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Ion/neutral complexes generated during unimolecular fragmentation: Intra-complex hydride abstraction by *tert*-butyl cations from electron-rich and electron-poor 1,3-diphenylpropanes

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Dedicated to Professor Diethard Böhme on the occasion of his 65th birthday.

Abstract

The hydride transfer and proton transfer occurring between the constituents of ion/neutral complexes of *tert*-butyl cations and electron-rich and electron-poor 1,3-diphenylpropanes, $[(CH_3)_3C^+ \quad C_6H_5CH_2CH_2CH_2C_6H_4X]$ were investigated by use of CI/MIKE spectrometry of nine 1-(*tert*-butylphenyl)-3-arylpropanes and 16 site-specific deuterium-labeled isotopomers. The competition between H^- abstraction by the $(CH_3)_3C^+$ ion from the neutral arene and H^+ transfer to it was found to be strongly affected by the electron-donating substituents, in particular by $X = OCH_3$, on the one hand, and $X = F$ and CF_3, on the other, suggesting that the 1,3-diphenylpropane molecule within the I/N complex acts and reacts as a bidentate solvating partner to the carbocation. The effect of the substituents X on the regioselectivity of the intra-complex hydride abstraction from the two benzylic CH_2 groups, $k_{\gamma\text{-H}}/k_{\alpha\text{-H}}$, and their influence on the kinetic isotope effect $(k_H/k_D)_\gamma$, operating during the abstraction from the substituted benzylic moiety, were determined in a semi-quantitative approach by assuming $(k_H/k_D)_\alpha = 1.60$, the generally observed value for the unsubstituted benzylic moiety. The regioselectivity range was found to span almost three orders of magnitude, from $k_{\gamma\text{-H}}/k_{\alpha\text{-H}} \geq 11.2$ for the complex $[(CH_3)_3C^+ \quad C_6H_5C^{\alpha}H_2CH_2C^{\gamma}H_2C_6H_4(p\text{-}OCH_3)]$ to $k_{\gamma\text{-H}}/k_{\alpha\text{-H}} \leq 0.04$ for the complex $[(CH_3)_3C^+ \quad C_6H_5C^{\alpha}H_2CH_2C^{\gamma}H_2C_6H_4(p\text{-}CF_3)]$.

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Keywords: Ion/neutral complexes; Hydride transfer; Proton transfer; Carbenium ions; Arenium ions

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1. Introduction

Hydride transfer reactions occurring in the course of unimolecular fragmentation reactions of gaseous organic ions can be used favorably as a probe for the formation of intermediate ion/molecule complexes [1–6]. In such systems, the positively charged I/N complexes consist of a cationic fragment as a Lewis acid and a neutral molecule reacting as a hydride ion donor, both constituents being mutually bound through ion/dipole and ion/induced-dipole interactions. In general, hydride transfer is much less common in organic ion/neutral complexes than proton transfer since many carbocations contain highly acidic C–H bonds, thus representing both Lewis and Brønsted acids. Nevertheless, hydride transfer reactions can compete with or even dominate over proton transfer if, for a given carbocation, the hydride donor reactivity and the basicity of the neutral partner of the complex are well-tuned [5–8]. Excellent examples to study this behavior are complexes consisting of a *tert*-butyl cation and an α,ω-diphenylalkane, as shown in Scheme 1 [9].

In the course of our research into the chemistry of ion/molecule complexes formed during the unimolecular fragmentation of protonated *tert*-butylbenzenes under CI conditions [5,9–13], we have extensively investigated the effect of methyl substituents at the aromatic nuclei of the neutral arene, e.g., the 1,3-diphenylpropane molecule generated from protonated **1**, on its reactivity within the I/N complex [9,11]. It became clear that methyl substitution on the neutral component of the I/N complexes generated from the precursors **2**–**4** and related hydrocarbons affects the hydride-versus-proton transfer compe-

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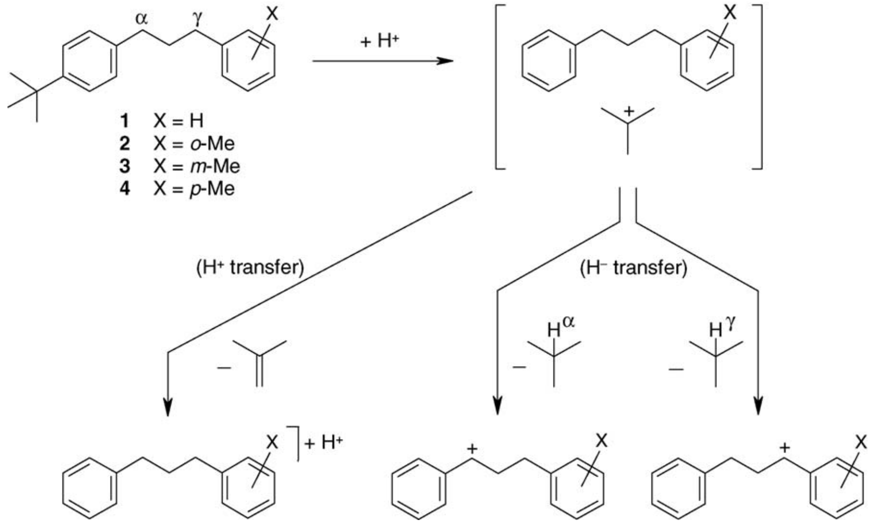


Scheme 1. Major fragmentation paths of metastable $[M+H]^+$ ions generated from α-(*tert*-butylphenyl)-γ-arylpropanes **1**–**4** by CI(CH_4), involving intra-complex proton and hydride transfer [5,9].

tition and the regioselectivity ($k_{\alpha\text{-H}}/k_{\gamma\text{-H}}$) of the intra-complex hydride transfer. However, the kinetic isotope effects operating on the H^- and D^- abstraction remained constant in all of the cases studied ($k_H/k_D = 1.6$). Of particular importance was the finding that *ortho*-methyl substituents, if electronically activated by additional methyl groups at the same arene ring, can act as strong hydride donors competing with the benzylic methylene groups, whereas *meta*- and *para*-methyl groups cannot [11].

In this work, we present the results of further experiments performed in this series with protonated 1-(4-*tert*-butylphenyl)-3-arylpropanes **5**–**13**, bearing more or less strongly electron-releasing and electron-withdrawing substituents (Chart 1). Instead of methyl substituents, some extended π-electron systems and, in particular, strongly electro-active groups, such as methoxy, fluoro and trifluoromethyl substituents, were introduced at the formally remote aromatic ring of the $[M+H]^+$ ions. Dissociation of the protonated 1,3-diarylpropanes and their isotopomers bearing deuterium-labeled benzylic methylene groups was studied on the microseconds' time scale in a sector-field mass spectrometer (MIKE spectrometry) and allowed us to gain further detailed insights on the regioselectivity of the intra-complex hydride abstraction and the kinetic isotope effects associated with this process. An independent study on the intermolecular reactions between *tert*-butyl cations and related

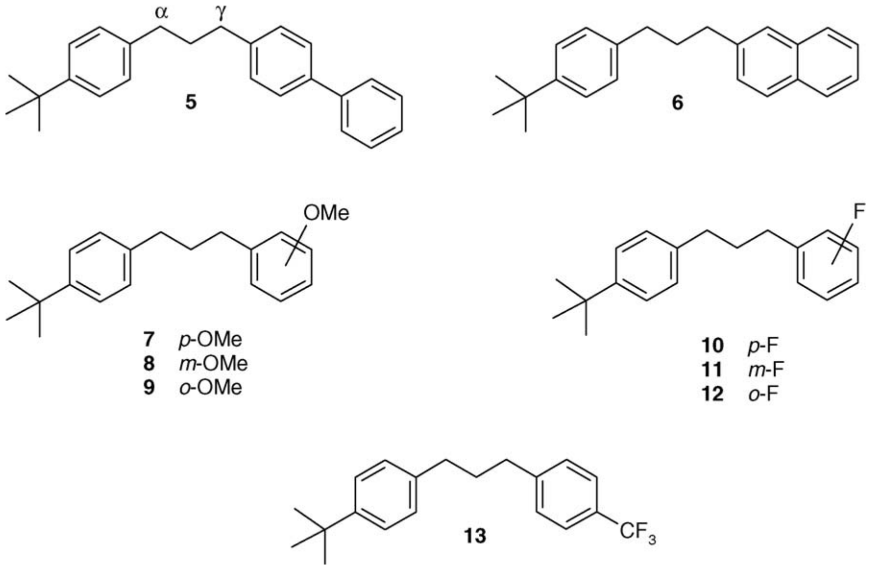


Chart 1. α-(*tert*-Butylphenyl)-γ-arylpropanes **5**–**13** studied by CI/MIKE spectrometry.

electron-rich and electron-poor ethylbenzenes has also been performed recently [14] (A. Cartoni, M. Mormann, D. Kuck, unpublished results).

2. Experimental

2.1. Measurements

All measurements were carried out on a double-focusing instrument, AutoSpec (Fisons, Manchester/UK) with a three-sector, EBE geometry. The compounds were introduced into the CI source via the heatable inlet rod. Methane was used as the reactant gas with the nominal pressure of 4×10^{-5} to 1×10^{-4} mbar. The electron energy was set at 70 eV, the trap current at 200 μA, the accelerating voltage at 8000 V, and the source temperature at 160–200 °C. Fragmentation of the metastable ions in the third field-free region was monitored by selecting the precursor ion by the magnetic field and scanning the field of the second electrostatic analyzer. The MIKE spectral data reported are representative examples for several independent measurements and the figures illustrate averaged data from at least 10 consecutive scans. Deconvolution of the peaks was performed graphically; the error limits denote the estimated uncertainty associated with this procedure.

2.2. Syntheses, general

The synthetic work on which the mass spectrometric measurements were based followed the general lines described in previous papers of this series [9,11]. The physical and spectroscopic data of the synthesis intermediates and the 1,3-diarylpropanes (Charts 1 and 2) are collected in Appendix A, and the synthesis methods used in the individual cases are named therein. The 1,3-diarylpropanes were synthesized starting by condensation of the suitably substituted benzaldehydes and acetophenones. Typically, both of these compounds (20 mmol each in most cases, see below) were dissolved in 20–30 ml of methanol and aqueous potassium hydroxide (20%) was added. The mixtures were stirred at ca. 25 °C for 12 h and the 1,3-diarylprop-1-en-3-ones (chalcones) **A5**–**A′14** were isolated by standard procedures (filtration of solid crude products or acidification with AcOH and Et_2O followed by extraction in case of non-precipitating crude products). Purification of the chalcones was effected by recrystallization or kugelrohr distillation, respectively. Conversion of the chalcones **A5**–**A′14** into the corresponding 1,3-diarylpropane-3-ones (dihydrochalcones) **B5**–**B′14** was achieved by catalytic hydrogenation of the chalcones in ethyl acetate (ca. 30 ml) at ca. 20 °C and 1 bar in the presence of Adam's catalyst, formed from $PtO_2 \times H_2O$ (30 mg) during the beginning each hydrogenation. After standard work-up, the dihydrochalcones were purified by recrystallized from ethanol or, were appropriate, by kugelrohr distillation. Reduction of the dihydrochalcones **B5**–**B′14** to the corresponding 1,3-diarylpropanes **5**–**13** (and to the intermediate **E14**) was performed either (i) by heterogeneous catalytic hydrogenolysis under medium pressure, (ii) by chloroalane reduction, or (iii), in the cases of the fluoroacetophenone derivatives **B′10**–**B′12**, by sequential reduction. The general protocols are given below.

In the cases of the dihydrochalcones bearing a fluorine substituent at the 1-phenyl group, introduction of a CD_2 group by chloroalane reduction proved to be unsuccessful. Therefore, labeling was achieved by preparing the [1,1,2-D_3]-isotopomers **10b**–**12b** by successive reduction of **B′10**–**B′12** with lithium aluminum deuteride to give the related [1-D]-3-(4-*t*-butylphenyl)-1-(fluorophenyl)propane-1-ols, **C′10**–**C′12**, elimination of HDO in DMSO at 160 °C to give the corresponding [1-D]-3-(4-*t*-butylphenyl)-1-(fluorophenyl)propenes, **D′10**–**D′12**, and, finally, addition of deuterium by homogenous catalysis using Wilkinson's catalyst, $[Rh(PPh_3)_3Cl]$, in benzene.

2.3. Catalytic hydrogenolysis

To a solution of the *tert*-butylated 1,3-diphenylpropan-1-one (1.0 mmol), or the corresponding 1,3-diphenylprop-2-en-1-one (1.0 mmol), in glacial acetic acid (5 ml) was added palladium on charcoal (10%, Merck) (40 mg) and the mixture was shaken in a Parr apparatus for 4 h at 20–25 °C under hydrogen (5 bar). The catalyst was removed by filtration, the filtrate was diluted with water (5 ml) and extracted thrice with 10-ml portions of *n*-hexane. The combined organic layers were dried over sodium sulfate and concentrated to dryness. The residue was purified by kugelrohr distillation to give the desired hydrocarbon as colorless liquids in yields of 50–80%.

2.4. Chloroalane reduction

A suspension of lithium aluminum hydride (1.0 mmol) or lithium aluminum deuteride (1.0 mmol) in anhydrous diethyl ether (5.0 ml) was cooled to ca. 0 °C and a solution of anhydrous aluminum trichloride (3.0 mmol) in diethyl ether (5.0 ml) was added rapidly. Cooling was maintained while a solution of the *tert*-substituted 1,3-diphenylpropan-1-one (1.0 mmol) in diethyl ether (5.0 ml) was added dropwise. The mixture was heated until the conversion was completed (ca. 2 h), as monitored by TLC (silica/CH_2Cl_2), then cooled to room temperature, hydrolysed with ice/water and acidified with 10N hydrochlorid acid. After extraction of the aqueous layer with diethyl ether, the combined organic layers were dried over sodium sulfate and concentrated to dryness. The residue was purified by kugelrohr distillation to give the desired products as colorless liquids (yields 60–80%). In several cases, the corresponding propenes, i.e., the product(s) of elimination were formed as mostly minor contaminations; in a few cases, the corresponding α- and/or γ-chloro-substituted diphenylpropane derivatives were also observed. No efforts were made to remove these contaminations since they did not affect the MIKE measurements.

In one case only (**6**), Wolff–Kishner reduction of a dihydrochalcone (**B′6**) was carried out by use of the standard Huang–Minlon procedure.

2.5. Sequential reduction

A suspension of lithium aluminum hydride (or deuteride) (1.5 mmol) in 15 ml of anhydrous diethyl ether was stirred while

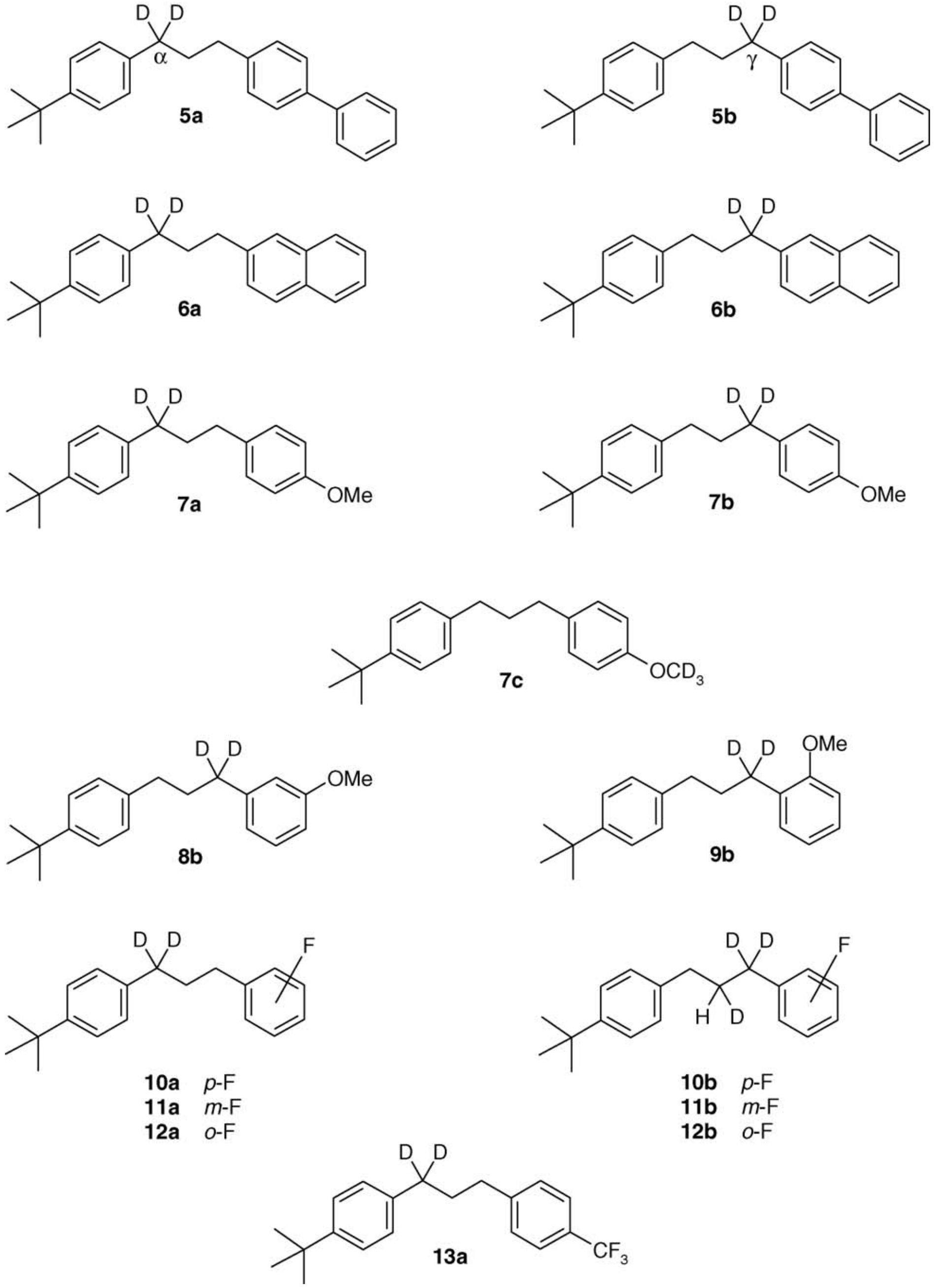


Chart 2. Deuterium-labeled isotopomers of the α-(*tert*-butylphenyl)-γ-arylpropanes **5**–**13** studied by CI/MIKE spectrometry.

a solution of the dihydrochalcone (5.0 mmol) in 20 ml of the same solvent was added dropwise. The mixture was heated under reflux until the reaction was completed (TLC monitoring, CH_2Cl_2). The mixture was cooled in an ice/water bath and hydrolyzed by addition of 2N sulfuric acid. The layers were separated and the aqueous layer was extracted with diethyl ether, and the combined organic solutions were dried over sodium sulphate and the solvent was removed. The residue was purified by kugelrohr distillation. In the next step, a solution of the 1,3-diarylpropanol thus obtained (4.0 mmol) in 4 ml of dimethyl sulfoxide was heated to 160 °C until the starting material was no longer detectable by TLC (ca. 6 h). The cooled mixture was extracted several times with *n*-hexane; the combined extracts were dried over sodium sulfate and the solvent was removed. The residue was purified by kugelrohr distillation. Finally, Wilkinson's catalyst [$Rh(P(Ph)_3)_3Cl$] (25 mg, 0.025 mmol) was added to a solution of the 1,3-diarylpropene obtained (0.5 mmol) in 4 ml of anhydrous benzene and the mixture was stirred under D_2 (1 bar) in a microhydrogenation apparatus at ambient temperature until >1.0 equiv. of the gas was absorbed. The solution was filtered through silica and the solvent was removed. The residue was purified first by column chromatography (CH_2Cl_2) and then

Table 1
Relative rates (in %Σ) of hydride abstraction (C_4H_{10} loss), proton transfer (C_4H_8 loss), and release of $C_4H_9^+$ ions from metastable protonated 1-(*tert*-butylphenyl)-3-arylpropanes [**5** + H]$^+$ to [**13** + H]$^{+}$[a]

[*M* + H]$^+$ ion	γ-Aryl group	C_4H_{10} loss	C_4H_8 loss	$C_4H_9^+$
[**5** + H]$^+$	4-Biphenylyl	53	47	0
[**6** + H]$^+$	2-Naphthyl	5	95	0
[**7** + H]$^+$	4-Methoxyphenyl	33	67	0
[**8** + H]$^+$	3-Methoxyphenyl	1	99	0
[**9** + H]$^+$	2-Methoxyphenyl	6	94	0
[**10** + H]$^+$	4-Fluorophenyl	98	0	2
[**11** + H]+	3-Fluorophenyl	89	7	4
[**12** + H]$^+$	2-Fluorophenyl	>99	0	<1
[**13** + H]$^+$	4-(Trifluoromethyl)phenyl	80	0	20

[a] From MIKE spectra after correction for minor contributions of C_4H_8 losses from $M^{\bullet+}$ ions containing naturally occurring ^{13}C.

by kugelrohr distillation. The 1,3-diarylpropanes were obtained as colorless liquids in good yields (70–90% for the last step).

3. Results and discussion

3.1. Competition between intra-complex hydride and proton transfer

The MIKE spectra of ions [**5** + H]$^+$ to [**13** + H]$^+$, reflecting the fragmentation of the long-lived (ca. 2×10^{-5} s) metastable species, are collected in Table 1. In all cases, either the hydride abstraction or proton transfer represents the dominant fragmentation path of these ions. Clearly, the ratio of isobutane versus isobutene losses depends on the electronic effects of the substituents on the heterolysis of the benzylic C^{γ}–H bonds, on the one hand, and on the basicity of the neutral 1,3-diphenylpropane component, on the other. Both processes are assumed to take place within the same ion/neutral complexes (cf. Scheme 1). The third possible channel, known to occur in the dissociation of simple, preferably α-branched alkylbenzenes upon protonation both in the gas phase [15–18] and in solution [19,20], namely the loss of alkyl cations and, in particular, the *t*-$C_4H_9^+$ ion from protonated arenes, occurs to a significant extent only in the case the trifluoromethyl-substituted ion [**13** + H]$^+$ and to minor extents also in the *para*- and *meta*-fluoro-substituted analogues [**10** + H]$^+$ and [**11** + H]$^+$. This observation can be attributed to the fact that both the hydride donor ability of the C^{γ}-H bonds and the basicity of the diphenylpropane in the ion/molecule complex are strongly decreased by the presence of the electron-withdrawing substituents. Thus we can expect the C^{α}-H bonds of the 1,3-diphenylpropane unit to be the major hydride donor site especially in the case of ions [**13** + H]$^+$ (vide infra). In addition, however, the competition between the (overall) three different fragmentation channels suggests once again that the bidentate 1,3-diarylalkane acts with both of its aryl groups as a solvating partner of the *t*-$C_4H_8^+$ ion [11,21–24], which may be regarded as an extension of the "simpler" cation–π interactions [4,25–29].

Release of the *t*-$C_4H_9^+$ does not occur from metastable ions that contain more or less electron-donating substituents. In all these cases, hydride abstraction and proton transfer compete and the electronic effects of the substituents dominate this competition. The *para*-phenyl group in ions [**5** + H]$^+$ obviously increases the proton affinity of the diphenylpropane unit more strongly than the hydride-donor ability of the C^{γ}-H bonds, as compared to the unsubstituted ion [**1** + H]$^+$, which exclusively undergoes isobutane loss. The annelated benzene nucleus in the 3-(β-naphthyl) analogue [**6** + H]$^+$ gives rise to a further strong increase of the proton affinity of the diarylpropane unit, as reflected by the far predominant loss of isobutene.

Proton transfer is also dominating for the set of the methoxy-substituted ions [**7** + H]$^+$ to [**9** + H]$^+$, in agreement with the increased proton affinity of anisole and the methylanisoles as compared to benzene and toluene, respectively [30–33]. Accordingly, this is most evident for the *meta* isomer [**8** + H]$^+$. However, the hydride transfer channel, i.e., loss of isobutane, is still significant for the *para*- and *ortho*-methoxy isomers. In line with expectation, the hydride-donor reactivity of the C^{γ}-H bonds is enhanced most strongly by the methoxy group at the *para*-position of ions [**7** + H]$^+$, whereas the basicity of the 1,3-diphenylpropane molecule is mostly increased by the *meta*-methoxy group present in ions [**8** + H]$^+$. The *ortho*-methoxy group of ions [**9** + H]$^+$ increases both the hydride-donor ability of the γ-CH_2 group and the basicity of the 1,3-diphenylpropane, the former probably being subject to steric hindrance similar to that found for the *ortho*-methyl analogue [**4** + H]$^+$ [9,11]. In fact, the ratios of isobutane versus isobutene losses from the methoxy-substituted ions [**7** + H]$^+$ to [**9** + H]$^+$ increase in the same order as those of the methyl-substituted ones, [**2** + H]$^+$ to [**4** + H]$^+$, that is, $\{[C_4H_{10}]:[C_4H_8]\}_{meta} < \{[C_4H_{10}]:[C_4H_8]\}_{ortho} < \{[C_4H_{10}]:[C_4H_8]\}_{para}$.

The ion/neutral complexes containing an electron-poor 1,3-diarylpropane component increasingly release the *t*-$C_4H_9^+$ ion in the order *ortho*-F < *para*-F < *meta*-F < *para*-CF_3. This finding reflects the decreasing stability of these I/N complexes. However, the competition of this direct fragmentation with the proton transfer channel is remarkable: only the I/N complex generated from the *meta*-fluoro-substituted ions [**11** + H]$^+$ undergoes a significant loss of isobutene. This indicates that the (yet unknown) gas-phase basicity of the 1-(3-fluorophenyl)-3-phenyl-propane neutral is probably significantly higher than those of the 1-(4-fluorophenyl)- and 1-(2-fluorophenyl)-3-phenylpropane isomers, generated within the complexes from ions [**10** + H]$^+$ and [**12** + H]$^+$, respectively. This assumption is in accordance with the known GB values of the three fluorotoluene isomers: $GB(3\text{-}FC_6H_4Me) - GB(4\text{-}FC_6H_4Me) = 20\,\mathrm{kJ\,mol^{-1}})$ [30,31]. At the same time, however, the *meta*-fluorine substituent in the I/N complex formed from ions [**11** + H]$^+$ may slightly destabilize the benzylic cation formed by hydride abstraction and thus hamper the loss of isobutene (see below). Finally, the particularly strong electron-withdrawing effect of the trifluoromethyl substituent is reflected by the fact that the relative abundance of [*M* + H]$^+$ ions in the CI(CH_4) spectrum of **13** is very low. The lack of isobutene loss and the relatively high abundance of *t*-$C_4H_9^+$ ions released from ions [**13** + H]$^+$ suggests that the (likewise unknown) gas-phase basicity of 1-phenyl-3-[(4-trifluoromethyl)phenyl]propane is significantly lower than that of 1,3-diphenylpropane itself [22].

3.2. Regioselectivity of intra-complex hydride abstraction

Site-specific deuterium labeling of the 1-(4-*tert*-butylphenyl)-3-arylpropanes allowed us to determine, on a semi-quantitative basis, the regioselectivities of the hydride abstraction reactions within the ion/neutral complexes formed as intermediates during the fragmentation of the metastable ions. To this end, 16 site-specific deuterium-labeled isotopomers of the nine disubstituted 1,3-diarylpropanes **5**–**13** were synthesized, viz. **5a**–**13a** (Chart 2). As will be shown, some of the electronic effects deduced from the overall fragmentation discussed above can be corroborated by MIKE spectrometry of the deuterium-labeled ions. Two pieces of information from previous work are crucial for the evaluation of the data. (i) The homobenzylic (C^{β}–H) bonds in the $[M+H]^+$ ions do not act as hydride donors [5,9–11] and (ii) the kinetic isotope effect operating on the intra-complex hydride abstraction from benzyl- or methylbenzyl groups is generally $k_H/k_D = 1.6$ [5,9–12]. To ensure that the methoxy groups do not react as hydride donors on their own, an OCD_3-substituted analogue was also synthesized and the fragmentation of the corresponding $[M+H]^+$ ions was studied by MIKE spectrometry. In some cases, the regioselectivity of the hydride transfer was hardly detectable due to the predominance of the proton transfer reaction. This holds in particular for the *meta*-methoxy derivative **8**, the [γ,γ-D_2] isotopomer of which, **8b**, was synthesized (see Section 2) but turned out to be unsuitable to yield information about the hydride transfer.

One special aspect is worth being noted concerning the synthesis of the labeled analogues. Introduction of two deuterium atoms at the α- or γ-positions of compounds **5a**–**9b** was achieved in similar ways as described previously [9,11]. In contrast, γ,γ-dideuteration of the fluorine-substituted analogues to yield isotopomers **10b**–**12b** required another synthetic methodology due to the fact that the fluorine substituents inhibited the chloroalane ($LiAlH_4/AlCl_3$) reduction of the corresponding fluoroacetophenones or 1-[D_1]-(fluorophenyl)propanols (see Section 2). However, dehydration of the latter compounds obtained by simple alanate ($LiAlH_4$) reduction to the corresponding 1-arylpropenes, followed by addition of deuterium under homogeneous catalysis afforded the generation of the γ-CD_2 group along with the introduction of a third deuterium atom at the β-position. In this way, compounds **10b**–**12b** were obtained with high isotopic purities and site-specificities. It is assumed that the secondary kinetic isotope effect due to the presence of a β-CHD group is neglible within the frame of our semi-quantitative evaluation.

The ratios of hydride versus deuteride abstraction from ions $[\mathbf{5a}+H]^+$ to $[\mathbf{13a}+H]^+$ are collected in Table 2. Fig. 1 illustrates the partial MIKE spectra (which represent ≥98% of the total fragment ion current, cf. Table 1) of three couples of isotopomeric ions: The deuterium-labeled *para*-phenyl-substituted isotopomers $[\mathbf{5a}+H]^+$ and $[\mathbf{5b}+H]^+$, the *para*-methoxy-substituted analogues $[\mathbf{7a}+H]^+$ and $[\mathbf{7b}+H]^+$, and the *para*-fluorine-substituted ions $[\mathbf{10a}+H]^+$ and $[\mathbf{10b}+H]^+$. It is evident from the MIKE spectra in Fig. 1a that the presence of a *para*-phenyl group at the initially remote arene ring of ions $[\mathbf{5}+H]^+$ gives rise to a dominant hydride abstraction from the γ-methylene position. Whereas α,α-dideuteration in ions $[\mathbf{5a}+H]^+$ gives intra-complex H^- versus D^- transfer to the t-$C_4H_9^+$ ion in the ratio of 6.3:1, the fragmentation of the γ,γ-dideuterated ions $[\mathbf{5b}+H]^+$ reflects a H^- versus D^- ratio of 1:2.4. Thus, irrespective of the kinetic isotope effect operating in favour of the H^- abstraction, the (biphenyl-4-yl)methyl group of the neutral component of the ion/neutral complex is a stronger hydride donor than the "simple" benzyl group. A first evaluation assuming the generally observed kinetic isotope effect $k_H/k_D = 1.6$, in analogy to many cases studied previously, gives a regioselectivity for hydride abstraction $k_{\gamma\text{-H}}/k_{\alpha\text{-H}} = 3.9$. This demonstrates that the activating effect of the *para*-phenyl substituent in ions $[\mathbf{5}+H]^+$ is similar and even somewhat stronger than that of a *para*-methyl group ($k_{\gamma\text{-H}}/k_{\alpha\text{-H}} = 3.3$) in ions $[\mathbf{4}+H]^+$ (Chart 1) [9].

A similar determination of the regioselectivity of the intra-complex hydride transfer applies to the fragmentation of the metastable protonated 1-(4-*tert*-butylphenyl)-3-(2-naphthyl)propane isotopomers, $[\mathbf{6a}+H]^+$ and $[\mathbf{6b}+H]^+$. Again, the larger aryl substituent at the remote position of the aliphatic chain activates the hydride transfer from there. However, the strong competition of the proton transfer renders the MIKE signals for the C_4H_{10} and C_4H_9D losses rather weak and the uncertainty limits relatively large. The H^- versus D^- transfer ratios measured for ions $[\mathbf{6a}+H]^+$ (ca. 4:1) and $[\mathbf{6b}+H]^+$ (ca.

Table 2
Ratios of H^- vs. D^- abstraction in the loss of isobutane from the metastable deuterium-labeled protonated 1-(*tert*-butylphenyl)-3-arylpropanes $[\mathbf{5a}+H]^+$ to $[\mathbf{7c}+H]^+$ and $[\mathbf{9a}+H]^+$ to $[\mathbf{13a}+H]^{+a}$

γ-Aryl group	[α,α-D_2]-labeled $[M+H]^+$ ion	$[C_4H_{10}]:[C_4H_9D]$	[γ,γ-D_2]-labeled $[M+H]^+$ ion	$[C_4H_{10}]:[C_4H_9D]$
4-Biphenylyl	$[\mathbf{5a}+H]^+$	6.3	$[\mathbf{5b}+H]^+$	0.42
2-Naphthyl	$[\mathbf{6a}+H]^+$	≈4.0	$[\mathbf{6b}+H]^+$	≈0.67
4-Anisyl	$[\mathbf{7a}+H]^+$	≥12	$[\mathbf{7b}+H]^+$	0.14
4-[MeO-D_3]-anisyl	$[\mathbf{7c}+H]^+$	$[C_4H_{10}]:[C_4H_9D] > 50$		
2-Anisyl	$[\mathbf{9a}+H]^+$	[b]	$[\mathbf{9b}+H]^+$	≈0.25
4-Fluorophenyl	$[\mathbf{10a}+H]^+$	1.20	$[\mathbf{10b}+H]^+$ [c]	2.5
3-Fluorophenyl	$[\mathbf{11a}+H]+$	0.29	$[\mathbf{11b}+H]^+$ [c]	12.3
2-Fluorophenyl	$[\mathbf{12a}+H]^+$	0.26	$[\mathbf{12b}+H]^+$ [c]	≥17
4-(Trifluoromethyl)phenyl	$[\mathbf{13a}+H]^+$	≤0.065	[b]	–

[a] Isotopomers $[\mathbf{8b}+H]^+$ did not exhibit sufficient hydride transfer (see text).

[b] Not studied due to poor relative abundance of the $[M+H-\text{isobutane}]^+$ ions.

[c] Labeling includes one D atom in the β-position (see text and Chart 2).

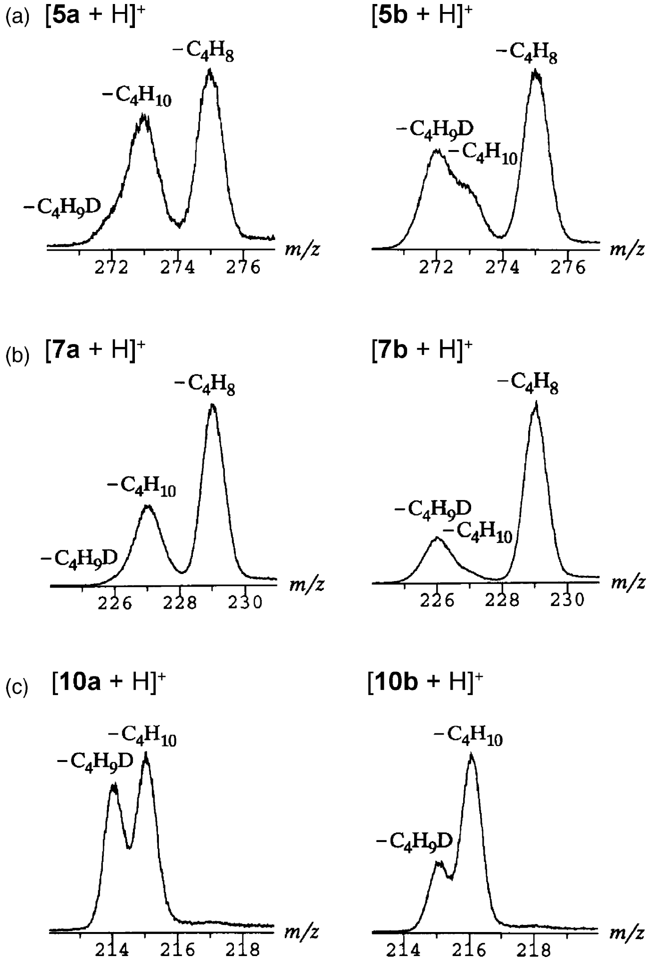


Fig. 1. Partial MIKE spectra of the $[M + \mathrm{H}]^+$ ions generated from [α,α-D_2]- and [γ,γ-D_2]-isotopomers of the (a) *para*-phenyl-substituted ions $[\mathbf{5} + \mathrm{H}]^+$ and (b) *para*-methoxy-substituted ions $[\mathbf{7} + \mathrm{H}]^+$, and of the (c) [α,α-$D_2$]- and [β,γ,γ-$D_3$]-isotopomers of the *para*-fluoro-substituted ions $[\mathbf{10} + \mathrm{H}]^+$ (cf. Chart 2).

1:1.5), a regioselectivity of $k_{\gamma\text{-H}}/k_{\alpha\text{-H}} \approx 2.4$ is determined. Thus, benzoannelation in the case of ions $[\mathbf{6} + \mathrm{H}]^+$ gives a significantly weaker preference for the hydride abstraction than introduction of the *para*-phenyl or *para*-methyl substituents, as discussed above. Notably, the regioselectivity of the isobutane loss from the $[M + \mathrm{H}]^+$ ions bearing a γ-(3,4-xylyl) group, being more closely comparable to the γ-(2-naphthyl) group in ions $[\mathbf{6} + \mathrm{H}]^+$, was found to be higher, viz. $k_{\gamma\text{-H}}/k_{\alpha\text{-H}} = 5.3$ [11].

It is obvious from these and our previous studies that electron-releasing aryl groups at the remote methylene group facilitate the intra-complex hydride abstraction, thus reflecting the increased thermodynamic stability of the benzylic fragment ions formed. Therefore, methoxy groups were expected to give rise to particularly high $k_{\gamma\text{-H}}/k_{\alpha\text{-H}}$ values. In fact, this expectation was confirmed when the MIKE spectra of ions $[\mathbf{7a} + \mathrm{H}]^+$ to $[\mathbf{9b} + \mathrm{H}]^+$ were studied, although the picture was partially disturbed by the interference of the strongly enhanced intra-complex proton transfer discussed above. In fact, the labeled *meta*-methoxy-substituted isotopomer $[\mathbf{8b} + \mathrm{H}]^+$, bearing the label adjacent to the electron-rich meta-anisyl group, was synthesized but did not undergo sufficient isobutane loss to yield reliable information on the regioselectivity of the hydride transfer in the I/M complex generated from ions $[\mathbf{8} + \mathrm{H}]^+$. By contrast, the MIKE spectrum of the *ortho*-methoxy-substituted isotopomer $[\mathbf{9b} + \mathrm{H}]^+$ gave significant data, in spite of the relatively slow isobutane loss (cf. Table 1). The *para*-methoxy isomers, however, were found to be most useful. The partial MIKE spectra of the isotopomers bearing the [D_2]-label in one of the benzylic positions, $[\mathbf{7a} + \mathrm{H}]^+$ and $[\mathbf{7b} + \mathrm{H}]^+$, are reproduced in Fig. 1b. As expected, both of these ions exhibit a strongly enhanced hydride abstraction from the γ-methylene group, leading to far predominant losses of C_4H_{10} from $[\mathbf{7a} + \mathrm{H}]^+$ and of C_4H_9D from $[\mathbf{7b} + \mathrm{H}]^+$. Use of the H^- versus D^- abstraction ratios of ≥12:1 obtained for the former and ca. 1:7 for the latter isotopomer, and assuming, as a first approximation, the generally observed kinetic isotope $k_\mathrm{H}/k_\mathrm{D} = 1.6$ to operate again at both of the benzylic donor positions, leads to a regioselectivity much in favour of the electron-rich donor group, but conflicting values, $8 \le k_{\gamma\text{-H}}/k_{\alpha\text{-H}} \le 11$. However, leaving the isotope effect as a variable, yields $k_\mathrm{H}/k_\mathrm{D} = 1.31$ and $k_{\gamma\text{-H}}/k_{\alpha\text{-H}} \approx 9.2$. Thus, in any case, this crude approximation shows that the activating effect of a *para*-methoxy substituent is considerably stronger than that of a *para*-methyl substituent.

In spite of the low relative abundance of the $[M + \mathrm{H}\text{-}\mathrm{Me_3C(H,D)}]^+$ ions in the MIKE spectrum of the [γ,γ-D_2]-labeled *ortho*-anisyl analogue $[\mathbf{9b} + \mathrm{H}]^+$, it is evident that D^- abstraction within the complex prevails over H^- abstraction. The ratio of C_4H_9D versus C_4H_{10} loss from ions $[\mathbf{9b} + \mathrm{H}]^+$ was found to be ca. 4:1, and thus much lower than for the corresponding *para* isomer, $[\mathbf{7b} + \mathrm{H}]^+$. With the kinetic isotope effect $k_\mathrm{H}/k_\mathrm{D} = 1.6$ operating during the intra-complex hydride transfer from both of the benzylic positions, a regioselectivity of $k_{\gamma\text{-H}}/k_{\alpha\text{-H}} \approx 6.4$ is obtained for ions $[\mathbf{9} + \mathrm{H}]^+$. Thus, the activating effect of a methoxy substituent in the *ortho* position towards hydride abstraction from the 1,3-diphenylpropane molecule appears to be strong but significantly lower than in the *para* position. The activation by the *ortho*-methoxy substituent in ions $[\mathbf{9} + \mathrm{H}]^+$ is in obvious contrast to the zero net effect of an *ortho*-methyl group in ions $[\mathbf{2} + \mathrm{H}]^+$ ($k_{\gamma\text{-H}}/k_{\alpha\text{-H}} = 1.0$), for which the electronic influence was found to be cancelled by the effect of steric hindrance [9,11].

To ascertain the role of the methoxy substituents in the fragmentation of anisole-derived ions $[\mathbf{7} + \mathrm{H}]^+$ and $[\mathbf{9} + \mathrm{H}]^+$, we synthesized isotopomer **7c**, bearing a *para*-trideuteromethoxy substituent, and studied the fragmentation of its $[M + \mathrm{H}]^+$ ions by MIKE spectrometry. It was relieving to find that, in fact, the methoxy group does not react as a hydride donor on its own (Table 2). This particularly important piece of information can be generalized for the other methoxy-substituted ions studied here, and recent independent studies performed on the *intermolecular* hydride transfer from the three isomeric ethylanisoles to $t\text{-}C_4H_9^+$ ions corroborate this [14] (A. Cartoni, M. Mormann, D. Kuck, unpublished results).

With this problem being fixed, a closer inspection of the regioselectivity of the intra-complex hydride abstraction from the methoxy- and also from the fluorine-substituted 1,3-diphenylpropanes (see below) has to account for the possibility that the kinetic isotope effect operating on the hydride abstraction from the initially remote benzylic methylene group may significantly differ from the value of $k_H/k_D = 1.6$ observed generally for the parent systems and for the methyl-substituted 1,3-diphenylalkanes. Therefore, we evaluated the regioselectivity from the experimentally obtained data by assuming that only the α-CH_2 group is subject to the "general" kinetic isotope effect, setting $(k_H/k_D)_\alpha \equiv 1.60$ but leaving the corresponding value for the γ-CH_2 group $(k_H/k_D)_\gamma$ variable. This appears justified by considering the transitions state for hydride abstraction from the α-CH_2 group to be essentially independent from the interaction of the electron density of the ("spectator") γ-aryl ring. With this second approximation, we determined both the regioselectivities, $k_{\gamma\text{-H}}/k_{\alpha\text{-H}}$, and the kinetic isotope effects involved in the intra-complex hydride abstraction from the γ-CH_2 group $(k_H/k_D)_\gamma$. For the sake of completeness, we also applied this evaluation to the 1-(biphenyl-4-yl)-3-phenyl and 1-(2-naphthyl)-3-phenylpropane neutrals undergoing the hydride transfer in the I/N complexes formed from ions $[\mathbf{5a}+\mathrm{H}]^+$ and $[\mathbf{5b}+\mathrm{H}]^+$ and $[\mathbf{6a}+\mathrm{H}]^+$ and $[\mathbf{6b}+\mathrm{H}]^+$, respectively. In fact, the latter cases turned out to justify our first approximation assuming a common $(k_H/k_D)_\alpha \equiv (k_H/k_D)_\gamma = 1.6$. The closer evaluation was based on Eqs. (1a) and (1b) and the data obtained are collected in Table 3, together with the regioselectivities obtained by the first approximation:

$$\left(\frac{[M+\mathrm{H}-\mathrm{C_4H_9D}]^+}{[M+\mathrm{H}-\mathrm{C_4H_{10}}]^+}\right)_{\alpha,\alpha\text{-}\mathrm{D}_2} = \frac{k_{\alpha\text{-H}}}{(k_\mathrm{H}/k_\mathrm{D})_\gamma\, k_{\gamma\text{-H}}} \tag{1a}$$

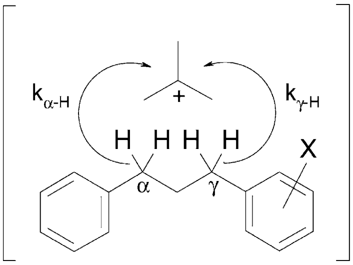
$$\left(\frac{[M+\mathrm{H}-\mathrm{C_4H_9D}]^+}{[M+\mathrm{H}-\mathrm{C_4H_{10}}]^+}\right)_{\gamma,\gamma\text{-}\mathrm{D}_2} = \frac{k_{\gamma\text{-H}}}{(k_\mathrm{H}/k_\mathrm{D})_\alpha\, k_{\alpha\text{-H}}} = \frac{k_{\gamma\text{-H}}}{1.60\, k_{\alpha\text{-H}}} \tag{1b}$$

It is obvious that the strong electro-active substituents, such as methoxy and fluoro do affect not only the regioselectivity but also the kinetic isotope effect involved in the hydride abstraction from the benzylic moiety bearing that substituent. Thus, our suspicion that $(k_H/k_D)_\gamma \neq 1.6$ in such cases is clearly confirmed.

As mentioned above, the fragmentation of the protonated fluorine- and trifluoromethyl-substituted 1-(4-*t*-butylphenyl)-3-phenylpropanes $[\mathbf{10}+\mathrm{H}]^+$, $[\mathbf{11}+\mathrm{H}]^+$ and $[\mathbf{12}+\mathrm{H}]^+$ takes place preferably by loss of isobutane, while the elimination of isobutene is largely suppressed due to the decreased basicity of the 1,3-diarylpropane partner in the ion/neutral complexes. Owing to the predominance of the isobutane loss, the regioselectivity of the intra-complex hydride transfer could be studied for all isotopomers of the three isomers, i.e., ions $[\mathbf{10a}+\mathrm{H}]^+$ to $[\mathbf{12b}+\mathrm{H}]^+$, as well as for the isotopomer $[\mathbf{13a}+\mathrm{H}]^+$. The partial MIKE spectra of the *para*-substituted isotopomers $[\mathbf{10a}+\mathrm{H}]^+$ and $[\mathbf{10b}+\mathrm{H}]^+$ are reproduced in Fig. 1c. As expected, the electron-withdrawing character of the fluorine substituent gives rise to a reduced hydride donor ability of the γ-methylene groups and a strong dependence of the site-specific isotope effect. Evaluation of the experimental data for ions $[\mathbf{10a}+\mathrm{H}]^+$ and $[\mathbf{10b}+\mathrm{H}]^+$ by use of Eqs. (1) and (2) yields a kinetic isotope effect $(k_H/k_D)_\gamma = 1.88$ and a regioselectivity of $k_{\gamma\text{-H}}/k_{\alpha\text{-H}} = 0.64$. Thus, the kinetic isotope effect operating during the intra-complex hydride abstraction from the γ-CH_2 group is considerably higher than that observed for the unsubstituted or methyl-substituted benzyl moiety $(k_H/k_D = 1.60)$. The isotope effects evaluated from the MIKE spectra of the *meta* and *para* isomers were found to be even higher, $(k_H/k_D)_\gamma = 2.30$ for $[\mathbf{11a}+\mathrm{H}]^+$ and $[\mathbf{11b}+\mathrm{H}]^+$ and $(k_H/k_D)_\gamma = 2.80$ for $[\mathbf{12a}+\mathrm{H}]^+$ and $[\mathbf{12b}+\mathrm{H}]^+$. The regioselectivity of the intra-complex hydride abstraction

Table 3

Regioselectivities and kinetic isotope effects operating during the loss of isobutane from metastable deuterium-labeled protonated 1-(*tert*-butylphenyl)-3-arylpropanes $[\mathbf{5a}+\mathrm{H}]^+$ to $[\mathbf{7c}+\mathrm{H}]^+$ and $[\mathbf{9a}+\mathrm{H}]^+$ to $[\mathbf{13a}+\mathrm{H}]^{+}$[a]



Precursor ion $[M+\mathrm{H}]^+$	X	Isotope effect $(k_H/k_D)_\gamma$ with $(k_H/k_D)_\alpha \equiv 1.60$	Regioselectivity $k_{\gamma\text{-H}}/k_{\alpha\text{-H}}$
$[\mathbf{5}+\mathrm{H}]^+$	4-C_6H_5	1.64	3.84 (3.9[b])
$[\mathbf{6}+\mathrm{H}]^+$	3,4-C_6H_4	1.67	2.40 (2.4[b])
$[\mathbf{7}+\mathrm{H}]^+$	4-OCH_3	1.07	≥11.2 (≈9.2[c])
$[\mathbf{9}+\mathrm{H}]^+$	2-OCH_3	–[b]	(≈6.4[b])
$[\mathbf{10}+\mathrm{H}]^+$	4-F	1.88	0.640
$[\mathbf{11}+\mathrm{H}]$+	3-F	2.30	0.128
$[\mathbf{12}+\mathrm{H}]^+$	2-F	2.80	0.094
$[\mathbf{13}+\mathrm{H}]^+$	4-CF_3	–[d]	≤0.04[d]

[a] Evaluated by use of the data given in Table 2 and Eqs. (1a) and (1b).

[b] Values in parentheses obtained by assuming $(k_H/k_D)_\alpha \equiv (k_H/k_D)_\gamma = 1.60$.

[c] Assuming a common isotope effect, calculated to be $(k_H/k_D)_\alpha \equiv (k_H/k_D)_\gamma = 1.31$.

[d] Obtained by assuming $(k_H/k_D)_\alpha = 1.60$.

was found to decrease in the same order, $k_{\gamma\text{-H}}/k_{\alpha\text{-H}} = 0.13$ for the *meta* isomer $[\mathbf{11}+\text{H}]^+$ and $k_{\gamma\text{-H}}/k_{\alpha\text{-H}} = 0.094$ for the *ortho* isomer $[\mathbf{12}+\text{H}]^+$. These high deactivating effects of the hydride abstraction from the initially remote benzylic position is still passed by the influence of the *para*-trifluoromethyl substituent in ions $[\mathbf{13}+\text{H}]^+$, leading to $k_{\gamma\text{-H}}/k_{\alpha\text{-H}} \leq 0.04$ and, thus, a 25-fold preference for the hydride abstraction from the "electro-neutral" α-methylene position.

As mentioned above, the closer approach based on $(k_\text{H}/k_\text{D})_\alpha \equiv 1.60$ yields only minor deviations for $(k_\text{H}/k_\text{D})_\gamma$ in the cases of the 4-biphenylyl and 2-naphthyl analogues, $[\mathbf{5a}+\text{H}]^+$ to $[\mathbf{6b}+\text{H}]^+$, and the regioselectivities obtained, $k_{\gamma\text{-H}}/k_{\alpha\text{-H}} = 3.84$ for ions $[\mathbf{5}+\text{H}]^+$ and $k_{\gamma\text{-H}}/k_{\alpha\text{-H}} = 2.40$ for ions $[\mathbf{6}+\text{H}]^+$ in favour of the activated γ-methylene group are also not changed significantly. Even the *para*-methoxy group in ions $[\mathbf{7a}+\text{H}]^+$ and $[\mathbf{7b}+\text{H}]^+$ was found to exert about the same high regioselectivity, $k_{\gamma\text{-H}}/k_{\alpha\text{-H}} \geq 11.2$ as obtained by the first approximation; however, it gives rise to a strongly reduced kinetic isotope effect for the hydride abstraction from the activated γ-methylene group $(k_\text{H}/k_\text{D})_\gamma = 1.07$. Thus, there seems to be a systematic correlation between electronic effect of the substituents and the kinetic isotope effect.

The regioselectivities of the intra-complex hydride abstraction obviously reflect the stabilizing and destabilizing effects of the substituents on the benzylic cations formed upon the loss of isobutane [34]. It appears that no recent experimental or theoretical data are available on the relative heats of formations of a set of appropriate model cations, such as the isomeric $XC_6H_4CH^+CH_3$ ions with $X = OCH_3$, F and CF_3. However, the substituent effects on the heats of formation of the simple benzyl cations, $XC_6H_4CH_2^+$, are known from semi-empirical calculations [35] and gas-phase equilibrium measurements [32,36]. From these data, the hydride abstraction from the γ-CH_2 group should be facilitated by the methoxy substituent in the order p-$OCH_3 > o$-$OCH_3 > m$-$OCH_3 >$ H and impeded by the fluorine substituent in the order m-F $> o$-F $>$ H $\approx p$-F. In fact, the regioselectivity observed for the I/N complexes generated from the methoxy-substituted ions $[\mathbf{7}+\text{H}]^+$ and $[\mathbf{9}+\text{H}]^+$ is in accordance with this order; however, the regioselectivities found for the fluorine-substituted analogues is not. The similarity of the hydride donor abilities of the *para*-fluorobenzyl and the unsubstituted benzyl moieties ($k_{\gamma\text{-H}}/k_{\alpha\text{-H}} = 0.64$) in the I/N complex from ions $[\mathbf{10}+\text{H}]^+$ is roughly in line with the very weakly stabilizing effect of the *para*-fluorine atom on the stability of the benzyl cation ($\Delta\Delta H_\text{f} = -2\,\text{kJ mol}^{-1}$) [36]. Also, the significantly decreased reactivity of the *meta*-fluorobenzyl moiety ($k_{\gamma\text{-H}}/k_{\alpha\text{-H}} = 0.13$) found for ions $[\mathbf{11}+\text{H}]^+$) corresponds to the strong destabilizing effect ($\Delta\Delta H_\text{f} = +24\,\text{kJ mol}^{-1}$) [36]. However, the even lower hydride donor ability found for the *ortho*-fluorobenzyl moiety in the I/M complexes generated from ions $[\mathbf{12}+\text{H}]^+$ ($k_{\gamma\text{-H}}/k_{\alpha\text{-H}} = 0.09$) is in contrast to the less pronounced destabilization of *ortho*-fluorobenzyl cations ($\Delta\Delta H_\text{f} = +9\,\text{kJ mol}^{-1}$) [36]. This discrepancy may be traced to a steric hindrance effect of the *ortho*-fluorine substituent on the hydride abstraction, in parallel to the steric hindrance exerted by *ortho*-methyl substituents [9,11].

4. Conclusion

This study has provided detailed insights on the substituent effects on the hydride and proton transfer reactions occurring in ion/neutral complexes generated by chemical ionization of deuterium-labeled model compounds, namely, *tert*-butyl-substituted 1,3-diphenylpropanes. In accordance with previous investigation in this series, the presence of electron-releasing or electron-withdrawing substituents at one of the benzyl moieties of the neutral component of the I/N complex strongly affects the regioselectivity, $k_{\gamma\text{-H}}/k_{\alpha\text{-H}}$, of the intra-complex hydride abstraction by the t-$C_4H_9^+$ ion. The *para*-methoxy substituent increases the H^- donor ability of the benzylic methylene group by a factor ≥11 and the *para*-trifluoromethyl substituent decreases it by a factor ≥25. Thus, the electron-rich and electron-poor character of the aromatic moieties within the neutral constituent of the I/N complexes is clearly reflected by a their intra-complex reactivity, spanning over almost three orders of magnitude. The competition of the hydride transfer with the (reciprocal) intra-complex proton transfer is also affected by the presence of substituents and appears to reflect the gas-phase basicity of the whole 1,3-diarylpropane molecule, rather than the individual basicity of the more electron-rich arene ring. These findings corroborate a two-fold cation–π interaction of the bidentate 1,3-diarylpropane molecule with the t-$C_4H_9^+$ ion, in line with previous results on the gas-phase ion chemistry of protonated and cationized α,ω-diphenylalkanes [9–12,21–24]. In addition, pronounced kinetic isotope effects were found to operate during the intra-complex hydride abstraction in these [$C_4H_9^+$ diphenylalkane] complexes. The generally observed value of $k_\text{H}/k_\text{D} = 1.6$ decreases to $k_\text{H}/k_\text{D} = 1.1$ along with strongly increased hydride donor ability, and it increases up to $k_\text{H}/k_\text{D} = 2.8$ along with decreased hydride donor ability of the benzylic methylene groups. It is hoped that further studies focusing on gaseous ion/neutral complexes formed during the unimolecular fragmentation will provide further insights into elementary ion/molecule reactions in the gas phase.

Acknowledgement

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Appendix A

The following intermediate products en route to the 1,3-diarylpropanes **5**–**13a** were obtained and characterized (Chart 3):

A.1. Tert-butylated 1,3-diphenylpropenones (tert-butylchalcones)

A.1.1. 3-(4-Biphenylyl)-1-(4-t-butylphenyl)prop-2-en-1-one (A5).

From 4-phenylbenzaldehyde (3.64 g) and 4-*t*-butylacetophenone (3.52 g); yield 4.21 g (62%), yellow

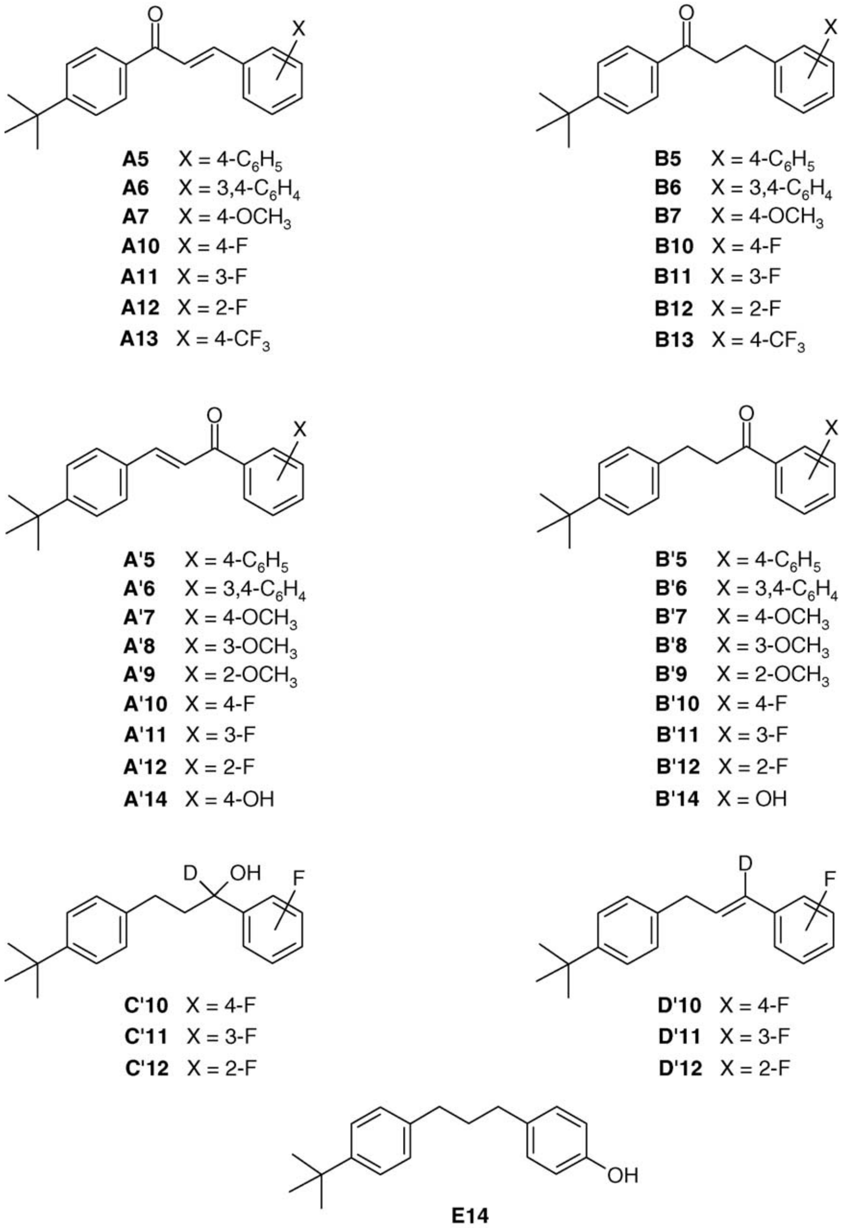

Chart 3. Intermediate compounds prepared in the course of the syntheses of the α-(*tert*-butylphenyl)-γ-arylpropanes **5**–**13** and their deuterium-labeled isotopomers.

needles, mp 143–146 °C (EtOH). ^{1}H NMR (CDCl$_3$): $\delta = 1.37$ (s, 9H), 7.39–7.50 (m, 3H), 7.54 and 8.00 (AA′BB′, $^3J = 8.6$ Hz, 4H), 7.59 and 7.86 (AB, $^3J = 15.7$ Hz, 2H), 7.63–7.68 (m, 2H), 7.64 and 7.73 (AA′BB′, $^3J = 8.4$ Hz, 4H); MS (EI, 70 eV): *m*/*z* (%) 340 (98, $M^{\bullet+}$), 339 (72), 325 (28), 297 (19), 283 (100), 263 (35), 207 (20), 178 (58), 165 (15), 161 (15), 152 (18), 118 (14), 115 (12), 91 (17), 77 (16); IR (KBr), $\tilde{\nu}$ (cm^{-1}): 3060, 2961, 2928, 2856, 1653, 1592, 1332, 1220, 1185, 819, 698. $C_{25}H_{24}O$ (340.47): Calcd. C 88.20, H 7.11; found C 87.44, H 7.16.

*A.1.2. 1-(4-Biphenylyl)-3-(4-t-butylphenyl)prop-2-en-1-one (**A′5**).*

From 4-acetylbiphenyl (3.92 g) and 4-*t*-butylbenzaldehyde (3.24 g, 20 mmol); yield 3.83 g (56%), yellow solid, mp 118 °C (EtOH). ^{1}H NMR (CDCl$_3$): $\delta = 1.33$ (s, 9H), 7.39–7.50 (m, 3H), 7.45 and 7.60 (AA′BB′, $^3J = 8.4$ Hz, 4H), 7.54 and 7.83 (AB, $^3J = 15.7$ Hz, 2H), 7.63–7.66 (m, 2H), 7.72 and 8.09 (AA′BB′, $^3J = 8.5$ Hz, 4H); MS (EI, 70 eV): *m*/*z* (%) 340 (40, $M^{\bullet+}$), 339 (25), 325 (63), 297 (11), 283 (100), 181 (24), 163 (11), 153 (22), 152 (37), 129 (14), 128 (13), 115 (12), 77 (9), 57 (14); IR (KBr), $\tilde{\nu}$ (cm^{-1}): 3035, 2967, 2868, 1656, 1606, 1592, 1332, 1308, 1222, 1032, 825, 772, 747, 693. $C_{25}H_{24}O$ (340.47): Calcd. C 88.20, H 7.11; found C 88.24, H 7.28.

*A.1.3. 1-(4-t-Butylphenyl)-3-(2-naphthyl)prop-2-en-1-one (**A6**).*

From 4-*t*-butylacetophenone (3.52 g) and 2-naphthaldehyde (3.12 g, 20 mmol); yield 4.00 g (64%), yellow solid, mp 145 °C (EtOH). ^{1}H NMR (CDCl$_3$): $\delta = 1.38$ (s, 9H), 7.52–7.56 (m, 2H), 7.55 and 8.02 (AA′BB′, $^3J = 8.6$ Hz, 4H), 7.66 and 7.98 (AB,

^3J = 15.6 Hz, 2H), 7.80–7.91 (m, 4H), 8.04 (br s, 1H); MS (EI, 70 eV): *m/z* (%) 314 (100, $M^{\bullet+}$), 313 (92), 299 (33), 271 (16), 257 (98), 181 (39), 161 (65), 153 (40), 152 (47), 135 (44), 127 (35), 118 (15), 115 (15), 91 (17), 77 (19), 57 (16); IR (KBr), $\tilde{\nu}$ (cm^{-1}): 3061, 2969, 2865, 1655, 1604, 1588, 1360, 1297, 1269, 1191, 1108, 1010, 987, 832, 819, 746, 692. $\mathrm{C_{23}H_{22}O}$ (314.43): Calcd. C 87.86, H 7.05; found C 87.75, H 7.28.

*A.1.4. 3-(4-t-Butylphenyl)-1-(2-naphthyl)prop-2-en-1-one (**A′6**)*

From 2-acetonaphthone (3.40 g) and 4-*t*-butylbenzaldehyde (3.24 g, 20 mmol); yield 4.18 g (66%), yellow crystals, mp 81 °C (EtOH). ^{1}H NMR (CDCl$_3$): δ = 1.36 (s, 9H), 7.47 and 7.64 (AA′BB′, ^3J = 8.4 Hz, 4H), 7.55–7.62 (m, 2H), 7.66 and 7.88 (AB, ^3J = 15.7 Hz, 2H), 7.89–8.01 (m, 3H), 8.09–8.12 (m, 1H), 8.54 (br s, 1H); MS (EI, 70 eV): *m/z* (%) 314 (39, $M^{\bullet+}$), 313 (21), 299 (66), 271 (10), 257 (100), 155 (20), 135 (10), 127 (47), 115 (10), 77 (10), 57 (12); IR (KBr), $\tilde{\nu}$ (cm^{-1}): 3054, 2965, 2867, 1661, 1625, 1600, 1361, 1325, 1178, 1128, 1047, 979, 819, 753. $\mathrm{C_{23}H_{22}O}$ (314.43): Calcd. C 87.86, H 7.05; found C 87.71, H 7.14.

*A.1.5. 1-(4-t-Butylphenyl)-3-(4-methoxyphenyl)prop-2-en-1-one (**A7**)*

From 4-*t*-butylacetophenone (3.32 g) and 4-methoxybenzaldehyde (2.72 g, 20 mmol); yield 3.21 g (55%), yellow oil, bp 145 °C (0.01 mbar, kugelrohr). ^{1}H NMR (CDCl$_3$): δ = 1.36 (s, 9H), 3.84 (s, 3H), 6.93 and 7.60 (AA′BB′, ^3J = 8.8 Hz, 4H), 7.43 and 7.79 (AB, ^3J = 15.6 Hz, 2H), 7.51 and 7.97 (AA′BB′, ^3J = 8.5 Hz, 4H); MS (EI, 70 eV): *m/z* (%) 294 (72, $M^{\bullet+}$), 293 (36), 279 (42), 237 (100), 135 (29), 91 (21), 77 (26), 57 (15); IR (film), $\tilde{\nu}$ (cm^{-1}): 2967, 2872, 1660, 1594, 1512, 1422, 1257, 1221, 1172, 1035, 820. Accurate mass (EI) $\mathrm{C_{20}H_{22}O_2}$: Calcd. 294.1620; found 294.1615.

*A.1.6. 3-(4-t-Butylphenyl)-1-(4-methoxyphenyl)prop-2-en-1-one (**A′7**)*

From 4-*t*-butylbenzaldehyde (3.24 g) and 4-methoxyacetophenone (3.00 g, 20 mmol); yield 4.52 g (77%), yellow crystals, mp 112 °C (EtOH). ^{1}H NMR (CDCl$_3$): δ = 1.35 (s, 9H), 3.90 (s, 3H), 6.99 and 8.04 (AA′BB′, ^3J = 8.9 Hz, 4H), 7.44 and 7.59 (AA′BB′, ^3J = 8.4 Hz, 4H), 7.52 and 7.80 (AB, ^3J = 15.6 Hz, 2H); MS (EI, 70 eV): *m/z* (%) = 294 (39, $M^{\bullet+}$), 293 (32), 279 (83), 237 (100), 135 (41), 77 (25), 57 (12); IR (KBr), $\tilde{\nu}$ (cm^{-1}): 3033, 2970, 2841, 1654, 1592, 1421, 1254, 1226, 1177, 1021, 995, 824. $\mathrm{C_{20}H_{22}O_2}$ (294.40): Calcd. C 81.60, H 7.53; found C 81.49, H 7.69.

*A.1.7. 3-(4-t-Butylphenyl)-1-(3-methoxyphenyl)prop-2-en-1-one (**A′8**)*

From 4-*t*-butylbenzaldehyde (3.24 g) and 3-methoxyacetophenone (3.00 g, 20 mmol); yield 2.21 g (38%), yellow solid, mp 47 °C (EtOH). ^{1}H NMR (CDCl$_3$): δ = 1.35 (s, 9H), 3.89 (s, 3H), 7.11–7.15 (m, 1H), 7.39–7.47 (m, 1H), 7.45 and 7.60 (AA′BB′, ^3J = 8.4 Hz, 4H), 7.49 and 7.81 (AB, ^3J = 15.7 Hz, 2H), 7.54–7.55 (m, 1H), 7.58–7.62 (m, 1H); MS (EI, 70 eV): *m/z* (%) 294 (36, $M^{\bullet+}$), 293 (23), 279 (64), 237 (100), 135 (25), 107 (18), 77 (28), 57 (21); IR (KBr), $\tilde{\nu}$ (cm^{-1}): 3076, 2960, 2907, 1664, 1591, 1331, 1254, 1170, 1000, 826, 793. $\mathrm{C_{20}H_{22}O_2}$ (294.40): Calcd. C 81.60, H 7.53; found C 81.30, H 7.70.

*A.1.8. 3-(4-t-Butylphenyl)-1-(2-methoxyphenyl)prop-2-en-1-one (**A′9**)*

From 4-*t*-butylbenzaldehyde (3.24 g) and 2-methoxyacetophenone (3.00 g, 20 mmol); yield 4.71 g (80%), yellow oil, bp 190 °C (0.06 mbar, kugelrohr). ^{1}H NMR (CDCl$_3$): δ = 1.33 (s, 9H), 3.89 (s, 3H), 6.98–7.07 (m, 2H), 7.33 and 7.61 (AB, ^3J = 15.9 Hz, 2H), 7.42 and 7.53 (AA′BB′, ^3J = 8.4 Hz, 4H), 7.43–7.48 (m, 1H), 7.59–7.62 (m, 1H); MS (EI, 70 eV): *m/z* (%) = 294 (63, $M^{\bullet+}$), 293 (35), 279 (89), 237 (100), 147 (39), 135 (61), 77 (55), 57 (39); IR (film), $\tilde{\nu}$ (cm^{-1}): 3041, 2966, 2872, 1657, 1599, 1484, 1462, 1331, 1243, 1027, 827, 753, 636. Accurate mass (EI) $\mathrm{C_{20}H_{22}O}$: Calcd. 294.1620; found 294.1613.

*A.1.9. 1-(4-t-Butylphenyl)-3-(4-fluorophenyl)prop-2-en-1-one (**A10**)*

From 4-fluorobenzaldehyde (2.53 g) and 4-*t*-butylacetophenone (3.52 g, 20.0 mmol); yield 3.12 g (55%), yellow crystals, mp 81–82 °C (EtOH). ^{1}H NMR (CDCl$_3$): δ = 1.37 (s, 9H), 7.09–7.14 (m, 2H), 7.48 and 7.78 (AB, ^3J = 15.7 Hz, 2H), 7.53 and 7.98 (AA′BB′, ^3J = 8.6 Hz, 4H), 7.62–7.66 (m, 2H); MS (EI, 70 eV): *m/z* (%) 282 (57, $M^{\bullet+}$), 281 (37), 267 (91), 225 (100), 161 (26), 149 (53), 121 (38), 101 (35), 91 (16); IR (KBr), $\tilde{\nu}$ (cm^{-1}): 3048, 2963, 2871, 1658, 1598, 1504, 1221, 1157, 1009, 985, 823. $\mathrm{C_{19}H_{19}FO}$ (282.36): Calcd. C 80.82, H 6.78; found C 80.89, H 6.98.

*A.1.10. 3-(4-t-Butylphenyl)-1-(4-fluorophenyl)prop-2-en-1-one (**A′10**)*

From 4-fluoroacetophenone (2.76 g) and 4-*t*-butylbenzaldehyde (3.25 g); yield 4.79 g (85%), pale-yellow needles, mp 93.5–94 °C. ^{1}H NMR (CDCl$_3$): δ = 1.35 (s, 9H), 7.15−7.21 (m, 2H), 7.45 and 7.59 (AA′BB′, ^3J = 8.4 Hz, 4H), 7.47 and 7.81 (AB, ^3J = 15.7 Hz, 2H), 8.03–8.08 (m, 2H); MS (EI, 70 eV): *m/z* (%) 282 (33, $M^{\bullet+}$), 281 (21), 267 (94), 225 (100), 129 (20), 123 (52), 95 (40), 57 (13); IR (KBr), $\tilde{\nu}$ (cm^{-1}): 3033, 2952, 2911, 2872, 1660, 1605, 1584, 1417, 1342, 1224, 1023, 990, 837, 822. $\mathrm{C_{19}H_{19}FO}$ (282.36): Calcd. C 80.82, H 6.78; found C 80.64, H 6.86.

*A.1.11. 1-(4-t-Butylphenyl)-3-(3-fluorophenyl)prop-2-en-1-one (**A11**)*

From 3-fluorobenzaldehyde (0.50 g) and 4-*t*-butylacetophenone (0.70 g, 4.0 mmol); yield 0.69 g (61%), yellow crystals, mp 72 °C (EtOH). ^{1}H NMR (CDCl$_3$): δ = 1.37 (s, 9H), 7.09–7.15 (m, 1H), 7.33–7.42 (m, 3H), 7.53 and 7.76 (AB, ^3J = 15.7 Hz, 2H), 7.53 and 7.98 (AA′BB′, ^3J = 8.6 Hz, 4H); MS (EI, 70 eV): *m/z* (%) 282 (65, $M^{\bullet+}$), 281 (44), 267 (100), 225 (61), 161 (29), 149 (53), 121 (33), 101 (32), 57 (19); IR (KBr), $\tilde{\nu}$ (cm^{-1}): 3069, 2971, 2874, 1658, 1600, 1581, 1248, 839, 784, 668. $\mathrm{C_{19}H_{19}FO}$ (282.36): Calcd. C 80.82, H 6.78; found C 80.69, H 6.76.

*A.1.12. 3-(4-t-Butylphenyl)-1-(3-fluorophenyl)prop-2-en-1-one (**A′11**)*

From 4-*t*-butylbenzaldehyde (2.45 g) and 3-fluoroacetophenone (2.09 g, 15.1 mmol); yield 1.60 g (37%), yellow solid, mp 61 °C (EtOH). ^{1}H NMR ($CDCl_3$): $\delta = 1.35$ (s, 9H), 7.28–7.32 (m, 1H), 7.45 and 7.83 (AB, $^3J = 15.6$ Hz, 2H), 7.46 and 7.60 (AA′BB′, $^3J = 8.5$ Hz, 4H), 7.47–7.52 (m, 1H), 7.68–7.72 (m, 1H), 7.79–7.82 (m, 1H); MS (EI, 70 eV): *m/z* (%) 282 (19, $M^{\bullet+}$), 281 (16), 267 (86), 225 (100), 123 (41), 95 (39), 57 (13); IR (KBr), $\tilde{\nu}$ (cm^{-1}): 3078, 2963, 2871, 1661, 1601, 1584, 1441, 1332, 1269, 1250, 990, 834, 827, 792. $C_{19}H_{19}FO$ (282.36): Calcd. C 80.82, H 6.78; found C 80.63, H 6.69.

*A.1.13. 1-(4-t-Butylphenyl)-3-(2-fluorophenyl)prop-2-en-1-one (**A12**)*

From 2-fluorobenzaldehyde (2.56 g) and 4-*t*-butylacetophenone (3.52 g, 20.0 mmol); yield 3.68 g (65%), yellow crystals, mp 65 °C (EtOH). ^{1}H NMR ($CDCl_3$): $\delta = 1.37$ (s, 9H), 7.10–7.23 (m, 2H), 7.35–7.42 (m, 1H), 7.53 and 7.99 (AA′BB′, $^3J = 8.6$ Hz, 4H), 7.64–7.68 (m, 1H), 7.66 and 7.91 (AB, $^3J = 15.9$ Hz, 2H); MS (EI, 70 eV): *m/z* (%) 282 (59, $M^{\bullet+}$), 281 (27), 267 (100), 263 (20), 225 (55), 161 (27), 149 (55), 121 (36), 101 (51), 91 (18), 57 (13); IR (KBr), $\tilde{\nu}$ (cm^{-1}): 3079, 2972, 2873, 1655, 1592, 1486, 1458, 1282, 1225, 1109, 1010, 840, 756. $C_{19}H_{19}FO$ (282.36): Calcd. C 80.82, H 6.78; found C 80.71, H 6.87.

*A.1.14. 3-(4-t-Butylphenyl)-1-(2-fluorophenyl)prop-2-en-1-one (**A′12**)*

From 4-*t*-butylbenzaldehyde (7.13 g) and 2-fluoroacetophenone (6.07 g, 44.0 mmol); yield 5.33 g (43%), yellow oil, bp 155 °C (0.01 mbar, kugelrohr). ^{1}H NMR ($CDCl_3$): $\delta = 1.34$ (s, 9H), 7.13–7.29 (m, 2H), 7.36 (A part of AB, $^3J = 15.8$ Hz, $J = 2.8$ Hz, 1H), 7.44 and 7.57 (AA′BB′, $^3J = 8.4$ Hz, 4H), 7.49–7.54 (m, 1H), 7.74 (B part of AB, $^3J = 15.8$ Hz, $J = 1.6$ Hz, 1H), 7.78–7.84 (m, 1H); MS (EI, 70 eV): *m/z* (%) 282 (24, $M^{\bullet+}$), 281 (17), 267 (86), 239 (14), 225 (100), 129 (18), 123 (45), 115 (14), 95 (27), 77 (9), 75 (11), 57 (13); IR (film), $\tilde{\nu}$ (cm^{-1}): 3040, 2969, 2873, 1665, 1611, 1479, 1452, 1331, 1269, 1204, 1100, 1019, 824, 769, 752, 630. Accurate mass (EI) $C_{19}H_{19}FO$: Calcd. 282.1420; found 282.1418.

*A.1.15. 1-(4-t-Butylphenyl)-3-(4-trifluoromethylphenyl)prop-2-en-1-one (**A13**)*

From 4-trifluoromethylbenzaldehyde (3.70 g) and 4-*t*-butylacetophenone (3.70 g, 21.0 mmol); yield 3.20 g (48%), yellow crystals, mp 168–175 °C (EtOH). ^{1}H NMR ($CDCl_3$): $\delta = 1.37$ (s, 9H), 7.54 and 7.99 (AA′BB′, $^3J = 8.6$ Hz, 4H), 7.61 and 7.81 (AB, $^3J = 15.8$ Hz, 2H), 7.68 and 7.75 (AA′BB′, $^3J = 8.5$ Hz, 4H); MS (EI, 70 eV): *m/z* (%) 332 (48, $M^{\bullet+}$), 331 (26), 317 (100), 289 (26), 275 (37), 199 (43), 171 (33), 161 (40), 151 (33), 110 (37), 91 (24), 77 (17), 57 (42); IR (KBr), $\tilde{\nu}$ (cm^{-1}): 2975, 2875, 1661, 1607, 1324, 1159, 1126, 1107, 1067, 820. $C_{20}H_{19}F_3O$ (332.37): Calcd. C 72.28, H 5.76; found C 72.29, H 5.95.

*A.1.16. 3-(4-t-Butylphenyl)-1-(4-hydroxyphenyl)prop-2-en-1-one (**A′14**)*

From 4-*t*-butylbenzaldehyde (3.40 g) and 4-hydroxyacetophenone (2.86 g, 21 mmol); yield 3.88 g (66%), light-red solid, mp 144–145 °C (Et_2O). ^{1}H NMR ($CDCl_3$): $\delta = 1.32$ (s, 9H), 6.92 and 7.98 (AA′BB′, $^3J = 8.6$ Hz, 4H), 7.48 and 7.79 (AB, $^3J = 15.6$ Hz, 2H), 7.42 and 7.57 (AA′BB′, $^3J = 8.3$ Hz, 4H); MS (EI, 70 eV): *m/z* (%) 280 (39, $M^{\bullet+}$), 265 (93), 223 (100). Accurate mass (EI) $C_{19}H_{20}O_2$: Calcd. 280.1463; found 280.1459.

A.2. tert-Butylated 1,3-diphenylpropanones (tert-butyldihydrochalcones)

*A.2.1. 3-(4-Biphenylyl)-1-(4-t-butylphenyl)propan-1-one (**B5**)*

From chalcone **A5** (3.00 g, 8.8 mmol); yield 2.05 g (68%), colorless needles, mp 115.5–116.5 °C (EtOH). ^{1}H NMR: $\delta = 1.34$ (s, 9H), 3.11 (t, $^3J = 7.7$ Hz, 2H), 3.33 (t, $^3J = 7.5$ Hz, 2H), 7.32–7.36 (m, 1H), 7.34 and 7.54 (AA′BB′, $^3J = 8.2$ Hz, 4H), 7.41–7.60 (m, 4H), 7.58 and 7.93 (AA′BB′, $^3J = 8.5$ Hz, 4H); MS (EI, 70 eV): *m/z* (%) 342 (35, $M^{\bullet+}$), 285 (30), 167 (37), 161 (100), 118 (15), 91 (13); IR (KBr), $\tilde{\nu}$ (cm^{-1}): 3029, 2969, 2873, 1677, 1602, 1487, 1406, 1213, 1188, 1106, 982, 825, 761, 701. $C_{25}H_{26}O$ (342.49): Calcd. C 87.68, H 7.65; found C 87.60, H 7.90.

*A.2.2. 1-(4-Biphenylyl)-3-(4-t-butylphenyl)propan-1-one (**B′5**)*

From chalcone **A′5** (3.83 g, 11.2 mmol); yield 2.25 g (58%), colorless solid, mp 105 °C (EtOH). ^{1}H NMR ($CDCl_3$): $\delta = 1.32$ (s, 9H), 3.06 (t, $^3J = 7.7$ Hz, 2H), 3.34 (t, $^3J = 7.8$ Hz, 2H), 7.21 and 7.34 (AA′BB′, $^3J = 8.3$ Hz, 4H), 7.39–7.50 (m, 3H), 7.61–7.64 (m, 2H), 7.68 and 8.04 (AA′BB′, $^3J = 8.5$ Hz, 4H); MS (EI, 70 eV): *m/z* (%) 342 (54, $M^{\bullet+}$), 327 (68), 285 (6), 181 (100), 153 (23), 152 (32), 131 (32), 117 (11), 91 (10), 57 (9); IR (KBr), $\tilde{\nu}$ (cm^{-1}): 3033, 2964, 2907, 2868, 1676, 1603, 1405, 1360, 1267, 1197, 981, 819, 760, 691. $C_{25}H_{26}O$ (342.49): Calcd. C 87.68, H 7.65; found C 87.58, H 7.71.

*A.2.3. 1-(4-t-Butylphenyl)-3-(2-naphthyl)propan-1-one (**B6**)*

From chalcone **A6** (1.14 g, 3.6 mmol); yield 620 mg (54%), colorless solid, mp 99–102 °C (EtOH). ^{1}H NMR ($CDCl_3$): $\delta = 1.34$ (s, 9H), 3.21–3.25 (m, 2H), 3.35–3.42 (m, 2H), 7.38–7.50 (m, 3H), 7.46 and 7.92 (AA′BB′, $^3J = 8.6$ Hz, 4H), 7.69 (br s, 1H), 7.78–7.86 (m, 3H); MS (EI, 70 eV): *m/z* (%) 316 (22, $M^{\bullet+}$), 259 (7), 161 (100), 155 (15), 141 (22); IR (KBr), $\tilde{\nu}$ (cm^{-1}): 3059, 2968, 2907, 2860, 1667, 1603, 1266, 1190, 1107, 984, 808, 748. $C_{23}H_{24}O$ (316.45): Calcd. C 87.30, H 7.64; found C 85.94, H 7.80.

*A.2.4. 3-(4-t-Butylphenyl)-1-(2-naphthyl)propan-1-one (**B′6**)*

From chalcone **A′6** (3.14 g, 10.0 mmol); yield 1.95 g (61%), colorless crystals, mp 78 °C (EtOH). ^{1}H NMR ($CDCl_3$): $\delta = 1.32$ (s, 9H), 3.10 (t, $^3J = 7.8$ Hz, 2H), 3.44 (t, $^3J = 7.8$ Hz, 2H), 7.24 and 7.35 (AA′BB′, $^3J = 8.3$ Hz, 4H), 7.52–7.63 (m, 2H), 7.86–7.96 (m, 3H), 8.03–8.06 (m, 1H), 8.46 (br s, 1H); MS (EI, 70 eV): *m/z* (%) 316 (53, $M^{\bullet+}$), 301 (61), 259 (7), 155 (100), 147 (11), 131 (45), 127 (60), 117 (14), 91 (13), 77 (10), 57 (12); IR (KBr), $\tilde{\nu}$ (cm^{-1}): 3033, 2963, 2904, 2867, 1677, 1360, 1299, 1181, 1124, 869, 830, 817, 782, 746. $C_{23}H_{24}O$ (316.45): Calcd. C 87.30, H 7.64; found C 87.36, H 7.40.

*A.2.5. 1-(4-t-Butylphenyl)-3-(4-methoxyphenyl)propan-1-one (**B7**)*

From chalcone **A7** (2.50 g, 8.5 mmol); yield 1.72 g (68%), colorless liquid, bp 150 °C (0.02 mbar, kugelrohr). ^{1}H NMR (CDCl$_3$): $\delta = 1.34$ (s, 9H), 3.00 (t, $^3J = 7.8$ Hz, 2H), 3.25 (t, $^3J = 7.8$ Hz, 2H), 3.79 (s, 3H), 6.84 and 7.17 (AA′BB′, $^3J = 8.7$ Hz, 4H), 7.47 and 7.90 (AA′BB′, $^3J = 8.6$ Hz, 4H); MS (EI, 70 eV): *m/z* (%) 296 (48, $M^{\bullet+}$), 281 (7), 239 (29), 135 (19), 121 (100), 91 (28), 77 (22), 57 (17); IR (film), $\tilde{\nu}$ (cm^{-1}): 2967, 2872, 1682, 1605, 1513, 1247, 1036, 822. Accurate mass (EI) $C_{20}H_{24}O_2$: Calcd. 296.1776; found 296.1776.

*A.2.6. 3-(4-t-Butylphenyl)-1-(4-methoxyphenyl)propan-1-one (**B′7**)*

From chalcone **A′7** (3.00 g, 10.2 mmol); yield 2.25 g (74%), colorless crystals, mp 76 °C (EtOH). ^{1}H NMR (CDCl$_3$): $\delta = 1.31$ (s, 9H), 3.02 (t, $^3J = 7.8$ Hz, 2H), 3.25 (t, $^3J = 8.0$ Hz, 2H), 3.87 (s, 3H), 6.92 and 7.95 (AA′BB′, $^3J = 9.0$ Hz, 4H), 7.20 and 7.33 (AA′BB′, $^3J = 8.3$ Hz, 4H); MS (EI, 70 eV): *m/z* (%) 296 (36, $M^{\bullet+}$), 281 (36), 147 (21), 135 (100), 131 (27), 91 (12), 77 (16), 57 (8); IR (KBr), $\tilde{\nu}$ (cm^{-1}): 3007, 2956, 2867, 1667, 1603, 1418, 1257, 1181, 1033, 817. $C_{20}H_{24}O_2$ (296.41): Calcd. C 81.04, H 8.16; found C 80.81, H 8.29.

*A.2.7. 3-(4-t-Butylphenyl)-1-(3-methoxyphenyl)propan-1-one (**B′8**)*

From chalcone **A′8** (2.00 g, 6.8 mmol); yield 1.55 g (77%), colorless liquid, bp 160 °C (0.03 mbar, kugelrohr). ^{1}H NMR (CDCl$_3$): $\delta = 1.31$ (s, 9H), 3.03 (t, $^3J = 7.8$ Hz, 2H), 3.28 (t, $^3J = 7.7$ Hz, 2H), 3.84 (s, 3H), 7.07–7.11 (m, 1H), 7.19 and 7.33 (AA′BB′, $^3J = 8.4$ Hz, 4H), 7.28–7.37 (m, 1H), 7.48–7.54 (m, 2H); MS (EI, 70 eV): *m/z* (%) 296 (84, $M^{\bullet+}$), 281 (100), 239 (22), 147 (30), 135 (85), 131 (92), 107 (34), 91 (35), 77 (41), 57 (33); IR (film), $\tilde{\nu}$ (cm^{-1}): 3059, 2965, 2870, 1687, 1597, 1485, 1463, 1429, 1288, 1260, 1040, 832, 773, 685. Accurate mass (EI) $C_{20}H_{24}O_2$: Calcd. 296.1776; found 296.1767.

*A.2.8. 3-(4-t-Butylphenyl)-1-(2-methoxyphenyl)propan-1-one (**B′9**)*

From chalcone **A′9** (3.00 g, 10.2 mmol); yield 2.53 g (83%), colorless liquid, bp 150 °C (0.01 mbar, kugelrohr). ^{1}H NMR (CDCl$_3$): $\delta = 1.31$ (s, 9H), 2.99 (t, $^3J = 7.8$ Hz, 2H), 3.30 (t, $^3J = 7.8$ Hz, 2H), 3.85 (s, 3H), 6.92–7.01 (m, 2H), 7.17 and 7.31 (AA′BB′, $^3J = 8.3$ Hz, 4H), 7.40–7.46 (m, 1H), 7.67–7.71 (m, 1H); MS (EI, 70 eV): *m/z* (%) 296 (38, $M^{\bullet+}$), 281 (26), 239 (10), 147 (16), 135 (100), 131 (34), 117 (16), 91 (15), 77 (33), 57 (11); IR (film), $\tilde{\nu}$ (cm^{-1}): 3030, 2966, 2871, 1673, 1598, 1485, 1464, 1436, 1243, 1023, 823, 755. Accurate mass (EI) $C_{20}H_{24}O_2$: Calcd. 296.1776; found 296.1770.

*A.2.9. 1-(4-t-Butylphenyl)-3-(4-fluorophenyl)propan-1-one (**B10**)*

From chalcone **A10** (2.82 g, 5.0 mmol); yield 2.37 g (84%), colorless liquid, bp 125 °C (0.02 mbar, kugelrohr). ^{1}H HMR (CDCl$_3$): $\delta = 1.34$ (s, 9H), 3.04 (t, $^3J = 7.5$ Hz, 2H), 3.26 (t, $^3J = 7.6$ Hz, 2H), 6.95–7.00 (m, 2H), 7.18–7.37 (m, 2H), 7.47 and 7.90 (AA′BB′, $^3J = 8.6$ Hz, 4H); MS (EI, 70 eV): *m/z* (%) 284 ($M^{\bullet+}$, 16), 269 (10), 227 (44), 163 (34), 161 (100), 109 (35), 91 (17), 57 (12); IR (film), $\tilde{\nu}$ (cm^{-1}): 3044, 2969, 2872, 1682, 1605, 1509, 1221, 824. Accurate mass (EI) $C_{19}H_{21}FO$: Calcd. 284.1576; found 284.1573.

*A.2.10. 3-(4-t-Butylphenyl)-1-(4-fluorophenyl)propan-1-one (**B′10**)*

From chalcone **A′10** (4.50 g, 16.0 mmol); yield 2.05 g (45%), colorless solid, mp 82–84 °C (EtOH). ^{1}H NMR (CDCl$_3$): $\delta = 1.31$ (s, 9H), 3.03 (t, $^3J = 7.7$ Hz, 2H), 3.27 (t, $^3J = 7.7$ Hz, 2H), 7.12–7.15 (m, 2H), 7.19 and 7.33 (AA′BB′, $^3J = 8.2$ Hz, 4H), 7.96–8.01 (m, 2H); MS (EI, 70 eV): *m/z* (%) 284 (41, $M^{\bullet+}$), 269 (100), 147 (13), 131 (42), 123 (48), 117 (19), 95 (30), 57 (18); IR (KBr), $\tilde{\nu}$ (cm^{-1}): 3026, 2973, 2954, 2870, 1677, 1595, 1503, 1410, 1296, 1227, 1204, 1157, 981, 845, 820. $C_{19}H_{21}FO$ (284.38): Calcd. C 80.25, H 7.44; found C 80.18, H 7.61.

*A.2.11. 1-(4-t-Butylphenyl)-3-(3-fluorophenyl)propan-1-one (**B11**)*

From chalcone **A11** (0.60 g, 2.1 mmol); yield 0.46 g (78%), colorless liquid, bp 140 °C (0.02 mbar, kugelrohr). ^{1}H NMR (CDCl$_3$): $\delta = 1.34$ (s, 9H), 3.06 (t, $^3J = 7.6$ Hz, 2H), 3.28 (t, $^3J = 7.7$ Hz, 2H), 6.87–7.04 (m, 3H), 7.21–7.30 (m, 1H), 7.47 and 7.90 (AA′BB′, $^3J = 8.5$ Hz, 4H); MS (EI, 70 eV): *m/z* (%) = 284 (13, $M^{\bullet+}$), 269 (13), 227 (42), 163 (52), 161 (100), 118 (19), 109 (28), 91 (21), 57 (21); IR, $\tilde{\nu}$ (cm^{-1}): 3062, 2969, 2872, 1681, 1605, 1449, 1252, 1108, 783, 690. Accurate mass (EI) $C_{19}H_{21}FO$: Calcd. 284.1576; found 284.1567.

*A.2.12. 3-(4-t-Butylphenyl)-1-(3-fluorophenyl)propan-1-one (**B′11**)*

From chalcone **A′11** (1.50 g, 5.3 mmol); yield 0.62 g (41%), colorless liquid, bp 125 °C (0.02 mbar, kugelrohr). ^{1}H NMR (CDCl$_3$): $\delta = 1.31$ (s, 9H), 3.03 (t, $^3J = 7.7$ Hz, 2H), 3.28 (t, $^3J = 7.8$ Hz, 2H), 7.18–7.31 (m, 1H), 7.19 and 7.33 (AA′BB′, $^3J = 8.5$ Hz, 4H), 7.35–7.46 (m, 1H), 7.61–7.66 (m, 1H), 7.71–7.75 (m, 1H); MS (EI, 70 eV): *m/z* (%) 284 (44, $M^{\bullet+}$), 269 (100), 147 (49), 131 (36), 91 (20), 57 (58); IR (film), $\tilde{\nu}$ (cm^{-1}): 3076, 2967, 2872, 1691, 1589, 1443, 1268, 1239, 681. Accurate mass (EI) $C_{19}H_{21}FO$: Calcd. 284.1576; found 284.1580.

*A.2.13. 1-(4-t-Butylphenyl)-3-(2-fluorophenyl)propan-1-one (**B12**)*

From chalcone **A12** (2.82 g, 10.0 mmol); yield 2.62 g (93%), colorless liquid, bp 125 °C (0.02 mbar, kugelrohr). ^{1}H NMR (CDCl$_3$): $\delta = 1.34$ (s, 9H), 3.09 (t, $^3J = 7.6$ Hz, 2H), 3.29 (t, $^3J = 7.8$ Hz, 2H), 7.00–7.32 (m, 4H), 7.47 and 7.91 (AA′BB′, $^3J = 8.7$ Hz, 4H); MS (EI, 70 eV): *m/z* (%) 284 (8, $M^{\bullet+}$), 269 (8), 227 (33), 163 (59), 161 (100), 117 (30), 109 (77), 91 (40), 77 (29), 57 (26); IR (film), $\tilde{\nu}$ (cm^{-1}): 3048, 2968, 2872, 1682, 1605, 1481, 1229, 755. Accurate mass (EI) $C_{19}H_{21}FO$: Calcd. 284.1576; found 284.1571.

*A.2.14. 3-(4-t-Butylphenyl)-1-(2-fluorophenyl)propan-1-one **B′12***

From chalcone **A′12** (5.27 g, 18.7 mmol); yield 4.09 g (77%), colorless liquid, bp 130 °C (0.01 mbar, kugelrohr). ^{1}H NMR ($CDCl_3$): $\delta = 1.31$ (s, 9H), 3.02 (t, $^3J = 7.7$ Hz, 2H), 3.31 (t, $^3J = 7.7$ Hz, $J = 3.4$ Hz, 2H), 7.09–7.30 (m, 2H), 7.19 and 7.32 (AA′BB′, $^3J = 8.4$ Hz, 4H), 7.47–7.55 (m, 1H), 7.85–7.90 (m, 1H); MS (EI, 70 eV): *m/z* (%) 284 (14, $M^{\bullet+}$), 269 (100), 227 (5), 147 (10), 131 (39), 123 (28), 117 (11), 105 (6), 95 (10), 91 (12), 57 (14); IR (film), $\tilde{\nu}$ (cm^{-1}): 1688, 1610. Accurate mass (EI) $C_{19}H_{21}FO$: Calcd. 284.1576; found 284.1575. The corresponding carbinol was detected by signals at $\delta = 1.30$ (s), 2.07–2.15 (m), 2.62–2.84 (m) and 7.47–7.55 (m) in the ^{1}H NMR spectrum (ca. 25%) and at $\tilde{\nu} = 3502\,\text{cm}^{-1}$ in the IR spectrum.

*A.2.15. 1-(4-t-Butylphenyl)-3-(4-trifluoromethylphenyl)-propan-1-one (**B13**)*

From chalcone **A13** (1.68 g, 5.0 mmol); yield 0.93 g (56%), colorless crystals, mp 39–40 °C (EtOH). ^{1}H NMR ($CDCl_3$): $\delta = 1.34$ (s, 9H), 3.12 (t, $^3J = 7.4$ Hz, 2H), 3.31 (t, $^3J = 7.8$ Hz, 2H), 7.37 and 7.54 (AA′BB′, $^3J = 8.1$ Hz, 4H), 7.47 and 7.90 (AA′BB′, $^3J = 8.7$ Hz, 4H); MS (EI, 70 eV): *m/z* (%) 334 (8, $M^{\bullet+}$), 319 (18), 315 (6), 277 (45), 161 (100), 118 (17), 91 (14), 57 (8); IR (KBr), $\tilde{\nu}$ (cm^{-1}): 3048, 2972, 2896, 1681, 1328, 1153, 1129, 1104, 1067, 835, 821. $C_{20}H_{21}F_3O$ (334.39): Calcd. C 71.84, H 6.33; found C 71.95, H 6.43.

*A.2.16. 3-(4-t-Butylphenyl)-1-(4-hydroxyphenyl)propan-1-one (**B′14**)*

From chalcone **A′14** (2.35 g, 8.4 mmol); yield 1.42 g (60%), beige crystals, mp 45–48 °C (EtOH). ^{1}H NMR ($CDCl_3$): $\delta = 1.29$ (s, 9H), 2.99–3.02 (t, $^3J = 7.8$ Hz, 2H), 3.21–3.24 (t, $^3J = 8.2$ Hz, 2H), 5.42 (s, 1H), 6.85 (d, $^3J = 8.7$ Hz, 2H), 7.17 (d, $^3J = 8.2$ Hz, 2H), 7.31 (d, $^3J = 8.2$ Hz, 2H), 7.89 (d, $^3J = 8.7$ Hz, 2H); MS (EI, 70 eV): *m/z* (%) 282 (50, $M^{\bullet+}$), 267 (84), 121 (100). Accurate mass (EI) $C_{19}H_{22}O_2$: Calcd. 282.1620; found 282.1620.

A.3. tert-Butylated 1,3-diphenylpropanes

*A.3.1. 1-(4-Biphenylyl)-3-(4-t-butylphenyl)propane (**5**)*

From dihydrochalcone **B′5** (342 mg, 1.00 mmol) by hydrogenolysis [method (i), see Section 2.2]; colorless liquid, bp 180 °C (0.01 mbar, kugelrohr). ^{1}H NMR ($CDCl_3$): $\delta = 1.31$ (s, 9H), 1.99 (quint, $^3J = 7.7$ Hz, 2H), 2.66 (t, $^3J = 7.7$ Hz, 2H), 2.70 (t, $^3J = 7.7$ Hz, 2H), 7.14 and 7.52 (AA′BB′, $^3J = 8.3$ Hz, 4H), 7.27–7.35 (m, 3H), 7.27 and 7.59 (AA′BB′, $^3J = 8.5$ Hz, 4H), 7.40–7.46 (m, 2H); MS (EI, 70 eV): *m/z* (%) = 328 (96, $M^{\bullet+}$), 313 (100), 194 (9), 181 (23), 167 (72), 165 (32), 157 (33), 155 (20), 131 (34), 117 (30), 105 (15), 92 (31), 91 (28), 77 (12), 57 (34); IR, $\tilde{\nu}$ (cm^{-1}): 3060, 3031, 2966, 2862, 1518, 1486, 1460, 1363, 1268, 831, 761, 697. Accurate mass (EI) $C_{25}H_{28}$: Calcd. 328.2191; found 328.2189.

*A.3.2. 3,3-[D_2]-1-(4-Biphenylyl)-3(4-t-butylphenyl)-propane (**5a**)*

From dihydrochalcone **B5** (342 mg, 1.00 mmol) by reduction with $LiAlD_4/AlCl_3$ [method (ii), see Section 2.2]; colorless liquid, bp 185 °C (0.01 mbar, kugelrohr). ^{1}H NMR ($CDCl_3$): $\delta = 1.31$ (s, 9H), 1.98 (t, $^3J = 7.7$ Hz, 2H), 2.70 (t, $^3J = 7.7$ Hz, 2H), 7.27–7.35 (m, 5H), 7.14 and 7.52 (AA′BB′, $^3J = 8.3$ Hz, 4H), 7.40–7.46 (m, 2H), 7.54–7.60 (m, 2H); MS (EI, 70 eV): *m/z* (%) = 330 (43, $M^{\bullet+}$), 315 (56), 192 (16), 180 (12), 179 (22), 178 (15), 167 (65), 165 (31), 152 (17), 142 (11), 133 (14), 132 (11), 130 (14), 129 (11), 116 (28), 92 (22), 91 (21), 57 (40). A reduction/elimination product was detected by ^{1}H NMR at $\delta = 1.31$ (s), 3.58 (d) and 6.34 (t) and by MS at *m/z* 327, 312 and 270. D content (MS): 85% (74% d_2, 23% d_1, 3% d_0).

*A.3.3. 1,1-[D_2]-1-(4-Biphenylyl)-3(4-t-butylphenyl)-propane (**5b**)*

From dihydrochalcone **B′5** (342 mg, 1.00 mmol) by reduction with $LiAlD_4/AlCl_3$; colorless liquid, bp 180 °C (0.01 mbar, kugelrohr). ^{1}H NMR ($CDCl_3$): $\delta = 1.31$ (s, 9H), 1.98 (t, $^3J = 7.7$ Hz, 2H), 2.66 (t, $^3J = 7.8$ Hz, 2H), 7.14 and 7.52 (AA′BB′, $^3J = 8.1$ Hz, 4H), 7.27–7.35 (m, 3H), 7.26 and 7.59 (AA′BB′, $^3J = 8.4$ Hz, 4H), 7.40–7.45 (m, 2H); MS (EI, 70 eV): *m/z* (%) = 330 (65, $M^{\bullet+}$), 315 (100), 195 (5), 183 (15), 169 (77), 157 (13), 147 (10), 131 (29), 117 (24), 105 (10), 93 (27), 91 (20), 57 (46). A reduction/elimination product was detected in very low amounts by MS (*m/z* 327, 312 and 270). D content (MS): 99% (97% d_2, 3% d_1).

*A.3.4. 1-(4-t-Butylphenyl)-3-(2-naphthyl)propane (**6**)*

From dihydrochalcone **B′6** (316 mg, 1.0 mmol) by Wolff–Kishner reduction; yield 60%, colorless liquid, bp 150 °C (0.01 mbar, kugelrohr). ^{1}H NMR ($CDCl_3$): $\delta = 1.31$ (s, 9H), 2.05 (quint, $^3J = 7.7$ Hz, 2H), 2.66 (t, $^3J = 7.7$ Hz, 2H), 2.83 (t, $^3J = 7.7$ Hz, 2H), 7.14 and 7.31 (AA′BB′, $^3J = 8.2$ Hz, 4H), 7.30–7.36 (m, 2H), 7.39–7.48 (m, 2H), 7.63 (br s, 1H), 7.76–7.82 (m, 2H); MS (EI, 70 eV): *m/z* (%) = 302 (32, $M^{\bullet+}$), 287 (21), 155 (15), 142 (100), 131 (23), 117 (20), 115 (25), 105 (8), 91 (18), 77 (6), 57 (16); IR (film), $\tilde{\nu}$ (cm^{-1}): 3057, 3026, 2966, 2863, 1508, 1461, 1363, 1269, 815, 745. Accurate mass (EI) $C_{23}H_{26}$: Calcd. 302.2035; found 302.2033.

*A.3.5. 1,1-[D_2]-1-(4-t-Butylphenyl)-3-(2-naphthyl)-propane (**6a**)*

From dihydrochalcone **B6** (316 mg, 1.00 mmol) by reduction with $LiAlD_4/AlCl_3$; colorless liquid, bp 150 °C (0.01 mbar, kugelrohr). ^{1}H NMR ($CDCl_3$): $\delta = 1.31$ (s, 9H), 2.03 (t, $^3J = 7.6$ Hz, 2H), 2.83 (t, $^3J = 7.7$ Hz, 2H), 7.14 and 7.31 (AA′BB′, $^3J = 8.4$ Hz, 4H), 7.30–7.36 (m, 2H), 7.39–7.48 (m, 2H), 7.63 (br s, 1H), 7.76–7.82 (m, 2H); MS (EI, 70 eV): *m/z* (%) = 304 (33, $M^{\bullet+}$), 289 (25), 143 (100); D content (MS): 96% (94% d_2, 5% d_1, 1% d_0).

*A.3.6. 3,3-[D_2]-1-(4-t-Butylphenyl)-3-(2-naphthyl)-propane (**6b**)*

From dihydrochalcone **B′6** (316 mg, 1.0 mmol) by reduction with $LiAlD_4/AlCl_3$; colorless liquid, bp 165 °C (0.01 mbar, kugelrohr). ^{1}H NMR (CDCl$_3$): $\delta = 1.31$ (s, 9H), 2.03 (t, $^3J = 7.7$ Hz, 2H), 2.66 (t, $^3J = 7.7$ Hz, 2H), 7.13 and 7.31 (AA′BB′, $^3J = 8.3$ Hz, 4H), 7.30–7.37 (m, 2H), 7.40–7.48 (m, 2H), 7.62 (br s, 1H), 7.74–7.81 (m, 2H); MS (EI, 70 eV): *m/z* (%) = 304 (35, $M^{\bullet+}$), 289 (21), 157 (13), 144 (100), 143 (60), 131 (22), 117 (24), 91 (18), 57 (29). D content (MS): 87% (77% d$_2$, 19% d$_1$, 4% d$_0$). Some reduction/elimination product was detected by ^{1}H NMR at $\delta = 1.32$ (s), 3.58 (d), 6.49 (t) and by MS at *m/z* 301, 286, 244.

*A.3.7. 1-(4-t-Butylphenyl)-3-(4-methoxyphenyl)propane (**7**)*

From dihydrochalcone **B7** (500 mg, 1.69 mmol) by hydrogenolysis; colorless liquid, bp 140 °C (0.02 mbar, kugelrohr). ^{1}H NMR (CDCl$_3$): $\delta = 1.31$ (s, 9H), 1.92 (quint, $^3J = 7.7$ Hz, 2H), 2.60 (t, $^3J = 7.7$ Hz, 2H), 2.61 (t, $^3J = 7.8$ Hz, 2H), 3.78 (s, 3H), 6.82 and 7.10 (AA′BB′, $^3J = 8.6$ Hz, 4H), 7.12 and 7.30 (AA′BB′, $^3J = 8.3$ Hz, 4H); MS (EI, 70 eV): *m/z* (%) 282 (47, $M^{\bullet+}$), 267 (46), 131 (41), 121 (100), 91 (42), 77 (23), 57 (25); IR (film), $\tilde{\nu}$ (cm^{-1}): 3028, 2966, 2863, 1513, 1245, 1038, 830. Accurate mass (EI) C$_{20}$H$_{26}$O: Calcd. 282.1984; found 282.1979.

*A.3.8. [1,1-D$_2$]-1-(4-t-Butylphenyl)-3-(4-methoxyphenyl)-propane (**7a**)*

From dihydrochalcone **B7** (300 mg, 1.01 mmol) by reduction with LiAlD$_4$/AlCl$_3$; colorless liquid, bp 150 °C (0.02 mbar, kugelrohr). ^{1}H NMR (CDCl$_3$): $\delta = 1.31$ (s, 9H), 1.90 (t, $^3J = 7.7$ Hz, 2H), 2.60 (t, $^3J = 7.7$ Hz, 2H), 3.79 (s, 3H), 6.83 and 7.11 (AA′BB′, $^3J = 8.7$ Hz, 4H), 7.12 and 7.30 (AA′BB′, $^3J = 8.5$ Hz, 4H); MS (EI, 70 eV): *m/z* (%) 284 (84, $M^{\bullet+}$), 269 (60), 133 (19), 121 (100), 94 (31), 93 (15), 91 (17), 57 (38); D content (MS): 92% (86% d$_2$, 12% d$_1$, 2% d$_0$).

*A.3.9. [3,3-D$_2$]-1-(4-t-Butylphenyl)-3-(4-methoxyphenyl)-propane (**7b**)*

From dihydrochalcone **B′7** (400 mg, 1.34 mmol) by reduction with LiAlD$_4$/AlCl$_3$; colorless liquid, bp 155 °C (0.01 mbar, kugelrohr). ^{1}H NMR (CDCl$_3$): $\delta = 1.31$ (s, 9H), 1.90 (t, $^3J = 7.8$ Hz, 2H), 2.61 (t, $^3J = 7.8$ Hz, 2H), 3.79 (s, 3H), 6.83 and 7.11 (AA′BB′, $^3J = 8.7$ Hz, 4H), 7.12 and 7.30 (AA′BB′, $^3J = 8.3$ Hz, 4H); MS (EI, 70 eV): *m/z* (%) = 284 (68, $M^{\bullet+}$), 269 (63), 131 (20), 123 (100), 93 (30), 91 (15), 57 (28); D content (MS): 97% (96% d$_2$, 3% d$_1$, 1% d$_0$).

*A.3.10. 1-(4-t-Butylphenyl)-3-[4-(trideuteromethoxy)-phenyl]propane (**7c**)*

From the phenol derivative **E14** (see below) by use of sodium hydride (1.5 equiv.) in THF and trideuteromethyl iodide (1.5 equiv.); yield 83%, colorless liquid, bp 155 °C (0.02 mbar, kugelrohr). ^{1}H NMR (CDCl$_3$): $\delta = 1.29$ (s, 9H), 1.90 (m, 2H), 2.57–2.60 (m, 4H), 6.81 (d, $^3J = 8.6$ Hz, 2H), 7.08–7.11 (m, 4H), 7.28 (d, $^3J = 8.2$ Hz, 2H); MS (EI, 70 eV): *m/z* (%) 285 (84, $M^{\bullet+}$), 270 (76), 124 (100). D content (MS): ≥99%. An impurity (ca. 5%) which is assumed to be a corresponding 1,3-diarylpropene [^{1}H NMR, MS: *m/z* (%) 282 ($M^{\bullet+}$)] was also detected.

*A.3.11. 1-(4-t-Butylphenyl)-3-(3-methoxyphenyl)-propane (**8**)*

From dihydrochalcone **B′8** (320 mg, 1.08 mmol) by hydrogenolysis; colorless liquid, bp 120 °C (0.01 mbar, kugelrohr). ^{1}H NMR (CDCl$_3$): $\delta = 1.31$ (s, 9H), 1.95 (quint, $^3J = 7.8$ Hz, 2H), 2.62 (t, $^3J = 7.7$ Hz, 2H), 2.64 (t, $^3J = 7.7$ Hz, 2H), 3.80 (s, 3H), 6.72–6.80 (m, 3H), 7.13 and 7.31 (AA′BB′, $^3J = 8.3$ Hz, 4H), 7.17–7.23 (m, 1H); MS (EI, 70 eV): *m/z* (%) = 282 (32, $M^{\bullet+}$), 267 (27), 131 (24), 122 (100), 91 (30), 77 (15), 57 (16); IR (film), $\tilde{\nu}$ (cm^{-1}): 3029, 2965, 2864, 1601, 1584, 1487, 1464, 1265, 1152, 1055, 830, 780, 695. Accurate mass (EI) C$_{20}$H$_{26}$O: Calcd. 282.1984; found 282.1983.

*A.3.12. [3,3-D$_2$]-1-(4-t-Butylphenyl)-3-(3-methoxyphenyl)-propane (**8b**)*

From dihydrochalcone **B′8** (600 mg, 2.03 mmol) by reduction with LiAlD$_4$/AlCl$_3$; colorless liquid, bp 150 °C (0.04 mbar, kugelrohr). ^{1}H NMR (CDCl$_3$): $\delta = 1.31$ (s, 9H), 1.94 (t, $^3J = 7.7$ Hz, 2H), 2.62 (t, $^3J = 7.8$ Hz, 2H), 3.79 (s, 3H), 6.71–6.80 (m, 3H), 7.12 and 7.30 (AA′BB′, $^3J = 8.3$ Hz, 4H), 7.17–7.23 (m, 1H); MS (EI, 70 eV): *m/z* (%) = 284 (37, $M^{\bullet+}$), 269 (23), 131 (19), 124 (100), 91 (25), 77 (10), 57 (20). Impurities by the reduction/elimination product (ca. 25%) were detected by ^{1}H NMR [$\delta = 1.31$ (s), 3.52 (d), 6.35 (t)] and MS (*m/z* 281, 266, 224). D contents (MS): 89% (81% d$_2$, 17% d$_1$, 2% d$_0$).

*A.3.13. 1-(4-t-Butylphenyl)-3-(2-methoxyphenyl)-propane (**9**)*

From dihydrochalcone **B′9** (500 mg, 1.69 mmol) by hydrogenolysis; colorless liquid, bp 170 °C (0.05 mbar, kugelrohr). ^{1}H NMR (CDCl$_3$): $\delta = 1.30$ (s, 9H), 1.92 (quint, $^3J = 7.8$ Hz, 2H), 2.64 (t, $^3J = 7.8$ Hz, 2H), 2.67 (t, $^3J = 7.8$ Hz, 2H), 3.79 (s, 3H), 6.81–6.90 (m, 2H), 7.14 and 7.30 (AA′BB′, $^3J = 8.3$ Hz, 4H), 7.12–7.20 (m, 2H); MS (EI, 70 eV): *m/z* (%) 282 (77, $M^{\bullet+}$), 267 (100), 131 (46), 121 (70), 91 (89), 77 (29), 57 (43); IR (film), $\tilde{\nu}$ (cm^{-1}): 3026, 2965, 2866, 1493, 1463, 1242, 1035, 831, 751. Accurate mass (EI) C$_{20}$H$_{26}$O: Calcd. 282.1984; found 282.1983.

*A.3.14. [3,3-D$_2$]-1-(4-t-Butylphenyl)-3-(2-methoxyphenyl)-propane (**9b**)*

From dihydrochalcone **B′9** (400 mg, 1.34 mmol) by reduction with LiAlD$_4$/AlCl$_3$; colorless liquid, bp 180 °C (0.06 mbar, kugelrohr). ^{1}H NMR (CDCl$_3$): $\delta = 1.31$ (s, 9H), 1.90 (t, $^3J = 7.9$ Hz, 2H), 2.64 (t, $^3J = 7.9$ Hz, 2H), 3.81 (s, 3H), 6.82–6.91 (m, 2H), 7.14 and 7.30 (AA′BB′, $^3J = 8.4$ Hz, 4H), 7.12–7.20 (m, 2H); MS (EI, 70 eV): *m/z* (%) 284 (72, $M^{\bullet+}$), 269 (100), 131 (34), 123 (68), 93 (56), 91 (28), 77 (11), 57 (42). D contents (MS): 91% (84% d$_2$, 13% d$_1$, 3% d$_0$). Some reduction/elimination product was observed by MS (*m/z* 281, 266, 224).

*A.3.15. 1-(4-t-Butylphenyl)-3-(4-fluorophenyl)propane (**10**)*

From dihydrochalcone **B10** (800 mg, 2.8 mmol) by hydrogenolysis at 5 bar; colorless liquid, bp 105 °C (0.01 mbar, kugelrohr). ^{1}H NMR (CDCl$_3$): $\delta = 1.31$ (s, 9H), 1.92 (quint, $^3J = 7.7$ Hz, 2H), 2.61 (t, $^3J = 7.6$ Hz, 2H), 2.63 (t, $^3J = 7.6$ Hz, 2H), 6.93–6.99 (m, 2H), 7.10–7.15 (m, 2H), 7.11 and 7.31 (AA′BB′, $^3J = 8.3$ Hz, 4H); MS (EI, 70 eV): *m/z* (%) = 270 (36, $M^{\bullet+}$), 255 (100), 131 (14), 117 (14), 109 (40), 91 (14), 57 (11); IR (film), $\tilde{\nu}$ (cm^{-1}): 3029, 2967, 2866, 1600, 1508, 1221, 821. Accurate mass (EI) $C_{19}H_{23}F$: Calcd. 270.1784; found 270.1781.

*A.3.16. [1,1-D$_2$]-1-(4-t-Butylphenyl)-3-(4-fluorophenyl)-propane (**10a**)*

From dihydrochalcone **B10** (800 mg, 2.8 mmol) by reduction with $LiAlD_4/AlCl_3$; colorless liquid, bp 105 °C (0.01 mbar, kugelrohr). ^{1}H NMR ($CDCl_3$): $\delta = 1.31$ (s, 9H), 1.91 (t, $^3J = 7.6$ Hz, 2H), 2.62 (t, $^3J = 7.6$ Hz, 2H), 6.93–6.99 (m, 2H), 7.09–7.15 (m, 2H), 7.11 and 7.31 (AA′BB′, $^3J = 8.3$ Hz, 4H); MS (EI, 70 eV): *m/z* (%) 272 (36, $M^{\bullet+}$), 257 (100), 133 (14), 119 (12), 109 (38), 93 (9), 57 (14); D contents (MS): 83% (69% d_2, 28% d_1, 3% d_0).

*A.3.17. [1-D]-3-(4-t-Butylphenyl)-1-(4-fluorophenyl)-propan-1-ol (**C′10**)*

From dihydrochalcone **B′10** (1.60 g, 5.6 mmol) by reduction with $LiAlD_4$ [method (iii), see above]; yield 1.47 g (92%), colorless oil, bp 180 °C (0.02 mbar, kugelrohr). ^{1}H NMR ($CDCl_3$): $\delta = 1.29$ (s, 9H), 1.85–2.07 (m, 2H), 2.49–2.68 (m, 2H), 2.70 (br s, 1H), 6.91–6.97 (m, 2H), 7.07 and 7.28 (AA′BB′, $^3J = 8.3$ Hz, 4H), 7.18–7.23 (m, 2H); MS (EI, 70 eV): *m/z* (%) 287 (27, $M^{\bullet+}$), 272 (27), 269 (50), 254 (73), 212 (67), 161 (12), 147 (29), 131 (46), 126 (100), 117 (35), 110 (24), 98 (53), 93 (46), 91 (38), 78 (25), 77 (22), 57 (94).

*A.3.18. [1-D]-3-(4-t-Butylphenyl)-1-(4-fluorophenyl)-propene (**D′10**)*

By heating alcohol **C′10** (1.20 g, 4.30 mmol) in DMSO (4.0 ml) [method (iii), see Section 2.2]; yield 250 mg (31%), colorless liquid, bp 120 °C (0.01 mbar, kugelrohr). ^{1}H NMR ($CDCl_3$): $\delta = 1.32$ (s, 9H), 3.51 (d, $^3J = 7.0$ Hz, 2H), 6.24–6.29 (m, 1H), 6.94–7.00 (m, 2H), 7.18 and 7.34 (AA′BB′, $^3J = 8.3$ Hz, 4H), 7.28–7.35 (m, 2H); MS (EI, 70 eV): *m/z* (%) 269 (30, $M^{\bullet+}$), 254 (100), 212 (60), 147 (6), 136 (24), 116 (16), 110 (21), 91 (9), 57 (14).

*A.3.19. [2,3,3-D$_3$]-1-(4-t-Butylphenyl)-3-(4-fluorophenyl)-propane (**10b**)*

By addition of deuterium to diarylpropene **D′10** (110 mg, 0.41 mmol) by homogeneous catalysis [method (iii), see Section 2.2]; bp 110 °C (0.01 mbar, kugelrohr). ^{1}H NMR ($CDCl_3$): $\delta = 1.31$ (s, 9H), 1.89 (br t, $^3J = 7.7$ Hz, 1H), 2.60 (d, $^3J = 7.7$ Hz, 2H), 6.93–6.99 (m, 2H), 7.10–7.15 (m, 2H), 7.11 and 7.31 (AA′BB′, $^3J = 8.3$ Hz, 4H); MS (EI, 70 eV): *m/z* (%) 273 (38, $M^{\bullet+}$), 258 (100), 147 (9), 132 (11), 117 (11), 111 (28), 93 (8), 92 (8), 91 (9), 57 (12). D contents (MS): 97% (93% d_3, 5% d_2, 1% d_1, 1% d_0).

*A.3.20. 1-(4-t-Butylphenyl)-3-(3-fluorophenyl)propane (**11**)*

From dihydrochalcone **B11** (150 mg, 0.53 mmol) by hydrogenolysis; colorless liquid, bp 115 °C (0.02 mbar, kugelrohr). ^{1}H NMR ($CDCl_3$): $\delta = 1.31$ (s, 9H), 1.94 (quint, $^3J = 7.7$ Hz, 2H), 2.62 (t, $^3J = 7.8$ Hz, 2H), 2.65 (t, $^3J = 7.8$ Hz, 2H), 6.84–6.97 (m, 3H), 7.12 and 7.31 (AA′BB′, $^3J = 8.3$ Hz, 4H), 7.19–7.25 (m, 1H); MS (EI, 70 eV): *m/z* (%) 270 (38, $M^{\bullet+}$), 255 (100), 131 (16), 117 (23), 109 (47), 91 (24), 57 (27); IR (film), $\tilde{\nu}$ (cm^{-1}): 3029, 2967, 2867, 1615, 1589, 1486, 1450, 1254, 1138, 831, 782, 691. Accurate mass (EI) $C_{19}H_{23}F$: Calcd. 270.1784; found 270.1782.

*A.3.21. [1,1-D$_2$]-1-(4-t-Butylphenyl)-3-(3-fluorophenyl)-propane (**11a**)*

From dihydrochalcone **B11** (150 mg, 0.53 mmol) by reduction with $LiAlD_4/AlCl_3$; colorless liquid, bp 110 °C (0.01 mbar, kugelrohr). ^{1}H NMR ($CDCl_3$): $\delta = 1.31$ (s, 9H), 1.93 (t, $^3J = 7.7$ Hz, 2H), 2.65 (t, $^3J = 7.7$ Hz, 2H), 6.87–6.97 (m, 3H), 7.12 and 7.31 (AA′BB′, $^3J = 8.3$ Hz, 4H), 7.21–7.26 (m, 1H); MS (EI, 70 eV): *m/z* (%) 272 (39, $M^{\bullet+}$), 257 (100), 133 (18), 119 (19), 109 (50), 91 (15), 57 (32). D contents (MS): 79% (65% d_2, 28% d_1, 7% d_0). A reduction/elimination product was detected as an impurity (ca. 15%) by ^{1}H NMR [$\delta = 1.31$ (s) and 3.53 (d)] and MS (*m/z* 269, 254, 212).

*A.3.22. [1-D]-3-(4-t-Butylphenyl)-1-(3-fluorophenyl)-propane-1-ol (**C′11**)*

From dihydrochalcone **B′11** (4.11 g, 14.5 mmol) by reduction with $LiAlD_4$; yield 2.38 g (57%), colorless oil, bp 135 °C (0.01 mbar, kugelrohr). ^{1}H NMR ($CDCl_3$): $\delta = 1.30$ (s, 9H), 1.94–2.13 (m, 3H), 2.57–2.77 (m, 2H), 6.91–6.98 (m, 1H), 7.04–7.13 (m, 2H), 7.12 and 7.30 (AA′BB′, $^3J = 8.3$ Hz, 4H), 7.23–7.32 (m, 1H); MS (EI, 70 eV): *m/z* (%) 287 (28, $M^{\bullet+}$), 272 (39), 269 (46), 254 (69), 212 (52), 161 (14), 147 (32), 131 (47), 126 (35), 117 (33), 98 (41), 93 (34), 92 (25), 91 (35), 77 (20), 57 (100). The ^{1}H NMR signal at $\delta = 4.68$ (t) indicated the presence of the [D$_0$]-alcohol, D contents (^{1}H NMR) 75%.

*A.3.23. [1-D]-3-(4-t-Butylphenyl)-1-(3-fluorophenyl)-propene (**D′11**)*

By heating of alcohol **C′11** (2.38 g, 8.3 mmol) in DMSO (11 ml); yield 0.17 g (8%), colorless liquid, bp 125 °C (0.01 mbar, kugelrohr). ^{1}H NMR ($CDCl_3$): $\delta = 1.32$ (s, 9H), 3.52 (d, $^3J = 6.9$ Hz, 2H), 6.34–6.39 (m, 1H), 6.85–6.92 (m, 1H), 7.03–7.13 (m, 2H), 7.17–7.30 (m, 1H), 7.17 and 7.34 (AA′BB′, $^3J = 8.4$ Hz, 4H); MS (EI, 70 eV): *m/z* (%) 269 (46), 254 (100), 212 (53), 136 (33), 117 (24), 116 (29), 115 (27), 110 (31), 109 (34), 91 (29), 77 (119, 57 (36).

*A.3.24. [2,2,3-D$_3$]-1-(4-t-Butylphenyl)-3-(3-fluorophenyl)-propane (**11b**)*

By addition of deuterium to diarylpropene **D′11** (110 mg, 0.41 mmol) by homogeneous catalysis; colorless liquid, bp 110 °C (0.01 mbar, kugelrohr). ^{1}H NMR ($CDCl_3$): $\delta = 1.31$ (s, 9H), 1.91 (br t, 1H), 2.61 (d, $^3J = 7.8$ Hz, 2H), 6.85–6.97 (m, 3H), 7.12 and 7.31 (AA′BB′, $^3J = 8.2$ Hz, 4H), 7.19–7.25 (m, 1H); MS (EI, 70 eV): *m/z* (%) 273 (26, $M^{\bullet+}$), 258 (100), 132 (11), 131 (10), 117 (16), 111 (23), 110 (19), 91 (14), 57 (13). D contents (MS): 92% (77% d_3, 22% d_2, 1% d_1).

*A.3.25. 1-(4-t-Butylphenyl)-3-(2-fluorophenyl)propane (**12**)*

From dihydrochalcone **B12** (800 mg, 2.8 mmol) by hydrogenolysis; colorless liquid, bp 110 °C (0.01 mbar, kugelrohr). ^{1}H NMR ($CDCl_3$): $\delta = 1.31$ (s, 9H), 1.94 (quint, $^3J = 7.8$ Hz, 2H), 2.64 (t, $^3J = 7.9$ Hz, 2H), 2.70 (t, $^3J = 7.9$ Hz, 2H), 6.97–7.07 (m, 2H), 7.12–7.21 (m, 2H), 7.13 and 7.31 (AA′BB′, $^3J = 8.3$ Hz, 4H); MS (EI, 70 eV): *m/z* (%) 270 (37, $M^{\bullet+}$), 255 (100), 147 (11), 131 (21), 117 (22), 109 (47), 91 (20), 57 (14); IR (film), $\tilde{\nu}$ (cm^{-1}): 3030, 2966, 2868, 1585, 1491, 1228, 830, 754. Accurate mass (EI) $C_{19}H_{23}F$: Calcd. 270.1784; found 270.1780.

*A.3.26. [1,1-D$_2$]-1-(4-t-Butylphenyl)-3-(2-fluorophenyl)-propane (**12a**)*

From dihydrochalcone **B12** (800 mg, 2.8 mmol) by reduction with $LiAlD_4/AlCl_3$; colorless liquid, bp 105 °C (0.01 mbar, kugelrohr). ^{1}H NMR ($CDCl_3$): $\delta = 1.31$ (s, 9H), 1.93 (t, $^3J = 7.4$ Hz, 2H), 2.69 (t, $^3J = 7.7$ Hz, 2H), 7.00–7.08 (m, 2H), 7.12–7.21 (m, 2H), 7.13 and 7.31 (AA′BB′, $^3J = 8.3$ Hz, 4H); MS (EI, 70 eV): *m/z* (%) 272 (32, $M^{\bullet+}$), 257 (100), 148 (8), 133 (17), 119 (14), 109 (60), 92 (12), 91 (11), 57 (14). D contents (MS): 74% (54% d_2, 40% d_1, 6% d_0).

*A.3.27. [1-D]-3-(4-t-Butylphenyl)-1-(2-fluorophenyl)-propane-1-ol (**C′12**)*

From dihydrochalcone **B′12** (4.03 g, 14.2 mmol) by reduction with $LiAlD_4$; yield 2.71 g (67%), colorless oil, bp 130 °C (0.01 mbar, kugelrohr). ^{1}H NMR ($CDCl_3$): $\delta = 1.30$ (s, 9H), 1.94 (br s, 1H), 2.05–2.12 (m, 2H), 2.60–2.80 (m, 2H), 6.98–7.04 (m, 1H), 7.11–7.16 (m, 1H), 7.13 and 7.30 (AA′BB′, $^3J = 8.3$ Hz, 4H), 7.20–7.28 (m, 1H), 7.43–7.49 (m, 1H); MS (EI, 70 eV): *m/z* (%) 287 (5, $M^{\bullet+}$), 272 (31), 269 (44), 254 (100), 212 (63), 161 (13), 147 (25), 131 (41), 126 (70), 117 (32), 110 (26), 105 (22), 98 (25), 93 (39), 92 (31), 91 (36), 77 (25), 57 (78). The presence of the [D$_0$]-alcohol was indicated by the ^{1}H NMR signal at $\delta = 5.03$ (t); D contents (NMR): 75%.

*A.3.28. [1-D]-3-(4-t-Butylphenyl)-1-(2-fluorophenyl)-propene (**D′12**)*

From alcohol **C′12** (2.46 g, 8.6 mmol) by heating in DMSO (10 ml); yield 0.28 g, 13%), colorless liquid, bp 120 °C (0.01 mbar, kugelrohr). ^{1}H NMR ($CDCl_3$): $\delta = 1.32$ (s, 9H), 3.55 (d, $^3J = 7.1$ Hz, 2H), 6.43 (t, $^3J = 7.1$ Hz, 1H), 6.90–7.08 (m, 2H), 7.13–7.20 (m, 1H), 7.19 and 7.34 (AA′BB′, $^3J = 8.4$ Hz, 4H), 7.41–7.44 (m, 1H); MS (EI, 70 eV): *m/z* (%) 269 (21, $M^{\bullet+}$), 254 (100), 212 (47), 136 (21), 116 (13), 110 (18), 109 (19), 91 (10), 57 (15). D contents (MS): 76%.

*A.3.29. [2,3,3-D$_3$]-1-(4-t-Butylphenyl)-3-(2-fluorophenyl)-propane (**12b**)*

By addition of deuterium to diarylpropene **D′12** (200 mg, 0.75 mmol) by homogeneous catalysis; bp 110 °C (0.01 mbar, kugelrohr). ^{1}H NMR ($CDCl_3$): $\delta = 1.31$ (s, 9H), 1.91 (br t, 1H), 2.63 (d, $^3J = 7.9$ Hz, 2H), 6.97–7.07 (m, 2H), 7.11–7.21 (m, 2H), 7.13 and 7.30 (AA′BB′, $^3J = 8.2$ Hz, 4H); MS (EI, 70 eV): *m/z* (%) 273 (23, $M^{\bullet+}$), 258 (100), 132 (11), 131 (9), 117 (13), 111 (21), 110 (20), 91 (11), 57 (11). D contents (MS): 91% (73% d_3, 26% d_2, 1% d_1).

*A.3.30. 1-(4-t-Butylphenyl)-3-(4-trifluoromethylphenyl)-propane (**13**)*

From dihydrochalcone **B13** (420 mg, 1.26 mmol) by hydrogenolysis; colorless liquid, bp 95 °C (0.01 mbar, kugelrohr). ^{1}H NMR ($CDCl_3$): $\delta = 1.31$ (s, 9H), 1.96 (quint, $^3J = 7.8$ Hz, 2H), 2.62 (t, $^3J = 7.7$ Hz, 2H), 2.70 (t, $^3J = 7.7$ Hz, 2H), 7.11 and 7.31 (AA′BB′, $^3J = 8.3$ Hz, 4H), 7.28 and 7.52 (AA′BB′, $^3J = 8.1$ Hz, 4H); MS (EI, 70 eV): *m/z* (%) 320 (23, $M^{\bullet+}$), 305 (100), 159 (29), 117 (14), 91 (15), 57 (11); IR (film), $\tilde{\nu}$ (cm^{-1}): 2968, 2868, 1618, 1326, 1163, 1123, 1067, 1018. Accurate mass (EI) $C_{20}H_{23}F_3$: Calcd. 320.1752; found 320.1746.

*A.3.31. [1,1-D$_2$]-1-(4-t-Butylphenyl)-3-(4-trifluoromethylphenyl)propane (**13a**)*

From dihydrochalcone **B13** (400 mg, 1.2 mmol) by reduction with $LiAlD_4/AlCl_3$; colorless liquid, bp 150 °C (0.03 mbar, kugelrohr). ^{1}H NMR ($CDCl_3$): $\delta = 1.31$ (s, 9H), 1.95 (t, $^3J = 7.8$ Hz, 2H), 2.70 (t, $^3J = 7.7$ Hz, 2H), 7.12 and 7.31 (AA′BB′, $^3J = 8.2$ Hz, 4H), 7.29 and 7.53 (AA′BB′, $^3J = 8.0$ Hz, 4H). MS (EI, 70 eV): *m/z* (%) 322 (31, $M^{\bullet+}$), 307 (100), 159 (33), 133 (17), 119 (19), 92 (12), 91 (11), 57 (21). D contents (MS): 89% (80% d_2, 18% d_1, 2% d_0). A reduction/elimination product was detected as an impurity (ca. 15%) by ^{1}H NMR [$\delta = 1.31$ (s), 3.59 (d), 6.28 (t)] and MS (*m/z* 319, 304, 262).

*A.3.32. 1-(4-t-Butylphenyl)-3-(4-hydroxyphenyl)-propane (**E14**)*

From dihydrochalcone **B′14** by chloroalane reduction in diethyl ether; colorless oil, bp 160–165 °C (0.05 mbar, kugelrohr), yield 80%. ^{1}H NMR ($CDCl_3$): $\delta = 1.29$ (s, 9H), 1.89 (m, 2H), 2.55–2.60 (m, 4H), 6.73 (d, $^3J = 8.4$ Hz, 2H), 7.04 (d, $^3J = 8.4$ Hz, 2H), 7.10 (d, $^3J = 8.3$ Hz, 2H), 7.28 (d, $^3J = 8.3$ Hz, 2H); MS (EI, 70 eV): *m/z* (%) 268 (57, $M^{\bullet+}$), 253 (100), 107 (75). Accurate mass (EI) $C_{19}H_{24}O$: Calcd. 268.1827; found 268.1824.

References

[1] P. Ausloos, S.G. Lias, J. Am. Chem. Soc. 92 (1970) 5037.

[2] (a) T.H. Morton, in: P.B. Armentrout (Ed.), The Encyclopedia of Mass Spectrometry, 1, Elsevier, Amsterdam, 2003, p. 467;
(b) T.H. Morton, in: N.M.M. Nibbering (Ed.), Encyclopedia of Mass Spectrometry, 4, Elsevier, Amsterdam, 2005, p. 165.

[3] Reviews on I/N complexes;
(a) P. Longevialle, Mass Spectrom. Rev. 11 (1992) 157;
(b) T.H. Morton, Tetrahedron 38 (1982) 3195;
(c) T.H. Morton, Org. Mass Spectrom. 27 (1992) 353;
(d) D.J. McAdoo, Mass Spectrom. Rev. 7 (1988) 363;
(e) R.D. Bowen, Acc. Chem. Res. 24 (1991) 264;
(f) D.J. McAdoo, T.H. Morton, Acc. Chem. Res. 26 (1993) 295;
(g) N. Heinrich, H. Schwarz, in: J.P. Meier (Ed.), Ion and Cluster Ion Spectroscopy and Structure, Elsevier, Amsterdam, 1989, p. 329.

[4] (a) H.E. Audier, C. Monteiro, P. Mourgues, D. Berthomieu, Org. Mass Spectrom. 25 (1990) 245;
(b) J.P. Denhez, H.E. Audier, D. Berthomieu, Rap. Commun. Mass Spectrom. 9 (1995) 1210;

(c) D. Berthomieu, V. Brenner, G. Ohanessian, J.P. Denhez, P. Millié, H.E. Audier, J. Phys. Chem. 99 (1995) 712.
[5] D. Kuck, C. Matthias, J. Am. Chem. Soc. 114 (1992) 1901.
[6] H.E. Audier, F. Dahhani, A. Milliet, D. Kuck, J. Chem. Soc., Chem. Commun. (1997) 429.
[7] (a) M.E. Crestoni, S. Fornarini, M. Lentini, M. Speranza, J. Chem. Soc., Chem. Commun. (1995) 121;
(b) M.E. Crestoni, S. Fornarini, M. Lentini, M. Speranza, J. Phys. Chem. 100 (1996) 8285.
[8] M. Mormann, D. Kuck, J. Phys. Org. Chem. 16 (2003) 746.
[9] C. Matthias, K. Weniger, D. Kuck, Eur. Mass Spectrom. 1 (1995) 445.
[10] C. Matthias, D. Kuck, Org. Mass Spectrom. 28 (1993) 1073.
[11] C. Matthias, S. Anlauf, K. Weniger, D. Kuck, Int. J. Mass Spectrom. 199 (2000) 155.
[12] C. Matthias, D. Kuck, Int. J. Mass Spectrom. 217 (2002) 131.
[13] C. Matthias, B. Bredenkötter, D. Kuck, Int. J. Mass Spectrom. 228 (2003) 321.
[14] D. Kuck, A. Cartoni, C. Matthias, M. Mormann, Proceedings of the Sixth European Symopsium on FT-ICR Mass Spectrometry, Rolduc/Kerkrade, NL, 16–19 October 2001; Book of Abstracts, p. 40.
[15] (a) A.G. Harrison, P.H. Lin, H.W. Leung, Adv. Mass Spectrom. 7B (1978) 1394;
(b) J.A. Herman, A.G. Harrison, Org. Mass Spectrom. 16 (1981) 423;
(c) A.G. Harrison, Chemical Ionization Mass Spectrometry, 2nd ed., CRC Press, Boca Raton, 1992.
[16] (a) D. Berthomieu, H.E. Audier, C. Monteiro, J.P. Denhez, Rap. Commun. Mass Spectrom. 5 (1991) 415;
(b) J.P. Denhez, H.E. Audier, D. Berthomieu, Org. Mass Spectrom. 28 (1993) 704.
[17] D.K. Sen Sharma, S. Ikuta, P. Kebarle, Can. J. Chem. 60 (1982) 2325.
[18] C. Wesdemiotis, H. Schwarz, C.C. Van de Sande, F. Van Gaever, Z. Naturforsch. B 34 (1979) 495.
[19] M.B. Smith, J. March, Advanced Organic Chemistry: Reactions, Mechanisms and Structure, Wiley, New York, 2001, pp. 730–734.
[20] (a) L. Lin, C.D. Gutsche, Tetrahedron 42 (1986) 1633;
(b) M. Iqbal, C.D. Gutsche, Org. Synth. 68 (1990) 234;
(c) V. Böhmer, Angew. Chem. 107 (1995) 785;
V. Böhmer, Angew. Chem. Int. Ed. Engl. 34 (1995) 713.
[21] M. Meot-Ner, P. Hamlet, E.P. Hunter, F.H. Field, J. Am. Chem. Soc. 100 (1978) 5466.
[22] M.E. Crestoni, S. Fornarini, D. Kuck, J. Phys. Chem. 99 (1995) 3150.
[23] (a) M.E. Crestoni, S. Fornarini, D. Kuck, J. Phys. Chem. 99 (1995) 3144;
(b) B. Chiavarino, M.E. Crestoni, S. Fornarini, D. Kuck, Int. J. Mass Spectrom. Ion Process. 148 (1995) 215;
(c) M.E. Crestoni, J. Phys. Chem. 97 (1993) 6197;
(d) B. Chiavarino, M.E. Crestoni, S. Fornarini, D. Kuck, J. Phys. Chem. A 107 (2003) 4619.
[24] J.F. Gal, P.C. Maria, O. Mó, M. Yáñez, D. Kuck, submitted for publication.
[25] J.F. Gal, P.C. Maria, M. Decouzon, O. Mó, M. Yáñez, Int. J. Mass Spectrom. 219 (2002) 445.
[26] D. Berthomieu, V. Brenner, G. Ohanessian, J.P. Denhez, P. Millié, H.E. Audier, J. Am. Chem Soc. 115 (1993) 2505.
[27] D. Heidrich, Angew. Chem. 114 (2002) 3343;
D. Heidrich, Angew. Chem. Int. Ed. 41 (2002) 3208.
[28] A. Filippi, G. Roselli, G. Renzi, F. Grandinetti, M. Speranza, Chem. Eur. J. 9 (2003) 2072.
[29] J.C. Ma, D.A. Dougherty, Chem. Rev. 97 (1997) 1303.
[30] NIST Standard Reference Database Number 69, March 2003 Release; National Institute of Standards and Technology, Gaithersburg, MD 20899. http://webbook.nist.gov/chemistry.
[31] E.P.L. Hunter, S.G. Lias, J. Phys. Chem. Ref. Data 27 (1998) 413.
[32] G. Lias, J.E. Bartmess, J.F. Liebman, J.L. Holmes, R.D. Levin, W.G. Mallard, J. Phys. Chem. Ref. Data 17 (Suppl. 1) (1988) 1.
[33] (a) E.S.E. van Beelen, T.A. Koblenz, S. Ingemann, S. Hammerum, J. Phys. Chem. A 108 (2004) 2787;
(b) E.S.E. van Beelen, Academisch Proefschrift, Universiteit van Amsterdam, 2005.
[34] For reviews on the gas-phase ion chemistry of alkylbenzenes, including benzyl and tropylium ions, see;
(a) D. Kuck, Mass Spectrom. Rev. 9 (1990) 583;
(b) D. Kuck, Mass Spectrom. Rev. 9 (1990) 181;
(c) D. Kuck, Int. J. Mass Spectrom. 213 (2002) 101;
(d) D. Kuck, in: N.M.M. Nibbering (Ed.), The Encyclopedia of Mass Spectrometry, 4, Elsevier, Amsterdam, 2005, p. 199.
[35] M.J.S. Dewar, D. Landman, J. Am. Chem. Soc. 99 (1977) 7439.
[36] R.B. Sharma, D.K.S. Sharma, K. Hiraoka, P. Kebarle, J. Am. Chem. Soc. 107 (1985) 3747.