Transition-Metal-Catalyzed Deuteration via Hydrogen Isotope Exchange

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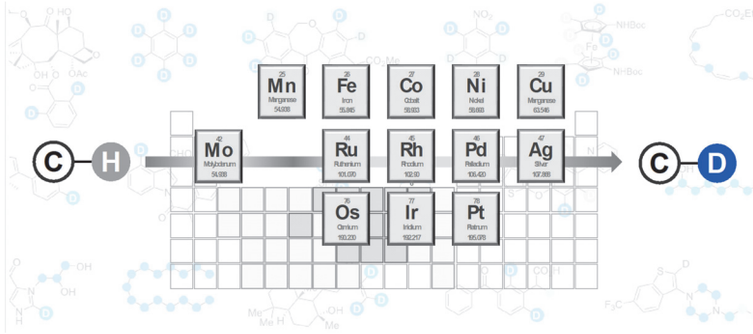


Received: 20.09.2024
Accepted after revision: 29.10.2024
Published online: 04.11.2024 (Accepted Manuscript), 11.12.2024 (Version of Record)
DOI: 10.1055/a-2460-7378; Art ID: SO-2024-09-0038-GR

Abstract Direct hydrogen isotope exchange represents a distinctive strategy for deuterium labelling, where the protium is directly replaced by deuterium. In this graphical review, we summarize the progress in deuteration via transition-metal-catalyzed hydrogen isotope exchange. The review is organized according to the mechanism of C–H bond activation relating to the homogeneous catalysis, and heterogeneous catalysis is also discussed according to the catalyst type. Representative mechanistic processes are depicted, and proven cases for tritiation are 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] These applications have been accompanied by the development of synthetic strategies for efficient deuterium incorporation, such as conventional chemical transformations by catalytic hydrogenation of unsaturated bonds and the defunctionalization of aromatic halides.[4] Meanwhile, in contrast to the transformations of functional groups, the direct hydrogen isotope exchange (HIE) of C–H bonds has 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 mass production of deuterium compounds. Therefore, the development of milder and environmentally friendly deuteration strategies remains a necessity, especially methods that are compatible with economical deuterium sources, such as heavy water or deuterium gas.

Accompanied with an in-depth understanding of the characteristics of C–H activation with transition metals,[5] a few examples of transition-metal-facilitated HIE have been used as a chemical tool to check the reversibility of the process. Thus, benefiting from mechanistic investigations, catalytic HIE has been enabled based on reversible manipulation of established catalytic systems.[6] For instance, Crabtree's catalyst, designed for hydrogenation, was found to facilitate dehydrogenation under a low H_2 pressure.[7a] This finding was further developed as a major type 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 the main source of deuterium. Similar HIE processes have also been employed with Ir, Rh, Ru, and Pt,[10–12g,13,15] whilst earth-abundant metals such as Fe, Co and Ni also show promising reactivities.[12f–h,14] On the other hand, the recently burgeoning strategy of concerted metalation–deprotonation (CMD) was also utilized in a reversible manner,[16–22] which employed D_2O or deuterated acids as the deuterium source. Despite the challenge associated with CMD of subsequent route control between functionalization and C–D bond reconstruction, *ortho*- or *meta*-selective, as well as undirected deuteration, have been developed, mainly based on Pd catalysis;[20–22] however, Mn,[21a] Co,[18d] Ni,[18f] and Ag[19] have also been recently reported to show HIE activity. Moreover, HIE can also be accomplished through the strategy of hydrogen borrowing by exploiting the remarkable kinetic isotope effect of deuterium.[23,24] As a reversible process, it has also been utilized in HIE with olefins.[25] Additionally, other specialized strategies have been reported, including Lewis acid enhanced local acidity of protons,[26] arene activation facilitated by an η^6 complex,[27] and σ-metathesis-enabled H/D exchange between a metal and D_2.[28] On the other hand, heterogeneous catalysts also comprise 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 nanoparticles collide,[38,39] and that the corresponding ligand-loaded nanoparticles[40] may also achieve astonishing regioselectivity compared to their homogeneous alternatives. Noticeably, in most cases, tritiation could be easily achieved by replacing the deuterium source with the corresponding tritium source. We hope that this graphical review will stimulate further research on the development of innovative HIE strategies within this rapidly evolving field.

Biosketches

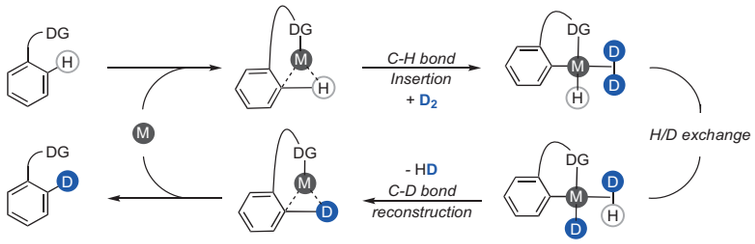
Zhi-Jiang Jiang was born in 1990 in Ningbo, China. He obtained his B.Sc. in pharmaceutical science at Zhejiang University of Technology. He completed his Ph.D. under the supervision of Prof. Wei-Ke Su and Prof. Alexandre. V. Dushkin at the Collaborative Innovation Center of Yangtze River Delta Region Green Pharmaceuticals, where he explored the phenomenon of liquid-assisted grinding in mechanochemistry. He subsequently joined the School of Biological and Chemical Engineering of NingboTech University as an assistant professor in 2019. Currently, his research interests focus on the development of tools and strategies for selective deuterium-labelling.

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 Prof. Lixin Wang. In the same year, he joined the group of Prof. P. Vogel as a postdoctoral researcher at the Swiss Federal Institute of Technology in Lausanne (EPFL). He continued his postdoctoral studies at Kyoto University in 2015, working with Prof. Keiji Maruoka. In 2019, he 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 applications of the site-specific synthesis of deuterium-labeled compounds.

Zhanghua Gao obtained his Ph.D. in 2005 under the supervision of Prof. Wei-Dong Z. Li at Lanzhou University. In 2006, he joined the group of Prof. Philip J. Kocienski at the University of Leeds as a postdoctoral associate, undertaking research in natural product synthesis. After a one-year stay in the chemical industry, in 2010, he joined the University of Oxford as a postdoctoral fellow working with Prof. Véronique Gouverneur and Prof. Benjamin G. Davis on fluorine-18 radiolabeling of amino acids and proteins. In 2015, he moved to Ningbo University as an associate professor and became a full professor in 2016. His research interests include isotope-labelling methodology/technology and its applications in drug discovery and functional materials.

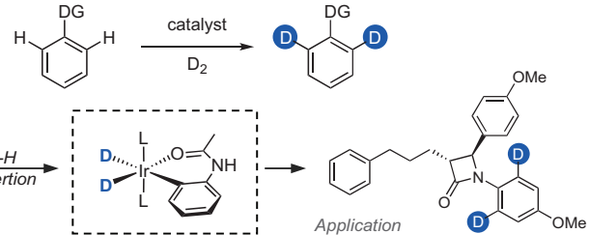
Basic process for OA based H/D exchange

- C-H bond cleavage via oxidative addition (OA)
- Deuterium gas (D_2) as deuterium source
- Labelling site selectivity under *ortho*-directing or non-directing system



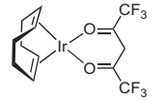
Seminal studies

Directing group led *ortho*-deuteration

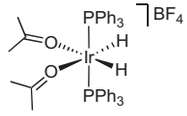


Crabtree's catalyst

(7a) Hesk, *J. Labelled Compd. Radiopharm.* **1995**, *36*, 497



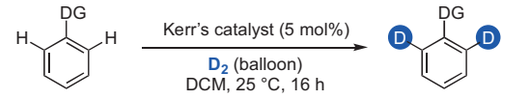
(7b) Lockley, *Tetrahedron Lett.* **2000**, *41*, 2705;
(7c) Lockley, *Tetrahedron Lett.* **2003**, *44*, 3959;
(7d) Lockley, *J. Labelled Compd. Radiopharm.* **2003**, *46*, 1191;
(7e) Lockley, *J. Labelled Compd. Radiopharm.* **2005**, *48*, 75.



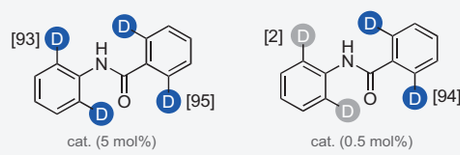
(7f) Heys, *J. Chem. Soc., Chem. Commun.* **1992**, 680;
(7g) Heys, *J. Labelled Compd. Radiopharm.* **1993**, *33*, 431;
(7h) Heys, *J. Organomet. Chem.* **1996**, *524*, 87;
(7i) Heys, *J. Labelled Compd. Radiopharm.* **1997**, *39*, 291;
(7j) Heys, *J. Labelled Compd. Radiopharm.* **1999**, *42*, 797;
(7k) Heys, *Tetrahedron Lett.* **2000**, *41*, 9015.

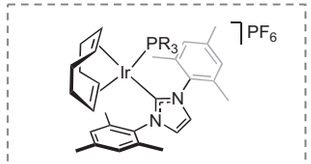
Further reading:
(7l) Herbert, *Tetrahedron* **2001**, *57*, 9487; (7m) Herbert, *Tetrahedron* **2003**, *59*, 3349; (7n) Herbert, *J. Labelled Compd. Radiopharm.* **2004**, *47*, 1; (7o) Salter, *J. Labelled Compd. Radiopharm.* **2003**, *46*, 489; (7p) Fels, *Eur. J. Org. Chem.* **2005**, 1402.

Kerr's catalysts

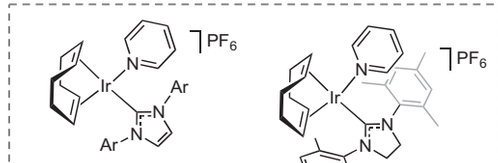


DG = Ac, Bz, $CONH_2$, $CONEt_2$, 2-Pyr, *N*-pyrazolyl, NO_2, NHAc, CONHPh, …

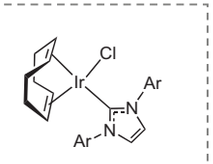




PR_3 = PPh_3, PBn_3, PMe_2Ph



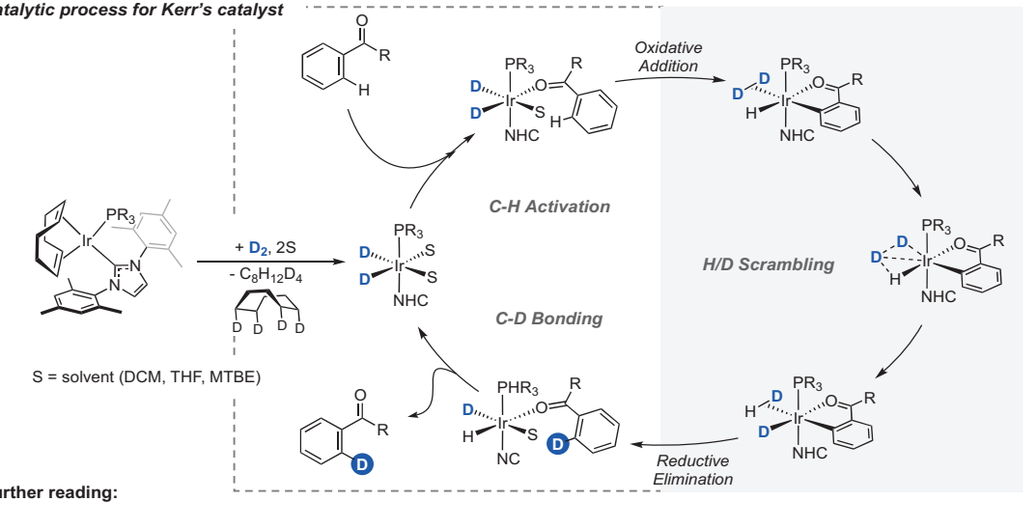
Ar = mesityl, 2,6-^{i}Pr$_2$C$_6$H$_3$



Ar = mesityl, 2,6-^{i}Pr$_2$C$_6$H$_3$

(8a) Kerr, *Chem. Commun.* **2008**, 1115; (8b) Nilsson and Kerr, *J. Labelled Compd. Radiopharm.* **2010**, *53*, 662; (8c) Kerr, *J. Labelled Compd. Radiopharm.* **2013**, *56*, 451; (8d). Kerr, *Synlett* **2015**, *27*, 111; (8e) Kerr, *Chem. Sci.* **2021**, *12*, 6747.

Catalytic process for Kerr's catalyst



Further reading:
For parameter effect: (8f) Kerr, *Org. Biomol. Chem.* **2014**, *12*, 3598; for counterion effect: (8g) Kerr, *Org. Biomol. Chem.* **2014**, *12*, 7927; (8h) Kerr, *J. Label. Compd. Radiopharm.* **2016**, *59*, 601; for mechanistic consideration: (8i) Kerr, *Adv. Synth. Catal.* **2014**, *356*, 3551; (8j) Kerr and Nelson, *Catal. Sci. Technol.* **2020**, *10*, 7249; (8k) Kerr, Lindsay and Nelson, *Catal. Sci. Technol.*, **2021**, *11*, 5498; for improved radioactivity: (8l) Derdau, *Green Chem.* **2022**, *24*, 4824.

Figure 1 HIE based on oxidative addition with directing groups (part 1): Early attempts using iridium catalysts[7a–p] and Kerr's iridium catalysts[8a–k]

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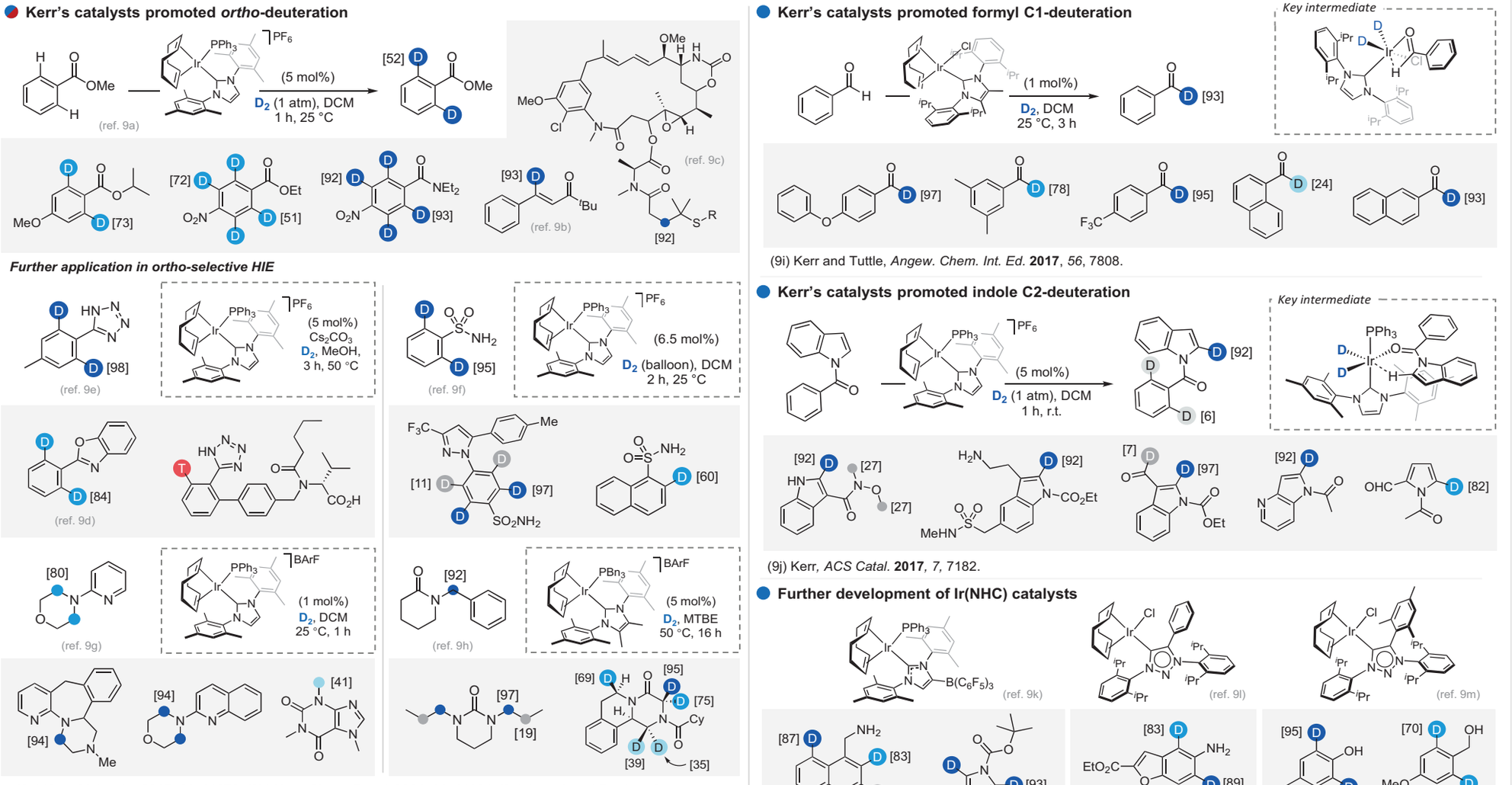

(9a) Kerr, *Molecules* **2015**, *20*, 11676; (9b) Kerr, *Chem. Eur. J.* **2014**, *20*, 14604; (9c) Atzrodt and Derdau, *Angew. Chem. Int. Ed.* **2018**, *57*, 8159; (9d) Derdau and Kerr, *Tetrahedron* **2015**, *71*, 1924; (9e) Kerr, *Chem. Commun.* **2016**, *52*, 6669; (9f) Kerr, *ACS Catal.* **2015**, *5*, 402; (9g) Kerr, *ACS Catal.* **2018**, *8*, 10895; (9h) Kerr, *Adv. Synth. Catal.* **2024**, *366*, 2577.

(9i) Kerr and Tuttle, *Angew. Chem. Int. Ed.* **2017**, *56*, 7808.

(9j) Kerr, *ACS Catal.* **2017**, *7*, 7182.

(9k) Tamm, *Adv. Synth. Catal.* **2020**, *362*, 3857; (9l) Zhao and Yan, *Org. Lett.* **2020**, *22*, 2210; (9m) Yan, *Org. Lett.* **2021**, *23*, 9297.

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

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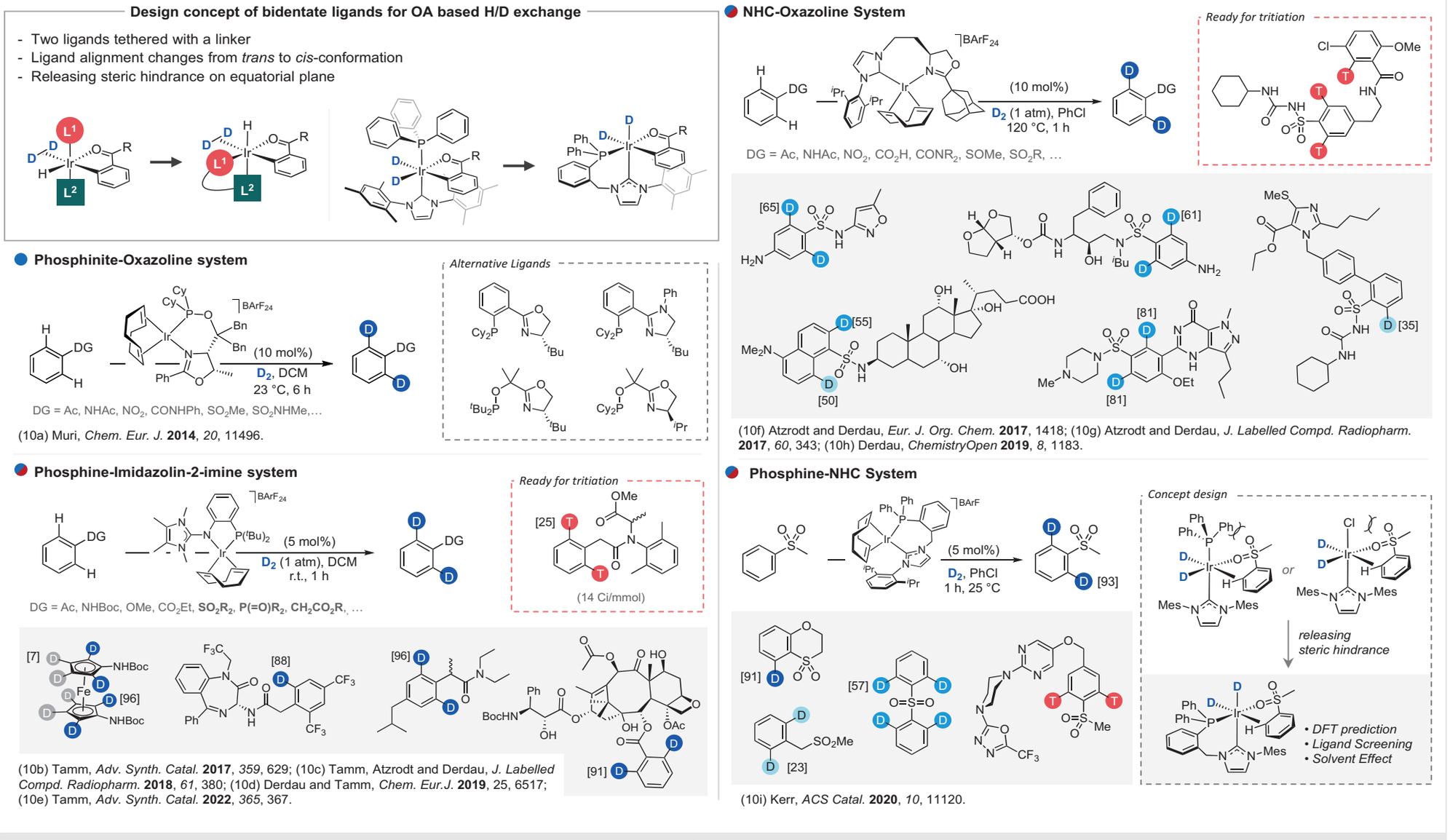
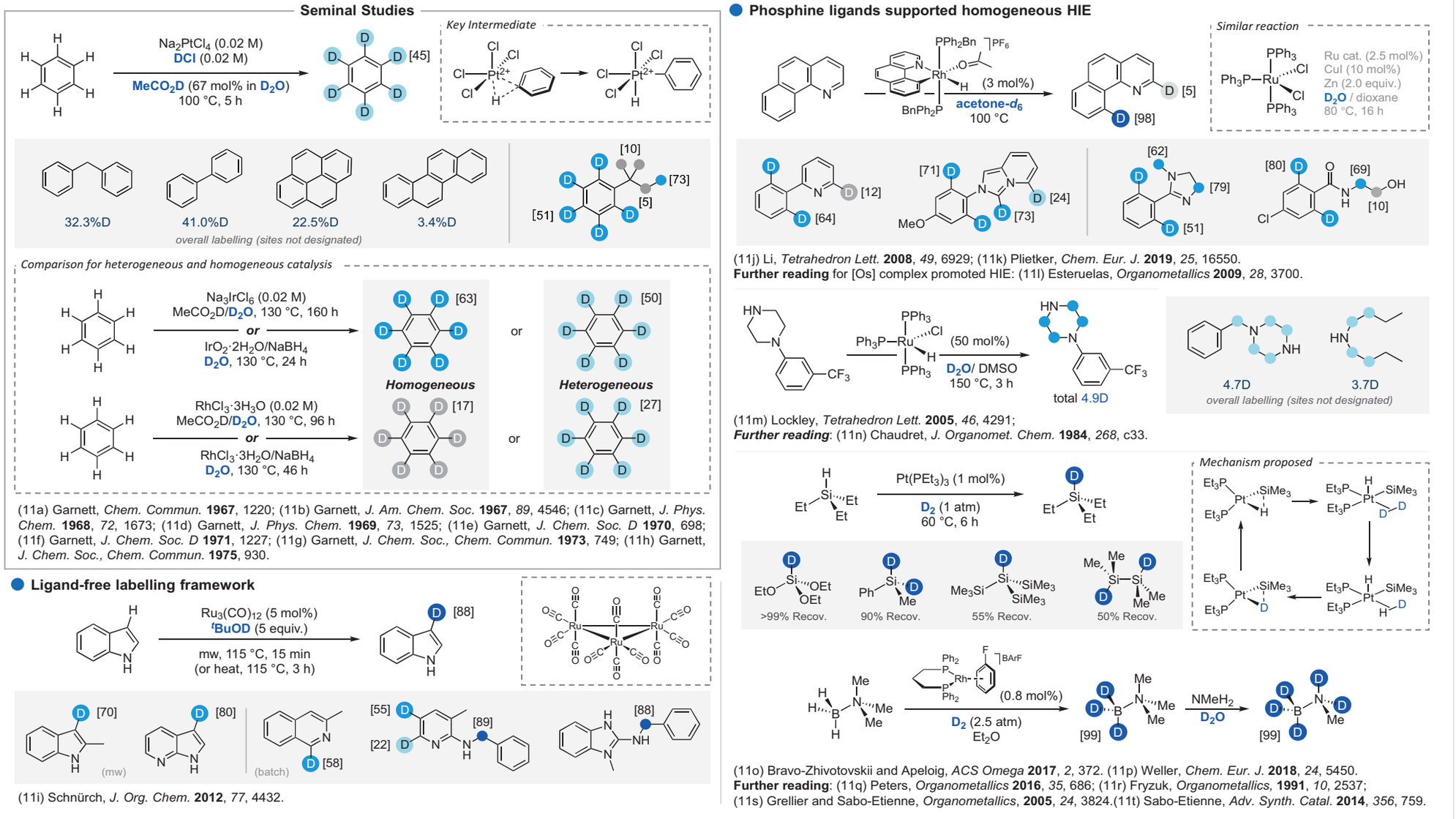


Figure 3 HIE based on oxidative addition with directing groups (part 3): Iridium catalysts with bidentate ligands[10a–i]



(11a) Garnett, *Chem. Commun.* **1967**, 1220; (11b) Garnett, *J. Am. Chem. Soc.* **1967**, *89*, 4546; (11c) Garnett, *J. Phys. Chem.* **1968**, *72*, 1673; (11d) Garnett, *J. Phys. Chem.* **1969**, *73*, 1525; (11e) Garnett, *J. Chem. Soc. D* **1970**, 698; (11f) Garnett, *J. Chem. Soc. D* **1971**, 1227; (11g) Garnett, *J. Chem. Soc., Chem. Commun.* **1973**, 749; (11h) Garnett, *J. Chem. Soc., Chem. Commun.* **1975**, 930.

(11i) Schnürch, *J. Org. Chem.* **2012**, *77*, 4432.

(11j) Li, *Tetrahedron Lett.* **2008**, *49*, 6929; (11k) Plietker, *Chem. Eur. J.* **2019**, *25*, 16550.
Further reading for [Os] complex promoted HIE: (11l) Esteruelas, *Organometallics* **2009**, *28*, 3700.

(11m) Lockley, *Tetrahedron Lett.* **2005**, *46*, 4291;
Further reading: (11n) Chaudret, *J. Organomet. Chem.* **1984**, *268*, c33.

(11o) Bravo-Zhivotovskii and Apeloig, *ACS Omega* **2017**, *2*, 372. (11p) Weller, *Chem. Eur. J.* **2018**, *24*, 5450.
Further reading: (11q) Peters, *Organometallics* **2016**, *35*, 686; (11r) Fryzuk, *Organometallics*, **1991**, *10*, 2537;
(11s) Grellier and Sabo-Etienne, *Organometallics*, **2005**, *24*, 3824.(11t) Sabo-Etienne, *Adv. Synth. Catal.* **2014**, *356*, 759.

Figure 4 HIE based on oxidative addition without directing groups (part 1): Phosphine-ligand-supported metal catalysts[11a–t]

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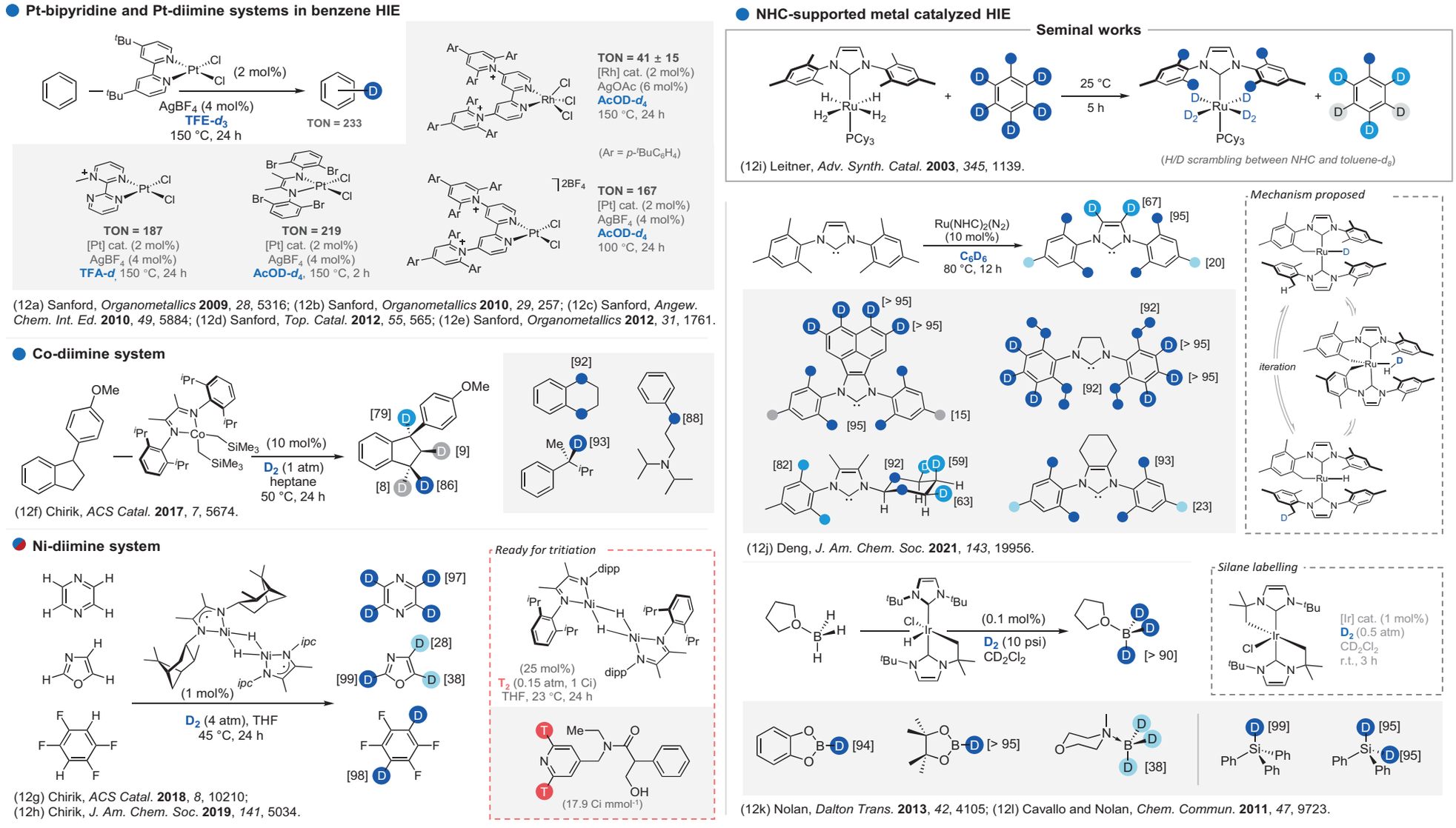

Figure 5 HIE based on oxidative addition without directing groups (part 2): Bipyridine-, imine-, and NHC-ligand-supported metal catalysts[12a–k]

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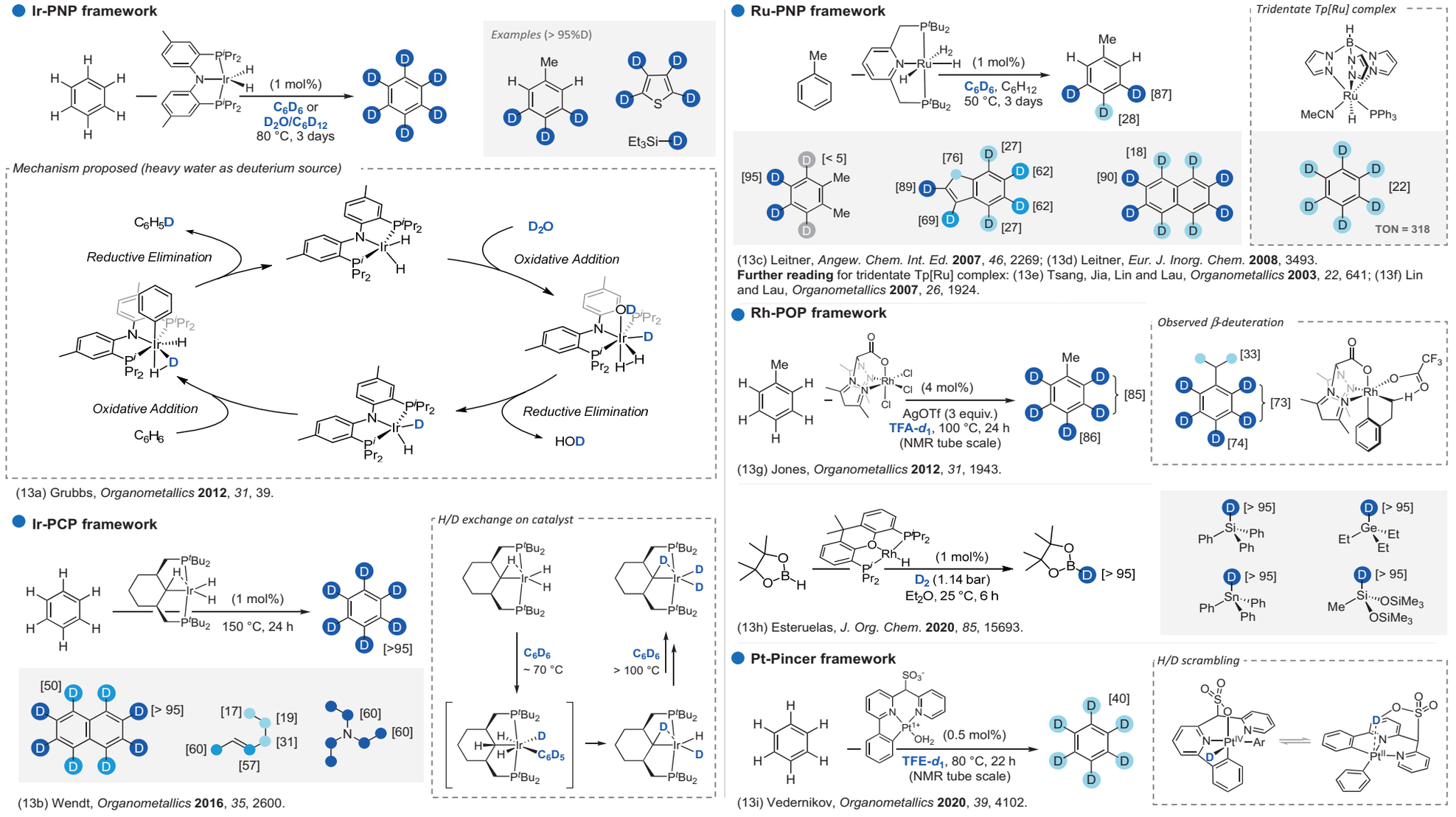

Figure 6 HIE based on oxidative addition without directing groups (part 3): Tridentate-ligand-supported noble metal catalysts[13a–i]

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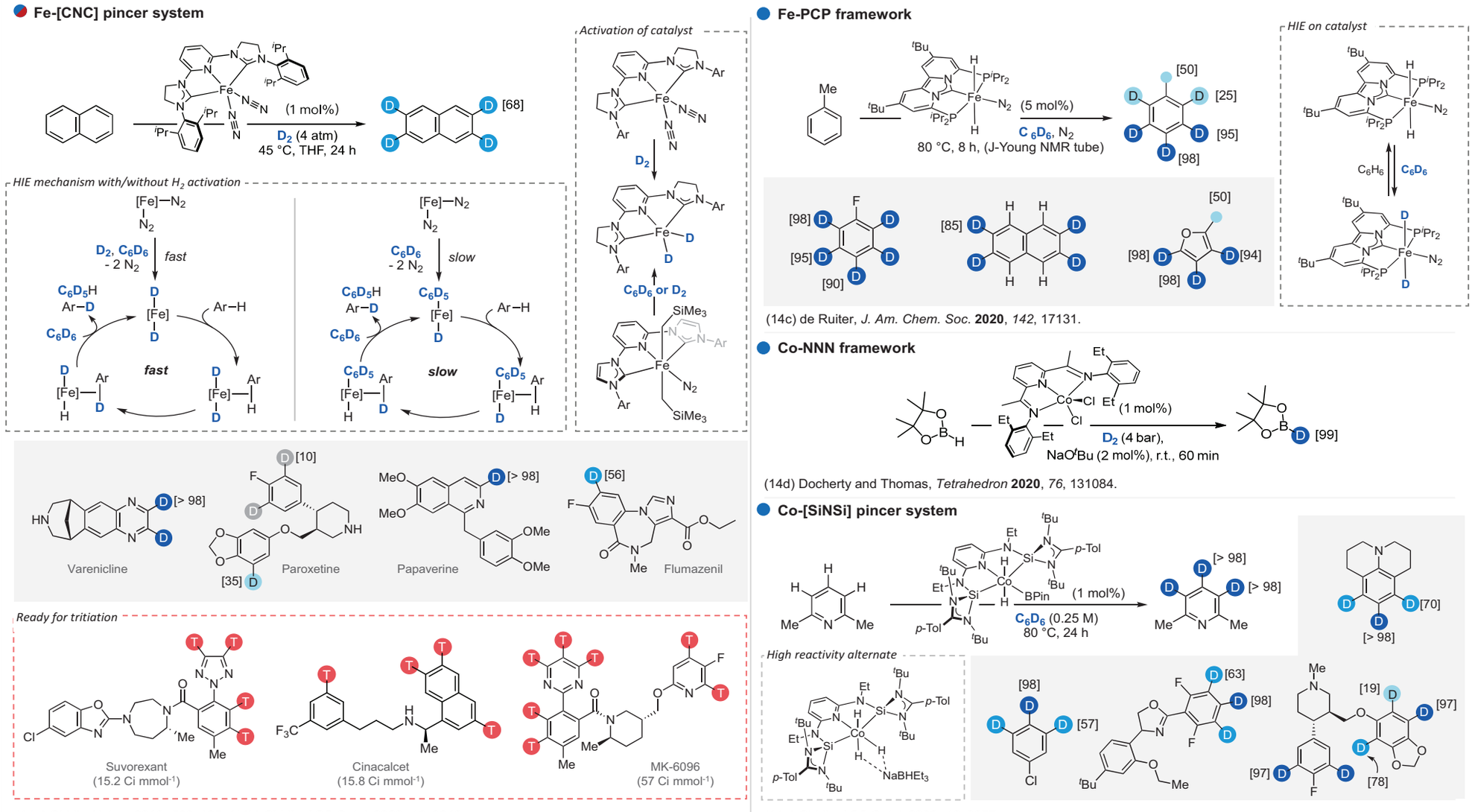

(14a) Chirik, *Nature* **2016**, *529*, 195; (14b) Chirik, *ACS Catal.* **2020**, *10*, 8640.

(14c) de Ruiter, *J. Am. Chem. Soc.* **2020**, *142*, 17131.

(14d) Docherty and Thomas, *Tetrahedron* **2020**, *76*, 131084.

(14e) Chirik, *ACS Catal.* **2022**, *12*, 8877.

Figure 7 HIE based on oxidative addition without directing groups (part 4): Tridentate-ligand-supported earth-abundant metal catalysts[14a–e]

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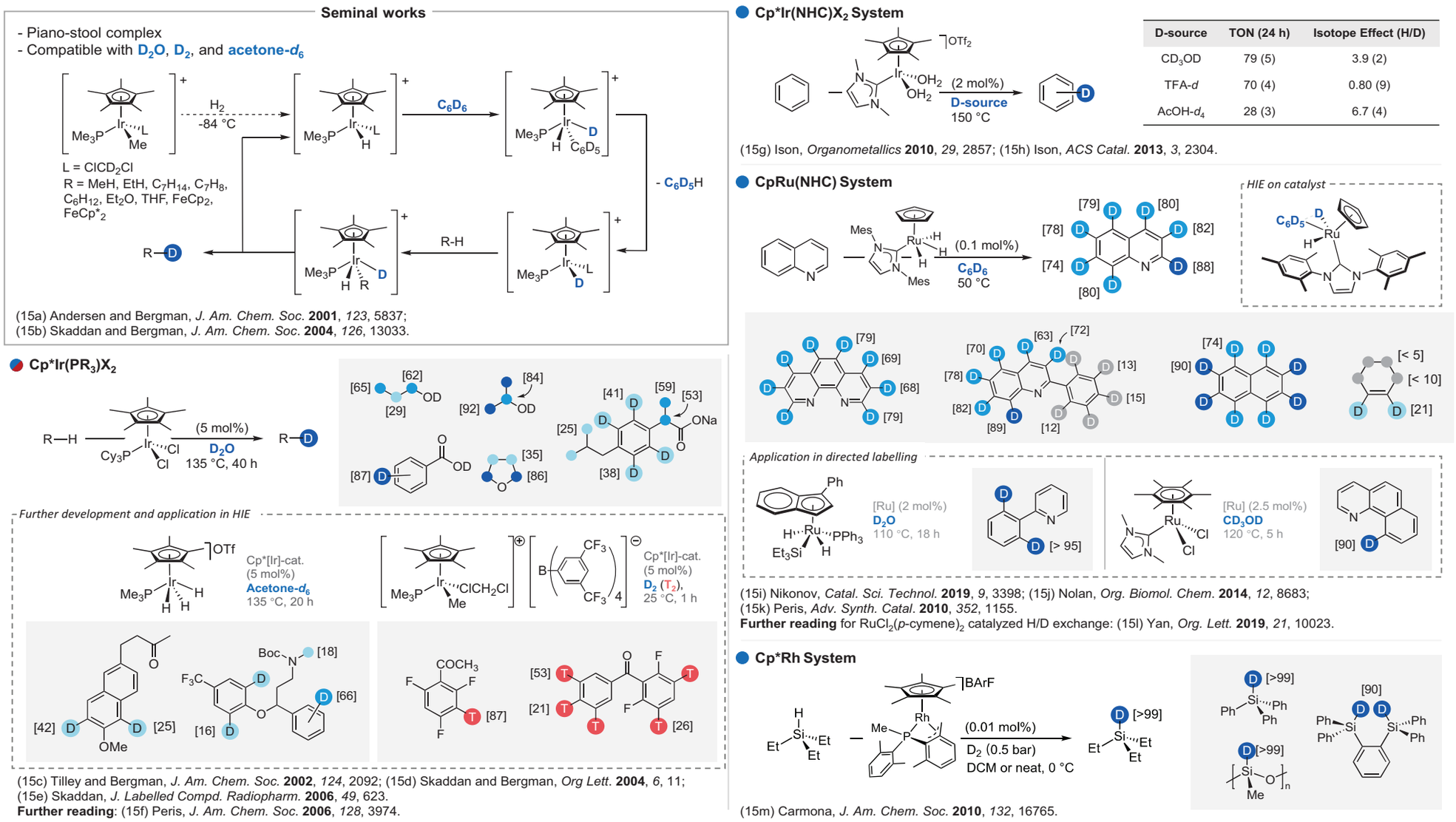

Figure 8 HIE based on oxidative addition without directing groups (part 5): Half-sandwich-type metal catalysts[15a–m]

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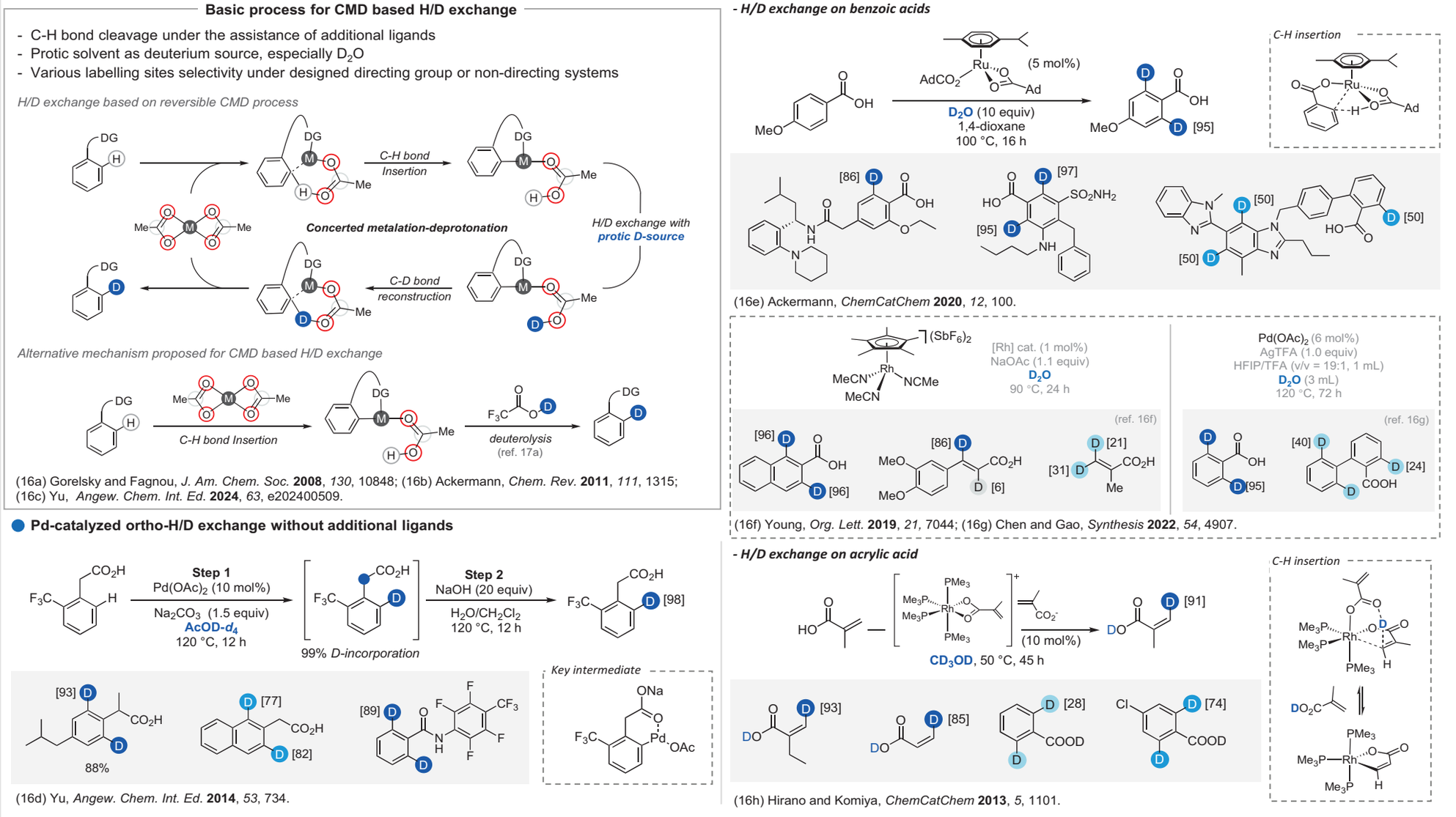

Figure 9 HIE based on concerted metalation–deprotonation (part 1): Directing-group-enabled *ortho*-selective deuteration[16a–h]

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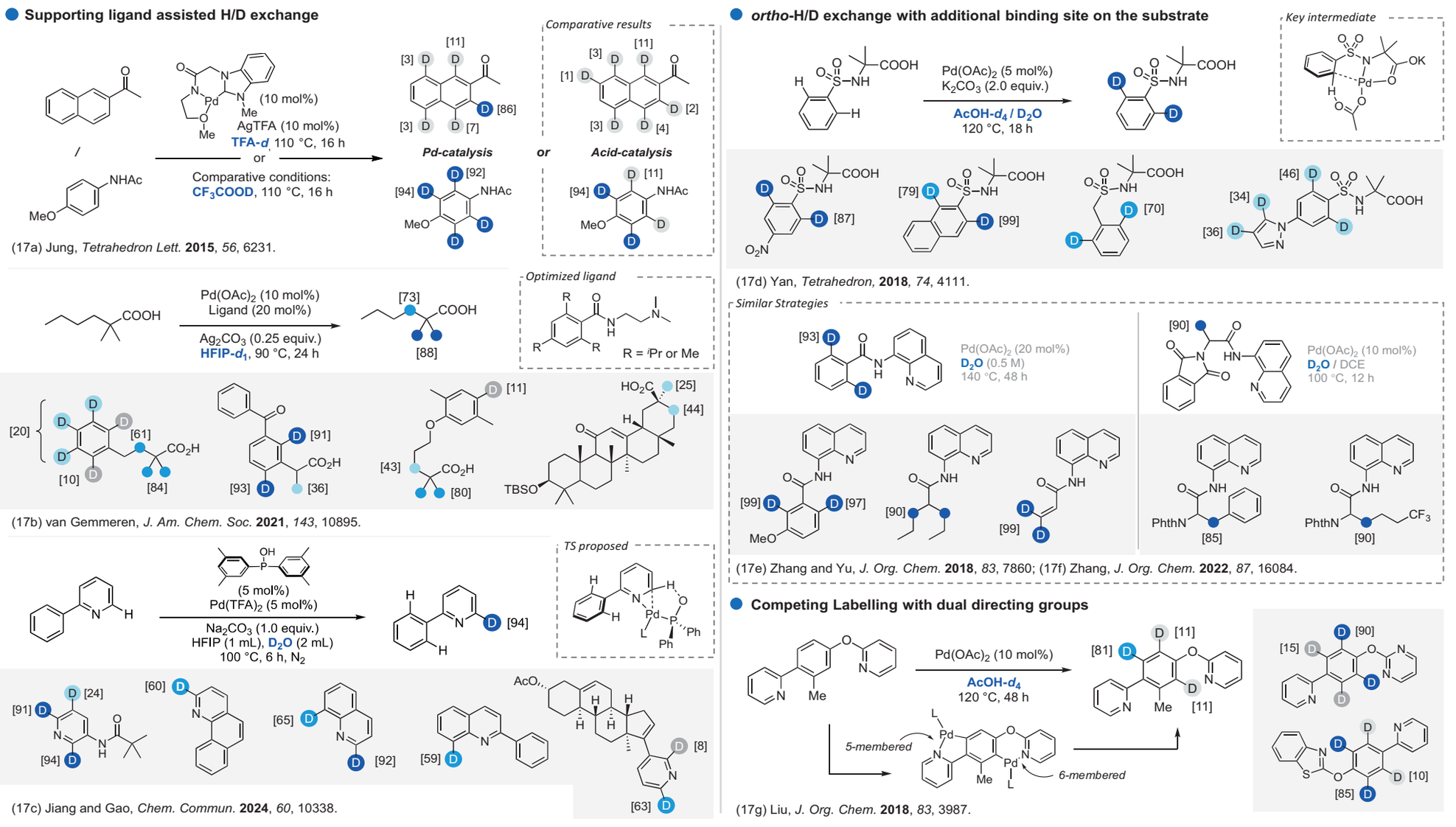


Figure 10 HIE based on concerted metalation–deprotonation (part 2): Supporting-ligand- and bidentate-substrate-enabled regioselective deuteration[17a–g]

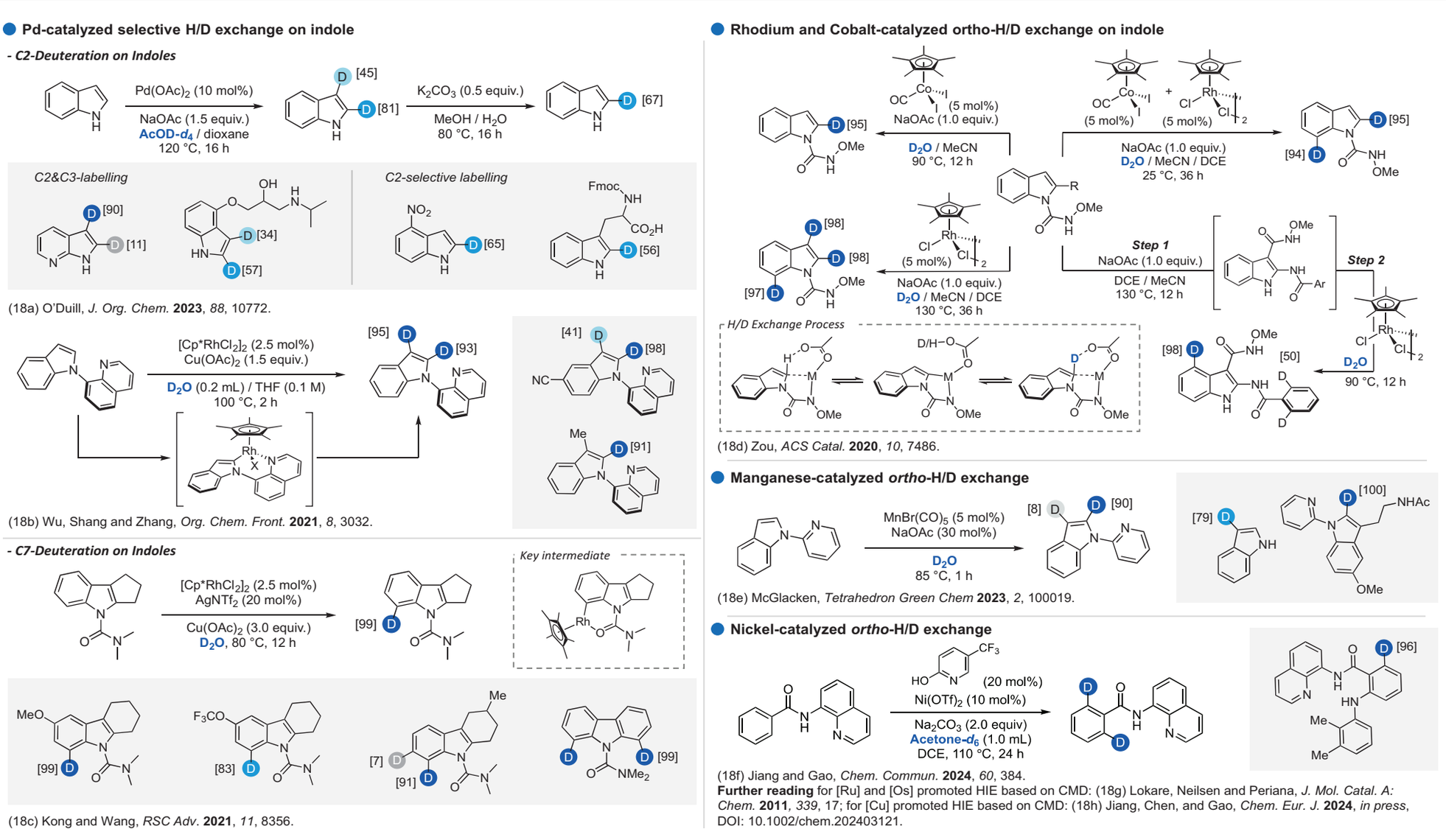
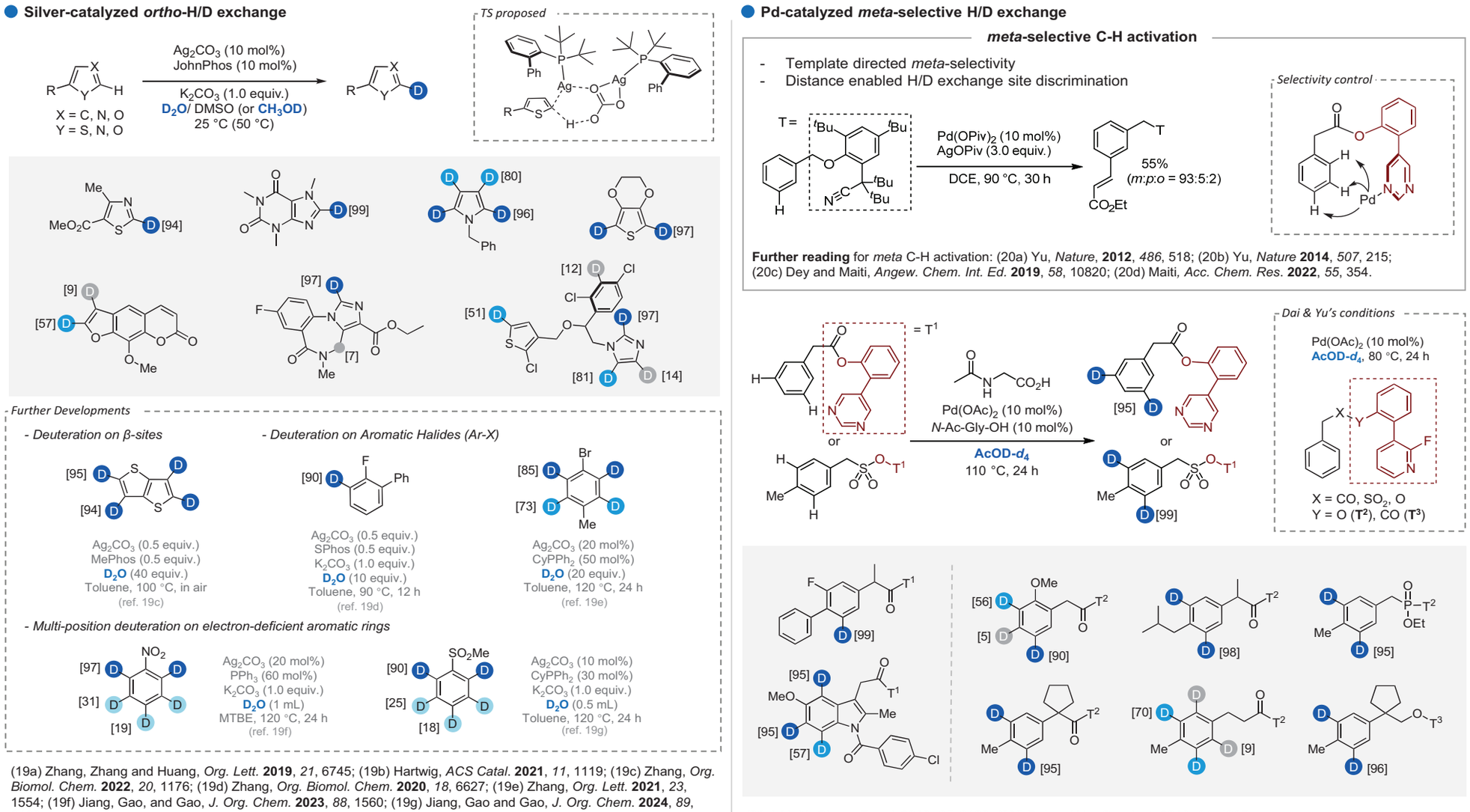


Figure 11 HIE based on concerted metalation–deprotonation (part 3): Regioselective deuteration of indoles, and earth-abundant-metal-catalyzed deuteration[18a–h]



(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 (part 4): Silver-catalyzed deuteration[19a–g] and *meta*-selective deuteration[20a–f]

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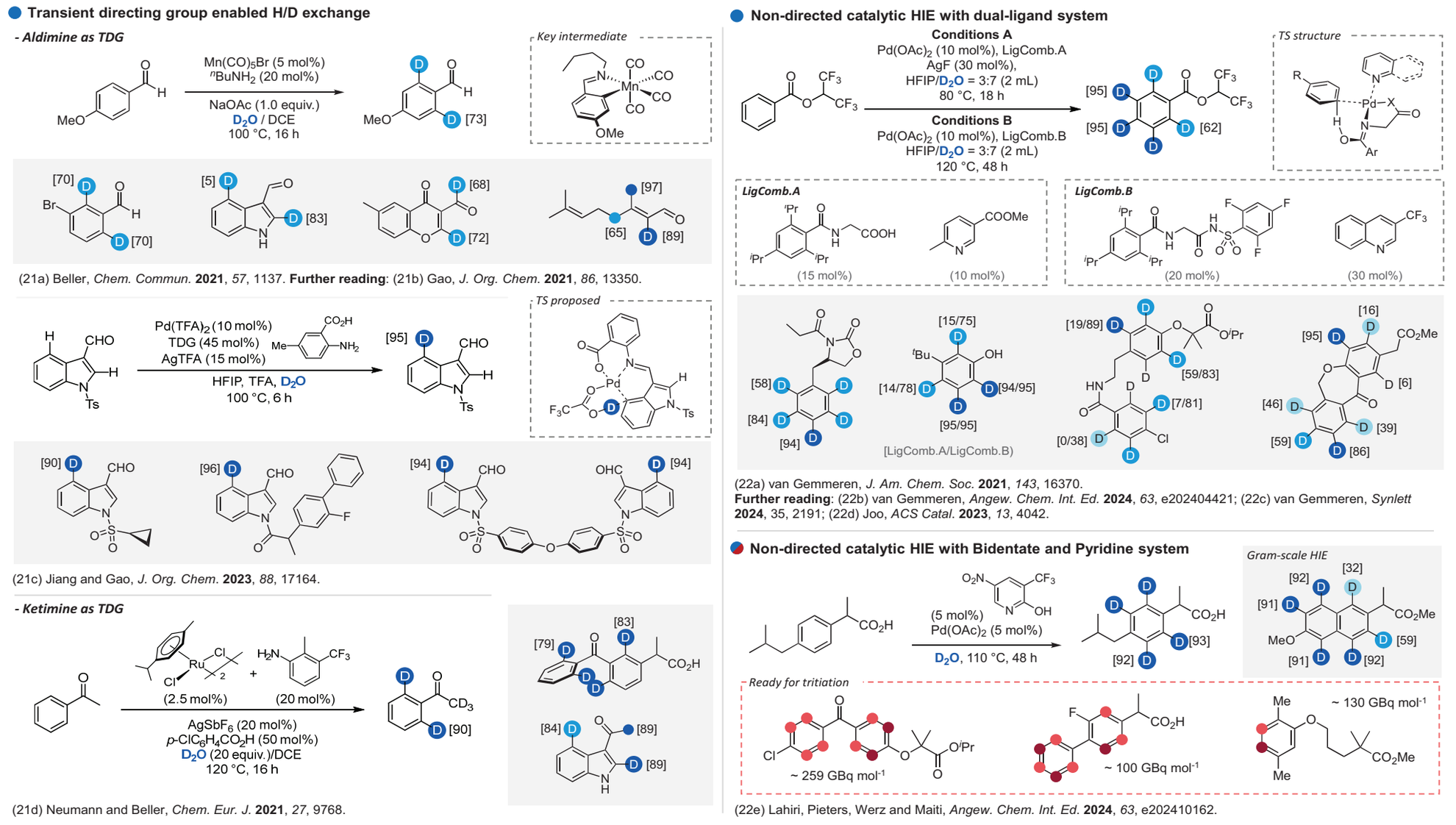
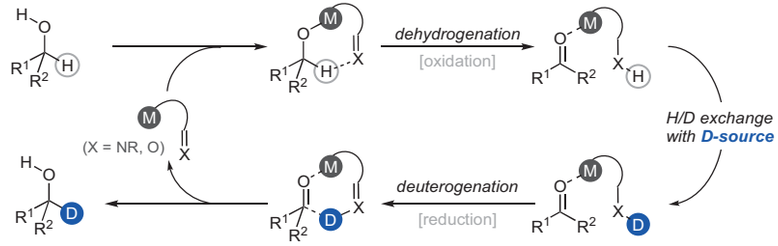


Figure 13 HIE based on concerted metalation–deprotonation (part 5): Application of a transient-directing-group (TDG) strategy[21a–d] and a non-directing strategy in deuteration[22a–e]

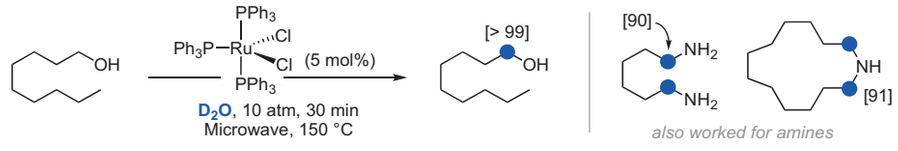
Basic process for hydrogen-borrowing based H/D exchange

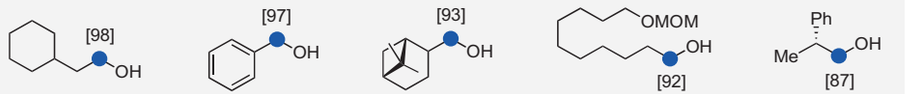
- Continuous oxidation and reduction promoted H/D exchange
- Ligand or metal-center act as hydrogen transferring center
- Available for H/D exchange of alcohols and amines



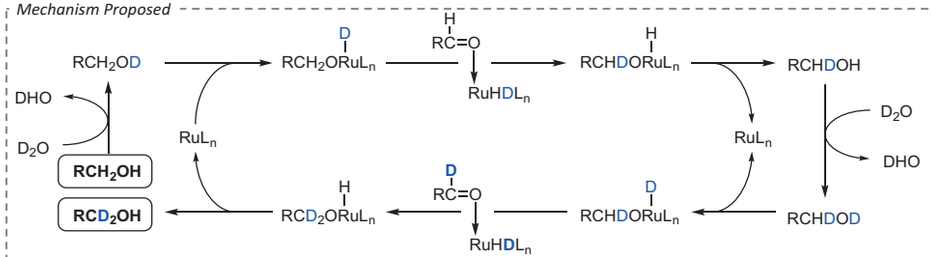
Further reading for hydrogen-borrowing strategy: (23a) Morrill, *ACS Cent. Sci.* **2021**, *7*, 570; (23b) Corma and Sabater, *Chem. Rev.* **2018**, *118*, 1410; for a review of labelling on heteroatom adjacent sites: (23c) Roche, *Synthesis* **2019**, *51*, 131.

Seminal studies





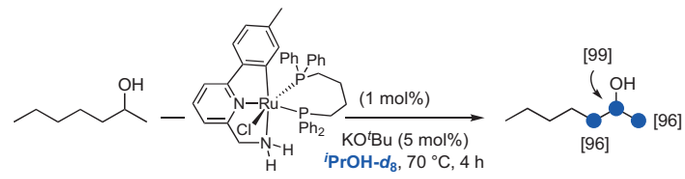
Mechanism Proposed



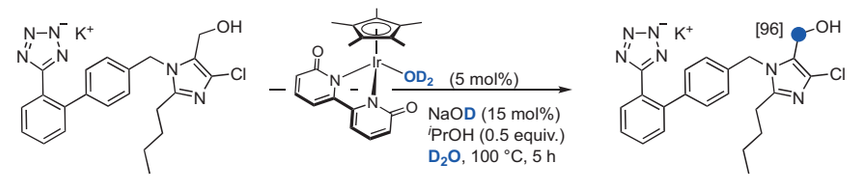
(23d) Matsubara, *Chem. Lett*, **2005**, *34*, 192.

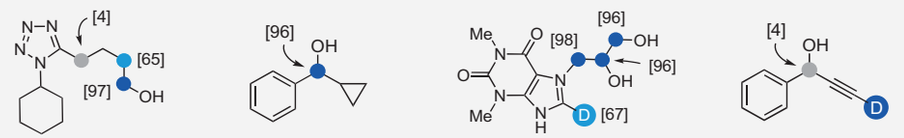
H/D exchange on alcohols

- H/D exchange without ligand participation

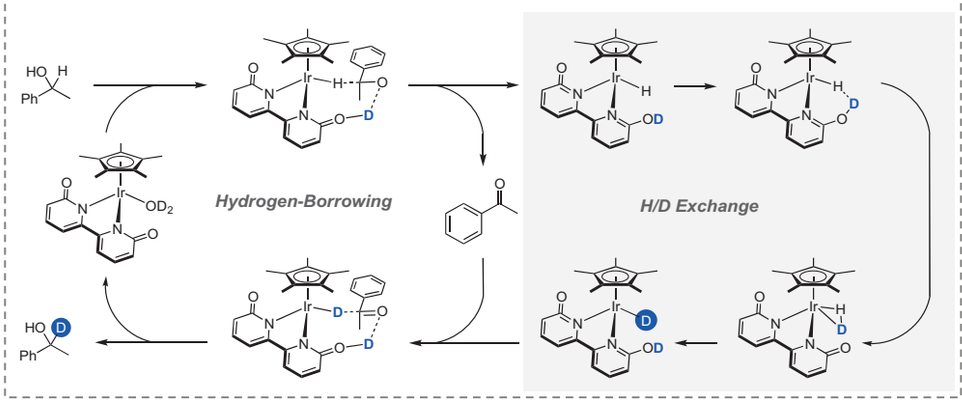


(23e) Baratta, *Dalton Trans*. **2011**, *40*, 8986





Mechanism proposed



(23f) Naka, *Chem. Sci.* **2022**, *13*, 8744.

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

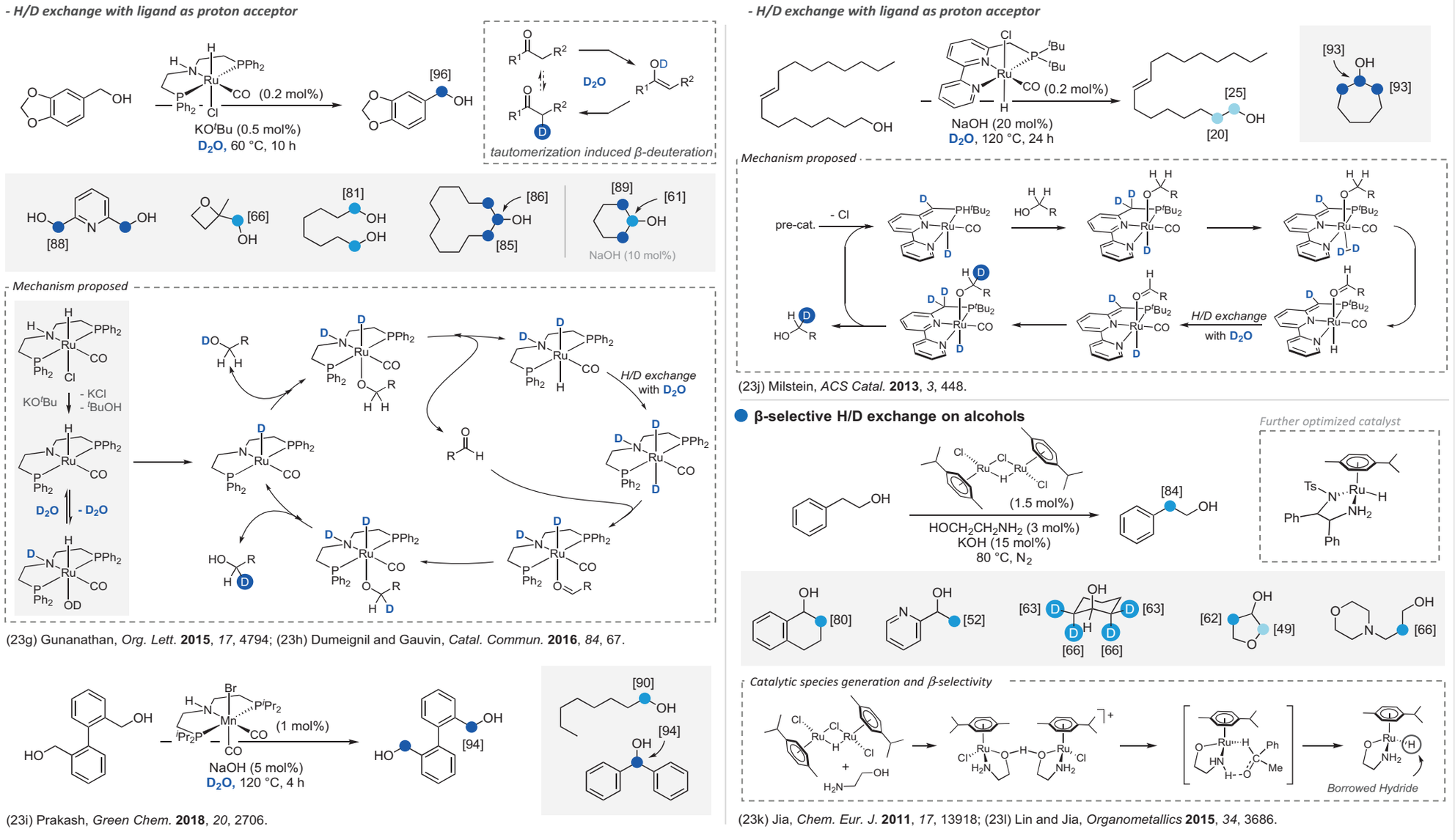


Figure 15 HIE based on hydrogen borrowing (part 2): α- and β-deuteration of alcohols via ligand-enabled hydride transfer[23g–l]

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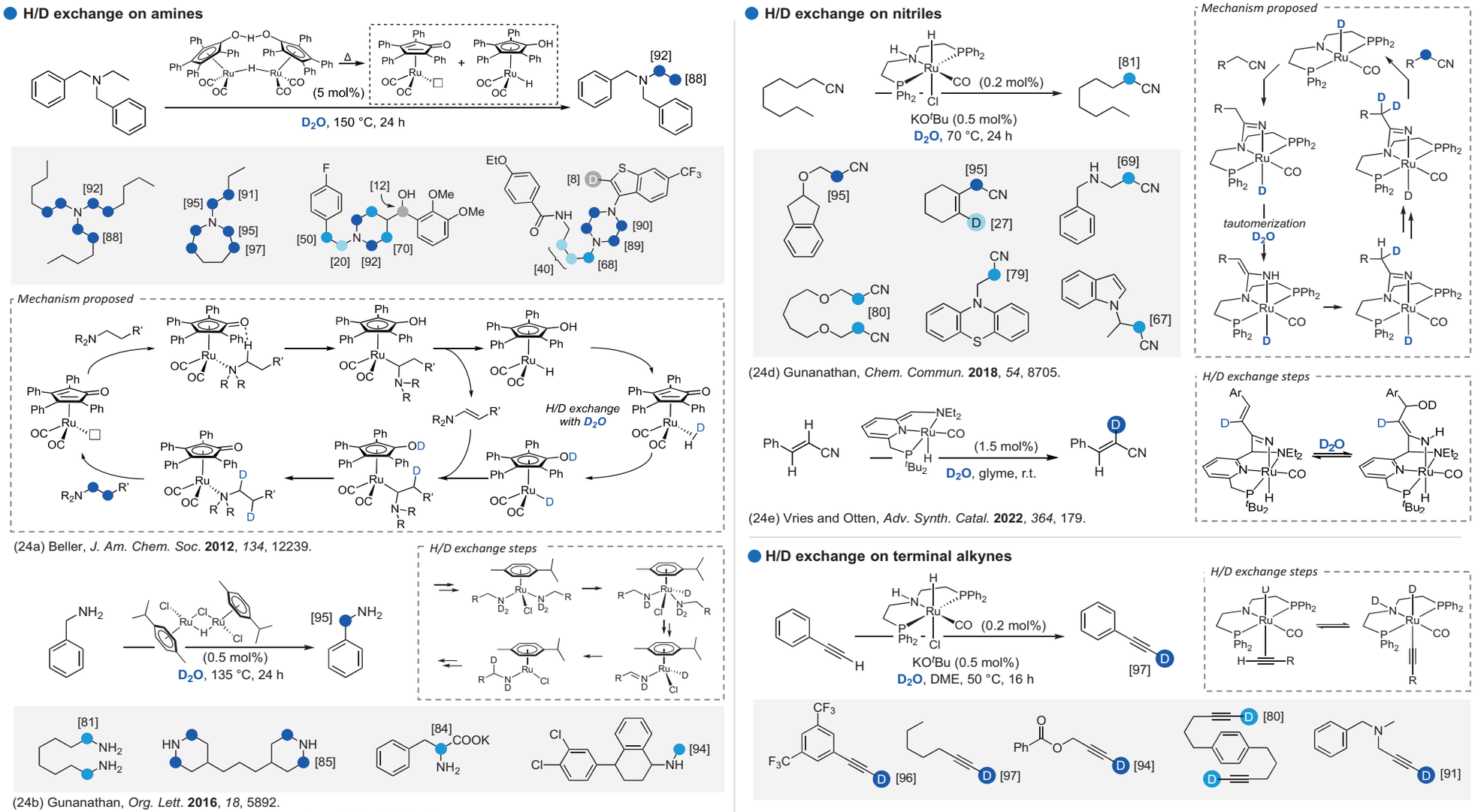
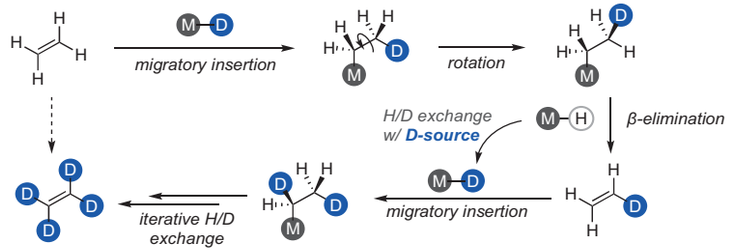


Figure 16 HIE based on hydrogen borrowing (part 3): Deuteration of amines, nitriles, and alkynes[24a–f]

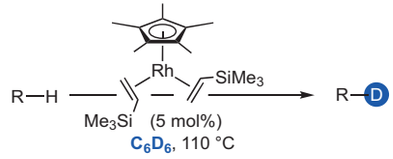
Basic process for migratory insertion /β-elimination based H/D exchange

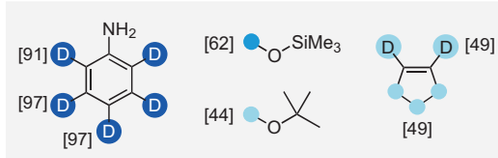
- Reversible migratory insertion / β-elimination under metal catalysis
- Preferred C-H bond cleavage based on kinetic isotope effect
- Iterative process enabled H/D exchange balance.



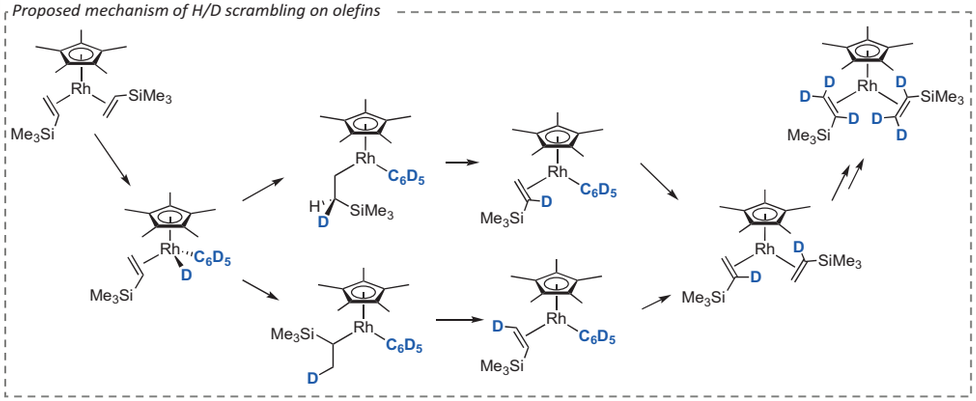
(25a) Faller, *Organometallics* **1989**, *8*, 602;
Further reading: (25b) Enders, *Organometallics* **2005**, *24*, 4774; (25c) Di Giuseppe, Castarlenas and Oro, *Chem. Eur. J.* **2014**, *20*, 8391.

H/D exchange on alkene ligands



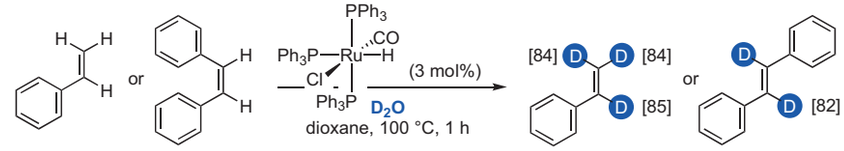


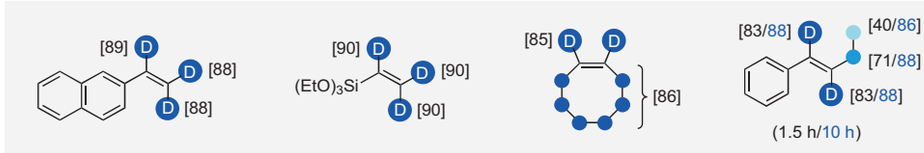
Proposed mechanism of H/D scrambling on olefins



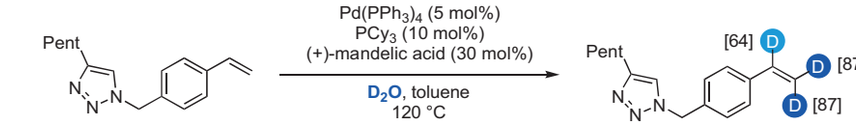
(25d) Brookhart, *J. Am. Chem. Soc.* **1999**, *121*, 4385; (25e) Brookhart, *Organometallics* **2000**, *19*, 1247.
Further reading: (25f) Brookhart, *J. Am. Chem. Soc.* **1997**, *119*, 3165; (25g) Brookhart, *J. Organomet. Chem.* **1997**, *528*, 199; (25h) Brookhart, *J. Am. Chem. Soc.* **1998**, *120*, 6965.

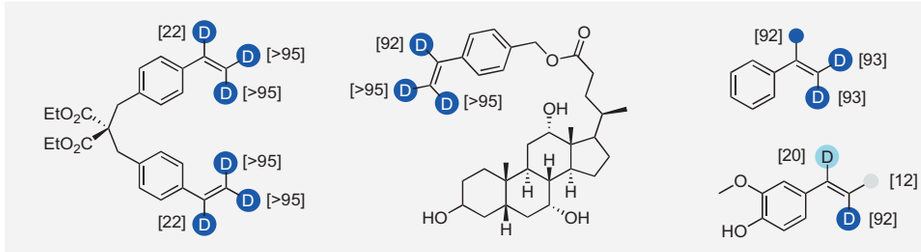
Catalytic H/D exchange of olefins





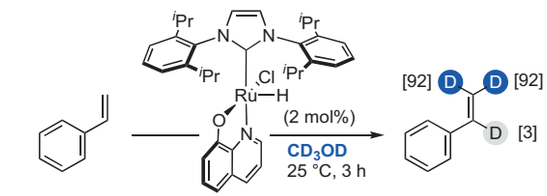
(25i) Lin and Jia, *Adv. Synth. Catal.* **2010**, *352*, 1512.

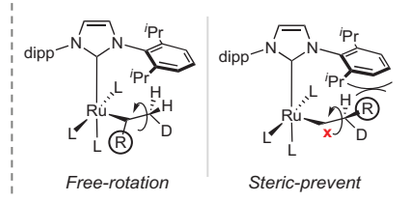




(25j) Maestri, *Synthesis* **2020**, *52*, 1762.
Further reading: (25k) Nishimura, *Org. Lett.* **2016**, *18*, 3674; (25l) Ackermann, *ChemCatChem* **2019**, *11*, 435.

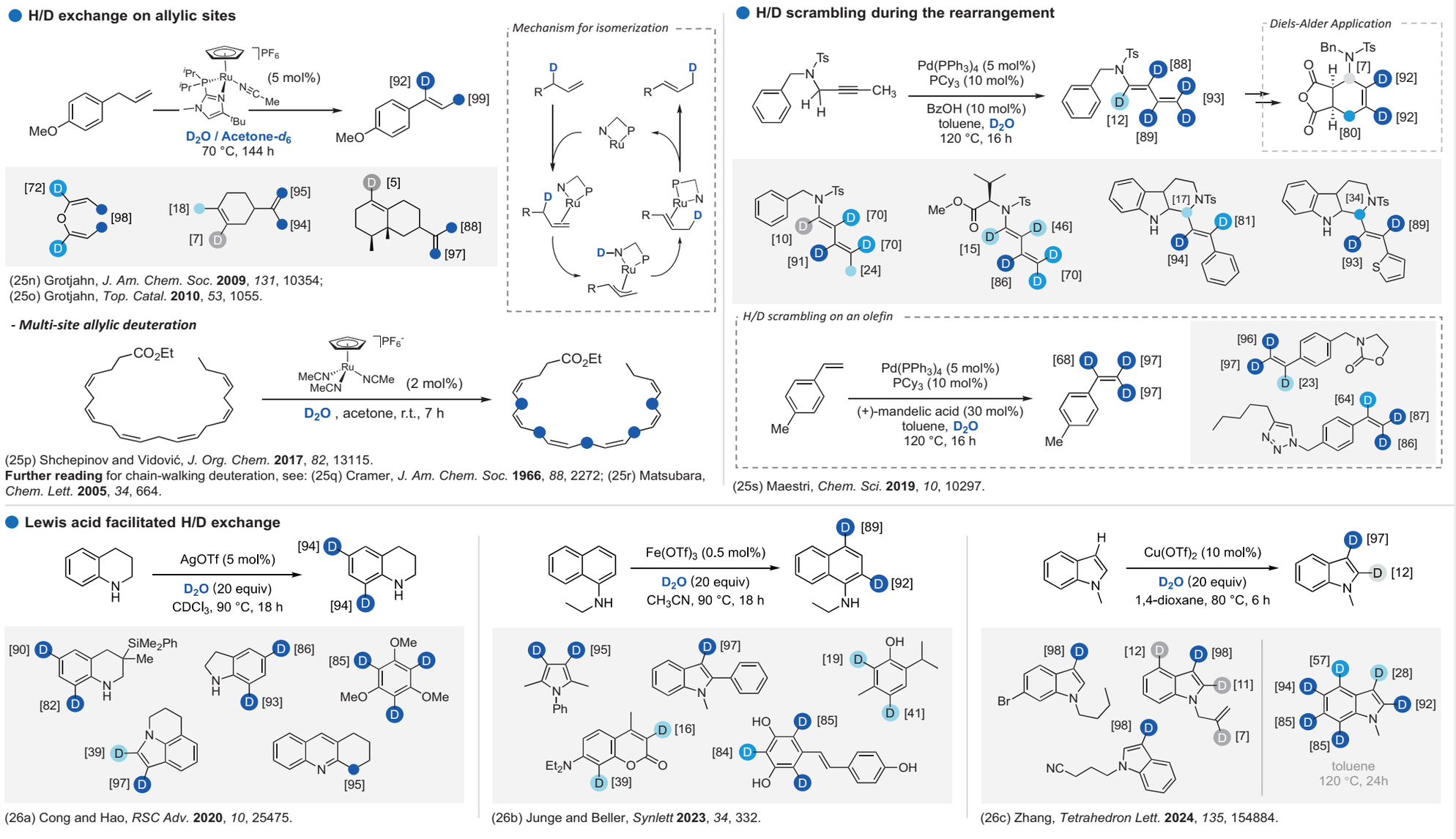
β-selective H/D exchange of olefins





(25m) Di Giuseppe, Castarlenas, and Oro, *Angew. Chem. Int. Ed.* **2011**, *50*, 3938.

Figure 17 HIE based on iterative migratory insertion/β-elimination (part 1): Deuteration of olefins[25a–m]



(25n) Grotjahn, *J. Am. Chem. Soc.* **2009**, *131*, 10354;
(25o) Grotjahn, *Top. Catal.* **2010**, *53*, 1055.

(25p) Shchepinov and Vidović, *J. Org. Chem.* **2017**, *82*, 13115.
Further reading for chain-walking deuteration, see: (25q) Cramer, *J. Am. Chem. Soc.* **1966**, *88*, 2272; (25r) Matsubara, *Chem. Lett.* **2005**, *34*, 664.

(25s) Maestri, *Chem. Sci.* **2019**, *10*, 10297.

(26a) Cong and Hao, *RSC Adv.* **2020**, *10*, 25475.

(26b) Junge and Beller, *Synlett* **2023**, *34*, 332.

(26c) Zhang, *Tetrahedron Lett.* **2024**, *135*, 154884.

Figure 18 HIE based on iterative migratory insertion/β-elimination (part 2): Deuteration of allyl groups and chain-walking deuteration.[25n–s] Miscellaneous cases of homogeneous HIE (part 1): Lewis acid catalyzed deuteration[26a–c]

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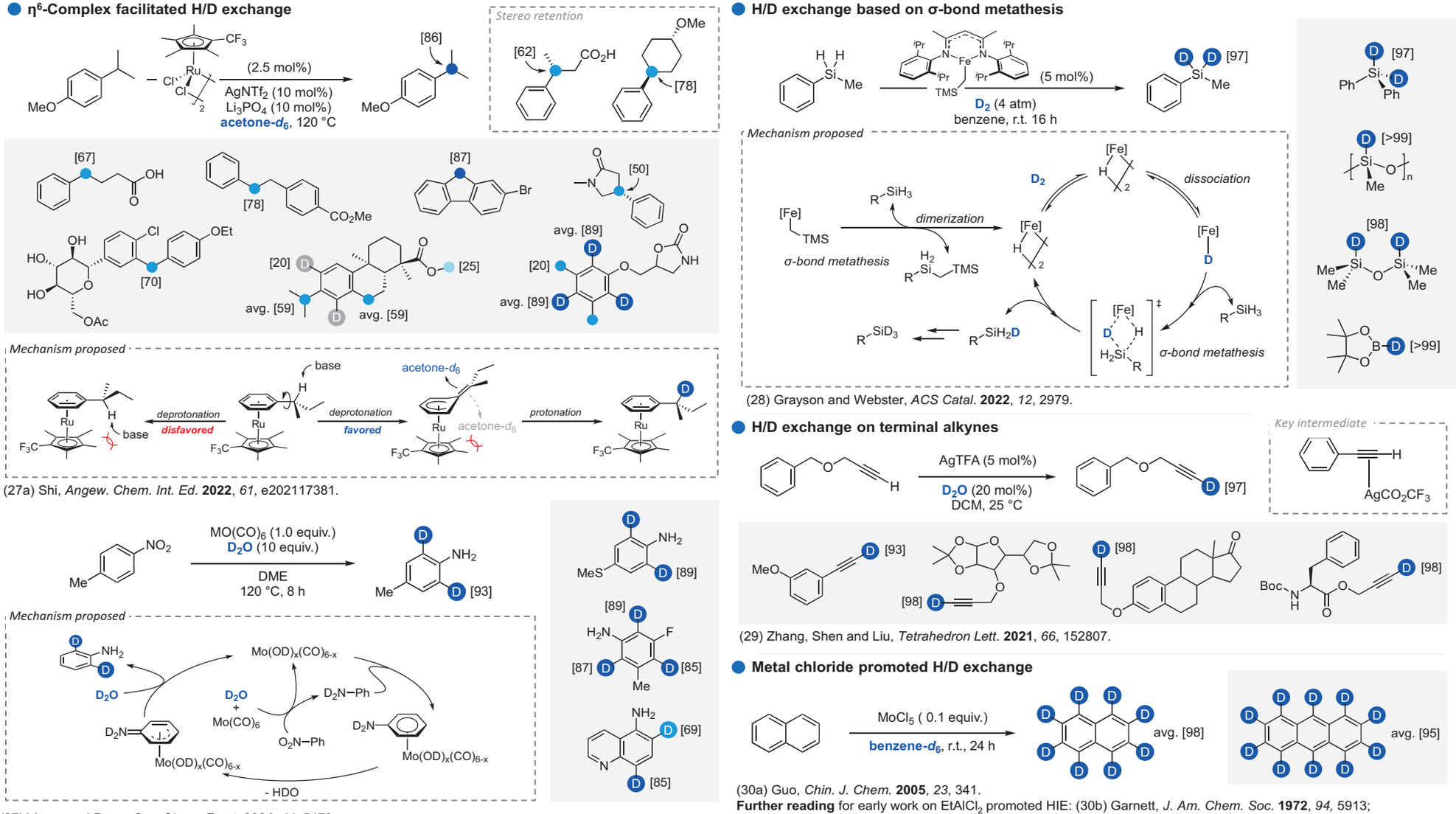

(27a) Shi, *Angew. Chem. Int. Ed.* **2022**, *61*, e202117381.

(28) Grayson and Webster, *ACS Catal.* **2022**, *12*, 2979.

(29) Zhang, Shen and Liu, *Tetrahedron Lett.* **2021**, *66*, 152807.

(27b) Lang and Peng, *Org. Chem. Front.* **2024**, *11*, 5473.

(30a) Guo, *Chin. J. Chem.* **2005**, *23*, 341.
Further reading for early work on $EtAlCl_2$ promoted HIE: (30b) Garnett, *J. Am. Chem. Soc.* **1972**, *94*, 5913; (30c) Garnett, *J. Am. Chem. Soc.* **1972**, *94*, 8632; (30d) Long, *J. Chem. Soc., Perkin Trans. 2* **1975**, 1298.

Figure 19 Miscellaneous cases of homogeneous HIE (part 2): Deuteration catalyzed by η⁶ complexes,[27a,b] σ-metathesis,[28] π-acids[29] and metal chlorides[30a–d]

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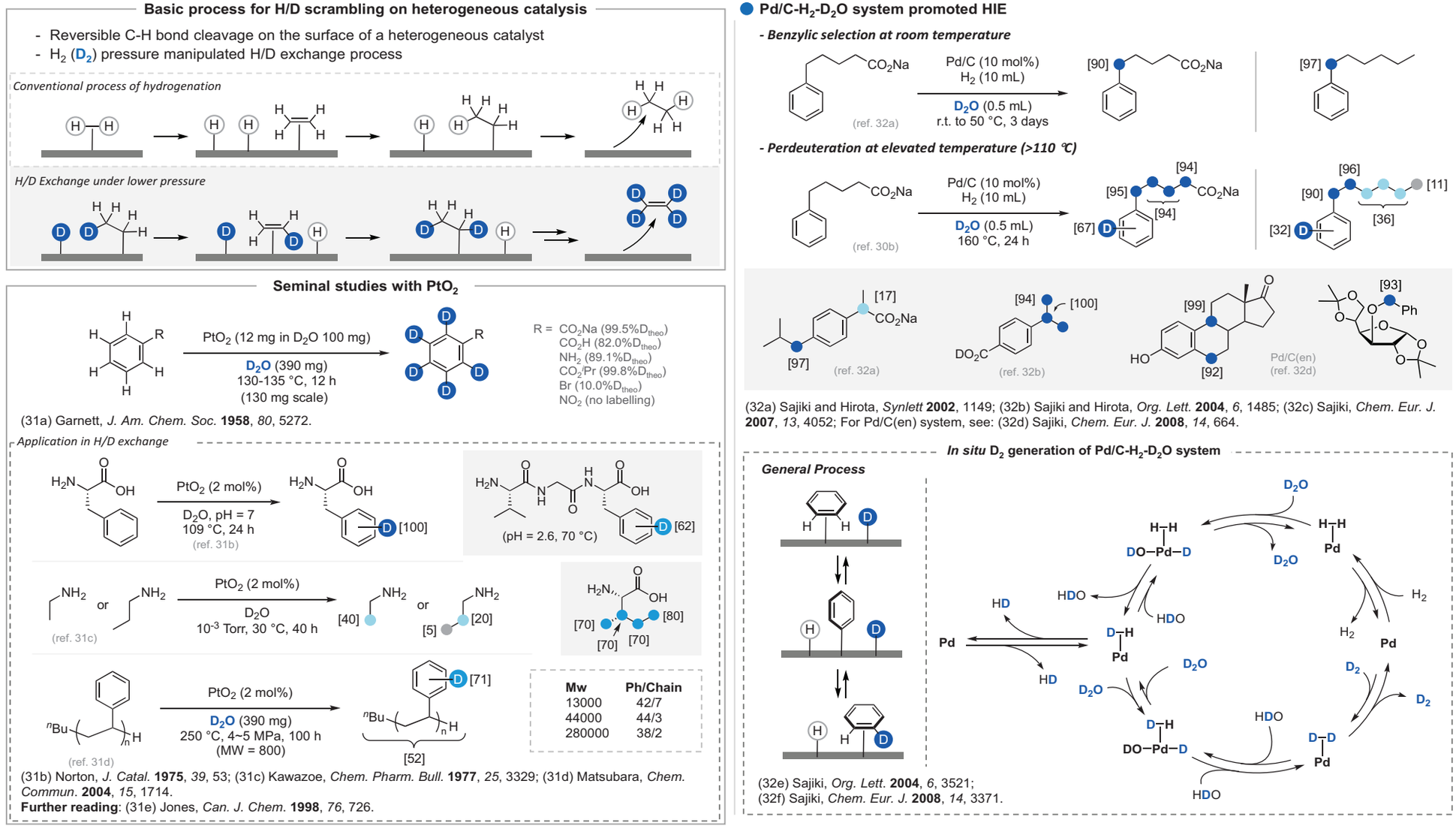

Figure 20 Heterogeneous HIE catalyzed by an active-carbon-supported metal catalyst (part 1): Seminal work with PtO_2[31a–e] and a Pd/C-H_2-D_2O system (part 1)[32a–f]

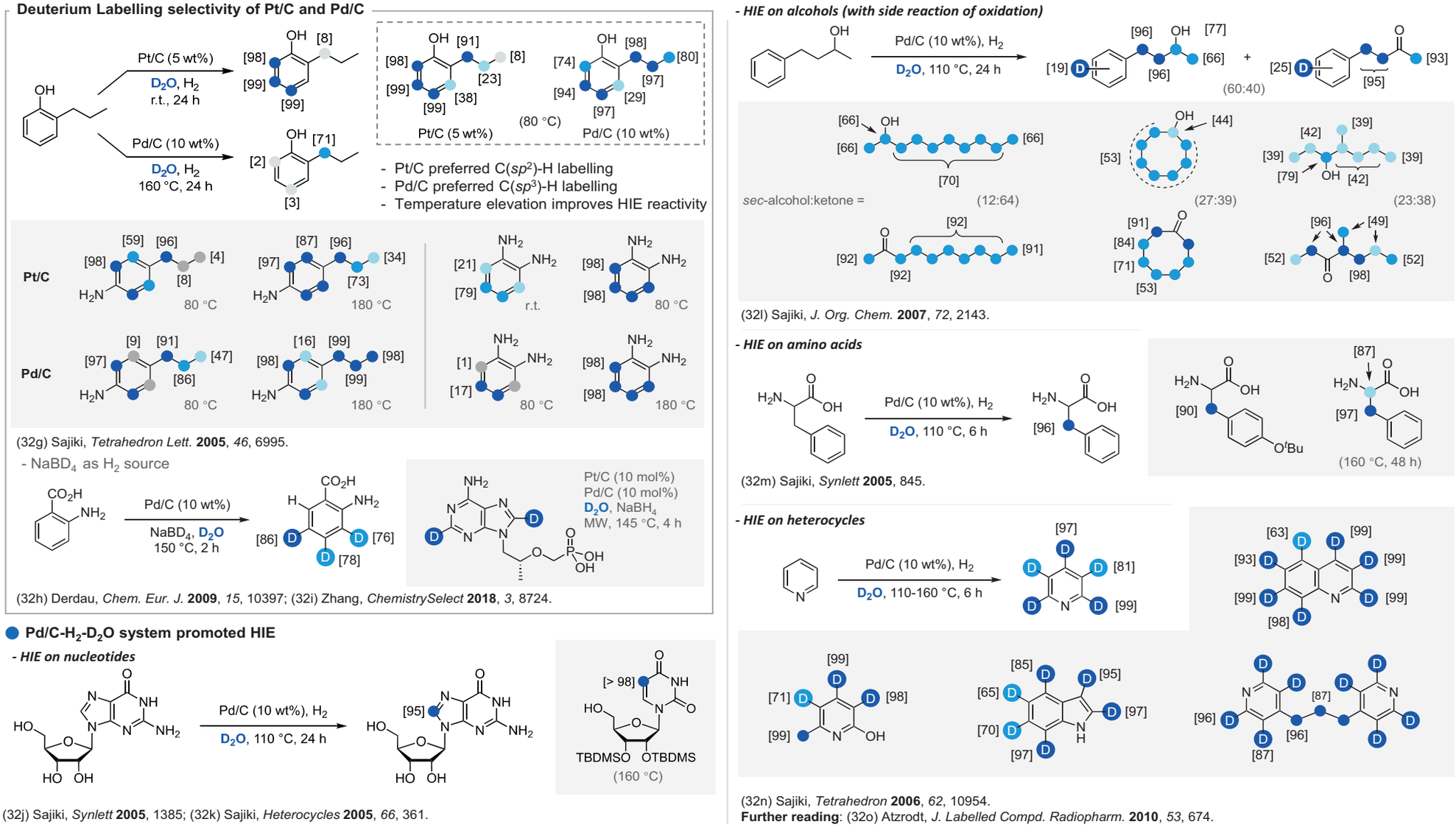

Figure 21 Heterogeneous HIE catalyzed by an active-carbon-supported metal catalyst (part 2): A Pd/C-H_2-D_2O system (part 2)[32g–o]

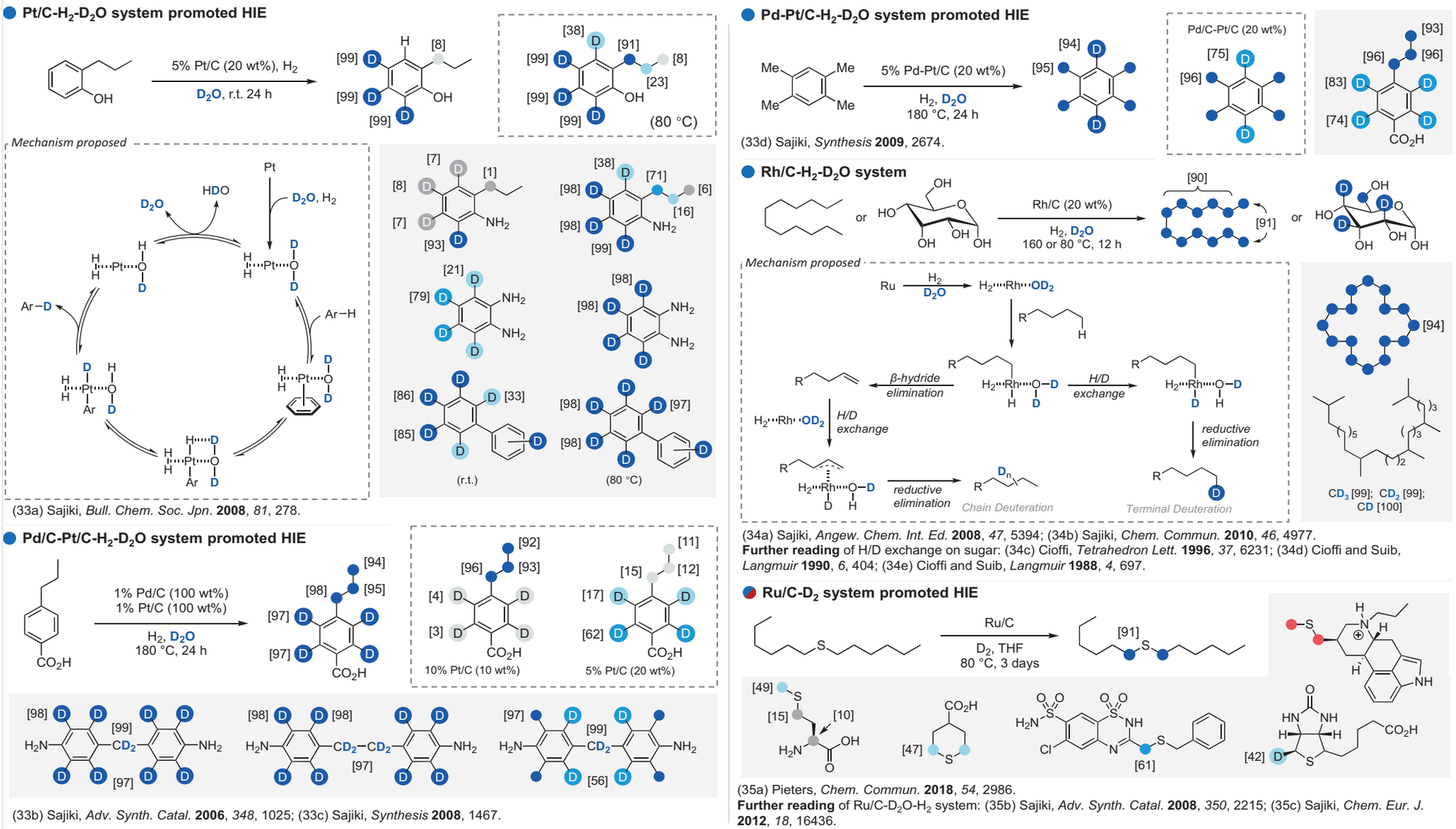

Figure 22 Heterogeneous HIE catalyzed by an active-carbon-supported metal catalyst (part 3): Further applications of M/C-H_2-D_2O systems, Pt/C,[33a–d] Rh/C[34a–e] and Ru/C[35a–c]

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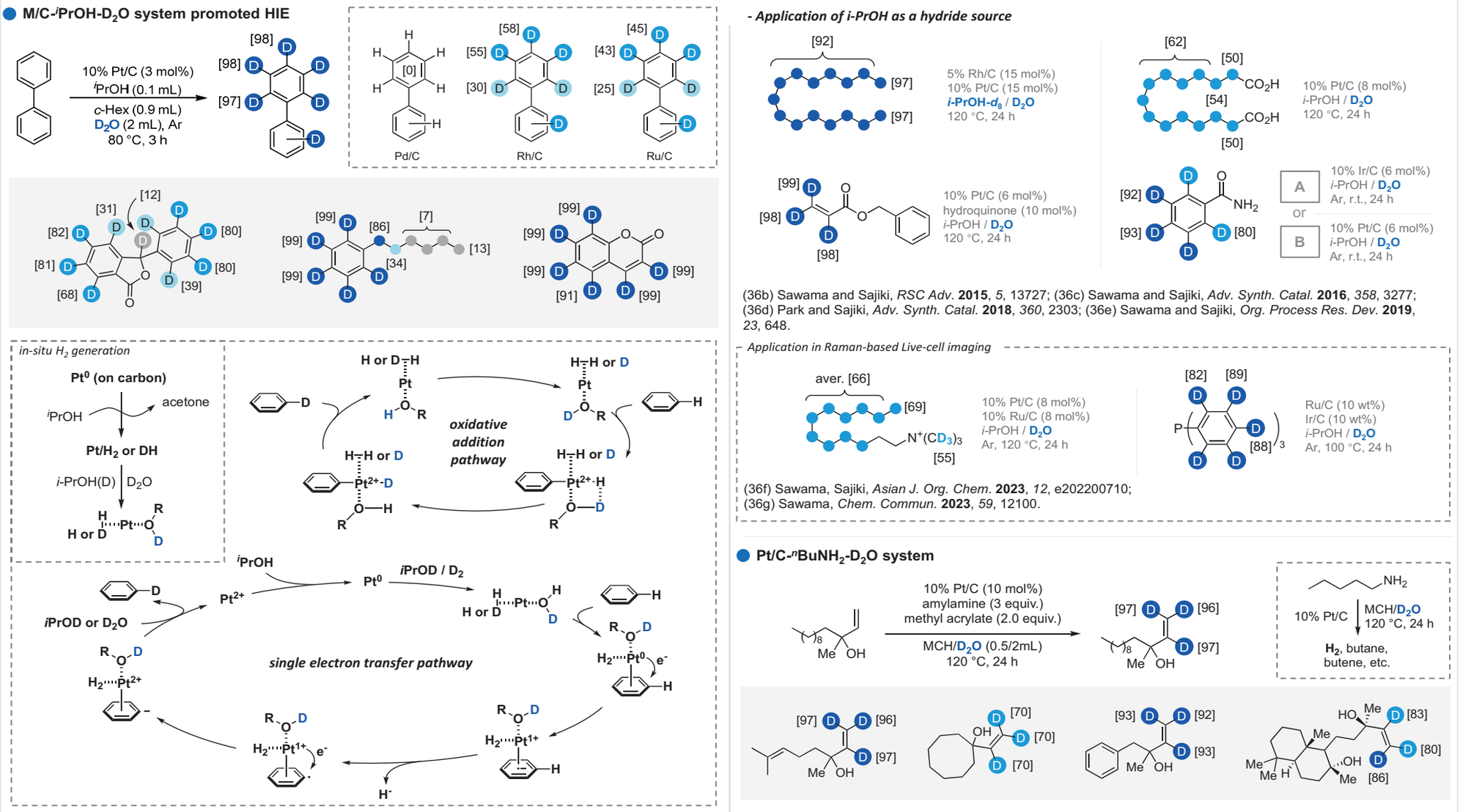

(36a) Sajiki, *Adv. Synth. Catal.* **2013**, *355*, 1529.

(36b) Sawama and Sajiki, *RSC Adv.* **2015**, *5*, 13727; (36c) Sawama and Sajiki, *Adv. Synth. Catal.* **2016**, *358*, 3277; (36d) Park and Sajiki, *Adv. Synth. Catal.* **2018**, *360*, 2303; (36e) Sawama and Sajiki, *Org. Process Res. Dev.* **2019**, *23*, 648.

(36f) Sawama, Sajiki, *Asian J. Org. Chem.* **2023**, *12*, e202200710; (36g) Sawama, *Chem. Commun.* **2023**, *59*, 12100.

(37) Park, Sajiki, *Org. Chem. Front.* **2022**, *9*, 1986.

Figure 23 Heterogeneous HIE catalyzed by an active-carbon-supported metal catalyst (part 4): M/C-^{i}PrOH-D_2O[36a–g] and Pt/C-^{n}BuNH$_2$-D_2O[37] systems

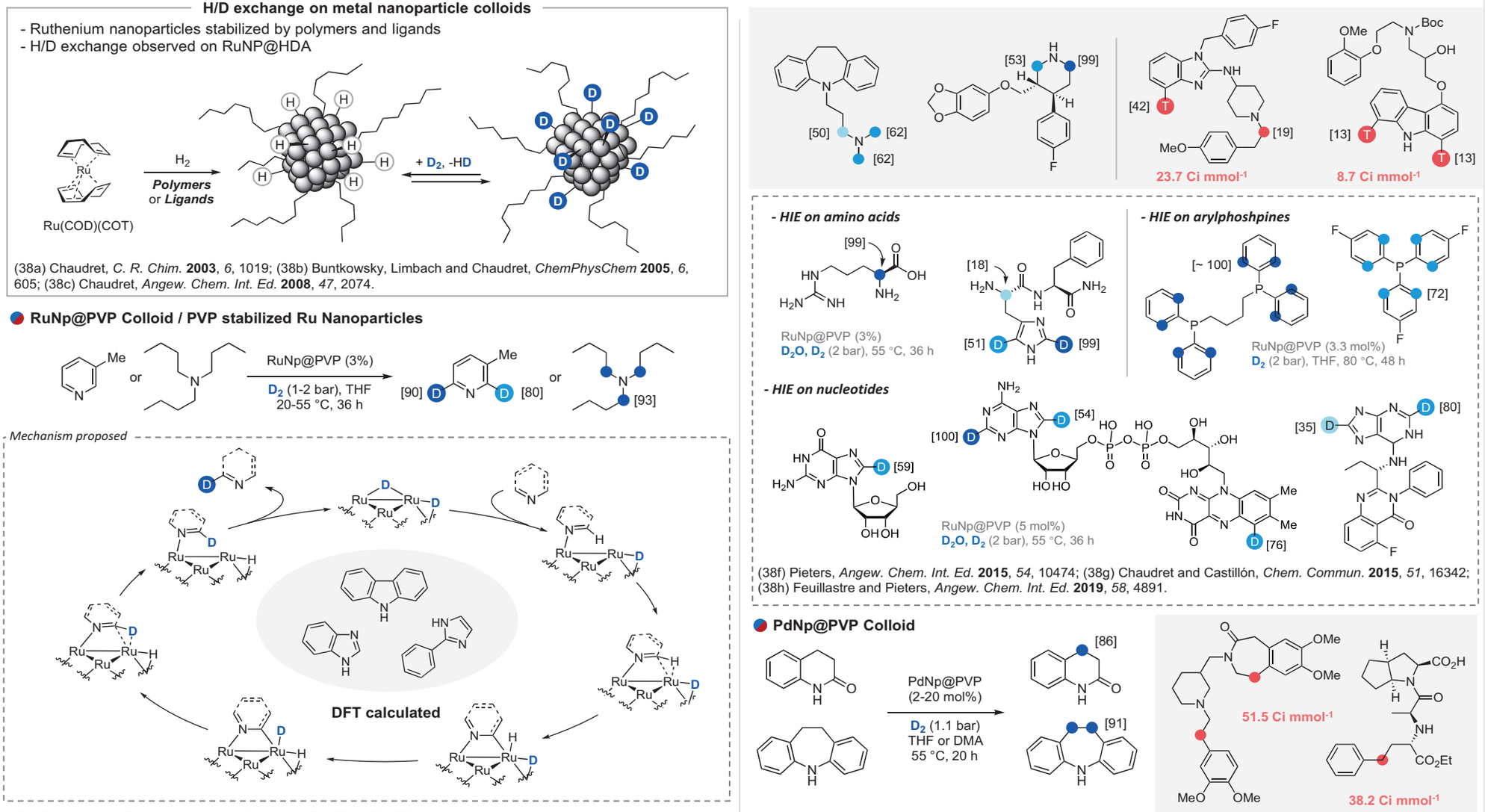

Figure 24 Heterogeneous HIE catalyzed by metal nanoparticles (part 1): PVP-supported metal nanoparticles[38a–j]

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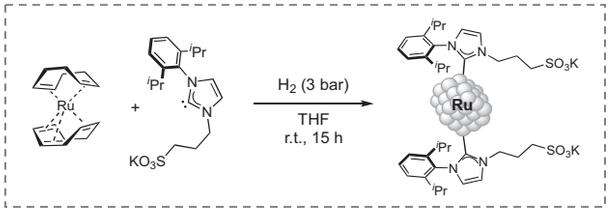
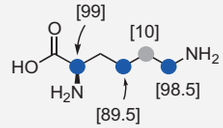
NHC Stabilized Nanoparticles

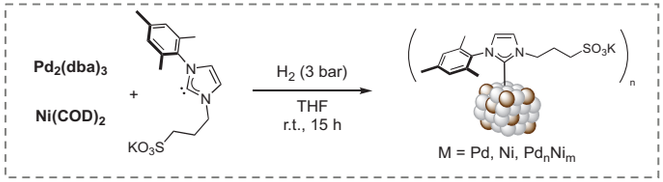
- Improve the solubility and stability of nanoparticles

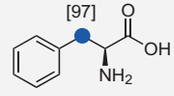




8% RuNP, D_2 (2 bar)
D_2O, pH = 13.2
55 °C, 42 h

(39a) Martínez-Prieto and Chaudret, *Chem. Commun.* **2017**, *53*, 5850.

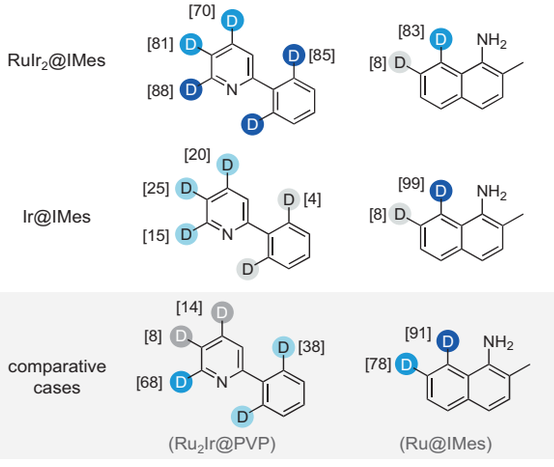


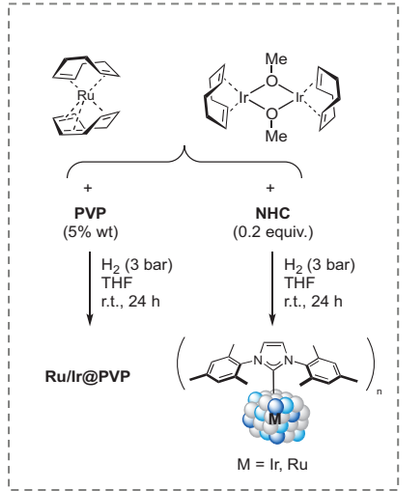


$Pd_{70}Ni_{30}$@IMesPrSO$_3$ (4 mol%)
D_2O (pH = 8-9), D_2 (2 bar)
55 °C, 48 h

(39b) Baquero, *Chem. Commun.* **2023**, *59*, 1062.

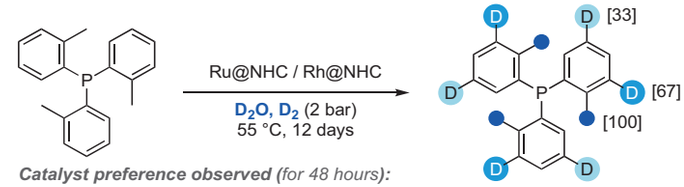
- Ligand enhanced regioselectivity of nanoparticles



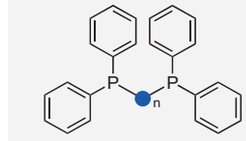


(39c) Mencia, Baquero and Chaudret, *Organometallics* **2022**, *41*, 3313.

- Ligand shifted regioselectivity of nanoparticles



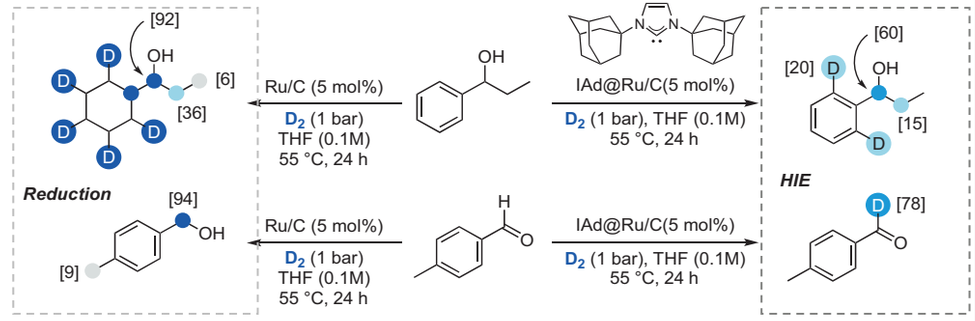
***Catalyst preference observed** (for 48 hours):*
Ru@NHC (D_{Ar}:D_{Me} = 47:53); Rh@NHC (D_{Ar}:D_{Me} = 17:83)



n = 1D (13%); 2D (86%)

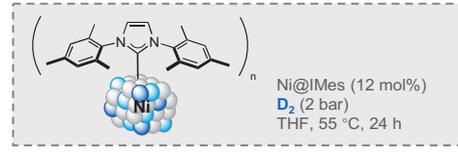
(39d) Carbó, Godard and Castillon, *Inorg. Chem.* **2023**, *62*, 4570.

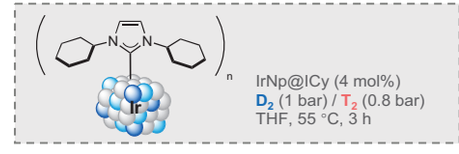
- Reactivity regulation on Ru/C

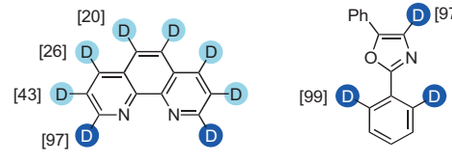


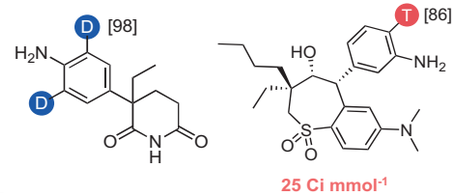
(39e) Pieters, *Angew. Chem. Int. Ed.* **2020**, *59*, 20879.

- Further applications







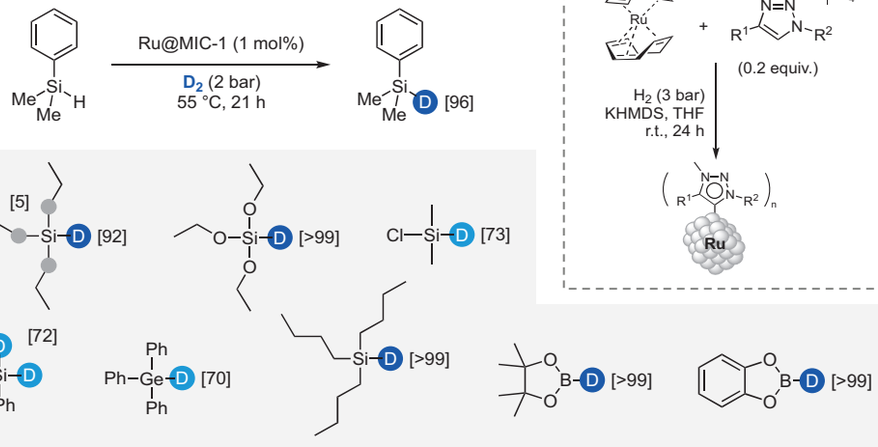


25 Ci mmol^{-1}

(39f) Asensio, Tricard and Chaudret, *Nanoscale*, **2020**, *12*, 15736;
(39g) Pieters, Chaudret and Derdau, *Angew. Chem. Int. Ed.* **2020**, *59*, 3517.

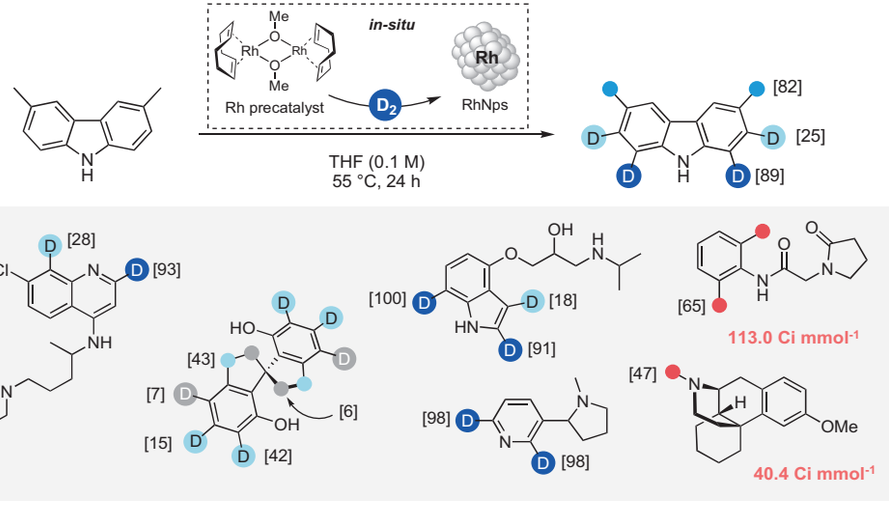
Figure 25 Heterogeneous HIE catalyzed by metal nanoparticles (part 2): NHC-supported metal nanoparticles (part 1)[39a–g]

Ru@MIC promoted HIE on Group XIV elements and borane



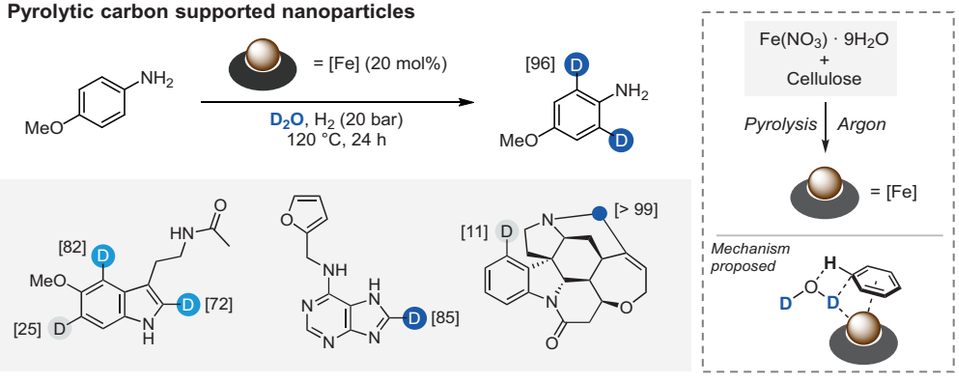
(39h) Rendón, Lara and Suárez, *Nanoscale* **2023**, *15*, 14488.

In situ generated Ru-nanoparticle catalyzed HIE

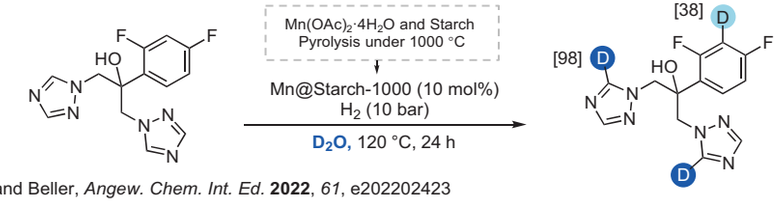


(39i) Feuillastre and Pieters, *JACS Au* **2022**, *2*, 801.

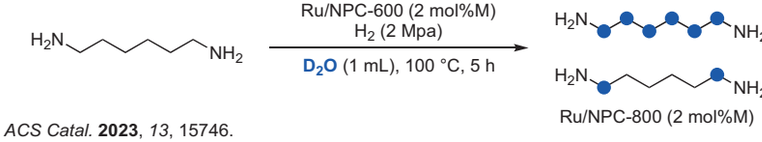
Pyrolytic carbon supported nanoparticles



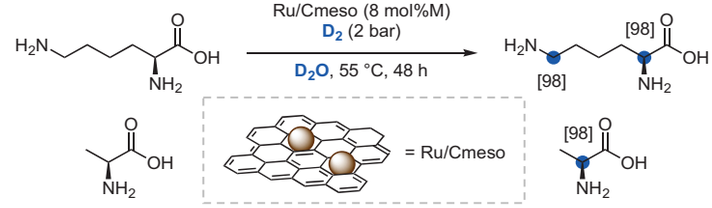
(40a) Brückner, Lei and Beller, *Nat. Chem.* **2022**, *14*, 344.



(40b) Junge and Beller, *Angew. Chem. Int. Ed.* **2022**, *61*, e202202423



(40c) Wang, *ACS Catal.* **2023**, *13*, 15746.



(40d) Chaudret, *Catal. Sci. Technol.* **2024**, *14*, 4904.
Further reading: (40e) Wang, *ChemSusChem* **2023**, *16*, e202202395; (40f) Shao and Wang, *Asian J. Org. Chem.* **2023**, *12*, e202200662.

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

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Conflict of Interest

The authors declare no conflict of interest.

Funding Information

Financial support from the National Natural Science Foundation of China [22308307 (Z.-J.J.) and 22001257 (J.F.B.)], the Natural Science Foundation of Ningbo Municipality [202003N4310 (Z.-J.J.)], and the Ningbo Municipal Bureau of Science and Technology under the CM2025 Programme [2020Z092 (Z.G.)] is acknowledged. J.F.B. thanks the NingboTech University Start-up Foundation (2022A229G).

Acknowledgment

We are grateful to Professor Bencan Tang of the University of Nottingham Ningbo China for constructive discussions, and to current and former members of the Gao group who have contributed to the development of this field. We also thank Ningbo Cuiying Chemical Technology Co. Ltd. for their continuous support of our research in this field.

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