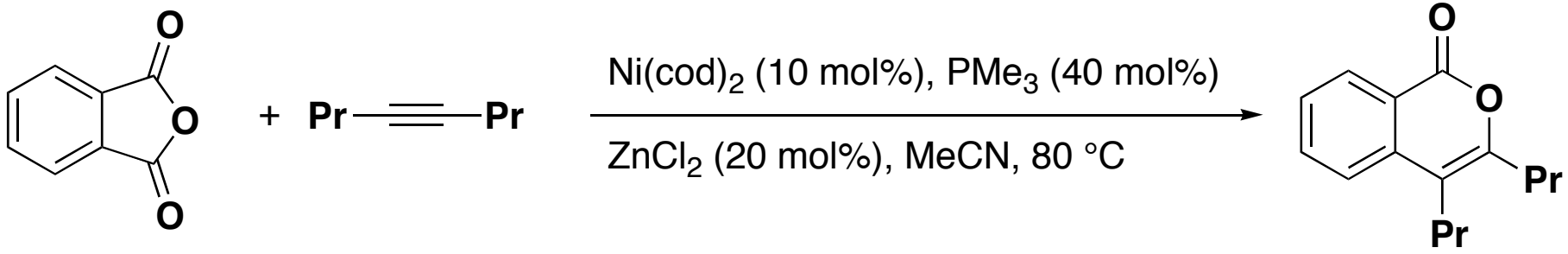
Nickel-Catalyzed Decarbonylative Addition of Anhydrides to Alkynes

Kajita, Y.; Kurahashi, T.; Matsubara, S.

J. Am. Chem. Soc. **2008**, *130*, 17226



Current Literature

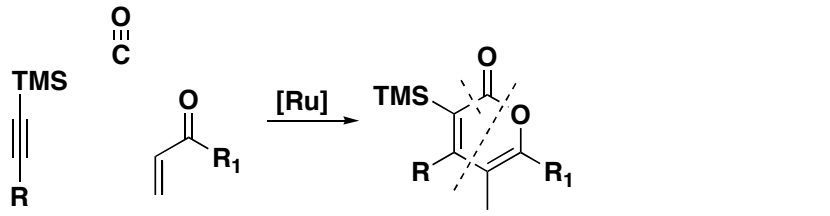
Kalyani Patil

12/20/08

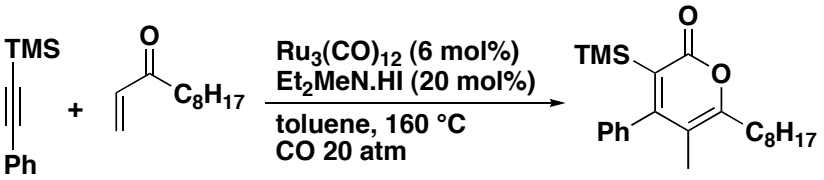
Outline

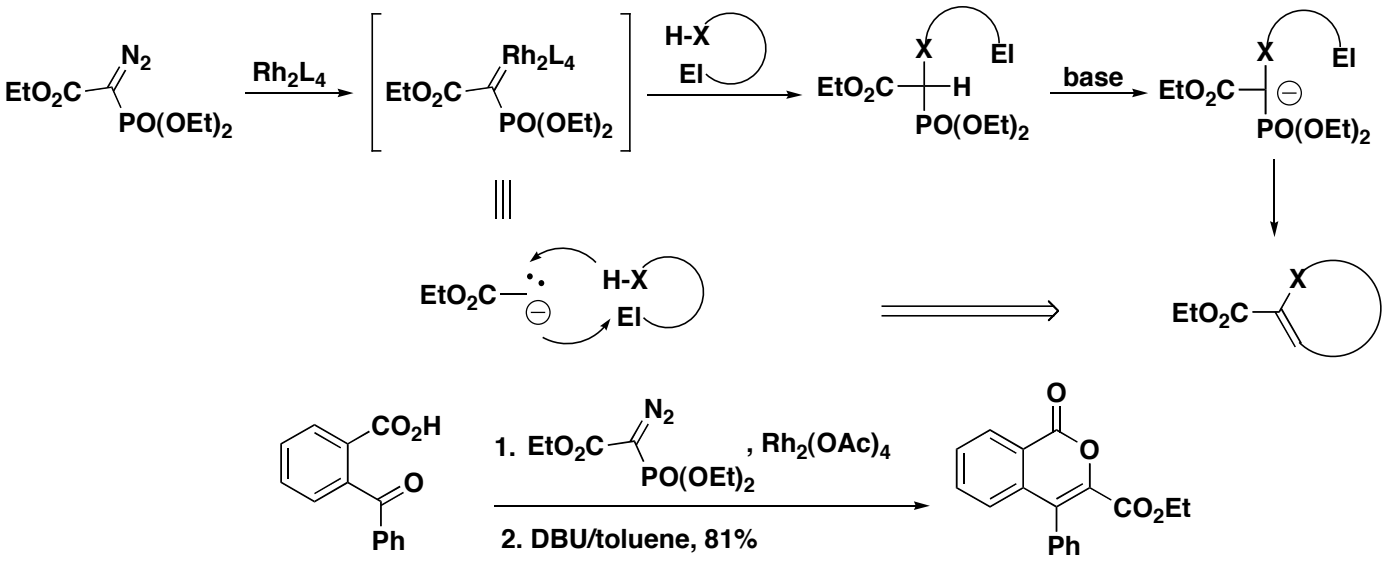
- Synthesis of Isocoumarins
- Nickel - LA Catalyzed Reactions
- Title Paper
- Summary

Synthesis of Isocoumarins/α-Pyrones



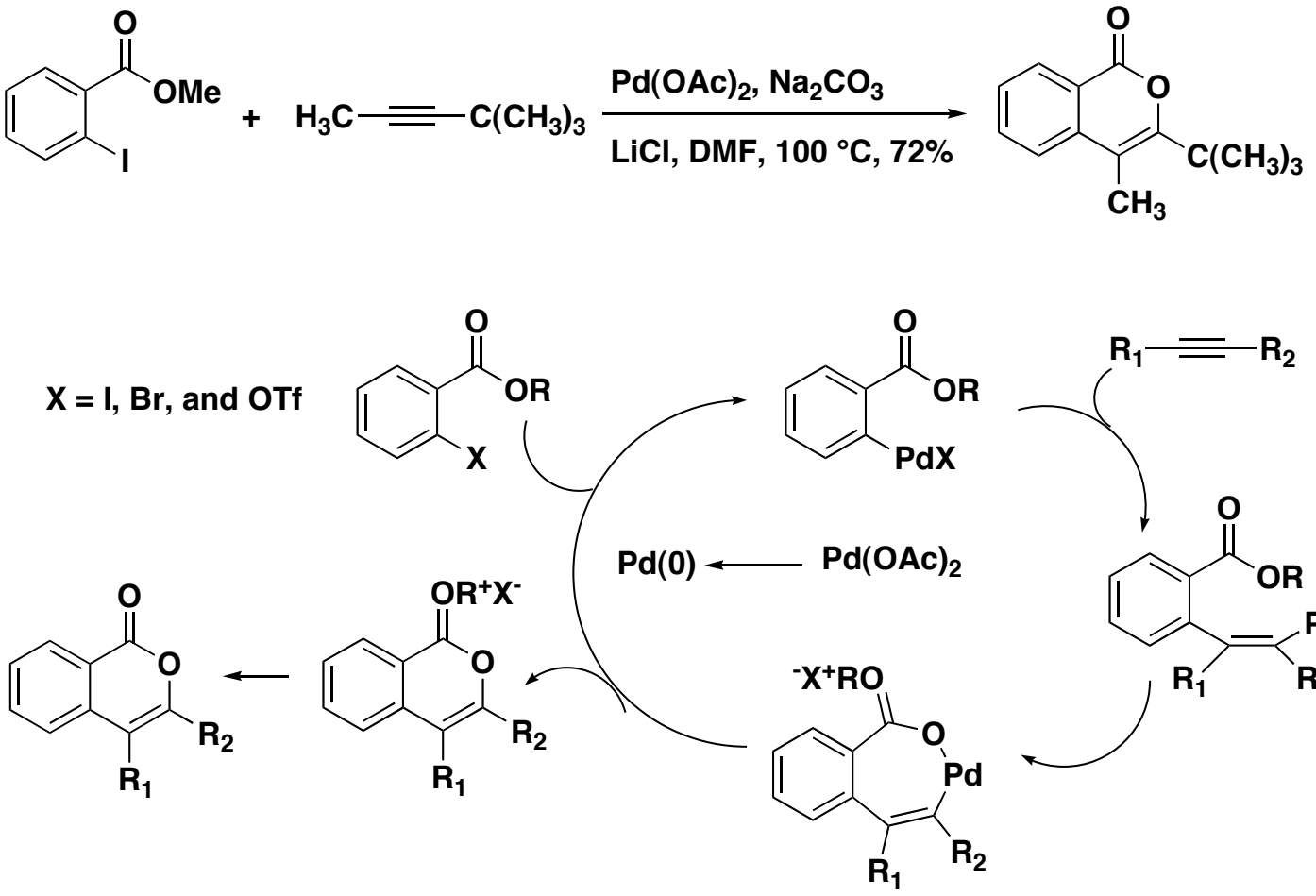
[3+2+1] cycloaddition





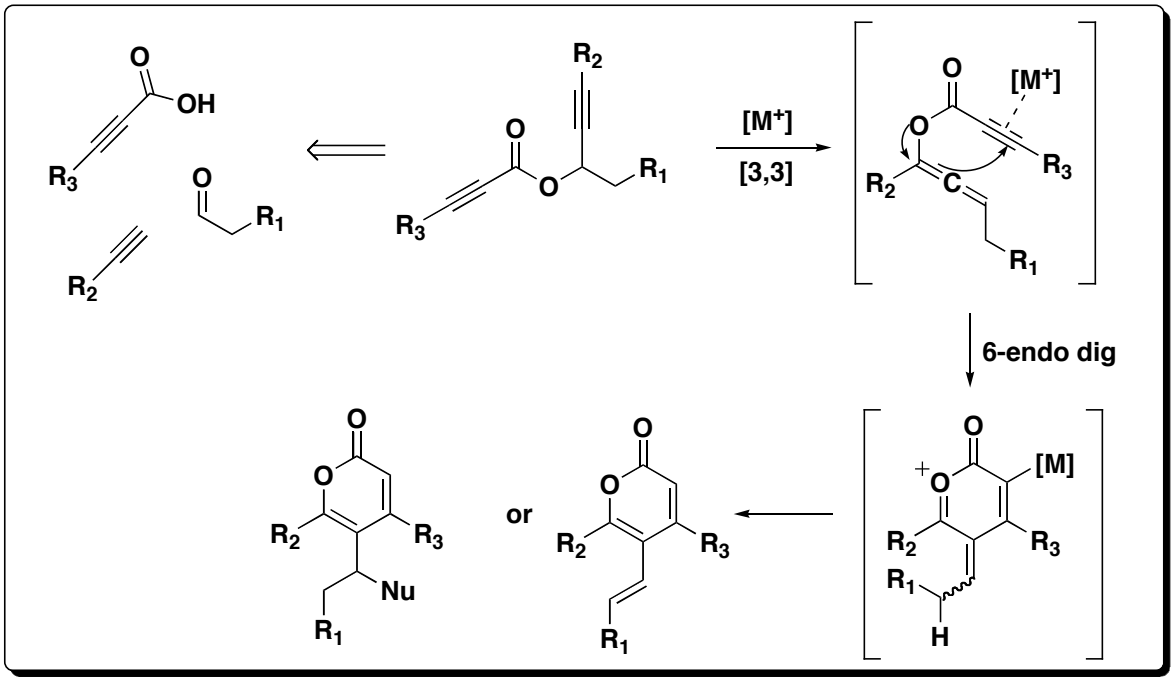
Fukuyama, T.; Higashibeppu, Y.; Yamaura, R.; Ryu, I. *Org. Lett.* **2007**, *9*, 587
Nakamura, Y.; Ukita, T. *Org. Lett.* **2002**, *4*, 2317

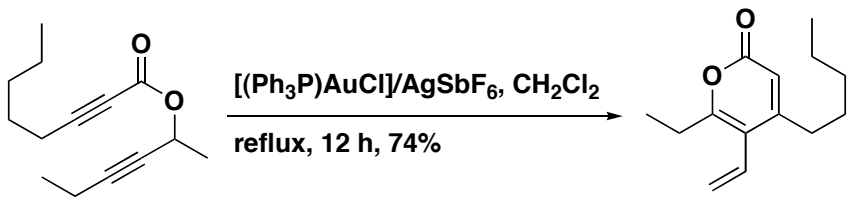
Synthesis of Isocoumarins

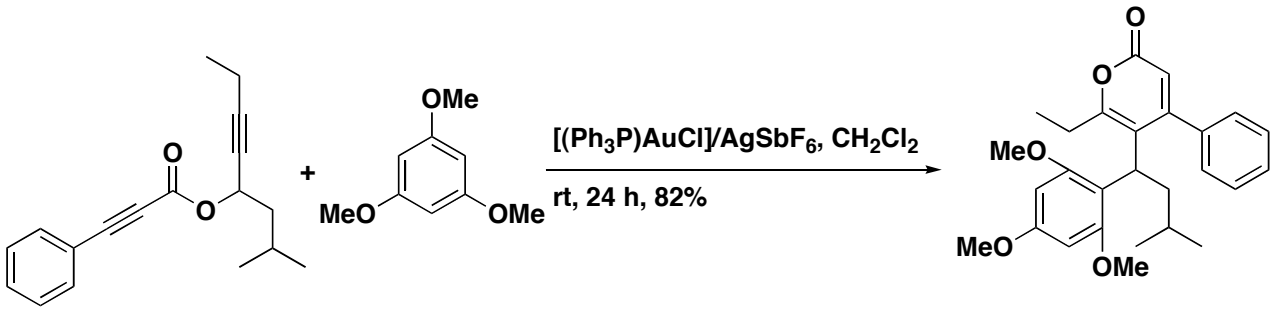


Larock, R. C.; Doty, M. J.; Han, X. *J. Org. Chem.* **1999**, *64*, 8770

Synthesis of Isocoumarins

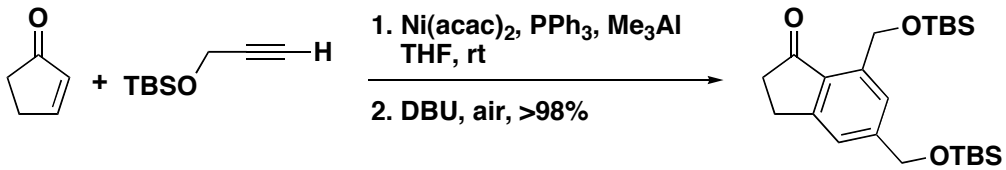




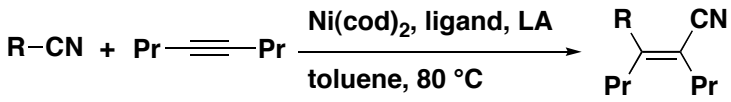


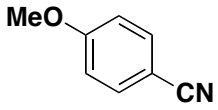
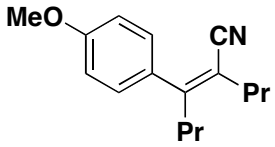
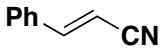
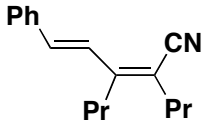
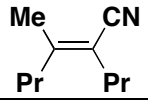
Luo, T.; Schreiber, S. L. *Angew. Chem. Int. Ed.* **2007**, *46*, 8250

Examples of Nickel-LA Catalyzed Reactions



Cyclic cotrimerization of α,β-enones and alkynes

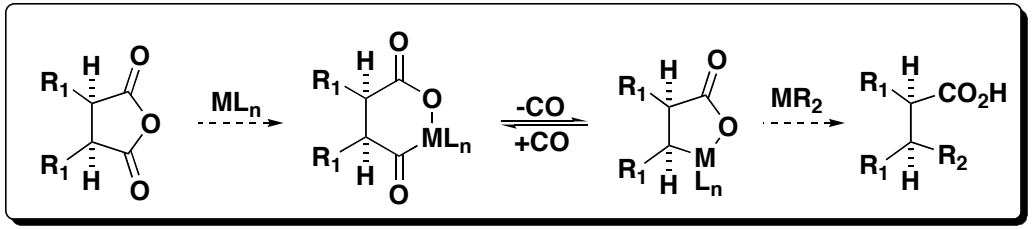


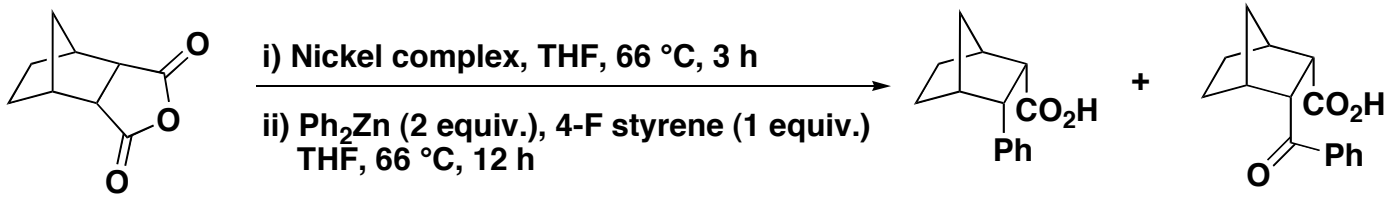
entry	substrate	ligand	LA	product (yield)
1.		$PPhMe_2$	$AlMe_2Cl$	 (96%)
2.		dppb	BPh_3	 (94%)
3.	Me–CN	$PPh_2(t\text{-}Bu)$	$AlMe_3$	 (71%)

Carbocyanation of alkynes

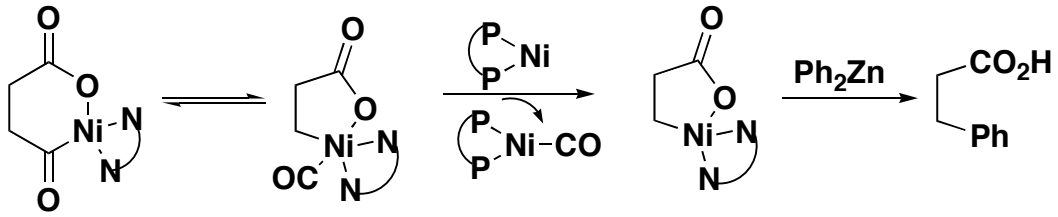
Ikeda, S-i.; Mori, N.; Sato, Y. *J. Am. Chem. Soc.* **1997**, 119, 4779
Nakao, Y.; Yada, A.; Ebata, S.; Hiyama, T. *J. Am. Chem. Soc.* **2007**, *129*, 2428

Decarbonylative Cross Coupling of Cyclic Anhydrides



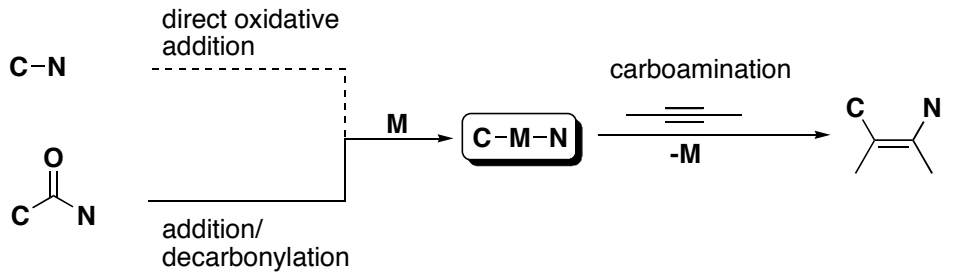


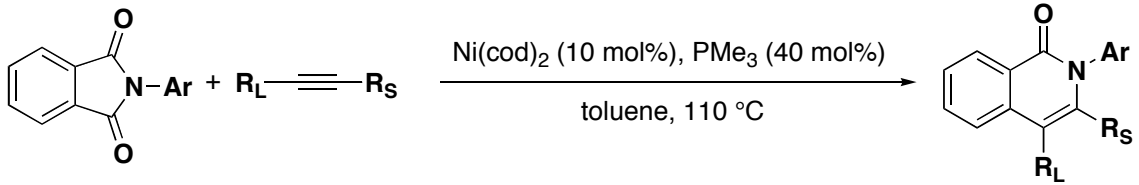
$Ni(COD)_2$/neocuproine (1:1)	**66:33**
$Ni(COD)_2$/neocuproine/dppb (1.5:1.0:0.5)	**>95:5 (77% yield)**

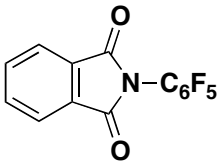
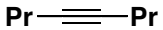
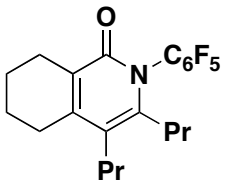
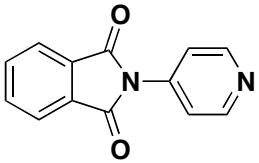
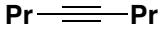
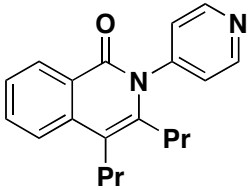
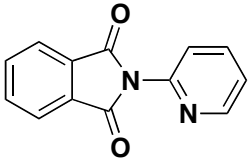
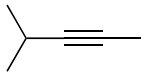
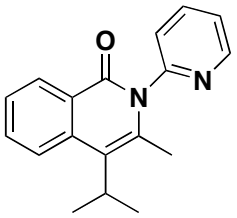


O'Brien, E. M.; Bercot, E. A..; Rovis, T. *J. Am. Chem. Soc.* **2003**, *125*, 10498

Decarbonylative Addition of Phthalimides to Alkynes

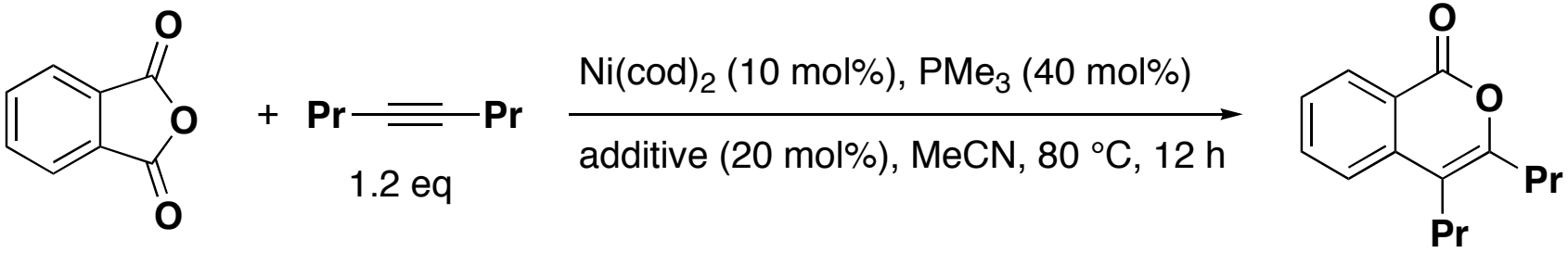




entry	phthalimide	alkyne	time (h)	product (yield)
1.			7	 (84%)
2.			7	 (72%)
3.			12	 (93%) 2:1

Kajita, Y.; Matsubara, S.; Kurahashi, T. *J. Am. Chem. Soc.* **2008**, *130*, 6058

Title Paper - Optimization Studies



entry	additive	yield (%)
1.	-	12
2.	$ZnCl_2$	96
3.	$Zn(OTf)_2$	92
4.	$ZnBr_2$	91
5.	ZnI_2	90
6.	BPh_3	92

entry	additive	yield (%)
7.	LiCl	76
8.	Bu_4NPF_6	54
9.	Bu_4NCl	72
10.	Bu_4NOTf	67
11.	Bu_4NBr	65
12.	Bu_4NI	52

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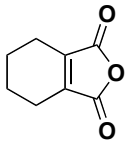
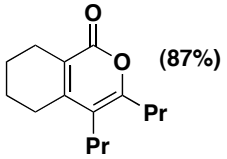
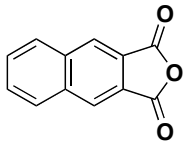
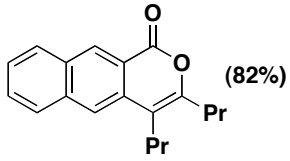
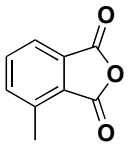
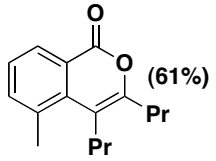
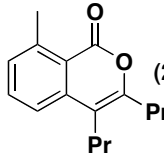
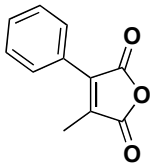
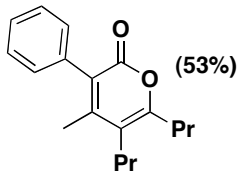
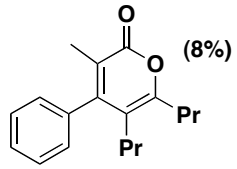
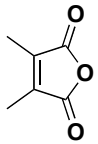
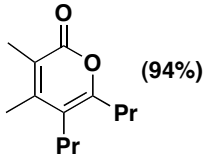
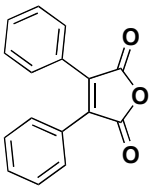
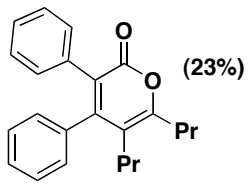
Ni Catalyzed Decarbonylative Addition of Anhydrides

entry	substrate	time (h)	product (yield)
1.		15	 (87%)
2.		18	 (82%)
3.		18	 (61%)  (29%)
4.		18	 (53%)  (8%)
5.		15	 (94%)
6.		18	 (23%)

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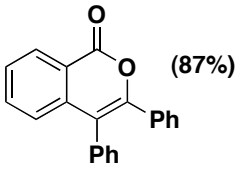
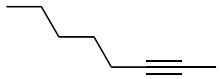
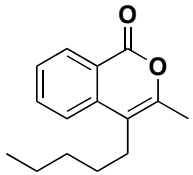
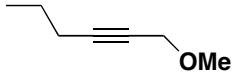
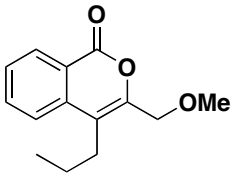
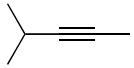
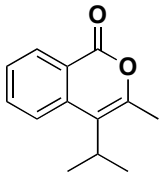
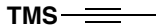
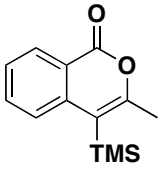
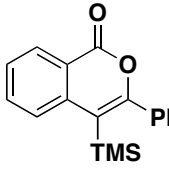
Ni Catalyzed Decarbonylative Addition of Anhydrides

entry	alkyne	time (h)	product (yield)
1.		12	 (87%)
2.		15	 (91%) (1:1)
3.		15	 (75%) (1:1)
4.		15	 (89%) (2:1)
5.		18	 93%
6.		24	 86%

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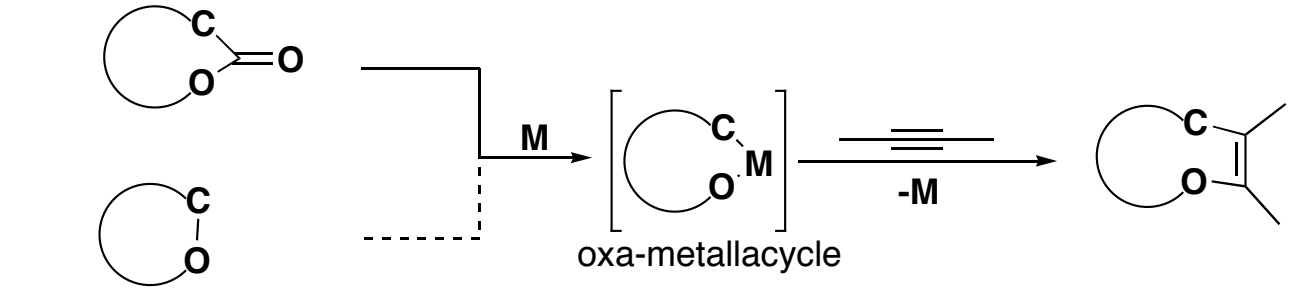
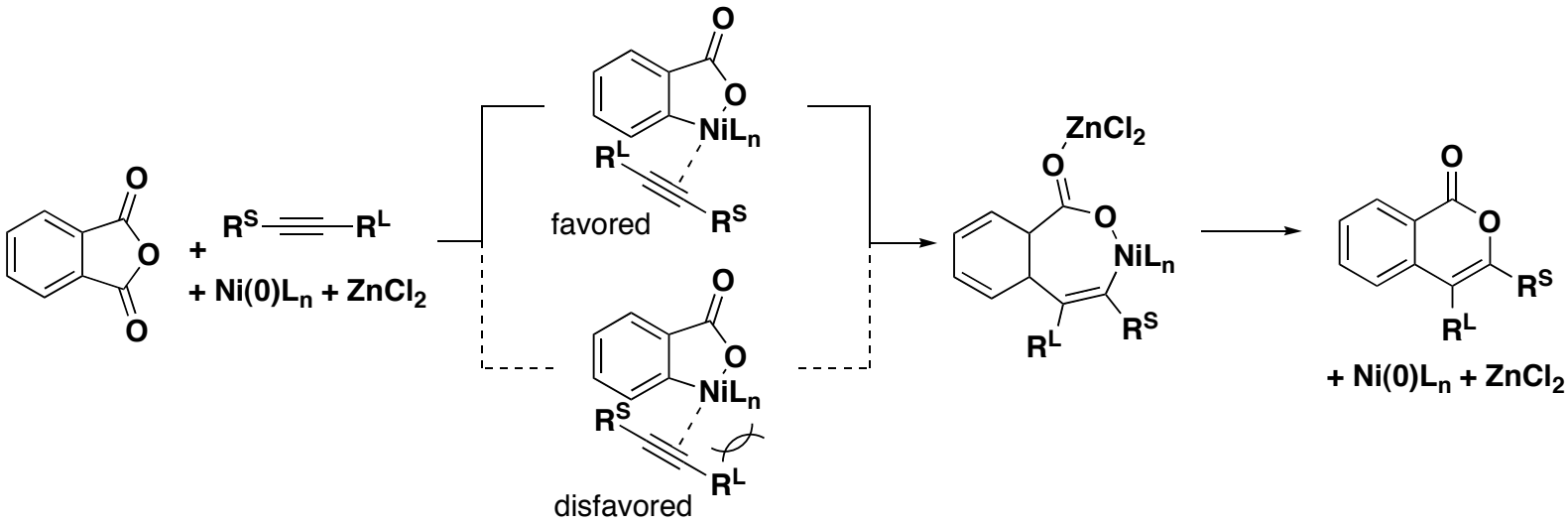
Title Paper - Plausible Mechanism





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Summary

- Synthesis of Isocoumarins/α-Pyrones in Good Yields
- Nickel Catalyzed Decarbonylative Addition of Cyclic Anhydrides to Alkynes
- Terminal Alkynes failed to Convert to the Product