Radical cascade reactions triggered by single electron transfer

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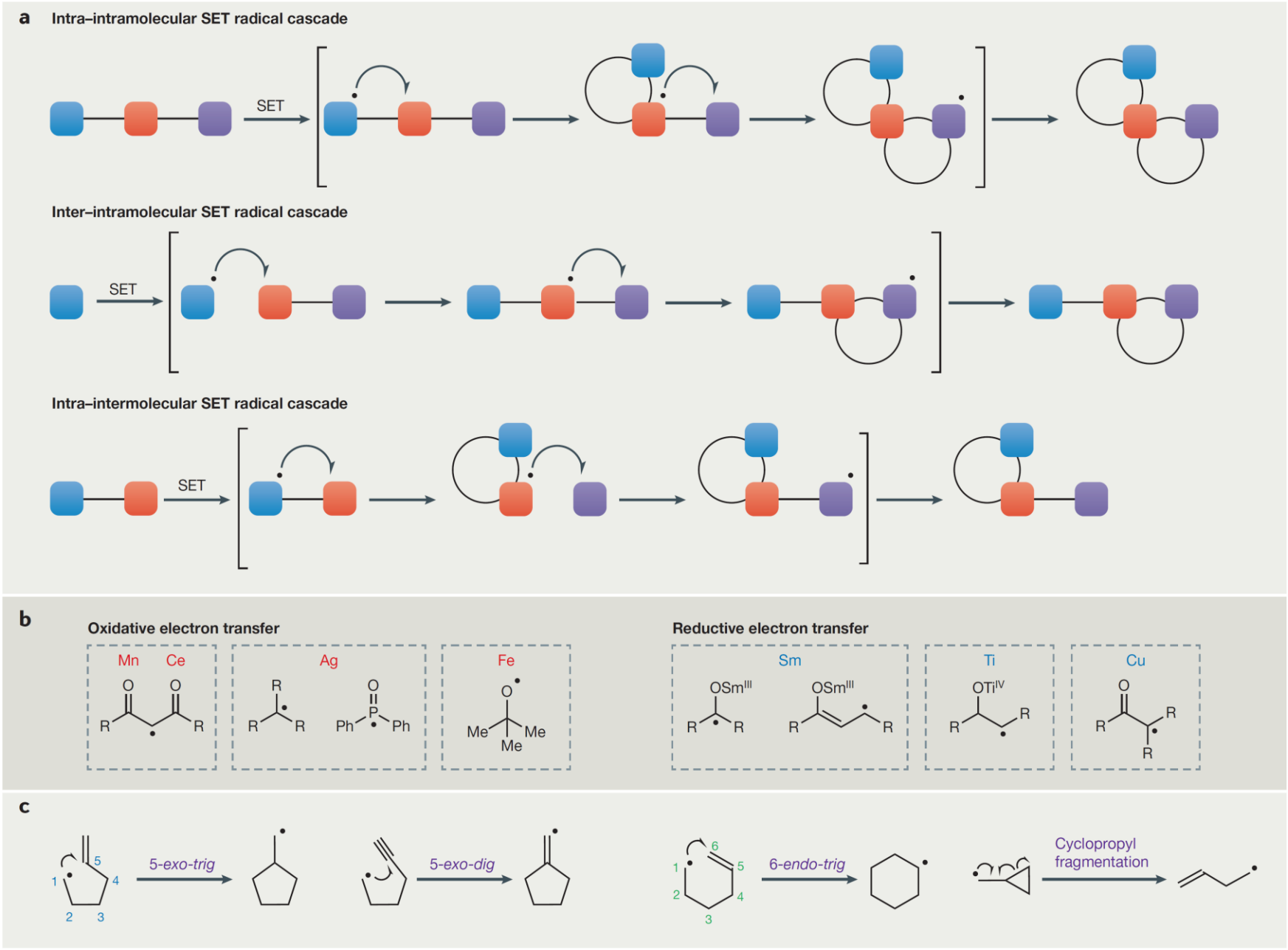
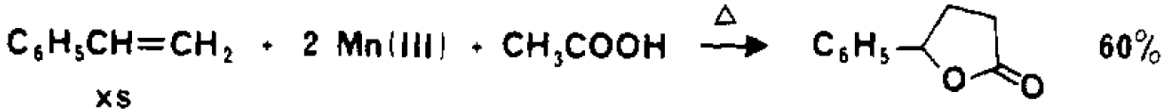
Introduction



Oxidative SET radical cascades

Manganese-mediated radical cascades- Total synthesis of limonin



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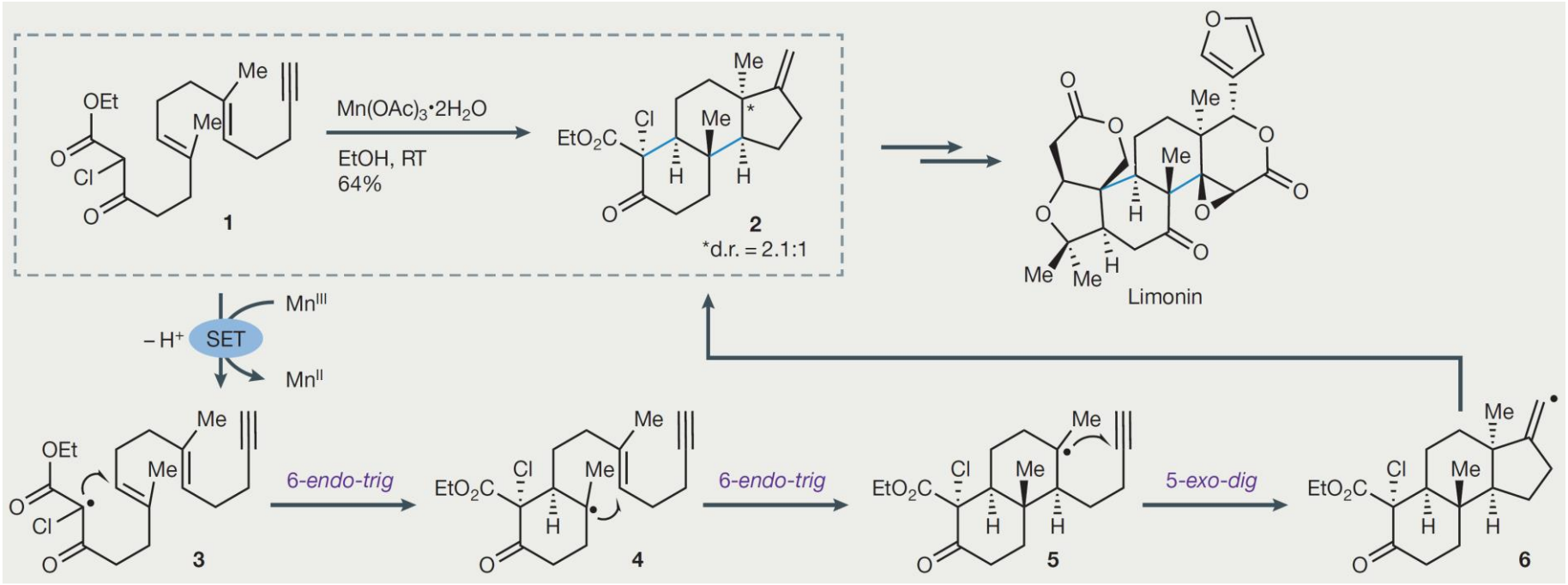

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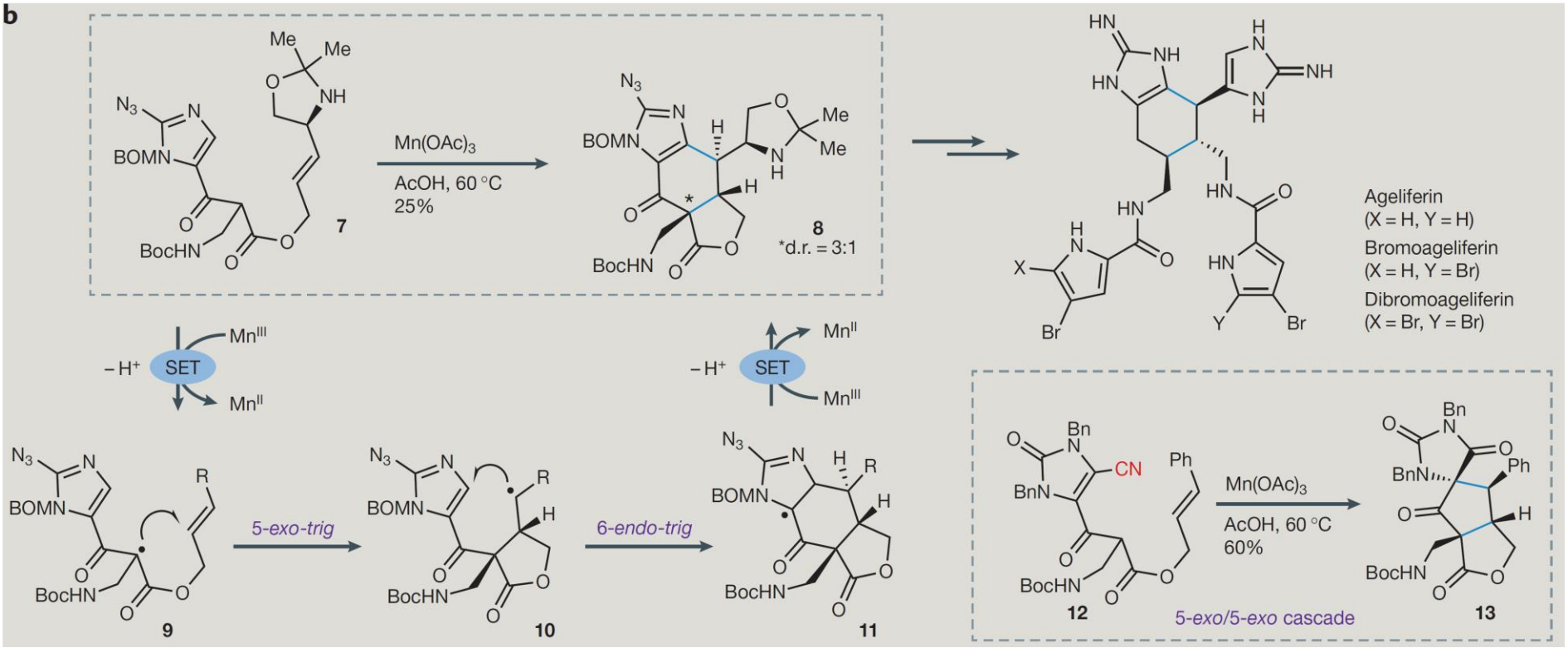
Oxidative SET radical cascades

Manganese-mediated radical cascades- Biomimetic route for construction of the [4+2] and [3+2] core skeletons of dimeric pyrrole-imidazole alkaloids and asymmetric synthesis of ageliferins



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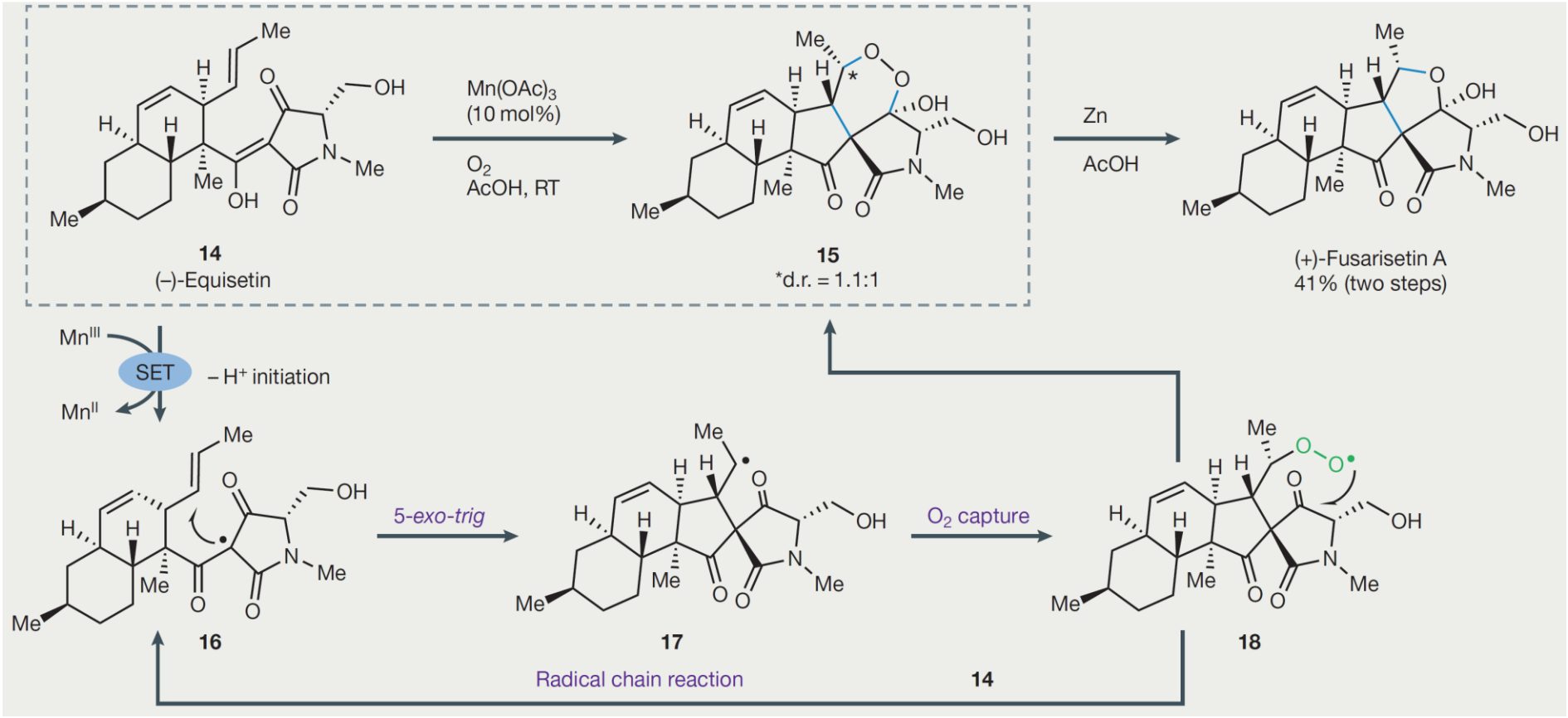
Oxidative SET radical cascades

Manganese-mediated radical cascades-Asymmetric synthesis and biosynthetic implications of (+)-fusarisetin A.



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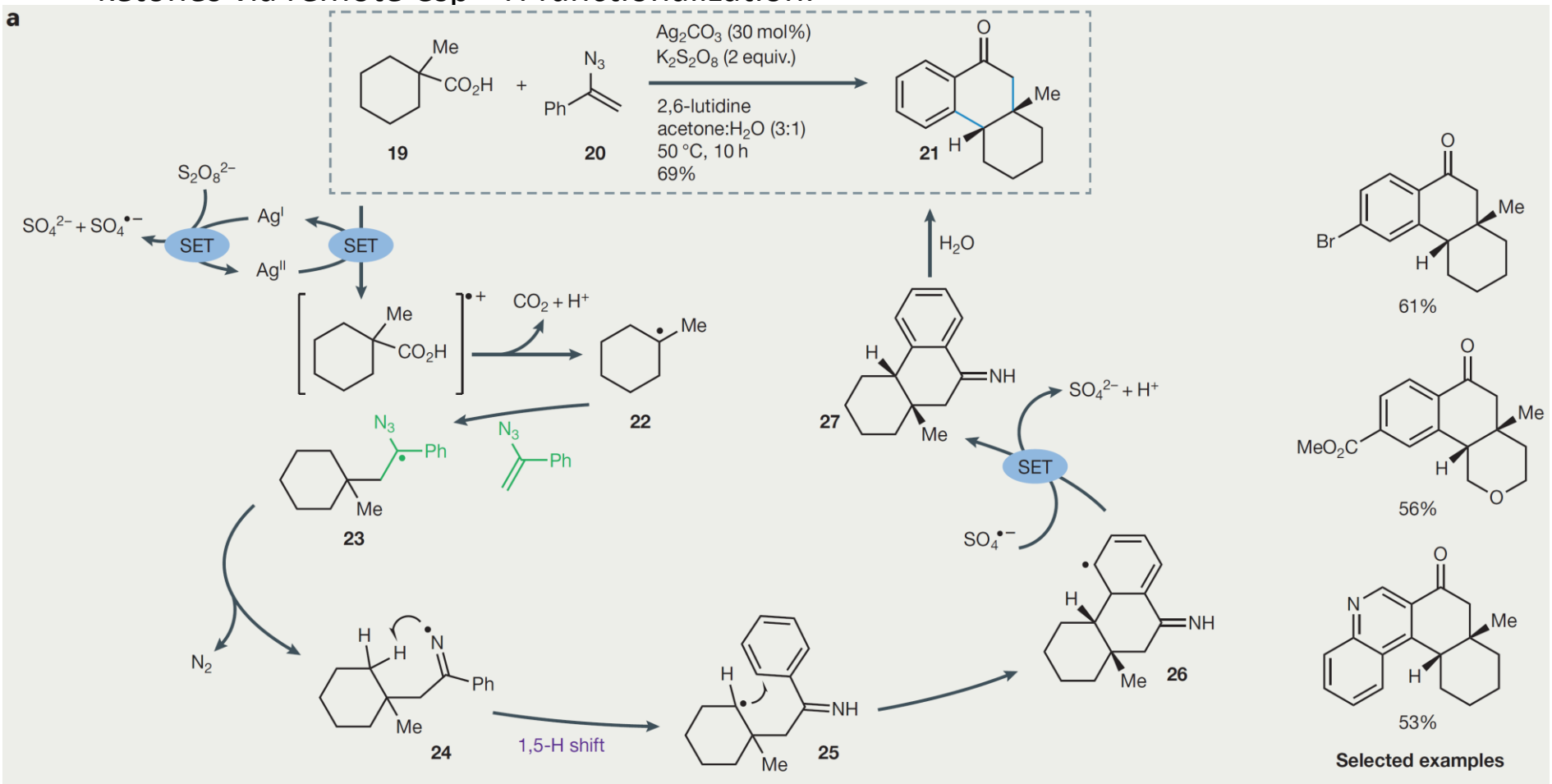
Oxidative SET radical cascades

Silver-mediated radical cascades-Expeditious diastereoselective synthesis of elaborated ketones via remote Csp^3–H functionalization.



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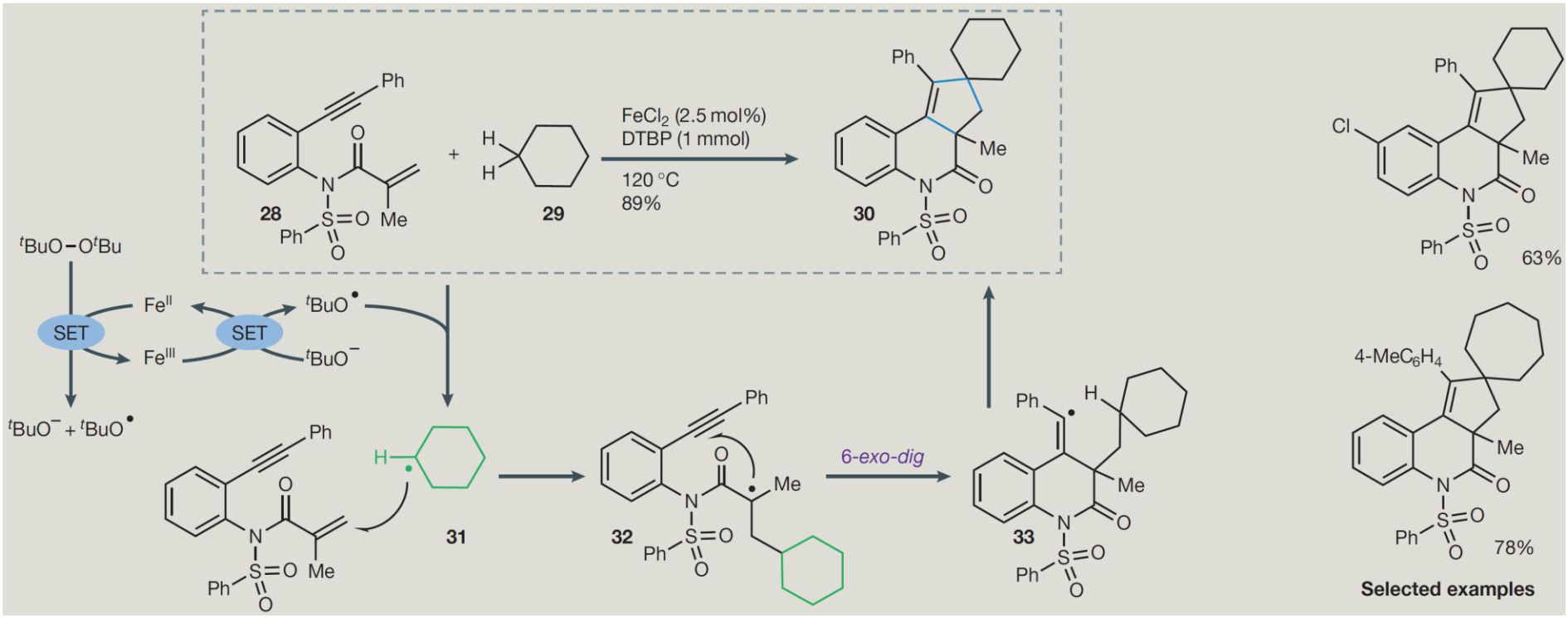
Oxidative SET radical cascades

Iron-mediated radical cascades-Catalytic dual 1,1-H-abstraction/ insertion for domino spirocyclizations.



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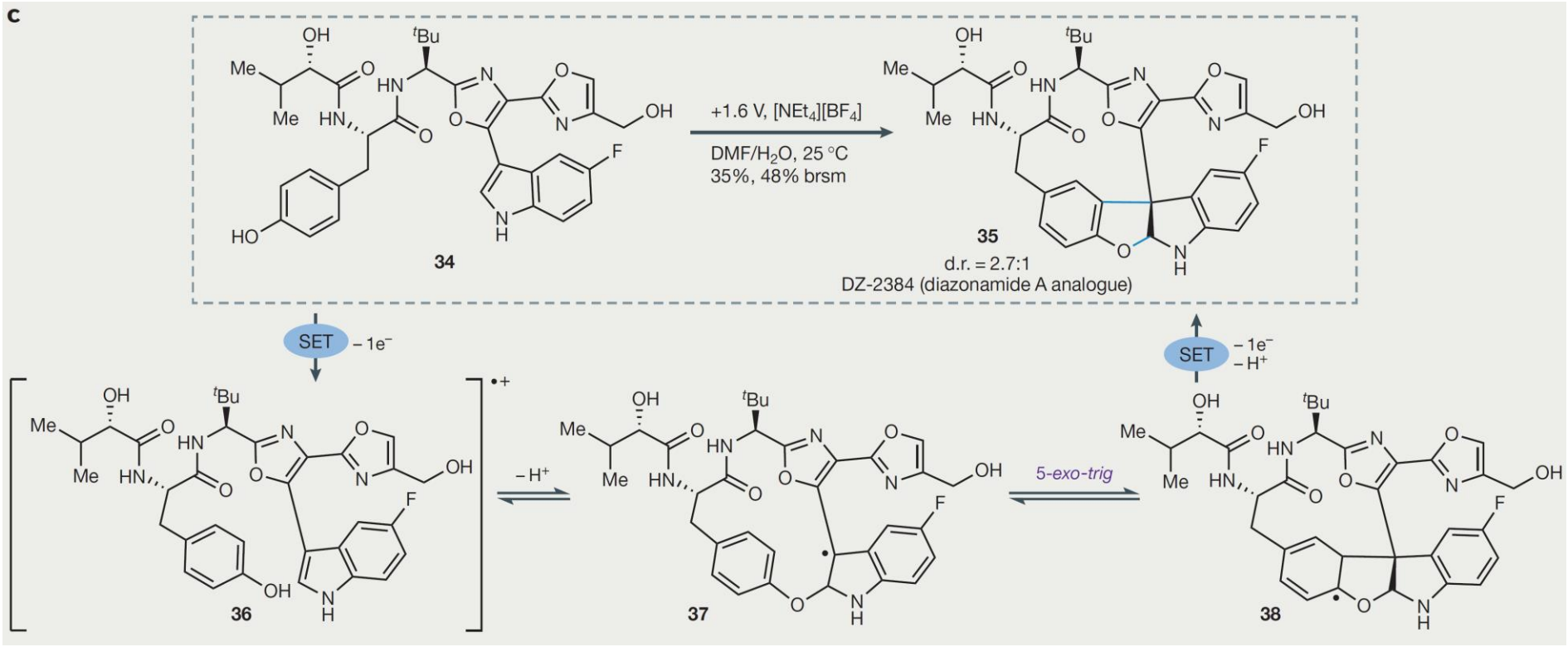
Oxidative SET radical cascades

Electrochemically mediated radical cascades-Electrolytic macrocyclizations: scalable synthesis of a diazonamide-based drug development candidate.



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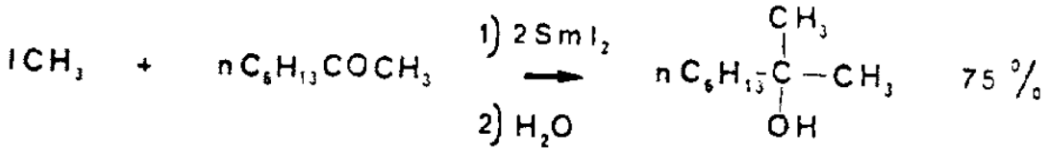
Reductive SET radical cascades

Samarium-mediated radical cascades- Total synthesis of (+)-crotogoudin.



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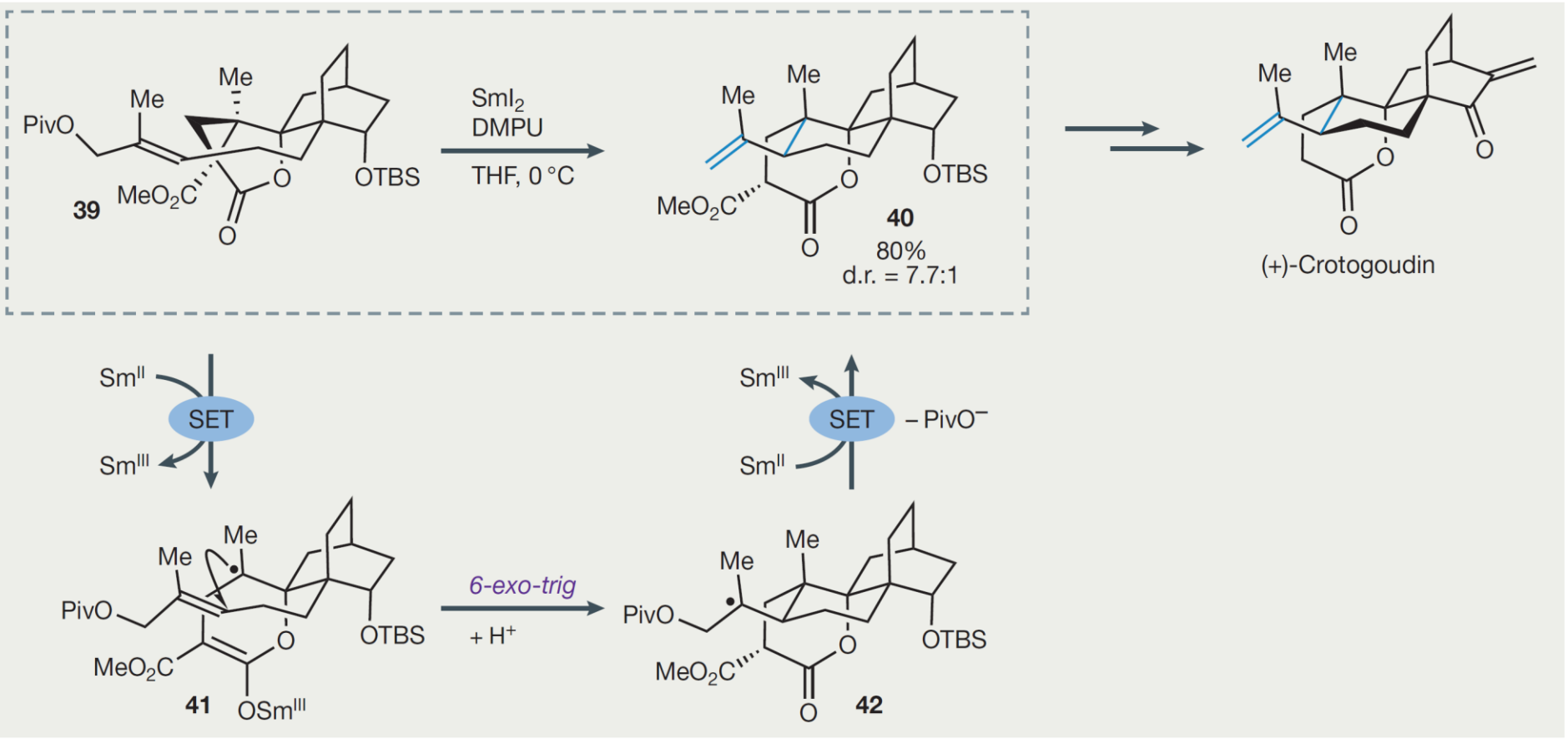

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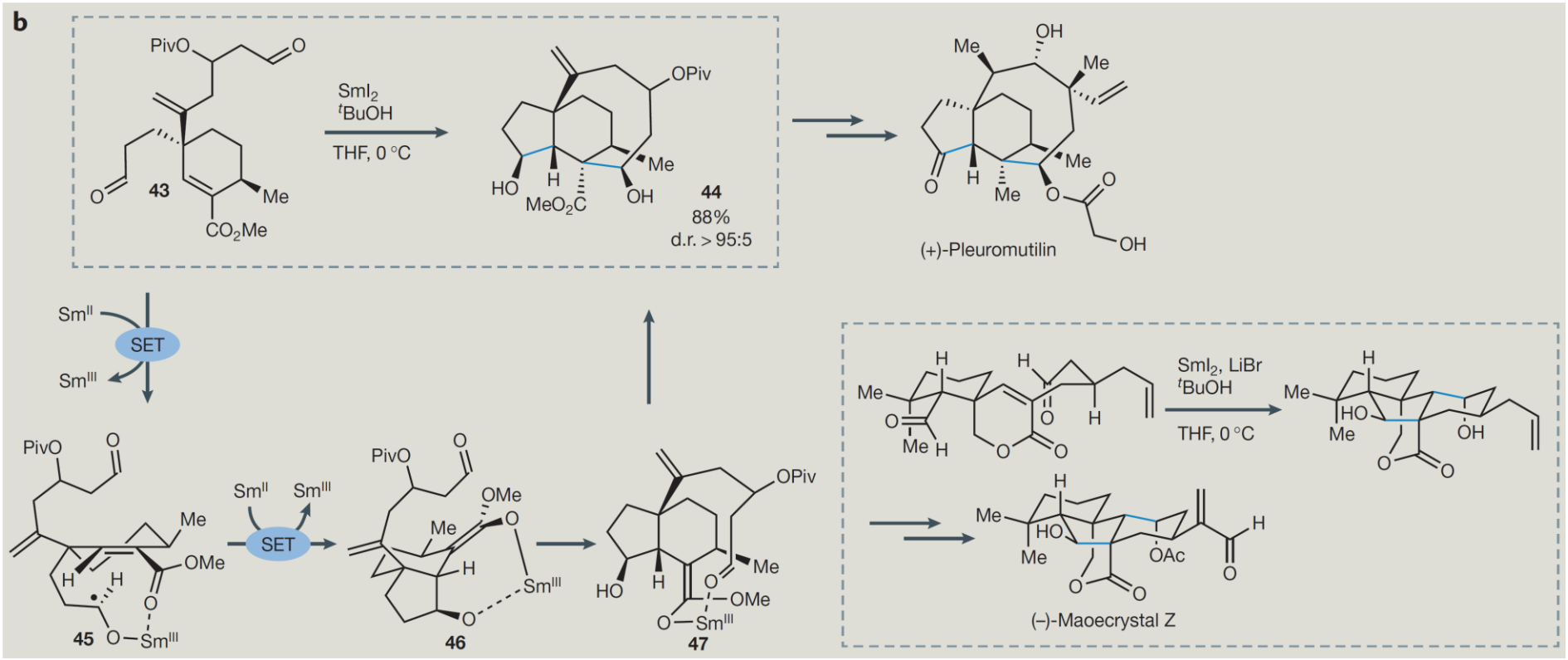
Reductive SET radical cascades

Samarium-mediated radical cascades-Total synthesis of (+)-pleuromutilin



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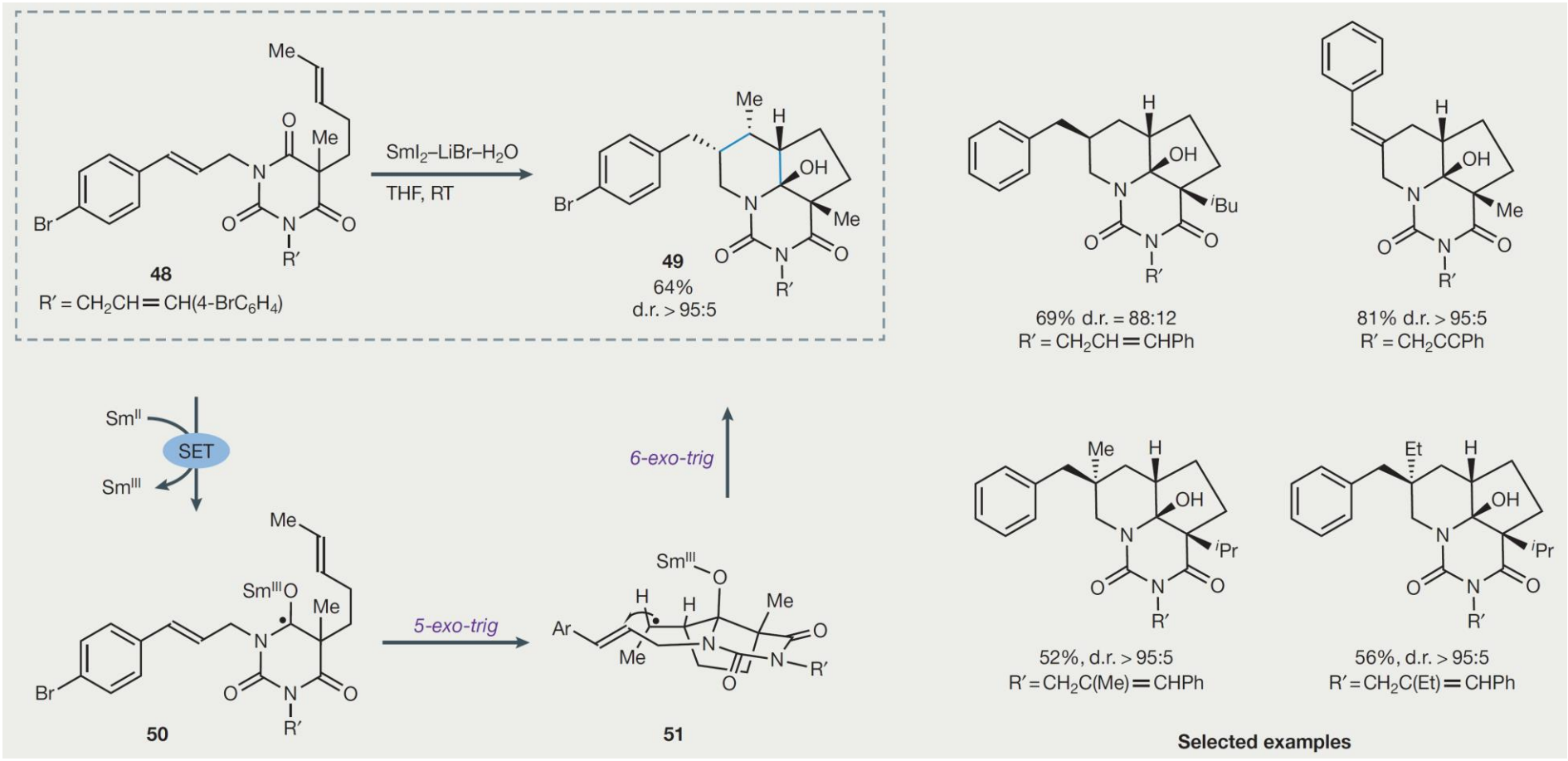
Reductive SET radical cascades

Samarium-mediated radical cascades- Radical–radical cyclization cascades of barbiturates triggered by electron-transfer reduction of amide-type carbonyls.



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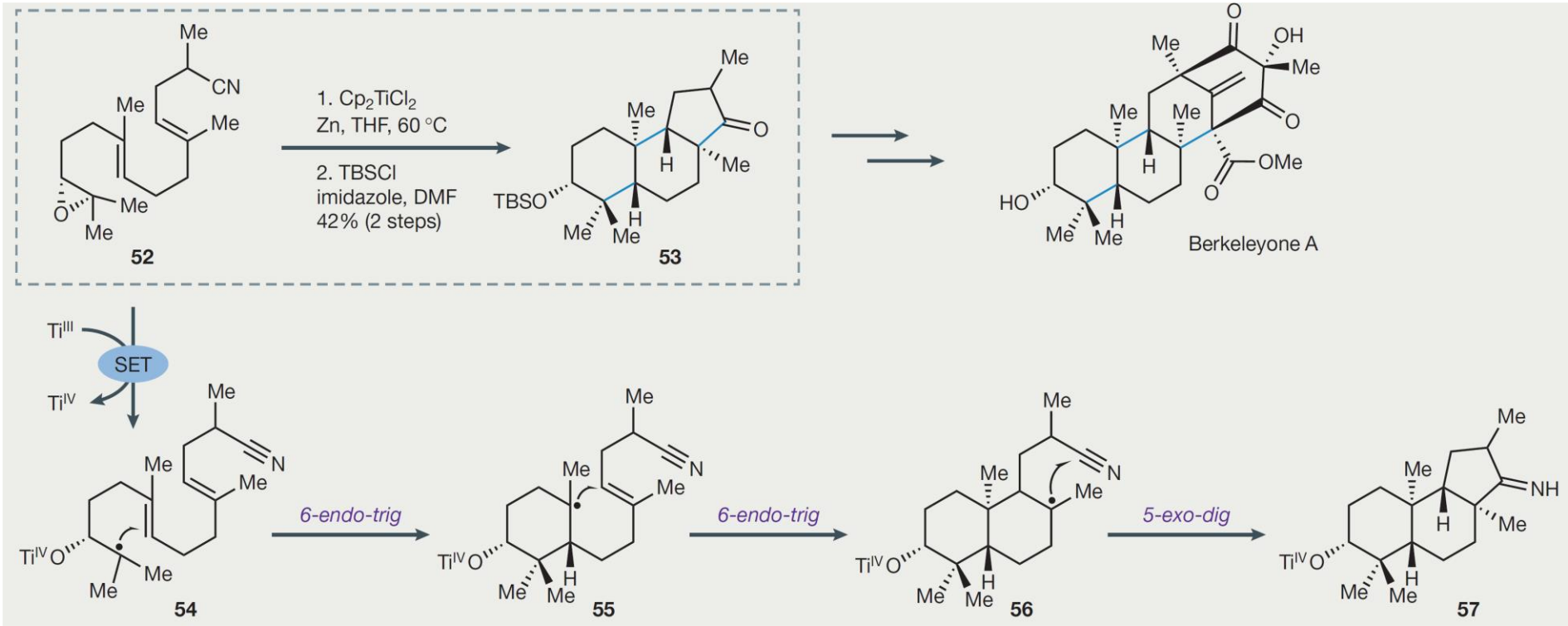
Reductive SET radical cascades

Titanium-mediated radical cascades-Annulative methods enable a total synthesis of the complex meroterpene berkeleyone



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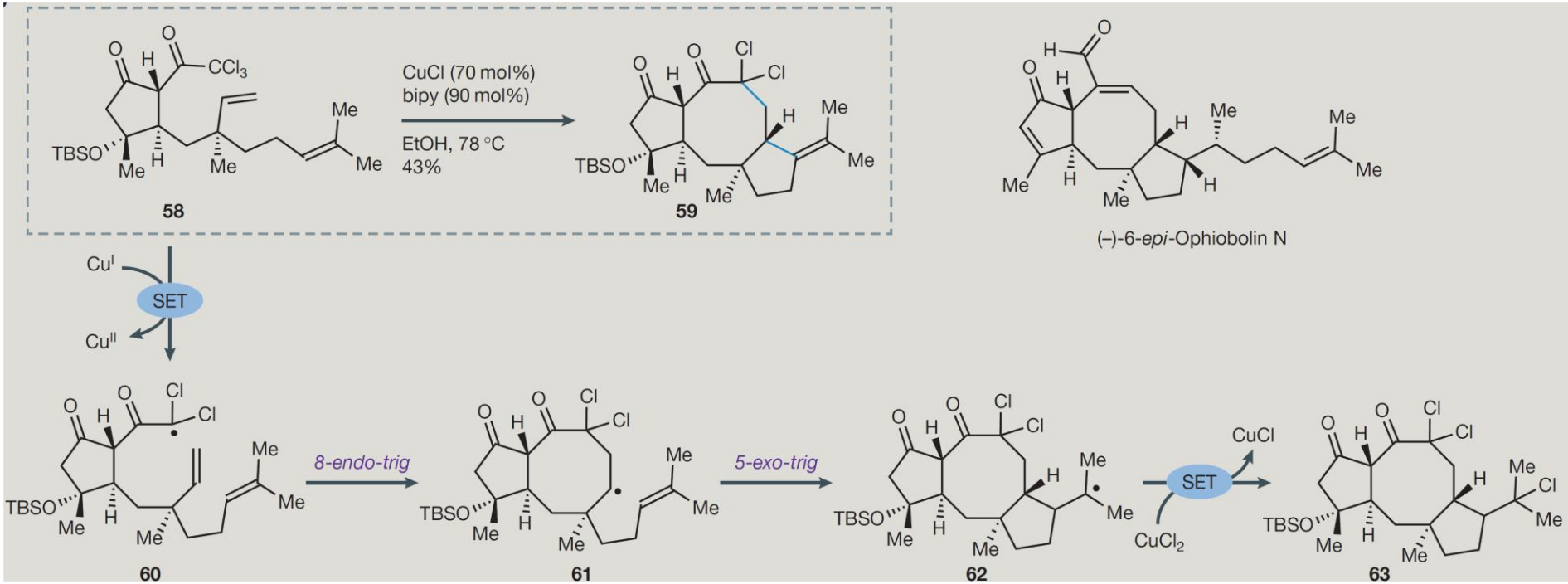
Reductive SET radical cascades

Copper-mediated radical cascades- Enantioselective synthesis of an ophiobolin sesterterpene via a programmed radical cascade.



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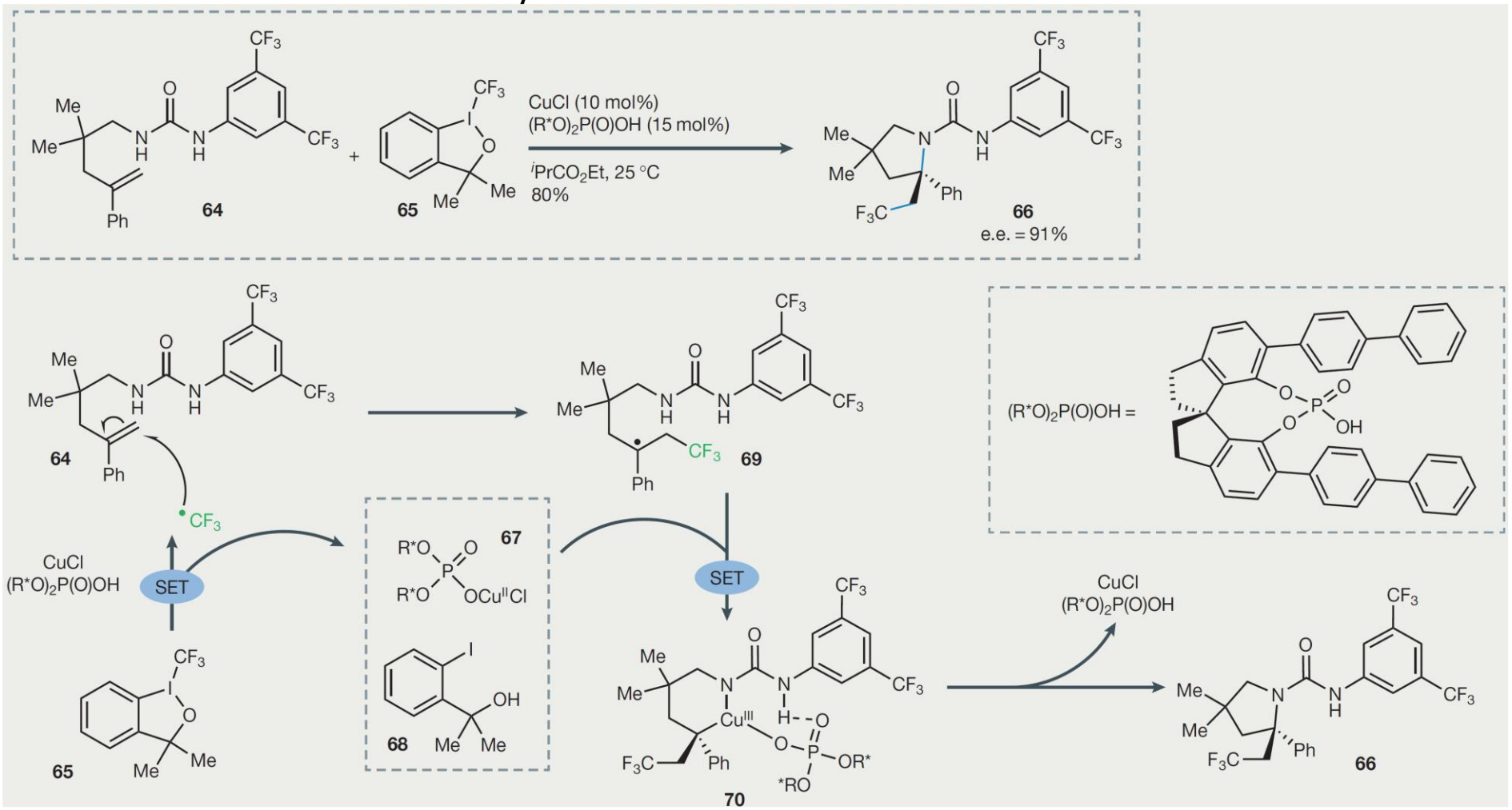
Reductive SET radical cascades

Copper-mediated radical cascades- A dual-catalytic strategy to direct asymmetric radical aminotrifluoromethylation of alkenes.



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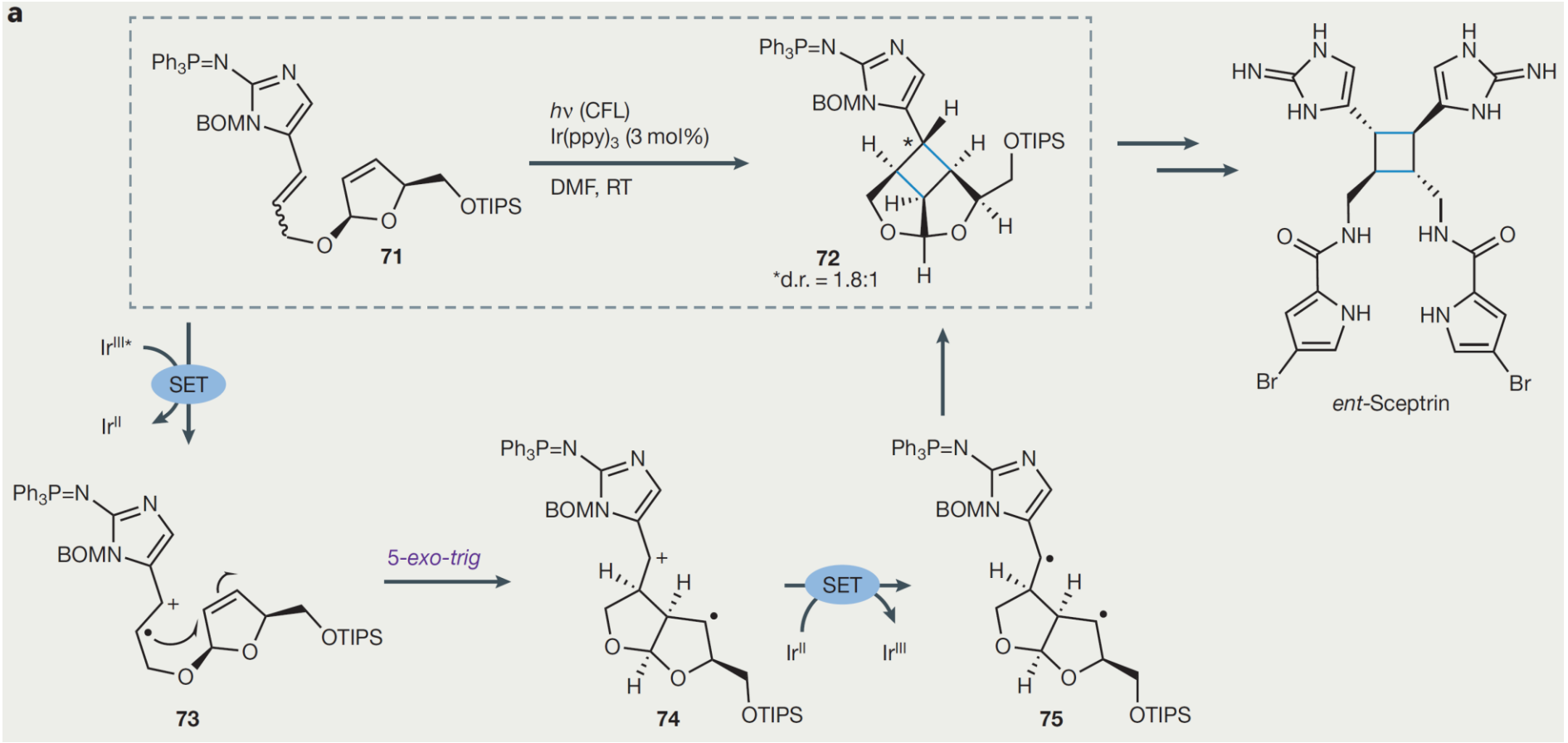
Photoredox catalysis in radical cascades

Oxidative photoredox radical cascades- Asymmetric syntheses of sceptrin and massadine and evidence for biosynthetic enantiodivergence.



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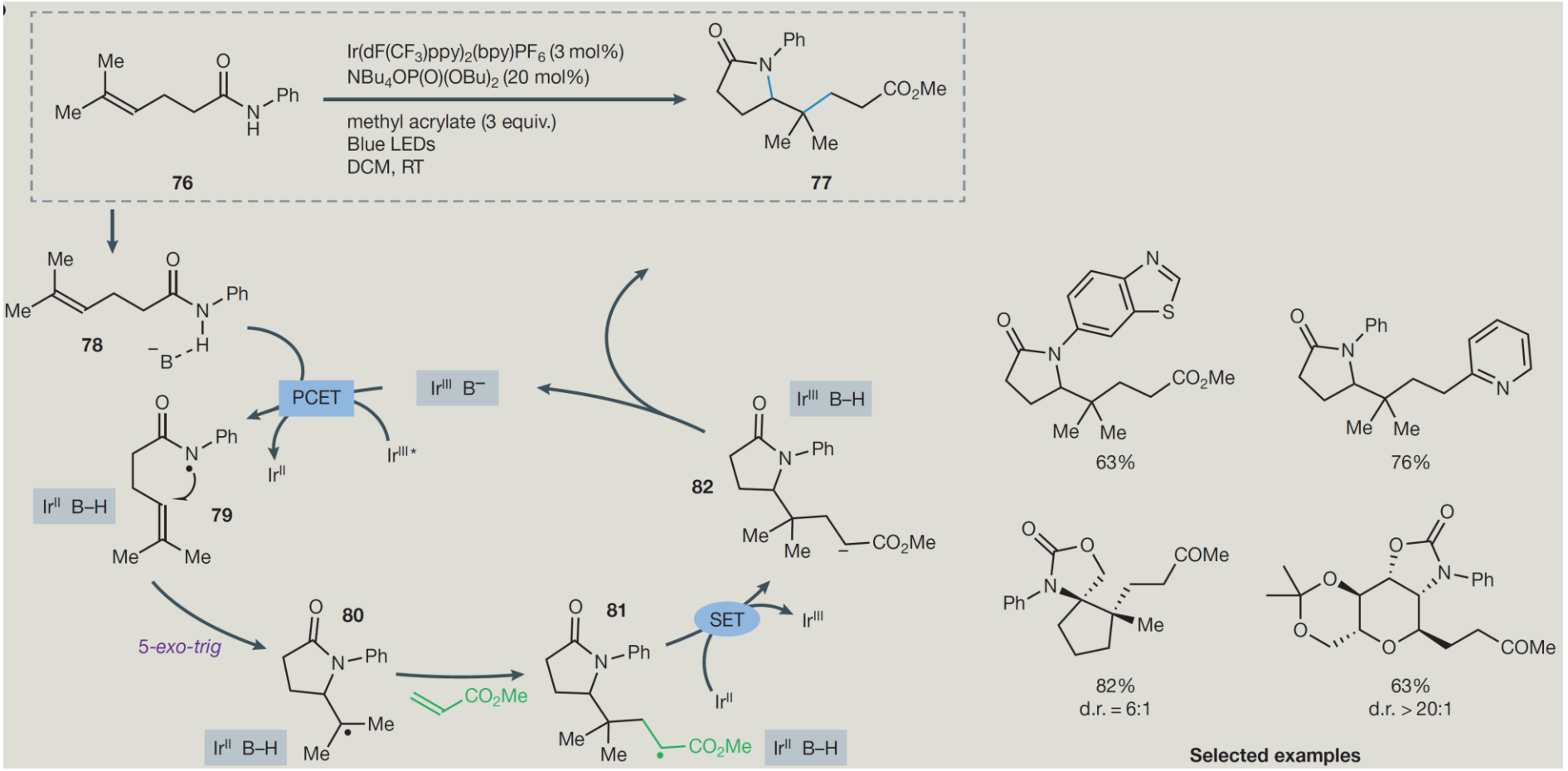
Photoredox catalysis in radical cascades

Oxidative photoredox radical cascades- Catalytic alkene carboaminations enabled by oxidative proton-coupled electron transfer.



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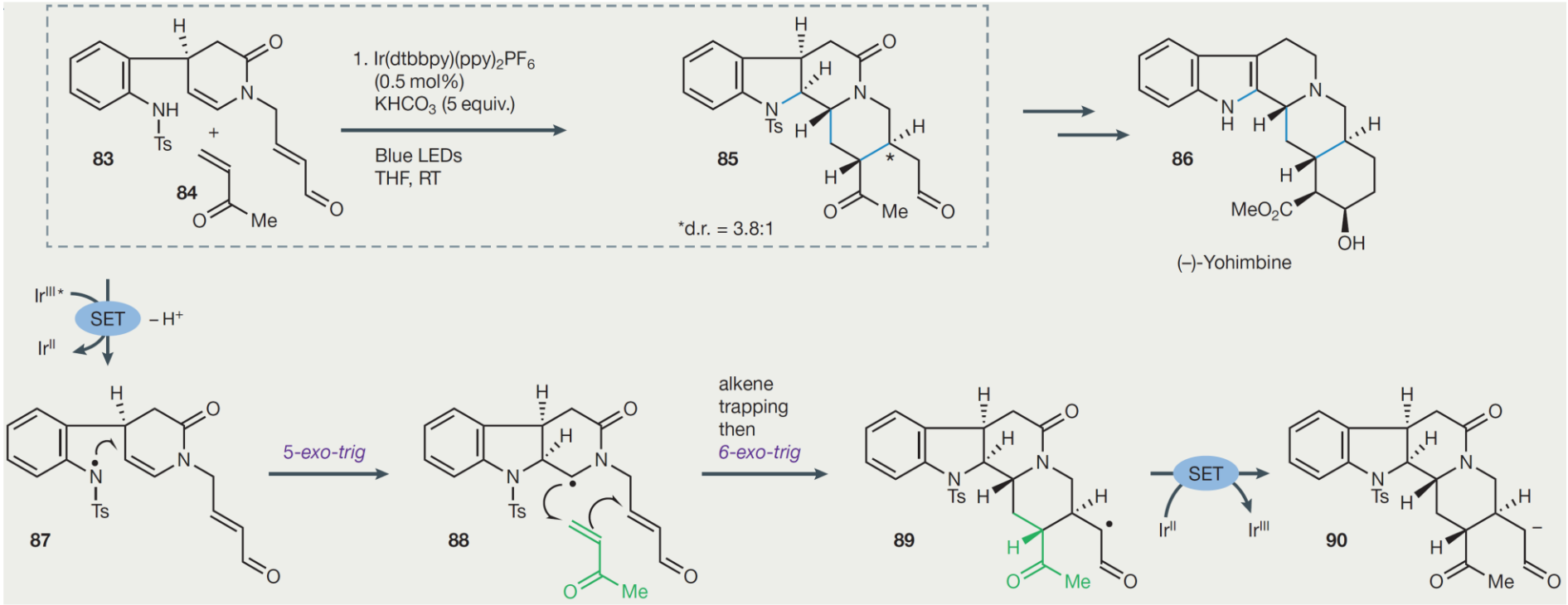
Photoredox catalysis in radical cascades

Oxidative photoredox radical cascades- A radical cascade enabling collective syntheses of natural products.



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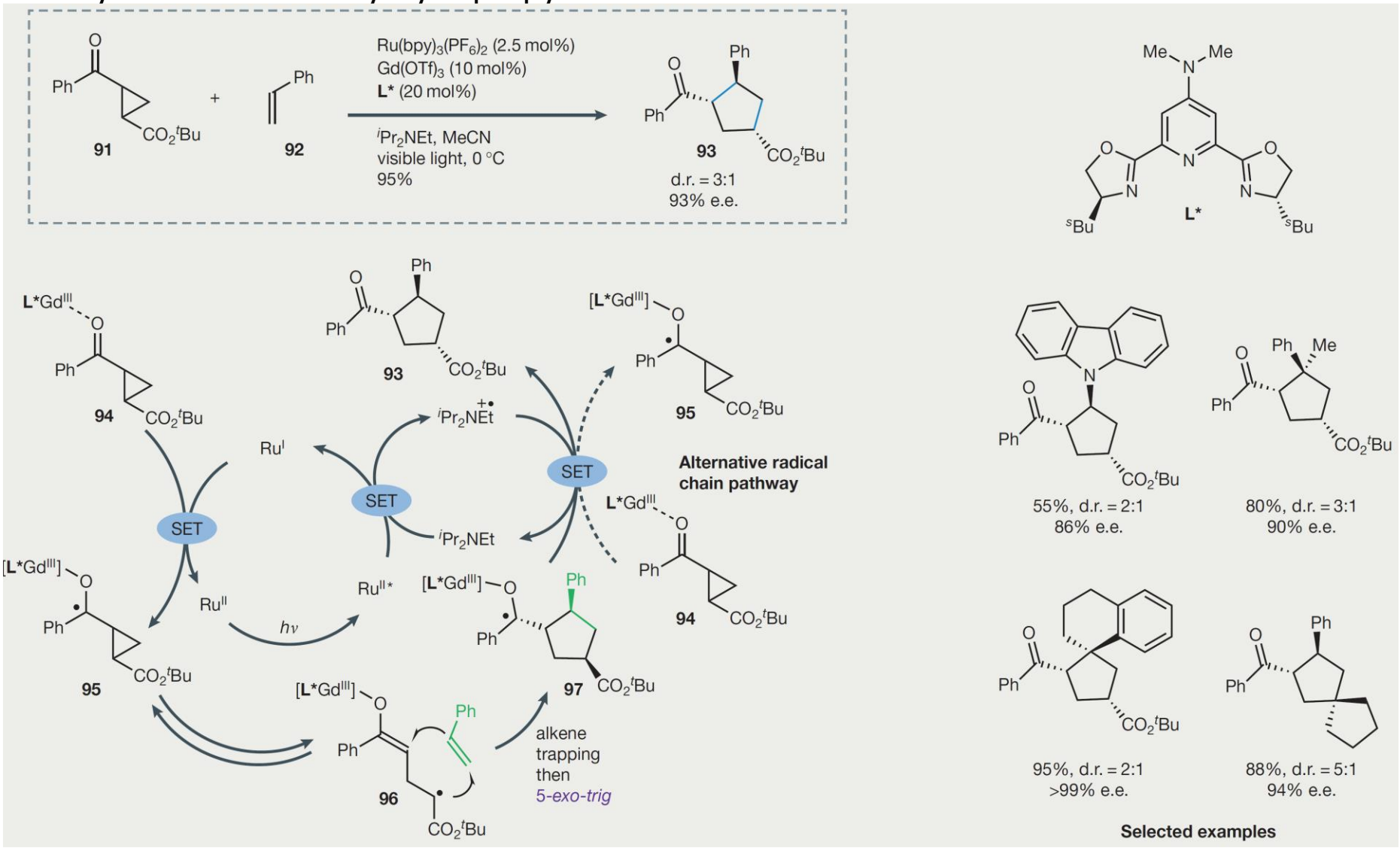
Photoredox catalysis in radical cascades

Reductive photoredox radical cascades-Enantioselective photocatalytic [3+2] cycloadditions of aryl cyclopropyl ketones.



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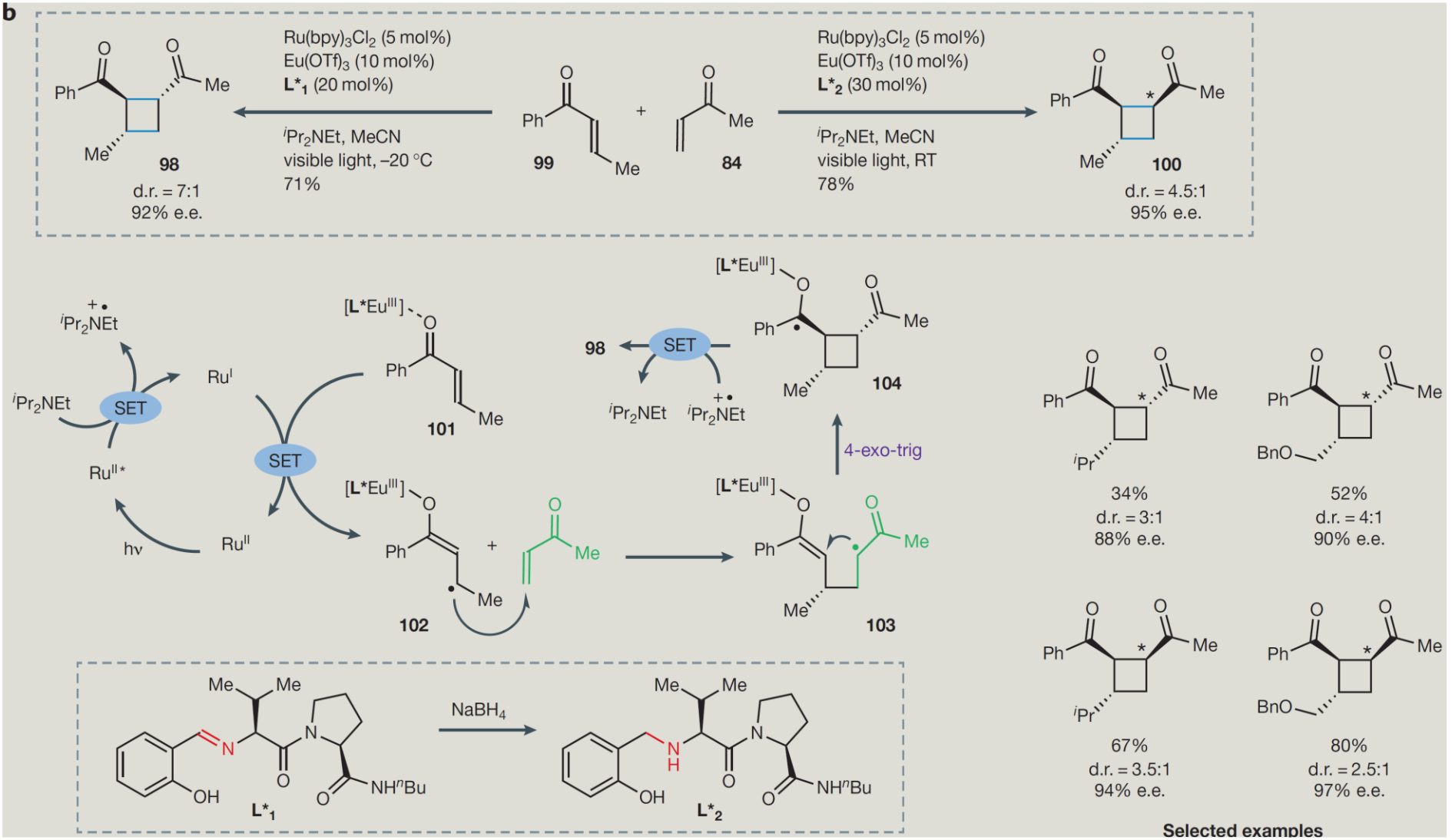
Photoredox catalysis in radical cascades

Reductive photoredox radical cascades-A dual-catalysis approach to enantioselective [2+2] photocycloadditions using visible light.



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Summary and Outlook

Cascade reactions reduces the time and cost of target chemical synthesis and the price paid in waste generation. Harnessing transient radical intermediates allows the exploration of reactivity beyond traditional ionic processes.

Can the use of stoichiometric SET reagents be rendered catalytic?
Can chiral ligands be used to control the asymmetry of radical cascades?

What if combine SET reagents with chiral BrØnsted acid catalysts or photoredox catalysts with chiral Lewis acids?

Can straightforward electrochemical SET cascade methods be developed for mainstream use?

Can new photoredox catalysts and photoredox substrate activation modes be developed for complexity-generating radical cascades ?

Silver(i) -catalyzed oxidative decarboxylation of acids by peroxydisulfate. Role of silver (ii)

I. Silver(I)-Catalyzed Decarboxylation[a]

$$Ag(I) + S_2O_8^{2-} \longrightarrow Ag(II) + SO_4^{2-} + SO_4\cdot^-$$

$$Ag(I) + SO_4\cdot^- \longrightarrow Ag(II) + SO_4^{2-}$$

$$Ag(II) + RCO_2H \longrightarrow Ag(I) + RCO_2\cdot + H^+$$

$$RCO_2\cdot \longrightarrow R\cdot + CO_2$$

$$R\cdot + HY \longrightarrow RH + Y\cdot$$

$$R\cdot + Ag(II) \longrightarrow [R^+]_{ox} + Ag(I) \text{ etc.}$$

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