

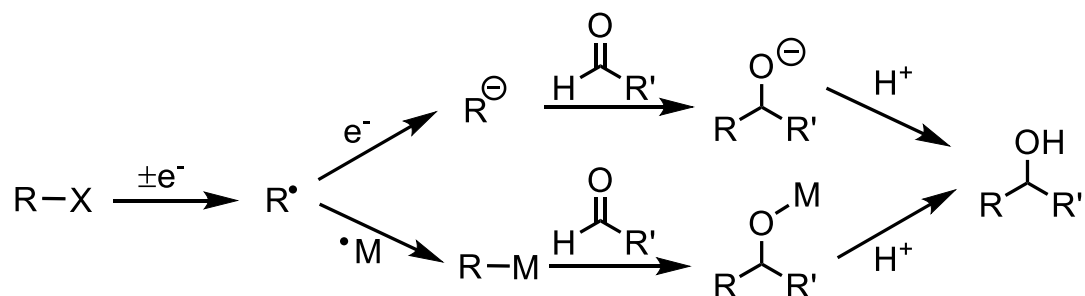
# REDUCTIVE RADICAL-POLAR CROSSOVER REACTIONS WITH CARBONYL GROUPS AS ELECTROPHILES

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## DESCRIPTION

In recent years, reductive radical-polar crossover reactions (RRPCO) have emerged as a powerful tool for the formation of C-C bonds.<sup>[1]</sup> Among these, reactions with carbonyl electrophiles proved to be the most versatile. The literature precedence is somewhat limited when it comes to the usage of carbonyl electrophiles in radical chemistry, which is attributed to the highly negative redox potential of the carbonyl group. On the other hand, ionic additions to carbonyl groups are very common, but suffer from low functional group tolerance. RRPCO overcomes these limitations as it represents a combination of radical and ionic pathways.<sup>[2]</sup> At first, a radical is formed which then, either gets reduced to an anion, or gets recombined with a transition metal to form a nucleophile that adds to a carbonyl group (Scheme 1).



Scheme 1. General reaction scheme for RRPCO.

The goal of this report is to summarize the most recent developments in RRPCO. The first two parts of the report are going to deal with recent methodologies developed in the field: photoredox catalyzed RRPCO and transition metal mediated RRPCO, showcasing in the end the combination of both by dual catalysis. The last part will cover RRPCO annulation and the appliance of this transformation in the total syntheses of nodulisporic acid and forskolin (Figure 1).<sup>[3,4]</sup>

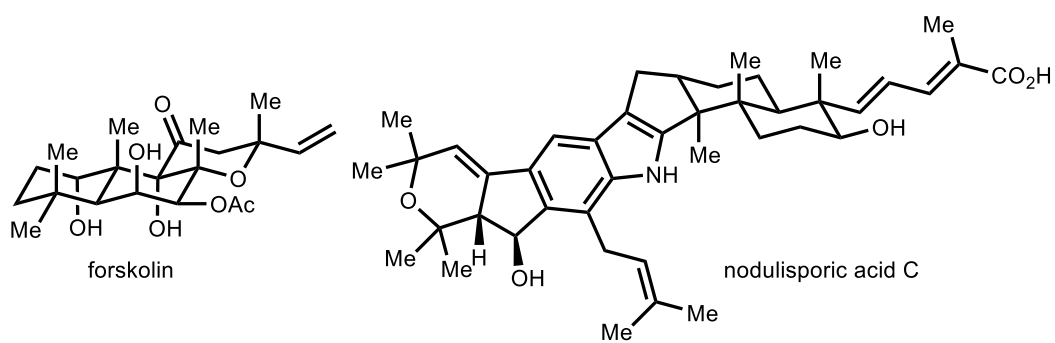


Figure 1. Total syntheses employing RRPCO.

## REFERENCES

1. *Chem. Sci.*, **2019**, *10*, 8285;
2. *Chem. Commun.*, **1997**, 1889;
3. *J. Am. Chem. Soc.* **2019**, *141*, 12246;
4. *J. Am. Chem. Soc.* **2018**, *140*, 12770.