Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

1,3,5-Triaryl 2-Pyridylidene: Base-promoted Generation and Complexation

Kazuhiro Hata, Yasutomo Segawa* and Kenichiro Itami*

Department of Chemistry, Graduate School of Science, Nagoya University,

Chikusa, Nagoya 464-8602, Japan

E-mail: ysegawa@nagoya-u.jp; itami.kenichiro@a.mbox.nagoya-u.ac.jp

---

Table of Contents

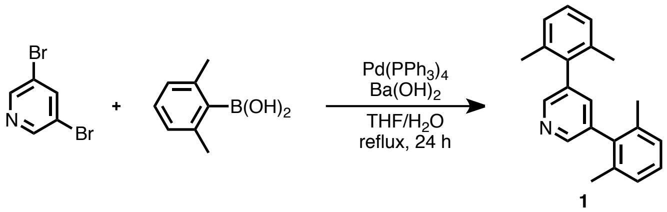
1. Experimental Section

General

Unless otherwise noted, all materials including dry solvents were obtained from commercial suppliers and used without further purification. Tetrahydrofuran (THF) and diethyl ether were purified by passing through a solvent purification system (Glass Contour). All reactions were performed using standard vacuum-line and Schlenk techniques. Work-up and purification procedures were carried out with reagent-grade solvents under air.

Analytical thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (0.25 mm). The developed chromatogram was analyzed by UV lamp (254 nm and 365 nm). Flash column chromatography was performed with E. Merck silica gel 60 (230–400 mesh). Preparative thin-layer chromatography (PTLC) was performed using Wako-gel® B5-F silica coated plates (0.75 mm) prepared in our laboratory. High-resolution mass spectra (HRMS) were obtained from a JEOL JMS700 (fast atom bombardment mass spectrometry, FAB MS) and a JEOL JMST100TD instrument (DART). Melting points were measured on a MPA100 Optimelt automated melting point system. Nuclear magnetic resonance (NMR) spectra were recorded on JEOL JNM-ECA-600 (^{1}H 600 MHz, ^{13}C 150 MHz) spectrometer and JEOL JNM-ECS-400 (^{1}H 400 MHz, ^{13}C 100 MHz) spectrometer. Chemical shifts for ^{1}H NMR are expressed in parts per million (ppm) relative to $CHCl_3$ (δ 7.26 ppm) and benzene-d_6 (δ 7.15 ppm). Chemical shifts for ^{13}C NMR are expressed in ppm relative to $CDCl_3$ (δ 77.0 ppm) and benzene-d_6 (δ 128.1 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet, br = broad), coupling constant (Hz), and integration.

Synthesis of 3,5-bis(2,6-dimethylphenyl)pyridine (1)

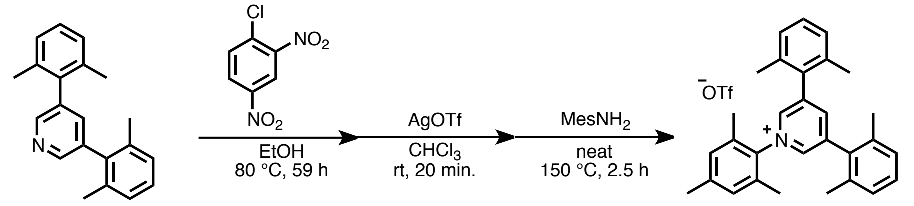


1
80%

A two-necked 300 mL flask equipped a reflux tube and containing a magnetic stirring bar was dried under vacuum and filled with argon after cooling to room temperature. 3,5-dibromopyridine (1.88 g, 7.95 mmol), 2,6-dimethylphenylboronic acid (2.49 g, 16.7 mmol), $Ba(OH)_2$ (5.45 g, 31.8 mmol), $Pd(PPh_3)_4$ (462 mg, 399 μmol) are added in dry THF (100 mL) and H_2O (10 mL) under argon atmosphere. The mixture was stirred at reflux for 24 h. After the reaction mixture was cooled to room temperature, the reaction mixture was quenched with 50 mL of water, extracted with EtOAc (50 mL × 4), dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (EtOAc/hexane = 1:10) to obtain **1** (1.83 g, 80%) as a white solid. Suitable single crystal for X-ray analysis was obtained from MeOH solution at –30 °C.

^{1}H NMR ($CDCl_3$, 600 MHz) δ 2.09 (s, 12H), 7.14 (d, J = 8 Hz, 4H), 7.21 (t, J = 8 Hz, 2H), 7.33 (t, J = 2 Hz, 1H), 8.43 (d, J = 2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 21.0 (CH_3), 127.5 (CH), 127.8 (CH), 136.2 (4°), 136.3 (4°), 137.5 (CH), 137.7 (4°), 148.4 (CH); mp: 132.9–134.9 °C; Anal. calcd. for $C_{21}H_{21}N$: C 87.76, H 7.36, N 4.87. found: C 87.65, H 7.31, N 4.62.

Synthesis of 3,5-bis(2,6-dimethylphenyl)-1-mesitylpyridinium triflate (3)



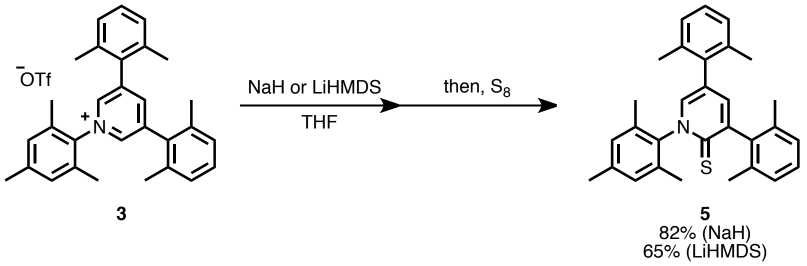
1

3
34%

A mixture of diarylpyridine **1** (574 mg, 2.00 mmol), 1-chloro-2,4-dinitrobenzene (405 mg, 2.00 mmol), and EtOH (3.0 mL) in a 10-mL Schlenk tube equipped a reflux tube and a magnetic stirring bar was stirred at 80 °C for 59 h under air. After the reaction mixture was cooled to room temperature, the reaction mixture was reprecipitated with acetone. The insoluble material was separated with filtration and dried under reduced pressure to obtain as a white solid. The solid was dissolved in $CHCl_3$ (20 mL), and AgOTf (513 mg, 2.00 mmol) was added to the solution. The mixture was stirred at room temperature for 20 min. The residue was filtered off with $CHCl_3$, and the solution was concentrated under reduced pressure. 2,4,6-Trimethylaniline (12 mL) was added to the mixture. The mixture was stirred at 150 °C for 2.5 h. After the reaction mixture was cooled to rt, the mixture was reprecipitated with toluene. Insoluble material was collected. The product was recrystallized with $CHCl_3$/toluene at rt to obtain pyridinium triflate **3**·toluene (446 mg, 34% 3 steps) as a colorless crystal.

^{1}H NMR ($CDCl_3$, 600 MHz) δ 2.14 (s, 6H), 2.17 (s, 12H), 2.38 (s, 3H), 7.13–7.16 (m, 2H), 7.21–7.24 (m, 4H), 7.32 (t, J = 8 Hz, 2H), 8.27 (s, 1H), 8.70 (d, J = 2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 17.3 (CH_3), 21.0 (CH_3), 21.1 (CH_3), 21.4 (CH_3), 120.6 (q, $^1J_{CF}$ = 320 Hz, CF_3), 125.2 (CH), 128.2 (CH), 128.5 (CH), 129.0 (CH), 130.28 (CH), 130.33 (CH), 131.7 (4°), 132.0 (4°), 135.3 (4°), 137.8 (4°), 138.7 (4°), 142.3 (4°), 143.1 (4°), 144.5 (CH), 148.9 (CH); mp: 206.2–208.2 °C; Anal. calcd. for $C_{38}H_{40}NO_3F_3S$: C 70.46, H 6.22, N 2.16. found: C 70.40, H, 6.29, N 1.88.

Synthesis of 3,5-bis(2,6-dimethylphenyl)-1-mesitylpyridine-2-thione (5)



Method A

A 10-mL Schlenk tube equipped reflux tube and containing stirring bar was dried under vacuum and filled with argon after cooling to room temperature. A mixture of pyridinium triflate **3** (32.3 mg, 50.0 μmol) and NaH (12.0 mg, 500 μmol) in dry THF (1.0 mL) was stirred at 50 °C for 1.5 h. After the reaction, the solution of S_8 in toluene (0.1 M, 1.0 mL) was added to the reaction mixture at room temperature. The reaction mixture was filtered and the solution was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (EtOAc/hexane = 1:5) and recrystallized with THF/pentane at room temperature to obtain **5** (17.9 mg, 82%) as a yellow crystal.

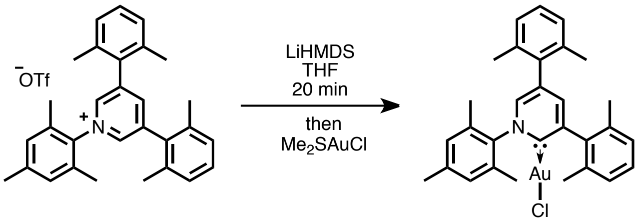
Method B

A 10-mL Schlenk tube equipped reflux tube and containing stirring bar was dried under vacuum and filled with argon after cooling to room temperature. A mixture of pyridinium triflate **3** (11.1 mg, 18.1 μmol) and LiHMDS (1.0 M, 40 μL, 40.0 μmol) in dry THF (1.0 mL) was stirred at room temperature for 20 min. After the reaction, the solution of S_8 in toluene (0.1 M, 0.5 mL) was added to the reaction mixture at room temperature. The reaction mixture was filtered and the solution was concentrated under reduced pressure. The crude product was purified by PTLC (EtOAc/hexane = 1:5) to obtain **5** (4.9 mg, 65%) as a yellow solid.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.15 (s, 6H), 2.21 (s, 6H), 2.23 (s, 6H), 2.32 (s, 3H), 7.00 (s, 2H), 7.10 (d, J = 7 Hz, 2H), 7.14 (d, J = 2 Hz, 1H), 7.17 (dd, J = 8 Hz, 7 Hz, 2H) 7.34

(d, *J* = 2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.9 (CH_3), 19.8 (CH_3), 20.9 (CH_3), 21.2 (CH_3), 125.1 (4°), 127.4 (CH), 127.6 (CH), 127.8 (CH), 128.3 (CH), 129.6 (CH), 133.0 (4°), 135.3 (4°), 135.4 (4°), 136.2 (4°), 137.1 (CH), 138.6 (4°), 138.8 (CH), 139.4 (4°), 141.3 (4°), 146.5 (4°), 178.3 (4°, C=S); HRMS (FAB-MS) *m/z* calcd. for $C_{30}H_{31}NSNa$ $[M+Na]^+$: 460.2075, found: 460.2069; mp: 260.3–262.3 (dec.).

Synthesis of 3,5-bis(2,6-dimethylphenyl)-1-mesitylpyridylidenechlorogold(I) (6)



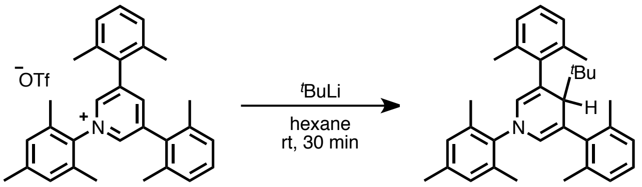
3

6
27%

A 10-mL Schlenk tube containing stirring bar was dried under vacuum and filled with argon after cooling to room temperature. A THF solution of LiHMDS (1.0 M, 115 μL, 115 μmol) was added to the solution of pyridinium triflate **3** (25.0 mg, 38.0 μmol) in dry THF (2.0 mL). The mixture was stirred at room temperature for 20 min. MeS_2AuCl (11.5 mg, 38.0 μmol) was added to the reaction mixture. The reaction solution was filtered and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography ($MeOH/CHCl_3$ = 1:20) and recrystallized with $CHCl_3$/toluene at room temperature to obtain **6**·toluene (6.8 mg, 27%) as a pale yellow crystal.

^1H NMR ($CDCl_3$, 400 MHz) δ 2.09 (s, 6H), 2.13 (brs, 12H), 2.35 (s, 3H), 7.03 (s, 2H), 7.12–7.18 (m, 4H), 7.21–7.27 (m, 2H), 7.71 (d, *J* = 2 Hz, 1H), 7.97 (d, *J* = 2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.6 (CH_3), 20.8 (CH_3), 21.1 (CH_3), 21.2 (CH_3), 125.2 (CH), 127.8 (CH), 128.1 (CH), 128.2 (CH), 128.5 (CH), 129.0 (4°), 129.2 (CH), 129.8 (CH), 131.6 (4°), 134.1 (4°), 135.1 (4°), 135.5 (4°), 135.6 (4°), 137.8 (4°), 139.4 (4°), 139.8 (4°), 140.3 (CH), 140.4 (4°), 144.9 (4°), 151.7 (4°), 189.3 (4°, $C_{carbene}$); mp: 253.4–263.4 °C (dec.); Anal. calcd. for $C_{37}H_{39}NAuCl$: C 60.87, H 5.38, N 1.92. found: C 60.67, H 5.25, N 1.90.

Synthesis of 4-(*tert*-butyl)-3,5-bis(2,6-dimethylphenyl)-1-mesityl-1,4-dihydropyridine (7)



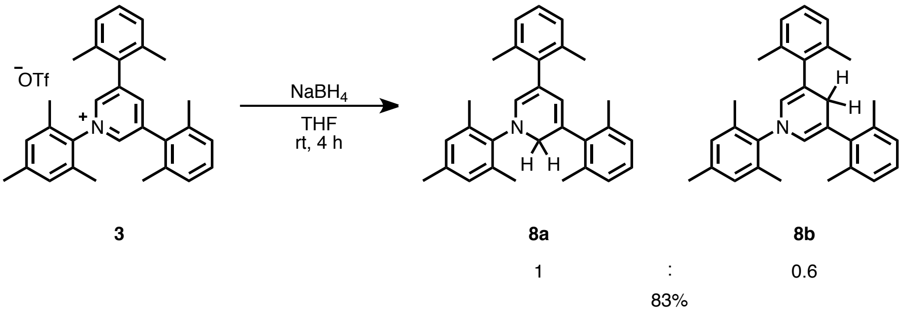
3

7
39%

A 10-mL Schlenk tube containing stirring bar was dried under vacuum and filled with argon after cooling to room temperature. A pentane solution of *t*-BuLi (1.6 M, 190 μL, 304 μmol) was added dropwise to the solution of pyridinium triflate **3** (64.7 mg, 100 μmol) in dry hexane (1.0 mL). The mixture was stirred at room temperature for 30 min. The reaction mixture was concentrated under reduced pressure. The crude product was purified by recrystallization with hexane at –25 °C to obtain **7** (18.0 mg, 39%) as a colorless crystal.

^{1}H NMR ($CDCl_3$, 600 MHz) δ 0.76 (s, 9H), 2.08 (s, 3H), 2.27 (s, 3H), 2.44 (s, 3H), 2.57 (s, 6H), 2.63 (s, 6H), 3.73 (s, 1H), 6.00 (s, 2H), 6.83 (s, 1H), 6.93 (s, 1H), 6.99–7.06 (m, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 17.5 (CH_3), 18.5 (CH_3), 20.9 (CH_3), 22.1 (CH_3), 22.4 (CH_3), 29.2 (CH_3), 40.6 (4°), 51.0 (CH), 109.9 (4°), 125.0 (CH), 127.8 (CH), 128.8 (CH), 129.4 (CH), 133.9 (CH), 135.7 (4°), 136.4 (4°), 136.6 (4°), 136.9 (4°), 137.2 (4°), 140.7 (4°), 144.2 (4°); HRMS (DART-MS); *m*/*z* calcd. for $C_{34}H_{42}N$ $[M+H]^+$: 464.3317, found: 464.3319; mp: 214.5–216.5 °C (dec.).

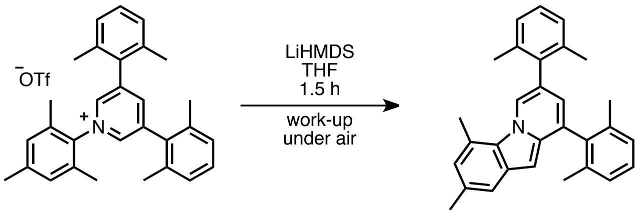
Synthesis of 3,5-bis(2,6-dimethylphenyl)-1-mesityl-1,2-dihydropyridine (8a) and 3,5-bis(2,6-dimethylphenyl)-1-mesityl-1,4-dihydropyridine (8b)



A 30-mL screw-capped vial containing stirring bar was dried and filled with argon after cooling to room temperature. $NaBH_4$ (8.0 mg, 0.21 mmol) was added to the solution of pyridinium triflate **3** (33.4 mg, 51.6 μmol) in dry THF (0.5 mL). The mixture was stirred at room temperature for 4 h. The reaction mixture was treated in glove box filled with argon and was concentrated under reduced pressure. The crude product was filtered with hexane and recrystallized with dry hexane at –30 °C to obtain **8a** and **8b** as a mixture (17.4 mg, 83%, **8a**/**8b** = 1:0.6) as a colorless crystal.

^{1}H NMR (benzene-d_6, 600 MHz) δ **8a**: 2.11 (s, 3H), 2.25 (s, 6H), 2.35 (s, 6H), 2.41 (s, 6H), 4.10 (d, *J* = 1 Hz, 2H), 5.42 (d, *J* = 1 Hz, 1H), 5.44 (dt, *J* = 1 Hz, 1 Hz, 1H), 6.71 (d, *J* = 1 Hz, 2H), 6.98–7.15 (m, 8H); **8b**: 2.11 (s, 3H), 2.21 (s, 6H), 2.42 (s, 12H), 3.14 (t, *J* = 1 Hz, 2H), 5.19 (t, *J* = 1 Hz, 2H), 6.69 (d, *J* = 1 Hz, 2H), 6.98–7.15 (m, 8H); ^{13}C NMR (benzene-d_6, 150 MHz) δ 18.1 (CH_3), 18.6 (CH_3), 20.0 (CH_3), 20.3 (CH_3), 21.0 (CH_3), 21.0 (CH_3), 21.3 (CH_3), 31.9 (CH_2), 52.5 (CH_2), 107.2 (4°), 107.9 (4°), 123.0 (4°), 126.4 (CH), 126.6 (CH), 126.8 (CH), 127.1 (CH), 127.7 (CH), 127.8 (CH), 127.8 (CH), 128.0 (4°), 128.1 (4°), 128.3 (4°), 128.5 (4°), 129.3 (CH), 129.7 (CH), 133.5 (CH), 136.3 (4°), 136.5 (4°), 136.6 (4°), 136.8 (4°), 136.9 (4°), 137.2 (4°), 137.9 (4°), 140.2 (4°), 140.8 (4°), 141.0 (4°), 141.1 (4°), 142.5 (4°); HRMS (FAB-MS) *m*/*z* calcd. for $C_{30}H_{32}N$ $[M–H]^+$: 406.2535, found: 406.2527.

Synthesis of 7,9-bis(2,6-dimethylphenyl)-2,4-dimethylpyrido[1,2-*a*]indole (9)



3

9
22%

A 10-mL Schlenk tube containing stirring bar was dried under vacuum and filled with argon after cooling to room temperature. LiHMDS (8.3 mg, 50 μmol) was added to the solution of pyridinium triflate **3** (32.3 mg, 50.0 μmol) in dry THF (1.0 mL). The mixture was stirred at room temperature for 1.5 h. The reaction mixture was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (EtOAc/hexane = 1:5) and recrystallized with EtOH (slow evapolation) to obtain pyrido[1,2-*a*]indole **9** (4.5 mg, 22%) as a yellow crystal.

^{1}H NMR ($CDCl_3$, 600 MHz) δ 2.15 (s, 6H), 2.25 (s, 6H), 2.46 (s, 3H), 2.87 (s, 3H), 6.15 (brs, 1H), 6.51 (d, J = 2 Hz, 1H), 6.86 (s, 1H), 7.17 (d, J = 7 Hz, 4H), 7.21 (dd, J = 7 Hz, 8 Hz, 1H), 7.24 (dd, J = 7 Hz, 8 Hz, 1H), 7.34 (s, 1H), 8.51 (s, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 19.8 (CH_3), 21.0 (CH_3), 21.4 (CH_3), 21.5 (CH_3), 92.0 (CH), 117.7 (CH), 120.0 (4°), 122.9 (4°), 123.7 (CH), 124.4 (CH), 124.5 (CH), 127.41 (CH), 127.49 (CH), 127.57 (CH), 127.61 (CH), 127.7 (4°), 130.4 (4°), 131.5 (4°), 132.0 (4°), 135.7 (4°), 136.7 (4°), 137.3 (4°), 137.6 (4°), 138.4 (4°); HRMS (FAB-MS) *m/z* calcd. for $C_{30}H_{29}N$ $[M]^+$: 403.2300, found: 403.2322; mp: 254.4–256.4 °C (dec.).

NMR yield of **9** by the reaction of **3** with KH was determined as follows. A 10-mL Schlenk tube equipped reflux tube and containing stirring bar was dried under vacuum and filled with argon after cooling to room temperature. A mixture of **3** (50.0 mg, 77.2 μmol) and KH (34.0 mg, 771 μmol) in dry THF (0.77 mL) was stirred at room temperature for 12 h. The reaction mixture was concentrated under reduced pressure to observed **9** (7%). CH_2Cl_4 (4.2 mg, 25.0 μmol) was added as an internal standard. ^{1}H NMR of the resulting mixture was measured with $CDCl_3$ as a solvent.

2. X-ray Crystallography

Details of the crystal data and a summary of the intensity data collection parameters for **1**, **3**·toluene, **5**, **6**·toluene, **7**, and **9** are listed in Table S1. In each case, a suitable crystal was mounted with mineral oil on a glass fiber and transferred to the goniometer of a Rigaku Saturn CCD diffractometer. Graphite-monochromated Mo Kα radiation ($\lambda = 0.71070$ Å) was used. The structures were solved by direct methods with (SIR-97)[S1] and refined by full-matrix least-squares techniques against F^2 (SHELXL-97).[S2] The intensities were corrected for Lorentz and polarization effects. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using AFIX instructions.

Table S1. Crystallographic data and refinement details for **1**, **3**·toluene, **5**, **6**·toluene, **7**, and **9.**

	1	**3**·toluene	**5**	**6**·toluene	**7**	**9**
formula	$C_{21}H_{21}N$	$C_{38}H_{40}F_3NO_3S$	$C_{30}H_{31}NS$	$C_{37}H_{39}AuClN$	$C_{34}H_{41}N$	$C_{30}H_{29}N$
fw	287.39	647.77	437.62	730.11	463.68	403.54
T (K)	123(2)	123(2)	123(2)	103(2)	123(2)	123(2)
λ (Å)	0.71070	0.71070	0.71070	0.71070	0.71070	0.71070
cryst syst	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/n$	P-1	P-1
a, (Å)	13.283(3)	14.1166(19)	11.751(4)	13.600(2)	9.355(4)	11.727(3)
b, (Å)	8.3330(14)	17.674(2)	19.429(6)	16.635(3)	13.050(5)	12.934(3)
c, (Å)	15.160(3)	14.3488(19)	22.402(7)	14.925(3)	13.097(4)	15.910(4)
α, (deg)	90	90	90	90	62.601(11)	98.919(2)
β, (deg)	101.272(2)	107.5846(18)	97.269(6)	111.5120(18)	79.653(16)	105.428(5)
γ, (deg)	90	90	90	90	89.316(18)	93.867
V, (Å^3)	1645.6(5)	3412.8(8)	5074(3)	3141.3(9)	1391.9(9)	2283.2(9)
Z	4	4	8	4	2	4
D_{calc}, (g / cm^3)	1.160	1.261	1.146	1.544	1.106	1.174
μ (mm^{-1})	0.067	0.148	0.144	4.794	0.063	0.067
F(000)	616	1368	1872	1456	1504	864
cryst size (mm)	0.15 × 0.15 × 0.10	0.20 × 0.15 × 0.15	0.10 × 0.10 × 0.02	0.05 × 0.05 × 0.05	0.20 × 0.10 × 0.10	0.15 × 0.03 × 0.01
2θ range, (deg)	3.08-25.00	3.03-25.00	3.16-25.00	3.00-25.00	3.04-25.00	3.08-25.00
reflns collected	10602	22492	33370	40677	9281	15506
indep reflns/R_{int}	2878/0.0288	5977/0.0338	8903/0.0760	5529/0.0441	4791/0.0392	7886/0.0618
params	203	423	591	370	326	571
GOF on F^2	1.045	1.067	1.088	1.139	0.968	1.062
R_1, wR_2 [I>2σ(I)]	0.0414, 0.0988	0.0435, 0.1028	0.1084, 0.2705	0.0421, 0.0882	0.0489, 0.1227	0.0770, 0.1595
R_1, wR_2 (all data)	0.0495, 0.1040	0.0503, 0.1081	0.1590, 0.3154	0.0477, 0.0913	0.0706, 0.1361	0.1384, 0.1913

[S1] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.*, 1999, **32,** 115–119.

[S2] G. M. Sheldrick, University of Göttingen: Göttingen, Germany, 1997.

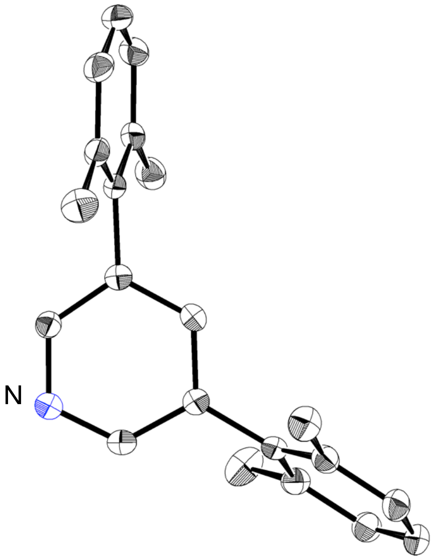


Figure S1. ORTEP drawing of **1** with 50% thermal ellipsoid. All hydrogen atoms and toluene molecule are omitted for clarity.

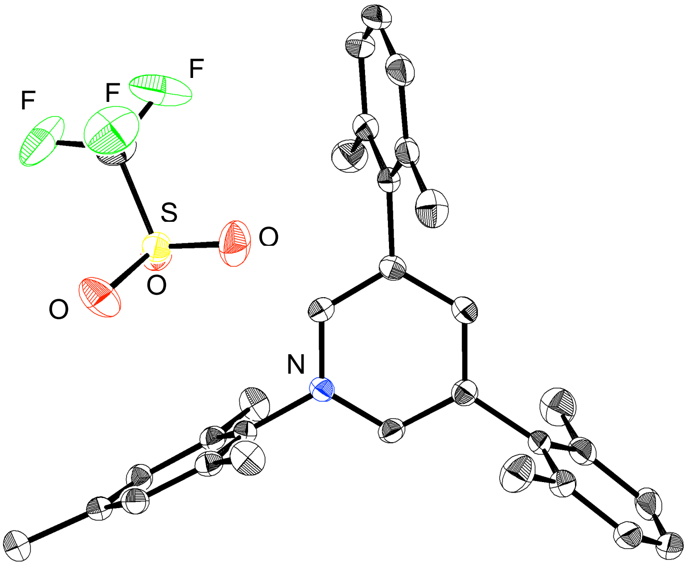


Figure S2. ORTEP drawing of **3** with 50% thermal ellipsoid. All hydrogen atoms and toluene molecule are omitted for clarity.

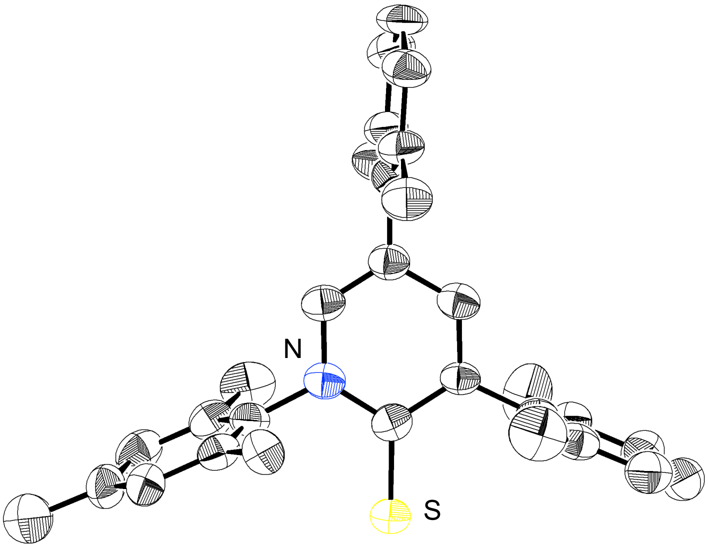


Figure S3. ORTEP drawing of **5** with 50% thermal ellipsoid. All hydrogen atoms are omitted for clarity.

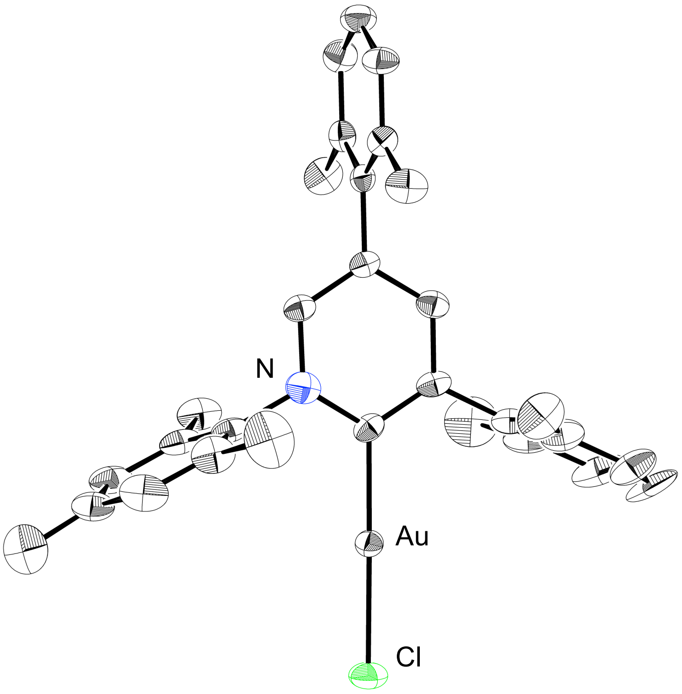


Figure S4. ORTEP drawing of **6** with 50% thermal ellipsoid. All hydrogen atoms and toluene molecule are omitted for clarity.

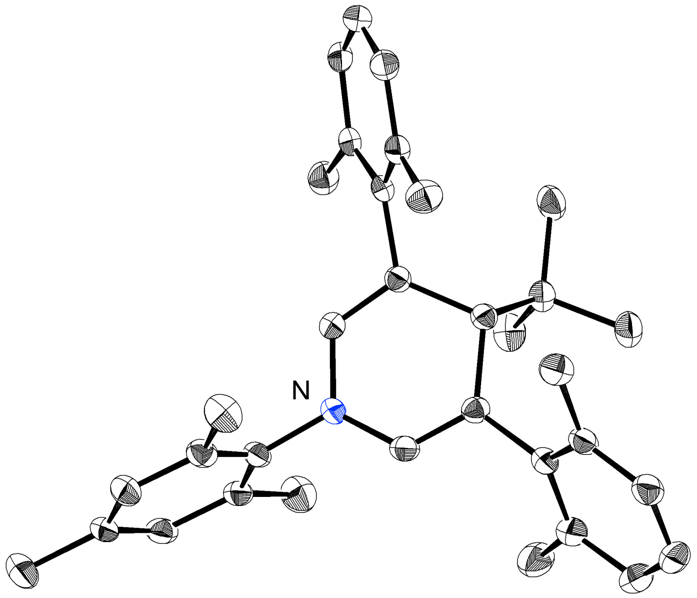


Figure S5. ORTEP drawing of **7** with 50% thermal ellipsoid. All hydrogen atoms are omitted for clarity.

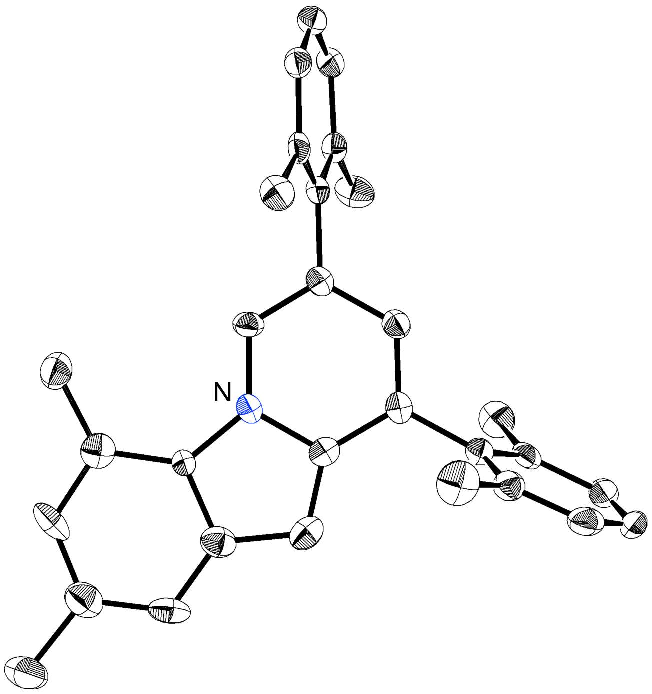


Figure S6. ORTEP drawing of **9** with 50% thermal ellipsoid. All hydrogen atoms are omitted for clarity.

3. Computational Study

The Gaussian 09 program[S3] running on a SGI Altix4700 system was used for optimization (B3LYP/6-31+G(d)). All structures were optimized without any symmetry assumptions. Zero-point energy, enthalpy, and Gibbs free energy at 298.15 K and 1 atm were estimated from the gas-phase studies. Harmonic vibration frequency calculation at the same level was performed to verify all stationary points as local minima (with no imaginary frequency). Visualization of the results was performed by use of GaussView 5.0.

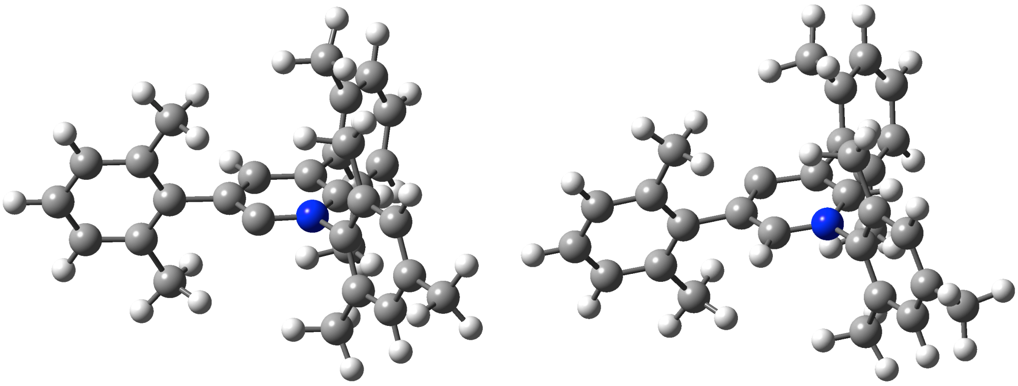


Figure S7. Optimized structures of 2-pyridylidene **4** (left) and 4-pyridylidene **4'** (right).

Table S2. Uncorrected and thermal-corrected energies of stationary points (Hartree).[a]

compound	*E*	*E* + *ZPE*	*H*	*G*
4	-1216.61973919	-1216.096649	-1216.064916	-1216.161509
4'	-1216.59836160	-1216.075584	-1216.043714	-1216.141343

a) *E*: electronic energy; *ZPE*: zero-point energy; *H* (= $E + ZPE + E_{vib} + E_{rot} + E_{trans} + RT$): sum of electronic and themal enthalpies; *G* (= $H - TS$): sum of electronic and thermal free energies.

---

[3] (Full reference of ref 12a) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, *Gaussian 09, Revision A.02*, Gaussian, Inc., Wallingford CT, 2009.

Table S3. Cartesian coordinates for optimized compounds.

Optimized structure of **4**

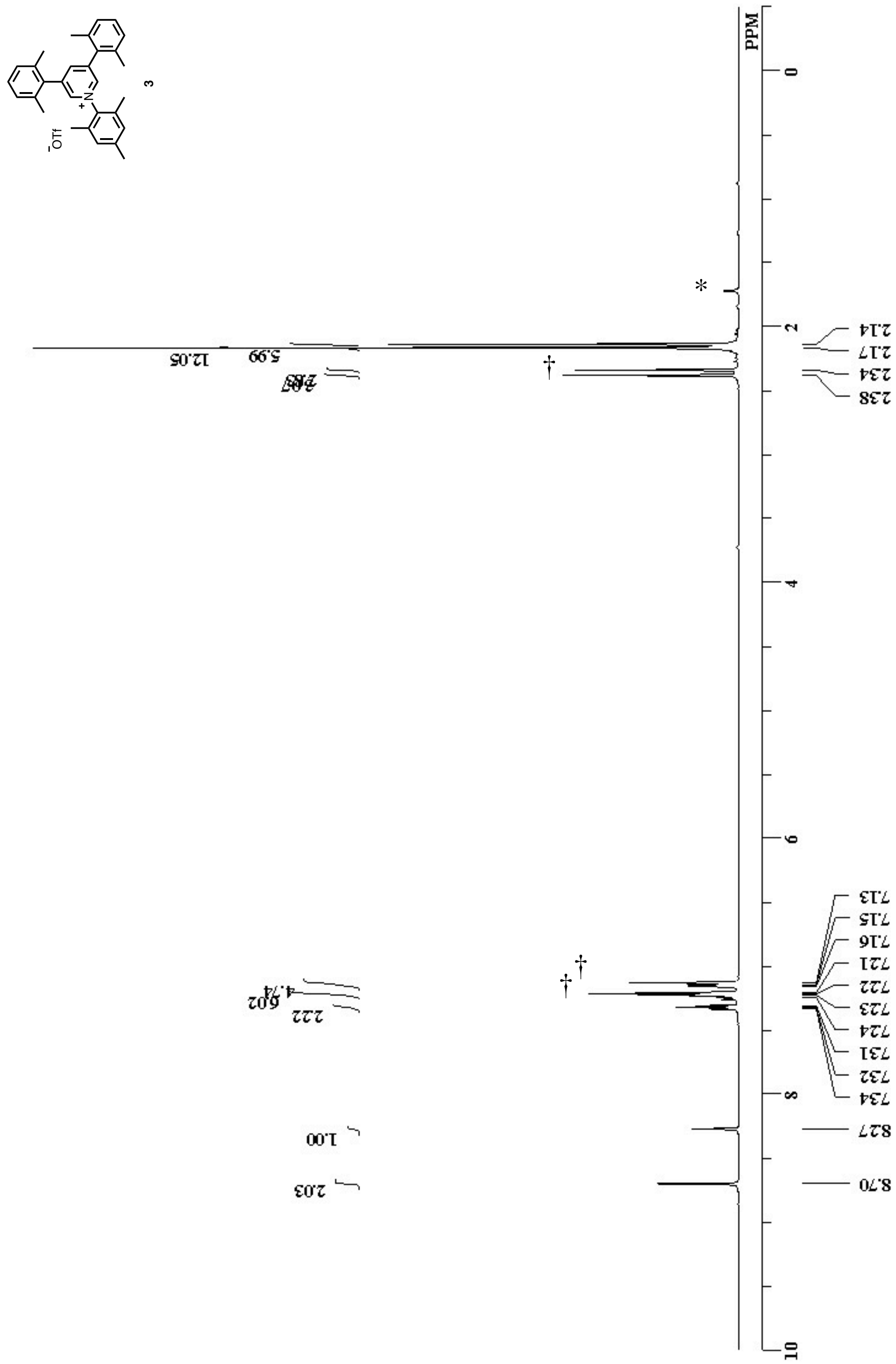
C	0.441010	-1.328289	-0.013784
C	-0.985989	-1.191178	-0.005421
C	-1.619355	0.045846	0.014964
C	-0.875807	1.249517	0.025656
C	0.495145	1.124285	0.011892
H	-2.707593	0.107178	0.022628
H	1.164328	1.979304	0.017737
C	2.541362	-0.143858	-0.021616
C	3.233275	-0.098115	1.196995
C	3.206261	-0.222726	-1.254866
C	4.633271	-0.120158	1.155608
C	4.605481	-0.241312	-1.242473
C	5.338048	-0.191905	-0.050420
H	5.184041	-0.085794	2.093877
H	5.135122	-0.302379	-2.191699
C	-1.814553	-2.444271	-0.024574
C	-2.422264	-2.871196	-1.225348
C	-1.977283	-3.195583	1.159913
C	-3.195440	-4.040311	-1.220810
C	-2.760871	-4.356355	1.128762
C	-3.370285	-4.779573	-0.051945
H	-3.658206	-4.374201	-2.147240
H	-2.888849	-4.934366	2.041663
H	-3.973441	-5.684349	-0.062279
C	-1.535478	2.594346	0.055241
C	-1.973307	3.131016	1.287022
C	-1.730092	3.309886	-1.147299
C	-2.598409	4.385020	1.296480
C	-2.359964	4.560855	-1.097491
C	-2.791786	5.098384	0.114177
H	-2.935394	4.802759	2.242493
H	-2.514204	5.114372	-2.021018
H	-3.279463	6.069839	0.136867
N	1.082756	-0.115827	-0.007688
C	2.444635	-0.317917	-2.555067
H	1.827267	-1.223997	-2.574417
H	1.769344	0.534105	-2.701725
H	3.133495	-0.350289	-3.404902
C	2.502675	-0.055980	2.518345
H	1.883755	0.844319	2.620329
H	1.834278	-0.918693	2.623056
H	3.211909	-0.068262	3.351721
C	-1.313562	-2.772127	2.451275
H	-0.222255	-2.762165	2.344157
H	-1.614819	-1.760916	2.753019
H	-1.573185	-3.457013	3.265516
C	-2.232771	-2.108171	-2.519538
H	-2.702969	-1.116947	-2.488408
H	-1.169923	-1.950407	-2.737997
H	-2.673881	-2.655665	-3.359118
C	-1.277346	2.751903	-2.479855
H	-0.184758	2.669118	-2.537456
H	-1.679559	1.747970	-2.659127
H	-1.604140	3.397947	-3.300948
C	-1.775135	2.382407	2.587645
H	-2.292200	1.415346	2.585465
H	-0.715642	2.172122	2.778085
H	-2.158515	2.964433	3.431738
C	6.849096	-0.247583	-0.067933
H	7.205056	-1.282403	-0.162887
H	7.261866	0.316307	-0.912338
H	7.275879	0.162378	0.853817

Optimized structure of **4'**

C	1.009078	1.196419	-0.016774
C	1.798574	0.003184	-0.000479
C	1.013159	-1.192712	0.017252
C	-0.372459	-1.179525	0.016495
H	-0.993103	-2.072049	0.026962
C	-2.511659	-0.004045	0.002562
C	-3.188043	-0.091960	1.229484
C	-3.189248	0.077224	-1.226307
C	-4.588627	-0.094945	1.200252
C	-4.587924	0.069205	-1.197765
C	-5.305829	-0.013225	0.002113
H	-5.129874	-0.164095	2.141572
H	-5.129594	0.127134	-2.139951
C	1.681172	2.542677	-0.038670
C	2.212430	3.036979	-1.249847
C	1.802860	3.294349	1.149776
C	2.841702	4.288481	-1.257450
C	2.442105	4.541169	1.106468
C	2.955722	5.041611	-0.089044
H	3.251260	4.670259	-2.190405
H	2.543025	5.118483	2.023280
H	3.450303	6.009898	-0.108589
C	1.689715	-2.536755	0.037793
C	2.226008	-3.028842	1.247656
C	1.810378	-3.288587	-1.150668
C	2.859064	-4.278439	1.254043
C	2.453579	-4.533414	-1.108618
C	2.972058	-5.031767	0.085662
H	3.272410	-4.658541	2.186009
H	2.553708	-5.110816	-2.025463
H	3.469640	-5.998533	0.104234
N	-1.059358	-0.001613	0.001982
C	-2.445741	0.168840	-2.539095
H	-1.868061	1.097979	-2.614586
H	-1.736039	-0.656807	-2.664770
H	-3.146206	0.142526	-3.378934
C	-2.445893	-0.186042	2.542866
H	-1.872686	-1.117916	2.619632
H	-1.732522	0.636382	2.668322
H	-3.146805	-0.155822	3.382203
C	1.286471	2.765377	2.471405
H	0.191046	2.689150	2.488634
H	1.680042	1.763437	2.679139
H	1.581798	3.424668	3.294477
C	2.127033	2.228945	-2.525347
H	2.622585	1.258458	-2.403694
H	1.087032	2.022991	-2.810968
H	2.602909	2.760439	-3.356364
C	1.288753	-2.761835	-2.471138
H	0.192979	-2.690162	-2.485867
H	1.677698	-1.758309	-2.679889
H	1.584868	-3.419998	-3.294829
C	2.141972	-2.220379	2.522965
H	2.635580	-1.249099	2.399691
H	1.102261	-2.016022	2.810719
H	2.620614	-2.750638	3.353183
C	-0.376483	1.178623	-0.013679
H	-1.000171	2.069033	-0.023179
C	-6.817213	0.006988	-0.001684
H	-7.225272	-0.357318	0.946699
H	-7.196585	1.026005	-0.155167
H	-7.223615	-0.615028	-0.807331

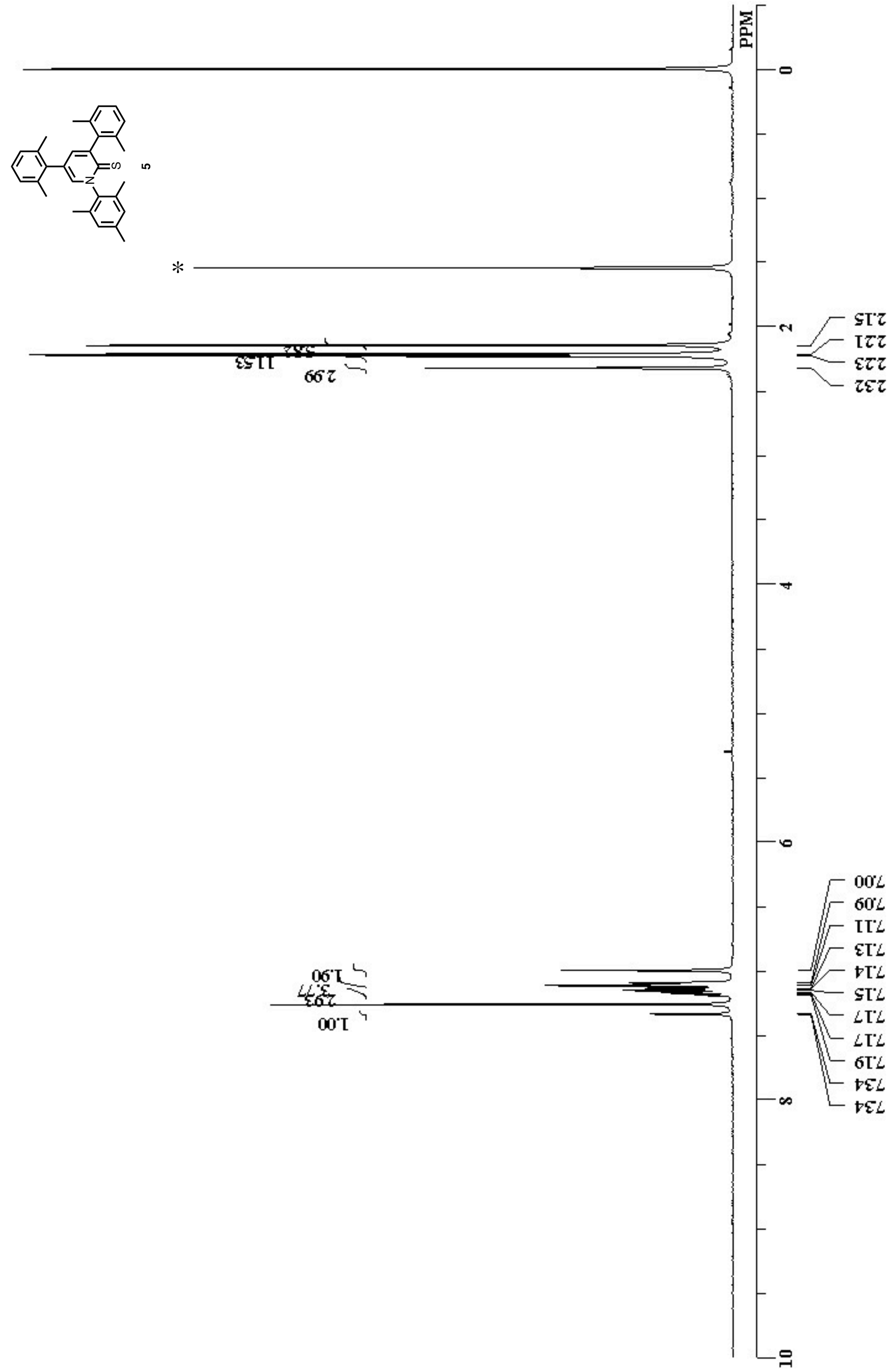
4. ^{1}H and ^{13}C NMR Spectra

^{1}H NMR spectrum of **3**·toluene (600 MHz, $CDCl_3$)



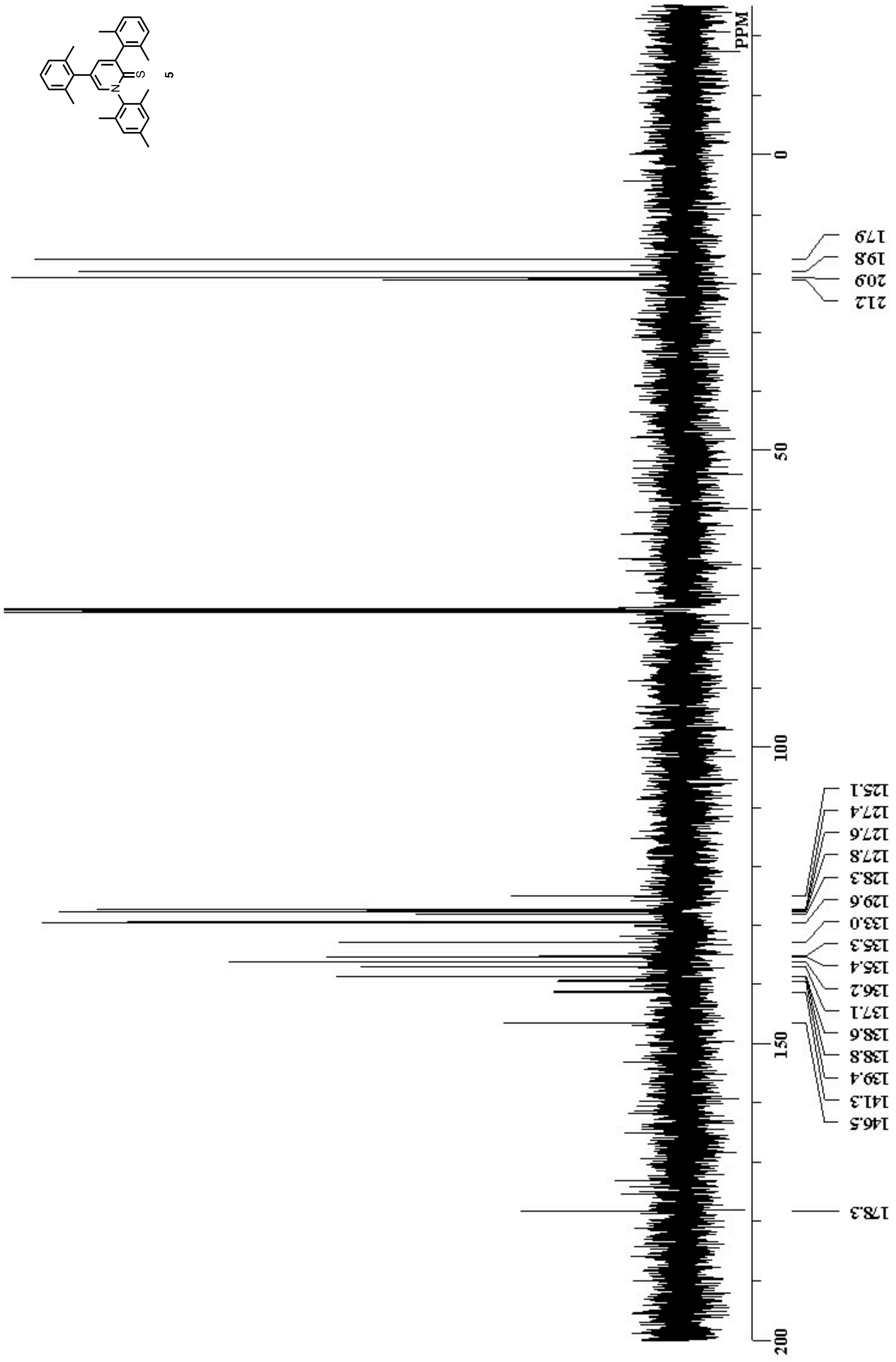
*: H_2O, †: toluene

^{1}H NMR spectrum of **5** (400 MHz, $CDCl_3$)

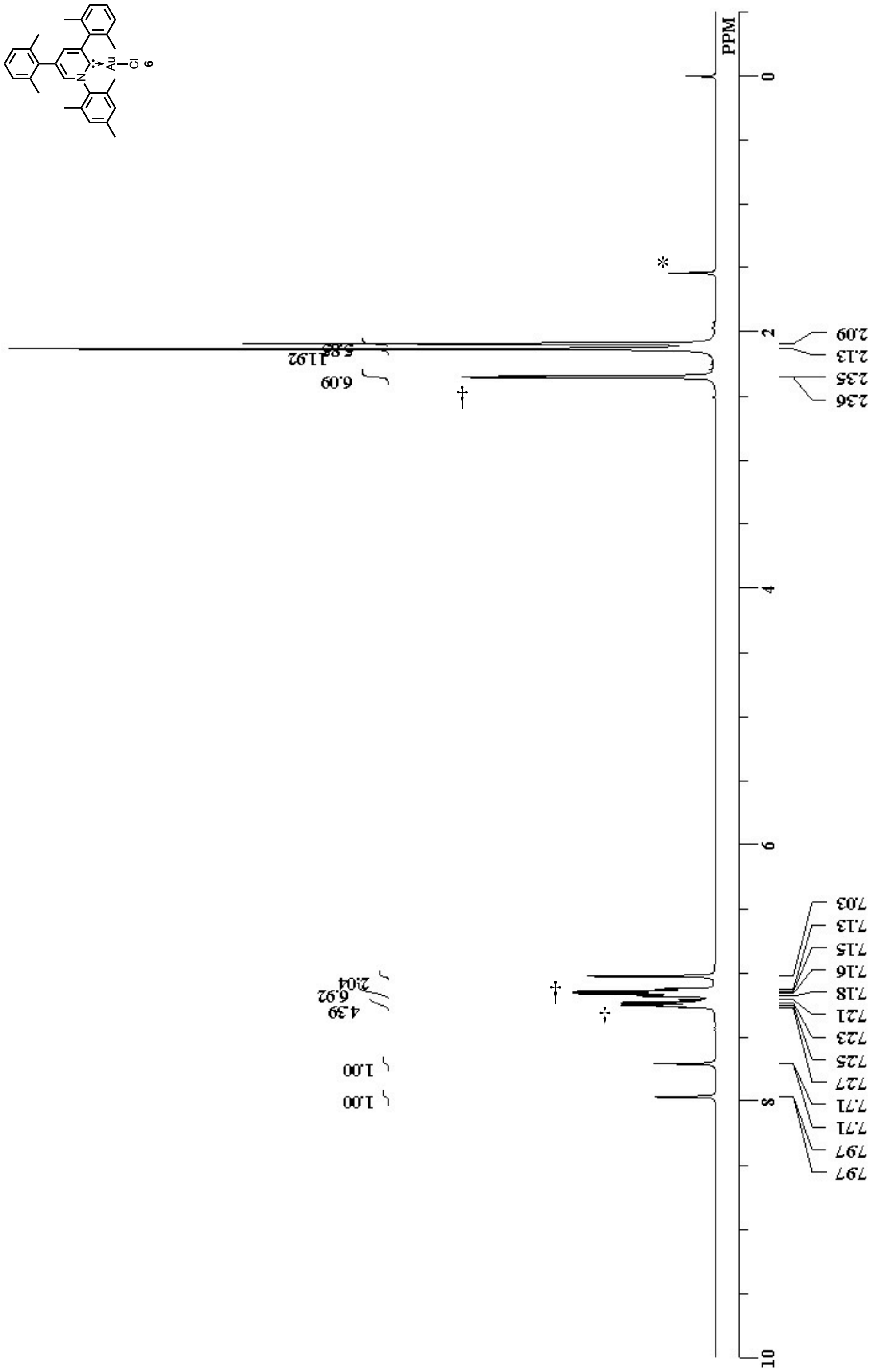


*: H_2O

^{13}C NMR spectrum of **5** (100 MHz, CDCl$_3$)

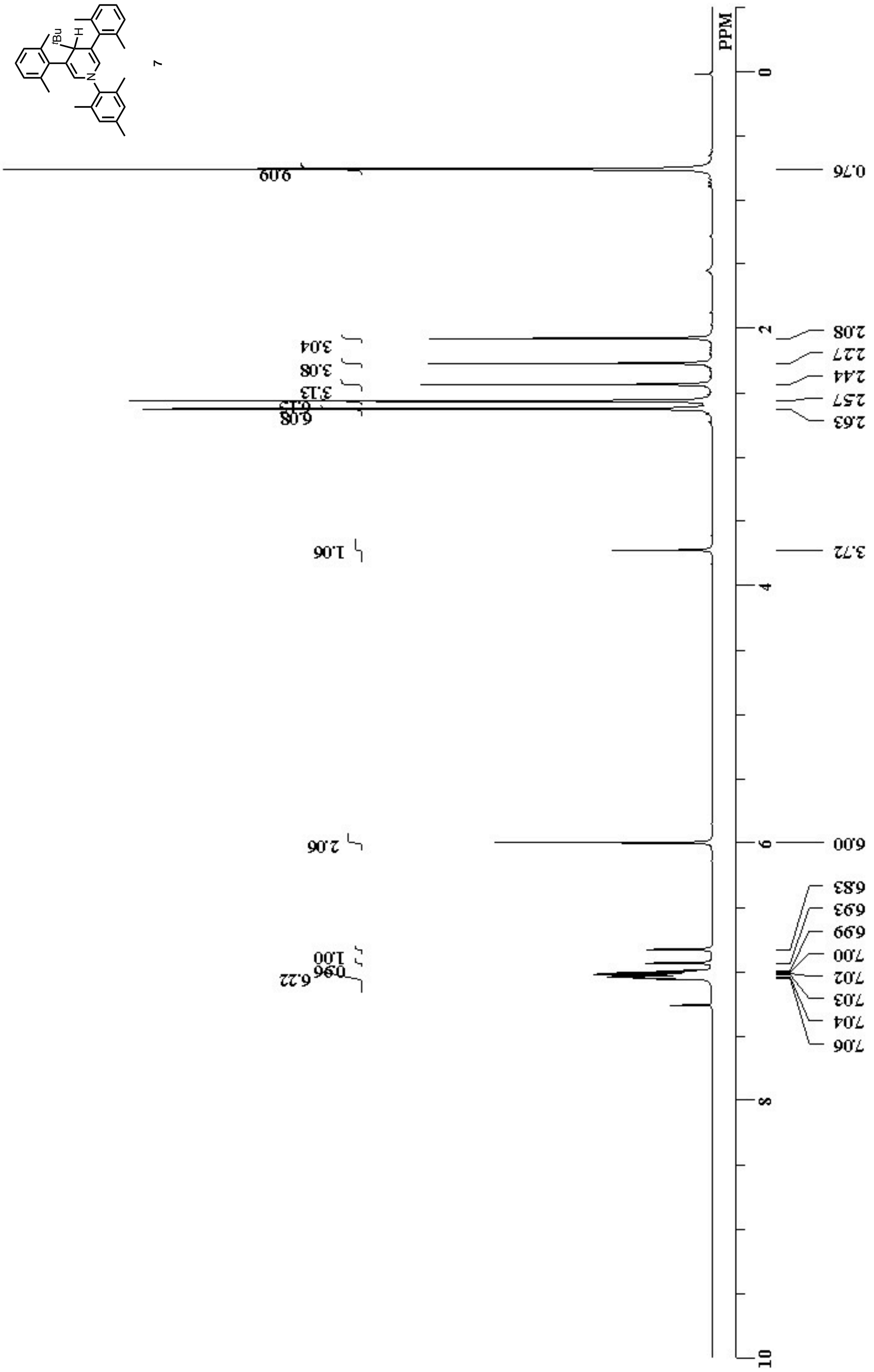


^{1}H NMR spectrum of single crystal of **6**·toluene (400 MHz, $CDCl_3$)

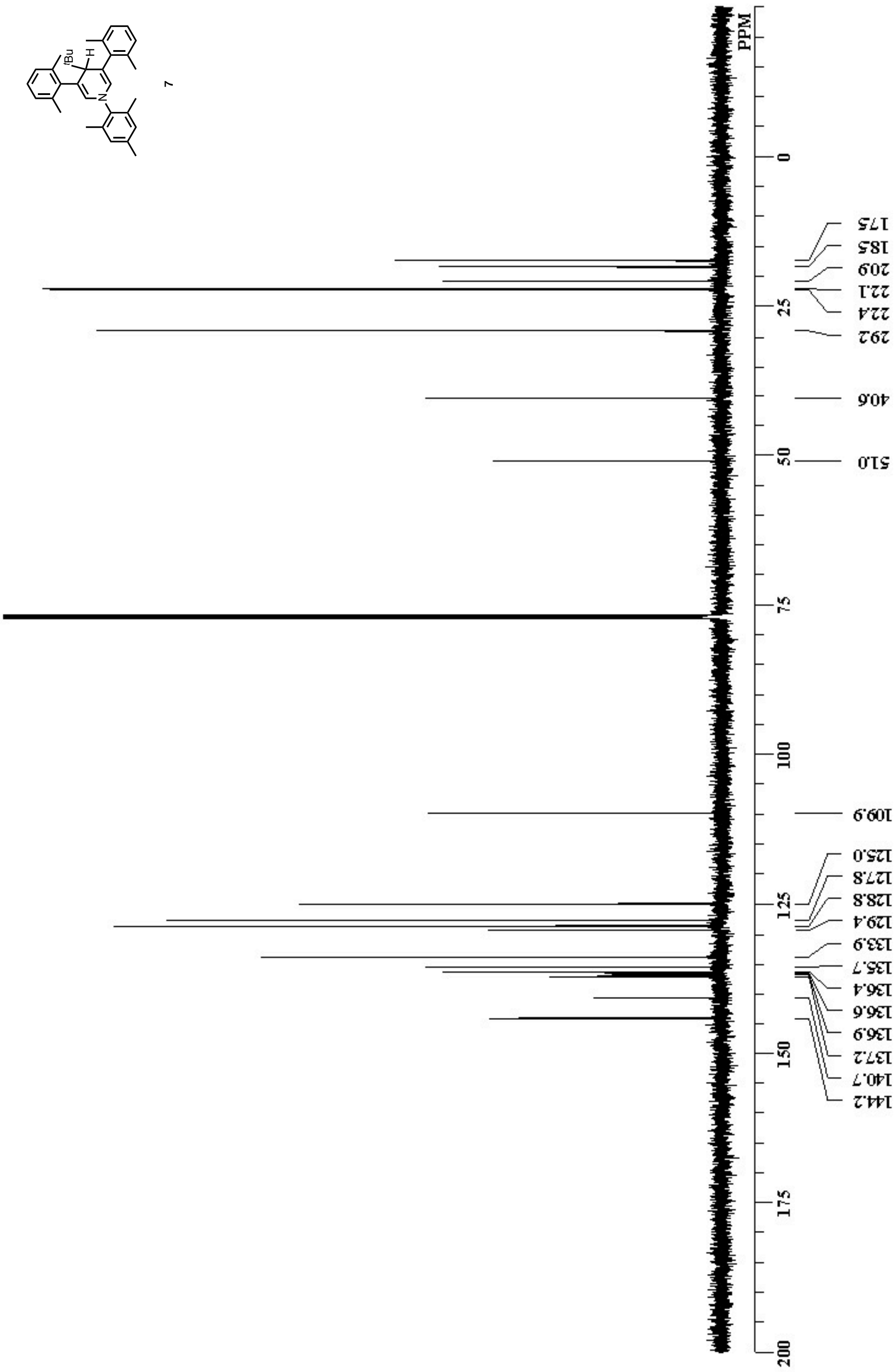


*: H_2O, †: toluene

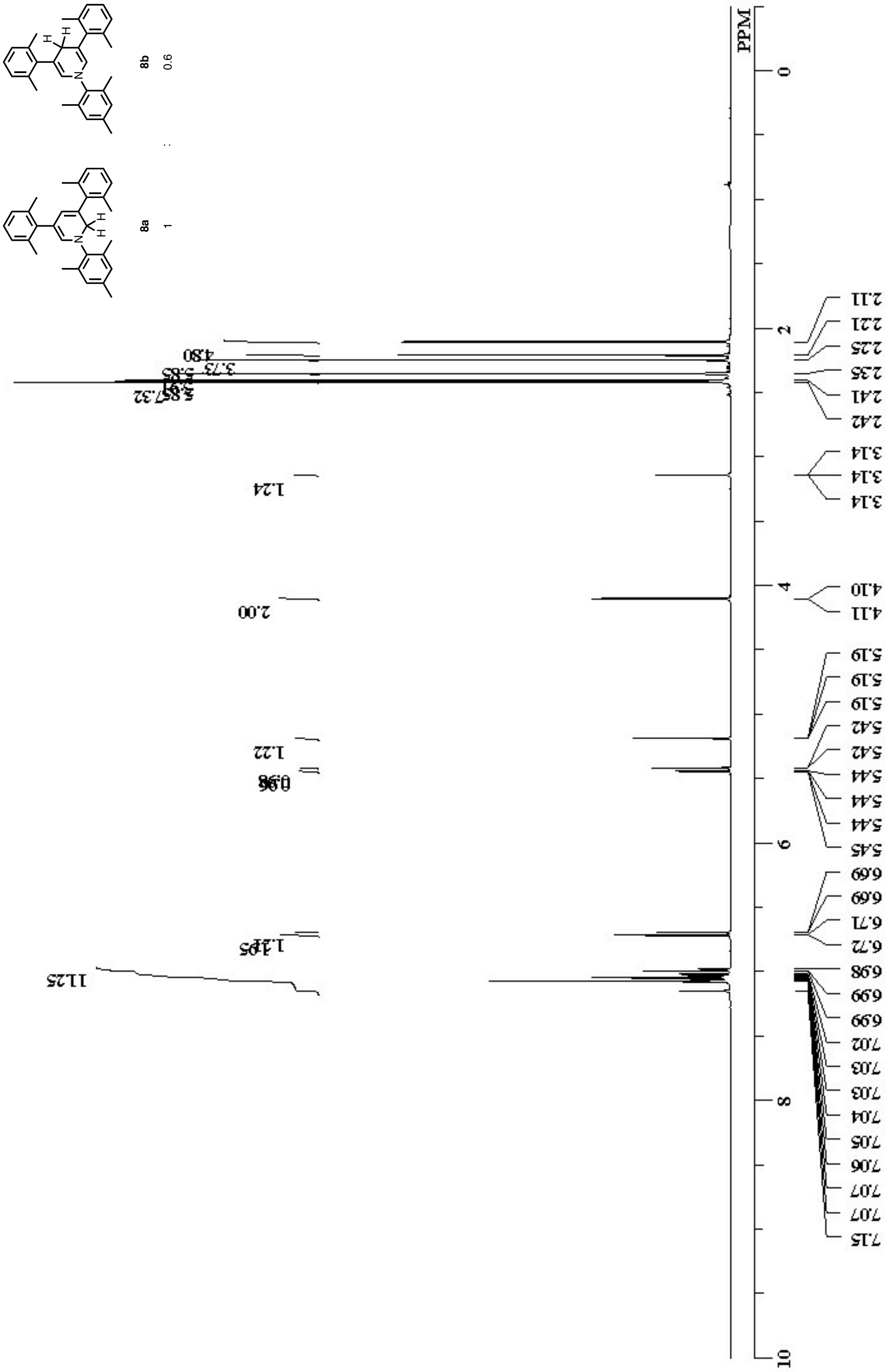
^{1}H NMR spectrum of **7** (600 MHz, CDCl$_3$)



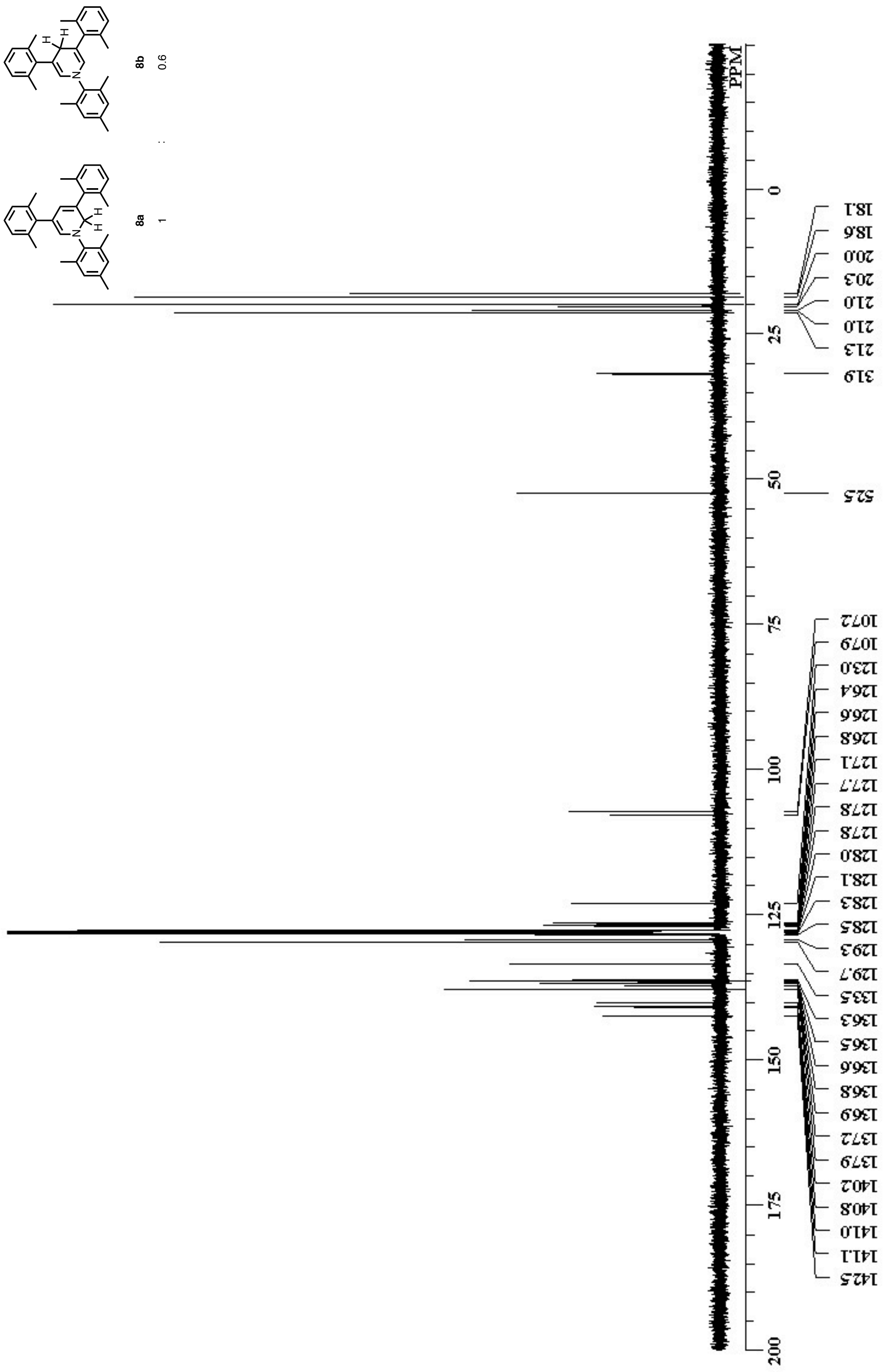
^{13}C NMR spectrum of **7** (150 MHz, CDCl$_3$)



^{1}H NMR spectrum of **8a** + **8b** (600 MHz, benzene-d_6)

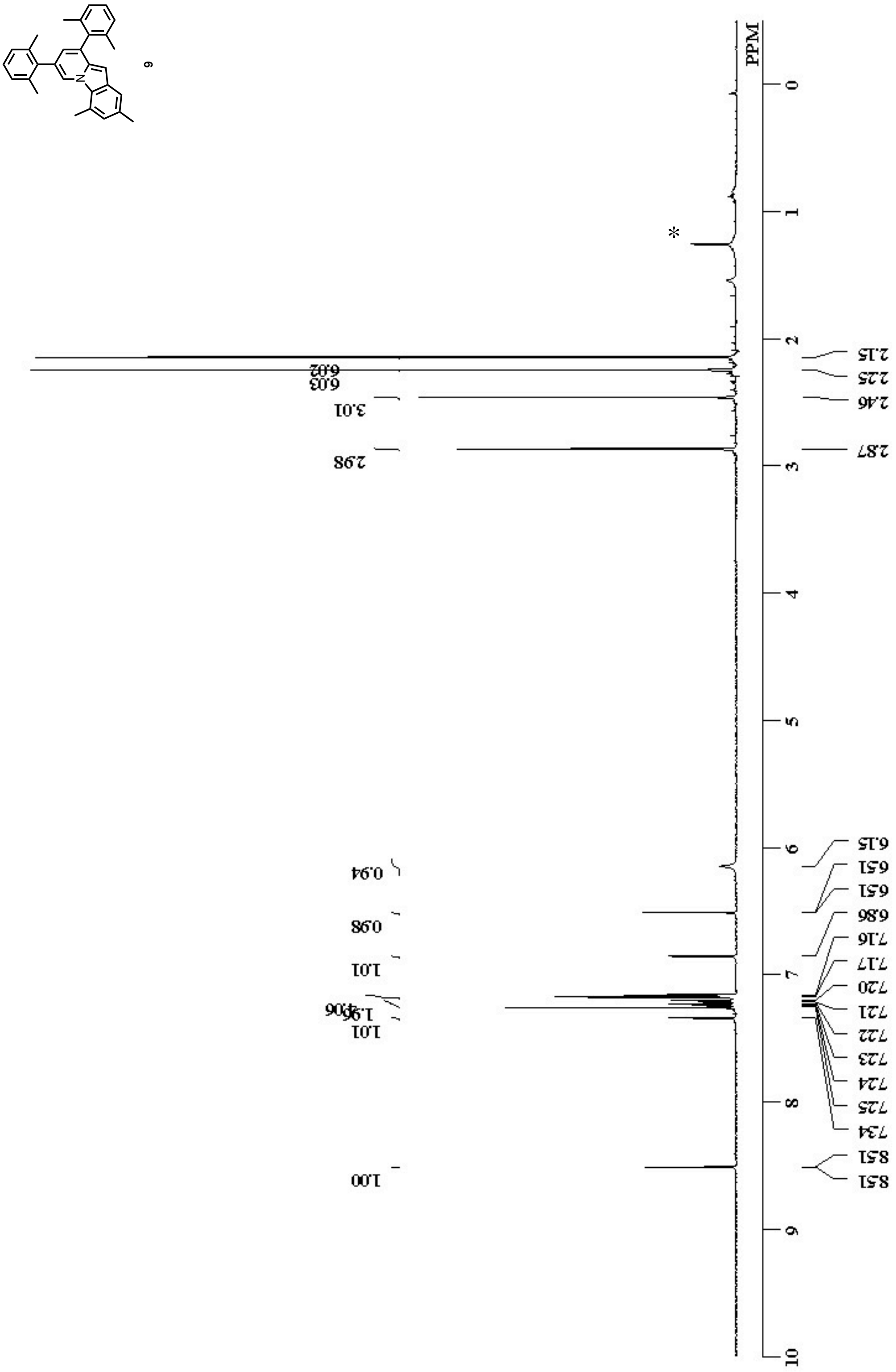


^{13}C NMR spectrum of **8a** + **8b** (150 MHz, benzene-d_6)



^{1}H NMR spectrum of **9** (600 MHz, $CDCl_3$)

9



*: H_2O

^{13}C NMR spectrum of **9** (150 MHz, $CDCl_3$)