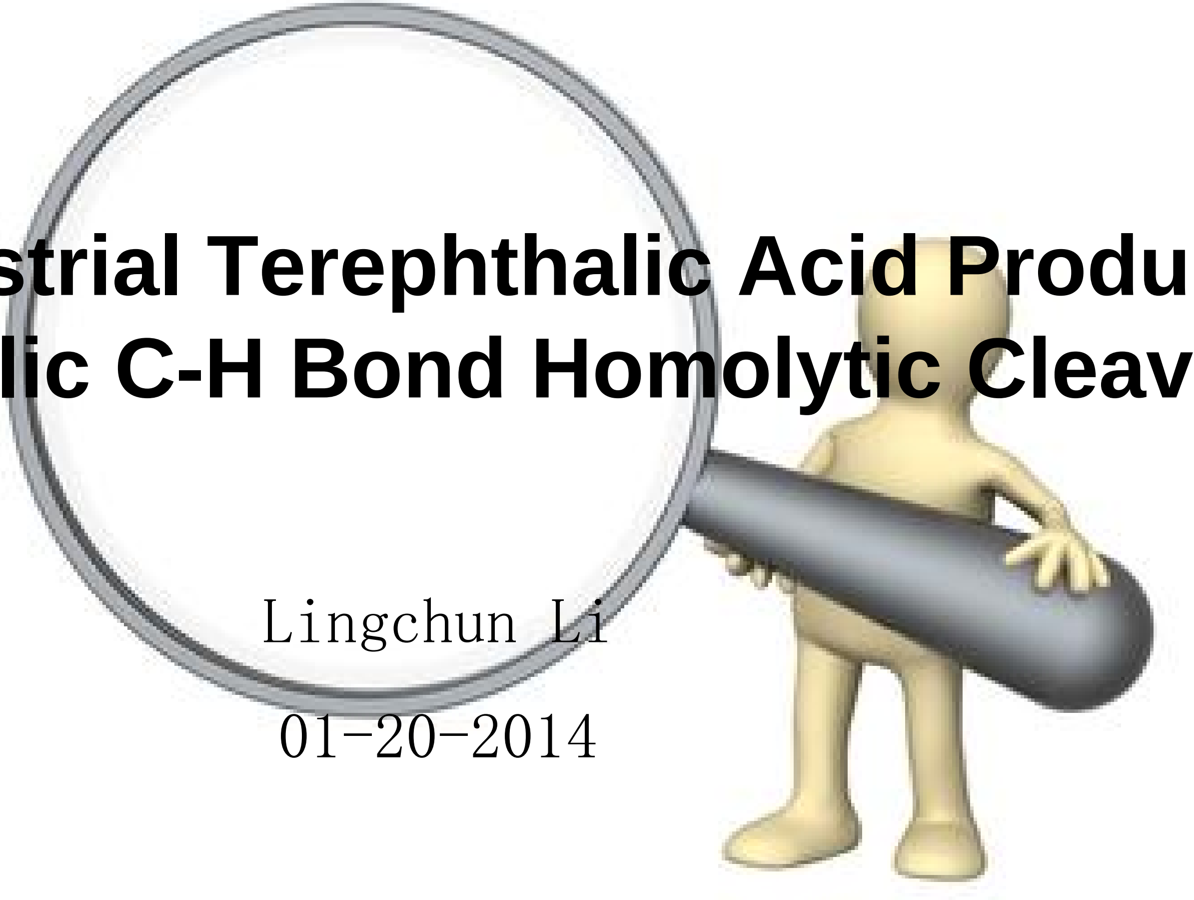


From Industrial Terephthalic Acid Production to Benzylic C-H Bond Homolytic Cleavage

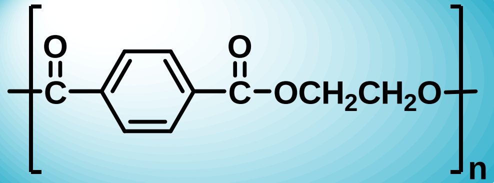
Lingchun Li

01-20-2014

Content

- **Background**
  - History of terephthalic acid preparation
  - Recent research trends in TA synthesis
- **Main text**
  - Use benzyl radical for C_{sp3}-X bond formation
  - Use benzyl radical for C_{sp3}-C bond formation
- **Summary and outlook**

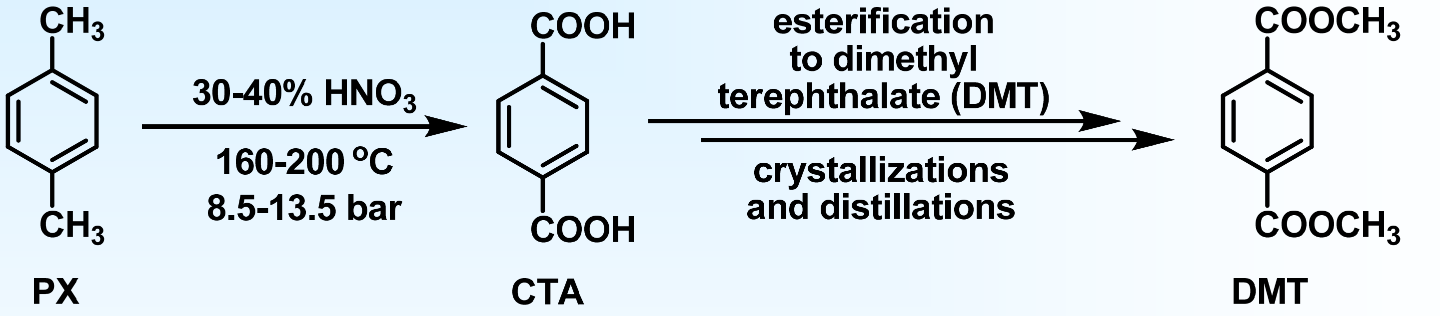
Background-History of terephthalic acid preparation



PET (PolyEthylene Terephthalate)

Background-History of terephthalic acid preparation

- Liquid-phase nitric acid *p*-xylene oxidation

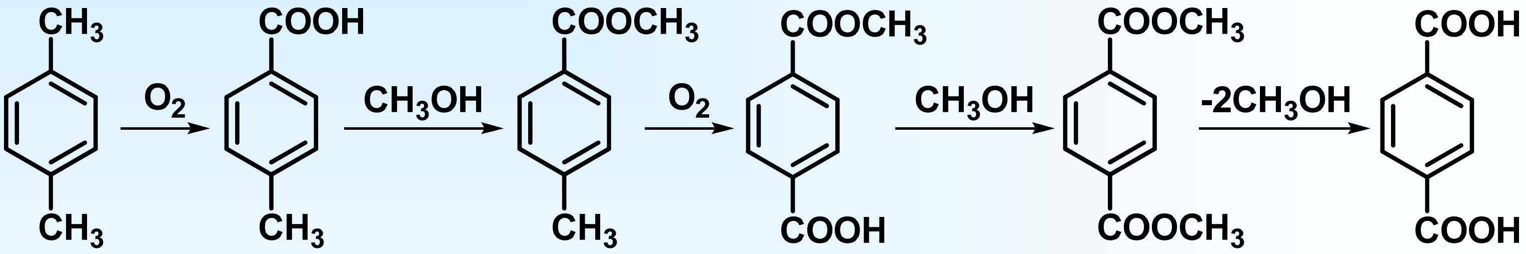


Raghavendrachar, P.; Ramachandran, S.

Ind. Eng. Chem. Res. **1992**, *31*, 453.

Background-History of terephthalic acid preparation

- Dynamit – Nobel process

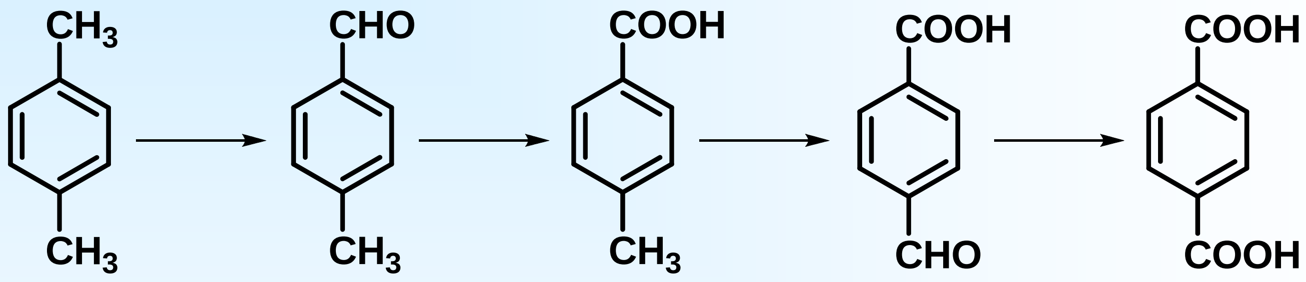


conditions: air, neat, 140-180 °C, 5-8 bar, cobalt catalyst

Sheehan, R. J. Terephthalic Acid, Dimethyl Terephthalate and Isophthalic Acid. *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH Verlag GmbH & Co.: Weinheim, 2005; Vol. *35*, pp 639−651.

Background-History of terephthalic acid preparation

- Mid-Century process (AMOCO MC process)



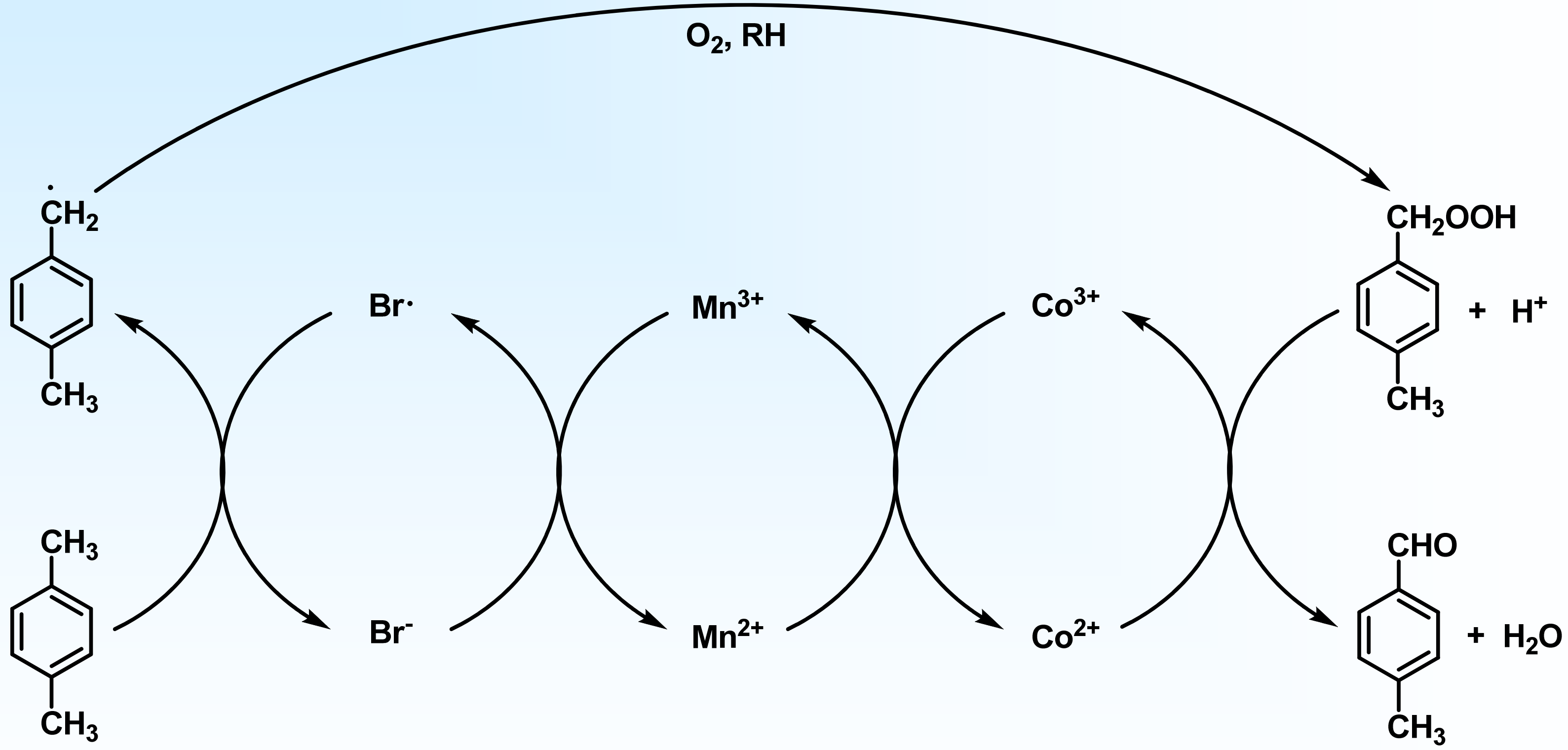
PX **_p_-TALD** **PT** **4-CBA** **CTA**

conditions: air, ~200 °C, 15-30 bar, Co/Mn/Br catalyst, in acetic acid

Saffer, A.; Barker, R. S. U.S. Patent 2833816, May 6, 1958.
Saffer, A.; Barker, R. S. GB Patent 807091, January 7, 1959.

Background-History of terephthalic acid preparation

- Catalytic pathway for AMOCO MC oxidation



Partenheimer, W. *Catal. Today* **1995**, *23*, 69.

Background-History of terephthalic acid preparation

- Kinetic mechanism of the AMOCO MC method

$$Br^{\cdot} + CH_3PhCH_3 \longrightarrow Br^{-} + CH_3PhCH_2^{\cdot} + H^{+}$$

$$CH_3PhCH_2^{\cdot} + O_2 \longrightarrow CH_3PhCH_2O_2^{\cdot}$$

$$CH_3PhCH_2O_2^{\cdot} + Co^{2+} + H^{+} \longrightarrow CH_3PhCHO + Co^{3+} + H_2O$$

$$CH_3PhCH_2O_2^{\cdot} + Mn^{2+} + H^{+} \longrightarrow CH_3PhCHO + Mn^{3+} + H_2O$$

$$Br^{\cdot} + CH_3PhCHO \longrightarrow Br^{-} + CH_3PhCO^{\cdot} + H^{+}$$

$$CH_3PhCO^{\cdot} + O_2 \longrightarrow CH_3PhCO_3^{\cdot}$$

$$CH_3PhCO_3^{\cdot} + Co^{2+} + H^{+} \longrightarrow CH_3PhCOOOH + Co^{3+} + H_2O$$

$$CH_3PhCO_3^{\cdot} + Mn^{2+} + H^{+} \longrightarrow CH_3PhCOOOH + Mn^{3+} + H_2O$$

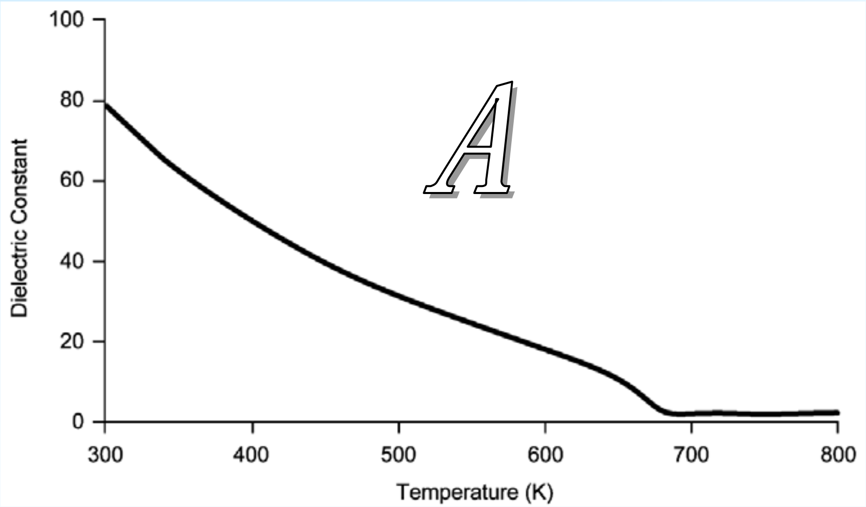
$$CH_3PhCOOOH + CH_3PhCHO \longrightarrow 2CH_3PhCOOH$$

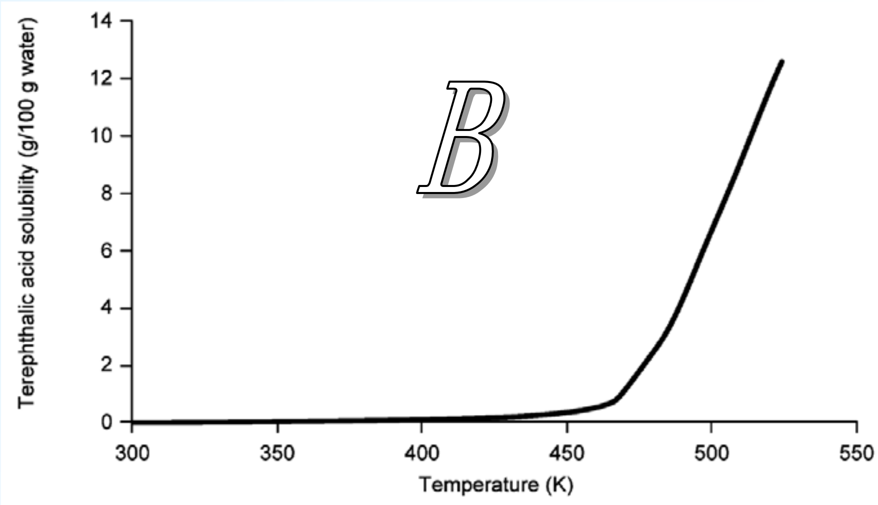
... ...

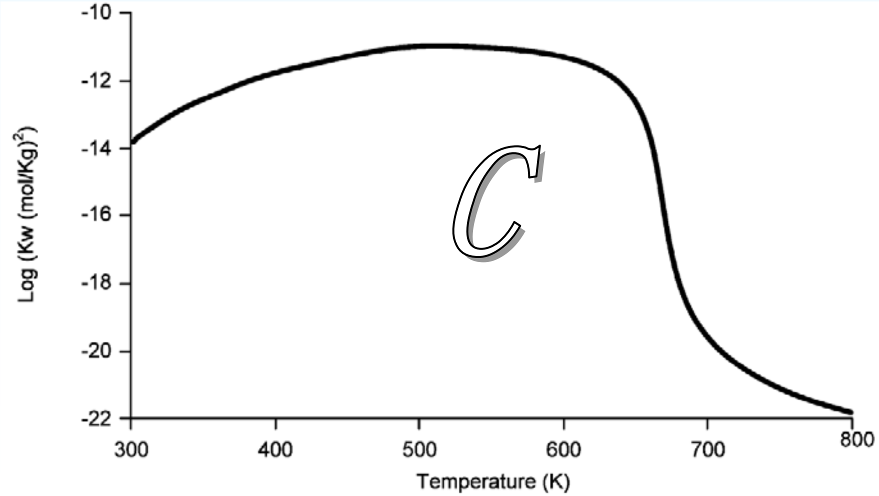
Wang, Q.; Cheng, Y.; Wang, L.; Li, X. *Ind. Eng. Chem. Res.* **2007**, *46*, 8980.

Background-Recent research trends in TA synthesis

- Oxidation in sub- and supercritical water





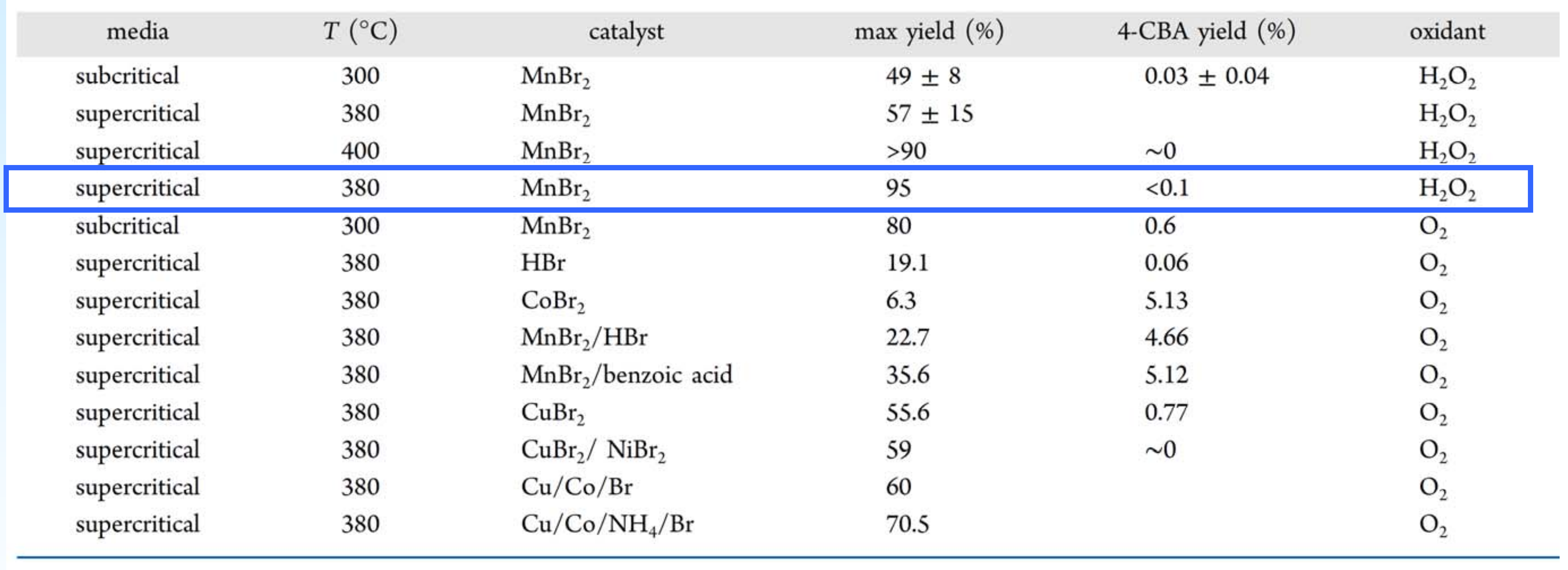


Properties of water as a function of temperature at 25 bar

Savage, P. E. J.
Supercrit. Fluids **2009**, *47*, 407.

Background-Recent research trends in TA synthesis

- Oxidation in sub- and supercritical water



media	*T* (°C)	catalyst	max yield (%)	4-CBA yield (%)	oxidant
subcritical	300	$MnBr_2$	49 ± 8	0.03 ± 0.04	H_2O_2
supercritical	380	$MnBr_2$	57 ± 15		H_2O_2
supercritical	400	$MnBr_2$	>90	~0	H_2O_2
supercritical	380	$MnBr_2$	95	<0.1	H_2O_2
subcritical	300	$MnBr_2$	80	0.6	O_2
supercritical	380	HBr	19.1	0.06	O_2
supercritical	380	$CoBr_2$	6.3	5.13	O_2
supercritical	380	$MnBr_2$/HBr	22.7	4.66	O_2
supercritical	380	$MnBr_2$/benzoic acid	35.6	5.12	O_2
supercritical	380	$CuBr_2$	55.6	0.77	O_2
supercritical	380	$CuBr_2$/ $NiBr_2$	59	~0	O_2
supercritical	380	Cu/Co/Br	60		O_2
supercritical	380	Cu/Co/NH_4/Br	70.5		O_2

Garcia-Verdugo, E.; Venardou, E.; Thomas, W. B.; Whiston, K.; Partenheimer, W.; Hamley, P. A.; Poliakoff, M. *Adv. Synth. Catal. 2004*, *346*, 307.
Garcia-Verdugo, E.; Fraga-Dubreuil, J.; Hamley, P. A.; Thomas, W. B.; Whiston, K.; Poliakoff, M. *Green Chem*. **2005**, *7*, 294.

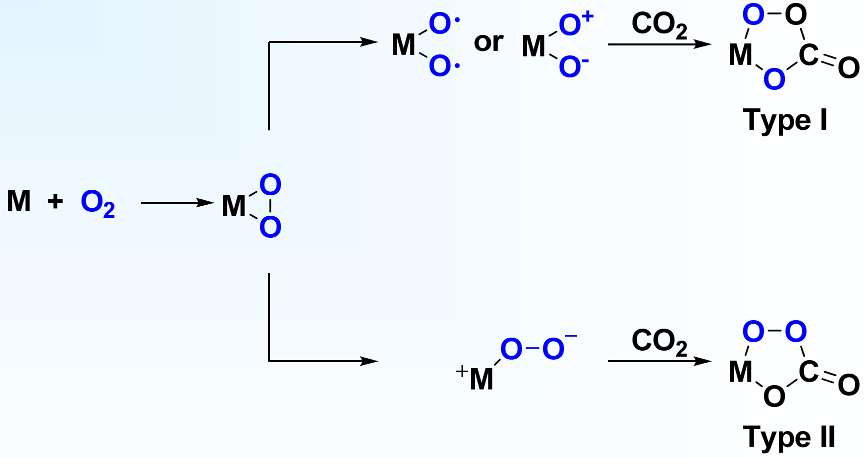
Background-Recent research trends in TA synthesis

➢ Alternative catalyst systems and cocatalyst

◆ Use carbon dioxide as co-oxidant

Beneficial effect:

- Suppressive effect in decarboxylation reactions
- Improvements in oxidation rate and product selectivity
- Increase solubility of oxygen

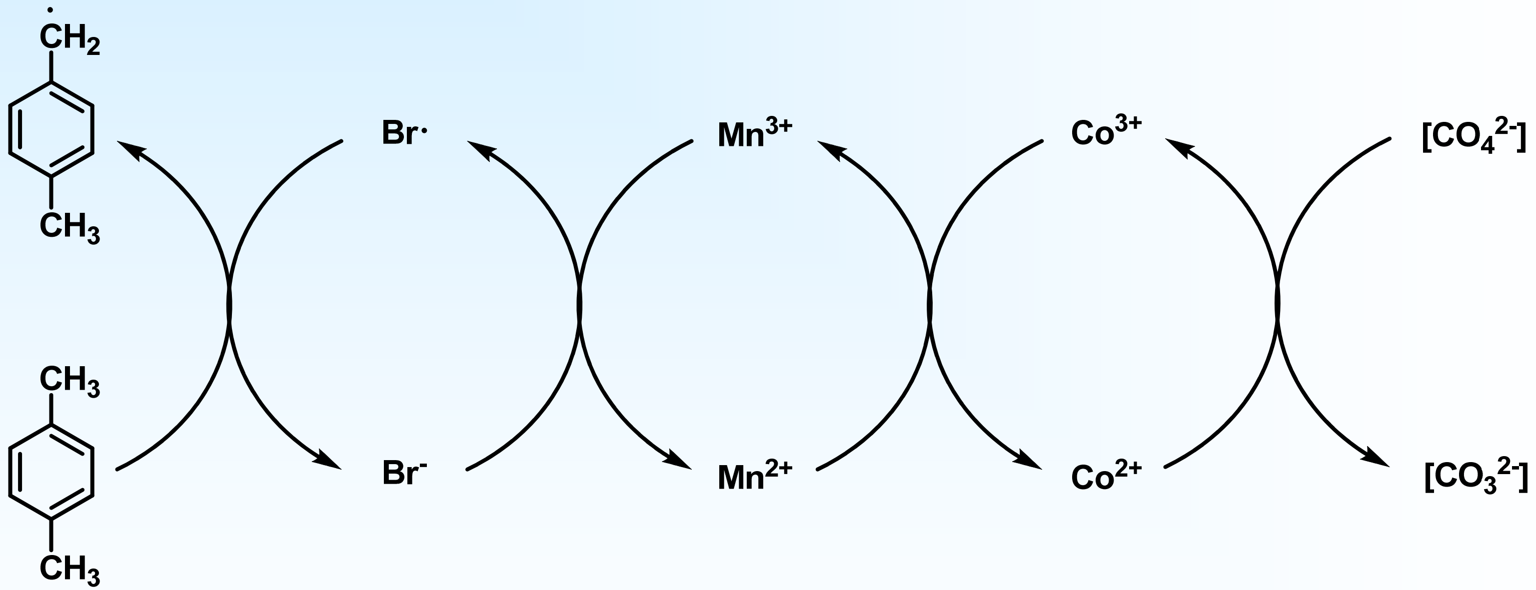


Yoo, J. S.; Jung, S.; Lee, K.; Park, Y. *Appl. Catal., A: Gen.* **2002**, *223*, 239.

Background-Recent research trends in TA synthesis

- Alternative catalyst systems and cocatalyst

  - Use carbon dioxide as co-oxidant

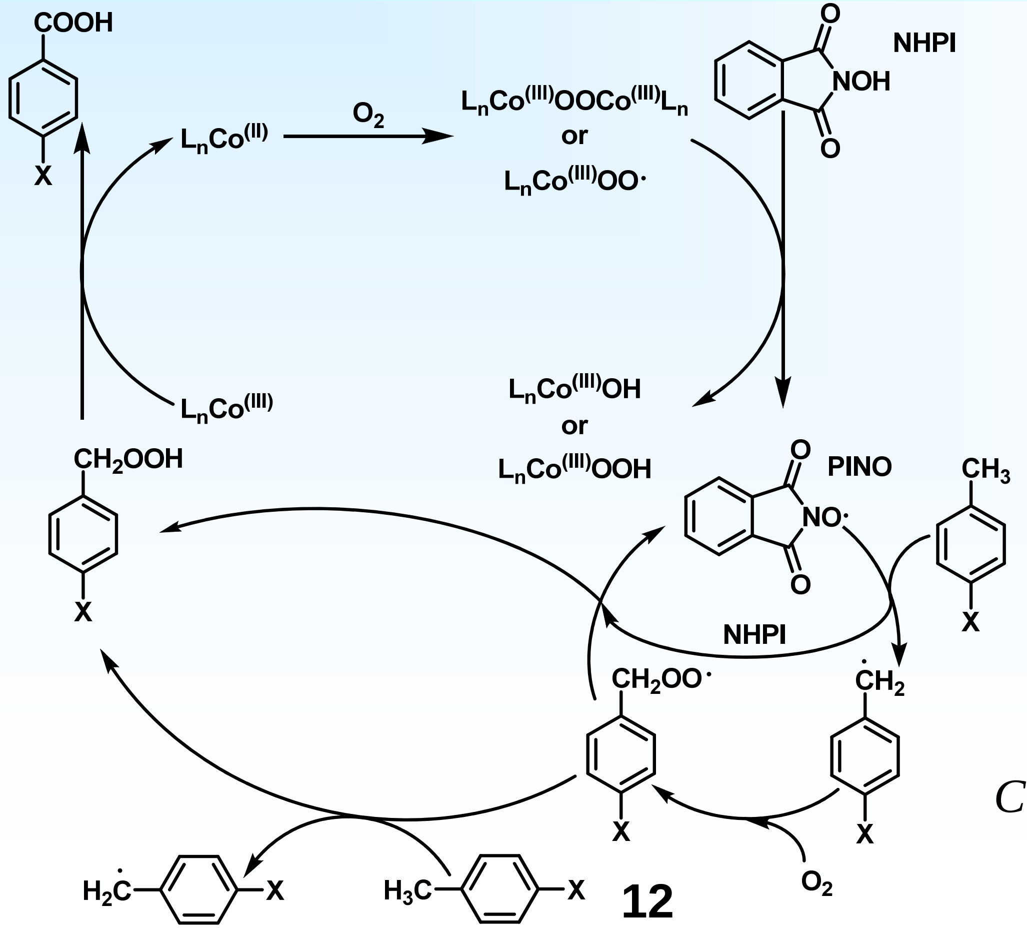


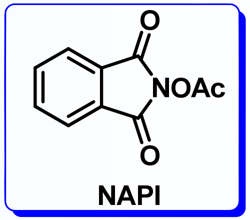
Postulated role of the peroxocarbonate species in the conventional AMOCO MC oxidation catalytic pathway.

Yoo, J. S.; Jung, S.; Lee, K.; Park, Y. *Appl. Catal., A: Gen.* **2002**, *223*, 239.

Background-Recent research trends in TA synthesis

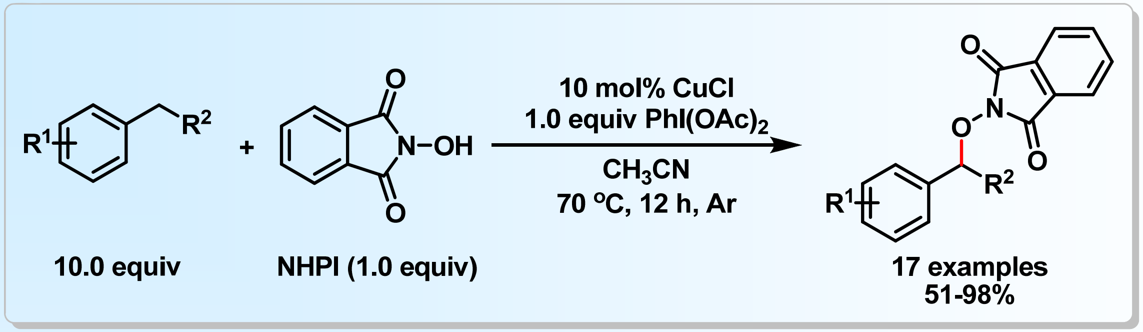
- Alternative catalyst systems and cocatalyst
  - Use *N*-hydroxyphthalimide (NHPI) instead of bromide



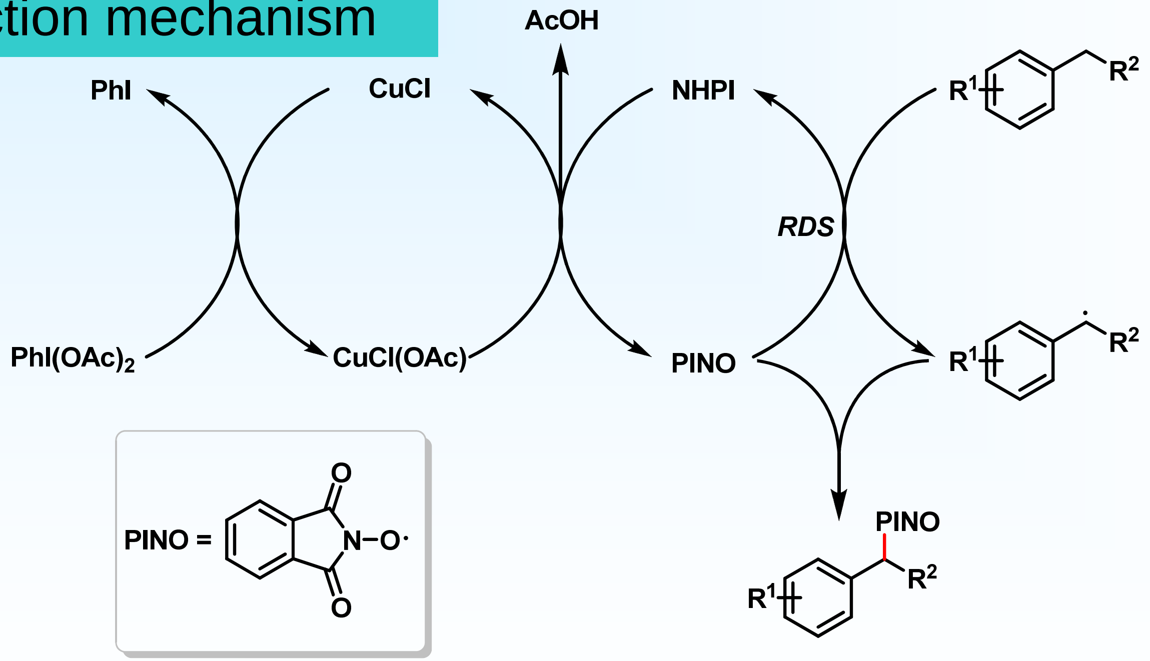


Ishii, Y.; Sakaguchi, S.
Catal. Today **2006**, *117*, 105.

Main text-Use benzyl radical for C_{sp3}-O bond formation

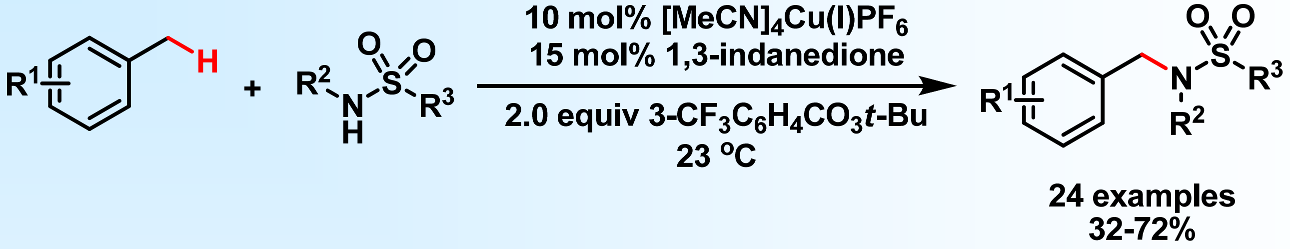


Proposed reaction mechanism

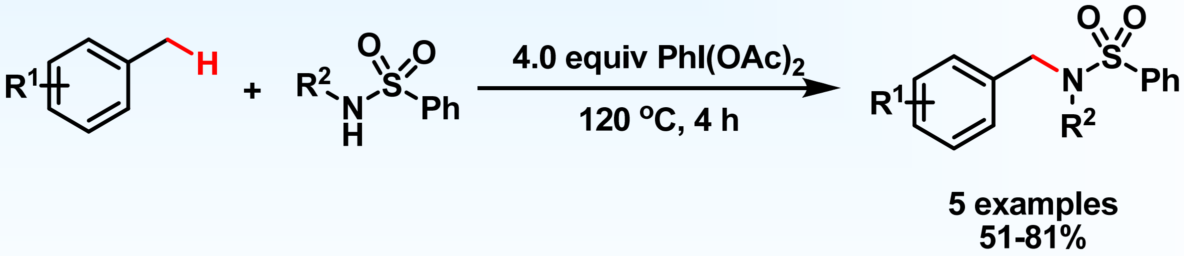


Lee, J. M.; Park, E. J.; Cho, S. H.; Chang, S. *J. Am. Chem. Soc.* **2008**, *130*, 7824.

Main text-Use benzyl radical for C_{sp3}-N bond formation

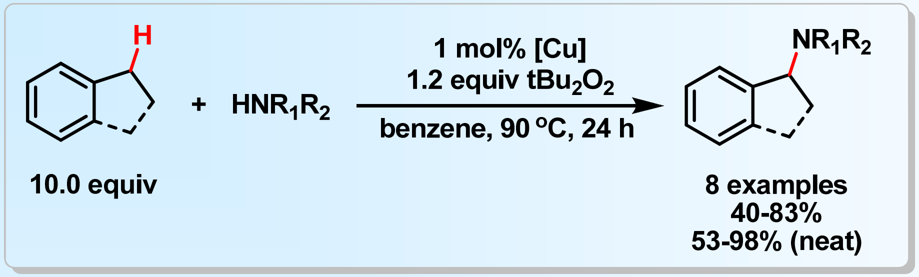


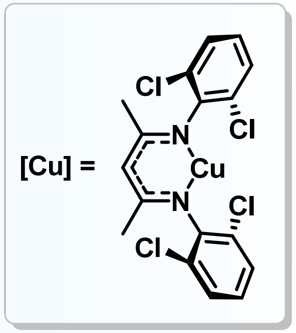
Powell, D. A.; Fan, H. *J. Org. Chem.* **2010**, *75*, 2726.



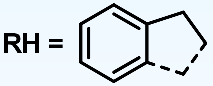
Kim, H. J.; Kim, J.; Cho, S. H.; Chang, S. *J. Am. Chem. Soc.* **2011**, *133*, 16382.

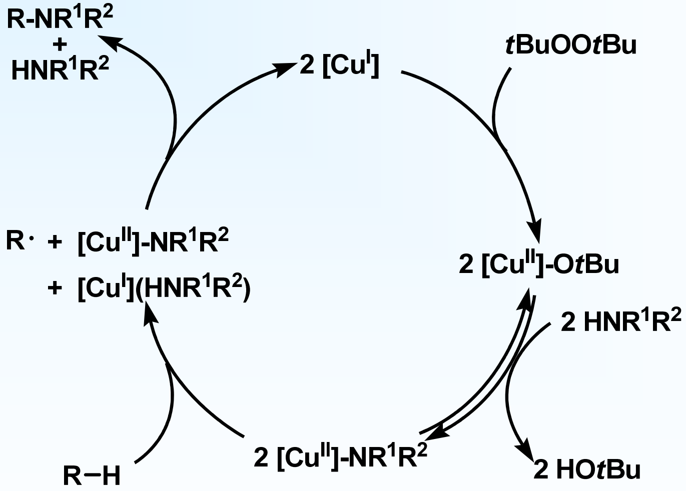
Main text-Use benzyl radical for C_{sp3}-N bond formation





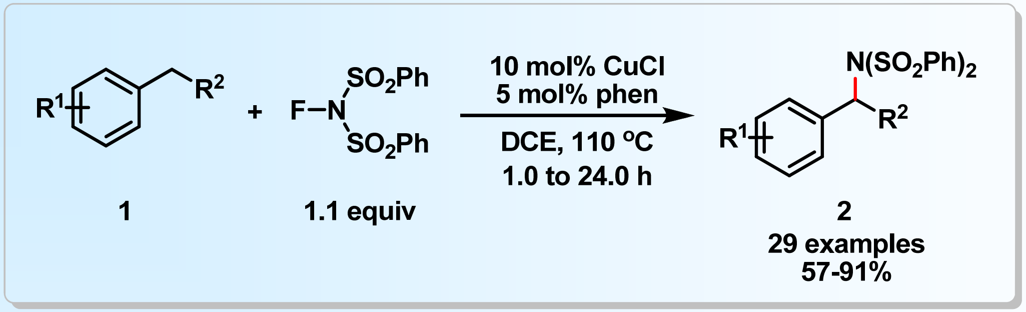
Proposed reaction mechanism



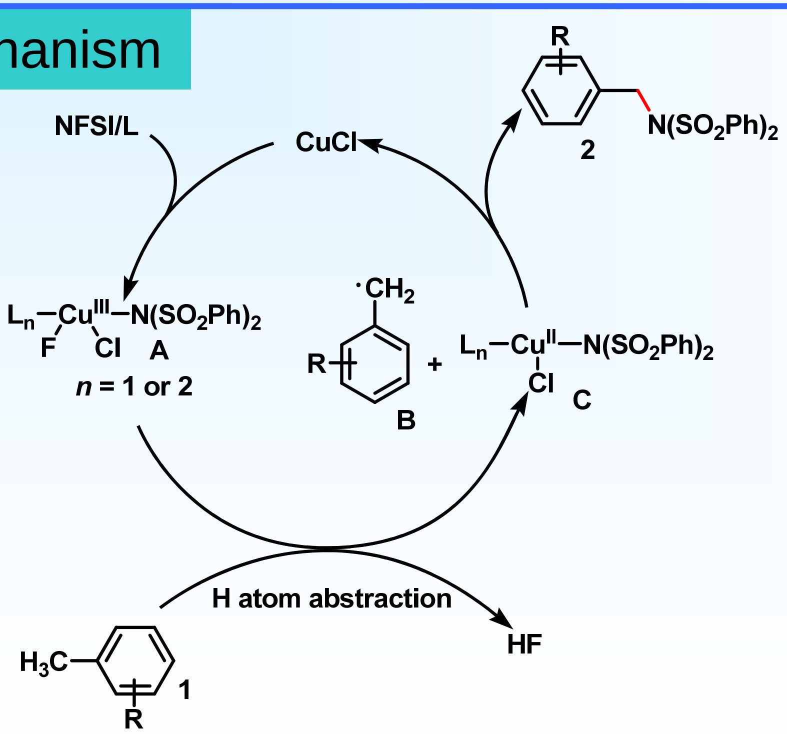


Wiese, S.; Badiei, Y. M.; Gephart, R. T.; Mossin, S.; Varonka, M. S.; Melzer, M. M.; Meyer, K.; Cundari, T. R.; Warren, T. H.; *Angew. Chem. Int. Ed.* **2010**, *49*, 8850.

Main text-Use benzyl radical for C_{sp3}-N bond formation

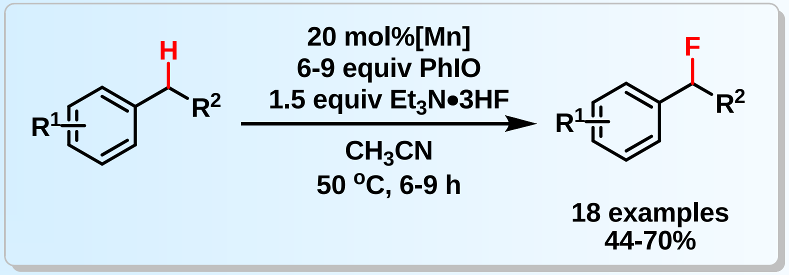


Proposed reaction mechanism

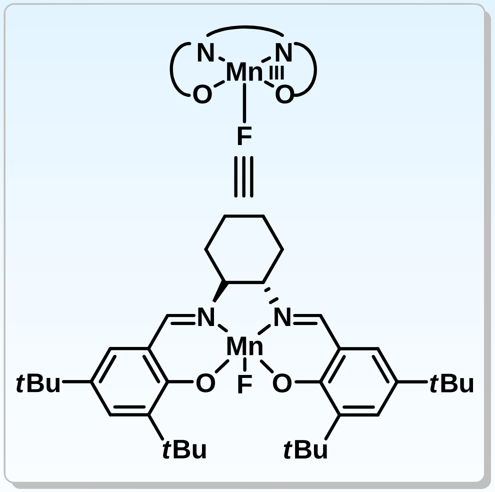


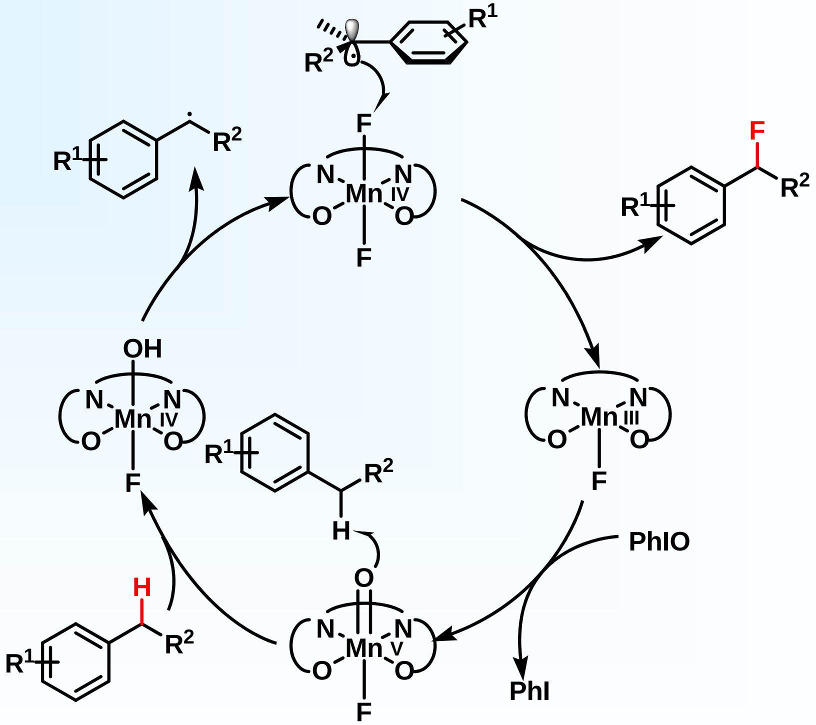
Ni, Z.; Zhang, Q.; Xiong, T.; Zheng, Y.; Li, Y.; Zhang, H.; Zhang, J.; Liu, Q. *Angew. Chem. Int. Ed.* **2012**, *51*, 1244.

Main text-Use benzyl radical for C_{sp3}-F bond formation



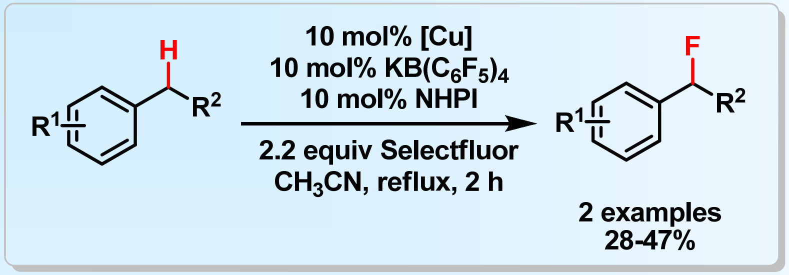
Proposed reaction mechanism

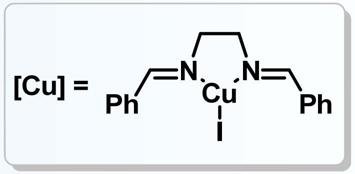




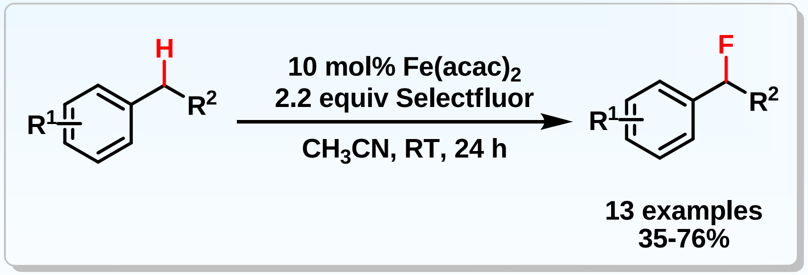
Liu, W.; Groves, J. T. *Angew. Chem. Int. Ed.* **2013**, *52*, 6024.

Main text-Use benzyl radical for C_{sp3}-F bond formation



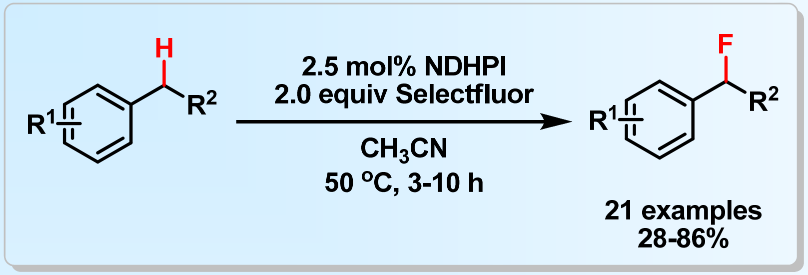


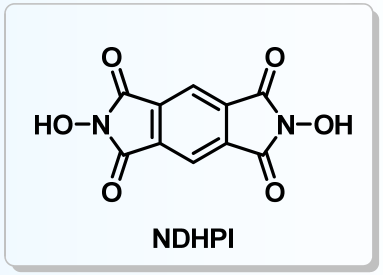
Bloom, S.; Pitts, C. R.; Miller, D. C.; Haselton, N.; Holl, M. G.; Urheim, E.; Lectka, T. *Angew. Chem. Int. Ed.* **2012**, *51*, 10580.



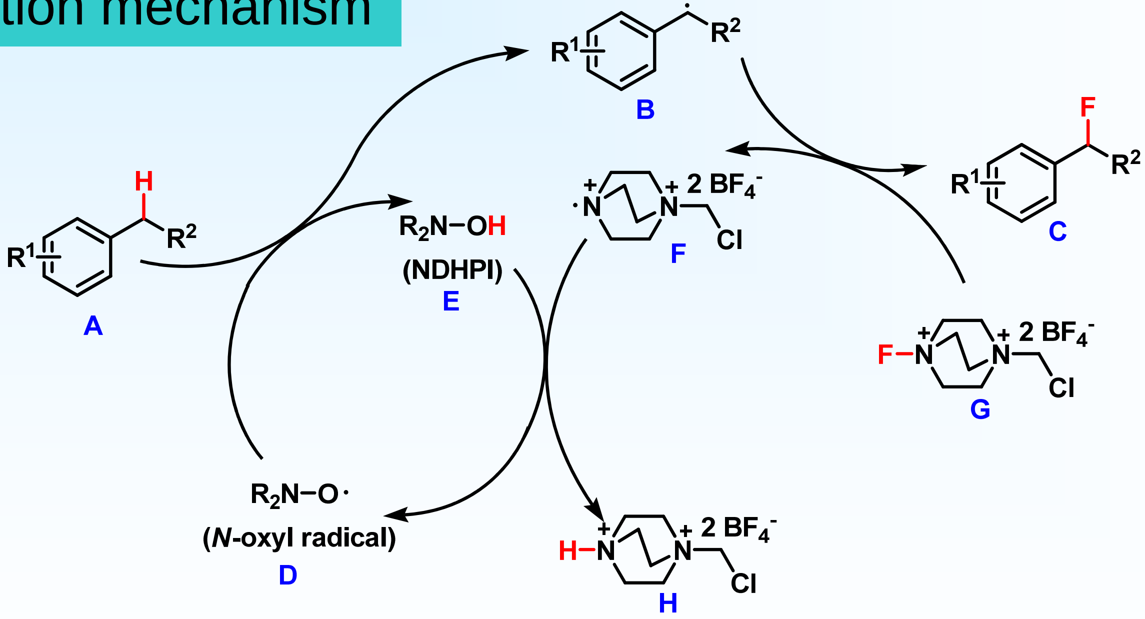
Bloom, S.; Pitts, C. R.; Woltornist, R.; Griswold, A.; Holl, M. G. Lectka, T. *Org. Lett.* **2013**, *15*, 1722.

Main text-Use benzyl radical for C_{sp3}-F bond formation



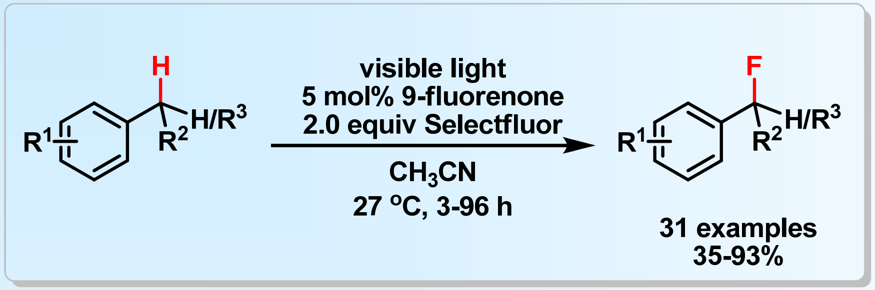


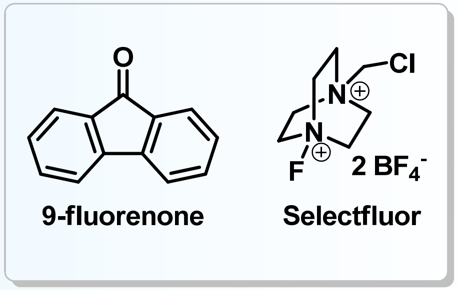
Proposed reaction mechanism



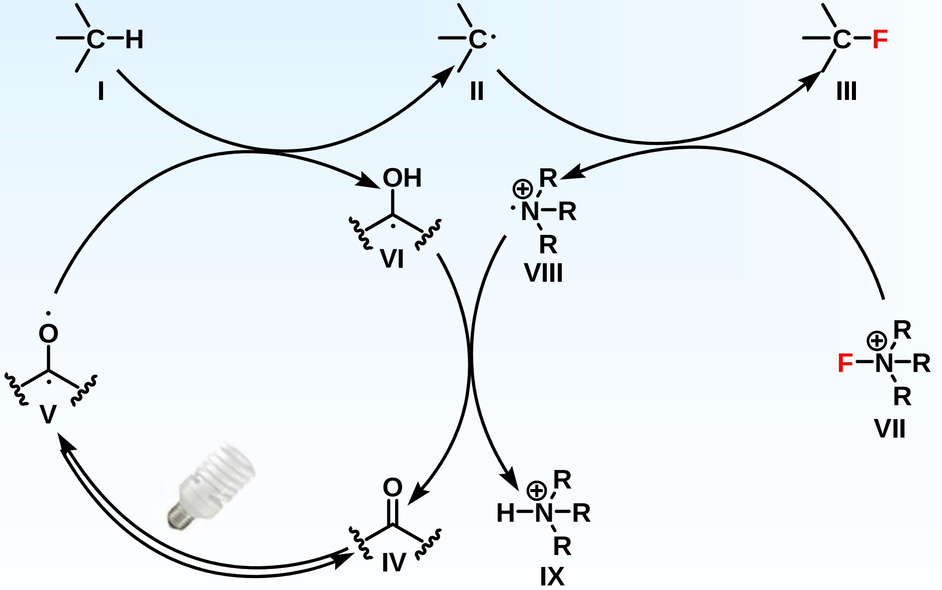
Amaoka, Y.; Nagatomo, M.; Inoue, M.; *Org. Lett.* **2013**, *15*, 2160.

Main text-Use benzyl radical for C_{sp3}-F bond formation



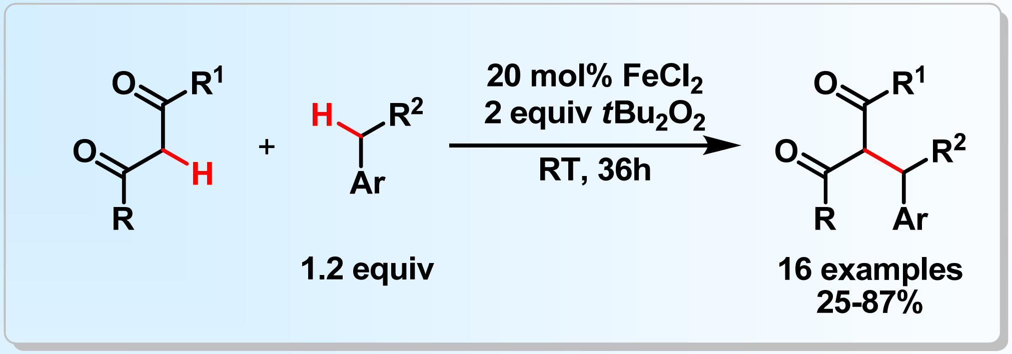


Proposed reaction mechanism

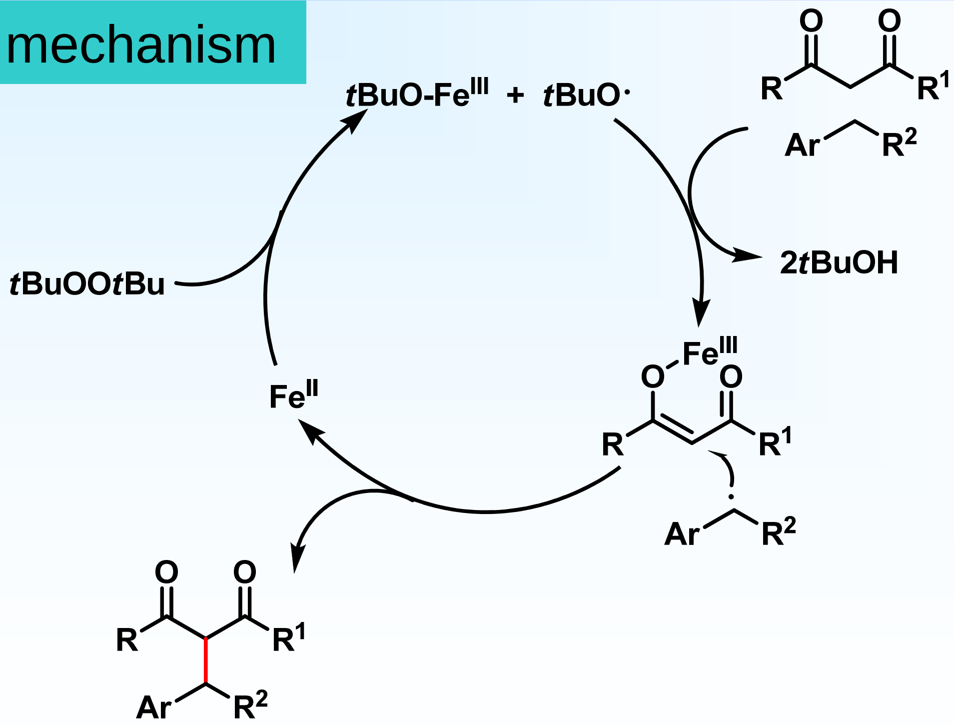


Xia, J.-B.; Zhu, C.; Chen, C. *J. Am. Chem. Soc.* **2013**, *135*, 17494.

Main text-Use benzyl radical for C_{sp3}-C bond formation

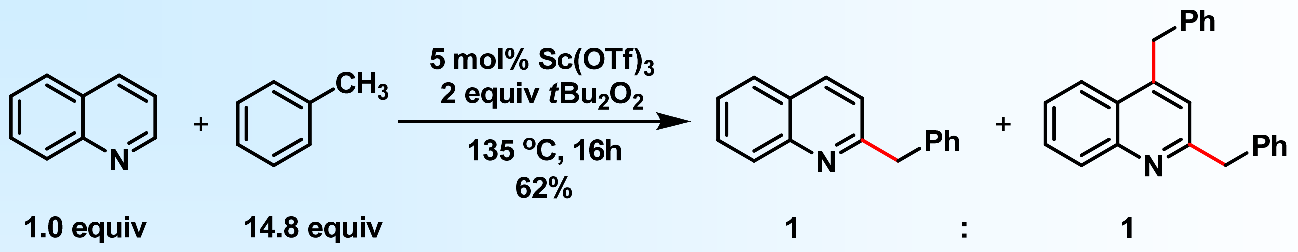


Proposed reaction mechanism

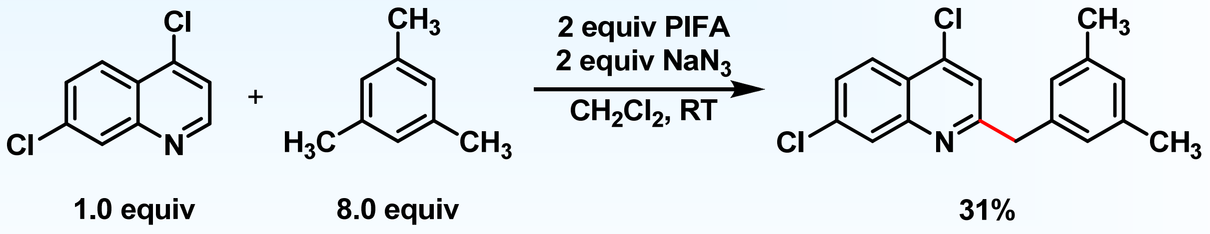


Li, Z.; Cao, L.; Li, C.-J. *Angew. Chem. Int. Ed.* **2007**, *46*, 6505.

Main text-Use benzyl radical for C_{sp3}-C bond formation



Geng, G.; Li, C.-J. *Org. Lett.* **2009**, *11*, 1171.

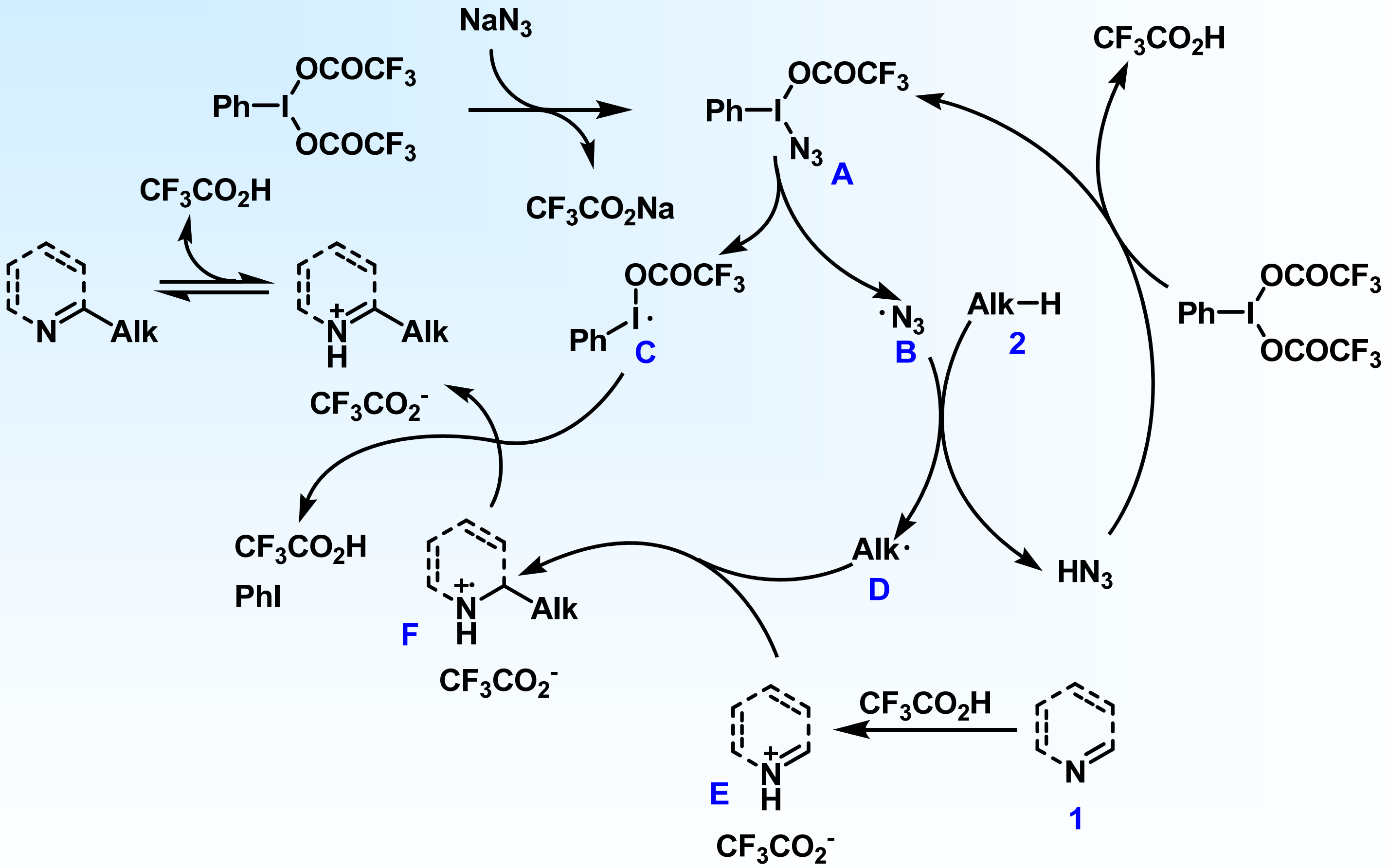


31%
for alkanes yield up to 92%

Antonchick, A. P.; Burgmann, L. *Angew. Chem. Int. Ed.* **2013**, *52*, 3267.

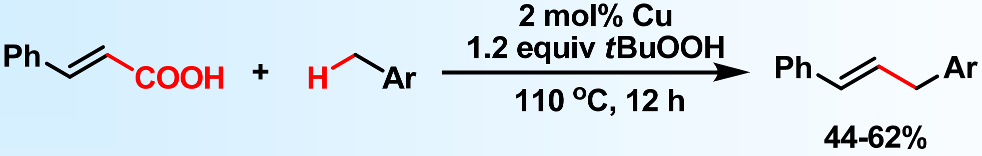
Main text-Use benzyl radical for C_{sp3}-C bond formation

Proposed reaction mechanism

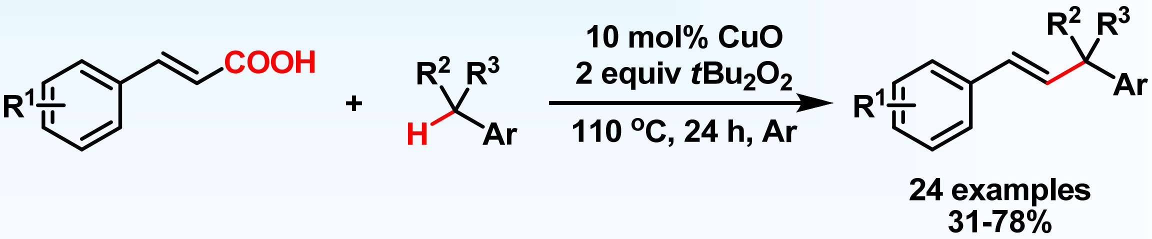


Antonchick, A. P.; Burgmann, L. *Angew. Chem. Int. Ed.* **2013**, *52*, 3267.

Main text-Use benzyl radical for C_{sp3}-C bond formation



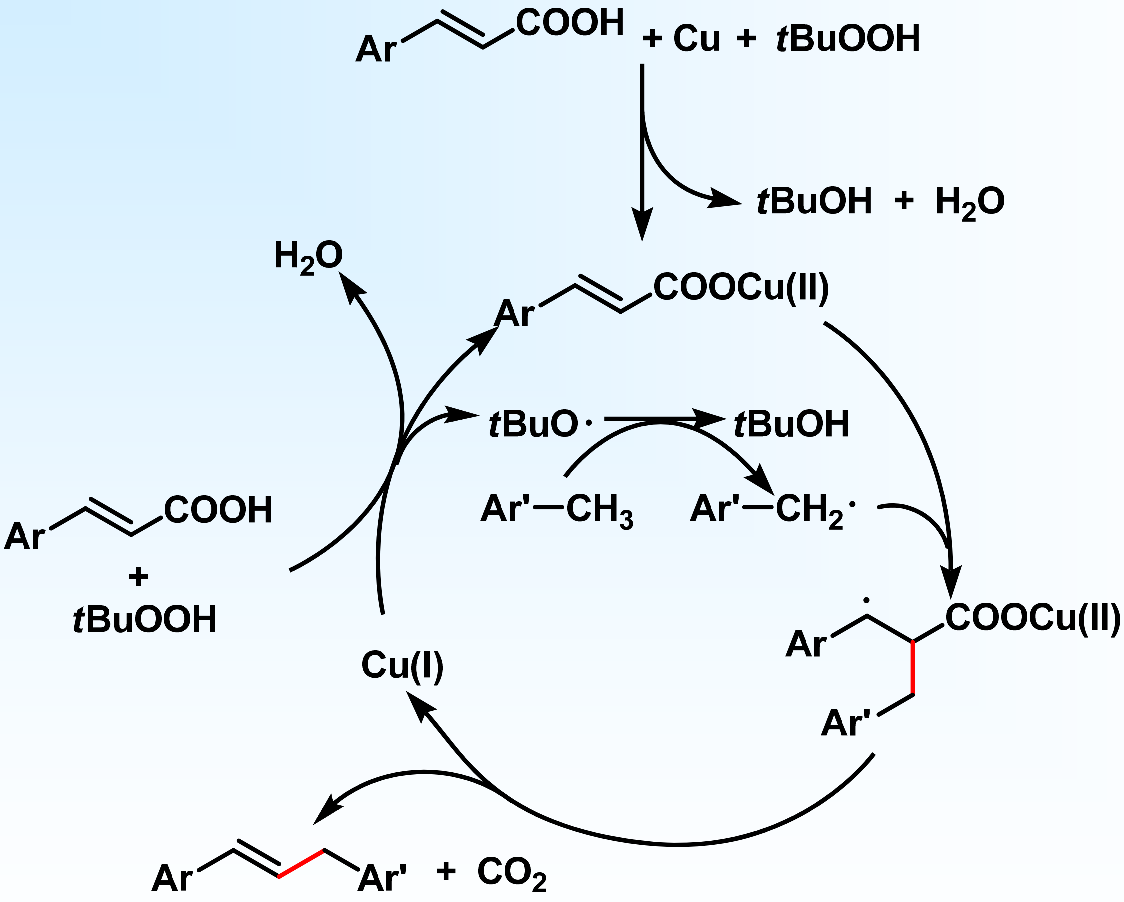
Cui, Z.; Shang, X.; Shao, X.-F.; Liu, Z.-Q. *Chem. Sci.* **2012**, *3*, 2853.



Yang, H.; Sun, P.; Zhu, Y.; Yan, H.; Lu, L.; Qu, X.; Li, T.; Mao, J.
Chem. Commun. **2012**, *48*, 7847.

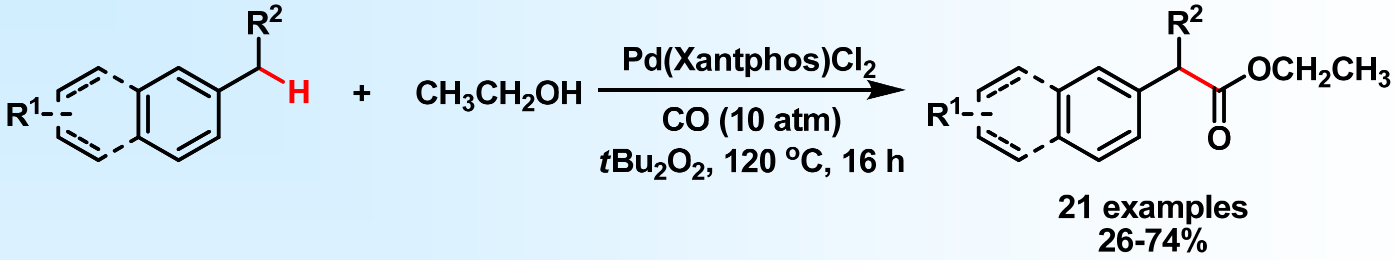
Main text-Use benzyl radical for C_{sp3}-C bond formation

Proposed reaction mechanism

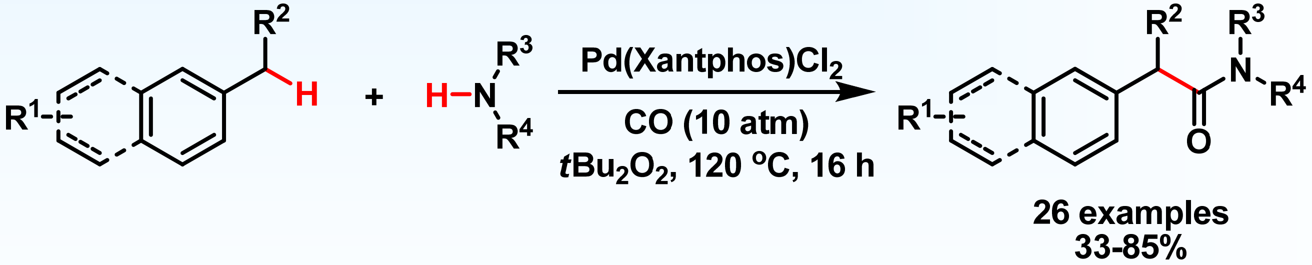


Cui, Z.; Shang, X.; Shao, X.-F.; Liu, Z.-Q. *Chem. Sci.* **2012**, *3*, 2853.

Main text-Use benzyl radical for C_{sp3}-C bond formation



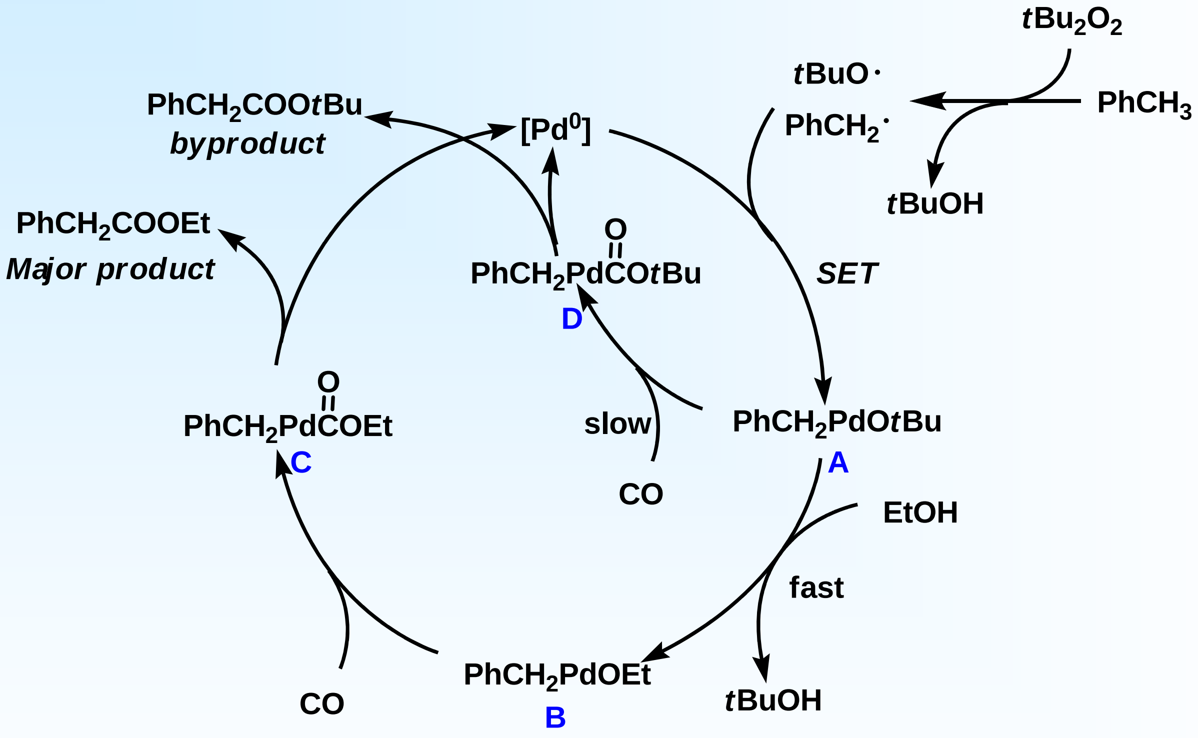
Xie, P.; Xie, Y.; Qian, B.; Zhou, H.; Xia, C.; Huang, H. *J. Am. Chem. Soc.* **2012**, *134*, 9902.



Xie, P.; Xia, C.; Huang, H. *Org. Lett.* **2013**, 15, 3370.

Main text-Use benzyl radical for C_{sp3}-C bond formation

Proposed reaction mechanism



Xie, P.; Xie, Y.; Qian, B.; Zhou, H.; Xia, C.; Huang, H.
J. Am. Chem. Soc. **2012**, *134*, 9902.

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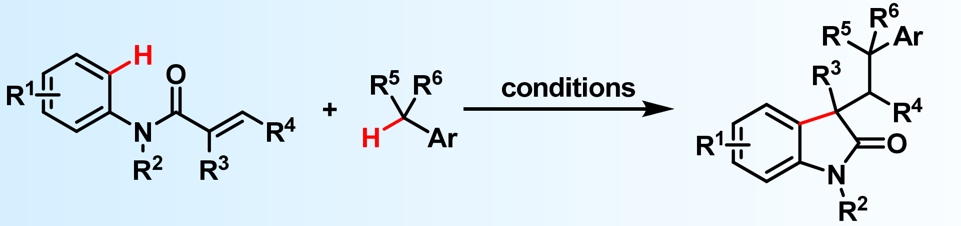


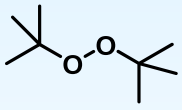
conditions:

$\xrightarrow[\text{120 °C, 24 h, Ar}]{\text{3 mol\% IrCl}_3\text{, 2.0 equiv DTBP}}$ 26 examples 67-88%

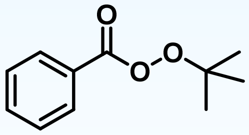
$\xrightarrow[\text{120 °C, 28 h}]{\text{2 mol\% Cu}_2\text{O, 2.0 equiv TBPB}}$ 23 examples 45-95%

$\xrightarrow[\text{110 °C, 22 h}]{\text{5 mol\% Cu}_2\text{O, 3.0 equiv DCP}}$ 7 examples 45-95%

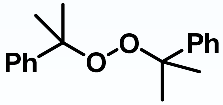
Proposed reaction mechanism



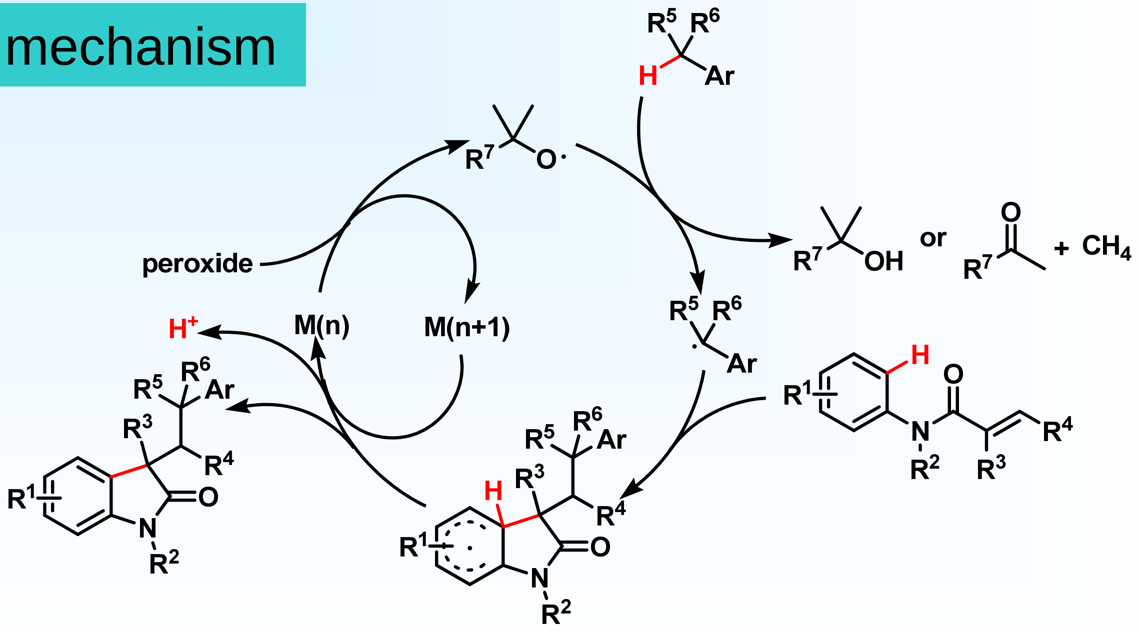
DTBP



TBPB



DCP



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Zhou, S.-L.; Duan, X.-H. et al *Chem. Eur. J.* **2013**, *19*, 12970.
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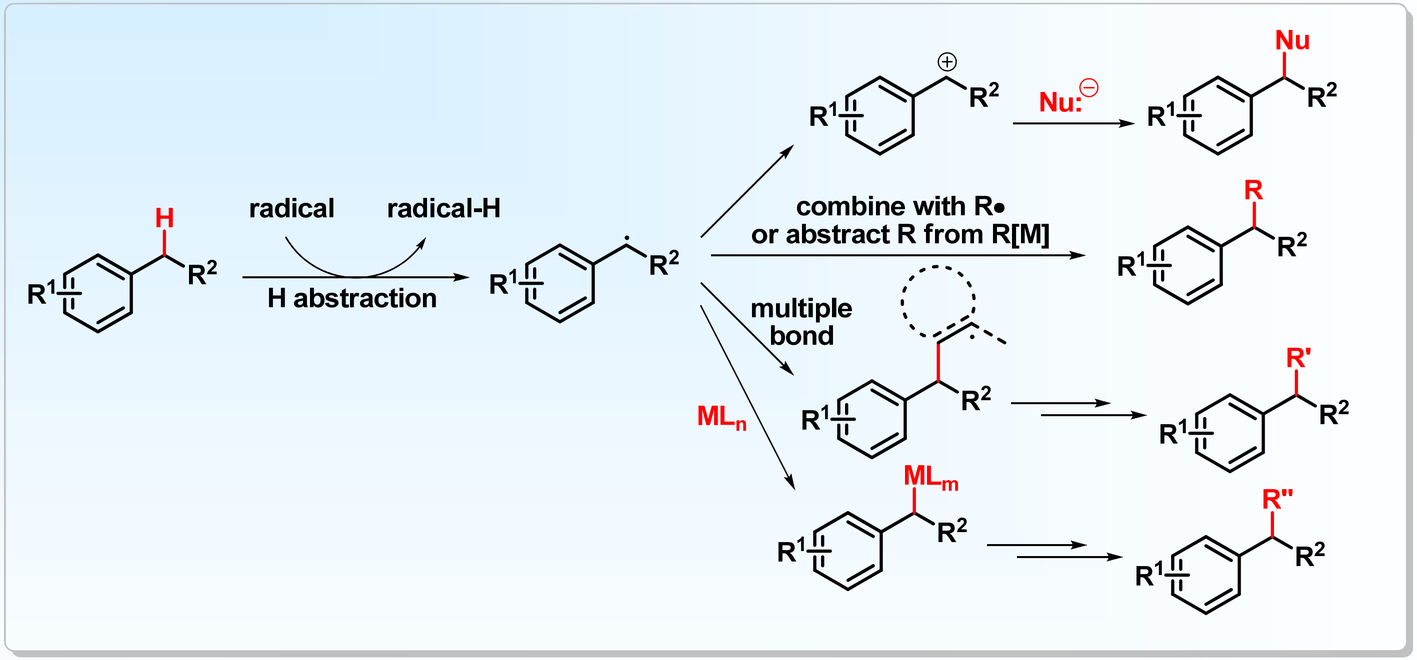
Summary and outlook

Summary



Summary and outlook

Outlook

- The oxidative coupling of C_{sp3}-H bond with different substrates supplements well-established coupling reactions of prefunctionalized starting materials and provides waste-minimized access to functionalized molecules more rapidly.
- It is of high interest to develop efficient catalyst systems for the selective activation of inert C_{sp3}-H bonds.
- Air has yet to be further established as a broadly available and safe oxidant.

Thanks !