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MERCURY(II) OXIDE/TETRAFLUOROBORIC ACID-PROMOTED VICINAL HYDROXY- AND ALKOXYLATION OF ALKENES

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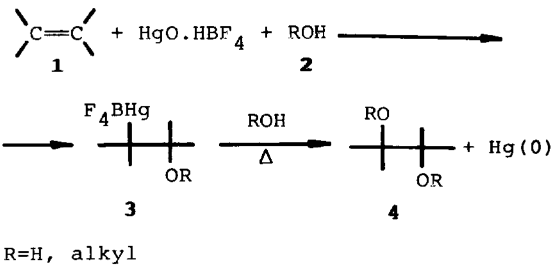
Abstract—The reaction of alkenes with mercury(II) oxide/tetrafluoroboric acid and alcohols or water involves reduction to Hg(O) and vicinal diethers or diols are produced in good yields. Olefins bearing benzylic hydrogens in an α position lead to cinnamyl ethers. Mechanisms are proposed to account for the products and their stereochemistry.

The oxidation of olefins with mercury(II) salts has been quite throughly studied.[1-3] The Deniges and the Treibs reactions which allows the transformation of alkenes into carbonyl compounds or allyl acetates respectively are the most general and studied processes.[2] A third route of oxidation is that leading to *vicinal* diols or diethers. The scope of this reaction appears to be constrained to the use of α-aryl substituted olefins since otherwise addition–elimination compounds[4] or Wagner–Meervein rearranged carbonyl derivatives are obtained. For instance, while the oxidation of 2-methyl-1-phenyl propene with mercury(II) nitrate in methanol gives a mixture of the 1,2- and 1,1-dimethoxyalkanes and some nitrate ester,[5] the reaction of cyclohexene with mercury(II) sulfate affords mainly cyclopentanecarboxaldehyde and minor amounts of cyclohexenone and cyclohexanone.[2] On the other hand, recently we have described the general mercury(II) oxide/tetrafluoroboric acid-promoted 1,2-diamination[6] and 1,2-hydroxy(alkoxy)-phenylamination[7] of alkenes.

On these grounds we felt it of interest to study the oxidation of olefins with this latter mercury(II) salt in aqueous and alcoholic media in the search of a general method of *vicinal* hydroxylation and alkoxylation.

RESULTS AND DISCUSSION

We have found that the mercury(II) oxide/tetrafluoroboric acid-promoted addition of water and alcohols **2** to olefins **1** followed by moderated heating (*ca* 70°) of the reaction mixture gives elemental mercury and the corresponding *vicinal* diols or diethers **4** (Scheme 1).



Scheme 1.

Reactions are carried out as a one pot, process in THF, dioxane or alcohol solution. From the preparative point of view, the use of alcohol as the solvent for the synthesis of diethers, is advantageous since side reactions are minimized or even completely avoided. When an ether cosolvent is employed, variable amounts of allyl ethers or alcohols **6** and/or carbonyl compounds **7** are also generated (see Table 1).

The intermediate Markovnikov oxymercurials **3** can be trapped if the adduct is formed at 0° and quenched with sodium acetate as soon as the solution gives a negative test for free mercury(II) with 1N potassium hydroxide (Scheme 2, path a).

When the starting olefin **1** does not bear α-aryl substituents the formation of diethers **4** is *trans*-stereospecific (Scheme 2, path b→c) and can be easily explained through the formation of the intermediate oxonium tetrafluoroborate **5** by anchimerically assisted displacement of mercury in **3**. If the concentration of **2** is diminished by addition of a cosolvent, the alternative reaction path b→d (Scheme 2) is also operative and variable amounts of compounds **6** are produced (see Table 1). The same effect is observed by steric crowding in the intermediate oxirane **5** (i.e. R = *iso*-propyl) which will slow down the reaction with **2** to accomplish the ring opening.

By contrast, olefins bearing α-arylsubstituents give rise to the formation of a mixture of diasteroisomers. Thus, *trans*-1-phenylpropene **1c** and anethole **1d** give equimolecular amounts of the *erythro* and *threo* diethers (Scheme 3).

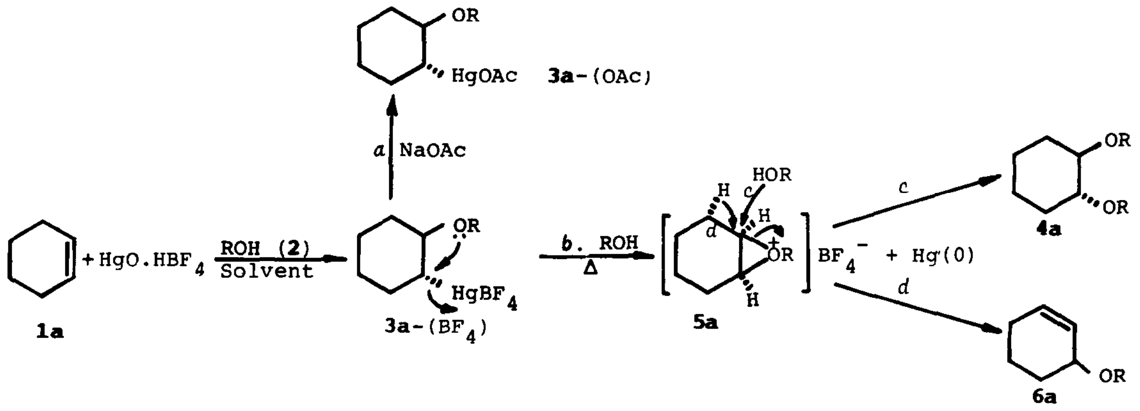
The possibility of Z-E isomerization of **1c** and **1d** in the mercuration step as an explanation for the formation of the mixture **4c, d** is disregarded since only one (**3d**) out of the two possible diastereoisomeric oxymercurials is produced.

Thus, two alternative reaction paths can be envisaged to explain this stereochemical result (Scheme 4). Path b implies that the intermediate oxirane **5c, d** formed from the regular Markovnikov adduct **3c, d** is in equilibrium with the benzylic cation **8c, d** and this latter undergoes the attack of the second molecule of alcohol to afford the mixture of diasteroisomers **4c, d**. On the other hand in path a the reverse orientation in the oxymercuration is proposed to give a benzylic oxymercurial **10c, d** which would be solvolyzed to

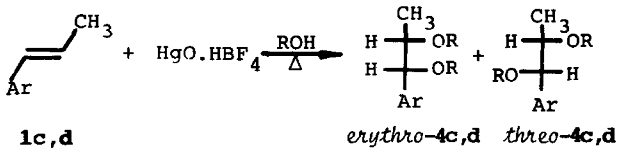
Table 1. Mercury(II) oxide/tetrafluoroboric acid-promoted oxidation of olefins[a]

1 (Olefin)	**2** (R)	Cosolvent	Yield (%)	**4** (Ratio)	**6** (Ratio)	**7** (Ratio)
a (Cyclohexene)	**a** (H)	Dioxane	60	**aa** (83)	**aa** (17)	-
a	**c** (C_2H_5)	-	51	**ac** (100)	-	-
a	**d** (*iso*-C_3H_7)	-	55	**ad** (90)	**ad** (10)	-
b (Cyclooctene)	**b** (CH_3)	-	50	**bb** (100)	-	-
c (*trans*-1-Phenyl-propene)	**c**	-	77	**cc**[b] (90)	-	**c** (5)
c	**c**	THF	76	**cc**[b] (65)	-	**c** (35)
d (Anethole)	**a**	Dioxane	72[c]	**da** (100)	-	-
d	**b**	-	90	**db**[b] (100)	-	-
e (Styrene)	**a**	Dioxane	83	**ea** (100)	-	-
e	**b**	-	63	**eb** (100)	-	-
e	**b**	THF	67	**eb** (100)	-	-
e	**c**	THF	56	**ec** (100)	-	-
e	**d**	THF	66	**ed** (100)	-	-
e	**e** (*n*-C_4H_9)	THF	68	**ee** (100)	-	-
g (1-Phenylcyclo-hexene)	**b**	THF	52	-	**gb** (60)	**g** (40)
g	**c**	-	67	-	**gc** (70)	**g** (30)
h (3-Phenyl-propene)	**b**	THF	71	-	**hb** (100)	-
h	**c**	THF	80	-	**hc** (100)	-
h	**d**	THF	68	-	**hd** (100)	-
h	**e**	THF	71	-	**he** (100)	-
h	**f** (*iso*-C_4H_9)	THF	66	-	**hf** (100)	-
h	**g** (*n*-C_5H_{11})	THF	76	-	**hg** (100)	-
h	**h** (*cyclo*-C_6H_{11})	THF	67	-	**hh** (100)	-
i (Indene)	**b**	-	65	**ib** (95)	-	**i** (5)
i	**b**	THF	56	**ib** (75)	**ib** (25)	-
i	**c**	THF	68	**ic** (70)	**ic** (25)	**i** (5)

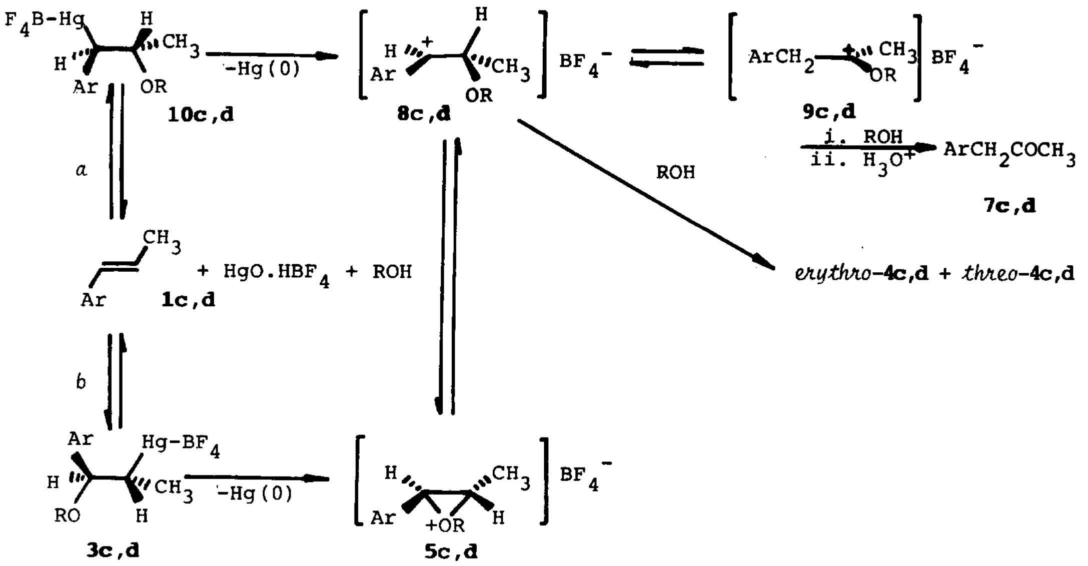
[a] Reactions were carried out at 70° (bath). Elemental mercury was recovered in nearly quantitative amount. [b] Equimolecular mixture of diasteroisomers. [c] Mercuration was carried out with mercury(II) acetate as described by Summerbell in Ref.8.



Scheme 2.



Scheme 3.

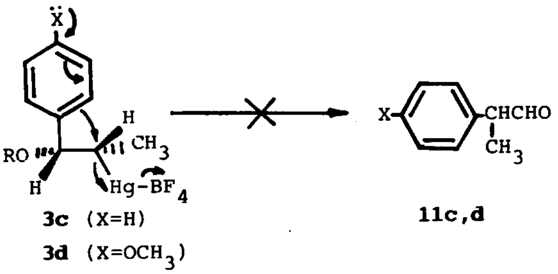


Scheme 4.

afford the products. This type of intermediate was also proposed by Summerbell *et al.*[8] The orientation in the oxymercuration of olefins is well documentated[9] and, indeed, compounds **3c, d** are the expected ones. In fact, we have isolated from anethole the bromomercury derivative **3d** (Br) after stirring for 10 h a mixture of **1d**, methanol and mercury(II) acetate followed by precipitation of the mercurial with an aqueous solution of potassium bromide. We failled to detect the anti-Markovnikov regioisomer **10d** by ^{13}C–NMR analysis of the crude reaction product. However, ^{13}C–NMR is not a very sensitive technique to perform such a detection and, hence, the possibility of the presence of small amounts of **10d** cannot be excluded. Since **10c, d** would loss mercury a much faster rate than **3c, d** due to the benzylic character of its C–Hg bond[10] and taking into account that the oxymercuration is a reversible process, the whole reaction could proceed through path a. This argument would account for the rule that double bonds adjacent to an o- or p-alkoxyphenyl group reduce mercury(II) salts to mercury[2] and also for the enhanced reaction rate observed in α-aryl substituted olefins relative to other alkenes.

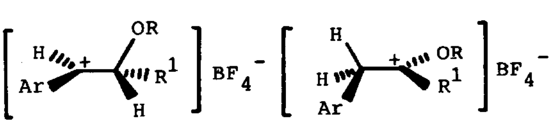
The possibility of formation of the anti-Markovnikov adduct **10** depends largely from the degree of substitution at Cβ · So, we found that p-methoxystyrene **1f** when allowed to react with mercury(II) acetate in water/dioxane solution does not yield the corresponding diol and elemental mercury even after fifteen days stirring at room temperature, while the oxymercurial derived from anethole **1d** start to decompose after twelve hours under similar reaction conditions.

If the reaction would follow the course shown in path b some type of aryl participation as depicted in **3** would be required to explain the differences observed in reaction rates. Consequently, rearranged products (i.e. aldehydes **11**) should be obtained in amounts increasing with the electron donating ability of the aryl substituent (Scheme 5). Conversely, no aldehyde is obtained in the oxidation of **1d**.



Scheme 5.

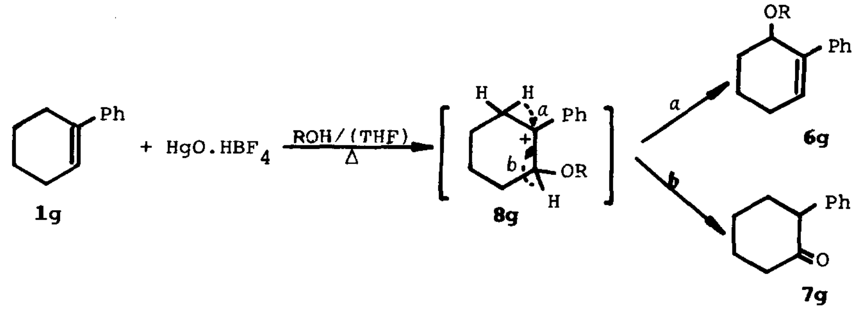
α-Aryl alkenes produce α-aryl carbonyl compounds **7** as side products in amounts that correlate well with the relative stability of ions **8** and **9**. So, p-methoxyphenylpropanone **7d** is not detected from **1d** and only trace amounts of phenylacetaldehyde **7e** (as dimethylacetal) are obtained from styrene **1e** due to the special stabilization of the benzylic cation **8d** by the p-methoxy group and to the lowered stability of **8c** and **9c** (Ar=C$_6$H$_5$; R^1=CH$_3$) will lie closer and compound **7c** is produced in up to 35% yield if a cosolvent is used instead of alcohol as reaction medium.



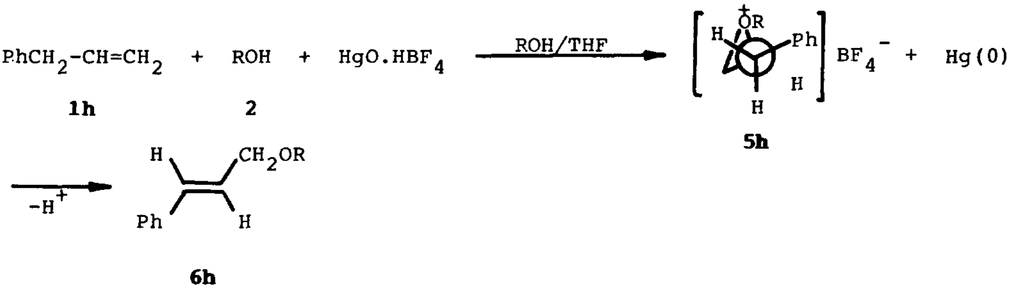
8 **9**

The reaction of α,α-alkylaryl alkenes (i.e. 1-phenylcyclohexene **1g**) gives only the corresponding allyl ether **6g** and ketone **7g** (Scheme 6).

The presence of a benzylic proton in α to the oxirane intermediate **5** gives rise to elimination and

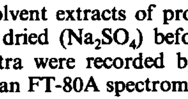


Scheme 6.

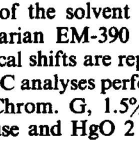


Scheme 7.

formation of olefin. So, allylbenzene **1h** reacts with mercury(II) oxide/tetrafluoroboric acid in alcohol or alcohol/THF to afford exclusively *trans*-cynnamyl ethers **6h**[4] (Scheme 7). Consequently, indene **1i** that can be regarded as an α-arylalkene or an allyl arene gives cleanly 1,2-diethers **4i** in alcoholic medium and a mixture of **4i** and allyl ether **6i** in alcohol/THF solution (see Table 1).



4i



6i

EXPERIMENTAL

Solvent extracts of products were appropriately washed and dried (Na_2SO_4) before removal of the solvent NMR spectra were recorded by using a Varian EM-390 and a Varian FT-80A spectrometers. Chemical shifts are reported in ppm (δ) down field from Me_4Si. GLC analyses performed on a Varian VISTA-6000 (column Chrom. G, 1.5% OV-101). Olefins were distilled prior to use and HgO 2 HBF_4 was prepared as reported.[6]

Synthesis of compounds **4**

(a) *In alcoholic medium.* To a soln of **1** (20 mmol) in alcohol **2** (25 ml) HgO HBF_4 (3.75 g, 10 mmol) was added. The mixture was heated at 70° for 4 h. The quantitative elemental mercury was filtered and the resulting solution treated with lN KOH and extracted with ether. After usual work-up procedure the residue was purified by vacuum distillation (0.01 torr) and analyzed by GLC and NMR. Yields in compounds **4** are summarized in Table 1. Spectral data are collected in Table 2.

(b) *In THF/alcoholic medium.* Olefin **1** (20 mmol) and alcohol **2** (30 mmol) were disolved in THF (25 mL) and the HgO/HBF_4 (3.75 g, 10 mmol) was added. The work-up procedure was similar to the above described.

(c) *In dioxane/water medium.* A mixture of dioxane (30 mL) and water (15 mL) was employed as the solvent for the preparation of diols **4**. The work-up procedure was similar to the above.

Trapping of the oxymercurial **3a**(*OAc*). A mixture of HgO HBF_4 (1.9 g, 5 mmol), **1a** (0.82 g, 10 mmol), and methanol (15 mL) was stirred at 0° until test for mercury(II) proved negative (30 min). Then potassium acetate (2 g) was added and the solvent was removed *in vacuo*. The oily residue was disolved in THF and filtered. The evaporation of the solution gave 3.65 g (100%) of the product. ^{1}H-NMR (CCl_4) δppm 1.30–2.20 (m, 8H), 1.85 (s, 3H), 3.30 (s, 3H), 3.30–3.60 (m, 1H). ^{13}C-NMR (CCl_4) δppm 24.77, 25.36, 29.85, 32.75, 34.47, 53.19, 57.03, 83.40, 177.59.

Preparation of **3d**(*Br*). Mercury(II) acetate (16.0 g, 50 mmol) was slowly added to a mixture of anethole **1d** (7.4 g, 50 mmol) and methanol (30 mL) and stirred until negative test of mercury(II) (10 h). The solution was filtered to remove the small amount of mercury(I) salt formed, and poured into an excess of aq KBr. The resulting white solid was filtered, washed, dried, and recrystallized from methanol giving 13.4 g (58%) of **3d**(*Br*). ^{1}H-NMR (DMSO-d_6) δppm 1.70(d, 3H), 3.20 (m, 1H), 3.50 (s, 3H), 4.15 (s, 3H), 4.80 (d, 1H), 7.20–7.70 (m, 4H). ^{13}C-NMR (DMSO-d_6) ppm 31.03, 59.33, 60.13, 61.95, 90.62, 118.01, 131.89, 139.68, 162.82.

Preparation of compounds **6h**. To a solution of **1h** (4.7 g, 40 mmol) and alcohol **2** (60 mmol) in THF (40 mL) was added HgO/HBF_4 (7.5 g, 20 mmol). The reaction was stirred under reflux for 2 h and then cooled. The mercury(0) precipitate was filtered off (nearly quantitative yield) and the solution hydrolyzed with 1N KOH and extracted with ether. Solvents were removed and the residue distilled under vacuum to yield **6h**. Yields and spectral data are summarized in Tables 1 and 2.

Table 2. NMR data for compounds **4**, **6** and **7**^{a}

Compound	^{1}H-MNR [CCl$_4$ or CDCl$_3$, δ (TMS)]	^{13}C-NMR [CCl$_4$ or CDCl$_3$, δ (TMS)]
4aa^{b,c}		
4ac	1.15(t,6H), 1.5–2.3(m,8H), 3.15(m,2H), 3.55(q,4H)	17.44, 24.61, 30.99, 66.27, 81.61
4ad	1.05(d,12H), 0.8-2.15(m,8H), 3.1(m,2H), 3.75(m,2H)	24.07, 24.30, 24.79, 32.30, 71.33, 79.52
4bb	1.20-2.50(m,12H), 3.25(s,6H), 3.25-3.60(m,2H)	24.38, 27.79, 31.26, 56.56, 81.47
4cc	1.05(t,3H), 1.15(t,3H), 1.2(d,3H), 3.55(m,4H), 4.20(dd,2H), 7.3(m,5H)	16.54, 17.67, 65.58, 79.49, 80.49, 86.21, 86.79, 128.69, 128.78, 128.90 129.72, 130.44
4db	0.95(dd,3H), 3.20(s,6H), 3.7(s,3H), 3.7-4.2(m,2H), 6.5-7.2 (m,4H)	16.50, 55.71, 57.49, 57.68, 81.11 and 81.83, 97.29 and 97.99, 114.53, 129.89, 132.27 and 132.98, 160.29
4ea^{b,c}		
4eb	3.25(s,3H), 3.3(s,3H), 3.5(m,2H), 4.35(m,1H), 7.35(m,5H)	56.29, 57.43, 76.88, 82.77, 126.55, 127.38, 127.80, 139.12
4ec	1.15(t,3H), 1.2(t,3H), 3.5(m,6H), 4.45(m,1H), 7.3(m,5H)	14.08, 14.33, 63.70, 65.88, 74.50, 80.63, 125.20, 126.74, 127.37, 139.50
4ed	1.15(m,12H), 3.5(m,4H), 4.5(m,1H), 7.3(m,5H)	21.43, 21.71, 21.86, 22.94, 69.74, 71.81, 73.27, 78.99, 125.96, 126.69 127.82, 141.31
4ee	0.7-1.75(m,18H), 3.45(m,2H), 4.4(m,1H), 7.3(m,5H)	12.72, 18.14, 30.66, 30.88, 68.01, 70.24, 74.53, 80.47, 125.79, 126.50, 127.14, 139.21
4ib	2.85(m,2H), 3.4(s,3H), 3.5(s,3H), 4.1(m,1H), 4.75(d,1H), 7.0-7.4(m,4H)	37.13, 57.92, 88.71, 89.45, 126.03, 126.31, 127.78, 129.51, 141.07, 141.93
4ic	1.2(t,3H), 1.35(t,3H), 3.1(m,2H), 3.65(q,2H), 3.75(q,2H), 4.2(q,2H), 7.0-7.4(m,4H)	14.41, 14.58, 35.45, 63.75, 63.89, 85.29, 86.34, 123.75, 123.84, 125.60, 127.13, 138.80, 140.22
6aa^{b,c}		
6ad	1.05(d,6H), 0.8-2.15(m,6H), 3.1(m,1H), 3.7(m,1H), 5.8(m,2H)	24.94, 25.19, 25.53, 31.55, 33.46, 74.32, 81.99, 130.28, 132.41
6gb	1.35-2.7(m,6H), 3.25(s,3H), 3.35(m,1H), 6.05(m,1H), 7.35 (m,5H)	18.38, 27.37, 27.72, 27.13, 75.45, 127.12, 128.28, 128.90, 129.73, 129.82, 139.22
6gc	1.1(t,3H), 1.25-2.6(m,8H), 3.4(m,1H), 6.5(m,1H), 7.65(m,5H)	16.90, 18.42, 27.04, 27.28, 64.87, 74.01, 127.12, 128.28, 128.90, 129.73, 129.82, 139.22
6hb	3.35(s,3H), 4.1(d,2H), 6.0-6.8(m,2H), 7.1-7.65(m,5H)	57.08, 71.94, 125.96, 126.96, 127.97, 131.59, 136.57
6hc	1.2(t,3H), 3.55(q,2H), 4.10(d,2H), 6.05–6.9(m,2H), 6.95-7.6(m,5H)	14.93, 55.42, 60.86, 126.26, 127.46, 127.29, 128.27, 131.81, 136.84
6hd	1.2(d,6H), 3.6(m,1HO, 4.1(d,2H), 6.0-6.8(m,2H), 7.0-7.5 (m,5H)	21.89, 68.33, 70.67, 126.18, 127.02, 127.13, 128.18, 131.21, 136.92
6he	0.7-1.9(m,7H), 3.5(t,2H), 4.15(d,2H), 6.05-6.85(m,2H), 7.0-7.55(m,5H)	13.59, 19.18, 31.75, 70.04, 71.09, 126.27, 126.61, 127.26, 128.27, 131.70 136.90
6hf	0.9(d,6H), 1.8(m,1H), 3.25(d,2H), 4.1(d,2H), 6.0-6.75 (m,2H), 7.0-7.6(m,6H)	18.96, 28.19, 71.02, 76.90, 126.02, 126.46, 126.99, 128.07, 131.26, 136.70
6hg	0.4-1.9(m,9H), 2.95-3.7(m,2H), 4.1(d,2H), 6.0-6.75(m,2H), 6.75–7.6(m,5H)	24.08, 25.88, 32.35, 68.35, 76.94, 126.43, 127.37, 127.45, 128.41, 131.43 137.19
6hh	0.85–2.15(m,10H), 3.5(m,1H), 4.15(d,2H), 6.05-6.8(m,2H), 7.0-7.6(m,5H)	23.63, 25.57, 31.95, 67.93, 76.45, 126.04, 126.94, 127.11, 127.72, 130.89 136.82
6ib	3.55(s,3H), 4.8(m,1H), 6.4-6.9(m,2H), 7.0-7.4(m,4H)	
6ic	1.25(t,3H), 3.5(q,2H), 4.85(d,1H), 6.2-6.7(m,2H), 7.0-7.4 (m,4H)	
7c^{b,c}		
7g^{b}		26.37, 28.94, 36.38, 43.18, 57.22, 127.10, 128.33, 129.50, 134.44, 187.20
7i^{b,c}		

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[a] Satisfactory microanalytical values were found for all compounds: C ± 0.35; H ± 0.15. [b] For ^{1}H-NMR see "The Aldrich Library of NMR Spectra", Aldrich Chem. Co., Inc., Milwaukee, WI, 1974. [c] For ^{13}C-NMR see "^{13}C-NMR Spectral Data", Verlag Chemie, Weinheim, Germany, 1982.

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