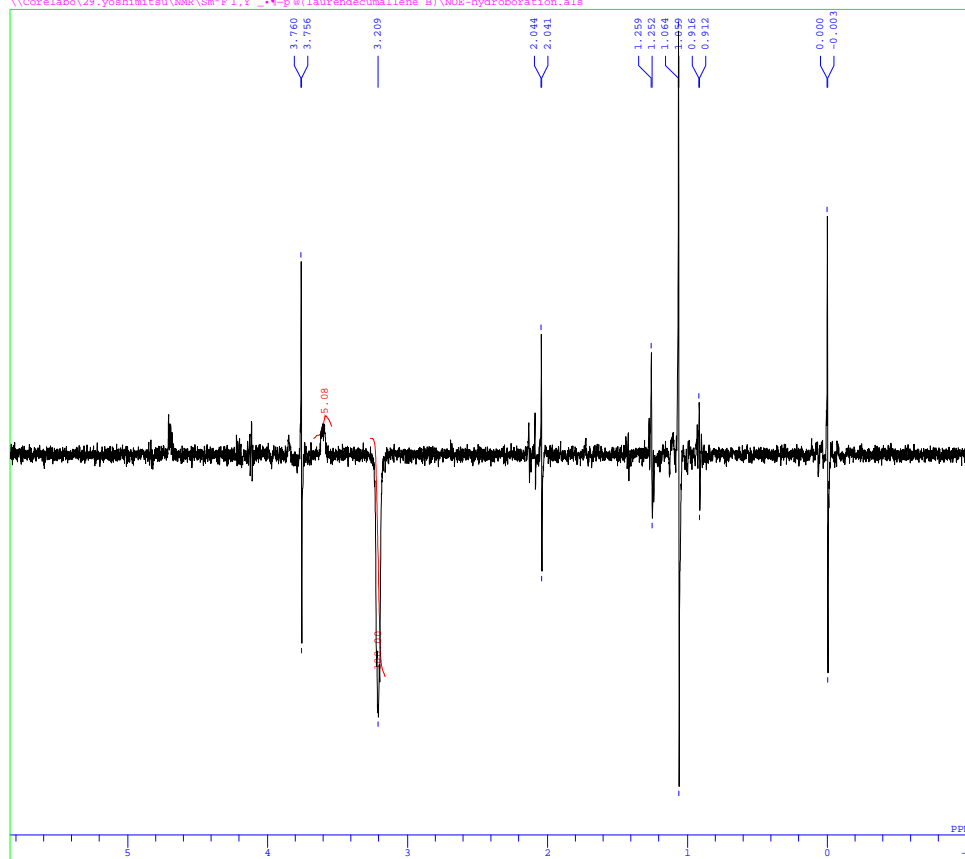


DFILE J-171-AcOH-data_Carbon-
COMNT single pulse decoupled
DATIM 2012-10-16 11:11:53
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 35
ACQTM 0.0000 sec
PD 2.0000 sec
PWL 3.00 usec
IRNUC 1H
CTEMP 24.3 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 60





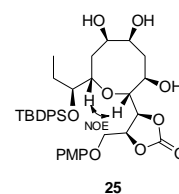
Difference NOE Experiment
\\Corelabo\29.yoshimitsu\NMR\5m³F 2, 5³...-p@(\laurendecumallene B)\NOE-hydroboration.als



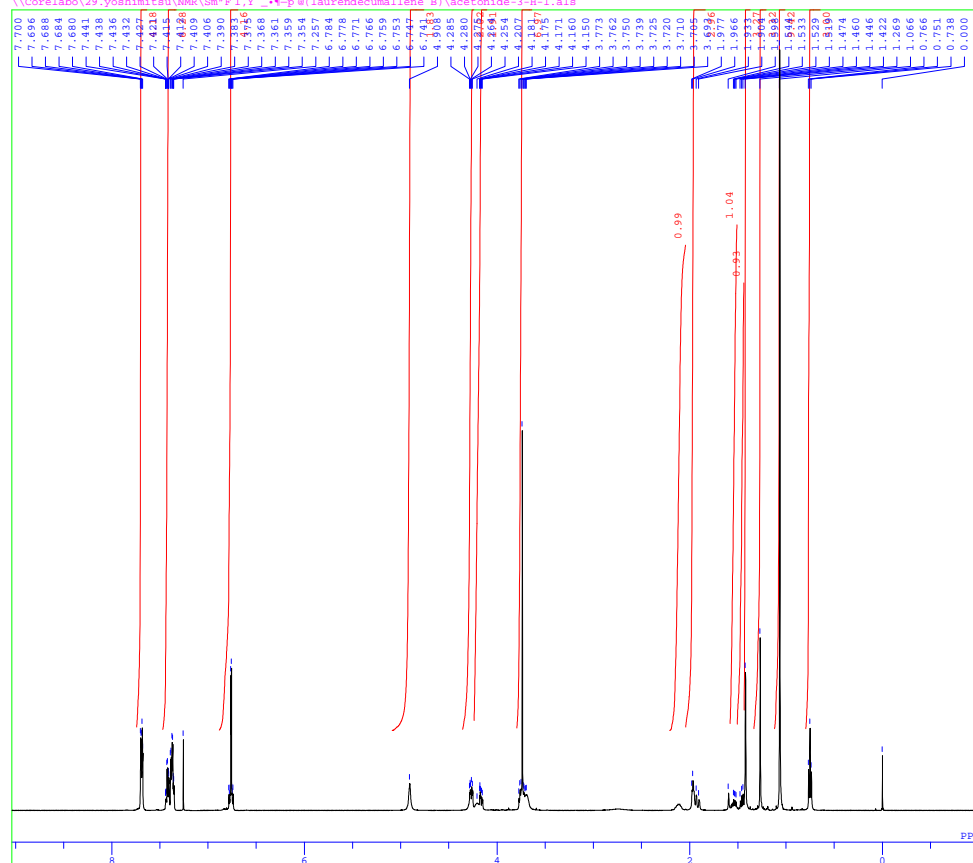
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DPFLE NOE-hydroboration.als
COMET difference NOE Experiment
DATIM 2012-10-11 21:33:58
ONUC 1H
EXMOD difference_noe_1
OBFREQ 500.16 MHz
OSSET 2.41 KHz
OBFIN 6.01 Hz
POINT 16364
FREQU 9384.38 Hz
SCANS 16
ACQTM 1.7459 sec
PD 7.0000 sec
PW1 13.00 usec
IRNUC 1H
CTEMP 26.1 c
SILVET
EXREF CDCL3
BF 0.00 ppm
BF 0.12 Hz
RGAIN 50

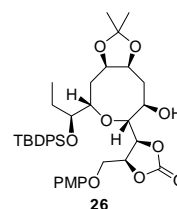
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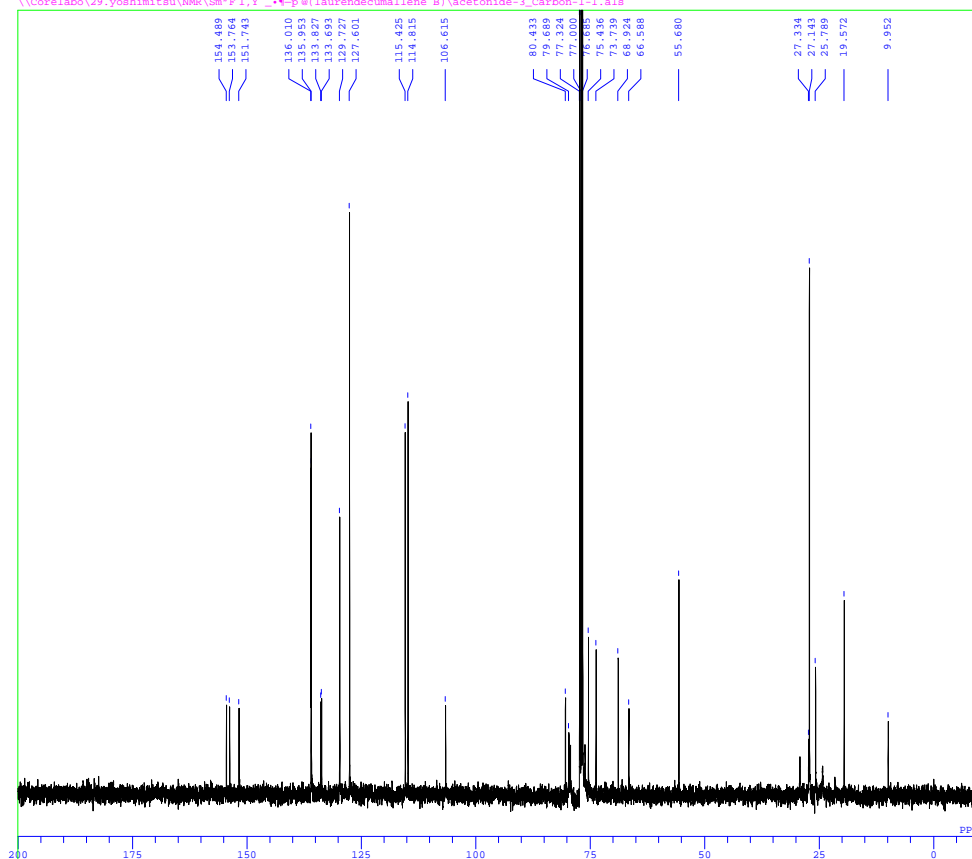
single_pulse
\\Corelabo\29.yoshimitsu\NMR\5m*F i, 2'-.*-p@lauredecumallene B)\acetonide-3-H-1.als



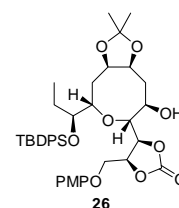
DFILE acetonide-3-H-1.als
COMNT single_pulse
DATIM 2013-03-11 16:07:56
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
AQTM 1.7459 sec
PD 5.0000 sec
PWL 6.50 usec
IRNUC 1H
CTEMP 25.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 38



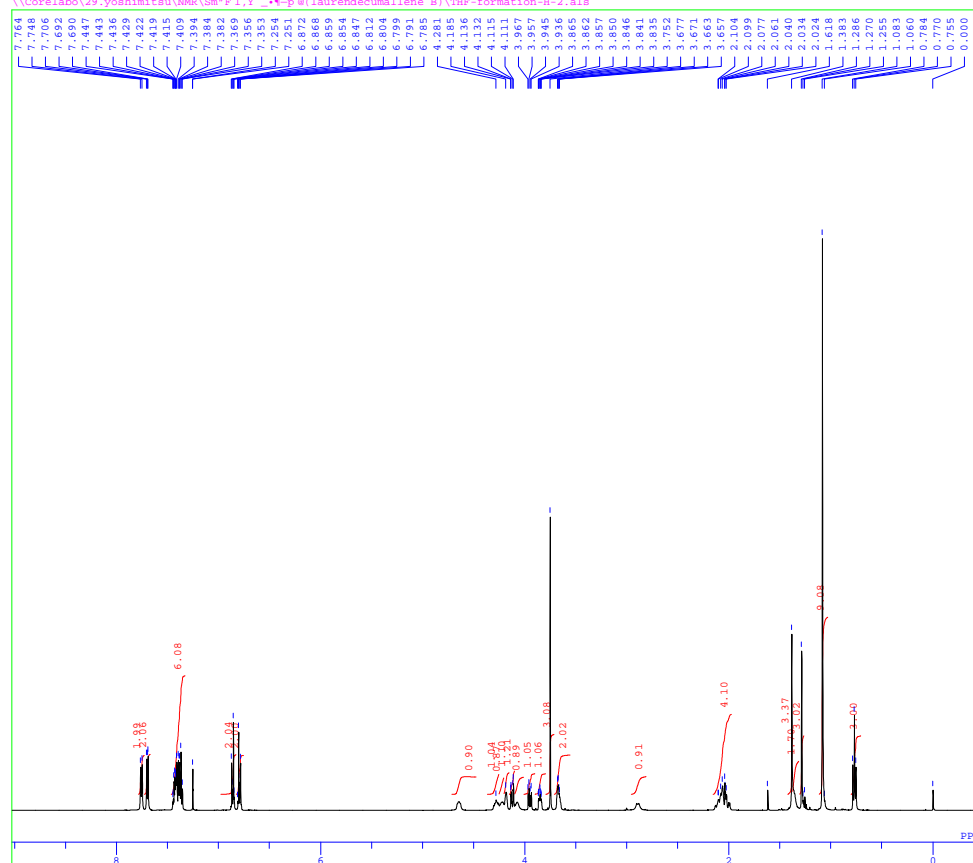
single pulse decoupled gated NMR
\\Corelabo\29.yoshimitsu\NMR\5m*F i, 2'-.*-p@lauredecumallene B)\acetonide-3-Carbon-1-1.als



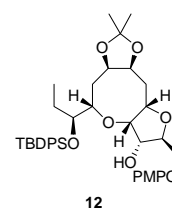
DFILE acetonide-3-Carbon-1-1
COMNT single pulse decoupled
DATIM 2013-03-11 16:39:37
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 500
AQTM 1.0433 sec
PD 2.0000 sec
PWL 3.00 usec
IRNUC 1H
CTEMP 24.8 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 60



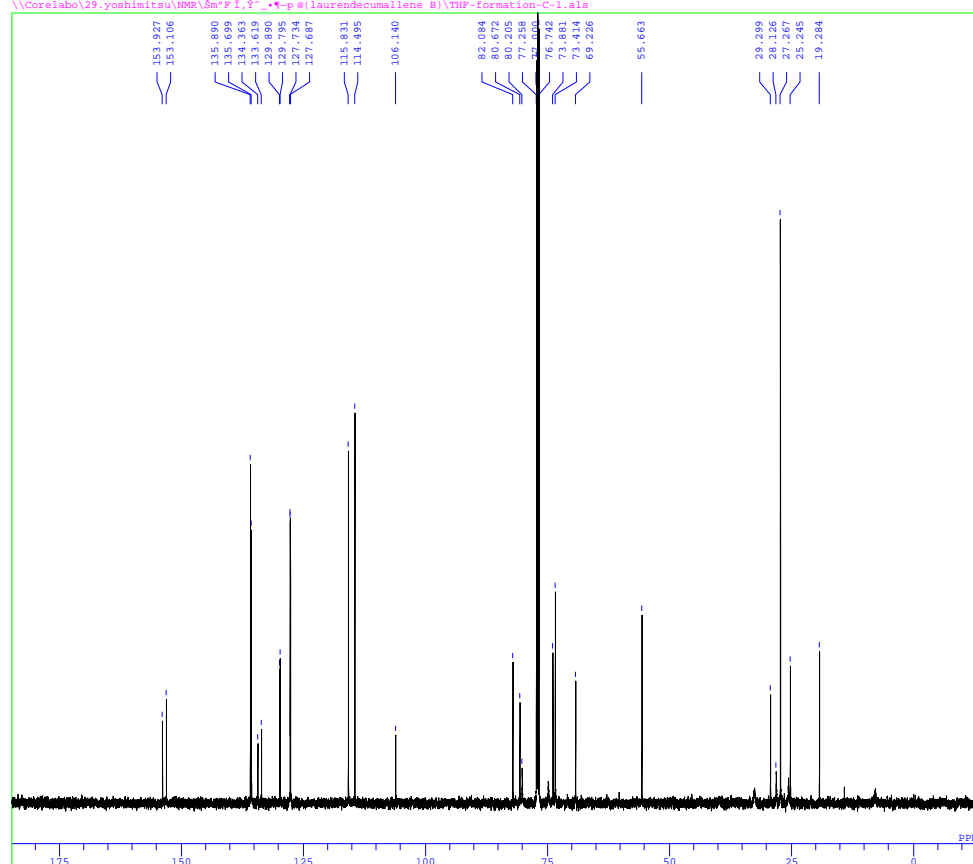
single_pulse
 \\Corelabo\29.yoshimitsu\NMR\5m*Ff.8~.4-p@lauredecumallene B\THF-formation-H-2.als



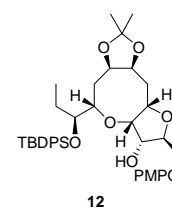
DFILE THF-formation-H-2.als
 COMNT single_pulse
 DATIM 2013-03-12 11:40:15
 OBNUC 1H
 EXMOD single_pulse.ex2
 OBFREQ 500.16 MHz
 OBSST 2.41 KHz
 OBFIN 6.01 Hz
 POINT 13107
 FREQU 7507.39 Hz
 SCANS 8
 ACQTM 1.7459 sec
 PD 5.0000 sec
 PW1 6.50 usec
 IRNUC 1H
 CTEMP 25.4 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 34



single_pulse decoupled gated NOE
 \\Corelabo\29.yoshimitsu\NMR\5m*Ff.8~.4-p@lauredecumallene B\THF-formation-C-1.als



DFILE THF-formation-C-1.als
 COMNT single_pulse decoupled
 DATIM 2013-03-12 12:07:46
 OBNUC 13C
 EXMOD single_pulse_dec
 OBFREQ 125.77 MHz
 OBSST 7.87 KHz
 OBFIN 4.21 Hz
 POINT 26214
 FREQU 31446.06 Hz
 SCANS 570
 ACQTM 0.8336 sec
 PD 2.0000 sec
 PW1 3.73 usec
 IRNUC 13C
 CTEMP 26.2 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 1.20 Hz
 RGAIN 54



[illegible]

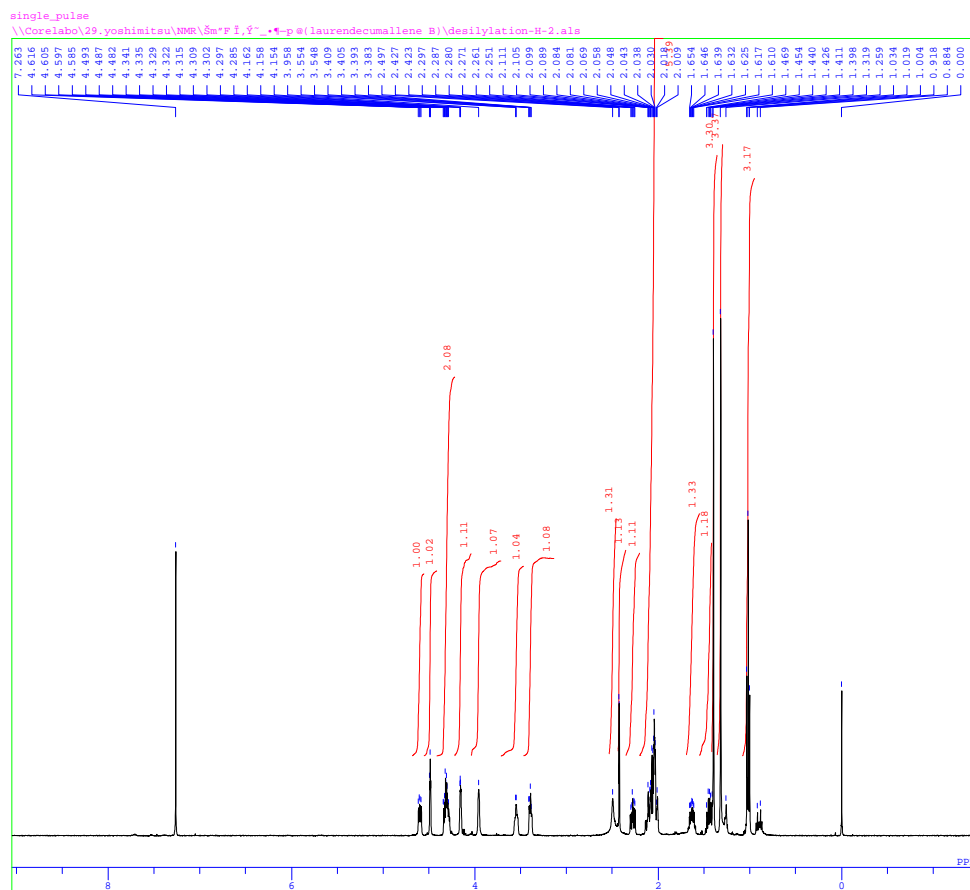
\\Corelabo\29_yoshimitsu\NMR\5M\F1.Y\2014-09-10-10-00-00\p@laurendecumaliene B\aiter-barton-C-13.ms

136.014
135.937
129.604
129.470
129.477
127.429

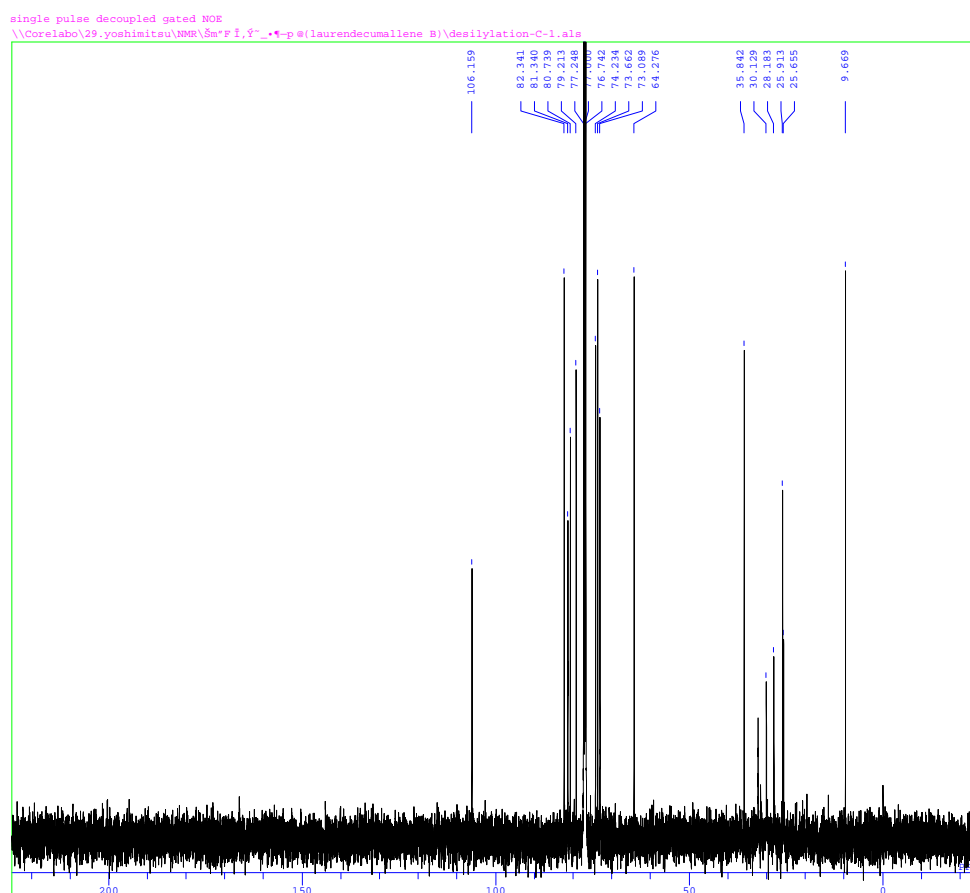
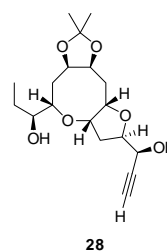
82.847
77.563
77.288
77.000
76.722
75.862

25.738
25.038
25.627

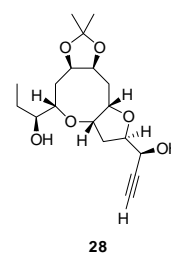
Chemical structure of compound 10, a bicyclic acetal. It features a central eight-membered ring fused to a five-membered ring. The eight-membered ring has a tert-butyldiphenylsilyloxy (TBDPSO) group and a hydroxyl group. The five-membered ring has a tert-butyldiphenylsilyloxy group and a hydroxyl group.

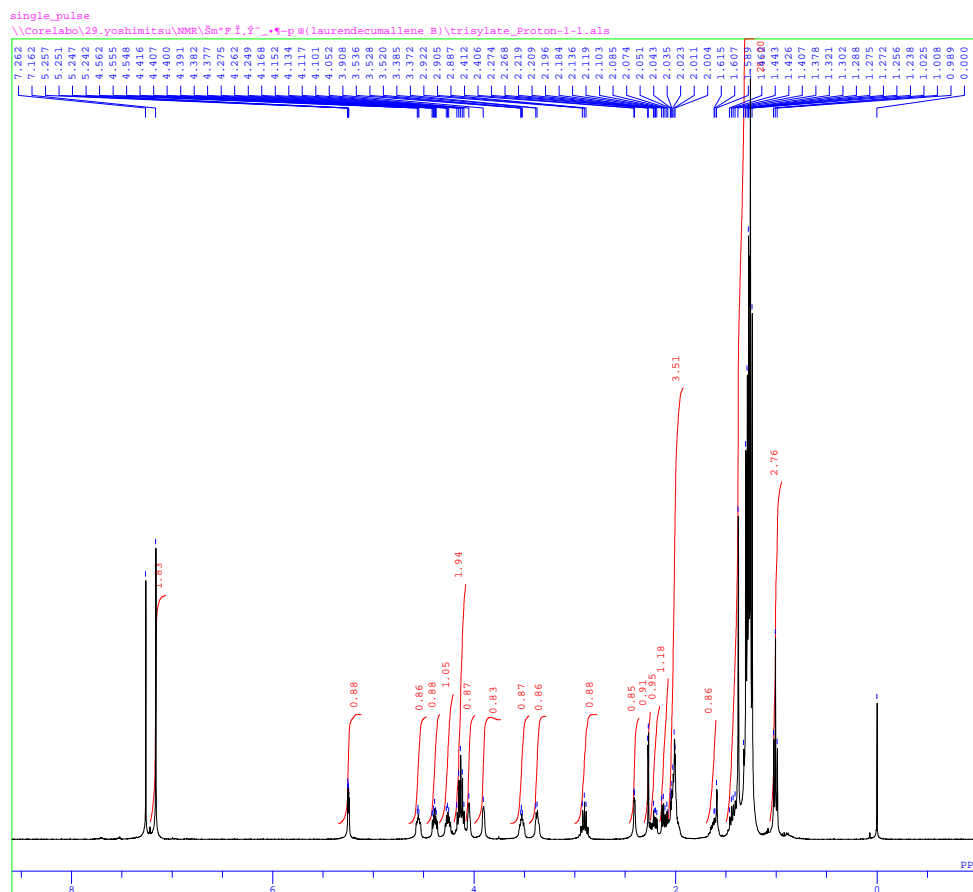


DFILE desilylation-H-2.als
COMNT single_pulse
DATIM 2013-03-16 10:37:25
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
AQTM 1.7459 sec
PD 5.0000 sec
FW1 6.50 usec
IRNUC 1H
CTEMP 25.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 46

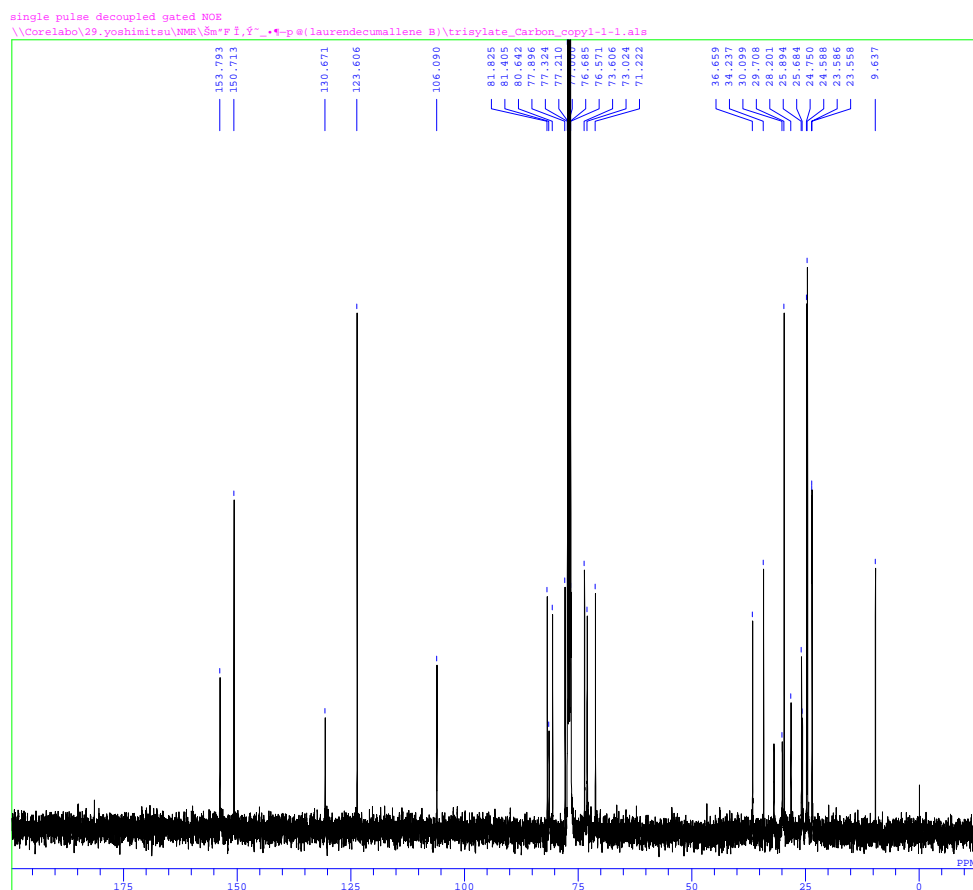
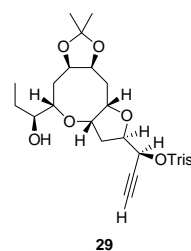


DFILE desilylation-C-1.als
COMNT single_pulse decoupled
DATIM 2013-03-16 11:53:42
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 1601
AQTM 0.8336 sec
PD 2.0000 sec
FW1 3.73 usec
IRNUC 1H
CTEMP 25.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 52

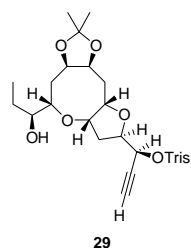


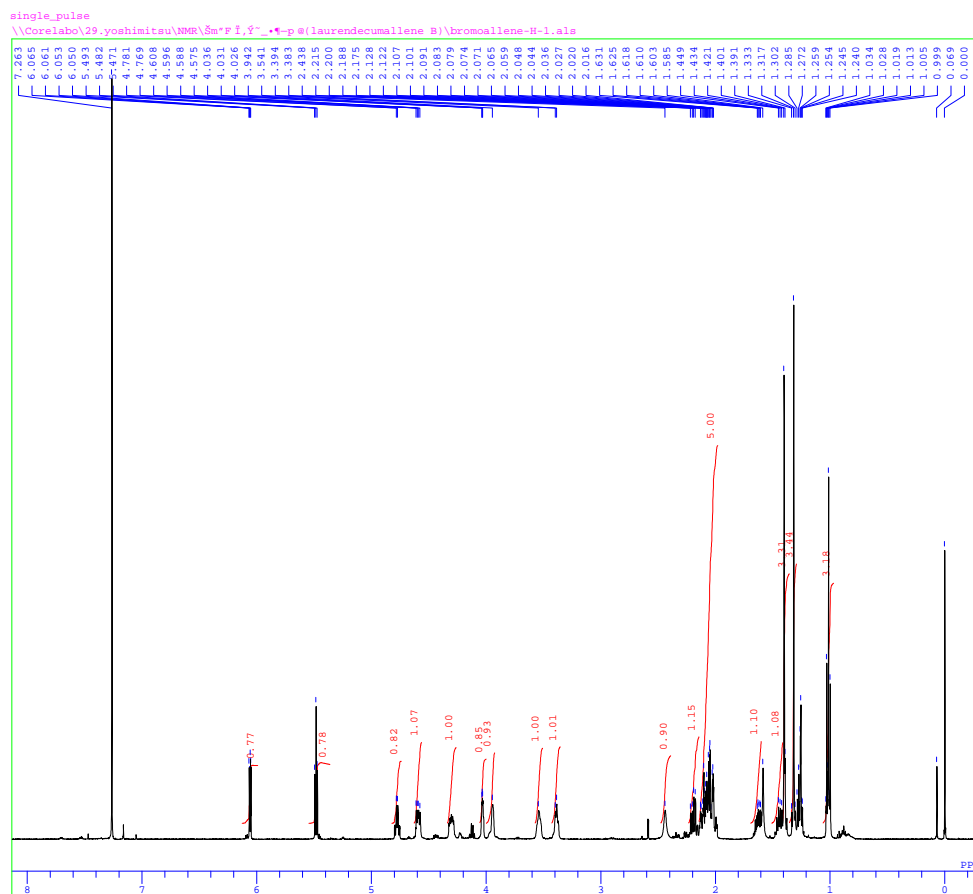


DFILE trisyate_Proton-1-1.a
COMNT single_pulse
DATIM 2013-03-16 19:45:46
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 7598.78 Hz
SCANS 8
AQTM 1.7249 sec
PD 5.0000 sec
PW1 4.65 usec
IRNUC 1H
CTEMP 25.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 38

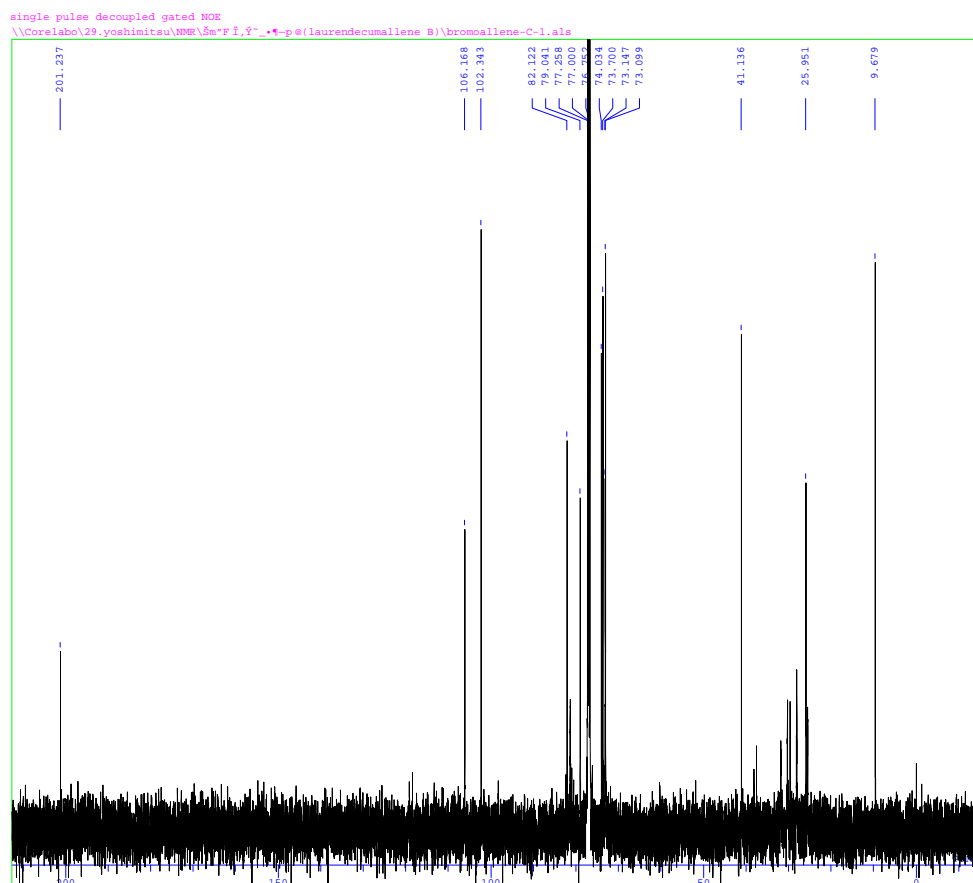
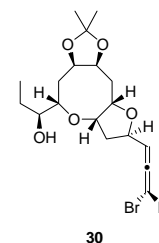


DFILE trisyate_Carbon_copy1-
COMNT single pulse decoupled
DATIM 2013-03-16 19:47:28
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 1010
AQTM 0.0000 sec
PD 2.0000 sec
PW1 3.00 usec
IRNUC 1H
CTEMP 25.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 60





DFILE bromoallene-H-1.als
COMNT single_pulse
DATIM 2013-03-18 16:11:02
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
AQTM 1.7459 sec
PD 5.0000 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 25.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 46



DFILE bromoallene-C-1.als
COMNT single pulse decoupled
DATIM 2013-03-18 17:08:18
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 1200
AQTM 0.8336 sec
PD 2.0000 sec
PW1 3.73 usec
IRNUC 1H
CTEMP 26.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 52

