Frustrated Lewis Pair Catalyzed Reactions

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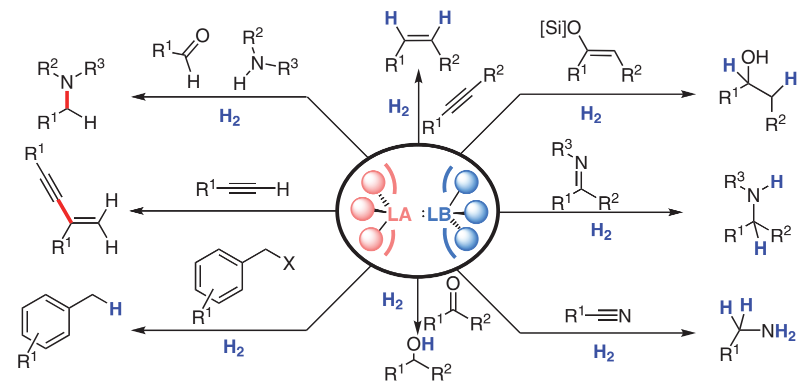

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Crowd-Reviewed

Abstract In recent years, frustrated Lewis pairs have been widely used for the activation of small molecules and in catalytic transformations. This graphical review aims to provide a fundamental understanding of frustrated Lewis pair reactivity and the exploitation thereof in catalytic reactions.

Key words frustrated Lewis pairs, boron, phosphine, nitrogen, hydrogenation, C–C bonds, C–N bonds

Since the seminal report by Douglas Stephan[1a] reporting the reversible heterolytic splitting of molecular H_2 by an intramolecular Lewis acid/Lewis base pair, the field of so-called frustrated Lewis pairs (FLP)[1b,1c] has evolved into one of the key research pillars in main group chemistry. A frustrated Lewis pair (FLP) consists of an electron-pair acceptor (Lewis acid) and an electron-pair donor (Lewis base) that cannot form a Lewis acid–base adduct because of steric reasons, thus leaving the individual reactivities available for synergistic activation with small molecules, e.g., hydrogen, carbon dioxide or nitrogen oxides.[1d] The activation of H_2 is certainly one of the most important applications of FLP catalysts.[1e–j] However, new applications of FLP catalysts beyond hydrogenations have also been elaborated, e.g., hydroaminations, oxidations and cycloisomerizations.[1k–m] This Graphical Review provides a general overview of the development of FLP-catalyzed reactions with a focus on initial findings and recent achievements.

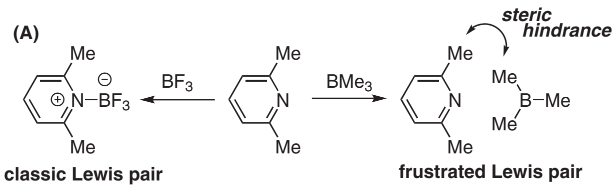
Rundong Zhou (left) was born in Shandong, P. R. of China. She earned her B.Sc. and M.Sc. degrees from Paderborn University (Germany). In 2019, she began her Ph.D. research at Paderborn University under the guidance of Prof. Dr. Jan Paradies. Her research is focused on frustrated Lewis pair catalyzed hydrogenations.

Zoleykha Pirhadi Tavandashti (center) was born in Borojerd, Iran. She received her M.Sc. in inorganic chemistry from Isfahan University of Technology (IUT) (Iran) in September 2018. In October 2021, she joined the group of Prof. Dr. Jan Paradies and started her Ph.D. research in the Department of Chemistry at Paderborn University. Her research is focused on asymmetric hydrogenations catalyzed by chiral boranes.

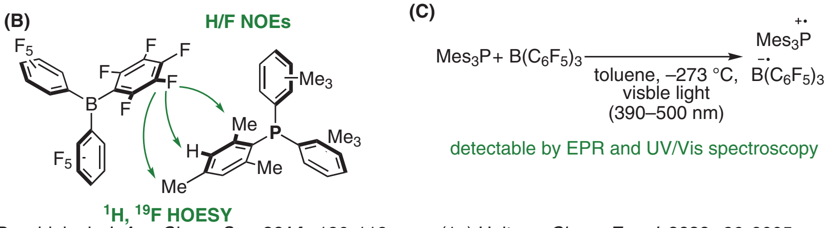
Jan Paradies (right) was born in Berlin and studied chemistry at the University of Münster and the University of Edinburgh. He received his diploma in chemistry in 2002 and joined the group of Prof. Dr. G. Erker at the University of Münster for his Ph.D. on the topic of photochemical reactions of organometallic compounds. After graduation in 2006, he joined the group of Prof. Dr. G. C. Fu at the Massachusetts Institute of Technology (MIT) as a DAAD postdoctoral fellow. In 2007, he started his independent career as a Liebig Fellow at the Karlsruhe Institute of Technology (KIT) under the mentorship of Prof. Dr. S. Bräse. After his habilitation in 2013 as a Heisenberg Fellow, he was appointed as a professor of organic chemistry at Paderborn University. His research is directed towards sulfur-rich heteroacenes and the exploration of frustrated Lewis pair chemistry.

1. Frustrated Lewis pairs:
- No formation of the Lewis acid–base adduct is observed
- The FLPs could be present as polar or radical-encounter complexes

The classic Lewis and frustrated Lewis pair (A), the polar (B) and radical (C) FLP counter complex

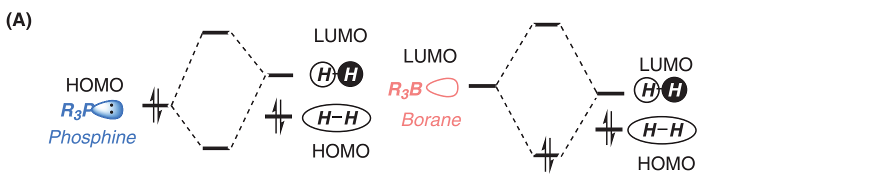


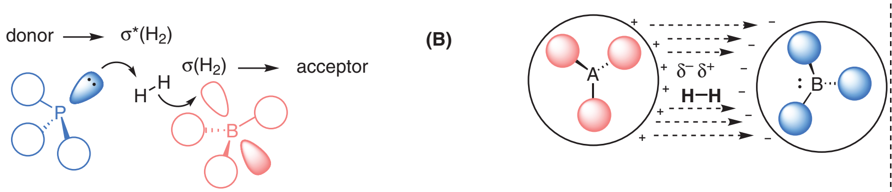
(1n) Brown, *J. Am. Chem. Soc.* **1942**, *64*, 325.



(1o) Rocchigiani, *J. Am. Chem. Soc.* **2014**, *136*, 112. (1p) Holtrop, *Chem. Eur. J.* **2020**, *26*, 9005.

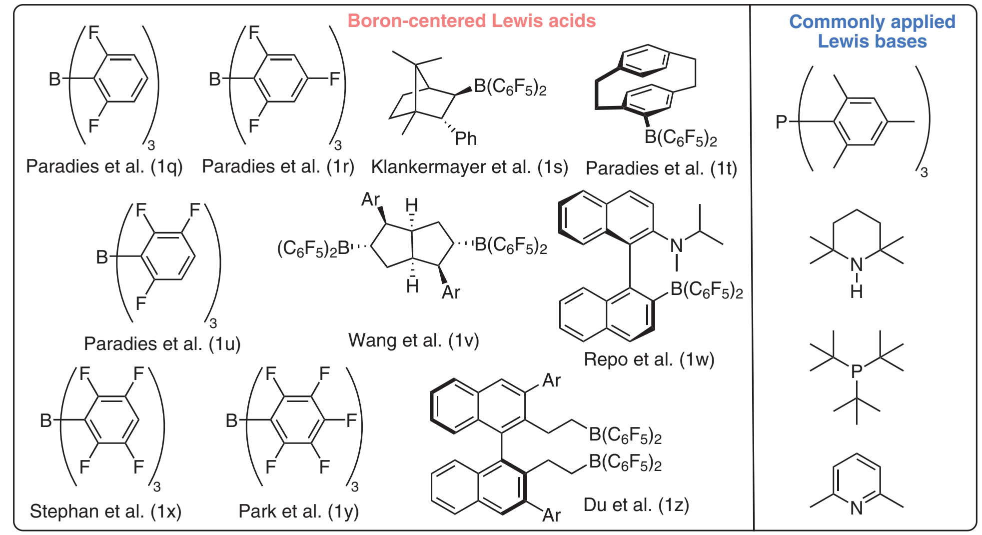
Two models for heterolytic splitting of the H–H bond, the electric transfer (ET) model (A) and the electric field (EF) model (B)





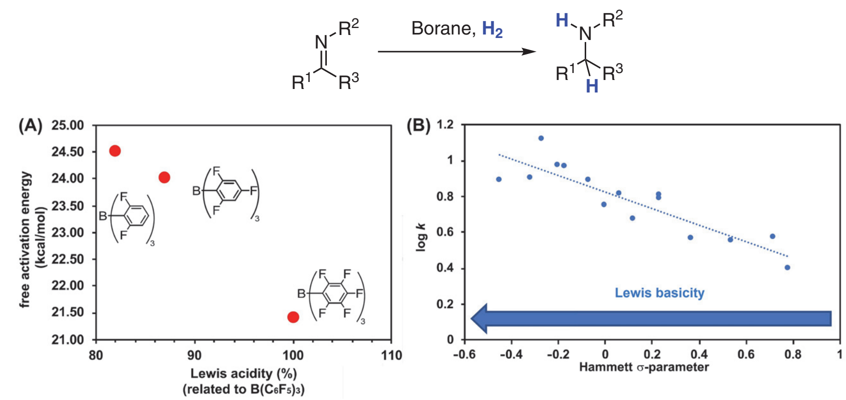
(1aa) Rokob, *Angew. Chem. Int. Ed.* **2008**, *47*, 2435. (1ab) Grimme, *Angew. Chem. Int. Ed.* **2010**, *49*, 1402.

The typical Lewis acids and Lewis bases



(1q) Greb, *Angew. Chem. Int. Ed.* **2013**, *52*, 5876.
(1r) Tussing, *Chem. Eur. J.* **2015**, *21*, 8056.
(1s) Chen, *Angew. Chem.* **2010**, *122*, 9665.
(1t) Greb, *Top. Curr. Chem.* **2013**, *334*, 81.
(1u) Köring, *Chem. Eur. J.* **2021**, *27*, 14179.
(1v) Tu, *Angew. Chem. Int. Ed.* **2018**, *57*, 15096.
(1w) Lindqvist, *J. Am. Chem. Soc.* **2015**, *137*, 4038.
(1x) Ullrich, *J. Am. Chem. Soc.* **2009**, *131*, 52.
(1y) Massey, *J. Organomet. Chem.* **1964**, *2*, 245.
(1z) Liu, *J. Am. Chem. Soc.* **2013**, *135*, 6810.

Free activation energy versus Lewis acidity for the hydrogenation of imine (A) and logarithmic plot of reaction rate constants (*k*) and Hammett parameters (B)



(1r) Tussing, *Chem. Eur. J.* **2015**, *21*, 8056. (1ac) Tussing, *Chem. Eur. J.* **2016**, 22, 7422.

Figure 1 Structure and reactivity of frustrated Lewis Pairs

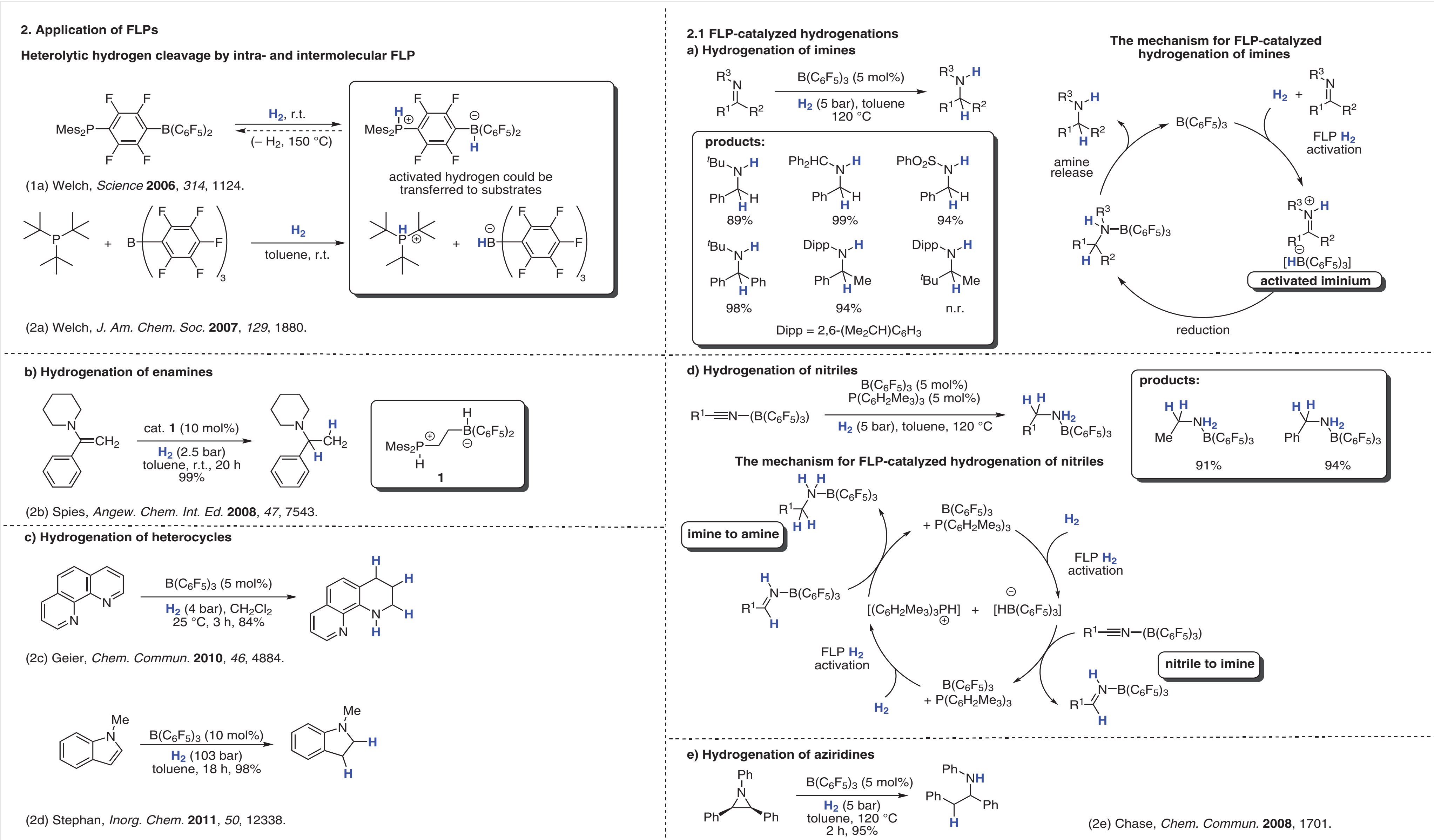
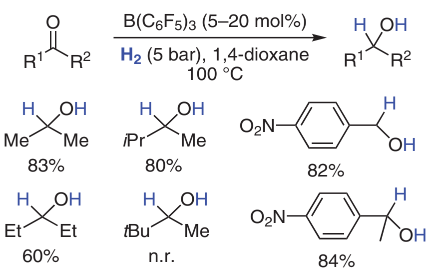
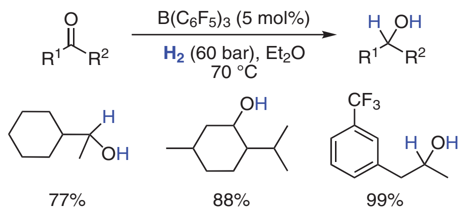


Figure 2 Frustrated Lewis pair catalaysed hydrogenations of a) imines, b) enamines, c) heterocycles, d) nitriles and e) aziridines

f) Hydrogenation of ketones



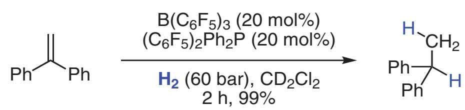
(2f) Scott, *J. Am. Chem. Soc.* **2014**, *136*, 15813.



(2g) Mahdi, *J. Am. Chem. Soc.* **2014**, *136*, 15809.

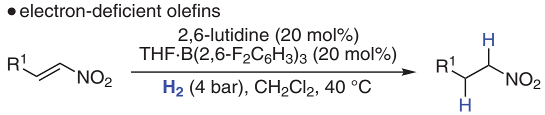
g) Hydrogenation of olefins

• electron-rich olefins



(2h) Greb, *Angew. Chem. Int. Ed.* **2012**, *51*, 10164.

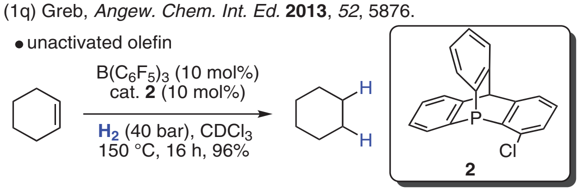
• electron-deficient olefins



R^1 = Ph, 24 h, 74%; R^1 = Cy, 36 h, >95%
R^1 = *p*-$MeOC_6H_4$, 24 h, >95%; R^1 = *i*Pr, 36 h, >95%

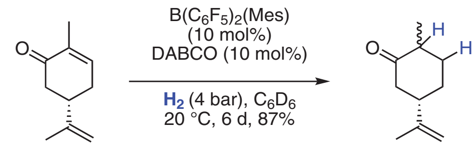
(1q) Greb, *Angew. Chem. Int. Ed.* **2013**, *52*, 5876.

• unactivated olefin



(2i) Mahaut, *ChemCatChem* **2022**, *14*, e202200294.

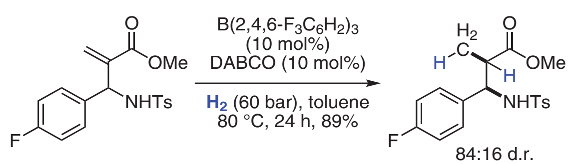
h) Hydrogenation of a,ß-unsaturated olefins



(2j) Eros, *Angew. Chem. Int. Ed.* **2010**, *49*, 6559.

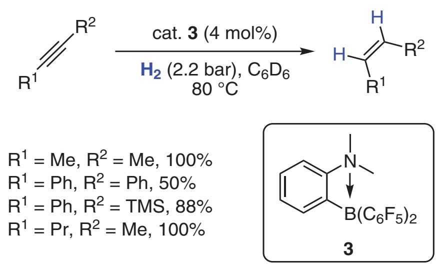
Further examples:
(2k) Reddy, *Organometallics* **2012**, *31*, 5638.
(2l) Nicasio, *Chem. Eur. J.* **2013**, *19*, 11016.
(2m) Wölke, *J. Organomet. Chem.* **2019**, *899*, 120879.

i) Hydrogenation of aza-Morita–Baylis–Hilman adducts



(2n) Khan, *ACS Catal.* **2017**, *7*, 7748.

j) Hydrogenation of alkynes



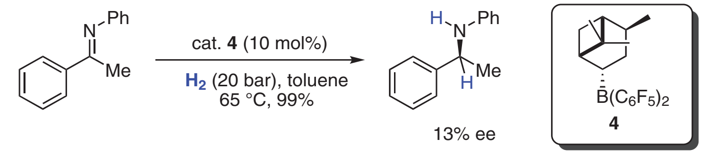
R^1 = Me, R^2 = Me, 100%
R^1 = Ph, R^2 = Ph, 50%
R^1 = Ph, R^2 = TMS, 88%
R^1 = Pr, R^2 = Me, 100%

(2o) Chernichenko, *Nat. Chem.* **2013**, *5*, 718.

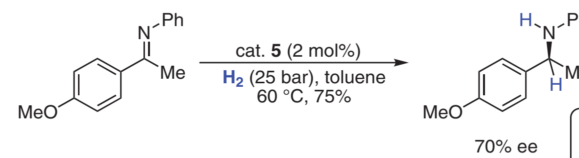
Further examples:
(2p) Wech, *Chem. Eur. J.* **2020**, *26*, 13445.
(2q) Wech, *ACS Catal.* **2022**, *12*, 5388.

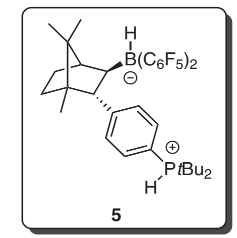
2.2 FLP-catalyzed asymmetric hydrogenations

a) Asymmetric hydrogenation of imines



(3a) Chen, *Chem. Commun.* **2008**, 2130.

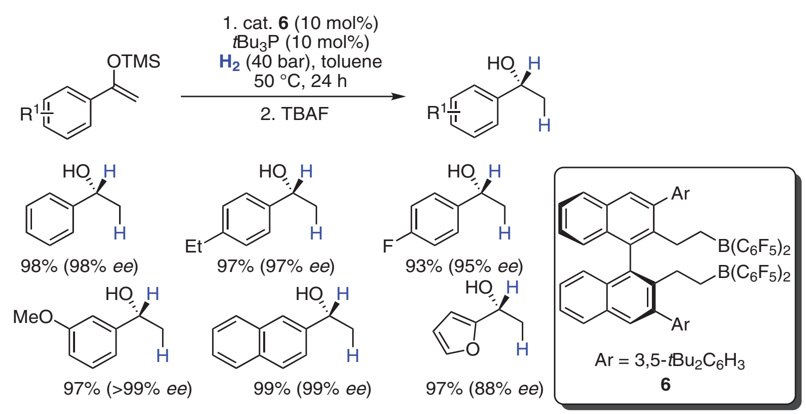




(3b) Ghattas, *Dalton Trans.* **2012**, *41*, 9026.

Further examples:
(1z) Liu, *J. Am. Chem. Soc.* **2013**, *135*, 6810.
(3c) Wang, *Adv. Synth. Catal.* **2014**, *356*, 1747.
(3d) Hamza, *ACS Catal.* **2020**, *10*, 14290.

b) Asymmetric hydrogenation of silyl enol ethers



(3e) Wei, *J. Am. Chem. Soc.* **2014**, *136*, 12261.

Figure 3 Frustrated Lewis pair catalaysed hydrogenations of f) ketones g) olefins h) electron-deficient olefins i) aza-morita-Hilman adducts and j) alkynes and frustrated Lewis pair catalaysed asymmetric hydrogenations

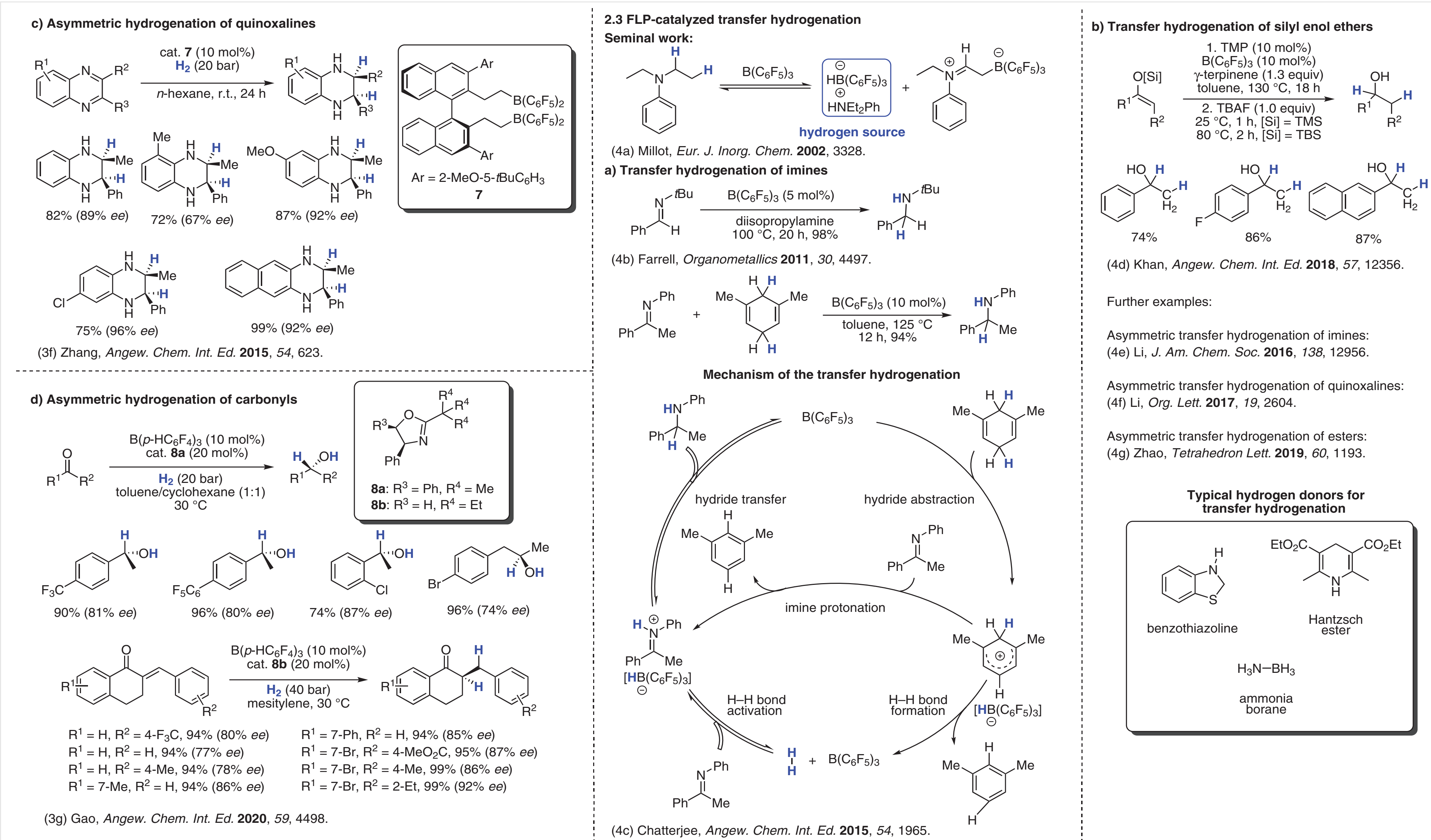


Figure 4 Frustrated Lewis pair catalaysed asymmetric hydrogenation of c) quinoxalines d) carbonyls and transfer hydrogenations

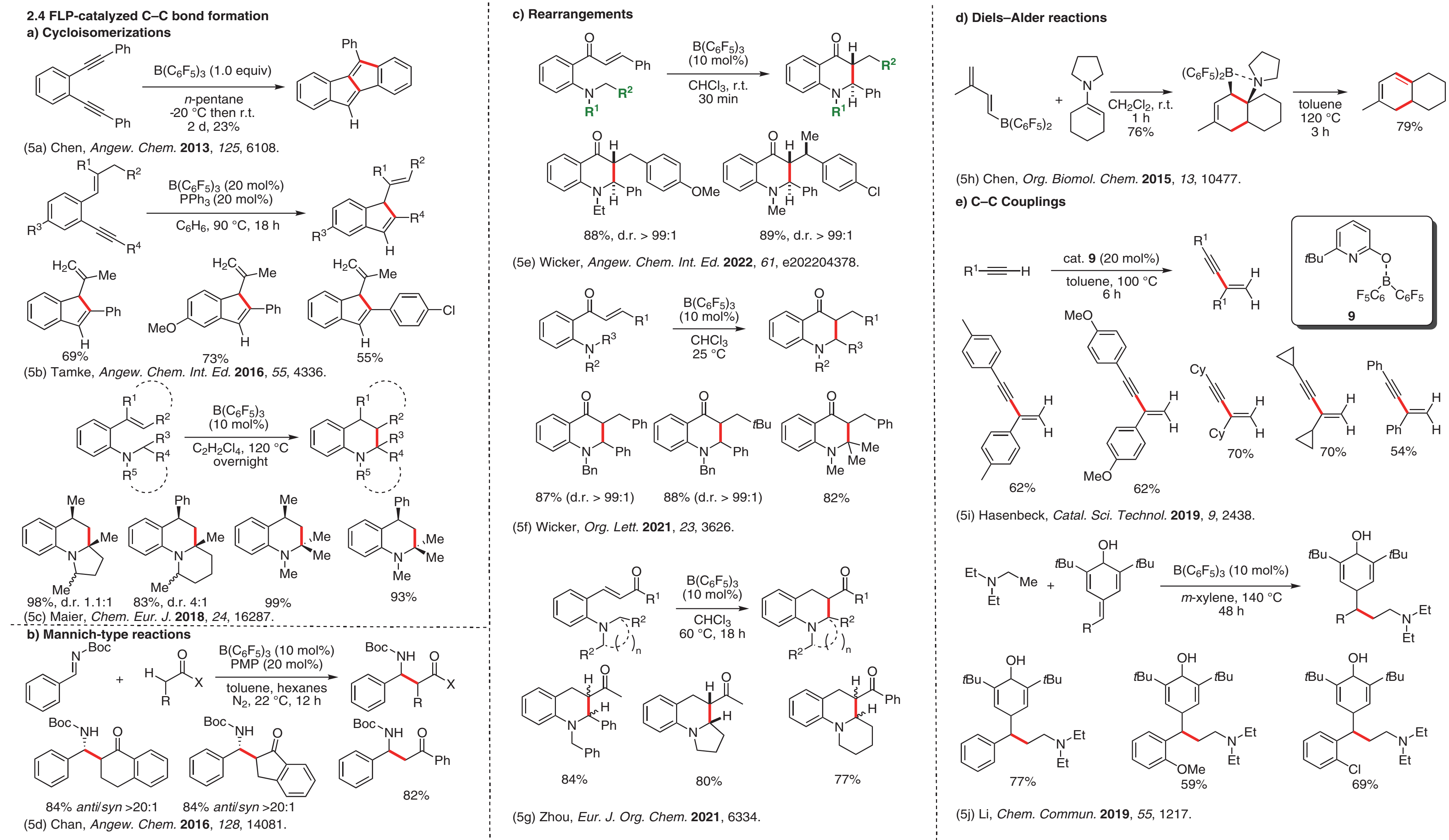
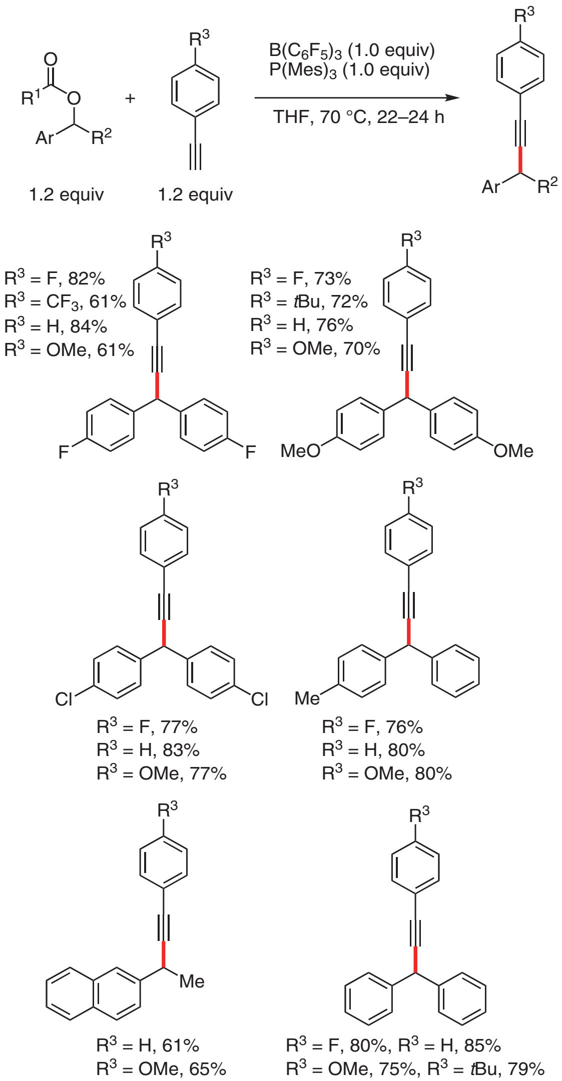


Figure 5 Frustrated Lewis pair catalysed C–C bond formation by a) cycloisomerizations b) Mannich-type reactions c) rearrangements d) Diels–Alder reactions and e) C–C couplings

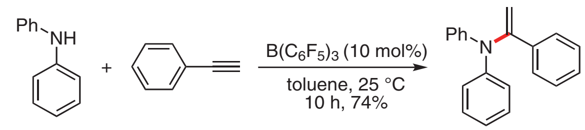
e) C–C Couplings (continued)



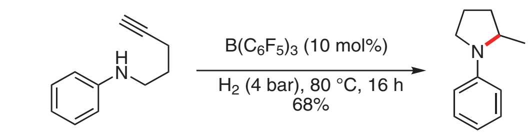
(5k) Dasgupta, *J. Am. Chem. Soc.* **2021**, *143*, 4451.

2.5 C–N Bond formation

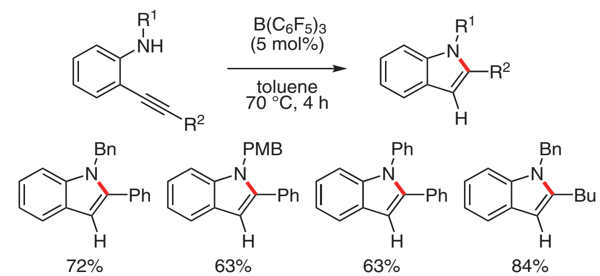
a) Hydroaminations



(6a) Mahdi, *Angew. Chem. Int. Ed.* **2013**, *52*, 12418.

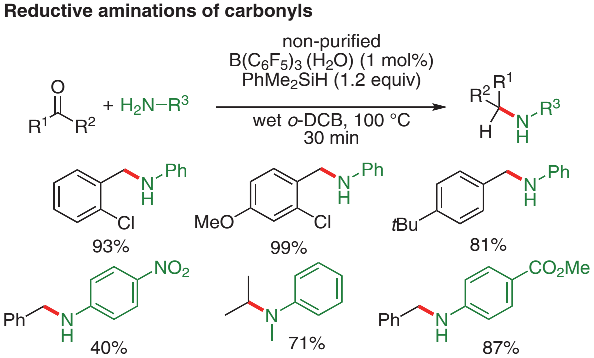


(6b) Mahdi, *Chem. Eur. J.* **2015**, *21*, 11134.



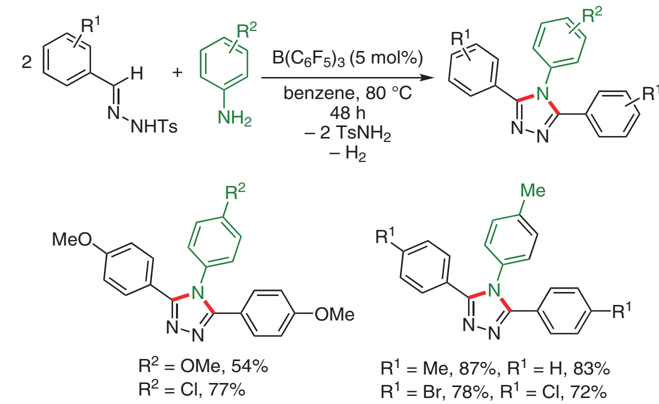
(6c) Tussing, *Dalton Trans.* **2017**, *46*, 1539.

c) Reductive aminations of carbonyls



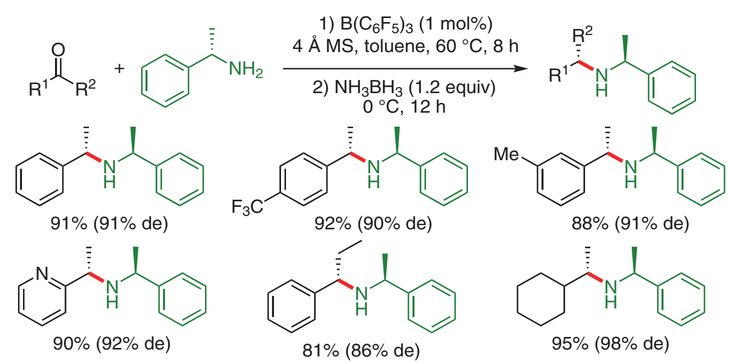
(6e) Fasano, *Chem. Eur. J.* **2017**, *23*, 1793.

b) Reductive aminations of hydrazones



(6d) Guru, *Chem. Sci.* **2019**, *10*, 7964.

d) Asymmetric reductive aminations of carbonyls

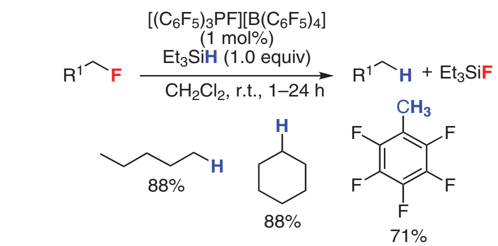


(6f) Pan, *J. Org. Chem.* **2018**, *83*, 11502.

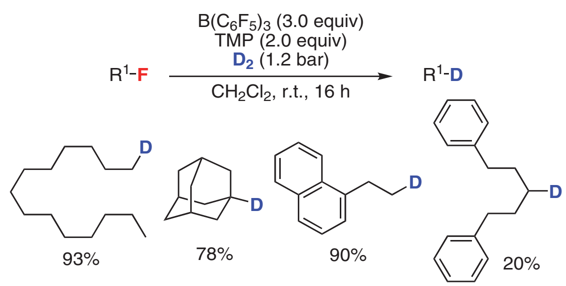
Further examples:
(6g) Dorkó, *Angew. Chem. Int. Ed.* **2017**, *56*, 9512.
(6h) Hoshimoto, *J. Am. Chem. Soc.* **2018**, *140*, 7292.

Figure 6 Frustrated Lewis pair catalysed C–C and C–N bond formations

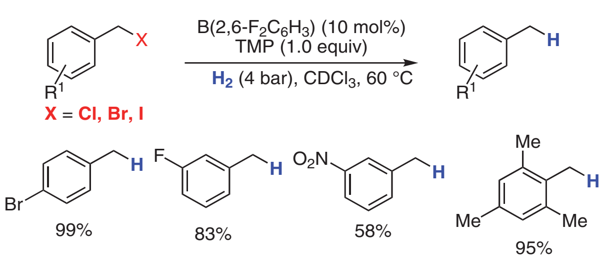
2.6 C–Hal bond activations



(7a) Caputo, *Science* **2013**, *341*, 1374.



(7b) Bro , *J. Labelled Compd. Radiopharm.* **2019**, *62*, 743.



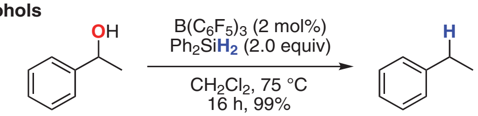
(7c) Wang, *Chem. Commun.* **2022**, *58*, 1175.

Further examples
C–F bond activation:
(7d) Mandal, *J. Am. Chem. Soc.* **2018**, *140*, 10682.
(7e) Caputo, *Organometallics* **2012**, *31*, 27.

2.7 FLP-catalyzed defunctionalizations

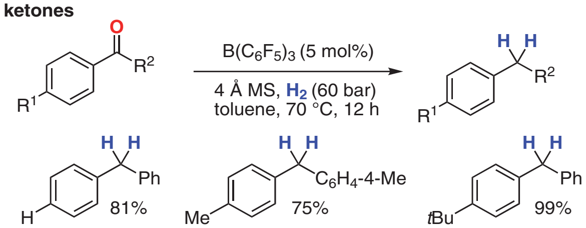
a) Deoxygenations of alcohols, ketones and esters

- **alcohols**



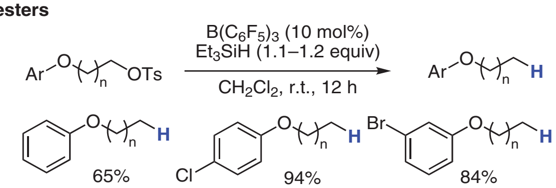
(8a) Tan, *Tetrahedron Lett.* **2009**, *50*, 4912.

- **ketones**



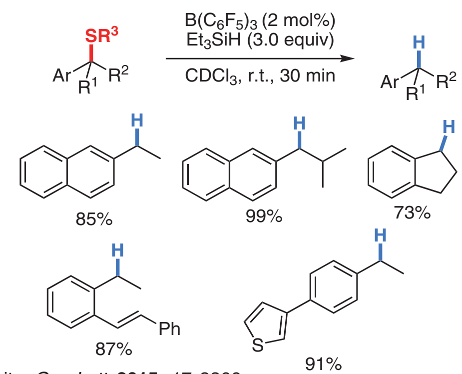
(8b) Mahdi, *Angew. Chem. Int. Ed.* **2015**, *54*, 8511.

- **esters**



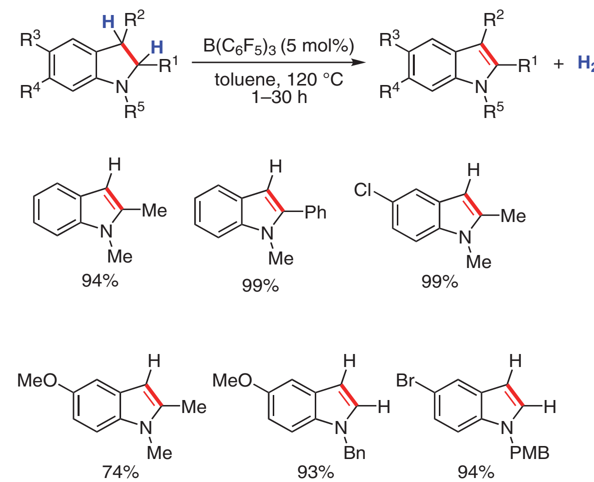
(8c) Chatterjee, *Angew. Chem. Int. Ed.* **2017**, *56*, 3389.

b) Hydrodesulfurizations



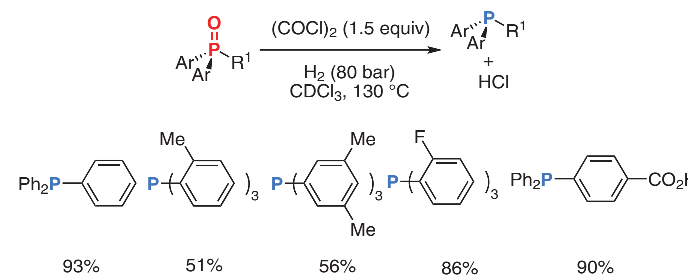
(8d) Saito, *Org. Lett.* **2015**, *17*, 3366.

c) Dehydrogenations



(8e) Maier, *Angew. Chem. Int. Ed.* **2016**, *55*, 12219.

d) Deoxygenations of phosphane oxides



(8f) Stepen, *Angew. Chem. Int. Ed.* **2018**, *57*, 15253.

Figure 7 Frustrated Lewis pair catalysed C–Hal bond activations and defunctionalizations by a) deoxygenation of alcohols, ketones and esters, b) hydrodesulfurization, c) dehydrogenations and d) deoxygenations of phosphane oxides

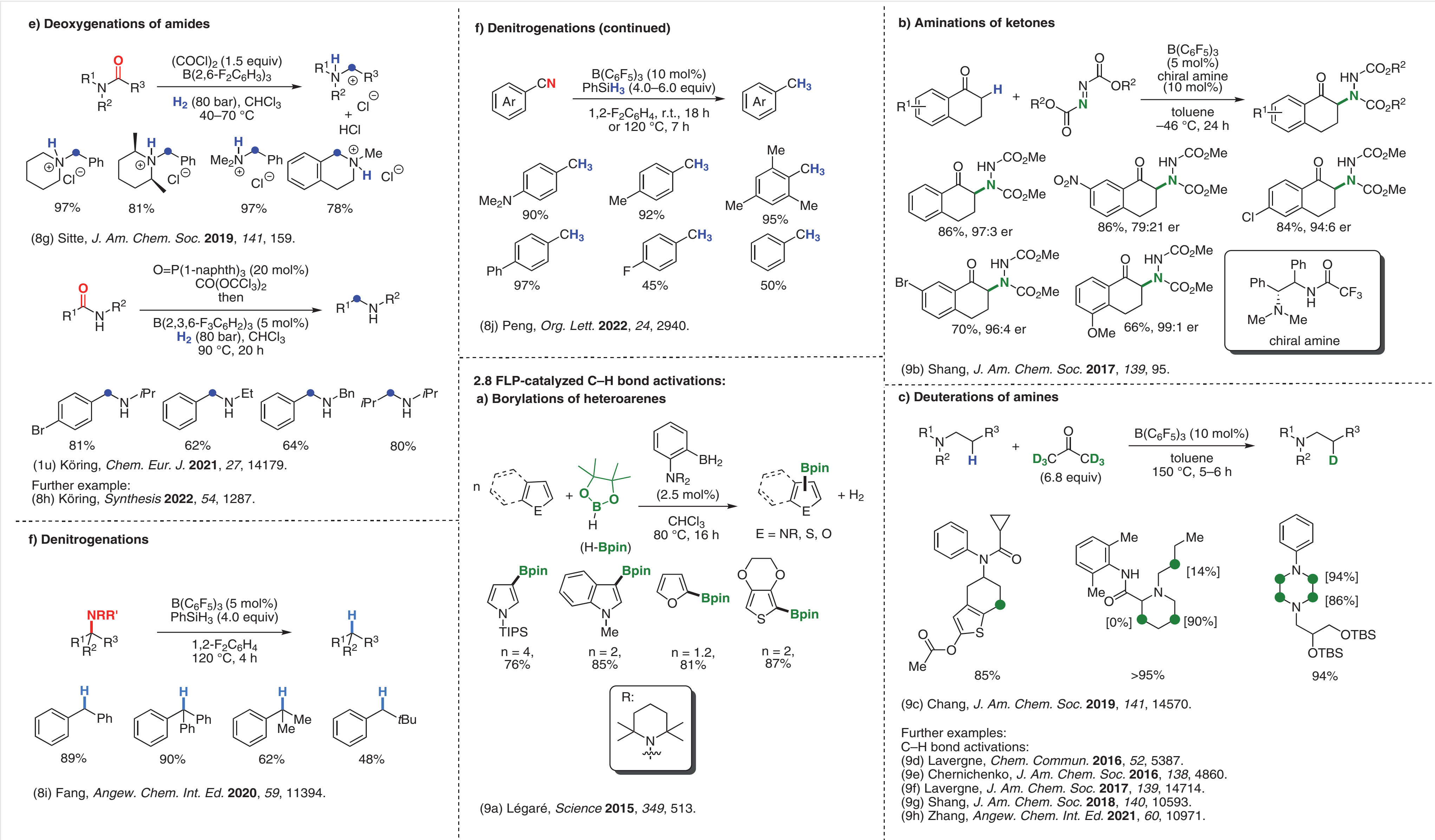
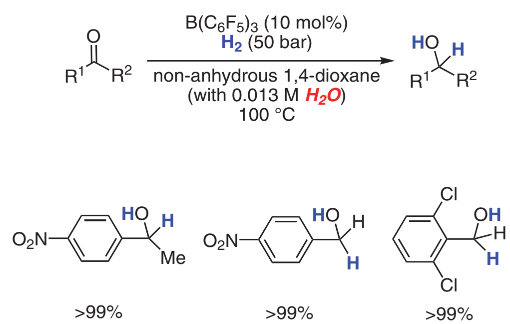


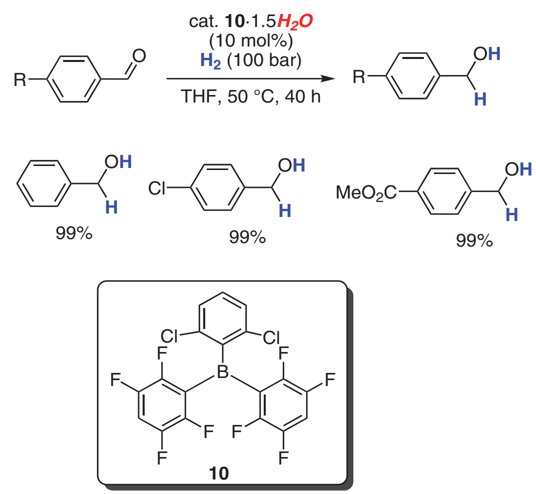
Figure 8 Frustrated Lewis pair reductive defunctionalizations of e) amides, f) amines, g) nitriles and frustrated Lewis pair catalaysed C–H bond activations

2.9 Moisture-tolerant FLP-catalyzed reactions

Hydrogenations of carbonyls

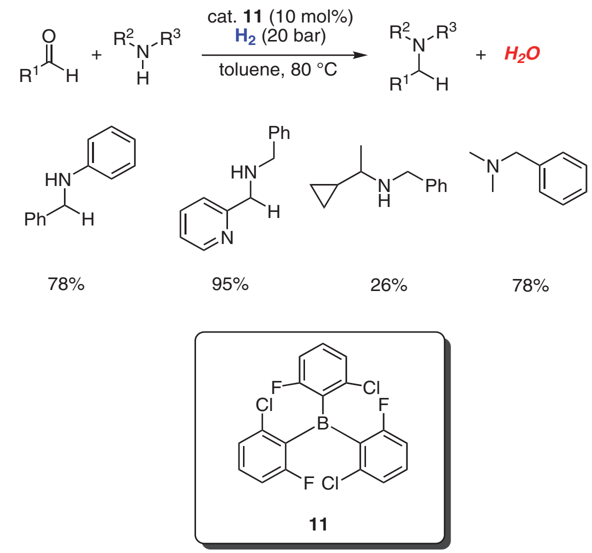


(10a) Gyömöre, *ACS Catal.* **2015**, *5*, 5366.



(10b) Scott, *ACS Catal.* **2015**, *5*, 5540.

Reductive aminations



(6g) Dorkó, *Angew. Chem. Int. Ed.* **2017**, *56*, 9512.

Further examples
(10c) Ghattas, *Chem. Commun.* **2017**, *53*, 3205.
(10d) Zhang, *RSC Adv.* **2020**, *10*, 16942.

Figure 9 Application of moisture-tolerant frustrated Lewis pairs

Conflict of Interest

The authors declare no conflict of interest.

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