Supporting Information

for

Metathesis Cleavage of an N=N Bond in Benzo[*c*]cinnolines and Azobenzenes by Triply-bonded Ditungsten Complexes

Hideaki Ikeda, Kohei Nishi, Hayato Tsurugi* and Kazushi Mashima*

Department of Chemistry, Graduate School of Engineering Science,

Osaka University, Toyonaka, Osaka 560-8531, Japan

E-mail: mashima@chem.es.osaka-u.ac.jp; tsurugi@chem.es.osaka-u.ac.jp

Contents:

1. General information for experimental details

General procedures

All manipulations involving air- and moisture-sensitive organometallic compounds were carried out under argon using the standard Schlenk technique or argon-filled glovebox. Hexane, THF, and toluene were dried and deoxygenated by using Grubbs column (Glass Counter Solvent Dispending System, Nikko Hansen & Co., Ltd.). Benzene-d_6, THF-d_8, and benzene were distilled over CaH_2 and thoroughly degassed by trap-to-trap distillation before use. Azobenzene, benzo[*c*]cinnoline, and trimethylsilyl trifluoromethanesulfonate were purchased and used as recieved. $W_2(O^tBu)_6$ (**1**),[1] $W_2(NMe_2)_6$ (**5**),[1] $W_2(NMe_2)_4(OTf)_2$ (**6**),[2] 4,4’-dimethylazobenzene,[3] and 4,4’-difluoroazobenzene[3] were prepared according to the literature procedures. 3,8-Disubstituted benzo[*c*]cinnolines were prepared by deoxygenative N=N bond formation from the corresponding 2,2’-dinitrobiaryl derivatives.

Physical measurement

^1H NMR (400 MHz) and $^{13}C\{^1H\}$ NMR (100 MHz) spectra were measured on BRUKER AVANCEIII-400 spectrometers. ^1H and $^{13}C\{^1H\}$ NMR Chemical shifts were reported in ppm and referenced to residual proton signal of the solvent (^1H, benzene-d_6 at δ 7.16) or the solvent itself ($^{13}C\{^1H\}$, benzene-d_6 at δ 128.06). High resolution mass spectra were recorded on a JEOL JMS-700. GC-MS analysis were performed with Shimadzu GCMS-QP505A spectrometer with Shimadzu GC-17A GC equipped with J&W Scientific DB-1 column. IR spectra were recorded on JASCO FT/IR-410 and JASCO FT/IR-4000. The elemental analyses were recorded by using Perkin Elmer 2400 at the Faculty of Engineering Science, Osaka University. All melting points were measured in sealed tubes under argon atmosphere.

2. Syntheses of complexes **2—4** and **7—9**

Synthesis of complex 2

To a solution of $W_2(O^tBu)_6$ (200 mg, 0.248 mmol) in benzene (3.0 mL) was added benzo[*c*]cinnoline (44.7 mg, 0.248 mmol). After stirring the deep brownish red solution at room temperature for 1 hour, all volatiles were removed under reduced pressure to give brownish red powder of **2** (244 mg, >99% yield), mp 140 °C (dec.).

^{1}H NMR (C_6D_6, 400 MHz, 303 K): δ 7.32 (d, J = 7.9 Hz, 2 H, Ar), 7.08 (dd, J = 7.9, 6.9 Hz, 2 H, Ar), 7.02 (d, J = 7.9 Hz, 2 H, Ar), 6.91 (dd, J = 7.9, 6.9 Hz, 2 H, Ar), 1.47 (brs, 54 H, O^tBu) ppm.

$^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz, 303 K): δ 157.8 (Ar), 141.3 (Ar), 135.0 (Ar), 127.9 (Ar), 127.2 (Ar), 124.9 (Ar), 80.6 ($O\mathit{C}(CH_3)_3$), 32.1 ($OC(\mathit{C}H_3)_3$) ppm.

Elemental Analysis: Calcd for $C_{36}H_{62}N_2O_6W_2$: C, 43.83; H, 6.33; N, 2.84. Found: C, 43.60; H, 6.34; N, 2.87.

Synthesis of complex 3

To a solution of $W_2(O^tBu)_6$ (50.2 mg, 0.0623 mmol) in benzene (4.0 mL) was added 3,8-dimethylbenzo[*c*]cinnoline (13.6 mg, 0.0654 mmol). After stirring the deep brownish red solution at room temperature for 24 hours, all volatiles were removed under reduced pressure to give dark red powder of **3** (63.2 mg, 99% yield), mp 162 °C (dec.)

^{1}H NMR (C_6D_6, 400 MHz, 303 K): δ 7.29 (d, J = 8.0 Hz, 2 H, Ar), 6.92 (s, 2 H, Ar), 6.76 (d, J = 8.0 Hz, 2 H, Ar), 2.09 (s, 6 H, CH_3), 1.48 (brs, 54 H, O^tBu) ppm.

$^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz, 303 K): δ 157.6 (Ar), 138.6 (Ar), 137.3 (Ar), 134.7 (Ar), 127.4 (Ar), 126.1 (Ar), 80.6 ($O\mathit{C}(CH_3)_3$), 32.1 ($OC(\mathit{C}H_3)_3$), 30.7 (CH_3) ppm.

Synthesis of complex 4

To a solution of $W_2(O^tBu)_6$ (50.0 mg, 0.0620 mmol) in benzene (4.0 mL) was added 3,8-dimethoxybenzo[*c*]cinnoline (14.9 mg, 0.0620 mmol). After stirring the deep brownish red solution at room temperature for 24 hours, all volatiles were removed under reduced pressure to give brownish red powder of **4** (64.0 mg, 99% yield), mp 147 °C (dec.)

^{1}H NMR (C_6D_6, 400 MHz, 303 K): δ 7.24 (d, J = 8.4 Hz, 2 H, Ar), 6.70 (s, 2 H, Ar), 6.66 (d, J = 8.6 Hz, 2 H, Ar), 3.40 (s, 6 H, CH_3), 1.49 (brs, 54 H, O^tBu) ppm.

$^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz, 303 K): δ 159.6 (Ar), 158.4 (Ar), 153.3 (Ar), 133.9 (Ar), 112.4 (Ar), 111.6 (Ar), 80.6 ($O\mathit{C}(CH_3)_3$), 54.9 (OCH_3), 32.1 ($OC(\mathit{C}H_3)_3$) ppm.

Synthesis of complex 7

To solution of $W_2(NMe_2)_6$ (51.7 mg, 0.0818 mmol) in benzene (3.0 mL) was added Me_3SiOTf (30.0 μL, 0.167 mmol) to generate $W_2(NMe_2)_4(OTf)_2$ *in situ*. After stirring the golden yellow solution at room temperature for 12 hours, azobenzene (15.2 mg, 0.0834 mmol) in benzene (2.0 mL) was added to the golden yellow solution. The mixture was exposed to blue light (450-470 nm) with stirring for 12 hours to give red precipitate and dark brownish red solution. The solution part was removed by decantation, then all volatiles were dried in vacuo to give red powder of **7** (61.5 mg, 73% yield), mp 148 ^oC (dec.).

Elemental Analysis: Calcd for $C_{44}H_{68}F_{12}N_{12}O_{12}S_4W_4$: C, 25.80; H, 3.35; N, 8.20. Found: C, 26.25; H, 3.26; N, 7.69.

Synthesis of complex 8

To solution of $W_2(NMe_2)_6$ (34.4 mg, 0.0544 mmol) in benzene (2.0 mL) was added Me_3SiOTf (19.6 μL, 0.109 mmol) to generate $W_2(NMe_2)_4(OTf)_2$ *in situ*. After keeping the golden yellow solution at room temperature for 12 hours, 4,4'-dimethylazobenzene (11.6 mg, 0.0552 mmol) in benzene (1.0 mL) was added to the golden yellow solution. The mixture was exposed to blue light (450-470 nm) for 12 hours to give dark red microcrystals and dark brownish red solution. The solution part was removed by decantation, then residual dark red microcrystals were washed with toluene (3 x 1 mL) and hexane (2 x 1 mL), dried in vacuo to give **8** (32.5 mg, 71% yield), mp 159 ^oC (dec.).

Elemental Analysis: Calcd for $(C_{48}H_{76}F_{12}N_{12}O_{12}S_4W_4)(C_6H_6)_2$: C, 31.87; H, 3.92; N, 7.43. Found: C, 31.62; H, 3.86; N, 7.48.

Synthesis of complex 9

To solution of $W_2(NMe_2)_6$ (30.2 mg, 0.0478 mmol) in benzene (2.0 mL) was added Me_3SiOTf (17.1 μL, 0.0949 mmol) to generate $W_2(NMe_2)_4(OTf)_2$ *in situ*. After keeping the golden yellow solution at room temperature for 12 hours, 4,4'-difluoroazobenzene (10.5 mg, 0.0482 mmol) in benzene (2.0 mL) was added to the golden yellow solution. The mixture was exposed to blue light (450-470 nm) for 12 hours to give red microcrystals and dark brownish red solution. The solution part was removed by decantation, then black red microcrystals were washed with benzene (3 x 1 mL), dried in vacuo to give **9** (42.3 mg, 83% yield), mp 156 ^oC (dec.).

Elemental Analysis: Calcd for $C_{44}H_{64}F_{16}N_{12}O_{12}S_4W_4$: C, 24.92; H, 3.04; N, 7.93. Found: C, 25.03; H, 3.09; N, 7.75.

3. NMR spectra of complexes **2**—**4**

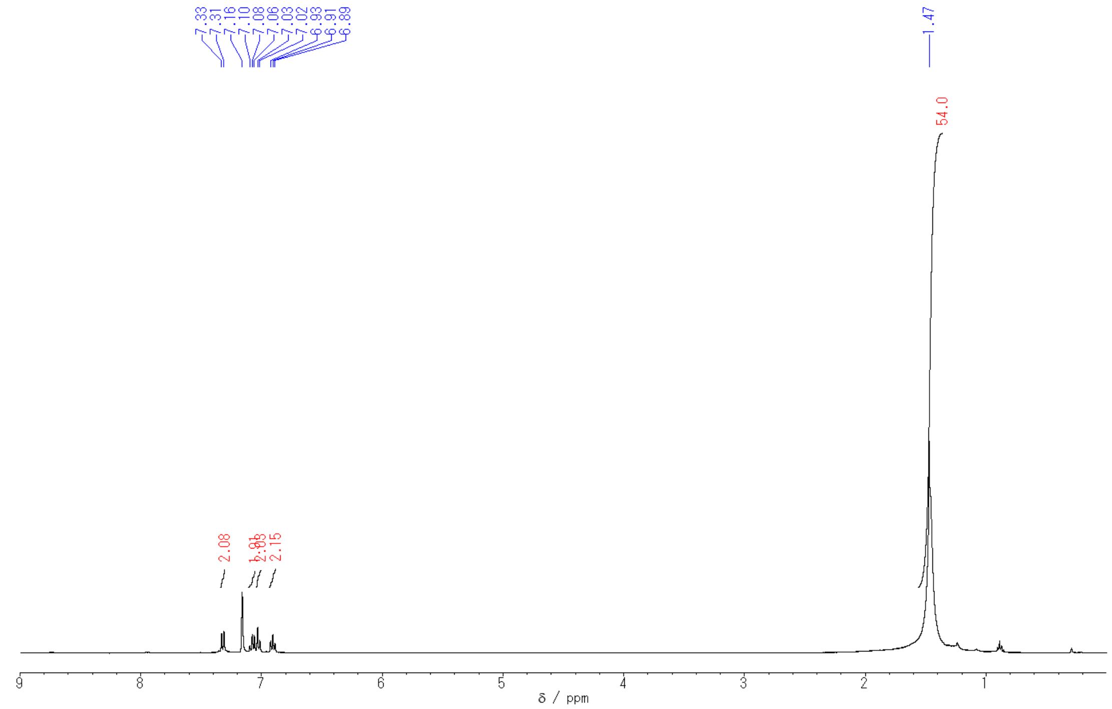


Figure S1. ^{1}H NMR spectrum of complex **2** in C_6D_6

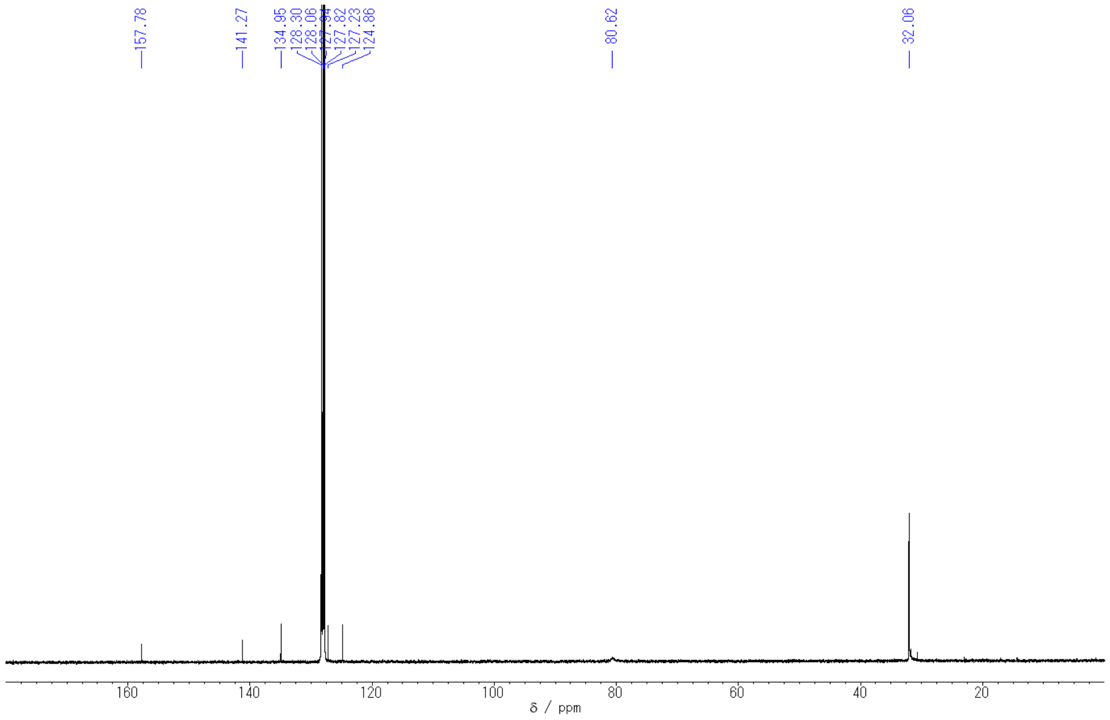


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of complex **2** in C_6D_6

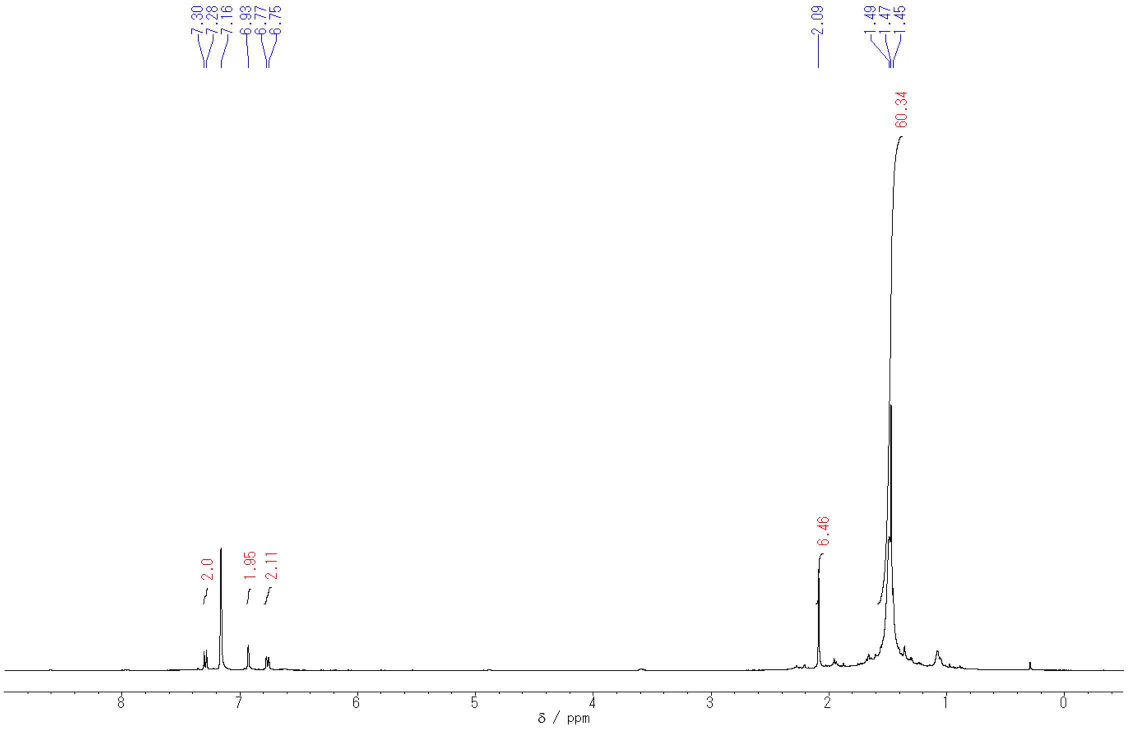


Figure S3. ^{1}H NMR spectrum of complex **3** in C_6D_6

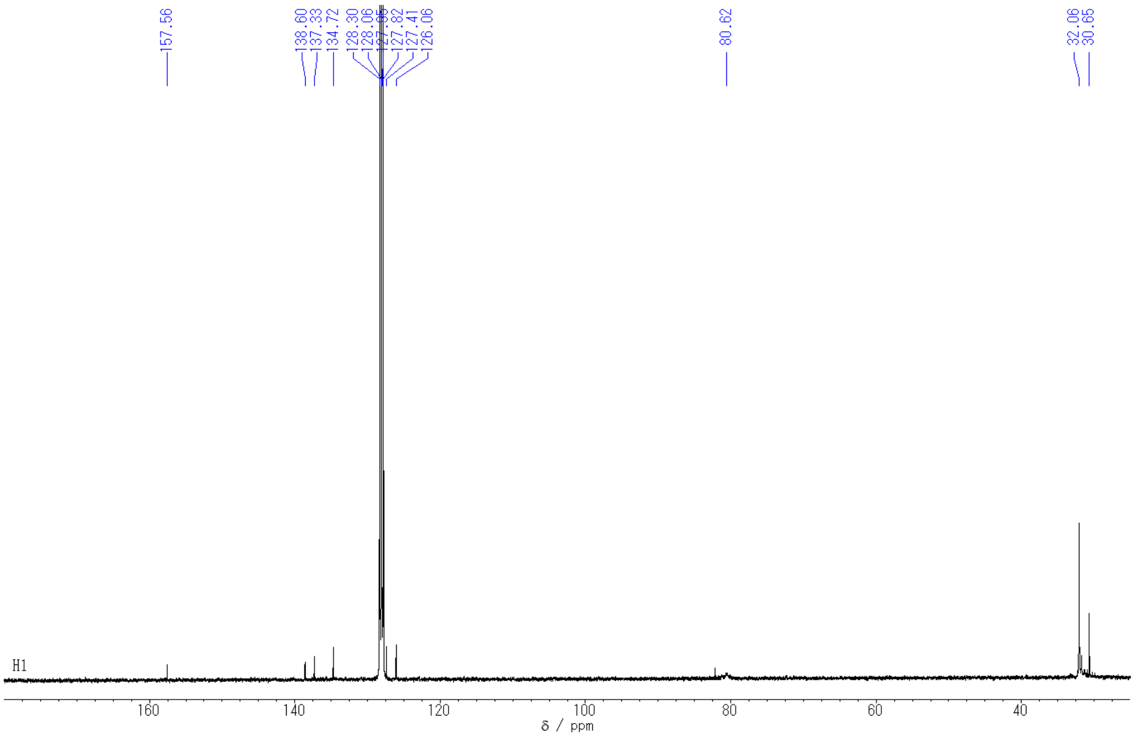


Figure S4. $^{13}C\{^1H\}$ NMR spectrum of complex **3** in C_6D_6

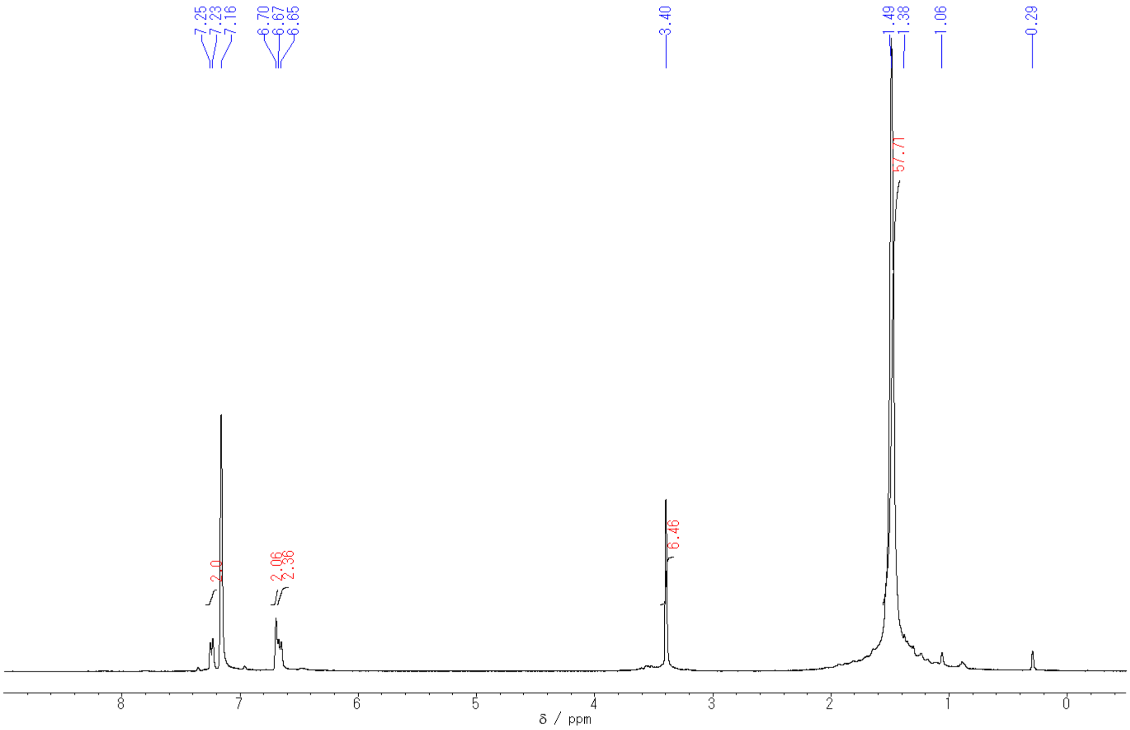


Figure S5. ^{1}H NMR spectrum of complex **4** in C_6D_6

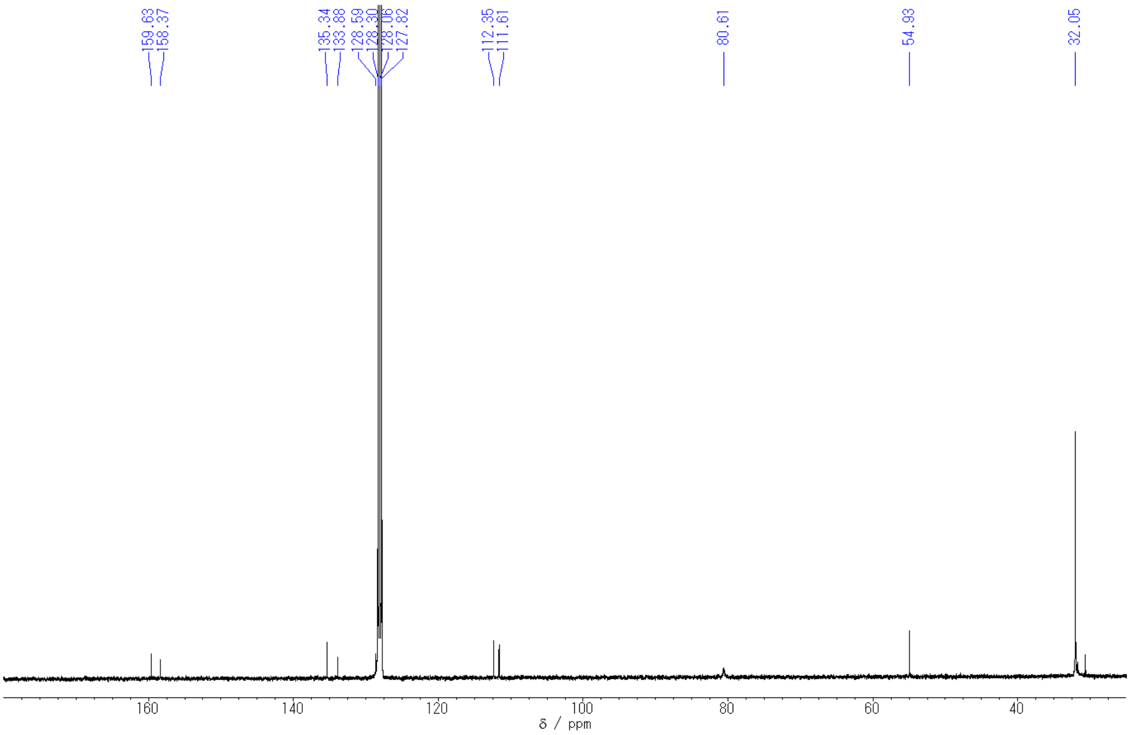
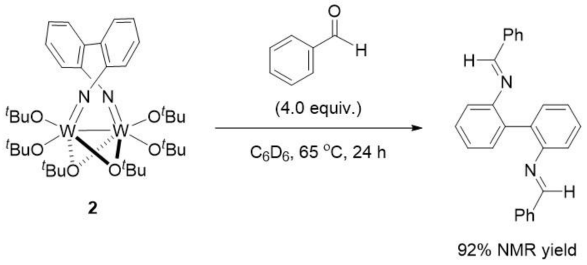


Figure S6. $^{13}C\{^1H\}$ NMR spectrum of complex **4** in C_6D_6

4. Reaction of **2** with benzaldehyde



(S1)

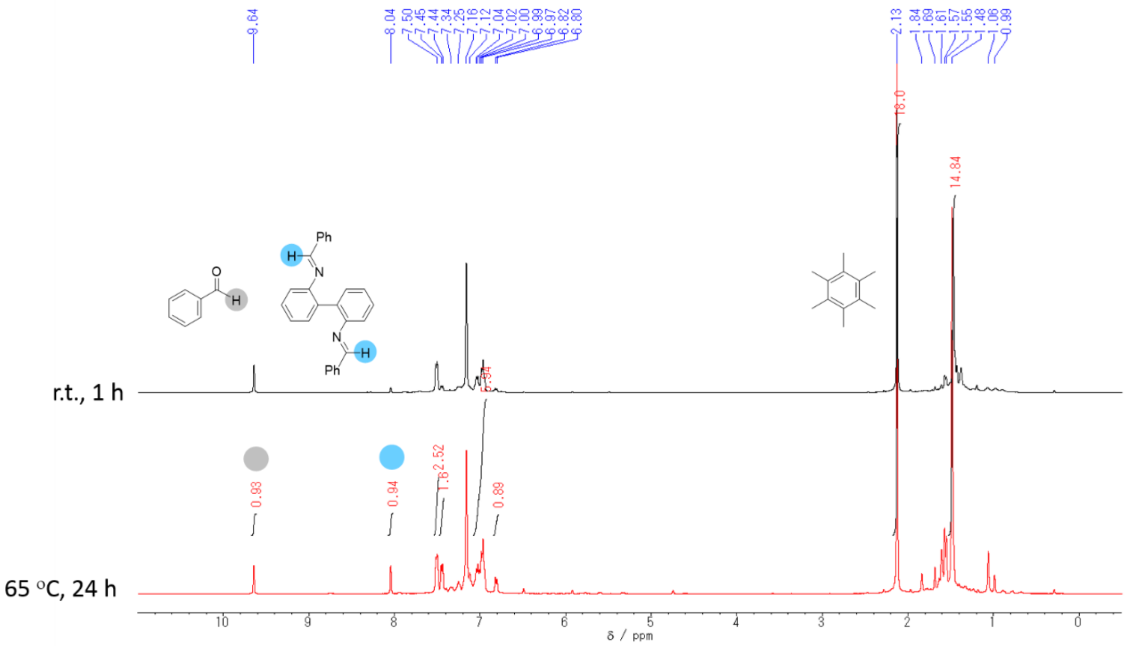
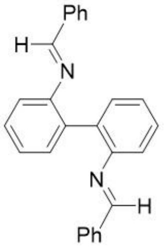


Figure S7. Reaction of complex **2** with benzaldehyde (4 equiv) in C_6D_6 (black line: r.t., 1 h; red line: 65 °C, 24 h)

Isolation of 2,2'-Bis(benzylideneamino)biphenyl



Addition of benzaldehyde (20.4 μL, 2 equiv) to the solution of **2** (99.4 mg, 0.101 mmol) in toluene (3 mL), and the mixture was stirred for 16 h at 60 °C. The reaction mixture was quenched by exposing to air with addition of ethyl acetate (10 mL), and then insoluble solids were removed by filtration. Evaporation of the solvent gave 2,2'-bis(benzylideneamino)biphenyl as brown colored oil (24.0 mg, 66% isolated yield). Although further purification by column chromatography was difficult due to the hydrolysis of the imine moiety, the ^{1}H NMR spectrum of the isolated product was identical to the authentic sample prepared from 2,2'-diaminobiphenyl and 2 equiv of benzaldehyde.[4]

^{1}H NMR (C_6D_6, 400 MHz, 303 K): δ 6.81 (dd, *J* = 7.6 and 1.3 Hz, 2H, Ar), 6.97-7.05 (m, 8H, Ar), 7.45 (dd, *J* = 6.7 and 1.6 Hz, 4H, *o*-Ph), 7.50 (dd, *J* = 7.3 and 1.7 Hz, 2H, Ar), 8.05 (s, 2H, *H*C=NAr) ppm. One resonance for doublet of doublet was overlapped with the residual proton signal of C_6D_6.

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 303 K): δ 118.3, 125.4, 126.7, 127.2, 128.5, 128.6, 128.7, 131.0, 131.1, 134.3, 136.5, 151.4, 160.1 ppm.

HRMS (FAB) (*m/z*): $[M+H]^+$ calculated. for $C_{26}H_{21}N_2$: 361.16; found 361.17.

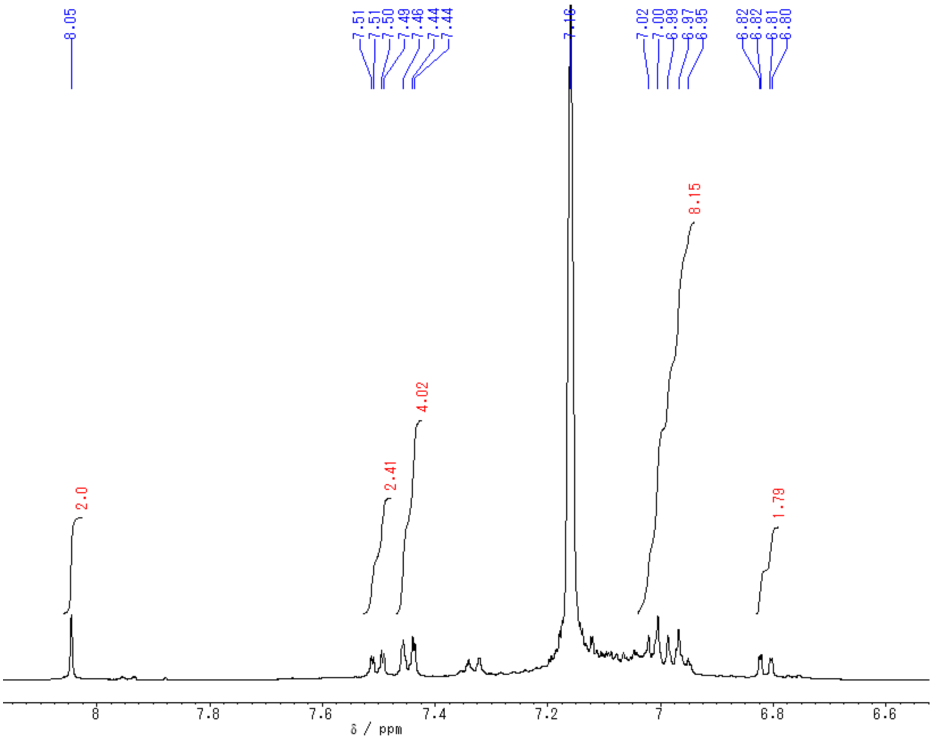


Figure S8. ^{1}H NMR spectrum of 2,2'-bis(benzylideneamino)biphenyl in C_6D_6

5. X-ray diffraction 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 XtaLAB P200 diffractometer using multi-layer mirror monochromated Mo-Kα (0.71075 Å) radiation. The structures were solved by SHELXS-2013,[5] and refined on F^2 by full-matrix least-squares method, using SHELXL-2013.[6] 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 $[\Sigma w(F\mathrm{o}^2 - F\mathrm{c}^2)^2]$ ($w = 1/[\sigma^2(F\mathrm{o})^2 + (a\mathrm{P})^2 + b\mathrm{P}]$), where $\mathrm{P} = (\mathrm{Max}(F\mathrm{o}^2, 0) + 2F\mathrm{c}^2)/3$ with $\sigma^2(F\mathrm{o}^2)$ from counting statistics. The function $R1$ and $wR2$ were $(\Sigma||F\mathrm{o}| - |F\mathrm{c}||)/\Sigma|F\mathrm{o}|$ and $[\Sigma w(F\mathrm{o}^2 - F\mathrm{c}^2)^2/\Sigma(wF\mathrm{o}^4)]^{1/2}$, respectively. The ORTEP-3 program[7] was used to draw the molecule.

Table S1. Crystal data and data collection parameters of **2**

	2
empirical formula	$C_{36}H_{62}N_2O_6W_2$
formula weight	986.60
crystal system	monoclinic
space group	$C2$ / c (#15)
a, Å	18.8904(18)
b, Å	16.4256(14)
c, Å	13.4978(9)
α, deg.	------------
β, deg.	106.8126(6)
γ, deg.	------------
V, Å^3	4009.2(6)
Z	4
D_{calcd}, g/cm^3	1.634
μ [Mo-Kα], mm^{-1}	5.7822
T, K	113(2)
crystal size, mm	0.170 x 0.100 x 0.080
θ range for data collection (deg.)	3.153 to 27.525
no. of reflections measured	21060
unique data (Rint)	4601 (0.0225)
data / restraints / parameters	4601 / 0 / 208
$R1$ ($I > 2.0\sigma(I)$)	0.0122
$wR2$ ($I > 2.0\sigma(I)$)	0.0313
$R1$ (all data)	0.0135
$wR2$ (all data)	0.0315
GOF on F^2	1.077
Δρ, e Å $^{-3}$	0.78, -0.70

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

Table S2. Crystal data and data collection parameters of **7**

	7
empirical formula	$C_{56}H_{80}F_{12}N_{12}O_{12}S_4W_4$
formula weight	2204.96
crystal system	monoclinic
space group	$P2_1 / c$ (#14)
a, Å	14.2203(15)
b, Å	11.6883(11)
c, Å	22.162(2)
α, deg.	------------
β, deg.	98.946(3)
γ, deg.	------------
V, Å^3	3638.8(6)
Z	4
D_{calcd}, g/cm^3	2.012
μ [Mo-$K\alpha$], mm^{-1}	6.5186
T, K	113(2)
crystal size, mm	0.160 x 0.130 x 0.110
θ range for data collection (deg.)	3.073 to 27.530
no. of reflections measured	29121
unique data (Rint)	8300 (0.0312)
data / restraints / parameters	8300 / 0 / 409
$R1$ ($I > 2.0\sigma(I)$)	0.0356
$wR2$ ($I > 2.0\sigma(I)$)	0.0930
$R1$ (all data)	0.0511
$wR2$ (all data)	0.1017
GOF on F^2	1.018
$\Delta\rho$, e Å^{-3}	2.10, -1.45

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

6. References

1. M. H. Chisholm, B. W. Eichhorn, K. Folting, J. C. Huffman, C. D. Ontiveros, W. E. Streib and W. G. Van Der Sluys, *Inorg. Chem.*, 1987, **26**, 3182.
2. M. H. Chisholm, K. S. Kramer, J. D. Martin, J. C. Huffman, E. B. Lobkovsky and W. E. Streib, *Inorg. Chem.*, 1992, **31**, 4469.
3. X. Geng and C. Wang, *Org. Lett.*, 2015, **17**, 2434.
4. K. Aikawa and K. Mikami, *Chem. Commun.* **2005,** 5799.
5. (a) G. M. Sheldrick, A Short History of SHELX, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 2008, 64, 112. (b) A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, SIR92 - A Program for Automatic Solution of Crystal Structures by Direct Methods, *J. Appl. Crystallogr.*, 1994, **27**, 435.
6. G. M. Sheldrick, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 2008, **64**, 112.
7. L. J. Farrugia, WinGX Suite for Small-Molecule SingleCrystal Crystallography, *J. Appl. Crystallogr.*, 1999, **32**, 837.