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The reaction of biphenyl radical anion and dianion with alkyl fluorides. From ET to S_N2 reaction pathways and synthetic applications

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ABSTRACT

The reaction of dilithium biphenyl ($Li_2C_{12}H_{10}$) with alkyl fluorides has been studied from the point of view of the distribution of products. Two main reaction pathways, the nucleophilic substitution (S_N2) and the electron transfer (ET), can compete to yield the same alkylation products in what is known as the S_N2–ET dichotomy. S_N2 seems to be the main mechanism operating with primary alkyl fluorides (*n*-RF). Alkylation proceeds in good yields, and the resulting alkylated dihydrobiphenyl anion (*n*-$RC_{12}H_{10}Li$) can be trapped with a second conventional electrophile (E^+) affording synthetically interesting dearomatized biphenyl derivatives (*n*-$RC_{12}H_{10}E$). The reaction gives a higher amount of ET products as we move to secondary (*s*-RF) and to tertiary alkyl fluorides (*t*-RF), in which case the mechanism seems to be dominated by ET. In this case, alkylation by radical coupling is still feasible, giving access to the synthesis of *t*-$RC_{12}H_{10}E$, although in lower yields. A rational interpretation of this S_N2–ET dichotomy is given on the basis of the full distribution of products observed when 5-hexenyl fluoride and 1,1-dimethyl-5-hexenyl fluoride were are used as radical probes in their reaction with $Li_2C_{12}H_{10}$ and $LiC_{12}H_{10}$.

1. Introduction

1.1. The radical anion and dianion of biphenyl

Radical anions and dianions of aromatic hydrocarbons of high reduction potential, such as naphthalene or biphenyl, should be considered among the strongest ET (electron transfer) reagents in solution.[1] They can be prepared, inter alia, by direct reaction of the aromatic hydrocarbon with an alkali metal. These anionic species have very high energy electrons, which are also highly delocalized in an extended π-cloud that spreads all over the molecule. This determines much of the reactivity displayed by these species, which is often dominated by ET to acceptors and reminiscent of the alkaline metal they originated from. Applications of these alkali metal-like solutions are well developed. Indeed, the use of naphthalene, biphenyl or alkylated derivatives (such as 4,4′-di-*tert*-butylbiphenyl) as an ET mediator in $Li_{(s)}$ reductions has been shown to be advantageous over the direct, non catalyzed $Li_{(s)}$ reduction,[2] and this has been rationalized by means of a quantitative consideration of the electron transfer kinetics involved.[3]

Lithium is the preferred alkali metal for these chemical reductions since the pair $Li_{(s)}/Li^+_{(H2O)}$ is the most negative among alkali metals, with a standard potential $E^\circ_{(Li/Li+)}=-3.04$ V, in water relative to SHE.[4] This allows in principle the highest reduction power in coordinating solvents.[5] Biphenyl (**1**, $C_{12}H_{10}$) has the highest first reduction potential E°_1 (giving rise to the radical anion), and the second higher E°_2 (which affords the dianion) among polycyclic arenes: $E^\circ_1=-2.68$ V, $E^\circ_2=-3.18$ V, in Me_2NH versus Ag/AgCl.[6] It is important noticing that these values rival with those of lithium metal itself, both in water and in THF, for which similar values are reported.[5] In spite of the imprecision inherent to the comparison of electrochemical data obtained from different sources under different experimental conditions, it is evident that there is only a narrow window for a feasible double reduction of biphenyl in solution. Indeed, the information found in the literature regarding the existence of the biphenyl dianion is ambiguous in that respect. The biphenyl dianion, **1**-Li_2 ($Li_2C_{12}H_{10}$) was suggested in early studies as a component of the $Li_{(s)}$–biphenyl solutions of stoichiometry 2:1 in THF, and was used for reductive-cleavage applications akin to $Li_{(s)}$.[7] Since **1**-Li_2 was not isolated or characterized in this work, the idea that some of the Li^+ in solution could come from side reactions prevailed. Further studies on Raman spectroscopy reported the view that the dianion of biphenyl was not a component of biphenyl–alkali metal solutions, in particular, in the case of sodium.[8] Later, descriptive work of the biphenyl dianion was reported, dealing with the ^1H NMR and ^{13}C NMR of **1**-Li_2 ($Li_2C_{12}H_{10}$) at −80 °C in THF-d_8.[9] In the solid phase there is better consensus. The UV and IR and Raman spectra of different alkali metal salts of biphenyl in sublimated layers and codeposits are described by different groups.[10] We have observed previously that, in the presence of an excess of $Li_{(s)}$, naphthalene is

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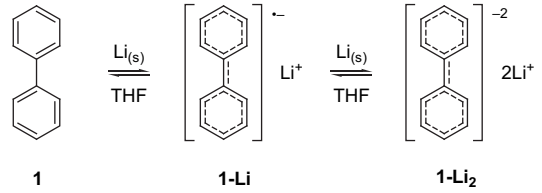
doubly reduced in THF or better in THP to its dianion,[11] and this has been substantiated with the determination of the crystal structure of the naphthalene dianion, $(Li^{+}TMEDA)_2C_{10}H_8^{-2}$, obtained by direct reduction of naphthalene with $Li_{(s)}$.[12] Based on reduction potential criteria,[1] biphenyl (**1**) would be also expected to be reduced to the corresponding dianion (**1**-Li_2) at least to some extent under similar conditions, according to Scheme 1.[13]



Scheme 1.

In this paper we report on the reactivity of biphenyl radical anion and dianion with different (primary, secondary, and tertiary) alkyl fluorides in order to establish the mechanistic and synthetic aspects of these reactions.

1.2. Alkyl fluorides as electron acceptors

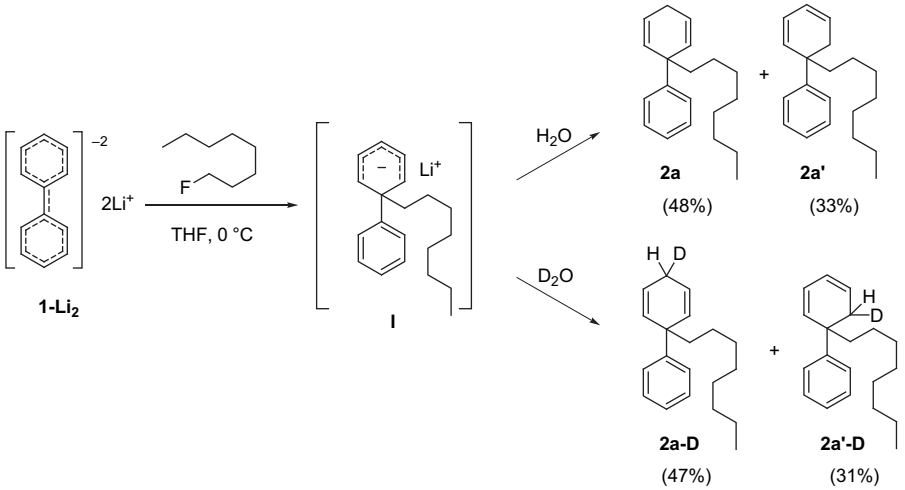
The carbon–fluoride bond cannot be electrochemically reduced below the solvent cut-off limit.[14] Solvents or supporting electrolytes are invariably reduced at lower potentials than that required for an alkyl fluoride, therefore there are no reports of cathodic reductions of regular alkyl fluorides by electrochemical means. They can however be the electron acceptor counterpart in homogeneous reactions with arene radical anions as ET reagents. In this regard, the alkyl halide series including alkyl fluorides (RI, RBr, RCl, and RF) has been the subject of numerous studies in their reactions with arene radical anions.[15] A widely accepted mechanism of reaction for alkyl halides has been described in identical terms for *all* alkyl halides, including alkyl fluorides.[16] It involves ET from the arene radical anion and dissociation of the alkyl halide with generation of the alkyl radical. Thus, the reaction of alkyl halides (R–X) with sodium naphthalene affords similar crude products mainly consisting in mixtures of reduction (R–H) and coupling products (R–$C_{10}H_9$, $R_2C_{10}H_8$), regardless the nature of X (F, Cl, Br or I). According to the authors, the lack of effect of halogen variation on the distribution of products mitigates the possibility of an S_N2 reaction pathway.[16] This statement remained unchallenged until a first hint suggesting a special behavior of alkyl fluorides was anticipated by Eberson.[17] He observed the failure of the alkyl fluorides to conform in a reasonable way with the Marcus theory of ET, which adequately fitted the ET reaction between arene radical anions and the rest of alkyl halides (RI, RBr, and RCl). The thermodynamic/electrochemical data needed (e.g., the unavailable E° of RX) were estimated from indirect thermodynamic measures, according to the method given by Hush.[18] After being overlooked for two decades, recent studies of competitive kinetics on lithium naphthalene ($LiC_{10}H_8$) and dilithium naphthalene ($Li_2C_{10}H_8$) confirmed an ET reactivity profile with alkyl chlorides (*n*-, *s*-, and *t*-octyl chlorides), while revealed an apparent mechanistic shift toward the S_N2 when alkyl fluorides (*n*-, *s*-, and *t*-octyl fluorides) were employed as electron acceptors.[19] The reactivity was shown to decrease in the order primary>secondary>tertiary for reactions of octyl fluorides in both the naphthalene radical anion and dianion, just the opposite behavior that would be intuitively expected if ET was the main process.

2. Results and discussion

We want to report here the differences in chemical reactivity between the lithium salts of biphenyl radical anion ($LiC_{12}H_{10}$, **1**-Li) and its dianion ($Li_2C_{12}H_{10}$, **1**-Li_2), specifically their differences when reacting with alkyl fluorides as an example of poor electron acceptors. The synthetic applications derived from this study are also evaluated.

2.1. Previous studies

Some aspects of the reactivity of these species (**1**-Li, **1**-Li_2), postulated as coexisting in more or less extension in solutions containing biphenyl and an excess of an alkali metal, have already been reported, in part as a preliminary communication.[20] For instance, **1**-Li_2 reacts with terminal alkenes, affording dearomatized carbolithiation products, which can be further functionalized in subsequent steps.[21] Instead, **1**-Li is unreactive under the same reaction conditions. Analogous results were obtained for lithium naphthalene dianion and the corresponding radical anion.[21] The reaction is not an ET process, but rather a nucleophilic attack to the alkene resulting a carbolithiation. Lithium naphthalene radical anion and dianion were also studied in concern with their roles with the mechanism of the arene-catalyzed lithiation.[11] Also, the reaction of a large number of dianions of polycyclic aromatic hydrocarbons (PAHs) with alkyl fluorides provided a route to alkylated dihydro-PAHs, which was



Scheme 2. Alkylation of dilithium biphenyl ($Li_2C_{12}H_{10}$) with *n*-fluorooctane. Yields were determined by quantitative GLC using pure isolated products for the calibration curve and dodecane as internal standard. 4-Deuterio-1-octyl-1,4-dihydrobiphenyl (**2a**-D, 47%, 53:47 dr, >98.5% deuterium incorporation) and 2-deuterio-1-octyl-1,2-dihydrobiphenyl (**2a**′-D, 31%, 62:38 dr, >99.8% deuterium incorporation) were obtained using D_2O for deuterolysis (diastereomeric ratio by ^1H NMR and ^{13}C NMR, deuterium incorporation by MS and ^1H NMR, natural isotopic distribution corrected). Product characterization: Ref. 22.

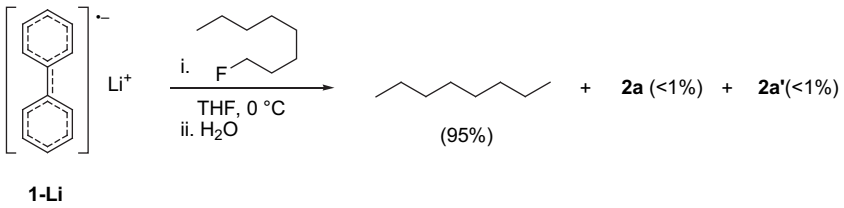
complementary to the classical Birch reductive alkylation of PAHs since a different set of regioisomers was obtained.[22]

2.2. Reactions with primary alkyl fluorides

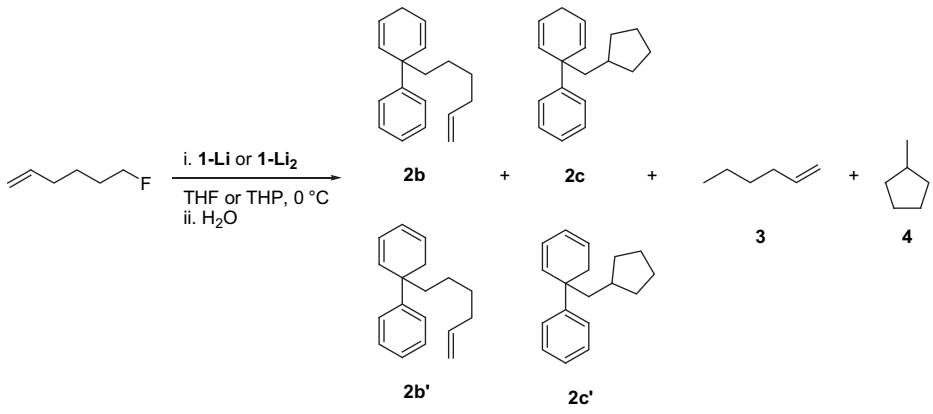
*2.2.1. Differences in the reactivity of **1**-Li and **1**-Li$_2$ with a primary alkyl fluoride.* The reaction of a solution of biphenyl with an excess of Li$_{(s)}$ powder in THF at 0 °C is assumed to afford lithium biphenyl dianion (**1**-Li$_2$, deep dark blue) in an unknown concentration, which is used throughout this work as such. Its reaction with *n*-fluorooctane affords, after hydrolysis with water, a mixture of two regioisomers **2a** and **2a**′ in 81% overall yield (Scheme 2). Further support of the participation of intermediate **I** in Scheme 2 was obtained from deuterolysis experiments. Deuterolysis employing D_2O afforded **2a**-D and **2a**′-D in 78% overall yield with excellent deuterium incorporation (see footnotes in Scheme 2). It points toward the presence of a living dianionic species in the reaction medium that is alkylated by *n*-fluorooctane, in agreement with Scheme 2.[22]

Still, the main evidence of the participation of the dianion comes from the analysis of the distribution of products in the absence of dianionic biphenyl. The analogous reaction carried out using the radical anion of biphenyl (**1**-Li, LiC$_{12}$H$_{10}$) has a very different outcome. Using a substoichiometric amount of Li$_{(s)}$ with respect to biphenyl in THF at 0 °C, a deep dark-blue solution of **1**-Li is generated. Using this reagent, *n*-fluorooctane is mainly reduced to *n*-octane (95%), with only trace amounts of **2a**+**2a**′ by quantitative GLC (Scheme 3).

2.2.2. Studies with a primary radical probe: 5-hexenyl fluoride. The use of 5-hexenyl radical probes was seen as an obvious choice to obtain data more sensible to the mechanism of the reactions. 6-Fluoro-1-hexene was prepared and used as alkylating reagent, in search for potential radical reaction pathways. The results are collected in Scheme 4 and Table 1. When 6-fluoro-1-hexene was reacted with an equivalent of **1**-Li$_2$ in THF at 0 °C (formal [**1**-Li$_2$]=0.2 M), the reaction crude afforded the non-rearranged products **2b** and **2b**′ in 75% overall yield, while the rearranged (cyclized) products **2c** and **2c**′ could not be detected by GLC (Table 1, entry 3). To confirm this finding beyond doubt, **2c** and **2c**′ were synthesized directly from fluoromethylcyclopentane by reaction with **1**-Li$_2$ (72% overall yield).[22] The pure compounds were used as control in GLC analyses. The amounts of **2c** and **2c**′ remained zero (undetectable) in experiments of dilution with formal [**1**-Li$_2$]=0.1, 0.05 and 0.01 M. On the other hand, the radical anion **1**-Li afforded mainly reduction products (**3** and **4**) in 92% overall yield, with a clear prevalence of the rearranged product (methylcyclopentane **4**, 91%, Table 1, entry 2). This reaction had to be carried out in THP since in THF a complete overlap of **4** by the solvent peak occurred. In spite of the information provided by these data regarding major products, the overall picture including the yields of the minor



Scheme 3. Reaction of lithium biphenyl radical anion (LiC$_{12}$H$_{10}$) with *n*-fluorooctane affords octane as the main reaction product, consistent with an ET mechanism. Yields were determined by quantitative GLC using pure commercial and isolated products for the calibration curve and *n*-dodecane as internal standard.



Scheme 4.

Table 1
Distribution of products from Scheme 4[a,b,c]

		Solvent	2b	2b′	2c	2c′	3	4	Total
1	**1**-Li	THF	1.6±1	1±0.9	0	0	7±4	—[d]	—
2		THP	0.6±1	0.4±0.9	0	0	1.4±0.6	91±2	93
3	**1**-Li$_2$	THF	45±8	30±10	0	0	2±1.7	—[d]	—

[a] Reactions performed by addition of the halide (0.2 mmol diluted in THF or THP at 0 °C, 30 min) to a 0.2 M solution of **1**-Li or **1**-Li$_2$ in THF or THP at 0 °C and hydrolysis at low temperature (−80 °C), followed by immediate GLC analysis.

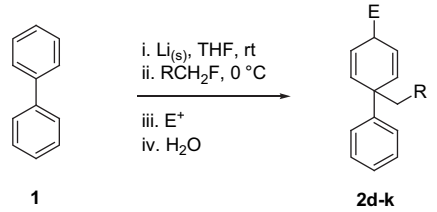
[b] Yields (%) followed by standard deviations were the average of 3–7 determinations (relative standard deviation, rsd=2–33% for major components), determined by quantitative GLC using pure isolated or commercially available compounds and *n*-decane as internal standard. Yield of coupling products were contrasted with 400 MHz ^{1}H NMR yields using *N*,*N*-diphenyl formamide as internal standard.

[c] Product characterization: Ref. 22.

[d] Hidden behind the solvent peak.

components proved to be very disperse in nature (relative standard deviations (rsd) of the minor yields spanning 57–225%) and very sensitive to small, undefined changes. A complete kinetic study of these reactions as a function of the concentration of **1**-Li or **1**-Li_2 was initially considered, but the overall results did not show well defined trends and was later dismissed given the lack of accuracy, especially in the determination of minor, yet key products. Interestingly, this erratic behavior had already been reported in the past by other groups, with no given explanation.[16c] It seems that the complexity of these blue solutions and their changing nature as a function of the concentration may play an important role in this misleading behavior.

2.2.3. Synthetic applications derived from ***1****-Li_2 and n-alkyl fluorides.* The results described in Schemes 2 and 4 leave an open door for potential synthetic applications. A second electrophile (E^+) can be added to the intermediate of alkylation (e.g., **I** in Scheme 2), giving rise to doubly functionalized dearomatized biphenyl derivatives according to Scheme 5 and Table 2.



Scheme 5.

Thus, the reaction of biphenyl (**1**) with an excess of lithium powder (ca. 1:12 molar ratio) in THF at room temperature gave a deeply colored dark-blue solution containing the dianion **1**-Li_2, which was alkylated with a primary alkyl fluoride (RCH_2F: *n*-$C_8H_{17}F$, *c*-$C_5H_9CH_2F$, $CH_2{=}CH(CH_2)_4F$; 1:1.1 molar ratio, 0 °C, 30 min). The resulting mixture was then treated with a conventional electrophile [E^+: *n*-C_4H_9Br, Et_2CO, $Me_2C(O)CH_2$, *i*-Pr_3SiCl; 1:1.1 molar ratio, −78 °C, 15 min], affording after final hydrolysis with water (−78 °C to rt) the corresponding 1,4-disubstituted compounds **2d**–**k**, as a mixture of cis/trans-diastereomers (Scheme 5 and Table 2).

The results reported in entries 7 and 8 back up the previously reported behavior with radical clocks. The reaction of **1**-Li_2 with 6-fluoro-1-hexene (Table 2, entries 7 and 8) affords good and fair yields of the expected products (86% of **2j** and 58% of **2k**). The corresponding cyclopentylmethyl rearranged products (i.e., products **2h** and **2i**, which were prepared from fluoromethylcyclopentane: Table 1, entries 5 and 6) could not be detected in the reaction crudes, at least within the detection limits of GLC. Again, this points toward a bimolecular substitution reaction as the key step of the process, rather than an ET reaction from the dianion intermediate **1**-Li_2 to 6-fluoro-1-hexene. After coupling with the primary alkyl fluoride, the resulting intermediate of type **I** reacts regio but not stereoselectively with the conventional electrophile to give, after hydrolysis, a cis/trans-mixture of the 1,4-disubstituted diastereomers **2**. From a preparative point of view it is worthy to note that both diastereomers could be separated by column chromatography in all cases except for the minor components *trans*-**2f**, *trans*-**2g** (Table 2, entries 3 and 4), which were contaminated with variable amounts of the major cis-diastereomer (ca. 30% for *trans*-**3f**) or other byproducts (ca. 20% for *trans*-**3g**). The stereochemistry of both cis and trans diastereomers was assigned in all cases by NMR experiments, specially by means of NOESY measurements.

Regarding the regiochemistry displayed at the electrophilic capture, E^+ is invariably introduced at the $C_{(4)}$ position yielding 1,4-dihydrobiphenyl derivatives. This is a special feature of the cyclohexadienyl anion (**I**) in its reaction with an electrophilic carbon (or silicon), but it was not so with protons or deuterons from water, as seen before (Scheme 2). When water or deuterium oxide was used as the electrophile, together with the expected mixture of 1,4-disubstituted deuterated products **2a** and **2a**-D, the corresponding mixture of 1,2-disubstituted deuterated adducts **2a**′ and **2a**′-D was also isolated (Scheme 2). It is well known that the cyclohexadienyl anion is kinetically more reactive at the central position (e.g., $C_{(4)}$ of **I** in Scheme 2).[23] This carbon supports a higher coefficient in the HOMO of the anion. However, for the highly polarized H–O (or D–O) bond of water (or D_2O), the protonation step may be primarily controlled by electrostatic interactions. The density of charge is more equally distributed between the $C_{(2)}$, $C_{(4)}$, and $C_{(6)}$ positions than the values for these atoms in the HOMO of **I**.[20] Therefore a loss of selectivity is expected in a reaction pathway driven by polar interactions.

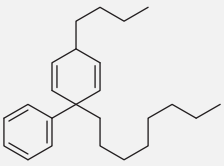
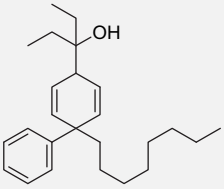
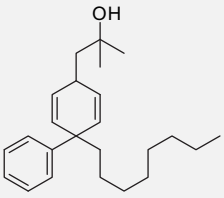
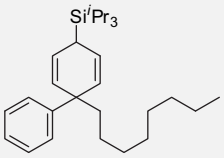
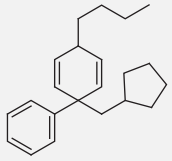
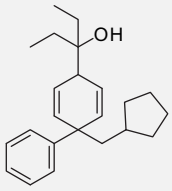
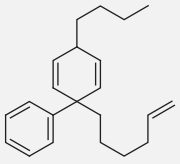
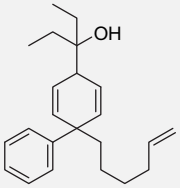
2.3. Reactions with secondary and tertiary alkyl fluorides

We next explored the potential use of this synthetically appealing methodology of alkylation/dearomatization for the case of secondary and tertiary alkyl fluorides. As the substrates become less prone to undergo S_N2 (i.e., with secondary and tertiary RF), the ET pathway should gain share and eventually become dominant. This would limit in principle the synthetic utility of the process. However, secondary and tertiary radicals generated from a hypothetic ET step are reduced to carbanions with increasing difficulty, so they should also tend to couple with the biphenyl radical anion (**1**-Li, always present in the reaction media) in greater extension than their primary counterparts. This alkylation by coupling of radicals affords, in principle, the same alkylated intermediates than a direct nucleophilic substitution, in what is called the S_N2–ET dichotomy. The final outcome is described below as an evolution from S_N to ET reaction pathways as we move from primary to secondary to tertiary alkyl fluorides. The experimental data that follow show that the yields of the alkylation products are indeed lower than those reported for primary alkyl fluorides, and a diminished regiochemical control is observed with tertiary alkyl fluorides.

2.3.1. Reaction of a sec-octyl fluoride and a tert-octyl fluoride with ***1****-Li_2.* The reaction of a solution of biphenyl with an excess of $Li_{(s)}$ in powder in THF at 0 °C (**1**-Li_2) followed by the addition of 2-fluorooctane or 2-fluoro-2-methylheptane afforded, after quenching with CH_3CN and then water, a mixture of the corresponding alkylation products **5a** (82%) and **6a** (45% as a mixture of *p*-**6a** and *m*-**6a**), along with the corresponding *n*-octane and isooctane, respectively (Scheme 6). The use of CH_3CN as a Brønsted acid weaker than water for the protonation step maximizes the formation of a major regioisomer of protonation, simplifying considerably the analysis of the crude mixture and separations.[22] The regiochemistry of alkylation is different for both substrates. We have observed that secondary alkyl fluorides alkylate the 1-position of biphenyl, while tertiary alkyl fluorides are directed to the 4-position and, in less extent, to the 3-position, in considerably lower yields. Again, the generation of two adjacent quaternary centers is disfavored. The reacting carbon of the biphenyl moiety shifts to the less hindered 4-position (and 3-position). This general behavior is maintained with other secondary and tertiary alkyl fluorides. Whether this regiochemical shift is connected or not with a shift in the main operating mechanism is still to be determined. But at this point it is tempting to attribute the decreased regioselectivity observed with tertiary alkyl fluorides to a poor selective mechanism of radical coupling.

2.3.2. Studies with a tertiary radical probe: 1,1-dimethyl-5-hexenyl fluoride. The use of a radical probe was again considered to study this reaction. 6-Fluoro-6-methylhept-1-ene (**7**) was synthesized

Table 2
Preparation of compounds **2d**–**l** according to Scheme 3

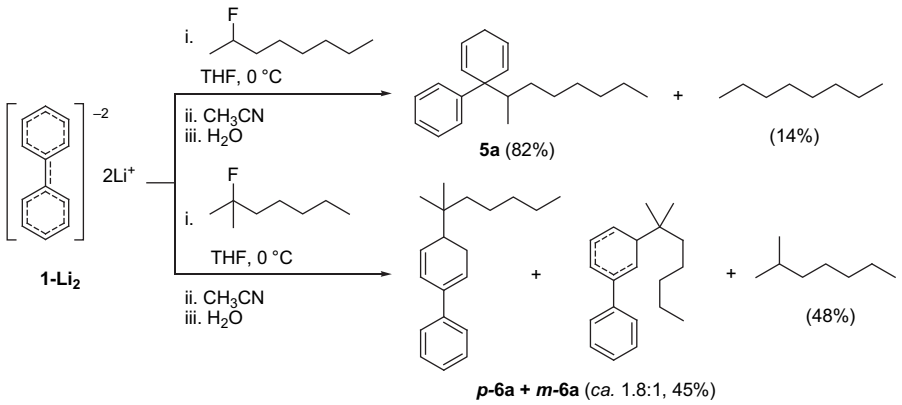
Entry	RF, E^+	Products **2d**–**k**				
		Structure[a]	No.	Yield[b]	cis/trans[c]	t_R values[d]
1	*n*-$C_8H_{17}F$, *n*-C_4H_9Br		**2d**	98	0.9:1	14.11:14.18
2	*n*-$C_8H_{17}F$, Et_2CO		**2e**	61	1:0.7	15.69:15.84
3	*n*-$C_8H_{17}F$, $Me_2C(O)CH_2$		**2f**	58	1:0.4	15.15:15.21
4	*n*-$C_8H_{17}F$, *i*-Pr_3SiCl		**2g**	82	1:0.4	16.77:17.00
5	*c*-$C_5H_9CH_2F$, *n*-C_4H_9Br		**2h**	81	0.9:1	13.38:13.48
6	*c*-$C_5H_9CH_2F$, Et_2CO		**2i**	59	0.5:1	14.70:14.87
7	$CH_2{=}CH(CH_2)_4F$, *n*-C_4H_9Br		**2j**	86	0.9:1	13.48:13.62
8	$CH_2{=}CH(CH_2)_4F$, Et_2CO		**2k**	58	1:0.6	14.57:14.77

[a] Both diastereomers of all compounds **2d**–**k** were isolated >95% pure, except for *trans*-**2f** (ca. 70%) and *trans*-**2g** (ca. 80%), as determined by GLC and/or 300/400 MHz ^1H NMR, and were fully characterized by spectroscopic means (IR, ^1H and ^{13}C NMR, LRMS, and HRMS). All the compounds gave consistent NMR correlations (DEPT, COSY, HSQC, and HMBC), which were used for signal assignment.

[b] Determined by quantitative NMR, using *N*,*N*-diphenyl formamide as internal standard and/or GLC using pure isolated products and decane as internal standard.

[c] Determined by GLC and/or 300 MHz ^1H NMR of the reaction crude. The cis/trans assignment of the stereochemistry was done after examination of the cross-signals in NOESY experiments.

[d] Measured with a Hewlett-Packard HP-5890 instrument equipped with a flame ionization detector and an HP-5 capillary column (30 m, 0.32 mm diam.), using nitrogen as gas carrier, $T_{injector}$=275 °C; $T_{detector}$=300 °C; T_{column}=60 °C (3 min) and 60–270 °C (15 min), P=12 psi; t_R (min) are given under these conditions.



Scheme 6. Alkylation of dilithium biphenyl ($Li_2C_{12}H_{10}$) with 2-fluorooctane and 2-fluoro-2-methylheptane. Yields of alkanes were determined by quantitative GLC using pure commercial products for the calibration curve and diphenylmethane as internal standard. Yields of coupling products were obtained by 400 MHz ^{1}H NMR using *N*,*N*-diphenyl formamide as internal standard, and was estimated for *m*-**6a**, which consisted in a decaying mixture of non isolable regioisomers.

Table 3
Distribution of products from Scheme 7[a,b]

Entry		c[c] (M)	**7**	**8**	**9**	**10**	*p*-**6b**	*m*-**6b**	% Total
1	**1**-Li	0.5	0	1.4±0.5	40±4	11±3	19±3	11±2	82
2	**1**-Li_2	0.1	0	2.8±1.3	45±8	9±3	23±4	13±6	93

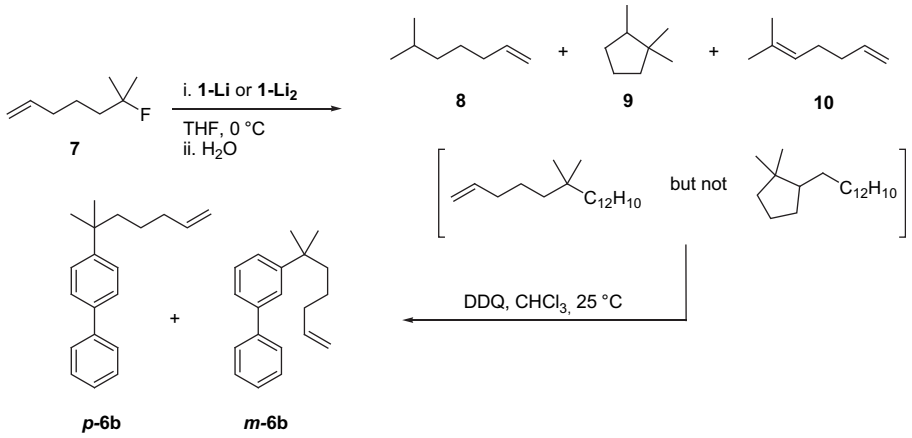
[a] Reactions performed by addition of the halide (0.2 mmol diluted in THF or THP at 0 °C, 30 min) to a solution of **1**-Li or **1**-Li_2 in THF at 0 °C and hydrolysis at low temperature (−80 °C), followed by immediate GLC analysis.

[b] Yields followed by standard deviations determined by quantitative GLC using pure isolated or commercially available compounds and *n*-decane as internal standard, and contrasted when necessary with 400 MHz ^{1}H NMR yields using *N*,*N*-diphenyl formamide as internal standard. Yields were the average of 3–5 determinations (relative standard deviation, rsd=±17–47%).

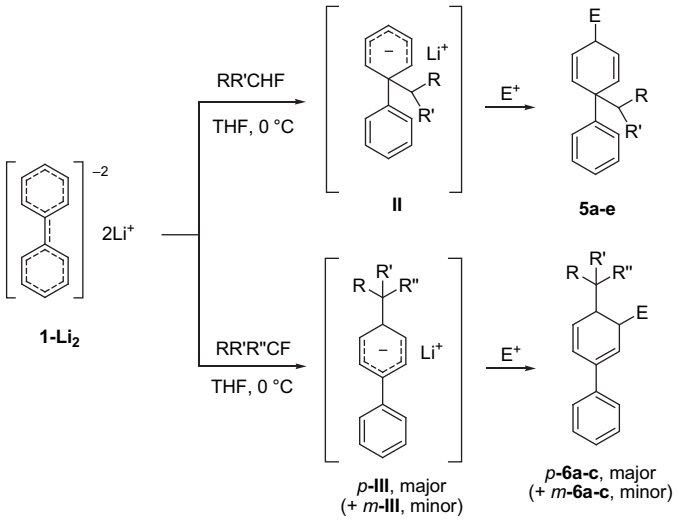
[c] Formal concentration of **1**-Li or **1**-Li_2, *not* actual concentration, which is unknown for **1**-Li_2.

and was reacted with an equivalent of **1**-Li_2 in THF at 0 °C (formal [**1**-Li_2]=0.1 M). Results are gathered in Table 3, entry 2. The reaction crude afforded a mixture of products that was first analyzed for volatiles (GLC), and subsequently was rearomatized using DDQ to afford a mixture of the non-rearranged coupling products *p*-**6b** and *m*-**6b** in limited yield (36% overall). The corresponding rearranged (cyclized) coupling products could not be detected in the reaction crude (GLC and 400 MHz ^{1}H NMR), and remained undetectable in experiments of dilution (formal [**1**-Li_2]=0.05, 0.02, and 0.01 M). The observed regioselectivity in the alkylation displayed in products *p*-**6** and *m*-**6** results remarkable: it is different to that found for products **2b** and **2c** in that the attack is directed to the 4- and 3-position of biphenyl, instead of the 1-position. This is so to preclude the formation of two contiguous quaternary centers, a significantly destabilizing situation. We found an analogous behavior in different reactions of attachment of a tertiary group to the biphenyl moiety in the 4-position, while primary or secondary groups generally reacted at the 1-position.[21a] Regarding low molecular weight products (C_8), the hydrocarbons 6-methylhept-1-ene (**8**), 1,1,2-trimethylcyclopentane (**9**), and 6-methylhepta-1,5-diene (**10**) were detected and quantified by GLC (Table 3, Scheme 7) using pure commercial or synthesized samples for the preparation of calibration curves. Rearranged product **9** was the major component of the reaction mixture (45%). Along with **9**, the presence of **10** (9%) also indicates the existence of an ET pathway. Compound **10** is likely originated from disproportionation of its precursor radical with other radicals. A decrease in the regioselective control of the formation of *p*-**6b** and *m*-**6b** may also be attributed to a radical course of the reaction. When the radical anion **1**-Li was used as a reagent, the rearranged product **9** was obtained as major reaction product (40%) as expected. A reasonable amount of coupling products *p*-**6b** and *m*-**6b** (30% overall) was also found in the reaction crude.

Again, the realization of a complete kinetic study as a function of the concentration of **1**-Li or **1**-Li_2 was not viable for the



Scheme 7.



Scheme 8.

aforementioned reasons. Still, in spite of the dispersed nature of data, the distribution of products found in Table 3 reveals that the data from entry 1 (results from the radical anion, **1**-Li) are statistically indistinguishable from that in entry 2 (from dianion, **1**-Li_2). This is significant, and supports a common reaction pathway initiated by an ET to the fluoride. Radicals so generated evolve according to their specific nature. Thus the long-lived tertiary radical is prone to give coupling products (**6**) [among others (**10**)] rather than being reduced to the corresponding carbanion. Conversely, upon unimolecular rearrangement, a primary radical arises, which is easily reduced now by ET to the corresponding carbanion, affording eventually **9**.

2.3.3. Synthetic applications derived from ***1****-Li_2 and sec- and tert-alkyl fluorides.* The methodology described in Scheme 8 entails again both dearomatization plus double functionalization of biphenyl in one pot. In addition to that the initial alkylation site can be chosen using either a secondary alkyl fluoride (RR′CHF) or a tertiary alkyl fluoride (RR′R″CF) (Scheme 8). This affords 1-alkylated or 4-alkylated carbanionic intermediates as major intermediates (**II** and **III** in Scheme 8), which can be further trapped with an appropriate electrophilic reagent (E^+). Thus, **1**-Li_2 was alkylated with different secondary and tertiary alkyl fluorides (RF, Table 4) and was reacted later with an electrophile (E^+: Et_2CO, CH_3CN, H_2O) followed by hydrolysis with water, all under the same conditions described before (Scheme 5 and Table 2), to afford the corresponding compounds **5b**–**e** and **6b**,**c**, along with the byproducts of reduction RH. The reaction product described in entry 6 was rearomatized using DDQ.

3. Conclusions

In this paper we report a new and different reactivity of the lithium biphenyl dianion (**1**-Li_2) in its reaction with a poor electron acceptor, namely an alkyl fluoride, as compared to that of lithium biphenyl radical anion (**1**-Li). The analysis of the distribution of products in the reaction of dilithium biphenyl (**1**-Li_2) with several alkyl fluorides in THF at 0 °C points toward a nucleophilic substitution, S_N2, as a competing mechanism with the general ET mechanism, in another example of S_N2–ET dichotomy. The picture that emerges from this study is based on the analysis of the distribution of products derived from the well known 5-hexenyl radical probes, which is best described with the help of Scheme 9. According to our findings, two main reaction pathways compete for the alkyl fluoride substrate. On one hand, the bimolecular nucleophilic substitution (k_{SN}), which prevails in the case of a primary substrate (R=H). On the other hand, also the bimolecular electron transfer (k_{ET}), which dominates in the case of a tertiary alkyl fluoride (R=Me). After ET, the corresponding radical clock evolves depending on its nature (substitution) in three competing ways: one unimolecular way (k_r) affording rearranged products, for which exact activation parameters are well documented,[24] and two bimolecular ways (k_{red} and k_{coupl}) that afford non-rearranged products. At this point, for the simplest case of reactions with the radical anion **1**-Li and making a few simplifying assumptions (as setting k_{ET} and k'_r=0), an evaluation of the ratio between the non-rearranged products and rearranged products versus the concentration of **1**-Li (in large excess) would afford a linear plot: [non-rearranged]/[rearranged]=(k_{red}+k_{coupl})[**1**-Li]/k_r. From it, all rate constants should be evaluated, and most importantly, the radical mechanism established. Unfortunately, this was not experimentally feasible for the aforementioned reasons. Even for the case of **1**-Li_2, which was also explored, the concentration of **1**-Li (now variable) could be expressed as a function of the advance of the reaction and the resulting differential equations integrated. Still, no well defined trends were found in this and other explored situations. The reaction network is complicated by the possible participation of anionic cyclizations (k'_r), which may be especially important in the case of a tertiary carbanion. In spite of that and although no absolute rates could be measured, the distribution of products is consistent with the two competing reaction pathways and the reaction network described in Scheme 9.

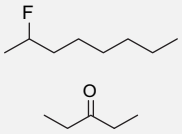
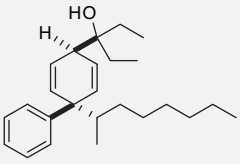
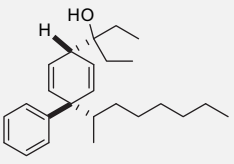
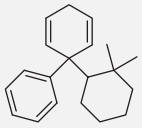
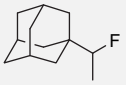
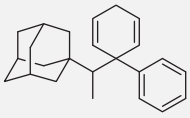
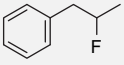
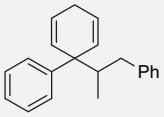
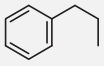
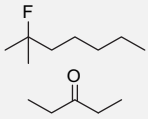
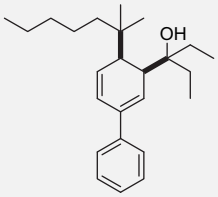
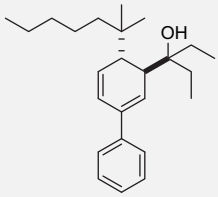
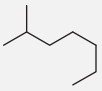
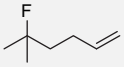
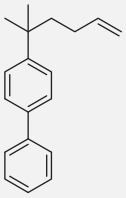
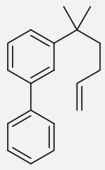
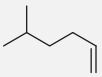
From a synthetic point of view, the successive reaction of the dianion of biphenyl (**1**-Li_2) with a primary alkyl fluoride as the first electrophile and with a second conventional electrophile works regioselectively affording 1-alkyl-4-substituted-1,4-dihydrobiphenyls in good yields (**2a**–**k**).[25]

4. Experimental section

4.1. General

All moisture sensitive reactions were carried out under argon atmosphere. THF and THP were dried and distilled over Na/K alloy right before use. Commercially available (Acros, Aldrich, Fluka) biphenyl, alkyl fluorides, and electrophiles were used without further purification. Deuterium oxide was 99.98% D grade. Lithium powder was prepared from lithium granules (Chemetall, 99%, high sodium content) using an impact grinding mill and was also commercially available (Medalchemy). All glassware were dried in an oven at 100 °C and cooled to room temperature under Ar before use. Column chromatography was performed with Merck silica gel 60 (0.040–0.063 μm, 240–400 mesh). Thin-layer chromatography (TLC) was performed on precoated silica gel plates (Merck 60, F_{254}, 0.25 mm). Detection was done by UV_{254} light and/or developing with phosphomolybdic acid spray; R_f values are given under these conditions. NMR spectra were recorded on a Bruker Avance 300 and Bruker Avance 400 (300 and 400 MHz for ^1H NMR, and 75 and 100 MHz for ^{13}C NMR, respectively) using $CDCl_3$ as solvent and TMS as internal standard. Mass spectra (EI) were obtained at 70 eV on a Shimadzu QP-5000 and Agilent 5973 spectrometers, fragment ions in *m*/*z* with relative intensities (%) in parenthesis. HRMS analyses were carried out on a Finnigan MAT95S spectrometer. Infrared (FTIR) spectra were obtained on a Nicolet Impact 400D spectrophotometer using NaCl plates. The purity of volatile compounds and the quantitative chromatographic analyses (GC) were carried out with a Hewlett-Packard HP-5890 instrument equipped with a flame ionization detector and a 30 m HP-5 capillary column (0.32 mm diam., 0.25 μm film thickness), using nitrogen as carrier gas (12 psi).

Table 4
Preparation of compounds **5b–e** and **6b**, **c** according to Scheme 7

Entry	RF	Products			
	E^+	Structures[a]	Yield[b] (%)	Ratio[c]	Yield RH
1		 *cis*-**5b**  *trans*-**5b**	55%	*c*-/*t*- 2.7:1	 37%
2	 CH_3CN	 **5c**	70%		 21%
3	 CH_3CN	 **5d**	40%		 51%
4	 CH_3CN	 **5e**	38%		 55%
5		 *cis*-**6b**  *trans*-**6b**	49%	*c*-/*t*- 1.3:1	 41%
6	 i. H_2O; ii. DDQ	 *p*-**6c**  *m*-**6c**	42%	*m*-/*p*- 1.8:1	 53%

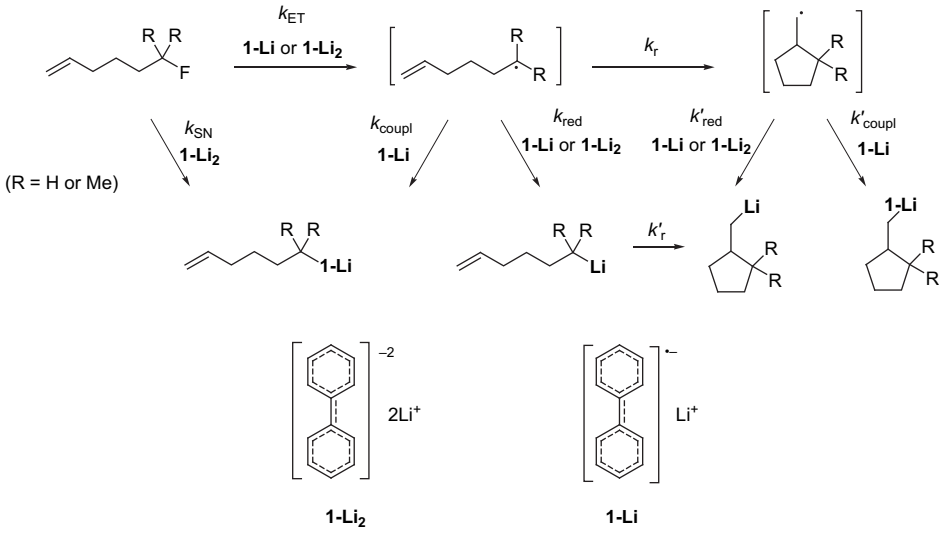
[a] Both isomers of **5b**, and **6b–c** were isolated >95% pure, as well as the remaining compounds, as determined by GLC and/or 300/400 MHz ^{1}H NMR, and were characterized by spectroscopic means (IR, ^{1}H and ^{13}C NMR, LRMS, and HRMS). All the compounds gave consistent NMR correlations (DEPT, COSY, HSQC, and HMBC), which were used for signal assignment.

[b] Determined by quantitative 400 MHz ^{1}H NMR, using *N*,*N*-diphenyl formamide as internal standard and/or GLC using pure isolated products and decane as internal standard.

[c] Determined by 300/400 MHz ^{1}H NMR from the reaction crude. The cis/trans assignment of the stereochemistry was done after examination of the cross-signals in NOESY experiments.

4.2. Preparation of the fluorinated reagents

All alkyl fluorides were colorless liquids. Octyl fluoride was commercially available (Aldrich) and was used as supplied. The preparation of 6-fluoro-1-hexene and fluoromethylcyclopentane was previously reported by us.[19] 2-Fluorooctane,[26] 2-fluoro-2-methylheptane,[27] 2-fluoro-1-phenylpropane,[28] 5-fluoro-5-methyl-1-hexene,[29] and 1-(1-fluoroethyl)adamantane[30] were prepared according to the corresponding literature procedures and were characterized by comparing their physical and spectroscopic data



Scheme 9. Proposed overall reaction network, including both S_N as well as ET reaction pathways. The corresponding hydrocarbon products of Tables 1 and 3 would be generated in a final hydrolysis step (not drawn).

with those already reported. Some characteristic data of these known compounds as well as the preparation of the two new fluorinated reagents follows.

4.2.1. 2-Fluorooctane[26]. Yield 50%; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H=0.89 (t, J=6.7 Hz, 3H, CH_2CH_3), 1.20–1.77 (m, 10H, 5×CH_2), 1.30 (dd, $^3J_{HF}$=23.8 Hz, $^3J_{HH}$=6.1 Hz, 3H, CH_3CHF), 4.49–4.80 (dm, $^2J_{HF}$=48.8 Hz, 1H, CHF); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C=14.05 (CH_2CH_3), 21.00 (d, $^3J_{CF}$=23.2 Hz, CH_3CHF), 22.55 (CH_2CH_3), 25.05 (d, $^3J_{CF}$=4.9 Hz), 29.10, 31.75 (CH_2CH_2CHF), 36.95 (d, $^2J_{CF}$=20.8 Hz, CHF), 91.05 (d, $^1J_{CF}$=164.8 Hz, CHF); MS (70 eV, EI): m/z (%)=112 (<1%, M^+−HF), 84 (14), 83 (25), 70 (50), 69 (19), 57 (26), 56 (56), 55 (72), 46 (27), 43 (88), 42 (54), 41 (100).

4.2.2. 2-Fluoro-2-methylheptane[27]. Yield 60%; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H=0.90 (t, J=7 Hz, 3H, CH_2CH_3), 1.20–1.48 [m with a dd at 1.35, $^3J_{HF}$=18.3 Hz, 12H, $CH_3(CH_2)_3$ and 2×CH_3CF], 1.48–1.70 (m, 2H, CH_2CF); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C=14.00 (CH_2CH_3), 22.60 (CH_3CH_2), 23.65 (d, $^3J_{CF}$=5.5 Hz, CFCH_2CH_2), 26.60 (d, $^2J_{CF}$=24.8 Hz, CH_3CFCH_3), 32.15 ($CH_3CH_2CH_2$), 41.45 (d, $^2J_{CF}$=22.9 Hz, CFCH_2), 95.85 (d, $^1J_{CF}$=164.1 Hz, CF); MS (70 eV, EI): m/z (%)=113 (<1%, M^+−F), 112 (1%, M^+−HF), 97 (15), 70 (15), 69 (13), 61 (100), 60 (45), 58 (10), 57 (29), 56 (54), 55 (63), 43 (35), 42 (12), 41 (64); HRMS: calcd for C_8H_{17} 113.1330; found 113.1305.

4.2.3. 2-Fluoro-1-phenylpropane[28]. Yield 60%; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H=1.35 (dd, $^3J_{HF}$=23.7 Hz, $^3J_{H-H}$=6.2 Hz, 3H, CH_3), 2.76–3.07 (m, 2H, CH_2), 4.72–5.01 (dm, $^1J_{H-F}$=54.0 Hz, $^1J_{H-H}$=6.2 Hz 1H, CHF), 7.18–7.34 (m, 5H, Ph); ^{13}C-NMR (75 MHz, $CDCl_3$): δ_C=20.53 (d, $^2J_{C-F}$=21.8 Hz, CH_3), 43.26 (d, $^2J_{C-F}$=20.7 Hz, CH_2), 90.04 (d, $^1J_{C-F}$=92.9 Hz, CHF), 126.51, 128.38 (2C), 129.35 (2C), 137.19 (d, $^3J_{C-F}$=4.4 Hz) (Ph); MS (70 eV, EI): m/z (%)=138 (24%, M^+), 92 (9), 91 (100), 65 (9).

4.2.4. 5-Fluoro-5-methyl-1-hexene[29]. Yield 70%; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H=0.90 (d, $^3J_{HF}$=21.4 Hz, 6H, 2×CH_3), 1.64–1.78 (m, 2H, CH_2CF), 2.16 (app q, J=6.9 Hz, 2H, CH_2C=C), 4.93–5.09 (m, 2H, CH_2=CH), 5.76–5.91 (m, 1H, CH_2=CH); ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C=26.62 (d, $^2J_{CF}$=25.91 Hz, 2C, 2×CH_3), 28.22 (d, $^3J_{CF}$=6.10 Hz, CH_2C=C), 40.47 (d, $^2J_{CF}$=22.9 Hz, CH_2CF), 95.87 (d, $^1J_{CF}$=164.6 Hz, CF), 114.48 (CH_2=CH), 138.35 (CH_2=CH).

4.2.5. 1-(1-Fluoroethyl)adamantane[30]. Yield 40%; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H=1.21 (dd, $^3J_{HF}$=25.3 Hz, $^3J_{HH}$=6.4 Hz, 3H, CH_3), 1.44–1.53 (m, 3H, 3×CH ring), 1.59–1.77, 1.97–2.03 (2m, 12H, 6×CH_2 ring), 4.13 (dq, $^1J_{HF}$=47.4 Hz, $^1J_{HH}$=6.4 Hz, 1H, CHF); ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C=14.22 (d, $^2J_{CF}$=24.4 Hz, CH_3), 28.06 (3×CH ring), 36.33 (d, $^2J_{CF}$=18.3 Hz, CCF), 36.97, 37.11, 37.31, 37.35, 37.48, 38.53 (6×CH_2 ring), 97.63 (d, $^1J_{CF}$=169.2 Hz, CF); MS (70 eV, EI): m/z (%)=169 (12%, M^+−CH), 168 (100), 154 (30), 139 (11), 133 (10), 125 (14), 119 (27), 112 (26), 11 (37), 109 (21), 108 (31), 107 (63), 106 (16), 105 (11), 99 (11), 98 (38), 97 (96), 96 (33), 95 (25), 94 (17), 93 (83), 92 (28), 91 (37), 85 (13), 81 (40), 80 (18), 79 (62), 78 (10), 77 (26), 68 (12), 67 (40), 65 (12), 59 (13), 55 (18), 53 (18).

4.2.6. 2-Fluoro-1,1-dimethylcyclohexane. To a suspension of magnesium (1.6 g, 67 mmol) in Et_2O (20 mL) was added dropwise a solution of 5-bromo-1-pentene (5.0 g, 53.5 mmol) in Et_2O (10 mL) and the mixture was stirred for 1 h. The resulting mixture was cooled at 0 °C, anhydrous acetone (3.7 mL, 30 mmol) was added and the resulting mixture was stirred for 1 h. After hydrolysis with water (40 mL), it was extracted with Et_2O (3×20 mL), the organic layer dried over $MgSO_4$ and the solvent evaporated at 15 Torr. The resulting oil was dissolved in hexane (20 mL) and the resulting solution was added to a 70% solution of HF in pyridine (10 mL) in a polyethylene flask. After 3 h stirring at −40 °C it was hydrolyzed with a saturated solution of $NaHCO_3$ (3×30 mL), extracted with hexane, and distilled in vacuo (15 Torr) to give the title compound (trapped at −78 °C) with 60% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H=0.89, 0.99 (2s, 6H, 2×CH_3), 1.16–1.48, 1.67–1.77, 1.89–2.03 (3m, 8H, 4×CH_2 ring), 4.53–4.80 (dm, $^1J_{HF}$=49.0 Hz, 1H, CHF); ^{13}C-NMR (75 MHz, $CDCl_3$): δ_C=19.68 (d, $^3J_{CF}$=9.8 Hz, CH_2CH_2CHF), 26.66, 31.72 (2C, 2×CH_3), 32.45 (d, $^2J_{C-F}$=18.5 Hz, CH_2CHF), 38.19 (d, $^4J_{CF}$=2.2 Hz, $CH_2CH_2CH_2$CHF), 44.89 (d, $^2J_{CF}$=16.4 Hz, CCHF), 90.60 (d, $^1J_{CF}$=168.0 Hz, CHF); MS (70 eV, EI) m/z (%)=130 (0.5%, M^+), 115 (29), 95 (100), 87 (20), 73 (19), 69 (20), 67 (16), 59 (11), 56 (20), 55 (28).

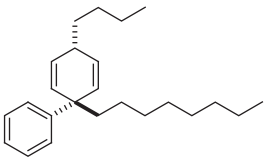
4.2.7. 6-Fluoro-6-methyl-1-heptene. The procedure was the same as described in Section 4.2.6 but the crude alcohols (after the Grignard reaction) were dissolved in triglyme (10 mL) and the resulting solution was added to (diethylamino)sulfur trifluoride (DAST; 1.8 mL, 15.28 mmol) at −30 °C and the mixture was stirred for 3 h at the same temperature. After hydrolysis with a saturated solution of $NaHCO_3$ (3×30 mL), it was extracted with hexane and distilled in vacuo (15 Torr) to give the title compound (trapped at −78 °C) with 40% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H=1.34 (d, $^3J_{H-F}$=21.6 Hz, 6H, 2×CH_3), 1.45–1.64, 1.57–1.64 (2m, 2H, CH_2CH_2CF), 2.07 (app

q, J=6.9 Hz, 2H, CH_2=CHCH_2), 4.93–5.06 (m, 2H, CH_2=CH), 5.74–5.86 (m, 1H, CH_2=CH); ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C=23.16 (CFCH_2CH_2), 26.60 (d, $^2J_{C-F}$=25.1 Hz, 2C, 2×CH_3), 33.89 (CH_2=CHCH_2), 40.80 (d, $^2J_{C-F}$=22.9 Hz, CH_2CF), 71.25 (d, $^1J_{C-F}$=99.3 Hz, CF), 114.70 (CH_2=CH), 138.51 (CH_2=CH); MS (70 eV): 130 (0.14%, M^+), 95 (75), 82 (12), 81 (18), 73 (27), 69 (53), 68 (13), 67 (18), 61 (100), 59 (14), 56 (70), 55 (47), 54 (68), 53 (14).

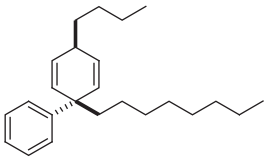
4.3. General procedure for the preparation of compounds 2d–k

To a stirred (rt, 30 min) greenish-blue suspension of a mixture of biphenyl (1 mmol) and lithium powder (12 mmol) in dry THF (10 mL) was added the corresponding alkyl fluoride (1.1 mmol) at 0 °C. After 30 min at the same temperature the mixture was cooled down to −78 °C. The second commercially available electrophile (1.1 mmol) was then added. After 15 min stirring, the resulting mixture was hydrolyzed with water (5 mL), allowing the temperature to rise to room temperature. The mixture was extracted with diethyl ether (3×20 mL), the organic layer dried over Na_2SO_4, and evaporated (15 Torr) to give a residue that was purified by column chromatography (silica gel, hexane/ethyl acetate). Yields of colorless liquid compounds **2** are given in Table 2; physical, analytical, and spectroscopic data for compounds **2d**–**k** follow, except for compounds *cis*- and *trans*-**2i**, which were fully described in the preliminary communication.[20]

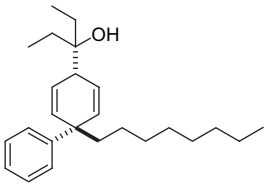
*4.3.1. cis-(4-Butyl-1-octylcyclohexa-2,5-dienyl)benzene (cis-**2d**).* t_R=14.11 min; IR (film): ν (cm^{-1})=30, 2926, 2854, 1492, 1465, 1377, 1115, 743, 697; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H=0.87 (t, J=6.9 Hz, 3H, CH_3CH$_2$), 0.90 (t, J=7.1 Hz, 3H, CH_3CH$_2$), 1.20–1.39 (m, 16H, 8×CH_2), 1.41–1.48 (m, 2H, CHCH_2), 1.74–1.81 (m, 2H, CCH$_2$), 2.65–2.72 [m, 1H, (CH=CH)$_2$CH], 5.59 [app dd, J=10.3, 1.9 Hz, 2H, (CH=CH)$_2$C(Ph)], 5.76 [app dd, J=10.3, 3.2 Hz, 2H, (CH=CH)$_2$CHCH$_2$CH$_2$], 7.13–7.19, 7.27–7.32, 7.34–7.39 (3m, 5H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C=14.03, 14.10 (2×CH_3), 22.66, 22.92, 24.86, 28.86, 29.37, 29.62, 30.30, 31.90 (8×CH_2), 35.39 (CHCH$_2$), 35.89 (CHCH_2), 40.21(CCH_2), 44.63 (CHPh), 125.70, 126.73 (2C), 128.15 (2C) (Ph), 128.34 [2C, (CH=CH)$_2$CH], 132.31[2C, (CH=CH)$_2$C], 148.22 (Ph); MS (70 eV, EI)=m/z (%): 326 (0.06%, M^++2), 325 (0.41, M^++1), 324 (1.60, M^+), 212 (16), 211 (93), 210 (12), 167 (14), 156 (13), 155 (100), 154 (16), 57 (36); HRMS: calcd for $C_{24}H_{36}$ 342.2817; found 324.2834.



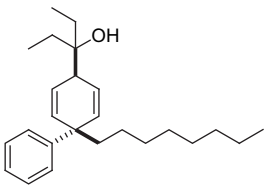
*4.3.2. trans-(4-Butyl-1-octylcyclohexa-2,5-dienyl)benzene (trans-**2d**).* t_R=14.18 min; IR (film): ν (cm^{-1})=3084, 3057, 3014, 2956, 2926, 2855, 1598, 1491, 1465, 1446, 1378, 1116, 1032, 925, 740, 697; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H=0.87 (t, J=6.9 Hz, 3H, CH_3CH$_2$), 0.91 (t, J=7.1 Hz, 3H, CH_3CH$_2$), 1.19–1.41 (m, 16H, 8×CH_2), 1.42–1.5 [m, 2H, (CH=CH)$_2$CHCH_2CH$_2$], 1.76–1.81 (m, 2H, CCH_2CH$_2$), 2.66–2.75 [m, 2H, (CH=CH)$_2$CHCH$_2$CH$_2$], 5.59 [app dd, J=10.3 Hz, J=2.0 Hz, 2H, (CH=CH)$_2$C(Ph)], 5.75 [dd, J=10.4 Hz, J=3.0 Hz, 2H, (CH=CH)$_2$CHCH$_2$CH$_2$], 7.13–7.19 (m, 1H, Ph), 7.26–7.32 (m, 2H, Ph), 7.33–7.39 (m, 2H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C=14.11 (2C, 2×CH_3), 22.67, 23.01, 25.46, 28.82, 29.33, 29.62, 30.28, 31.91 (8×CH_2), 35.18 (CHCH$_2$), 35.89 (CHCH_2), 39.85 (CCH_2), 44.52 (CHPh), 125.76, 126.62 (2C), 128.20 (2C) (Ph), 128.33 [2C, (CH=CH)$_2$CH], 132.38 [2C, (CH=CH)$_2$C], 148.22 (Ph); MS (70 eV, EI): m/z (%)=326 (0.06%, M^++2), 325 (0.37, M^++1), 1324 (1.44, M^+), 212 (17), 211 (99), 167 (11), 156 (13), 155 (100), 154 (14), 57 (30); HRMS: calcd for $C_{24}H_{36}$ 342.2817; found 324.2838.



*4.3.3. cis-3-(4-Octyl-4-phenylcyclohexa-2,5-dienyl)pentan-3-ol (cis-**2e**).* t_R=15.69 min; IR (film): ν (cm^{-1})=3478, 3023, 2961, 2927, 2854, 1492, 1462, 1446, 1378, 1123, 1032, 938, 831, 819, 799, 763, 698; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H=0.88 (t, J=7.0 Hz, 3H, CH_3CH$_2$CH$_2$), 0.89 (t, J=7.5 Hz, 6H, 2×CH$_2$CH_3), 1.18–1.33 (m, 12H, 6×CH_2), 1.46–1.63 (m, 5H, 2×CH_2CO, OH), 1.72–1.82 (m, 2H, CCH_2CH$_2$), 2.92–2.98 (m, 1H, CHCO), 5.81–5.91 [m, 4H, C(CH=CH)$_2$], 7.14–7.20, 7.27–7.33, 7.34–7.40 (3m, 5H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C=7.61 (2C), 14.11 (3×CH_3), 22.66, 24.76, 28.81, 29.34, 29.57, 30.20, 31.88, 41.18 (8×CH_2), 42.36 (CHCO), 44.43 (CPh), 124.27 [2C, (CH=CH)$_2$], 125.80, 126.47 (2C), 128.28 (2C) (Ph), 134.97 [2C, (CH=CH)$_2$], 147.89 (Ph); MS (70 eV, EI): m/z (%)=336 (<1%, M^+−18), 268 (20), 156 (13), 155 (82), 154 (43), 153 (10), 87 (100); HRMS: calcd for $C_{25}H_{36}$ 336.2817; found 336.2817.

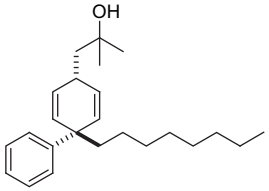


*4.3.4. trans-3-(4-Octyl-4-phenylcyclohexa-2,5-dienyl)pentan-3-ol (trans-**2e**).* t_R=15.84 min; IR (film): ν (cm^{-1})=3453, 3024, 2928, 2855, 1727, 1599, 1491, 1463, 1378, 1290, 1124, 1032, 938, 796, 762, 698; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H=0.87 (t, J=7.0 Hz, 3H, CH_3CH$_2$CH$_2$), 0.93 (t, J=7.5 Hz, 6H, 2×CH_2CH$_3$), 1.18–1.35 (m, 12H, 6×CH_2), 1.56–1.69 (2m, 5H, 2×CH_2CO, OH), 1.78–1.88 (m, 2H, CCH_2CH$_2$), 2.94–3.00 (m, 1H, CHCOH), 5.80 [app dd, J=10.7, 1.9 Hz, 2H, (CH=CH)$_2$C] 5.86 [dd, J=10.7 Hz, J=2.3 Hz, 2H, (CH=CH)$_2$CH], 7.12–7.20, 7.24–7.37 (2m, 5H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C=7.55 (2C), 14.08 (3×CH_3), 22.65, 25.36, 29.02, 29.25, 29.54, 30.23, 31.89, 40.29 (8×CH_2), 42.26 (CHCO), 44.39 (CPh), 123.95 [2C, (CH=CH)$_2$], 125.89, 126.59 (2C), 128.29 (2C) (Ph), 135.10 [2C, (CH=CH)$_2$], 147.48 (Ph); MS (70 eV, EI): m/z (%)=336 (3.90%, M^+−18), 307 (10), 268 (11), 223 (31), 181 (17), 167 (38), 156 (12), 155 (72), 154 (39), 153 (11), 87 (100), 69 (12), 57 (14); HRMS: calcd for $C_{25}H_{36}$ 336.2817; found 336.2796.

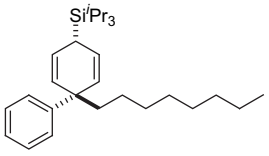


*4.3.5. cis-2-Methyl-1-(4-octyl-4-phenylcyclohexa-2,5-dienyl)propan-2-ol (cis-**2f**).* t_R=15.15 min; IR (film): ν (cm^{-1})=3383, 3057, 3018, 2959, 2927, 2854, 1491, 1466, 1446, 1377, 1223, 1130, 909, 764, 741, 697; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H=0.88 (t, J=6.6 Hz, 3H, CH_3CH$_2$), 1.19–1.37 (m, 13H, 6×CH_2, OH), 1.28 [s, 6H, (CH_3)$_2$CO], 1.62 [d, J=6.0 Hz, 2H, (CH$_2$CO)], 1.72–1.84 (m, 2H, CCH$_2$), 2.86–2.97 (m, 1H, CHCH$_2$CO), 5.59 [app dd, J=10.3, 1.7 Hz, 2H, (CH=CH)$_2$C], 5.89 [app dd, J=10.3, 3.4 Hz, 2H, (CH=CH)$_2$CH], 7.10–7.21, 7.25–7.40 (2m, 5H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C=14.11 (CH_3CH$_2$), 22.65, 24.92, 29.35, 29.60 (4×CH_2), 30.04 [2C, (CH_3)$_2$CO], 30.26, 31.88 (2×CH_2), 32.01 (CHCH$_2$), 40.28 (CCH_2), 44.12 (CPh), 50.00 (CH_2CO), 71.51

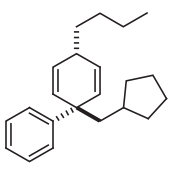
(CO), 125.77, 126.61 (2C), 128.22 [2C, (CH=*C*H)$_2$CH], 129.18 (2C, Ph), 131.92 [2C, (CH=*C*H)$_2$C], 147.94 (Ph); MS (70 eV, EI): *m*/*z* (%)=322 (1.92%, M$^+$−18), 210 (17), 209 (100), 168 (13), 167 (51); HRMS: calcd for $C_{24}H_{34}$ 322.2661; found 322.2657.



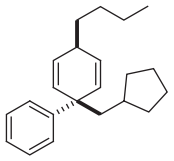
*4.3.6. cis-Triisopropyl(4-octyl-4-phenylcyclohexa-2,5-dienyl)silane (cis-**2g**).* t_R=16.77 min; IR (film): ν (cm^{-1})=3021, 2927, 2865, 1464, 1101, 1016, 902, 883, 761, 735, 698; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H=0.87 (t, *J*=6.7 Hz, 3H, C*H*$_3$CH$_2$), 1.00 [d, *J*=6.8 Hz, 18H, 3×SiCH(C*H*$_3$)$_2$], 1.05–1.14 [m, 3H, SiC*H*(CH$_3$)$_2$], 1.19–1.31 (m, 12H, 6×CH$_2$), 1.62–1.71 (m, 2H, CCH$_2$), 2.65–2.69 (m, 1H, C*H*Si^{i}Pr), 5.64 [app dd, *J*=10.4, 2.0 Hz, 2H, (CH=C*H*)$_2$C], 5.90 [app dd, *J*=10.4, 3.3 Hz, 2H, (CH=C*H*)$_2$CH], 7.10–7.16, 7.23–7.30, 7.31–7.36 (3m, 5H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C=11.07 [3C, Si*C*H(CH$_3$)$_2$], 14.13 (*C*H$_3$CH$_2$), 18.93 [6C, SiCH(*C*H$_3$)$_2$], 22.67, 25.15 (2×CH$_2$), 26.96 [SiCH(CH$_3$)$_2$], 29.38, 29.59, 30.24, 31.91 (4×CH$_2$), 43.62 (*C*Ph), 43.99 (C*C*H$_2$), 125.33, 126.08 (2C), 126.41 [2C, (CH=*C*H)$_2$CH], 127.95 (2C, Ph), 128.99 [2C, (CH=*C*H)$_2$C], 149.38 (Ph); MS (70 eV, EI): *m*/*z* (%)=267 (1.66%, M$^+$−Si^{i}Pr$_3$), 158 (15), 157 (100), 154 (14), 115 (46), 87 (17), 73 (19), 59 (23).



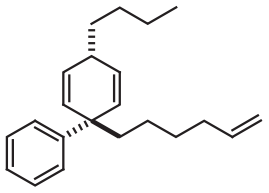
*4.3.7. cis-(4-Butyl-1-(cyclopentylmethyl)cyclohexa-2,5-dienyl)benzene (cis-**2h**).* t_R=13.38 min; IR (film): ν (cm^{-1})=3084, 3057, 3014, 2954, 2928, 2858, 1597, 1491, 1446, 1377, 1033, 952, 914, 743, 697; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H=0.88 (t, *J*=7.0 Hz, 3H, CH$_3$), 1.02–1.16 (m, 2H, 2×C*H*H cyclopentyl), 1.25–1.39 (m, 4H, C*H*$_2$C*H*$_2$CH$_3$), 1.40–1.50 (2m, 4H, CHC*H*$_2$, 2×C*H*H cyclopentyl), 1.51–1.63 (m, 2H, 2×C*H*H cyclopentyl), 1.72–1.85 [2m, 3H, 2×C*H*H cyclopentyl, CH$_2$C*H*(CH$_2$)$_2$], 1.92 (d, *J*=5.9 Hz, 2H, CCH$_2$), 2.68–2.76 [m, 1H, (CH=CH)$_2$C*H*CH$_2$], 5.66 [app dd, *J*=10.4, 1.9 Hz, 2H, (CH=C*H*)$_2$C], 5.75 [app dd, *J*=10.4, 3.2 Hz, 2H, (CH=C*H*)$_2$CH], 7.12–7.18, 7.26–7.32, 7.34–7.40 (3m, 5H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C=14.03 (CH$_3$), 22.91 (*C*H$_2$CH$_3$), 25.12 [2C, CH(CH$_2$*C*H$_2$)$_2$], 28.89 (CH$_2$), 34.80 [2C, CH(*C*H$_2$CH$_2$)$_2$], 35.34 [(CH=CH)$_2$*C*H], 35.90 (CH$_2$), 37.23 [CH$_2$*C*H(CH$_2$)$_2$], 44.91 [(CH=CH)$_2$*C*], 47.31 (C*C*H$_2$), 125.65 (Ph), 126.67 [2C, (CH=*C*H)$_2$CH], 128.05 (2C), 128.12 (2C) (Ph), 133.00 [2C, (CH=*C*H)$_2$*C*], 148.60 (Ph); MS (70 eV, EI): *m*/*z* (%)=296 (0.05%, M$^+$+2), 295 (9.91, M$^+$+1), 294 (0.97, M$^+$), 212 (14), 211 (84), 210 (14), 167 (11), 156 (13), 155 (100), 154 (17), 153 (10), 57 (25), 55 (11); HRMS: calcd for $C_{22}H_{30}$ 294.2348; found 294.2370.



*4.3.8. trans-(4-Butyl-1-(cyclopentylmethyl)cyclohexa-2,5-dienyl)benzene (trans-**2h**).* t_R=13.48 min; IR (film): ν (cm^{-1})=3016, 2952, 2927, 2857, 1491, 1445, 764, 740, 696; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H=0.91 (t, *J*=7.0 Hz, 3H, CH$_3$), 1.02–1.13 (m, 2H, 2×C*H*H cyclopentyl), 1.28–1.39 (m, 4H, C*H*$_2$C*H*$_2$CH$_3$), 1.40–1.50 (2m, 4H, CHC*H*$_2$, 2×C*H*H cyclopentyl), 1.51–1.62 (m, 2H, 2×C*H*H cyclopentyl), 1.74–1.86 [2m, 3H, 2×C*H*H cyclopentyl, CH$_2$C*H*(CH$_2$)$_2$], 1.91 (d, *J*=4.9 Hz, 2H, CCH$_2$), 2.65–2.75 [m, 1H, (CH=CH)$_2$C*H*CH$_2$], 5.67 [app dd, *J*=10.4, 2.0 Hz, 2H, (CH=C*H*)$_2$C], 5.74 [app dd, *J*=10.4, 2.7 Hz, 2H, (CH=C*H*)$_2$CH], 7.10–7.18, 7.24–7.32, 7.33–7.40 (3m, 5H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C=14.10 (CH$_3$), 23.01 (*C*H$_2$CH$_3$), 25.03 [2C, CH(CH$_2$*C*H$_2$)$_2$], 28.82 (CH$_2$), 34.84 [2C, CH(*C*H$_2$CH$_2$)$_2$], 35.12 [(CH=CH)$_2$*C*H], 35.87 (CH$_2$), 37.13 [CH$_2$*C*H(CH$_2$)$_2$], 44.90 [(CH=CH)$_2$*C*], 47.02 (C*C*H$_2$), 125.73 (Ph), 126.59 [2C, (CH=*C*H)$_2$CH], 128.04 (2C), 128.17 (2C) (Ph), 133.11 [2C, (CH=*C*H)$_2$C], 148.54 (Ph); MS (70 eV, EI): *m*/*z* (%)=296 (0.04%, M$^+$+2), 295 (0.29, M$^+$+1), 294 (1.21, M$^+$), 212 (15), 211 (86), 210 (10), 167 (12), 156 (13), 155 (100), 154 (18), 153 (10), 57 (25), 55 (11); HRMS: calcd for $C_{22}H_{30}$ 294.2348; found 294.2321.

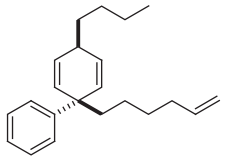


*4.3.9. cis-(4-Butyl-1-(hex-5-enyl)cyclohexa-2,5-dienyl)benzene (cis-**2j**).* t_R=13.48 min; IR (film): ν (cm^{-1})=3082, 3066, 3022, 2957, 2929, 2858, 1640, 1591, 1503, 1471, 1443, 995, 919, 761, 695; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H=0.88 (m, 3H, CH$_2$C*H*$_3$), 1.18–1.48 (2m, 10H, C*H*$_2$C*H*$_2$C*H*$_2$CH$_3$, CCH$_2$C*H*$_2$C*H*$_2$), 1.76–1.82 (m, 2H, CCH$_2$), 2.00–2.10 (m, 2H, C*H*$_2$CH=CH$_2$), 2.64–2.72 (m, 1H, C*H*CH$_2$), 4.89–5.03 (m, 2H, CH=C*H*$_2$), 5.58 [app dd, *J*=10.4, 1.9 Hz, 2H, (CH=C*H*)$_2$C], 5.77 [app dd, *J*=10.3, 3.3 Hz, 2H, (CH=C*H*)$_2$CH], 5.70–5.88 (m, 1H, C*H*=CH$_2$), 7.14–7.20, 7.27–7.39 (2m, 5H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C=14.05 (CH$_3$), 22.91 (CH$_3$*C*H$_2$), 24.42 (CCH$_2$*C*H$_2$), 28.84 (*C*H$_2$CH$_2$CH$_3$), 29.56 (*C*H$_2$CH$_2$CH=CH$_2$), 33.78 (*C*H$_2$CH=CH$_2$), 35.34 (CHCH$_2$), 35.86 (CH$_2$CH$_2$CH$_2$CH$_3$), 39.93 (CCH$_2$*C*H$_2$), 44.56 (*C*Ph), 114.14 (CH=*C*H$_2$), 125.74, 126.69 (2C), 128.17 (2C) (Ph), 128.43 [2C, (CH=*C*H)$_2$CH], 132.16 [2C, (CH=*C*H)$_2$C], 139.13 (*C*H=CH$_2$), 148.09 (Ph); MS (70 eV, EI): *m*/*z* (%)=296 (0.03%, M$^+$+2), 295 (0.21, M$^+$+1), 294 (0.91, M$^+$), 212 (15), 211 (89), 167 (25), 156 (13), 155 (100), 154 (14), 153 (10), 57 (27); HRMS: calcd for $C_{22}H_{30}$ 294.2348; found 294.2330.

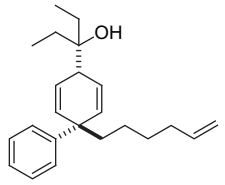


*4.3.10. trans-(4-Butyl-1-(hex-5-enyl)cyclohexa-2,5-dienyl)benzene (trans-**2j**).* t_R=13.62 min; IR (film): ν (cm^{-1})=3071, 3011, 2918, 2864, 1640, 1591, 1498, 1454, 1034, 913, 695; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H=0.92 (t, *J*=7.0 Hz, 3H, CH$_3$), 1.19–1.49 (2m, 10H, C*H*$_2$C*H*$_2$C*H*$_2$CH$_3$, CCH$_2$C*H*$_2$C*H*$_2$), 1.75–1.81 (m, 2H, CCH$_2$), 2.01–2.09 (m, 2H, C*H*$_2$CH=CH$_2$), 2.68–2.74 (m, 1H, C*H*CH$_2$), 4.92 (app d, *J*=10.1 Hz, 1H, CH=CH*H*), 4.98 (app d, *J*=17.0 Hz, 1H, CH=C*H*H), 5.59 [app dd, *J*=10.2, 2.0 Hz, 2H, (CH=C*H*)$_2$C(Ph)], 5.76 [app dd, *J*=10.2, 2.9 Hz, 2H, (CH=C*H*)$_2$CH], 5.74–5.86 (m, 1H, C*H*=CH$_2$), 7.14–7.18 (m, 1H, Ph), 7.27–7.37 (m, 4H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C=14.09 (CH$_3$), 22.97 (CH$_3$*C*H$_2$), 25.01 (CCH$_2$*C*H$_2$), 28.77 (CH$_2$CH$_2$CH$_3$), 29.54 (*C*H$_2$CH$_2$CH=CH$_2$), 33.82 (*C*H$_2$CH=CH$_2$), 35.15 [(CH=CH)$_2$*C*HCH$_2$], 35.84 (*C*H$_2$CH$_2$CH$_2$CH$_3$), 39.60 (C*C*H$_2$), 44.49

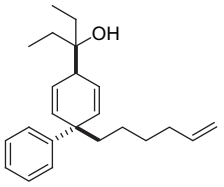
(*C*Ph), 114.19 (CH=*C*H$_2$), 125.79, 126.58 (2C), 128.21 (2C) (Ph), 128.43 [2C, (CH=*C*H)$_2$CH], 132.25 [2C, (CH=*C*H)$_2$C], 139.08 (*C*H=CH$_2$), 148.12 (Ph); MS (70 eV, EI): *m*/*z* (%)=296 (0.02%, M$^+$+2), 295 (0.21, M$^+$+1), 294 (0.90, M$^+$), 212 (15), 211 (88), 167 (25), 156 (13), 155 (100), 154 (13), 153 (10), 91 (10), 57 (25); HRMS: calcd for $C_{22}H_{30}$ 294.2348; found 294.2355.



*4.3.11. cis-3-(4-(Hex-5-enyl)-4-phenylcyclohexa-2,5-dienyl)pentan-3-ol (cis-**2k**).* t_R=14.57 min; IR (film): ν (cm^{-1})=3492, 3028, 2968, 2935, 2847, 1646, 1591, 1487, 1449, 1121, 914, 804, 761, 755; ^{1}H NMR (400 MHz, CDCl$_3$): δ_H=0.88 (t, *J*=7.5 Hz, 6H, 2×CH$_3$), 1.19–1.32 (m with a br s at 123, 3H, CCH$_2$*CH*$_2$, OH), 1.34–1.45 (m, 2H, *CH*$_2$CH$_2$CH=CH$_2$), 1.46–1.62 (m, 4H, 2×*CH*$_2$CH$_3$), 1.75–1.82 (m, 2H, CCH$_2$), 1.98–2.06 (m, 2H, *CH*$_2$CH=CH$_2$), 2.93–2.97 (m, 1H, CHCO), 4.92 (app d, *J*=10.2 Hz, 1H, CH=CH*H*), 4.98 (app d, *J*=17.0 Hz, 1H, CH=C*H*H), 5.74–5.85 (m, 1H, C*H*=CH$_2$), 5.83 [app dd, *J*=10.4, 1.7 Hz, 2H, (CH=C*H*)$_2$CH], 5.85 [app dd, *J*=10.8, 2.7 Hz, 2H, (CH=C*H*)$_2$C], 7.14–7.19, 7.27–7.39 (2m, 5H, Ph); ^{13}C NMR (100 MHz, CDCl$_3$): δ_C=7.60 (2C, 2×CH$_3$), 24.28 (CCH$_2$*CH*$_2$), 28.83 (2C, 2×*CH*$_2$CH$_3$), 29.46 (*CH*$_2$CH$_2$CH=CH$_2$), 33.70 (*CH*$_2$CH=CH$_2$), 40.97 (*CCH*$_2$), 42.35 (*CHCO*), 44.41 (*CO*), 114.18 (*CH*$_2$=CH), 124.39 [2C, (CH=*CH*)$_2$CH], 125.84, 126.45 (2C), 128.29 (2C) (Ph), 134.84 [2C, (CH=*CH*)$_2$C], 139.04 (*CH*=CH$_2$), 147.80 (Ph); MS (70 eV, EI): *m*/*z* (%)=308 (0.16%, M$^+$+2), 307 (1.18, M$^+$+1), 306 (4.77, M$^+$), 277 (10), 238 (11), 224 (12), 223 (64), 181 (36), 179 (15), 178 (13), 168 (15), 167 (85), 166 (10), 165 (20), 156 (12), 155 (81), 154 (46), 153 (20), 152 (19), 91 (10), 87 (100), 69 (20), 55 (14); HRMS: calcd for $C_{23}H_{30}$ 306.2348; found 306.2345.



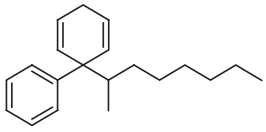
*4.3.12. trans-3-(4-(Hex-5-enyl)-4-phenylcyclohexa-2,5-dienyl)pentan-3-ol (trans-**2k**).* t_R=14.77 min; IR (film): ν (cm^{-1}) =3437, 3071, 3028, 2968, 2924, 2853, 1777, 1738, 1689, 1640, 1492, 1460, 1443, 1170, 1127, 935, 908, 793, 733, 695; ^{1}H NMR (400 MHz, CDCl$_3$): δ_H=0.94 (t, *J*=7.5 Hz, 6H, 2×CH$_3$), 1.18–1.35 (m with a br s at 1.32, 3H, CCH$_2$*CH*$_2$, OH), 1.36–1.45 (m, 2H, *CH*$_2$CH$_2$CH=CH$_2$), 1.50–1.67 (m, 4H, 2×*CH*$_2$CH$_3$), 1.80–1.86 (m, 2H, CCH$_2$), 2.00–2.08 (m, 2H, *CH*$_2$CH=CH$_2$), 2.95–2.99 (m, 1H, CHCO), 4.92 (app d, *J*=10.2 Hz, 1H, CH=CH*H*), 4.97 (app d, *J*=17.0 Hz, 1H, CH=C*H*H), 5.73–5.85 (m, 1H, C*H*=CH$_2$), 5.80 [app dd, *J*=10.6, 2.0 Hz, 2H, (CH=C*H*)$_2$CH], 5.86 [app dd, *J*=10.6, 2.5 Hz, 2H, (CH=C*H*)$_2$C], 7.15–7.20, 7.27–7.38 (2m, 5H, Ph); ^{13}C NMR (100 MHz, CDCl$_3$): δ_C=7.54 (2C, 2×CH$_3$), 24.93 (CCH$_2$*CH*$_2$), (2C, 2×*CH*$_2$CH$_3$), 29.49 (*CH*$_2$CH$_2$CH=CH$_2$), 33.77 (*CH*$_2$CH=CH$_2$), 40.07 (*CCH*$_2$), 42.22 (*CHCO*), 44.37 (*CO*), 114.30 (*CH*$_2$=CH), 124.05 [2C, (CH=*CH*)$_2$CH], 125.93, 126.46 (2C), 128.30 (2C) (Ph), 134.95 ((CH=*CH*)$_2$C), 138.98 (*CH*=CH$_2$), 147.39 (Ph); MS (70 eV, EI): *m*/*z* (%)=308 (0.13%, M$^+$+2), 307 (1.71, M$^+$+1), 306 (7.29, M$^+$), 277 (14), 224 (14), 223 (72), 207 (12), 181 (45), 179 (22), 178 (18), 168 (17), 167 (100), 166 (12), 165 (28), 156 (10), 155 (75), 154 (42), 153 (19), 152 (20), 115 (11), 91 (14), 87 (96), 69 (20), 57 (10), 55 (16).



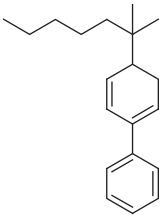
4.4. General procedure for the preparation of compounds 5a–d and 6a–c

Compounds **5a–d** and **6a–c** were synthesized as colorless liquids using the same procedure as for the above described compounds **2d–k**. Yields are given in Table 4; physical, analytical, and spectroscopic data follow.

*4.4.1. [1-(1-Methylheptyl)cyclohexa-2,5-dien-1-yl]benzene (**5a**).* R_f=0.64 (hexane); ^{1}H NMR (300 MHz, CDCl$_3$): δ_H=0.81 (d, *J*=6.7 Hz, 3H, CHC*H*$_3$), 0.86 (t, *J*=7.0 Hz, 3H, CH$_2$C*H*$_3$), 1.10–1.45 (m, 10H, 5×CH$_2$), 1.92–2.05 (m, 1H, C*H*CH$_3$), 2.52–2.73 [m, 2H, (CH=CH)$_2$C*H*$_2$], 5.71 [app dt, *J*=10.7, 1.7 Hz, 2H, (CH=C*H*)$_2$C], 5.86 [app t, *J*=10.9 Hz, 2H, (CH=C*H*)$_2$CH$_2$], 7.14–7.19, 7.27–7.35 (2m, 5H, Ph); ^{13}C NMR (75 MHz, CDCl$_3$): δ_C=14.10 (*C*H$_3$CH), 14.70 (*C*H$_3$CH$_2$), 22.65 (*C*H$_2$CH$_3$), 26.47 [(CH=CH)$_2$*C*H$_2$], 28.32, 29.51, 31.76, 31.89 (4×CH$_2$), 40.97 (*C*HCH$_3$), 48.10 (*C*Ph), 123.98, 124.55 [(CH=*C*H)$_2$CH$_2$], 125.45, 126.73 (2C), 128.19 (2C) (Ph), 131.10, 131.27 [2C, (CH=*C*H)$_2$C], 147.97 (Ph); MS (70 eV, IE): *m*/*z* (%)=269 (0.05%, M$^+$+1), 268 (0.17, M$^+$), 156 (13), 155 (100), 154 (15), 153 (12); HRMS: calcd for $C_{20}H_{28}$ 268.2191; found 268.2163.

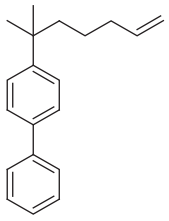


*4.4.2. [4-(1,1-Dimethylhexyl)-1,5-cyclohexadien-1-yl]-benzene (p-**6a**).* R_f=0.58 (hexane); IR (film): ν (cm^{-1}): 3031, 2971, 2925, 2851, 2804, 1936, 1622, 1602, 1502, 1475, 1375, 1355, 1168, 988, 794, 767, 714; ^{1}H NMR (300 MHz, CDCl$_3$): δ_H=0.64, 0.73 [2s, 2×3H, C(CH$_3$)$_2$], 0.83 (t, *J*=7.1 Hz, CH$_2$C*H*$_3$), 0.94–1.27 (m, 8H, 4×CH$_2$), 2.67–2.89 [m, 2H, C=CHC*H*$_2$], 3.30–3.38 [m, 1H, C*H*C(CH$_3$)$_2$], 5.92–5.98 [m, 3H, C*H*=C*H*(Ph)C=C*H*], 7.16–7.22, 7.25–7.32 (2m, 5H, Ph); ^{13}C NMR (75 MHz, CDCl$_3$): δ_C=14.1 (CH$_2$*C*H$_3$), 22.67, 23.48 (2×CH$_2$), 25.06, 26.28 (2×CCH$_3$), 28.44 (C=CHCH$_2$), 32.72 (CH$_3$*C*H$_2$), 40.56 [(CH$_3$)$_2$CCH$_2$], 41.20 [(CH$_3$)$_2$*C*CH$_2$], 46.16 [(CH$_3$)$_2$*C*CHCH=CH], 125.90 (Ph), 126.09 (*C*H=CPh), 126.09 (2C, Ph), 127.34 (*C*H=CHCPh), 128.10 (2C, Ph), 129.10 (CH=*C*HCPh), 140.59 (CH$_2$CH=*C*Ph), 145.89 (*C*$_{Ph}$); MS (70 eV, IE): *m*/*z* (%)=270 (0.04, M$^+$+2), 269 (0.36, M$^+$+1), 268 (1.54, M$^+$), 157 (20), 156 (100), 155 (100), 154 (100), 153 (31), 152 (18), 128 (12), 115 (11), 77 (19), 71 (33), 57 (32); HRMS: calcd for $C_{20}H_{28}$ 268.2191; found 268.2211.

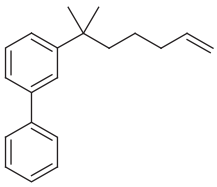


*4.4.3. 4-(1,1-Dimethylhex-5-en-1-yl)biphenyl (p-**6b**).* R_f=0.40 (hexane): IR (film): ν (cm^{-1})=3092, 3058, 3031, 2978, 2931, 2851,

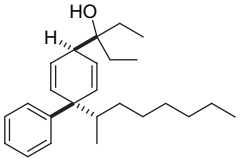
1629, 1589, 1482, 1368, 1255, 1088, 1014, 908, 827, 754, 727, 701; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H=1.14–1.26 (m, 2H, $CH_2CH_2CH_2$), 1.33 [s, 6H, $C(CH_3)_2$], 1.60–1.68 (m, 2H, CH_2C), 1.98 (app q, J=7.2 Hz, 2H, $CH_2CH{=}CH_2$), 4.91 (app d, 1H, J=10.2 Hz, CH=CH*H*), 4.95 (app d, 1H, J=17.1 Hz, CH=CH*H*), 5.74 (ddt, J=17.1, 10.2, 6.7 Hz, 1H, $CH{=}CH_2$), 7.32 (app t, J=7.4 Hz, 1H, Ar), 7.36–7.47 (m, 4H, Ar), 7.53 (app d, J=8.6 Hz, 2H, Ar), 7.60 (app d, J=8.2 Hz, 2H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C=24.09 ($CH_2CH_2CH{=}CH_2$), 28.96 [2C, $C(CH_3)_2$], 34.35 ($CH_2CH{=}CH_2$), 37.48 [$(CH_3)_2C$], 44.02 (CCH_2), 114.33 ($CH{=}CH_2$), 126.23 (2C, Ar), 126.69 (2C, Ar), 126.96 (Ar), 126.96 (2C, Ar), 128.67 (2C, Ar), 138.12 (Ar), 138.96 ($CH{=}CH_2$), 140.99 (Ar), 148.73 (Ar); MS (70 eV, IE): m/z (%)=266 (0.22%, M^++2), 265 (2.27, M^++1), 264 (10.06, M^+), 196 (16), 195 (100), 167 (18); HRMS: calcd for $C_{20}H_{24}$ 264.1878; found 264.1854.



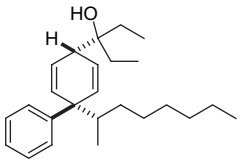
*4.4.4. 3-(1,1-Dimethylhex-5-en-1-yl)biphenyl (m-**6b**).* R_f=0.42 (hexane): IR (film): ν (cm^{-1})=3048, 2970, 2908, 2851, 1729, 1640, 1469, 1427, 1256, 1053, 1012, 913, 757; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H=1.17 (s, 6H, 2×CH_3), 1.35–1.44 (m, 4H, CH_2CH_2C), 1.88 (app q, J=7.1 Hz, 2H, $CH_2CH{=}CH_2$), 4.89 (app d, J=10.3 Hz, 2H, CH=CH*H*), 4.93 (app d, J=17.0 Hz, 2H, CH=CH*H*), 5.73 (ddt, J=17.0, 10.2 Hz, 6.7 Hz, 1H, $CH{=}CH_2$), 6.99 (app dd, J=7.5, 1.6 Hz, 1H, Ar), 7.16 (app dt, J=7.5, 1.2 Hz, 1H, Ar), 7.26–7.35 (m, 6H, Ar), 7.42 (app d, J=8.1 Hz, 1H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C=24.40 ($CH_2CH_2CH{=}CH_2$), 31.06 (2C, 2×CH_3), 34.20 ($CH_2CH{=}CH_2$), 39.67 [$(CH_3)_2C$], 43.21 (CCH_2), 114.17 ($CH{=}CH_2$), 124.82, 126.52, 127.04 (3C, Ar), 127.13 (2C, Ar), 127.56 (Ar), 129.66 (2C, Ar), 132.50 (Ar), 139.06 ($CH{=}CH_2$), 142.02, 145.16 (2C, Ar), 145.71 (Ar); MS (70 eV, IE): m/z (%)=264 (1.90%, M^+), 207 (10), 196 (19), 195 (100), 193 (13), 180 (13), 179 (20), 178 (17), 167 (22), 165 (29), 152 (10); HRMS: calcd for $C_{20}H_{24}$ 264.1878; found 264.1883.



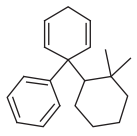
*4.4.5. 3-[cis-4-(1-Methylheptyl)-4-phenylcyclohexa-2,5-dien-1-yl]-pentan-3-ol (cis-**5b**).* IR (film): ν (cm^{-1})=3479 (br), 3082, 3057, 3027, 2962, 2929, 2855, 1597, 1491, 1460, 1446, 1377, 1322, 1267, 1237, 1153, 1125, 1034, 939, 910, 830, 795, 734, 700, 647; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H=0.78 (d, J=6.7 Hz, 3H, $CHCH_3$), 0.85 [t, J=7.5 Hz, 9H, $CH_2CH_2CH_3$, $OC(CH_2CH_3)_2$], 1.09–1.30 (m, 10H, 5×CH_2), 1.35 (br s, 1H, OH), 1.41–1.57 (m, 4H, 2×$OCCH_2CH_3$), 1.89–2.04 (m, 1H, $CHCH_3$), 2.93–2.96 (m, 1H, CHCO), 5.85–5.94 [m, 4H, $(CH{=}CH)_2$], 7.10–7.16, 7.24–7.32 (2m, 5H, Ph); ^{13}C NMR (100 MHz): δ_C=7.61, 7.61 (2C×CH_2CH_3), 14.09 ($CH_2CH_2CH_3$), 14.53 ($CHCH_3$), 22.64 (CH_2CH_3), 28.29 (CH_2), 28.80, 28.80 (2×CH_2CH_3), 29.44 (CH_2), 31.59 ($CHCH_2$), 31.87 (CH_2), 41.58 ($CHCH_2$), 42.82 (CHCO), 48.43 (CPh), 76.84 (CO), 124.94 (Ph), 125.48, 125.48 [2C, $(CH{=}CH)_2CH$], 126.70 (2C), 128.27 (2C) (Ph), 133.54, 133.54 [$(CH{=}CH)_2C$], 147.50 (Ph); MS: m/z (%)=354 (0.00%, M^+), 336 (0.17, M^+−18), 167 (10), 155 (71), 154 (73), 153 (17), 152 (11), 88 (14), 87 (100), 69 (13), 57 (24); HRMS: calcd for $C_{25}H_{36}$ 336.2817; found 336.2769.



*4.4.6. 3-[trans-4-(1-Methylheptyl)-4-phenylcyclohexa-2,5-dien-1-yl]pentan-3-ol (trans-**5b**).* IR (film): ν (cm^{-1})=3456 (br), 3030, 2965, 2924, 2858, 1639, 1598, 1491, 1468, 1444, 1367, 1148, 1119, 941, 799, 734, 692; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H=0.81 (d, J=6.8 Hz, 3H, $CHCH_3$), 0.85 (t, J=7.0 Hz, 3H, $CH_2CH_2CH_3$), 0.91 [t, J=7.5 Hz, 6H, $OC(CH_2CH_3)_2$], 1.18–1.42 (m, 10H, 5×CH_2), 1.30 (br s, 1H, OH), 1.56–1.68 [m, 4H, $OC(CH_2CH_3)_2$], 1.97–2.07 (m, 1H, $CHCH_3$), 2.85–2.89 (m, 1H, CHCOH), 5.85–5.95 [m, 4H, $(CH{=}CH)_2$], 7.13–7.18, 7.28–7.33 (2m, 5H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C=7.49, 7.49 (2×$CH_2CH_2CH_3$), 14.09 ($CH_2CH_2CH_3$), 15.22 ($CHCH_3$), 22.65, 28.21 (2×CH_2), 29.15, 29.15 (2×CCH_2CH_3), 29.46 (CH_2), 31.79 ($CHCH_2$), 32.39 (CH_2), 40.77 ($CHCH_3$), 42.48 (CHCO), 48.47 (CPh), 76.25 (CO), 124.92 (Ph), 125.39, 125.63 [2C, $(CH{=}CH)_2CH$], 126.63 (2C), 128.34 (2C) (Ph), 133.08, 133.21 [$(CH{=}CH)_2C$], 147.36 (Ph); MS (70 eV, IE): m/z (%)=336 (0.11%, M^+−18), 155 (21), 154 (22), 87 (100), 57 (12).

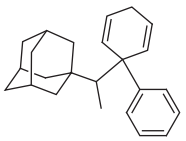


*4.4.7. (1-(2,2-Dimethylcyclohexyl)cyclohexa-2,5-dienyl)benzene (**5c**).* IR (film): ν (cm^{-1}): 3032, 2925, 2851, 1742, 1602, 1495, 1455, 1362, 1028, 954, 908, 727, 694; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H=0.84, 0.90 (2s, 6H, 2×CH_3), 1.18–1.45 (m, 8H, 4×CH_2), 1.97–2.10 [m, 1H, $CHC(CH_3)_2$], 2.58–2.64 [m, 2H, $(CH{=}CH)_2CH_2$], 5.67–5.78 [m, 2H, $(CH{=}CH)_2C$], 5.81–5.93 [m, 2H, $(CH{=}CH)_2CH_2$], 7.12–7.19, 7.28–7.34 (2m, 5H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C=22.72 (CH_2), 24.52 (CH_3), 26.45 [$(CH{=}CH)_2CH_2$], 27.72 (CH_2), 31.08 [$CH_2CH_2C(CH_3)_2$], 33.61 (CH_3), 39.41 (CH_2), 41.77 (CCH), 46.81 [$C(CH_3)_2$], 46.94 (CPh), 124.08, 124.54 [2C, $(CH{=}CH)_2CH_2$], 125.43, 126.68 (2C), 128.30 (2C) (Ph), 131.25, 131.60 [$(CH{=}CH)_2C$], 147.57 (Ph); MS (70 eV, IE): m/z (%): 268 (0.03%, M^++2), 267 (0.10, M^++1), 266 (0.45, M^+), 156 (14), 155 (100), 154 (43), 153 (10); HRMS: calcd for $C_{20}H_{26}$ 266.2034; found 266.2022.

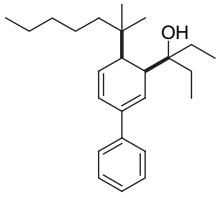


*4.4.8. 1-[1-(1-Phenylcyclohexa-2,5-dien-1-yl)ethyl]adamantane (**5d**).* IR (film): ν (cm^{-1})=3025, 2926, 2859, 1716, 1609, 1495, 1454, 1382, 1355, 1028, 1355, 1029, 908, 834, 761, 699; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H=0.87 (m, 3H, CH_3), 1.20–1.70 (m, 15H, 6×CH_2, 3×CH adamantyl), 1.99–2.12 (m, 1H, $CHCH_3$), 2.62–2.71 [m, 2H, $CH_2(CH{=}CH)_2$], 5.64–5.85 [m, 4H, $CH_2(CH{=}CH)_2$], 7.12–7.35 (m, 5H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C=14.02 (CH_3), 22.74, 22.89 (2×CH_2), 24.52 (CH adamantyl), 27.67, 28.74 (2 ×CH_2), 31.08 (C adamantyl), 33.63 (CH adamantyl), 35.49 [$CH_2(CH{=}CH)_2$], 35.75 (CH adamantyl), 39.49, 40.37 (2×CH_2 adamantyl), 41.62 ($CHCH_3$),

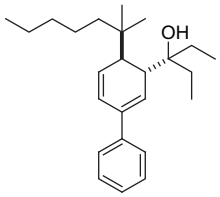
47.54 (*C*Ph), 125.37, 126.75 (2C), 128.19 (2C) (Ph), 129.03, 129.58 [$CH_2(CH{=}CH)_2$], 130.43, 131.23 [$C(CH{=}CH)_2$], 147.49 (Ph).



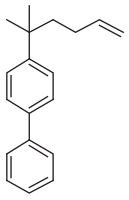
*4.4.9. 3-[cis-6-(1,1-Dimethylhexyl)-3-phenylcyclohexa-2,4-dien-1-yl]pentan-3-ol (cis-**6b**).* IR (film): ν (cm^{-1})=3476 (br), 3030, 2952, 2926, 2864, 1734, 1604, 1490, 1464, 1386, 1360, 1262, 945; ^1H NMR (300 MHz, $CDCl_3$): δ_H=0.83, 0.87 (2s, 6H, 2×CCH_3), 0.86–0.92 (2m, 6H, $OCCH_2CH_3$, $CH_2CH_2CH_3$), 0.97 (t, *J*=7.5 Hz, 3H, $OCCH_2CH_3$), 1.18–1.38 (m, 9H, 4×CH_2, OH), 1.50–1.70 [m, 4H, $OC(CH_2CH_3)_2$], 2.40 [d, *J*=6.1 Hz, 1H, $CHC(CH_3)_2$], 2.58 [d, *J*=6.3 Hz, 1H, CHCO], 5.80 [d, *J*=7.4 Hz, 1H, (C=*CH*CHCOH)], 5.99 (dd, *J*=9.9, 5.9 Hz, 1H, PhCCH=*CH*CH), 6.30 (d, *J*=9.9 Hz, 1H, PhCC*H*=CH), 7.18–7.43 (m, 5*H*, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C=7.55, 7.95 (2×CH_2CH_3), 14.15 ($CH_2CH_2CH_3$), 22.74, 23.60 (2×CH_2), 24.04, 24.15 (2×CCH_3), 27.08, 27.92 (2×CH_2), 32.97 (CH_2), 38.79 [$C(CH_3)_2$], 39.03 (CH_2), 40.24 (*C*HCO), 40.24 [*C*H$C(CH_3)_2$], 78.90 (CO), 123.27 (PhC=*C*HCHCOH), 124.87 (PhCCH=CH), 125.47 (2C), 127.02, 128.40 (2C) (Ph), 130.85 (PhCCH=*C*HCH), 135.85 (Ph*C*), 140.83 (Ph); MS (70 eV, IE): *m*/*z* (%)=336 (0.42%, M^+−18), 167 (11), 156 (71), 155 (74), 154 (85), 153 (14), 87 (100), 71 (32), 69 (13), 57 (51); HRMS: calcd for $C_{25}H_{36}$ 336.2817; found 336.2823.



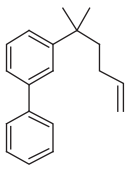
*4.4.10. 3-[trans-6-(1,1-Dimethylhexyl)-3-phenylcyclohexa-2,4-dien-1-yl]pentan-3-ol (trans-**6b**).* IR (film): ν (cm^{-1})=3445 (br), 3035, 2952, 2932, 2859, 1656, 1588, 1459, 1376, 1148; ^1H MRN (400 MHz, $CDCl_3$): δ_H=0.64, 0.72 (2s, 6H, 2×CCH_3), 0.84 (t, *J*=7.3 Hz, 3H, $CH_2CH_2CH_3$), 0.89 (t, *J*=7.5 Hz, 3H, $OCCH_2CH_3$), 0.90 (t, *J*=7.3 Hz, 3H, $OCCH_2CH_3$), 0.94–1.27 (m, 8H, 4×CH_2), 1.32 (br s, 1H, OH), 1.45–1.65 [m, 4H, $OC(CH_2CH_3)_2$], 2.95–3.01 (m, 1H, *CH*COH), 3.32 [app t, *J*=5.3 Hz, 1H, $CHC(CH_3)_2$], 5.93–6.06 [m, 3H, *CH*=*CH*(Ph)C=*CH*], 7.17–7.22, 7.26–7.34 (2m, 5H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C=7.45, 7.45 (2×$OCCH_2CH_3$), 14.08 ($CH_2CH_2CH_3$), 22.66, 23.45 (2×CH_2), 25.24, 26.44 (2×CCH_3), 29.23, 29.29 (2×CH_2CH_3), 32.68 (CH_2), 40.66 [$(CH_3)_2C$], 41.16 (CH_2), 44.14 (*C*HCO), 46.42 [*C*H$C(CH_3)_2$], 76.01(CO), 126.17, 126.31 (2C) (Ph), 126.89 (PhC=*C*HCH), 128.09 (2C) (Ph), 128.46 (PhCCH=*C*HCH), 130.06 (PhC*C*H=CH), 141.40 (Ph*C*), 145.91 (Ph); MS (70 eV, IE): *m*/*z* (%)=336 (0.01%, M^+−18), 156 (46), 155 (30), 154 (51), 153 (12), 87 (100), 71 (16), 69 (10), 57 (28).



*4.4.11. 4-(1,1-Dimethylpent-4-en-1-yl)biphenyl (p-**6c**).* R_f=0.35 (hexane); IR (film): ν (cm^{-1})=3069, 3027, 2965, 2918, 2845, 1640, 1609, 1484, 1370, 1313, 1110, 1006, 918, 851, 767, 736; ^1H NMR (300 MHz, $CDCl_3$): δ_H=1.35 (s, 6H, 2×CH_3), 1.70–1.78 [m, 2H, $CH_2C(CH_3)_2$], 1.81–1.91 (m, 2H, $CH_2CH{=}CH_2$), 4.89 (app d, *J*=10.2 Hz, 1H, CH=CH*H*), 4.95 (app dd, *J*=17.2, 1.6 Hz, 1H, CH=CH*H*), 5.77 (ddt, *J*=17.3, 10.3, 6.4 Hz, 1H, $CH{=}CH_2$), 7.28–7.36, 7.37–7.47, 7.51–7.63 (3m, 9H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C=28.91 (2C, 2×CH_3), 29.22 ($CH_2CH{=}CH_2$), 37.46 [$(CH_3)_2C$], 43.59 [$(CH_3)_2CCH_2$], 113.86 ($CH{=}CH_2$), 126.24, 126.75, 126.96, 128.68, 138.24 (Ar), 139.29 ($CH{=}CH_2$), 140.96, 148.35 (Ar); MS (70 eV, IE): *m*/*z* (%)=253 (0.04%, M^++3), 252 (0.64%, M^++2), 251 (6.15%, M^++1), 250 (30.70%, M^+), 196 (35), 195 (100), 194 (8), 181 (9), 179 (13), 178 (22), 167 (41), 165 (19), 155 (14), 152 (14); HRMS: calcd for $C_{19}H_{22}$ 250.1721; found 250.1736.



*4.4.12. 3-(1,1-Dimethylpent-4-en-1-yl)biphenyl (m-**6c**).* R_f=0.33 (hexane): IR (film): ν (cm^{-1})=3058, 2958, 2918, 2845, 1642, 1475, 1262, 1008, 908, 761, 701; ^1H NMR (300 MHz, $CDCl_3$): δ_H=1.20 (s, 6H, 2×CH_3), 1.46–1.55 [m, 2H, $CH_2C(CH_3)_2$], 1.76–1.86 (m, 2H, $CH_2CH{=}CH_2$), 4.81–4.94 (2m, 2H, CH=CH_2), 5.68 (ddt, *J*=17.0, 10.4, 6.1 Hz, 1H, $CH{=}CH_2$), 7.0 (app dd, *J*=7.5, 1.5 Hz, 1*H*, Ar), 7.17 (app dt, *J*=7.4, 1.1 Hz, 1H, Ar), 7.22–7.36, 7.39–7.46, 7.50–7.63 (3m, 7H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C=29.42 ($CH_2CH{=}CH_2$), 30.99 (2C, 2×CH_3), 39.63 [$(CH_3)_2C$], 42.48 [$(CH_3)_2CCH_2$], 113.71 ($CH{=}CH_2$), 124.94, 126.56, 127.08 (Ar), 127.15 (2C, Ar), 127.55, 129.68 (2C), 132.56 (Ar), 139.14 ($CH{=}CH_2$), 142.09, 145.03, 145.29 (Ar); MS (70 eV, IE): *m*/*z* (%)=252 (0.06%, M^++2), 251 (0.72, M^++1), 250 (3.10, M^+), 196 (19), 195 (100), 194 (10), 193 (11), 180 (12), 179 (26), 178 (22), 167 (25), 166 (10), 165 (32), 152 (10); HRMS: calcd for $C_{19}H_{22}$ 250.1721; found 250.1721.



Acknowledgements

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References and notes

1. Meerholz, K.; Heinze, J. *J. Am. Chem. Soc.* **1989**, *111*, 2325–2326.
2. This has resulted in numerous synthetic applications: Yus, M. In *The Chemistry of Organolithium Compounds*; Rappoport, Z., Marek, I., Eds.; Wiley: Chichester, UK, 2004; Vol. 1, Part 2, pp 657–747.
3. Rees, N. V.; Baron, R.; Kershaw, N. M.; Donohoe, T. J.; Compton, R. G. *J. Am. Chem. Soc.* **2008**, *130*, 12256–12257.
4. *CRC Handbook of Chemistry and Physics*, 85th ed.; Lide, Dr., Ed.; CRC: Boca Raton, FL, 2004; pp 8–33.
5. For reduction potentials of Li (a) A reported half-peak potential for the pair $Li_{(s)}$/$Li^+_{(THF)}$ in THF is found, $E_{1/2(Li/Li^+)}$=−3.07 V, in THF/$LiBPh_4$ versus Ag/AgCl: Mortensen, J.; Heinze, J. *Tetrahedron Lett.* **1985**, *26*, 415–418; (b) The formal $Li_{(s)}$/$Li^+_{(THF)}$ potential in THF was measured recently, E^f_0=−3.48 V versus Fc/

$Fc^{+}PF^{6-}$: Paddon, C. A.; Ward Jones, S. E.; Bhatti, F. L.; Donohoe, T. J.; Compton, R. G. *J. Phys. Org. Chem.* **2007**, *20*, 677–684.
6. E°_1 for biphenyl is some 0.15 V higher than that of naphthalene ($C_{10}H_8$, $E^{\circ}_1=-2.53$ V, E°_2=beyond the experimental limit), which on the other hand holds the highest—yet to be measured—second reduction potential E°_2: See reference 1.
7. Eisch, J. J. *J. Org. Chem.* **1963**, *28*, 707–710.
8. Takahashi, C.; Maeda, S. *Chem. Phys. Lett.* **1974**, *24*, 584–588.
9. Huber, W.; May, A.; Muellen, K. *Chem. Ber.* **1981**, *114*, 1318–1336.
10. (a) Sidorov, A. N. *Opt. Spektrosk.* **1979**, *47*, 678–683; *Chem. Abstr.* **1980**, *92*, 110107; (b) Devlin, J. P.; McKennis, J. S.; Thornton, C.; Moore, J. C. *J. Phys. Chem.* **1982**, *86*, 2613–2616.
11. (a) Herrera, R. P.; Guijarro, A.; Yus, M. *Tetrahedron Lett.* **2001**, *42*, 3455–3458; (b) Herrera, R. P.; Guijarro, A.; Yus, M. *Chem.—Eur. J.* **2002**, *8*, 2574–2584.
12. Melero, C.; Guijarro, A.; Yus, M. *Dalton Trans.* **2009**, 1286–1289.
13. The actual extent to which this reduction takes place (i.e., the concentration of the dianion in Scheme 1) has not been established quantitatively. The dynamics of these heterogeneous equilibria depend on a number of variables including, in addition to the reduction potentials of biphenyl (E°_1, E°_2) and lithium ($E^{\circ}_{(Li/Li+)}$) in THF,[5] the stabilization due to ion-pairing equilibria of the dissolved species, the solvent, the concentration and the temperature, all of which can be further complicated by the appearance of new phases. Disproportionation equilibria are profoundly affected by the medium (e.g., by small changes in the solvent; Levin, G.; Holloway, B. E.; Szwarc, M. *J. Am. Chem. Soc.* **1976**, *98*, 5706–5709), and the complex kinetics inherent to heterogeneous ET processes on metal surfaces along with the intrinsic high reactivity of the species involved makes difficult the determination of the actual composition of the reaction media. For all this, in addition to spectroscopic claims, we included available electrochemical data on the generation of biphenyl dianion, so the arguments concerning the generation and stability of some of these highly reduced species do not rest exclusively on spectroscopic grounds.
14. Casanova, J.; Eberson, L. In *Chemistry of the Carbon–Halogen Bond*; Patai, S., Ed.; Interscience: New York, NY, 1974; Chapter 15, p 982.
15. (a) Garst, J. F.; Ayers, P. W.; Lamb, R. C. *J. Am. Chem. Soc.* **1966**, *88*, 4260–4261; (b) Sargent, G. D.; Cron, J. N.; Bank, S. *J. Am. Chem. Soc.* **1966**, *88*, 5363–5364; (c) Bank, S.; Juckett, D. A. *J. Am. Chem. Soc.* **1975**, *97*, 567–573; (d) Bank, S.; Juckett, D. A. *J. Am. Chem. Soc.* **1976**, *98*, 7742–7746.
16. (a) Garst, J. F. *Acc. Chem. Res.* **1971**, *4*, 400–406; (b) Garst, J. F.; Barton, F. E., II. *Tetrahedron Lett.* **1969**, 587–590; (c) Garst, J. F.; Barton, F. E., II. *J. Am. Chem. Soc.* **1974**, *96*, 523–529.
17. Eberson, L. *Acta Chem. Scand., B* **1982**, *36*, 533–543.
18. Hush, N. S. *Z. Elektrochem.* **1957**, *61*, 734–738.
19. Herrera, R. P.; Guijarro, A.; Yus, M. *Tetrahedron Lett.* **2003**, *44*, 1309–1312.
20. Melero, C.; Perez, H.; Guijarro, A.; Yus, M. *Tetrahedron Lett.* **2007**, *48*, 4105–4109.
21. (a) Melero, C.; Guijarro, A.; Baumann, V.; Perez-Jimenez, A. J.; Yus, M. *Eur. J. Org. Chem.* **2007**, 5514–5526; (b) Melero, C.; Guijarro, A.; Yus, M. *Tetrahedron Lett.* **2006**, *47*, 6267–6271.
22. Melero, C.; Herrera, R. P.; Guijarro, A.; Yus, M. *Chem.—Eur. J.* **2007**, *13*, 10096–10107.
23. Dewar, M. J. S.; Dougherty, R. C. *The PMO Theory of Organic Chemistry*; Plenum: New York, NY, 1975; Chapter 7.7.
24. (a) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317–323; (b) Lusztyuk, J.; Maillard, B.; Deycard, S.; Lindsay, D. A.; Ingold, K. U. *J. Org. Chem.* **1987**, *52*, 3509–3514; (c) Chatgilialoglu, C.; Dickhaut, J.; Giese, B. *J. Org. Chem.* **1991**, *56*, 6399–6403.
25. The reaction has an identical outcome in the case of secondary alkyl fluorides, affording products **5a**–**e**, while the regiochemistry of alkylation switches to 4-alkyl-3-substituted-1,4-dihydrobiphenyls (**6a**–**c**) for tertiary alkyl fluorides, which are obtained in lower yields. As a whole, it should be emphasized that using this methodology biphenyl is partially dearomatized and doubly derivatized in a one pot reaction.
26. Flosser, D. A.; Olofson, R. A. *Tetrahedron Lett.* **2002**, *43*, 4275–4279.
27. Olah, G. A.; Nojima, M.; Kerekes, I. *Synthesis* **1973**, 786–787.
28. (a) Isogai, K.; Nishizawa, N.; Saito, T.; Sakai, J.-i. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1555–1556; (b) Dax, K. *Science of Synthesis*; George Thieme Verlag: Stuttgart, 2006; Vol. 34, pp 71–148.
29. Lettre, H.; Woelke, U. *Justus Liebigs Ann. Chem.* **1967**, *708*, 75–85.
30. (a) Sorochinskii, A. E.; Aleksandrov, A. M.; Gamaleya, V. F.; Kukhar, V. P. *Zh. Org. Khim.* **1981**, *17*, 1642–1648; *Chem. Abstr.* **1981**, *95*, 186706; (b) Stulgies, B.; Prinz, P.; Magull, J.; Rauch, K.; Meindl, K.; Ruchl, S.; de Meijere, A. *Chem.—Eur. J.* **2005**, *11*, 308–320.