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SYNTHESIS AND CONFORMATION OF 2-SILYLETHYNYL-SUBSTITUTED 2,4,4,6-TETRAMETHYL-1,3-DIOXANES

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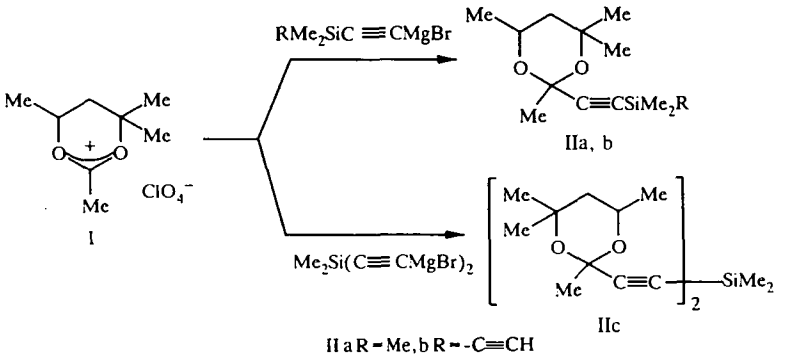
Reaction of 2,4,4,6-tetramethyl-1,3-dioxanium perchlorate with Iotsich reagents led to the synthesis of new silylethynyl-substituted 2,4,4,6-tetramethyl-1,3-dioxanes. According to the data of ^1H and ^{13}C NMR and x-ray diffraction analysis, it was established that the 1,3-dioxane ring of the products obtained has the chair conformation.

The 1,3-dioxanium salts are not only active reagents, but also substances for the investigation of conformational transitions of the six-membered 1,3-dioxa ring under the influence of substituents at positions 2, 4, and 6, as well as the positive charge on the meso-carbon atom of the $O=C^+=O$ portion [1-7]. The 1,4-twist conformation of the six-membered ring of the acyloxonium ion — the 2,4,4,6-tetramethyl-1,3-dioxanium cation — was previously established [4]. The last is a precursor of the little-studied 2,2,4,4,6-substituted 1,3-dioxanes. In the case of 2-methyl- and 2-(4-bromophenyl)-2,4,4,6-tetramethyl-1,3-dioxanes, it was shown by the methods of ^1H and ^{13}C NMR that the ring of the first compound can occur both in the 1,4-twist conformation [8] and the 2,5-twist conformation [9, 10], and the second has the form of a chair with the axial disposition of the 4-bromophenyl and methyl substituents at positions 2 and 6 [9, 10], whereby the conformation of its molecule is unchanged in the solid state according to the data of X-ray diffraction analysis [11].

We showed [12, 13] that the reaction of 1,3-dioxanium salts with the silicon-containing Iotsich reagents affords 2-silylethynyl-substituted 1,3-dioxanes. In the continuation of these investigations, it seemed expedient to study the reactivity of 2,4,4,6-tetramethyl-1,3-dioxanium perchlorate (I) in the conditions of the organomagnesium synthesis with the aim of synthesizing new 2,2,4,4,6-substituted 1,3-dioxanes of interest in a stereochemical regard.

Reaction of the salt (I) with mono- and diethynylmagnesium bromides gave, for the first time, the 2-silylethynyl-1,3-dioxanes (IIa-c).



The reaction was accomplished at room temperature by the addition of the perchlorate (I) to the silicon-containing Iotsich complex. The structure of the resulting compounds (IIa-c), obtained with the yield of 38-60%, was confirmed by results of the elemental analysis (Table 1) as well as the data of IR, mass spectra, and NMR (Table 2).

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TABLE 1. Characteristics of the Synthesized 1,3-Dioxanes (IIa-c)

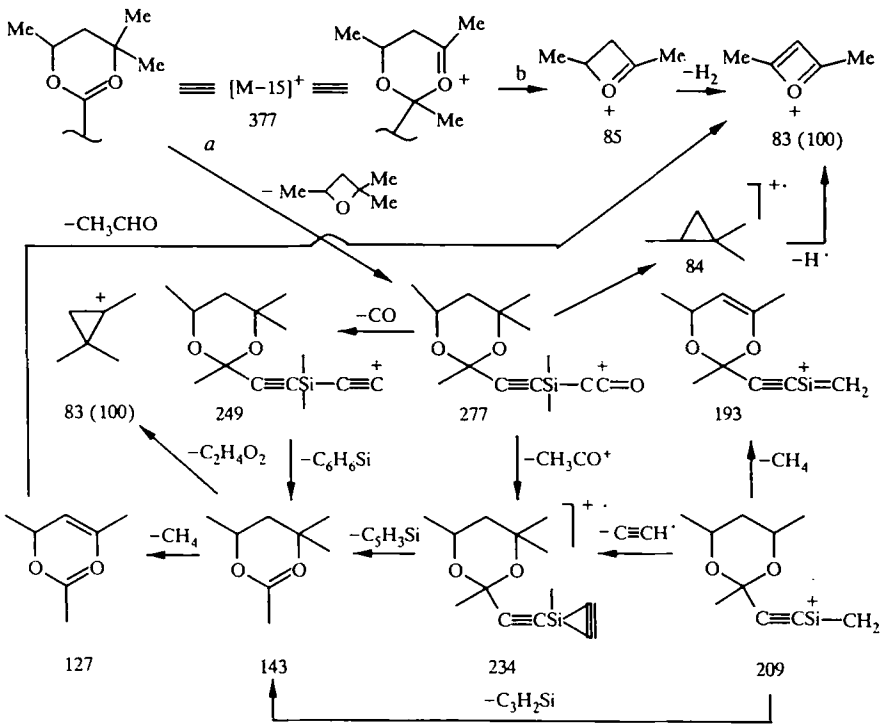
Compound	Empirical formula	Found, % / Calculated, %			R_f*	bp, °C (mm of Hg)	d^{20}_4	n^{20}_D	Yield, %
		C	H	Si					
IIa	$C_{13}H_{24}O_2Si$	65,62 65,18	10,32 10,10	11,54 11,72	0.92	99...101 (10)	0,8914	1,4425	54
IIb	$C_{14}H_{22}O_2Si$	67,36 67,15	8,94 8,85	11,46 11,21	0,80	145...146 (10)	0,9737	1,4559	38
IIc	$C_{22}H_{36}O_4Si$	67,65 67,30	9,37 9,24	7,40 7,15	0,80	61-62†	—	—	60

*The eluent is the 20:2 mixture of toluene–ethanol, and the developer is $KMnO_4$.

†The mp (°C) after recrystallization from 50% aqueous ethanol.

The mass spectrum of the 1,3-dioxane (IIc) contains the peak of the $[M - 15]^+$ ion, characteristic of such a type of compound, confirming the molecular mass of this product. It is known [14] that the $[M - 15]^+$ ions can arise as a result of the removal of the methyl radical from the $C_{(2)}$ or $C_{(4)}$ atom of the ring with their subsequent fragmentation in the directions *a* and b (see Scheme 1). Path *a* results in the formation of the acylium ion with the m/z 277. The last breaks down further according to the scheme typical of 2,4,4,6-substituted 1,3-dioxanes [14, 15]. The ion with the m/z 83, having the peak of maximum intensity, is formed from the oxonium ions with the m/z 143, 127, and 85 by the release of molecules of acetic acid, acetaldehyde, and hydrogen correspondingly [3, 5, 14].

Scheme 1



According to the ^1H NMR spectral data, on the basis of the vicinal and geminal spin–spin coupling constants ($^3J_{Aa}$ = 11.25 Hz, $^3J_{Ae}$ = 3.75 Hz, and $^2J_{ae}$ = −15.40 Hz), the preferred 1,4-twist conformation of the ring was assigned to the 2,4,4,6-tetramethyl-1,3-dioxanium hexachloroantimonate [4]. It is also shown that the geminal protons H_a and H_e did not undergo the phenomenon of the inversion of their constants of nuclear magnetic shielding, typical of 1,3-dioxanes in the chair conformation [16]. The parameters of the PMR spectrum of the 2,4,4,6-tetramethyl-1,3-dioxanium cation are not tested for the influence of the anion since they are analogous to those previously described for the hexachloroantimonate in the case of the perchlorate (I) (see the Experimental section). Therefore, in the analysis of PMR spectral data of the 1,3-dioxanes (IIa-c),

TABLE 2. Data of the IR Spectra and PMR of the 1,3-Dioxanes (IIa-c)

Compound	IR spectrum, cm^{-1}				PMR spectrum, chemical shifts, δ, ppm, SSCC (J), Hz				
	C≡C(≡C-H)	Si-Me	O-C-O	Si-C	$SiMe_3$, $SiMe_2$, s	2-Me, s	4-Me_2, 6-Me	5-CH_2	6-CH, m
(IIa)*	2170	1260	1060, 1110, 1160, 1190	760, 840 880, 910	0,06 (9H)	1,42 (3H)	1,07 (3H, s) 1,42 (3H) 1,05 (3H, d $^3J_{HCH3}$ = 6,0)	1,23 (2H, m)	4,05 (1H)
(IIb)†	2180, 2060, (3290)	1260	1100, 1160, 1190	790, 830 900, 980	0,26 (6H)	1,43 (3H)	1,10 (3H, s) 1,40 (3H, s) 1,11 (3H, d, $^3J_{HCH3}$ = 6,0)	1,39 (2H, m)	4,12 (1H)
(IIc)*	2170	1260	1040, 1090 1160, 1180	780, 830 860	0,23 (6H)	1,45 (6H)	1,08 (6H, s) 1,45 (6H, s) 1,13 (6H, d $^3J_{HCH3}$ = 6,0)	1,26 (4H, m)	4,14 (2H)
(IIc)‡	–	–	–	–	0,30 (6H)	1,58 (6H)	1,17 (6H, s) 1,54 (6H, s) 1,20 (6H, d $^3J_{HCH3}$ = 6,0)	1,39 (2H, d) 1,46 (2H, d) $^2J_{HH}$ = −1,37	4,33 (2H)

*The solvent CCl_4.

†The chemical shift of ≡C−H is 2.3 ppm.

‡The solvent $CDCl_3$.

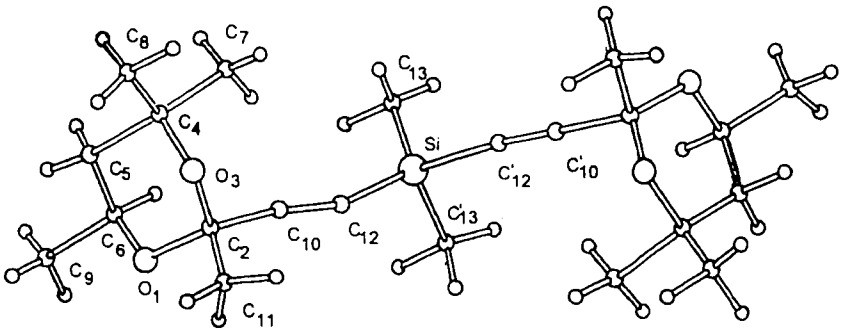
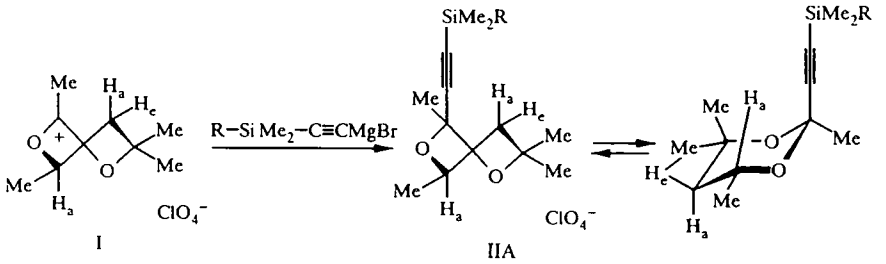


Fig. 1. Structure of the 1,3-dioxane (IIc) determined by the method of x-ray diffraction analysis.

we considered two possibilities for the conformation of their ring, arising on the approach of the nucleophilic part of the molecule of the Iotsich reagents to the meso-carbon atom of the $O=C^{+}=O$ portion of the 1,3-dioxanium cation having the 1,4-twist conformation. The first assumed the retention of the indicated conformation (A) on the basis of known data for 2,4,4,6-tetramethyl-1,3-dioxane [6,7] and 2-(1-methyl-2-benzimidazolyl)-2,4,4-trimethyl-1,3-dioxane [2], and the second assumed the conversion of the flexible 1,4-twist conformation (by virtue of the anomeric effect) to the chair conformation (B) with the axial disposition of the $C\equiv C-Si$ portion [12, 17].



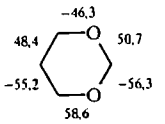
According to the ^{1}H and ^{13}C NMR data, the 1,3-dioxane rings in the molecule of compound (IIc) stay chiefly in the chair conformation with the axial orientation of the ethynyl portion at the $C_{(2)}$ atom. This is indicated by the fact of the inversion of the nuclear screening constant of the protons at the $C_{(5)}$ atom (δ_{Ha} = 1.46 ppm, δ_{He} = 1.39 ppm) and the geminal SSCC $^{2}J_{HaHe}$ of 11.37 Hz, typical for 1,3-dioxane systems having the chair conformation ($^{2}J_{HH}$ = −11.5 Hz) [16]. Moreover, the geminal methyl groups at the $C_{(4)}$ atom in the indicated conformation are distinguished by significant anisochronicity ($\Delta\delta$ = 0.37 ppm) similarly observed in the spectrum of 2,4,4-trimethyl-1,3-dioxane [2], for which the ring conformation was determined to be the pure chair. In the given case, the cause of the inversion of the chemical shifts of the protons of the gem-dimethyl groups may be the magnetic–anisotropic and electrical effects of the axially disposed ethynyl group at the $C_{(2)}$ atom of the ring [12, 17]. The chair conformation of 2,4,4,6-tetramethyl-1,3-dioxanes can certainly be judged from the value of the chemical shift of the $C_{(5)}$ atom in the ^{13}C NMR spectrum of compound (IIc), equal to 43.22 ppm. For 2,4,4,6,6-pentamethyl-1,3-dioxane, the chemical shift of the $C_{(5)}$ atom in the chair conformation equals 41.4 ppm, and it increases in the twist conformation (it is 48.3 ppm for the $C_{(5)}$ atom of 4,4,6,6-tetramethyl-2-chloro-1,3,2-dioxaarsine) [8-10, 19].

Therefore, it can be assumed that the compounds (IIa-c) in solution have the chair conformation B of the six-membered 1,3-dioxa ring with the cis-diequatorial disposition of the methyl groups at positions 2 and 6.

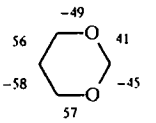
With the object of establishing the precise geometry and conformation of the molecule having substituents at positions 2, 4, and 6, x-ray diffraction analysis was performed on dimethylbis[(2,4,4,6-tetramethyl-1,3-dioxan-2-yl)ethynyl]silane (IIc). The majority of the 1,3-dioxane molecules studied by x-ray diffraction analysis have differences in the nature of substituents at positions 2 and 5 [20]. The influence of substituents at positions 2, 2, 4, 4, and 6 of the 1,3-dioxa ring has been virtually unstudied besides the investigation of the structure of 2-(p-bromophenyl)-2,4,4,6-tetramethyl-1,3-dioxane (III) [11]. However, this work, one of the first in which 1,3-dioxanes have been studied by x-ray diffraction analysis, was insufficiently correct (R = 11%).

According to X-ray diffraction data for compound (IIc), the crystallographic axis of symmetry 2 goes through the Si atom and the middle of the sections $C_{(10)}...C_{(11)}$ and $C_{(10')}...C_{(11')}$ (Fig. 1). Therefore, only one of the two dioxane rings is considered subsequently.

The ring conformation is a highly distorted chair. Analysis of the individual torsion angles indicates that the mirror symmetry characteristic of unsubstituted 1,3-dioxane is broken. The difference in the torsion angles in the acetal portion comprises 5.6°; the difference in the aliphatic portion comprises −6.8°, and that in the central portion comprises −12.4°.



IIa



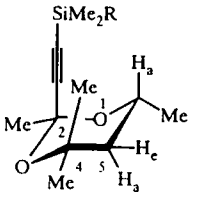
III

However, the alternation of the signs (+, −) of the torsion angles indicates that the conformation of the ring is retained. A similar ring structure was also established for compound (III) and, although the corresponding values of the torsion angles do not agree, the tendency to distortion is retained.

It should be noted that the side of the ring containing the gem-dimethyl substituents ($C_{(5)}-C_{(4)}-O_{(3)}-C_{(2)}$, τ_{mean} = 48.5°) is significantly compressed by comparison with the other side ($C_{(5)}-C_{(6)}-O_{(1)}-C_{(2)}$, τ_{mean} = 56.7°), whereby if the torsion angles of the $C_{(5)}-C_{(6)}-O_{(1)}-C_{(2)}$ portion can be compared with the corresponding torsion angles of molecules with 2,2-substituents [20], the torsion angles of the $C_{(5)}-C_{(4)}-O_{(3)}-C_{(2)}$ portion do not have analogs.

In contrast to the "standard" 1,3-dioxane where the base of the ring is formed by the atoms $C_{(4)}-O_{(3)}-C_{(6)}-O_{(1)}$ lying in one plane, the base in the molecule of compound (IIc) can be taken as the plane formed by the atoms $C_{(5)}-C_{(4)}-C_{(2)}-O_{(1)}$ and the deviation of the atoms $O_{(3)}$ and $C_{(6)}$ from it comprises 0.521 Å and −0.667 Å correspondingly. The methyl groups at the positions 2 and 6 occupy the equatorial position, and the acetylene portion occupies the axial position. The strong syn-axial interactions of the axial methyl group at the position 4 and the acetylene portion obviously lead to significant ring distortions, but they are insufficiently strong to change its conformation.

The bond lengths $C_{(2)}-O_{(3)}$, $C_{(4)}-O_{(3)}$, and $C_{(4)}-C_{(5)}$ are somewhat higher than those of the bonds $C_{(2)}-O_{(1)}$, $C_{(6)}-O_{(1)}$, and $C_{(6)}-C_{(5)}$ (Δl = 0.021, 0.017, and 0.011 Å correspondingly). On the whole, the bonds $C_{(2)}-O$ and $C_{(4,6)}-O$ are longer than their analogous bonds in all molecules previously investigated. The bond angles at the oxygen atoms underwent change the most strongly. Thus, the angle $C_{(4)}-O_{(3)}-C_{(2)}$ increased to 117.7°, which is much higher than the angle $C_{(6)}-O_{(1)}-C_{(2)}$ of 113.5°, as well as the mean statistical angle of 111.4°. The remaining bond angles in the ring are also increased by 1-2°; only the angle $O_{(3)}-C_{(4)}-C_{(5)}$ is decreased by 2.1°.



IIc

Therefore, the data of X-ray diffraction analysis of the molecule (IIc) once again confirm that tensions in the dioxane ring are removed by its compression, and not by the transition to the non-chair form of conformation, although the situation in solutions may be somewhat different [2].

EXPERIMENTAL

The IR spectra were recorded on the Specord 71 instrument at room temperature in a thin layer, and for a suspension in mineral oil. The PMR spectra of compounds (IIa-c) were obtained on the Tesla BS-467 instrument (60 MHz, the internal standard HMDS, and the solvent $CDCl_3$). The PMR spectrum of compound (IIc) was obtained on the Bruker AC-200 instrument (200 MHz, the internal standard TMS, and the solvent $CDCl_3$). The ^{13}C NMR spectrum was recorded on the Bruker

AC-200P instrument in $CDCl_3$, with the internal standard TMS. The mass spectra were obtained on the Varian MAT 311A instrument with the application of the direct introduction of the substance at the ion source, the 200°C temperature of the ionization chamber, and the 70 eV energy of the ionizing electrons.

Monitoring of the course of reaction and the discreteness of substances was accomplished by the method of TLC on plates of Silufol UV-254 with the eluent comprising the 95:5 mixture of hexane–ether, and the developer comprising the aqueous solution of $KMnO_4$. The purity of the 1,3-dioxanes (IIa, b) was determined on the Khrom-5 instrument with a flame-ionization detector on a column of length 2.5 m (15% PMPS-4 on Chromaton N-AW DMCS) with the nitrogen gas carrier flow rate of 30 cm^3/min, the vaporizer temperature of 200°C, the column temperature of 145°C, the detector temperature of 150°C, and the 0.1 μl quantity of the introduced microsample.

X-Ray Diffraction Investigation of Compound (IIc). Transparent colorless monoclinic crystals were developed from the 3:7 mixture of acetone–alcohol. Exposure and interpretation of the structure were carried out on the CAD-4-SDP-11/23 autodiffractometric system (MoKα emission, graphite monochromator, ω-2/3θ-scanning) according to the ENX-SDP complex of programs. The crystal of size 0.21 by 0.36 by 1.18 mm gave 4442 reflections (τ_{max} = 30°). Parameters of the elementary cell are as follows: a = 27.366(10) Å, b = 5.805(11) Å, c = 14.851(5) Å, β = 90.54(5)°, Z = 4, and the space group C2/c. The structure was determined by the direct method (MULTAN) from the E synthesis with the best evaluations of 13 and 14 crystallographic independent nonhydrogen atoms (the molecule occupies a particular position on the axis 2). The remaining C atom was localized from the Fourier difference synthesis, and positional parameters of the H atoms were calculated from geometrical considerations. Anisotropic specification (isotropic for hydrogen atoms) by the MLS (2492 reflections with I > 3σ(I), single weight scheme) was performed on the PC-UNIPAC-256 instrument using the SHELX-76 program. The final value is R = R_W = 0.053. Data on the atomic coordinates, bond lengths, and bond angles can be obtained from the author of the paper, M. A. Khusainov.

2,4,4,6-Tetramethyl-1,3-dioxanium Perchlorate (I). This was obtained by the method of the work [2]. The yield is 98%. The mp is 45-47°C. The IR spectrum is as follows: 1560 cm^{-1}, 1520 cm^{-1}, 1480 cm^{-1}, 1440 cm^{-1}, 1200 cm^{-1}, 1110 cm^{-1}, 800 cm^{-1}, and 600 cm^{-1}. The PMR spectrum ($C_6D_5NO_2$) is as follows: 1.81 and 1.76 ppm (6H, s, s, 4-Me_2), 1.71 ppm (3H, d, 6-Me, $^3J_{HCH3}$ = 6 Hz), 2.65 ppm (2H, m, 5-CH_2), 2.70 ppm (3H, s, 2-Me), and 5.35 ppm (1H, m, 6-CH). The literature PMR spectrum (CD_3CN) is as follows: 1.68 ppm (6H, s, 4-Me_2), 1.58 ppm (3H, d, 6-Me, $^3J_{HCH3}$ = 6 Hz), 2.50 ppm (2H, m, 5-CH_2), 2.55 ppm (3H, s, 2-Me), and 5.1 ppm (1H, m, 6-CH) [7].

2,4,4,6-Tetramethyl-2-trimethylsilylethynyl-1,3-dioxane (IIa). To the Iotsich complex, obtained from 2.4 g (100 mmole) of magnesium, 10.9 g (100 mmole) of ethyl bromide, and 9.8 g (97 mmole) of trimethylethynylsilane in 150 ml of dry ether are added, slowly in portions at room temperature, 7.98 g (33 mmole) of the perchlorate (I). The reaction mass is stirred for 30 min at room temperature prior to decomposition with 50 ml of a saturated solution of ammonium chloride using cooling with ice. The organic layer is separated, and the aqueous layer is extracted twice with ether. The combined ether extracts are dried with anhydrous sodium sulfate. The ether is distilled off on a water bath, and 4 g of compound (IIa) are isolated from the residue by fractionation *in vacuo*.

Dimethyl(ethynyl)[(2,4,4,6-tetramethyl-1,3-dioxan-2-yl)ethynyl]silane (IIb). Using the method described above, 2.4 g of magnesium, 10.9 g of ethyl bromide, 10.8 g of dimethyldiethynylsilane, and 7.98 g of the perchlorate (I) afford 2.53 g of compound (IIb).

Dimethylbis[(2,4,4,6-tetramethyl-1,3-dioxan-2-yl)ethynyl]silane (IIc). By analogy with the synthesis of compound (IIb), the product (IIc) is obtained from the same reagents, but with the utilization of the twofold molar amount of ethyl bromide in relation to dimethyldiethynylsilane. The product (IIc) is isolated by crystallization of the residue (after the distillation of the ether) from hexane or petroleum ether. The mass spectrum, given as the m/z (I_{rel}, %), is as follows: 377 (23.1), 277 (4.7), 249 (4.5), 234 (30.6), 209 (37.1), 194 (15.6), 193 (47.4), 151 (15.4), 143 (32.7), 127 (4.4), 85 (16.8), 84 (42.7), 83 (100), 69 (12.7), 56 (20.9), and 44 (59.7). The ^{13}C NMR spectrum is as follows: 21.67 and 25.51 ppm (4-Me_2), 31.33 ppm (6-Me), 32.94 ppm (2-Me), 43.22 ppm ($C_{(5)}$), 64.72 ppm ($C_{(6)}$), 73.25 ppm ($C_{(4)}$), 84.95 ppm ($C_{(2)}$), and 91.23 and 107.13 ppm (C≡C).

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