

ALIPHATIC DIOLS IN THE SYNTHESIS OF BIS(CYCLOPENTADIENYLIRON) ARENE COMPLEXES

ALAA S. ABD-EL-AZIZ,* YUN LEI and CHRISTINE R. DE DENUS

Department of Chemistry, University of Winnipeg, Winnipeg, Manitoba, R3B 2E9 Canada

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Abstract—Aromatic nucleophilic substitution reactions (S_NAr) of chloroarene cyclopentadienyliron complex cations with potassium salts of dihydroxyalkanes in a THF/DMF mixture were found to give bis(cyclopentadienyliron) arene dicationic complexes with aliphatic ether linkages. A series of diols were used to produce the diiron complexes (**3a–m**). Increasing the length of the aliphatic chain resulted in more soluble dicationic complexes. Photolytic demetallation of these diiron complexes provided an alternative route to the synthesis of terminal diphenoxyalkanes (**4a–m**).

Interest in the field of bimetallic complexes largely stems from their important catalytic and electrochemical properties.^{1–8} One of the most common routes to the synthesis of bis(cyclopentadienyliron) arene complexes is the ligand exchange reaction, where an excess of ferrocene reacts with the polyaromatic compound.^{9–13} This method suffers from low yields and the lack of being able to introduce arenes with some functional groups. Over the past few years we have developed a unique route to the synthesis of di- and polyiron arene complexes with various heteroatom linkages.^{14–18} The synthesis of these types of diiron complexes involves the reaction of a chloroarene cyclopentadienyliron complex with the appropriate dinucleophile in the presence of a weak base such as potassium carbonate, in either pure DMF or a DMF/THF solvent mixture. The use of dihydroxyaromatic nucleophiles have proven to be successful, leading to the formation of the di- or polyiron arene complexes in very high yields.^{14,17} Other metal-containing moieties, such as chromium tricarbonyl, manganese tricarbonyl and cyclopentadienyl ruthenium, have also been used in the activation of the arene ring towards nucleophilic substitution reactions, leading to the formation of di- or polymetallic complexes with aromatic ether linkages.^{19–23} Baldoli and co-workers have also reported the synthesis of dichromium arene com-

plexes which possess aliphatic ether bridges.²⁴ They first reacted the aliphatic diols with sodium hydride to generate the sodium salt, and subsequently added the chloroarene chromium tricarbonyl complex which led to the formation of the bimetallic complex.

In this article, we report further investigation of the nucleophilic aromatic substitution reactions (S_NAr) of a variety of cyclopentadienyliron arene complexes with a homologous series of aliphatic diols.

RESULTS AND DISCUSSION

Our initial studies in the synthesis of bimetallic complexes containing aliphatic ether bridges were carried out following the same synthetic strategy that we developed for the synthesis of bis(cyclopentadienyliron) arene complexes with aromatic ether linkages. We carried out the reaction of the chlorobenzene complex with ethylene glycol in the presence of potassium carbonate as a base in DMF. However, this reaction failed to give either the desired diiron or monoiron complex. This was accounted for by the difference in the pK_a values of aromatic phenols compared to aliphatic diols.²⁵ Owing to the lower reactivity of the aliphatic diols, a much stronger base was required in the generation of the dinucleophiles. It was found that reaction of 2.0 mmol of the diol (**2a–f**) with 2.4 mmol of

* Author to whom correspondence should be addressed.

potassium tert-butoxide in THF for 45 min, led to the generation of the potassium salt. Two mmol of the chloroarene complex (**1a–e**) was then added and the reaction mixture stirred under nitrogen for a period of 16 h (Scheme 1). Following the workup procedure (see Experimental) the bis(cyclopentadienyliron) arene complexes **3a–m** were isolated in 45–86% yield. It is very important to note that the logical use of a 2:1:2 molar ratio of the base:diol:complex resulted in a mixture of products which consisted of the desired diiron complex as well as unreacted starting materials. In this investigation, we have noticed that the use of a slight excess of the base to the diol, along with an equimolar ratio of the diol to the starting complex, produced the dicationic complexes in a consistent manner. ^1H and ^{13}C NMR spectroscopy and elemental analysis were used to characterize the prepared diiron complexes **3a–m**. It was also noted for complexes **3k–m** that there was an increase in the product yield as the chain length of the diols increased. The elemental analyses of these complexes were also found to be satisfactory. The NMR data and yields of these complexes are summarized in Tables 1 and 2. The above described methodology further demonstrates the flexibility and efficiency of the nucleophilic substitution reaction as a route to the synthesis of diiron arene complexes. These materials could be used as building blocks in the synthesis of polymeric materials with pendent cyclopentadienyliron moieties.¹⁷

Since our research has been directed to the synthesis, functionalization and applications of cyclopentadienyliron arene complexes,^{14–18,26–28} we have investigated the possibility of demetallation as a

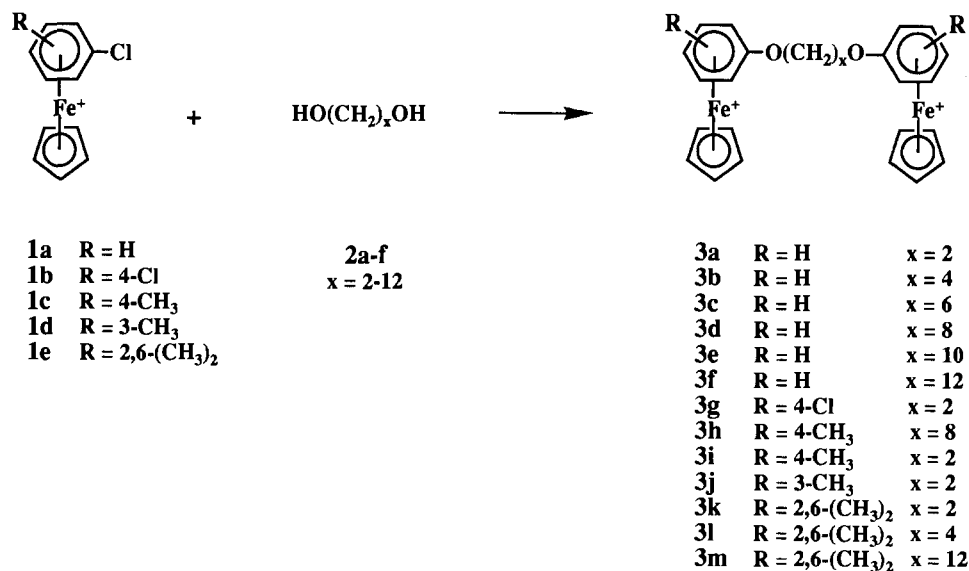
means to provide the free arenes. Photolytic demetallation has provided a unique route to the synthesis of terminal diaryloxyalkanes²⁹ (Scheme 2). The usual route to the synthesis of these compounds is *via* the Williamson's reaction,^{30–33} the cleavage of tetrahydrofuran by benzyne,³⁴ or the coupling of cyclohexanone cyclic ketals.³⁵ The identities of all free arenes prepared in this study were confirmed by ^1H and ^{13}C NMR spectroscopy, MS and m.ps. The major difference in the NMR spectra of these compounds was the absence of the cyclopentadienyl peaks and the downfield shift of the arene peaks. While the characterization of some of the free arenes has been reported^{31–41} complete spectroscopic data of all compounds are listed in Tables 3 and 4.

In conclusion, this work further demonstrates our ability to prepare bis(cyclopentadienyliron) arene complexes with aliphatic ether bridges. As well, photolytic demetallation provides a simple and efficient route to the synthesis of the diphenoxyalkanes. Both types of these materials could be used as building blocks in polyether synthesis.

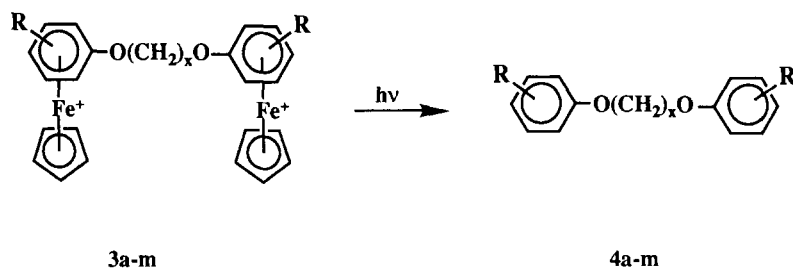
EXPERIMENTAL

Measurements

^1H and ^{13}C NMR spectra were recorded at 200 and 50 MHz, respectively, on a Varian Gemini 200 NMR spectrometer, with chemical shifts (ppm) being calculated from the solvent signals. Deuteroacetone or deuterodimethyl sulphoxide, and deuteriochloroform were used as solvents for the complexed and free arenes, respectively. Coupling constants were cal-



Scheme 1.



Scheme 2.

Table 1. Yield and ^1H NMR data for complexes **3a-m**

Complex no.	Yield (%)	Cp	Complexed Ar	δ (DMSO- d_6 , ppm)	
					Others
3a''	56	5.23	6.28 (m, 2H) 6.49 (m, 8H)	4.81 (s, 4H, CH ₂)	
3b	62	5.11	6.15 (m, 2H) 6.32 (m, 8H)	1.97 (br.s, 4H, CH ₂) 4.28 (br.s, 4H, CH ₂)	
3c	81	5.07	6.02 (m, 2H) 6.27 (m, 8H)	1.52 (br.s, 4H, CH ₂) 1.81 (br.s, 4H, CH ₂) 4.19 (t, 4H, $J = 6.0$ Hz, CH ₂)	
3d	71	5.06	6.02 (m, 2H) 6.27 (m, 8H)	1.41 (m, 8H, CH ₂) 1.76 (br.s, 4H, CH ₂) 4.16 (t, 4H, $J = 6.2$ Hz, CH ₂)	
3e	75	5.06	6.06 (m, 2H) 6.27 (m, 8H)	1.30 (m, 12H, CH ₂) 1.72 (br.s, 4H, CH ₂) 4.16 (t, 4H, $J = 6.2$ Hz, CH ₂)	
3f	86	5.06	6.07 (m, 2H) 6.27 (m, 8H)	1.27 (m, 16H, CH ₂) 1.73 (br.s, 4H, CH ₂) 4.15 (t, 4H, $J = 6.0$ Hz, CH ₂)	
3g''	51	5.33	6.56 (d, $J = 7.0$ Hz, 4H) 6.77 (d, $J = 7.0$ Hz, 4H)	4.76 (s, 4H, CH ₂)	
3h''	62	5.13	6.32 (s, 8H)	1.49 (br.s, 8H, CH ₂) 1.84 (m, 4H, CH ₂) 2.47 (s, 6H, CH ₃) 4.28 (t, 4H, $J = 6.6$ Hz, CH ₂)	
3i''	45	5.17	6.31 (d, $J = 6.8$ Hz, 4H) 6.40 (d, $J = 7.0$ Hz, 4H)	2.49 (s, 6H, CH ₃) 4.74 (s, 4H, CH ₂)	
3j''	49	5.15	6.19 (m, 2H) 6.37 (br.s, 6H)	2.56 (s, 6H, CH ₃) 4.76 (s, 4H, CH ₂)	
3k''	61	5.11	6.18 (t, $J = 6.0$ Hz, 2H) 6.40 (d, $J = 6.2$ Hz, 4H)	2.74 (s, 12H, CH ₃) 4.74 (s, 4H, CH ₂)	
3l''	68	5.07	6.14 (t, $J = 6.2$ Hz, 2H) 6.35 (d, $J = 6.2$ Hz, 4H)	2.18 (br.s, 4H, CH ₂) 2.64 (s, 12H, CH ₃) 4.13 (t, 4H, $J = 6.0$ Hz, CH ₂)	
3m''	82	5.05	6.11 (t, $J = 6.0$ Hz, 2H) 6.32 (d, $J = 6.2$ Hz, 4H)	1.31 (br.s, 16H, CH ₂) 1.87 (quintet, 4H, $J = 7.2$ Hz, CH ₂) 2.59 (s, 12H, CH ₃) 3.99 (t, 4H, $J = 6.4$ Hz, CH ₂)	

^aThe solvent for the NMR study was (CD₃)₂CO instead of DMSO- d_6 .

culated in Hz. MS were obtained on a Hewlett-Packard 5970 Series Mass Selective Detector, by electron impact (70 V). Signal positions are given in m/z units.

M.p.s were measured in a capillary using a Mel-Temp II and were uncorrected. All new compounds gave satisfactory elemental analyses.

Table 2. ^{13}C NMR data for complexes **3a–m**

Complex no.	Cp	δ (DMSO- d_6 , ppm)	
		Complexed Ar	Others
3a^a	77.56	75.99 (4C), 85.26 (2C), 87.65 (4C), 134.46 (2C, <i>ipso</i>)	68.76 (2C, CH ₂)
3b	76.10	74.33 (4C), 83.82 (2C), 86.38 (4C), 133.40 (2C, <i>ipso</i>)	24.98 (2C, CH ₂), 68.76 (2C, CH ₂)
3c	76.07	74.31 (4C), 83.75 (2C), 86.38 (4C), 133.52 (2C, <i>ipso</i>)	24.95 (2C, CH ₂), 28.20 (2C, CH ₂), 69.30 (2C, CH ₂)
3d	76.06	74.30 (4C), 83.73 (2C), 86.37 (4C), 133.54 (2C, <i>ipso</i>)	25.24 (2C, CH ₂), 28.27 (2C, CH ₂), 28.65 (2C, CH ₂), 69.36 (2C, CH ₂)
3e	76.01	74.24 (4C), 83.65 (2C), 86.30 (4C), 133.52 (2C, <i>ipso</i>)	25.17 (2C, CH ₂), 28.22 (2C, CH ₂), 28.62 (2C, CH ₂), 28.86 (2C, CH ₂), 69.32 (2C, CH ₂)
3f	76.08	74.32 (4C), 83.72 (2C), 86.38 (4C), 133.60 (2C, <i>ipso</i>)	25.24 (2C, CH ₂), 28.29 (2C, CH ₂), 28.71 (2C, CH ₂), 28.98 (2C, CH ₂), 29.00 (2C, CH ₂), 69.32 (2C, CH ₂)
3g^a	79.74	75.16 (4C), 87.45 (4C), 104.20 (2C, <i>ipso</i>), 133.53 (2C, <i>ipso</i>)	68.94 (2C, CH ₂)
3h	76.51	73.48 (4C), 86.42 (4C), 98.95 (2C, <i>ipso</i>), 132.49 (2C, <i>ipso</i>)	19.14 (2C, CH ₃), 25.18 (2C, CH ₂), 28.26 (2C, CH ₂), 28.69 (2C, CH ₂), 69.41 (2C, CH ₂)
3i^a	77.91	75.09 (4C), 87.65 (4C), 100.70 (2C, <i>ipso</i>), 133.27 (2C, <i>ipso</i>)	19.76 (2C, CH ₃), 68.76 (2C, CH ₂)
3j^a	77.65	73.90 (2C), 76.89 (2C), 85.39 (2C), 86.50 (2C), 103.40 (2C, <i>ipso</i>), 133.97 (2C, <i>ipso</i>)	19.76 (2C, CH ₃), 68.55 (2C, CH ₂)
3k	77.50	84.56 (2C), 87.24 (4C), 97.31 (4C, <i>ipso</i>), 129.04 (2C, <i>ipso</i>)	16.06 (4C, CH ₃), 72.94 (2C, CH ₂)
3l	77.30	84.23 (2C), 87.09 (2C), 96.96 (4C, <i>ipso</i>), 129.34 (2C, <i>ipso</i>)	15.86 (4C, CH ₃), 26.08 (2C, CH ₂), 73.71 (2C, CH ₂)
3m	77.27	84.15 (2C), 87.07 (4C), 96.90 (4C, <i>ipso</i>), 129.50 (2C, <i>ipso</i>)	15.87 (4C, CH ₃), 25.22 (2C, CH ₂), 28.67 (2C, CH ₂), 28.89 (4C, CH ₂), 29.53 (2C, CH ₂), 74.13 (2C, CH ₂)

^aThe solvent for the NMR study was (CD₃)₂CO instead of DMSO- d_6 .

Reagents

Starting complexes **1a–e** were prepared by ligand exchange reactions.^{42,43} Anhydrous aluminium chloride, aluminium powder, ferrocene, chloroarenes, aliphatic diols, potassium tert-butoxide and ammonium hexafluorophosphate were commercially available and were used without further purification. All solvents (reagent grade) were used without further purification, with the exception of freshly distilled THF. Silica gel, 60–100 mesh was used in the column chromatographic purification of the liberated arenes.

Synthesis of bis(cyclopentadienyliron) arene complexes

In a 50 cm³ round-bottom flask equipped with a stirbar was placed 0.2693 g (2.4 mmol) of potassium tert-butoxide, 2.0 mmol of the appropriate aliphatic

diol and 3.0 cm³ of tetrahydrofuran (THF). This white cloudy reaction mixture was then stirred under nitrogen for 45 min, after which another 3.0 cm³ of THF and 1.0 cm³ of DMF was added and the reaction mixture stirred for 5 min. To this mixture, 2.0 mmol of the desired chloroarene iron-cyclopentadienyl complex was then added, and the reaction mixture stirred further at room temperature, under nitrogen for 17 h. The red reaction mixture was then filtered into 20 cm³ of 10% HCl. The reaction flask was washed with acetone and the latter added to the filtrate. The acetone was removed under reduced pressure at 25°C using a rotary evaporator (Buchi RE-111), and concentrated aqueous ammonium hexafluorophosphate was added to the reaction mixture. The product was then extracted with CH₂Cl₂ (2 × 30 cm³), and washed with distilled water (2 × 50 cm³). After drying over MgSO₄, the solution was concentrated by rotary evaporation of the

Table 3. Yield, m.p. and ^1H NMR data for compounds **4a–m**

Compound no.	Yield (%)	M.p. ($^{\circ}\text{C}$)	δ (CDCl_3 , ppm)	
			Ar	Others
4a	85	93–94 ^{33,34}	6.96 (m, 6H) 7.29 (t, $J = 7.3$ Hz, 4H)	4.32 (s, 4H, CH_2)
4b	78	77–78	6.92 (m, 6H) 7.29 (t, $J = 7.3$ Hz, 4H)	1.99 (br.s, 4H, CH_2) 4.04 (br.s, 4H, CH_2)
4c	77	78–79.5	6.92 (m, 6H) 7.28 (t, $J = 7.4$ Hz, 4H)	1.56 (m, 4H, CH_2) 1.83 (t, 4H, $J = 6.6$ Hz, CH_2) 3.98 (t, 4H, $J = 6.1$ Hz, CH_2)
4d	92	76–77.5	6.93 (m, 6H) 7.29 (t, $J = 7.3$ Hz, 4H)	1.44 (m, 8H, CH_2) 1.80 (t, 4H, $J = 6.6$ Hz, CH_2) 4.98 (t, 4H, $J = 6.3$ Hz, CH_2)
4e	82	76.5–78	6.91 (m, 6H) 7.27 (t, $J = 7.1$ Hz, 4H)	1.32 (m, 12H, CH_2) 1.77 (m, 4H, CH_2) 3.94 (t, 4H, $J = 6.5$ Hz, CH_2)
4f	91 34	85–86	6.91 (m, 6H) 7.26 (t, $J = 7.1$ Hz, 4H)	1.29 (m, 16H, CH_2) 1.77 (m, 4H, CH_2) 3.94 (t, 4H, $J = 6.4$ Hz, CH_2)
4g	82	127–128 ³⁵	6.87 (d, $J = 7.7$ Hz, 4H) 7.25 (d, $J = 7.8$ Hz, 4H)	4.29 (s, 4H, CH_2)
4h	85	oil	6.77 (d, $J = 8.3$ Hz, 4H) 7.05 (d, $J = 7.7$ Hz, 4H)	1.34 (br.s, 8H, CH_2) 1.73 (m, 4H, CH_2) 2.26 (s, 6H, CH_3) 3.90 (t, $J = 6.6$ Hz, 4H, CH_2)
4i	84	127–128.5	6.82 (d, $J = 8.0$ Hz, 4H) 7.07 (d, $J = 8.0$ Hz, 4H)	2.27 (s, 6H, CH_3) 4.26 (s, 4H, CH_2)
4j	87	oil	6.87 (m, 6H) 7.15 (t, $J = 7.3$ Hz, 2H)	2.31 (s, 6H, CH_3) 4.29 (s, 4H, CH_2)
4k	95	oil	6.97 (m, 2H) 7.03 (m, 4H)	2.36 (s, 12H, CH_3) 4.14 (s, 4H, CH_2)
4l	90	oil	7.25 (m, 6H)	2.05 (m, 4H, CH_2) 2.28 (s, 12H, CH_3) 3.84 (m, 4H, CH_2)
4m	92	oil	6.97 (m, 6H)	1.29 (br.s, 16H, CH_2) 1.79 (quintet, 4H, $J = 7.0$ Hz, CH_2) 2.27 (s, 12H, CH_3) 3.75 (t, 4H, $J = 6.4$, CH_2)

solvent. Addition of diethyl ether resulted in a yellow precipitate which was filtered and dried *in vacuo* before analysis.

Photolytic demetallation

Each of the complexes **3a–m** was separately dissolved in a mixture of CH_2Cl_2 – CH_3CN ($30\text{ cm}^3/10\text{ cm}^3$) in a Pyrex tube. The solution was then deoxygenated by bubbling nitrogen through it after which the reaction tube was fitted into a photochemical apparatus equipped with a xenon lamp, and irradiated at room temperature for 4 h. The solvent was concentrated to a volume of 1–2 cm^3

using rotary evaporation. The residue was applied to a silica gel column which was then washed with hexane and eluted with chloroform. Removal of the solvent from the eluate gave the expected liberated arenes.

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Table 4. Mass spectral and ^{13}C NMR data for complexes **4a–m**

Compound no.	m/z (M^+)	Ar	δ (CDCl_3 , ppm)	Others
4a	214 (57%)	114.68 (4C), 121.08 (2C), 129.49 (4C), 158.61 (2C, <i>ipso</i>)	66.42 (2C, CH_2)	
4b	242 (11%)	114.49 (4C), 120.61 (2C), 129.44 (4C), 158.98 (2C, <i>ipso</i>)	26.06 (2C, CH_2), 67.34 (2C, CH_2)	
4c	270 (62%)	114.47 (4C), 120.47 (2C), 129.39 (4C), 159.04 (2C, <i>ipso</i>)	25.89 (2C, CH_2), 29.24 (2C, CH_2), 67.67 (2C, CH_2)	
4d	298 (52%)	114.42 (4C), 120.39 (2C), 129.33 (4C), 159.04 (2C, <i>ipso</i>)	25.95 (2C, CH_2), 29.22 (2C, CH_2), 29.24 (2C, CH_2), 67.74 (2C, CH_2)	
4e	326 (35%)	114.47 (4C), 120.42 (2C), 129.36 (4C), 159.10 (2C, <i>ipso</i>)	26.03 (2C, CH_2), 29.27 (2C, CH_2), 29.36 (2C, CH_2), 29.47 (2C, CH_2), 67.83 (2C, CH_2)	
4f	354 (33%)	114.46 (4C), 120.40 (2C), 129.34 (4C), 158.08 (2C, <i>ipso</i>)	26.03 (2C, CH_2), 29.27 (2C, CH_2), 29.37 (2C, CH_2), 29.53 (4C, CH_2), 67.83 (2C, CH_2)	
4g	282 (87%) 284 (58%)	115.97 (4C), 129.39 (4C), 126.10 (2C, <i>ipso</i>), 157.17 (2C, <i>ipso</i>)	66.78 (2C, CH_2)	
4h	326 (84%)	114.33 (4C), 129.80 (4C), 136.18 (2C, <i>ipso</i>), 157.48 (2C, <i>ipso</i>)	20.42 (2C, CH_3), 25.97 (2C, CH_2), 29.28 (4C, CH_2), 67.97 (2C, CH_2)	
4i	242 (100%)	114.57 (4C), 129.90 (4C), 130.29 (2C, <i>ipso</i>), 156.54 (2C, <i>ipso</i>)	20.47 (2C, CH_3), 66.67 (2C, CH_2)	
4j	242 (71%)	111.50 (2C), 115.54 (2C), 121.85 (2C), 129.19 (2C), 139.51 (2C, <i>ipso</i>), 158.62 (2C, <i>ipso</i>)	21.50 (2C, CH_3), 66.35 (2C, CH_2)	
4k	270 (2%)	123.88 (2C), 128.83 (4C), 131.01 (4C, <i>ipso</i>), 155.87 (2C, <i>ipso</i>)	16.36 (4C, CH_3), 71.35 (2C, CH_2)	
4l	298 (1%)	123.70 (2C), 128.79 (4C), 131.01 (4C, <i>ipso</i>), 155.87 (2C, <i>ipso</i>)	16.26 (4C, CH_3), 27.25 (2C, CH_2), 71.83 (2C, CH_2)	
4m	410 (1%)	123.48 (2C), 128.65 (4C), 130.82 (4C, <i>ipso</i>), 155.98 (2C, <i>ipso</i>)	16.18 (4C, CH_3), 26.09 (2C, CH_2), 29.38 (2C, CH_2), 29.53 (4C, CH_2), 30.37 (2C, CH_2), 72.20 (2C, CH_2)	

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