Supplementary Information

Data-Driven Discovery of Active Phosphine Ligand Space for Cross-Coupling Reaction

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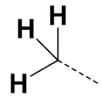
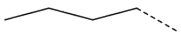
Me	Et	n-Pr	i-Pr	n-Pe	n-Bu
					
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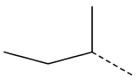		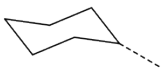	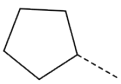	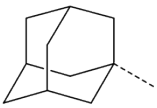	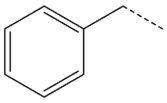
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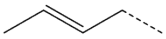	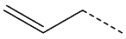				
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			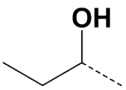	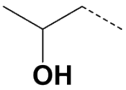	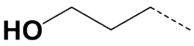
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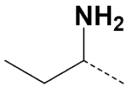	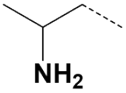	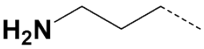		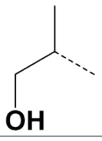	
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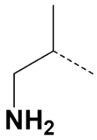	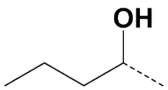	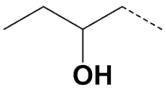	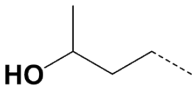	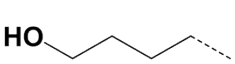	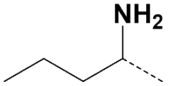
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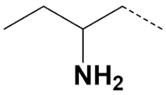	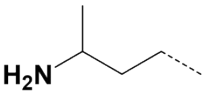	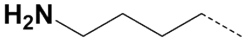	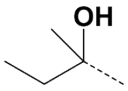		
iBu1NH2	**iBu2NH2**	**iBu3NH2**	**tBuOH**	**tBuNH2**	**BMeN**
BEtN	**BiPrN**	**BnPrN**	**MeEtN**	**MePhN**	**EtPhN**
nPrPhN	**BPhN**	**OMe**	**OEt**	**OPr**	**OPh**
OiPr	**OnBu**	**O2nBu**	**OiBu**	**OtBu**	**Ph**

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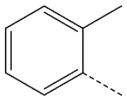

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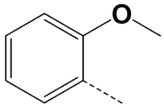

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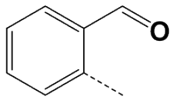

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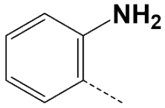

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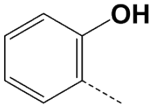

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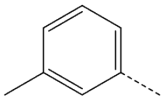

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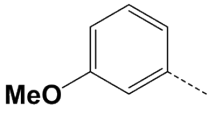

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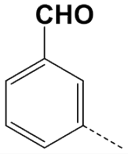

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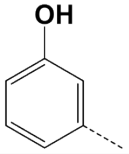

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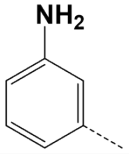

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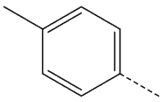

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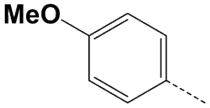

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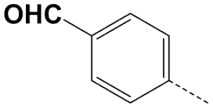

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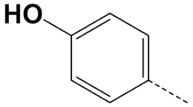

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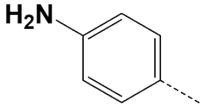

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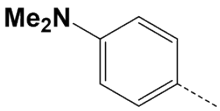

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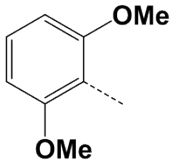

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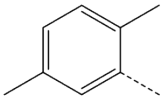

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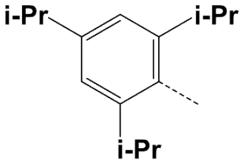

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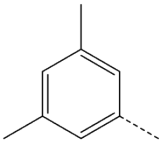

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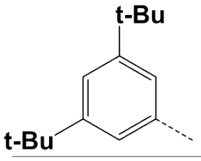

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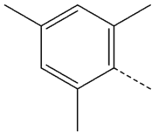

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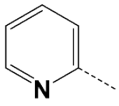

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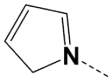

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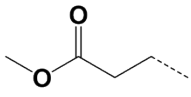

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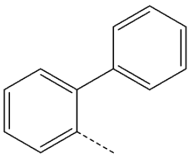

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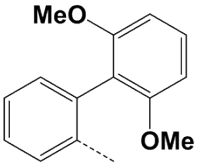

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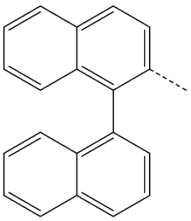

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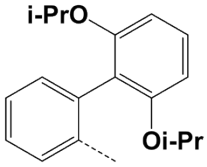
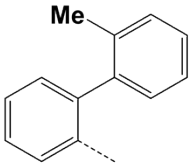
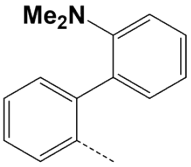


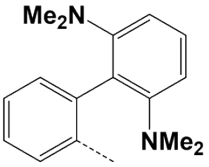
2MeBPh



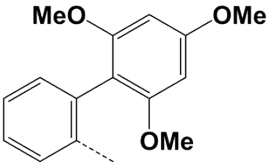
22MeNBPh



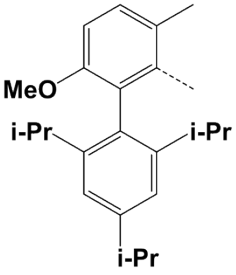
26B2MeNBPh



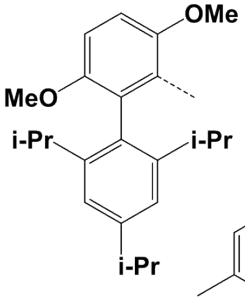
TOMeBPh



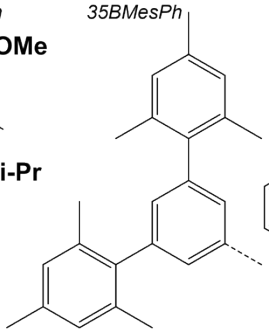
3OMe6Me2TRIPPh



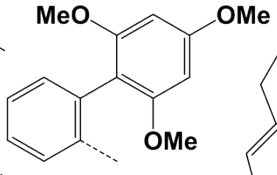
36OMe2TRIPPh



35BMesPh



TOMeBPh



Trop

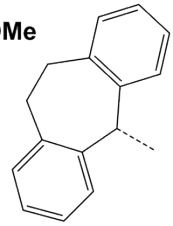


Figure S1. The substitution groups for P-ligand construction and their abbreviation name in MPCD.

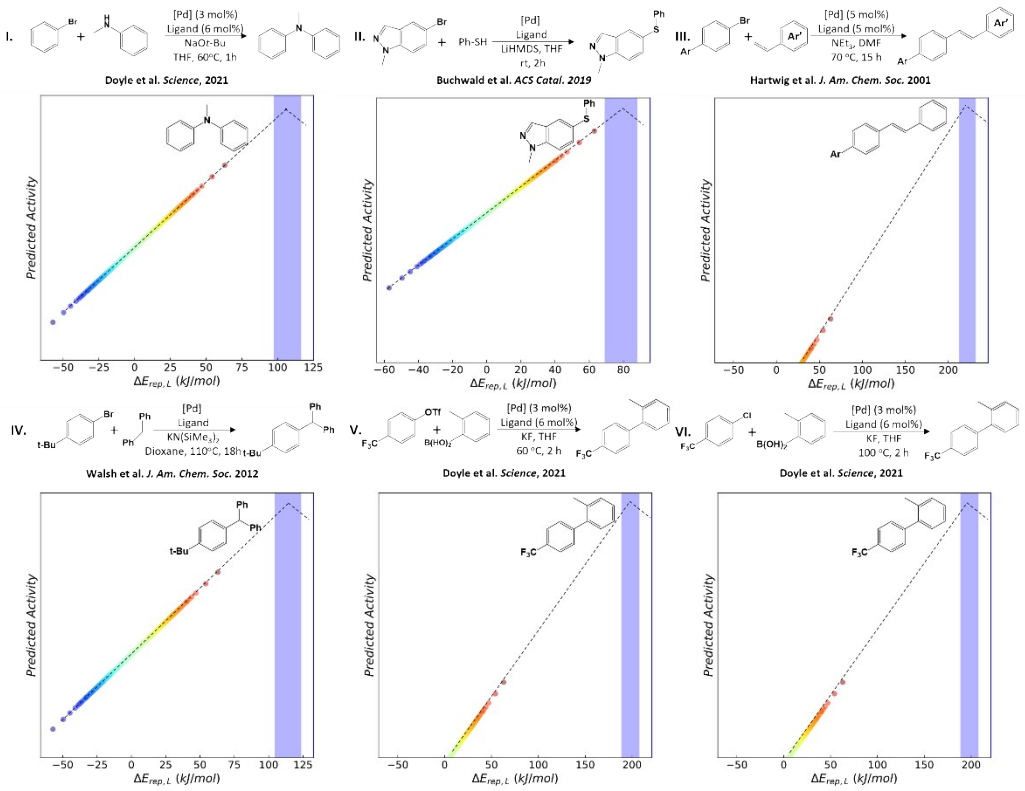


Figure S2. The MPCD-based volcano plot analysis for Pd catalyzed cross-coupling reactions with the coupling products as the key reaction species to match with P-ligand.

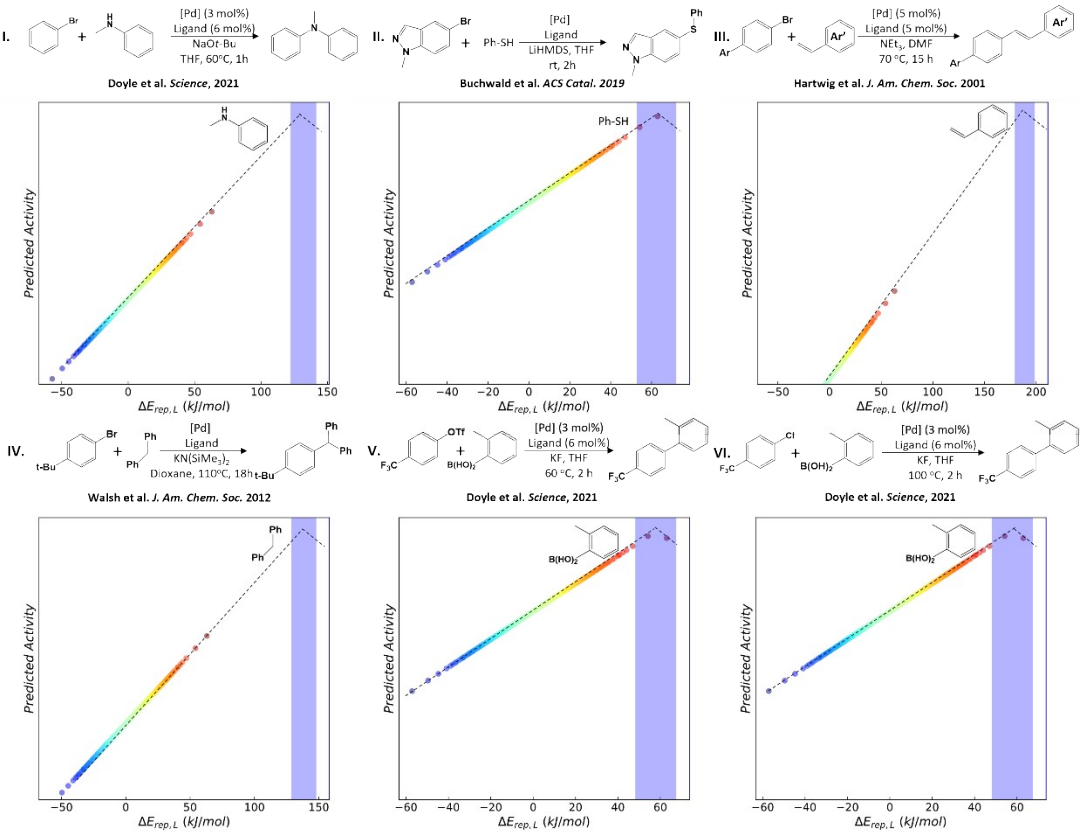


Figure S3. The MPCD-based volcano plot analysis for Pd catalyzed cross-coupling reactions with the coupling partners as the key reaction species to match with P-ligand.

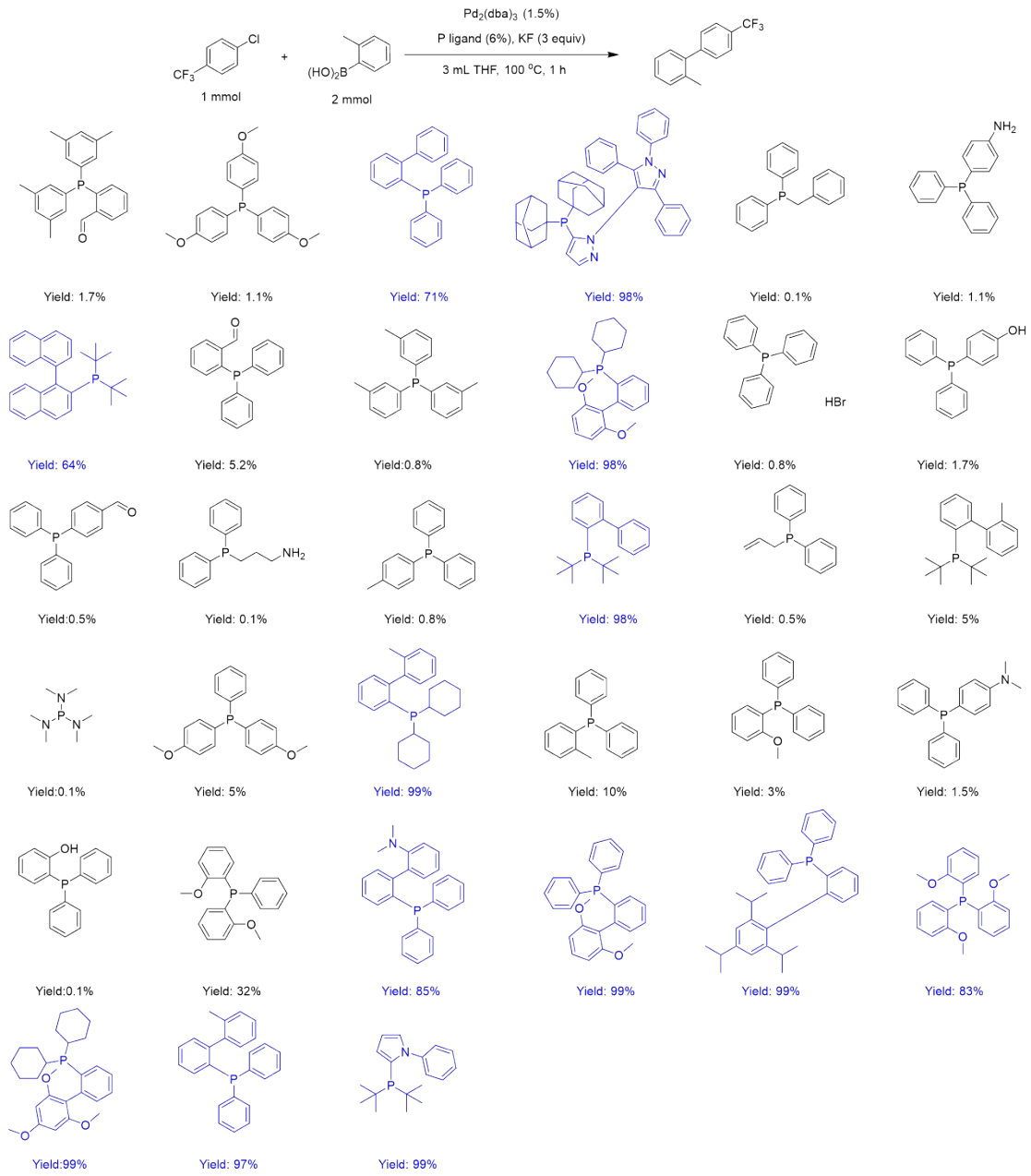


Figure S4. The product yield of reaction VI catalyzed by different P-ligands.

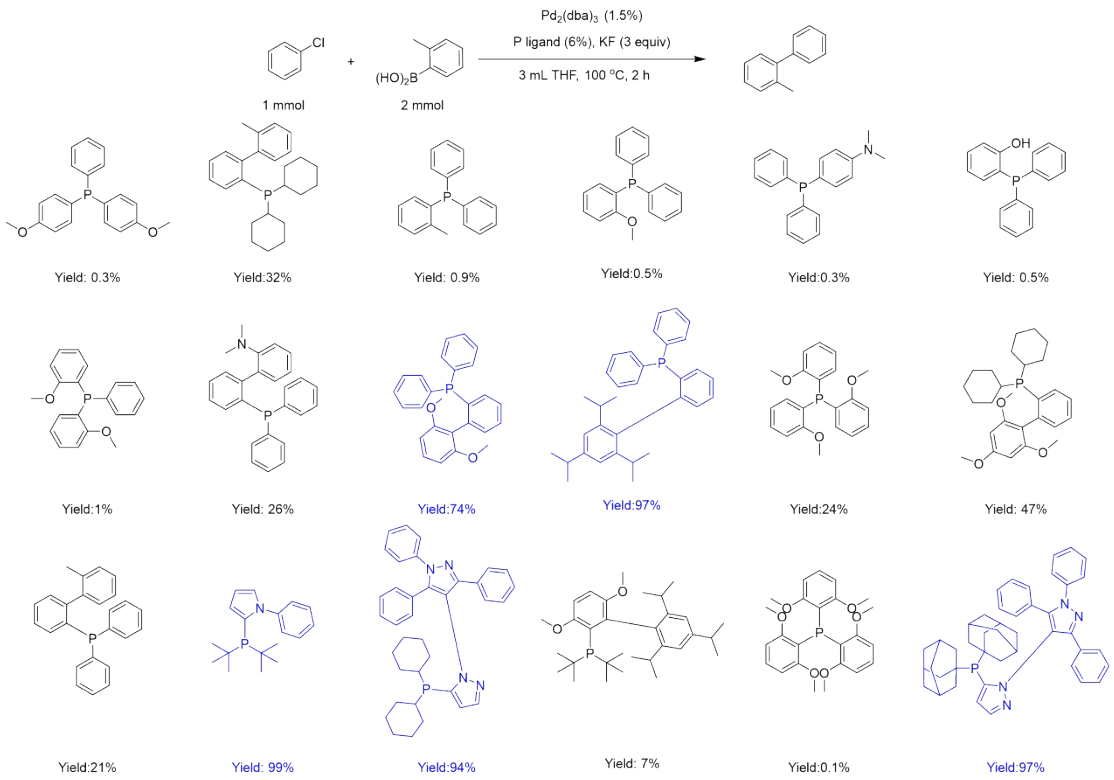


Figure S5. The product yield of reaction VII catalyzed by different P-ligands.

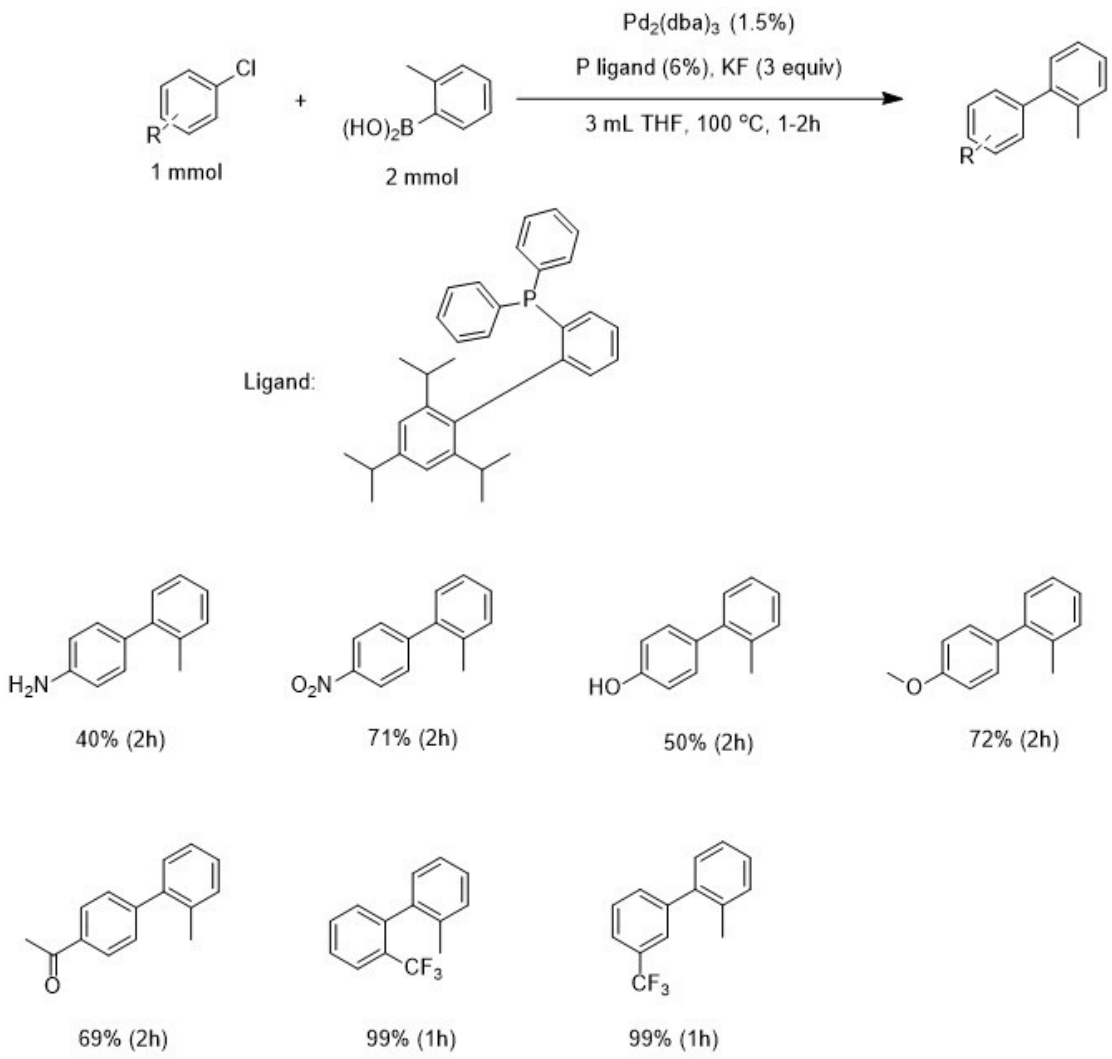


Figure S6. Scope of the Pd-catalyzed Suzuki-Miyaura coupling reaction between different aryl chloride and *o*-tolylboronic acid.

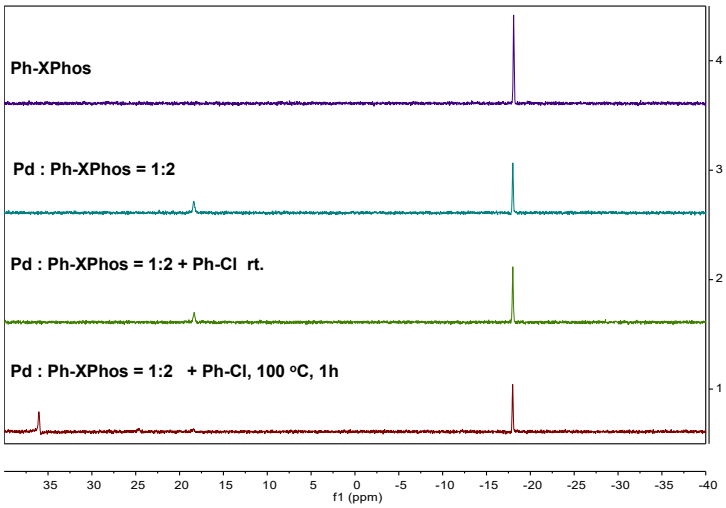


Figure S7. The ^{31}P NMR spectrum of Ph-XPhos during the activation of PhCl.

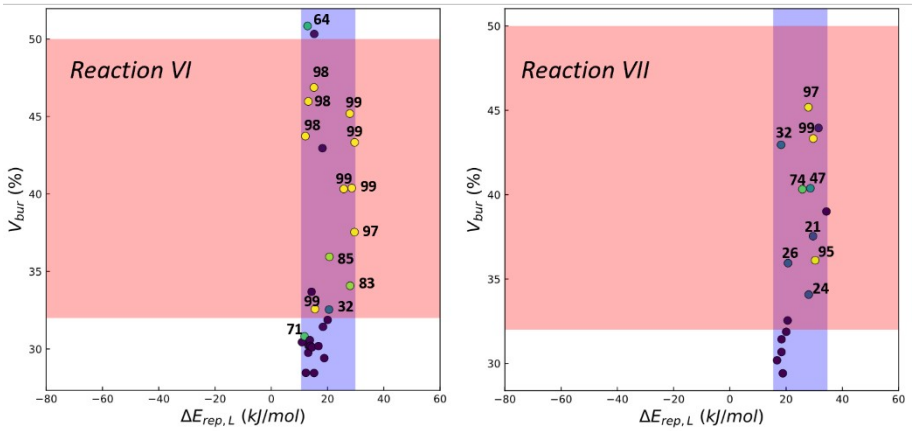


Figure S8. The V_{bur} Threshold and $\Delta E_{rep,L}$ analysis of reaction activity for reaction VI and VII. The reaction activities larger than 20 % are labeled in the plot.

Experimental standard curves

The standard curves were drawn through mixing biphenyls and dodecane as internal standard with various mass concentrations. m(i): mass of biphenyls, m(s): mass of internal standard (dodecane), A(i): peak area of biphenyls, A(s): peak area of internal standard (dodecane), k: correction factor. After correct the data, the yields of biphenyls in the reaction were calibrated.

$$\frac{m(i)}{m(s)} = k\frac{A(i)}{A(s)} \quad (1)$$

$$\text{Yield } (\%) = \frac{Yields\ of\ biphenyls}{\text{Theoretical yield}} \times 100\% \quad (2)$$

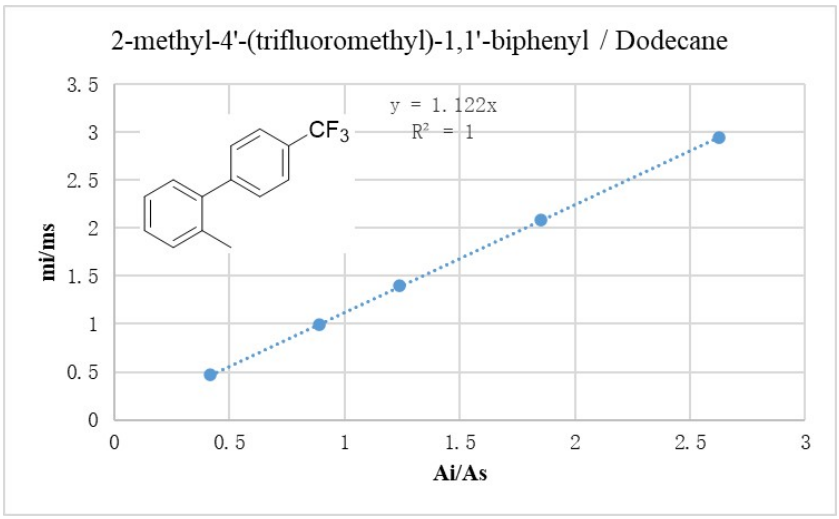


Figure S9. Standard curves for 2-methyl-4'-(trifluoromethyl)-1,1'-biphenyl and dodecane.

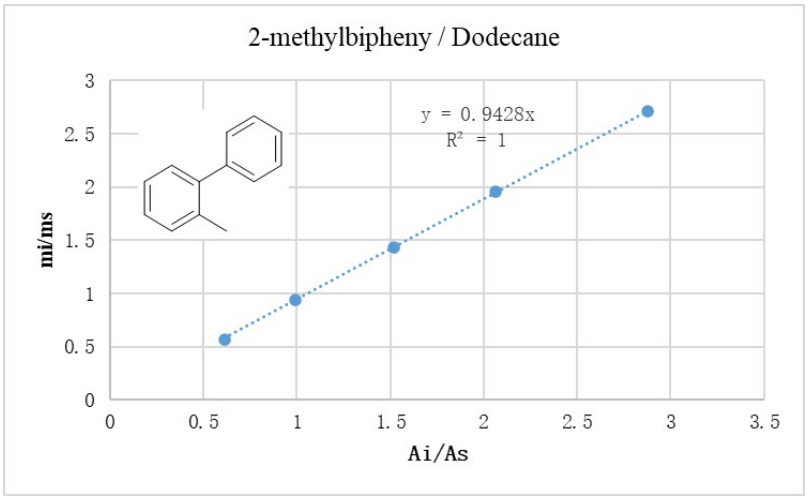


Figure S10. Standard curves for 2-methylbiphenyl and dodecane.

Table S1. The $\Delta E_{rep}(R)$ values of common molecules.

Molecule	$\Delta E_{rep}(R)$ (kJ/mol)
CO	-26.1
PhI	-6.8
p-*t*-Bu-PhBr	2.9
p-Et-PhBr	3.9
PhBr	4.8
p-CF_3-PhOTf	5.8
2,6-bi-Me-PhBr	5.8
2,4-bi-Cl-Pyridine	9.6
m-CN-PhCl	17.4
p-CN-PhCl	18.3
p-COOEt-PhCl	19.3
p-CF_3-PhCl	20.3
PhCl	25.1
C_2H_2	28.0
C_2H_4	32.8

Table S2. The $\Delta E_{rep}(L)$ values of commercially available P-ligands with Pd in MPCD.

name	G1	G2	G3	$\Delta E_{rep}(L)$ (kJ/mol)
P_Cy_Cy_Cy	Cy	Cy	Cy	-28.0
P_n_Bu_n_Bu_n_Bu	n_Bu	n_Bu	n_Bu	-23.2
P_Cy_o_Tol_o_Tol	o_Tol	Cy	o_Tol	-18.3
P_Cy_Cy_Et	Et	Cy	Cy	-16.4
P_t_Bu_t_Bu_TiPrBPh	t_Bu	TiPrBPh	t_Bu	-10.6
P_Cy_Cy_Ph	Ph	Cy	Cy	-8.7
P_Ph_OMe_OMe	OMe	Ph	OMe	-8.7
P_n_Bu_Adm_Adm	n_Bu	Adm	Adm	-8.7
P_Et_Et_Et	Et	Et	Et	-7.7
P_Cy_Cy_p_Tol	p_Tol	Cy	Cy	-6.8
P_Cy_Cy_Bn	Bn	Cy	Cy	-6.8
P_36OMe2TRIPPh_Cy_Cy	36OMe2TRIPPh	Cy	Cy	-5.8
P_Cy_4NMe2Ph_4NMe2Ph	Cy	4NMe2Ph	4NMe2Ph	-5.8
P_Ph_nPr3NH2_nPr3NH2	nPr3NH2	Ph	nPr3NH2	-3.9
P_t_Bu_t_Bu_n_Bu	n_Bu	t_Bu	t_Bu	-3.9
P_Cyp_Cyp_Cyp	Cyp	Cyp	Cyp	-3.9
P_t_Bu_t_Bu_t_Bu	t_Bu	t_Bu	t_Bu	-3.9
P_Adm_Adm_Adm	Adm	Adm	Adm	-2.9
P_iPr_iPr_iPr	iPr	iPr	iPr	-2.9
P_Cy_t_Bu_t_Bu	t_Bu	Cy	t_Bu	-1.9
P_Cy_Cy_o_Tol	o_Tol	Cy	Cy	-1.9
P_iPr_iPr_Ph	Ph	iPr	iPr	-1.9
P_MeOH_MeOH_MeOH	MeOH	MeOH	MeOH	0.0
P_Et_Et_Ph	Et	Ph	Et	1.0
P_Me_t_Bu_t_Bu	Me	t_Bu	t_Bu	1.0
P_Me_Me_Ph	Me	Ph	Me	1.0
P_Cy_Cy_4NMe2Ph	4NMe2Ph	Cy	Cy	1.9
P_Cy_Cy_25BMePh	Cy	25BMePh	Cy	1.9
P_Cy_BPh_Cy	BPh	Cy	Cy	1.9
P_Ph_Ph_OEt	OEt	Ph	Ph	1.9
P_Bn_Bn_Bn	Bn	Bn	Bn	2.9
P_Adm_Adm_oPhNH2	Adm	oPhNH2	Adm	2.9
P_Adm_Bn_Adm	Bn	Adm	Adm	2.9
P_Cy_Ph_Ph	Cy	Ph	Ph	2.9
P_Cy_35Bt_BuPh_35Bt_BuPh	Cy	35Bt_BuPh	35Bt_BuPh	3.9
P_TiPrBPh_Cy_Cy	TiPrBPh	Cy	Cy	3.9
P_Ph_m_Tol_m_Tol	Ph	m_Tol	m_Tol	3.9
P_iPr_Ph_Ph	iPr	Ph	Ph	4.8
P_Et_Ph_Ph	Et	Ph	Ph	4.8
P_25BMePh_25BMePh_25BMePh	25BMePh	25BMePh	25BMePh	4.8
P_Cy_Cy_BNap	BNap	Cy	Cy	4.8
P_BNap_35Bt_BuPh_35Bt_BuPh	BNap	35Bt_BuPh	35Bt_BuPh	4.8

P_Ph_Ph_oPhNH2	oPhNH2	Ph	Ph	5.8
P_Ph_mPhNH2_mPhNH2	mPhNH2	Ph	mPhNH2	5.8
P_Cy_Cy_1PhIn	1PhIn	Cy	Cy	5.8
P_Ph_t_Bu_t_Bu	Ph	t_Bu	t_Bu	5.8
P_t_Bu_t_Bu_22MeNBPh	22MeNBPh	t_Bu	t_Bu	5.8
P_Ph_OEt_OEt	Ph	OEt	OEt	5.8
P_iPr_iPr_1PhPyr	1PhPyr	iPr	iPr	6.8
P_t_Bu_t_Bu_TPhBPyz	TPhBPyz	t_Bu	t_Bu	6.8
P_Me_Ph_Ph	Me	Ph	Ph	6.8
P_o_CHOPh_o_CHOPh_o_CHOPh	o_CHOPh	o_CHOPh	o_CHOPh	6.8
P_t_Bu_t_Bu_4NMe2Ph	4NMe2Ph	t_Bu	t_Bu	6.8
P_Ph_Ph_Et2NH2	Et2NH2	Ph	Ph	6.8
P_pPhOH_pPhOH_pPhOH	pPhOH	pPhOH	pPhOH	6.8
P_35Bt_BuPh_35Bt_BuPh_35Bt_BuPh	35Bt_BuPh	35Bt_BuPh	35Bt_BuPh	7.7
P_pPhNH2_pPhNH2_pPhNH2	pPhNH2	pPhNH2	pPhNH2	7.7
P_o_Tol_o_Tol_o_Tol	o_Tol	o_Tol	o_Tol	7.7
P_p_Tol_p_Tol_o_CHOPh	o_CHOPh	p_Tol	p_Tol	7.7
P_Ph_Ph_OMe	OMe	Ph	Ph	8.7
P_m_OMePh_m_OMePh_m_OMePh	m_OMePh	m_OMePh	m_OMePh	8.7
P_p_Tol_p_Tol_p_Tol	p_Tol	p_Tol	p_Tol	8.7
P_Ph_o_CHOPh_o_CHOPh	o_CHOPh	Ph	o_CHOPh	8.7
P_Ph_Ph_n_Pr	n_Pr	Ph	Ph	8.7
P_4NMe2Ph_4NMe2Ph_4NMe2Ph	4NMe2Ph	4NMe2Ph	4NMe2Ph	9.6
P_Cy_Cy_26B2MeNBPh	Cy	26B2MeNBPh	Cy	9.6
P_35BMePh_35BMePh_35BMePh	35BMePh	35BMePh	35BMePh	9.6
P_Cy_Cy_Mes	Mes	Cy	Cy	9.6
P_t_Bu_t_Bu_1PhIn	1PhIn	t_Bu	t_Bu	10.6
P_Ph_Ph_t_Bu	t_Bu	Ph	Ph	10.6
P_35BMePh_35BMePh_o_CHOPh	o_CHOPh	35BMePh	35BMePh	10.6
P_p_OMePh_p_OMePh_p_OMePh	p_OMePh	p_OMePh	p_OMePh	10.6
P_t_Bu_Adm_Adm	t_Bu	Adm	Adm	10.6
P_Ph_BPh_Ph	BPh	Ph	Ph	11.6
P_mPhOH_mPhOH_mPhOH	mPhOH	mPhOH	mPhOH	11.6
P_TPhBPyz_Adm_Adm	TPhBPyz	Adm	Adm	12.5
P_Ph_Ph_Bn	Bn	Ph	Ph	12.5
P_Ph_Ph_mPhNH2	mPhNH2	Ph	Ph	12.5
P_t_Bu_t_Bu_BNap	BNap	t_Bu	t_Bu	12.5
P_Ph_Ph_o_CHOPh	o_CHOPh	Ph	Ph	12.5
P_m_Tol_m_Tol_m_Tol	m_Tol	m_Tol	m_Tol	13.5
P_Cy_Cy_BOMeBPh	Cy	BOMeBPh	Cy	13.5
P_Ph_Ph_Ph	Ph	Ph	Ph	13.5
P_Ph_Ph_m_CHOPh	m_CHOPh	Ph	Ph	13.5
P_Ph_p_Tol_p_Tol	p_Tol	Ph	p_Tol	13.5
P_Ph_Ph_pPhOH	pPhOH	Ph	Ph	13.5

P_Ph_Ph_pCHOPh	Ph	pCHOPh	Ph	13.5
P_Ph_Ph_nPr3NH2	nPr3NH2	Ph	Ph	14.5
P_o_OMePh_o_OMePh_o_CHOPh	o_CHOPh	o_OMePh	o_OMePh	14.5
P_Ph_Ph_p_Tol	p_Tol	Ph	Ph	14.5
P_t_Bu_t_Bu_BPh	BPh	t_Bu	t_Bu	15.4
P_Ph_Ph_Aly	Aly	Ph	Ph	15.4
P_t_Bu_t_Bu_2MeBPh	2MeBPh	t_Bu	t_Bu	15.4
P_BMeN_BMeN_BMeN	BMeN	BMeN	BMeN	15.4
P_Ph_p_OMePh_p_OMePh	Ph	p_OMePh	p_OMePh	16.4
P_Cy_Cy_2MeBPh	2MeBPh	Cy	Cy	18.3
P_Ph_Ph_o_Tol	o_Tol	Ph	Ph	18.3
P_Ph_Ph_o_OMePh	o_OMePh	Ph	Ph	18.3
P_t_Bu_t_Bu_BOMeBPh	t_Bu	BOMeBPh	t_Bu	18.3
P_Ph_Ph_4NMe2Ph	4NMe2Ph	Ph	Ph	19.3
P_Ph_Ph_oPhOH	oPhOH	Ph	Ph	20.3
P_Ph_o_OMePh_o_OMePh	Ph	o_OMePh	o_OMePh	20.3
P_22MeNBPh_Ph_Ph	22MeNBPh	Ph	Ph	20.3
P_Mes_Mes_Cyp	Mes	Cyp	Mes	24.1
P_Ph_Ph_BOMeBPh	Ph	BOMeBPh	Ph	26.1
P_Ph_Ph_TiPrBPh	TiPrBPh	Ph	Ph	28.0
P_o_OMePh_o_OMePh_o_OMePh	o_OMePh	o_OMePh	o_OMePh	28.0
P_TOMeBPh_Cy_Cy	TOMeBPh	Cy	Cy	28.9
P_Ph_Ph_2MeBPh	Ph	2MeBPh	Ph	29.9
P_t_Bu_t_Bu_1PhPyr	1PhPyr	t_Bu	t_Bu	29.9
P_Cy_Cy_TPhBPyz	TPhBPyz	Cy	Cy	29.9
P_t_Bu_t_Bu_36OMe2TRIPPh	36OMe2TRIPPh	t_Bu	t_Bu	31.8
P_26BOMePh_26BOMePh_26BOMePh	26BOMePh	26BOMePh	26BOMePh	34.7
P_Mes_Mes_Mes	Mes	Mes	Mes	35.7

Table S3. The predicted P-ligands for *p*-CF_3-PhCl activation via MPCD-based ALS and their reported catalytic performance in literature for Pd-catalyzed cross-coupling reaction.

	name	G1	G2	G3	$\Delta E_{rep}(L)$ (kJ/mol)	Vbur (%)	Price (CNY/g)	Yield (%)[a]
1	P_p_OMePh_p_OMePh_p_OMePh	p_OMePh	p_OMePh	p_OMePh	10.6	30.4	20	1
2	P_t_Bu_Adm_Adm	t_Bu	Adm	Adm	10.6	39.7		
3	P_Ph_BPh_Ph	BPh	Ph	Ph	11.6	30.8	21	71
4	P_mPhOH_mPhOH_mPhOH	mPhOH	mPhOH	mPhOH	11.6	29.8		
5	P_TPhBPyz_Adm_Adm	TPhBPyz	Adm	Adm	12.5	43.7	1871	98
6	P_Ph_Ph_Bn	Bn	Ph	Ph	12.5	28.5	40	0
7	P_Ph_Ph_mPhNH2	mPhNH2	Ph	Ph	12.5	30.6		
8	P_t_Bu_t_Bu_BNap	BNap	t_Bu	t_Bu	12.5	50.8	1097	64
9	P_m_Tol_m_Tol_m_Tol	m_Tol	m_Tol	m_Tol	13.5	29.8	10	1
10	P_Cy_Cy_BOMeBPh	Cy	BOMeBPh	Cy	13.5	46.0	24	98
11	P_Ph_Ph_Ph	Ph	Ph	Ph	13.5	30.2		
12	P_Ph_Ph_Ph	Ph	Ph	Ph	13.5	30.2	1	0
13	P_Ph_p_Tol_p_Tol	p_Tol	Ph	p_Tol	13.5	30.0		
14	P_Ph_Ph_pPhOH	pPhOH	Ph	Ph	13.5	30.6	2203	2
15	P_Ph_Ph_pCHOPh	Ph	pCHOPh	Ph	13.5	30.2	1098	0
16	P_Ph_Ph_nPr3NH2	nPr3NH2	Ph	Ph	14.5	33.7	640	0
17	P_Ph_Ph_p_Tol	p_Tol	Ph	Ph	14.5	30.1	10	0
18	P_t_Bu_t_Bu_BPh	BPh	t_Bu	t_Bu	15.4	46.9	30	98
19	P_Ph_Ph_Aly	Aly	Ph	Ph	15.4	28.4	289	0
20	P_t_Bu_t_Bu_2MeBPh	2MeBPh	t_Bu	t_Bu	15.4	50.3	33	5
21	P_BMeN_BMeN_BMeN	BMeN	BMeN	BMeN	15.4	32.6	10	0
22	P_Ph_p_OMePh_p_OMePh	Ph	p_OMePh	p_OMePh	16.4	30.2	103	0
23	P_Cy_Cy_2MeBPh	2MeBPh	Cy	Cy	18.3	43.0	28	99
24	P_Ph_Ph_o_Tol	o_Tol	Ph	Ph	18.3	30.7	76	10
25	P_Ph_Ph_o_OMePh	o_OMePh	Ph	Ph	18.3	31.4	286	3
26	P_t_Bu_t_Bu_BOMeBPh	t_Bu	BOMeBPh	t_Bu	18.3	51.4		
27	P_Ph_Ph_4NMe2Ph	4NMe2Ph	Ph	Ph	19.3	29.4	20	2
28	P_Ph_Ph_oPhOH	oPhOH	Ph	Ph	20.3	31.9	359	0
29	P_Ph_o_OMePh_o_OMePh	Ph	o_OMePh	o_OMePh	20.3	32.5	123	32
30	P_22MeNBPh_Ph_Ph	22MeNBPh	Ph	Ph	20.3	35.9	35	85
31	P_Mes_Mes_Cyp	Mes	Cyp	Mes	24.1	41.4		
32	P_Ph_Ph_BOMeBPh	Ph	BOMeBPh	Ph	26.1	40.3	46	99
33	P_Ph_Ph_TiPrBPh	TiPrBPh	Ph	Ph	28.0	45.2	37	99
34	P_o_OMePh_o_OMePh_o_OMePh	o_OMePh	o_OMePh	o_OMePh	28.0	34.1	21	83
35	P_TOMeBPh_Cy_Cy	TOMeBPh	Cy	Cy	28.9	40.4	1711	99
36	P_Ph_Ph_2MeBPh	Ph	2MeBPh	Ph	29.9	37.5	53	97
37	P_t_Bu_t_Bu_1PhPyr	1PhPyr	t_Bu	t_Bu	29.9	43.3	1450	99

[a] Reaction **VI** in manuscript.

Table S4. TOF values for the representative catalytic system in the literature in the Suzuki coupling of *p*-CF_3-PhCl/PhCl and *o*-tolylboronic acid.

	P-ligand	Temp (°C)	Time (h)	Yield (%)	TOF (h^{-1})	Price (CNY/g)	Ref.
PhCl	2-(2-methoxyphenyl)-1-(dicyclohexylphosphino)ferrocene	95	24	83	3.4		1
	P-cyclohexyl-4-hydroxy-2,2,6,6-tetramethylphosphorinane	110	16	85	5.3		2
	(2-mesityl-1H-inden-3-yl)-dicyclohexylphosphine	100	8	79	6.6		3
	[PdCl2((Ph2PCH2)2NC6H4-2-(CF3))]	80	7	98	14		4
	Our work	**100**	**2**	**97**	**16**	**37**	
***p*-CF_3-PhCl**	[Me2NCH2(Cl)C=C(CH2)2OP(i-Pr)2-κNκCκP]PdCl	130	27	85	6.3		5
	Adbippyphos	100	1	99	33	1871	6
	Our work	**100**	**1**	**99**	**33**	**37**	

Table S5. The predicted P-ligands for PhCl activation via MPCD-based ALS and their reported catalytic performance in literature for Pd-catalyzed cross-coupling reaction.

	name	G1	G2	G3	$\Delta E_{rep}(L)$ (kJ/mol)	Vbur (%)	Price (CNY/g)	Yield (%)[a]
1	P_Ph_p_OMePh_p_OMePh	Ph	p_OMePh	p_OMePh	16.4	30.2	103	0
2	P_Cy_Cy_2MeBPh	2MeBPh	Cy	Cy	18.3	43.0	28	32
3	P_Ph_Ph_o_Tol	o_Tol	Ph	Ph	18.3	30.7	83	0
4	P_Ph_Ph_o_OMePh	o_OMePh	Ph	Ph	18.3	31.4	286	0
5	P_t_Bu_t_Bu_BOMeBPh	t_Bu	BOMeBPh	t_Bu	18.3	51.4	7190	
6	P_Ph_Ph_4NMe2Ph	4NMe2Ph	Ph	Ph	19.3	29.4	20	0
7	P_Ph_Ph_oPhOH	oPhOH	Ph	Ph	20.3	31.9	359	0
8	P_Ph_o_OMePh_o_OMePh	Ph	o_OMePh	o_OMePh	20.3	32.5	123	1
9	P_22MeNBPh_Ph_Ph	22MeNBPh	Ph	Ph	20.3	35.9	35	26
10	P_Mes_Mes_Cyp	Mes	Cyp	Mes	24.1	41.4		
11	P_Ph_Ph_BOMeBPh	Ph	BOMeBPh	Ph	26.1	40.3	46	74
12	P_Ph_Ph_TiPrBPh	TiPrBPh	Ph	Ph	28.0	45.2	37	97
13	P_o_OMePh_o_OMePh_o_OMePh	o_OMePh	o_OMePh	o_OMePh	28.0	34.1	21	24
14	P_TOMeBPh_Cy_Cy	TOMeBPh	Cy	Cy	28.9	40.4	1711	47
15	P_Ph_Ph_2MeBPh	Ph	2MeBPh	Ph	29.9	37.5	53	21
16	P_t_Bu_t_Bu_1PhPyr	1PhPyr	t_Bu	t_Bu	29.9	43.3	1450	99
17	P_Cy_Cy_TPhBPyz	TPhBPyz	Cy	Cy	29.9	36.1	1141	95
18	P_t_Bu_t_Bu_36OMe2TRIPPh	36OMe2TRIPPh	t_Bu	t_Bu	31.8	44.0	258	7
19	P_26BOMePh_26BOMePh_26BOMePh	26BOMePh	26BOMePh	26BOMePh	34.7	39.0	23	1

[a] Reaction **VII** in manuscript.

Table S6. The reaction yields for the representative catalytic system in the literature for the Suzuki coupling of ArCl with *o*-tolylboronic acid.

ArCl	Ligand	Temp (°C)	Time (h)	Yield (%)	Ref.
p-NH_2-PhCl	Ph-XPhos	100	2	40	This work
	NHC	50	24	89	[7]
p-NO_2-PhCl	Ph-XPhos	100	3	90	This work
	N-ligand	85	5.5	68	[8]
p-OH-PhCl	Ph-XPhos	100	2	50	This work
	polymeric imidazole Pd	100	12	90	[9]
p-CH_3O-PhCl	Ph-XPhos	100	2	72	This work
	NHC	80	6	99	[10]
	NHC	80	4	99	[11]
p-CH_3CO-PhCl	Ph-XPhos	100	2	69	This work
	(t-Bu-Ph-phosphinomethyl)polystyrene		20	86	[12]
o-CF_3-PhCl	Ph-XPhos	100	1	99	This work
	NHC	130	27	71	[5]
m-CF_3-PhCl	Ph-XPhos	100	1	99	This work
	Ferrocence-based phosphine (with phenylboronic acid)	r.t.	12	99	[13]
	$P[OiPr]_3$ (phenylboronic acid)	120	18	88	[14]

Table S7. The calculated $\Delta E_{rep}(L)$ results by using PBE functional in VASP and B3LYP functional in Gaussion 09 packages and their absolute energy differences ($|E_{diff}|$). The unit of energy is kJ/mol.

Name	$\Delta E_{rep}(L)$ with PBE functional	$\Delta E_{rep}(L)$ with B3LYP functional	$\|E_{diff}\|$
P_Cyp_35BTRIPPh_35BTRIPPh	1.9	0.0	1.9
P_35Bt_BuPh_35Bt_BuPh_35BTRIPPh	3.9	1.9	1.9
P_Cyp_35BMesPh_35BMesPh	0.0	1.9	1.9
P_TPhBPyz_Adm_Adm	12.5	12.5	0.0
P_Cy_Cy_35BTRIPPh	-3.9	-1.9	1.9
P_Cyp_Cyp_35BTRIPPh	-1.9	1.0	2.9
P_35Bt_BuPh_35Bt_BuPh_35Bt_BuPh	7.7	3.9	3.9
P_Cy_Cy_TPhBPyz	-40.5	-28.0	12.5
P_36OMe2TRIPPh_Cy_Cy	-5.8	-7.7	1.9
P_t_Bu_t_Bu_TPhBPyz	16.4	20.3	3.9
P_26BOMePh_26BOMePh_26BOMePh	34.7	30.9	3.9
P_t_Bu_t_Bu_36OMe2TRIPPh	17.4	32.8	15.4
P_Cy_35Bt_BuPh_35Bt_BuPh	-1.9	-1.0	1.0
P_Ph_35Bt_BuPh_35Bt_BuPh	5.8	6.8	1.0
P_Cy_Cy_BOiPrBPh	4.8	6.8	1.9
P_Cyp_35Bt_BuPh_35Bt_BuPh	-1.0	1.0	1.9
P_TiPrBPh_Cy_Cy	3.9	5.8	1.9
P_Ph_Ph_TiPrBPh	28.0	19.3	8.7
P_TOMeBPh_Cy_Cy	28.9	18.3	10.6
P_n_Bu_35Bt_BuPh_35Bt_BuPh	2.9	3.9	1.0
P_t_Bu_35Bt_BuPh_35Bt_BuPh	5.8	6.8	1.0
P_35BPhPyzPh_t_Bu_t_Bu	3.9	6.8	2.9
P_BOMeBPh_o_Tol_o_Tol	21.2	24.1	2.9
P_Cy_Cy_26B2MeNBPh	9.6	13.5	3.9
P_Adm_Adm_Adm	-2.9	1.0	3.9
P_Cy_Cy_BOMeBPh	13.5	11.6	1.9
P_Ph_Ph_BOMeBPh	26.1	16.4	9.6
P_o_OMePh_o_OMePh_26BOMePh	1.0	0.0	1.0
P_t_Bu_t_Bu_TiPrBPh	14.5	10.6	3.9
P_t_Bu_t_Bu_BNap	12.5	19.3	6.8
P_22MeNBPh_Cy_Cy	0.0	-1.0	1.0
P_Cy_Cy_1PhIn	5.8	3.9	1.9
P_22MeNBPh_Ph_Ph	20.3	24.1	3.9
P_Adm_Bn_Adm	2.9	1.9	1.0
P_Mes_Mes_Mes	35.7	39.6	3.9
P_Ph_Ph_Trop	5.8	0.0	5.8
P_p_OMePh_p_OMePh_p_OMePh	10.6	2.9	7.7
P_o_OMePh_o_OMePh_o_OMePh	28.0	24.1	3.9
P_Cy_Cy_2OMe1PhPyr	8.7	5.8	2.9
P_Cy_Cy_2MeBPh	18.3	13.5	4.8

P_t_Bu_r5_r5	13.5	11.6	1.9
P_n_Bu_Adm_Adm	-8.7	-6.8	1.9
P_t_Bu_Adm_Adm	10.6	16.4	5.8
P_Cy_p_OMePh_p_OMePh	3.9	4.8	1.0
P_t_Bu_t_Bu_NapPyz	29.9	32.8	2.9
P_PrO2Me_PrO2Me_PrO2Me	-7.7	-10.6	2.9
P_OPh_OPh_OPh	5.8	1.9	3.9
P_t_Bu_t_Bu_22MeNBPh	5.8	11.6	5.8
P_3OMe6Me2TRIPPh_t_Bu_t_Bu	9.6	13.5	3.9
P_Cy_Cy_1PhPyr	-6.8	7.7	14.5
P_t_Bu_t_Bu_1PhIn	10.6	12.5	1.9
P_Mes_Mes_Cyp	24.1	21.2	2.9
P_Cyp_p_OMePh_p_OMePh	-1.0	0.0	1.0
P_t_Bu_t_Bu_2OMe1PhPyr	6.8	10.6	3.9
P_Cy_Cy_4NMe2Ph	1.9	-6.8	8.7
P_BEtN_OBn_OBn	1.0	2.9	1.9
P_Cy_Cy_Mes	12.5	20.3	7.7
P_t_Bu_t_Bu_2MeBPh	15.4	20.3	4.8
P_Cyp_35BMePh_35BMePh	0.0	1.0	1.0
P_p_Tol_p_Tol_p_Tol	8.7	5.8	2.9
P_m_Tol_m_Tol_m_Tol	13.5	5.8	7.7
P_o_Tol_o_Tol_o_Tol	7.7	14.5	6.8
P_Bn_Bn_Bn	2.9	5.8	2.9
P_t_Bu_t_Bu_BPh	15.4	13.5	1.9
P_Cy_o_Tol_o_Tol	-18.3	-10.6	7.7
P_t_Bu_t_Bu_1PhPyr	29.9	32.8	2.9
P_Cy_Cy_o_Tol	1.9	5.8	3.9
P_Mes_Cyp_Cyp	11.6	21.2	9.6
P_Ph_Ph_p_Tol	14.5	8.7	5.8
P_Ph_Ph_o_Tol	4.8	5.8	1.0
P_Ph_Ph_Bn	2.9	4.8	1.9
P_Cy_Cy_Cy	-28.0	-24.1	3.9
P_t_Bu_t_Bu_Adm	-1.9	1.9	3.9
P_Cy_Cy_Ph	-1.9	-1.0	1.0
P_iPr_BPh_iPr	-2.9	-1.9	1.0
P_Cy_Ph_Ph	2.9	2.9	0.0
P_Ph_Ph_Ph	13.5	7.7	5.8
P_Ph_Ph_Cyp	11.6	5.8	5.8
P_BEtN_BEtN_BEtN	-1.9	0.0	1.9
P_Cy_Cy_t_Bu	-4.8	-3.9	1.0
P_t_Bu_OtBu_OtBu	-5.8	-1.0	4.8
P_Ph_Cyp_Cyp	0.0	-1.0	1.0
P_Ph_Ph_t_Bu	10.6	4.8	5.8
P_Ph_Ph_OEt	1.9	-5.8	7.7

P_Cyp_Cyp_Cyp	-3.9	-1.0	2.9
P_t_Bu_t_Bu_Bn	1.0	2.9	1.9
P_iPr_Ph_Ph	4.8	3.9	1.0
P_Prol_Prol_Prol	3.9	11.6	7.7
P_Ph_Ph_Aly	1.0	1.9	1.0
P_Cy_t_Bu_t_Bu	-1.9	0.0	1.9
P_Ph_t_Bu_t_Bu	5.8	2.9	2.9
P_Me_BPh_Me	4.8	5.8	1.0
P_EtCN_EtCN_EtCN	-6.8	-2.9	3.9
P_n_Bu_n_Bu_n_Bu	-23.2	-24.1	1.0
P_i_Bu_i_Bu_i_Bu	-1.0	8.7	9.6
P_t_Bu_t_Bu_n_Bu	-3.9	-2.9	1.0
P_t_Bu_t_Bu_t_Bu	-3.9	0.0	3.9
P_OEt_OEt_OEt	-10.6	-23.2	12.5
P_iPr_t_Bu_t_Bu	-17.4	-14.5	2.9
P_BMeN_BMeN_BMeN	15.4	16.4	1.0
P_n_Pr_n_Pr_n_Pr	-2.9	-1.9	1.0
P_iPr_iPr_iPr	-2.9	-1.9	1.0
P_Me_t_Bu_t_Bu	1.0	1.0	0.0
P_Aly_Aly_Aly	-5.8	-3.9	1.9
P_Et_Et_Et	-7.7	-6.8	1.0
P_Me_Me_Me	0.0	0.0	0.0
Mean absolute error			3.7

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