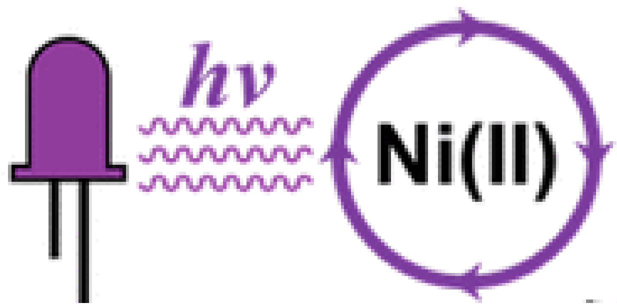
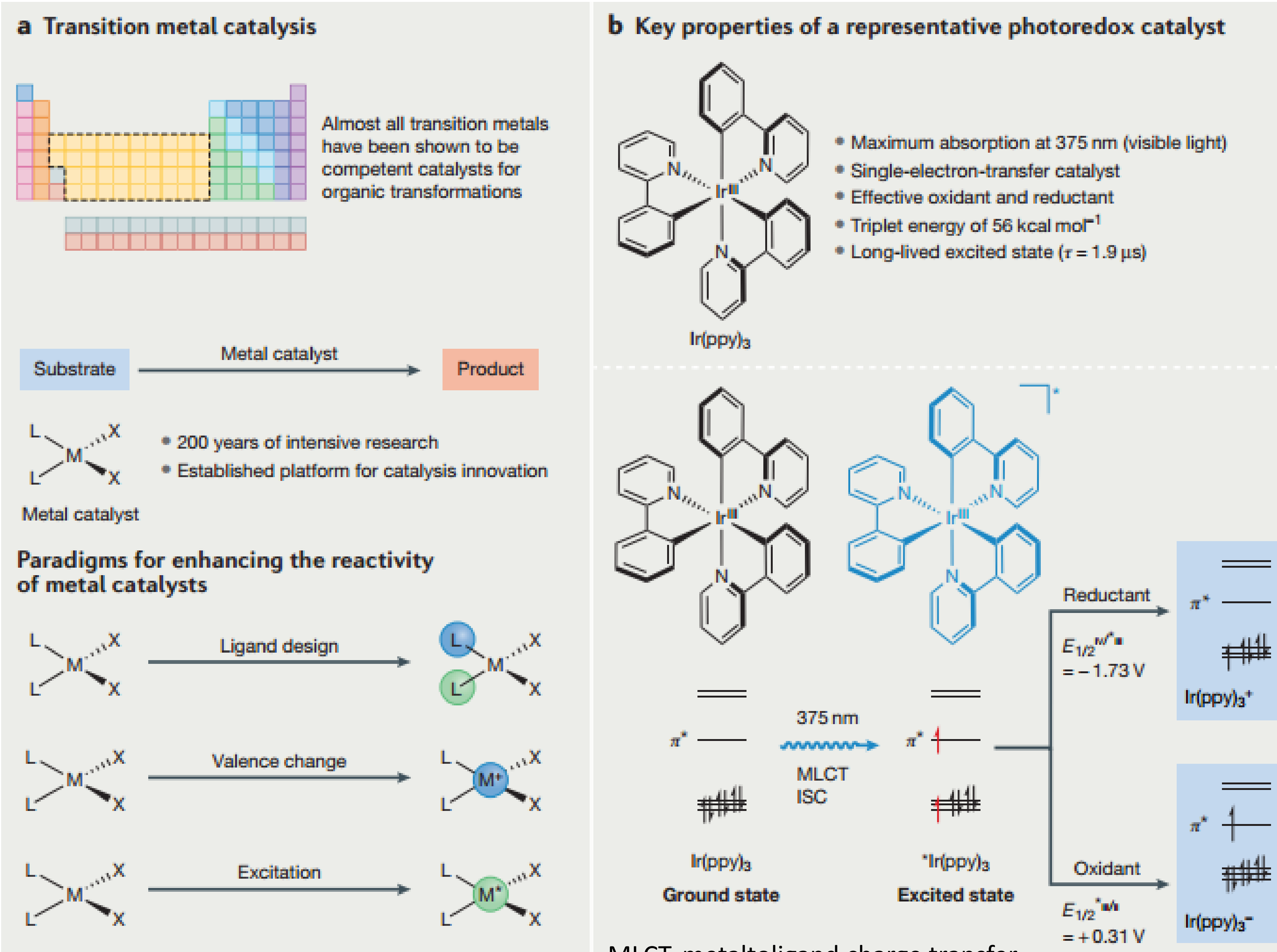
Nickel/Photocatalytic



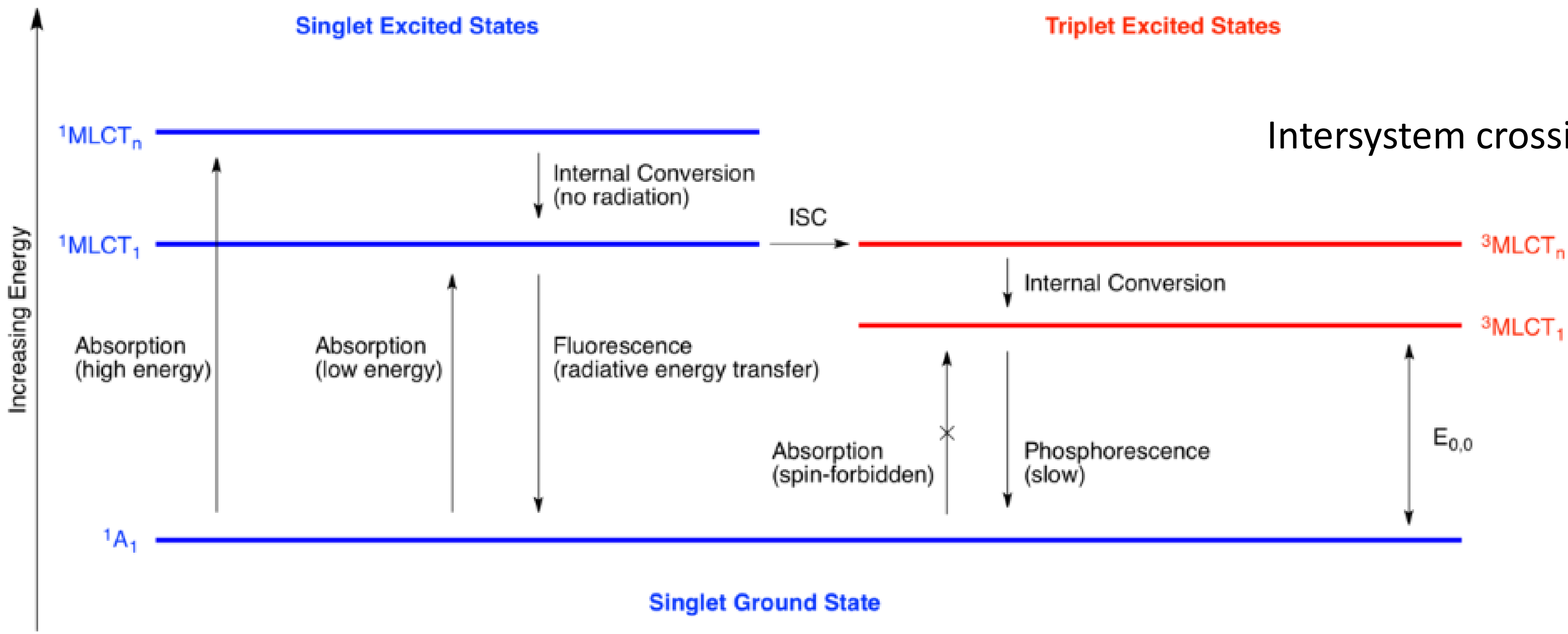
Yadong Gao
20180613



MLCT, metaltoligand charge transfer

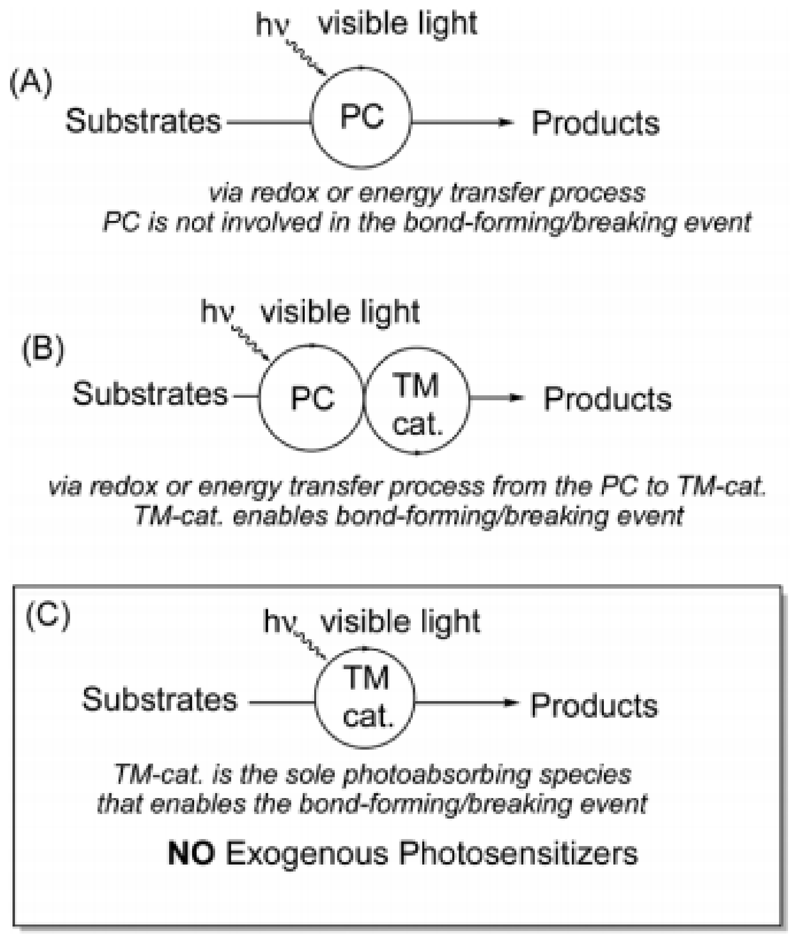
David W. C. MacMillan *Nat. Rev. Chem.* 1, 0052 (2017).

Photoexcitation



Intersystem crossing

Photoredox catalysis - Wikipedia
https://en.wikipedia.org/wiki/Photoredox_catalysis

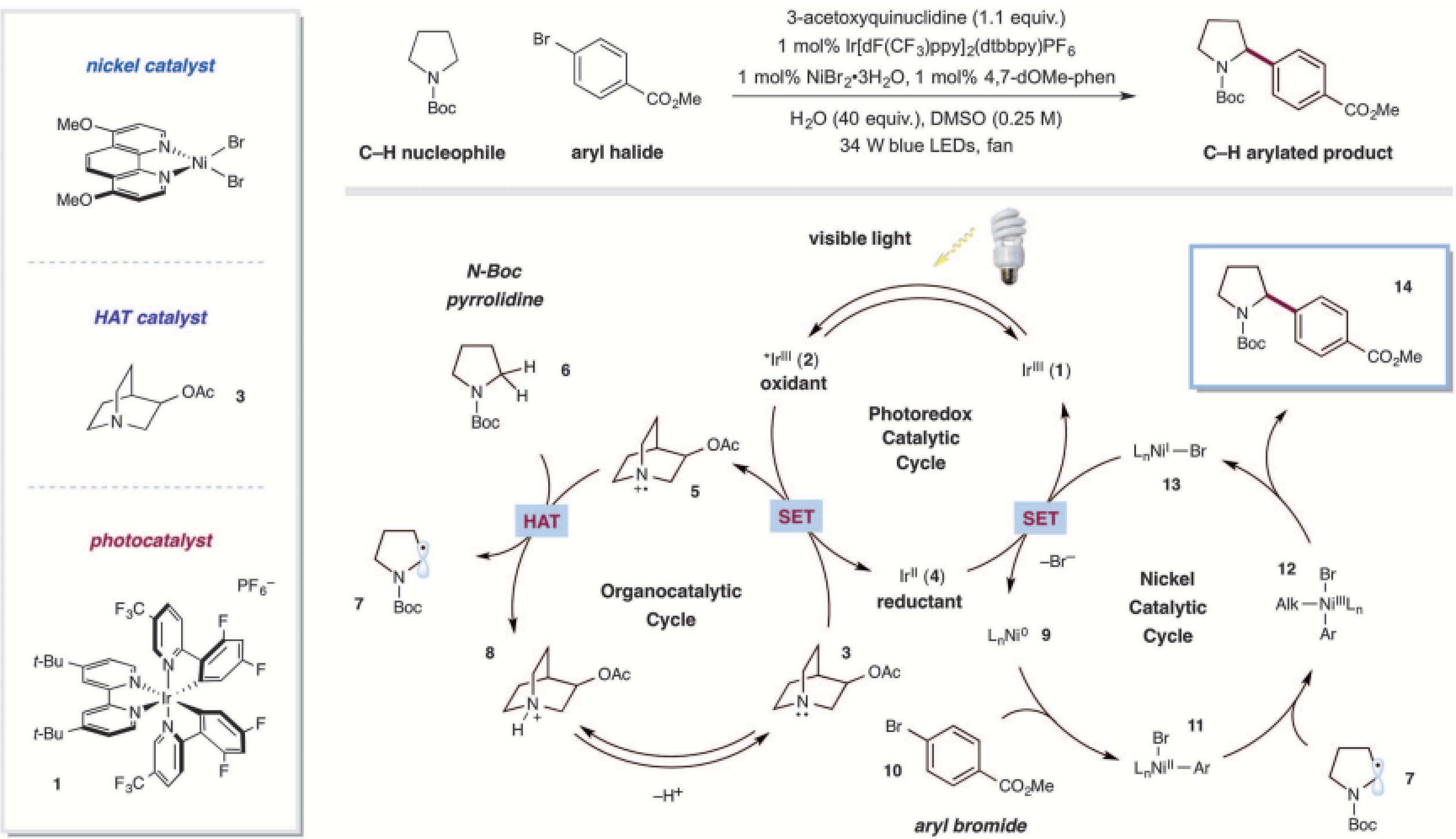


(TM = Co, Fe, Cu, Pd, Pt, Au)

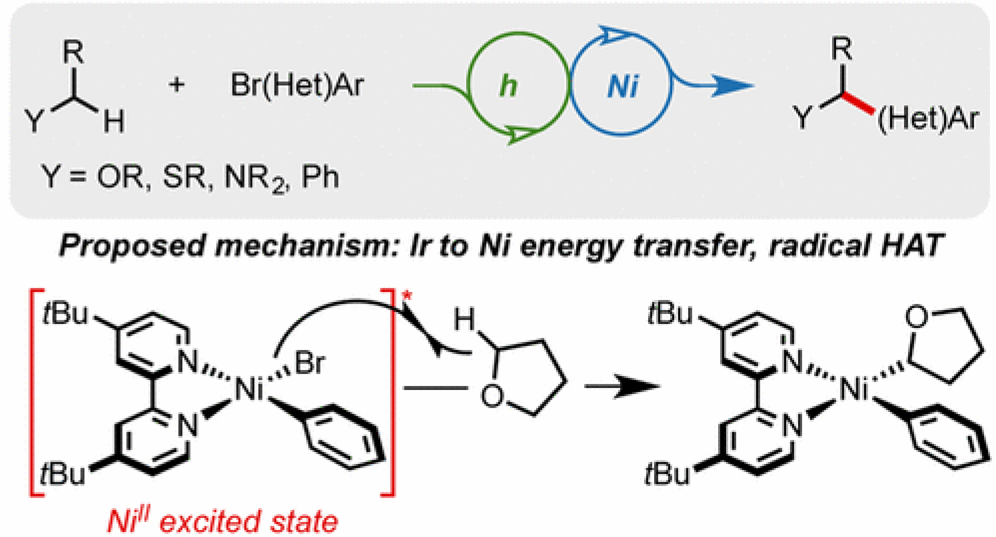
Fig. 1 Photocatalytic approaches: (A) traditional photocatalysis. (B) Cooperative/dual photocatalysis. (C) Visible light-induced transition metal catalysis: focus of this tutorial review.

Ni

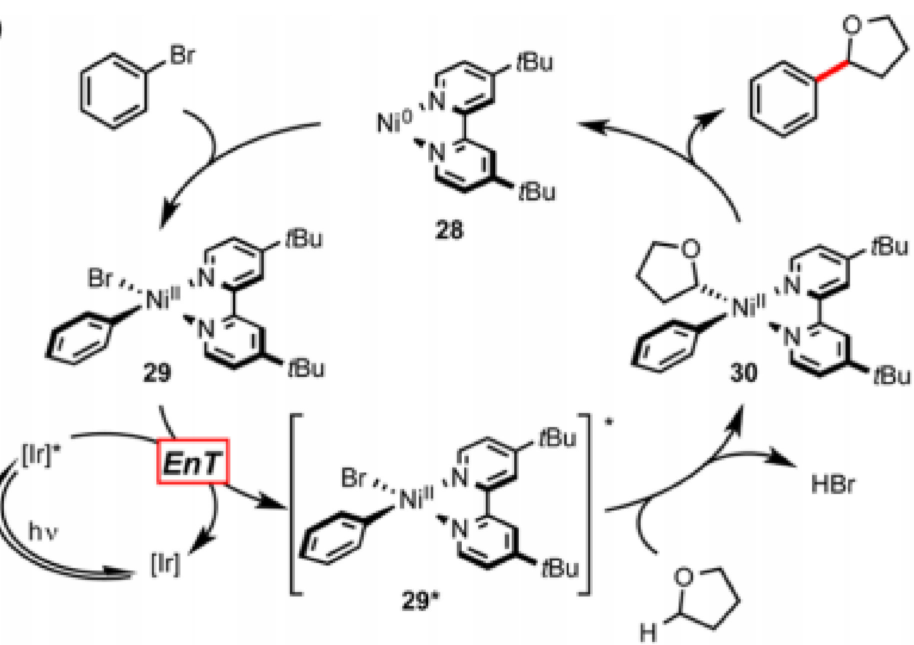
Chem. Soc. Rev., 2017, 46, 6227--6240



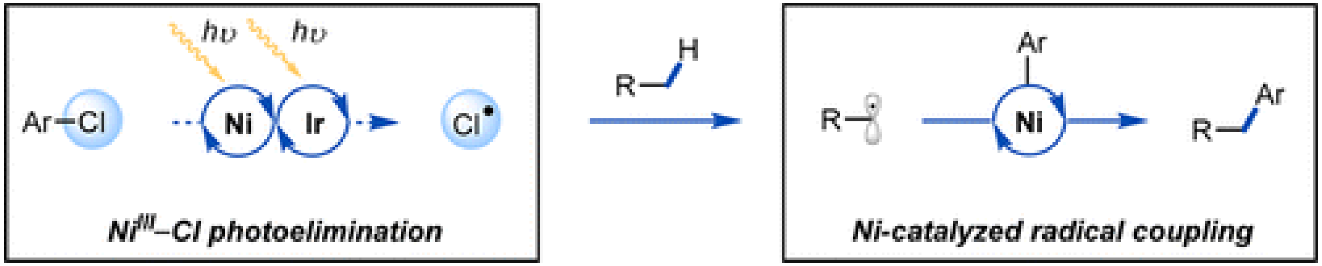
David W. C. MacMillan Science, 2016, 352(6291): 1304-1308.

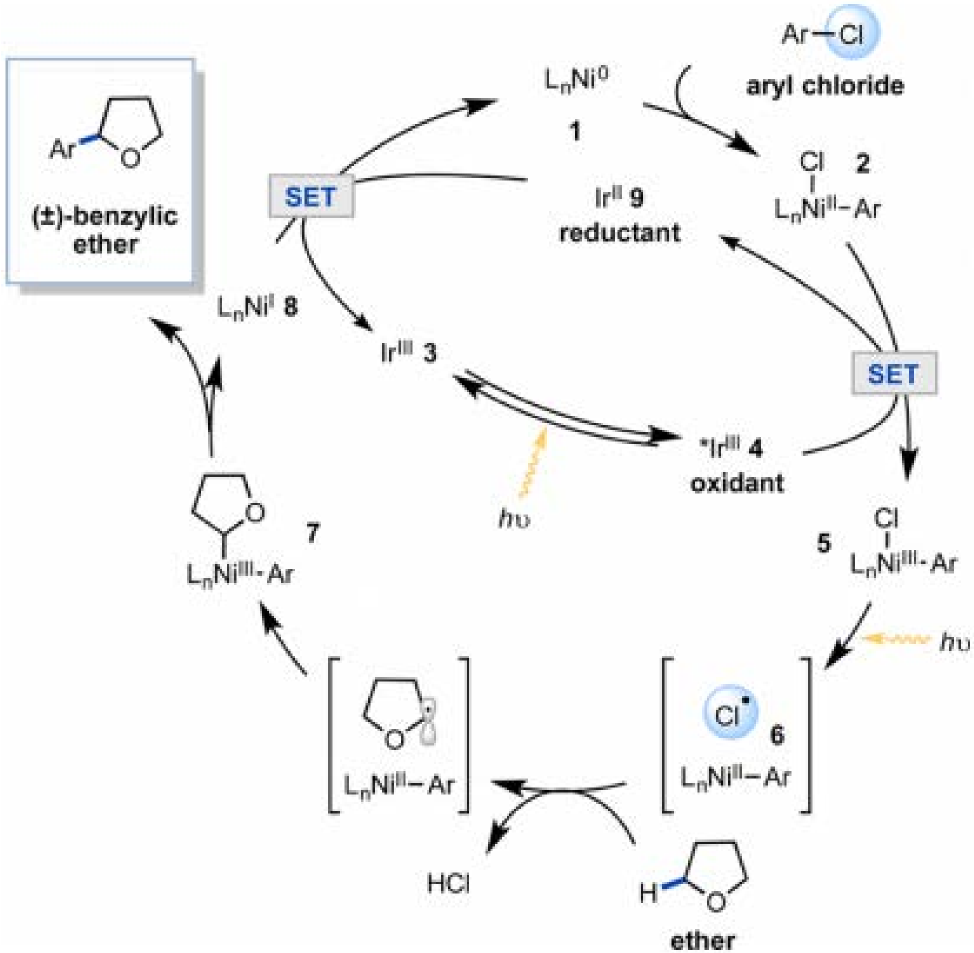


(A)



Gary A. Molander* *J. Am. Chem. Soc.* 2016, 138, 39, 12715-12718





photocatalyst **3** (2 mol%)
Ni(cod)$_2$ (10 mol%)
dtbbpy (15 mol%)

K_3PO_4 (2 eq), 0.04 M
34 W Blue LED, 23 °C

Abigail G. Doyle* *J. Am. Chem. Soc.* 2016, 138, 39, 12719-12722

10.1002/ajoc.201700115

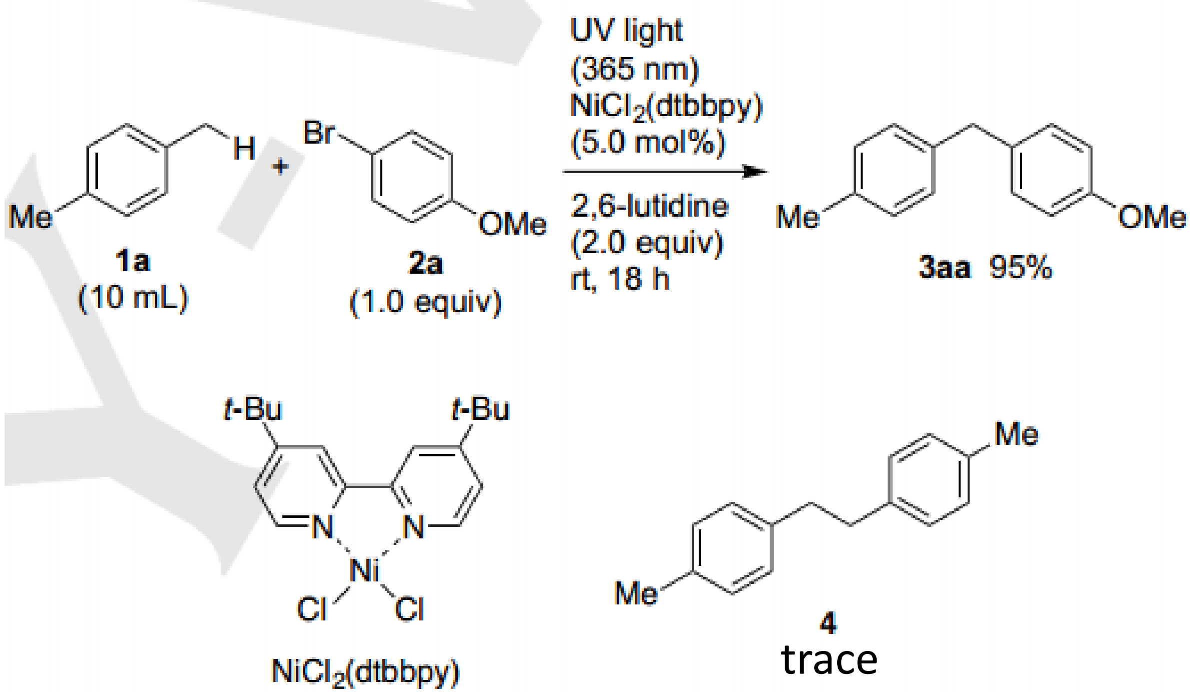
No. 1

WILEY-VCH

COMMUNICATION

Cooperation of a Nickel/Bipyridine Complex with Light for Benzylic C–H Arylation of Toluene Derivatives

Naoki Ishida, Yusuke Masuda, Norikazu Ishikawa, and Masahiro Murakami*[a]



Asian Journal of Organic Chemistry, 2017, 6(6): 669-672.

Table 1. Scope of Aryl Bromides.[a]

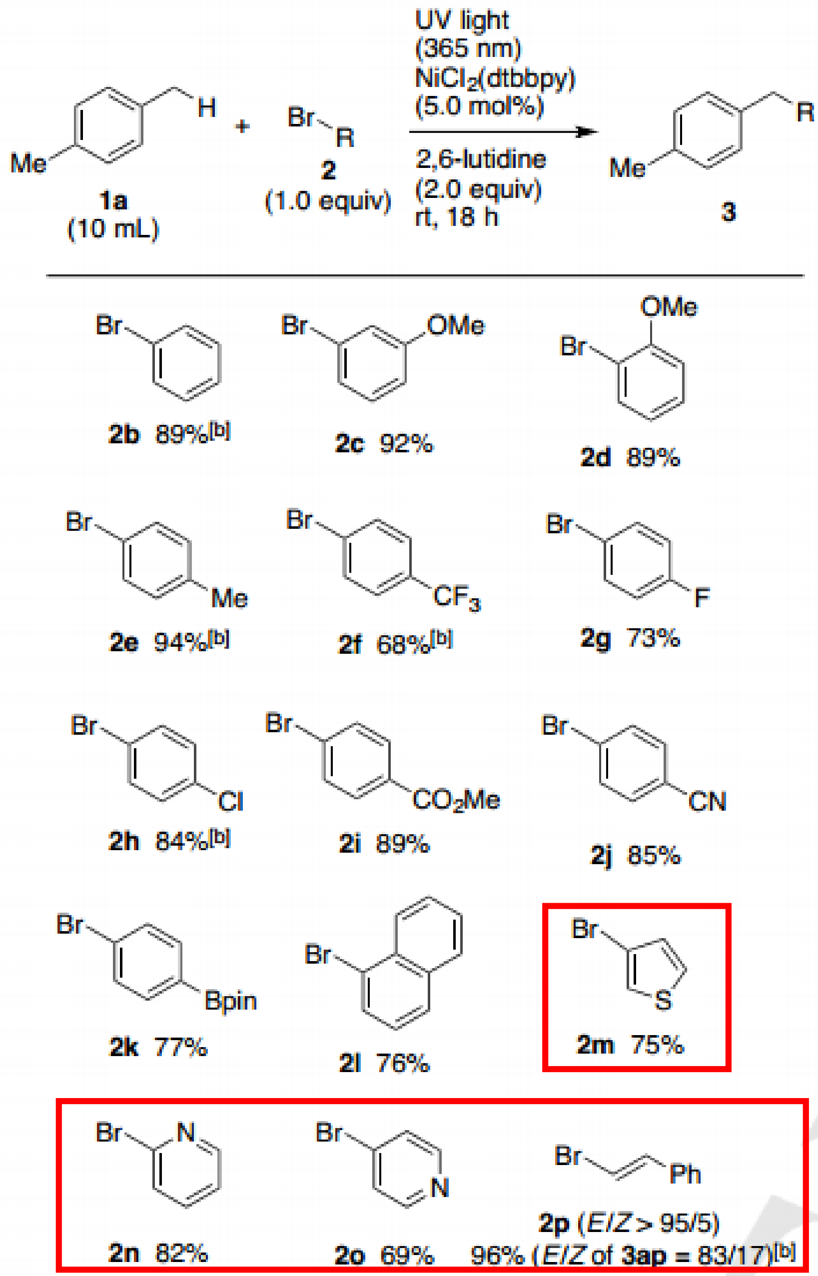
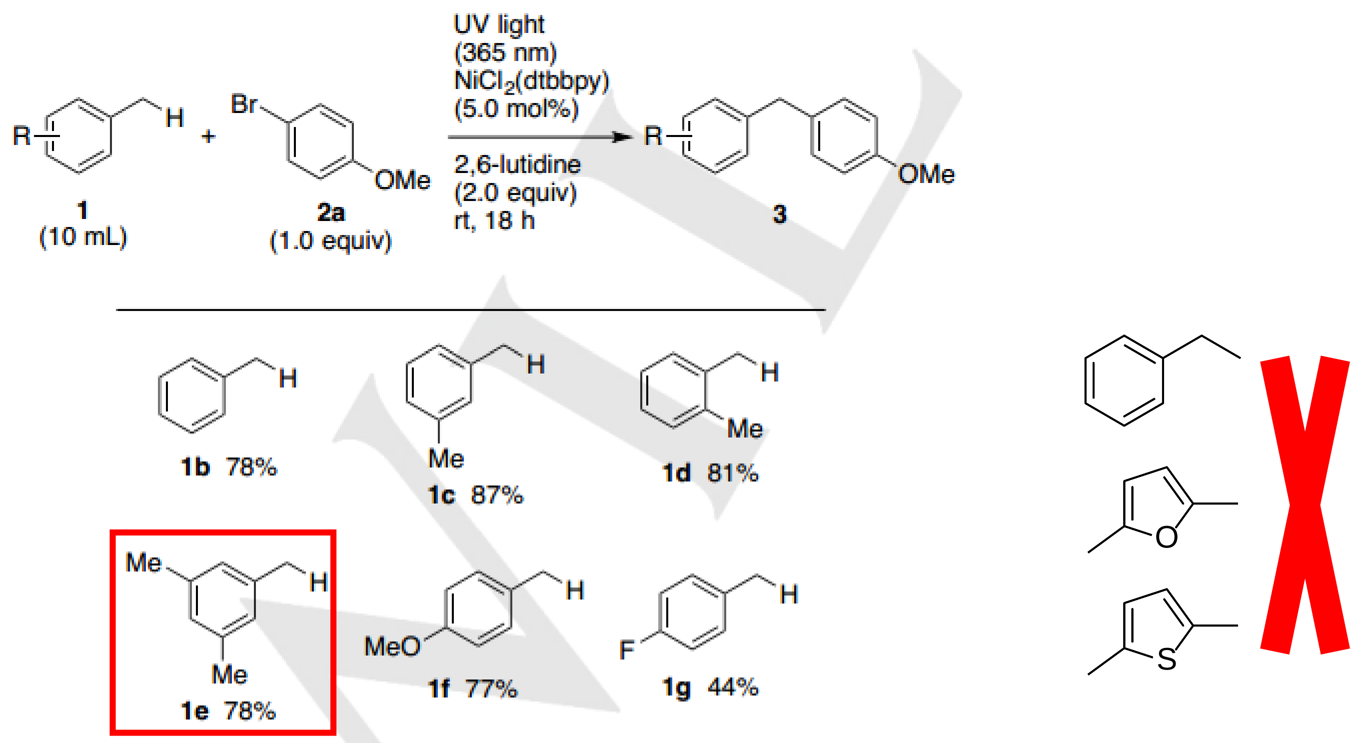
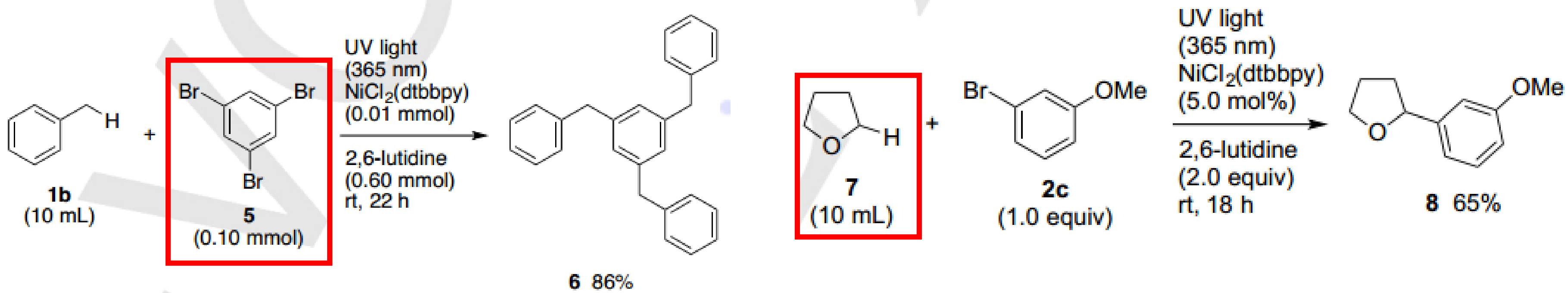


Table 2. Scope of Aromatic Hydrocarbons.[a]





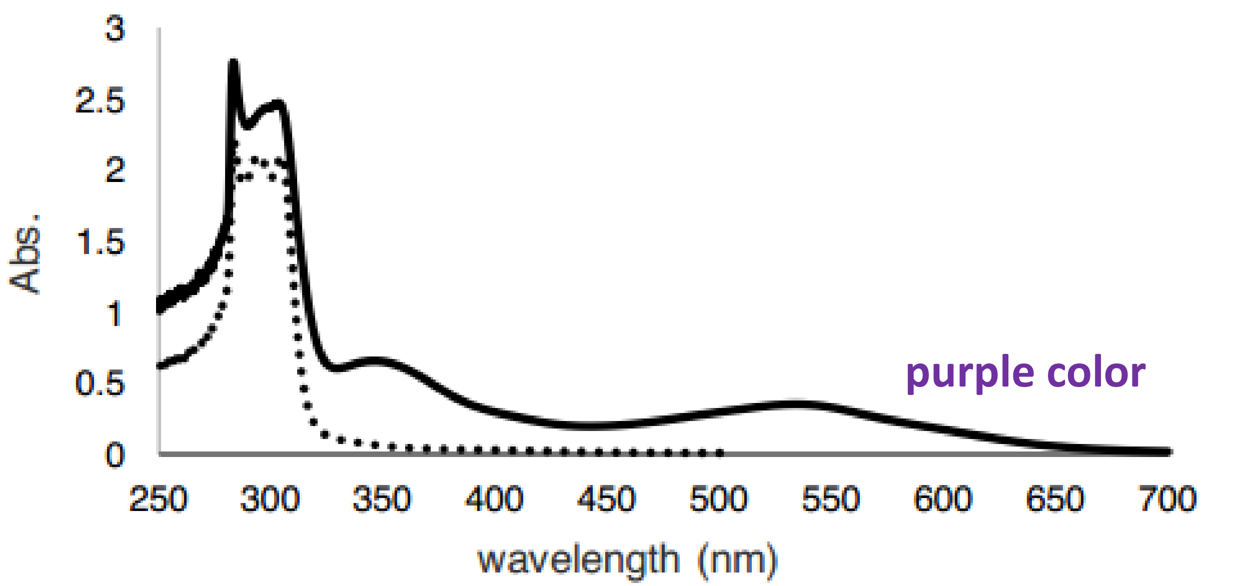
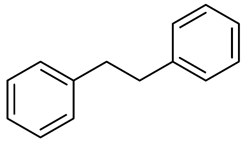
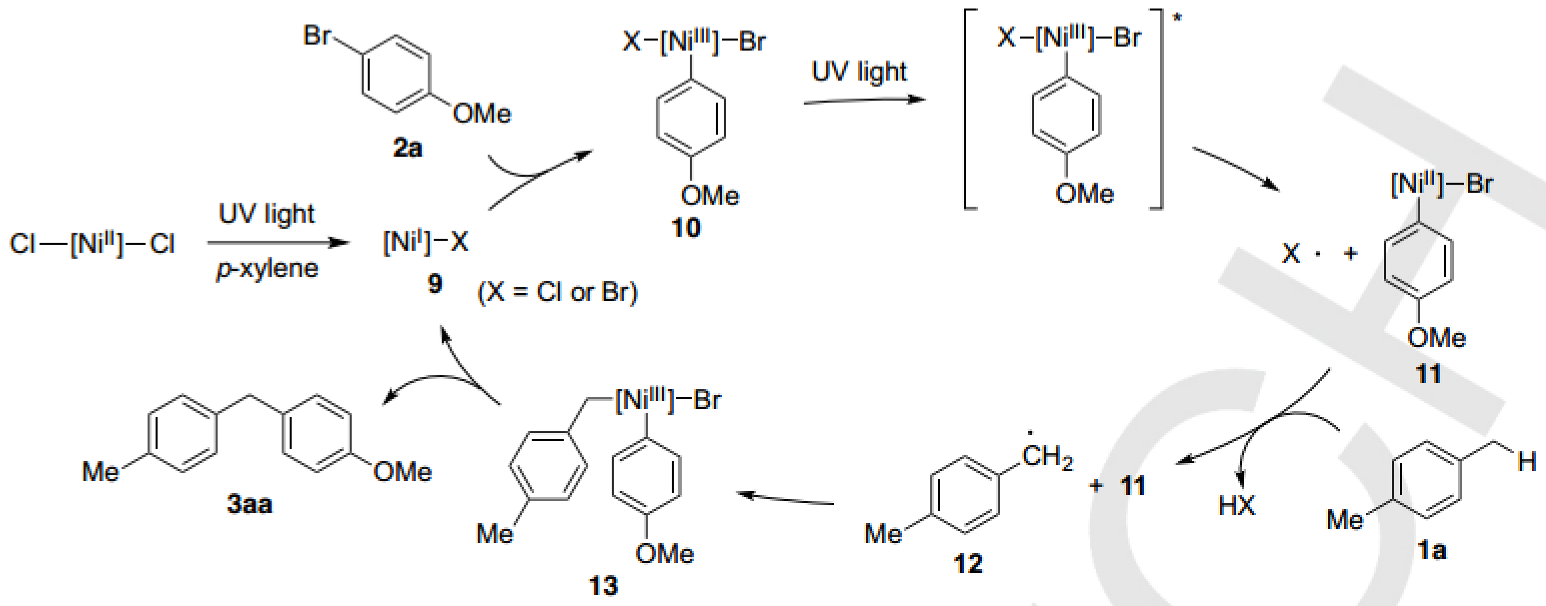


Figure 1. A Shift of UV-Vis Absorption Spectrum by Photolysis of a Mixture of $NiCl_2$(dtbbpy) and 2,6-Lutidine in Toluene. Dot line: before UV irradiation, plain line: after UV irradiation for 1h.

Only NiCl2(dtbbpy) exhibited absorption around 365 nm

maximum absorptions at 346 and 535 nm (Figure 1), which are ascribed to a reduced nickel species.
GC-MS analysis of the reaction mixture confirmed the generation of 2,2-diphenylethane as a byproduct,
Suggesting that toluene serves as the reductant.





Scheme 4. Possible Mechanisms.

No. 2

JACS JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

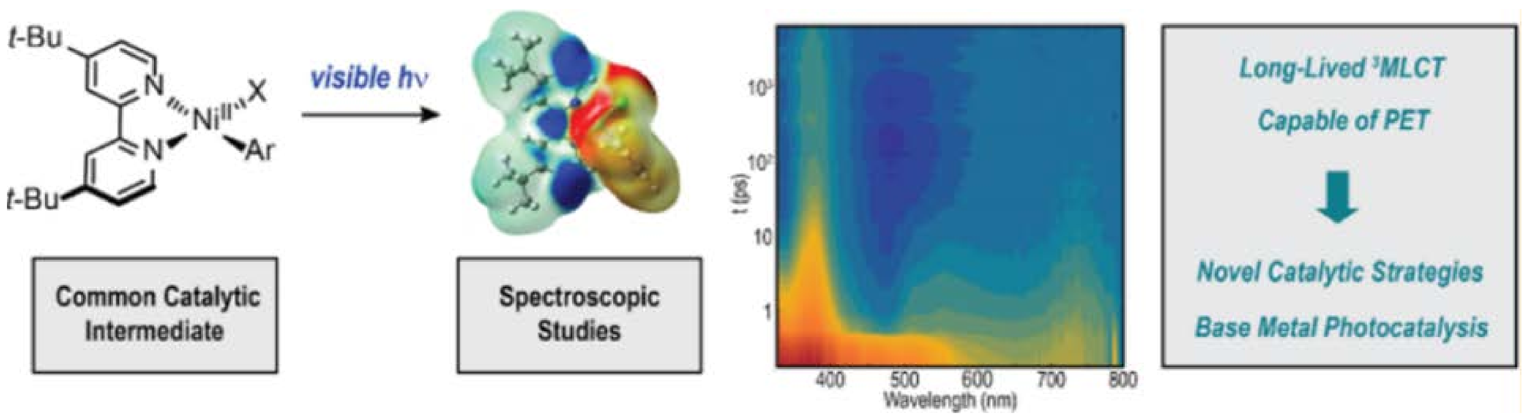
Article

Cite This: *J. Am. Chem. Soc.* 2018, 140, 3035−3039

pubs.acs.org/JACS

Long-Lived Charge-Transfer States of Nickel(II) Aryl Halide Complexes Facilitate Bimolecular Photoinduced Electron Transfer

Benjamin J. Shields, Bryan Kudisch, Gregory D. Scholes, and Abigail G. Doyle*



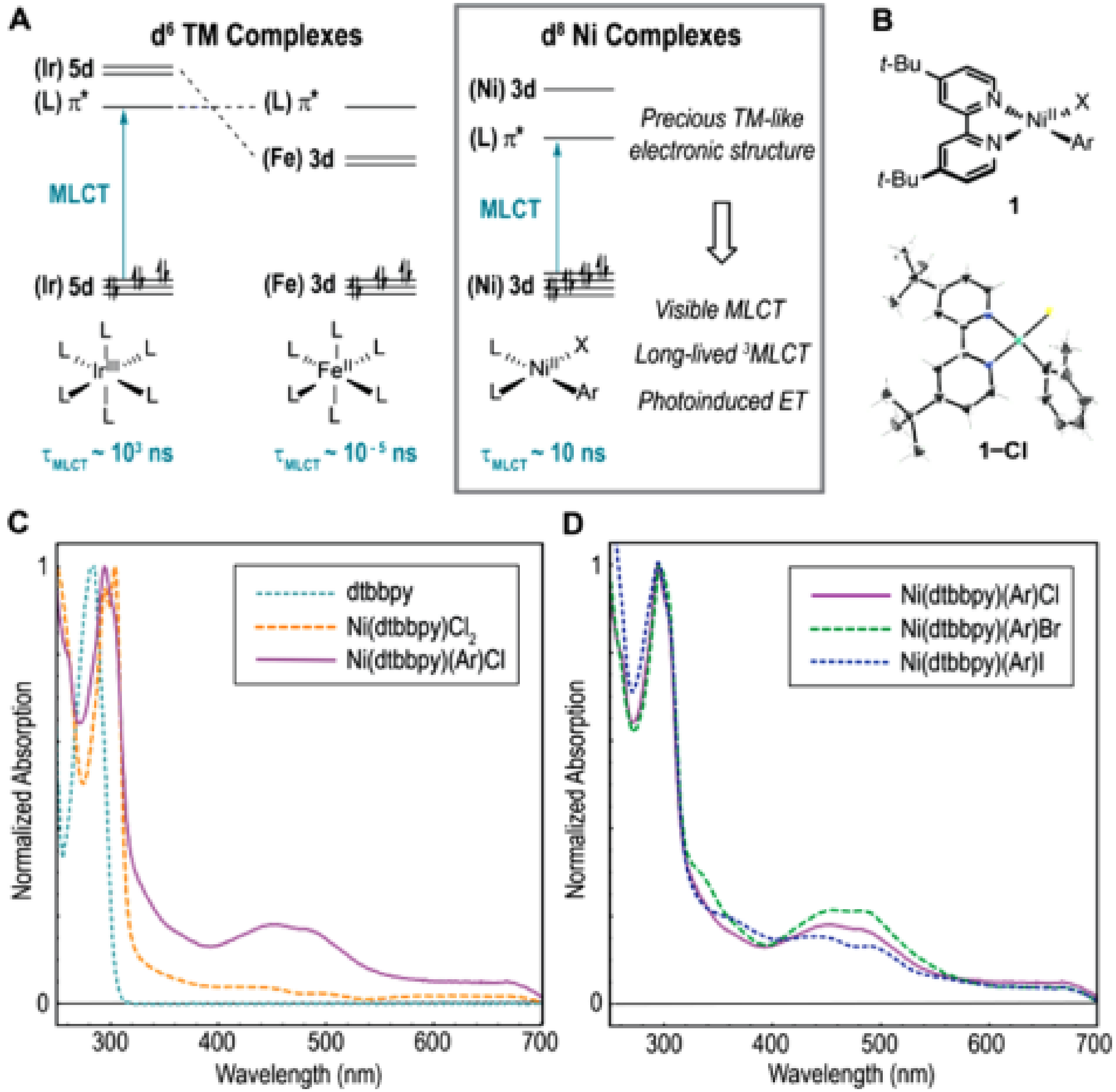


Figure 1. (A) Electronic structure of d^6 photocatalysts compared to Ni(II) aryl halide complexes. (B) Structure of Ni complexes and X-ray crystal structure of **1-Cl**. (C) Comparison of component absorption spectra. (D) Absorption spectra for aryl halide complexes.

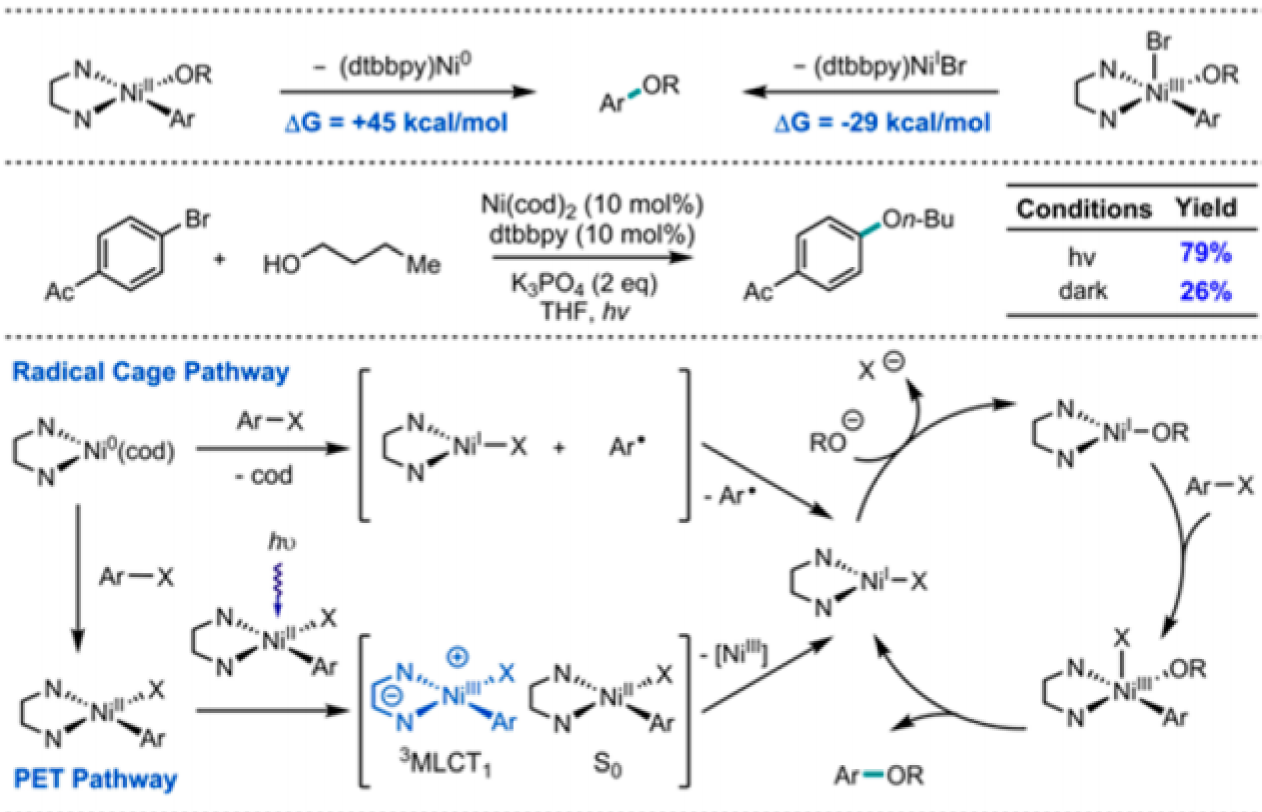


Figure 6. Ni-catalyzed C–O coupling and proposed mechanism. Yields determined by GC-FID using 1-fluoronaphthalene as an external standard.

No. 3

A Journal of the Gesellschaft Deutscher Chemiker

Angewandte Chemie

GDCh

International Edition

www.angewandte.org

The two earth-abundant metals zinc and nickel enable the formation of new $C(sp^3)$–$C(sp^2)$ bonds under irradiation with visible light. In their Communication (DOI: 10.1002/anie.201802656), J. Alcázar and co-workers describe how these reaction conditions lead to a direct acceleration of the well-known nickel-catalyzed Negishi cross-coupling without requiring the addition of an exogenous photosensitizer.

WILEY-VCH

Photocatalysis

International Edition: DOI: 10.1002/anie.201802656
German Edition: DOI: 10.1002/ange.201802656

Visible-Light-Induced Nickel-Catalyzed Negishi Cross-Couplings by Exogenous-Photosensitizer-Free Photocatalysis

*Irini Abdiaj, Alberto Fontana, M. Victoria Gomez, Antonio de la Hoz, and Jesús Alcázar**

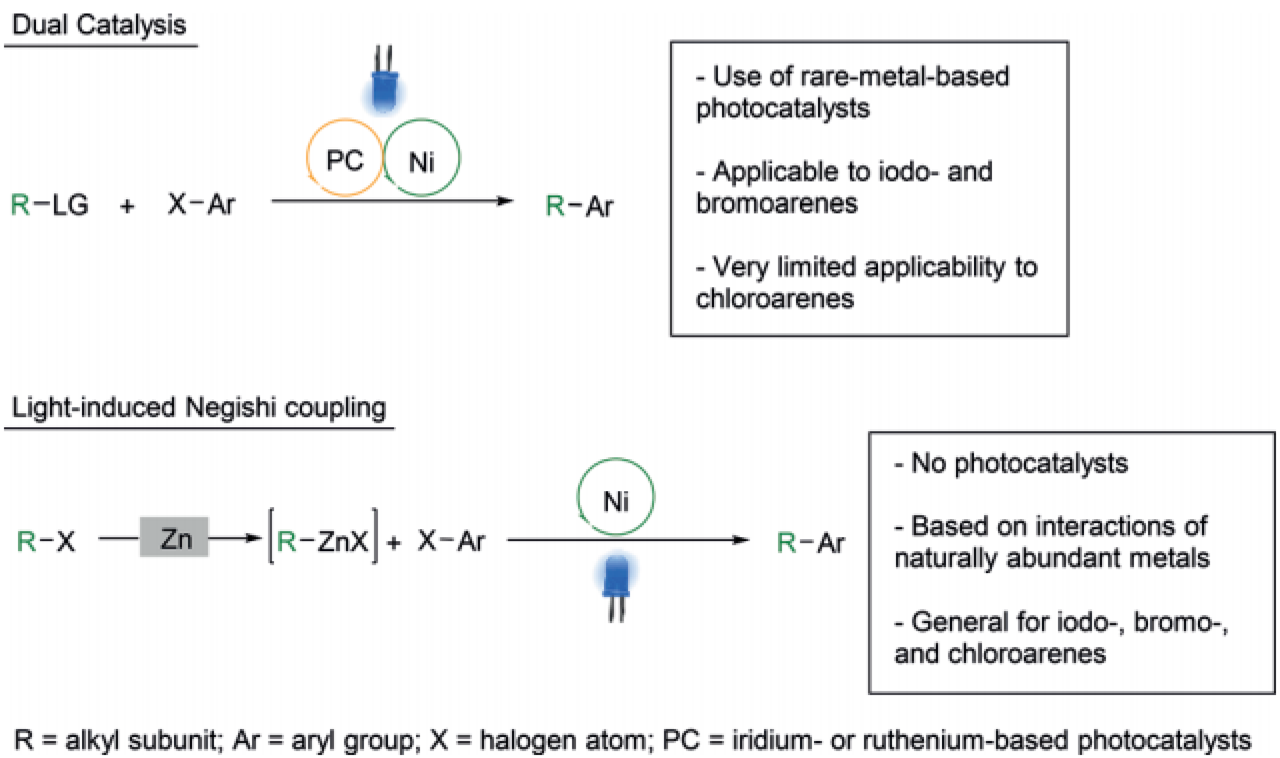
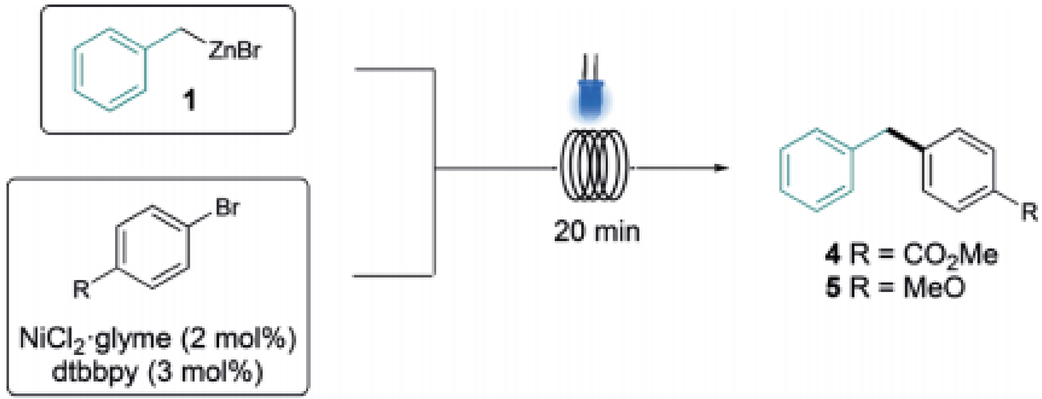


Table 1: Optimization of the flow reaction.

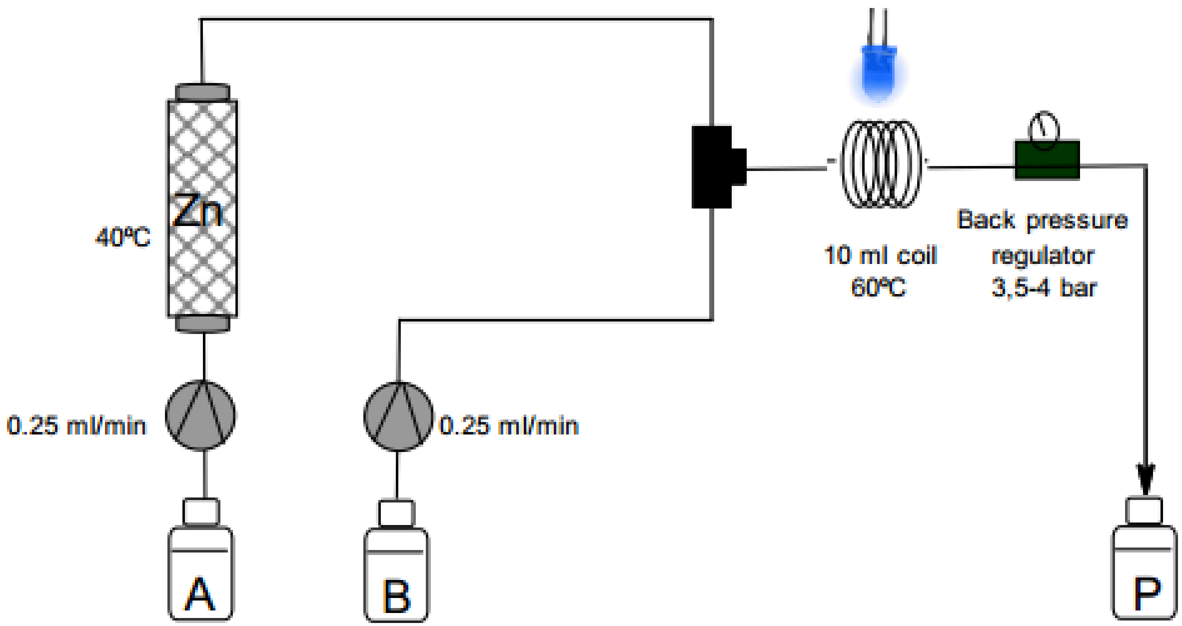


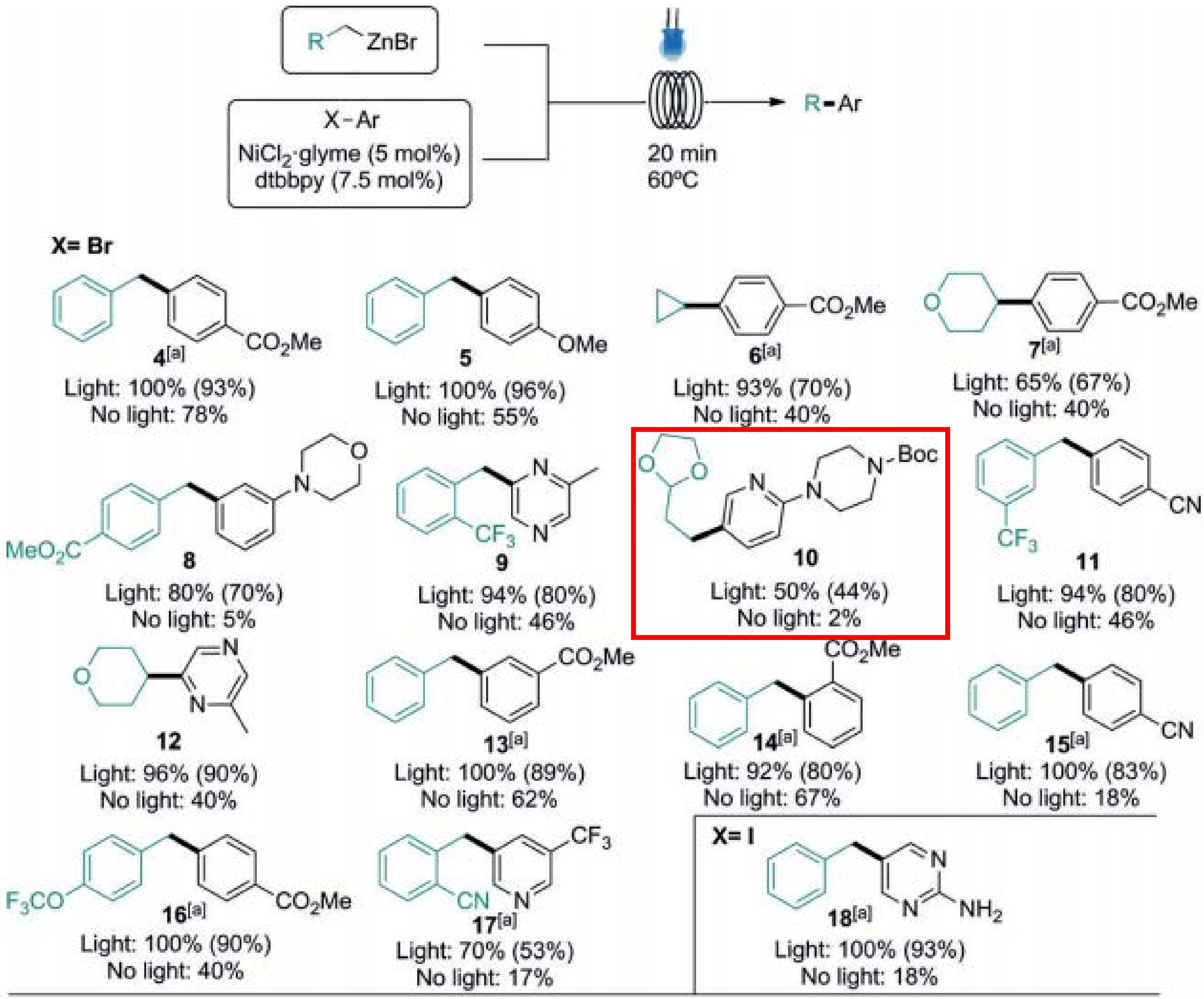
2 R = CO_2Me
3 R = MeO

Entry	*T* [°C]	R	Irradiation	Photocatalyst	Conv. [%]
1	40	CO_2Me	450 nm	*fac*-Ir(ppy)$_3$	64
2	40	CO_2Me	450 nm	–	70
3	40	CO_2Me	–	–	4
4	60	CO_2Me	450 nm	–	100
5[a]	60	CO_2Me	–	–	78
6	60	MeO	450 nm	–	0
7[a]	60	MeO	450 nm	–	53
8[a,b]	60	MeO	450 nm	–	100
9[a,b]	60	MeO	–	–	55

[a] Organozinc reagent prepared in flow. [b] With 5 mol% of the nickel catalyst. dtbbpy = 4,4′-di-*tert*-butyl-2,2′-dipyridyl.

Scale up procedure





R ZnBr
X - Ar
NiCl2·glyme (5 mol%)
dtbbpy (7.5 mol%)
20 min
60°C
R - Ar
X= Br
4[a]
Light: 100% (93%)
No light: 78%
5
Light: 100% (96%)
No light: 55%
6[a]
Light: 93% (70%)
No light: 40%
7[a]
Light: 65% (67%)
No light: 40%
8
Light: 80% (70%)
No light: 5%
9
Light: 94% (80%)
No light: 46%
10
Light: 50% (44%)
No light: 2%
11
Light: 94% (80%)
No light: 46%
12
Light: 96% (90%)
No light: 40%
13[a]
Light: 100% (89%)
No light: 62%
14[a]
Light: 92% (80%)
No light: 67%
15[a]
Light: 100% (83%)
No light: 18%
16[a]
Light: 100% (90%)
No light: 40%
17[a]
Light: 70% (53%)
No light: 17%
X= I
18[a]
Light: 100% (93%)
No light: 18%

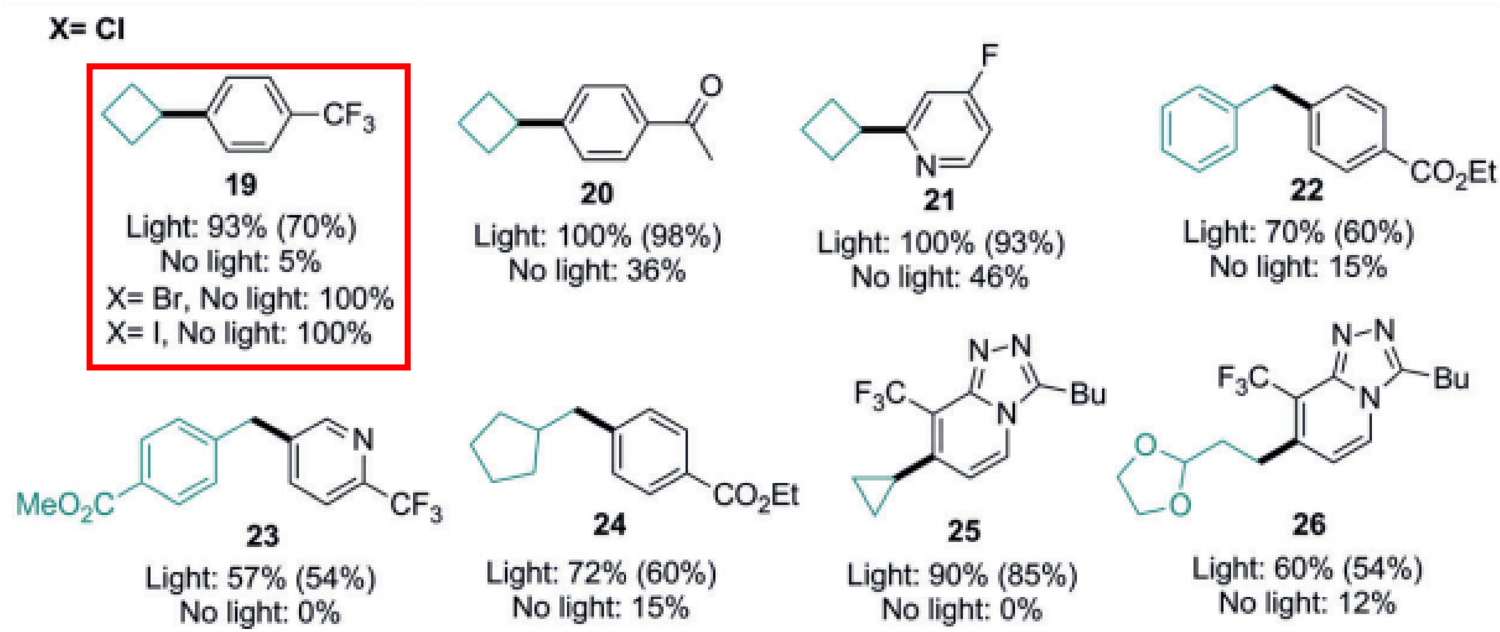


Figure 2. Scope of the light-induced nickel-catalyzed Negishi coupling with respect to the organozinc and haloarene coupling partners. Conversions determined by liquid chromatography. Yields of isolated products given in parentheses. [a] With 2 mol% of catalyst. See the Supporting Information for details.

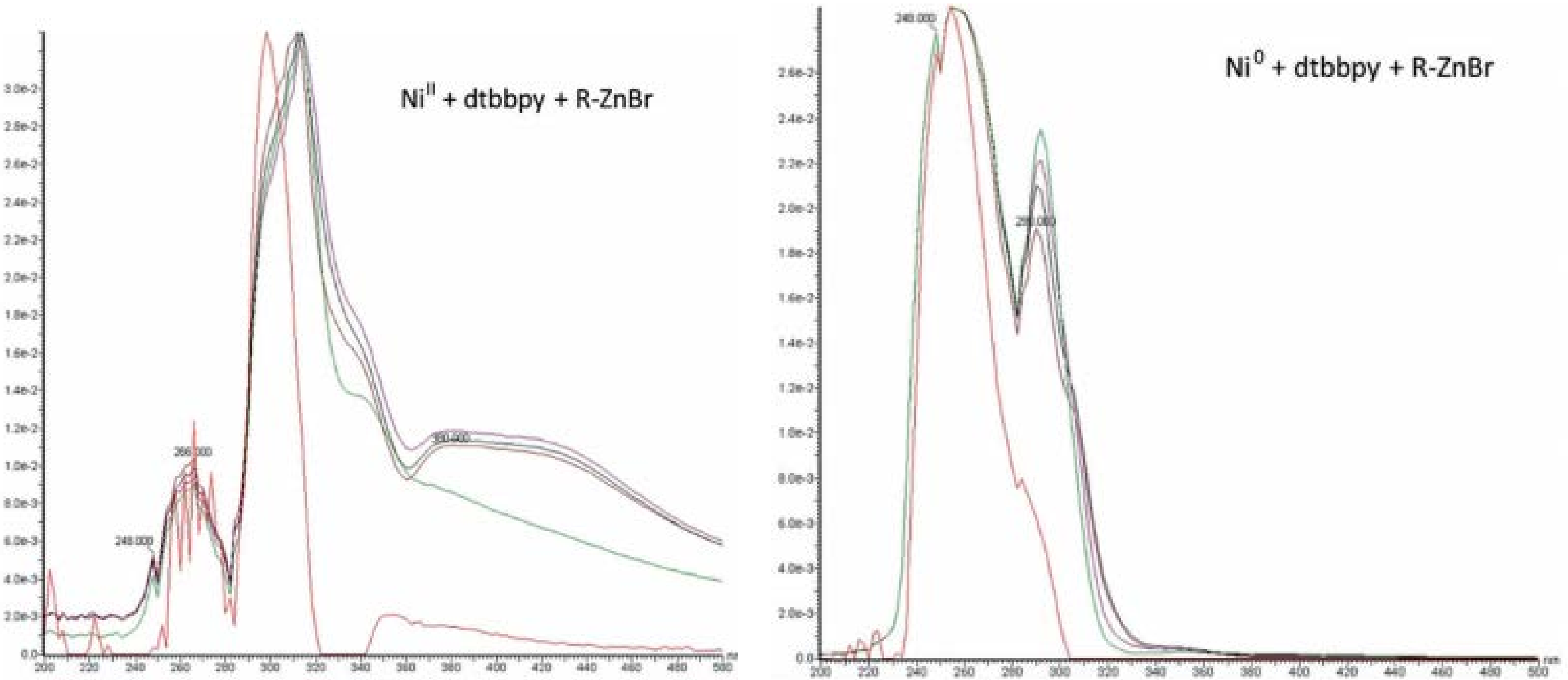


Figure 3. Absorption spectra of mixtures of nickel complexes with the organozinc reagent. Evolution of the absorption recorded over 20 min.

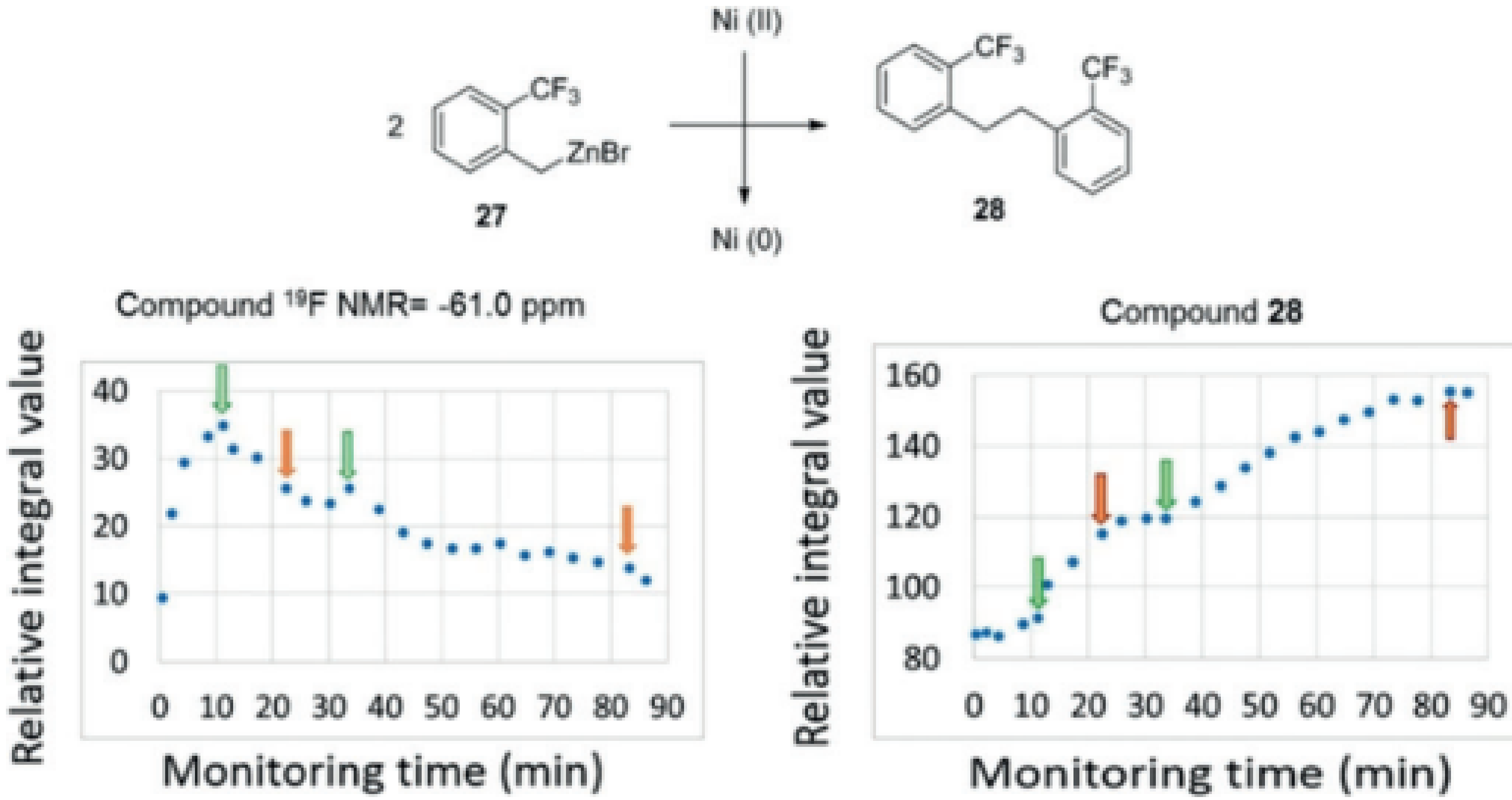
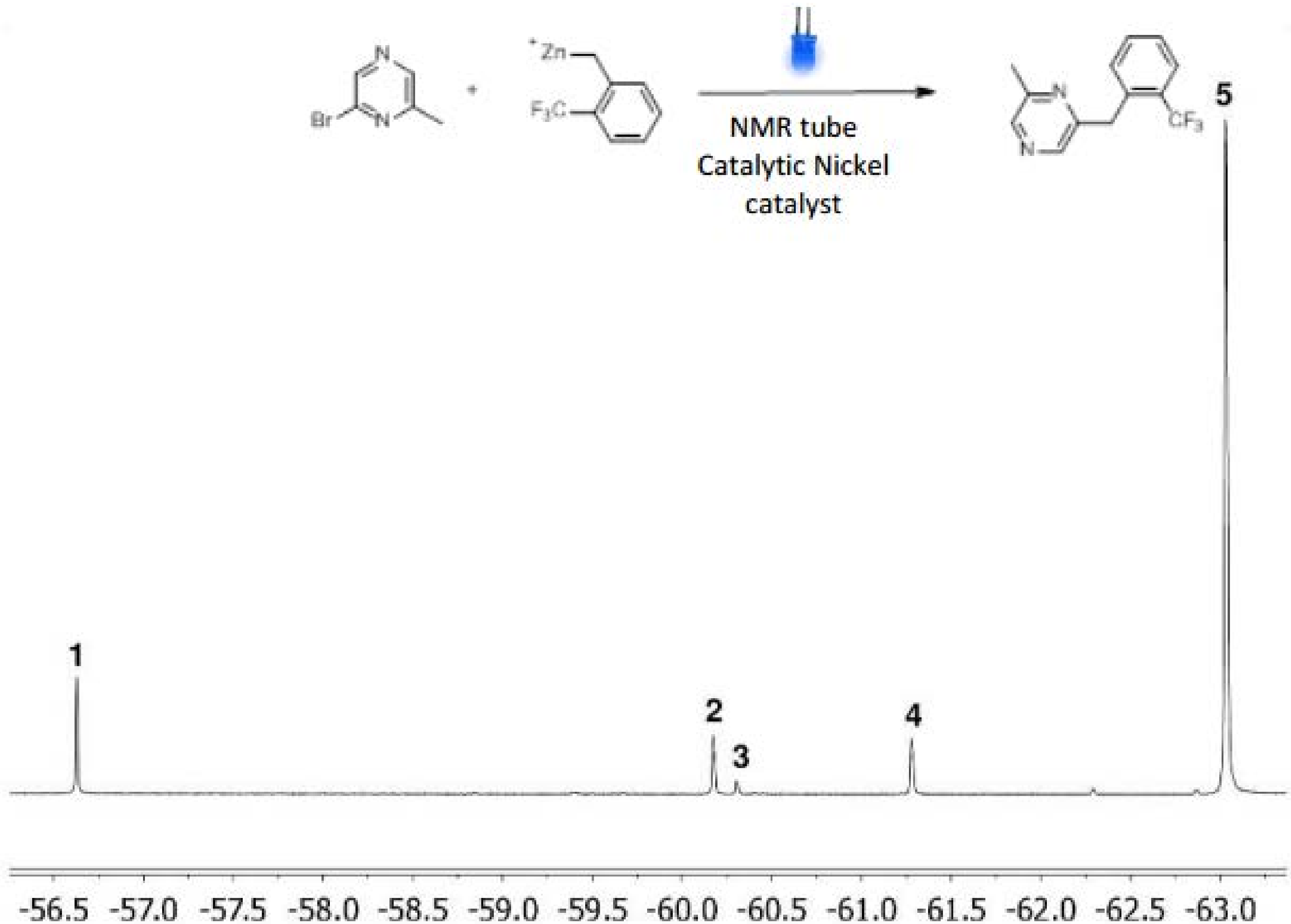
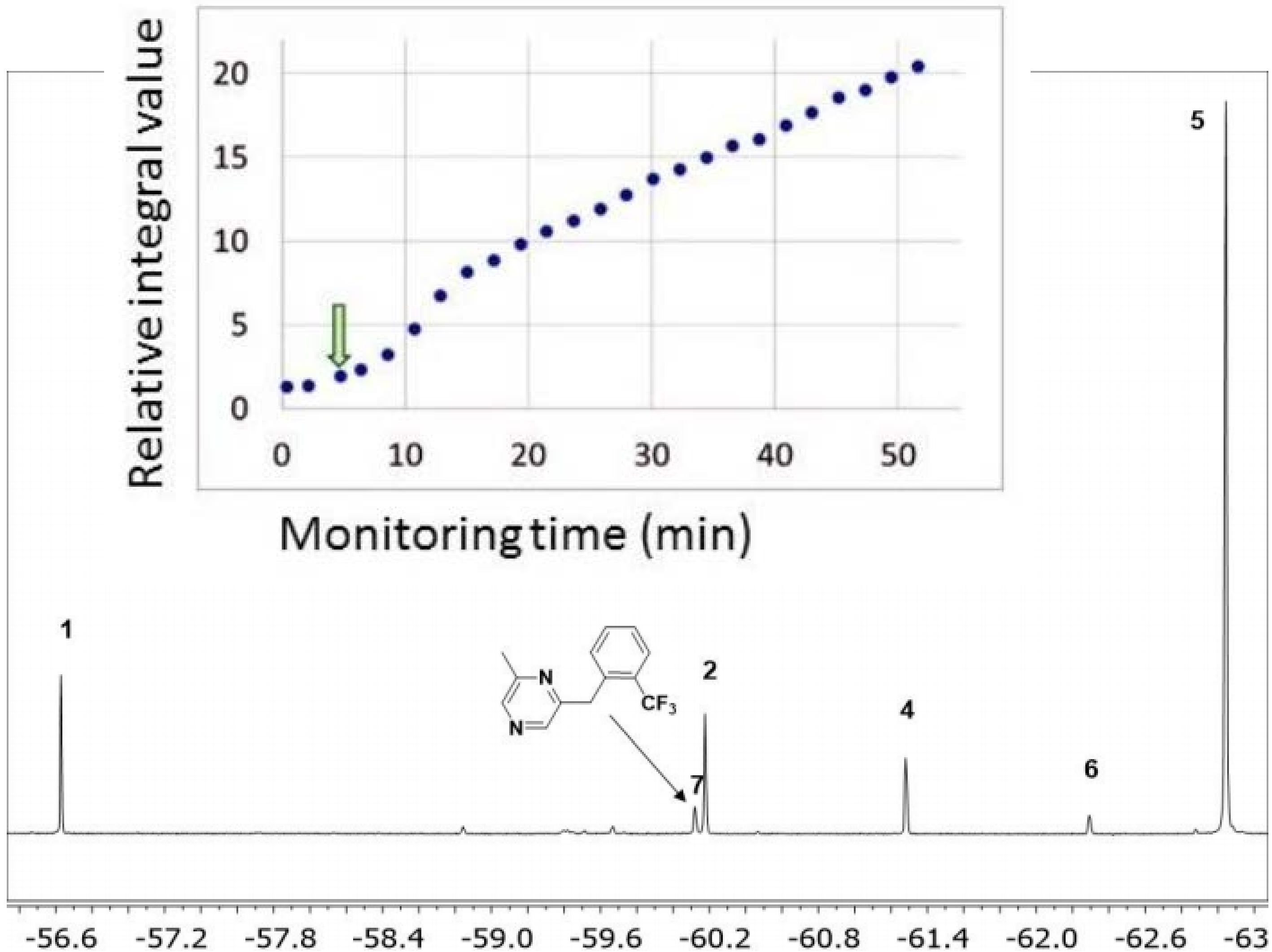


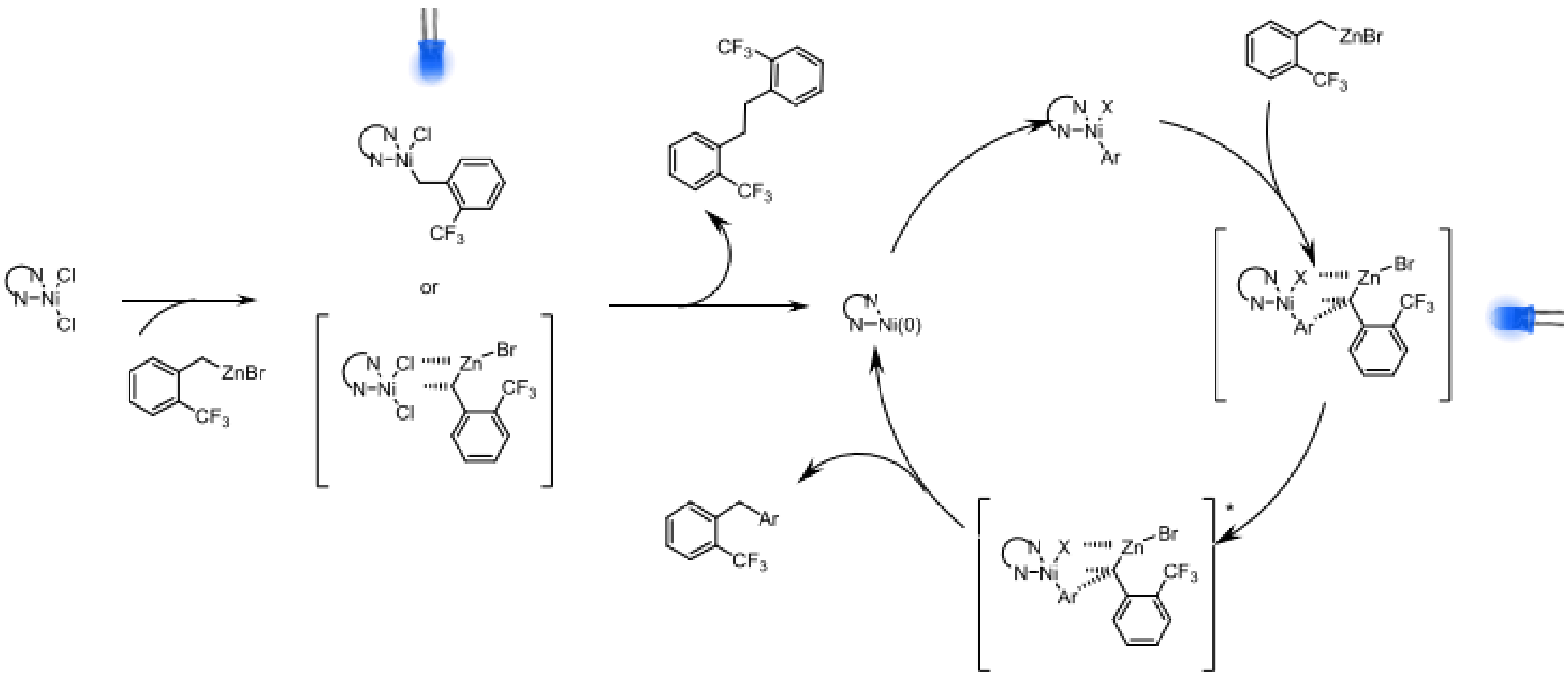
Figure 4. The effect of light irradiation on the degradation of an intermediate signal and the acceleration of the formation of dimer **28**. Green arrows indicated when the light was turned on, and orange arrows indicated when the light was turned off.



Br
N
N
+
Zn
F3C
NMR tube
Catalytic Nickel
catalyst
N
N
CF3
1
2
3
4
5
-56.5 -57.0 -57.5 -58.0 -58.5 -59.0 -59.5 -60.0 -60.5 -61.0 -61.5 -62.0 -62.5 -63.0



Relative integral value
Monitoring time (min)
0
5
10
15
20
0
10
20
30
40
50
1
2
4
5
6
7
N
N
CF3
-56.6
-57.2
-57.8
-58.4
-59.0
-59.6
-60.2
-60.8
-61.4
-62.0
-62.6
-63



Scheme S3: Proposed mechanism for the Visible light induced nickel-catalyzed Negishi cross-coupling. Steps potentially accelerated by light are highlighted with blue leds.

No. 4

JACS JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Article

Cite This: J. Am. Chem. Soc. XXXX, XXX, XXX−XXX

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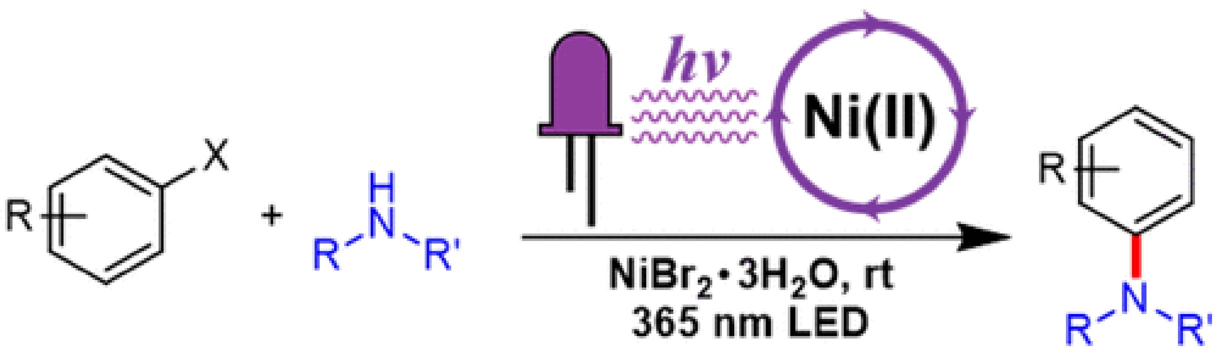
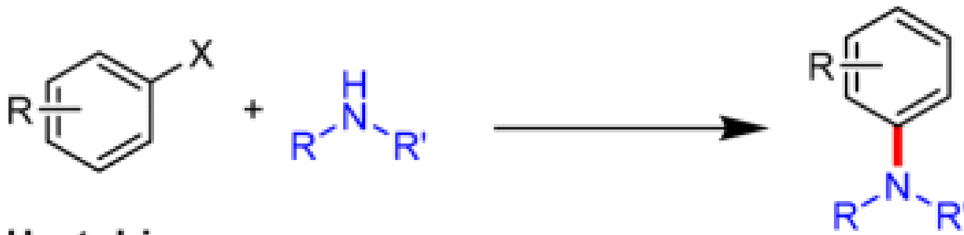
C−N Cross-Coupling via Photoexcitation of Nickel−Amine Complexes

Chern-Hooi Lim, Max Kudisch, Bin Liu, and Garret M. Miyake*

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523, United States



Scheme 1. Historical Development of the C−N Cross-Coupling Reaction



Heat-driven

a) Cu, ligand, high temp., mild base

b) Pd, ligand, high temp., strong base

c) Ni(0), ligand, high temp., strong base

Light or electricity-driven

d) Cu(I), room temp., UV light (e.g. 254 nm), strong base

e) Ni(II)/Ir PC, room temp., blue LED, mild base

f) Ni(II)/organic PC, room temp., white LED, mild base

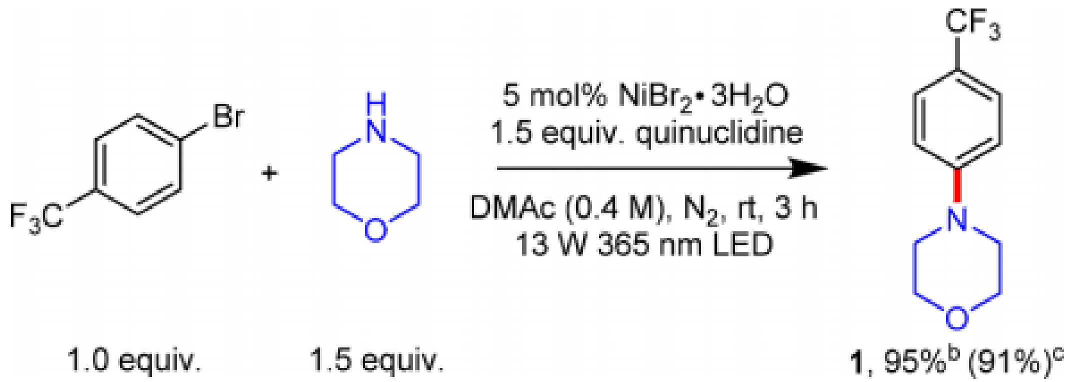
g) Ni(II), ligand, room temp., electricity, no added base

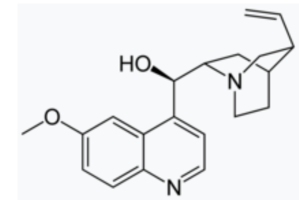
This work

h) $NiBr_2 \cdot 3H_2O$, room temp., 365 nm LED

- no added photoredox catalyst
- no added ligand and base
- cost-effective and abundant Ni source
- tolerant to O_2 and H_2O
- broad scope (40 examples)

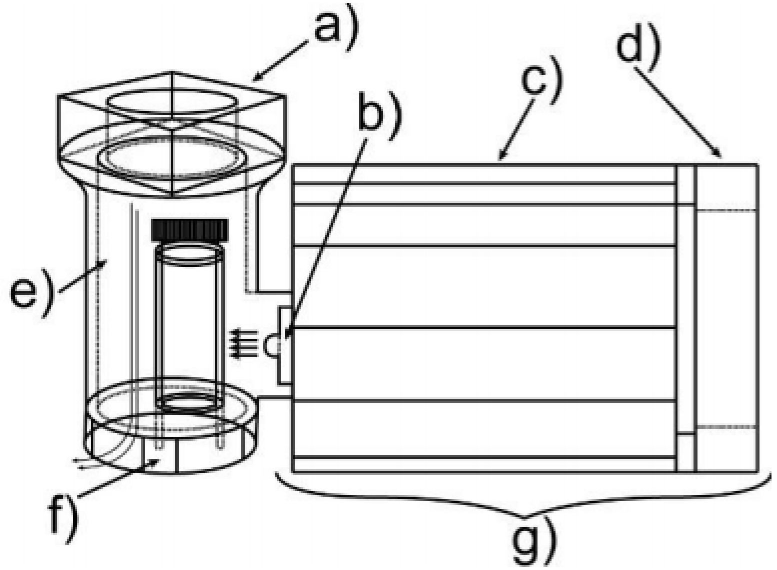
Table 1. Reaction Development and Control Experiments[a]



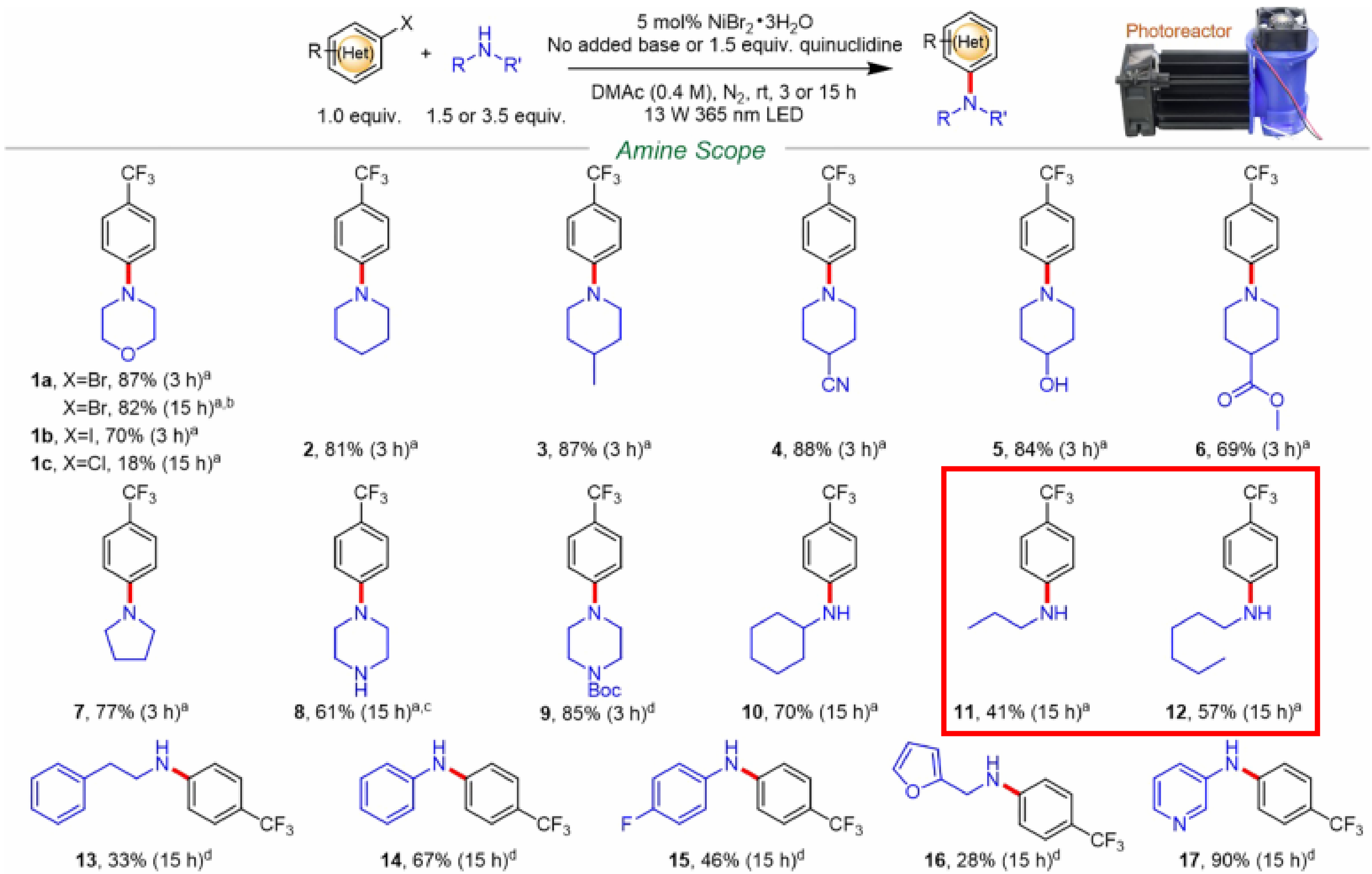


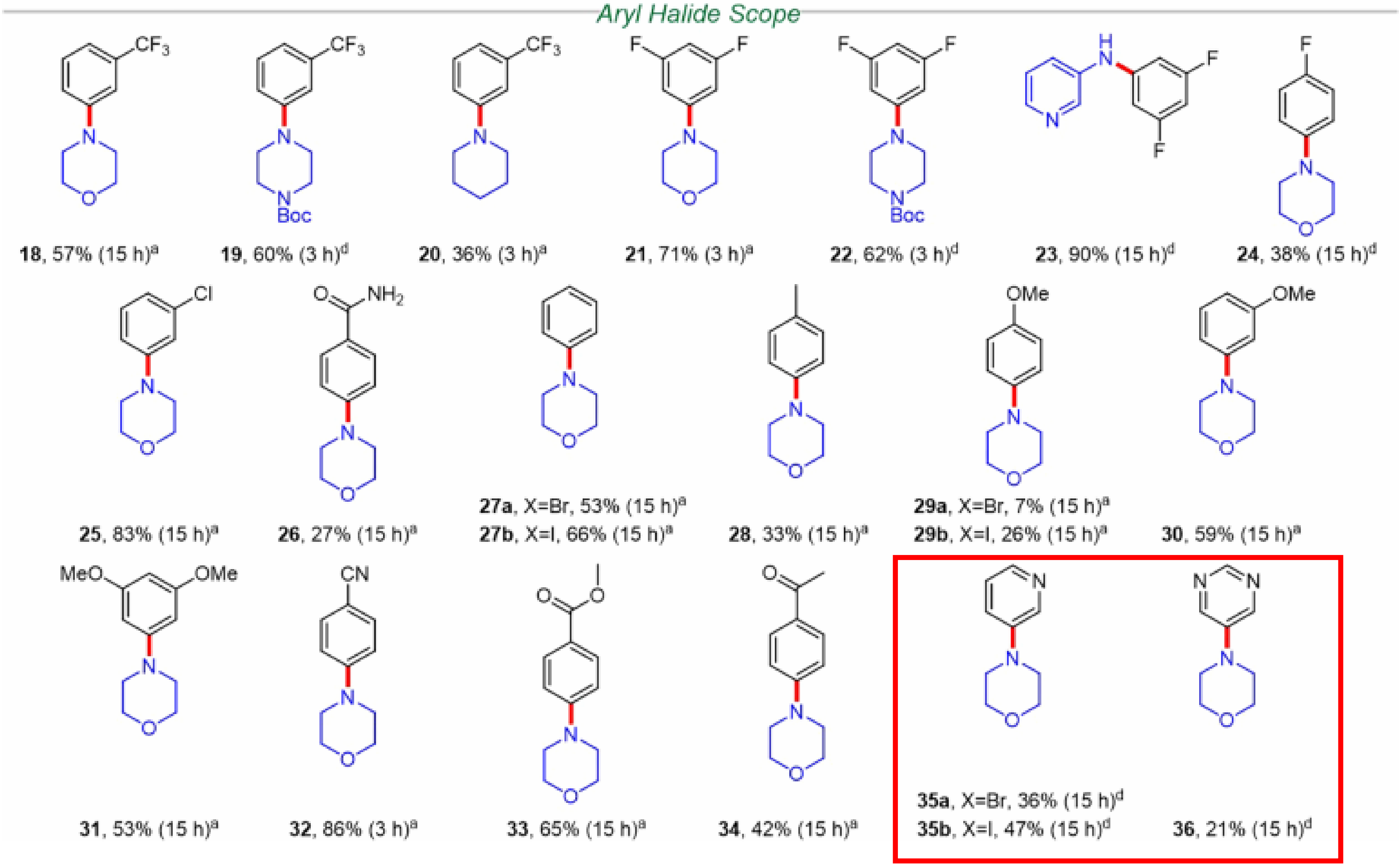
entry	deviation from conditions above	yield[b] (%)
1	no light (rt or 80 °C)	0
2	13 W 405 nm LED	93
3	no nickel salt	0
4	5 mol% $NiBr_2 \cdot glyme$	95
5	5 mol% $NiCl_2 \cdot 6H_2O$	95
6	no quinuclidine base	55
7	no quinuclidine, 3.5 equiv morpholine	94 (87)[c]
8	1.5 equiv DBU base	2
9	same as entry 7, presence of oxygen[d]	91
10	1 h	72

[a]0.4 mmol scale. Abbreviations: DMAc, *N,N*-dimethylacetamide; rt, room temperature; LED, light-emitting diode; DBU, 1,8-diazabicyclo-[5.4.0]undec-7-ene. [b]Yield determined by ^{19}F NMR. [c]Isolated yield. [d]Deoxygenated reaction mixture sparged with air for 2 min prior to light irradiation.

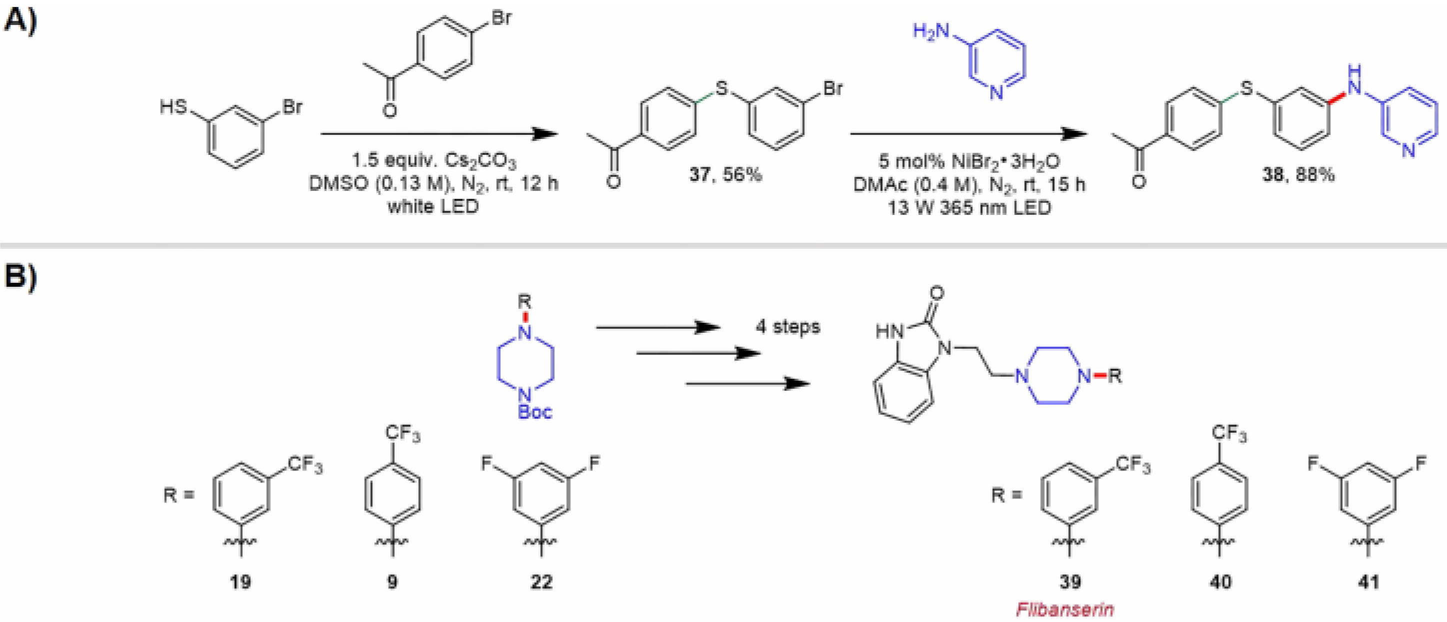

a)
d)
c)
b)
e)
f)
g)

Scheme 2. C–N Cross-Coupling via Photoexcitation of Nickel–Amine Complexes: Amine and Aryl Halide Scope

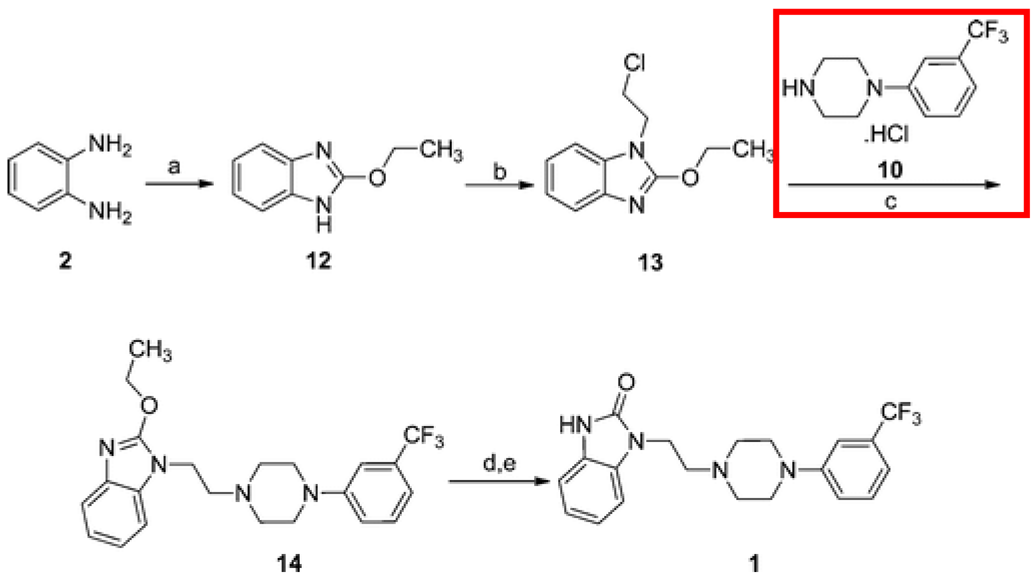




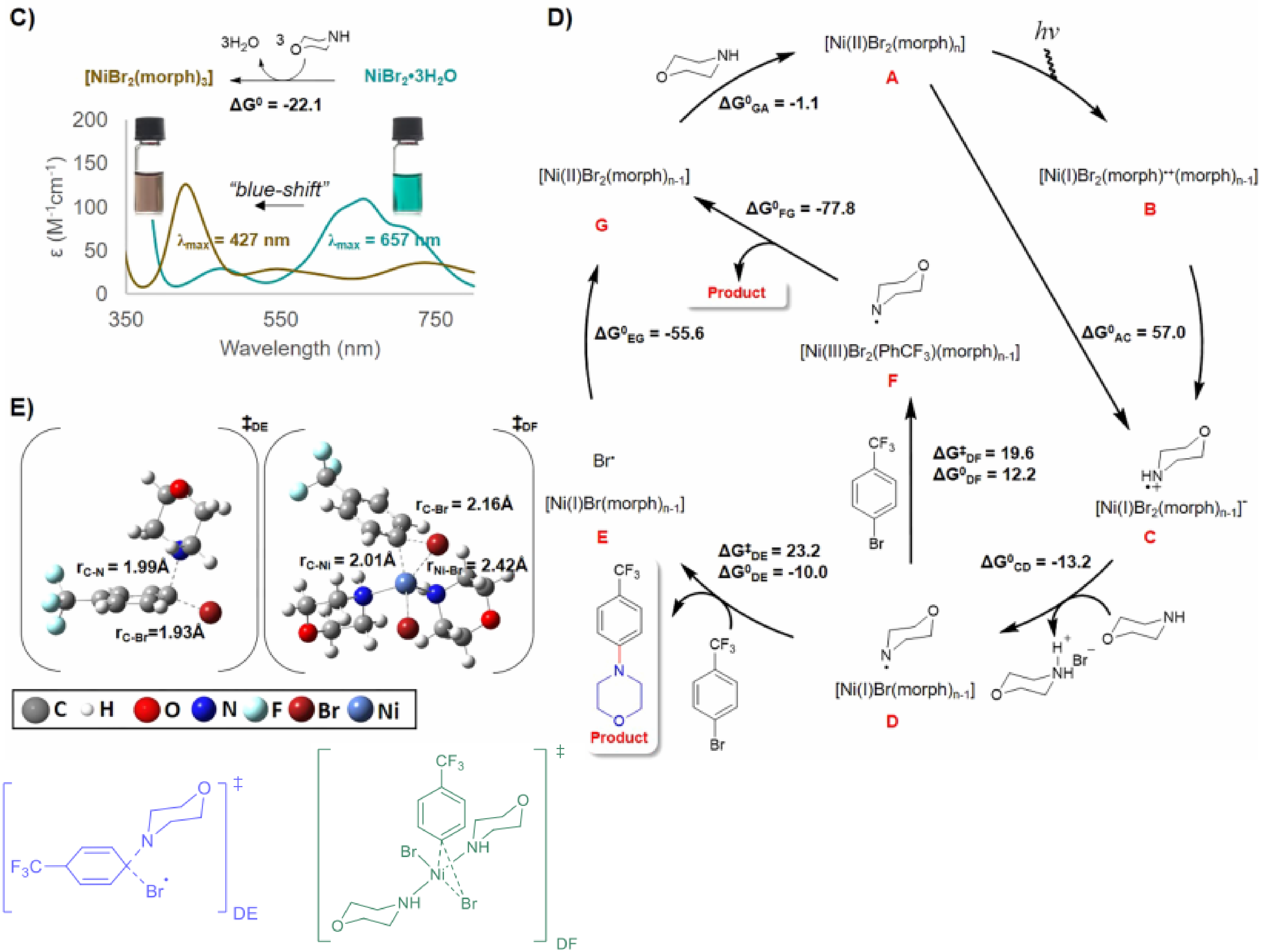
Aryl Halide Scope
CF3
N
O
Boc
F
H
N
OMe
MeO
Cl
NH2
CN
18, 57% (15 h)[a]
19, 60% (3 h)[d]
20, 36% (3 h)[a]
21, 71% (3 h)[a]
22, 62% (3 h)[d]
23, 90% (15 h)[d]
24, 38% (15 h)[d]
25, 83% (15 h)[a]
26, 27% (15 h)[a]
27a, X=Br, 53% (15 h)[a]
27b, X=I, 66% (15 h)[a]
28, 33% (15 h)[a]
29a, X=Br, 7% (15 h)[a]
29b, X=I, 26% (15 h)[a]
30, 59% (15 h)[a]
31, 53% (15 h)[a]
32, 86% (3 h)[a]
33, 65% (15 h)[a]
34, 42% (15 h)[a]
35a, X=Br, 36% (15 h)[d]
35b, X=I, 47% (15 h)[d]
36, 21% (15 h)[d]



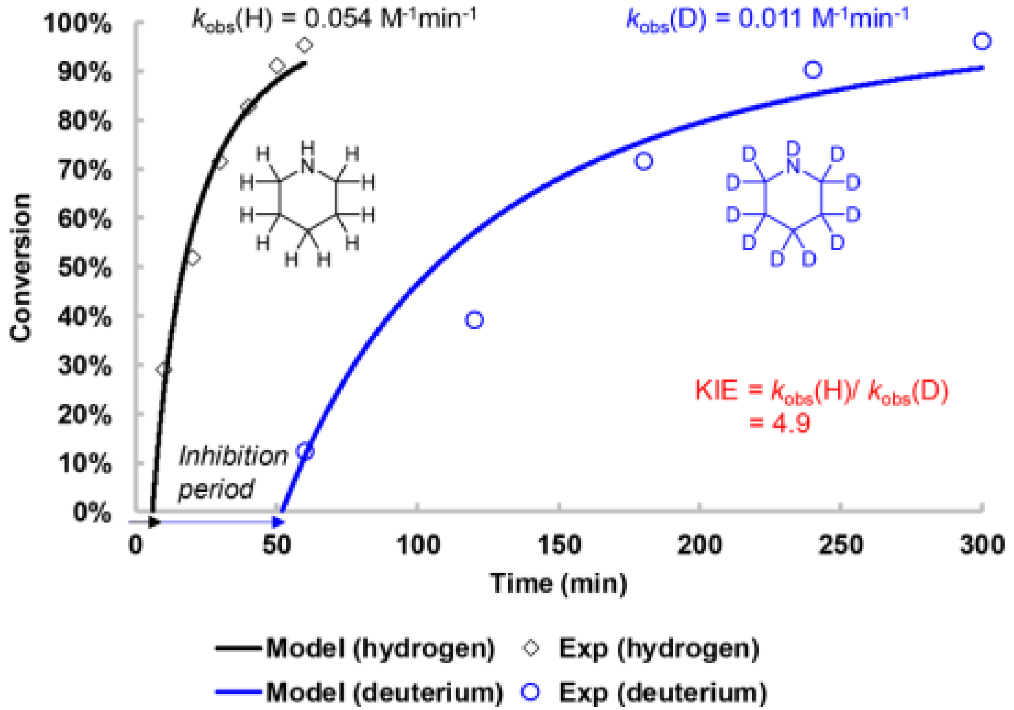
50%, 40%, and 70%



[*Org. Process Res. Dev.* 2016, 20, 9, 1576-1580]



C)
3H2O
3
NH
O
[NiBr2(morph)3]
NiBr2•3H2O
ΔG0 = -22.1
200
150
100
50
0
ε (M-1cm-1)
"blue-shift"
λmax = 427 nm
λmax = 657 nm
350
550
750
Wavelength (nm)
D)
[Ni(II)Br2(morph)n]
A
hv
ΔG0GA = -1.1
[Ni(I)Br2(morph)•+(morph)n-1]
B
[Ni(II)Br2(morph)n-1]
G
ΔG0FG = -77.8
Product
ΔG0EG = -55.6
[Ni(III)Br2(PhCF3)(morph)n-1]
F
ΔG0AC = 57.0
[Ni(I)Br2(morph)n-1]-
C
Br•
[Ni(I)Br(morph)n-1]
E
CF3
Br
ΔG‡DF = 19.6
ΔG0DF = 12.2
ΔG‡DE = 23.2
ΔG0DE = -10.0
ΔG0CD = -13.2
[Ni(I)Br(morph)n-1]
D
Product
E)
‡DE
‡DF
rC-N = 1.99Å
rC-Br=1.93Å
rC-Br = 2.16Å
rC-Ni = 2.01Å
rNi-Br = 2.42Å
C
H
O
N
F
Br
Ni
F3C
Br•
DE
DF
Ni
NH



A = amine; B = aryl halide; C = C-N coupled product.

$$\frac{d[A]}{dt} = -2k_{obs}[A][B], [A]_0 = 1.4M$$

$$\frac{d[B]}{dt} = -k_{obs}[A][B], [B]_0 = 0.4M$$

$$\frac{d[C]}{dt} = k_{obs}[A][B], [C]_0 = 0.0M$$

No. 5

Volume 9 | Number 20 | 28 May 2018 | Pages 4537–4720

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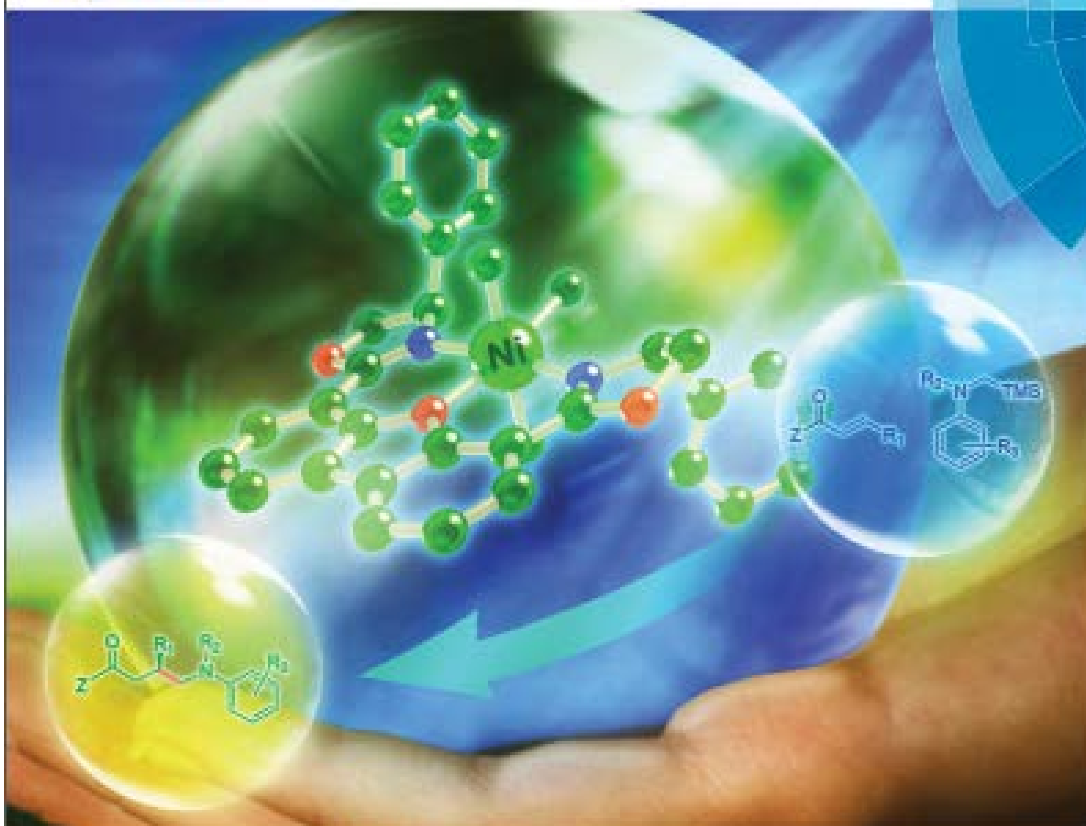

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A chiral nickel DBFOX complex as a bifunctional catalyst for visible-light-promoted asymmetric photoredox reactions†

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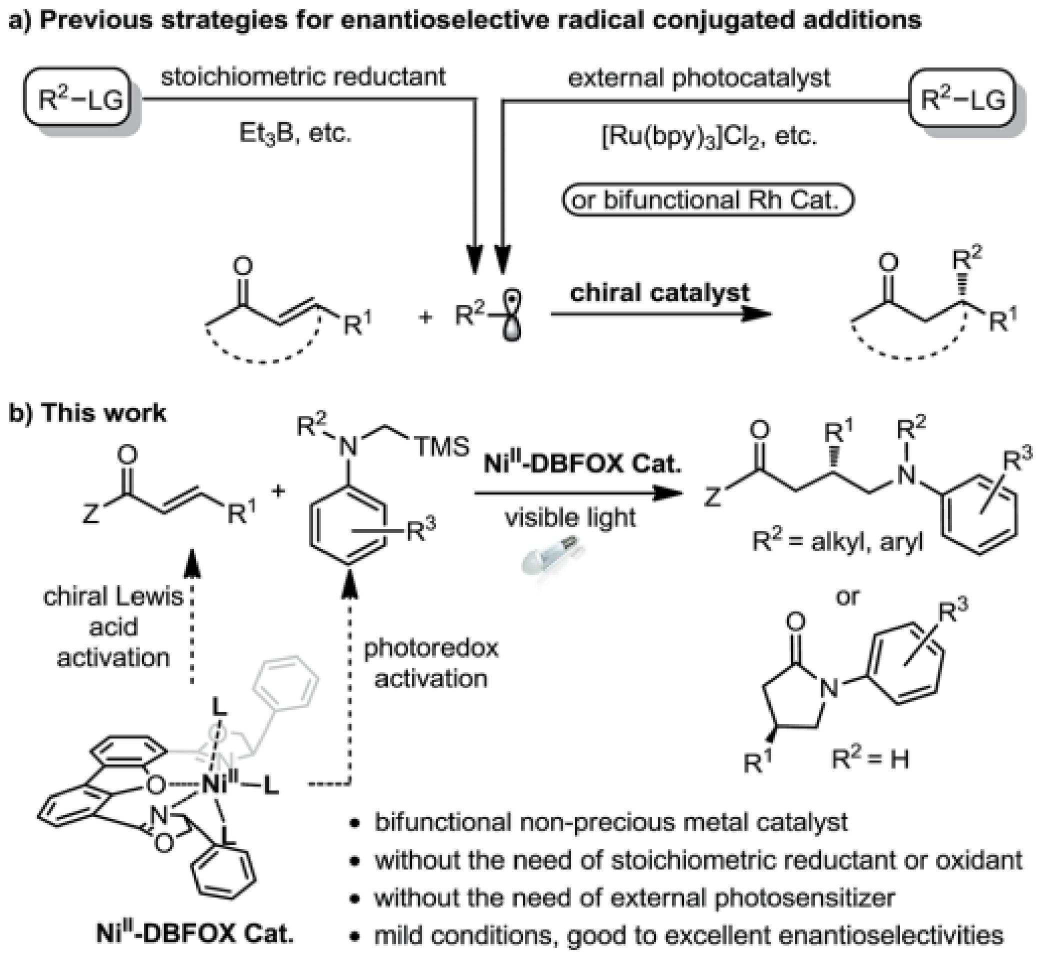
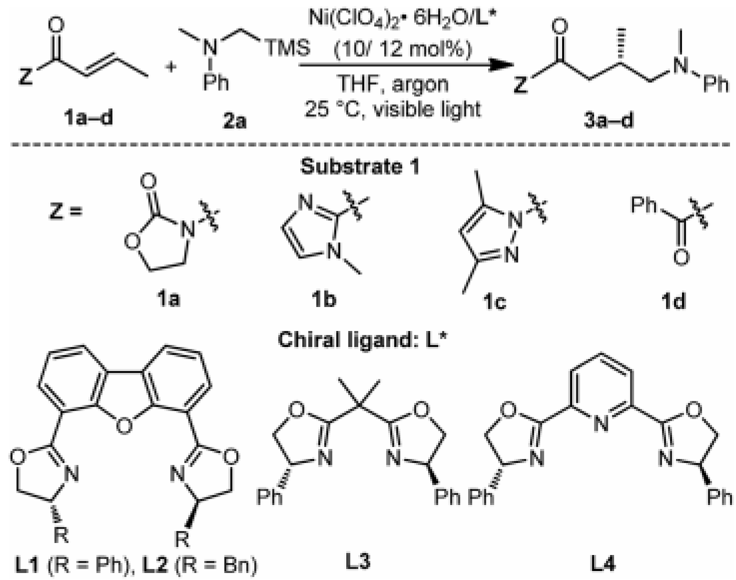
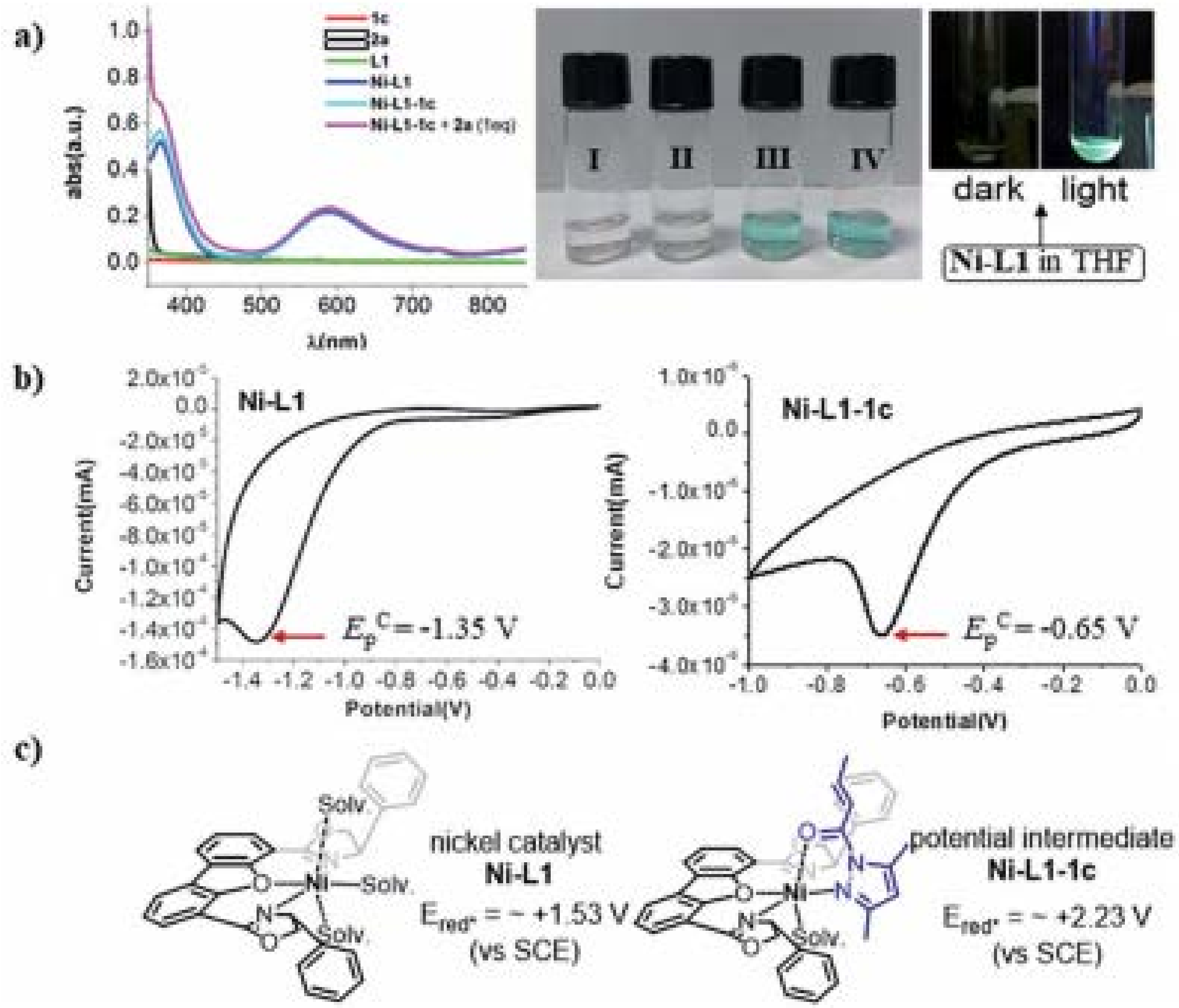
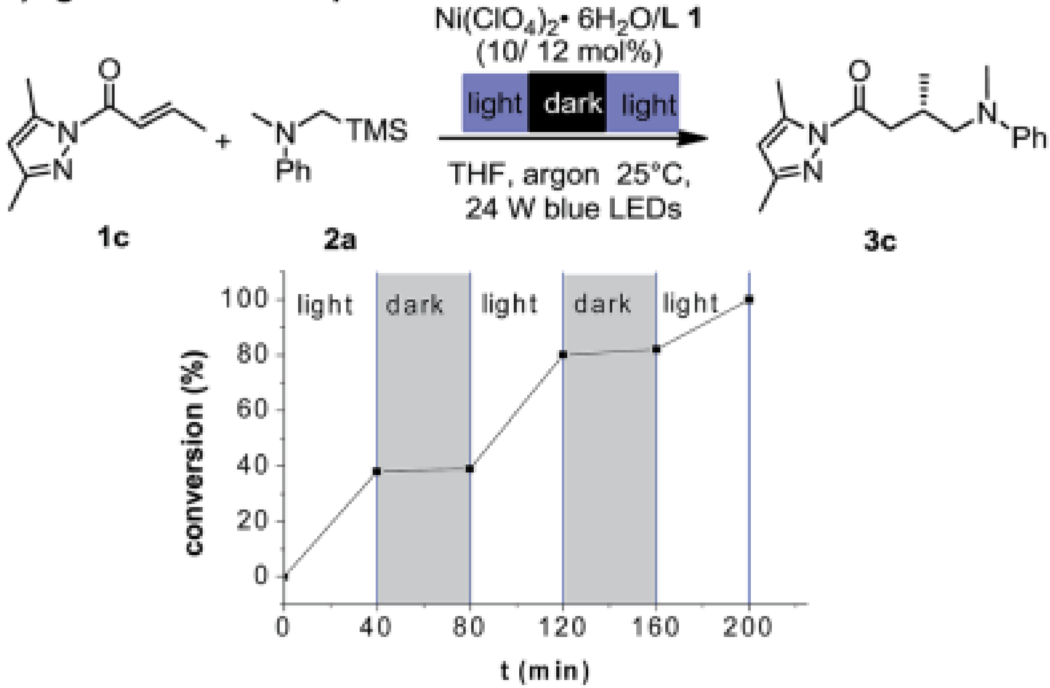




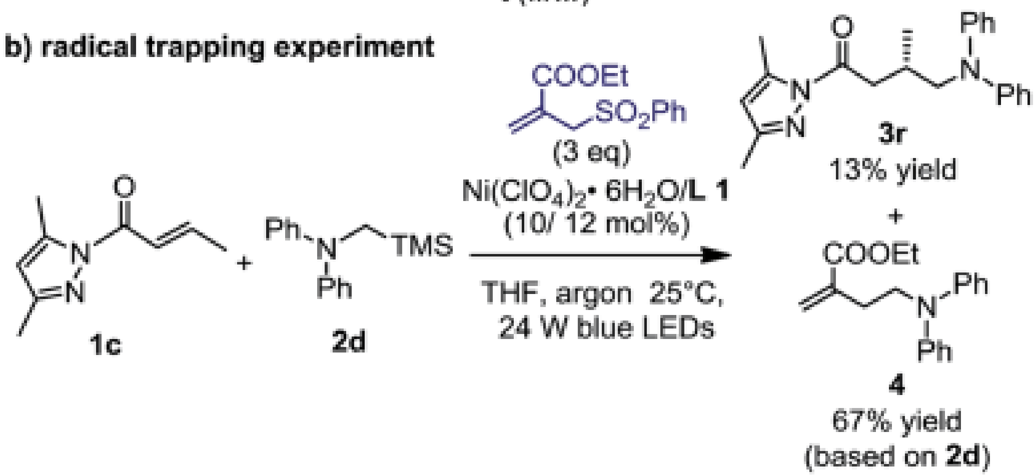
Entry	Substrate	Ligand	Light source	Additives	*t* (h)	Product	Conv.[b] (%)	ee[c] (%)
1	**1a**	**L1**	White CFL	None	12	**3a**	0	n.a.
2	**1b**	**L1**	White CFL	None	12	**3b**	22	78
3	**1c**	**L1**	White CFL	None	6	**3c**	95	91
4	**1d**	**L1**	White CFL	None	12	**3d**	0	n.a.
5	**1c**	**L2**	White CFL	None	12	**3c**	23	0
6	**1c**	**L3**	White CFL	None	12	**3c**	21	n.d.
7	**1c**	**L4**	White CFL	None	12	**3c**	0	n.a.
8	**1c**	**L1**	Blue LEDs	None	3	**3c**	95	91
9	**1c**	**L1**	Red LEDs	None	12	**3c**	<5	n.d.
10	**1c**	**L1**	Yellow LEDs	None	12	**3c**	0	n.a.
11	**1c**	**L1**	UV (365 nm)	None	6	**3c**	90	91
12[d]	**1c**	**L1**	Blue LEDs	None	12	**3c**	0	n.a.
13[e]	**1c**	**L1**	Blue LEDs	None	12	**3c**	0	n.a.
14[f]	**1c**	**L1**	Blue LEDs	None	12	**3c**	0	n.a.
15	**1c**	None	Blue LEDs	None	12	**3c**	0	n.a.
16	**1c**	**L1**	None	None	12	**3c**	<5	n.a.
17[g]	**1c**	**L1**	Blue LEDs	None	12	**3c**	0	n.a.
18	**1c**	**L1**	Blue LEDs	1 eq. TEMPO	12	**3c**	0	n.a.
19	**1c**	**L1**	Blue LEDs	3 eq. BHT	12	**3c**	0	n.a.


a)
1c
2a
L1
Ni-L1
Ni-L1-1c
Ni-L1-1c + 2a (1eq)
abs(a.u.)
λ(nm)
I
II
III
IV
dark
light
Ni-L1 in THF
b)
Ni-L1
Current(mA)
Potential(V)
E_p^C = -1.35 V
Ni-L1-1c
E_p^C = -0.65 V
c)
Solv.
nickel catalyst
Ni-L1
E_{red^*} = ~ +1.53 V
(vs SCE)
potential intermediate
Ni-L1-1c
E_{red^*} = ~ +2.23 V
(vs SCE)

a) light-dark interval experiments



b) radical trapping experiment



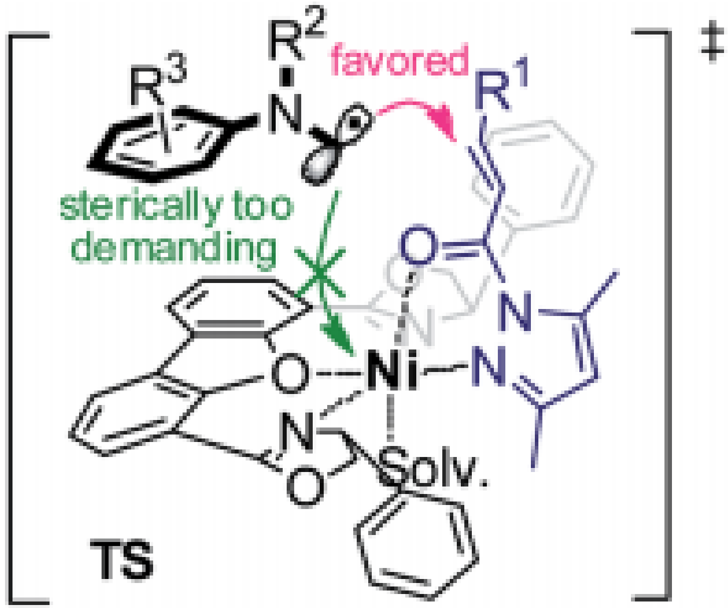


Fig. 5 proposed transition state for radical addition.

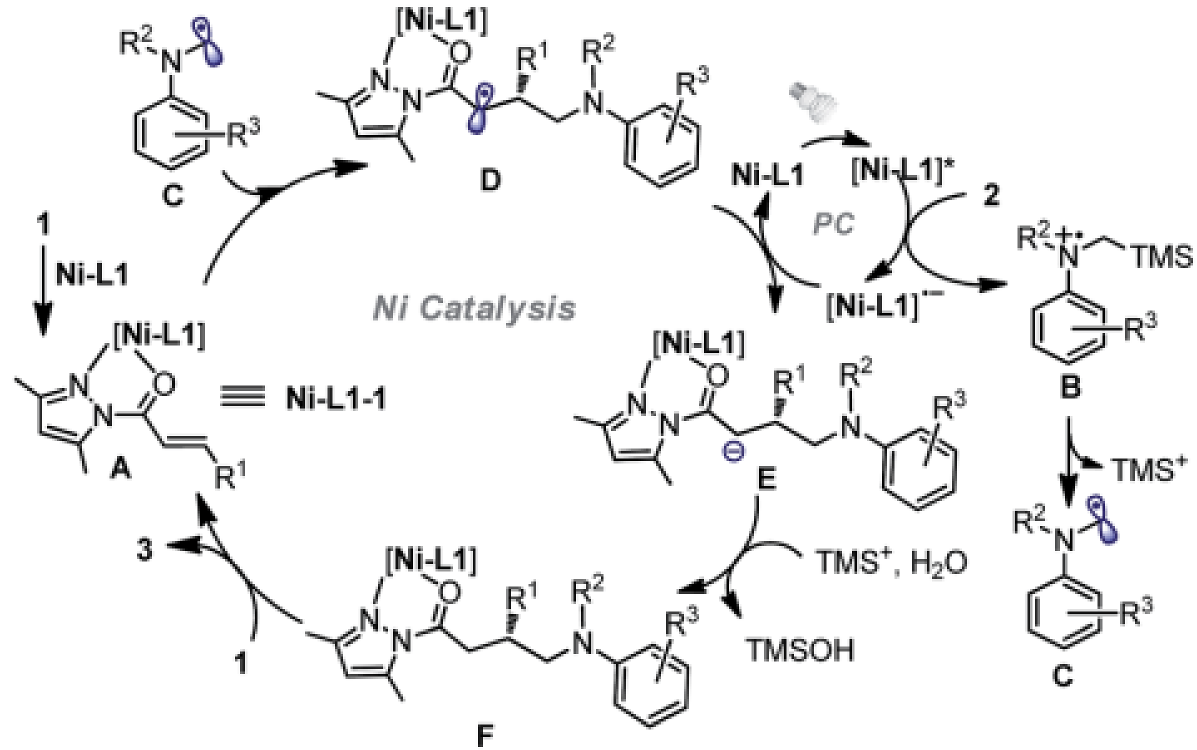


Fig. 4 A proposed reaction mechanism for the nickel-catalyzed enantioselective photoredox reaction of α,β-unsaturated carbonyl compounds and α-silylamines.

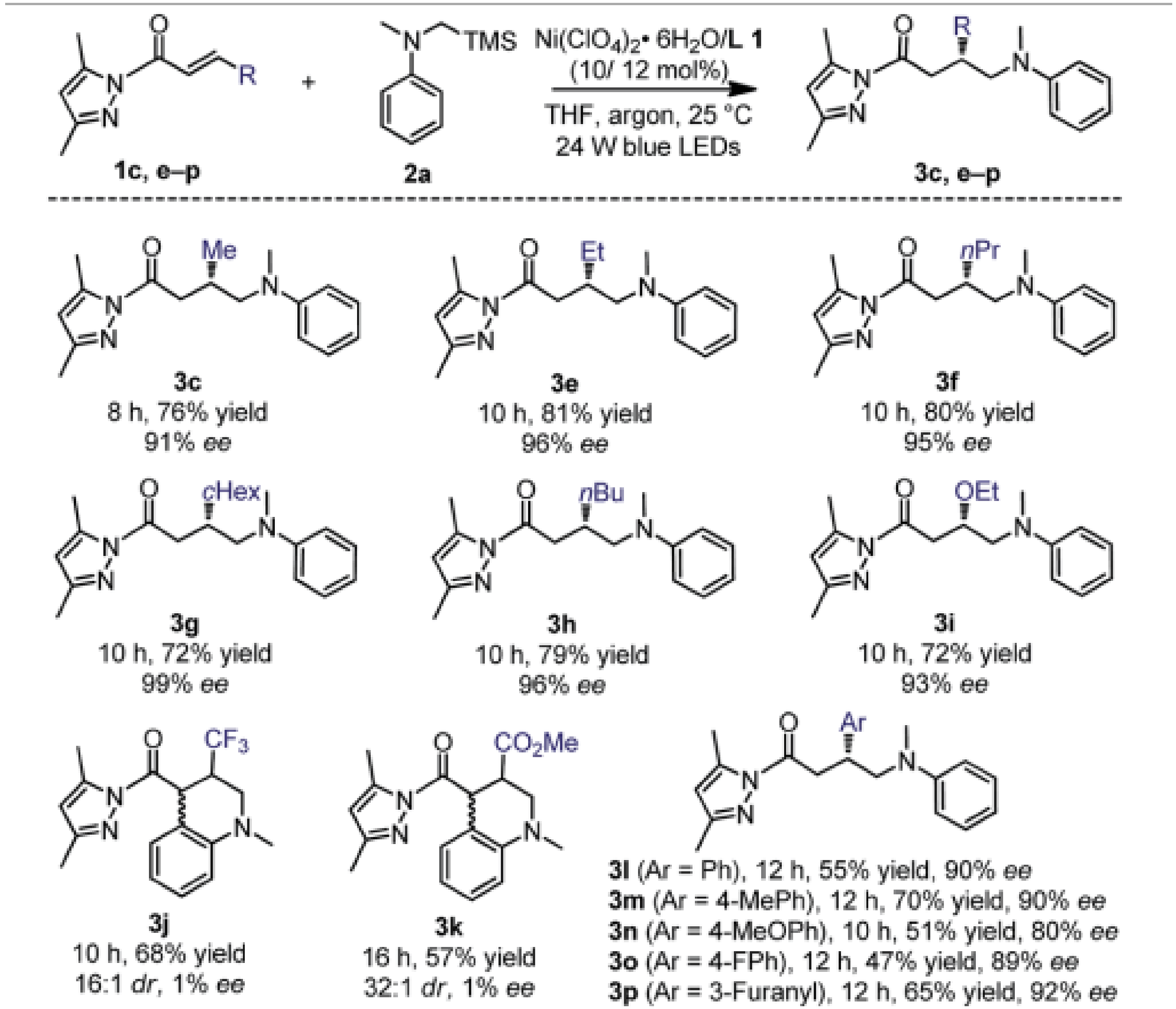


Fig. 6 Substrate scope with respect to α,β-unsaturated *N*-acyl pyrazoles.

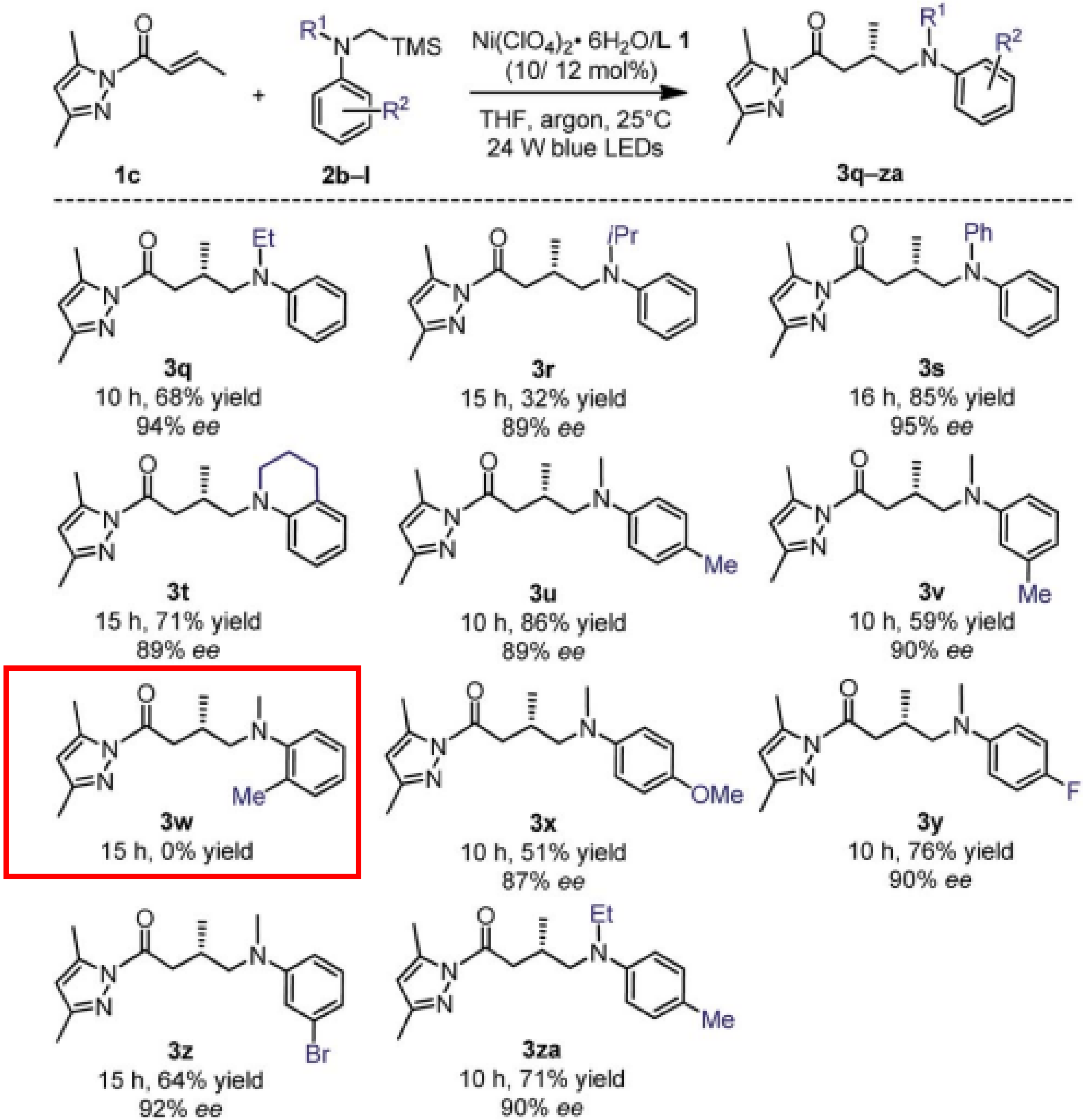


Fig. 7 Substrate scope with respect to tertiary α-silylamines.

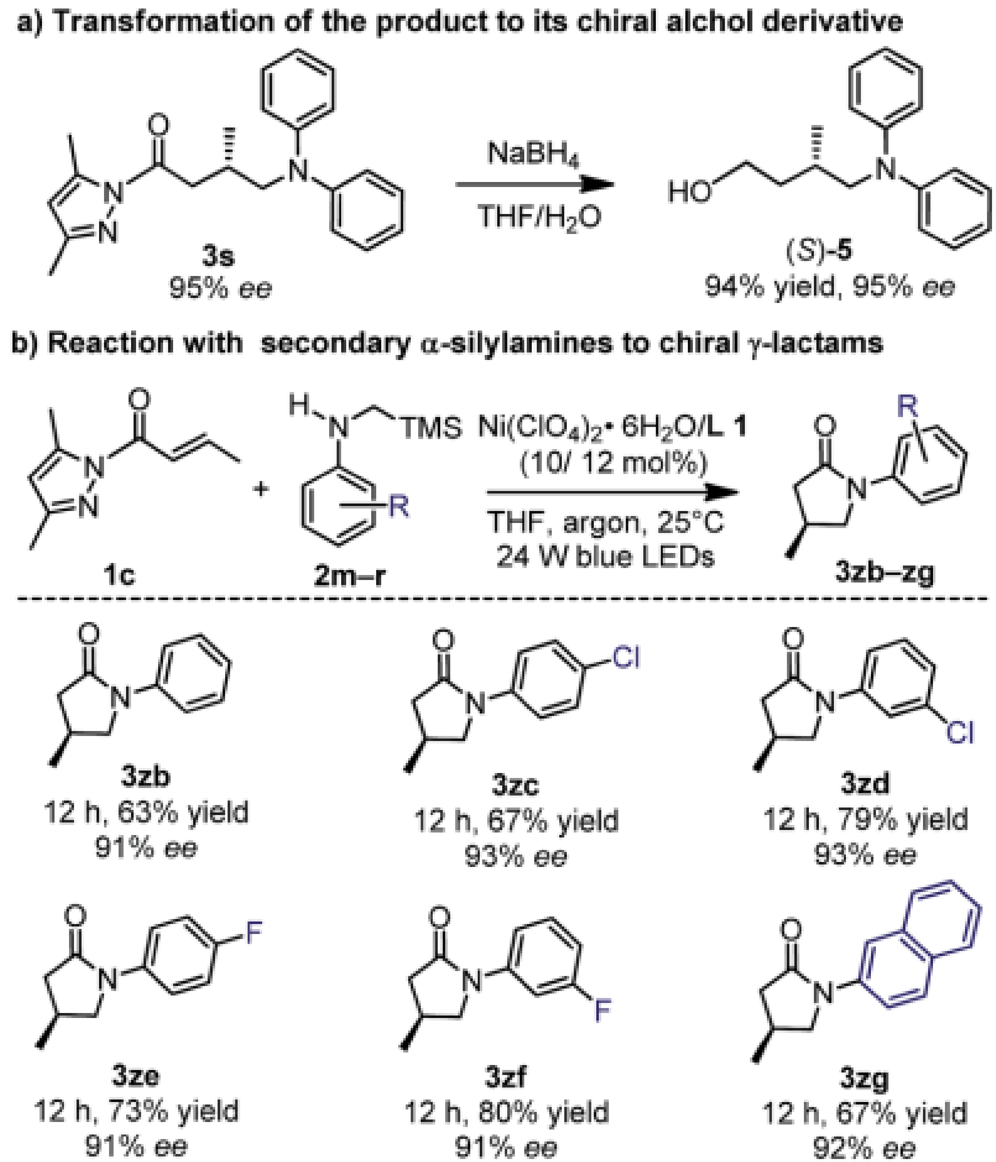
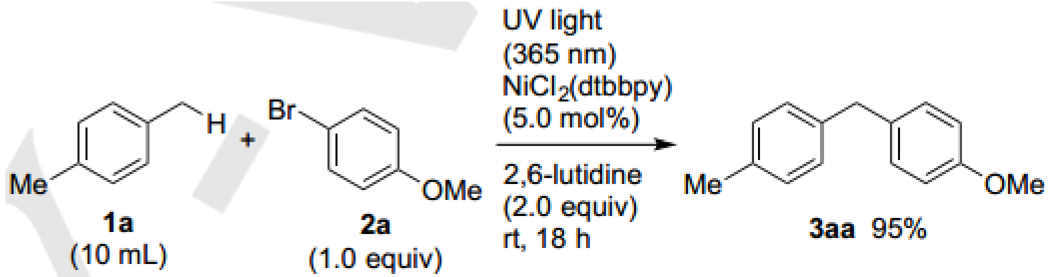


Fig. 8 Synthetic applications of the methodology.



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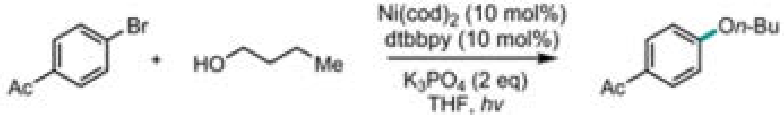

Conditions	Yield
hv	79%
dark	26%

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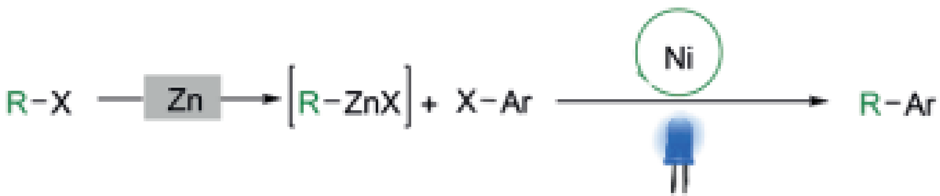
Light-induced Negishi coupling



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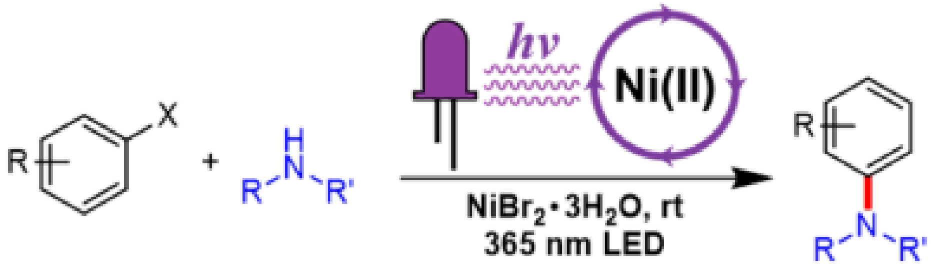

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This work

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Thanks