Straightforward Synthesis of Nonconjugated Cyclohex-3-enone and Conjugated 4-Methylenecyclohex-2-enone Derivatives

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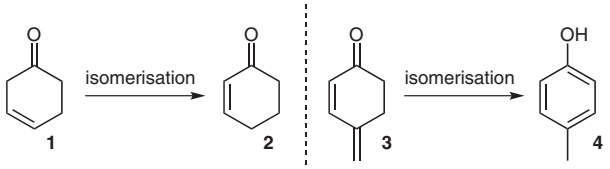
Abstract: The synthesis of nonconjugated cyclohex-3-enones via the regiodivergent cobalt-catalysed Diels–Alder reactions of 2-(trimethylsilyloxy)buta-1,3-diene with alkynes and hydrolysis of the dihydroaromatic intermediates is described. The application of bidentate phosphine ligands versus pyridine–imine ligands led to the regioselective formation of one out of the two possible regioisomeric products when terminal or unsymmetrically substituted alkynes were applied. The cyclohex-3-enone products were isolated mostly in good yields without isomerisation of the carbon–carbon double bond into conjugation based on the mild reaction conditions. The use of acetoxymethyl-substituted alkynes led to the conjugated 4-methylenecyclohex-2-enones after deprotection of the silyl enol ether.

Key words: alkynes, catalysis, cobalt, Diels–Alder reaction, dienes, nonconjugation

For a wide variety of functionalisation reactions, the cyclohex-2-enone skeleton is a versatile playground and a huge number of applications of the cyclohex-2-enone scaffold have been described thus far. Nevertheless, the chemistry of nonconjugated cyclohex-3-enones such as **1**[1] is far less explored than the transformations associated with cyclohex-2-enone derivatives such as **2** (Scheme 1). Even less explored than the chemistry of materials of type **1** are 4-methylenecyclohex-2-enone derivatives such as **3**.[2]



Scheme 1 Isomeric cyclohexenones and their interconversions

This is mostly due to the small number of efficient approaches for the selective synthesis of various derivatives of **1** and **3**.[3] In addition, basically any harsh reaction conditions will cause double-bond migration in **1** to generate the corresponding conjugated derivatives of type **2**. Intermediates of type **3** are sensitive as well, generating phenol derivatives such as **4** upon double-bond migration and keto–enol tautomerisation.[4]

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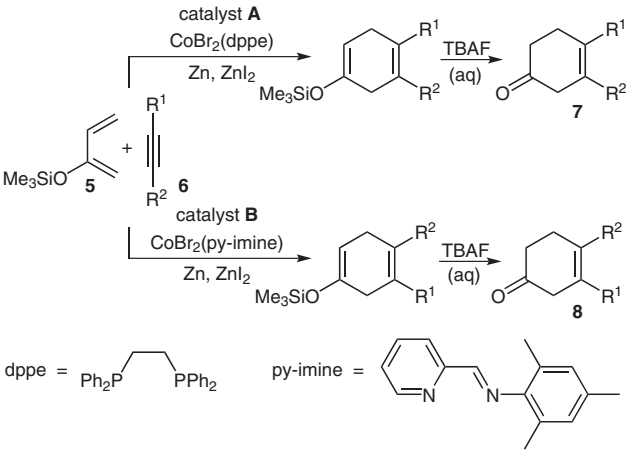
We envisaged that a cobalt-catalysed Diels–Alder reaction combined with appropriate workup conditions of suitable intermediates could be utilised for the synthesis of structures such as **1** and **3**. At best, the synthesis of **1** and **3** should be accomplished from readily available starting materials in as few chemical steps as possible.

For this purpose, we investigated the regiodiverse cobalt-catalysed Diels–Alder reactions of 2-(trimethylsilyloxy)buta-1,3-diene (**5**) with alkynes **6** for the selective synthesis of either the cyclohex-3-enone derivative **7** or the regioisomeric cyclohex-3-enone derivative **8** (Scheme 2).[5] The elegance and simplicity of this approach is that both regioisomers **7** and **8** are addressable from the same starting materials by utilising two different ligands[6] in the cobalt catalyst systems.

The silyl enol ether intermediates are directly converted into the much less oxidation-sensitive ketones **7**/**8**, realising the desired one-pot approach for the synthesis of these derivatives.



Scheme 2 Regiodiverse synthesis of the cyclohex-3-enone derivatives **7** or **8**

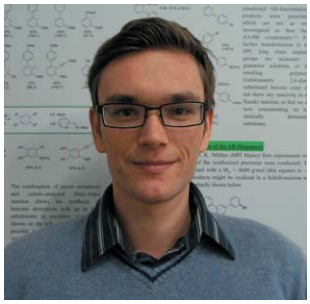
The synthesis of nonconjugated cyclohex-3-enone derivatives was first tested utilising symmetrical internal alkynes ($R^1 = R^2$). At first, the two complementary cobalt catalyst systems were tested with hex-3-yne as substrate. Catalyst system **A**, comprising $CoBr_2$(dppe), zinc powder and zinc iodide, furnished the desired product **7a** in 67% yield, while catalyst system **B**, comprising $CoBr_2$(py-imine), zinc powder and zinc iodide, gave **7a** in 76% yield.[7] Accordingly, entries 1 and 3 (Table 1) were tested using

catalyst **B** and good overall yields for the two-step procedure were obtained. Although in these cases no discrimination between **7** and **8** is possible, the general approach leads to products with synthetic potential. The investigation was then expanded toward terminal alkynes **6** (R^2 = H) which led predominantly to the formation of the 4-substituted cyclohex-3-enones **7** when catalyst system **A** was used. Complementary to these reactions, the transformations of terminal alkynes **6** utilising the alternative $CoBr_2$(py-imine) catalyst precursor (catalyst **B**) generated the regioisomeric 3-substituted cyclohex-3-enone products of type **8**. The results of this investigation utilising symmetrical internal alkynes as well as terminal alkynes for the cobalt-catalysed Diels–Alder reactions with diene **5** are summarised in Table 1.

The high degree of regiodiversity when utilising the two different cobalt catalyst systems has been demonstrated in a number of applications and is merely based on steric interactions of the ligands with the starting materials coordinated to the cobalt centre.[5e] Also in this series of experiments good to excellent regiodiversity was obtained with these two catalyst systems. Most importantly, the mild reaction conditions of the cobalt-catalysed Diels–Alder reaction and the direct silyl enol ether cleavage utilising a buffered aqueous potassium fluoride solution led to the exclusive formation of the desired nonconjugated cyclohex-3-enones **7** or **8** without isomerisation to the corresponding cyclohex-2-enone derivatives of type **2**. The improved hydrolysis conditions applying a buffered aqueous potassium fluoride solution is preferable over the hydrolysis with Brønsted acids as we reported earlier,[8] because isomerisation toward the conjugated cyclohex-2-enone derivatives is not observed even upon stirring for a prolonged reaction time.

The high functional group tolerance of the cobalt-catalysed Diels–Alder reaction found in previous investigations was also observed in the present reactions; alkyl, ether, aryl, alkenyl and ester functionalities are well accepted.

Biographical Sketches



Julian Kuttner was born in Bad Arolsen (Germany) in 1985. He studied chemistry at the Philipps-University in Marburg, obtaining his diploma in 2010. He is currently working as a Ph.D. student in the group of Prof. G. Hilt on cobalt(I)-catalysed reactions and their application in organic synthesis.

Svenja Warratz was born in Marburg (Germany) in 1987. She studied chemistry at the Philipps-University in Marburg and the Heriot-Watt University in Edinburgh. She obtained her bachelors degree in 2009 and her masters degree in 2011 with Prof. G. Hilt. Svenja is currently planning her Ph.D. thesis in organic chemistry.

Gerhard Hilt was born in Andernach (Germany) in 1968. He studied chemistry in Bonn, where he obtained his diploma in 1992 and his Ph.D. in 1996 with Prof. E. Steckhan on indirect electrochemical regeneration of enzymatic cofactors in asymmetric biosynthesis. From 1996 to 1998 he worked as a postdoctoral fellow with Prof. M. F. Semmelhack (Princeton, U.S.A.) on stoichiometric organometallic chemistry and from 1998 to 1999 in the group of Prof. R. Noyori (Nagoya, Japan) on mechanistic investigations in asymmetric catalysis. From late 1999 to 2002 he was at the Ludwig-Maximilians-University (Munich, Germany) for his habilitation, associated with the group of Prof. P. Knochel. In 2002 he moved to Marburg to his current position as an associate professor in organic chemistry. His research interests are electron-transfer-activated transition-metal complexes of cobalt and iron and their application as catalysts in atom-economic organic transformations. Another aspect of his research is the quantification of Lewis acidities and the relation to reaction rates of Lewis acid catalysed organic transformations.

The use of a nonconjugated ester functionality (Table 1, entry 10) results in the formation of product **8h**. Under the present reaction conditions, the carbon–carbon double bond did not isomerise to yield the corresponding α,β-unsaturated ester with an exocyclic double bond nor the α,β-unsaturated ketone with an endocyclic double bond.

Next, we investigated the application of unsymmetrical internal alkynes ($R^2 \neq H$) in the regiodivergent cobalt-catalysed Diels–Alder reaction. We expected that the steric hindrance of the internal alkyne would reduce the reactivity and in combination with the trimethylsilyloxy group of the diene **5** overcrowding might occur. Also, the regiodifferentiation might be reduced when the steric bulkiness of the two substituents R^1 and R^2 in alkyne **6** (Scheme 2) becomes similar. Therefore, we focused our attention in this series of experiments mostly on aryl–alkyl-substituted alkynes. The results of the transformation of unsymmetrical internal alkynes with diene **5** are summarised in Table 2.

Table 1 Synthesis of Nonconjugated Cyclohex-3-enone Derivatives from Symmetrical Internal Alkynes and Terminal Alkynes via a Cobalt-Catalysed Diels–Alder Reaction

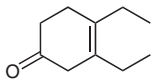
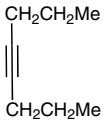
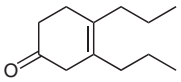
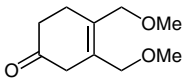
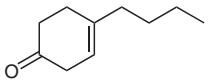
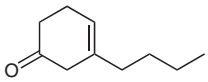
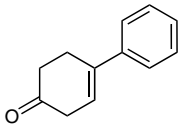
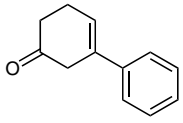
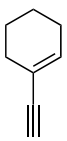
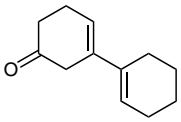
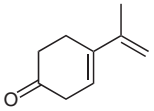
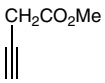
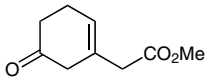
Entry	Catalyst	Alkyne **6**	Main product **7** or **8**	Ratio **7**/**8**	Yield (%)
1	**A** **B**		 **7a**	–	67 76
2	**A**		 **7b**	–	68
3	**A** **B**		 **7c**	–	61 83
4	**A**		 **7d**	>20:1	60
5	**B**		 **8d**	1:3.5	43
6	**A**		 **7e**	>20:1	83
7	**B**		 **8e**	1:>20	65
8	**B**		 **8f**	1:>20	53
9	**A**		 **7g**	>20:1	95
10	**B**		 **8h**	1:15	42

Table 2 Synthesis of Nonconjugated Cyclohex-3-enone Derivatives from Unsymmetrical Internal Alkynes via a Regiodivergent Cobalt-Catalysed Diels–Alder Reaction

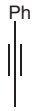
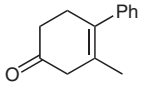
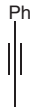
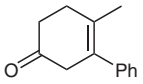
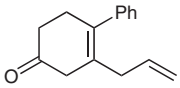
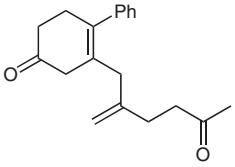
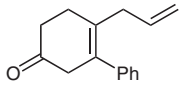
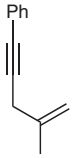
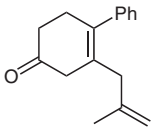
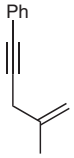
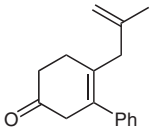
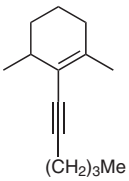
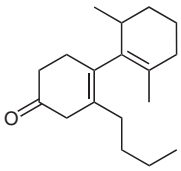
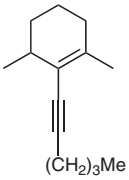
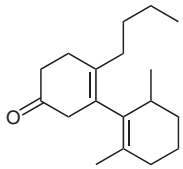
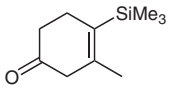
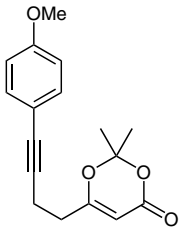
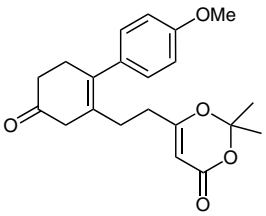
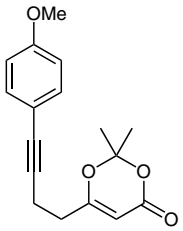
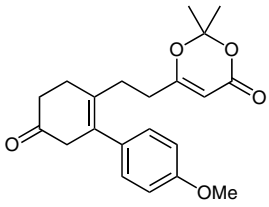
Entry	Catalyst	Alkyne **6**	Main product **7** or **8**	Ratio **7**/**8**	Yield (%)
1	**A**		 **7i**	5.5:1	92
2	**B**		 **8i**	1:>20	81
3	**A**		 **7j**	5.8:1	58
			 **7k**	4.0:1	13
4	**B**		 **8j**	1:>20	77
5	**A**		 **7l**	4.0:1	93
6	**B**		 **8l**	1:>20	82
7	**A**		 **7m**	>20:1	62
8	**B**		 **8m**	1:>20	30
9	**A**		 **7n**	>20:1	70

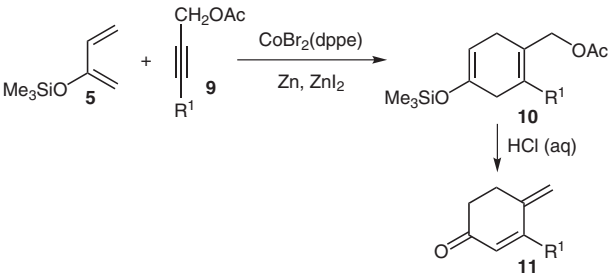
Table 2 Synthesis of Nonconjugated Cyclohex-3-enone Derivatives from Unsymmetrical Internal Alkynes via a Regiodivergent Cobalt-Catalysed Diels–Alder Reaction (continued)

Entry	Catalyst	Alkyne **6**	Main product **7** or **8**	Ratio **7**/**8**	Yield (%)
10	**A**		 **7o**	9.0:1	99
11	**B**		 **8o**	1:>20	33 75[a]

[a] Yield based on recovered starting material.

The regioselectivity for the two complementary catalyst systems was good to excellent in most cases. While catalyst system **A** generated the desired products of type **7**, the alternatively used catalyst system **B** furnished products of type **8**. The yields for the products of types **7** and **8** were also good; it was only when sterically hindered alkynes were applied that catalyst **B** gave reduced yields (Table 2, entries 8 and 11). When the $CoBr_2$(py-imine) catalyst system **B** was used, even a terminal double bond in the nonconjugated enyne was accepted (Table 2, entry 4). In contrast, when the $CoBr_2$(dppe) catalyst precursor was used in this case (Table 2, entry 3), a 1,4-hydrovinylation of the terminal double bond was also obtained and the product **7k** was isolated in 13% yield as an interesting side product.[9] The pyridine–imine-type catalysts applied in entry 4 are unreactive in 1,4-hydrovinylation reactions which led to product **8j** without the formation of such a side product. On the other hand, when the substrate with a 1,1-disubstituted double bond was applied (Table 2, entries 5 and 6) neither of the two catalyst systems led to a 1,4-hydrovinylation or isomerisation of this subunit. In many cases the regioselectivity was good to excellent so that the products can be applied in follow-up transformations without further purification. In this investigation the oxidation of the dihydroaromatic intermediates such as **10** (see Scheme 3) to the corresponding phenol derivatives was not taken into account but represents an alternative follow-up reaction for the formation of 3,4-disubstituted phenol derivatives.

Another possibility for an interesting follow-up transformation is the acidic workup of the cycloaddition products bearing an acetate group in the side chain (Scheme 3). Under these reaction conditions, the acidic hydrolysis of intermediates of type **10** can be used for the formation of conjugated 4-methylenecyclohex-2-enones **11** in a one-pot procedure.



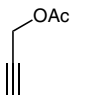
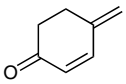
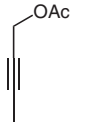
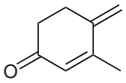
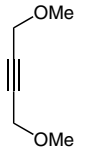
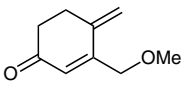
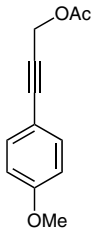
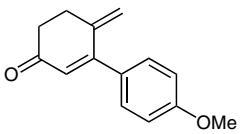
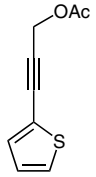
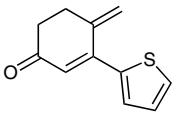
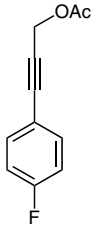
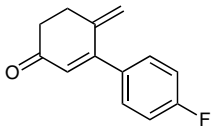
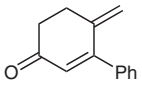
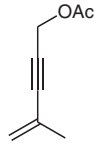
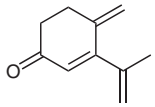
Scheme 3 Synthesis of 4-methylenecyclohex-2-enone derivatives **11**

The results of the cobalt-catalysed Diels–Alder reaction/hydrolysis sequence for the synthesis of 4-methylenecyclohex-2-enone derivatives **11** are summarised in Table 3.

The desired products could be obtained in all cases; however, the yields for most of the transformations were only moderate. The yields for the unsubstituted derivative **11a** and for the aryl-substituted products **11d–g**, particularly for the thienyl-substituted product **11e**, were in an acceptable range (Table 3, entries 1 and 4–7). Nevertheless, in this work we were able to show that the desired 4-methylenecyclohex-2-enone derivatives of type **11** can be obtained. The critical step is the hydrolysis and elimination from **10** to **11** and we have not yet been able to identify milder conditions that lead to lower yields of side products.

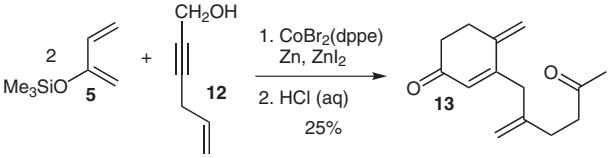
Finally, the transformation of the bisfunctionalised starting material **12** led to a regioselective cobalt-catalysed Diels–Alder reaction and to a 1,4-hydrovinylation of the terminal double bond with a second equivalent of diene **5** (Scheme 4). Similar to the reaction sequence outlined in Scheme 3, the hydrolysis with aqueous hydrochloric acid led to the formation of two keto functionalities and to the

Table 3 Synthesis of Conjugated 4-Methylenecyclohex-2-enone Derivatives via a Cobalt-Catalysed Diels–Alder Reaction/Hydrolysis Sequence

Entry	Catalyst	Alkyne **9**	Product **11**	Yield (%)
1	**A**		 **11a**	61
2	**A**		 **11b**	14
3	**A**		 **11c**	11[a]
4	**B**		 **11d**	35
5	**B**		 **11e**	53
6	**B**		 **11f**	32
7	**B**		 **11g**	43
8	**B**		 **11h**	26

[a] In this case, the symmetrical 1,4-dimethoxybut-2-yne was used as starting material.

elimination reaction to form **13** in 25% yield. Relative to the functional group density in **13** and the very short access route, the yield can be considered acceptable.



Scheme 4 Synthesis of the 4-methylenecyclohex-2-enone derivative **13**

In conclusion, we were able to show that the application of two cobalt catalyst systems with complementary regioselectivity can be applied for the facile synthesis of a wide range of nonconjugated cyclohex-3-enone derivatives. The simplicity of the synthetic approach and the high functional group tolerance of the catalysts will allow the synthesis of such building blocks for the evaluation of their follow-up chemistry. Furthermore, the application of acetoxymethyl-functionalised alkynes in the cobalt-catalysed Diels–Alder reaction and acidic hydrolysis led to the generation of 4-methylenecyclohex-2-enone derivatives. Although the yields are not very good at this stage, further research into milder methods for the hydrolysis could furnish a valuable method for the synthesis of such building blocks. An outline for the possibilities embedded in this synthetic approach has been demonstrated in the synthesis of derivative **13**, a product with many possibilities for follow-up transformations.

Column chromatography was performed using silica gel (Macherey-Nagel, 230–400 mesh size) and TLC was carried out using silica gel plates (Merck). IR spectra were obtained using a Bruker Physics IFS 200 Interferometer, a Nicolet Magna IR 750, or a Bruker Alpha-P spectrophotometer. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded using a Bruker Avance-300 instrument with $CDCl_3$ as the solvent. Low-resolution mass spectra were recorded using a Varian MAT CH 7A or a Micromass VG 7070 spectrometer for EI measurements, or a Micromass VG Autospec spectrometer for ESI measurements. HRMS were obtained using a Finnigan MAT 95S instrument for EI measurements or a Micromass VG Autospec spectrometer for ESI measurements.

Preparative Cobalt-Catalysed [4+2] Cycloaddition; Typical Procedure

A Schlenk flask was charged with [1,2-bis(diphenylphosphino)ethane]dibromocobalt(II) complex [$CoBr_2$(dppe); 62 mg, 0.1 mmol, 10 mol%] or [2,4,6-trimethyl-*N*-(pyridin-2-ylmethylene)aniline]dibromocobalt(II) complex [$CoBr_2$(py-imine); 44 mg, 0.1 mmol, 10 mol%], anhyd ZnI_2 (64 mg, 0.2 mmol, 20 mol%) and zinc powder (13 mg, 0.2 mmol, 20 mol%) under argon atmosphere. After addition of anhyd CH_2Cl_2 (1.0 mL), 2-(trimethylsilyloxy)buta-1,3-diene (**5**; 1.5 mmol) and the alkyne (1.0 mmol) were added. The mixture was stirred at r.t. and the conversion was monitored by GC/MS. After the conversion was complete, the mixture was either directly subjected to deprotection of the silyl ether or diluted with pentane to precipitate the metal salts and filtered through a small plug of silica gel using pentane or Et_2O–pentane as eluent to yield the cyclohexadiene product.

Trimethylsilyl Deprotection Using In Situ Generated TBAF; Typical Procedure

A Schlenk flask was charged with TBAB (150–200 mg) and sat. aq KF soln (2 mL), which was brought to pH 7.0 by the addition of 1 M AcOH. The above cycloaddition reaction mixture was taken up

in THF–H_2O (5:1, 10 mL) and was added to this suspension. The mixture was stirred vigorously at r.t. and the conversion was monitored by TLC. After complete conversion, the phases were separated, and the organic layer was taken up in Et_2O (40 mL) and washed once with H_2O (20 mL). The combined aqueous phases were extracted with Et_2O (2 × 20 mL) and the combined organic phases were washed once with brine (20 mL), dried ($MgSO_4$) and filtered through a small plug of silica gel. After the solvent was removed, the crude product was purified by column chromatography on silica gel.

Hydrolysis; Typical Procedure

The cyclohexadiene (1.0 mmol) was dissolved in THF (2.0 mL) and aq 1.0 M HCl (2.0 mL) was added. The mixture was stirred at r.t. and the conversion was monitored by GC/MS. After complete conversion, the phases were separated, and the organic layer was taken up in Et_2O (30 mL) and washed once with H_2O (20 mL). The combined aqueous phases were extracted with Et_2O (2 × 20 mL) and the combined organic phases were washed once with brine (20 mL), dried ($MgSO_4$) and filtered through a small plug of silica gel. The solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel.

3,4-Diethylcyclohex-3-enone (7a)

Eluent: pentane–Et_2O, 5:1; colourless oil.

Catalyst **A**: yield: 203 mg (1.33 mmol, 67%).

Catalyst **B**: yield: 230 mg (1.51 mmol, 76%).

R_f = 0.26 (pentane–Et_2O, 5:1).

IR (neat): 2966, 2933, 2873, 1721, 1459, 1403, 1375, 1361, 1296, 1244, 1218, 1190, 515 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 2.78 (s, 2 H), 2.43–2.34 (m, 4 H), 2.07 (q, *J* = 7.6 Hz, 2 H), 2.02 (q, *J* = 7.7 Hz, 2 H), 0.96 (t, *J* = 7.6 Hz, 3 H), 0.93 (t, *J* = 7.6 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 211.7, 132.3, 128.9, 43.0, 38.9, 28.9, 25.40, 25.36, 13.0, 12.8.

MS (EI, 70 eV): *m*/*z* (%) = 152 (78) $[M]^+$, 110 (54), 95 (100), 81 (40), 67 (24).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{10}H_{16}O$: 152.1201; found: 152.1202.

3,4-Dipropylcyclohex-3-enone (7b)

Eluent: pentane–Et_2O, 5:1; colourless oil.

Catalyst **A**: yield: 245 mg (1.36 mmol, 68%).

R_f = 0.29 (pentane–Et_2O, 5:1).

IR (neat): 2960, 2932, 2871, 1720, 1465, 1403, 1378, 1362, 1263, 1214, 1186, 515 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 2.79 (s, 2 H), 2.43–2.33 (m, 4 H), 2.09–1.98 (m, 4 H), 1.45–1.30 (m, 4 H), 0.89 (t, *J* = 7.3 Hz, 3 H), 0.88 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 212.0, 131.6, 128.1, 43.6, 38.9, 34.6, 34.5, 29.3, 21.5, 21.2, 14.0, 13.9.

MS (EI, 70 eV): *m*/*z* (%) = 180 (42) $[M]^+$, 109 (100), 95 (37), 81 (33), 67 (24).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{12}H_{20}O$: 180.1514; found: 180.1515.

3,4-Bis(methoxymethyl)cyclohex-3-enone (7c)

Eluent: pentane–Et_2O, 1:1; yellow oil.

Catalyst **A**: yield: 223 mg (1.23 mmol, 61%).

Catalyst **B**: yield: 603 mg (3.31 mmol, 83%).

R_f = 0.14 (pentane–Et_2O, 1:1).

IR (neat): 2979, 2927, 2819, 1718, 1449, 1384, 1355, 1296, 1193, 1082, 952, 929, 908 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 4.00 (s, 2 H), 3.95 (s, 2 H), 3.30 (s, 3 H), 3.29 (s, 3 H), 2.96 (s, 2 H), 2.58–2.53 (m, 2 H), 2.47–2.42 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 210.0, 133.2, 130.3, 70.68, 70.66, 58.04, 58.00, 41.8, 38.3, 27.5.

MS (EI, 70 eV): *m*/*z* (%) = 184 (1) $[M]^+$, 152 (100), 137 (12), 123 (9), 109 (23), 93 (20), 79 (31), 67 (13), 53 (10).

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{10}H_{16}O_3Na$: 207.0992; found: 207.0995.

4-Butylcyclohex-3-enone (7d)

Eluent: pentane–Et_2O, 5:1; colourless oil.

Yield: 458 mg (3.01 mmol, 60%).

R_f = 0.25 (pentane–Et_2O, 5:1).

IR (neat): 2957, 2929, 2872, 1719, 1466, 1443, 1405, 1379, 1340, 1190, 1019, 973 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 5.41 (tt, *J* = 3.6, 1.2 Hz, 1 H), 2.82 (dt, *J* = 3.5, 1.7 Hz, 2 H), 2.49–2.34 (m, 4 H), 2.11–1.93 (m, 2 H), 1.44–1.22 (m, 4 H), 0.88 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 211.0, 138.9, 117.5, 39.6, 38.6, 36.7, 29.7, 28.5, 22.3, 13.9.

MS (EI, 70 eV): *m*/*z* (%) = 152 (6) $[M]^+$, 151 (57), 95 (39), 68 (100).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{10}H_{16}O$: 152.1201; found: 152.1213.

3-Butylcyclohex-3-enone (8d)

Eluent: pentane–Et_2O, 5:1; colourless oil.

Yield: 130 mg (0.86 mmol, 43%); **7d**/**8d** = 1:3.5.

R_f = 0.25 (pentane–Et_2O, 5:1).

IR (neat): 2957, 2927, 2859, 1715, 1458, 1402, 1344, 1289, 1193, 884, 755, 500 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 5.60–5.59 (m, 1 H), 2.78 (s, 2 H), 2.50–2.38 (m, 4 H), 2.04–1.95 (m, 2 H), 1.45–1.22 (m, 4 H), 0.89 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 210.9, 136.3, 120.3, 42.9, 38.5, 36.3, 29.4, 24.9, 22.2, 13.9.

MS (EI, 70 eV): *m*/*z* (%) = 152 (16) $[M]^+$, 110 (28), 95 (26), 68 (100).

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{10}H_{16}ONa$: 175.1093; found: 175.1095.

4-Phenylcyclohex-3-enone (7e)

Eluent: pentane–Et_2O, 5:1; yellow solid.

Yield: 713 mg (4.15 mmol, 83%).

R_f = 0.16 (pentane–Et_2O, 5:1).

IR (KBr): 3036, 2929, 1716, 1493, 1443, 1414, 1394, 1340, 1237, 1197, 985, 756, 696, 473, 444 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.42–7.25 (m, 5 H), 6.10 (tt, *J* = 3.9, 1.2 Hz, 1 H), 3.07 (dt, *J* = 3.8, 1.8 Hz, 2 H), 2.91 (td, *J* = 6.9, 1.6 Hz, 2 H), 2.65 (t, *J* = 6.9 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 209.9, 140.7, 137.8, 128.4, 127.4, 125.2, 120.9, 39.9, 38.7, 27.9.

MS (EI, 70 eV): *m*/*z* (%) = 172 (71) $[M]^+$, 130 (100), 129 (94), 115 (58).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{12}H_{12}O$: 172.0888; found: 172.0898.

3-Phenylcyclohex-3-enone (8e)
Eluent: pentane–Et_2O, 5:1; yellow solid.

Yield: 449 mg (2.61 mmol, 65%).

R_f = 0.16 (pentane–Et_2O, 5:1).

IR (KBr): 3053, 2911, 1703, 1493, 1444, 1398, 1335, 1247, 1195, 1069, 886, 747, 692, 421, 411 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.25 (m, 5 H), 6.34 (tt, *J* = 4.2, 1.9 Hz, 1 H), 3.28 (d, *J* = 1.9 Hz, 2 H), 2.70–2.63 (m, 2 H), 2.58–2.54 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 209.9, 139.7, 134.9, 128.5, 127.5, 125.0, 123.5, 41.9, 37.9, 25.2.

MS (EI, 70 eV): *m*/*z* (%) = 172 (68) $[M]^+$, 144 (34), 130 (84), 129 (100), 115 (70).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{12}H_{12}O$: 172.0888; found: 172.0901.

3-(Cyclohex-1-enyl)cyclohex-3-enone (8f)
Eluent: pentane–Et_2O, 5:1; colourless solid.

Yield: 186 mg (1.06 mmol, 53%).

R_f = 0.26 (pentane–Et_2O, 5:1).

IR (KBr): 2925, 1711, 1426, 1406, 1345, 1284, 1242, 1188, 923, 792, 518, 413 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 5.94 (t, *J* = 3.9 Hz, 1 H), 5.71 (t, *J* = 3.8 Hz, 1 H), 3.04 (d, *J* = 1.3 Hz, 2 H), 2.56–2.45 (m, 4 H), 2.23–2.14 (m, 4 H), 1.73–1.54 (m, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 210.9, 135.5, 135.0, 123.5, 120.0, 40.6, 38.4, 25.8, 25.6, 25.2, 22.9, 22.3.

MS (EI, 70 eV): *m*/*z* (%) = 176 (100) $[M]^+$, 133 (17), 119 (32), 105 (23), 91 (33), 79 (20).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{12}H_{16}O$: 176.1201; found: 176.1195.

4-(Prop-1-en-2-yl)cyclohex-3-enone (7g)
Eluent: pentane–Et_2O, 5:1; yellow oil.

Yield: 224 mg (1.65 mmol, 95%).

R_f = 0.28 (pentane–Et_2O, 5:1).

IR (neat): 3093, 2970, 2858, 1724, 1609, 1443, 1399, 1341, 1269, 1195, 890, 819, 412 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 5.87 (t, *J* = 4.0 Hz, 1 H), 5.03 (s, 1 H), 4.97 (s, 1 H), 3.00 (d, *J* = 3.6 Hz, 2 H), 2.69 (t, *J* = 6.9 Hz, 2 H), 2.53 (t, *J* = 6.8 Hz, 2 H), 1.94 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 210.3, 142.1, 137.6, 120.8, 111.9, 39.8, 38.5, 25.8, 20.7.

MS (EI, 70 eV): *m*/*z* (%) = 136 (86) $[M]^+$, 94 (28), 93 (50), 79 (100).

HRMS: *m*/*z* $[M]^+$ calcd for $C_9H_{12}O$: 136.0888; found: 136.0893.

Methyl 2-(5-Oxocyclohex-1-enyl)acetate (8h)
Eluent: pentane–Et_2O, 1:1; yellow oil.

Yield: 352 mg (2.10 mmol, 42%); **7h**/**8h** = 1:15.

R_f = 0.30 (pentane–Et_2O, 1:1).

IR (neat): 2954, 2851, 1712, 1436, 1342, 1258, 1195, 1161, 1062, 1007, 970, 889, 846, 754, 705, 498 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 5.78 (s, 1 H), 3.68 (s, 3 H), 3.05 (s, 2 H), 2.91 (s, 2 H), 2.46 (s, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 209.3, 171.3, 129.2, 125.5, 51.9, 42.9, 41.9, 37.9, 24.8.

MS (EI, 70 eV): *m*/*z* (%) = 168 (68) $[M]^+$, 126 (100), 108 (100), 97 (34), 79 (92), 67 (38).

HRMS: *m*/*z* $[M]^+$ calcd for $C_9H_{12}O_3$: 168.0786; found: 168.0785.

3-Methyl-4-phenylcyclohex-3-enone (7i)
Eluent: pentane–Et_2O, 5:1; colourless oil.

Yield: 172 mg (0.92 mmol, 92%); **7i**/**8i** = 5.5:1.

R_f = 0.17 (pentane–Et_2O, 5:1).

IR (neat): 2909, 2852, 1714, 1492, 1443, 1399, 1357, 1251, 1187, 759, 700, 484 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.38–7.32 (m, 2 H), 7.28–7.23 (m, 1 H), 7.18–7.13 (m, 2 H), 2.96 (s, 2 H), 2.76–2.71 (m, 2 H), 2.62–2.58 (m, 2 H), 1.65 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 210.5, 142.1, 132.7, 128.2, 128.1, 126.9, 126.6, 45.5, 39.2, 31.7, 20.2.

MS (EI, 70 eV): *m*/*z* (%) = 186 (40) $[M]^+$, 144 (20), 129 (100), 115 (20).

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{13}H_{15}O$: 187.1117; found: 187.1119.

4-Methyl-3-phenylcyclohex-3-enone (8i)
Eluent: pentane–Et_2O, 5:1; yellow oil.

Yield: 753 mg (4.05 mmol, 81%).

R_f = 0.17 (pentane–Et_2O, 5:1).

IR (neat): 3055, 2912, 1717, 1493, 1442, 1362, 1247, 1210, 762, 702 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.38–7.32 (m, 2 H), 7.28–7.22 (m, 1 H), 7.16–7.13 (m, 2 H), 3.13 (d, *J* = 1.7 Hz, 2 H), 2.62–2.52 (m, 4 H), 1.71 (t, *J* = 2.0 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 210.5, 141.5, 130.2, 129.6, 128.3, 128.2, 126.7, 45.3, 38.5, 31.5, 20.2.

MS (EI, 70 eV): *m*/*z* (%) = 186 (92) $[M]^+$, 144 (68), 129 (100), 115 (22), 43 (22).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{13}H_{14}O$: 186.1045; found: 186.1036.

3-Allyl-4-phenylcyclohex-3-enone (7j)
Eluent: pentane–Et_2O, 5:1; colourless oil.

Yield: 122 mg (0.58 mmol, 58%); **7j**/**8j** = 5.8:1.

R_f = 0.21 (pentane–Et_2O, 5:1).

IR (neat): 3075, 3021, 2970, 2901, 2846, 1714, 1635, 1491, 1438, 1358, 1293, 1252, 1190, 994, 914, 756, 700, 563, 487 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.38–7.32 (m, 2 H), 7.30–7.24 (m, 1 H), 7.19–7.15 (m, 2 H), 5.71 (ddt, *J* = 16.9, 10.2, 6.5 Hz, 1 H), 5.07–4.98 (m, 2 H), 2.98 (s, 2 H), 2.78–2.71 (m, 4 H), 2.62–2.58 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 210.5, 141.8, 135.5, 134.5, 128.7, 128.3, 127.8, 126.8, 116.5, 43.1, 39.0, 38.2, 31.9.

MS (EI, 70 eV): *m*/*z* (%) = 212 (28) $[M]^+$, 197 (35), 169 (48), 155 (75), 141 (100), 128 (77), 115 (53), 91 (34), 77 (26).

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{15}H_{16}ONa$: 235.1093; found: 235.1094.

3-[2-(3-Oxobutyl)prop-2-enyl]-4-phenylcyclohex-3-enone (7k)
Eluent: pentane–EtOAc, 3:1; yellow oil.

Yield: 36 mg (0.13 mmol, 13%); **7k**/**8k** = 4:1.

R_f = 0.16 (pentane–EtOAc, 3:1).

IR (neat): 2903, 1710, 1644, 1491, 1437, 1357, 1253, 1189, 1160, 895, 760, 702, 485 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.37–7.31 (m, 2 H), 7.29–7.23 (m, 1 H), 7.18–7.13 (m, 2 H), 4.78–4.77 (m, 2 H), 2.92 (s, 2 H), 2.79–

2.75 (m, 2 H), 2.70 (s, 2 H), 2.60 (t, *J* = 6.8 Hz, 2 H), 2.35–2.29 (m, 2 H), 2.15–2.09 (m, 2 H), 2.05 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 210.5, 207.8, 145.4, 141.8, 135.6, 128.34, 128.26, 127.8, 126.9, 111.5, 43.0, 41.5, 40.3, 38.9, 32.0, 29.8, 29.4.

MS (EI, 70 eV): *m*/*z* (%) = 282 (46) $[M]^+$, 264 (19), 239 (18), 224 (100), 211 (90), 193 (39), 181 (72), 167 (90), 155 (93), 141 (64), 128 (76), 115 (52), 91 (41), 77 (19).

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{19}H_{22}O_2Na$: 305.1512; found: 305.1511.

4-Allyl-3-phenylcyclohex-3-enone (8j)
Eluent: pentane–Et_2O, 5:1; yellow oil.

Yield: 326 mg (1.54 mmol, 77%).

R_f = 0.21 (pentane–Et_2O, 5:1).

IR (neat): 3077, 3056, 2973, 2902, 2844, 1714, 1635, 1492, 1442, 1361, 1296, 1251, 1196, 992, 913, 755, 700, 476 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.37–7.32 (m, 2 H), 7.29–7.24 (m, 1 H), 7.17–7.14 (m, 2 H), 5.71 (ddt, *J* = 16.8, 10.4, 6.3 Hz, 1 H), 5.08–5.01 (m, 2 H), 3.16 (s, 2 H), 2.78 (d, *J* = 6.3 Hz, 2 H), 2.57 (s, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 210.3, 141.1, 136.0, 132.0, 131.5, 128.4, 127.9, 127.0, 116.1, 45.7, 38.6, 38.1, 28.7.

MS (EI, 70 eV): *m*/*z* (%) = 212 (88) $[M]^+$, 197 (30), 169 (70), 155 (100), 141 (90), 129 (82), 115 (45), 91 (95), 77 (39).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{15}H_{16}O$: 212.1201; found: 212.1198.

3-(2-Methallyl)-4-phenylcyclohex-3-enone (7l)
Eluent: pentane–Et_2O, 5:1; colourless oil.

Yield: 210 mg (0.93 mmol, 93%); **7l**/**8l** = 4:1.

R_f = 0.24 (pentane–Et_2O, 5:1).

IR (neat): 2968, 2907, 1714, 1647, 1492, 1441, 1359, 1251, 1189, 890, 757, 700, 484 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.37–7.31 (m, 2 H), 7.29–7.23 (m, 1 H), 7.20–7.15 (m, 2 H), 4.80 (s, 1 H), 4.71 (s, 1 H), 2.95 (s, 2 H), 2.80–2.75 (m, 2 H), 2.69 (s, 2 H), 2.62–2.58 (m, 2 H), 1.60 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 210.7, 142.9, 141.9, 135.2, 128.6, 128.3, 127.8, 126.8, 111.9, 43.0, 41.9, 39.0, 32.0, 22.4.

MS (EI, 70 eV): *m*/*z* (%) = 226 (42) $[M]^+$, 211 (80), 183 (40), 169 (100), 155 (97), 141 (96), 128 (85), 115 (65), 91 (50), 77 (34).

HRMS: *m*/*z* $[M + Na]^+$ calcd for $C_{16}H_{18}ONa$: 249.1250; found: 249.1252.

4-(2-Methallyl)-3-phenylcyclohex-3-enone (8l)
Eluent: pentane–Et_2O, 5:1; colourless oil.

Yield: 372 mg (1.64 mmol, 82%).

R_f = 0.24 (pentane–Et_2O, 5:1).

IR (neat): 3076, 3022, 2968, 2933, 1718, 1648, 1493, 1443, 1362, 1298, 1251, 1195, 890, 759, 703, 418 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.37–7.32 (m, 2 H), 7.29–7.23 (m, 1 H), 7.19–7.15 (m, 2 H), 4.83 (s, 1 H), 4.72 (s, 1 H), 3.18 (s, 2 H), 2.75 (s, 2 H), 2.61–2.48 (m, 4 H), 1.63 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 210.5, 143.6, 141.1, 132.1 (2 C), 128.3, 127.8, 126.9, 111.5, 45.7, 41.9, 38.7, 28.5, 22.6.

MS (EI, 70 eV): *m*/*z* (%) = 226 (60) $[M]^+$, 211 (22), 183 (19), 169 (37), 155 (100), 142 (38), 128 (21), 115 (13), 91 (14), 77 (18).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{16}H_{18}O$: 226.1358; found: 226.1349.

3-Butyl-4-(2,6-dimethylcyclohex-1-enyl)cyclohex-3-enone (7m)
The product was obtained as a 1:1 mixture of axially chiral diastereomers which could not be separated by simple silica gel column chromatography.

Eluent: pentane–Et_2O, 6:1; yellow oil.

Yield: 161 mg (0.62 mmol, 62%).

R_f = 0.39 (pentane–Et_2O, 5:1).

IR (neat): 2956, 2927, 2869, 1718, 1495, 1456, 1371, 1291, 1182, 1112, 1045, 982, 802 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.96–2.80 (m, 2 H), 2.49–2.41 (m, 3 H), 2.30–1.52 (m, 9 H), 1.49–1.48 (m, 3 H), 1.45–1.16 (m, 5 H), 0.97–0.85 (m, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 212.02, 211.98, 137.0, 135.7, 134.4, 132.0, 129.9, 129.4, 128.3, 127.8, 42.7, 42.5, 38.9, 38.8, 34.8, 33.3, 32.9, 31.9, 31.3 (4 C), 30.7, 29.8, 29.3, 28.7, 23.2, 22.7, 20.65, 20.63, 20.52, 20.49, 20.13, 20.09, 14.0, 13.9.

MS (EI, 70 eV): *m*/*z* (%) = 260 (80) $[M]^+$, 245 (33), 217 (100), 175 (31), 159 (44), 133 (30), 119 (30), 105 (50), 91 (48).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{18}H_{28}O$: 260.2140; found: 260.2135.

4-Butyl-3-(2,6-dimethylcyclohex-1-enyl)cyclohex-3-enone (8m)
The product was obtained as a 1:1 mixture of axially chiral diastereomers which could not be separated by simple silica gel column chromatography.

Eluent: pentane–Et_2O, 6:1; yellow oil.

Yield: 78 mg (0.30 mmol, 30%).

R_f = 0.39 (pentane–Et_2O, 5:1).

IR (neat): 2956, 2932, 2871, 1716, 1676, 1456, 1377, 1251, 1205, 1035, 841 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.93–2.59 (m, 2 H), 2.50–2.32 (m, 4 H), 2.21–2.12 (m, 1 H), 2.06–1.83 (m, 4 H), 1.78–1.49 (m, 3 H), 1.47 (s, 3 H), 1.41–1.17 (m, 5 H), 0.95–0.84 (m, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 211.9, 211.7, 135.9, 135.0, 133.5, 133.1, 130.8, 128.9, 128.63, 128.59, 46.0, 43.2, 38.70, 38.66, 34.8, 33.5, 33.1, 31.9, 31.32, 31.31, 31.30, 30.4, 30.0, 29.4, 28.0, 27.7, 23.3, 22.8, 20.5 (2 C), 20.40, 20.37, 20.1, 19.9, 14.0, 13.9.

MS (EI, 70 eV): *m*/*z* (%) = 260 (69) $[M]^+$, 245 (32), 217 (100), 187 (29), 159 (61), 133 (30), 119 (34), 105 (52), 91 (50).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{18}H_{28}O$: 260.2140; found: 260.2151.

3-Methyl-4-(trimethylsilyl)cyclohex-3-enone (7n)
Eluent: pentane–Et_2O, 5:1; colourless oil.

Yield: 253 mg (1.39 mmol, 70%).

R_f = 0.27 (pentane–Et_2O, 5:1).

IR (neat): 1718, 1247, 832, 752, 688, 501 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.84 (s, 2 H), 2.48–2.33 (m, 4 H), 1.82 (s, 3 H), 0.16 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 211.6, 141.0, 130.9, 47.4, 38.7, 28.9, 23.1, 0.0.

MS (EI, 70 eV): *m*/*z* (%) = 182 (43) $[M]^+$, 167 (74), 151 (12), 75 (32), 73 (100), 59 (16).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{10}H_{18}OSi$: 182.1127; found: 182.1131.

6-(2-[2-(4-Methoxyphenyl)-5-oxocyclohex-1-enyl]ethyl)-2,2-dimethyl-4*H*-1,3-dioxin-4-one (7o)
Eluent: pentane–Et_2O, 1:3; colourless solid.

Yield: 354 mg (0.99 mmol, 99%); **7o**/**8o** = 9:1.

R_f = 0.16 (pentane–Et_2O, 1:3).

IR (neat): 1714, 1633, 1607, 1511, 1390, 1375, 1291, 1251, 1197, 1179, 1041, 1012, 902, 829, 798, 760, 509 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.04 (d, *J* = 8.5 Hz, 2 H), 6.89 (d, *J* = 8.4 Hz, 2 H), 5.09 (s, 1 H), 3.81 (s, 3 H), 2.96 (s, 2 H), 2.70 (t, *J* = 6.5 Hz, 2 H), 2.57 (t, *J* = 6.4 Hz, 2 H), 2.29–2.18 (m, 4 H), 1.59 (s, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 209.7, 170.6, 161.0, 158.6, 135.5, 133.6, 128.9, 128.1, 113.9, 106.3, 93.3, 55.2, 42.9, 38.7, 32.2, 32.0, 29.9, 24.9.

MS (EI, 70 eV): *m*/*z* (%) = 356 (1) $[M]^+$, 298 (56), 272 (62), 214 (44), 172 (40), 121 (26), 58 (28), 43 (100).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{21}H_{24}O_5$: 356.1624; found: 356.1621.

6-(2-[2-(4-Methoxyphenyl)-4-oxocyclohex-1-enyl]ethyl)-2,2-dimethyl-4*H*-1,3-dioxin-4-one (8o)
Eluent: pentane–Et_2O, 1:3; yellow solid.

Yield: 119 mg (0.33 mmol, 33%).

R_f = 0.16 (pentane–Et_2O, 1:3).

IR (thin film, CH_2Cl_2): 1715, 1631, 1608, 1510, 1389, 1374, 1271, 1245, 1201, 1176, 1032, 1017, 901, 833, 809, 732, 701, 509 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.02 (d, *J* = 8.8 Hz, 2 H), 6.88 (d, *J* = 8.8 Hz, 2 H), 5.10 (s, 1 H), 3.81 (s, 3 H), 3.09 (s, 2 H), 2.56–2.55 (m, 4 H), 2.35–2.23 (m, 4 H), 1.59 (s, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 209.6, 170.8, 161.0, 158.6, 132.9, 132.2, 131.5, 128.9, 114.0, 106.3, 93.2, 55.3, 46.0, 38.4, 32.2, 29.9, 28.6, 24.9.

MS (EI, 70 eV): *m*/*z* (%) = 356 (1) $[M]^+$, 298 (11), 227 (3), 214 (7), 186 (5), 171 (6), 58 (66), 43 (100).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{21}H_{24}O_5$: 356.1624; found: 356.1624.

4-Methylenecyclohex-2-enone (11a)
Eluent: pentane–Et_2O, 10:1; yellow oil.

Yield: 132 mg (1.22 mmol, 61%).

R_f = 0.12 (pentane–Et_2O, 10:1).

^1H NMR (300 MHz, $CDCl_3$): δ = 7.08 (d, *J* = 9.9 Hz, 1 H), 5.95 (d, *J* = 9.9 Hz, 1 H), 5.33 (s, 1 H), 5.29 (s, 1 H), 2.78–2.71 (m, 2 H), 2.56–2.48 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.9, 147.3, 140.5, 128.0, 119.2, 37.1, 29.1.

The analytical data were in accordance with literature data.[10]

3-Methyl-4-methylenecyclohex-2-enone (11b)
Eluent: pentane–Et_2O, 5:1; yellow oil.

Yield: 17 mg (0.14 mmol, 14%).

R_f = 0.08 (pentane–Et_2O, 10:1).

^1H NMR (300 MHz, $CDCl_3$): δ = 5.90 (s, 1 H), 5.35 (s, 1 H), 5.33 (s, 1 H), 2.74 (t, *J* = 7.0 Hz, 2 H), 2.72 (t, *J* = 7.0 Hz, 2 H), 2.05 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.4, 154.3, 142.2, 127.8, 115.4, 37.6, 31.3, 20.0.

The analytical data were in accordance with literature data.[11]

3-(Methoxymethyl)-4-methylenecyclohex-2-enone (11c)
Eluent: pentane–Et_2O, 2:1; yellow oil.

Yield: 17 mg (0.11 mmol, 11%).

R_f = 0.13 (pentane–Et_2O, 2:1).

IR (neat): 3407, 2928, 2350, 1667, 1448, 1283, 1189, 1091, 910 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.13 (d, *J* = 0.8 Hz, 1 H), 5.36–5.27 (m, 2 H), 4.24 (d, *J* = 1.4 Hz, 2 H), 3.40 (s, 3 H), 2.78–2.69 (m, 2 H), 2.56–2.47 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.2, 153.0, 139.5, 125.7, 114.7, 71.3, 58.8, 37.8, 31.8.

MS (EI, 70 eV): *m*/*z* (%) = 152 (21) $[M]^+$, 122 (78), 109 (63), 91 (71), 81 (66), 79 (100), 77 (63).

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_9H_{12}O_2Na$: 175.0730; found: 175.0731.

3-(4-Methoxyphenyl)-4-methylenecyclohex-2-enone (11d)
Eluent: pentane–Et_2O, 2:1; yellow oil.

Yield: 74 mg (0.35 mmol, 35%).

R_f = 0.16 (pentane–Et_2O, 2:1).

IR (neat): 3406, 2955, 2839, 1663, 1605, 1576, 1559, 1510, 1443, 1421, 1369, 1295, 1247, 1174, 1033, 840, 533 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.37–7.32 (m, 2 H), 6.95–6.90 (m, 2 H), 6.05 (d, *J* = 1.1 Hz, 1 H), 5.56–5.51 (m, 1 H), 5.21 (s, 1 H), 3.84 (s, 3 H), 2.89–2.81 (m, 2 H), 2.59 (t, *J* = 7.0 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.3, 160.8, 158.0, 142.1, 130.5, 130.3, 125.7, 119.7, 113.8, 55.3, 38.2, 32.7.

MS (EI, 70 eV): *m*/*z* (%) = 214 (100) $[M]^+$, 186 (31), 171 (76), 158 (49), 155 (31), 128 (28), 115 (43).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{14}H_{14}O_2$: 214.0994; found: 214.0984.

4-Methylene-3-(2-thienyl)cyclohex-2-enone (11e)
Eluent: pentane–Et_2O, 5:1; yellow oil.

Yield: 101 mg (0.53 mmol, 53%).

R_f = 0.07 (pentane–Et_2O, 10:1).

IR (neat): 3473, 3100, 2954, 1662, 1558, 1423, 1367, 1273, 1244, 1176, 922, 854, 709, 527 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.46 (dd, *J* = 5.1, 1.1 Hz, 1 H), 7.33 (dd, *J* = 3.7, 1.1 Hz, 1 H), 7.11 (dd, *J* = 5.1, 3.7 Hz, 1 H), 6.21 (d, *J* = 1.1 Hz, 1 H), 5.62 (s, 1 H), 5.58 (t, *J* = 1.2 Hz, 1 H), 2.84 (t, *J* = 6.7 Hz, 2 H), 2.59 (t, *J* = 6.7 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.6, 150.4, 141.6, 140.1, 129.6, 128.5, 127.9, 125.1, 119.4, 38.4, 32.9.

MS (EI, 70 eV): *m*/*z* (%) = 190 (100) $[M]^+$, 161 (33), 147 (30), 134 (38), 129 (14).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{11}H_{10}OS$: 190.0452; found: 190.0456.

3-(4-Fluorophenyl)-4-methylenecyclohex-2-enone (11f)
Eluent: pentane–MTBE, 10:1; yellow oil.

Yield: 65 mg (0.32 mmol, 32%).

R_f = 0.09 (pentane–MTBE, 10:1).

IR (neat): 3068, 2954, 2357, 1662, 1595, 1504, 1367, 1226, 1165, 843, 482 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.41–7.32 (m, 2 H), 7.15–7.05 (m, 2 H), 6.03 (d, *J* = 1.2 Hz, 1 H), 5.56–5.51 (m, 1 H), 5.15 (s, 1 H), 2.92–2.83 (m, 2 H), 2.59 (t, *J* = 7.1 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.0, 163.5 (d, *J* = 249.6 Hz), 157.2, 141.9, 134.0 (d, *J* = 3.2 Hz), 130.8 (d, *J* = 8.4 Hz), 126.7, 120.0, 115.5 (d, *J* = 21.7 Hz), 38.0, 32.4.

MS (EI, 70 eV): *m*/*z* (%) = 202 (76) $[M]^+$, 187 (18), 173 (40), 159 (72), 146 (100), 133 (26), 120 (25).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{13}H_{11}OF$: 202.0794; found: 202.0799.

4-Methylene-3-phenylcyclohex-2-enone (11g)
Eluent: pentane–Et_2O, 5:1; yellow oil.

Yield: 80 mg (0.43 mmol, 43%).

R_f = 0.17 (pentane–Et_2O, 5:1).

IR (neat): 3048, 2952, 2901, 1661, 1563, 1491, 1441, 1317, 1172, 916, 876, 736, 694, 455 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.44–7.34 (m, 5 H), 6.06 (d, *J* = 1.2 Hz, 1 H), 5.55–5.50 (m, 1 H), 5.17 (s, 1 H), 2.93–2.83 (m, 2 H), 2.61 (t, *J* = 7.0 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.1, 158.3, 141.9, 138.1, 129.4, 129.0, 128.3, 126.7, 120.0, 38.0, 32.5.

MS (EI, 70 eV): *m*/*z* (%) = 184 (96) $[M]^+$, 169 (15), 155 (59), 141 (72), 128 (100), 115 (25), 102 (24).

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{13}H_{12}ONa$: 207.0780; found: 207.0781.

4-Methylene-3-(prop-1-en-2-yl)cyclohex-2-enone (11h)
Eluent: pentane–Et_2O, 5:1; yellow oil.

Yield: 38 mg (0.26 mmol, 26%).

R_f = 0.21 (pentane–Et_2O, 5:1).

IR (neat): 3088, 2956, 1662, 1561, 1440, 1368, 1269, 1228, 1178, 1017, 910, 729, 450 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 5.88 (d, *J* = 1.1 Hz, 1 H), 5.45–5.40 (m, 1 H), 5.34 (s, 1 H), 5.28–5.23 (m, 1 H), 5.19–5.15 (m, 1 H), 2.77–2.69 (m, 2 H), 2.52 (t, *J* = 7.0 Hz, 2 H), 1.95 (dd, *J* = 1.4, 0.9 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.7, 159.8, 141.9, 140.4, 124.5, 118.8, 118.3, 38.3, 32.6, 22.3.

MS (EI, 70 eV): *m*/*z* (%) = 148 (96) $[M]^+$, 133 (35), 120 (74), 105 (97), 92 (32), 91 (100), 79 (29).

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{10}H_{13}O$: 149.0961; found: 149.0962.

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