

SUPPORTING INFORMATION

Ligand Tuning in Pyridine-Alkoxide Ligated Cp*Ir^{III} Oxidation Catalysts

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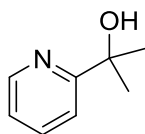
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Contents

1. Ligand Syntheses.....	3
2. Original NMR spectra	6
3,3,5,5-Tetramethyl-1-(2-pyridyl)cyclohexanol, L6	6
1,1-Diphenyl-1-(2-quinolyl)methanol, L7	7
$[\eta^5(\text{C}_5\text{Me}_5)\text{Ir}^{\text{III}}\{2,2,4,4\text{-Tetramethyl-3-(2-pyridyl)-3-pentanoate-}\kappa\text{O},\kappa\text{N}\}][\text{SbF}_6]$, 3.....	9
$[\eta^5(\text{C}_5\text{Me}_5)\text{Ir}^{\text{III}}\{1\text{-(2-Pyridyl)cyclohexanoate-}\kappa\text{O},\kappa\text{N}\}\text{Cl}]$, 4	10
$[\eta^5(\text{C}_5\text{Me}_5)\text{Ir}^{\text{III}}\{2\text{-(2-Quinolyl)-2-propanoate-}\kappa\text{O},\kappa\text{N}\}\text{Cl}]$, 5	11
$[\eta^5(\text{C}_5\text{Me}_5)\text{Ir}^{\text{III}}\{3,3,5,5\text{-Tetramethyl-1-(2-pyridyl)cyclohexanoate-}\kappa\text{O},\kappa\text{N}\}\text{Cl}]$, 6.....	12
$[\eta^5(\text{C}_5\text{Me}_5)\text{Ir}^{\text{III}}\{\text{Diphenyl(2-quinolyl)methanoate-}\kappa\text{O},\kappa\text{N}\}\text{Cl}]$, 7	13
3. ^1H NMR analysis of precatalyst activation.....	14
4. 2D UV-vis plots of precatalyst activation	18
5. X-Ray crystallography	26
6. References.....	26

1. Ligand Syntheses

2-(2-Pyridyl)-2-propanol¹, L1



A solution of 2-acetyl pyridine (20 mmol, 2.42g) in diethyl ether (50 mL) was placed in a flame dried round bottom flask and cooled to 0 °C. Methyl magnesium bromide (3 M in diethyl ether, 22 mmol, 7.3 mL) was added dropwise via a dropping funnel and the resultant solution was stirred at room temperature for 1 hour. The reaction was quenched by addition of water (50 mL) and conc. HCl (3 mL). The product was extracted with diethyl ether (3 x 50 mL), the combined organic extracts dried over MgSO₄, filtered and dried *in vacuo* to give a pale yellow oil.

Purification: Upon addition of hexane (5 mL) and storage at -20 °C colourless crystals formed, which were collected from their yellow supernatant and dried *in vacuo*.

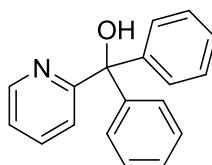
Yield: 1.70 g (62 %).

¹H-NMR (400 MHz, CDCl₃): δ = 8.48 (d, J = 4.8 Hz, 1H, H_{arom}), 7.67 (t, J = 7.8 Hz, 1H, H_{arom}), 7.36 (d, J = 8.0 Hz, 1H, H_{arom}), 7.16 (t, J = 6.3 Hz, 1H, H_{arom}), 5.09 (s, 1H, OH), 1.52 (s, 6H, [CH₃]₂).

General procedure for L2-L7

2-bromo pyridine or 2-bromo quinoline (20 mmol) was degassed by careful application of vacuum, dissolved in dry THF (40 mL) and the solution cooled to -78°C. n-BuLi (1.6 M in hexanes, 22 mmol) was added via a dropping funnel over 20 mins. The resulting yellow solution was stirred for 1.5 hours at -78°C and a series of colour changes was observed (yellow -> orange -> brown). A solution of the desired ketone (20 mmol) in dry THF (10 mL) was added to the dropping funnel and added to the solution over 10 mins. The solution was left to warm to room temperature and stirred for 18 hours, after which time it had turned dark green. The reaction was quenched by addition of 1 M NaOH (25 mL) and water (25 mL), changing to yellow. The product was extracted with diethyl ether (3 x 50 mL), the combined organic extracts dried over MgSO₄, filtered and dried *in vacuo* to afford the crude product as an oil.

Diphenyl(2-pyridyl)methanol², L2

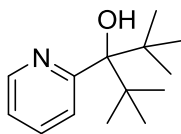


Purification: The crude product (a dark orange oil) was recrystallized from hexane (20 mL) and the yellow supernatant removed. The resulting solid was washed with hexane (2 x 20 mL), giving a creamy white, microcrystalline solid.

Yield: 1.69 g (32 %).

¹H-NMR (400 MHz, CDCl₃): δ = 8.60 (d, J = 4.9 Hz, 1H, H_{arom}), 7.64 (t, J = 7.7 Hz, 1H, H_{arom}), 7.29 (s + m, 11H, H_{arom} + CH_{phenyl}), 7.12 (d, J = 9.7 Hz, 1H, H_{arom}), 6.30 (s, 1H, OH).

2,2,4,4-Tetramethyl-3-(2-pyridyl)-3-pentanol³, L3

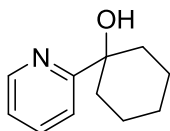


Purification: The crude product (a dark brown oil) was purified via sublimation under high vacuum at 45 °C onto a cold finger at -78 °C, yielding colourless crystals.

Yield: 0.53 g (34 %).

¹H-NMR (400 MHz, CDCl₃): δ = 8.49 (d, J = 5.0 Hz, 1H, H_{arom}), 7.62 (m, 2H, H_{arom}), 7.19 (t, J = 5.9 Hz, 1H, H_{arom}), 6.66 (s, 1H, OH), 1.03 (s, 18H, [CH₃]₆).

1-(2-Pyridyl)cyclohexanol⁴, L4

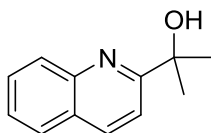


Purification: The crude product (a dark brown oil) was purified via sublimation under high vacuum at 50 °C onto a cold finger at -78 °C, yielding a colourless solid.

Yield: 0.77 g (22 %).

¹H-NMR (400 MHz, CDCl₃): δ = 8.51 (d, J = 4.1 Hz, 1H, H_{arom}), 7.69 (t, J = 7.7 Hz, 1H, H_{arom}), 7.39 (d, J = 8.1 Hz, 1H, H_{arom}), 7.19 (t, J = 6.2 Hz, 1H, H_{arom}), 4.88 (s, 1H, OH), 1.76 (m, 6H, CH_{hexyl}).

2-(2-Quinolyl)-2-propanol⁵, L5

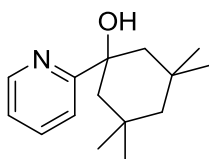


Purification: The product was extracted with diethyl ether (3 x 50 mL), the combined organic extracts dried over MgSO₄, filtered and dried *in vacuo* to afford a brown oil that was pure by NMR analysis.

Yield: 0.32 g (72 %).

¹H-NMR (400 MHz, CDCl₃): δ = 8.18 (d, J = 8.6 Hz, 1H, H_{arom}), 8.06 (d, J = 8.5 Hz, 1H, H_{arom}), 7.81 (d, J = 8.2 Hz, 1H, H_{arom}), 7.72 (t, J = 7.7 Hz, 1H, H_{arom}), 7.54 (t, J = 7.5 Hz, 1H, H_{arom}), 7.45 (d, J = 8.6 Hz, 1H, H_{arom}), 5.92 (s, 1H, OH), 1.61 (s, 6H, [CH₃]₂).

3,3,5,5-Tetramethyl-1-(2-pyridyl)cyclohexanol, L6



Purification: The crude product (a dark red oil) was recrystallised from cold hexane (20 mL, -78°C) and the supernatant removed to give brown crystals which were dried *in vacuo*.

Yield: 0.65 g (28 %).

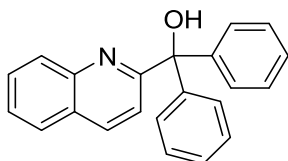
¹H-NMR (400 MHz, CDCl₃): δ = 8.50 (d, J = 4.8 Hz, 1H, H_{arom}), 7.68 (t, J = 8.0 Hz, 1H, H_{arom}), 7.40 (d, J = 8.0 Hz, 1H, H_{arom}), 7.16 (t, J = 8.0 Hz, 1H, H_{arom}), 4.99 (bs, 1H, OH), 1.56 (s, 4H, H_{cyclohex}), 1.51 (d, J = 13.6 Hz, 2H, H_{cyclohex}), 1.34 (s, 6H, [CH₃]₂), 0.94 (s, 6H, [CH₃]₂)

¹³C-NMR (100 MHz, CD₂Cl₂): δ = 166.7 (C_{pyridine}), 147.2 (CH_{pyridine}), 136.8 (CH_{pyridine}), 121.6 (CH_{pyridine}), 118.92 (CH_{pyridine}), 75.5 (C), 51.8 (CH₂), 49.7 (CH₂), 36.6 (CH₃), 31.7 (C), 28.2 (CH₃).

HR ESI-MS (+): m/z calculated for C₁₅H₂₃NO: [M+H]⁺ 234.1849, 235.1882; found 234.1852, 235.1885.

Elemental analysis: calculated for C₁₅H₂₃NO: C 77.21, H 9.94, N 6.00; found: C 77.05, H 10.01, N 6.12.

1,1-Diphenyl-1-(2-quinolyl)methanol, L7



Purification: The product was recrystallied from DCM (5 mL) by addition of hexane (30 mL) and storage at -20°C for 24 hours. The supernatant was removed and the pale yellow solid was dried *in vacuo*.

Yield: 0.13 g (17 %).

¹H-NMR (400 MHz, CDCl₃): δ = 8.11 (t, J = 8.4 Hz, 2H, H_{arom}), 7.82 (d, J = 8.4 Hz, 1H, H_{arom}), 7.75 (t, J = 8.0 Hz, 1H, H_{arom}), 7.57 (t, J = 8.0 Hz, 1H, H_{arom}), 7.35-7.28 (m, 10H, H_{phenyl}), 7.15 (s, 1H, H_{arom}), 5.30 (s, 1H, OH);

¹³C-NMR (100 MHz, CD₂Cl₂): δ = 162.6 (C_{quinoline}), 146.1 (C_{quinoline}), 145.8 (C_{quinoline}), 136.7 (CH_{arom}), 130.1 (CH_{arom}), 129.1 (CH_{arom}), 128.4 (CH_{arom}), 128.1 (CH_{arom}), 127.6 (CH_{arom}), 127.5 (CH_{arom}), 127.3 (CH_{arom}), 127.0 (CH_{arom}), 120.9 (CH_{quin-arom}), 80.9 (C) ;

HR ESI-MS (+): m/z calculated for C₂₂H₁₇NO: [M+H]⁺ 312.1383, 313.1417; found 312.1375, 313.1407; [M-H₂O]⁺ 294.1277; found: 294.1273.

Elemental analysis: calculated for C₂₂H₁₇NO: C 84.86, H 5.50, N 4.50; found: C 84.78, H 5.42, N, 4.41.

2. Original NMR spectra

3,3,5,5-Tetramethyl-1-(2-pyridyl)cyclohexanol, **L6**

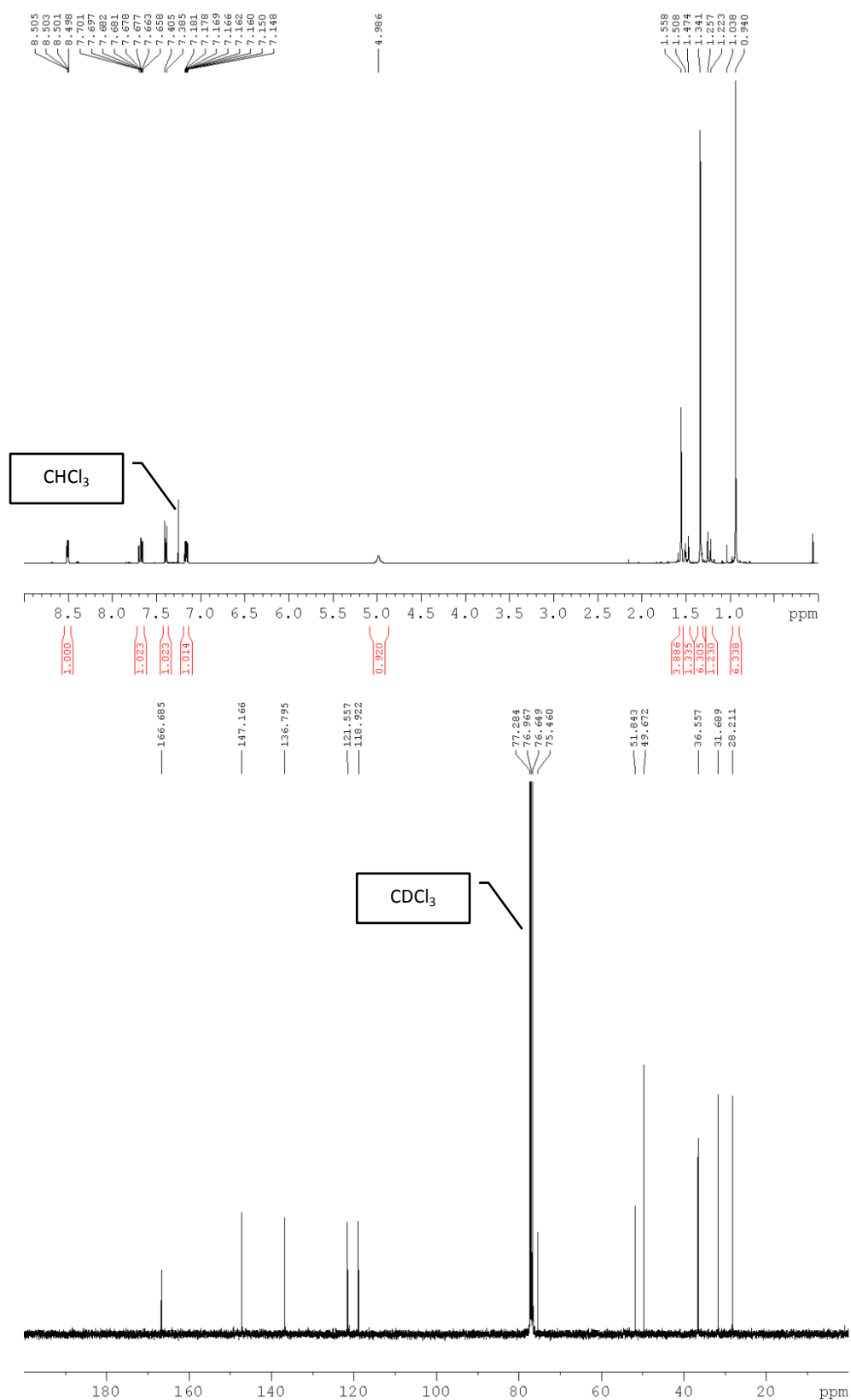
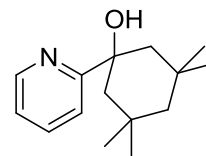


Figure S1. Original ¹H (above) and ¹³C (below) NMR spectra of compound **L6**

1,1-Diphenyl-1-(2-quinolyl)methanol, L7

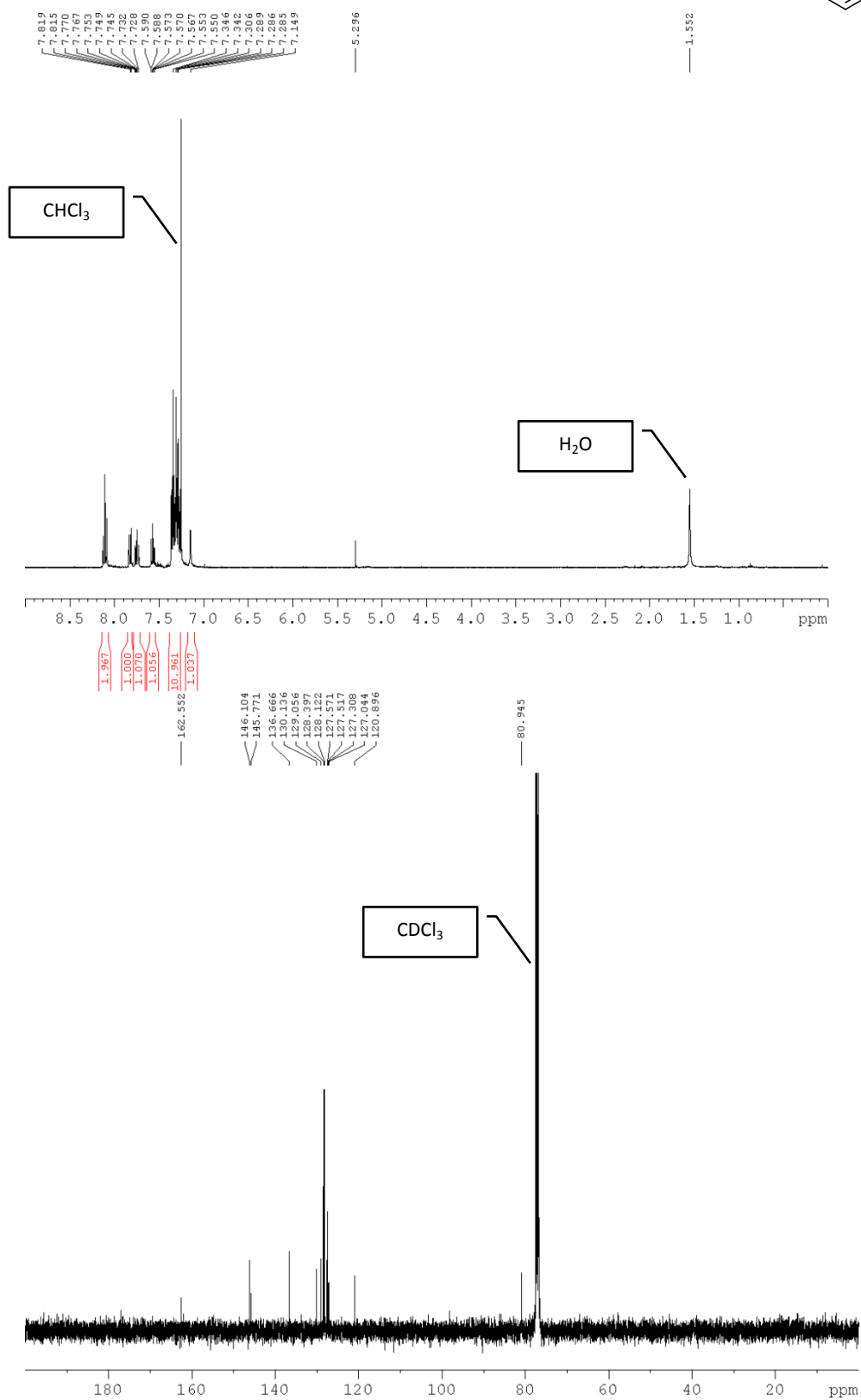
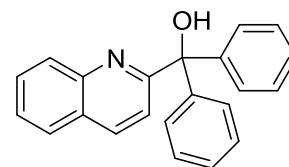


Figure S2. Original ^1H (above) and ^{13}C (below) NMR spectra for compound L7

$[\eta^5(\text{C}_5\text{Me}_5)\text{Ir}^{\text{III}}\{\text{Diphenyl}(2\text{-pyridyl})\text{methanolate-}\kappa\text{O},\kappa\text{N}\}\text{Cl}], \mathbf{2}$

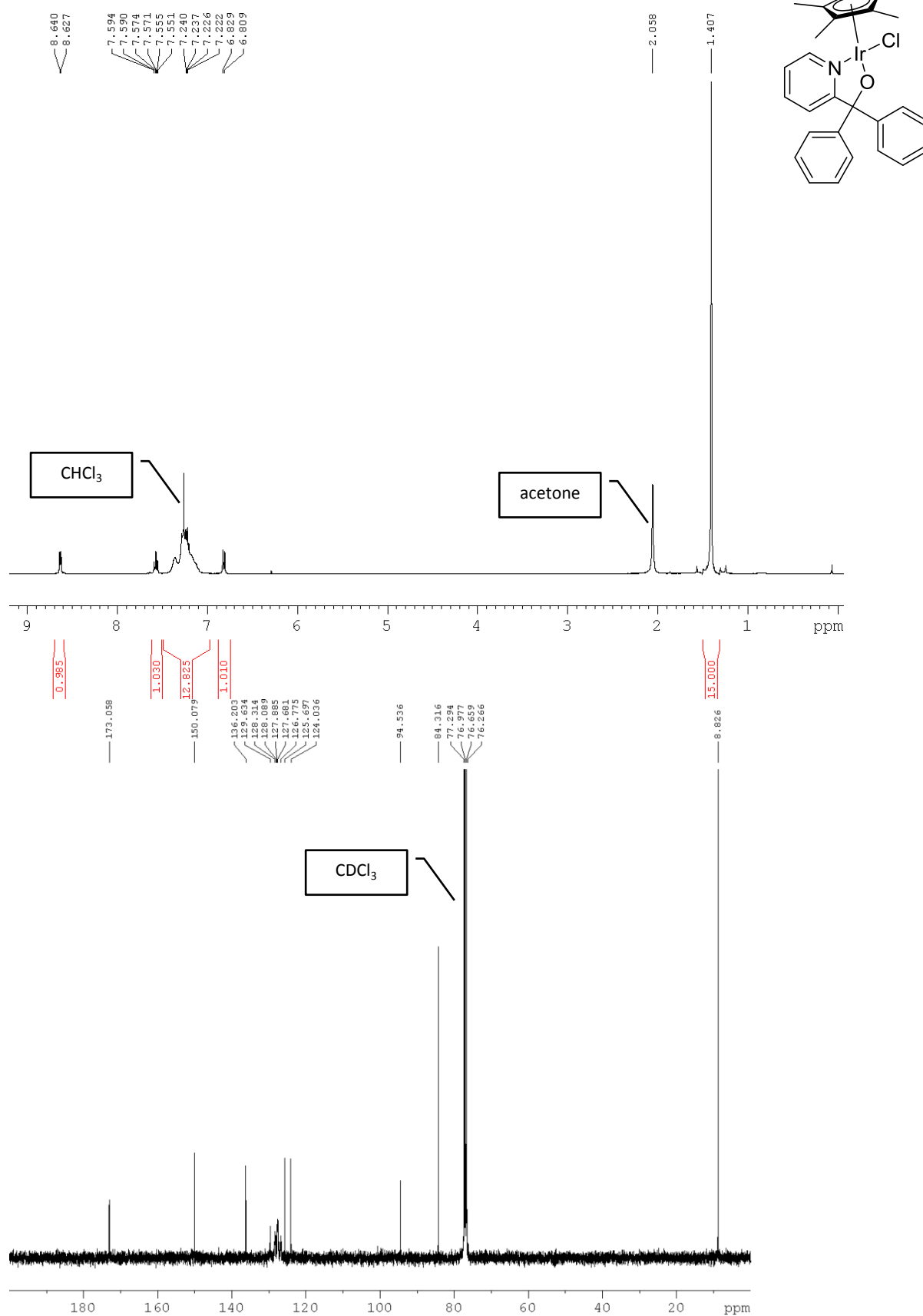


Figure S3. Original ^1H (above) and ^{13}C (below) NMR spectra for compound **2**

$[\eta^5(\text{C}_5\text{Me}_5)\text{Ir}^{\text{III}}\{2,2,4,4\text{-Tetramethyl-3-(2-pyridyl)-3-pentanolate-}\kappa\text{O},\kappa\text{N}\}][\text{SbF}_6]$, **3**

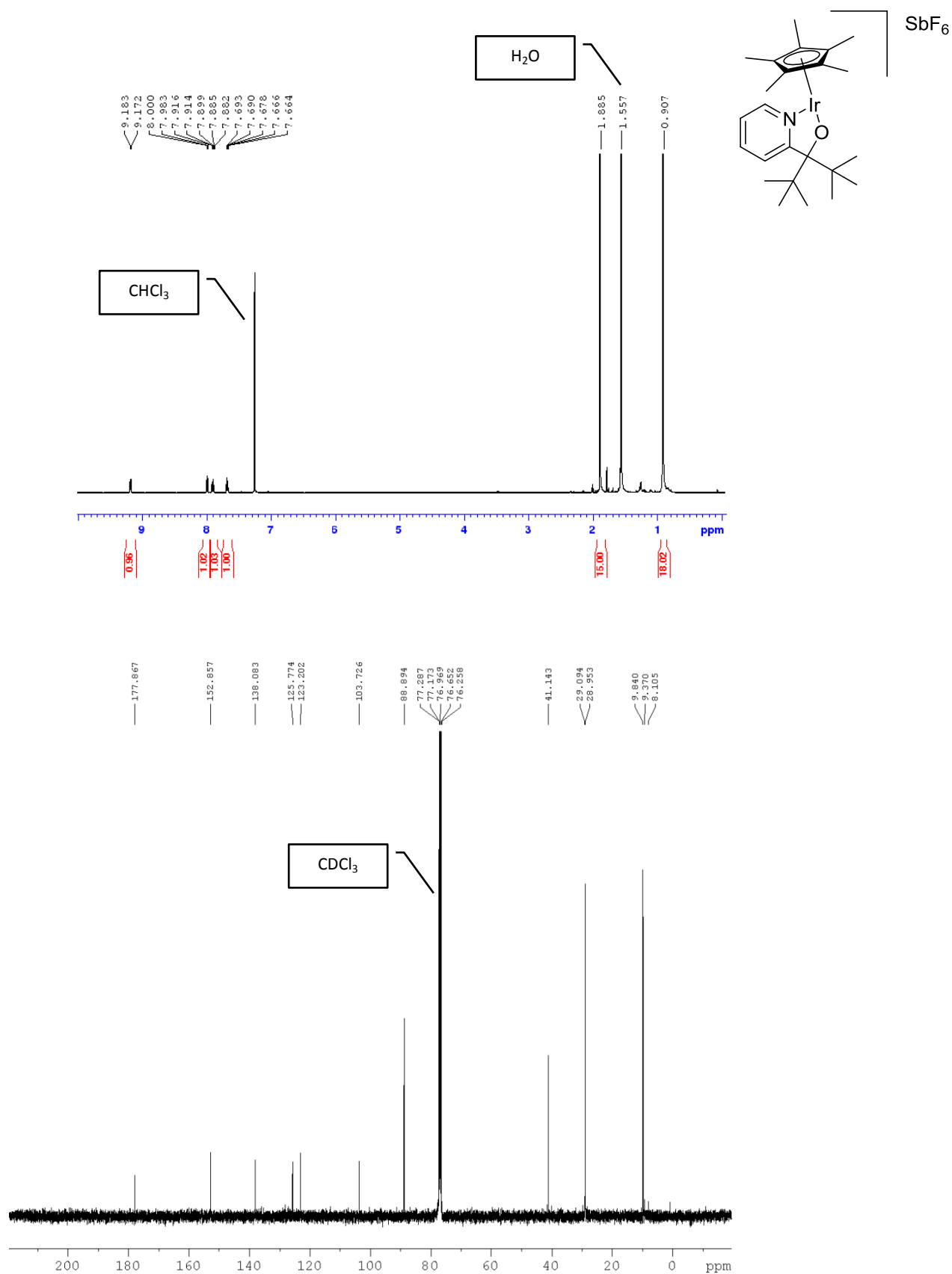


Figure S4. Original ^1H (above) and ^{13}C (below) NMR spectra for compound **3**

$[\eta^5(\text{C}_5\text{Me}_5)\text{Ir}^{\text{III}}\{1-(2\text{-Pyridyl})\text{cyclohexanolate-}\kappa\text{O},\kappa\text{N}\}\text{Cl}], \mathbf{4}$

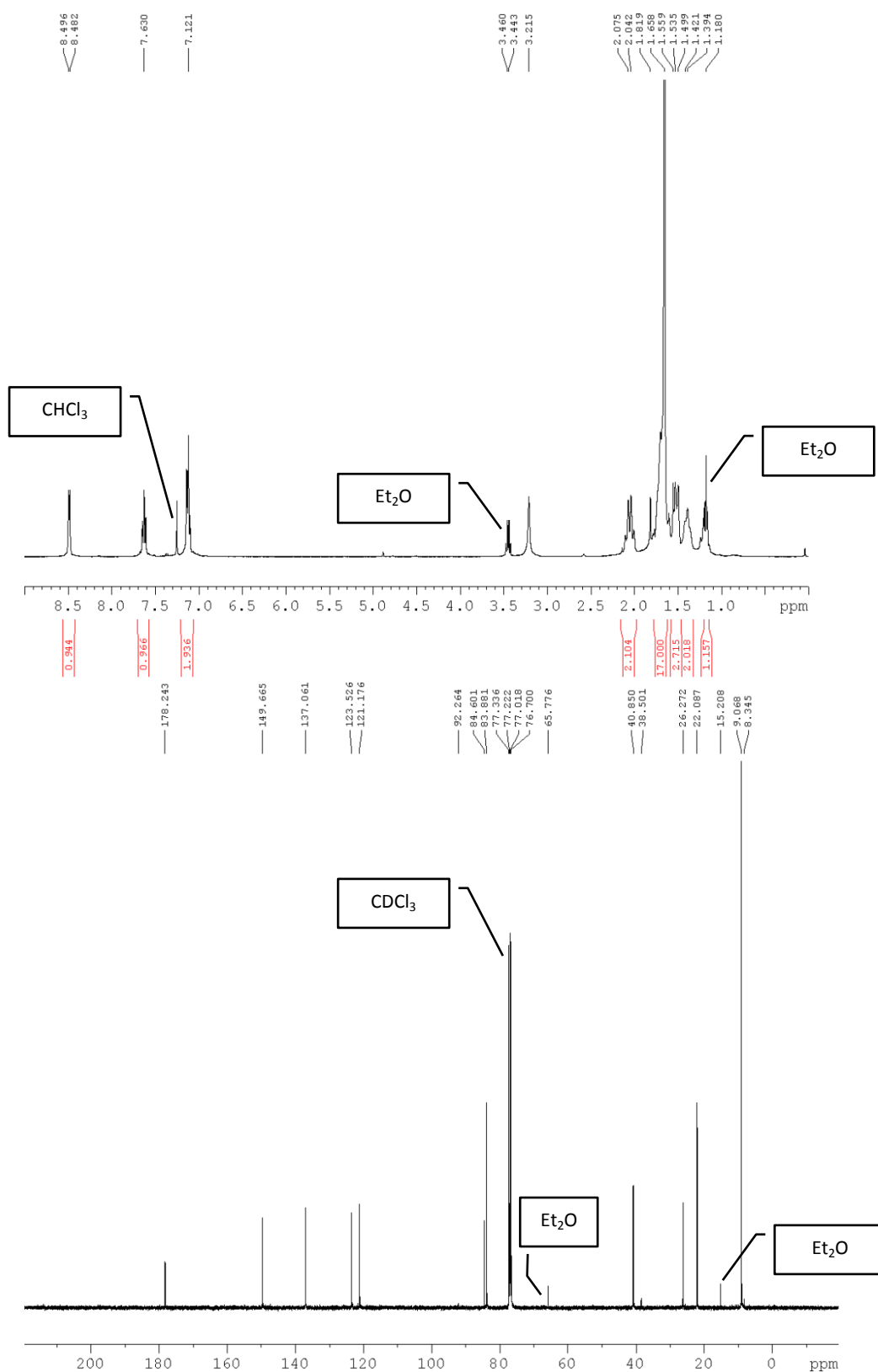
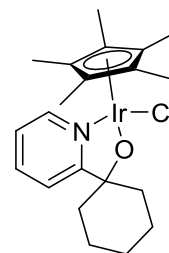


Figure S5. Original ^1H (above) and ^{13}C (below) NMR spectra for compound **4**

$[\eta^5(\text{C}_5\text{Me}_5)\text{Ir}^{\text{III}}\{2-(2\text{-Quinoly})\text{-2-propanolate-}\kappa\text{O},\kappa\text{N}\}\text{Cl}], \mathbf{5}$

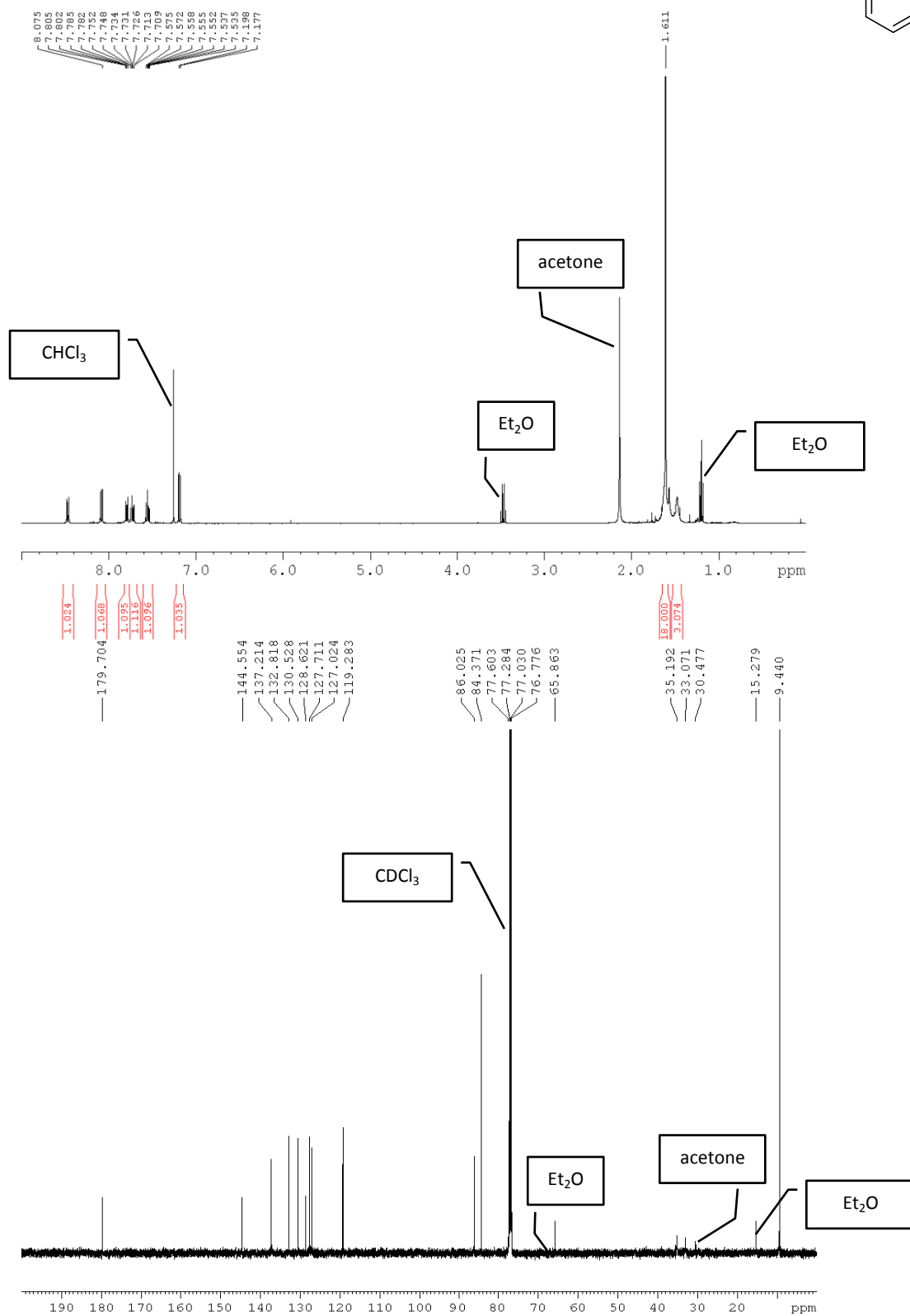
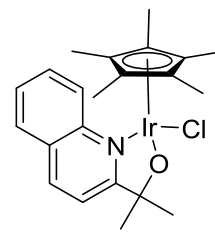


Figure S6. Original ^1H (above) and ^{13}C (below) NMR spectra for compound **5**

$[\eta^5(\text{C}_5\text{Me}_5)\text{Ir}^{\text{III}}\{3,3,5,5\text{-Tetramethyl-1-(2-pyridyl)cyclohexanolate-}\kappa\text{O},\kappa\text{N}\}\text{Cl}]$, **6**

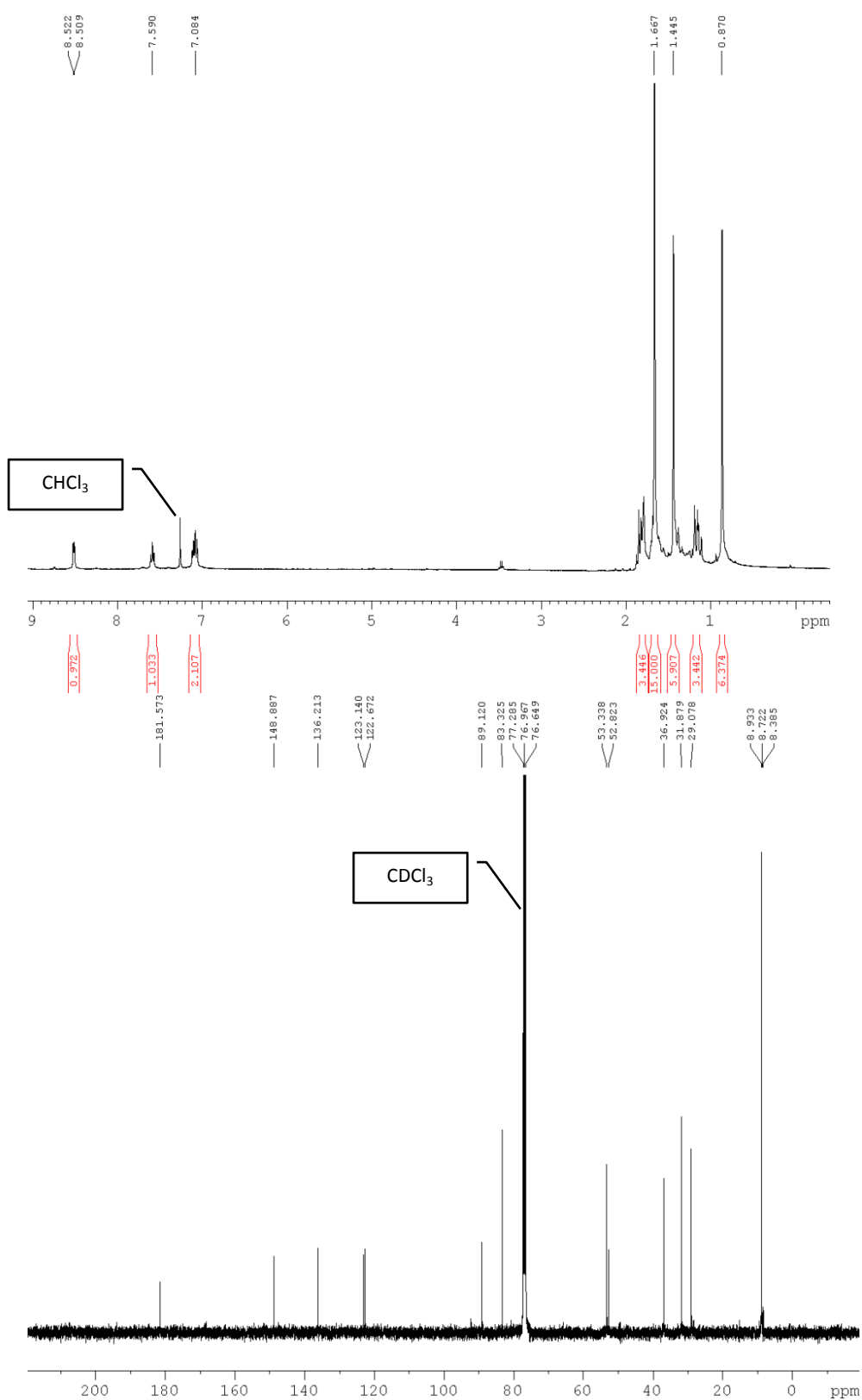
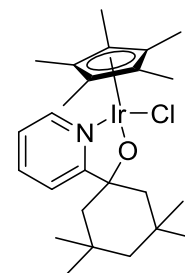


Figure S7. Original ^1H (above) and ^{13}C (below) NMR spectra for compound **6**

$[\eta^5(\text{C}_5\text{Me}_5)\text{Ir}^{\text{III}}\{\text{Diphenyl}(2\text{-quinolyl})\text{methanolate-}\kappa\text{O},\kappa\text{N}\}\text{Cl}], \mathbf{7}$

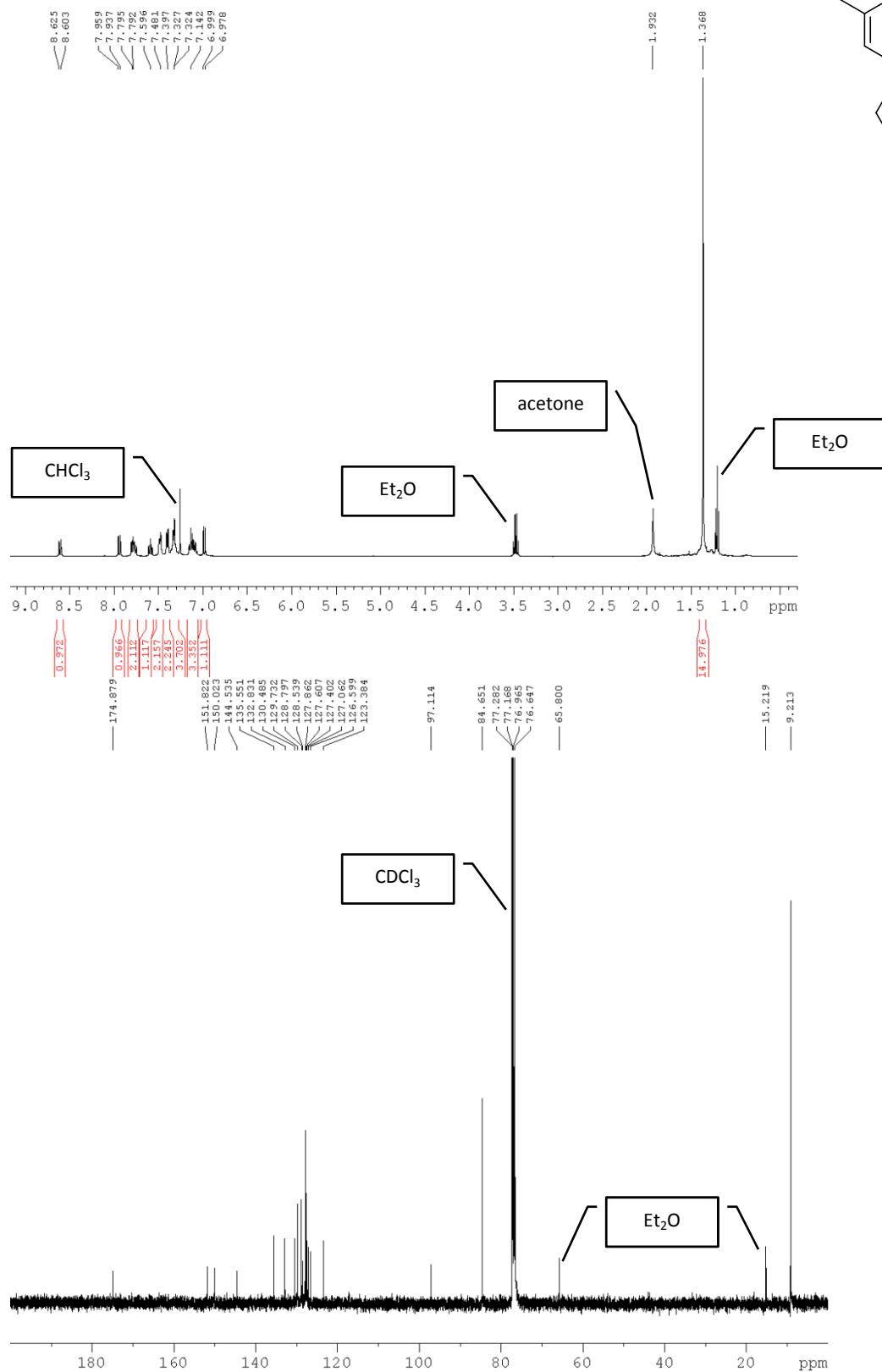
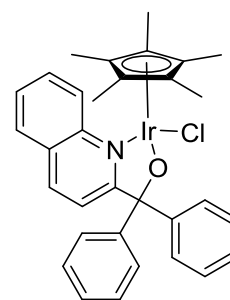
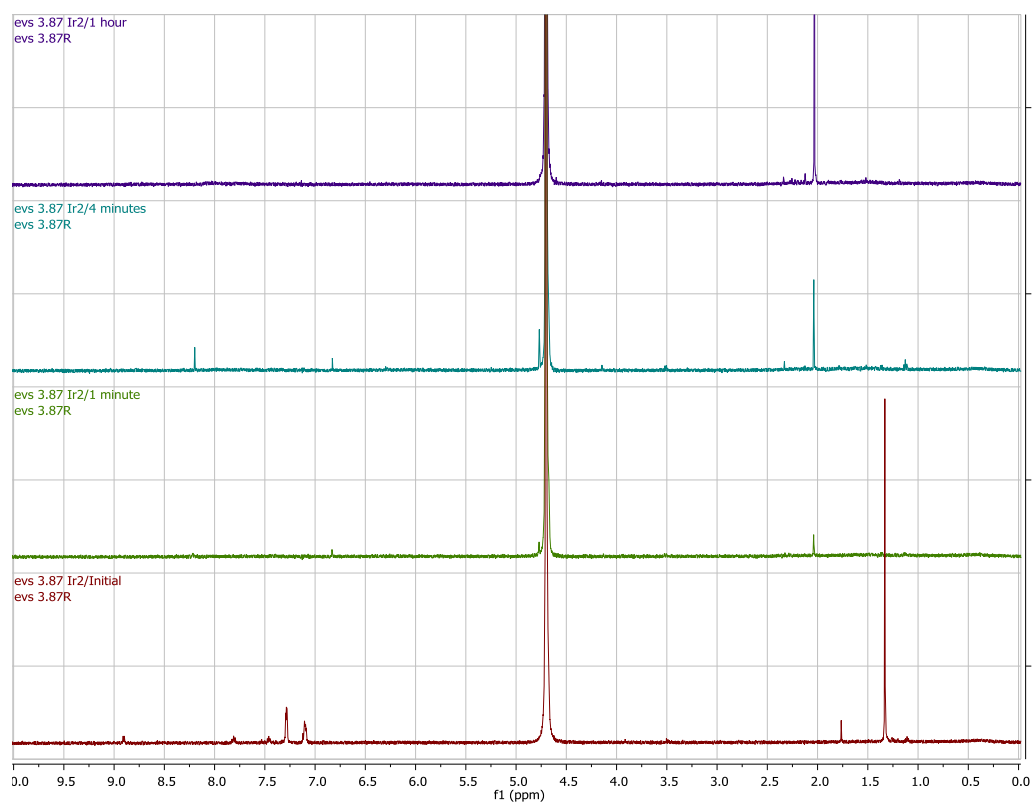
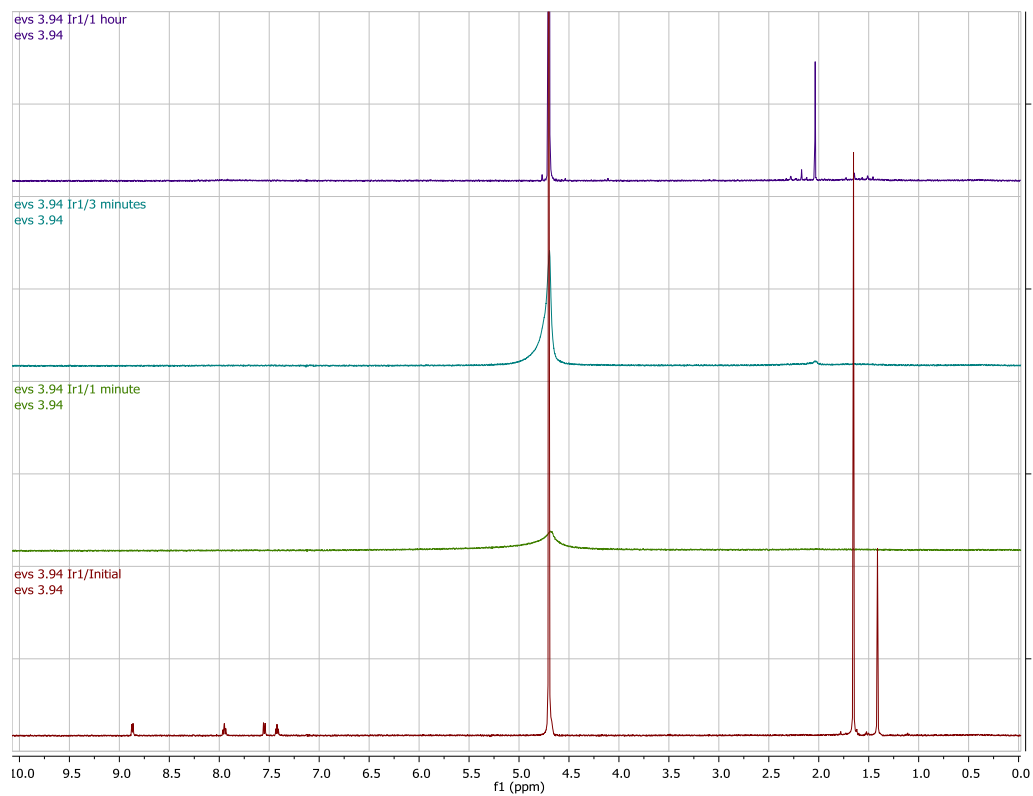
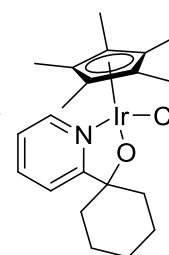
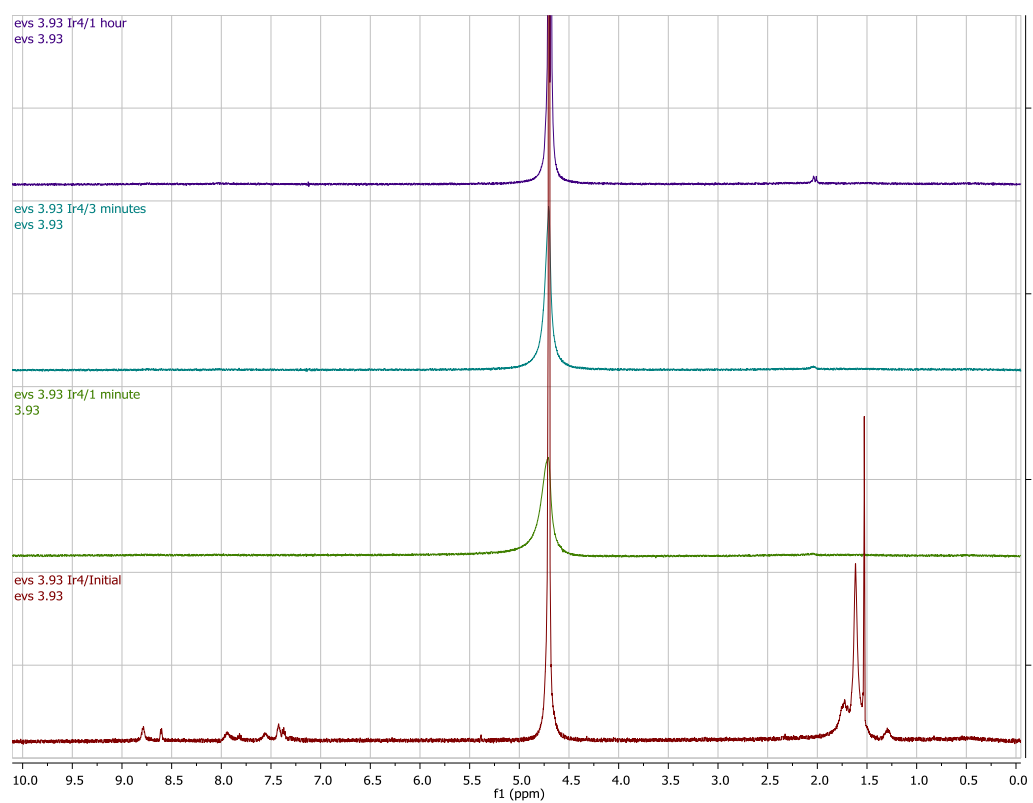
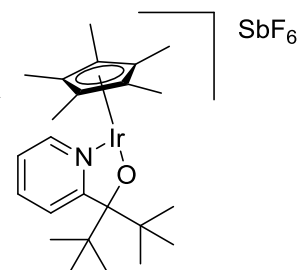
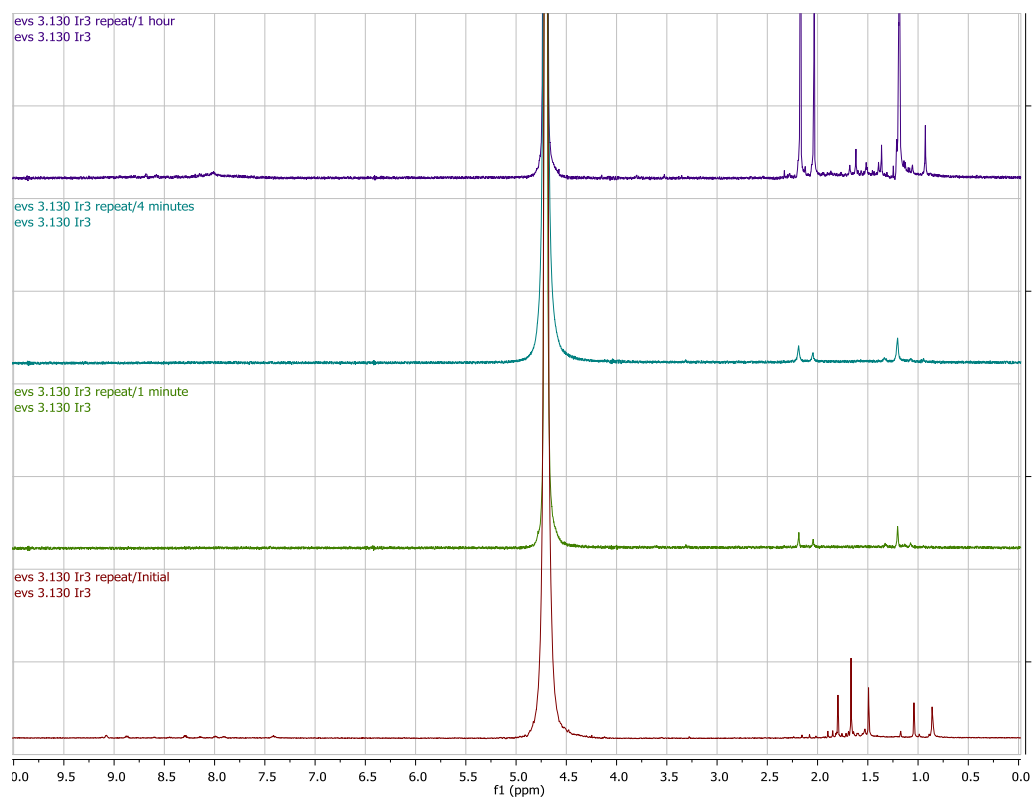
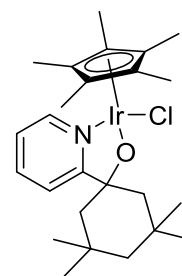
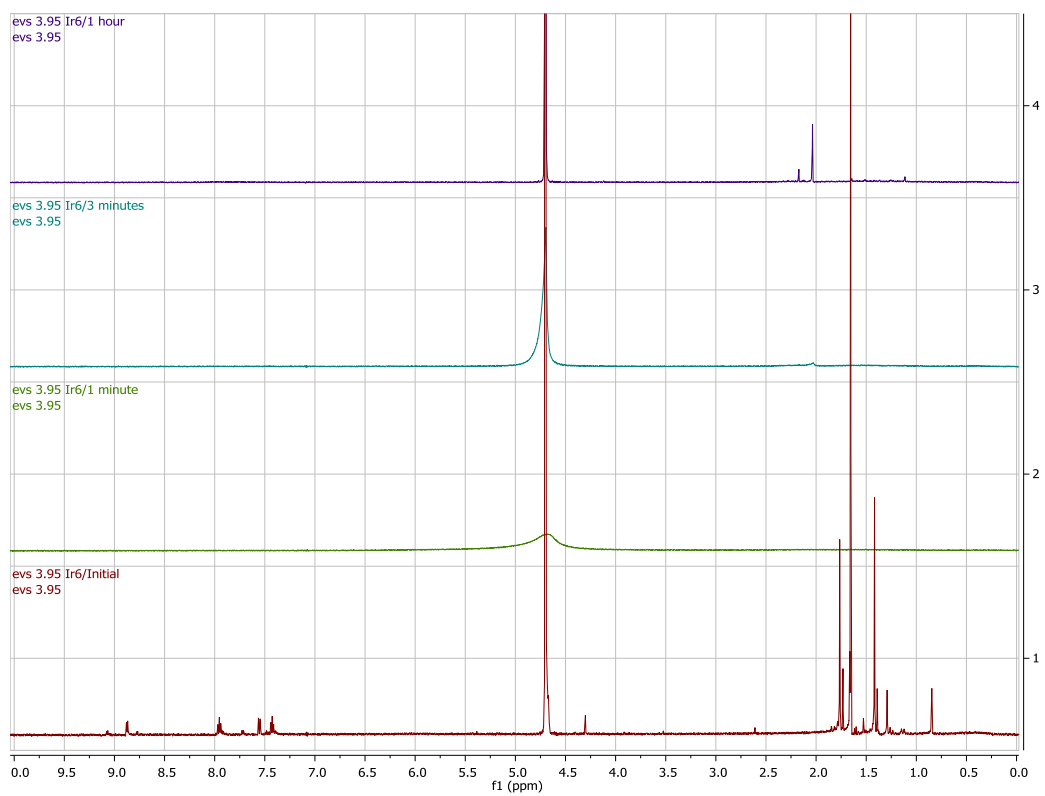
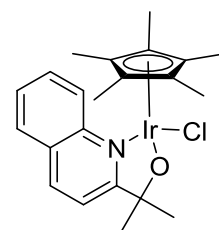
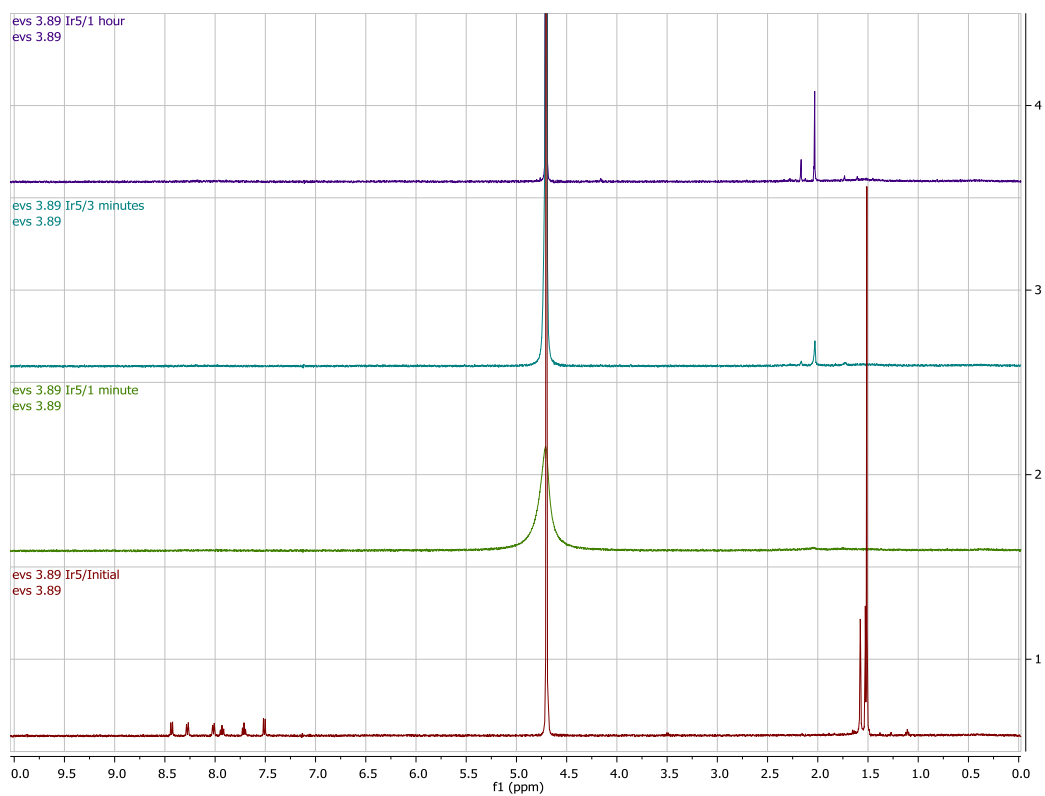


Figure S8. Original ^1H (above) and ^{13}C (below) NMR spectra for compound **7**

3. ^1H NMR analysis of precatalyst activation







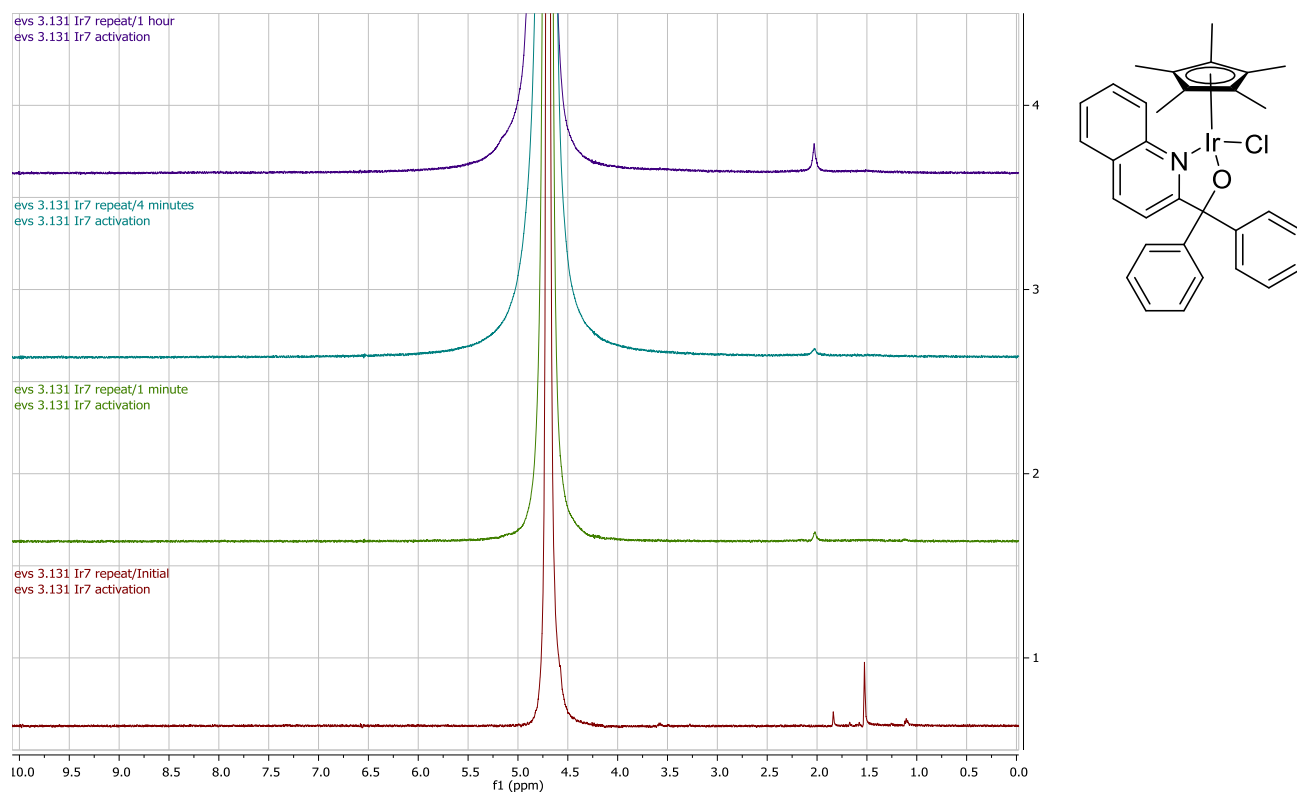


Figure S9A-G: ^1H NMR spectra of compounds **1-7** during precatalyst activation at $t = 0$ min, $t = 1$ min, $t = 3$ or 4 mins, $t = 60$ mins (from bottom to top). 5 mM [Ir] with 25 mM NaIO_4 in D_2O at room temperature.

4. 2D UV-vis plots of precatalyst activation

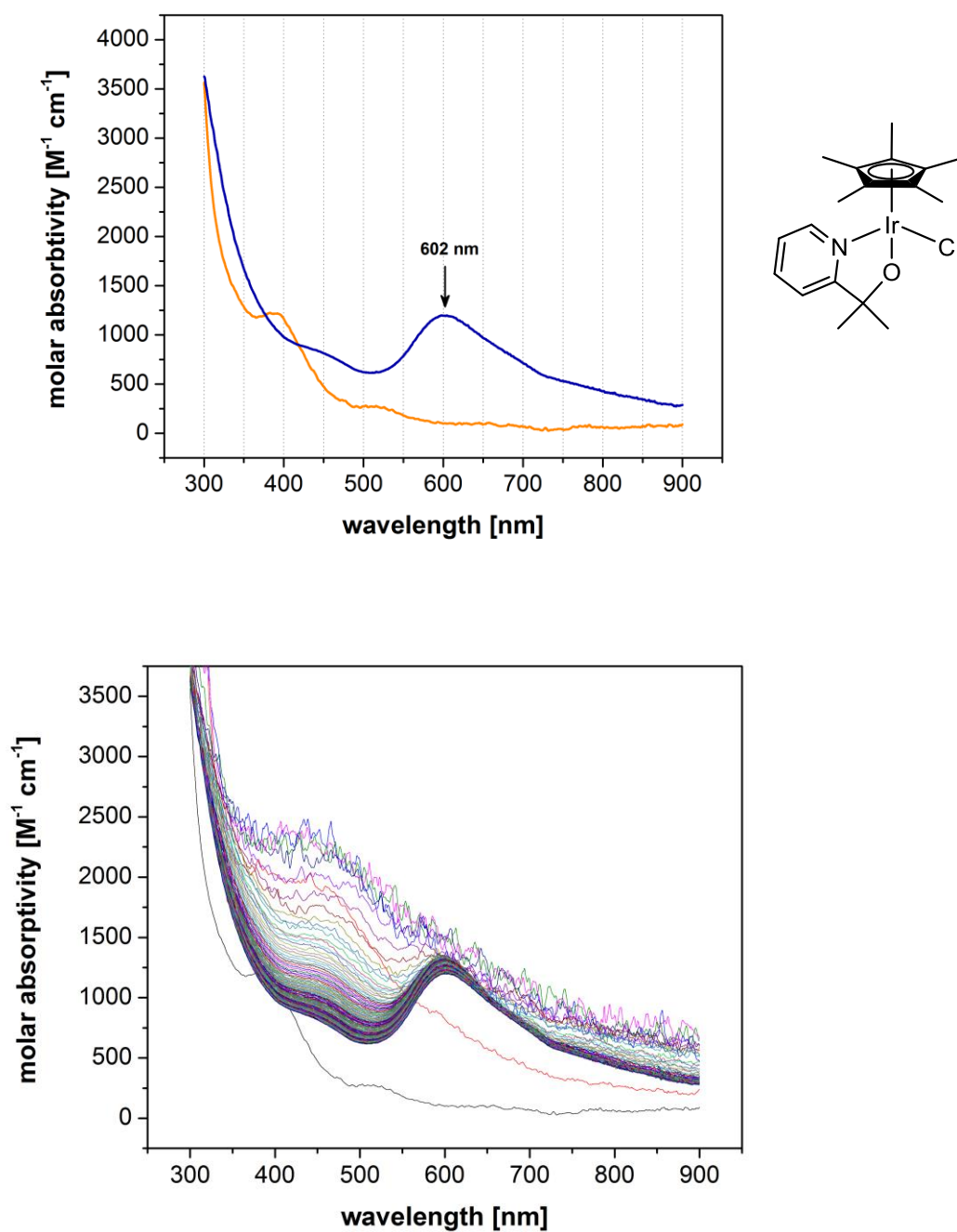


Figure S10A, top: UV-vis spectra of compound **1** before (orange) and after (blue) the reaction shown in scheme 2 (0.5 mM [Ir] with 25 mM $NaIO_4$ in 4:1 $H_2O/BuOH$ at room temperature). **Bottom:** 2D projection of time-course data shown in figure 6.

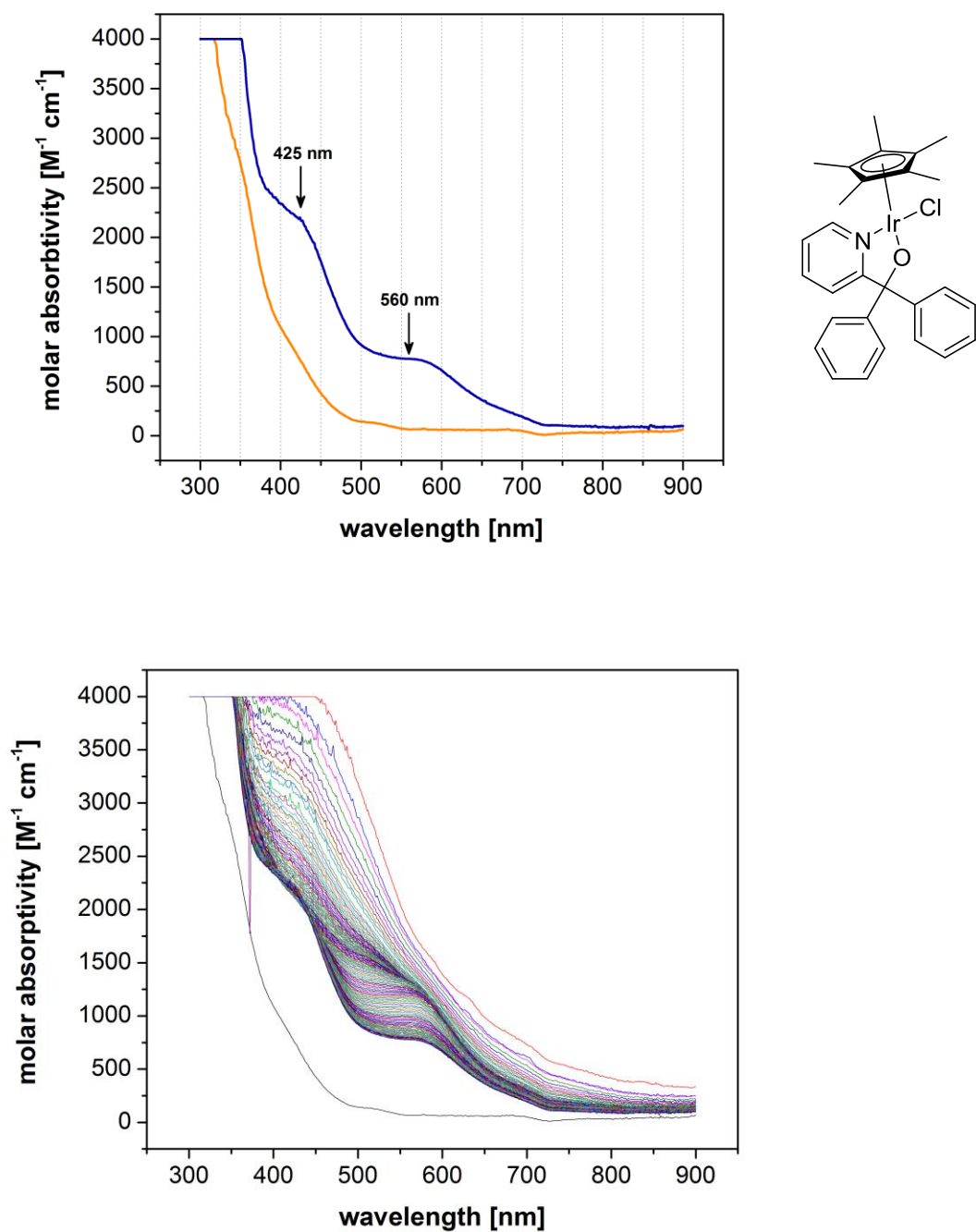


Figure S10B, top: UV-vis spectra of compound **2** before (orange) and after (blue) the reaction shown in scheme 2 (0.5 mM [Ir] with 25 mM $NaIO_4$ in 4:1 $H_2O/BuOH$ at room temperature). **Bottom:** 2D projection of time-course data shown in figure 6.

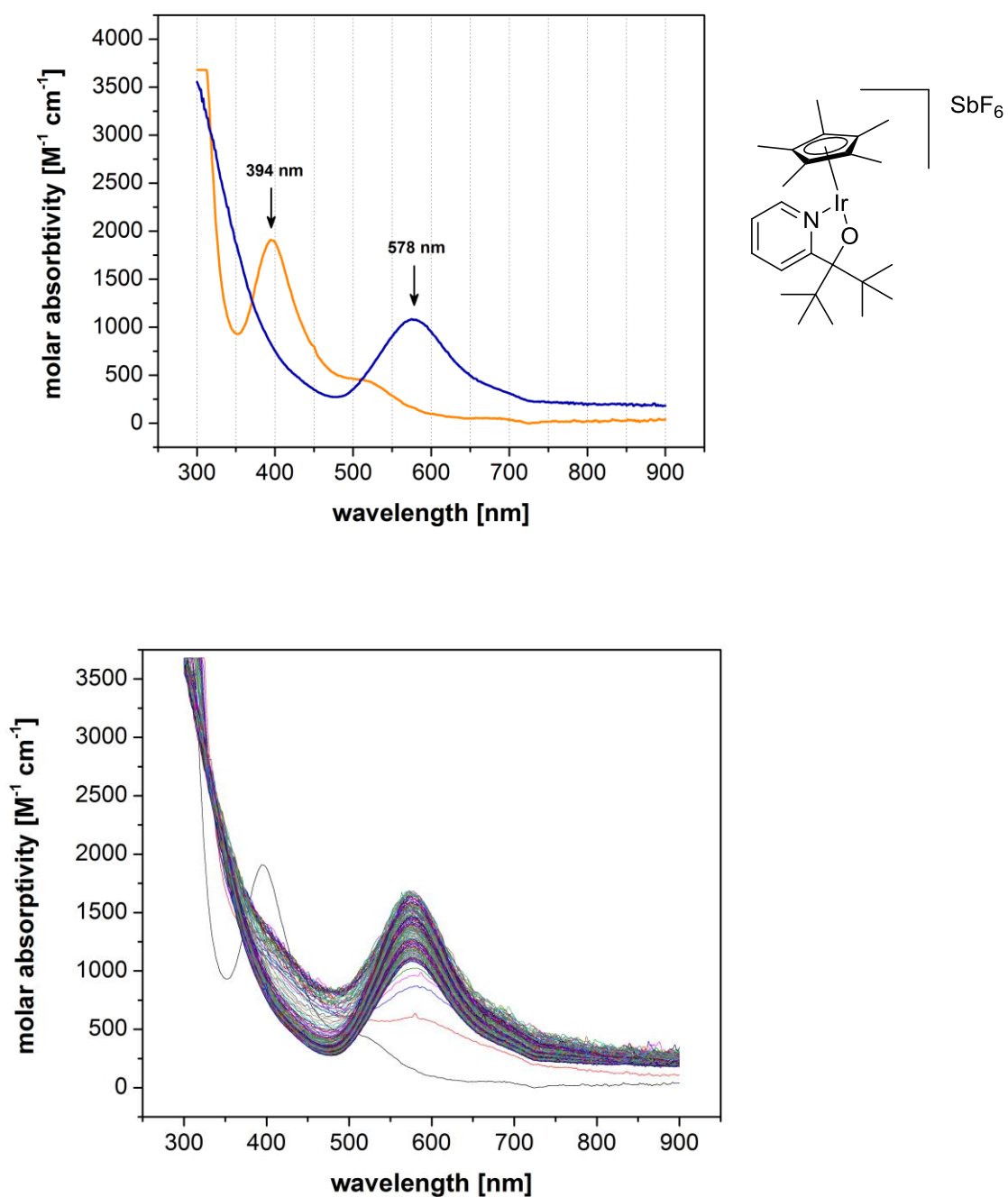


Figure S10C, top: UV-vis spectra of compound **3** before (orange) and after (blue) the reaction shown in scheme 2 (0.5 mM [Ir] with 25 mM $NaIO_4$ in 4:1 $H_2O/BuOH$ at room temperature). **Bottom:** 2D projection of time-course data shown in figure 6.

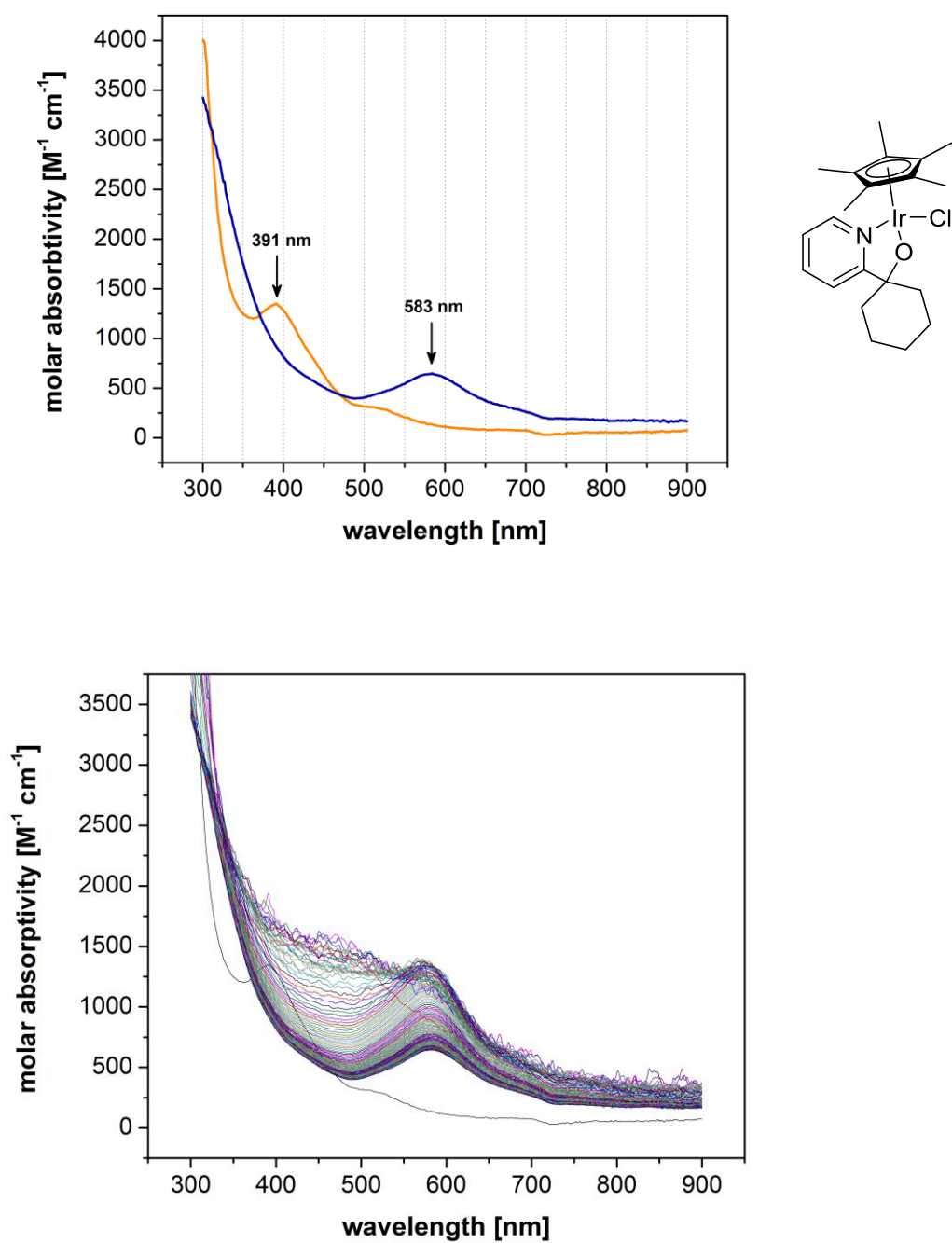


Figure S10D, top: UV-vis spectra of compound **4** before (orange) and after (blue) the reaction shown in scheme 2 (0.5 mM [Ir] with 25 mM $NaIO_4$ in 4:1 $H_2O/BuOH$ at room temperature). **Bottom:** 2D projection of time-course data shown in figure 6.

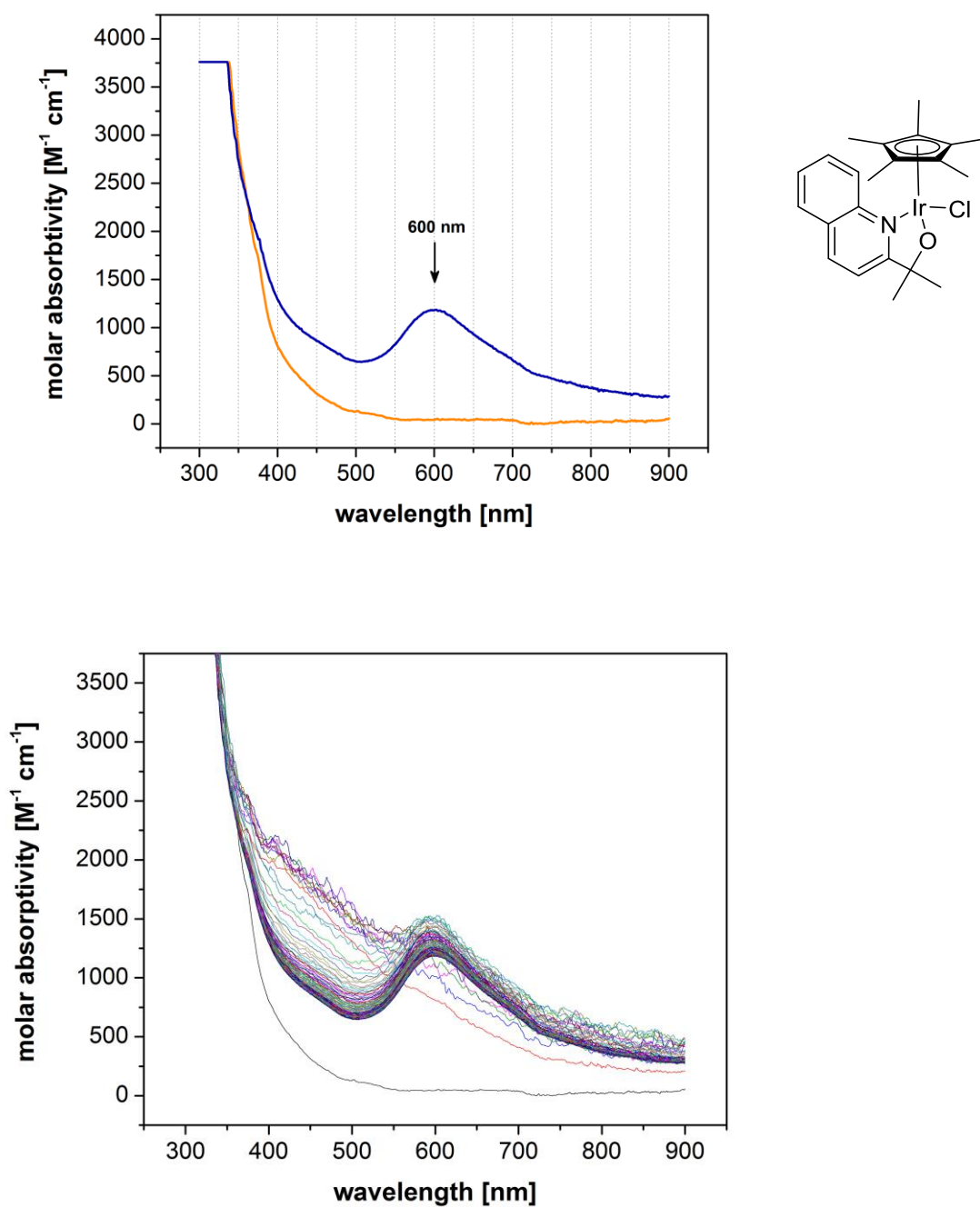


Figure S10E, top: UV-vis spectra of compound **5** before (orange) and after (blue) the reaction shown in scheme 2 (0.5 mM [Ir] with 25 mM NaIO_4 in 4:1 $\text{H}_2\text{O}/\text{BuOH}$ at room temperature). **Bottom:** 2D projection of time-course data shown in figure 6.

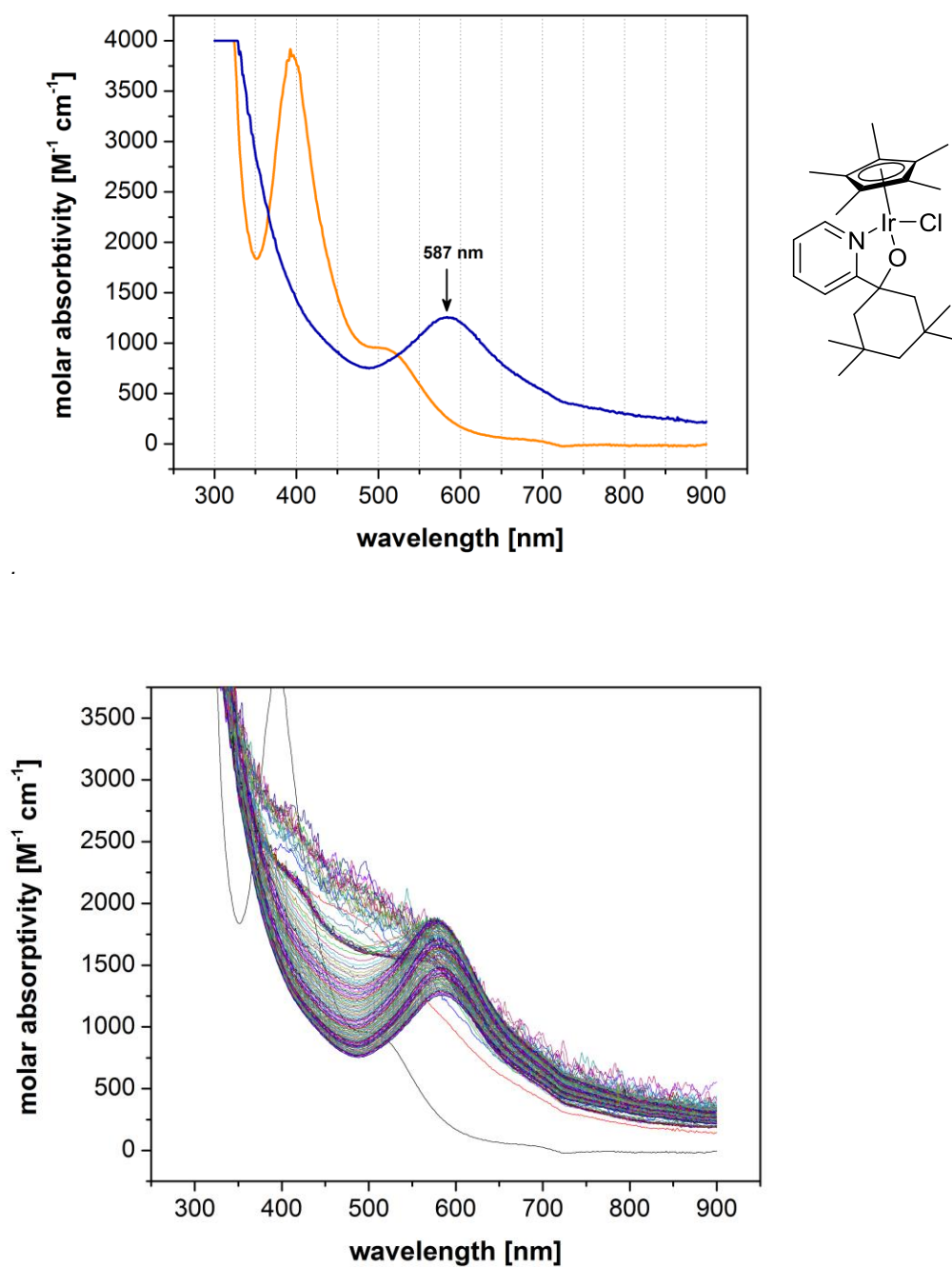


Figure S10F, top: UV-vis spectra of compound **6** before (orange) and after (blue) the reaction shown in scheme 2 (0.5 mM [Ir] with 25 mM NaIO₄ in 4:1 H₂O/BuOH at room temperature). **Bottom:** 2D projection of time-course data shown in figure 6.

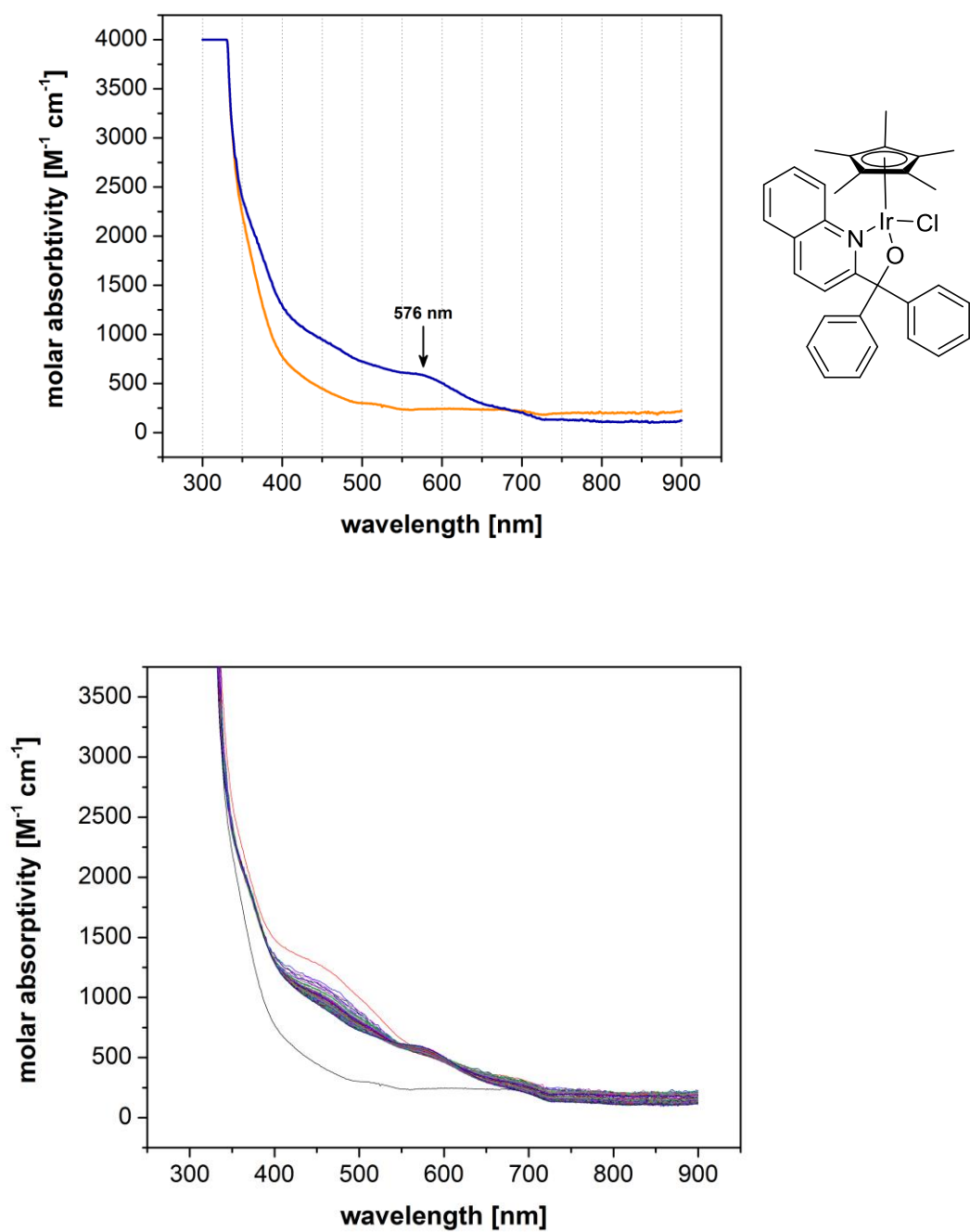


Figure S10G, top: UV-vis spectra of compound **7** before (orange) and after (blue) the reaction shown in scheme 2 (0.5 mM [Ir] with 25 mM $NaIO_4$ in 4:1 $H_2O/BuOH$ at room temperature). **Bottom:** 2D projection of time-course data shown in figure 6.

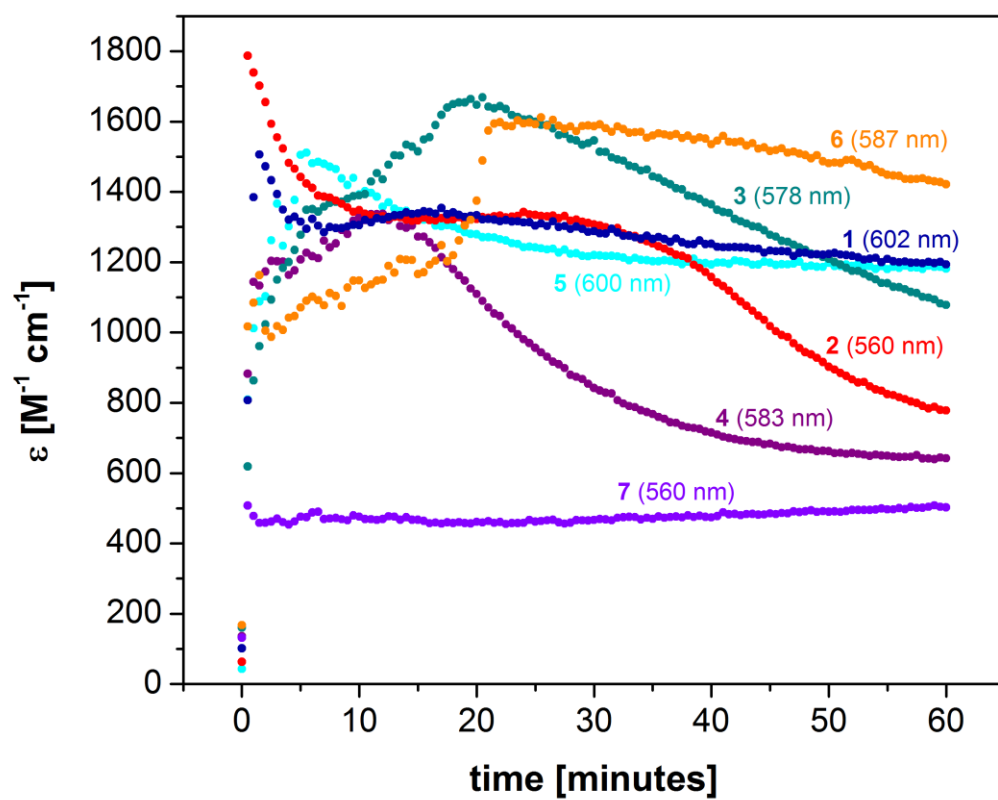


Figure S11. Plot of final maximum absorption intensities for 1-7 over time.

5. X-Ray crystallography

Intensity data for all structures were collected at 150 K using an Oxford Cryostream. Data for **2** and **3** were collected on a Nonius KappaCCD diffractometer and were processed using the Nonius Software⁶. Data for **4**, **5** and **6** were collected on an Agilent Supernova diffractometer, data for **7** on an Agilent Xcalibur diffractometer and processed using the CrysAlisPro software⁷. For all structures a symmetry-related (multi-scan) absorption correction has been applied. Structure solution, followed by full-matrix least squares refinement was performed using the WINGX-v2014 suite of programs throughout.⁸ Non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms of water were located in the difference Fourier map and refined with bond lengths restraints, while all other hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters riding on the corresponding parent atoms.

CCDC 1413039-1413044 contain the supplementary crystallographic data for **2-7**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax:(+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

6. References

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