Supporting Information

Enolizable Ketones as Activators of Palladium(II) Precatalysts in Amine Arylation Reactions

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NMR Spectra of Isolated Compounds

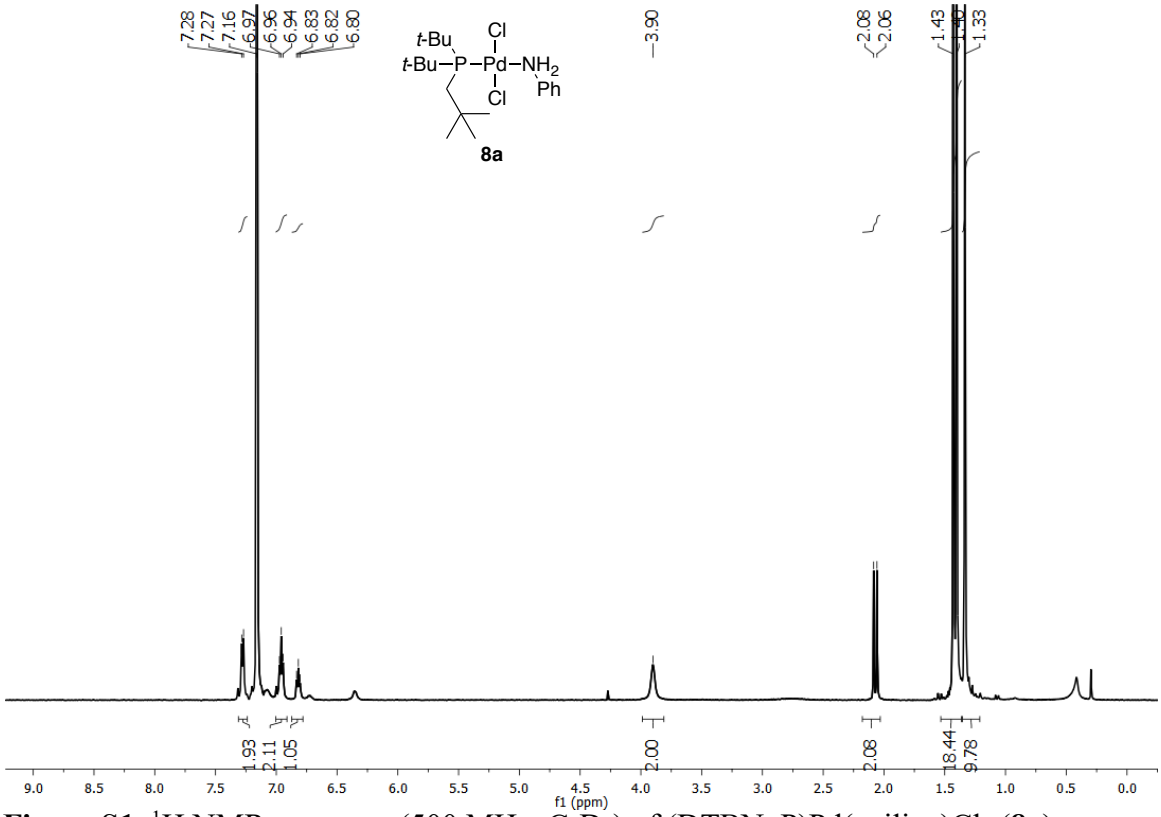

Figure S1. ^{1}H NMR spectrum (500 MHz, C_6D_6) of (DTBNpP)Pd(aniline)Cl_2 (**8a**)

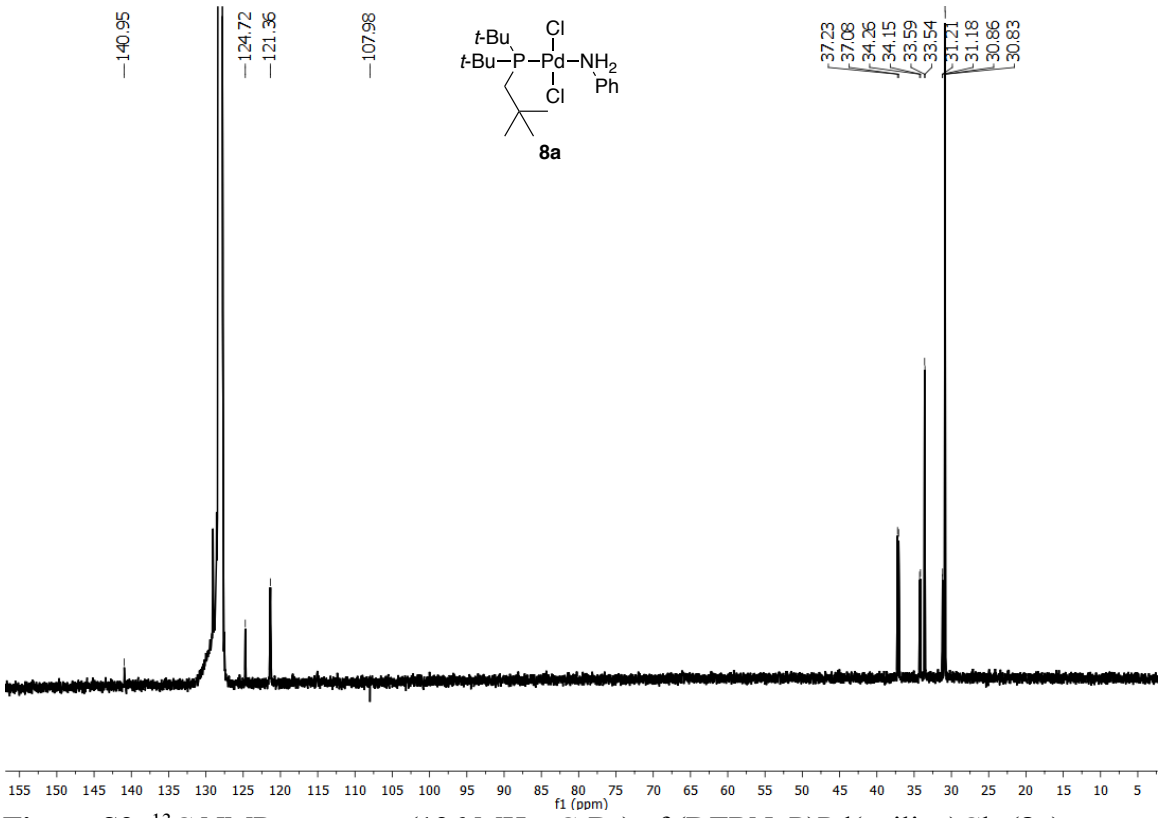

Figure S2. ^{13}C NMR spectrum (126 MHz, C_6D_6) of (DTBNpP)Pd(aniline)Cl_2 (**8a**)

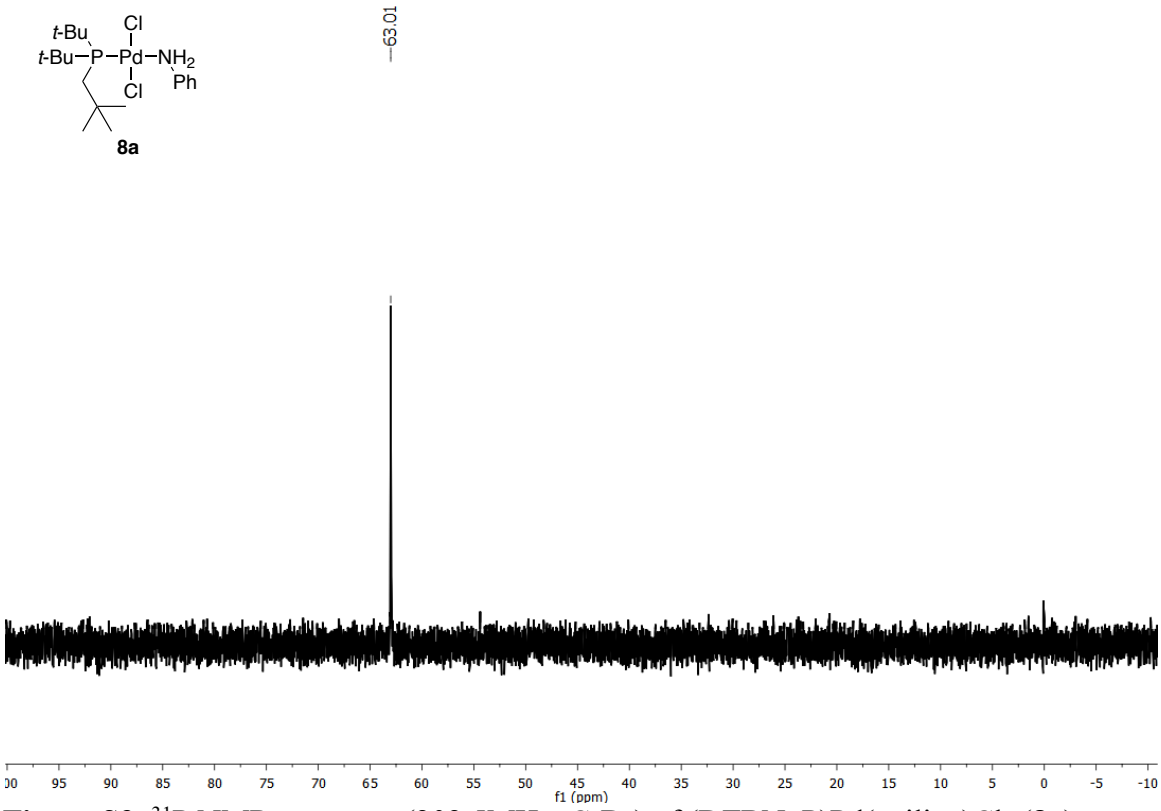

Figure S3. ^{31}P NMR spectrum (202.5MHz, C_6D_6) of (DTBNpP)Pd(aniline)Cl_2 (**8a**)

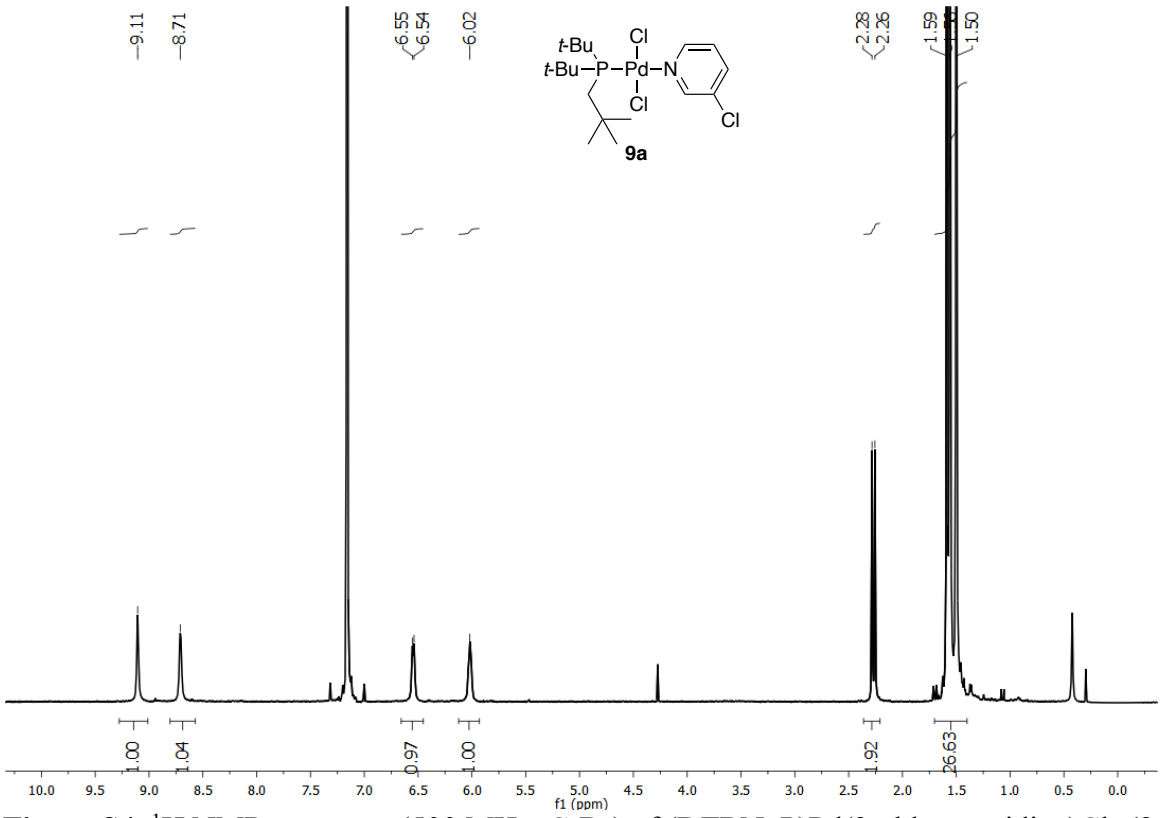

Figure S4. ^{1}H NMR spectrum (500 MHz, C_6D_6) of (DTBNpP)Pd(3-chloropyridine)Cl_2 (**9a**)

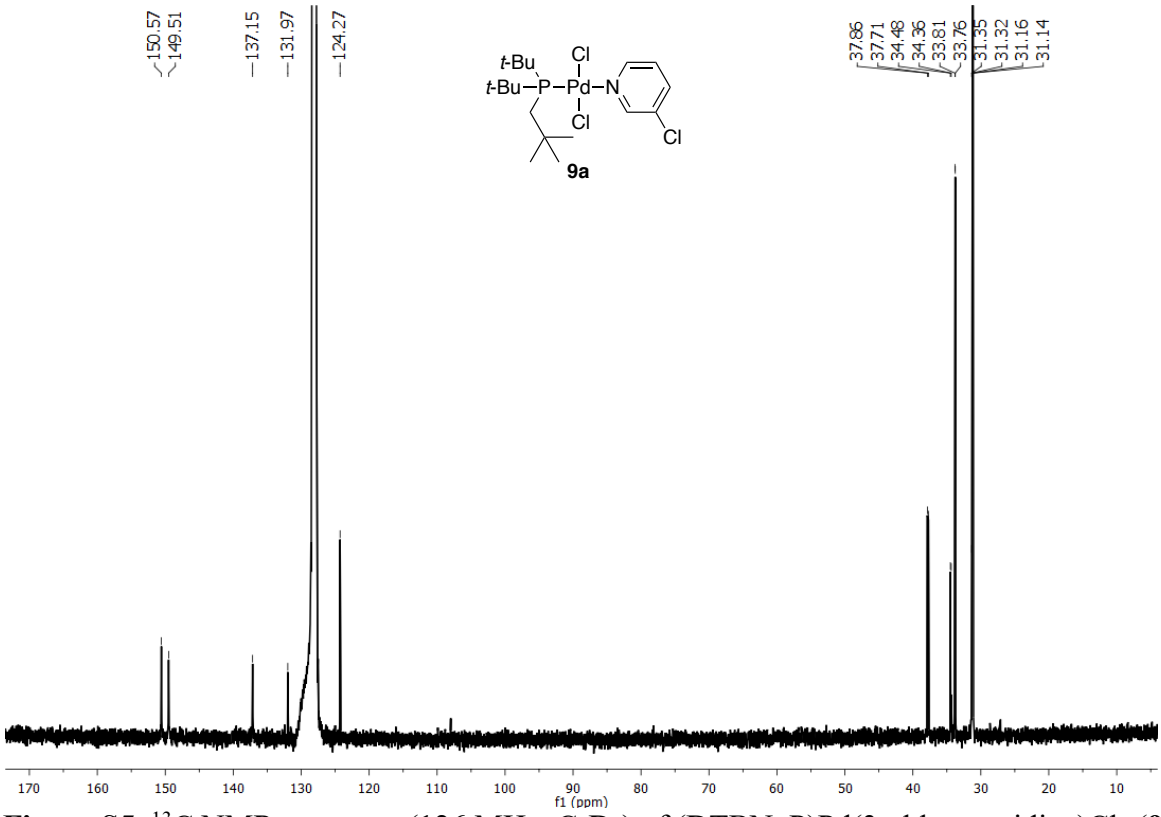

Figure S5. ^{13}C NMR spectrum (126 MHz, C_6D_6) of (DTBNpP)Pd(3-chloropyridine)Cl_2 (**9a**)

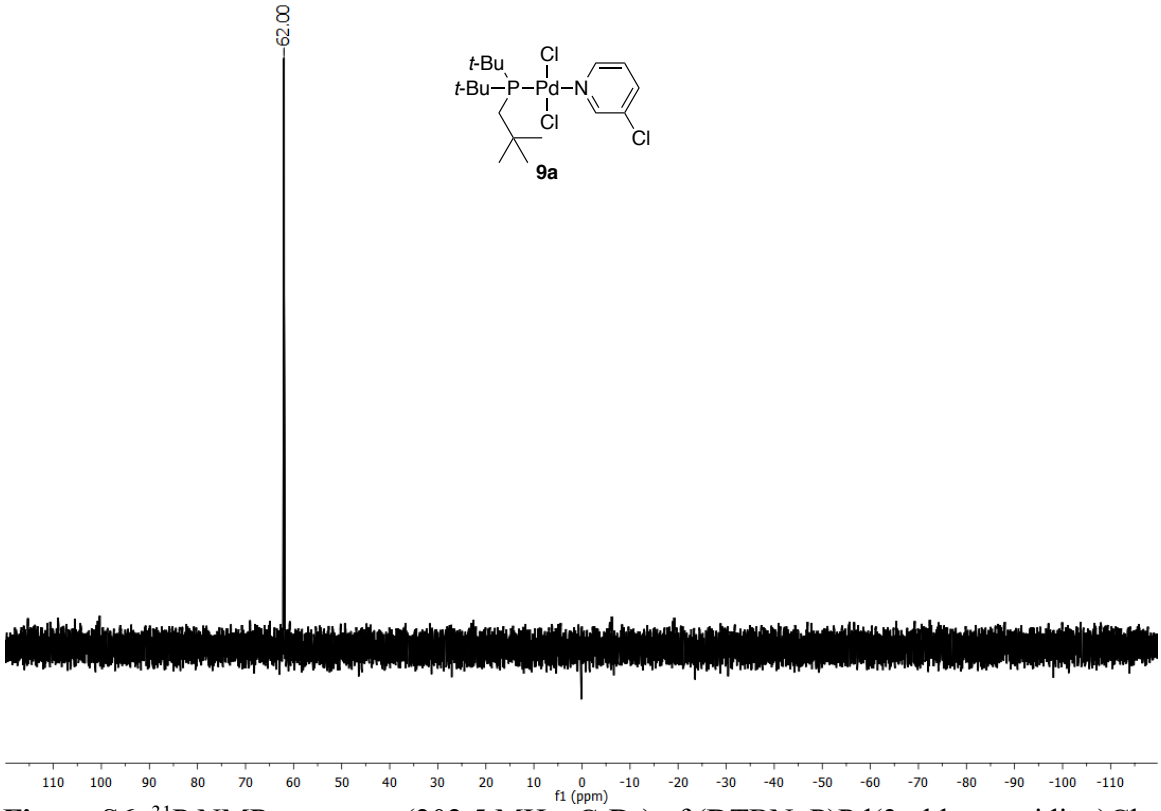

Figure S6. ^{31}P NMR spectrum (202.5 MHz, C_6D_6) of (DTBNpP)Pd(3-chloropyridine)Cl_2 (**9a**)

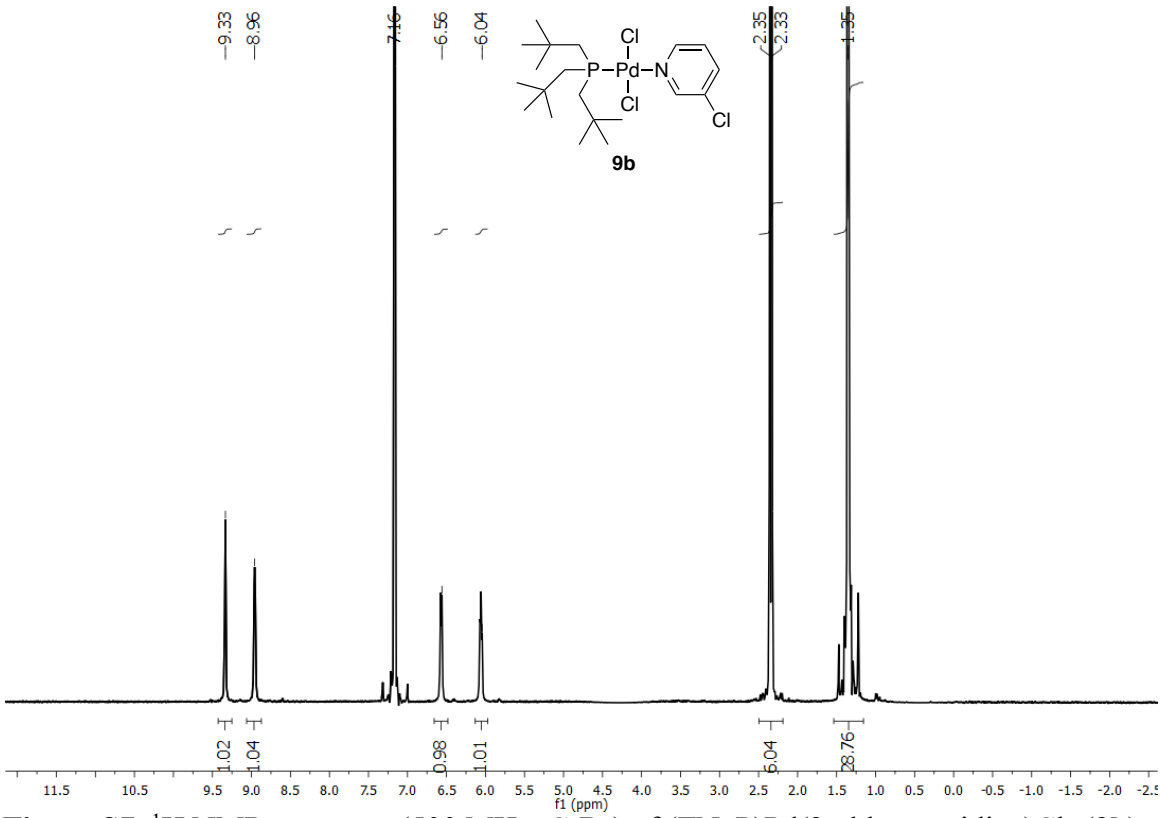

Figure S7. ^{1}H NMR spectrum (500 MHz, C_6D_6) of (TNpP)Pd(3-chloropyridine)Cl_2 (**9b**)

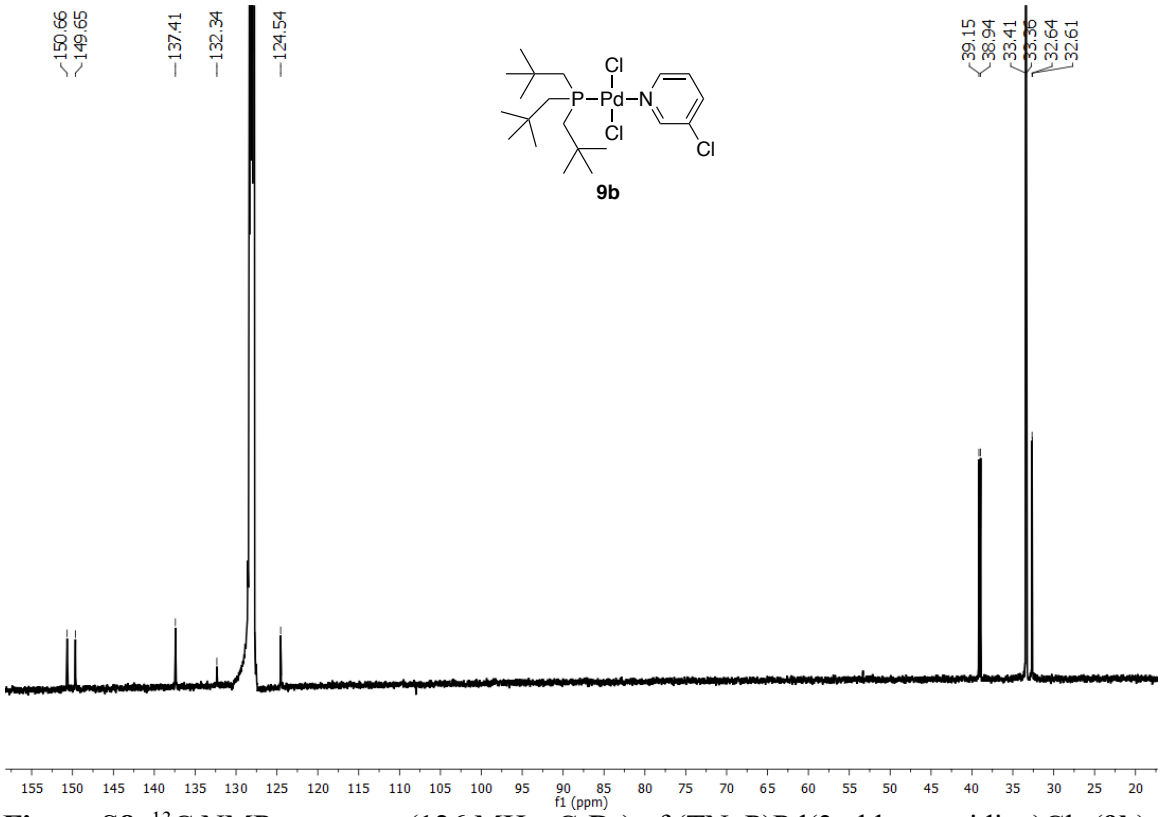

Figure S8. ^{13}C NMR spectrum (126 MHz, C_6D_6) of (TNpP)Pd(3-chloropyridine)Cl_2 (**9b**)

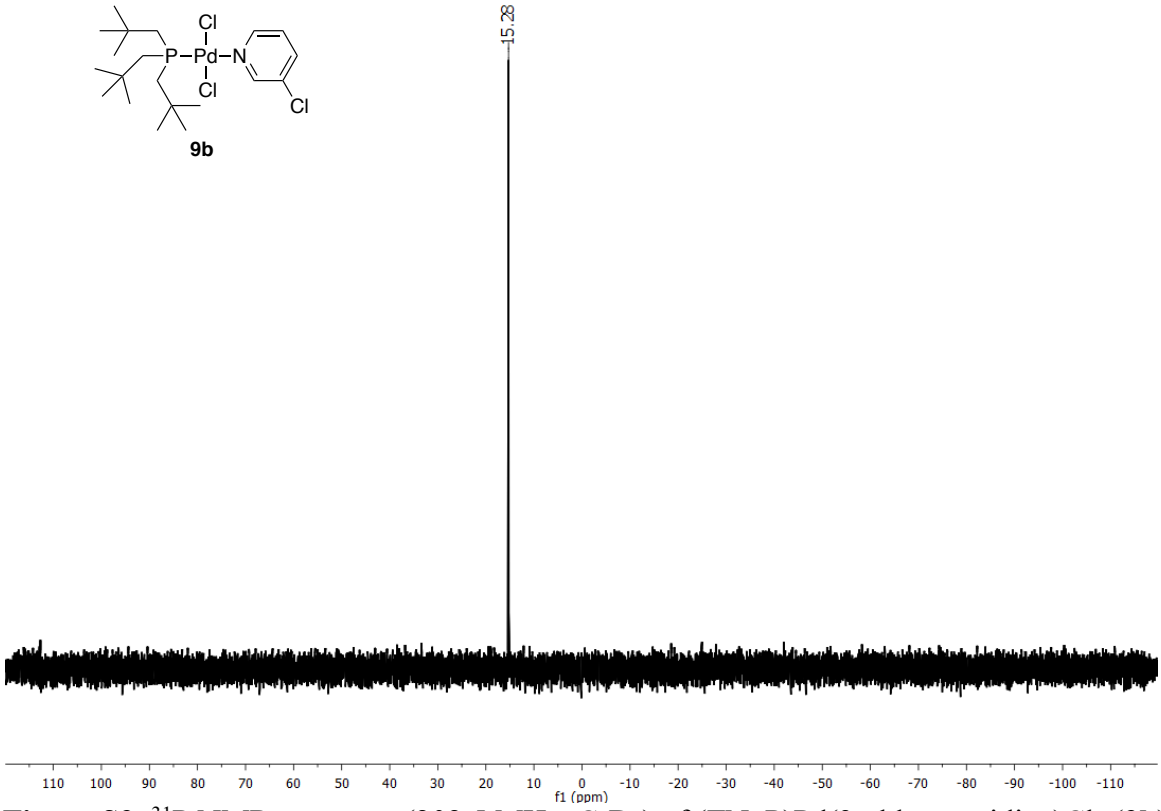

Figure S9. ^{31}P NMR spectrum (202.5 MHz, C_6D_6) of (TNpP)Pd(3-chloropyridine)Cl_2 (**9b**)

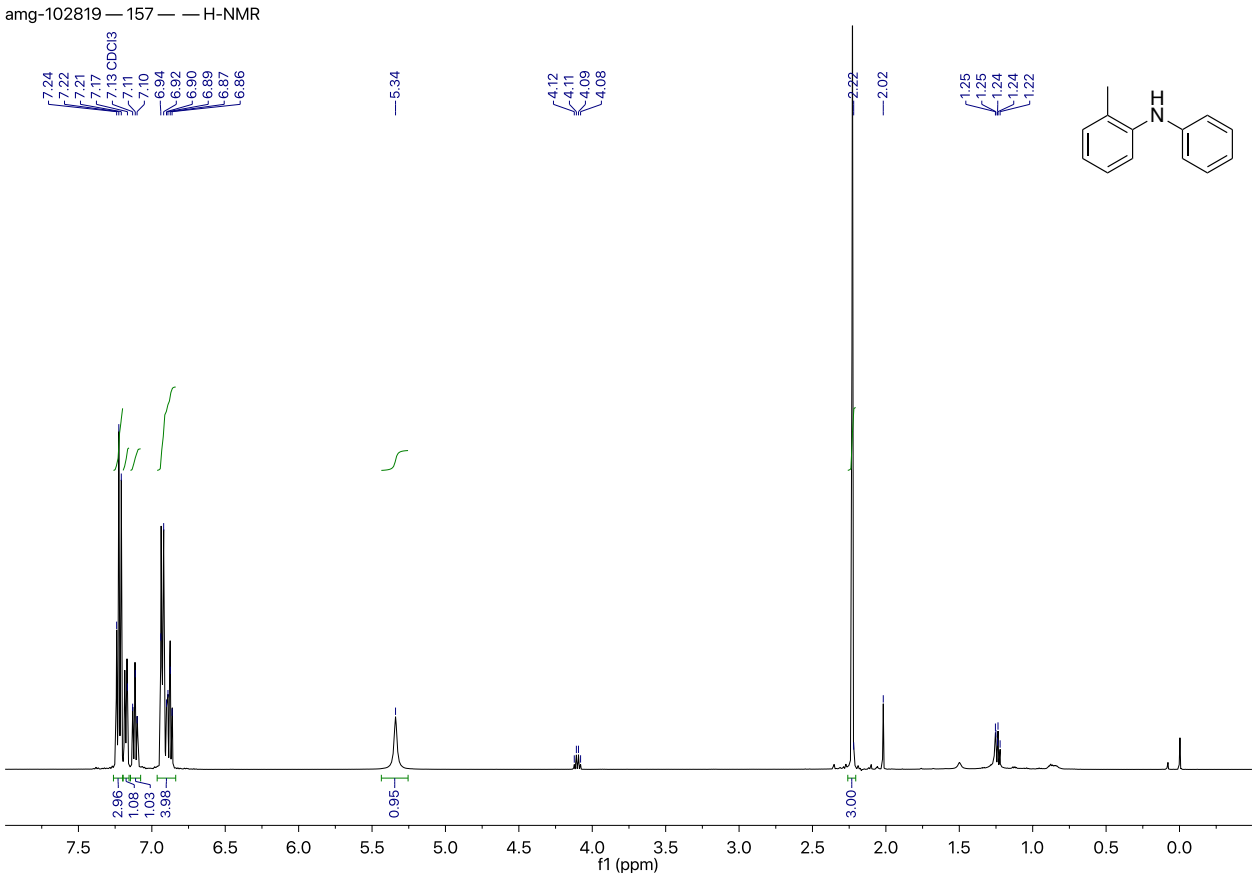

Figure S10. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of *N*-phenyl 2-toluidine

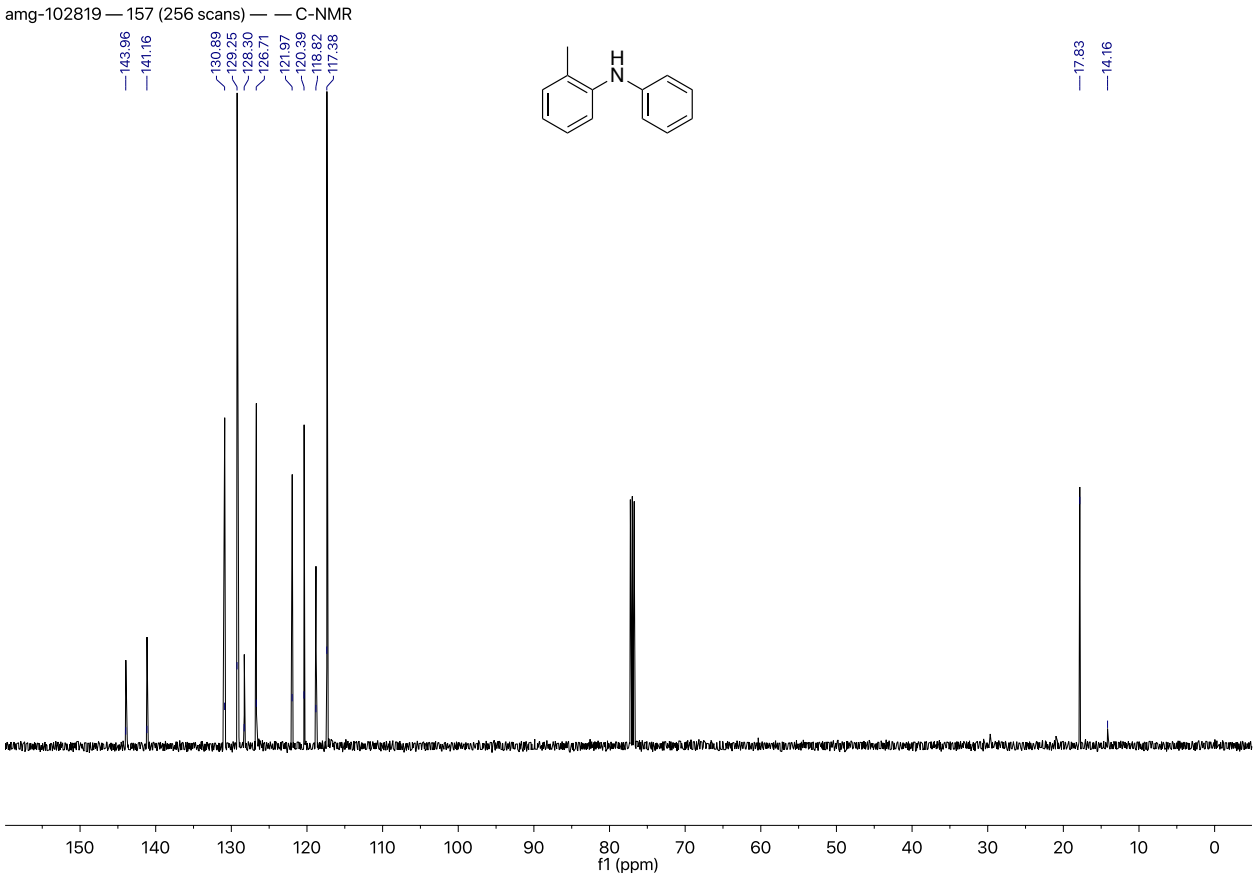

Figure S11. ^{13}C NMR spectrum ($CDCl_3$, 126 MHz) of *N*-phenyl 2-toluidine

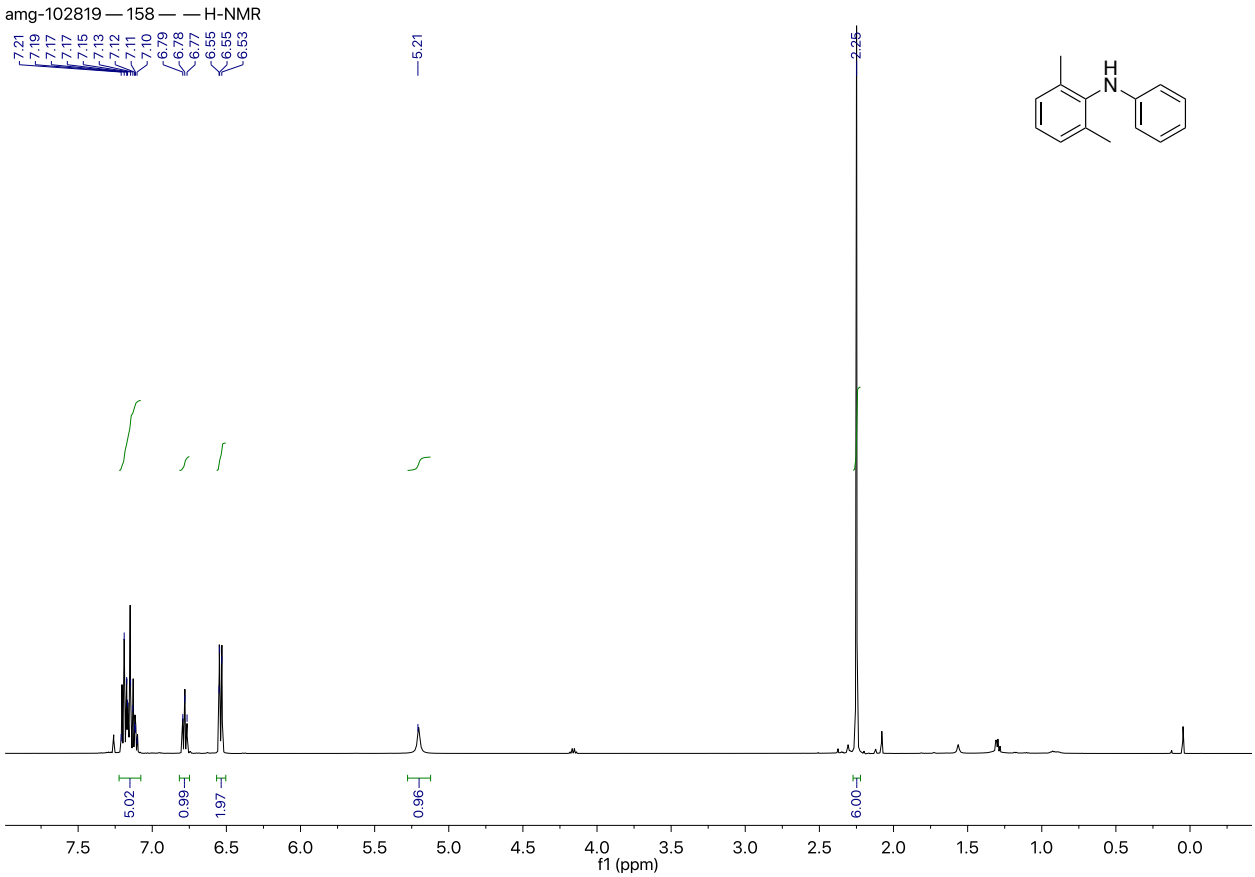

Figure S12. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of *N*-phenyl 2,6-dimethylaniline

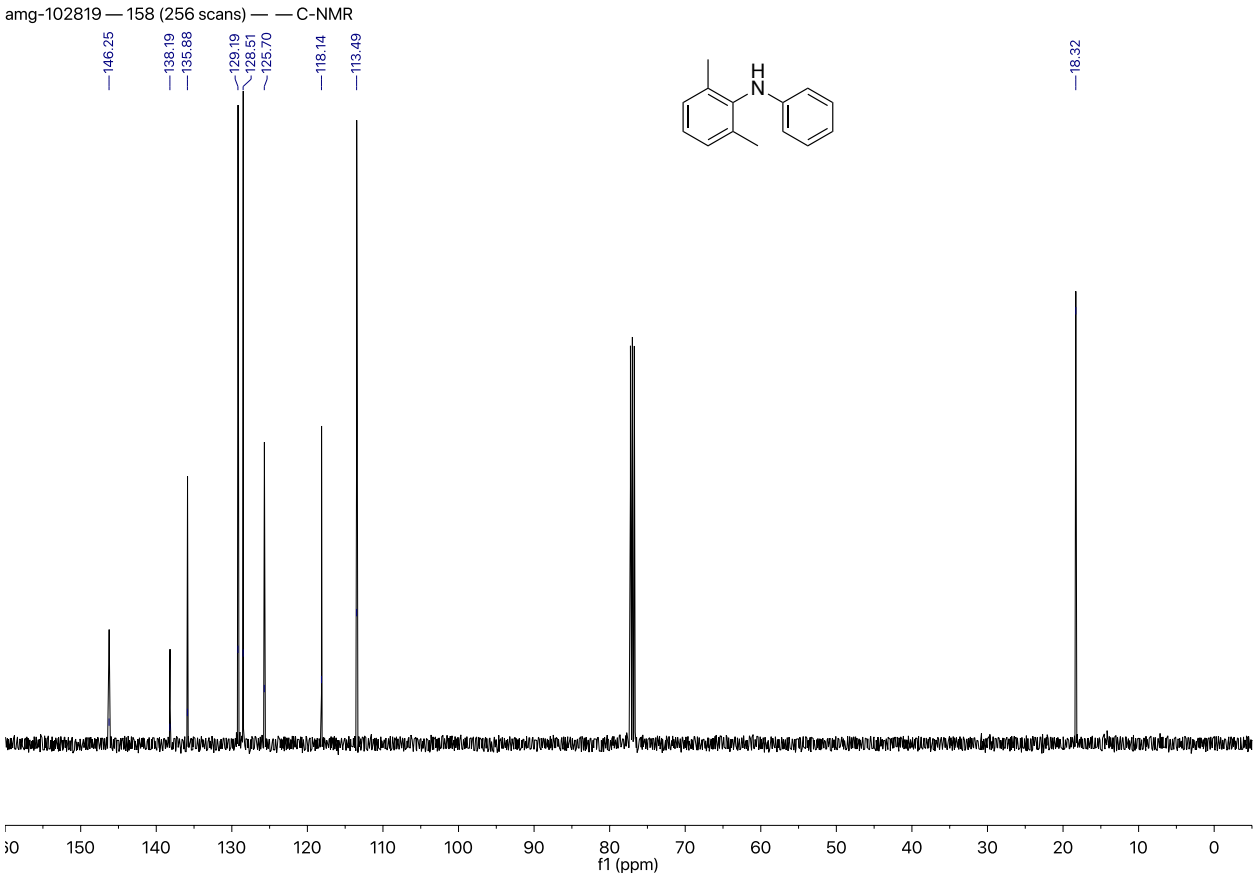

Figure S13. ^{13}C NMR spectrum ($CDCl_3$, 126 MHz) of *N*-phenyl 2,6-dimethylaniline

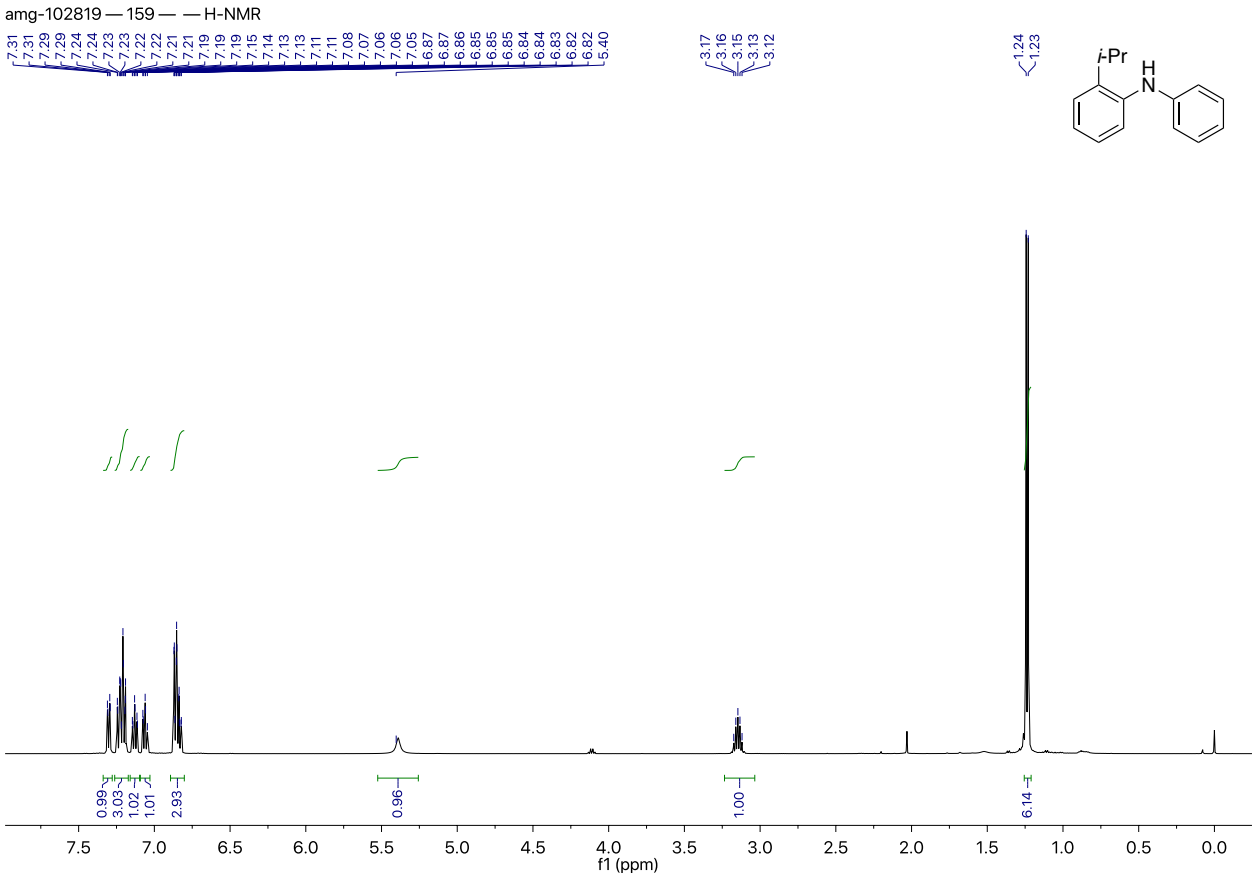

Figure S14. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of *N*-phenyl 2-isopropylaniline

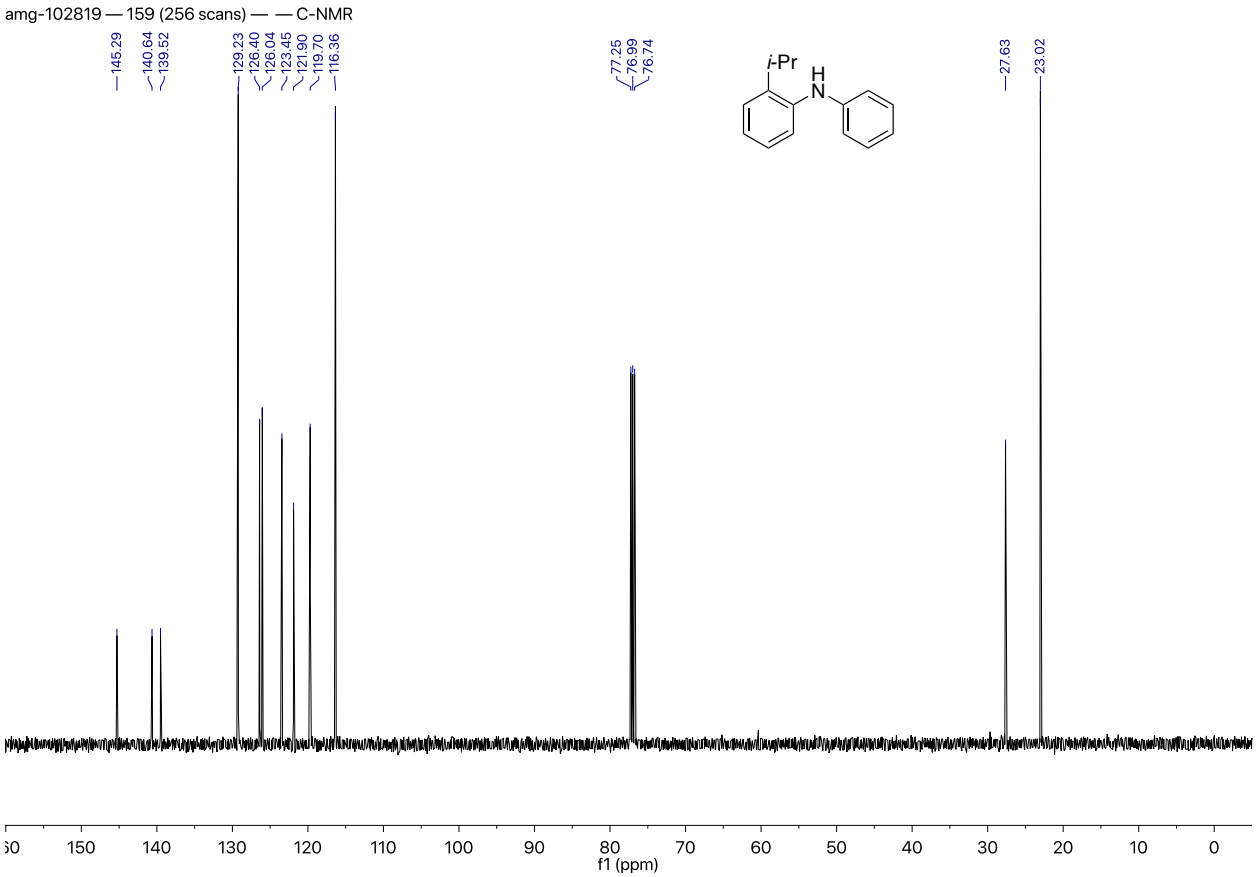

Figure S15. ^{13}C NMR spectrum ($CDCl_3$, 126 MHz) of *N*-phenyl 2-isopropylaniline

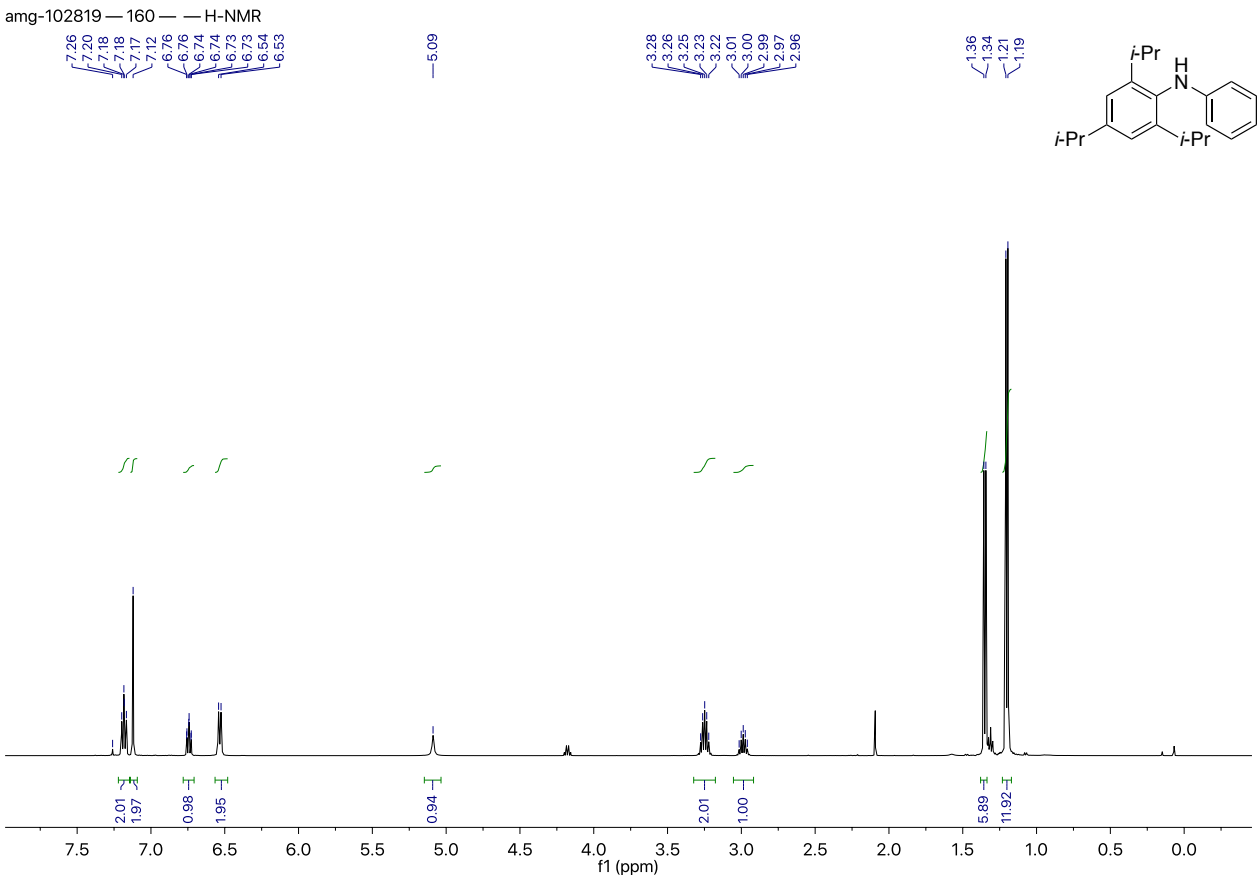

Figure S16. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of *N*-phenyl 2,4,6-triisopropylaniline

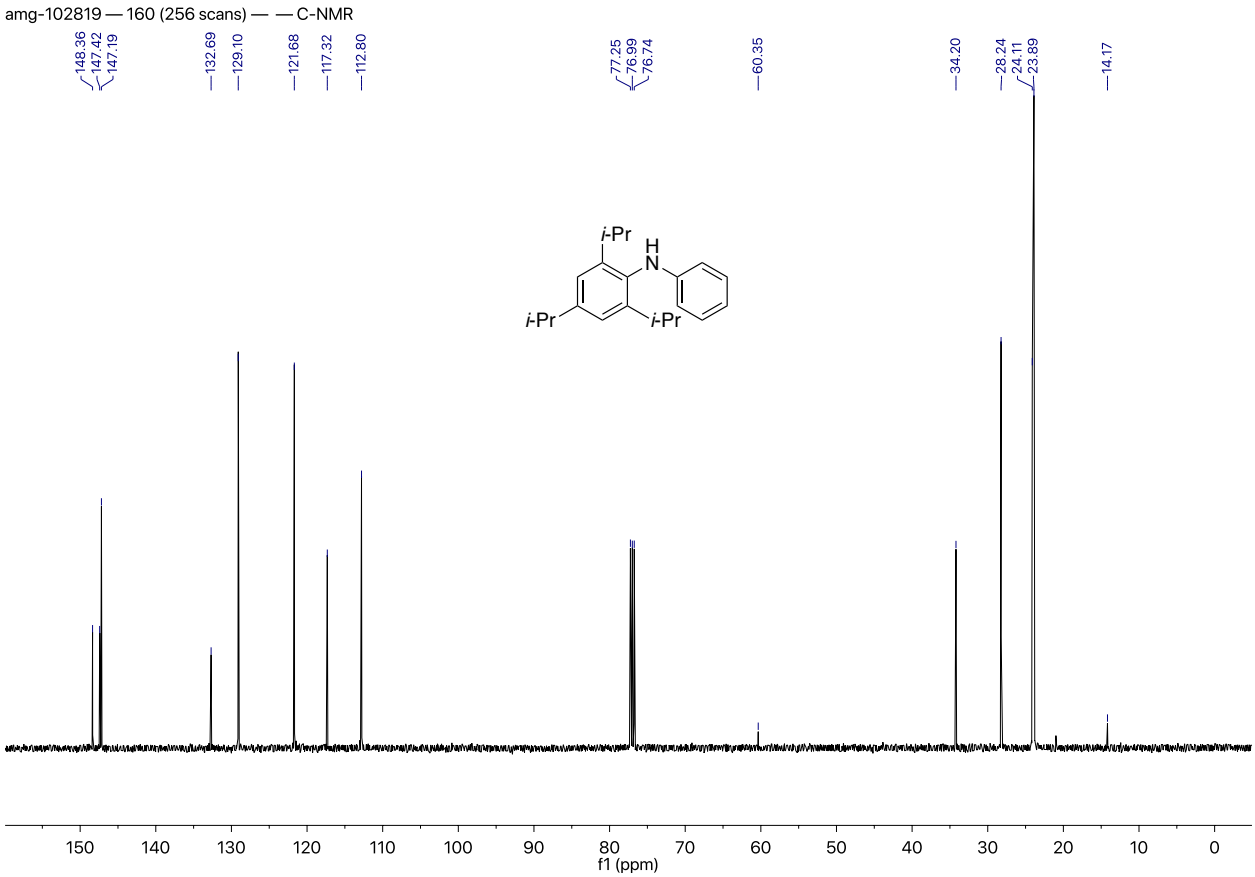

Figure S17. ^{13}C NMR spectrum ($CDCl_3$, 126 MHz) of *N*-phenyl 2,4,6-triisopropylaniline

X-ray Crystallographic Data

Table S1. Crystallographic data and structure refinement parameters for $(PNp_3)Pd(C_5H_3NCl)Cl_2$

Formula	$C_{20}\ H_{37}\ Cl_3NP\ Pd$	γ (deg)	90
Formula weight	535.27	V(Å^3)	4888.71(13)
T (K)	101(2) K	Z	8
Wavelength (Å)	0.71073	D_{calcd} (gcm^{-3})	1.4544
Space group	C2/c	μ(mm^{-1})	1.158
Crystal system	monoclinic	F(000)	2205.0
a (Å)	17.8460(3)	θ_{max} (deg)	26.022
b (Å)	15.0741(2)	Reflection collected	31885
c (Å)	18.2288(3)	unique reflections	7172
α (deg)	90	R1, wR2 ($I \geq 2\sigma(I)$)	0.0160, 0.0393
β (deg)	94.4920(10)		

Ketone Loading Study with Precatalyst 7a

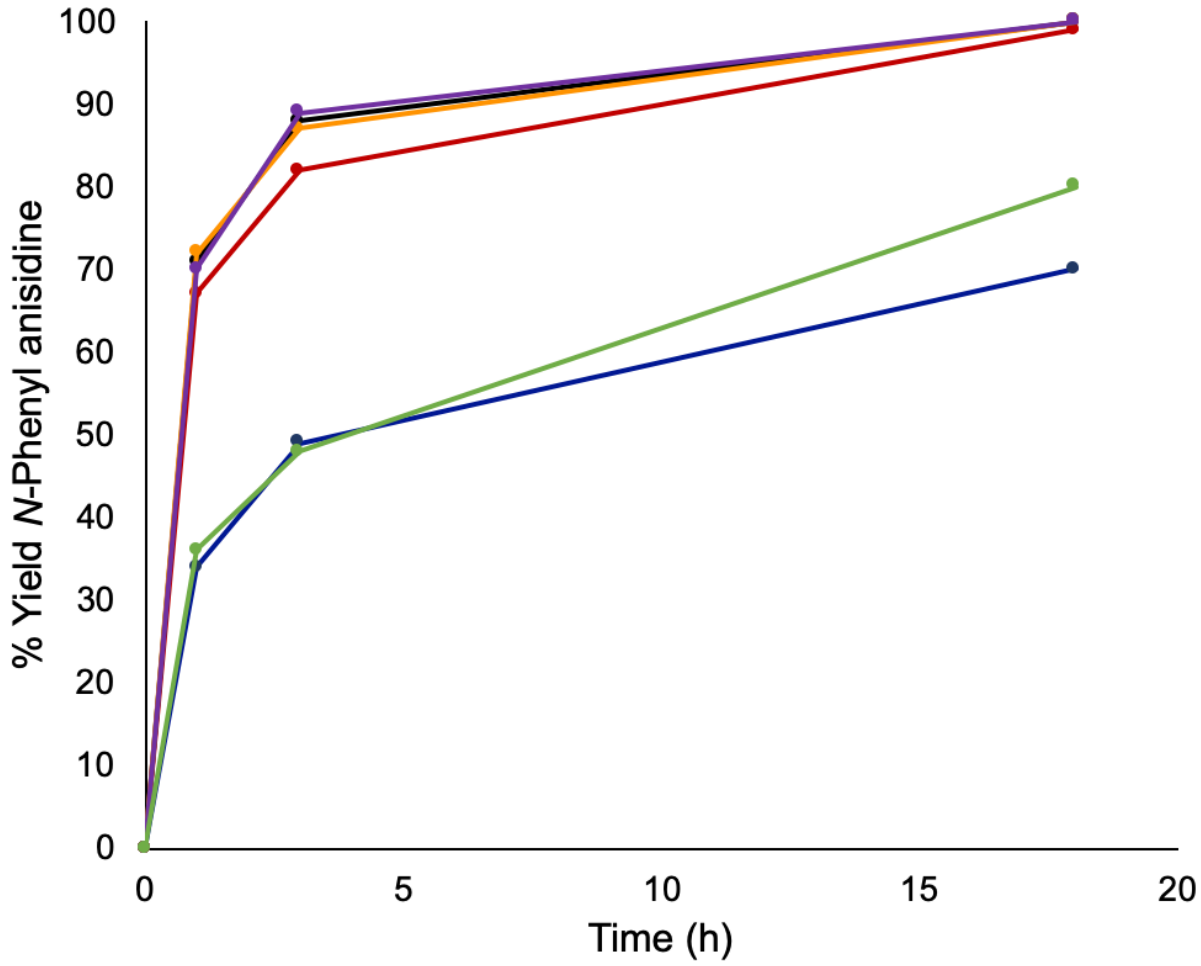

Figure S18. Reaction profile for the coupling of 4-bromoanisole and aniline at room temperature using precatalyst **7a** with 2–20 mol% 3-pentanone: 2 mol% (blue), 5 mol% (red), 8 mol% (black), 11 mol% (orange), 14 mol% (purple), 20 mol% (green)

Table S2. GC conversions for each trial in ketone loading study (Figure S18)

		2 mol%	5mol%	8mol%	11mol%	14mol%	20mol%
1 h GC conv	1	31%	62%	67%	69%	67%	34%
	2	35%	69%	74%	76%	73%	39%
	3	37%	70%	72%	71%	70%	35%
	average	34%	67%	71%	72%	70%	36%
	std dev	3%	4%	4%	4%	3%	3%
3h GC conv	1	51%	85%	91%	87%	88%	47%
	2	51%	80%	87%	86%	91%	50%
	3	45%	81%	86%	88%	88%	47%
	average	49%	82%	88%	87%	89%	48%
	std dev	3%	3%	3%	1%	2%	2%
18h GC convd	1	69%	99%	100%	100%	100%	77%
	2	73%	99%	100%	100%	100%	81%
	3	68%	99%	100%	100%	100%	82%
	average	70%	99%	100%	100%	100%	80%
	std dev	3%	0%	0%	0%	0%	3%