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Carbolithiation of Simple Terminal and Strained Internal Alkenes by the Naphthalene and the Biphenyl Dianion: New Modes of Reactivity of Highly Reduced Organic Species in Solution

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Dianions derived from arenes of high reduction potential (biphenyl, naphthalene) and $Li_{(s)}$ can carbometallate propene, isobutene or norbornene among other alkenes, in an intermolecular fashion. This reaction runs at room temperature to afford partially dearomatized alkylated aryl anions that are susceptible to further functionalization by electrophilic capture. This form of reactivity, typical of the arene dianion, deviates from the specific alkali metal-like reactivity displayed by these complexes, affording regio- and in many cases stereo-controlled products. DFT calculations help to figure out the regiochemical outcome of this reaction, where some of the most inexpensive organic starting materials are involved. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2007)

Introduction

The carbolithiation of alkenes is a synthetically useful strategy that allows the formation of a new carbon–carbon bond, while at the same time a new organolithium center is generated. This provides the opportunity of further processing of the molecule by electrophilic capture, making the whole one-pot process especially attractive. In practice, most carbolithiations described in the literature are of the *intramolecular* type, often taking advantage of favorable 5-*exo-trig* cyclizations as a main reaction pathway.[1] *Intermolecular* carbolithiations remain, otherwise, much more uncommon. They are restricted to the use of alkenes activated by conjugation or by other carbanion-stabilizing substituents,[2] as well as the carbolithiation of ethylene.[3] However, so far no nucleophilic addition of an organoalkali compound to propene or isobutene has ever been reported under mild conditions.

With the exception of benzene, which does not form its radical anion in a synthetically significant concentration in most solvents, arenes of less negative reduction potential do form complexes with alkali metals in ethereal solvents. In the case of lithium, complexes with naphthalene or 4,4′-di-*tert*-butylbiphenyl are well shifted to the right and have seen much success as reductive-cleaving reagents, giving rise to a variety of organolithium compounds used in preparative organic chemistry.[4,5] We focused recently our attention on the differences in reactivity between the different species postulated as coexisting in these solutions, namely the radical anion ($LiC_{10}H_8$) and dianion ($Li_2C_{10}H_8$) in the case of naphthalene, in relation to their roles in the mechanism of the arene-catalyzed lithiations.[6] For instance, both $LiC_{10}H_8$ as well as $Li_2C_{10}H_8$ display an ET reactivity profile before alkyl chlorides, generating high yields of organolithium compounds.[7] Intrinsically different electronic configurations between radical-anions and dianions (with an open and closed shell, respectively) anticipate, however, the occurrence of a markedly different reactivity when substrates are appropriately chosen. Among the reagents that are capable of discriminating between both kind of reagents, we found the case of low-strained cyclic ethers.[6] It is also the case of many arene dianions reacting with alkyl fluorides as alkylating reagents, since the corresponding radical anions remain unreactive under identical conditions,[8] except for a few arenes of very high reduction potential. In this article we would like to present the reaction of lithium dianions of three common aromatic hydrocarbons, biphenyl (**1**), naphthalene (**2**) and, to a lesser extent, phenanthrene (**3**), with terminal non-functionalized alkenes, as well as with one example of a strained internal alkene. This reaction affords, after electrophilic quenching, regiochemically functionalized alkylated dihydroarenes through an intermolecular carbolithiation as the key step of the synthesis.[9] It is also

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an additional example of a specific reaction of the dianions of arene, since the corresponding radical anions remain unreactive under identical reaction conditions (see below).

Results and Discussion

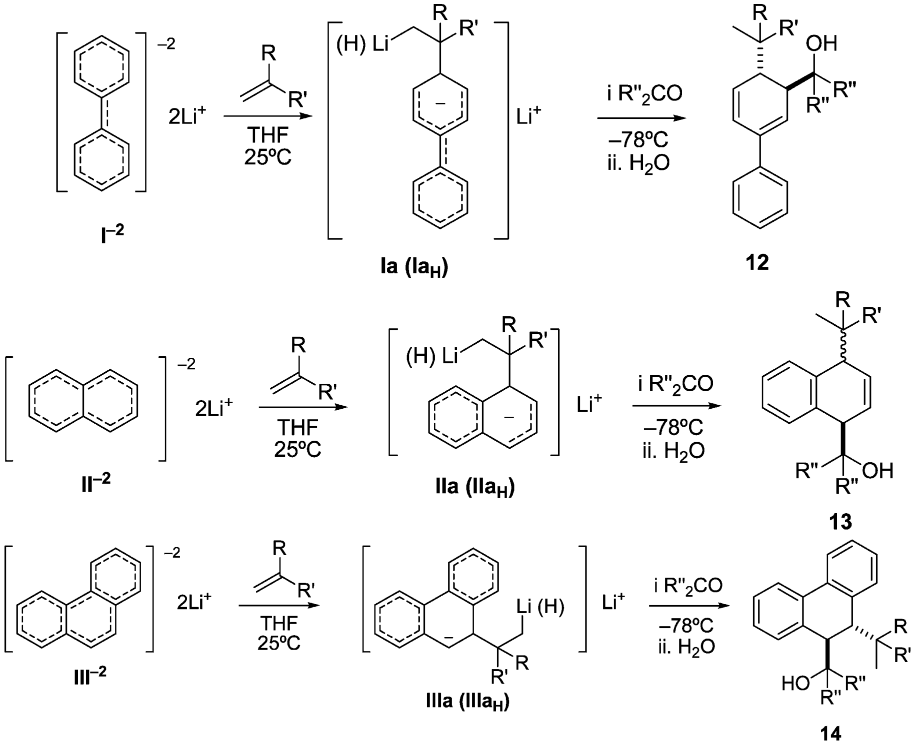
Arene dianions of high reduction potential arenes are exceedingly reactive and rather elusive species. Previous descriptions of the arene dianions employed in this work were done in more or less depth elsewhere. Dilithionaphthalene (**II-Li$_2$**) was prepared by double deprotonation of 1,4-dihydronaphthalene and crystallized as a dilithium salt coordinated with TMEDA, its structure being determined by X-rays diffraction.[10] Low-temperature ^{1}H- and ^{13}C-NMR spectra of dilithiophenanthrene (**III-Li$_2$**) have been reported.[11,15] For dilithiobiphenyl (**I-Li$_2$**) one ^{1}H- and ^{13}C-NMR spectrum at –70 °C was also reported,[12] as well as the UV and IR spectra of sublimed layers.[13] In addition to spectroscopic claims, there is electrochemical evidence in the literature on the generation of the dianions **I^{-2}** and **III^{-2}**, so the arguments concerning the generation and stability of some of these highly reduced species do not rest exclusively on spectroscopic grounds. Biphenyl (**1**) has the highest reduction potential ($E°_1$ = –2.68 V, $E°_2$ = –3.18 V) followed by naphthalene (**2**) ($E°_1$ = –2.53 V) and phenanthrene (**3**) ($E°_1$ = –2.49 V, $E°_2$ = –3.13 V), all vs. Ag/AgCl under identical experimental conditions by cyclic voltammetry.[14] Interestingly, the second-reduction-wave does not follow the same sequence. The biphenyl dianion (**I^{-2}**, $C_{12}H_{10}^{-2}$) is formed at a less negative cathodic potential than the corresponding dianion of naphthalene (**II^{-2}**, $C_{10}H_8^{-2}$), for which the second reduction potential is beyond the cathodic limit. The effect could be interpreted as an attainment of the Hückel aromatic character of **I^{-2}**, the opposite being true for **II^{-2}** (and phenanthrene dianion $C_{14}H_{10}^{-2}$, **III^{-2}**). This has been observed also as a paratropic NMR shift in the ^{1}H NMR spectrum of **III-Li$_2$** (and other dianions derived from larger, more easily reducible polycyclic aromatic hydrocarbons of benzenoid structure)[15] which is not ascribed solely to electronic shielding.

We have observed previously that, in the presence of an excess of Li$_{(s)}$, **2** is doubly reduced in THF (or better in THP) to its dianion, **II-Li$_2$**, to a certain extent.[6,7] Based on reduction potential criteria,[14] the remaining arenes are also expected to be reduced to the corresponding dianion under the same conditions according to Equation (1).

$$\mathrm{Arene_{(THF)}} \overset{\mathrm{Li_{(s)}}}{\rightleftharpoons} \mathrm{Arene^{-\bullet}\,Li^{+}_{(THF)}} \overset{\mathrm{Li_{(s)}}}{\rightleftharpoons} \underset{\textbf{I, II or III}}{\mathrm{Arene^{-2}}}\ \mathrm{2\,Li^{+}_{(THF)}} \tag{1}$$

The proposed reaction scheme for the species **I-Li$_2$**, **II-Li$_2$** and **III-Li$_2$** with terminal alkenes followed by electrophilic capture is described in Scheme 1.

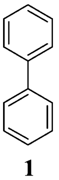
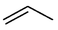
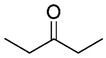
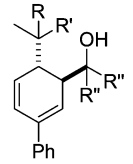
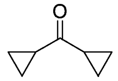
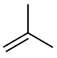
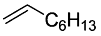
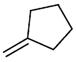
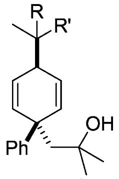
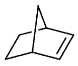
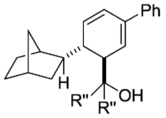
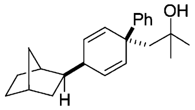
The reactions described in Scheme 1 were carried out using simple equipment in a one-pot fashion. The carbolithiation step can be followed appropriately by change in color: the arene dianion changes from greenish-blue (**I-Li$_2$**), purple (**II-Li$_2$**) or dark magenta (**III**) to brown or brownish tones within the times indicated in Table 1 and Table 2, indicating the consumption of **I-III-Li$_2$**. Terminal alkenes such as propene, isobutene, 1-octene and methylenecyclo-



Scheme 1.

pentane were carbometallated by **I-III-Li$_2$**, followed by in situ electrophilic capture and hydrolysis to afford products **12a–h**, **13** and **14** (Table 1, entries 1–8 and Table 2). In general, nonstrained internal (*cis-* or *trans-*)alkenes failed to react at a reasonable rate. However, slightly strained ones such as norbornene afforded products in moderate yield (Table 1, entries 9–10). While the site of the arene attack is adequately confirmed by the HOMO coefficients of **I**$^{-2}$ (e.g. C^4 for biphenyl, see Figure 1), the final electrophilic capture seems to depend on the nature of the electrophile itself. As electrophiles, non-prochiral electrophiles such as symmetric ketones or oxiranes were preferred to assess the scope of the process and to avoid tedious separations. Regarding the solvent, relatively short reaction times and the convenience of using THF vs. THP (m.p. –45 °C) prompted us to choose THF in most cases to the detriment of THP, despite the better stability known for THP in these very reactive media.[6] In the case of ketones **9–10**, addition occurs at C^3

Table 1. Reaction of biphenyl dianion (**I-Li$_2$**) with alkenes and capture with electrophiles.

Entry	Arene	Alkene	*t* [h]	Electrophile	R	R'	R''	Product[a]	%[b]
1	 **1**	 **4**	1	 **9**	H	Me	Et	 **12a**	62
2	**1**	**4**		 **10**	H	Me		**12b**	80
3	**1**	 **5**	1.5	**9**	Me	Me	Et	**12c**	63
4	**1**	**5**		**10**	Me	Me		**12d**	76
5	**1**	 **6**	1.5	**9**	H	Hx	Et	**12e**[c]	67
6	**1**	 **7**	1.5	**9**	[CH$_2$]$_4$		Et	**12f**	58
7	**1**	**7**		**10**	[CH$_2$]$_4$			**12g**	59
8	**1**	**7**		 **11**	[CH$_2$]$_4$			 **12h**[d]	43
9	**1**	 **8**	3	**9**			Et	 **12i**[e]	68
10	**1**	**8**		**11**				 **12j**[f]	56

[a] Unless otherwise stated, all compounds were isolated (>94% purity by GLC and/or 300/500 MHz ^{1}H NMR) giving consistent NMR spectra and correlations (^{1}H-, ^{13}C-, DEPT, COSY, HSQC and HMBC), as well as HRMS and IR spectra. The stereochemistry is based on NOESY experiments. [b] Yield based on arene **1**. [c] 1:1 Mixture of diastereomers corresponding to the two possible configurations of the 1-methylheptyl moiety. [d] Separated *cis-* (major, shown in Table) and *trans*-stereoisomer (minor) in 6:1 ratio. [e] Separated two *exo-trans*-stereoisomers in 1.1:1 ratio, one of them shown in Table (the major *exo-trans* stereoisomer was separated with 64% purity, contaminated with a 36% of minor *exo-trans* stereoisomer). The *exo-endo* stereochemistry was assigned by comparison with published NMR studies on assignment of substituted norbornane derivatives; see ref.[17]. [f] Separated *cis* (major, shown in Table) and *trans* stereoisomer (minor) in 1.7:1 ratio, both with the *exo* configuration in the norbornane moiety determined as above. This reaction was carried out in THP.

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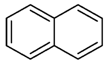
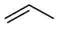
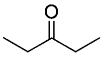
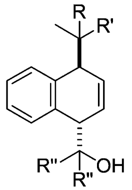
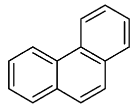
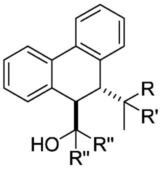
Table 2. Reaction of naphthalene dianion (**II-Li$_2$**) and phenanthrene dianion (**III-Li$_2$**) with propene and capture with electrophiles.

Entry	Arene	Alkene	t [h]	Electrophile	R	R'	R''	Product[a]	%[b]
1	 **2**	 **4**	2	 **9**	H	Me	Et	 **13**[c]	58
2	 **3**	**4**	2.5	**9**	H	Me	Et	 **14**	20

[a] All compounds were isolated (>95% purity by GLC and/or 300/500 MHz ^{1}H NMR) giving consistent NMR spectra and correlations (^{1}H, ^{13}C, DEPT, COSY, HSQC and HMBC), as well as HRMS and IR spectra. Stereochemistry was determined in base of NOESY experiments. [b] Yield based on arene **2**, **3**. [c] Separated *trans*- (major, shown in Table) and *cis*-stereoisomers (minor) in 3.5:1 ratio.[19]

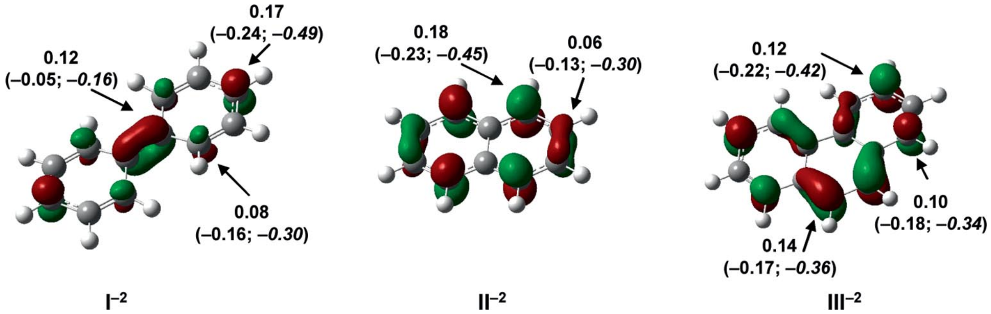


Figure 1. HOMO atomic coefficients, Mulliken charges (in parentheses) and atomic charges from NPA (in parentheses, italics) for $C_{12}H_{10}^{-2}$ (**I^{-2}**, point group C_{2h}), $C_{10}H_8^{-2}$ (**II^{-2}**, D_{2h}) and $C_{14}H_{10}^{-2}$ (**III^{-2}**, C_2), from B3LYP calculations at the 6-311G(d,p) level in the gas phase.

yielding substituted 3,4-dihydrobiphenyls of *trans*-configuration, presumably to avoid the generation of two adjacent quaternary centers, which is a sterically compromised situation (Table 1, Entries 1–7, 9). On the contrary, for sterically less demanding outcomes such as trapping with isobutylene oxide (**11**), reaction at C^1 is preferred, affording substituted 1,4-dihydrobiphenyls, although with low *cis-*/*trans*-stereoselectivity (Table 1, Entries 8, 10).[16]

In Table 2, the products obtained by carbolithiation of propene with the naphthalene dianion (**II-Li$_2$**) or phenanthrene dianion (**III-Li$_2$**), followed by capture with 3-pentanone, are described. Roughly, for arenes with a second reduction potential less-negative than phenanthrene ($E°_2$ = –3.13 V under the given conditions),[14] the reaction with alkenes does not proceed in a synthetically useful way. Indeed, yields are low for phenanthrene itself (Table 2, entry 2) and drop sharply for other polycyclic arenes of less-negative second reduction potential, such as anthracene ($E°_1$ = –2.04 V, $E°_2$ = –2.64 V), pyrene ($E°_1$ = –2.13 V, $E°_2$ = –2.86 V), both in DMA/TBAB vs. Ag/AgCl,[14] or chrysene, [$E_{1/2(1)}$ = –2.31 V, $E_{1/2(2)}$ = –2.82 V], in DMF/TMAB vs. Ag/AgCl,[14,18] (this last value is only approximate, given the different experimental conditions and expression of the potentials from different sources, but still a good approach for our purposes).

Semiempirical calculations are a first qualitative approach to the theoretical description of the reactivity of **I^{-2}–III^{-2}** that proved to be helpful in the past[8] and so are in the present case.[9] Density Functional Theory calculations,[20] using the B3LYP exchange-correlation functional,[21] have been performed here to support the theoretical description of the reactivity of **I^{-2}–III^{-2}**. The geometries of the isolated dianions have been optimized both in the gas phase and in the presence of the THF solvent described by a continuum model,[22,23] using the 6-311G(d,p) basis set.[24] The corresponding Mulliken charges, the atomic charges derived from a NPA (Natural Population Analysis)[25] and the atomic gross populations for the HOMO are reported in Figure 1, and clearly indicate that the alkene attack takes place at the carbon atom of the arene supporting the highest contribution to the HOMO of the dianion, rather than at the carbon of highest calculated charge. This conclusion is also supported when standard diffuse functions,[26] are included in the basis set, provided that the solvent is considered, as can be seen from the B3LYP/6-31+G(d,p) results reported in the electronic supporting in-

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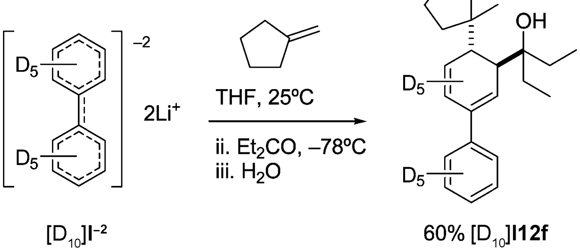
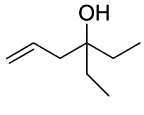
formation. Without the stabilizing effect of the solvent the tendency of high-energy electrons to escape from the dianion leads to large coefficients for several diffuse functions in the HOMO, which spreads throughout space, yielding meaningless values for the Mulliken charges and HOMO gross populations. This deleterious effect has been noted previously for a number of organic,[27] and inorganic dianions.[28] It should be stated that, for the qualitative purpose of pinpointing the reactive site in a kinetically-driven reaction of the arene dianion, both semiempirical and DFT calculations afford the same information. The atomic gross populations for the HOMO (DFT, this paper) correlate well with the HOMO coefficients (semiempirical, preliminary communication),[9] indicating the place in the molecule where the alkene attack will take place most probably.[29] Calculated charge distributions afford also the same qualitative results, in spite of the population analysis employed.[30]

With the results of Tables 1 and 2 in hand, we tried to execute the same kind of reactions by using the radical anions of **1**, **2** and **3** (i.e. **I-Li**, **II-Li** or **III-Li**). The results were clear and also significant concerning the reactivity of the species involved. The reaction of the corresponding arene radical anions **I-Li**, **II-Li** or **III-Li** with alkenes did not take place at all (0% carbolithiation using a 1:1 Li/arene ratio for **1**–**3**, THF, room temp.).

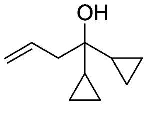
Regarding the mechanism in Scheme 1, the intermediates **Ia**–**IIIa** are postulated after carbolithiation of the corresponding alkenes by $\mathbf{I^{-2}}$–$\mathbf{III^{-2}}$. These species carry two well differentiated organolithium centers, one primary alkyllithium and one highly conjugated organolithium center (benzylic type or both benzyic-allylic type depending on the arene). We have not been able to capture the primary organolithium compound by any means. By the time the carbolithiation is complete, the primary alkyllithium is already quenched by the reaction media. In order to clarify this point, a reaction employing [D$_8$]THF was carried out. After 3 h of reaction of **I-Li$_2$** with propene in [D$_8$]THF and H_2O hydrolysis, analysis of the crude products showed no deuterium incorporation at all (non-separated mixture of 4-isopropyl-3,4-dihydrobiphenyl and *trans*- and *cis*-4-isopropyl-1,4-dihydrobiphenyl, **15a**–**c**, 90%, in ratios **15a**/**15b**/**15c** = 46:33:21). When D_2O was used for quenching, an analogous mixture of monodeuterated products was observed {[D$_1$]**15a**–**c** (Scheme 2), monodeuterium incorporation >99.5%, natural isotopic abundance for $C_{15}H_{17}D$ corrected}. Deuterium incorporation took place exclusively at the ring, as could be determined both by ^{1}H NMR and MS fragmentations (Scheme 1). The reaction employing [D$_{10}$]biphenyl was examined at this point. After reaction with $Li_{(s)}$ in THF and methylenecyclopentane (2 h), and electrophilic capture with 3-pentanone, [D$_{10}$]**12f**, with all 10 D in ring positions was isolated and characterized, proving that biphenyl or subsequent intermediates were not source of quenchable protons in this reaction (Scheme 3). The only remaining source of protons is the alkene. Sufficient (although indirect) evidence of the alkene participation in the protonation step **Ia**–**IIIa** → $\mathbf{Ia_H}$-$\mathbf{IIIa_H}$ (Scheme 1) was obtained upon detection of alcohols **16**–**21** as side-products in variable yields (in parenthesis) in the reaction crudes (Table 1, entries 1–4, 6,7). The presence of these side-products was confirmed by independent synthesis of **16**–**21** (see Exp. Sect.) and quantitative reexamination of the corresponding reaction crudes.



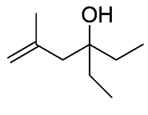
Scheme 3.



16 (20%)



17 (55%)



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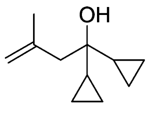

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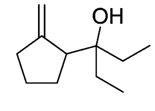
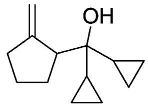
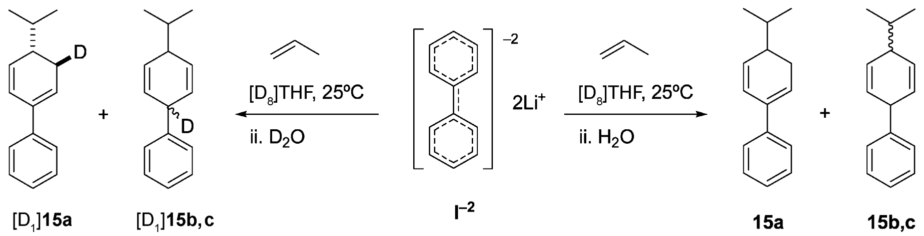


20 (27%)



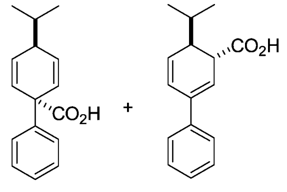
21 (25%)

We also tried to set the limits for the regioselectivity displayed by the electrophilic capture. The reaction of $\mathbf{Ia_H}$ (with R = H, R′ = Me) with CO_2 followed by hydrolysis and extractive work up afforded a separable mixture of two carboxylic acids characterized as **22a** and **22b** in a 70:30 ratio. Indeed, delocalized carbanion $\mathbf{Ia_H}$, which is of the cyclohexadienyl type, is expected to react with electrophiles at the C^1 or C^3 positions, affording substituted 3,4- and 1,4-



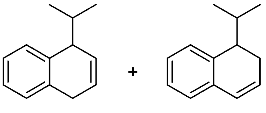
Scheme 2.

dihydrobiphenyls, respectively, showing a priori a preference for the addition at C^1 (PM3 HOMO coefficients: $C_1 = 0.60$; $C_3 = -0.40$. Mulliken charge: $C_1 = -0.40$; $C_3 = -0.44$).[31,32] This is evidenced by the 70:30 ratio of carboxylic acids, **22a** being the major component of the crude.[33] However, for ketones only 3,4-dihydroderivatives **12a**–**g** could be isolated. As pointed out before, the reason for this behavior seems to be merely steric. The occurrence of two contiguous quaternary centers should severely hamper the reaction pathways towards 1,4-dihydrobiphenylic tertiary alcohols, i.e., the regioisomers of **12a**–**g**, which could not be detected. Indeed, this substitution pattern is only observed with electrophiles of low steric demand like oxirane **11**, CO_2 or H_2O (**15a**–**c**). For the naphthalene framework, the reaction of $\mathbf{IIa_H}$ (with R = H, R′ = Me) with H_2O also affords a mixture of two separable hydrocarbon isomers in 76% yield, characterized as **23a** and **23b** in 52:48 ratio. A little preference for 1-isopropyl-1,4-dihydronaphthalene (**23a**) over the isomeric 1,2-dihydro derivative **23b** is, again, observed, also in reasonable agreement with calculations on $\mathbf{IIa_H}$ (PM3).[31]



22a **22b**

56% (70:30)



23a **23b**

76% (52:48)

Conclusions

New reactivity patterns have been identified for lithium dianions of polycyclic arenes of high reduction potential. Largely unexplored, the reactivity displayed by these highly reduced species ($\mathbf{I}^{-2}$, $\mathbf{II}^{-2}$ and to less extent $\mathbf{III}^{-2}$) other than ET is notable and has straightforward synthetic uses. They react nucleophilically with terminal alkenes and norbornene through an intermolecular carbolithiation as the key step, the resulting organolithium intermediate generated being trapped with conventional electrophiles. This synthesis affords highly elaborated, regiochemically and in many cases stereochemically well defined products, which are obtained after processing of among some of the most low-cost organic starting materials. The reaction involves partial dearomatization and produces doubly functionalized 2-phenyl-1,3-cyclohexadienes as well as functionalized 1,4-dihydronaphthalenes and 9,10-dihydrophenanthrenes when starting from biphenyl, naphthalene and phenanthrene, respectively. Besides the synthetic scope, the relevance of this work comes from its contributions in two fronts: from one side, as a reaction in which arene radical anion and dianion display clear-cut different reactivity. From the other side, as one of the few reactions of arene dianions of high reduction potential displaying reactivity profiles other than alkali-metal-like soluble forms. Interestingly, nucleophilic reactivity is manifested vs. substituted alkenes, such as propene and isobutene, which only very seldomly undergo nucleophilic substitution processes, especially in the absence of transition metal catalysts.

Experimental Section

General: All moisture-sensitive reactions were carried out under argon atmosphere. THF was dried and distilled from Na/K alloy right before use. Starting arenes, olefins and electrophiles were commercially available (Acros, Aldrich, Fluka) and used without further purification. Deuterated reagents were of the following grade: [D$_8$]THF (99.5% D), D_2O (99.9% D) and $C_{12}D_{10}$ (99% D). Lithium powder was prepared from lithium granules (99%, high sodium content) using an impact grinding mill and was also commercially available (MEDALCHEMY S. L.). All glassware was 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, F254, 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, Bruker Avance 400 or Bruker Avance DRX500 (300, 400 and 500 MHz for ^{1}H NMR, and 75, 100 and 125 MHz for ^{13}C NMR, respectively) using $CDCl_3$ as solvent and TMS as internal standard. Multiplicity is reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br. s = broad singlet, app. = apparent. 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 (FT-IR) spectra were obtained on a Nicolet Impact 400D spectrophotometer using NaCl plates. The purity of volatile compounds and the chromatographic analyses (GC) were determined with a Hewlett–Packard HP-5890 instrument equipped with a flame ionization detector and a 12 m HP-1 capillary column (0.2 mm diam, 0.33 µm film thickness, OV-1 stationary phase), using nitrogen (2 mL min^{-1}) as carrier gas.

General Procedure for the Preparation of Compounds 12a–d: To a deeply colored solution of biphenyl (3 mmol) and lithium powder ($Li_{(s)}$, 12 mmol) in dry THF (10 mL) at 25 °C with vigorous stirring under Ar, propene or isobutene was delivered using a balloon (approx. 3 L, 1 atm). Proper evacuation of Ar is critical for the reaction with gaseous alkenes in order not to unnecessarily lengthen the reaction times. After ca. 1 h for propene or 1.5 h for isobutene, the initial greenish-blue color of **I** turned brown. The reaction was then cooled down to –78 °C and 3-pentanone (**9**) or diisopropyl ketone (**10**) (6 mmol) was added. After 15 min the reaction was hydrolyzed (H_2O) and worked up as usual (3 × 20 mL diethyl ether, Na_2SO_4, 15 Torr), purifying **12a**–**d** by flash chromatography (silica gel, Hx/EtOAc); 0.5 wt.-% of hydroquinone was added for stabilisation during storage (see ref.[6]).

3-[(1*RS*,6*SR*)-6-Isopropyl-3-phenylcyclohexa-2,4-dienyl]pentan-3-ol (12a): R_f = 0.36 (9:1, hexane/ethyl acetate). IR (film): $\tilde{\nu}$ = 3583, 3486, 3032, 2963, 2879, 1599, 1494, 1461, 1447, 1384, 1367, 1123, 948, 917, 771, 750, 697 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H = 0.88 (t, 3 H, *J* = 7.6, $C\mathit{H}_3CH_2$), 0.92 (d, *J* = 6.6 Hz, 3 H, $C\mathit{H}_3CH$), 0.93 (d, *J* = 6.9 Hz, 3 H, $C\mathit{H}_3CH$), 0.95 (t, *J* = 7.7 Hz, 3 H, $C\mathit{H}_3CH_2$), 1.49 (br. s, 1 H, OH), 1.51–1.70 (m, 5 H, 2× $C\mathit{H}_2CH_3$, $CH_3C\mathit{H}CH_3$), 2.42–2.48 (2 m, 2× 1 H, C=CHC*H*COH and CH=CHC*Hi*Pr), 5.82 (app. d, *J* = 6.4 Hz, 1 H, C=C*H*CHCOH), 5.88 (app. dd, *J* = 10.0, *J* = 6.2 Hz, 1 H, CH=C*H*CH*i*Pr), 6.28 (app. d, *J* = 9.8 Hz, 1 H, CH=C*H*CPh), 7.24–7.42 (m, 5 H, Ph) ppm. ^{13}C NMR (75 MHz): δ_C = 7.61, 7.89 (2× CH_3CH_2), 18.45, 19.43 ($\mathit{C}H_3CH\mathit{C}H_3$), 27.11, 27.99 (2× $\mathit{C}H_2CH_3$), 34.72 ($CH_3\mathit{C}HCH_3$), 38.38 (CH=CH*C*H*i*Pr), 43.12 (C=CH*C*HCOH), 78.81 (*C*OH), 122.57 (C=*C*HCHCOH), 124.33 (C*C*H=CHCH*i*Pr), 125.49 (2 C, Ph_{oC}), 127.04 (Ph_{pC}), 128.40 (2 C, Ph_{mC}), 130.70 (CH=*C*HCH*i*Pr), 136.12 [CH=*C*(Ph)CH], 140.78 (Ph_{iC}) ppm. MS: *m*/*z* (%) = 268 (0.09) [(M$^+$ – 18) + 2], 267 (0.49) [(M$^+$ – 18) + 1], 266 (2.16) [M$^+$ – 18], 198 (34), 155 (100), 154 (32), 87 (34). HRMS: calcd. for $C_{20}H_{28}O$: 284.2140; found 284.2092.

Dicyclopropyl[(1*RS*,6*SR*)-6-isopropyl-3-phenylcyclohexa-2,4-dienyl]-methanol (12b): R_f = 0.36 (9:1, hexane/ethyl acetate). IR (film): $\tilde{\nu}$ = 3583, 3490, 3082, 3008, 2956, 2927, 2869, 1599, 1493, 1462, 1447, 1384, 1366, 1021, 1007, 948, 911, 771, 745, 697 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H = 0.20–0.49 (m, 8 H, 4× $C\mathit{H}_2$ of cyclopropyl), 0.92 (app. d, *J* = 6.9 Hz, 3 H, $C\mathit{H}_3CHCH_3$), 0.94 (app. d, *J* = 6.9 Hz, 3 H, $CH_3CHC\mathit{H}_3$), 0.94–1.02 (m, 2 H, 2× C*H* of cyclopropyl), 1.25 (br. s, 1 H, OH), 1.63–1.74 (m, 1 H, $CH_3C\mathit{H}CH_3$), 2.57 (app. dd, *J* = 6.2, 1.6 Hz, 1 H, C=CHC*H*COH), 2.63 (app. t, *J* = 5.6 Hz, 1 H, CH=CHC*Hi*Pr), 5.88 (app. dd, *J* = 9.8, 5.9 Hz, 1 H, CH=C*H*CH*i*Pr), 6.06 (app. d, *J* = 6.1 Hz, 1 H, C=CHC*H*COH), 6.27 (app. d, *J* = 9.8 Hz, 1 H, CH=C*H*CPh), 7.22–7.43 (m, 5 H, Ph) ppm. ^{13}C NMR (75 MHz): δ_C = –0.49, –0.31, 1.33, 1.52 (4× C*H*$_2$ of cyclopropyl), 16.33, 17.17 (2× C*H* of cyclopropyl), 18.76, 19.25 ($\mathit{C}H_3CH\mathit{C}H_3$), 34.22 ($CH_3\mathit{C}HCH_3$), 38.70 (CH=CH*C*H*i*Pr), 48.02 (C=CH*C*HCOH), 74.11 (*C*OH), 123.43 (C=*C*HCHCOH), 124.23 (C*C*H=CHCH*i*Pr), 125.47 (2 C, Ph_{oC}), 126.85 (Ph_{pC}), 128.38 (2 C, Ph_{mC}), 130.54 (CH=*C*HCH*i*Pr), 135.47 [CH=*C*(Ph)CH], 141.08 (Ph_{iC}) ppm. MS: *m*/*z* (%) = 308 (0.01) [M$^+$], 290 (0.12) [M$^+$ – 18], 198 (19), 155 (41), 154 (18), 111 (100), 69 (44). HRMS: calcd. for $C_{22}H_{28}O$ 308.2140; found 308.2135.

3-[(1*RS*,6*SR*)-6-*tert*-Butyl-3-phenylcyclohexa-2,4-dienyl]pentan-3-ol (12c): R_f = 0.39 (9:1, hexane/ethyl acetate). IR (film): $\tilde{\nu}$ = 3584, 3500, 3036, 2964, 2879, 1599, 1494, 1463, 1447, 1392, 1365, 1224, 1151, 1128, 994, 945, 856, 767, 750, 699, 638 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H = 0.87 (t, *J* = 7.5 Hz, 3 H, $C\mathit{H}_3CH_2$), 0.91 (s, 9 H, 3× $C\mathit{H}_3C$), 0.97 (t, *J* = 7.5 Hz, 3 H, $C\mathit{H}_3CH_2$), 1.47 (br. s, 1 H, OH), 1.54–1.68 (m, 4 H, 2× $CH_3C\mathit{H}_2$), 2.30 (app. d, *J* = 5.9 Hz, 1 H, CH=CHC*Ht*Bu), 2.59 (app. d, *J* = 6.4 Hz, 1 H, C=CHC*H*COH), 5.80 (app. d, *J* = 6.4 Hz, 1 H, C=C*H*CHCOH), 5.93 (app. dd, *J* = 6.1, 9.9 Hz, 1 H, CH=C*H*CH*t*Bu), 6.31 (app. d, *J* = 9.8 Hz, 1 H, CH=C*H*CPh), 7.23–7.41 (m, 5 H, Ph) ppm. ^{13}C NMR: δ_C = 7.53, 7.92 (2× CH_3CH_2), 26.77 [3 C, $(\mathit{C}H_3)_3C$], 26.99, 27.87 (2× $\mathit{C}H_2CH_3$), 36.17 ($\mathit{C}CH_3$), 40.47 (C=CH*C*HCOH), 41.96 (CH=CH*C*H*t*Bu), 78.82 (*C*OH), 123.04 (C=*C*HCHCOH), 124.59 (C*C*H=CHCH*t*Bu), 125.45 (2 C, Ph_{oC}), 127.02 (Ph_{pC}), 128.41 (2 C, Ph_{mC}), 130.67 (CH=*C*HCH*t*Bu), 135.69 [CH=*C*(Ph)CH], 140.73 (Ph_{iC}) ppm. MS: *m*/*z* (%) = 282 (0.16) [(M$^+$ – 18) + 2], 281 (0.94) [(M$^+$ – 18) + 1], 280 (3.73) [M$^+$ – 18], 212 (28), 156 (44), 155 (100), 154 (59), 153 (12), 87 (61), 57 (24). HRMS: calcd. for $C_{21}H_{28}$ 280.2191; found 280.2197.

Dicyclopropyl[(1*RS*,6*SR*)-6-*tert*-butyl-3-phenylcyclohexa-2,4-dienyl]-methanol (12d): R_f = 0.44 (9:1, hexane/ethyl acetate). IR (film): $\tilde{\nu}$ = 3584, 3082, 3008, 2960, 2904, 2866, 1599, 1492, 1465, 1447, 1392, 1364, 1021, 1005, 951, 910, 766, 744, 697 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H = 0.21–0.49 (m, 8 H, 4× C*H*$_2$ of cyclopropyl), 0.92 (s, 9 H, 3× $C\mathit{H}_3C$), 0.94–1.02 (m, 2 H, 2× C*H* of cyclopropyl), 1.15 (br. s, 1 H, OH), 2.48 (app. d, *J* = 5.9 Hz, 1 H, CH=CHC*Ht*Bu), 2.73 (app. d, *J* = 6.4 Hz, 1 H, C=CHC*H*COH), 5.91 (app. dd, *J* = 6.2, *J* = 9.9 Hz, 1 H, CH=C*H*CH*t*Bu), 6.07 (app. d, *J* = 5.9 Hz, 1 H, C=C*H*CHCOH), 6.30 (app. d, *J* = 10.1 Hz, 1 H, CH=C*H*CPh), 7.26 (app. t, *J* = 7.3 Hz, 1 H, Ph_{pH}), 7.34 (app. t, *J* = 7.3 Hz, 2 H, Ph_{mH}) 7.40 (app. d, *J* = 7.3 Hz, 2 H, Ph_{oH}) ppm. ^{13}C NMR (75 MHz): δ_C = –0.39, –0.15, 1.38, 1.57 (4× C*H*$_2$ of cyclopropyl), 16.30, 17.27 (2× C*H* of cyclopropyl), 26.79 [3 C, $(CH_3)_3C$], 36.14 [$(CH_3)_3\mathit{C}$], 42.33 (CH=CH*C*H*t*Bu), 45.79 (C=CH*C*HCOH), 74.10 (*C*OH), 123.96 (C=*C*HCHCOH), 124.68 (*C*H=CHCH*t*Bu), 125.43 (2 C, Ph_{oC}), 126.84 (Ph_{pC}), 128.38 (2 C, Ph_{mC}), 130.12 (CH=*C*HCH*t*Bu), 135.15 [CH=*C*(Ph)CH], 141.01 (Ph_{iC}) ppm. MS: *m*/*z* (%) = 322 (0.005) [M$^+$], 304 (0.08) [M$^+$ – 18], 212 (12), 155 (18), 154 (22), 111 (100), 69 (39), 57 (16). HRMS: calcd. for $C_{23}H_{30}O$ 322.2297; found 322.2278.

General Procedure for the Preparation of Compounds 12e–f, [D$_{10}$]12f, 12g–j: To a deeply colored solution of biphenyl or [D$_{10}$]-biphenyl (3 mmol) and lithium powder ($Li_{(s)}$, 12 mmol) in dry THF (10 mL) at 25 °C with stirring under Ar, the corresponding alkene (methylenecyclopentane, 3 mmol, 1-octene or norbornene, 3.3 mmol) was added. After ca. 1.5 h the initial greenish-blue color of **I-Li$_2$** or [D$_{10}$]**I-Li$_2$** turned brown. The reaction was then cooled down to –78 °C and 3-pentanone (**8**, 6 mmol), dicyclopropyl ketone (**9**, 6 mmol) or isobutene oxide (**11**) was added. After 15 min the reaction was hydrolyzed (H_2O) and worked up as usual (3× 20 mL diethyl ether, Na_2SO_4, 15 Torr), purifying **12e**–**j** by flash chromatography (silica gel, Hx/EtOAc), respectively; 0.5 wt.-% of hydroquinone was added for stabilisation during storage (see ref.[6]).

3-[(1*RS*,6*SR*)-6-(1-Methylheptyl)-3-phenylcyclohexa-2,4-dienyl]pentan-3-ol (12e, 1:1 mixture of diastereomers): R_f = 0.41 (9:1, hexane/ethyl acetate). IR (film): $\tilde{\nu}$ = = 3583, 3490, 3032, 2961, 2927, 2872, 2856, 1599, 1495, 1460, 1448, 1378, 1302, 1261, 1150, 1124, 1004, 993, 945, 911, 857, 772, 750, 736, 697 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 0.84–0.91 (m, 9 H, $C\mathit{H}_3CH_2CO$, $C\mathit{H}_3CHCH_2$, $C\mathit{H}_3CH_2CH_2$), 0.85–0.92 (m, 9 H, $C\mathit{H}_3CH_2CO$, $C\mathit{H}_3CHCH_2$, $C\mathit{H}_3CH_2CH_2$), 0.94 (t, *J* = 7.3 Hz, 3 H, $C\mathit{H}_3CH_2CO$), 0.95 (t, *J* = 7.3 Hz, 3 H, $C\mathit{H}_3CH_2CO$), 1.21–1.32 [m, 10 H, $(C\mathit{H}_2)_5$], 1.21–1.32 [m, 10 H, $(C\mathit{H}_2)_5$], 1.36 (br. s, 1 H, OH), 1.36 (br. s, 1 H, OH), 1.39–1.45 (m, 1 H, $CH_3C\mathit{H}CH_2$), 1.45–1.53 (m, 1 H, $CH_3C\mathit{H}CH_2$), 1.56–1.63 (m, 4 H, 2× $CH_3C\mathit{H}_2CO$), 1.56–1.63 (m, 4 H, 2× $CH_3C\mathit{H}_2CO$), 2.40 (app. d, *J* = 5.0 Hz, 1 H, C=CHC*H*COH), 2.45 (app. d, *J* = 5.9 Hz, 1 H, C=CHC*H*COH), 2.52 (m, 1 H, $C\mathit{H}CHCH_3$), 2.59 (m, 1 H, $C\mathit{H}CHCH_3$), 5.78–5.84 [m, 2 H, C*H*=C(Ph)CH=C*H*], 5.78–5.84 [m, 1 H, C*H*=C(Ph)CH=CH], 5.86 [app. dd, *J* = 9.6, 5.5 Hz, 1 H, CH=C(Ph)CH=C*H*], 6.25 [app. d, *J* = 9.6 Hz, 1 H, CH=C(Ph)C*H*=CH], 6.29 [app. d, *J* = 10.1 Hz, 1 H, CH=C(Ph)C*H*=CH], 7.25 (app. t, *J* = 7.8 Hz, 1 H, Ph_{pH}), 7.26 (app. t, *J* = 7.8 Hz, 1 H, Ph_{pH}), 7.33 (app. t, *J* = 6.9 Hz, 2 H, Ph_{mH}), 7.33 (app. t, *J* = 6.9 Hz, 2 H, Ph_{mH}), 7.39 (app. d, *J* = 8.2 Hz, 2 H, Ph_{oH}), 7.39 (app. d, *J* = 8.2 Hz, 2 H, Ph_{oH}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ_C = 7.52, 7.55, 7.82, 7.82, 14.06, 14.06, 15.27, 15.89 (8× CH_3), 22.64, 22.64, 27.08, 27.14, 27.50, 27.64, 27.89, 27.89, 29.52, 29.58, 31.86, 31.91, 32.44, 33.39 (14× CH_2), 36.74, 37.54 (2× *C*HCHCH$_3$), 39.37, 41.16 (2× CH*C*HCH$_3$), 42.26, 44.33 (2× *C*HCOH), 78.70, 78.80 (2× *C*OH), 122.69, 122.73 [2× *C*H=C(Ph)CH=CH], 123.95, 124.74 [2× CH=C(Ph)*C*H=CH], 125.42 (2 C), 125.42 (2 C, 4× Ph_{oC}), 126.92, 126.92 (2× Ph_{pC}), 128.30 (2 C), 128.30 (2 C, 4× Ph_{mC}), 129.87, 131.37 [2× CH=C(Ph)CH=*C*H], 136.10, 136.14 [2× CH=*C*(Ph)CH], 140.81, 140.81 (2 × Ph$_{iC}$) ppm. MS: *m*/*z* (%) = 354 (0.01) [M$^+$], 336 (0.60) [M$^+$ – 18], 268 (21) 156 [30], 155 (100), 154 (52), 111 (100), 87 (35), 57 (10). HRMS: calcd. for $C_{25}H_{36}$ 336.2817; found 336.2824.

3-[(1*RS*,6*SR*)-6-(1-Methylcyclopentyl)-3-phenylcyclohexa-2,4-dienyl]pentan-3-ol (12f): R_f = 0.45 (9:1, hexane/ethyl acetate). IR (film): $\tilde{\nu}$ = 3483, 3033, 2958, 2876, 1599, 1494, 1460, 1447, 1376, 1124, 1004, 947, 911, 855, 748, 734, 698 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ_H = 0.85 (s, 3 H, CH_3C), 0.87 (app. t, *J* = 7.5 Hz, 3 H, CH_3CH$_2$), 0.97 (t, *J* = 7.3 Hz, 3 H, CH_3CH$_2$), 1.25 (br. s, 1 H, OH), 1.36–1.68 [m, 8 H, (CH_2)$_4$], 1.55–1.68 (m, 4 H, 2 × CH_2CH$_3$), 2.41 (app. d, *J* = 5.8 Hz, 1 H, CH=CHC*H*CCH$_3$), 2.55 (app. d, *J* = 6.2 Hz, 1 H, C=CHC*H*COH), 5.81 (d, *J* = 6.4 Hz, 1 H, C=C*H*CHCOH), 5.90 (app. dd, *J* = 10.0, 5.9 Hz, 1 H, CH=C*H*CHCCH$_3$), 6.29 (app. d, *J* = 10.0 Hz, 1 H, CH=C*H*CPh), 7.25–7.42 (m, 5 H, Ph) ppm. ^{13}C NMR (75 MHz): δ_C = 7.50, 7.86 (2 × CH_3CH$_2$), 21.30 (CH$_3$C), 23.35, 23.93 (CH$_2$$CH_2CH_2$C), 27.05, 27.79 (2 × CH$_2CH_3$), 37.07, 37.33 [CH$_2$C(CH$_3$)CH$_2$], 42.22 (C=CHCHCOH), 42.37 [CH=CHCHC(CH$_3$)], 48.56 [CH$_2$$C$(CH$_3$)-CH$_2$], 78.73 ($C$OH), 123.14 [$C$H=C(Ph)CH=CH], 124.62 [CH=C(Ph)CH=CH], 125.45 (2 C, Ph$_{oC}$), 127.01 (Ph$_{pC}$), 128.39 (2 C, Ph$_{mC}$), 131.13 (CH=CHCHC), 135.93 [CH=C(Ph)CH], 140.83 (Ph$_{iC}$) ppm. MS: *m*/*z* (%) = 324 (0.002) [M$^+$], 306 (1.75) [M$^+$ – 18], 238 (18), 236 (11), 221 (19), 167 (17), 157 (12), 156 (100), 155 (81), 154 (74), 153 (14), 152 (11), 87 (64), 83 (37), 57 (10), 55 (17). HRMS: calcd. for $C_{23}H_{30}$ 306.2348; found 306.2343.

3-[(1*RS*,6*SR*)-6-(1-Methylcyclopentyl)-3-(2,3,4,5,6-pentadeuteriophenyl)-1,2,4,5,6-pentadeuteriocyclohexa-2,4-dienyl]pentan-3-ol ([D$_{10}$]12f): ^{1}H NMR (300 MHz, CDCl$_3$): δ_H = 0.85 (s, 3 H, CH_3C), 0.86 (app. t, *J* = 7.4 Hz, 3 H, CH_3CH$_2$), 0.97 (t, *J* = 7.3 Hz, 3 H, CH_3CH$_2$), 1.35 (br. s, 1 H, OH), 1.37–1.69 [m, 8 H, (CH_2)$_4$], 1.56–1.69 (m, 4 H, 2 × CH_2CH$_3$) ppm. ^{13}C NMR (75 MHz): δ_C = 7.50, 7.86 (2 × CH$_3$CH$_2$), 21.31 (CH$_3$C), 23.38, 23.94 (CH$_2$$CH_2CH_2$C), 27.07, 27.79 (2 × CH$_2CH_3$), 37.03, 37.31 [CH$_2$C(CH$_3$)CH$_2$], 41.59 (t, *J* = 18.8 Hz, C=CHCDCOH), 41.62 [t, *J* = 18.8 Hz, CH=CHCDC(CH$_3$)], 48.46 [CH$_2$$C$(CH$_3$)CH$_2$], 78.67 ($C$OH), 122.64 [t, *J* = 24.3 Hz, CH=C(Ph)CH=CH], 124.21 [t, *J* = 24.3 Hz, CH=C(Ph)CH=CH], 125.01 (t, *J* = 24.3 Hz, 2 C, Ph$_{oC}$), 126.48 (t, *J* = 24.3 Hz, Ph$_{pC}$), 127.88 (t, *J* = 24.3 Hz, 2 C, Ph$_{mC}$), 130.58 (t, *J* = 24.3 Hz, CH=CHCHC), 135.74 [CH=C(Ph)CH], 140.60 (Ph$_{iC}$) ppm. MS: *m*/*z* (%) = 317 (0.06) [(M$^+$ – 18) + 1], 316 (0.24) [M$^+$ – 18], 248 (19), 167 (13), 166 (100), 165 (77), 164 (50), 163 (32),162 (11), 87 (53), 83 (32), 55 (13). HRMS: calcd. for $C_{23}H_{20}D_{10}$ 316.2975; found 316.2929.

Dicyclopropyl[(1*RS*,6*SR*)-6-(1-methylcyclopentyl)-3-phenylcyclohexa-2,4-dienyl]methanol (12g): R_f = 0.48 (9:1, hexane/ethyl acetate). IR (film): $\tilde{\nu}$ = 3582, 3082, 3007, 2954, 2869, 1599, 1491, 1447, 1376, 1020, 1005, 910, 953, 761, 740, 697 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ_H = 0.20–0.49 (m, 8 H, 4 × CH_2 of cyclopropyl), 0.87 (s, 3 H, CH_3C), 0.94–1.04 (m, 2 H, 2 × C*H* of cyclopropyl), 1.25 (br. s, 1 H, OH), 1.38–1.69 (m, 8 H, 4 × CH_2 of cyclopentyl), 2.60 (app. d, *J* = 5.9 Hz, 1 H, CH=CHC*H*CCH$_3$), 2.68 (app. d, *J* = 6.3 Hz, 1 H, C=CHC*H*COH), 5.89 (app. dd, *J* = 9.9, 5.9 Hz, 1 H, CH=C*H*CHCCH$_3$), 6.08 (app. d, *J* = 6.2 Hz, C=C*H*CHCOH) 6.29 (app. d, *J* = 9.9 Hz, 1 H, CH=C*H*CPh), 7.23–7.43 (m, 5 H, Ph) ppm. ^{13}C NMR (75 MHz): δ_C = –0.50, –0.17, 1.43, 1.61 (4 × CH$_2$ of cyclopropyl), 16.31, 17.22 (2 × CH of cyclopropyl), 21.45 (CH$_3$C), 23.49, 24.05 (CH$_2$$CH_2$$CH_2CH_2$), 37.13, 37.26 ($CH_2CH_2CH_2$$CH_2$), 42.54 (CH=CH$C$HCCH$_3$), 47.53 (C=CH$C$HCOH), 48.52 (CH$_3$$C$), 74.09 ($C$OH), 124.03 (C=$C$HCHCOH), 124.74 (C$C$H=CHCHCCH$_3$) 125.45 (2 C, Ph$_{oC}$), 126.83 (Ph$_{pC}$), 128.39 (2 C, Ph$_{mC}$), 130.60 (CH=$C$HCHCCH$_3$), 135.42 [CH=$C$(Ph)CH], 141.13 (Ph$_{iC}$) ppm. MS: *m*/*z* (%) = 331 (0.01) [(M$^+$ – 18) + 1], 330 (0.12) [M$^+$ – 18], 156 (20), 155 (12), 154 (22), 111 (100), 83 (18), 69 (36), 55 (12). HRMS: calcd. for $C_{25}H_{32}O$ 348.2453; found 348.2454.

***cis*-2-Methyl-1-[4-(1-methylcyclopentyl)-1-phenylcyclohexa-2,5-dienyl]propan-2-ol (*cis*-12h):** R_f = 0.48 (8:2, hexane/ethyl acetate). ^{1}H NMR (300 MHz): δ_H = 0.69 (s, 3 H, CH_3C), 1.27 [s, 6 H, (CH_3)$_2$-COH], 1.40–1.55 (m, 4 H, 4 × C*H*H of cyclopentyl), 1.58–1.69 (m, 4 H, 4 × CH*H* of cyclopentyl), 2.14 (s, 2 H, CCH_2COH), 2.25 (br. s, 1 H, OH), 2.57–2.63 [m, 1 H, (CH=CH)$_2$C*H*CCH$_3$], 5.87 [app. dd, *J* = 10.6, *J* = 3.1 Hz, 2 H, (CH=C*H*)$_2$CH], 6.14 [dd, *J* = 10.6, *J* = 2.0 Hz, 2 H, (CH=C*H*)$_2$C(Ph)], 7.12–7.20 (m, 1 H, Ph), 7.25–7.32 (m, 2 H, Ph), 7.35–7.41 (m, 2 H, Ph) ppm. ^{13}C NMR (75 MHz): δ_C = 23.14 (CH$_3$C), 24.18 (2 × CH$_2$ of cyclopentyl), 31.29 [2 C, (CH$_3$)$_2$COH], 38.35 (2 × CH$_2$ of cyclopentyl), 43.59 [(CH=CH)$_2$$C$(Ph)], 46.27 (CH$_3$$C$), 46.62 [(CH=CH)$_2$$C$H], 53.67 (C$CH_2$COH), 72.31 (COH), 125.79 (CH$_{Ph}$), 126.13 (2 C, CH$_{Ph}$), 127.21 [2 C, (CH=CH)$_2$CH], 128.21 (2 C, CH$_{Ph}$), 134.36 [2 C, (CH=CH)$_2$C(Ph)], 148.77 (C$_{Ph}$) ppm. IR (film): $\tilde{\nu}$ = 3436, 3020, 2956, 2869, 1597, 1492, 1446, 1373, 1216, 1161, 912, 803, 744, 698 cm^{-1}. MS: *m*/*z* (%) = 311 (0.01) [M$^+$ + 1], 310 (0.02) [M$^+$], 292 (2.4), 236 (14), 221 (14), 210 (14), 209 (54), 178 (10), 168 (14), 167 (86), 165 (16), 155 (35), 154 (100), 153 (18), 152 (17), 83 (95), 55 (33). HRMS: calcd. for $C_{22}H_{28}$: 292.2191; found 292.2161.

***trans*-2-Methyl-1-[4-(1-methylcyclopentyl)-1-phenylcyclohexa-2,5-dienyl]propan-2-ol (*trans*-12h):** R_f = 0.47 (8:2, hexane/ethyl acetate). ^{1}H NMR (300 MHz): δ_H = 0.88 (s, 3 H, CH_3C), 1.29 [s, 6 H, (CH_3)$_2$-COH], 1.51–1.58 (m, 4 H, 4 × C*H*H of cyclopentyl), 1.62–1.72 (m, 4 H, 4 × C*H*H of cyclopentyl), 2.06 (br. s, 1 H, OH), 2.17 (s, 2 H, CCH_2COH), 2.52–2.56 [m, 1 H, (CH=CH)$_2$C*H*], 5.90 [app. dd, *J* = 10.4, *J* = 2.3 Hz, 2 H, (CH=C*H*)$_2$CH], 6.10 [app. dd, *J* = 10.4, *J* = 2.5 Hz, 2 H, (CH=C*H*)$_2$C(Ph)], 7.13–7.21 (m, 1 H, Ph), 7.27–7.41 (m, 4 H, Ph) ppm. ^{13}C NMR (75 MHz): δ_C = 23.57 (CH$_3$C), 24.28 (2 × CH$_2$ of cyclopentyl), 31.62 [2 C, (CH$_3$)$_2$COH], 38.51 (2 × CH$_2$ of cyclopentyl), 43.78 [(CH=CH)$_2$$C$(Ph)], 45.91 (CH$_3$$C$), 46.52 [(CH=CH)$_2$$C$H], 52.89 (C$CH_2$COH), 72.34 (COH), 125.99 (2 C, CH$_{Ph}$), 126.02 (CH$_{Ph}$), 127.42 [(CH=CH)$_2$CH], 128.42 (2 C, CH$_{Ph}$), 134.73 [2 C, (CH=CH)$_2$C(Ph)], 148.32 (C$_{Ph}$) ppm. IR (film): $\tilde{\nu}$ = 3445, 3021, 2955, 2869, 1597, 1491, 1445, 1372, 1140, 914, 741, 697 cm^{-1}. MS: *m*/*z* (%) = 311 (0.02) [M$^+$ + 1], 310 (0.11%) [M$^+$], 292 (1.6), 221 (13), 209 (18), 167 (45), 165 (11), 155 (21), 154 (71), 153 (10), 83 (100), 55 (28). HRMS: calcd. for $C_{22}H_{28}$: 292.2191; found 292.2228.

3-{*trans*-[6-(*exo*-2-Norbornyl)-3-phenylcyclohexa-2,4-dienyl]}pentan-3-ol (*trans-exo*-12i, minor isomer): R_f = 0.29 (8:2, hexane/ethyl acetate). ^{1}H NMR (300 MHz): δ_H = 0.85 (app. t, *J* = 7.5 Hz, 3 H, CH_3CH$_2$), 0.93 (app. t, *J* = 7.5 Hz, 3 H, CH_3CH$_2$), 1.01–1.67 (m, 14 H, 4 × CH_2 and $H^{2\text{-}endo}$ of norbornyl, 2 × CH_2CH$_3$, OH), 2.14 (app. dd, *J* = 10.7, *J* = 6.0 Hz, 1 H, CH=CHC*H*), 2.19–2.29 (m, 2 H, H^1, H^4 of norbornyl), 2.32 (app. d, *J* = 6.4 Hz, 1 H, C=CHC*H*COH), 5.85 (app. d, *J* = 6.4 Hz, 1 H, C=C*H*CHCOH), 6.14 (app. dd, *J* = 9.9, *J* = 5.8 Hz, 1 H, CH=C*H*CH), 6.22 (app. dd, *J* = 9.8, *J* = 1.4 Hz, 1 H, CH=C*H*CPh), 7.26–7.30 (m, 1 H, Ph), 7.31–7.39 (m, 2 H, Ph), 7.40–7.46 (m, 2 H, Ph) ppm. ^{13}C NMR (75 MHz): δ_C = 7.59, 7.98 (2 × CH$_3$), 27.26, 28.27 (2 × CH$_2$CH$_3$), 28.81, 30.47, 35.70 (3 × CH$_2$), 36.56 (CH), 36.74 (CH$_2$), 36.89 (CH=CHCH), 38.63 (CH), 42.34 (C=CHCHCOH), 46.28 (CH), 78.78 (COH), 121.56 (C=CHCHCOH), 122.94 (CCH=CHCH), 125.52 (2 C, Ph$_{oC}$), 127.12 (Ph$_{pC}$), 128.41 (2 C, Ph$_{mC}$), 133.72 (CH=CHCH), 136.18 [CH=C(Ph)CH], 140.39 (Ph$_{iC}$) ppm. IR (film): $\tilde{\nu}$ = 3441, 2947, 2867, 1660, 1644, 1633, 1494, 1454, 748, 733, 696 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 320 (0.45) (M$^+$ – 18) + 2], 319 (1.84) [(M$^+$ – 18) + 1], 318 (6.90) [M$^+$ – 18], 289 (10), 251

(14), 250 (68), 223 (19), 181 (14), 167 (24), 156 (25), 155 (100), 154 (80), 153 (12), 95 (67), 87 (46), 67 (15). HRMS: calcd. for $C_{24}H_{30}$: 318.2348; found 318.2370.

3-{*trans*-[6-(*exo*-2-Norbornyl)-3-phenylcyclohexa-2,4-dienyl]}pentan-3-ol (*trans-exo*-12i, major isomer): ^{1}H NMR (300 MHz): δ_H = 0.87 (t, *J* = 7.4 Hz, 3 H, CH_3CH_2), 0.94 (t, *J* = 7.4 Hz, 3 H, CH_3CH_2), 1.02–1.18 (m, 3 H, $H^{7\text{-}anti}$, $H^{6\text{-}endo}$ and $H^{5\text{-}endo}$ of norbornyl), 1.32–1.68 (m, 10 H, $H^{7\text{-}syn}$, $H^{2\text{-}endo}$, $H^{3\text{-}exo}$, $H^{3\text{-}endo}$, $H^{5\text{-}exo}$ and $H^{6\text{-}exo}$ of norbornyl, 2 × CH_2CH_3), 2.10–2.30 (m, 4 H, CH=CHC*H*, H^1 and H^4 of norbornyl, OH), 2.54 (app. d, *J* = 6.3 Hz, C=CHC*H*COH), 5.85 (app. d, *J* = 6.4 Hz, 1 H, C=C*H*CHCOH), 6.01 (app. dd, *J* = 9.9, *J* = 6.0 Hz, 1 H, CH=C*H*CH), 6.24 (app. d, 1 H, CH=C*H*CPh), 7.26–7.30 (m, 1 H, Ph), 7.30–7.38 (m, 2 H, Ph), 7.40–7.46 (m, 2 H, Ph) ppm. ^{13}C NMR (75 MHz): δ_C = 7.63, 7.94 (2 × CH_3), 27.18, 28.21 (2 × CH_2CH_3), 28.65, 30.41, 35.60, 35.85 (4 × CH_2), 36.43 (CH), 36.71 (CH=CH*C*H), 38.40 (CH), 44.54 (C=CH*C*HCOH), 46.52 (CH), 121.66 (C=*C*HCHCOH), 123.75 (C*C*H=CHCH), 125.48 (2 C, Ph_{oC}), 127.08 (Ph_{pC}), 128.39 (2 C, Ph_{mC}), 132.04 (CH=*C*HCH), 136.15 [CH =*C*(Ph)CH], 140.38 (Ph_{iC}) ppm. MS (70 eV, EI): *m/z* (%) = 337 (0.03) [M^+ + 1], 336 (0.10) [M^+], 318 (11), 289 (16), 251 (17), 250 (85), 223 (24), 181 (17), 167 (26), 165 (11), 156 (24), 155 (100), 154 (87), 153 (14), 152 (11), 95 (58), 87 (41), 67 (16). HRMS: calcd. for $C_{24}H_{30}$: 318.2348; found 318.2303

***cis*-2-Methyl-1-[4-(*exo*-2-norbornyl)-1-phenylcyclohexa-2,5-dienyl]-propan-2-ol (*trans*-12h):** R_f = 0.31 (8:2, hexane/ethyl acetate). ^{1}H NMR (400 MHz): δ_H = 1.06–1.13 (m, 3 H, $H^{7\text{-}anti}$, $H^{6\text{-}endo}$, $H^{5\text{-}endo}$ of norbornyl), 1.26 (2s, 6 H, 2 × CH_3), 1.26–1.39 (m, 4 H, $H^{7\text{-}syn}$, $H^{2\text{-}endo}$, $H^{3\text{-}exo}$, $H^{3\text{-}endo}$ of norbornyl), 1.44–1.50 (m, 2 H, $H^{5\text{-}exo}$, $H^{6\text{-}exo}$ of norbornyl), 2.15 (app. s, 2 H, CCH_2COH), 2.19–2.25 (m, 2 H, H^1, H^4 of norbornyl), 2.21 (br. s, 1 H, OH), 2.45–2.51 [m, 1 H, $(CH=CH)_2CH$], 5.80–5.85 [m, 1 H, (CH=C*H*)CH], 5.90–6.01 [m, 3 H, (CH=C*H*)CH, $(CH=CH)_2CH$], 7.15–7.21 (m, 1 H, Ph_p), 7.27–7.33 (m, 2 H, Ph_o), 7.34–7.40 (m, 2 H, Ph_m) ppm. ^{13}C NMR (100 MHz): δ_C = 28.52, 30.56 (2 × CH_2), 31.36, 31.37 (2 × CH_3), 35.75, 35.94 (2 × CH_2), 36.67, 38.58 (2 × CH), 39.81 [$(CH=CH)_2$-*C*H], 43.86 [$(CH=CH)_2C$(Ph)], 47.98 (CH), 52.95 (CH_2COH), 72.30 (COH), 125.90 (CH_{Ph}), 126.16 (2 C, CH_{Ph}), 126.94, 127.86 [$(CH=CH)_2CH$], 128.32 (2 C, CH_{Ph}), 133.29, 133.65 [$(CH=CH)_2$-CH], 148.58 (C_{Ph}) ppm. IR (film): ṽ = 3436, 3020, 2949, 2867, 1596, 1491, 1454, 1372, 1139, 744, 697 cm^{-1}. MS (70 eV, EI): *m/z* (%) = 324 (0.003) [M^+ + 2], 323 (0.06) [M^+ + 1], 322 (0.24) [M^+], 248 (16), 209 (10), 168 (11), 167 (27), 154 (21), 95 (100), 67 (16). HRMS: calcd. for $C_{23}H_{28}$ 304.2191; found 304.2182.

***trans*-2-Methyl-1-[4-(*exo*-2-norbornyl)-1-phenylcyclohexa-2,5-dienyl]-propan-2-ol (*trans*-12h):** R_f = 0.47 (8:2, hexane/ethyl acetate). ^{1}H NMR (300 MHz): δ_H = 1.10–1.18 (m, 3 H, $H^{7\text{-}anti}$, $H^{6\text{-}endo}$, $H^{5\text{-}endo}$ of norbornyl), 1.29 (2s, 6 H, 2 × CH^3), 1.22–1.57 (m, 6 H, $H^{7\text{-}syn}$, $H^{2\text{-}endo}$, $H^{3\text{-}exo}$, $H^{3\text{-}endo}$, $H^{5\text{-}exo}$, $H^{6\text{-}exo}$ of norbornyl), 2.18 (app. s, 2 H, CCH_2COH), 2.20 (br. s, 1 H, OH), 2.24–2.29 (m, 1 H, H^4 of norbornyl), 2.29–2.35 (m, 1 H, H^1 of norbornyl), 2.36–2.44 [m, 1 H, $(CH=CH)_2CH$], 5.82–5.89 [m, 1 H, (CH=C*H*)CH], 5.93–6.04 [m, 3 H, (CH=C*H*)CH, $(CH=CH)_2C$(Ph)], 7.13–7.20 (m, 1 H, Ph_o), 7.24–7.40 (m, 4 H, Ph) ppm. ^{13}C NMR (75 MHz): δ_C = 28.53, 30.52 (2 × CH_2), 31.63, 31.69 (2 × CH_3), 35.59, 36.37 (2 × CH_2), 36.74, 38.60 (2 × CH), 39.67 [$(CH=CH)_2CH$], 43.84 [$(CH=CH)_2$-*C*(Ph)], 47.52 (CH), 52.51 (CCH_2COH), 72.35 (COH), 125.99 (CH_{Ph}), 126.03 (2 C, CH_{Ph}), 126.75, 127.52 [$(CH=CH)_2CH$], 128.35 (2 C, CH_{Ph}), 133.37, 133.62 [$(CH=CH)_2CH$], 148.25 (C_{Ph}) ppm. IR (film): ṽ = 3435, 3022, 2950, 2868, 1667, 1597, 1491, 1454, 1372, 1299, 1214, 1033, 916, 743, 697 cm^{-1}. MS (70 eV, EI): *m/z* (%) = 324 (0.005) [M^+ + 2], 323 (0.04) [M^+ + 1], 322 (0.15) [M^+], 304 (1.6), 248 (10), 167 (22), 154 (17), 95 (100), 67 (14). HRMS: calcd. for $C_{23}H_{28}$: 304.2191; found 304.2173.

Preparation of Compounds *trans*-13, *cis*-13 and 14: To a deeply colored solution of naphthalene or phenanthrene (3 mmol) and lithium powder [$Li_{(s)}$, 12 mmol] in dry THF (10 mL) at 25 °C with vigorous stirring under Ar, propene was delivered using a ballon (approx. 3 L, 1 atm), ensuring a complete evacuation of the Ar. After ca. 2 h the reaction was then cooled down to –78 °C and 3-pentanone (**8**) (6 mmol) was added. After 15 min the reaction was hydrolyzed (H_2O) and worked up as usual (3 × 20 mL diethyl ether, Na_2SO_4, 15 Torr), purifying ***trans*-13**, ***cis*-13** or **14**, respectively, by flash chromatography (silica gel, Hx/EtOAc); 0.5 wt.-% of hydroquinone was added for stabilisation during storage (see ref.[6]).

3-[(1*RS*,4*RS*)-4-Isopropyl-1,4-dihydronaphth-1-yl]pentan-3-ol (*trans*-13): R_f = 0.39 (9:1, hexane/ethyl acetate). IR (film): ṽ = 3582, 3537, 3489, 3060, 3035, 2962, 2936, 2880, 1485, 1462, 1384, 1367, 1154, 1121, 1089, 938, 823, 750 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H = 0.55 (d, *J* = 6.9 H, 3 H, CH_3CHCH_3), 0.78 (app. t, *J* = 7.5 Hz, 3 H, CH_3CH_2), 1.00 (app. t, *J* = 7.4 Hz, 3 H, CH_3CH_2), 1.19 (d, *J* = 6.9 Hz, 3 H, CH_3CHCH_3), 1.39 (br. s, 1 H, OH), 1.41–1.53 (m, 2 H, CH_2CH_3), 1.52–1.64 (m, 2 H, CH_2CH_3), 2.52–2.64 (m, 1 H, CH_3CHCH_3), 3.28–3.32 (m, 1 H, CH=CHC*H*iPr), 3.59–3.63 (m, 1 H, CH=CHC*H*COH), 6.02–6.11 (m, 2 H, C*H*=C*H*CHCOH), 7.14–7.29 (m, 3 H, CHC*H*=CHCCHCO), 7.39 (app. d, *J* = 7.7 Hz, 1 H, CH=C*H*CCH*i*Pr) ppm. ^{13}C NMR (75 MHz): δ_C = 7.48, 7.70 (2 × CH_3CH_2), 16.08, 21.07 (CH_3CHCH_3), 27.91, 28.07 (2 × CH_2CH_3), 30.18 (CH_3CHCH_3), 43.22 (CH=CH*C*H*i*Pr), 46.99 (CH=CH*C*HCOH), 79.24 (COH), 125.12, 125.99, 126.19 (3 × CH_{ar}), 127.77, 128.27 (*C*H=*C*HCH*i*Pr), 129.32 (CH_{ar}), 136.04, 139.85 (2 × C_{ar}) ppm. MS: *m/z* (%) = 241 (0.11) [(M^+ – 18) + 1], 240 (0.53) [M^+ – 18], 172 (25), 130 (11), 129 (100), 128 (51), 87 (35). HRMS: calcd. for $C_{18}H_{24}$ 240.1878; found 240.1881.

3-[(1*RS*,4*SR*)-4-Isopropyl-1,4-dihydronaphth-1-yl]pentan-3-ol (*cis*-13): R_f = 0.45 (9:1, hexane/ethyl acetate). IR (film): ṽ = 3582, 3507, 3058, 3031, 2964, 2880, 2868, 1486, 1461, 1382, 1365, 1247, 1157, 1125, 971, 952, 936, 846, 825, 752 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H = 0.88 (app. t, *J* = 7.6 Hz, 3 H, CH_3CH_2), 1.00 (app. t, *J* = 7.6 Hz, 3 H, CH_3CH_2), 1.02 (d, *J* = 6.9 Hz, 3 H, CH_3CHCH_3), 1.10 (d, *J* = 6.6 Hz, 3 H, CH_3CHCH_3), 1.22 (br. s, 1 H, OH), 1.39–1.47 (m, 1 H, C*H*HCH$_3$), 1.51–1.65 (m, 2 H, CH_2CH_3), 1.66–1.76 (m, 1 H, CH*H*CH$_3$), 1.93–2.03 (m, 1 H, CH_3CHCH_3), 2.98–3.03 (m, 1 H, CH=CHC*H*iPr), 3.60–3.65 (m, 1 H, CH=CHC*H*COH), 5.93 (app. dd, *J* = 10.4, 5.1 Hz, 1 H, CH=C*H*CHCOH), 6.21 (app. dd, *J* = 10.4, 5.0 Hz, 1 H, CH=C*H*CH*i*Pr), 7.14–7.31 (m, 3 H, CH_{ar}), 7.32 (app. d, *J* = 6.3 Hz, 1 H, CH_{ar}) ppm. ^{13}C NMR (75 MHz): δ_C = 7.85, 7.89 (CH_3CH_2), 21.10, 22.67 (CH_3CHCH_3), 29.12, 29.15 (CH_2CH_3), 35.58 (CH_3CH), 46.98 (CH=CH*C*HCOH), 47.54 (CH=CH*C*H*i*Pr), 76.75 (*C*OH), 125.18, 125.52 (CH_{ar}), 126.52 (CH=*C*HCHCOH), 129.98, 130.47 (CH_{arom}), 131.34 (CH=*C*HCH*i*Pr), 135.48, 140.13 (C_{ar}) ppm. MS: *m/z* (%) = 241 (0.06) [(M^+ – 18) + 1], 240 (0.30) [M^+ – 18], 172 (24), 130 (11), 129 (100), 128 (49), 87 (56). HRMS: calcd. for $C_{18}H_{24}$ 240.1878: found 242.1904.

3-[(9*RS*,10*RS*)-10-Isopropyl-9,10-dihydrophenanthren-9-yl]pentan-3-ol (14): R_f = 0.27 (9:1, hexane/ethyl acetate). IR (film): ṽ = 3585, 3482, 3066, 3031, 2965, 2880, 1726, 1482, 1461, 1438, 1383, 1256, 1156, 1132, 975, 938, 910, 741 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H = 0.70 (d, *J* = 6.4 Hz, 3 H, CH_3CHCH_3), 0.76 (app. t, *J* = 7.3 Hz, 3 H, CH_3CH_2), 0.87 (app. t, *J* = 7.3 Hz, 3 H, CH_3CH_2), 0.91 (d, *J* = 6.9 Hz, 3 H, CH_3CHCH_3), 1.22–1.32 (m, 2 H, CH_2CH_3), 1.27 (br. s, 1 H, OH), 1.38–1.49 (m, 2 H, CH$_3$CH*H*COH, CH_3CHCH_3), 1.52–1.60 (m, 1 H, CH$_3$C*H*HCOH),

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2.58 (app. d, J = 8.7 Hz, 1 H, CC*Hi*Pr), 3.11 (app. s, 1 H, CC*H*COH), 7.12–7.35 (m, 6 H, $\mathrm{CH_{ar}}$), 7.70 (app. d, J = 7.8 Hz, 1 H, $\mathrm{CH_{ar}}$), 7.74 (app. d, J = 7.3 Hz, 1 H, $\mathrm{CH_{ar}}$) ppm. ^{13}C NMR (75 MHz): δ_C = 7.54, 8.10 ($\mathrm{CH_3}C\mathrm{H_2}$), 21.00, 21.51 ($C\mathrm{H_3CH}C\mathrm{H_3}$), 28.04, 28.38 ($C\mathrm{H_2CH_3}$), 31.37 ($\mathrm{CH_3}C\mathrm{HCH_3}$), 46.99 (C*C*H*i*Pr), 47.27 (C*C*HCOH), 77.1 (*C*OH), 123.60, 123.60, 127.03, 127.21, 127.30, 127.44, 130.01, 131.58 ($\mathrm{CH_{ar}}$), 134.53, 135.17, 135.74, 138.99 ($\mathrm{C_{ar}}$) ppm. MS: *m/z* (%): 291 (0.13) [(M^+ – 18) + 1], 290 (0.55) [M^+ – 18], 222 (22), 180 (14), 179 (100), 178 (41), 87 (11). HRMS: calcd. for $\mathrm{C_{22}H_{26}}$ 290.2035: found 290.2038.

Preparation of Compounds 15a–c and [D$_1$]15a–c: To a deeply colored solution of biphenyl (3 mmol) and lithium powder [$\mathrm{Li_{(s)}}$, 12 mmol] in dry THF (10 mL), at 25 °C with vigorous stirring under Ar, propene was delivered using a ballon (approx. 3 L, 1 atm), ensuring complete evacuation of the Ar atmosphere. After ca. 3 h the reaction was then cooled down to –78 °C and $\mathrm{D_2O}$ (20 mmol in 2 mL of THF) or $\mathrm{H_2O}$ (20 mmol in 2 mL of THF), respectively, was added drop by drop via syringe. Afterwards, the reaction was hydrolyzed ($\mathrm{H_2O}$) and worked up as usual (3 × 20 mL diethyl ether, $\mathrm{Na_2SO_4}$, 15 Torr), purifying **15a**–**c** and [D$_1$]**15a**–**c** by flash chromatography (silica gel doped with 1 wt.-% of hydroquinone, Hx/EtOAc); 0.5 wt.-% of hydroquinone was added for stabilisation during storage (see ref.[6]). The reactions carried out in [D$_8$]THF (2 mL) were run and worked up under analogous reaction conditions, scaling down all the reagents appropriately.

4-Isopropyl-3,4-dihydrobiphenyl (15a) and *trans*- and *cis*-4-Isopropyl-1,4-dihydrobiphenyl (15b and 15c, respectively). Mixture of Isomers: **15a** (major isomer): ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ_H = 0.94 (d, J = 6.9 Hz, 3 H, $\mathrm{C}H_3\mathrm{CHCH_3}$), 0.95 (d, J = 6.9 Hz, 3 H, $\mathrm{CH_3CHC}H_3$), 1.68–1.82 (m, 1 H, $\mathrm{CH_3C}H\mathrm{CH_3}$), 2.18–2.25 (2 m, 2 × 1 H, C*H*HC*Hi*Pr), 2.25–2.40 (m, 1 H, CH*H*CH*i*Pr), 5.92 (app. dd, J = 9.8, 2.6 Hz, 1 H, CH=C*H*CH*i*Pr), 6.05–6.10 (m, 1 H, $\mathrm{C{=}C}H\mathrm{CH_2}$), 6.32 (app. dt, J = 9.8, 1.8 Hz, 1 H, C*H*=CHCH*i*Pr), 7.19–7.41 (m, 5 H, Ph) ppm. MS: *m/z* (%) = 200 (0.29) [M^+ + 2], 199 (3.69%) [M^+ + 1], 198 (22.58%) [M^+], 156 (14), 155 (100), 154 (32), 153 (16), 77 (10). HRMS: calcd. for $\mathrm{C_{15}H_{18}}$ 198.1409: found 198.1382. **15b** (second major isomer): ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ_H = 0.98 (d, J = 6.8 Hz, 6 H, $\mathrm{C}H_3\mathrm{CHC}H_3$), 1.70–1.88 (m, 1 H, $\mathrm{CH_3C}H\mathrm{CH_3}$), 2.69–2.78 (m, 1 H, C*Hi*Pr), 3.94–4.02 (m, 1 H, PhCH), 5.67–5.81 [m (app. AA′BB′), 4 H, $\mathrm{PhCH(C}H{=}\mathrm{C}H)_2$CH*i*Pr], 7.19–7.41 (m, 5 H, Ph) ppm. MS: *m/z* (%): 200 (0.31, [M^++2]), 199 (2.44%, [M^++1]), 198 (14.91%, [M^+]), 156 (13), 155 (100), 154 (22), 153 (14), 77 (11). HRMS: calcd. for $\mathrm{C_{15}H_{18}}$ 198.1409: found 198.1393. **15c** (minor isomer): ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ_H = 0.95 (d, J = 6.8 Hz, 6 H, $\mathrm{C}H_3\mathrm{CHC}H_3$), 1.70–1.88 (m, 1 H, $\mathrm{CH_3C}H\mathrm{CH_3}$), 2.70–2.80 (m, 1 H, C*Hi*Pr), 3.86–3.93 (m, 1 H, PhCH), 5.67–5.83 [m, 4 H, $\mathrm{PhCH(C}H{=}\mathrm{C}H)_2$CH*i*Pr], 7.19–7.41 (m, 5 H, Ph) ppm. MS: *m/z* (%) = 200 (0.21) [M^+ + 2], 199 (2.24%) [M^+ + 1], 198 (13.20%) [M^+], 156 (14), 155 (100), 154 (20), 153 (14), 77 (11). HRMS: calcd. for $\mathrm{C_{15}H_{18}}$ 198.1409: found 198.1385.

(3*RS*,4*SR*)-3-Deuterio-4-isopropyl-3,4-dihydrobiphenyl ([D$_1$]15a) and *trans*- and *cis*-1-Deuterio-4-isopropyl-1,4-dihydrobiphenyl ([D$_1$]15b and [D$_1$]15c, respectively). Mixture of Isomers: [D$_1$]**15a** (major isomer): ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ_H = 0.93 (d, J = 6.9 Hz, 3 H, $\mathrm{C}H_3\mathrm{CHCH_3}$), 0.95 (d, J = 6.9 Hz, 3 H, $\mathrm{CH_3CHC}H_3$), 1.70–1.80 (m, 1 H, $\mathrm{CH_3C}H\mathrm{CH_3}$), 2.17–2.21 [2 m, 2 × 1 H, C*H*DC*Hi*Pr], 5.90 (app. d, J = 9.9 Hz, 1 H, CH=C*H*CH*i*Pr), 6.05 (app. br. s, 1 H, C=C*H*CHD), 6.32 (app. d, J = 10.1 Hz, 1 H, C*H*=CHCH*i*Pr), 7.19–7.41 (m, 5 H, Ph) ppm. MS: *m/z* (%) = 201 (0.34) [M^+ + 2], 200 (4.09%) [M^+ + 1], 199 (23.92%) [M^+], 198 (0.00%) [M^+ – 1], 157 (14), 156 (100), 155 (29), 154 (18). HRMS: calcd. for $\mathrm{C_{15}H_{17}D}$ 199.1471: found 199.1463. [D$_1$]**15b** (second major isomer): ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ_H = 0.97 (d, J = 6.8 Hz, 6 H, $\mathrm{C}H_3\mathrm{CHC}H_3$), 1.75–1.86 (m, 1 H, $\mathrm{CH_3C}H\mathrm{CH_3}$), 2.69–2.77 (m, 1 H, C*Hi*Pr), 5.67–5.81 [m (app. AA′BB′), 4 H, $\mathrm{PhCD(C}H{=}\mathrm{C}H)_2$CH*i*Pr], 7.19–7.41 (m, 5 H, Ph) ppm. MS: *m/z* (%) = 201 (0.22) [M^+ + 2], 200 (2.62%) [M^+ + 1], 199 (15.43%) [M^+], 198 (0.00%) [M^+ – 1], 157 (13), 156 (100), 155 (17), 154 (17). HRMS: calcd. for $\mathrm{C_{15}H_{17}D}$ 199.1471: found 199.1471. [D$_1$]**15c** (minor isomer): ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ_H = 0.94 (d, J = 6.8 Hz, 6 H, $\mathrm{C}H_3\mathrm{CHC}H_3$), 1.75–1.86 (m, 1 H, $\mathrm{CH_3C}H\mathrm{CH_3}$), 2.69–2.77 (m, 1 H, C*Hi*Pr), 5.67–5.83 [m, 4 H, $\mathrm{PhCH(C}H{=}\mathrm{C}H)_2$CH*i*Pr], 7.19–7.41 (m, 5 H, Ph) ppm. MS: *m/z* (%) = 201 (0.19) [M^+ + 2], 200 (2.42%) [M^+ + 1], 199 (14.56%) [M^+], 198 (0.00%) [M^+ – 1], 157 (13), 156 (100), 155 (15), 154 (18). HRMS: calcd. for $\mathrm{C_{15}H_{17}D}$ 199.1471: found 199.1465.

Preparation of Minor Products 16–19: Allyl bromide (1 mmol) or 3-bromo-2-methylpropene (1 mmol) was added to a suspension of Mg (5 mmol) in dry THF (5 mL) and was stirred vigorously at room temperature. After 1 h, 3-pentanone (1 mmol) or dicyclopropyl ketone (1 mmol) was added, allowing the mixture to react during 15 min. The reaction was then hydrolyzed ($\mathrm{H_2O}$), extracted (3 × 20 mL diethyl ether, $\mathrm{Na_2SO_4}$, 15 Torr) and the resulting products **16** (ca. 60%), **17** (ca. 60%), **18** (ca. 55%), **19** (ca. 65%) (unoptimized yields) were purified by column chromatography (silica gel, Hx/EtOAc).

3-Ethyl-5-hexen-3-ol (16)[34] and **3-ethyl-5-methyl-5-hexen-3-ol (18)**[34] were prepared according to the above-mentioned procedure. The spectroscopic data are identical to those described in the literature.

1,1-Dicyclopropylbut-3-en-1-ol (17): IR (film): $\tilde{\nu}$ = 3422, 2925, 1728, 1644, 1463, 1261, 1074, 797 cm^{-1}. ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ_H = 0.26–0.43 (m, 8 H, 4 × $\mathrm{C}H_2$ of cyclopropyl), 0.80–0.92 (m, 2 H, 2 × C*H* of cyclopropyl), 1.03 (br. s, 1 H, OH), 2.35 (d, J = 7.3 Hz, 2 H, $\mathrm{C}H_2\mathrm{CH{=}CH_2}$), 5.08–5.15 (2 m, 2 × 1 H, $\mathrm{C}H_2\mathrm{{=}CH}$), 5.97–6.09 (m, 1 H, $\mathrm{CH_2C}H\mathrm{{=}CH_2}$) ppm. ^{13}C NMR (75 MHz): δ_C = –0.48 (2 C), 0.64 (2 C, 4 × $C\mathrm{H_2}$ of cyclopropyl), 18.73 (2 C, 2 × *C*H of cyclopropyl), 47.16 ($C\mathrm{H_2CH{=}CH_2}$), 118.13 ($C\mathrm{H_2{=}CH}$), 134.49 ($C\mathrm{H{=}CH_2}$) ppm. MS: *m/z* (%) = 134 (M^+ – 18) [0.03], 111 (100), 69(99), 55 (11). HRMS: calcd. for $\mathrm{C_7H_{11}O}$: 111.0810; found 111.0814.

1,1-Dicyclopropyl-3-methylbut-3-en-1-ol (19): IR (film): $\tilde{\nu}$ = 3548, 3084, 3007, 2918, 1643, 1438, 1374, 1230, 1171, 1122, 1022, 991, 893, 828 cm^{-1}. ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ_H = 0.26–0.48 (m, 8 H, 4 × $\mathrm{C}H_2$ of cyclopropyl), 0.80–0.87 (m, 2 H, 2 × C*H* of cyclopropyl), 1.24 (br. s, 1 H, OH), 1.91 (app. s, 3 H, $\mathrm{C}H_3\mathrm{C{=}CH_2}$), 2.31 [app. s, 2 H, $\mathrm{C}H_2\mathrm{C(CH_3){=}CH_2}$], 4.77, 4.91 [2 app. s, 2 × 1 H, $\mathrm{C}H_2\mathrm{{=}C(CH_3)}$] ppm. ^{13}C NMR (75 MHz): δ_C = –0.26 (2 C), 1.01 (2 C, 4 × $C\mathrm{H_2}$ of cyclopropyl), 19.18 (2 C, 2 × *C*H of cyclopropyl), 25.01 [$\mathrm{CH_2C(}C\mathrm{H_3){=}CH_2}$], 49.94 [$C\mathrm{H_2C(CH_3){=}CH_2}$], 69.90 (COH), 114.53 ($C\mathrm{H_2{=}C}$), 143.10 ($C\mathrm{{=}CH_2}$) ppm. MS: *m/z* (%) = 111 (1.05) [M^+ – $\mathrm{C_4H_7}$], 110 (13), 109 (13), 69 (100). HRMS: calcd. for $\mathrm{C_{11}H_{18}O}$: 166.1358; found 166.1377.

Preparation of Minor Products 20 and 21: To a solution of 1-methylcyclopentene (2 mmol) in dry cyclohexane (10 mL), TMEDA (2 mmol) and *tert*-butyllithium (1.5 mmol, 1.7 M in pentane) was added, the mixture being stirred for 1 h at room temperature. The reaction was then cooled down to 0 °C and 3-pentanone (1.5 mmol), or dicyclopropyl ketone (1.5 mmol) was added, respectively. After 15 min the reaction was hydrolyzed ($\mathrm{H_2O}$) and worked up as usual (3 × 20 mL diethyl ether, $\mathrm{Na_2SO_4}$, 15 Torr), purifying compounds **20** (60%) and **21** (50%) (unoptimized yields) by flash chromatography (silica gel, Hx/EtOAc).

3-(2-Methylenecyclopentyl)pentan-3-ol (20): IR (film): ṽ = 3419, 2925, 1651, 1455, 1120 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H = 0.88 (app. t, 3 H, *J* = 7.5 Hz, $C\mathit{H}_3CH_2$), 0.91 (app. t, *J* = 7.5 Hz, 3 H, $C\mathit{H}_3CH_2$), 1.31 (br. s, 1 H, OH), 1.40–1.70 (2 m, 4 H, 2×$C\mathit{H}_2CH_3$), 1.41–1.54 (m, 1 H, $CH\mathit{H}CH_2C{=}CH_2$), 1.51–1.68 (m, 1 H, $CH_2CH\mathit{H}CHCOH$), 1.69–1.82 (m, 1 H, $C\mathit{H}HCH_2C{=}CH_2$), 1.78–1.91 (m, 1 H, $CH_2C\mathit{H}HCHCOH$), 2.12–2.34 (m, 2 H, $C\mathit{H}_2C{=}CH_2$), 2.65 (app. td, *J* = 8.3, 1.7 Hz, 1 H, $CH_2{=}CC\mathit{H}COH$), 4.92, 5.05 (app. 2s, 2×1 H, $C\mathit{H}_2{=}C$) ppm. ^{13}C NMR (75 MHz): δ_C = 7.69, 7.85 (2×CH_3CH_2), 25.17 ($\mathit{C}H_2CH_2C{=}CH_2$), 27.73 ($\mathit{C}H_2CH_3$), 28.10 ($CH_2\mathit{C}H_2CHCOH$), 28.74 ($\mathit{C}H_2CH_3$), 36.69 ($\mathit{C}H_2C{=}CH_2$), 49.49 ($CH_2{=}C\mathit{C}HCOH$), 108.32 ($\mathit{C}H_2{=}C$), 153.99 ($\mathit{C}{=}CH_2$) ppm. MS: *m*/*z* (%) = 150 (0.20) [M$^+$ – 18], 87 (100), 82 (31), 80 (11), 69 (15), 67 (31), 57 (68). HRMS: calcd. for $C_{11}H_{18}$: 150.1409; found 150.1463.

Dicyclopropyl(2-methylenecyclopentyl)methanol (21): IR (film): ṽ = 3542, 3085, 3007, 2956, 2869, 1647, 1469, 1433, 1376, 1303, 1180, 1112, 1022, 992, 912, 890, 834 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H = 0.25–0.50 (m, 8 H, 4×$C\mathit{H}_2$ of cyclopropyl), 0.80–0.88 (m, 2 H, 2×$C\mathit{H}$ of cyclopropyl), 1.26 (br. s, 1 H, OH), 1.08–1.12, 1.78–1.89 (2 m, 2×1 H, $C\mathit{H}_2CH_2C{=}CH_2$), 1.83–2.00 (m, 2 H, $CH_2C\mathit{H}_2CHCOH$), 2.29–2.42 (m, 2 H, $C\mathit{H}_2C{=}CH_2$), 2.67–2.73 (m, 1 H, $CH_2{=}CC\mathit{H}COH$), 5.01, 5.05 (2 app. s, 2×1 H, $C\mathit{H}_2{=}C$) ppm. ^{13}C NMR (75 MHz): δ_C = –1.38, –0.83, 1.12, 1.73 (4×$\mathit{C}H_2$ of cyclopropyl), 16.38, 16.89 (2×$\mathit{C}H$ of cyclopropyl), 25.03 ($\mathit{C}H_2CH_2C{=}CH_2$), 28.36 ($\mathit{C}H_2CHC{=}CH_2$), 35.67 ($\mathit{C}H_2C{=}CH_2$), 54.78 ($CH_2\mathit{C}HC{=}CH_2$), 71.84 (COH), 108.11 ($\mathit{C}H_2{=}C$), 154.22 ($\mathit{C}{=}CH_2$) ppm. MS: *m*/*z* (%) = 174 (0.08) [M$^+$ – 18], 111 (100), 69 (68).

Preparation of Carboxylic Acids 22a–b: To a solution containing dilithium biphenyl (**I**) prepared as described before for compounds **12**, propene was delivered using a balloon (approx. 3 L, 1 atm) previous evacuation of Ar. After ca. 1 h, the initial greenish-blue color of **I**$^{-2}$ turned brown. The reaction was then cooled down to –78 °C and $CO_{2(g)}$ was passed through. After 15 min, the reaction was hydrolyzed with water. The aqueous layer was acidified (12 M HCl) and extracted with diethyl ether (3×20 mL). The diethyl ether extract was then dried (Na_2SO_4) and concentrated under reduce pressure, purifying **22a**–**b** by flash chromatography (silica gel, Hx/EtOAc); 0.5 wt.-% of hydroquinone was added for stabilisation during storage (see ref.[6]).

4-*trans*-Isopropyl-1-phenylcyclohexa-2,5-dienecarboxylic Acid (22a): R_f = 0.47 (7:3, hexane/ethyl acetate). IR (film): ṽ = 3034, 2958, 2871, 2621, 1704, 1490, 1386, 1275, 1235, 916, 830, 733, 697 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H = 0.92 (d, *J* = 6.9 Hz, 6 H, $C\mathit{H}_3CHC\mathit{H}_3$), 1.80–1.91 (m, 1 H, $CH_3C\mathit{H}CH_3$), 2.65–2.72 (m, 1 H, $C\mathit{H}i$Pr), 5.89 [app. dd, *J* = 10.3, 3.3 Hz, 2 H, $(CH{=}C\mathit{H})_2CH\mathit{i}Pr$], 6.12 [app. dd, *J* = 10.4, 1.9 Hz, 2 H, $(CH{=}C\mathit{H})_2C(Ph)CO_2H$], 7.20–7.40 (m, 5 H, Ph), 13.10 (very br. s, 1 H, CO_2H) ppm. ^{13}C NMR (75 MHz): δ_C = 19.14 (2 C, $\mathit{C}H_3CH\mathit{C}H_3$), 31.11 ($CH_3\mathit{C}HCH_3$), 41.25 ($\mathit{C}H\mathit{i}Pr$), 52.88 [$(CH{=}CH)_2\mathit{C}(Ph)CO_2H$], 126.31 (2 C), 127.05, 127.79 (2 C), 128.61 (2 C), 128.73 (2 C, $(\mathit{C}H{=}\mathit{C}H)_2CH\mathit{i}Pr$, Ph_{CH}], 143.04 (Ph_{iC}), 179.44 ($\mathit{C}O_2H$) ppm. MS: *m*/*z* (%) = 243 (0.08) [M$^+$ + 1], 242 (0.33%) [M$^+$], 197 (31), 181 (13), 156 (13), 155 (100), 154 (17), 153 (16), 152 (14), 77 (10). HRMS: calcd. for $C_{16}H_{18}O_2$: 242.1307; found 242.1290.

(1*RS*,6*SR*)-6-Isopropyl-3-phenylcyclohexa-2,4-dienecarboxylic Acid (22b) (impure sample contaminated with acid 22a): ^{1}H NMR (300 MHz, $CDCl_3$): δ_H = 0.94 (d, *J* = 6.7 Hz, 3 H, $C\mathit{H}_3CHCH_3$), 0.98 (d, *J* = 6.7 Hz, 3 H, $CH_3CHC\mathit{H}_3$), 1.74–1.92 (m, 1 H, $CH_3C\mathit{H}CH_3$), 2.73–2.84 (m, 1 H, $C\mathit{H}i$Pr), 3.43 [app. dd, *J* = 8.5, 5.3 Hz, 1 H, $(C\mathit{H}CO_2H)$], 5.85–5.97 [2 m, 2×1 H, $C\mathit{H}{=}CHC(Ph){=}C\mathit{H}$], 6.34 [app. d, *J* = 10.0 Hz, 1 H, $CH{=}C\mathit{H}C(Ph){=}CH$], 7.22–7.44 (m, 5 H, Ph), 10.20 (very br. s, 1 H, CO_2H) ppm. MS: *m*/*z* (%) = 244 (0.47) [M$^+$ + 2], 243 (4.22%) [M$^+$ + 1], 242 (23.3%) [M$^+$], 181 (12), 156 (13), 155 (100), 154 (17), 153 (17), 152 (14).

Preparation of Dihydronaphthalenes 23a and 23b: To a deeply colored solution of naphtalene (3 mmol) and lithium powder [$Li_{(s)}$, 12 mmol] in dry THF (10 mL) at 25 °C under Ar, propene was delivered using a ballon (approx. 3 L, 1 atm) ensuring complete evacuation of the Ar. After ca. 2 h, the initial purple color of **II**$^{-2}$ turned brown. The reaction was then cooled down to –78 °C and the reaction was hydrolyzed (H_2O) and worked up as usual (3×20 mL diethyl ether, Na_2SO_4, 15 Torr), purifying **23a** and **23b** by flash chromatography (silica gel was doped with 1 wt.-% of hydroquinone, Hx/EtOAc); 0.5 wt.-% of hydroquinone was added for stabilisation during storage (see ref.[6]).

1-Isopropyl-1,4-dihydronaphthalene (23a): R_f = 0.58 (hexane). IR (film): ṽ = 3029, 2958, 2927, 2869, 2869, 2820, 1492, 1456, 1424, 1382, 1365, 745 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H = 0.68 (d, *J* = 6.9 Hz, 3 H, $C\mathit{H}_3CHCH_3$), 0.98 (d, *J* = 6.9 Hz, 3 H, $CH_3CHC\mathit{H}_3$), 2.00–2.12 (m, 1 H, $CH_3C\mathit{H}CH_3$), 3.21–3.44 (m, 3 H, $C\mathit{H}_2CH{=}CHC\mathit{H}i$Pr), 5.88–5.94 (m, 1 H, $CH_2C\mathit{H}{=}CHCH\mathit{i}$Pr), 6.04–6.08 (m, 1 H, $CH_2CH{=}C\mathit{H}CH\mathit{i}$Pr), 7.08–7.18 (m, 4 H, $C\mathit{H}_{ar}$) ppm. ^{13}C NMR (75 MHz): δ_C = 17.42, 20.47 ($\mathit{C}H_3CH\mathit{C}H_3$), 30.45 ($\mathit{C}H_2$), 36.07 ($CH_3\mathit{C}HCH_3$), 45.80 ($\mathit{C}H\mathit{i}$Pr), 125.51, 125.71, 126.27, 126.69,127.93, ($\mathit{C}H{=}\mathit{C}HCH_2$, 4×$CH_{ar}$), 135.26, 138.48 (2×$C_{ar}$) ppm. MS: *m*/*z* (%) = 174 (0.03) [M$^+$ + 2], 173 (0.56) [M$^+$ + 1], 172 (3.80) [M$^+$], 130 (11), 129 (100), 128 (60), 127 (14). HRMS: calcd. for $C_{13}H_{16}$ 172.1252: found 172.1258.

1-Isopropyl-1,2-dihydronaphthalene (23b): R_f = 0.55 (hexane). IR (film): ṽ = 3032, 2956, 2869, 2831, 1484, 1462, 1450, 1431, 1384, 1366, 792, 757, 728, 686 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H = 0.82 (d, *J* = 6.9 Hz, 3 H, $C\mathit{H}_3CHCH_3$), 0.90 (d, *J* = 6.9 Hz, 3 H, $CH_3CHC\mathit{H}_3$), 1.90–1.99 (m, 1 H, $CH_3C\mathit{H}CH_3$), 2.35–2.50 (m, 3 H, $CH{=}CHC\mathit{H}_2C\mathit{H}i$Pr), 5.87–5.95 (m, 1 H, $CH{=}C\mathit{H}CH_2$), 6.39 (app. d, *J* = 9.2 Hz, 1 H, $C\mathit{H}{=}CHCH_2$), 7.00 (app. d, *J* = 6.9 Hz, 1 H, CH_{ar}), 7.05–7.16 (m, 3 H, CH_{ar}) ppm. ^{13}C NMR (75 MHz): δ_C = 20.03, 21.26 ($\mathit{C}H_3CH\mathit{C}H_3$), 25.40 ($\mathit{C}H_2$), 30.61 ($CH_3\mathit{C}HCH_3$), 43.53 ($\mathit{C}H\mathit{i}$Pr), 125.92, 126.32, (3×$CH_{ar}$), 127.42, 127.57 ($\mathit{C}H{=}\mathit{C}HCH_2$), 128.58 ($CH_{ar}$), 133.91, 138.28 (2×$C_{ar}$) ppm. MS: *m*/*z* (%) = 174 (0.20) [M$^+$ + 2], 173 (3.01) [M$^+$ + 1], 172 (21.51) [M$^+$], 130 (13), 129 (100), 128 (64), 127 (16). HRMS: calcd. for $C_{13}H_{16}$ 172.1252: found 172.1258.

Supporting Information (see also the footnote on the first page of this article): Table S1 showing HOMO atomic contributions and population analysis data of arene dianions **I**$^{-2}$–**III**$^{-2}$ from B3LYP calculations.

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