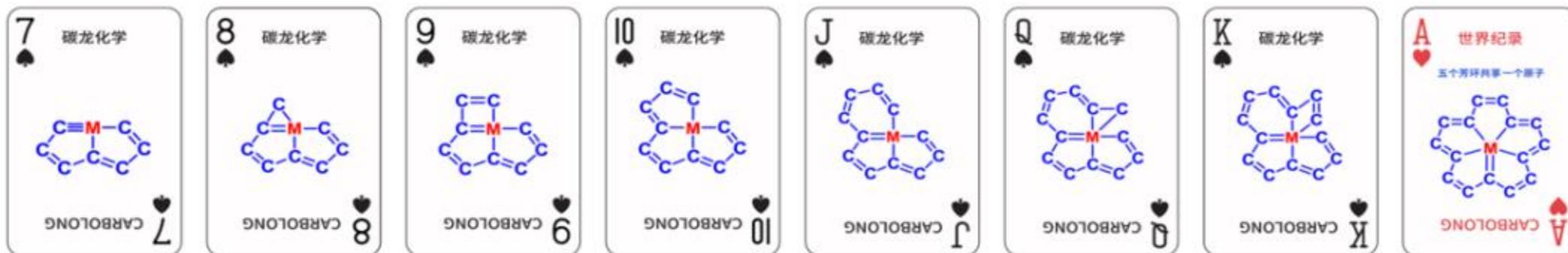




Carbolong Chemistry



汇报人：杨懿
指导老师：麻生明 教授
钱辉 副教授
汇报时间：2025年12月5日



- 一. 背景介绍
- 二. 简单金属杂芳烃构筑
- 三. 碳龙骨架构筑及反应性
- 四. 总结与展望

一. 背景介绍

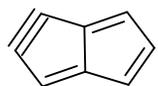
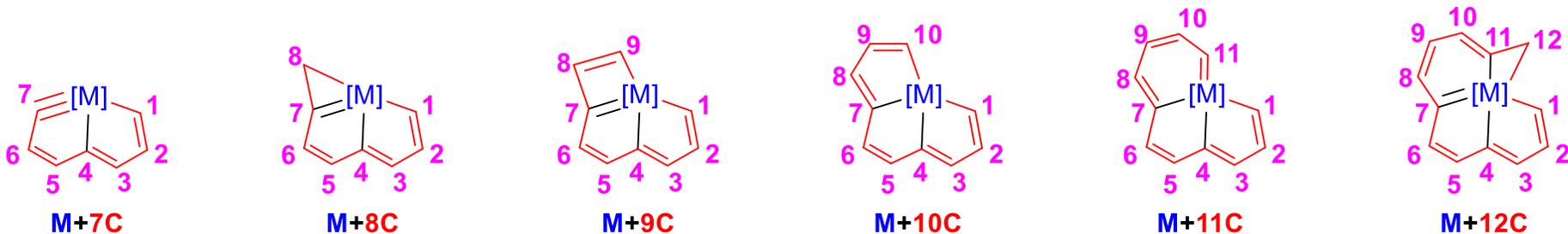
二. 简单金属杂芳烃构筑

三. 碳龙骨架构筑及反应性

四. 总结与展望

1.1 碳龙化学简介

碳龙化合物 (Carbolong): 一条平面共轭的碳链 (碳数 ≥ 7) 通过至少3个碳-金属键整合一个过渡金属形成的化合物。



Pentalyne

光致发光材料

Nat. Chem. **2013**, 5, 698.

均相催化

J. Am. Chem. Soc. **2022**, 144, 2301.

太阳能电池

Nat. Commun. **2020**, 11, 4651.

Adv. Mater. **2021**, 33, e2101279.

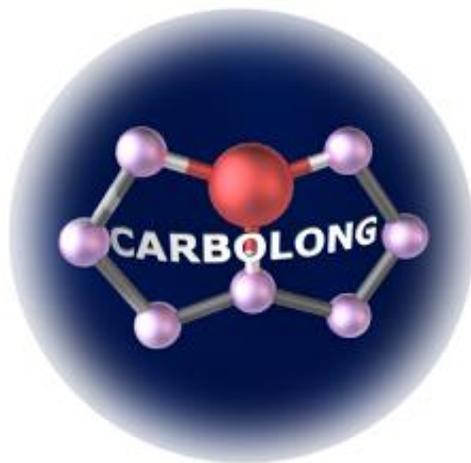
J. Am. Chem. Soc. **2021**, 143, 7759.

Adv. Sci. **2022**, 2203640.

Adv. Funct. Mater. **2023**, 2300359.

分子电子学

J. Am. Chem. Soc. **2017**, 139, 14344.



响应性高分子材料

ACS Macro Lett. **2018**, 7, 1034.

ACS Macro Lett. **2020**, 9, 344.

光声成像

Angew. Chem. Int. Ed. **2015**, 54, 6181.

光热治疗

Sci. Adv. **2016**, 2, e1601031.

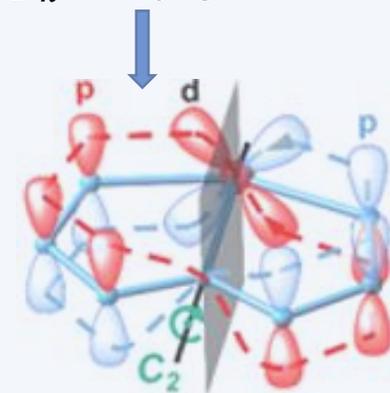
光动力学治疗

Nat. Commun. **2022**, 13, 2245.

光热海水淡化

SusMat **2022**, 2, 679.

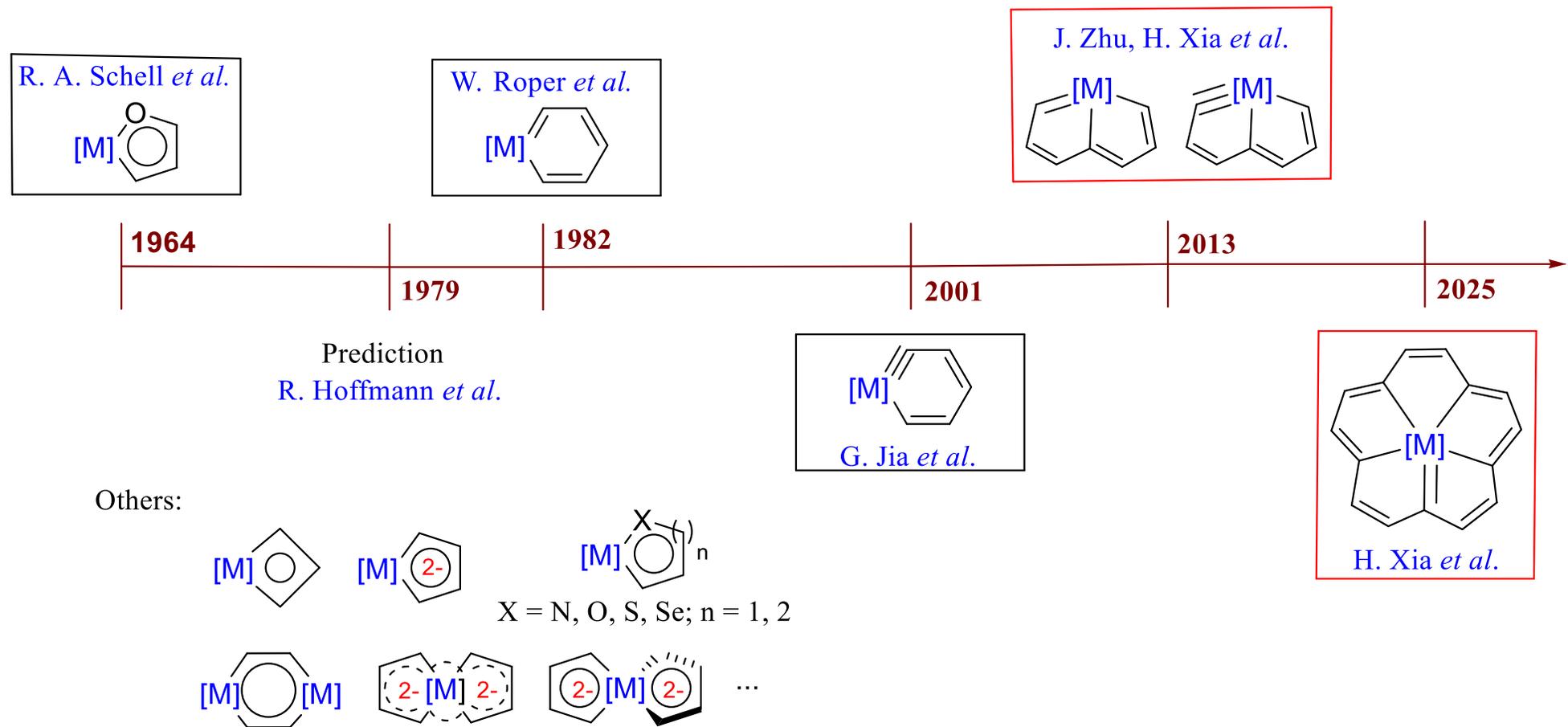
$d_{\pi}-p_{\pi}$ Conjugation



Phase Inversion

Craig aromaticity

1.1 碳龙化学发展





1.2 芳香性判定—常见实验判据

➤ 平面性

芳香性化合物往往相较于非芳香及反芳香化合物具有更好的平面性。

➤ 键长平均化

由于芳香环中存在显著的共轭作用，环上的每个单键或双键的键长将趋于均衡，表现为键长平均化。

➤ NMR化学位移（环电流）

在外部磁场作用下，芳香环上的环电流将在环外产生去屏蔽区，使得环外原子的NMR信号产生向低场的化学位移。

1.2 芳香性判定—常见理论判据

➤ 共轭电子数

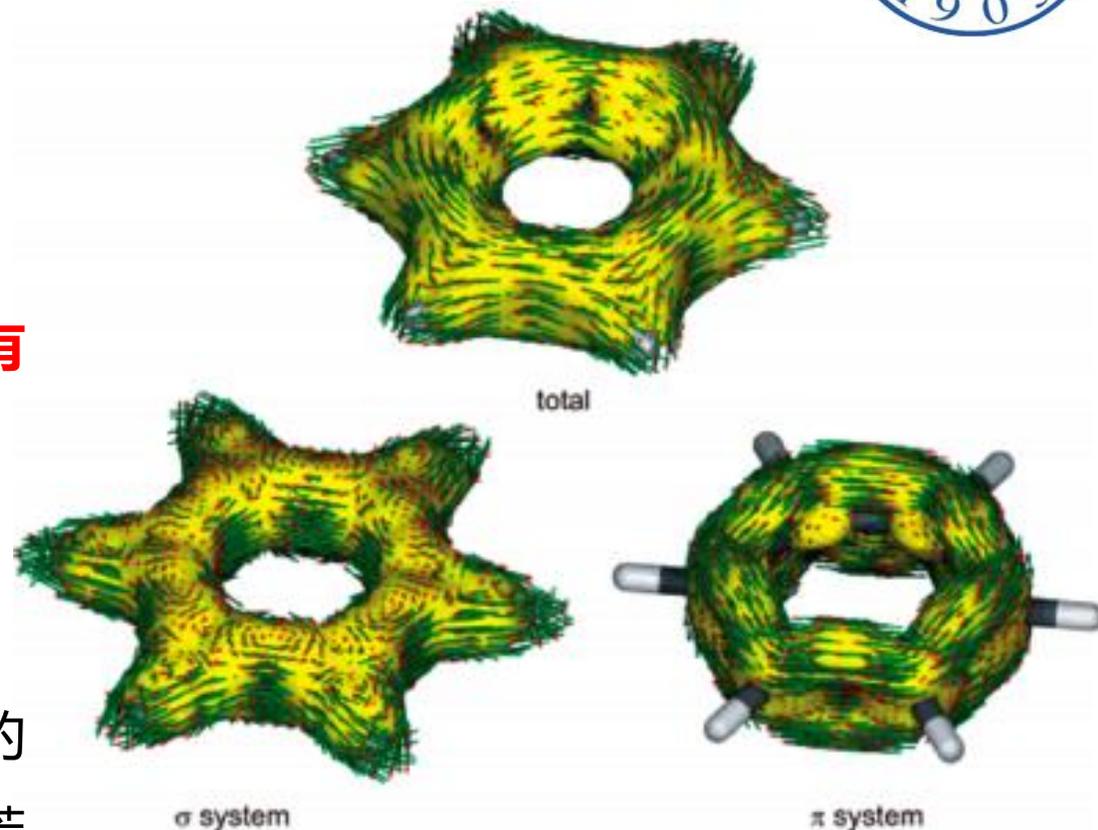
Hückel体系 $[4n+2]$ 及Möbius体系 $[4n]$ 电子判据。

➤ 核独立化学位移 (NICS)

芳香环平面中心点处磁屏蔽值的负值，**负值表明分子具有芳香性，正值则表示反芳香性，零表示非芳香性。**

➤ 感应电流密度各向异性 (AICD)

感应电流密度是一个矢量场，通过绘制特定轨道截面上的**电流密度二维矢量图**，可以可视化地定性判断化合物的芳香性。



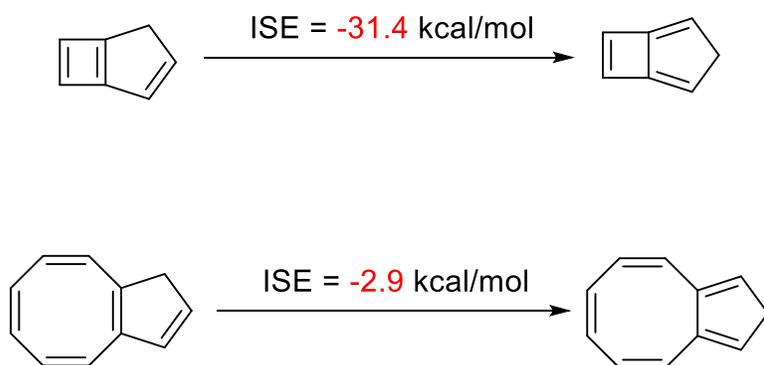
苯分子的AICD等值面

1.2 芳香性判定—常见理论判据

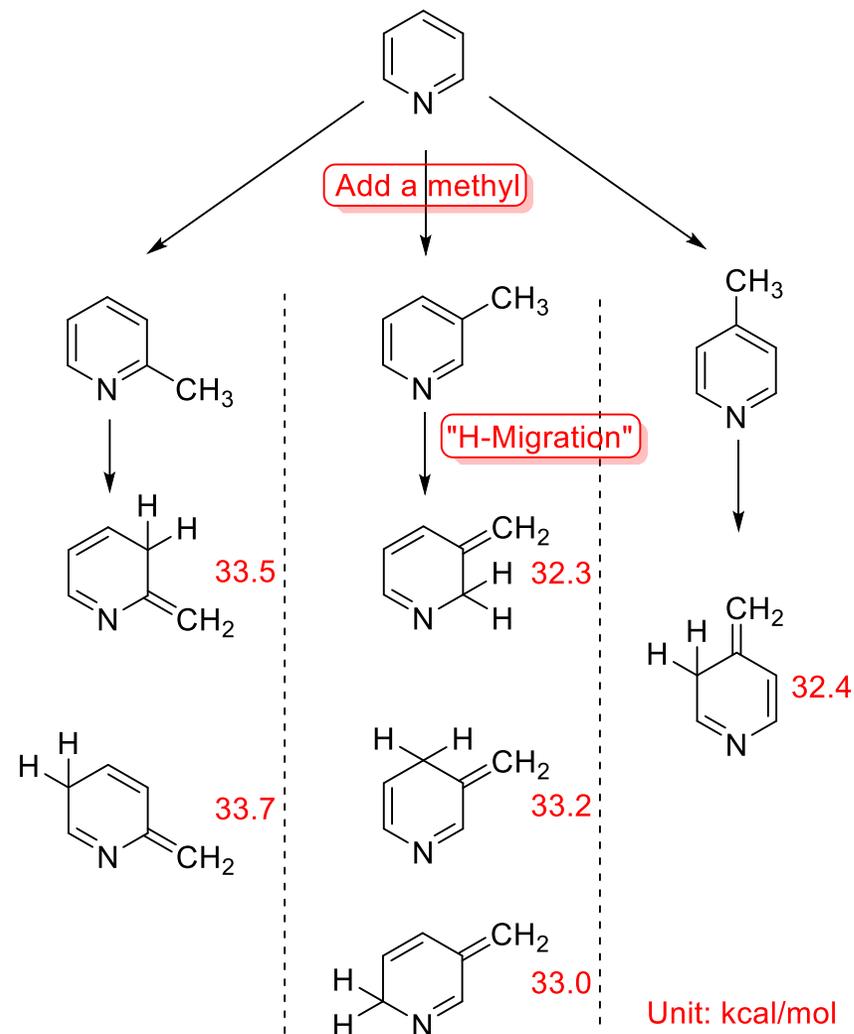
➤ 异构稳定化能 (ISE)

构建芳环与其去芳构化异构体之间的假想等键反应，
 计算得到的反应能量称为异构稳定化能 (ISE)，该能量差可被视为芳香性的贡献。

茚-异茚异构法:



甲基-亚甲基异构法:



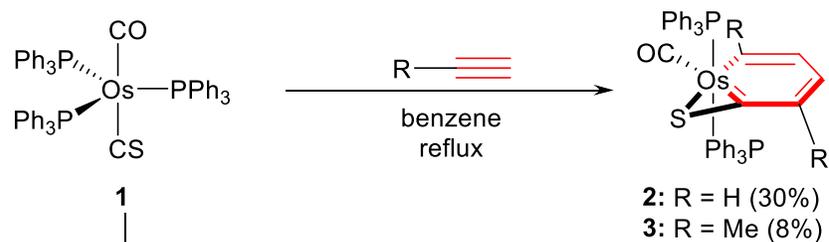
一. 背景介绍

二. 简单金属杂芳烃构筑

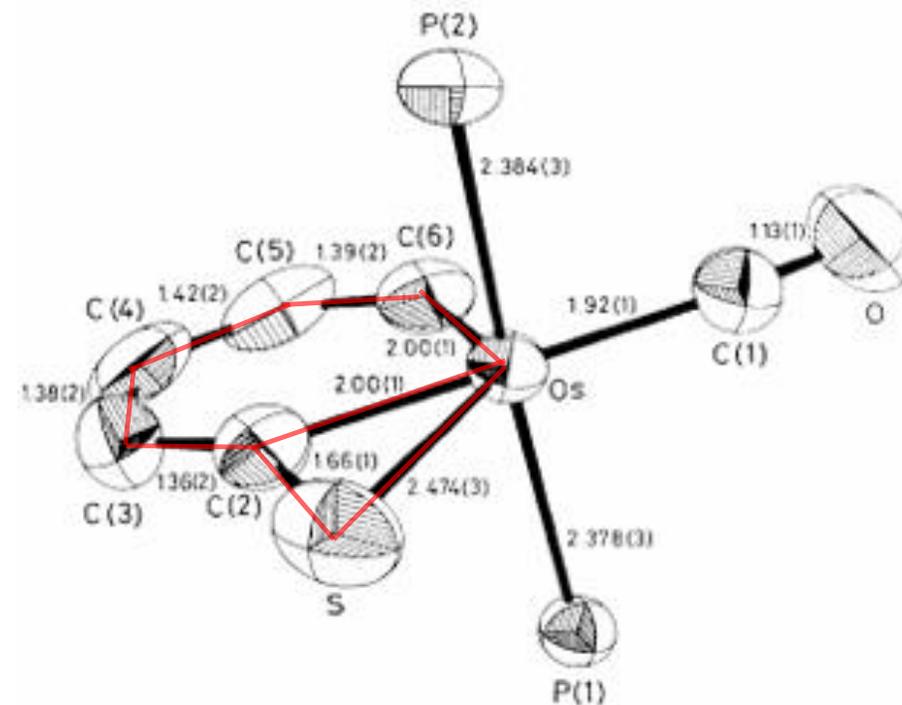
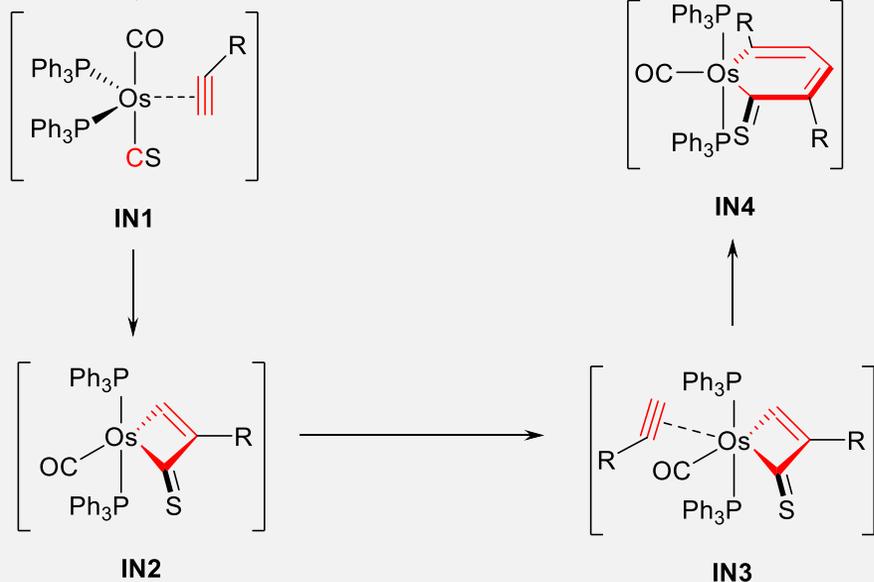
三. 碳龙骨架构筑及反应性

四. 总结与展望

2.1 简单金属杂芳烃构筑—钌苯



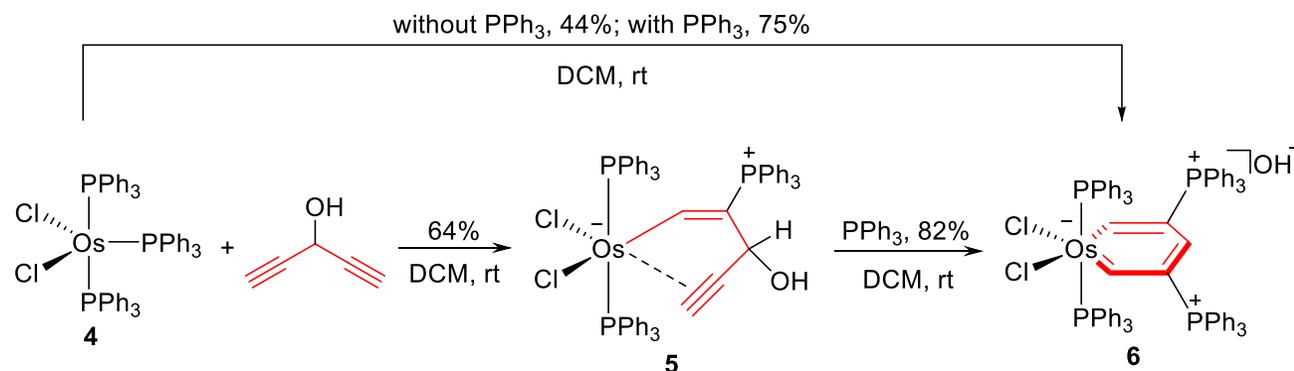
Mechanism:



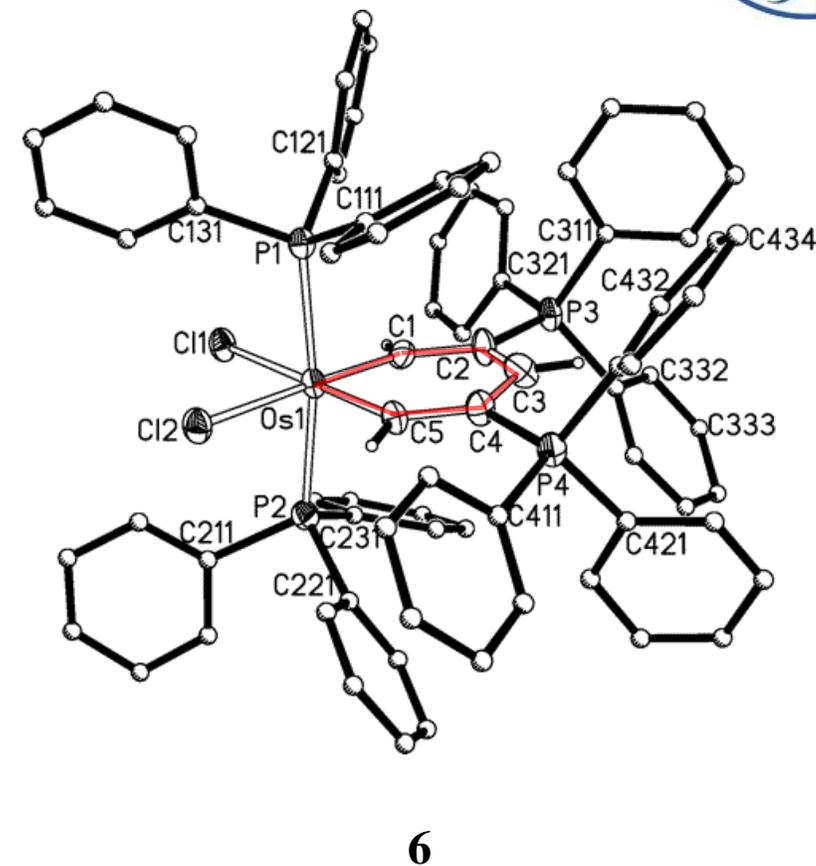
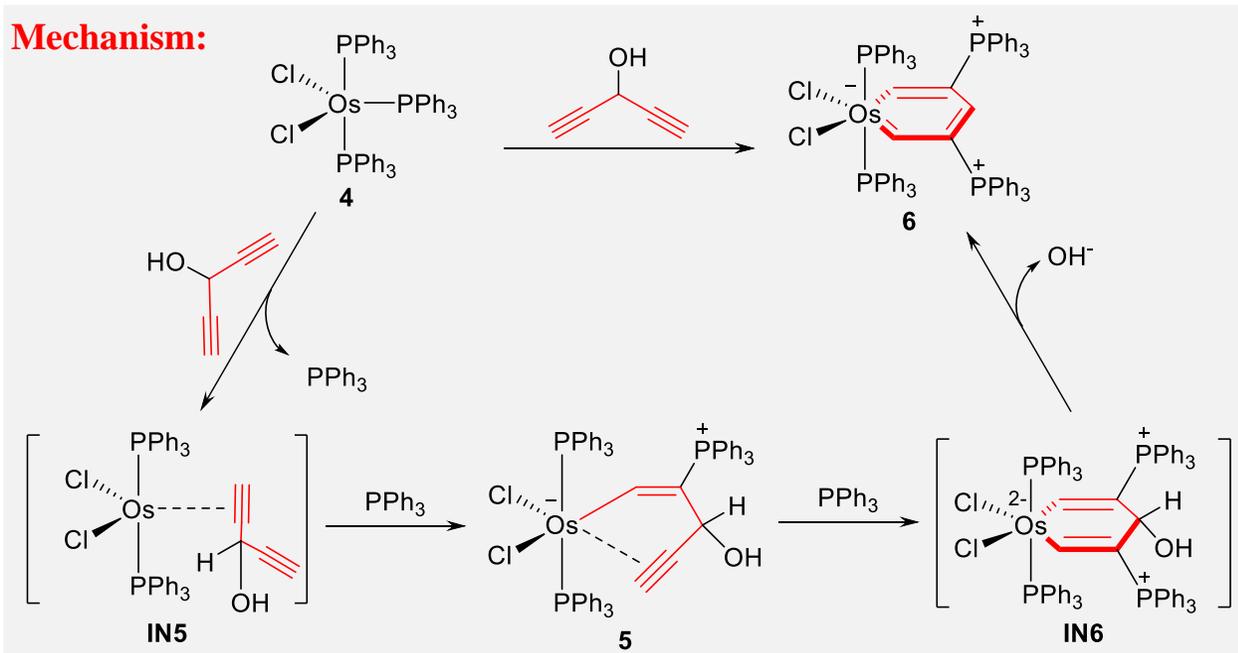
2

碳碳单键: 1.54 Å
 碳碳双键: 1.34 Å
 苯环内碳碳键: 1.40 Å

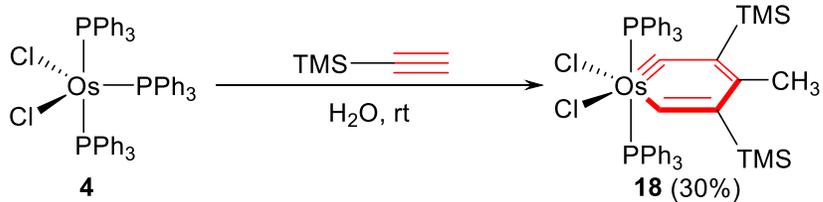
2.1 简单金属杂芳烃构筑—钌苯



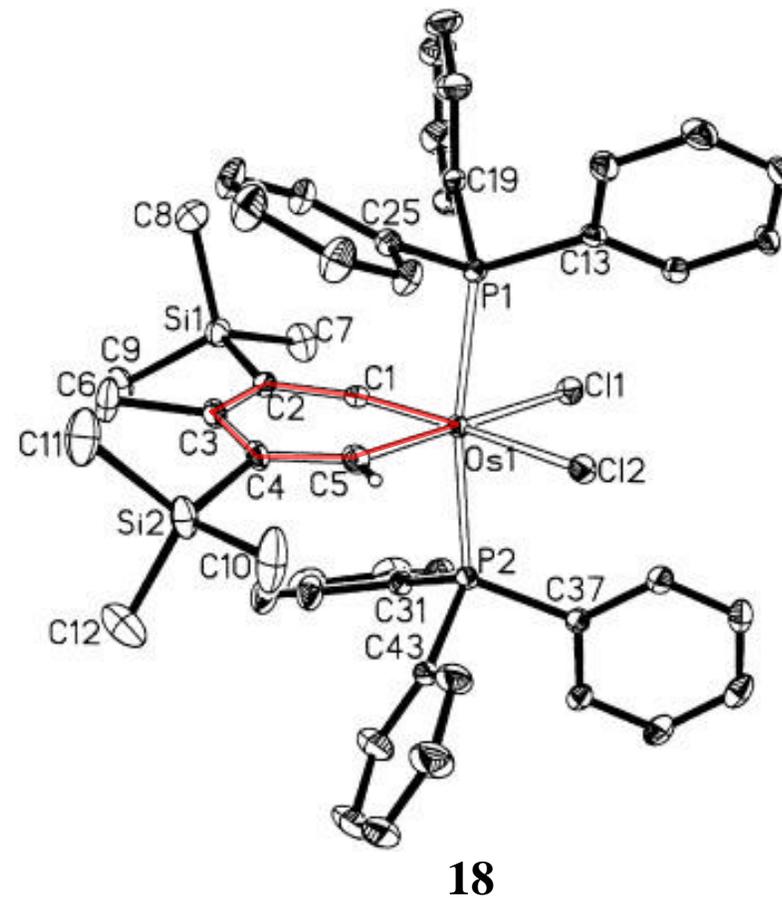
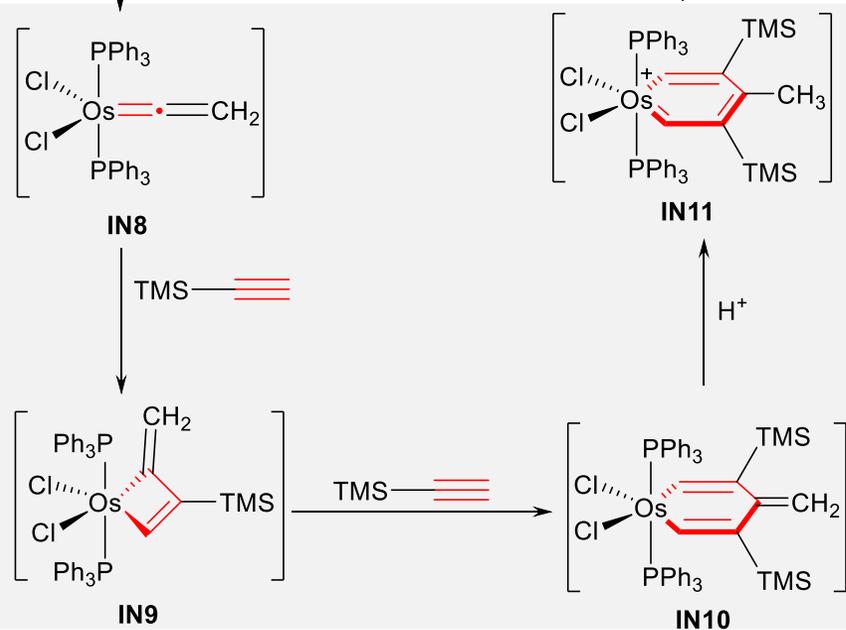
Mechanism:



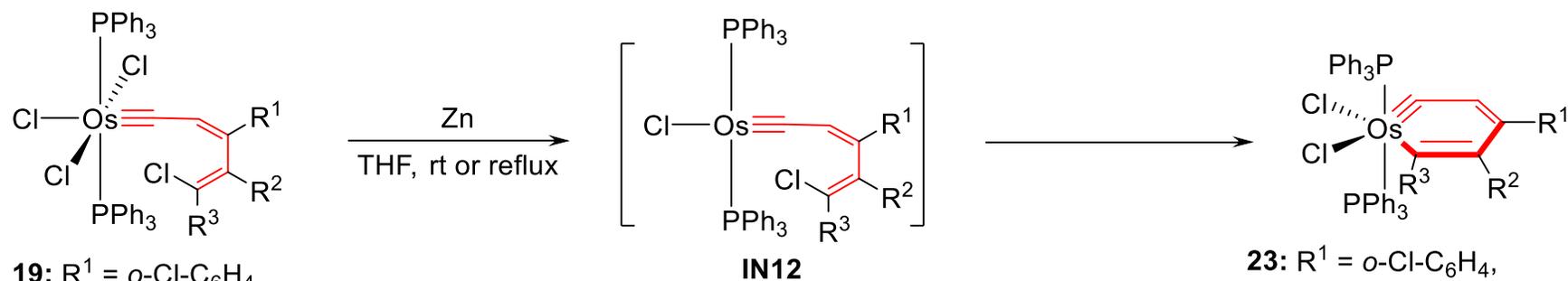
2.2 简单金属杂芳烃构筑—钌苯炔



Mechanism:



2.2 简单金属杂芳烃构筑—钌苯炔



19: $R^1 = o\text{-Cl-C}_6\text{H}_4$,

$R^2, R^3 = \text{CH=CH-CH=CH}$

20: $R^1 = t\text{-Bu}, R^2 = R^3 = \text{H}$

21: $R^1 = t\text{-Bu}, R^2 = \text{H}, R^3 = n\text{-pentyl}$

22: $R^1 = 1\text{-adamantyl}, R^2 = R^3 = \text{H}$

23: $R^1 = o\text{-Cl-C}_6\text{H}_4$,

$R^2, R^3 = \text{CH=CH-CH=CH}$ (25%)

24: $R^1 = t\text{-Bu}, R^2 = R^3 = \text{H}$ (NMR detection)

25: $R^1 = t\text{-Bu}, R^2 = \text{H}, R^3 = n\text{-pentyl}$ (62%)

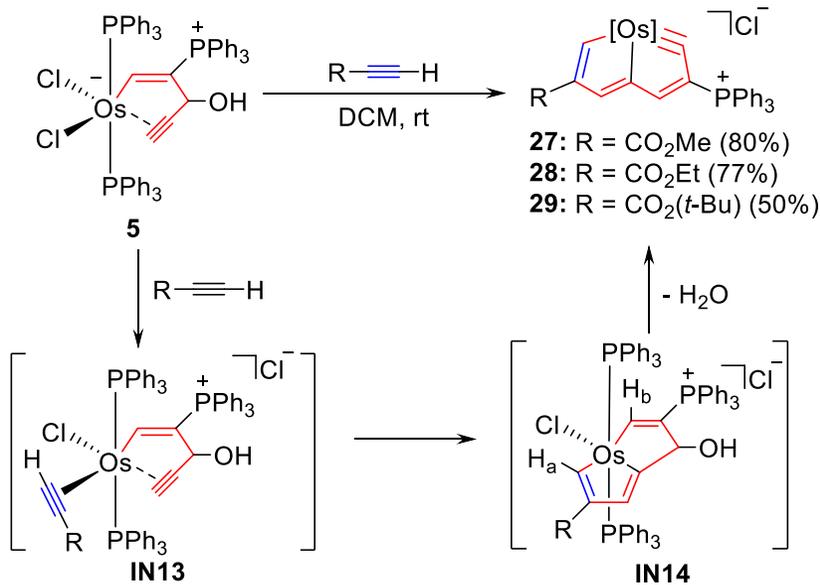
26: $R^1 = 1\text{-adamantyl}, R^2 = R^3 = \text{H}$

(NMR detection)

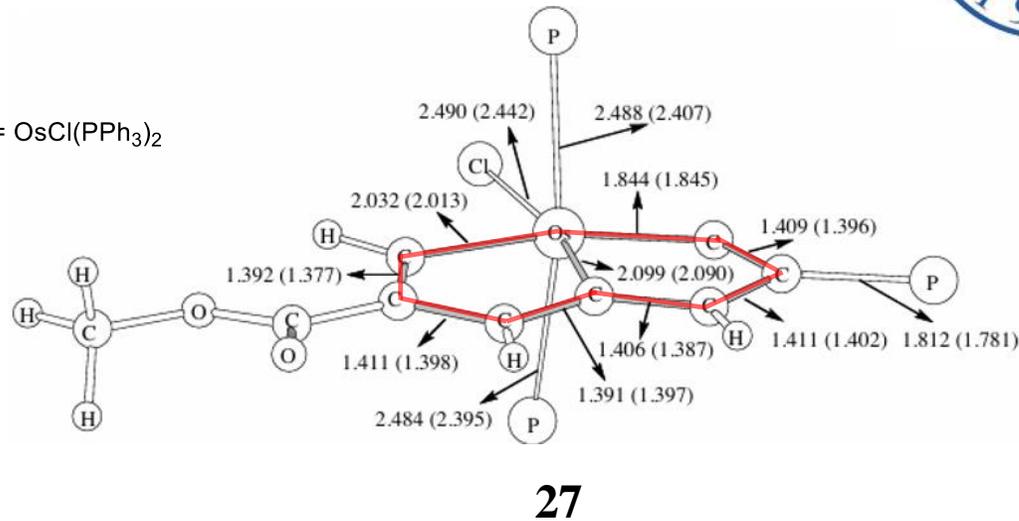
- 一. 背景介绍
- 二. 简单金属杂芳烃构筑
- 三. 碳龙骨架构筑及反应性
- 四. 总结与展望

3.1 7C碳龙-骨架构筑

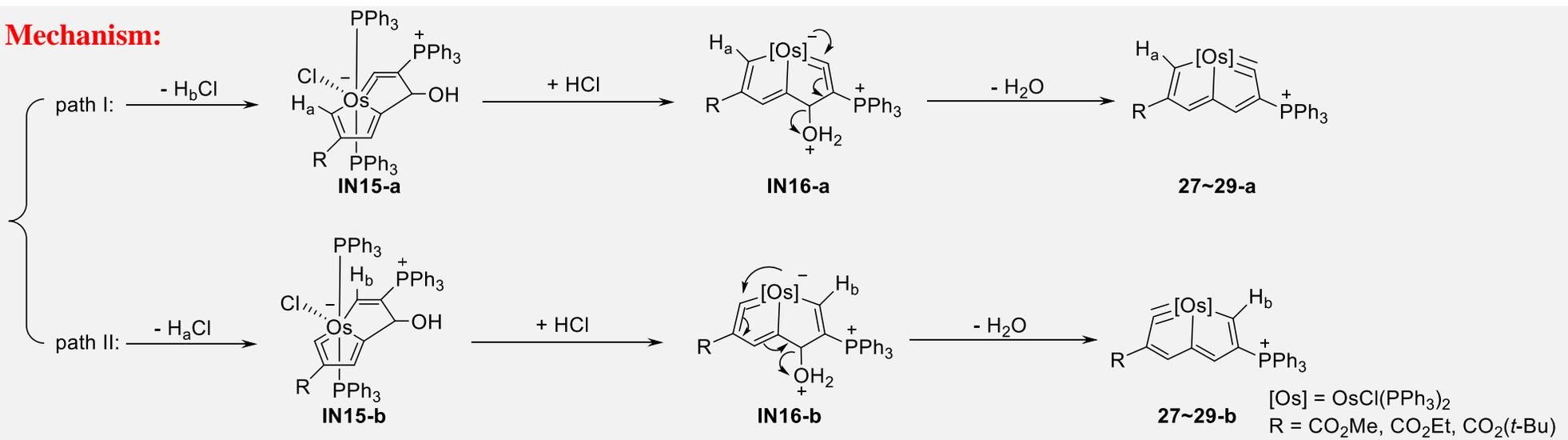
"5+2"



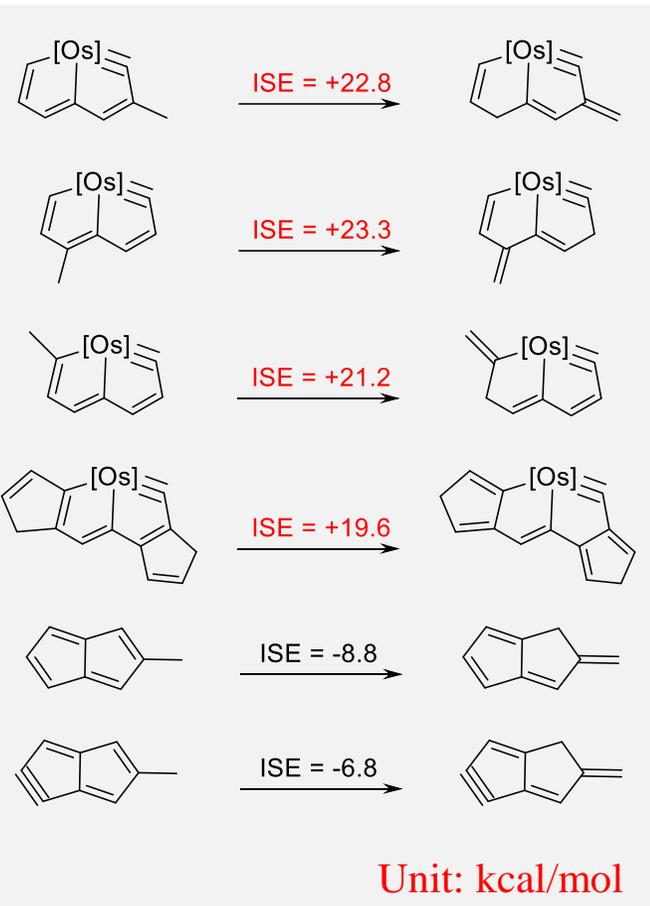
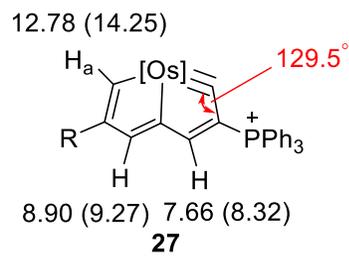
[Os] = OsCl(PPh₃)₂



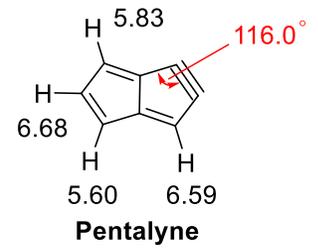
Mechanism:



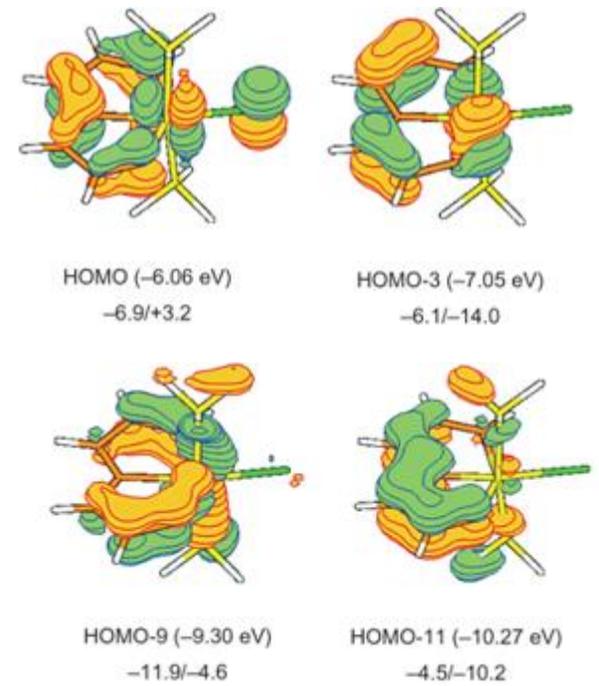
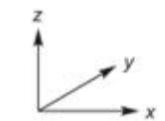
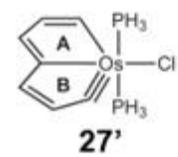
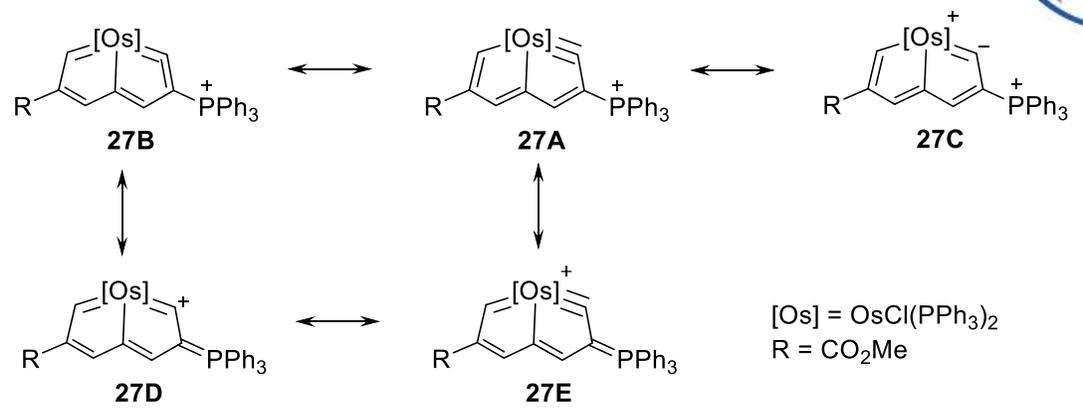
3.1 7C碳龙-骨架构筑



戊搭炔及钺杂戊搭炔ISE值计算



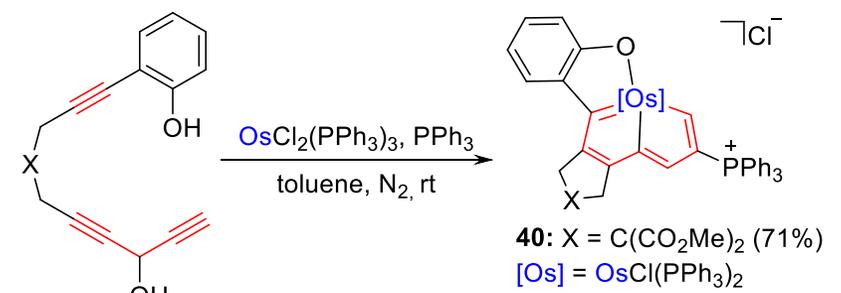
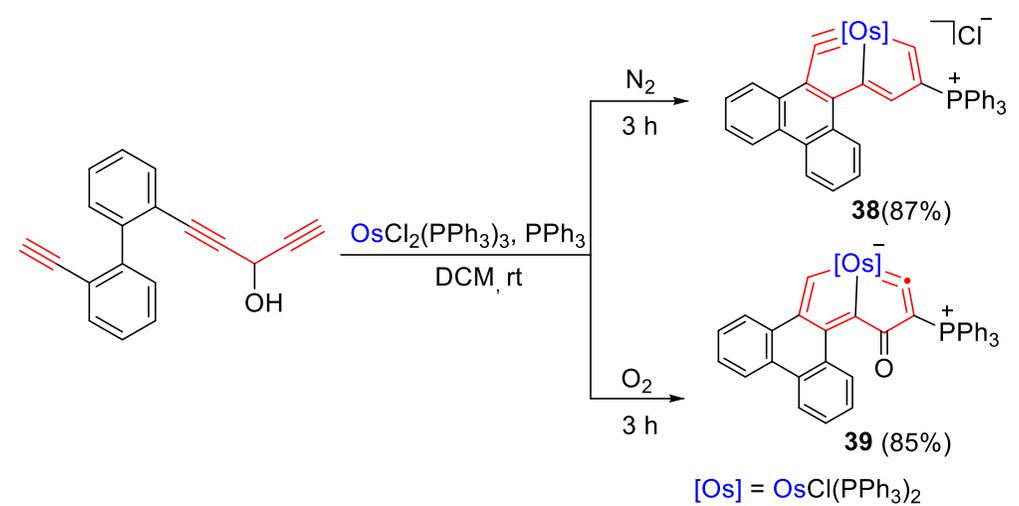
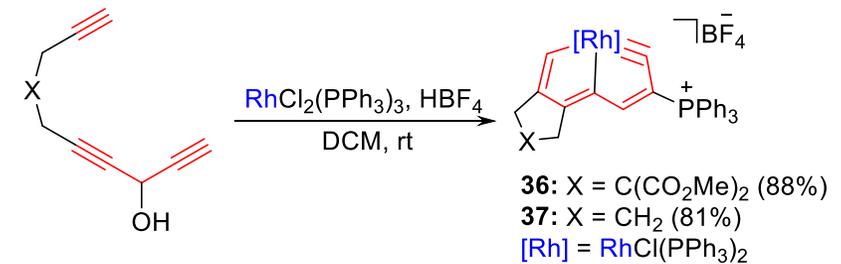
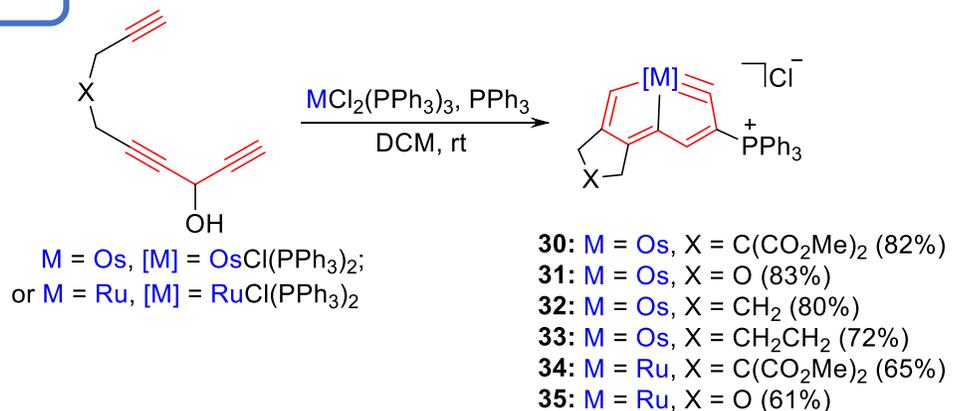
钺杂戊搭炔**49**共振式:



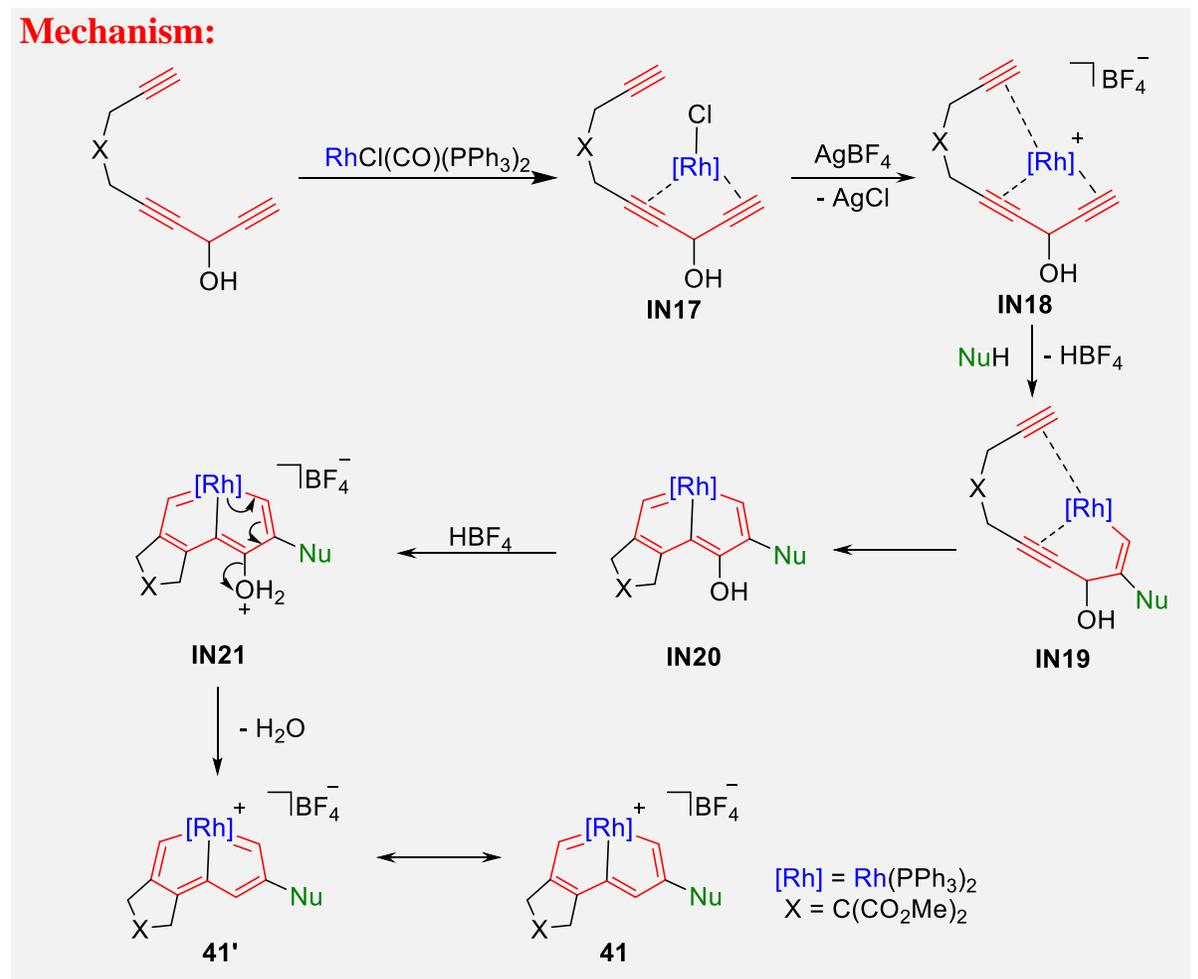
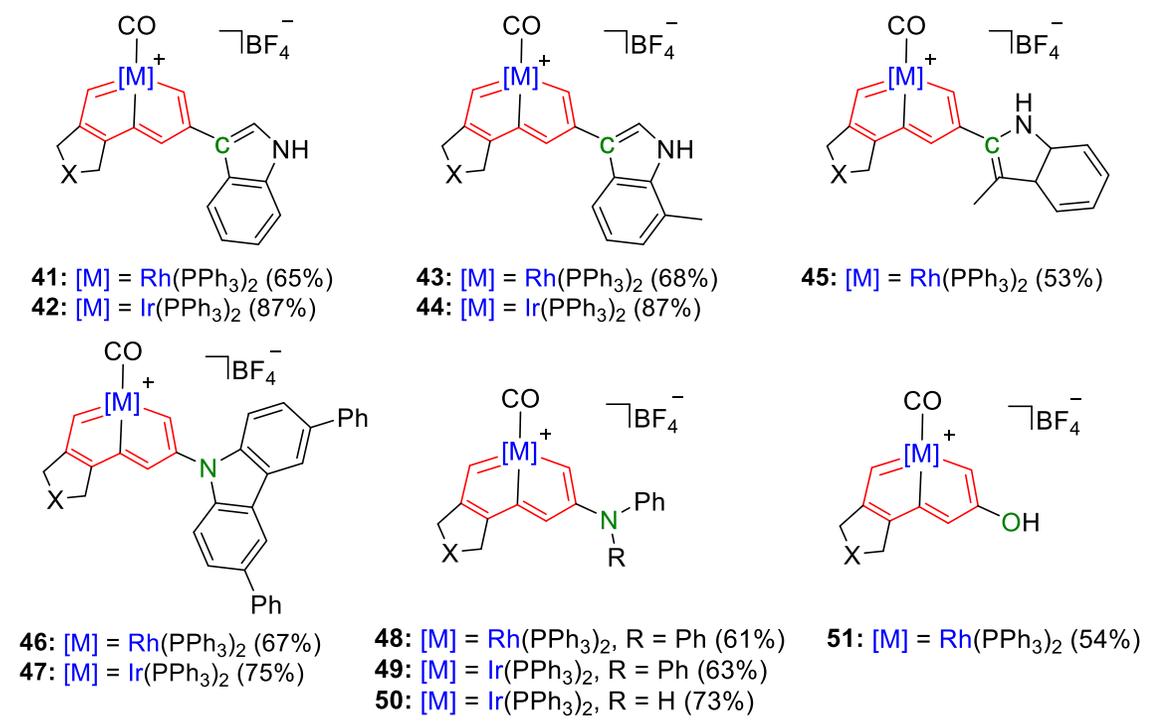
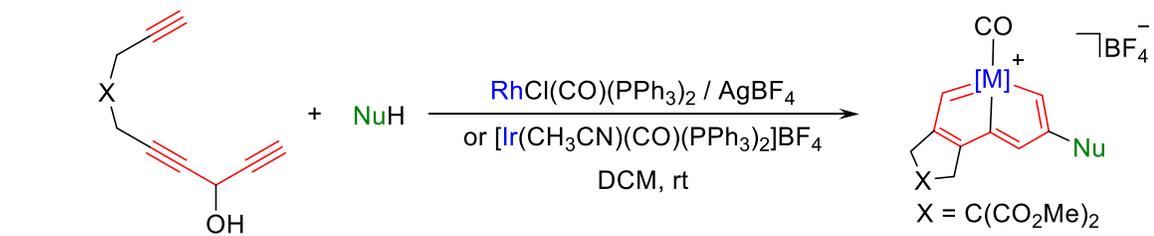
钺杂戊搭炔**27'**的π对称性前线轨道及相应NICS值 (ppm)

3.1 7C碳龙-骨架构筑

"One-Pot"

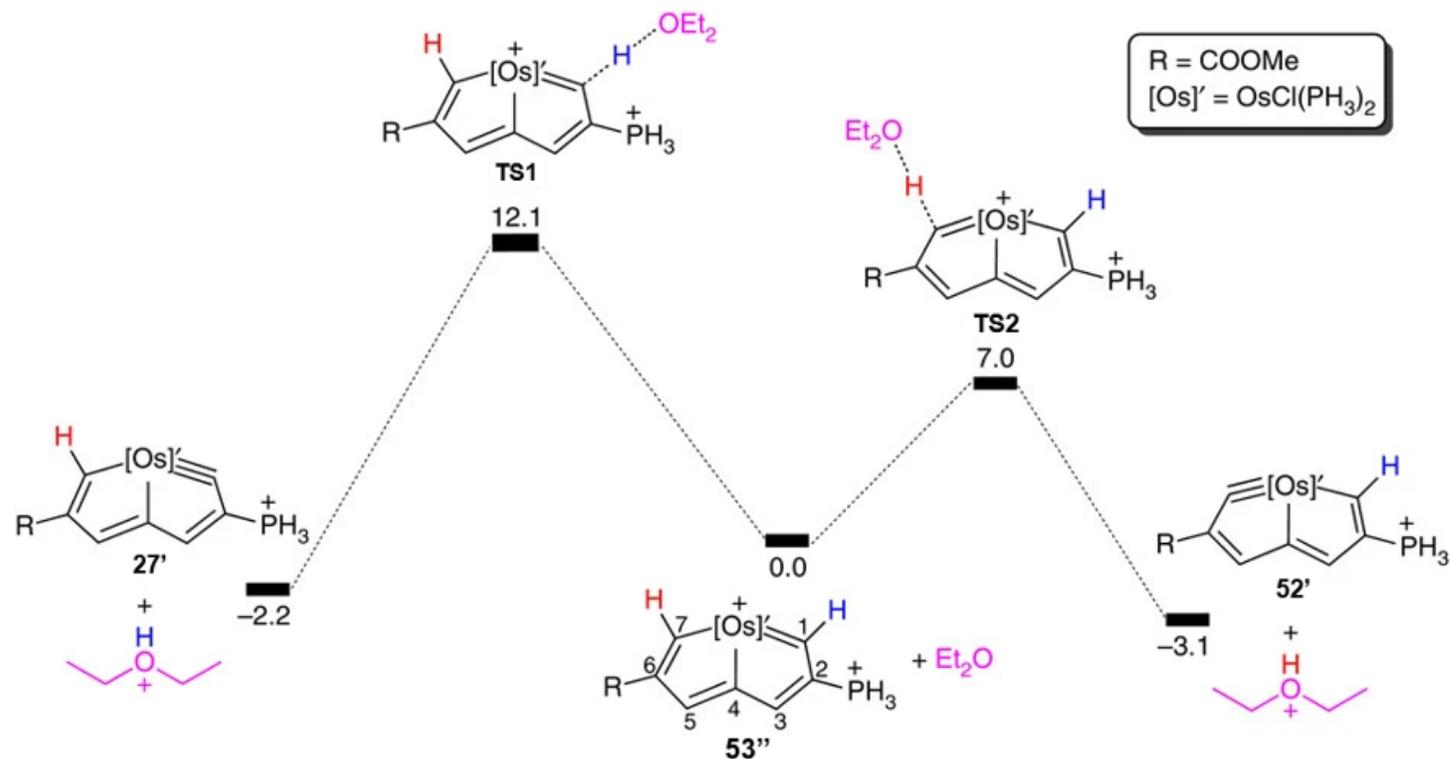
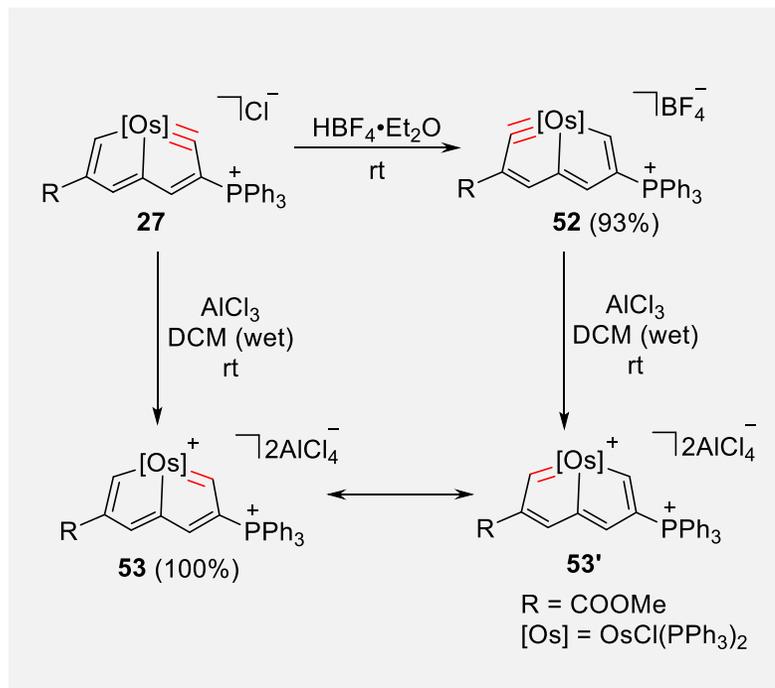


3.1 7C碳龙-骨架构筑

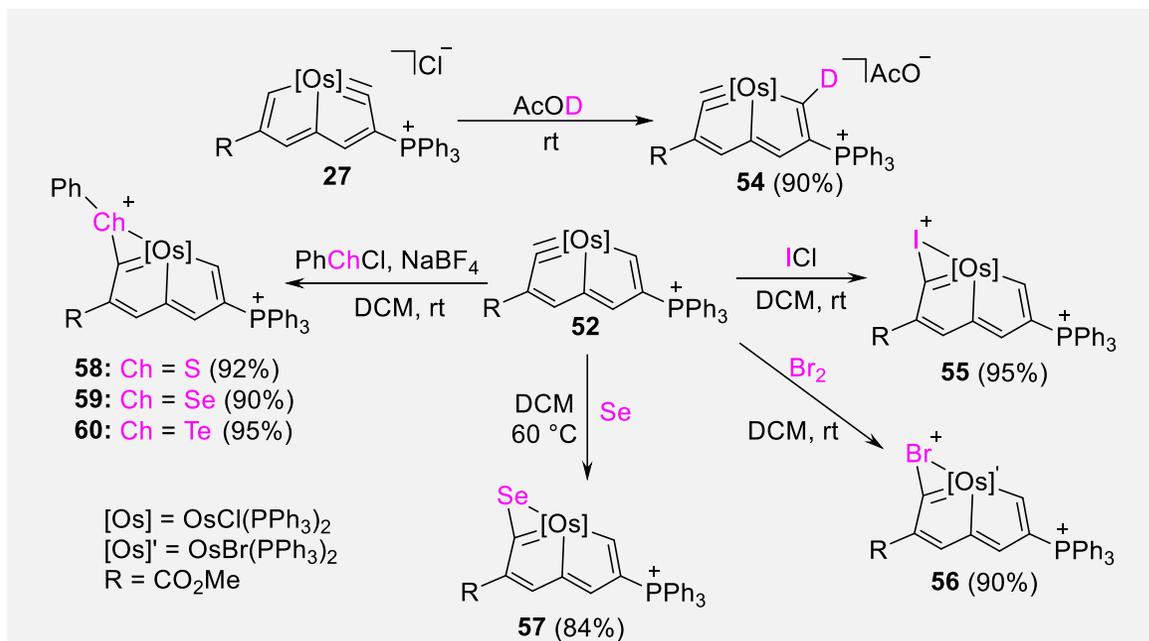


3.1 7C碳龙-反应性

Mechanism:



3.1 7C碳龙-反应性



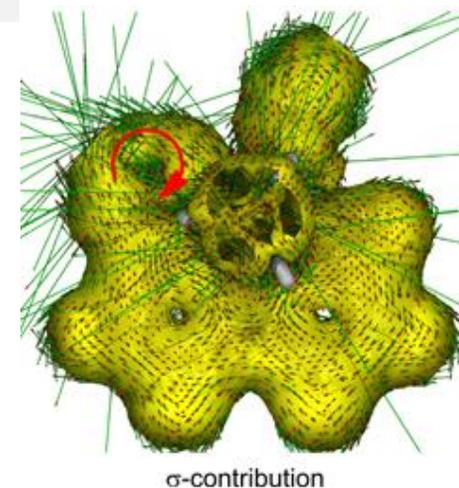
σ-Aromaticity

57'的前线轨道及相应NICS值 (ppm) :

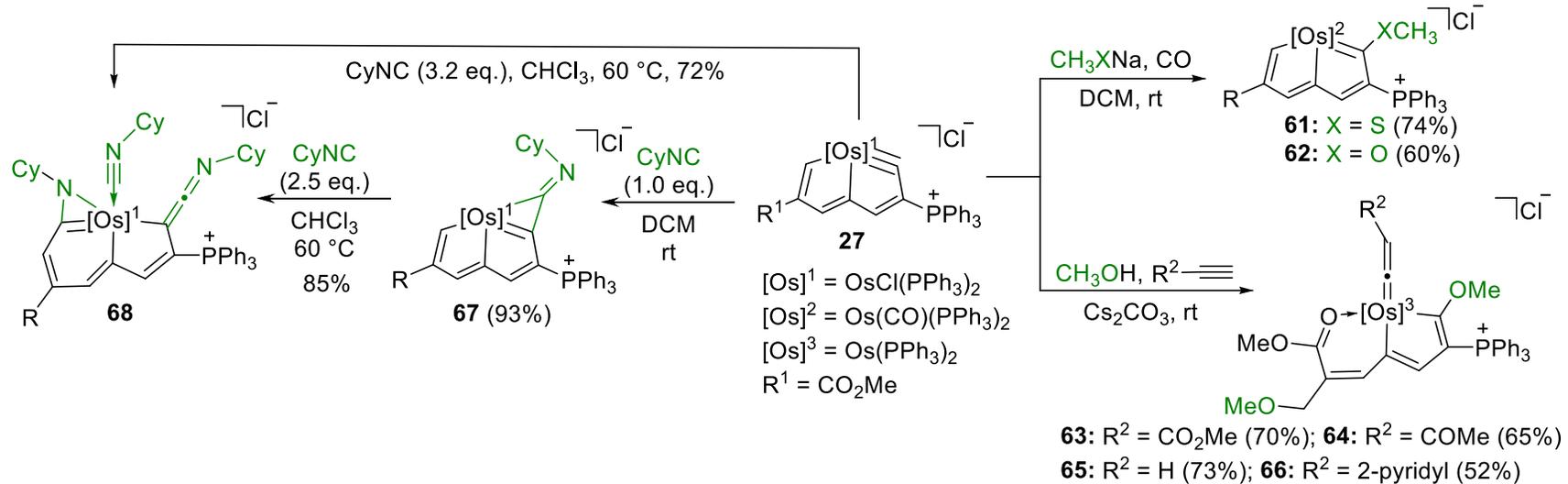


Orbitals	NICS(0)		
	a	b	c
HOMO HOMO-1			
HOMO-3 HOMO-4	-2.6	-3.4	-3.6
HOMO-11 HOMO-13			
All σ orbitals	-27.5	-6.7	-4.9
Total	-30.1	-10.1	-8.5

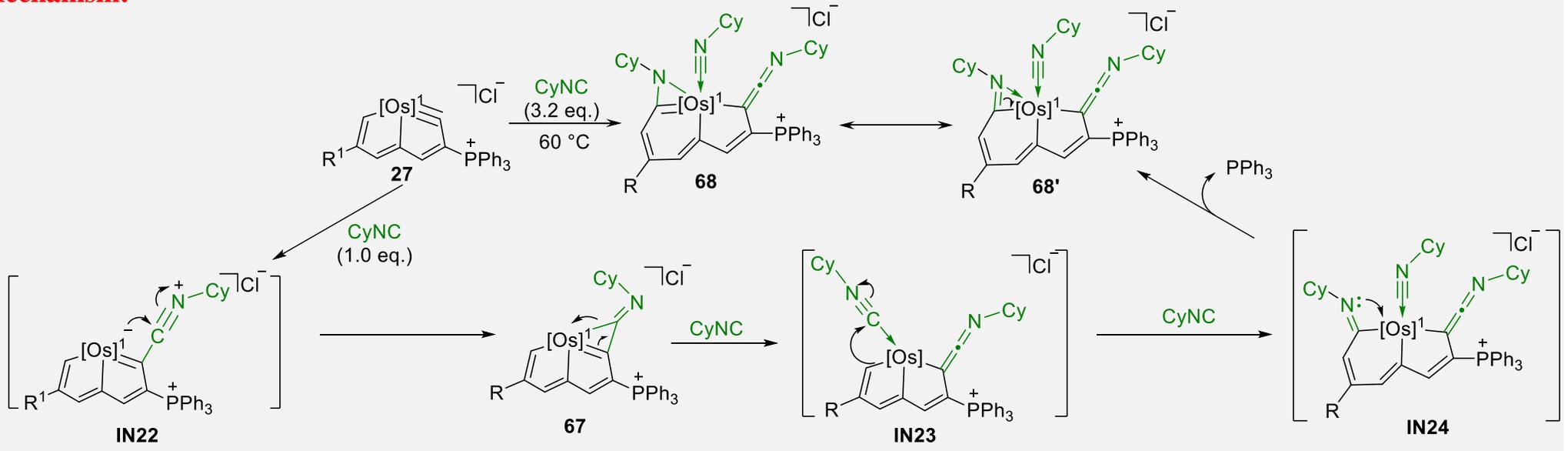
57的σ轨道AICD等值面:



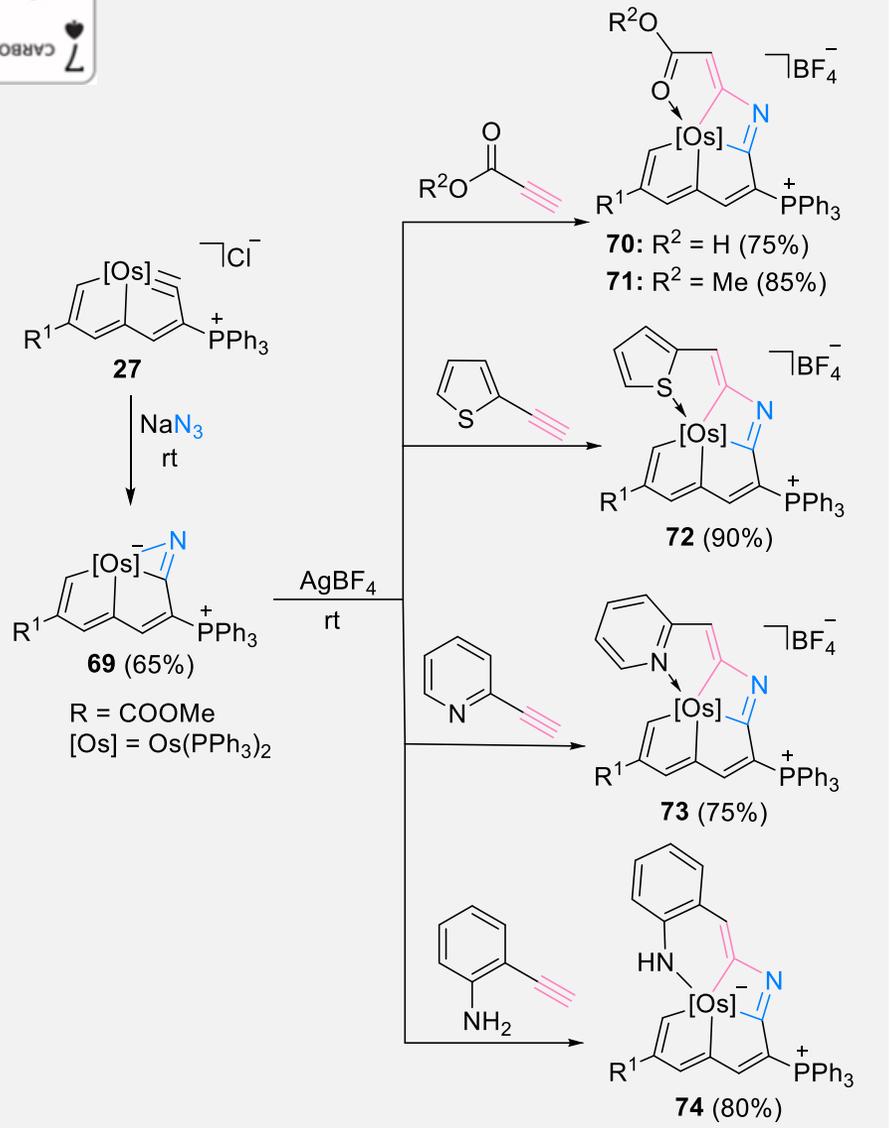
3.1 7C碳龙-反应性



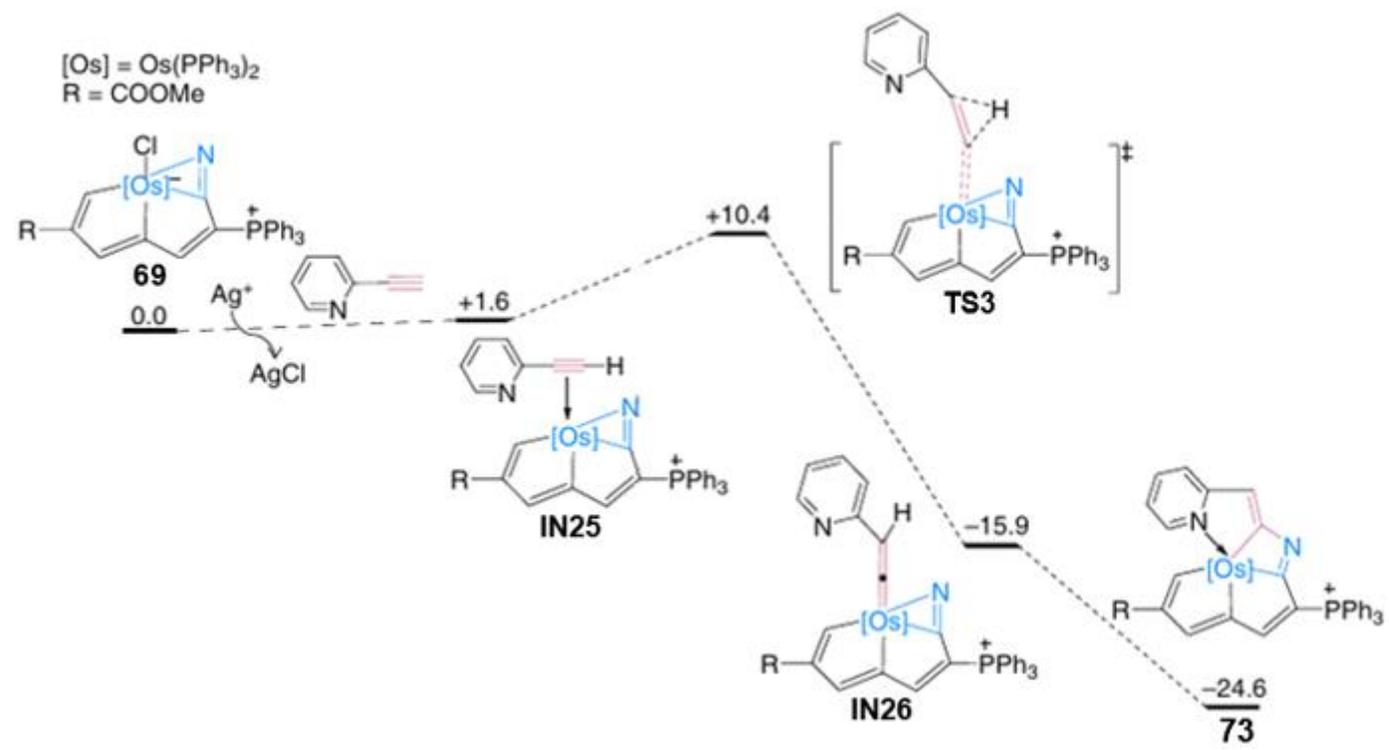
Mechanism:



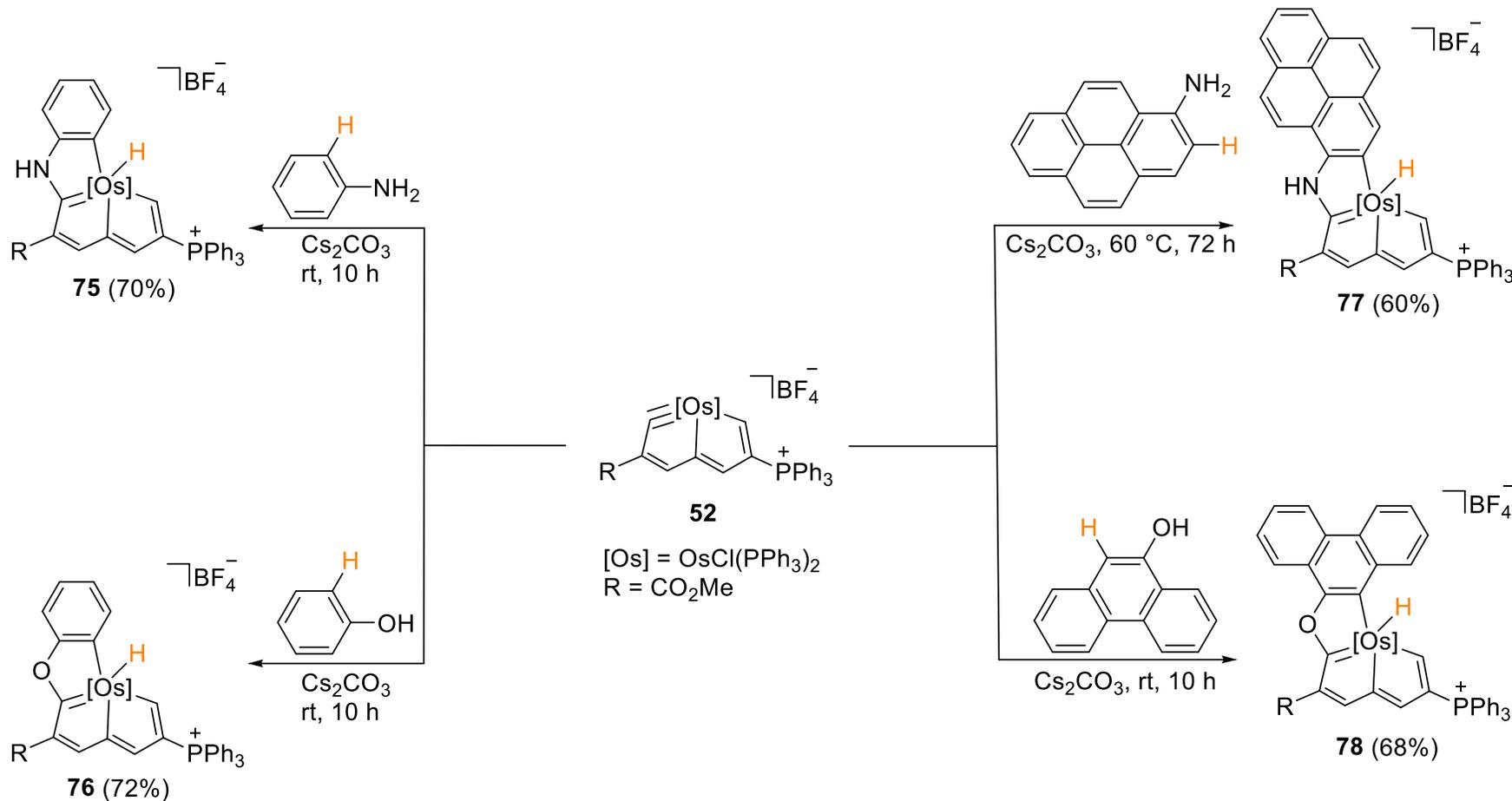
3.1 7C碳-反应性



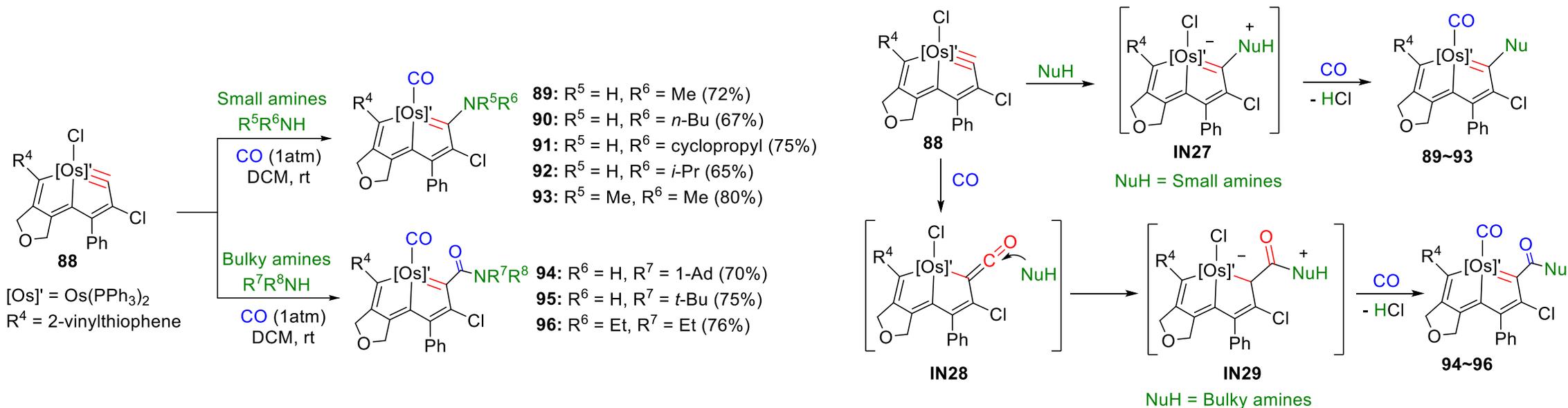
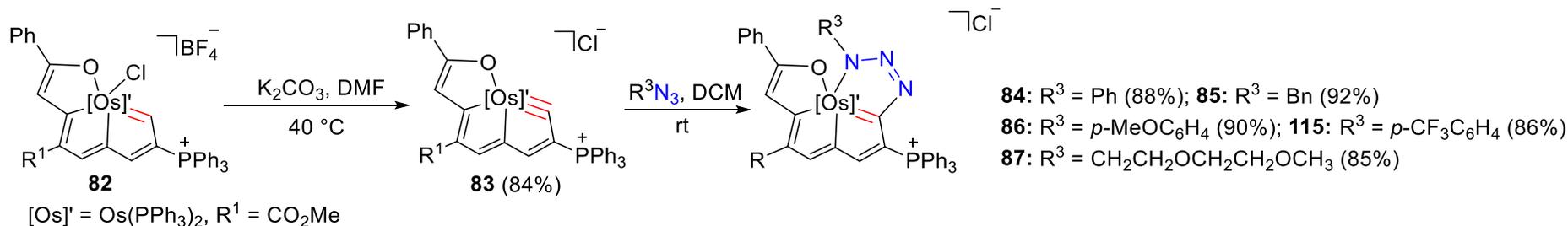
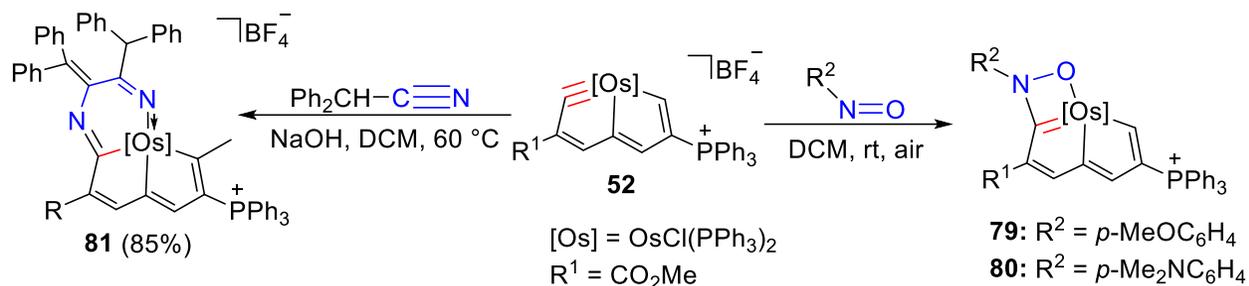
Mechanism:



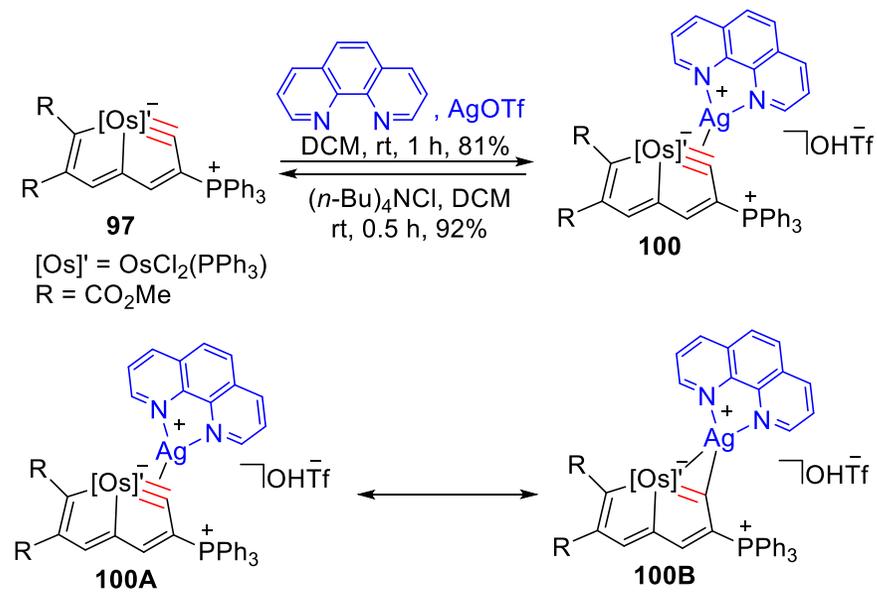
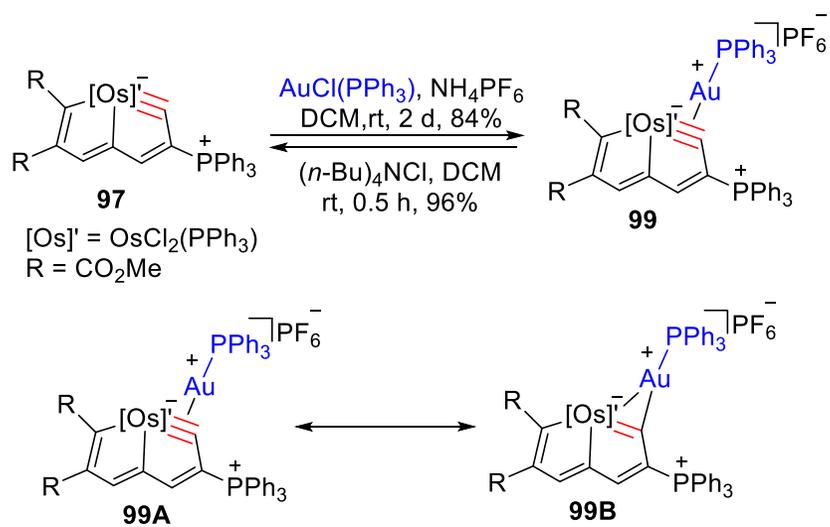
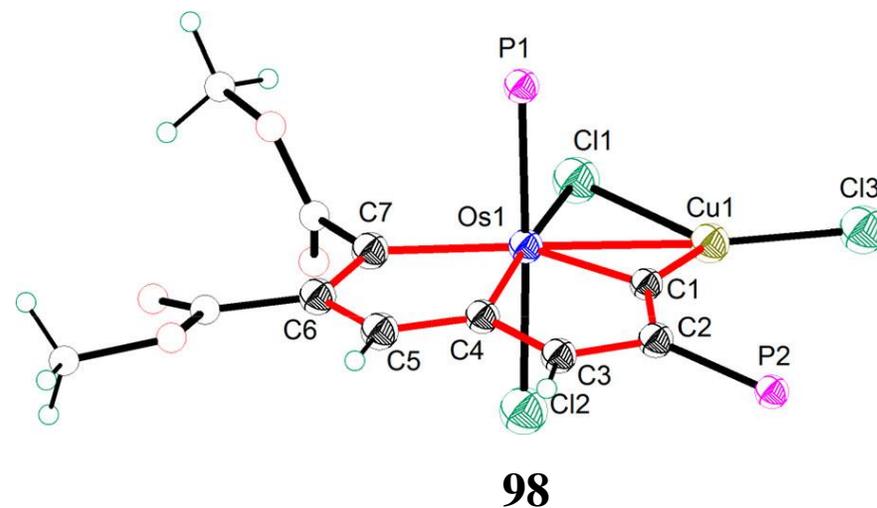
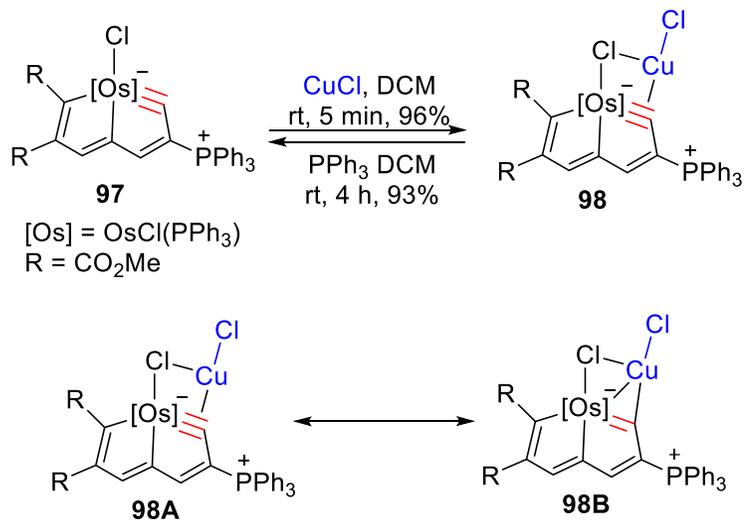
3.1 7C碳龙-反应性



3.1 7C碳龙-反应性

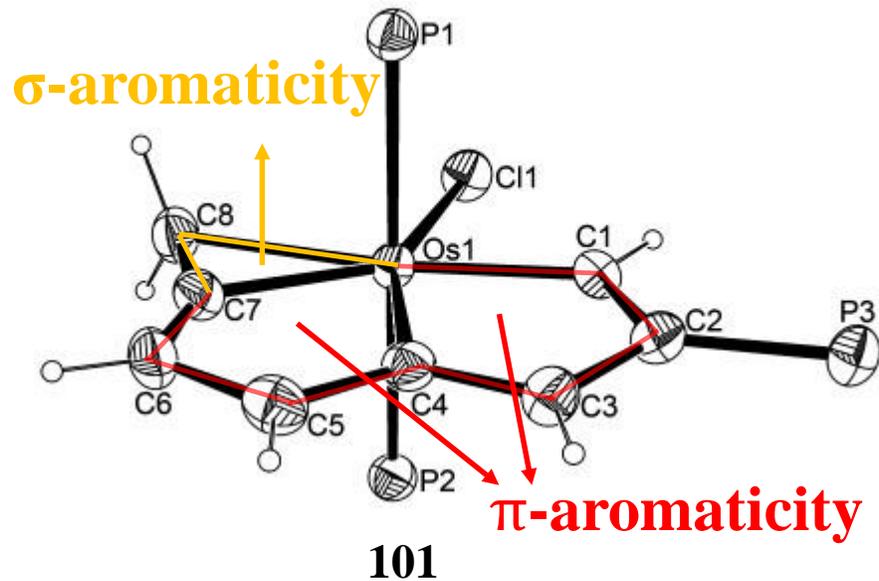
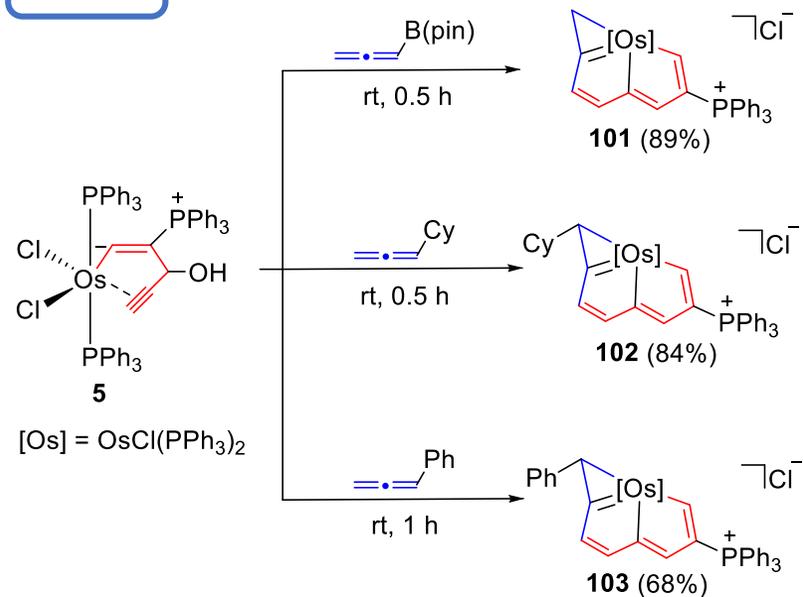


3.1 7C碳龙-反应性

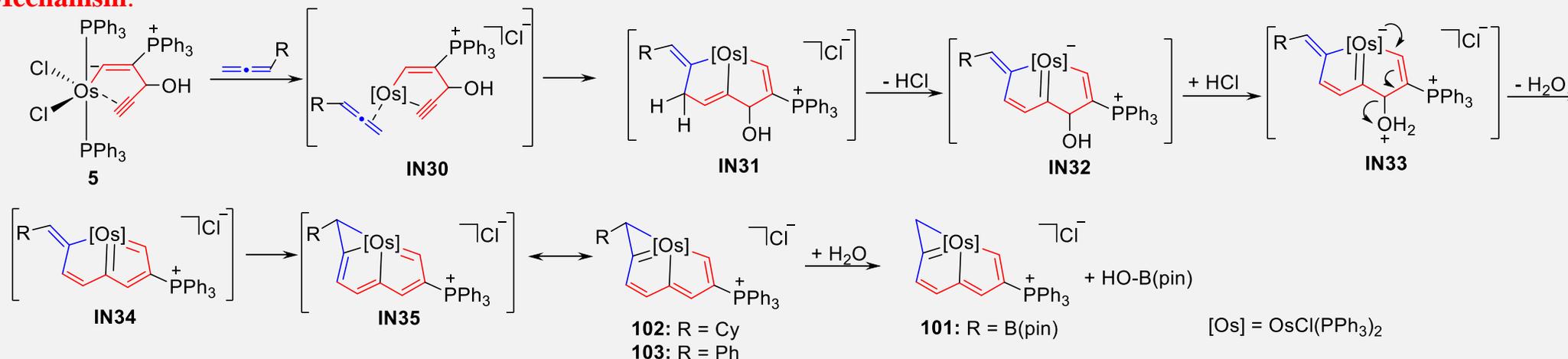


3.2 8C碳龙-骨架构筑

"5+3"

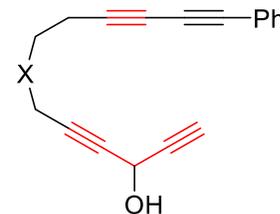
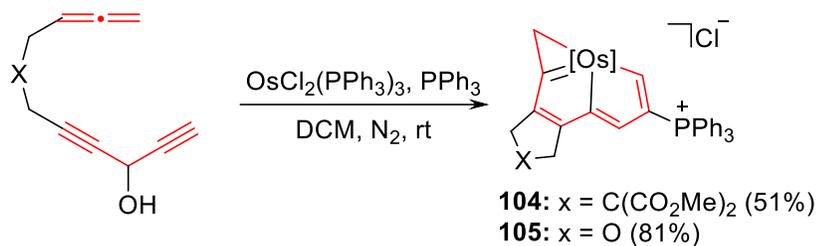


Mechanism:



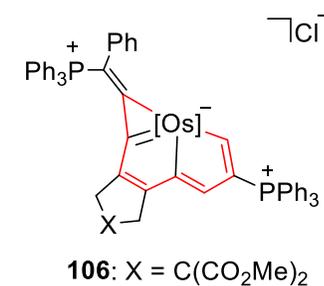
3.2 8C碳龙-骨架构筑

"One-Pot"

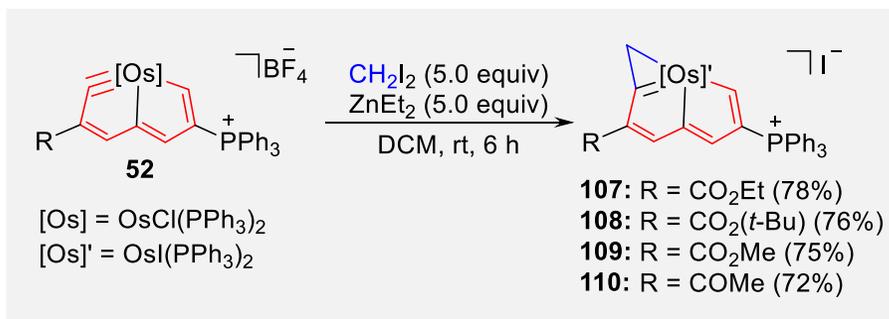


Method A:
 $OsCl_2(PPh_3)_3, PPh_3$
 HCl (aq), rt, air, 1 h
73%

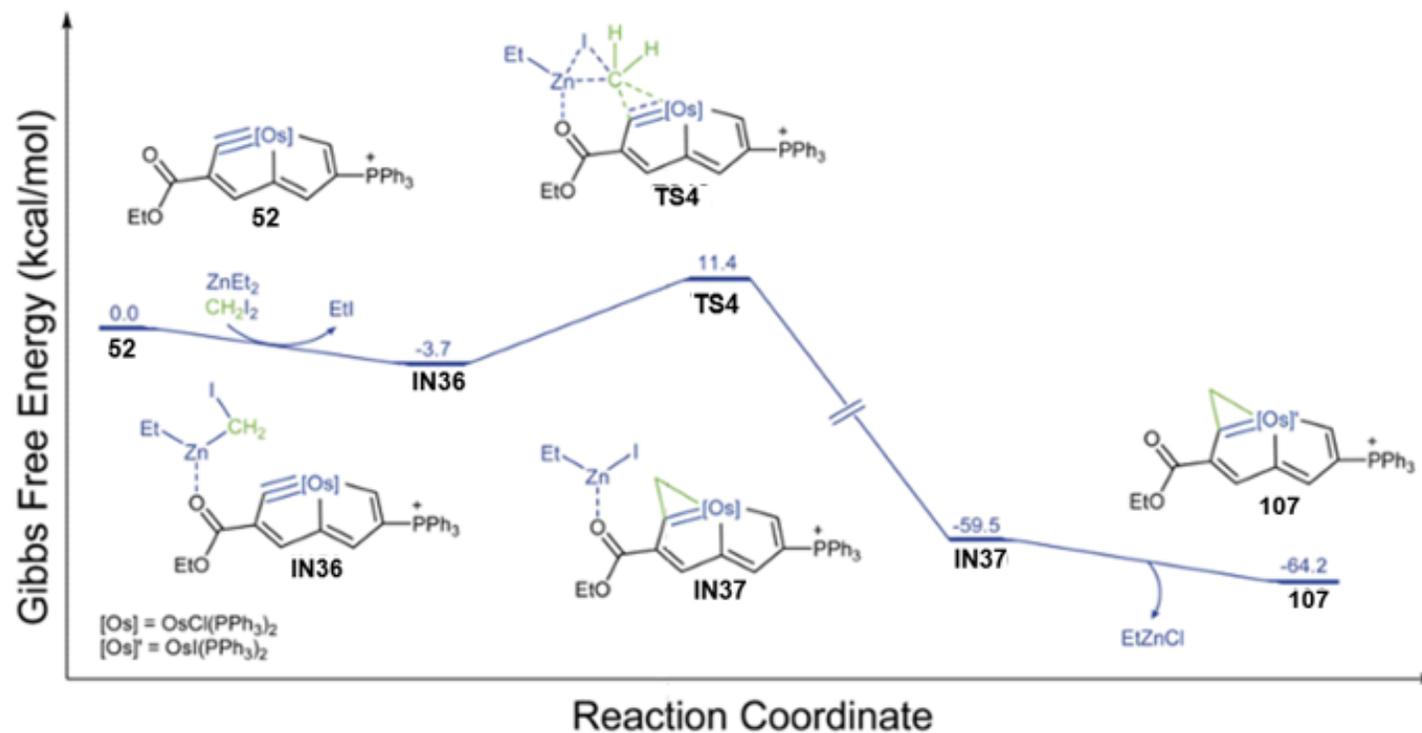
Method B:
 K_2OsCl_6, PPh_3
 $80^\circ C$, air, 4 h
47%



"7+1"

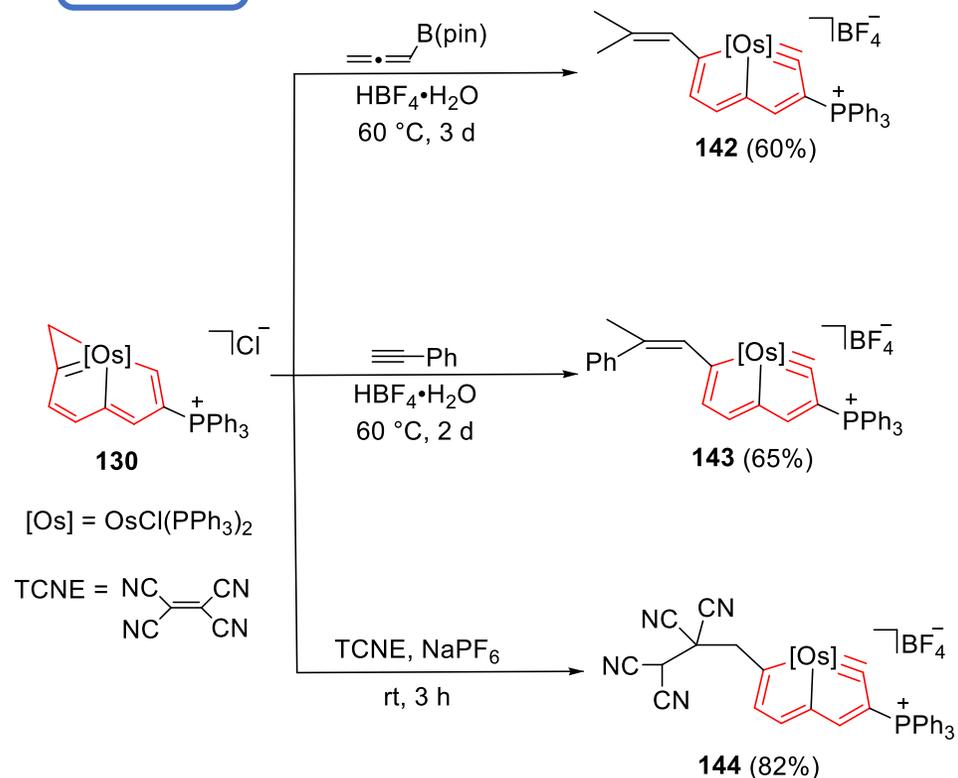


Mechanism:

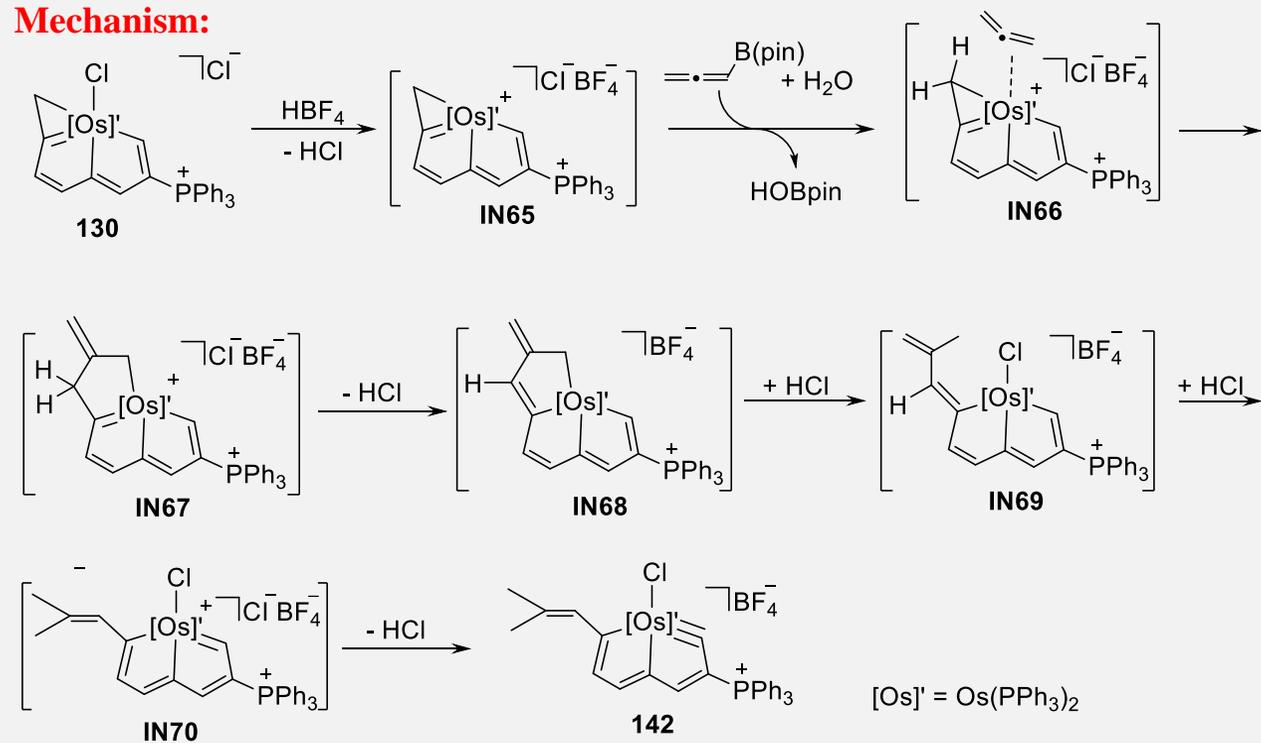


3.2 8C碳龙-反应性

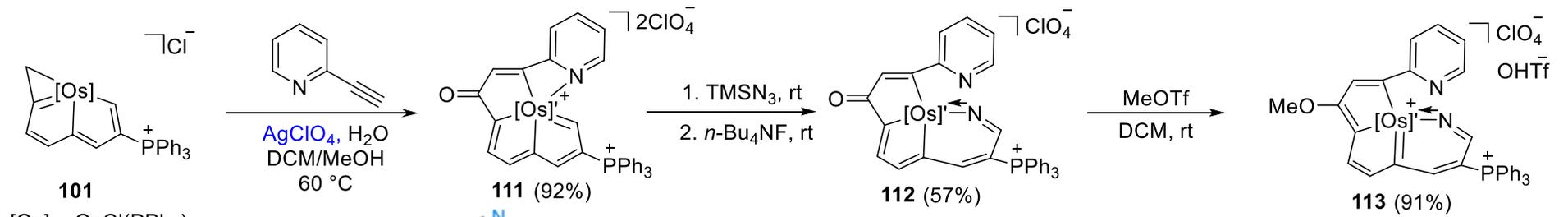
"8-1"



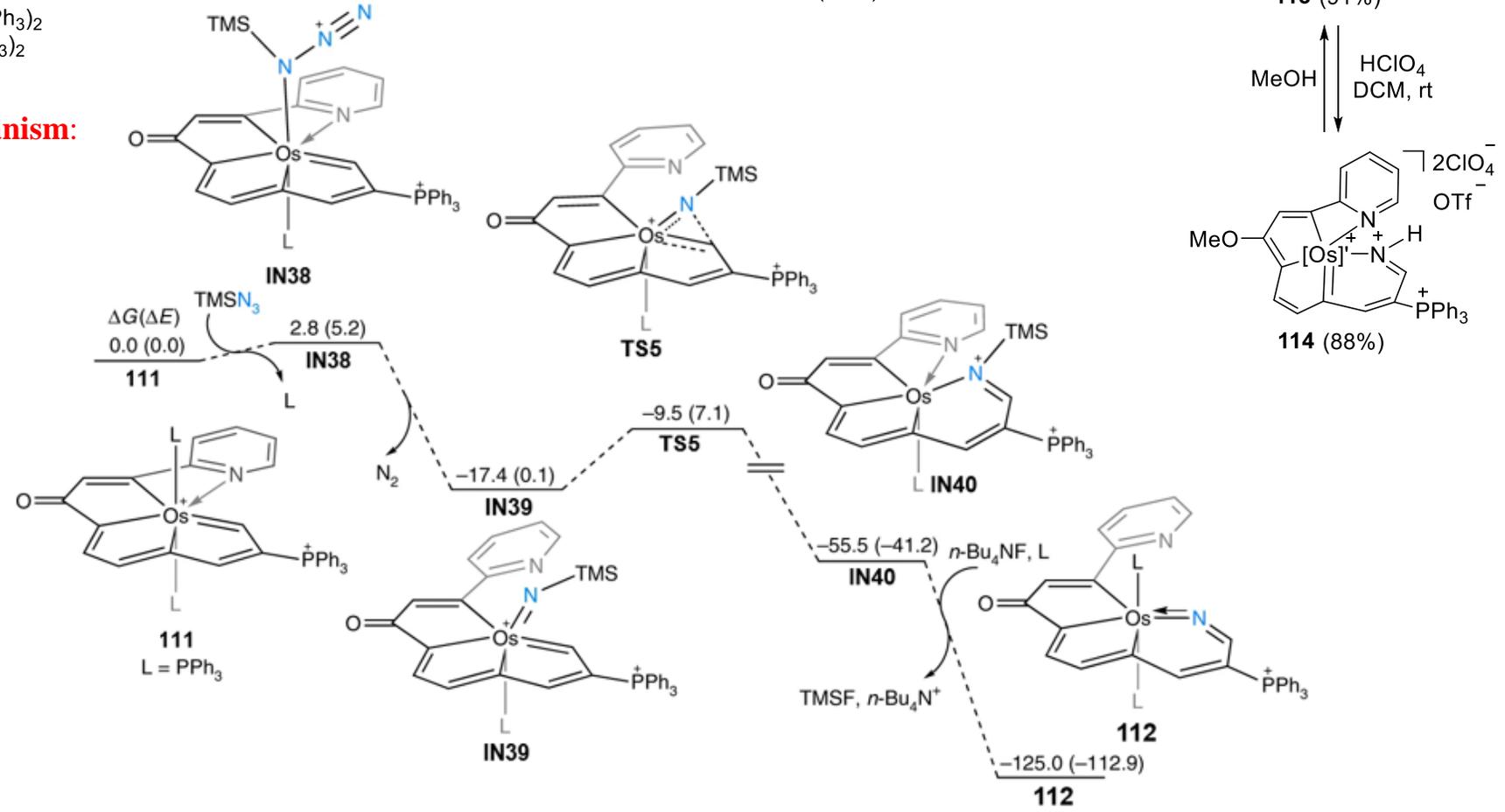
Mechanism:



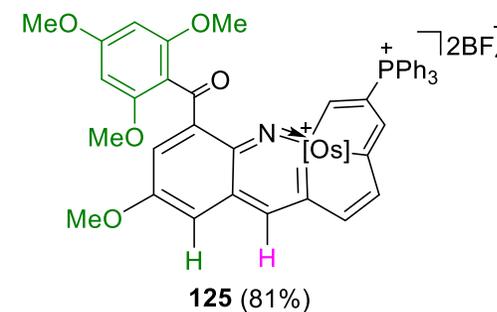
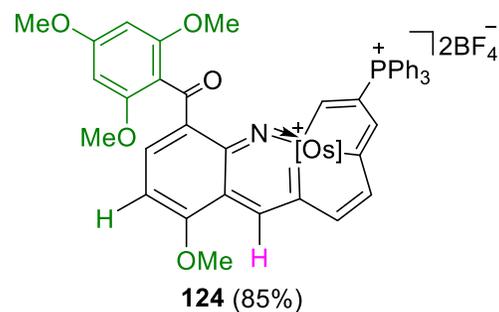
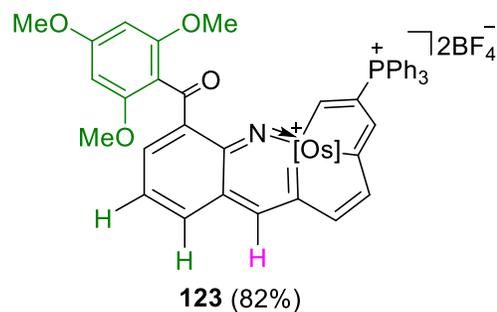
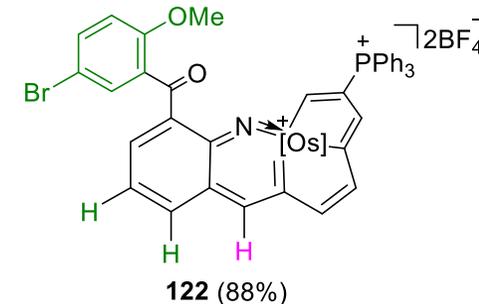
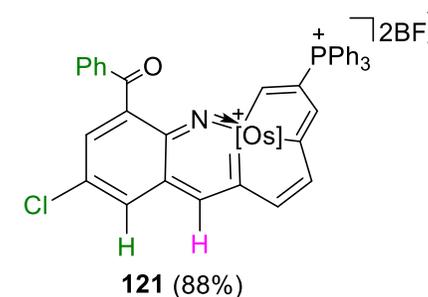
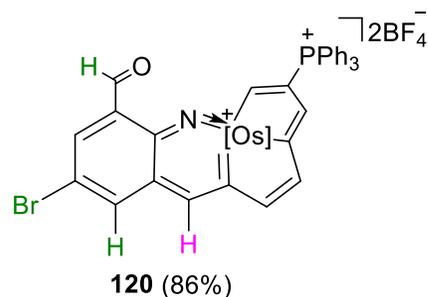
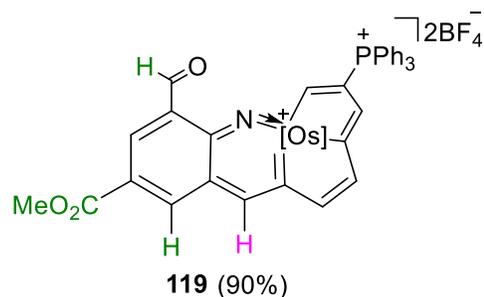
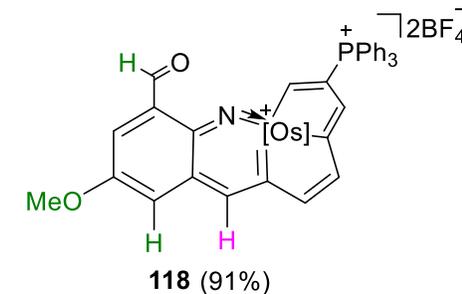
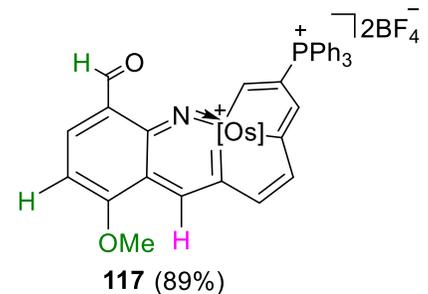
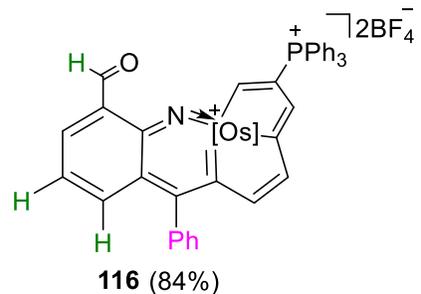
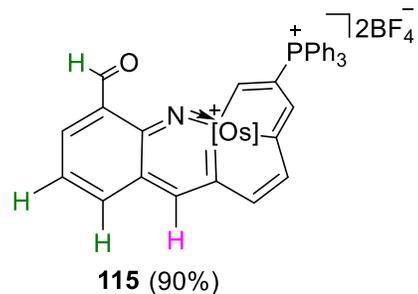
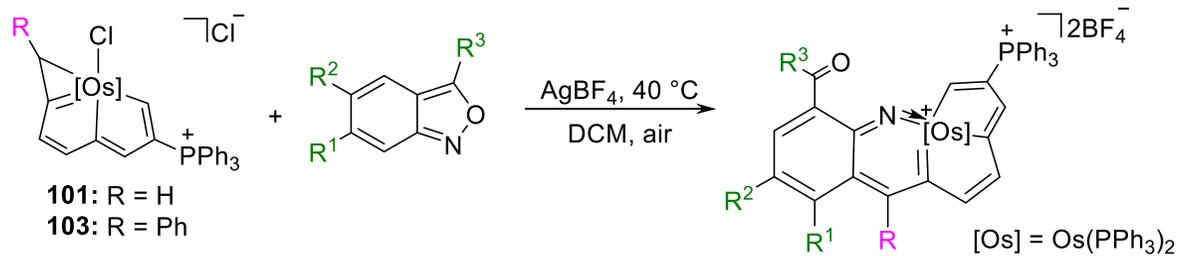
3.2 8C碳龙-反应性



Mechanism:

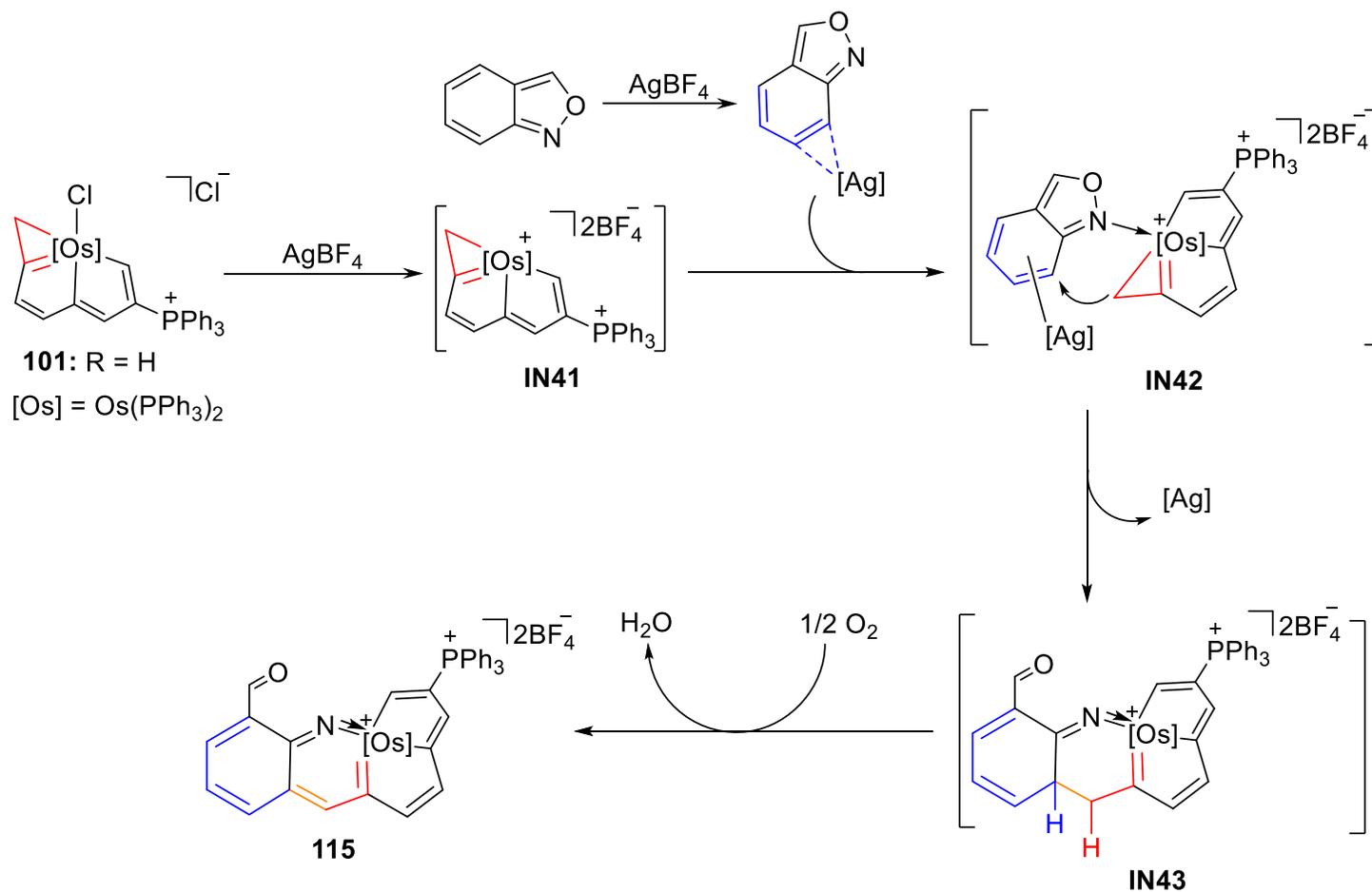


3.2 8C碳龙-反应性



3.2 8C碳龙-反应性

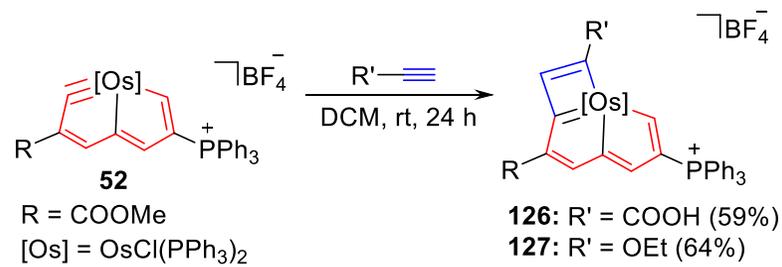
Mechanism:



3.3 9C碳龙骨架构筑及反应性

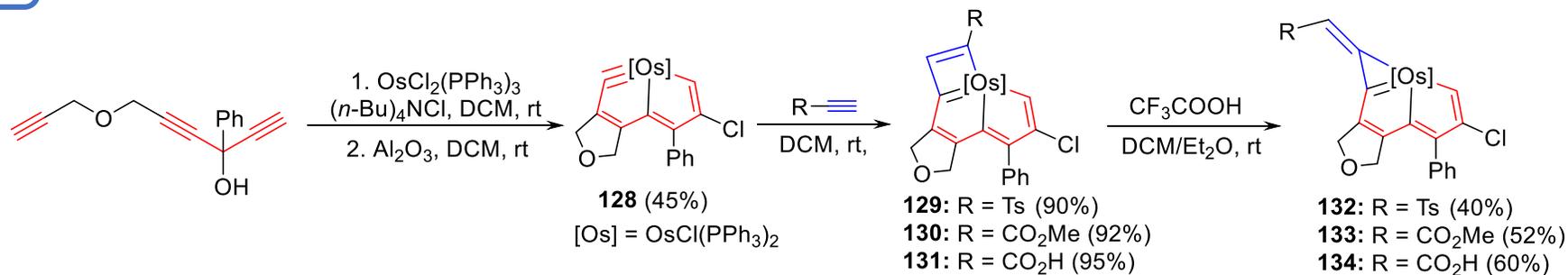
骨架构筑:

"7+2"



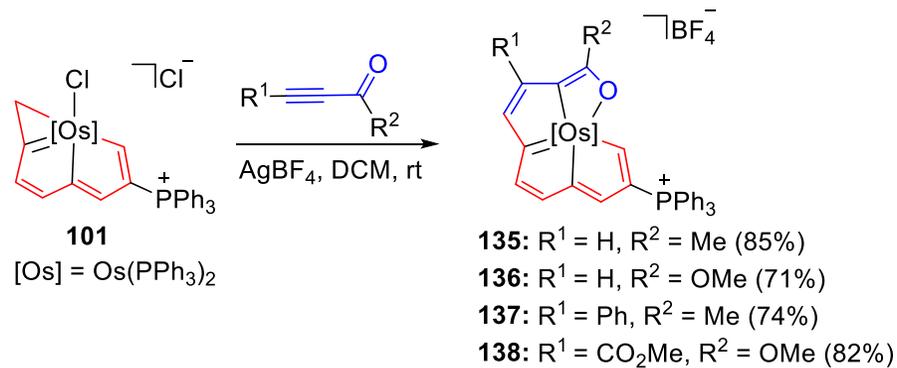
反应性:

"9-1"

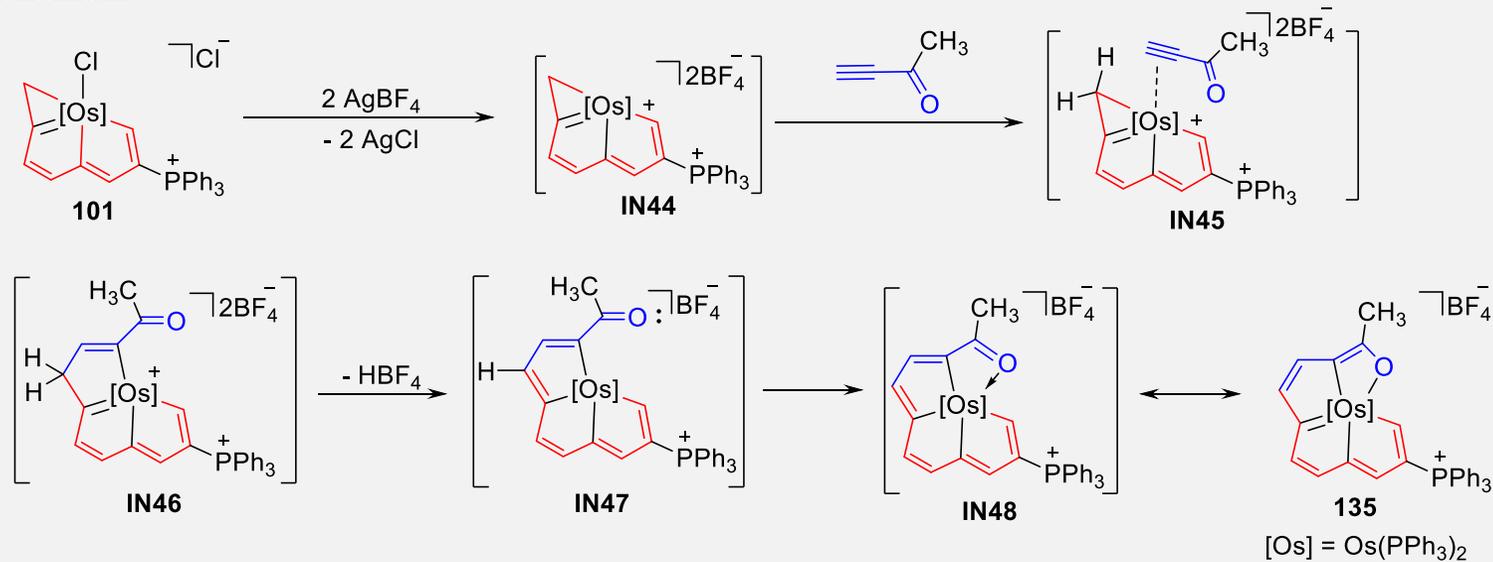


3.4 10C碳龙-骨架构筑

"8+2"

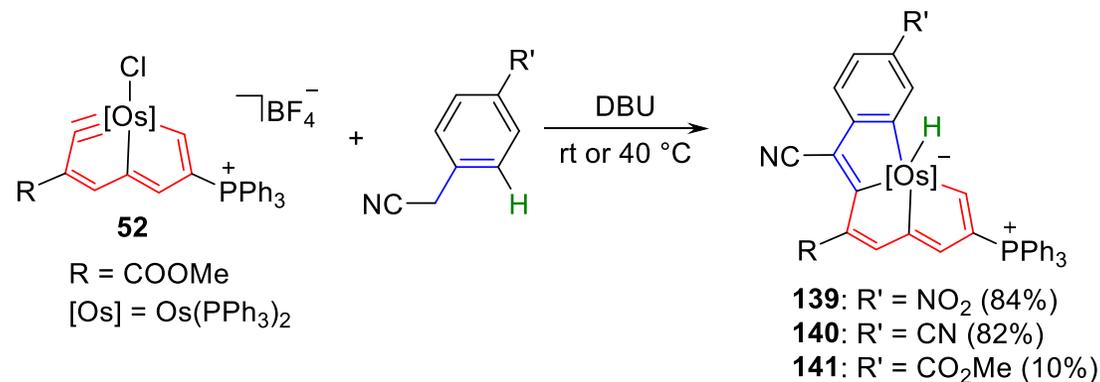


Mechanism:

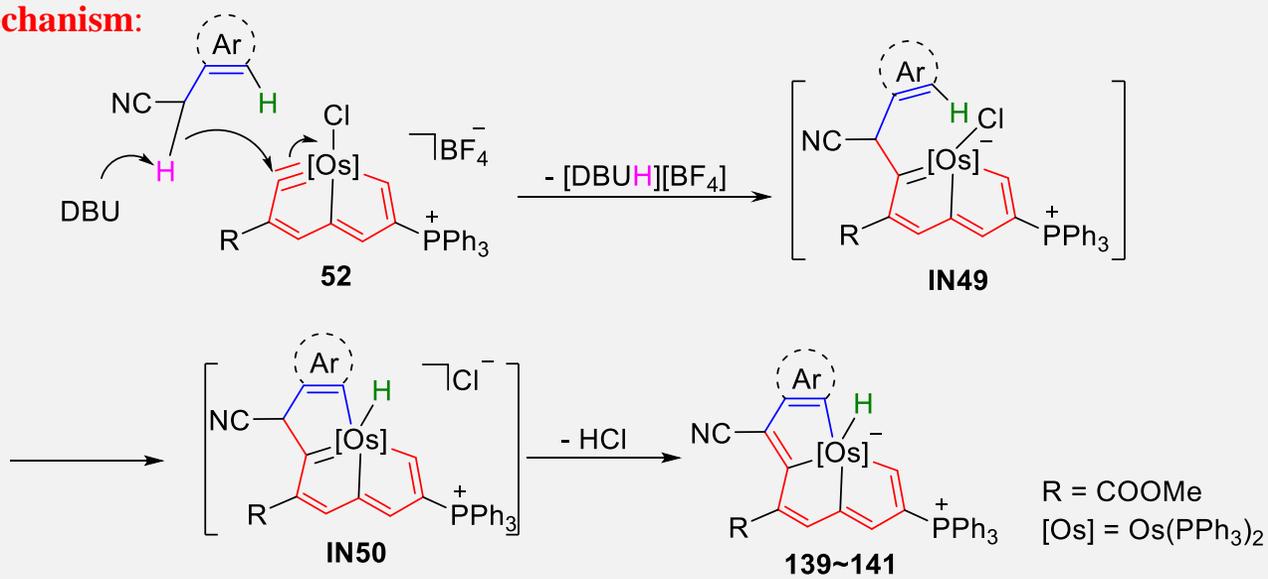


3.4 10C碳龙-骨架构筑

"7+3"

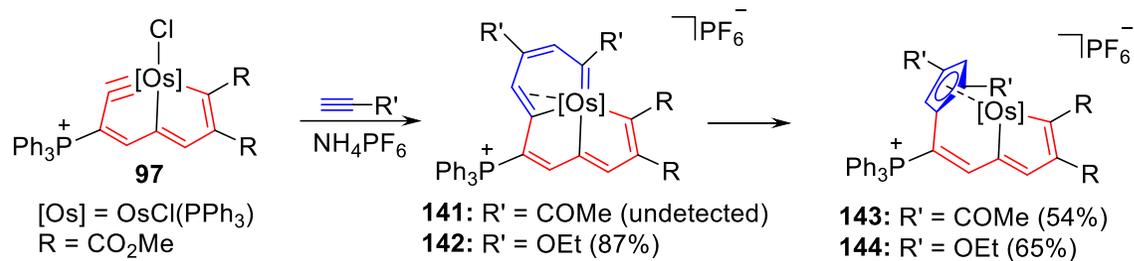


Mechanism:

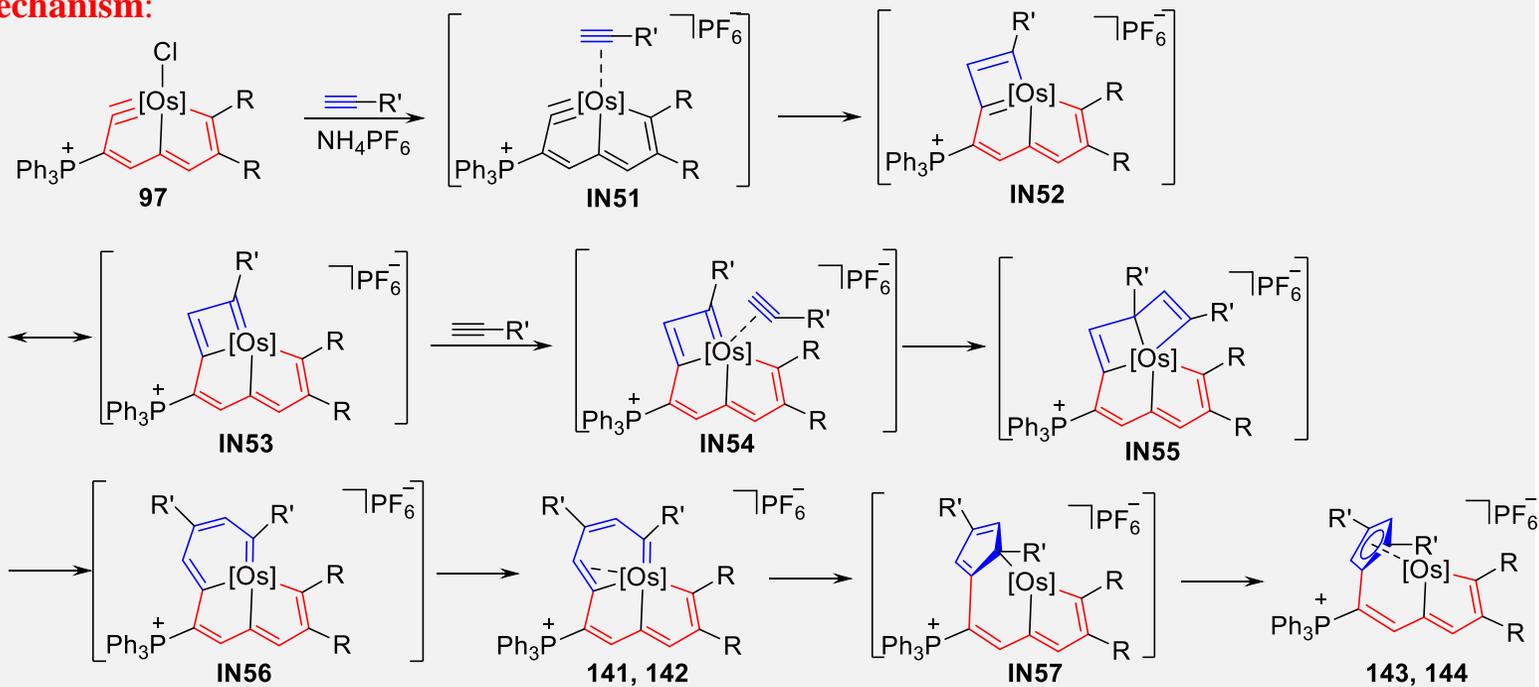


3.5 ¹¹C碳龙-骨架构筑

"7+2+2"



Mechanism:

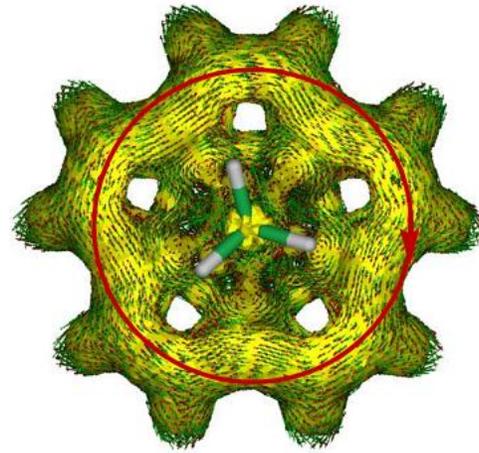


3.5 ¹¹C碳龙-反应性

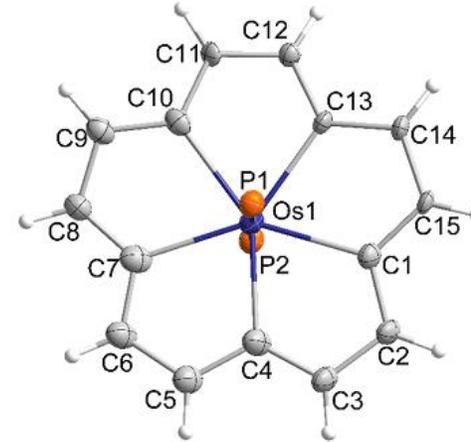


金属杂轮烯合成难点:

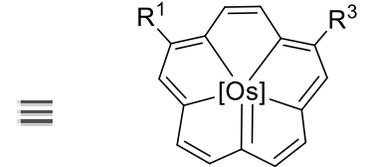
- 缺少合适的轮烯骨架
- 缺少活化方式



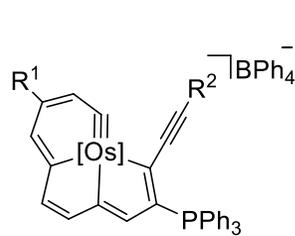
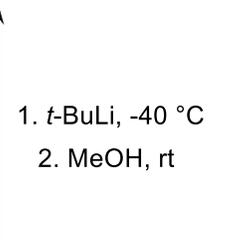
157的π轨道AICD等值面



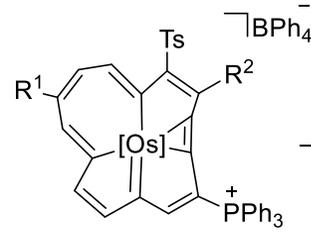
157
 D_{5h}



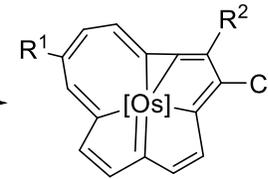
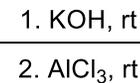
- 157: $R^1 = H, R^3 = H$ (80%)
- 158: $R^1 = Ph, R^3 = Ph$ (72%)
- 159: $R^1 = Me, R^3 = Ph$ (75%)



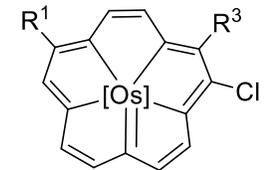
- 145: $R^1 = H, R^2 = TMS$
- 146: $R^1 = Ph, R^2 = Ph$
- 147: $R^1 = Me, R^2 = Ph$



- 148: $R^1 = H, R^2 = TMS$ (20%)
- 149: $R^1 = Ph, R^2 = Ph$ (57%)
- 150: $R^1 = Me, R^2 = Ph$ (50%)



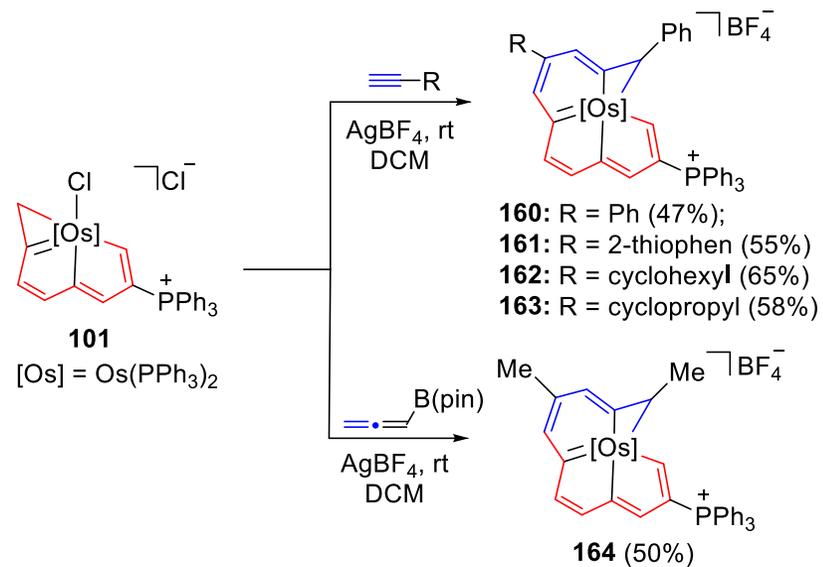
- 151: $R^1 = H, R^2 = TMS$ (64%)
- 152: $R^1 = Ph, R^2 = Ph$ (77%)
- 153: $R^1 = Me, R^2 = Ph$ (74%)



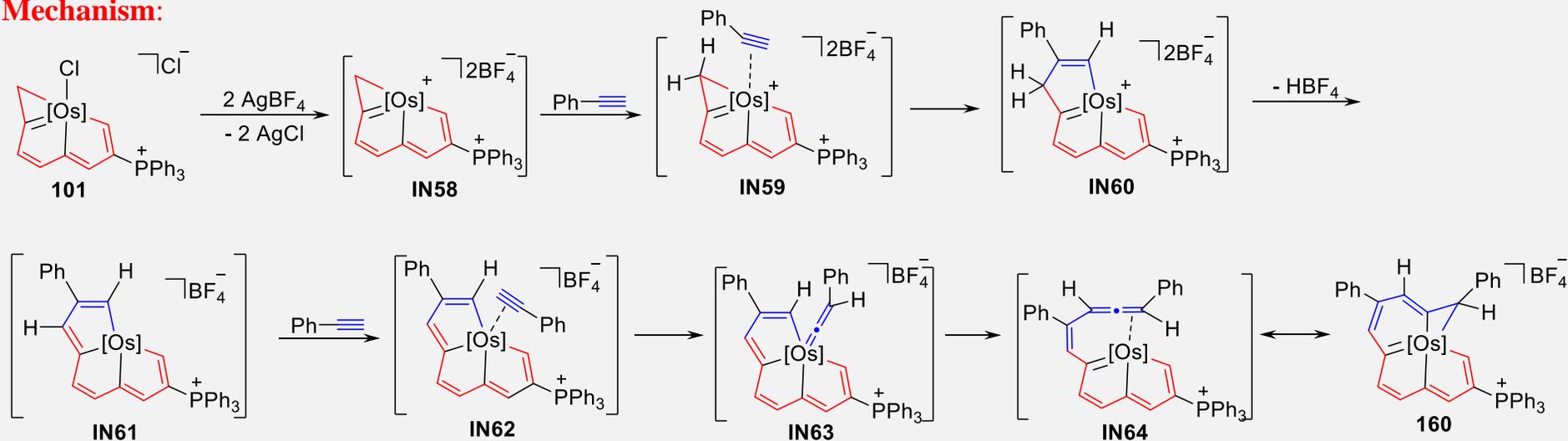
- 154: $R^1 = H, R^3 = H$ (70%)
- 155: $R^1 = Ph, R^3 = Ph$ (34%)
- 156: $R^1 = Me, R^3 = Ph$ (61%)

3.6 12C碳龙骨架构筑

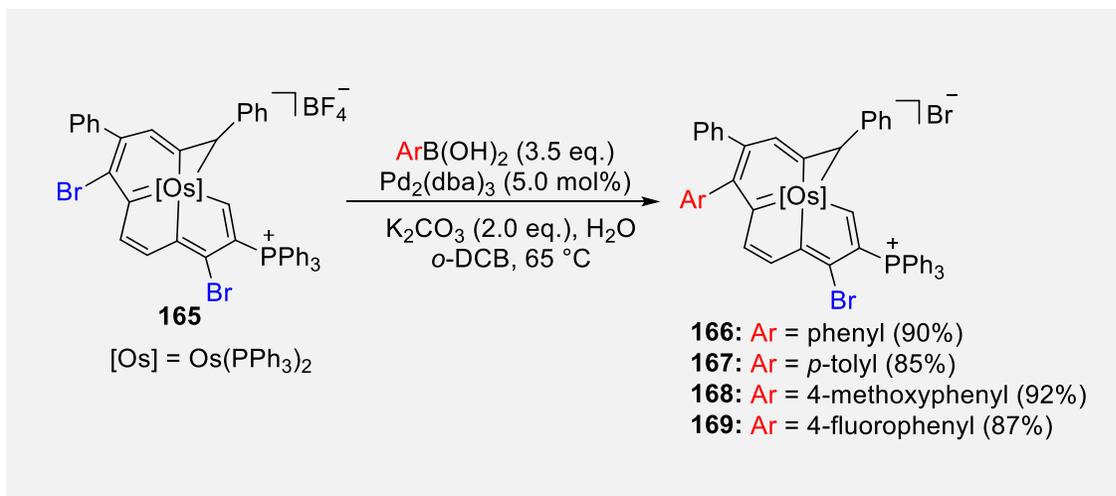
"8+2+2"



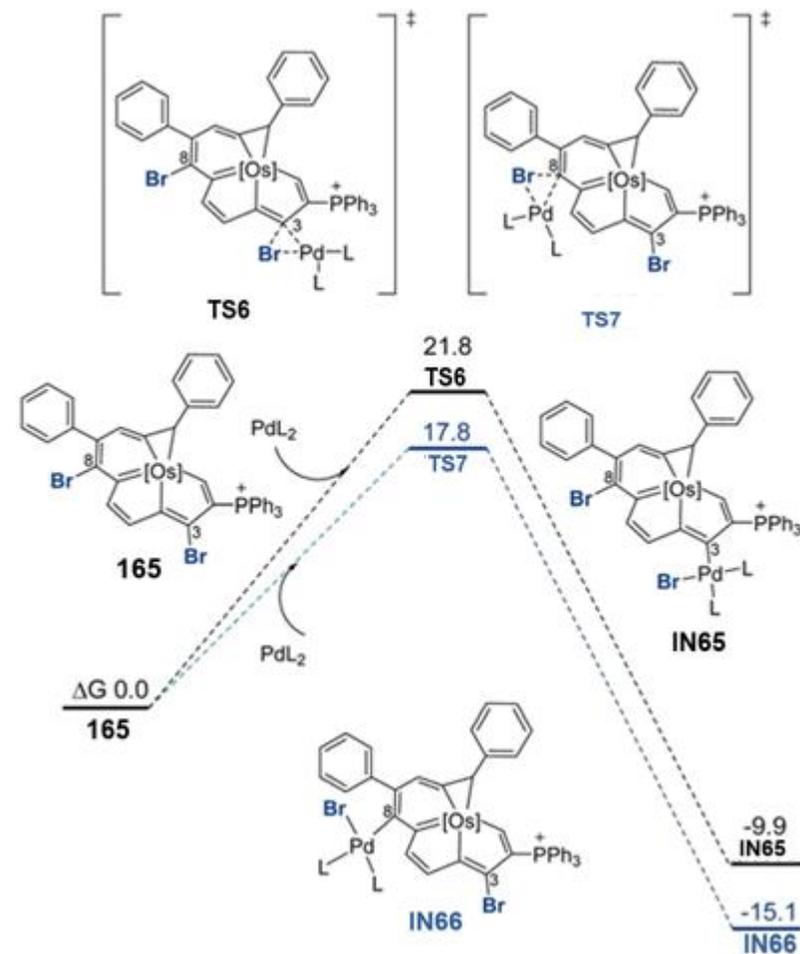
Mechanism:



3.6 12C碳龙-反应性



Mechanism:



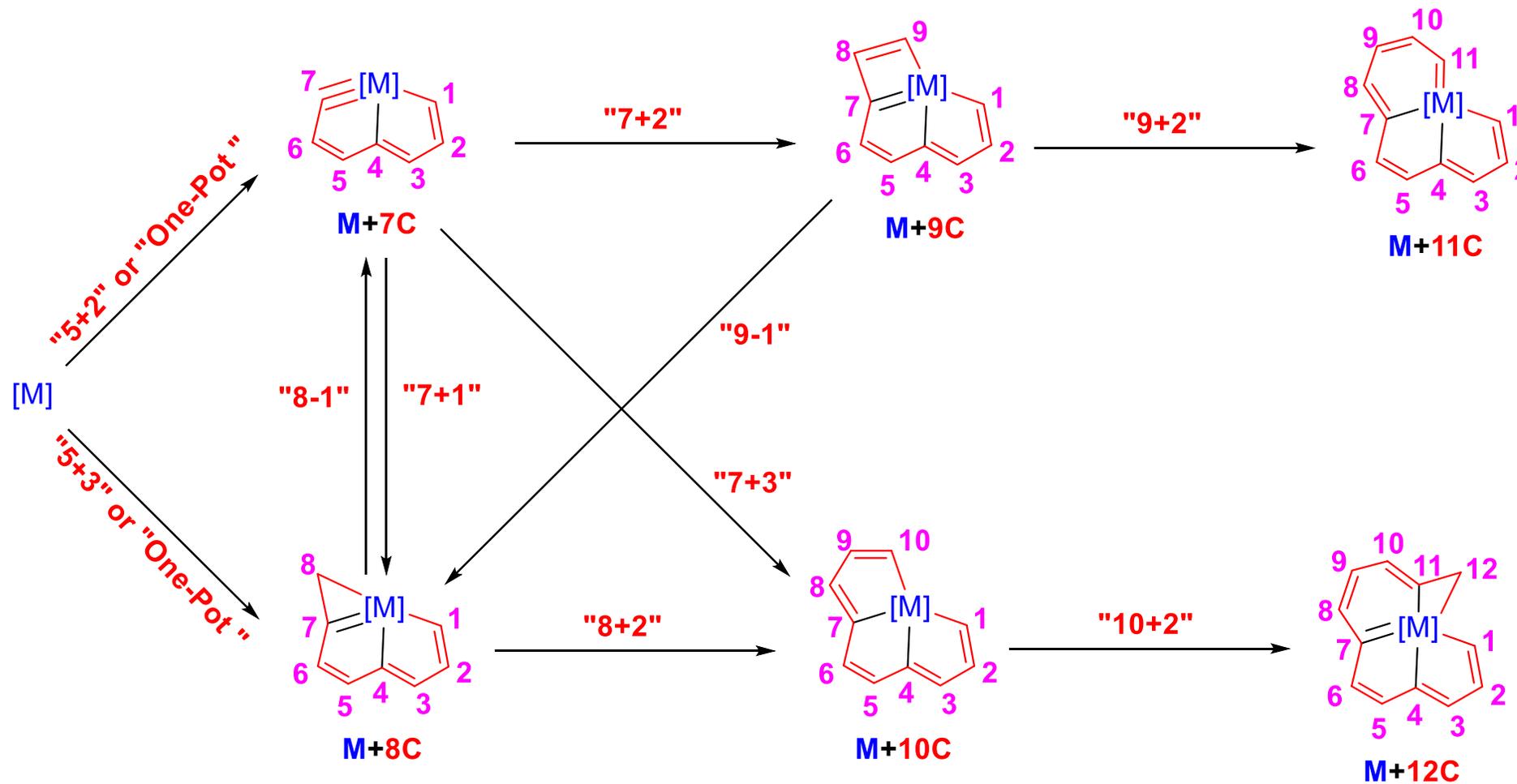
一. 背景介绍

二. 简单金属杂芳烃构筑

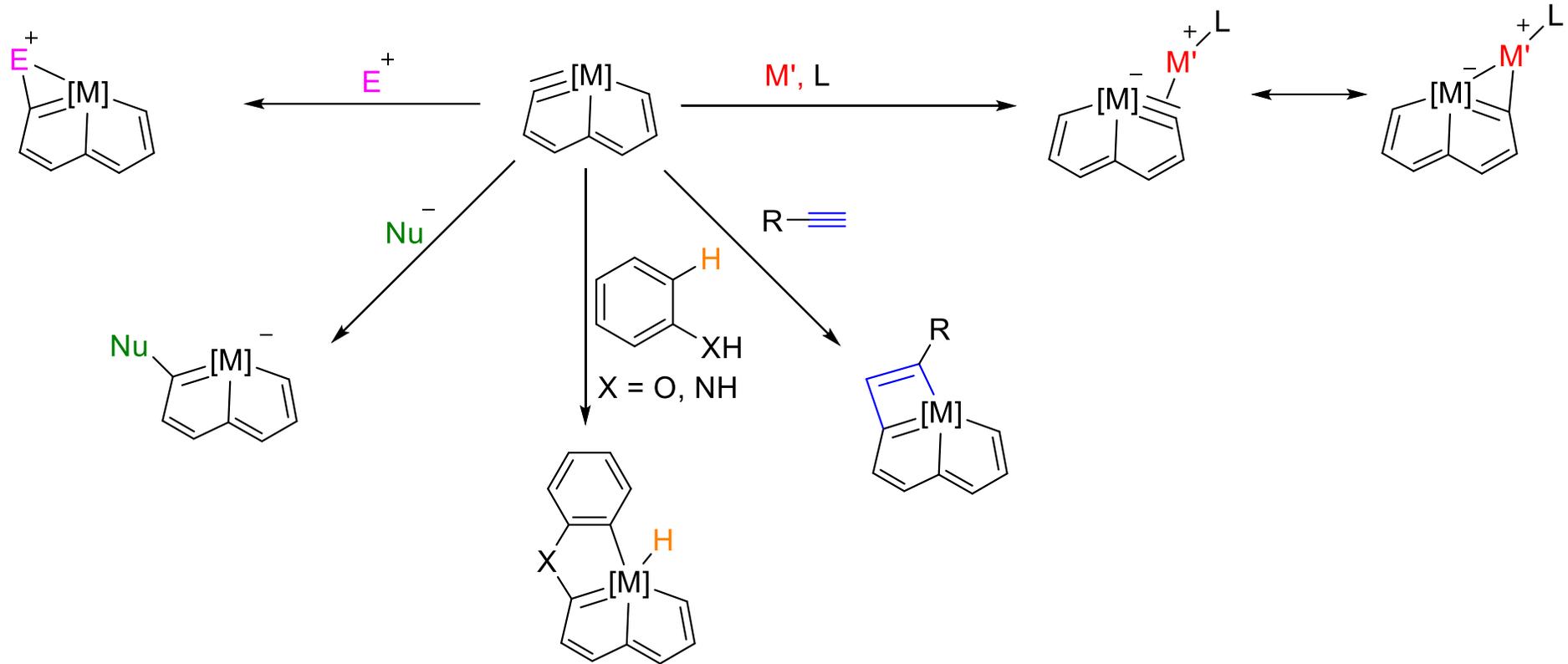
三. 碳龙骨架构筑及反应性

四. 总结与展望

4.1 碳龙化学总结-骨架构筑

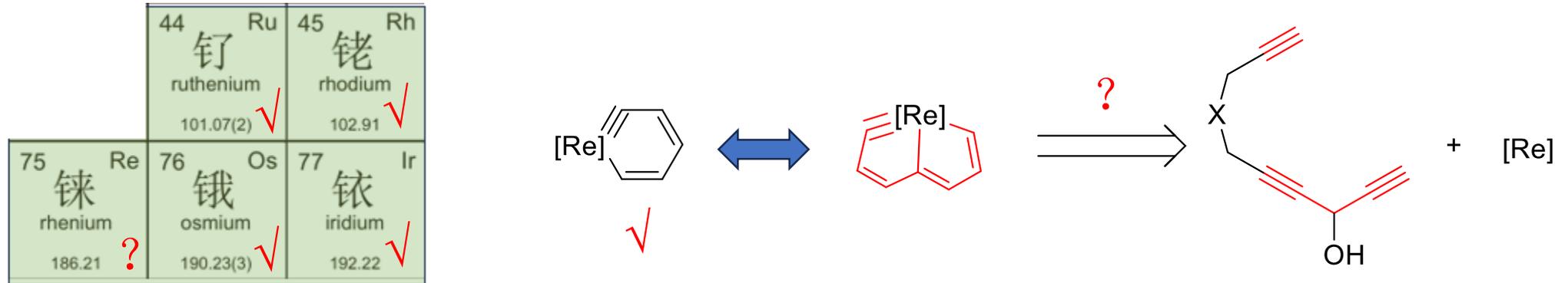


4.1 碳龙化学总结-反应性

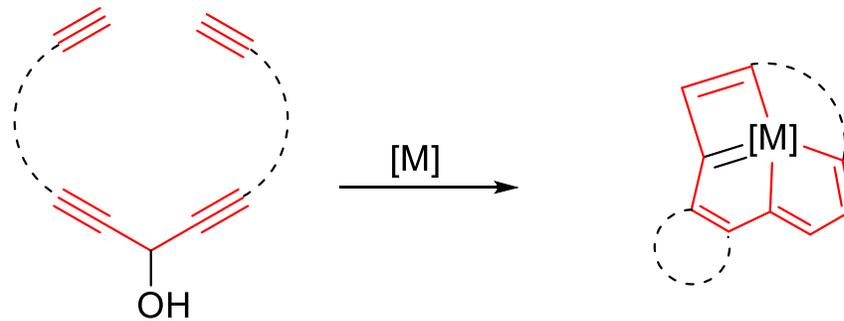


4.2 碳龙化学展望

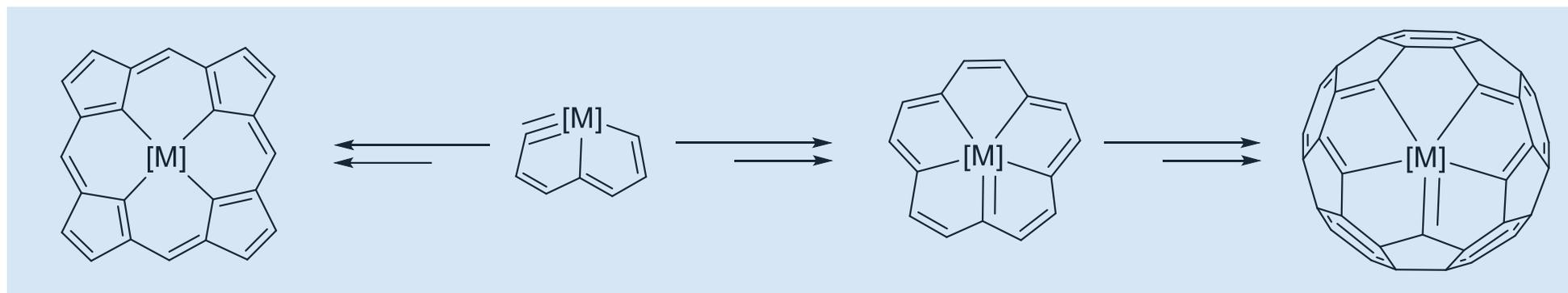
- 目前仅有部分第八族过渡金属碳龙化合物的合成报道。



- 通过底物设计发展简洁高效合成9-12C碳龙骨架新方法。

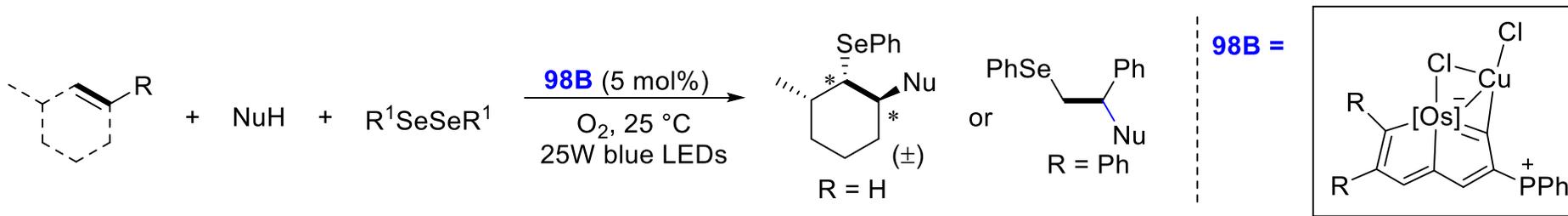
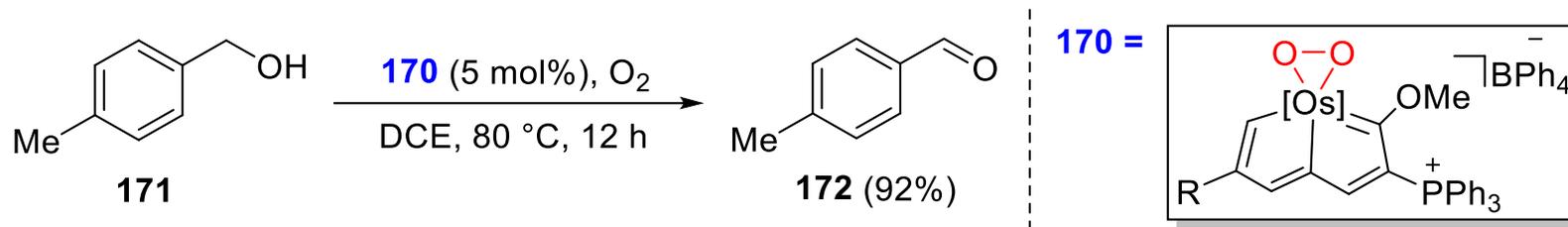


- 通过碳龙合成多样的金属轮烯乃至金属富勒烯、金属全碳卟啉及金属石墨烯。

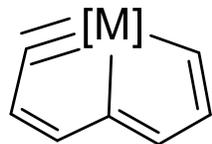


4.2 碳龙化学展望

● 碳龙催化的反应



As catalyst :



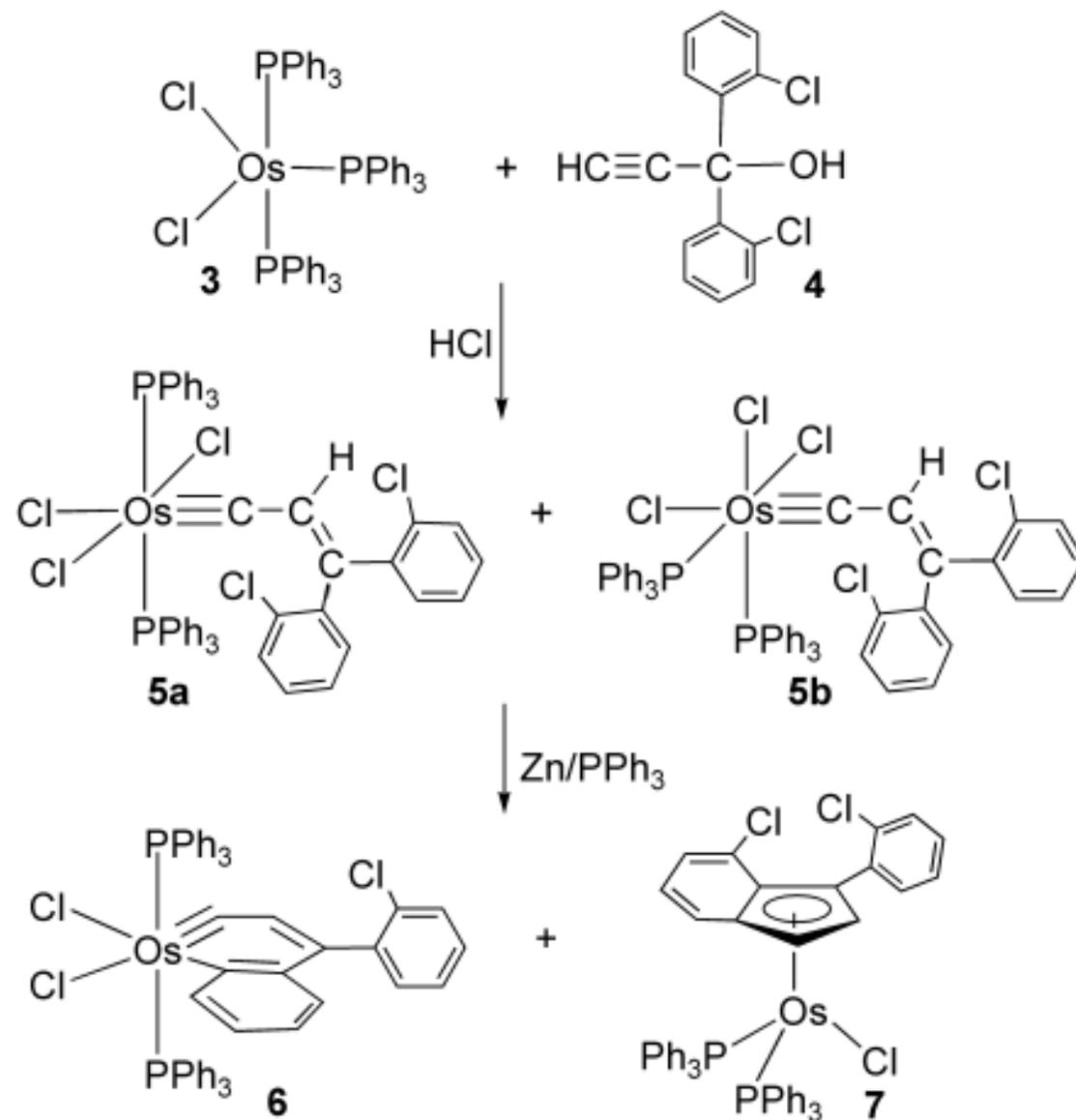
dehydrogenation, multicomponent coupling, C-H activation ...

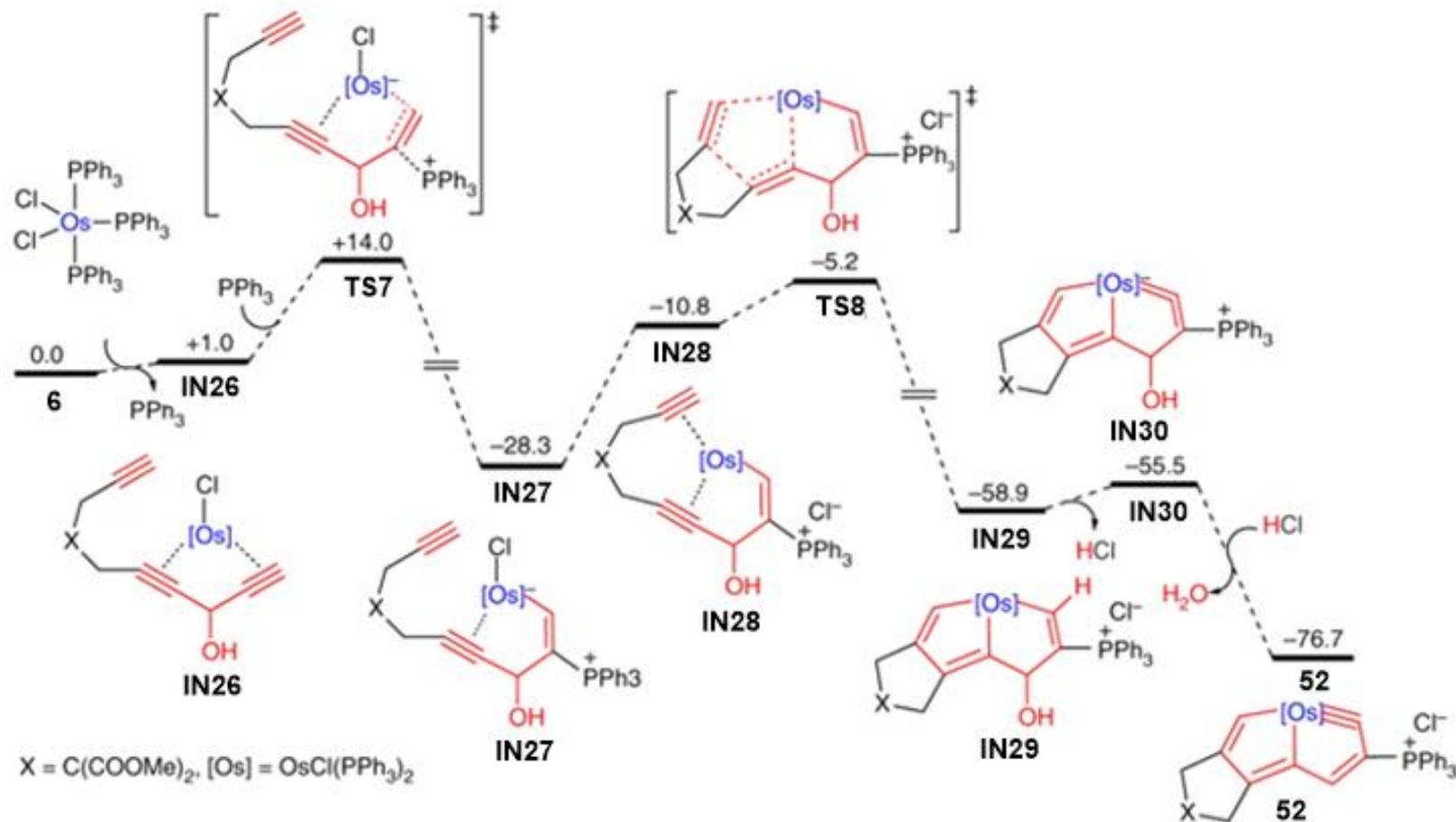
?

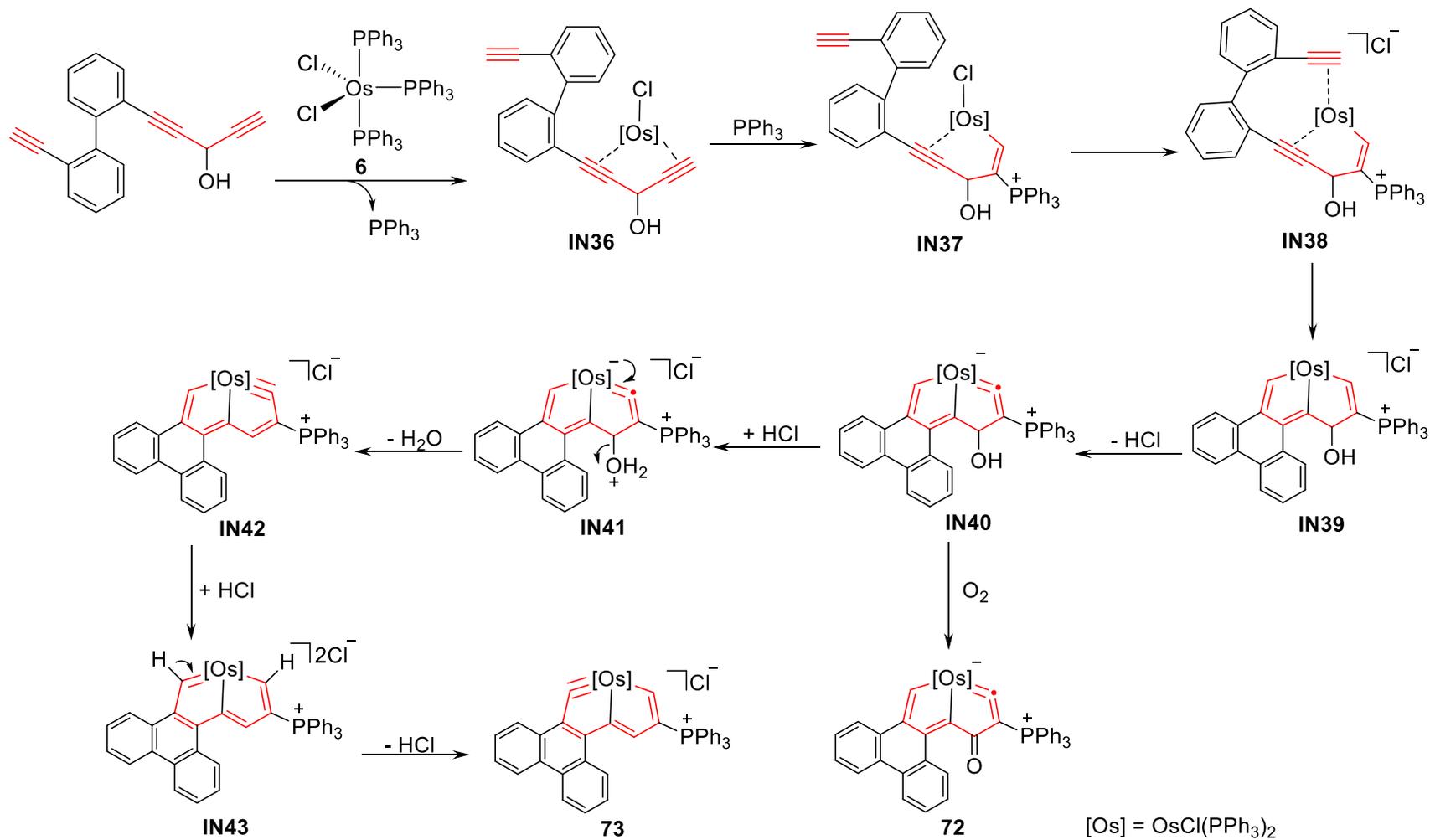


Thanks for your listening

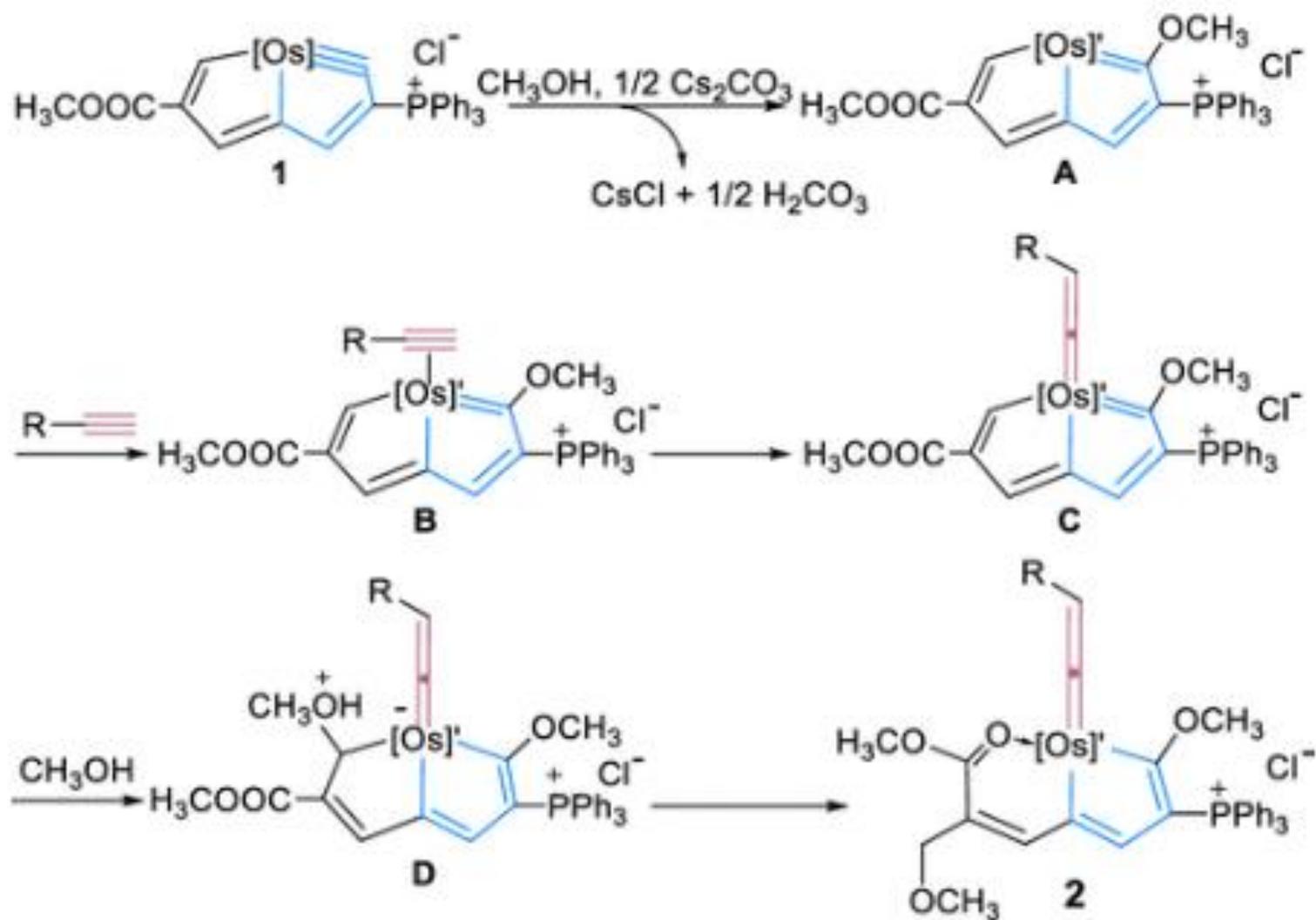
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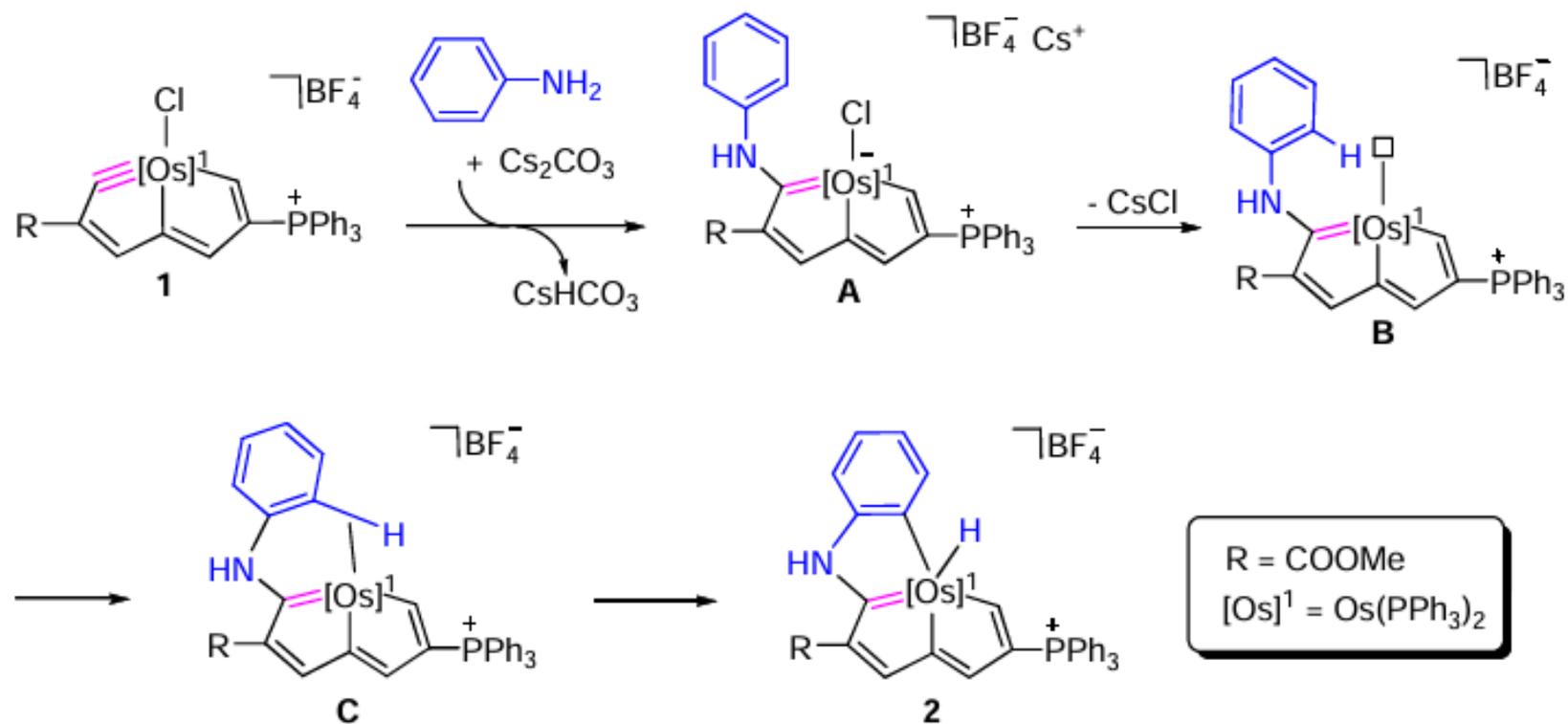




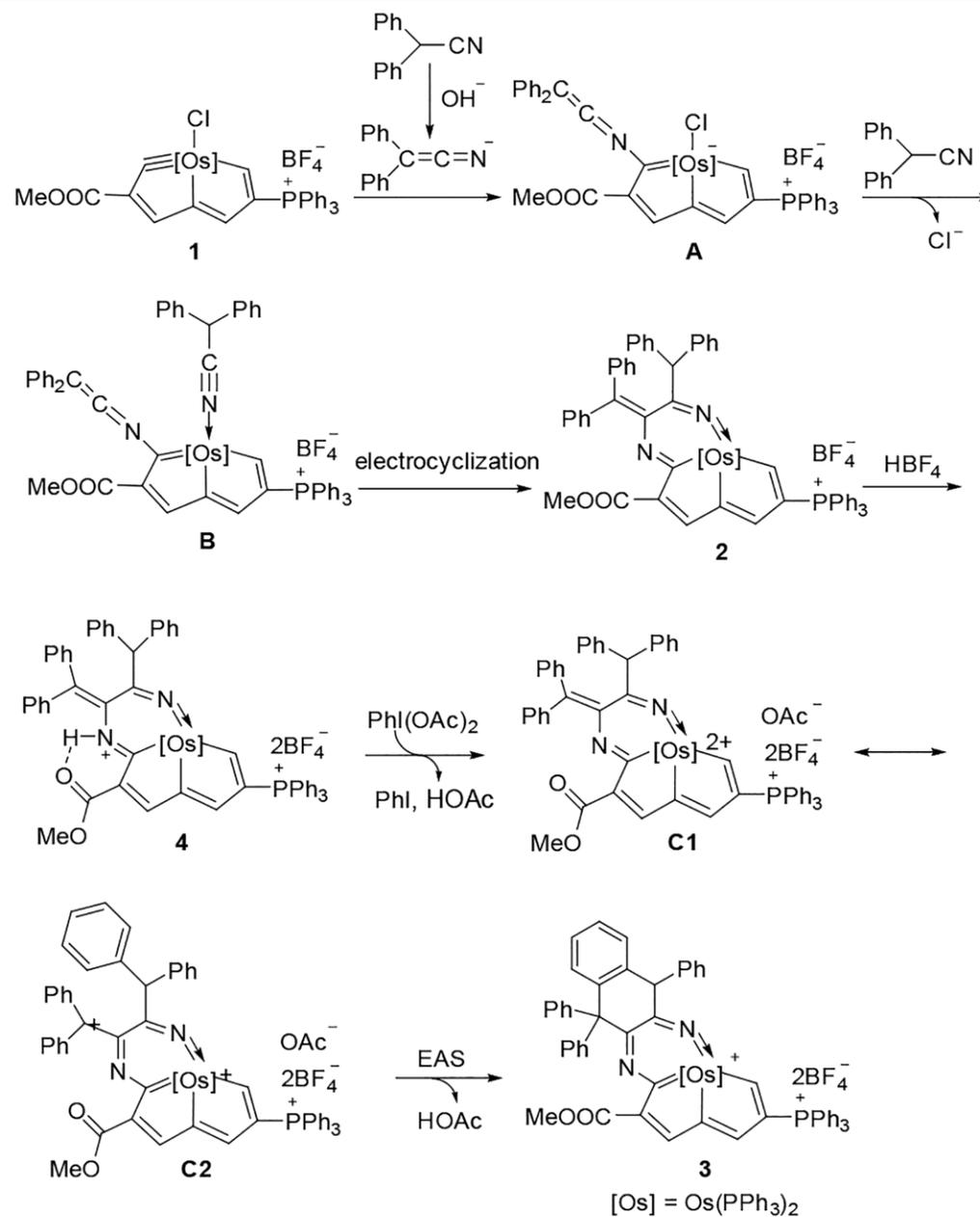


22

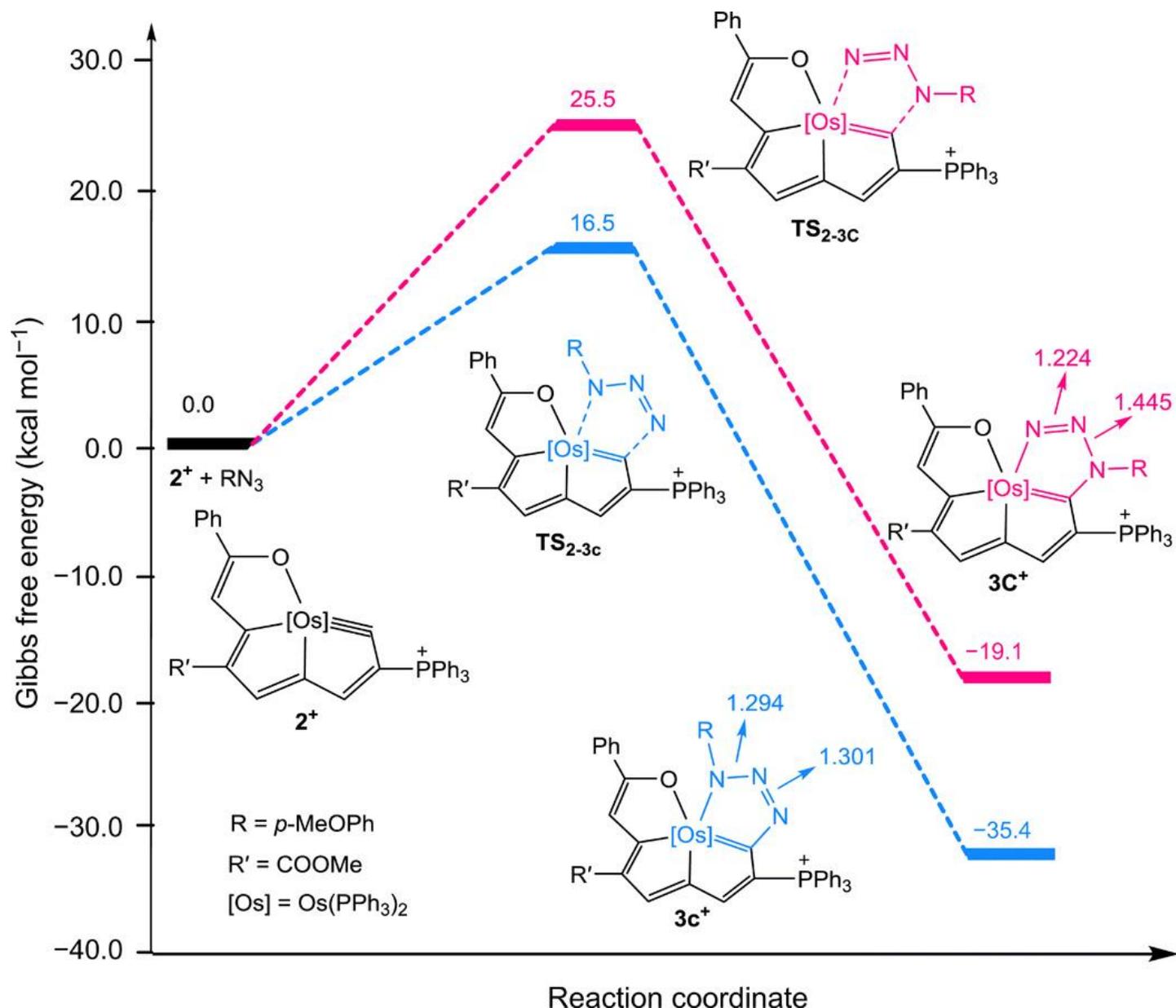




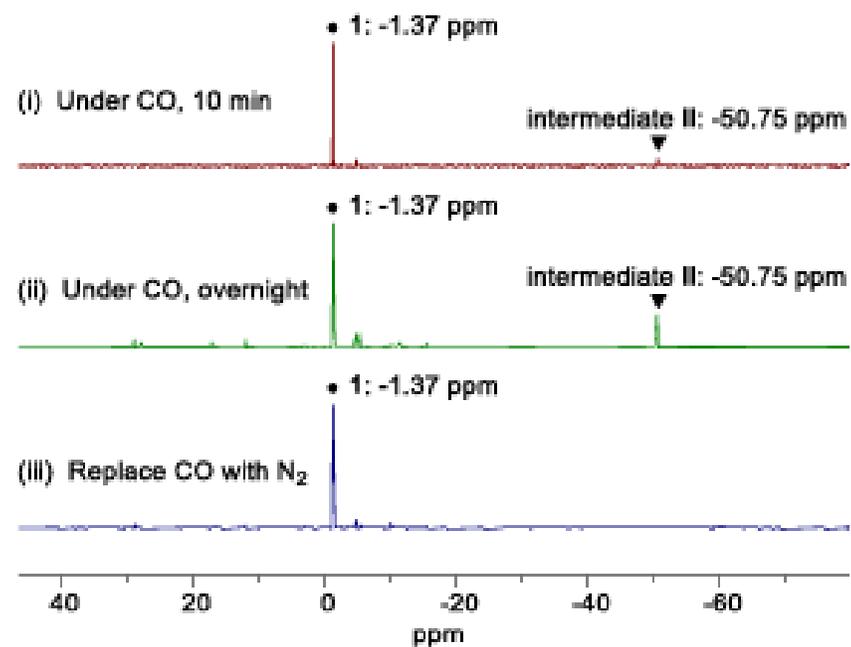
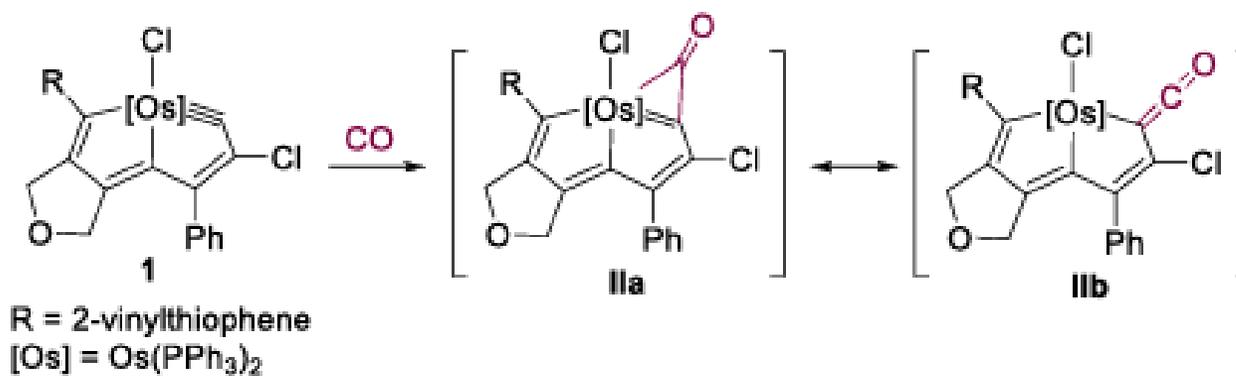
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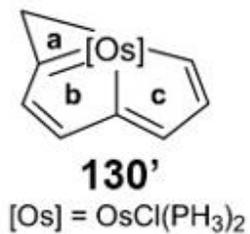
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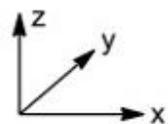
25



27



Orbitals		NICS(0): a / b / c
HOMO	HOMO-2	-5.8 / -6.1 / -13.6
HOMO-3	HOMO-10	
HOMO-12		
All σ orbitals		-34.8 / +0.4 / +9.4
Total		-40.6 / -5.7 / -4.2



HOMO (-5.93 eV)
-1.9 / -3.4 / +0.8



HOMO-2 (-6.25 eV)
+3.7 / +2.9 / -0.4



HOMO-3 (-6.80 eV)
-1.7 / 0.0 / -2.4

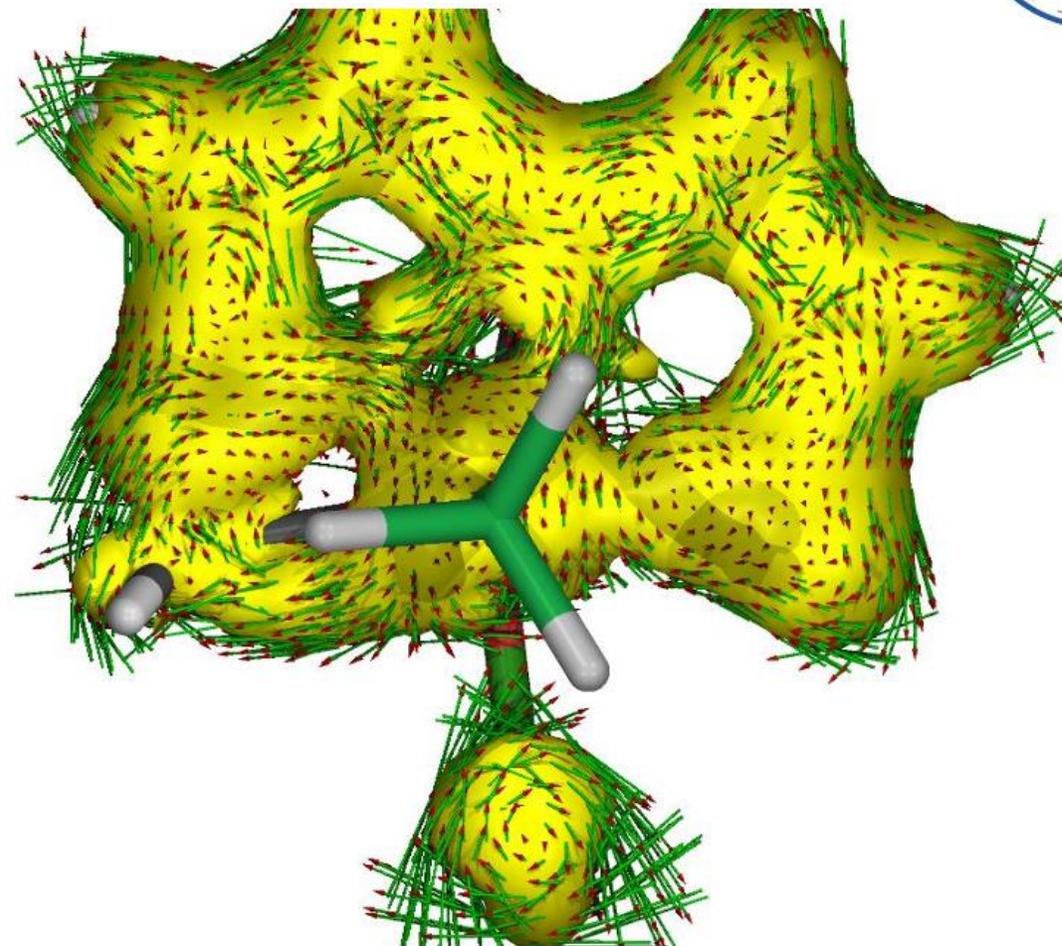


HOMO-10 (-9.09 eV)
-4.7 / -6.0 / -1.2



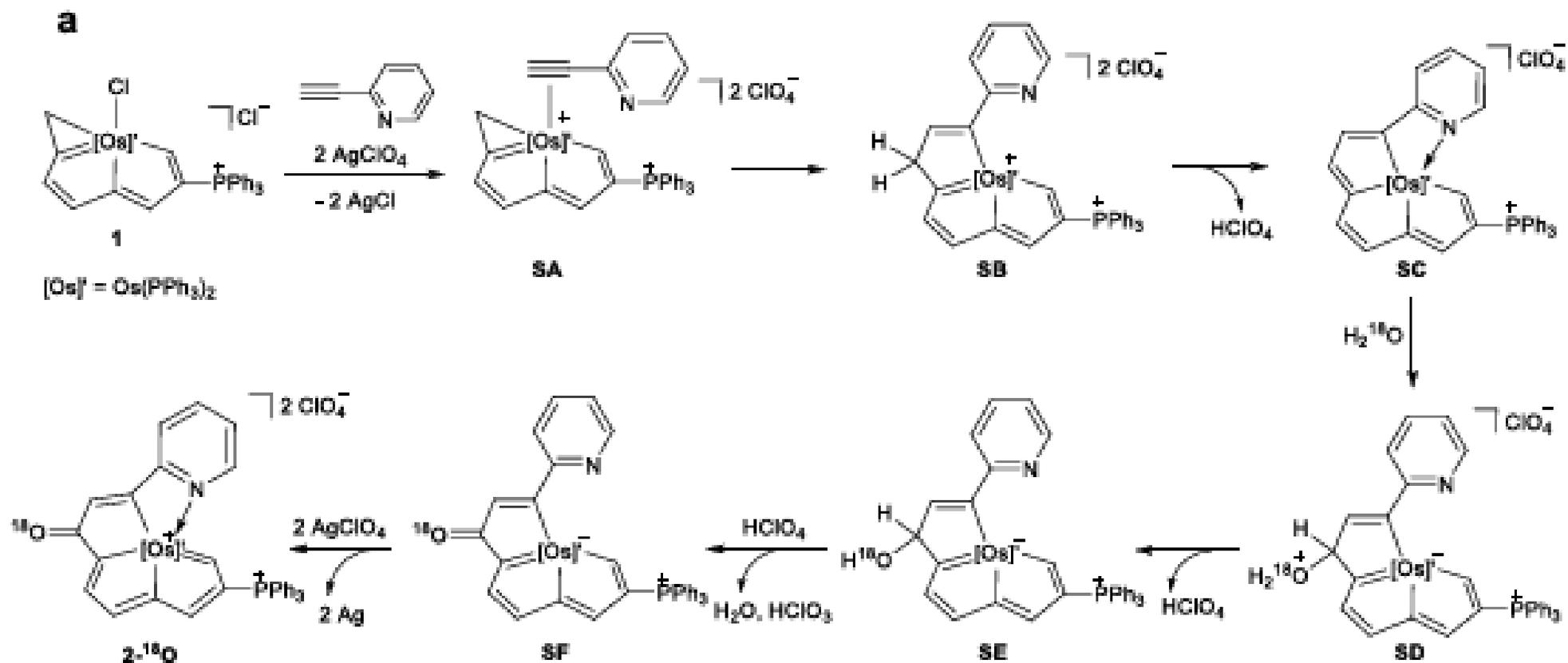
HOMO-12 (-10.04 eV)
-1.2 / +0.4 / -10.4

130' 的前线轨道及相应NICS值 (ppm)

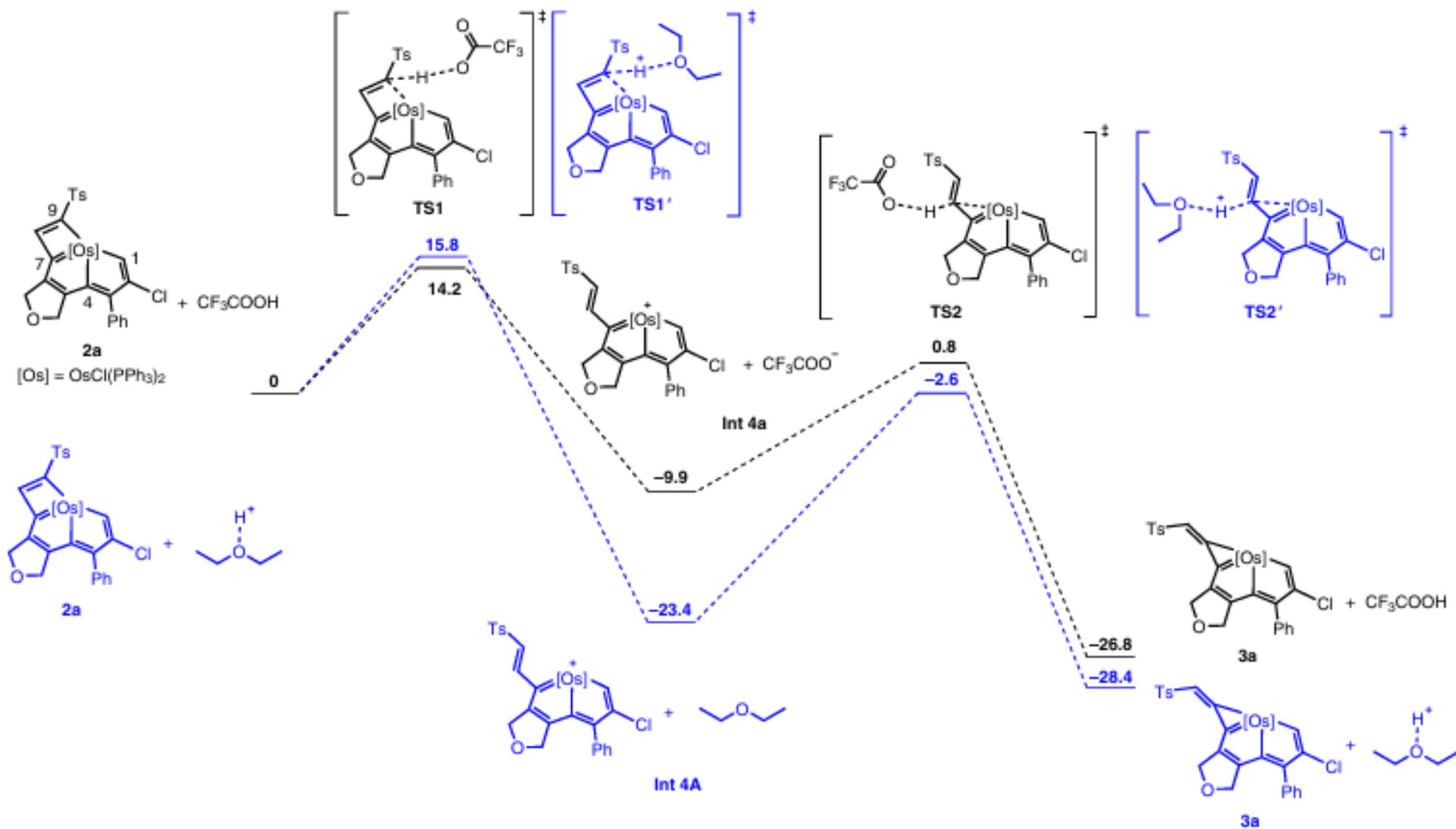


130的 σ 轨道AICD等值面

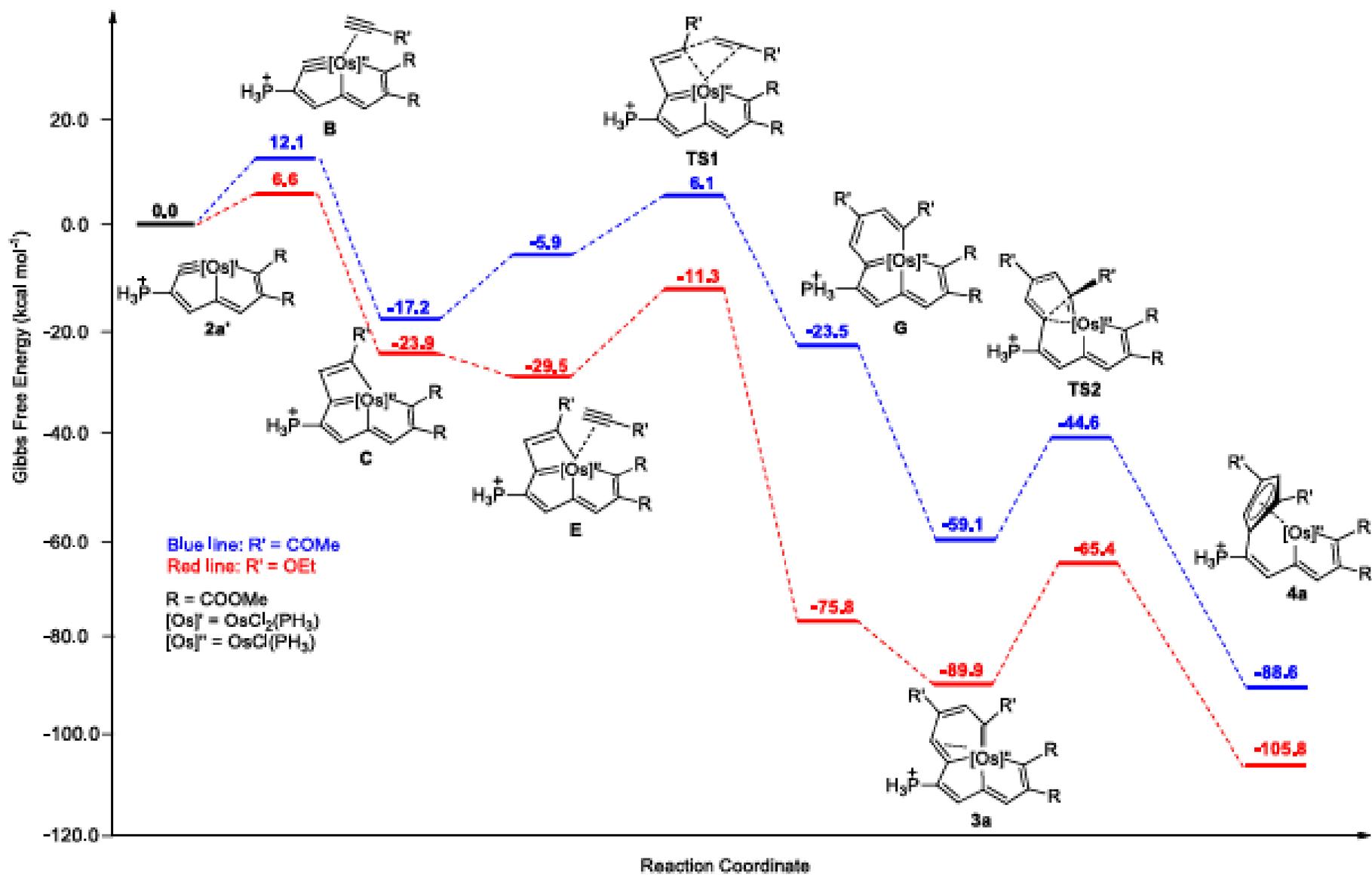
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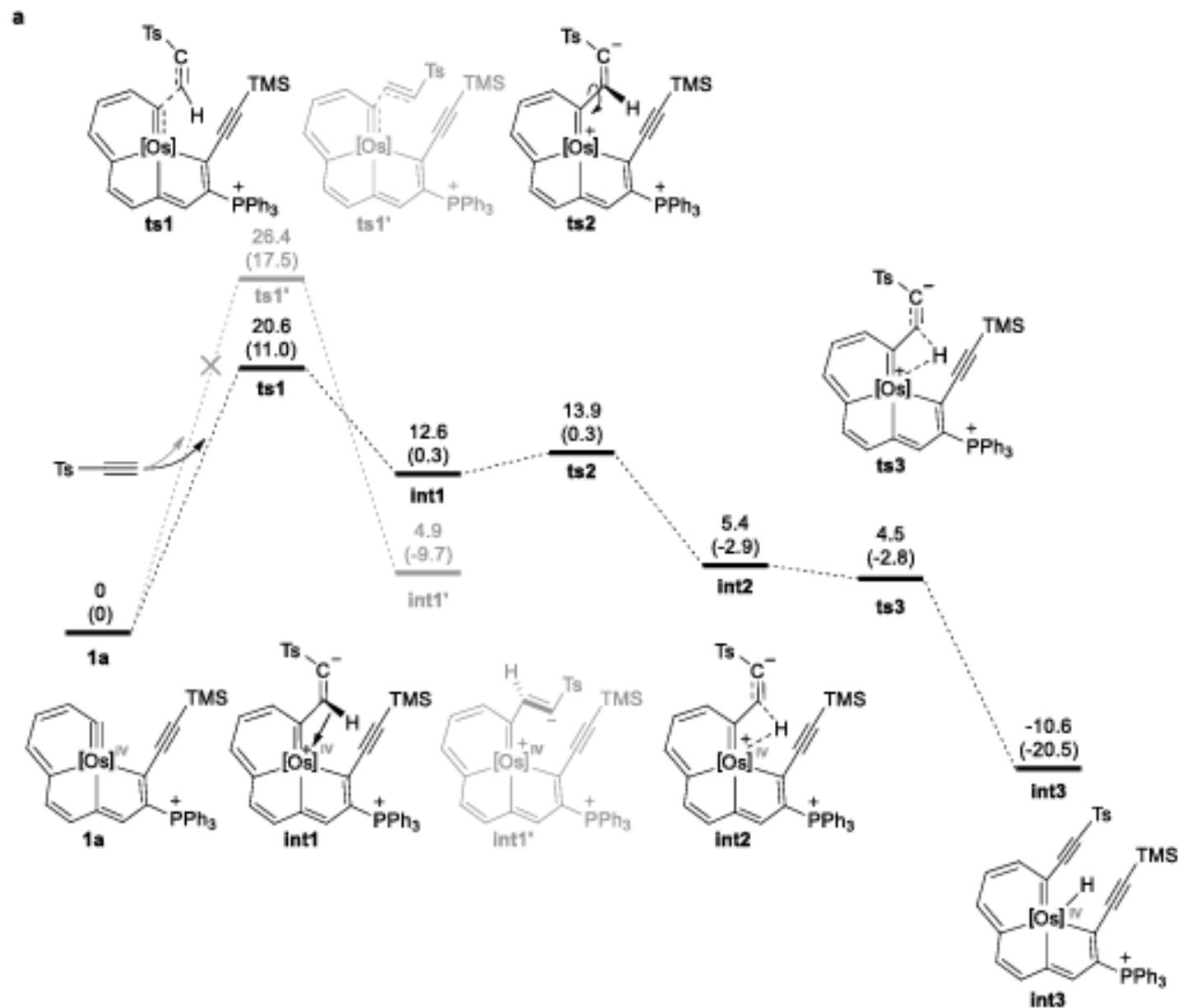
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36

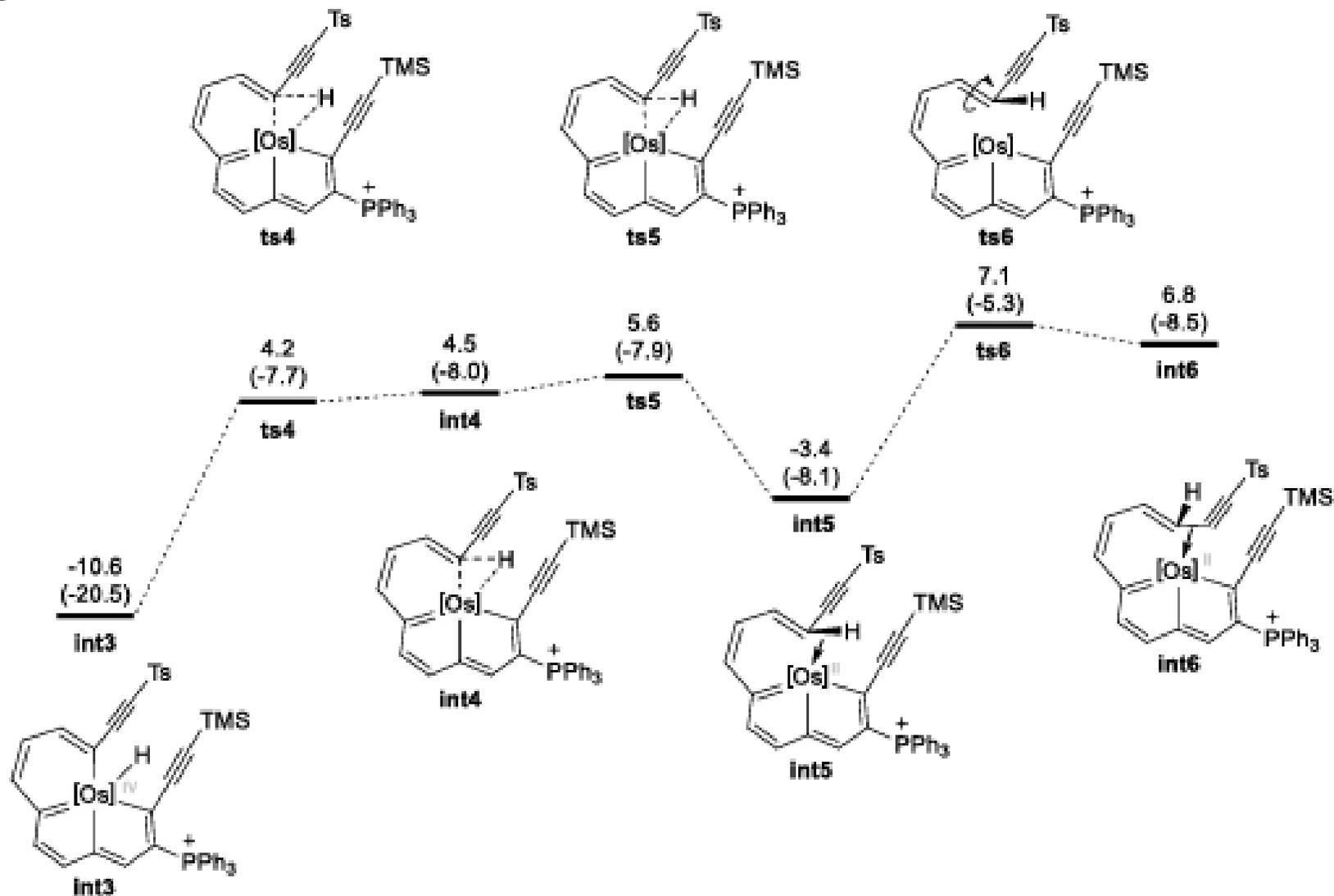


37

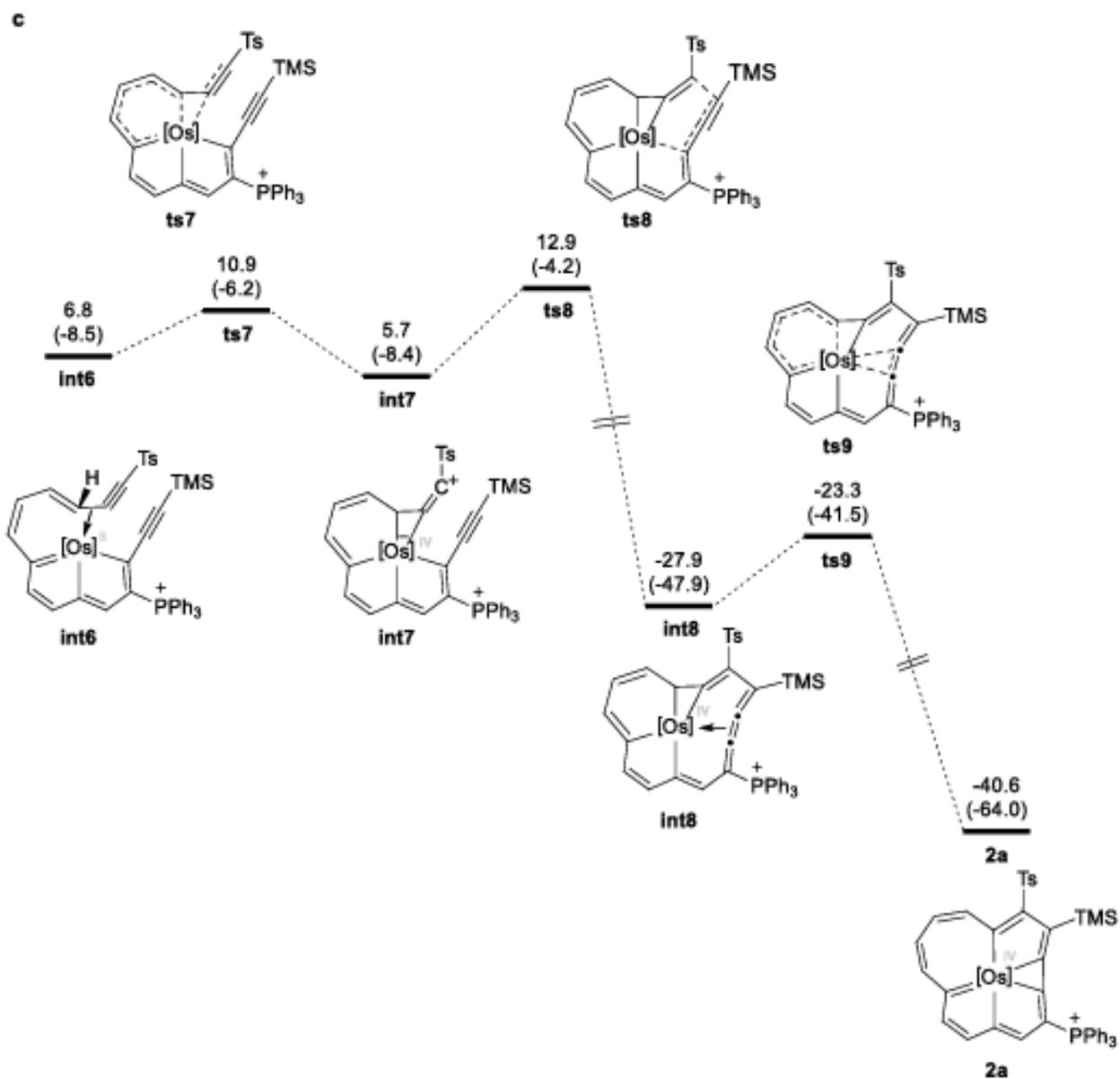


37

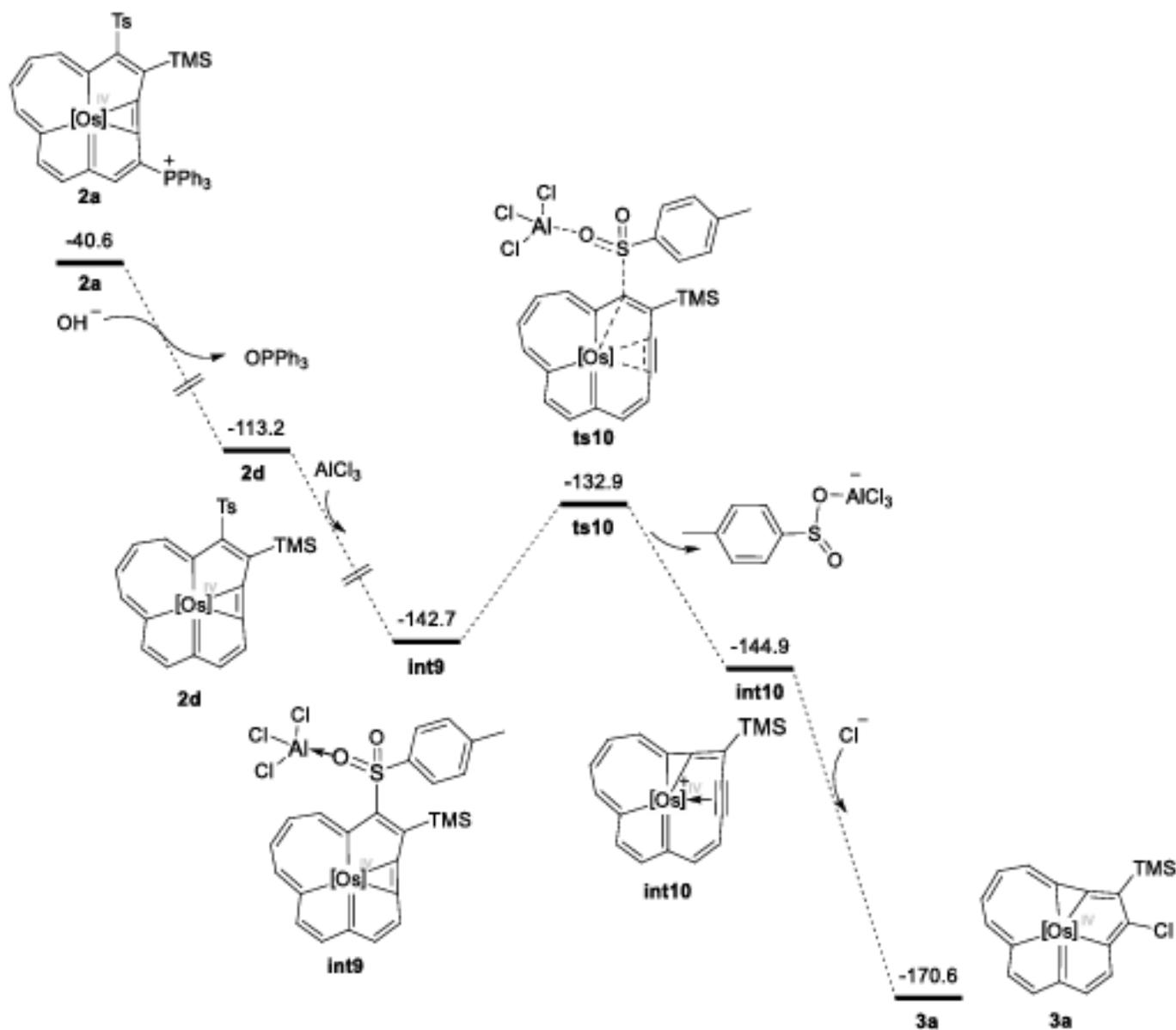
b



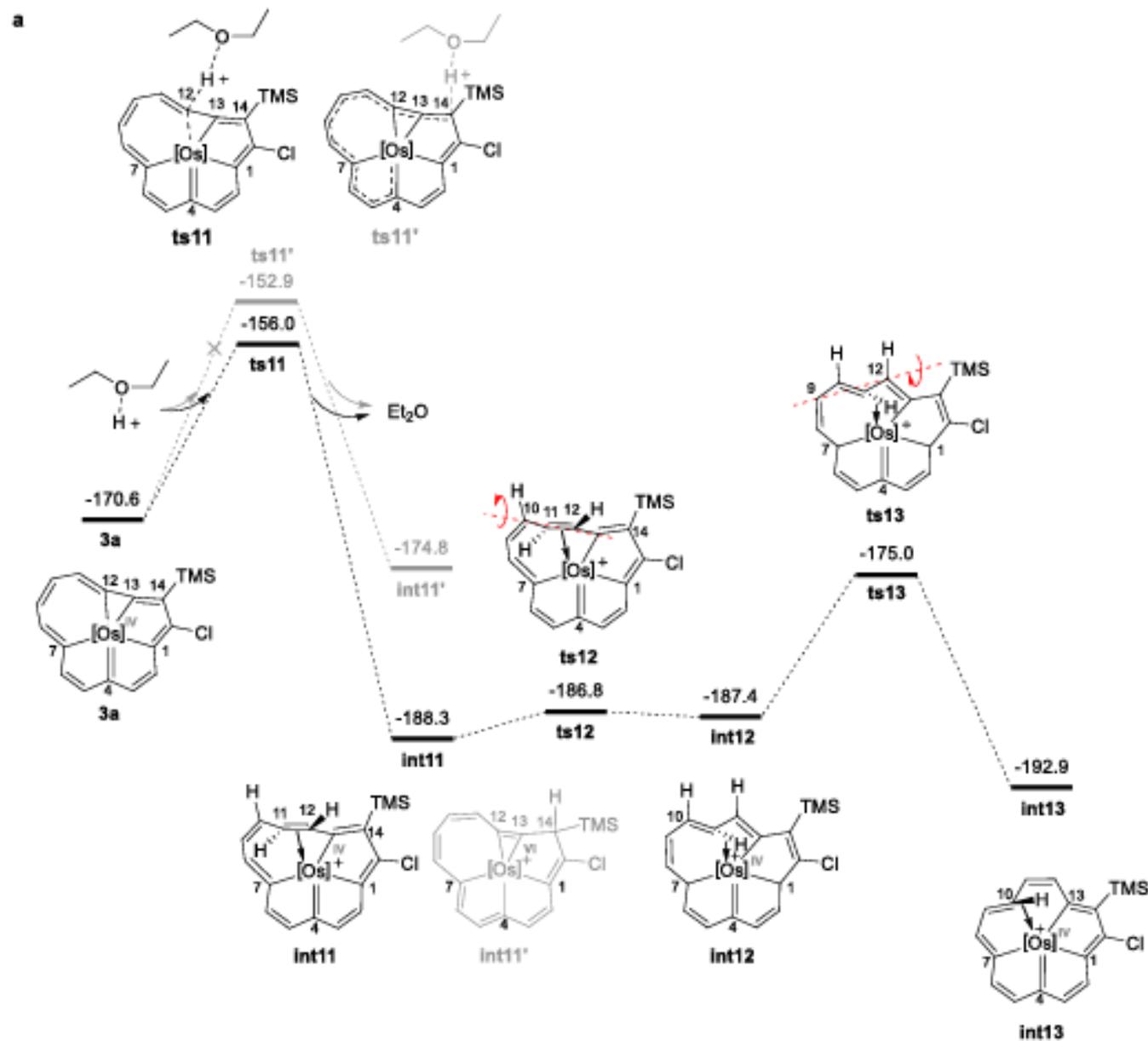
37



37

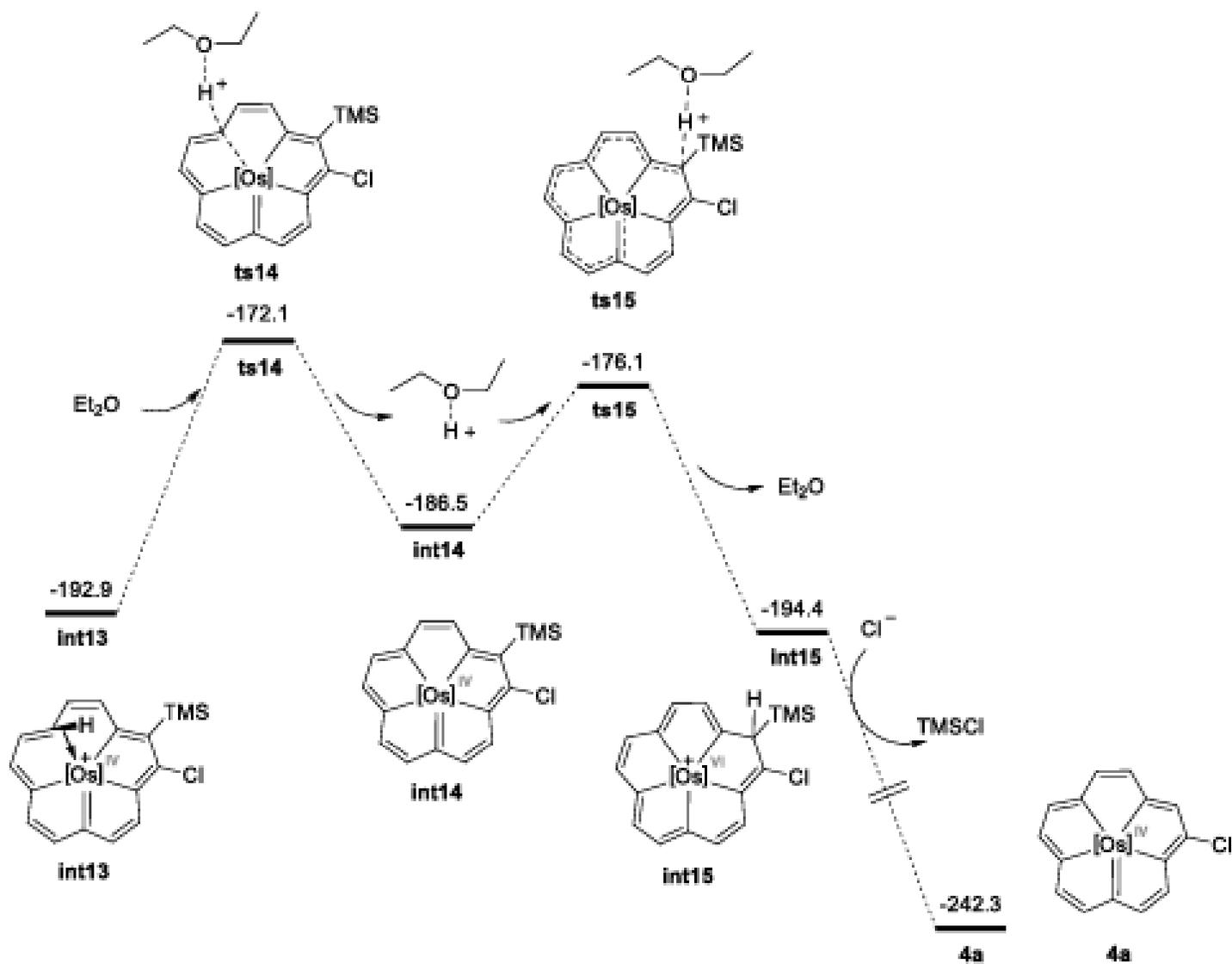


37

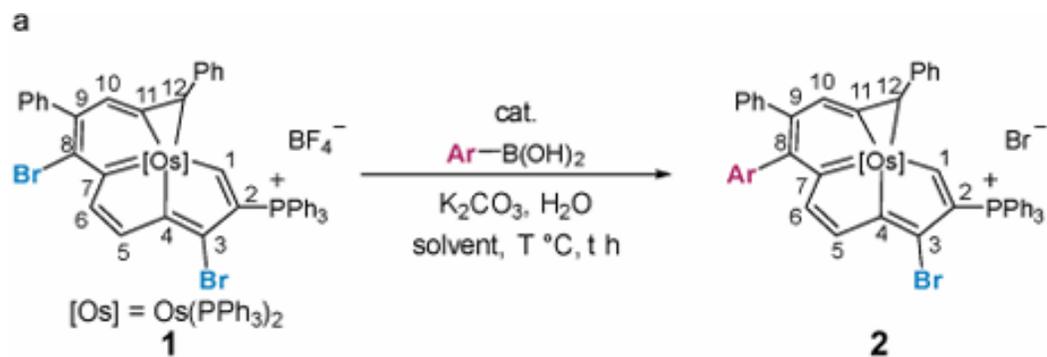


37

b



39



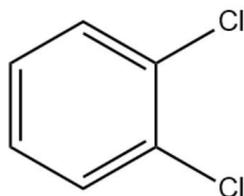
entry	cat.	solvent	t (h)	T (°C)	yield (%)
1	Pd(PPh ₃) ₄	<i>o</i> -DCB	24	65	0
2	Pd(dba) ₂	<i>o</i> -DCB	24	65	0
3	Pd(OAc) ₂	<i>o</i> -DCB	24	65	0
4	Pd ₂ (dba) ₃	<i>o</i> -DCB	24	25	0
5	Pd ₂ (dba) ₃	<i>o</i> -DCB	24	65	92
6	Pd ₂ (dba) ₃	<i>o</i> -DCB	8	80	82
7*	Pd ₂ (dba) ₃	<i>o</i> -DCB	24	65	0
8	Pd ₂ (dba) ₃	CB	24	65	20
9	Pd ₂ (dba) ₃	1,4-dioxane	24	65	0

Reaction conditions: **1** (0.1 mmol), **Ar** = 4-methoxyphenyl (0.35 mmol), catalyst (10 mol% [Pd]), K₂CO₃ (0.2 mmol), solvent (5.0 mL). *Ligands: P(*t*Bu)₃/P(*o*-tol)₃/PPh₃/DPPF/Sphos/BIPHEP.

d

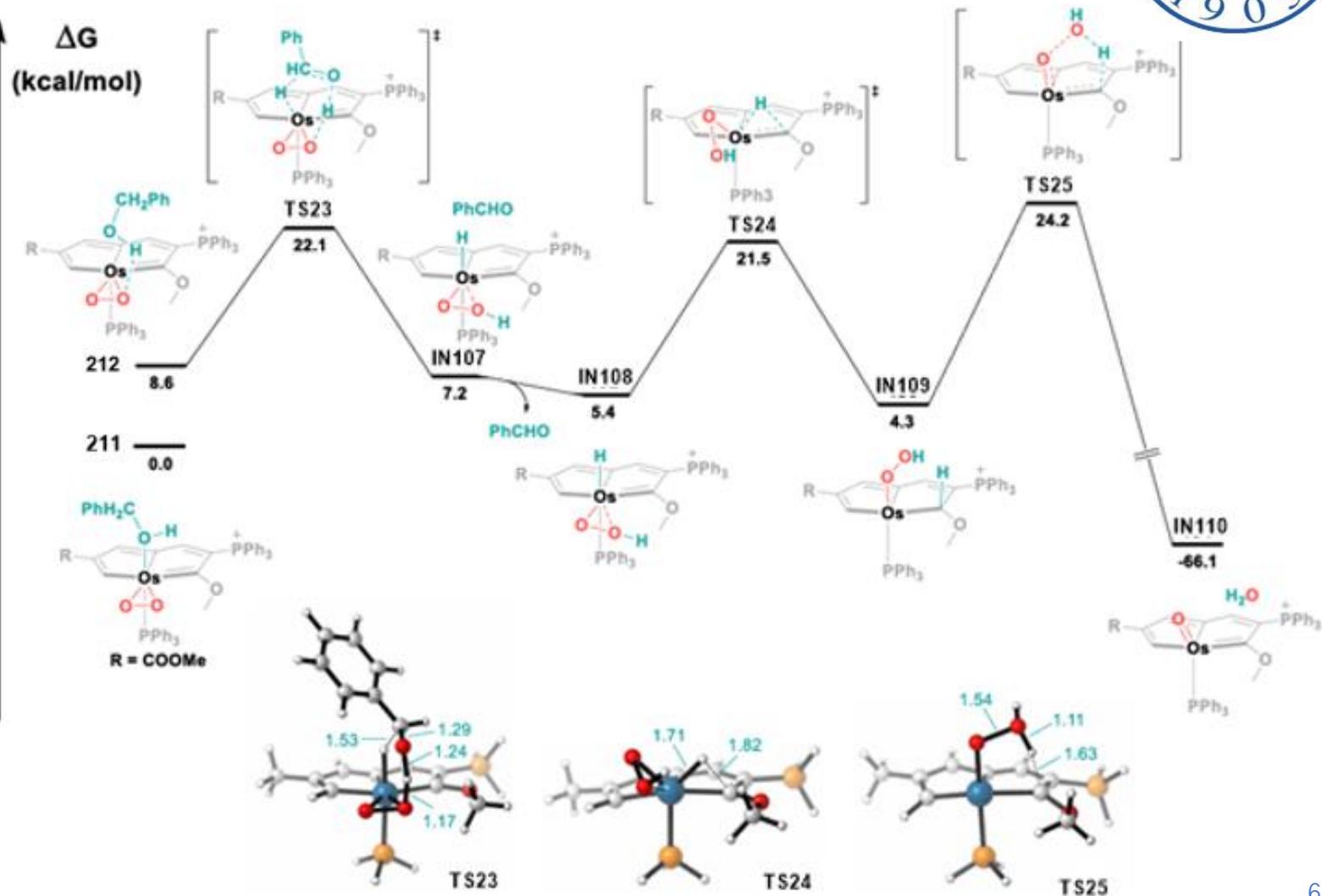
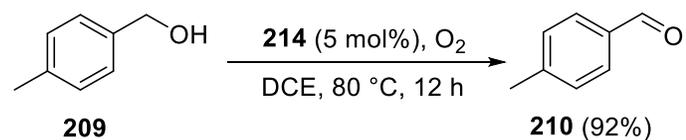
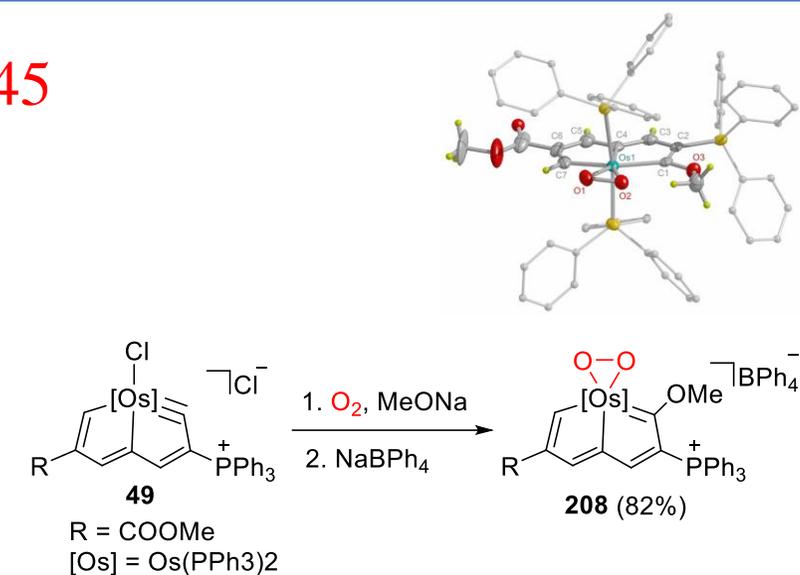
entry	substrate (Ar)	product	yield (%)
1	phenyl	2a	90
2	<i>p</i> -tolyl	2b	85
3	4-ethylphenyl	2c	82
4	4-butylphenyl	2d	87
5	4-isopropylphenyl	2e	83
6	4-(<i>tert</i> -butyl)phenyl	2f	85
7	4-methoxyphenyl	2g	92
8	4-(diphenylamino)phenyl	2h	88
9	4-fluorophenyl	2i	87
10	naphthalen-2-yl	2j	81

Standard conditions: **1** (0.1 mmol), substrate (**Ar**) (0.35 mmol), Pd₂(dba)₃ (10 mol% [Pd]), K₂CO₃ (0.2 mol), *o*-DCB (5.0 mL), t, 24 h, T, 65 °C.

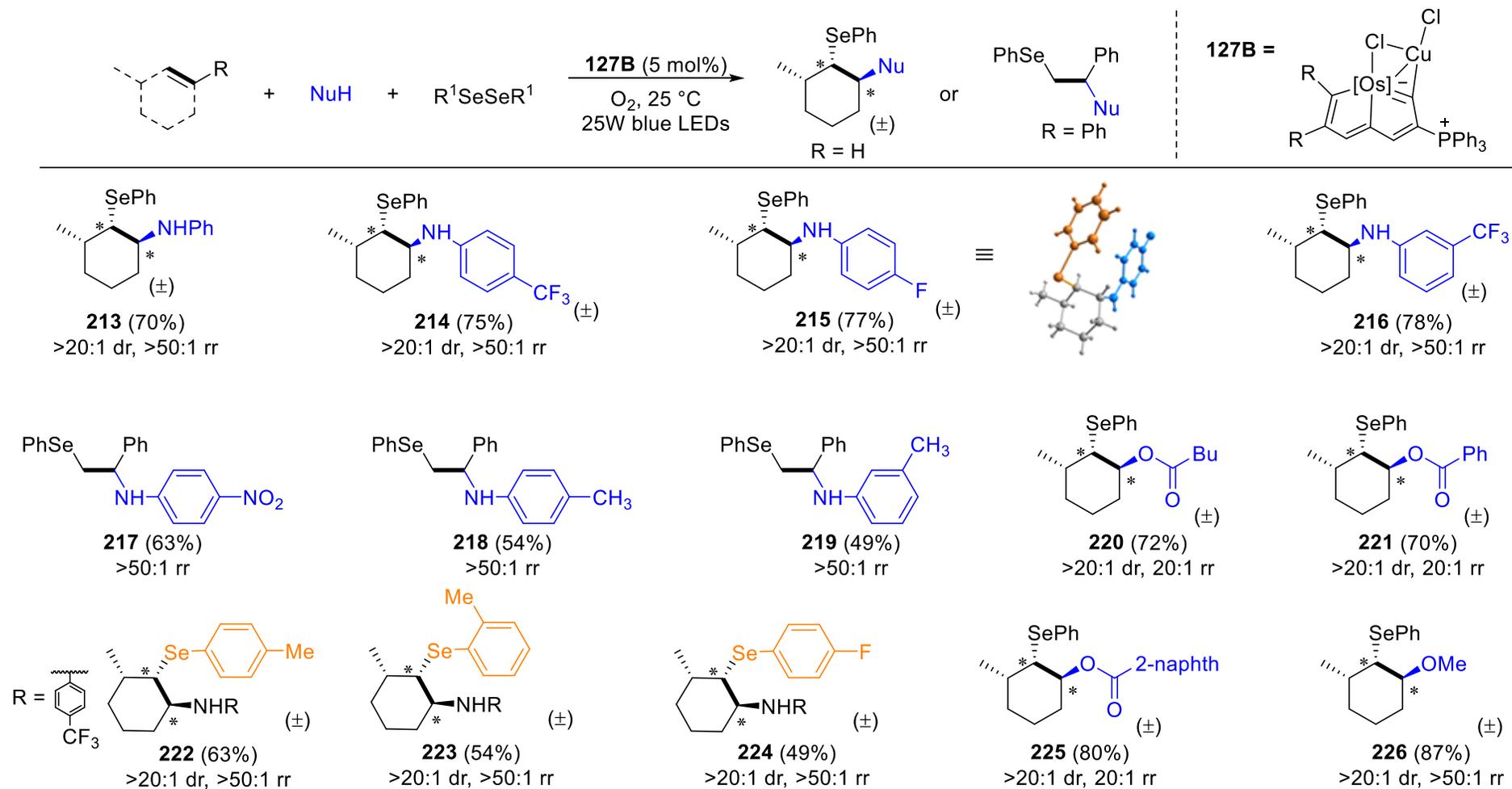


4、 Supporting Information

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3.2 碳龙催化烯炔双官能团化

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Mechanism:

