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Regioselective Synthesis of Alkylarenes by Two-Step *ipso*-Substitution of Aromatic Dicarboxylic Acids

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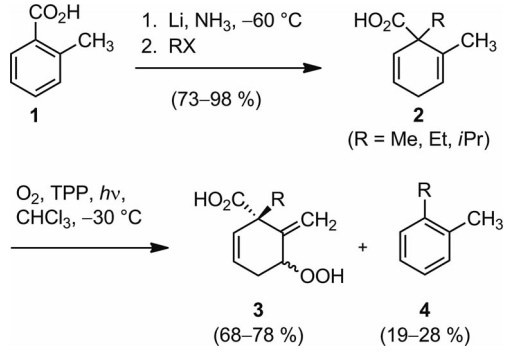
A strategy for the regioselective alkylation of arenes was developed, starting from commercially available and inexpensive terephthalic acid or naphthalene-1,4-dicarboxylic acid. The method entails a formal *ipso*-substitution of the carboxylate groups by a sequence of reductive alkylation under Birch conditions and subsequent acid-mediated rearomatization with loss of carbon monoxide and carbon dioxide. More than 20 different arenes with various side-chains were synthesized. With naphthalene-1,4-dicarboxylic acid as starting material, we were able to control the degree of alkylation by choosing the appropriate electrophile in the Birch reduction. Thus, bisalkylated naphthalenes and naphthoic acids became available chemoselectively. All reactions afforded a single regioisomer exclusively in high yields. Overall, aromatic dicarboxylic acids are suitable substrates for a two-step *ipso*-substitution that allows the selective synthesis of alkylated benzenes and naphthalenes.

Introduction

The efficient functionalization of arenes has always been an important target in organic chemistry and industrial processes.[1] In this context, the formation of C–C bonds is of special interest, and it has given rise to many publications concerning different synthetic routes. Classical methods such as Friedel–Crafts alkylation often give insufficient regioselectivities, and bisalkylations are especially difficult to realize using such methods.[2] The more selective Friedel–Crafts acylation[3] requires subsequent reduction of the carbonyl group.[4] Modern strategies[5] such as Stille,[6] Heck,[7] Sonogashira,[8] or Suzuki couplings,[9] often starting from aryl halides, proceed under mild conditions and result in the fomation of a single regioisomer. Yet many methods require laborious syntheses of starting materials, or expensive Pd catalysts, or involve the use of toxic metal organyls. In addition, many procedures are limited to the formation of C–C bonds to sp^2- or sp-centers due to competing β-hydride elimination. One exception is the iron(III)-catalyzed alkylation of chloroarenes with Grignard reagents, which leads to alkyl-substituted arenes in high yields.[10] The substitution of the carboxylate group of aromatic carboxylic acids offers an interesting alternative to the already mentioned methodologies, since these acids are commercially available and often inexpensive industrial bulk products. Gooßen et al. and Myers et al. have developed, respectively, copper- and palladium-catalyzed C–C coupling protocols proceeding with the evolution of carbon dioxide.[11] However, in these cases, only arylations and vinylations were possible, and no alkylations were described.

During the course of our investigations on singlet-oxygen chemistry, we discovered an unexpected aromatization of 1,4-cyclohexadienes **2** derived from *o*-toluic acid (**1**) by reductive alkylation under Birch conditions (Scheme 1).[12] The reaction proceeded under acidic conditions, and was accompanied by the formation of carbon monoxide. Based on these results, we developed an efficient two-step *ipso*-substitution of different aromatic monocarboxylic acids by alkyl groups, applying a sequence of alkylative Birch reduction and subsequent treatment with the strongly acidic and hygroscopic chlorosulfonic acid.[13]



Scheme 1. Unexpected formation of arenes **4** during the photooxygenation of 1,4-cyclohexadienes **2**.

However, in our initial studies, we only investigated monocarboxylic acids. Very recently, we became interested in the *ipso*-substitution of terephthalic acid (**5**), and described

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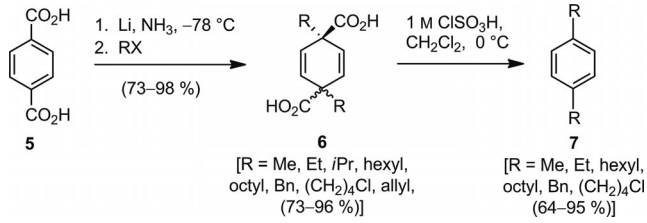
our results in a communication.[14] Birch reduction and subsequent alkylation was realized with this arene for the first time, with cyclohexadienes **6** being formed in good yields (Scheme 2). Reaction with chlorosulfonic acid resulted in rearomatization, and gave easy access to 1,4-dialkylbenzenes **7** with excellent regioselectivities. In addition, we found evidence for an interesting mechanism involving two subsequent C–C bond cleavages with the evolution of carbon monoxide and carbon dioxide, which we called a tandem decarbonylation–decarboxylation.



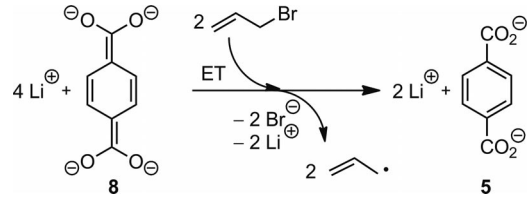
Scheme 2. *ipso*-Substitution of terephthalic acid (**5**).

In our recent communication we investigated only the *ipso*-substitution of terephthalic acid with a few alkyl halides.[14] To extend our methodology, we became interested in the introduction of other functional groups, and also in the use of another diacid as starting material. In this paper, we describe our results on the Birch reduction of terephthalic acid in the presence of other electrophiles, and on the subsequent rearomatization of the cyclohexadienes. We found some interesting mechanistic features, and we will discuss the scope and limitations of such *ipso*-substitutions. Additionally, we present the first successful Birch reduction of naphthalene-1,4-dicarboxylic acid (**15**) with subsequent alkylation. The rearomatization of the resulting dihydronaphthalenes proceeded smoothly to give alkylated naphthalenes as single regioisomers in high yields. We want to demonstrate in this full paper, that the mechanistically interesting *ipso*-substitution of aromatic diacids is a convenient method for the regioselective synthesis of various bisalkylated arenes.

Results and Discussion

ipso-Substitution of Terephthalic Acid

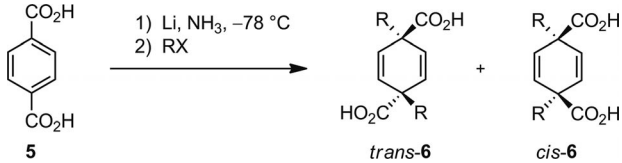
Terephthalic acid (**5**) is a commercially available and inexpensive starting material. Although the Birch reduction is an established and often used transformation in organic chemistry,[15] we succeeded in the reductive alkylation of this aromatic diacid only very recently.[14] It was important to have a high dilution in liquid ammonia, due to the low solubility of the intermediate tetraanions **8**. We applied these conditions to electrophiles bearing different functional groups to examine the scope and limitations, and to gain mechanistic insight into such Birch reductions (Table 1). Indeed, 4-bromo-1-butene afforded cyclohexadiene **6b** in full conversion, and remarkably in a higher yield than that obtained with allyl bromide (Table 1, entries 1 and 2). This is a further proof of our hypothesis that an electron transfer from the intermediate tetraanion **8** to allyl bromide results in lower conversions, and in the reisolation of terephthalic acid (Scheme 3).



Scheme 3. Competing electron transfer (ET) from tetraanion **8** to allyl bromide.

Additionally, other functional groups like ethers or acetals are tolerated during the bisalkylation of terephthalic acid (**5**) under Birch conditions (Table 1, entries 3 and 4). Thus, the electrophiles 3-(2-bromoethoxy)prop-1-ene[16] and 2-(2-bromoethyl)-1,3-dioxolane reacted smoothly to give the corresponding 1,4-cyclohexadienes (i.e., **6c** and **6d**) in good to high yields. All the reactions showed a preference for the formation of the *trans*-configured products *trans*-**6**.

Table 1. Birch reduction and alkylation of terephthalic acid (**5**).

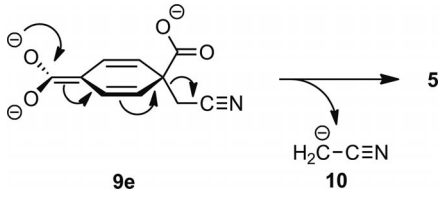


Entry	RX (10 equiv.)	Product (yield [%])[a]	*trans*/*cis*[b]
1	allyl bromide	**6a** (74)[c]	60:40
2	4-bromo-1-butene	**6b** (87)	65:35
3	3-(2-bromoethoxy)prop-1-ene[d]	**6c** (93)	80:20
4	2-(2-bromoethyl)-1,3-dioxolane	**6d** (78)	85:15
5	2-chloroacetonitrile	**6e** (0)	–
6	ethyl 4-bromobutyrate	**13f** (89)[e]	–
7	4-bromobutyronitrile	**13g** (85)[e]	–

[a] Yield of purified product. [b] Determined from the NMR spectra of the crude products. [c] Lower yield, due to incomplete conversion (Ref.[14]). [d] Synthesis over two steps.[16] [e] Formation of monoalkylated 1,3-cyclohexadienes **13f** and **13g**.

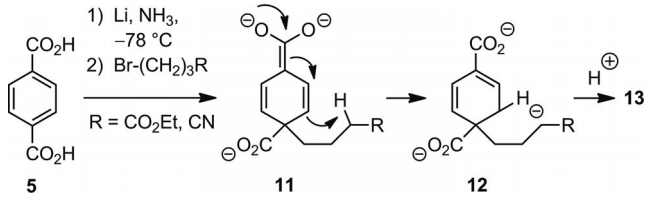
This can be rationalized by steric interactions in the second alkylation step, consistent with our previous studies.[14]

Although we could introduce ethyl acetate or acetonitrile substituents during the Birch reduction of toluic or naphthoic acid,[13] these reactions failed with terephthalic acid (**5**), since no consumption of the starting material was observed (Table 1, entry 5). We explain this behavior by a fragmentation of the monoalkylated intermediate **9e** by cleavage of a stabilized carbanion **10**. The terephthalate is finally protonated during work-up to reform the starting material (Scheme 4).



Scheme 4. Proposed fragmentation of monoalkylated anion **9e**.

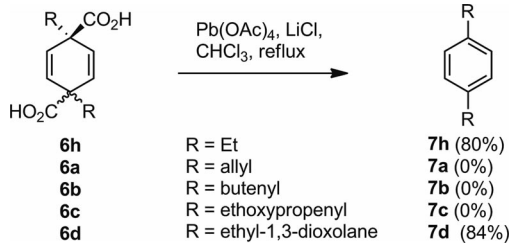
To overcome this problem of fragmentation, we used electrophiles with longer alkyl chains between the halide leaving group and the ester and nitrile functional groups. Indeed, ethyl 4-bromobutyrate and 4-bromobutyronitrile gave full conversion of terephthalic acid, and cyclohexadienes were isolated in high yields (Table 1, entries 6 and 7). Surprisingly, it was not the expected 1,4-bisalkylated 2,5-cyclohexadienes (i.e., **6**) that were formed, but rather monoalkylated 1,3-dienes **13f** and **13g**. Although a double-bond migration during the Birch reduction, as discussed by other groups,[17] cannot be completely ruled out, the striking difference between entries 6 and 7 on the one hand and all other Birch reductions on the other suggests that another explanation is required. Our mechanistic rationale is based on monoalkylated intermediates **11**, with acidic CH protons α to the ester or nitrile groups (Scheme 5). Thus, intramolecular proton-transfer to the double bond is possible, and this would give 1,3-cyclohexadienes **13** after work-up. This new hypothesis might be interesting for the discussion of the regioselectivity of the Birch reduction in general.



Scheme 5. Proposed mechanism for the formation of 1,3-cyclohexadienes **13** by intramolecular proton transfer during the Birch reduction.

For the final *ipso*-substitution, we first used chlorosulfonic acid, which was a suitable reagent for the rearomatization of simple alkyl-substituted compounds.[14] However, with hitherto unknown cyclohexadienes **6b** and **6c** with double bonds in the side-chain, only a brown sticky material was obtained, indicating that polymerization had occurred under the strongly acidic reaction conditions. In the attempted reaction of dioxolanyl-substituted diacid **6d**, some aldehyde signals were seen in the NMR spectrum of the crude reaction mixture, due to cleavage of the protecting group. Again, no defined product could be isolated after column chromatography.

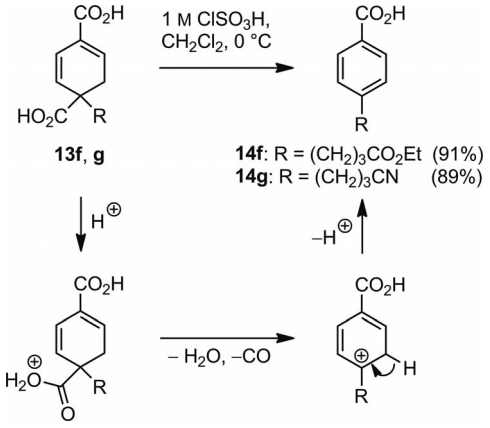
To overcome the problem of the strongly acidic conditions, we turned our attention to reactions in the presence of lead tetraacetate and lithium chloride. This method was developed for aromatizations of cyclohexa-2,5-diene-1-carboxylic acids with concomitant decarboxylation by a radical pathway.[18] Since only the reaction of monoacids has only been described to date, we tested this reagent on simple diacid **6h** with two ethyl substituents. Indeed, 1,4-diethylbenzene (**7h**) was isolated in 80% yield (Scheme 6). Although toxic reagents have to be used, this is the first example of a C–C double-bond cleavage in the presence of $Pb(OAc)_4$, and this method might be used for the regioselective synthesis of other arenes. Unfortunately, alkenyl-substituted cyclohexadienes **6a**–**c** were again unstable under the reaction conditions, presumably because of lead-mediated additions to the double bonds.[19] On the other hand, the dioxolane ring was not cleaved by lead tetraacetate, which allowed the introduction of this functional group and the regioselective synthesis of 1,4-bisalkyl benzene **7d** in 84% yield (Scheme 6).



Scheme 6. Decarboxylations of cyclohexadienes **6**.

For the aromatization of 1,3-cyclohexadienes **13f** and **13g**, we could use our previously developed procedure with the less toxic chlorosulfonic acid in dry dichloromethane at 0 °C. Thus, *p*-substituted benzoic acids **14f** and **14g** were isolated in high yields, presumably by a tandem dehydration–decarbonylation sequence (Scheme 7). This demonstrates that functional groups like esters or nitriles, which are of interest for further transformations like reductions, are tolerated under the reaction conditions. Thus, this first example of an aromatization of a 1,3-cyclohexadiene under acidic conditions opens a regioselective access to *p*-substituted benzoic acids from terephthalic acid.

In summary, we have been able to extend the scope of the Birch reduction and subsequent alkylation of terephthalic acid to tolerate other functional groups, like ethers, acetals, esters, and nitriles. With certain electrophiles, we observed hitherto unknown fragmentations or intramolecular proton transfers during the reactions. The formation of 1,3-cyclohexadienes might be particularly interesting in the context of the general mechanism of Birch reductions. Some functional groups are not stable in the presence of



Scheme 7. Proposed mechanism of the rearomatization of 1,3-cyclohexadienes **13**.

chlorosulfonic acid, but esters and nitriles are tolerated. Lead tetraacetate was used for the aromatization of diacids for the first time, which allowed the introduction of more sensitive acetal groups. Finally, the aromatization of 1,3-cyclohexadienes proceeded under mild conditions, which allowed the selective synthesis of *p*-substituted benzoic acids from terephthalic acid.

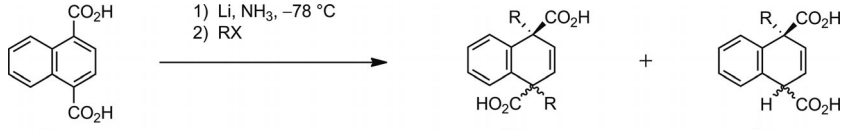
ipso-Substitution of Naphthalene-1,4-dicarboxylic Acid

To extend the scope of the *ipso*-substitution of aromatic dicarboxylic acids, we chose naphthalene-1,4-dicarboxylic acid (**15**) as starting material. This is an inexpensive, commercially available arene, and its Birch reduction was hitherto unknown. In principle, both aromatic rings might be reduced and the degree of alkylation after the addition of alkyl halides had to be examined. Furthermore, the conditions for the subsequent aromatization had to be carefully optimized.

The first reactions were conducted with a 50 mM concentration of naphthalene-1,4-dicarboxylic acid (**15**) in liquid ammonia and lithium as reducing agent, conditions different from those used with terephthalic acid. Iodomethane was used as the electrophile, since it allowed an easy interpretation of the NMR spectra of the crude products. The reaction proceeded to full conversion, and yielded bis- and monomethylated 1,4-dihydronaphthalene-1,4-dicarboxylic acids **16a** and **17a** as a mixture of *trans* and *cis* isomers (Table 2, entry 1). Importantly, no further reduction of the second, unfunctionalized aromatic ring was observed, due to its higher electron density. The ratio of **16a**/**17a** was 4:1, thus bisalkylation predominated. To obtain a higher selectivity for monoalkylation, we protonated with 1–2 equiv. *tert*-butyl alcohol before adding iodomethane. This alcohol has often been used as a proton source in Birch reductions.[15] However, the resulting mixture just contained 10% more monoalkylation product **17a** than was seen in the first experiment (Table 2, entry 2). This observation can be rationalized with the HSAB (hard/soft acid/base) concept.[20] Protons are hard Lewis acids, and prefer protonation of the strongly Lewis basic amide anions or the carboxylate oxygen instead of the weakly Lewis basic C1 or C4. Consequently, the resulting enolate is still reactive for bisalkylation. Thus, the degree of alkylation could not be influenced by the addition of alcohols, and depends only on the corresponding alkylation agent (vide infra). However, a separation of mono- and bisalkylated products **16a** and **17a** was possible by column chromatography, and the overall yield was 91%.

To examine the scope of the Birch reduction of naphthalene-1,4-dicarboxylic acid (**15**), we investigated other halides and the degree of alkylation (Table 2, entries 3–10). We did not use electrophiles with double bonds, because of the expected problems during rearomatization. Interestingly, less sterically demanding reagents like iodomethane or

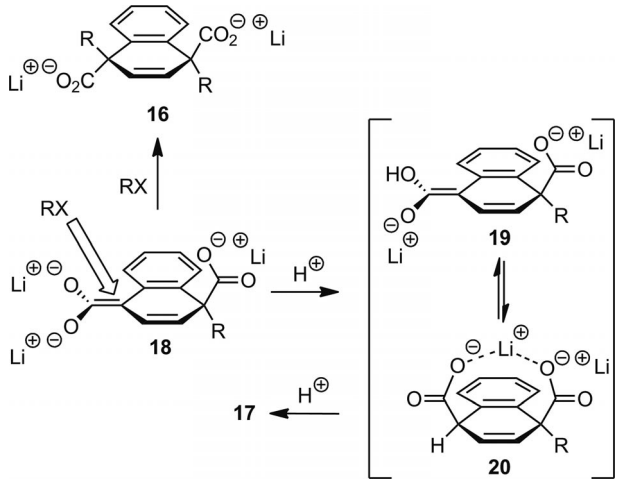
Table 2. Birch reduction of naphthalene-1,4-dicarboxylic acid (**15**).



15 **16** **17**

Entry	RX (10 equiv.)	Product (yield [%])[a]	*trans*/*cis*[b]	Product (yield [%])[a]	*trans*/*cis*[b]
1	MeI	**16a** (73)	60:40	**17a** (18)	50:50
2	MeI[c]	**16a** (62)	50:50	**17a** (27)	40:60
3	EtBr	**16b** (71)	70:30	**17b** (24)	40:60
4	*i*PrBr[d]	**16c** (54)	90:10	**17c** (9)	20:80
5	*n*HexBr	**16d** (5)	> 95:5	**17d** (90)	30:70
6	*n*OctBr	**16e** (5)	> 95:5	**17e** (91)	10:90
7	BnBr	**16f** (< 5)	–	**17f** (80)	< 5:95
8	1-bromo-4-chlorobutane	**16g** (63)	80:20	**17g** (27)	30:70
9	ethyl 4-bromobutyrate	**16h** (5)	–	**17h** (91)	< 5:95
10	4-bromobutyronitrile	**16i** (5)	–	**17i** (87)	< 5:95

[a] Yield of isolated product after column chromatography or crystallization. [b] Determined from NMR spectra. [c] Addition of 1 equiv. *tert*-butyl alcohol before adding iodomethane. [d] Yields of dihydronaphthalenes **16c** and **17c** were lower because of the formation of 4-isopropylnaphthalenecarboxylic acid (**22c**; 30%).



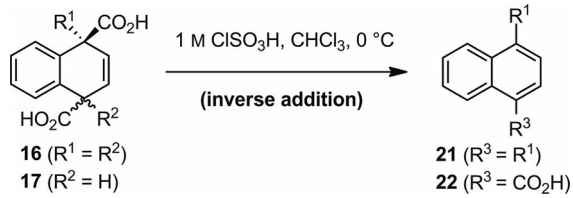
Scheme 8. Different reaction pathways of intermediate trianion **18**.

bromoethane show a preference for bisalkylation (to give **16**), whereas bulkier alkyl halides (e.g., bromohexane, bromooctane, benzyl bromide) gave monoalkylated dihydronaphthalenes **17** almost exclusively. This can be rationalized by an electronic stabilization of the intermediate trianion (i.e., **18**) by the adjacent benzene ring (Scheme 8). Furthermore, this ring causes steric hindrance. Thus, the alkylations proceeded more slowly than with terephthalic acid, allowing competing protonation, which results in monoalkylated product **17**.

Interestingly, monoalkylated 1,4-dihydronaphthalenes **17** are formed mainly as *cis* isomers, in contrast to bisalkylated products **16**. The predominant *trans* configuration of products **16** is consistent with the results from terephthalic acid (Table 1 and ref.[14]), and can be rationalized by steric interactions with the alkyl group (Scheme 8). This explains why more sterically demanding halides give high *trans* selectivities (Table 2). On the other hand, protonation, which leads to monoalkylated 1,4-dihydronaphthalenes **17**, should occur at the oxygen, due to the HSAB concept (vide supra). Thus, enol **19** is formed in the first step, which can tautomerize to acid **20**, stabilized by intramolecular coordination with lithium ions. After work-up, the *cis* isomer is formed predominantly (Scheme 8).

All Birch reductions of naphthalene-1,4-dicarboxylic acid (**15**) proceeded smoothly to give eight alkylated 1,4-dihydronaphthalenes **16** and **17** in very good yields (Table 2). Although the separation of *cis* and *trans* isomers was not possible, their structures were assigned by NMR spectroscopy and X-ray analysis (see Supporting Information). Furthermore, the monoalkylated products (i.e., **16**) could be isolated in analytically pure form by column chromatography or crystallization (see Experimental Section). Another advantage is that mixtures of *cis* and *trans* isomers can be used directly for the rearomatizations (vide infra). Only the Birch reduction with 2-bromopropane as electrophile showed different behavior, giving 1,4-dihdronaphthalenes **16c** and **17c** in remarkably lower yields (Table 2, entry 4). Additionally, the formation of a gas was observed already during the acidic work-up, indicating a proton-catalyzed rearomatization, as discussed below. Indeed, 4-isopropyl-1-naphthalenecarboxylic acid (**22c**) was isolated in 30% yield as a by-product.

Table 3. Rearomatization of dihydronaphthalenes **16** and **17**.



Entry	Dihydronaphthalene	R^1	R^2	R^3	Naphthalene (yield [%])[a]
1[b]	**16b**	Et	Et	Et	**21b** (56)[c]
2	**16a**	Me	Me	Me	**21a** (85)
3	**16b**	Et	Et	Et	**21b** (86)
4	**16c**	*i*Pr	*i*Pr	CO_2H	**22c** (84)
5	**16d**	*n*Hex	*n*Hex	*n*Hex	**21d** (91)
6	**16e**	*n*Oct	*n*Oct	*n*Oct	**21e** (90)
7	**16g**	$(CH_2)_4Cl$	$(CH_2)_4Cl$	$(CH_2)_4Cl$	**21g** (89)
8	**17a**	Me	H	CO_2H	**22a** (91)
9	**17b**	Et	H	CO_2H	**22b** (86)
10	**17c**	*i*Pr	H	CO_2H	**22c** (90)
11	**17d**	*n*Hex	H	CO_2H	**22d** (85)
12	**17e**	*n*Oct	H	CO_2H	**22e** (86)
13	**17f**	Bn	H	CO_2H	**22f** (81)
14	**17g**	$(CH_2)_4Cl$	H	CO_2H	**22g** (92)
15	**17h**	$C_3H_6CO_2Et$	H	CO_2H	**22h** (89)
16	**17i**	$(CH_2)_3CN$	H	CO_2H	**22h** (85)

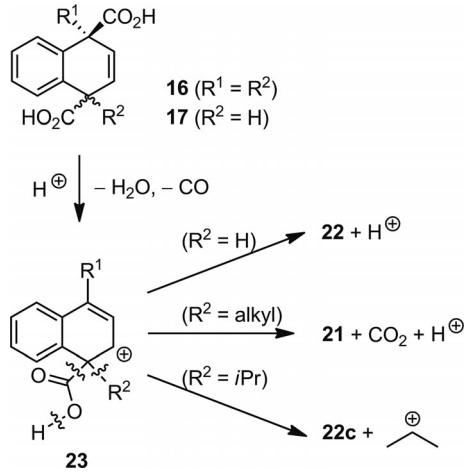
[a] Yield of analytically pure product, isolated by column chromatography. [b] Addition of chlorosulfonic acid (1 M) to the dihydronaphthalene. All other reactions (entries 2–16) were performed by the inverse addition method. [c] Formation of sulfonation products.

For the rearomatization of the 1,4-dihydronaphthalene-1,4-dicarboxylic acids, we used chlorosulfonic acid again, which worked well for simple alkyl-substituted terephthalic acid.[14] However, the higher reactivity of naphthalenes than benzenes in $S_E(Ar)$ reactions had to be taken into account. Furthermore, the solubility of the diacids in dichloromethane was very low. Therefore, we optimized the conditions with bisethylated compound **16b**, which was easy to analyze by NMR spectroscopy. Thus, 2 equiv. $ClSO_3H$ (1 M) was added to a suspension of the starting material in dichloromethane at 0 °C. Due to the low solubility, the reaction proceeded slowly, and full consumption of starting material was only achieved after 30 min. The NMR spectrum of the crude reaction mixture was complex and indicated the presence of sulfonation products as well as 1,4-diethylnaphthalene (**21b**), which was finally isolated in only 56% yield after column chromatography (Table 3, entry 1).

Neither changing the solvent (chloroform) nor varying the temperature (25, –15, –30 °C) resulted in higher yields. Obviously, the contact time of the arene product with chlorosulfonic acid was too long, and this resulted in the formation of sulfonation by-products. Finally, we solved this problem by adding dihydronaphthalene **16b** to a 1 M solution of chlorosulfonic acid in chloroform at 0 °C. The reaction was quenched after only 2 min by adding the mixture to a saturated sodium carbonate solution (5 mL). Indeed, the desired 1,4-diethylnaphthalene (**21b**) was now isolated in 86% yield after column chromatography in analytically pure form (Table 3, entry 3). This *inverse addition* is a remarkable improvement compared to our previous studies, and it might be used in other *ipso*-substitutions as well.

We used this successful procedure for all other mono- and bisalkylated 1,4-dihydronaphthalenes **16** and **17** (Table 3). In all, 15 different naphthalenes were isolated in analytically pure form in high yields as single regioisomers (see Exp. Section). Bisalkylated starting materials **16** gave 1,4-dialkylnaphthalenes **21** (Table 3, entries 1–3 and 5–7), whereas monoalkylated 1,4-dihydronaphthalenes **17** yielded exclusively 4-alkyl-1-naphthalenecarboxylic acids **22** (Table 3, entries 8–16). Only 1,4-bisisopropyl derivative **16c** showed a different reactivity and afforded 4-isopropyl-1-naphthalenecarboxylic acid (**22c**) in 84% yield (Table 3, entry 4). The formation of these various products supports our previous mechanistic hypothesis for *ipso*-substitutions of other aromatic carboxylic acids,[13,14] which is summarized in Scheme 9.

In the first step, protonation of one carboxylic acid group with the strong chlorosulfonic acid affords, after dehydration and *decarbonylation*, carbenium ion **23**. Now three different reaction pathways are possible. For monoalkylated 1,4-dihydronaphthalenes **17** (R^2 = H) deprotonation is obvious, leading directly to 4-alkyl-1-naphthalenecarboxylic acids **22**. Bisalkylated derivatives **16** (R^2 = alkyl) cannot react by this pathway. Thus, cleavage of the C–C bond to the carboxylic acid takes place to give 1,4-bisalkyl naphthalenes **21** in high yields by a *decarboxylation*. Finally, for 1,4-diisopropyl-1,4-dihydronaphthalene (**16c**) (R^2 = *i*Pr), the cleavage of a stabilized carbenium ion



Scheme 9. Proposed mechanisms for the aromatizations to naphthalenes **21** and **22**.

is faster, which results in product **22c** and finally 2-chloropropane, which was detected in the NMR spectra.

In summary, we have realized the Birch reduction of 1,4-naphthalenedicarboxylic acid for the first time. Mono- and bisalkylated 1,4-dihydronaphthalenes were isolated in high yields, although the degree of alkylation could not be controlled. The formation of *cis* and *trans* isomers in different ratios is interesting in the context of the mechanism of Birch reductions. For the rearomatizations, a new experimental protocol with chlorosulfonic acid was developed, which afforded naphthalenes as single regioisomers in high yields. The formation of the different products can be explained by a general mechanism of *decarbonylations* and *decarboxylations*, which should also operate in other *ipso*-substitutions. Overall, starting from the inexpensive precursor naphthalene-1,4-dicarboxylic acid, various alkyl-substituted naphthalenes were synthesized in only two steps as single regioisomers in high yields.

Conclusions

Aromatic dicarboxylic acids are suitable starting materials for the regioselective synthesis of alkylarenes. Terephthalic and naphthalene-1,4-dicarboxylic acids are inexpensive precursors that undergo Birch reduction and subsequent alkylation in high yields. We used electrophiles containing ester, nitrile, and acetal groups for the first time, thus extending the scope of this method. Interesting fragmentations or intramolecular proton transfers during the Birch reductions gave mechanistic insight in this reaction. With naphthalene-1,4-dicarboxylic acid as precursor, the different ratios of mono- and bisalkylated products and *cis* and *trans* isomers were rationalized by a change in the reaction pathway. More than 20 new dihydro derivatives were isolated in high yields in analytically pure form.

For the subsequent rearomatizations, we used inexpensive chlorosulfonic acid. We developed a new experimental protocol for 1,4-dihydronaphthalenes, which afforded higher yields of naphthalenes. Some functional groups were

not stable under the strongly acidic conditions, but we could use lead tetraacetate for the aromatization of diacids for the first time. The formation of mono- and bisalkylated naphthalenes was important from the point of view of the mechanism of the reactions in the presence of chlorosulfonic acid. Thus, a deprotonation, a tandem decarbonylation–decarboxylation sequence or the cleavage of an isopropyl group can compete. Overall, we have extended the scope of the *ipso*-substitution of aromatic carboxylic acids to tolerate other functional groups, and applied the method to naphthalene-1,4-dicarboxylic acid for the first time. Starting from inexpensive precursors, various alkyl-substituted arenes were synthesized in only two steps as single regioisomers in high yields.

Experimental Section

General Methods: Commercially available chemicals and solvents were used as purchased or purified by standard methods. TLC was performed on aluminium sheets coated with silica gel 60 F_{254} (Merck). Column chromatography was carried out with silica gel LC60A 40–63 μM (Davisil). NMR spectra were recorded with Bruker Avance 300 MHz and 500 MHz spectrometers. Deuterated solvents were used as internal standards. Melting points were measured with MEL-TEMP II and Electrothermal BI 9100 instruments. IR spectra were recorded with a Nicolet 6700 FT-IR spectrometer. Elemental analyses were performed with a Vario EL III (ELEMENTAR) apparatus. Mass spectra were recorded with ESI-Q-TOF (Waters) and Thermo DSQII (Axel Semrau GmbH) spectrometers.

General Procedure for the Birch Reductions of Terephthalic Acid (5): Lithium (555 mg, 80 mmol) was added in small portions at –78 °C to a suspension of terephthalic acid (1.66 g, 10.0 mmol) in liquid ammonia (500 mL) until the blue color persisted. After 5 h at this temperature, the alkyl halide (100 mmol, 10 equiv.) was added slowly. The ammonia was evaporated overnight, and the solid residue was dissolved in water (100 mL). After cooling to 0 °C, concentrated aqueous HCl was slowly added until pH 1 was reached, and the resulting precipitate was filtered off and dried in a desiccator. Products **6** and **13** were purified by recrystallization.

1,4-Diallylcyclohexa-2,5-diene-1,4-dicarboxylic Acid (6a):[14] White solid (1.83 g, 74%); m.p. 176–178 °C. R_f = 0.35 (dichloromethane/methanol, 10:1). ^{1}H NMR (300 MHz, [D$_6$]DMSO, *cis* and *trans* isomers overlapping): δ = 2.33 (d, J = 7.2 Hz, 4 H, 4-H), 4.95–5.06 (m, 4 H, 6-H), 5.50–5.65 (m, 2 H, 5-H), 5.81 (s, 4 H, 2-H), 11.59 (br. s, 2 H, -CO*OH*) ppm. *trans* isomer: ^{13}C NMR (75 MHz, CDCl$_3$): δ = 44.0 (t, C-4), 48.1 (s, C-1), 118.7 (t, C-6), 128.7 (d, C-2), 133.8 (d, C-5), 174.7 (s, C-3) ppm. *cis* isomer: ^{13}C NMR (75 MHz, CDCl$_3$): δ = 44.2 (t, C-4), 48.0 (s, C-1), 118.8 (t, C-6), 128.6 (d, C-2), 133.9 (d, C-5), 174.6 (s, C-3) ppm. IR (KBr): $\tilde{\nu}$ = 3080, 2916, 1691, 1234, 915 cm^{-1}. $C_{14}H_{16}O_4$ (248.28): calcd. C 67.73, H 6.50; found C 67.68, H 6.56.

1,4-Di(but-3-enyl)cyclohexa-2,5-diene-1,4-dicarboxylic Acid (6b): White solid (87%); m.p. 230–233 °C. R_f = 0.32 (dichloromethane/methanol = 10:1). ^{1}H NMR (300 MHz, [D$_6$]DMSO, *cis* and *trans* isomers overlapping): δ = 1.60–1.97 (m, 8 H, 4- and 5-H), 4.87–5.02 (m, 4 H, 7-H), 5.68–5.87 (m, 2 H, 6-H), 5.82 (s, 4-H, 2-H), 12.63 (br. s, 2 H, -CO*OH*) ppm. *trans* isomer: ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 28.8, 38.1 (t, C-4 and C-5), 48.0 (s, C-1), 115.4 (t, C-7), 128.9 (d, C-2), 138.7 (d, C-6), 175.2 (s, C-3) ppm. *cis* isomer: ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 29.1, 38.6 (t, C-4 and C-5), 47.9 (s, C-1), 115.5 (t, C-7), 128.9 (d, C-2), 138.6 (d, C-6), 174.9 (s, C-3) ppm. IR (methanol): $\tilde{\nu}$ = 2945, 2857, 2628, 1686, 1640, 1414, 1399, 1281, 1252, 1093, 991, 951, 915, 791 cm^{-1}. $C_{16}H_{20}O_4$ (276.33): calcd. C 69.55, H 7.30; found C 69.19, H 7.183.

1,4-Bis[2-(allyloxy)ethyl]cyclohexa-2,5-diene-1,4-dicarboxylic Acid (6c): White solid (93%); m.p. 160–162 °C. R_f = 0.43 (dichloromethane/methanol = 10:1). *trans* isomer: ^{1}H NMR (300 MHz, [D$_6$]-DMSO): δ = 1.87 (t, J = 7.2 Hz, 4 H, 4-H), 3.26 (t, J = 7.2 Hz, 4 H, 5-H), 3.80 (dt, J = 5.4, J = 1.5 Hz, 4 H, 6-H), 5.12 (ddd, J = 17.3, J = 10.4, J = 2.0 Hz, 4 H, 8-H), 5.73–5.83 (m, 2 H, 7-H), 5.79 (s, 4 H, 2-H), 12.57 (br. s, 1 H, -CO*OH*) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 38.4 (t, C-4), 46.5 (s, C-1), 66.4 (t, C-5), 71.3 (t, C-6), 116.6 (t, C-8), 128.5 (d, C-2), 135.6 (d, C-7), 174.7 (s, C-3) ppm. *cis* isomer: ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 1.89 (t, J = 7.2 Hz, 4 H, 4-H), 3.28 (t, J = 7.2 Hz, 4 H, 5-H), 3.85 (dt, J = 5.3, J = 1.5 Hz, 4 H, 6 H), 5.15 (ddd, J = 17.3, J = 10.4, J = 2.0 Hz, 4 H, 8-H), 5.80–5.88 (m, 2 H, 7-H), 5.79 (s, 4 H, 2-H), 12.57 (br. s, 1 H, -CO*OH*) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 38.3 (t, C-4), 46.6 (s, C-1), 66.7 (t, C-5), 71.2 (t, C-6), 116.7 (t, C-8), 128.7 (d, C-2), 135.7 (d, C-7), 174.5 (s, C-3) ppm. IR (methanol): $\tilde{\nu}$ = 2970, 2855, 1690, 1455, 1417, 1397, 1348, 1270, 1106, 1012, 953, 914, 812, 785, 739 cm^{-1}. $C_{18}H_{24}O_6$ (336.38): calcd. C 64.27, H 7.19; found C 64.12, H 7.09.

1,4-Bis[2-(1,3-dioxolan-2-yl)ethyl]cyclohexa-2,5-diene-1,4-dicarboxylic Acid (6d): White solid (78%); m.p. 249–253 °C. R_f = 0.28 (dichloromethane/methanol = 10:1). ^{1}H NMR (300 MHz, [D$_6$]DMSO, *cis* and *trans* isomers overlapping): δ = 1.30–1.46 (m, 4 H, 4-H), 1.59–1.72 (m 4 H, 5-H), 3.69–3.87 (m, 8 H, 7-H), 4.71 (t, J = 4.6 Hz, 2 H, 6-H), 5.76 (s, 4 H, 2-H) ppm, -CO*OH* not detected. *trans* isomer: ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 29.3 (t, C-4), 33.4 (t, C-5), 47.9 (s, C-1), 65.1 (t, C-7), 104.1 (d, C-6), 129.3 (d, C-2), 175.6 (s, C-3) ppm. *cis* isomer: ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 29.6 (t, C-4), 33.8 (t, C-5), 48.0 (s, C-1), 65.1 (t, C-7), 104.1 (d, C-6), 129.3 (d, C-2), 175.7 (s, C-3) ppm. IR (methanol): $\tilde{\nu}$ = 2950, 2881, 2360, 1686, 1398, 1264, 1140, 1028, 992, 942, 886, 799, 766 cm^{-1}. $C_{18}H_{24}O_8$ (368.38): calcd. C 58.69, H 6.57; found C 58.40, H 6.415.

1,4-Diethylcyclohexa-2,5-diene-1,4-dicarboxylic Acid (6h):[14] White solid (93%); m.p. 189–191 °C. R_f = 0.43 (dichloromethane/methanol, 5:1). *trans* isomer: ^{1}H NMR (300 MHz, [D$_4$]methanol): δ = 0.84 (t, J = 7.5 Hz, 6 H, 5-H), 1.76 (q, J = 7.5 Hz, 4 H, 4-H), 5.92 (s, 4 H, 2-H), 12.46 (br. s, 2 H, -CO*OH*) ppm. ^{13}C NMR (75 MHz, [D$_4$]methanol): δ = 7.9 (q, C-5), 32.2 (t, C-4), 48.9 (s, C-1), 128.7 (d, C-2), 176.9 (s, C-3) ppm. *cis* isomer: ^{1}H NMR (300 MHz, [D$_4$]methanol): δ = 0.89 (t, J = 7.5 Hz, 6 H, 5-H), 1.77 (q, J = 7.5 Hz, 4 H, 4-H), 5.92 (s, 4 H, 2-H), 12.46 (br. s, 2 H, -CO*OH*) ppm. ^{13}C NMR (75 MHz, [D$_4$]methanol): δ = 8.4 (q, C-5), 32.3 (t, C-4), 49.0 (s, C-1), 128.9 (d, C-2), 175.7 (s, C-3 ppm). IR (KBr): $\tilde{\nu}$ = 2976, 1684, 1410, 1272, 1118, 1073, 946, 912, 776 cm^{-1}. $C_{12}H_{16}O_4$ (224.26): calcd. C 64.27, H 7.19; found C 64.33, H 7.19.

4-(4-Ethoxy-4-oxobutyl)cyclohexa-1,3-diene-1,4-dicarboxylic Acid (13f): White solid (89%); m.p. 295–299 °C. R_f = 0.43 (dichloromethane/methanol = 10:1). ^{1}H NMR (300 MHz, [D$_4$]methanol): δ = 1.58 (t, J = 7.0 Hz, 3 H, 14-H), 1.32–1.63 (m, 4 H, 9- and 10-H), 2.10 (t, J = 6.6 Hz, 2 H, 11-H), 2.33 (dd, J = 20.0, 4.0 Hz, 1 H, 5-H$_a$), 2.75 (dd, J = 20.0, 4.0 Hz, 1 H, 5-H$_b$), 3.92 (q, J = 7.0 Hz, 2 H, 13-H), 5.77 (d, J = 9.9 Hz, 1 H, 3-H), 6.24 (d, J = 9.9 Hz, 1 H, 2-H), 6.77 (t, J = 4.0 Hz, 1 H, 6-H) ppm, -CO*OH* not detected. ^{13}C NMR (75 MHz, [D$_4$]methanol): δ = 14.1 (q, C-14), 20.2 (t, C-10), 31.4, 34.5 (t, C-9 and C-11), 37.0 (t, C-5), 45.4 (s, C-4), 60.7 (t, C-13), 121.8, 130.0, 136.7 (d, C-2, C-3, C-6), 127.6 (s, C-1),

167.8, 174.0, 177.6 (s, C-7, C-8, C-12) ppm. IR (dichloromethane): $\tilde{\nu}$ = 2945, 2554, 2371, 2244, 1692, 1653, 1417, 1285, 1121, 1089, 939, 772, 731 cm^{-1}. HRMS: calcd. for $C_{14}H_{18}O_6$ $[M + H]^+$ 283.12; found 283.1211.

4-(3-Cyanopropyl)cyclohexa-1,3-diene-1,4-dicarboxylic Acid (13g): White solid (85%); m.p. 335–338 °C. R_f = 0.44 (dichloromethane/methanol = 10:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.53–1.90 (m, 4 H, 9- and 10-H), 2.44 (t, J = 6.8 Hz, 2 H, 11-H), 2.53 (dd, J = 19.1, 5.1 Hz, 1 H, 5-H_a), 2.93 (dd, J = 19.1, 5.1 Hz, 1 H, 5-H_b), 5.96 (d, J = 9.9 Hz, 1 H, 3-H), 6.44 (d, J = 9.9 Hz, 1 H, 2-H), 6.95 (t, J = 4.6 Hz, 1 H, 6-H) ppm, -CO*OH* not detected. ^{13}C NMR (75 MHz, [D$_4$]methanol): δ = 16.8, 20.4, 31.1 (t, C-9–C-11), 36.00 (t, C-5), 44.7 (s, C-4), 119.1 (s, C-12), 121.7, 128.8, 135.8 (d, C-2, C-3, C-6), 127.3 (s, C-1), 167.0, 176.6 (s, C-7, C-8) ppm. IR (dichloromethane): $\tilde{\nu}$ = 2937, 2544, 2362, 2245, 1689, 1646, 1421, 1280, 1107, 1091, 939, 763, 724 cm^{-1}. $C_{12}H_{13}NO_4$ (235.24): calcd. C 61.27, H 5.57, N 5.95; found C 61.10, H 5.45, N 5.83. HRMS: calcd. for $C_{12}H_{13}NO_4$ $[M + Na]^+$ 258.0742; found 258.0727.

General Procedure for the Halodecarboxylation of Cyclohexadiene-dicarboxylic Acids 6: Cyclohexadiene **6** (2.0 mmol) was suspended in chloroform (100 mL), and lead tetraacetate (5.0 mmol, 2.5 equiv.) and lithium chloride (5.0 mmol, 2.5 equiv.) were added. The yellow reaction mixture was heated at reflux for 3 h. The white suspension was washed with saturated $Na_2S_2O_3$ solution (2 × 20 mL) and water (20 mL), and the organic fraction was dried with $MgSO_4$. After removal of the solvent, arenes **7** were purified by column chromatography (dichloromethane).

1,4-Bis[2-(1,3-dioxolan-2-yl)ethyl]benzene (7d): White solid (84%); m.p. 70–72 °C. R_f = 0.63 (dichloromethane). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.92–2.02 (m, 4 H, CH_2), 2.72 (t, J = 8.2 Hz, 4 H, CH_2), 3.82–4.02 (m, 8 H, CH_2), 4.89 (t, J = 4.7 Hz, 2 H, CH), 7.13 (s, 4 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.8 (t, C-3), 35.6 (t, C-4), 65.0 (t, C-6), 104.0 (d, C-5), 128.5 (d, C-2), 139.2 (s, C-1) ppm. IR (dichloromethane): $\tilde{\nu}$ = 3011, 2942, 1736, 1519, 1447, 1409, 1231, 1199, 1133, 1071, 1029, 971, 943, 887, 762 cm^{-1}. HRMS: calcd. for $C_{16}H_{22}O_4$ $[M]^+$ 278.1518; found 278.1509.

1,4-Diethylbenzene (7h):[21] Colorless liquid (85%); n_D^{20} = 1.4948 (lit. n_D^{20} = 1.4947); R_f = 0.89 (dichloromethane). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.22 (t, J = 7.6 Hz, 6 H, CH_3), 2.61 (q, J = 7.6 Hz, 4 H, CH_2), 7.11 (s, 4 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.6 (q, CH_3), 28.4 (t, CH_2), 127.8 (d, C-Ar), 141.4 (s, C-Ar) ppm.

General Procedure for the Rearomatization of 1,3-Cyclohexadiene-dicarboxylic Acids 13: Cyclohexadiene **13** (2.0 mmol) was suspended in dry dichloromethane (10 mL) and cooled to 0 °C. A solution of chlorosulfonic acid (2.0 to 4.0 mmol, 1 M in dichloromethane) was added dropwise with evolution of CO, until TLC showed full conversion. The solution was poured into ice-cold water, and the aqueous phase was extracted with dichloromethane (3 × 10 mL). The combined organic phases were dried with $MgSO_4$. After removal of the solvent, arenes **14** were purified by column chromatography (dichloromethane/methanol).

4-(4-Ethoxy-4-oxobutyl)benzoic Acid (14f): White solid (91%); m.p. 65–67 °C. R_f = 0.10 (dichloromethane/methanol = 50:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.23 (t, J = 7.1 Hz, 3 H, CH), 1.96 (quint, J = 7.5 Hz, 2 H, 7-H), 2.32 (t, J = 7.4 Hz, 2 H, 8-H), 2.70 (t, J = 7.6 Hz, 2 H, 6-H), 4.11 (q, J = 7.1 Hz, 2 H, 10-H), 7.26, 8.01 (d, J = 8.3 Hz, 2 H, 2-H and 3-H), 12.43 (br. s, 1 H, -CO*OH*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.2 (q, C-11), 26.1, 33.5, 35.1 (t, C-6–C-8), 60.5 (t, C-10), 127.2 (s, C-4), 128.6, 130.4 (d, C-2 and C-3), 148.0 (s, C-1), 172.1, 173.5 (s, C-5 and C-9) ppm. IR (dichloromethane): $\tilde{\nu}$ = 3170, 2950, 1727, 1677, 1611, 1575, 1427, 1380, 1321, 1289, 1257, 1174, 1020, 938, 863 cm^{-1}. $C_{13}H_{16}O_4$ (236.27): calcd. C 66.09, H 6.83; found C 66.11, H 6.629.

4-(3-Cyanopropyl)benzoic Acid (14g):[22] White solid (89%); m.p. 156–158 °C (lit. m.p. 158–160 °C). R_f = 0.26 (dichloromethane/methanol = 30:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.04 (quint, J = 7.3 Hz, 2 H, 7-H), 2.37 (t, J = 7.0 Hz, 2 H, 8-H), 2.88 (t, J = 7.5 Hz, 2 H, 6-H), 7.32, 8.08 (d, J = 8.2 Hz, 2 H, 2-H and 3-H), 9.95 (br. s, 1 H, -CO*OH*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.6, 26.7, 34.6 (t, C-6–C-8), 119.2 (t, C-9), 127.9 (s, C-4), 128.8, 130.8 (d, C-2 and C-3), 146.3 (s, C-1), 171.7 (s, C-5) ppm. IR (dichloromethane): $\tilde{\nu}$ = 2923, 2547, 2244, 1683, 1609, 1575, 1515, 1425, 1292, 1218, 1182, 1128, 929, 867, 844, 826 cm^{-1}. $C_{11}H_{11}NO_2$ (189.21): calcd. C 69.83, H 5.86, N 7.40; found C 69.65, H 5.736, N 7.233.

General Procedure for the Birch Reductions of Naphthalene-1,4-dicarboxylic Acid (15): Lithium (555 mg, 80 mmol) was added in small portions at –78 °C to a suspension of naphthalene-1,4-dicarboxylic acid (**15**) (2.16 g, 10.0 mmol) in liquid ammonia (150 mL) until the blue color persisted. After 2 h at this temperature, the alkyl halide (100 mmol, 10 equiv.) was added slowly. The reaction mixture was warmed up to –35 °C before adding 1-bromohexane, 1-bromooctane, and benzyl bromide. The ammonia was evaporated overnight, and the solid residue was dissolved in water (100 mL). After cooling to 0 °C, concentrated HCl was slowly added until pH 1 was reached, and the resulting precipitate was continuously extracted with chloroform. After removal of the solvent, products **16** and **17** were purified by column chromatography.

1,4-Dimethyl-1,4-dihydronaphthalene-1,4-dicarboxylic Acid (16a): White solid (73%). R_f = 0.23 (dichloromethane/methanol = 100:1). *trans* isomer: ^1H NMR (300 MHz, [D$_4$]methanol): δ = 1.60 (s, 6 H, 7-H), 5.93 (s, 2 H, 2-H), 7.28 (dd, J = 5.8, J = 3.6 Hz, 2 H, 3-H), 7.40 (dd, J = 5.8, J = 3.6 Hz, 2 H, 4-H) ppm, -CO*OH* not detected. ^{13}C NMR (75 MHz, [D$_4$]methanol): δ = 28.6 (t, C-7), 48.4 (s, C-1), 128.3, 128.5, 130.6 (d, C-2–C-4), 137.6 (s, C-5), 178.2 (s, C-6) ppm. *cis* isomer: ^1H NMR (300 MHz, [D$_4$]methanol): δ = 1.60 (s, 6 H, 7-H), 5.87 (s, 2 H, 2-H), 7.25 (dd, J = 5.9, J = 3.8 Hz, 2 H, 3-H), 7.36 (dd, J = 5.9, J = 3.8 Hz, 2 H, 4-H) ppm, -CO*OH* not detected. ^{13}C NMR (75 MHz, [D$_4$]methanol): δ = 28.2 (t, C-7), 48.3 (s, C-1), 128.1, 128.2, 130.2 (d, C-2–C-4), 137.9 (s, C-5), 178.4 (s, C-6) ppm. IR (methanol): $\tilde{\nu}$ = 2977, 2925, 2638, 1702, 1469, 1435, 1383, 1275, 1261, 1201, 1093, 971, 849 cm^{-1}. HRMS: calcd. for $C_{14}H_{14}O_4$ $[M]^+$ 246.0892; found 246.0885.

1-Methyl-1,4-dihydronaphthalene-1,4-dicarboxylic Acid (17a): White solid (18%); m.p. 155–158 °C. R_f = 0.12 (dichloromethane/methanol = 100:1). *trans* isomer: ^1H NMR (300 MHz, [D$_4$]methanol): δ = 1.59 (s, 3 H, 12-H), 4.45 (d, J = 3.7 Hz, 1 H, 4-H), 6.01 (d, J = 10.0 Hz, 1 H, 2-H), 6.05 (dd, J = 10.0, J = 3.7 Hz, 1 H, 3-H), 7.19–7.38 (m, 4 H, 5-H–8-H) ppm, -CO*OH* not detected. ^{13}C NMR (75 MHz, [D$_4$]methanol): δ = 27.5 (t, C-12), 48.6 (d, C-4), 48.8 (s, C-1), 124.5, 128.1, 128.4, 128.7, 129.6 (d, C-2, C-3, C-5–C-8), 132.2, 138.2 (s, C-9 and C-10), 176.0, 177.0 (s, C-11 and C-12) ppm. *cis* isomer: ^1H NMR (300 MHz, [D$_4$]methanol): δ = 1.60 (s, 3 H, 13-H), 4.45 (d, J = 3.7 Hz, 1 H, 4-H), 5.98 (d, J = 10.0 Hz, 1 H, 2-H), 6.08 (dd, J = 10.0, J = 3.7 Hz, 1 H, 3-H), 7.19–7.38 (m, 4 H, 5-H–8-H) ppm, -CO*OH* not detected. ^{13}C NMR (75 MHz, [D$_4$]methanol): δ = 28.2 (t, C-12), 47.5 (d, C-4), 48.6 (s, C-1), 123.6, 128.0, 128.5, 128.6, 129.8 (d, C-2, C-3, C-5–C-8), 132.9, 139.0 (s, C-9 and C-10), 176.4, 178.5 (s, C-11 and C-12) ppm. IR (methanol): $\tilde{\nu}$ = 3034, 2970, 2934, 2626, 1698, 1489, 1450, 1381, 1286, 1260, 1207, 1085, 968, 856 cm^{-1}. $C_{13}H_{12}O_4$ (232.24): calcd. C 67.23, H 5.21; found C 67.25, H 5.23.

1,4-Diethyl-1,4-dihydronaphthalene-1,4-dicarboxylic Acid (16b): White solid (71%); m.p. 243–244 °C. R_f = 0.27 (dichloromethane/methanol = 100:1). *trans* isomer: ^{1}H NMR (300 MHz, [D$_4$]methanol): δ = 0.66 (t, J = 7.3 Hz, 6 H, 8-H), 2.12 (dt, J = 14.7, J = 7.3 Hz, 2 H, 7-H$_a$), 2.35 (dt, J = 14.7, J = 7.3 Hz, 2 H, 7-H$_b$), 5.95 (s, 2 H, 2-H), 7.30 (dd, J = 5.9, J = 3.4 Hz, 2 H, 3-H), 7.45 (dd, J = 5.9, J = 3.4 Hz, 2 H, 3-H) ppm, -CO*OH* not detected. ^{13}C NMR (75 MHz, [D$_4$]methanol): δ = 9.4 (q, C-8), 32.6 (t, C-7), 52.9 (s, C-1), 128.3, 128.6, 131.2 (d, C-2–C-4), 136.5 (s, C-5), 177.8 (s, C-6); *cis* isomer: ^{1}H NMR (300 MHz, [D$_4$]methanol): δ = 0.65 (t, J = 7.5 Hz, 6 H, 8-H), 2.05 (dt, J = 14.8, J = 7.5 Hz, 1 H, 7-H$_a$), 2.18 (dt, J = 14.8, J = 7.5 Hz, 1 H, 7-H$_b$), 5.89 (s, 2 H, 2-H), 7.24 (dd, J = 5.9, J = 3.4 Hz, 2 H, 3-H), 7.40 (dd, J = 5.9, J = 3.4 Hz, 2 H, 3-H) ppm, -CO*OH* not detected. ^{13}C NMR (75 MHz, [D$_4$]methanol): δ = 9.1 (q, C-8), 34.2 (t, C-7), 52.8 (s, C-1), 127.9, 128.2, 130.0 (d, C-2–C-4), 137.1 (s, C-5), 178.1 (s, C-6) ppm. IR (methanol): $\tilde{\nu}$ = 2971, 2936, 2879, 2619, 1702, 1489, 1450, 1381, 1263, 1207, 1088, 1025, 924, 857 cm^{-1}. $C_{16}H_{18}O_4$ (274.32): calcd. C 70.06, H 6.61; found C 69.99, H 6.55.

1-Ethyl-1,4-dihydronaphthalene-1,4-dicarboxylic Acid (17b): White solid (24%); m.p. 277–278 °C. R_f = 0.18 (dichloromethane/methanol = 100:1). ^{1}H NMR (300 MHz, [D$_4$]methanol, *cis* and *trans* isomers overlapping): δ = 0.55 (t, J = 7.3 Hz, 3 H, 14-H), 2.03 (dt, J = 14.0, J = 7.3 Hz, 1 H, 13-H$_a$), 2.32 (dt, J = 14.0, J = 7.3 Hz, 1 H, 13-H$_b$), 4.46 (d, J = 4.0 Hz,1 H, 4-H), 5.87 (d, J = 10.0 Hz, 1 H, 2-H), 6.20 (dd, J = 10.0, J = 4.0 Hz, 1 H, 3-H), 7.20–7.44 (m, 4 H, 5-H–8-H) ppm, -CO*OH* not detected. *trans* isomer: ^{13}C NMR (75 MHz, [D$_4$]methanol): δ = 8.0 (q, C-14), 31.0 (t, C-13), 46.8 (d, C-4), 51.7 (s, C-1), 124.6, 126.9, 127.4, 127.9, 128.4, 130.7 (d, C-2, C-3, C-5–C-8), 131.4, 133.9 (s, C-9 and C-10), 175.1, 176.2 (C-11 and C-12) ppm. *cis* isomer: ^{13}C NMR (75 MHz, [D$_4$]methanol): δ = 8.5 (q, C-14), 31.6 (t, C-13), 46.1 (d, C-4), 51.2 (s, C-1), 123.8, 127.1, 127.3, 127.6, 128.4, 130.8 (d, C-2, C-3, C-5–C-8), 131.6, 134.4 (s, C-9 and C-10), 175.0, 176.4 (C-11 and C-12) ppm. IR (methanol): $\tilde{\nu}$ = 3149, 2967, 2936, 2878, 1720, 1684, 1669, 1489, 1445, 1381, 1232, 1183, 1150, 982, 876 cm^{-1}. $C_{14}H_{14}O_4$ (246.26): calcd. C 68.28, H 5.73; found C 68.29, H 5.766.

1,4-Diisopropyl-1,4-dihydronaphthalene-1,4-dicarboxylic Acid (16c): White solid (54%). R_f = 0.35 (dichloromethane/methanol = 100:1). *trans* isomer: ^{1}H NMR (300 MHz, [D$_4$]methanol): δ = 0.46 (d, J = 6.7 Hz, 3 H, 8-H), 1.02 (d, J = 6.7 Hz, 3 H, 8-H′), 2.72 (septet, J = 6.7 Hz, 1 H, 7-H), 5.97 (s, 2 H, 2-H), 7.27 (dd, J = 6.0, J = 3.4 Hz, 2 H, 3-H), 7.63 (dd, J = 5.9, J = 3.4 Hz, 2 H, 2-H) ppm, -CO*OH* not detected. ^{13}C NMR (75 MHz, [D$_4$]methanol): δ = 18.7, 18.9 (q, C-8 and C-8′), 36.4 (d, C-7), 53.8 (s, C-1), 125.6, 126.8, 127.3 (d, C-2–C-4), 135.9 (s, C-5), 175.3 (s, C-6) ppm. *cis* isomer: ^{1}H NMR (300 MHz, [D$_4$]methanol): δ = 0.39 (d, J = 6.7 Hz, 6 H, 8-H), 0.97 (d, J = 6.7 Hz, 6 H, 8-H′), 2.55 (septet, J = 6.7 Hz, 2 H, 7-H), 5.97 (s, 2 H, 2-H), 7.24 (dd, J = 6.0, J = 3.4 Hz, 2 H, 3-H), 7.58 (dd, J = 5.9, J = 3.4 Hz, 2 H, 2-H) ppm, -CO*OH* not detected. ^{13}C NMR (75 MHz, [D$_4$]methanol): δ = 17.8, 19.1 (q, C-8 and C-8′), 37.9 (d, C-7), 53.6 (s, C-1), 125.4, 126.8, 127.3 (d, C-2–C-4), 136.4 (s, C-5), 175.7 (s, C-6) ppm. IR (methanol): $\tilde{\nu}$ = 2966, 2875, 2622, 1692, 1489, 1466, 1389, 1261, 1215, 1007, 928 cm^{-1}. HRMS: calcd. for $C_{24}H_{34}O_4$ [M]$^+$ 386.2457; found 386.2446.

1-Isopropyl-1,4-dihydronaphthalene-1,4-dicarboxylic Acid (17c): White solid (9%). R_f = 0.26 (dichloromethane/methanol = 100:1). ^{1}H NMR (300 MHz, [D$_4$]methanol, *cis* and *trans* isomers overlapping): δ = 0.49 (d, J = 6.9 Hz, 3 H, 14-H), 1.13 (d, J = 6.9 Hz, 3 H, 14′-H), 2.85 (septet, J = 6.9 Hz, 1 H, 13-H), 4.41 (d, J = 3.9 Hz, 1 H, 4-H), 6.05 (d, J = 10.0 Hz, 1 H, 2-H), 6.26 (dd, J = 10.0, J = 3.9 Hz, 1 H, 3-H), 7.18–7.36 (m, 4 H, 5–8 H) ppm, -CO*OH* not detected. *trans* isomer: ^{13}C NMR (75 MHz, [D$_4$]methanol): δ = 17.8, 19.1 (q, C-14 and C-14′), 36.3 (d, C-13), 49.1 (d, C-4), 56.1 (s, C-1), 126.4, 126.7, 127.4, 127.8, 128.3, 129.1 (d, C-2, C-3, C-5–C-8), 133.3, 136.3 (s, C-9 and C-10), 177.0, 177.2 (C-11 and C-12) ppm. *cis* isomer: ^{13}C NMR (75 MHz, [D$_4$]methanol): δ = 18.1, 18.6 (q, C-14 and C-14′), 38.7 (d, C-13), 46.6 (d, C-4), 54.8 (s, C-1), 125.2, 126.0, 127.3, 127.6, 128.2, 130.2 (d, C-2, C-3, C-5–C-8), 132.7, 136.4 (s, C-9 and C-10), 177.4, 177.7 (C-11 and C-12) ppm. IR (methanol): $\tilde{\nu}$ = 2965, 2874, 2630, 1698, 1495, 1455, 1436, 1388, 1365, 1259, 1217, 1007, 929, 750 cm^{-1}. $C_{15}H_{16}O_4$ (260.29): calcd. C 69.22, H 6.20; found C 69.03, H 6.15.

***trans*-1,4-Dihexyl-1,4-dihydronaphthalene-1,4-dicarboxylic Acid (16d):** White solid (5%); m.p. 218–221 °C. R_f = 0.41 (dichloromethane/methanol = 100:1). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.83 (t, J = 6.8 Hz, 6 H, 12-H), 1.05–1.28 (m, 16 H, 8–11-H), 2.01 (dt, J = 12.3, J = 4.1 Hz, 2 H, 7-H$_a$), 2.35 (dt, J = 12.3, J = 4.1 Hz, 2 H, 7-H$_b$), 5.91 (s, 2 H, 2-H), 7.30 (dd, J = 5.9, J = 3.4 Hz, 2 H, 3-H), 7.41 (dd, J = 5.9, J = 3.4 Hz, 2 H, 4-H), 9.91 (br. s, 2 H, -CO*OH*) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 14.1 (q, C-12), 22.6, 24.7, 29.6, 31.7 (t, C-11–C-8), 38.1 (t, C-7), 51.4 (s, C-1), 127.2, 128.3, 130.2 (d, C-2–C-4), 134.3 (s, C-5), 178.6 (s, C-6) ppm. IR (chloroform): $\tilde{\nu}$ = 2955, 2928, 2858, 2629, 1697, 1489, 1466, 1446, 1403, 1272, 935, 780 cm^{-1}. $C_{24}H_{34}O_4$ (386.53): calcd. C 74.58, H 8.87; found C 74.45, H 8.659.

***cis*-1-Hexyl-1,4-dihydronaphthalene-1,4-dicarboxylic Acid (17d):** White solid (90%). R_f = 0.36 (dichloromethane/methanol = 100:1). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.84 (t, J = 7.1 Hz, 3 H, 17-H), 0.95–1.34 (m, 8 H, 14-H–16-H), 2.01 (t, J = 13.0 Hz, 1 H, 13-H$_a$), 2.36 (t, J = 13.0 Hz, 1 H, 13-H$_b$), 4.48 (d, J = 4.4 Hz, 1 H,4-H), 5.88 (d, J = 9.9 Hz, 1 H, 2-H), 6.15 (dd, J = 9.9, J = 4.4 Hz, 1 H, 3-H), 7.20–7.47 (m, 4 H, 5-H–8-H), 11.0 (br. s, 2 H, -CO*OH*) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 14.3 (q, C-18), 22.9, 24.4, 29.8, 31.9 (t, C-17–C-14), 38.4 (t, C-13), 47.4 (d, C-4), 51.8 (s, C-1), 124.7, 127.6, 128.1, 128.6, 129.2, 131.7 (d, C-2, C-3, C-5–C-8), 131.4, 134.5 (s, C-9 and C-10), 177.7, 178.8 (s, C-11 and C-12) ppm. IR (methanol): $\tilde{\nu}$ = 2927, 2855, 2359, 1694, 1491, 1461, 1398, 1263, 938, 802, 754 cm^{-1}. $C_{18}H_{22}O_4$ (302.37): calcd. C 71.50, H 7.33; found C 71.23, H 7.16.

***trans*-1,4-Dioctyl-1,4-dihydronaphthalene-1,4-dicarboxylic Acid (16e):** White solid (5%); m.p. 169–171 °C. R_f = 0.46 (dichloromethane/methanol = 100:1). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.86 (t, J = 6.8 Hz, 6 H, 14-H), 1.03–1.33 (m, 24 H, 8-H–13-H), 2.00 (dt, J = 13.1, J = 3.8 Hz, 2 H, 7-H$_a$), 2.33 (dt, J = 12.3, J = 4.1 Hz, 2 H, 7-H$_b$), 5.91 (s, 2 H, 2-H), 7.29 (dd, J = 5.9, J = 3.4 Hz, 2 H, 3-H), 7.41 (dd, J = 5.9, J = 3.4 Hz, 2 H, 4-H), 10.22 (br. s, 2 H, -CO*OH*) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 14.2 (q, C-14), 22.7, 24.8, 29.3, 29.5, 30.0, 32.0 (t, C-13–C-8), 38.2 (t, C-7), 51.5 (s, C-1), 127.3, 128.4, 130.2 (d, C-2–C-4), 134.3 (s, C-5), 178.5 (s, C-6) ppm. IR (chloroform): $\tilde{\nu}$ = 2922, 2854, 2630, 1693, 1489, 1466, 1445, 1403, 1270, 936 cm^{-1}. $C_{28}H_{46}O_4$ (446.67): calcd. C 75.98, H 9.56; found C 75.85, H 9.23.

***cis*-1-Octyl-1,4-dihydronaphthalene-1,4-dicarboxylic Acid (17e):** White solid (91%). R_f = 0.41 (dichloromethane/methanol = 100:1). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.87 (t, J = 6.8 Hz, 3 H, 20-H), 0.98–1.38 (m, 12 H, 14–18-H), 1.96–2.08 (m, 2 H, 13-H), 4.49 (d, J = 4.5 Hz, 1 H, 4-H), 5.91 (d, J = 10.0 Hz, 1 H, 2-H), 6.18 (dd, J = 10.0, J = 4.5 Hz, 1 H, 3-H), 7.20–7.48 (m, 4 H, 5-H–8-H), 10.94 (br. s, 2 H, -CO*OH*) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 14.1 (q, C-20), 22.7, 24.1, 29.2, 29.3, 29.8, 31.8 (t, C-19–C-14), 38.2 (t, C-13), 46.8 (d, C-4), 51.3 (s, C-1), 124.2, 127.4, 127.8, 128.3, 128.9, 131.4 (d, C-2, C-3, C-5–C-8), 131.0, 134.1 (s, C-9 and C-10), 177.3, 178.6 (s, C-11 and C-12) ppm. IR (methanol): $\tilde{\nu}$ = 2951, 2922, 2853,

2620, 1688, 1493, 1466, 1398, 1247, 1214, 940 cm^{-1}. HRMS: calcd. for $C_{20}H_{26}O_4$ $[M]^+$ 330.1831; found 330.1828.

***cis*-1-Benzyl-1,4-dihydronaphthalene-1,4-dicarboxylic Acid (17f):** White solid (80%); m.p. 156–158 °C. R_f = 0.35 (dichloromethane/methanol = 100:1). ^1H NMR (300 MHz, [D$_4$]methanol): δ = 3.31 (d, J = 13.9 Hz, 1 H, 12-H$_a$), 3.50 (d, J = 13.9 Hz, 1 H, 12-H$_b$), 4.40 (d, J = 4.1 Hz, 1 H, 4-H), 5.76 (d, J = 10.1 Hz, 1 H, 2-H), 5.84 (dd, J = 10.1, J = 4.1 Hz, 1 H, 3-H), 7.13–7.30 (m, 9 H, 5-H–8-H and 14–16-H) ppm, -CO*OH* not detected. ^{13}C NMR (75 MHz, [D$_4$]methanol): δ = 43.9 (t, C-12), 49.6 (d, C-4), 49.8 (s, C-1), 124.8, 127.5, 127.8, 128.6, 128.8, 128.9, 129.8, 130.1, 131.4 (d, C-2, C-3, C-5–C-8, C-14–C-16), 130.7, 135.1 (s, C-9 and C-10), 177.0, 177.9 (s, C-11 and C-12) ppm. IR (chloroform): $\tilde{\nu}$ = 3028, 2963, 2933, 2865, 2601, 1693, 1485, 1454, 1378, 1251, 1013 cm^{-1}. $C_{19}H_{16}O_4$ (308.33): calcd. C 74.01, H 5.23; found C 73.83, H 5.09.

1,4-(4-Chlorbutyl)-1,4-dihydronaphthalene-1,4-dicarboxylic Acid (16g): White solid (63%). R_f = 0.36 (dichloromethane/methanol = 100:1). ^1H NMR (300 MHz, [D$_4$]methanol, *cis* and *trans* isomers overlapping): δ = 0.84–1.01, 1.20–1.42, 1.60–1.82 (m, 8 H, 8- and 9-H), 2.05 (dt, J = 13.2, J = 4.2 Hz, 2 H, 7-H$_a$), 2.38 (dt, J = 13.2, J = 4.2 Hz, 2 H, 7-H$_b$), 3.40–3.51 (m, 4 H, 10-H), 5.96 (s, 2 H, 2-H), 7.32 (dd, J = 5.8, J = 3.4 Hz, 2 H, 3-H), 7.42 (dd, J = 5.8, J = 3.4 Hz, 2 H, 4-H), 9.37 (br. s, 2 H, -CO*OH*) ppm. *trans* isomer: ^{13}C NMR (75 MHz, [D$_4$]methanol): δ = 22.2 (t, C-8), 32.6, 37.3 (t, C-7 and C-9), 44.8 (t, C-10), 51.2 (s, C-1), 127.2, 128.7, 130.2 (d, C-2–C-4), 133.9 (s, C-5), 178.0 (s, C-6) ppm. *cis* isomer: ^{13}C NMR (75 MHz, [D$_4$]methanol): δ = 22.1 (t, C-8), 32.8, 38.9 (t, C-7 and C-9), 44.7 (t, C-10), 50.9 (s, C-1), 127.0, 128.3, 129.7 (d, C-2–C-4), 134.5 (s, C-5), 179.9 (s, C-6) ppm. IR (methanol): $\tilde{\nu}$ = 3035, 2939, 2869, 2612, 1936, 1697, 1489, 1447, 1371, 1279, 1199, 1022, 928, 872 cm^{-1}. $C_{20}H_{24}Cl_2O_4$ (399.31): calcd. C 60.16, H 6.06; found C 59.98, H 5.94.

1-(4-Chlorbutyl)-1,4-dihydronaphthalene-1,4-dicarboxylic Acid (17g): White solid (27%). R_f = 0.31 (dichloromethane/methanol = 100:1). ^1H NMR (300 MHz, $CDCl_3$, *cis* and *trans* isomers overlapping): δ = 0.72–0.92, 1.10–1.31, 1.59–1.77 (m, 4 H, 14- and 15-H), 1.99 (dt, J = 13.2, J = 4.1 Hz, 1 H, 13-H$_a$), 2.45 (dt, J = 13.2, J = 4.1 Hz, 1 H, 13-H$_b$), 3.37–3.48 (m, 2 H, 16-H), 4.50 (d, J = 4.7 Hz, 1 H, 4-H), 5.80 (d, J = 10.0 Hz, 1 H, 2-H), 6.19 (dd, J = 10.0, J = 4.7 Hz, 1 H, 3-H), 7.15–7.40 (m, 4 H, 5-H–8-H), 8.75 (br. s, 2 H, -CO*OH*) ppm. *trans* isomer: ^{13}C NMR (75 MHz, [D$_4$]methanol): δ = 21.4 (t, C-14), 32.6, 36.7 (t, C-13 and C-15), 44.5 (t, C-16), 49.3 (d, C-4), 52.1 (s, C-1), 125.4, 126.3, 127.4, 127.6, 128.1, 130.6 (d, C-2, C-3, C-5–C-8), 132.6, 134.3 (s, s, C-9 and C-10), 176.2, 176.8 (s, C-11 and C-12) ppm. *cis* isomer: ^{13}C NMR (75 MHz, [D$_4$]methanol): δ = 21.6 (t, C-14), 32.7, 36.3 (t, C-13 and C-15), 44.8 (t, C-16), 49.3 (d, C-4), 53.4 (s, C-1), 125.7, 126.7, 127.3, 127.5, 128.6, 130.2 (d, C-2, C-3, C-5–C-8), 132.6, 134.2 (s, C-9 and C-10), 176.5, 177.0 (s, C-11 and C-12) ppm. IR (methanol): $\tilde{\nu}$ = 3035, 2939, 2869, 2612, 1936, 1697, 1489, 1447, 1371, 1279, 1199, 1022, 928, 872 cm^{-1}. HRMS: calcd. for $C_{16}H_{17}ClO_4$ $[M]^+$ 308.0815; found 308.0809.

***cis*-1-(4-Ethoxy-4-oxobutyl)-1,4-dihydronaphthalene-1,4-dicarboxylic Acid (17h):** White solid (91%); m.p. 249–252 °C. R_f = 0.39 (dichloromethane/methanol = 100:1). ^1H NMR (300 MHz, [D$_4$]methanol): δ = 1.18 (t, J = 7.1 Hz, 3 H, 18-H), 0.95–1.09 and 1.28–1.43 (m, 2 H, 14-H), 1.99 and 2.39 (dt, J = 13.1, J = 4.5 Hz, 2 H, 13-H), 2.20 (t, J = 7.4 Hz, 2 H, 15-H), 4.04 (q, J = 7.1 Hz, 2 H, 17-H), 4.48 (d, J = 4.5 Hz, 1 H, 4-H), 5.88 (d, J = 10.0 Hz, 1 H, 2-H), 6.19 (dd, J = 10.0, J = 4.5 Hz, 1 H, 3-H), 7.19–7.43 (m, 4 H, 5-H–8-H), 11.18 (br. s, 2 H, -CO*OH*) ppm. ^{13}C NMR (75 MHz, [D$_4$]methanol): δ = 14.1 (q, C-18), 19.6, 30.1, 34.3 (t, C-13–C-15), 46.9 (d, C-4), 50.9 (s, C-1), 60.4 (t, C-17), 124.8, 127.0, 127.9, 128.3, 128.8, 130.9 (d, C-2, C-3, C-5–C-8), 131.0, 133.5 (s, C-9 and C-10), 173.4, 177.7, 178.8 (s, C-11, C-12 and C-16) ppm. IR (methanol): $\tilde{\nu}$ = 2941, 1704, 1490, 1446, 1374, 1263, 1197, 1104, 1022, 911, 761 cm^{-1}. $C_{18}H_{20}O_6$ (332.35): calcd. C 65.05, H 6.07; found C 64.99, H 5.98.

***cis*-1-(3-Cyanopropyl)-1,4-dihydronaphthalene-1,4-dicarboxylic Acid (17i):** White solid (87%); m.p. 268–270 °C. R_f = 0.32 (dichloromethane/methanol = 100:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.98–1.12 (m, 1 H, 14-H$_a$), 1.32–1.49 (m, 1 H, 14-H$_b$), 2.11 (t, J = 13.0 Hz, 1 H, 13-H$_a$), 2.22 (t, J = 7.1 Hz, 2 H, 15-H), 2.36 (t, J = 13.0 Hz, 1 H, 13-H$_b$), 4.51 (d, J = 4.5 Hz, 1 H, 4-H), 5.87 (d, J = 10.1 Hz, 1 H, 2-H), 6.22 (dd, J = 10.1, J = 4.5 Hz, 1 H, 3-H), 7.23–7.47 (m, 4 H, 5-H–8-H), 11.09 (br. s, 2 H, -CO*OH*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.0, 20.4 (t, C-14 and C-15), 36.9 (t, C-13), 46.3 (d, C-4), 50.7 (s, C-1), 119.2 (s, C-16), 125.1, 126.9, 128.2, 128.6, 129.1, 130.0 (d, C-2, C-3, C-5–C-8), 130.6, 132.9 (s, C-9 and C-10), 176.9, 177.4 (s, C-11 and C-12) ppm. IR (methanol): $\tilde{\nu}$ = 2948, 2250, 1701, 1489, 1147, 1422, 1266, 1203, 1020, 910, 857 cm^{-1}. $C_{16}H_{15}NO_4$ (285.30): calcd. C 67.36, H 5.30, N 4.91; found C 67.12, H 5.06, N 4.80.

General Procedure for the Rearomatization of 1,4-Dihydronaphthalenedicarboxylic Acids 16: Dihydronaphthalene **16** (1.0 mmol) was added to a solution of chlorosulfonic acid (5 mL, 1 M in chloroform) at 0 °C. After 1–2 min, the reaction mixture was poured into saturated sodium carbonate solution (5 mL). After separation of the organic layer, the aqueous phase was xtracted with chloroform (3 × 5 mL) and the combined organic phases were dried with $MgSO_4$. After removal of the solvents, arenes **21** were purified by column chromatography (hexane).

1,4-Dimethylnaphthalene (21a):[23] Colorless liquid (85%). n_D^{20} = 1.6135 (lit. n_D^{20} = 1.6132). R_f = 0.41 (hexane). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.64 (s, 6 H, CH_3), 7.18 (s, 2 H, Ar-H), 7.45 (dd, J = 6.5, J = 3.3 Hz, 2 H, Ar-H), 7.97 (dd, J = 6.5, J = 3.3 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.3 (q, CH_3), 124.6, 125.3, 126.2 (d, C-Ar), 132.2, 138.8 (s, C-Ar) ppm.

1,4-Diethylnaphthalene (21b):[24] Colorless liquid (86%). n_D^{20} = 1.5951 (lit. $n_D^{13.1}$ = 1.597). R_f = 0.43 (hexane). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.53 (t, J = 7.5 Hz, 6 H, CH_3), 3.24 (q, J = 7.5 Hz, 4 H, CH_2), 7.42 (s, 2 H, Ar-H), 7.65 (dd, J = 6.5, J = 3.3 Hz, 2 H, Ar-H), 8.23 (dd, J = 6.5, J = 3.3 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.31 (q, CH_3), 26.1 (t, CH_2), 124.7, 124.9, 125.4 (d, C-Ar), 132.4, 138.5 (s, C-Ar) ppm.

1,4-Dihexylnaphthalene (21d):[13d] Colorless liquid (91%). R_f = 0.56 (hexane). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.95 (t, J = 6.5 Hz, 6 H, CH_3), 1.35–1.52 (m, 12 H, CH_2), 1.79 (quint, J = 7.7 Hz, 4 H, CH_2), 3.08 (t, J = 7.5 Hz, 4 H, CH_2), 7.28 (s, 2 H, Ar-H), 7.53 (dd, J = 6.5, J = 3.3 Hz, 2 H, Ar-H), 8.11 (dd, J = 6.5, J = 3.3 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.3 (q, CH_3), 22.9, 29.7, 31.0, 32.0, 33.2 (t, CH_2), 124.7, 125.2, 125.7 (d, C-Ar), 132.4, 137.2 (s, C-Ar) ppm.

1,4-Dioctylnaphthalene (21e): Colorless liquid (90%). R_f = 0.59 (hexane). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.97 (t, J = 7.0 Hz, 6 H, CH_3), 1.20–1.61 (m, 20 H, CH_2), 1.82 (quint, J = 7.5 Hz, 4 H, CH_2), 3.08 (t, J = 7.8 Hz, 4 H, CH_3), 7.30 (s, 2 H, Ar-H), 7.55 (dd, J = 6.5, J = 3.3 Hz, 2 H, Ar-H), 8.14 (dd, J = 6.5, J = 3.3 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.2 (q, CH_3), 22.8, 29.5, 29.7, 30.1, 31.1, 32.1, 33.3 (t, CH_2), 124.7, 125.2, 125.7 (d, C-Ar), 132.4, 137.2 (s, C-Ar) ppm. IR (chloroform): $\tilde{\nu}$ = 3085, 2941, 2870, 1868, 1599, 1525, 1463, 1399, 1314, 1178, 1028, 987, 835, 801 cm^{-1}. $C_{26}H_{40}$ (352.60): calcd. C 88.57, H 11.43; found C 88.25, H 11.31.

1,4-Bis(4-chlorbutyl)naphthalene (21g): Colorless liquid (89%). R_f = 0.40 (hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.88–1.96 (m, 8 H, 8- and 9-H), 3.10 (t, J = 7.3 Hz, 4 H, 7-H), 3.60 (t, J = 6.2 Hz, 4 H, 10-H), 7.26 (s, 2 H, 2-H), 7.54 (dd, J = 6.5, J = 3.3 Hz, 2 H, 3-H), 8.08 (dd, J = 6.5, J = 3.3 Hz, 2 H, 4-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.1, 32.4, 32.7 (t, C-7–C-9), 45.0 (t, C-10), 124.6, 125.5, 125.8 (d, C-2–C-4), 132.3, 136.5 (s, C-1 and C-5) ppm. IR (chloroform): $\tilde{\nu}$ = 3071, 2938, 2865, 1877, 1595, 1516, 1461, 1392, 1309, 1163, 1031, 980, 839, 814 cm^{-1}. $C_{18}H_{22}Cl_2$ (309.28): calcd. C 69.90, H 7.17; found C 69.57, H 7.338.

General Procedure for the Rearomatization of 1,4-Dihydronaphthalenedicarboxylic Acids 17: Dihydronaphthalene **17** (1.0 mmol) was added to a solution of chlorosulfonic acid (5 mL, 1 M in chloroform) at 0 °C. After 1–2 min, the reaction mixture was poured into ice-cold water (10 mL). After separation of the organic layer, the aqueous phase was extracted with chloroform (3 × 5 mL), and the combined organic phases were dried with $MgSO_4$. After removal of the solvents, arenes **22** were purified by column chromatography (dichloromethane/methanol).

4-Methyl-1-naphthalenecarboxylic Acid (22a):[25] Colorless crystals (91%); m.p. 178–181 °C (lit; m.p. 179–181 °C). R_f = 0.36 (dichloromethane/methanol = 10:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.72 (s, 3 H, CH_3), 7.41 (d, J = 7.4 Hz, 1 H, Ar-H), 7.51–7.65 (m, 2 H, Ar-H), 8.03 (d, J = 8.2 Hz, 1 H, Ar-H), 8.19 (d, J = 7.4 Hz, 1 H, Ar-H), 9.05 (d, J = 8.2 Hz, 1 H, Ar-H) ppm, -CO*OH* not detected. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.1 (q, CH_3), 124.5, 125.6, 126.1, 126.5, 127.4, 131.1 (d, C-Ar), 128.2, 131.7, 133.0, 141.0 (s, C-Ar), 171.2 (s, C-11) ppm.

4-Ethyl-1-naphthalenecarboxylic Acid (22b):[26] Colorless crystals (86%); m.p. 123–126 °C (lit; m.p. 125–127 °C). R_f = 0.42 (dichloromethane/methanol = 10:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.41 (d, J = 7.5 Hz, 6 H, CH_3), 3.85 (q, J = 7.5 Hz, 1 H, CH_2), 7.41 (d, J = 7.5 Hz, 1 H, Ar-H), 7.55–7.69 (m, 2 H, Ar-H), 8.14 (d, J = 8.6 Hz, 1 H, Ar-H), 8.33 (d, J = 7.5 Hz, 1 H, Ar-H), 9.16 (d, J = 8.3 Hz, 1 H, Ar-H) ppm, -CO*OH* not detected. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.8 (q, CH_3), 26.6 (d, CH_2), 123.9, 124.2, 126.2, 126.8, 127.5, 131.7 (d, C-Ar), 125.0, 132.1, 132.3, 147.3 (s, C-Ar), 172.5 (s, C-11) ppm.

4-Isopropyl-1-naphthalenecarboxylic Acid (22c):[27] Colorless crystals (90%); m.p. 150–152 °C (lit; m.p. 153–153.5 °C). R_f = 0.21 (dichloromethane/methanol = 50:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.45 (d, J = 6.8 Hz, 6 H, CH_3), 3.85 (septet, J = 6.8 Hz, 1 H, CH), 7.52 (d, J = 7.8 Hz, 1 H, Ar-H), 8.06–8.21 (m, 2 H, Ar-H), 8.25 (d, J = 9.1 Hz, 1 H, Ar-H), 8.41 (d, J = 7.7 Hz, 1 H, Ar-H), 9.20 (d, J = 8.2 Hz, 1 H, Ar-H), 12.38 (br. s, 1 H, -CO*OH*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.5 (q, CH_3), 29.3 (d, CH), 121.0, 123.8, 126.2, 126.9, 127.4, 132.0 (d, C-Ar), 124.0, 132.2, 132.3, 152.0 (s, C-Ar), 173.5 (s, C-11) ppm. IR (dichloromethane): $\tilde{\nu}$ = 3060, 2965, 2629, 1678, 1580, 1518, 1462, 1432, 1410, 1385, 1365, 1277, 1251, 1149, 1063, 1042, 1021, 924, 850, 775 cm^{-1}. $C_{14}H_{14}O_2$ (214.26): calcd. C 78.48, H 6.59; found C 78.18, H 6.65.

4-Hexyl-1-naphthalenecarboxylic Acid (22d): White solid (85%); m.p. 149–151 °C. R_f = 0.08 (dichloromethane/methanol = 100:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.77 (t, J = 6.8 Hz, 3 H, CH_3), 1.11–1.33 (m, 6 H, CH_2), 1.57 (quint, J = 7.5 Hz, 2 H, CH_2), 2.98 (t, J = 7.5 Hz, 2 H, CH_2), 7.34 (d, J = 7.5 Hz, 1 H, Ar-H), 7.50–7.62 (m, 2 H, Ar-H), 8.04 (d, J = 7.5 Hz, 1 H, Ar-H), 8.07 (d, J = 8.3 Hz, 1 H, Ar-H), 8.92 (d, J = 7.8 Hz, 1 H, Ar-H) ppm, -CO*OH* not detected. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.5 (q, CH_3), 22.7, 29.3, 30.9, 31.7, 33.3 (t, CH_2), 124.8, 125.5, 126.2, 126.7, 126.8, 127.6, 130.2 (d, C-Ar), 126.6, 131.8, 132.3, 144.7 (s, C-Ar), 169.4 (s, C-11) ppm. IR (methanol): $\tilde{\nu}$ = 2950, 1672, 1587, 1517, 1461, 1432, 1272, 1249, 1201, 1136, 918 cm^{-1}. $C_{17}H_{20}O_2$ (256.34): calcd. C 79.65, H 7.86; found C 79.23, H 7.37.

4-Octyl-1-naphthalenecarboxylic Acid (22e): White solid (86%); m.p. 129–131 °C. R_f = 0.15 (dichloromethane/methanol = 100:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.75 (t, J = 6.8 Hz, 3 H, CH_3), 1.05–1.36 (m, 10 H, CH_2), 1.62 (quint, J = 7.6 Hz, 2 H, CH_2), 2.98 (t, J = 7.6 Hz, 2 H, CH_2), 7.22 (d, J = 7.4 Hz, 1 H, Ar-H), 7.36–7.51 (m, 2 H, Ar-H), 7.97 (d, J = 8.0 Hz, 1 H, Ar-H), 8.01 (d, J = 7.4 Hz, 1 H, Ar-H), 8.87 (d, J = 8.2 Hz, 1 H, Ar-H) ppm, -CO*OH* not detected. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0 (q, CH_3), 22.7, 29.3, 29.5, 29.8, 30.7, 31.9, 33.6 (t, CH_2), 124.3, 124.8, 125.9, 126.7, 127.1, 130.8 (d, C-Ar), 126.6, 132.0, 132.3, 145.4 (s, C-Ar), 170.8 (s, C-11) ppm. IR (methanol): $\tilde{\nu}$ = 3013, 2929, 1682, 1463, 1408, 1280, 1249, 1017 cm^{-1}. $C_{19}H_{34}O_2$ (294.48): calcd. C 80.24, H 8.51; found C 80.16, H 8.296.

4-Benzyl-1-naphthalenecarboxylic Acid (22f): White solid (81%); m.p. 135–138 °C. R_f = 0.85 (dichloromethane/methanol = 5:1). ^{1}H NMR (300 MHz, [D$_4$]methanol): δ = 4.47 (s, 2 H, CH_2), 7.11–7.29 (m, 5 H, Ar-H), 7.33 (d, J = 7.5 Hz, 1 H, Ar-H), 7.44–7.54 (m, 2 H, Ar-H), 8.07 (d, J = 8.7 Hz, 1 H, Ar-H), 8.12 (d, J = 7.5 Hz, 1 H, Ar-H), 8.93 (d, J = 8.7 Hz, 1 H, Ar-H) ppm, -CO*OH* not detected. ^{13}C NMR (75 MHz, [D$_4$]methanol): δ = 40.0 (t, CH_2), 125.5, 126.8, 126.9, 127.2, 127.7, 129.2, 129.4, 130.6, 130.7 (d, C-Ar), 127.6, 130.8, 132.7, 133.4, 143.2 (s, C-Ar), 172.0 (s, C-11) ppm. IR (methanol): $\tilde{\nu}$ = 3035, 3011, 2921, 1695, 1468, 1480, 1312, 1265, 1258, 1023, 998 cm^{-1}. HRMS: calcd. for $C_{18}H_{14}O_2$ [M]$^+$ 262.0994; found 262.0989.

4-(4-Chlorbutyl)-1-naphthalenecarboxylic Acid (22g): White solid (92%); m.p. 158–161 °C. R_f = 0.56 (dichloromethane/methanol = 10:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.85–1.96 (m, 4 H, 13- and 14-H), 3.12 (t, J = 7.1 Hz, 2 H, 12-H), 3.57 (t, J = 6.1 Hz, 2 H, 15-H), 7.34 (d, J = 7.5 Hz, 1 H, Ar-H), 7.53–7.66 (m, 2 H, Ar-H), 8.08 (d, J = 8.4 Hz, 1 H, Ar-H), 8.11 (d, J = 7.5 Hz, 1 H, Ar-H), 9.00 (d, J = 8.2 Hz, 1 H, Ar-H) ppm, -CO*OH* not detected. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.8, 32.5, 32.7 (t, C-12–C-14), 44.7 (t, C-15), 124.0, 124.9, 126.2, 126.7, 127.2, 129.8 (d, C-Ar), 126.3, 131.9, 132.2, 143.6 (s, C-Ar), 167.7 (s, C-11) ppm. IR (chloroform): $\tilde{\nu}$ = 3029, 2966, 1723, 1675, 1579, 1458, 1426, 1365, 1346, 1264, 1166, 1089, 1012, 907 cm^{-1}. $C_{15}H_{15}ClO_2$ (262.74): calcd. C 68.57, H 5.75; found C 68.42, H 5.793.

4-(4-Ethoxy-4-oxobutyl)-1-naphthalenecarboxylic Acid (22h): White solid (89%); m.p. 97–101 °C. R_f = 0.18 (dichloromethane/methanol = 50:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.28 (t, J = 7.4 Hz, 3 H, 17-H), 2.05–2.18 (m, 2 H, 13-H), 2.44 (t, J = 7.2 Hz, 2 H, 14-H), 3.20 (t, J = 7.4 Hz, 2 H, 12-H), 4.17 (q, J = 7.4 Hz, 2 H, 16-H), 7.41 (d, J = 7.5 Hz, 1 H, Ar-H), 7.57–7.69 (m, 2 H, Ar-H), 8.17 (d, J = 8.0 Hz, 1 H, Ar-H), 8.33 (d, J = 7.5 Hz, 1 H, Ar-H), 9.15 (d, J = 8.2 Hz, 1 H, Ar-H), 11.46 (br. s, 1 H, -CO*OH*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.4 (q, C-17), 25.8 (t, C-13), 33.1 (t, C-12), 34.1 (t, C-14), 60.6 (t, C-16), 124.4, 125.3, 126.5, 126.8, 127.8, 131.7 (d, C-Ar), 124.5, 132.2, 132.4, 145.0 (s, C-Ar), 173.0, 173.4 (s, C-11 and C-15) ppm. IR (dichloromethane): $\tilde{\nu}$ = 3025, 2956, 1727, 1687, 1590, 1463, 1426, 1412, 1374, 1339, 1321, 1264, 1248, 1166, 1075, 1025, 908, 870, 790 cm^{-1}. $C_{17}H_{18}O_4$ (286.33): calcd. C 71.31, H 6.34; found C 71.22, H 6.214.

4-(3-Cyanopropyl)-1-naphthalenecarboxylic Acid (22i): White solid (85%); m.p. 191–194 °C. R_f = 0.15 (dichloromethane/methanol = 50:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.86 (quint, J = 7.4 Hz, 2 H, 13-H), 2.21 (t, J = 7.0 Hz, 2 H, 14-H), 3.05 (t, J = 7.6 Hz, 2 H, 12-H), 7.15 (d, J = 7.4 Hz, 1 H, Ar-H), 7.31–7.38 (m, 2 H, Ar-H), 7.83 (d, J = 9.6 Hz, 1 H, Ar-H), 7.89 (d, J = 7.4 Hz, 1 H, Ar-H), 8.73 (d, J = 9.6 Hz, 1 H, Ar-H) ppm, -CO*OH* not detected. ^{13}C

NMR (75 MHz, $CDCl_3$): δ = 17.2, 27.5, 33.0 (t, C-12–C-14), 121.0 (s, C-15), 124.9, 126.4, 127.4, 127.8, 128.1, 130.7 (d, C-Ar), 129.8, 133.2, 133.3, 143.2 (s, C-Ar), 171.2 (s, C-11) ppm. IR (dichloromethane): $\tilde{\nu}$ = 3069, 2927, 2362, 1678, 1585, 1516, 1456, 1429, 1321, 1282, 1206, 1136, 954, 856 cm^{-1}. HRMS: calcd. for $C_{15}H_{13}NO_2$ [M + Na]$^+$ 262.08; found 262.0833.

Supporting Information (see footnote on the first page of this article): NMR spectra of all products and X-ray structures of compounds *trans*-**6c** and *cis*-**17c**.

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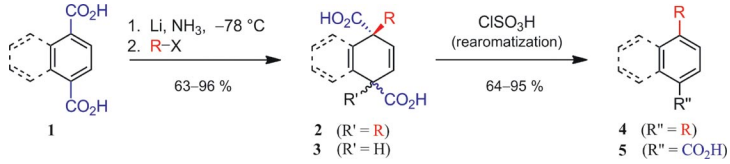

The transformation from acid to alkyl groups is the result of a simple two-step sequence that allows the regioselective synthesis of substituted benzenes and naphthalenes **4** or **5** from inexpensive terephthalic acid or naphthalene-1,4-dicarboxylic acid **1** in high yields. The formation of intermediates **2** and **3** is interesting in the context of the mechanism of the Birch reduction, and the rearomatizations proceed by different reaction pathways.

Keywords: Synthetic methods / Alkylation / Birch reduction / Arenes / Regioselectivity

