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Abstract:
Direct hydrogen isotope exchange represents a distinctive strategy for deuterium labelling, where the protium is directly replaced by deuterium. In this graphic review, we summarized the progress in deuteration via transition metal catalyzed hydrogen isotope exchange. The review was organized according to the mechanism of C-H bond activation in the homogeneous catalysis, and the heterogeneous catalysis was also discussed according to the catalyst type. Representative mechanistic processes were depicted, and proven cases for tritiation were also highlighted.

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Transition Metal Catalyzed Deuteration via Hydrogen Isotope Exchange

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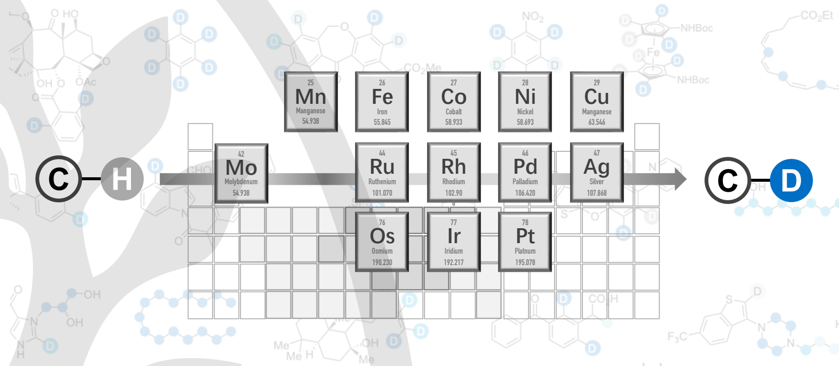

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Abstract Direct hydrogen isotope exchange represents a distinctive strategy for deuterium labelling, where the protium is directly replaced by deuterium. In this graphic review, we summarized the progress in deuteration via transition metal catalyzed hydrogen isotope exchange. The review was organized according to the mechanism of C-H bond activation in the homogeneous catalysis, and the heterogeneous catalysis was also discussed according to the catalyst type. Representative mechanistic processes were depicted, and proven cases for tritiation were also highlighted.

Key words H/D exchange, C-H activation, hydrogen-borrowing, deuterium labelling, heavy water, deuterium gas

Deuterium labelling has become an increasingly important tool in biomedical and materials science, with its successful applications in drug development,[1] biological compound imaging and tracking[2] and organic light-emitting diodes (OLEDs).[3] Their application has been accompanied by the development of synthetic strategies for efficient deuterium incorporation, such as conventional chemical transformation by catalytic hydrogenation on unsaturated bonds, and the defunctionalization of aromatic halides.[4] Meanwhile, in contrast to the transformation of functional groups, the direct hydrogen isotope exchange (HIE) of C-H bonds had also been extensively developed since the early days of deuterium incorporation, especially under a pH-dependent manner with harsh acid or base environments, which is still employed industrially in the current production of massive deuterium compounds. Therefore, the strategy development of milder and environmentally friendly deuteration remains a necessity, especially with which is compatible with economic deuterium sources, such as heavy water or deuterium gas.

Accompanied with the in-depth understanding of the characteristic of C-H activation with transition metals,[5] scattered cases of transition metal facilitated HIE have been used as a chemical tool to check the reversibility of the unit reaction. Thus, benefiting from the mechanistic investigation, catalytic HIE was enabled based on reversible manipulation of established catalytic systems.[6] For instance, Crabtree's catalyst designed for hydrogenation was found to facilitate dehydrogenation under low H_2 pressure.[7a] This finding was further developed as a major genre of HIE process based on reversible oxidative addition, catalyzed by a family of iridium catalysts such as Kerr's catalysts,[8-9] with D_2 gas as main source of deuterium. Similar HIE processes had also been employed with HIEs with Ir, Rh, Ru, and Pt,[10–12g,13,15] and earth-abundant metals such as Fe, Co and Ni had also shown promising reactivities.[12f-h,14] On the other hand, the recently burgeoning strategy of concerted metalation-deprotonation (CMD) was also converted in a reversible manner,[16-22] which employing D_2O or deuterated acids as deuterium source. Despite the CMD's challenge of subsequent route control between functionalization and C-D bond reconstruction, *ortho*- or *meta*-selective, as well as undirected deuteration had been developed mainly based Pd-catalysis,[20-22] where Mn,[21a] Co,[18d] Ni,[18f] and Ag[19] had also shown their HIE activity recently. Moreover, HIE could also be accomplished through scheme of hydrogen borrowing strategy by exploiting the remarkable kinetic isotope effect of deuterium.[23-24] Its reversible process had also been utilized in HIE on olefins.[25] Additionally, some other specialized strategies had also been reported, including Lewis acid enhanced local acidity of proton,[26] η^6 complex facilitated arenes activation,[27] and σ-metathesis enabled H/D exchange between metal and D_2.[28] On the other hand, heterogeneous catalysts also compromise a large family for HIE based on a similar strategy of reversibility control under low D_2 pressure,[31-37] where recent findings suggest that the nanoparticle collides,[38-39] and corresponding ligand-loaded nanoparticles[40] may also achieve astonishing regioselectivity as their homogeneous alternatives. Noticeably, in most cases, the tritiation could be easily achieved by replacing the deuterium sources with the corresponding tritium sources. We hope that this graphical review will stimulate further research on the development of innovative HIE strategies in this rapid evolving field.

Biosketches

	**Dr. Zhi-Jiang Jiang** was born in 1990 in Ningbo, China. He obtained his B. Sc. in pharmaceutical science at Zhejiang University of Technology. He completed his Ph.D. under the supervision of Prof. Wei-Ke Su and Prof. Alexandre. V. Dushkin at Collaborative Innovation Center of Yangtze River Delta Region Green Pharmaceuticals, where he explored the phenomenon of liquid-assisted grinding in mechanochemistry. He joined the school of biological and chemical engineering of NingboTech University as assistant professor in 2019. Currently, his research interests focused on the development of tools and strategies for selective deuterium-labelling.
	**Dr. Jian-Fei Bai** graduated from Lanzhou University in 2007 and received his Ph.D. from the University of Chinese Academy of Sciences in 2012 under the supervision of Professor Lixin Wang. In the same year, he joined the group of Professor P. Vogel as a postdoctoral researcher at the Swiss Federal Institute of Technology in Lausanne (EPFL). He continued his postdoctoral work at Kyoto University in 2015, working with Professor Keiji Maruoka. In 2019, Dr. Bai was appointed as an associate professor at the Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, before moving to NingboTech University in 2021. His research focuses on the development and application of site-specific synthesis of deuterium-labeled compounds.
	**Dr. Zhanghua Gao** obtained his Ph.D. (2005) under the supervision of Prof. Wei-Dong Z. Li from Lanzhou University. He joined the group of Prof. Philip J. Kocienski FRS at University of Leeds (2006) as a postdoctoral associate, continuing the research in natural product synthesis. After a one-year stay in chemical industry, he joined the University of Oxford (2010), working with Prof. Véronique Gouverneur FRS and Prof. Benjamin G. Davis FRS on fluorine-18 radiolabelling of amino acids and protein. He moved to Ningbo University (2015) as an associated professor and became a full professor in 2016 at NingboTech University. His research interests include isotope labelling methodology/technology and its application in drug discovery and functional materials.

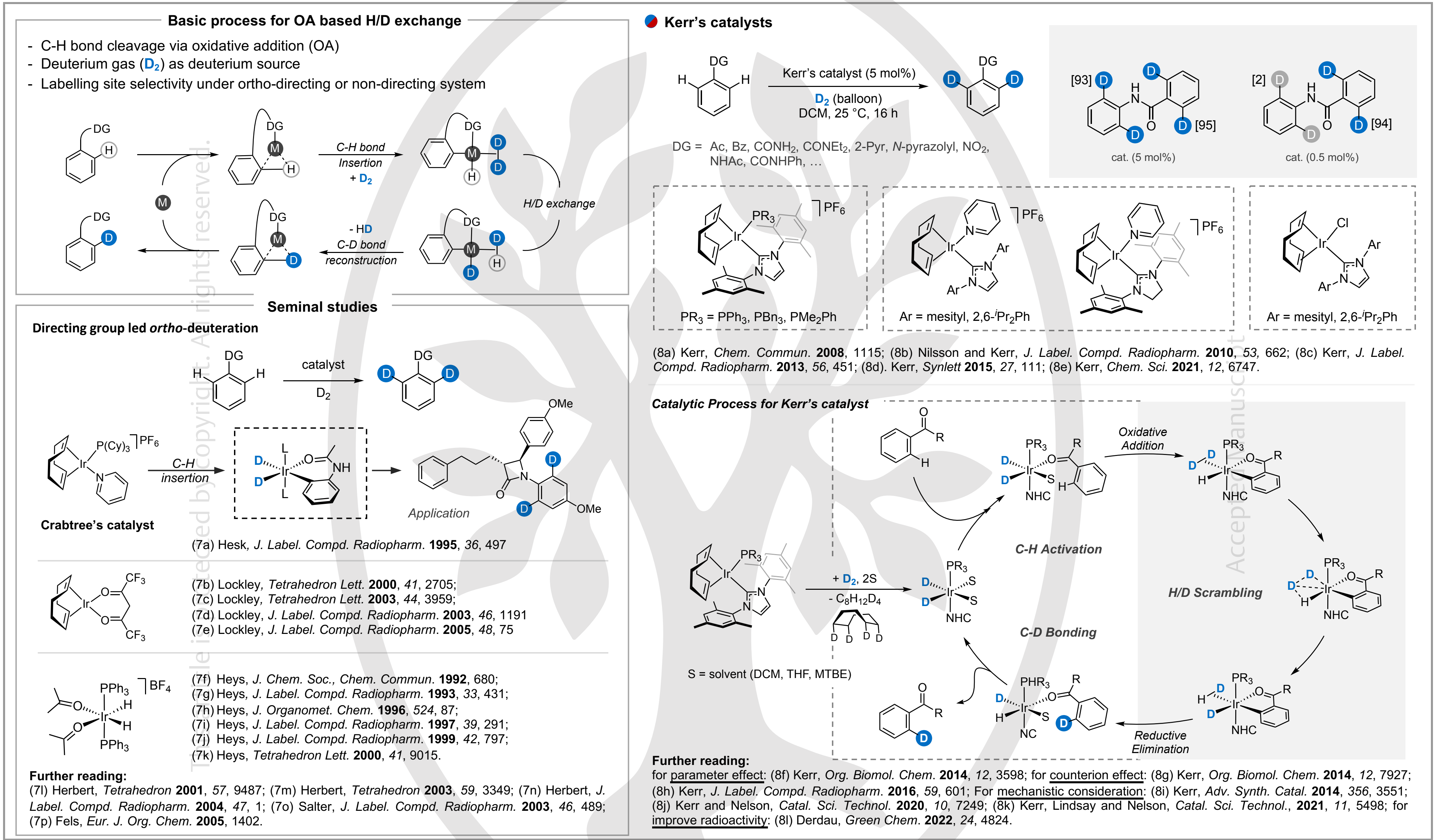


Figure 1 HIE based on oxidative addition with directing group (1): Early attempts of iridium catalysts,[7a-p] and Kerr's iridium catalysts.[8a-k]

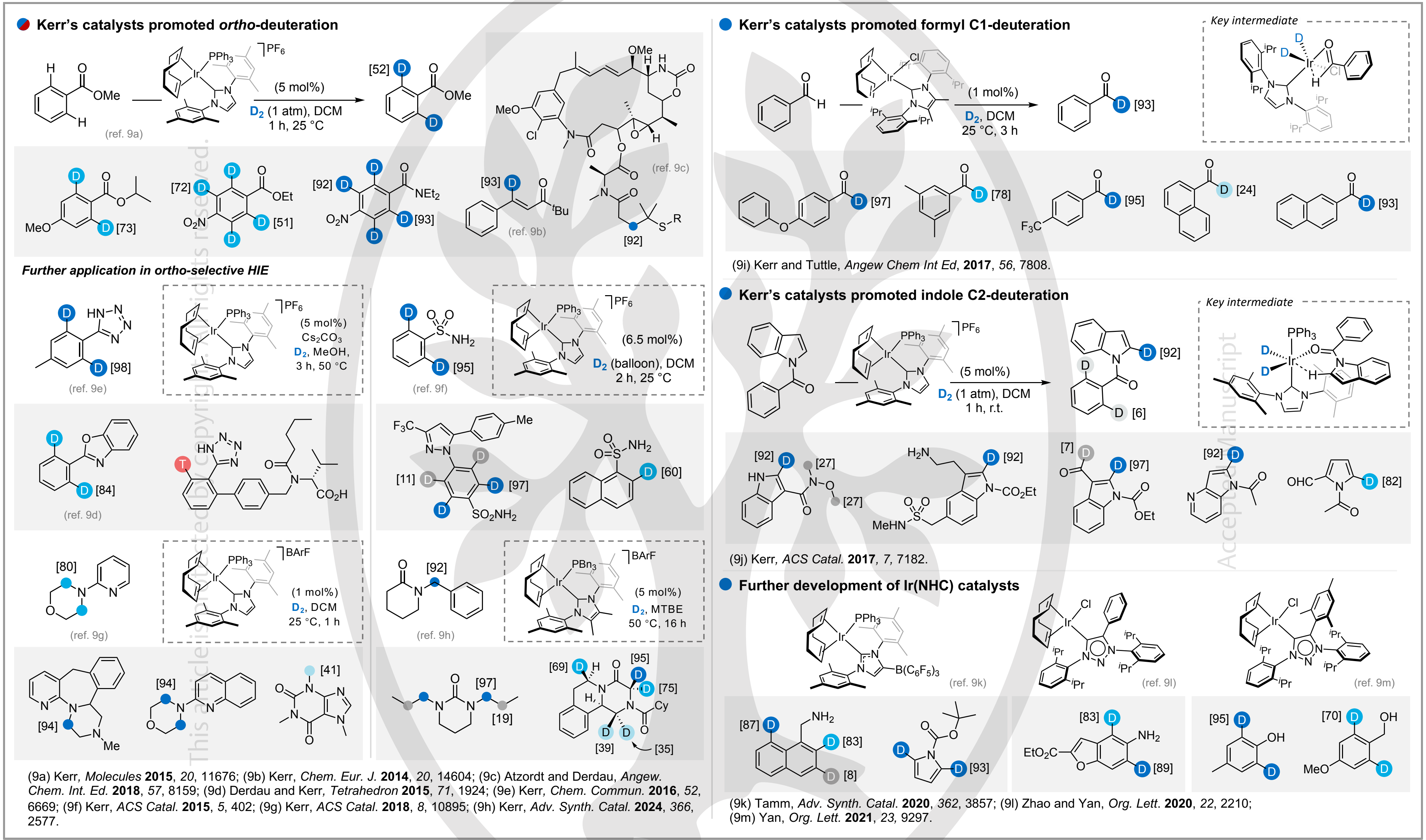


Figure 2 HIE based on oxidative addition with directing group (2): Application of Kerr's iridium catalysts.[9a-m]

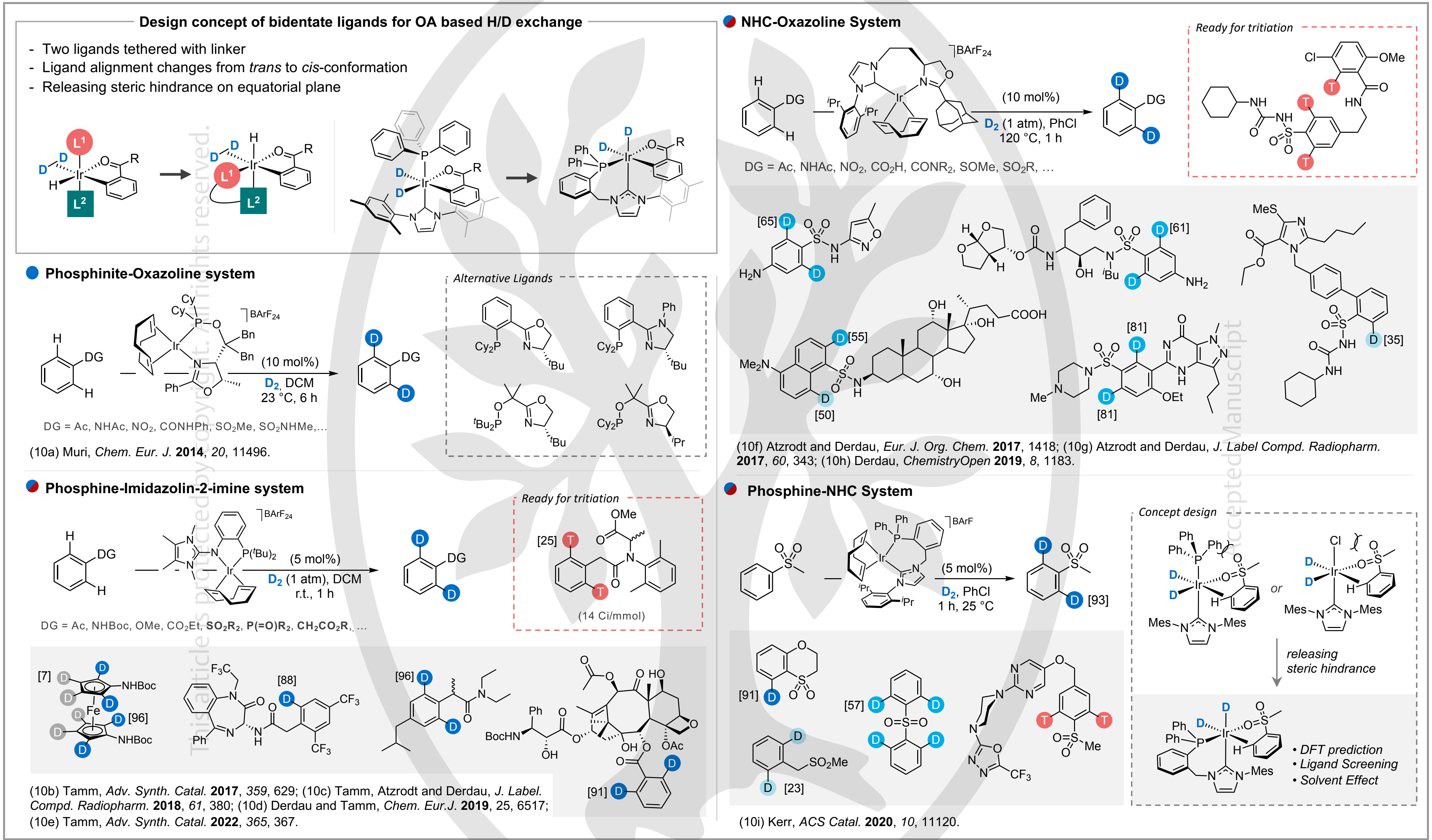


Figure 3 HIE based on oxidative addition with directing group (3): Iridium catalysts with bidentate ligands.[10a-i]

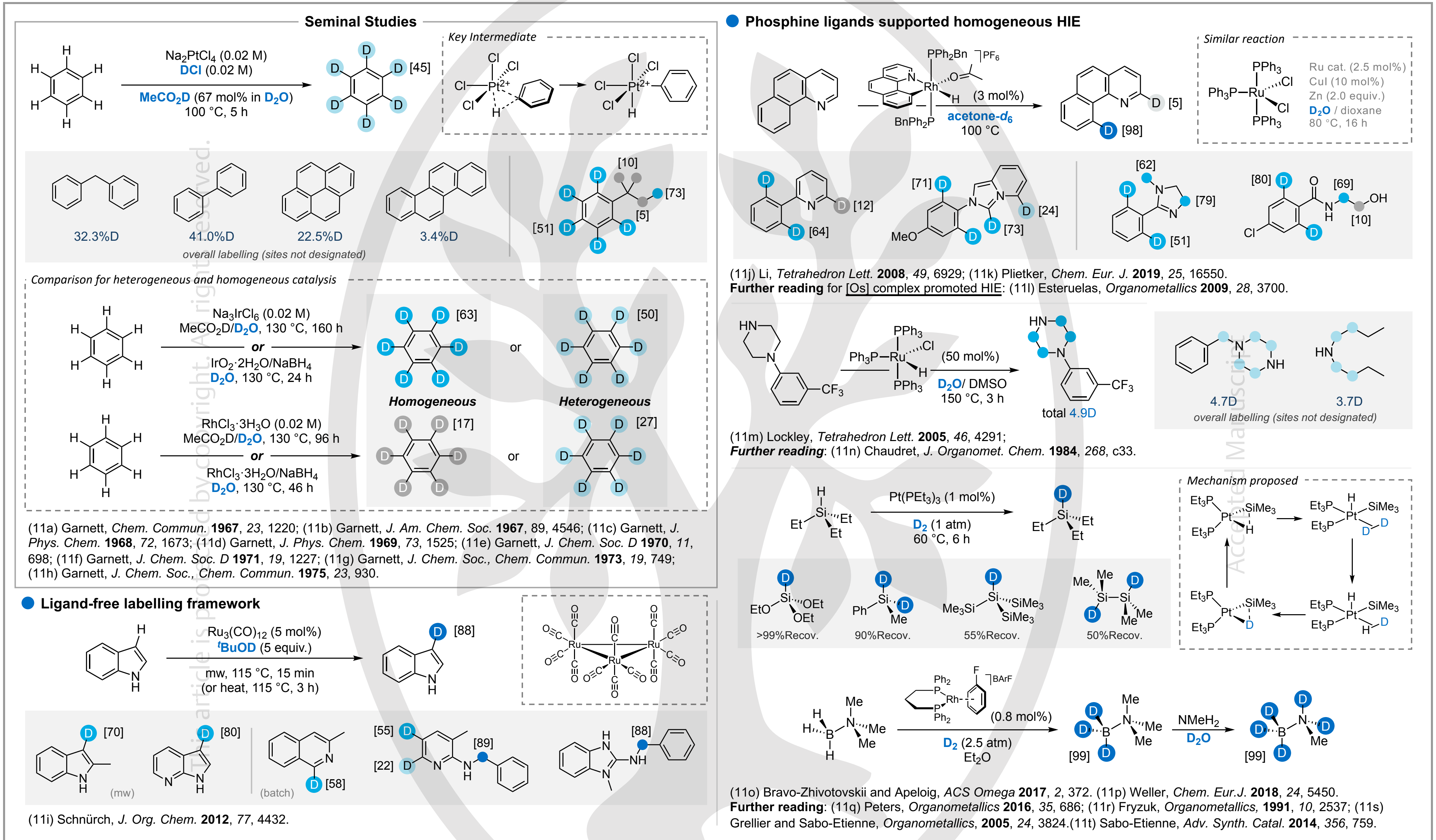


Figure 4 HIE based on oxidative addition without directing group (1): phosphine ligands supported metal catalysts.[11]

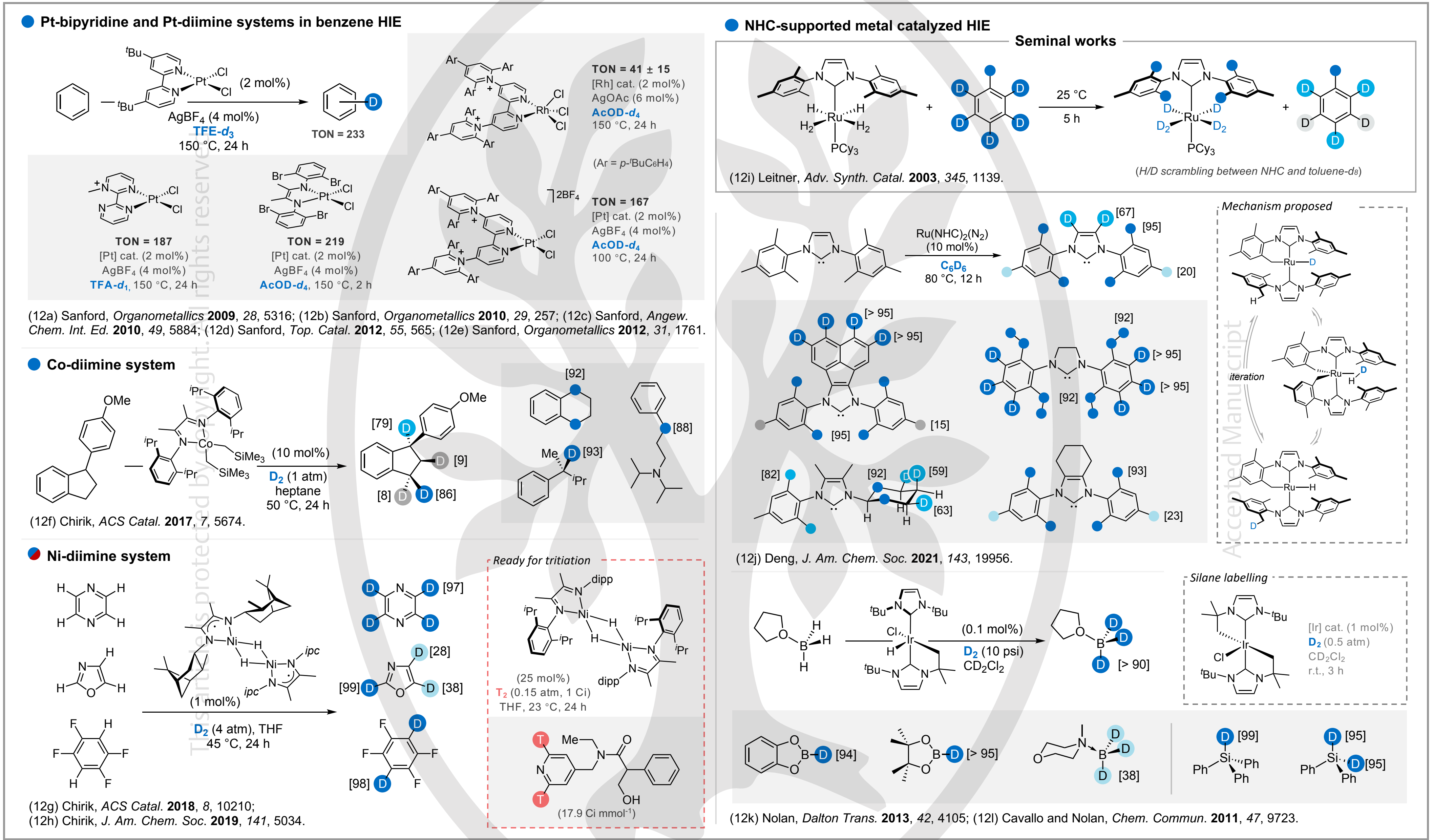


Figure 5 HIE based on oxidative addition without directing group (2): Bipyridine, imine, NHC ligands supported metal catalysts [12a-k]

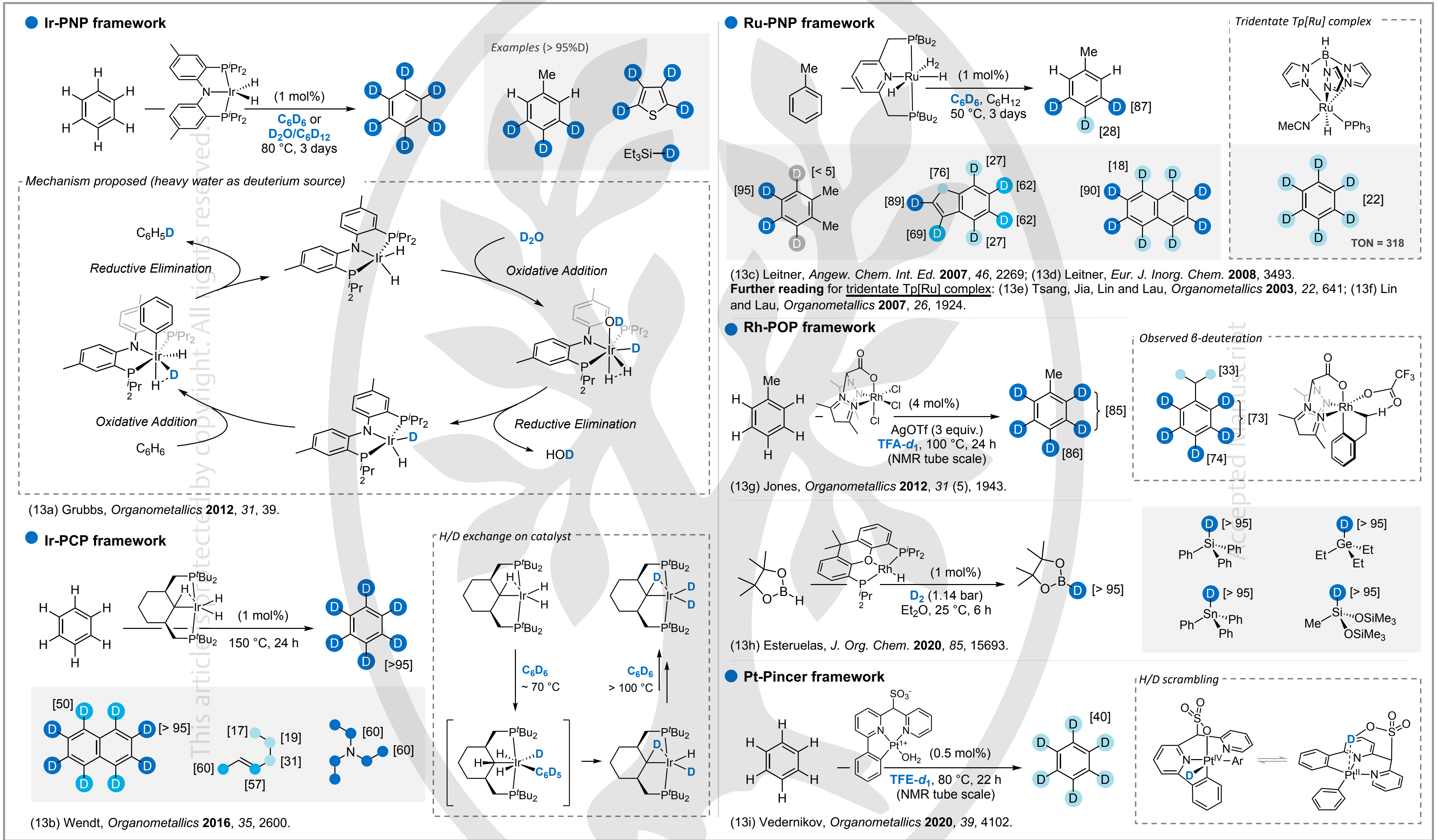


Figure 6 HIE based on oxidative addition without directing group (3): Tridentate ligands supported noble metal catalysts.[13a-i]

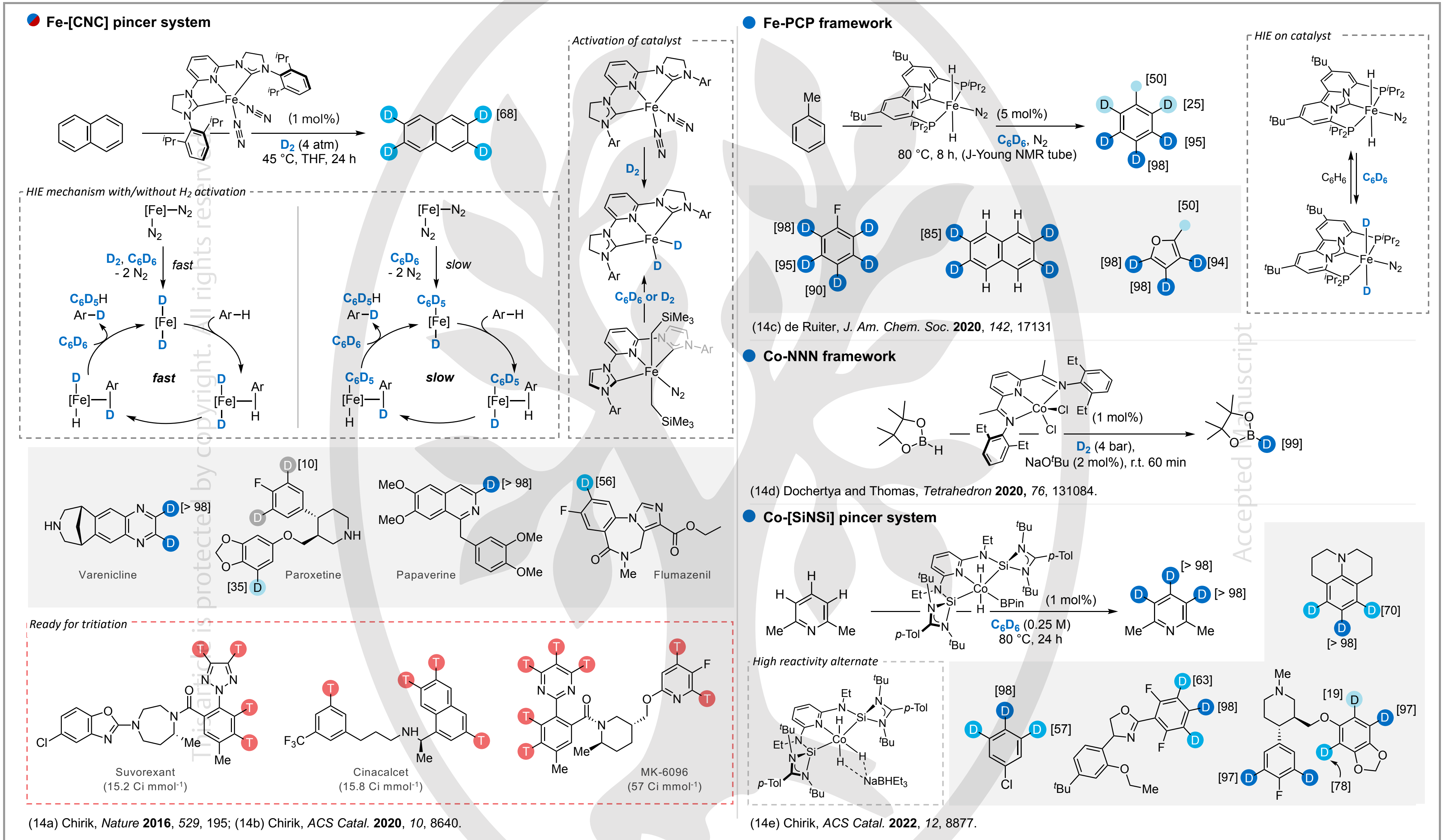


Figure 7 HIE based on oxidative addition without directing group (4): Tridentate ligands supported earth-abundant metal catalysts.[14a-e]

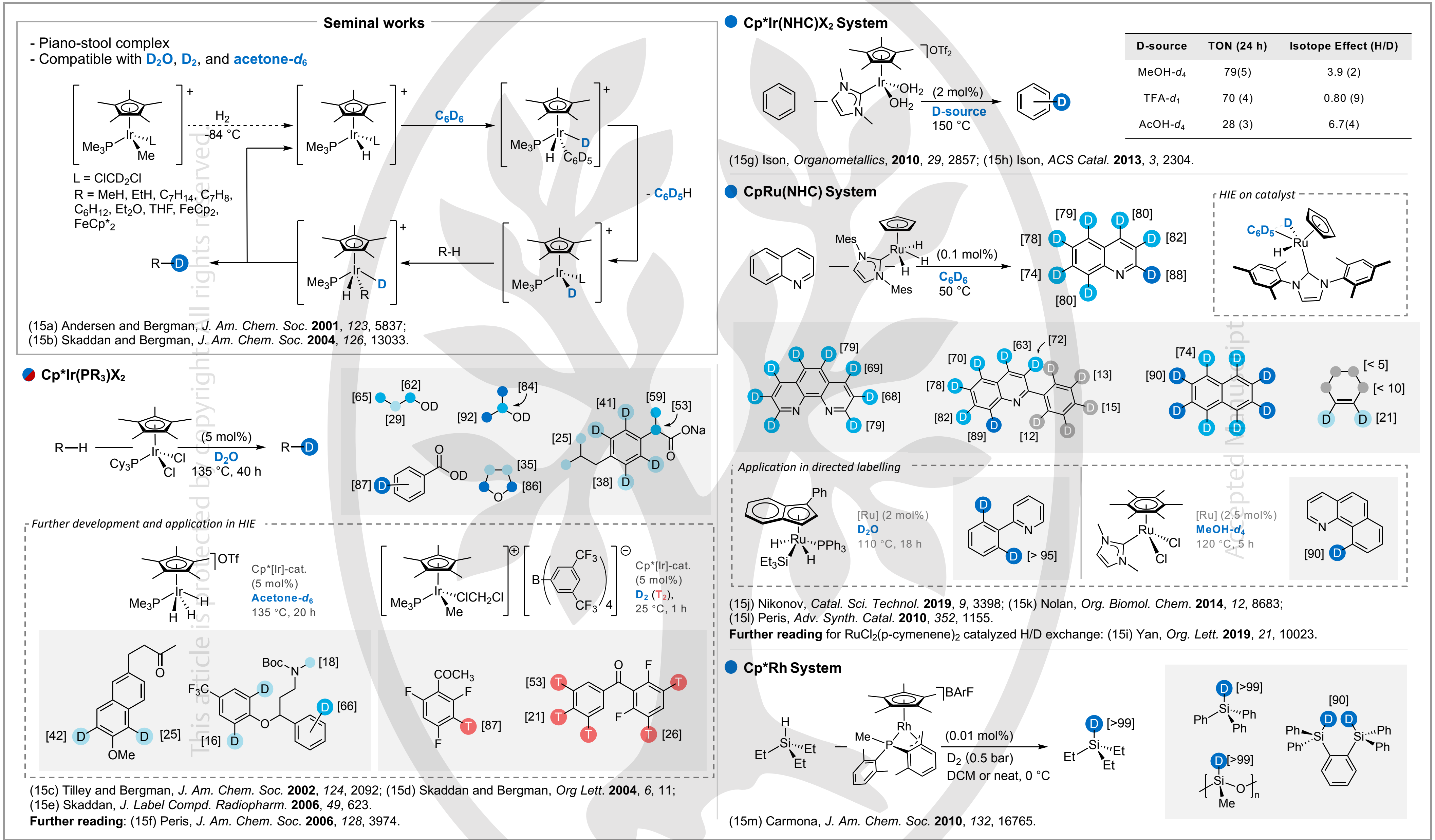


Figure 8 HIE based on oxidative addition without directing group (5): Half-sandwich type metal catalysts [15a-m]

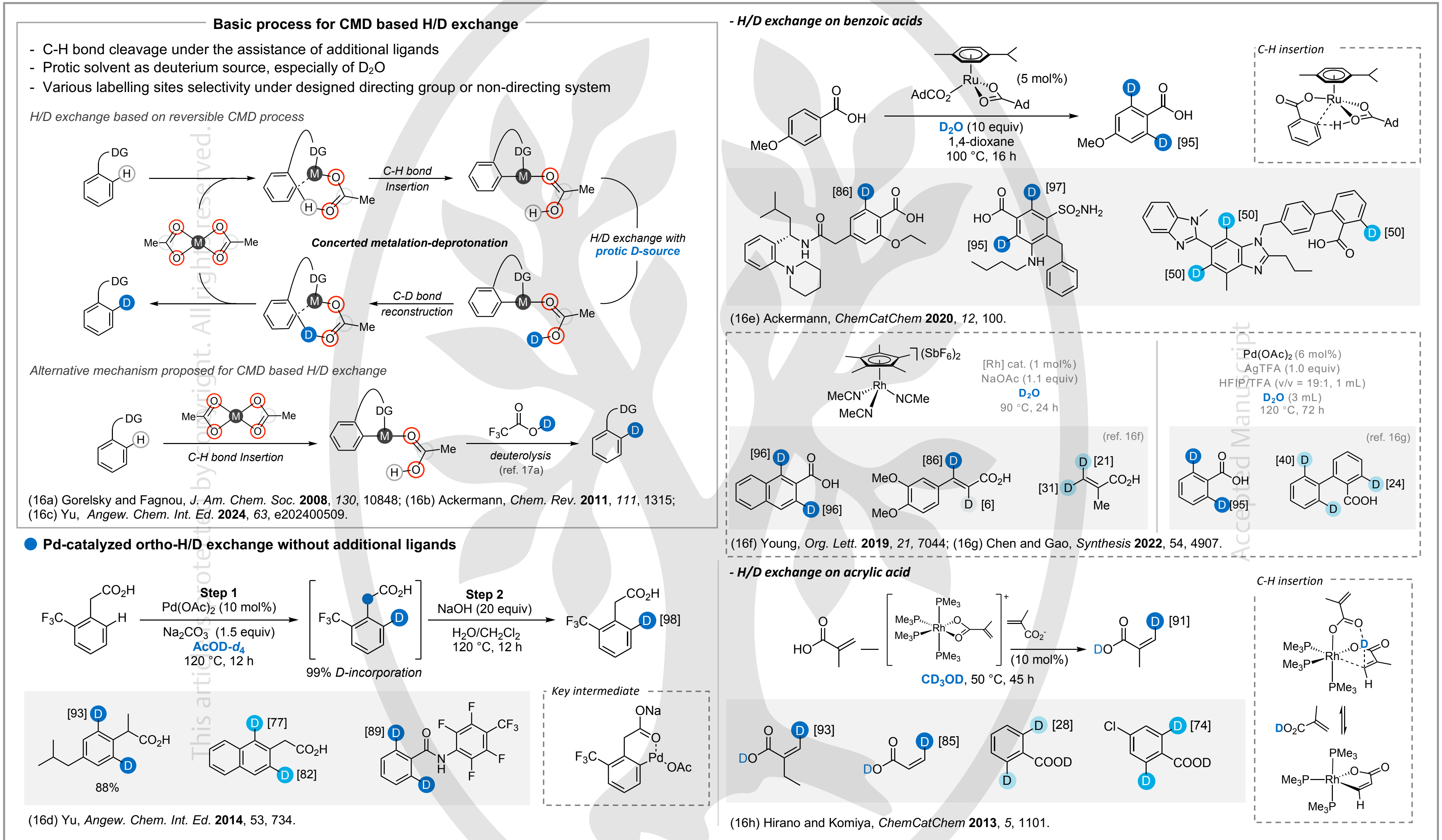


Figure 9 HIE based on concerted metalation-deprotonation (1): Directing group enabled *ortho*-selective deuteration.[16a-h]

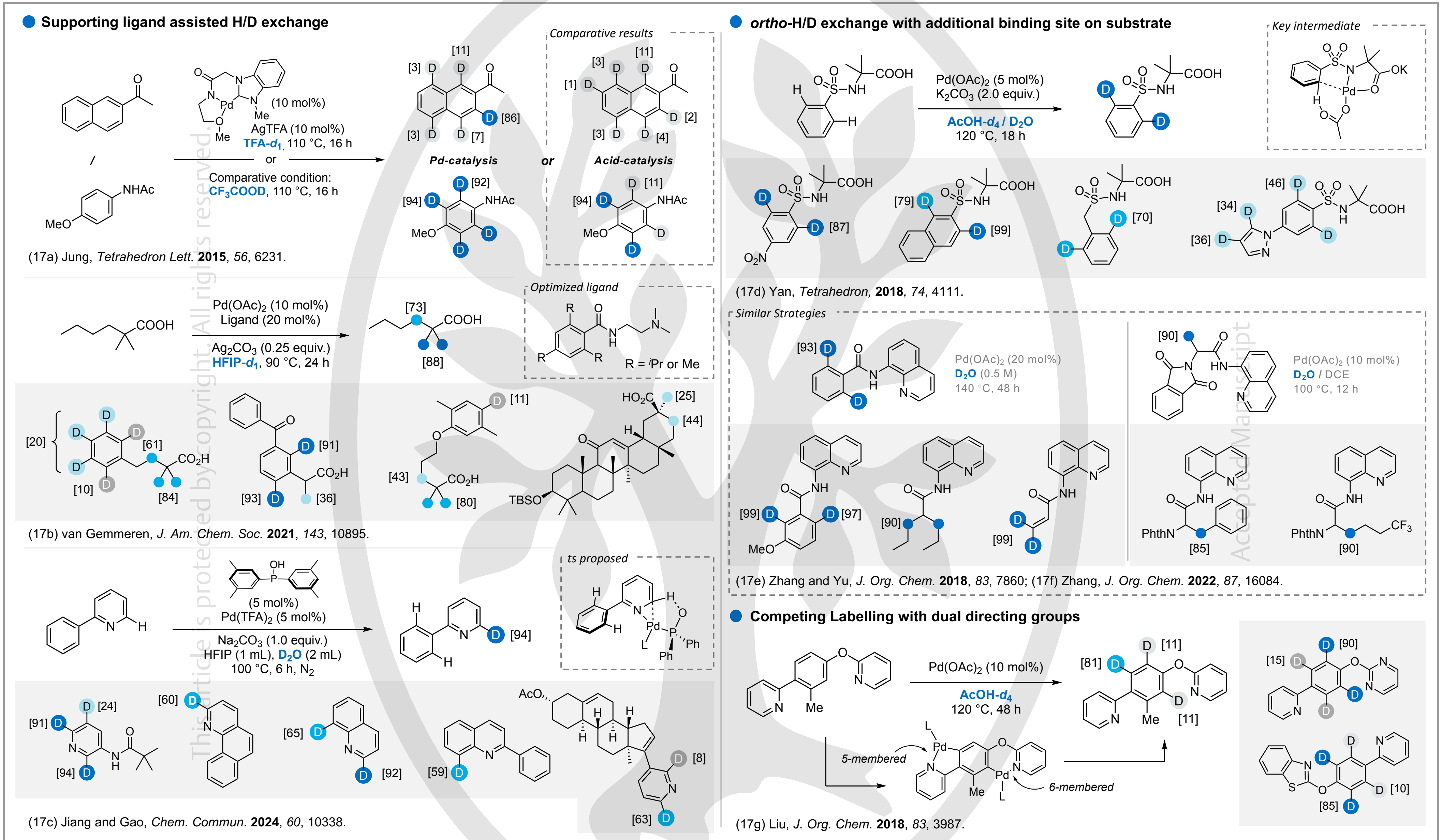


Figure 10 HIE based on concerted metalation-deprotonation (2): Supporting ligands and bidentate substrate enabled regioselective deuteration.[17a-g]

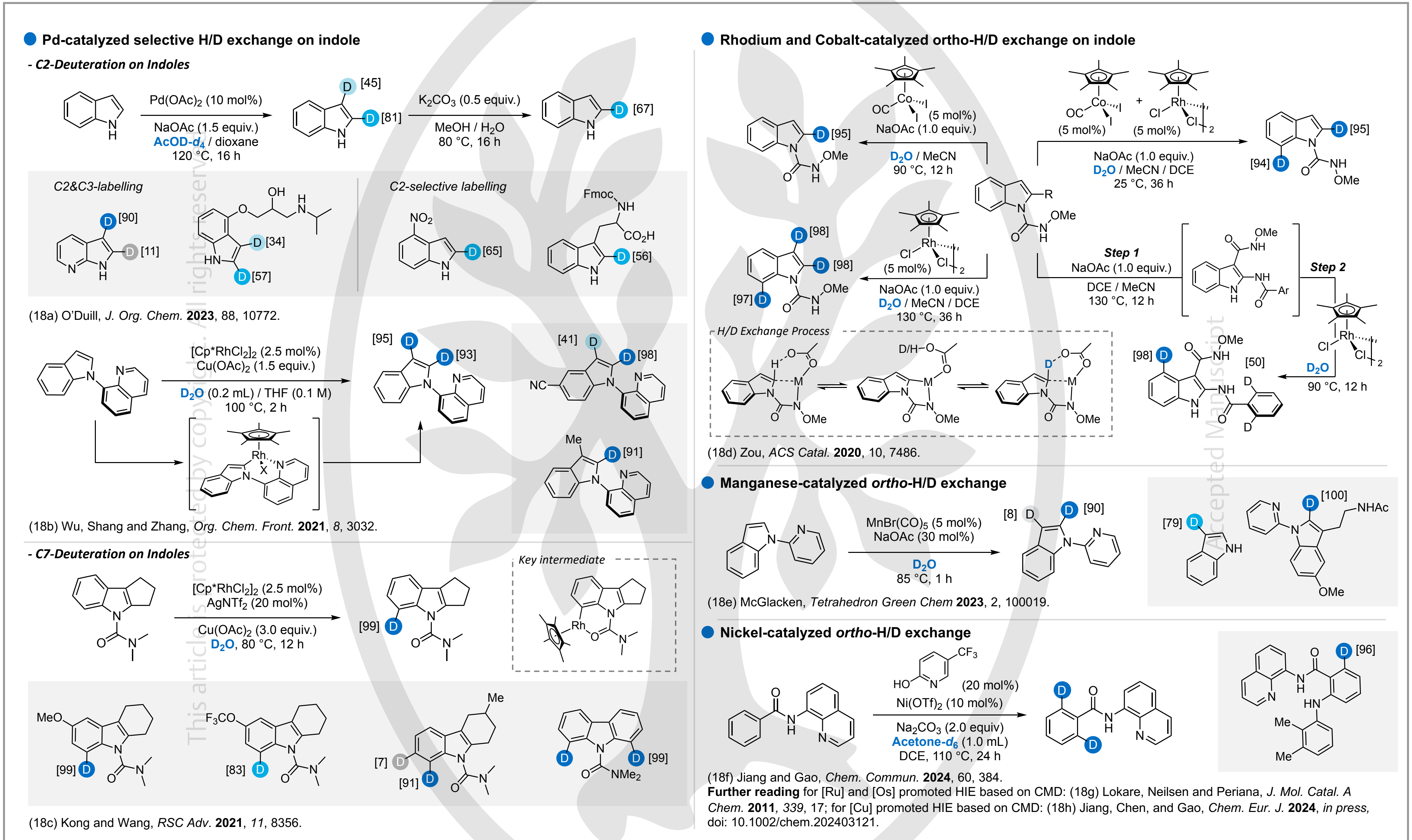
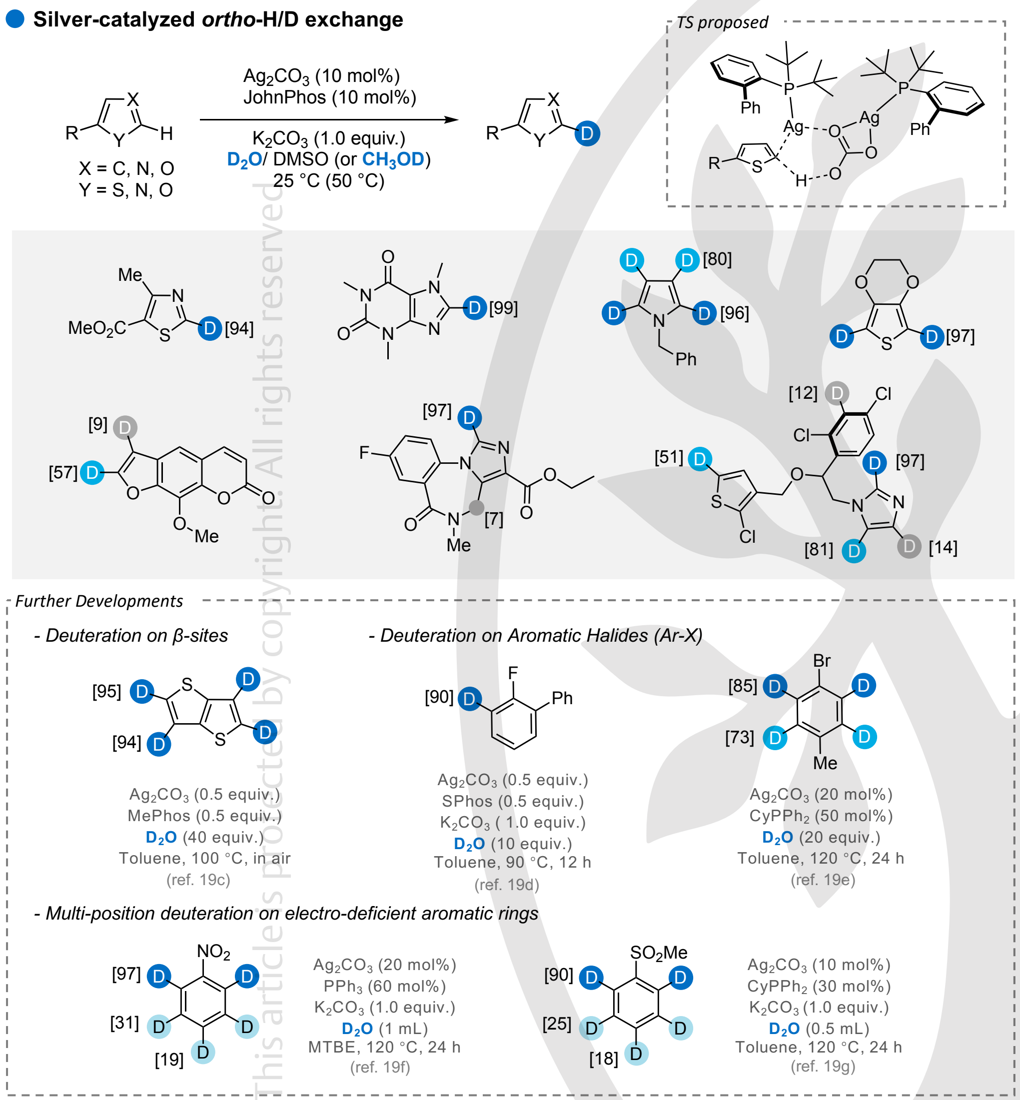
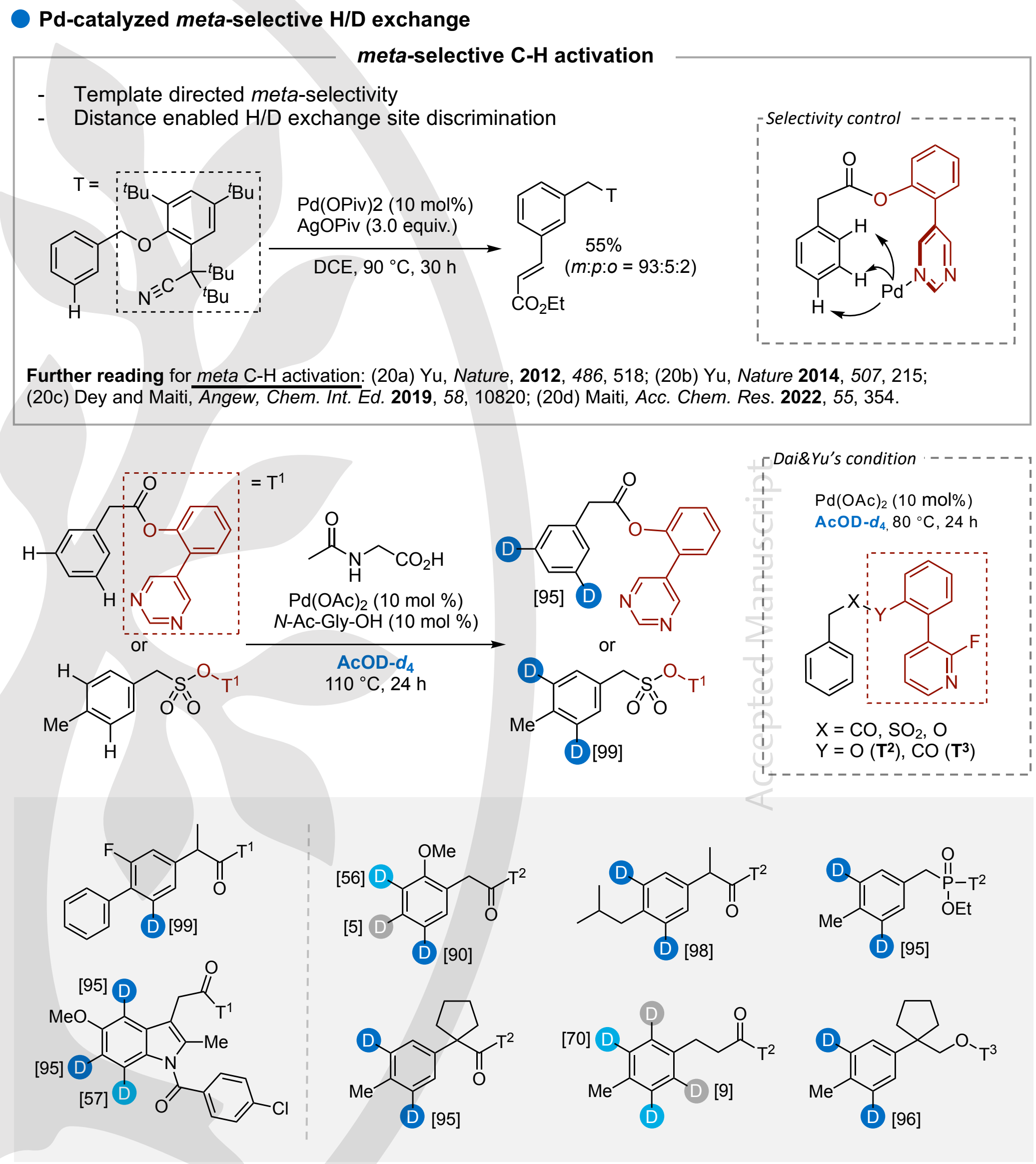


Figure 11 HIE based on concerted metalation-deprotonation (3): Regioselective deuteration on indoles, and earth abundant metal catalyzed deuteration.[18a-g]



(19a) Zhang, Zhang and Huang, *Org. Lett.* **2019**, *21*, 6745; (19b) Hartwig, *ACS Catal.* **2021**, *11*, 1119; (19c) Zhang, *Org. Biomol. Chem.* **2022**, *20*, 1176; (19d) Zhang, *Org. Biomol. Chem.* **2020**, *18*, 6627; (19e) Zhang, *Org. Lett.* **2021**, *23*, 1554; (19f) Jiang, Gao, and Gao, *J. Org. Chem.* **2023**, *88*, 1560; (19g) Jiang, Gao and Gao, *J. Org. Chem.* **2024**, *89*, 8468.



(20e) Maiti, *Chem. Eur. J.* **2019**, *25*, 9433; (20f) Dai and Yu, *Org. Lett.* **2019**, *21*, 4887.

Figure 12 HIE based on concerted metalation-deprotonation (4): Silver catalyzed deuteration,[19a-g] and *meta*-selective deuteration[20a-e]

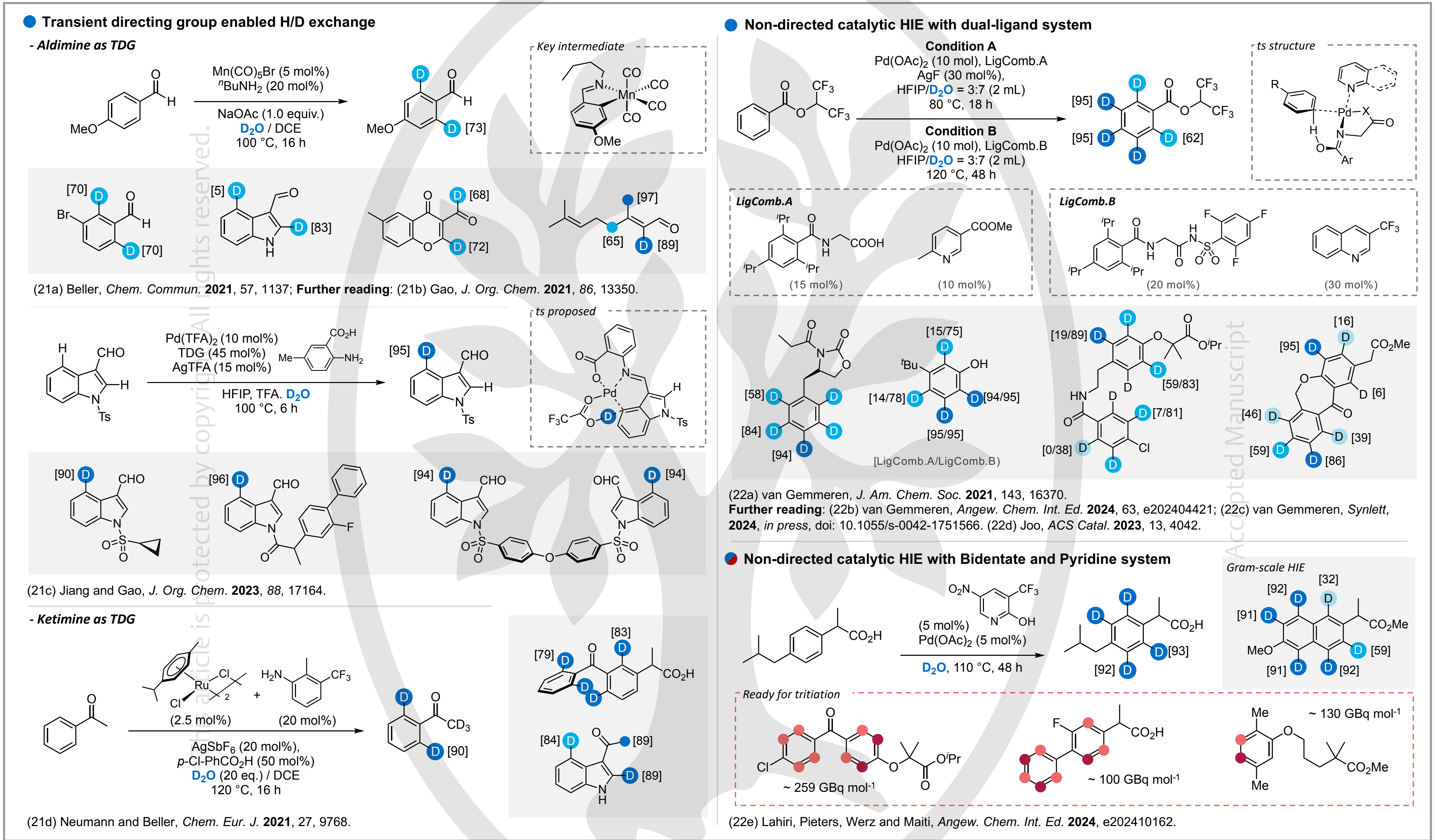


Figure 13 HIE based on concerted metalation-deprotonation (5): Application of transient-directing strategy,[21a-d] and non-directing strategy in deuteration.[22a-e]

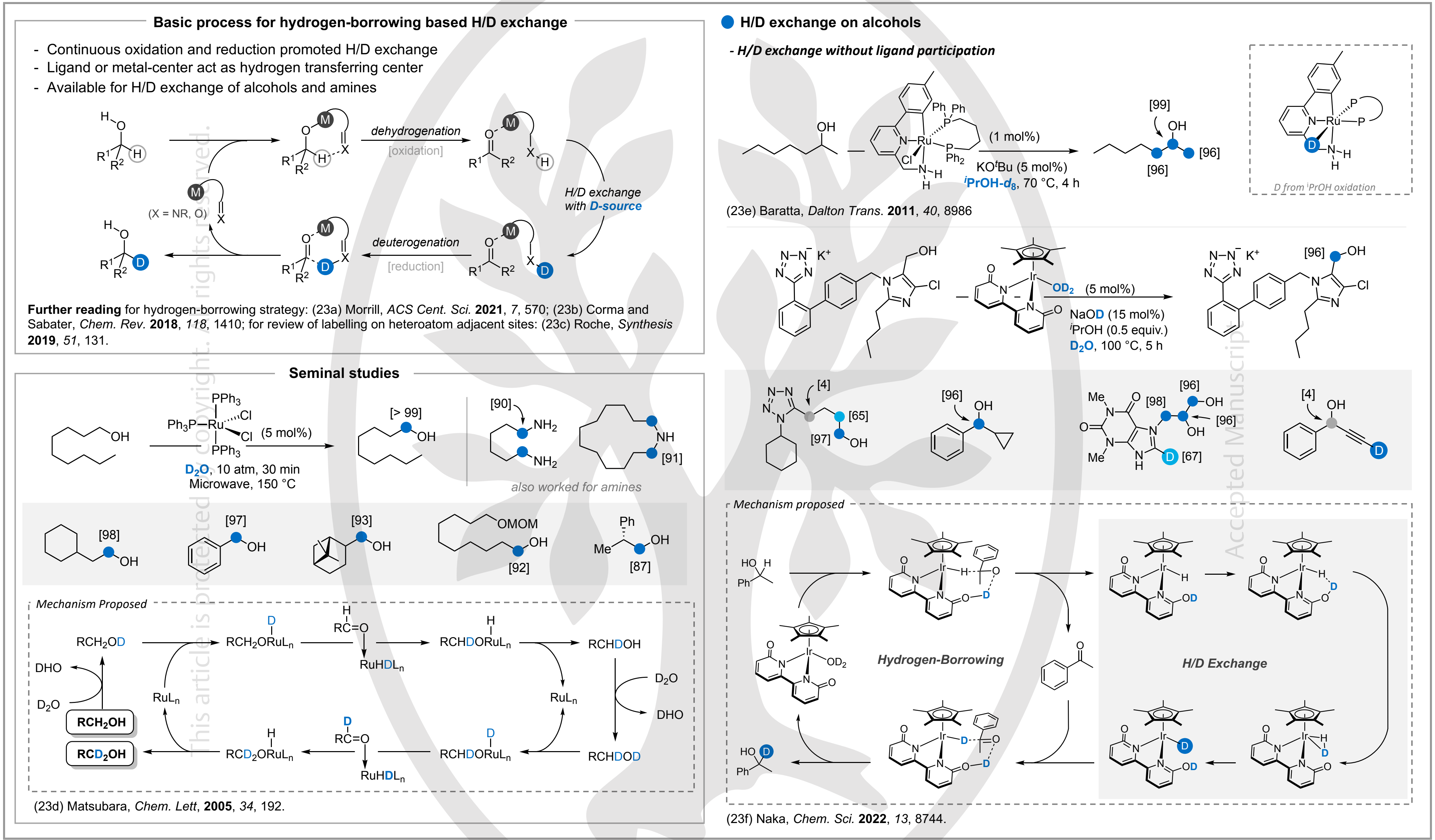


Figure 14 HIE based on hydrogen-borrowing (1): Principles, seminal work, and α-deuteration on alcohols via metal hydride intermediate.[23a-f]

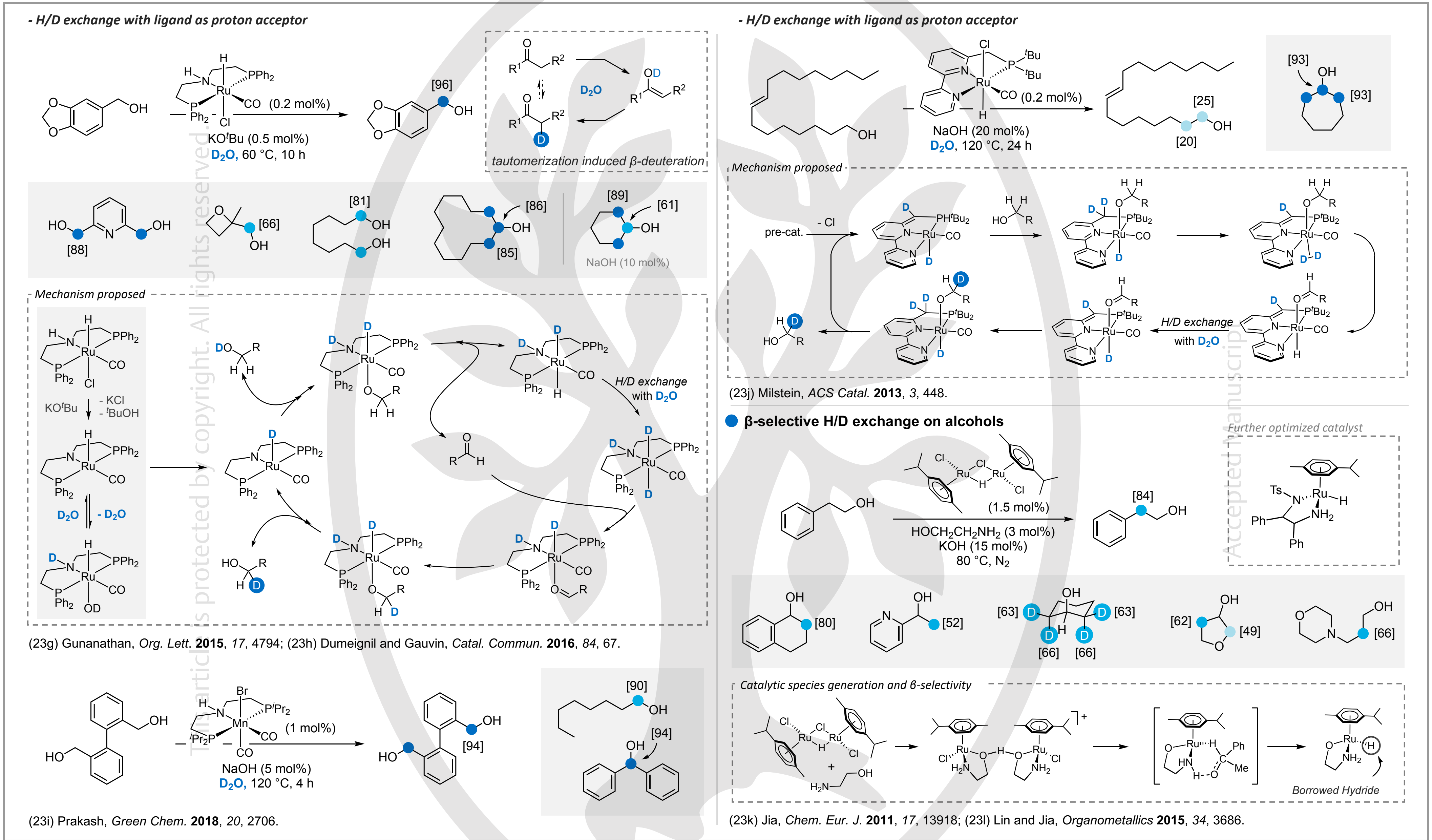


Figure 15 HIE based on hydrogen-borrowing (2): α- and β-deuteration on alcohols via ligand enabled hydride transfer.[23g-j]

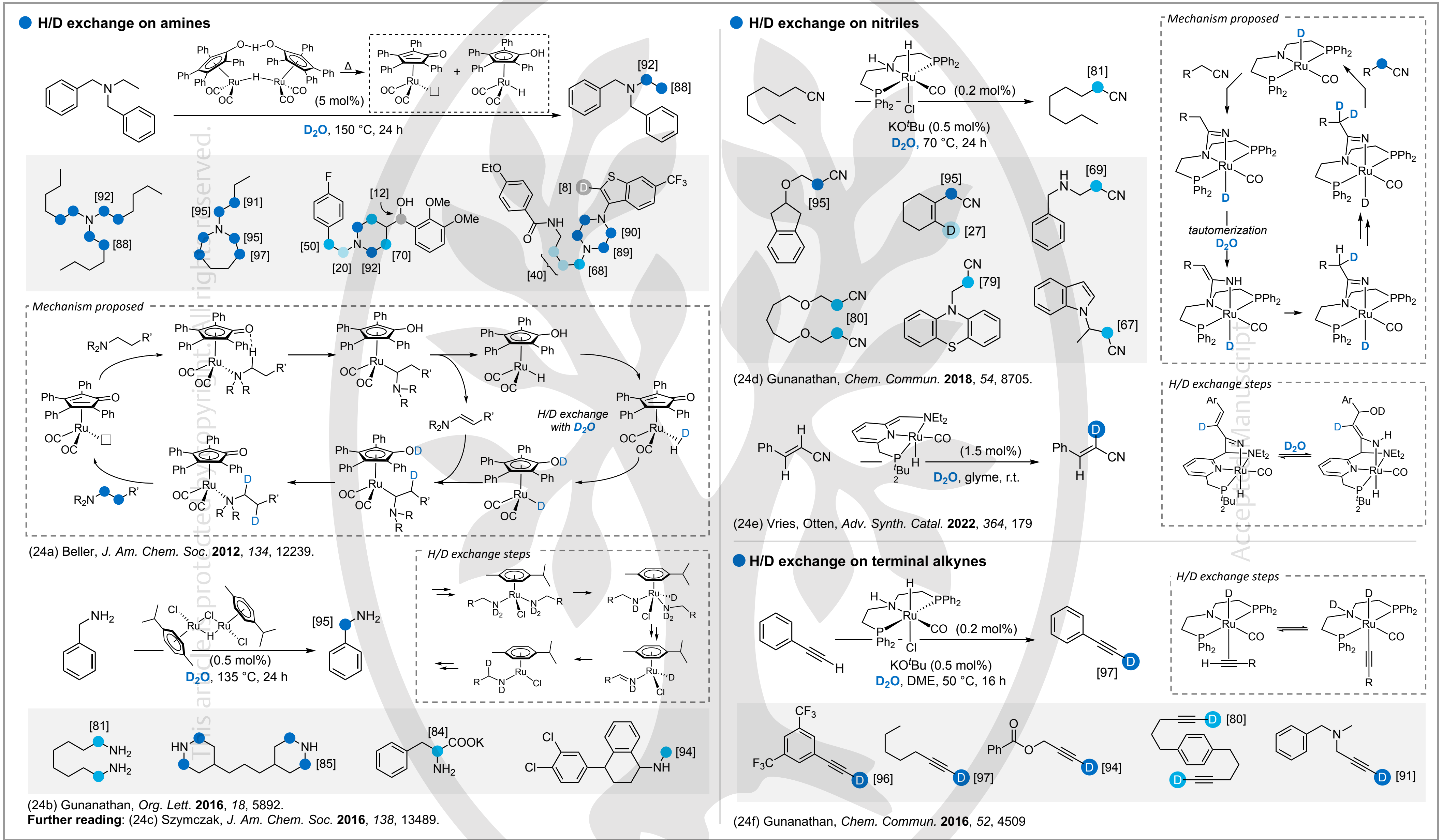


Figure 16 HIE based on hydrogen-borrowing (3): deuteration on amines, nitriles, and alkynes.[24a-f]

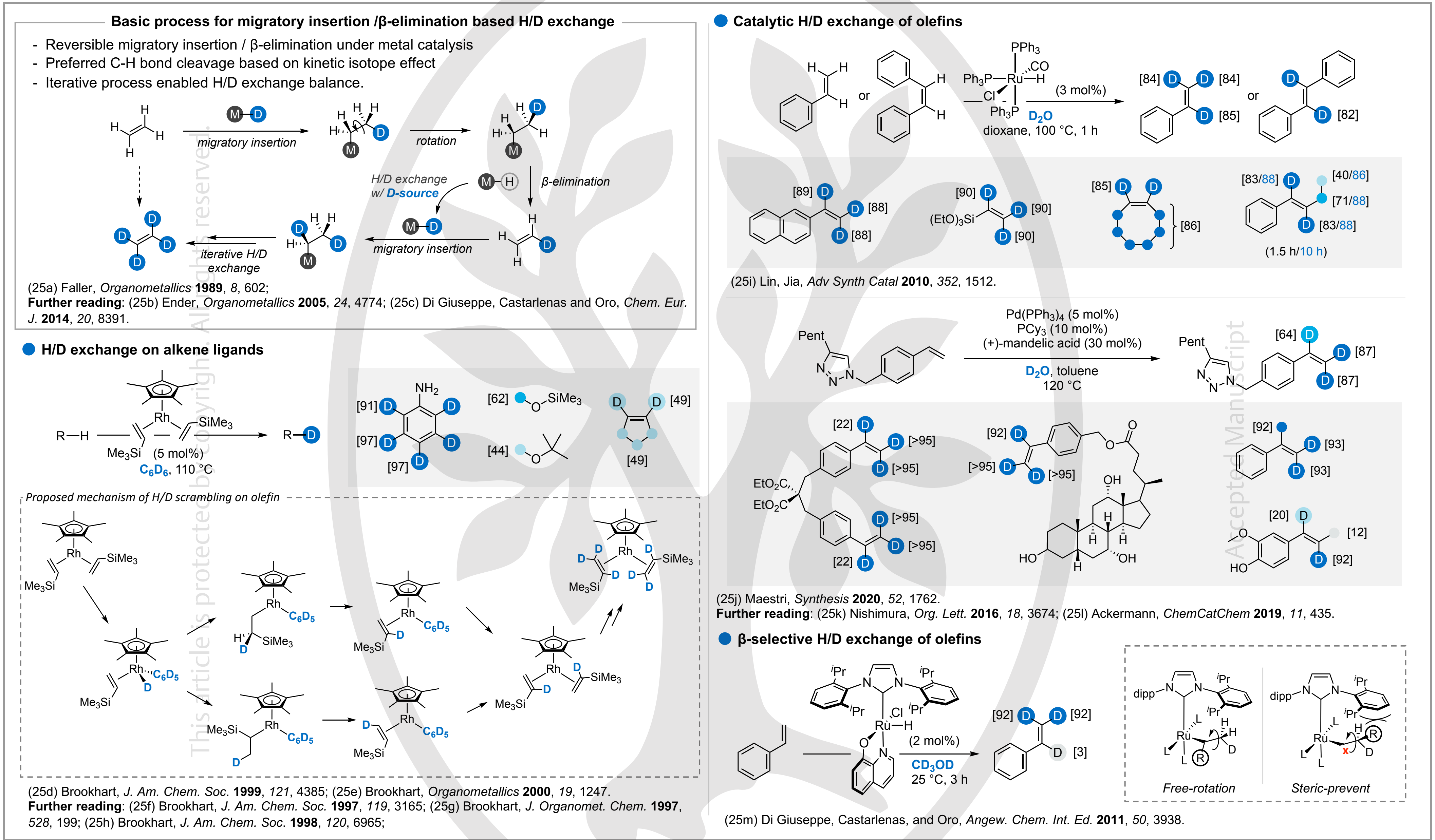


Figure 17 HIE based on iterative migratory insertion/β-elimination (1): deuteration on olefins.[25a-l]

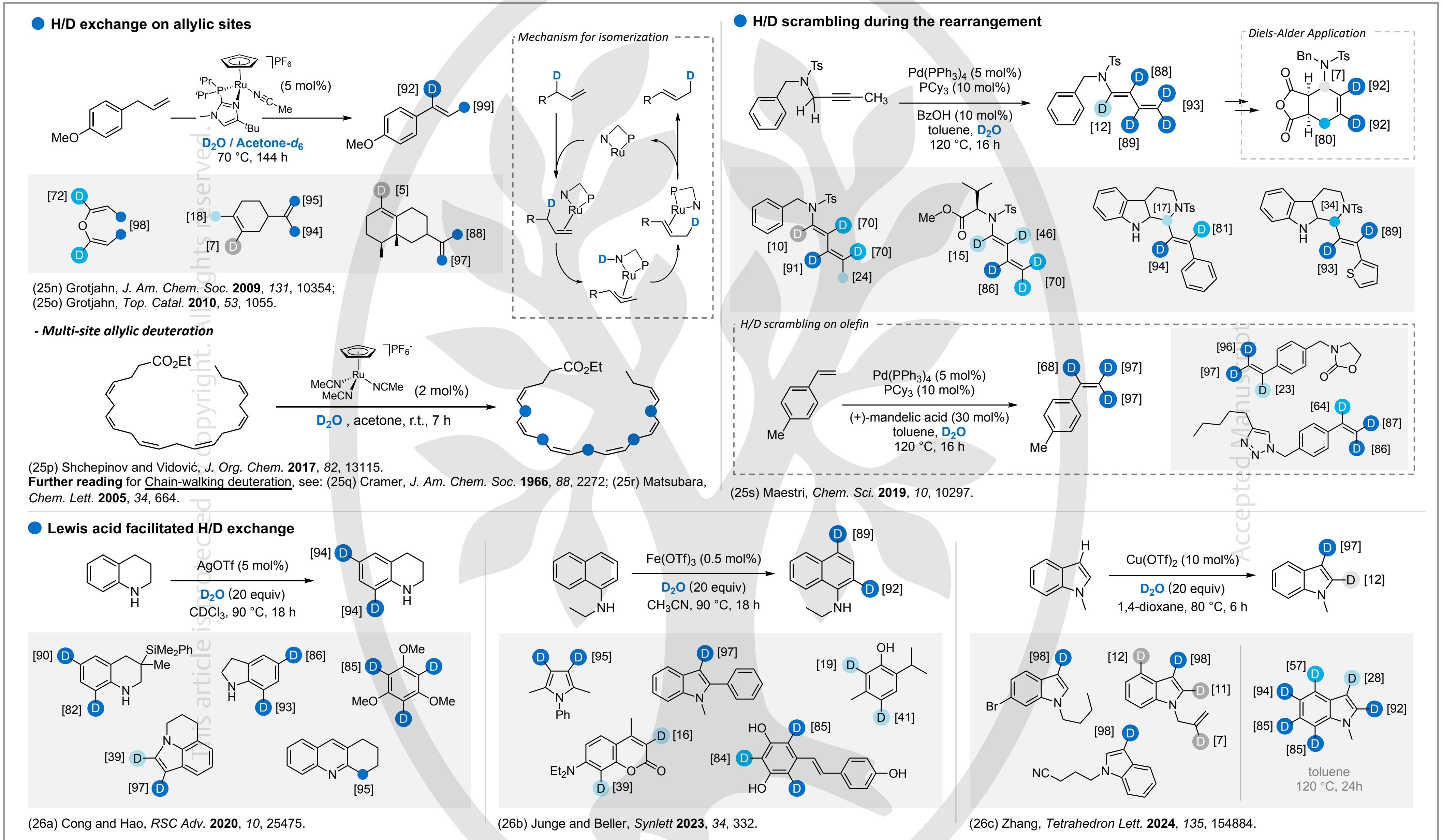


Figure 18 HIE based on iterative migratory insertion/β-elimination (2): deuteration on allyl and chain-walking deuteration.[25m-r] Miscellaneous case of homogenous HIE (1): Lewis acid catalyzed deuteration.[26a-c]

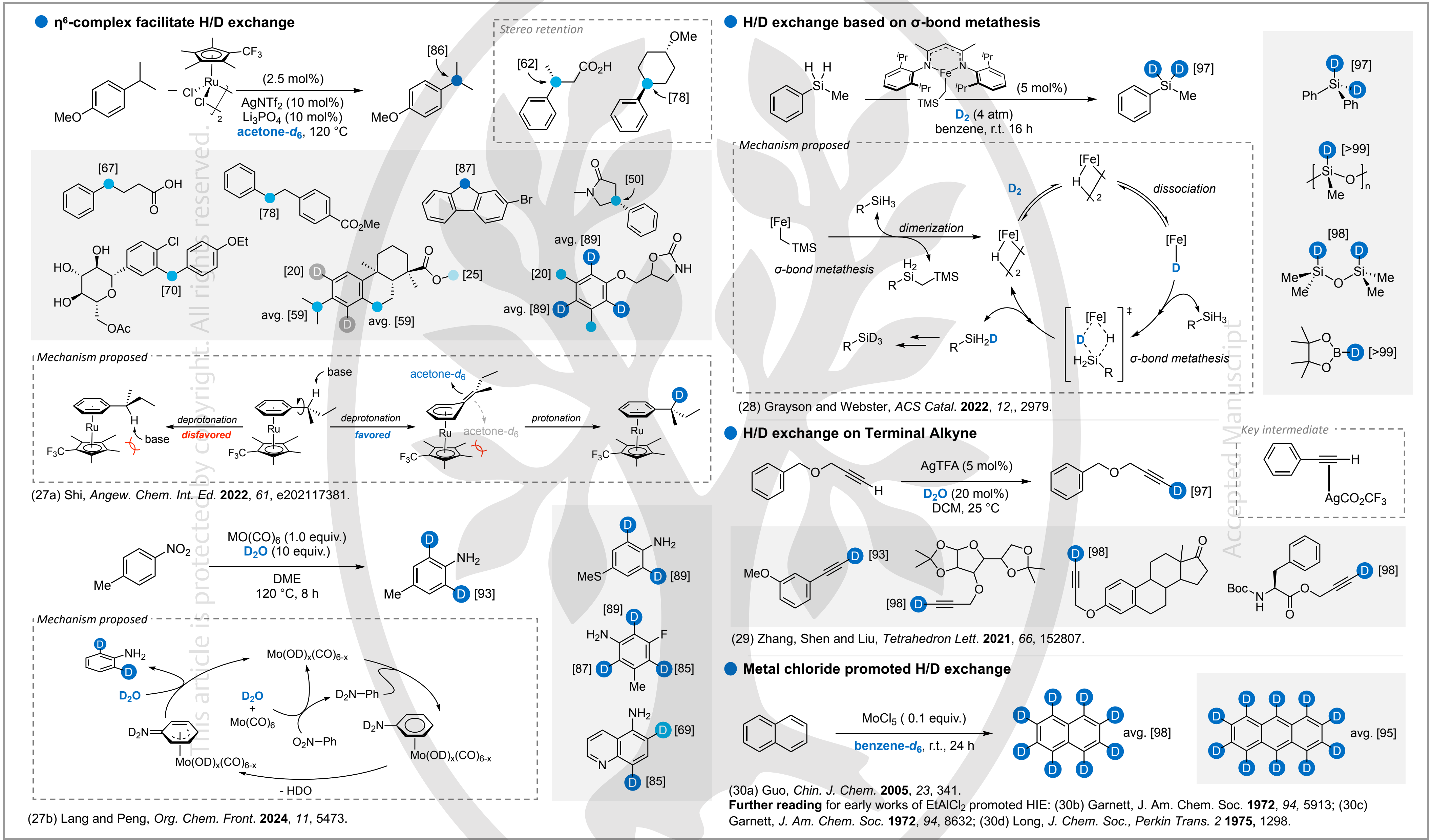


Figure 19 Miscellaneous case of homogenous HIE (2): deuteration catalyzed by η6 complex[27a-b], σ-metathesis[28], π -acid[29], and metal chloride.[30a-d]

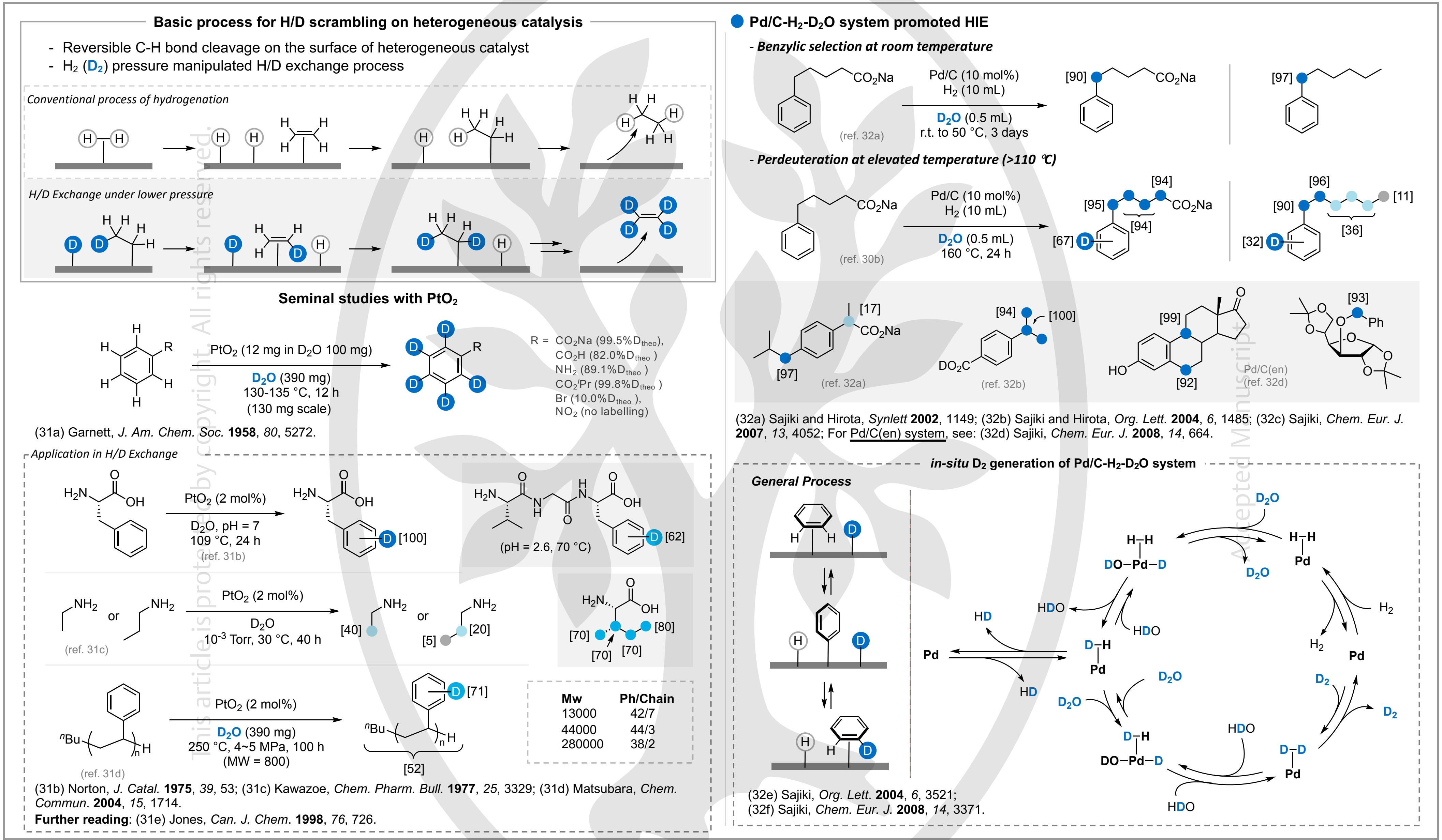


Figure 20 Heterogeneous HIE catalyzed by active carbon supported metal catalyst (1): seminal works of PtO_2,[31a-e] and Pd/C-H_2-D_2O system (1).[32a-f]

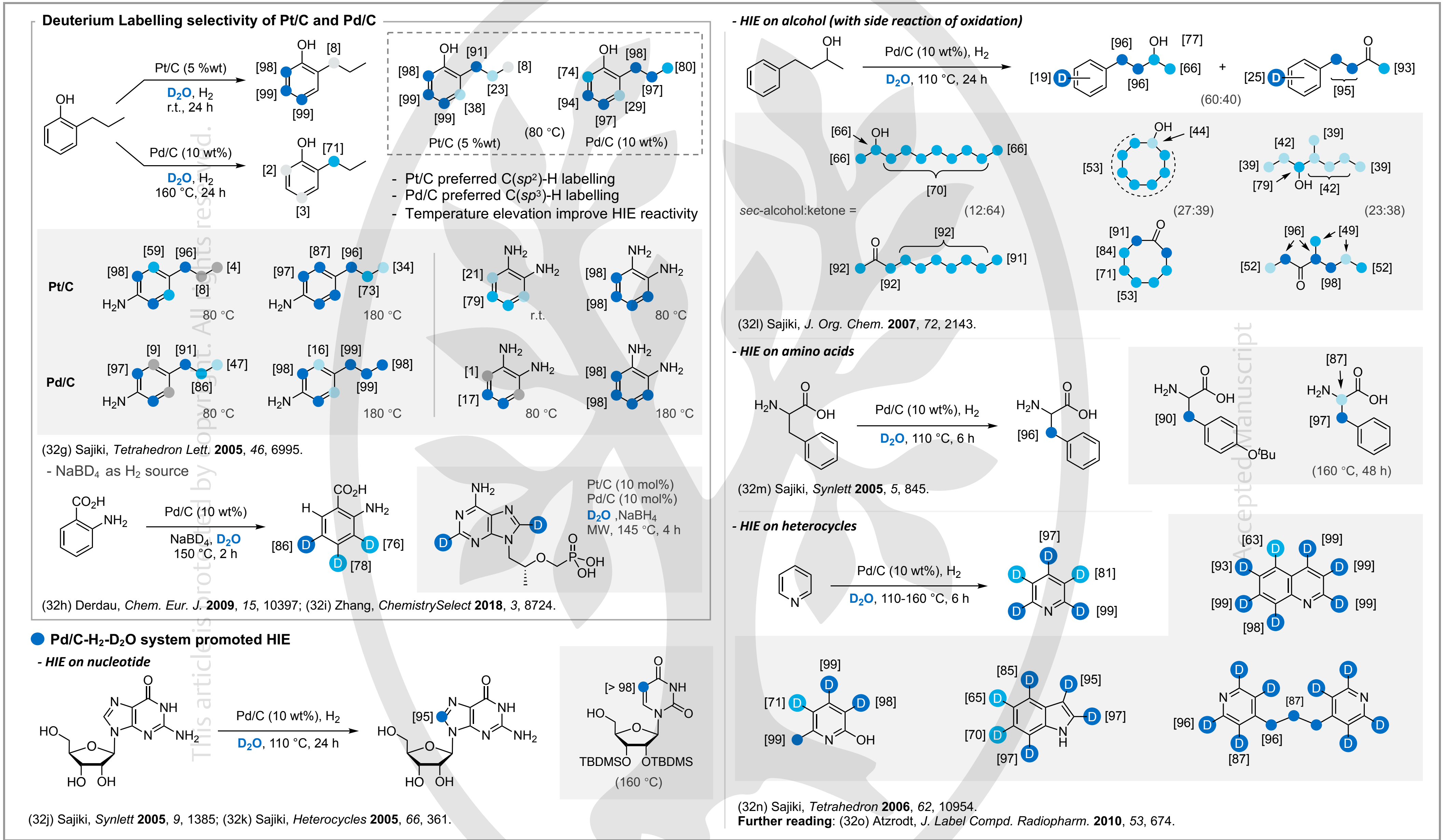


Figure 21 Heterogeneous HIE catalyzed by active carbon supported metal catalyst (2): Pd/C-H_2-D_2O System(2).[32g-o]

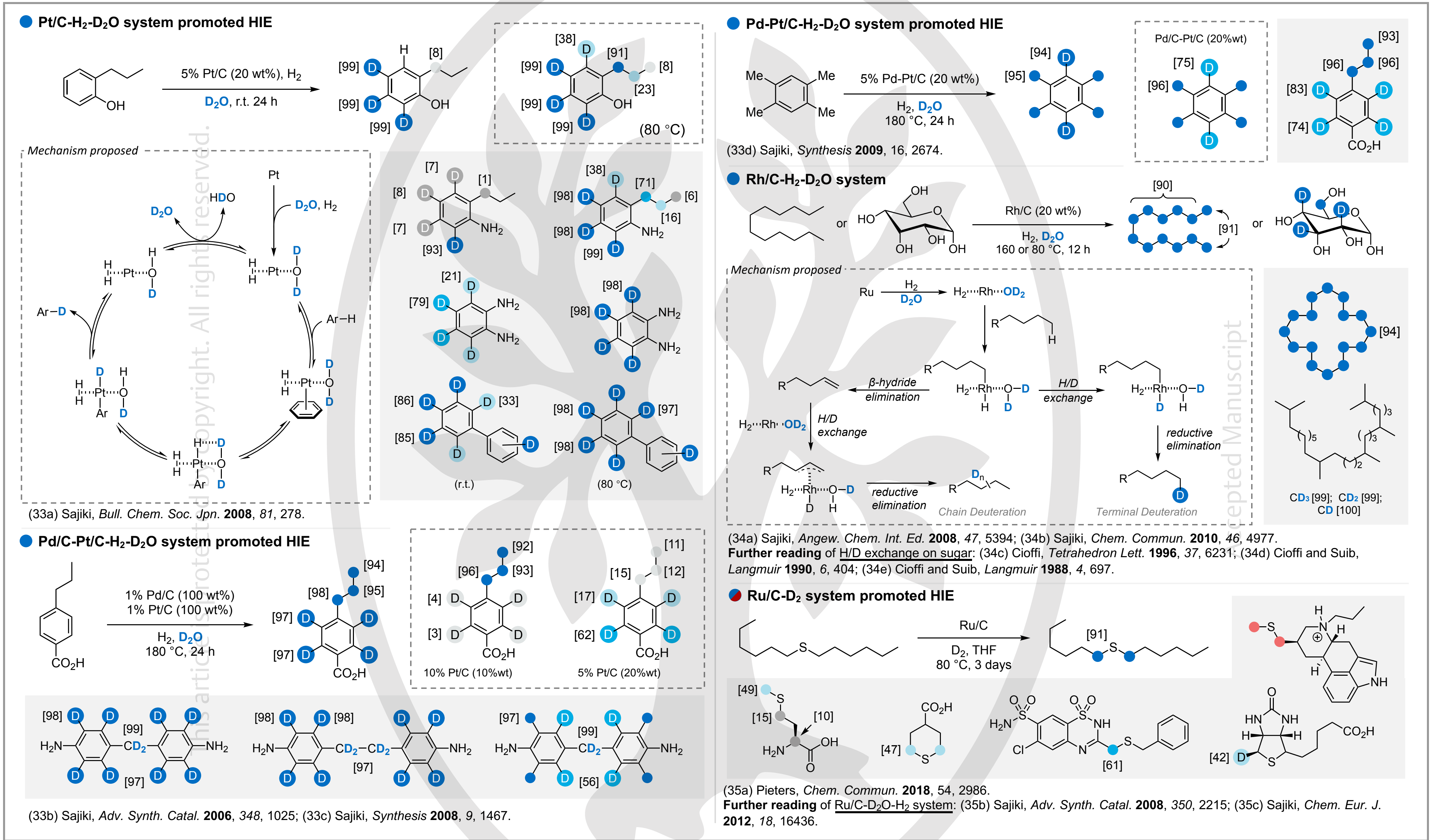


Figure 22 Heterogeneous HIE catalyzed by active carbon supported metal catalyst (3): Further application of M/C-H2-D2O systems, Pt/C[33a-c], Rh/C [34a-e], and Ru/C.[35a-c]

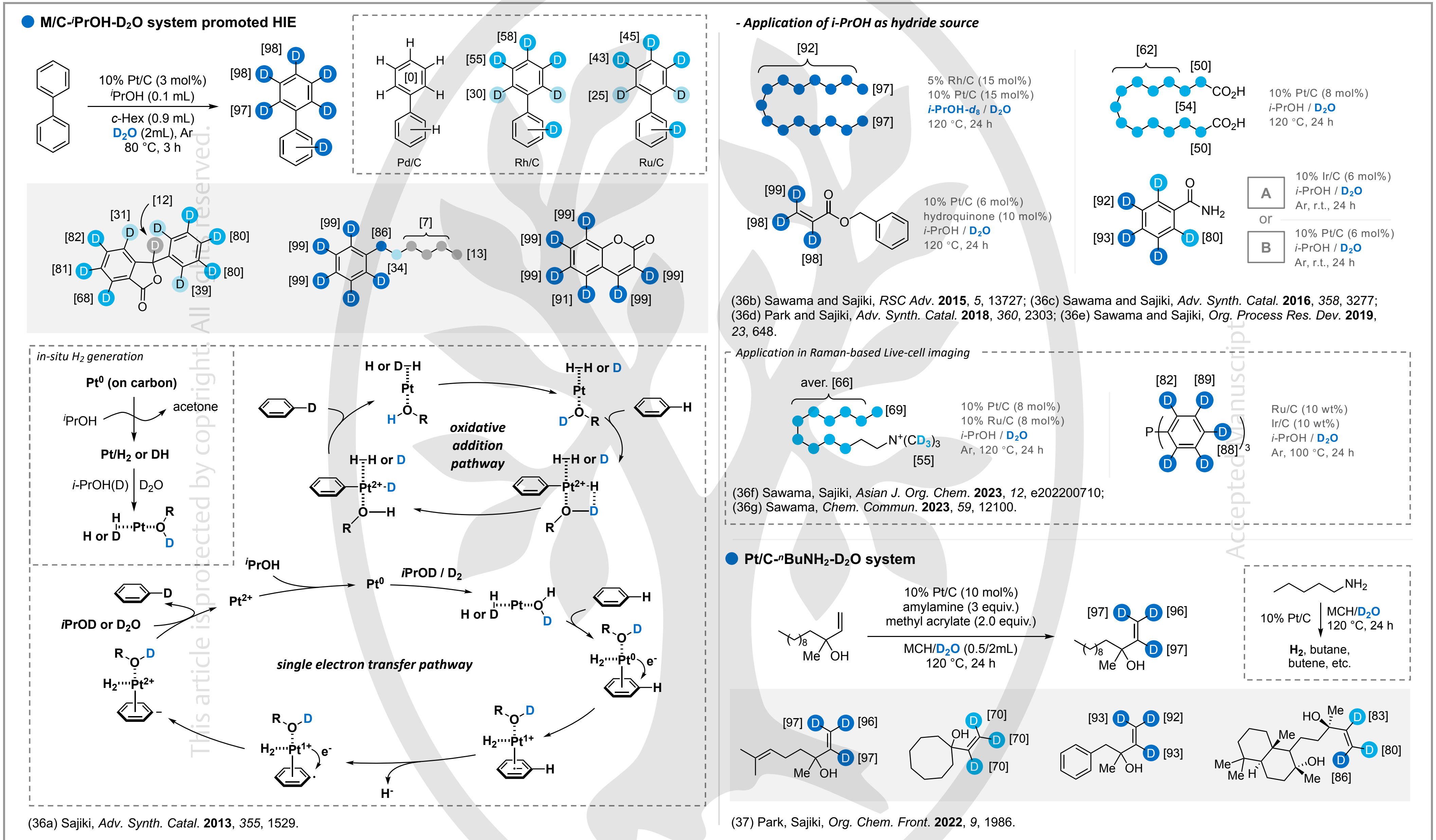


Figure 23 Heterogeneous HIE catalyzed by active carbon supported metal catalyst (4): M/C-^{i}PrOH-D$_2$O system[36a-g], and Pt/C-^{n}BuNH$_2$-D$_2$O.[37]

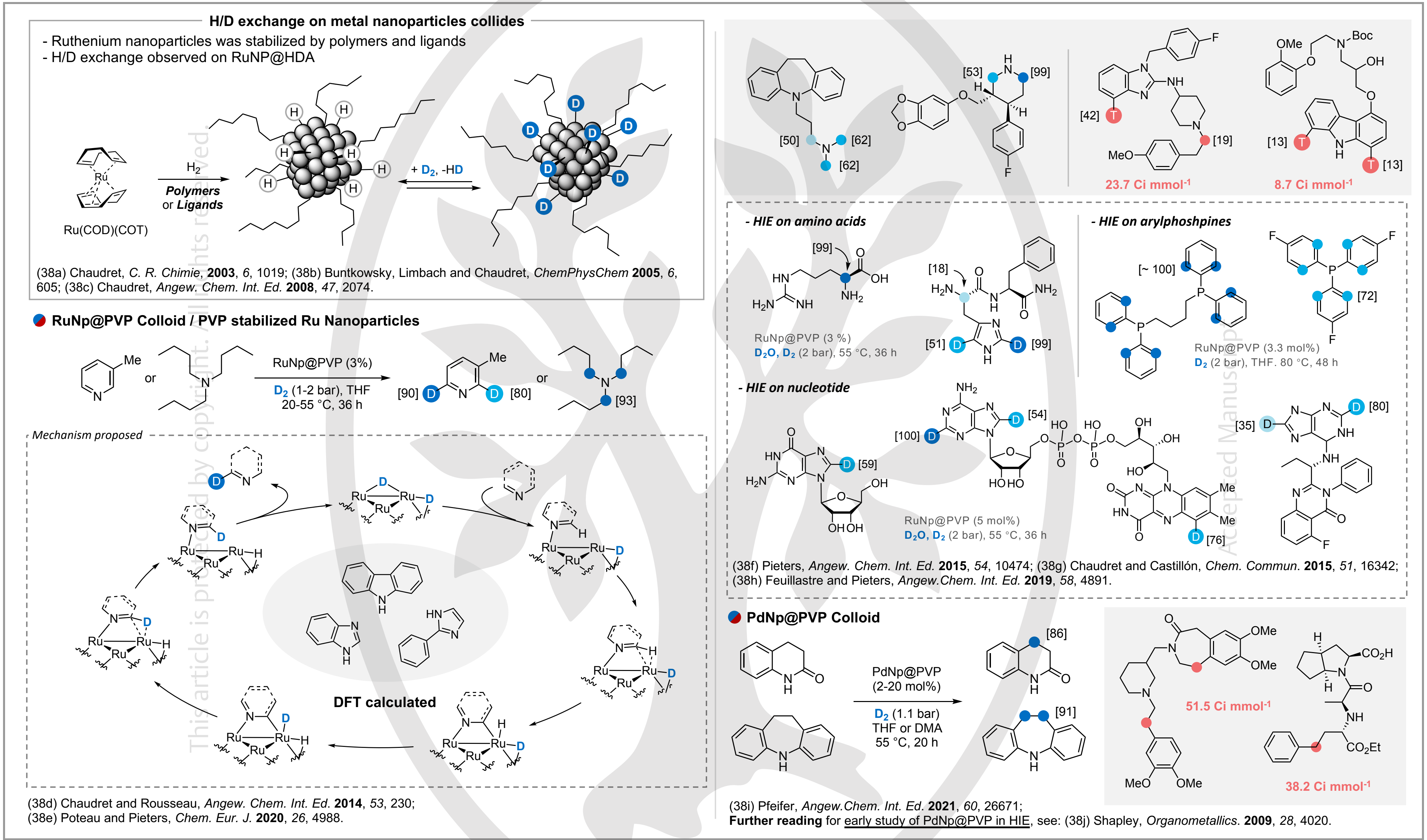


Figure 24 Heterogeneous HIE catalyzed by metal nanoparticles (1): PVP supported metal nanoparticle.[38a-i]

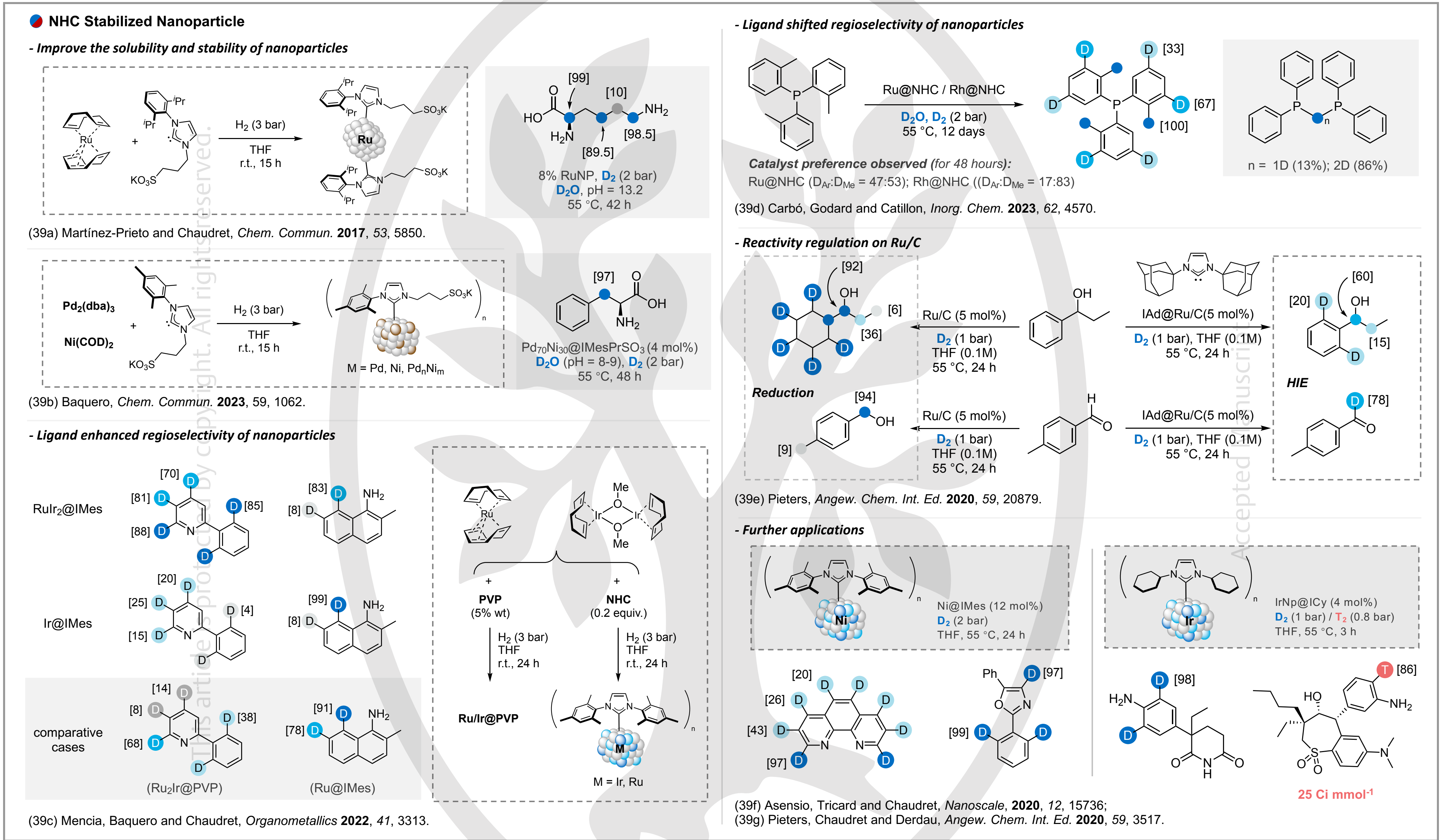


Figure 25 Heterogeneous HIE catalyzed by metal nanoparticles (2): NHC supported metal nanoparticles (1).[39a-g]

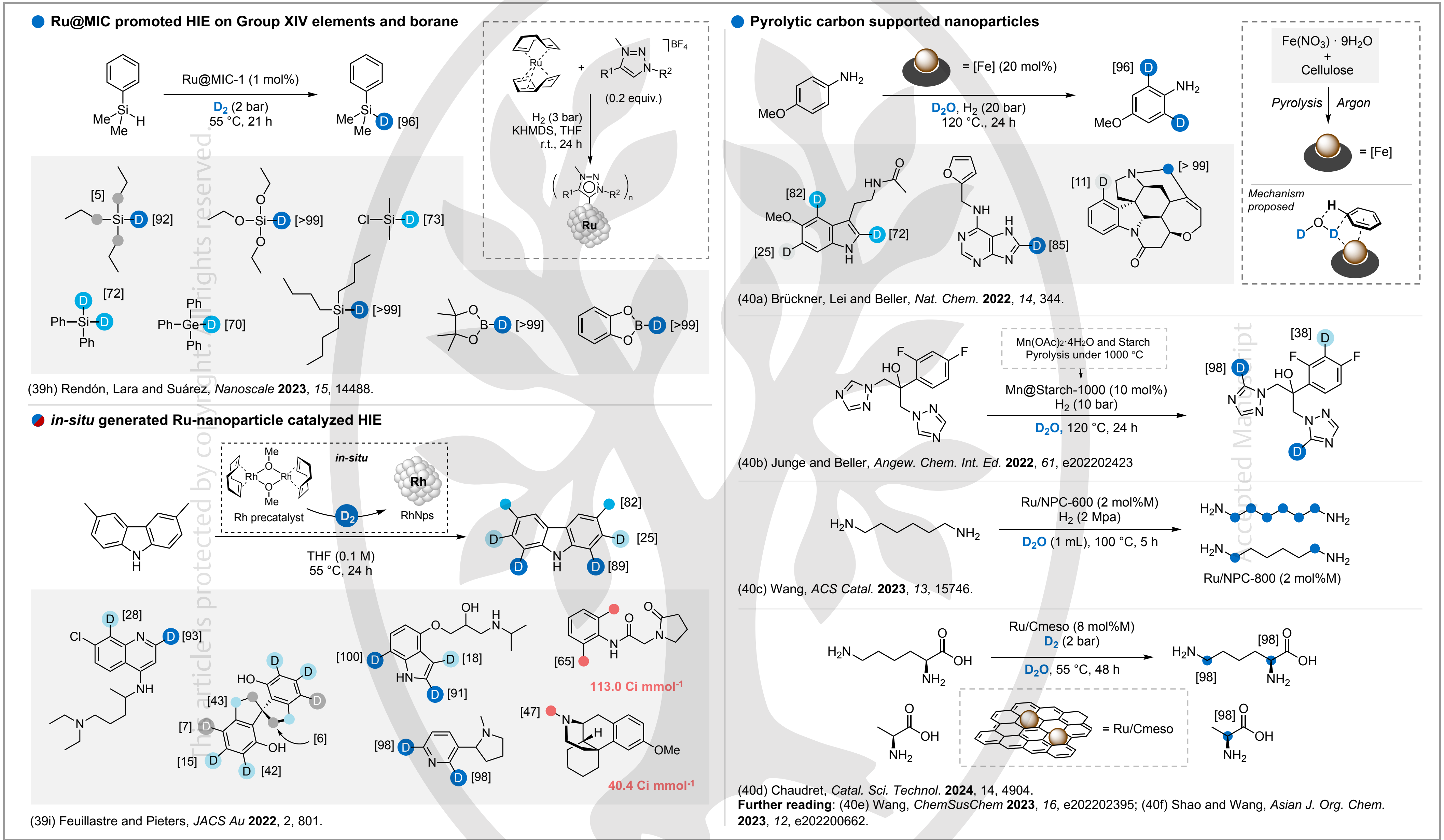


Figure 26 Heterogeneous HIE catalyzed by metal nanoparticles (3): NHC supported metal nanoparticles (2),[39h-i] and pyrolytic carbon supported novel metal nanoparticle.[40a-f]

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Conflict of Interest

The authors declare no conflict of interest.

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