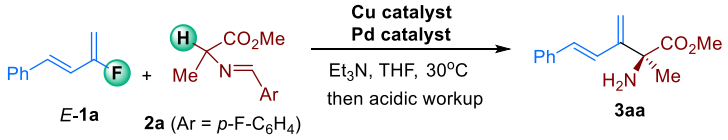
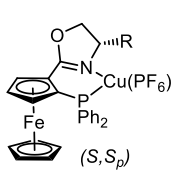
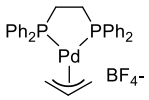
Table 1. Optimization of catalyst system for the cross-coupling reaction. [a]

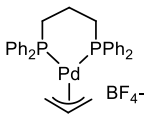




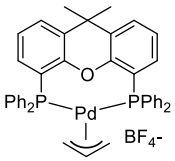
R = Ph, **L1-Cu**
R = ^{t}Bu, **L2-Cu**
R = ^{i}Pr, **L3-Cu**



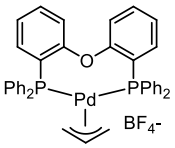
L4-Pd



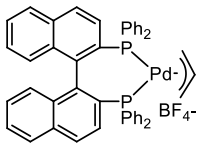
L5-Pd



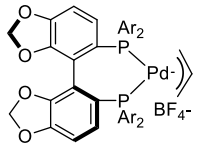
L6-Pd



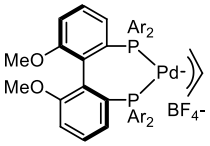
L7-Pd



L8-Pd



Ar = Ph, **L9-Pd**
Ar = 3,5-^{t}Bu$_2$-4-MeO-C$_6$H$_2$, **L10-Pd**

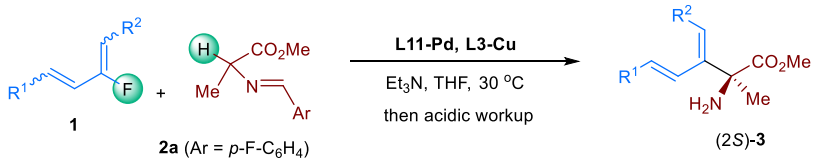


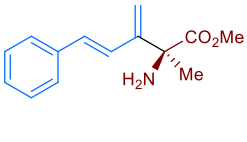
Ar = 3,5-^{t}Bu$_2$-C$_6$H$_3$, **L11-Pd**

Entry	**Pd catalyst**	**Cu catalyst**	Yield [%] [b]	ee [%] [c]
1	**L4-Pd**	**L1-Cu**	<5	n.d.
2	**L5-Pd**	**L1-Cu**	<5	n.d.
3	**L6-Pd**	**L1-Cu**	<5	n.d.
4	**L7-Pd**	**L1-Cu**	<5	n.d.
5	**L8-Pd**	**L1-Cu**	53	96
6	**L9-Pd**	**L1-Cu**	50	98
7	**L10-Pd**	**L1-Cu**	73	99
8	**L11-Pd**	**L1-Cu**	87	96
9	**L11-Pd**	**L2-Cu**	75	98
10	**L11-Pd**	**L3-Cu**	86	99
11	*ent*-**L11-Pd**	**L3-Cu**	82	93
12	**L11-Pd**	—	n.r.	n.d.
13	—	**L3-Cu**	n.r.	n.d.

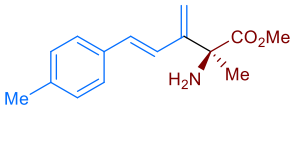
[a] Reaction conditions: i) **1a** (0.2 mmol), **2a** (0.1 mmol), **Pd catalyst** (4 mol%)**, Cu catalyst** (5 mol%), Et$_3$N (200 mol%), THF (0.5 mL), 30 °C, 24 h; ii) citric acid (10 wt%, 4 mL). [b] Isolated yields are provided. [c] The ee values were determined by HPLC using a column with a chiral stationary phase; n.d. = not determined; n.r. = no reaction.

Table 2. Substrate scope with respect to the dienyl fluorides. [a]

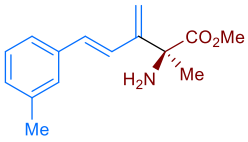




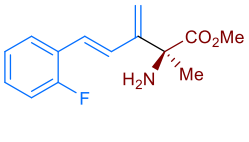
3aa, 86% yield, 99% ee



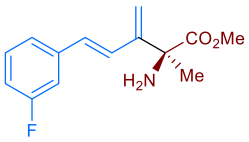
3ba, 81% yield, 98% ee



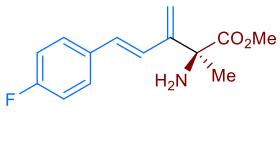
3ca, 79% yield, >99% ee



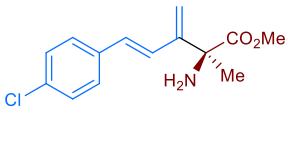
3da, 80% yield, 98% ee



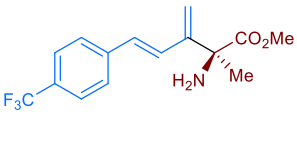
3ea, 81% yield, 98% ee



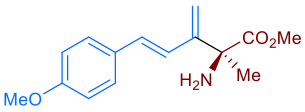
3fa, 87% yield, 99% ee



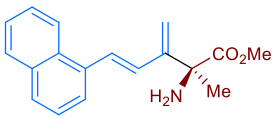
3ga, 82% yield, 99% ee



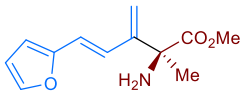
3ha, 71% yield, 98% ee



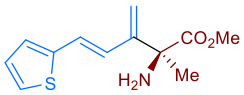
3ia, 80% yield, >99% ee



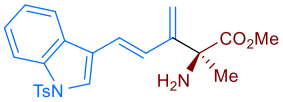
3ja, 76% yield, >99% ee



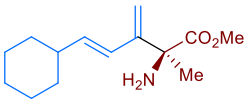
3ka, 70% yield, 97% ee



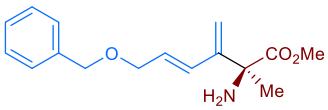
3la, 70% yield, >99% ee



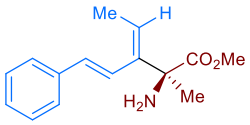
3ma, 68% yield, 99% ee



3na, 63% yield, 94% ee



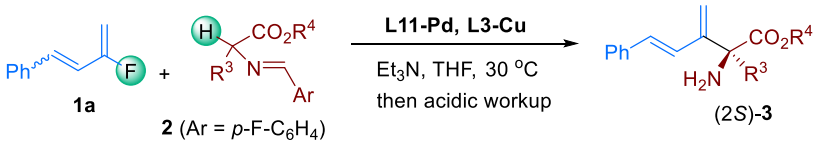
3oa, 60% yield, 99% ee

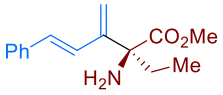


3pa, 50% yield, >99% ee [b]

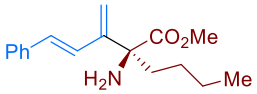
[a] Reaction conditions: i) **1a** (0.4 mmol), **2a** (0.2 mmol), **L11-Pd** (4 mol%)**, L3-Cu** (5 mol%), Et_3N (200 mol%), THF (0.5 mL), 30 °C, 24 h; ii) citric acid (10 wt%, 4 mL). Isolated yields are provided. The ee values were determined by HPLC on a column with a chiral stationary phase. [b] **L11-Pd** (8 mol%), **L3-Cu** (10 mol%), THF (0.2 mL), 40 °C, 120 h.

Table 3. Substrate scope with respect to the aldimine esters. [a]

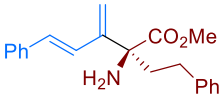




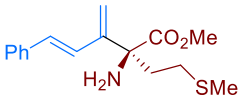
3ab, 71% yield, 92% ee



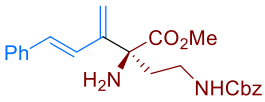
3ac, 69% yield, 96% ee



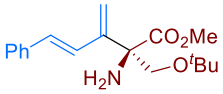
3ad, 58% yield, 92% ee



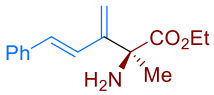
3ae, 67% yield, 95% ee



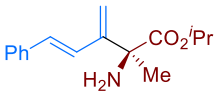
3af, 45% yield, 88% ee



3ag, 48% yield, 96% ee

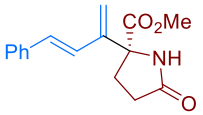


3ah, 65% yield, >99% ee

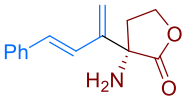


3ai, 77% yield, 97% ee

3aj, 85% yield, 91% ee



3ak, 58% yield, 92% ee



3al, 55% yield, 98% ee

3am, 89% yield, 99% ee

3an, 76% yield, >99% ee

[a] Reaction conditions: i) **1a** (0.4 mmol), **2a** (0.2 mmol), **Pd-8** (4 mol%)**, Cu-3** (5 mol%), Et_3N (200 mol%), THF (0.5 mL), 30 °C, 48 h; ii) citric acid (10 wt%, 4 mL). Isolated yields are provided. The ee values were determined by HPLC on a column with a chiral stationary phase.