



同濟大學
TONGJI UNIVERSITY

LMCT-Driven Fe,Ti Photocatalysis: Mechanistic Insights and Synthetic Applications

汇报人：黄振

时 间：2026. 10. 16

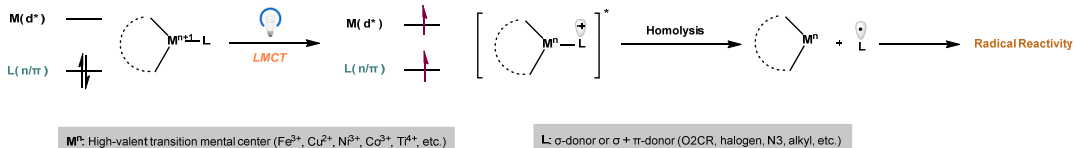
1, 金属的LMCT总述

2, 钛催化的LMCT

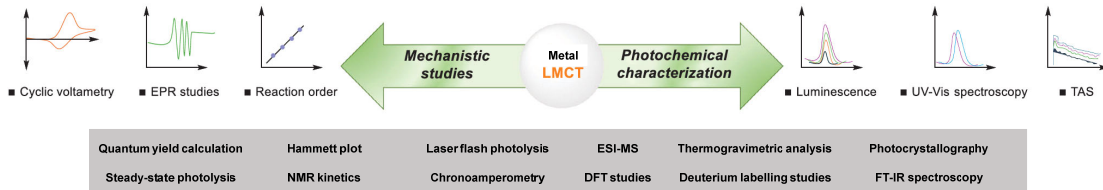
3, 铁催化的LMCT

4, proposal

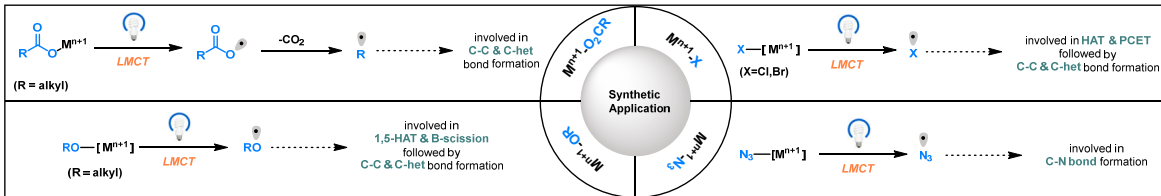
A) General Mechanism of LMCT-Mediated Reactivity



B. Photochemical Characterization and Mechanistic Investigation of Iron-LMCT



C. Types of M-L Bond Undergoes LMCT/Homolysis Sequence



pubs.acs.org/JACS

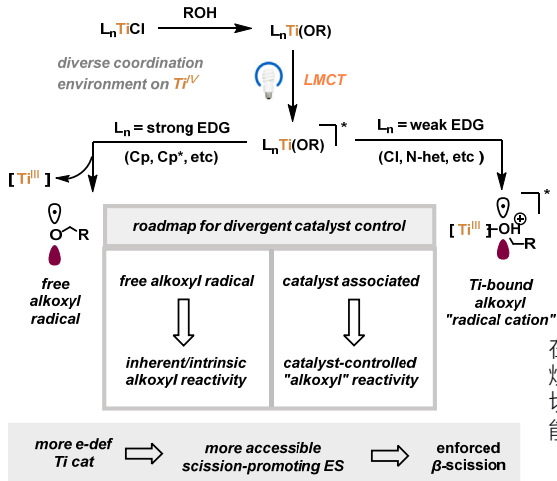
Article

Leveraging Divergent Ligand-to-Metal Charge-Transfer Excited State Pathways for Catalyst Control over Alkoxyl Radical Reactivity

Zilu Tang,[#] Yetong Lin,[#] Arshad Mehmood, Ashley E. Lojko, Jagrut A. Shah, Noah J. Schwartzapfel, Benjamin G. Levine, and Jeffrey M. Lipshultz*

利用多样化的配体到金属电荷转移 (LMCT) 激发态路径, 实现催化剂对烷氧自由基反应性的调控。

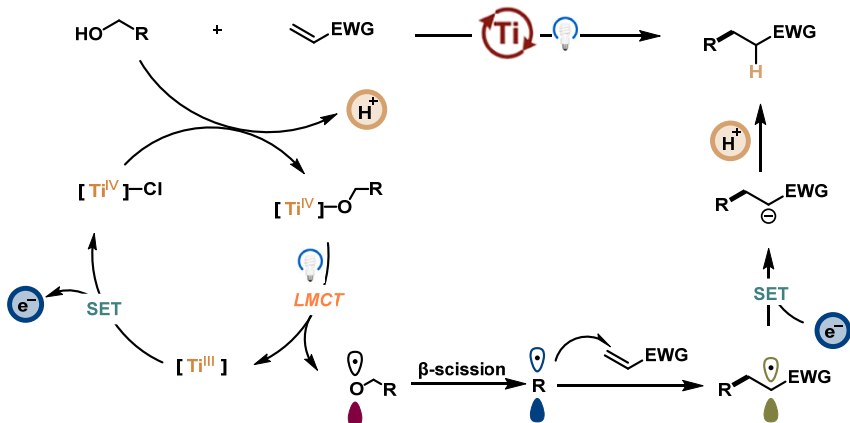
J. M. Lipshultz, *J. Am. Chem. Soc.* **2026**, *148*, 6665-6673.

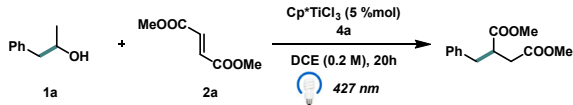
Proposal: Divergent Ti-LMCT Catalysis: Inherent vs Enforced Scission


Ti 配体电子性质	强给电子配体: Cp、Cp* 等	弱给电子/吸电子配体: Cl、N-杂原子配体等
Ti 中心电子性	给电子配体降低 Ti 缺电子性, Ti 受体能力弱	弱给电子/吸电子配体增强 Ti 缺电子性, Ti 受体能力强
促进断裂的 LMCT 激发态	能量高, 不易接近	能量低, 更易接近
主要光化学路径	VLIH: Ti-O 均裂, 释放游离 RO $\cdot$	从 LMCT 激发态直接促进 C α -C β 断裂; 可看作 Ti 结合的烷氧自由基阳离子
烷氧自由基状态	游离烷氧自由基	催化剂结合的烷氧自由基阳离子/激发态物种
反应性由谁决定	游离 RO $\cdot$ 的固有反应性	催化剂控制烷氧自由基反应性

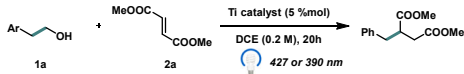
在 Ti-LMCT 催化中, 通过调控 Ti 配体电子性质, 可在“游离烷氧自由基固有反应性”与“催化剂强制激发态 β -断裂”之间切换; Ti 越缺电子, 越易接近促进断裂的 LMCT 激发态, 越能强制 β -断裂。

Proposed Deconstructive Alkylation via Free Alkoxy Radical

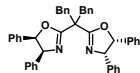




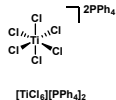
entry	deviation from standard	yield (%)
1	—	88
2	Cp ₂ TiCl ₂ in place of 4a	81
3	FeCl ₃ , CeCl ₃ , CeCl ₆ ²⁻ , or CpZrCl ₃ in place of 4a	<1
4	1.5 equiv 1a	94
5	1.5 equiv 2a	>99
6	CH ₂ Cl ₂ / PhCl solvent	83/72
7	Et ₂ O/THF solvent	28/30
8	450 nm LED	74
9	390 nm LED	80
10	0 mol% 4a / in dark	0/0

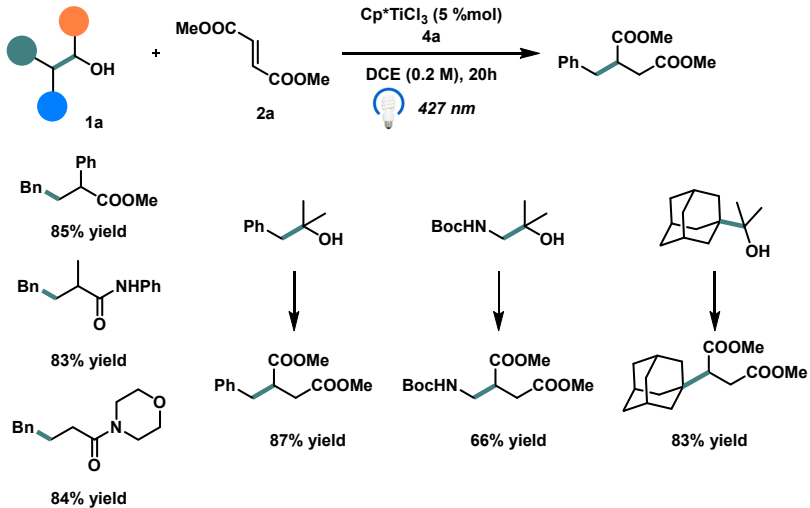


entry	Ti catalyst	LEDs	yield (%)
1	4a	427 nm	26
2	Cp ₂ TiCl ₂	427 nm	25
3	Cp*TiCl ₃	427 nm	29
4	4a	390 nm	35
5	Cp ₂ TiCl ₂	390 nm	31
6	Cp*TiCl ₃	390 nm	39
7	TiCl ₄ + Box* (10 mol%)	390 nm	56 ^a
8	TiCl ₄ + dCF ₃ bpy (10 mol%)	390 nm	63
9	TiCl ₄ + dOMebpy (10 mol%)	390 nm	73
10	TiCl ₄ + PPh ₄ Cl (10 mol%)	390 nm	67
11	[TiCl ₆][PPh ₄] ₂ (4b)	390 nm	79

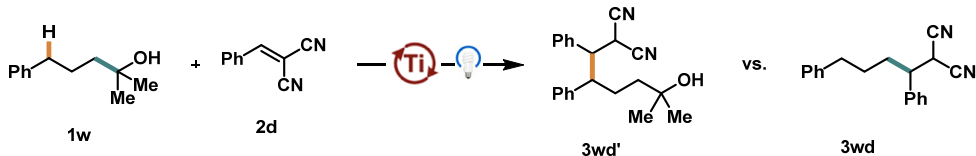


Box*

[TiCl₆][PPh₄]₂



Competition Study: Catalyst Control over Alkoxy Radical Reaction Pathways



catalyst-control effect

more e--deficient Ti catalyst

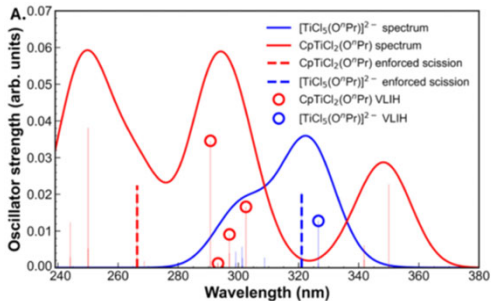
 10^2 - 10^3 relative rate enhancement

via 1,5-HAT

via β -scission

4a	16%	12%
4b	0%	73%, 69%
TiCl ₄ , dCF ₃ bpy	0%	72%
TiCl ₄ , Box*	0%	79%

TD-DFT 计算实验



Ti 配体电子性质可调控 LMCT 激发态路径

氯配体使断裂相关 LMCT 跃迁红移, Cp 配体使其蓝移

缺电子 Ti 更容易实现强制 β -断裂 $[\text{TiCl}_3(\text{OPr})]^{2-}$ 的断裂相关 LMCT 态能量更低, 更易被 390 nm 光激发

富电子 Ti 更倾向 VLIH/游离自由基

 $\text{CpTiCl}_2(\text{OPr})$ 的断裂相关 LMCT 态高能难接近, 低能 VLIH 占主导

激发态具有“Ti 结合烷氧自由基阳离子”特征

空穴分布在烷氧氧和配体, 并延伸到 $\text{C}\alpha\text{-C}\beta$ σ 键; 同时沿 Ti-O 键有正力, 支持 Zuo 的“协同双均裂”

实验观察到的催化二分法有电子结构基础

计算与实验一致: Cp-Ti 走游离自由基路径, 氯饱和 Ti 走强制 β -断裂路径

Degradative Alcohol Functionalization by Titanocene Photocatalysis

Jagrut Atul Shah, Ashley E. Lojko, Zilu Tang, Yetong Lin, Emma H. Scher, Celeste A. Barefoot, and Jeffrey M. Lipshultz*



Cite This: *ACS Catal.* 2025, 15, 15315–15323



[Read Online](#)

二茂钛光催化实现的醇降解性/解构性官能团化

J. M. Lipshultz, *ACS Catal.* **2025**, 15, 15315-15323.

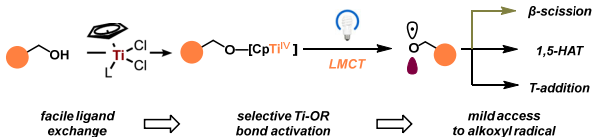
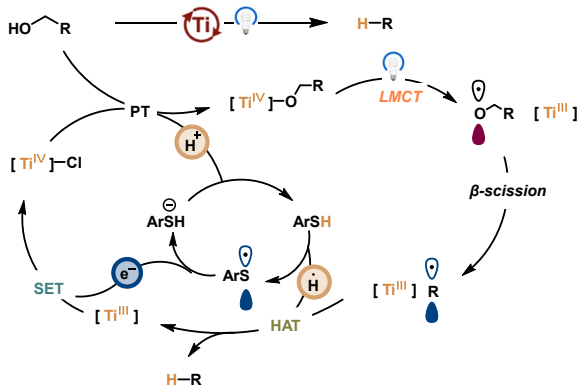
Ligand-to-Metal Charge-Transfer Catalysis

commonly used metals

 Ce^{IV}
strong
oxidant

 Fe^{II}
 Ni^{III}
 Cu^{II}
weak
oxidant

Design: Ti-LMCT Alcohol Functionalization via Alkoxy Radical

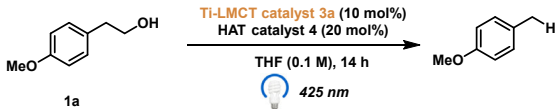
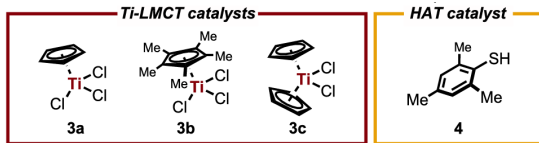

 tunable Ti^{III}
redox potentials
 $E_{1/2}$ VS. Fc^+/Fc
 CpTiCl_3 Cp^*TiCl_3 Cp_2TiCl_2 $\text{Cp}^*_2\text{TiCl}_2$

-0.79V

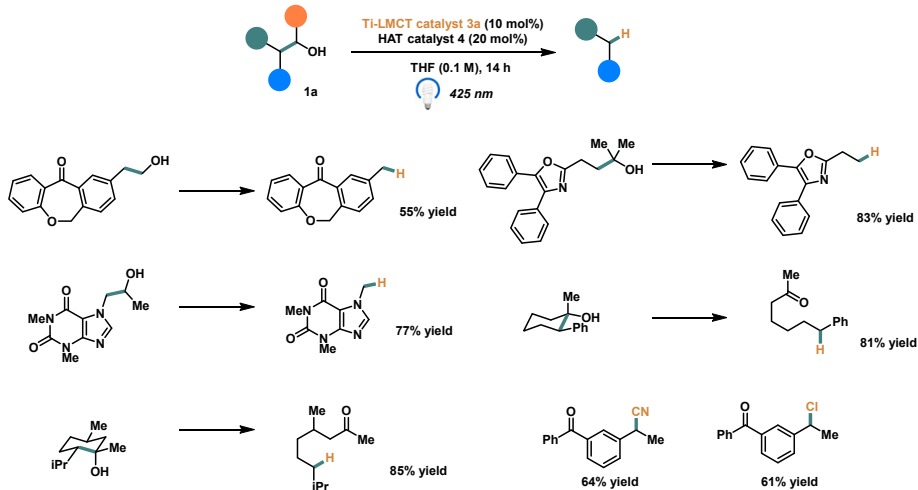
-1.12V

-1.19V

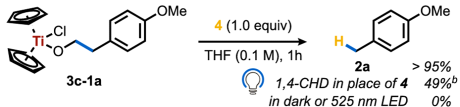
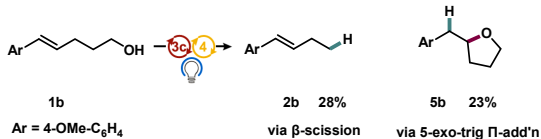
-1.55 V



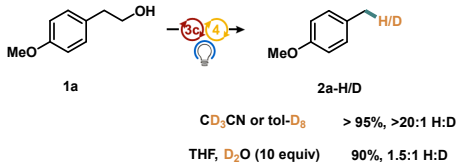
entry	deviation from standard	yield (%)
1	—	> 95
2	3b in place of 3a	> 95
3	3c in place of 3a	92
4	450 nm	92
5	475 nm	81
6	390 nm	> 95
7	525 nm, in dark, no 3a, or no 4	0



A. Isolated titanocene alkoxide undergoes photochemical degradation

B. Evidence of alkoxy radical: β -scission vs. Π -addition

C. Evidence of C-radical trapping by HAT catalyst 4: deuteration



Chiral Ti(BOX)–LMCT Catalysis Integrating Alcohol C–C Bond Cleavage with Enantioselective Radical Conjugate Addition

Hexiang Wang, Yunzhi Lin, and Zhiwei Zuo*



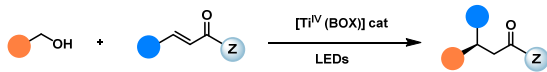
Cite This: *J. Am. Chem. Soc.* 2026, 148, 42904–42912



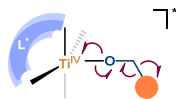
Read Online

Z. Zuo, *J. Am. Chem. Soc.* **2026**, 148, 42904–42912.

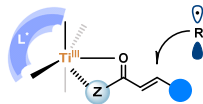
Enantioselective radical conjugate addition through Ti(BOX)-LMCT induced alcohol C-C bond cleavage



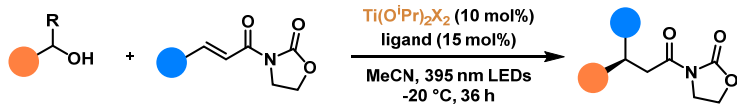
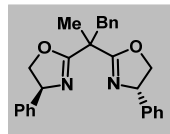
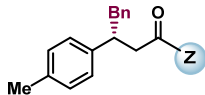
LMCT temporarily couples carbon-radical generation with stereocontrolled bond formation



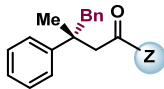
Ti^{IV} -LMCT
C-C bond cleavage



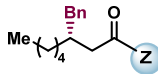
Chiral Ti^{III} -LA
asymmetric C-C bond formation



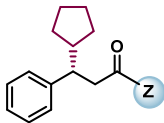
62% yield, 94:6 er



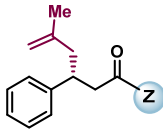
55% yield, 95:5 er



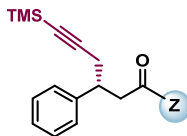
54% yield, 97:3 er



51% yield, 90:10 er

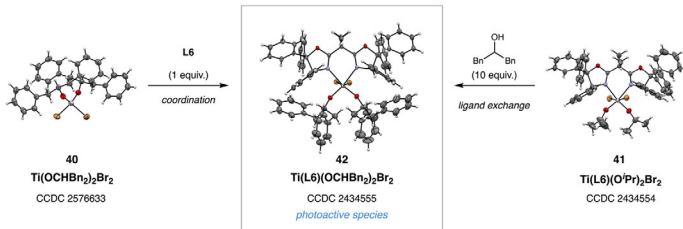


72% yield, 96:4 er



63% yield, 96:4 er

Synthesis and structure characterization of photoactive Ti(BOX)-alkoxide complexes

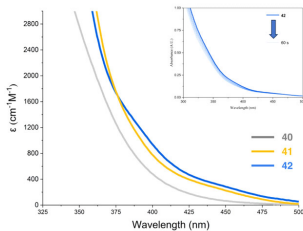


Catalytic performance validation

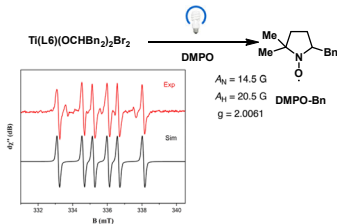


10 mol% 40, 10 mol% L6	61% yield	94:6 er
10 mol% 41	64% yield	92:8 er
10 mol% 42	58% yield	95:5 er

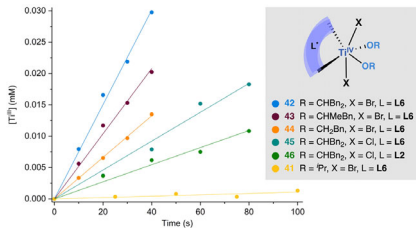
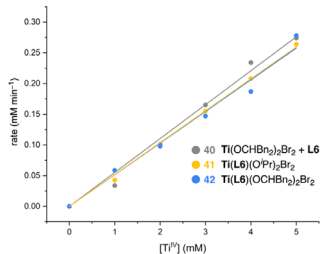
UV-vis spectra of Ti(IV) complexes



Operando EPR experiment



Photolysis rate of Ti(BOX)-alkoxide complexes

Kinetic experiments of Ti^{IV} complexes

ORGANIC CHEMISTRY

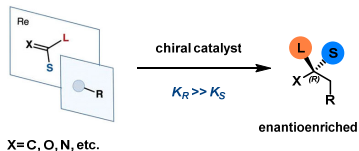
Multiplicative enhancement of stereoenrichment by a single catalyst for deracemization of alcohols

Lu Wen[†], Jia Ding[†], Lingfei Duan[†], Shun Wang, Qing An, Hexiang Wang, Zhiwei Zuo*

单一催化剂对醇去消旋化中立体富集的倍增式增强”

Z. Zuo, *Science* **382**, 458–464 (2023)

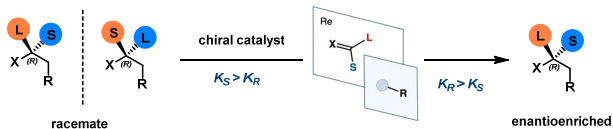
A) Established enantioselective C-C bond formations



stringent requirement for high enantioinduction: $er = k_R/k_S$

principle of microscopic reversibility: $k_{-R} >> k_{-S}$

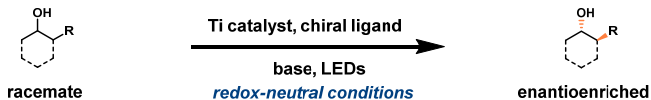
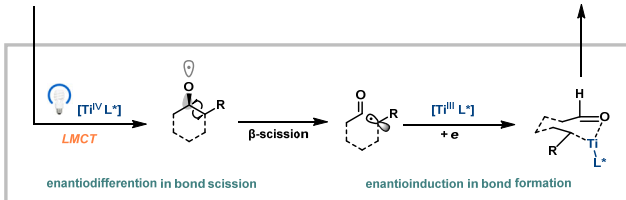
B) Catalytic deracemization via enantioselective C-C bond scission and formation



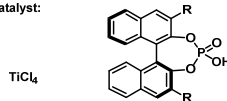
multiplicative enhancement of stereoenrichment: $er = (k_{-S} k_R)/(k_{-R} k_S)$

one chiral catalyst + two distinct enantioinduction steps $\Rightarrow$ high stereoselectivity

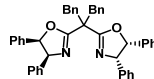
Deracemization of free alcohols enabled by asymmetric LMCT catalysis



catalyst:



for cyclic alcohols



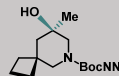
for acyclic alcohols



up to 81% yield,
8.9:1 d.r., 93:7 er

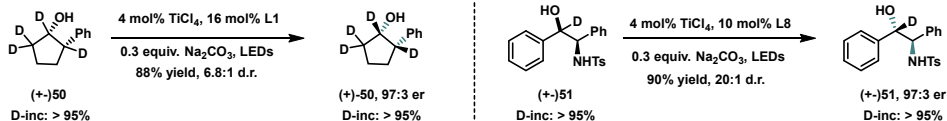


up to 99% yield,
20:1 d.r., 99:1 er

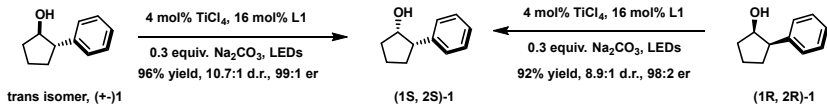


90% yield, 93:7 er

A) Isotope labeling experiments preclude alcohol oxidation/reduction and HAT pathways for deracemization

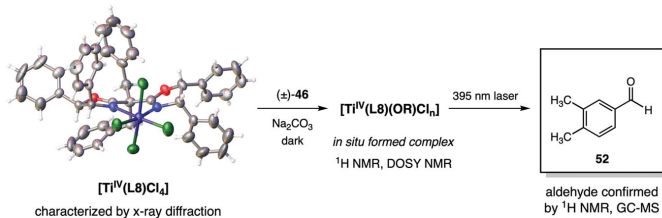
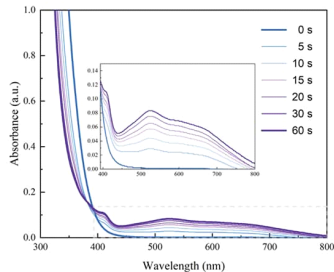


B) enantioconvergent transformations support deracemization through a shared, achiral intermediate

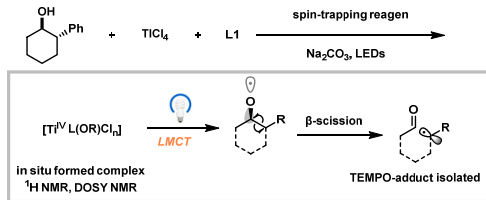
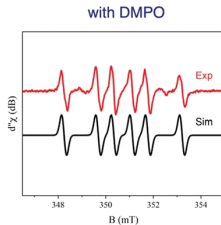
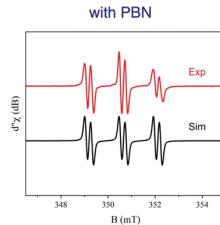


钛催化的LMCT

C) steady state photolysis experiments validate the LMCT-homolysis of Ti(IV) alkoxide complex

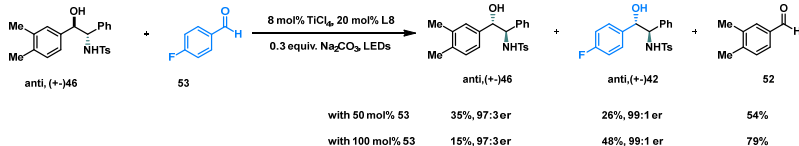


D) spin-trapping EPR experiments validate the generation of alkyl radical in the bond scission event

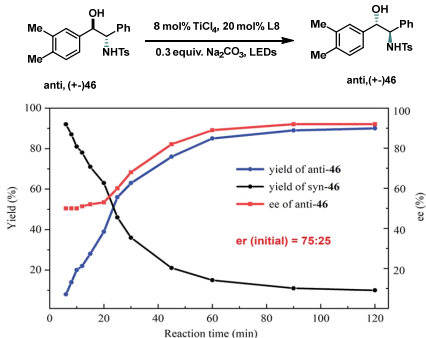


钛催化的LMCT

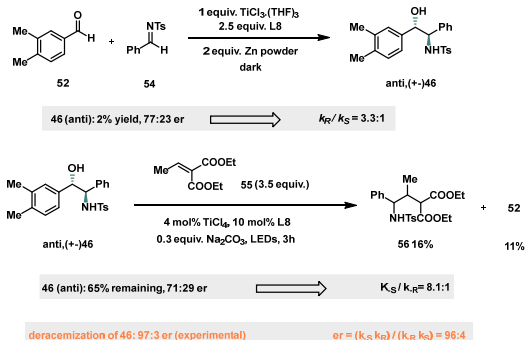
E) cross-over experiments validate the intermediacy of aldehydes in the bond forming event



F) time-course study reveals synergistic enantioinduction



G) asymmetric induction validated in decoupled bond scission and forming events



Oxidative Hetero-Coupling: Iron- and Copper-Mediated 1,2-Dicarbofunctionalization

Chandru Murugan, Bincy Chindan, Sanjai R. Yogaraj, Sheryl C. Parakkal, Venkadesh Balakrishnan,* and Ramesh Rasappan*



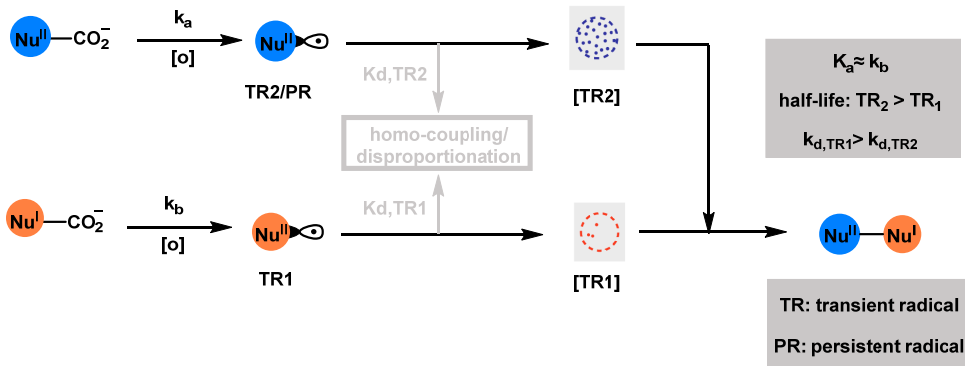
Cite This: *J. Am. Chem. Soc.* 2026, 148, 23577–23584

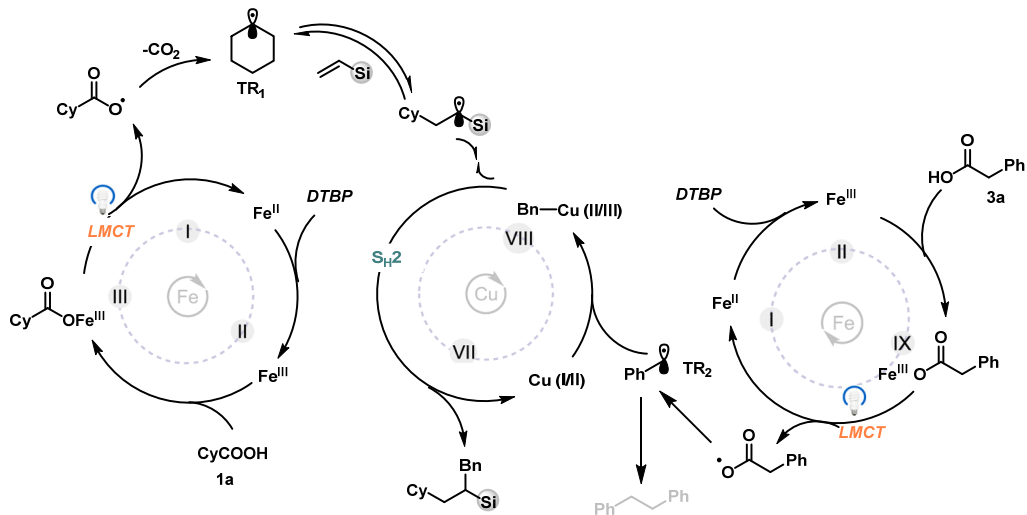


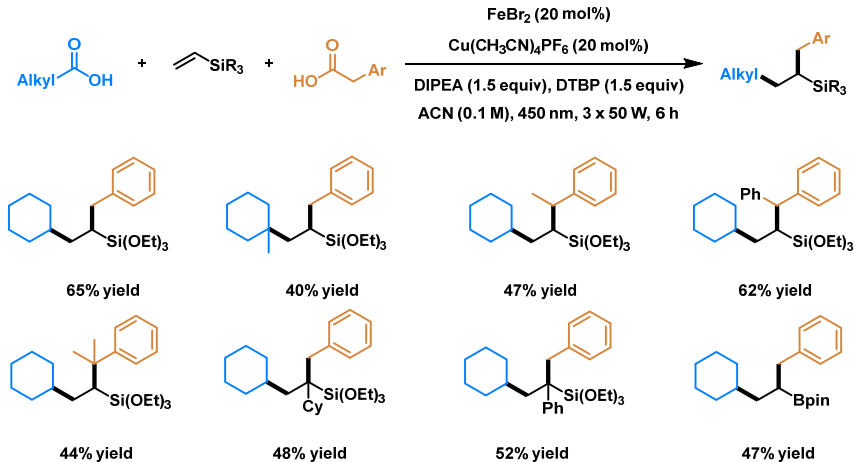
Read Online

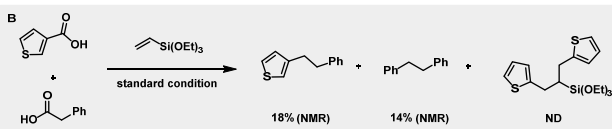
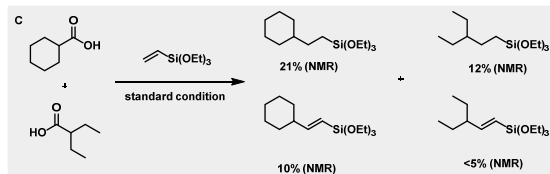
R. Rasappan, *J. Am. Chem. Soc.* **2026**, 148, 23577-23584.

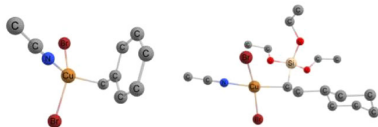
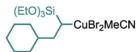
Oxidative coupling via persistent radical



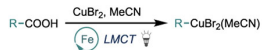




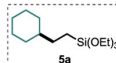
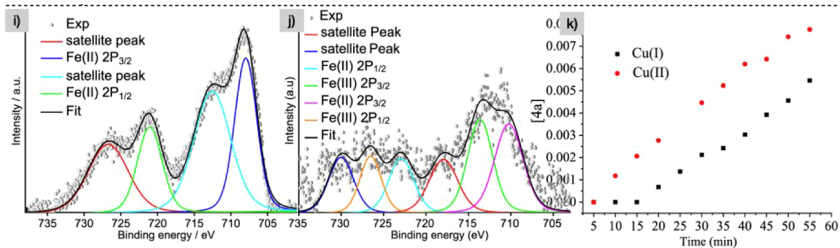


Bn-CuBr₂MeCN

bond	theoretical BDFE
Bn-CuL _n	9.72 kcal/mol
C(Si)-CuL _n	6.10 kcal/mol



h) Not an intermediate



Decarboxylative Cross-Coupling Enabled by Fe and Ni Metallaphotoredox Catalysis

Reem Nsouli, Sneha Nayak,^{||} Venkadesh Balakrishnan,^{||} Jung-Ying Lin,^{||} Benjamin K. Chi, Hannah G. Ford, Andrew V. Tran, Ilia A. Guzei, John Bacsá, Nicholas R. Armada, Fedor Zenov, Daniel J. Weix,^{*} and Laura K. G. Ackerman-Biegasiewicz^{*}

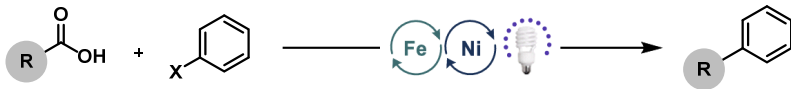


Cite This: *J. Am. Chem. Soc.* 2024, 146, 29551–29559

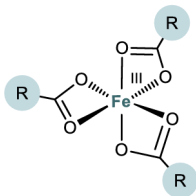


Read Online

G. Ackerman-Biegasiewicz, *J. Am. Chem. Soc.*, **2024**, 146, 29551-29559.



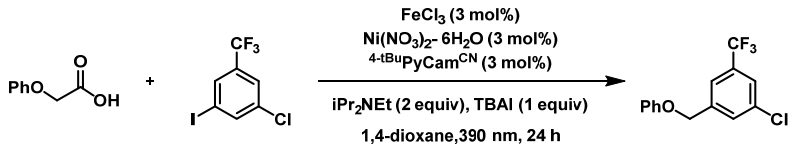
underexplored Fe photocatalysts



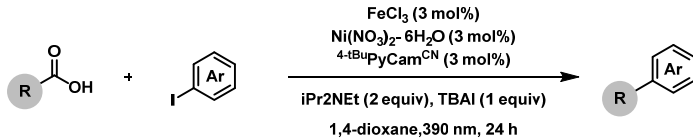
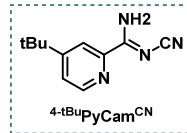
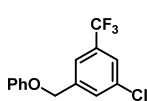
- *circumvents the need for long-lived excited states*
- *enables ligand design due to substrate binding*
- *activates substrates beyond redox potentials*
- *possesses moisture and oxygen tolerance*

Fe carboxylates formed in situ

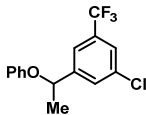
carboxylate activation via inner-sphere SET



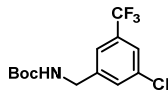
entry	deviation from standard	yield (%)
1	—	86
2	no Fe catalyst	19
3	no Ni catalyst	0
4	no TBAI	73
5	with 0.5 equiv of phthalimide	90
6	427 nm iastead of 390 nm	62



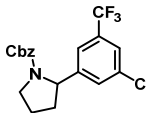
76% yield



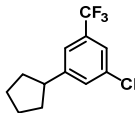
63% yield



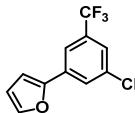
70% yield



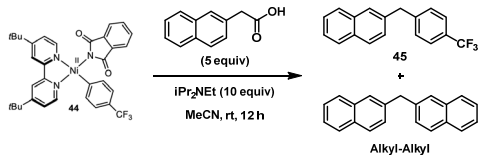
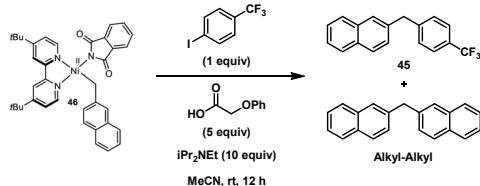
65% yield



53% yield

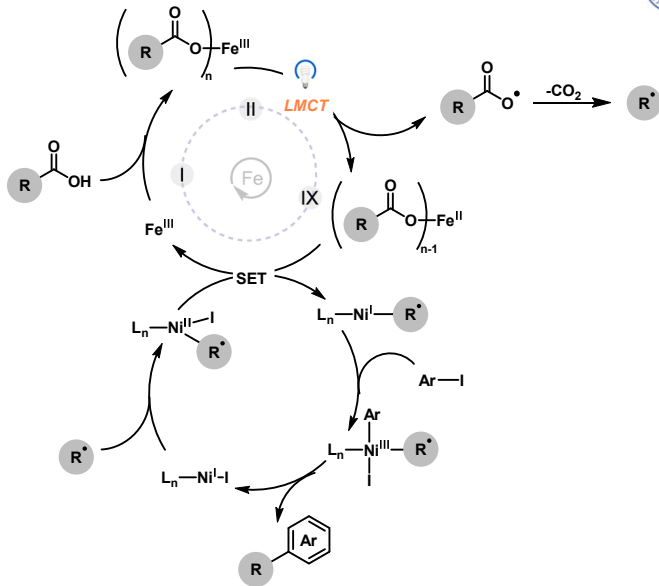


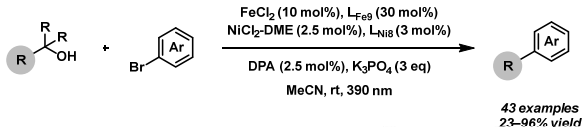
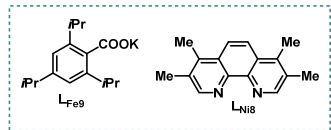
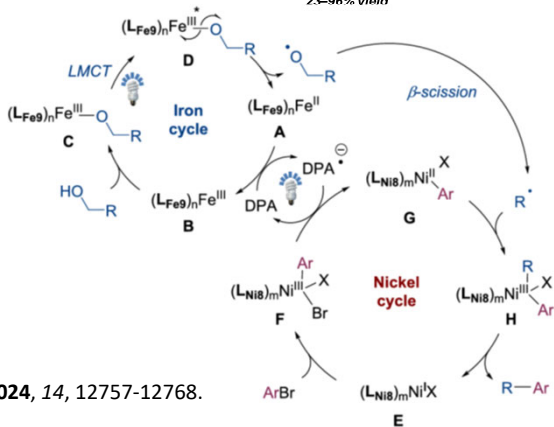
0% yield



entry	condition	yield 45 (%)	yield Alkyl-Alkyl (%)
1	FeCl_2 (1 equiv)	0	0
2	FeCl_3 (1 equiv)	0	0
3	FeCl_3 (1 equiv), 390 nm	2	15
4	FeCl_3 (1 equiv), KNPhth (5 equiv), 390 nm	13	9

entry	condition	yield 45 (%)	yield Alkyl-Alkyl (%)
1	as in scheme	28	25
2	no $\text{PhOCH}_2\text{CO}_2\text{H}$, $i\text{Pr}_2\text{NEt}$	48	47
3	FeCl_2 (1 equiv)	59	31
4	FeCl_2 (1 equiv), 390 nm	60	34
5	FeCl_2 (2 equiv)	58	39
6	FeCl_3 (1 equiv)	10	71
7	FeCl_3 (1 equiv), 390 nm	10	71
8	Cp^*Co (1 equiv), no $\text{PhOCH}_2\text{CO}_2\text{H}$, $i\text{Pr}_2\text{NEt}$	62	0



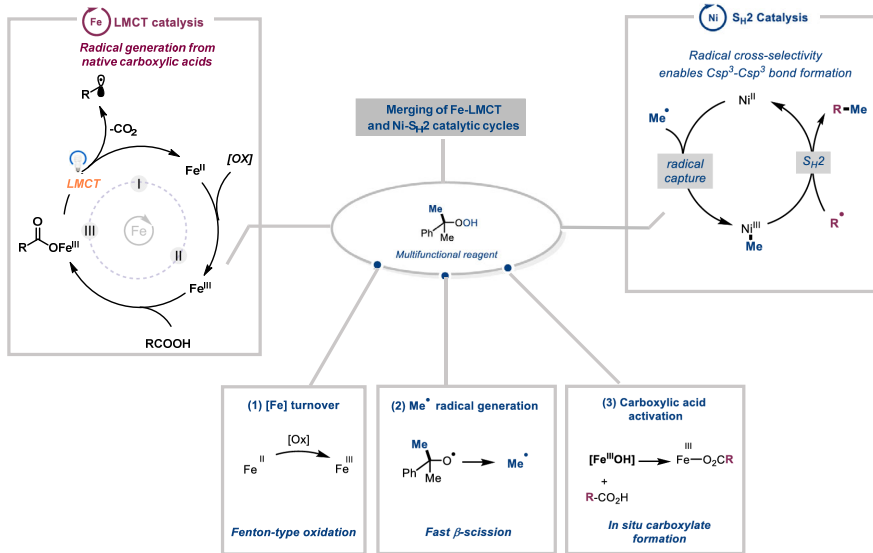


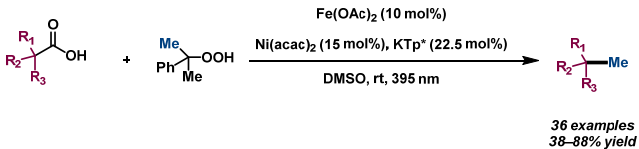
A. Amgoune, *ACS Catal.*, **2024**, 14, 12757-12768.

Cooperative Fe–LMCT and Ni–S_H2 Catalysis for Native Carboxylic Acid Methyl Editing

Mohammad Jaber  | Mikaël Le Roch  | Gaël Tran  | Abderrahmane Amgoune 

Abderrahmane Amgoune, *Angew.Chem.Int.Ed.* **2026**, e3306470





Key Features

1°, 2°, and 3° carboxylic acids

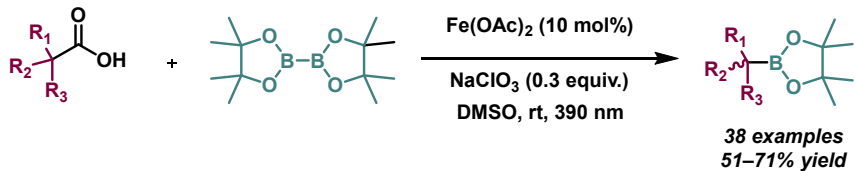
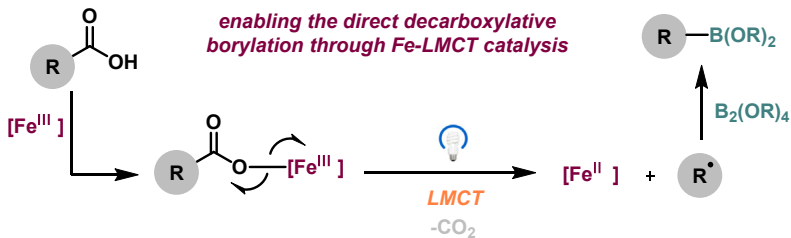
No overmethylation at positions prone to HAT

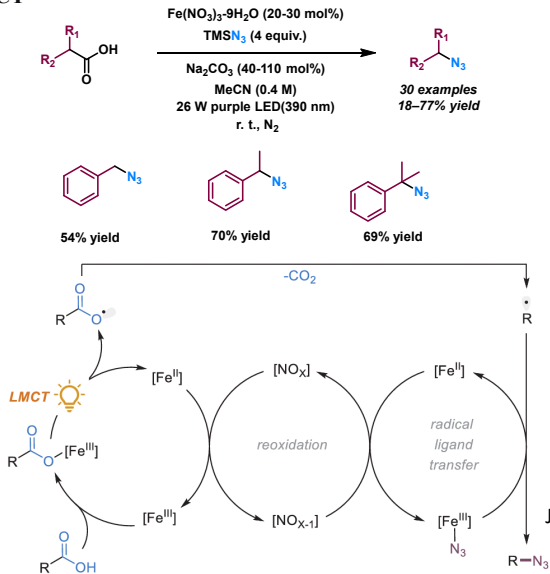
No dimerization of the radical intermediate

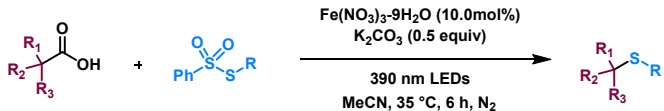
Compatible with unstabilized, benzylic or α to heteroatoms radicals

Good functional group tolerance

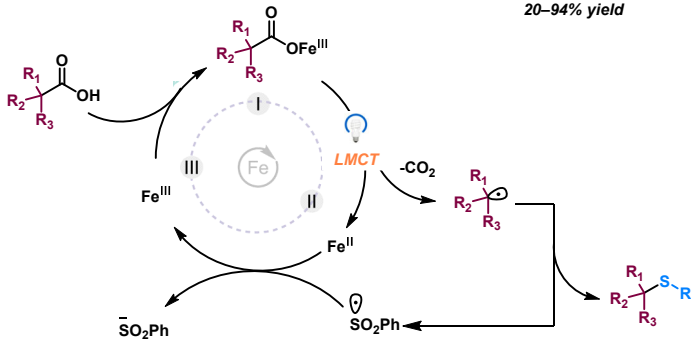
Single set of standard conditions

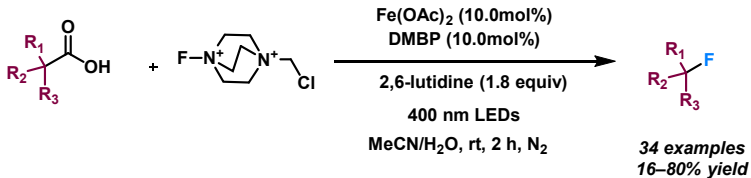
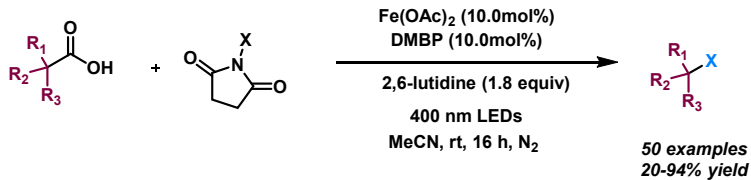



 J. G. West, *Chem Catalysis*, **2023**, 3, 100603.

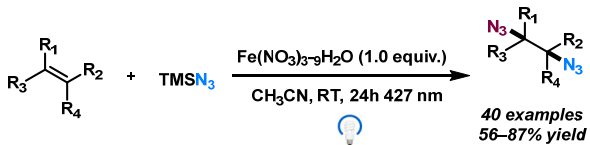
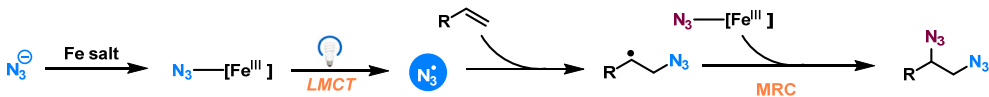


60 examples
20–94% yield





a) P. Hu, *Org. Lett.*, **2022**, 24, 5972–5976. b) P. Hu, *Chem. Commun.*, **2024**, 60, 2764–2767.



J. G. West, *Nat. Commun.*, **2022**, 13, 7881

