

Synthesis of Medium-Sized Carbocycles by Gallium-Catalyzed Tandem Carbonyl-Olefin Metathesis/Transfer Hydrogenation.

Supporting Information

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Table of Contents

1	GENERAL REMARKS	2
2	ADDITIONAL EXPERIMENTS	3
3	FT-IR EXPERIMENTS	4
4	EXPERIMENTAL PROCEDURES	6
4.1	GENERAL PROCEDURE (A) FOR THE SYNTHESIS OF STARTING MATERIALS 1A-O	6
4.2	CHARACTERIZATION OF THE STARTING MATERIALS 1A-O	7
4.3	GENERAL PROCEDURE (B) FOR THE SYNTHESIS OF STARTING MATERIALS 4A-N	13
4.4	CHARACTERIZATION OF STARTING MATERIALS 4A-O	14
5	CATALYTIC REACTIONS	21
5.1	EXPERIMENTAL PROCEDURE (C) FOR THE HYDROGENATIVE RING CLOSING CARBONYL-OLEFIN METATHESIS (TABLE 1).....	21
5.2	SCALE-UP	21
5.3	EXPERIMENTAL PROCEDURE (D) FOR THE HYDROGENATIVE CARBONYL-OLEFIN METATHESIS (SCHEMES 2 AND 3) AND CHARACTERIZATION OF PRODUCTS 3A-O AND 5A-N.	21
6	TRANSFORMATIONS OF ETHYL CIS-2-PHENYLCYCLO-PENTANECARBOXYLATE 3A	32
7	SINGLE-CRYSTAL X-RAY STRUCTURE ANALYSIS OF COMPOUND 3H	34
8	CALCULATIONS	36
9	REFERENCES	43

1 General Remarks

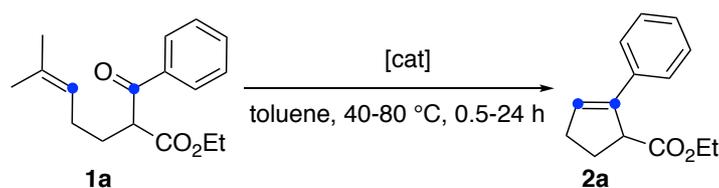
All reactions were performed in oven-dried flasks under argon. Reactions in overheated solvent were performed in 10 mL reaction tubes sealed with a Teflon-coated Rodaviss stopper and immersed in a pre-heated oil bath. Reactions were monitored using thin-layer chromatography (TLC) on silica gel plates (0.25 mm) precoated with a fluorescent indicator. The spots were visualized with ultraviolet light and/or phosphomolybdic acid stain with heat as revealing agent. Flash chromatography (FC) was performed with CombiFlash System on 40-63 μm silica gel with mixtures of ethyl acetate (EtOAc), diethylether (Et₂O), cyclohexane (Cy), pentane, or petroleum ether (PE). Yields refer to chromatographically and spectroscopically pure compounds. NMR characterization data was collected at 296 K on a AM 250, AV 300, or AV 360 spectrometer operating at 250, 300, or 360 MHz respectively for ¹H NMR. ¹H NMR chemical shifts are reported in ppm using residual solvent peak as reference (CDCl₃: δ = 7.26 ppm or C₆D₆: δ = 7.16 ppm). Data for ¹H NMR are presented as follows: chemical shift δ (ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), coupling constant *J* (Hz) and integration; ¹³C NMR spectra were recorded at 63, 75, or 90 MHz using broadband proton decoupling and chemical shifts are reported in ppm using residual solvent peaks as reference (CDCl₃: δ = 77.16 ppm or C₆D₆: δ = 128.06 ppm). Multiplicity was defined by DEPT 135 analysis. IR characterization data were recorded on a FT-IR spectrometer (Perkin-Elmer). High-resolution mass spectra (HRMS) was performed by a TOF instrument (MicrOTOFq Bruker spectrometer) using ESI-TOF (electrospray ionization-time of flight). Compounds **3h**, **3i**, **3l** proved too apolar and too sensitive to allow mass spectroscopy analysis.

Materials: Reagents were purchased from commercial suppliers (*Alfa Aesar*, *Sigma Aldrich*, *TCI* or *Strem*) and used as received. Solvents were dried by distillation under argon from the followings: tetrahydrofuran (sodium/benzophenone); toluene (sodium); 1,2-dichloroethane (calcium hydride). IPr-GaCl₃ and IPr-InBr₃ were synthesized according to literature procedures.¹

NMR spectra of compounds **1b**, **1e**, **1f**, **1g**, **1i**, **1j**, **1k**, **1l**, **1m**, **4a**, **4b**, **4c**, **4d**, **4e**, **4f**, **4g**, **4h**, **4i**, **4j**, **4k**, **4l**, **4m**, **4n**, **3a**, **3b**, **3c**, **3d**, **3f**, **3h**, **3i**, **3j**, **3m**, **3n**, **5a**, **5b**, **5c**, **5d**, **5e**, **5f**, **5g**, **5h**, **5i**, **5j**, **5m**, **5n** are shown in the appendix.

2 Additional Experiments

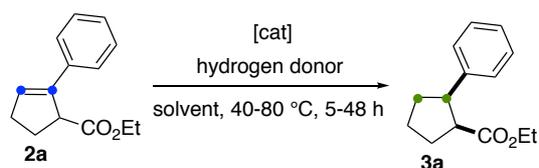
Table S1: Complete Screening of Catalysts for Ring Closing Carbonyl-Ene Metathesis of 1a



Entry	Catalyst/additive (x/y mol%)	Temp. (°C)	Time (h)	1a/2a ratio (yield %) ^a
1	IPr·GaCl ₃ /AgSbF ₆ (5/7)	80	2.5	0/100 (93)
2	IPr·GaCl ₃ /AgSbF ₆ (5/7)	80	1	7/93 (79)
3	IPr·GaCl ₃ (5)	80	24	NR
4	IPr·GaCl ₃ /AgSbF ₆ (5/7)	40	1	99/1 (86)
5	AgSbF ₆ (7)	80	24	NR
6	GaCl ₃ (5)	80	24	NR
7	GaCl ₃ /AgSbF ₆ (5/7)	80	0.5	0/100 (89)
8	FeCl ₃ (5)	80	24	92/8
9	IPr·InBr ₃ /AgSbF ₆ (5/7)	80	0.5	0/100 (38)
10	IPr·InBr ₃ /AgSbF ₆ (5/7)	40	24	15/85
11	[Ga(PhF) ₂][Al(pftb) ₄] (5)	80	24	93/7
12	Ga ₂ Cl ₄ (5)	80	24	94/6
13	InCl ₃ (5)	80	48	35/65
14	PPh ₃ AuCl/AgSbF ₆ (5/5)	80	1	0/100 (92)
15	B(C ₆ F ₅) ₃ (5)	80	17	99/1
16	Tf ₂ NH (2.5)	80	24	95/5
17	Tf ₂ NH (5)	80	3	0/100 (87) ^b
18	[(JohnPhos)Au(MeCN)][SbF ₆] (5)	80	17	68/32

^a Estimated by ¹H NMR spectroscopic analysis, isolated yield in parenthesis. ^b Complex mixture

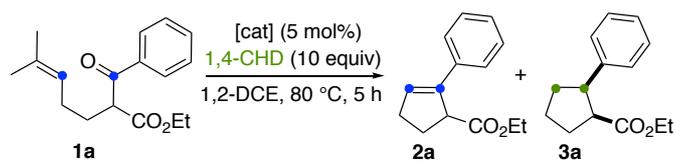
Table S2: Screening of Catalysts and Hydrogen Donor for Transfer Hydrogenation of 2a



Entry	Catalyst/additive (x/y mol%)	H ₂ Donor (equiv)	Solvent	Temp. (°C)	Time (h)	2a/3a ratio (yield %) ^a
1	IPr·GaCl ₃ /AgSbF ₆ (5/7)	1,4-CHD (3)	toluene	80	48	92/8
2	IPr·GaCl ₃ /AgSbF ₆ (5/7)	1,3,5-CHD (3+3)	toluene	80	5	NR
3	IPr·GaCl ₃ /AgSbF ₆ (5/7)	1,4-CHD	1,2-DCE	40	20	45/55 (52)
4	IPr·GaCl ₃ /AgSbF ₆ (5/7)	1,3,5-CHD (3+3)	1,2-DCE	40	5	95/5
5	IPr·GaCl ₃ /AgSbF ₆ (5/7)	Et ₃ SiH (10)	1,2-DCE	80	17	90/10
6	FeCl ₃ (5)	1,4-CHD (10)	1,2-DCE	80	17	58/42 (41)
7	B(C ₆ F ₅) ₃ (5)	1,4-CHD (10)	1,2-DCE	80	17	99/1
8	Tf ₂ NH (5)	1,4-CHD (10)	1,2-DCE	80	17	47/53 (42)

^a Estimated by ¹H NMR spectroscopic analysis, diastereomeric ratio *cis/trans* 4/1 (isolated yield in parenthesis).

Table S3: Screening of Catalysts for the Hydrogenative Ring Closing Carbonyl-Olefin Metathesis, Generation of Stronger Superelectrophiles with MCl_3 and MBr_3 .



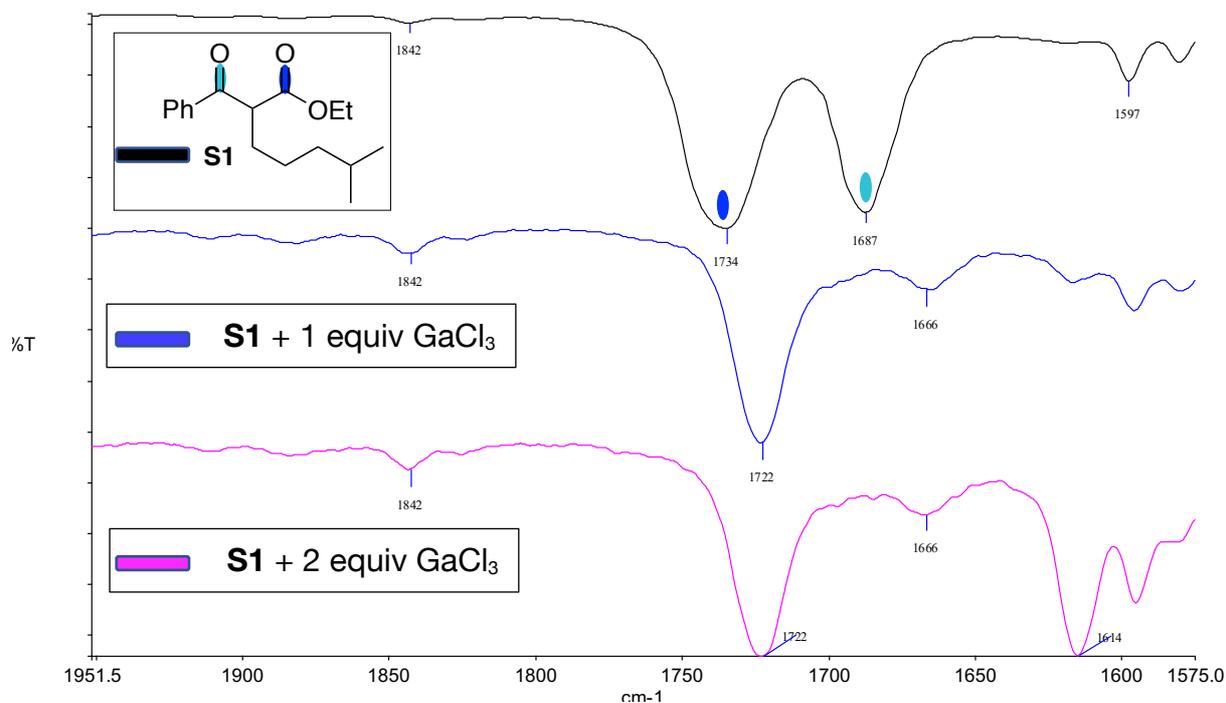
Entry	Catalyst (mol%)	2a/3a ratio ^a
1	GaCl_3 (5)	91/1
2	GaBr_3 (5)	96/4
3	$\text{GaCl}_3/\text{GaBr}_3$ (5/5)	50/50
4	$[\text{IPr}\cdot\text{GaCl}_2][\text{SbF}_6]$ (5)	16/84
5	$[\text{IPr}\cdot\text{GaBr}_2][\text{SbF}_6]$ (5)	32/68
6	$[\text{IPr}\cdot\text{GaCl}_2][\text{SbF}_6]/[\text{IPr}\cdot\text{GaBr}_2][\text{SbF}_6]$ (5/5)	40/60
7	FeCl_3 (5)	32/0
8	FeBr_3 (5)	6/0
9	$\text{FeCl}_3/\text{FeBr}_3$ (5/5)	39/0
10	$[\text{IPr}\cdot\text{GaCl}_2][\text{SbF}_6]$ (2.5)	12/88
11	$[\text{IPr}\cdot\text{GaCl}_2][\text{SbF}_6]$ (1)	96/4

^a Estimated by ^1H NMR spectroscopic analysis.

3 FT-IR Experiments

FT-IR experiments were carried out to get some pieces of information regarding the role of Ga(III) homodimers, by using a substrate which cannot cyclize (**S1**). Transmission IR spectra were recorded on a Perkin Elmer FT-IR spectrometer using 0.30 mm path length KBr solution cell.

IR measurements of compound **S1** with A) no additive, B) 1 equiv GaCl_3 and C) 2 equiv GaCl_3



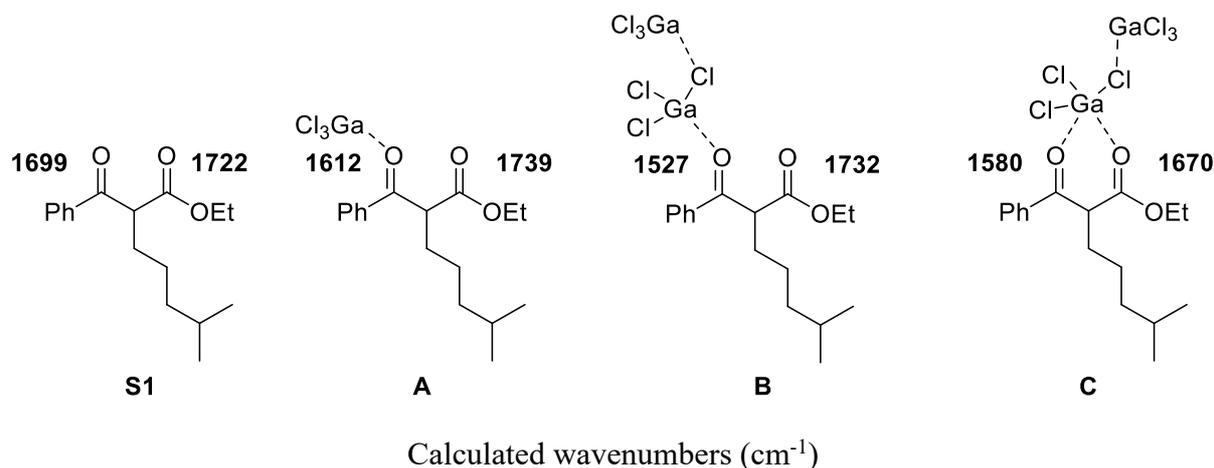
Compound S1 + no additive: to a 1 dram vial was added **S1** (5.0 mg, 0.018 mmol) along with 1 mL of DCE. Then 150 μ L of this solution was transferred *via* syringe into a transmission IR solution cell and the IR spectrum was immediately recorded.

Compound S1 + 1 equiv GaCl₃: to a 1 dram vial was added **S1** (5.0 mg, 0.018 mmol) along with 0.5 mL of 1,2-DCE. The resultant solution was then added to a mixture of GaCl₃ (3.2 mg; 0.018 mmol) in 1,2-DCE (0.5 mL). Then 150 μ L of this solution was transferred *via* syringe into a transmission IR solution cell and the IR spectrum was immediately recorded.

Compound S1 + 2 equiv GaCl₃: to a 1 dram vial was added **S1** (5.0 mg, 0.018 mmol) along with 0.5 mL of 1,2-DCE. The resultant solution was then added to a mixture of GaCl₃ (5.4 mg; 0.036 mmol) in 1,2-DCE (0.5 mL). Then 150 μ L of this solution was transferred *via* syringe into a transmission IR solution cell and the IR spectrum was immediately recorded.

Of note, the IR spectrum of β -keto esters usually exhibit the keto rather than the enol form.² The observed band at 1734 cm⁻¹ is thus attributed to the ester carbonyl stretching, and the band at 1687 cm⁻¹ is attributed to the ketone carbonyl stretching. Upon addition of 1 equiv of GaCl₃, the ketone C=O band vanishes. Addition of a second equiv of GaCl₃ promotes the appearance of a stronger band at 1614 cm⁻¹.

IR spectra were simulated by DFT computations at the level described in Section 8 of this Supporting Information. For **S1**, the calculated wavenumbers are 1699 (exp 1687) and 1722 (exp 1734) cm⁻¹ for the keto and ester carbonyl respectively. Coordination of GaCl₃ to the ketone function leads to a peak at 1612 cm⁻¹ (**A**), and that of Ga₂Cl₆ to a peak at 1527 cm⁻¹ (**B**). As further discussed in Section 7, GaCl₃ is a monocoordinating Lewis acid that normally do not form pentavalent species, unless a homodimer is formed. A chelate is therefore possible with Ga₂Cl₆, as in **C**. A peak at 1580 cm⁻¹ corresponds to the antisymmetric stretch of the two carbonyls (more pronounced for the ketone), while the peak at 1670 cm⁻¹ corresponds to the symmetric stretch of the two carbonyls (more pronounced for the ester).

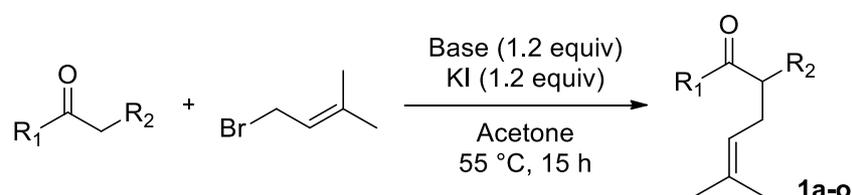


⁷¹Ga NMR is not very useful here since complexes of type LGaCl₃ usually give very broad signals. In contrast, highly symmetrical gallium species such as GaCl₄⁻ provide a diagnostic sharp peak. Importantly, the mixture composed of **S1** and 2 equiv of GaCl₃ did not show the presence of GaCl₄⁻ by ⁷¹Ga NMR.

Based on all these elements, we conclude that the band at 1614 cm⁻¹ can only be explained by the existence of **C** in the mixture when 2 equiv of GaCl₃ are used. This experiment supports the role of gallium(III) homodimers. The case is not clear with only one equiv of GaCl₃ because of the low resolution of the spectra when the Lewis acid is present.

4 Experimental Procedures

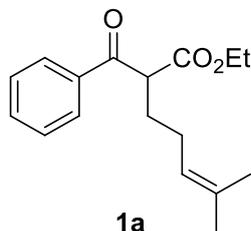
4.1 General Procedure (A) for the Synthesis of Starting Materials 1a-o



A 250 mL round bottom flask equipped with a magnetic stir bar was charged with a base (1.2 equiv) and KI (1.2 equiv). Dry acetone (0.2 M) was then added, followed by the starting ketone (1-1.2 equiv) and 5-bromo-2-methylpent-2-ene (1 equiv). The resulting mixture was heated at reflux with a condenser and stirred overnight. The reaction was then cooled to rt, quenched with H₂O and extracted twice with Et₂O. The combined organic extracts were washed with H₂O and brine, dried over MgSO₄, filtered and concentrated under reduced pressure by rotary evaporation. Purification by FC (SiO₂, Cy/EtOAc) afforded the desired substrate **1a-o**.

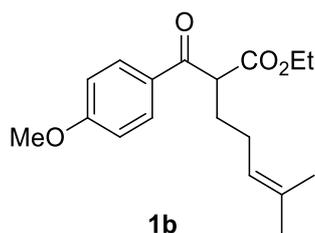
4.2 Characterization of the Starting Materials 1a-o

Ethyl 2-benzoyl-6-methylhept-5-enoate 1a



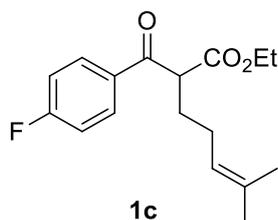
The general procedure **A** was followed with 5-bromo-2-methylpent-2-ene (850 mg, 5.20 mmol), ethyl 3-oxo-3-phenylpropanoate (1.2 g, 6.24 mmol) and K_2CO_3 as base. Purification by FC (SiO_2 , Cy/EtOAc, 97/3) afforded **1a** as a clear oil (985 mg, 3.59 mmol, 69%). 1H NMR (250 MHz, $CDCl_3$): δ 7.98-7.94 (m, 2H), 7.60-7.54 (m, 1H), 7.49-7.43 (m, 2H), 5.14-5.09 (m, 1H), 4.33 (ddd, $J = 7.0, 4.6, 2.8$ Hz, 1H), 4.13 (q, $J = 7.1$ Hz, 2H), 2.05-2.03 (m, 4H), 1.65 (s, 3H), 1.50 (s, 3H), 1.20 (t, $J = 7.1$ Hz, 3H). These data correspond to those previously reported in the literature.³

1-(4-Methoxyphenyl)-2-(4-methylpent-3-en-1-yl)butane-1,3-dione 1b



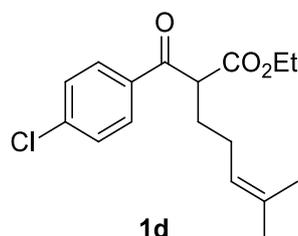
The general procedure **A** was followed with 5-bromo-2-methylpent-2-ene (880 mg, 5.40 mmol), ethyl 3-(4-methoxyphenyl)-3-oxopropanoate (1.0 g, 4.50 mmol) and K_2CO_3 as base. Purification by FC (SiO_2 , Cy/EtOAc, 95/5) afforded **1b** as a clear oil (206 mg, 0.68 mmol, 15%). 1H NMR (250 MHz, $CDCl_3$): δ 7.97 (d, $J = 8.8$ Hz, 2H), 6.94 (d, $J = 8.8$ Hz, 2H), 5.16-5.05 (m, 1H), 4.29-4.23 (m, 1H), 4.14 (q, $J = 7.1$ Hz, 2H), 3.87 (s, 3H), 2.07-2.00 (m, 4H), 1.67 (s, 3H), 1.51 (s, 3H), 1.18 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (90 MHz, $CDCl_3$): δ 193.6 (C), 170.0 (C), 163.7 (C), 132.9 (C), 130.8 (2CH), 129.2 (C), 123.0 (CH), 113.7 (2CH), 61.0 (CH_2), 55.3 (CH_3), 52.9 (CH), 29.0 (CH_2), 25.8 (CH_3), 25.5 (CH_2), 17.4 (CH_3), 13.9 (CH_3). FT-IR (neat, cm^{-1}): 3074, 2980, 2933, 2858, 1742, 1689, 1599, 1507, 1447, 1409, 1368, 1300, 1234, 1158, 1025. HRMS (ESI⁺): m/z calcd. for $C_{18}H_{24}O_4Na$ $[M+Na]^+$ 327.1566, found 327.1561.

Ethyl 2-(4-fluorobenzoyl)-6-methylhept-5-enoate 1c



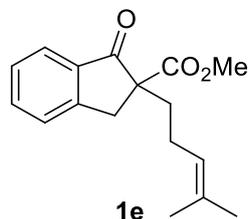
The general procedure **A** was followed with 5-bromo-2-methylpent-2-ene (930 mg, 5.70 mmol), ethyl 3-(4-fluorophenyl)-3-oxopropanoate (1.0 g, 4.76 mmol) and K_2CO_3 as base. Purification by FC (SiO_2 , Cy/EtOAc, 97/3) afforded **1c** as a clear oil (1.03 g, 3.50 mmol, 74%). **1H NMR (250 MHz, $CDCl_3$):** δ 8.04-7.95 (m, 2H), 7.17-7.07 (m, 2H), 5.11-5.03 (m, 1H), 4.28-4.21 (m, 1H), 4.12 (q, $J = 7.0$ Hz, 2H), 2.06-2.00 (m, 4H), 1.64 (s, 3H), 1.48 (s, 3H), 1.15 (t, $J = 7.0$ Hz, 3H). These data correspond to those previously reported in the literature.³

Ethyl 2-(4-chlorobenzoyl)-6-methylhept-5-enoate 1d



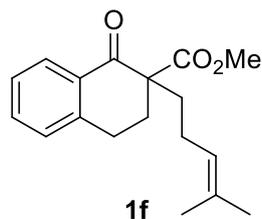
The general procedure **A** was followed with 5-bromo-2-methylpent-2-ene (1.0 g, 6.13 mmol), ethyl 3-(4-chlororophenyl)-3-oxopropanoate (1.67 g, 7.36 mmol) and K_2CO_3 as base. Purification by FC (SiO_2 , Cy/EtOAc, 97/3) afforded **1c** as a clear oil (993 mg, 3.22 mmol, 52%). **1H NMR (300 MHz, $CDCl_3$):** δ 7.96-7.90 (m, 2H), 7.48-7.43 (m, 2H), 5.14-5.06 (m, 1H), 4.15 (q, $J = 7.1$ Hz, 2H), 2.09-2.03 (m, 4H), 1.67 (s, 3H), 1.52 (s, 3H), 1.19 (t, $J = 7.1$ Hz, 3H). These data correspond to those previously reported in the literature.³

Methyl 2-(4-methylpent-3-en-1-yl)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate 1e



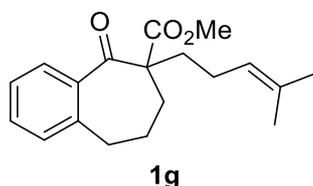
The general procedure **A** was followed with 5-bromo-2-methylpent-2-ene (1.0 g, 6.30 mmol), methyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate⁴ (1.0 g, 5.26 mmol) and K_2CO_3 as base. Purification by FC (SiO_2 , Cy/EtOAc, 97/3) afforded **1e** as a clear oil (183 mg, 0.67 mmol, 13%). **1H NMR (300 MHz, $CDCl_3$):** δ 7.73 (d, $J = 7.7$ Hz, 1H), 7.61 (ddd, $J = 7.7, 7.2, 1.7$ Hz, 1H), 7.49 (d, $J = 7.7$ Hz, 1H), 7.38 (ddd, $J = 7.7, 7.2, 1.7$ Hz, 1H), 5.07-4.99 (m, 1H), 3.72 (d, $J = 17.4$ Hz, 1H), 3.66 (s, 3H), 3.11 (d, $J = 17.4$ Hz, 1H), 2.21-2.09 (m, 1H), 2.00-1.81 (m, 3H), 1.60 (s, 3H), 1.48 (s, 3H). **^{13}C NMR (63 MHz, $CDCl_3$):** δ 202.4 (C), 171.5 (C), 153.0 (C), 135.3 (C), 132.6 (CH + C), 127.7 (CH), 126.4 (CH), 124.7 (CH), 123.2 (CH), 60.6 (C), 52.6 (CH₃), 36.6 (CH₂), 34.9 (CH₂), 25.6 (CH₃), 23.6 (CH₂), 17.5 (CH₃). **FT-IR (neat, cm^{-1}):** 3064, 3023, 2949, 2854, 1730, 1692, 1618, 1570, 1453, 1434, 1375, 1271, 1215, 1080. **HRMS (ESI⁺):** m/z calcd. for $C_{17}H_{20}O_3Na$ [$M+Na$]⁺ 295.1307, found 295.1304.

Methyl-2-(4-methylpent-3-en-1-yl)-1-oxo-1,2,3,4 tetrahydronaphthalene-2-carboxylate 1f



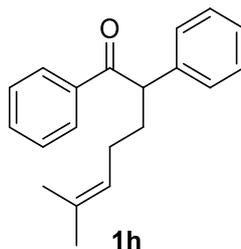
The general procedure **A** was followed with 5-bromo-2-methylpent-2-ene (960 mg, 5.88 mmol), methyl 1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate⁴ (1.0 g, 4.90 mmol) and Cs₂CO₃ as a base. Purification by FC (SiO₂, Cy/EtOAc, 95/5) afforded **1f** as a clear oil (362 mg, 1.26 mmol, 26%). **¹H NMR (300 MHz, CDCl₃):** δ 8.05 (d, *J* = 7.5, 1.3 Hz, 1H), 7.47 (td, *J* = 7.5, 1.3 Hz, 1H), 7.32 (d, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 7.5 Hz, 1H), 5.15-5.09 (m, 1H), 3.68 (s, 3H), 3.08 (ddd, *J* = 17.3, 9.7, 4.8 Hz, 1H), 2.93 (td, *J* = 17.3, 5.3 Hz, 1H), 2.59 (ddd, *J* = 14.3, 5.3, 4.8 Hz, 1H), 2.17 (ddd, *J* = 14.3, 9.7, 4.8 Hz, 1H), 2.11-2.05 (m, 1H), 2.04-1.85 (m, 3H), 1.67 (s, 3H), 1.61 (s, 3H). **¹³C NMR (63 MHz, CDCl₃):** δ 195.4 (C), 172.3 (C), 143.1 (C), 133.4 (CH), 132.4 (C), 132.0 (C), 128.7 (CH), 128.1 (CH), 126.7 (CH), 123.5 (CH), 57.5 (C), 52.3 (CH₃), 34.0 (CH₂), 30.5 (CH₂), 25.9 (CH₂), 25.6 (CH₂), 23.5 (CH₃), 17.6 (CH₃). **FT-IR (neat, cm⁻¹):** 3091, 2952, 2923, 2858, 1740, 1695, 1600, 1448, 1376, 1325, 1303, 1253, 1209, 1167, 1087. **HRMS (ESI⁺):** *m/z* calcd. for C₁₈H₂₂O₃Na [M+Na]⁺ 309.1461, found 309.1464.

Methyl 6-(4-methylpent-3-en-1-yl)-5-oxo-6,7,8,9-tetrahydro-5H-benzo[7]annulene-6-carboxylate 1g



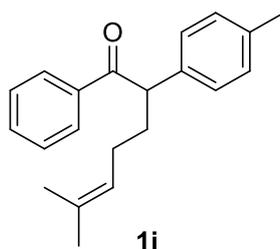
The general procedure **A** was followed with 5-bromo-2-methylpent-2-ene (269 mg, 1.65 mmol), methyl 5-oxo-6,7,8,9-tetrahydro-5H-benzo[7]annulene-6-carboxylate⁴ (300 g, 1.37 mmol) and Cs₂CO₃ as base. Purification by FC (SiO₂, Cy/EtOAc, 97/3) afforded **1g** as a clear oil (335 mg, 1.12 mmol, 81%). **¹H NMR (250 MHz, CDCl₃):** δ 7.42 (d, *J* = 7.6 Hz, 1H), 7.35 (dd, *J* = 7.4, 7.4 Hz, 1H), 7.26 (dd, *J* = 7.4, 7.4 Hz, 1H), 7.12 (d, *J* = 7.4 Hz, 1H), 5.12-5.02 (m, 1H), 3.59 (s, 3H), 2.95 (ddd, *J* = 14.7, 10.1, 4.3 Hz, 1H), 2.78 (ddd, *J* = 14.7, 6.4, 4.3 Hz, 1H), 2.46-2.30 (m, 1H), 2.15-1.95 (m, 2H), 1.94-1.77 (m, 5H), 1.66 (s, 3H), 1.57 (s, 3H). **¹³C NMR (90 MHz, CDCl₃):** δ 204.0 (C=O), 172.1 (C=O), 140.5 (C), 138.0 (C), 131.6 (C), 130.6 (CH), 128.7 (CH), 128.2 (CH), 125.9 (CH), 123.1 (CH), 61.4 (C), 51.4 (CH₃), 36.4 (CH₂), 32.7 (CH₂), 31.8 (CH₂), 25.8 (CH₂), 23.9 (CH₂), 23.2 (CH₃), 17.8 (CH₃). **FT-IR (neat, cm⁻¹):** 3093, 3047, 2947, 2858, 1740, 1690, 1599, 1449, 1376, 1351, 1325, 1253, 1237, 1209, 1167, 1117, 1087. **HRMS (ESI⁺):** *m/z* calcd. for C₁₉H₂₄O₃Na [M+Na]⁺ 323.1622, found 323.1617.

6-Methyl-1,2-diphenylhept-5-en-1-one **1h**



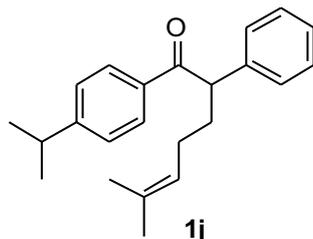
The general procedure **A** was followed with 5-bromo-2-methylpent-2-ene (697 mg, 4.28 mmol), 2-phenylacetophenone (700 mg, 3.57 mmol) and *t*BuOK as base. Purification by FC (SiO₂, Cy/EtOAc, 90/10) afforded **1h** as a clear oil (321.8 mg, 1.16 mmol, 32%). **¹H NMR (300 MHz, CDCl₃):** δ 7.98-7.94 (m, 2H), 7.50-7.46 (m, 1H), 7.41-7.36 (m, 2H), 7.32-7.27 (m, 4H), 7.22-7.17 (m, 1H), 5.14-5.09 (m, 1H), 4.59 (t, *J* = 7.2 Hz, 1H), 2.30-2.21 (m, 1H), 1.98-1.93 (m, 2H), 1.90-1.83 (m, 1H), 1.66 (s, 3H), 1.47 (s, 3H). These data correspond to those previously reported in the literature.³

6-Methyl-2-phenyl-1-(*p*-tolyl)hept-5-en-1-one **1i**



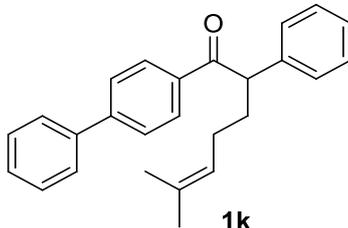
The general procedure **A** was followed with 5-bromo-2-methylpent-2-ene (1.86 g, 11.41 mmol), 2-(4-methylphenyl)-1-phenylethan-1-one (2.0 g, 9.51 mmol) and *t*BuOK as base. Purification by FC (SiO₂, Cy/EtOAc, 100/0 to 97/3) afforded **1i** as a clear oil (1.3 g, 4.46 mmol, 47%). **¹H NMR (300 MHz, CDCl₃):** δ 8.29 (d, *J* = 7.1 Hz, 2H), 7.80-7.73 (m, 1H), 7.71-7.64 (m, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 8.1 Hz, 2H), 5.45 (t, *J* = 7.1 Hz, 1H), 4.87 (t, *J* = 7.1 Hz, 1H), 2.58 (s, 3H), 2.65-2.51 (m, 1H), 2.35-2.26 (m, 2H), 2.25-2.11 (m, 1H), 1.99 (s, 3H), 1.81 (s, 3H). **¹³C NMR (90 MHz, CDCl₃):** δ 199.5 (C), 154.2 (C), 140.0 (C), 134.8 (C), 132.3 (C), 129.0 (C), 128.8 (2CH), 128.3 (2CH), 126.9 (2CH), 126.6 (2CH), 124.0 (CH), 52.7 (CH), 34.2 (CH₂), 26.0 (CH₃), 25.8 (CH₂), 23.6 (CH₃), 17.7 (CH₃). **FT-IR (neat, cm⁻¹):** 3053, 3023, 2923, 2857, 1681, 1596, 1579, 1511, 1447, 1376, 1257, 1112. **HRMS (ESI⁺):** *m/z* calcd. for C₂₁H₂₄ONa [M+Na]⁺ 315.1719, found 315.1724.

1-(4-Isopropylphenyl)-6-methyl-2-phenylhept-5-en-1-one 1j



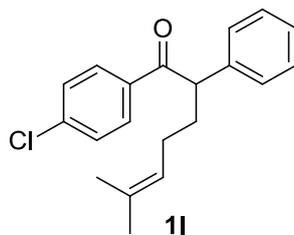
The general procedure **A** was followed with 5-bromo-2-methylpent-2-ene (1.64 g, 10.07 mmol), 2-phenyl-1-[4-(propan-2-yl)phenyl]ethan-1-one (2.0 g, 8.39 mmol) and *t*BuOK as base. Purification by FC (SiO₂, Cy/EtOAc, 100/0 to 97/3) afforded **1j** as a clear oil (710 mg, 2.21 mmol, 26%). **¹H NMR (300 MHz, CDCl₃):** δ 7.99-7.94 (m, 2H), 7.39-7.33 (m, 2H), 7.32-7.22 (m, 4H), 7.22-7.15 (m, 1H), 5.22-5.12 (m, 1H), 4.61 (t, *J* = 7.1 Hz, 1H), 2.90 (hept, *J* = 6.9 Hz, 1H), 2.38-2.23 (m, 1H), 2.06-1.96 (m, 2H), 1.96-1.83 (m, 1H), 1.69 (s, 3H), 1.51 (s, 3H), 1.22 (d, *J* = 6.9 Hz, 6H). **¹³C NMR (75 MHz, CDCl₃):** δ 199.9 (C), 137.0 (C), 136.7 (C), 136.4 (C), 132.6 (C), 129.5 (2CH), 128.6 (2CH), 128.6 (CH), 128.4 (2CH), 128.1 (2CH), 124.0 (CH), 52.4 (CH), 34.1 (CH), 26.9 (CH₂), 26.0 (CH₂), 25.8 (CH₃), 20.9 (2CH₃), 17.7 (CH₃). **FT-IR (neat, cm⁻¹):** 3061, 3027, 2963, 2927, 2870, 1678, 1605, 1453, 1415, 1259, 1218, 1178. **HRMS (ESI⁺):** *m/z* calcd. for C₂₃H₂₈ONa [M+Na]⁺ 343.2032, found 343.2032.

1-([1,1'-Biphenyl]-4-yl)-6-methyl-2-phenylhept-5-en-1-one 1k



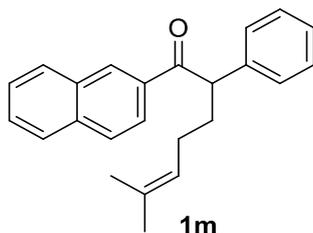
The general procedure **A** was followed with 5-bromo-2-methylpent-2-ene (1.44 g, 8.81 mmol), 2-phenyl-1-(4-phenylphenyl)ethan-1-one (2.0 g, 7.34 mmol) and *t*BuOK as base. Purification by FC (SiO₂, Cy/EtOAc, 100/0 to 96/4) afforded **1k** as a clear oil (441 mg, 1.24 mmol, 17%). **¹H NMR (360 MHz, CDCl₃):** δ 8.06 (d ap, *J* = 8.5 Hz, 2H), 7.66-7.56 (m, 4H), 7.49-7.42 (m, 2H), 7.42-7.38 (m, 1H), 7.37-7.29 (m, 4H), 7.22 (m, 1H), 5.16 (tdd, *J* = 5.8, 2.7, 1.4 Hz, 1H), 4.62 (t, *J* = 7.1 Hz, 1H), 2.37-2.24 (m, 1H), 2.05-1.98 (m, 2H), 1.96-1.84 (m, 1H), 1.69 (s, 3H), 1.51 (s, 3H). **¹³C NMR (90 MHz, CDCl₃):** δ 199.7 (C), 145.5 (C), 140.0 (C), 139.9 (C), 135.8 (C), 132.6 (C), 129.3 (2CH), 129.0 (2CH), 128.9 (2CH), 128.4 (2CH), 128.3 (CH), 127.4 (2CH), 127.3 (2CH), 127.1 (CH), 124.0 (C), 52.9 (CH), 34.2 (CH₂), 26.1 (CH₃), 25.9 (CH₂), 17.9 (CH₃). **FT-IR (neat, cm⁻¹):** 3058, 3028, 2964, 2924, 2857, 1676, 1603, 1450, 1404, 1258, 1178. **HRMS (ESI⁺):** *m/z* calcd. for C₂₆H₂₆ONa [M+Na]⁺ 377.1862 found, 377.1876.

1-(4-Chlorophenyl)-6-methyl-2-phenylhept-5-en-1-one **1l**



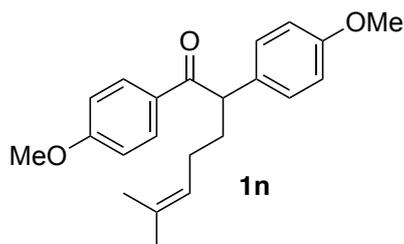
The general procedure **A** was followed with 5-bromo-2-methylpent-2-ene (1.28 g, 7.84 mmol), 2-(4-chlorophenyl)-1-phenylethan-1-one (1.17 g, 5.1 mmol) and *t*BuOK as base. Purification by FC (SiO₂, Cy/EtOAc, 100/0 to 97/3) afforded **1l** as a clear oil (400 mg, 1.28 mmol, 25%). **¹H NMR (400 MHz, CDCl₃):** δ 7.90 (d, *J* = 8.6 Hz, 2H), 7.35 (d, *J* = 8.6 Hz, 2H), 7.30-7.28 (m, 4H), 7.24-7.18 (m, 1H), 5.16-5.10 (m, 1H), 4.51 (t, *J* = 7.1 Hz, 1H), 2.27 (td, *J* = 14.2, 7.1 Hz, 1H), 2.03-1.94 (m, 2H), 1.87 (dt, *J* = 14.2, 7.1 Hz, 1H), 1.68 (s, 3H), 1.49 (s, 3H). **¹³C NMR (100 MHz, CDCl₃):** δ 198.8 (C), 139.5 (C), 139.2 (C), 135.3 (C), 132.6 (C), 130.2 (2 CH), 129.0 (2CH), 128.9 (2CH), 128.3 (2CH), 127.2 (CH), 123.8 (CH), 52.9 (CH), 34.0 (CH₂), 26.0 (CH₂), 25.8 (CH₃), 17.8 (CH₃). **FT-IR (neat, cm⁻¹):** 3061, 3026, 2963, 2923, 1682, 1587, 1570, 1489, 1399, 1259, 1174, 1093, 1013, 815, 757, 700. **HRMS (ESI⁺):** *m/z* calcd. for C₂₀H₂₁ONa [M+Na]⁺ 335.1161 found, 335.1173.

6-Methyl-1-(naphthalen-2-yl)-2-phenylhept-5-en-1-one **1m**



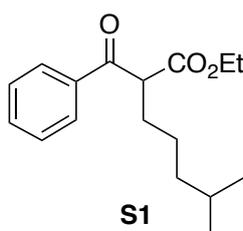
The general procedure **A** was followed with 5-bromo-2-methylpent-2-ene (1.27 g, 7.8 mmol), 2-1-(naphthalen-2-yl)-2-phenylethan-1-one (1.6 g, 6.5 mmol) and *t*BuOK as base. Purification by FC (SiO₂, Cy/EtOAc, 100/0 to 97/3) afforded **1m** as a clear oil (595 mg, 1.81 mmol, 28%). **¹H NMR (300 MHz, CDCl₃):** δ 8.55 (s, 1H), 8.08 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.98-7.91 (m, 1H), 7.87-7.80 (m, 2H), 7.60-7.49 (m, 2H), 7.46-7.41 (m, 2H), 7.37-7.30 (m, 2H), 7.26-7.19 (m, 1H), 5.22 (ddd, *J* = 7.3, 5.8, 1.4, 1H), 4.81 (t, *J* = 7.1 Hz, 1H), 2.40 (dt, *J* = 13.7, 7.3 Hz, 1H), 2.15-2.04 (m, 2H), 2.05-1.93 (m, 1H), 1.73 (s, 3H), 1.54 (s, 3H). **¹³C NMR (90 MHz, CDCl₃):** δ 200.1 (C), 139.9 (C), 135.5 (C), 134.4 (C), 132.6 (C), 130.4 (C), 129.7 (CH), 128.9 (2CH), 128.4 (2CH), 127.8 (CH), 127.0 (CH), 126.7 (CH), 124.6 (CH), 124.0 (CH), 52.9 (CH), 34.1 (CH₂), 26.1 (CH₂), 25.8 (CH₃), 17.8 (CH₃). **FT-IR (neat, cm⁻¹):** 3060, 3026, 2964, 2924, 2856, 1674, 1627, 1598, 1452, 1276, 1173, 1124. **HRMS (ESI⁺):** *m/z* calcd. for C₂₄H₂₄ONa [M+Na]⁺ 351.1704, found 351.1719.

1,2-bis(4-methoxyphenyl)-6-methylhept-5-en-1-one **1n**



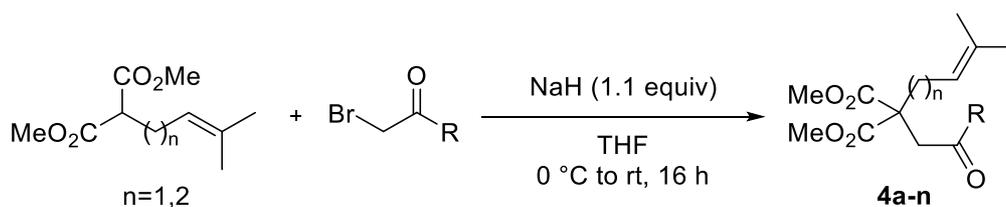
The general procedure **A** was followed with 5-bromo-2-methylpent-2-ene (392 mg, 2.40 mmol), 4'-methoxy-2-(4-methoxyphenyl)acetophenone (400 mg, 1.56 mmol) and *t*BuOK as base. Purification by FC (SiO₂, Cy/EtOAc, 100/0 to 97/3) afforded **1n** as a clear oil (400 mg, 1.18 mmol, 76%). ¹H NMR (300 MHz, CDCl₃): δ 7.95 (d, *J* = 9.0 Hz, 2H), 7.21 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 9.0 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 5.15-5.08 (m, 1H), 4.47 (t, *J* = 7.2 Hz, 1H), 3.82 (s, 3H), 3.75 (s, 3H), 2.28-2.14 (m, 1H), 2.00-1.90 (m, 2H), 1.88-1.75 (m, 1H), 1.67 (s, 3H), 1.48 (s, 3H). These data correspond to those previously reported in the literature.³

Ethyl 2-benzoyl-6-methylheptanoate **S1**



The general procedure **A** was followed with 5-bromo-2-methylpentane (510 mg, 3.02 mmol), ethyl 3-oxo-3-phenylpropanoate (776 mg, 3.63 mmol) and K₂CO₃ as base. Purification by FC (SiO₂, Cy/EtOAc, 100/0 to 95/5) afforded **S1** as a clear oil (729 mg, 2.64 mmol, 87%). ¹H NMR (300 MHz, CDCl₃): δ 7.95 (d, *J* = 7.4 Hz, 2H), 7.57-7.47 (m, 1H), 7.46-7.37 (m, 2H), 4.26 (t, *J* = 7.1 Hz, 1H), 4.09 (q, *J* = 6.7 Hz, 2H), 2.00-1.88 (m, 2H), 1.49 (sept, *J* = 6.6 Hz, 1H), 1.40-1.25 (m, 2H), 1.23-1.07 (m, 4H), 0.80 (d, *J* = 6.6 Hz, 6H). ¹³C NMR (75 MHz, CDCl₃): δ 195.3 (C), 170.1 (C), 136.3 (C), 133.4 (CH), 128.7 (2CH), 128.6 (2CH), 61.3 (CH), 54.4 (CH₂), 38.6 (CH₃), 29.2 (CH₂), 27.7 (CH₂), 25.4 (CH₂), 22.5 (2CH₃), 14.0 (CH). HRMS (ESI⁺): *m/z* calcd. for C₁₇H₂₅O₃ [M+H]⁺ 277.1798, found 277.1789.

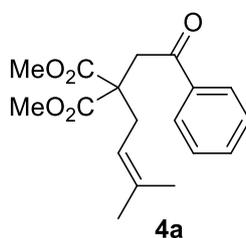
4.3 General Procedure (B) for the Synthesis of Starting Materials 4a-n



To a three-neck round-bottom flask equipped with an addition funnel was added NaH (1.1 equiv) followed by THF (0.1 M) under argon. The resulting suspension was then cooled to 0 °C and a solution of dimethyl 2-(3-methylbut-2-en-1-yl)malonate or dimethyl 2-(4-methylpent-3-en-1-yl)malonate (1.0 equiv) in THF (0.5 M) was added dropwise over 20 min. The cooling bath was removed and the reaction mixture was allowed to warm to rt over 45 min. A solution of starting bromo-ketone (1.1 equiv) in THF (0.6 M) was rapidly added and the resulting orange-red mixture was stirred at rt for 16 h. The mixture was carefully poured into 75 mL of 1M hydrochloric acid, and the resulting mixture was stirred for 10 min and extracted twice with EtOAc. The combined organic extracts were dried over MgSO₄ and concentrated under reduced pressure. Purification by FC (SiO₂, Cy/EtOAc, 100/0 to 95/5) afforded the desired product **4a-n**.

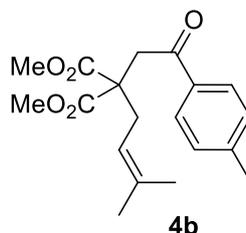
4.4 Characterization of Starting Materials 4a-o

Dimethyl 2-(3-methylbut-2-en-1-yl)-2-(2-oxo-2-phenylethyl)malonate 4a



The general procedure **B** was followed with 1,3-dimethyl 2-(3-methylbut-2-en-1-yl)propanedioate (700 mg, 3.50 mmol) and 2-bromoacetophenone (765 mg, 3.85 mmol) to afford **4a** as a clear oil (533 mg, 1.67 mmol, 48%). ¹H NMR (360 MHz, CDCl₃): δ 7.90-7.85 (m, 2H), 7.51-7.45 (m, 1H), 7.41-7.34 (m, 2H), 4.88 (t, *J* = 7.3, 1H), 3.66 (s, 6H), 3.60 (s, 2H), 2.78 (d, *J* = 7.8 Hz, 2H), 1.54 (s, 3H), 1.34 (s, 3H). ¹³C NMR (90 MHz, CDCl₃): δ 196.8 (C), 171.0 (2C), 136.4 (C), 133.2 (CH), 128.5 (2CH), 127.8 (2CH), 117.9 (CH), 55.3 (C), 52.5 (2CH₃), 40.9 (CH₂), 31.6 (CH₂), 25.8 (CH₃), 17.6 (CH₃). FT-IR (neat, cm⁻¹): 3059, 2952, 2928, 2860, 1738, 1689, 1597, 1581, 1449, 1435, 1356, 1290, 1197, 1064, 1002. HRMS (ESI⁺): *m/z* calcd. for C₁₈H₂₂O₅Na [M+Na]⁺ 341.1351, found 341.1359.

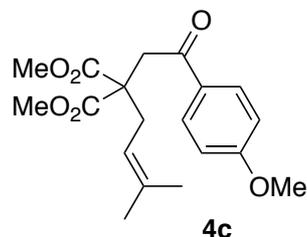
Dimethyl 2-(3-methylbut-2-en-1-yl)-2-(2-oxo-2-(p-tolyl)ethyl)malonate 4b



The general procedure **B** was followed with 1,3-dimethyl 2-(3-methylbut-2-en-1-yl)propanedioate (600 mg, 3.00 mmol) and 2-bromo-4'-methylacetophenone (702 mg, 3.30 mmol) to afford **4b** as a clear oil (500 mg, 1.50 mmol, 50%). ¹H NMR (360 MHz, CDCl₃): δ 7.83 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 4.95-4.87

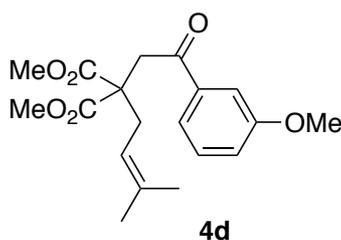
(m, 1H), 3.71 (s, 6H), 3.61 (s, 2H), 2.81 (d, $J = 7.8$ Hz, 2H), 2.37 (s, 3H), 1.59 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (90 MHz, CDCl_3): δ 196.5 (C), 171.3 (2C), 144.1 (C), 136.5 (C), 134.1 (C), 129.2 (2CH), 128.1 (2CH), 118.0 (CH), 55.4 (C), 52.7 (2CH₃), 40.9 (CH₂), 31.7 (CH₂), 25.9 (CH₃), 25.6 (CH₃), 17.7 (CH₃). FT-IR (neat, cm^{-1}): 2952, 2926, 1737, 1684, 1607, 1572, 1435, 1407, 1354, 1289, 1257, 1225, 1179, 1066. HRMS (ESI⁺): m/z calcd. for $\text{C}_{19}\text{H}_{24}\text{O}_5\text{Na}$ $[\text{M}+\text{Na}]^+$ 355.1523, found 355.1515.

Dimethyl 2-(2-(4-methoxyphenyl)-2-oxoethyl)-2-(3-methylbut-2-en-1-yl)malonate 4c



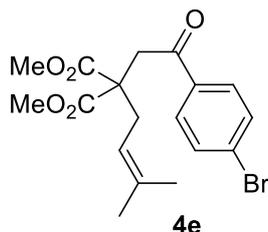
The general procedure **B** was followed with 1,3-dimethyl 2-(3-methylbut-2-en-1-yl)propanedioate (488 mg, 2.44 mmol) and 2-bromo-4'-methoxyacetophenone (614 mg, 2.68 mmol) to afford **4c** as a clear oil (105.6 mg, 0.30 mmol, 12%). ^1H NMR (300 MHz, CDCl_3): δ 7.92 (d, $J = 8.9$ Hz, 2H), 6.90 (d, $J = 8.9$ Hz, 2H), 4.91 (t, $J = 7.8$ Hz, 1H), 3.84 (s, 3H), 3.72 (s, 6H), 3.59 (s, 2H), 2.81 (d, $J = 7.8$ Hz, 2H), 1.60 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 195.5 (C), 171.5 (2C), 163.7 (C), 136.6 (C), 130.4 (2CH), 129.7 (C), 118.1 (CH), 113.8 (2CH), 55.5 (CH₃), 55.5 (C) 52.8 (2CH₃), 40.7 (CH₂), 31.8 (CH₂), 26.0 (CH₃), 17.8 (CH₃). FT-IR (neat, cm^{-1}): 2953, 2842, 1735, 1677, 1601, 1576, 1511, 1434, 1355, 1290, 1259, 1224, 1170, 1028. HRMS (ESI⁺): m/z calcd. for $\text{C}_{19}\text{H}_{24}\text{O}_6\text{Na}$ $[\text{M}+\text{Na}]^+$ 371.1573, found 371.1452.

Dimethyl 2-(2-(3-methoxyphenyl)-2-oxoethyl)-2-(3-methylbut-2-en-1-yl)malonate 4d



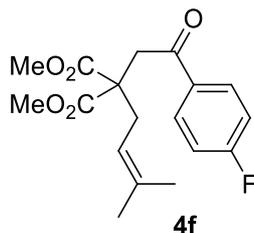
The general procedure **B** was followed with 1,3-dimethyl 2-(3-methylbut-2-en-1-yl)propanedioate (600 mg, 3.00 mmol) and 2-bromo-3'-methoxyacetophenone (755 mg, 3.30 mmol) to afford **4d** as a clear oil (489 mg, 1.40 mmol, 47%). ^1H NMR (300 MHz, CDCl_3): δ 7.48-7.43 (m, 1H), 7.37 (dd, $J = 2.5, 1.5$ Hz, 1H), 7.27 (t, $J = 7.9$ Hz, 1H), 7.02 (ddd, $J = 7.9, 2.5, 0.9$ Hz, 1H), 4.86 (t, $J = 7.8$ Hz, 1H), 3.74 (s, 3H), 3.65 (s, 6H), 3.56 (s, 2H), 2.75 (d, $J = 7.8$ Hz, 2H), 1.54 (s, 3H), 1.34 (s, 3H). ^{13}C NMR (90 MHz, CDCl_3): δ 196.9 (C), 171.3 (2C), 159.9 (C), 137.9 (C), 136.8 (C), 129.7 (CH), 120.8 (CH), 120.1 (CH), 118.0 (CH), 112.1 (CH), 55.5 (C + CH₃), 52.8 (2CH₃), 41.3 (CH₂), 31.9 (CH₂), 26.3 (CH₃), 17.9 (CH₃). FT-IR (neat, cm^{-1}): 3064, 2954, 1734, 1689, 1597, 1485, 1454, 1378, 1352, 1196, 1116, 1055, 1023. HRMS (ESI⁺): m/z calcd. for $\text{C}_{19}\text{H}_{24}\text{O}_6\text{Na}$ $[\text{M}+\text{Na}]^+$ 371.1448, found 371.1465.

Dimethyl 2-(2-(4-bromophenyl)-2-oxoethyl)-2-(3-methylbut-2-en-1-yl)malonate 4e



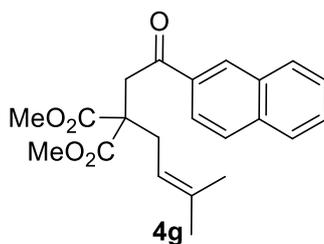
The general procedure **B** was followed with 1,3-dimethyl 2-(3-methylbut-2-en-1-yl)propanedioate (600 mg, 3.00 mmol) and 2,4'-dibromoacetophenone (1 g, 3.60 mmol) to afford **4e** as a clear oil (503 mg, 1.26 mmol, 42%). **¹H NMR (360 MHz, CDCl₃):** δ 7.73 (d, J = 8.6 Hz, 2H), 7.50 (d, J = 8.6 Hz, 2H), 4.85 (t, J = 7.8 Hz, 1H), 3.65 (s, 6H), 3.53 (s, 2H), 2.74 (d, J = 7.8 Hz, 2H), 1.53 (s, 3H), 1.33 (s, 3H). **¹³C NMR (63 MHz, CDCl₃):** δ 195.9 (C), 170.9 (2C), 136.5 (C), 135.2 (C), 131.8 (2CH), 129.4 (2CH), 128.4 (C), 117.9 (CH), 55.3 (C), 52.6 (2 CH₃), 40.9 (CH₂), 37.1 (CH₂), 25.8 (CH₃), 17.6 (CH₃). **FT-IR (neat, cm⁻¹):** 3091, 2976, 2951, 2855, 1751, 1698, 1585, 1568, 1455, 1399, 1353, 1256, 1174, 1108, 1004. **HRMS (ESI⁺):** m/z calcd. for C₁₈H₂₁O₅BrNa [M+Na]⁺ 419.0464, found 419.0446.

Dimethyl 2-(2-(4-fluorophenyl)-2-oxoethyl)-2-(3-methylbut-2-en-1-yl)malonate 4f



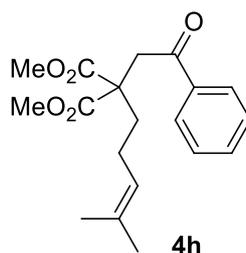
The general procedure **B** was followed with 1,3-dimethyl 2-(3-methylbut-2-en-1-yl)propanedioate (600 mg, 3.00 mmol) and 2-bromo-4'-fluoroacetophenone (780 mg, 3.60 mmol) to afford **4f** as a clear oil (626 mg, 1.86 mmol, 62%). **¹H NMR (360 MHz, CDCl₃):** δ 7.93-7.86 (m, 2H), 7.06-6.99 (m, 2H), 4.85 (t, J = 7.8 Hz, 1H), 3.64 (s, 6H), 3.54 (s, 2H), 2.74 (d, J = 7.7 Hz, 2H), 1.51 (s, 3H), 1.32 (s, 3H). **¹³C NMR (63 MHz, CDCl₃):** δ 195.2 (C), 171.0 (2 C), 165.7 (d, J^{CF} = 255 Hz, C), 136.4 (C), 132.9 (d, J^{CF} = 1.5 Hz, C), 130.6 (d, J^{CF} = 9.6 Hz, 2CH), 117.9 (CH), 115.6 (d, J^{CF} = 21.1 Hz, 2 CH), 55.3 (C), 52.5 (2CH₃), 40.8 (CH₂), 31.7 (CH₂), 25.7 (CH₃), 17.5 (CH₃). **¹⁹F NMR (235 MHz, CDCl₃):** δ -104.8. **FT-IR (neat, cm⁻¹):** 3074, 2975, 2953, 2863, 1750, 1690, 1599, 1507, 1436, 1353, 1291, 1207, 1115, 1066, 1005. **HRMS (ESI⁺):** m/z calcd. for C₁₈H₂₁O₅FNa [M+Na]⁺ 359.1265, found 359.1258

Dimethyl 2-(3-methylbut-2-en-1-yl)-2-(2-(naphthalen-2-yl)-2-oxoethyl)malonate 4g



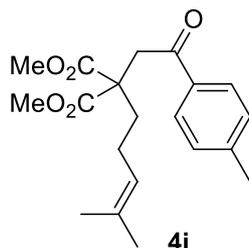
The general procedure **B** was followed with 1,3-dimethyl 2-(3-methylbut-2-en-1-yl)propanedioate (600 mg, 3.00 mmol) and 2-bromo-1-(naphthalen-2-yl)ethenone (821 mg, 3.30 mmol) to afford **4g** as a clear oil (624 mg, 1.69 mmol, 57%). **¹H NMR (300 MHz, CDCl₃):** δ 8.45 (s, 1H), 7.97 (dd, J = 8.6, 1.7 Hz, 1H), 7.90 (d, J = 7.6 Hz, 1H), 7.85-7.77 (m, 2H), 7.57-7.45 (m, 2H), 4.99 (t, J = 7.8 Hz, 1H), 3.81 (s, 2H), 3.74 (s, 6H), 2.90 (d, J = 7.8 Hz, 2H), 1.58 (s, 3H), 1.39 (s, 3H). **¹³C NMR (90 MHz, CDCl₃):** δ 196.7 (C), 171.1 (2C), 136.5 (C), 135.5 (C), 133.7 (C), 132.3 (C), 129.7 (CH), 129.5 (CH), 128.5 (CH), 128.3 (CH), 127.6 (CH), 126.7 (CH), 123.4 (CH), 117.9 (CH), 55.4 (C), 52.6 (2CH₃), 40.9 (CH₂), 31.7 (CH₂), 25.8 (CH₃), 17.6 (CH₃). **FT-IR (neat, cm⁻¹):** 3058, 2951, 2860, 1734, 1627, 1596, 1507, 1436, 1361, 1198, 1073, 1023. **HRMS (ESI⁺):** m/z calcd. for C₂₂H₂₄O₅Na [M+Na]⁺ 391.1501, found 391.1515.

Dimethyl 2-(4-methylpent-3-en-1-yl)-2-(2-oxo-2-phenylethyl)malonate 4h



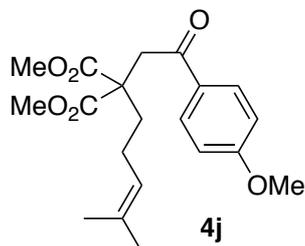
The general procedure **B** was followed with 1,3-dimethyl 2-(4-methylpent-3-en-1-yl)propanedioate (700 mg, 3.27 mmol) and 2-bromoacetophenone (715 mg, 3.59 mmol) to afford **4h** as a clear oil (364 mg, 1.10 mmol, 34%). **¹H NMR (300 MHz, CDCl₃):** δ 7.91 (dd, J = 8.3, 1.2 Hz, 2H), 7.55-7.45 (m, 1H), 7.44-7.35 (m, 2H), 4.95 (tdd, J = 4.0, 2.6, 1.2 Hz, 1H), 3.67 (s, 6H), 3.66 (s, 2H), 2.14-2.06 (m, 2H), 1.87 (dd, J = 15.8, 7.3 Hz, 2H), 1.51 (s, 3H), 1.46 (s, 3H). **¹³C NMR (90 MHz, CDCl₃):** δ 196.5 (C), 171.3 (2C), 136.4 (C), 133.3 (CH), 132.4 (C), 128.5 (2CH), 127.9 (2CH), 122.9 (CH), 55.1 (C), 52.5 (2CH₃), 41.4 (CH₂), 33.1 (CH₂), 25.4 (CH₂), 23.4 (CH₃), 17.4 (CH₃). **FT-IR (neat, cm⁻¹):** 3059, 2953, 2928, 2857, 1734, 1689, 1597, 1581, 1449, 1435, 1356, 1272, 1219, 1072, 1002. **HRMS (ESI⁺):** m/z calcd. for C₁₉H₂₄O₅Na [M+Na]⁺ 355.1505, found 355.1515.

Dimethyl 2-(4-methylpent-3-en-1-yl)-2-(2-oxo-2-(p-tolyl)ethyl)malonate 4i



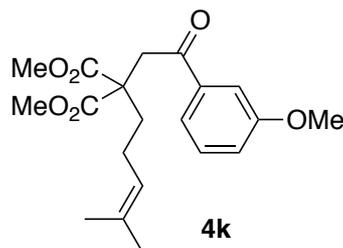
The general procedure **B** was followed with 1,3-dimethyl 2-(4-methylpent-3-en-1-yl)propanedioate (600 mg, 2.80 mmol) and 2-bromo-4'-methylacetophenone (656 mg, 3.08 mmol) to afford **4i** as clear oil (644 mg, 1.86 mmol, 66%). **¹H NMR (360 MHz, CDCl₃):** δ 7.80 (d, $J = 8.2$ Hz, 2H), 7.17 (d, $J = 8.2$ Hz, 2H), 4.98-4.89 (m, 1H), 3.65 (s, 6H), 3.64 (s, 2H), 2.31 (s, 3H), 2.12-2.03 (m, 2H), 1.85 (dd, $J = 15.9, 7.3$ Hz, 2H), 1.50 (s, 3H), 1.45 (s, 3H). **¹³C NMR (90 MHz, CDCl₃):** δ 195.8 (C), 171.2 (2C), 143.9 (C), 133.9 (C), 132.2 (C), 129.1 (2CH), 127.9 (2CH), 122.9 (CH), 54.9 (C), 52.3 (2CH₃), 41.2 (C), 33.0 (CH₂), 25.3 (CH₂), 23.3 (CH₃), 21.3 (CH₃), 17.3 (CH₃). **FT-IR (neat, cm⁻¹):** 2953, 2926, 2731, 1735, 1685, 1607, 1573, 1434, 1408, 1353, 1271, 1222, 1179, 1070. **HRMS (ESI⁺):** m/z calcd. for C₂₀H₂₆O₅Na [M+Na]⁺ 369.1668, found 369.1672.

Dimethyl 2-(2-(4-methoxyphenyl)-2-oxoethyl)-2-(4-methylpent-3-en-1-yl)malonate 4j



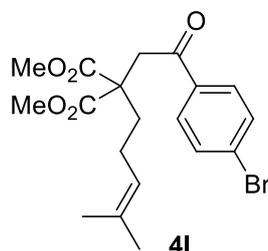
The general procedure **B** was followed with 1,3-dimethyl 2-(4-methylpent-3-en-1-yl)propanedioate (600 mg, 2.80 mmol) and 2-bromo-4'-methoxyacetophenone (706 mg, 3.08 mmol) to afford **4j** as a clear oil (271 mg, 0.75 mmol, 27%). **¹H NMR (300 MHz, CDCl₃):** δ 7.89 (d, $J = 8.9$ Hz, 2H), 6.87 (d, $J = 8.9$ Hz, 2H), 4.95 (t, $J = 7.0$ Hz, 1H), 3.79 (s, 3H), 3.67 (s, 6H), 3.63 (s, 2H), 2.11-2.04 (m, 2H), 1.85 (dd, $J = 15.5, 7.0$ Hz, 2H), 1.52 (s, 3H), 1.46 (s, 3H). **¹³C NMR (75 MHz, CDCl₃):** δ 195.0 (C), 171.5 (2C), 163.6 (C), 132.4 (C), 130.2 (2CH), 129.5 (C), 123.0 (CH), 113.7 (2CH), 55.5 (CH₃), 55.1 (C), 52.5 (2CH₃), 41.0 (CH₂), 33.1 (CH₂), 25.5 (CH₂), 23.4 (CH₃), 17.4 (CH₃). **FT-IR (neat, cm⁻¹):** 3054, 2953, 2843, 1739, 1681, 1601, 1576, 1511, 1436, 1421, 1375, 1236, 1112, 1028. **HRMS (ESI⁺):** m/z calcd. for C₂₀H₂₆O₆Na [M+Na]⁺ 385.1729, found 391.1608.

Dimethyl 2-(2-(3-methoxyphenyl)-2-oxoethyl)-2-(4-methylpent-3-en-1-yl)malonate 4k



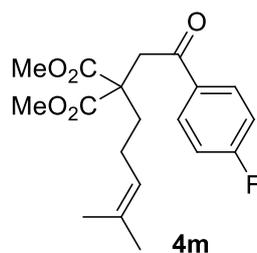
The general procedure **B** was followed with 1,3-dimethyl 2-(4-methylpent-3-en-1-yl)propanedioate (600 mg, 2.80 mmol) and 2-bromo-3'-methoxyacetophenone (705 mg, 3.08 mmol) to afford **4k** as a clear oil (367 mg, 1.01 mmol, 36%). **¹H NMR (300 MHz, CDCl₃):** δ 7.53-7.48 (m, 1H), 7.42 (dd, $J = 2.5, 1.6$ Hz, 1H), 7.31 (t, $J = 7.9$ Hz, 1H), 7.05 (ddd, $J = 7.9, 2.5, 0.7$ Hz, 1H), 4.95 (t, $J = 7.4$ Hz, 1H), 3.77 (s, 3H), 3.68 (s, 6H), 3.66 (s, 2H), 2.13-2.04 (m, 2H), 1.86 (dd, $J = 15.9, 7.4$ Hz, 2H), 1.52 (s, 3H), 1.47 (s, 3H). **¹³C NMR (90 MHz, CDCl₃):** δ 196.6 (C), 171.6 (2C), 159.9 (C), 137.9 (C), 132.8 (C), 129.7 (CH), 123.1 (CH), 120.8 (CH), 120.2 (CH), 112.1 (CH), 55.5 (CH₃), 55.3 (C), 52.8 (2CH₃), 41.7 (CH₂), 33.3 (CH₂), 25.7 (CH₂), 23.6 (CH₃), 17.7 (CH₃). **FT-IR (neat, cm⁻¹):** 3074, 2953, 2875, 1738, 1689, 1597, 1583, 1486, 1450, 1352, 1263, 1071, 1026. **HRMS (ESI⁺):** m/z calcd. for C₂₀H₂₆O₆Na [M+Na]⁺ 385.1605, found 385.1621.

Dimethyl 2-(2-(4-bromophenyl)-2-oxoethyl)-2-(4-methylpent-3-en-1-yl)malonate 4l



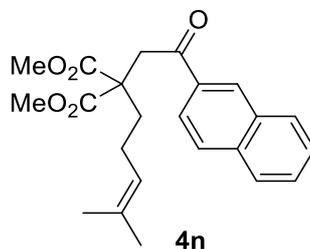
The general procedure **B** was followed with 1,3-dimethyl 2-(4-methylpent-3-en-1-yl)propanedioate (600 mg, 2.80 mmol) and 2,4-dibromoacetophenone (934 mg, 3.36 mmol) to afford **4l** as a clear oil (711 mg, 1.73 mmol, 62%). **¹H NMR (360 MHz, CDCl₃):** δ 7.83 (d, $J = 8.5$ Hz, 2H), 7.61 (d, $J = 8.5$ Hz, 2H), 5.00 (t, $J = 7.0$ Hz, 1H), 3.74 (s, 6H), 3.66 (s, 2H), 2.17-2.09 (m, 2H), 1.90 (dd, $J = 16.0, 7.0$ Hz, 2H), 1.59 (s, 3H), 1.53 (s, 3H). **¹³C NMR (63 MHz, CDCl₃):** δ 195.3 (C), 170.9 (2C), 135.1 (C), 132.3 (C), 131.7 (2CH), 129.3 (2CH), 128.2 (C), 122.9 (CH), 55.0 (C), 52.4 (2CH₃), 41.2 (CH₂), 33.1 (CH₂), 25.3 (CH₃), 23.3 (CH₂), 17.3 (CH₃). **FT-IR (neat, cm⁻¹):** 3060, 2952, 2927, 2857, 1743, 1691, 1586, 1434, 1397, 1354, 1271, 1208, 1070, 1001. **HRMS (ESI⁺):** m/z calcd. for C₁₉H₂₃O₅BrNa [M+Na]⁺ 433.0600, found 433.0621.

Dimethyl 2-(2-(4-fluorophenyl)-2-oxoethyl)-2-(4-methylpent-3-en-1-yl)malonate 4m



The general procedure **B** was followed with 1,3-dimethyl 2-(4-methylpent-3-en-1-yl)propanedioate (600 mg, 2.80 mmol) and 2-bromo-4'-fluoroacetophenone (729 mg, 3.36 mmol) to afford **4m** as a clear oil (607 mg, 1.73 mmol, 62%). **¹H NMR (360 MHz, CDCl₃):** δ 7.91 (dd, $J = 8.9, 5.4$ Hz, 2H), 7.03 (t ap, $J = 8.9$ Hz, 2H), 4.90 (t, $J = 7.1$ Hz, 1H), 3.63 (s, 6H), 3.61 (s, 2H), 2.08-2.00 (m, 2H), 1.83 (dd, $J = 15.9, 7.1$ Hz, 2H), 1.47 (s, 3H), 1.42 (s, 3H). **¹³C NMR (63 MHz, CDCl₃):** δ 194.9 (C), 171.1 (2C), 165.7 (d, $J^{CF} = 255$ Hz, C), 132.9 (C), 132.4 (C), 130.6 (d, $J^{CF} = 9.1$ Hz, 2CH), 122.9 (CH), 115.4 (d, $J^{CF} = 22.0$ Hz, 2CH), 55.1 (C), 52.4 (2CH₃), 41.3 (C), 33.1 (CH₂), 25.3 (CH₃), 23.4 (CH₂), 17.3 (CH₃). **¹⁹F NMR (235 MHz, CDCl₃):** δ -104.8. **FT-IR (neat, cm⁻¹):** 3075, 2953, 2929, 2858, 1737, 1691, 1598, 1507, 1435, 1410, 1354, 1209, 1158, 1069, 1003. **HRMS (ESI⁺):** m/z calcd. for C₁₉H₂₃O₅FNa [M+Na]⁺ 373.1421, found 373.1409.

Dimethyl 2-(4-methylpent-3-en-1-yl)-2-(2-(naphthalen-2-yl)-2-oxoethyl)malonate 4n



The general procedure **B** was followed with 1,3-dimethyl 2-(4-methylpent-3-en-1-yl)propanedioate (600 mg, 2.80 mmol) and bromomethyl 2-naphthyl ketone (767 mg, 3.08 mmol) to afford **4n** as a clear oil (589 mg, 1.54 mmol, 55%). **¹H NMR (360 MHz, CDCl₃):** δ 8.49 (s, 1H), 8.00 (dd, $J = 8.6, 1.7$ Hz, 1H), 7.93 (d, $J = 7.8$ Hz, 1H), 7.83 (t, $J = 8.6$ Hz, 2H), 7.58-7.48 (m, 2H), 5.02 (t, $J = 7.1$ Hz, 1H), 3.88 (s, 2H), 3.75 (s, 6H), 2.25-2.16 (m, 2H), 1.96 (dd, $J = 15.9, 7.1$ Hz, 2H), 1.56 (s, 3H), 1.52 (s, 3H). **¹³C NMR (90 MHz, CDCl₃):** δ 196.5 (C), 171.5 (2C), 135.6 (C), 133.8 (C), 132.6 (C), 132.4 (C), 129.7 (CH), 129.5 (CH), 128.6 (CH), 128.4 (CH), 127.7 (CH), 126.8 (CH), 123.5 (CH), 123.0 (CH), 55.3 (C), 52.6 (2CH₃), 41.5 (CH₂), 33.2 (CH₂), 25.5 (CH₃), 23.5 (CH₂), 17.5 (CH₃). **FT-IR (neat, cm⁻¹):** 3058, 2951, 2860, 1730, 1689, 1627, 1596, 1578, 1436, 1360, 1201, 1067, 1000. **HRMS (ESI⁺):** m/z calcd. for C₂₃H₂₆O₅Na [M+Na]⁺ 405.1657, found 405.1672.

5 Catalytic Reactions

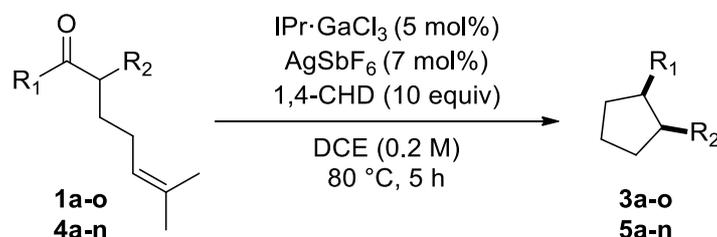
5.1 Experimental Procedure (C) for the Hydrogenative Ring Closing Carbonyl-Olefin Metathesis (Table 1)

The catalyst (5 mol%), dry solvent (0.2 M) and ethyl 2-benzoyl-6-methylhept-5-enoate **1a** (50 mg, 0.18 mmol, 1 equiv) were charged in a 10 mL tube equipped with a Teflon-coated magnetic stir bar, under argon. The hydrogen donor (173.8 μ l, 1.82 mmol, 10 equiv) was added to this solution and the resulting mixture was stirred in a preheated oil bath at 80 °C for 5 h. The reaction mixture was diluted with Et₂O, filtered through a pad of celite (thoroughly rinsed with Et₂O) and concentrated under reduced pressure by rotary evaporation. Purification by FC over silica gel (pentane/Et₂O, 100/0 to 96/4) afforded **3a** as a clear oil. The *cis/trans* diastereomeric ratio was determined by ¹H NMR analysis of the crude reaction mixture.

5.2 Scale-up

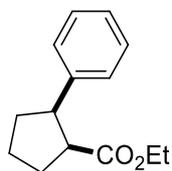
The general procedure C was followed with **1a** (500 mg, 1.82 mmol, 1 equiv), IPr·GaCl₃ (51.4 mg, 0.09 mmol, 5 mol%), AgSbF₆ (43.8 mg, 0.09 mmol, 7 mol%) and 1,4-cyclohexadiene (1.74 mL, 18.22 mmol, 10 equiv) in 1,2-DCE (12 mL). Purification by FC (SiO₂, pentane/Et₂O, 100/0 to 96/4) afforded **3a** (270 mg, 68%) as a clear oil.

5.3 Experimental Procedure (D) for the Hydrogenative Carbonyl-Olefin Metathesis (Schemes 2 and 3) and Characterization of Products 3a-o and 5a-n.



IPr·GaCl₃ (5 mol%) and AgSbF₆ (7 mol%) were charged in a 10 mL tube equipped with a Teflon-coated magnetic stir bar in the glovebox. Dry 1,2-DCE (0.2 M) was added and the mixture was stirred at rt for 10 min; then was added starting material **1a-o** or **4a-n** (0.10 mmol). The 1,4-CHD (10 equiv) was finally added and the resulting mixture was stirred for 5 h in a preheated oil bath at 80 °C, unless otherwise specified. The reaction mixture was diluted with Et₂O, filtered through a pad of celite (thoroughly rinsed with Et₂O) and concentrated under reduced pressure by rotary evaporation. Purification by FC over silica gel (pentane/Et₂O) afforded desired product **3a-n** and **5a-n**. For **3a-n**, the *cis/trans* diastereomeric ratio was determined by ¹H NMR analysis of the crude reaction mixture.

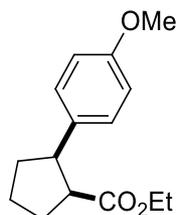
cis-Ethyl 2-phenylcyclopentanecarboxylate **3a**



3a

The general procedure **D** was followed with **1a** (80 mg, 0.30 mmol). Purification by FC (SiO₂, pentane/Et₂O, 100/0 to 96/4) afforded **3a** as a clear oil (43.1 mg, 0.20 mmol, 68%, *dr* = 5/1). **¹H NMR (360 MHz, CDCl₃): (major isomer) δ** 7.60-7.41 (m, 5H), 4.06-3.85 (m, 2H), 3.70 (dt, *J* = 16.4, 8.3 Hz, 1H), 3.46-3.38 (m, 1H), 2.49-2.20 (m, 6H), 1.10 (t, *J* = 7.2 Hz, 3H); **(minor isomer) δ** 7.60-7.41 (m, 5H), 4.34 (q, *J* = 7.1 Hz, 2H), 3.70 (dt, *J* = 16.4, 8.3 Hz, 1H), 3.09 (dd, *J* = 17.8, 8.3 Hz, 1H), 2.05-1.93 (m, 6H), 1.43 (t, *J* = 7.1 Hz, 3H). **¹³C NMR (63 MHz, C₆D₆): (major isomer) δ** 174.1 (C=O), 141.4 (C), 127.7 (2CH), 127.6 (2CH), 126.0 (CH), 59.3 (CH₂), 49.3 (CH), 48.9 (CH), 31.0 (CH₂), 28.3 (CH₂), 24.5 (CH₂), 13.4 (CH₃); **(minor isomer) δ** 174.1 (C=O), 138.8 (C), 128.0 (2CH), 126.9 (2CH), 126.0 (CH), 59.8 (CH₂), 51.8 (CH), 49.6 (CH), 34.7 (CH₂), 30.4 (CH₂), 24.7 (CH₂), 13.9 (CH₃). **HRMS (ESI⁺):** *m/z* calcd. for C₁₄H₁₈O₂Na [M+Na]⁺ 241.1194, found 241.1199. Spectroscopic data for **3a** match those previously reported in literature for *cis*-methyl-2-phenylcyclopentane-carboxylate.⁵

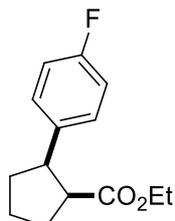
cis-Ethyl 2-(4-methoxyphenyl)cyclopentanecarboxylate **3b**



3b

The general procedure **D** was followed with **1b** (80 mg, 0.26 mmol). Purification by FC (SiO₂, PE/Et₂O, 100/0 to 94/6) afforded **3b** as a clear oil (34.4 mg, 0.14 mmol, 53%, *dr* = 4/1). **¹H NMR (300 MHz, C₆D₆): (major isomer) δ** 7.15 (d, *J* = 8.8 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 3.69 (q, *J* = 7.2 Hz, 2H), 3.34 (s, 3H), 3.18-3.07 (m, 1H), 3.03-2.95 (m, 1H), 2.29-2.07 (m, 2H), 2.00-1.69 (m, 3H), 1.51-1.36 (m, 1H), 0.71 (t, *J* = 7.2 Hz, 3H); **(minor isomer) δ** 7.15 (d, *J* = 8.8 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 3.92 (q, *J* = 7.1 Hz, 2H), 3.33 (s, 3H), 3.16 – 3.08 (m, 1H), 2.79 (dt, *J* = 9.8, 8.9 Hz, 2H), 2.28 – 2.07 (m, 2H), 2.00-1.69 (m, 3H), 1.51 – 1.37 (m, 1H), 0.88 (t, *J* = 7.1 Hz, 3H). **¹³C NMR (90 MHz, C₆D₆): (major isomer) δ** 174.2 (C=O), 158.8 (C), 134.0 (C), 129.4 (2CH), 113.7 (2CH), 59.6 (CH₂), 54.7 (CH₃), 49.9 (CH), 48.8 (CH), 31.8 (CH₂), 28.2 (CH₂), 25.0 (CH₂), 14.0 (CH₃), **(minor isomer) δ** 174.2 (C=O), 158.8 (C), 134.0 (C), 128.5 (2CH), 114.2 (2CH), 60.1 (CH₂), 54.7 (CH₃), 52.6 (CH), 49.7 (CH), 30.9 (CH₂), 30.4 (CH₂), 25.1 (CH₂), 14.2 (CH₃). **HRMS (ESI⁺):** *m/z* calcd. for C₁₅H₂₀O₃Na [M+Na]⁺ 271.1298, found 271.1305.

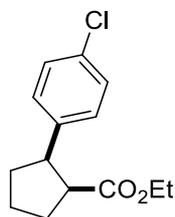
cis-Ethyl 2-(4-fluorophenyl)cyclopentanecarboxylate **3c**



3c

The general procedure **D** was followed, in HFIP instead of 1,2-DCE, with **1c** (40 mg, 0.14 mmol). Purification by FC (SiO₂, PE/Et₂O, 100/0 to 98/2) afforded **3c** as a clear oil (17 mg, 0.07 mmol, 53%, *dr* = 5/1). ¹H NMR (360 MHz, CDCl₃): (**major isomer**) δ 7.16 (dd, *J* = 8.6, 5.5 Hz, 2H), 6.94 (t, *J* = 8.6 Hz, 2H), 3.81-3.60 (m, 2H), 3.39 (dd, *J* = 17.0, 8.6 Hz, 1H), 3.16-3.07 (m, 1H), 2.20-1.91 (m, 5H), 1.72-1.68 (m, 1H), 0.87 (t, *J* = 7.1 Hz, 3H); (**minor isomer**) δ 7.16 (dd, *J* = 8.6, 5.5 Hz, 2H), 6.94 (t, *J* = 8.6 Hz, 2H), 4.06 (q, *J* = 7.1 Hz, 2H), 3.34-3.24 (m, 1H), 2.75 (dd, *J* = 18.4, 8.6 Hz, 1H), 2.20-1.91 (m, 5H), 1.82-1.68 (m, 1H), 1.15 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (90 MHz, CDCl₃): (**major isomer**) δ 174.7 (C=O), 161.7 (d, *J* = 244.2 Hz, C), 137.5 (C), 129.5 (d, *J*^{CH} = 7.5 Hz, 2CH), 114.8 (d, *J*^{CH} = 21 Hz, 2CH), 60.0 (CH₂), 49.8 (CH), 48.5 (CH), 31.6 (CH₂), 28.7 (CH₂), 24.9 (CH₂), 14.0 (CH₃); (**minor isomer**) δ 174.7 (C=O), 161.7 (d, *J* = 244.2 Hz, C), 137.5 (C), 128.7 (d, *J*^{CH} = 8.3 Hz), 115.3 (d, *J*^{CH} = 21.2 Hz), 60.5 (CH₂), 52.5 (CH), 49.3 (CH), 30.7 (CH₂), 30.4 (CH₂), 25.0 (CH₂), 14.3 (CH₃). HRMS (ESI⁺): *m/z* calcd. for C₁₄H₁₇FO₂Na [M+Na]⁺ 258.2810, found 258.2818.

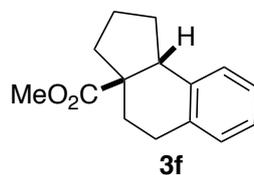
***cis*-Ethyl 2-(4-chlorophenyl)cyclopentanecarboxylate 3d**



3d

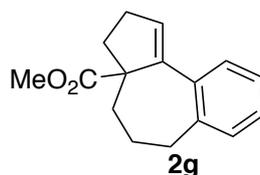
The general procedure **D** was followed, in HFIP instead of 1,2-DCE, with **1d** (50 mg, 0.16 mmol). Purification by FC (SiO₂, PE/Et₂O, 100/0 to 97/3) afforded **3d** as a clear oil (33 mg, 0.13 mmol, 81%, *dr* = 4/1). ¹H NMR (360 MHz, CDCl₃): (**major isomer**) δ 7.22 (d, *J* = 8.5 Hz, 2H), 7.13 (d, *J* = 8.5 Hz, 2H), 3.81-3.62 (m, 2H), 3.37 (dd, *J* = 17.0, 8.6 Hz, 1H), 3.12 (ddd, *J* = 9.0, 8.6, 6.0 Hz, 1H), 2.19-1.91 (m, 5H), 1.76-1.63 (m, 1H), 0.87 (t, *J* = 7.1 Hz, 3H); (**minor isomer**) δ 7.22 (d, *J* = 8.5 Hz, 2H), 7.13 (d, *J* = 8.5 Hz, 2H), 4.06 (q, *J* = 7.2 Hz, 2H), 3.32-3.24 (m, 1H), 2.85-2.70 (m, 1H), 2.19-1.91 (m, 5H), 1.76-1.63 (m, 1H), 1.16 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (90 MHz, CDCl₃): (**major isomer**) δ 174.6 (C=O), 140.4 (C), 132.1 (C), 129.5 (2CH), 128.2 (2CH), 60.0 (CH₂), 49.7 (CH), 48.6 (CH), 31.5 (CH₂), 28.7 (CH₂), 24.9 (CH₂), 13.9; (**minor isomer**) 175.7 (C=O), 142.5 (C), 132.0 (C), 128.7 (2CH), 128.6 (2CH), 60.5 (CH₂), 52.3 (CH), 49.3 (CH), 35.2 (CH₂), 30.8 (CH₂), 25.0 (CH₂), 14.4 (CH₃). HRMS (ESI⁺): *m/z* calcd. for C₁₄H₁₇ClO₂Na [M+Na]⁺ 275.0802, found 275.0809.

***cis*-Methyl 2,3,3a,4,5,9b-hexahydro-1H-cyclopenta[*a*]naphthalene-3a-carboxylate 3f**



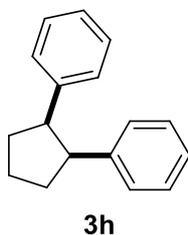
The general procedure **D** was followed with **1f** (40 mg, 0.14 mmol). Purification by FC (SiO₂, pentane/Et₂O, 99/1) afforded **3f** as a clear oil (16.9 mg, 0.07 mmol, 42%, *dr* = 4/1). **¹H NMR (400 MHz, C₆D₆, mixture of diastereoisomers):** δ 7.19-6.97 (m, 4H), 3.08 (s, 3H), 3.01-2.88 (m, 1H), 2.84-2.71 (m, 1H), 2.66-2.51 (m, 3H), 2.43-2.32 (m, 1H), 2.16-2.02 (m, 2H), 1.96-1.83 (m, 1H), 1.79-1.64 (m, 2H), 1.52-1.30 (m, 3H). **¹³C NMR (63 MHz, CDCl₃): (major isomer)** δ 176.0 (C=O), 139.8 (C), 135.7 (C), 128.1 (CH), 125.7 (CH), 125.6 (CH), 125.1 (CH), 54.3 (C), 51.4 (CH₃), 50.4 (CH), 36.9 (CH₂), 33.0 (CH₂), 28.0 (CH₂), 25.6 (CH₂), 22.5 (CH₂); **(minor isomer)** 176.0 (C=O), 139.8 (C), 135.7 (C), 129.2 (CH), 128.5 (CH), 126.1 (CH), 125.6 (CH), 54.3 (C), 52.1 (CH₃), 45.6 (CH), 38.6 (CH₂), 36.5 (CH₂), 30.1 (CH₂), 27.4 (CH₂), 24.2 (CH₂). **HRMS (ESI⁺):** *m/z* C₁₅H₁₈O₂Na [M+Na]⁺ 253.1199, found 253.1201.

Methyl 2,3,3a,4,5,6-hexahydrobenzo[e]azulene-3a-carboxylate 2g



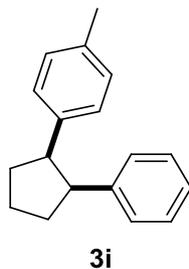
The general procedure **D** was followed with **1g** (40 mg, 0.13 mmol). Purification by FC (SiO₂, pentane/Et₂O, 95/5) afforded **2g** as a clear oil (32.5 mg, 0.13 mmol, 99%). **¹H NMR (400 MHz):** δ 7.26-7.20 (m, 1H), 7.18-7.09 (m, 2H), 7.06-6.99 (m, 1H), 5.74 (t, *J* = 2.3 Hz, 1H), 3.49 (s, 3H), 2.75-2.63 (m, 2H), 2.62-2.58 (m, 1H), 2.56-2.48 (m, 2H), 2.44-2.30 (2H), 2.03-1.84 (m, 2H), 1.77-1.66 (m, 1H). **¹³C NMR (63 MHz, CDCl₃):** δ 176.6 (C), 147.9 (C), 140.6 (C), 138.2 (C), 130.6 (CH), 130.1 (CH), 128.8 (CH), 127.1 (CH), 125.9 (CH), 59.8 (C), 51.7 (CH₃), 39.6 (CH₂), 39.2 (CH₂), 36.9 (CH₂), 30.8 (CH₂), 24.8 (CH₂). **HRMS (ESI⁺):** *m/z* C₁₆H₁₈O₂Na [M+Na]⁺ 265.1199, found 265.1195.

cis-1,2-Diphenylcyclopentane 3h



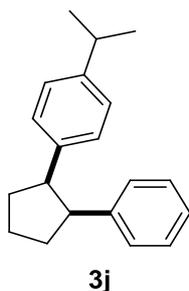
The general procedure **D** was followed with **1h** (100 mg, 0.36 mmol). Purification by FC (SiO₂, pentane, 100%) afforded **3h** as a clear oil (49.5 mg, 0.22 mmol, 61%, *dr* = 24/1). **¹H NMR (360 MHz, C₆D₆):** δ 7.09-7.01 (m, 6H), 6.85-6.77 (m, 4H), 3.49-3.37 (m, 2H), 2.15-2.05 (m, 5H), 2.00-1.89 (m, 1H). **¹³C NMR (63 MHz, CDCl₃):** δ 142.7 (2C), 128.6 (4CH), 127.5 (4CH), 125.7 (2CH), 51.1 (2CH), 30.5 (2CH₂), 24.0 (CH₂). These data correspond to those previously reported in the literature⁶ and confirmed by X-ray diffraction (see section 7).

cis-1-Methyl-4-(2-phenylcyclopentyl)benzene 3i



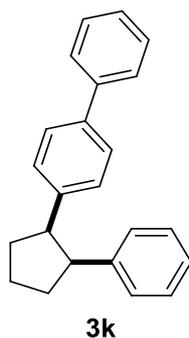
The general procedure **D** was followed with **1i** (40 mg, 0.14 mmol). Purification by FC (SiO₂, PE, 100%) afforded **3i** as a clear oil (17.1 mg, 0.07 mmol, 53%, *dr* = 24/1). ¹H NMR (300 MHz, C₆D₆): δ 7.05-6.92 (m, 3H), 6.87-6.79 (m, 4H), 6.75-6.70 (m, 2H), 3.25-3.19 (m, 2H), 2.04 (s, 3H), 2.02-1.84 (m, 5H), 1.75-1.62 (m, 1H). ¹³C NMR (75 MHz, CDCl₃): δ 142.8 (C), 139.5 (C), 135.0 (C), 128.7 (2CH), 128.5 (2CH), 128.3 (2CH), 127.5 (2CH), 125.6 (CH), 51.1 (CH), 50.8 (CH), 30.7 (CH₂), 30.5 (CH₂), 23.9 (CH₂), 21.1 (CH₃).

cis-1-Isopropyl-4-(2-phenylcyclopentyl)benzene 3j



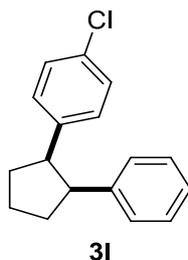
The general procedure **D** was followed with **1j** (40 mg, 0.12 mmol). Purification by FC (SiO₂, PE, 100%) afforded **3j** as a clear oil (25.9 mg, 0.1 mmol, 78%, *dr* = 24/1). ¹H NMR (300 MHz, C₆D₆): δ 7.04-6.89 (m, 5H), 6.82-6.73 (m, 4H), 3.29-3.17 (m, 2H), 2.64 (sept, *J* = 7.0 Hz, 1H), 2.10-1.84 (m, 5H), 1.78-1.61 (m, 1H), 1.10 (d, *J* = 7.0 Hz, 6H). ¹³C NMR (90 MHz, CDCl₃): δ 146.2 (C), 142.8 (C), 139.9 (C), 128.7 (2CH), 128.5 (2CH), 127.4 (2CH), 125.6 (CH), 125.5 (2CH), 51.2 (CH), 50.8 (CH), 33.7 (CH₂), 30.5 (2CH₂), 24.2 (2CH₃), 23.9 (CH). HRMS (ESI⁺): *m/z* calcd. for C₂₀H₂₄Na [M+Na]⁺ 287.1760, found 287.1770. The relative *cis*-stereochemistry of the product was determined by NOESY.

cis-4-(2-Phenylcyclopentyl)-1,1'-biphenyl 3k



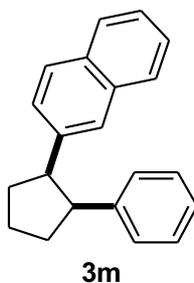
The general procedure **D** was followed with **1k** (60 mg, 0.17 mmol). Purification by FC (SiO₂, PE/Et₂O, 100/0 to 98/2) afforded **3k** as a clear oil (34.1 mg, 0.11 mmol, 68%, *dr* = 24/1). **¹H NMR (360 MHz, C₆D₆):** δ 7.46-7.40 (d, *J* = 8.2, 1.2 Hz, 2H), 7.41 (d, *J* = 8.2, 2H), 7.32-7.28 (m, 2H), 7.23-7.18 (m, 1H), 7.14-7.07 (m, 3H), 6.94-6.90 (m, 4H), 3.36-3.32 (m, 2H), 2.16-1.97 (m, 5H), 1.87-1.77 (m, 1H). **¹³C NMR (90 MHz, C₆D₆):** δ 142.8 (C), 141.9 (C), 141.5 (C), 138.9 (C), 129.3 (2CH), 128.9 (2CH), 127.9 (2CH), 127.6 (2CH), 127.2 (2CH), 127.1 (CH), 126.0 (2CH), 51.3 (CH), 51.0 (CH), 30.9 (CH₂), 30.7 (CH₂), 24.0 (CH₂). **HRMS (ESI⁺):** *m/z* calcd. for C₂₃H₂₂Na [M+Na]⁺ 321.1595, found 321.1614.

cis-1-Chloro-4-(2-phenylcyclopentyl)benzene **3l**



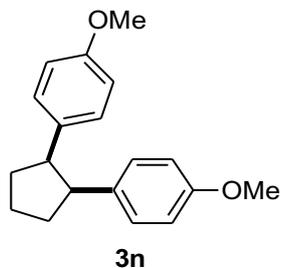
The general procedure **D** was followed with **1l** (80 mg, 0.26 mmol). Purification by FC (SiO₂, pentane, 100%) afforded **3l** (16 mg, 0.06 mmol, 24%, *dr* = 24/1) as a clear oil. **¹H NMR (360 MHz, CDCl₃):** δ 7.13-7.02 (m, 5H), 6.82 (dd, *J* = 7.7, 1.8 Hz, 2H), 6.73 (d, *J* = 8.5 Hz, 2H 2H), 3.47-3.38 (m, 2H), 2.18-2.02 (m, 5H), 1.98-1.88 (m, 1H). **¹³C NMR (75 MHz, CDCl₃):** δ 142.3 (C), 141.2 (C), 131.4 (C), 129.9 (2CH), 128.6 (2CH), 127.7 (2CH), 127.6 (2CH), 125.9 (CH), 51.0 (CH), 50.6 (CH), 30.6 (CH₂), 30.4 (CH₂), 23.9 (CH₂).

cis-2-(2-Phenylcyclopentyl)naphthalene **3m**



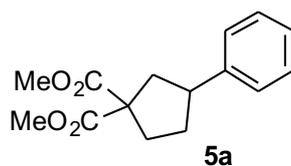
The general procedure **D** was followed with **1m** (40 mg, 0.12 mmol). Purification by FC (SiO₂, PE/Et₂O, 100/0 to 99/1) afforded **3m** as clear oil (31.2 mg, 0.11 mmol, 95%, *dr* = 24/1). **¹H NMR (300 MHz, C₆D₆):** δ 7.59-7.53 (m, 2H), 7.42 (d, *J* = 8.5 Hz, 1H), 7.30 (s, 1H), 7.21 (ddd, *J* = 14.1, 7.1, 1.5 Hz, 2H), 6.92-6.81 (m, 4H), 6.75 (dd, *J* = 7.1, 1.5 Hz, 2H), 3.40-3.20 (m, 2H), 2.12-1.92 (m, 5H), 1.80-1.66 (m, 1H). **¹³C NMR (90 MHz, CDCl₃):** δ 142.6 (C), 140.4 (C), 133.3 (C), 132.0 (C), 128.6 (2CH), 127.9 (CH), 127.7 (CH), 127.6 (2CH), 127.5 (CH), 126.7 (CH), 126.6 (CH), 125.7 (CH), 125.6 (CH), 125.0 (CH), 51.3 (CH), 51.1 (CH), 30.7 (2CH₂), 24.0 (CH₃). **HRMS (ESI⁺):** *m/z* calcd. for C₂₁H₂₀Na [M+Na]⁺ 295.1449, found 295.1457.

cis-1,2-Bis(4-methoxyphenyl)cyclopentane **3n**



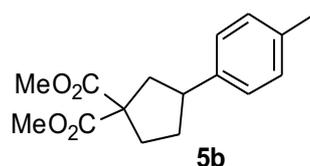
The general procedure **D** was followed with **1n** (40 mg, 0.12 mmol). Purification by FC (SiO₂, PE/Et₂O, 100/0 to 90/10) afforded **3n** as clear oil (29.2 mg, 0.10 mmol, 87%, *dr* = 9/1). **¹H NMR (360 MHz, CDCl₃): (major isomer)** δ 6.71 (d, *J* = 8.8 Hz, 4H), 6.63 (d, *J* = 8.8 Hz, 4H), 3.73 (s, 6H), 3.33 (td, *J* = 5.1, 2.6 Hz, 2H), 2.14-1.97 (m, 5H), 1.97-1.83 (m, 1H), **(minor isomer)** δ 7.03 (d, *J* = 8.8 Hz, 4H), 6.75 (d, *J* = 8.8 Hz, 4H), 3.75 (s, 6H), 3.01-2.95 (m, 2H), 2.11-2.00 (m, 5H), 1.94-1.85 (m, 1H). **¹³C NMR (63 MHz, CDCl₃): (major isomer)** δ 157.6 (2C), 134.9 (2C), 129.5 (4CH), 113.0 (4CH), 55.2 (2CH₃), 50.3 (2CH), 30.7 (2CH₂), 23.7 (CH₂), **(minor isomer)** δ 157.6 (2C), 136.7 (2C), 128.4 (4CH), 113.7 (4CH), 53.4 (2CH₃), 50.3 (2CH), 35.4 (2CH₂), 24.4 (CH₂). **HRMS (ESI⁺):** *m/z* calcd. for C₁₅H₁₈O₄Na [M+Na]⁺ 305.1765, found 305.1773.

Dimethyl 3-phenylcyclopentane-1,1-dicarboxylate 5a



The general procedure **D** was followed with **4a** (40 mg, 0.13 mmol). Purification by FC (SiO₂, pentane/Et₂O, 100/0 to 94/6) afforded **5a** as a clear oil (25.5 mg, 0.1 mmol, 77%). **¹H NMR (360 MHz, CDCl₃):** δ 7.61-7.45 (m, 5H), 4.04 (s, 3H), 4.03 (s, 3H), 3.45 (tt, *J* = 11.1, 7.1 Hz, 1H), 3.05 (ddd, *J* = 8.8, 7.3, 1.2 Hz, 1H), 2.79 (ddd, *J* = 13.6, 8.5, 2.9 Hz, 1H), 2.58 (ddd, *J* = 13.6, 10.2, 7.3 Hz, 1H), 2.48 (dd, *J* = 13.5, 11.2 Hz, 1H), 2.46-2.39 (m, 1H), 2.07 (dddd, *J* = 13.6, 11.2, 10.2, 8.8 Hz, 1H). **¹³C NMR (90 MHz, CDCl₃):** δ 173.2 (C=O), 173.1 (C=O), 143.6 (C), 128.5 (2CH), 127.2 (2CH), 126.5 (CH), 60.0 (C), 52.9 (CH₃), 52.9 (CH₃), 45.3 (CH), 42.2 (CH₂), 34.3 (CH₂), 34.0 (CH₂). **HRMS (ESI⁺):** *m/z* calcd. for C₁₅H₁₈O₄Na [M+Na]⁺ 285.1087, found 285.1097. Spectroscopic data for **5a** match those previously reported in literature.⁷

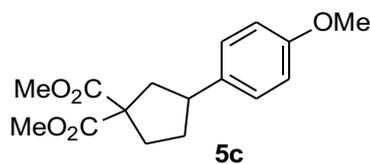
Dimethyl 3-(p-tolyl)cyclopentane-1,1-dicarboxylate 5b



The general procedure **D** was followed with **4b** (40 mg, 0.12 mmol). Purification by FC (SiO₂, pentane/Et₂O, 100/0 to 95/5) afforded **5b** as a clear oil (32.9 mg, 0.12 mmol, 98%). **¹H NMR (360 MHz, CDCl₃):** δ 7.17-7.06 (m, 4H), 3.76 (s, 3H), 3.74 (s, 3H), 3.13 (tt, *J* = 11.4, 7.1 Hz, 1H), 2.74 (ddd, *J* = 13.4, 7.4, 1.2 Hz, 1H),

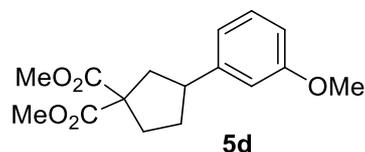
2.50 (ddd, $J = 13.4, 8.5, 2.9$ Hz, 1H), 2.32 (s, 3H), 2.35-2.25 (m, 1H), 2.20-2.06 (m, 1H), 2.17 (dd, $J = 13.4, 11.4$ Hz, 1H), 1.85-1.68 (m, 1H). **^{13}C NMR (90 MHz, CDCl_3):** δ 173.2 (C=O), 173.1 (C=O), 140.5 (C), 136.0 (C), 129.2 (2CH), 127.0 (2CH), 59.9 (C), 52.9 (CH₃), 52.8 (CH₃), 44.9 (CH), 42.3 (CH₂), 34.3 (CH₂), 34.1 (CH₂), 21.1 (CH₃). **HRMS (ESI⁺):** m/z calcd. for C₁₆H₂₀O₄Na [M+Na]⁺ 299.1244, found 299.1253.

Dimethyl 3-(4-methoxyphenyl)cyclopentane-1,1-dicarboxylate **5c**



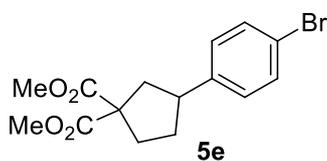
The general procedure **D** was followed with **4c** (30 mg, 0.09 mmol). Purification by FC (SiO₂, pentane/Et₂O, 100/0 to 96/4) afforded **5c** as a clear oil (19.9 mg, 0.07 mmol, 79%). **^1H NMR (300 MHz, CDCl_3):** δ 7.17 (d, $J = 8.6$ Hz, 2H), 6.84 (d, $J = 8.6$ Hz, 2H), 3.79 (s, 1H), 3.76 (s, 1H), 3.74 (s, 1H), 3.12 (tt, $J = 11.4, 7.2$ Hz, 1H), 2.73 (ddd, $J = 13.5, 7.2, 1.1$ Hz, 1H), 2.49 (ddd, $J = 13.5, 8.5, 2.9$ Hz, 1H), 2.28 (ddd, $J = 13.5, 10.1, 7.4$ Hz, 1H), 2.18-2.05 (m, 1H), 2.15 (dd, $J = 13.5, 11.4$ Hz, 1H), 1.84-1.67 (m, 1H). **^{13}C NMR (75 MHz, CDCl_3):** δ 173.2 (2C=O), 158.3 (C), 135.7 (C), 128.1 (2CH), 114.0 (2CH), 60.0 (C), 55.4 (CH₃), 52.9 (2CH₃), 44.6 (CH), 42.4 (CH₂), 34.3 (CH₂), 34.2 (CH₂). **HRMS (ESI⁺):** m/z calcd. for C₁₆H₂₀O₅Na [M+Na]⁺ 315.1201, found 315.1202.

Dimethyl 3-(3-methoxyphenyl)cyclopentane-1,1-dicarboxylate **5d**



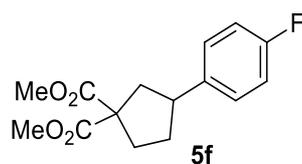
The general procedure **D** was followed with **4d** (40 mg, 0.11 mmol). Purification by FC (SiO₂, pentane/Et₂O, 100/0 to 96/4) afforded **5d** as a clear oil (26.3 mg, 0.10 mmol, 78%). **^1H NMR (300 MHz, CDCl_3):** δ 7.25 (dd, $J = 14.5, 6.6$ Hz, 1H), 6.90-6.74 (m, 3H), 3.82 (s, 2H), 3.78 (s, 3H), 3.76 (s, 3H), 3.17 (ddd, $J = 11.3, 7.0$ Hz, 4.0 Hz 1H), 2.78 (dd, $J = 13.5, 7.0$ Hz, 1H), 2.53 (ddd, $J = 13.5, 8.6, 2.9$ Hz, 1H), 2.37-2.27 (m, 1H), 2.21 (dd, $J = 13.5, 11.3$ Hz, 2H), 1.90-1.73 (m, 1H). **^{13}C NMR (90 MHz, CDCl_3):** δ 173.2 (C=O), 173.1 (C=O), 159.8 (C), 145.3 (C), 129.5 (CH), 119.5 (CH), 113.1 (CH), 111.6 (CH), 59.9 (C), 55.3 (CH₃), 52.9 (CH₃), 52.9 (CH₃), 45.3 (CH), 42.1 (CH₂), 34.3 (CH₂), 33.9 (CH₂). **HRMS (ESI⁺):** m/z calcd. for C₁₆H₂₀O₅Na [M+Na]⁺ 315.1189, found 315.1202.

Dimethyl 3-(4-bromophenyl)cyclopentane-1,1-dicarboxylate **5e**



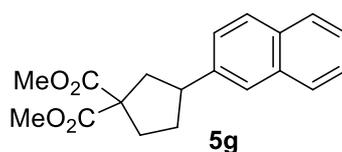
The general procedure **D** was followed with **4e** (40 mg, 0.10 mmol). Purification by FC (SiO₂, pentane/Et₂O, 100/0 to 95/5) afforded **5e** as a clear oil (26.6 mg, 0.08 mmol, 77%). **¹H NMR (300 MHz, CDCl₃):** δ 7.41 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 3.76 (s, 3H), 3.74 (s, 3H), 3.12 (ddd, *J* = 13.5, 9.2, 5.6 Hz, 1H), 2.73 (dd, *J* = 13.5, 7.4 Hz, 1H), 2.50 (dd, *J* = 13.5, 8.5 Hz, 1H), 2.29 (ddd, *J* = 13.5, 9.2, 7.4 Hz, 1H), 2.15 (dd, *J* = 13.5, 11.4 Hz, 1H), 2.21-2.07 (m, 1H), 1.83-1.64 (m, 1H). **¹³C NMR (90 MHz, CDCl₃):** δ 173.1 (C=O), 173.0 (C=O), 142.6 (C), 131.6 (2CH), 129.0 (2CH), 120.2 (C), 59.9 (C), 53.0 (2CH₃), 44.7 (CH), 42.1 (CH₂), 34.2 (CH₂), 34.0 (CH₂). **HRMS (ESI⁺):** *m/z* calcd. for C₁₅H₁₇BrO₄Na [M+Na]⁺ 363.0182, found 363.0202.

Dimethyl 3-(4-fluorophenyl)cyclopentane-1,1-dicarboxylate **5f**



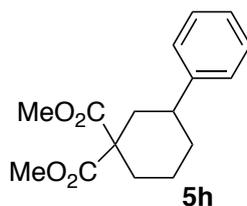
The general procedure **D** was followed with **4f** (40 mg, 0.12 mmol). Purification by FC (SiO₂, pentane/Et₂O, 100/0 to 95/5) afforded **5f** as a clear oil (28 mg, 0.10 mmol, 84%). **¹H NMR (360 MHz, CDCl₃):** δ 7.24-7.16 (m, 2H), 7.02-6.93 (m, 2H), 3.76 (s, 3H), 3.74 (s, 3H), 3.16 (tt ap, *J* = 11.2, 7.3 Hz, 1H), 2.75 (ddd, *J* = 13.7, 7.3, 1.8 Hz, 1H), 2.52 (ddd, *J* = 13.6, 8.5, 2.8 Hz, 1H), 2.30 (ddd, *J* = 13.7, 10.1, 7.4 Hz, 1H), 2.19-2.08 (m, 1H), 2.17 (dd, *J* = 13.6, 11.3 Hz, 1H), 1.76 (dddd, *J* = 12.5, 11.2, 10.1, 8.5 Hz, 1H). **¹³C NMR (90 MHz, CDCl₃):** δ 173.1 (2C=O), 161.6 (d, *J*^{CF} = 244.2 Hz, C), 139.2 (d, *J*^{CF} = 2.8 Hz, C), 128.4 (d, *J*^{CF} = 7.9 Hz, 2CH), 115.2 (d, *J*^{CF} = 21.3 Hz, 2CH), 59.9 (C), 52.9 (2CH₃), 44.6 (CH), 42.3 (CH₂), 34.2 (CH₂), 34.1 (CH₂). **¹⁹F NMR (235 MHz, CDCl₃):** δ -117.0. **HRMS (ESI⁺):** *m/z* calcd. for C₁₅H₁₇FO₄Na [M+Na]⁺ 303.0998, found 303.1003.

Dimethyl 3-(naphthalen-2-yl)cyclopentane-1,1-dicarboxylate **5g**



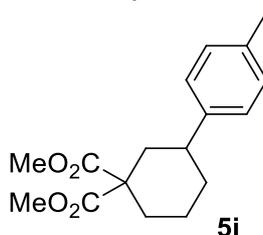
The general procedure **D** was followed with **4g** (40 mg, 0.11 mmol). Purification by FC (SiO₂, pentane/Et₂O, 100/0 to 93/7) afforded **5g** as a clear oil (33.1 mg, 0.11 mmol, 98%). **¹H NMR (300 MHz, CDCl₃):** δ 7.83-7.76 (m, 3H), 7.68 (s, 1H), 7.50-7.37 (m, 3H), 3.79 (s, 3H), 3.77 (s, 3H), 3.36 (dd, *J* = 11.0, 7.0 Hz, 1H), 2.84 (dd, *J* = 13.5, 7.0 Hz, 1H), 2.56 (ddd, *J* = 13.5, 8.5, 2.9 Hz, 1H), 2.42-2.31 (m, 2H), 2.30-2.18 (m, 1H), 1.91 (dddd, *J* = 12.4, 11.0, 9.9, 8.5 Hz, 1H). **¹³C NMR (90 MHz, CDCl₃):** δ 173.2 (C=O), 173.1 (C=O), 141.0 (C), 133.6 (C), 132.4 (C), 128.2 (CH), 127.7 (2CH), 126.2 (CH), 125.9 (CH), 125.5 (CH), 125.3 (CH), 60.1 (C), 53.0 (2CH₃), 45.4 (CH), 42.2 (CH₂), 34.4 (CH₂), 34.0 (CH₂). **HRMS (ESI⁺):** *m/z* calcd. for C₁₉H₂₀O₄Na [M+Na]⁺ 335.1241, found 335.1253.

Dimethyl 3-phenylcyclohexane-1,1-dicarboxylate **5h**



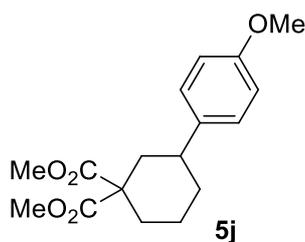
The general procedure **D** was followed with **4h** (40 mg, 0.12 mmol). Purification by FC (SiO₂, pentane/Et₂O, 100/0 to 96/4) afforded **5h** as a clear oil (23.5 mg, 0.09 mmol, 71%). **¹H NMR (300 MHz, CDCl₃):** δ 7.34-7.27 (m, 2H), 7.25-7.16 (m, 3H), 3.80 (s, 3H), 3.70 (s, 3H), 2.69 (tt, $J = 12.5, 3.2$ Hz, 1H), 2.54 (ddd, $J = 13.2, 4.7, 3.2$ Hz, 1H), 2.48-2.39 (m, 1H), 1.94-1.66 (m, 4H), 1.62-1.38 (m, 2H). **¹³C NMR (360 MHz, CDCl₃):** δ 172.9 (C=O), 171.4 (C=O), 146.1 (C), 128.6 (2CH), 127.0 (2CH), 126.4 (CH), 55.8 (C), 52.8 (CH₃), 52.7 (CH₃), 40.4 (CH), 38.6 (CH₂), 32.9 (CH₂), 31.1 (CH₂), 23.3 (CH₂). **HRMS (ESI⁺):** m/z calcd. for C₁₆H₂₀O₄Na [M+Na]⁺ 299.1250, found 299.1253. Spectroscopic data for **5h** match those previously reported in literature.⁸

Dimethyl 3-(*p*-tolyl)cyclohexane-1,1-dicarboxylate **5i**



The general procedure **D** was followed with **4i** (40 mg, 0.12 mmol). Purification by FC (SiO₂, pentane/Et₂O, 100/0 to 96/4) afforded **5i** as a clear oil (33 mg, 0.11 mmol, 98%). **¹H NMR (300 MHz, CDCl₃):** δ 7.12 (s ap, 4H), 3.79 (s, 3H), 3.70 (s, 3H), 2.66 (tt, $J = 12.5, 3.1$ Hz, 1H), 2.52 (dd, $J = 13.2, 1.9$ Hz, 1H), 2.48-2.38 (m, 1H), 2.32 (s, 3H), 1.93-1.65 (m, 4H), 1.59-1.38 (m, 2H). **¹³C NMR (90 MHz, CDCl₃):** δ 172.9 (C=O), 171.7 (C=O), 143.2 (C), 135.9 (C), 129.2 (2CH), 126.8 (2CH), 55.8 (C), 52.8 (CH₃), 52.6 (CH₃), 44.9 (CH), 42.3 (CH₂), 38.7 (CH₂), 34.3 (CH₂), 34.1 (CH₂), 21.1 (CH₃). **HRMS (ESI⁺):** m/z calcd. for C₁₇H₂₂O₄Na [M+Na]⁺ 313.1405, found 313.1410.

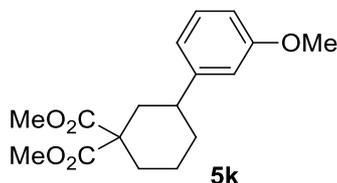
Dimethyl 3-(4-methoxyphenyl)cyclohexane-1,1-dicarboxylate **5j**



The general procedure **D** was followed with **4j** (27 mg, 0.07 mmol). Purification by FC (SiO₂, pentane/Et₂O, 100/0 to 96/4) afforded **5j** as a clear oil (18 mg, 0.06 mmol, 79%). **¹H NMR (360 MHz, CDCl₃):** δ 7.14 (d, $J = 8.7$ Hz, 2H), 6.84 (d, $J = 8.7$ Hz, 2H), 3.79 (s, 3H),

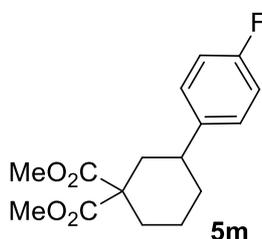
3.79 (s, 3H), 3.69 (s, 3H), 2.64 (tt, $J = 12.4, 3.1$ Hz, 1H), 2.55-2.47 (m, 1H), 2.46-2.38 (m, 1H), 1.88-1.81 (m, 2H), 1.80-1.66 (m, 2H), 1.59-1.48 (m, 1H), 1.42-1.36 (m, 1H). ^{13}C NMR (75 MHz, CDCl_3): 172.9 (C=O), 171.7 (C=O), 158.2 (C), 138.4 (C), 127.8 (2CH), 113.9 (2CH), 55.9 (CH₃), 55.4 (C), 52.8 (CH₃), 52.6 (CH₃), 39.5 (CH), 38.9 (CH₂), 33.1 (CH₂), 31.1 (CH₂), 23.3 (CH₂). HRMS (ESI⁺): m/z calcd. for $\text{C}_{17}\text{H}_{22}\text{O}_5\text{Na}$ $[\text{M}+\text{Na}]^+$ 329.1349, found 329.1359.

Dimethyl 3-(3-methoxyphenyl)cyclohexane-1,1-dicarboxylate **5k**



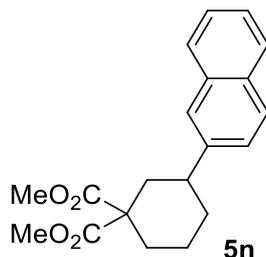
The general procedure **D** was followed with **4k** (40 mg, 0.11 mmol). Purification by FC (SiO_2 , pentane/ Et_2O , 100/0 to 96/4) afforded **5k** as a clear oil (15 mg, 0.05 mmol, 44%). ^1H NMR (360 MHz, CDCl_3): 7.10 (d, $J = 7.8$, 1H), 6.97 (s, 1H), 6.77 (dd, $J = 7.8, 1.6$ Hz, 1H), 6.68 (d, $J = 1.6$ Hz, 1H), 3.81 (s, 3H), 3.79 (s, 3H), 3.69 (s, 3H), 2.94-2.82 (m, 1H), 2.66 (ddd, $J = 12.4, 7.8, 3.2$ Hz, 1H), 2.54 (d, $J = 13.5$ Hz, 1H), 2.41 (d, $J = 12.4$ Hz, 1H), 1.90-1.60 (m, 5H). ^{13}C NMR (100 MHz, CDCl_3): 172.7 (C=O), 171.6 (C=O), 159.7 (C), 147.7 (C), 129.4 (CH), 119.2 (CH), 112.8 (CH), 111.4 (CH), 55.7 (C), 55.2 (CH₃), 52.7 (CH₃), 52.5 (CH₃), 40.3 (CH), 38.4 (CH₂), 32.7 (CH₂), 30.9 (CH₂), 23.1 (CH₂). HRMS (ESI⁺): m/z calcd. for $\text{C}_{17}\text{H}_{23}\text{O}_5$ $[\text{M}+\text{H}]^+$ 307.1528, found 307.1540.

Dimethyl 3-(4-fluorophenyl)cyclohexane-1,1-dicarboxylate **5m**



The general procedure **D** was followed with **4m** (40 mg, 0.11 mmol). Purification by FC (SiO_2 , pentane/ Et_2O , 100/0 to 96/4) afforded **5m** as a clear oil (21 mg, 0.07 mmol, 63%). ^1H NMR (300 MHz, CDCl_3): δ 7.21-7.13 (m, 2H), 7.02-6.94 (m, 2H), 3.79 (s, 3H), 3.70 (s, 3H), 2.68 (tt, $J = 12.4, 3.0$ Hz, 1H), 2.56-2.46 (m, 1H), 2.46-2.38 (m, 1H), 1.90-1.80 (m, 2H), 1.73-1.65 (m, 2H), 1.61-1.45 (m, 2H). ^{13}C NMR (90 MHz, CDCl_3): δ 172.8 (C=O), 171.7 (C=O), 161.5 (d, $J^{\text{CF}} = 244.0$ Hz, C), 141.8 (C), 128.3 (d, $J^{\text{CH}} = 7.8$ Hz, 2CH), 115.3 (d, $J^{\text{CH}} = 21.1$ Hz, 2CH), 55.8 (C), 52.9 (CH₃), 52.7 (CH₃), 39.6 (CH), 38.8 (CH₂), 33.0 (CH₂), 31.0 (CH₂), 23.2 (CH₂). ^{19}F NMR (235 MHz, CDCl_3): δ -117.1. HRMS (ESI⁺): m/z calcd. for $\text{C}_{16}\text{H}_{19}\text{O}_4\text{FNa}$ $[\text{M}+\text{Na}]^+$ 317.1153, found 317.1159.

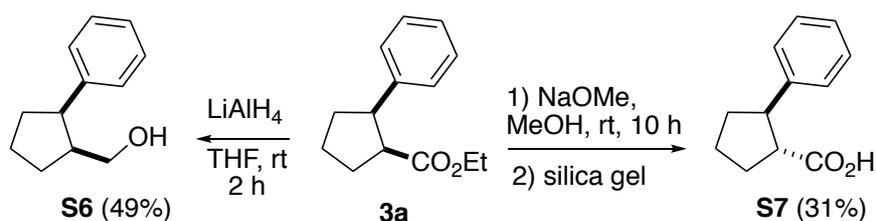
Dimethyl 3-(naphthalen-2-yl)cyclohexane-1,1-dicarboxylate **5n**



The general procedure **D** was followed with **4n** (40 mg, 0.11 mmol). Purification by FC (SiO₂, pentane/Et₂O, 100/0 to 96/4) afforded **5n** as a clear oil (28.3 mg, 0.09 mmol, 83%). **¹H NMR (300 MHz, CDCl₃):** δ 7.84-7.76 (m, 3H), 7.66 (s, 1H), 7.50-7.35 (m, 3H), 3.83 (s, 3H), 3.71 (s, 3H), 2.87 (tt, $J = 12.1, 3.2$ Hz, 1H), 2.63 (ddd, $J = 7.1, 5.0, 3.2$ Hz, 1H), 2.53-2.43 (m, 1H), 2.03-1.85 (m, 3H), 1.84-1.72 (m, 1H), 1.66-1.51 (m, 2H). **¹³C NMR (90 MHz, CDCl₃):** δ 173.2 (C=O), 173.1 (C=O), 141.0 (C), 133.6 (C), 132.4 (C), 128.2 (CH), 127.7 (2CH), 126.2 (CH), 125.9 (CH), 125.5 (CH), 125.3 (CH), 60.1 (C), 53.0 (CH₃), 52.9 (CH₃), 45.4 (CH), 42.2 (CH₂), 42.2 (CH₂), 34.4 (CH₂), 33.9 (CH₂). **HRMS (ESI⁺):** m/z calcd. for C₂₀H₂₂O₄Na [M+Na]⁺ 349.1393, found 349.1410.

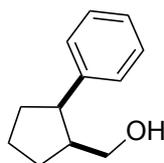
6 Transformations of Ethyl *cis*-2-Phenylcyclopentanecarboxylate **3a**

cis-2-phenylcyclopentanecarboxylate **3a** was reduced with LiAlH₄ in THF at room temperature. The corresponding alcohol **S6** was isolated in 49% yields (Scheme S1) with stereoretention. In addition, epimerization of **3a** with sodium ethoxide in MeOH led, after acidic treatment, to the thermodynamically more stable *trans*-2-phenylcyclopentanecarboxylic acid **S7**.



Scheme S1. Selected Modifications of Ethyl *cis*-2-phenylcyclopentanecarboxylate **3a**

cis-2-Phenylcyclopentyl)methanol **S6**

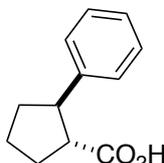


S6

A 25 mL round bottom flask equipped with a magnetic stir bar was charged with ethyl 2-phenylcyclopentane-1-carboxylate **3a** (138 mg, 0.63 mmol, 1 equiv) and THF (0.18 M). The mixture was cooled to 0 °C and LiAlH₄ (36 mg, 0.95 mmol, 1.5 equiv) was added. The mixture was stirred at 0 °C for 1 h and then passed through a short silica plug Et₂O (20 mL). The filtrate was concentrated under reduced pressure and the crude material was purified by FC (SiO₂, Cy/EtOAc, 100/0 to 80/20) to afford **S6** as a clear oil (55.1 mg, 0.31 mmol, 49%).

¹H NMR (300 MHz, CDCl₃) δ 7.38-7.28 (m, 2H), 7.27-7.20 (m, 3H), 3.33 (dd, *J* = 10.9, 7.1 Hz, 1H), 3.23 (dd, *J* = 10.9, 6.9 Hz, 1H), 2.51-2.33 (m, 1H), 2.14-2.02 (m, 1H), 2.00-1.88 (m, 2H), 1.80-1.69 (m, 1H), 1.61-1.51 (m, 1H). ¹³C NMR (90 MHz, CDCl₃): δ 142.7 (C), 128.5 (2CH), 128.3 (2CH), 126.3 (CH), 64.3 (CH₂), 47.3 (CH), 46.4 (CH), 31.0 (CH₂), 28.6 (CH₂), 24.3 (CH₂). HRMS (ESI): *m/z* calcd. for C₁₂H₁₄OK [M-H₂+K]⁻ 213.0682, found 213.06883.

trans-2-Phenylcyclopentanecarboxylic acid **S7**



S7

An oven-dried round bottom flask was charged with a solution of **3a** (200 mg, 0.94 mmol, 1 equiv) in MeOH (0.08 M) and NaOMe (3.5 equiv). The resulting mixture was refluxed for 1 h. Then, the solvent was evaporated and the crude product was purified by FC (SiO₂, pentane/Et₂O, 100/0 to 70/30) to afford **S7** as a clear oil (54 mg, 0.28 mmol, 31%)

¹H NMR (300 MHz, CDCl₃): δ 7.33-7.18 (m, 5H), 3.35 (dd, *J* = 17.7, 8.2 Hz, 1H), 2.87 (dd, *J* = 17.7, 8.2 Hz, 1H), 2.26-1.95 (m, 3H), 1.92-1.71 (m, 3H). ¹³C NMR (90 MHz, CDCl₃): δ 182.6 (C=O), 143.8 (C), 128.6 (2CH), 127.3 (2CH), 126.5 (CH), 51.9 (CH), 49.6 (CH), 35.4 (CH₂), 31.1 (CH₂), 25.3 (CH₂). HRMS (ESI⁺): *m/z* calcd. for C₁₂H₁₃O₂Na [M+Na]⁺ 189.0919, found 189.0921. Spectroscopic data for **S7** match those previously reported in literature.⁹

7 Single-Crystal X-ray Structure Analysis of Compound 3h

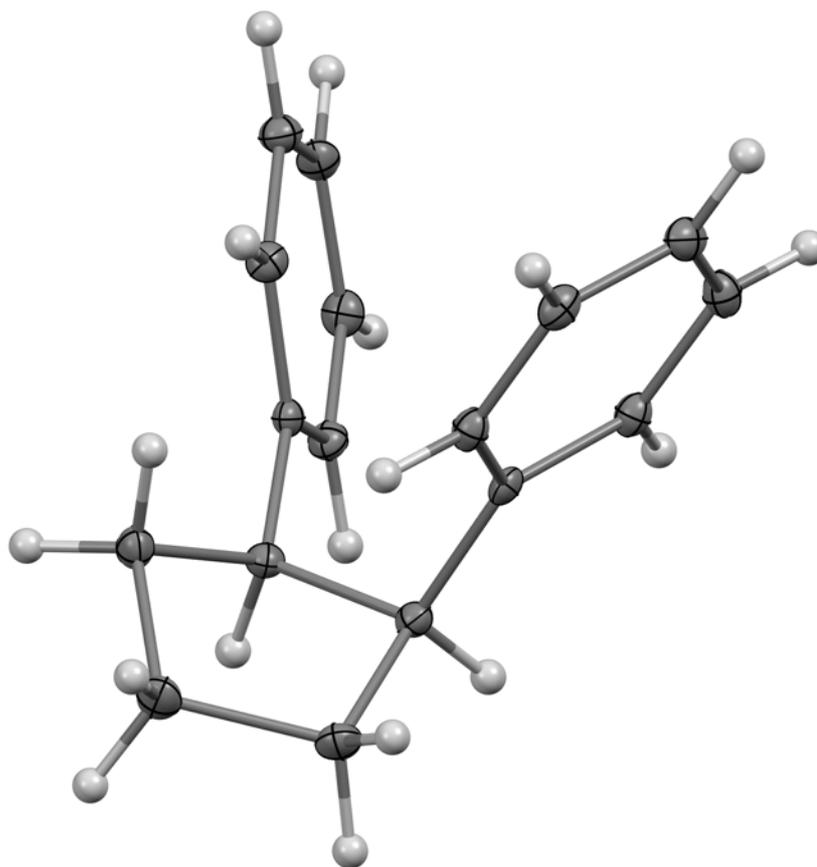


Figure S1. ORTEP drawing for crystal structure of compound **3h**. Thermal ellipsoids are shown at the 30% level at 100K.

X-ray diffraction data for compound **3h** was collected by using a Kappa X8 APPEX II Bruker diffractometer with graphite-monochromated MoK α radiation. Crystal was mounted on a CryoLoop (Hampton Research) with Paratone-N (Hampton Research) as cryoprotectant and then flashfrozen in a nitrogen-gas stream at 100 K. For compound, the temperature of the crystal was maintained at the selected value by means of a 700 series Cryostream cooling device to within an accuracy of ± 1 K. The data were corrected for Lorentz polarization, and absorption effects. The structures were solved by direct methods using SHELXS-97¹⁰ and refined against F^2 by full-matrix least-squares techniques using SHELXL-2018¹¹ with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were located on a difference Fourier map and introduced into the calculations as a riding model with isotropic thermal parameters. All calculations were performed by using the Crystal Structure crystallographic software package WINGX.¹²

The crystal data collection and refinement parameters are given in Table S4.

CCDC 1920340 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via <http://www.ccdc.cam.ac.uk/Community/Requestastructure>.

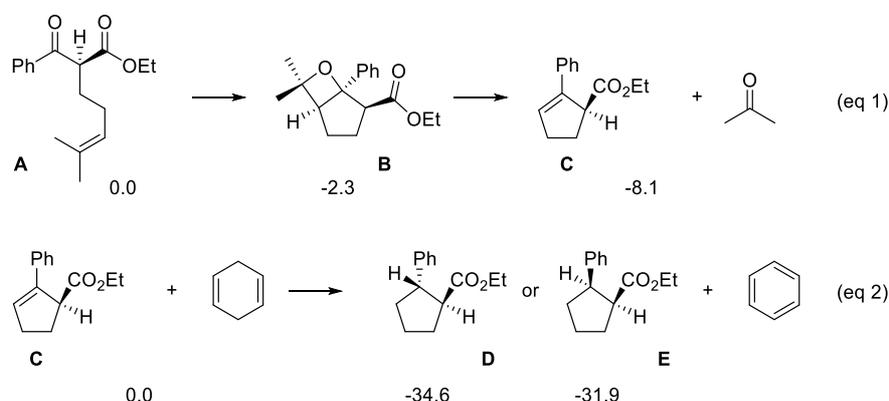
Table S4. Crystallographic data and structure refinement details.

Compound	3h
CCDC	1920340
Empirical Formula	C ₁₇ H ₁₈
<i>M_r</i>	222.31
Crystal size, mm ³	0.24 x 0.04 x 0.02
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i> '
a, Å	13.8695(10)
b, Å	5.7371(3)
c, Å	16.5766(10)
α, °	90
β, °	110.981(3)
γ, °	90
Cell volume, Å ³	1231.56(13)
Z ; Z'	4 ; 1
T, K	100(1)
Radiation type ; wavelength Å	MoKα ; 0.71073
F ₀₀₀	480
μ, mm ⁻¹	0.067
θ range, °	1.572 - 33.213
Reflection collected	28 538
Reflections unique	4 683
R _{int}	0.1194
GOF	1.028
Refl. obs. (<i>I</i> >2σ(<i>I</i>))	2 469
Parameters	154
wR ₂ (all data)	0.1426
R value (<i>I</i> >2σ(<i>I</i>))	0.0585
Largest diff. peak and hole (e ⁻ ·Å ⁻³)	0.311 ; -0.293

8 Calculations

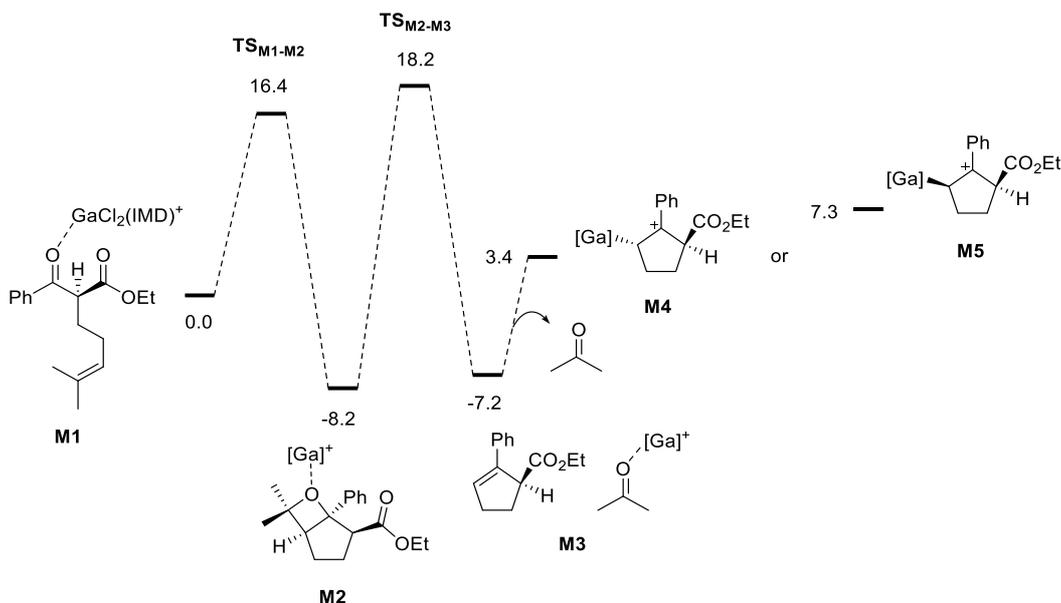
To get an insight into the reaction mechanism, DFT computations were carried out using the Gaussian 09 software package.¹³ Geometries of minima and transition states were optimized using the ω B97-XD¹⁴ functional. The 6-31G(d)¹⁵ basis set for selected all atoms. The values presented are ΔG in kcal/mol at 298.15 K. They include solvation correction for 1,2-dichloroethane, obtained using the CPCM method.¹⁶

Compound **A** (Scheme S2) was used as model substrate. At the chosen level of theory, the putative [2+2] cycloadduct **B**³ is more stable than **A** by 2.3 kcal/mol, and the metathesis product **C** and acetone by 8.1 kcal/mol (eq 1). The reduction of **C** with 1,4-cyclohexadiene to give the *trans* product **D** or the *cis* product **E** and benzene is strongly exergonic by 34.6 and 31.9 kcal/mol respectively. Thus, the experimentally observed *cis* product is less stable than the *trans* one by 2.7 kcal/mol.



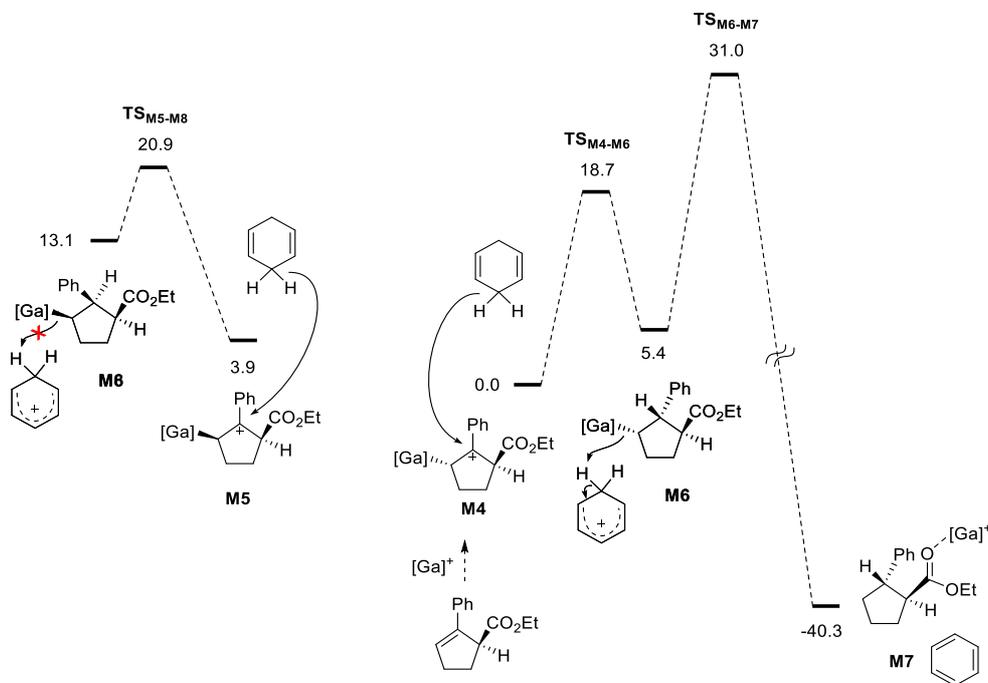
Scheme S2. Free Energies of the Putative Intermediates (ΔG , kcal/mol)

Using 1,3-dimethylimidazol-2-ylidene as model NHC (noted IMD) and [(IMD)GaCl₂]⁺ as model active species (noted [Ga]⁺), the carbonyl-olefin metathesis was computed as a two-step process (Scheme S3). The [2+2] cycloaddition requires 16.4 kcal/mol of free energy of activation from **M1** and is exergonic by 8.2 kcal/mol. The following retro-[2+2] transition state lies at 18.2 kcal/mol on the free energy surface, which means 26.4 kcal/mol from **M2**. This step is endergonic by 1.0 kcal/mol. Removal of acetone from the system and coordination of the gallium fragment to the alkene function led to the diastereomeric complexes **M4** and **M5**, found at 3.4 and 7.3 kcal/mol respectively on the surface. The *trans* one, **M4**, was found 3.9 kcal/mol more stable than the *cis* isomer, **M5**. Thus; although this concerted (i.e. non cationic) mechanism is consistent with the one reported by Schindler et al with FeCl₃,¹⁷ the computations do not support it.



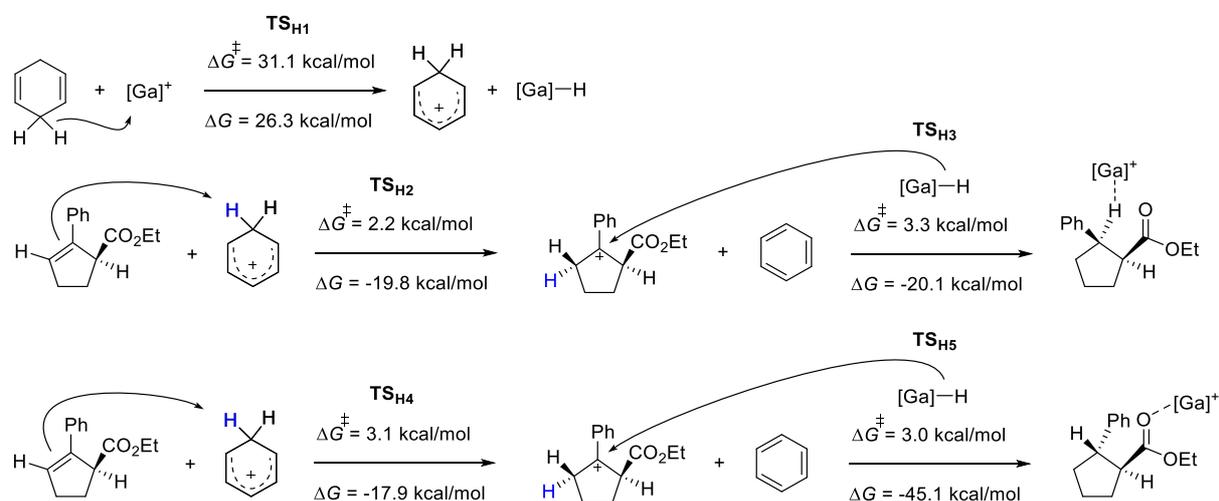
Scheme S3. Free Energies Profile of the $[(\text{IMD})\text{GaCl}_2]^+$ -catalyzed Carbonyl-Olefin Metathesis (ΔG , kcal/mol): **Hypothesis 1a**

The transfer of a hydride from 1,4-cyclohexadiene to **M4** or **M5** could not be achieved on the gallium side due to the steric hindrance. On the opposite side, both transfer could be modeled (Scheme S4). The corresponding transition states were found at 18.7 and 20.9 kcal/mol for **M4** and **M5** respectively. These steps are markedly endergonic. Cleavage of the strong C_{sp^3} -Ga bond by the cyclohexadienyl cation to give **M7** proved very difficult, the transition state being located at 32.0 kcal/mol. In the case of **M8**, manifold efforts failed to locate it. Overall, the pathway through **M4** seems favored, but the free energy of activation to cleave the C_{sp^3} -Ga bond is prohibitively high and leads to the unobserved *trans* stereoisomer of the final product.



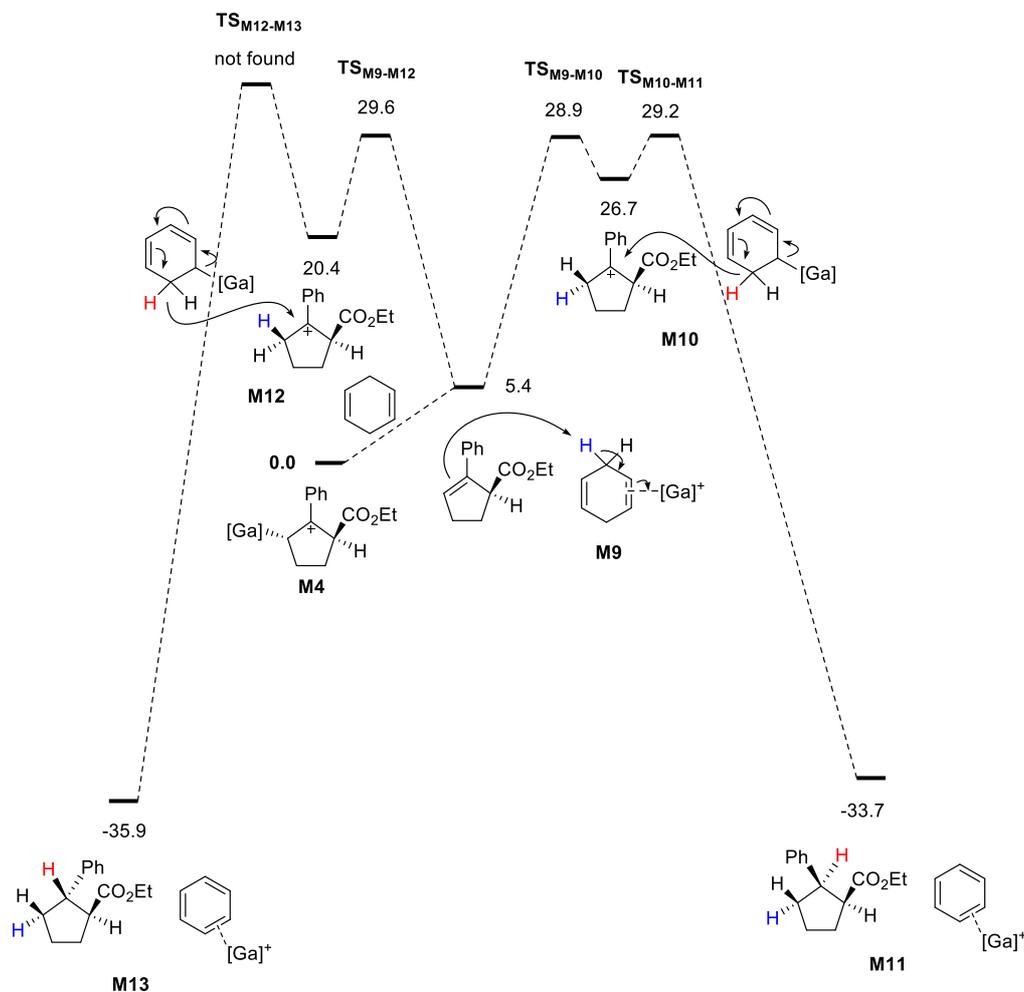
Scheme S4. Free Energies Profile of the $[(\text{IMD})\text{GaCl}_2]^+$ -catalyzed Transfer Hydrogenation of the Carbonyl-Olefin Metathesis Product (ΔG , kcal/mol): **Hypothesis 2a**

We then envisaged a direct reaction between $[(\text{IMD})\text{GaCl}_2]^+$ and 1,4-cyclohexadiene to furnish the cyclohexadienyl cation and the gallium hydride $[(\text{IMD})\text{GaCl}_2\text{H}]$ (Scheme S5). However, the hydride transfer requires a high free energy of activation of 31.1 kcal/mol and is endergonic by 26.3 kcal/mol. Of note, even if the cyclohexadienyl cation was formed, there would be virtually no selectivity between the *cis* and *trans* final products according to computations, the protonation of the alkene function (*trans* or *cis* relatively to the ester) and the following hydride transfer exhibiting quite low barriers of 2-3 kcal/mol.



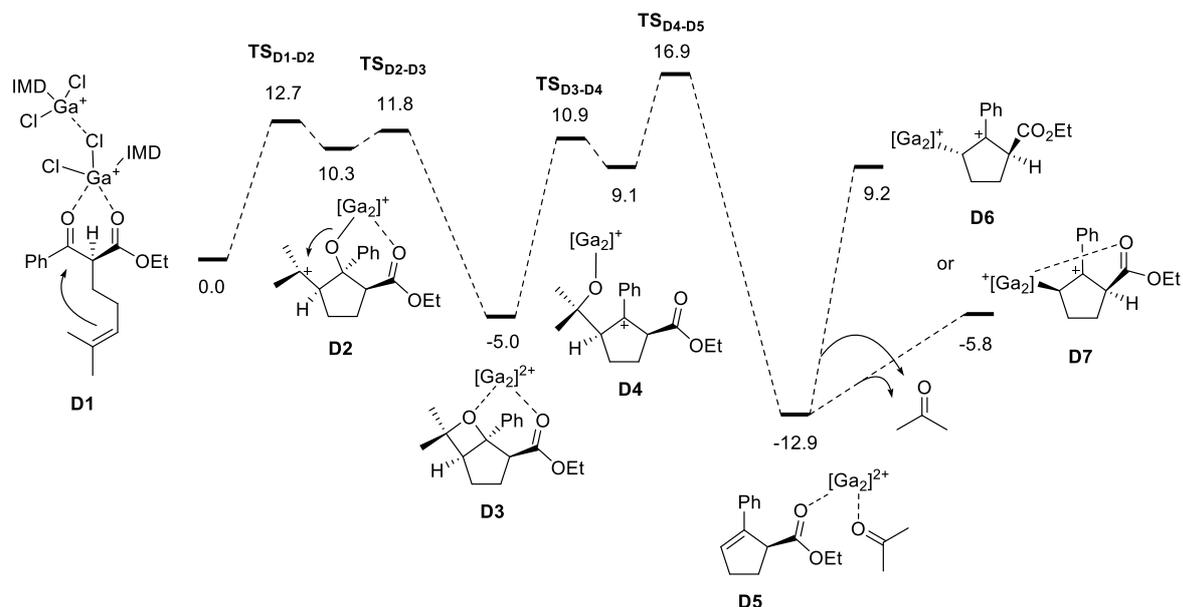
Scheme S5. $[(\text{IMD})\text{GaCl}_2]^+$ -catalyzed Transfer Hydrogenation of the Carbonyl-Olefin Metathesis Product through a Gallium Hydride Species: **Hypothesis 3a**

We next studied a mechanistic hypothesis that would neither involve the protonolysis of a $\text{C}_{sp^3}\text{-Ga}$ bond nor the formation of a Ga-H bond. We supposed that the coordination of the $[\text{Ga}]^+$ fragment to 1,4-cyclohexadiene might increase its acidity and allow a direct proton transfer to the alkene function of the metathesis product. However, the barriers for the *trans* or *cis* proton transfer to give **M10** or **M12** respectively were still significantly high, actually close to 30 kcal/mol when referenced to **M4**. This means that a direct proton transfer remains more favorable (Scheme S4, 18.7 kcal/mol). It is yet interesting to note that this hypothesis leads to the experimentally observed *cis* diastereomer. Due to the steric hindrance on the ester side, the hydride transfer from the large cyclohexadienyl gallium complex became impossible to model, suggesting that **M11** is obtained more easily than **M13**.



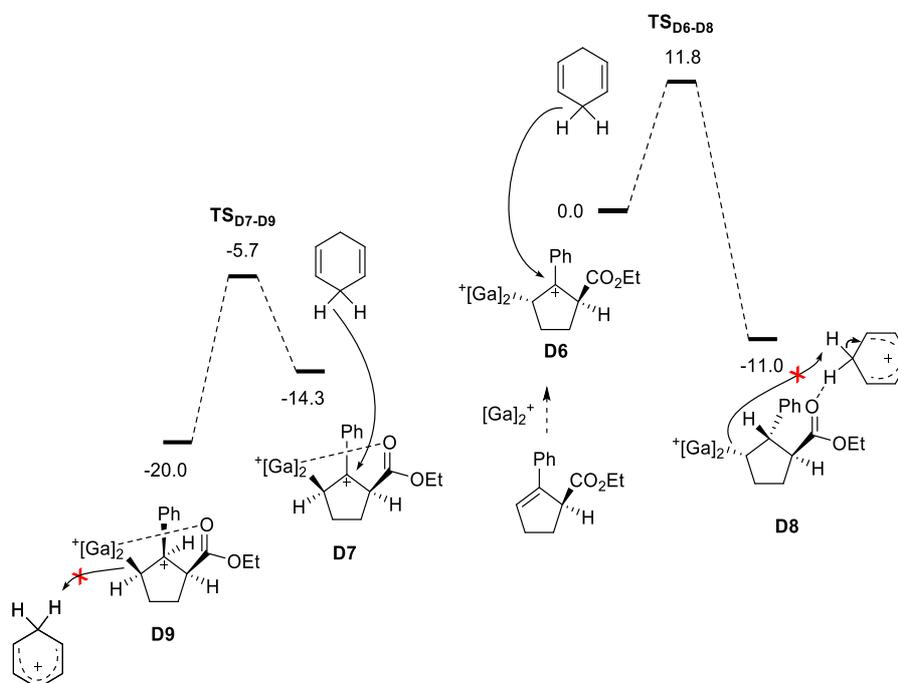
Scheme S6. $[(\text{IMD})\text{GaCl}_2]^+$ -catalyzed Transfer Hydrogenation of the Carbonyl-Olefin Metathesis Product by Activation of 1,4-cyclohexadiene: **Hypothesis 4a**

Because the energy profiles of the carbonyl-Olefin metathesis (Scheme S3) and of the three above transfer hydrogenation hypotheses (Schemes S4-S6) were not convincing, we reinvestigated these pathways using the superelectrophilic $\{[(\text{IMD})\text{GaCl}_2]_2\}^{2+}$ active species (noted $[\text{Ga}_2]^{2+}$). In such a complex, a $[(\text{IMD})\text{GaCl}_2]^+$ unit is bonded to a chlorine atom of another, which is likely to increase its electrophilicity (Scheme S7).¹⁷ Indeed, the effect of the coordination of an additional $[(\text{IMD})\text{GaCl}_2]^+$ now allows the formation of the chelate complex **D1** in which one gallium atom is pentavalent. The [2+2] process is not concerted anymore and first leads to the tertiary carbocation **D2**. This step is endergonic, but the corresponding transition state was found lying at only 12.7 kcal/mol on the free energy surface. The formation of a C-O bond to give chelate **D3** follows at the expense of only 1.5 kcal/mol of free energy of activation from **D2**. This complex is more stable than **D1** by 5.0 kcal/mol. The elimination of acetone is also a two-step process. It starts with the cleavage of the C-O bond to give carbocation **D4**. The transition state and **D4** were located at 10.9 and 9.1 kcal/mol on the free energy surface respectively. Cleavage of the C-C is then achieved through **TS_{D4-D5}**, which is the highest-lying transition state, located at 16.9 kcal/mol. The resulting complex **D5** unites the metathesis product and acetone at the gallium cluster. This complex is more stable than **D1** by 12.9 kcal/mol. Elimination of acetone leads to the *trans* complex **D6** found at 9.2 kcal/mol, or to the *syn* complex **D7** lying at -5.8 kcal/mol. The latter is stabilized by the coordination of the ester carbonyl to gallium, a situation that was not possible with only one $[(\text{IMD})\text{GaCl}_2]^+$ unit.



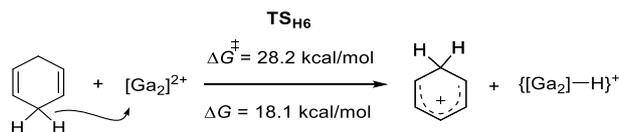
Scheme S7. Free Energies Profile of the $\{[(\text{IMD})\text{GaCl}_2]_2\}^{2+}$ -catalyzed Carbonyl-Olefin Metathesis (ΔG , kcal/mol): **Hypothesis 1b**

Again, the transfer of a hydride from 1,4-cyclohexadiene to **D6** or **D7** could not be achieved on the gallium side due to the steric hindrance. On the opposite side, both transfers could be modeled (Scheme S8). Of note, because of the possible formation of a chelate in this digallium series, **D7** is 14.3 kcal/mol more stable than **D6**. The hydride transfer transition states were found at 11.8 and -5.7 kcal/mol for **D6** and **D7** respectively. These steps are exergonic this time. However, these pathways are dead-end since the protodegallation proved unworkable because of the steric demand on the gallium cluster side.



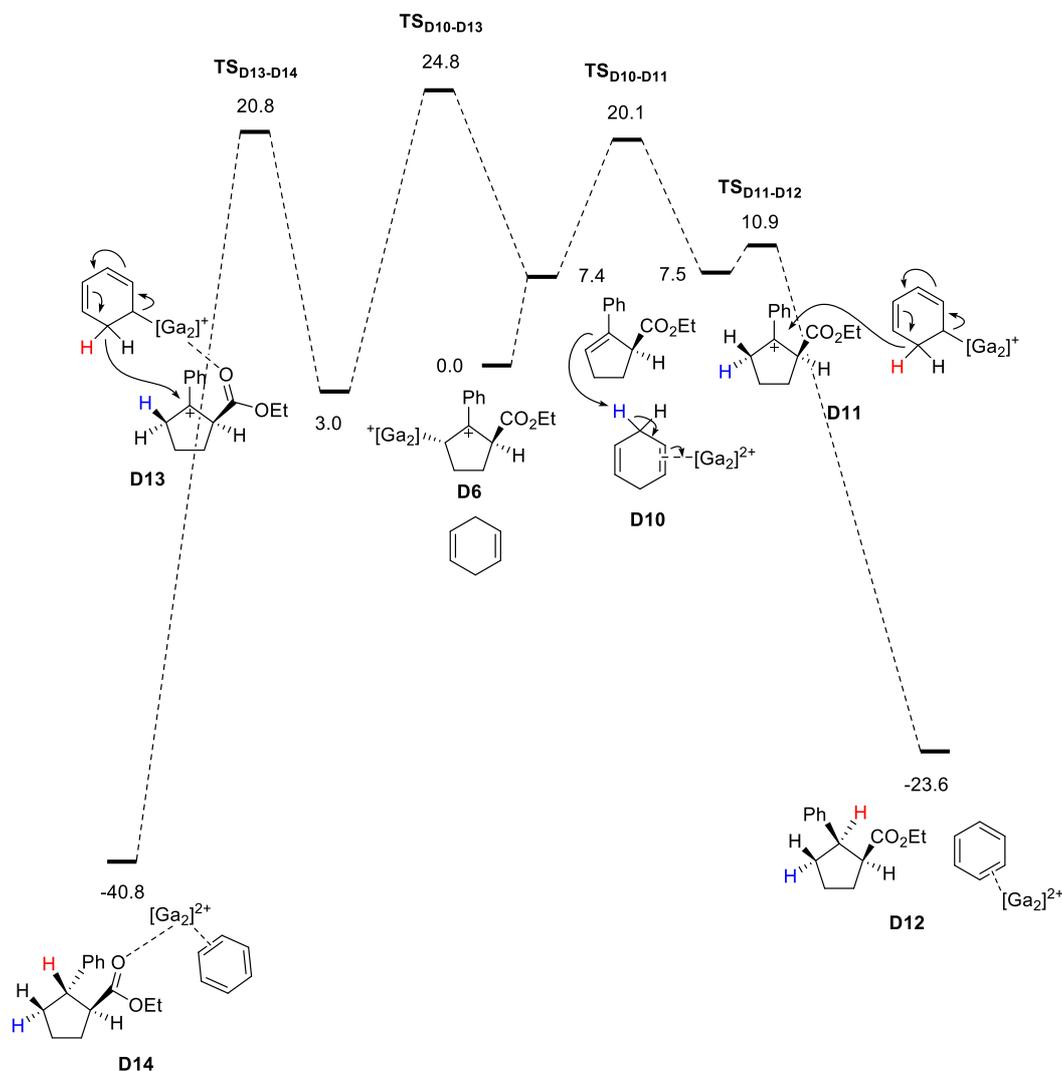
Scheme S8. Free Energies Profile of the $\{[\text{GaCl}_2(\text{IMD})]_2\}^{2+}$ -catalyzed Transfer Hydrogenation of the Carbonyl-Olefin Metathesis Product (ΔG , kcal/mol): **Hypothesis 2b**

The formation of a gallium hydride also remained an unfavorable process within the two gallium series (Scheme S9).



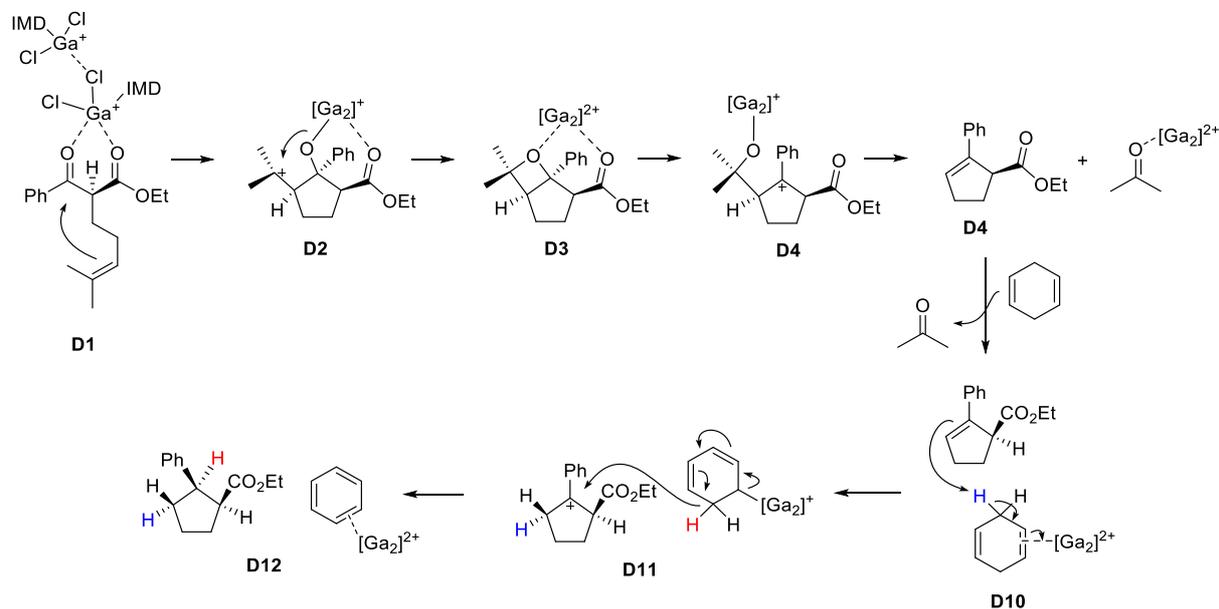
Scheme S9. Formation of a through a Di-Gallium Hydride Species: **Hypothesis 3b**

We finally revisited the mechanistic hypothesis that involves the activation of cyclohexadiene by coordination. Compared to the mono-gallium series presented in Scheme S6, there is now a more efficient activation, as shown by the lower free energies of activation for the proton and the hydride transfers. The slowest step is the protonation of the alkene, which has to overcome a barrier of 20.1 kcal/mol on its less hindered face, or of 24.8 kcal/mol on its more crowded one. From **D11**, the hydride transfer requires a low free energy of activation of 3.4 kcal/mol to reach **TS_{D11-D12}**, located 10.9 kcal/mol above **D6**. The hydride transfer from **D13** on the other hand requires 17.8 kcal/mol of free energy of activation (20.8 kcal/mol from **D6**). Thus, this hypothesis becomes viable and rationalize the stereoselectivity observed in this reaction.



Scheme S10. $\{[(\text{IMD})\text{GaCl}_2]_2\}^{2+}$ -Catalyzed Transfer Hydrogenation of the Carbonyl-Olefin Metathesis Product by Activation of 1,4-cyclohexadiene: **Hypothesis 4b**

In conclusion, the best mechanistic hypothesis involves the superelectrophilic species $\{[(\text{IMD})\text{GaCl}_2]_2\}^{2+}$, both for the carbonyl-olefin metathesis and the transfer hydrogenation. It involves the activation of cyclohexadiene, which becomes more acidic upon coordination to the gallium cluster and therefore able to protonate the alkene generated during the metathesis step. This pathway avoids the protodegallation of a strong $\text{Csp}^3\text{-Ga}$ bond. Scheme S11 summarizes the best mechanistic proposal arising from the computations.



Scheme S11. Preferred Mechanistic Hypothesis (Based on Hypotheses **1b** and **4b**).

The coordinates (x,y,z) of the computed species is available the “Computed Structures.xyz” file that allows to see them in 3 dimensions with usual softwares such as Mercury.

9 References

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