Supporting Information

On-Demand Hydrogen Production from Formic Acid by Light-Active Dinuclear Iridium Catalysts

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Experimental Procedures

General. All experiments were carried out under a nitrogen atmosphere using standard Schlenk techniques. All solvents were treated with appropriate drying agents, distilled, and stored under nitrogen atmosphere. All the chemicals were purchased from common commercial suppliers. ^{1}H (400 MHz), ^{13}C (100 MHz), and ^{31}P (162 MHz) spectra were acquired on a JEOL JNM-AL400 FT-NMR spectrometers. Solvents for NMR measurements (CD_3OD, $(CD_3)_2CO$, CD_2Cl_2, THF-d_8, CD_3NO_2) were dried over molecular sieves, degassed, and stored under N_2 atmosphere. UV−vis absorption spectra were obtained on a JASCO V-670 spectrometer.

Preparation and spectral data of 1d.

To an acetone (2.0 mL) solution of $[Ir(cod)_2]BF_4$ (49.6 mg, 0.10 mmol), a THF solution (1.2 mL) of xylBINAP (2,2'-Bis[di(3,5-xylyl)phosphino]-1,1'-binaphthyl) (7.27 mg, 0.10 mmol) was added. After stirring for 1.5 h, the red-purple solution was concentrated under vacuum and Et_2O was added for recrystallization. $[Ir(xylBINAP)(cod)]BF_4$ was obtained as red-purple crystal (108.8 mg, 0.097 mmol, 98%).

A methanol (1 mL) solution of $[Ir(xylBINAP)(cod)]BF_4$ (40.0 mg, 0.035 mmol) was degassed by freeze-pump-thaw method, and then 1 atm H_2 gas was introduced. After stirring the solution for 3 h, the solution became cloudy, and Et_2O was directly added to isolate **1d** as yellow powder (27.9 mg, 0.014 mmol, 82%).

^{1}H NMR (400 MHz, CD_2Cl_2, δ / ppm) 8.21 (d, J = 6.0 Hz, 4 H, Ph + naphthyl), 7.80 (brs, 4 H), 7.57 (d, J = 8.0 Hz, 2 H), 7.49 (d, J = 8.0 Hz, 2 H), 7.42 (d, J = 8.0 Hz, 2 H), 7.27-7.39 (m, 6 H), 7.22 (t, J = 6.6 Hz, 4 H), 7.18-7.05 (m, 8 H), 6.86-7.03 (m, 8 H), 6.66 (s, 2 H), 6.27 (s, 2 H), 5.93 (s, 2 H), 2.43 (s, 12 H, C_6H_3-2CH_3), 2.16 (s, 12 H, C_6H_3-2CH_3), 1.79 (s, 12 H, C_6H_3-2CH_3), 0.92 (s, 12 H, C_6H_3-2CH_3), -6.78 (d, J = 74.4 Hz, 2 H, Ir-H), -7.78 (t, J = 63.8 Hz, 1 H, Ir-H), -21.12 (brs, 2 H, Ir-H)

^{31}P{^{1}H} NMR (162 MHz, acetone-d_6, δ / ppm) 34.4, 22.5 (br).

^{13}C (100MHz, CD_2Cl_2, δ / ppm) 139.0–122.0 (*Ar*), 20.22 (Ar-*C*H$_3$), 20.13 (Ar-*C*H$_3$), 20.04 (Ar-*C*H$_3$), 19.03 (Ar-*C*H$_3$).

Anal. Calcd. for $C_{104}H_{101}Ir_2P_4BF_4\cdot CH_2Cl_2$: C, 62.09; H, 5.11. Found: C, 62.00; H, 5.30.

Preparation and spectral data of 1e.

To a acetone (2.0 mL) solution of $[Ir(cod)_2]BF_4$ (46.5 mg, 0.094 mmol), a THF (1.5 mL) solution of DADMP-BINAP(2,2'-Bis[bis(4-dimethylamino-3,5-dimethylphenyl)phosphino]-1,1'-binaphthyl) (81.0 mg, 0.089 mmol) was added. After stirring for 1.5 h, the red-purple solution was concentrated under vacuum and Et_2O and hexane was added for precipitation. $[Ir(DADMP-BINAP)(cod)]BF_4$ was obtained as red powder (113.6 mg, 0.087 mmol, 97%).

A methanol (1 mL) solution of $[Ir(DADMP-BINAP)(cod)]BF_4$ (61.1 mg, 0.047 mmol) was degassed by freeze-pump-thaw method, and then 1 atm H_2 gas was introduced. After stirring the solution for 3 h, Et_2O and hexane was added to isolate **1e** as yellow powder (47.8 mg, 0.021 mmol, 89%).

^{1}H NMR (400 MHz, MeOH-d_4, δ / ppm) 8.33 (d, J = 12.0 Hz, 4 H, Ph + naphthyl), 7.60-7.69 (m, 4 H), 7.47 (d, J = 8.0 Hz, 2 H), 7.35-7.44 (m, 6 H), 7.14-7.43 (m, 12 H), 6.96 (s, 2 H), 6.89 (d, J = 4.8 Hz, 2 H), 6.70 (s, 4 H), 7.18-7.05 (m, 8 H), 6.86-7.03 (m, 8 H), 6.66 (s, 2 H), 6.27 (s, 2 H), 5.93 (s, 2 H), 2.93 (s, 26 H, N-2CH_3), 2.65 (s, 12 H, N-2CH_3), 2.49 (s, 12 H, N-2CH_3), 2.29 (s, 14 H, C_6H_3-2CH_3), 2.01 (s, 12 H, C_6H_3-2CH_3), 1.89 (s, 12 H, C_6H_3-2CH_3),0.88 (brs, 10H, C_6H_3-2CH_3) -6.92 (d, J = 74.4 Hz, 2 H, Ir-H), -7.74 (t, J = 63.8 Hz, 1 H, Ir-H), -20.95 (brs, 2 H, Ir-H)

^{31}P{^{1}H} NMR (162 MHz, acetone-d_6, δ / ppm) 34.6, 20.1 (br).

Anal. Calcd. for $C_{120}H_{141}Ir_2P_4N_8BF_4\cdot 3H_2O$: C, 61.47; H, 6.32; N, 4.78. Found: C, 61.14; H, 5.92; N, 4.58.

Preparation and spectral data of monoformate complex **A**^{a}.

To a MeOH (1.5 mL) solution of **1a** (25.9 mg, 15.0 mmol), HCOOH (2.3 µL, 4.0 eq) was added and irradiated (395 nm) for 15 minutes. The solvent was removed under reduced pressure to yield **A**^{a} as yellow powder quantitatively.

^{1}H NMR (400 MHz, acetone-d_6, δ / ppm) 8.77 (d, *J* = 14.8 Hz, 2 H, Ar), 8.34-8.25 (m, 4 H, Ar), 7.85 (brs, 1 H, OC*H*O), 7.71-7.21 (m, 26 H, Ar), 7.18-7.00 (m, 14 H, Ar), 6.95-6.72 (m, 8 H, Ar), 6.65 (d, *J* = 7.6 Hz, 2H, Ar), 6.48 (d, *J* = 8.4 Hz, 2 H, Ar), 6.42 (t, *J* = 7.5 Hz, 2 H, Ar), 6.25 (d, *J* = 8.4 Hz, 2 H, Ar), 6.18 (t, *J* = 7.5 Hz, 2 H, Ar), -8.43 (dt, J_{PH} = 64 Hz, 2 H, Ir-*H*), -21.03 (m, 2 H, Ir-*H*).

^{31}P{^{1}H} NMR (162 MHz, acetone-d_6, δ / ppm) 15.0, 6.1.

Preparation and spectral data of monoformate complex **B**^{a}.

Complex **1a** (40.0 mg, 23.2 mmol) was dissolved into HCOOH (0.5 mL) and irradiated (395 nm) for 6 h. The solvent was removed under reduced pressure to yield **B**^{a} as yellow powder quantitatively.

^{1}H NMR (400 MHz, acetone-d_6, δ / ppm) 7.92-7.87 (m, 3 H, OC*H*O + Ar), 7.83-7.76 (m, 4 H, Ar), 7.66-7.47 (m, 22 H, Ar), 7.42-7.32 (m, 6 H, Ar), 7.30-7.09 (m, 5 H, Ar), 6.79-6.57 (m, 6 H, Ar), 6.53-6.43 (m, 8 H, Ar), 6.25-6.19 (m, 4 H, Ar), -13.14 (dt, J_{PH} = 58 Hz, 2 H, Ir-*H*), -24.70 (s, 2 H, Ir-*H*).

^{31}P{^{1}H} NMR (162 MHz, acetone-d_6, δ / ppm) 5.3, -9.1.

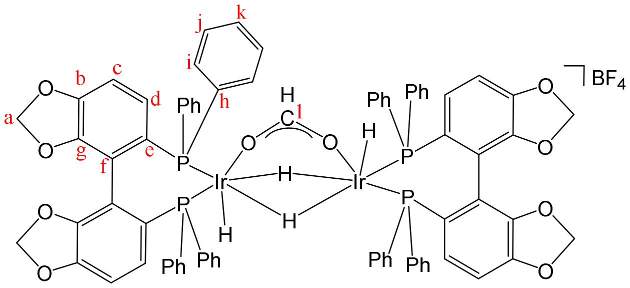
Preparation and spectral data of monoformate complex **A**^{c}.

The monoformate complex **A**^{c} was prepared as the same procedure as that for **A**^{a}.

^{1}H NMR (400 MHz, acetone-d_6, δ / ppm) 7.97-7.25 (m, 38 H, Ar), 7.04-6.92 (m, 12 H, Ar), 6.82 (t, *J* = 8.0 Hz, 4H, Ar), 6.69-6.59 (m, 4 H), 6.47 (d, *J* = 8.0 Hz, 4 H, Ar), 6.23 (m, 2 H, Ar), 6.02(s, 2 H, methyl), 5.98 (s, 2 H, methyl), 5.85 (s, 6 H, methyl), -8.39 (dt, *J* = 64.2 Hz, *J* = 9.2 Hz, 2 H, Ir-H), -21.45 (t, *J* = 17.6 Hz, 2 H, Ir-H).

^{31}P{^{1}H} NMR (162 MHz, acetone-d_6, δ / ppm) 13.87 (brs), 6.17 (brs).

^{13}C NMR (100.8 MHz, acetone-d_6, δ / ppm) 174.9 (s, l (OCHO)), 149.7 (d, $J_{C\text{-}O}$ = 15.3 Hz, b), 147.2 (d, $J_{C\text{-}O}$ = 13.5 Hz, g), 146.9 (d, $J_{C\text{-}O}$ = 14.0 Hz, g), 134.9 (d, $J_{C\text{-}P}$ = 10.6 Hz, h), 134.6 (d, $J_{C\text{-}P}$ = 11.5 Hz, h), 133.8(d, $J_{C\text{-}P}$ = 8.7 Hz, h), 133.2 (d, $J_{C\text{-}P}$ = 10.6 Hz, h), 131.5, 131.2, 130.8, 130.4, 130.2, 130.0 (s, i), 129.3-127.6 (m, d, f, j), 126.9(d, $J_{C\text{-}P}$ = 8.7 Hz, e), 125.8 (d, $J_{C\text{-}P}$ = 8.4 Hz, e), 125.3,124.7, 123.8, 123.2 (s, k), 117.9, 117.2 (m, c), 107.5–107.9 (m, a), 102.2 (s, a), 102.1 (s, a).



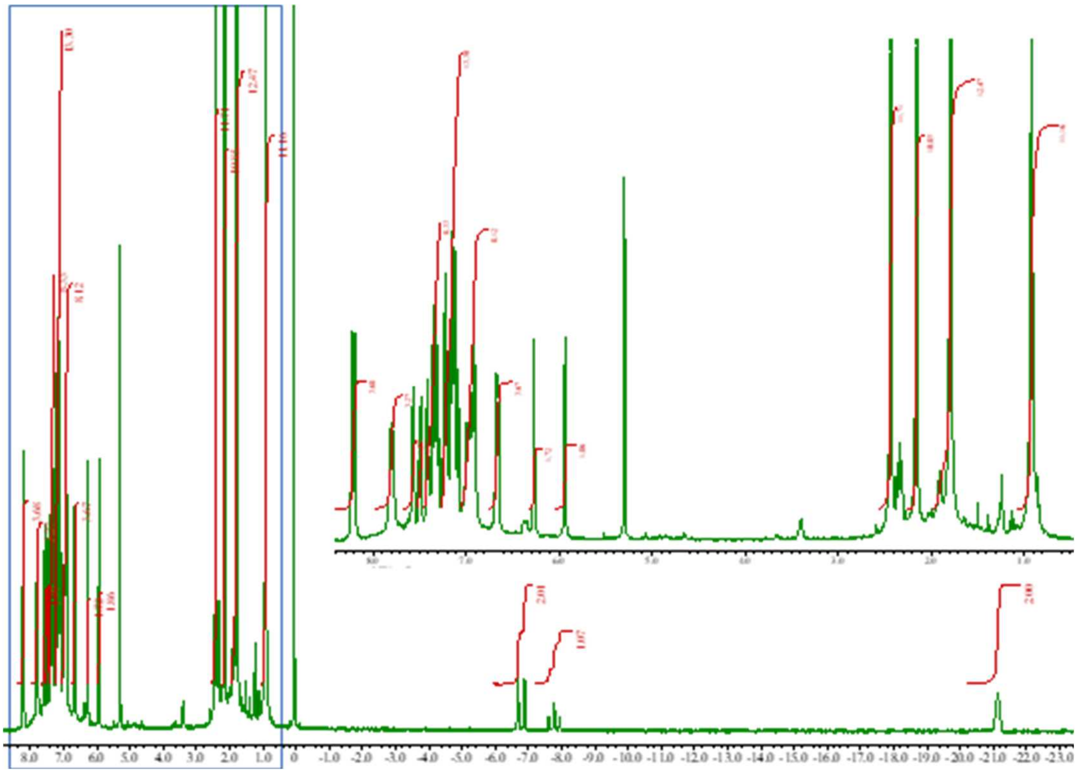


Figure S1. ^{1}H NMR spectra of **1d** (400 MHz, CD_2Cl_2, r.t.).

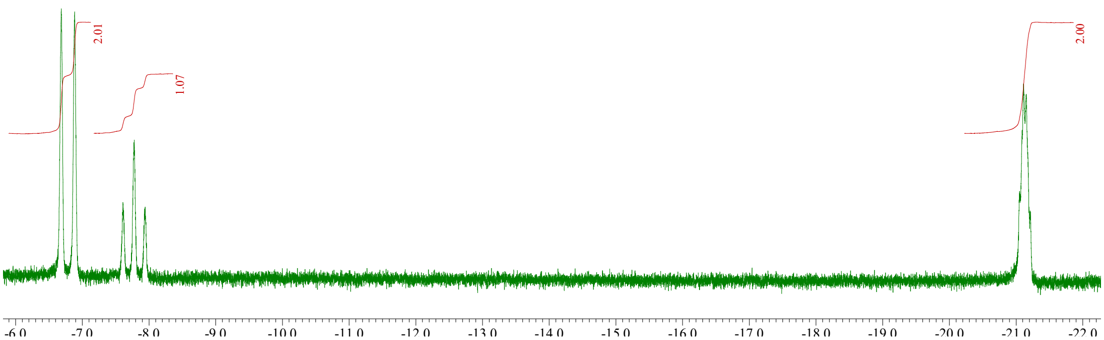


Figure S2. ^{1}H NMR spectra of hydride region of **1d** (400 MHz, CD_2Cl_2, r.t.).

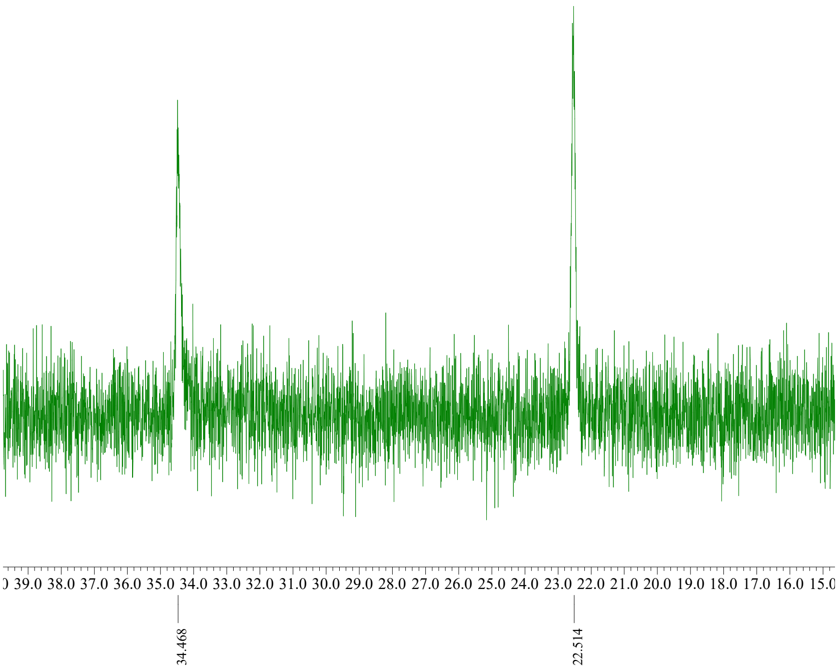


Figure S3. ^{31}P NMR spectra of **1d** (161.8 MHz, CD_2Cl_2, r.t.).

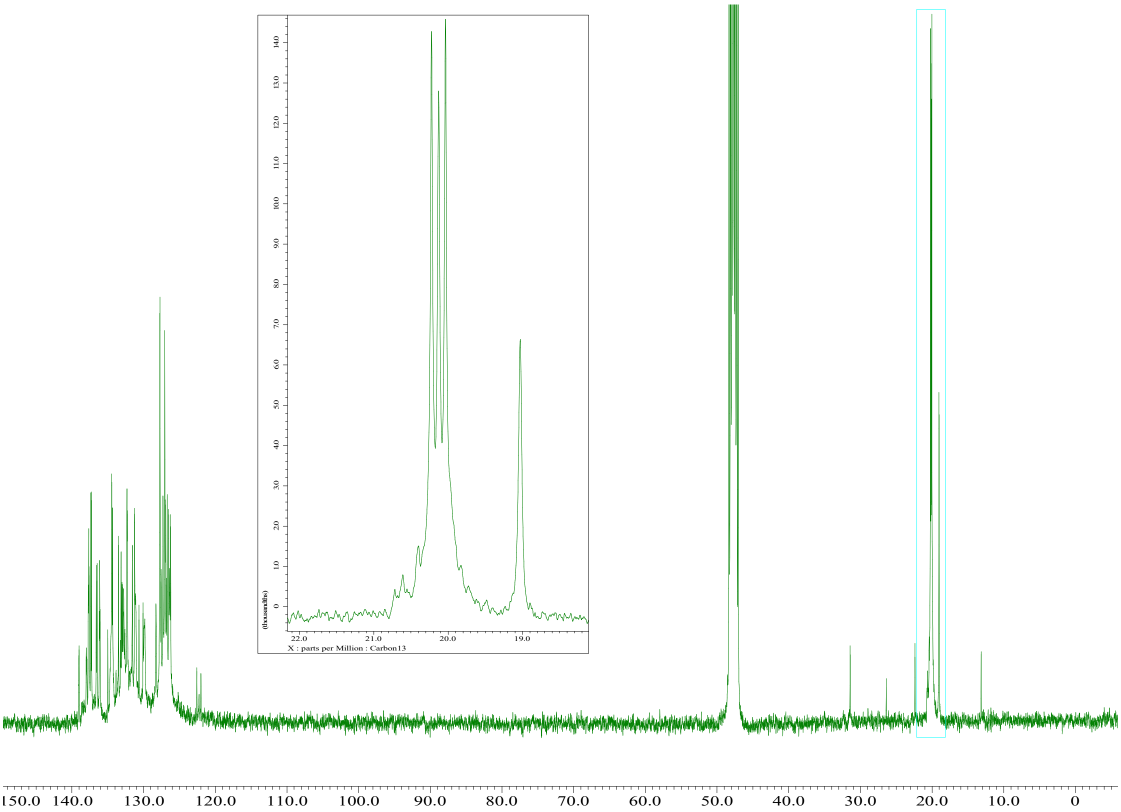


Figure S4. ^{13}C NMR spectra of **1d** (100 MHz, CD_2Cl_2, r.t.).

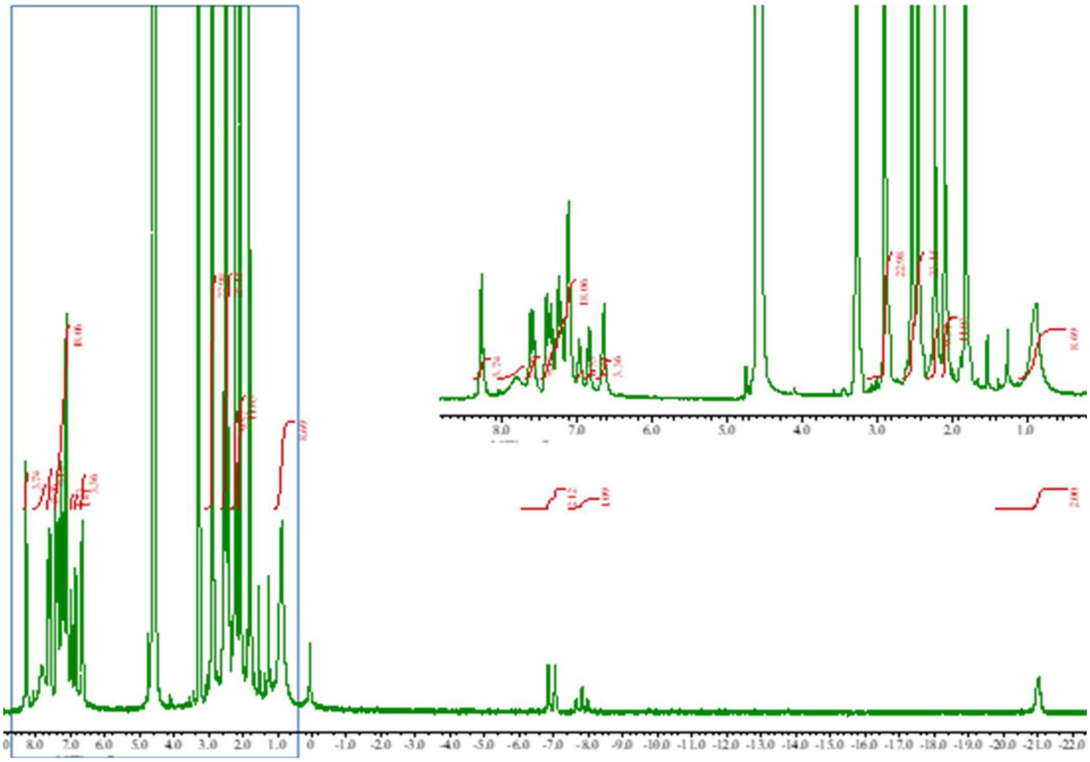


Figure S5. ^{1}H NMR spectra of **1e** (400 MHz, MeOH-d_4, 323 K).

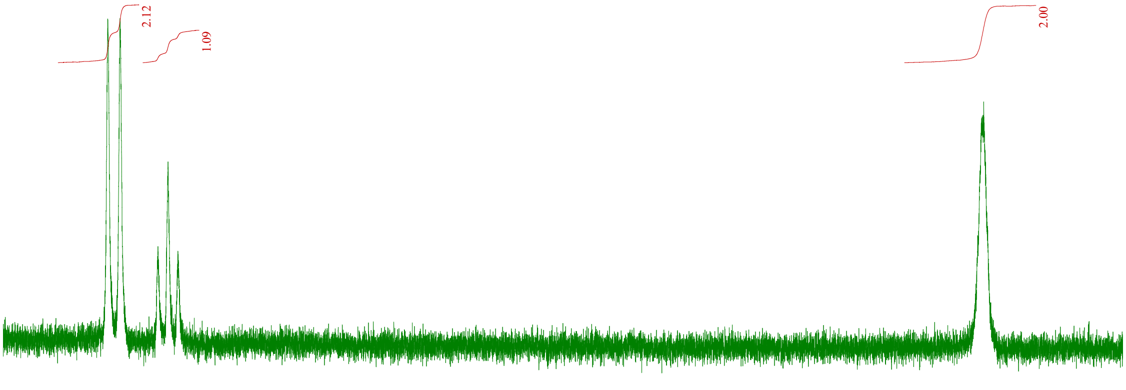


Figure S6. ^{1}H NMR spectra of hydride region of **1e** (400 MHz, MeOH-d_4, 323 K).

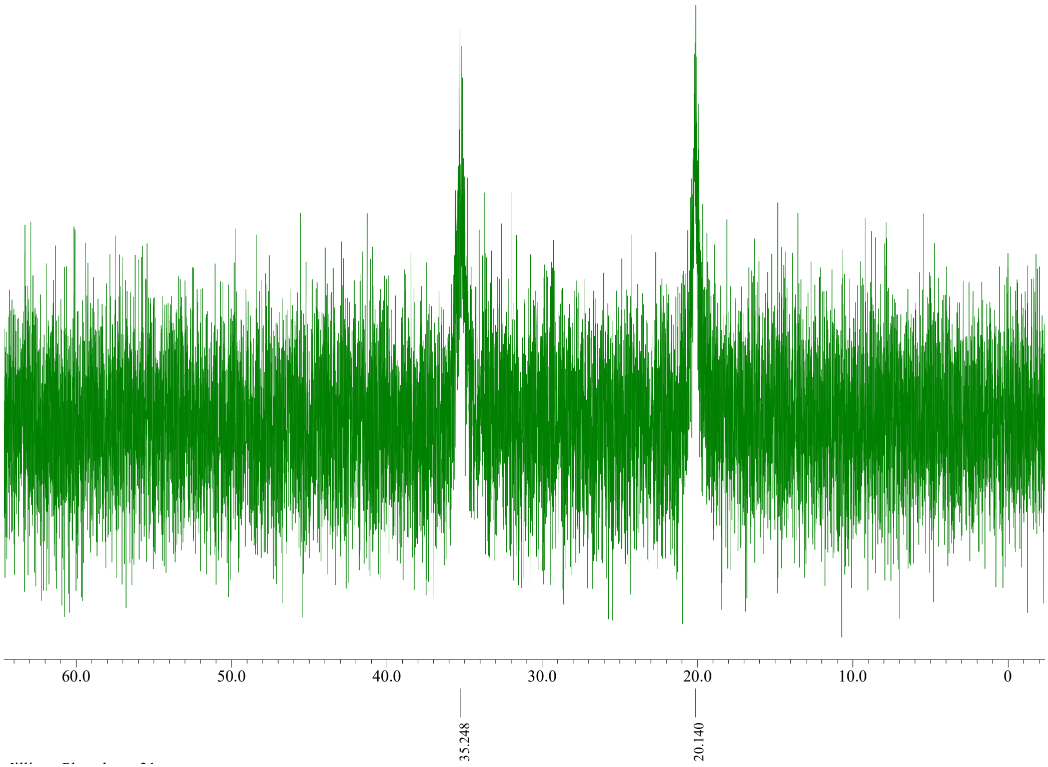


Figure S7. ^{31}P NMR spectra of **1e** (161.8 MHz, MeOH-d_4, r.t.).

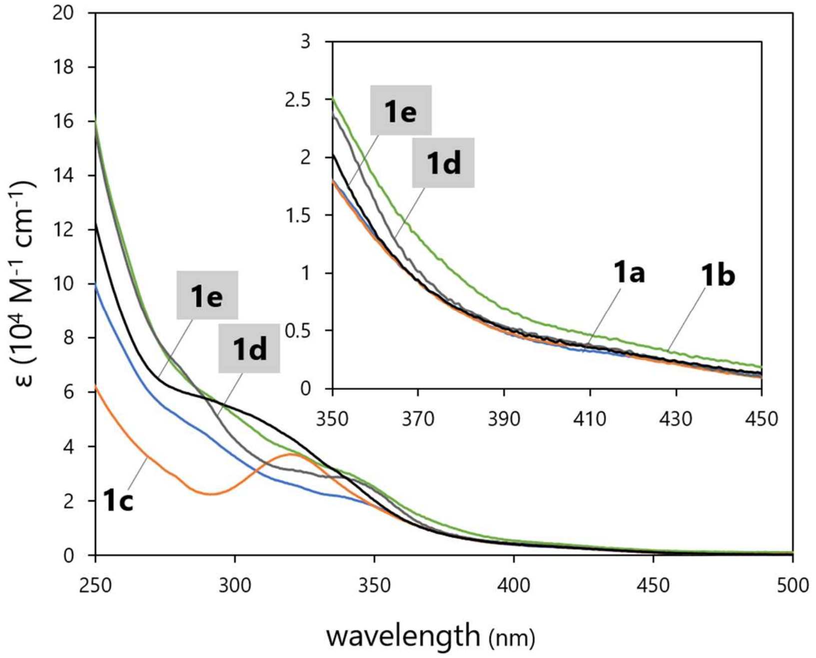


Figure S8. UV-vis absorption spectra of **1a-e** measured in CD_2Cl_2 at r.t.

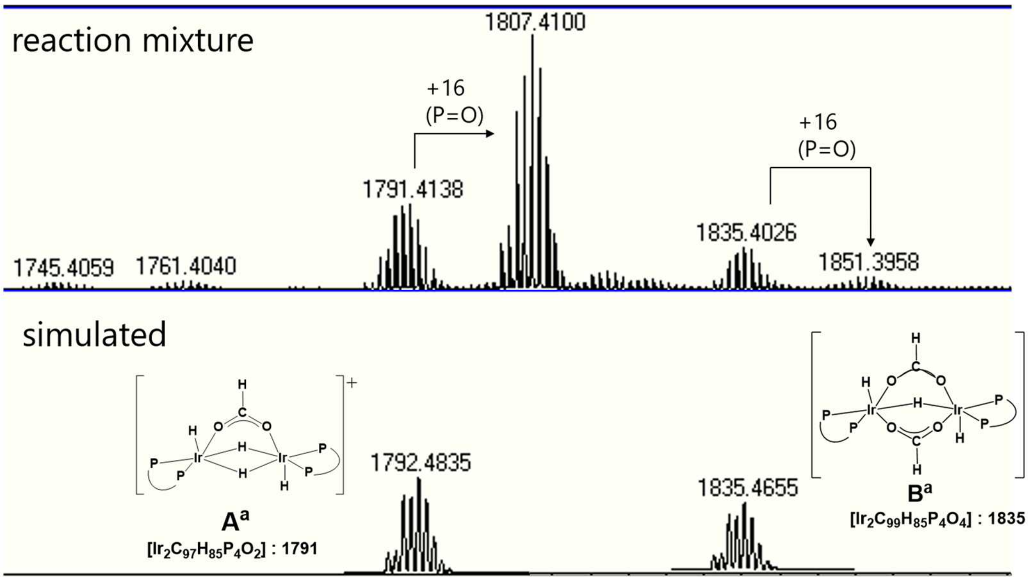


Figure S9. ESI-MS spectra of the reaction mixture of the photocatalytic reaction by **1a** (CH_3CN, r.t.).

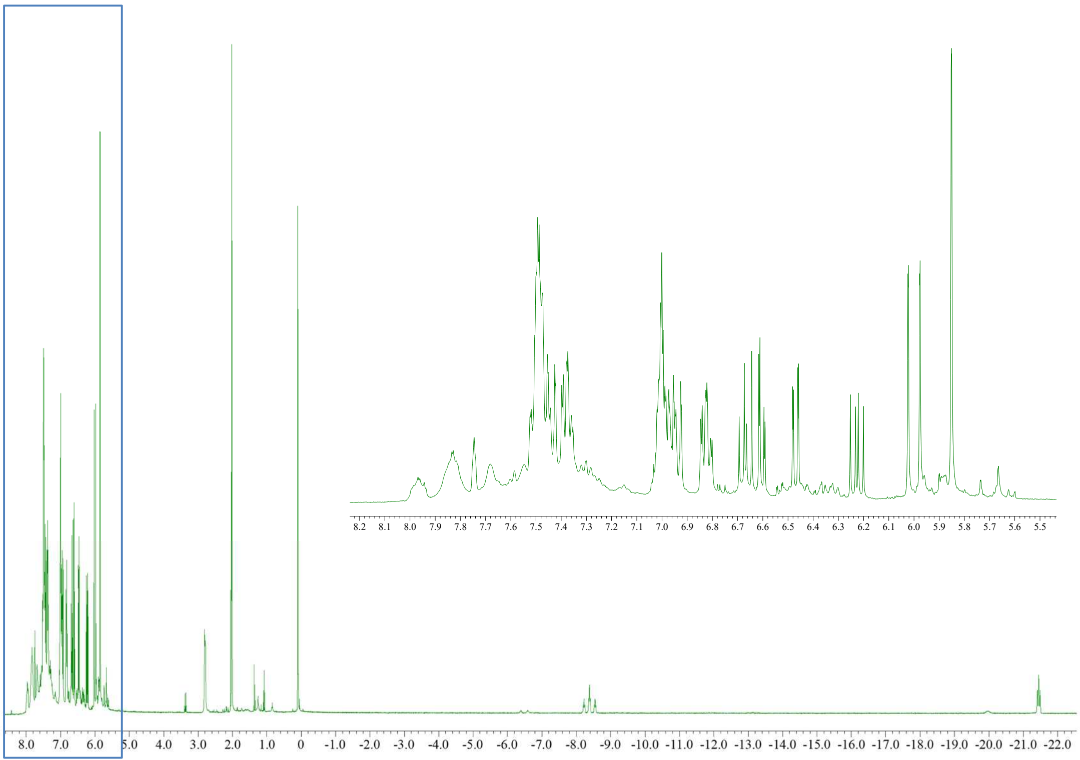


Figure S10. ^{1}H NMR spectra of **A^c** (400 MHz, acetone-d_6, r.t.).

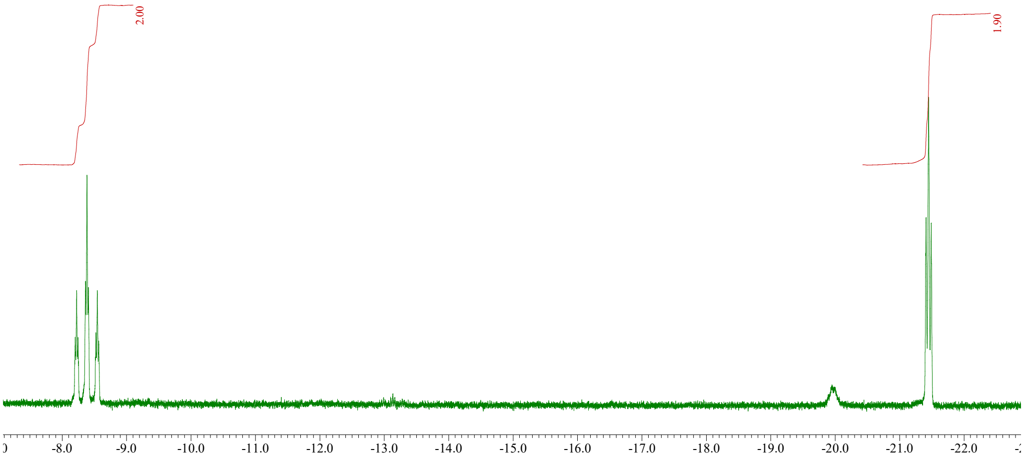


Figure S11. ^{1}H NMR spectra of hydride region of **A^c** (400 MHz, acetone-d_6, r.t.).

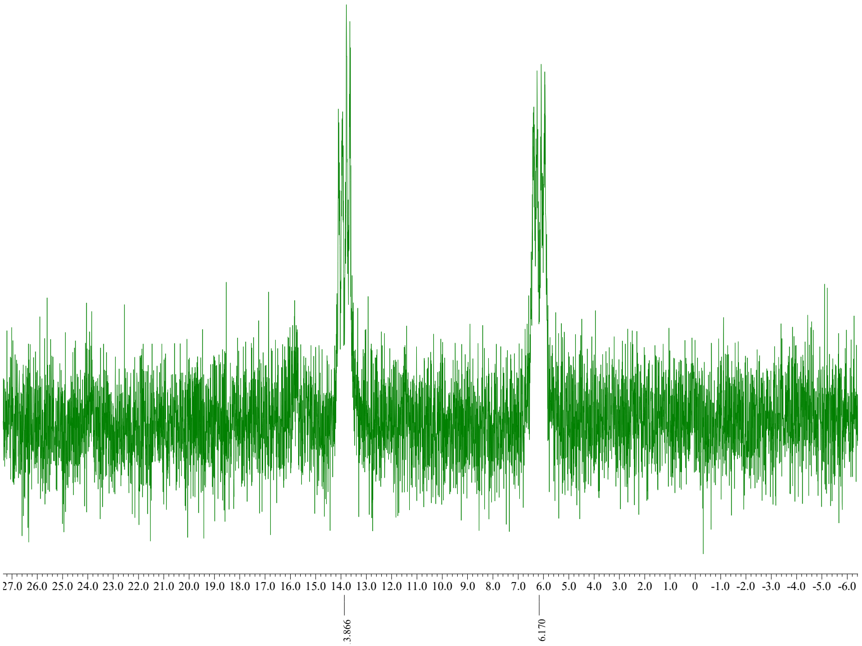


Figure S12. ^{31}P NMR spectra of **A**^{c} (161.8 MHz, acetone-d_6, r.t.).

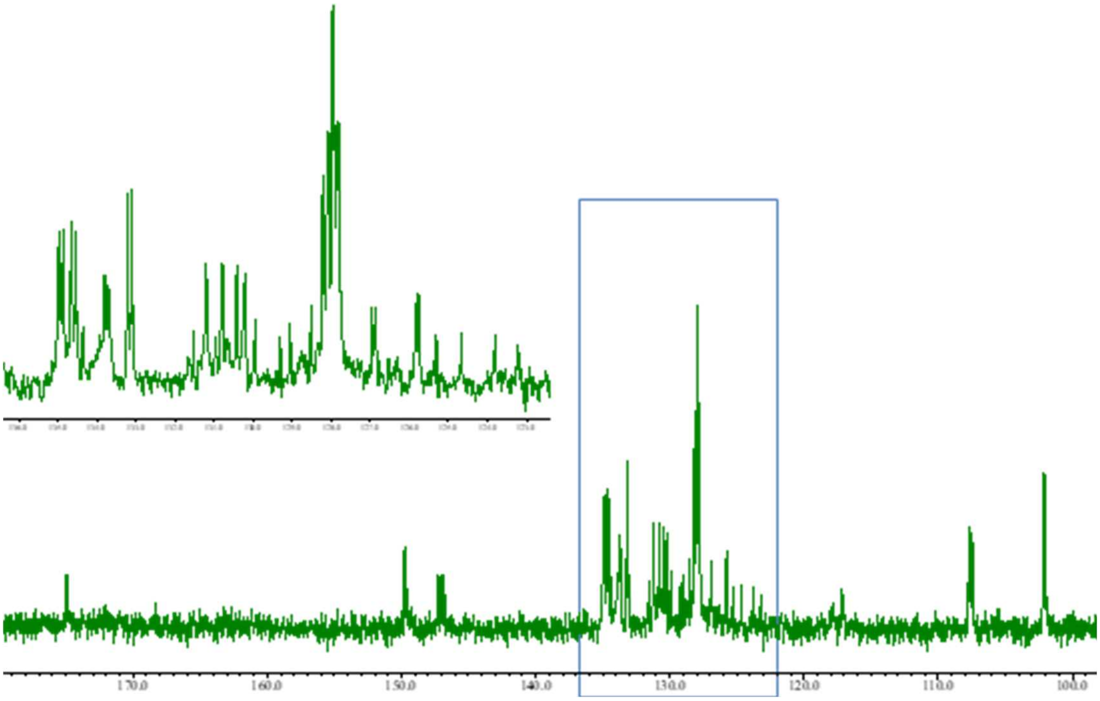


Figure S13. ^{13}C NMR spectra of **A**^{c} (100 MHz, acetone-d_6, r.t.).

X-ray Structural Determinations.

The diffraction data of **B^b** were collected on a Rigaku XtaLAB P100 diffractometer with graphite monochromated MoKα(λ=0.71073Å). The data were collected at a temperature of -180 ± 1°C to a maximum 2θ value of 55.1°. The crystal-to-detector distance was 45.00 mm. Readout was performed in the 0.172 mm pixel mode. Data were collected and processed using CrystalClear (Rigaku).[1] An empirical absorption correction was applied. The data were corrected for Lorentz and polarization effects.

The crystal structures were solved by direct method (SHELXS-97[2] or SHELXT[3]) and expanded using Fourier techniques, which are subsequently completed by Fourier recycling using the SHELXL 2014 program.[3] Non-hydrogen atoms were refined by anisotropic displacement parameters. Crystallographic data, data collection and refinement parameters for **B^b** are listed in Table S1.

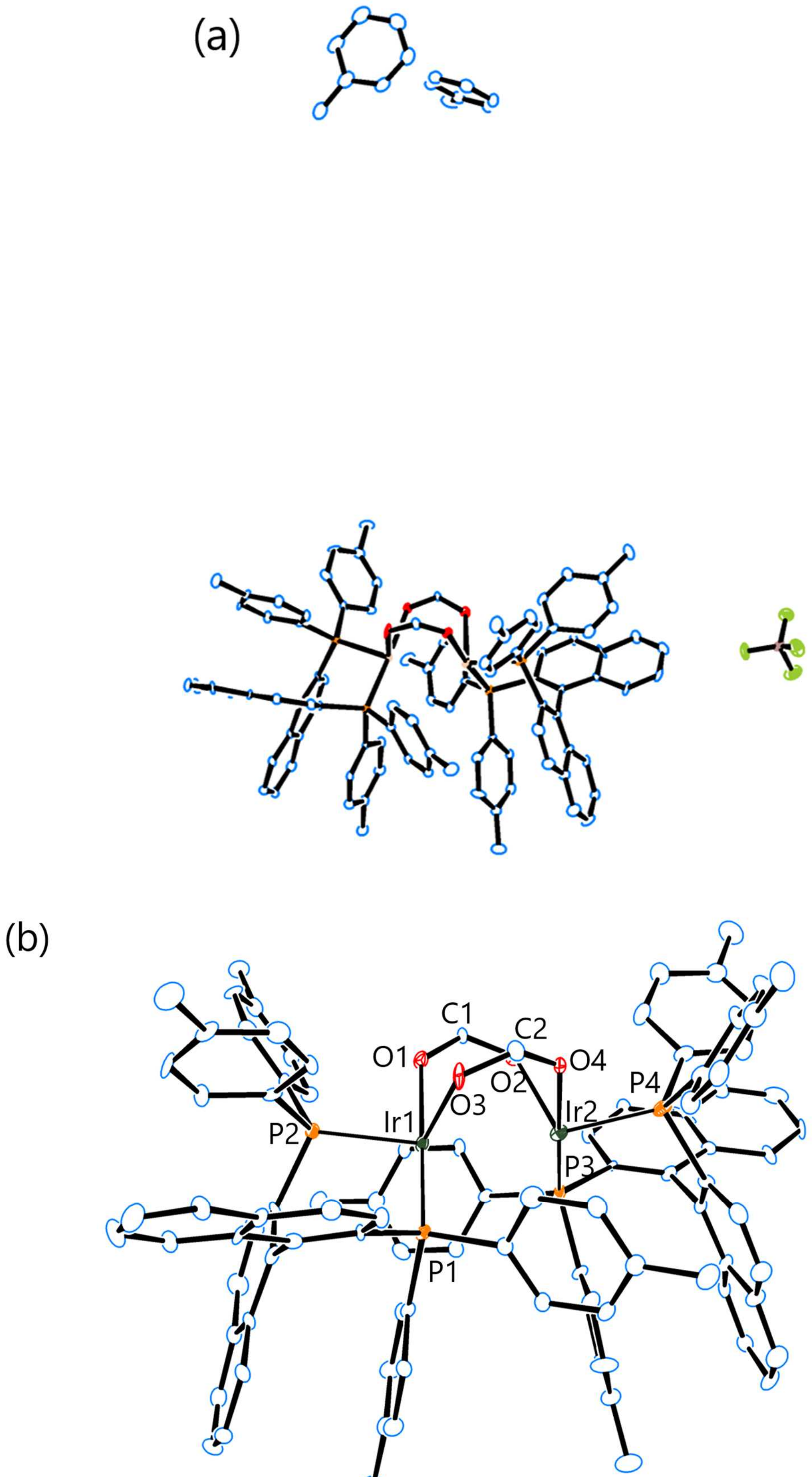


Figure S14. ORTEP diagram of complex $\mathbf{B^b}$ (a) including solvent and anion, (b) cationic unit.

Table S1. Crystal data and structure refinement for **B**$^{\mathbf{b}}$.

Complex	**B**$^{\mathbf{b}}$
Empirical formula	C112 H98 B F4 Ir2 O4 P4
Formula weight	2102.99
Temperature	93(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	a = 15.3077(3) Å b = 17.0493(3) Å c = 35.2582(8) Å
	α= 90° β = 90° γ = 90°
Volume	9201.9(3) Å^3
Z	4
Density (calculated)	1.518 Mg/m^3
Absorption coefficient	3.023 mm^{-1}
F(000)	4228
Crystal size	0.390 x 0.360 x 0.090 mm ^{3}
Theta range for data collection	2.735 to 27.499°
Index ranges	-19<=h<=19, -21<=k<=16, -45<=l<=43
Reflections collected	67280
Independent reflections	19583 [R(int) = 0.0537]
Completeness to theta = 27.50°	99.6 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	19583 / 0 / 1154
Goodness-of-fit on F^2	1.009
Final R indices [I>2sigma(I)]	*R*1 = 0.0689, *wR*2 = 0.1663
R indices (all data)	*R*1 = 0.0726, *wR*2 = 0.1687
Largest diff. peak and hole	13.584 and -4.386 e.Å^{-3}

(1) CrystalClear: Data Collection and Processing Software, Rigaku Corporation (1998-2015). Tokyo 196-8666, Japan.
(2) SHELXS Version 2013/1: Sheldrick, G. M. (2008). Acta Cryst. A64, 112-122.
(3) SHELXT Version 2014/5: Sheldrick, G. M. (2014). Acta Cryst. A70, C1437.

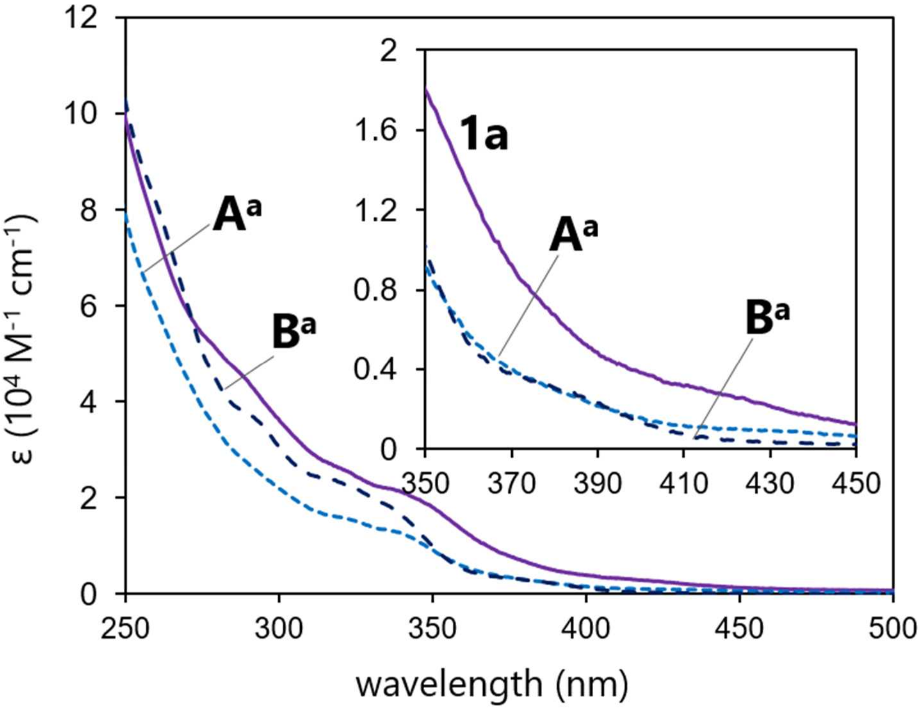


Figure S15. UV-vis absorption spectra of **1a**, **A^a**, and **B^a** measured in CD_2Cl_2 at r.t.