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Synthesis of a sumanenyl hafnocene complex

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Convex-bound sumanenyl hafnocene complex Cp*(sumanenyl)HfCl₂ (Cp* = C₅Me₅) was selectively synthesized. The catalytic activity of the sumanenyl hafnocene and zirconocene was also demonstrated in the hydroethylation reaction of allylbenzene via carboalumination. This is a first example demonstrated the catalytic activity of sumanenyl metallocenes. Furthermore, the sumanenyl ligand was found to exhibit the higher reactivity as compared to fluorenyl and Cp* ligands.

Introduction

Since the first report of C₆₀ metal complex, research on the coordination of a curved carbon π surface to a metal is of interest from a fundamental point of view including issues such as the coordination mode and molecular shape.¹⁻⁴ The open-ended molecular bowl as represented by a fullerene fragment (geodesic polyarene, buckybowl, or π bowl, a π bowl is used here) also has a curved carbon π face.^{5,6} Representative examples of such compounds include corannulene and sumanene (**1**, Scheme 1a). From a coordination chemistry viewpoint, the π bowl is very unique since it has a concave surface as well as a convex surface for coordination to the metal. For this reason, these structures have attracted wide attention because they not only represent a source of basic knowledge and information but also provide possibilities as future catalysts and materials. π -Bowl complexes made up of various transition metals in several coordination modes have been studied over the past 20 years, mainly using corannulene and corannulene derivatives as ligands.⁷ The history of research on mono- and multi-alkali metal complexes of corannulene is even a few more years longer.⁸ In this context, we have studied π -complexation of a sumanene ligand.⁹ A complex [CpFe (η^6 -sumanene)]PF₆ (Cp = C₅H₅) coordinated from the concave surface was confirmed in both solution and solid states.^{9a} In addition, supramolecular alkali metal coordination complexes have also been reported recently.¹⁰

Group 4 metallocene type complexes are used as catalysts in various reactions including polymerization and carboalumination reactions.¹¹ However, despite the unique structural properties and the possibility of catalytic application of π -bowl complexes, group 4 metallocene type complexes have been less studied. The only examples are zirconocene and titanocene complexes with fluorenyl type ligands prepared by the partial hydrogenation of corannulene.^{12,13} The only report of catalytic applications includes the polymerization of styrene using a titanocene complex.¹³ In the organometallic chemistry of fullerenes, metallocene complexes with cyclopentadienyl type ligands prepared by the collapse of fullerene π conjugation have been reported since the development of buckyferrocene by Nakamura and co-workers.¹⁴ On the other hand, in previous studies, we reported that sumanenyl mono-, di- and trianion can be selectively produced by treatment with a strong base.¹⁵ It is generally believed that such cyclopentadienyl-like anions can provide mononuclear and polynuclear metallocene type complexes (Scheme 1b). Indeed, we reported on the synthesis of the mononuclear and trinuclear zirconocene complexes **2a**, **2b**, and **3a** (Scheme 1c).¹⁶ Here we report on the synthetic study of the sumanenyl hafnocene complexes **4** and **3b**, and the catalytic activity of **4** and **2b** for the carboalumination of allylbenzene (**5**) (Scheme 1d).

Results and discussion

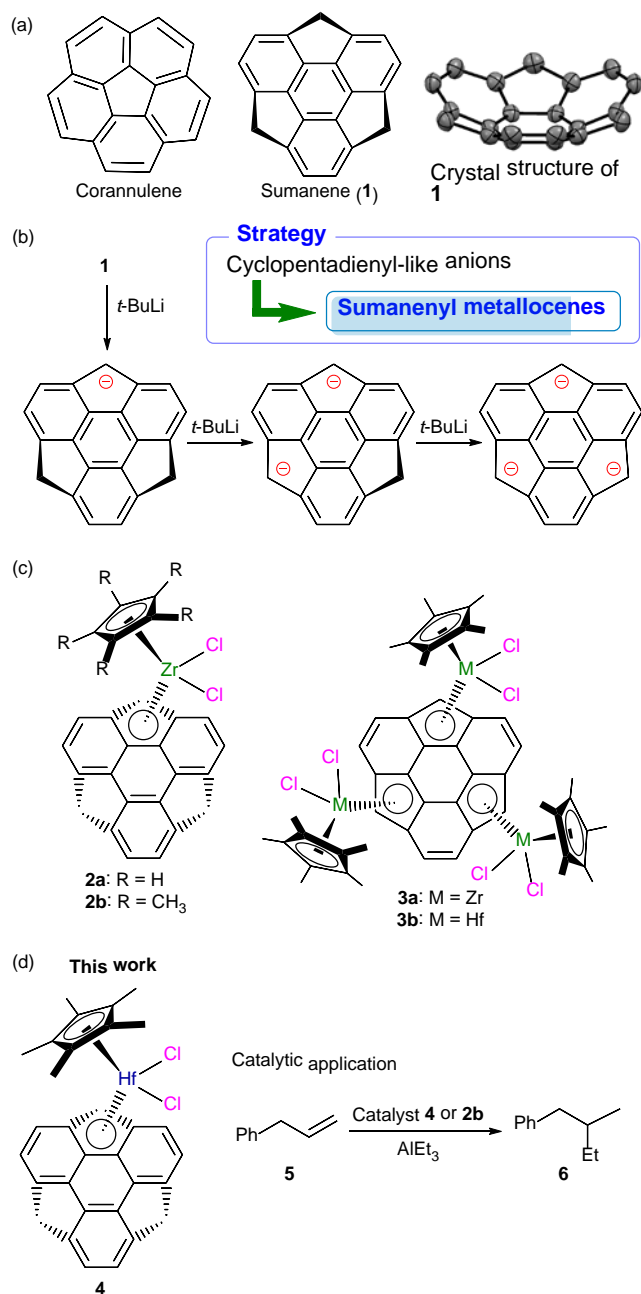
Scheme 2a shows the synthesis of the sumanenyl hafnocene complex **4**. Sumanene (**1**) was treated with *n*-BuLi (1.08 equiv) in anhydrous THF at -40 °C to generate the corresponding benzylic monoanion. The solvent was then evaporated in vacuo to give the lithium salt of the monoanion as a red solid, which was dissolved in anhydrous Et₂O. To the deep red colored solution of the monoanion was added Cp*HfCl₃ (1.02 equiv) at room temperature. The color of the mixture changed to a deep orange. The sumanenyl hafnocene complex **4** was formed in 90% yield, calculated by the integral ratio [**4**/(**4** + **1**) x 100] in the ¹H NMR spectrum. The use of Et₂O as a solvent instead of THF

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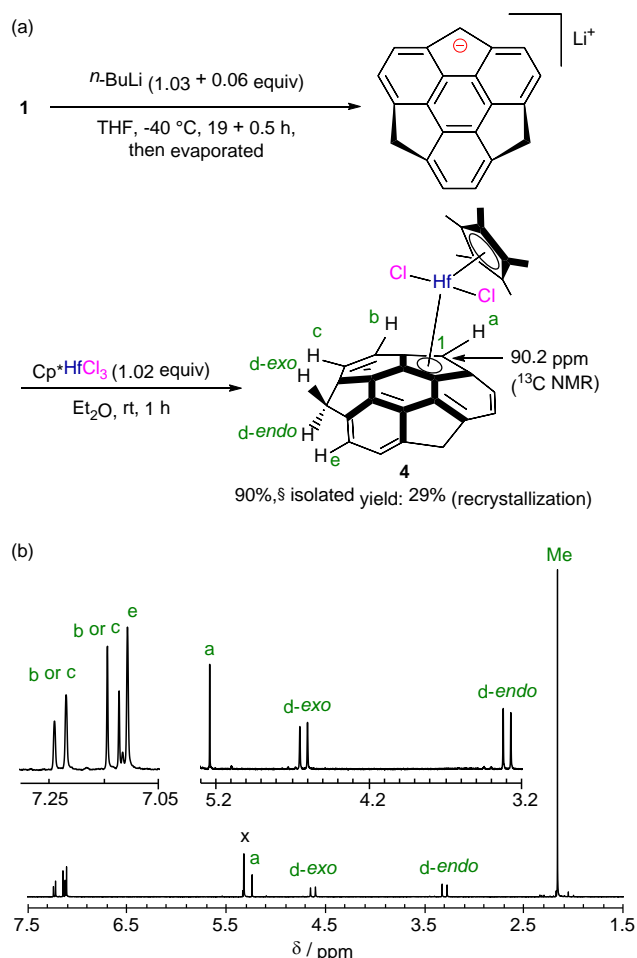
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†This paper is dedicated to Professor Julius Rebek, Jr. on the occasion of his 75th birthday. Electronic Supplementary Information (ESI) available: ¹³C NMR spectrum for **4**, ¹H and ¹³C NMR spectra for Cp*HfCl₂ and **6**. See DOI: 10.1039/x0xx00000x



Scheme 1 (a). Corannulene and sumanene (**1**), and the crystal structure of **1**. (b) Selective generation of mono-, di-, and tribenzylic anions of **1**, and a strategy for the synthesis of sumanenyl metallocenes. (c) Previously synthesized mononuclear sumanenyl zirconocene complexes **2a** and **2b**, and trinuclear zirconocene complex **3a**. (d) This work: synthesis of sumanenyl hafnocene complex **4** and its use as a catalyst for the carboalumination of allylbenzene (**5**).

in the synthesis was necessary because the complex **4** is not completely stable in THF. Synthesis of trinuclear hafnocene complex **3b** was also attempted. Formation of **3b** was suggested from the ¹H NMR spectrum (Scheme S1 in Electronic Supplementary Information) although isolation and complete characterization were not established.



Scheme 2 (a). Synthesis of **4** and (b) its ¹H NMR spectrum.

¹H NMR spectrum of **4** after recrystallization is shown in Scheme 2b. The spectrum showed a pair of doublets for the benzylic protons [$\delta = 4.63$ ($J = 20.0$ Hz, *d-exo*) and 3.31 ($J = 20.0$ Hz, *d-endo*) ppm], a singlet for *H_a* ($\delta = 5.24$ ppm), and a pair of doublets and a singlet in the aromatic region. Thus, the large separation of the chemical shifts for the *exo*- and *endo*-benzylic protons is typical in cases of bowl-shaped sumanene derivatives,^{6b} which can be accounted for by ring current effects. The peak for the methyl protons of Cp* was observed as a singlet, indicating that the Cp rings rotate rapidly compared to the NMR time scale at room temperature. As a whole, the spectrum is consistent with the C_s symmetric structure. To investigate the face selectivity of the coordination, the chemical shifts for the Cp and methyl protons of Cp* were compared to those for the corresponding fluorenyl complexes Cp*(fluorenyl)HfCl₂. The signal for the methyl protons of Cp* in **4** at $\delta = 2.16$ ppm was shifted $\Delta\delta = 0.08$ ppm to lower field than the corresponding protons of Cp*(fluorenyl)HfCl₂ ($\delta = 2.08$ ppm). This lower-field shift can be explained by the *anti*-shielding effect of the ring current, suggesting the existence of convex binding. In the ¹³C NMR spectrum, the carbon at C1 in **4** is located at $\delta = 90.2$ ppm (Scheme 2a), which is lower than the corresponding carbon in Cp*(fluorenyl)HfCl₂ ($\delta = 81.8$ ppm). These values are similar to those for the corresponding

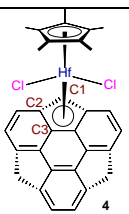
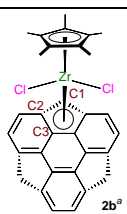
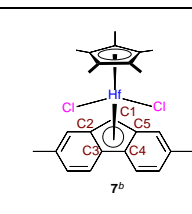
zirconocene complex. The value for the hapticity of **4**, suggests the existence of a state between η^3 - and η^5 -hapticity using the trends for zirconocene complexes.¹⁷ A more η^5 -bonding character of **4** is indicated as compared to the corresponding

fluorenyl complex Cp*(fluorenyl)HfCl₂. This is similar to that of **2b**.

Recrystallization of **4** from CH₂Cl₂/hexane afforded single orange colored crystals suitable for X-ray crystallographic analysis. Figure 1 shows the structure of **4**,¹⁸ indicating C_s symmetry and the convex binding of the Cp*Hf unit to the sumanenyl ligand. The observed structure of **4** is similar to the sumanenyl zirconocene complex **2b**. Bond lengths between Hf and the coordinating 5-membered ring in **4**, **2b**, and the fluorenyl hafnocene complex **7**¹⁹ are summarized in Table 1. The C1-Hf bond length is 2.425(8) Å, which is shorter than the other bonds (C2-Hf and C3-Hf: 2.616(6) and 2.621(6) Å, respectively). This can be attributed to disturbed η^5 -bonding. These findings suggest that the η^5 -bonding character of **4** is stronger than that of **7** (C1-Hf: 2.389(4) Å, C2 and C5-Hf: 2.599(3) and 2.552(3) Å, and C3 and C4-Hf: 2.764(3) and 2.750(3) Å). As compared to the zirconocene complex **2b**, all of the bonds (C_n-Hf, n = 1-3) in **4** are shorter than those in **2b**. This suggests the existence of strong coordination. The bowl depth was measured as the perpendicular distance from the bottom plane of the sumanene skeleton to the benzylic carbon atoms of the five-membered rings or the rim carbon atoms of the six-membered rings (Figure 1). Around the coordinating site (five-membered ring: 0.918 Å, six-membered ring: 1.106 to 1.116 Å), it became shallower as compared with the zirconocene complex (five-membered ring: 0.936 Å, six-membered ring: 1.112 to 1.126 Å). In addition, the side opposite the coordinating site (five-membered ring: 0.951 Å, six-membered ring: 1.213 Å) was deeper than the zirconocene complex (five-membered ring: 0.939 Å, six-membered ring: 1.201 Å). A π -orbital axis vector (POAV) angle²⁰ was employed to evaluate the curvature. The POAV angle is defined as $\theta_{\sigma\pi} - 90$ (Figure 1), which indicates the extent of pyramidalization. Selected values are depicted in Figure 1. The POAVs for **4** at the hub benzene ring (C4, C6, and C7) are 8.9, 9.8, and 9.1°, respectively, the values of which are slightly larger as compared to that for sumanene (**1**, 8.8°). In the packing structure of **4**, CH/ π interactions between the methyl protons of Cp* and the cyclopentadienyl-like moiety of the sumanenyl ligand were observed, inducing a columnar packing of **4** (see Figure S1 in Electronic Supplementary Information).

Figure 1 ORTEP drawings (thermal ellipsoids set at the 50% probability level), bowl depth, and POAV of **4**.

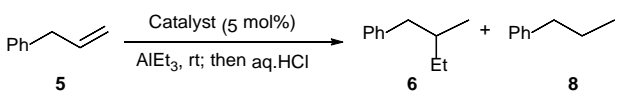
Table 1 Bond lengths between Hf and coordinating 5-membered rings in **4**, **2b**, and **7**

Bond	Bond length (Å)		
			
C1-M	2.425(8)	2.447(5)	2.389(4)
C2-M	2.616(6)	2.630(4)	2.599(3), 2.552(3) ^c
C3-M	2.621(6)	2.639(4)	2.764(3), 2.750(3) ^d

^aReference 16. ^b Reference 19. ^c Bond length of C5-M. ^d Bond length of C4-M.

weak electron donating character induced by curved structure resulted in a high Lewis acidity compared to Cp*(fluorenyl)HfCl₂ and Cp*₂HfCl₂. In the comparison of the hafnocene and zirconocene catalysts, the zirconocene derivatives are more active than the hafnocene derivatives.

Table 2 Catalytic activity of the metallocene complexes for the carboalumination of **5**



Entry	Catalyst	Time/h	Yield/%		
			6	8	5
1	4 ^a	91	75	13	11
2	2b ^a	10	93	7	0
3	Cp*(fluorenyl)HfCl ₂	91	6	13	81
4	Cp*(fluorenyl)ZrCl ₂	10	67	27	6
5	Cp* ₂ HfCl ₂	91	2	10	88
6	Cp* ₂ ZrCl ₂	10	5	7	88

^aUsed as a mixture with **1** because **1** could not be removed after the purification (weight ratio: **4**/**1** = 72: 28, **2b**/**1** = 79: 21).

Conclusions

In conclusion, the sumanenyl hafnocene complex **4** was synthesized and its convex-bound structure was characterized. The catalytic activity of **4** was also demonstrated in the hydroethylation reaction of allylbenzene (**5**) via carboalumination. This is a first example of the catalytic activity of a sumanenyl metallocene. It should also be noted that the sumanenyl ligand conferred a higher reactivity as compared to the fluorenyl and Cp* ligands. Further investigations of the use of sumanenyl metallocenes in catalytic applications is currently underway.

Experimental

General: ¹H (400 MHz) and ¹³C (100 MHz) NMR spectra were obtained on a JEOL JNM-ECS 400 spectrometer. CD₂Cl₂ and CDCl₃ were used as solvents. The residual peaks (δ 5.32 and 7.26 for ¹H, respectively), and CD₂Cl₂ and CDCl₃ peaks (δ 53.8 and 77.0 for ¹³C, respectively) were used as references for NMR. Anhydrous THF, hexane, and toluene were prepared using a Glass Contour Solvent Dispensing System. CD₂Cl₂, THF-*d*₈, and toluene-*d*₈ were dried with MS4A. Other reagents were purchased from commercial sources and used without further purification. Sumanene (**1**)²² and Cp*HfCl₃²³ were prepared according to the previously reported methods, respectively. All manipulations were conducted in a N₂-filled glove box unless otherwise noted.

Synthesis of 4. Sumanene (**1**, 23.9 mg, 9.03 x 10⁻² mmol) was dissolved in anhydrous THF (5 mL) and the resulting solution was cooled to -40 °C. To the solution was added dropwise a 1.60 M hexane solution of *n*-BuLi (58 μ L, 9.28 x 10⁻² mmol) at -40 °C. After stirring the reaction mixture for 19 h at the same

temperature, a small amount of the reaction mixture was collected to confirm the generation of an anion by ¹H NMR. As approximately 5% of **1** was still observed in the ¹H NMR spectrum, 0.06 equivalents of *n*-BuLi (3.4 μ L, 5.42 x 10⁻³ mmol) was further added to the mixture at -40 °C. After 0.5 h, the solvent was evaporated in vacuo to give a red solid. Anhydrous Et₂O (5 mL) was then added to the mixture. The suspension of Cp*HfCl₃ (38.7 mg, 9.64 x 10⁻² mmol) in Et₂O (1 mL) was added to the solution by means of a pipette at room temperature, where additional Et₂O (0.5 mL x 2) was used to transfer the Cp*HfCl₃ completely. After stirring the reaction mixture for 1 h, the solvent was evaporated in vacuo. The yield (90%) was determined by the integral ratio [**4**/(**4** + **1**) x 100] in the ¹H NMR spectrum. For purification, a mixed solution of anhydrous toluene (5 mL) and anhydrous CH₂Cl₂ (3 mL) was added to the solid, and the suspension was filtered through a membrane filter. The filtrate was slowly evaporated until some solid material appeared. The suspension was moved to a sample tube. The sample tube was allowed to stand in a freezer (-30 °C), then a red solid was formed. The supernatant solution was removed and the solid was thoroughly washed with hexane, and dried in vacuo to give the desired complex **4** as a red solid [17.1 mg, 2.64 x 10⁻² mmol, 29% yield (97% purity, containing 3% of **1**)]. Single crystals for an X-ray crystallographic analysis were grown as follows. The red solid of **4** was dissolved in a minimal amount of anhydrous CH₂Cl₂, where dry CH₂Cl₂. The same amount of hexane was then carefully and slowly added on wall surface. After allowing the solution to stand in the freezer (-30 °C) for a period, orange crystals were obtained. ¹H NMR (400 MHz, CD₂Cl₂): the spectrum was shown in Scheme 1b in the text, δ = 7.23 (d, *J* = 8.4 Hz, 2H, b or c), 7.14 (s, 2H, e), 7.11 (d, *J* = 8.4 Hz, 2H, b or c), 5.24 (s, 1H, a), 4.63 (d, *J* = 20.0 Hz, 2H, d-*exo*), 3.30 (d, *J* = 20.0 Hz, 2H, d-*endo*), 2.16 (s, 15H, -CH₃) ppm; ¹³C NMR (100MHz, CD₂Cl₂): δ = 150.9, 150.4, 149.2, 148.1, 145.6, 136.7, 127.7, 124.9, 124.5, 122.3, 90.2, 42.9, 12.3 ppm.

Synthesis of 3b. Sumanene (**1**, 5.0 mg, 1.89 x 10⁻² mmol) was added to a dried J-Young valve-attached NMR tube. Anhydrous THF-*d*₈ (0.6 mL) was added to the tube. The resulting solution was cooled to -40 °C. To the solution was added dropwise a 1.77 M pentane solution of *t*-BuLi [50 μ L, 8.85 x 10⁻² mmol, added in three portion (20, 20, and 10 μ L)] at -40 °C, and the tube was shaken for 1 min each addition. Then, the complete generation of trianion was confirmed by ¹H NMR. The suspension of Cp*HfCl₃ (38.7 mg, 6.10 x 10⁻² mmol) in THF-*d*₈ (0.2 mL) was added to the solution by means of a pipette at room temperature, where additional THF-*d*₈ (0.1 mL x 2) was used to transfer the Cp*HfCl₃ completely. The tube was shaken for 1 min. After that, the reaction mixture was concentrated in vacuo. Toluene-*d*₈ (0.5 mL) was added to the mixture, which was concentrated in vacuo. CD₂Cl₂ (0.6 mL) was added to the mixture. The crude ¹H NMR spectrum suggested the formation of **3b** (Scheme S1b for the spectrum). ¹H NMR (400 MHz, CD₂Cl₂): δ = 6.92 (s, 6H, b'), 5.24 (s, 3H, a'), 2.18 (s, 45H, c') ppm.

Synthesis of Cp*(fluorenyl)HfCl₂. Based on the synthesis of **7** in reference 19, Cp*(fluorenyl)HfCl₂ was synthesized from the reaction of Cp*HfCl₃ and the fluorenyl anion generated with *n*-BuLi. The crude product was recrystallized from toluene to give

the desired product in 19% isolated yield. ¹H NMR (400 MHz, CD₂Cl₂): δ = 7.99 (br-d, *J* = 8.7 Hz, 2H), 7.54 (ddd, *J* = 0.9, 7.8, and 7.8 Hz, 2H), 7.43 (br-d, *J* = 8.7 Hz, 2H), 7.26 (ddd, *J* = 0.9, 7.8, and 7.8 Hz, 2H), 6.20 (s, 1H), 2.08 (s, 15H) ppm; ¹³C NMR (100MHz, CD₂Cl₂): δ = 128.4, 128.2, 126.8, 125.9, 124.3, 123.5, 122.8, 81.8, 12.5 ppm.

Catalytic Reaction. 5 Mol% (20 μmol) of the sumanenyli metallocene complex **2b** or **4** (**2b**: containing **1**, **4**/**1** = 79: 21 weight ratio, 5.4 mg; **4**: containing **1**, **2b**/**1** = 72: 28 weight ratio, 7.1 mg) was placed in a brown screw-capped vial. A 1.0 M hexane solution of AlEt₃ (450 μL, 450 μmol, 1.2 equiv.) was added to the vial at room temperature and hexane was then allowed to evaporate. Allylbenzene (44.3 mg, 375 μmol, 1.0 equiv) was added to the vial at room temperature. After stirring the reaction mixture for 10 or 91 h, anhydrous Et₂O was added to the mixture. The the vial was then removed from the glove-box. An aqueous 3 M HCl solution was added to the mixture. 1,3,5-Tribromobenzene was added as an internal standard. An adequate amount of the reaction mixture was collected to quantify by ¹H NMR, where the concentration was carefully carried out to avoid evaporation of the products. The yield of **6** was calculated based on the integral ratio in the ¹H NMR spectrum (93% yield using **2b**; 75% yield using **4**). An authentic sample of **6** was prepared according to the literature.²¹ NMR data for **6**, ¹H NMR (400MHz, CDCl₃): δ = 7.25-7.30 (m, 2H, -Ph), 7.13-7.21 (m, 3H, -Ph), 2.64 (dd, *J* = 6.0 and 13.5 Hz, 1H, -CH₂Ph), 2.37 (dd, *J* = 7.8 and 13.5 Hz, 1H, -CH₂Ph), 1.60-1.70 (m, 1H, -CH(Me)Et), 1.34-1.44 (m, 1H, -CH₂Me), 1.12-1.23 (m, 1H, -CH₂Me), 0.91 (dd, *J* = 7.3 and 7.3 Hz, 3H, -CH₂CH₃), 0.85 (d, *J* = 6.9 Hz, 3H, -CH(CH₃)Et) ppm; ¹³C NMR (100MHz, CDCl₃): δ = 141.7, 129.2, 128.0, 125.5, 43.3, 36.7, 29.2, 18.9, 11.5 ppm.

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