Supporting information of
Air-stable Pd(0) catalyst bearing dual phosphine ligands: a detailed evaluation of air stability and catalytic property in cross-coupling reactions

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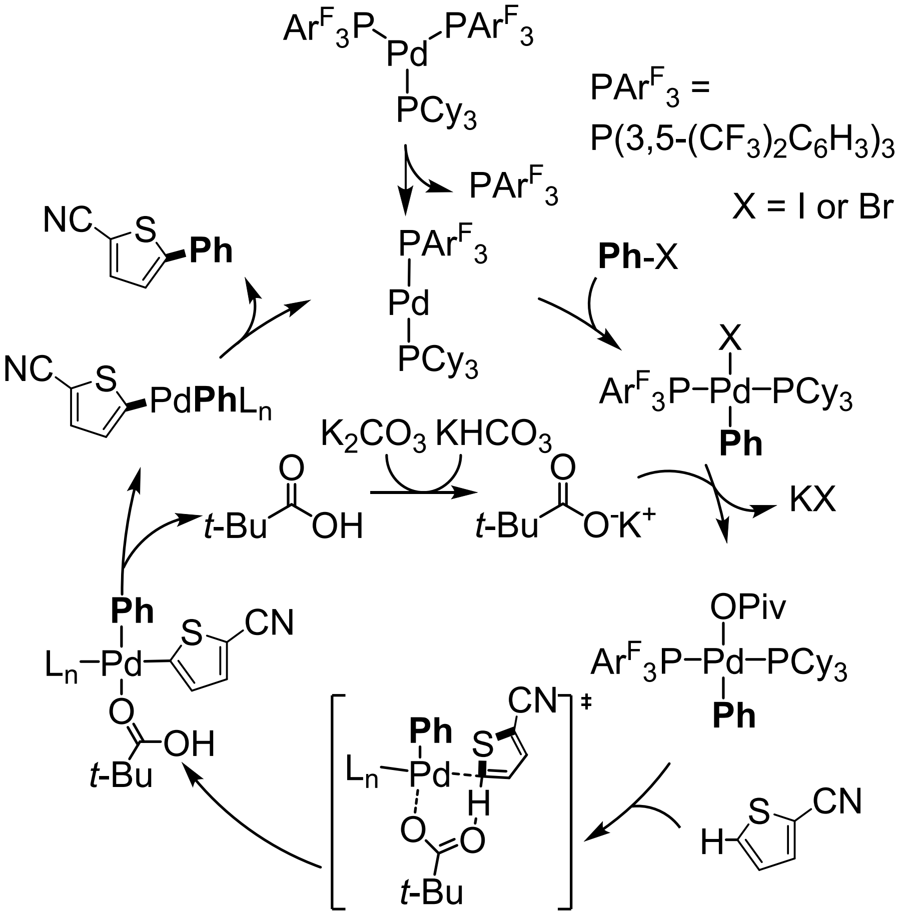


Figure S1. Plausible reaction mechanism of direct C-H arylation reaction by Complex 1.

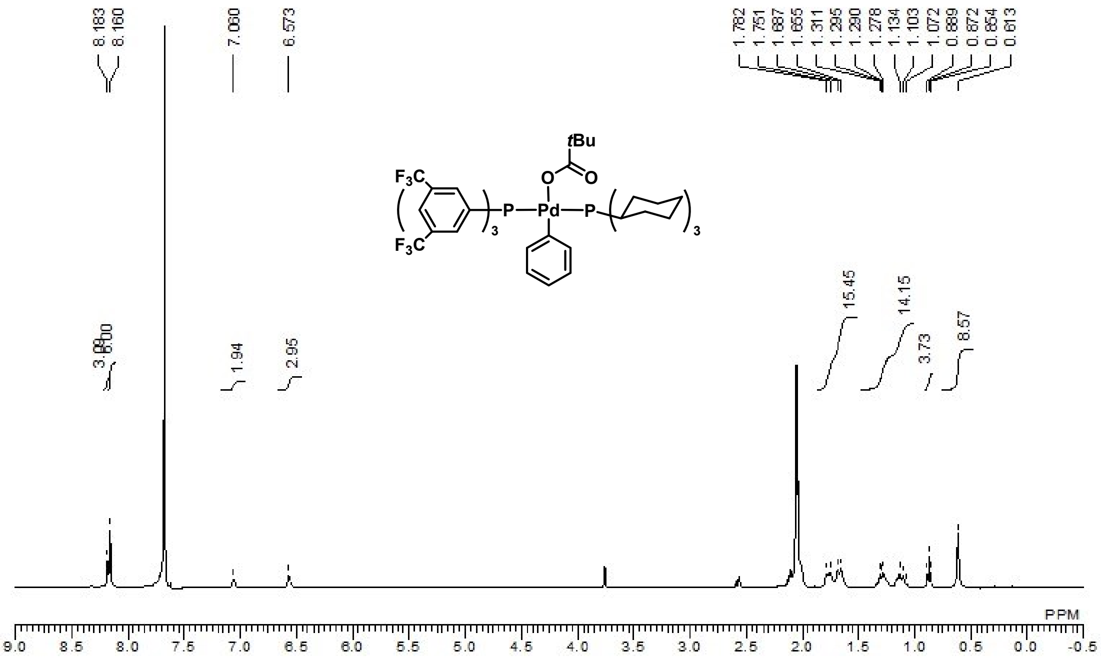


Figure S2. ^{1}H NMR spectrum of Complex 3 (400 MHz, acetone-d_6, r.t., under N_2).

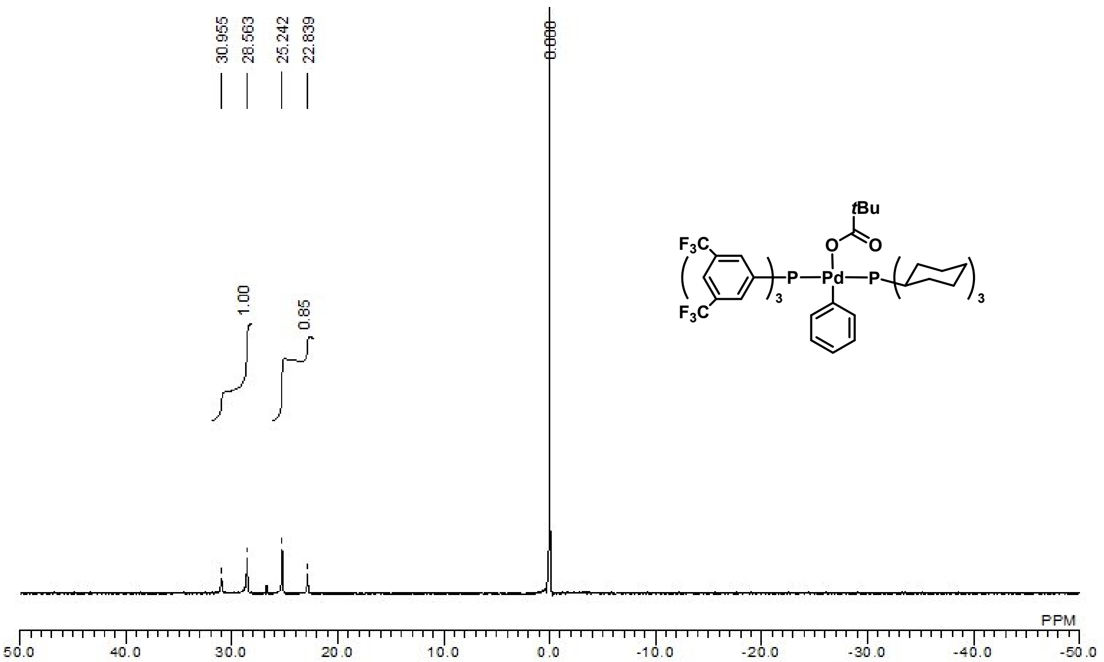


Figure S3. ^{31}P NMR spectrum of Complex 3 (162 MHz, acetone-d_6, r.t., under N_2, external standard: 85% H_3PO_4 0 ppm).

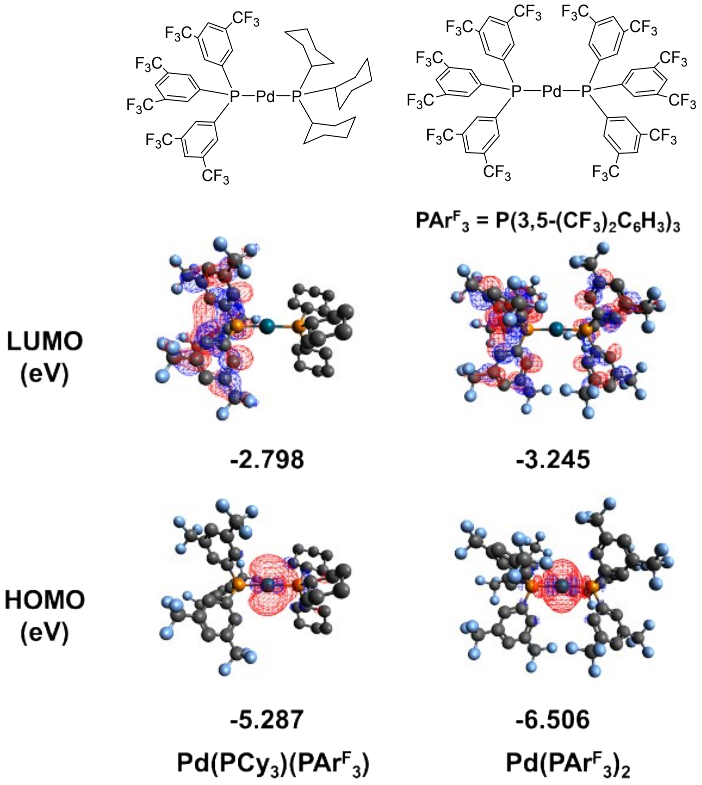


Figure S4. Chemical structures (top), HOMO and LUMO distribution and energy levels of Pd(PCy_3)($PAr^F{}_3$) and Pd($PAr^F{}_3$)$_2$ based on DFT calculations (bottom).

The high energy Pd-centred HOMO of Pd(PCy_3)($PAr^F{}_3$) may contribute to high reactivity in the oxidative addition step. Theoretical calculations have revealed that a transition state of an oxidative addition step involves interaction between an occupied 4d orbital of a Pd centre and an unoccupied σ^*(and π^*) orbital of a substrate.[S1] The high energy Pd-centred orbital is able to make strong interaction to the high-lying σ^*(and π^*) orbital of the substrate,[S2] which resulted in the low activation energy of the oxidative addition step. Form these insights, an energy level of Pd-centred orbital is expected to be a simple guideline for estimating activity for oxidative addition of the complex.

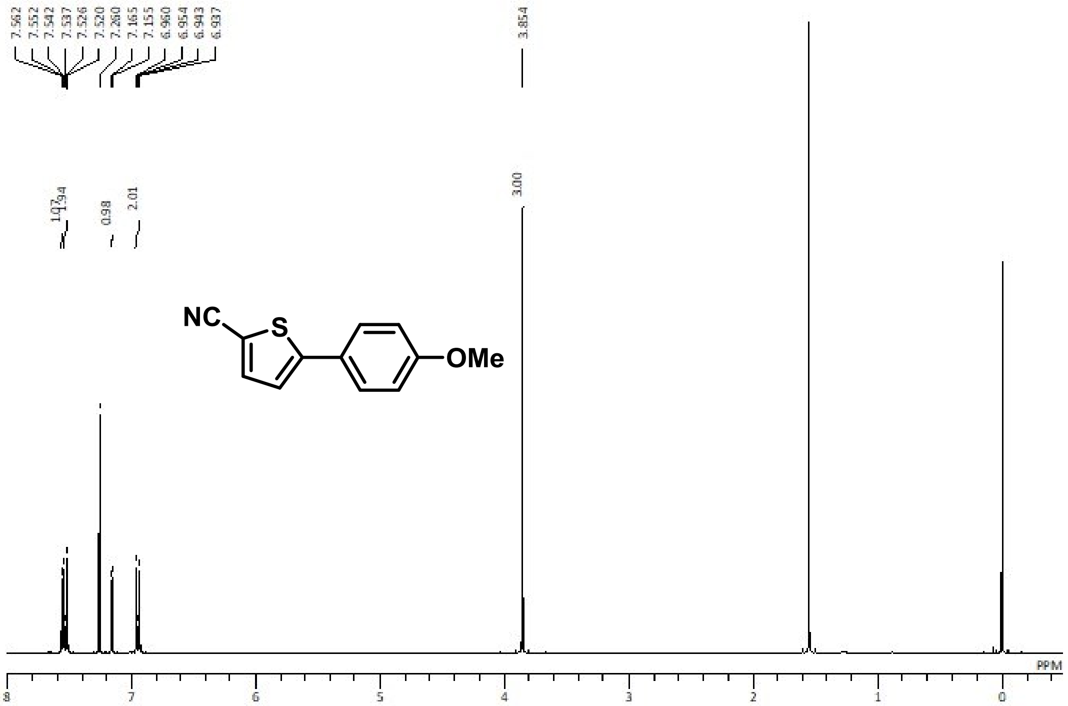


Figure S5. ^{1}H NMR spectrum of 5-(4-methoxyphenyl)-2-cyanothiophene (400 MHz, chloroform-*d*, r.t.).

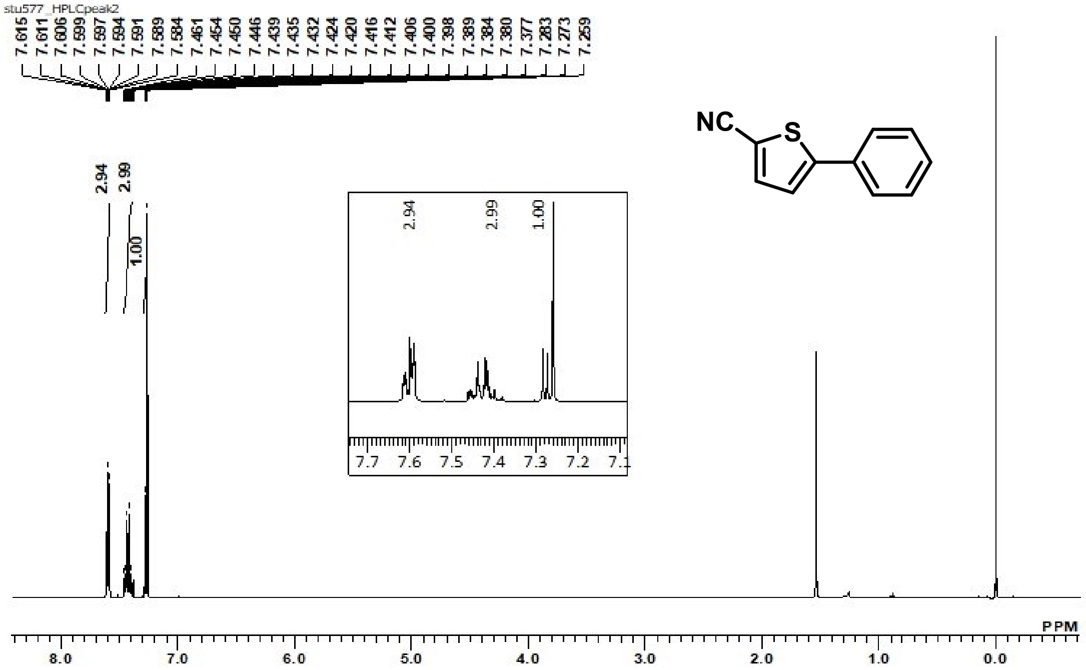


Figure S6. ^{1}H NMR spectrum of 5-phenyl-2-cyanothiophene (400 MHz, chloroform-*d*, r.t.).

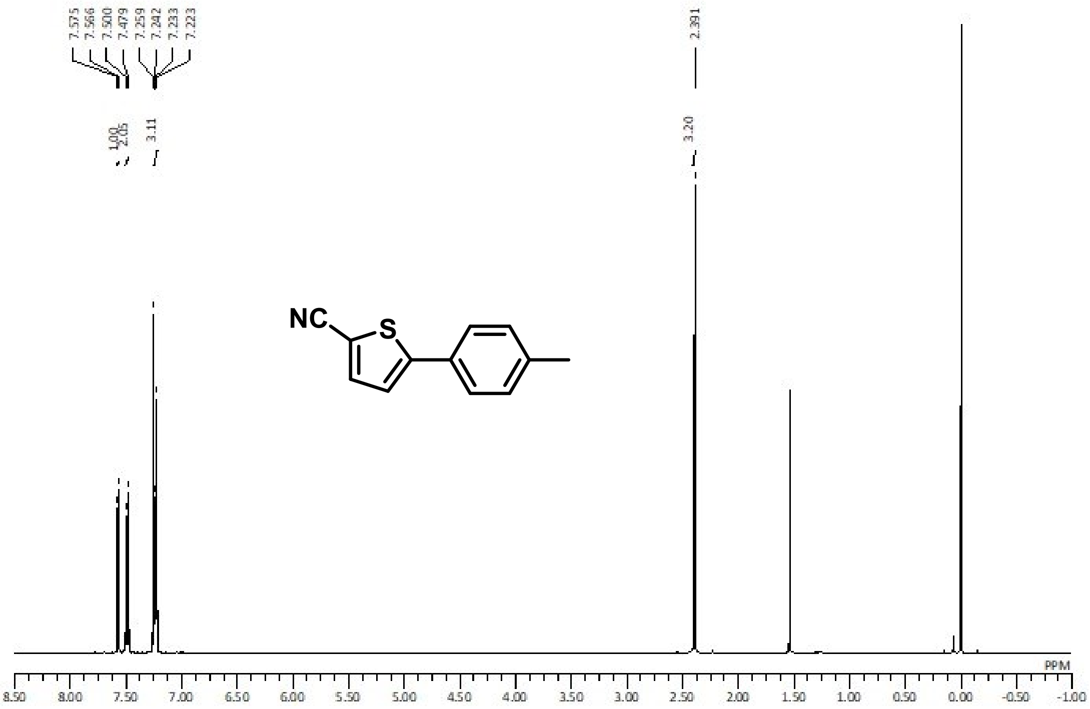


Figure S7. ^{1}H NMR spectrum of 5-(4-methylphenyl)-2-cyanothiophene (400 MHz, chloroform-*d*, r.t.).

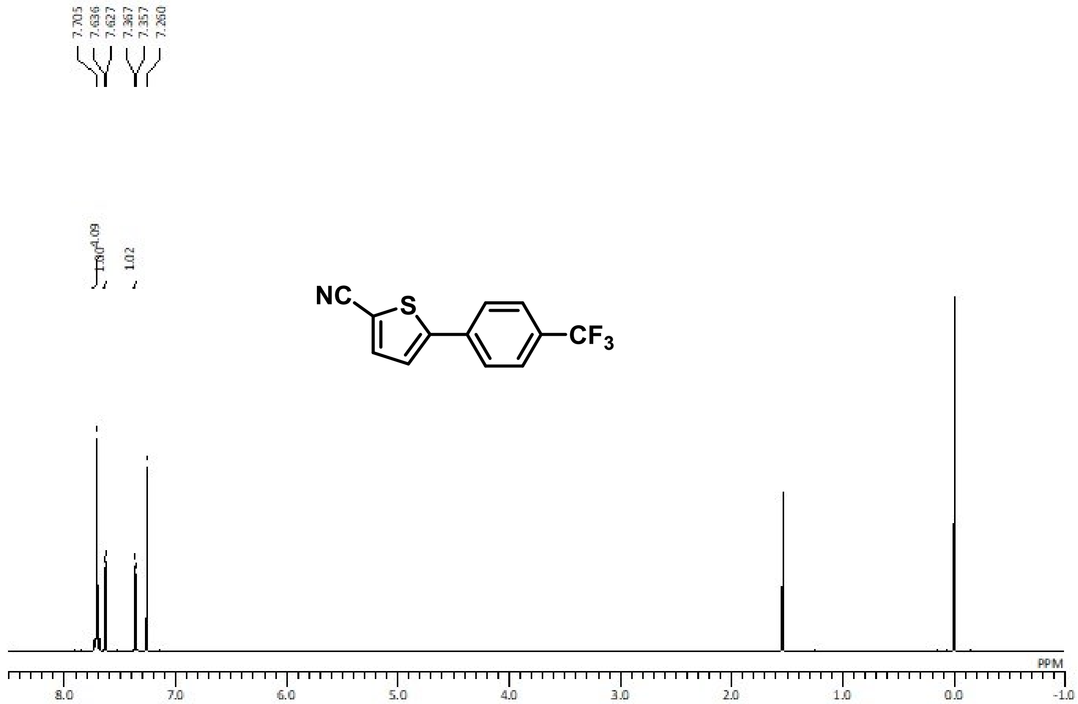


Figure S8. ^{1}H NMR spectrum of 5-(4-trifluoromehylphenyl)-2-cyanothiophene (400 MHz, chloroform-*d*, r.t.).

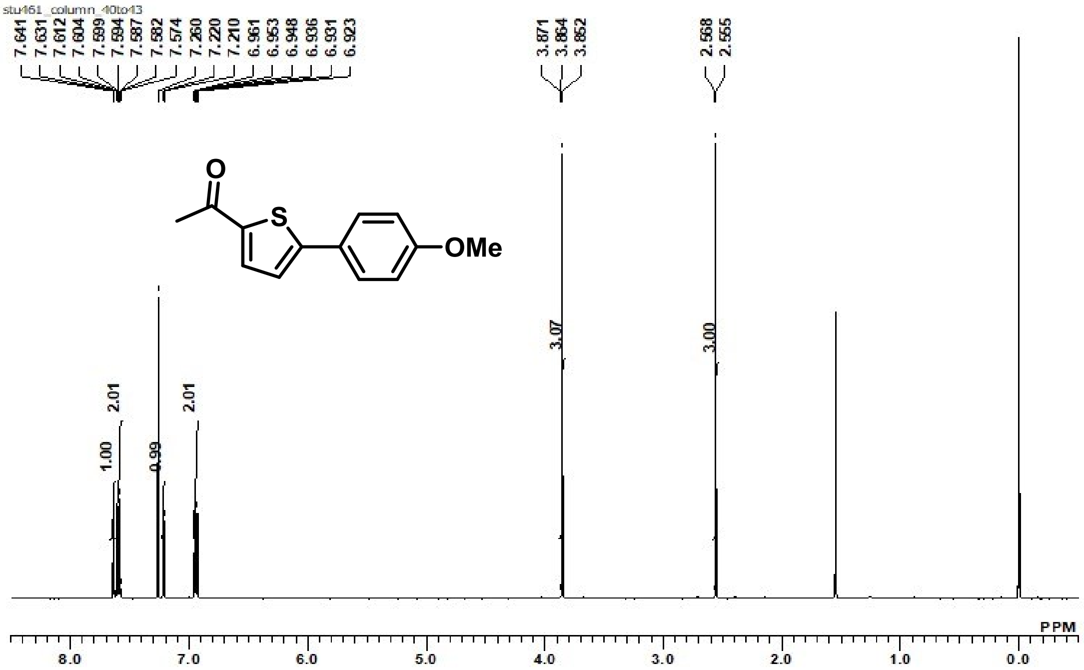


Figure S9. ^{1}H NMR spectrum of 5-(4-methoxyphenyl)-2-cyanothiophene (400 MHz, chloroform-*d*, r.t.).

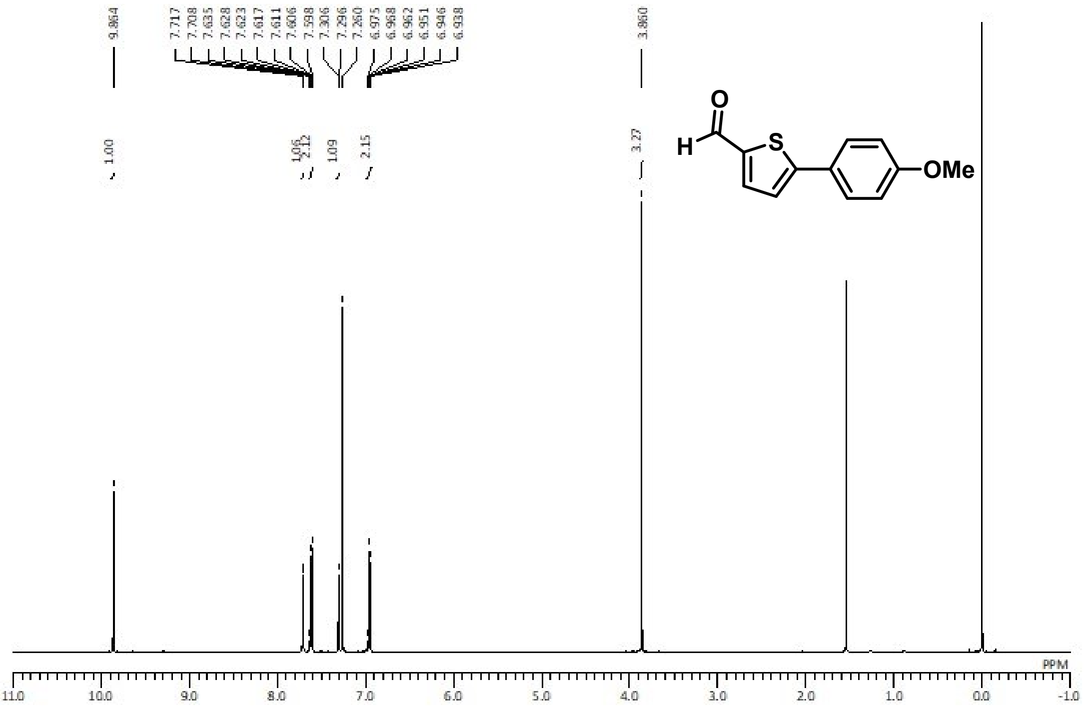


Figure S10. ^{1}H NMR spectrum of 5-(4-methoxyphenyl)-2-formylthiophene (400 MHz, chloroform-*d*, r.t.).

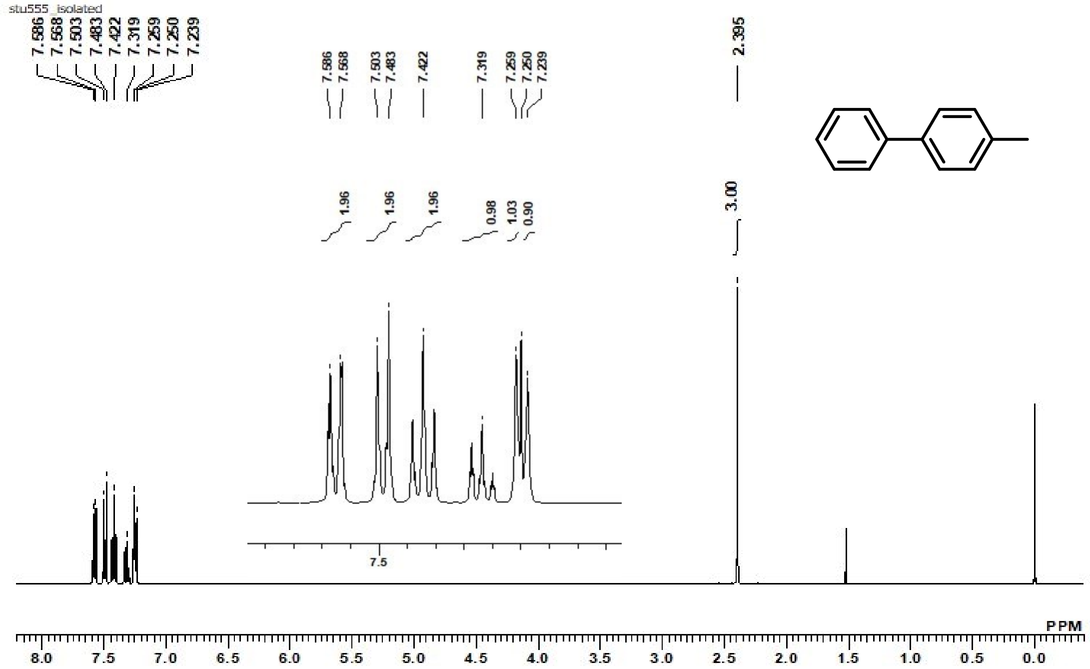


Figure S11. ^{1}H NMR spectrum of 4-methylbiphenyl (400 MHz, chloroform-*d*, r.t.).

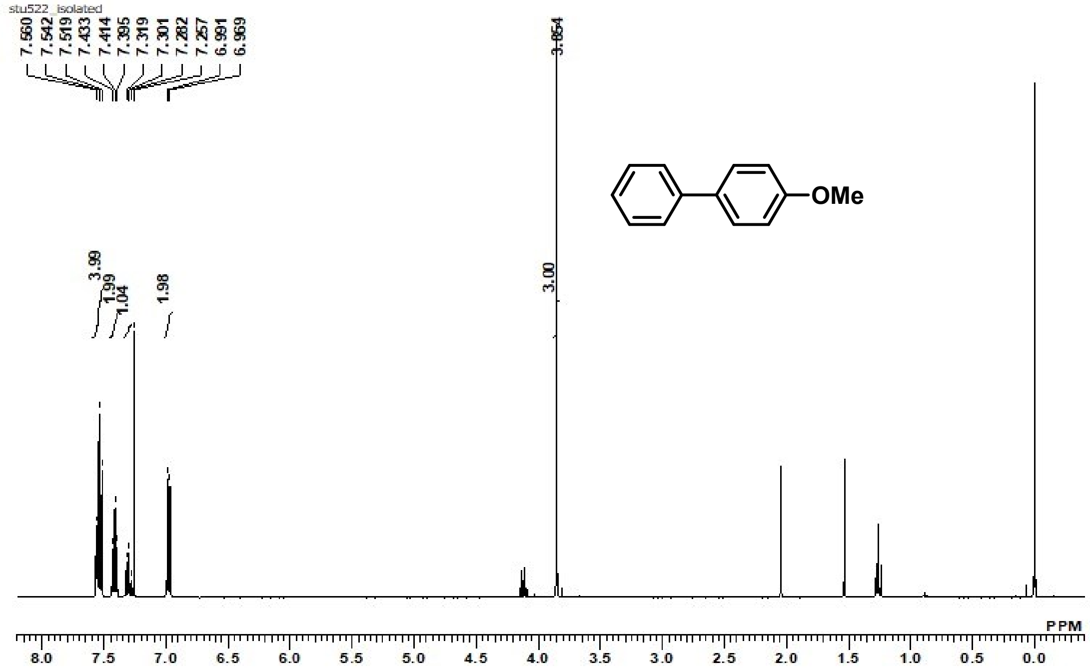


Figure S12. ^{1}H NMR spectrum of 4-methoxylbiphenyl (400 MHz, chloroform-*d*, r.t.).

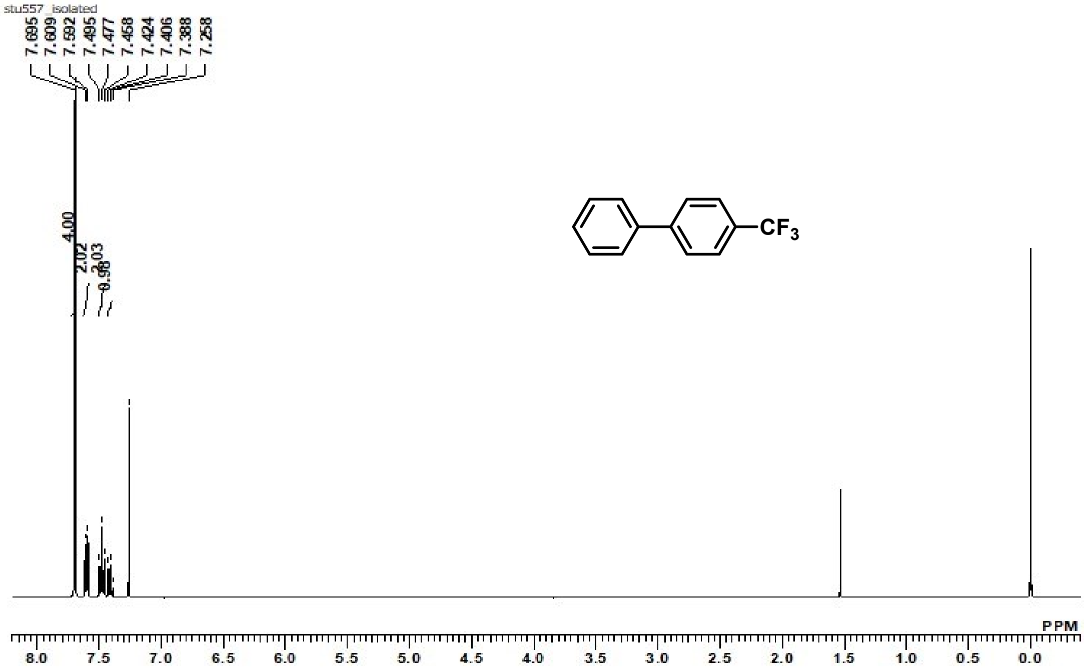


Figure S13. ^{1}H NMR spectrum of 4-trifluoromethylbiphenyl (400 MHz, chloroform-*d*, r.t.).

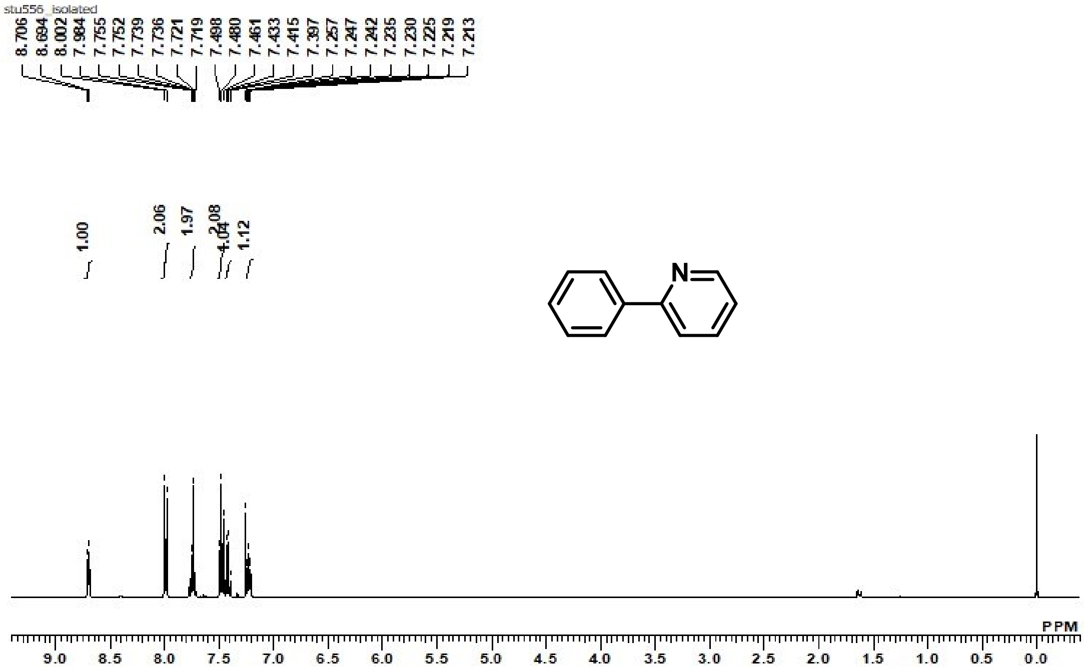
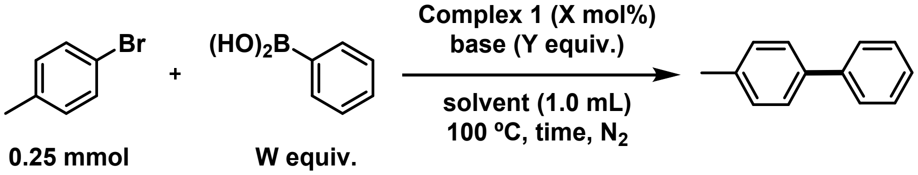


Figure S14. ^{1}H NMR spectrum of 2-phenylpyridine (400 MHz, chloroform-*d*, r.t.).

Table S1. Optimizing reaction condition of Suzuki-Miyaura cross-coupling reaction.



entry	W	X	base	Y	solvent	time (h)	NMR yield[a] (%)
S1	1.05	1	Cs_2CO_3	1	DMF	5	74
S2	1.05	1	Cs_2CO_3	1	toluene	5	35
S3	1.05	1	Cs_2CO_3	1	1,4-dioxane	5	88
S4	1.2	1	Cs_2CO_3	1	1,4-dioxane	5	77
S5	1.05	1	Cs_2CO_3	2	1,4-dioxane	5	94
S6[b]	1.05	0.5	Cs_2CO_3	2	1,4-dioxane	4	96
S7[b]	1.05	0.5	K_2CO_3	2	1,4-dioxane	4	quant.

[a]The yield was determined by ^{1}H NMR analyses of a crude product with ferrocene as an internal standard. [b]0.5 mmol scale.

Table S2. Crystallographic data of Complex 3

	Complex 3
Empirical Formula	$C_{53}H_{56}F_{18}O_2P_2Pd\cdot C_{3.5}O$
Formula Weight	1293.38
Crystal Color	colorless
Crystal Dimensions / mm	0.35 x 0.25 x 0.2
Crystal System	triclinic
Lattice Parameters	
a / Å	14.2183(11)
b / Å	14.2230(9)
c / Å	15.4574(11)
α / deg.	102.2520(10)
β / deg.	92.1720(10)
γ / deg.	110.8340(10)
V / Å^3	2832.9(3)
Space Group	P-1 (#2)
Z	2
D / gcm^{-3}	1.516
F000	1314.0
μ(MoKα) / cm^{-1}	4.864
Reflection/Parameter Ratio	17.07
R1 ($I > 2.00\sigma(I)$)	0.0443
R (All reflections)	0.0473
wR2 (All reflections)	0.1178
Goodness of Fit Indicator	1.061

The crystal contains disordered toluene molecules and water molecules as cocrystalizing species.

References

S1 A. Ariafard and Z. Lin, *Organometallics*, 2006, **25**, 4030–4033.
S2 L. P. Wolters, W. J. Van Zeist and F. M. Bickelhaupt, *Chem. Eur. J.*, 2014, **20**, 11370–11381.