

Green Azoarene Reduction: Au Nanoparticle-Catalyzed Hydrazoarene Synthesis with Ammonia Borane in Ethanol

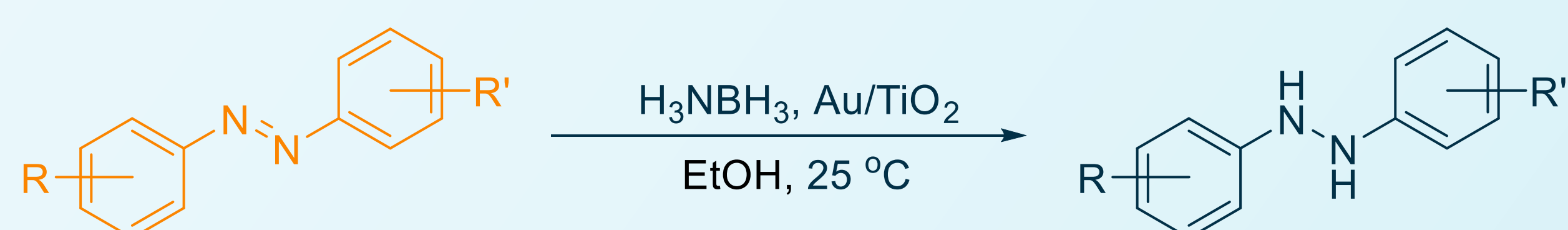
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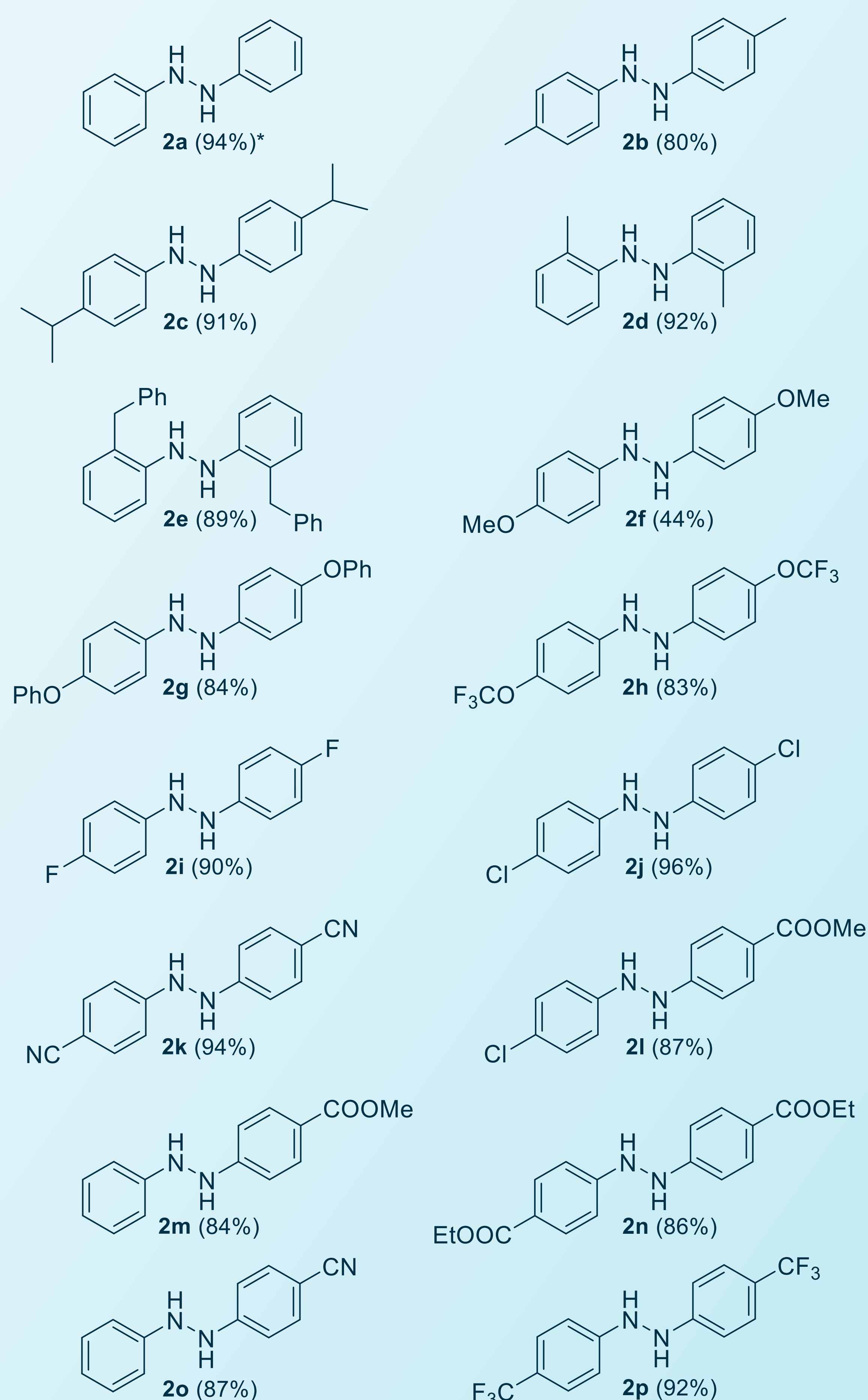
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Azoarenes are quantitatively converted into hydrazoarenes via transfer hydrogenation by ammonia borane complex (2.5 molar equivalents) catalyzed by minute amounts of Au nanoparticles supported on TiO₂ (0.1 mol%).^[1] The reaction takes place at room temperature in protic solvents, e.g., ethanol. Increasing the catalyst loading level to 1 mol%, the desirable conversion is achieved instantaneously. The reverse transformation, the oxidation of hydrazoarenes to azoarenes, occurs smoothly under aerobic conditions by Au/TiO₂ in the absence of reducing agent. The catalyst is recyclable and reusable for five consecutive runs of azoarene reduction with no loss of activity. To our knowledge, the above protocol is superior to existing analogous ones^[2-4] that also employ ammonia borane as a reductant.

Reduction of Azoarenes to Hydrazoarenes by Ammonia Borane Catalyzed by Au/TiO₂

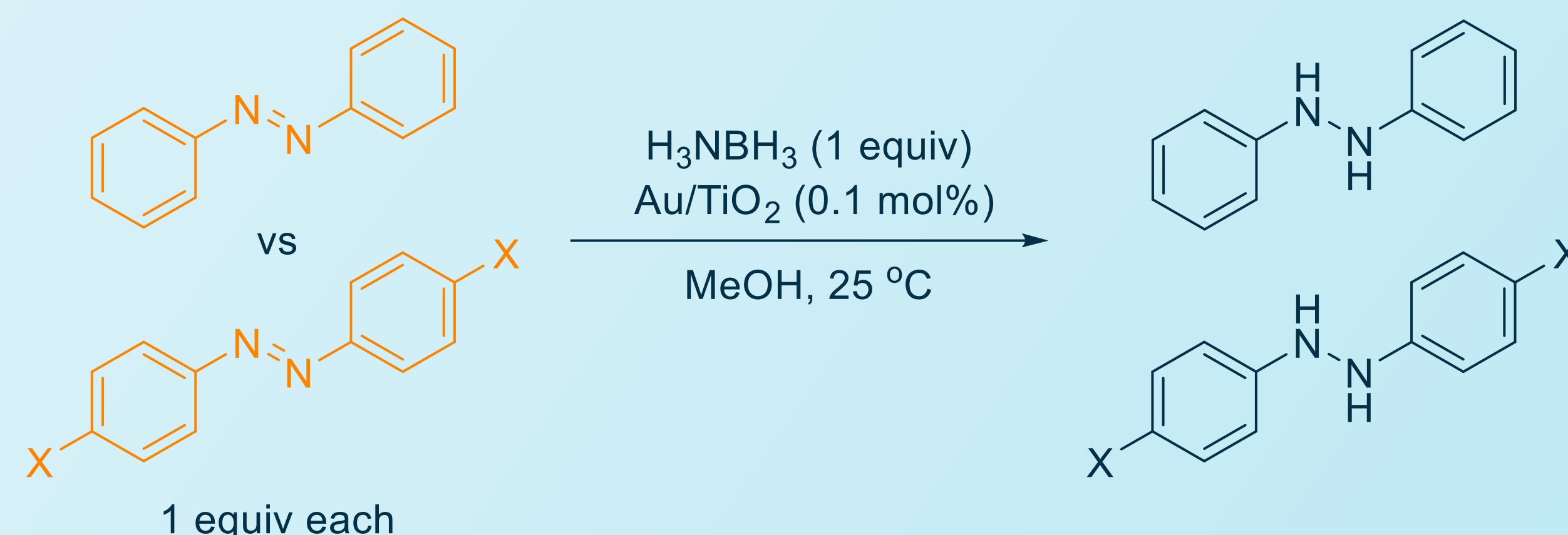


Conditions A: 2.5 equiv H₃NBH₃, 0.1 mol% Au, 10-40 min
Conditions B: 2.5 equiv H₃NBH₃, 1 mol% Au, < 1 min

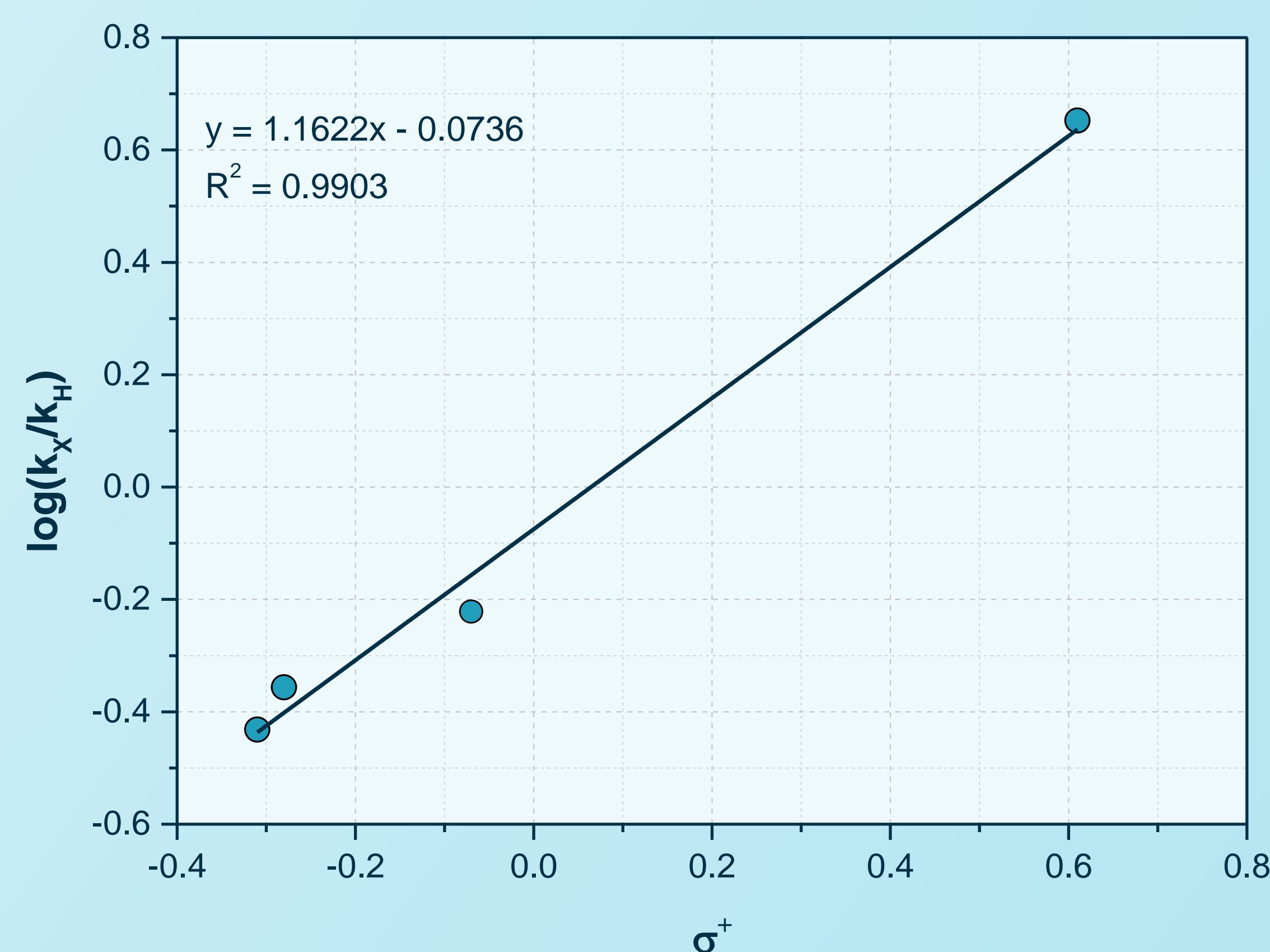


* Yields obtained under conditions A.

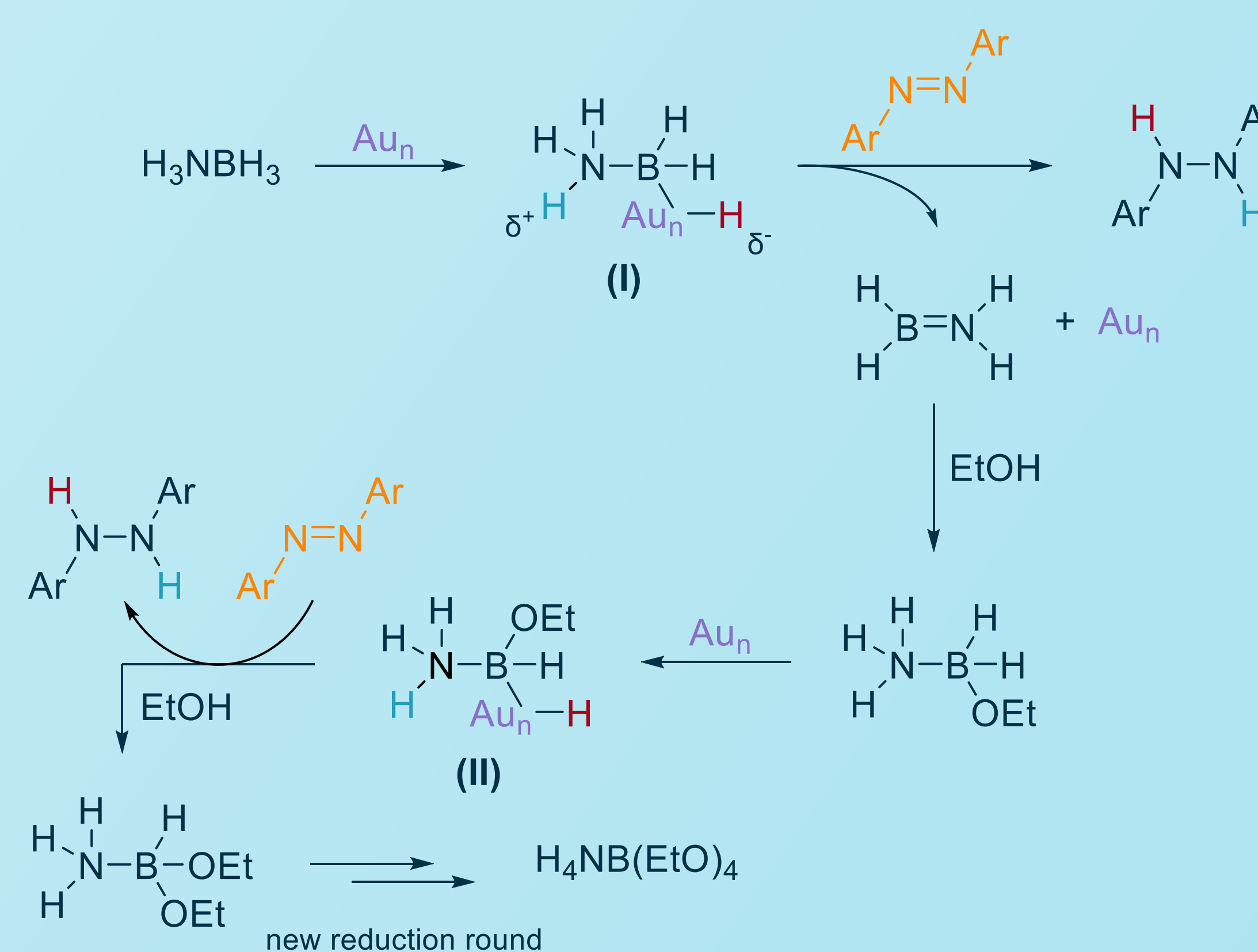
Hammett Kinetics in the Reduction of Azoarenes



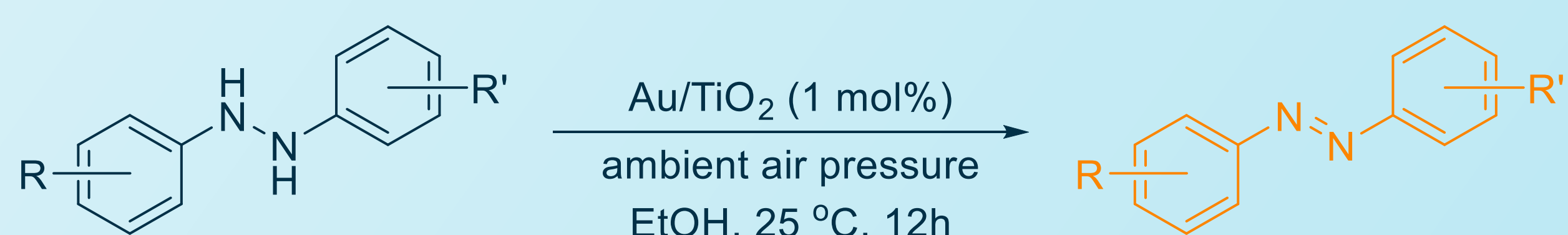
para-X	k _X /k _H	log(k _X /k _H)	σ ⁺
-Me	0.37	-0.43	-0.31
-iPr	0.44	-0.35	-0.28
-F	0.60	-0.22	-0.07
-CF ₃	4.49	+0.65	+0.61



Proposed Mechanism of Azoarene Reduction



Oxidation of Hydrazoarenes to Azoarenes under Atmospheric O₂ Catalyzed by Au/TiO₂



References

- [1] E. M. Zantioti-Chatzouda, D. Malliotaki, M. Stratakis, *Adv. Synth. Catal.*, 365 (2023) 2982.
- [2] C. C. Chong, H. Hirao, R. Kinjo, *Angew. Chem. Int. Ed.*, 53 (2014) 3342.
- [3] M. A. Chacón-Terán, R. E. Rodríguez-Lugo, R. Wolf, V. R. Landaeta, *Eur. J. Inorg. Chem.*, 2019 (2019) 4336.
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