Supporting Information

Aminomethylation Reaction of *ortho*-Pyridyl C-H Bonds Catalyzed by Group 3 Metal Triamido Complexes

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Contents:

1. General procedure for catalytic aminomethylation reaction by $Ln[N(SiMe_3)_2]_3$.

General

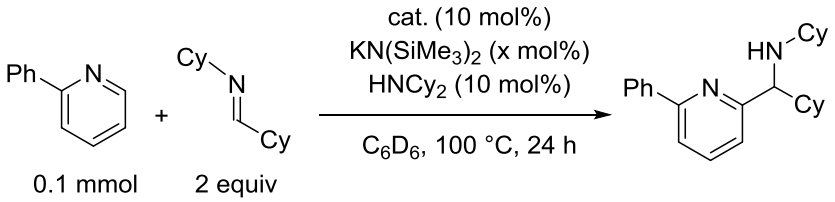
All manipulations involving air- and moisture-sensitive organometallic compounds were carried out under argon using the standard Schlenk technique or argon-filled glovebox. $LiCH_2SiMe_3$[S1] and $Y(CH_2SiMe_3)_3(THF)_2$[S2] were prepared according to the literatures. $Y[N(SiMe_3)_2]_3$, $Ln[N(SiMe_3)_2]_3$ (Ln = La, Nd, Sm, Gd, Yb), YCl_3, $ScCl_3$, $LuCl_3$, $CeCl_3$, $ZrCl_4$, $HfCl_4$, Cp_2ZrCl_2, $NbCl_5$, $TaCl_5$, $KN(SiMe_3)_2$, amines and aldehydes to synthesis imines, and $MgSO_4$ were purchased and used as received. Substituted pyridines, *N*-heteroaromatics, and amines as additive were purchased and purified by distillation over CaH_2. Hexane, pentane, toluene and benzene-d_6 were distilled over CaH_2 and thoroughly degassed by trap-to-trap distillation before use. NMR spectra were recorded on a Bruker AV 400M spectrometer in 5 mm NMR tube. Chemical shifts were reported in parts per million and referenced to residual proton signal of the solvent (^{1}H benzene-d_6, δ = 7.15; chloroform, δ = 7.26) or the solvent itself ($^{13}C\{^1H\}$ benzene-d_6, δ = 128.06; chloroform, δ = 77.16). Melting points were recorded by a BUCHI Melting Point M-565. IR spectra were recorded on a JASCO FT/IR 4000 spectrometer. Mass spectra were recorded on a JEOL JMS-700 spectrometer. The elemental analyses were recorded by using Perkin Elmer 2400 at the Faculty of Engineering Science, Osaka University. Flash column chromatography was performed using silica gel 60 (0.040–0.063 mm, 230–400 mesh ASTM).

2. Catalysts screening for aminomethylation reaction.

General procedure for catalysts screening of aminoalkylation reaction

In a glovebox under argon, catalyst (0.010 mmol, 10 mol%), **1a** (14.1 μL, 15.3 mg, 0.100 mmol), **2a** (38.6 mg, 0.200 mmol, 2 equiv) and C_6D_6 (0.5 mL) were added to a J-young capped NMR tube. The NMR tube was heated in oil bath at 100 °C for 24 h. After cooling to room temperature, the reaction mixture was diluted with Et_2O (1.5 mL) and filtered short silica gel plug to remove metal residues. The obtained solution was concentrated under reduced pressure at room temperature. 1,1,2,2-Tetrachloroethane (0.050 mmol) was added to the residue as an internal standard. Yield of the product **3aa** was determined by integral ratios of ^{1}H NMR signals of 1,1,2,2-tetrachloroethane and CyNC*H*(Ar)Cy proton.

Table S1. Screening of catalyst precursors.



0.1 mmol 2 equiv

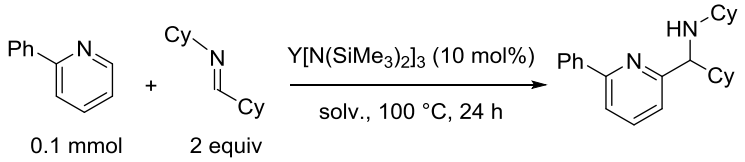
entry	cat.	$KN(SiMe_3)_2$ (mol%)	yield (%)[a]
1	$YCl_3(thf)_{3.5}$	30	50
2	$ScCl_3(thf)_3$	30	n.d.
3	$LuCl_3(thf)_3$	30	n.d.
4	$CeCl_3(thf)_2$	30	17
5	$ZrCl_4$	40	n.d.
6	$HfCl_4$	40	n.d.
7	Cp_2ZrCl_2	20	n.d.
8	$NbCl_5$	50	n.d.
9	$TaCl_5$	50	n.d.

[a] Determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane (0.05 mmol) as an internal standard.

3. Optimization of catalytic aminomethylation reaction.

In a glovebox under argon, $Y[N(SiMe_3)_2]_3$ (5.7 mg, 0.010 mmol, 10 mol%), **1a** (14.3 μL, 15.5 mg, 0.100 mmol), **2a** (38.7 mg, 0.200 mmol, 2 equiv) and solvent (total volume, 0.50 mL) were added to an oven-dried 3-mL vial. The vial was capped with a PTFE-lined cap, and heated by aluminum block bath with stirrer at 80 °C or 100 °C for 24 h in the absence or presence of amines (10 mol%). After cooling to room temperature, the reaction mixture was diluted with Et_2O (1.5 mL) and filtered through short silica gel plug. The obtained solution was concentrated under reduced pressure at room temperature. 1,1,2,2-Tetrachloroethane (0.050 mmol) was added to the residue as an internal standard.

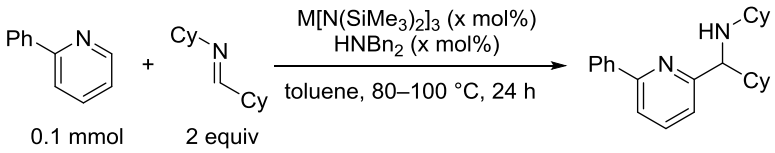
Table S2. Screening of solvents.



entry	solv.	yield (%)[a]
1	C_6D_6	48
2	Toluene	54
3	Mesitylene	43
4	Nonane	42
5	C_6H_5Cl	29
6[b]	THF-d_8	0
7[b]	C_6D_6/THF-d_8= 9:1	34
8[b]	pyridine-d_5	0
9[b]	C_6D_6/pyridine-d_5= 9:1	0

[a] Determined by ^1H NMR using 1,1,2,2-tetrachloroethane (0.05 mmol) as an internal standard. [b] Complex **4** was used as catalyst.

Table S3. Optimization of catalyst loading and temperature.

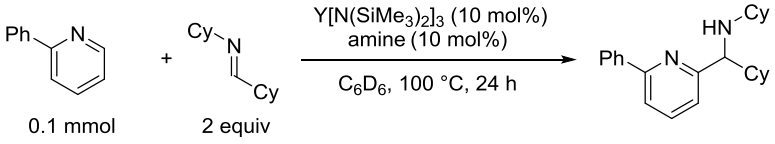


0.1 mmol 2 equiv

entry	M (mol%)	temp (°C)	conv. (%)[a]
1	Y (10)	100	77
2	Y (10)	80	36
3	Y (5)	100	42
4	Y (5)	80	12
5	Gd (10)	100	85
6	Gd (10)	80	49
7	Gd (5)	100	69
8	Gd (5)	80	21

[a] Determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane (0.05 mmol) as an internal standard.

Table S4. Screening of amines.



0.1 mmol 2 equiv

entry	amine	18 h yield (%)[a]	24 h yield (%)[a]	48 h yield (%)[a]
1	HTMP	16	29	71
2	HN(^{t}Bu)(^{i}Pr)	17	31	70
3	$HNCy_2$	34	53	84
4	HNCy(^{i}Pr)	29	45	70
5	HNCyMe	60	66	78
6	$HNBn_2$	70	78	87
7	HN(^{n}Bu)$_2$	-	63	76
8	H_2N(1-Ad)	69	75	86
9	H_2NCy	-	44	63
10	H_2NBn	-	0	-
11	$H_2N(^nC_6H_{13})$	-	0	-

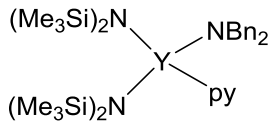
[a] Determined by ^{1}H NMR related to fluorene (0.05 mmol).

4. Preparation and characterization of yttrium complexes 4-6.

Preparation of $[(SiMe_3)_2N]_2YNBn_2(thf)$ (4):

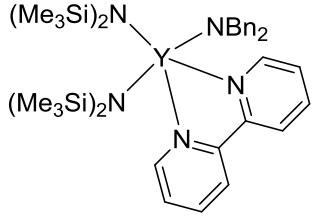
A solution of 1,1,1,3,3,3-hexamethyldisilazane (429 μL, 326 mg, 2.02 mmol) in hexane (3 mL) was added to a solution of $Y(CH_2SiMe_3)_3(thf)_2$ (500 mg, 1.01 mmol) in hexane (5 mL) at room temperature, and then a solution of dibenzylamine (194 μL, 199 mg, 1.01 mmol) in hexane (2 mL) was added to the reaction mixture. The reaction mixture was stirred for overnight. The reaction mixture was filtered, and the volatiles were evaporated to afford yellow solid. The resulting solid was washed with pentane (2 mL x 2). Drying in vacuo gave complex **4** as white powders (260 mg, 0.384 mmol, 38% yield). The hexane washing layer was cooled at -40 °C to afford pale yellow crystals (191 mg, 0.281 mmol, 28% yield). mp 114-117 °C. ^{1}H NMR (400 MHz, C_6D_6, 30 °C): δ 7.32 (d, ^3J = 7.4 Hz, 4H, *o*-Ph), 7.21 (dd, ^3J = 7.5 Hz, ^3J = 7.4 Hz, 4H, *m*-Ph), 7.09 (t, ^3J = 7.5 Hz, 2H, *p*-Ph), 4.48 (s, 4H, CH_2Ph), 3.69 (br m, 4H, α-THF), 1.05 (br m, 4H, β-THF), 0.39 (s, 36H, $Si(CH_3)_3$); $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 30 °C): δ 142.7 (Ph), 128.9 (Ph), 128.3 (Ph, overlapped with C_6D_6), 126.5 (Ph), 72.4 (CH_2Ph), 53.5 (α-THF), 24.8 (β-THF), 5.3 ($Si(CH_3)_3$); Anal. Calcd for $C_{30}H_{57}N_3OSi_4Y$: C, 53.22; H, 8.49; N, 6.21. Found: C, 53.02; H, 8.68; N, 6.12.

Preparation of $[(SiMe_3)_2N]_2YNBn_2(py)$ (5):



A solution of pyridine (48.3 μL, 0.600 mmol, 3 equiv) in pentane (2 mL) was added to a solution of complex **4** (135.6 mg, 0.200 mmol) in pentane at room temperature. The pale yellow reaction mixture was stirred for 15 h and small amount of precipitate was removed by filtration. All volatiles were removed under reduced pressure to obtain pale yellow powder (121.3 mg, 0.177 mmol, 89% yield). mp 98-100 °C. ^{1}H NMR (400 MHz, C_6D_6, 30 °C): δ 8.67 (d, ^3J = 5.8 Hz, 2H, *o*-Py), 7.21-7.10 (m, 8H, *o*- and *m*-Ph), 7.06 (t, ^3J = 6.8 Hz, 2H, *p*-Ph), 6.79 (t, ^3J = 7.8 Hz, 1H, *p*-Py), 6.49 (dd, ^3J = 7.8 Hz, ^3J = 5.8 Hz, 2H, *m*-Py), 4.48 (s, 4H, CH_2Ph), 0.42 (s, 36H, $Si(CH_3)_3$); $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 30 °C): δ 150.1 (*o*-py), 142.4 (*ipso*-Ph), 138.5 (br s, *p*-py), 129.0 (*o*-Ph), 128.2 (*m*-Ph), 126.3 (*p*-Ph), 124.4 (*m*-py), 53.4 (CH_2Ph), 5.3 ($Si(CH_3)_3$).

Preparation of $[(SiMe_3)_2N]_2YNBn_2$(2,2'-bipyridyl) (6):



A solution of 2,2'-bipyridyl (31.2 mg, 0.200 mmol, 1 equiv) in pentane (2 mL) was added to a solution of complex **4** (136.5 mg, 0.200 mmol) in pentane at room temperature to give orange suspension. The suspension was stirred for 1 h and the supernatant was removed by decantation. All volatiles were removed under reduced pressure to obtain orange powder (137.5 mg, 0.180 mmol, 90% yield). mp 128 °C. ^{1}H NMR (400 MHz, C_6D_6, 30 °C): δ 9.55 (d, ^3J = 5.1 Hz, 2H, 6-bpy), 6.92-6.85 (m, 10H), 6.81-6.76 (m, 4H), 6.64 (dt, ^3J = 5.1 Hz, ^4J = 3.5 Hz, 2H, bpy), 4.36 (s, 4H, CH_2Ph), 0.47 (s, 36H, $Si(CH_3)_3$); $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 30 °C): δ 153.2 (2-bpy), 152.7 (6-bpy), 142.6 (*ipso*-Ph), 139.2 (bpy), 128.8 (*o*-Ph), 127.8 (*m*-Ph), 125.6 (*p*-Ph), 124.8 (bpy), 121.0 (bpy), 54.0 (CH_2Ph), 6.6 ($Si(CH_3)_3$).

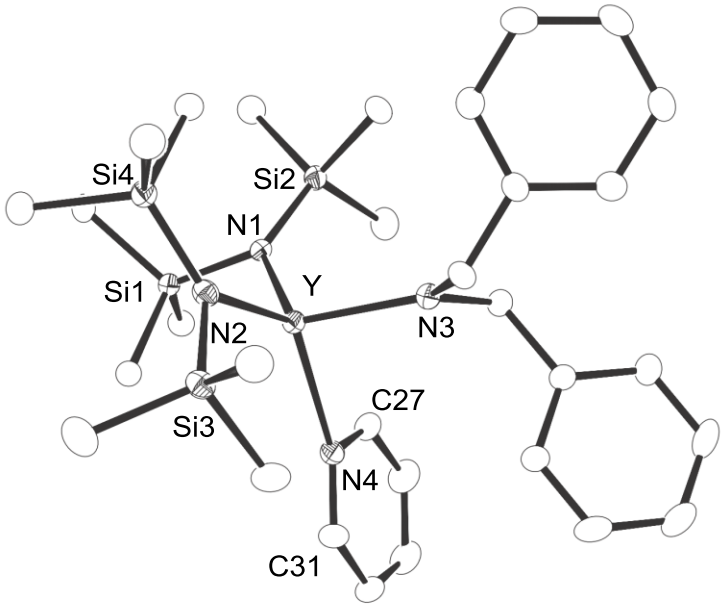


Figure S1A. Crystal structure of complex **5** with 30% thermal ellipsoids. All H atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Y—N1, 2.250(3); Y—N2, 2.259(3); Y—N3, 2.179(3); Y—N4, 2.549(4); Y—Si1, 3.2549(15); Y—Si3, 3.2955(14); Y—N1—Si1, 109.26(16); Y—N1—Si2, 129.65(18); Y—N2—Si3, 111.58(17); Y—N2—Si4, 125.61(18); Y—N4—C27, 108.8(3); Y—N4—C31, 135.2(3).

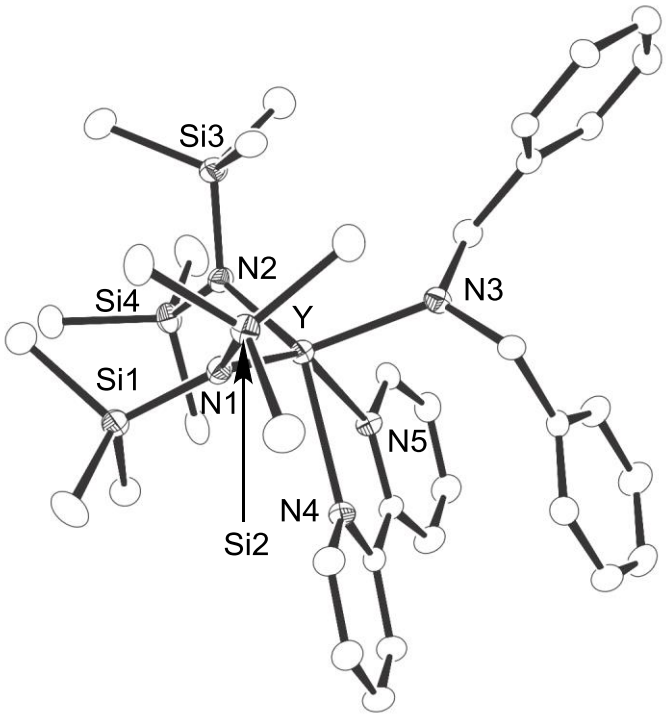


Figure S1B. Crystal structure of complex **6** with 30% thermal ellipsoids. All H atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Y—N1, 2.298(5); Y—N2, 2.302(5); Y—N3, 2.191(6); Y—N4, 2.515(5); Y—N5, 2.472(5); Y—Si1, 3.352(2); Y—Si3, 3.342(2); Y—N1—Si1, 112.3(3); Y—N1—Si2, 128.0(3); Y—N2—Si3, 111.3(3); Y—N2—Si4, 130.8(3).

5. Kinetic analysis of the catalytic aminomethylation reaction.

In a glovebox under argon, catalyst, **1a**, **2a**, fluorene (0.05 mmol), and C_6D_6 (0.5 mL) were added to a J-young capped NMR tube. The NMR tube was heated in oil bath. Yield of the product **3aa** and consumption of 2-phenylpyridine were determined by integral ratios of ^{1}H NMR signals of fluorene, CyNC*H*(Ar)Cy, and 2-phenylpyridine proton.

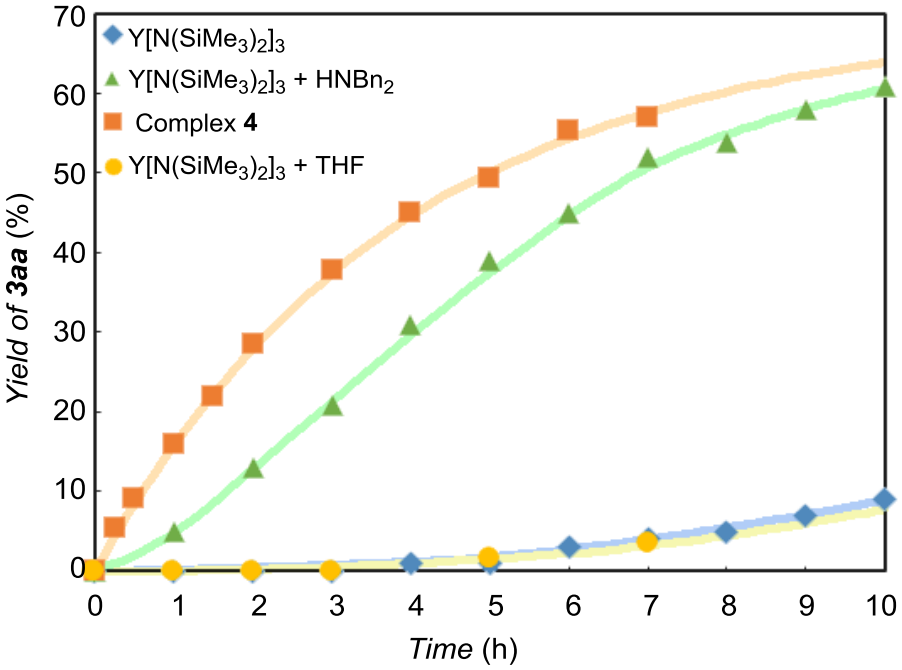


Figure S2. Reaction profiles for the aminoalkylation.

Following mechanistic studies were carried out by using mixed ligated yttrium triamido complex **4**. Dependence on the catalyst, imine, and 2-phenylpyridine concentration for the product yield was checked at 100 °C by ^{1}H NMR measurement.

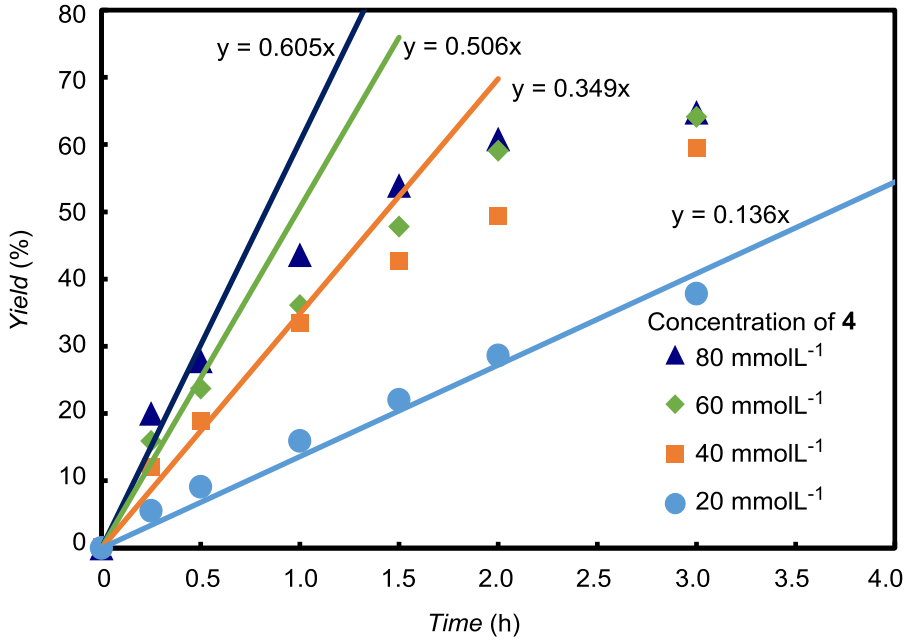


Figure S3. Time dependence on catalyst concentration for the aminoalkylation.

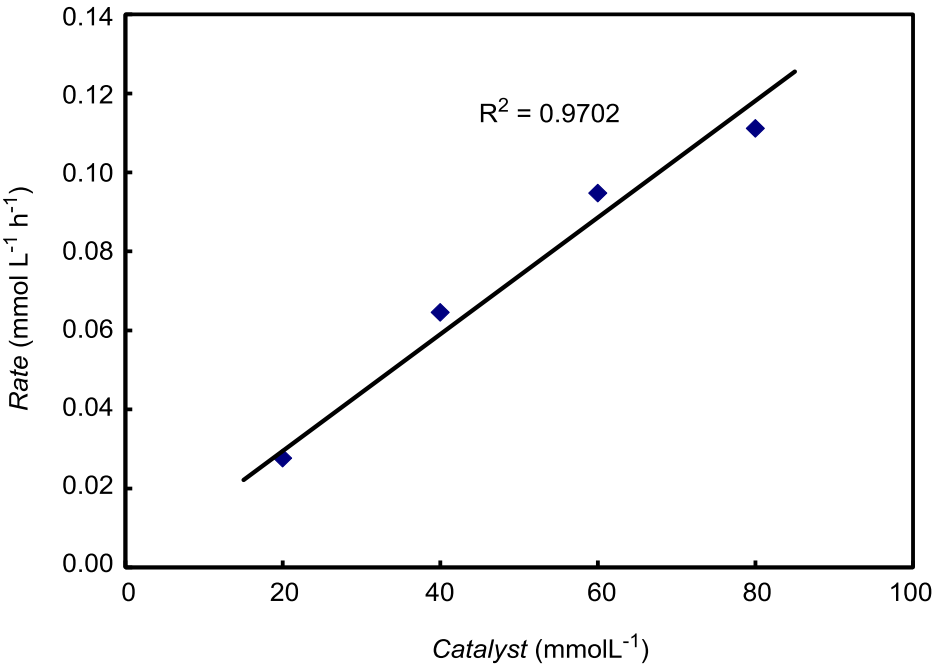


Figure S4. Initial reaction rate dependence on catalyst concentration for the aminoalkylation.

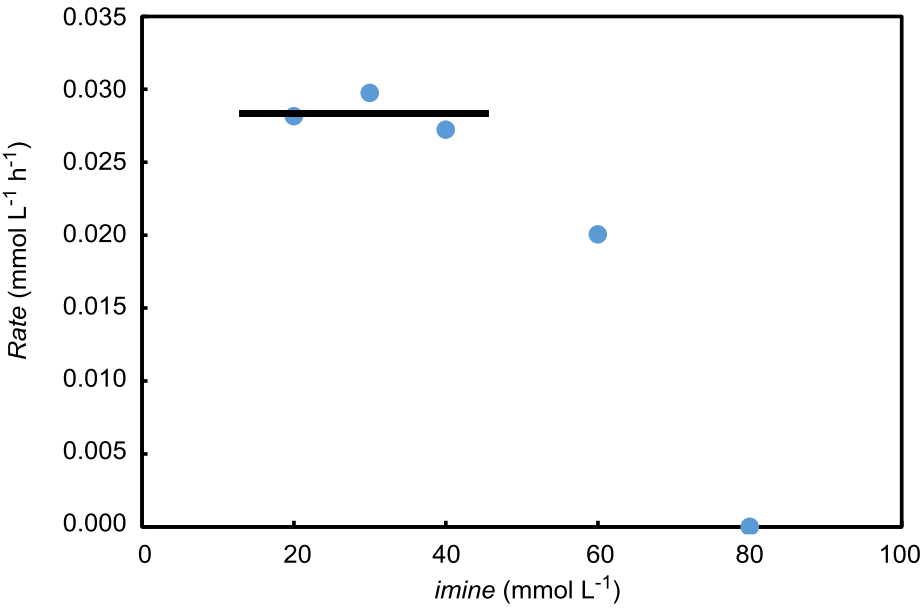


Figure S5. Initial reaction rate dependence on imine concentration for the aminoalkylation.

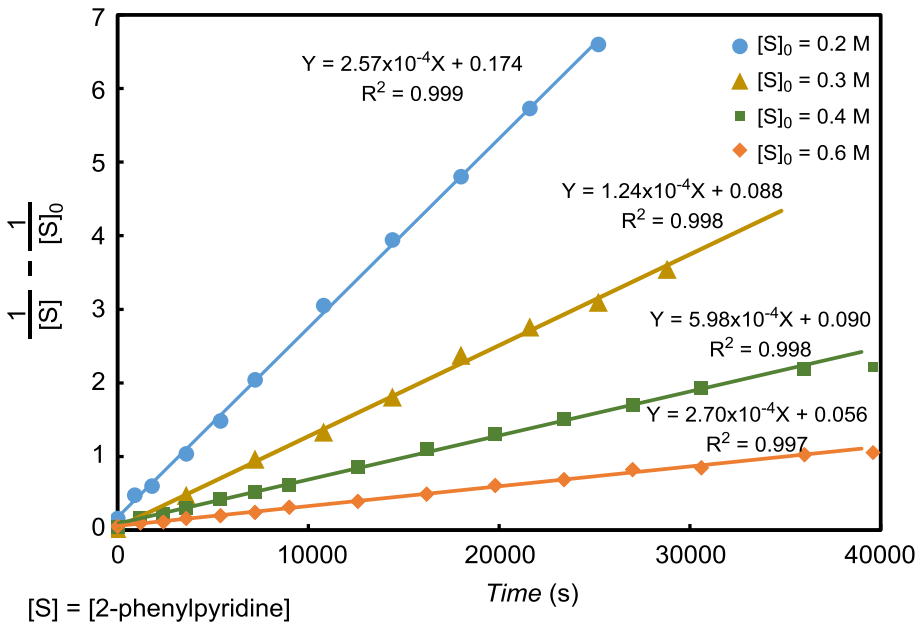


Figure S6. Second order plot on 2-phenylpyridine concentration for the aminoalkylation.

In a glovebox under argon, complex **4** (0.010 mmol, 10 mol%), **1a** (14.1 μL, 15.3 mg, 0.100 mmol), **2a** (38.6 mg, 0.200 mmol, 2 equiv), fluorene (0.050 mmol, 50 mol%) additives, and C_6D_6 (0.5 mL) were added to a J-young capped NMR tube to check the additive effect. The NMR tube was heated in oil bath at 100 °C and monitored by ^{1}H NMR spectrum. The addition of 50 mol% of THF-d_8 did not inhibit the catalytic reaction. When $HN(SiMe_3)_2$ (30 mol% and 60 mol%) was added to the reaction mixture, reaction rate constants were decreased by 10% and 23% respectively.

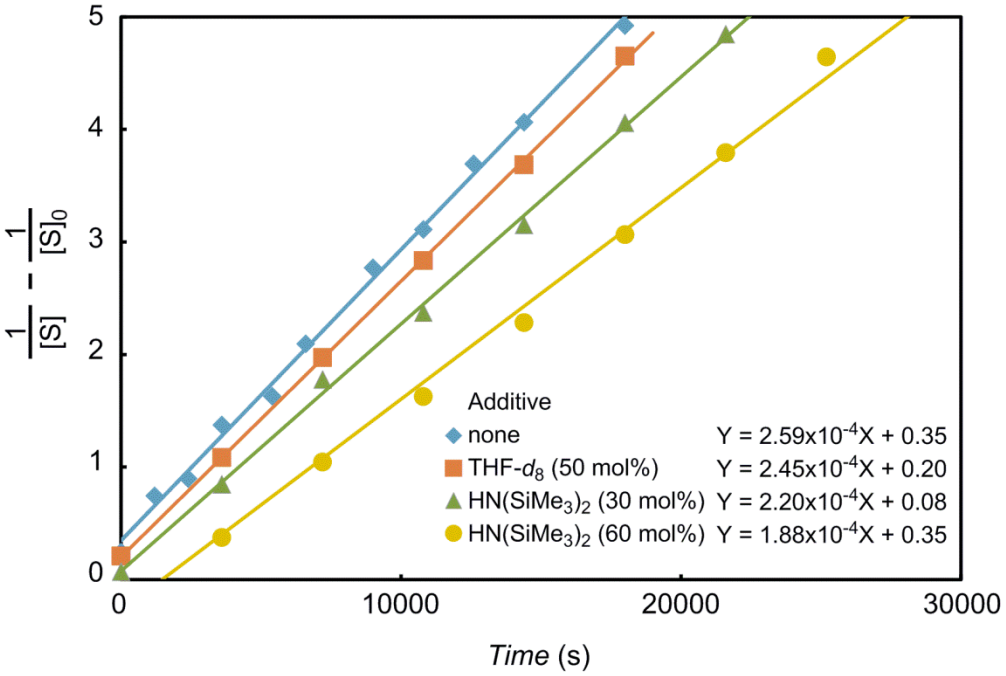


Figure S7. Additive effect of THF and amine.

The reaction rate constants were monitored by ^{1}H NMR spectroscopy over a temperature ranging from 89 to 110 °C under optimized condition (complex **4** (0.010 mmol, 10 mol%), **1a** (14.1 μL, 15.3 mg, 0.100 mmol), **2a** (38.6 mg, 0.200 mmol, 2 equiv), fluorene (0.050 mmol, 50 mol%), and C_6D_6 (0.5 mL)). A deuterium-labeling experiment by using 2-phenylpyridine-d_9 as a substrate was carried out to obtain a KIE value (3.19).

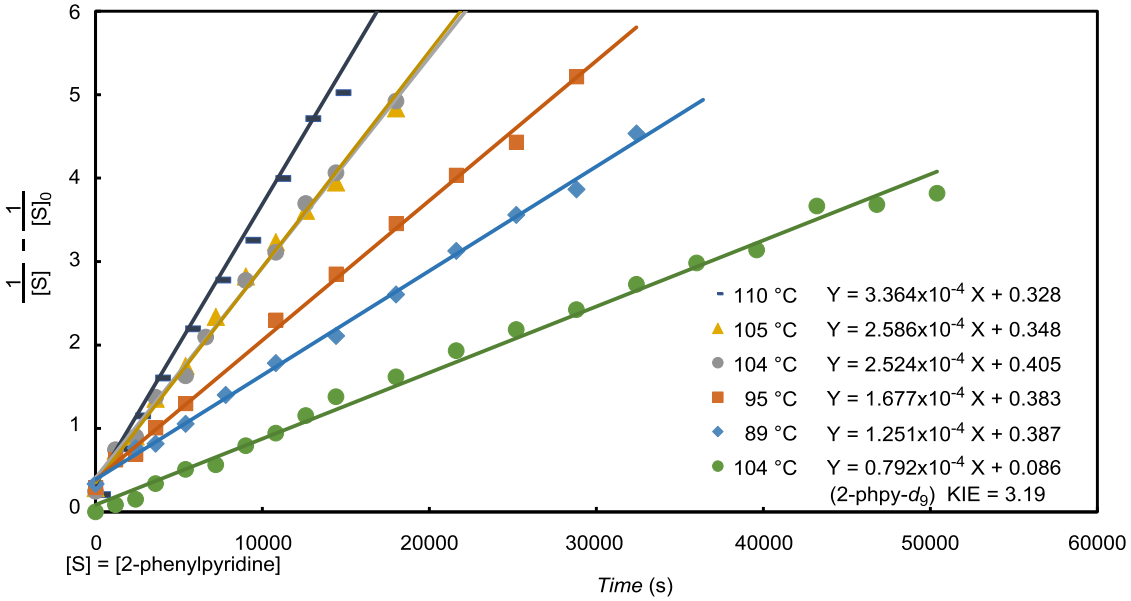


Figure S8. Second order plot on 2-phenylpyridine at several temperature.

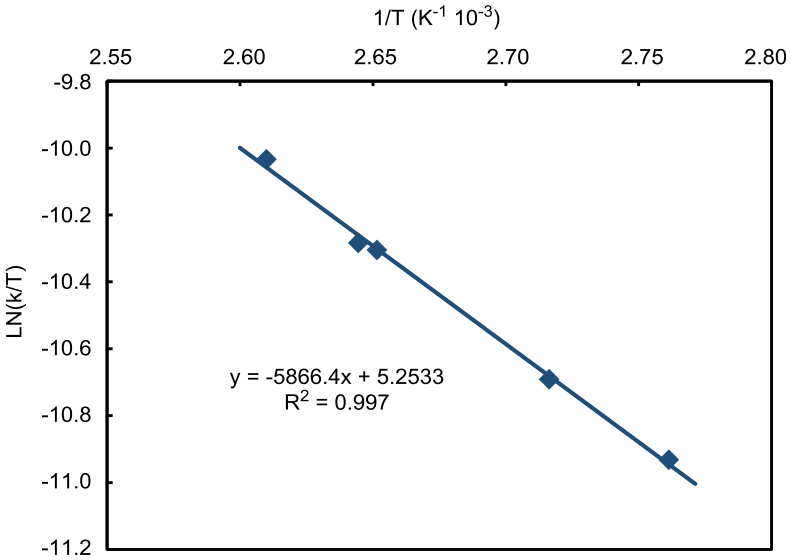


Figure S9. Eyring plot for the aminoalkylation.

$\Delta H^{\ddagger} = 48.8 \pm 1.5$ kJmol^{-1}, $\Delta S^{\ddagger} = -153.9 \pm 4.0$ a.u. $\Delta G^{\ddagger}(298K) = 94.6 \pm 2.7$ kJ mol^{-1}.

6. X-Ray crystallographic analysis.

All crystals were handled similarly. The crystals were mounted on the CryoLoop (Hampton Research Corp.) with a layer of light mineral oil and placed in a nitrogen stream at 113(1) K. All measurements were made on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Mo-Kα (0.71075 Å) radiation. Crystal data and structure refinement parameters were listed below (Table S5). The structures were solved by SIR-2008[S3] and refined on F^2 by full-matrix least-squares method, using SHELXL-2013.[S4] Non-hydrogen atoms were anisotropically refined. H-atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was $[\Sigma w(Fo^2 - Fc^2)^2]$ ($w = 1 / [\sigma^2 (Fo^2) + (aP)^2 + bP]$), where $P = (\mathrm{Max}(Fo^2,0) + 2Fc^2) / 3$ with $\sigma^2(Fo^2)$ from counting statistics. The function $R1$ and $wR2$ were $(\Sigma||Fo| - |Fc||) / \Sigma|Fo|$ and $[\Sigma w(Fo^2 - Fc^2)^2 / \Sigma(wFo^4)]^{1/2}$, respectively. The ORTEP-3 program was used to draw the molecule.[S5]

Table S5. Crystal data and data collection parameters of complexes **4**–**6**.

	4	**5**
empirical formula	$C_{30}H_{58}N_3OSi_4Y$	$C_{31}H_{53}N_4Si_4Y$
formula weight	678.06	685.04
crystal system	*monoclinic*	*monoclinic*
space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
a, Å	11.082(6)	30.617(8)
b, Å	17.774(9)	17.608(5)
c, Å	19.160(10)	21.674(6)
α, deg.	-	-
β, deg.	93.361(6)	100.565(3)
γ, deg.	-	-
V, Å^3	3768(3)	11487(5)
Z	4	12
*D*calcd, g/cm^{-3}	1.195	1.187
μ [Mo-*K*α], mm^{-1}	1.700	1.672
T, K	113(2)	113(2)
crystal size, mm	0.36 x 0.23 x 0.23	0.29 x 0.28 x 0.20
θ range for data collection (deg.)	3.164 to 27.473	3.052 to 27.612
no. of reflections measured	35961	109783
unique data (*R*int)	8539 (0.0457)	26140 (0.1007)
data / restraints / parameters	8539 / 0 / 382	26140 / 0 / 1116
*R*1 ($I > 2.0\sigma(I)$)	0.0394	0.0767
*wR*2 ($I > 2.0\sigma(I)$)	0.0873	0.1225
*R*1 (all data)	0.0534	0.1331
*wR*2 (all data)	0.0941	0.1451
GOF on F^2	1.061	1.098
Δρ, e Å^{-3}	0.466, -0.499	0.841, -0.683

a) $R1 = (\Sigma||Fo| - |Fc||)/(\Sigma|Fo|)$ b) $wR2 = [\{\Sigma w(Fo^2\text{-}Fc^2)^2\}/\{\Sigma w(Fo^4)\}]^{1/2}$

Table S5. Crystal data and data collection parameters of complexes **4**-**6**.

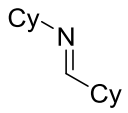
	6
empirical formula	$C_{36}H_{58}N_5Si_4Y$
formula weight	762.14
crystal system	*orthorhombic*
space group	*Pca*2$_1$ (No. 29)
a, Å	25.749(13)
b, Å	12.001(6)
c, Å	27.085(14)
α, deg.	-
β, deg.	-
γ, deg.	-
V, Å^3	8369(7)
Z	8
*D*calcd, g/cm^{-3}	1.210
μ [Mo-*K*α], mm^{-1}	1.538
T, K	113(2)
crystal size, mm	0.27 x 0.26 x 0.07
θ range for data collection (deg.)	3.01 to 27.48
no. of reflections measured	79513
unique data (*R*int)	19125 (0.1029)
data / restraints / parameters	19125 / 1 / 853
*R*1 ($I > 2.0\sigma(I)$)	0.0554
*wR*2 ($I > 2.0\sigma(I)$)	0.1027
*R*1 (all data)	0.0789
*wR*2 (all data)	0.1159
GOF on F^2	1.040
$\Delta\rho$, e Å^{-3}	0.811, -0.650

a) $R1 = (\Sigma||Fo| - |Fc||)/(\Sigma|Fo|)$ b) $wR2 = [\{\Sigma w(Fo^2\text{-}Fc^2)^2\}/\{\Sigma w(Fo^4)\}]^{1/2}$

7. Characterization of imines and aminomethylated products.

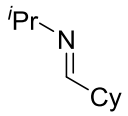
General procedure for preparation of imine derivatives

All imine derivatives were prepared by condensation of the corresponding amines and aldehyde in Et_2O with excess amount of $MgSO_4$ at room temperature. After removing $MgSO_4$ by filtration, all volatiles were removed under reduced pressure. Products were purified by distillation under reduced pressure or by using Kugelrohr.



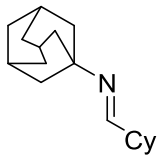
N,1-dicyclohexylmethanimine (**2a**)

^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 7.42 (d, ^3J = 5.6 Hz, 1H, N=CH), 2.81 (tt, ^3J = 10.6 Hz, ^3J = 4.1 Hz, 1H, NCH), 2.14-2.02 (m, 1H, N=CHCy), 1.78-1.65 (m, 6H, Cy), 1.65-1.50 (m, 4H, Cy), 1.47-1.33 (m, 2H, Cy), 1.32-1.06 (m, 8H, Cy); ^{1}H NMR (400 MHz, C_6D_6, 30 ˚C): δ 7.42 (d, ^3J = 5.6 Hz, 1H, N=CH), 2.85 (tt, ^3J = 9.1 Hz, ^3J = 5.0 Hz, 1H, NCH), 2.14-2.01 (m, 1H, N=CHCy), 1.84-1.70 (m, 4H, Cy), 1.70-1.57 (m, 6H, Cy), 1.57-1.45 (m, 2H, Cy), 1.34-1.01 (m, 8H, Cy); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C): δ 166.6 (N=CH), 69.6 (NCH), 43.5 (N=CHCy), 34.5, 29.9, 26.0, 25.6, 25.4, 24.9; HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{13}H_{23}N$, 193.1830; found, 193.1828.



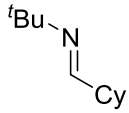
1-cyclohexyl-*N*-isopropylmethanimine (**2b**)

^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 7.36 (d, ^3J = 4.8 Hz, 1H, N=CH), 3.12 (sept, ^3J = 6.3 Hz, 1H, NC*H*$(CH_3)_2$), 2.08-1.97 (m, 1H, N=CHCy), 1.84-1.73 (m, 2H, Cy), 1.66-1.57 (m, 2H, Cy), 1.54-1.45 (m, 1H, Cy), 1.28-1.03 (m, 5H, Cy), 1.16 (d, ^3J = 6.3 Hz, 6H, NCH(C*H*$_3)_2$); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C): δ 164.4 (N=CH), 61.8 (NCH), 43.2 (N=CHCy), 30.1, 26.6, 25.9, 24.7; HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{10}H_{19}N$, 153.1517; found, 153.1516.



N-(1-adamantyl)-1-cyclohexylmethanimine (**2c**)

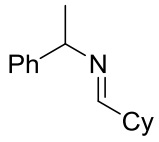
^{1}H NMR (400 MHz, C_6D_6, 30 °C): δ 7.39 (d, ^3J = 6.0 Hz, 1H, N=CH), 2.01-2.06 (m, 4H), 1.78-1.58 (m, 17H), 1.36-1.10 (m, 5H); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 30 °C): δ 163.0 (N=CH), 56.5 (NCH), 44.4, 43.4, 36.8, 30.2, 29.8, 26.1, 25.6; HRMS-FAB (*m/z*): $[M+H]^+$ calcd for $C_{17}H_{28}N$, 246.2222; found, 246.2224.



N-*tert*-buthyl-1-cyclohexylmethanimine (**2d**)

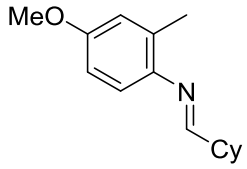
^{1}H NMR (400 MHz, C_6D_6, 30 °C): δ 7.39 (d, ^3J = 4.1 Hz, 1H, N=CH), 2.14-2.01 (m, 1H), 1.83-1.71 (m, 2H), 1.70-1.58 (m, 2H), 1.58-1.48 (m, 1H),

1.28-1.04 (m, 5H), 1.15 (s, 9H, $C(CH_3)_3$); $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 30 °C): δ 162.9 (N=CH), 56.2 (NCH), 44.1, 30.0, 29.7, 26.0, 25.4; HRMS-FAB (*m/z*): $[M]^+$ calcd for $C_{11}H_{21}N$, 167.1674; found,167.1673.



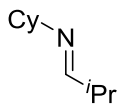
1-cyclohexyl-*N*-(1-phenylethyl)methanimine (**2e**)

^1H NMR (400 MHz, C_6D_6, 30 °C): δ 7.44 (d, ^3J = 7.3 Hz, 2H, *o*-Ph), 7.44 (d, ^3J = 4.0 Hz, 1H, N=CH), 7.22 (dd, ^3J = 7.4 Hz, ^3J = 7.3 Hz, 2H, *m*-Ph), 7.09 (t, ^3J = 7.4 Hz, 1H, *p*-Ph), 4.11 (q, ^3J = 6.6 Hz, 1H, NCH), 2.09-1.98 (m, 1H, N=CHCy), 1.80-1.70 (m, 2H, Cy), 1.65-1.55 (m, 2H, Cy), 1.54-1.43 (m, 1H, Cy), 1.45 (d, ^3J = 6.6 Hz, 3H, CH_3), 1.27-1.00 (m, 5H, Cy); $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 30 °C): δ 166.1 (N=CH), 146.5, 128.6, 126.9_4, 126.9_0, 70.4 (NCH), 43.3 (N=CHCy), 29.9, 26.5, 26.0, 25.9; HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{15}H_{21}N$, 215.1674; found, 215.1666.



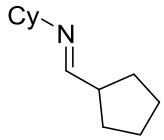
1-Cyclohexyl-*N*-(4-methoxy-2-methylphenyl)methanimine (**2f**)

^1H NMR (400 MHz, C_6D_6, 30 °C): δ 7.50 (d, ^3J = 4.0 Hz, 1H, N=CH), 6.76 (s, 1H), 6.69-6.66 (m, 2H), 3.40 (s, 3H, OCH_3), 2.34 (s, 3H, CH_3), 2.23-2.11 (m, 1H), 1.88-1.78 (m, 2H), 1.70-1.61 (m, 2H), 1.57-1.48 (m, 1H), 1.37-1.05 (m, 5H); $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 30 °C): δ 166.7 (N=CH), 158.1, 145.5, 133.1, 118.7, 116.1, 112.0, 55.0 (NCH), 44.0, 29.9, 26.6, 25.9, 18.3; HRMS-FAB (*m/z*): $[M+H]^+$ calcd for $C_{15}H_{22}NO$, 232.1701; found, 232.1698.



N-cyclohexyl-2-methylpropan-1-imine (**2g**)

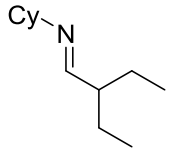
^1H NMR (400 MHz, C_6D_6, 30 °C): δ 7.37 (d, ^3J = 4.1 Hz, 1H, N=CH), 2.84 (tt, ^3J = 9.1 Hz, ^3J = 4.6 Hz, 1H, NCy), 2.32-2.22 (dsept, ^3J = 6.8 Hz, ^3J = 4.1 Hz, 1H, C*H*$(CH_3)_2$), 1.77-1.46 (m, 7H), 1.32-1.09 (m, 3H), 0.98 (d, ^3J = 6.8 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 30 °C): δ 165.6 (N=CH), 69.7 (NCH), 35.1, 34.0, 26.2, 25.0, 19.5; HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{10}H_{19}N$, 153.1517; found,153.1516.



N-cyclohexyl-1-cyclopentylmethanimine (**2h**)

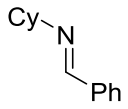
^1H NMR (400 MHz, C_6D_6, 30 °C): δ 7.42 (d, ^3J = 4.9 Hz, 1H, N=CH), 2.86 (tt, ^3J = 9.2 Hz, ^3J = 4.6 Hz, 1H, NCH), 2.05-1.94 (dt, ^3J = 7.5 Hz, ^3J = 4.9 Hz, 1H, N=CHC*H*), 1.79-1.08 (m, 18H); $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 30 °C): δ 164.3 (N=CH), 69.7 (NCH), 45.4, 35.1, 30.1, 26.2, 25.7, 25.0; HRMS-FAB (*m/z*): $[M+H]^+$ calcd for $C_{12}H_{22}N$, 180.1752; found, 181.1760.

N-cyclohexyl-2-ethylbutan-1-imine (**2i**)



^{1}H NMR (400 MHz, C_6D_6, 30 °C): δ 7.27 (d, ^{3}J = 5.8 Hz, 1H, N=CH), 3.12 (tt, ^{3}J = 9.0 Hz, ^{3}J = 5.1 Hz, 1H, NCH), 2.05-1.94 (m, 1H, N=CHC*H*Et$_2$), 1.77-1.68 (m, 2H), 1.67-1.47 (m, 5H), 1.45-1.10 (m, 7H), 0.86 (t, ^{3}J = 7.4 Hz, 6H, CH_3); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 30 °C): δ 164.5 (N=CH), 70.1 (NCH), 48.0 (N=CH*C*HEt$_2$), 35.2, 26.2, 25.3, 25.0, 11.8; HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{12}H_{23}N$, 181.1830; found, 181.1837.

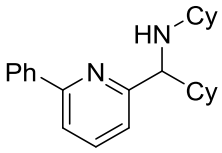
N-cyclohexyl-1-phenylmethanimine (**2j**)



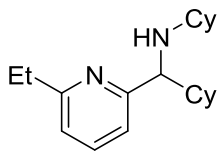
^{1}H NMR (400 MHz, C_6D_6, 30 °C): δ 8.05 (s, 1H, N=CH), 7.77 (d, ^{3}J = 7.8 Hz, 2H, *o*-Ph), 7.18-7.06 (m, 3H, *m* and *p*-Ph), 3.05 (tt, ^{3}J = 8.2 Hz, ^{3}J = 5.4 Hz, 1H, NCH), 1.82-1.63 (m, 6H), 1.59-1.50 (m, 1H), 1.37-1.13 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 30 °C): δ 158.0 (N=CH), 137.5, 130.3, 128.6, 128.5, 70.0 (NCH), 34.9, 26.1, 24.9; HRMS-FAB (*m/z*): $[M+H]^+$ calcd for $C_{13}H_{18}N$, 188.1439; found, 188.1441.

General procedure for Gd-catalyzed aminoalkylation reaction

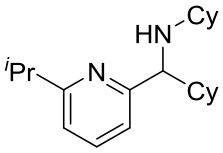
In an Ar-filled glovebox, $Gd[N(SiMe_3)_2]_3$ (31.9 mg, 0.0500 mmol, 10 mol%), **1** (0.500 mmol), dibenzylamine (9.6 μL, 9.9 mg, 0.0500 mmol, 10 mol%), **2** (1.00 mmol, 2 equiv) and toluene (total volume, 1.0 mL) were added to an oven-dried 3-mL vial. The vial was capped with a PTFE-lined cap, and heated by aluminum block bath with stirrer at 100 °C for 24 h. After cooling to room temperature, the reaction mixture was diluted with Et_2O (1.5 mL) and filtered short silica gel plug. The obtained solution was concentrated under reduced pressure at 100 °C for at least 1 h to remove starting materials. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 10:1) to give aminoalkylpyridine **3** as a pale yellow oil or solid. In ^{1}H NMR spectra of products, some NH signals were not assigned because the broad NH signals were not observed.



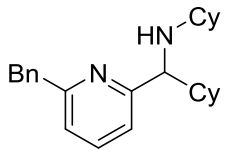
N-[cyclohexyl-(6-phenylpyridin-2-yl)methyl]cyclohexyanamine (**3aa**)
^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 8.07 (d, ^3J = 7.3 Hz, 2H, *o*-Ph), 7.68 (t, ^3J = 7.3 Hz, 1H, 4-Py), 7.58 (d, ^3J = 7.3 Hz, 1H, 3- or 5-Py), 7.49 (dd, ^3J = 7.4 Hz, ^3J = 7.3 Hz, 2H, *m*-Ph), 7.41 (t, ^3J = 7.4 Hz, 1H, *p*-Ph), 7.15 (d, ^3J = 7.3 Hz, 1H, 5- or 3-Py), 3.66 (d, ^3J = 6.6 Hz, 1H, NC*H*(Ar)Cy), 2.31-2.09 (m, 2H, NCy and NH), 2.06-1.91 (m, 2H, Cy), 1.81-1.42 (m, 9H, Cy), 1.33-0.99 (m, 10H, Cy); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C): δ 163.6, 156.2, 139.8, 136.2, 128.8, 128.7, 126.9, 121.5, 118.0, 66.1 (NCHCy), 54.7 (NCy), 44.1, 34.8, 33.2, 30.1_1, 30.0_6, 26.7, 26.5_3, 26.4_8, 26.3, 25.2, 24.9; IR (NaCl film, ν/cm^{-1}): 3307 w, 3060 w, 2924 s, 2850 s, 2666 w, 1589 m, 1445 s, 1123 m, 760 s, 693 m; HRMS-FAB (*m/z*): $[M+H]^+$ calcd for $C_{24}H_{33}N_2$, 349.2644; found, 349.2646.



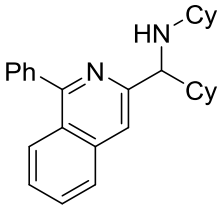
N-[cyclohexyl-(6-ethylpyridin-2-yl)methyl]cyclohexanamine (**3ba**)
^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 7.44 (t, ^3J = 7.6 Hz, 1H, 4-Py), 6.98 (d, ^3J = 7.6 Hz, 1H, 3- or 5-Py), 6.92 (d, ^3J = 7.6 Hz, 1H, 5- or 3-Py), 3.50 (d, ^3J = 6.7 Hz, 1H, NC*H*(Ar)Cy), 2.76 (q, ^3J = 7.6 Hz, 2H, CH_2CH$_3$), 2.16-1.82 (m, 4H, NCy, Cy and NH), 1.71-1.44 (m, 8H, Cy), 1.35-0.87 (m, 11H, Cy), 1.24 (t, ^3J = 7.6 Hz, 3H, CH$_2$CH_3); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C): δ 163.3, 162.6, 135.7, 119.9, 119.5, 66.3 (NCHCy), 54.7 (NCy), 44.0, 34.8, 33.2, 31.5, 30.2, 29.9, 26.7, 26.5_0, 26.4_7, 26.3, 25.2, 24.8, 14.1; IR (NaCl film, ν/cm^{-1}): 3057 w, 2924 s, 2851 s, 2667 w, 1589 m, 1575 m, 1463 m, 1449 s, 1124 w, 818 w, 750 w; HRMS-FAB (*m/z*): $[M+H]^+$ calcd for $C_{20}H_{33}N_2$, 301.2644; found, 301.2644.



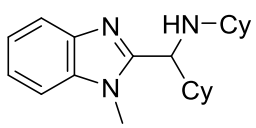
N-[cyclohexyl-(6-isopropylpyridin-2-yl)methyl]cyclohexanamine (**3ca**) ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 7.45 (t, ^3J = 7.7 Hz, 1H, 4-Py), 6.94 (d, ^3J = 7.7 Hz, 2H, 3- and 5-Py), 3.50 (d, ^3J = 6.4 Hz, 1H, NC*H*(Ar)Cy), 3.01 (sept, ^3J = 6.8 Hz, 1H, C*H*$(CH_3)_2$), 2.18 (br s, 1H, NH), 2.12-2.03 (m, 1H, Cy), 1.95-1.82 (m, 2H, Cy), 1.78-1.44 (m, 9H, Cy), 1.40-1.31 (m, 1H, Cy), 1.26 (d, ^3J = 6.8 Hz, 6H, CH(C*H*$_3)_2$), 1.21-0.86 (m, 9H, Cy); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C): δ 166.3, 162.7, 135.7, 120.2, 117.9, 66.0 (NCHCy), 54.7 (NCy), 44.2, 36.3, 34.7, 33.2, 30.0_2, 30.0_1, 26.8, 23.6, 26.5, 26.3, 25.3, 24.9, 22.8, 22.5; IR (NaCl film, ν/cm^{-1}): 3056 w, 2925 s, 2851 s, 2667 w, 1589 m, 1575 m, 1469 m, 1449 m, 1368 m, 1157 m, 1122 m, 818 w, 751 w; HRMS-FAB (*m/z*): $[M+H]^+$ calcd for $C_{21}H_{35}N_2$, 315.2800; found, 315.2805.



N-[cyclohexyl-(6-benzylpyridin-2-yl)methyl]cyclohexanamine (**3da**) ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 7.46 (t, ^3J = 7.6 Hz, 1H, 4-Py), 7.30-7.22 (m, 4H, *o*- and *m*-Ph), 7.22-7.14 (m, 1H, *p*-Ph) 7.20 (d, ^3J = 7.6 Hz, 1H, 3- or 5-Py), 6.92 (d, ^3J = 7.6 Hz, 1H, 5- or 3-Py), 4.14 (s, 2H, CH_2Ph), 3.55 (d, ^3J = 6.8 Hz, 1H, NC*H*(Ar)Cy), 2.14-1.89 (m, 4H, NCy, Cy and NH), 1.77-1.49 (m, 8H, Cy), 1.40-0.91 (m, 11H, Cy); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C): δ 163.5, 160.1, 140.2, 136.0, 129.1, 128.4, 126.2, 120.7, 120.4, 66.1 (NCHCy), 54.6 (NCy), 44.8, 44.0, 34.7, 33.1, 30.1, 30.0, 26.7, 26.5, 26.4_6, 26.3, 25.2, 24.8; IR (NaCl film, ν/cm^{-1}): 3061 w, 3027 w, 2925 s, 2851 s, 1559 m, 1573 m, 1495 m, 1449 s, 750 m, 699 m; HRMS-FAB (*m/z*): $[M+H]^+$ calcd for $C_{25}H_{35}N_2$, 363.2800; found, 363.2796.

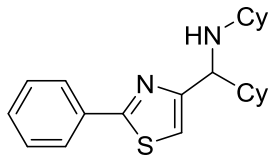


N-[cyclohexyl(1-phenylisoquinolin-3-yl)methyl]cyclohexanamine (**3ea**) mp 105-112 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 8.08 (d, ^3J = 8.4 Hz, 1H, Ar), 7.86 (d, ^3J = 8.2 Hz, 1H, Ar), 7.71 (d, ^3J = 6.7 Hz, 2H, *o*-Ph), 7.64 (t, ^3J = 7.1 Hz, 1H, *p*-Ph), 7.59-7.43 (m, 5H), 3.79 (d, ^3J = 6.7 Hz, 1H, NC*H*(Ar)Cy), 2.31-2.20 (m, 1H, NCy), 2.13-1.92 (m, 3H, Cy and NH), 1.86-1.41 (m, 9H, Cy), 1.35-0.99 (m, 10H, Cy); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C): δ 160.0, 156.2, 140.2, 137.1, 130.2 (Ph), 129.8, 128.5, 128.3 (Ph), 127.5, 127.1, 126.4, 125.7, 118.1, 66.0 (NCHCy), 54.6 (NCy), 43.8, 34.9, 33.2, 30.5, 30.1, 26.8, 26.6, 26.5, 26.4, 25.3, 24.9; IR (NaCl film, ν/cm^{-1}): 3057 w, 2924 s, 2850 s, 1322 m, 1560 m, 1448 m, 753 m, 740 m, 700 m; HRMS-FAB (*m/z*): $[M+H]^+$ calcd for $C_{28}H_{35}N_2$, 399.2800; found, 399.2793.



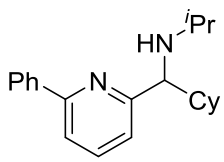
N-[cyclohexyl(1-methyl-1*H*-benzo[*d*]imidazol-2-yl)methyl]-cyclohexanamine (**3fa**)

^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 7.70-7.61 (m, 1H, Ar), 7.28-7.20 (m, 1H, Ar), 7.20-7.11 (m, 2H, Ar), 3.78 (d, ^3J = 7.7 Hz, 1H, NC*H*(Ar)Cy), 3.75 (s, 3H, NCH_3), 2.17-1.36 (m, 12H, Cy and NH), 1.24-0.89 (m, 11H, Cy); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C): δ 157.4, 142.5, 136.0, 121.9, 121.8, 119.4, 109.4, 58.6, 54.8, 43.4, 34.4, 33.0, 30.5, 30.2, 30.0, 26.5, 26.2_1, 26.1_7(2C), 24.9, 24.7; IR (NaCl film, ν/cm^{-1}): 3316 m, 3052 m, 2925 s, 2852 s, 2667 w, 1612 m, 1464 s, 1450 s, 1398 m, 1332 m, 1273 m, 1237 m, 1118 m, 1007 m, 888 m, 765 m, 742 s, 702 w; HRMS-FAB (*m/z*): $[M+H]^+$ calcd for $C_{21}H_{32}N_3$, 326.2596; found, 326.2597.



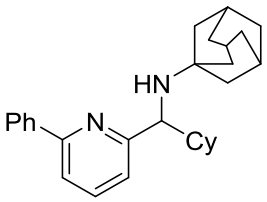
N-[cyclohexyl(2-phenylthiazol-4-yl)methyl]cyclohexanamine (**3ga**)

^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 7.96 (dd, ^3J = 7.9 Hz, ^4J = 1.7 Hz, 2H, *o*-Ph), 7.46-7.35 (m, 3H, *m*- and *p*-Ph), 6.95 (s, 1H, Ar), 3.67 (d, ^3J = 6.6 Hz, 1H, NC*H*(Ar)Cy), 2.32-2.20 (m, 1H, NCy), 2.02-1.89 (m, 2H, Cy), 1.80-1.45 (m, 10H, Cy and NH), 1.32-0.93 (m, 10H, Cy); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C): δ 167.3, 161.1, 134.2, 129.7, 128.9, 126.6, 114.0, 61.5 (NCHCy), 54.3 (NCy), 43.3, 34.7, 33.1, 30.1, 30.0, 26.8, 26.5, 26.4, 26.3, 25.2, 24.8; IR (NaCl film, ν/cm^{-1}): 3062 w, 2923 s, 2851 s, 2666 w, 1511 m, 1497 m, 1462 s, 1449 s, 1369 m, 1348 m, 1310 m, 1263 m, 1369 m, 1115 m, 1002 s, 795 m, 763 s, 740 s, 689 s, 605 m; HRMS-FAB (*m/z*): $[M+H]^+$ calcd for $C_{22}H_{31}N_2S$, 355.2208; found, 355.2209.



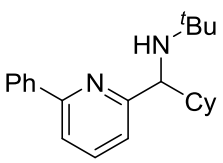
N-[cyclohexyl-(6-phenylpyridin-2-yl)methyl]ispropylamine (**3ab**)

^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 8.05 (d, ^3J = 7.0 Hz, 2H, *o*-Ph), 7.65 (t, ^3J = 7.7 Hz, 1H, 4-Py), 7.57 (d, ^3J = 7.7 Hz, 1H, 3- or 5-Py), 7.47 (t, ^3J = 7.0 Hz, 2H, *m*-Ph), 7.41 (t, ^3J = 7.0 Hz, 1H, *p*-Ph), 7.11 (d, ^3J = 7.7 Hz, 1H, 5- or 3-Py), 3.58 (d, ^3J = 6.6 Hz, 1H, NC*H*(Ar)Cy), 2.53 (sept, ^3J = 6.0 Hz, 1H, NC*H*$(CH_3)_2$), 2.03-1.85 (m, 3H, Cy and NH), 1.77-1.56 (m, 4H, Cy), 1.50-1.40 (br d, 1H, Cy), 1.30-0.95 (m, 4H, Cy), 1.03 (d, ^3J = 6.0 Hz, 3H, NCH(C*H*$_3)_2$), 0.99 (d, ^3J = 6.0 Hz, 3H, NCH(C*H*$_3)_2$); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C): δ 163.4, 156.3, 139.9, 136.2, 128.8_4, 128.7_5, 127.0, 121.7, 118.1, 66.6 (NCHCy), 45.5, 44.1, 30.3, 30.0, 26.8, 26.6_2, 26.5_6, 24.6, 22.4; IR (NaCl film, ν/cm^{-1}): 3061 m, 2960 s, 2924 s, 2851 s, 1590 m, 1570 s, 1445 s, 1378 m, 1366 m, 1174 m, 760 s, 694 s, 624 m; HRMS-FAB (*m/z*): $[M+H]^+$ calcd for $C_{21}H_{29}N_2$, 309.2331; found, 309.2332.



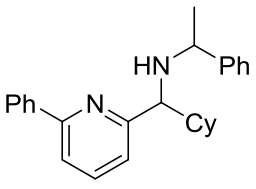
N-[cyclohexyl(6-phenylpyridin-2-yl)methyl]adamantan-1-amine (**3ac**)

^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 8.06 (d, ^3J = 7.0 Hz, 2H, *o*-Ph), 7.64 (t, ^3J = 7.6 Hz, 1H, 4-Py), 7.53 (d, ^3J = 7.3 Hz, 1H, 3- or 5-Py), 7.47 (dd, ^3J = 7.1 Hz, ^3J = 7.0 Hz, 2H, *m*-Ph), 7.40 (t, ^3J = 7.1 Hz, 1H, *p*-Ph), 7.21 (d, ^3J = 7.3 Hz, 1H, 5- or 3-Py), 3.69 (d, ^3J = 6.8 Hz, 1H, NC*H*(Ar)Cy), 2.11 (br s, 1H, NH),1.95 (br s, 4H), 1.75-1.33 (m, 17H), 1.27-0.94 (m, 5H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C): δ 166.2, 155.7, 140.0, 136.2, 128.8(2C), 127.0, 121.4, 117.7, 61.1 (NCHCy), 51.0 (NAd), 45.3, 44.2, 36.9, 30.7, 29.9, 29.8, 26.8, 26.7, 26.6; IR (NaCl film, ν/cm^{-1}): 3305 w, 3061 m, 2915 s, 2847 s, 2657 m, 1570 s, 1444 s, 1357 m, 1310 m, 1261 m, 1216 m, 1183 m, 1145 m, 1099 m, 818 m, 759 s, 694 s, 668 m; HRMS-FAB (*m/z*): $[M+H]^+$ calcd for $C_{28}H_{37}N_2$, 401.2957; found, 401.2961.



N-[cyclohexyl(6-phenylpyridin-2-yl)methyl]-2-methylpropan-2-amine (**3ad**)

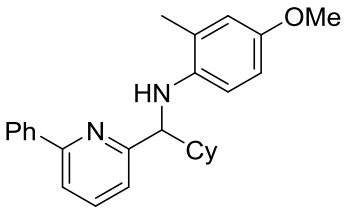
^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 8.07-8.03 (m, 2H, *o*-Ph), 7.62 (t, ^3J = 7.7 Hz, 1H, 4-Py), 7.53 (dd, ^3J = 7.8 Hz, ^4J = 0.9 Hz, 1H, 3- or 5-Py), 7.50-7.44 (m, 2H, *m*-Ph), 7.40 (tt, ^3J = 7.3 Hz, ^4J = 1.3 Hz, 1H, *p*-Ph), 7.20 (dd, ^3J = 7.5 Hz, ^4J = 0.9 Hz, 1H, 5- or 3-Py), 3.59 (d, ^3J = 6.6 Hz, 1H, NC*H*(Ar)Cy), 2.07-1.82 (br m, 2H, Cy and NH), 1.76-1.46 (m, 4H), 1.42-1.33 (m, 1H), 1.29-0.97 (m, 5H), 0.96 (s, 9H, $C(CH_3)_3$); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C): δ 166.0, 155.8, 140.0, 136.2, 128.7$_7$, 128.7$_6$, 127.0, 121.4, 117.8, 63.4 (NCHCy), 51.0 (N^{t}Bu), 45.3, 30.7, 30.4, 29.8, 26.8, 26.7, 26.6; IR (NaCl film, ν/cm^{-1}): 3312 w, 3061 m, 2961 s, 2924 s, 2851 s, 1569 s, 1445 s, 1387 m, 1361 m,1228 m, 1027 m, 821 w, 759 s, 694 s, 624 w; HRMS-FAB (*m/z*): $[M+H]^+$ calcd for $C_{22}H_{31}N_2$, 323.2487; found, 323.2494.



N-[cyclohexyl-(6-phenylpyridin-2-yl)methyl]-1-phenylethylamine (**3ae**)

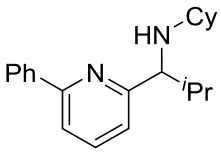
^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 8.08 (d, ^3J = 7.0 Hz, 2H, *o*-Ph), 7.66-7.58 (m, 2H, 4-Py and 3- or 5-Py), 7.49 (t, ^3J = 7.3 Hz, 2H, *m*-Ph), 7.45-7.39 (m, 1H, *p*-Ph), 7.36-7.29 (m, 4H, *o*- and *m*-Ph), 7.25-7.19 (m, 1H, *p*-Ph), 6.89 (dd, ^3J = 6.8 Hz, ^4J = 1.5 Hz, 1H, 5- or 3-Py), 3.42 (q, ^3J = 6.5 Hz, 1H, NC*H*(Ph)CH_3), 3.18 (d, ^3J = 7.4 Hz, 1H, NC*H*(Ar)Cy), 2.18-2.09 (br d, 1H, NH), 1.79-1.52 (m, 5H, Cy), 1.30-0.86 (m, 6H, Cy), 1.26 (d, ^3J = 6.5 Hz, 3H, NCH(Ph)CH_3); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C): δ 163.3, 156.7, 146.4, 139.9, 136.2, 128.9,

128.8, 128.3, 127.3, 127.0, 126.8, 122.3, 118.2, 66.3 (NCHCy), 55.9 (N*C*H(Ph)CH_3), 44.0, 30.5, 30.1, 26.8, 26.6, 26.5, 26.0; IR (NaCl film, ν/cm^{-1}): 3061 m, 3028 m, 2924 s, 2851 s, 1951 w, 1885 w, 1807 w, 1725 w, 1687 w, 1589 s, 1569 s, 1492 m, 1446 s, 1368 m, 1265 s, 1157 m, 1121 s, 1027 m, 992 m, 821 m, 762 s, 701 s, 624 m; HRMS-FAB (*m/z*): $[M+H]^+$ calcd for $C_{26}H_{31}N_2$, 371.2487; found, 371.2487.



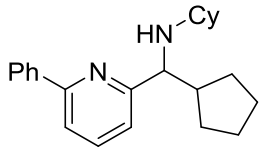
N-[cyclohexyl(6-phenylpyridin-2-yl)methyl]-4-methoxy-2-methylaniline (**3af**)

^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 8.09-8.04 (m, 2H, *o*-Ph), 7.62 (t, ^3J = 7.7 Hz, 1H, 4-Py), 7.56 (dd, ^3J = 7.7 Hz, ^4J = 1.1 Hz, 1H, 3- or 5-Py), 7.52 (m, 2H, *m*-Ph), 7.42 (tt, ^3J = 7.2 Hz, ^4J = 1.3 Hz, 1H, *p*-Ph), 7.13 (dd, ^3J = 7.7 Hz, ^3J = 1.1 Hz, 1H, 5- or 3-Py), 6.67 (d, ^4J = 3.5 Hz, 1H, 3-Ar), 6.56 (dd, ^3J = 8.7 Hz, ^4J = 3.5 Hz, 1H, 5-Ar), 6.47 (d, ^3J = 8.7 Hz, 1H, 6-Ar), 4.48-4.24 (br s, 1H, NH), 4.35 (d, ^3J = 5.8 Hz, 1H, NC*H*(Ar)Cy), 3.69 (s, 3H, OCH_3), 2.26 (s, 3H, CH_3), 2.01-1.91 (m, 2H), 1.86-1.48 (m, 4H), 1.34-1.06 (m, 5H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 30 °C): δ 162.1, 156.5, 151.5, 140.5, 139.8, 136.7, 128.9, 128.8, 127.0, 124.0, 120.7, 118.5, 117.0, 112.3, 111.7, 65.0 (NCHCy), 55.9, 44.0, 30.4, 29.5, 26.7, 26.6, 26.5, 18.1; IR (NaCl film, ν/cm^{-1}): 3421 w, 3377 w, 3061 m, 3005 m, 2925 s, 2851 m, 1570 m, 1509 s, 1447 s, 1419 m, 1289 m, 1224 s, 1159 m, 1051 m, 760 s, 695 m; HRMS-FAB (*m/z*): $[M]^+$ calcd for $C_{26}H_{30}N_2O$, 386.2358; found, 386.2358.



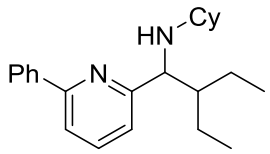
N-[2-methyl-1-(6-phenylpyridin-2-yl)propyl]cyclohexanamine (**3ag**)

^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 8.07-8.02 (m, 2H, *o*-Ph), 7.66 (t, ^3J = 7.8 Hz, 1H, 4-Py), 7.57 (dd, ^3J = 7.8 Hz, ^4J = 1.1 Hz, 1H, 3- or 5-Py), 7.49-7.44 (m, 2H, *m*-Ph), 7.40 (tt, ^3J = 7.3 Hz, ^4J = 1.3 Hz, 1H, *p*-Ph), 7.16 (dd, ^3J = 7.8 Hz, ^3J = 1.1 Hz, 1H, 5- or 3-Py), 3.61 (d, ^3J = 6.3 Hz, 1H, NC*H*(Ar)^{i}Pr), 2.25-2.14 (m,1H), 2.08-1.92 (m, 2H, C*H*$(CH_3)_2$ and Cy), 1.86 (br s, 1H, NH), 1.74-1.47 (m, 4H), 1.20-1.03 (m, 5H), 0.96 (d, ^3J = 6.7 Hz, 3H, one CH_3 of ^{i}Pr), 0.84 (d, ^3J = 6.7 Hz, 3H, one CH_3 of ^{i}Pr); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 30 °C): δ 163.8, 156.3, 140.0, 136.3, 128.8_3, 128.7_7, 127.0, 121.5, 118.2, 66.7 (NCH^{i}Pr), 54.9 (NCy), 34.9, 34.3, 33.4, 26.4, 25.3, 25.0, 19.8, 19.4; IR (NaCl film, ν/cm^{-1}): 3309 w, 3061 m, 2925 s, 2852 s, 1570 s, 1445 s, 1368 m, 1114 m, 760 s, 693 s; HRMS-FAB (*m/z*): $[M+H]^+$ calcd for $C_{21}H_{29}N_2$, 309.2331; found, 309.2327.



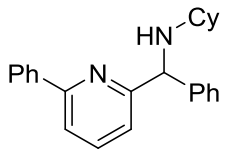
N-[cyclopentyl(6-phenylpyridin-2-yl)methyl]cyclohexyanamine (**3ah**)

^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 8.04 (d, ^3J = 7.3 Hz, 2H, *o*-Ph), 7.66 (t, ^3J = 7.7 Hz, 1H, 4-Py), 7.57 (d, ^3J = 7.7 Hz, 1H, 3- or 5-Py), 7.47 (t, ^3J = 7.3 Hz, 2H, *m*-Ph), 7.39 (tt, ^3J = 7.3 Hz, ^4J = 1.3 Hz, 1H, *p*-Ph), 7.20 (d, ^3J = 7.3 Hz, 1H, 5- or 3-Py), 3.68 (d, ^3J = 8.3 Hz, 1H, NC*H*(Ar)*c*-C_5H_9), 2.26-2.10 (m, 2H), 2.05-1.94 (m, 1H), 1.93-1.76 (m, 2H, C-H and NH), 1.73-1.38 (m, 9H), 1.38-1.21 (m, 2H), 1.19-1.01 (m, 5H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C): δ 164.7, 156.3, 140.0, 136.5, 128.8$_1$, 128.7$_7$, 127.0, 121.0, 118.3, 66.0 (NCHc-C_5H_9), 54.6 (NCy), 45.8, 35.0, 33.3, 30.4, 29.9, 26.4, 25.5, 25.4, 25.3, 25.0; IR (NaCl film, ν/cm^{-1}): 3308 w, 3060 m, 2926 s, 2852 s, 1570 s, 1445 s, 1122 m, 760 s, 694 s, 624 m; HRMS-FAB (*m/z*): $[M+H]^+$ calcd for $C_{23}H_{31}N_2$, 335.2487; found, 335.2484.



N-[(2-ethyl)buthyl-(6-phenylpyridin-2-yl)methyl]cyclohexyan amine (**3ai**)

^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 8.05 (d, ^3J = 7.5 Hz, 2H, *o*-Ph), 7.65 (t, ^3J = 7.7 Hz, 1H, 4-Py), 7.57 (d, ^3J = 7.7 Hz, 1H, 3- or 5-Py), 7.47 (t, ^3J = 7.3 Hz, 2H, *m*-Ph), 7.39 (t, ^3J = 7.3 Hz, 1H, *p*-Ph), 7.16 (d, J = 7.7 Hz, 1H, 5- or 3-Py), 3.86 (d, ^3J = 5.8 Hz, 1H, NC*H*(Ar)CHEt_2), 2.25-2.13 (m, 1H, NCy), 2.01-1.91 (m, 1H, C*H*Et_2), 1.79 (br s, 1H, NH), 1.73-1.31 (m, 8H), 1.23-0.99 (m, 6H), 0.92-0.80 (m, 6H, CH_2CH_3); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C): δ 164.2, 156.1, 139.9, 136.3, 128.8$_1$, 128.7$_6$, 127.0, 121.4, 118.0, 62.4 (N*C*HEt_2), 54.8 (NCy), 47.7, 35.0, 33.4, 26.4, 25.4, 25.0, 22.6, 21.6, 12.0, 11.6; IR (NaCl film, ν//cm-1): 3061 w, 2959 m, 2926 s, 2852 m, 1589 m, 1569 m, 1445 s, 1377 w, 755 m, 692 m; HRMS-FAB (*m/z*): $[M+H]^+$ calcd for $C_{23}H_{33}N_2$, 337.2644; found, 337.2652.



N-[phenyl(6-phenylpyridin-2-yl)methyl]cyclohexanamine (**3aj**)

^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 8.06-8.02 (m, 2H, *o*-Ph), 7.63 (t, ^3J = 7.7 Hz, 1H, 4-Py), 7.56 (dd, ^3J = 7.9 Hz, ^4J = 0.9 Hz, 1H, 3- or 5-Py), 7.50-7.45 (m, 4H, *m*-Ph and Ph), 7.41 (tt, ^3J = 7.2 Hz, ^4J = 1.4 Hz, 1H, *p*-Ph), 7.33-7.28 (m, 2H, Ph), 7.22 (tt, ^3J = 7.3 Hz, ^4J = 1.3 Hz, 1H, *p*-Ph), 7.17 (dd, ^3J = 7.7 Hz, ^4J = 0.9 Hz, 1H, 5- or 3-Py), 5.15 (s, 1H, NC*H*(Ar)Ph), 2.48-2.36 (m, 1H), 2.10 (br s, 1H, NH), 2.02-1.88 (m, 2H), 1.78-1.49 (m, 3H), 1.30-1.08 (m, 5H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C): δ 162.8, 156.5, 143.7, 139.7, 137.2, 129.0, 128.8, 128.6, 127.9, 127.1$_3$, 127.0$_9$, 120.8, 118.5, 65.0 (NCHPh), 54.2 (NCy), 34.2, 33.7, 26.4, 25.2$_4$, 25.1$_8$; IR (NaCl film, ν/cm^{-1}): 3310 w, 3061 m, 3028 m, 2925 s, 2851 s, 1569 s, 1445 s, 1027 m, 758 s, 697 s, 624 m; HRMS-FAB (*m/z*): $[M+H]^+$ calcd for $C_{24}H_{27}N_2$, 343.2174; found, 343.2174.

8. ^{1}H and ^{13}C NMR spectra of aminomethylated products and complexes 4-6.

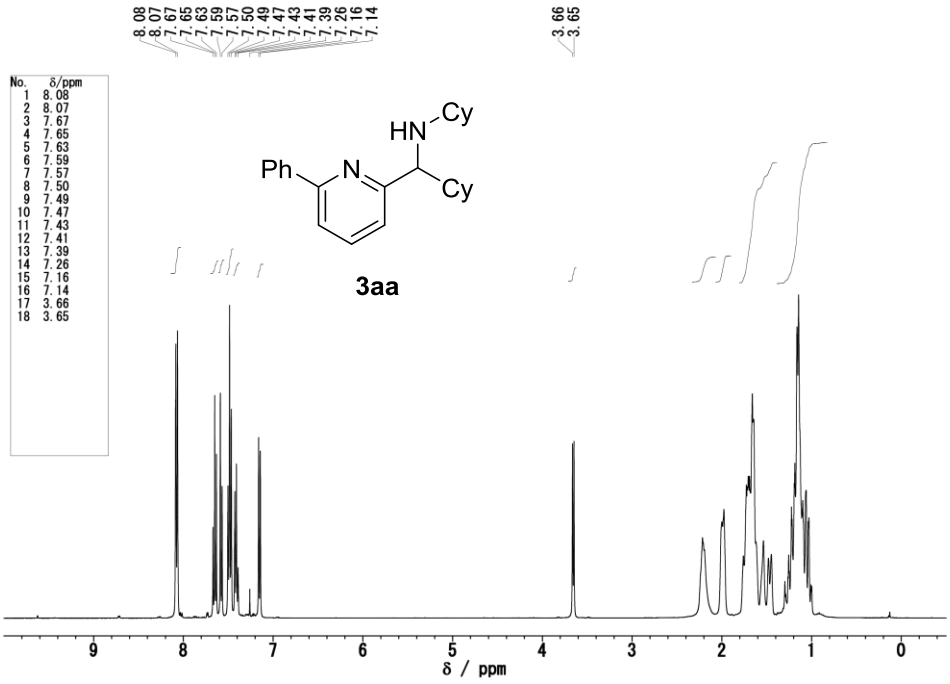


Figure S10. ^{1}H NMR spectrum of compound **3aa**.

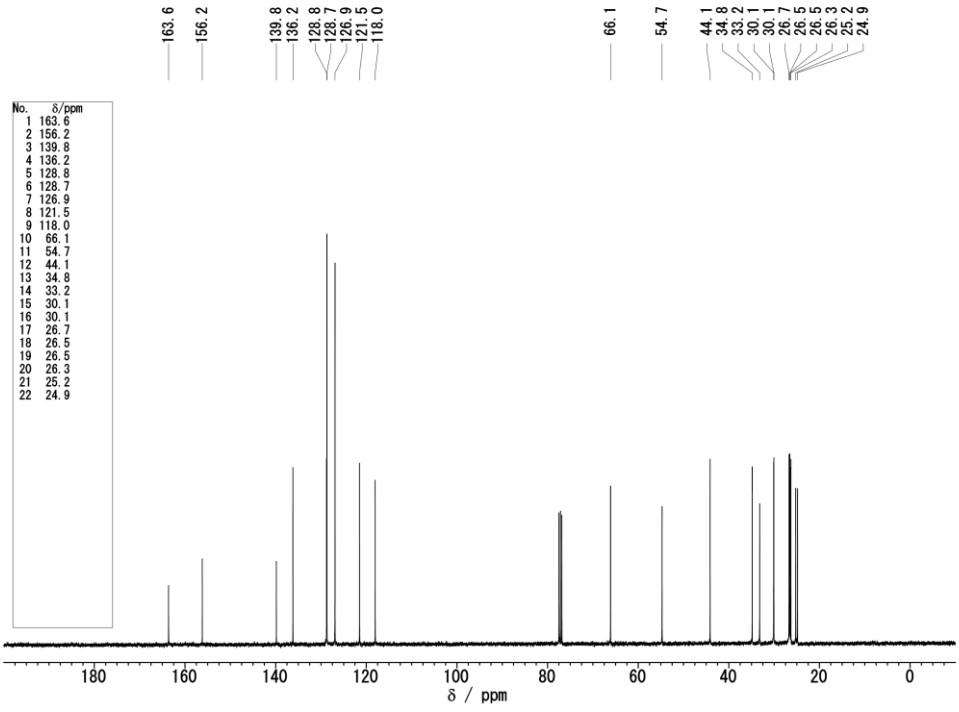


Figure S11. ^{13}C NMR spectrum of compound **3aa**.

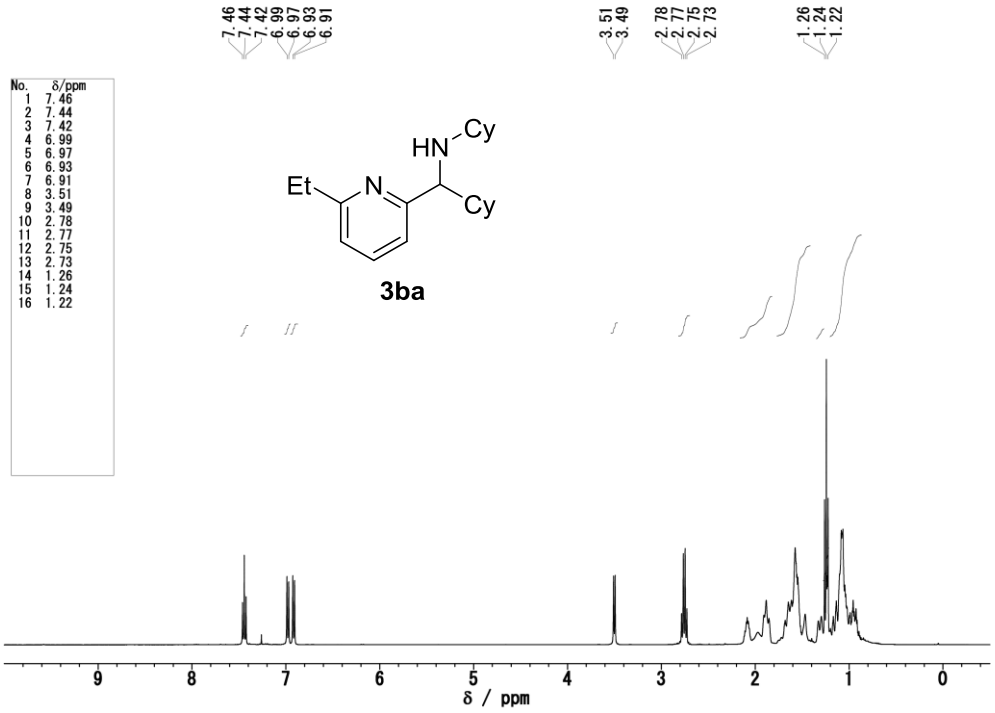


Figure S12. ^{1}H NMR spectrum of compound **3ba**.

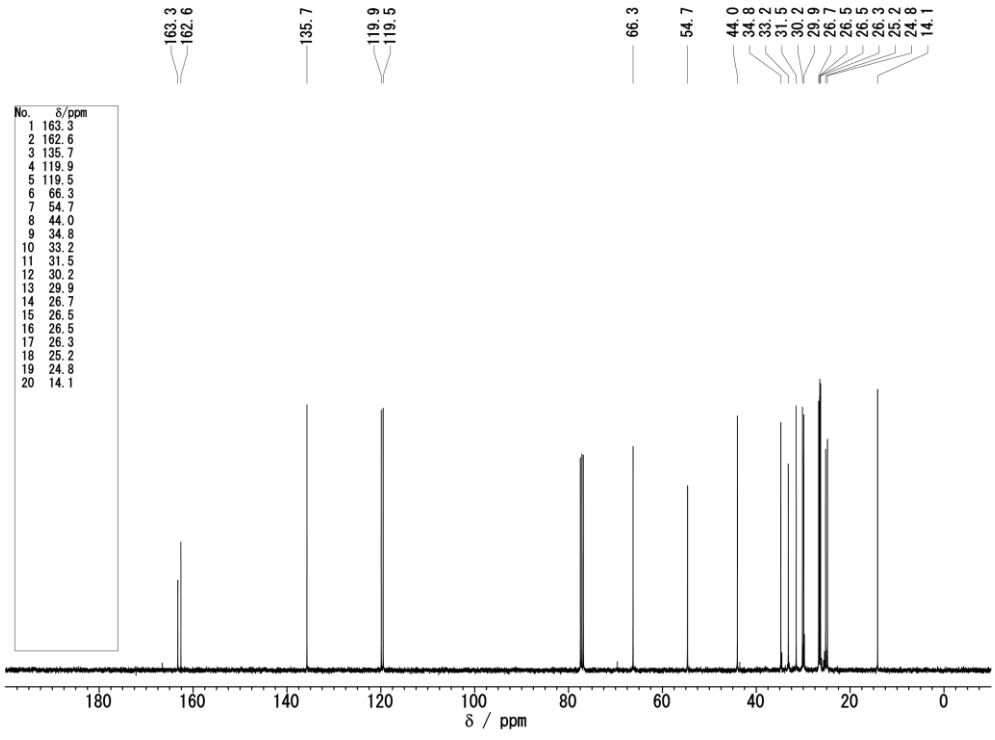


Figure S13. ^{13}C NMR spectrum of compound **3ba**.

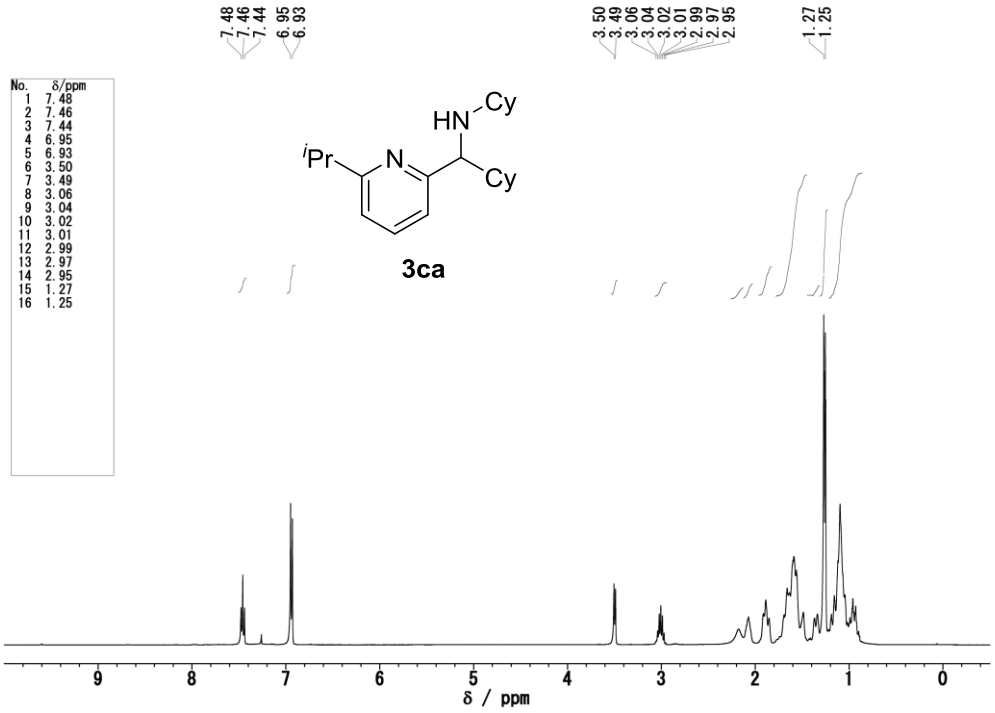


Figure S14. ^{1}H NMR spectrum of compound **3ca**.

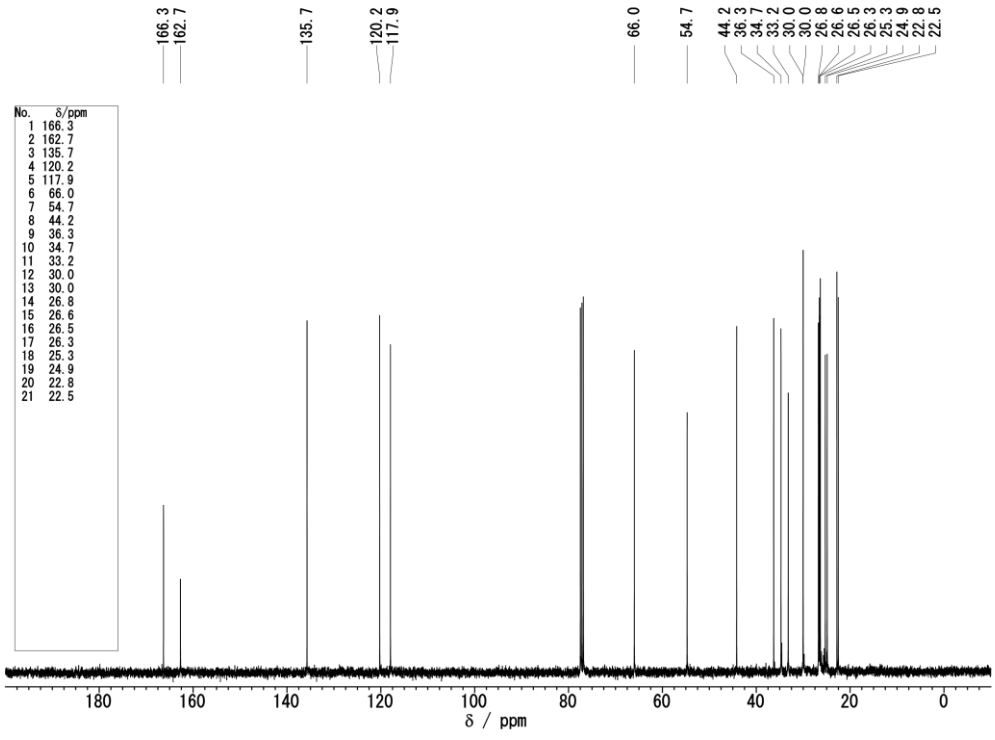


Figure S15. ^{13}C NMR spectrum of compound **3ca**.

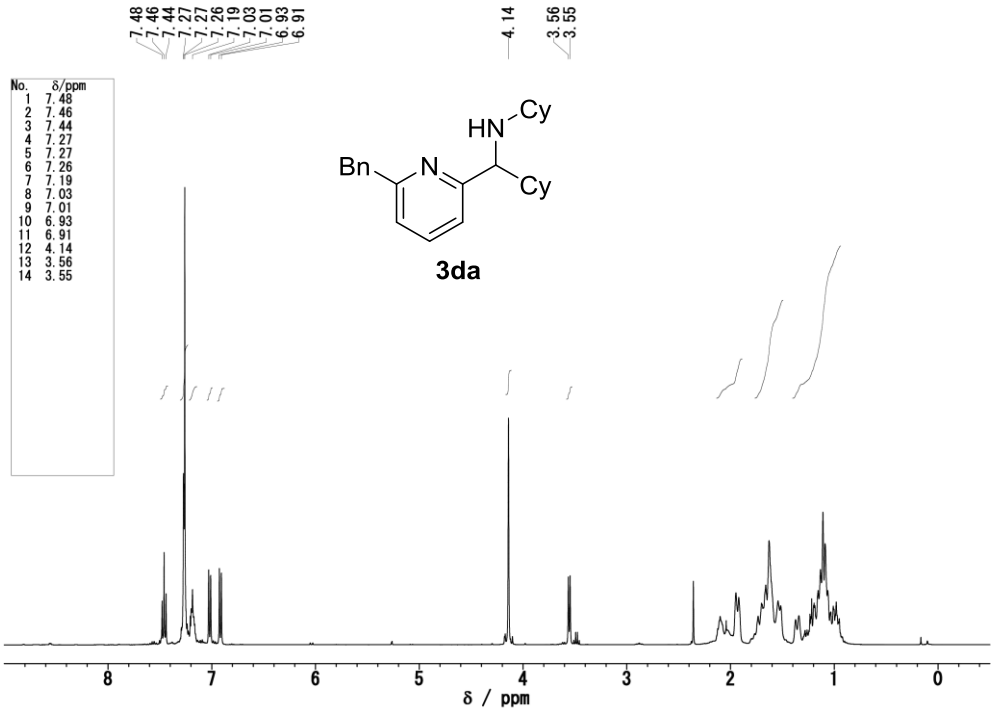


Figure S16. ^{1}H NMR spectrum of compound **3da**.

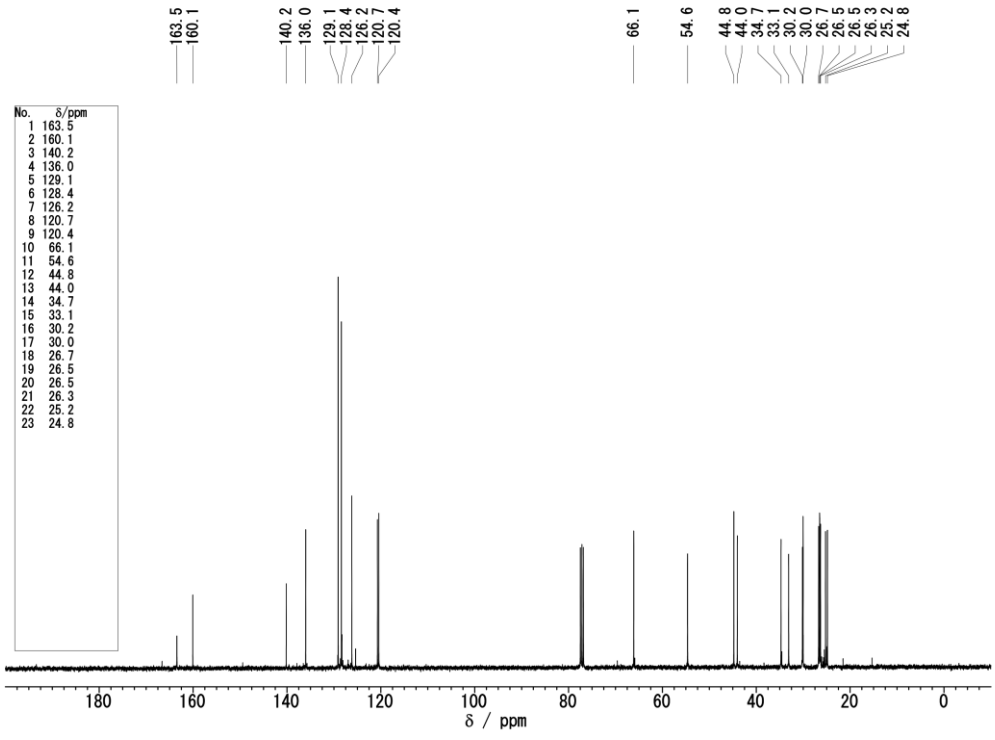


Figure S17. ^{13}C NMR spectrum of compound **3da**.

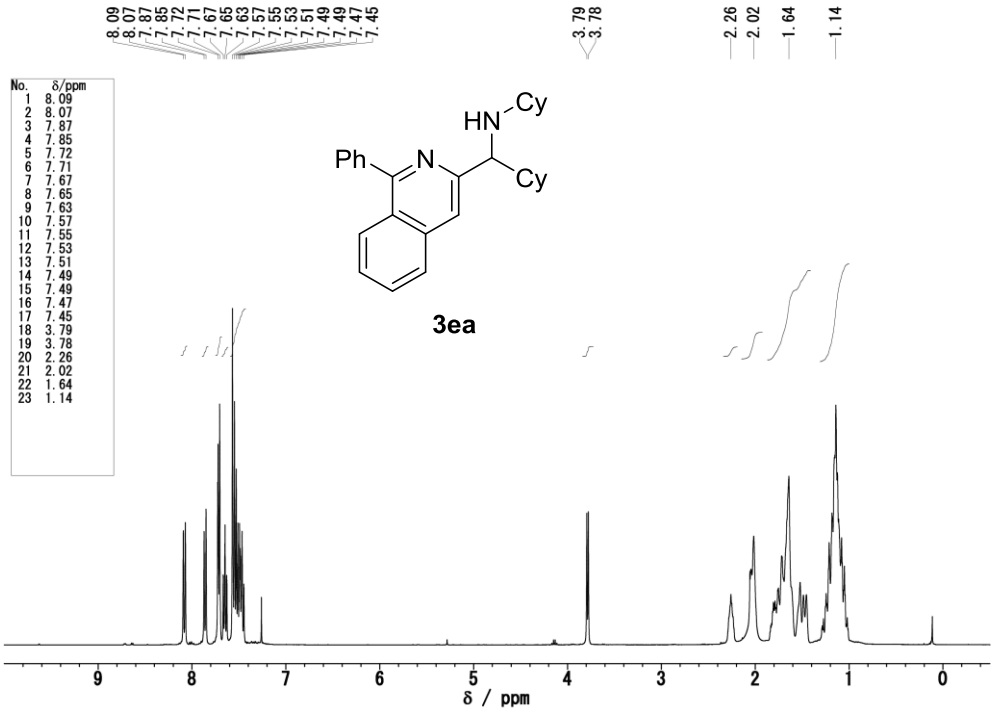


Figure S18. ^{1}H NMR spectrum of compound **3ea**.

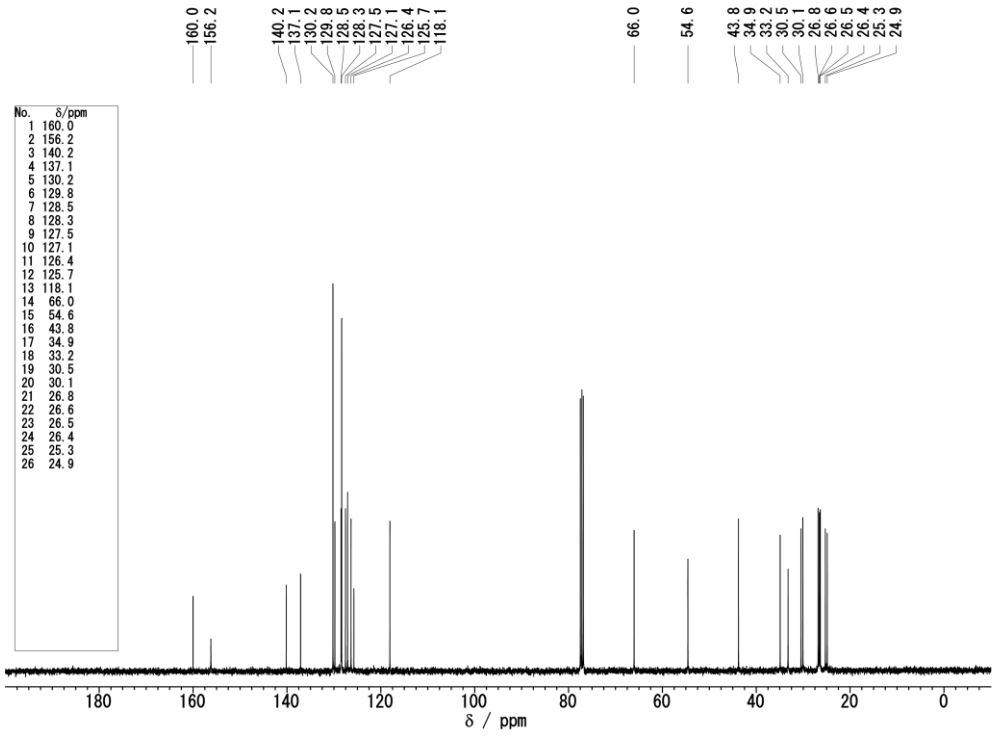


Figure S19. ^{13}C NMR spectrum of compound **3ea**.

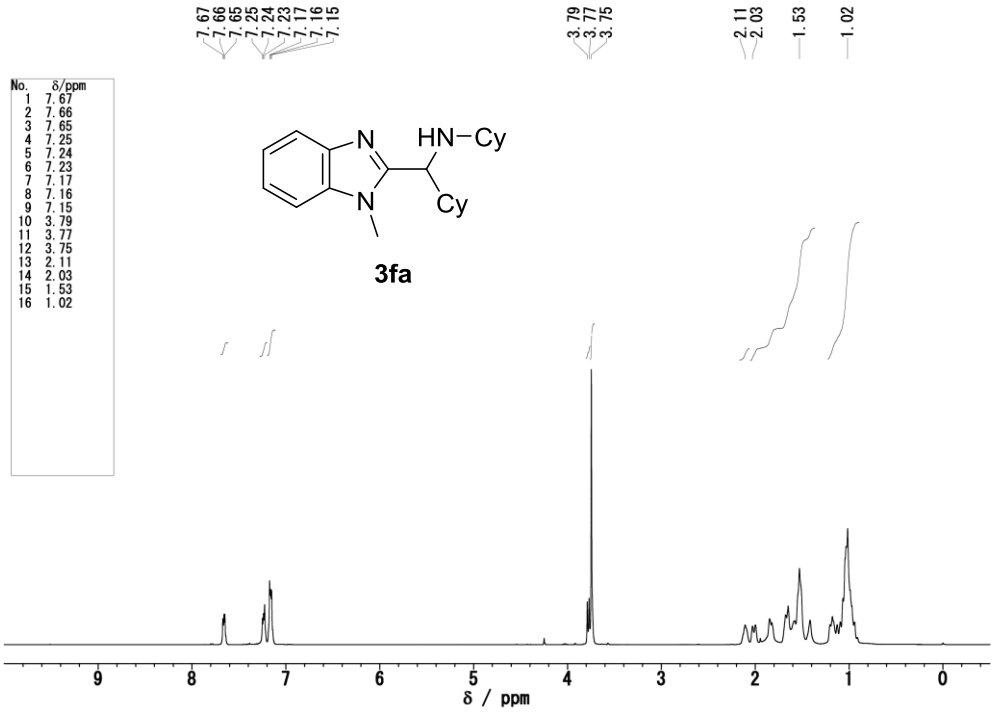


Figure S20. ^{1}H NMR spectrum of compound **3fa**.

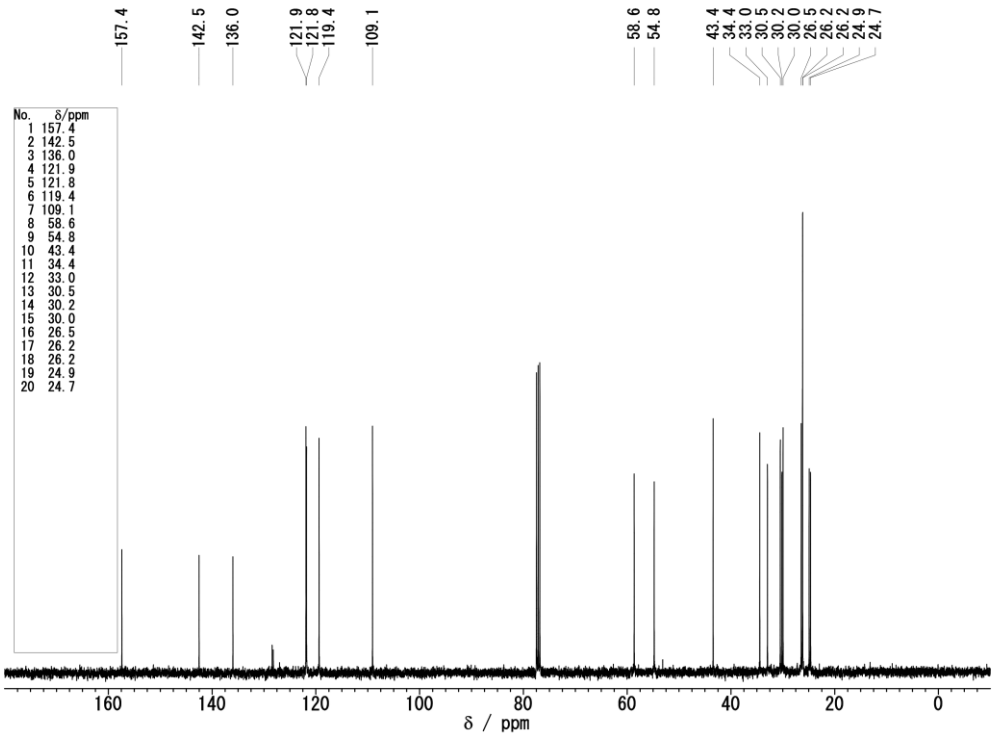


Figure S21. ^{13}C NMR spectrum of compound **3fa**.

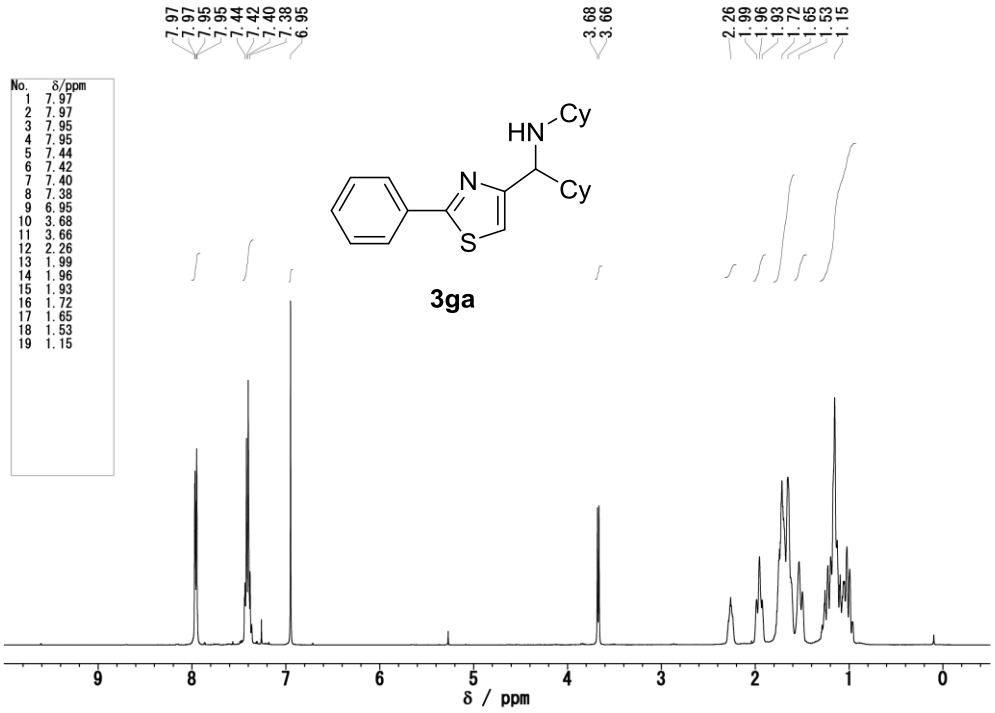


Figure S22. ^{1}H NMR spectrum of compound **3ga**.

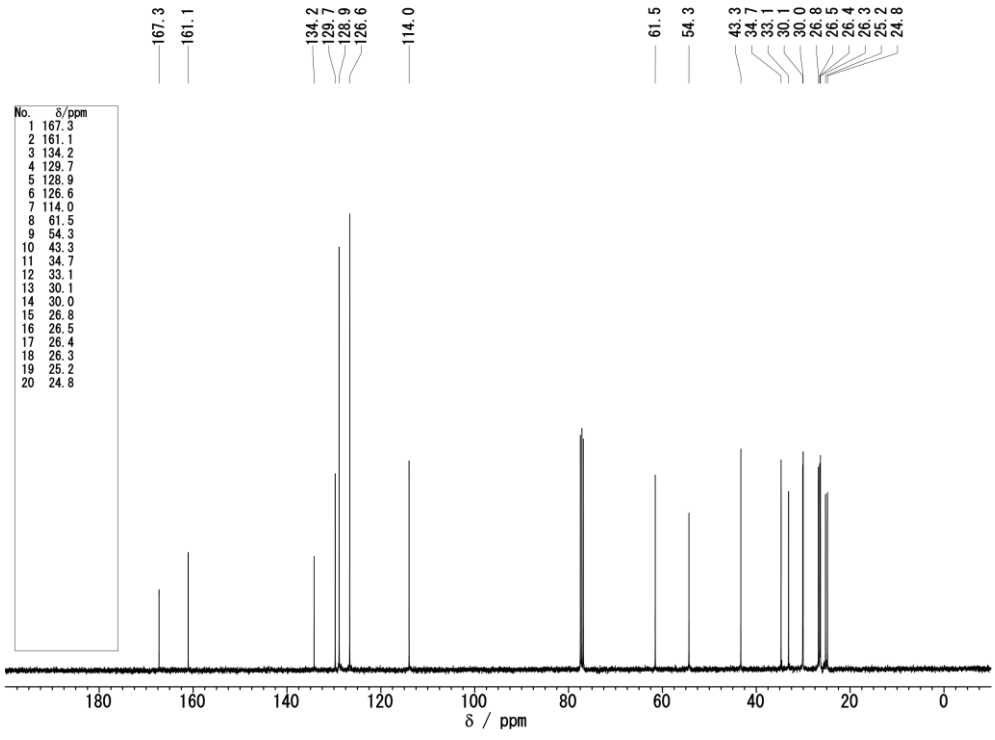


Figure S23. ^{13}C NMR spectrum of compound **3ga**.

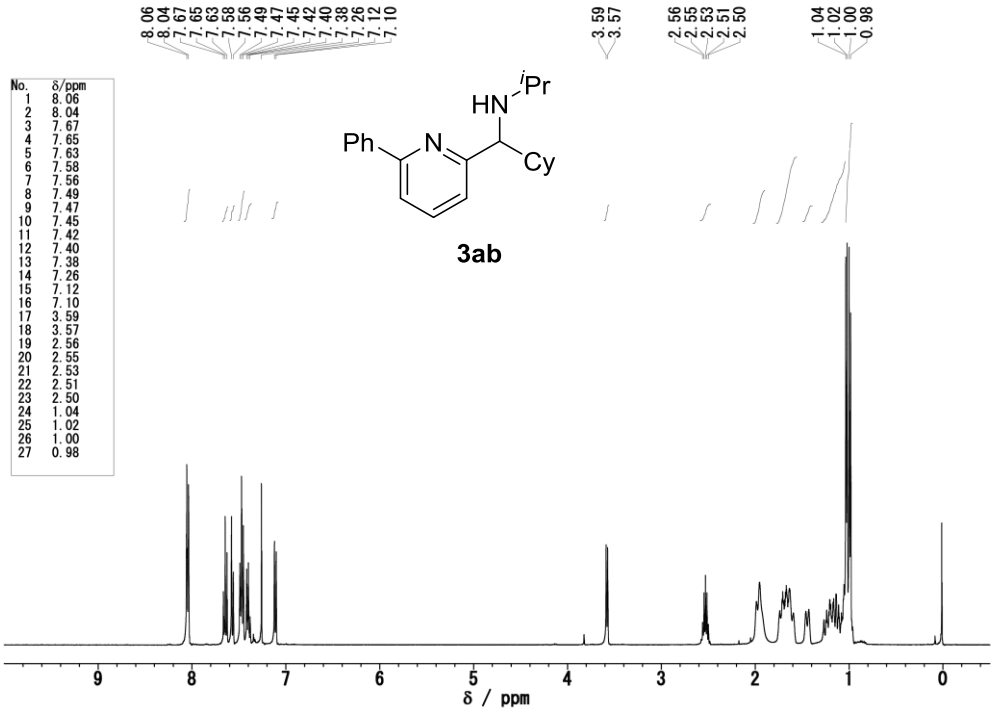


Figure S24. ^{1}H NMR spectrum of compound **3ab**.

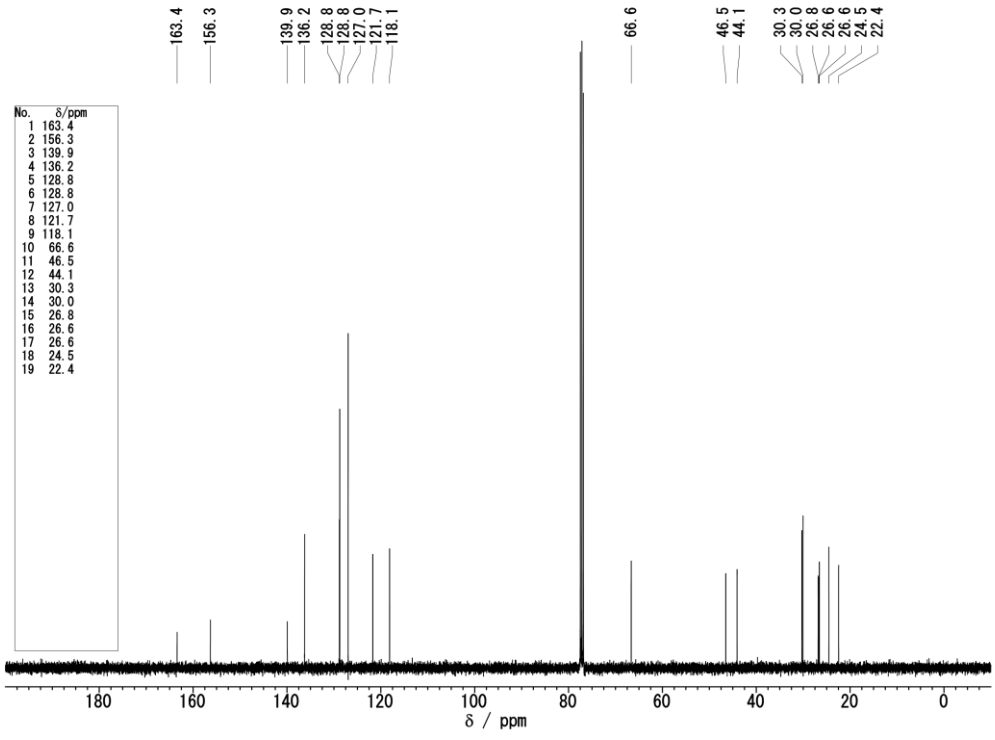


Figure S25. ^{13}C NMR spectrum of compound **3ab**.

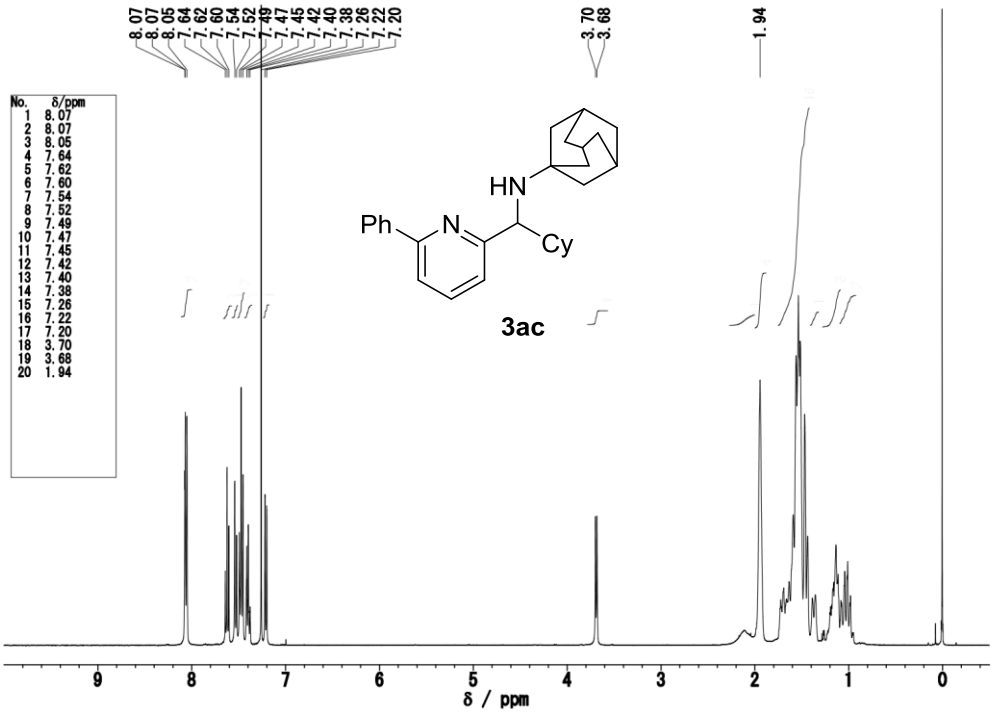


Figure S26. ^{1}H NMR spectrum of compound **3ac**.

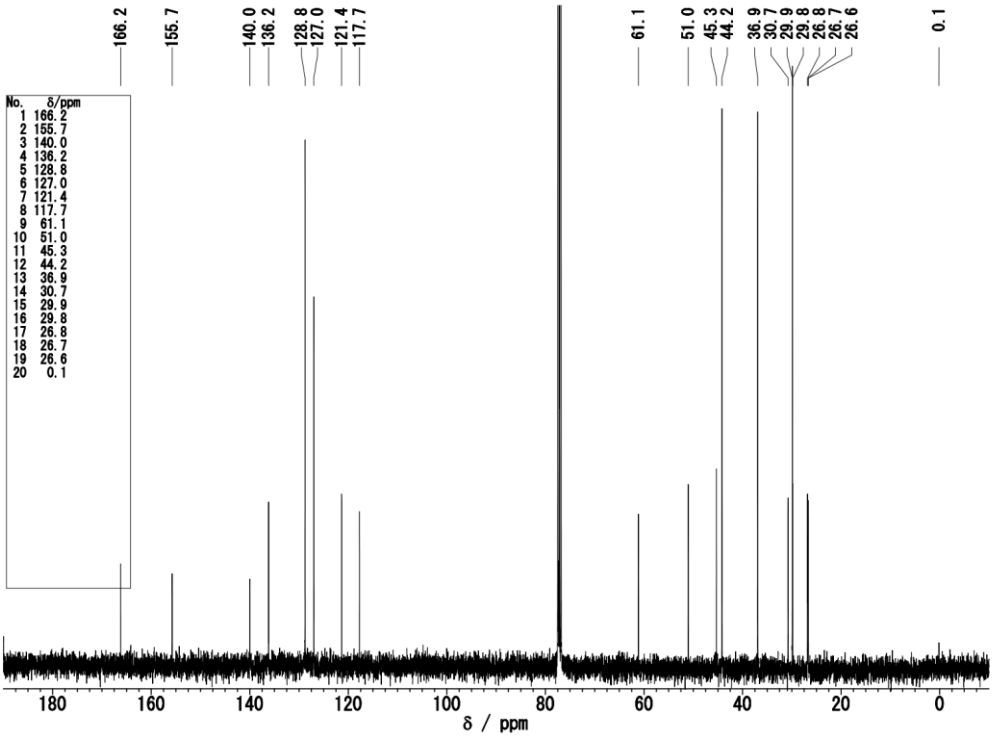


Figure S27. ^{13}C NMR spectrum of compound **3ac**.

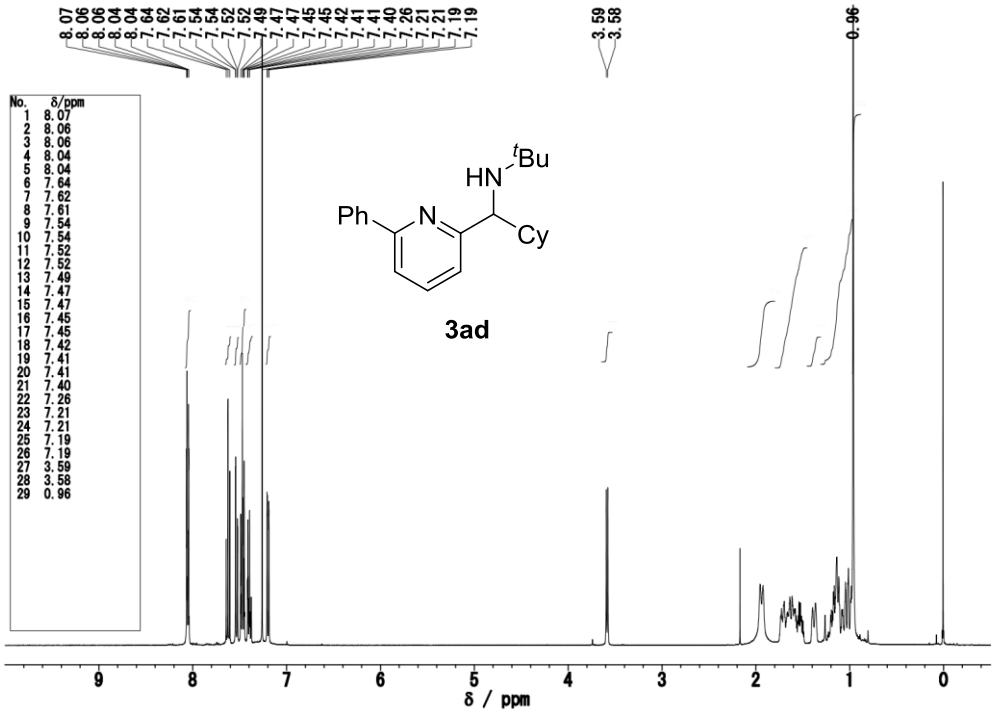


Figure S28. ^{1}H NMR spectrum of compound **3ad**.

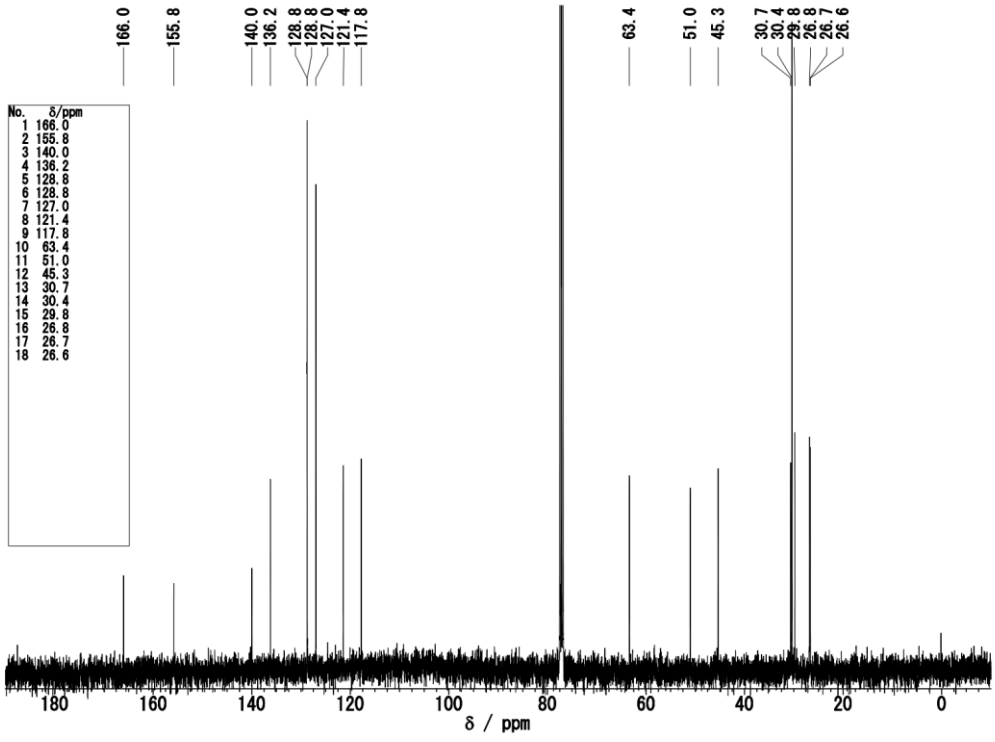


Figure S29. ^{13}C NMR spectrum of compound **3ad**.

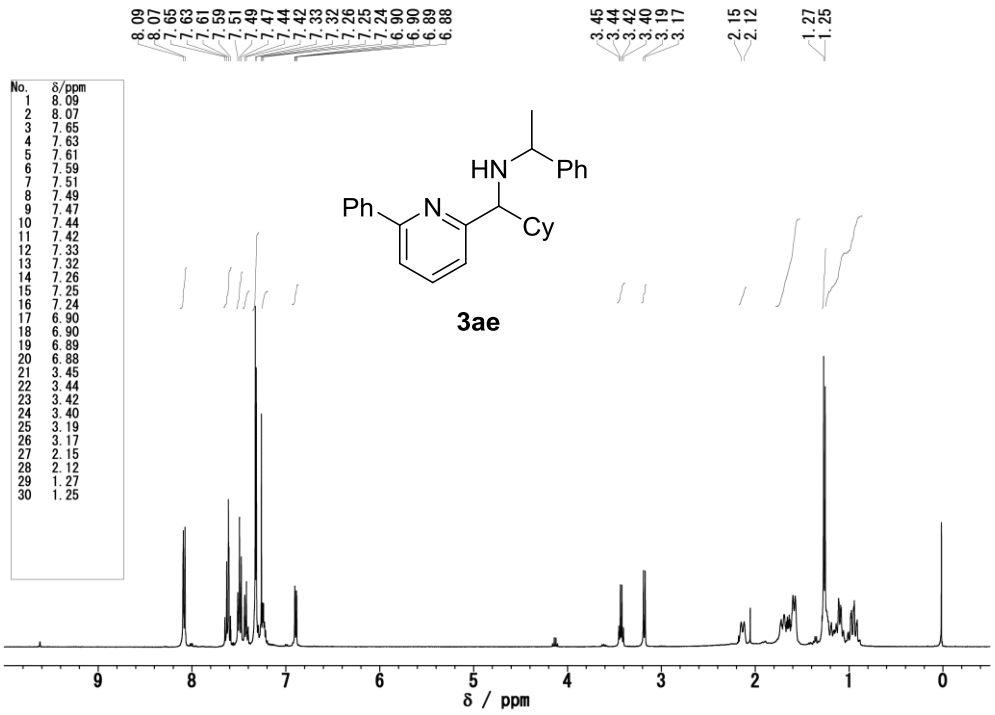


Figure S30. ^{1}H NMR spectrum of compound **3ae**.

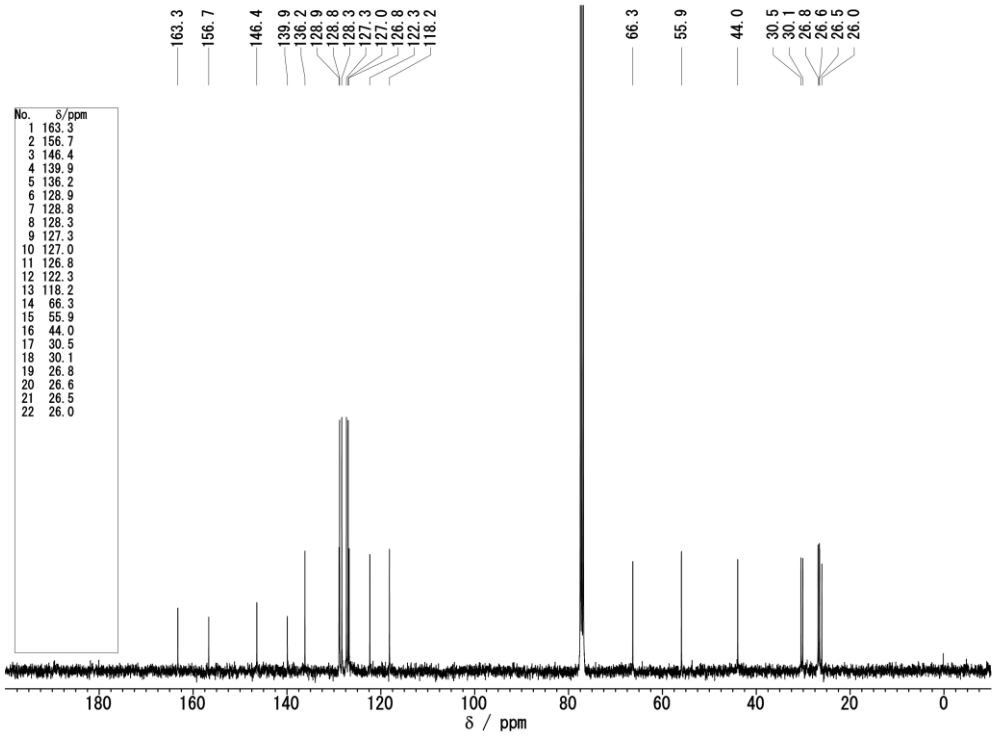


Figure S31. ^{13}C NMR spectrum of compound **3ae**.

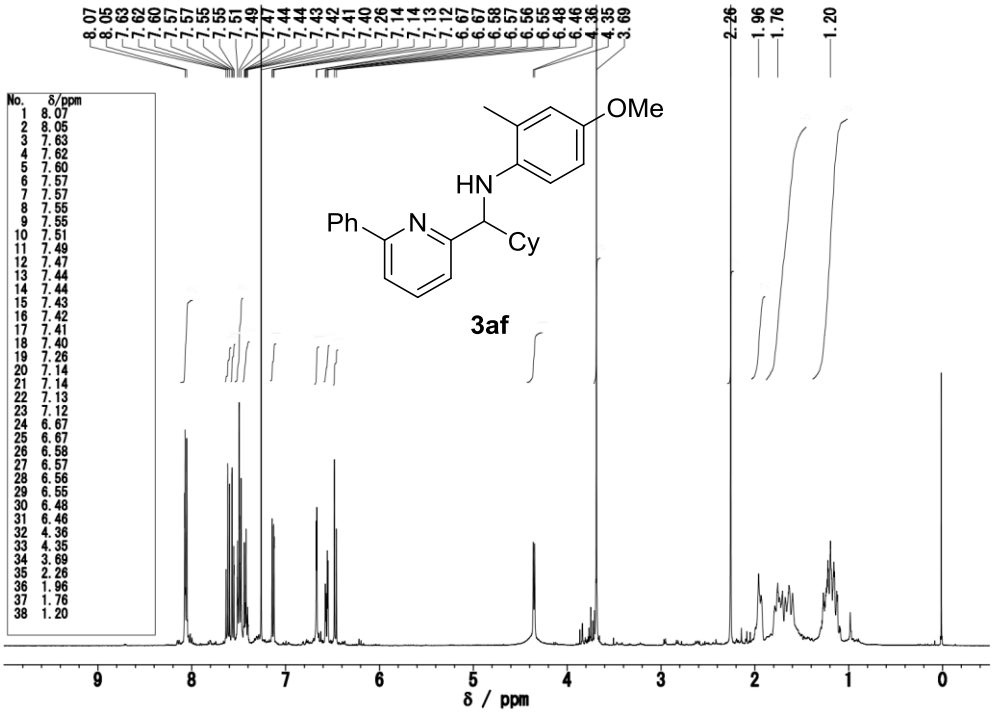


Figure S32. ^{1}H NMR spectrum of compound **3af**.

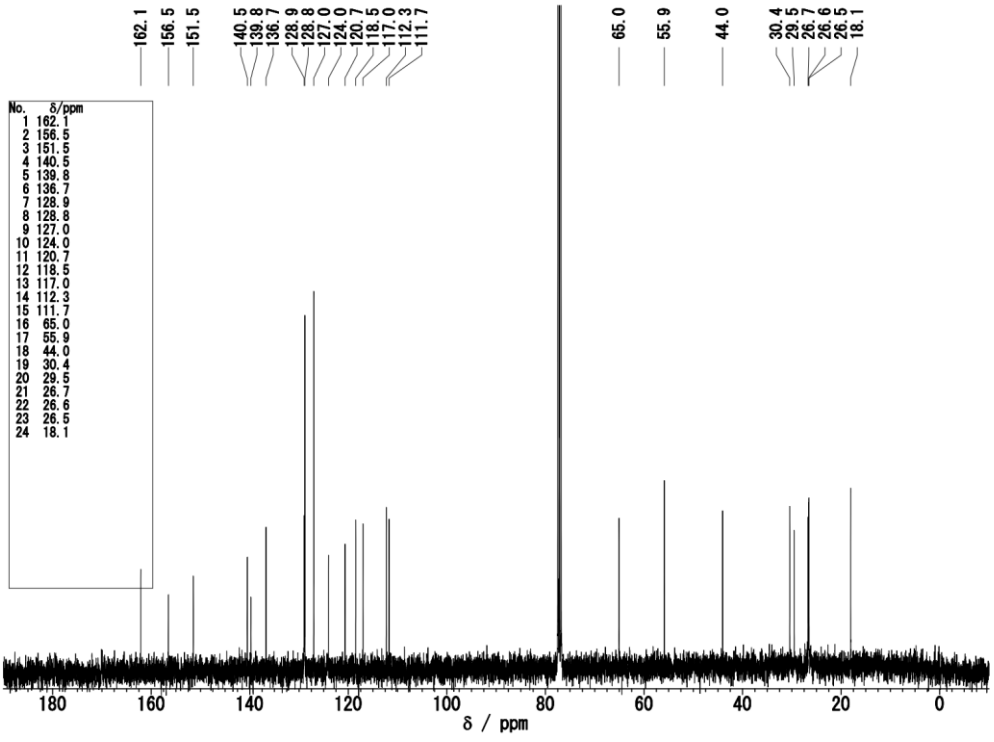


Figure S33. ^{13}C NMR spectrum of compound **3af**.

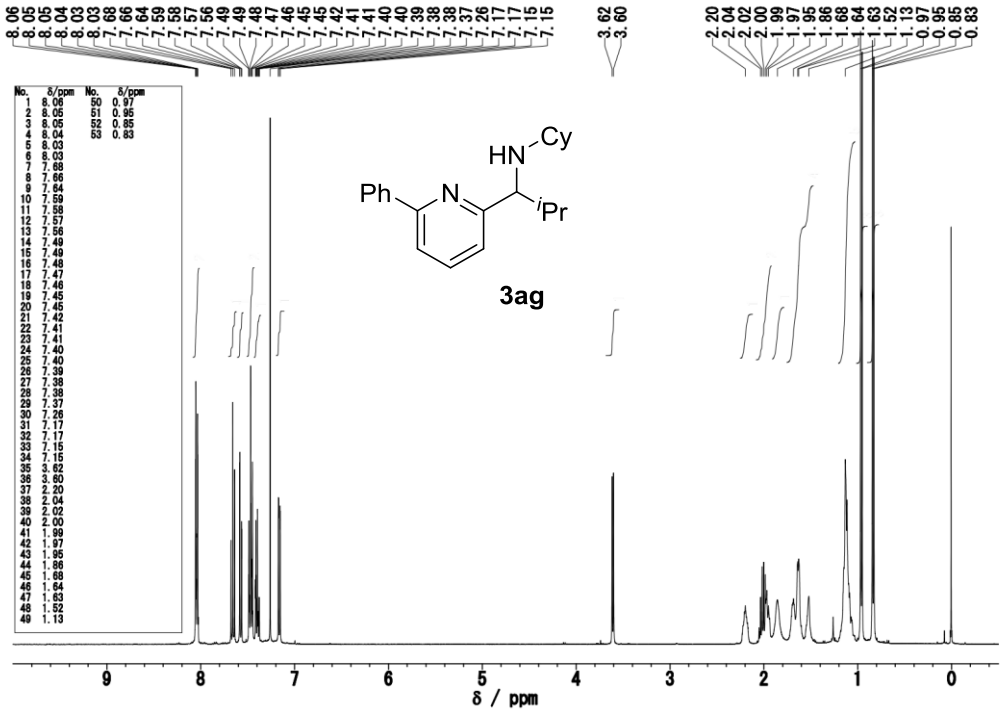


Figure S34. ^{1}H NMR spectrum of compound **3ag**.

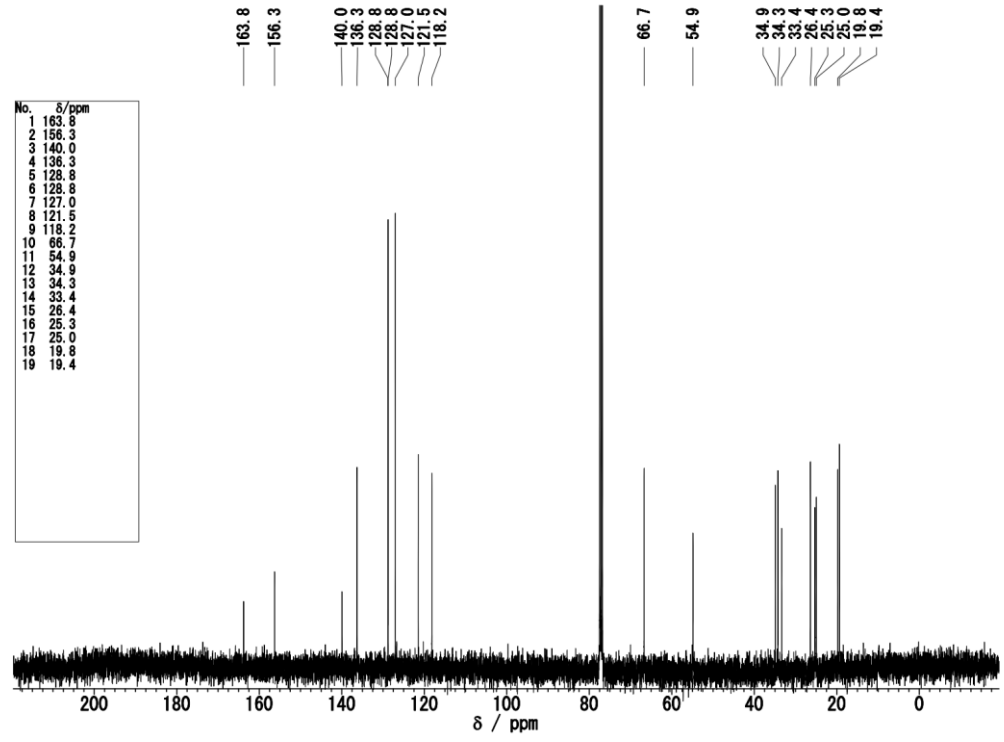


Figure S35. ^{13}C NMR spectrum of compound **3ag**.

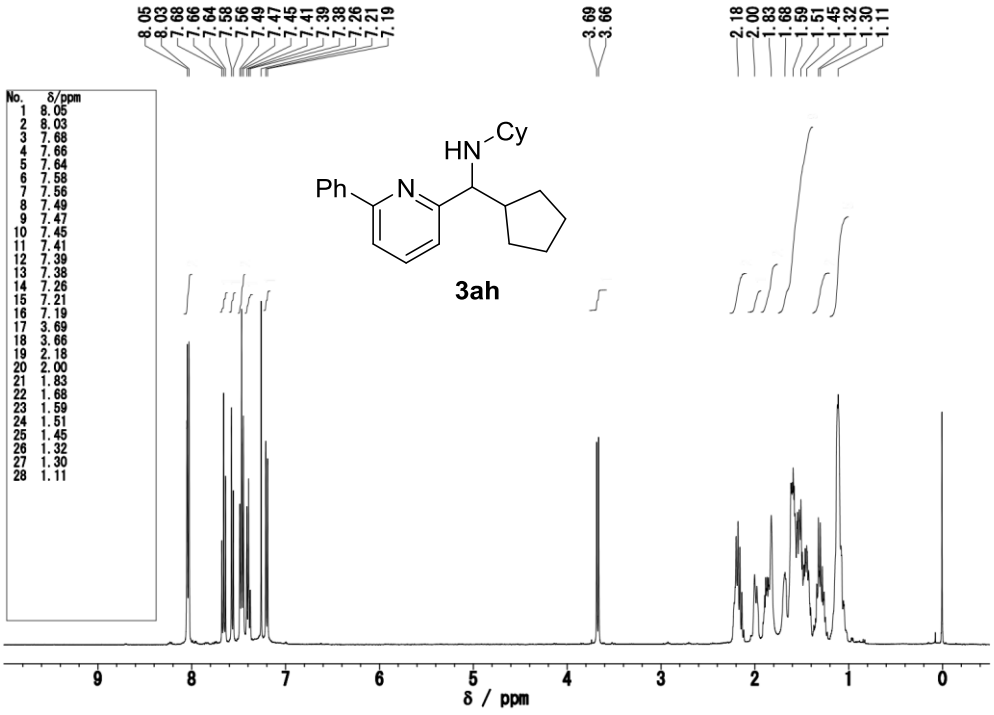


Figure S36. ^{1}H NMR spectrum of compound **3ah**.

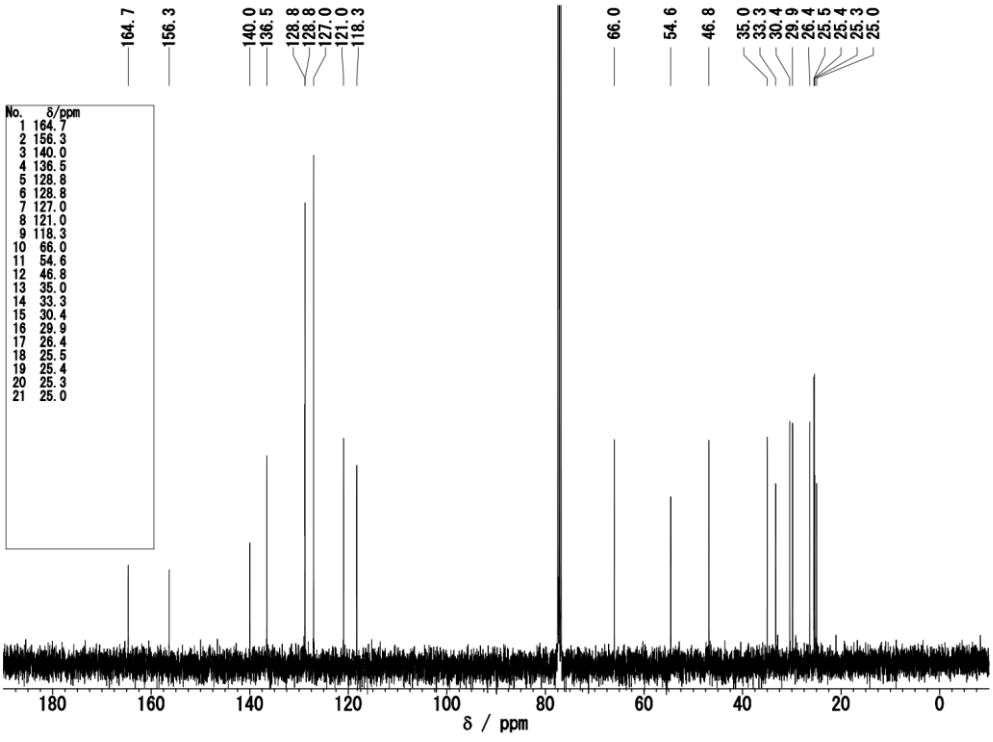


Figure S37. ^{13}C NMR spectrum of compound **3ah**.

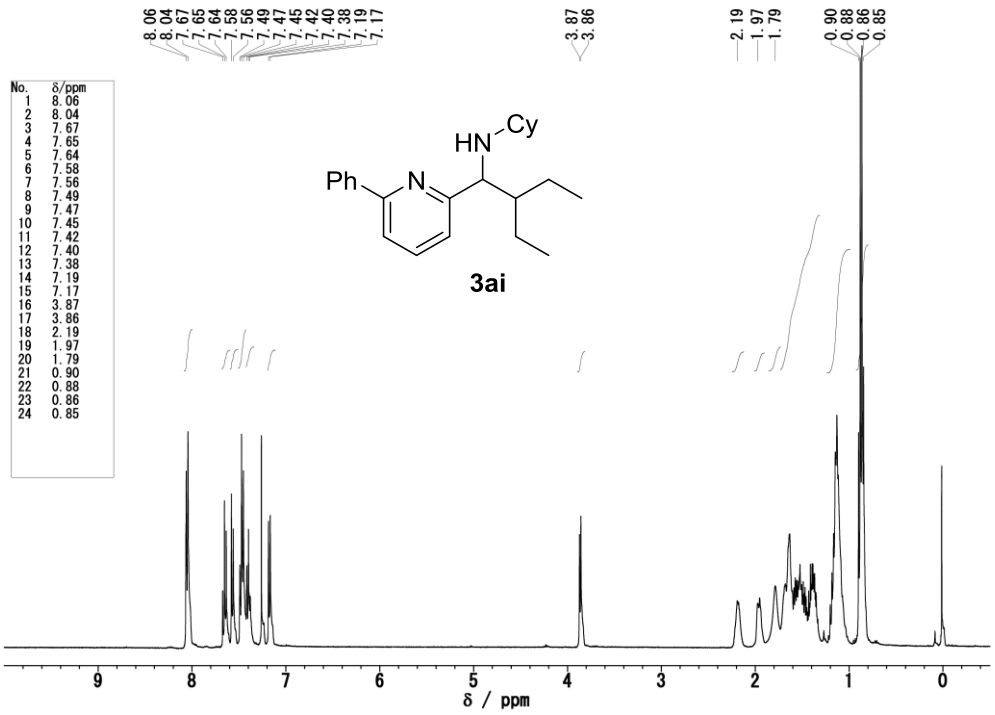


Figure S38. ^{1}H NMR spectrum of compound **3ai**.

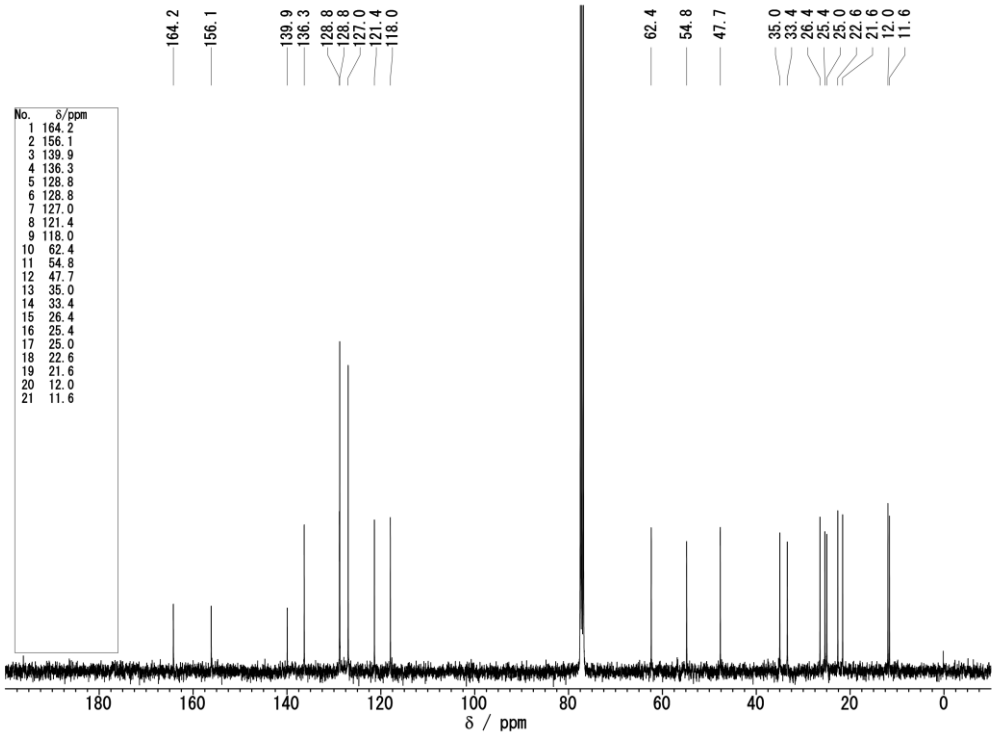


Figure S39. ^{13}C NMR spectrum of compound **3ai**.

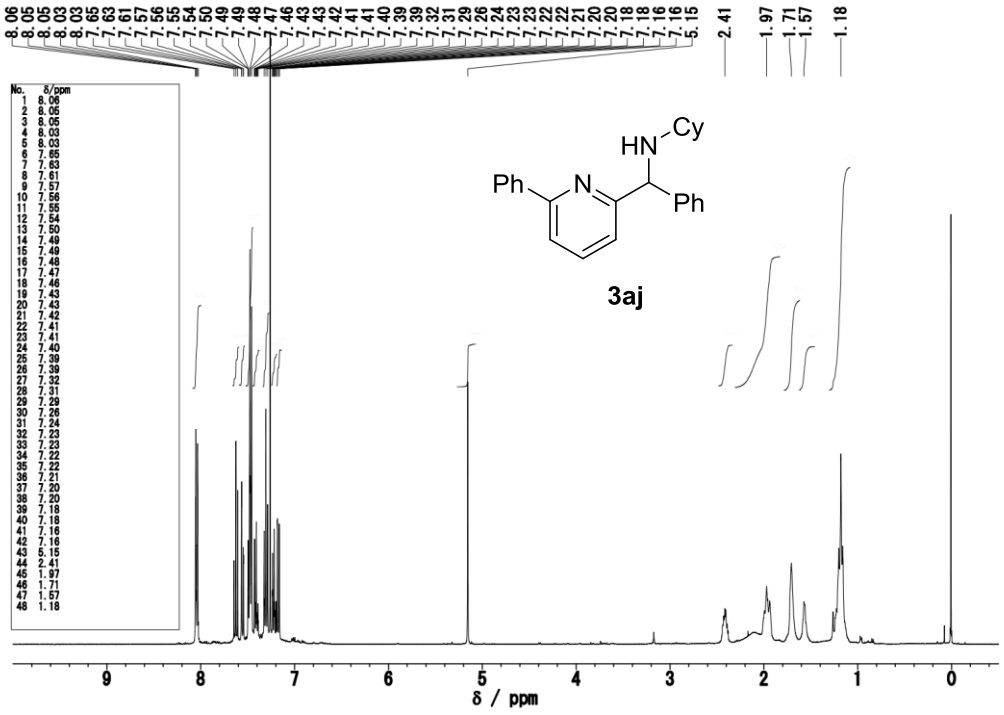


Figure S40. ^{1}H NMR spectrum of compound **3aj**.

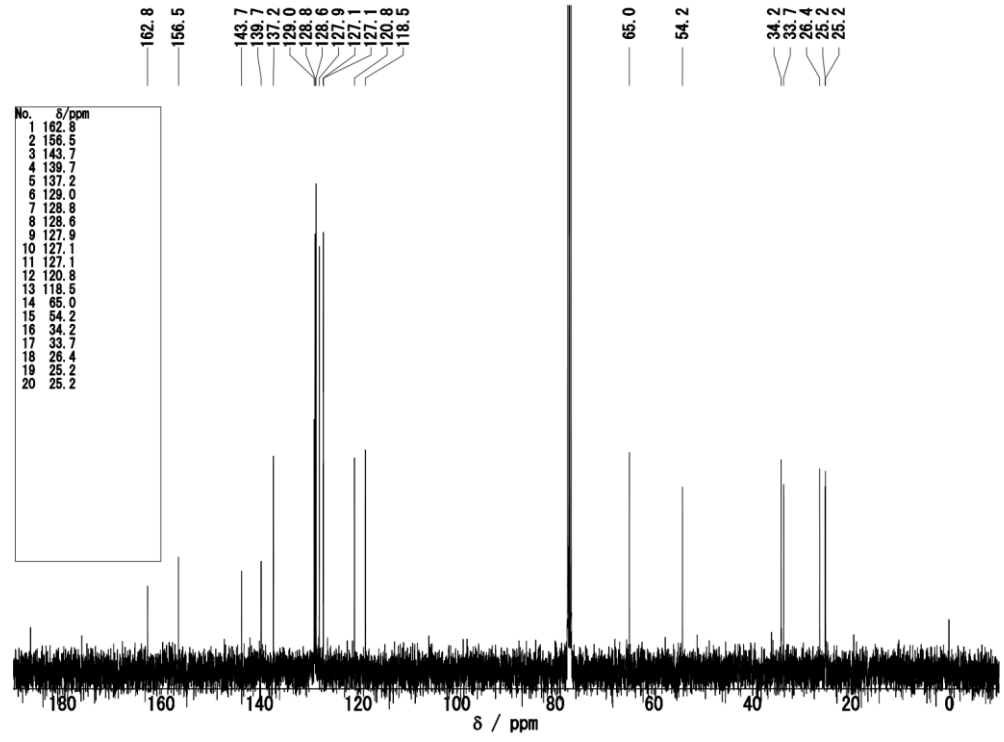


Figure S41. ^{13}C NMR spectrum of compound **3aj**.

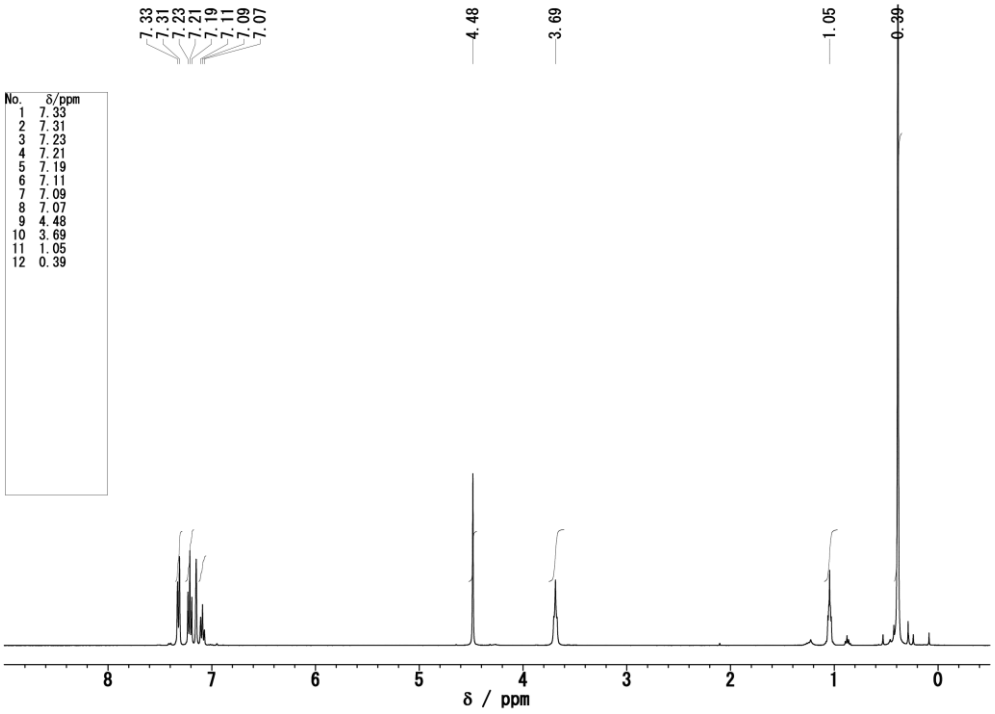


Figure S42. ^{1}H NMR spectrum of complex **4**.

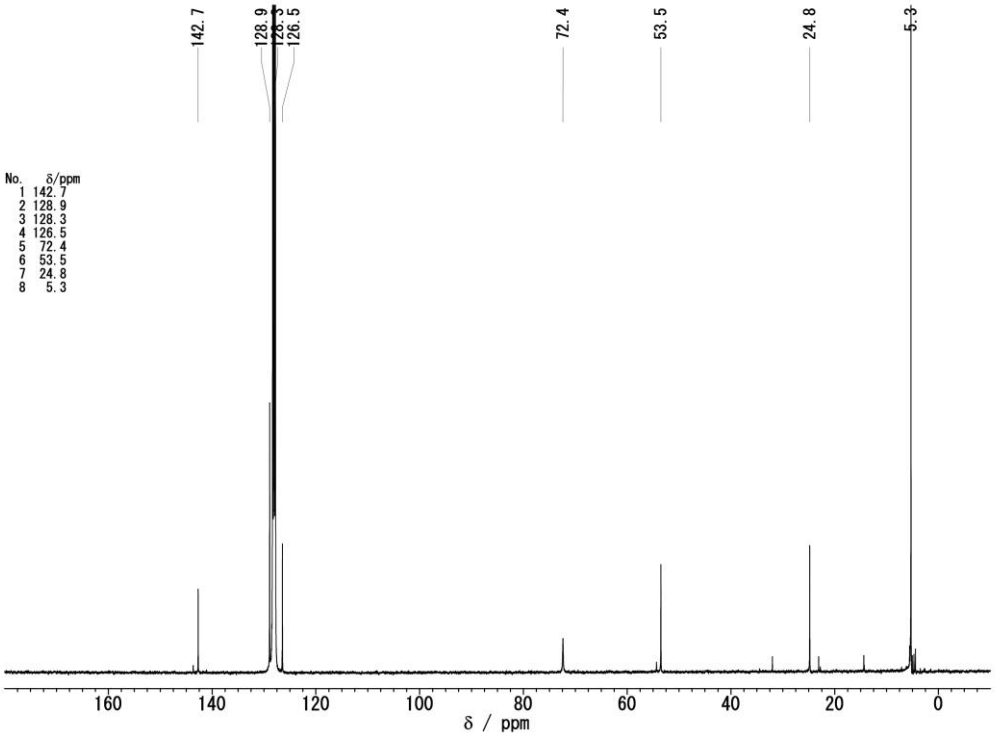


Figure S43. ^{13}C NMR spectrum of complex **4**.

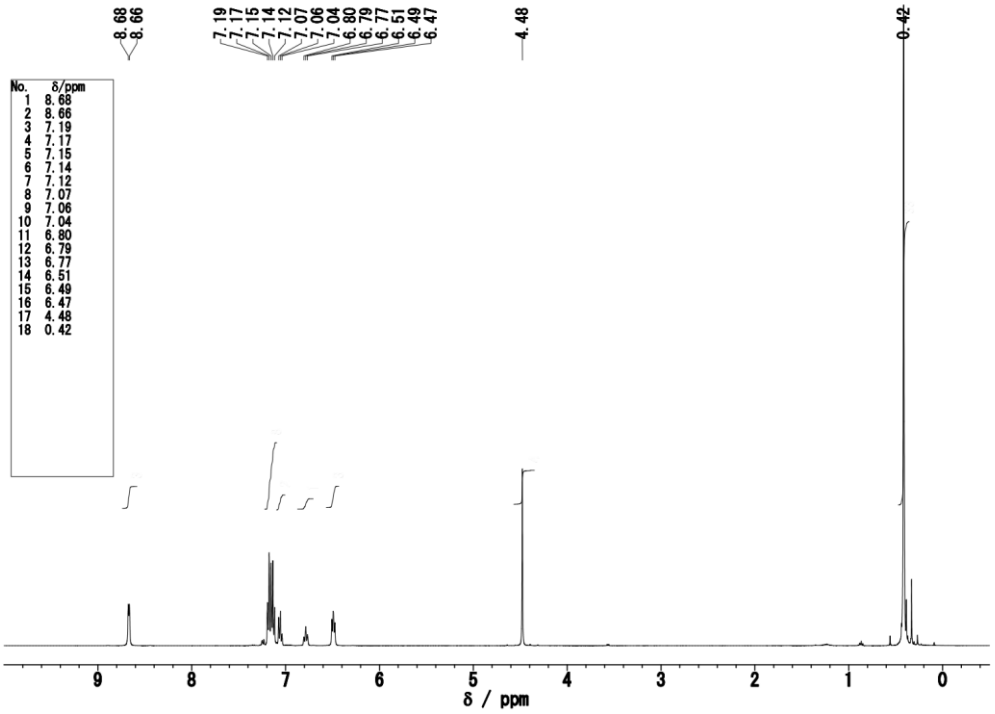


Figure S44. ^{1}H NMR spectrum of complex **5**.

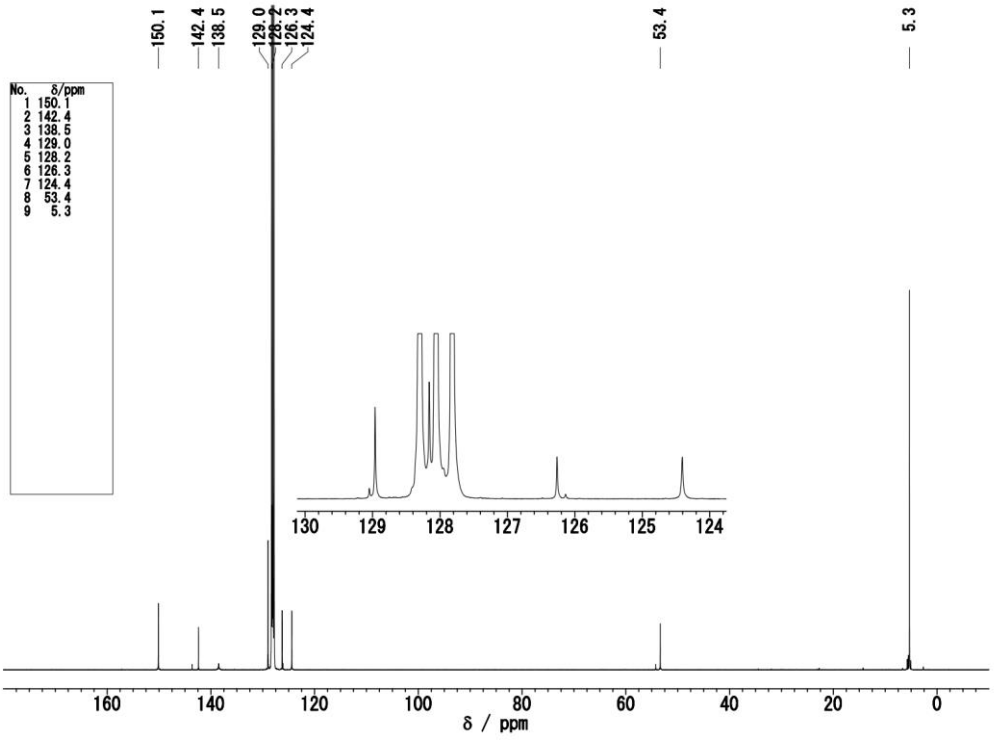


Figure S45. ^{13}C NMR spectrum of complex **5**.

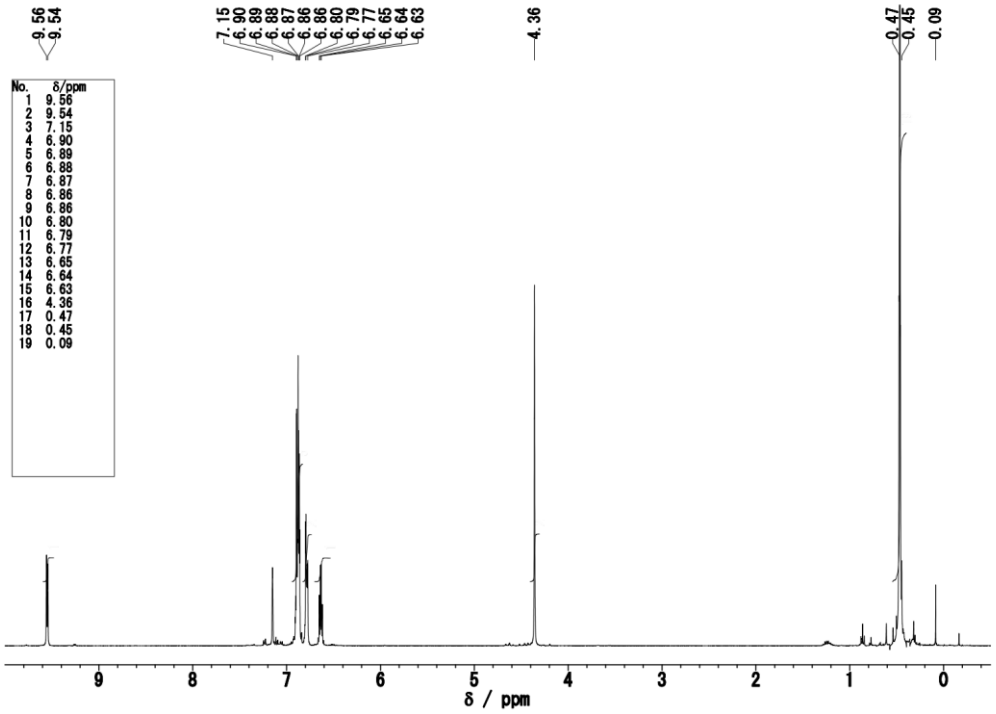


Figure S46. ^{1}H NMR spectrum of complex **6**.

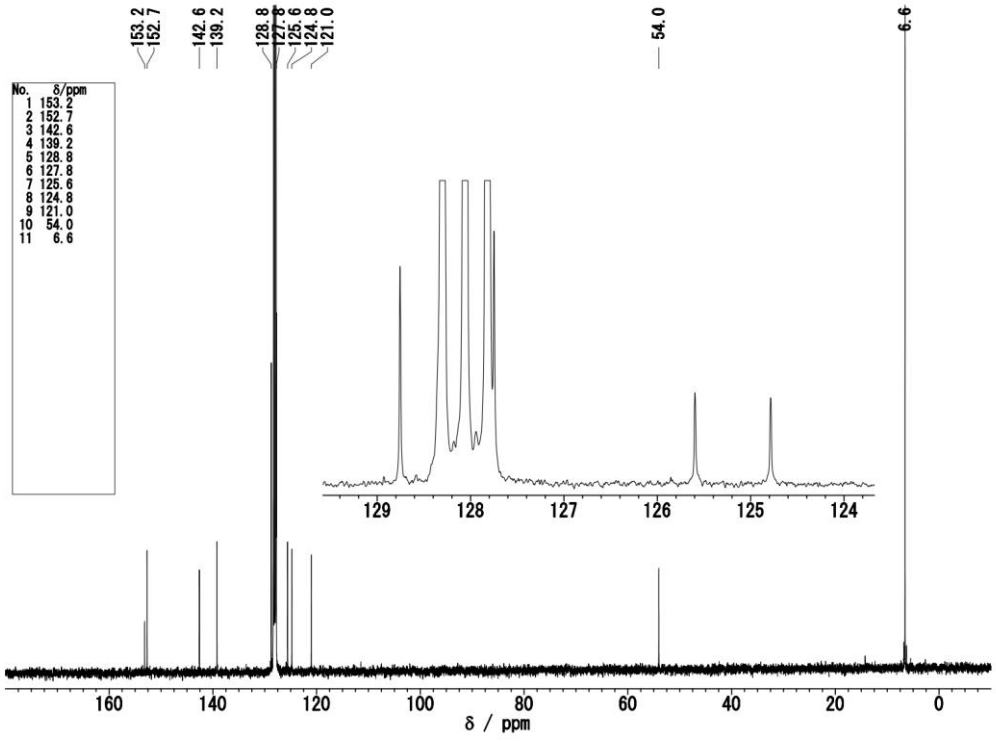


Figure S47. ^{13}C NMR spectrum of complex **6**.

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