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Unsaturated Aldehydes as Alkene Equivalents in the Diels–Alder Reaction

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Abstract: A one-pot procedure is described for using α,β-unsaturated aldehydes as olefin equivalents in the Diels–Alder reaction. The method combines the normal electron demand cycloaddition with aldehyde dienophiles and the rhodium-catalyzed decarbonylation of aldehydes to afford cyclohexenes with no electron-withdrawing substituents. In this way, the aldehyde group serves as a traceless control element to direct the cycloaddition reaction. The Diels–Alder reactions are performed in a diglyme solution in the presence of a catalytic amount of boron trifluoride etherate. Subsequent quenching of the Lewis acid, addition of 0.3% of [Rh-(dppp)$_2$Cl] and heating to reflux achieves the ensuing decarbonylation to afford the product cyclohexenes. Under these conditions, acrolein, crotonaldehyde and cinnamaldehyde have been reacted with a variety of 1,3-dienes to afford cyclohexenes in overall yields between 53 and 88%. In these transformations, the three aldehydes serve as equivalents of ethylene, propylene and styrene, respectively.

Keywords: aldehydes · cycloalkenes · decarbonylation · Diels–Alder reaction · homogeneous catalysis

Introduction

The Diels–Alder reaction is one of the most powerful methods in organic chemistry for synthesis of six-membered carbocyclic compounds.[1,2] The [4+2] cycloaddition between a 1,3-diene and a dienophile gives rise functionalized cyclohexenes with good control of both regio-, enantio-, and diastereoselectivity.[2,3] The reaction has found widespread application in the synthesis of natural products and other biologically active molecules.[4,5] In the normal Diels–Alder reaction the reactivity is governed by the energy difference between the HOMO of the diene and the LUMO of the dienophile. The energy of the latter is lowered by electron-withdrawing substituents and the most common dienophiles contain carbonyl, cyano, sulfonyl or nitro groups. The effect is enhanced by coordination to Lewis acids which are known to accelerate Diels–Alder reactions substantially. For the same reason, the cycloaddition with simple olefins as dienophiles is a poor reaction which requires high temperature and pressure.[6] Instead, olefin equivalents have been developed by using electron-withdrawing groups on the dienophile that can be removed in a subsequent reduction. The most popular group is the phenylsulfonyl group,[7,8] but ethylthio,[9] nitro[10] and dichloroboryl[11] groups have also been employed. In all four cases, the Diels–Alder reaction is achieved under thermal conditions while the subsequent removal of the electron-withdrawing group is accomplished in the presence of either sodium amalgam (for $PhSO_2$),[7] Raney-Nickel (for EtS),[9] Bu_3SnH/AIBN (for NO_2),[10] or by a three-step sequence (for BCl_2) involving oxidation ($NaOH/H_2O_2$), mesylation (MsCl/pyridine) and reduction ($LiEt_3BH$).[11] However, the use of stoichiometric reducing agents for the removal of these groups diminishes the atom economy of the overall transformation. Hence, we envisioned to use α,β-unsaturated aldehydes for the Diels–Alder reaction followed by removal of the aldehyde group by a metal-catalyzed decarbonylation in the same pot. This tandem Diels–Alder decarbonylation sequence would offer a more expedient procedure for the cycloaddition with olefin equivalents and at the same time be able to maintain the regio- and stereoselectivity that characterizes the normal Diels–Alder reaction.

The catalytic decarbonylation of aldehydes can be achieved with rhodium catalysts at elevated temperatures.[12,13] The most reactive catalysts are rhodium(I) complexes containing bi- or tridentate phosphine ligands.[13] In a recent study, 1,3-bis(diphenylphosphino)propane (dppp) was shown to be the ligand of choice for this transformation among a

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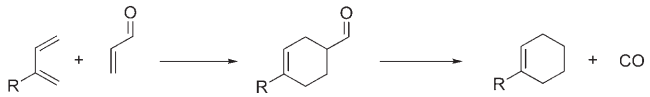
range of phosphine ligands.[14] The corresponding complex [Rh(dppp)$_2$Cl] has been used for decarbonylation of a variety of different aldehydes ranging from unprotected carbohydrates[15] to aldehydes in natural product syntheses.[16] The complex can be prepared in two steps from commercially available $RhCl_3 \cdot 3H_2O$ by conversion into [Rh(cyclooctene)$_2$Cl]$_2$ followed by ligand exchange with dppp.[17] Alternatively, the active catalyst can be generated *in situ* from the same components if the decarbonylation is performed in a diglyme solution.[14] Very recently, the mechanism for the decarbonylation was studied by experimental and theoretical methods and shown to proceed by an oxidative addition into the aldehyde C–H bond followed by a rate-limiting extrusion of carbon monoxide and reductive elimination.[18]

Herein, we describe the development of α,β-unsaturated aldehydes as alkene equivalents in the Diels–Alder reaction. Acrolein and substituted acroleins are added to various 1,3-dienes followed by a rhodium-catalyzed decarbonylation in the same pot to remove the aldehyde group (Scheme 1).



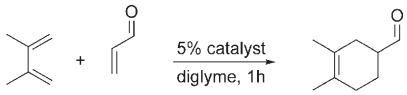
Scheme 1. One-pot Diels–Alder decarbonylation reaction.

Results and Discussion

Acrolein as dienophile: The initial experiments were carried out under thermal conditions in the presence of [Rh(dppp)$_2$Cl]. Acrolein (b.p. 53 °C) was selected as the dienophile and reacted with isoprene (b.p. 34 °C) and 2 % of [Rh(dppp)$_2$Cl] in an autoclave. The thermal Diels–Alder reaction between acrolein and simple dienes will occur at temperatures around 100 °C[19] while the catalytic decarbonylation requires a temperature around 150 °C.[14–16] Therefore, we were confident that the Diels–Alder reaction would occur before the decarbonylation. Indeed, when the autoclave was heated to 170 °C for 24 h, the reaction mixture consisted of 66 % of 1-methylcyclohexene and 34 % of the Diels–Alder adduct that had not undergone decarbonylation. Unfortunately, it was not possible to push the decarbonylation to completion under these conditions. By comparison, the decarbonylation of the same aldehyde in an open flask at 170 °C only required 4 h for full conversion. Thus, it was apparent that the liberated carbon monoxide hampered the decarbonylation in the autoclave and it was therefore decided to pursue the tandem reaction in an open system. In this case, 2,3-dimethyl-1,3-butadiene (b.p. 68 °C) was selected as the diene and reacted with acrolein at reflux. However, due to the low boiling point of acrolein, the cycloaddition required 30 h for complete conversion. More hindered dienes required even longer reaction times and this procedure was therefore not suitable for general use.

As a result, it was decided to use Lewis acid catalysis to increase the rate of the cycloaddition reaction. Several Lewis acids were selected and the reactions were investigated under neat conditions as well as in the presence of a solvent (Table 1). In the latter case, diglyme was chosen as the solvent since it had shown good results in the decarbonylation reaction.[14,15] Zinc chloride was found to be an excellent catalyst under neat conditions with full conversion in 40 min while no reaction occurred in a diglyme solution (entries 1 and 2). Furthermore, subsequent addition of [Rh(dppp)$_2$Cl] and heating to 170 °C resulted in complete decarbonylation. However, extensive isomerization of the double bond in the product also occurred, which is most likely caused by the presence of zinc chloride at elevated temperature. Thus, it appears necessary to remove or quench the Lewis acid prior to increasing the temperature in order to avoid product isomerization. Unfortunately, it was not possible to quench zinc chloride with reagents like water or ethylenediamine. Instead, a number of other Lewis acids were investigated (entries 3–8). Aluminum chloride and $BF_3 \cdot OEt_2$ gave rise to a highly exothermic reaction under neat conditions which led to instantaneous decomposition of the starting materials. In diglyme, however, the reactivity of the two Lewis acids was lowered significantly and an efficient Diels–Alder reaction could be achieved with the latter. The cycloaddition went to completion in 10 min at room temperature with 5 % of $BF_3 \cdot OEt_2$ and afforded the product in 89 % isolated yield. The conversion with aluminum chloride and other Lewis acids were slower.

Table 1. Diels–Alder reaction with acrolein catalyzed by various Lewis acids.[a]



Entry	Catalyst	Conversion of diene [%][b]
1	$ZnCl_2$	0
2[c]	$ZnCl_2$	>99
3	$AlCl_3$	43
4[d]	$BF_3 \cdot OEt_2$	>99
5[e]	$FeCl_3$	37
6	$La(OTf)_3$	0
7	$Sc(OTf)_3$	66
8	$Bi(OTf)_3$	75

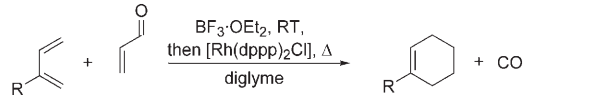
[a] To a solution of 2,3-dimethyl-1,3-butadiene (5 mmol) and acrolein (7.5 mmol) in diglyme (5 mL) was added the Lewis acid (0.25 mmol) and the mixture was stirred at room temperature for 60 min. [b] Determined by GC. [c] Under neat conditions for 40 min. [d] Reaction time 10 min with 89 % isolated yield of 3,4-dimethyl-3-cyclohexene-1-carbaldehyde. [e] Some by-products are visible by GC analysis.

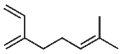
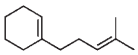
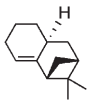
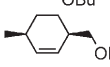
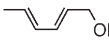
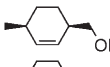
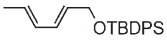
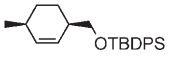
Again, it was necessary to quench the Lewis acid before the decarbonylation could be achieved. This could be performed by adding one equivalent of K_2HPO_4 relative to $BF_3 \cdot OEt_2$ together with a small amount of water which did not interfere with the ensuing decarbonylation reaction. On the contrary, neutralizing $BF_3 \cdot OEt_2$ with Na_2CO_3 or K_2CO_3

caused the decarbonylation to proceed slowly and gave rise to side products and precipitation of rhodium metal.

Earlier studies on simple aldehydes had shown that the decarbonylation could be achieved with an *in situ* generated catalyst from $RhCl_3 \cdot 3H_2O$ and dppp.[14] Addition of these two reagents to the Diels–Alder adduct did result in the desired decarbonylation upon heating, but the reaction was accompanied by severe double bond isomerization. It was not possible to add $RhCl_3 \cdot 3H_2O$ and dppp before the Diels–Alder reaction since dppp catalyzes a rapid polymerization of acrolein. Therefore, it was decided to use $[Rh(dppp)_2Cl]$ for the decarbonylation. This complex was prepared by a new one-step procedure where $RhCl_3 \cdot 3H_2O$ was treated with two equivalents of dppp in an ethanol solution at reflux for 30 min followed by removal of the solvent in vacuo. This afforded a crude $[Rh(dppp)_2Cl]$ complex which was equal in reactivity to the catalyst formed by the previous two-step procedure.[17] With 0.3% of the crude complex the decarbonylation could be achieved in 20 h to afford the desired 1,2-dimethylcyclohexene in 86% isolated yield from the starting diene (Table 2, entry 1). The progress of the decarbonylation could be monitored by measuring the evolution of carbon monoxide. Diglyme was removed in an aqueous work-up and the product was isolated by extraction with pentane and subsequent distillation.

Table 2. Acrolein as ethylene synthon in the Diels–Alder reaction.[a]



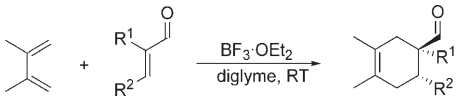
Entry	Diene	Product	Yield [%][b]
1			86
2			65
3			77
4			75
5			81
6			84
7[c]			79
8			66
9[d]			53
10[c]			61

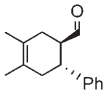
[a] Reactions were carried out on a 5–40 mmol scale in diglyme (1 M solution) with 6–10% of $BF_3 \cdot OEt_2$ for the Diels–Alder reaction (10–300 min at RT) and 0.3% of $[Rh(dppp)_2Cl]$ for the decarbonylation (8–20 h at reflux). [b] Isolated yield. [c] 1% $[Rh(dppp)_2Cl]$ was used. [d] Decarbonylation took 42 h.

To examine the scope and limitations of this new one-pot protocol, a number of other dienes were also subjected to the reaction with acrolein (Table 2, entries 2–10). In general, the Diels–Alder decarbonylation sequence worked very well for a variety of hydrocarbon dienes where yields around 80% were typically obtained (entries 2–6). It should be noted that some of the products are highly volatile and thus difficult to isolate quantitatively. Ether and ester functionalities can also be accommodated in the diene (entries 7–10), although the 1,4-disubstituted dienes in entries 8–10 reacted significantly slower than the other dienes. The longer reaction time in the Diels–Alder reaction resulted in a slightly decreased yield of the product cyclohexenes due to a slow acid-catalyzed decomposition of the allyl ether and ester dienes. No sign of a retro Diels–Alder reaction was observed when the intermediate aldehydes were heated to 162 °C during the decarbonylation reaction. Several dienes failed to undergo the cycloaddition in the presence of $BF_3 \cdot OEt_2$. Furan underwent polymerization while dienes with conjugating electron-withdrawing groups such as sorbic aldehyde and β-ionone did not react with acrolein. In all cases, except for entry 1, did the Diels–Alder reaction furnish more than one aldehyde (regioisomers and *exo*/*endo* isomers). Particularly, the reaction with the 1,4-disubstituted dienes led to the formation of all four isomeric aldehydes. However, after decarbonylation they all gave rise to the same cyclohexene product which illustrates the benefit of the one-pot procedure where no work-up of the intermediate aldehyde is required.

Other α,β-unsaturated aldehydes as dienophiles: With the successful application of acrolein as an ethylene equivalent the studies were now extended to other unsaturated aldehydes. Since the Diels–Alder reaction is also highly sensitive to substituents in the dienophile it was decided first to examine the rate of the $BF_3 \cdot OEt_2$-catalyzed cycloaddition reaction with various aldehydes. As shown above, the reaction between 2,3-dimethyl-1,3-butadiene and acrolein goes to completion within 10 min in diglyme with 5% of $BF_3 \cdot OEt_2$ (Table 1, entry 4). Changing the solvent to diethyl ether had no influence on the rate of the cycloaddition (Table 3, entry 1). However, the reactions with substituted acroleins were slower and it was necessary to use a larger amount of the Lewis acid. With 10% of $BF_3 \cdot OEt_2$ the reaction with methacrolein went to completion in 30 min and proceeded very cleanly to give the product in high yield (entry 2). The reactions with crotonaldehyde and cinnamaldehyde were significantly more sluggish, but full conversion could still be obtained within a reasonable timeframe (Figure 1 and Table 3, entries 3 and 4). This, however, was not possible with 3-methylcrotonaldehyde where only trace amounts of the cycloaddition product was obtained even with very long reaction times and up to 30% of $BF_3 \cdot OEt_2$ (Figure 1). The use of other Lewis acids such as zinc chloride and bismuth triflate did not improve the yield of the cycloaddition product. In this connection, it should be noted that 3-methylcrotonaldehyde is known to give a poor yield in the thermal

Table 3. $BF_3{\cdot}OEt_2$-catalyzed Diels–Alder reaction with 2,3-dimethyl-1,3-butadiene and α,β-unsaturated aldehydes.[a]



Entry	Dienophile	$BF_3{\cdot}OEt_2$ loading [%]	Reaction time	Product	Yield [%][b]
1[c]		5	10 min		87
2		10	30 min		95
3		10	6 h		89
4		15	24 h		74

[a] Reactions were performed with 30 mmol of diene and 45 mmol of dienophile in 30 mL of diglyme. [b] Isolated yield. [c] Diethyl ether was used instead of diglyme.

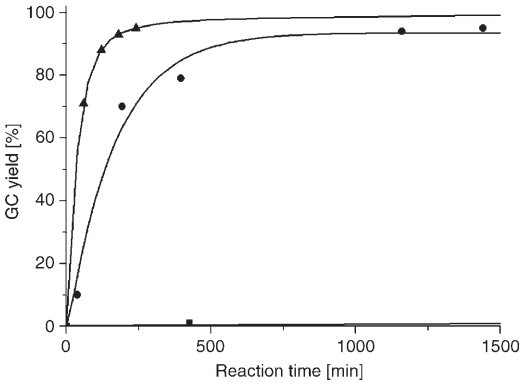
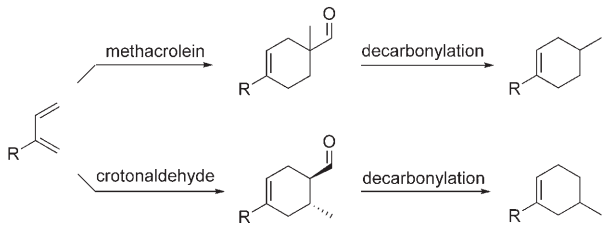


Figure 1. Comparison of the cycloaddition rate for crotonaldehyde (▲: 10% $BF_3{\cdot}OEt_2$), cinnamaldehyde (●: 15% $BF_3{\cdot}OEt_2$) and 3-methylcrotonaldehyde (■: 10% $BF_3{\cdot}OEt_2$) in the reaction with 2,3-dimethyl-1,3-butadiene.

Diels–Alder reaction[19] and we are not aware of any successful Lewis acid-catalyzed cycloadditions with this dienophile.

With the optimized cycloaddition reaction available the stage was now set to investigate the one-pot sequence with the substituted dienophiles. Methacrolein and crotonaldehyde can both serve as propylene equivalents, but will give rise to different regioisomeric products. Methacrolein will mainly afford the "*para*" product after decarbonylation while crotonaldehyde will furnish the corresponding "*meta*" product (Scheme 2). Unfortunately, the decarbonylation of the Diels–Alder adduct from methacrolein did not proceed at 162 °C. This is probably due to the steric bulk in the α-tribranched aldehyde (see Table 3, entry 2) and has previously been observed with a similar hindered aldehyde.[14] The temperature was therefore raised and it turned out that the neat tribranched aldehyde could be decarbonylated slowly at a temperature around 215 °C. However, under these forcing conditions the reaction was accompanied by small amounts of product from double-bond isomerization which could not be separated. As a result, it was decided to abandon methacrolein as a propylene synthon.

Instead, crotonaldehyde was examined and in this case the decarbonylation proceeded at 162 °C without any side reactions. Three different dienes were subjected to the one-pot Diels–Alder decarbonylation sequence in diglyme to afford the product cyclohexenes in good yields (Table 4, entries 1–3). In the latter two cases very small amounts of the corresponding regioisomers were also obtained according to analysis by GC-MS.



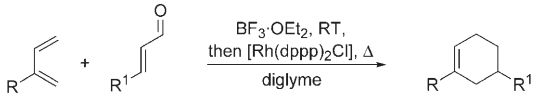
Scheme 2. Regioselectivity with methacrolein and crotonaldehyde.

Cinnamaldehyde can serve as a styrene equivalent in the Diels–Alder reaction when followed by the decarbonylation. Although, the cycloaddition reaction with cinnamaldehyde is slower than for crotonaldehyde, the same three dienes still reacted to completion within 24 h (entries 4–6). Subsequent quenching of $BF_3{\cdot}OEt_2$ and heating with the rhodium catalyst achieved the decarbonylation in a satisfying overall yield and with excellent regioselectivity for the last two cases. It should be noted that this procedure with olefin equivalents gives rise to the opposite regioisomer as compared to the thermal Diels–Alder reaction with substituted olefins.[20] For example, the thermal reaction between isoprene and styrene at 200 °C affords the product in entry 5 as a 2:7 mixture of "*meta*" and "*para*" in 31% yield.[21]

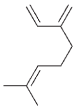
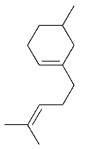
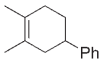
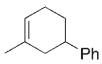
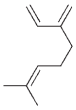
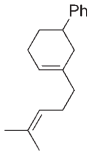
Conclusion

In summary, we have shown that α,β-unsaturated aldehydes can serve as olefin equivalents in the $BF_3{\cdot}OEt_2$-catalyzed Diels–Alder reaction with 1,3-dienes when the cycloaddition

Table 4. Diels–Alder decarbonylation protocol with various α,β-unsaturated aldehydes.[a]



R^1 = CH_3 or Ph

Entry	Diene	Dienophile	Major product	Regioisomer ratio	Yield [%][b]
1[c]				–	86
2[c]				24:1	67
3[c]				24:1	88
4[d]				–	73
5[d]				39:1	59
6[d]				39:1	75

[a] Reactions were carried out with 10–15% of $BF_3{\cdot}OEt_2$ for the Diels–Alder reaction and 0.3% of [Rh(dppp)$_2$Cl] for the decarbonylation (14–30 h). [b] Isolated yield of both isomers. [c] 10% of $BF_3{\cdot}OEt_2$ was used for 5–6 h. [d] 15% of $BF_3{\cdot}OEt_2$ was used for 24 h.

is combined with a rhodium-catalyzed decarbonylation in the same pot. In this way, the aldehyde group functions as a traceless control element which directs both reactivity and regioselectivity in the overall transformation. Acrolein, crotonaldehyde and cinnamaldehyde were shown to act as synthons for ethylene, propylene and styrene, respectively, and good yields were obtained of the product cyclohexenes. Although, the decarbonylation is performed at 162 °C, the reaction still tolerates a number of functional groups in the substrates including esters, silyl ethers and isolated olefins.[22] The two-step procedure generates only a minimum amount of waste compared to previous methods[7–11] since both reactions are performed with only a catalytic amount of an additive. Thus, we believe this procedure will be a valuable new tool for synthesis of certain cyclohexenes from cheap starting materials in an atom-economical fashion.

Experimental Section

General procedure for Diels–Alder decarbonylation sequence: A solution of $RhCl_3{\cdot}3H_2O$ (29.3 mg, 0.111 mmol) and dppp (95.6 mg, 0.225 mmol) in ethanol (10 mL) was degassed and heated to reflux for 30 min. The mixture was then concentrated to afford crude [Rh(dppp)$_2$Cl] as a yellow solid which was dissolved in diglyme (2 mL). Another flask was charged with diglyme (40 mL), diene (39 mmol) and aldehyde (60 mmol) followed by addition of $BF_3{\cdot}OEt_2$ (0.30–0.74 mL, 2.4–5.9 mmol). The mixture was stirred at room temperature until the cycloaddition had gone to completion according to GC or TLC. The mixture was quenched with $K_2HPO_4{\cdot}3H_2O$ (0.60–1.2 g, 2.4–5.9 mmol) and water (0.25 mL). The above catalyst solution was added and the reaction was degassed and heated to reflux until the decarbonylation had gone to completion. The mixture was cooled to room temperature, diluted with water (50 mL) and extracted with pentane (5×50 mL). The combined organic phases were washed with water (5×50 mL) and dried with anhydrous Na_2SO_4. Pentane was removed by distillation followed by isolation of the product cyclohexene by either distillation or flash chromatography. The decarbonylation could be monitored by measuring the evolution of carbon monoxide. This was achieved by connecting the reaction flask to a burette filled with water. The bottom of the burette was further connected to a reservoir flask with water. In this way, carbon monoxide from the reaction forces water from the burette into the reservoir flask.

1,2-Dimethylcyclohexene: b.p. 134–136 °C (lit.[11] b.p. 135–136 °C); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.50–1.60 (m, 4H), 1.61 (s, 6H), 1.86–1.97 ppm (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 19.14, 23.46, 31.71, 125.60 ppm; MS: m/z: 110 $[M]^+$.

1-Methylcyclohexene: b.p. 107–110 °C (lit.[23] b.p. 106–110 °C); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.49–1.67 (m, 4H), 1.64 (s, 3H), 1.87–2.01 (m, 4H), 5.36–5.42 ppm (tdd, 1H, J = 1.5, 3.4, 5.2 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 22.37, 22.99, 23.94, 25.28, 30.02, 121.10, 134.05 ppm; MS: m/z: 96 $[M]^+$.

1-(4-Methyl-3-pentenyl)cyclohexene: b.p. 100–102 °C at 17 mm Hg; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.48–1.66 (m, 4H), 1.60 (s, 3H), 1.68 (s, 3H), 1.88–2.12 (m, 8H), 5.06–5.15 (m, 1H), 5.37–5.42 ppm (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 17.65, 22.57, 23.02, 25.23, 25.69, 26.46, 28.37, 38.09, 120.66, 124.47, 131.23, 137.72 ppm; MS: m/z: 164 $[M]^+$. NMR data are in accordance with literature values.[7b]

Bicyclo[2.2.2]-2-octene: ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.10–1.19 (m, 4H), 1.36–1.46 (m, 4H), 2.35–2.43 (m, 2H), 6.12–6.19 ppm (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 25.75, 29.46, 134.21 ppm; MS: m/z: 108 $[M]^+$. NMR data are in accordance with literature data.[7b]

9,9-Dimethyltricyclo[4,4,0,1^{8,10}]-1-undecene: b.p. 115–120 °C at 15 mm Hg (lit.[7b] b.p. 118–123 °C at 15 mm Hg); $[\alpha]_D^{20}$ = −29.9 (c = 2.2, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.84 (d, 1H, J = 9.3 Hz), 0.97 (s, 3H), 1.13–1.23 (m, 1H), 1.25 (s, 3H), 1.40–1.48 (m, 1H), 1.56–1.71 (m, 1H), 1.76–1.90 (m, 2H), 1.94–2.11 (m, 3H), 2.11–2.24 (m, 1H), 2.41 (t, 1H, J = 5.8 Hz), 2.45–2.61 (m, 2H), 5.14 ppm (q, 1H, J = 3.3 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 22.79, 23.57, 24.53, 27.19, 32.56, 33.37, 33.55, 35.59, 39.56, 42.17, 52.22, 116.88, 146.73 ppm; MS: m/z: 176 $[M]^+$.

1-Phenylcyclohexene: b.p. 122–125 °C at 13 mm Hg (lit.[24] b.p. 128 °C at 16 mm Hg); R_f = 0.45 (EtOAc/hexane 1:99); ^{1}H NMR ($CDCl_3$, 300 MHz):

δ = 1.63–1.73 (m, 2H), 1.75–1.84 (m, 2H), 2.18–2.27 (m, 2H), 2.39–2.47 (m, 2H), 5.13–5.19 (m, 1H), 7.19–7.42 ppm (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 22.40, 23.31, 26.12, 27.63, 125.00, 125.16, 126.73, 128.40, 136.80, 142.92 ppm; MS: *m*/*z*: 130 $[M-C_2H_4]^+$.

1-(Butoxymethyl)cyclohexene: b.p. 95–102 °C at 15 mm Hg; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.90 (t, 3H, *J* = 7.3 Hz), 1.30–1.43 (m, 2H), 1.49–1.68 (m, 6H), 1.93–2.05 (m, 4H), 3.35 (t, 2H, *J* = 6.6 Hz), 3.78–3.80 (m, 2H), 5.63–5.69 ppm (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 13.92, 19.39, 22.42, 22.52, 24.97, 25.86, 31.85, 69.62, 75.56, 124.47, 135.21 ppm; HRMS: *m*/*z*: calcd for $C_{11}H_{20}ONa$: 191.1412 $[M+Na]^+$; found: 191.1403.

3-(Butoxymethyl)-6-methylcyclohexene: R_f = 0.67 (Et_2O/pentane 1:19); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.87–0.97 (m, 6H), 1.21–1.45 (m, 3H), 1.48–1.72 (m, 5H), 2.09–2.39 (m, 2H), 3.19–3.31 (m, 2H), 3.36–3.46 (m, 2H), 5.52–5.66 ppm (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 13.94, 19.37, 21.43, 23.15, 27.95, 29.99, 31.81, 35.26, 70.81, 74.56, 127.25, 134.88 ppm; HRMS: *m*/*z*: calcd for $C_{12}H_{22}ONa$: 205.1568 $[M+Na]^+$; found: 205.1563.

(4-Methyl-2-cyclohexenyl)methyl benzoate: R_f = 0.55 (EtOAc/heptane 1:99); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.00 (d, 3H, *J* = 7.1 Hz), 1.30–1.45 (m, 1H), 1.56–1.79 (m, 3H), 2.15–2.27 (m, 1H), 2.50–2.61 (m, 1H), 4.20 (d, 1H, *J* = 1.3 Hz), 4.22 (s, 1H), 5.58–5.76 (m, 2H), 7.40–7.59 (m, 3H), 8.03–8.08 ppm (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 21.27, 23.03, 27.73, 29.82, 34.42, 67.90, 125.81, 128.29, 129.51, 130.36, 132.81, 135.95, 166.56 ppm; HRMS: *m*/*z*: calcd for $C_{15}H_{18}O_2Na$: 253.1205 $[M+Na]^+$; found: 253.1206.

***tert*-Butyl((4-methyl-2-cyclohexenyl)methoxy)diphenylsilane**: R_f = 0.30 (EtOAc/heptane 1:39); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.99 (d, 3H, *J* = 3.7 Hz), 1.11 (s, 9H), 1.22–1.34 (m, 1H), 1.63–1.75 (m, 3H), 2.13–2.42 (m, 2H), 3.50–3.65 (m, 2H), 5.57–5.70 (m, 2H), 7.37–7.49 (m, 6H), 7.70–7.76 ppm (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 19.30, 21.39, 22.72, 26.87, 27.97, 29.99, 37.74, 67.32, 127.28, 127.56, 129.48, 133.98, 134.89, 135.60; HRMS: *m*/*z*: calcd for $C_{24}H_{32}OSiNa$: 387.2120 $[M+Na]^+$; found: 387.2120.

1,2,4-Trimethylcyclohexene: b.p. 150–154 °C (lit.[25] b.p. 154 °C); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.94 (d, 3H, *J* = 2.6 Hz), 1.08–1.23 (m, 1H), 1.24–1.70 (m, 9H), 1.85–2.11 ppm (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 18.86, 19.10, 21.95, 29.32, 31.73, 31.98, 40.53, 125.14, 125.16 ppm; MS: *m*/*z*: 124 $[M]^+$.

1,5-Dimethylcyclohexene: b.p. 132–133 °C (lit.[26] b.p. 127–129 °C); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.93–0.98 (m, 3H), 1.03–1.19 (m, 1H), 1.51–1.73 (m, 6H), 1.87–2.06 (m, 3H), 5.33–5.40 ppm (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 21.97, 23.74, 25.36, 28.89, 30.63, 38.73, 120.64, 133.65 ppm; MS: *m*/*z*: 110 $[M]^+$.

5-Methyl-1-(4-methyl-3-pentenyl)cyclohexene: b.p. 107–108 °C at 12 mm Hg; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.96 (d, 3H, *J* = 2.7 Hz), 1.05–1.22 (m, 1H), 1.54–1.75 (m, 9H), 1.87–2.13 (m, 7H), 5.06–5.16 (m, 1H), 5.35–5.41 ppm (br s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 17.67, 22.00, 25.33, 25.70, 26.49, 28.92, 30.83, 37.07, 37.91, 120.26, 124.47, 131.22, 137.29 ppm; MS: *m*/*z*: 178 $[M]^+$.

1,2-Dimethyl-4-phenylcyclohexene: b.p. 130–131 °C at 13 mm Hg (lit.[27] b.p. 128–130 °C at 11 mm Hg); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.65–1.70 (m, 6H), 1.71–2.29 (m, 6H), 2.73–2.86 (m, 1H), 7.18–7.38 ppm (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 18.87, 19.05, 30.29, 32.35, 40.05, 40.91, 125.32, 125.48, 125.85, 126.84, 128.28, 147.32 ppm; MS: *m*/*z*: 186 $[M]^+$.

1-Methyl-5-phenylcyclohexene: b.p. 122–123 °C at 13 mm Hg; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.58–1.74 (m, 1H), 1.68 (s, 3H), 1.83–1.93 (m, 1H), 2.01–2.20 (m, 4H), 2.78–2.90 (m, 1H), 5.42–5.49 (br s, 1H), 7.14–7.33 ppm (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 23.62, 25.82, 29.45, 38.31, 40.54, 120.86, 125.91, 126.86, 128.32, 133.77, 147.30 ppm; MS: *m*/*z*: 172 $[M]^+$. ^{13}C NMR data are in accordance with literature data.[28]

5-Phenyl-1-(4-methyl-3-pentenyl)cyclohexene: b.p. 113–115 °C at 0.1 mm Hg; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.65 (s, 3H), 1.74 (s, 3H), 1.67–1.80 (m, 1H), 1.90–2.27 (m, 9H), 2.76–2.90 (m, 1H), 5.13–5.21 (m, 1H), 5.53 (br s, 1H), 7.20–7.39 ppm (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 17.70, 25.71, 25.83, 26.45, 29.61, 36.81, 37.79, 40.59, 120.47, 124.30, 125.91, 126.86, 128.32, 131.38, 137.45, 147.37 ppm; MS: *m*/*z*: 240 $[M]^+$; elemental analysis (%) calcd for $C_{18}H_{24}$: C 89.94, H 10.06; found: C 89.58, H 10.12.

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