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Supplementary Information Caesium Fluoride-Mediated Hydrocarboxylation of Alkenes and Allenes: Scope and Mechanistic Insights

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General considerations

Commercially available starting materials, reagents, catalysts and anhydrous and degassed solvents were used without further purification. Flash column chromatography was performed with Merck silica gel 60 (230-400 mesh). The solvents for column chromatography were distilled before use. Thin layer chromatography was carried out using Merck TLC Silica gel 60 F_{254} and visualized by short-wavelength ultraviolet light or by treatment with potassium permanganate (KMnO₄) stain. ¹H, ¹³C and ¹⁹F NMR spectra were recorded on a Bruker Avance 400 MHz at 20°C. All ¹H NMR spectra are reported in parts per million (ppm) downfield of TMS and were measured relative to the signals for CHCl₃ (7.26 ppm), methanol (4.87ppm, 3.31ppm) and DMSO (2.50 ppm). All ¹³C NMR spectra were reported in ppm relative to residual CDCl₃ (77.20 ppm), methanol (49.1 ppm) or DMSO (39.70 ppm) and were obtained with ¹H decoupling. Coupling constants, *J*, are reported in Hertz (Hz). High-resolution mass spectra (HRMS) were recorded from methanol solutions on an LTQ Orbitrap XL (Thermo Scientific) either in negative or in positive electrospray ionization (ESI) mode. Chromatographic analysis was performed on a Waters Acquity UPC² system, equipped with a Torus DIOL column (2.1 mm x 50 mm, 130 Å, 1.7 µmeter) and coupled to QDa Detector with electrospray ionisation (ESI) and single-quadropole mass detector. The mobile phase for SFC analysis was a gradient of MeOH + 0.5% Ammonia solution (25%) in supercritical CO₂ over 2.0 min (gradient 0-20%). Melting points were measured using Stuart SMP50 automatic melting point detector.

Warning!

Most of the reactions were performed in specialized glassware under pressure. The glassware should always be examined for damages before any manipulation. All laboratory safety procedures must be followed strictly and the work with pressure tubes must be conducted behind a shield.

Optimization of reaction

General experimental procedure. For general setup, see Figure S1-S4.

Inside of glove box 45 mL pressure tube was charged with *trans*-stilbene (0.444 mmol), (9-BBN)₂ (1 equiv.) and corresponding dry solvent (3 mL). The flask was closed with suitable cap, removed from the glove box and heated to 70°C for 24h. Afterwards, the pressure tube was transferred back to the glove box. To the reaction mixture at 20°C was added the base (0-3 equiv.) and (in case of Cu-catalysed experiments) previously prepared solution of catalyst (the mixture of CuI (5 mol%), IPrHCl (6 mol%) and NaO*t*Bu (6 mol%) in appropriate dry solvent (1 mL) was stirred at 20°C for 30 min). The pressure tube was closed with the cap and removed from the glove box. Afterwards CO_2 (120 mL) was added *via* a syringe, which was followed by stirring of reaction mixture at 120°C for 24h. Next, the reaction mixture was diluted with 15 mL Et₂O and transferred into 250 mL separating funnel. The resulting mixture was extracted with 15 mL saturated basic (NaHCO₃, 1M KOH) solution (3 times). Resulting basic solution was washed with 10 mL Et₂O (once), acidified (25-30 mL 6M HCl) and extracted with 15 mL Et₂O (3 times). The resulting solution of Et₂O was distilled to dryness to give corresponding acid.

In cases of diglyme, triglyme and PEG400 the final Et₂O solution was washed with 10 mL distilled water (3 times) before evaporation.

Table S1. Reaction Optimization.^a



Entry	Catalyst (mol%)	Ligand (mol%)	Additive (mol%)	Base (equiv.)	Solvent	T, ⁰C	h	Yield % ^b
1	CuI	IPrHCl	NaOtBu	CsF (3)	Dioxane	120	24	78
2	-	-	-	CsF (3)	Dioxane	120	24	83
3	-	-	-	CsF (3)	THF	120	24	61
4	-	-	-	CsF (3)	Diglyme	120	24	67
5	-	-	-	CsF (3)	Triglyme	120	24	64
6	-	-	-	CsF (3)	PEG400	120	24	0
7	-	-	-	CsF (3)	DME	120	24	87
8	-	-	-	CsF (3)	DMA	120	24	0
9	-	-	-	CsF (3)	MeCN	120	24	0
10	-	-	-	CsF (3)	Toluene	120	24	70
11	-	-	-	CsF (3)	Cyclohexane	120	24	12
12	-	-	-	CsF (3)	ODCB	120	24	65
13	-	-	-	CsF (3)	DCE	120	24	0
14	-	-	-	CsF (3)	CCl ₄	120	24	0
15	-	-	-	$Cs_2CO_3(3)$	DME	120	24	71
16	-	-	-	CsOAc (3)	DME	120	24	34
17	-	-	-	Rb ₂ CO ₃ (3)	DME	120	24	65
18	-	-	-	KF (3)	DME	120	24	50

19	-	-	-	KOtBu (3) ^c	DME	120	24	47
20	-	-	-	K ₂ CO ₃ (3)	DME	120	24	67
21	-	-	-	K ₃ PO ₄ (3)	DME	120	24	0
22	-	-	-	NaOtBu (3) ^c	DME	120	24	33
23	-	-	-	NaF (3)	DME	120	24	0
24	-	-	-	CsF (2)	DME	120	24	57
25	-	-	-	-	DME	120	24	0
26	-	-	-	CsF (3)	DME	80	24	59
27	-	-	-	CsF (3)	DME	80	72	74
28	-	-	-	CsF (3)	DME	120	16	78
29	-	-	-	CsF (3)	DME	120	28	85
30	CuI (5)	IPrHCl (6)	NaOtBu (6)	CsF (3)	DME	120	24	86

^a Reaction conditions: 1) 1a (0.444 mmol), (9-BBN)₂ (1 equiv.), Solvent (3 mL), 70°C, 24h. 2) (CuI (5 mol%), IPrHCl (1,3-bis(2,6-

diisopropylphenyl)imidazolium chloride, 6 mol%), NaOtBu (6 mol%)), base (0-3 equiv.), CO₂ 120 mL, 80-120°C, 16-72h. ^b Isolated yields. ^c Before addition of CO₂ the reaction mixture, containing the base, was mixed at 20°C for 30 min.



Control experiments for comparison with Cu-containing conditions Cul (5 mol%), IPrHCl (6 mol%), NaOtBu (6 mol%) Me Me Cs₂CO₃ (2 equiv.), DME, 120°C, 24h CO₂H CO₂H 3j 3j 95% recovery Cs₂CO₃ (2 equiv.), DME, 120°C, 24h Me Me CO₂H CO₂H 3j 3j 99% recovery

Scheme S1. Control experiments on Cu-catalysed decarboxylation.



Scheme S2. Cu-catalysed hydrocarboxylation of indene and 1,2-dihydronaphthalene.

Starting material used in the study



Scheme S3. List of starting materials used in the work.

Control experiments on benzylboronic esters

(A) CsF-mediated carboxylation of benzylboronic acid pinacol ester



(B) Control experiment on LiBH4-catalysed hydroboration using catecholborane



(C) CsF-mediated hydrocarboxylation using catecholborane



Scheme S4. Control experiments on benzylboronic esters.

Carboxylation of enantiomerically enriched organoborane

(A) Asymmetric hydroboration-oxidation of trans-ß-methylstyrene



Scheme S5. Asymmetric hydroboration-oxidation of *trans*- β -methylstyrene (A) and carboxylation of enantiomerically enriched organoborane intermediate (B).

${\it Setup of the reaction}$



Figure S1. 45mL pressure tube with suitable stabilizer and septa.





Figure S2. 45mL pressure tube with suitable stabilizer and septa.

Figure S3. Syringe with CO₂ ready for injection.



Figure S4. First injection of CO₂.





Figure S5. Gram scale hydrocarboxylation in diglyme.

General procedures

Preparation of starting materials for 2e, 3b, 3c, 3d and 6b by Wittig reaction.



50mL round bottom flask was charged with phosphonium salt (1.2 equiv.), sealed with a rubber septa, evacuated and back filled with Ar. Afterwards, an Ar balloon was added to the system followed by addition of dry THF (15 mL). The reaction mixture was transferred into isopropanol bath (-78°C), which was followed by addition of BuLi (2.5M in hexanes, 1.2 equiv., dropped). The reaction mixture was allowed to reach 20°C. Next, it was transferred back to the isopropanol bath (-78°C), which was followed by addition of carbonyl compound (6 mmol, solid carbonyl compounds were dissolved in 4-6 mL dry THF before addition). Further, the reaction mixture was allowed to reach 20°C where it was stirred for 12h. The formed mixture was evaporated to dryness and purified by column chromatography.

Preparation of starting material for 3e.



50mL round bottom flask was charged with cinnamyl alcohol (7.5 mmol), sealed with a rubber septa, evacuated and beck filled with Ar. An Ar balloon was added to the system, which was followed by addition of dry THF (15 mL). The reaction mixture was transferred into isopropanol bath (-78°C), which was followed by addition of BuLi (2.5M in hexanes, 1 equiv., dropped). The reaction mixture was allowed to reach 20°C. Afterwards, the reaction mixture was transferred back to the isopropanol bath (-78°C) that was followed by addition of benzoyl chloride (1.2 equiv., dropped). The reaction mixture was allowed to reach 20°C and was stirred at 20°C for 6h. Afterwards, the reaction mixture was evaporated to dryness and purified by column chromatography.

Preparation of starting materials for 5d-f.¹



Step 1: To the stirring mixture of corresponding styrene (50 mmol), bromoform (2 equiv.), and TBAB (0.1 equiv.) in 50 mL round bottom flask was added sodium hydroxide (2 equiv.) in water (7.5 mL, dropped). The resulting mixture was stired at 50°C for 8h. Next, the reaction was quenched with brine (50 mL) and extracted with DCM (3×50 mL). Combined organic fractions were washed with brine (50 mL), evaporated to dryness and used for the next step without purification.

Step 2: To a stirred solution of gem-dibromocyclopropane in dry THF (40 mL), was added EtMgBr (1.1 equiv., 1M in THF). The reaction mixture was stirred at 20°C for 1.5h. Next, the reaction was quenched with brine (10 mL) that was followed by addition of 6M HCl (50 mL) and extraction using Et₂O (3×50 mL). The resulting solution of Et₂O was dried (Na₂SO₄) and evaporated. The resulting mixture was purified by column chromatography.

General procedure for metal-free hydrocarboxylation of stilbenes and 8-substituted styrenes. For general setup, see Figure S1-S4.

R¹
$$R^2$$
 R^2 R^2

Inside of glove box 45 mL pressure tube was charged with corresponding olefin (1.5 mmol), $(9\text{-BBN})_2$ (1 equiv.) and dry DME (7 mL). The flask was closed with suitable cap, removed from the glove box and heated to 70°C for 24h. Afterwards, the pressure tube was transferred back to the glove box. To the reaction mixture at 20°C was added CsF (3 equiv.). The pressure tube was closed with the cap and removed from the glove box. Afterwards CO₂ (120 mL) was added *via* a syringe, which was followed by stirring of reaction mixture at 120°C for 24h. Next, the reaction mixture was diluted with 30 mL Et₂O and transferred into 500 mL separating funnel. The resulting mixture was extracted with 30 mL saturated basic (NaHCO₃, 1M KOH) solution (3 times). Resulting basic solution was washed with 15 mL Et₂O (once), acidified (50-55 mL 6M HCl) and extracted with 30 mL Et₂O (3 times). The resulting solution of Et₂O was distilled to dryness to give corresponding acid.

¹ K. Semba, M. Shinomiya, T. Fujihara, J. Terao and Y. Tsuji, <u>Chem. Eur. J.</u>, 2013, **19**, 7125-7132.

General procedure for metal-free hydrocarboxylation of allenes. For general setup, see Figure S1-S4.



Inside of glove box 45 mL pressure tube was charged with corresponding allene (1.5 mmol), (9-BBN)₂ (0.7 equiv.) and dry DME (7 mL). The flask was closed with suitable cap, removed from the glove box and heated to 50°C for 24h (in case of **5c** this step was runned at 20°C). Afterwards, the pressure tube was transferred back to the glove box. To the reaction mixture at 20°C was added CsF (3 equiv.). The pressure tube was closed with the cap and removed from the glove box. Afterwards CO_2 (120 mL) was added *via* a syringe, which was followed by stirring of reaction mixture at 120°C for 24h. Next, the reaction mixture was diluted with 30 mL Et₂O and transferred into 500 mL separating funnel. The resulting mixture was extracted with 30 mL saturated basic (NaHCO₃, 1M KOH) solution (3 times). Resulting basic solution was washed with 15 mL Et₂O (once), acidified (50-55 mL 6M HCl) and extracted with 30 mL Et₂O (3 times). The resulting solution of Et₂O was distilled to dryness to give corresponding acid (in case of **5c** the final solution of Et₂O was dried using Na₂SO₄, which was followed by careful evaporation of solvents).

General procedure for preparation of Butetamate.



Inside of glove box 45 mL pressure tube was charged with *trans*- β -methylstyrene (1.5 mmol), (9-BBN)₂ (1 equiv.) and dry DME (7 mL). The flask was closed with suitable cap, removed from the glove box and heated to 70°C for 24h. Afterwards, the pressure tube was transferred back to the glove box. To the reaction mixture at 20°C was added CsF (3 equiv.). The pressure tube was closed with the cap and removed from the glove box. Afterwards CO₂ (120 mL) was added *via* a syringe, which was followed by stirring of reaction mixture at 120°C for 24h. Next, the reaction mixture was diluted with 30 mL Et₂O and transferred into 500 mL separating funnel. The resulting mixture was extracted with 30 mL saturated basic (NaHCO₃, 1M KOH) solution (3 times). Resulting basic solution was washed with 15 mL Et₂O (once), acidified (50-55 mL 6M HCl) and extracted with 30 mL Et₂O (3 times). The resulting solution of Et₂O was distilled to dryness to give corresponding acid.

An oven dried 25mL Schlenk flask was charged with the acid, sealed with rubber septa, evacuated and beck filled with Ar (3 times). Next, an Ar balloon was added to the system, which was followed by addition of dry DCM (4 mL), dry DMF (0.5 equiv) and SOCl₂ (1.2 equiv., dropwise). The reaction mixture was stirred at 20°C for 3h that was followed by removal of volatiles and addition of dry THF (4 mL). To the resulting mixture at 0°C was added (dropwise) previously prepared solution of corresponding alkoxide (at 0°C, under Ar atmosphere to the solution of 2-(diethylamino)ethanol (1.4 equiv.) in dry THF (4 mL) was added BuLi (2.5M in hexanes, 1.4 equiv., dropped), which was followed by stirring of the reaction mixture at 20°C for 30 min). The resulting mixture was stirred at 20°C for 6h, evaporated to dryness and purified using column chromatography.

General procedure for preparation of Butibufen.



Inside of glove box 45 mL pressure tube was charged with corresponding olefin (1.148 mmol), $(9\text{-BBN})_2(1 \text{ equiv.})$ and dry DME (5 mL). The flask was closed with suitable cap, removed from the glove box and heated to 70°C for 24h. Afterwards, the pressure tube was transferred back to the glove box. To the reaction mixture at 20°C was added CsF (3 equiv.). The pressure tube was closed with the cap and removed from the glove box. Afterwards CO₂ (120 mL) was added *via* a syringe, which was followed by stirring of reaction mixture at 120°C for 24h. Next, the reaction mixture was diluted with 30 mL Et₂O and transferred into 500 mL separating funnel. The resulting mixture was extracted with 30 mL saturated basic (NaHCO₃, 1M KOH) solution (3 times). Resulting basic solution was washed with 15 mL Et₂O (once), acidified (50-55 mL 6M HCl) and extracted with 30 mL Et₂O (3 times). The resulting solution of Et₂O was distilled to dryness to give corresponding acid.

General procedure for gram scale hydrocarboxylation of *trans*-stilbene. For general setup, see Figure S5.



Inside of glove box 50 mL Schlenk flask was charged with *trans*-stilbene (1.5 g, 8.322 mmol), $(9-BBN)_2(1 \text{ equiv.})$ and dry Diglyme (18 mL). The flask was closed with rubber septa, removed from the glove box and heated to 70°C for 24h. Afterwards, the flask was transferred back to the glove box. To the reaction mixture at 20°C was added CsF (3.792 g.). The flask was closed with rubber septa and removed from the glove box. Next, the flask was carefully evacuated (once), which was followed by addition of CO₂ balloon. The reaction mixture was stirred

at 120°C for 24h. Further, the reaction mixture was diluted with 90 mL Et_2O and transferred into 1000 mL separating funnel. The resulting mixture was extracted with 90 mL saturated basic (NaHCO₃, 1M KOH) solution (3 times). Resulting basic solution was washed with 45 mL Et_2O (once), acidified (160 mL 6M HCl) and extracted with 90 mL Et_2O (3 times). The resulting solution of Et_2O was washed with 30 mL distilled water (3 times) and evaporated to dryness to give corresponding acid.

General procedure for Cu-catalysed hydrocarboxylation of indene and 1,2-dihydronaphthalene. For general setup, see Figure S1-S4.



Inside of glove box 45 mL pressure tube was charged with corresponding olefin (1.5 mmol), (9-BBN)₂ (1 equiv.) and dry DME (5 mL). The flask was closed with suitable cap, removed from the glove box and heated to 70°C for 24h. Afterwards, the pressure tube was transferred back to the glove box. To the reaction mixture at 20°C was added CsF (3 equiv.) and previously prepared solution of catalyst (the mixture of CuI (5 mol%), IPrHCl (6 mol%) and NaOtBu (6 mol%) in dry DME (2 mL) was stirred at 20°C for 30 min). The pressure tube was closed with the cap and removed from the glove box. Afterwards CO_2 (120 mL) was added *via* a syringe, which was followed by stirring of reaction mixture at 120°C for 24h. Next, the reaction mixture was diluted with 30 mL Et₂O and transferred into 500 mL separating funnel. The resulting mixture was extracted with 30 mL saturated basic (NaHCO₃, 1M KOH) solution (3 times). Resulting basic solution was washed with 15 mL Et₂O (once), acidified (50-55 mL 6M HCl) and extracted with 30 mL Et₂O (3 times). The resulting solution of Et₂O was distilled to dryness to give corresponding acid.

Control experiment on Cu-catalysed decarboxylation.



Inside of glove box 45 mL pressure tube was charged with 2-phenylpropionic acid (1.5 mmol), DME (5 mL), Cs_2CO_3 (2 equiv.) and previously prepared solution of catalyst (the mixture of CuI (5 mol%), IPrHCl (6 mol%) and NaO*t*Bu (6 mol%) in dry DME (2 mL) was stirred at 20°C for 30 min). The pressure tube was closed with the cap and removed from the glove box, which was followed by stirring of reaction mixture at 120°C for 24h. Next, the reaction mixture was diluted with 30 mL Et₂O and transferred into 500 mL separating funnel. The resulting mixture

was extracted with 30 mL saturated basic (NaHCO₃, 1M KOH) solution (3 times). Resulting basic solution was washed with 15 mL Et_2O (once), acidified (50-55 mL 6M HCl) and extracted with 30 mL Et_2O (3 times). The resulting solution of Et_2O was distilled to dryness to give corresponding acid.

Control experiment on Cu-free decarboxylation.



Inside of glove box 45 mL pressure tube was charged with 2-phenylpropionic acid (1.5 mmol), DME (5 mL) and Cs_2CO_3 (2 equiv.). The pressure tube was closed with the cap and removed from the glove box, which was followed by stirring of reaction mixture at 120°C for 24h. Next, the reaction mixture was diluted with 30 mL Et₂O and transferred into 500 mL separating funnel. The resulting mixture was extracted with 30 mL saturated basic (NaHCO₃, 1M KOH) solution (3 times). Resulting basic solution was washed with 15 mL Et₂O (once), acidified (50-55 mL 6M HCl) and extracted with 30 mL Et₂O (3 times). The resulting solution of Et₂O was distilled to dryness to give corresponding acid.

Control experiment on LiBH₄-catalysed hydroboration using catecholborane.



Inside of glove box 25 mL round bottom flask was charged with *trans*-stilbene (1.110 mmol), catecholborane (1.5 equiv.), DME (6 mL) and LiBH₄ (10 mol%). The flask was closed with a rubber septa, removed from the glove box and stirred at 20°C for 12h. Afterwards, the reaction mixture was transferred into 250 mL round bottom flask. To the mixture sequentially were added EtOH (15 mL), 1M NaOH (15 mL) and aq. H_2O_2 (30%, 12 mL). The resulting mixture was stirred at 20°C for 18h. Then it was quenched with aq. $Na_2S_2O_3$ (10%, 60 mL). This was followed by extraction using 40 mL DCM (3 times). The organic fractions were collected, evaporated to dryness and purified using column chromatography.

Asymmetric hydroboration-oxidation of *trans*-ß-methylstyrene.



Inside of glove box, a 45 mL pressure tube was charged with (-)-isopinocampheylborane TMEDA complex ((-)-(Ipc-BH₂)₂xTMEDA) (1.0 mmol) and BF₃xTHF (1.0 mmol) in dry DME (2 mL). The flask was closed with suitable cap, removed from the glove box and stirred for 1h. *Trans*-beta-methylstyrene (0.5 mmol) was added with syringe and heated to 70°C for 20h. To the intermediate borane compound was added 1 mL 3M NaOH and 0.5 mL H₂O₂ and reacted 10 min. The phases were allowed to settle and the organic phase was removed. The aqueous phase was extracted with 1 mL EtOAc and the organic phase was filtered through a pad of Na₂SO₄ and evaporated. The residue was purified by automated flash chromatography on a 10g Biotage SNAP column with a 0-30% EtOAc in heptane gradient. The resulting blank oil is 1-phenylpropanol in an approximate 3:1 mixture with oxidized (-)-Ipc reagent shown by NMR. Chiral SFC was performed using Waters Trefoil CEL2 (2.5 µm, 3.0 x 150 mm), backpressure: 1500 psi, column temperature 40°C, mobile phase B: 1:1:1 EtOH:*i*PrOH:MeCN with 20 mM NH₄OAc. Gradient 1-6 % 4.5 min, 6 % 1.5 min. The 1-phenylpropanol has an *ee* of 36% and the (-)-Ipc reagent is invisible by UV detection.

Carboxylation of enantiomerically enriched organoborane intermediate.



Inside of glove box, a 45 mL pressure tube was charged with (-)-isopinocampheylborane TMEDA complex ((-)-(Ipc-BH₂)₂xTMEDA) (1.0 mmol) and BF₃xTHF (1.0 mmol) in dry DME (2 mL). The flask was closed with suitable cap, removed from the glove box and stirred for 1h. *Trans*-beta-methylstyrene (0.5 mmol) was added with syringe and heated to 70°C for 20h. The pressure tube was then transferred back to the glove box where at 20°C was added CsF (3 equiv.). The pressure tube was closed with the cap and removed from the glove box. Afterwards CO_2 (120 mL) was added *via* a syringe, which was followed by stirring of reaction mixture at 120°C for 19h. Next, the reaction mixture was diluted with 30 mL Et₂O and transferred into a 250 mL separating funnel. The resulting mixture was extracted with 15 mL 1M KOH solution (3 times). The resulting basic solution was washed with 30 mL Et₂O, acidified (30 mL 2M HCl) and extracted with 15 mL Et₂O (3 times). The resulting solution of Et₂O was dried with Na₂SO₄ and distilled to dryness.

The acid base extraction after carboxylation yields an approximate 2:2:1 ratio of 2-phenylbutyric acid, 1-phenylpropanol and oxidized (-)-Ipc reagent, determined by NMR. SFC was performed with Waters Trefoil CEL1 (2.5 μ m, 3.0 x 150 mm), backpressure: 1500 psi, column temperature 40°C, mobile phase B: 1:1 MeOH:*i*PrOH with 20 mM TFA. Gradient 1-10 % 4.5 min, 10 % 1.5 min. The 2-phenylbutyric acid has 0.9% *ee* and the 1-phenylpropanol has 15% *ee* (favoring the same enantiomer as for the oxidized intermediate). Note that the retention of 2-phenylbutyric acid varies between runs with up to 0.5 min.

Characterization of products



1-Fluoro-4-(1-(p-tolyl)prop-1-en-2-yl)benzene, mixture of stereoisomers, 1e. Starting from 10.86 mmol of corresponding carbonyl compound the product was obtained as a colourless viscous oil as a 1:1 mixture of isomers, yield 99% (2.444 g). ¹H NMR (400 MHz, CDCl₃): δ = 2.18 (d, 1.5H, *J* = 1.6 Hz, Me), 2.26-2.27 (m, 3H, Me), 2.38 (s, 1.5H, Me), 6.45-6.46 (m, 0.45H, olefin), 6.76 (s, 0.49H, olefin), 6.84 (d, *J* = 8.1 Hz, 1H, Ar), 6.92-7.00 (m, 2H, Ar), 7.03-7.09 (m, 1H, Ar), 7.13-7.21 (m, 2H, Ar), 7.24-7.28 (m, 1H, Ar), 7.46-7.51 (m, 1H, Ar).

¹³**C NMR** (101 MHz, CDCl₃): δ = 17.8, 21.3, 21.4, 27.2, 115.1, 115.3, 115.4, 115.6, 127.0, 127.6, 127.7, 127.8, 128.9, 129.0, 129.1, 129.2, 130.0, 130.1, 134.7, 135.5, 135.9, 136.1, 136.5, 136.8.



1-Fluoro-4-(prop-1-en-1-yl)benzene, mixture of stereoisomers, 1g.² Starting from 12.09 mmol of corresponding carbonyl compound the product was obtained as a colorless liquid as a 1:3 mixture of isomers, yield 90% (1.487 g). ¹H NMR (400 MHz, CDCl₃): $\delta = 1.88$ -1.91 (m, 3H, Me), 5.80 (dq, J = 11.6, 7.2 Hz, 0.27H, olefin), 6.17 (dq, J = 15.7, 6.6 Hz, 0.74H, olefin), 6.36-6.43 (m, 1H, olefin), 6.97-7.07 (m, 2H, Ar), 7.26-7.33 (m, 2H, Ar). ¹³C NMR

 $(101 \text{ MHz}, \text{CDCl}_3): \delta = 14.7, 18.6, 115.0, 115.3, 115.4, 115.6, 125.5, 125.6, 126.8, 127.3, 127.4, 129.0, 130.0, 130.5, 130.6, 134.3, 160.8, 163.3.$



1-Methoxy-4-(prop-1-en-1-yl)benzene, mixture of stereoisomers, 1h.³ Starting from 11.02 mmol of corresponding carbonyl compound the product was obtained as a colorless liquid as a 1:9 mixture of isomers, yield 94% (1.534 g). ¹H NMR (400 MHz, CDCl₃): $\delta = 1.85$ -1.91 (m, 3H, Me), 3.80-3.82 (m, 3H, OMe), 5.71 (dq, J = 11.5, 7.2 Hz, 0.11H, olefin), 6.10 (dq, J = 15.7, 6.6 Hz, 0.9H, olefin), 6.33-6.40 (m, 1H, olefin), 6.82-

6.90 (m, 2H, Ar), 7.24-7.35 (m, 2H, Ar).¹³**C NMR** (101 MHz, CDCl₃): $\delta = 18.6, 55.5, 113.7, 114.1, 123.7, 127.1, 130.2, 130.5, 131.0, 158.8.$



1-Methoxy-4-(4-phenylbut-1-en-1-yl)benzene, mixture of stereoisomers, 1i.⁴ Starting from 5.876 mmol of corresponding carbonyl compound the product was obtained as a colourless viscous oil as a 1:4 mixture of isomers, yield 83% (1.162 g). ¹H NMR (400 MHz, CDCl₃): δ = 2.51-2.58 (m, 1.57H, CH₂), 2.66-2.73 (m, 0.46H, CH₂), 2.79-2.84 (m, 2H, CH₂), 3.82-3.83 (m, 3H, OMe), 5.65 (dddd, *J* = 11.5, 8.8, 7.0, 2.3 Hz, 0.22H, olefin), 6.11-6.19 (m, 0.78H, olefin), 6.37-6.42 (m, 1H, olefin), 6.85-

²L. Zheng, F. Gao, C. Yang, G.-L. Gao, Y. Zhao, Y. Gao and W. Xia, *Org. Lett.* 2017, **19**, 5086-5089.

³I. R. Green and N. October, <u>ARKIVOC</u> 2010, 2, 71-96.

⁴S. Hajra, B. Maji and D. Mal, <u>Adv. Synth. Catal.</u> 2009, **351**, 859-864.

6.90 (m, 2H, Ar), 7.21-7.35 (m, 7H, Ar). ¹³**C NMR** (101 MHz, CDCl₃): δ = 30.6, 35.1, 36.2, 36.3, 55.4, 113.8, 114.1, 126.0, 126.1, 127.2, 128.0, 128.5, 128.6, 129.0, 129.9, 130.1, 130.4, 130.7, 142.1, 158.9.



Cinnamyl benzoate, **1j.**⁵ Starting from 7.453 mmol of cinnamyl alcohol the product was obtained as a colourless viscous oil, yield 95% (1.682 g). ¹H NMR (400 MHz, CDCl₃): $\delta = 4.78$ (dd, J = 6.4, 1.4 Hz, 2H, CH₂), 6.20 (dt, J = 15.9, 6.4 Hz, 1H, olefin), 6.54 (d, J = 15.9 Hz, 1H, olefin), 7.04-7.08 (m, 1H, Ar), 7.11-7.14 (m, 2H, Ar), 7.20-7.26 (m, 4H, Ar), 7.33-7.38 (m, 1H, Ar), 7.87-7.89 (m, 2H, Ar). ¹³C NMR (101 MHz, CDCl₃): $\delta = 65.7$, 123.5, 126.8, 128.3, 128.5, 128.6, 128.8, 129.7, 129.8, 130.4, 133.2, 134.4,

136.4, 166.6.



1-Isobutyl-4-(prop-1-en-1-yl)benzene, mixture of stereoisomers, 1m.⁶ Starting from 9.246 mmol of corresponding carbonyl compound the product was obtained as a colorless liquid, yield 94% (1.511 g). ¹H NMR (400 MHz, CDCl₃): δ = 0.94-0.97 (m, 6H, 2xMe), 1.84-1.97 (m, 4H, Me, CH), 2.48-2.52 (m, 2H, CH₂), 5.80 (dq, *J* = 11.5, 7.2 Hz, 0.21H, olefin), 6.24 (dq, *J* = 15.7, 6.6 Hz, 0.79H, olefin), 6.40-6.47 (m,

1H, olefin), 7.10-7.17 (m, 2H, Ar), 7.26-7.30 (m, 2H, Ar). ¹³**C** NMR (101 MHz, CDCl₃): $\delta = 14.9$, 18.6, 22.5, 22.6, 30.4, 45.3, 124.8, 125.7, 126.2, 128.8, 129.1, 129.4, 130.0, 131.1, 135.6, 140.5.



2,3-Diphenylpropanoic acid, 2a.⁷ Starting from 0.444 mmol of corresponding stilbene the product was obtained as a white solid, yield 87% (0.087 g), m.p. = 77-80°C. ¹H NMR (400 MHz, CDCl₃): δ = 3.13 (dd, *J* = 13.9, 7.0 Hz, 1H, CH₂), 3.50 (dd, *J* = 13.8, 8.4 Hz, 1H, CH₂), 3.95 (dd, *J* = 8.4, 7.0 Hz, 1H, CH), 7.17-7.21 (m, 2H, Ar), 7.24-7.33 (m, 3H, Ar), 7.34-7.41 (m, 5H, Ar), 11.45 (br s, 1H, CO₂H). ¹³C NMR (101 MHz, CDCl₃): δ = 39.4, 53.6, 126.6, 127.8, 128.3, 128.5, 128.9, 129.1, 138.1, 138.8, 179.7. HRMS-EI (m/z) [M-H]⁻ calcd. for C₁₅H₁₃O₂225.0921

found 225.0923.

⁵C.-T. Chen, J.-H. Kuo, V. D. Pawar, Y. S. Munot, S.-S. Weng, C.-H. Ku and C.-Y. Liu, *J. Org. Chem.* 2005, **70**, 1188-1197.

⁶S. Movahhed, J. Westphal, M. Dindaroglu, A. Falk and H.-G. Schmalz, <u>*Chem. Eur. J.*</u> 2016, **22**, 7381-7384.

⁷ M. Juhl, S. L. R. Laursen, Y. Huang, D. U. Nielsen, K. Daasbjerg and T. Skrydstrup, <u>ACS Catal.</u> 2017, 7, 1392-1396.



253.1229 found 253.1234.



2,3-Di-p-tolylpropanoic acid, 2b.⁸ Starting from 0.336 mmol of corresponding stilbene the product was obtained as a white solid, yield 91% (0.078 g), m.p. = 138-140°C. ¹H NMR (400 MHz, CDCl₃): δ = 2.31 (d, *J* = 14.7 Hz, 6H, 2xMe), 2.98 (dd, *J* = 13.9, 6.8 Hz, 1H, CH₂), 3.35 (dd, *J* = 13.9, 8.5 Hz, 1H, CH₂), 3.81 (dd, *J* = 8.5, 6.8 Hz, 1H, CH), 7.00-7.05 (m, 4H, Ar), 7.13 (d, *J* = 7.9 Hz, 2H, Ar), 7.21 (d, *J* = 8.1 Hz, 2H, Ar), 10.25 (br s, 1H, CO₂H). ¹³C NMR (101 MHz, CDCl₃): δ = 21.2, 21.3, 38.9, 53.2, 128.1, 128.9, 129.2, 129.6, 135.2, 135.9, 136.0, 137.5, 179.5. HRMS-EI (m/z) [M-H]⁻ calcd. for C₁₇H₁₇O₂

2,3-Bis(4-chlorophenyl)propanoic acid, 2c.⁸ Starting from 0.0803 mmol of corresponding stilbene the product was obtained as a white solid, yield 51% (0.012 g), m.p. > 200°C. ¹H NMR (400 MHz, MeOHd4): $\delta = 2.97$ (dd, J = 13.7, 7.6 Hz, 1H, CH₂), 3.30-3.35 (m, 1H, CH₂), 3.84 (t, J = 7.9 Hz, 1H, CH), 7.10-7.12 (m, 2H, Ar), 7.18-7.21 (m, 2H, Ar), 7.26-7.32 (m, 4H, Ar). ¹³C NMR (101 MHz, MeOH-d4): $\delta = 40.0$, 54.1, 129.4, 129.7, 130.9, 131.8, 133.3, 134.3, 139.1, 139.2. HRMS-EI (m/z) [M-H]⁻ calcd. for C₁₅H₁₁Cl₂O₂ 293.0136 found 293.0142.



2,3-Diphenylbutanoic acid, mixture of diastereomers, NMR-ratio 10:1, LC-MS-ratio 85:15, 2d. Starting from 0.772 mmol of corresponding stilbene the product was obtained as a white solid, yield 70% (0.130 g), m.p. = 128-131°C. ¹H NMR (400 MHz, CDCl₃): $\delta = 1.06$ (d, J = 6.7 Hz, 0.31H, Me of second diastereomere), 1.48 (d, J = 7.0 Hz, 3H, Me), 3.46-3.54 (m, 1H, CH), 3.74-3.80 (m, 1H, CH), 7.00-7.21 (m, 10H, Ar), 7.30-7.51 (m, 0.99H, Ar of second diastereomere), 11.40 (br s, 1H, CO₂H). ¹³C NMR (101 MHz, CDCl₃): $\delta = 20.2$, 21.3, 43.2, 43.6, 59.1, 59.4,

126.4, 126.9, 127.4, 127.5, 127.7, 128.0, 128.3, 128.4, 128.7, 128.8, 128.9, 129.0, 137.0, 143.4, 179.2, 180.1. **HRMS-EI** (m/z) $[M-H]^-$ calcd. for $C_{16}H_{15}O_2$ 239.1072 found 239.1076.



3-(4-Fluorophenyl)-2-(p-tolyl)butanoic acid, mixture of diastereomers, NMR-ratio 12:1, LC-MS-ratio 92:8, 2e. Starting from 0.884 mmol of corresponding stilbene the product was obtained as a white solid, yield 55% (0.133 g), m.p. = 148-151°C. ¹H NMR (400 MHz, CDCl₃): δ = 1.04 (d, *J* = 6.9 Hz, 0.24H, Me of minor diastereomere), 1.44 (dd, *J* = 6.7, 1.1 Hz, 3H, Me), 2.24 (s, 3H, Me), 2.38 (s, 0.26H, Me of minor diastereomere), 3.45-3.52 (m, 1H, CH), 3.65-3.70 (m, 1H, CH), 6.80-6.84 (m, 2H, Ar), 6.95-6.99 (m, 4H, Ar), 7.05-7.08 (m, 2H, Ar), 7.20-7.37 (m, 0.71H, Ar of minor diastereomere), 11.52 (br s, 1H, CO₂H). ¹³C

NMR (101 MHz, CDCl₃): δ = 20.2, 21.1, 21.3, 21.4, 30.5, 42.4, 42.7, 59.1, 59.3, 71.6, 115.1 (d, *J* = 21.2 Hz), 115.4, 115.6, 128.6, 128.7,

⁸ J. Dai, W. Ren, J. Li and Y. Shi, *Org. Chem. Front.* 2018, **5**, 561-565.

128.9, 129.1 (d, J = 7.8 Hz), 129.2, 129.7, 133.8, 137.2, 137.8, 139.3 (d, J = 3.3 Hz), 161.4 (d, J = 244.0 Hz), 179.4, 180.2. **HRMS-EI** (m/z) [M-H]⁻ calcd. for C₁₇H₁₆FO₂ 271.1134 found 271.1136.



2-Phenylbutanoic acid, 3a.⁹ Starting from 1.690 mmol of corresponding β-substituted styrene the product was obtained as a white solid, yield 94% (0.262 g), m.p. = 39-42°C. ¹H NMR (400 MHz, CDCl₃): δ = 0.91 (t, *J* = 7.4 Hz, 3H, Me), 1.76-1.87 (m, 1H, CH₂), 2.06- 2.17 (m, 1H, CH₂), 3.46 (t, *J* = 7.7 Hz, 1H, CH), 7.25-7.35 (m, 5H, Ar), 10.76 (br s, 1H, CO₂H). ¹³C NMR (101 MHz, CDCl₃): δ = 12.3, 26.5, 53.5, 127.6, 128.3, 128.8, 138.5. HRMS-EI (m/z) [M-H]⁻ calcd. for C₁₀H₁₁O₂ 163.0759 found 163.0788.



2-(4-Fluorophenyl)*butanoic acid*, **3b.** Starting from 1.470 mmol of corresponding β-substituted styrene the product was obtained as a white solid, yield 75% (0.201 g), m.p. = 54-56°C. ¹H NMR (400 MHz, CDCl₃): δ = 0.84 (t, *J* = 7.4 Hz, 3H, Me), 1.73 (dt, *J* = 13.7, 7.5 Hz, 1H, CH₂), 2.03 (dt, *J* = 13.6, 7.4 Hz, 1H, CH₂), 3.39 (t, *J* = 7.7 Hz, 1H, CH), 6.93-6.99 (m, 2H, Ar), 7.19-7.25 (m, 2H, Ar), 10.13 (br s, 1H, CO₂H). ¹³C NMR (101 MHz, CDCl₃): δ = 12.2, 26.6, 52.7, 115.7 (d, *J* = 22.4 Hz), 129.8 (d, *J* = 7.9 Hz), 134.2 (d, *J* = 3.2 Hz), 162.4 (d, *J* = 246.0 Hz), 180.2. calcd for Cypheret Content of the Equation (181.0672).

HRMS-EI (m/z) $[M-H]^-$ calcd. for $C_{10}H_{10}FO_2$ 181.0665 found 181.0672.



2-(4-Methoxyphenyl)butanoic acid, 3c.¹⁰ Starting from 1.350 mmol of corresponding β-substituted styrene the product was obtained as a white solid, yield 63% (0.164 g), m.p. = 57-60°C. ¹H NMR (400 MHz, CDCl₃): δ = 0.84 (t, *J* = 7.4 Hz, 3H, Me), 1.72 (dt, *J* = 13.7, 7.4 Hz, 1H, CH₂), 2.02 (dt, *J* = 13.7, 7.4 Hz, 1H, CH₂), 3.35 (t, *J* = 7.7 Hz, 1H, CH), 3.73 (s, 3H, OMe), 6.79-6.83 (m, 2H, Ar), 7.16-7.20 (m, 2H, Ar), 11.29 (br s, 1H, CO₂H). ¹³C NMR (101 MHz, CDCl₃): δ = 12.2, 26.4, 52.6, 55.4, 114.2, 129.3, 130.6, 159.1, 180.9. HRMS-EI (m/z) [M-

H]⁻ calcd. for $C_{11}H_{13}O_3$ 193.0865 found 193.0872.



2-(4-Methoxyphenyl)-5-phenylpentanoic acid, 3d. Starting from 0.839 mmol of corresponding β-substituted styrene the product was obtained as a colourless viscous oil, yield 52% (0.123 g). ¹H NMR (400 MHz, CDCl₃): δ = 1.49-1.62 (m, 2H, CH₂), 1.73-1.81 (m, 1H, CH₂), 1.99-2.08 (m, 1H, CH₂), 2.51-2.63 (m, 2H, CH₂), 3.46 (t, *J* = 7.7 Hz, 1H, CH), 3.73 (s, 3H, OMe), 6.79-6.82 (m, 2H, Ar), 7.07.7.27 (m, 7H, Ar), 11.01 (br s, 1H, CO₂H). ¹³C NMR (101 MHz, CDCl₃): δ = 29.3, 32.7, 35.7,

⁹J. A. Mukhlall, B. C. Noll and W. H. Hersh, <u>J. Sulfur Chem.</u> 2011, **32**, 199-212.

¹⁰ A. H. Mermerian and G. C. Fu, *J. Am. Chem. Soc.* 2005, **127**, 5604-5607.

50.7, 55.4, 114.2, 125.9, 128.4, 128.5, 128.8, 129.2, 130.5, 142.0, 159.1, 180.6. **HRMS-EI** (m/z) [M-H]⁻ calcd. for C₁₈H₁₉O₃ 283.1334 found 283.1335.



4-(*Benzoyloxy*)-2-phenylbutanoic acid, 3e. Starting from 0.839 mmol of corresponding β-substituted styrene the product was obtained as a colourless viscous oil, yield 51% (0.122 g). ¹H NMR (400 MHz, CDCl₃): $\delta = 2.44$ (dddd, J = 12.8, 10.3, 9.2, 8.2 Hz, 1H, CH₂), 2.72 (dddd, J = 12.6, 9.0, 6.7, 3.4 Hz, 1H, CH₂), 3.84 (dd, J = 10.2, 9.0 Hz, 1H, CH), 4.36 (td, J = 9.2, 6.7 Hz, 1H, CH₂), 4.49 (td, J = 8.7, 3.4 Hz, 1H, CH₂), 7.28-7.33 (m, 2H, Ar), 7.36-7.39 (m, 2H, Ar), 7.49 (t, J = 7.7 Hz, 3H, Ar), 7.60-7.64 (m, 1H,

Ar), 8.12-8.15 (m, 2H, Ar), 11.40 (br s, 1H, CO₂H). ¹³C NMR (101 MHz, CDCl₃): δ = 31.7, 45.7, 66.9, 127.8, 128.0, 128.6, 129.1, 129.4, 130.3, 134.0, 136.7, 172.4, 178.2. HRMS-EI (m/z) [M-H]⁻ calcd. for C₁₇H₁₅O₄283.0970 found 283.0976.



2,3-Dihydro-1H-indene-1-carboxylic acid, 3f.¹¹ Starting from 1.722 mmol of corresponding β-substituted styrene the product was obtained as a yellowish viscous oil, yield 46% (0.142 g). ¹H NMR (400 MHz, CDCl₃): δ = 2.31-2.49 (m, 2H, CH₂), 2.89-2.96 (m, 1H, CH₂), 3.07-3.15 (m, 1H, CH₂), 4.08 (dd, *J* = 8.5, 6.0 Hz, 1H, CH), 7.17-7.26 (m, 3H, Ar), 7.41-7.43 (m, 1H, Ar), 10.97 (br s, 1H, CO₂H). ¹³C NMR (101 MHz, CDCl₃): δ = 28.8, 31.9, 50.1, 124.9, 125.1, 126.7, 127.9, 140.1, 144.3, 180.6. HRMS-EI (m/z) [M-H]⁻ calcd. for C₁₀H₉O₂ 161.0603 found 161.0610.



1,2,3,4-Tetrahydronaphthalene-1-carboxylic acid, **3g.**¹² Starting from 1.540 mmol of corresponding β-substituted styrene the product was obtained as a white solid, yield 92% (0.248 g), m.p. = 76-79°C. ¹H NMR (400 MHz, CDCl₃): δ = 1.80-1.91 (m, 1H, CH₂), 1.99-2.13 (m, 2H, CH₂), 2.21-2.30 (m, 1H, CH₂), 2.78-2.94 (m, 2H, CH₂), 3.91 (t, *J* = 5.7 Hz, 1H, CH), 7.16-7.31 (m, 4H, Ar), 11.82 (br s, 1H, CO₂H).

¹³C NMR (101 MHz, CDCl₃): δ = 20.6, 26.6, 29.2, 44.6, 126.0, 127.2, 129.6, 129.8, 132.6, 137.4, 181.9.

HRMS-EI (m/z) $[M-H]^-$ calcd. for $C_{11}H_{11}O_2 175.0759$ found 175.0763.



Propa-1,2-dien-1-ylbenzene, 4d.^{1,13} Starting from 28.800 mmol of corresponding styrene the product was obtained as a colorless liquid, yield 27% (0.917 g). ¹H NMR (400 MHz, CDCl₃): $\delta = 5.16$ (d, J = 6.8 Hz, 2H, allene), 6.18 (t, J = 6.8 Hz, 1H, allene), 7.19-7.24 (m, 1H, Ar), 7.30-7.34 (m, 4H, Ar).

¹³**C NMR** (101 MHz, CDCl₃): δ = 78.9, 94.1, 126.9, 127.1, 128.8, 134.1, 210.0.

¹¹ J. Pietruszka, R. C. Simon, F. Kruska and M. Braun, *Eur. J. Org. Chem.* 2009, 6217-6224.

¹²L.-L. Liao, G.-M. Cao, J.-H. Ye, G.-Q. Sun, W.-J. Zhou, Y.-Y. Gui, S.-S. Yan, G. Shen, and D.-G. Yu, *J. Am. Chem. Soc.* 2018, 140, 17338-17342.



1-Methyl-4-(propa-1,2-dien-1-yl)benzene, **4e.**¹³ Starting from 25.390 mmol of corresponding styrene the product was obtained as a colorless liquid, yield 42% (1.401 g). ¹H NMR (400 MHz, CDCl₃): δ = 2.34 (s, 3H, Me), 5.14 (d, J = 6.8 Hz, 2H, allene), 6.15 (t, J = 6.8 Hz, 1H, allene), 7.13 (d, J = 7.9 Hz, 2H, Ar), 7.20 (d, J = 8.1 Hz, 2H, Ar). ¹³C NMR (101 MHz, CDCl₃): δ = 21.4, 78.8, 93.9, 126.3, 126.8, 129.4, 129.5, 131.1, 136.8, 209.8.



1-Methyl-3-(propa-1,2-dien-1-yl)benzene, **4f.**¹³ Starting from 16.920 mmol of corresponding styrene the product was obtained as a colorless liquid, yield 42% (0.921 g). ¹H NMR (400 MHz, CDCl₃): $\delta = 2.34$ (s, 3H, Me), 5.14 (d, J = 6.8 Hz, 2H, allene), 6.14 (t, J = 6.8 Hz, 1H, allene), 7.02 (d, J = 7.6 Hz, 1H, Ar), 7.10-7.13 (m, 2H, Ar), 7.19-7.24 (m, 1H, Ar).

¹³**C NMR** (101 MHz, CDCl₃): δ = 21.5, 78.8, 94.1, 124.1, 127.5, 127.9, 128.7, 133.9, 138.4, 210.0.



2-*Cyclohexylbut-3-enoic acid*, **5a.**¹⁴ Starting from 1.637 mmol of corresponding allene the product was obtained as a white solid, yield 76% (0.208 g), m.p. = 67-69°C. ¹H NMR (400 MHz, CDCl₃): δ = 0.84-0.93 (m, 1H, Cy), 1.00-1.31 (m, 4H, Cy), 1.61-1.78 (m, 6H, Cy), 2.76 (dd, *J* = 9.6, 8.1 Hz, 1H, CH), 5.10-5.18 (m, 2H, olefin), 5.78 (dt, *J* = 17.0, 9.9 Hz, 1H, olefin), 11.66 (br s, 1H, CO₂H).

¹³C NMR (101 MHz, CDCl₃): δ = 26.1, 26.2, 26.3, 30.1, 31.3, 39.9, 57.4, 118.7, 134.6, 180.8. HRMS-EI (m/z) [M-H]⁻ calcd. for C₁₀H₁₅O₂ 167.1072 found 167.1081.



I-Vinylcyclohexane-1-carboxylic acid, **5b.**¹⁵ Starting from 1.850 mmol of corresponding allene the product was obtained as a colourless viscous oil, yield 63% (0.179 g). ¹H NMR (400 MHz, CDCl₃): δ = 1.26-1.33 (m, 1H, Cy), 1.40-1.64 (m, 6H, Cy), 1.75-1.80 (m, 1H, Cy), 2.08-2.13 (m, 2H, Cy), 5.16-5.21 (m, 2H, olefin), 5.83 (dd, *J* = 17.5, 10.7 Hz, 1H, olefin), 11.18 (br s, 1H, CO₂H).

¹³**C NMR** (101 MHz, CDCl₃): $\delta = 23.2, 25.8, 33.4, 49.6, 115.3, 141.8.$ **HRMS-EI** (m/z) [M-H]⁻ calcd. for C₉H₁₃O₂ 153.0916 found 153.0927.

HO₂C Me Me *2,2-Dimethylbut-3-enoic acid*, **5c**.¹⁶ Starting from 2.936 mmol of corresponding allene the product was obtained as a colourless liquid, yield 65% (0.217 g). ¹H NMR (400 MHz, CDCl₃): $\delta = 1.33$ (s, 6H, 2xMe), 5.10-5.17 (m, 2H, olefin), 6.05

¹³ J. Liu, Z. Han, X. Wang, Z. Wang and K. Ding, *J. Am. Chem. Soc.* 2015, **137**, 15346-15349.

¹⁴E. M. Brun, S. Gil, R. Mestres and M. Parra, *Synthesis* 2000, **8**, 1160-1165.

¹⁵ H. A. Duong, P. B. Huleatt, Q.-W. Tan and E. L. Shuying, *Org. Lett.* 2013, **15**, 4034-4037.

¹⁶ C. Zhu, J. Takaya and N. Iwasawa, <u>*Org. Lett.*</u> 2015, **17**, 1814-1817.

 $(dd, J = 17.4, 10.6 \text{ Hz}, 1\text{H}, \text{olefin}), 10.93 (br s, 1\text{H}, CO_2\text{H}).$ ¹³C NMR (101 MHz, CDCl₃): $\delta = 24.6, 44.9, 113.6, 142.1, 183.0.$ HRMS-EI (m/z) [M-H]⁻ calcd. for C₆H₉O₂ 113.0603 found 113.0612.



4-Phenylbut-3-enoic acid 5da, 2-phenylbut-3-enoic acid 5db, 2phenylbut-2-enoic acid 5dc, NMR-ratio 10:1.5:4.5, LC-MS-ratio of 5 isomers 66:18:6:6:3.¹⁷ Starting from 1.722 mmol of corresponding allene the product was obtained as a yellowish viscous oil, yield 72% (0.202 g). ¹H NMR (400 MHz, CDCl₃): $\delta = 1.80$ (d, J = 7.2 Hz, 0.56H, 5dc Me),

2.18 (d, J = 7.3 Hz, 1.02H, **5dc** Me), 3.32 (dd, J = 7.1, 1.5 Hz, 2H, **5da**, CH₂), 4.36-4.39 (m, 0.11H, **5db**, CH), 5.20-5.30 (m, 0.25H, **5db**, olefin), 5.82-5.87 (m, 0.14H, **5db**, olefin), 6.21-6.34 (m, 1.11H, **5da/5dc**, olefin), 6.47 (q, J = 7.3 Hz, 0.34H, **5dc**, olefin), 6.51-6.56 (m, 0.99H, **5da**, olefin), 7.18-7.43 (m, 11.34H, **5da/5db/5dc**, Ar), 11.72 (br s, 2.68H, **5da/5db/5dc**, CO₂H). ¹³C NMR (101 MHz, CDCl₃): $\delta = 15.9$, 16.6, 30.5, 33.9, 38.2, 38.7, 55.7, 118.2, 120.9, 121.6, 122.4, 126.5, 126.9, 127.4, 127.7, 127.8, 128.1, 128.2, 128.3, 128.4, 128.5, 128.7, 128.8, 128.9, 129.6, 129.9, 134.2, 134.4, 135.1, 136.4, 136.8, 137.3, 138.3, 140.8, 143.5, 150.9, 173.8, 178.5. **HRMS-EI** (m/z) [M-H]⁻ calcd. for C₁₀H₉O₂ 161.0603 found 161.0612.



4-(*p*-Tolyl)but-3-enoic acid 5ea, 2-(*p*-tolyl)but-3-enoic acid 5eb, 2-(*p*-tolyl)but-2-enoic acid 5ec, NMR-ratio 10:1.8:4.3, LC-MSratio of 5 isomers 80:8:5:4:3. Starting from 1.540 mmol of corresponding allene the product was obtained as a yellowish viscous oil, yield 68% (0.185 g). ¹H NMR (400 MHz, CDCl₃): δ = 1.88 (d, *J* = 7.2 Hz, 0.27H, 5ec, Me), 2.24 (d, *J* = 7.3 Hz, 0.56H, 5ec,

Me), 2.43-2.47 (m, 5.82H, **5ea/5eb/5ec**, Me), 3.37 (dd, J = 7.2, 1.5 Hz, 2H, **5ea**, CH₂), 4.41 (d, J = 8.0 Hz, 0.26H, **5eb**, CH), 5.26-5.33 (m, 0.40H, **5eb**, olefin), 5.88-5.96 (m, 0.18H, **5eb**, olefin), 6.27-6.36 (m, 1.25H, **5ea/5ec**, olefin), 6.51 (q, J = 7.3 Hz, 0.18H, **5ec**, olefin), 6.55-6.59 (m, 1H, **5ea**, olefin), 7.14-7.42 (m, 8.55H, **5ea/5eb/5ec**, Ar), 12.07 (br s, 2.33H, **5ea/5eb/5ec**, CO₂H). ¹³C NMR (101 MHz, CDCl₃): $\delta = 15.9$, 16.5, 21.1, 21.2, 21.3, 21.4, 34.0, 35.0, 38.2, 38.3, 55.3, 118.0, 119.8, 121.4, 121.7, 126.4, 127.9, 128.1, 128.2, 128.7, 128.8, 129.0, 129.2, 129.3, 129.4, 129.5, 129.6, 129.8, 130.6, 132.6, 134.0, 134.2, 134.3, 134.5, 135.2, 135.5, 136.5, 137.0, 137.4, 137.5, 137.6, 138.3, 140.0, 143.1, 151.1, 172.4, 173.1, 174.0, 176.9, 178.7, 179.3. **HRMS-EI** (m/z) [M-H]⁻ calcd. for C₁₁H₁₁O₂ 175.0759 found 175.0767.

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4-(*m*-Tolyl)but-3-enoic acid 5fa, 2-(*m*-tolyl)but-3-enoic acid 5fb, 2-(*m*-tolyl)but-2-enoic acid 5fc, NMR-ratio 10:1.1:4.1, LC-MS-ratio of 5 isomers 71:11:8:6:4. Starting from 1.536 mmol of corresponding allene the product was obtained as a yellowish viscous oil, yield 53% (0.142 g). ¹H NMR (400 MHz, CDCl₃): $\delta = 1.81$ (d, J = 7.2 Hz, 0.42H,

5fc, Me), 2.18 (d, J = 7.3 Hz, 0.81H, **5fc**, Me), 2.37-2.40 (m, 5.99H, **5fa/5fb/5fc**, Me), 3.32 (dd, J = 7.1, 1.4 Hz, 2H, **5fa**, CH₂), 4.34 (d, J = 8.1 Hz, 0.08H, **5fb**, CH), 5.20-5.30 (m, 0.18H, **5fb**, olefin), 5.83-5.88 (m, 0.11H, **5fb**, olefin), 6.26-6.33 (m, 1.13H, **5fa/5fc**, olefin), 6.46 (q, J = 7.3 Hz, 0.28H, **5fc**, olefin), 6.50-6.54 (m, 1H, **5fa**, olefin), 6.99-7.36 (m, 8.82H, **5fa/5fb/5fc**, Ar), 11.53 (br s, 2.41H, **5fa/5fb/5fc**, CO₂H). **¹³C NMR** (101 MHz, CDCl₃): $\delta = 15.9$, 16.5, 21.5, 21.6, 30.5, 34.0, 38.2, 38.6, 55.7, 118.1, 120.6, 121.5, 123.7, 125.1, 125.2, 125.8, 125.9, 126.9, 127.1, 127.7, 128.2, 128.5, 128.6, 128.7, 128.8, 128.9, 129.7, 130.5, 134.3, 134.6, 135.2, 136.7, 137.9, 138.2, 138.6, 140.3, 143.3, 151.0, 173.8, 178.5. **HRMS-EI** (m/z) [M-H]⁻ calcd. for C₁₁H₁₁O₂ 175.0759 found 175.0769.



2-(Diethylamino)ethyl 2-phenylbutanoate (Butetamate), **6a.** Starting from 1.830 mmol of corresponding acid the product was obtained as a colourless liquid, yield 91% (0.436 g). ¹H NMR (400 MHz, CDCl₃): $\delta = 0.93$ (dt, J = 33.3, 7.3 Hz, 9H, 3xMe), 1.74-1.85 (m, 1H, CH₂), 2.04-2.15 (m, 1H, CH₂), 2.50 (q, J = 7.1 Hz, 4H, 2xCH₂), 2.65 (t, J = 6.2 Hz, 2H, CH₂), 3.45 (t, J = 7.7 Hz, 1H, CH), 4.09-4.19 (m, 2H, CH₂), 7.23-7.31 (m, 5H, Ar). ¹³C NMR (101 MHz, CDCl₃): $\delta = 12.1$, 12.3, 26.9, 47.8, 51.2, 53.7, 63.2, 127.3, 128.2, 128.7, 139.3, 1⁺ calcd for CycHa NOa 264 1958 found 264 1958

174.2. **HRMS-EI** (m/z) $[M+H]^+$ calcd. for C₁₆H₂₆NO₂ 264.1958 found 264.1958.



2-(4-Isobutylphenyl)butanoic acid (Butibufen), 6b. Starting from 1.148 mmol of corresponding β-substituted styrene the product was obtained as a colourless viscous oil, yield 64% (0.162 g). ¹H NMR (400 MHz, CDCl₃): $\delta = 0.89$ -0.93 (m, 9H, 3xMe), 1.76-1.88 (m, 2H, CH₂), 2.04-2.15 (m, 1H, CH), 2.45 (d, J = 7.1 Hz, 2H, CH₂), 3.42-3.44 (m, 1H, CH), 7.09-7.11 (m, 2H, Ar), 7.20-7.22 (m, 2H, Ar), 10.25 (s, 1H, CO₂H). ¹³C NMR (101 MHz, CDCl₃): $\delta = 12.3$, 22.6, 26.5, 30.3, 30.5, 45.2, 53.1, 127.9, 129.5, 135.7,

141.1, 180.4. **HRMS-EI** (m/z) [M-H]⁻ calcd. for C₁₄H₁₉O₂ 219.1385 found 219.1392.



2,3-Dihydro-1H-indene-1-carboxylic acid 3f, 2,3-dihydro-1H-indene-2-carboxylic acid 3f', LC-MS-ratio 4:1. Starting from 1.720 mmol of corresponding β -substituted styrene the product was obtained as a yellowish viscous oil, yield 68% (0.190 g). ¹H NMR (400 MHz, CDCl₃): δ = 2.29-2.49 (m, 2H, CH₂ 3f/3f'), 2.76 (t, *J* = 7.3 Hz, 0.29H, CH₂ from 3f'), 2.89-2.96 (m, 1H, CH₂ 3f), 3.05-3.15 (m, 1H, CH₂ 3f/3f'), 3.19-3.55 (m, 1.39H, CH₂, CH 3f'), 4.08 (dd, *J* = 8.5,

6.0 Hz, 1H, CH **3f**), 7.15-7.30 (m, 4.3H, Ar **3f/3f'**), 7.42-7.44 (m, 1H, Ar **3f/3f'**), 11.55 (br s, 1H, CO₂H **3f/3f'**). ¹³C **NMR** (101 MHz, CDCl₃): $\delta = 28.8, 30.5, 31.0, 31.8, 34.3, 36.1, 43.5, 50.1, 59.0, 124.5, 124.8, 124.9, 125.1, 126.6, 126.7, 126.8, 126.9, 127.9, 129.2, 140.1, 141.4, 144.3, 144.6, 176.6, 180.8.$ **HRMS-EI**(m/z) [M-H]⁻ calcd. for C₁₀H₉O₂ 161.0603 found 161.0609.



1,2-Diphenylethan-1-ol, 9a.¹⁸ Starting from 1.110 mmol of *trans*-stilbene the product was obtained as a colourless viscous oil, yield 96% (0.212 g). ¹H NMR (400 MHz, CDCl₃): $\delta = 2.18$ (s, 1H, OH), 3.00-3.10 (m, 2H, CH₂), 4.90 (dd, J = 8.1, 5.3 Hz, 1H, CH), 7.21-7.42 (m, 10H, Ar). ¹³C NMR (101 MHz, CDCl₃): $\delta = 46.2, 75.4, 126.0, 126.7, 127.7, 128.5, 128.6, 129.6, 138.2, 144.0.$

¹⁸ M. R. Hollerbach and T. J. Barker, *<u>Organometallics</u>* 2018, **37**, 1425-1427.

Copies of spectra












































Chromatogram of compound 2d









Chromatogram of compound 2e


























































Compound 5da/5db/5dc







Compound 5ea/5eb/5ec







Compound 5fa/5fb/5fc













Cu-catalyzed hydrocarboxylation of indene





Chromatogram of Cu-catalyzed hydrocarboxylation of indene









Cu-catalyzed hydrocarboxylation of 1,2-dihydronaphthalene



Chromatogram of Cu-catalyzed hydrocarboxylation of 1,2-dihydronaphthalene vs 3g





Asymmetric hydroboration-oxidation of trans-ß-methylstyrene



Asymmetric hydroboration-oxidation of trans-ß-methylstyrene





Asymmetric hydroboration-oxidation of *trans*-ß-methylstyrene


Carboxylation of enantiomerically enriched organoborane intermediate



Carboxylation of enantiomerically enriched organoborane intermediate



Carboxylation of enantiomerically enriched organoborane intermediate

Computational details

Models: Full molecular models of **b1**, **b2** and **b3** were computed. For CsF, we observed in computations that a CsF dimer is much more stable than 2 CsF monomers. The CsF dimer was therefore used as a reference point, implying that addition of 1 molecule of CsF was computed as addition of $\frac{1}{2}$ (CsF)₂. This reference point affects the resting state (i1) of the preferred reaction mechanisms **B** and **C** and therefore the overall barriers of the reaction.

Geometry optimizations with Gaussian: All DFT calculations were performed using the Gaussian16 Revision B.01 software package.¹⁹ The DFT functional employed was ω -B97XD.²⁰ Other DFT functionals (PBE+GD3BJ,²¹ PBE0+GD3BJ,²² B3LYP+GD3²³ and CAM-B3LYP+GD3BJ²⁴) were tested but with these we were unable to identify the TSs for reaction mechanism **C**. This might be a results of the missing description of long-range interaction for most of the functionals, which are important for mechanism **C**. Geometry optimizations utilized basis set BS1, consisting of the SDD basis set for Cs and 6-31+G* for all other elements. Symmetry was not used. Solvation effects were included via the model IEFPCM (1,4-dioxane). Obtained minima and transition states (TS) geometries were controlled via vibrational mode analysis to show zero (minimum) or only one (TS) imaginary frequency. Gibbs energies were computed at 393.15 K (120 °C) at the BS1 level.

GRRM calculations: A number of initial structures for the TS optimization were generate by using the MC-AFIR²⁵ (Multi-Component Artificial Force Induced Reaction) method from the GGRM14 software.²⁶ The software was interfaced with Gaussian09 Revision D.01²⁷ and

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the same level of theory as described above was used. The termination criterion for the calculation was set to 20 runs without new results (NFault = 20).

Coupled-cluster single point calculations: SP electronic energies on the coupled-cluster level were obtained with the ORCA 4.1.1²⁸ software using the geometries optimized with w-B97XD. The used method was DLPNO-CCSD(T)²⁹ together with the scalar-relativistic ZORA Hamiltonian.³⁰ The basis set was SARC-ZORA-TZVPP for Cs and ZORA-def2-QZVPP for all other elements. Calculations were accelerated by using the RIJCOSX approximation³¹ with auxiliary basis set SARC/J and def2-TZVP/C. An example of the ORCA input can be found below.

Energies: Standard state conversions (SS) were computed at 393.15 K. Two sets of energies are compared below: DFT-based Gibbs free energies ($\Delta G_{\omega-B97XD}$) and DPLNO-CCSD(T)–based Gibbs free energies ($\Delta G_{DPLNO-CCSD(T)//\omega-B97XD}$).

The *DFT Gibbs free energies* were obtained by computing single point electronic energies (including IEFPCM) with basis set 2 (BS2), which corresponds to def2-TZVP level for all elements (with SDD ECP for Cs). Counterpoise (CP_{BS2}) corrections were computed at the same level of theory, providing the following final DFT energies:

 $\Delta G_{\omega\text{-B97XD}} = \Delta G_{\omega\text{-B97XD/IEFPCM/BS1}} - \Delta E_{\omega\text{-B97XD/IEFPCM/BS1}} + \Delta E_{\omega\text{-B97XD/IEFPCM/BS2}} + CP_{BS2} + SS.$

The DPLNO-CCSD(T)-based Gibbs free energies were computed by combining the DPLNO-CCSD(T) single point energies with the DFTbased vibrational, entropic and temperature corrections, and the standard state corrections (SS, 393.15 K). Counter poise corrections were not included. The final DPLNO-CCSD(T)-based energies (which are those discussed in the main text) are:

 $\Delta G_{DPLNO-CCSD(T)//\omega-B97XD} = \Delta G_{\omega-B97XD/IEFPCM/BS1} - \Delta E_{\omega-B97XD/IEFPCM/BS1} + \Delta E_{DPLNO-CCSD(T)} + SS.$

We further tested if addition of DFT solvent corrections (computed as the difference between vacuum and IEFPCM single points, $\Delta E_{sol_\omega-B97XD/IEFPCM/BS1} = \Delta E_{\omega-B97XD/IEFPCM/BS1} - \Delta E_{\omega-B97XD/VACUUM/BS1}$) affected the DPLNO-CCSD(T)–based Gibbs free energies. As shown in Table S2-S4 (energies in brackets), the solvent correction does not affect the overall barriers significantly and it was therefore not included in the energies given in the main text.

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EXAMPLE INPUT DPLNO-CCSD(T):

!DLPNO-CCSD(T) ZORA TightSCF SlowConv RIJCOSX !Printbasis !Smallprint % maxcore 5000 %PAL NProcs 16 END %BASIS Basis "ZORA-def2-QZVPP" Aux "SARC/J" AuxC "def2-TZVP/C" NewGTO Cs "SARC-ZORA-TZVPP" end END %SCF Convergence Tight MaxIter 1000 END * xyz 0 1 "Cartesian coordinates" *

DFT and DLPNO-CCSD(T) results



Table S2: Computed energies (kcal/mol) for mechanism A for substrates b1, b2 and
b3. Numbers in bold are $\Delta G_{DPLNO-CCSD(T)/\omega-B97XD}$ energies (given in the main text),
numbers in brackets are $\Delta G_{DPLNO-CCSD(T)//\omega-B97XD}$ energies with solvent corrections added
$(\Delta E_{sol \ \omega-B97XD/BS1})$, whereas energies in parentheses are pure DFT $\Delta G_{\omega-B97XD}$ energies.

Substrate	TS _{i0-i3}	i3	p1	Overall barrier
b1	57.4	-2.5	-17.7	72.9
	[58.1]	[-2.8]	[-15.3]	[68.4]
	(62.5)	(-3.6)	(-12.9)	(75.4)
b2	52.9	-4.1	-14.5	67.5
	[53.4]	[-4.5]	[-13.6]	[63.0]
	(56.8)	(-6.1)	(-10.7)	(68.5)
b3	57.7	-6.1	-17.2	57.7
	[58.2]	[-6.4]	[-16.9]	[58.2]
	(62.1)	(-10.3)	(-10.0)	(62.1)

Figure S6. Reaction mechanism A.



Table S3: Computed energies (kcal/mol) for mechanism **B** for substrates **b1**, **b2** and **b3**. Numbers in bold are $\Delta G_{DPLNO-CCSD(T)//\omega-B97XD}$ energies (given in the main text), numbers in brackets are $\Delta G_{DPLNO-CCSD(T)//\omega-B97XD}$ energies with solvent corrections added ($\Delta E_{sol_\omega-B97XD/BS1}$), whereas energies in parentheses are pure DFT $\Delta G_{\omega-B97XD}$ energies.

Substrate	i1	TS _{i1-p1}	p1	Overall barrier
b1	-15.5	36.3	-17.2	51.9
	[-10.3]	[39.6]	[-15.3]	[49.9]
	(-12.8)	(34.7)	(-12.9)	(47.6)
b2	-14.6	37.7	-14.5	52.3
	[-9.5]	[40.6]	[-13.6]	[50.1]
	(-11.7)	(36.6)	(-10.7)	(48.3)
b3	1.0	44.4	-17.2	44.4
	[3.1]	[47.6]	[-16.9]	[47.6]
	(6.2)	(47.6)	(-10.0)	(47.6)

Figure S7. Reaction mechanism B.



Figure S8. Reaction mechanism C.

Table S4: Computed energies (kcal/mol) for mechanism C for substrates b1, b2 and b3. Numbers in bold are $\Delta G_{DPLNO-CCSD(T)//(\omega-B97XD)}$ energies									
(given in the main text), numbers in brackets are $\Delta G_{DPLNO-CCSD(T)//\omega-B97XD}$ energies with solvent corrections added ($\Delta E_{sol_{\omega}-B97XD/BS1}$), whereas									
energies in parentheses are pure DFT $\Delta G_{\omega-B97XD}$ energies.									
Substrate	i1	TS _{i1-i2}	i2	TS _{i2-p1}	p1	Overall			
						barrier			
b1	-15.5	18.6	7.4	14.2	-17.2	34.0			
	[-10.3]	[24.4]	[9.9]	[19.2]	[-15.3]	[34.7]			
	(-12.8)	(19.6)	(8.6)	(16.1)	(-12.9)	(32.5)			
b2	-14.6	22.1	12.7	19.9	-14.5	36.7			
	[-9.5]	[27.4]	[12.3]	[21.1]	[-13.6]	[36.9]			
	(-11.7)	(22.4)	(15.3)	(24.3)	(-10.7)	(34.0)			
b3	1.0	44.8	37.2	51.1	-17.2	51.1			
	[3.1]	[49.5]	[36.8]	[52.3]	[-16.9]	[52.3]			
	(6.2)	(49.2)	(43.8)	(57.1)	(-10.0)	(57.1)			



Figure S9. Comparison of optimized TS structures for C-CO₂ bond formation with substrate **b1** in Mechanism C. The outer/acyclic TS [**TS**_{i2-} **p1I** (b1), left] is preferred by 0.7 kcal/mol ($\Delta G_{DPLNO-CCSD(T)//\omega-B97XD}$) in comparison to the inner/cyclic TS [**TS**_{i2-p1}**II** (b1), right].



Figure S10. Comparison of optimized TS structures for C-CO₂ bond formation with substrate **b2** in Mechanism C. The inner/cyclic TS [**TS**_{i2}. **p1I** (**b2**), left] is preferred by 1.4 kcal/mol ($\Delta G_{DPLNO-CCSD(T)//\omega-B97XD}$) in comparison to the outer/acyclic TS [**TS**_{i2-p1}**II** (**b2**), right].