

Terpyridine Diphosphine Ruthenium Complexes as Efficient Photocatalysts for the Transfer Hydrogenation of Carbonyl Compounds

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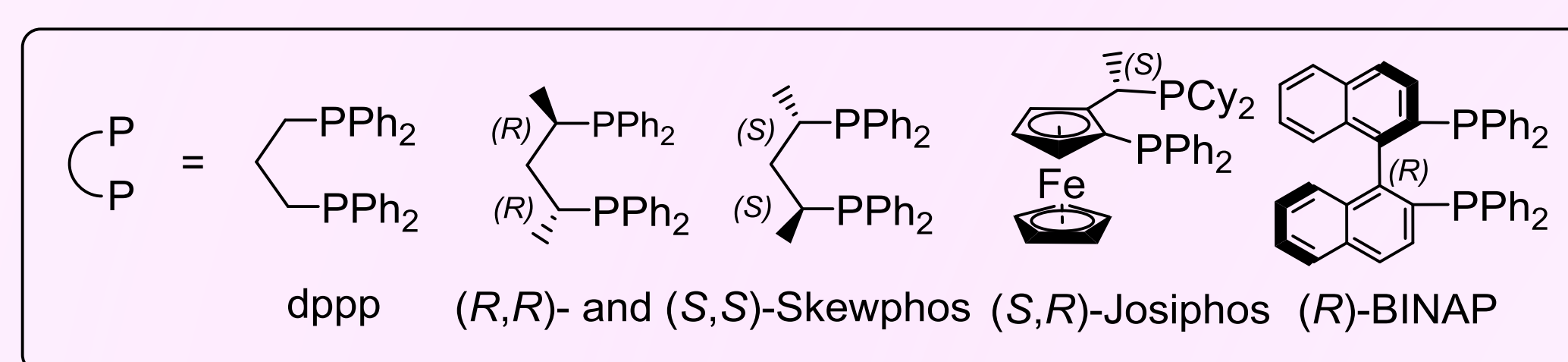
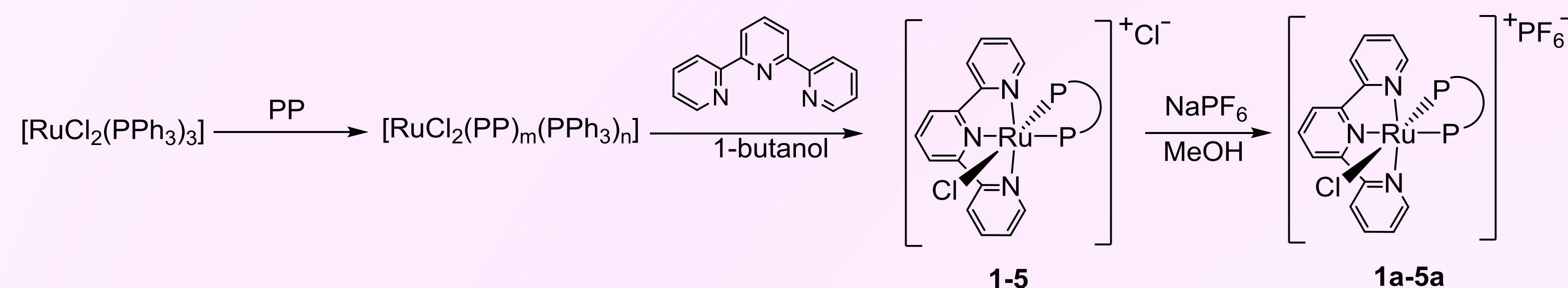
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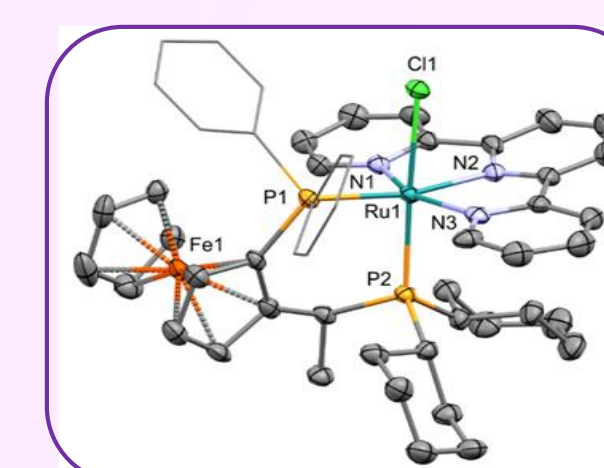
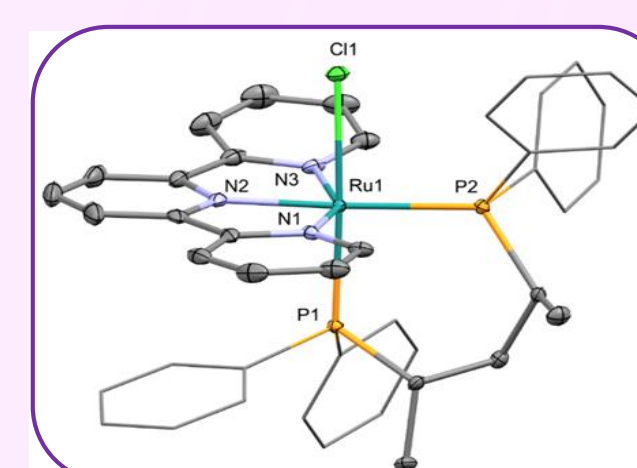
Introduction

- Over the past decade, visible-light photoredox catalysis or photocatalysis has grown to become a commonly employed powerful tool in organic synthesis leading to new unique and valuable molecular transformations, inaccessible from thermally activated processes.^[1]
- Photocatalysis can be conducted in homogeneous conditions as well as employing heterogeneous transition metal or solid semiconductors.^[2]
- The commonly employed homogeneous visible-light photocatalysts are homoleptic Ru and Ir polypyridyl complexes, like $[\text{Ru}(\text{bpy})_3]_2^+$ and $[\text{Ir}(\text{ppy})_3]$ (bpy = 2,2'-bipyridine; ppy = 2-phenylpyridine). These compounds, when excited by visible light undergo a metal-to-ligand-charge transfer (MLCT) transitions from HOMO and LUMO orbitals of the ligand.^[3]
- The 2,2':6',2''-terpyridine (tpy) is an NNN-type Pincer ligand, which can give tight chelation of various metal cations in a nearly planar geometry. The presence of the electron-deficient pyridine cycles make it a strong σ -donor and also as a very good π -receptor, moreover the presence of low energetic LUMO levels allows it to participate in the redox reactions as a non-innocent ligand.^[4]

Synthesis of $[\text{RuCl}(\text{PP})(\text{tpy})]\text{X}$ complexes (X = Cl, PF₆; PP = diphosphine)^[5]



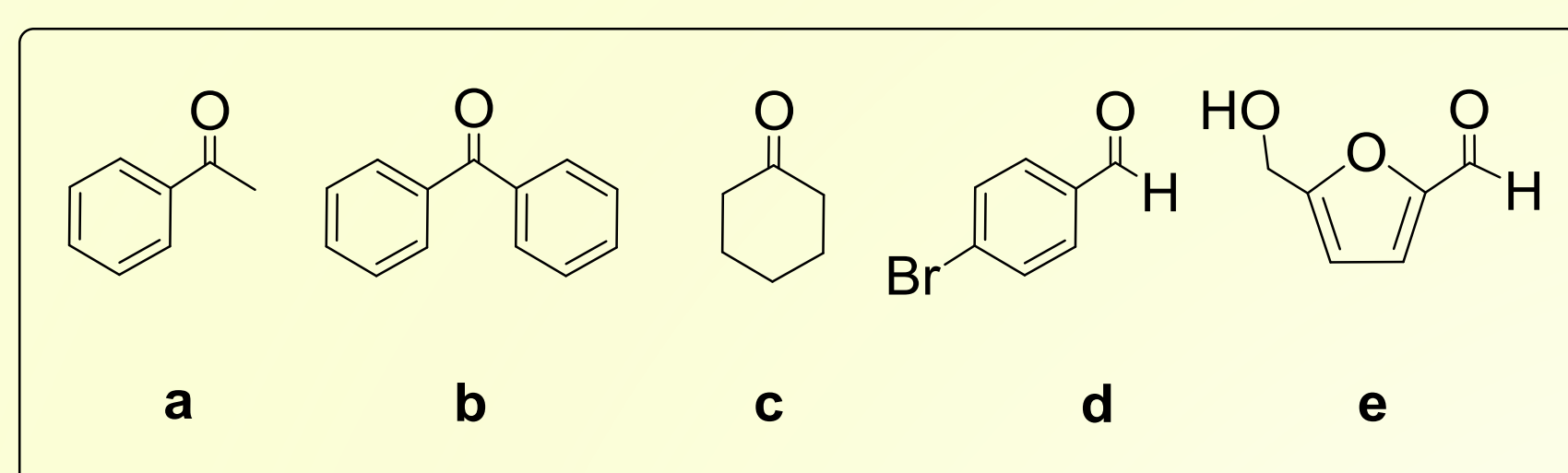
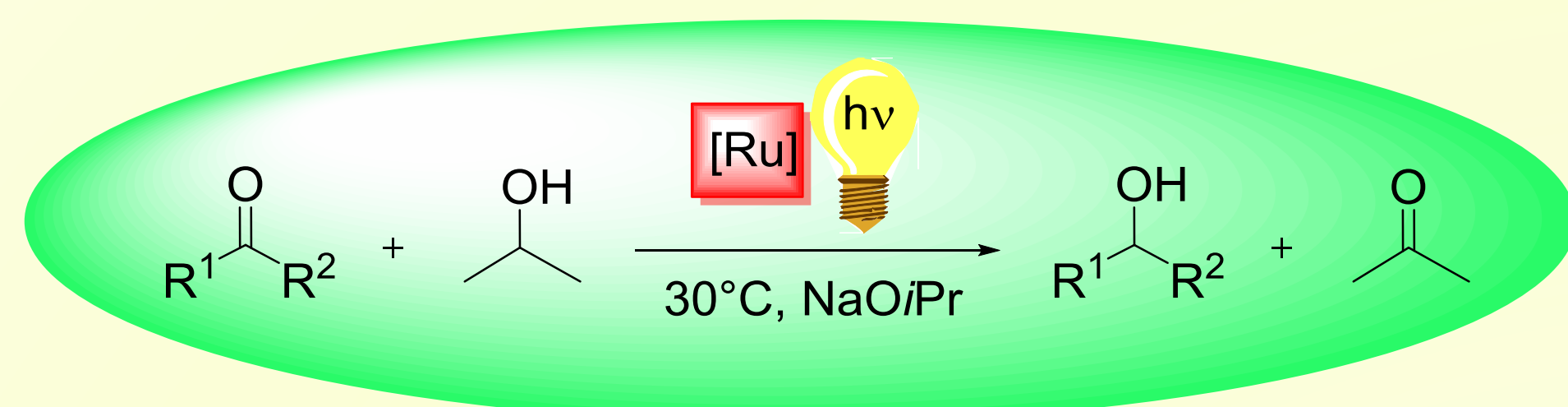
Complex	PP
1,1a	dppp
2,2a	(R,R)-Skewphos
3,3a	(S,S)-Skewphos
4,4a	(S,R)-Josiphos
5,5a	(R)-BINAP



$[\text{RuCl}((S,S)\text{-Skewphos})(\text{tpy})]\text{PF}_6$ (3a) $[\text{RuCl}((S,R)\text{-Josiphos})(\text{tpy})]\text{PF}_6$ (4a)

Complexes were isolated as single stereoisomers using chiral diphosphines

Photocatalytic transfer hydrogenation (TH) of carbonyl compounds^[5]

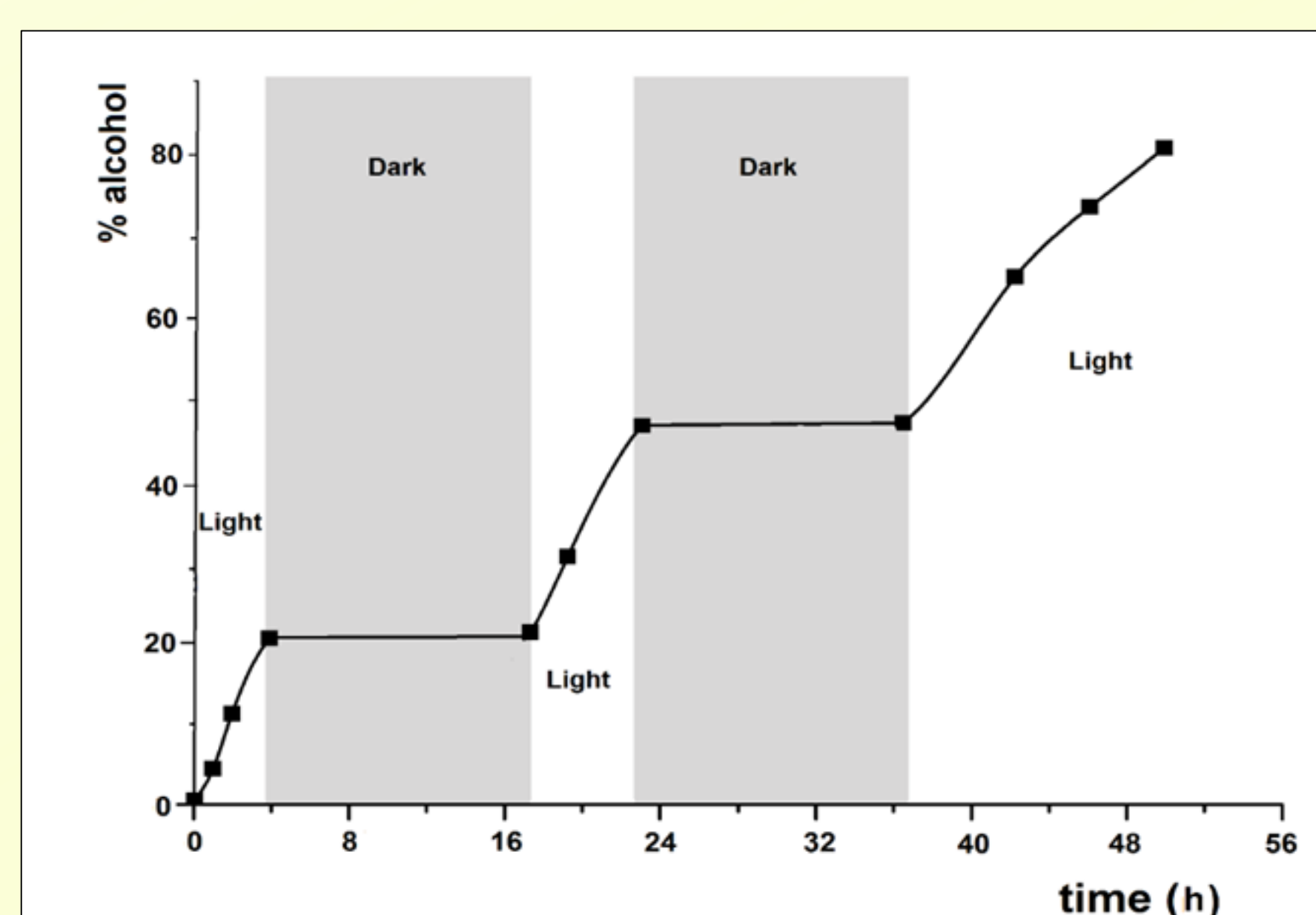


Conditions:

- Light irradiation with a solar simulator (300 W Xenon Arc Lamp)
- Reactions conducted at 30 °C without the use of sacrificial reductants (e.g. triethanolamine) or photosensitizers
- i*PrOH (or *i*PrOH/MeOH mixture (1:1)) as hydrogen donor
- Employment of NaOiPr (usually 2 mol%) as base

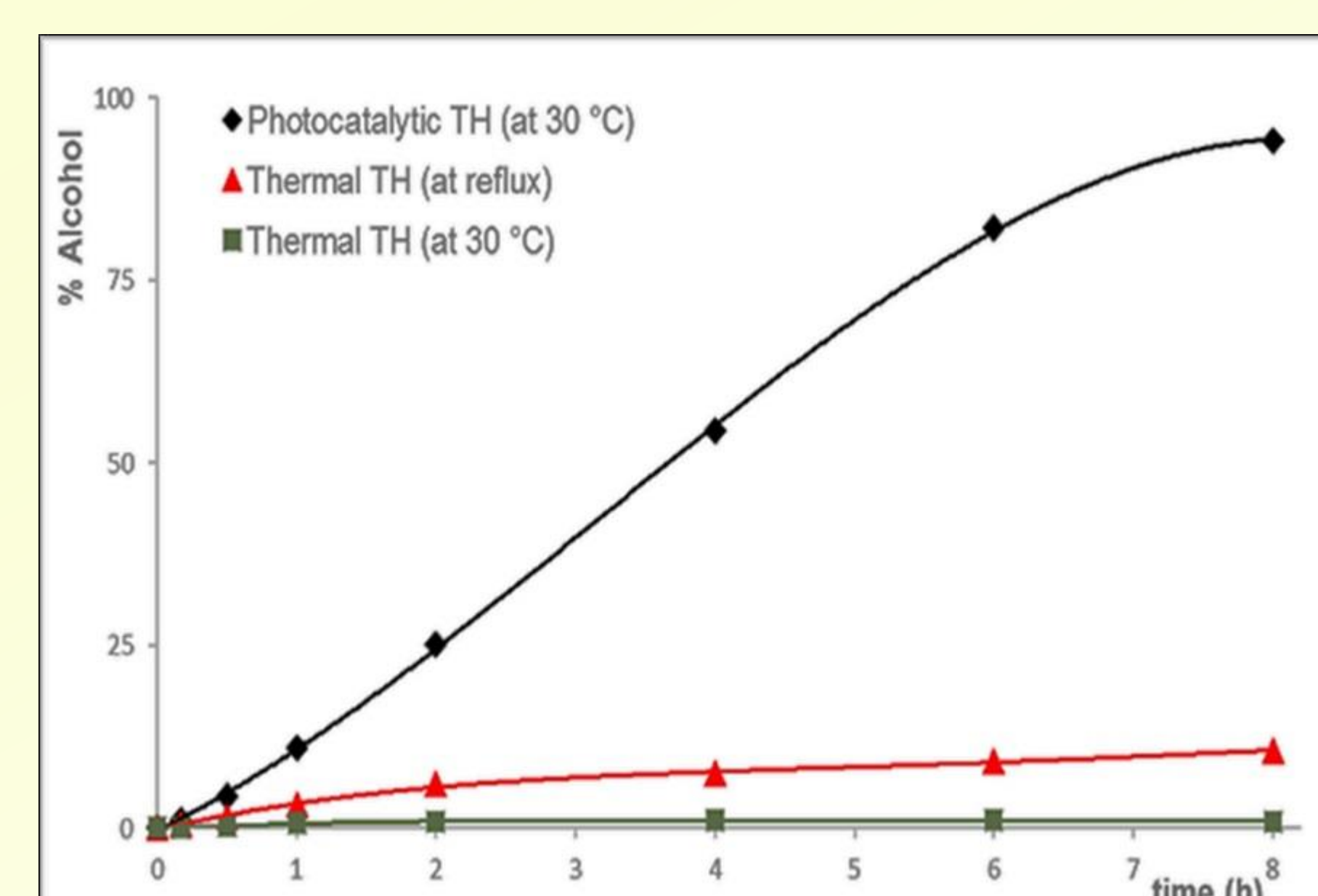
Properties of the photocatalytic TH of carbonyl compounds

Cycling between illumination and dark periods in the photocatalyzed TH of acetophenone (a) with complex 2



- Conc. substrate = 0.1 M
- Solvent: *i*PrOH
- Substrate/Catalyst ratio (S/C) = 5000
- NaOiPr (2 mol%)
- T = 30 °C

Comparison between the photocatalytic and thermal TH of acetophenone (a) catalyzed by complex 2



- Conc. substrate = 0.1 M
- Solvent: *i*PrOH
- S/C = 1000
- NaOiPr (2 mol%)

Results of the photocatalytic TH of carbonyl compounds

Photocatalytic TH of acetophenone (a)

Complex	NaOiPr [mol%]	Time ^[a] [h]	Conv. ^[b] [%]	TOF ^[c] [h ⁻¹]
1	2.0	16	94	74
2	2.0	8	96	148
2a	2.0	8	98	141
2 ^[d]	2.0	24	86	205
2	1.0	15	95	66
2	5.0	8	92	122
2	10.0	15	94	92
3	2.0	8	98	139
3a	2.0	10	99	144
4a	2.0	14	95	94
5a	2.0	14	98	88
$[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$	2.0	8	61	73

- Conc. substrate = 0.1 M
- Solvent: *i*PrOH
- S/C = 1000
- T = 30 °C

Photocatalytic TH of ketones and aldehydes

Complex	Substrate	S/C	Time ^[a] [h]	Conv. ^[b] [%]	TOF ^[c] [h ⁻¹]
1	b	1000	12	98	115
2	b	1000	6	99	264
2	b	5000	22	95	256
1	c	1000	18	91	82
2	c	1000	8	98	138
2	c	5000	25	97	207
4a	c	500	21	99	25
1	d	1000	21	88	46
2	d	1000	18	99	75
2	d ^[d]	1000	18	88	49
2	e	1000	24	96	40

- Conc. substrate = 0.1 M
- Solvent: *i*PrOH
- S/C = 1000
- NaOiPr (2 mol%)
- T = 30 °C

Asymmetric photocatalytic TH of acetophenone (a)

Complex	Time ^[a] [h]	Conv. ^[b] [%]	TOF ^[c] [h ⁻¹]	ee ^[b] [%]
2	24	89	54	51 S
2a	24	84	51	51 S
3	24	87	54	52 R
3a	27	90	56	52 R
4a	24	88	39	14 S
5a	30	89	38	18 S

- Conc. substrate = 0.1 M
- Solvent: *i*PrOH/MeOH (1:1)
- S/C = 1000
- NaOiPr (2 mol%)
- T = 30 °C

* best results are highlighted in orange

[a] Irradiation hours. [b] The conversions and e.e. were determined by GC analysis. [c] Turnover frequency (moles of ketone converted to alcohol per mole of catalyst per hour) at 50% conversion. [d] S/C = 5000.

References

- [1] a) Li, Y.; Ye, Z.; Cai, J.; Gong, L. *Synthesis* **2021**, *53*, 1570;
b) Skubi, K. L.; Blum, T. R.; Yoon, T. P. *Chem. Rev.* **2016**, *116*, 10035.
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- [4] Wei, C.; He, Y.; Shi, X.; Song, Z. *Coord. Chem. Rev.* **2019**, *385*, 1.
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Conclusions

- Synthesis in high yield of new cationic achiral and chiral terpyridine diphosphine ruthenium complexes $[\text{RuCl}(\text{PP})(\text{tpy})]\text{X}$ (X = Cl, PF₆).
- The tpy complexes with NaOiPr display high photocatalytic activity in the TH of carbonyl compounds (conversions up to 99%) using *i*PrOH as the only hydrogen donor and visible light at 30 °C, at remarkably high S/C (up to 5000) and TOF values up to 264 h⁻¹.
- The chiral enantiomers 2 and 3 induce the asymmetric photocatalytic TH of acetophenone, affording (S)- and (R)-1-phenylethanol with 51-52% ee, in a MeOH/*i*PrOH mixture.