

Supporting Information for

Luminescent Rhenium(I)-Dipyrrin Complexes

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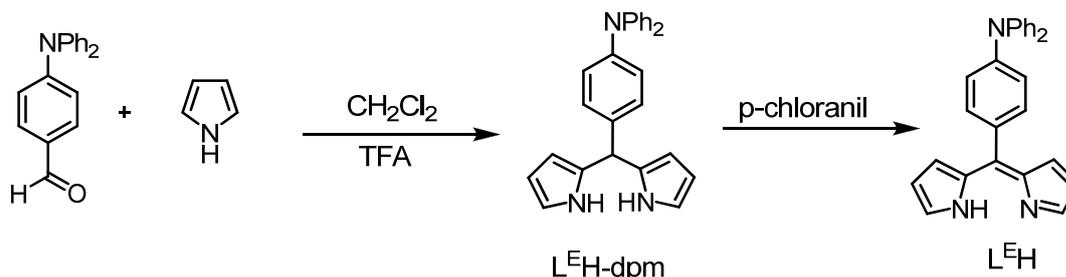
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1. Synthesis details

(a) Materials and reagents

$\text{Re}(\text{CO})_5\text{Cl}$ (Sigma-Aldrich), triphenylphosphine (PPh_3) (ACROS Organics), tributylphosphine (PBu_3) (BDH chemicals) were used without further purification. Triethylamine (Sigma-Aldrich) was dried over CaH_2 and stored over molecular sieves. With the exception of $\text{L}^{\text{E}}\text{H}$, the ligands ($\text{L}^{\text{A}}\text{H}$ - $\text{L}^{\text{D}}\text{H}$) were prepared by literature procedures.¹ The synthetic details for $\text{L}^{\text{E}}\text{H}$ are outlined below. All solvents were of analytical grade and used without further purification unless otherwise stated. All procedures were carried out under argon conditions using the standard Schlenk techniques, unless otherwise stated. It was assumed the products were light sensitive and therefore all products were stored in the dark.

(b) Synthesis of $\text{L}^{\text{E}}\text{H}$



Step 1. A solution of dry CH_2Cl_2 (100 mL), freshly distilled pyrrole (50 mL, 704 mmol) and TFA (0.205 mL, 0.275 mmol) were combined under Ar. 4-diphenylaminobenzaldehyde (504 mg, 1.84 mmol) was dissolved in dry CH_2Cl_2 (10 mL) and added dropwise with stirring through a septum to the pyrrole solution. The mixture was stirred at room temperature under Ar for 1.5 hrs. The reaction mixture was washed with 1 M aqueous KOH before the CH_2Cl_2 was removed by rotary-evaporation. The resulting solution was dried over MgSO_4 and the excess pyrrole removed by vacuum distillation. $\text{L}^{\text{E}}\text{H-dpm}$ was isolated from the residue by dissolution in CH_2Cl_2 then flash chromatography on deactivated neutral alumina using CH_2Cl_2 /hexane (60/40) as the eluent.

Step 2. L^EH-dpm (0.714 g, 1.84 mmol) was dissolved in dry CH₂Cl₂ (50 mL) and to this was added dropwise a solution of *p*-chloranil (0.631 g, 2.58 mmol) in dry CH₂Cl₂ (10 mL) under Ar. The reaction mixture was stirred at rt for 19 h before the solvent was removed. Column chromatography on deactivated neutral alumina, using CH₂Cl₂/hexane (60/40) with 0.1–0.2% methanol as the eluent provided the product as a dark crystalline solid (which appears as a purple band on the alumina column and yellow in solution). Yield: 0.519 g, 73% (over two steps). ¹H NMR (500 MHz, acetone-d₆): δ (ppm) 7.71 (s, 1H), 7.39 (m, 3H), 7.20 (d, J = 3.2 Hz, 2H), 7.12 (m, 2H), 6.69 (dd, 1H), 6.42 (dd, 1H); ¹³C NMR (100 MHz, acetone-d₆): δ (ppm) 149.71, 148.07, 132.76, 131.29, 130.32, 129.06, 125.90, 124.56, 121.66, 118.04; ESI-MS (+ve mode): 388.70 *m/z* ([M+H]⁺). Anal. Calcd for L_EH C₂₇H₂₁N₃ · 0.67CH₃OH: C, 81.27; H, 5.84; N, 10.28. Found: C, 81.21; H, 5.71; N, 10.57.

(c) Synthesis of 1A, [ReL^A(CO)₃Cl][NEt₃H]

Re(CO)₅Cl (56.0 mg, 0.15 mmol) and LH (1 equivalent) were dissolved in dry toluene (3 mL) and heated to 100 °C under argon. Dry triethylamine (~2 equivalents) was then added via a syringe through a septum. Heating at 100 °C was continued for 1 h, at which point TLC indicated disappearance of the dipyrin ligand. All volatiles were removed under reduced pressure before the residue was purified by recrystallisation from hot hexane and CH₂Cl₂. A crystalline orange solid formed upon cooling to room temperature.

(b) General synthesis of [ReL(CO)₃PR₃] complexes

(i) Method 2a, conventional heating

Re(CO)₅Cl (0.252 g, 0.70 mmol) and LH (1 equivalent) were dissolved in dry toluene (15 mL) and heated to 100 °C under argon. Dry triethylamine (~2 equivalents) was added via a syringe through a septum and heating continued for 1 h. PR₃ (1 equivalent) was then added and heating continued for a further 1 h. All volatiles were removed under reduced pressure before the residue was purified by chromatography on neutral deactivated alumina (specific details for individual complexes given below).

(ii) Method 2b, microwave heating

Re(CO)₅Cl (0.128 g, 0.354 mmol) and LH (1.25 equivalent) were dissolved in dry toluene (5 mL). Dry triethylamine (~2 equivalents) was added and the reaction was heated to 100 °C for 15 mins in a CEM microwave synthesizer (open vessel mode, power = 200 W) under argon. PR₃ (1 equivalent) was then added and heating continued for a further 15 mins. All volatiles were removed under reduced pressure before the residue was purified by chromatography on neutral deactivated alumina (specific details for individual complexes given below).

(c) General synthesis of [ReL(CO)₂(PR₃)(PR'₃)] complexes

(i) Method 3a, conventional heating

[ReL(CO)₃PR₃] (0.0248 g, 0.027 mmol) and PR'₃ (~2.5 equivalents) were combined in 11 mL dry toluene. The reaction was heated to 100 °C for ~48 hours. The reaction was monitored by TLC to check for the disappearance of [ReL(CO)₃PR₃]. All volatiles were removed under reduced pressure before the crude product was adsorbed onto deactivated neutral alumina and purified by column chromatography on deactivated neutral alumina (specific details for individual complexes given below).

(ii) Method 3b, microwave heating

[ReL(CO)₃PR₃] (0.139 g, 0.185 mmol) and PR'₃ (~5.5 equivalents) were combined in 5 mL toluene. The reaction was heated to 130 °C for 45 mins in a CEM microwave synthesizer (closed vessel mode, power = 200 W, pressure = 250 psi). All volatiles were removed under reduced pressure before the crude product was adsorbed onto deactivated neutral alumina and purified by column chromatography on deactivated neutral alumina (specific details for individual complexes given below).

2. Characterisation details

Instrumentation: NMR spectra were recorded in CDCl₃ or CD₃CN on 400 MHz and 500 MHz Bruker spectrometers at 25 °C (unless otherwise stated). Chemical shifts are reported relative to solvent peaks for ¹H and ¹³C spectra and to H₃PO₄ (0 ppm) for ³¹P spectra. Solution UV-Vis spectra were recorded on either a Shimadzu UV-3101PC UV-VIS-NIR spectrophotometer or a CARY 100 Bio UV-Vis spectrophotometer using either 1 cm or 0.1 cm quartz cells. Mass spectrometry was performed on either a Micromass ZMD 400 electrospray spectrometer or a Waters Micromass MALDI spectrometer using a α -cyano-4-hydroxycinnamic acid, α -CHCA, matrix. IR spectra were recorded on a Nicolet 5700 FT-IR from Thermo Electron Corporation using an ATR attachment (Ge crystal). Emission spectra were recorded using FluoroMax-4 spectrofluorimeter from Horiba Scientific. All samples were dissolved in dichloromethane and subjected to 3 or 4 freeze pump thaw (FPT) cycles to remove dissolved oxygen before the emission spectra was recorded. Fluorescence cells were dried, fitted with a septum, and oxygen was removed from the fluorescence cells by bubbling argon through the cell, before injecting the sample into the cell under argon. For complexes **1A** and **2A-2E** an excitation wavelength of 485 nm was used with slit widths of 7 nm, while for complexes **2F** and **3D** an excitation wavelength of 480 nm was used with slit widths of 10 nm. Relative quantum yields were determined in dichloromethane relative to cresyl violet in MeOH ($\Phi_F = 0.54 \pm 0.03$, $\lambda_{ex} = 540$ nm),² using:

$$\Phi_{F(X)} = \left(\frac{A_S}{A_X} \right) \left(\frac{F_X}{F_S} \right) \left(\frac{n_X}{n_S} \right)^2 \Phi_{F(S)}$$

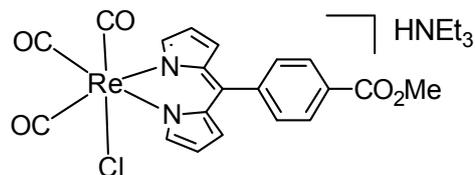
where Φ_F is the emission quantum yield, A is the absorbance at the excitation wavelength, F is the area under the corrected emission curve, and n is the refractive index of the solvents used. The subscripts s and x refer to the standard and the unknown, respectively. Quenching of the emission from **2A-2E** was carried out by injecting air into each sample or by titrating in methyl viologen (Sigma). From the methyl viologen quenching study and using:

$$\frac{\phi^0}{\phi} = 1 + K_{SV}[Q]$$

where the Stern-Volmer quenching constant, K_{SV} , could be obtained from the Stern-Volmer plots ($\frac{\phi^0}{\phi} - 1$ as a function of $[Q]$).

[ReL^A(CO)₃Cl][NEt₃H], 1A

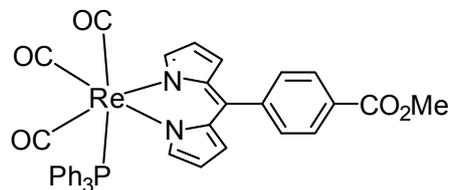
Yield: 75%. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 1.26 (t, *J* = 7.20 Hz, 9H), 2.93 (q, *J* = 7.20 Hz, 6H), 3.97 (s, 3H), 6.35 (dd, *J* = 4.20, 1.60 Hz, 2H), 6.45 (dd, *J* = 4.20, 1.60 Hz, 2H), 7.44 (dd, *J* = 7.80, 1.60 Hz,



1H), 7.59 (dd, *J* = 7.80, 1.60 Hz, 1H), 8.05 (m, 3H), 8.09 (dd, *J* = 7.80, 1.60 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 8.66, 46.22, 52.29, 117.86, 128.18, 128.49, 129.83, 130.08, 130.72, 130.82, 136.24, 143.75, 146.45, 154.02, 166.87, 193.48, 198.89; Anal. Calcd for C₂₆H₂₉ClN₃O₅Re: C, 45.58; H, 4.27; N, 6.13. Found C, 45.77; H, 4.38; N, 6.12; UV-Vis (DMSO): λ_{max} / nm (ε / L mol⁻¹ cm⁻¹): 487 (33 800), 308 (10 100); ESI-MS (-ve mode): *m/z* 583.7 ([M⁻]); IR (cm⁻¹): 729 (m), 762 (m), 829 (w), 897 (w), 995 (m), 1030 (s), 1242 (m), 1279 (m), 1340 (m), 1377 (m), 1551 (m), 1716 (m), 1863 (s), 1888 (s), 2004 (s).

[ReL^A(CO)₃PPh₃], 2A, synthesised via Method 2b

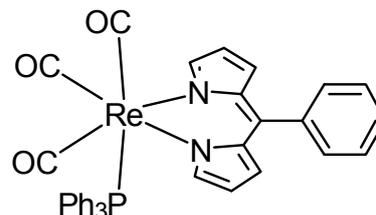
Purification for this complex was achieved by dissolving the crude product in minimal hexane/CH₂Cl₂ (1/2) and loading on to neutral deactivated alumina and eluting with CH₂Cl₂/hexane (1/7). Yield: 0.384 g, 87%.



¹H NMR (500 MHz, CDCl₃): δ (ppm) 3.96 (s, 3H), 6.38 (m, 2H), 6.42 (m, 2H), 6.78 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.01 (m, 6H), 7.37 (m, 6H), 7.48 (m, 3H), 7.52 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.78 (d, *J* = 1.4 Hz, 2H), 8.01 (dd, *J* = 7.9, 1.4 Hz, 1H), 8.09 (dd, *J* = 7.9, 1.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 52.24, 119.16, 128.14, 128.36, 128.45, 129.80, 129.83, 129.99, 130.01, 130.42, 130.83, 131.58, 133.42, 133.53, 136.10, 143.14, 146.39, 154.63, 166.94, 189.53, 196.4; ³¹P NMR (161.9 MHz, CDCl₃): δ (ppm) 11.26; Anal. Calcd for C₃₈H₂₈N₂O₅PRe: C, 56.36; H, 3.49; N, 3.46. Found C, 56.62; H, 3.70; N, 3.47; UV-Vis (CH₂Cl₂) λ_{max}/nm (ε / L mol⁻¹ cm⁻¹): 491 (36 600), 302 (sh, 11 100), 262 (sh, 18 100); MALDI-MS: *m/z* = 809.2 ([M⁺]), 726.3 ([ReLPPH₃ + H]); IR (cm⁻¹): 723 (m), 750 (m), 829 (m), 893 (w), 993 (s), 1036 (s), 1099 (w), 1240 (m), 1277 (m), 1342 (m), 1381 (m), 1541 (m), 1727 (m), 1880 (s), 1913 (s), 2015 (s).

[ReL^B(CO)₃PPh₃], 2B, synthesised via Method 2b:

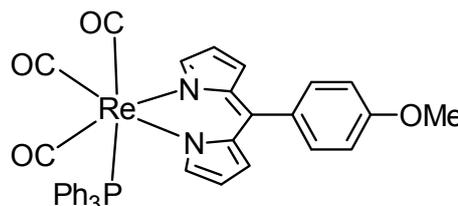
Purification for this complex was achieved by dissolving the crude product in minimal hexane/CH₂Cl₂ (1/2) and loading on to neutral deactivated alumina and eluting with CH₂Cl₂/hexane (1/7). The gradient was gradually increased



to CH₂Cl₂/hexane (1/5). Further purification was achieved by recrystallisation from hot hexane and CH₂Cl₂. Yield: 0.139 g, 37%. ¹H NMR (500 MHz, CDCl₃): δ 6.29 (d, *J* = 4.4 Hz, 2H), 6.40 (d, *J* = 4.4 Hz, 2H), 6.53 (d, *J* = 7.6 Hz, 1H), 6.93 (m, 6H), 7.24 (m, 7H), 7.36 (m, 6H), 7.68 (m, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 118.59, 126.69, 127.06, 128.00, 128.32, 128.39, 129.70, 129.91, 130.24, 130.56, 130.88, 131.87, 133.45, 133.54, 136.68, 138.54, 147.84, 154.21 196.51; ³¹P NMR (161.9 MHz, CDCl₃): δ (ppm) 19.80; Calcd for (C₃₆H₂₆N₂O₃PRe): C, 57.51; H, 3.49; N, 3.73. Found: C, 57.22; H, 3.45; N, 3.70; UV-Vis (CH₂Cl₂) λ_{max} (ε / L mol⁻¹ cm⁻¹): 489 (38 100), 316 (sh, 7 400), 270 (sh, 13 900); ESI-MS (+ve mode): 753.8 *m/z* ([M + H]); IR (cm⁻¹): 697 (m), 722 (m), 744 (s), 773 (w), 837 (w), 872 (w), 885 (w), 993 (s), 1030 (s), 1091 (w), 1193 (w), 1206 (w), 1240 (m), 1341 (m), 1379 (m), 1407 (w), 1435 (w), 1544 (s), 1890 (s), 1909 (s), 2010 (s).

[ReL^C(CO)₃PPh₃], 2C, synthesised via Method 2b:

Purification for this complex was achieved by dissolving the crude product in CH₂Cl₂ and adsorbing to neutral deactivated alumina and eluting with CH₂Cl₂/hexane (1/7). The gradient was gradually

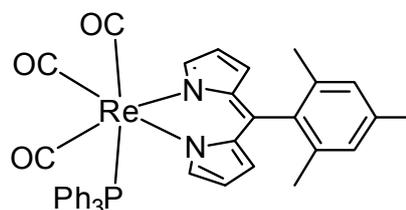


increased to CH₂Cl₂/hexane (1/5). Further purification was achieved by recrystallisation from hot hexane and CH₂Cl₂. Yield: 0.166 g, 49%. ¹H NMR (500 MHz, CDCl₃, -10 °C): δ (ppm) 3.86 (s, 3H), 6.30 (dd, *J* = 1.5, 4.4 Hz, 2H), 6.36 (dd, *J* = 2.4, 8.4 Hz, 1H), 6.46 (dt, *J* = 1.5, 4.4 Hz, 2H), 6.79 (dd, *J* = 2.4, 8.4 Hz, 1H), 6.89 (m, 7H), 7.23 (td, *J* = 2.2, 8.0 Hz, 6H), 7.30 (dd, *J* = 2.4, 8.4 Hz, 1H), 7.35 (m, 3H), 7.69 (d, *J* = 1.5 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 55.32, 112.32, 118.46, 128.30, 128.37, 128.88, 128.89, 130.57, 130.90, 131.02, 131.84, 133.45, 133.54, 137.00, 147.90, 154.03, 159.54, 196.51; ³¹P NMR (161.9 MHz, CDCl₃): δ (ppm) 11.31; Anal. Calcd for (C₃₇H₂₈N₂O₄PRe) · 0.25C₆H₁₄: C, 57.56; H,

3.95; N, 3.49. Found: C, 57.32; H, 3.66; N, 3.64; UV-Vis (CH₂Cl₂) λ_{\max} / nm (ϵ / L mol⁻¹ cm⁻¹): 488 (37 700), 357 (5 700), 274 (13 700); ESI-MS (+ve mode): 783.7 *m/z* ([M + H]); IR (cm⁻¹): 694 (m), 729 (m), 750 (m), 769 (m), 820 (m), 888 (w), 993 (s), 1034 (s), 1092 (w), 1175 (m), 1239 (s), 1290 (w), 1340 (m), 1379 (m), 1410 (w), 1434 (w), 1537 (m), 1883 (s), 1910 (s), 2013 (s).

[ReL^D(CO)₃PPh₃], 2D, synthesised via Method 2a:

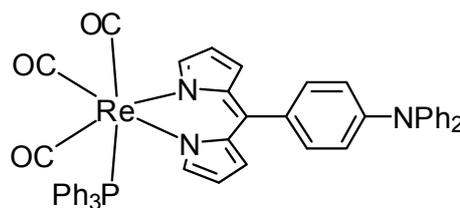
Purification for this complex was achieved by dissolving the crude product in CH₂Cl₂ and adsorbing to neutral deactivated alumina and then eluting with a gradient of CH₂Cl₂ in hexane. Yield: 0.23g, 93%. ¹H



NMR (500 MHz, CDCl₃): δ (ppm) 1.63 (s, 3H), 1.94 (s, 3H), 2.33 (s, 3H), 6.18 (dd, *J* = 1.5, 4.4 Hz, 2H), 6.37 (dt, *J* = 1.5, 4.4 Hz, 2H), 6.82 (s, 1H), 6.86 (s, 1H), 7.04 (m, 6H), 7.23 (tt, *J* = 2.0, 6.5 Hz, 6H), 7.33 (m, 3H), 7.47 (d, *J* = 1.5 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 19.40, 19.57, 21.08, 118.73, 127.30, 127.66, 128.29, 128.37, 129.96, 130.15, 130.74, 131.07, 133.64, 133.72, 135.23, 135.73, 136.03, 137.01, 137.06, 146.98, 153.96; ³¹P NMR (161.9 MHz, CDCl₃): δ (ppm) 12.97; Anal. Calcd for (C₃₉H₃₂N₂O₃Pre): C, 59.00; H, 4.06; N, 3.49. Found: C, 59.28; H, 4.20; N, 3.53; UV-Vis (CH₂Cl₂) λ_{\max} (ϵ / L mol⁻¹ cm⁻¹): 490 (42 100), 280 (11 600); ESI-MS (+ve mode): 833.7 *m/z* ([M + K]); IR (cm⁻¹): 695 (m), 723 (m), 729 (m), 746 (m), 772 (m), 836 (m), 864 (w), 887 (w), 993 (s), 1031 (s), 1092 (w), 1194 (w), 1244 (m), 1342 (m), 1378 (m), 1409 (w), 1436 (w), 1548 (s), 1885 (s), 1916 (s), 2012 (s).

[ReL^E(CO)₃PPh₃], 2E, synthesised via Method 2a:

Purification for this complex was achieved by dissolving the crude product in CH₂Cl₂ and adsorbing to neutral deactivated alumina and then eluting with CH₂Cl₂/hexane (1/7). Further purification was

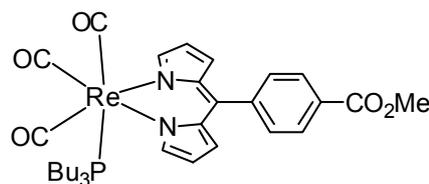


achieved by recrystallisation from hot hexane and CH₂Cl₂. Yield: 0.099 g (0.108 mmol, 36%). ¹H NMR (500 MHz, CDCl₃, -10 °C): δ (ppm) 6.26 (dd, *J* = 2.0, 8.30 Hz, 1H), 6.34

(dd, $J = 1.50, 4.40$ Hz, 2H), 6.56 (dt, $J = 1.50, 4.40$ Hz, 2H), 6.84 (m, 6H), 6.91 (dd, $J = 2.0, 8.30$ Hz, 1H), 7.03 (dd, $J = 2.0, 8.30$ Hz, 1H), 7.08 (t, $J = 7.3$ Hz, 2H), 7.16 (m, 4H), 7.22 (m, 7H), 7.32 (m, 7H), 7.69 (d, $J = 1.5$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 118.43, 123.34, 124.86, 128.28, 128.36, 129.41, 129.88, 129.89, 130.55, 130.88, 131.78, 132.19, 133.44, 133.53, 136.82, 147.51, 147.83, 148.01, 153.98, 196.43; ^{31}P NMR (161.9 MHz, CDCl_3): δ (ppm) 11.35; Calcd for $(\text{C}_{48}\text{H}_{35}\text{N}_3\text{O}_3\text{PRe}) \cdot 0.33\text{C}_6\text{H}_{14}$: C, 63.55; H, 3.92; N, 4.66. Found: C, 63.36; H, 4.22; N, 4.44; UV-Vis (CH_2Cl_2) λ_{max} ($\epsilon / \text{L mol}^{-1} \text{cm}^{-1}$): 490 (40 500), 302 (34 800); ESI-MS (+ve mode): 920.7 m/z ($[\text{M} + \text{H}]$); IR (cm^{-1}): 697 (s), 717 (m), 733 (m), 758 (m), 821 (m), 889 (w), 994 (s), 1035 (s), 1092 (w), 1192 (m), 1239 (m), 1282 (w), 1331 (m), 1341 (m), 1379 (m), 1409 (m), 1435 (w), 1486 (m), 1533 (m), 1590 (m), 1881 (s), 1912 (s), 2011 (s).

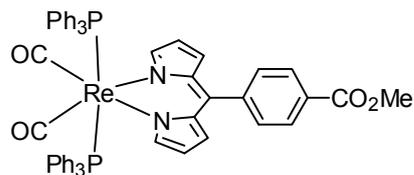
$[\text{ReL}^{\text{A}}(\text{CO})_3\text{PBu}_3]$, 2F, synthesised via Method 2b:

Purification for this complex was achieved by dissolving the crude product in $\text{CH}_2\text{Cl}_2/\text{hexane}$ (1/4) and loading onto neutral deactivated alumina and eluting with $\text{CH}_2\text{Cl}_2/\text{hexane}$ (1/7). The gradient was gradually



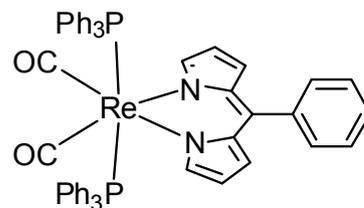
increased to $\text{CH}_2\text{Cl}_2/\text{hexane}$ (1/3). Further purification was achieved by recrystallisation from hot hexane and CH_2Cl_2 . Yield: 0.308 g, 78%. ^1H NMR (500 MHz, CDCl_3): δ (ppm) 0.83 (t, $J = 7.1$ Hz, 9H), 1.12 (m, 12H), 1.43 (m, 6H), 3.97 (s, 3H), 6.40 (dd, $J = 1.4, 4.4$ Hz, 2H), 6.50 (d, $J = 1.1, 4.4$ Hz, 2H), 7.37 (d, $J = 7.9$ Hz, 1H), 7.55 (d, $J = 7.9$ Hz, 1H), 7.96 (q, $J = 1.4$ Hz, 2H), 8.10 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 13.59, 23.47, 23.66, 24.43, 24.53, 25.09, 25.11, 52.32, 118.68, 128.40, 128.63, 129.68, 130.11, 130.65, 131.38, 136.12, 143.30, 146.05, 154.66, 166.75, 196.69; ^{31}P NMR (161.9 MHz, CDCl_3): δ (ppm) -7.60; Calcd for $(\text{C}_{32}\text{H}_{40}\text{N}_2\text{O}_5\text{PRe})$: C, 51.26; H, 5.38; N, 3.74. Found: C, 51.37; H, 5.37; N, 3.74; UV-Vis (CH_2Cl_2) λ_{max} ($\epsilon / \text{L mol}^{-1} \text{cm}^{-1}$): 485 (36 400), 303 (8 700); ESI-MS (+ve mode): 789.8 m/z ($[\text{M} + \text{K}]$); IR (cm^{-1}): 727 (m), 759 (w), 781 (w), 832 (w), 893 (w), 966 (w), 986 (m), 994 (m), 1034 (s), 1112 (w), 1194 (w), 1241 (m), 1282 (m), 1343 (m), 1378 (m), 1410 (m), 1436 (w), 1539 (m), 1569 (m), 1609 (w), 1723 (m), 1881 (s), 1910 (s), 2010 (s), 2873 (w), 2934 (w), 2960 (w).

[ReL^A(CO)₂(PPh₃)₂], 3A, synthesised via Method 3a:



Purification for this complex was achieved by dissolving the crude product in CH₂Cl₂ and adsorbing to neutral deactivated alumina and then eluting with CH₂Cl₂/hexane (1/7). Further purification was achieved by recrystallisation from hot hexane and CH₂Cl₂. Yield: 0.272 g, 49%. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 3.97 (s, 3H), 5.84 (dd, *J* = 1.3, 4.3 Hz, 2H), 6.07 (dd, *J* = 1.3, 4.3 Hz, 2H), 6.93 (d, *J* = 8.3 Hz, 2H), 7.09 (m, 14H), 7.17 (t, *J* = 7.4 Hz, 12H), 7.25 (t, *J* = 7.4 Hz, 6H), 7.98 (d, *J* = 8.3 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 52.30, 118.77, 127.77, 127.81, 127.84, 128.17, 129.01, 129.43, 129.90, 130.40, 133.10, 133.22, 133.44, 133.58, 133.61, 133.66, 135.22, 144.04, 144.46, 153.87, 166.93, 203.90; ³¹P NMR (161.9 MHz, CDCl₃): δ (ppm) 19.79; Anal. Calcd for (C₅₅H₄₃N₂O₄P₂Re): C, 63.27; H, 4.15; N, 2.68. Found: C, 63.24; H, 4.19; N, 2.54; UV-Vis (CH₂Cl₂) λ_{max} / nm (ε / L mol⁻¹ cm⁻¹): 480 (25 500), 307 (16 300); ESI-MS(+ve mode): 1045.7 *m/z* ([M + H]); IR (cm⁻¹): 693 (s), 723 (m), 746 (m), 827 (m), 893 (w), 990 (s), 1032 (s), 1092 (m), 1193 (w), 1243 (s), 1274 (m), 1343 (m), 1378 (m), 1410 (w), 1433 (m), 1482 (w), 1550 (m), 1724 (m), 1836 (s), 1912 (s).

[ReL^B(CO)₂(PPh₃)₂], 3B, via Method 3b:

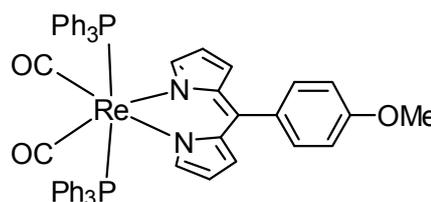


Purification for this complex was achieved by dissolving the crude product in hexane/CH₂Cl₂ (1/2) and loading on to neutral deactivated alumina and eluting with CH₂Cl₂/hexane (1/7). The gradient was gradually increased to CH₂Cl₂/hexane (1/3). Further purification was achieved by recrystallisation from hot hexane and CH₂Cl₂. Yield: 0.145 g, 80%. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 5.81 (d, *J* = 4.2 Hz, 2H), 6.13 (d, *J* = 4.2 Hz, 2H), 6.89 (d, *J* = 7.8 Hz, 2H), 7.03 (s, 2H), 7.10 (m, 12H), 7.16 (t, *J* = 7.8 Hz, 12H), 7.23 (m, 6H), 7.30 (m, 2H), 7.35 (m, 1H); ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 118.36, 126.75, 127.56, 127.73, 127.76, 127.80, 128.92, 129.84, 130.72, 133.19, 133.36, 133.53, 133.60, 133.64, 133.68, 135.80, 139.34, 145.82, 153.47; ³¹P NMR (161.9 MHz, CDCl₃): δ (ppm) 19.86; Calcd for (C₅₃H₄₁N₂O₂P₂Re) 3H₂O: C, 61.20; H, 4.55; N, 2.69. Found: C, 61.16; H, 4.28; N, 4.66; UV-Vis (CH₂Cl₂) λ_{max} (ε / L

mol⁻¹ cm⁻¹): 481 (27 300), 312 (14 600); ESI-MS (+ve mode): 986.8 *m/z* ([M⁺]); IR (cm⁻¹): 695 (s), 721 (m), 743 (m), 771 (w), 836 (w), 993 (m), 1031 (s), 1093 (w), 1195 (w), 1244 (m), 1282 (w), 1343 (m), 1378 (m), 1410 (w), 1432 (w), 1481 (w), 1552 (m), 1827 (s), 1906 (s).

[ReL^C(CO)₂(PPh₃)₂], 3C, synthesised via Method 3b:

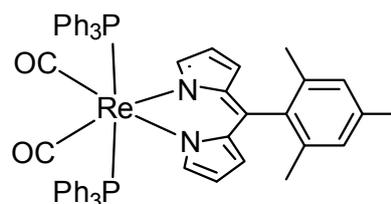
This complex was purified by chromatography on neutral deactivated alumina, eluting with a gradient of CH₂Cl₂ in hexane (1/7 to 1/4). Further purification was achieved by recrystallisation from hot hexane and



CH₂Cl₂. Yield: 0.073 g, 86%. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 3.87 (s, 3H), 5.83 (dd, *J* = 1.3, 4.2 Hz, 2H), 6.20 (d, *J* = 4.2 Hz, 2H), 6.83 (m, 4H), 7.04 (s, 2H), 7.09 (m, 12H), 7.16 (t, *J* = 7.4 Hz, 12H), 7.23 (t, *J* = 7.4 Hz, 6H); ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 55.32, 112.21, 118.24, 127.71, 127.75, 127.78, 128.91, 130.71, 131.71, 131.85, 133.21, 133.38, 133.55, 133.61, 133.65, 133.69, 136.16, 145.87, 153.41, 159.28, 204.03; ³¹P NMR (161.9 MHz, CDCl₃): δ (ppm) 19.76; Anal. Calcd for (C₅₄H₄₃N₂O₃P₂Re) 3H₂O: C, 60.65; H, 4.44; N, 2.57. Found: C, 60.61; H, 4.62; N, 2.62. UV-Vis (CH₂Cl₂) λ_{max} (ε / L mol⁻¹ cm⁻¹): 481 (25 400), 321 (12 200); ESI-MS (+ve mode) 1016.6 *m/z* ([M⁺]); IR (cm⁻¹): 695 (s), 727 (m), 771 (w), 803 (m), 813 (m), 887 (w), 899 (w), 994 (m), 1030 (m), 1093 (m), 1172 (w), 1248 (m), 1292 (w), 1343 (m), 1377 (m), 1410 (w), 1432 (w), 1481 (w), 1554 (m), 1610 (w), 1822 (s), 1904(s)

[ReL^D(CO)₂(PPh₃)₂], 3D, synthesised via Method 3a:

Purification for this complex was achieved by dissolving the crude product in CH₂Cl₂ and adsorbing to neutral deactivated alumina and then eluting with a gradient of CH₂Cl₂ in hexane. Yield: 0.049 g, 95% ¹H NMR (500 MHz, CDCl₃): δ (ppm) 1.57 (s, 6H), 2.30 (s, 3H), 5.87 (d, *J*

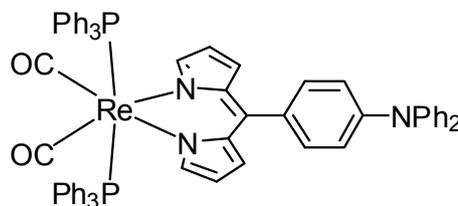


= 5.0 Hz, 2H), 6.14 (d, *J* = 5.0 Hz, 2H), 6.78 (s, 2H), 6.99 (t, *J* = 5.0 Hz, 2H), 7.06 (m, 12H),

7.15 (t, $J = 10.0$ Hz, 12H), 7.22 (t, $J = 10.0$ Hz, 6H); ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 19.64, 21.01, 29.71, 118.88, 127.41, 127.74, 127.78, 128.95, 133.16, 133.33, 133.85, 133.89, 133.93, 135.00, 135.83, 136.60, 153.42, 194.83; ^{31}P NMR (161.9 MHz, CDCl_3): δ (ppm) 18.89; Anal. Calcd for $(\text{C}_{56}\text{H}_{47}\text{N}_2\text{O}_2\text{P}_2\text{Re}) \cdot 0.25\text{CH}_2\text{Cl}_2 \cdot 0.33\text{C}_6\text{H}_{14}$: C, 64.89; H, 4.87; N, 2.60. Found: C, 64.63; H, 5.05; N, 2.53; UV-Vis (CH_2Cl_2) λ_{max} ($\epsilon / \text{L mol}^{-1} \text{cm}^{-1}$): 487 (27 600), 315 (12 600); ESI-MS (+ve mode): 1067.7 m/z ($[\text{M} + \text{K}]$); IR (cm^{-1}): 696 (s), 741 (m), 774 (w), 834 (m), 864 (w), 885 (w), 985 (m), 1030 (m), 1090 (w), 1193 (w), 1242 (m), 1343 (m), 1376 (m), 1410 (w), 1433 (w), 1481 (w), 1550 (m), 1834 (s), 1909 (m).

$[\text{ReL}^{\text{E}}(\text{CO})_2(\text{PPh}_3)_2]$, **3E, via Method 3a:**

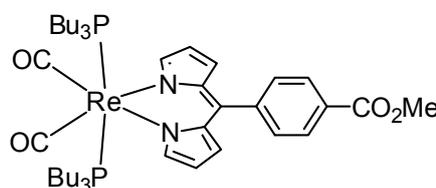
This complex was purified by chromatography on neutral deactivated alumina, eluting with CH_2Cl_2 /hexane (1/7). Further purification was achieved by recrystallisation from hot hexane and



CH_2Cl_2 . Yield: 0.053 g, 59%. ^1H NMR (500 MHz, CDCl_3): δ (ppm) 5.88 (dd, $J = 1.4, 4.3$ Hz, 2H), 6.32 (d, $J = 4.3$ Hz, 2H), 6.78 (d, $J = 6.6$ Hz, 2H), 7.01 (d, $J = 8.6$ Hz, 2H), 7.07 (m, 2H), 7.10 (m, 14H), 7.17 (t, $J = 7.4$ Hz, 16H), 7.24 (t, $J = 7.7$ Hz, 6H), 7.32 (m, 4H); ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 118.21, 121.40, 123.17, 124.70, 127.73, 127.77, 127.80, 128.94, 129.40, 130.67, 130.96, 133.20, 133.25, 133.54, 133.62, 133.66, 133.70, 135.96, 145.94, 147.39, 147.67, 153.34; ^{31}P NMR (161.9 MHz, CDCl_3): δ (ppm) 19.80; Anal. Calcd for $(\text{C}_{65}\text{H}_{50}\text{N}_3\text{O}_2\text{P}_2\text{Re})$: C, 67.69; H, 4.37; N, 3.64. Found: C, 67.55; H, 4.42; N, 3.73; UV-Vis (CH_2Cl_2) λ_{max} ($\epsilon / \text{L mol}^{-1} \text{cm}^{-1}$): 481 (27 200), 303 (39 500); IR (cm^{-1}): 695 (s), 722 (m), 808 (m), 889 (w), 986 (s), 1023 (s), 1091 (w), 1180 (w), 1194 (w), 1245 (m), 1282 (w), 1342 (m), 1379 (m), 1410 (w), 1432 (w), 1485 (w), 1543 (m), 1589 (w), 1832 (s), 1907 (m).

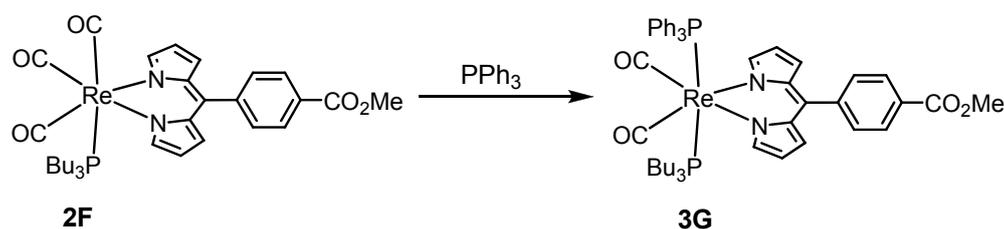
$[\text{ReL}^{\text{A}}(\text{CO})_2(\text{PBu}_3)_2]$, **3F, via Method 3b:**

This complex was purified by dissolving the crude product in minimum amount of hexane/ CH_2Cl_2 (2/1) and loading on to a column of neutral deactivated alumina



and eluting with CH₂Cl₂/hexane (1/7). Yield: 0.111 g, 92%. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 0.82 (t, *J* = 7.1 Hz, 18H), 1.19 (m, 24H), 1.45 (m, 12H) 3.96 (s, 3H), 6.35 (dd, *J* = 1.3, 4.4 Hz, 2H), 6.43 (dd, *J* = 1.3, 4.3 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.95 (t, *J* = 1.3 Hz, 2H), 8.08 (d, *J* = 8.2 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 13.71, 24.51, 24.55, 24.60, 25.00, 25.11, 25.15, 25.20, 52.26, 118.18, 128.42, 129.77, 130.06, 130.37, 135.88, 144.08, 144.62, 153.59, 166.84, 204.32; ³¹P NMR (161.9 MHz, CDCl₃): δ (ppm) -5.87; Calcd for (C₄₃H₆₇N₂O₄P₂Re): C, 55.88; H, 7.31; N, 3.03. Found: C, 56.16; H, 7.57; N, 2.87; UV-Vis (CH₂Cl₂) λ_{max} (ε / L mol⁻¹ cm⁻¹): 474 (40 900), 300 (9 500); MALDI-MS: 924.51 *m/z* ([M⁺]); IR (cm⁻¹): 723 (m), 760 (m), 774 (w), 826 (w), 873 (w), 893 (w), 985 (m), 1027 (s), 1097 (w), 1111 (w), 1191 (w), 1209 (w), 1240 (m), 1275 (m), 1340 (m), 1376 (m), 1407 (w), 1436 (w), 1544 (m), 1569 (w), 1610 (w), 1729 (m), 1825 (s), 1903 (s), 2871 (w), 2932 (w), 2957 (w).

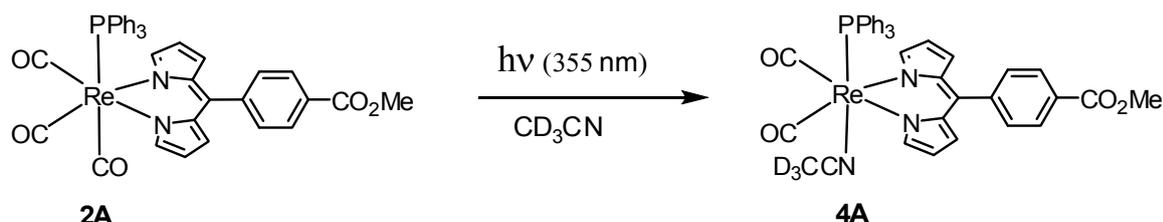
[ReL^A(CO)₂(PBu₃)(PPh₃)], 3G, synthesised via Method 3b:



Purification of this complex was achieved by dissolving the crude product in ethyl acetate/hexane (1/1) and loading on to a column of neutral deactivated alumina then eluting with ethyl acetate/hexane (1/40). Further purification was achieved by recrystallisation from hot MeOH/ H₂O. Yield: 0.055 g, 47%. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 0.83 (t, *J* = 6.7 Hz, 9H), 1.21 (m, 12H), 1.52 (m, 6H), 4.00 (s, 3H), 6.14 (dd, *J* = 1.3, 4.4 Hz, 2H), 6.28 (dd, *J* = 1.3, 4.4 Hz, 2H), 7.03 (dd, *J* = 1.8, 7.9 Hz, 1H), 7.12 (m, 6H), 7.21 (m, 6H), 7.26 (m, 3H), 7.35 (dd, *J* = 1.8, 7.9 Hz, 1H), 7.54 (t, *J* = 1.3 Hz, 2H), 8.06 (m, 2H); ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 13.66, 24.46, 24.55, 24.88, 25.09, 52.26, 118.48, 127.73, 127.80, 128.29, 128.33, 128.86, 129.61, 129.80, 130.14, 130.40, 130.49, 133.57, 133.89, 135.56, 144.03, 144.51, 153.76; ³¹P NMR (161.9 MHz, CDCl₃): δ (ppm) 21.46 and 20.19 (d), -4.70 and -5.92 (d); Calcd for (C₄₉H₅₅N₂O₄P₂Re): C, 59.80; H, 5.63; N, 2.85. Found: C, 59.79; H, 5.60; N, 2.86; UV-Vis (CH₂Cl₂) λ_{max} (ε / L mol⁻¹ cm⁻¹): 474 (32 200), 301 (14 000); MALDI-MS:

984.4 m/z ($[M+]$); IR (cm^{-1}): 723 (m), 760 (m), 774 (w), 826 (w), 873 (w), 893 (w), 985 (m), 1027 (s), 1097 (w), 1111 (w), 1191 (w), 1209 (w), 1240 (m), 1275 (m), 1340 (m), 1376 (m), 1407 (w), 1436 (w), 1544 (m), 1569 (w), 1610 (w), 1729 (m), 1825 (s), 1903 (s), 2871 (w), 2932 (w), 2957 (w).

3. Photochemical ligand substitution (PLS) in complex 2A



2A (~ 0.0070 g, ~ 8.6 μmol) was dissolved (with sonication) in CD_3CN or acetone- d_6 (~ 0.8 mL). The OD of this solution at 355 nm is ~12. The sample was irradiated (with stirring) using 355 nm excitation from a Quantel Brilliant B Nd:YAG pulsed laser (10 ns pulses) with a power output of 40-45 mW for ~ 2.5 hours. The sample was half wrapped in aluminium foil to improve the efficiency of the reaction. The temperature of the solution was monitored and found to reach a maximum of 29 $^\circ\text{C}$. The progress of the reaction was monitored by ^1H NMR, ^{31}P NMR, UV-Vis and IR spectroscopies. After 2 hours ~95% conversion was observed by ^1H NMR spectroscopy. Exhaustive attempts to isolate the product for a full characterisation were made, however the product is unstable. ^1H NMR (500 MHz, CD_3CN): δ (ppm): 3.92 (s, 3H), 6.15 (dd, $J = 1.3, 4.1$ Hz, 2H), 6.22 (dd, $J = 0.9, 4.4$ Hz, 2H), 7.07 (m, 6H), 7.10 (d, $J = 7.1$ Hz, 1H), 7.22 (td, $J = 1.6, 7.2$ Hz, 6H), 7.28 (tq, $J = 1.3, 7.1$ Hz, 3H), 7.44 (dd, $J = 2.0, 8.8$ Hz, 1H), 7.62 (s, 2H), 8.02 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (125 MHz, CD_3CN): δ (ppm) 51.89, 118.32, 127.81, 127.89, 128.06, 128.13, 129.18, 129.86, 130.13, 130.27, 130.56, 131.66, 131.74, 133.06, 133.13, 134.72, 135.10, 135.71, 143.66, 145.68, 153.83, 159.68, 166.52, 203.13; ^{31}P NMR (161.9 MHz, CD_3CN): δ (ppm) 29.92; UV-Vis (CD_3CN) λ_{max} : 472, 300 nm; IR (cm^{-1}) ($\text{C}\equiv\text{O}$ only): 1834 (s), 1914 (s).

In acetone- d_6 , the PLS reaction still takes place in the presence of excess triethylamine and methylviologen, which are potential redox excited state quenchers.

4. Supplementary Absorption, Resonance Raman, Emission and NMR Spectra

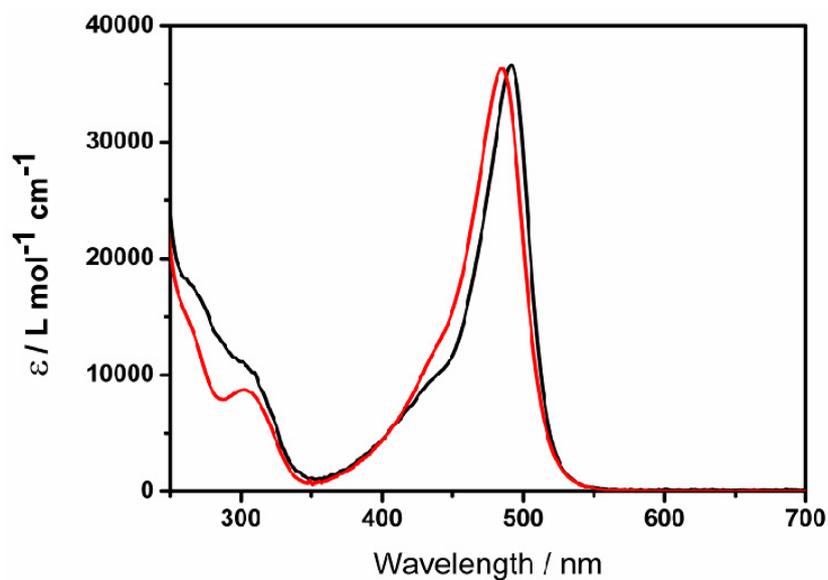


Figure S1. Absorbance spectra of **2A** (black) and **2F** (red) recorded in CH_2Cl_2 .

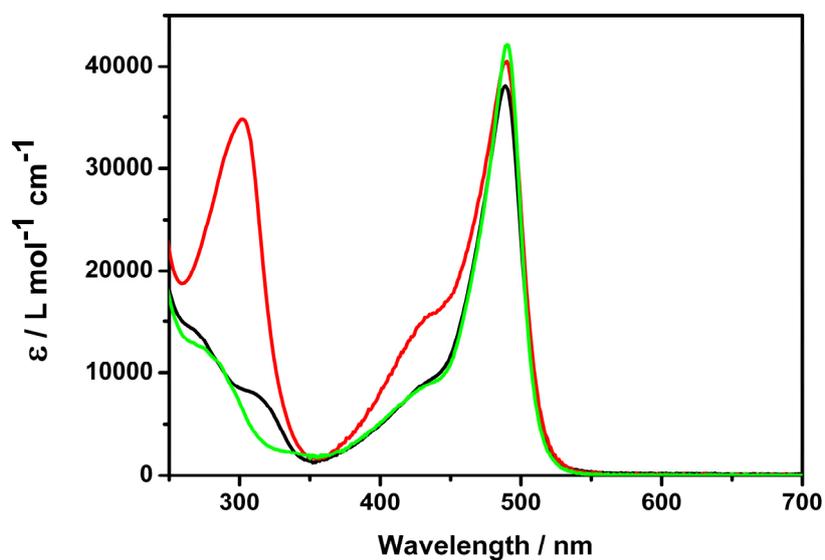


Figure S2. Absorbance spectra of **2B** (black), **2D** (green), and **2E** (red) recorded in CH_2Cl_2 .

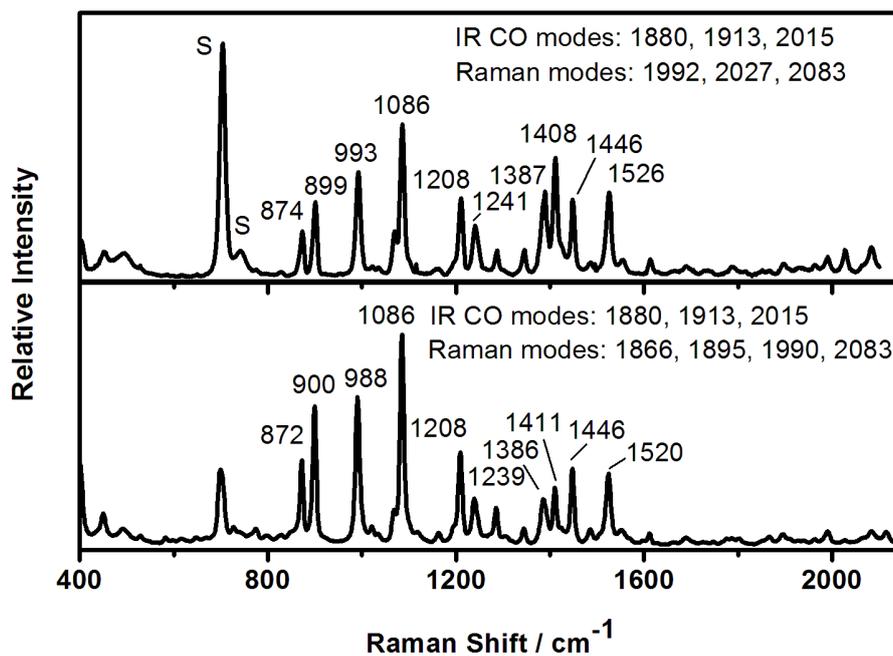


Figure S3. Resonance Raman spectrum of **2A** in CH_2Cl_2 . $\lambda_{\text{exc}} = 458$ nm (top), 488 nm (bottom).

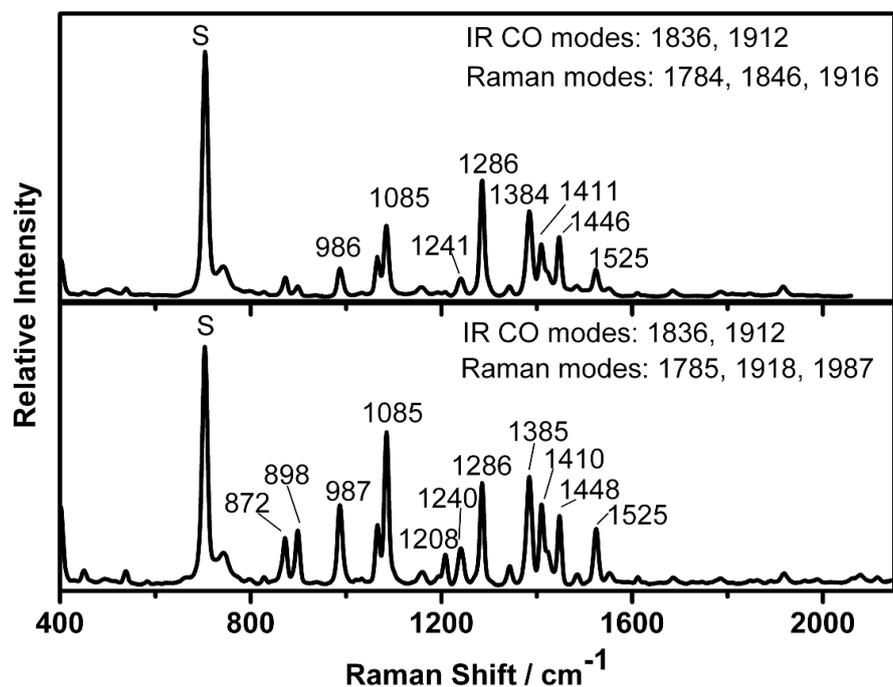


Figure S4. Resonance Raman of **3A** in CH_2Cl_2 . $\lambda_{\text{exc}} = 458$ nm (top), 488 nm (bottom)

Note: the weak overtones and combinations in the region $1700 - 2200$ cm^{-1} .

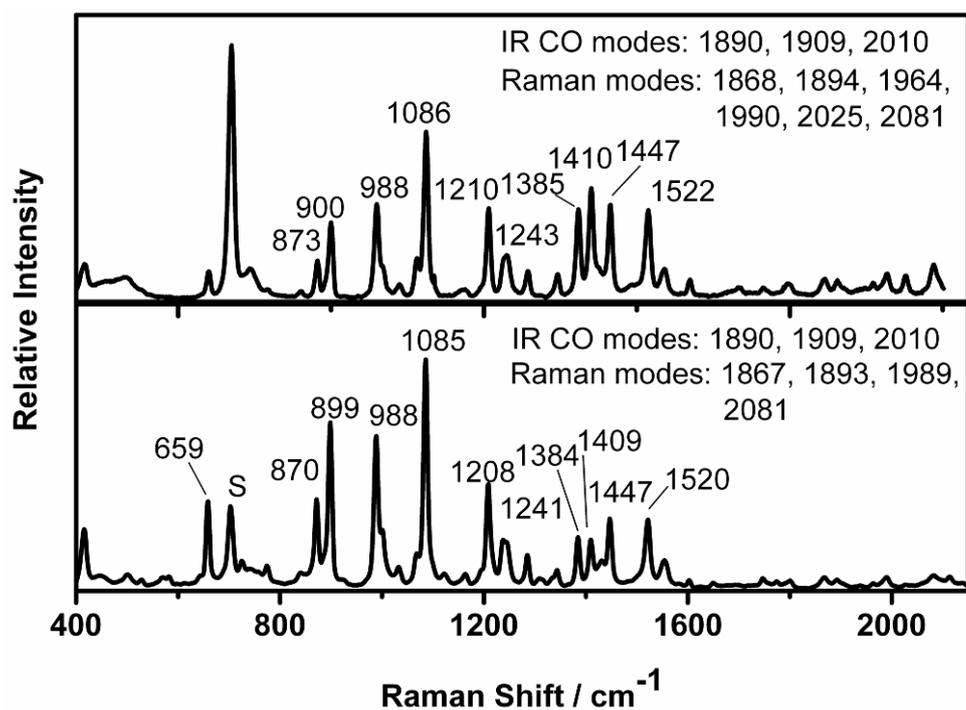


Figure S5. Resonance Raman spectrum of **2B** in CH_2Cl_2 . $\lambda_{\text{exc}} = 458$ nm (top), 488 nm (bottom).

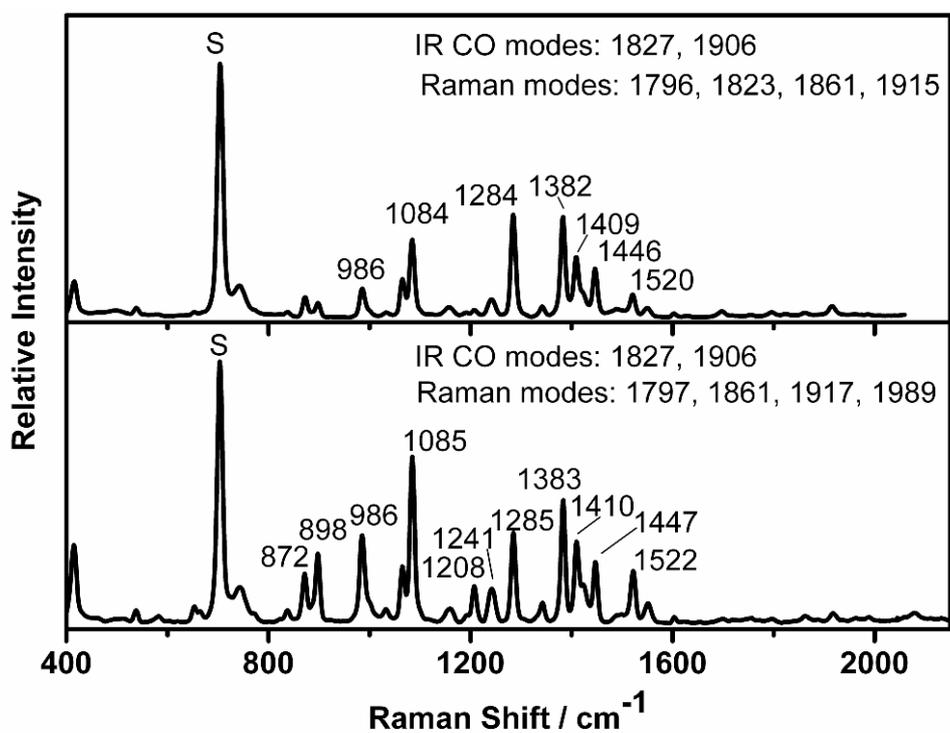


Figure S6. Resonance Raman spectrum of **3B** in CH_2Cl_2 . $\lambda_{\text{exc}} = 458$ nm (top), 488 nm (bottom).

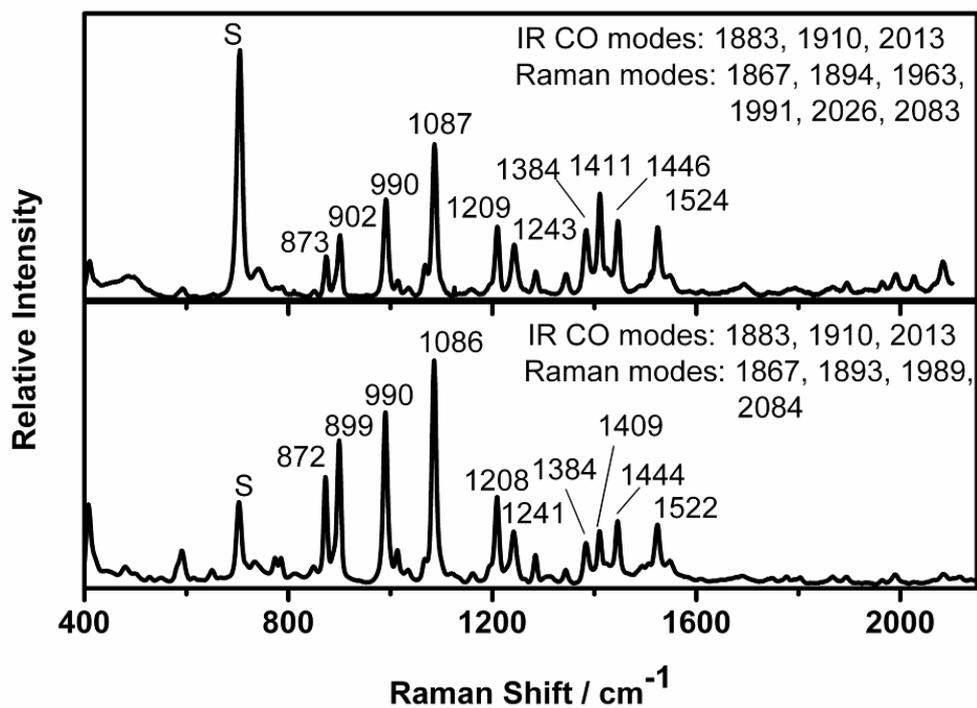


Figure S7. Resonance Raman spectrum of **2C** in CH_2Cl_2 . $\lambda_{\text{exc}} = 458 \text{ nm}$ (top), 488 nm (bottom).

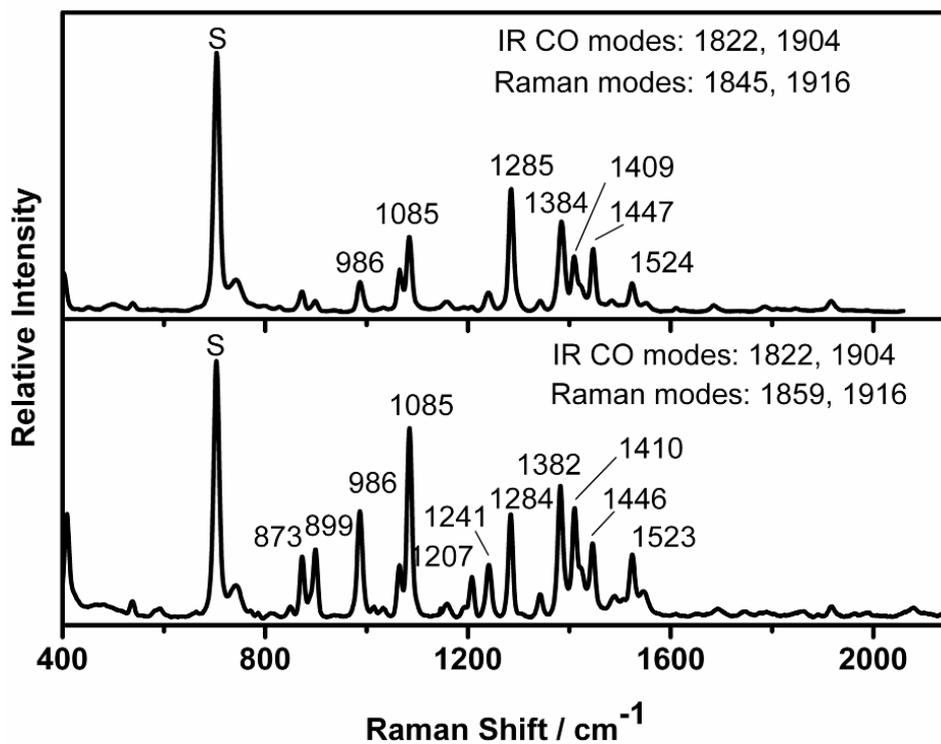


Figure S8. Resonance Raman spectrum of **3C** in CH_2Cl_2 . $\lambda_{\text{exc}} = 458 \text{ nm}$ (top), 488 nm (bottom).

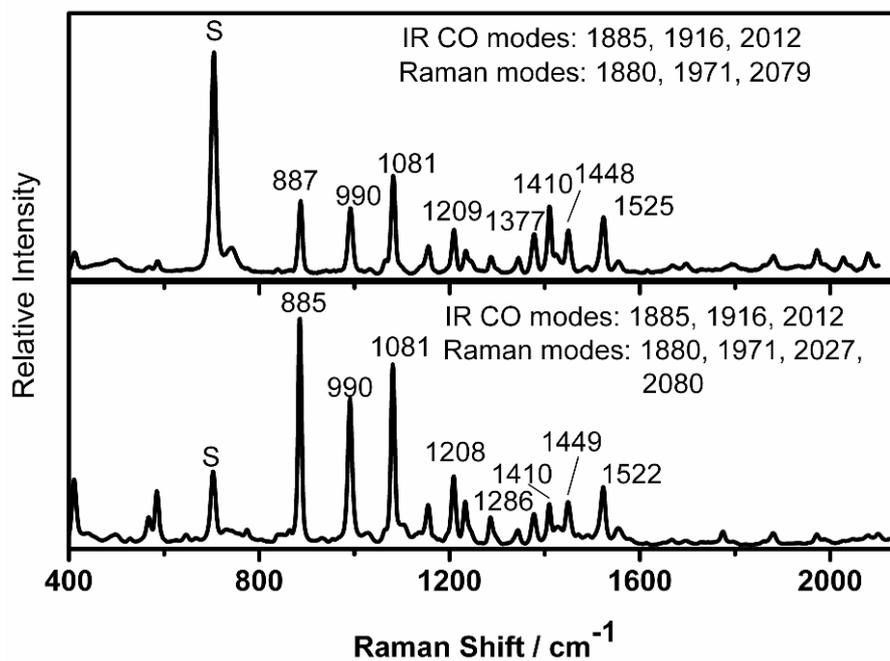


Figure S9. Resonance Raman spectrum of **2D** in CH_2Cl_2 . $\lambda_{\text{exc}} = 458 \text{ nm}$ (top), 488 nm (bottom).

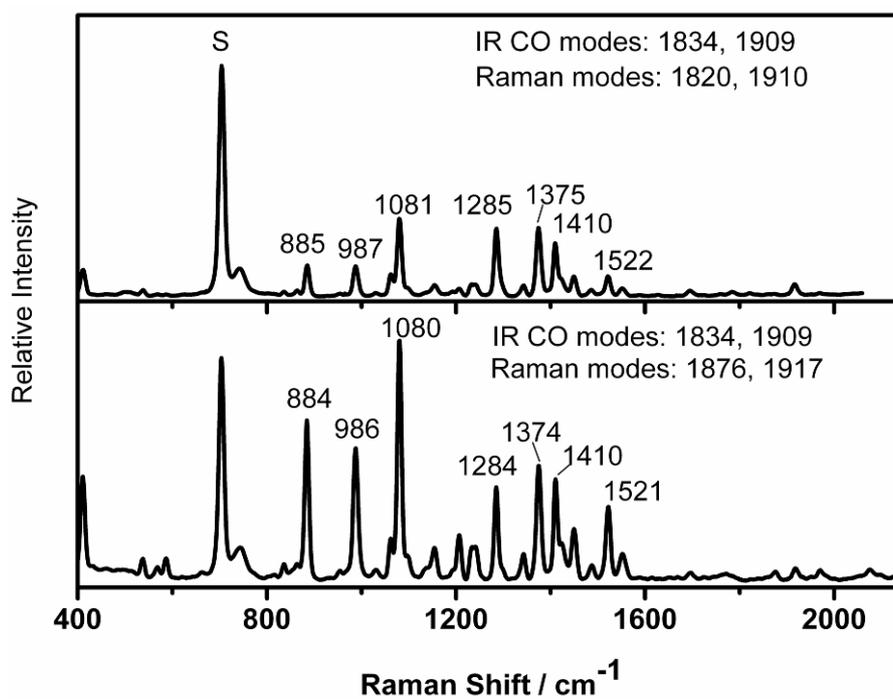


Figure S10. Resonance Raman spectrum of **3D** in CH_2Cl_2 . $\lambda_{\text{exc}} = 458 \text{ nm}$ (top), 488 nm (bottom).

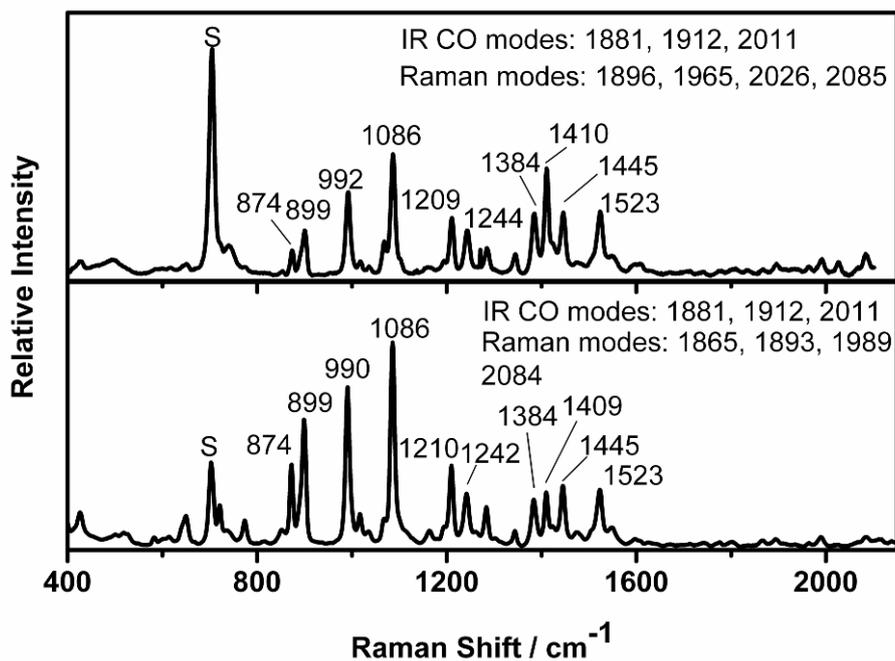


Figure S11. Resonance Raman spectrum of **2E** in CH_2Cl_2 . $\lambda_{\text{exc}} = 458$ nm (top), 488 nm (bottom).

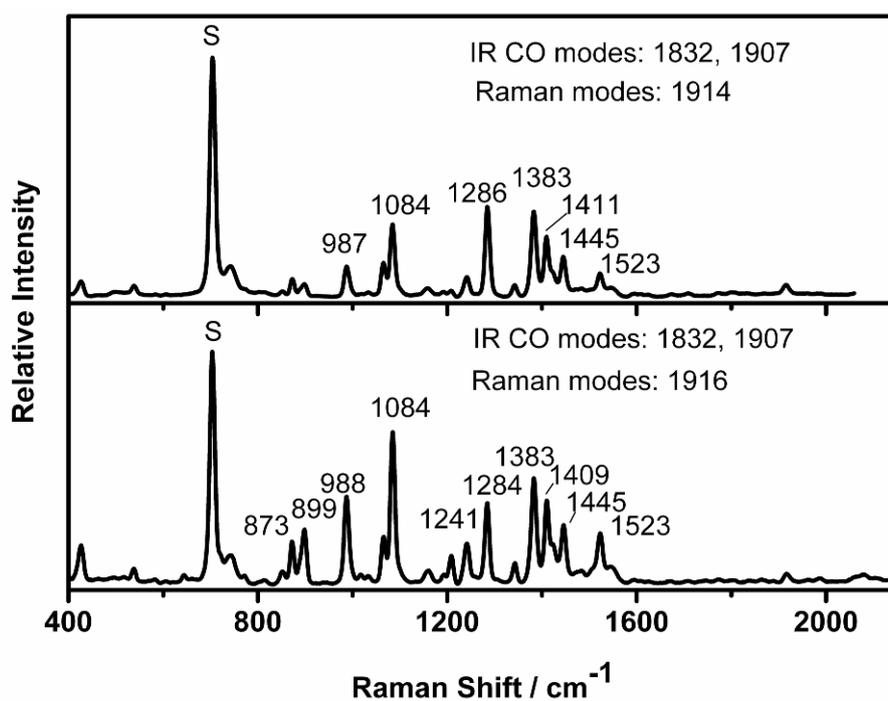


Figure S12. Resonance Raman spectrum of **3E** in CH_2Cl_2 . $\lambda_{\text{exc}} = 458$ nm (top), 488 nm (bottom).

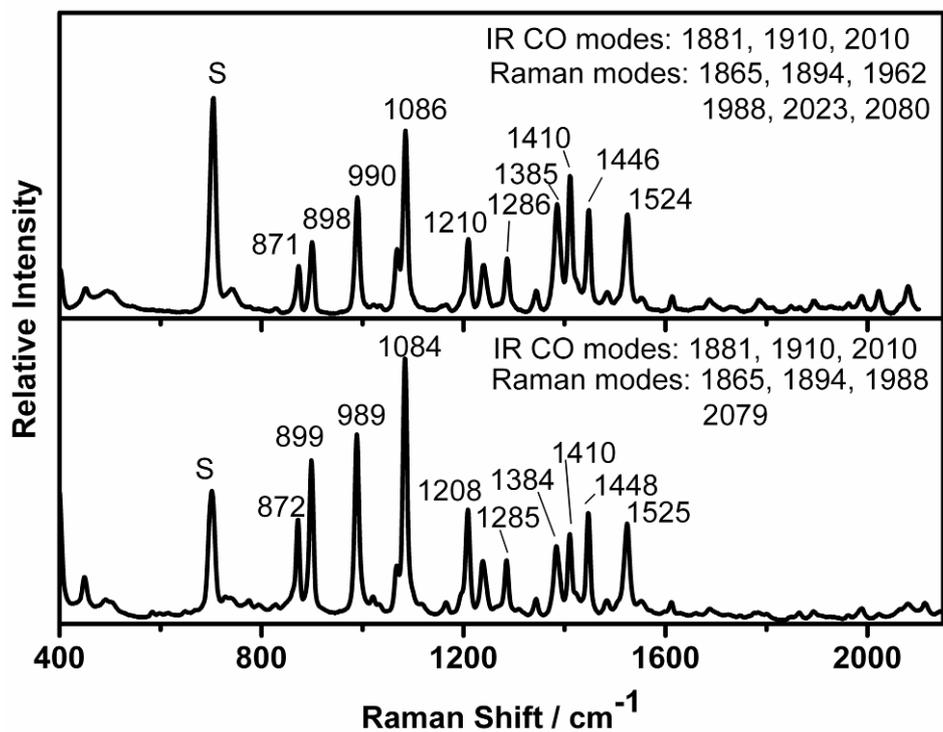


Figure S13. Resonance Raman spectrum of **2F** in CH_2Cl_2 . $\lambda_{\text{exc}} = 458$ nm (top), 488 nm (bottom).

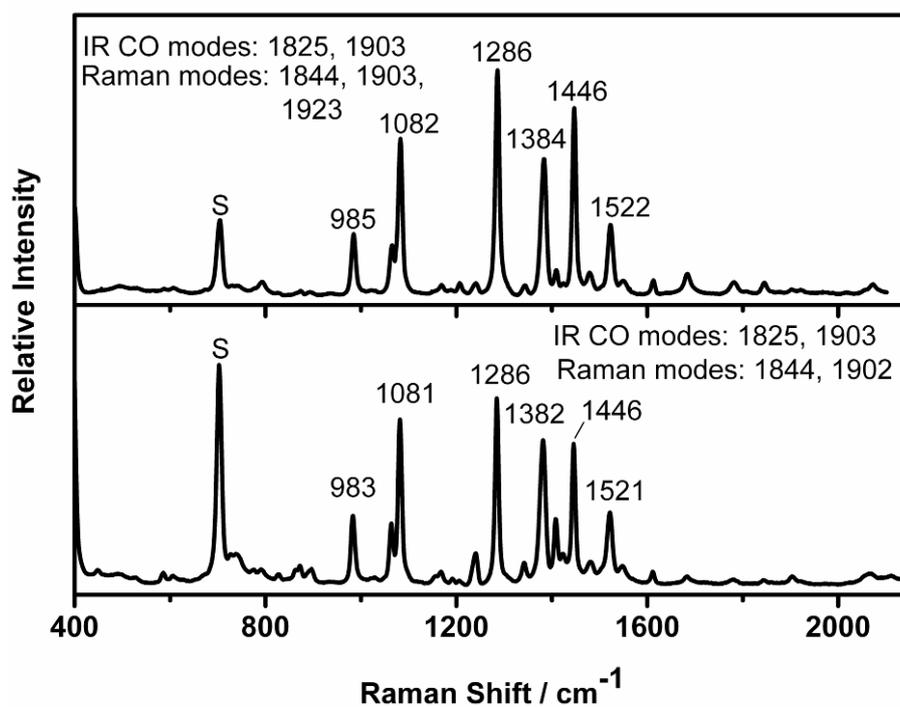


Figure S14. Resonance Raman spectrum of **3F** in CH_2Cl_2 . $\lambda_{\text{exc}} = 458$ nm (top), 488 nm (bottom).

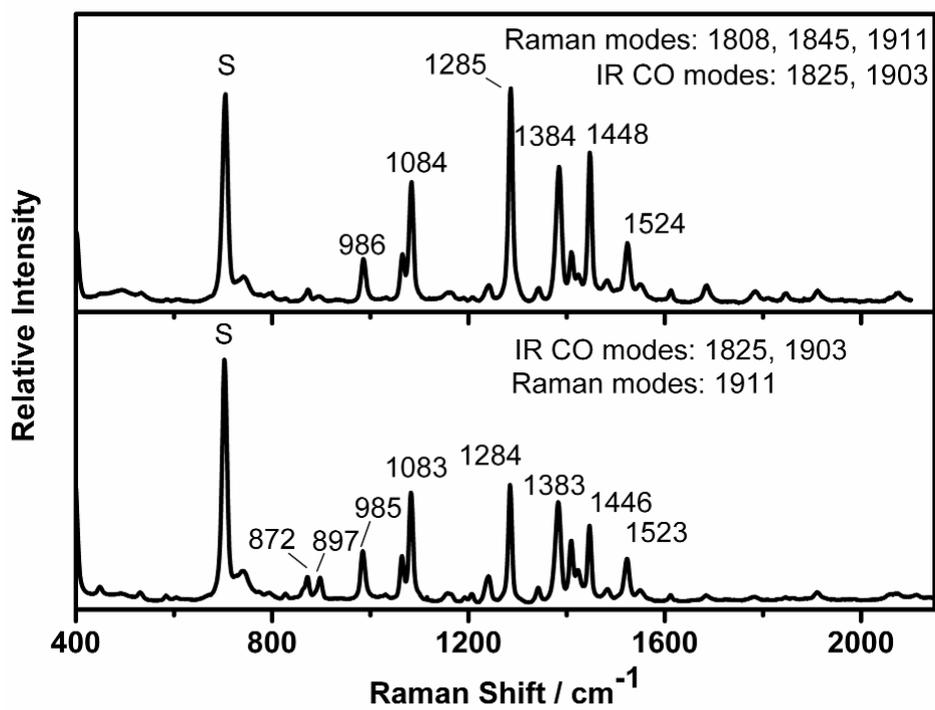


Figure S15. Resonance Raman spectrum of 3G in CH_2Cl_2 . $\lambda_{\text{exc}} = 458 \text{ nm}$ (top), 488 nm (bottom).

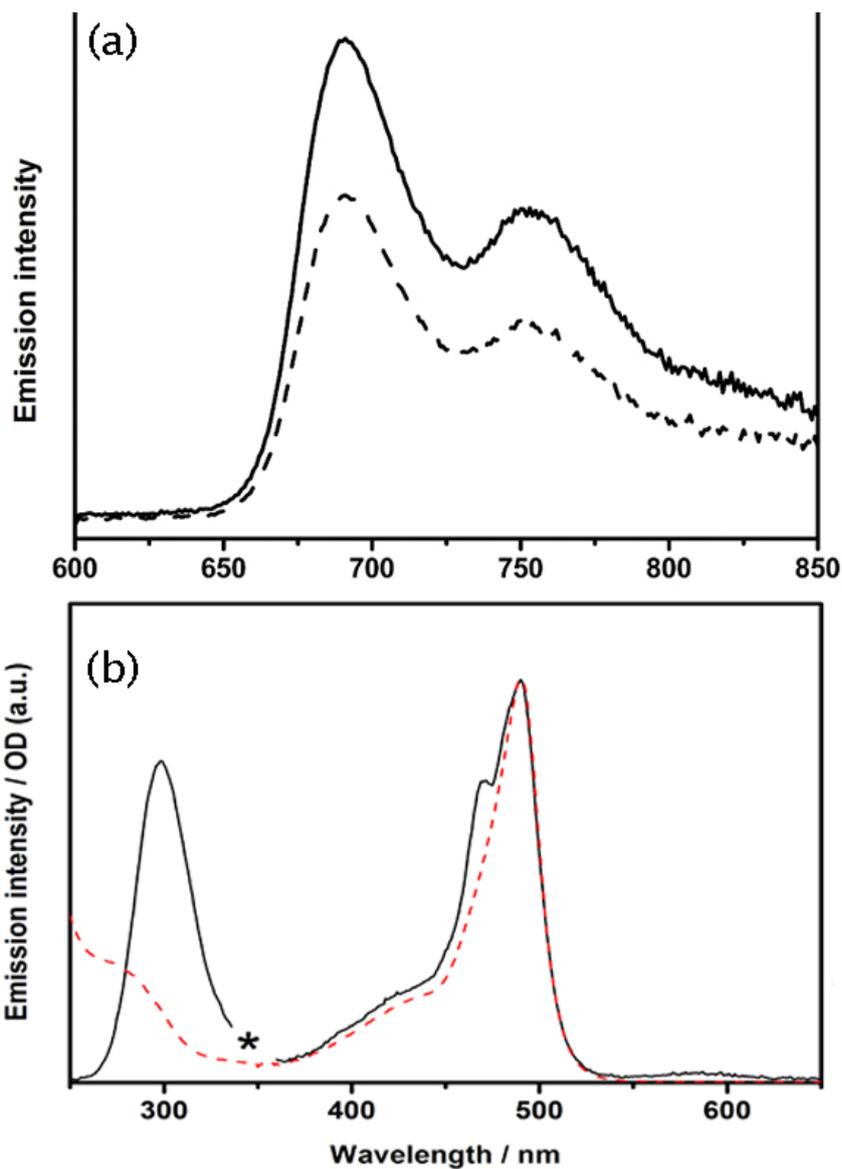


Figure S16. (a) Emission spectra of **2E** in CH₂Cl₂ ($\lambda_{\text{ex}} = 485$ nm). The solid curve was measured following rigorous deoxygenation of the solvent, and the dotted curve was measured after 2 mL of air was bubbled through the sample. (b) Excitation spectrum ($\lambda_{\text{em}} = 700$ nm) of **2D** in CH₂Cl₂ (solid black curve; the asterix denotes where an artefact peak was removed) overlaid with the absorption spectrum of **2D** in CH₂Cl₂ (dashed red curve).

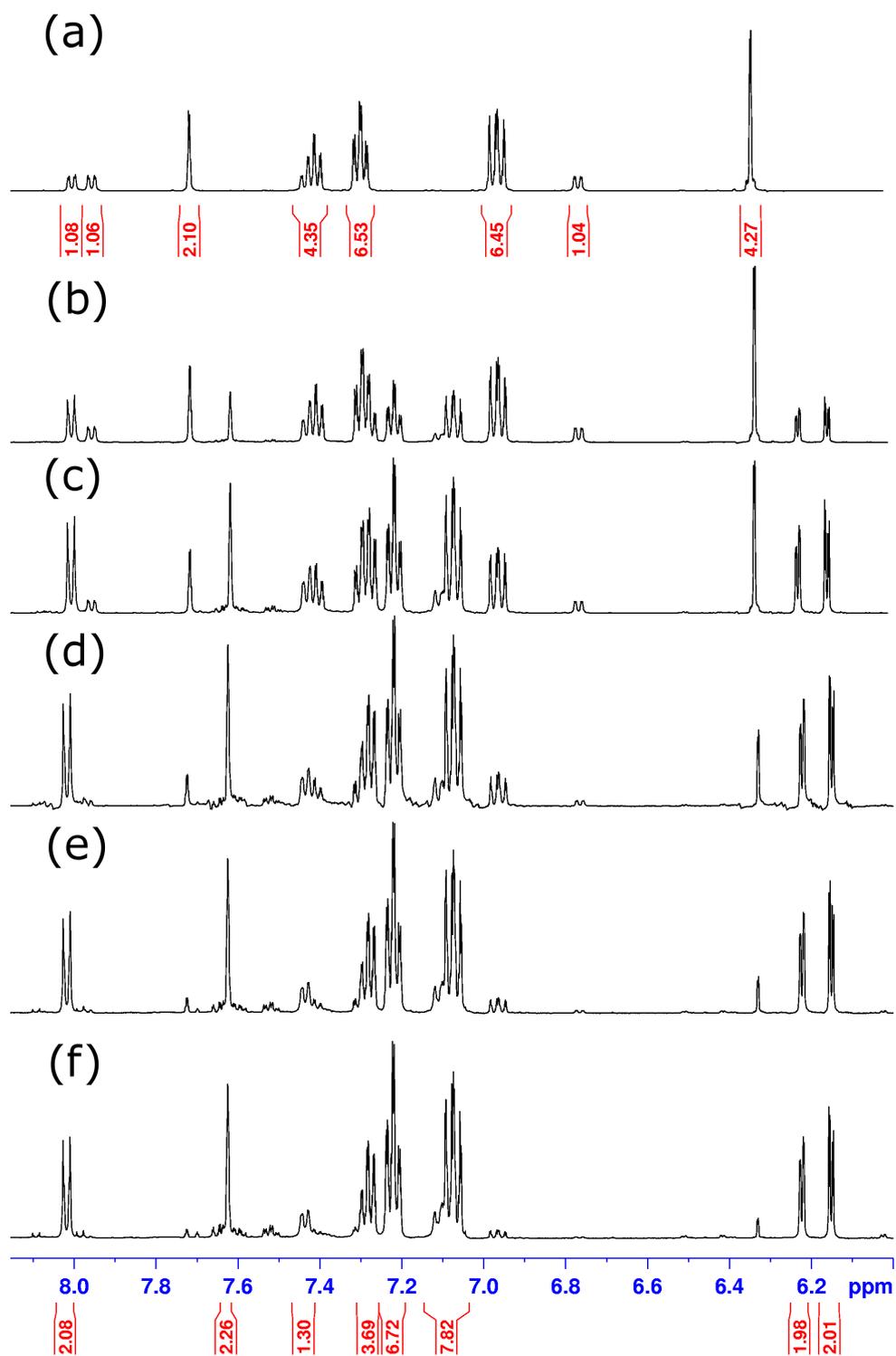


Figure S17. Aromatic region of the ^1H NMR spectrum (CD_3CN) of the PLS reaction of **2A**. (a) Starting material, **2A**; (b) after 30 mins irradiation, (c) after 60 mins irradiation, (d) after 90 mins irradiation, (e) after 120 mins irradiation, and (f) after 150 mins irradiation (proposed complex, **4A**).

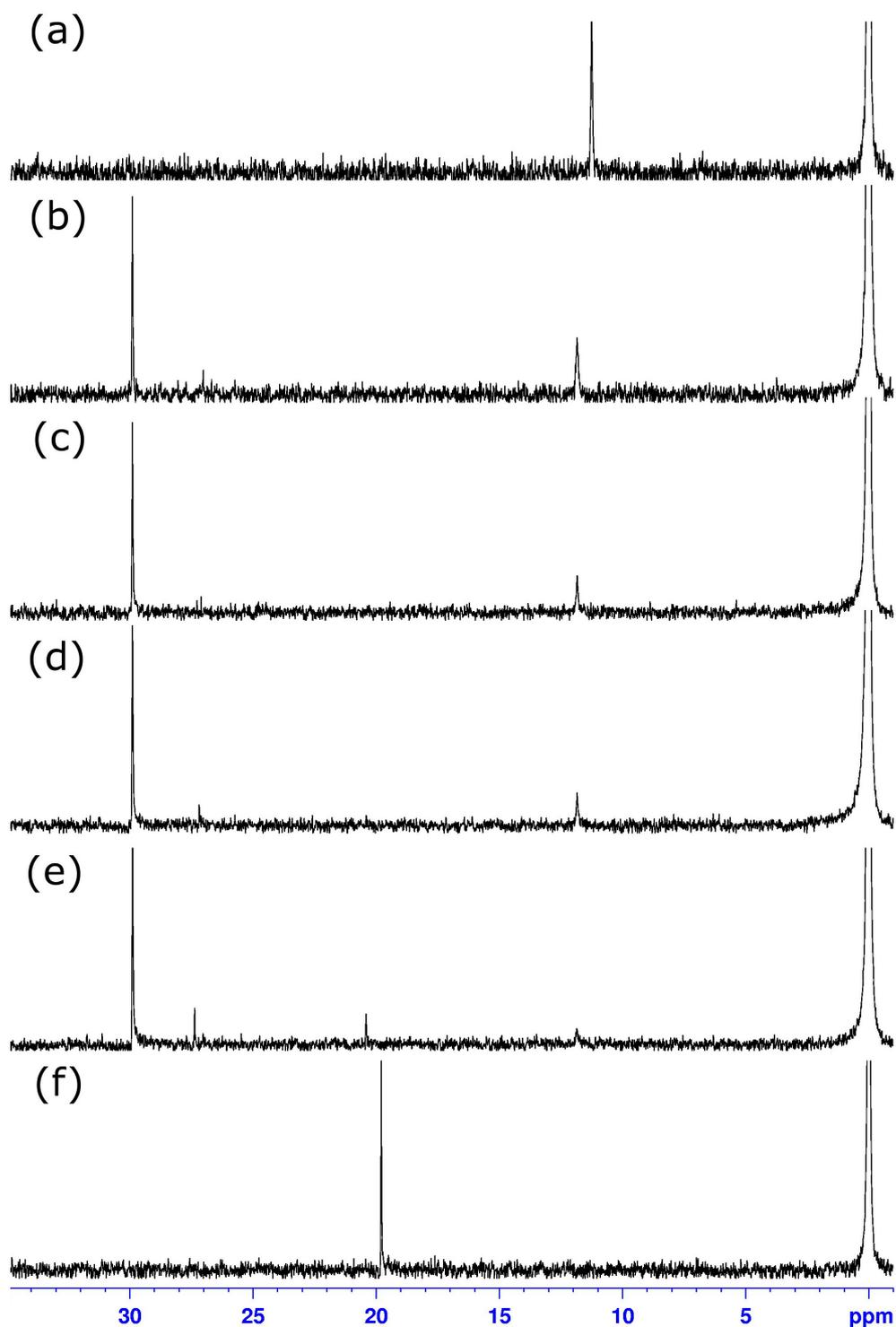


Figure S18. ^{31}P NMR spectroscopy was used to monitor the PLS reaction of **2A**. (a) Starting material, **2A** (in CDCl_3), (b) after 60 mins irradiation in CD_3CN , (c) after 90 mins irradiation in CD_3CN , (d) after 120 mins irradiation in CD_3CN , (e) after 150 mins irradiation in CD_3CN . (f) For comparison, the spectrum of **3A** in CDCl_3 is shown. For all spectra, the peak at 0 ppm is the internal reference (H_3PO_4 in a capillary).

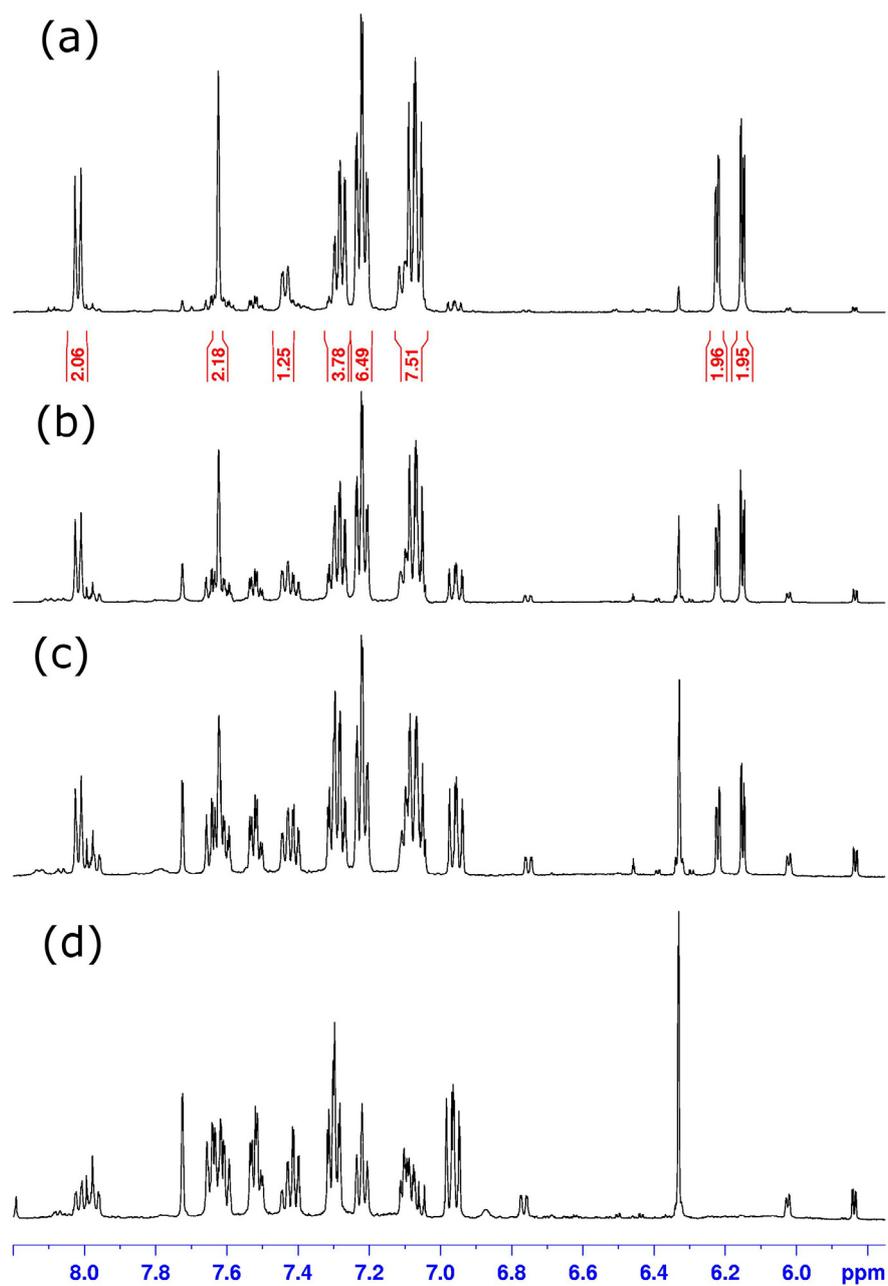


Figure S19. ^1H NMR spectroscopy (CD_3CN , 25°C) was used to monitor the decomposition reaction of **4A** following its generation by the PLS reaction of **2A**. (a) Complex **4A** (b) 1 day after the reaction; (c) 2 days after the reaction; (d) 13 days after the reaction.

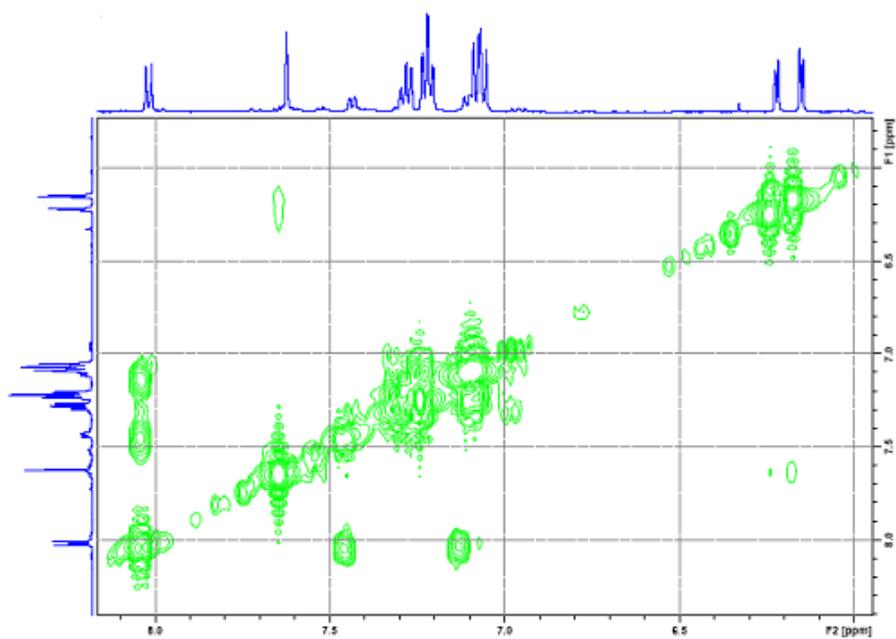


Figure S20. 2D-COSY NMR spectrum of **4A** generated by irradiation of **2A** with 355 nm laser light for 2 hours.

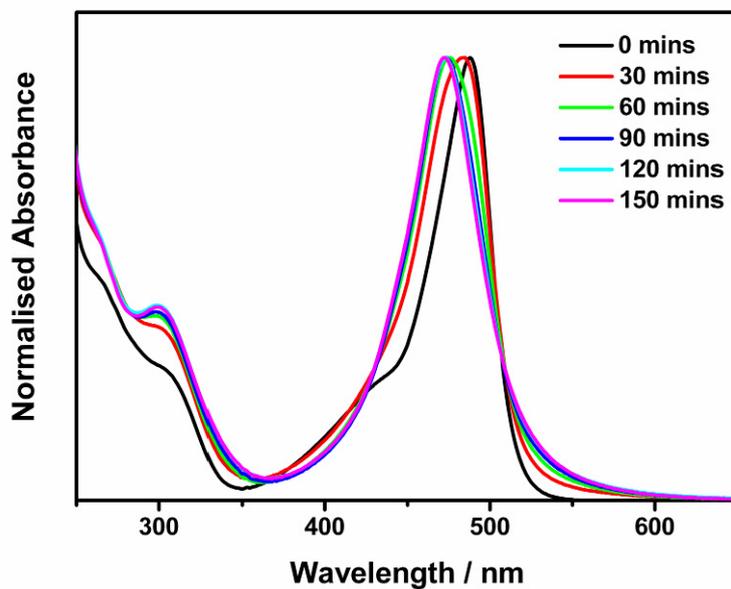


Figure S21. The photochemical conversion of **2A** to **4A** in CD_3CN monitored by absorption spectroscopy over the period of 150 mins. Note that the spectra have been normalized.

5. DFT calculations

Gaussian 09 software was employed.³ Calculations were carried out using density functional theory (DFT) with the B3LYP exchange-correlation functional and the SDD basis set. Solvent effects were accounted for using self-consistent reaction field methods, specifically the polarizable continuum model (PCM) of Barone.⁴ The geometry of **2A** was optimised and good agreement was found with the molecular structure of the compound determined by X-ray crystallography. The electronic excited states were calculated using time-dependent DFT (TD-DFT).

Table S1. Electronic transitions calculated for **2A** using TD-DFT.

λ (nm)	Dominant one-electron promotions (% contribution)	Oscillator strength
444	HOMO-2→LUMO (63), HOMO-1→LUMO (-18), HOMO→LUMO (13)	0.039
435	HOMO-2→LUMO (11), HOMO-1→LUMO (75)	0.088
412	HOMO-2→LUMO (-21), HOMO→LUMO (56)	0.340
360	HOMO→LUMO+1 (96)	0.043
316	HOMO-6→LUMO (37), HOMO-5→LUMO (38)	0.047
314	HOMO-9→LUMO (-18), HOMO-7→LUMO (36), HOMO-2→LUMO+2 (16), HOMO-2→LUMO+3 (-10)	0.057
299	HOMO-3→LUMO+3 (27), HOMO-1→LUMO+3 (34)	0.035
289	HOMO-3→LUMO+1 (-11), HOMO-3→LUMO+3 (48), HOMO-1→LUMO+3 (-11)	0.030
267	HOMO-2→LUMO+5 (47)	0.049

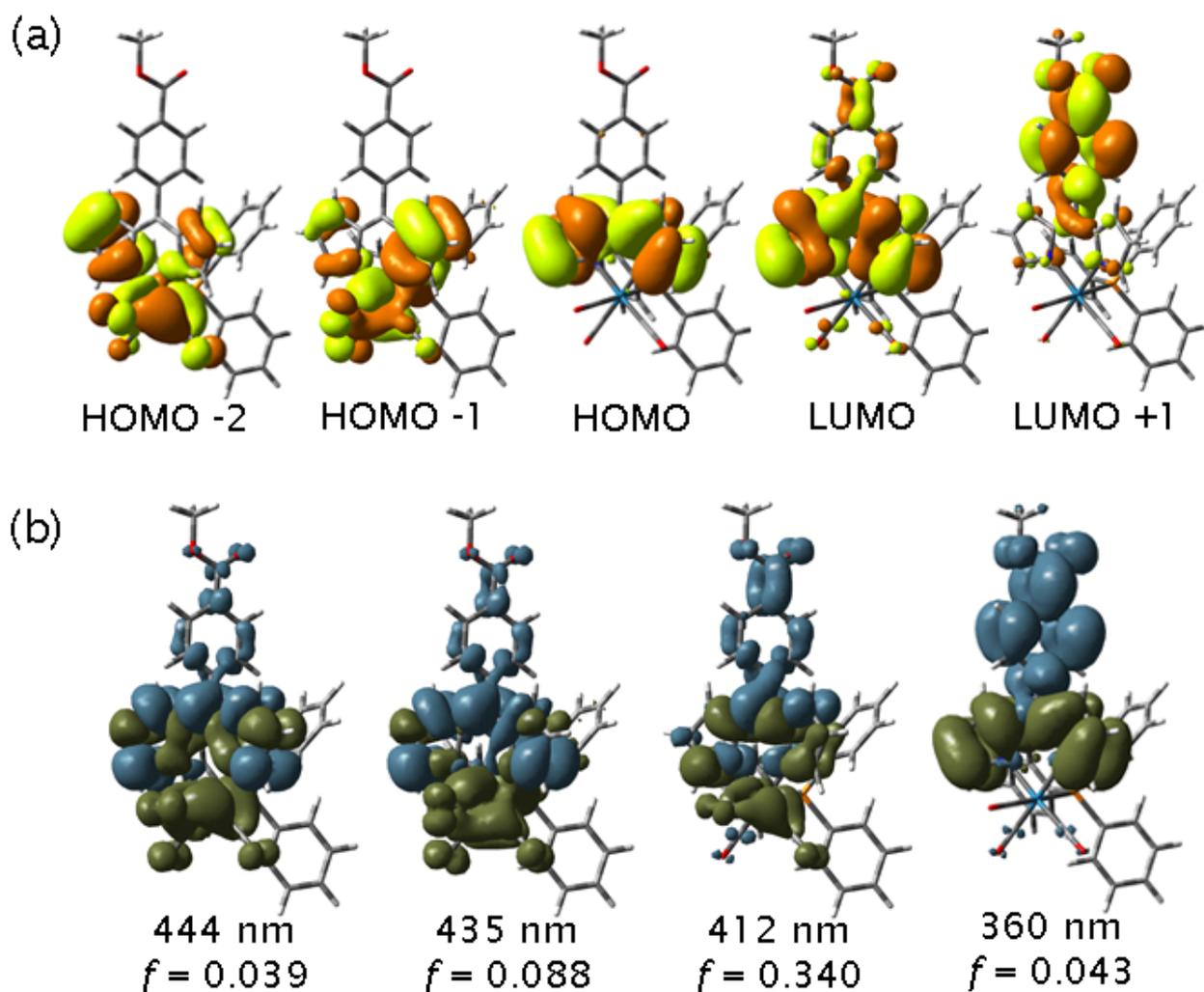


Figure S22. (a) Frontier molecular orbitals of **2A** as calculated by DFT. (b) Electron density difference plots for the four lowest-energy electronic transitions of **2A**, as calculated by TD-DFT. Green represents depletion of electron density and blue represents accumulation of electron density.

6. References

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