

Electronic supplementary information

Solid-phase cyclopalladation in *S,C,S'*-pincer systems: rising alternative for synthesis in solution

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IR spectral data

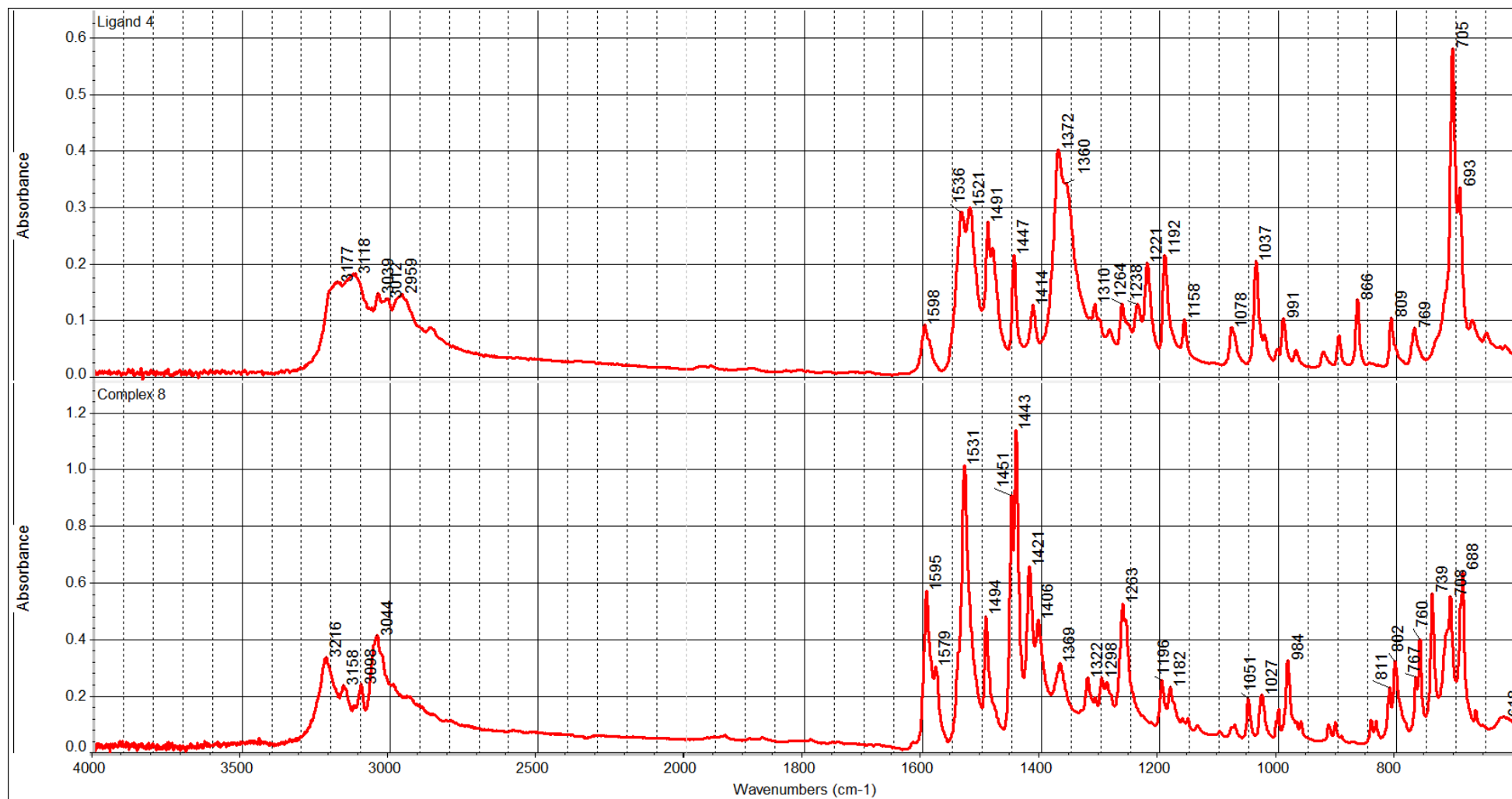
Fig. S1. IR spectra of unsymmetrical bis(thioamide) pincer ligand **4** (upper) and its Pd(II) complex **8** (lower).

Fig. S2. Extended fragments of IR spectra of unsymmetrical bis(thioamide) pincer ligand **4** (upper) and its Pd(II) complex **8** (lower).

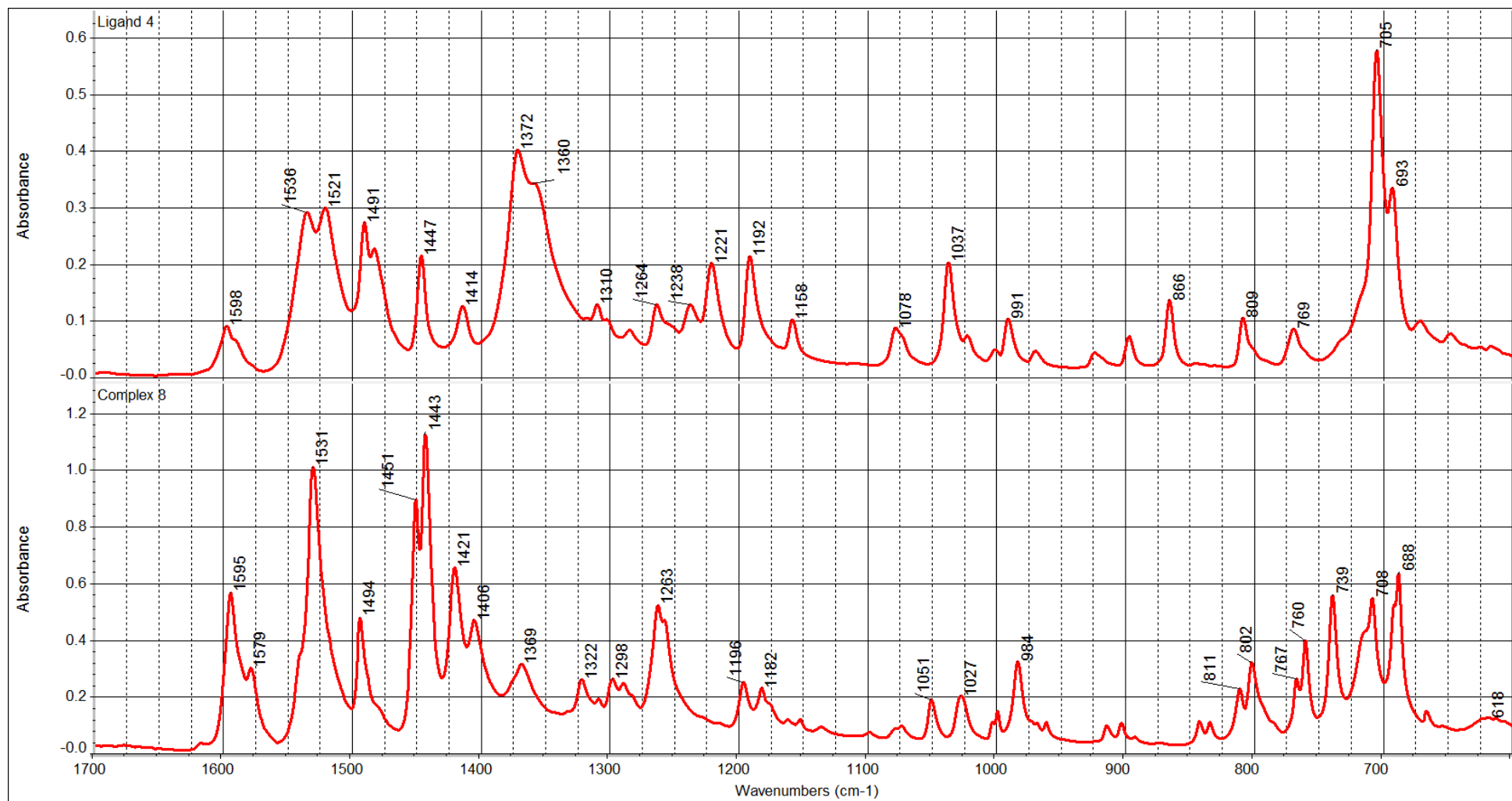
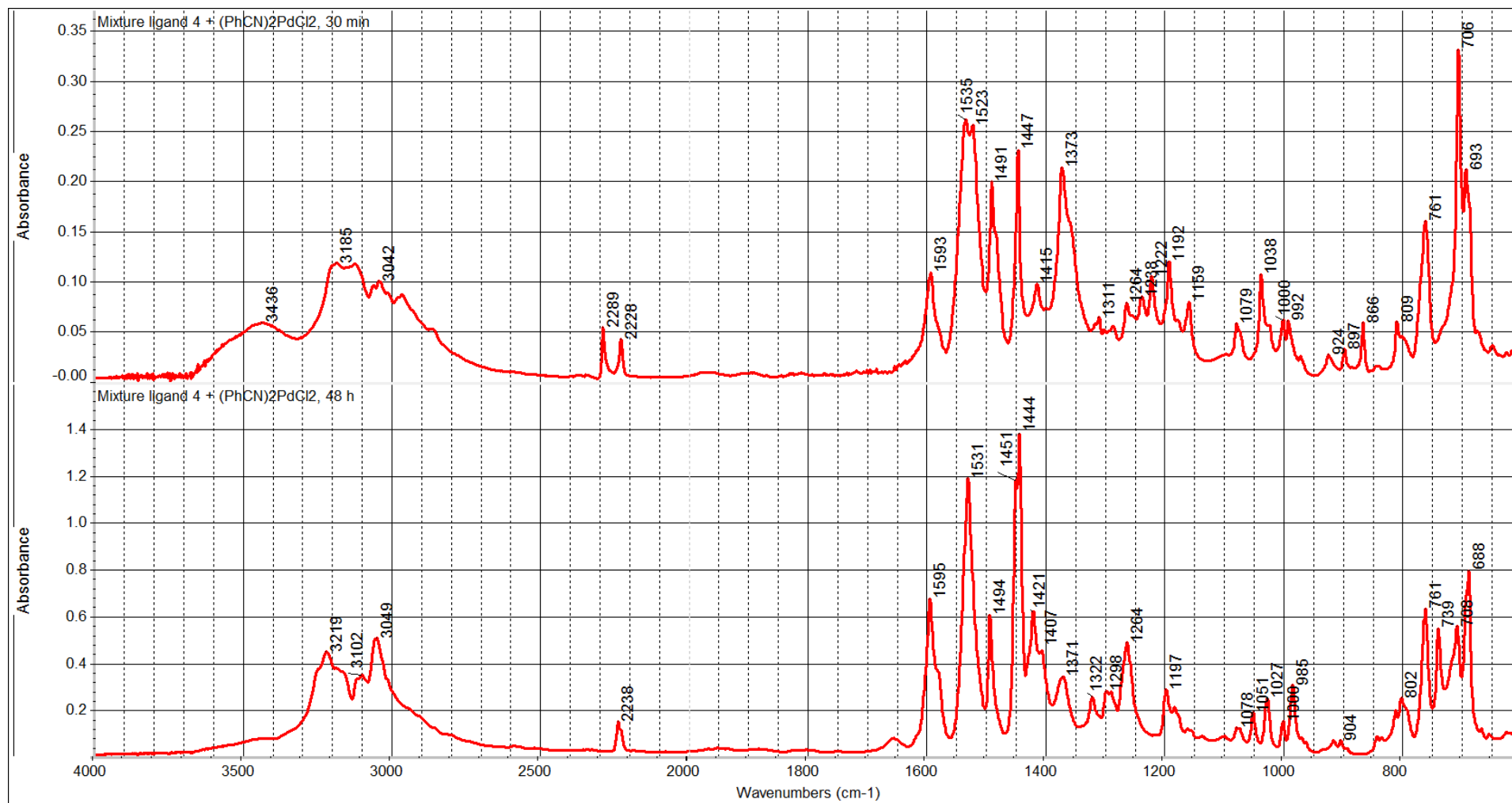


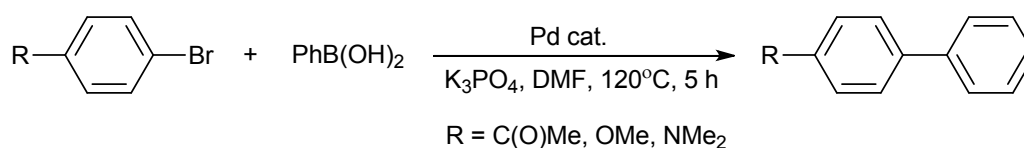
Fig. S3. IR spectra of a homogeneous mixture of ligand **4** and PdCl₂(NCPh)₂ in 30 min (upper) and 2 days (lower) after manual grinding in a mortar.



Catalytic activity of complexes 5–8 in the Suzuki cross-coupling

In a typical experiment, a solution of 0.25 mmol of aryl bromide, 0.375 mmol of PhB(OH)_2 , 0.5 mmol of K_3PO_4 , and the mentioned amount of the corresponding palladium complex (used as titrated solutions in DMF) in 1 mL of DMF was heated at 120 °C for 5 h. To determine the conversion of aryl bromide, aliquots of the reaction mixture were treated with water, extracted with benzene, and analyzed by GC (Chrom-5 instrument, 25 m capillary column with SE-30 stationary phase, FID detector, temperature programming 150→250°C at 15°C/min). Since both starting aryl bromides and the cross-coupling products were stable enough and seemed unlikely to undergo resinification or other loss during the processing, internal standard was not used. To define molar ratios from the peak areas, a simplified approach based on FID detector sensitivity towards carbon ions (acceptable for compounds of close chemotypes) was used. For this, the observed peak areas were divided by the number of carbon atoms in the corresponding molecule, and the obtained revised values (theoretically proportional to molar fractions) were used in further calculations.

Table S1. Catalytic activity of palladacycles 5–8 in the Suzuki cross-coupling



Entry	Aryl bromide	Cat. load. (mol %)	Pd cat./conversion, %			
			5	6	7	8
1	4-bromoacetophenone	1	n/d	n/d	100	100
2	4-bromoacetophenone	0.1	100	100	100	100
3	4-bromoacetophenone	0.01	7	100	98	98
	4-bromoacetophenone	0.001	0	0	n/d	n/d
4	4-bromoanisole	1	95	100	92	10
5	4-bromoanisole	0.1	99	97	73	0
	4-bromoanisole	0.01	0	0	n/d	n/d
6	4-bromo- <i>N,N</i> -dimethylaniline	1	35	27 ^a	10	2
7	4-bromo- <i>N,N</i> -dimethylaniline	0.1	6	28	n/d	n/d

n/d not defined

^aThe reaction is accompanied by precipitation of Pd black