Asymmetric Intermolecular Carbene Insertion to Non-activated C(sp^3)-H Bonds

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Apr 12 2024

Contents

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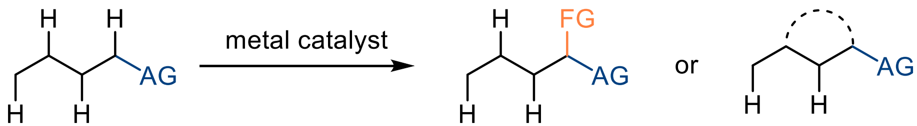
Introduction

Strategies for C(sp^3)-H functionalization

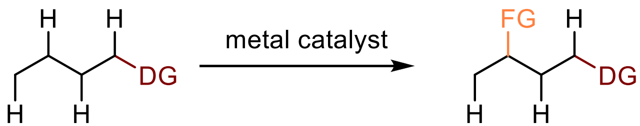
Site-selective C-H functionalization

✓ Controlled selectivity with an activating group (AG):

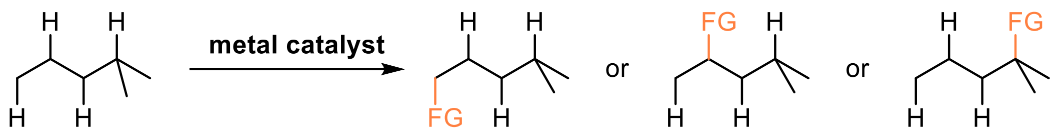


FG: functional group
AG: activating group
DG: directing group

✓ Controlled selectivity with a directing group (DG):



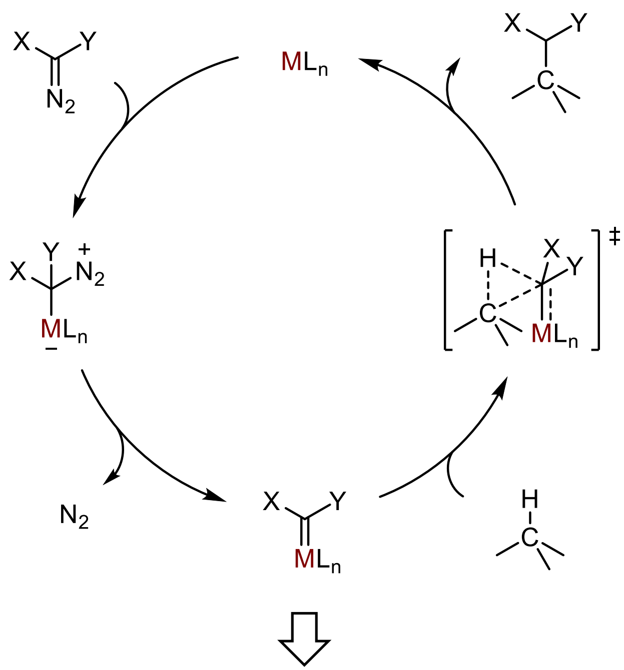
◆ *How to control the selectivity in non-activated C(sp^3)-H bonds?*



Davies, H. M. L.; Liao, K., *Nat. Rev. Chem.* **2019**, *3*, 347-360.

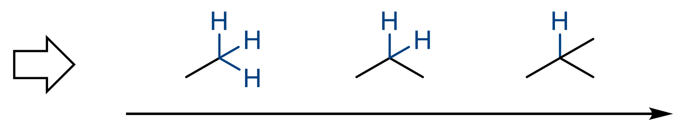
General mechanism and reactivity

Catalytic cycle

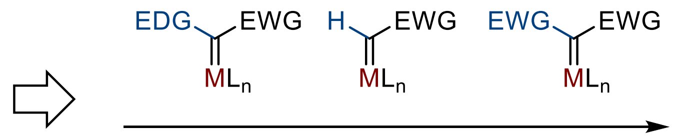


***Electrophilic** metal carbene*

Regular reactivity



electronically favourable
sterically less favourable



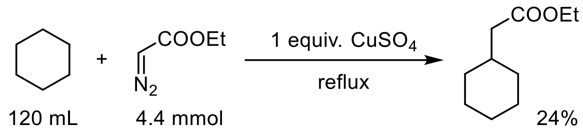
more reactive
less selective

EWG = CO_2R, COR, CN, $PO(OR)_2$
EDG = Aryl, heteroaryl, vinyl

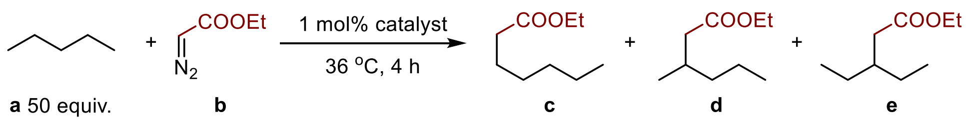
Doyle, M. P.; Duffy, R.; Ratnikov, M.; Zhou, L., *Chem. Rev.* **2010**, *110*, 704-724.

Site-selectivity and stereoselectivity

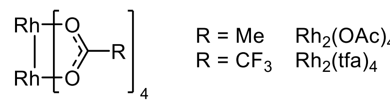
- The first example of intermolecular carbene insertion to non-activated C-H bonds (Scott, 1974)



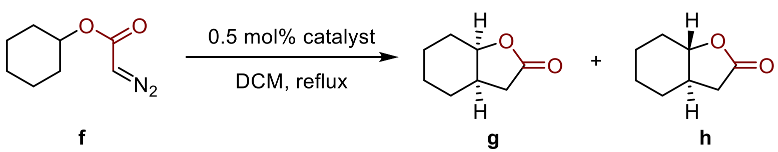
- Pioneer studies with moderate site-selectivity (Teyssié, 1984)

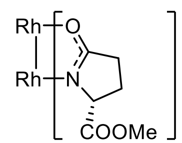


catalyst	total yield / %	**c:d:e**
$Rh_2(OAc)_4$	20	4:63:33
$Rh_2(tfa)_4$	65	8:66:27



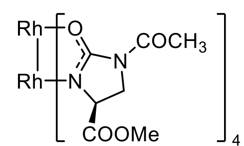
- Asymmetric intramolecular C-H insertion (Doyle, 1994)





$Rh_2(5S\text{-MEPY})_4$

catalyst	total yield / %	**g:h**	% ee	
			g	**h**
$Rh_2(5R\text{-MEPY})_4$	65	75:25	97	91
$Rh_2(4S\text{-MACIM})_4$	70	99:1	97	65



$Rh_2(4S\text{-MACIM})_4$

➢ *Can we control the site- and stereoselectivity in an intermolecular reaction?*

Scott, L. T.; Decicco, G. J., *J. Am. Chem. Soc.* **1974**, *96*, 322-323.
Demonceau, A.; Noels, A. F.; Hubert, A. J.; Teyssie, P., *Bull. Soc. Chim. Belg.* **1984**, *93*, 945-948.
Doyle, M. P.; Dyatkin, A. B.; Roos, G. H. P.; Canas, F.; Pierson, D. A.; Vanbasten, A.; Muller, P.; Polleux, P., *J. Am. Chem. Soc.* **1994**, *116*, 4507-4508.

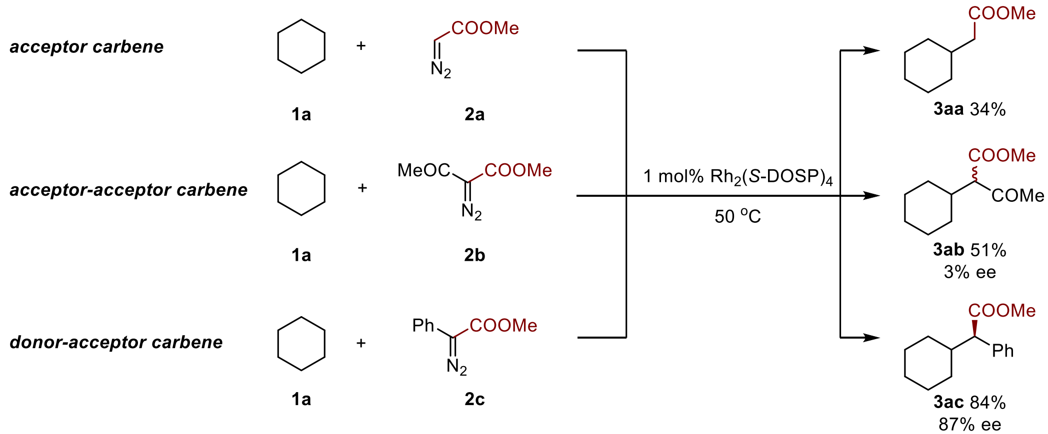
2.1

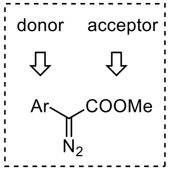
Seminal works

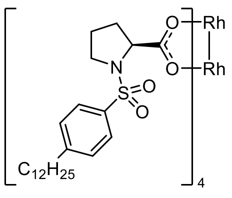
Seminal works: the first example

The first example of asymmetric intermolecular carbene insertion to non-activated C–H bonds

Reaction of cyclohexane

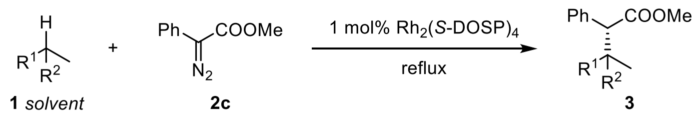


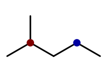
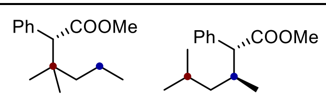
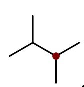
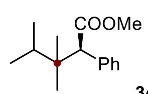
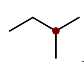
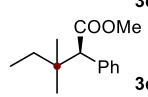




$Rh_2(S\text{-}DOSP)_4$

Reaction of acyclic alkanes

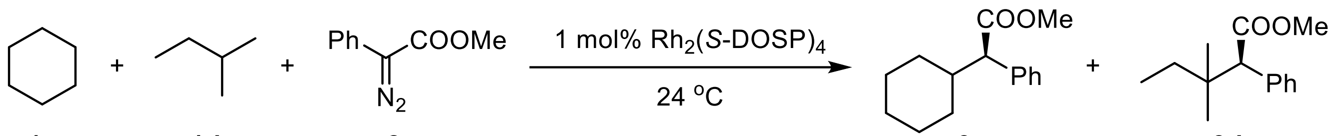


entry	substrates	products	yield / %	ee / %
1	 **1b**	 **3bc** **4bc**	75 (**3bc**:**4bc**=58:42)	26(**3bc**), 86(**4bc**, 4:1 dr)
2	 **1c**	 **3cc**	24	46
3	 **1d**	 **3dc**	60	68

Davies, H. M. L.; Hansen, T., *J. Am. Chem. Soc.* **1997**, *119*, 9075-9076.
Davies, H. M. L.; Hansen, T.; Churchill, M. R., *J. Am. Chem. Soc.* **2000**, *122*, 3063-3070.

Seminal works: the first example

The rate of reaction between secondary and tertiary sites

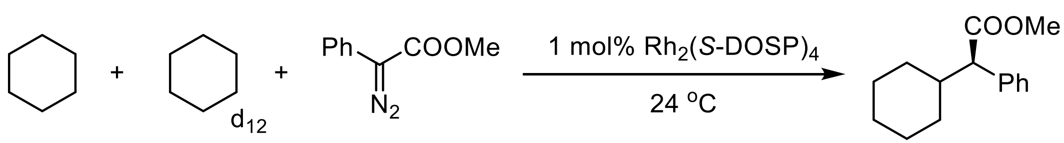


1a : **1d** **2c** → **3ac** : **3dc**

1 : *4.6* → *76* : *24*

rate of secondary:tertiary = 1.2:1

KIE experiment



1 : *1*

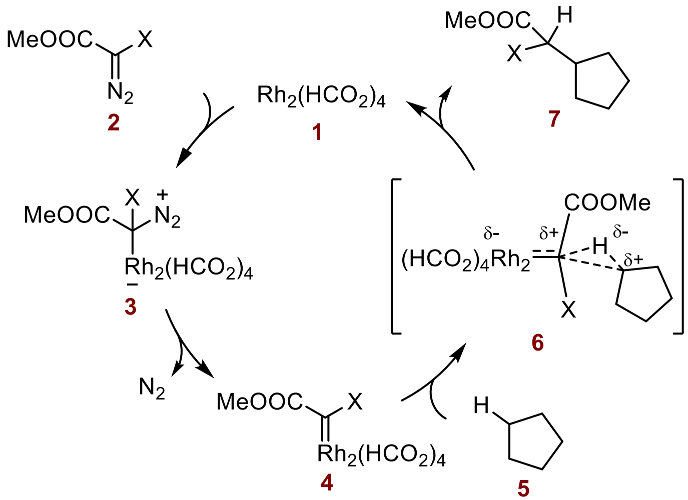
$k_H/k_D = 2.0$

Davies, H. M. L.; Hansen, T.; Churchill, M. R., *J. Am. Chem. Soc.* **2000**, *122*, 3063-3070.

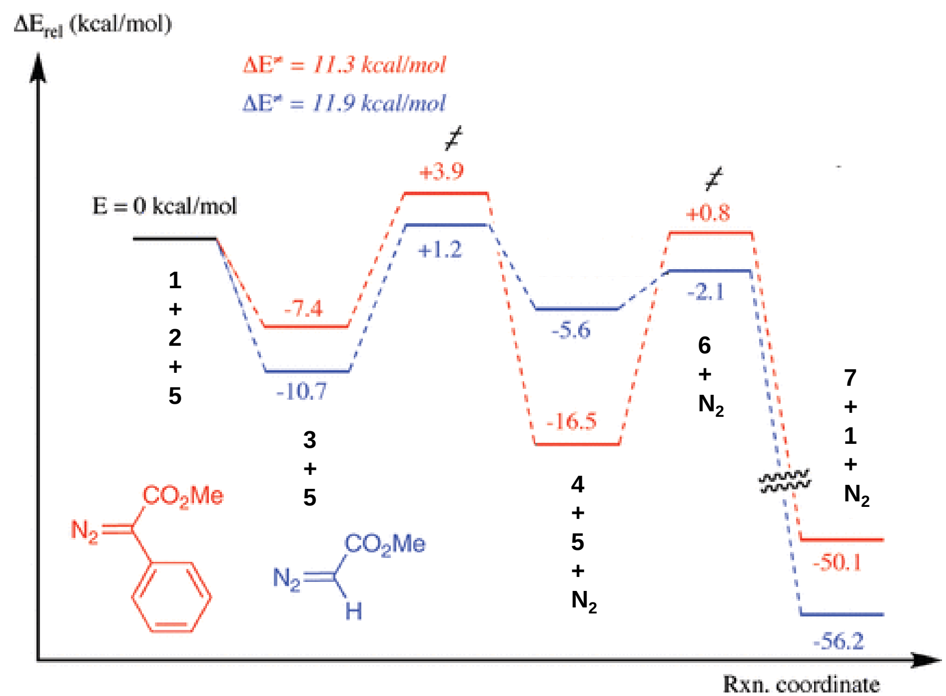
Seminal works: mechanism

Reaction pathway

X = H or Ph



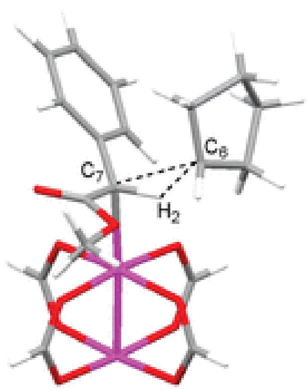
Relative energies



Calculated structures

for X = Ph ∠(C_6-C_2-C_7) = 126.5°

Bond	d (Å)	BO
C_6-H_2	1.543	0.19
C_7-H_2	1.148	0.69
C_6-C_7	2.409	0.36

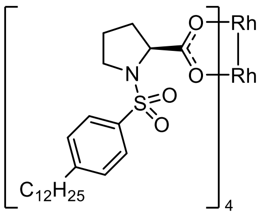


- transition state **6**: **concerted and asynchronous**

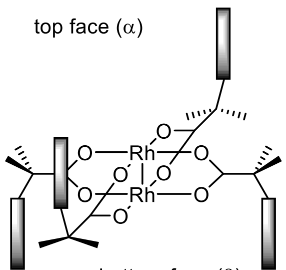
Hansen, J.; Autschbach, J.; Davies, H. M. L., *J. Org. Chem.* **2009**, *74*, 6555-6563.

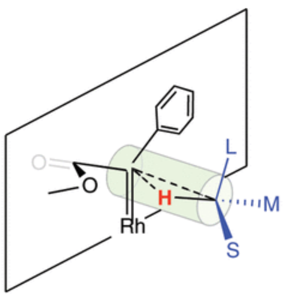
Seminal works: model

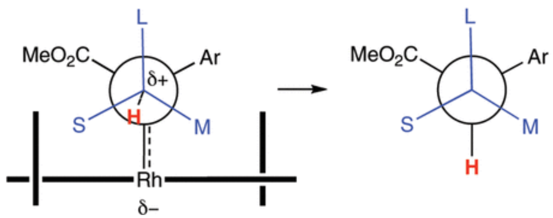
Newman-projection model



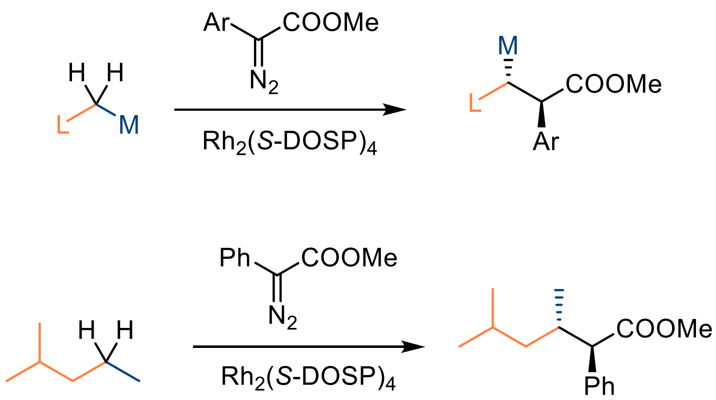
Rh_2(*S*-DOSP)$_4$







Enantio- and diastereoselectivity

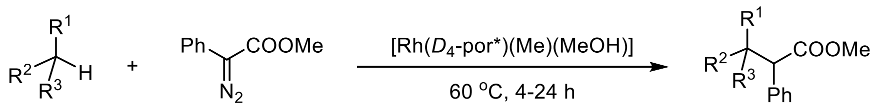


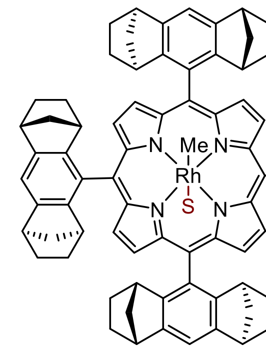
32% yield
86% ee
4:1 dr

Hansen, J.; Autschbach, J.; Davies, H. M. L., *J. Org. Chem.* **2009**, *74*, 6555-6563.

Seminal works: bulky catalysts

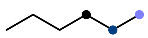
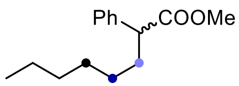
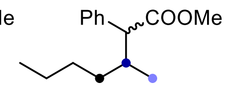
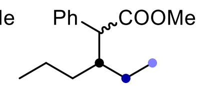
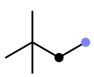
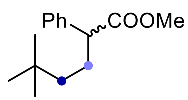
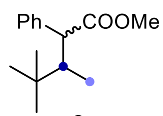
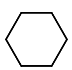
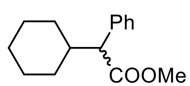
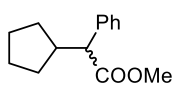
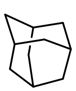
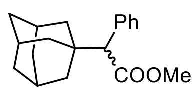
Insertion to primary C-H bonds





S = MeOH

[Rh(D_4-por*)(Me)(MeOH)]

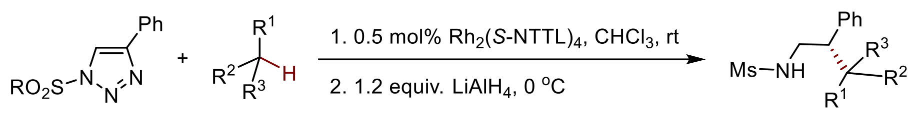
entry	substrates	products	total yield / %	ee / % [a]	1° : 2° [b]
1	 **1a**	 **1b**  **1c**  **1d**	66	68 (**1a**)	3.5 : 1
2	 **2a**	 **2b**  **2c**	55	65 (**2a**)	3.8 : 1
3	 **3a**	 **3b**	80	92	
4	 **4a**	 **4b**	64	93	
5	 **5a**	 **5b**	78	88	

Reaction conditions: $N_2C(Ph)CO_2Me$ (0.1 mmol); **1a**, **2a**, **3a**, **4a** (4 mL); **5a** (2 equiv.) in DCE (4 mL); catalyst (0.1 mol% for **3a**, **4a**, **5a**, 1.5 mol% for **1a** and **2a**). [a] Absolute configuration not determined. [b] Normalized for the relative number of hydrogen atoms.

Thu, H.-Y.; Tong, G. S.-M.; Huang, J.-S.; Chan, S. L.-F.; Deng, Q.-H.; Che, C.-M., *Angew. Chem. Int. Ed.* **2008**, *47*, 9747-9751.

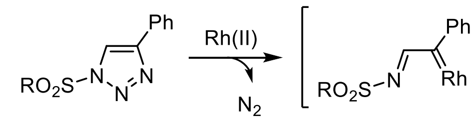
Seminal works: azavinyl carbenes

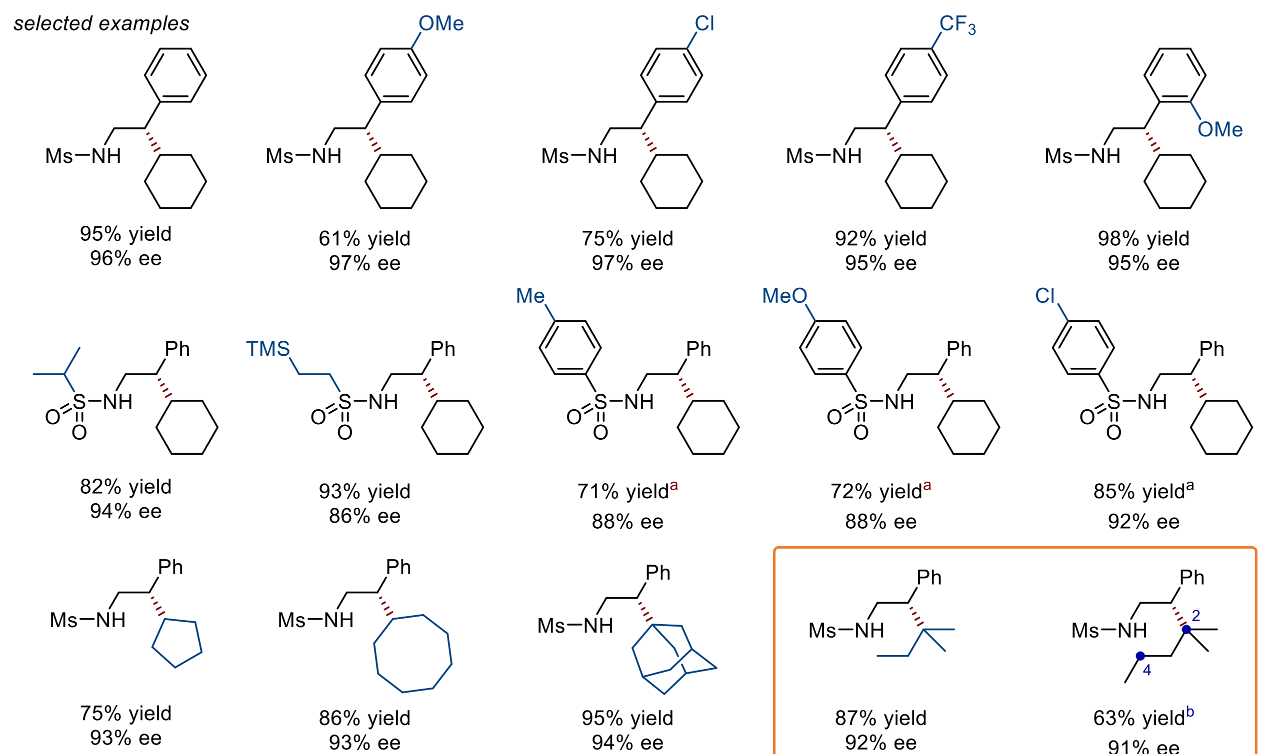
Selected examples

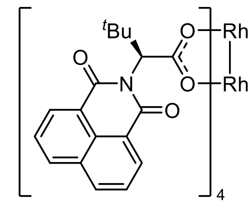


1 **2** **3**

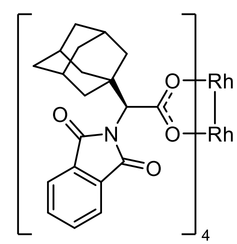
Formation of rhodium carbene







$Rh_2(S\text{-NTTL})_4$



$Rh_2(S\text{-PTAD})_4$

Reaction conditions: **1** (1 mmol), **2** (2.5 mL), $CHCl_3$ (2.5 mL) at room temperature. [a] $Rh_2(S\text{-PTAD})_4$ (0.5 mol%), 40 °C. [b] 12% of C-4 insertion product was observed.

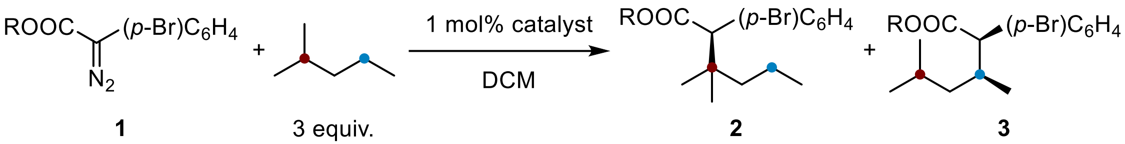
Chuprakov, S.; Malik, J. A.; Zibinsky, M.; Fokin, V. V., *J. Am. Chem. Soc.* **2011**, *133*, 10352-10355.

2.2

Acyclic Systems

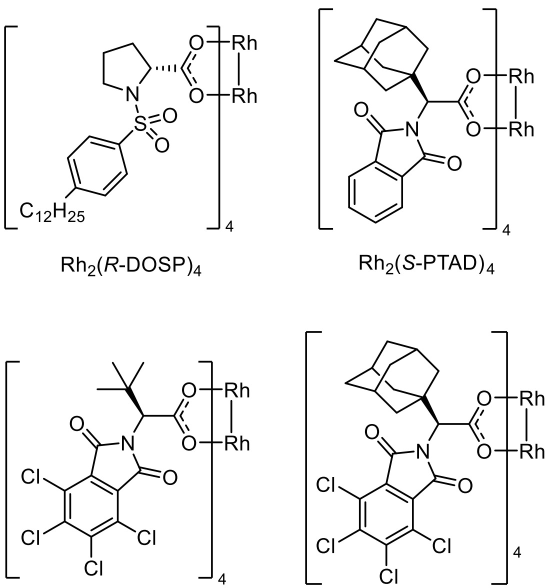
Acyclic Systems: tertiary C-H bonds

Optimization of reaction conditions



entry	catalyst	R	t / °C	yield / %	rr of **2**:**3**	ee of **2** / %
1	$Rh_2(R\text{-DOSP})_4$	CH_3	39	83	85:15	-43
2	$Rh_2(S\text{-PTAD})_4$	CH_3	39	50	74:26	-34
3	$Rh_2(S\text{-TCPTTL})_4$	CH_3	39	86	86:14	77
4	$Rh_2(S\text{-TCPTAD})_4$	CH_3	39	89	87:13	79
5	**$Rh_2(S\text{-TCPTAD})_4$**	**CH_2CF_3**	**39**	**92 (83)**	**90:10**	**77**
6	$Rh_2(S\text{-TCPTAD})_4$	CH_2CF_3	24	85 (77)	91:9	80
7	$Rh_2(S\text{-TCPTAD})_4$	CH_2CF_3	0	85 (79)	93:7	82
8	**$Rh_2(S\text{-TCPTAD})_4$**	**CH_2CF_3**	**-40**	**80 (77)**	**96:4**	**86**

The percentage yields refer to the combined yield of products **2** and **3**. The isolated yield of **2** is given in parentheses.



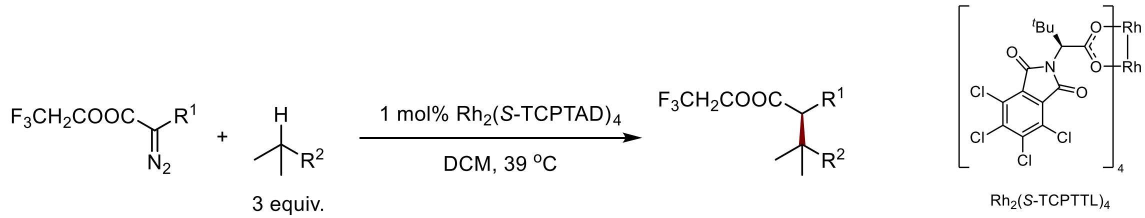
$Rh_2(R\text{-DOSP})_4$ $Rh_2(S\text{-PTAD})_4$

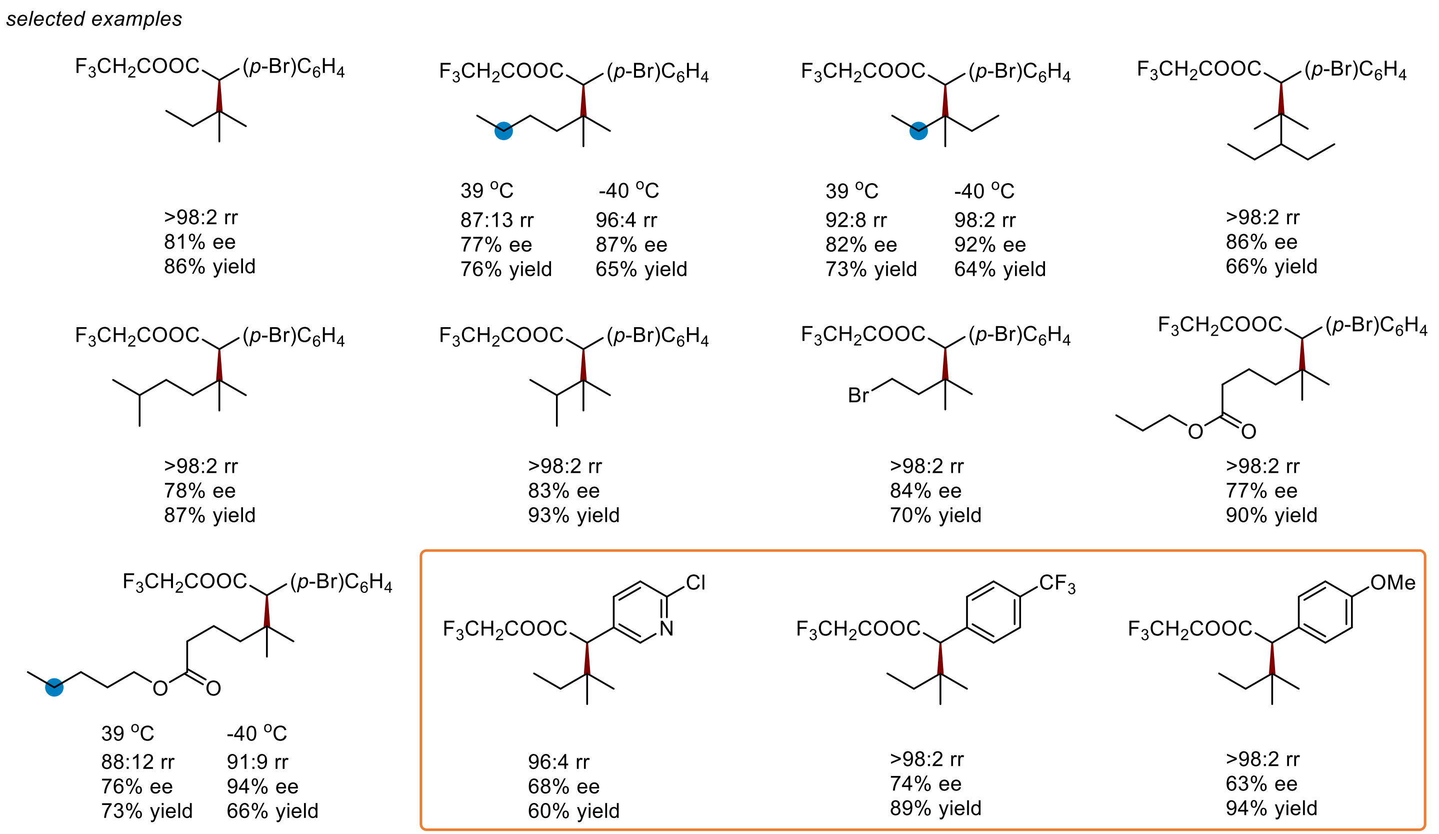
$Rh_2(S\text{-TCPTTL})_4$ $Rh_2(S\text{-TCPTAD})_4$

Liao, K.; Pickel, T. C.; Oyarskikh, V. B.; Acsa, J. B.; Usaev, D. G. M.; Davies, H. M. L., *Nature* **2017**, *551*, 609-613.

Acyclic Systems: tertiary C-H bonds

Scopes



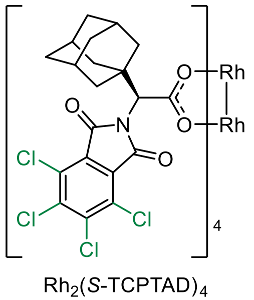


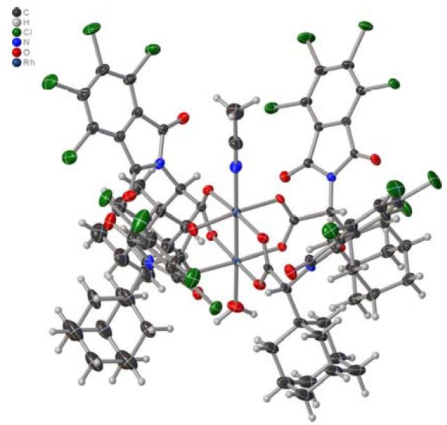
Some of the C–H functionalization occurred at the most accessible secondary position **(marked in blue)** of the substrates.

Liao, K.; Pickel, T. C.; Oyarskikh, V. B.; Acsa, J. B.; Usaev, D. G. M.; Davies, H. M. L., *Nature* **2017**, *551*, 609-613.

Acyclic Systems: chiral pocket

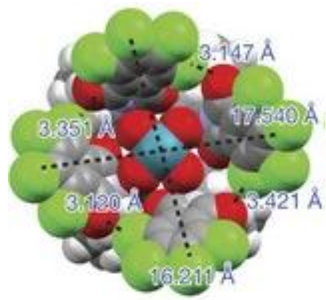
Structural information





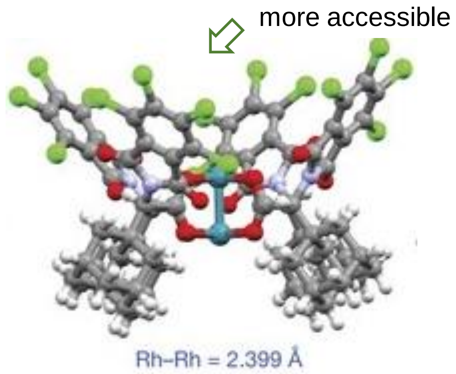
X-ray structure

- phthalimido groups on the top side
- slightly distorted C_4 symmetric structure

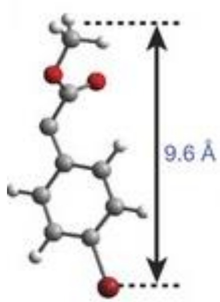


top view

bottom view

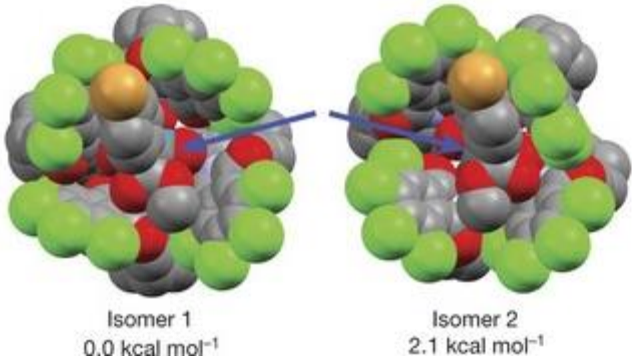


side view



length of carbene

- π-stacking between phthalimido and aryl groups
- preferred attack at the *Re* face

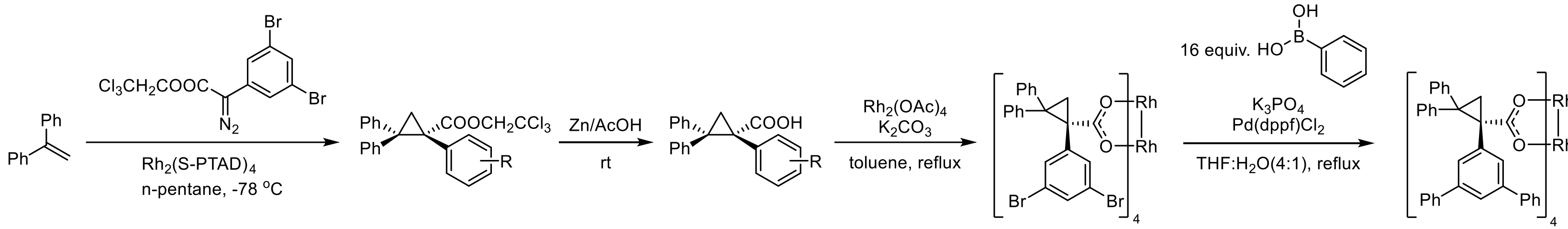


two most stable isomers

Liao, K.; Pickel, T. C.; Oyarskikh, V. B.; Acsa, J. B.; Usaev, D. G. M.; Davies, H. M. L., *Nature* **2017**, *551*, 609-613.

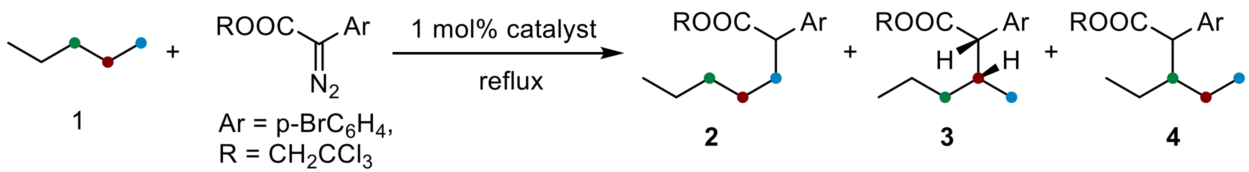
Acyclic Systems: secondary C-H bonds

Synthesis of catalysts



entry 4 entry 5

Optimization

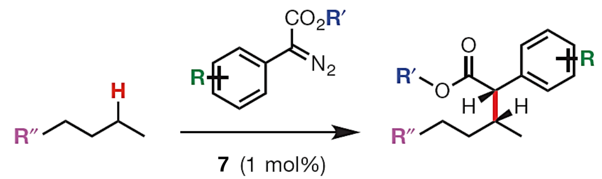


entry	catalyst	**2:3:4**	dr of **3**	ee% of **3**	yield / %
1	Rh_2(*S*-DOSP)$_4$	nd:29:1	3:1	82	98
2	Rh_2(*R*-*p*-PhTPCP)$_4$	1:2:nd	14:1	92	97
3	Rh_2(*R*-*p*-BrTPCP)$_4$	1:4:nd	6:1	91	98
4	Rh_2(*R*-3,5-di-BrTPCP)$_4$	1:26:nd	5:1	78	95
5	Rh_2(*R*-3,5-di-PhTPCP)$_4$	1:22:nd	5:1	96	95
6	Rh_2[*R*-3,5-di-(3,5-diPhC$_6$H$_3$)TPCP]$_4$	1:5:nd	16:1	97	98
7	Rh_2[*R*-3,5-di(*p*-^{t}BuC$_6$H$_4$)TPCP]$_4$	1:25:nd	20:1	99	99

Liao, K.; Negretti, S.; Musaev, D. G.; Bacsa, J.; Davies, H. M. L., *Nature* **2016**, *533*, 230-234.

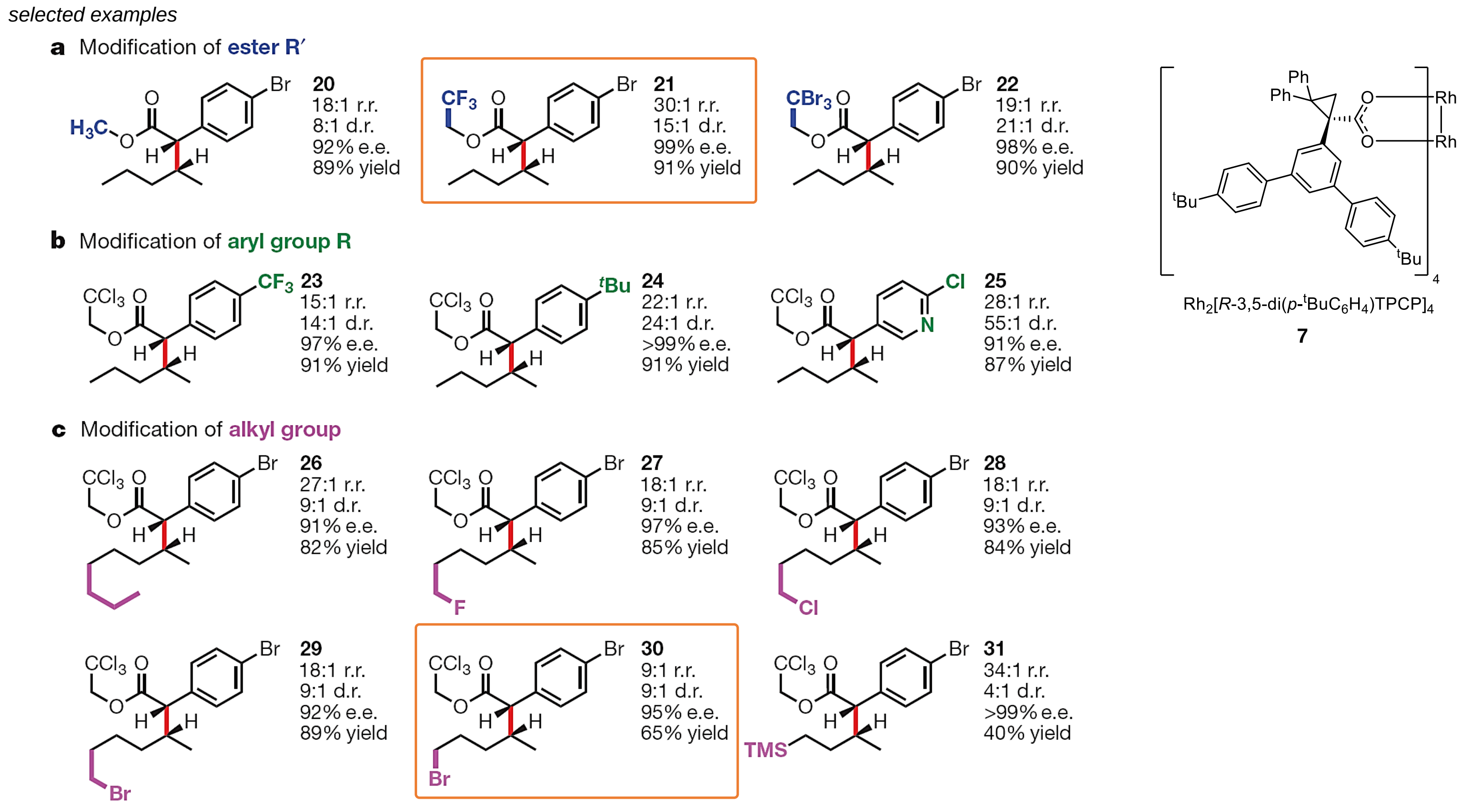
Acyclic Systems: secondary C-H bonds

Scopes



Condition A (20-25): pentane as solvent

Condition B (26-31): 3 equiv. of substituted alkanes with ~~dichloromethane~~ as solvent



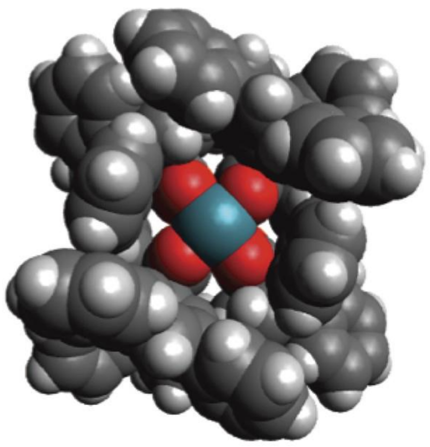
Liao, K.; Negretti, S.; Musaev, D. G.; Bacsa, J.; Davies, H. M. L., *Nature* **2016**, *533*, 230-234.

Acyclic Systems: secondary C-H bonds

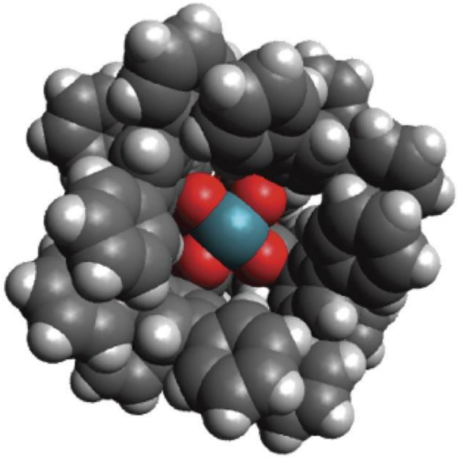
Structural information

computational structure	*computational structure*	*X-ray crystal structure*

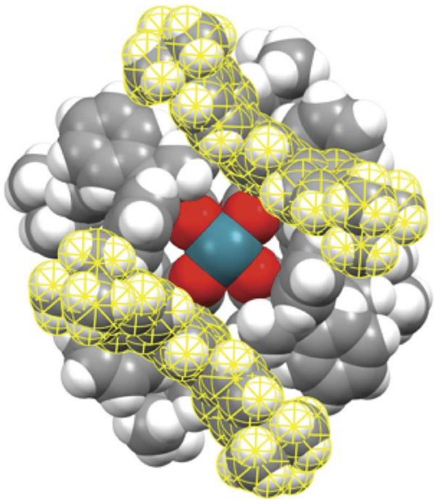
a



b



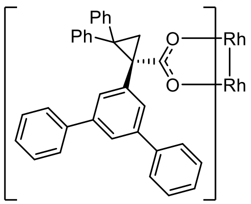
c



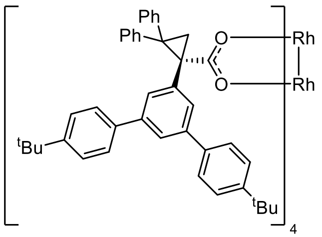
5
Rh_2[R-3,5-diPhTPCP]$_4$
α, β, α, β form
***D*$_2$ symmetry**

5
Rh_2[R-3,5-diPhTPCP]$_4$
α, α, α, α form
***C*$_4$ symmetry**
5 kcal mol^{-1} less stable than α, β, α, β form

7
Rh_2[R-3,5-di(*p*-^{t}BuC_6H_4)TPCP]$_4$
α, β, α, β form
***D*$_2$ symmetry**



Rh_2[*R*-3,5-diPhTPCP]$_4$

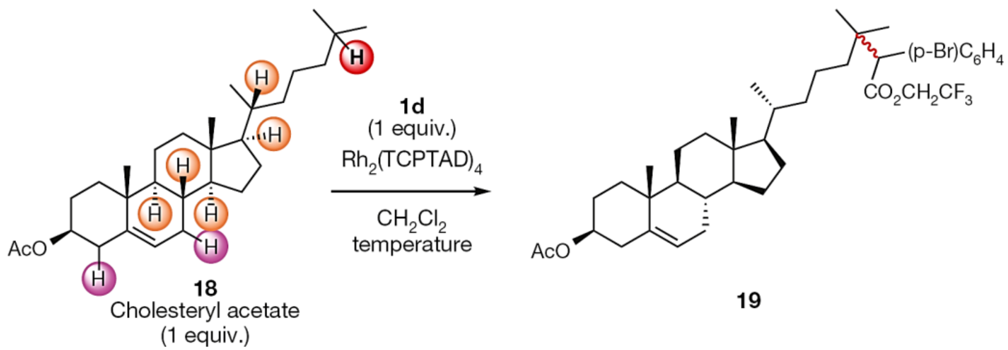


Rh_2[*R*-3,5-di(*p*-^{t}BuC_6H_4)TPCP]$_4$

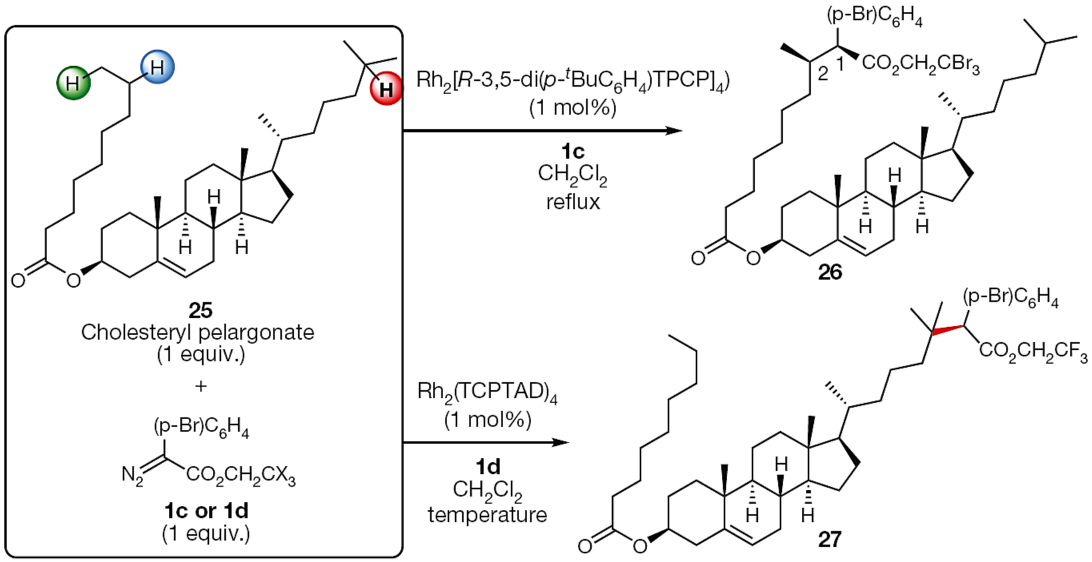
Liao, K.; Negretti, S.; Musaev, D. G.; Bacsa, J.; Davies, H. M. L., *Nature* **2016**, *533*, 230-234.

Acyclic Systems: secondary *vs* tertiary

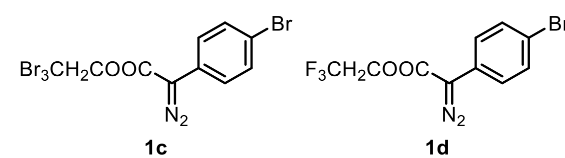
Controlled site-selectivity in elaborate substrates



$Rh_2(TCPTAD)_4$	19	Temperature	r.r.	d.r.	Yield (%)
S, 1 mol%	*R*	39 °C	>98:2	11:1	78
R, 1 mol%	*S*	39 °C	>98:2	11:1	86
R, 0.1 mol%	*S*	39 °C	>98:2	9:1	83
R, 1 mol%	*S*	24 °C	>98:2	13:1	80
R, 1 mol%	*S*	0 °C	>98:2	16:1	60



r.r.	d.r. of C1/steroid	d.r. of C1/C2	Yield (%)
87:10:3	39:1	9:1	68

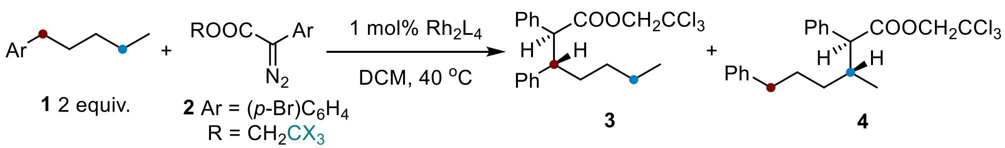


$Rh_2(TCPTAD)_4$	27	Temperature	r.r.	d.r.	Yield (%)
R	*S*	39 °C	87:13	6:1	74
R	*S*	24 °C	89:11	>20:1	68
R	*S*	0 °C	92:8	>20:1	65

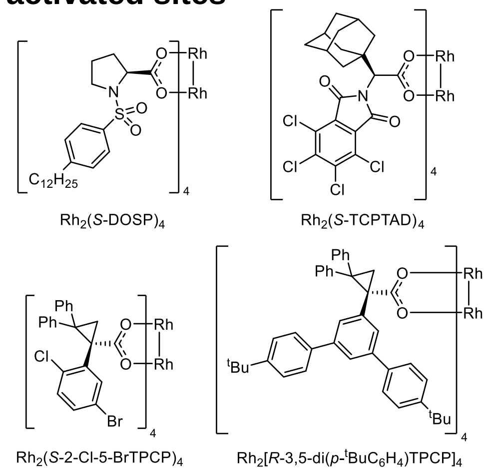
Liao, K.; Pickel, T. C.; Oyarskikh, V. B.; Acsa, J. B.; Usaev, D. G. M.; Davies, H. M. L., *Nature* **2017**, *551*, 609-613.

Acyclic Systems: secondary *vs* benzylic

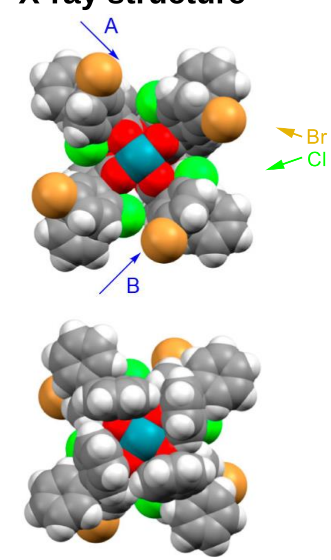
Optimization: non-activated C-H bonds in the presence of electronically activated sites



entry	Rh_2L_4	X	yield / %	rr of 3:4	major product (3 or 4) dr	major product (3 or 4) ee / %
1	Rh_2(*S*-DOSP)$_4$	Cl	68	6:1	4:1	77
2	Rh_2(*S*-TCPTAD)$_4$	Br	75	11:1	16:1	90
3	Rh_2[*R*-3,5-di(*p*-^{t}BuC_6H_4)TPCP]$_4$	Cl	69	1:3	7:1	89
4	Rh_2(*S*-2-Cl-5-BrTPCP)$_4$	Cl	87	1:20	30:1	89
5	Rh_2(*S*-2-Cl-5-BrTPCP)$_4$	F	86	1:24	28:1	91

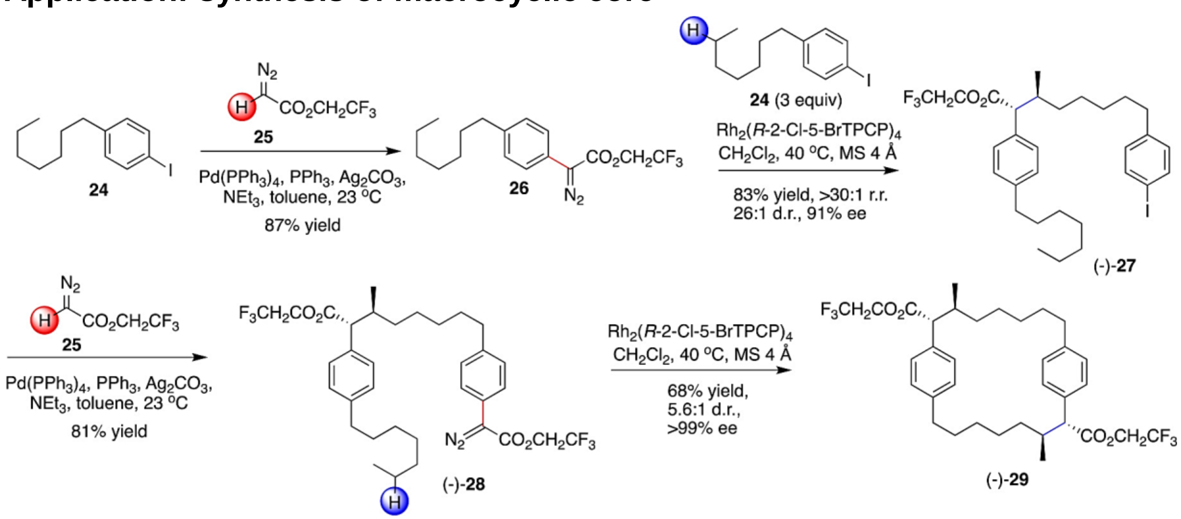


X-ray structure



Rh_2(*S*-2-Cl-5-BrTPCP)$_4$
***C_4* symmetry**

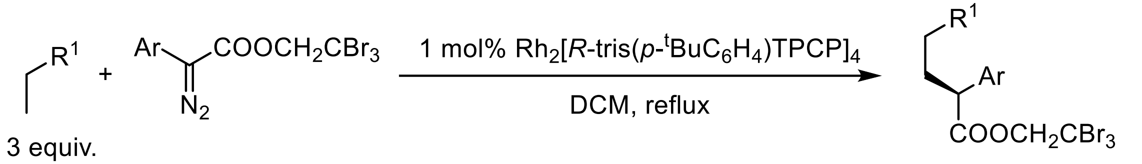
Application: synthesis of macrocyclic core

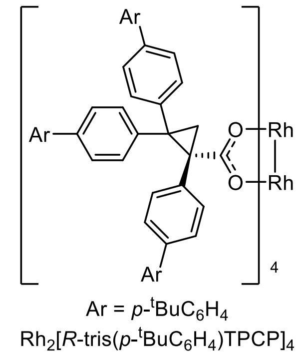


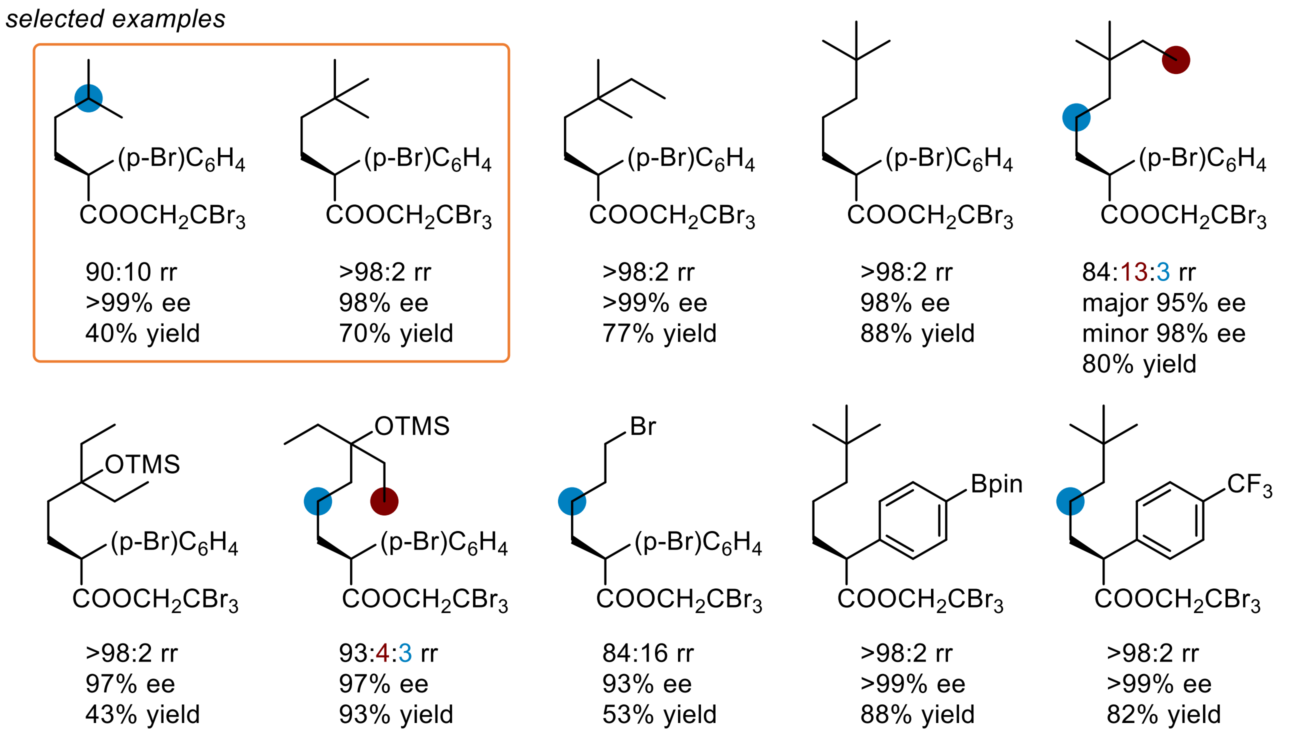
Liu, W.; Ren, Z.; Bosse, A. T.; Liao, K.; Goldstein, E. L.; Bacsa, J.; Musaev, D. G.; Stoltz, B. M.; Davies, H. M. L., *J. Am. Chem. Soc.* **2018**, *140*, 12247-12255.

Acyclic Systems: primary C-H bonds

Scopes



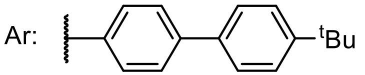




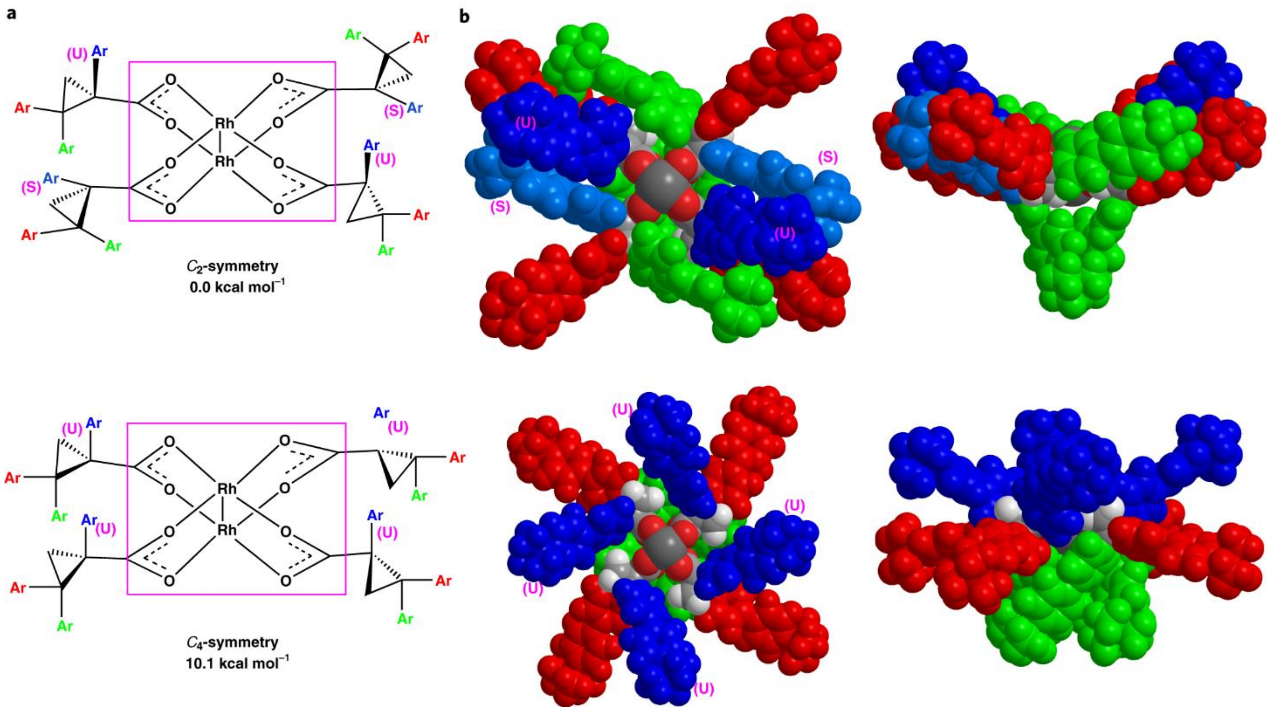
Some of the C–H functionalization occurred at the tertiary or secondary position **(marked in blue)** of the substrates.
Some of the C–H functionalization occurred at the primary position **(marked in red)** of the substrates.

Liao, K.; Yang, Y.-F.; Lie, Y.; Sanders, J. N.; Houk, K. N.; Musaev, D. G.; Davies, H. M. L., *Nat. Chem.* **2018**, *10*, 1048-1055.

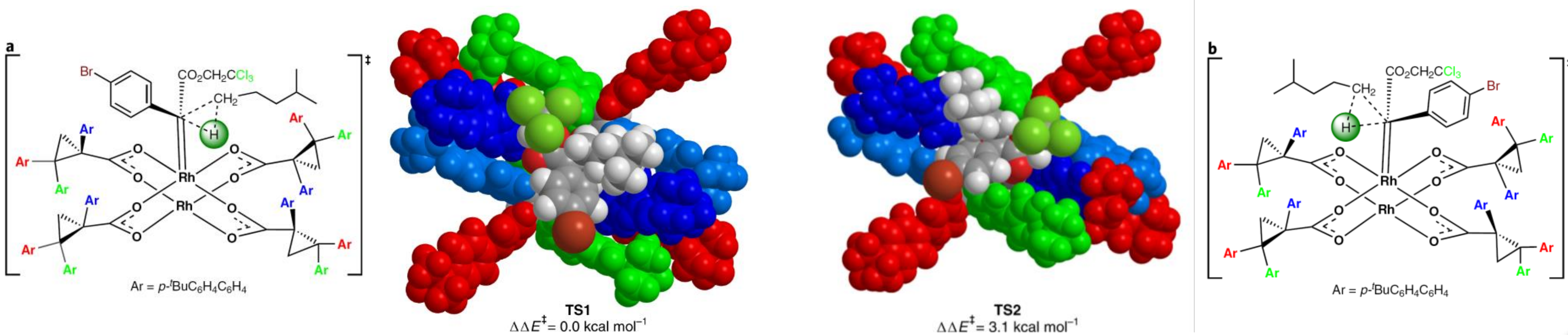
Acyclic Systems: primary C-H bonds



Computational structure



Transition state



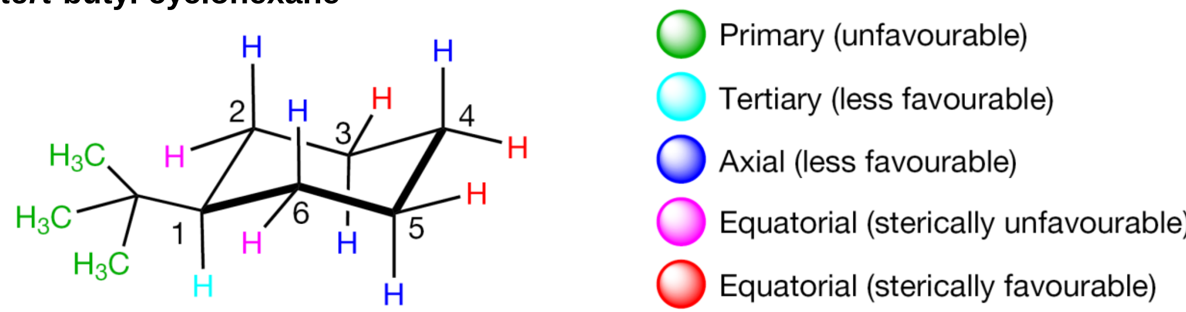
Liao, K.; Yang, Y.-F.; Lie, Y.; Sanders, J. N.; Houk, K. N.; Musaev, D. G.; Davies, H. M. L., *Nat. Chem.* **2018**, *10*, 1048-1055.

2.3

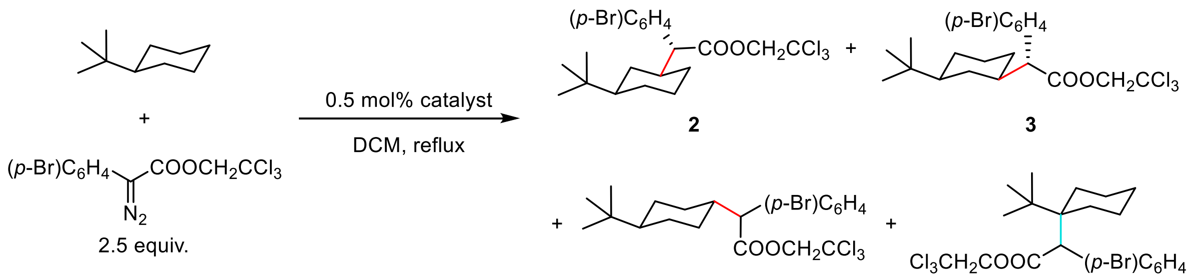
Cyclic Systems

Cyclic Systems: desymmetrization of cyclohexanes

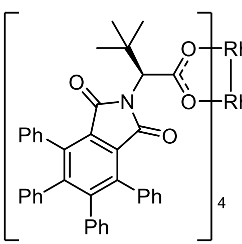
The structure of *tert*-butyl cyclohexane



Screen of catalyst



catalyst	product ratio			
	2	**3**	**4**	**5**
$Rh_2(S\text{-DOSP})_4$	60.8	9.7	24.1	5.3
$Rh_2(S\text{-TCPTTL})_4$	49.6	9.3	40.6	nd
$Rh_2[R\text{-3,5-di}(p\text{-}^tBuC_6H_4)TPCP]_4$	29.4	8.4	62.2	nd
$Rh_2[R\text{-tris}(p\text{-}^tBuC_6H_4)TPCP]_4$	70.3	17.2	12.4	nd
$Rh_2(S\text{-TPPTTL})_4$	91.3	8.7	nd	nd

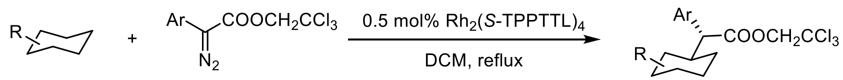


$Rh_2(S\text{-TPPTTL})_4$

Fu, J.; Ren, Z.; Bacsa, J.; Musaev, D. G.; Davies, H. M. L., *Nature* **2018**, *564*, 395-399.

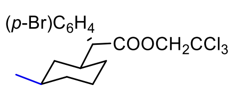
Cyclic Systems: cyclohexanes

Scopes

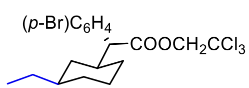


2.5 equiv.

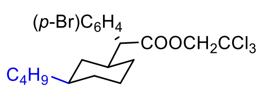
selected examples



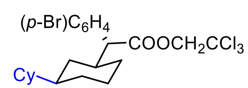
1, 85%, 97% ee
12.5:1 rr.
4.0:1 dr[a]



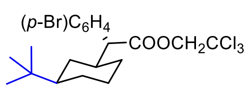
2, 81%, 96% ee
>50:1 rr
4.2:1 dr[a]



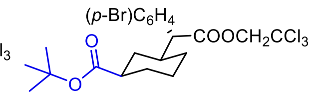
3, 77%, 90% ee
>50:1 rr
3.7:1 dr[a]



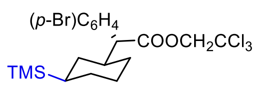
4, 85%, 95% ee
40:1 rr
12:1 dr[a]



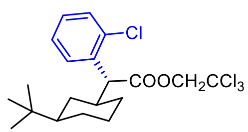
5, 80%, 95% ee
>50:1 rr
11:1 dr[a]



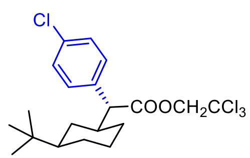
6, 58%, 96% ee
9.9:1 rr
7.7:1 dr[a]



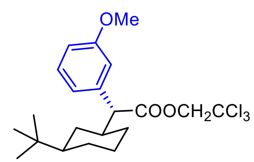
7, 80%, 97% ee
19.0:1 rr
14:1 dr[a]



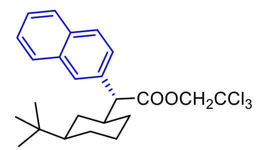
8, 64%, 92% ee
50:1 rr
15:1 dr[a]



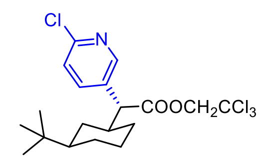
9, 89%, 97% ee
>50:1 rr
11:1 dr[a]



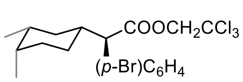
10, 61%, 96% ee
>50:1 rr
16:1dr[a]



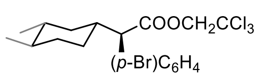
11, 81%, 98% ee
>50:1 rr
11 :1 dr[a]



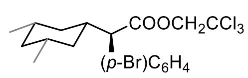
12, 58%, 98% ee
>50:1 rr
9.8:1 dr[a]



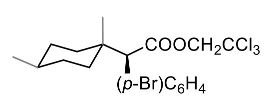
13, 70%, 98% ee
16:1 rr
3.7:1 dr[a]



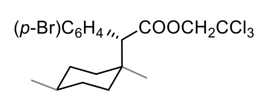
14, 75%, 85% ee
>50:1 rr
25:1 dr[a]



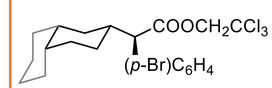
15, 62%, 59% ee
15:1 rr
>50:1 dr[b]



16, 80%, 91% ee
>50:1 rr
>50:1 dr[b]



17, 77%, 94% ee
4.8:1 rr
>50:1 dr[b]



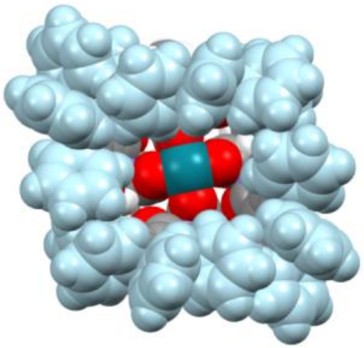
18, 68%, 98% ee
>50:1 rr
6.7:1 dr[a]

[a] No ring diastereomers were observed. [b] Owing to symmetry, there are no side-chain diastereomers.

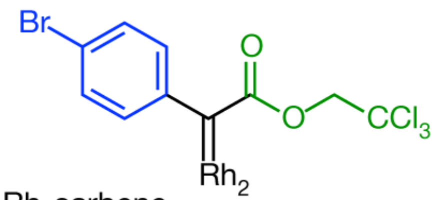
Fu, J.; Ren, Z.; Bacsa, J.; Musaev, D. G.; Davies, H. M. L., *Nature* **2018**, *564*, 395-399.

Cyclic Systems: cyclohexanes

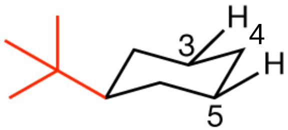
Computational studies



Isomer **47b**
***C_4* symmetry**

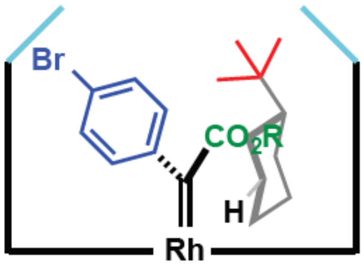


Rh-carbene

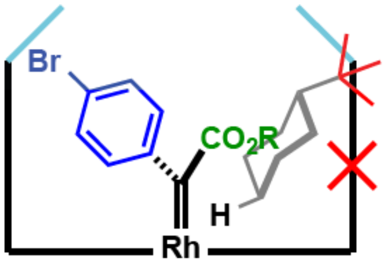


Substrate

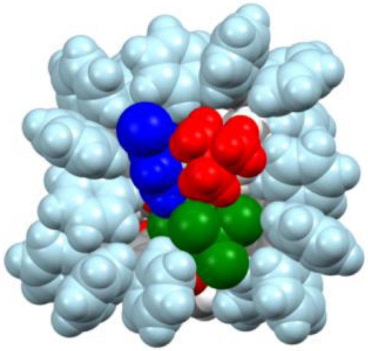
Rh-carbene-substrate complex



C3 insertion
side view

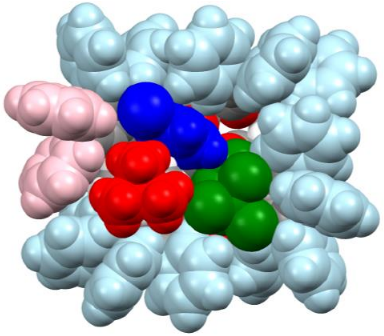


C4 insertion
side view



Isomer 46
ΔG = 0.0 kcal mol^{-1}

C3 insertion
top view



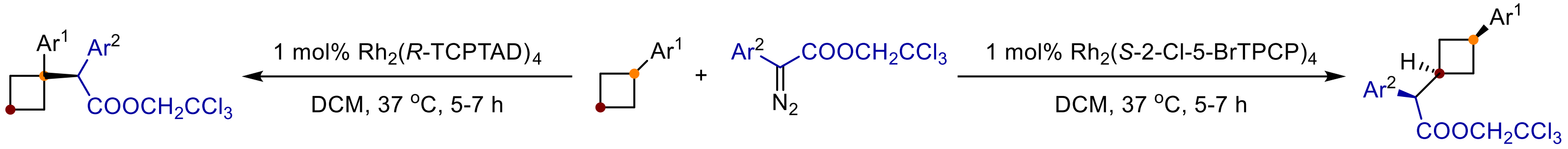
Isomer 46S
ΔG = 5.4 kcal mol^{-1}

C5 insertion
top view

Fu, J.; Ren, Z.; Bacsa, J.; Musaev, D. G.; Davies, H. M. L., *Nature* **2018**, *564*, 395-399.

Cyclic Systems: BCPs and cyclobutanes

C-H functionalization of cyclobutanes

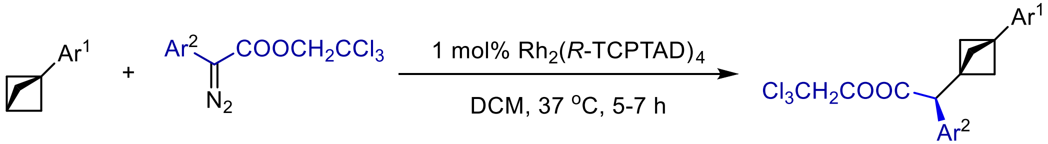


yield: 36-98%
ee: 88-99%

yield: 29-87%
cis:*trans*: 85:15->95:5
ee: 74-94%

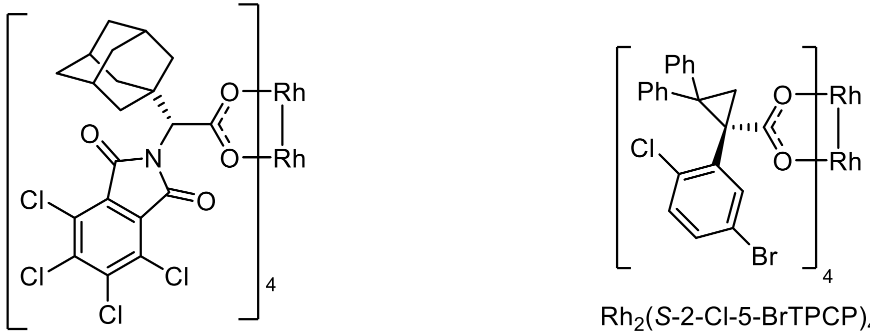
Garlets, Z. J.; Wertz, B. D.; Liu, W. B.; Voight, E. A.; Davies, H. M. L., *Chem* **2020**, *6*, 538-538.

C-H functionalization of bicyclo[1.1.1]pentanes



yield: 42-99%
ee: 65-94%

Garlets, Z. J.; Sanders, J. N.; Malik, H.; Gampe, C.; Houk, K. N.; Davies, H. M. L., *Nat. Catal.* **2020**, *3*, 351-357.



$Rh_2(R\text{-TCPTAD})_4$

$Rh_2(S\text{-2-Cl-5-BrTPCP})_4$

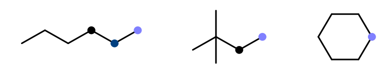
2.3

Summary and Outlook

Summary: catalyst-controlled reactivity

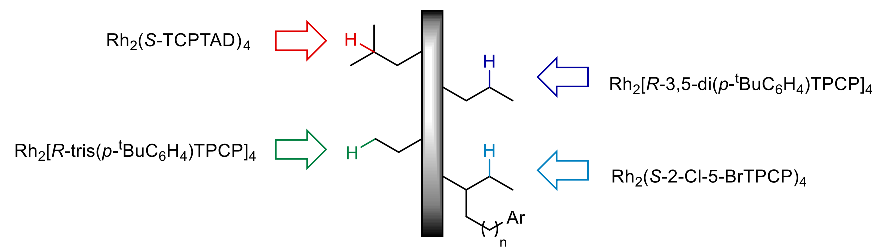
Seminal works

- Well-established catalysts
- Preliminary investigation on site- and stereoselectivity



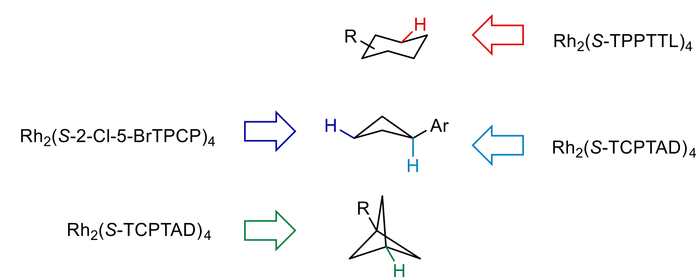
Comprehensive studies on acyclic systems

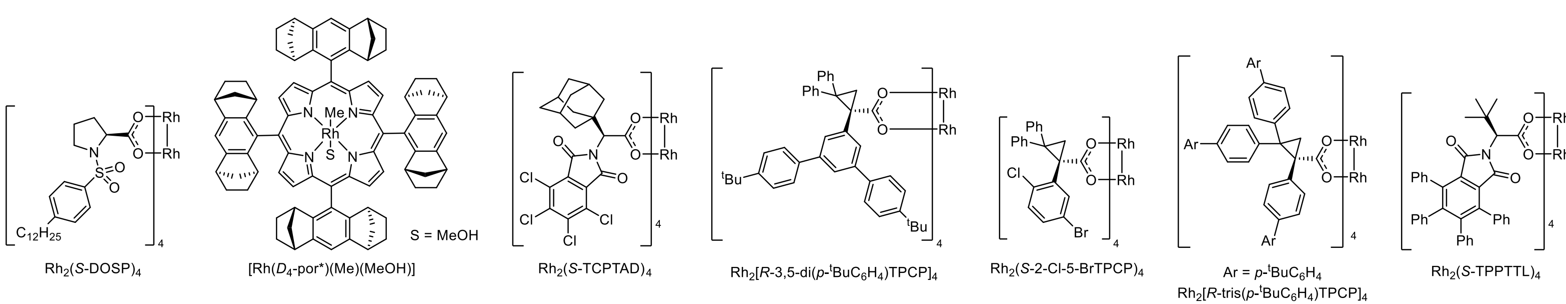
- Design of **new catalysts**
- C-H functionalization at **different sites**
- Excellent **enantio- and diastereoselectivity**



Further studies on cyclic systems

- Application of catalyst family
- Discrimination in **different conformation**





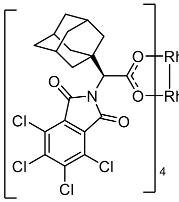
Summary: overview of the catalyst

Sterically hindered / electronically favoured site

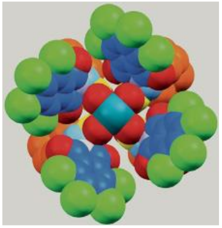
tertiary C-H

secondary C-H

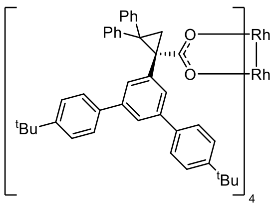
primary C-H



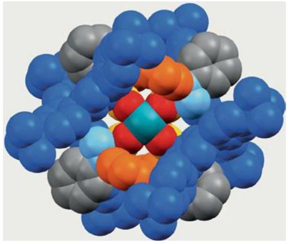
$Rh_2(S\text{-TCPTAD})_4$



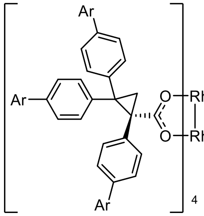
X-ray structure
***C_4* symmetry**



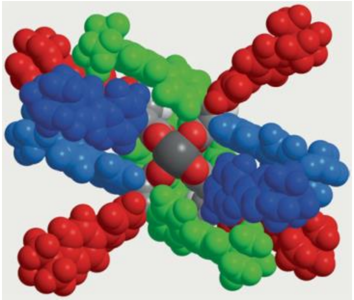
$Rh_2[R\text{-3,5-di}(p\text{-}^tBuC_6H_4)TPCP]_4$



X-ray structure
***D_2* symmetry**



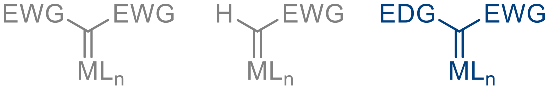
Ar = $p\text{-}^tBuC_6H_4$
$Rh_2[R\text{-tris}(p\text{-}^tBuC_6H_4)TPCP]_4$



computational structure
***C_2* symmetry**

Bulky ligand

Donor-acceptor carbene



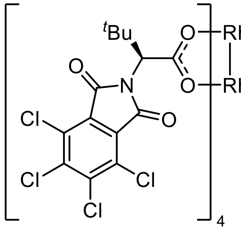
improved selectivity

EWG = CO_2R, COR, CN, $PO(OR)_2$
EDG = Aryl, heteroaryl, vinyl

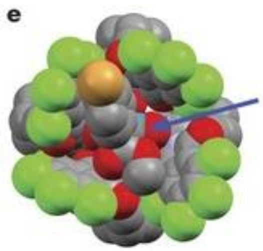
Davies, H. M. L.; Liao, K., *Nat. Rev. Chem.* **2019**, *3*, 347-360.

Outlook

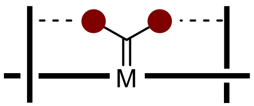
- Incorporation of other noncovalent interactions into the catalyst



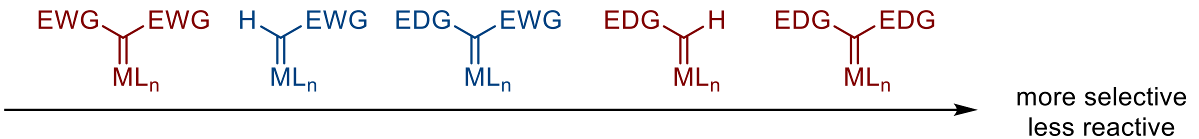
Rh_2(*S*-TCPTTL)$_4$



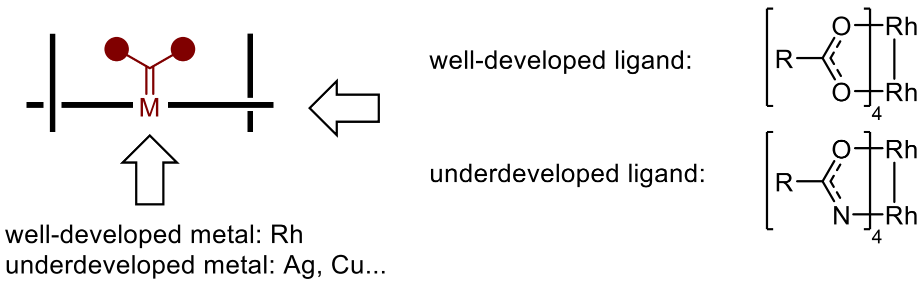
***π-stacking** between phthalimido and aryl groups*



- Application of other types of carbenoid



- Development of new catalysts



Davies, H. M. L.; Liao, K., *Nat. Rev. Chem.* **2019**, *3*, 347-360.
Doyle, M. P.; Duffy, R.; Ratnikov, M.; Zhou, L., *Chem. Rev.* **2010**, *110*, 704-724.
Caballero, A.; Díaz-Requejo, M. M.; Fructos, M. R.; Olmos, A.; Urbano, J.; Pérez, P. J., *Dalton Trans.* **2015**, *44*, 20295-20307.

THANKS FOR YOUR ATTENTION!