Electronic Supporting Information

Dual luminescence and infrared circularly polarized luminescence up to 900 nm with platinum complexes bearing helical donor-acceptor ligand

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1. General Information

General information and materials

Anhydrous 1,4-dioxane were obtained by distillation over Na/benzophenone. Other solvents such as cyclohexane, ethyl acetate (EtOAc), dichloromethane (DCM), chloroform, dimethoxyethane (DME), toluene, and isopropanol were purchased in chromatographic purity and used as received. Bromoisoquinoline and boronic acids was supplied by BLDpharm, and [$Pd(PPh_3)_4$] and Na(acac) were provided by Strem and Alfa Aesar, respectively. [$Pt(DMSO)_2Cl_2$] was synthesized according to previously described methodology.[1]

All synthetic transformations were done in oven-dried Schlenk tubes under inert (N_2) atmosphere. Thin-layer chromatography (TLC) was performed on aluminum sheets precoated with Merck 5735 Kieselgel 60F254. Column chromatography was carried out with Merck 5735 Kieselgel 60F (0.040-0.063 mm mesh). Chemicals were purchased from Sigma-Aldrich, Alfa Aesar or TCI Europe and used as received.

The 1H- and 13C-NMR spectra were measured on a DRX-400 spectrometer (Bruker) at 400 MHz or 100 MHz, and on an *AVANCE III 400 BRUKER* or an *AVANCE I 500 BRUKER* at Centre Régional de Mesures Physiques de l'Ouest (CRMPO), Université de Rennes 1. Chemical shifts δ are given in ppm and coupling constants *J* in Hz. 1H and ^{13}C chemical shifts were referenced to the residual solvent peak (7.26 and 77.1 ppm respectively). ^{31}P NMR spectra were referenced to an external 85% solution of H_3PO_4. Multiplicity of signals: s – singlet, d – doublet, t – triplet, q – quartet, br s – broad signal, m – multiplet.

Low-temperature diffraction data were collected on a Bruker D8 Quest APEX-III single crystal diffractometer, equipped with a Photon III detector and a IμS 3.0 microfocus X-ray source. Data were collected by means of ω and φ scans using monochromatic radiation λ(Mo Kα1) = 0.71073 Å. The diffraction images collected were processed and scaled using APEX-4 v2021.4-0 software. The structures were solved with SHELXT and was refined against F2 on all data by full-matrix least squares with SHELXL,5 using Olex2 as graphical interface.6 All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at

[1] Romeo, R.; Scolaro, L. M. *Inorg. Synth.,* **1998**, *32*, 153-158.

geometrically calculated positions and refined using a riding model, unless otherwise noted. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups).

High-resolution mass (HR-MS) determinations were performed at CRMPO on a Bruker MaXis 4G by ASAP (+ or -) or ESI and MALDI with CH_2Cl_2 as solvent techniques. Experimental and calculated masses are given with consideration of the mass of the electron.

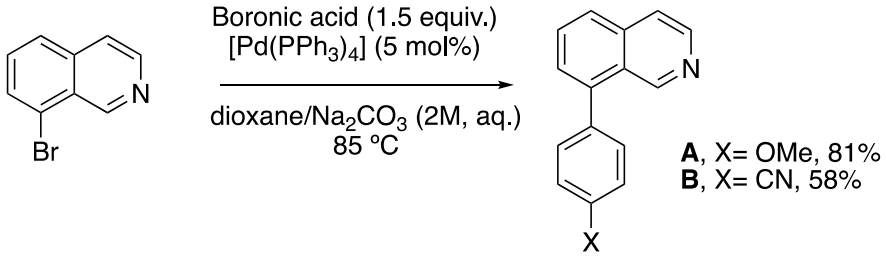
UV-Visible (UV-vis, in M^{-1} cm^{-1}) absorption spectra were recorded on a UV-2401PC Shimadzu spectrophotometer. Steady-state luminescence spectra were measured using an Edinburgh FS920 Fluorimeter combined with a FL920 Fluorescence Lifetime Spectrometer. The spectra were corrected for the wavelength dependence of the detector, and the quoted emission maxima refer to the values after correction. Life-times measurements were conducted with 375 nm diode laser excitation (EPL-series) plugged to a TCSPC pulsed source interface. Absolute fluorescence quantum yields ϕ were recorded with a Hamamatsu C9920-03 integrating sphere.

Electronic circular dichroism (ECD, in $M^{-1}cm^{-1}$) was measured on a Jasco J-1700 Circular Dichroism Spectrometer. The absorption and ECD spectra of the complexes have been measured in both dichloromethane and toluene, which afforded similar responses. The data in dichloromethane are shown to have the full spectra in the UV region, specially to see the complete ECD couplet signal from the binaphtyl unit around 250 nm (UV cut off of toluene is around 290 nm).

The circularly polarized luminescence (CPL) measurements were performed using a JASCO 300 CPL spectrofluoropolarimeter. The following parameters were used: emission slit width ≈ 20 mm, integration time = 4 sec, scan speed = 50 nm/min, accumulations = 8. The concentration of all the samples was *ca*. 10^{-5}–10^{-6} M. Excitation of the samples was performed at 380 nm.

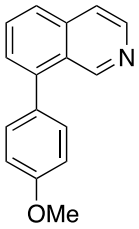
2. Synthesis of the ligands.

The ligands **L1** and **L5-L6** were synthesized following previously described procedures,[2] and these were applied for the synthesis of the other ligands **L2-L4**.



General procedure for the synthesis of **A-B**: A Schlenk tube was charged with 8-bromoisoquinoline (1 eq), boronic acid (1.5 eq) and [$Pd(PPh_3)_4$] (5 mol%). After N_2/vacuum cycles (3x), deoxygenated 1,4-dioxane (4mL/mmol) and a deoxygenated 2 M solution of Na_2CO_3 in water (2mL/mmol) were added, and the resulting reaction mixture was stirred at 85 °C for 16h. The reaction mixture was then cooled to rt, diluted in water (20 mL) and extracted with EtOAc (3 x 10 mL). The combined organic phases where dried with $MgSO_4$, filtered and evaporated under reduced pressure. The resulting crude was purified by column chromatography on silica gel.

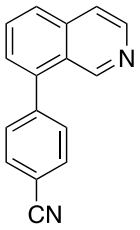
Synthesis of **A**.



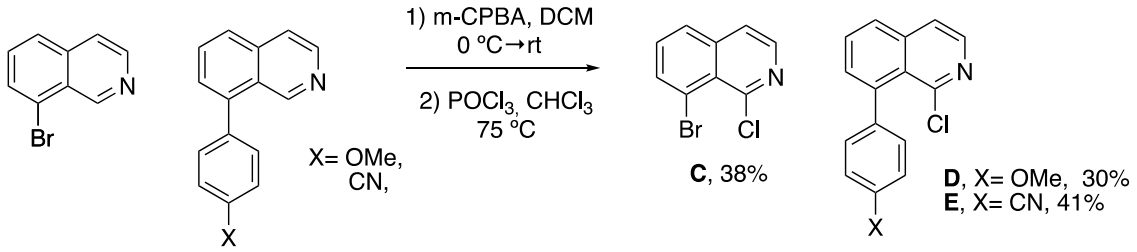
Following the *general procedure* starting from 5 mmol of 8-bromoisoquinoline, purification by flash chromatography (Cyclohexane/EtOAc 2:1) afforded **A** as a white solid (952 mg, 81%). **^{1}H-RMN (400 MHz, $CDCl_3$, 298K):** δ 9.34 (s, 1H, 8.54 (d, 1H, *J* = 5.4 Hz), 7.79 (d, 1H, *J* = 8.1 Hz) 7.73-7.69 (m, 2H), 7.51 (d, 1H, *J* = 7.0. Hz,), 7.44 (d, 2H, *J* = 8.4 Hz), 7.05 (d, 2H, *J* = 8.4 Hz), 3.90 (s, 3H, OMe). **^{13}C-RMN (100 MHz, $CDCl_3$, 298K):** δ 159.4, 151.1, 142.6, 140.8, 136.3, 131.2 (2xC), 130.9, 130.0, 128.2, 126.8, 125.6, 120.6, 114.0 (2xC), 55.4 (OMe). **HRMS(ESI)** calculated for $C_{16}H_{14}NO$ ($M + H^+$) 236.1070. Found 236.1068.

[2] Vázquez-Domínguez, P.; Rizo, J. F.; Arteaga, J. F.; Jacquemin, D.; Favereau, L.; Ros, A.; Pischel, U. *Org. Chem. Front.*, **2024**, *11*, 843-853.

Synthesis of **B**.



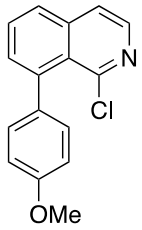
Following the *general procedure* starting from 5 mmol of 8-bromoisoquinoline, purification by flash chromatography (Cyclohexane/EtOAc 2:1→EtOAc) afforded **B** as a white solid (667 mg, 58%). **^{1}H-RMN (400 MHz, $CDCl_3$, 298K):** δ 9.21 (s, 1H), 8.60 (br s, 1H), 7.91 (d, 1H, *J* = 8.2 Hz), 7.83 (d, 2H, *J* = 8.2 Hz), 7.80-7.76 (m, 2H), 7.64 (d, 2H, *J* = 8.2 Hz), 7.53 (d, 1H, *J* = 7.0 Hz). **^{13}C-RMN (100 MHz, $CDCl_3$, 298K):** δ 150.0, 143.3, 142.8, 139.0, 136.3, 132.4 (2xC), 130.8 (2xC), 130.1, 128.4, 127.6, 120.9, 118.6 (CN), 112.0. **HRMS(ESI)** calculated for $C_{16}H_{11}N_2$ ($M + H^+$) 231.0917. Found 231.0919.



General procedure for the synthesis of **C-E**: Over a round bottom flask containing a solution of **A-B** in CH_2Cl_2 (11 mL/mmol), *m*-CPBA (77%, 1.6 equiv.) was slowly added in portions. The reaction was stirred overnight at room temperature, and then, a saturated $NaHCO_3$ aqueous solution (11mL/mmol) was added reaction and the two phases system was vigorously stirred for 30 min. The was organic phase was separated, the aqueous was extracted 2 times with CH_2Cl_2. The organics were dried over $MgSO_4$, filtered and evaporated to dryness. The reaction crude was used in the chlorination step assuming 100% yield.

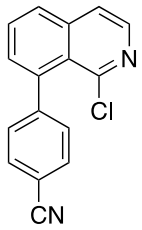
Over a solution of the previous *N*-oxidation crude in chloroform (1.5 mL/mmol), $POCl_3$ (6 equiv.) was added and the reaction was stirred 3h at 75 °C. Then, the reaction was cooled to rt, and it was carefully quenched with H_2O and saturated $NaHCO_3$ aqueous solution (CAUTION: vigorous CO_2 loosening was observed). The aqueous phase was extracted with dichloromethane. The combined organic phases were dried over $MgSO_4$, filtered and concentrated to dryness. The raw product was purified by column chromatography on silica gel.

Synthesis of **D**.



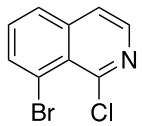
Following the *general procedure* starting from 4.1 mmol of **A**, purification by flash chromatography (Cyclohexane/EtOAc 8:1) afforded **D** as a light brown solid (331 mg, 30%). **^{1}H-RMN (400 MHz, $CDCl_3$, 298K):** δ 8.28 (d, 1H, *J* = 5.5 Hz), 7.84 (d, 1H, *J* = 8.Hz), 7.70 (t, 1H, *J* = 7.5 Hz), 7.65 (d, 1H, *J* = 5.Hz), 7.53 (d, 1H, *J* = 7.5 Hz), 7.24 (d, 2H, *J* = 8.7 Hz), 6.96 (d, 2H, *J* = 8.7 Hz), 3.89 (s, 3H, OMe). **^{13}C-RMN (100 MHz, $CDCl_3$, 298K):** δ 159.1, 150.3, 140.9, 140.7, 139.4, 134.4, 132.4, 130.5 (2xC), 129.8, 126.9, 125.2, 121.2, 113.1 (2xC), 55.3 (OMe). **HRMS(ESI)** calculated for $C_{16}H_{13}ONCl$ (M + H+) 270.0680. Found 270.0679.

Synthesis of **E**.



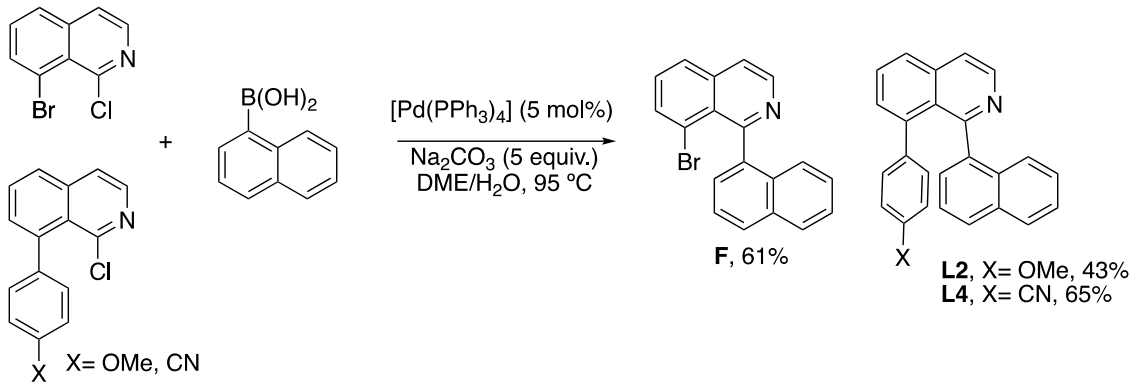
Following the *general procedure* starting from 3.5 mmol of **B**, purification by flash chromatography (Cyclohexane/EtOAc 3:1) afforded **E** as a light yellow solid (379 mg, 41%). **^{1}H-RMN (400 MHz, $CDCl_3$, 298K):** δ 8.35 (d, 1H, *J* = 5.5 Hz), 7.96 (d, 1H, *J* = 8.3 Hz), 7.79-7.72 (m, 4H), 7.52-7.48 (m, 3H). **^{13}C-RMN (100 MHz, $CDCl_3$, 298K):** δ 149.6, 147.1, 141.6, 139.4, 138.7, 132.0, 131.5 (2xC), 130.2 (2xC), 129.8, 128.2, 124.6, 121.4, 118.8 (CN), 111.3. **HRMS(ESI)** calculated for $C_{16}H_{10}N_2Cl$ (M + H+) 265.0529. Found 265.0527.

Synthesis of **C**.



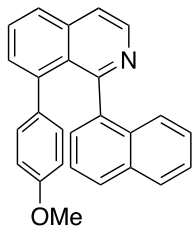
Following the *general procedure* starting from 20 mmol of 8-bromoisoquinoline, purification by flash chromatography (Cyclohexane/EtOAc 8:1) afforded **C** as a light yellow solid (1.84 g, 38%). The spectroscopic data were in agreement with the described in the literature.[3]

[3] Marx, M. A.;, Blake, J. F.; Fell, J. B.; Fischer, J. P.; Mejia, M. J. ARRAY BIOPHARMA - **WO2020/47192, 2020, A1**.



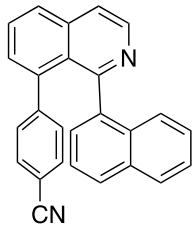
General procedure for the synthesis of **L2-L4**: A Schlenk tube was charged with **D-F** (1 eq), boronic acid (1.1-1.3 equiv.) and [$Pd(PPh_3)_4$] (5 mol%). After N_2/vacuum cycles (3x), deoxygenated DME (3 mL/mmol) and a deoxygenated solution of Na_2CO_3 (2-5 equiv.) in water (0.5 mL/mmol) were added, and the reaction was stirred at 90 °C for 5h-overnight. The reaction mixture was then cooled to rt, diluted in water (20 mL) and extracted with DCM (3 x 10 mL). The combined organic phases where dried with $MgSO_4$, filtered and evaporated under reduced pressure. The resulting crude was purified by column chromatography on silica gel.

Synthesis of **L2**.



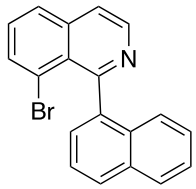
Following the *general procedure* starting from 0.45 mmol of **D**, and using 1.3 equiv. of the corresponding boronic acid, 1.2 mL of DME and 0.45 mL of Na_2CO_3 (2M), purification by flash chromatography (Cyclohexane/EtOAc 3:1) afforded **L2** as a light yellow solid (70 mg mg, 43%). **^{1}H-RMN (400 MHz, $CDCl_3$, 298K):** δ 8.74 (d, 1H, *J* = 5.6 Hz), 7.97 (d, 1H, *J* = 8.2 Hz), 7.85 (d, 1H, *J* = 5.6 Hz), 7.75 (t, 1H, *J* = 8.2 Hz), 7.67 (d, 1H, *J* = 8.5 Hz), 7.54 (dd, 1H, *J* = 6.7 Hz and *J* =2.6 Hz), 7.41-7.35 (m, 3H) , 7.30-7.26 (m, 2H), 7.26-7.19 (m, 2H), 6.79 (br d, 1H, *J* = 6.5 Hz), 6.36 (br d, 1H, *J* = 6.5 Hz), 6.34 (br d, 1H, *J* = 6.5 Hz), 5.78 (br d, 1H, *J* = 6.5 Hz), 3.58 (s, 3H, OMe). **^{13}C-RMN (100 MHz, $CDCl_3$, 298K):** δ 159.6, 157.5, 141.6, 141.4, 139.7, 138.1, 133.5, 133.3, 131.8, 131.3, 130.0, 129.4, 129.3, 128.1, 127.8, 127.8, 126.9, 126.7, 125.7, 125.7, 125.2, 124.9, 120.6, 112.6, 110.6, 55.1 (OMe). **HRMS(ESI)** calculated for $C_{26}H_{20}ON$ (M + H+) 362.1539. Found 362.1537.

Synthesis of **L4**.



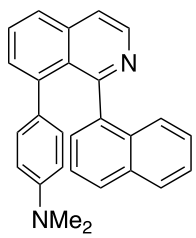
Following the *general procedure* starting from 0.3 mmol of **E**, and using 1.3 equiv. of the corresponding boronic acid, 0.75 mL of DME and 0.3 mL of Na_2CO_3 (2M), purification by flash chromatography (Cyclohexane/EtOAc 3:1) afforded **L4** as a light yellow solid (70 mg mg, 65%). **^{1}H-RMN (400 MHz, $CDCl_3$, 298K):** δ 8.79 (d, 1H, *J* = 5.6 Hz), 8.04 (d, 1H, *J* = 8.0 Hz), 7.87 (d, 1H, *J* = 5.6 Hz), 7.76 (t, 1H, *J* = 8.0 Hz), 7.69 (d, 1H, *J* = 8.0 Hz), 7.59 (d, 1H, *J* = 8.0 Hz), 7.40 (t, 1H, *J* = 7.4 Hz), 7.32-7.02 (m, 5H), 7.04 (d, 1H, *J* = 7.8 Hz), 6.89 (d, 1H, *J* = 8.0 Hz), 6.57 (d, 1H, *J* = 8.0 Hz), 6.53 (d, 1H, *J* = 7.8 Hz). **^{13}C-RMN (100 MHz, $CDCl_3$, 298K):** δ 158.8, 145.2, 142.1, 139.6, 139.3, 137.9, 133.1, 131.6, 131.2, 129.6, 129.4, 129.3, 129.0, 128.5, 128.3, 128.2 (2xC), 128.1, 126.2, 126.0, 125.7, 125.3, 124.9, 120.8, 118.7 (CN), 109.3. **HRMS(ESI)** calculated for $C_{26}H_{17}N_2^+$ (M + H+) 357.1386. Found 357.1390.

Synthesis of **F**.



Following the *general procedure* starting from 1.0 mmol of **C**, and using 1.1 equiv. of the corresponding boronic acid, 7 mL of DME and 3.2 mL of Na_2CO_3 (5M), purification by flash chromatography (Cyclohexane/EtOAc 8:1) afforded **F** as a yellow solid (205 mg, 62%). **^{1}H-RMN (400 MHz, $CDCl_3$, 298K):** δ 8.71 (d, 1H, *J* = 5.6 Hz), 7.96 (d, 1H, *J* = 8.2 Hz), 7.93 (d, 1H, *J* = 7.7 Hz), 7.92 (d, 1H, *J* = 8.1 Hz), 7.82 (d, 1H, *J* = 7.4 Hz), 7.78 (d, 1H, *J* = 5.6 Hz), 7.56 (t, 1H, *J* = 8.0 Hz), 7.54- 7.45 (m, 2H), 7.42 (d, 1H, *J* = 8.0 Hz), 7.36-7.29 (m, 2H). **^{13}C-RMN (100 MHz, $CDCl_3$, 298K):** δ 159.3, 142.1, 139.3, 139.0, 134.7, 133.4, 133.2, 130.3, 128.5, 128.1, 127.5, 127.5, 126.9, 126.2, 125.7, 125.6, 125.2, 120.8. **HRMS(ESI)** calculated for $C_{19}H_{13}BrN$ (M + H^+) 334.0226 (^{79}Br), 336.0205 (^{79}Br, ^{81}Br). Found 334.0227, 336.0202.

Synthesis of **L3**.



A dried Schlenk tube was charged with **F** (0.3 mmol, 100 mg), 4-Dimethylamino-phenyl boronic acid (0.9 mmol, 149 mg), [$Pd(PPh_3)_4$] (5 mol%, 17.3 mg) and Na_2CO_3 (0.54 mmol, 57.2 mg). After N_2/vacuum cycles (3x), deoxygenated 1,4-dioxane (1.4 mL) and deoxygenated water (0.7 mL) were added, and the reaction was

stirred overnight at 85 °C. The reaction mixture was then cooled to rt, diluted in water (20 mL) and extracted with DCM (3 x 10 mL). The combined organic phases where dried with $MgSO_4$, filtered and evaporated under reduced pressure. The resulting crude was purified by column chromatography on silica gel (Cyclohexane/EtOAc 5:1) to afford **L3** as a yellow solid (91 mg, 81%). **^{1}H-RMN (400 MHz, $CDCl_3$, 298K):** δ 8.69 (d, 1H, *J* = 5.5 Hz), 7.91 (d, 1H, *J* = 7.9 Hz), 7.78 (d, 1H, *J* = 5.5 Hz), 7.71 (t, 1H, *J* = 7.9 Hz), 7.63 (d, 1H, *J* = 8.1 Hz), 7.45-7.39 (m, 3H), 7.36 (t, 1H, *J* = 8.1 Hz), 7.29- 7.25 (m, 1H), 7.19-7.12 (m, 2H), 6.75 (br s, 1H), 6.30 (br s, 1H), 6.21 (br s, 1H), 5.58 (br s, 1H), 2.70 (s, 6H, NMe_2). **^{13}C-RMN (100 MHz, $CDCl_3$, 298K):** δ 159.9, 148.8, 142.2, 141.5, 140.2, 138.1, 133.5, 131.9, 131.0, 129.9, 129.3 (3xC), 128.1, 127.7, 127.7, 127.1, 126.2, 125.9, 125.6, 125.1, 124.8, 111.6 (br s), 110.6 (br s), 40.6. **HRMS(ESI)** calculated for $C_{27}H_{23}N_2^+$ ($M + H^+$) 375.1856. Found 375.1858.

3. Synthesis of Pt-complexes 1-6 and 5(acac)-6(acac).

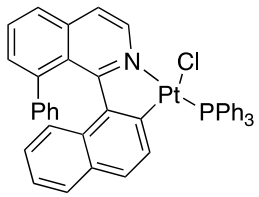
Procedure A. Synthesis of Pt-PPh_3 complexes **1-7**:

A dried Schlenk tube was charged with the substrates **L1-L7** (0.1 mmol), $[Pt(DMSO)_2Cl_2]$ (0.12 mmol, 51.2 mg) and Na_2CO_3 (0.2 mmol, 21.2 mg). After cycles of vacuum-N_2, anhydrous and deoxygenated toluene (4 mL) was added and the resulting reaction mixture was stirred at 110°C for 16 h. Then, reaction was cooled to rt, filtered through a pad of celite, washed with CH_2Cl_2 and concentrated to dryness in the rotavap. Reaction crude was analyzed by NMR to corroborate the total consumption of the starting **L1-L7**, and used in the next step without purification. This reaction crude was placed in a Schlenk tube, and after cycles of vacuum-Ar, deoxygenated DCM (3 mL) was added. Then, a solution of PPh_3 (1.1 equiv.) in DCM (1.5 mL) was dropwise added at rt and the resulting solution was heated at 40°C overnight. Then, the reaction crude was concentrated in the rovatavapor and purified by column chromatography (Cyclohexane/EtOAc mixtures) to give the corresponding complex **L1-L7**.

Procedure B. Synthesis of Pt-acac complexes **5(acac)-9(acac)**:

The cycloplatination step was similar to the procedure A, and then, the resulting reaction crude was dissolved in 6 mL of anhydrous EtOH/acetone 2:1 mixture, and was transferred via cannula (N_2 current) to a Schlenk tube containing sodium acac (0.5 mmol, 70 mg). The reaction mixture was stirred overnight at rt, diluted with CH_2Cl_2 (20 mL), washed with water (10 mL), and the organic phase dried over $MgSO_4$ and purified by column chromatography (Cyclohexane/EtOAc mixtures).

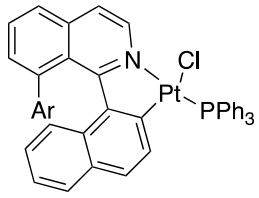
Synthesis of **1**.



Following the *procedure A*, purification by column chromatography (Cyclohexane/EtOAc 2:1), to afford **1** as a orange solid (75 mg, 95%). **^{1}H-RMN (400 MHz, $CDCl_3$, 298K):** δ 9.79 (dd, 1H, $J_{H,H}$ = 5.8Hz, $J_{P,H}$ = 3.5 Hz), 7.95-7.91 (m, 7H,), 7.86 (t, 1H, *J* = 8.2 Hz), 7.76 (d, 1H, *J* = 5.8 Hz), 7.55 (d, 1H, *J* = 7.0 Hz), 7.52-7.41 (m, 10H), 7.18 (d, 1H, *J* = 8.5 Hz), 7.08 (t, 1H, *J* = 7.2 Hz) 6.99-6.92 (m, 2H), 6.87 (d, 2H, *J* = 7.4 Hz), 6.74-6.64 (m, 5H). **^{13}C-RMN (100 MHz, $CDCl_3$, 298K):** δ 168.8 (d, $J_{P,C}$ = 2 Hz), 144.6, 142.4, 140.6 (d, $J_{P,C}$ = 6 Hz), 140.0, 139.7, 139.1, 135.4 (d, $J_{P,C}$ = 11 Hz, 6 x C*o*-

PPh_3), 134.5 (d, $J_{P,C}$ = 7 Hz), 134.5, 131.4, 131.3, 131.3, 130.8, 130.8 (d, $J_{P,C}$ = 4 Hz, 3 x C*p*-PPh_3), 130.2, 128.5 (d, $J_{P,C}$ = 2 Hz), 127.9 (d, $J_{P,C}$ = 11 Hz, 6 x C*m*-PPh_3), 127.6, 126.1, 125.7, 125.2, 123.5 (d, J = 2 Hz), 123.3, 123.2, 118.4 (d, $J_{P,C}$ = 3 Hz). **^{31}P NMR (162 MHz, $CDCl_3$, 298K):** δ 23.6 (s+d, $J_{Pt,P}$ = 4441Hz). **HRMS(ESI)** calculated for $C_{43}H_{31}NPPt$ ($M + H^+$) 787.1836. Found 787.1831.

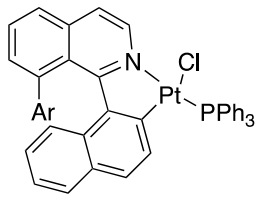
Synthesis of **2**.



Ar= *p*-MeO-Ph

Following the *procedure A*, purification by column chromatography (Cyclohexane/EtOAc 3:1), to afford **2** as a orange solid (73 mg, 89 %). **^{1}H-RMN (400 MHz, $CDCl_3$, 298K) :** δ 9.77 (dd, 1H, $J_{H,H}$ = 6.2 Hz, $J_{P,H}$ = 3.5 Hz), 7.96-7.88 (m, 7H), 7.84 (t, 1H , $J_{H,H}$ =7.5 Hz), 7.75 (d, 1H, $J_{H,H}$ = 6.2 Hz), 7.54-7.41 (m, 10H), 7.22 (d, 1H, $J_{H,H}$ = 8.1 Hz), 7.08 (m, 1H), 6.93 (br s, 2H), 6.76 (d, 2H, $J_{H,H}$ = 7.9 Hz), 6.73-6.69 (m, 2H), 6.15 (d, 2H, $J_{H,H}$ = 7.9 Hz), 3.54 (s, 3H, OMe). **^{13}C-RMN (100 MHz, $CDCl_3$, 298K):** δ 168.9 (d, $J_{P,C}$ = 2 Hz), 157.8, 144.7, 142.0, 140.3 (d, $J_{P,C}$ = 6 Hz), 139.8, 139.1, 135.4 (d, $J_{P,C}$ = 11 Hz, 6 x C*o*-PPh_3), 134.5 (d, $J_{P,C}$ = 7 Hz), 132.3, 131.4, 131.3, 131.1 (d, $J_{P,C}$ = 47 Hz, C*ipso*-PPh_3), 130.8 (s, 3 x C*p*-PPh_3), 130.2, 128.3, 127.9 (d, $J_{P,C}$ = 11 Hz, 6 x C*m*-PPh_3), 127.6, 125.2 (d, $J_{P,C}$ = 4 Hz), 123.7 (d, $J_{P,C}$ = 2 Hz), 123.4, 123.1, 118.4 (d, $J_{P,C}$ = 3 Hz), 111.4 (br s), 55.1. **^{31}P-RMN (162 MHz, $CDCl_3$, 298K):** δ 23.5 (s+d, $J_{Pt,P}$ = 4454 Hz). **HRMS(ESI)** calculated for $C_{44}H_{33}ONPPt$ ($M + H^+$) 817.1942. Found 817.1936.

Synthesis of **3**.

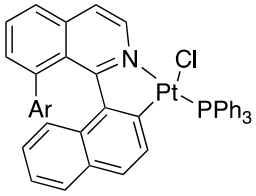


Ar= *p*-NMe_2-Ph

Following the *procedure A*, purification by column chromatography (Cyclohexane/EtOAc 4:1), to afford **3** as a orange-red solid (83 mg, 96 %). **^{1}H-RMN (400 MHz, $CDCl_3$, 298K):** δ 9.71 (dd, 1H, $J_{H,H}$ = 6.0 Hz, $J_{P,H}$ = 3.4 Hz), 7.92 (dd, 6H, $J_{P,H}$ = 11.4Hz, $J_{H,H}$ = 7.8 Hz), 7.82-7.78 (m, 2H), 7.70 (d, 1H, J = 6.0 Hz), 7.52 (dd, 1H, J = 6.0 and 1.8 Hz), 7.46-7.40 (m, 9H), 7.15 (d, 1H, J = 8.0Hz), 7.04 (t, 1H, J = 7.8 Hz), 6.92-6.86 (m, 2H), 6.71-6.62 (m, 4H), 5.93 (d, 2H, J = 7.0 Hz), 2.65 (s, 6H, NMe_2). **^{13}C-RMN (100 MHz, $CDCl_3$, 298K):** δ 169.1, 148.9, 145.0, 142.7, 139.8 (d, $J_{P,C}$ = 6 Hz), 139.6, 139.1, 135.4 (d, $J_{P,C}$ = 11 Hz, 6 x C*o*-PPh_3), 134.5 (d, $J_{P,C}$ =7 Hz), 131.4, 131.1 (d, $J_{P,C}$ = 22 Hz, 3 x C^{ipso}-PPh_3), 130.7 (s, 3 x C*p*-PPh_3), 130.3 (d, $J_{P,C}$ = 10

Hz), 129.6, 129.1 (br s), 128.4, 128.3, 127.8 (d, $J_{P,C}$ = 11 Hz, 6 x C*m*-PPh_3), 127.6, 125.0, 124.4, 123.9, 123.3, 123.2, 118.4, 110.7, 40.6. **^{31}P NMR (162 MHz, $CDCl_3$, 298K):** δ 23.6 (s+d, $J_{Pt,P}$ = 4471 Hz). **HRMS(ESI)** calculated for $C_{45}H_{37}ClN_2PPt$ ($M + H^+$) 866.2025. Found 866.2004.

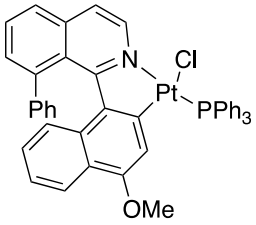
Synthesis of **4**.



Ar= *p*-CN-Ph

Following the *procedure A*, purification by column chromatography (Cyclohexane/EtOAc 3:1), to afford **4** as a orange solid (75 mg, 84 %). **^{1}H-RMN (400 MHz, $CDCl_3$, 298K):** δ 9.83 (dd, 1H, $J_{H,H}$ = 6.0 Hz and $J_{P,H}$ = 3.5 Hz), 8.00 (d, 1H, *J* = 8.3 Hz), 7.91-7.86 (m, 7H), 7.80 (d, 1H, *J* = 6.0 Hz), 7.54-7.50 (m, 4H), 7.46-7.42 (m, 6H), 7.23 (d, 1H, *J* = 8.4 Hz) ,7.10 (t, 1H, *J* = 7.4 Hz), 6.95 (t, 1H, 8.0 Hz), 6.90-6.82 (br s, 4H), 6.74 (s, 2H). **^{13}C-RMN (100 MHz, $CDCl_3$, 298K):** δ 168.5, 144.1, 141.7 (d, $J_{P,C}$ = 6 Hz), 140.8, 140.4, 139.4, 135.7 (d, $J_{P,C}$ = 11 Hz, 6 x C*o*-PPh_3), 135.0 (d, $J_{P,C}$ = 7Hz), 131.6, 131.4, 131.4 (s, 3 x C*p*-PPh_3), 131.2, 130.5 (d, $J_{P,C}$ = 62 Hz, 3 x C^{ipso}-PPh_3), 130.4, 129.1, 128.3 (d, $J_{P,C}$ = 10Hz, 6 x C*m*-PPh_3), 127.4, 125.9, 123.9, 123.2, 123.1 (d, $J_{P,H}$ = 2 Hz), 119.0, 109.5 (CN). **^{31}P NMR (162 MHz, $CDCl_3$, 298K):** δ 22.9 (s+d, $J_{Pt,P}$ = 4435 Hz). **HRMS(ESI)** calculated for $C_{45}H_{37}ClN_2PPt$ ($M + H^+$) 866.2025. Found 866.2004.

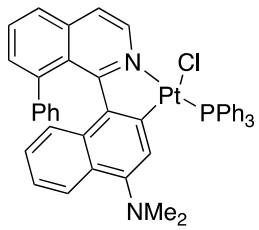
Synthesis of **5**.



Following the *procedure A*, purification by column chromatography (Cyclohexane/EtOAc 2:1), to afford **5** as a red solid (53 mg, 62 %). **^{1}H NMR (400 MHz, $CDCl_3$, 298K):** δ (ppm) 9.65 (dd, J = 6.1, 3.5 Hz, 1H), 7.93 (s, 1H), 7.92 – 7.89 (m, 3H), 7.89 – 7.86 (m, 2H), 7.85 (s, 1H), 7.83 – 7.77 (m, 1H), 7.64 – 7.61 (m, 1H), 7.55 (d, J = 8.4 Hz, 1H), 7.49 (s, 1H), 7.48 (s, 1H), 7.47 – 7.45 (m, 2H), 7.45 – 7.43 (m, 2H), 7.41 (d, J = 1.9 Hz, 3H), 7.40 (d, J = 2.0 Hz, 1H), 7.05 (ddd, J = 8.2, 6.3, 1.6 Hz, 1H), 6.98 – 6.88 (m, 2H), 6.83 (d, J = 7.1 Hz, 2H), 6.75 – 6.68 (m, 1H), 6.64 (t, J = 7.3 Hz, 2H), 6.12 (d, J = 3.0 Hz, 1H), 2.86 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$, 298K):** δ (ppm) 142.5, 139.8, 139.7, 139.3, 137.3, 135.6, 135.5, 135.0, 134.7, 134.6, 132.2, 131.3, 131.0, 130.8, 130.4, 130.3, 128.1, 128.0, 126.0, 125.9, 125.6, 123.0, 122.9, 122.2, 121.7, 117.2, 117.1, 114.7, 114.6, 54.8. **^{31}P NMR (162 MHz, $CDCl_3$,**

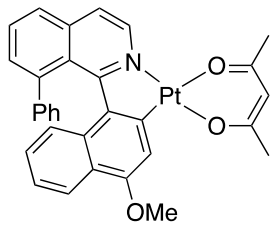
298K): δ (ppm) 38.15, 24.49, 10.84. **HRMS(ESI)** calculated for $C_{44}H_{33}ClNOPPt$ (M + H^+) 853.17089. Found 853.1715.

Synthesis of **6**.



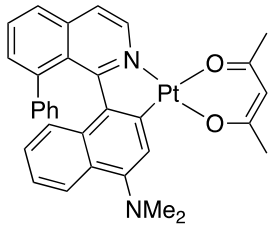
Following the *procedure A*, purification by column chromatography (Tol/EtOAc 5:1), to afford **6** as a red-purple solid (48 mg, 56 %). **^{1}H NMR (400 MHz, $CDCl_3$, 298K):** δ (ppm) 9.67 (dd, *J* = 6.1, 3.5 Hz, 1H), 7.95 – 7.90 (m, 3H), 7.90 – 7.86 (m, 3H), 7.85 (s, 1H), 7.82 – 7.76 (m, 1H), 7.63 – 7.60 (m, 1H), 7.50 – 7.44 (m, 5H), 7.43 – 7.41 (m, 2H), 7.41 – 7.39 (m, 2H), 7.39 (d, *J* = 2.2 Hz, 1H), 7.17 (d, *J* = 8.3 Hz, 1H), 7.06 – 7.01 (m, 1H), 6.98 (d, *J* = 9.1 Hz, 1H), 6.91 – 6.85 (m, 1H), 6.81 (d, *J* = 1.8 Hz, 2H), 6.68 – 6.59 (m, 3H), 6.18 (d, *J* = 3.1 Hz, 1H), 2.03 (s, 6H). **^{13}C-RMN (100 MHz, $CDCl_3$, 298K):** δ 157.1, 140.0, 135.8, 135.7, 135.0, 134.9, 131.3, 131.1, 131.0, 130.6, 130.6, 128.7, 128.6, 128.2, 128.1, 128.0, 126.4, 125.8, 125.3, 124.9, 124.4, 123.8, 122.9, 117.2, 43.8. **^{31}P NMR** (162 MHz, $CDCl_3$, 298K): δ (ppm) 24.91. **HRMS(ESI)** calculated for $C_{45}H_{36}ClN_2PPt$ (M + H^+) 866.20253. Found 866.2023.

Synthesis of **5-acac**.



Following the *procedure B*, purification by column chromatography (Cyclohexane/EtOAc 10:1), to afford **5-acac** as a pink solid (62 mg, 95 %). **^{1}H-RMN (400 MHz, $CDCl_3$, 298K):** δ 8.78 (d, 1H, *J*= 6.2 Hz. ^{195}Pt satellites signals with $^3J_{Pt,H}$ = 38 Hz), 7.79-7.72 (m, 3H), 7.48 (dd, 1H, *J*= 6.8 and 1.6 Hz), 7.41 (d, 1H, *J*= 6.2 Hz), 7.24 (d, 1H, *J*= 8.3 Hz), 7.11 (s, 1H. ^{195}Pt satellites signals with $^3J_{Pt,H}$ = 42 Hz), 7.07 (ddd, 1H, *J*= 8.2, 6.8 and 1.2 Hz), 6.96 (ddd, 1H, *J*= 8.4, 6.8 and 1.4 Hz), 6.84 (br s, 2H), 6.73-6.65 (m, 3H), 5.53 (s, 1H), 4.03 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H). **^{13}C-RMN (100 MHz, $CDCl_3$, 298K):** δ 186.1, 183.9, 171.1, 156.0, 144.3, 142.3, 139.9, 138.9, 138.1, 135.3, 132.4, 130.7, 130.3, 128.8, 126.3, 125.9, 125.7, 125.1, 123.4, 122.4, 122.4, 122.2, 122.1, 116.5, 105.6, 102.7, 55.4, 28.3, 27.3. **HRMS(ESI)** calculated foR $C_{31}H_{26}NO_3Pt$ (M + H^+) 655.1555. Found 655.1550.

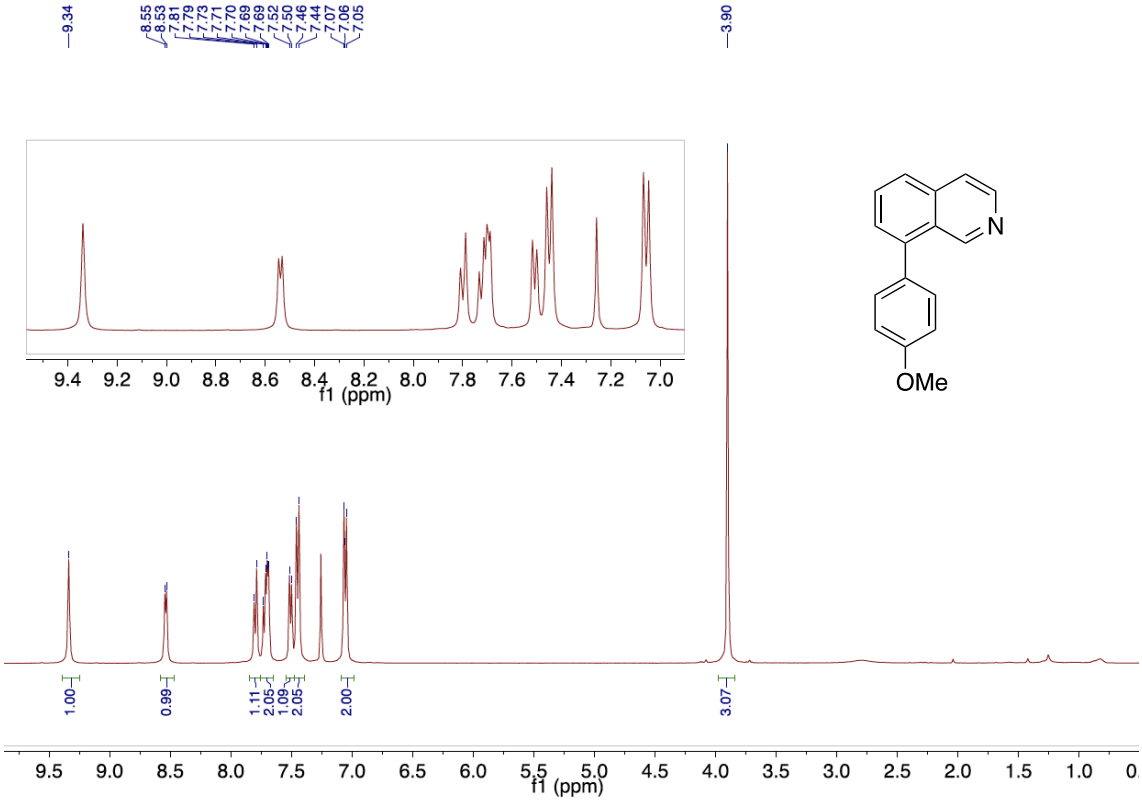
Synthesis of **6-acac**.



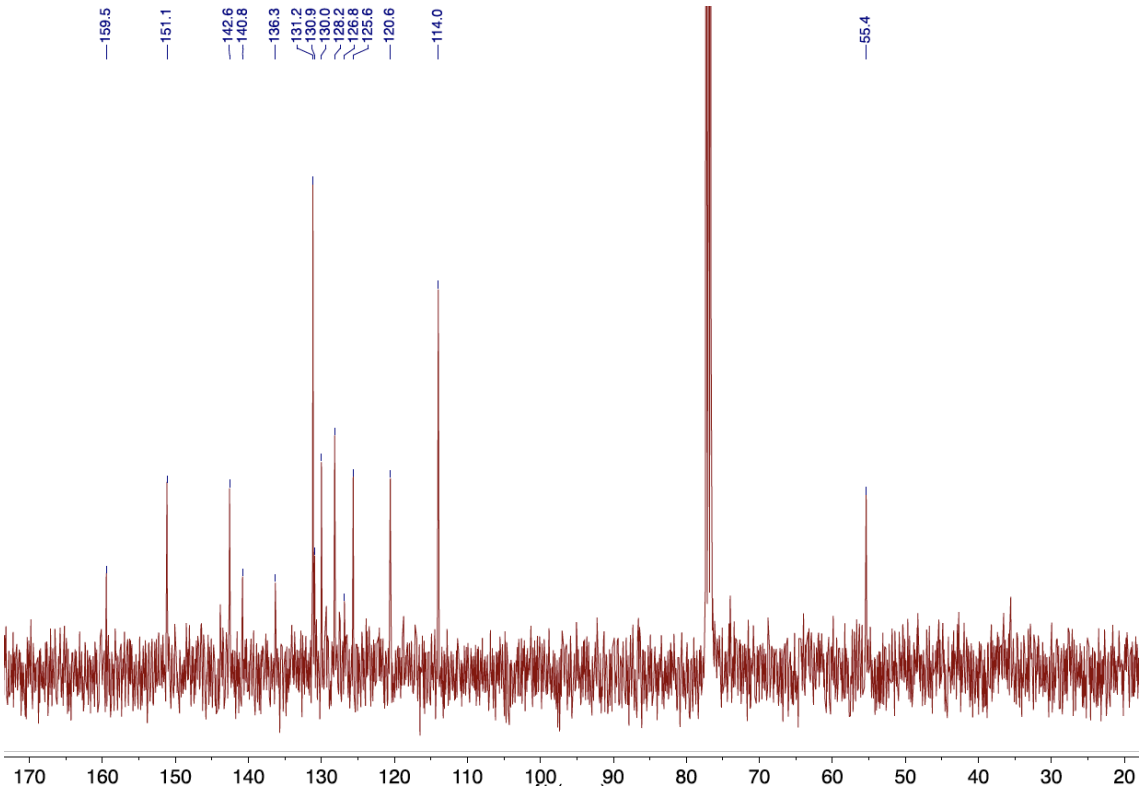
Following the *procedure B*, purification by column chromatography (Cyclohexane/EtOAc 10:1), to afford **6-acac** as a purple solid (40 mg, 60 %). **^{1}H-RMN (400 MHz, $CDCl_3$, 298K):** δ 8.78 (d, 1H, *J*= 6.2 Hz. ^{195}Pt satellites signals with $^3J_{Pt,H}$ = 38 Hz), 7.77 (dd, 1H, *J* = 8.2 and 1.4 Hz), 7.77 (dd, 1H, *J*= 8.2 and 6.9Hz), 7.63 (dd, 1H, *J* = 8.2 and 1.3 Hz), 7.47 (dd, 1H, *J* = 6.9 and 1.5Hz), 7.38 (d, 1H, *J* = 6.2 Hz), 7.22 (d, 1H, *J* = 8.4 Hz), 7.09 (s, 1H), 7.03 (ddd, 1H, *J* = 8.2, 6.8 and 1.2 Hz), 6.89 (ddd, 1H, *J* = 8.4, 6.8 and 1.3 Hz), 6.65 (br s, 5H), 5.50 (s, 1H), 2.89 (s, 6H), 2.05 (s, 3H), 2.03 (s, 3H). **^{13}C-RMN (100 MHz, $CDCl_3$, 298K):** δ 186.0, 183.9, 170.7, 151.6, 142.1, 140.2, 138.8, 138.3, 136.3, 133.0, 130.6, 130.3, 128.7, 126.2, 125.6, 125.1, 125.0 (2xC), 122.9, 122.2, 121.8, 116.1, 112.5, 102.6, 43.8, 28.3, 27.2. One CH and Cq are missing, perhaps are overlapped with other signals. **HRMS(ESI)** calculated for $C_{32}H_{29}N_2O_2Pt$ ($M + H^+$) 668.1871. Found 668.1858.

4. NMR spectra.

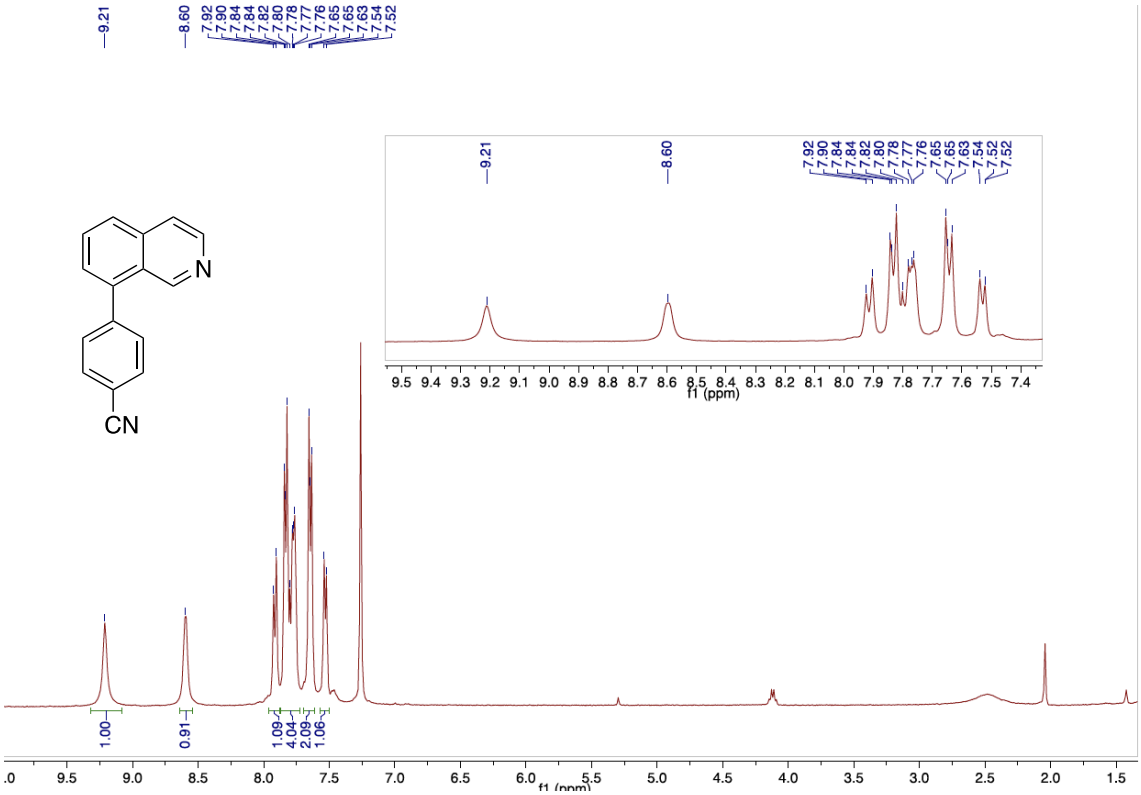
^{1}H-NMR (400MHz, $CDCl_3$, 298K):



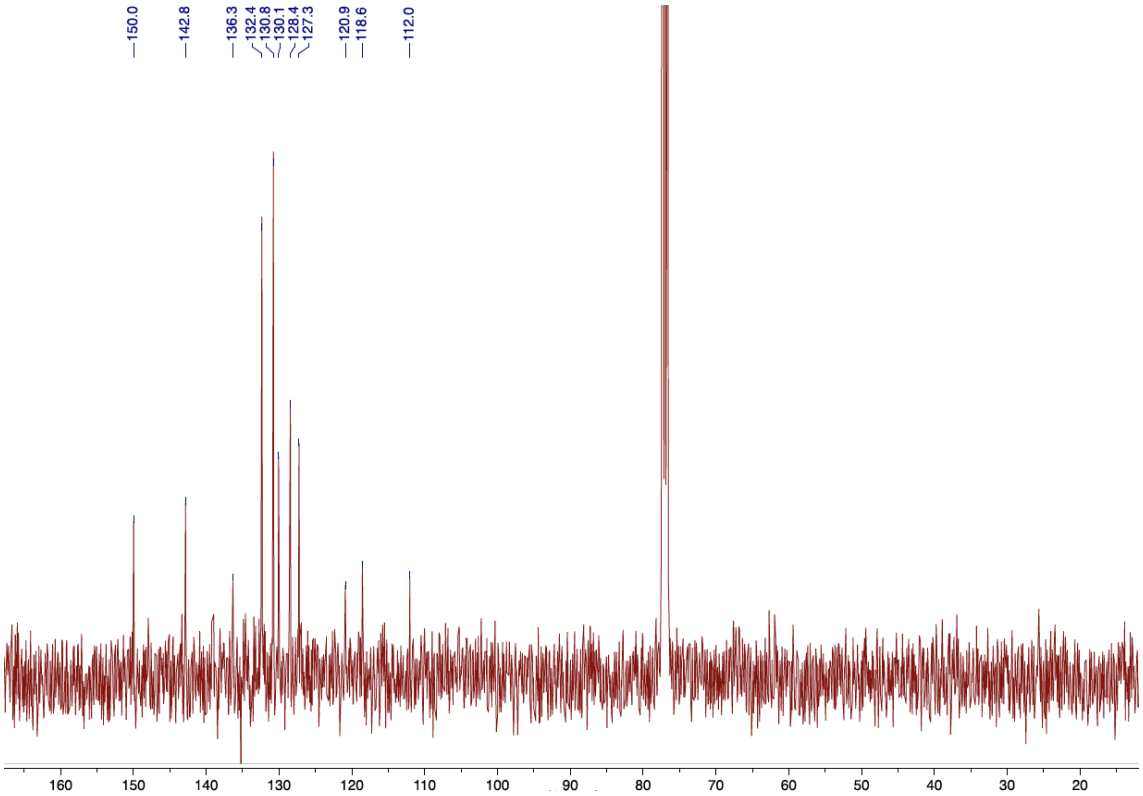
^{13}C-NMR (100MHz, $CDCl_3$, 298K):



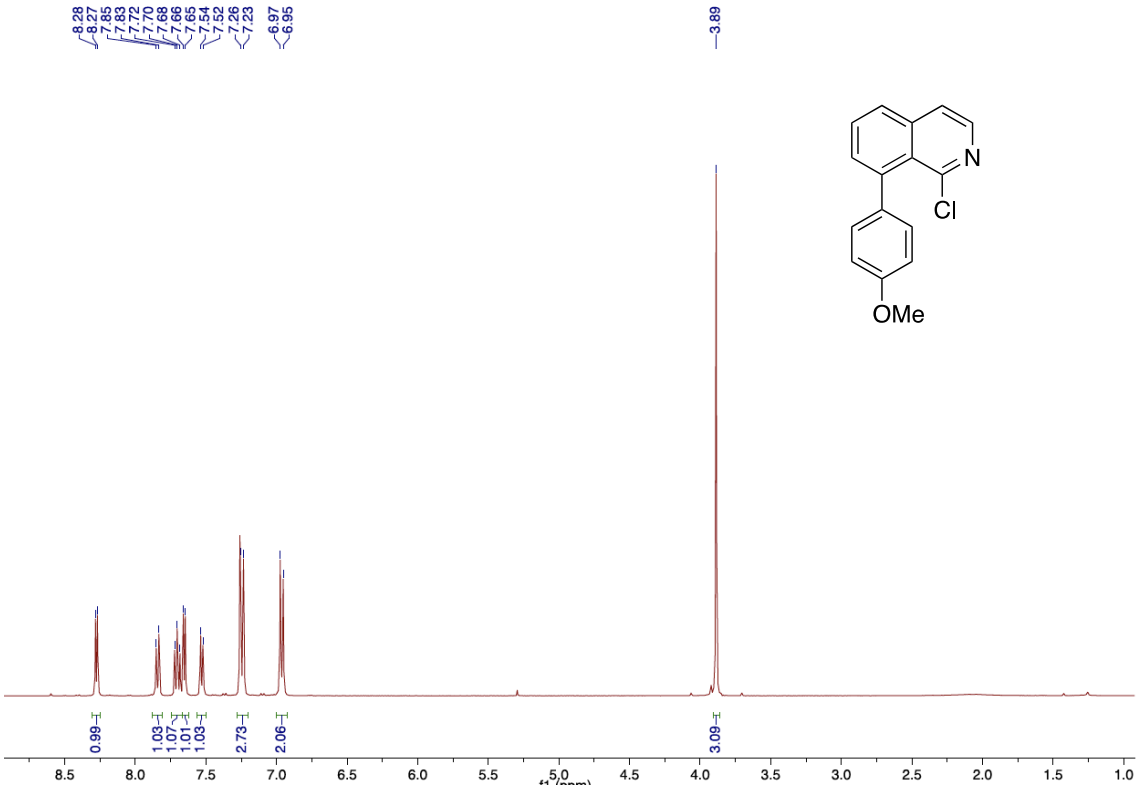
^{1}H-NMR (400MHz, $CDCl_3$, 298K):



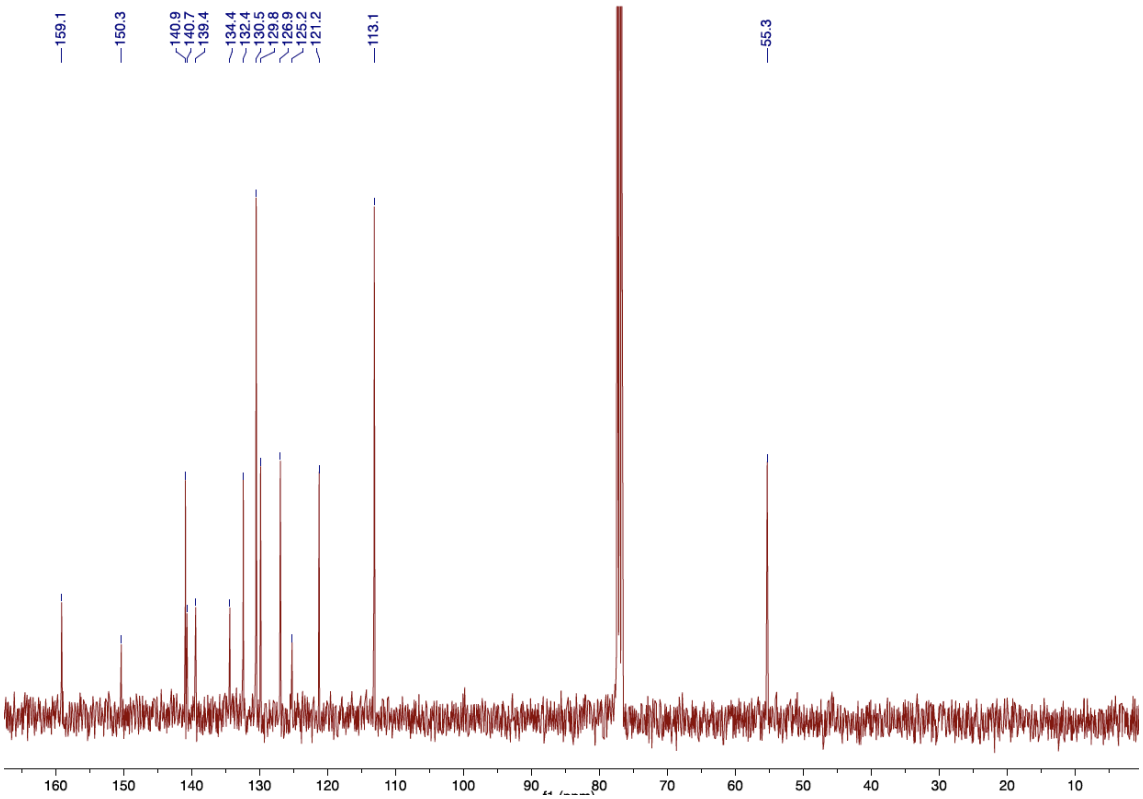
^{13}C-NMR (100MHz, $CDCl_3$, 298K):



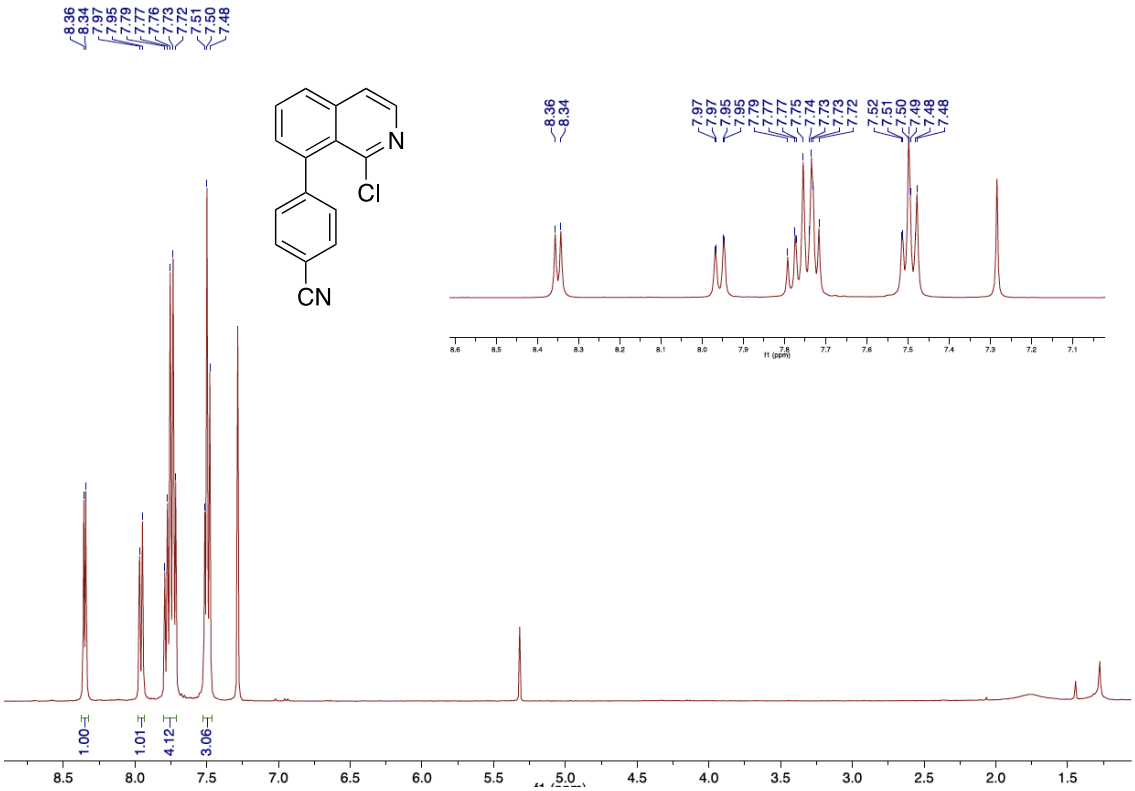
^{1}H-NMR (400MHz, $CDCl_3$, 298K):



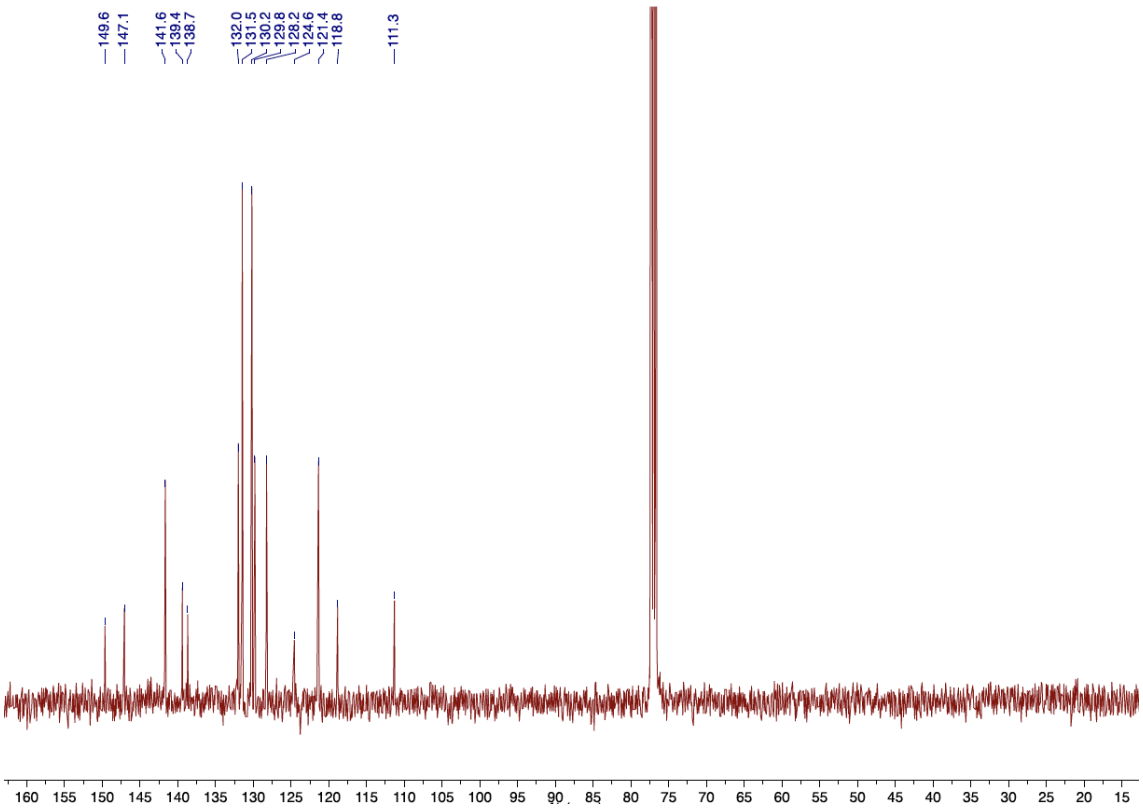
^{13}C-NMR (100MHz, $CDCl_3$, 298K):



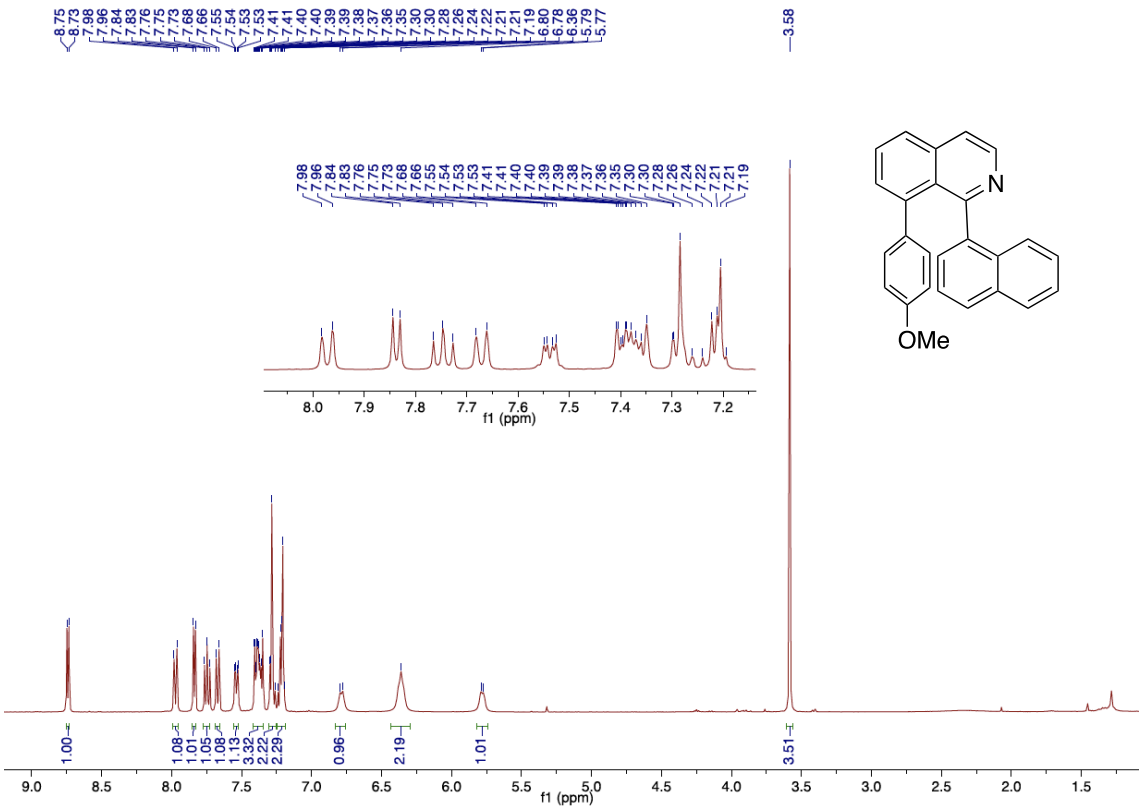
^{1}H-NMR (400MHz, $CDCl_3$, 298K):



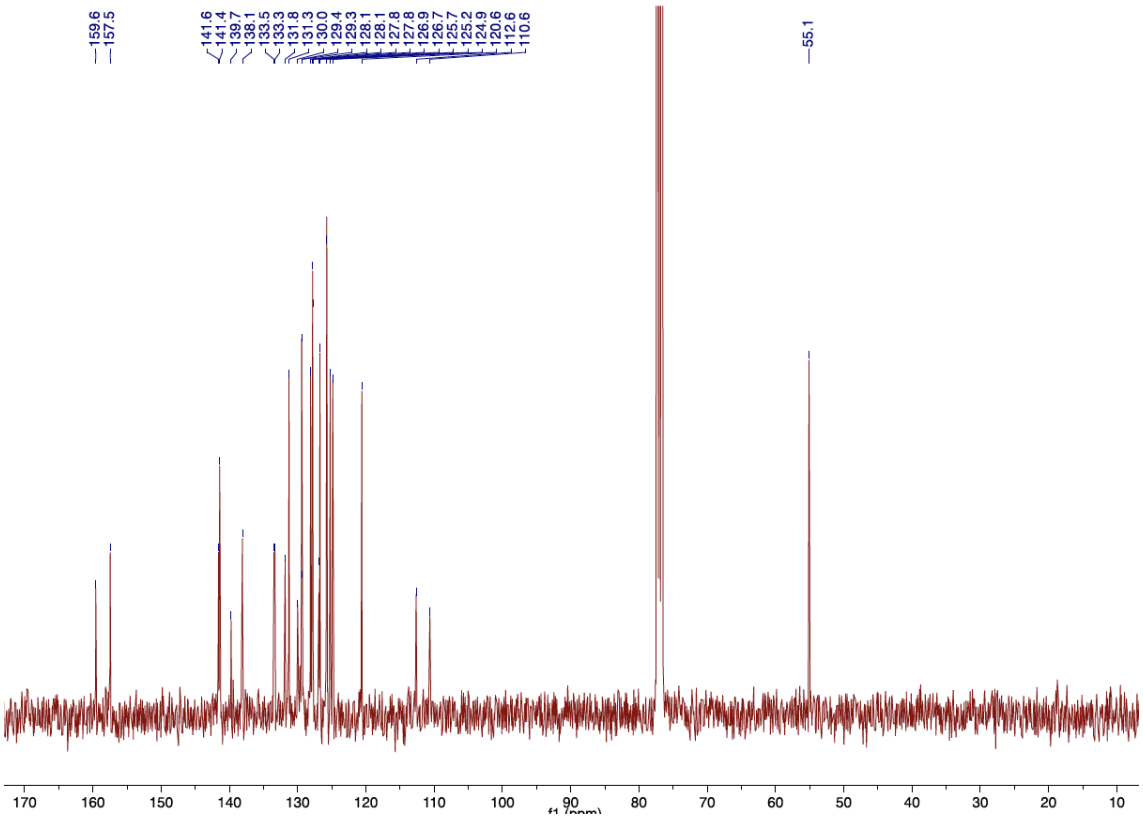
^{13}C-NMR (100MHz, $CDCl_3$, 298K):



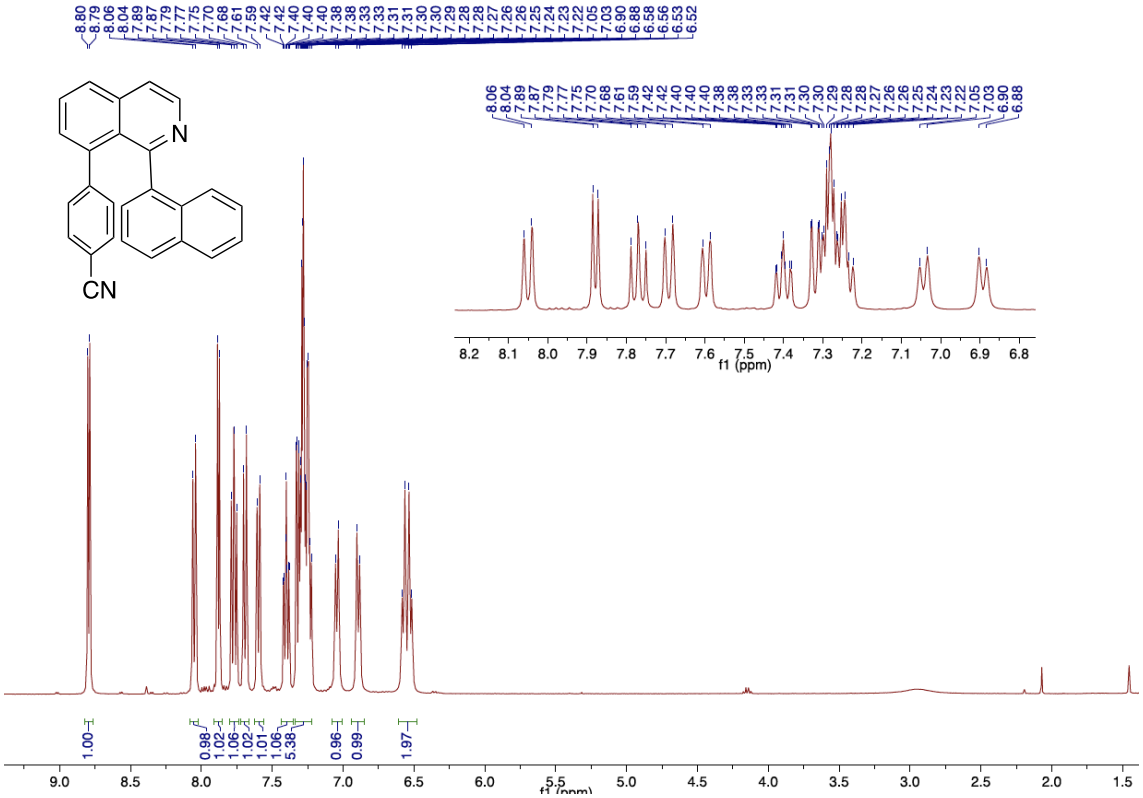
^{1}H-NMR (400MHz, $CDCl_3$, 298K):



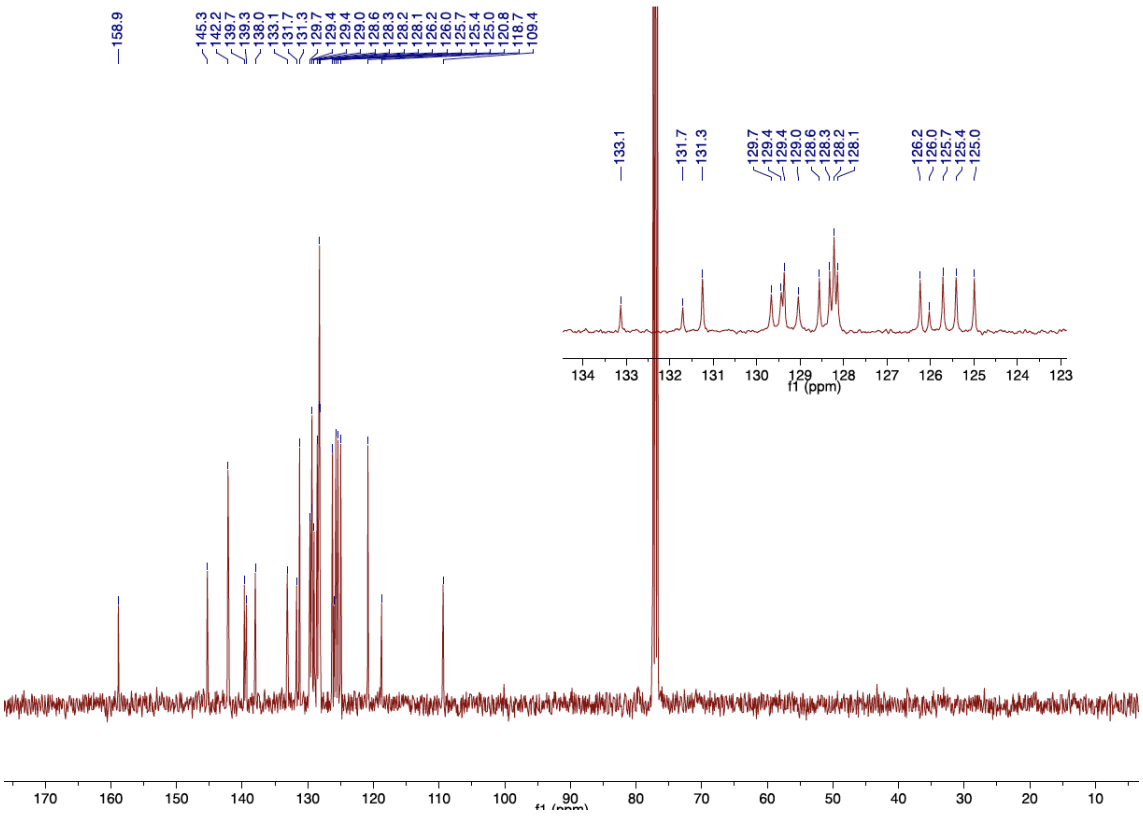
^{13}C-NMR (100MHz, $CDCl_3$, 298K):



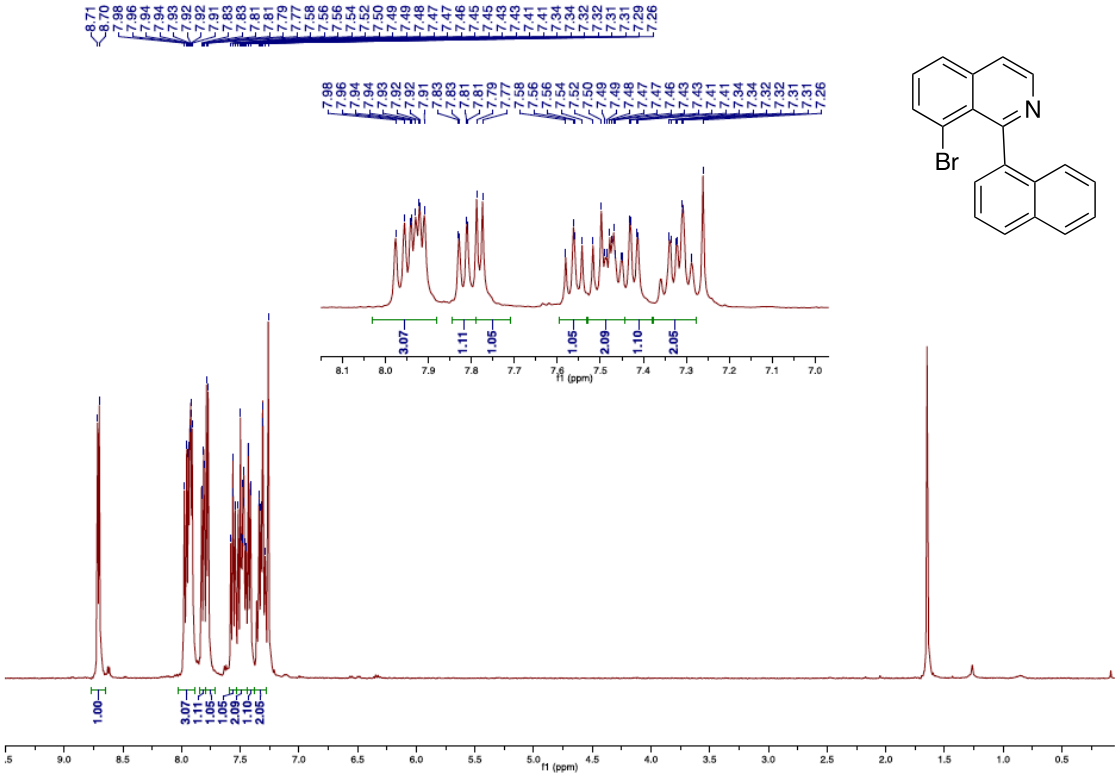
^{1}H-NMR (400MHz, $CDCl_3$, 298K):



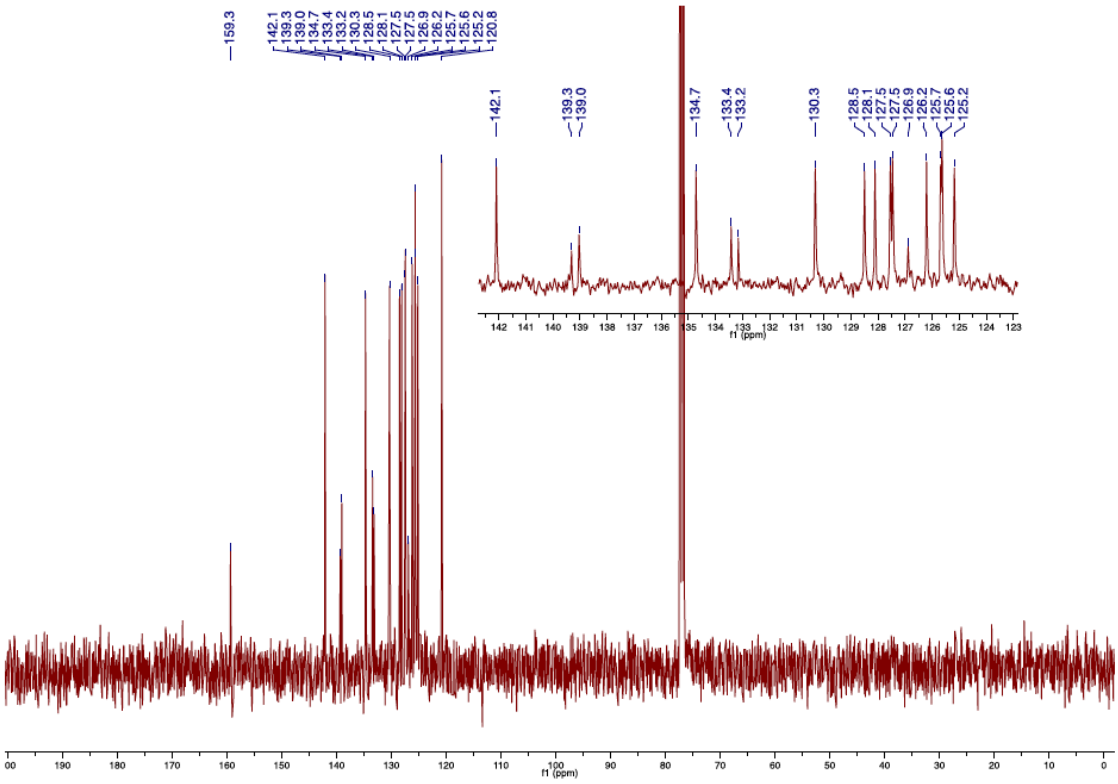
^{13}C-NMR (100MHz, $CDCl_3$, 298K):



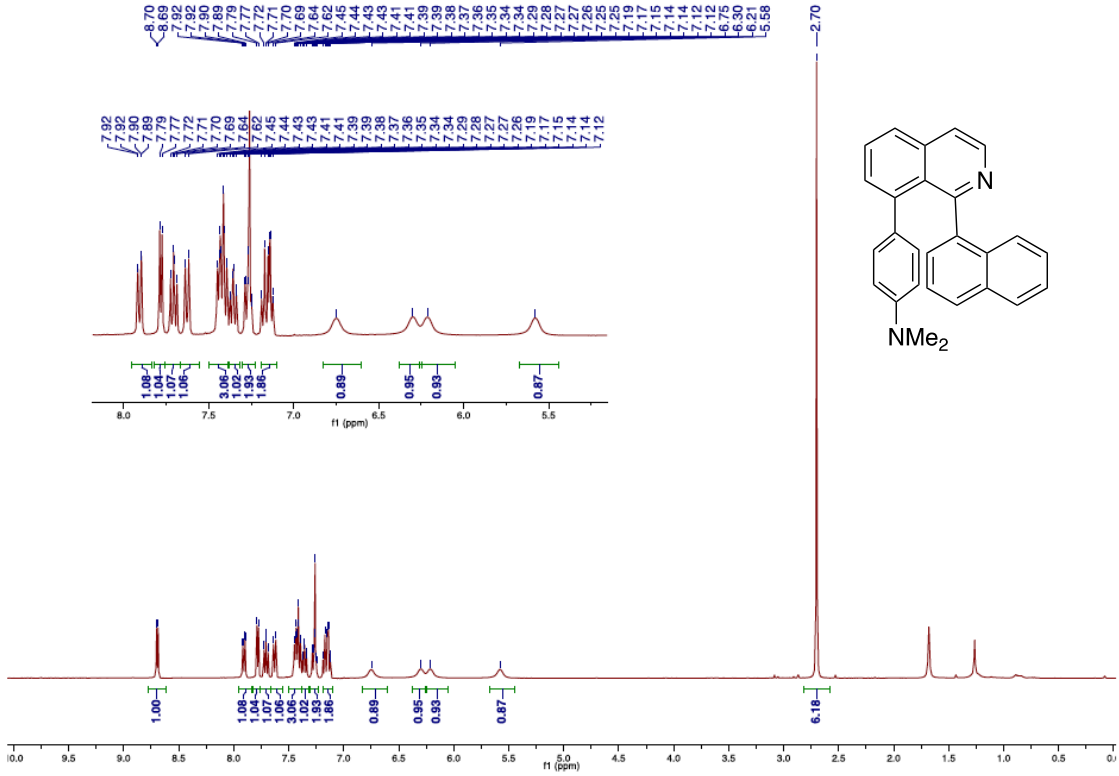
^{1}H-NMR (400MHz, $CDCl_3$, 298K):



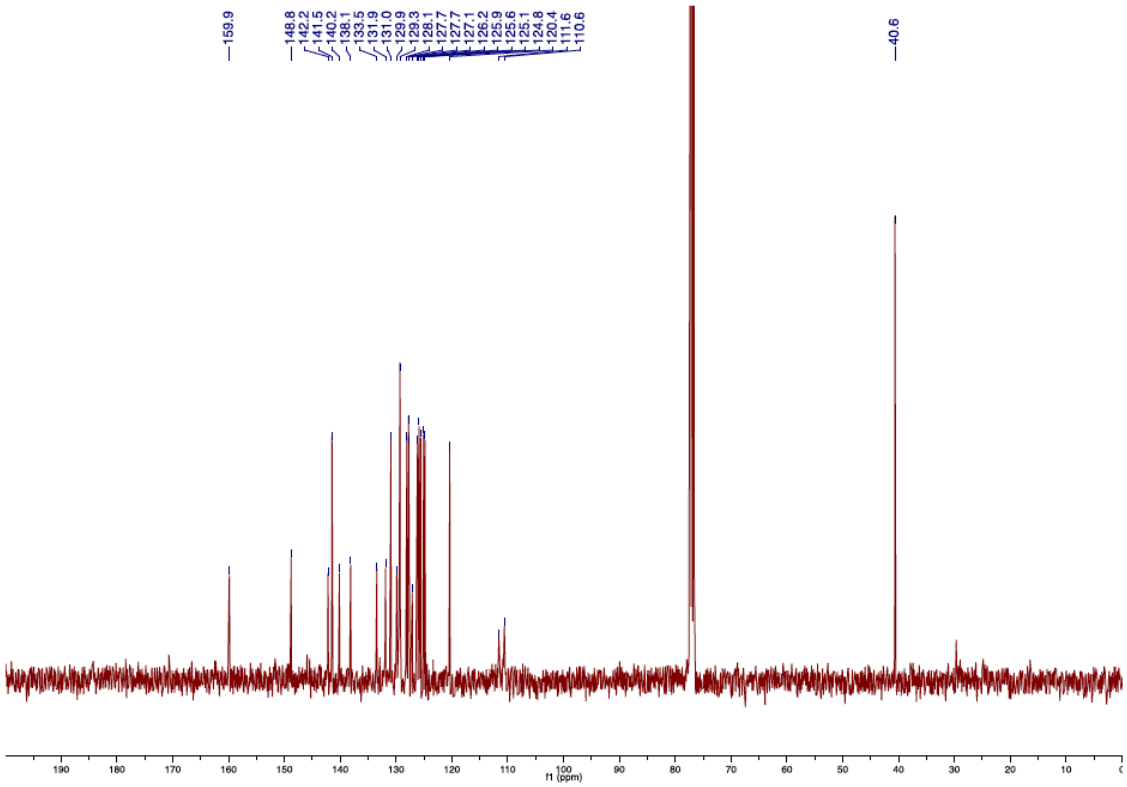
^{13}C-NMR (100MHz, $CDCl_3$, 298K):



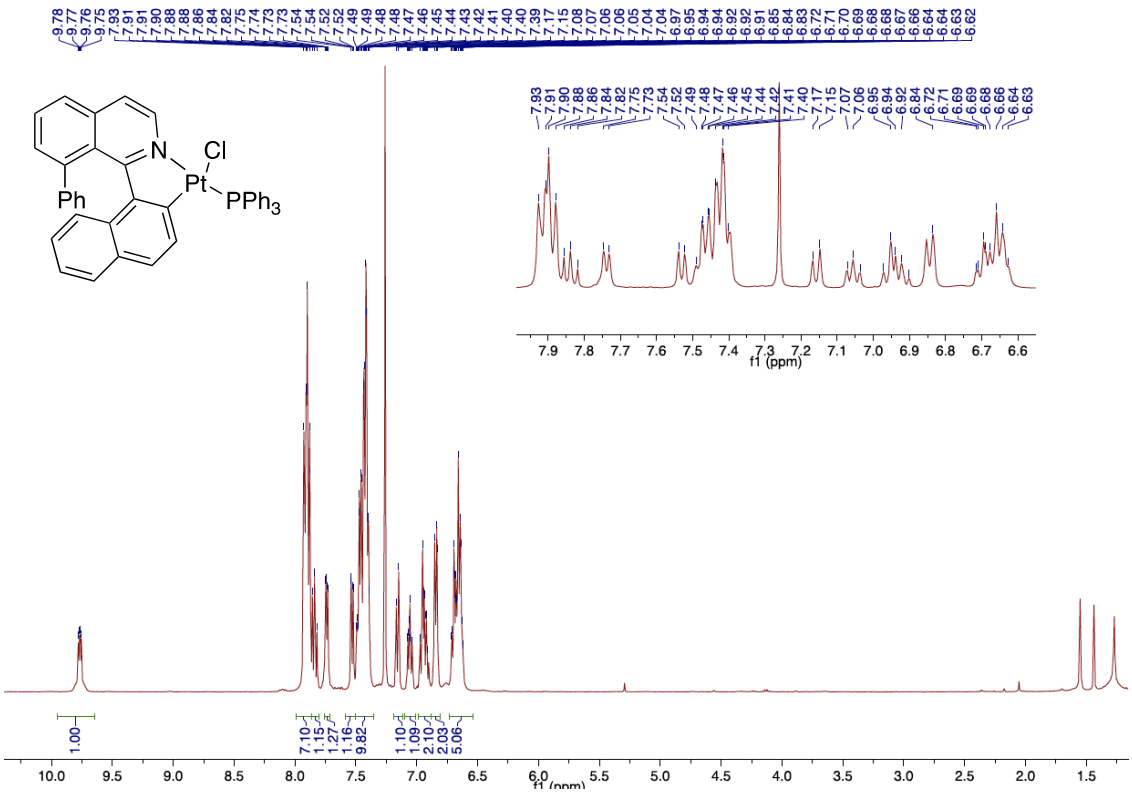
^{1}H-NMR (400MHz, $CDCl_3$, 298K):



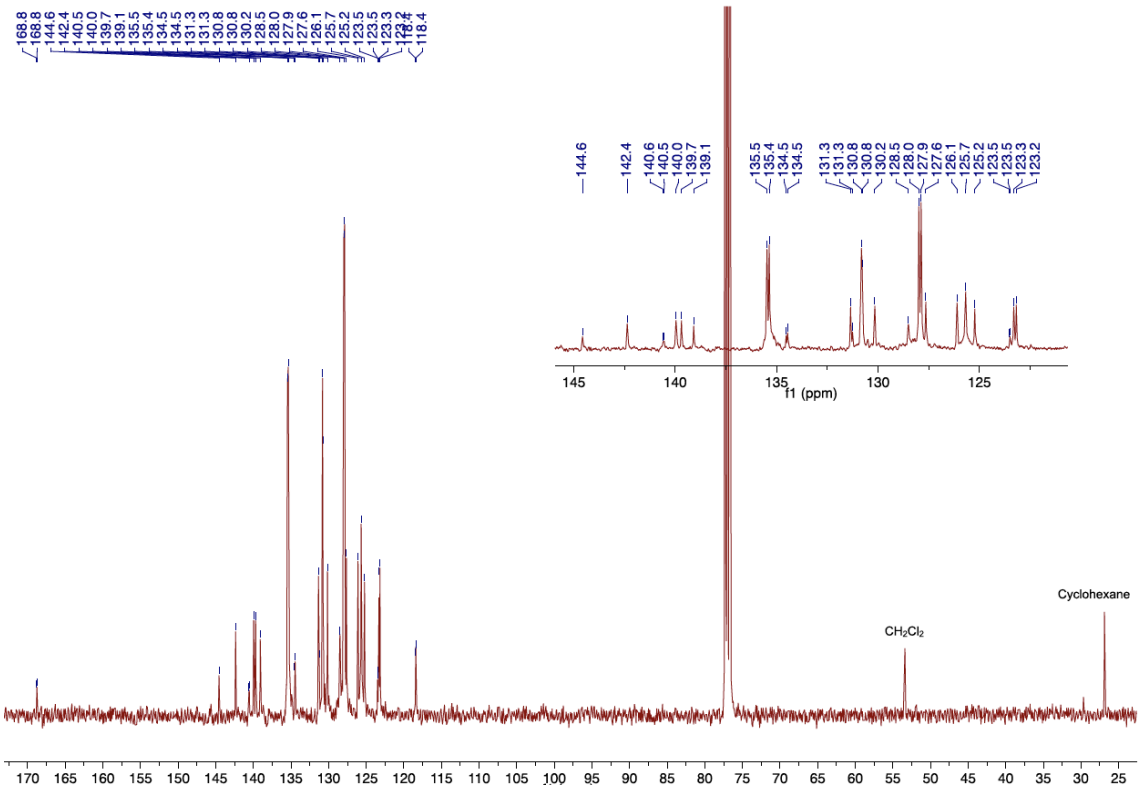
^{13}C-NMR (100MHz, $CDCl_3$, 298K):



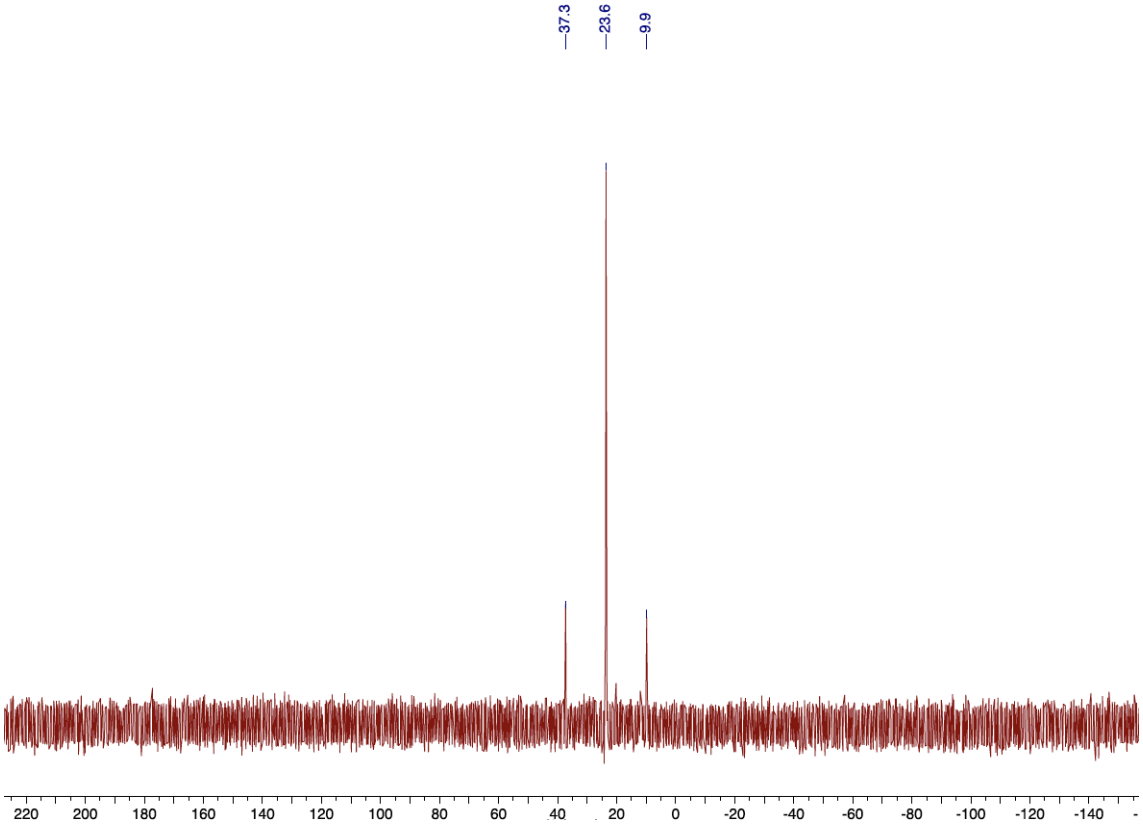
^{1}H-NMR (400MHz, $CDCl_3$, 298K):



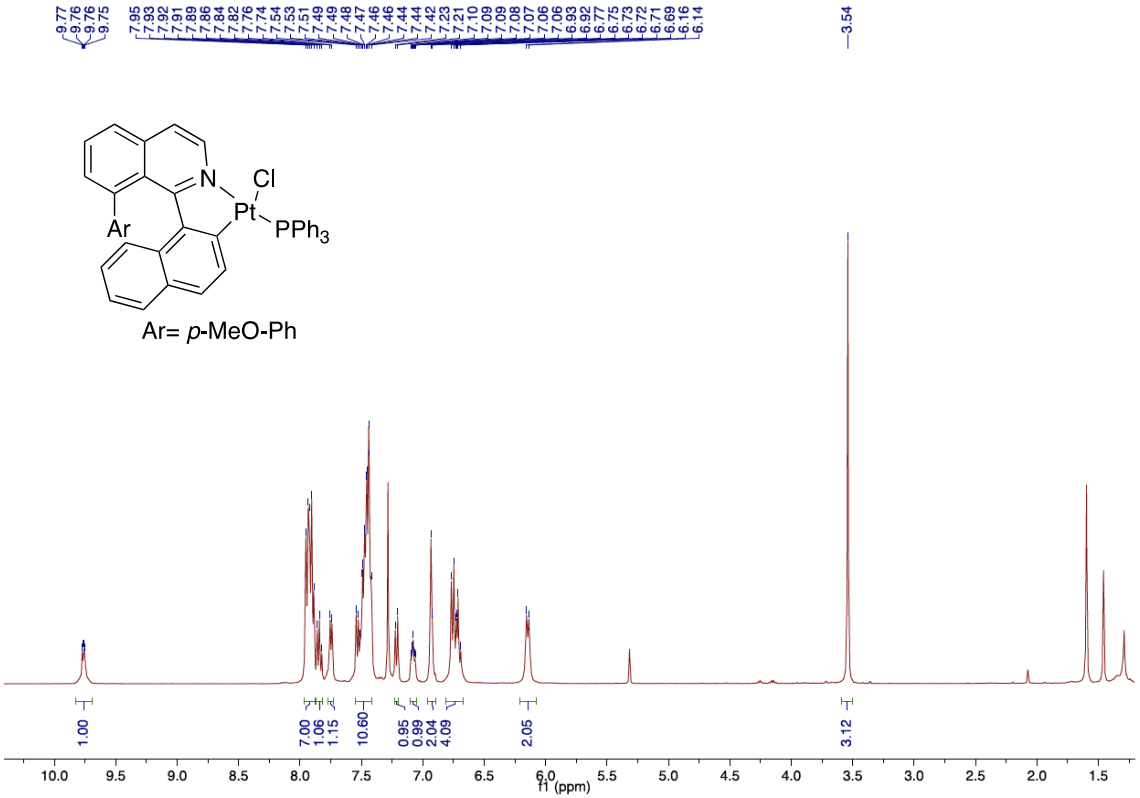
^{13}C-NMR (100MHz, $CDCl_3$, 298K):



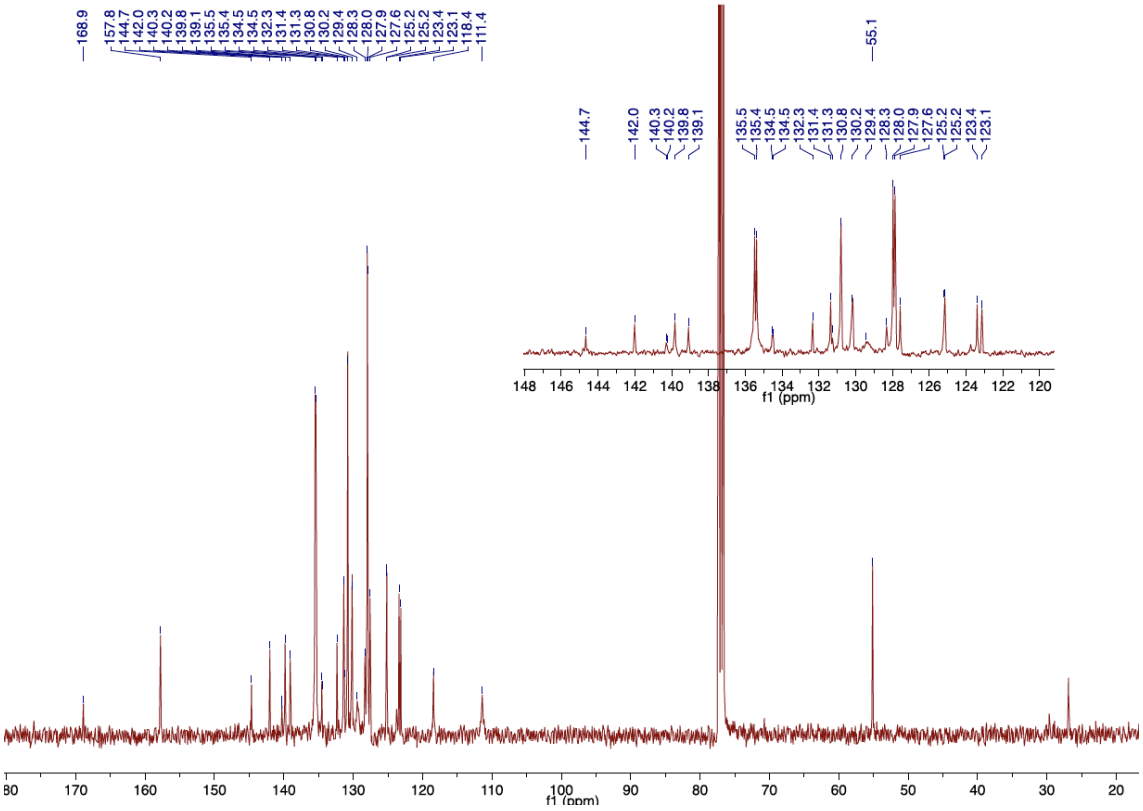
^{31}P-NMR (162MHz, $CDCl_3$, 298K):



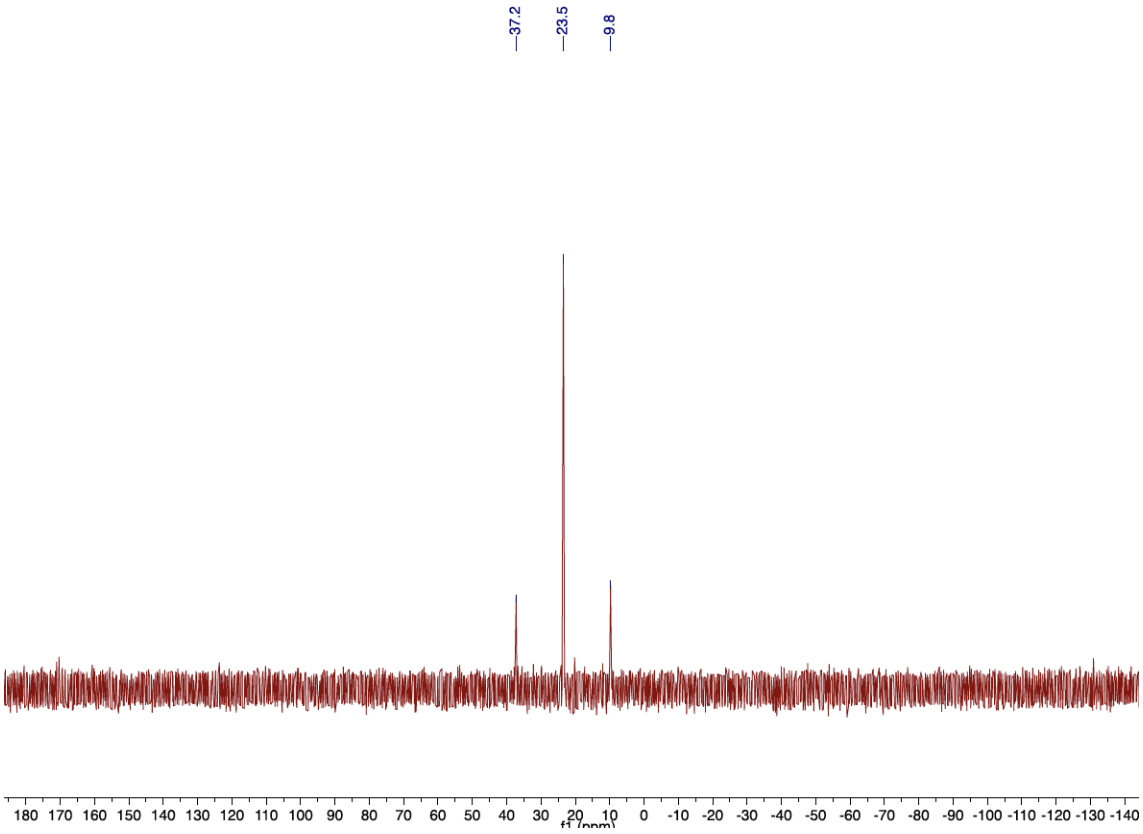
^{1}H-NMR (400MHz, $CDCl_3$, 298K):



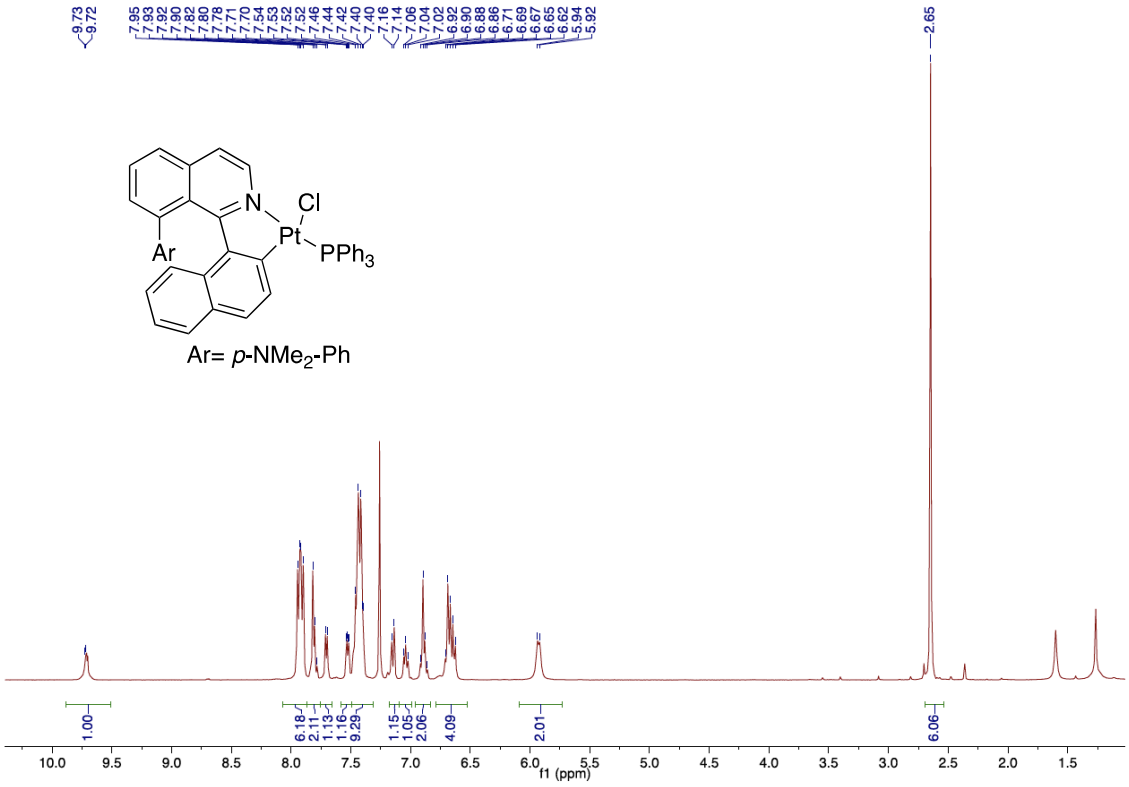
^{13}C-NMR (100MHz, $CDCl_3$, 298K):



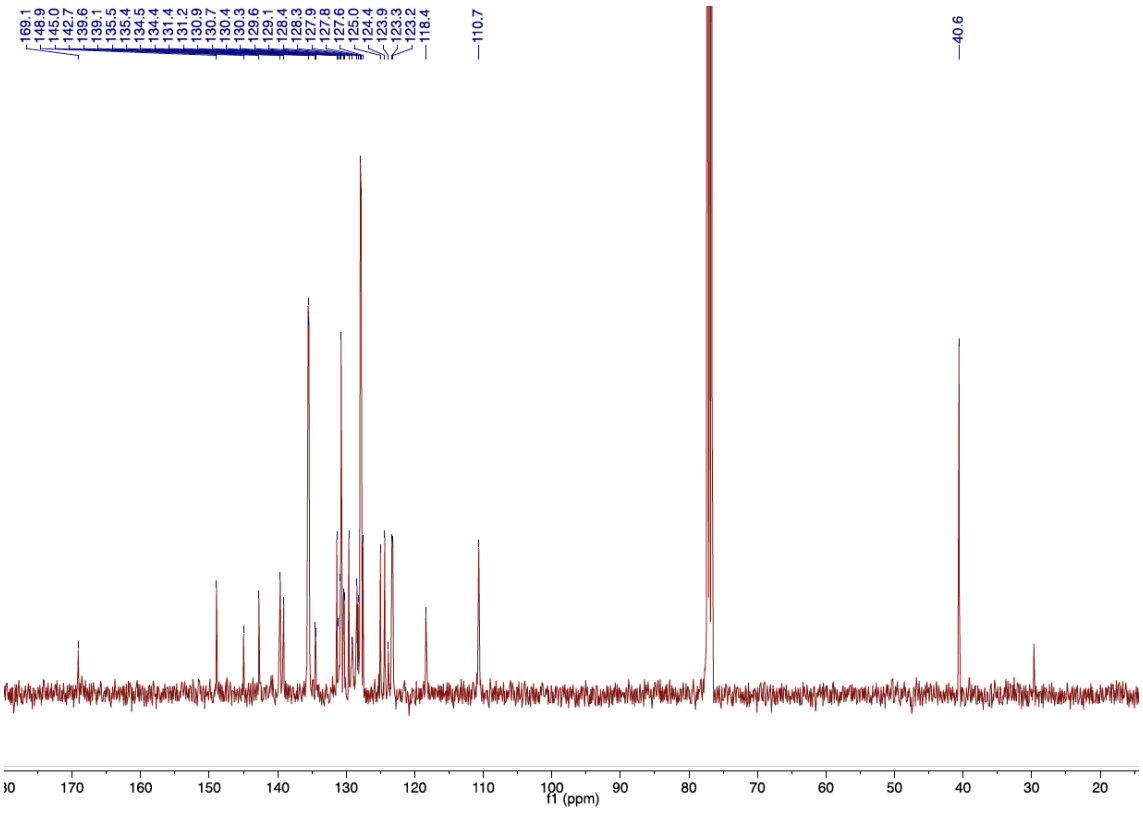
^{31}P-NMR (162MHz, $CDCl_3$, 298K):



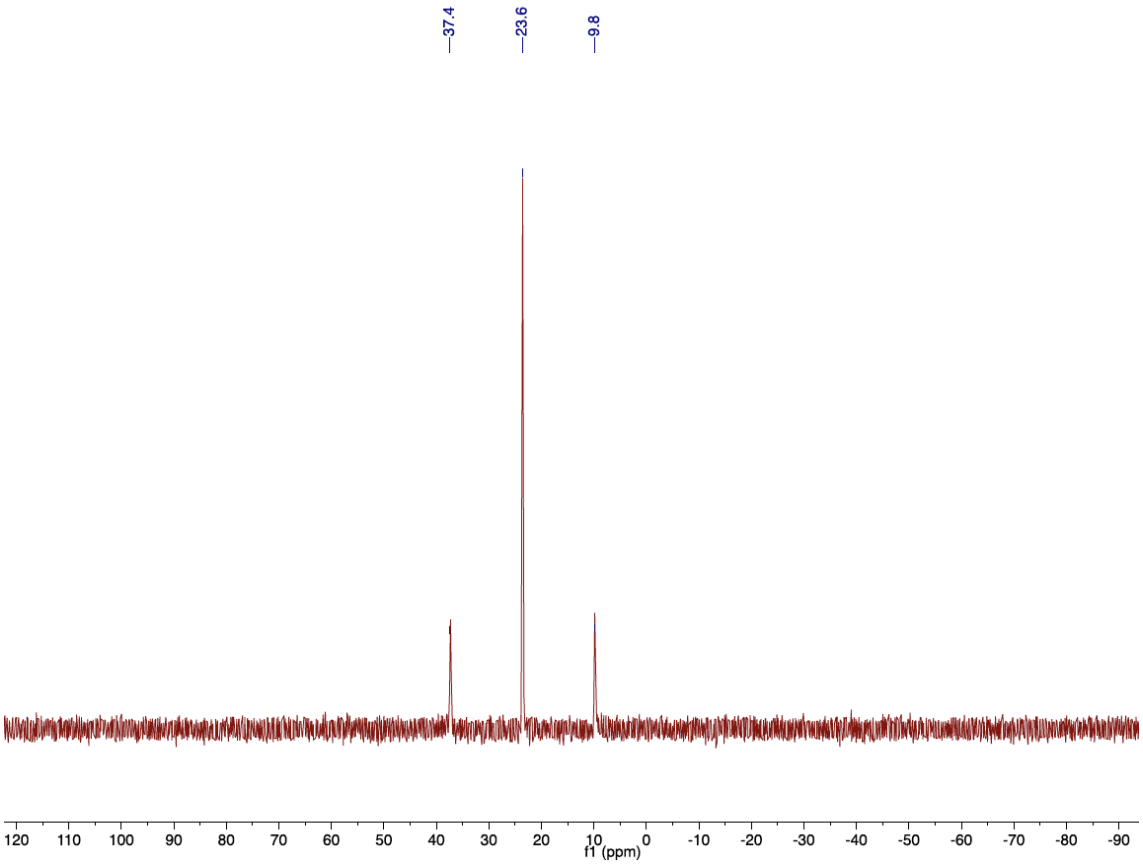
^{1}H-NMR (400MHz, $CDCl_3$, 298K):



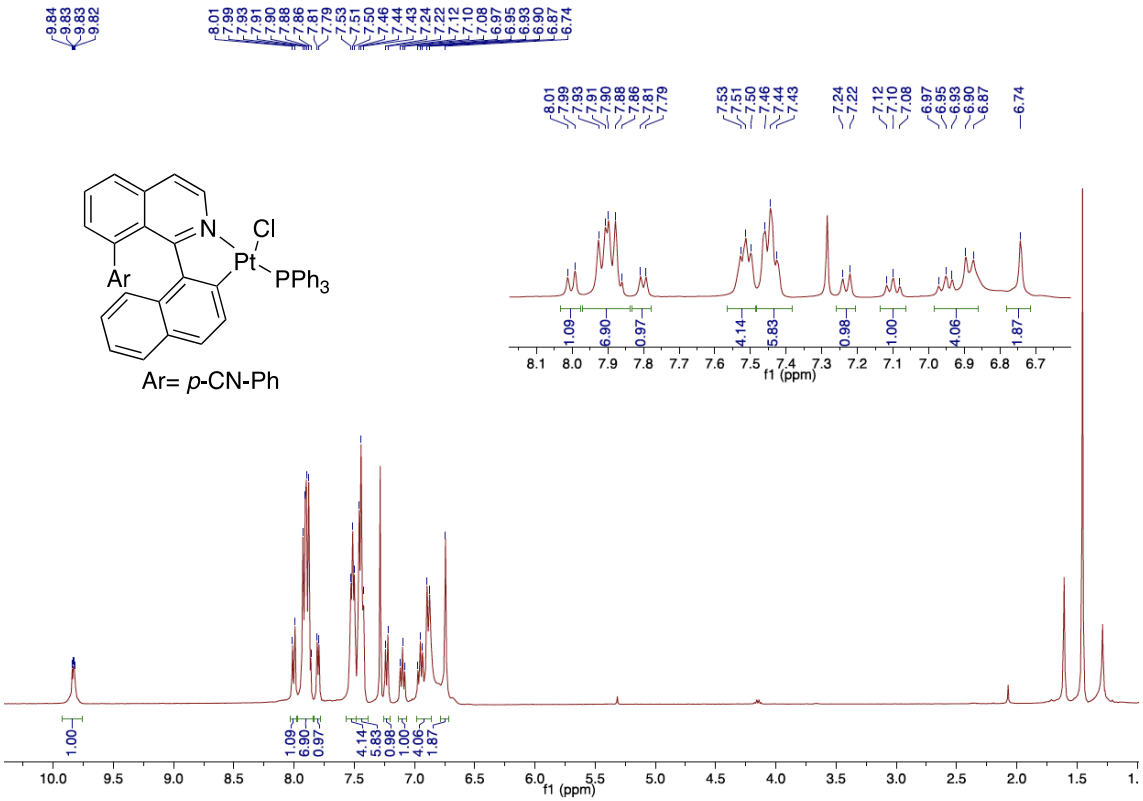
^{13}C-NMR (100MHz, $CDCl_3$, 298K):



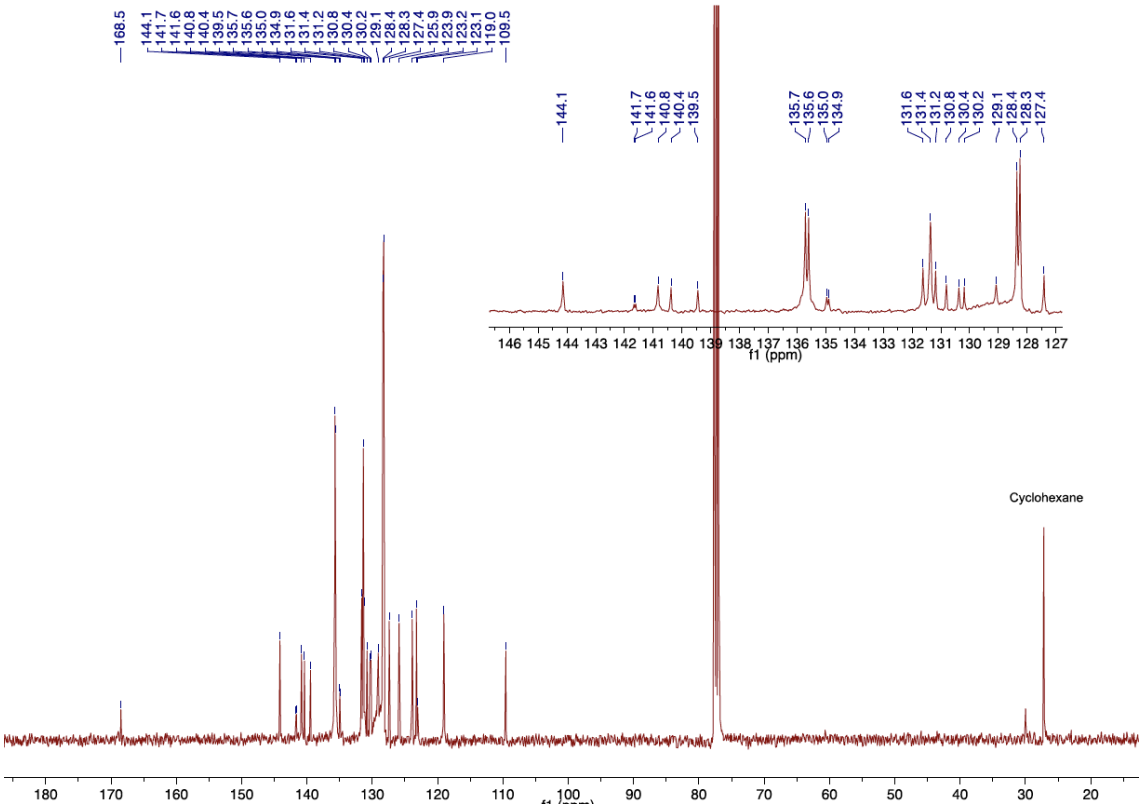
^{31}P-NMR (162MHz, $CDCl_3$, 298K):



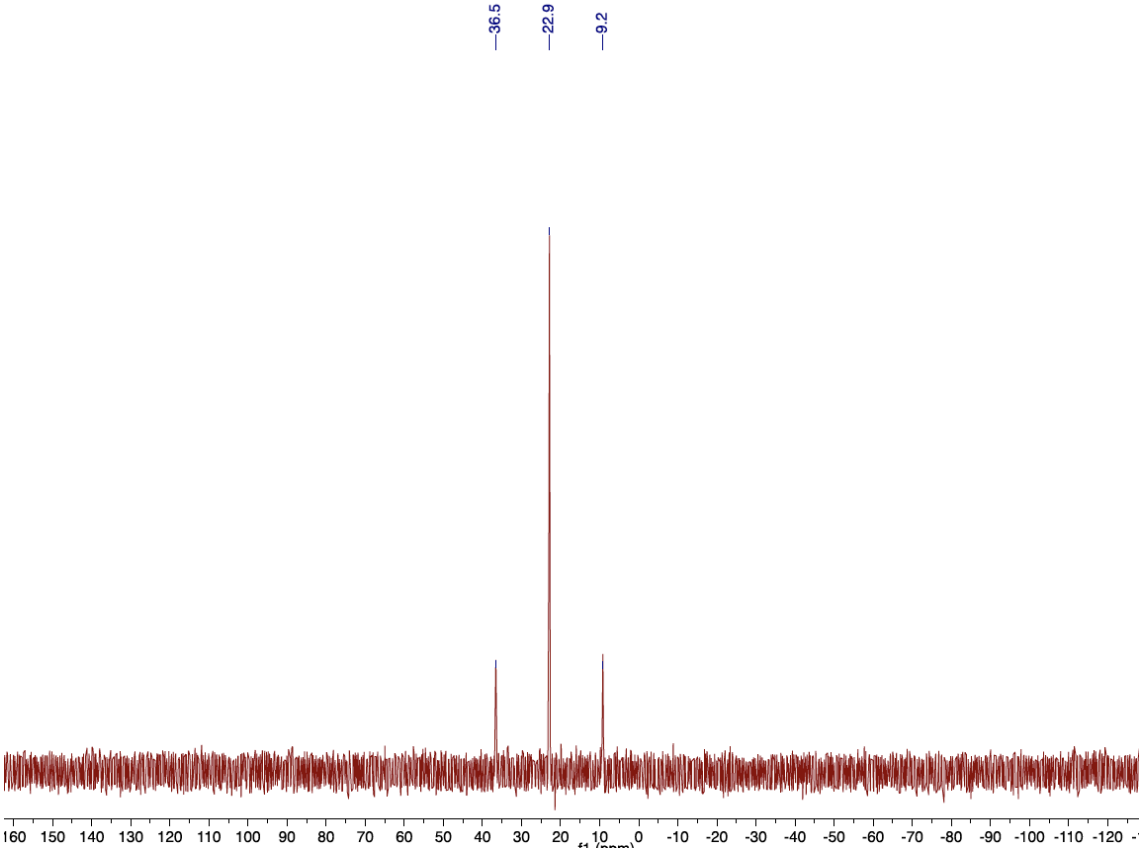
^{1}H-NMR (400MHz, $CDCl_3$, 298K):



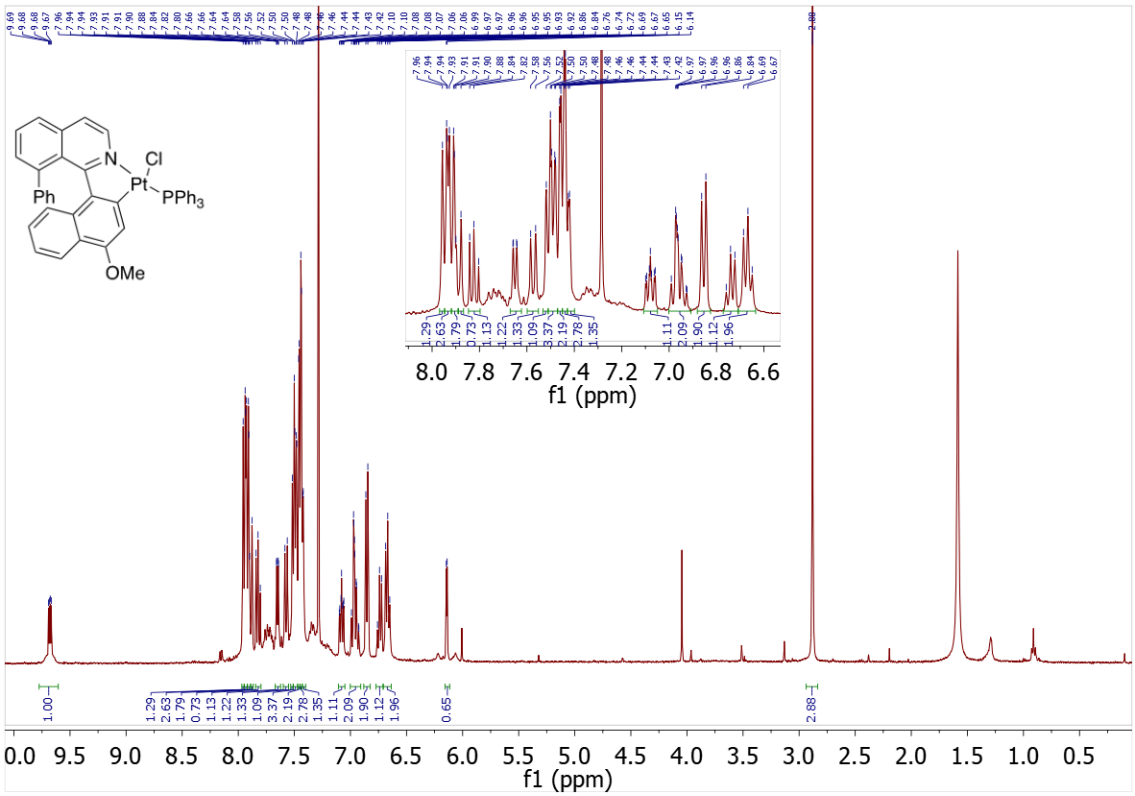
^{13}C-NMR (100MHz, $CDCl_3$, 298K):



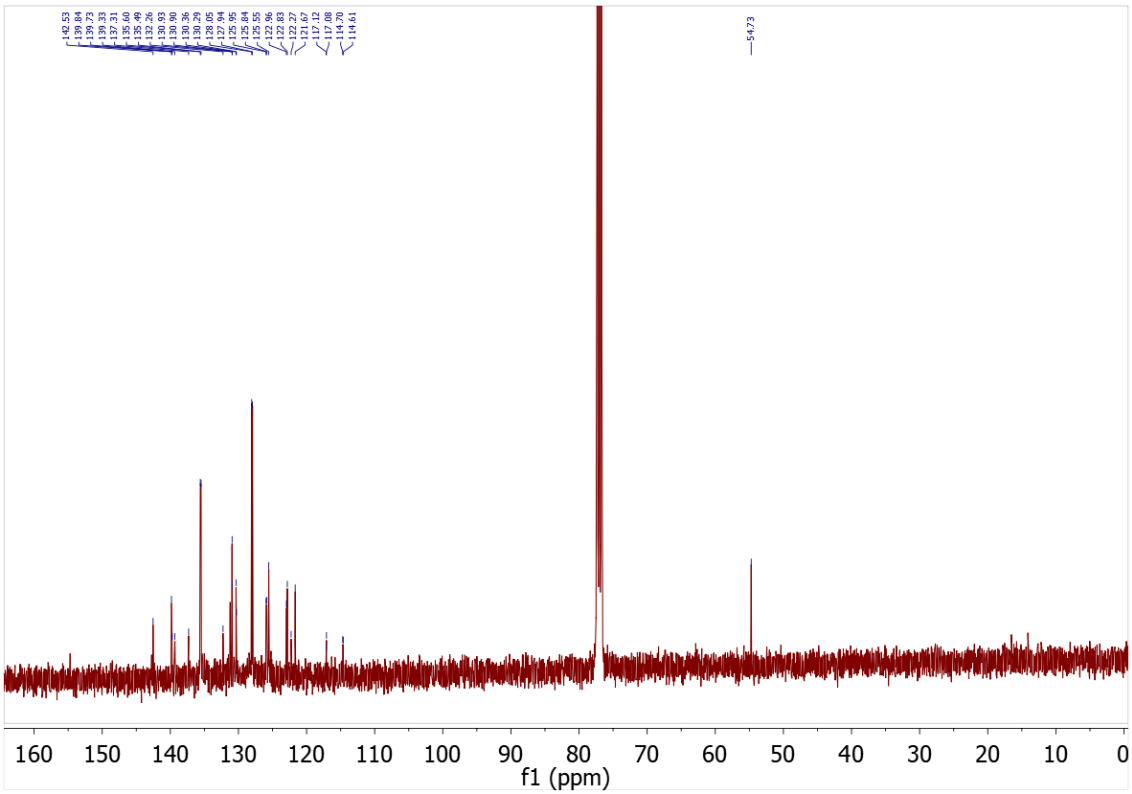
^{31}P-NMR (162MHz, $CDCl_3$, 298K):



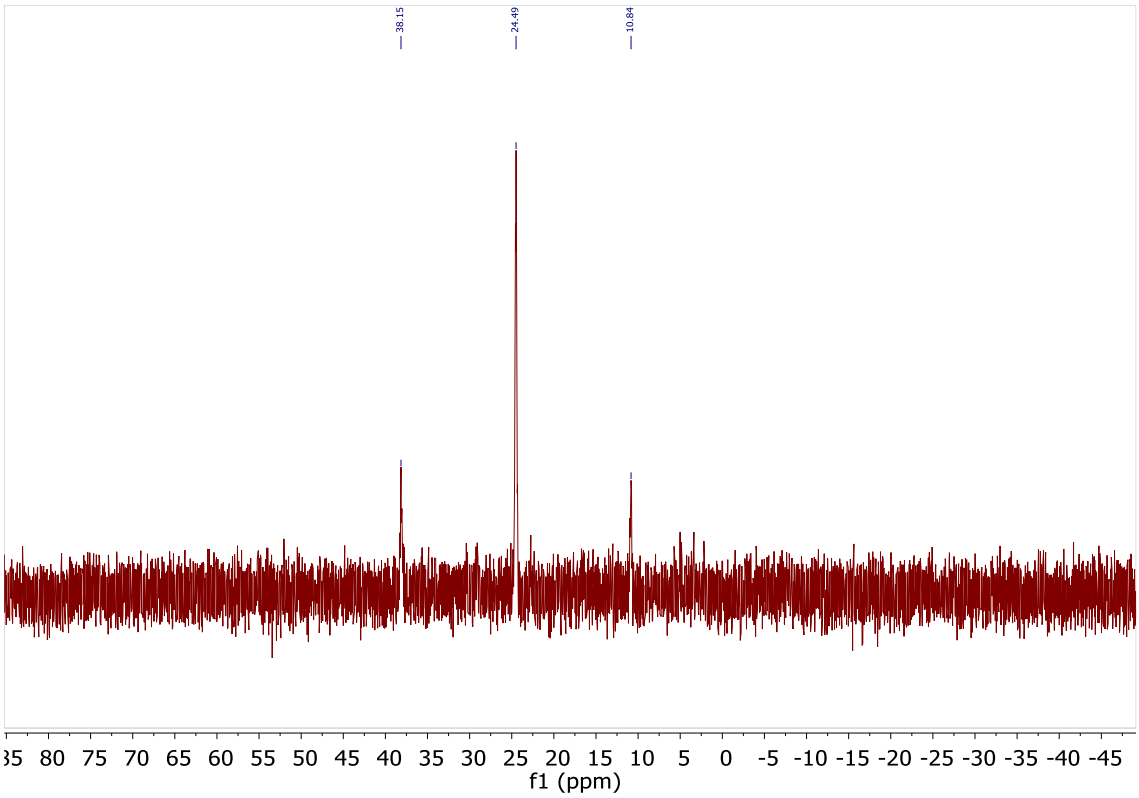
^{1}H-NMR (400MHz, $CDCl_3$, 298K):



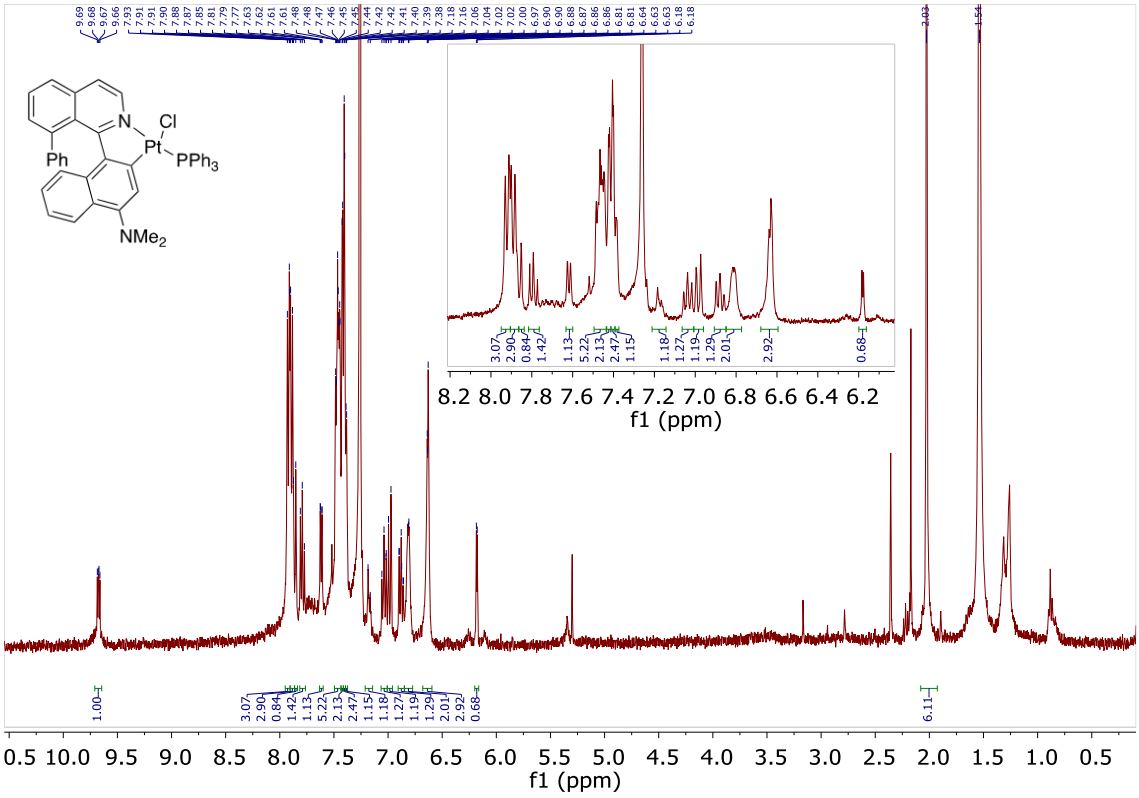
^{13}C-NMR (100MHz, $CDCl_3$, 298K):



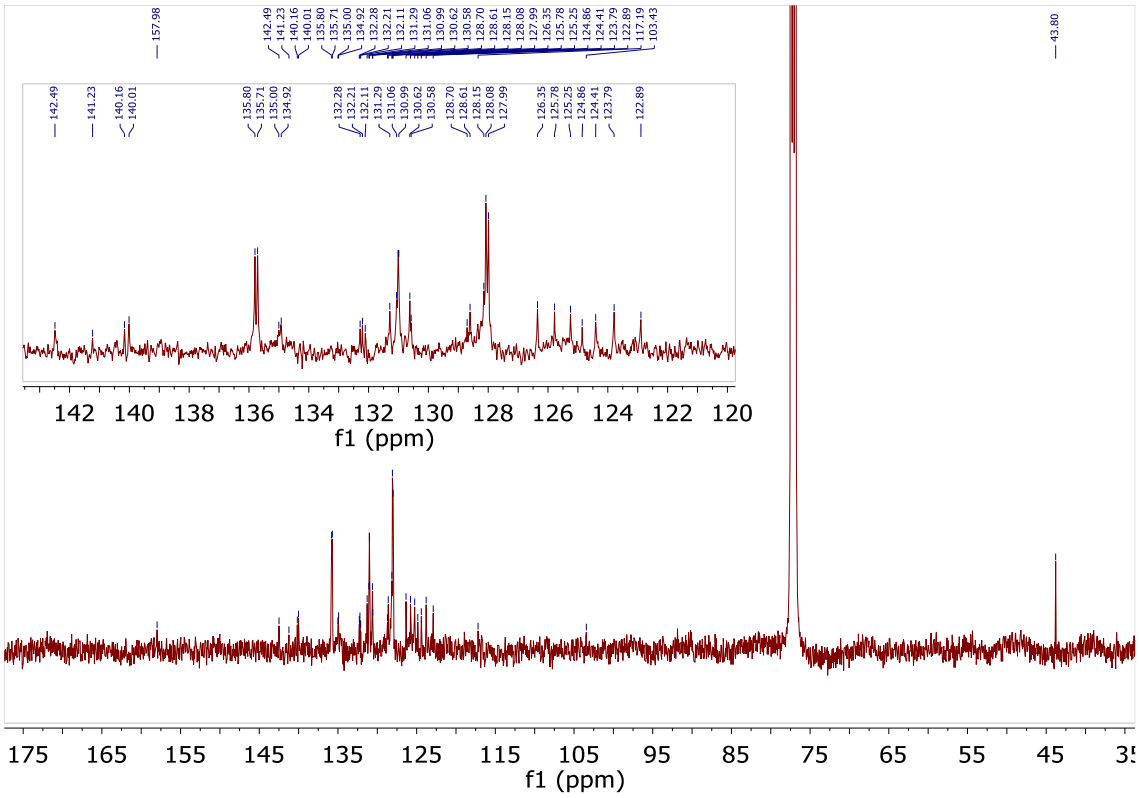
^{31}P-NMR (162MHz, $CDCl_3$, 298K):



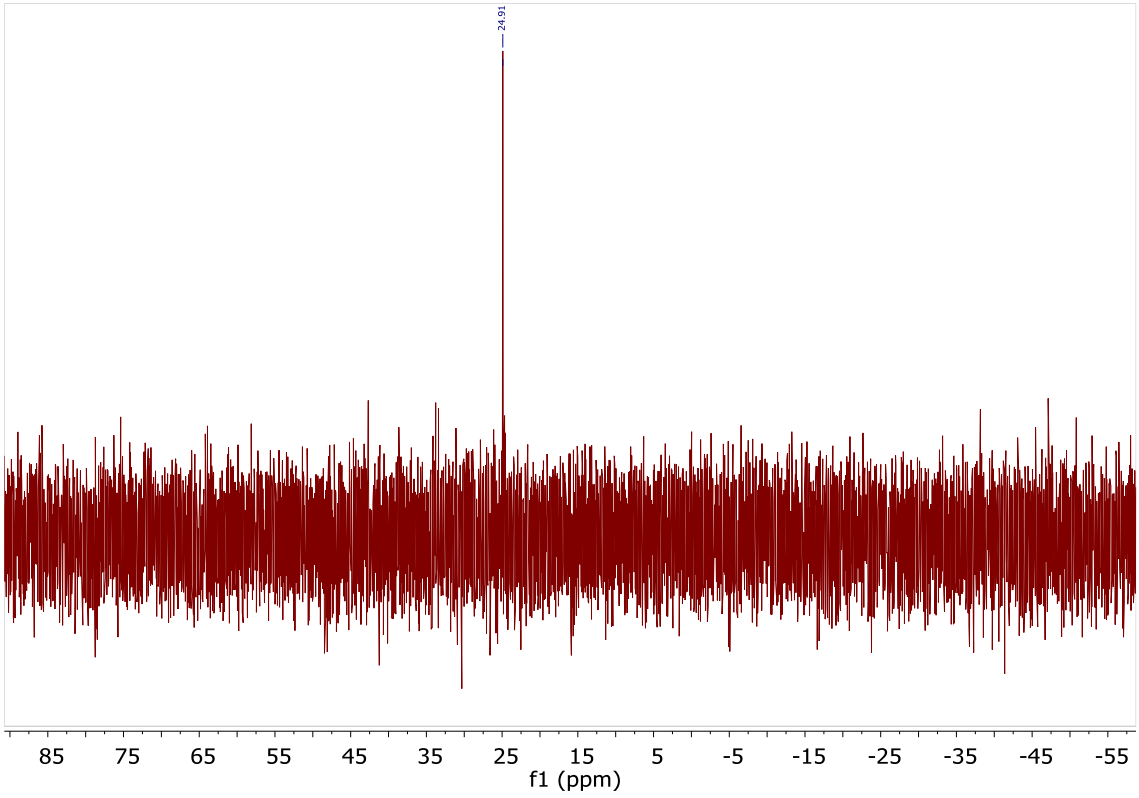
^{1}H-NMR (400MHz, $CDCl_3$, 298K):



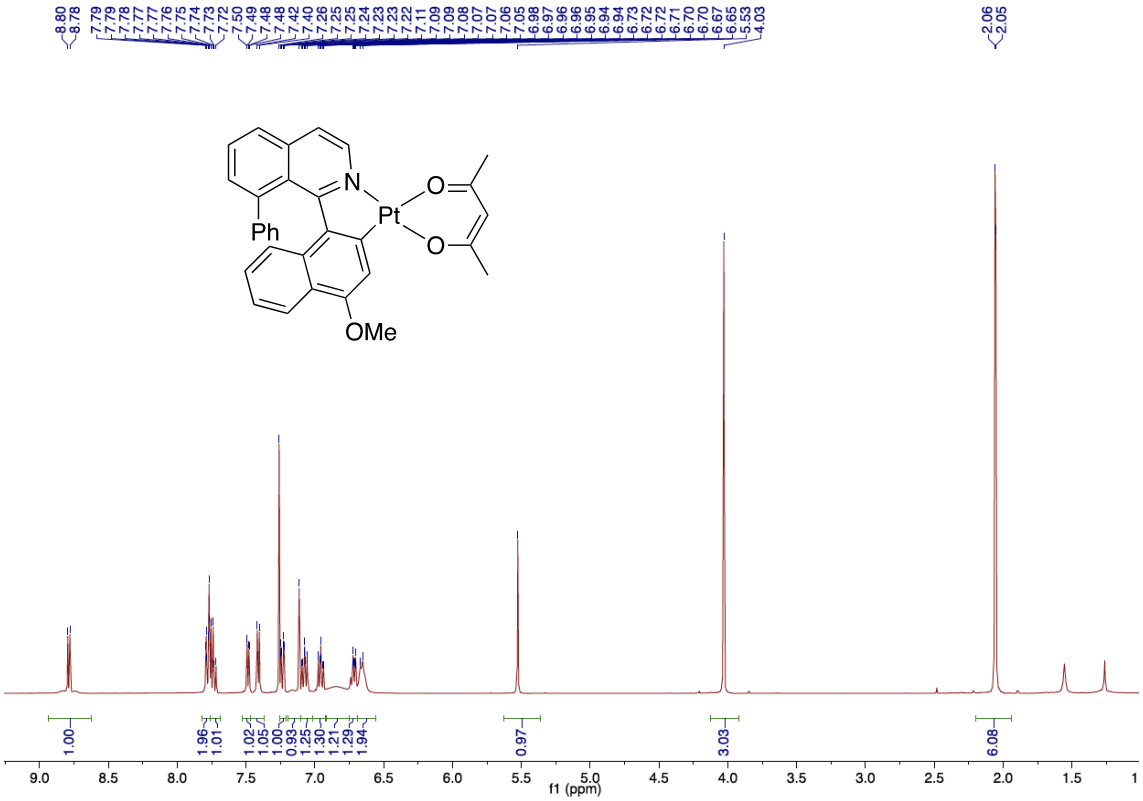
^{13}C-NMR (100MHz, $CDCl_3$, 298K):



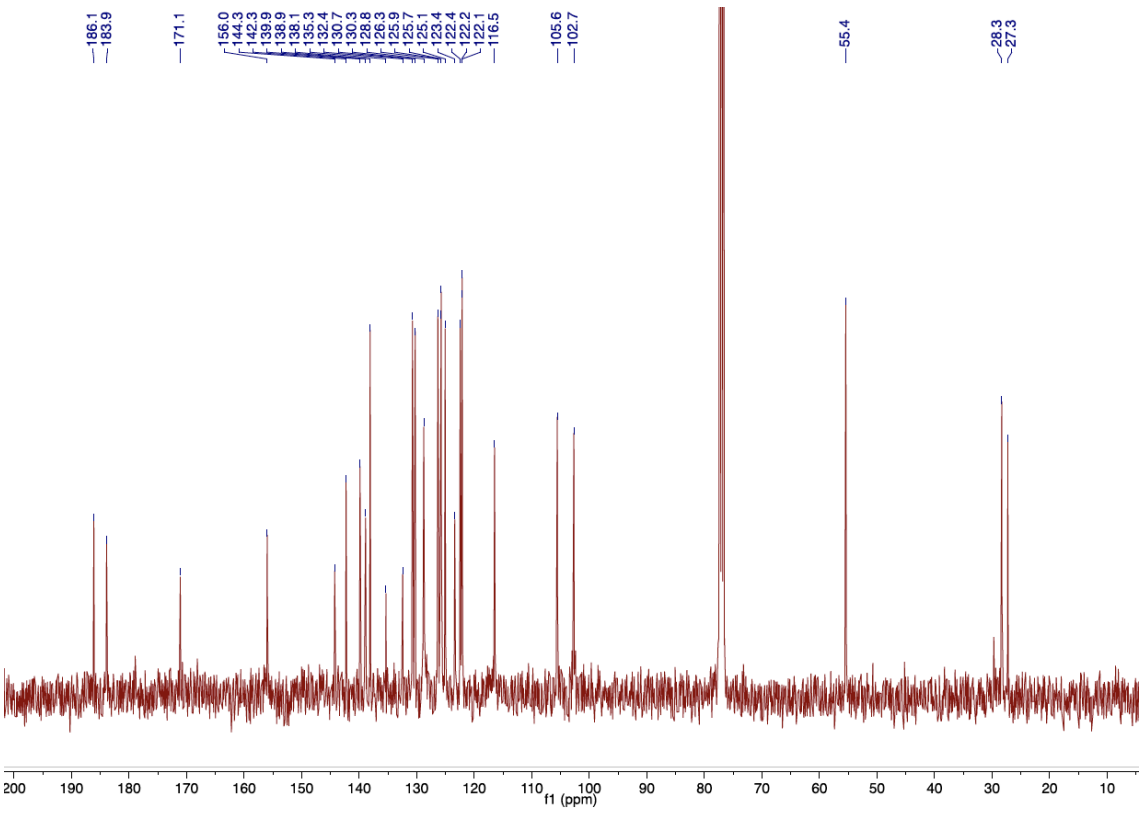
^{31}P-NMR (162MHz, $CDCl_3$, 298K):



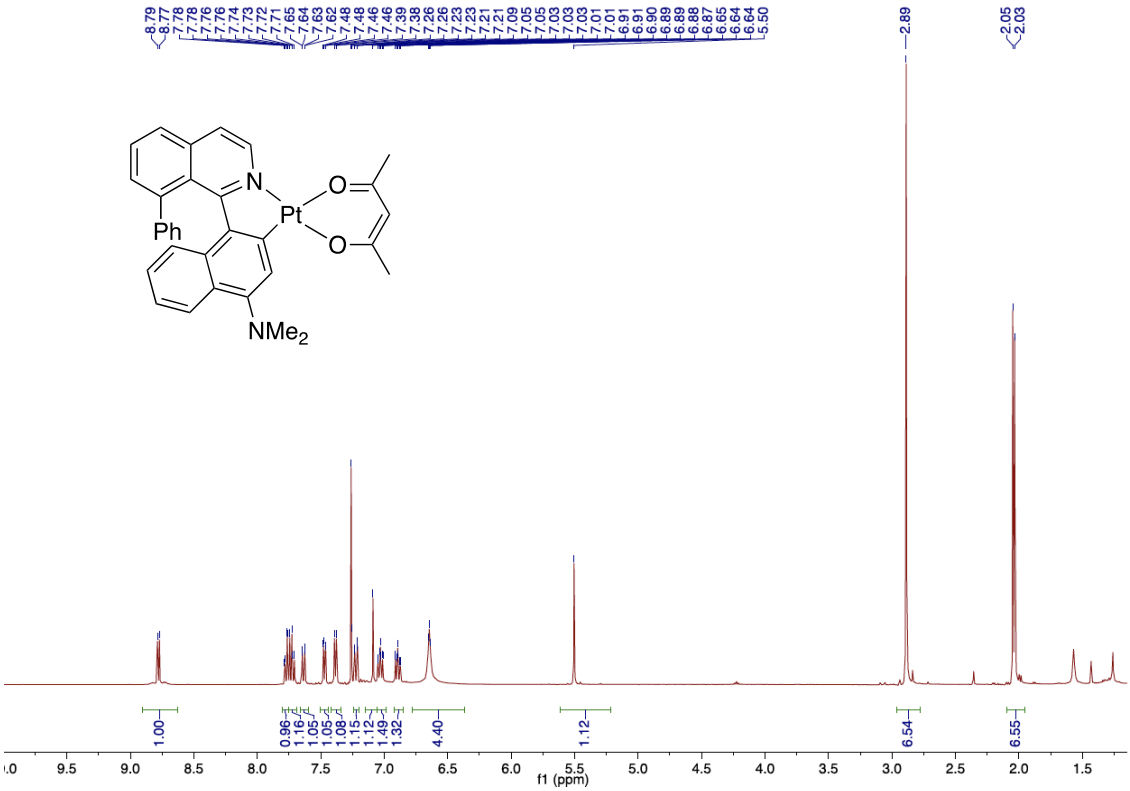
^{1}H-NMR (400MHz, $CDCl_3$, 298K):



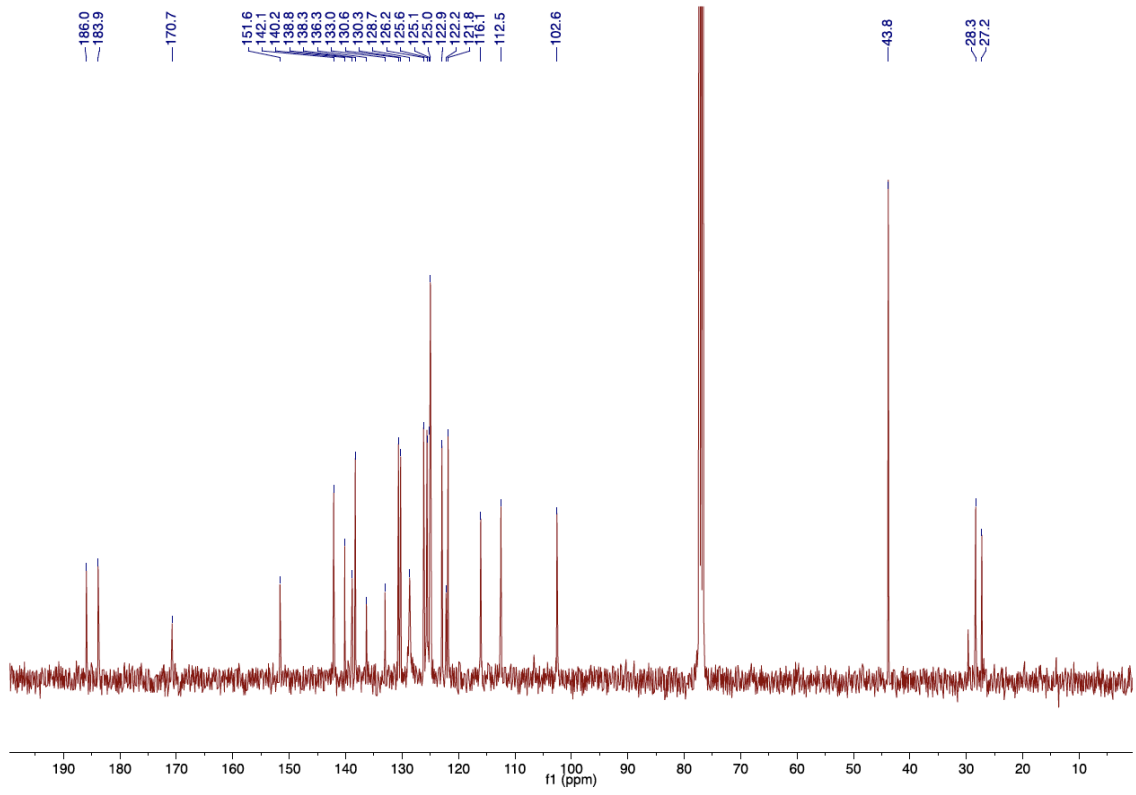
^{13}C-NMR (100MHz, $CDCl_3$, 298K):



^{1}H-NMR (400MHz, $CDCl_3$, 298K):



^{13}C-NMR (100MHz, $CDCl_3$, 298K):



4. UV-vis spectra of ligands and lifetime characterizations.

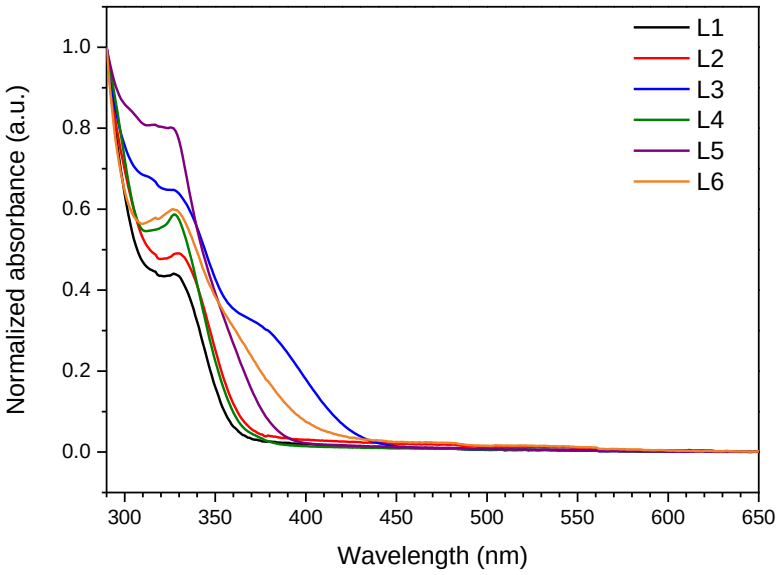


Figure S1: Normalized UV-vis absorption spectra of ligands **L1-L6** in toluene at room temperature.

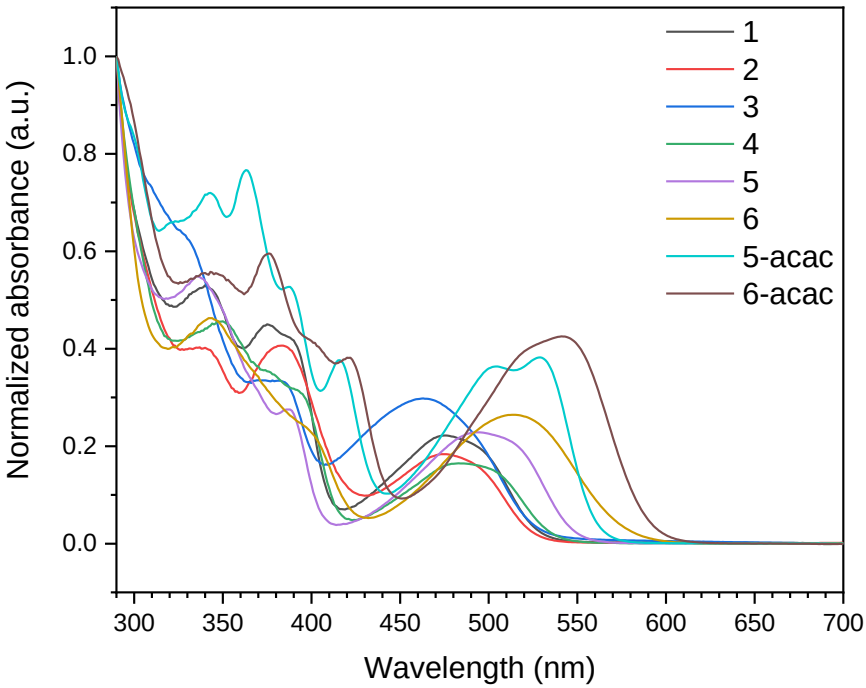


Figure S2: Normalized UV-vis absorption spectra of complexes **1**-**6**, **5-acac** and **6-acac** in toluene at room temperature.

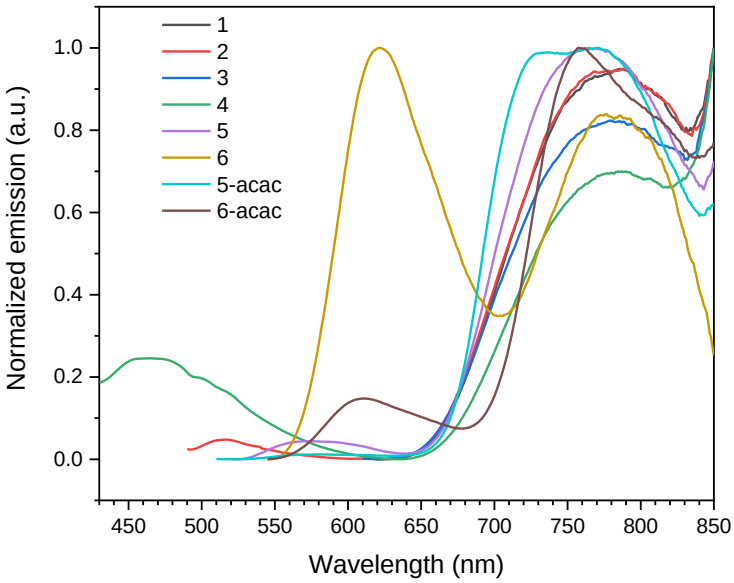


Figure S3: Normalized emission spectra recorded in aerated toluene at room temperatura of complexes **1**-**6**, **5-acac** and **6-acac**, λ_{ex} = 300 nm.

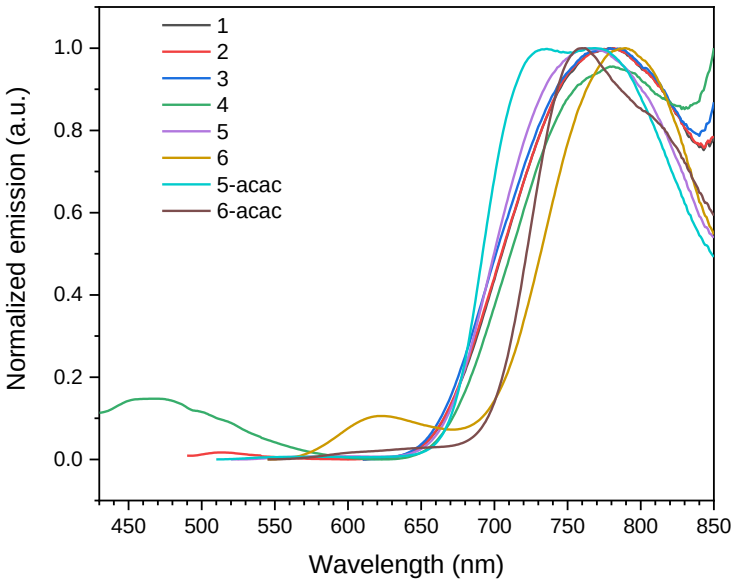


Figure S4: Normalized emission spectra recorded in degassed toluene at room temperatura of complexes **1**-**6**, **5-acac** and **6-acac**, λ_{ex} = 300 nm.

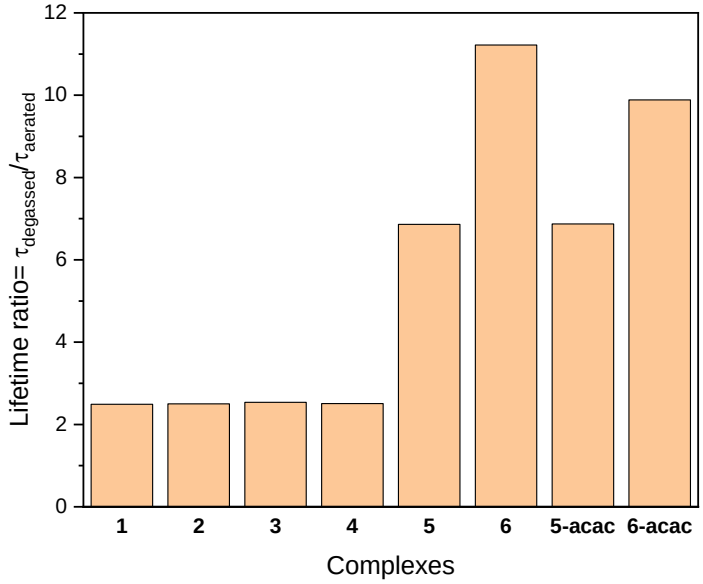


Figure S5: Phosphorescence lifetimes ratio in aerated and degassed toluene solution for complexes **1-6**, **5-acac** and **6-acac** at room temperature.

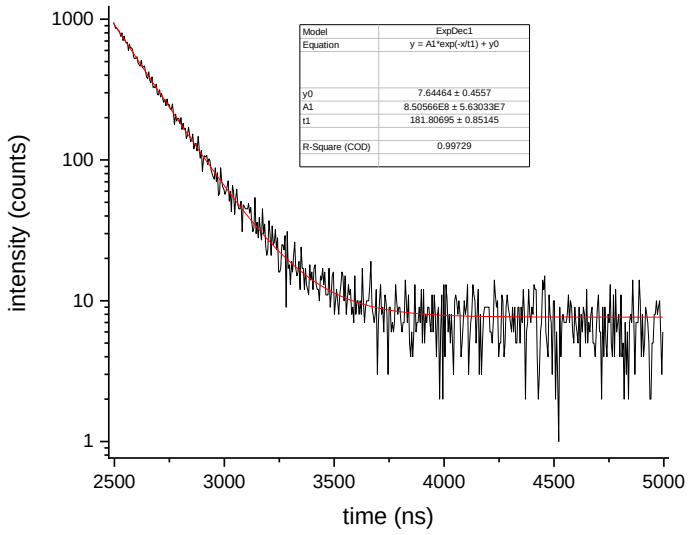


Figure S6: Phosphorescence decay of complex **1** in aerated toluene at room temperature. λ_{ex}= 400 nm, λ_{em}= 750 nm.

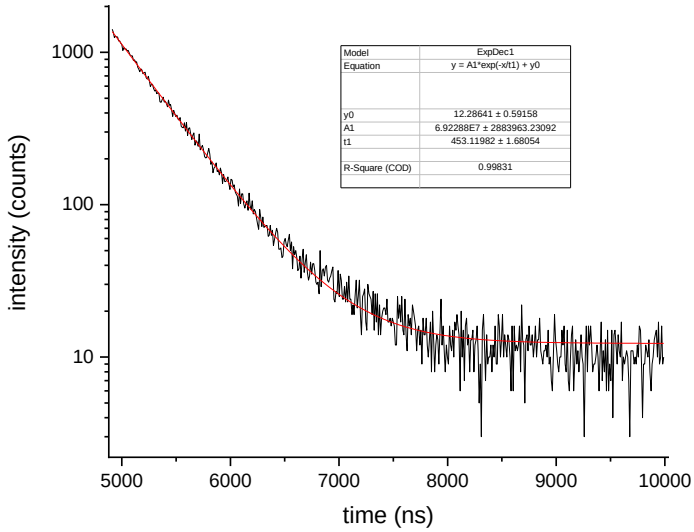


Figure S7: Phosphorescence decay of complex **1** in degassed toluene at room temperature. λ_{ex}= 400 nm, λ_{em}= 750 nm.

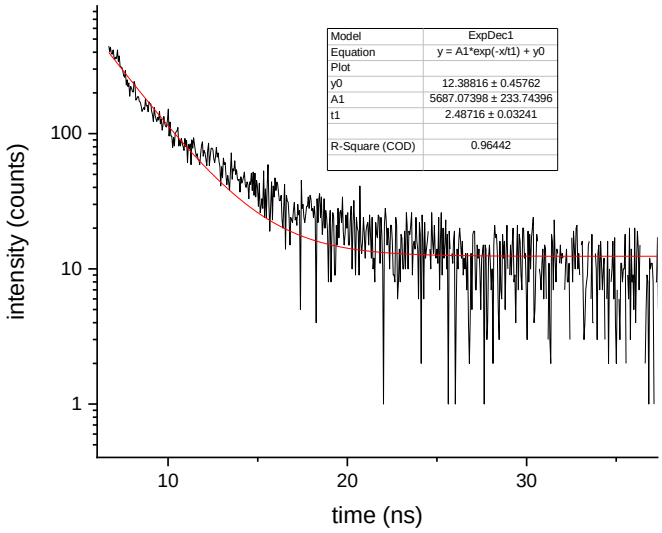


Figure S8: Fluorescence decay of complex **2** in aerated toluene at room temperature. λ_{ex}= 400 nm, λ_{em}= 520 nm.

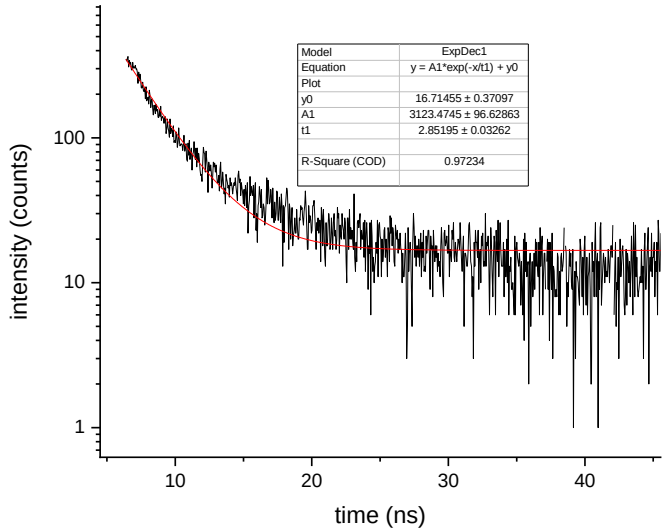


Figure S9: Fluorescence decay of complex **2** in degassed toluene at room temperature. λ_{ex}= 400 nm, λ_{em}= 520 nm.

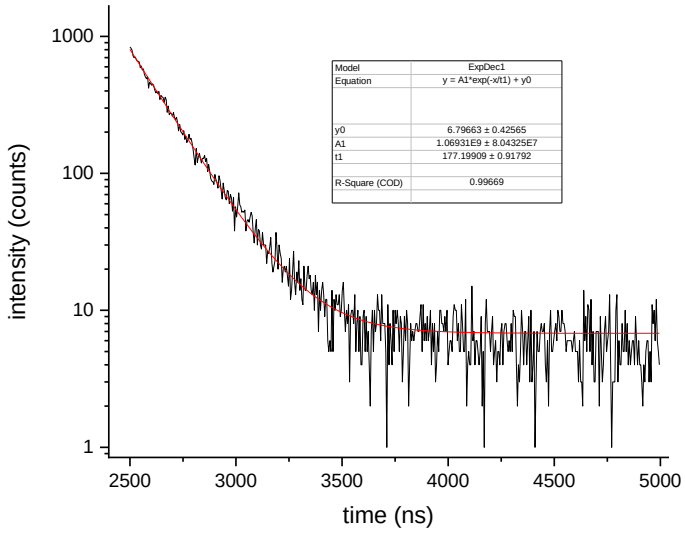


Figure S10: Phosphorescence decay of complex **2** in aerated toluene at room temperature. λ_{ex}= 400 nm, λ_{em}= 750 nm.

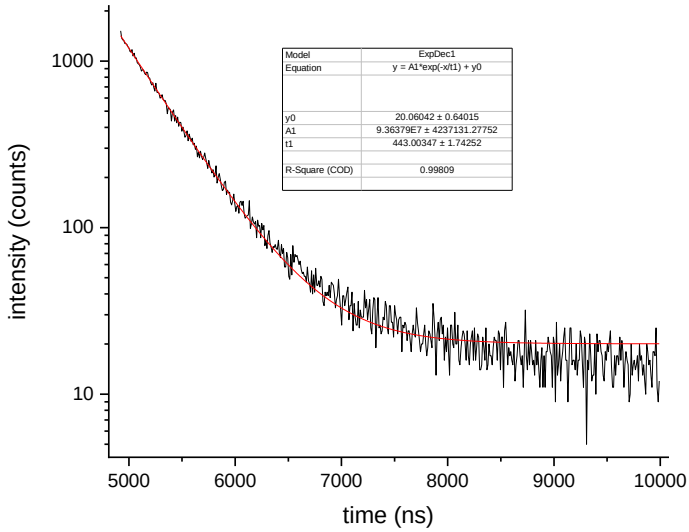


Figure S11: Phosphorescence decay of complex **2** in degassed toluene at room temperature. λ_{ex}= 400 nm, λ_{em}= 750 nm.

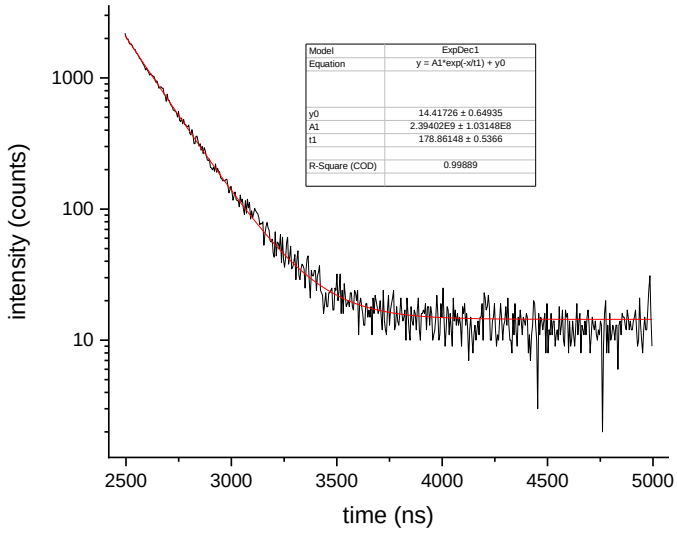


Figure S12: Phosphorescence decay of complex **3** in aerated toluene at room temperature. λ_{ex}= 400 nm, λ_{em}= 750 nm.

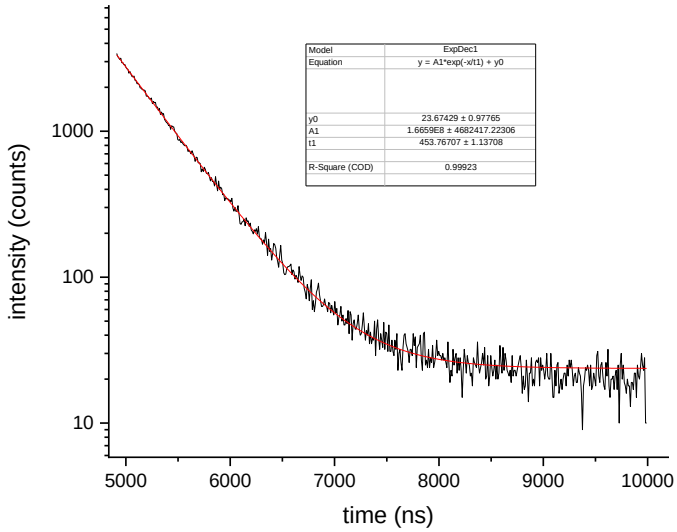


Figure S13: Phosphorescence decay of complex **3** in degassed toluene at room temperature. λ_{ex}= 400 nm, λ_{em}= 750 nm.

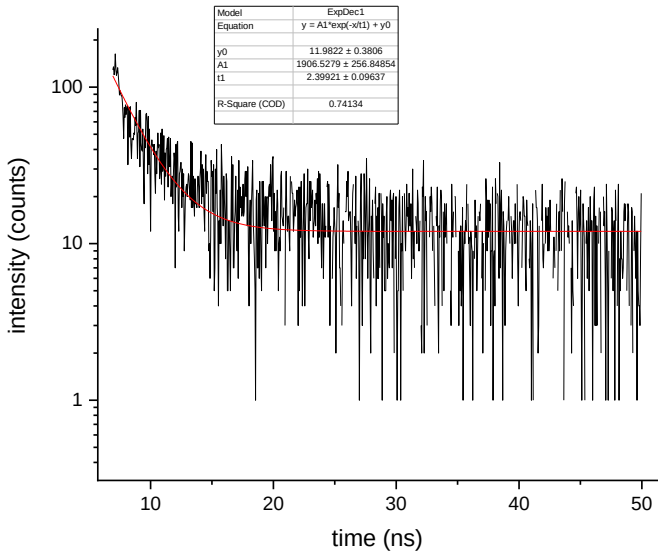


Figure S14: Fluorescence decay of complex **4** in aerated toluene at room temperature. λ_{ex}= 400 nm, λ_{em}= 460 nm.

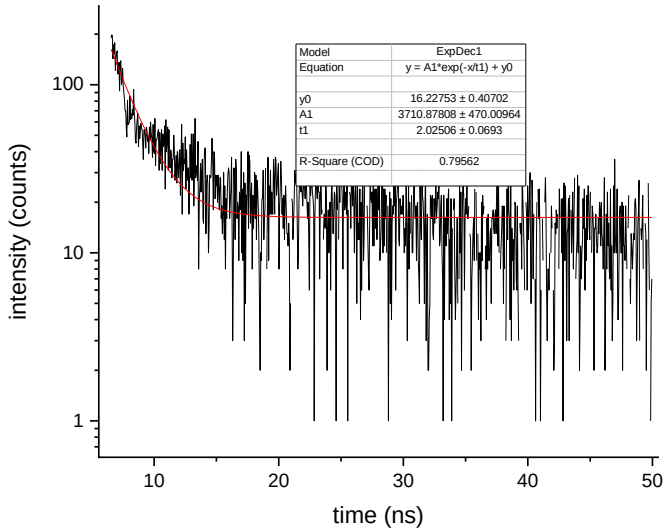


Figure S15: Fluorescence decay of complex **4** in degassed toluene at room temperature. λ_{ex}= 400 nm, λ_{em}= 460 nm.

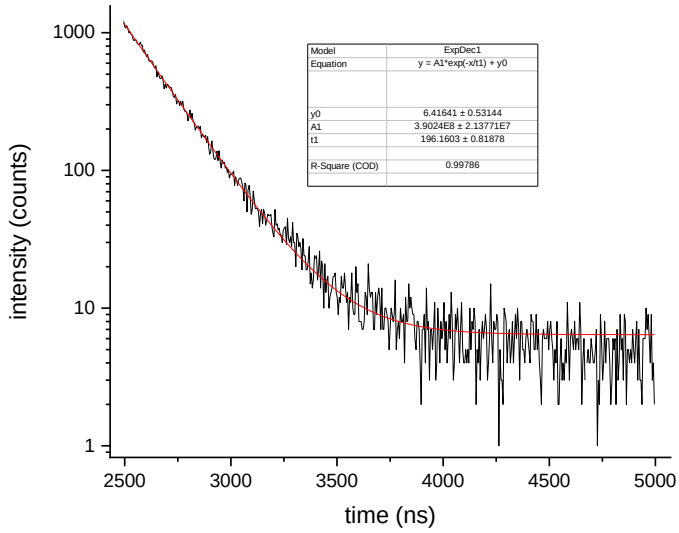


Figure S16: Phosphorescence decay of complex **4** in aerated toluene at room temperature. λ_{ex}= 400 nm, λ_{em}= 750 nm.

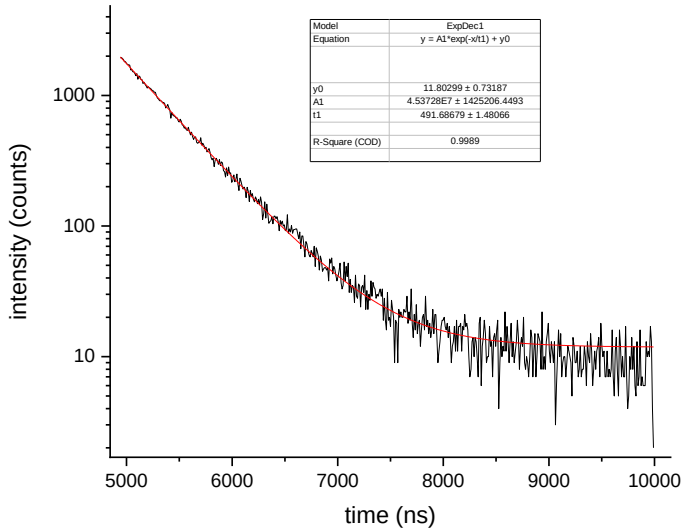


Figure S17: Phosphorescence decay of complex **4** in degassed toluene at room temperature. λ_{ex}= 400 nm, λ_{em}= 750 nm.

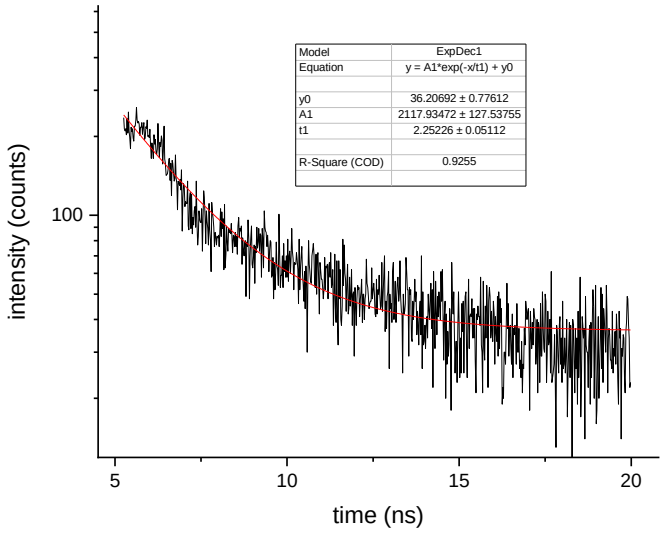


Figure S18: Fluorescence decay of complex **5** in aerated toluene at room temperature. λ_{ex}= 400 nm, λ_{em}= 575 nm.

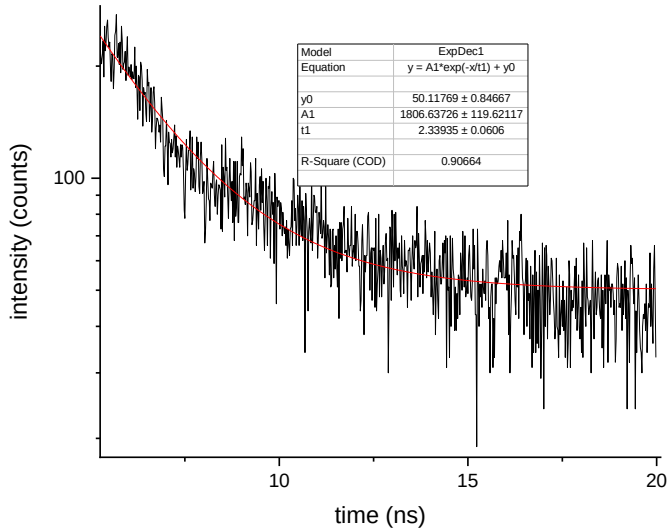


Figure S19: Fluorescence decay of complex **5** in degassed toluene at room temperature. λ_{ex}= 400 nm, λ_{em}= 575 nm.

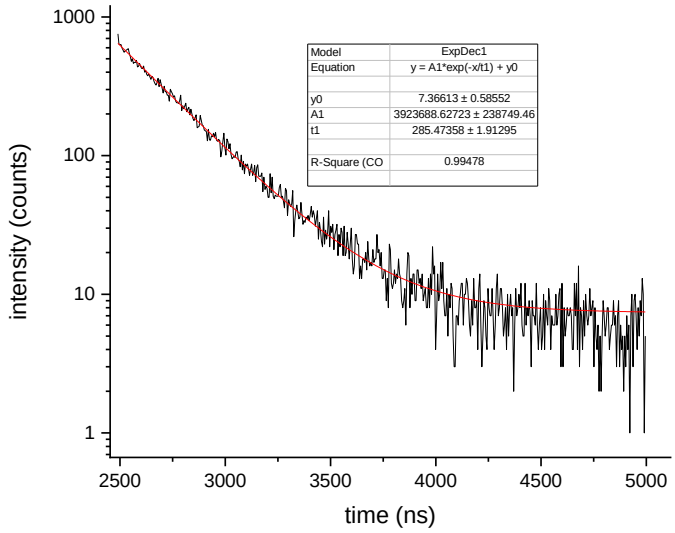


Figure S20: Phosphorescence decay of complex **5** in aerated toluene at room temperature. λ_{ex}= 400 nm, λ_{em}= 750 nm.

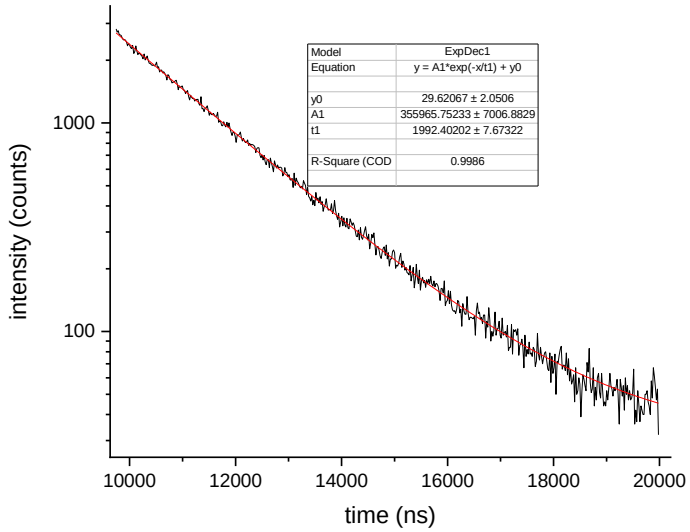


Figure S21: Phosphorescence decay of complex **5** in degassed toluene at room temperature. λ_{ex}= 400 nm, λ_{em}= 750 nm.

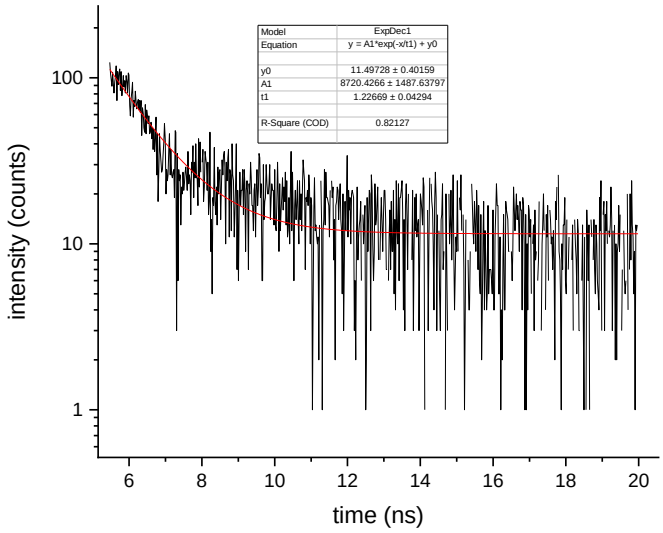


Figure S22: Fluorescence decay of complex **6** in aerated toluene at room temperature. λ_{ex}= 400 nm, λ_{em}= 620 nm.

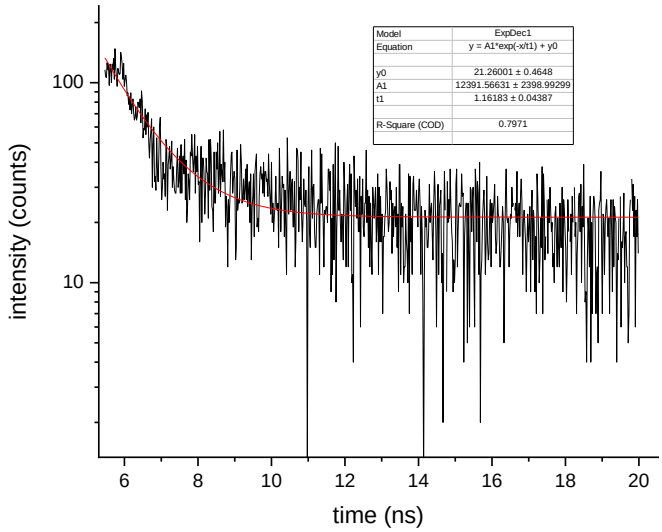


Figure S23: Fluorescence decay of complex **6** in degassed toluene at room temperature. λ_{ex}= 400 nm, λ_{em}= 620 nm.

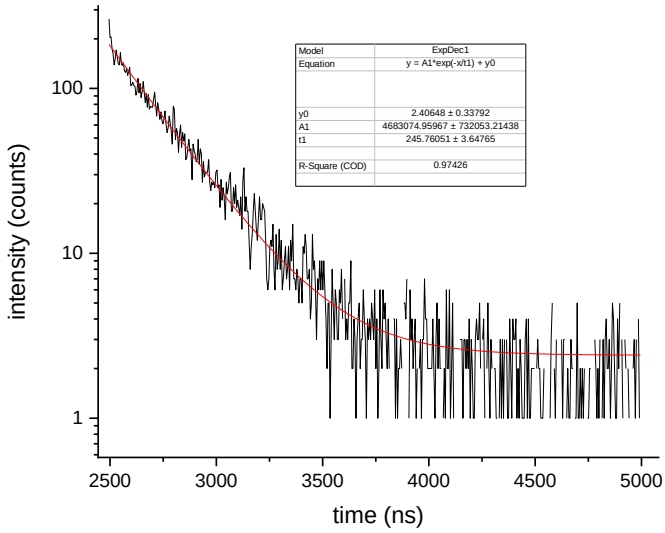


Figure S24: Phosphorescence decay of complex **6** in aerated toluene at room temperature. λ_{ex}= 400 nm, λ_{em}= 750 nm.

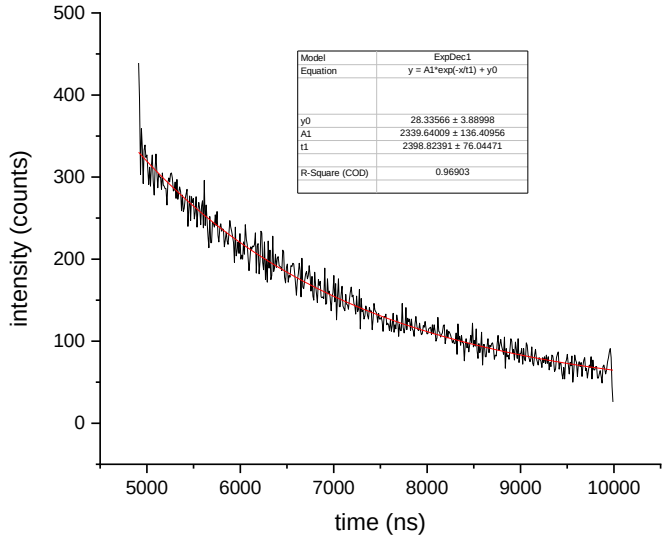


Figure S25: Phosphorescence decay of complex **6** in degassed toluene at room temperature. λ_{ex}= 400 nm, λ_{em}= 750 nm.

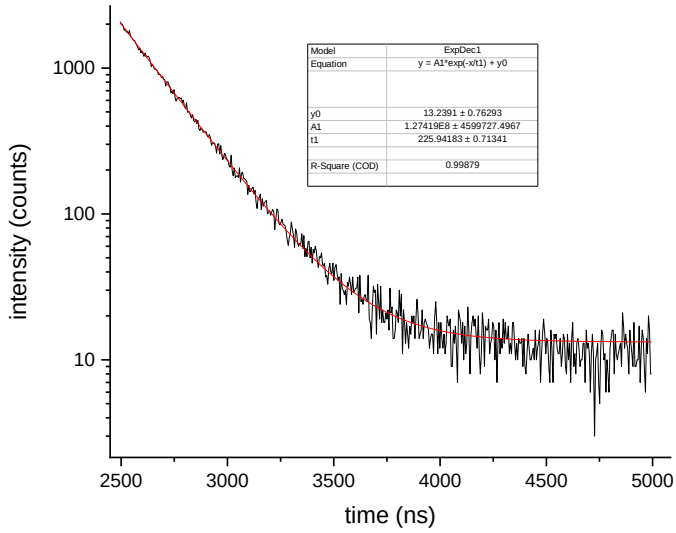


Figure S26: Phosphorescence decay of complex **5-acac** in aerated toluene at room temperature. λ_{ex}= 400 nm, λ_{em}= 750 nm.

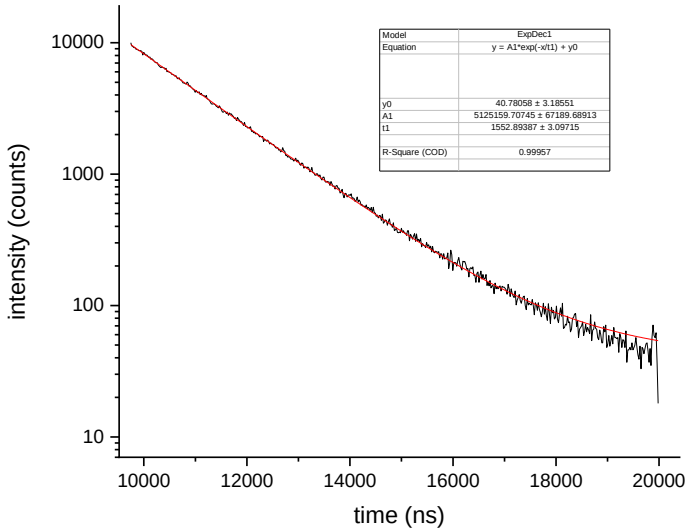


Figure S27: Phosphorescence decay of complex **5-acac** in degassed toluene at room temperature. λ_{ex}= 400 nm, λ_{em}= 750 nm.

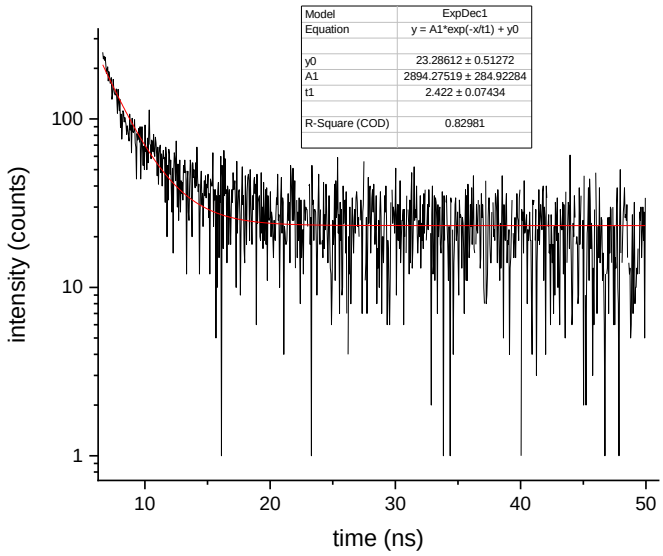


Figure S28: Fluorescence decay of complex **6-acac** in aerated toluene at room temperature. λ_{ex}= 400 nm, λ_{em}= 610 nm.

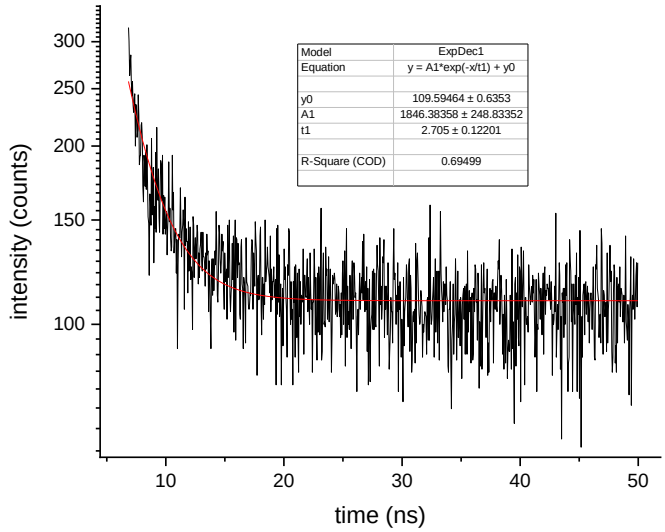


Figure S29: Fluorescence decay of complex **6-acac** in degassed toluene at room temperature. λ_{ex}= 400 nm, λ_{em}= 610 nm.

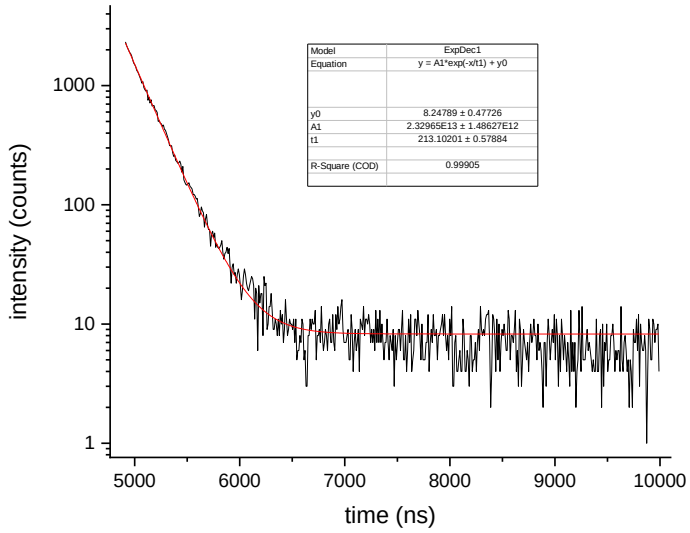


Figure S30: Phosphorescence decay of complex **6-acac** in aerated toluene at room temperature. λ_{ex}= 400 nm, λ_{em}= 750 nm.

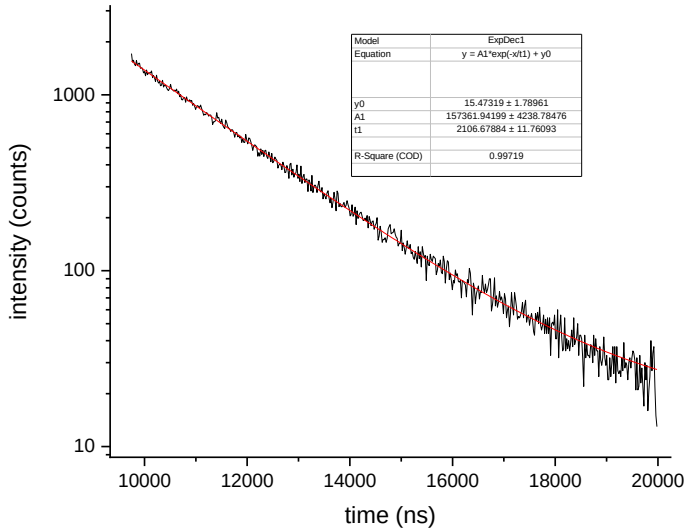


Figure S31: Phosphorescence decay of complex **6-acac** in degassed toluene at room temperature. λ_{ex}= 400 nm, λ_{em}= 750 nm.

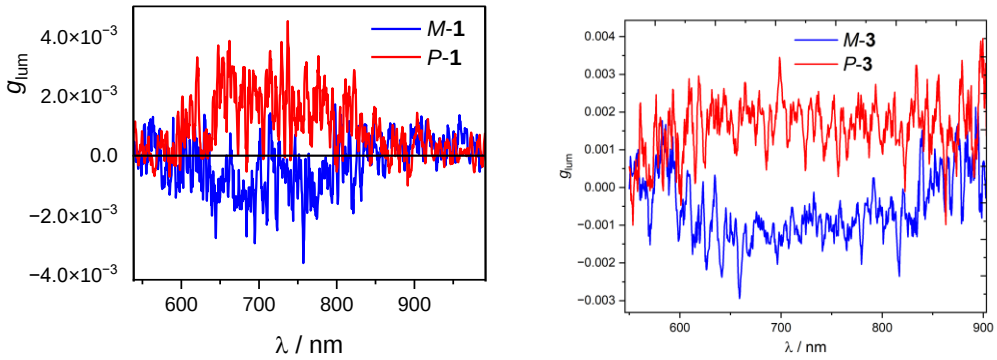


Figure S32: Luminescence dissymmetry factor g_{lum} spectra of complex **1** (left) and **3** (right) in degassed toluene at room temperature.

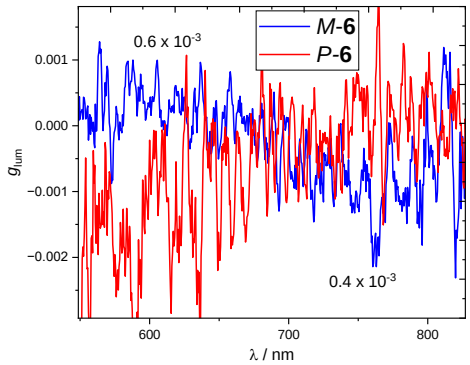
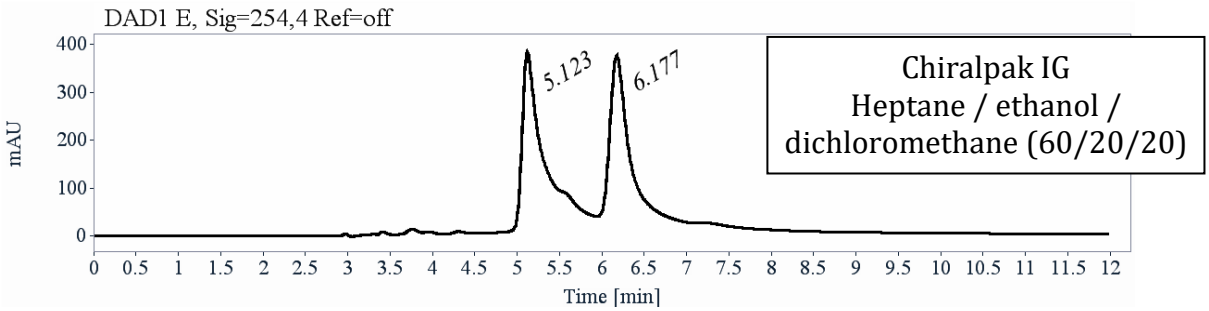


Figure S33: Luminescence dissymmetry factor g_{lum} spectra of complex **6** in degassed toluene at room temperature.

6. Chiral HPLC separation.

Analytical chiral HPLC separation for compound **1**

• The sample is dissolved in dichloromethane, injected on the chiral column, and detected with an UV detector at 254 nm. The flow-rate is 1 mL/min.



RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
5.12	7267	51.40	0.74		
6.18	6870	48.60	1.09	1.48	2.97
Sum	14137	100.00			

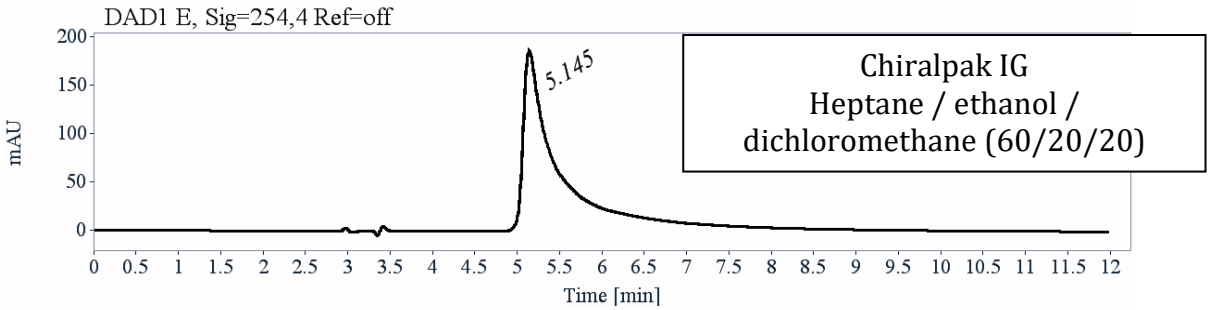
Preparative separation for compound **1**:

• Sample preparation: About 50 mg of compound **1** are dissolved in 3.5 mL of dichloromethane.

• Chromatographic conditions: Chiralpak IG (250 x 10 mm), hexane / ethanol / dichloromethane (60/20/20) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm.

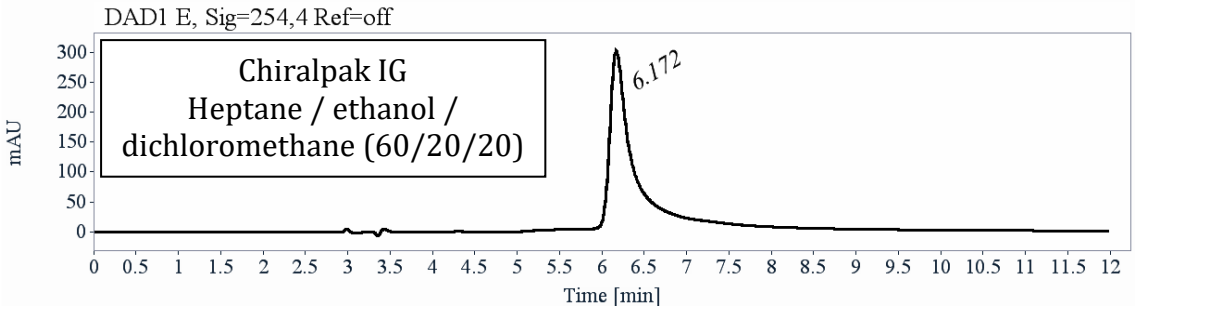
• Injections (stacked): 50 times 70 μL, every 7.4 minutes.

• First fraction: 23 mg of the first eluted enantiomer with ee > 99.5%



RT [min]	Area	Area%
5.15	5282	100.00
Sum	5282	100.00

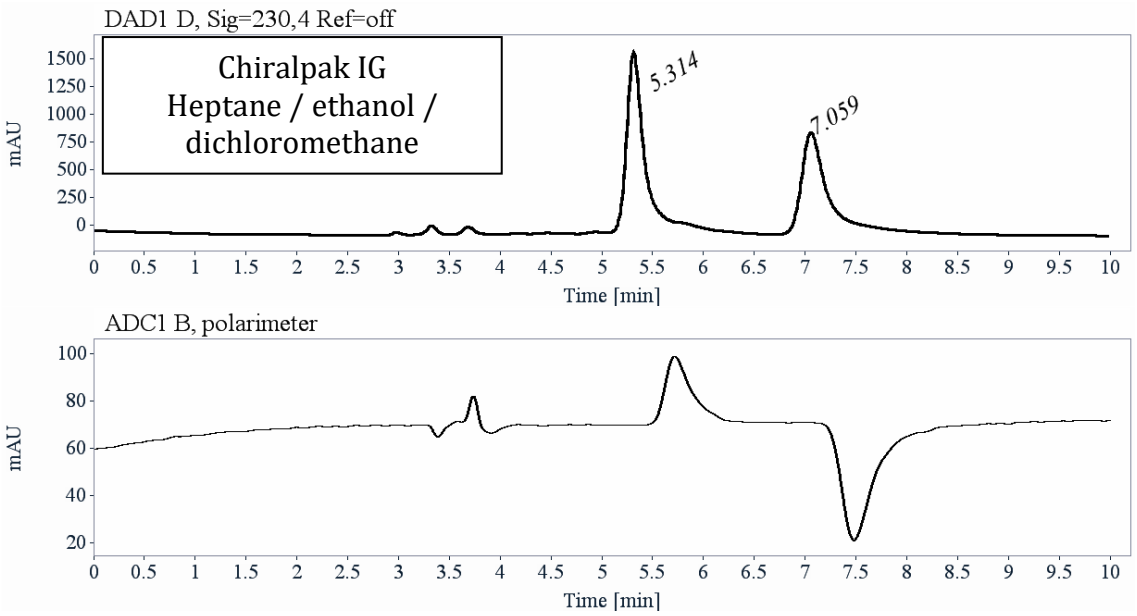
• Second fraction: 21 mg of the second eluted enantiomer with ee >99.5 %



RT [min]	Area	Area%
6.17	5997	100.00
Sum	5997	100.00

Analytical chiral HPLC separation for compound **2**

• The sample is dissolved in dichloromethane, injected on the chiral column, and detected with an UV detector at 230 nm and a polarimetric detector. The flow-rate is 1 mL/min.



RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
5.31	22297	58.14	0.80		
7.06	16053	41.86	1.39	1.74	5.19
Sum	38351	100.00			

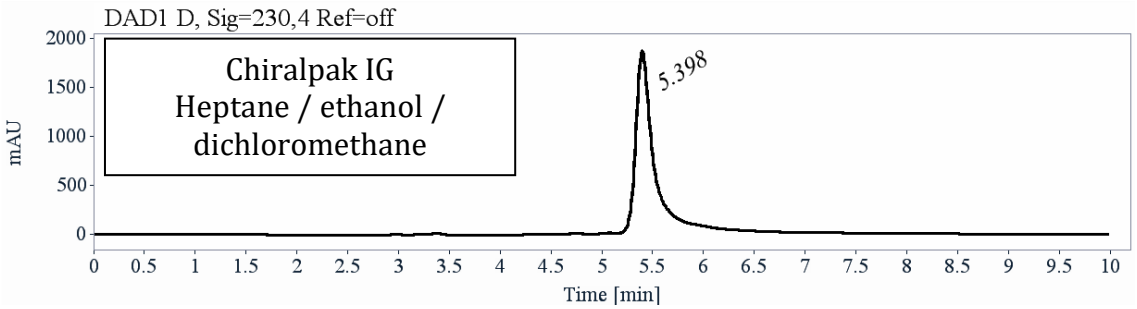
Preparative separation for compound **2**:

• Sample preparation: About 60 mg of compound **2** are dissolved in 5 mL of dichloromethane.

• Chromatographic conditions: Chiralpak IG (250 x 10 mm), hexane / ethanol / dichloromethane (60/20/20) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm.

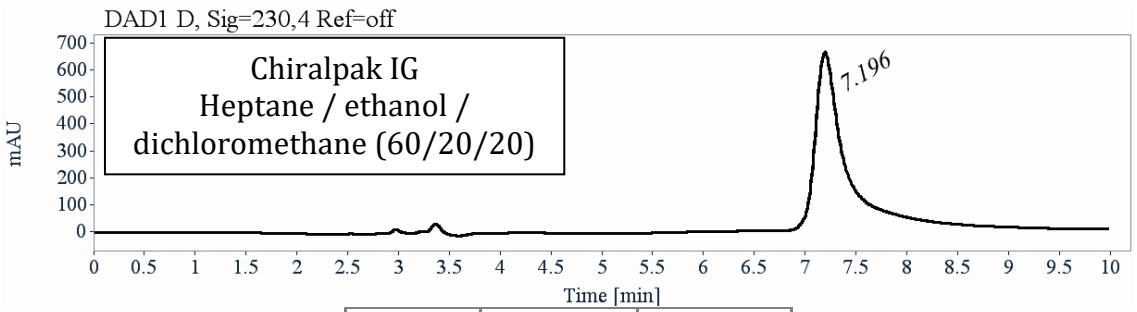
• Injections (stacked): 50 times 100 µL, every 9.3 minutes.

• First fraction: 31 mg of the first eluted enantiomer with ee > 99.5 %



RT [min]	Area	Area%
5.40	25993	100.00
Sum	25993	100.00

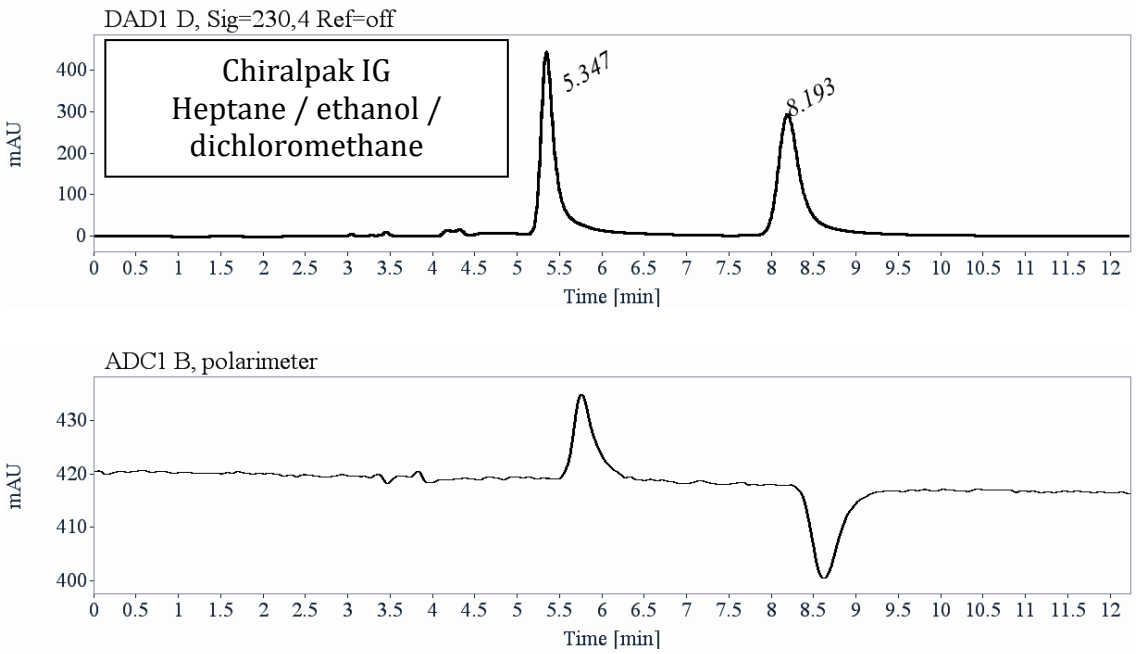
• Second fraction: 27 mg of the second eluted enantiomer with ee > 99.5%



RT [min]	Area	Area%
7.20	11625	100.00
Sum	11625	100.00

Analytical chiral HPLC separation for compound **3**

• The sample is dissolved in dichloromethane, injected on the chiral column, and detected with an UV detector at 230 nm and a polarimeter. The flow-rate is 1 mL/min.



RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
5.35	5658	49.34	0.81		
8.19	5808	50.66	1.78	2.19	7.83
Sum	11466	100.00			

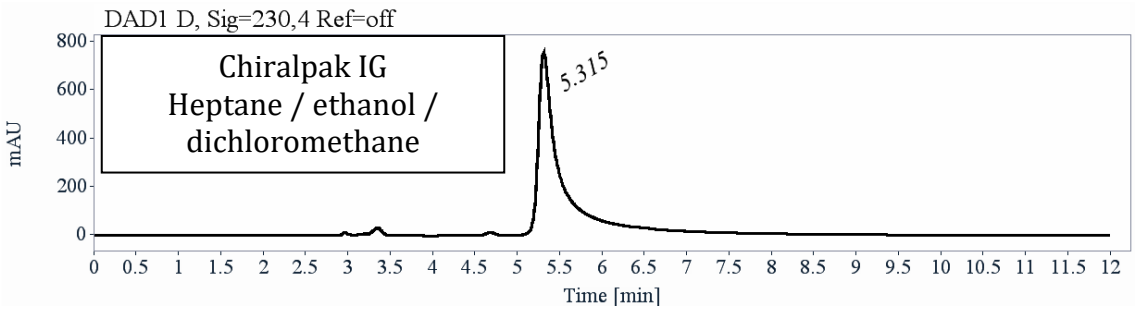
Preparative separation for compound **3**:

• Sample preparation: About 75 mg of compound **3** are dissolved in 3 mL of dichloromethane.

• Chromatographic conditions: Chiralpak IG (250 x 10 mm), hexane / ethanol / dichloromethane (60/20/20) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm.

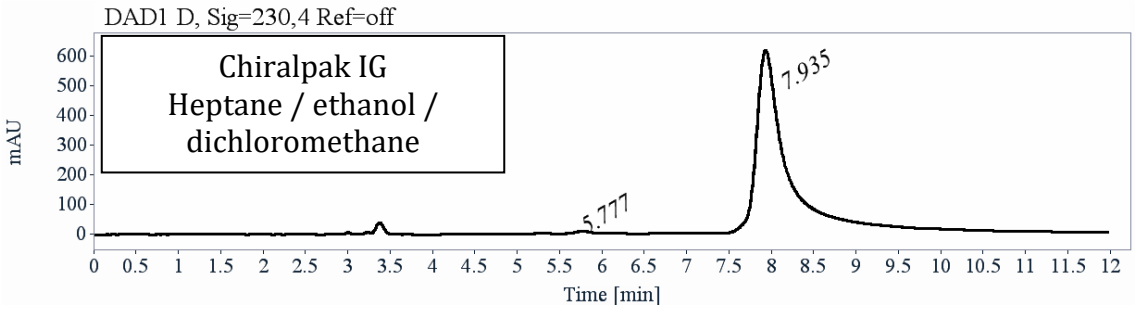
• Injections (stacked): 20 times 150 µL, every 12 minutes.

• First fraction: 36 mg of the first eluted enantiomer with ee > 99.5%



RT [min]	Area	Area%
5.32	15232	100.00
Sum	15232	100.00

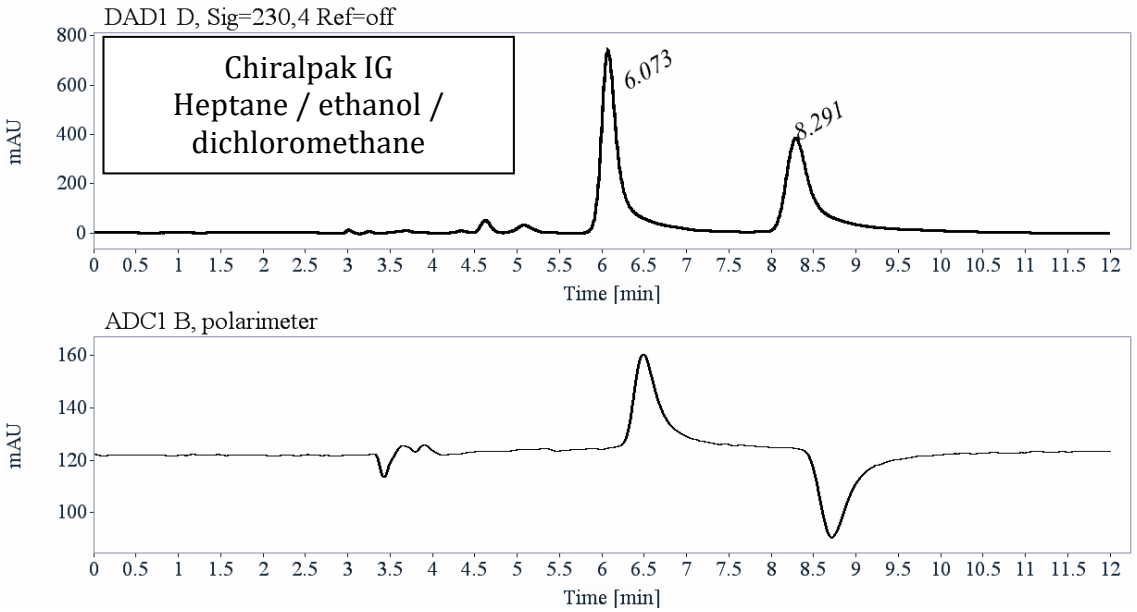
• Second fraction: 35 mg of the second eluted enantiomer with ee > 98.5 %



RT [min]	Area	Area%
5.78	86	0.57
7.93	15010	99.43
Sum	15096	100.00

Analytical chiral HPLC separation for compound **4**

• The sample is dissolved in dichloromethane, injected on the chiral column, and detected with an UV detector at 230 nm and a polarimetric detector. The flow-rate is 1 mL/min.



RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
6.07	11693	55.79	1.06		
8.29	9266	44.21	1.81	1.71	5.46
Sum	20959	100.00			

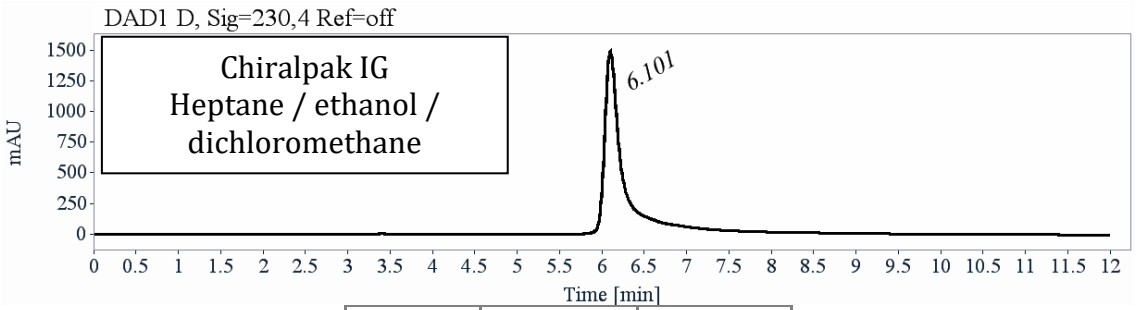
Preparative separation for compound **4**:

• Sample preparation: About 70 mg of compound **4** are dissolved in 5 mL of dichloromethane.

• Chromatographic conditions: Chiralpak IG (250 x 10 mm), hexane / ethanol / dichloromethane (60/20/20) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm.

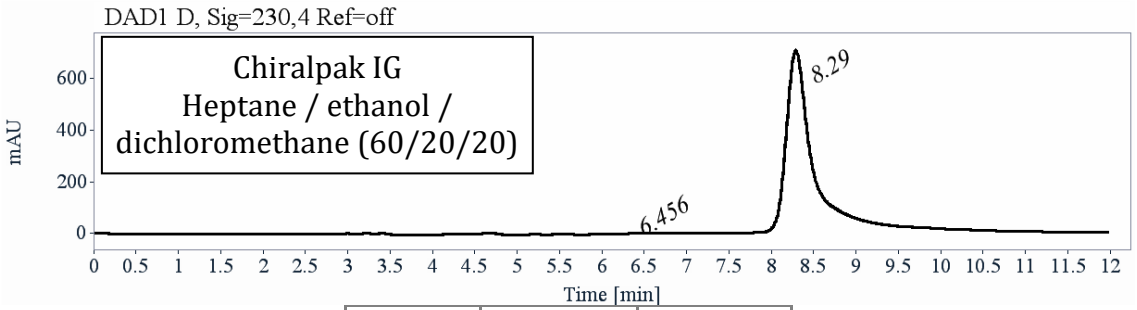
• Injections (stacked): 42 times 120 µL, every 11.3 minutes.

• First fraction: 30 mg of the first eluted enantiomer with ee > 99.5%



RT [min]	Area	Area%
6.10	24529	100.00
Sum	24529	100.00

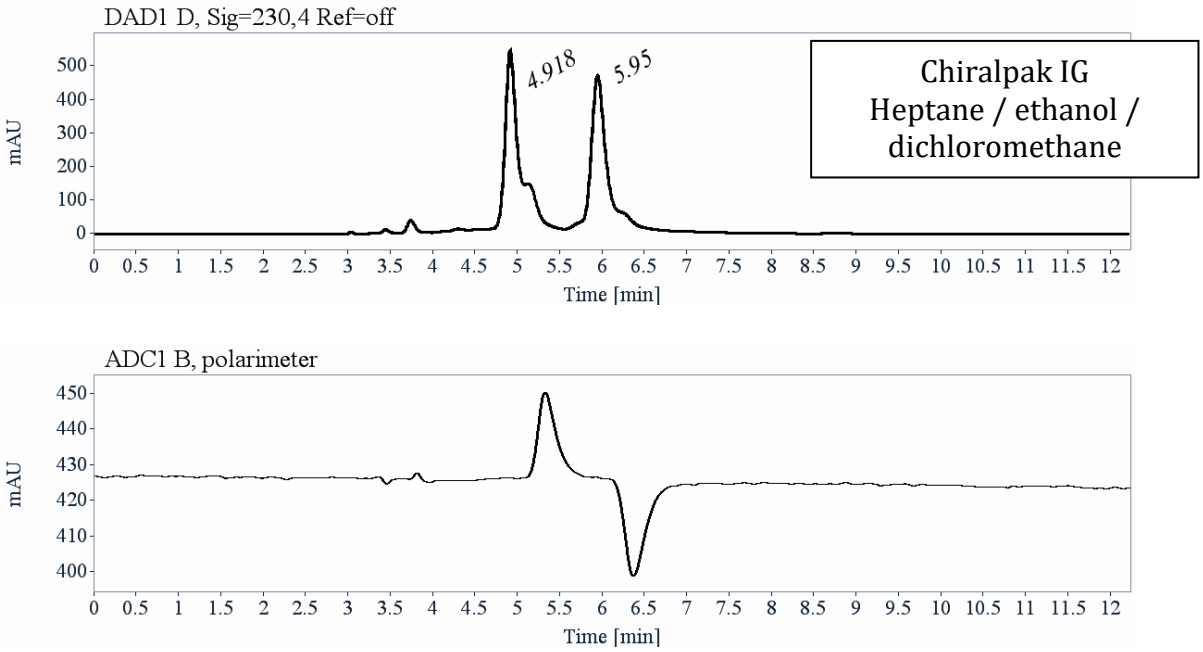
• Second fraction: 29 mg of the second eluted enantiomer with ee > 98.5 %



RT [min]	Area	Area%
6.46	86	0.54
8.29	15848	99.46
Sum	15934	100.00

Analytical chiral HPLC separation for compound **5**

• The sample is dissolved in dichloromethane, injected on the chiral column, and detected with an UV detector at 230 nm and a polarimeter. The flow-rate is 1 mL/min.



RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
4.92	5179	44.57	0.67		
5.95	6440	55.43	1.02	1.52	3.83
Sum	11619	100.00			

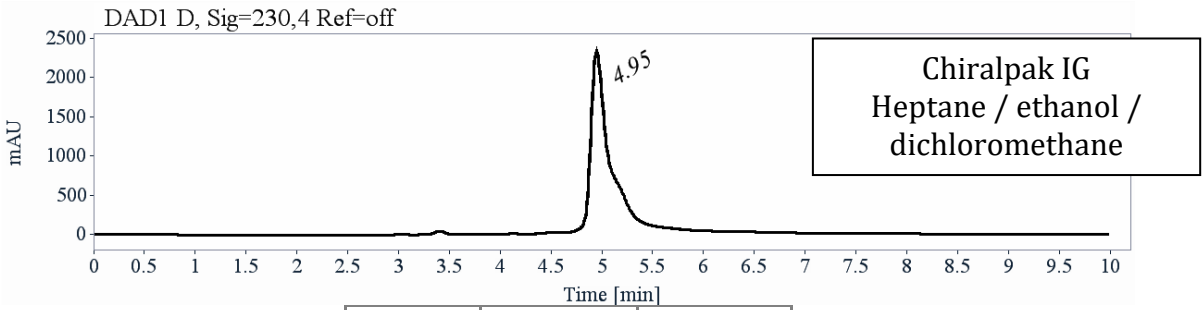
Preparative separation for compound **5**:

• Sample preparation: About 32 mg of compound **5** are dissolved in 4.5 mL of dichloromethane.

• Chromatographic conditions: Chiralpak IG (250 x 10 mm), hexane / ethanol / dichloromethane (60/20/20) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm.

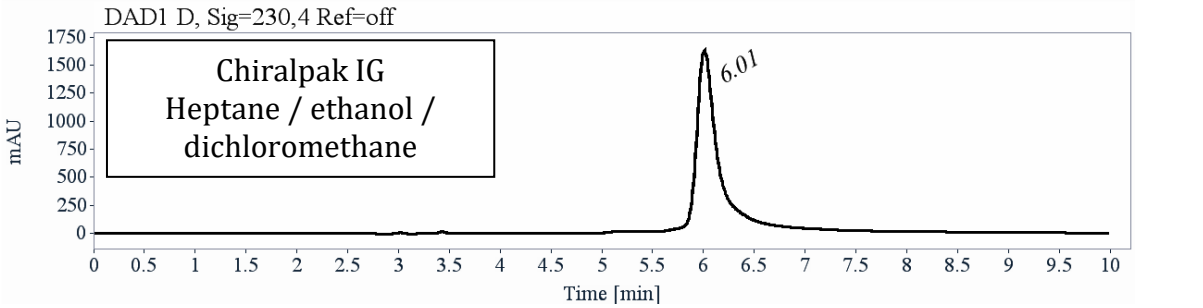
• Injections (stacked): 75 times 60 µL, every 7.8 minutes.

• First fraction: 10 mg of the first eluted enantiomer with ee > 99.5%



RT [min]	Area	Area%
4.95	32307	100.00
Sum	32307	100.00

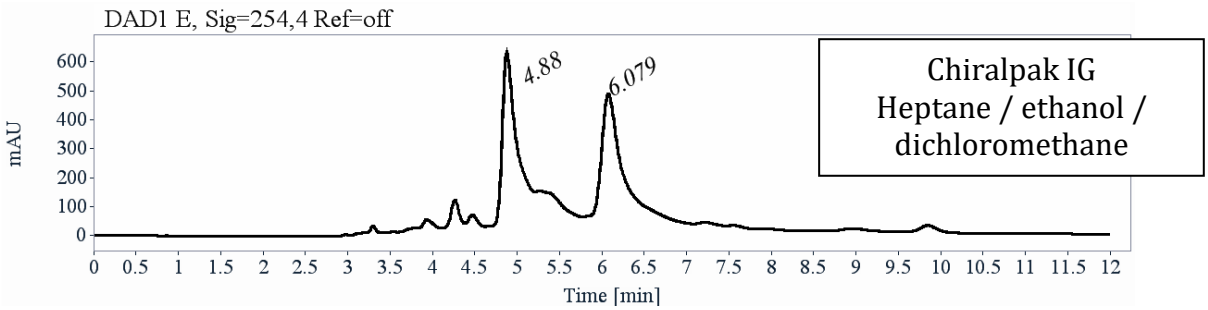
• Second fraction: 8 mg of the second eluted enantiomer with ee > 99.5 %



RT [min]	Area	Area%
6.01	27934	100.00
Sum	27934	100.00

Analytical chiral HPLC separation for compound **6**

• The sample is dissolved in dichloromethane, injected on the chiral column, and detected with an UV detector at 230 nm and a polarimetric detector. The flow-rate is 1 mL/min.



RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
4.88	7573	47.56	0.65		
6.08	8348	52.44	1.06	1.62	3.72
Sum	15921	100.00			

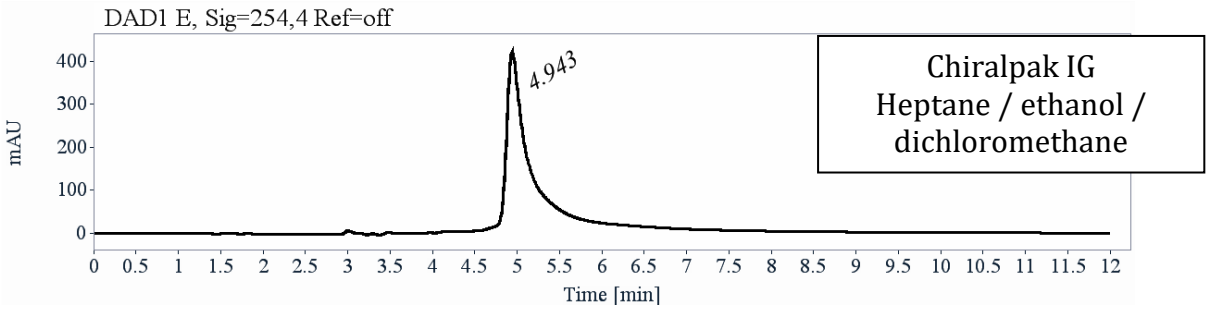
Preparative separation for compound **6**:

• Sample preparation: About 9 mg of compound **6** are dissolved in 2.8 mL of dichloromethane.

• Chromatographic conditions: Chiralpak IG (250 x 10 mm), hexane / ethanol / dichloromethane (60/20/20) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm.

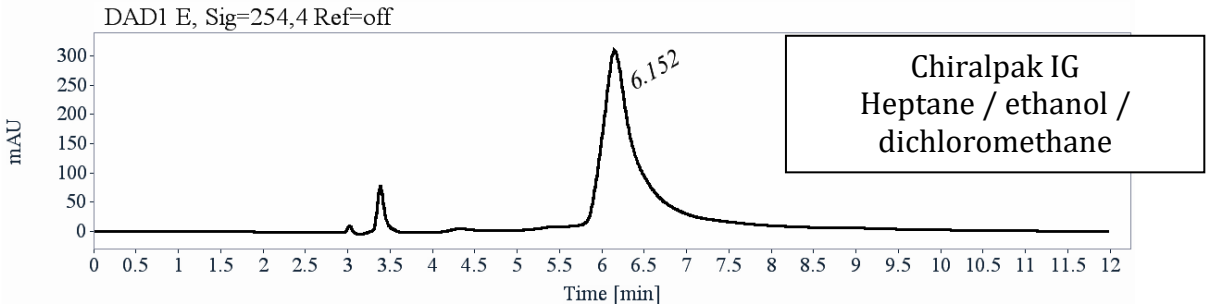
• Injections (stacked): 40 times 70 µL, every 7.6 minutes.

• First fraction: 3 mg of the first eluted enantiomer with ee > 99.5 %



RT [min]	Area	Area%
4.94	8269	100.00
Sum	8269	100.00

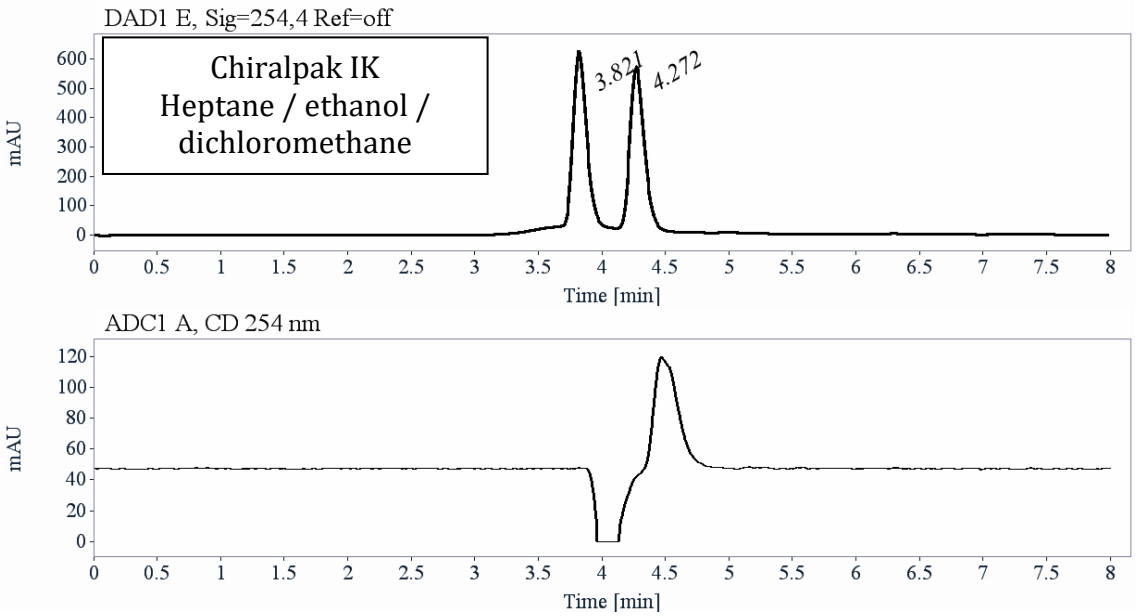
• Second fraction: 2 mg of the second eluted enantiomer with ee > 99.5 %



RT [min]	Area	Area%
6.15	7077	100.00
Sum	7077	100.00

Analytical chiral HPLC separation for compound **5-acac**

• The sample is dissolved in dichloromethane, injected on the chiral column, and detected with an UV detector at 254 nm and a circular dichroism detector at 254 nm. The flow-rate is 1 mL/min.



RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
3.82	4359	50.13	0.30		
4.27	4337	49.87	0.45	1.52	2.25
Sum	8696	100.00			

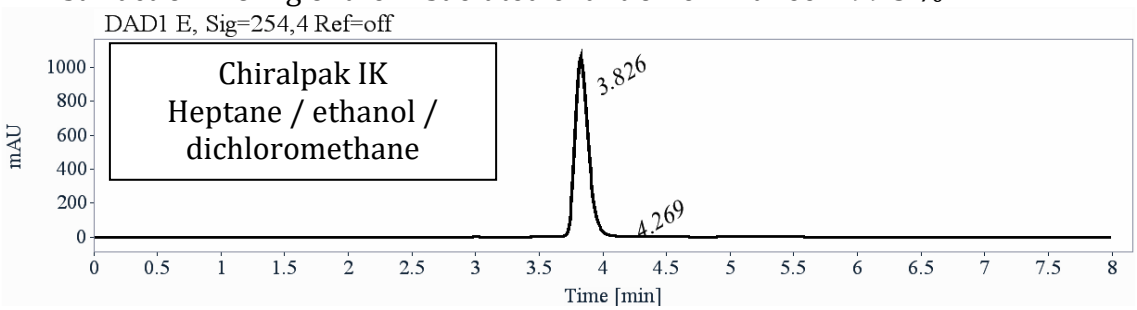
Preparative separation for compound **5-acac**:

• Sample preparation: About 55 mg of compound **5-acac** are dissolved in 7 mL of a mixture of dichloromethane and hexane (50/50).

• Chromatographic conditions: Chiralpak IK (250 x 10 mm), hexane / ethanol / dichloromethane (60/20/20) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm.

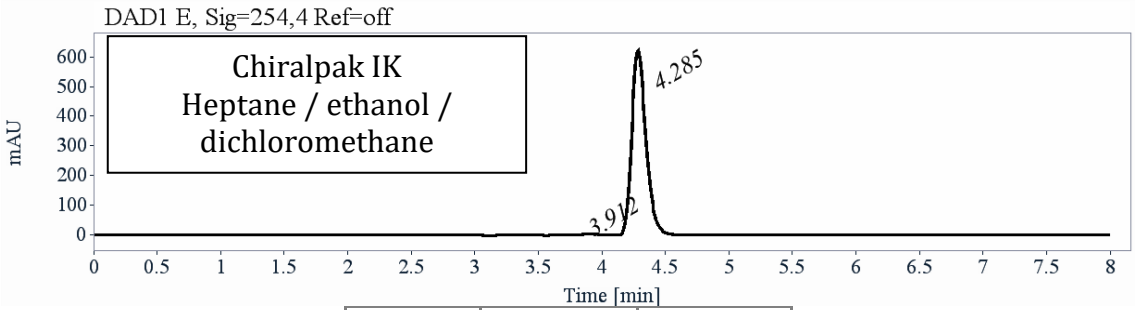
• Injections (stacked): 200 times 35 µL, every 1.8 minutes.

• First fraction: 26 mg of the first eluted enantiomer with ee > 99.5 %



RT [min]	Area	Area%
3.83	7691	99.91
4.27	7	0.09
Sum	7698	100.00

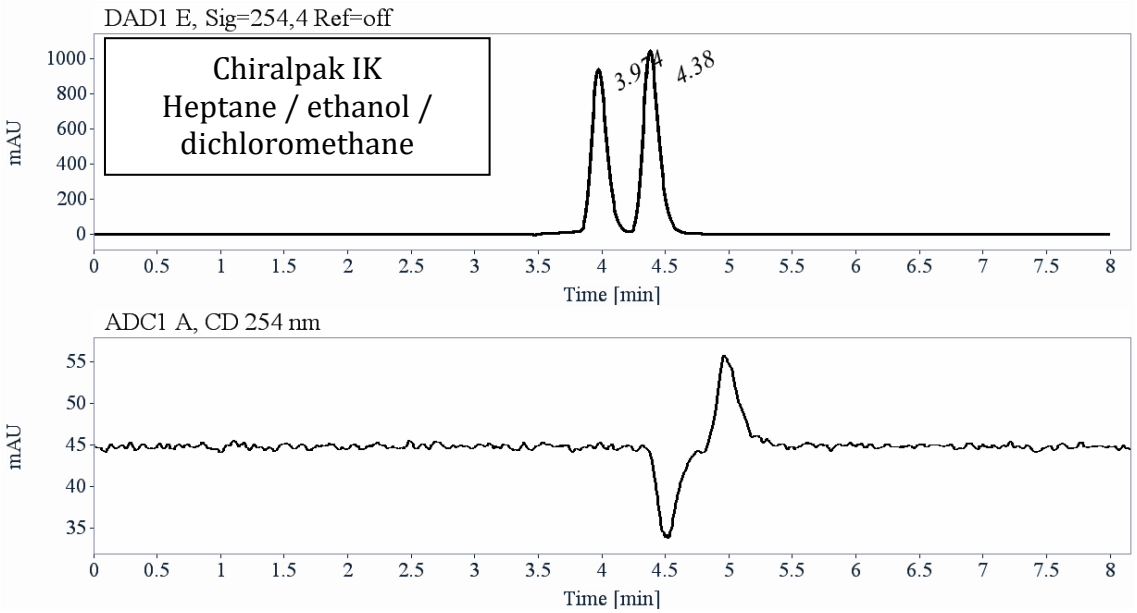
• Second fraction: 26 mg of the second eluted enantiomer with ee > 98.5 %



RT [min]	Area	Area%
3.91	31	0.63
4.28	4841	99.37
Sum	4872	100.00

Analytical chiral HPLC separation for compound **6-acac**

• The sample is dissolved in dichloromethane, injected on the chiral column, and detected with a UV detector at 254 nm and a circular dichroism detector at 254 nm. The flow-rate is 1 mL/min.



RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
3.97	7900	46.43	0.35		
4.38	9116	53.57	0.48	1.40	1.79
Sum	17016	100.00			

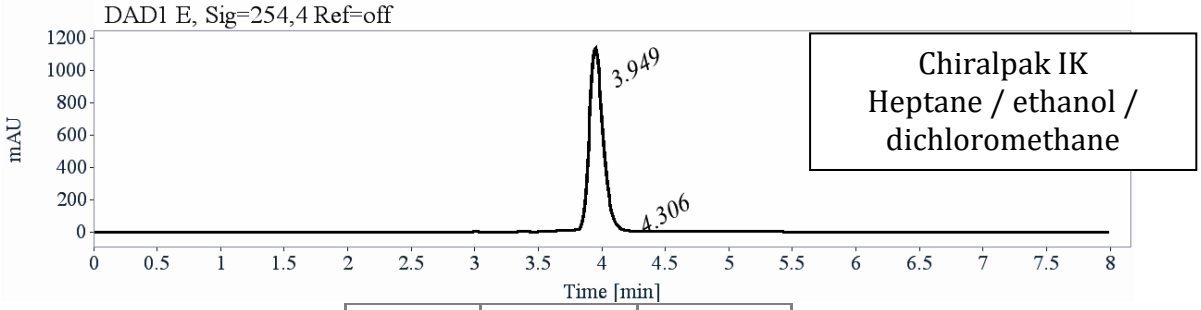
Preparative separation for compound **6-acac**:

• Sample preparation: About 18 mg of compound **6-acac** are dissolved in 4 mL of a mixture of dichloromethane and hexane (50/50).

• Chromatographic conditions: Chiralpak IK (250 x 10 mm), hexane / ethanol / dichloromethane (60/20/20) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm.

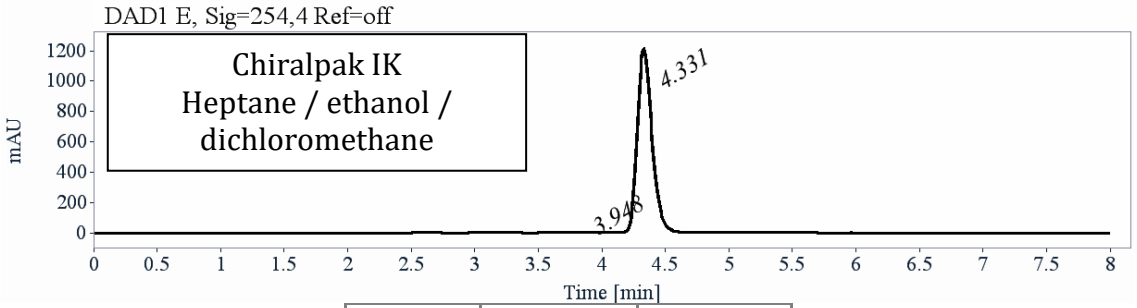
• Injections (stacked): 80 times 50 μL, every 1.8 minutes.

• First fraction: 9 mg of the first eluted enantiomer with ee > 99.5 %



RT [min]	Area	Area%
3.95	8571	99.86
4.31	12	0.14
Sum	8584	100.00

• Second fraction: 9 mg of the second eluted enantiomer with ee > 99.5 %



RT [min]	Area	Area%
3.95	23	0.23
4.33	9814	99.77
Sum	9837	100.00

7.Computational Methods

The total, transition energies, as well as the geometries and vibrations of all systems have been computed at the (Time-Dependent) Density Functional Theory (TD-DFT) level whereas the environmental effects have been modelled using the polarizable continuum model (PCM).[1] Toluene was considered as solvent as it is the solvent used in the emission experiments. No structure simplification was performed.

All calculations have been performed using the Gaussian16.A03 program,[2] but for the SOC calculations and related S-T gapes that have been achieved with ORCA.[3]

In Gaussian used tightened self-consistent field (10^{-10} a.u.) and geometry optimization (10^{-5} a.u.) convergence thresholds, and a large DFT integration grid (so-called *ultrafine* grid, a pruned 99,590 grid). These (TD-)DFT calculations relied on the M06-2X hybrid functional for absorption and emission.[3] The basis sets used for geometry optimization and frequency calculations are 6-311G(d,p) for all atoms, but Pt that was treated with LanL2TZ(f). Vertical absorption and emission transition energies were obtained adding diffuse orbitals on the "light" atoms, i.e., applying 6-311+G(d,p). The ground states were optimized with DFT, the lowest triplet with U-DFT and the lowest excited singlet with TD-DFT. The nature of the ground-state stationary points was confirmed by analytical Hessian calculations that returned 0 (minima) imaginary vibrational modes. The values reported below are vertical absorption and emission, as obtained by TD-DFT, whereas the phosphorescence vertical values were determined using ΔSCF on the optimal T1 geometry.

The ECD spectra were simulated by convoluting the TD-DFT "stick" contributions with a Gaussian showing a HWHM of 1400 cm^{-1}. For these calcultions, we use the ground-state geometry determined above and the B3LYP functional.

Eventually the spin-orbit coupling elements were computed using the same M06-2X hybrid functional, the ZORA Hamiltonian, the *def2*-TVP basis set and the CPCM(SMD) solvent model for the calculations. TDA was used. The reported SOC values reported in the text have been computed as:

$$\sqrt{\frac{1}{3}S_x^2 + \frac{1}{3}S_y^2 + \frac{1}{3}S_z^2}$$

For the sake of consistency, the S-T gaps given in the main text when studying the ISC process have been computed with ORCA and the same methodology.

[1] J. Tomasi, B. Mennucci, R. Cammi, *Chem. Rev*. **2005**, *105*, 2999–3094.

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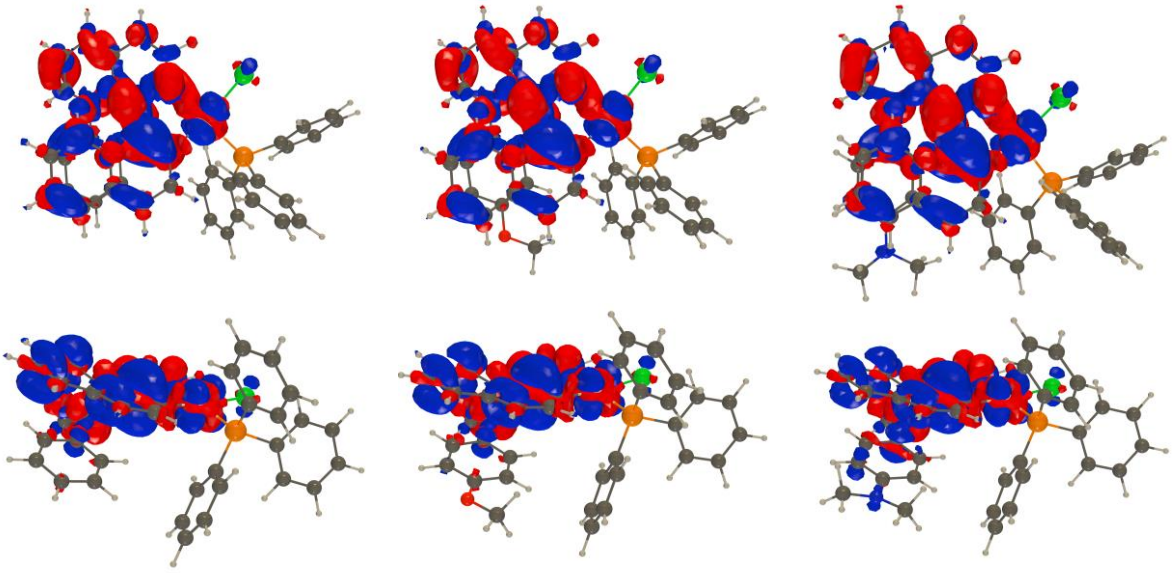
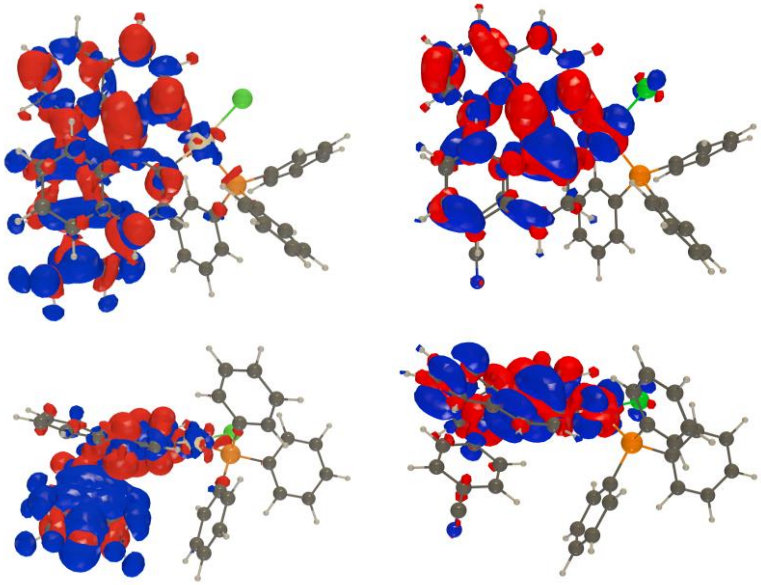
EDD plots



1 (S_0-S_1) **2** (S_0-S_1) **3** (S_0-S_1)



4 (S_0-S_2) **4** (S_0-S_1)

Figure S34 : Electron density difference plots for the lowest absorption of complexes **1-4**. The blue and red lobes correspond to region of decrease and increase of density upon excitation, respectively. Contour threshold: 0.001 au. We present two views for all systems.

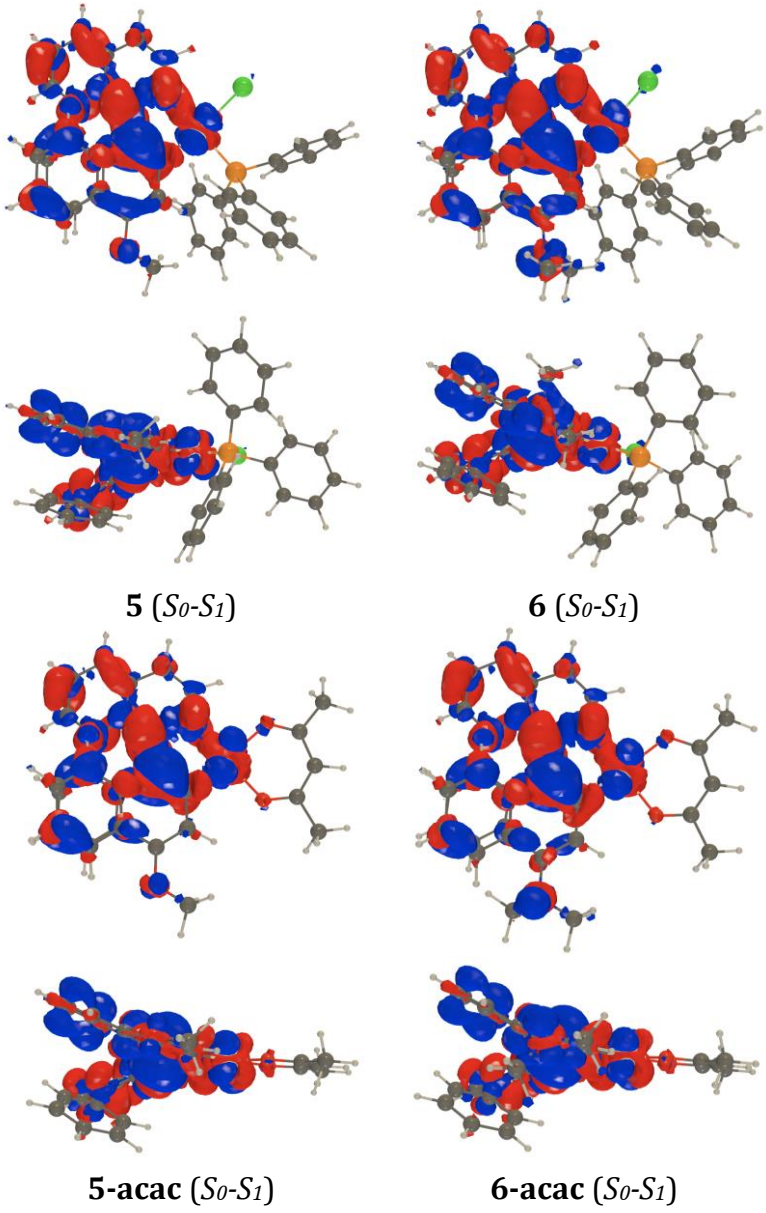


Figure S35 : Electron density difference plots for the lowest absorption of complexes **5-6** and the corresponding **acac** series**.** See caption of Figure **S32** for more details.

Table S1 : Main theoretical results. We report the key vertical absorption (in nm) together with the associated oscillator strength (*f*, in parenthesis), as well as the vertical fluorescence and phosphorescence wavelength (in nm). The two latter are always computed from the lowest singlet and triplet, respectively (transition applied only for absorption).

Compound	Transition	Absorption	Fluorescence	Phosphorescence
1	S_0-S_1	407 (*0.14*)	514	819
2	S_0-S_1	405 (*0.13*)	511	813
3	S_0-S_1	405 (*0.13*)	510	815
	S_0-S_2	398 (*0.17*)		
4	S_0-S_1	419 (*0.13*)	515	812
5	S_0-S_1	428 (*0.19*)	523	-
6	S_0-S_1	430 (*0.21*)	544	780
5-acac	S_0-S_1	446 (*0.22*)	528	747
6-acac	S_0-S_1	459 (*0.27*)	543	768

Table S2 : Theoretical investigation of ISC. We report the S_1-T_1 and S_1-T_2 gaps (in eV) computed on the optimal S_1 geometries together with the associated SOCs (in cm^{-1}). For the gaps, a negative value indicate that the triplet is below the singlet.

Compound	Transition	Gap	SOC
1	S_1-T_1	-0.77	14.1
	S_1-T_2	+0.22	97.1
2	S_1-T_1	-0.77	15.7
	S_1-T_2	+0.12	94.0
3	S_1-T_1	-0.77	16.2
	S_1-T_2	-0.02	74.3
4	S_1-T_1	-0.74	16.5
	S_1-T_2	+0.22	98.1
5	S_1-T_1	-0.73	10.7
	S_1-T_2	+0.31	66.1
6	S_1-T_1	-0.70	7.8
	S_1-T_2	+0.34	53.0
5-acac	S_1-T_1	-0.71	22.5
	S_1-T_2	+0.36	144.1
6-acac	S_1-T_1	-0.72	16.6
	S_1-T_2	+0.40	59.3

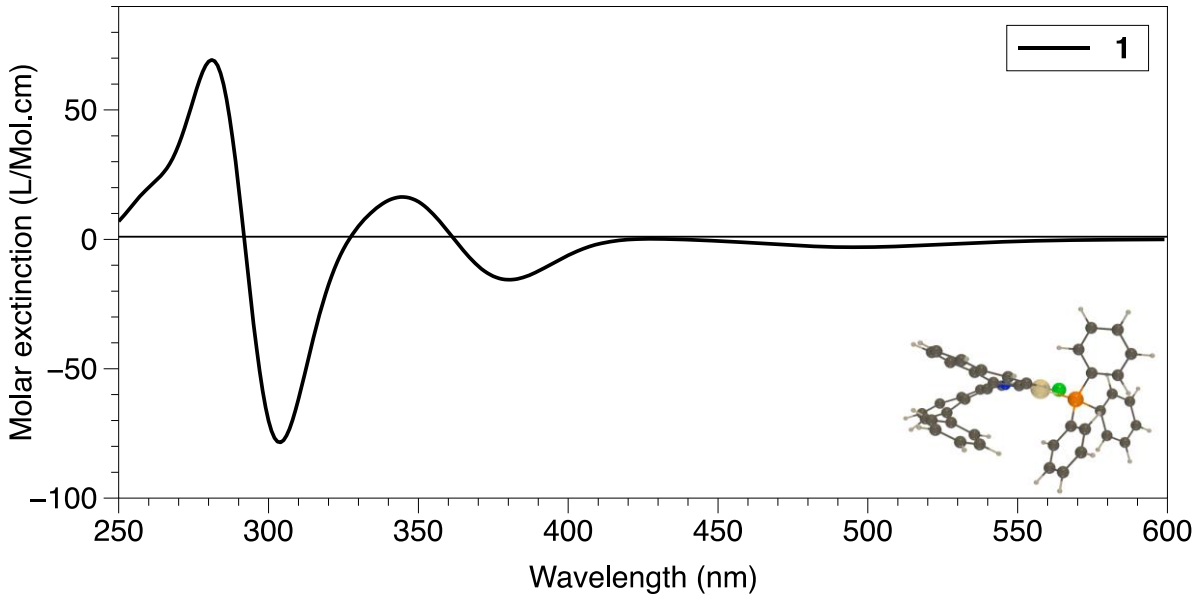


Figure S36 : Simulated ECD spectrum of **1.**

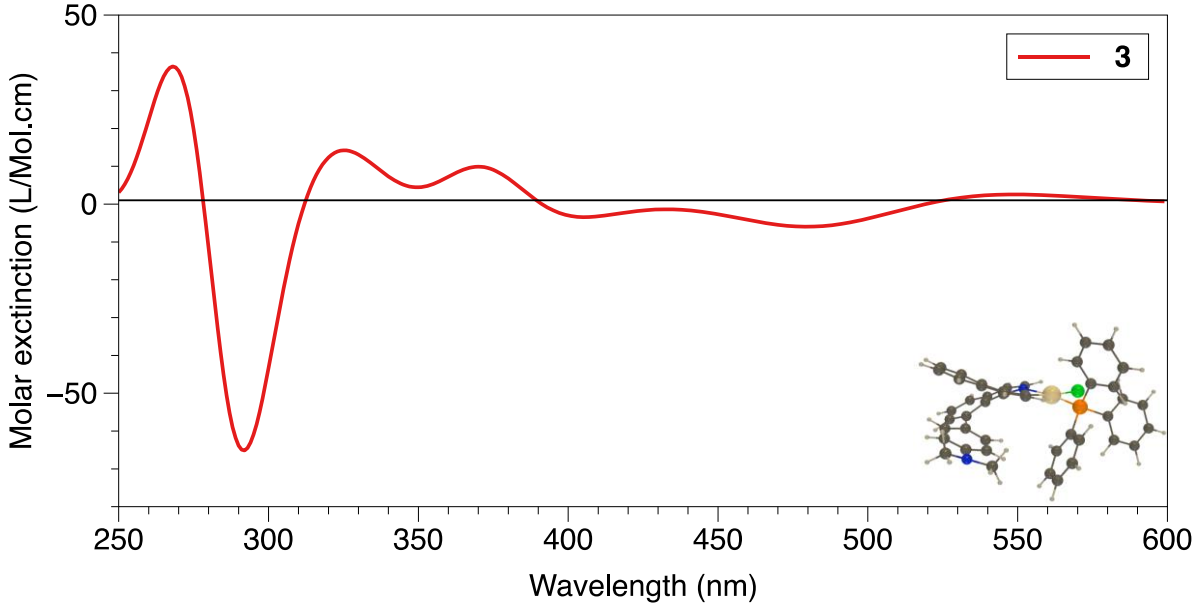


Figure S37 : Simulated ECD spectrum of **3**.

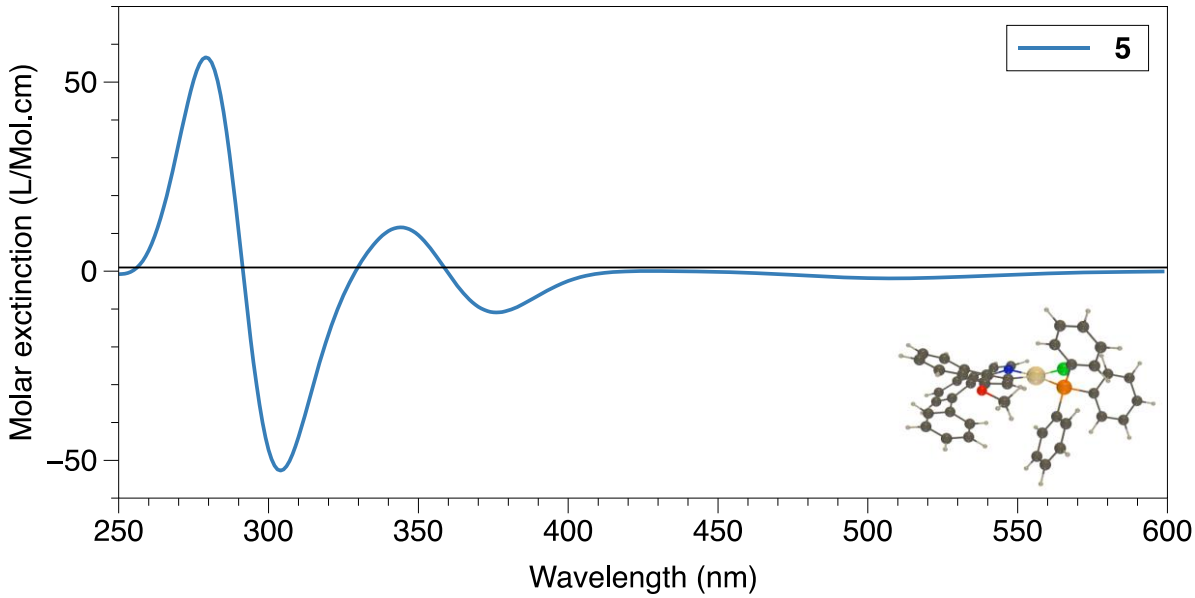


Figure S38 : Simulated ECD spectrum of **5**.

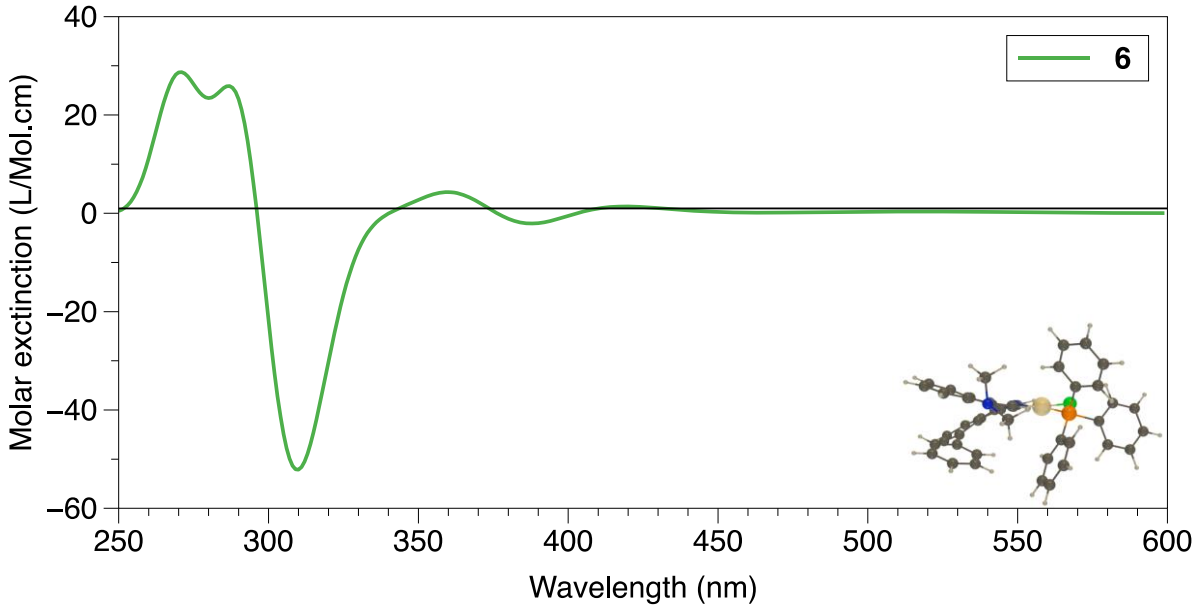


Figure S39 : Simulated ECD spectrum of **6**.