

## Supporting Information

### Mass Efficiency of Alkene Syntheses with Tri- and Tetrasubstituted Double Bonds

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Figure S 1b Environmental factor related to 1 mol of product of some alkene syntheses (Table 2), determined<sup>72</sup> according to the literature. Its relation to 1 kg can be found in Figure 1. The underlying data are given in ESI Table S 3 and ESI Table S 4. Quantities of solvents, salts, acids and bases are not shown in the columns, but as numbers in the table below Figure 1. Auxiliary materials such as salts (e.g. brine), acids and bases (e.g. hydrochloric acid) are also detailed listed separately (see ESI Table S 5). The solvent applications are given in ESI Table S 9. Assumptions made are presented in ESI Table S 10. Work-up procedures, which were not described quantitatively in literature and had to be omitted, are listed in ESI Table S 11. Reaction equations and conditions are shown in ESI Table S 7 and Table S 8. ....S11

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**Table S 1** Method specific auxiliary materials of syntheses according to Table 1. For a full presentation of all synthetic steps and reaction details see ESI Table S 7 and Table S 8.

No.	Method	Lite- ra- ture	Substrates	important / characteristic auxiliary materials	Product(s)
1	$\beta$ -Elimination (Tschugaeff)	19		$\xrightarrow{\text{CS}_2}$	
2a	Wittig Reaction	20		$\xrightarrow{\text{P(Ph)}_3, \text{Base}}$	
2b	Wittig Reaction (catalytic)	21		$\xrightarrow{\text{Phospholane oxide (10%), Diphenylsilane}}$	
3	Carbene Dimerisation.	22		$\xrightarrow{\text{PBr}_3, \text{Zn}}$	
4a	Barton-Kellogg's extrusion process	23		$\xrightarrow{\text{N}_2\text{H}_4, \text{S-source, oxidant}}$	
4b	Barton-Kellogg's extrusion process (asymmetric variant)	24		$\xrightarrow{\text{N}_2\text{H}_4, \text{S-source}^{[c]}, \text{oxidant}}$	
5a-g	McMurry Coupling	25-29 30 31		$\xrightarrow{\text{TiCl}_n \text{ or Ti reductant (e.g. Li)}}$	
6	Claisen rearrangement	32		$\xrightarrow{\text{Mg}}$	
7	Alkylation – elimination process	33 34		$\xrightarrow{\text{Lithium amide, MnCl}_2}$	
8	Suzuki-Miyaura (Zhou, Larock)	35		$\xrightarrow{\text{Mg, B(OX)}_3, \text{Pd(OAc)}_2, \text{mol. sieves}}$	
9	Hydroarylation <sup>[n]</sup>	36		$\xrightarrow{\text{Mg, B(OX)}_3, \text{Pd(OAc)}_2, \text{mol. sieves, CuOAc}}$	
10	Arylzincation	37		$\xrightarrow{\text{Zn, LiCl}}$	

			$\text{Ar}^3\text{-Br} \quad \text{R}^1\text{-}\equiv\text{R}^2 \quad \xrightarrow{\quad\quad\quad} \quad \text{R}^1\text{-CH=CH-R}^2 \quad \text{R}^1\text{-CH=CH-R}^2$ $\quad \quad \quad (+ \text{E (Electrophil)}) \quad \quad \quad \left( \begin{array}{c} \text{R}^1 \quad \text{R}^2 \\ \text{Ar}^3 \quad \text{E} \end{array} \right) \quad \left( \begin{array}{c} \text{R}^1 \quad \text{R}^2 \\ \text{E} \quad \text{Ar}^3 \end{array} \right)$	
11	Method of Coupling by Negishi	38	$\text{R}^1\text{-Br} \quad \text{R}^3 \quad \xrightarrow{\text{CCl}_4, \text{N}_2\text{H}_5\text{OH}, \text{Zn}, \text{Mg}} \quad \text{R}^1\text{-CH=CH-R}^3$ $\text{R}^2\text{-Br} \quad \text{O} \quad \text{H}$	
12	Shapiro <sup>[p]</sup>	39	$\text{O} \quad \text{R}^3 \quad \xrightarrow{\text{2,4,6-Triisopropylbenzene-sulfonylhydrazide, sec.-BuLi}} \quad \text{R}^1\text{-CH=CH-R}^3$ $\text{R}^1 \quad \text{R}^2 \quad \text{Alk}^3\text{-Br}$	
13	Peterson <sup>[q]</sup>	40	$\text{R}^1\text{-C(=O)-R}^2 \quad \text{O} \quad \text{R}^3 \quad \xrightarrow{\text{PhMe}_2\text{SiCl}, \text{CCl}_4, \text{PPh}_3, \text{Mg}, \text{CuBr}\cdot\text{Me}_2\text{S}, \text{p-TsOH}} \quad \text{R}^1\text{-CH=CH-R}^3$ $\text{R}^2 \quad \text{O} \quad \text{Cl} \quad \text{Li} \quad \text{R}^4$	
14	Julia-Lythgoe	41	$\text{R}^1 \quad \text{R}^3 \quad \xrightarrow{\text{LDA, BzCl, N,N-dimethylaminopropanol, SmI}_2, \text{HMPA}} \quad \text{R}^1\text{-CH=CH-R}^3$ $\text{R}^2 \quad \text{O} \quad \text{R}^4$	
15	Thiolester conversion	42	$\text{R}^1 \quad \text{R}^3 \quad \xrightarrow{\text{Pyridine, BuLi, Diisopropylamine, silica gel}} \quad \text{R}^1\text{-CH=CH-R}^3$ $\text{R}^2 \quad \text{O} \quad \text{R}^4$	
16	Heck	43	$\text{Ar}^1\text{-Cl} \quad \text{R}^2 \quad \text{R}^3 \quad \xrightarrow{\text{Pd(P}(t\text{-Bu)}_3)_2, \text{Cy}_2\text{NMe}} \quad \text{R}^2\text{-CH=CH-R}^3$ $\text{Ar}^1 \quad \text{R}^4$	
17	Heck	44	$\text{Ar}^2\text{-I} \quad \text{I} \quad \text{Ar}^3 \quad \xrightarrow{\text{2xMg (Grignard), Mercaptopyrimidine, TsCN, Pd(PPh}_3)_4, \text{DDQ, Pd}_2(\text{dba})_3} \quad \text{Ar}^2\text{-CH=CH-Ar}^3$ $\text{Ar}^1\text{-I} \quad \text{Br} \quad \text{Ar}^4$	
18	Arylmagnesiation of Aryl(alkyl)acetylenes	45	$\text{I} \quad \text{Ar}^2 \quad \text{Ar}^3\text{-Br} \quad \text{R}^1\text{-}\equiv\text{R}^2 \quad \xrightarrow{\text{Mg (Grignard), Pd(PPh}_3)_4, \text{Et}_3\text{N, Fe(acac)}_3} \quad \text{Ar}^3\text{-CH=CH-Ar}^2$	
19a	Coupling of Vinylbromides (Suzuki)	46,47	$\text{Ar}^1\text{-CH=CH-Ar}^2 \quad (\text{HO})_2\text{B-Ar}^3 \quad \xrightarrow{\text{Br}_2, \text{Base}} \quad \text{Ar}^1\text{-CH=CH-Ar}^2$ $\text{Ar}^1 \quad \text{Ar}^3$	
19b	Coupling of Vinylbromides (Suzuki)	46-48	$\text{Ar}^1\text{-CH}_2\text{-Hal} \quad \text{Hal-Ar}^3 \quad \xrightarrow{\text{P(OEt)}_3, \text{Br}_2, \text{Base, Mg, B(OX)}_3^{[d]}} \quad \text{Ar}^1\text{-CH=CH-Ar}^3$ $\text{O} \quad \text{Ar}^2$	
19c	Coupling of Vinylbromides (Suzuki)	46-49	$\text{Ar}^1\text{-CH}_2\text{-Hal} \quad \text{Hal-Ar}^3 \quad \xrightarrow{\text{P(OEt)}_3, \text{HBr, Base, Mg, B(OX)}_3} \quad \text{Ar}^1\text{-CH=CH-Ar}^3$ $\text{O} \quad \text{Ar}^2$	

20	Coupling of Vinylbromides (Negishi)	46,47 $\begin{array}{c} \text{Ar}^1\text{---CH}_2\text{---Hal} \\ \text{O}=\text{C---Ar}^2 \\ \text{Stillbene} \\ \text{intermediate} \\ \text{via e.g.}^{20} \text{ or }^{56} \end{array}$	$\text{Hal---R}$	$\text{Br}_2, \text{Base, ZnCl}_2, \text{Pd-cat}$	$\text{Ar}^1\text{---CH=CH---Ar}^2$ $\text{R}$
21	Ynolate conversion (Shindo)	50 $\begin{array}{c} \text{R}^1\text{---C(=O)---O---R}^2 \\ \text{Hal} \end{array}$	$\begin{array}{c} \text{Si} \\ \diagup \quad \diagdown \\ \text{O}=\text{C} \quad \text{R}^3 \end{array}$	$\text{Br---C(Cl)(Cl)---Br}$ , two Li-comp. <sup>[e][f]</sup>	$\begin{array}{c} \text{HO} \quad \text{O} \\ \diagup \quad \diagdown \\ \text{C}=\text{C} \\ \text{R}^1 \quad \text{R}^3 \end{array}$
22	Opening of cyclopropenes (Wang)	9 [g] (51-54) $\begin{array}{c} \text{R}^1\text{---O---C(=O)---EWG} \\ \text{Cyclopropene} \end{array}$	3 $\text{Hal---R}^3$	Al	$\begin{array}{c} \text{R}^1\text{---O---C(=O)---EWG} \\ \text{Alkene} \end{array}$ $\text{R}^2 \quad \text{R}^3$
23	Allylation of Alkenylalanes	55 $\begin{array}{c} \text{R}^1\text{---C}\equiv\text{C} \\ \text{R}^2\text{---Al---R}^2 \end{array}$	$\text{Cl---R}^3$ (R <sup>3</sup> = allyl)	$(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}_2, \text{Pd(Ph}_3\text{P)}_4$	$\begin{array}{c} \text{R}^1\text{---C=C---R}^3 \\ \text{R}^2 \end{array}$ $\text{[I]}$
24	Organozinc reagents and carbonyl compounds (Wang)	56 $\text{Ar}^1\text{---CH}_2\text{---Br}$	$\begin{array}{c} \text{O} \\ \text{C} \\ \text{Ar}^2 \end{array}$	Zn; Me <sub>3</sub> SiCl <sup>[h]</sup>	$\text{Ar}^1\text{---CH=CH---Ar}^2$
25	Cross-coupling of alkenylcarboxylates with Grignard reagents	57 $\begin{array}{c} \text{R}^1\text{---CH}_2\text{---C(=O)---R}^2 \\ \text{mostly} \\ \text{cyclic} \end{array}$	$\text{ClMg---R}^3$	NaH, Pivalic acid, FeCl <sub>2</sub> , 1,3-bis(2,4,6-trimethylphenyl)imidazolinium chloride	$\begin{array}{c} \text{R}^1\text{---CH=CH---R}^3 \\ \text{R}^2 \end{array}$ $\text{[o]}$
26	Three component reaction (Li)	58 $\begin{array}{c} \text{Ar}^1\text{---C}\equiv\text{C} \\ \text{[i]} \end{array}$	$\begin{array}{c} \text{OH} \\ \text{R}^1\text{---C---R}^2 \end{array}$	Ar <sup>2</sup> H $\text{AgNO}_3, \text{FeCl}_3, \text{Tf}_2\text{O}$	$\begin{array}{c} \text{Ar}^2\text{---CH=CH---R}^2 \\ \text{Ar}^1 \quad \text{R}^1 \end{array}$ $\begin{array}{c} \text{Ar}^1\text{---CH=CH---R}^2 \\ \text{Ar}^2 \quad \text{R}^1 \end{array}$
27	Alkylative or Arylative Carboxylation of Alkynes	59,60 $\text{R}^1\text{---C}\equiv\text{C} \quad \text{CO}_2$	$\text{Hal---R}^2$	Zn, Ni(COD) <sub>2</sub> <sup>[j]</sup> , DBU <sup>[k]</sup>	$\begin{array}{c} \text{R}^1\text{---CH=CH---CO}_2\text{H} \\ \text{R}^2 \end{array}$
28	Olefin Metathesis <sup>[b]</sup>	61 $\begin{array}{c} \text{R}^1\text{---C(R}^2\text{)=C(R}^3\text{)---R}^4 \end{array}$	$\begin{array}{c} \text{R}^5\text{---C(R}^6\text{)=C(R}^7\text{)---R}^8 \end{array}$	e.g. Grubbs catalyst	$\begin{array}{c} \text{R}^1\text{---C(R}^6\text{)=C(R}^5\text{)---R}^2 \\ \text{R}^3\text{---C(R}^7\text{)=C(R}^8\text{)---R}^4 \end{array}$ $\begin{array}{c} \text{R}^1\text{---C(R}^7\text{)=C(R}^8\text{)---R}^2 \\ \text{R}^3\text{---C(R}^5\text{)=C(R}^6\text{)---R}^4 \end{array}$
29a-d	Geminal dihalides	62-65 $\text{Ar---C(=O)---R}$	$\text{CX}_4$ (X = halogen)	Hydrazinium hydroxide or PPh <sub>3</sub>	$\begin{array}{c} \text{X} \\ \text{C}=\text{C} \\ \text{Ar} \quad \text{R} \end{array}$

[a] Yield and atom economy<sup>79,80</sup> in chosen examples (for details see ESI Table S 7 and Table S 8)

[b] Usually substrates are chosen so that one product is obtained. For an *Organic Syntheses* protocol for a ring-closing metathesis see the literature.<sup>175,176</sup>

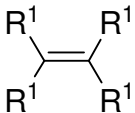
[c] Lawesson's reagent<sup>177,178</sup>

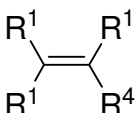
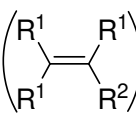
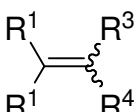
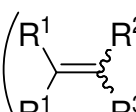
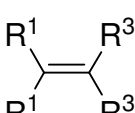
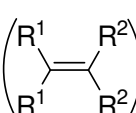
[d] For a review of such compounds see the literature.<sup>179,180</sup>

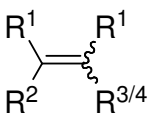
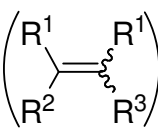
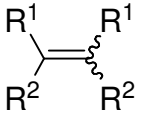
[e] Lithiumorganyles such as butyllithium can be omitted in the synthesis of lithium diisopropylamide.<sup>181</sup>

- [f] Instead of tert.-butyllithium a catalytic procedure using lithium naphthalenide can be used for larger scale.<sup>182</sup>
- [g] Malonic acid esters undergo decarboxylations<sup>183,184</sup> so that trisubstituted  $\beta, \gamma$  – unsaturated acid derivatives should be producible.
- [h] They used quite a large amount of Me<sub>3</sub>SiCl as a catalyst. Recently Peng et al. applied AlCl<sub>3</sub> producing 17% less yield.<sup>185</sup>
- [i] At least one of R<sup>1</sup> and R<sup>2</sup> is an aryl compound.
- [j] For further applications of nickel in alkene synthesis see the literature.<sup>186,187</sup>
- [k] For a review concerning bicyclic amidines as reagents in organic syntheses see the literature.<sup>188</sup>
- [l] If desired, decarboxylation is possible. Internal alkynes deliver alkenes with tetrasubstituted double bond. However, asymmetric internal alkynes result in the formation of regioisomers. For another  $\alpha$ -diazoester utilization see the literature.<sup>189</sup>
- [m] Rounded values. The underlying data are given in ESI Table S 3 and ESI Table S 4.
- [n] Considered yield is 77%. However, yield of other reactions is up to 94%.
- [o] According to another protocol<sup>190</sup> R<sup>3</sup> can be a carboxylic substituent.
- [p] The application of hydrazones can also be found in other methodologies.<sup>191-194 195 196,197</sup>
- [q] Four *Organic Syntheses* protocols: a) other copper complex applications consider an alkyne as substrate<sup>198</sup>, deliver alkenols<sup>199</sup> and enable a stereoselective isoprenoid chain extension.<sup>200</sup> b) Current applications using silicon compounds use e.g. organosilanol.<sup>201,202</sup>

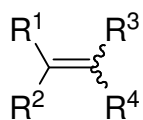
**Table S 2** Overview of trisubstituted (one R=H) and tetrasubstituted (R $\neq$ H) alkenes and stilbenes. (Commentary: although not all entries in this table were noted completely during its preparation, the information we collected should still be made available.)

Design of rests R <sup>1</sup> to R <sup>4</sup>		R=H	R $\neq$ H	entry or reference	Yield [%]		Stereo-selectivity	Regio-selectivity E/Z	Constraints / Commentary
according to... Scheme 1	according to... (... a common numbering (see Table 2))					kind of alkene i.e. of rests			Group R <sup>1</sup> can be any alkyl-, cycloalkyl- or aryl group but R <sup>1</sup> = C(CH <sub>3</sub> ) <sub>3</sub> cannot be prepared by any method
R <sup>1</sup> =R <sup>2</sup> =R <sup>3</sup> =R <sup>4</sup>				5a-g	80	any alkyl or aryl	-	-	McMurry reaction
		X		3	52	adamantylidene-adamantane	-	-	Carbene dimersiation <sup>[d]</sup>
		X		4a	50	adamantylidene-adamantane	-	-	Another type of Barton-Kellogg reaction in entry 4b
					25	Tetramesityl-ethylene			Carbene dimerization starting from dimesitylcarbene

$R^1=R^2=R^3$	 	-	X	101 203 204	84 80	aryl R1=CH <sub>3</sub> , R2=aryl R1=C(CH <sub>3</sub> ) <sub>3</sub> , R2=CH <sub>3</sub>	- good moderate to good	- E only E only	Other McMurry reactions in entries 5a-e Coupling of vinyl bromides with „Tedicyp“, Elimination of water from alcohols or hydrogen halides from alkyl halides
$R^1=R^2$ $R^3 \neq R^4$	 	X	X	7 101 205 206	20 51-91 50-70	alkyl aryl R1=aryl, R2=vinyl, R3=subst. vinyl R1=COOR, R2=alkyl, R3=aryl	- cross-coupling moderate good	-	Other McMurry reactions in entries 5a-e Coupling via iodide template Coupling by a modified Knoevenagel condensation
$R^1=R^2$ $R^3=R^4$ [a]	 	-	X	28 207 4b	32	cycloalkyl R1=alkyl, R2=aryl Aryl	n.s. very good	trans preferred	Horner-Wadsworth-Emmons Reaction Another Barton-Kellogg reaction in entry 4a

$R^1=R^3$ or $=R^4$ $R^2\neq R^3$ or $\neq R^4$			x	x	208		aryl	-	1:2.3	Other Negishi-Coupling see 20
			x	x [c]	8 10		aryl aryl, alkyl	- regioisomers (position of R <sup>2</sup> and R <sup>4</sup> ), e.g. 55:45 or 99:1	cis	
				x	209	28-88	Alkyl- and carbomethoxy, R1=CH3		99.5/0.5	Carbocupration of alkynoates
			x		210	52-89	Alkyl and carbomethoxy, R1=CH3		4/6	Organocuprate addition acetylenic esters.
			x	x	211	31-65	R1=phenyl, R2=COOR, R3=alkyl	high	Z-only	Carbozirconation of acetylene derivatives
			x		212	62-73	2 phenyls (E), special aryls, ethyl, Tamoxifen-type alkenes	high	95/5	Carbolithiation of diphenylacetylene
			x		213	64-72	R1=CH3, R2=vinyl, R3=phenylethyl			Peterson olefination, only for special cases
$R^1=R^3$ or $=R^4$ $R^2=R^4$ or $=R^3$ [a]			x		214	90	R1=alkyl, R2=aryl	good	Z isomers only	
			x		66	60-80	R1=alkyl1, R2=alkyl2		mixtures	McMurry coupling of asymmetric ketones

$R^1 \neq R^2 \neq R^3 \neq R^4$   
(all rests are  
different)



X	1	36	alkly	regioisom ers		
X	2	86	aryl, alkyl		n.s.	
-	X <sup>101</sup>		aryl	cross- coupling	n.s.	Other McMurry reactions in entries 5a-e
X	-	28	cycloalkyl	n.s.	trans	
X	-	11	aryl, alkyl		E>98%	
X	X	14			97:3	
X	X	17	aryl	Full selectivit y control	>93%	
X	[b]	18	aryl, alkyl	1% regio- isomer	89:11	
X	[c]	10	aryl, alkyl	regioisom ers (position of R <sup>2</sup> and R <sup>4</sup> ), e.g. 55:45 or 99:1		
X		2b	aryl, alkyl		83:17	
X		19	Aryl		Z	
	X	21	Alkyl, Carboxyl	normally R <sup>1</sup> will be R <sup>3</sup>	99:1	
X		22	42, 52- 92	Alkyl or aryl	5:1 to 10:1 regio- meric ratio	E
X		24	76	2xAryl, alkyl	E	
X		26	82	2xAryl, alkyl	>93:7	
X		27	79	alkyl, carboxyl	E or Z	
X		6	60.7	Alkyl, ester	E	
X		16	95	Aryl, alkyl, (carboxyl)	E:Z>20: 1	



X		9	77-97	Aryl, alkyl, ester		syn	
X		12	38.7	Alkyl	mixtures	mixtures	
X		23	83	Allyl, Alkenyl	High to mixtures	Partly >98%	
X		25	94	Alkyl	High		
X	X	15	68	Alkyl	Medium to High (by-products identified)		
X	X	13	32	Alkyl	high		
X	X	215		Aryl, fluor		Up to 97/3	
X		216	78-92	R1= aryl, R2=CH3, R3=COOR,	low	mixtures	One-pot route from alkynes
X	X	217 210	80				Carbocupration of alkynyl acetals
(X)	X	218 219 220 221 222	ca. 60	n-Alkyl,aryl			Addition of borontrialkyls to alkynes
X		223	52-95	n-alkyl, phenyl, NHR-group			Addition of imines and organoboranes, (Ni-catalysis)
X	X	224	36-73	n-alkyl, phenyl	high		Addition of acylstannanes to alkynes
X		225 226	86-92	Alkyl, 2-hydroxalky, aryl	high		Carbomagnesation of propargylic alkynes
		227	82-91	Phenyl, n-alkyl, -COR, CHOHa	High	Varies, Z is preferred	Carbozincation of alkynes by Cu[i] catalysis
		228	Ca. 85	Various substituents	high		Alkylative carboxylation of alkynes, (Ni-catalysis), tamoxifen 36% in 8 steps
		229	66-97	R1and R2, five- and six membered rings	Low, mixtur		Trans-selective addition of organoboron reagents to alkynes (Pd-cat.); 1 step
		230	81	R1=CH3, R''=aryl, R3=COOR, R4=n-alkyl	low		Hydropalladation-transmetallation of allenes; 4 steps
		231	ca. 72	3 different aryls, R4=ethyl,Tamoxifen	Very high		three component coupling of aryl iodides, alkynes and aryl boronic acids

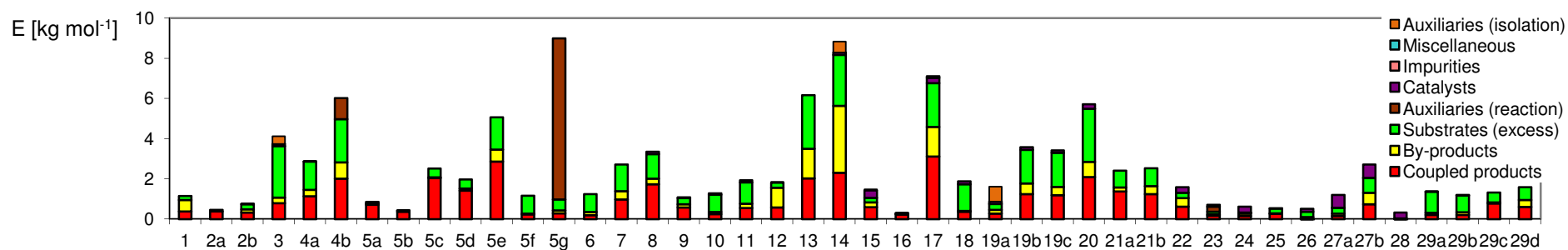
	232-236	15-69	5-membered cyclic enones	high	
	237	60-67	5-membered lactones		Coupling of cyclic dichloroenones,
X	238	26-92	R1=alkyl, R2=aryl1, R3=aryl2, R4=aryl3	good	Coupling of gem-dibromoalkenes
	239 240	80-85	R1=ethyl, R2=aryl1, R3=aryl2, R4=aryl4	good	Coupling of gem dibromo alkenes via gem boron compounds,
	241	43-61	R1=alkyl, R2=aryl1, R3=aryl2, R4=COOR	Moderate, mixture	Coupling of 2,3-dibromoalkenoates; side products
	242 243	75-95	R1=CF3, R2=alkyl, R3=1-hydroxyalkyl, R4=aryl	good	Carbolithiation of trifluoromethylenolethers
	244	21-72	four different aryl groups	good	Carbomagnesation of alkynyl(2pyridyl)silanes

<sup>[a]</sup> Consider also those entries that have been allocated to the alkene derivative not showing 2 + 2 but only 2 different rests. It should also be possible to apply these methods here.

<sup>[b]</sup> Instead of quenching with water, the intermediate alkenyl magnesium reagent may also be versatile to produce alkenes with tetrasubstituted double bond.

<sup>[c]</sup> Instead of quenching with water, with Pd<sub>2</sub>(dba)<sub>3</sub> (2.5mol%) PPh<sub>3</sub> (10mol%) and ArI (4equiv) alkenes with tetrasubstituted double bond can be synthesized.

<sup>[d]</sup> Carbene-Dimerization does only work if there are no hydrogen atoms in gamma position! Otherwise, the carbene prefers C-H insertions to give the cyclopropyl derivative. Dimesityl carbene, formed from the photolysis of the diazo compound give tetramesitylethylene <sup>245</sup>



**Figure S 1b** Environmental factor related to 1 mol of product of some alkene syntheses (Table 2), determined<sup>72</sup> according to the literature. Its relation to 1 kg can be found in Figure 1. The underlying data are given in ESI Table S 3 and ESI Table S 4. Quantities of solvents, salts, acids and bases are not shown in the columns, but as numbers in the table below Figure 1. Auxiliary materials such as salts (e.g. brine), acids and bases (e.g. hydrochloric acid) are also detailed listed separately (see ESI Table S 5). The solvent applications are given in ESI Table S 9. Assumptions made are presented in ESI Table S 10. Work-up procedures, which were not described quantitatively in literature and had to be omitted, are listed in ESI Table S 11. Reaction equations and conditions are shown in ESI Table S 7 and Table S 8.

**Table S 3** Data related to Figure 1

Entry:	1	2a	2b	3	4a	4b	5a	5b	5c	5d	5e	5f	5g	6	7	8
Category:																
Coupled products	2.7315	2.0008	1.8966	2.9381	4.2515	5.8401	2.6867	1.3546	7.6221	5.297	17.4401	0.7329	0.8672	1.0206	4.3625	5.5669
By-products	4.1639	0.3515	0.8652	1.0668	1.1876	2.3824	0.229	0.229	0.1283	0.4098	3.6581	0.1106	0.4668	0.7763	1.8705	0.8785
Substrates (excess)	1.4917		1.422	9.57	5.2315	6.2214	0.313	0.0416	1.6281	1.6494	9.7754	2.6477	1.6347	4.5264	5.9046	3.919
Auxiliaries (reaction)	0	0	0	0	0	3.0524	0	0	0	0	0	0	24.4402	0	0	0
Catalysts			0.1431	0.3651	0.0007											0.4045
Impurities																
Miscellaneous	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Auxiliaries (isolation)	0	0	0	1.4298	0	0	0	0	0	0	0	0	0	0	0	0
E-factor	8.3871	2.3523	4.3269	15.3698	10.6713	17.4963	3.2287	1.6252	9.3785	7.3562	30.8736	3.4912	27.4089	6.3233	12.1376	10.7689

Continued:

9	10	11	12	13	14	15	16	17	18	19a	19b	19c	20	21a	21b
2.1967	1.0297	2.4381	2.9941	11.1398	12.8103	3.0122	1.0619	7.8969	1.4001	1.0454	4.592	4.3901	10.0849	8.0078	7.246
0.5827	0.4456	0.8696	5.1527	8.0672	18.5063	1.2596	0.1085	3.7631	0.1439	0.647	1.9646	1.5229	3.6317	1.1415	2.2953
1.1678	3.5027	4.648	1.329	14.6563	14.0481	1.1401	0.1722	5.4928	5.0054	1.0929	6.2199	6.2896	12.6834	4.8348	5.164
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
0.1183	0.31245	0.4589			0.6273	1.8712	0.0738	0.6727	0.5114	0.4515	0.4953	0.4504	1.0832		
0	0	0	0	0	0	0	0	0.2066	0	0	0	0	0	0	0
0	0	0	0.199	0	3.0576	0.2705	0	0	0	2.7702	0	0	0	0	0
4.0655	5.29045	8.4146	9.6748	33.8633	49.0496	7.5536	1.4164	18.0321	7.0608	6.007	13.2718	12.653	27.4832	13.9841	14.7053

Continued:

22	23	24	25	26	27a	27b	28	29a	29b	29c	29d
2.2494	0.8095	0.7791	1.2145	0.0464	0.5476	2.4923	0.1116	0.9613	1.1965	2.9728	3.2687
1.5432	0.3706	0.5345	0.1088	0.2297	0.3997	1.9548	0.0112	0.449	0.7718	0.2292	1.8295
0.9642	0.6564	0.2358	1.1502	0.6663	0.9139	2.4451		4.7514	4.8494	1.8414	3.4126
0	1.1823	0.0345	0	0	0.0388	0.0388	0	0	0	0	0
1.0207	0.4817	1.4237	0.0393	0.3876	2.1727	2.2423	1.0729	0.052	0.1546		
0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0
5.7775	3.5005	3.0076	2.5128	1.33	4.0727	9.1733	1.1957	6.2137	6.9723	5.0434	8.5108

**Table S 4** Data related to Figure S 1b (see this ESI)

Entry:	1	2a	2b	3	4a	4b	5a	5b	5c	5d	5e	5f	5g	6	7	8
Category:																
Coupled products	0.377	0.389	0.334	0.789	1.141	2.012	0.721	0.364	2.046	1.422	2.865	0.244	0.285	0.200	0.979	1.739
By-products	0.575	0.068	0.152	0.286	0.319	0.821	0.061	0.061	0.034	0.110	0.601	0.037	0.153	0.152	0.420	0.274
Substrates (excess)	0.206		0.251	2.569	1.404	2.143	0.084	0.011	0.437	0.443	1.606	0.880	0.537	0.888	1.325	1.224
Auxiliaries (reaction)						1.051							8.026			
Catalysts			0.025	0.098	0.000											0.126
Impurities																
Miscellaneous Auxiliaries (isolation)				0.384												
Sum:	1.159	0.457	0.762	4.126	2.865	6.027	0.867	0.436	2.518	1.975	5.072	1.161	9.001	1.240	2.724	3.365

Continued:

9	10	11	12	13	14	15	16	17	18	19a	19b	19c	20	21a	21b
0.585	0.252	0.562	0.576	2.031	2.310	0.592	0.232	3.115	0.373	0.283	1.242	1.187	2.101	1.380	1.248
0.155	0.109	0.200	0.991	1.471	3.337	0.247	0.024	1.484	0.038	0.175	0.531	0.412	0.756	0.197	0.395
0.311	0.856	1.071	0.256	2.673	2.533	0.224	0.038	2.167	1.333	0.295	1.682	1.701	2.642	0.833	0.890
0.032	0.076	0.106			0.113	0.367	0.016	0.265	0.136	0.122	0.134	0.122	0.226		
								0.081							
			0.038		0.551	0.053				0.749					
1.083	1.293	1.939	1.861	6.175	8.845	1.483	0.309	7.113	1.881	1.624	3.588	3.421	5.725	2.409	2.534

Continued:

22	23	24	25	26	27a	27b	28	29a	29b	29c	29d
0.622	0.165	0.162	0.260	0.018	0.162	0.739	0.031	0.213	0.207	0.779	0.611
0.426	0.076	0.111	0.023	0.089	0.118	0.579	0.003	0.099	0.134	0.060	0.342
0.266	0.134	0.049	0.247	0.259	0.271	0.725		1.052	0.839	0.482	0.638
	0.242	0.007			0.011	0.011					
0.282	0.098	0.297	0.008	0.151	0.644	0.664	0.300	0.012	0.027		
1.596	0.715	0.626	0.539	0.517	1.207	2.718	0.334	1.376	1.206	1.321	1.592

Additional information: Molecular weights of the products in [g mol<sup>-1</sup>]

Entry:	1	2a	2b	3	4a	4b	5a	5b	5c	5d	5e	5f	5g	6	7	8
MW	138.14	194.27	176.21	268.44	268.44	344.45	268.44	268.44	268.44	268.44	164.29	332.44	328.41	196.15	224.43	312.45

Entry:	9	10	11	12	13	14	15	16	17	18	19a	19b	19c	20	21a	21b
MW	266.339	244.41	230.39	192.34	182.35	180.33	196.3752	218.13	394.48	266.38	270.37	270.37	270.37	208.3	172.3	172.3

Entry:	22	23	24	25	26	27a	27b	28	29a	29b	29c	29d
MW	276.33	204.35	208.3	214.35	388.54	296.32	296.32	279.4	221.51	173.041	261.94	187.07

Molecular weight (MW) of the product is the factor between Figure S 1b and Figure 1, i.e.

Figure S 1b = Figure 1 · MW(product).

Example: the coupled product mass of entry 1 in Table S 3 is 2.7315 kg kg<sup>-1</sup>. The multiplication with the molecular mass....

$$2.7315 \text{ kg kg}^{-1} \cdot 138.14 \frac{\text{g}}{\text{mol}} \text{ means } \frac{2.7315 \text{ kg coupled product}}{1 \text{ kg product}} \cdot 138.14 \frac{\text{g}}{\text{mol}} = \frac{2.7315 \text{ kg coupled product}}{1000 \text{ g product}} \cdot \frac{138.14 \text{ g}}{\text{mol}}$$

$$= \frac{2.7315 \text{ kg coupled product}}{1000 \cancel{\text{g}} \text{ product}} \cdot \frac{138.14 \cancel{\text{g}}}{\text{mol}} = \frac{0.377 \text{ kg coupled product}}{\text{mol product}} = 0.377 \text{ kg mol}^{-1}$$

... results in the value given in Table S 4.

**Table S 5** Supporting information for Figure 1: neat substances and their amounts [kg / kg product] in aqueous solutions. No water amounts are indicated here!

entry	1- 4a	4b	6a	5bc	5d	5e	5f	5g	6	7	8
Substances (auxiliary material)	-	Sodium chloride (5.1451), Ammonium chloride (aq, conc.) (14.2494)	Sodium sulfate (0.4383), Potassium carbonate (10%) (1.8407)	-	Florisil (4.8055)	Copper sulfate (0.9623)	-	-	Propionic acid (0.0202), NaHCO3 (aq, conc.) (0.2692), Sodium chloride (aq, conc.) (0.8085), Hydrochloric acid (5%) (0.1978)	-	Molecular sieves (4 A) (3.2005), Sodium chloride (84.1981)
9	10	11	12	13		14			15		
Hydrochloric acid (5%) (0.1046)	Ammonium chloride (7.6172)	Hydrochloric acid (aq, 1 M) (7.2741)	Hydrochloric acid (1M) (0.199)	Ammonium chloride (6.8195 +23.3045), Sodium hydrogen carbonate (7.0025), Sodium chloride (6.9636+5.7079),		Hydrochloric acid (50.3055), Ammonium chloride (aq, conc.) (87.5776), Sodium thiosulfate (38.2435), Sodium chloride (aq, conc.) (100.611)			Hydrochloric acid (1.0061), Sodium chloride (2.527+2.3724), Sodium carbonate (2.7053)		
16	17	18	19a	19b		19c			20		
Sodium chloride (4.0273)	Ammonium chloride (4.5909), Ammonia (3.0988), Copper iodide (0.5284), Sodium hydroxide (0.3963)	-	Sodium chloride (10.2424), Sodium hydroxide (1.5572)	Potassium hydroxide (10%) (0.4424), Sodium chloride (brine) (2.3278), Sodium chloride (10.2424), Sodium hydroxide (1.5572)		Potassium hydroxide (10%) (0.4424), Sodium chloride (brine) (2.3278), Sodium chloride (10.2424), Sodium hydroxide (1.5572)			Potassium hydroxide (10%) (0.6062), Sodium chloride (brine) (3.1893)		
21a			21b	22		23	24	25	26		
Sodium hydrogen carbonate (aq, conc.) (0.7135), Sodium chloride (2.9081), Magnesium sulfate (0.4422), Sodium hydroxide (1 M) (1.4419), Sodium chloride (aq, conc.) (4.7419), Magnesium sulfate (0.6008)			Sodium hydrogen carbonate (aq, conc.) (0.7135), Sodium chloride (2.9081), Magnesium sulfate (0.4422), Sodium hydroxide (1 M) (0.7209), Sodium chloride (aq, conc.) (4.7419), Magnesium sulfate (0.6008)		Rochelle salt (aq) (42.2198)		Hydrochloric acid (1.1823)	Ammonium chloride (1.4094)	Sodium hydroxide (0.5207), Sodium chloride (2.6091+2.557)		
27a	27b	28	29a	29b	29c	29d					
-	Sulfuric acid (conc.) (0.01)	0	Hydrochloric acid (2.7034), Silica gel (3.1496)	Hydrochloric acid (aq, 1 M) (8.5421)	0	0					

**Table S 6** Data related to Figure 2.

	1	2a	2b	3	4a	4b	5a	5b	5c	5d	5e	5f	5g	6	7	8
Step 1	9.387	2.2351	0.1431	8.149	2.156	5.8021	2.912	1.5182	9.1486	6.8835	12.5814	4.4912	3.9686	1.9231	3.5269	10.0587
Step 2		0.13	5.1839	6.4259	0.1921	3.2111	1.3167	1.3167	1.2299	1.4726	18.0605			5.4003	4.5827	0.7207
Step 3		0.9873			6.2243	3.6106					1.2317				5.028	0.5848
Step 4					3.0981	[a]										
Step 5						2.8202										
Step 6																
Sum:	9.387	3.3524	5.327	14.5749	11.6705	15.444	4.2287	2.8349	10.3785	8.3561	31.8736	4.4912	3.9686	7.3234	13.1376	11.3642

continued:

9	10	11	12	13	14	15	16	17	18	19a	19b	19c	20	21a	21b
3.9416	5.0584	6.6571	7.045	6.1524	5.504	2.9757	2.3426	3.1471	5.7316	1.9272	3.0716	2.6189	4.2085	2.0019	2.0019
1.0056	0.9197	1.5266	3.4308	11.3285	3.8248	3.4733		1.1147	1.7436	1.2229	5.5846	4.7616	7.6514	2.0544	2.0544
		0.7922		18.7901	3.484	0		5.2216	0.0743	0.6352	0.9427	1.6445	1.2916	3.9596	3.9596
					2.4705			4.7304			1.2229	1.2229	1.6755	2.5843	7.6893
					4.0319			3.9388			2.3493	2.3493	5.7458	0.9777	
					27.0495					0.1683	0.1683	6.8272	3.4064		
4.9472	5.9781	8.9759	10.4758	36.271	46.3647	6.449	2.3426	18.1526	7.5495	3.7853	13.3394	12.7655	27.4	14.9843	15.7052

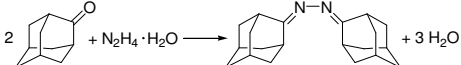
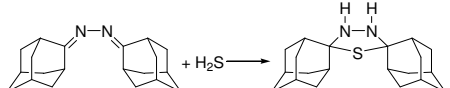
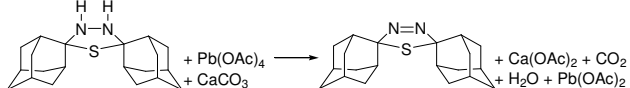
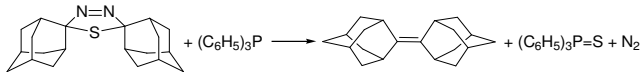
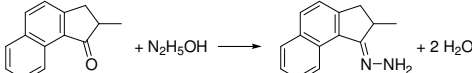
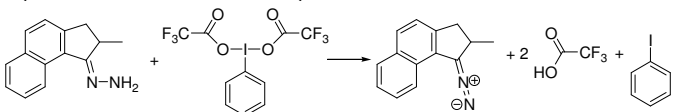
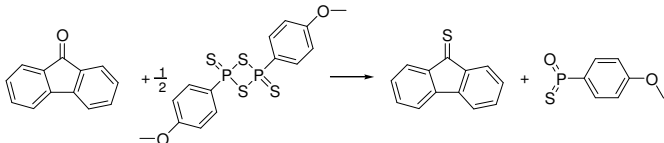
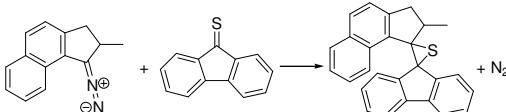
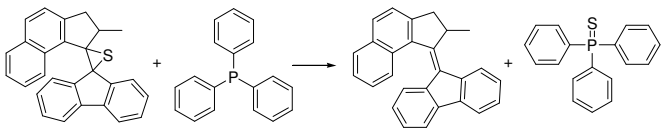
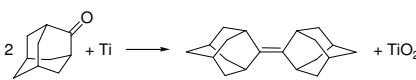
continued:

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2.3258	1.3884	2.5494	1.8003	1.9425	2.1937	5.4229	1.1228	1.5369	7.8176	5.0386	9.5108
1.1928	1.4481		1.6735		0.6674	1.7809		5.6767		0.5547	
1.4859						2.1937				0.4502	
0.7525						0.6674					
5.757	2.8365	2.5494	3.4738	1.9425	2.8611	10.0649	1.1228	7.2136	7.8176	6.0435	9.5108

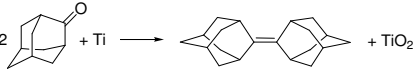
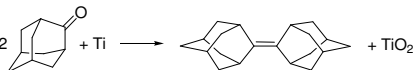
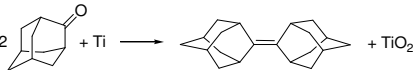
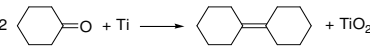

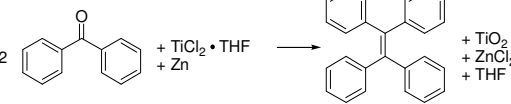
<sup>[a]</sup> In step 4 no new raw materials were used. The raw materials result from the convergent synthesis sequence of step 2 and 3.

**Table S 7** Selected methods for the preparation of alkenes with tri- and tetrasubstituted double bond: yields, atom economies and reaction conditions. Detail information related to Table 1 and Table 2.

No.	Method	Step	Reaction scheme	Ref.	Yield [%] <sup>[c]</sup>	AE <sup>[a]</sup> [%]	AE <sup>[b]</sup> [%]	Conditions
1	$\beta$ -Elimination of xanthates, prepared from alcohols			19	65	62	62	reflux, i.e. 111°C 32h
				19	56 (36.4)	56.1	34.8	Reflux, 145-155°C 1h 6h
2a	Wittig	1		20	90	100	100	130°C 20h
		2		20	100 <sup>[d]</sup>	73.5	73.5	80°C (nitrogen atm.) 45min + rt 10min
		3		20	95 (85.5)	41.1	33.6	rt 3h
2b	Wittig (catalytic)	1		21	100	100		rt, 20bar, 1mL/min n
		2		21	77	34.5		100°C 24h
3	Carbene Dimerisation	1		22	96	69.9	69.9	70°C 1h
		2		22	75 (72)	37.3	27.6	heating cooling in ice Reflux few minutes 10 min

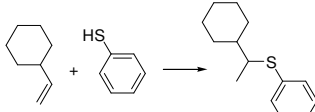
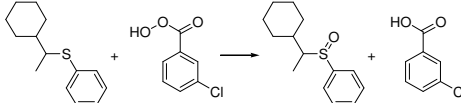
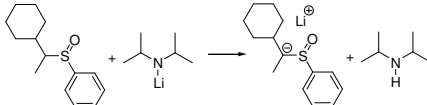
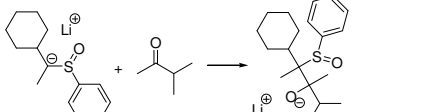
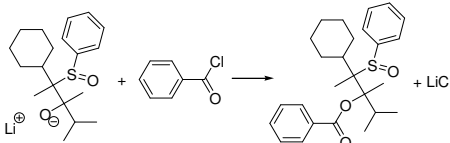
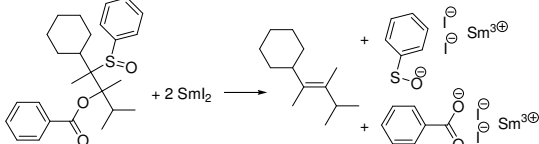
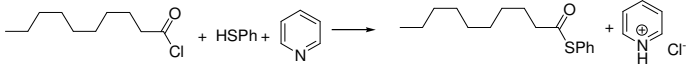
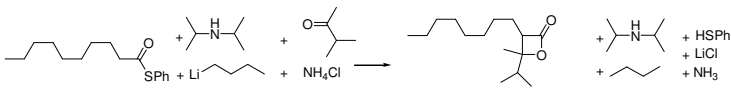
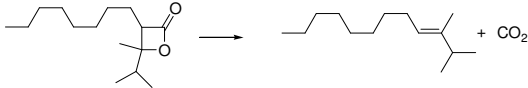
No.	Method	Step	Reaction scheme	Ref.	Yield [%] <sup>[c]</sup>	AE <sup>[a]</sup> [%]	AE <sup>[b]</sup> [%]	Conditions	
4a	Barton-Kellogg's extrusion process	1		23	98	84.6	84.6	Reflux (i.e. 82°C)	12,75 h
		2		23	95	100	85.9	ambient temp.	12h
		3		23	94	37.6	35.4	0°C ambient temp.	110min 8h
		4		23	74 ( <b>64.8</b> )	45.4	<b>22.6</b>	125°C-130°C (nitrogen atm.)	12h
4b	Barton-Kellogg's extrusion process	1		24	83	85.4	85.4 <sup>[n]</sup>	Reflux (i.e. 120°C)	3d
		2		24	100 <sup>[d]</sup>	32.5	30.8 <sup>[n]</sup>	-30°C	allowed to warm to rt
		3		24	100 <sup>[d]</sup>	51.3	51.3 <sup>[n]</sup>	80°C (nitrogen atm.)	1.5h
		4		24	48	93.1	35.6 <sup>[n]</sup>	see step2	see step2
		5		24	81 ( <b>32.3</b> )	53.9	<b>26.1</b>	Reflux (i.e. about 138°C)	3h
5a	McMurry  (variation using TiCl4/Zn)	1	$\text{TiCl}_4 + 2 \text{Zn} \longrightarrow \text{Ti} + 2 \text{ZnCl}_2$	25 <sup>[f]</sup>	100 <sup>[d]</sup>	14.9	14.9	0°C (inert atm.)	not spec.: dropping
		2		25	85 ( <b>85</b> )	77.1	<b>43.2</b>	reflux (i.e. ≈66°C)	20h



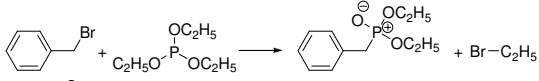
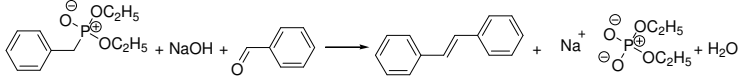
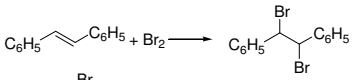
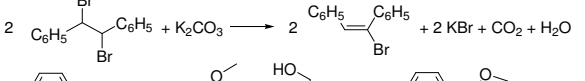
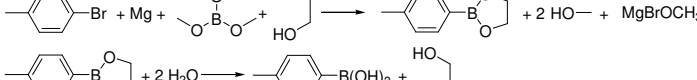
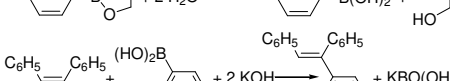
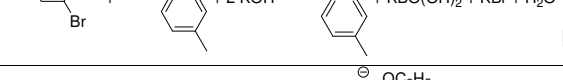
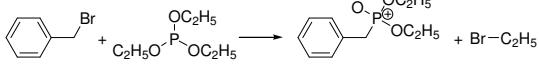

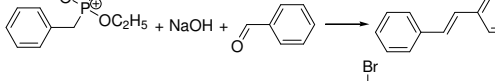
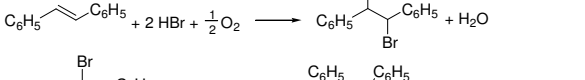
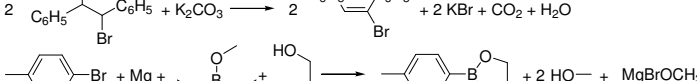
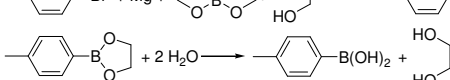
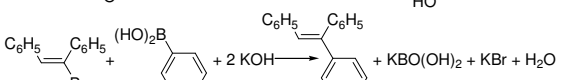
No.	Method	Step	Reaction scheme	Ref.	Yield [%] <sup>[c]</sup>	AE <sup>[a]</sup> [%]	AE <sup>[b]</sup> [%]	Conditions	
5b	McMurry (variation using TiCl <sub>3</sub> /LiAlH <sub>4</sub> )	1	$8 \text{ TiCl}_3 + 3 \text{ LiAlH}_4 \longrightarrow 8 \text{ Ti} + 3 \text{ AlCl}_3 + 3 \text{ LiCl} + 12 \text{ HCl}^{[g]}$	26	100 <sup>[d]</sup>	28.4	28.4	nitrogen atm.	not spec.
		2			85 <b>(85)</b>	77.1	<b>57.2</b>	reflux (i.e. ≈66°C)	4h
5c	McMurry (variation using TiCl <sub>3</sub> /K)	1	$\text{TiCl}_3 + 3 \text{ K} \longrightarrow \text{Ti} + 3 \text{ KCl}$	27	100 <sup>[d]</sup>	17.6	17.6	reflux (i.e. ≈66°C)	45min
		2			91 <b>(91)</b>	77.1	<b>46.9</b>	reflux (i.e. ≈66°C)	12h
5d	McMurry (variation using TiCl <sub>3</sub> /Li)	1	$\text{TiCl}_3 + 3 \text{ Li} \longrightarrow \text{Ti} + 3 \text{ KLi}$	28	100 <sup>[d]</sup>	27.4	27.4	120°C (argon atm.)	12h
		2		28	76 <sup>[h]</sup> <b>(76)</b>	77.1	<b>56.5</b>	Reflux (i.e. 84°C)	18h
5e	McMurry (variation using TiCl <sub>3</sub> DME <sub>1.5</sub> /Zn-Cu) <sup>29</sup>	0	$\text{Zn} \longrightarrow \text{Zn}$ (Preparation of zinc-copper-couple)	29	100 <sup>[d]</sup>			rt (nitrogen atm.)	15min
		1	$\text{TiCl}_3 + 1.5 \text{ } \text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3 \longrightarrow \text{TiCl}_3(\text{C}_4\text{H}_{10}\text{O}_2)_{1.5}$	29	80	100	100	Reflux, i.e. 84°C (argon atm.)	2d
		2	$2 \text{ TiCl}_3(\text{C}_4\text{H}_{10}\text{O}_2)_{1.5} + 3 \text{ Zn} \longrightarrow 2 \text{ Ti} + 3 \text{ ZnCl}_2 + 3 \text{ C}_4\text{H}_{10}\text{O}_2$	29	100 <sup>[d]</sup>	12.4	12.4	Reflux, i.e. 84°C (argon atm.)	2h
		3		29	97 <b>(97<sup>[li]</sup>)</b>	67.3	<b>12.4</b>	Reflux, i.e. 84°C (argon atm.)	8h
5f	McMurry (variation using Ti and Me <sub>3</sub> SiCl)			30	<b>94</b>	57.7	<b>57.7</b>	Reflux	67h + 4h
5g	McMurry (variation using TiCl <sub>2</sub> and Zn)			31	<b>80</b>	53.6	<b>53.6</b>	Ball milling	120min

No.	Method	Step	Reaction scheme	Ref.	Yield [%] <sup>[c]</sup>	AE <sup>[a]</sup> [%]	AE <sup>[b]</sup> [%]	Conditions	
6	Claisen	1		32	69	57	57	30°C (nitrogen atm.) 138–142°C	>30min >45min >1.5h until ethanol no longer distills from the reaction flask
	rearrangement	2		32	88 ( <b>60.7</b> )	68.1	<b>51.2</b>		
7	Alkylation – elimination process	1		33	100 <sup>[e]</sup>	76.3	76.3	0°C	
		2		34 33	acc. to 100 <sup>[j]</sup>	64.1	58.2	-78°C (nitrogen atm.)	1h
		3		34	62 ( <b>62</b> )	32.8	<b>23.7</b>	0°C 0°C	20min 1h
8	Suzuki-Miyaura (Zhou, Larock)	1		48	93	44.8	44.8	Reflux	overnight
		2			100 <sup>[e]</sup>	68.7	34.2		
		3		35 [l]	80 ( <b>80<sup>[m]</sup></b> )	74.7	<b>33.2</b>	-50°C	24h
9	Hydroarylation	1	See steps 1-2 in 8	48			34.2		
		2		36	77	77.8	44.1	28°C (nitrogen atm.)	24h
10	Arylzincation (Murakami Oshima)	1		246	100 <sup>[d]</sup>	100	100	rt (drying, argon)	24h
		2		37	82	49.3	<b>49.3</b>	60°C	4h

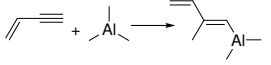
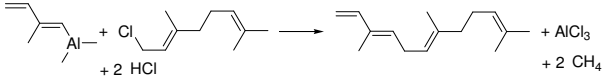
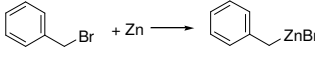
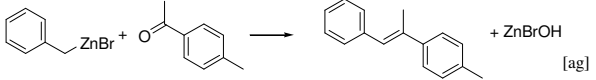
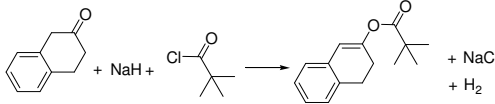
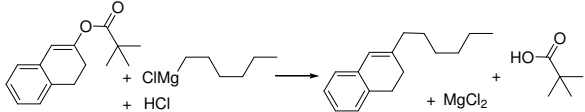
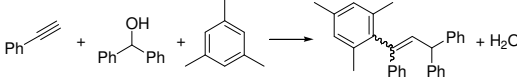
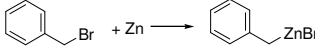
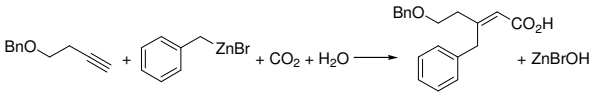
No.	Method	Step	Reaction scheme	Ref.	Yield [%] ( <sup>[c]</sup> )	AE <sup>[a]</sup> [%]	AE <sup>[b]</sup> [%]	Conditions	
11	Coupling of geminal 1,1-dihalides (Negishi, Tan)	1		see entry 29b <sup>63</sup> 38	74	45.5	45.5	rt 20°C	3h 10min
		2			90	58.1	39.3	rt 50°C	4h 12h
		3		[o] 38	100	100		reflux	2h
		4			100 (66.6)	62.3	30.4	appr. temp.	
12	Shapiro type	1		39	53	96.3	96.3	rt -10°C	overnight 4h
		2		39	Not isolated			Nitrogen -55°C	?min 15-20min 2h 20min
		3		39	73 (38.7)	26.2	25.6	Ice bath rt	10min overnight
13	Peterson	1		40	82	69.9	69.9	0°C (argon) -78°C	16h addition of substrate
		2		40	74	39.1	33.8	0°C Reflux (argon)	1h 12h
		3		40	52 (31.6)	15.9	11.1	Reflux (argon) -78°C to -10°C rt -78°C	3h addition of substrate 3h 1.5h+2h

No.	Method	Step	Reaction scheme	Ref.	Yield [%] <sup>[c]</sup>	AE <sup>[a]</sup> [%]	AE <sup>[b]</sup> [%]	Conditions	
14	Julia-Lythgoe	1	See step 1 in entry 21	50	100	64.8	64.8	-71°C (argon atm.)	26min
		2		[p] (247)	87	100	100	ice bath	2h + 0.5h
		3		[q]	88	60.2	60.2	n.s.	n.s.
		4		41	100 <sup>[d]</sup>	70.5	43.4	-78°C	0.5h
		5		41	100 <sup>[d]</sup>	100	51	-78°C	2h
		6		41	100 <sup>[d]</sup>	91	54.4	-78°C -78°C to rt rt	0.5h 1h 0.5h+0.16h
		7		41	29 ( <b>22.2</b> )	14.6	<b>11.3</b>	-78°C	0.5h
15	Thiolester conversion	1		42	98	69.6	69.6	0°C rt	30min 1h
		2		42	75.1	42.2	35.1	0°C -78°C → 0°C	10min 30+30min
		3		42	91.7 (67.5)	81.7	<b>28.7</b>	reflux (cyclohexane) rt	1 h 5min

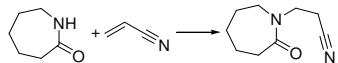
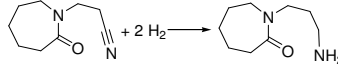
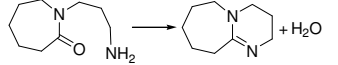
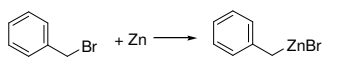
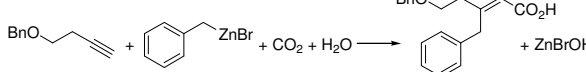
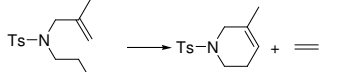
No.	Method	Step	Reaction scheme	Ref.	Yield [%] <sup>[c]</sup>	AE <sup>[a]</sup> [%]	AE <sup>[b]</sup> [%]	Conditions	
16	Heck	1		43	95	48.5	<b>48.5</b>	100°C	22h
17	Heck (Itami)	1		248	80	43.2	43.2	rt	2h
		2		249	97	51.5	30.8	0°C	1h
		3		44	89	42.2	30.3	60°C (argon) 90°C	3h 18h
		4		44	82	48.9	27.1	-78°C (argon) 0°C 50°C rt	0.5h 2h 3h 0.5h
		5		44	52 ( <b>29.4</b> )	59.2	<b>20.5</b>	90°C (argon)	20h
18	Alkynes (Yamagami)	1		45 [r]	100 <sup>[d]</sup>	40.9	40.9	60°C	12-24h
		2		45	100 <sup>[d]</sup>	100		rt	2h
		3		45	91 ( <b>91</b> )	68.7	<b>43.2</b>	rt 60°C	5min 16h
19a	Suzuki-Coupling of Vinyl-bromides	3		46	81	100	100	rt	1.25 h
		4		47	88	63.3	63.3	Reflux	1h
		7		47	95 ( <b>67.7</b> )	68.4	<b>49.6</b>	rt	1h

No.	Method	Step	Reaction scheme	Ref.	Yield [%] <sup>[c]</sup>	AE <sup>[a]</sup> [%]	AE <sup>[b]</sup> [%]	Conditions	
19b	Suzuki-Coupling of Vinyl-bromides	1		20	90	67.7	67.7	150-155°C	5h
		2		20	70	48.2	37.3	90°C	30min
		3		46	81	100	52.9	rt	1.25 h
		4		47, 250	88	63.3	36.4	Reflux	1h
		5		48	93	44.8	[s]	Reflux	overnight
		6			100 <sup>[e]</sup>	68.7	[s]		
		7	 [u]	47	94 (42.2 <sup>[t]</sup> )	53.3	22.1	rt	1h
19c	Suzuki-Coupling of Vinyl-bromides	1		20 [v]	90	67.7	67.7	150-155°C	5h
		2		20	70	48.2	37.3	90°C	30min
		3		49	95	95	51.4	rt	12 h
		4		47, 250	88	63.3	35.5	Reflux	1h
		5		48	93	44.8	[s]	Reflux	overnight
		6			100 <sup>[e]</sup>	68.7	[s]		
		7	 [u]	47	94 (49.5 <sup>[t]</sup> )	53.3	21.8	rt	1h

No.	Method	Step	Reaction scheme	Ref.	Yield [%] <sup>[c]</sup>	AE <sup>[a]</sup> [%]	AE <sup>[b]</sup> [%]	Conditions
20	Negishi-Coupling of vinyl bromides	1-4	See 19b					
		5		251	89	31.2	[s]	reflux 1h
		6		47	100 <sup>[d]</sup>	100	[s]	rt 1h
		7		47	90 (47.4 <sup>[t]</sup> )	53.5	<b>21.3</b>	rt 2h
21	Ynolate conversion (Shindo)	1		50	100 <sup>[d]</sup>	64.8	64.8	-71°C (argon atm.) 26min
		2		50	100 <sup>[d]</sup>	64.9	54	-71°C (argon atm.) 52min
		3		50	90	50.7	38.7	-71°C (argon atm.) 40min
		4		50	100 <sup>[d]</sup>	16	7.7	-72°C (argon atm.) 177min
		5		50	100 <sup>[d]</sup>	100	19.5	2°C 30min
a		6		50	69 (62.1)	80.3	<b>18.1</b>	rt 60min
b		4-6 <sup>[x]</sup>		50	69 (62.1)	26.2	<b>16.1</b>	see above acidification during work-up see above
22	Ring-Opening Reactions of cyclopropenes (Wang, Y.)			53 [y]	100 <sup>[d]</sup>	77.1	77.1	- 1h
				52 [z]	91	48	40.8	rt 3h + 15h
				9	59	90.3	50.3	rt 8h
				9 [aa]	78 (41.9)	78.9	<b>45.4</b>	0°C; rt 1h; 15.5h

No.	Method	Step	Reaction scheme	Ref.	Yield [%] ( <sup>[c]</sup> )	AE <sup>[a]</sup> [%]	AE <sup>[b]</sup> [%]	Conditions	
23	Allylation of Alkenylal anes	1		55	100 <sup>[d]</sup>	100	<b>100</b>	nitrogen rt	12h
		2		55	83 ( <b>83</b> )	55.3	<b>55.3</b>	rt	6h
24	Organo- zinc re- agents and carbonyl com- pounds (Wang)	1		252	98	100	100	5°C	1-4h
		2		56	78 ( <b>76.4</b> )	56.2	<b>56.2</b>	60°C (inert atm.) -28°C, rt	10min 8h
25	Cross- coupling of alke- nylcar- boxylates with Grignard reagents	1		57	98	79,2	79,2	nitrogen rt	10+108min
		2		57	96 ( <b>94.1</b> )	52.1	<b>45.4</b>	nitrogen rt -5 to 0°C 25°C	10+20min 43+90min 15min
26	three compo- nents (Li)			58	82	95.6	<b>95.6</b>	10°C	21h
27a	Alkyla- tive or Arylative Carboxyl ation of Alkynes	1		252 <sup>[ab]</sup>	98	100	100	5°C	1-4h
		2		60 <sup>[ac]</sup>	81 ( <b>79.4</b> )	64.6	<b>64.6</b>	0°C	1h+2h
27b	see 27a	1	$\text{Ni}(\text{C}_5\text{H}_7\text{O}_2)_2 + 2 \text{C}_8\text{H}_{12} + 2 \text{Bu}_2\text{AlH} \longrightarrow \text{Ni}(\text{C}_8\text{H}_{12})_2 + 2 \text{Bu}_2\text{Al}(\text{C}_5\text{H}_7\text{O}_2) + \text{H}_2$	253 <sup>[ad]</sup>	72	36.3		-78°C to 0°C, N <sub>2</sub> atm.	1h

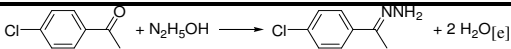
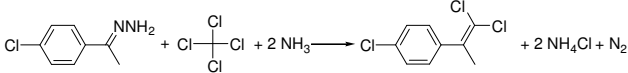
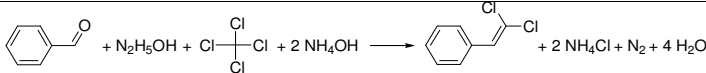
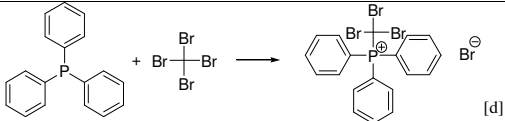
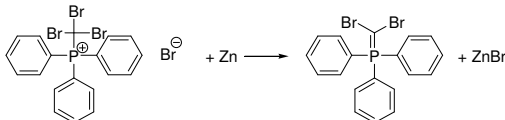
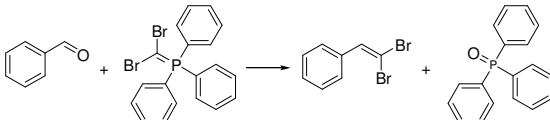
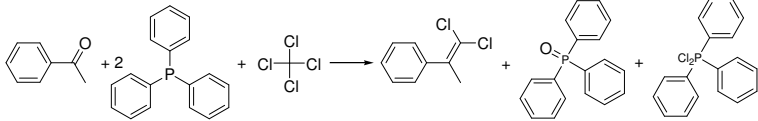


2		188 <sup>[ae]</sup>	100 <sup>[d]</sup>	100	80°C	3.5h			
3		188 <sup>[ae]</sup>	84	100	100°C (120atm)				
4		188 <sup>[ae]</sup>	88	89.4	reflux, i.e. about 138°C 5°C	10-12h			
5		252 <sup>[ab]</sup>	98	100	100	1-4h			
6		60 <sup>[ac]</sup>	81 ( <b>79.4</b> )	64.6	<b>64.6</b>				
28	Metathesis	1		61	99 <sup>[k]</sup>	90	90	rt	3h

<sup>[a]</sup> Atom economy of a single synthesis; <sup>[b]</sup> Atom economy of the synthesis sequence until this reaction; <sup>[c]</sup> Overall yield of synthesis sequence; <sup>[d]</sup> The intermediate was not isolated. Therefore, quantitative yield was assumed. <sup>[e]</sup> A published protocol does not exist for this reaction. Thus, a relatively ideal synthesis (dioxaborolane, 2 mass equiv. of aqueous hydrochloric acid (5%), 100% yield, no work up) is assumed resulting in a 100% yield. <sup>[f]</sup> according to <sup>66</sup> and <sup>254</sup>, <sup>[g]</sup> There are no details given in the experimental description. Instead of masses, the authors indicate 'equivalents'. Therefore, the amounts of converted materials do not seem to be complete. The stoichiometry is not known. We assume aluminum chloride, lithium chloride and hydrogen chloride to result from the reaction. <sup>[h]</sup> Concentration of the mother liquor and same work up results in 9-11% more product, which, however, is slightly impure. <sup>[i]</sup> The yield (97%) refers to cyclohexanone, i.e. the isolation of  $\text{TiCl}_3(\text{DME})_{1.5}$  with 80% yield was not considered for calculation of the overall yield. <sup>[j]</sup> A published protocol does not exist for this reaction. The authors refer to the literature procedure<sup>33</sup>. Thus, a relatively ideal synthesis is assumed resulting in a 100% yield. <sup>[k]</sup> The yield of a protocol delivering an alkene with tetrasubstituted double bond was 66%. <sup>[l]</sup> The coupled product is not known. The authors supposed  $(\text{OH})_2\text{B-B}(\text{OH})_2$  in their Scheme 2. However, this is stoichiometrically not possible without further assumptions. If one considers something like the  $\alpha$ -form of the metaboric acid ( $\text{B}_3\text{H}_3\text{O}_6$ ) as a potential coupled product, though not verified, the stoichiometry is correct. <sup>[m]</sup> The yield refers to the alkyne, explaining why the yield of preceding steps resulting in the boronic acid is not included. <sup>[n]</sup> Step 4 is a convergent synthesis resulting in one pot from step 3 and the sequence of step 1 and step 2. <sup>[o]</sup> The preparation of Grignard compounds often uses nearly equimolar amounts of alkyl halide and magnesium. For example, the protocol of Boeckman et al.<sup>255</sup> describes the conversion of 1.086 mol magnesium with 1 mol vinylbromide (75 mL) in tetrahydrofuran (200 mL) within two hours. Another protocol reports the reaction of 0.4 mol of magnesium and 0.4 mol of iodomethane (56.7 g) in 200 mL diethyl ether within 2.5 hours.<sup>256</sup> Therefore, we assume the following: magnesium (1 mol), methylbromide (1 mol) react to 100% in diethyl ether (150 mL) within 2 hours. <sup>[p]</sup> Personal communication with I. Marko enabled us to identify the protocol: 1 equiv. vinylcyclohexane, 1 equiv. thiophenol, 0.25 equiv.  $\text{HClO}_4$  (aq, 70%) were converted according to the literature<sup>247</sup> yielding 87% of the product. <sup>[q]</sup> Personal communication with I. Marko enabled us to identify the protocol: 1 equiv thioether, 1.02 equiv. mCPBA in dichloromethane resulted in a yield of 88%. No more details were available. <sup>[r]</sup> The preparation of 4-methoxyphenyl magnesium bromide is not sufficiently described in literature. Information was used as it was and 100% yield was assumed. According to the synthesis of 4-methylphenyl magnesium bromide<sup>257</sup> (yield 95%) this Grignard reaction is supposed to have a high yield as well. <sup>[s]</sup> Step 5 and 6 do not continue step 1-4, but represent a second path for the convergent synthesis step 7. <sup>[t]</sup> Yield related to triethylphosphite, ignoring the yield of step 5 and 6. <sup>[u]</sup> We assumed  $\text{KBO}(\text{OH})_2$  as the formula for the coupled product. See e.g.<sup>258</sup> for boronic acid salts. <sup>[v]</sup> Variants such as Horner-Wadsworth-Emmons (e.g.<sup>259,260</sup>) can directly deliver alkenes with tetrasubstituted double bond. <sup>[w]</sup> In ref.<sup>50</sup> the authors suggest to use lithium naphthalenide<sup>182</sup> instead of *tert*-butyllithium for larger scale, as naphthalene could be used catalytically. <sup>[x]</sup> In step 5 the mixture is poured onto 1 M aqueous lithium hydroxide. This can be understood as a reaction that can be summarized with step 4 and 6. While the overall mass balance is not affected, the atom economy is slightly reduced because of the neutralization step. <sup>[y]</sup> According to the literature<sup>51</sup> the preparation of dimethyl diazomalonate can be performed reasonably using tosyl azide.<sup>52</sup> <sup>[z]</sup> A polymer-bound tosyl azide<sup>54</sup> could be an alternative azide source to the considered literature.<sup>53</sup> <sup>[aa]</sup> Malonic acid esters undergo decarboxylations<sup>183,184</sup> so that trisubstituted  $\beta, \gamma$ -unsaturated acid derivatives should be producible. <sup>[ab]</sup> The authors<sup>60</sup> produce benzyl zinc bromide according to literature<sup>59</sup>. However, according to literature<sup>252</sup>, which is also applied in entry 24, a higher yield is conceivable. An alternative procedure to prepare

benzylzinc reagents was reported by Harada et al.<sup>261</sup> [ac] The catalyst Ni(COD)<sub>2</sub>, for which synthesis is described in references<sup>262</sup> and <sup>253</sup>, was applied in nearly stoichiometrical amounts. [ad] As no stoichiometric equation has been indicated in literature, we assume the one shown here. [ae] In literature, the synthesis not of DBU but of DBN was presented! This protocol was adapted, i.e. instead of the five-ring pyrrolidone, the sept-ring azepan-2-one was considered using the amounts and yields of DBN-synthesis. [af] The stoichiometry is not completely known. Copper acetate, which is used in a certain amount, is considered to be a catalyst. [ag] Trimethylsilylchloride (Me<sub>3</sub>SiCl) is applied twice as much using 0.02 mol as the carbonyl compound. The mechanism presages the transformation to Me<sub>3</sub>SiOH. Therefore, a corresponding reaction equation could also be formulated, which would reduce the atom economy.

**Table S 8** Methods for the preparation of geminal dihalogenids: yields, atom economies and reaction conditions. Detail information related to Table 1 and Table 2.

No.	Method	Step	Reaction scheme	Ref.	Yield [%] <sup>[c]</sup>	AE <sup>[a]</sup> [%]	AE <sup>[b]</sup> [%]	conditions
29a	Nenajdenko 2005	1		62	87	82.4	82.4	Reflux (i.e. 78°C) 3h
		2		62	86 <b>(74.8)</b>	56.4	<b>51.2</b>	rt overnight
29b	Nenajdenko 2001	1		63	74	45.5	<b>45.5</b>	rt 20°C 3h rt 10min 4h
29c	Corey	1		64	100 <sup>[d]</sup>	100	100	23°C 24-30h
		2		64	100 <sup>[d]</sup>	65.8	65.8	
		3		64	90 ( <b>90</b> )	48.5	<b>34.2</b>	1-2h
29d	Patil	1		65	<b>70</b>	23.4	<b>23.4</b>	Reflux, i.e. 39.7°C 48h

<sup>[a-c]</sup> See Table S 7

<sup>[d]</sup> Step 1 to Step 3 need to be considered together: all substrates are mixed in one pot. Addition of benzaldehyde takes place after about 24-30h.

<sup>[e]</sup> More syntheses of mono- and dihaloalkenes (also dibromo-compounds) were presented in the literature.<sup>263</sup>

**Table S 9** Solvent utilization (Note: four decimal places are probably not necessary, but they were given by the software <sup>69</sup> and simply noted here.)

						Function of solvent			Removal of solvent		Aqueous solutions			
No.	Method	Step	Ref.	Name	Mass	Reaction	Extraction	washing (dilution)	Recrystallisation	Chromatography	Distillation	Filtration	Decantation	washing
1	$\beta$ -Elimination of xanthates, prepared from alcohols	1	19	Toluene	2.7724	☒					☒			
		1		Diethyl ether	5.6729	☒				☒				
		1		Diethyl ether	not spec.			☒		☒				
		1		Ethanol	5.0319			☒			☒		water to precipitate	
2a	Wittig	1	20	Toluene	7.8285	☒								
		1	20	Toluene	not spec.			☒						
		2	20	Pentane	not spec.			☒						
		2/3	20	Dimethylsulfoxide	8.9401	☒					☒			water
		3	20	Pentane	not spec.		☒				☒			water
2b	Wittig (catalytic)	1	21	Methanol	10.9306	☒							☒	
		2	21	Toluene	2.1038	☒							☒	
		2	21	Benzene (with solvent next line)	not spec.					☒			☒	
		2	21	Pentane	not spec.					☒			☒	
3	Carbene Dimerisation	1	22	Dichloromethane	not spec.		☒				☒			NaOH(aq)
		2	22	Acetic acid	24.5118·6/16	☒					☒			
				Acetic acid	24.5118·10/16			☒			☒			
				Diethyl ether	94.9276·40/65			☒			☒			
				Tetrahydrofuran	25.9722	☒					☒			
				Diethyl ether	not spec.			☒			☒			
				Diethyl ether	94.9276·25/65		☒				☒			water
				Methanol	17.3455			☒				☒		

						Function of solvent					Removal of solvent	Aqueous solutions			
No.	Method	Step	Ref.	Name	Mass	Reaction	Extraction	washing (dilution)	Recrystallisation	Chromatography	Distillation	Filtration	Decantation	washing	
4a	Barton-Kellogg's extrusion process	1	23	t-Butanol	19.4756	☒					☒			water	
		1	23	Diethyl ether	93.0887		☒				☒			brine	
		1	23	Hexane	not spec.				☒			☒			
		2	23	Acetone	8.126	☒					☒				
		2	23	Benzene	26.9724	☒					☒				
		3	23	Benzene	78.2275	☒					b) ☒		a) ☒	water	
		3	23	Diethyl ether	not spec.		☒				☒			brine	
		4	23	Hexane	not spec.					☒	☒				
	Barton-Kellogg's extrusion process	1	24												water
		1	24	Diethyl ether	27.6929		☒					☒			brine
		2	24	Dimethylformamid	14.0378	☒						☒			
		3	24	Toluene	19.3766										
		3/4	24	Hexane / CH2Cl2	not spec.					☒	☒				NH4Cl(aq)
		4	24	Diethyl ether	not spec.		☒				☒				water
4		24	Pentane / Ether	not spec.					☒	☒					
5		24	Xylol	30.8234						☒					
5a	McMurry (variation using TiCl4/Zn)	1	66	Tetrahydrofuran	21.8232	☒					☒				
		2	66	Tetrahydrofuran	11.6884	☒					☒			K2CO3(10%)	
		2	66	Cyclohexane	17.0921		☒				☒			water	
		2	66	Ethanol / Cyclohexane	not spec.				☒						
5b	McMurry (variation using TiCl3/LiAlH4)	1	26	Tetrahydrofuran	not spec.	☒					☒				
		2		Tetrahydrofuran	not spec.	☒					☒				

						Function of solvent					Removal of solvent	Aqueous solutions			
No.	Method	Step	Ref.	Name	Mass	Reaction	Extraction	washing (dilution)	Recrystallisation	Chromatography	Distillation	Filtration	Decantation	washing	
5c	McMurry (variation using TiCl <sub>3</sub> /K)	1	27	Tetrahydrofuran	145.6025	☒					☒				
		2		Tetrahydrofuran	14.557	☒				☒					
		2		Ethanol	not spec.			☒		☒					
5d	McMurry (variation using TiCl <sub>3</sub> /Li)	1	28	1,2-dimethoxyethane	50.1692	☒					☒				
		2	28	Petroleum ether	88.8053			☒			☒				
		2	28	Methanol	269.8807·1500/3550			☒			☒				
		2	28	Methanol	269.8807·2000/3550			☒				☒			
		2	28	Methanol	269.8807·50/3550			☒				☒			
5e	McMurry (variation using TiCl <sub>3</sub> DME <sub>1.5</sub> /Zn-Cu)	0	29	Acetone	not spec.			☒				☒			
		0		Diethyl ether	not spec.			☒			☒				
		1		Dimethoxyethane	108.8568	☒				☒					
				Pentane	not spec.			☒			☒				
		2		Dimethoxyethane	242.6352	☒				☒					
		3		Dimethoxyethane	24.2635	☒				☒					
3	Pentane	175.7014			(☒)		☒								
5f		1	30	Dimethoxyethane	11.1174	☒					☒				
		1		Tetrahydrofuran	113.824		☒			☒					
		1		Hexane / ethyl acetate, 10:1	not spec.				☒	☒					
5g		1	31	Dichloromethane	24.9102 (assumption of 10 mL)		☒				☒				
6	Claisen	1	32	Diethyl ether	5.9838	☒					☒				NaHCO <sub>3</sub> (aq, conc.), NaCl(aq, conc.)
		1	32	Diethyl ether	8.7037	☒					☒				NaHCO <sub>3</sub> (aq, conc.), NaCl(aq, conc.)
		2	32	Propionic acid	0.0202	☒					☒				

						Function of solvent					Removal of solvent	Aqueous solutions			
No.	Method	Step	Ref.	Name	Mass	Reaction	Extraction	washing (dilution)	Recrystallisation	Chromatography	Distillation	Filtration	Decantation	washing	
7	Alkylation – elimination process	1	<sup>33</sup>	Tetrahydrofuran	12.7780	☒					☒			Water (hydrolysis)	
		1	<sup>33</sup>	Hexane, n-	5.1126	☒					☒			Water (hydrolysis)	
		2	<sup>34</sup>	Tetrahydrofuran	12.7780	☒								Water (hydrolysis)	
		2	<sup>34</sup> acc. to <sup>33</sup>	Diethyl ether	not spec.		☒				☒			water	
		3	<sup>34</sup> acc. to <sup>33</sup>	Tetrahydrofuran	76.6678	☒					☒			Water	
		3	<sup>34</sup>	Hexane, n-	16.8715	☒					☒			Water	
		3	<sup>34</sup>	Hexane not spec.	284.1623		☒				☒	☒			
8	Suzuki-Miyaura (Zhou, Laroc)	1-2	<sup>35</sup>	See 19b steps 5-6											
				DMSO	35.2052	☒					☒			NaCl(conc.)	
				Diethyl ether	1019.6714		☒				☒				
				not spec.						☒	☒				
9	Hydro-arylation	1-2		See 19b steps 5-6											
		3		Methanol	7.714	☒						☒			
		Acetic acid ethyl ester		0.0325			☒				☒				
		Hexane		3.1919			☒				☒				
hexanes/ethyl acetate	Approximately 1L for ca. 6.5 g product						☒	☒							
10	Arylzincation	1	<sup>246</sup>	THF	13.3068	☒							☒		
		1	<sup>37</sup>	Acetonitrile	1.1765	☒							☒	NH4Cl (aq)	
		2	<sup>37</sup>	Hexane	0.3288	☒							☒	NH4Cl (aq)	
		2	<sup>37</sup>	Ethyl acetate			☒						☒	NH4Cl (aq)	
		2	<sup>37</sup>	Hexane	not spec.						☒	☒			

11	Negishi-Tan	1	<sup>63</sup>	Dimethylsulfoxide	7.3152	☒		☒	HCl (1M)
		1	<sup>63</sup>	Dichloromethane	132.1718		☒	☒	HCl (1M)
		2	<sup>38</sup>	Dimethylformamide	13.8775	☒		☒	HCl(aq), brine
		2		Diethyl ether	not spec.		☒	☒	brine
		3		Diethyl ether	0.7055	☒			
		4		Tetrahydrofuran	7.8748	☒		☒	NH <sub>4</sub> C 1 (conc.) , brine
		4		Diethyl ether not spec.	not spec.		☒	☒ ☒ ☒	brine
12	Shapiro type	1	<sup>39</sup>	Acetonitrile	5.281	☒		☒	HCl (aq)
		1	<sup>39</sup>	Dichloromethane	15.5793		☒	☒	
		2	<sup>39</sup>	n-Hexane	9.632	☒		☒	water
		2	<sup>39</sup>	n-Hexane	14.0532	☒		☒	water
		2	<sup>39</sup>	tetramethylethylenediamine	16.5269	☒		☒	water
		3	<sup>39</sup>	Diethyl ether	15.0981	☒		☒	Water
13	Peterson method	1	<sup>40</sup>	Tetrahydrofuran	61.182	☒		☒	NH <sub>4</sub> Cl(aq), NaCl(aq)
		1	<sup>40</sup>	Diethyl ether	18.7405		☒	☒	NH <sub>4</sub> Cl(aq), NaCl(aq)
		2	<sup>40</sup>	Tetrahydrofuran	46.8414	☒		☒	
		2	<sup>40</sup>	Hexane; n-	62.5008		☒	☒	
		3	<sup>40</sup>	Tetrahydrofuran	70.2086	☒		☒	
		3	<sup>40</sup>	Isopropanol	17.0316	☒		☒	
		3	<sup>40</sup>	Diethyl ether	82.9495	☒		☒	
		3	<sup>40</sup>	Hexane; n-	40.0341	☒		☒	NaHCO <sub>3</sub> (conc.), NaCl(aq)
		3	<sup>40</sup>	Diethyl ether	15.361		☒	☒	NaHCO <sub>3</sub> (conc.), NaCl(aq)



						Function of solvent				Removal of solvent		Aqueous solutions			
No.	Method	Step	Ref.	Name	Mass	Reaction	Extraction	washing (dilution)	Recrystallisation	Chromatography	Distillation	Filtration	Decantation	washing	
14	Julia-Lythgoe	1	<sup>50</sup>	Tetrahydrofuran (see step 1 in entry 21)	39.9068	☒					☒			NaHCO <sub>3</sub> (conc.)	
		1		Hexane (see step 1 in entry 21)	7.5389	☒					☒			NaHCO <sub>3</sub> (conc.)	
		2		Benzene	16.3719		☒				☒			NaOH (aq)	
		3		Dichloromethane	not spec.	☒					n.s.				
		4	<sup>247</sup>	Tetrahydrofuran	169.9924	☒					☒				HCl (1M), water, brine
		5	<sup>247</sup>	Tetrahydrofuran	8.4996	☒					☒				HCl (1M), water, brine
		6	<sup>247</sup>	Tetrahydrofuran	8.4996	☒					☒				HCl (1M), water, brine
		6	<sup>247</sup>	Diethyl ether	67.691		☒				☒				HCl (1M), water, brine
		7	<sup>247</sup>	Tetrahydrofuran	590.0096	☒					☒				NH4Cl (sat.), Na2S2O3 (10% aq), water, brine
		7	<sup>247</sup>	Tetrahydrofuran	8.4996	☒					☒				dito
		7	<sup>247</sup>	HMPA	0.0121			☒			☒				dito
		7	<sup>247</sup>	Diethyl ether not spec.	812.2922			☒			☒	☒			dito
15	Thiolester conversion	1	<sup>42</sup>	Dichloromethane	15.1513	☒					☒			H2O (with HCl, NaCl)	
		2	<sup>42</sup>	Hexane	1.2219	☒					☒			H2O (with NH4Cl, Na2CO3, NaCl)	
		2	<sup>42</sup>	Tetrahydrofuran	12.426	☒					☒			See above	
		2	<sup>42</sup>	Hexane	5.9427		☒				☒			See above	
		3	<sup>42</sup>	Cyclohexane	8.7923	☒					☒				
		3	<sup>42</sup>	Hexane	(20 mL per min, 120-mL fractions)					☒	☒				

No.	Method	Step	Ref.	Name	Mass	Function of solvent					Removal of solvent	Aqueous solutions		
						Reaction	Extraction	washing (dilution)	Recrystallisation	Chromatography	Distillation	Filtration	Decantation	washing
16	Heck	1	43	Toluene	4.2373	☒								
			43	Diethyl ether	27.0954		☒			☒			H2O/brine	
			43	hexane/diethyl ether 19/1	Not spec.					☒				
17	Heck	1	248	THF	57.3933	☒							☒	H2O
		1	248	CHCl3	not spec.		☒						☒	H2O
		1	248	Benzene	not spec.					☒			☒	
		1	248	CHCl3	not spec.					☒			☒	
		2	249	THF	14.0940	☒							☒	H2O
		2	249	CHCl3	not spec.		☒						☒	H2O
		2	249	Hexane	not spec.					☒			☒	
		2	249	Dichloromethane	not spec.					☒			☒	
		3	44	Toluene	29.8861	☒							☒	
		3	44	Hexane (with solvent next line)	not spec.					☒			☒	
		3	44	Acetic acid ethyl ester	not spec.					☒			☒	
		3	44	Acetic acid ethyl ester	not spec.								☒	
		4	44	THF	44.0423	☒								NaOH (aq, 1%)
		4	44	Pentane	5.3812	☒								same
		4	44	THF	Integrated into first	☒								same
		4	44	THF	THF figure	☒								same
		4	44	Unknown (extractive workup)	not spec.		☒							same
		4	44	Hexane (with solvent next line)	not spec.					☒				
		4	44	Acetic acid ethyl ester	not spec.					☒				
		5	44	Toluene	85.4750	☒								☒
		5	44	THF	16.2393									☒
		5	44	Acetic acid ethyl ester	not spec.									☒
		5	44	Hexane (with solvent next line)	not spec.					☒				☒
		5	44	Acetic acid ethyl ester	not spec.					☒				☒

						Function of solvent			Removal of solvent			Aqueous solutions		
No.	Method	Step	Ref.	Name	Mass									
						Reaction	Extraction	washing (dilution)	Recrystallisation	Chromatography	Distillation	Filtration	Decantation	washing
18	Alkynes (Yamagami)	1	45	Et3N (substrate excess)	4.0997	☒							☒	
		1	45	Acetic acid ethyl ester	not spec.				(☒)				☒	
		1	45	Hexane	not spec.					☒				
		2	45	THF	18.3369	☒							☒	
		3	45	THF	6.6013									H2O
		3	45	Diethyl ether (TLC)	not spec.					☒			☒	
		3	45	Hexane (TLC)	not spec.					☒			☒	
19a	Suzuki-Coupling of Vinyl-bromides	3	46	Diethyl ether	11.6011	☒						☒		
		4	47, 250	Tetrahydrofuran	7.8661	☒					☒			
		4	47, 250	Methanol	6.9990	☒					☒			
		4	47, 250	Diethyl ether	12.5292			☒			☒			
		7	47	Methanol	7.6989	☒					☒			NaOH (aq), brine
		7	47	Tetrahydrofuran	8.6528	☒					☒			NaOH (aq), brine
		7	47	Diethyl ether	82.6927			☒			☒			NaOH (aq), brine
		7	47	Cyclohexane	not. spec.					☒	☒			
19b	Suzuki-Coupling of Vinyl-bromides	1	20	-										
		2	20	Toluene	8.0992	☒					☒			water
		3	46	Diethyl ether	11.6011	☒						☒		
		4	47, 250	Tetrahydrofuran	7.8661	☒					☒			
		4	47, 250	Methanol	6.9990	☒					☒			
		4	47, 250	Diethyl ether	12.5292			☒			☒			
		5	48	Tetrahydrofuran	4.4659	☒					☒			
		5	48	Toluene	2.1727	☒					☒			

		5	<sup>48</sup>	Ethylene glycol	2.4763	☒		☒	
		7	<sup>47</sup>	Methanol	7.6989	☒		☒	NaOH (aq), brine
		7	<sup>47</sup>	Tetrahydrofuran	8.6528	☒		☒	NaOH (aq), brine
		7	<sup>47</sup>	Diethyl ether	82.6927		☒	☒	NaOH (aq), brine
		7	<sup>47</sup>	Cyclohexane	not. spec.			☒ ☒	
19c	Suzuki- Coupling of Vinyl- bromides	1	<sup>20</sup>	-					
		2	<sup>20</sup>	Toluene	6.9057	☒		☒	water
		3	<sup>49</sup>	Acetonitrile	7.3208	☒		☒	
		4	<sup>47</sup> , <sup>250</sup>	Tetrahydrofuran	7.8661	☒		☒	
		4	<sup>47</sup> , <sup>250</sup>	Methanol	6.9990	☒		☒	
		4	<sup>47</sup> , <sup>250</sup>	Diethyl ether	12.5292		☒	☒	
		5	<sup>48</sup>	Tetrahydrofuran	4.4659	☒		☒	
		5	<sup>48</sup>	Toluene	2.1727	☒		☒	
		5	<sup>48</sup>	Ethylene glycol	2.4763	☒		☒	
		7	<sup>47</sup>	Methanol	7.6989	☒		☒	NaOH (aq), brine
		7	<sup>47</sup>	Tetrahydrofuran	8.6528	☒		☒	NaOH (aq), brine
		7	<sup>47</sup>	Diethyl ether	82.6927		☒	☒	NaOH (aq), brine
		7	<sup>47</sup>	Cyclohexane	not. spec.			☒ ☒	

						Function of solvent				Removal of solvent		Aqueous solutions			
No.	Method	Step	Ref.	Name	Mass	Reaction	Extraction	washing (dilution)	Recrystallisation	Chromatography	Distillation	Filtration	Decantation	washing	
20		1-4		See 19b											
		5	251	-	-										
		5		Hexane						☒	☒				
		6	47	Hexane	2.1923	☒					☒				
		7	47	Tetrahydrofuran	25.2909	☒					☒				
		7	47	Hexane	not. spec.					☒	☒				
21	Shindo	1	50	Tetrahydrofuran	22.9296	☒					☒			NaHCO <sub>3</sub> (conc.)	
	Ynolate	1		Hexane	4.3317	☒					☒			NaHCO <sub>3</sub> (conc.)	
	conversion	2		Tetrahydrofuran	1.9654										
		3		Tetrahydrofuran	3.9308	☒					☒				NaHCO <sub>3</sub> (conc.)
		3		Hexane	14.5691			☒			☒				water, brine
		4		Tetrahydrofuran	24.7033	☒					☒				NaOH (1M), brine
		4		Pentane	12.8891	☒					☒				NaOH (1M), brine
		5		Tetrahydrofuran	2.6706	☒					☒				NaOH (1M), brine
		5		Ethylacetate	32.5161			☒			☒				NaOH (1M), brine
		6		Ethylacetate	48.7742			☒			☒				brine
	4-6		See above												

						Function of solvent					Removal of solvent	Aqueous solutions		
No.	Method	Step	Ref.	Name	Mass	Reaction	Extraction	washing (dilution)	Recrystallisation	Chromatography	Distillation	Filtration	Decantation	washing
22	Wang	1	<sup>53</sup>	Ethanol (95%)	7.5122	☒					☒			Water
		2	<sup>52</sup>	Benzene	7.8907	☒					☒			
		2	<sup>52</sup>	Hexane; n-	1.6999	☒					☒			
		3	<sup>9</sup>	Dichloromethane	18.1468	☒					☒			
		3	<sup>9</sup>	EtOAc/hexane	not. spec.					☒	☒			
		4	<sup>9</sup>	Tetrahydrofuran	41.2455	☒					☒			Rochelle's salt (aq)
		4	<sup>9</sup>	Hexane; n-	3.0575	☒					☒			Rochelle's salt (aq)
		4	<sup>9</sup>	Dichloromethane	307.3695			☒			☒			Rochelle's salt (aq)
		4	<sup>9</sup>	Dichloromethane	1383.1626			☒			☒			Rochelle's salt (aq)
		4		EtOAc/hexane	not. spec.						☒	☒		
23	Allylation of Alkenyl-alanes	1	<sup>55</sup>	1,2-dichloroethane	7.405	☒					☒			HCl(aq)
		1	<sup>55</sup>	Xylene	0.3679	☒					☒			HCl(aq)
		1	<sup>55</sup>	Toluene	4.7107	☒					☒			HCl(aq)
		2	<sup>55</sup>	Tetrahydrofuran	5.2413	☒					☒			HCl(aq)
		2	<sup>55</sup>	Pentane	not. spec.			☒			☒			HCl(aq), water, NaHCO <sub>3</sub> (aq)
		2	<sup>55</sup>	Hexane	not. spec.						☒	☒		
		2	<sup>55</sup>	Hexane	not. spec.						☒	☒		
24		1	<sup>252</sup>	Tetrahydrofuran	6.5659	☒					☒			
		2	<sup>56</sup>	Tetrahydrofuran	3.6849	☒					☒			NH <sub>4</sub> Cl(conc.)
		2	<sup>56</sup>	Diethyl ether	4.3576			☒			☒			
		2		petroleum/ ethyl acetate	not. spec.						☒	☒		

						Function of solvent				Removal of solvent		Aqueous solutions		
No.	Method	Step	Ref.	Name	Mass	Reaction	Extraction	washing (dilution)	Recrystallisation	Chromatography	Distillation	Filtration	Decantation	washing
25	Cross-coupling of alkenyl-carboxylates with Grignard reagents	1	57	Tetrahydrofuran	10.1393	☒					☒			
		1	57	Acetic acid ethyl ester	8.9457		☒				☒			Partly water, NaOH(aq), NaCl(aq)
		1	57	Dichloromethane	39.4227					☒	☒			
		1	57	Hexane; n-	75.1611					☒	☒			
		2	57	Tetrahydrofuran (from HexylMgCl)	3.281	☒					☒			HCl (aq), NaCl(aq)
		2	57	Tetrahydrofuran	6.0483	☒					☒			HCl (aq), NaCl(aq)
		2	57	Acetic acid ethyl ester	19.287		☒				☒			HCl (aq), NaCl(aq)
		2	57	Hexane; n-	61.4883					☒	☒			
26		1	58	Nitromethane	3.578	☒				(☒)	☒			
		1	58	petroleum ether	not. spec.					☒	☒			
27a	Alkylative or Arylative Carboxyla - tion of Alkynes	1	252	Tetrahydrofuran	4.1379	☒					☒			HCl (10%) (hydrolysis)
		2	60	Tetrahydrofuran	53.6979	☒					☒			HCl (10%) (hydrolysis)
		2	60	Tetrahydrofuran	7.8325	☒					☒			HCl (10%) (hydrolysis)
		2	60	Diethyl ether	4.4535	☒					☒			HCl (10%) (hydrolysis)
		2	60	Acetic acid ethyl ester	not spec.		☒				☒			brine
		2	60	hexane/EtOAc/AcOH	not. spec.					☒	☒			
27b	see 27a	1	253	Tetrahydrofuran	17.9061	☒							☒	
		1	253	Diethyl ether	13.1666		☒						☒	
		2	188	-										
		3	188	Methanol	0.214	☒					☒			
		3	188	Ammonia	0.4166	☒					☒			
		4	188	Xylene	1.4877	☒					☒			
		See 27a for syntheses 5 and 6												

						Function of solvent			Removal of solvent	Aqueous solutions				
No.	Method	Step	Ref.	Name	Mass	Reaction	Extraction	washing (dilution)	Recrystallisation	Chromatography	Distillation	Filtration	Decantation	washing
28	Olefin	1	<sup>61</sup>	Acetic acid ethyl ester	845.8273		☒	☒			☒			(water was solvent)
	metathesis	1	<sup>61</sup>	12% Acetic acid ethyl ester / hexanes	not spec.					☒	☒			
29a	Nenajdenko, 2005		<sup>62</sup>	Ethanol	0.4079			☒					☒	HCl (5%)
			<sup>62</sup>	Acetone	0.4105			☒					☒	
			<sup>62</sup>	Diethyl ether	0.3679			☒					☒	
		1	<sup>62</sup>	Ethanol	4.7364	☒					☒			
		1	<sup>62</sup>	Ethanol	0.4736			☒					☒	
		1	<sup>62</sup>	Hexane	1.5905			☒					☒	
		2	<sup>62</sup>	Dimethylsulfoxide	5.7763	☒					☒			
		2	<sup>62</sup>	Hexane	13.8372			☒			☒			
		2	<sup>62</sup>	Hexane	13.8372					☒	☒			
29b	Nenajdenko, 2001	1	<sup>63</sup>	Dimethylsulfoxide	8.5904	☒					☒			HCl (1M)
		1	<sup>63</sup>	Dichloromethane	155.2120		☒				☒			HCl (1M)
29c	Corey 1972			not spec.						☒	☒			
		1-3	<sup>64</sup>	Methylene chloride	not spec.	☒							☒	
		3	<sup>64</sup>	Pentane	not spec.		☒						☒	
		3	<sup>64</sup>	Methylene chloride	not spec.								☒	
29d	Patil 2002			not spec.										
		1	<sup>65</sup>	Dichloromethane	20.2371	☒					☒			
				not spec.						☒	☒			



**Table S 10** Assumptions that were made for the examination of alkene syntheses (Figure 1, Figure 2).

Entry	Lit.	Assumption
2b	<sup>21</sup>	Step1: "under 20 bar H <sub>2</sub> , at 1 mL/min flow rate" cannot be entered. Thus, the minimum amount was assumed.
5e	<sup>29</sup>	Step1: the authors produce the Zn-Cu-couple with 150 mmol of zinc. They use 69 mmol of this Zn-Cu-couple. As they used 0.75 g of coppersulfate to produce the Zn-Cu-couple, we assume 0.345 g of coppersulfate to be used in synthesis of cyclohexylidenecyclohexane. ( $0.345 \text{ g} = 0.75 \text{ g} \cdot 69 : 150$ )
5g	<sup>29</sup>	Step1: 10 mL solvent for extraction
6	<sup>32</sup>	A "small chrystal of iodine" is assumed to be about 0.001g. Washing with sodium hydrogen carbonate: Solubility in water 6.9g in 100ml at 0°C (at 60°C: 16.4g) (Lit: Handbook of Chemistry and Physiks, David R. Lide, 73RD Edition 1992-1993, ISBN 0-8493-0473-3, S. 4-98) So the purity is $6.9/106.9 = 6.454\%$ . As the density is not known it is supposed, that 1 ml is 1 g. Washing with sodium chloride (aq): Solubility in water 35,7g in 100ml at 0°C (at 100°C: 39,12g) (Lit: Handbook of Chemistry and Physiks, David R. Lide, 73RD Edition 1992-1993, ISBN 0-8493-0473-3, S. 4-98) So the purity is $35,7/135,7 = 26,308\%$ . As the density is not known it is supposed, that 1 ml is 1 g.
7	<sup>33-34</sup>	Step 2: in literature <sup>34</sup> the preparation of 1,1,1-tribromo-2-methyl-2-heptanol is not described. There is a reference to the literature. <sup>33</sup> Thus, the general protocol of the literature <sup>33</sup> was applied to the production of 1,1,1-tribromo-2-methyl-2-heptanol. In order to avoid a discrimination of this procedure, a yield of 100% was assumed.
9	<sup>36</sup>	The authors did not denote the coupled product. As a hydrogen source is necessary and only methanol is available, the first conceivable coupled product is CH <sub>3</sub> OB(OH) <sub>2</sub> . Possibly it will form the trimethyl ester in another conversion.
10	<sup>246-37</sup>	Step2: 0.03 mL hexane. In fact, the actual amount will differ a bit, because a 1M solution of the catalyst (P(C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> ) in 0.03 mL is used. I.e. there is also another compound in this amount.
11		The preparation of Grignard compounds often uses nearly equimolar amounts of alkyl halide and magnesium. E.g. the protocol of Boeckman et al. <sup>255</sup> describes the conversion of 1.086 mol magnesium with 1 mol vinylbromide (75 mL) in tetrahydrofuran (200 mL) within two hours. The reaction of 0.4 mol of magnesium and 0.4 mol of iodomethane (56.7 g) in 200 mL diethyl ether within 2.5 hours is reported in another protocol. <sup>256</sup> Therefore, we assume the following: magnesium (1 mol), methylbromide (1 mol) react to 100% in diethyl ether (150 mL) within 2 hours.
12	<sup>39</sup>	Step2: instead of 1.29 M solution of sec.-butyllithium, we considered 1.62 M, because data of such a concentration was readily available. We assumed 2,4,6-tri-isopropylphenylsulfonic acid to be the coupled product, because nitrogen evolves during the reaction.
13	<sup>40</sup>	Step1: the literature quantity of 1.06 mol of lithium compared to the necessary amount of 0.335 mol is very exaggerated. In order to obtain a more realistic overview of the synthesis, the ideal amount of 0.335 mol was assumed. Step2: the coupled product in the stoichiometric equation is not clear, therefore all atoms of potential coupled products were collected to one formular? Step3: copper bromide-dimethyl sulfide is considered to be a catalyst which has to be used in stoichiometric amounts. Therefore, it was entered as substrate and as product. Step3: methyllithium was used as 1.4 M solution in hexane. However, no information concerning the density was available. Therefore, another example could be helpful: the density of a 1.6 M solution in diethyl ether is 0.732 g/mL or 732g/L. Such a solution contains 30.76598 g/L (=1.4 mol/L x (21.9757 g/mol)). Thus, the purity is 0.04203 (= 30.76598 g/L / 732g/L) and the amount of diethyl ether in 1000 mL is 701.23 g (= 732g - 30.76598 g). A simple approximation of the amount of hexane could be 700 mL.
15	<sup>42</sup>	Step2/3: the authors obtained 41.5 g of the product in the proceeding step 2 (synthesis of the lactone). However, according to the molecular masses of the substrate (264.425 g/mol) and the product (240.385 g/mol) and the quantities (substrate 0.17mol; product 41.5g=0.172639mol), the yield would be 101.55%. Apparently, the crude product is impure. In note 15 the authors describe which by-products they obtain, even the quantities. Though note 15 belongs to the third step, the by-products can only result from the

		second step. Therefore, the following by-products will be listed under 'By-products' in step 2 (synthesis of the lactone) and the crude product is considered to contain 30.7g of the product (=41.5g - 10.8g), which has to be entered in the third step. Thus, the yield in the second step is 75.1% (=30.7g/240.385g/mol / 0.17mol) in best case. In the third step the yield is not 69% (authors) but 91.7% (= 23g/196.375g/mol / 30.7g/240.385g/mol). The overall yield for step 2 and 3 is 68.8%(= 75.1% x 91.7%), which corresponds to the yield of 69% (authors). Including step 1, the overall yield is 67.5%(= 98% x 75.1% x 91.7%).
		By-products found: thiophenol 5g; diphenyl disulfide 0.2g; dinonyl ketone 2.4g; S-phenyl decanoate 0.8g; enol of 2-methyl-3,5-diketotetradecane 2.4g; Sum=10.8g
18	45	Step1: 100% yield Step2: 100% yield, and minimal amount of Mg
19b		Step3: instead of 80uL water, the stoichiometrical minimal amount of 0.2 mmol was assumed
20	251	Step 4: Assuming that at minimum the twofold quantity of hydrochloric acid ((substrate, 1mol = 162g)) would be necessary, one could note 2*161g=322g Hydrochloric acid (aq, 1 M). As 2 mol of water have been allocated to the substrates, 322g - 2*18g = 286g of hydrochloric acid are considered. No further work up was considered and the yield is assumed to be 100%.
21	30	Step5: Instead of 130g of Zn-Cu-couple, 120 g of zinc and 10 g CuO were considered from which this couple is made. The utilization of hydrogen was ignored.
22	9	Step1: The amount of hexane (58.78 mL) of the butyllithium solution is calculated: With $M(C_4H_9Li) = 64.0561 \text{ g/mol}$ and $c(C_4H_9Li) = 1.62 \text{ mol/L}$ there are $64.0561 \text{ g/mol} * 1.62 \text{ mol/L} = 103.770882 \text{ g/L}$ . Therefore, 0.102 L contain $m(C_4H_9Li) = 103.770882 \text{ g/L} * 0.102 \text{ L} = 10.58462996 \text{ g}$ and $69.36 \text{ g} - 10.58462996 \text{ g} = 58.77537004 \text{ g}$ hexane Step4: The density of a 1.7 M solution (t-butyllithium) is 0.652 g/mL. $M(t\text{-BuLi}) = 64.0561 \text{ g/mol}$ . Therefore, there are 108.89537 g/L (=64.0561 g/mol * 1.7 mol/L) of t-BuLi in solution. This means a purity of 108.89537 g/L : 652 g/L = 0.1670174. Literature: "1.72 M solution of tert-butyllithium in pentane (158 mL, 272 mmol, 4.9 equiv)" Assumption: Instead of a 1.72 M solution a 1.7 M solution is assumed.
23	35	Step 1: No further work up was considered and the yield is assumed to be 100%
24	252 36	Step 4: 2 M solution of trimethyl aluminum in hexane is used. Two equivalents (i.e.0.0004 mol) of trimethyl aluminum are used. Thus about 0.0004 mol / 2 mol/L = 0.0002 L hexane are used. The purity of Rochelle salt solution is assumed to be 9.1% = 0.091 = 0.1g (salt) / (0.1g (salt) + 1g (water)). The density is not known. Thus 1 g/mL are assumed. 0,0002 mol water were allocated to the substrates to fullfill stoichiometry.
27b	253 188	The aqueous work-up using HCl is considered to contribute to the stoichiometry, because the alane will be decomposed. Step1: General procedure A was considered. The hint "GLC analysis showed complete conversion in 2 h with less than 2% Wurtz coupling." was interpreted in that way that 2% of Wurtz coupling product was formed, i.e. a yield of 98% was assumed. Step 1: As no stoichiometric equation has been indicated in literature <sup>253</sup> , we assume the one shown here. The quantity of tetrahydrofurane soluting DIBAH (1.0 M solution) is considered to be 0.0454 mol / (1 mol/L) = 0.0454 L. Step2-Step4: In literature <sup>188</sup> , the synthesis not of DBU but of DBN is presented! This protocol was adapted, i.e. instead of the five-ring pyrrolidone the sept-ring azepan-2-one was considered using the amounts and yields of the DBN-synthesis. Assumption: 100% yield of 3-(2-oxoazepan-1-yl)propanenitrile are assumed.
29c	64	The range of yield was quoted with 80-90%. The best result, i.e. 90% is assumed.

**Table S 11** Work-up procedures of syntheses in Table 1 which are not considered in a quantitative way.

Entry	Method	Lit.	Work-up procedures not considered
1	Elimination	<sup>19</sup>	Step1: Washing with ether. Addition of water to precipitate.
2a	Wittig	<sup>20</sup>	Step2: Preparation of NaH by washing with pentane. Step3: Extraction with pentane (several times). Washing with water. Drying with sodium sulphate. Distillation of solvent. Filtration of pentane solution with Al <sub>2</sub> O <sub>3</sub> and elution with pentane.
2b	Wittig Catalytic	<sup>21</sup>	Step1: catalyst cartridge containing 10% Pd/C Step2: flash column chromatography (benzene/pentane, 60:40)
3	Carbene Dimerisation	<sup>22</sup>	Step1: Pouring into water. Extraction with dichloromethane. Washing with aqueous sodium hydroxide. Drying. Treating with charcoal and filtration. Distillation of the solvent. Step2: Distillation of the solvent. Washing of the organic layer with water, drying, and evaporation to dryness. Drying in vacuo.
4a	Barton-Kellogg	<sup>23</sup>	Step1: Distillation of the solvent. Washing with brine. Drying with MgSO <sub>4</sub> . Concentration. Recrystallisation from hexane. Step2: Potential excess of bubbling hydrogen sulphide. Removal of the solvent. Step3: Separation and saturation of the aqueous layer with NaCl. Extraction with ether. Washing the combined organic portions with brine and drying (MgSO <sub>4</sub> ). Concentration. Step4: Column chromatography over silica gel with hexane
4b	Barton-Kellogg (Feringa)	<sup>24</sup>	Step1: Drying with anhydrous sodium sulphate Step3: Amount of SiO <sub>2</sub> was not indicated. Elution with a mixture of hexane /CH <sub>2</sub> Cl <sub>2</sub> 9:1 Step4: Extraction with diethyl ether, washing with water and drying with magnesium sulphate. Chromatography with SiO <sub>2</sub> , pentane:ether=9:1 Step5: Removing volatile components under reduced pressure. Chromatography with SiO <sub>2</sub> , pentane:ether=9:1
5a	McMurry (Zink)	<sup>66</sup>	Step2: Recrystallisation from ethanol / cyclohexane
5b	McMurry (Lithium aluminum hydride)	<sup>26</sup>	Step1+2: Tetrahydrofuran
5c	McMurry (Potassium)	<sup>27</sup>	Step2: Quenching with ethanol
5d	McMurry (Lithium)	<sup>28</sup>	Step1: Cleaning of lithium with methanol and petroleum ether
5e	McMurry Zn-Cu DME	<sup>29</sup>	Step0: Washing with acetone and ether. Drying under vacuum. Step1: Washing with pentane. Drying under vacuum. Step3: Filtration through Florisil
5f	McMurry Ti-TMSCl	<sup>30</sup>	Step1: Filtration through silica, chromatography (hexane/ethyl acetate, 10:1)
5g	McMurry TiCl <sub>2</sub> (ball mill)	<sup>31</sup>	Step 1: Isolation of the product. The yield of about 80% was determined with gaschromatography
6	Claisen rearrangement	<sup>32</sup>	Step 1: The quantity of drying agent is not indicated in literature. Therefore, it is ignored quantitatively.
7	Alkylation – elimination process	<sup>33, 34</sup>	Step2: Extractive workup: Ether, washing water, drying over Na <sub>2</sub> SO <sub>4</sub> . Purification by column chromatography (benzene) Step3: Pouring into water, drying over Na <sub>2</sub> SO <sub>4</sub> , column chromatography
8	Suzuki-Miyaura, ZhouLarock	<sup>35</sup>	Step3: drying over MgSO <sub>4</sub> , chromatography
9	Hydroarylation	<sup>36</sup>	the reaction mixture is filtered through a pad of Celite®

			93 g SiliaFlash P60 silica gel (230-400 mesh) using hexanes/ethyl acetate (24:1) as the eluent. Approximately 1 L of the solvent mixture was used.
10	Arylzincation (MurokamiOshima)	<sup>246-37</sup>	Step2: extraction with ethyl acetate, drying over Na <sub>2</sub> SO <sub>4</sub> , chromatography (silica gel, hexane)
11	Negishi-Tan	<sup>38</sup>	Step2: Quenching with diluted HCl. Extraction with diethyl ether. Washing of combined organic layers with brine. Drying over MgSO <sub>4</sub> , filtration and concentration. Purification by flash column chromatography. Step4: Quenching with saturated NH <sub>4</sub> Cl and extraction with diethyl ether. Washing of combined organic layers with brine. Drying over MgSO <sub>4</sub> , filtration and concentration. Purification by flash column chromatography.
12	Shapiro	<sup>39</sup>	Step2: Drying over MgSO <sub>4</sub>
13	Peterson	<sup>40</sup>	Step1: dried over MgSO <sub>4</sub> ; Purification via flash column chromatography (silica gel 230-400 mesh, 450 g of oil, loaded with hexanes, eluant 10:1 hexanes:diethyl ether) Step2: flash column chromatography (silica gel 230-400 mesh, 450 g, eluant hexanes) Step3: filtered through a 75-g layer of Celite 545, dried over MgSO <sub>4</sub> , [...]. Purification of the residue via flash column chromatography (silica gel 230-400 mesh, 450 g, eluant hexanes)
14	Julia-Lythgoe (Markó)	<sup>247</sup> <sup>41</sup>	Step2: Sodium hydroxide solution. Separation of benzene layer and drying over anhydrous MgSO <sub>4</sub> . Recrystallization from hexane Step6: drying over MgSO <sub>4</sub> Step6: drying over MgSO <sub>4</sub> , chromatography
15	Thiolester conversion	<sup>42</sup>	Step1: dried over anhydrous magnesium sulfate Step2: butyllithium in hexane: Instead of a 2.53 M a 2.5 M solution was considered Step2: dried over anhydrous sodium sulphate Step3: This crude material is applied to the top of a 4.8-cm x 30-cm column of 210 g of 230-400 mesh silica gel 60 and eluted with hexane (20 mL per min, 120-mL fractions)
16	Heck	<sup>43</sup>	Step1: Flash column chromatography was performed using silica gel (6 cm diameter x 35 cm height), eluting with 19/1 hexane/diethyl ether
17	Heck (Itami)	Step 1 <sup>248</sup> Step 2 <sup>249</sup> Step 3-5 <sup>44</sup>	Step1: pouring into ice-H <sub>2</sub> O, extraction with CHCl <sub>3</sub> , washing with H <sub>2</sub> O, drying over Na <sub>2</sub> SO <sub>4</sub> . Concentration and column chromatography (SiO <sub>2</sub> , benzene, then CHCl <sub>3</sub> Step2: Extraction with CHCl <sub>3</sub> , washing with H <sub>2</sub> O, drying Na <sub>2</sub> SO <sub>4</sub> , column chromatography (SiO <sub>2</sub> , hexane, CH <sub>2</sub> Cl <sub>2</sub> ) Step3: Filtration (silica gel pad, EtOAc), chromatography (SiO <sub>2</sub> , hexane, EtOAc) Step4: Extractive work-up, chromatography (SiO <sub>2</sub> , hexane, EtOAc) Step5: Filtration (silica gel pad, EtOAc), chromatography (SiO <sub>2</sub> , hexane, EtOAc)
18	Yamagami Alkyne	<sup>45</sup>	Step1: pad of silica gel with EtOAc, concentration under vacuum, chromatography (SiO <sub>2</sub> hexane) Step3: pad of silica gel with EtOAc, concentration under vacuum, silica gel preparative TLC (hexane/Et <sub>2</sub> O)
19b	Suzuki (Nunes)		Step2: Drying over Na <sub>2</sub> SO <sub>4</sub> . Recrystallization. Step3: Washing the product with ether Step4: Drying over MgSO <sub>4</sub> Step6: Workup procedures were not considered, because no protocol exists for this hydrolysis.

19c	Suzuki (Nunes)		Step7: Drying over MgSO <sub>4</sub> . Purification with chromatography (silica gel, cyclohexane) Step2: Drying over Na <sub>2</sub> SO <sub>4</sub> . Recrystallization. Step4: Drying over MgSO <sub>4</sub> Step6: Workup procedures were not considered, because no protocol exists for this hydrolysis. Step7: Drying over MgSO <sub>4</sub> . Purification with chromatography (silica gel, cyclohexane)
20	Negishi (Nunes)		Step1-4 see 19b Step 5: Purification by flash chromatography on silica gel with hexane
22	Wang	<sup>53</sup> <sup>52</sup>  <sup>9</sup>	Step1: Washing thrice with water. Drying over sodium sulfate. Step3: Filtration through a short pad of celite eluting with dichloromethane. Purification of the residue by column chromatography (hexane → 10% EtOAc/hexane) Step4: Combination and drying of organic layers (MgSO <sub>4</sub> ). Concentration in vacuo. Purification of the residue by column chromatography. Purification by column chromatography (hexane→10% EtOAc/hexane)
23	Allylation of Alkenylalanes	<sup>55</sup>	The organic layer is separated and the aqueous layer is extracted twice with pentane. The combined organic layer is washed with water, saturated aqueous sodium bicarbonate, and water again. After the organic extract is dried over anhydrous magnesium sulfate, the solvent is removed thoroughly using a rotary evaporator (15–20 mm), and the crude product is passed through a short (15–20-cm) silica gel column (60–200 mesh) using hexane as an eluent.
24	Wang	<sup>56</sup>	Step2: Drying anhydrous MgSO <sub>4</sub> . Chromatography (silica gel column using petroleum/ ethyl acetate as an eluent)
25	Cross-coupling of alkenyl-carboxylates with Grignard reagents	<sup>57</sup>	Step1: The yellow organic phase is dried over anhydrous Na <sub>2</sub> SO <sub>4</sub> and gravity filtered through a cotton plug and the filtrate collected in a 1-L round-bottomed flask. The crude oil is loaded onto a fritted chromatography column (8.0 cm outer diameter) that had been drypacked with silica gel (300 g) and wetted with hexanes under air pressure. Step2: A fritted chromatography column (8.0 cm outer diameter) is dry-packed with 180.0 g of silica gel (Note 10) and wetted with hexanes under air pressure.
26	Li	<sup>58</sup>	Purification by silica gel column chromatography eluting with petroleum ether
27a	Alkylative or Arylative Carboxylation of Alkynes	<sup>60</sup>	Step2: Hydrolyzation with 10 % HCl aq. at 0 °C and extraction of the aqueous layer with EtOAc. The combined organic layer was washed with brine, dried over Na <sub>2</sub> SO <sub>4</sub> , and concentrated. The residue was purified by silica gel column chromatography (hexane/EtOAc/AcOH=80/20/1).
27b	see 27a	<sup>253</sup>	Step1: Washing with cold diethyl ether (15mL portions) Step4: Presence of p-toluenesulfonic acid
28	Lipshutz (Metathese)	<sup>61</sup>	Flash chromatography on silica gel (12% EtOAc/hexanes)
29a	Nenajdenko, 2005	<sup>62</sup>	Step2: Drying with anhydrous sodium sulphate
29b	Nenajdenko, 2001	<sup>63</sup>	Drying over Na <sub>2</sub> SO <sub>4</sub> . Purification by column chromatography in SiO <sub>2</sub> .
29c	Corey 1972	<sup>64</sup>	Step1-3: Methylene chloride as solvent for reaction Step3: Addition of pentane (4 vol.). Additional cycles of methylene chloride extraction and pentane precipitation.
29d	Patil	<sup>65</sup>	Addition of SiO <sub>2</sub> (3g) and loading of a SiO <sub>2</sub> (30g) column.

