

Supplementary Information

An Ir₃L₂ complex with anion binding pockets: photocatalytic *E–Z* isomerization via molecular recognition

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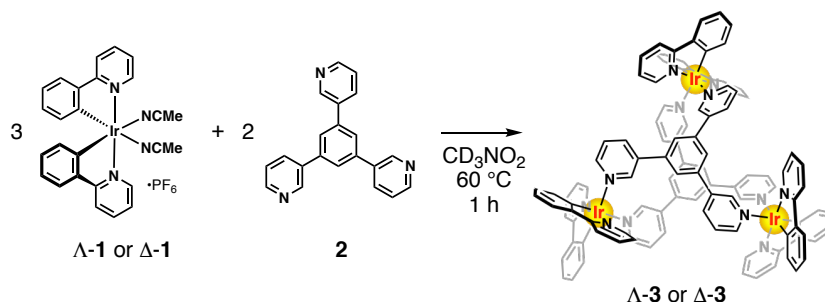
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1. Materials and instrumentations

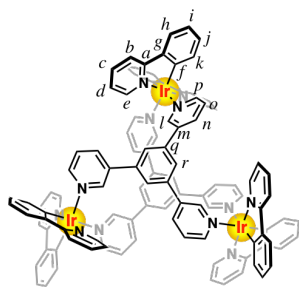
^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 500 MHz spectrometer equipped with a CP-TCI cryoprobe or a Bruker AVANCE III HD 500 MHz spectrometer equipped with a PABBO probe (500 MHz for ^1H NMR and 125MHz for ^{13}C NMR) at 300K unless otherwise stated. Chemical shifts are reported in δ (ppm) relative to the deuterated solvent signals ($\text{CD}_2\text{HNO}_2 = 4.33$ ppm, $\text{CDHCl}_2 = 5.32$ ppm). ESI-MS data were recorded on a Bruker maXis. Single crystal X-ray diffraction data were collected on a Synergy-S diffractometer (Rigaku Oxford Diffraction) equipped with a micro-focus CuK_α radiation source ($\lambda = 1.5418 \text{ \AA}$), a high-sensitive CCD detector, and a low temperature system using cold nitrogen stream (100 K). Optical measurements were carried out in 10 mm quartz cuvettes at ambient temperature unless otherwise stated. IR measurement was carried out using a DIGILAB Scimitar FTS-2000 instrument. GC-MS spectra were obtained on an Agilent 5977B Mass Selective Detector equipped with a 7820A GC system and an EI source. CD spectra were recorded on a Jasco J-820 spectropolarimeter. UV-Vis absorption spectrum was recorded on a Shimadzu UV-1900 spectrophotometer equipped with a 20 W halogen lamp and a deuterium lamp. Fluorescence spectra were measured with a Shimadzu RF-6000 spectrofluorophotometer equipped with a 150 W xenon arc lamp. Visible-light reactions were performed with SynLED Parallel Photoreactor (Sigma-Aldrich Co.) equipped with 1 W LEDs (465–470 nm) with a 45-degree lens, and a built-in cooling fan to maintain reaction temperatures at approximately 30 °C. Solvents and reagents were purchased from TCI Co., Ltd., FUJIFILM Wako Pure Chemical Corp., Sigma-Aldrich Co. LLC., and Kanto Chemical Co., Inc. and used without further purification. Deuterated solvents were acquired from ISOTECH Stable Isotopes at Sigma-Aldrich (CD_3NO_2) and Kanto Chemical (CD_2Cl_2) and used as supplied for the complexation reactions and NMR measurements. **Λ -1**, **Δ -1**,^{S1} and **2**^{S2} were prepared according to the reported methods.

2. Synthesis and physical properties of chiral coordination disk 3

Synthesis of Λ -3 and Δ -3



Λ -[Ir(ppy)₂(NMe)](PF₆) (Λ -1, 110 mg, 0.151 mmol) and 2,4,6-tri(3-pyridyl)benzene (**2**, 31.6 mg, 0.102 mmol) were dissolved in nitromethane (5.0 mL) and stirred at 60 °C for 1 h. Quantitative formation of complex Λ -3 was confirmed by NMR. The resulted mixture was cooled to room temperature and diethyl ether (30 mL) was added. The resulted precipitate was corrected by filtration, washed with diethyl ether, and dried in vacuo to give Λ -3 as a yellow crystalline powder (118 mg, 0.0461 mmol, 92%). Δ -3 was synthesized in the same manner as Λ -3 by using Δ -1 instead of Λ -1.



Physical data of Λ -3: ¹H NMR (500 MHz, 300 K, CD₃NO₂) : δ 8.92 (s, 6H, H_l), 8.73–8.71 (m, 12H, H_e and H_p), 8.10–8.03 (m, 18H, H_b, H_c and H_n), 7.73 (d, J = 7.5 Hz, 6H, H_h), 7.64 (t, J = 7.5 Hz, 6H, H_d), 7.55 (s, 6 H, H_r), 7.54 (t, J = 7.5 Hz, 6H, H_o), 7.02 (t, J = 6.5 Hz, 6H, H_i), 6.98 (t, J = 6.5 Hz, 6H, H_j), 6.54 (d, J = 7.5 Hz, 6H, H_k); ¹³C{¹H} NMR (125 MHz, 300 K, CD₃NO₂): δ 169.0 (C_a), 153.5 (C_p), 150.9 (C_e), 150.6 (C_i), 148.6 (C_l), 145.9 (C_g), 140.4 (C_c), 138.82, 328.78 (C_m, C_q), 137.6 (C_n), 133.7 (C_k), 131.9 (C_j), 127.7 (C_o),

126.6 (C_r), 125.9 (C_h), 125.1 (C_d), 124.3 (C_i), 121.3 (C_b); DOSY-NMR (CD₃NO₂, m²/s): D = 4.17×10^{-10} ; IR (ATR, cm⁻¹): 3049, 1607, 1583, 1479, 1439, 1421, 1393, 1228, 1197, 1165, 1116, 1064, 1032, 836, 759, 732, 710, 556; HRMS (ESI-pos) m/z : calcd. for [(C₂₂H₁₆IrN₂)₃(C₂₁H₁₅N₃)₂(F₆P)]²⁺, 1132.2485; found: 1132.2448; m.p.: >250 °C (decomposed).

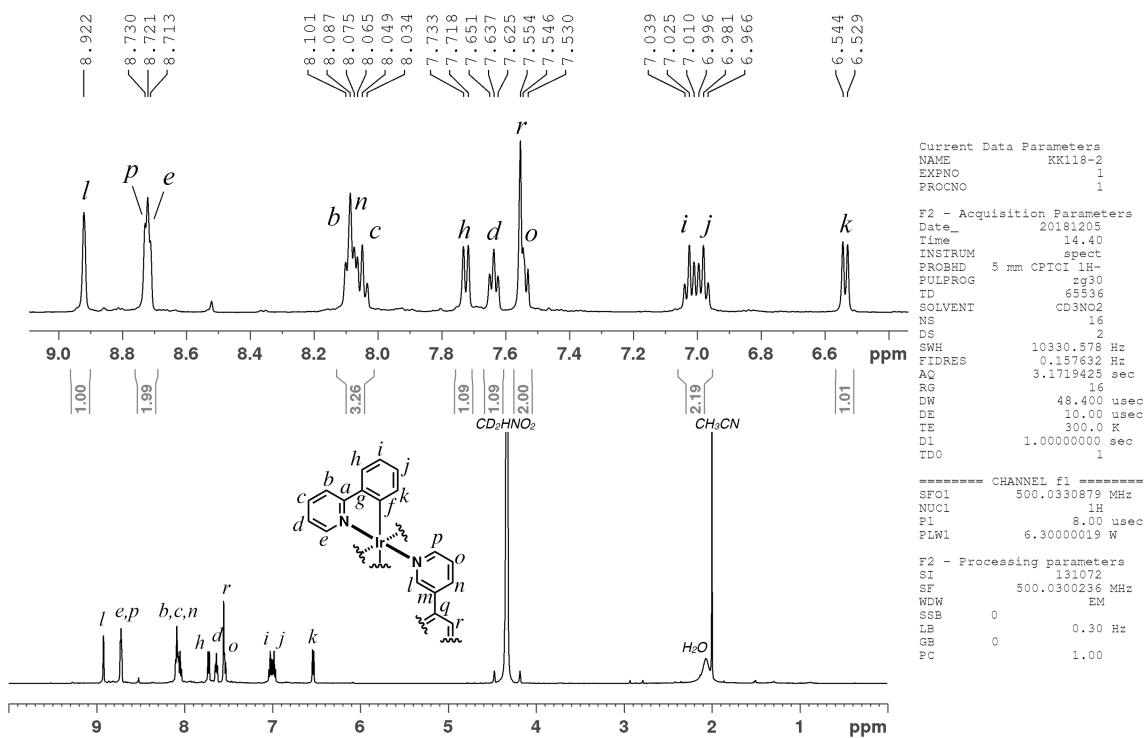


Figure S1. ^1H NMR (500 MHz, 300 K, CD_3NO_2) spectrum of Λ -3.

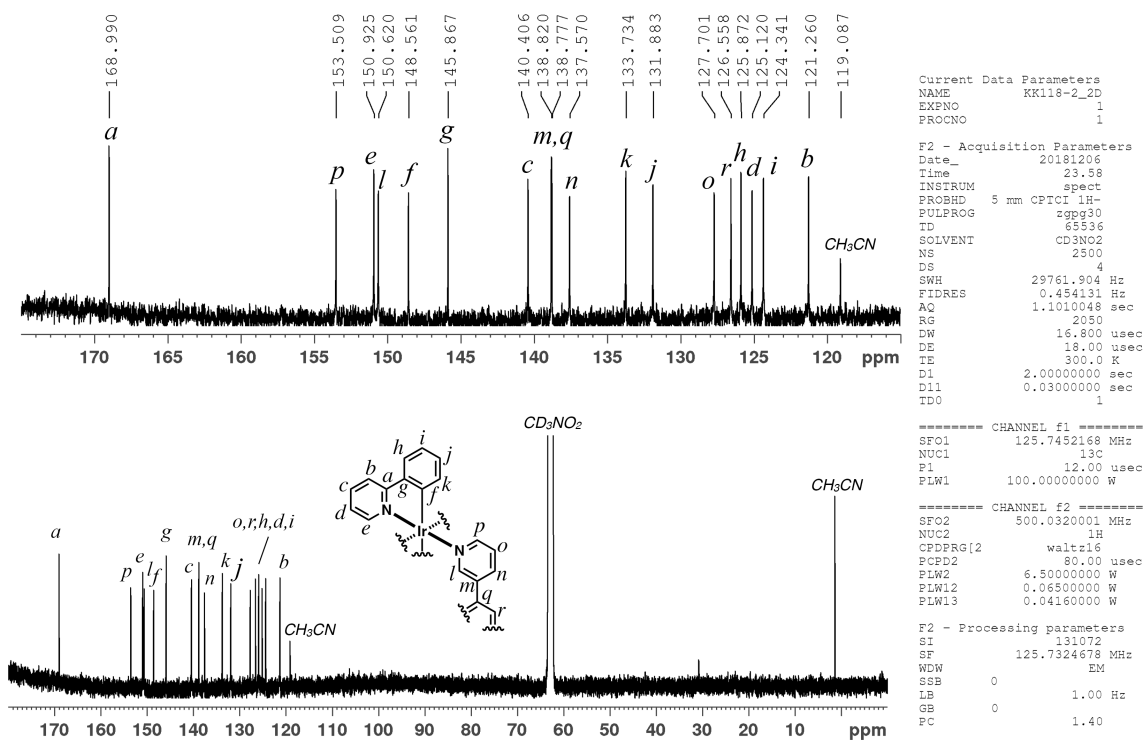


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 300 K, CD_3NO_2) spectrum of Λ -3.

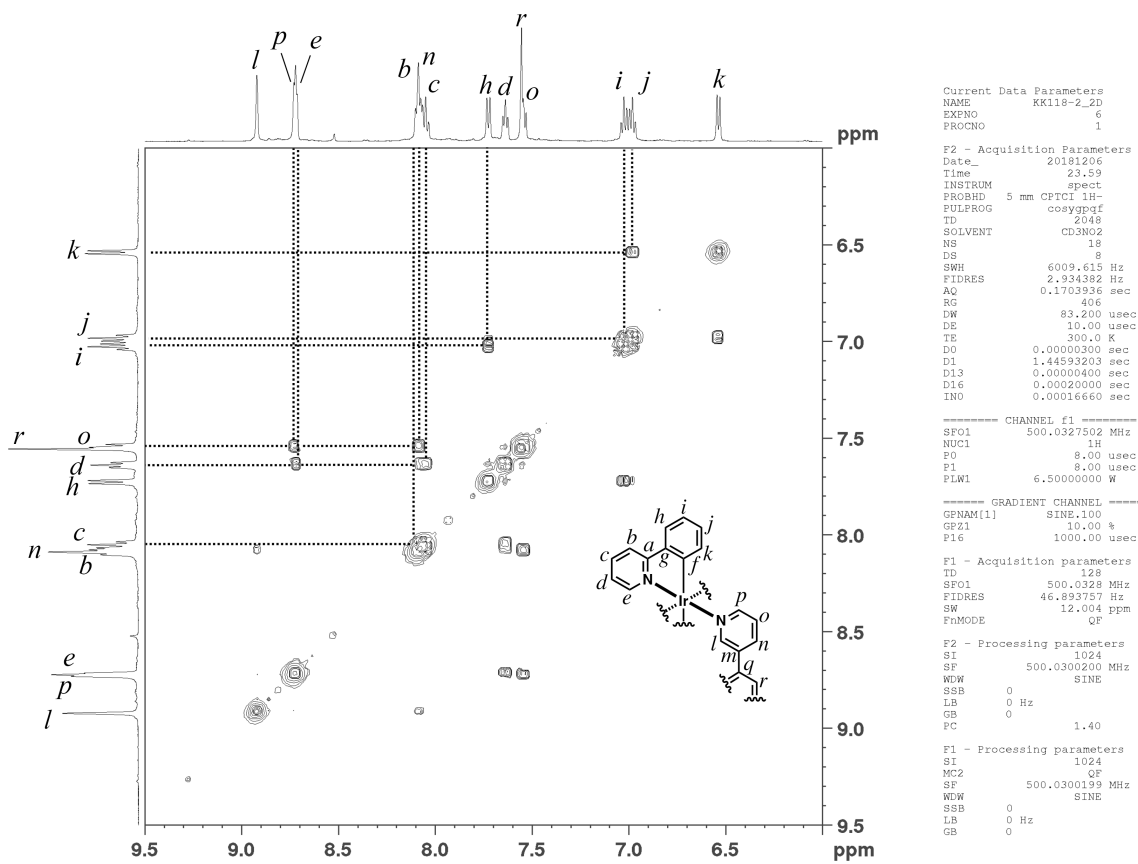


Figure S3. ^1H - ^1H COSY NMR (500 MHz, 300 K, CD_3NO_2) spectrum of Λ -3.

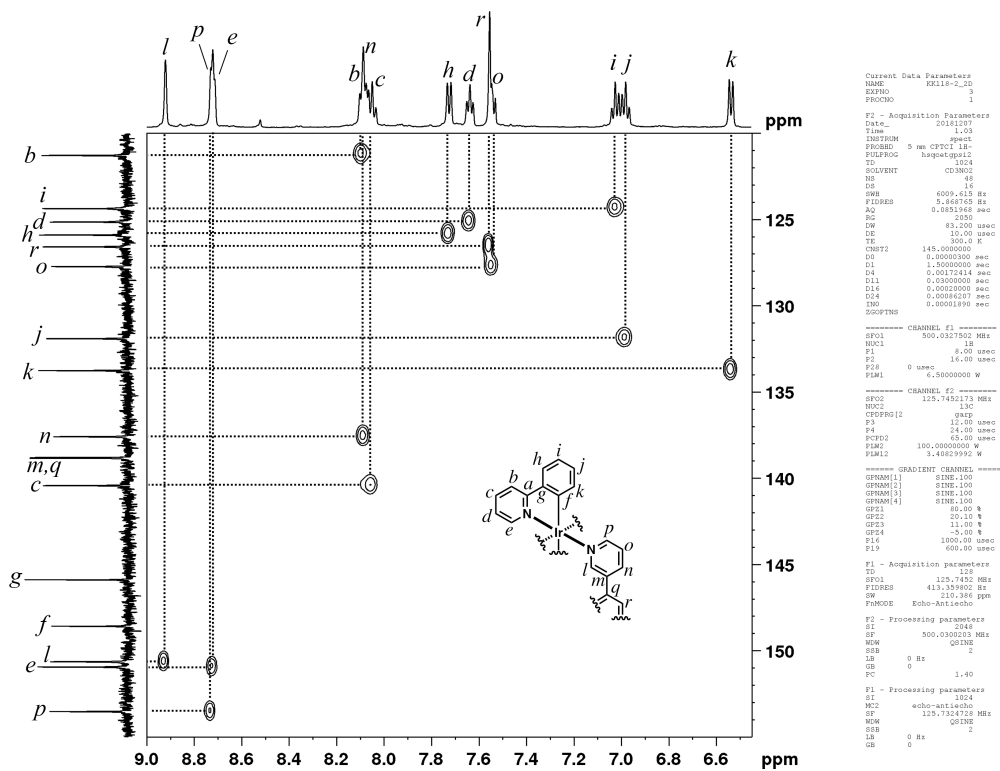


Figure S4. ^1H - ^{13}C HSQC NMR (500 MHz, 300 K, CD_3NO_2) spectrum of Λ -3.

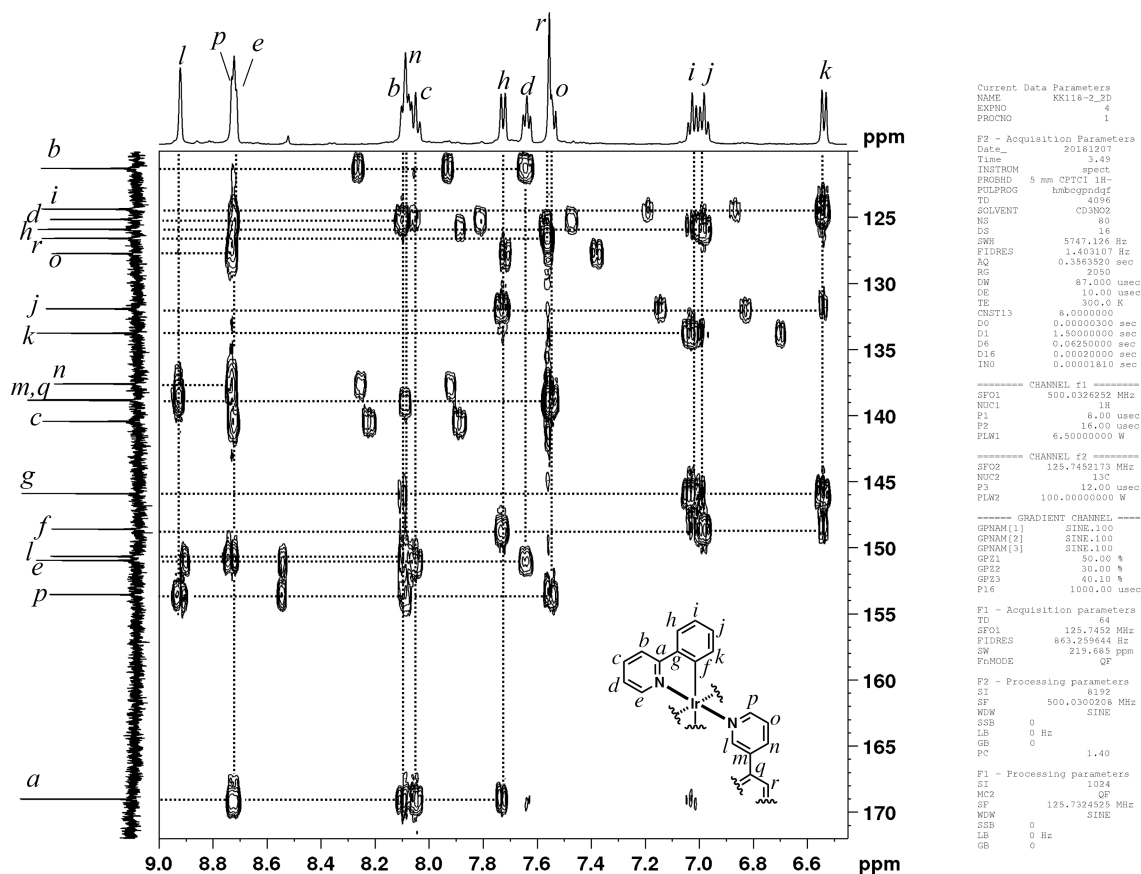


Figure S5. ^1H - ^{13}C HSQC NMR (500 MHz, 300 K, CD_3NO_2) spectrum of Λ -3.

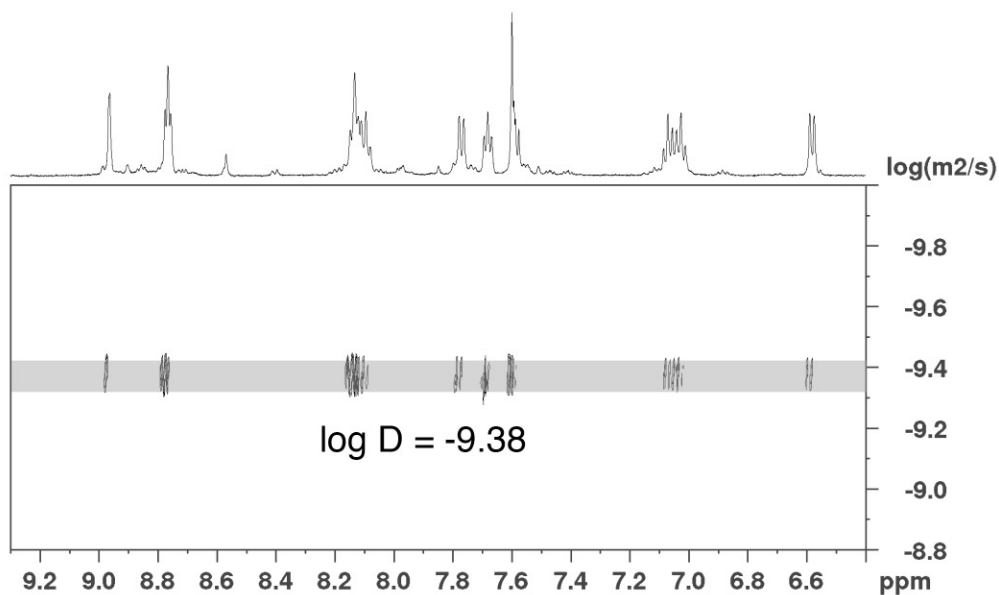


Figure S6. ^1H DOSY NMR spectrum (500 MHz, 300 K, CD_3NO_2) of Λ -3.

Analysis Info

Analysis Name D:\Data\Koyamada\KK062-1_1-F,1_01_1893.d
Method esi_pos_wide.m
Sample Name KK062-1
Comment

Acquisition Date 10/2/2018 2:07:51 PM

Operator BDAL@DE
Instrument maXis 30

Acquisition Parameter

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Scan End	3000 m/z	Set Collision Cell RF	1000.0 Vpp	Set Divert Valve	Source

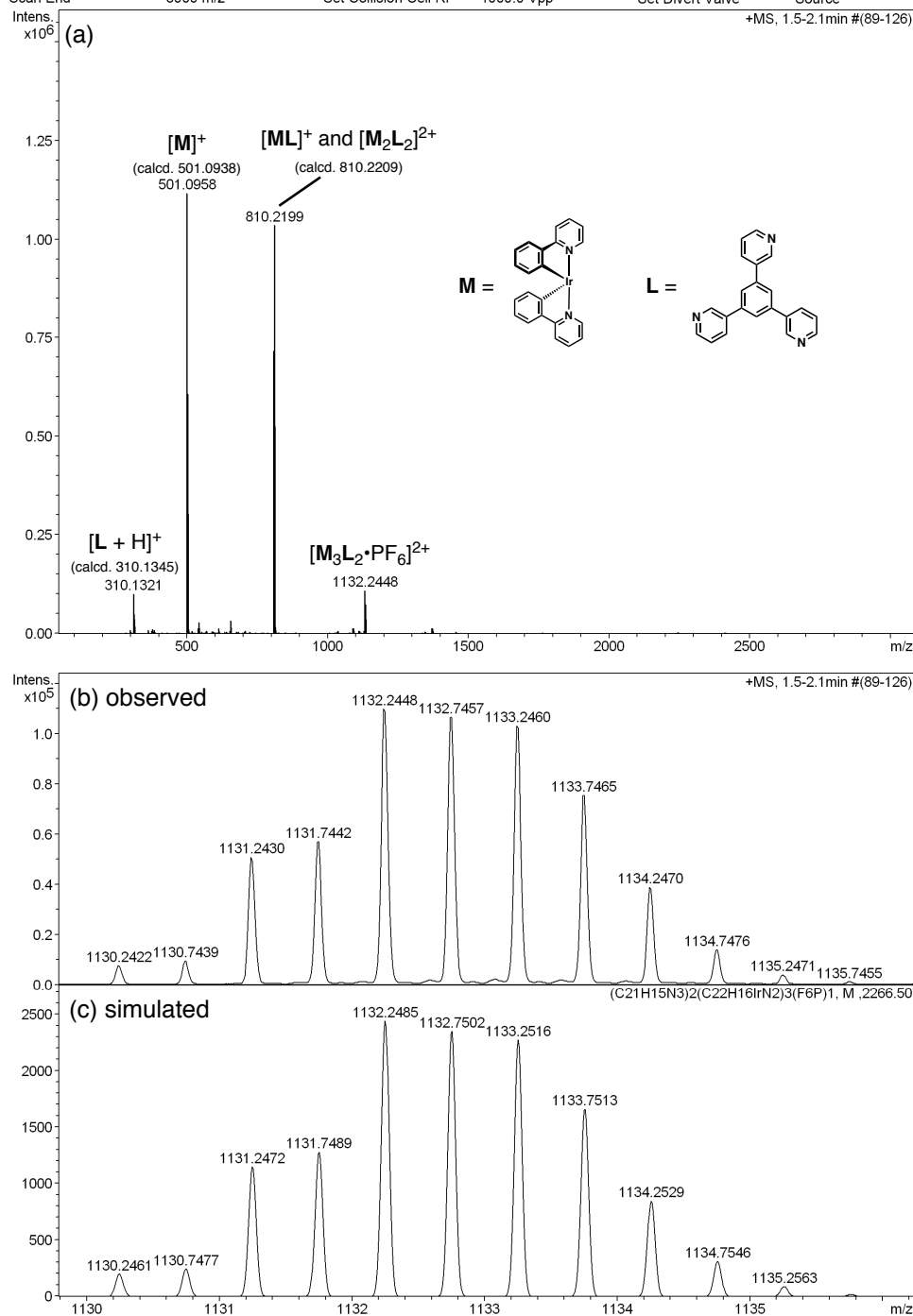


Figure S7. (a) ESI-TOF mass spectrum of Λ -3. Extended images of (b) observed and (c) simulated isotope patterns of $[M_3L_2 \cdot PF_6]^{2+}$.

Self-assembly with *rac-1*

rac-[Ir(ppy)₂(NCMe)](PF₆) (*rac-1*, 110 mg, 0.151 mmol) and 2,4,6-tri(3-pyridyl)benzene (**2**, 31.6 mg, 0.102 mmol) were dissolved in nitromethane (5.0 mL) and stirred at 60 °C for 5 h.

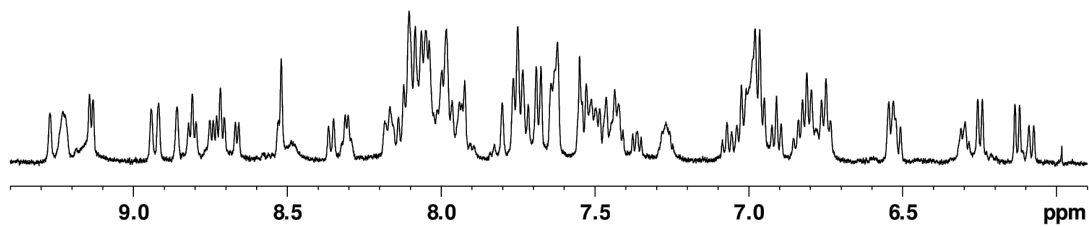


Figure S8. ¹H NMR (500 MHz, 300 K, CD₃NO₂) spectrum after self-assembly of *rac-1* with **2**.

3. UV-Vis absorption, fluorescence, and circular dichroism spectroscopy

Sample preparation for UV-Vis spectroscopy

Λ -3 (1.49 mg, 1.05 μmol) was dissolved in CH_2Cl_2 (4.2 mL) and filtered through a 0.2 μm PTFE membrane. The clear pale-yellow solution (3 mL) was transferred into a quartz cuvette, and then used for the absorption measurement.

Sample preparation for fluorescence spectroscopy

Λ -3 (0.61 mg, 0.24 μmol) was dissolved in degassed CH_2Cl_2 (3.0 mL) and filtered through a 0.2 μm PTFE membrane. The clear pale-yellow solution was transferred into a quartz cuvette and used for the fluorescence measurement.

Sample preparation for circular dichroism spectroscopy

Λ -3 or Δ -3 (2.0 μmol) was dissolved in $\text{CH}_2\text{ClCH}_2\text{Cl}$ (2.0 mL) and filtered through a 0.2 μm PTFE membrane. The solution was diluted to adjust the concentration to 0.10 mM and then transferred into a 1 mm quartz cell and used for the circular dichroism measurement.

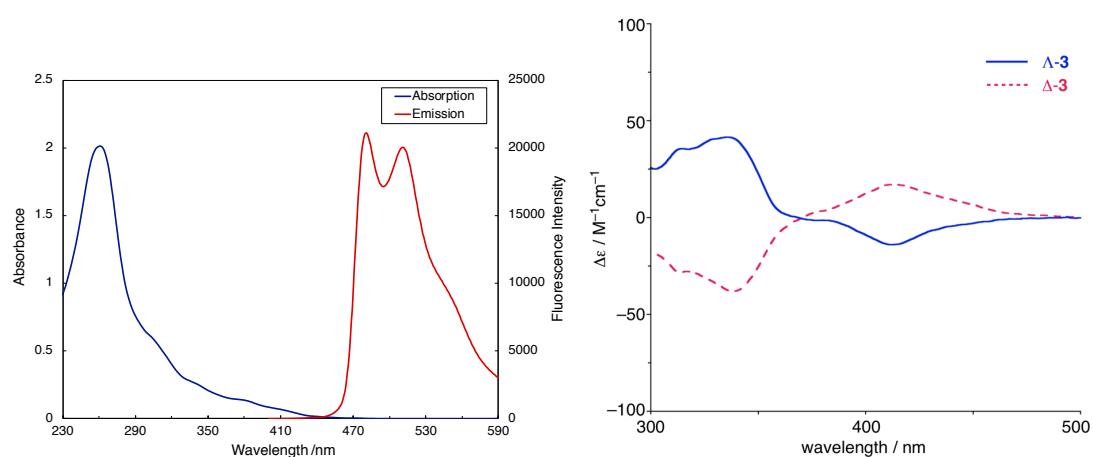


Figure S9. (left) UV-Vis absorption and fluorescence spectra of Λ -3 in CH_2Cl_2 (background-subtracted with a CH_2Cl_2 blank.). (right) Circular dichroism spectra of Λ -3 (blue solid line) and Δ -3 (red dashed line) in $\text{CH}_2\text{ClCH}_2\text{Cl}$.

4. X-ray crystallographic analyses

Crystallization of Λ -3

From nitromethane solution (MeNO₂ adduct)

A single crystal suitable for the X-ray analysis was obtained by vapor diffusion of 2-propanol into a 10 mM solution of Λ -3 in nitromethane.

From THF solution

A single crystal suitable for the X-ray analysis was obtained by vapor diffusion of ethyl acetate into a saturated solution of Λ -3 in THF.

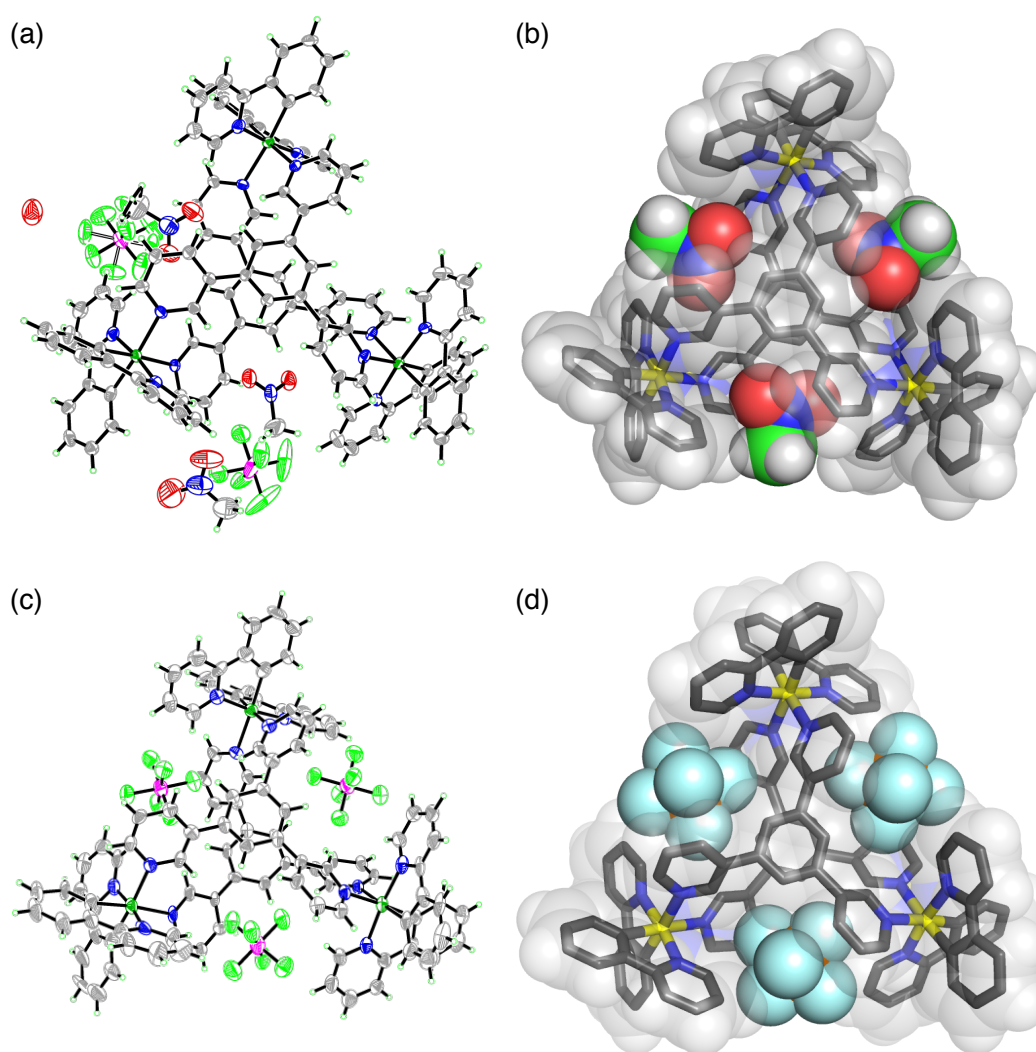


Figure S10. Crystal structures of Λ -3 (CCDC reference number 2083211 and 2083212). (a) ORTEP drawing (50% probability ellipsoids) of Λ -3 (MeNO₂ adduct). (b) Three molecules of nitromethane are interacted with Λ -3. (c) ORTEP drawing (50% probability ellipsoids) of Λ -3. (d) Three PF₆⁻ anions are interacted with Λ -3.

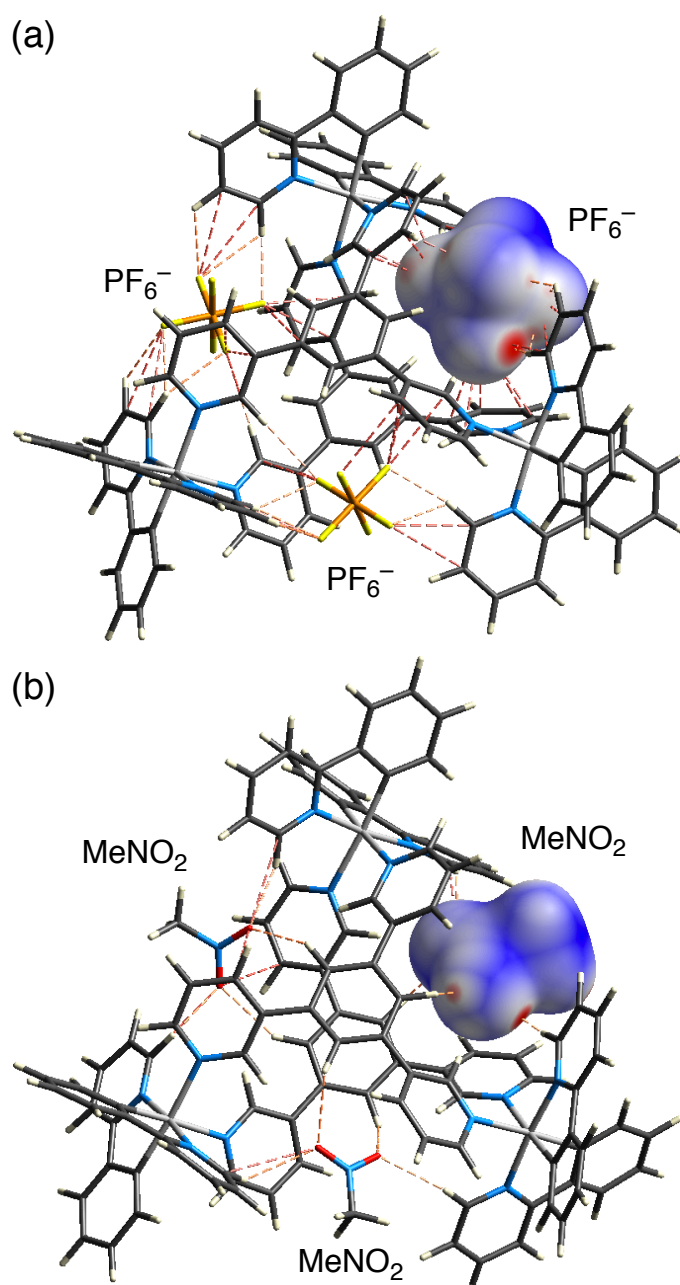
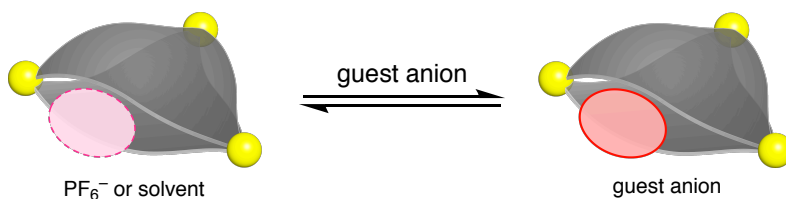


Figure S11. Short contacts between the bound guests and host Λ -3 in crystal structures of (a) Λ -3 and (b) the MeNO₂ adduct of Λ -3, plotted by *CrystalExplorer 17*.^[S3] One of the guest molecules is shown in a promolecular surface mapped with normalized contact distances, d_{norm} (the red areas show contact areas within the sum of the van der Waals radii).^[S4] The dashed lines represent short contacts within the sum of the van der Waals radii between the two atoms.

Table S1. Crystal data and structural refinement for Λ -3 (MeNO₂ adduct) and Λ -3.

	Λ -3 (MeNO ₂ adduct)	Λ -3
Identification code	exp_3833	exp_3863
CCDC number	2083211	2083212
Empirical formula	C ₁₁₃ H ₉₃ F ₁₈ Ir ₃ N ₁₇ O ₁₁ P ₃	C ₁₀₈ H ₇₈ F ₁₈ Ir ₃ N ₁₂ P ₃
Formula weight	2876.62	2555.33
Temperature	100.01(10) K	100.02(10) K
Wavelength	1.54184 Å	1.54184 Å
Crystal system	Orthorhombic	Orthorhombic
Space group	<i>C</i> 222 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁
Unit cell dimensions	<i>a</i> = 15.67350(12) Å <i>b</i> = 34.7800(3) Å <i>c</i> = 21.94284(18) Å $\alpha = \beta = \gamma = 90^\circ$	<i>a</i> = 16.8732(2) Å <i>b</i> = 20.5915(2) Å <i>c</i> = 32.4982(5) Å $\alpha = \beta = \gamma = 90^\circ$
Volume	11961.59(17) Å ³	11291.3(2) Å ³
<i>Z</i>	4	4
Density (calculated)	1.597 Mg/m ³	1.503 Mg/m ³
Absorption coefficient	7.501 mm ⁻¹	7.781 mm ⁻¹
<i>F</i> (000)	5664	4992
Crystal size	0.05 × 0.05 × 0.04 mm ³	0.10 × 0.02 × 0.02 mm ³
Theta range for data	3.093 to 76.181°	2.5403 to 76.5647°
Index ranges	-19 ≤ <i>h</i> ≤ 9, -43 ≤ <i>k</i> ≤ 43, -27 ≤ <i>l</i> ≤ 27	-20 ≤ <i>h</i> ≤ 21, -25 ≤ <i>k</i> ≤ 25, -40 ≤ <i>l</i> ≤ 15
Reflection collected	49594	51626
Independent reflections	12216 [<i>R</i> _{int} = 0.0496]	21763 [<i>R</i> _{int} = 0.0989]
Completeness	99.6 % ($\theta = 67.684^\circ$)	98.5 % ($\theta = 74.3338^\circ$)
Max. and min. transmission	1.00000 and 0.86456	1.00000 and 0.90861
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	12216 / 0 / 790	21763 / 36 / 1297
Goodness-of-fit on <i>F</i> ²	1.062	0.962
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0310, <i>wR</i> ₂ = 0.0790	<i>R</i> ₁ = 0.0489, <i>wR</i> ₂ = 0.1004
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0341, <i>wR</i> ₂ = 0.0802	<i>R</i> ₁ = 0.0846, <i>wR</i> ₂ = 0.1152
Absolute structure parameter	-0.031(4)	-0.027(6)
Largest diff. peak and hole	0.616 and -1.207 e•Å ⁻³	0.827 and -1.250 e•Å ⁻³

5. Anion recognition with Λ -3 and Δ -3



Recognition of carboxylates and a phosphate with Λ -3

Excess amount of a guest (ca. 64 eq.) was added to a CD_2Cl_2 solution of Λ -3 (0.8 mM, 0.7 mL, 1 eq.) and the mixture was stirred at room temperature for 2.5 h under dark conditions. After removal of the residual guest by filtration or centrifugation, ^1H NMR spectrum of the solution was measured.

Chiral recognition of an axially chiral phosphate S1 with Λ -3 and Δ -3

R-(-)-1,1'-binaphthyl-2,2'-diyl sodium phosphate (S1, 0.18 mg, 0.53 μmol , 3 eq.) was added to a CD_2Cl_2 solution of Λ -3 or Δ -3 (0.25 mM, 0.7 mL, 1 eq.) and the mixture was stirred at room temperature for 2.5 h under dark conditions then filtered. ^1H NMR spectra of the solution were measured at 300 K and 283 K.

NMR titration of Λ -1 with $\text{TBA}\cdot\text{NTf}_2$: a general procedure

Λ -3 (0.35 mg, 0.14 μmol) was dissolved in CD_2Cl_2 (1.5 mL). After filtration through a 0.2 μm PTFE membrane, 1 mL of the resulted solution was transferred into an NMR tube. For an NMR titration experiment, each sample containing Λ -3 (1 eq.) and $\text{TBA}\cdot\text{NTf}_2$ (0.5 – 27.0 eq.) was prepared by adding the colorless solution of $\text{TBA}\cdot\text{NTf}_2$ (50 mM in CD_2Cl_2) directly into the NMR tube and mixed well by inverting the tube several times. Other titration experiments were conducted in the same manner.

Table S2. List of titration experiments.

Entry	Titration	
	to	with
1	Λ -3	$\text{TBA}\cdot\text{SbF}_6$
2	Λ -3	$\text{TBA}\cdot\text{NTf}_2$
3	Λ -3	$\text{TBA}\cdot\text{N}(\text{SO}_2\text{Ph})_2$
4	Λ -3	(<i>E</i>)-4

Chemical shift changes in ^1H NMR spectra (Λ -3•carboxylates and Λ -3•phosphate)

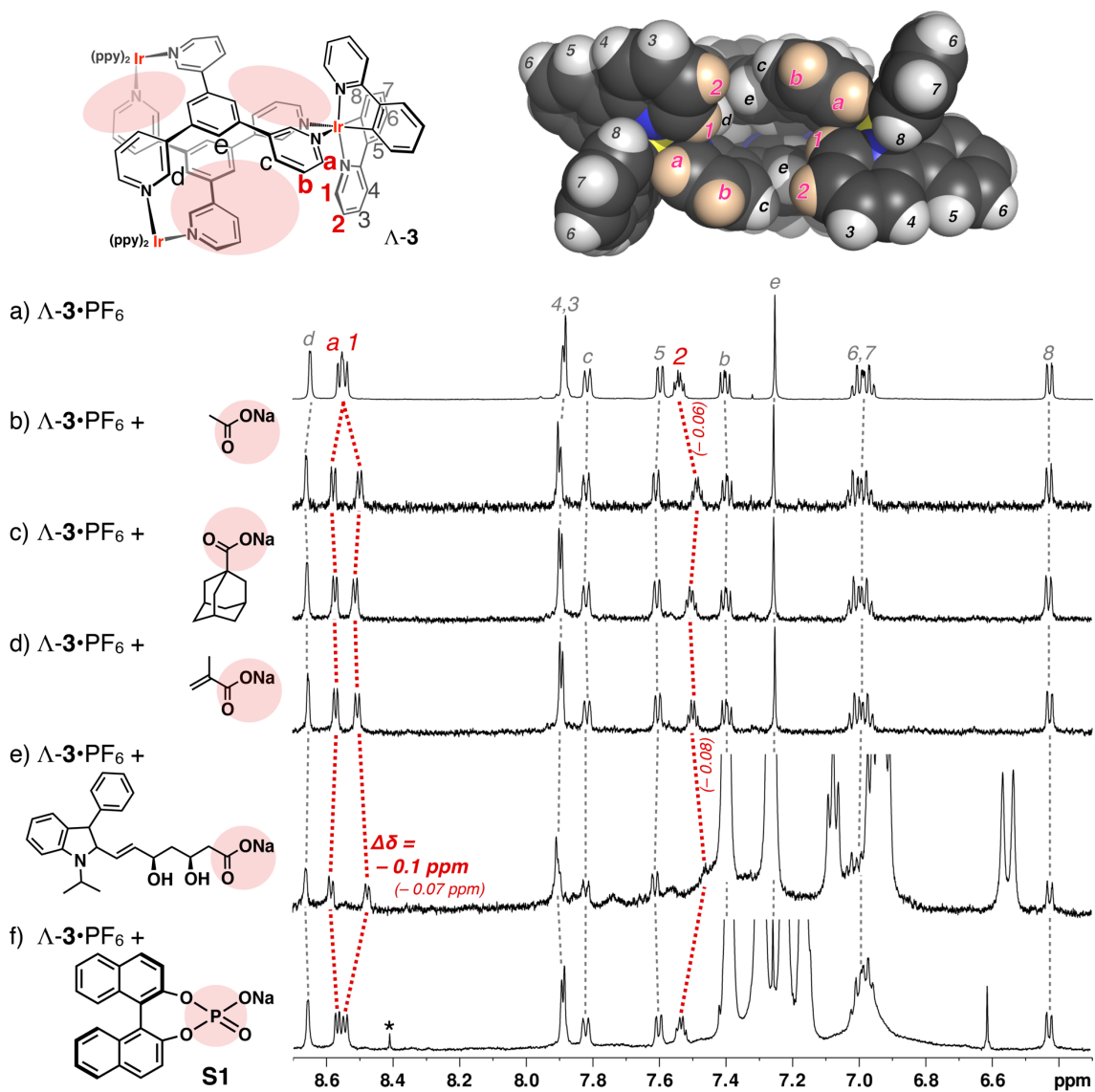


Figure S12. ^1H NMR spectra of a) Λ -3, b–e) Λ -3•carboxylate, f) Λ -3• S1 (CD_2Cl_2 , *: solvent impurity).

Chemical shift changes in ^1H NMR spectra (Λ -3•phosphate and Δ -3•phosphate)

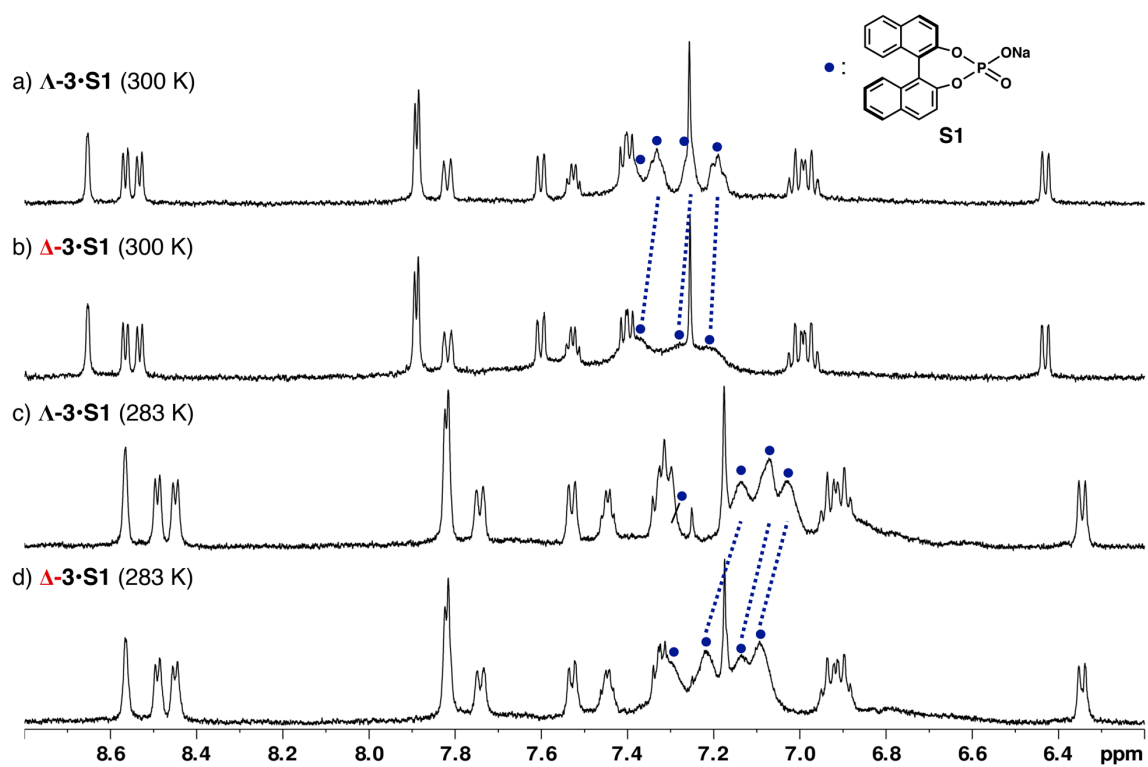


Figure S13. ^1H NMR spectra of a), c) Λ -3•S1, b), d) Δ -3•S1, (a), b) 300 K, c), d) 283 K; CD_2Cl_2)

NMR spectra of the anion titration experiments

Titration of Λ -3 with TBA·SbF₆

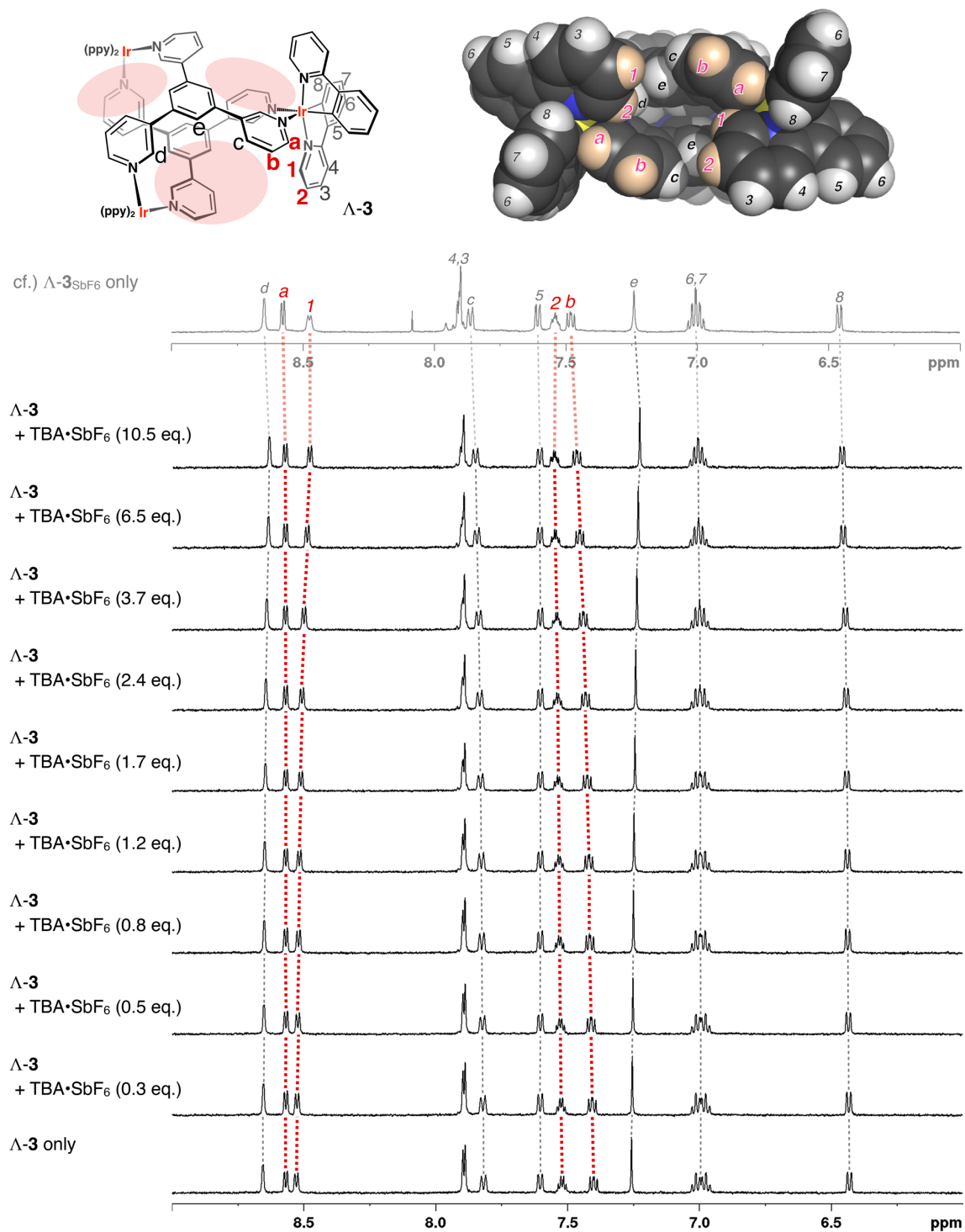


Figure S14. ¹H NMR spectra of Λ -3 titrated with TBA·SbF₆ (CD₂Cl₂).

Titration of Λ -3 with TBA \cdot NTf₂

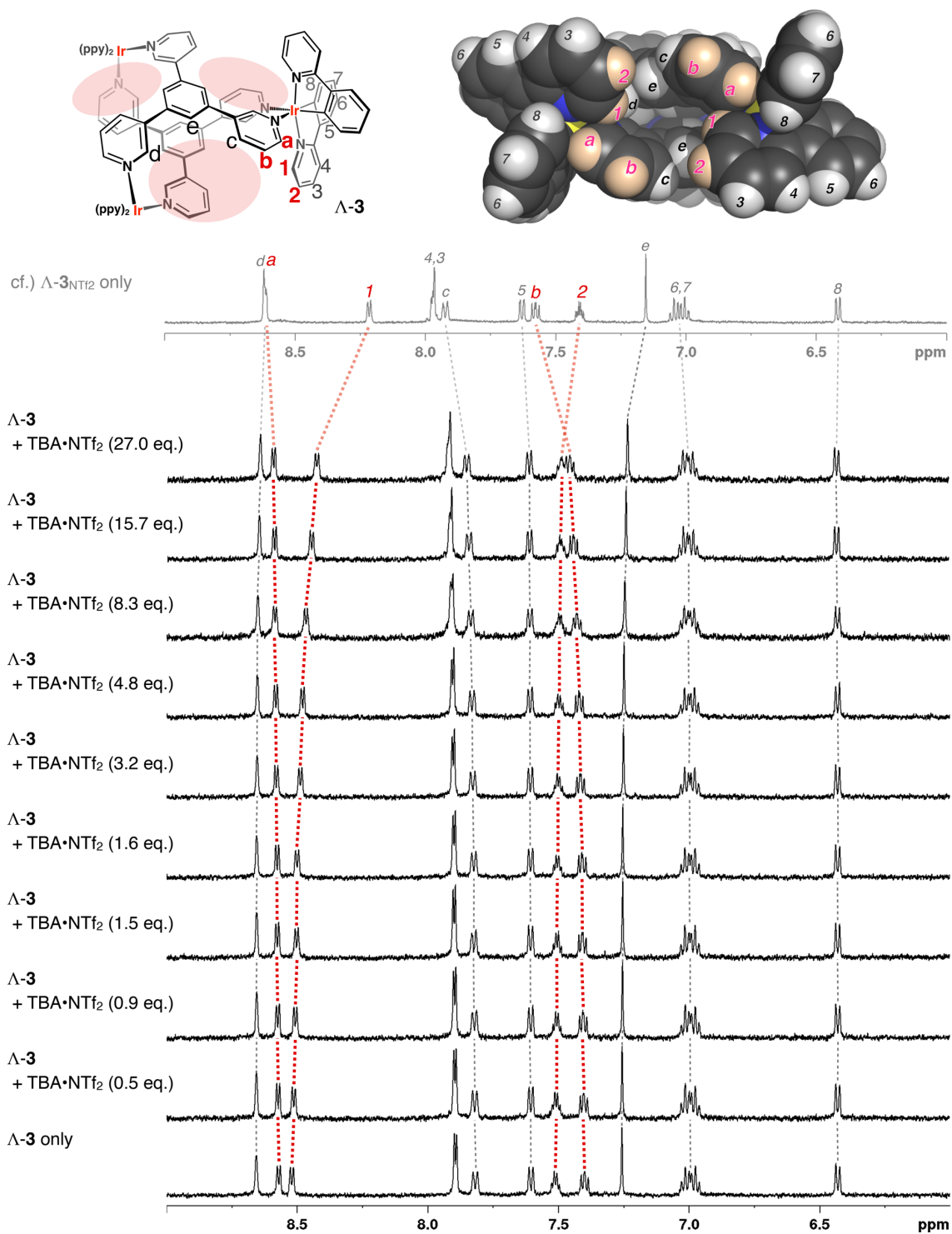


Figure S15. ¹H NMR spectra of Λ -3 titrated with TBA \cdot NTf₂ (CD₂Cl₂).

Titration of Λ -3 with $\text{TBA}\cdot\text{N}(\text{SO}_2\text{Ph})_2$

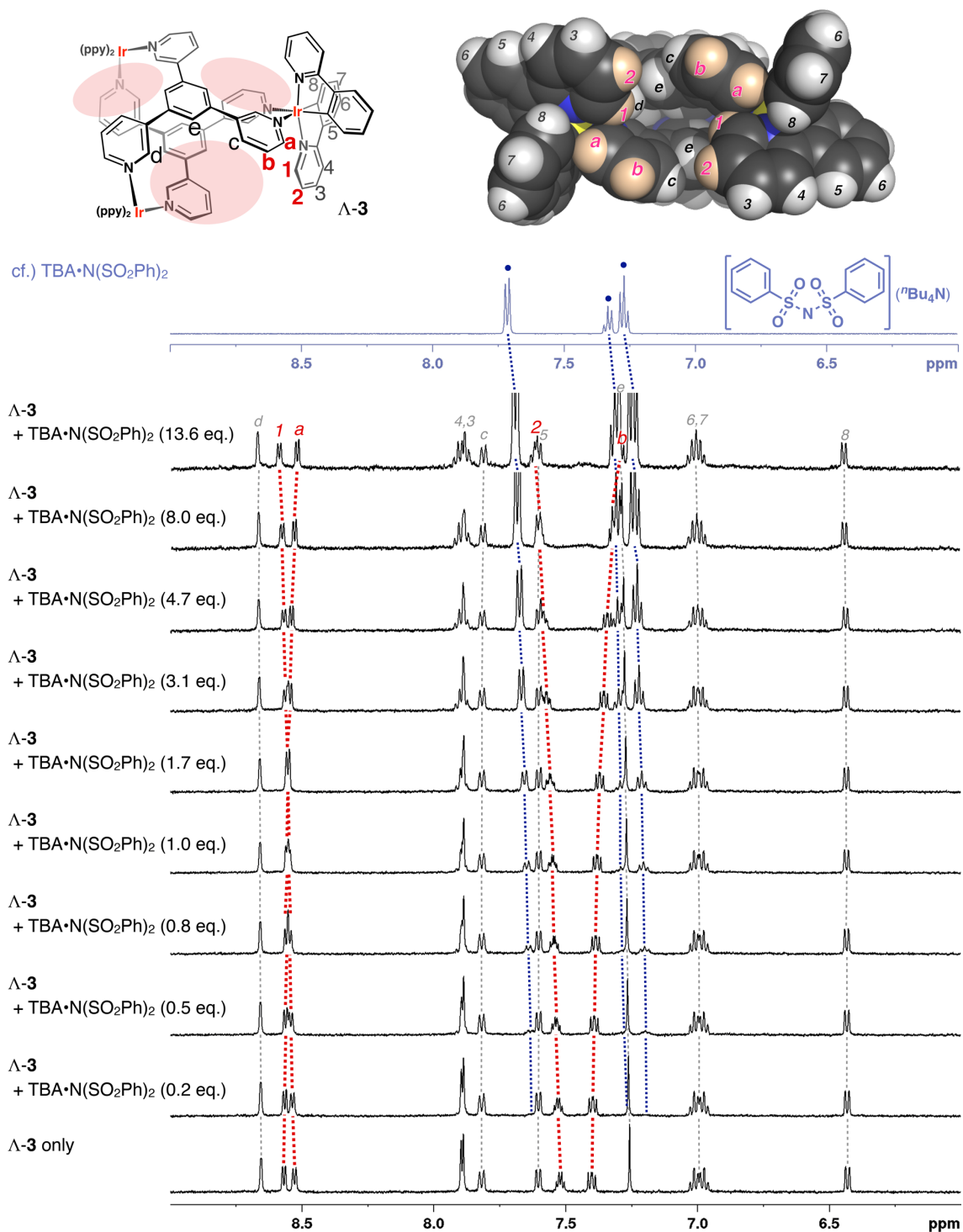


Figure S16. ^1H NMR spectra of Λ -3 titrated with $\text{TBA}\cdot\text{N}(\text{SO}_2\text{Ph})_2$ (CD_2Cl_2).

Titration of Λ -3 with TBA·F₃B–CH=CHPh ((*E*)-4)

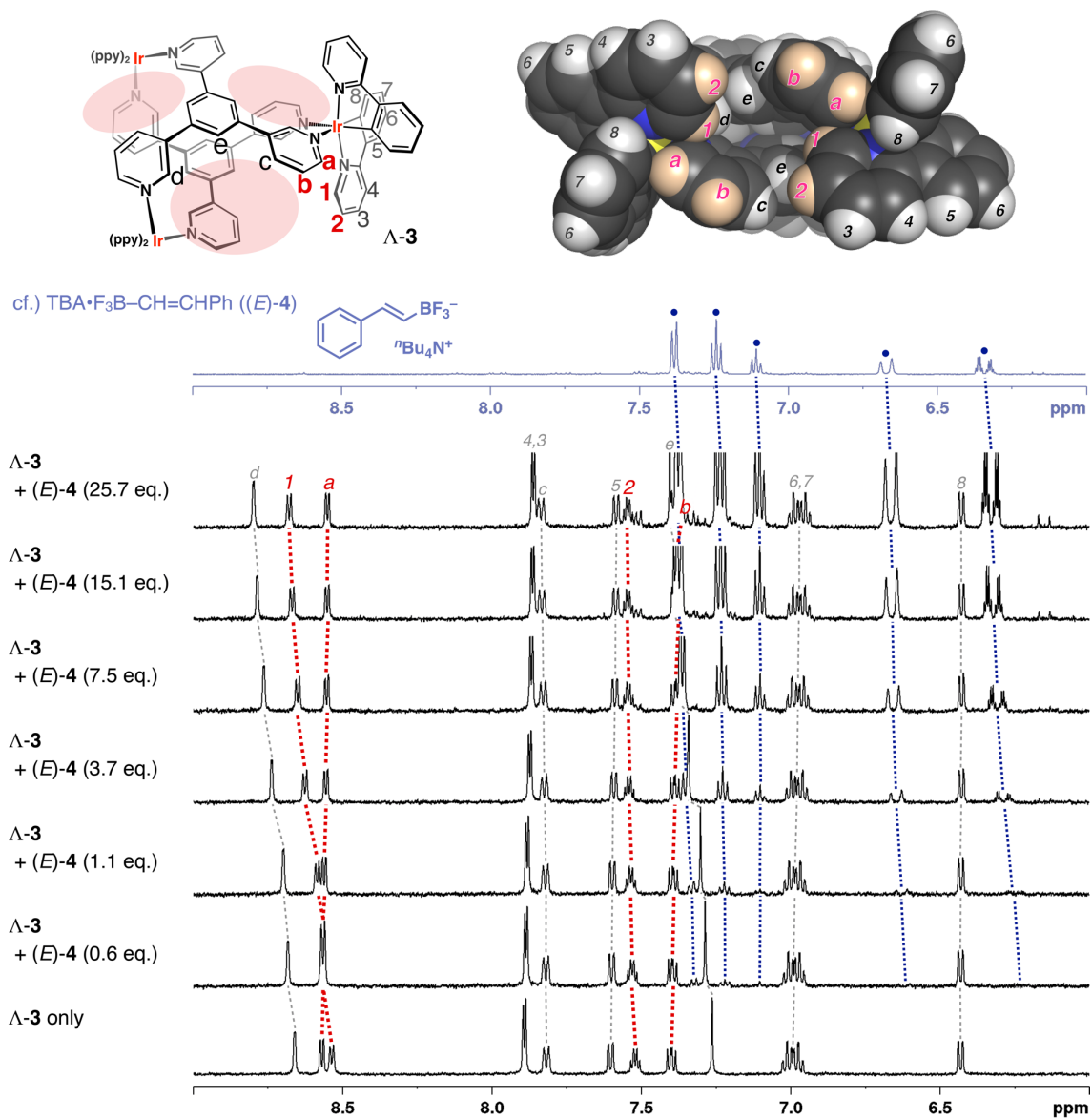


Figure S17. ¹H NMR spectra of Λ -3 titrated with TBA·F₃B–CH=CHPh ((*E*)-4) (CD₂Cl₂).

Determination of the binding constants from the anion titration experiments

The binding constants (the first binding: K_{11} , the second binding: K_{12}) of each anion were determined by fitting the NMR titration data to a 1:2 Host-Guest binding model using the online fitting program Bindfit.^{[S5][S6]} Although host **3** is expected to uptake up to three anions, the fitting curves with a 1:2 binding model showed good compatibility with the experimental results. It probably suggests that the binding of the third anion is weak and negligible.

[Settings for calculation]

Fitter: NMR 1:2

K_{11} guess: 1000 M^{-1}

K_{12} guess: 100 M^{-1}

Flavour: None (Full)

Method: Nelder-Mead

Titration of **A-3** with TBA•SbF₆

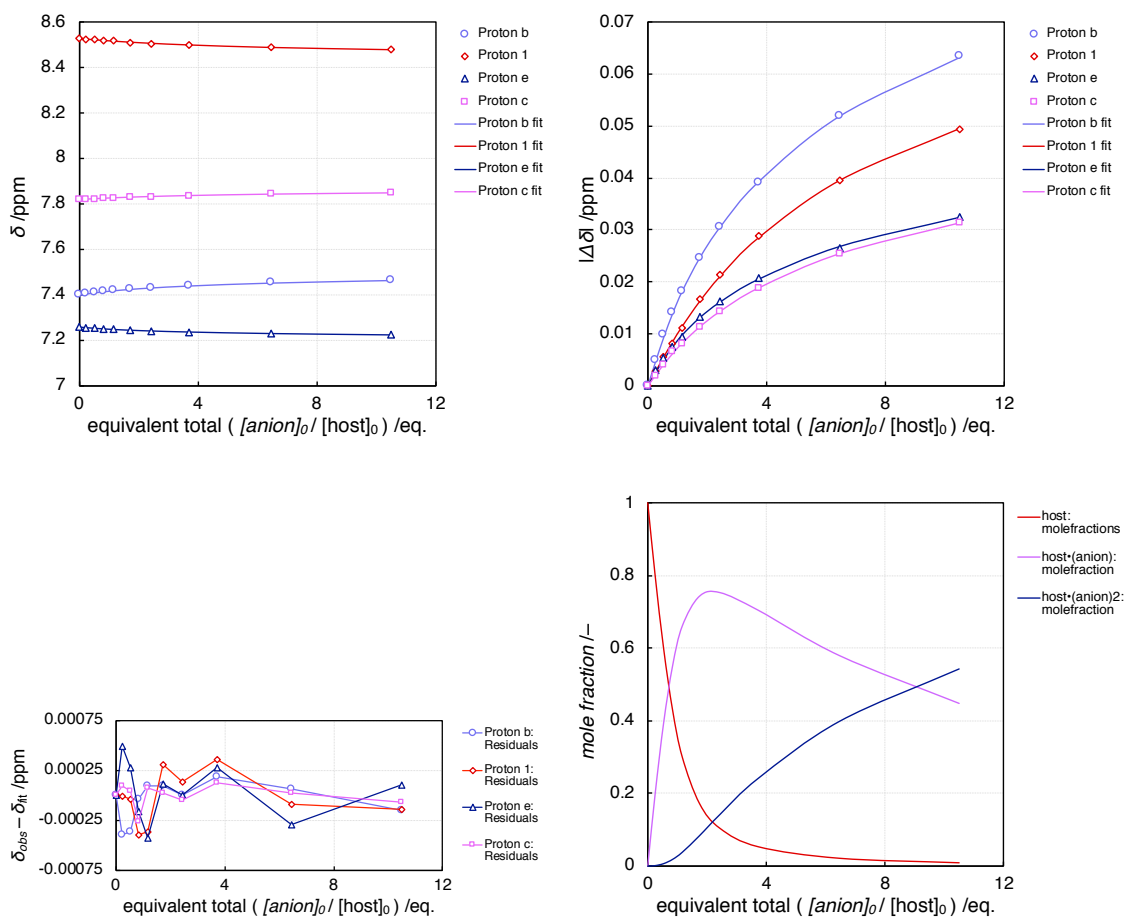


Figure S18. Titration curves for determination of the binding constants for SbF₆⁻.

Titration of Λ -3 with TBA \cdot NTf $_2$

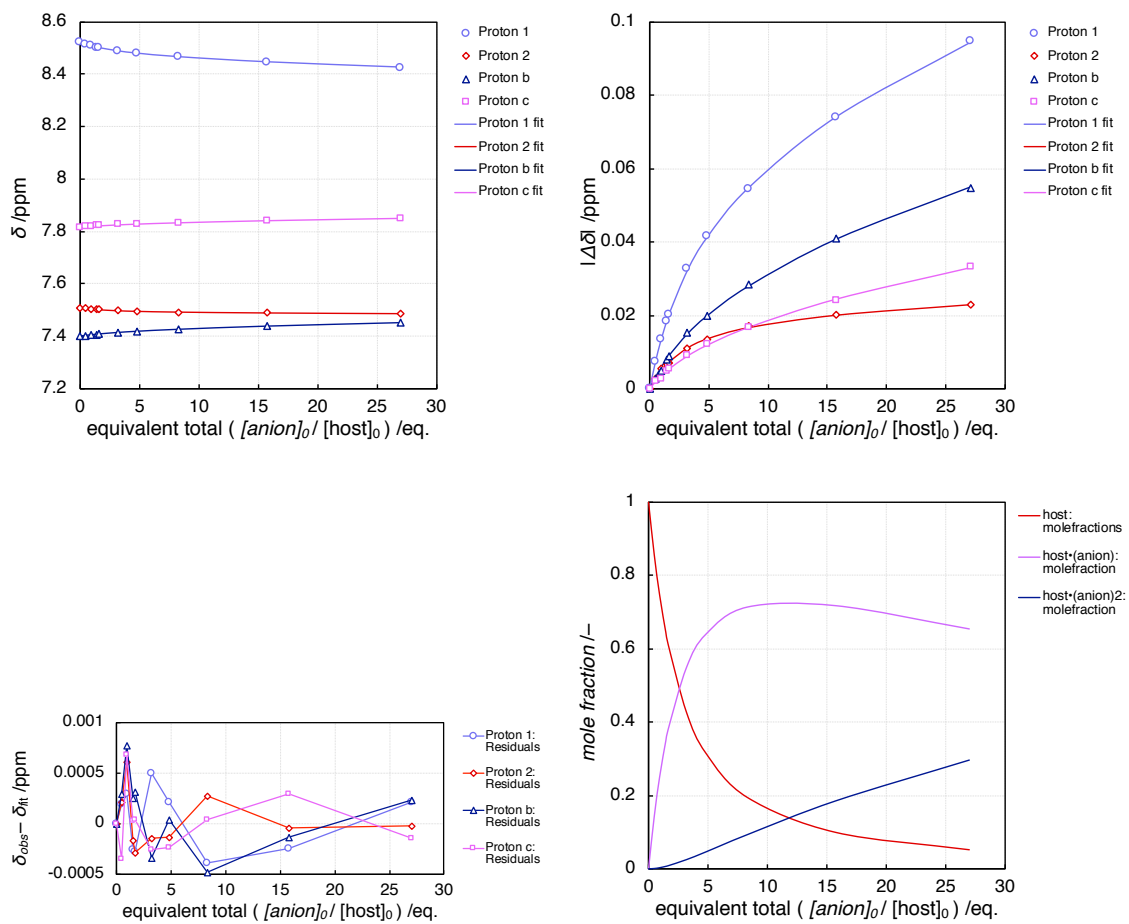


Figure S19. Titration curves for determination of the binding constants for NTf $_2^-$.

Titration of Λ -3 with TBA•N(SO₂Ph)₂

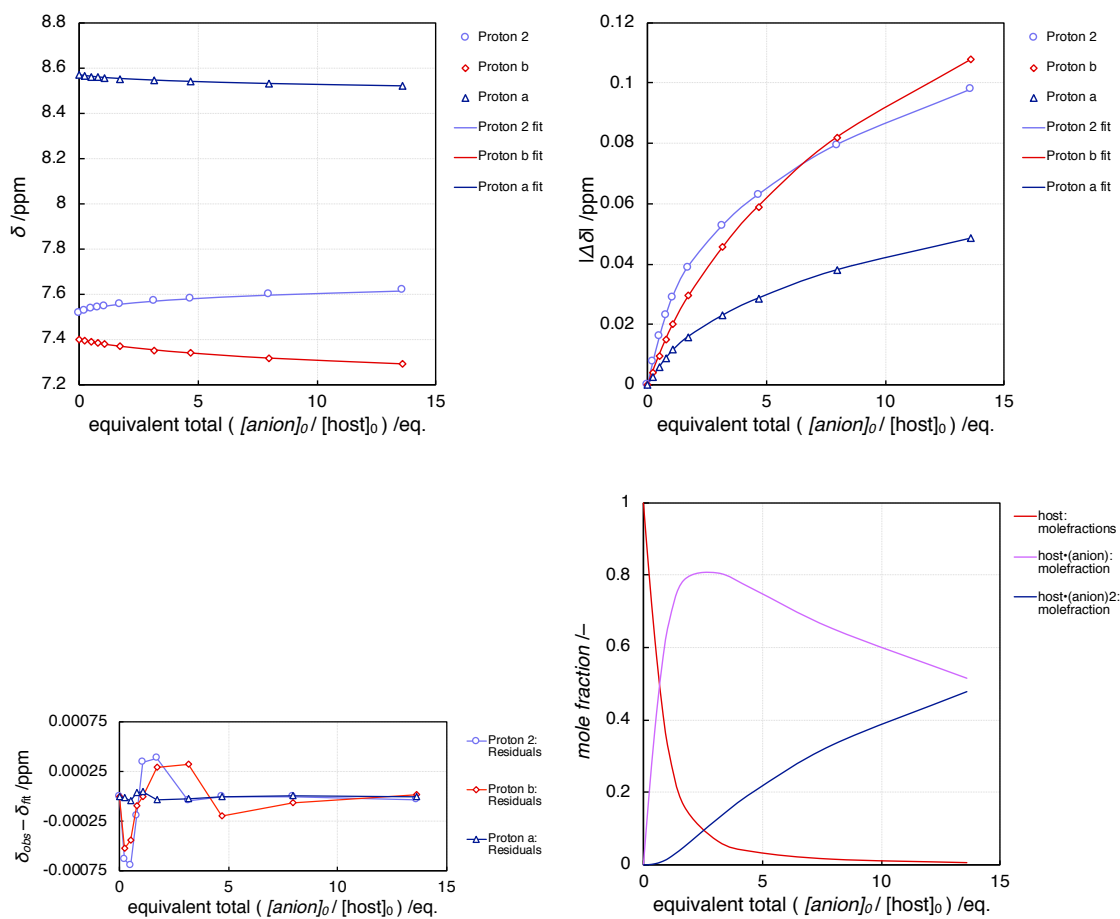


Figure S20. Titration curves for determination of the binding constants for N(SO₂Ph)₂⁻.

Titration of Λ -3 with TBA•F₃B–CH=CHPh ((E)-4)

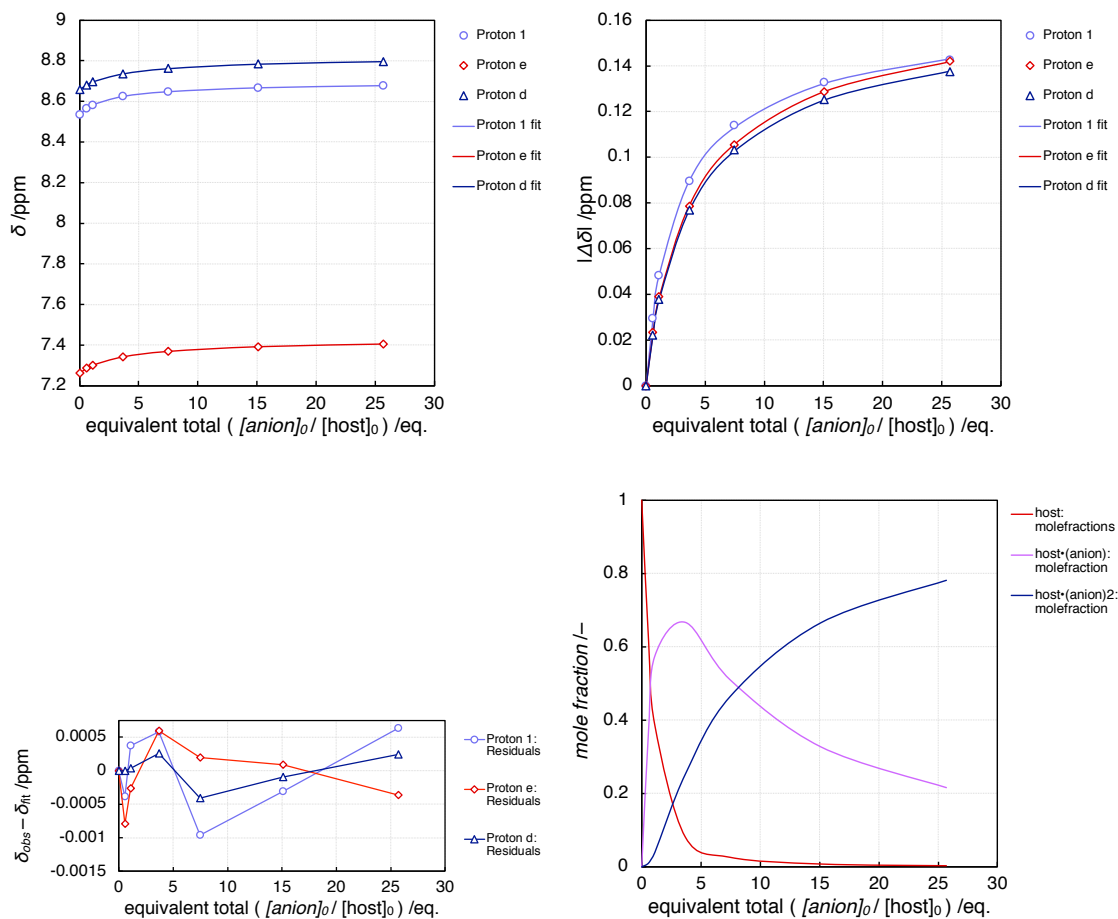


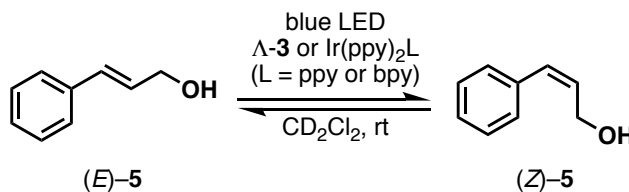
Figure S21. Titration curves for determination of the binding constants for (E)-4.

Table S3. List of the observed binding constants (K_{11} , K_{12}).

Entry	Titrant	Observed binding constants	
		K_{11} [10^3 M^{-1}]	K_{12} [10^3 M^{-1}]
1	TBA•SbF ₆	57 ± 4	1.50 ± 0.02
2	TBA•NTf ₂	5.5 ± 0.1	0.195 ± 0.003
3	TBA•N(SO ₂ Ph) ₂	65 ± 4	0.85 ± 0.01
4	(E)-4	37 ± 2	1.68 ± 0.03

6. Visible-light induced *E-Z* isomerization

(*E*)-cinnamyl alcohol ((*E*)-5)



Reaction with $\Lambda\text{-3}$ (a general procedure): (*E*)-cinnamyl alcohol (**5**) (8.0 μmol , 1.07 mg) was added to a degassed CD_2Cl_2 solution of $\Lambda\text{-3}$ (0.1 mM, 0.8 mL, 1mol%) in a 4 mL screw capped vial filled with Ar. The mixture was stirred at room temperature for 30 min under dark conditions. The solution was then irradiated with blue LED at room temperature. The reaction was monitored for 20 minutes by ^1H NMR and conversions and yields were determined.

Control experiments with other catalysts: The reaction was performed according to the procedure with $\Lambda\text{-3}$. A solution of a mononuclear Ir complex (0.3 mM), Ir(ppy)_3 or $[\text{Ir(ppy)}_2(\text{bpy})](\text{PF}_6)$, was used instead of the solution of $\Lambda\text{-3}$.

Control experiments in the presence of oxygen: The reactions were carried out under an anaerobic condition. The solvent was bubbled with air before adding a catalyst and the substrate.

Physical data of (Z)-5: ^1H NMR (CD_2Cl_2) δ : 7.39 (t, $J = 7.4$ Hz, 2H, ArH), 7.31 (d, $J = 5.9$ Hz, 1H, ArH), 7.26 (d, $J = 7.4$ Hz, 2H, ArH), 6.60 (t, $J = 11.8$ Hz, 1H, CCH), 5.90 (dt, $J = 11.8$ Hz, 5.9 Hz, 1H, CH_2CH), 4.45 (d, $J = 5.9$ Hz, 2H, CH_2)

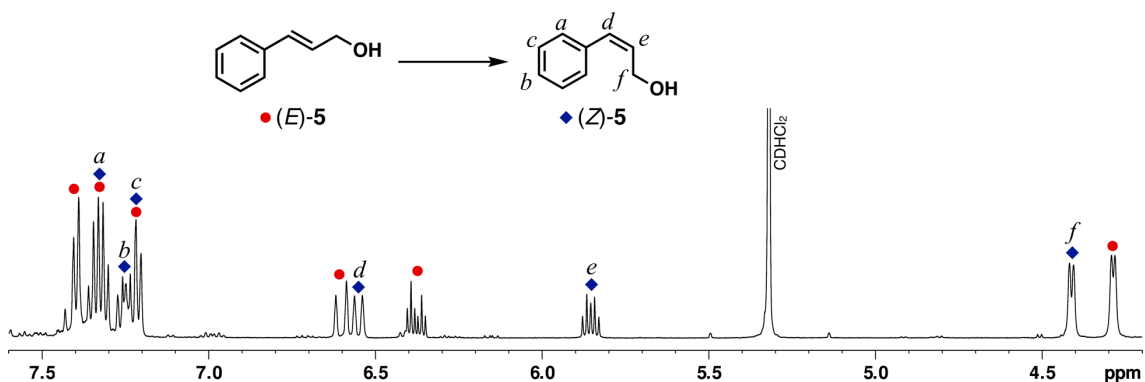
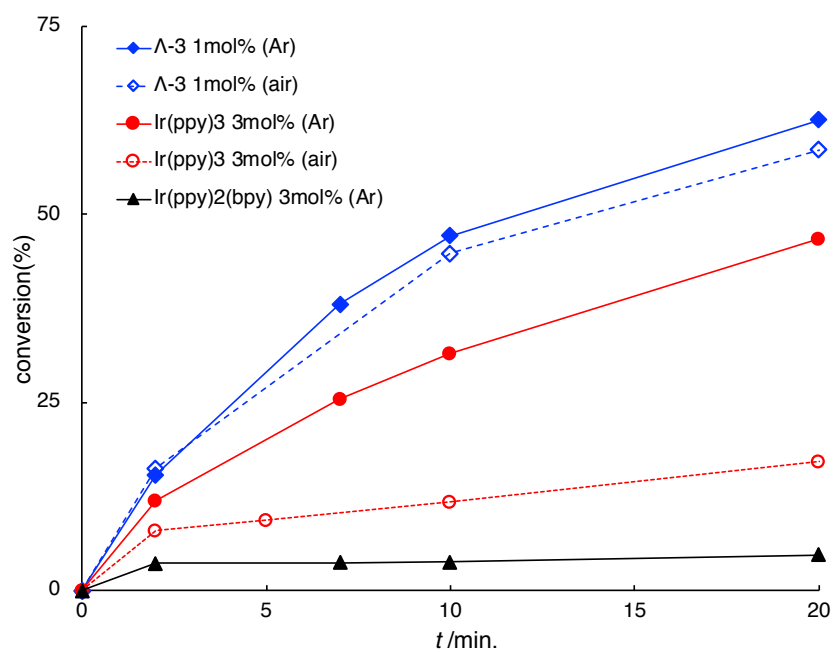


Figure S22. ^1H NMR spectrum after 10 min reaction with 1 mol% $\Lambda\text{-3}$ (CD_2Cl_2).

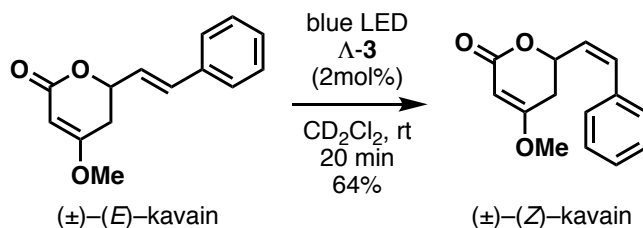
Table S4. List of conversions after photoirradiation of (*E*)-**5** with an Ir catalyst.

Entry	Catalyst	Atmosphere	Cat. load. [mol%]	Ir load. [mol%]	<i>t</i> [min]	Conv. [%]
1	Λ-3	Ar	1	3	20	62
2	Ir(ppy) ₃	Ar	3	3	20	47
3	Ir(ppy) ₂ (bpy)	Ar	3	3	20	5
4	none	Ar	–	–	20	<1
5	Λ-3	air	1	3	20	59
6	Ir(ppy) ₃	air	6	6	20	17
7	none	air	–	–	20	<1
8 ^a	Λ-3	Ar	6	6	20	<1

^a The reaction was conducted in the dark condition

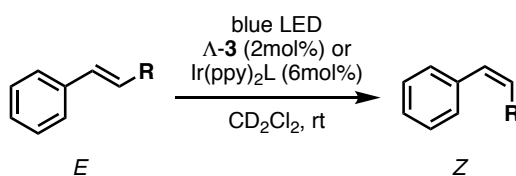
**Figure S23.** Time-conversion plots for the *E*–*Z* isomerization of **5** with 3 mol% Ir.

Other neutral substrates



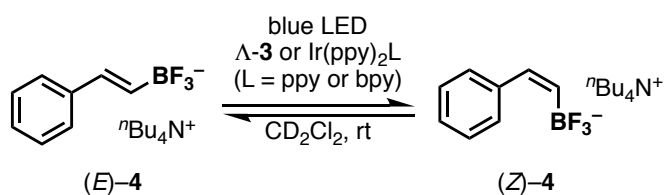
General procedure: $(\pm)\text{-}(E)\text{-kavain}$ (15.0 μmol , 3.45 mg) was added to a degassed CD_2Cl_2 solution of $\Lambda\text{-3}$ (0.2 mM, 1.5 mL, 2mol%) in a 4 mL screw capped vial filled with Ar. The mixture was stirred at room temperature for 20 min under dark conditions. The solution was then irradiated with blue LED at room temperature. Conversions and yields were determined by ^1H NMR analyses of the crude mixtures. In control experiments, a solution of a mononuclear Ir complex (0.6 mM), $\text{Ir}(\text{ppy})_3$ or $[\text{Ir}(\text{ppy})_2(\text{bpy})](\text{PF}_6)$ was used instead of the solution of $\Lambda\text{-3}$.

Table S5. List of yields



Substrate	Catalyst (6 mol% Ir)	t [min]	Yield (Conv.) [%]
R = CH ₂ OH (5)	$\Lambda\text{-3}$	50	73
	$\text{Ir}(\text{ppy})_3$	50	72
	$\text{Ir}(\text{ppy})_2(\text{bpy})$	50	14
R = Me	$\Lambda\text{-3}$	20	77
	$\text{Ir}(\text{ppy})_3$	20	64
	$\text{Ir}(\text{ppy})_2(\text{bpy})$	20	13
R = COOH	$\Lambda\text{-3}$	35	50
	$\text{Ir}(\text{ppy})_3$	35	59
	$\text{Ir}(\text{ppy})_2(\text{bpy})$	35	55
	none	35	3
Piperine	$\Lambda\text{-3}$	30	(41)
$(\pm)\text{-}(E)\text{-kavain}$	$\Lambda\text{-3}$	20	(64)

E-styryltrifluoroborate ((*E*)-4)



Reaction with Λ -3: (*E*)-styryltrifluoroborate (**4**, 8.0 μmol , 3.31 mg) was added to a degassed CD_2Cl_2 solution of Λ -3 (0.1 mM, 0.8 mL, 1mol%) in a 4 mL screw capped vial filled with Ar. The mixture was stirred at room temperature for 5 min under dark conditions. The solution was then irradiated with blue LED at room temperature. The reaction was monitored for 20 minutes by ^1H NMR and conversions and yields were determined.

Control experiments with other catalysts: The reaction was performed according to the procedure with Λ -3. A solution of a mononuclear Ir complex (0.3 mM), Ir(ppy)_3 or $[\text{Ir(ppy)}_2(\text{bpy})](\text{PF}_6)$ was used instead of the solution of Λ -3.

Physical data of (*Z*)-4: ^1H NMR (CD_2Cl_2) δ : 7.64 (d, $J = 7.9$ Hz, 2H, ArH), 7.22 (t, $J = 7.6$ Hz, 2H, ArH), 7.09 (t, $J = 7.3$ Hz, 1H, ArH), 6.63 (br, 1H, CCH), 5.71 (dq, $J = 14.4$ Hz, 6.5 Hz, 1H, CHCHBF₃), 3.14–3.07 (m, 8H, CH₂N), 1.62–1.54 (m, 8H, CH₂CH₂N), 1.40 (tq, $J = 7.4$ Hz, 7.4 Hz, 8H, CH₃CH₂(CH₂)₂N), 0.99 (t, $J = 7.3$ Hz, 12H, CH₃)

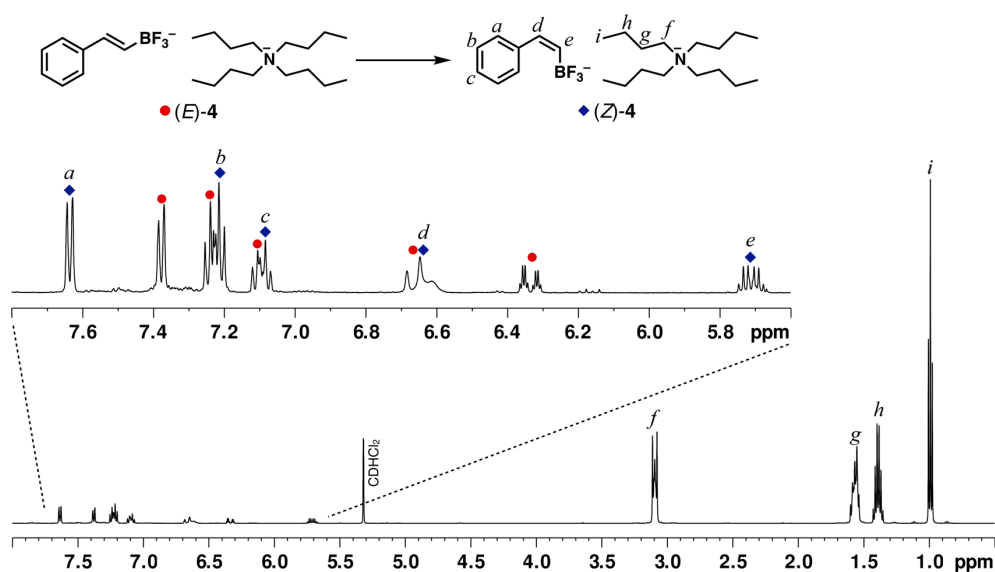


Figure S24. ^1H NMR spectrum after 10 min reaction with 2 mol% Λ -3 (CD_2Cl_2)

Table S6. List of conversions after 5-min photoirradiation for (*E*)-**4** with an Ir catalyst.

Entry	Catalyst	Atmosphere	Cat. load. [mol%]	Ir load. [mol%]	<i>t</i> [min]	Conv. [%]
1	Λ-3	Ar	1	3	5	51
2	Ir(ppy) ₃	Ar	3	3	5	29
3	Ir(ppy) ₂ (bpy)	Ar	3	3	5	6
4	none	Ar	–	–	20	<1
5	Λ-3	air	1	3	5	51
6	Ir(ppy) ₃	air	6	6	5	7
7 ^a	Λ-3	Ar	6	6	20	<1

^a The reaction was conducted in the dark condition

Comparison between Λ-3, Ir(ppy)₃, and Ir(ppy)₂(bpy)

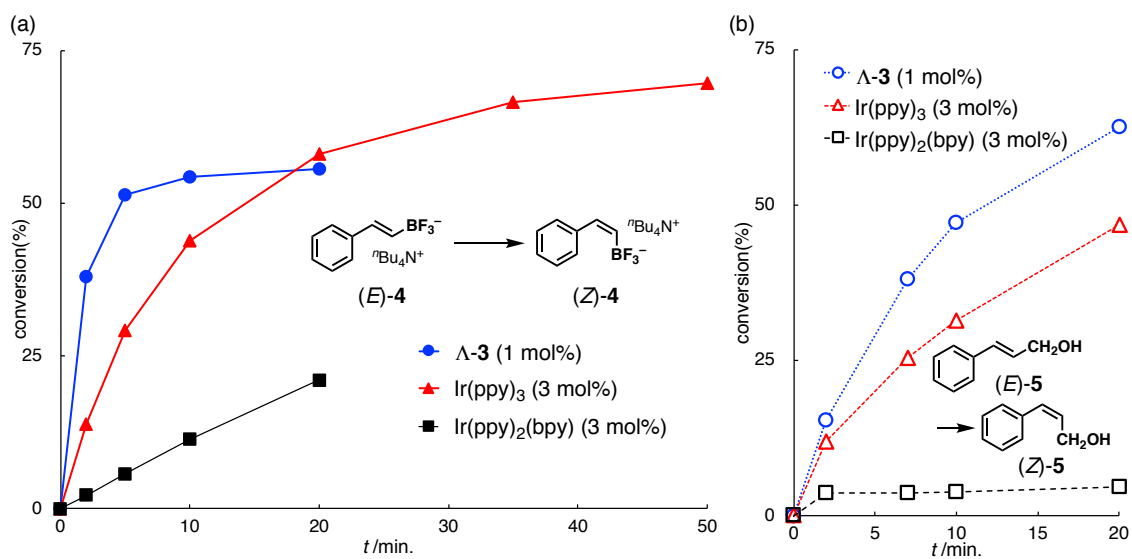


Figure S25. Time-conversion plots for the photo *E*–*Z* isomerizations of (a) **4** and (b) **5** with **Λ-3** (blue), Ir(ppy)₃ (red), and Ir(ppy)₂(bpy) (black).

Investigation on a binding affinity difference between (*E*)-4 and (*Z*)-4 : To a CD₂Cl₂ solution of ~1:1 mixture of (*E*)-4 and (*Z*)-4 (ca. 10 mM, 120 μL) was added a CD₂Cl₂ solution of **Λ-3** (0.1 mM, 0.8 mL), stirred at room temperature for 5 min under dark conditions. The NMR spectrum of the resulting mixture revealed that there are no much differences between (*E*)-4 and (*Z*)-4 in chemical shift changes ($\Delta \delta$) induced by **Λ-3**. This indicates the similar affinities of (*E*)-4 and (*Z*)-4 to **Λ-3**.

a) 1:1 mixture of (*E*)-4 and (*Z*)-4

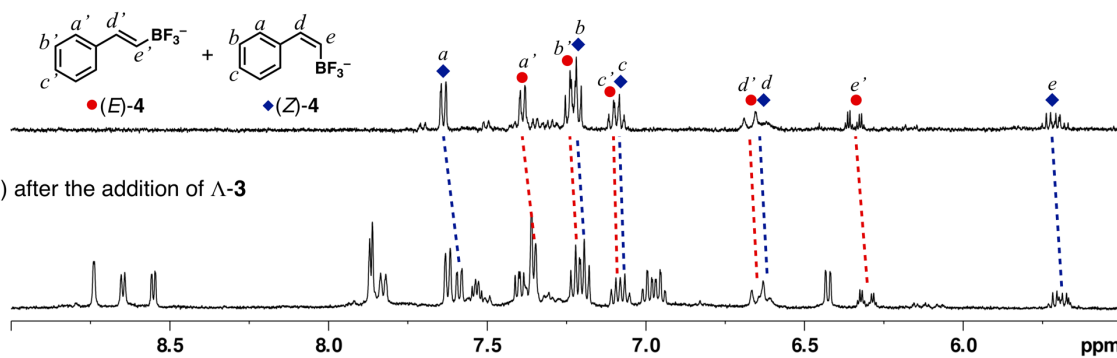
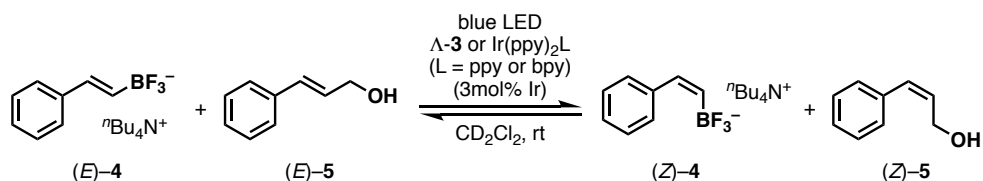


Figure S26. ¹H NMR spectra of ~1:1 mixture of (*E*)-4 and (*Z*)-4 (a) before and (b) after addition of **Λ-3** (CD₂Cl₂).

1:1 mixture of *E*-styryltrifluoroborate (*E*-4) and *E*-cinnamyl alcohol (*E*-5)



Reaction with Λ -3: *E*-styryltrifluoroborate (**4**, 4.0 μmol , 1.65 mg) and (*E*)-cinnamyl alcohol (**5**, 4.0 μmol , 0.54 mg) was added to a degassed CD_2Cl_2 solution of Λ -3 (0.1 mM, 0.8 mL, 1 mol%) in a 4 mL screw capped vial filled with Ar. The mixture was stirred at room temperature for 5 min under dark conditions. The solution was then irradiated with blue LED at room temperature. The reaction was monitored for 20 minutes by ^1H NMR measurements. Conversions were determined by ^1H NMR analyses of the crude mixtures.

Control experiments with other catalysts: The reaction was performed according to the procedure with Λ -3. A solution of a mononuclear Ir complex (0.3 mM), Ir(ppy)_3 or $[\text{Ir(ppy)}_2(\text{bpy})](\text{PF}_6)$ was used instead of the solution of Λ -3.

Table S7. List of molecular ratios and conversions after photoirradiation into a 1:1 mixture of (*E*)-4 and (*E*)-5 with an Ir catalyst.

Cat.	<i>t</i> [min]	Conversion [%]	
		(<i>E</i>)-4 to (<i>Z</i>)-4	(<i>E</i>)-5 to (<i>Z</i>)-5
Λ -3	0	0	0
	2	45	3
	5	56	8
	10	57	17
	20	57	34
Ir(ppy)_3	0	0	0
	2	6	14
	5	14	27
	10	25	43
	20	37	59
$\text{Ir(ppy)}_2(\text{bpy})$	0	0	0
	2	4	0
	5	9	0
	10	16	1
	20	33	4

7. References

- S1. S.-Y. Yao, Y.-L. Ou, B.-H. Ye, *Inorg. Chem.* **2016**, *55*, 6018–6026.
- S2. A. Pun, D. A. Hanifi, G. Kiel, E. O'Brien, Y. Liu, *Angew. Chem. Int. Ed.* **2012**, *51*, 13119–13122.
- S3. M. J. Turner, J. J. McKinnon, S. K. Wolff, D. J. Grimwood, P. R. Spackman, D. Jayatilaka and M. A. Spackman, *CrystalExplorer17* (2017). University of Western Australia. <https://hirshfeldsurface.net>.
- S4. J. J. McKinnon, D. Jayatilaka, M. A. Spackman, *Chem. Commun.*, **2007**, *43*, 3814–3816.
- S5. (a) <http://supramolecular.org>, (b) D. B. Hibbert and P. Thordarson, *Chem. Commun.*, **2016**, *52*, 12792–12805.
- S6. Links to saved fits:
- (a) <http://app.supramolecular.org/bindfit/view/75827ec1-bdf8-4282-b1ae-1638ca3fb15c>,
- (b) <http://app.supramolecular.org/bindfit/view/06f6ee8d-2da1-4c12-9f48-e08daedbf0be>,
- (c) <http://app.supramolecular.org/bindfit/view/1ec773f8-8af1-4bfc-9cfd-89b0dd0808ee>,
- (d) <http://app.supramolecular.org/bindfit/view/d28a47b9-6164-4fa1-b487-5e20bdfb6413>