Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Decarboxylative reactions with and without light – a comparison

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1. Definition of atom economy

The calculation of the atom economy (AE) or atomic efficiency shows how much of the reactants is converted into the final product. This concept has been introduced by Barry M. Trost in 1991.[1] Catalytic amounts of reagents and materials or solvents as well as reaction yields are ignored for the calculations.[1-2] Molar excesses of reactants are neglected, but the reaction stoichiometry is taken into account. The calculation does not reflect actual experimental masses and volumes, but shows the theoretical efficiency of a transformation. For an ideal reaction, the AE is 100%, which means that all reactant atoms form the desired product.

The calculation of the atom economy for the synthesis of the desired product C is shown in Scheme S1. The AE can be determined without any experimental work, only by consideration of the correctly balanced chemical equation. Therefore, the reaction mechanism should be known.

$$\text{A + B} \xrightarrow[\text{solvent}]{\text{catalyst}} \text{C + D}$$

$$\text{atom economy (\%)} = \frac{\text{MW(C)}}{\text{MW(A+B)}} \times 100\%$$

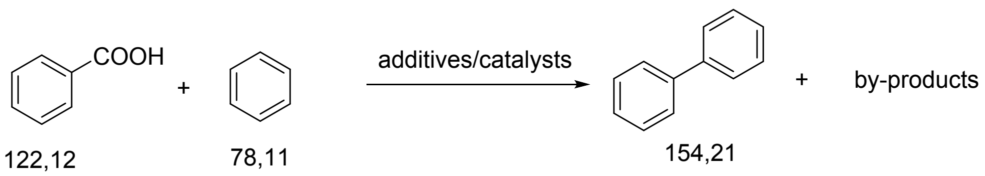
Scheme S1 Calculation of atom economy for product C; MW = molecular weight.

2. Calculations of atom economy for decarboxylative reactions

For comparison of different methods for one type of decarboxylative reaction, the same substrates have been chosen for this reaction, although these exact substrates may not occur within the scope of each method. In the following, the chemical equations show for which reactants the AE has been calculated exemplarily. Catalysts, solvents, by-products and catalytic amounts of reagents are not given within these equations, as they do not have any influence on the AE. The general chemical equations and the stoichiometric additives for each method are given with their corresponding molecular weights.

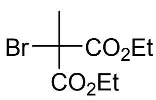
2.1. Aromatic carboxylic acids

Arylation



A) Ag_2CO_3 (275,74) AE = 154,21/(122,12+78,11+275,74) = **32%**

B) 0.5 equiv. $K_2S_2O_8$ (270,31) AE = 154,21/(122,12+78,11+0,5*270,31) = **47%**

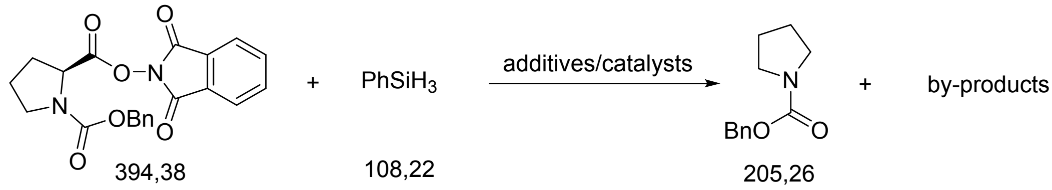
C) Cs_2CO_3 (325,82) 

(253,09) AE = 154,21/(122,12+78,11+325,82+253,09) = **20%**

2.2. Alkyl carboxylic acids

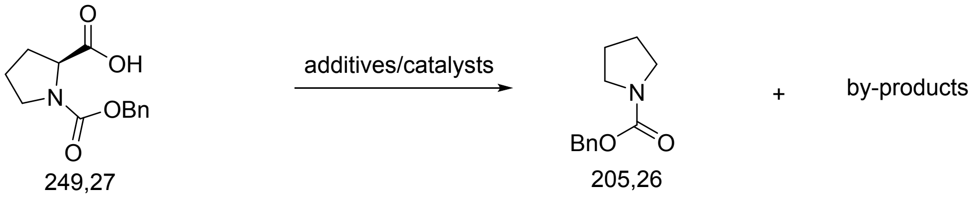
Protodecarboxylation

A)



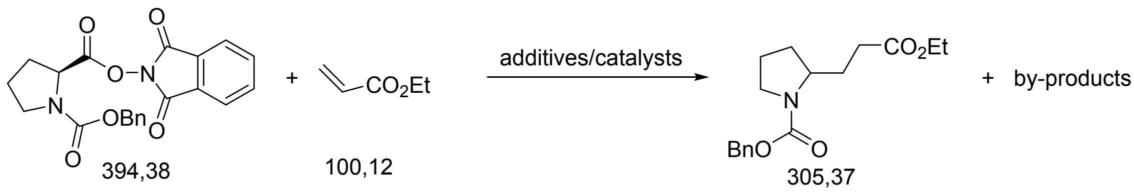
AE = 205,26/(394,38+108,22) = **41%**

B)



AE = 205,26/249,27 = **82%**

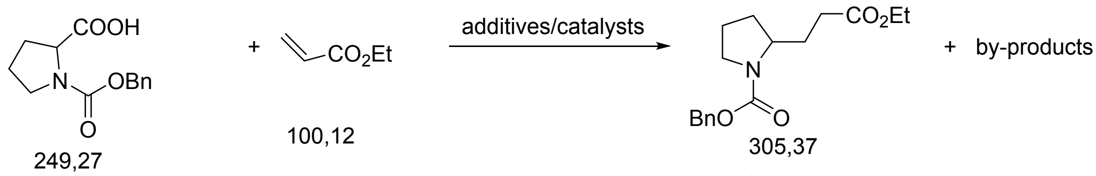
Alkylation



A) $LiCl_3$ (113,29), Zn (65,38) AE = 305,37/(394,38+100,12+113,29+65,38) = **45%**

B) DIPEA (129,25) AE = 305,37/(394,38+100,12+129,25) = **49%**

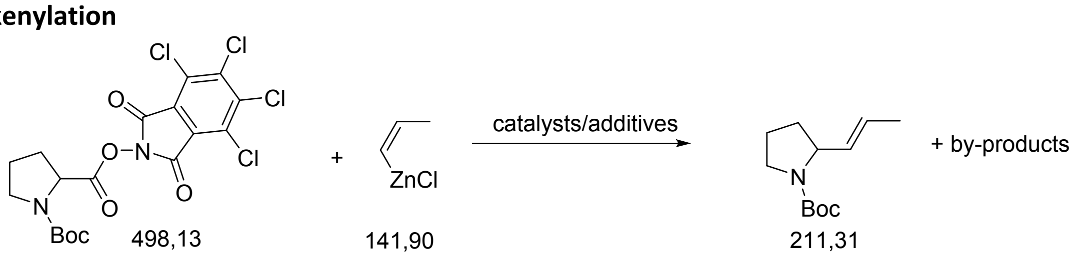
C)



AE = 305,37/(249,27+100,12) = **87%**

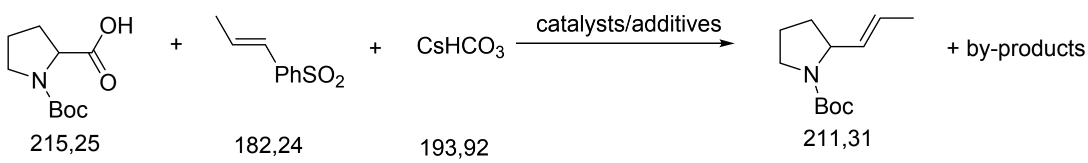
Alkenylation

A)



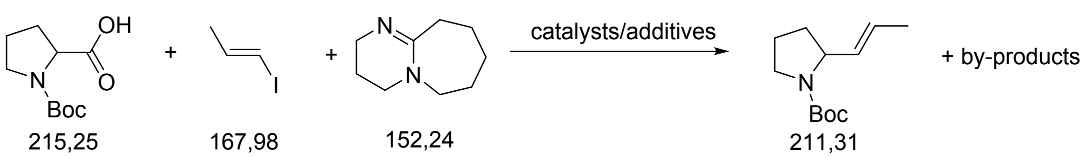
AE = 211,31/(498,13+141,90) = **33%**

B)



AE = 211,31/(215,25+182,24+193,92) = **36%**

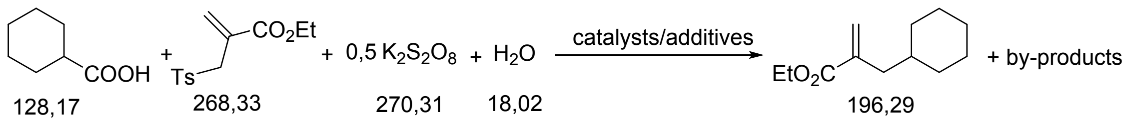
C)



AE = 211,31/(215,25+167,98+152,24) = **39%**

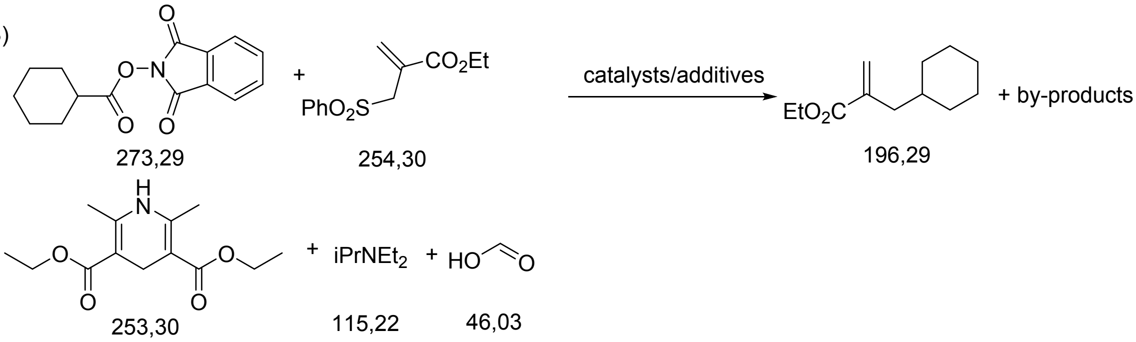
Allylation (intermolecular)

A)



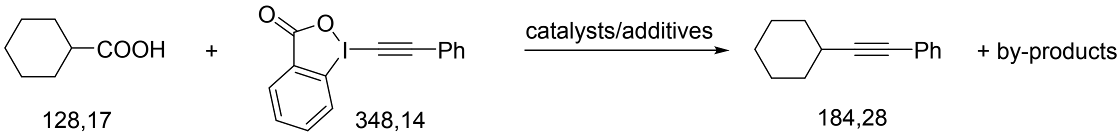
AE = 196,29/(128,17+268,33+0,5*270,31+18,02) = **36%**

B)



AE = 196,29/(273,29+254,30+253,30+115,22++46,03) = **21%**

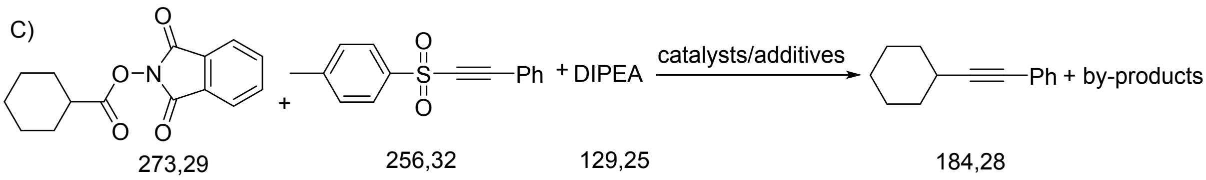
Alkynylation via C–LG activation



A) 0,5 $K_2S_2O_8$ (270,31) AE = 184,28/(128,17+348,14+0,5*270,31) = **30%**

B) K_2CO_3 (138,20) AE = 184,28/(128,17+348,14+138,20) = **30%**

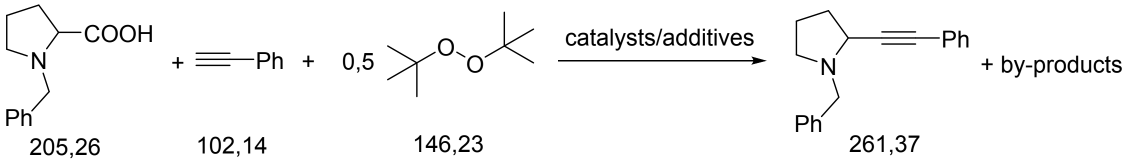
C)



AE = 184,28/(273,29+256,32+129,25) = **28%**

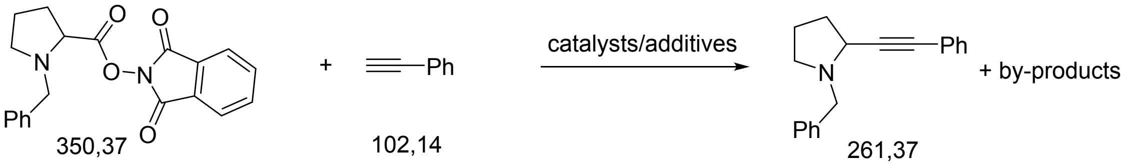
Alkynylation via C–H activation

A)



AE = 261,37/(205,26+102,14+0,5*146,23) = **69%**

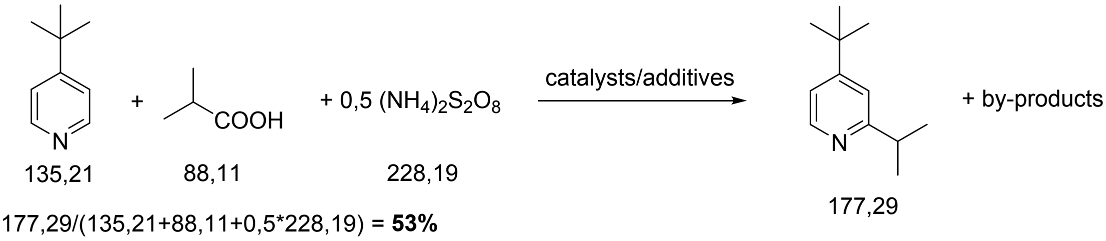
B)



AE = 261,37/(350,37+102,14) = **58%**

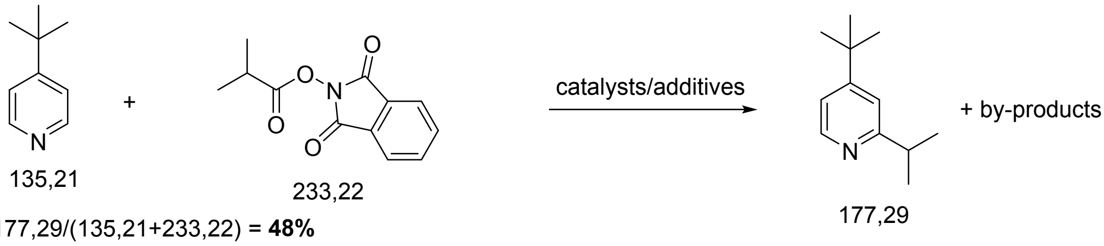
Arylation via C–H activation

A+B)



AE = 177,29/(135,21+88,11+0,5*228,19) = **53%**

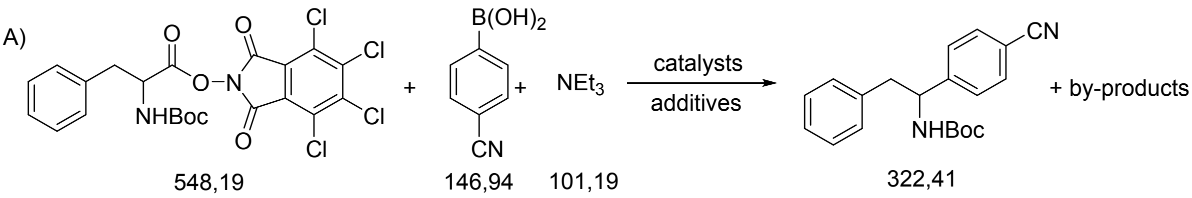
C)



AE = 177,29/(135,21+233,22) = **48%**

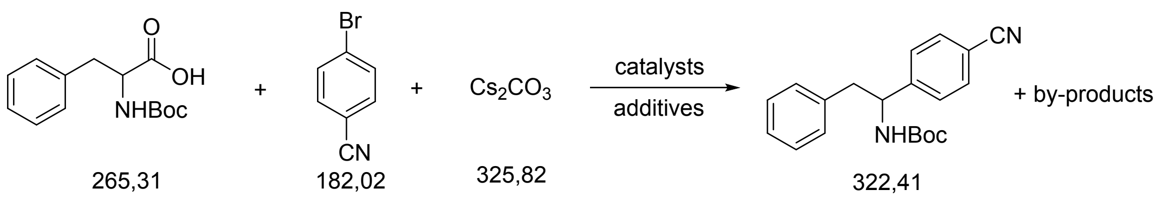
Arylation via C–LG activation

A)



AE = 322,41/(548,19+146,94+101,19) = **40%**

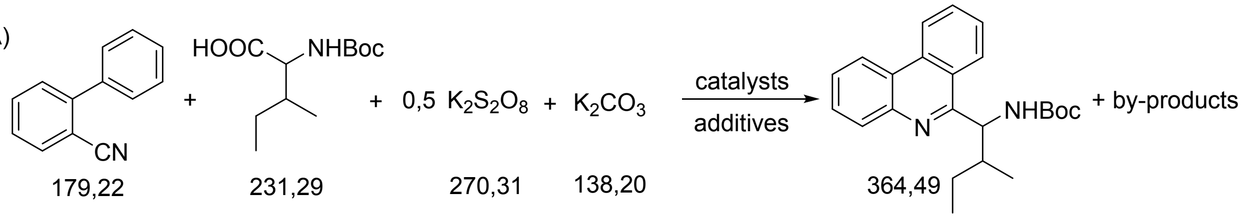
B)



AE = 322,41/(265,31+182,02+325,82) = **42%**

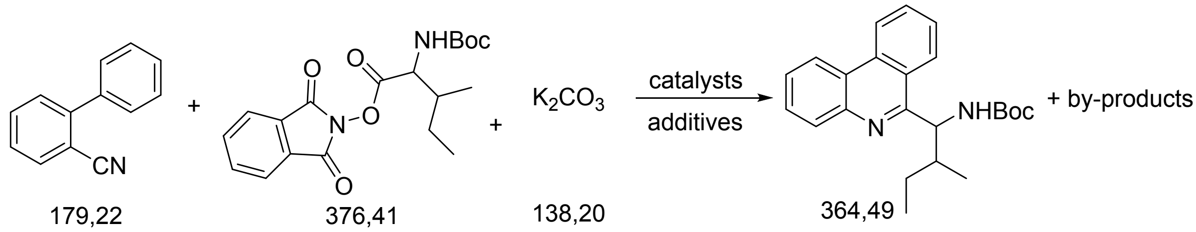
Cyclization to phenantridines

A)



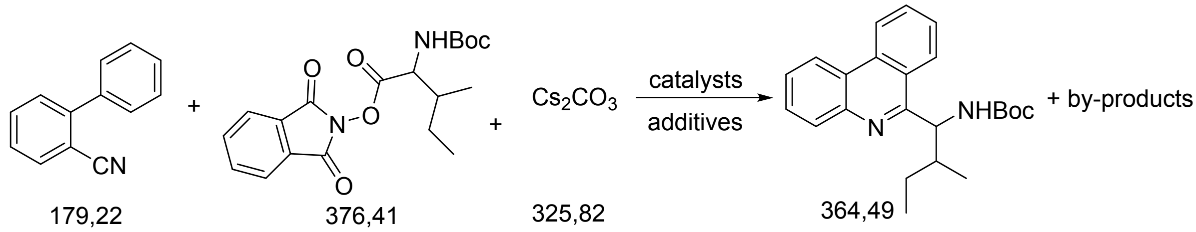
AE = 364,49/(179,22+231,29+0,5*270,31+138,20) = **53%**

B)



AE = 364,49/(179,22+376,41+138,20) = **53%**

C)



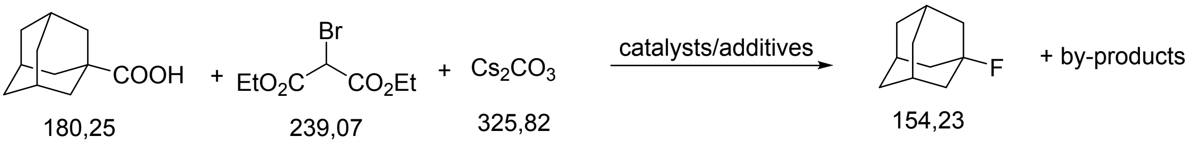
AE = 364,49/(179,22+376,41+325,82) = **39%**

Chlorination

B)

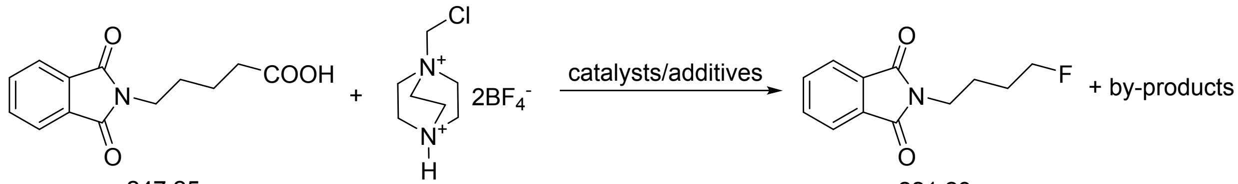
AE = 154,23/(180,25+0,5*286,87) = **48%**

C)



AE = 154,23/(180,25+239,07+325,82) = **21%**

Fluorination



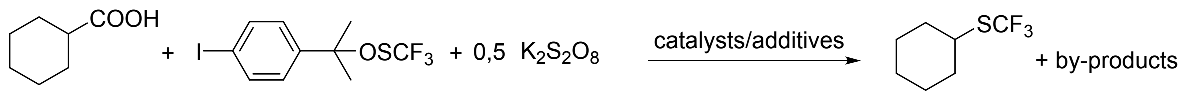
247,25 354,26 221,23

A) AE = 221,23/(247,25+354,26) = **37%**

B) Cs_2CO_3 (325,82) AE = 221,23/(247,25+354,26+325,82)= **24%**

Trifluoromethylthiolation

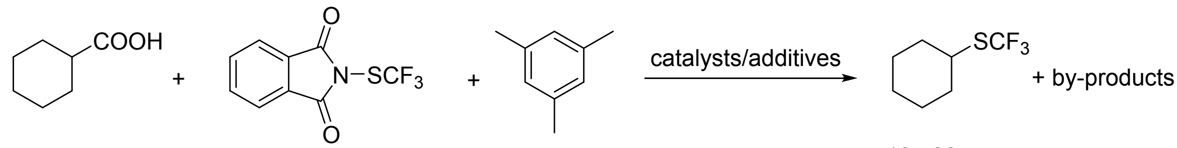
A)



128,17 362,15 270,31 184,22

AE = 184,22/(128,17+362,15+0,5*270,31) = **29%**

B)

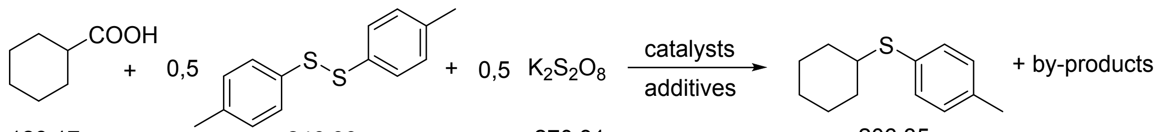


128,17 247,19 120,20 184,22

AE = 184,22/(128,17+247,19+120,20) = **37%**

Arylthiolation

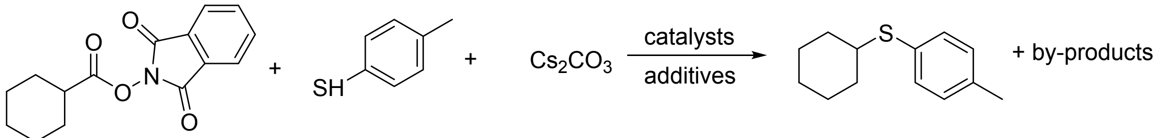
A)



128,17 246,39 270,31 206,35

AE = 206,35/(128,17+0,5*246,39+0,5*270,31) = **53%** (according to the proposed mechansim, $AgNO_3$ is regarded as a catalyst,although 1 equiv. is used)

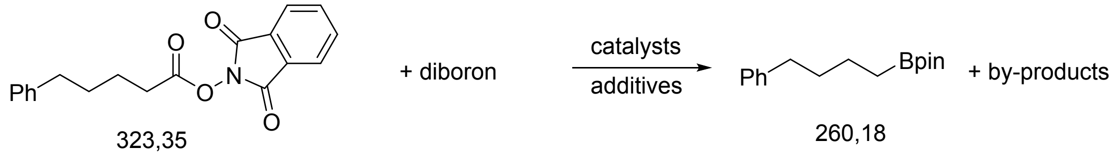
B)



273,29 124,20 325,82 206,35

AE = 206,35/(273,29+124,20+325,82) = **29%**

Borylation



A) B_2pin_2 (253,94), CH_3Li (21,98), $MgBr_2$*OEt_2 (258,24) AE = 260,18/(323,35+253,94+21,98+258,24) = **30%**

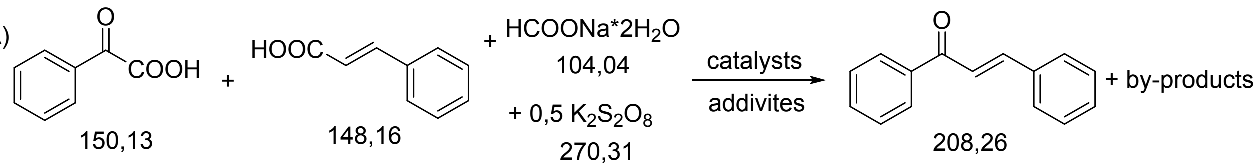
B) B_2cat_2 (237,81), pinacol (118,17), Et_3N (101,19) AE = 260,18/(323,35+237,81+118,17+101,19) = **33%**

C) B_2pin_2 (253,94) AE = 260,18/(323,35+253,94) = **45%**

2.3. α-Keto acids

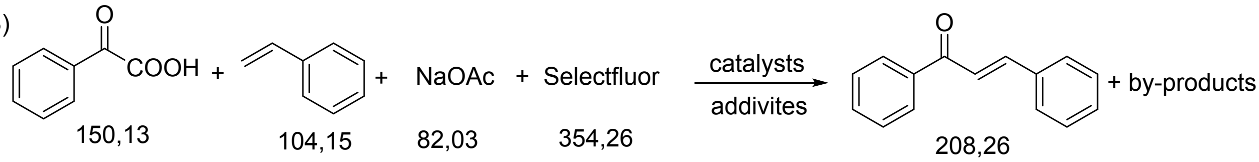
Vinylation

A)



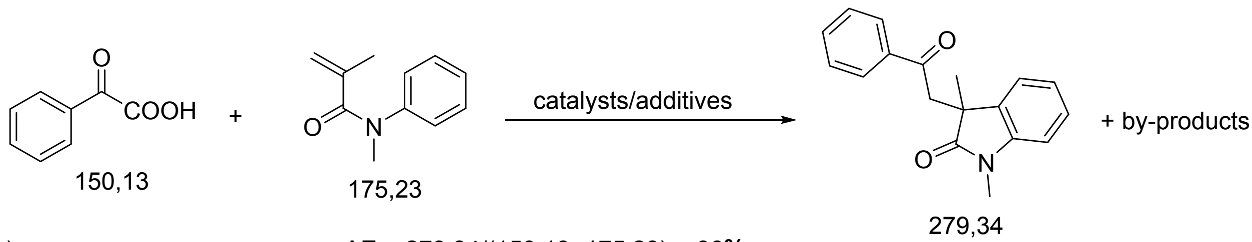
AE = 208,26/(150,13+148,16+104,04+0,5*270,31) = **39%**

B)



AE = 208,26/(150,13+104,15+82,03+354,26) = **30%**

Alkylation with acrylamides + ring-closure

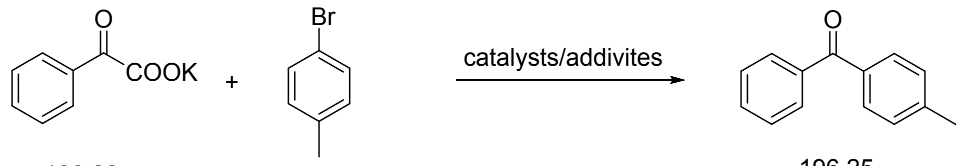


A) AE = 279,34/(150,13+175,23) = 86**%**

B) 0,5 $K_2S_2O_8$ (270,31) AE = 279,34/(150,13+175,23+0,5*270,31) = 61**%**

Arylation via C–X activation

A)

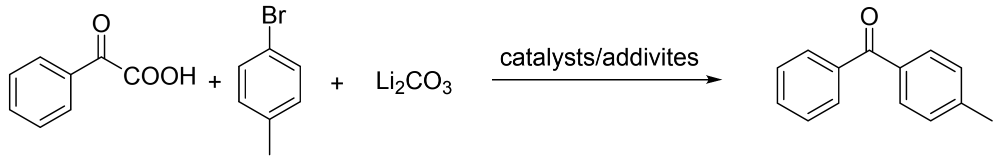


+ by-products

188,22 171,04 196,25

AE = 196,25/(188,22+171,04) = **55%**

B)

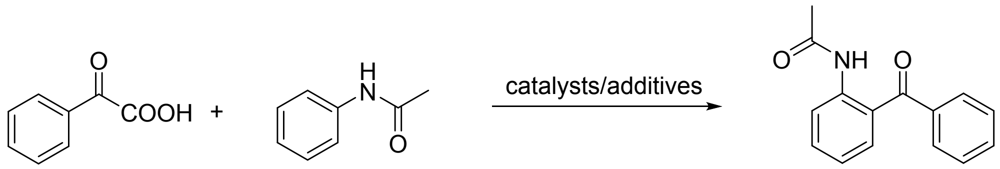


+ by-products

150,13 171,04 73,89 196,25

AE = 196,25/(150,13+171,04+73,89) = **50%**

Arylation via C–H activation with arylamides



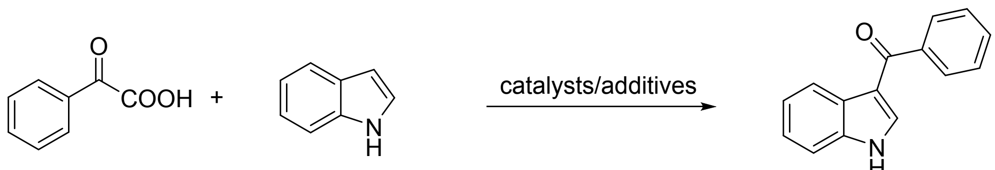
+ by-products

150,13 135,17 239,27

A) 0,5 $(NH_4)_2S_2O_8$ (228,19) AE = 239,27/(150,13+135,17+0,5*228,19) = **60%**

B) O_2 (32,00) AE = 239,27/(150,13+135,17+32,00) = **75%**

Arylation via C–H activation with indoles



+ by-products

150,13 117,15 221,26

A) 0,5 Ag_2CO_3 (275,74) AE = 221,26/(150,13+117,15+0,5*275,74) = **55%**

B) AE = 221,26/(150,13+117,15) = **83%**

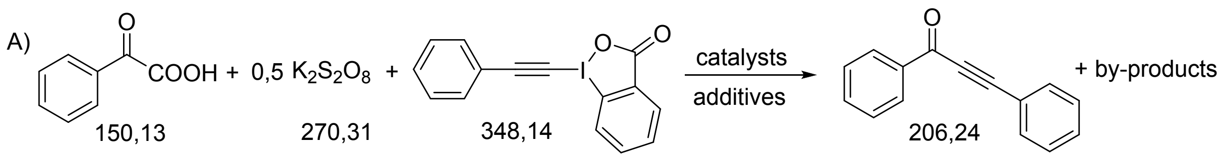
C) Cs_2CO_3 (325,82), I_2 (253,81) AE = 221,26/(150,13+117,15+325,82+0,5*253,81) = **31%**

Arylation via C–H activation with azobenzenes

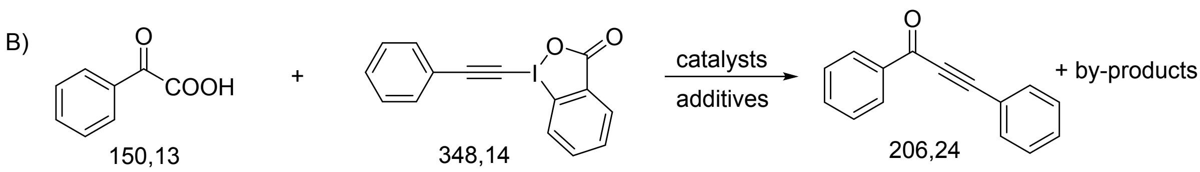
A) AE = 286,33/(150,13+182,23) = **86%**

B) 0,5 $K_2S_2O_8$ (270,31) AE = 286,33/(150,13+182,23+0,5*270,31) = **61%**

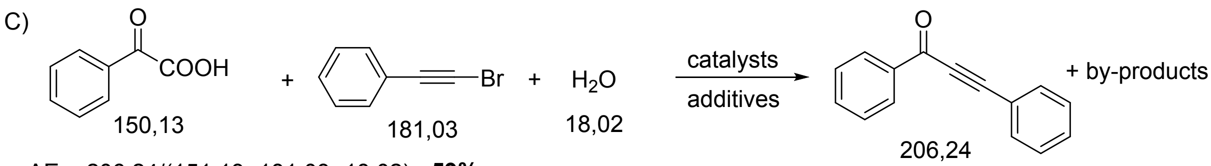
Alkynylation



AE = 206,24/(150,13+0,5*270,31+348,14) = **33%**



AE = 206,24/(150,13+348,14) = **41%**

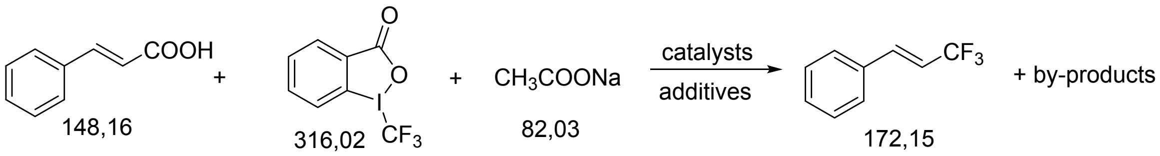


AE = 206,24/(151,13+181,03+18,02)= **59%**

2.4. α,β-Unsaturated carboxylic acids

Trifluoromethylation

A)

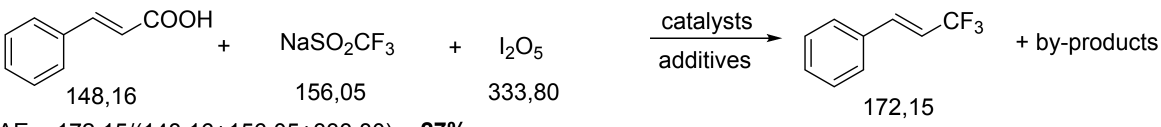


AE = 172,15/(148,16+316,02+82,03) = **32%**

B) without CH_3COONa:

AE = 172,15/(148,16+316,02) = **37%**

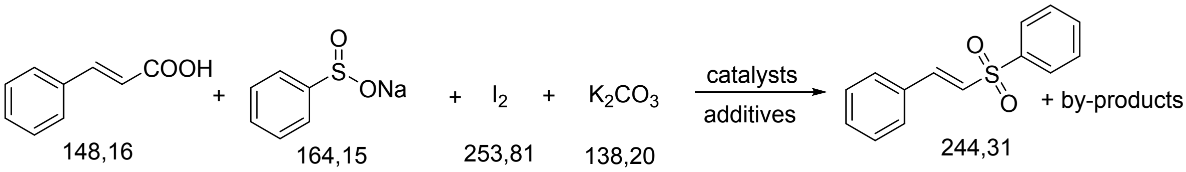
C)



AE = 172,15/(148,16+156,05+333,80) = **27%**

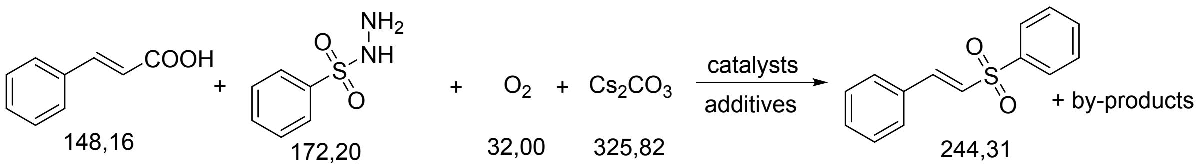
Sulfonylation

A)



AE = 244,31/(148,16+164,15+253,81+138,20) = **35%**

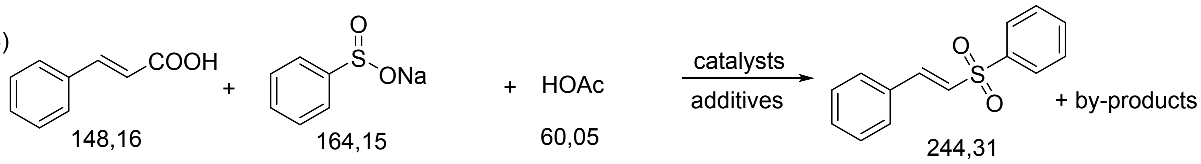
B)



(KI: catalytically)

AE = 244,31/(148,16+172,20+32,00+325,82) = **36%**

C)



AE = 244,31/(148,16+164,15+60,05) = **66%**

3. References

1. B. Trost, *Science*, 1991, 254, 1471-1477.
2. (a) D. J. C. Constable, A. D. Curzons and V. L. Cunningham, *Green Chem.*, 2002, 4, 521-527; (b) A. P. Dicks and A. Hent, in *Green Chemistry Metrics: A Guide to Determining and Evaluating Process Greenness*, Springer International Publishing, Cham, 2015, pp. 17-44**.**