Literature Report

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Palladium(II)-Catalyzed Direct Carboxylation of Alkenyl C–H Bonds with CO_2

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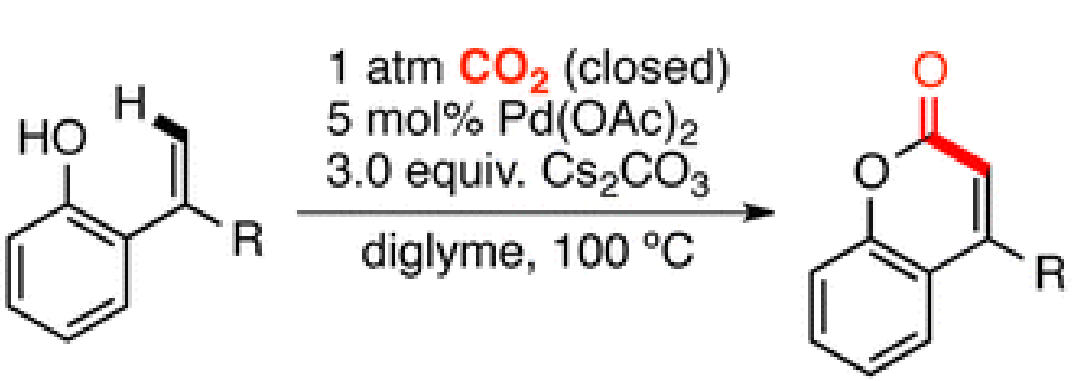
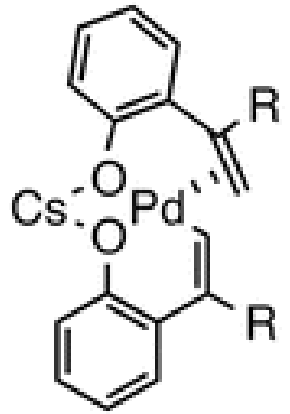
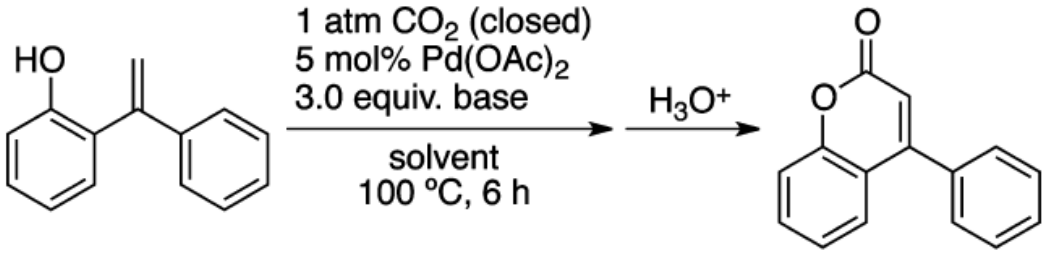


Direct Alkenyl C-H Carboxylation with CO_2

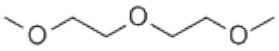


Key intermediate

Screening of Reaction Conditions



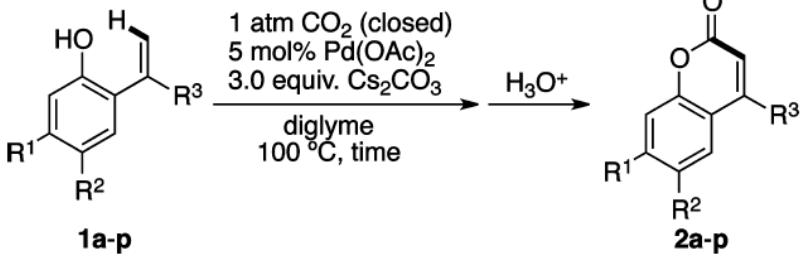
1a **2a**



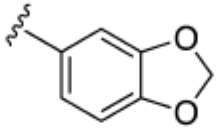
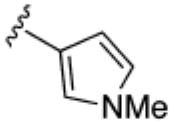
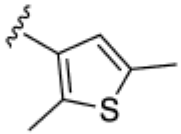
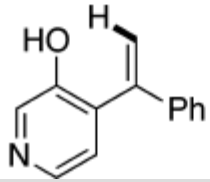
entry	solvent	base	**2a** (%)[a]	**1a** (%)[a]
1	diglyme	none	0	quant.
2	diglyme	LiO*t*-Bu	2	96
3	diglyme	KO*t*-Bu	16	75
4	diglyme	K_2CO_3	0	quant.
5	diglyme	$CsOH{\cdot}H_2O$	0	98
6	diglyme	Cs_2CO_3	86[b]	8
7	cyclooctane	Cs_2CO_3	80	14
8	1,4-dioxane	Cs_2CO_3	72	24
9	DMF	Cs_2CO_3	73	16
10	DMSO	Cs_2CO_3	69	25

[a]Based on ^1H NMR. [b]Isolated yield.

Generality

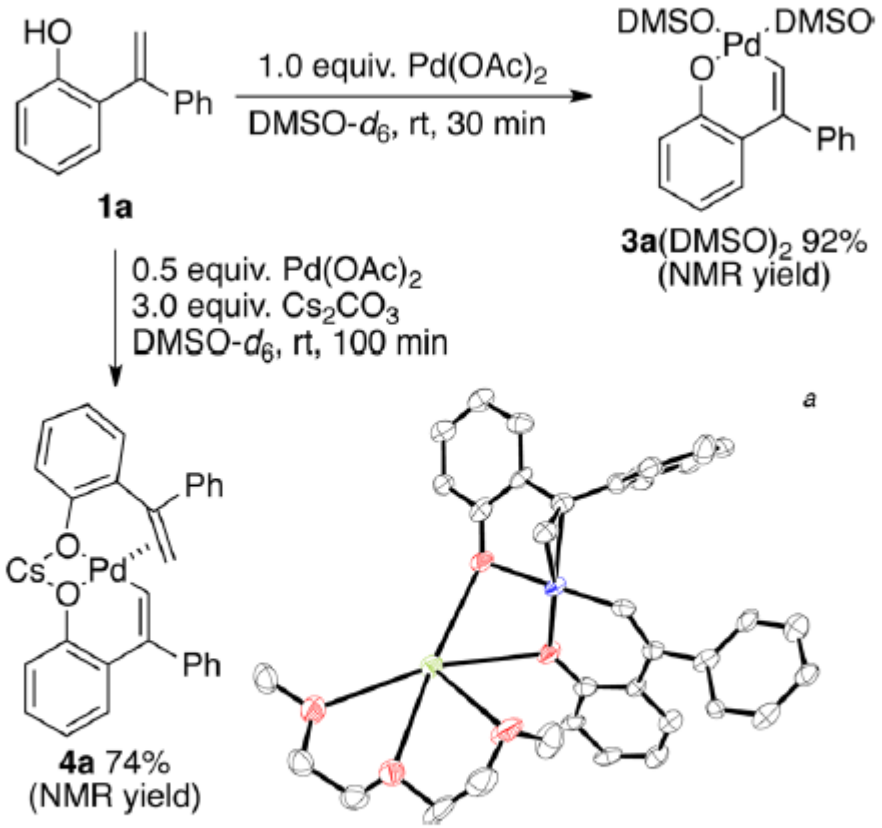


1a-p **2a-p**

Entry	R^1	R^2	R^3		time	Yield
1	H	H	Ph	**1a**	8 h	**2a** 86%
2			*p*-$MeOC_6H_4$	**1b**	7 h	**2b** 83%
3			*p*-MeC_6H_4	**1c**	12 h	**2c** 82%
4			*o*-MeC_6H_4	**1d**	18 h	**2c** 78%
5			*p*-$CF_3C_6H_4$	**1e**	6 h	**2e** 81%
6			*p*-NCC_6H_4	**1f**	6 h	**2f** 90%
7				**1g**	7 h	**2g** 88%
8				**1h**	6 h	**2h** 74%
9				**1i**	10 h	**2i** 81%
10			*p*-BrC_6H_4	**1j**	4 h	**2j** 82%
11[a]			Me	**1k**	10 h	**2k** 83%
12			H	**1l**	8 h	**2l** 73%
13	MeO	H	Ph	**1m**	6 h	**2m** 84%
14[b]	H	MeO	Ph	**1n**	12 h	**2n** 80%
15[b]	H	Me	Ph	**1o**	12 h	**2o** 75%
16[c]				**1p**	15 h	**2p** 50%

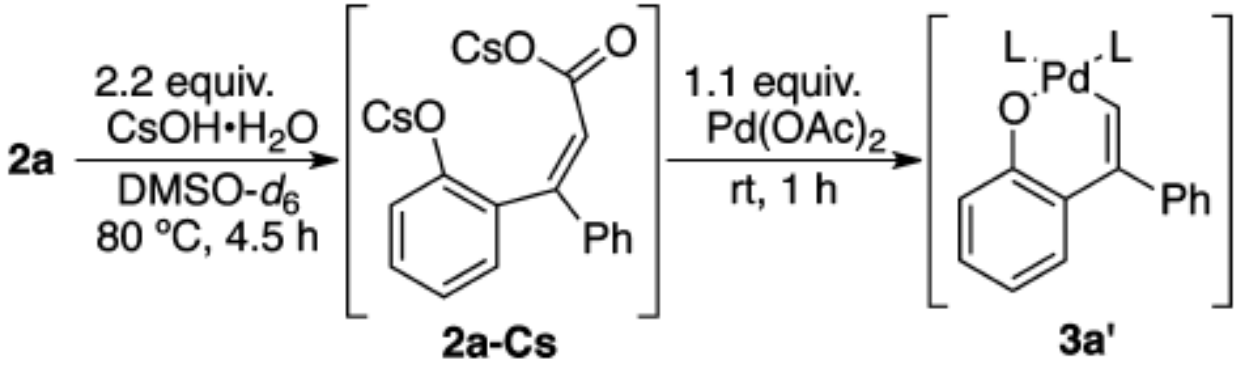
[a]Cyclooctane was used as solvent. [b]7.5 mol % of $Pd(OAc)_2$ employed. [c]10 mol % of $Pd(OAc)_2$ was employed.

Formation of Alkenylpalladium Complexes

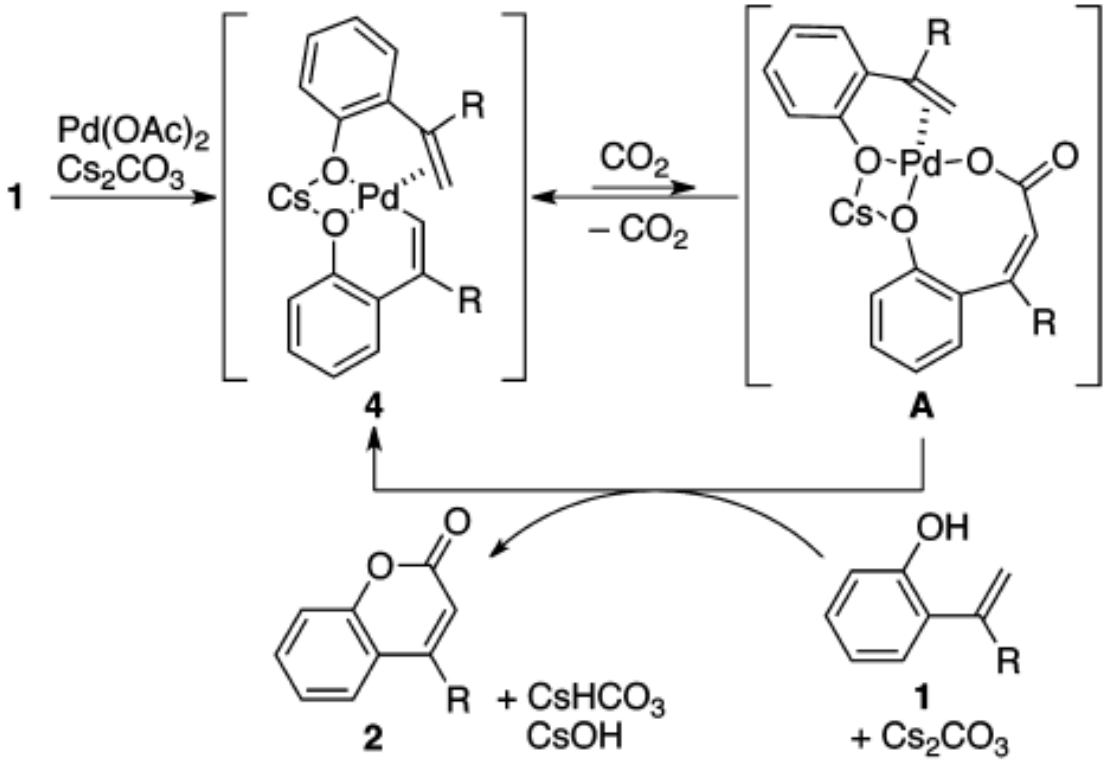


[a]ORTEP diagram of alkenylpalladium complex **4a·diglyme** at the 50% probability level (H atoms have been omitted for clarity). The diagram shows half of a dimerized symmetric structure.

Decarboxylation of Pd Carboxylate Complexes



Proposed Mechanism



Acknowledgment

- Prof. Jing Zhao
- Everyone in F-302

Thanks for your listening!