Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

A Kinetic Resolution Strategy for the Synthesis of Chiral Octahedral NHC-Iridium(III) Catalysts

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1. General Experimental procedures

All commercial chemicals were used as received unless otherwise noted. Toluene, THF, dichloromethane and diethylether were dried and distilled using a Solvant Purification System (SPS) MBRAUN. Reactions were monitored by thin-layer chromatography (TLC) carried out on aluminium backed silica gel 60 (F254) plates from MERCK (grain-size distribution 60/20 mm); visualized using 254nm UV light and $KMnO_4/K_2CO_3$/NaOH in water for staining. Column chromatography was performed with silica gel (spherical, particle size 40 µm, neutral). The eluents employed are reported as volume (volume percentages). Melting points were measured on a Stuart® SMP 10 melting point apparatus in open capillary tubes and are uncorrected. Optical rotations were recorded on a polarimeter Optical Activity Pekin Elmer 341 using a 1 mL cell with 1 dm path length. All samples were carried out in acetone or dichloromethane in 2 mL volumetric flask. Specific rotations are reported in $deg.dm^{-1}.cm^3.g^{-1}$ for a wave length related to sodium line spectrum (589 nm) according to the Biot relation and are uncorrected. NMR spectra (proton, carbon, 2D) were recorded on a spectrometer of nuclear magnetic resonance Bruker ARX-400 (^{1}H: 400 MHz, ^{13}C: 100 MHz, ^{19}F: 301 MHz, ^{31}P: 162 MHz) with complete proton decoupling for nucleus other than ^{1}H. Chemical shifts are reported in parts per million with the solvent resonance as the internal standard ($CDCl_3$: 1H, δ 7.26 ppm; ^{13}C, δ 77.16 ppm; CD_2Cl_2: ^{1}H, δ 5.32 ppm; ^{13}C, δ 53.83 ppm; CD_3OD: ^{1}H, δ 3.31 ppm; ^{13}C, δ 49.00 ppm, CD_3CN: 1H, δ 1.94 ppm; ^{13}C, δ 1.32, 118.26 ppm); Coupling constants (J) are reported in hertz (Hz). Multiplicities in ^{1}H NMR are reported using following abbrevations: s = singlet, br s = broad singlet, d = doublet, dd = double doublet, ddd = double double doublet, dt = double triplet, t = triplet, q = quartet, quint = quintet, sept = septet, m = multiplet. Mass spectrometric analyses were performed at Centre Régional de Mesures Physiques de l'Ouest (CRMPO), Université de Rennes 1. High-resolution mass spectroscopy (HMRS) was recorded on a Q-TOF spectrometer using electrospray ionization. UV-Visible (UV-vis, in M-1 cm-1) absorption spectra were recorded on a UV-2401PC Shimadzu spectrophotometer. Fluorescence spectra were recorded on a FL 920 Edimburgh fluorimeter. Luminescence quantum yields Φ were measured in diluted solution using the following equation, where: A(λ) is the absorbance at the excitation wavelength λ, *n* is the refractive index, D is the integrated intensity, and "r" and "x" stand for reference and sample, respectively.

$$\frac{\Phi_x}{\Phi_r} = \left(\frac{\mathrm{A}_r(\lambda)}{\mathrm{A}_x(\lambda)}\right)\left(\frac{n_x^2}{n_r^2}\right)\left(\frac{\mathrm{D}_x}{D_r}\right)$$

The fluorescence quantum yields were measured relative to $[Ru(bpy)_3]Cl_2$ in aqueous solution as the standard (Φ_{lum} = 0.042); estimated uncertainty in Φ_{lum} is ± 10%. Excitation of reference and sample compounds was performed at the same wavelength. Electrochemical measurements were performed with a potentiostat-galvanostat AutoLab PGSTAT 302N controlled by resident GPES (General Purpose Electrochemical System 4.9) software using a conventional single-compartment three-electrode cell. The working and auxiliary electrodes were platinum electrodes and the reference electrode was the saturated potassium chloride calomel electrode (SCE). Electronic circular dichroism (ECD, in M^{-1} cm^{-1}) was measured on a Jasco J-815 Circular Dichroism Spectrometer (IFR140 facility - Biosit - Université de Rennes 1). IR and VCD spectra were recorded on a Jasco FSV-6000 spectrometer. The circularly

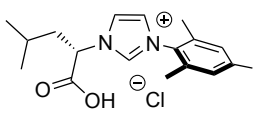
polarized luminescence (CPL) measurements were performed using a home-built CPL spectrofluoropolarimeter. The samples were excited using a 90° geometry with a Xenon ozone-free lamp 150 W LS. The following parameters were used: emission slit width ≈ 2 mm, integration time = 4 sec, scan speed = 50 nm/min, accumulations = 5. The concentration of all the samples was ~10^{-5} M. Excitation of the samples were performed at 350 nm. Enantiomeric excesses were measured on a Alliance e2695 Waters® HPLC with a UV/visible detector 2489 Waters® at 254nm. Single-crystal X-ray diffraction measurements were recorded on a D8 Venyure ASX diffractometer at T = 150K.

2. Synthesis of Iridium-NHC complexes

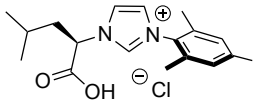
2.1. Preparation of the imidazolium salts.

The imidazolium salts were prepared according to the procedure reported by our laboratory[1]: In a round-bottomed flask were placed 2,4,6-trimethylaniline (2.8 mL, 20 mmol, 1.0 equiv.), *(L or D)*-Leucine (2.63 g, 20 mmol, 1.0 equiv.), acetic acid (5.2 mL, 90 mmol, 4.5 equiv.) and the mixture was heated at 60 °C for 5 min (mixture A). In another round bottomed flask were placed glyoxal (2.3 mL, 20 mmol, 1.0 equiv., 40 % wt in aqueous solution), formaldehyde (1.5 mL, 20 mmol, 1.0 equiv., 37 % wt in aqueous solution) and acetic acid (5.2 mL, 9 mmol, 4.5 equiv.) and the mixture was heated at 60 °C for 5 min (mixture B). At 60 °C, mixture B was added to mixture A (1.0 mL of AcOH was used to rince the flask) and the resulting mixture was stirred at 60 °C for 1h then cooled down to room temperature. Diethylether (200 mL) and water (200 mL) were added and the aqueous layer was washed with diethylether (3 x 200 mL). Brine (100 mL) was added and the aqueous layer was washed with diethylether (3 x 200 mL). The aqueous layer was placed in a round-bottomed flask with dichloromethane (250 mL) and potassium hexafluorophosphate (3,74 g, 20 mmol, 1.0 equiv.). The biphasic mixture was stirred at room temperature for one night. The organic layer was separated, dried over anhydrous magnesium sulphate, filtered and the solvent were evaporated under reduced pressure. The desired imidazolium.PF_6 salts were isolated by column chromatography on silica gel (eluent system: 100% DCM to 90:10 DCM/MeOH). The pure imidazolium.PF_6 salts dissolved in a minimum of solvent (50/50 acetone (HPLC grade)/ Milli Q water) was loaded on ion exchange Dowex® resin (activated by HCl 37%, 2 volumes) and slowly eluted using the same eluent. After removal of acetone and water under reduced pressure, the residue was dissolved in CH_2Cl_2, dried over dried $MgSO_4$, filtered and concentrated under reduced pressure to afford the desired imidazolium chloride salts (*S*)-**S1.Cl** or (*R*)-**S1.Cl**.

[1] C. Jahier-Diallo, M. S. T. Morin, P. Queval, M. Rouen, I. Artur, P. Querard, L. Toupet, C. Crévisy, O. Baslé, M. Mauduit. *Chem. Eur. J.* 2015, **21**, 993-997.



(*S*)-**S1.Cl**

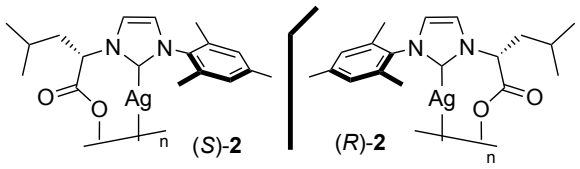


(*R*)-**S1.Cl**

(*S*)-**S1.Cl** (beige solid, 34% yield), (*R*)-**S1.Cl** (beige solid, 32% yield). ^{1}H NMR (400 MHz, MeOD): δ (ppm) δ 9.40 (t, *J* = 1.5Hz, 1H), 7.99 (t, *J* = 1.5 Hz, 1H), 7.72 (t, *J* = 1.5Hz, 1H), 7.14 (s, 2H), 5.15-5.10 (m, 1H), 2.37 (s, 3H), 2.17 (m, 2H), 2.09 (s, 3H), 2.09 (s, 3H), 1.52-1.42 (m, 1H), 1.03 (d, *J* = 6.6 Hz, 3H), 0.99 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, MeOD): δ (ppm) δ 173.3, 142.6, 139.1, 135.9, 135.7, 132.6, 130.7, 128.8, 124.7, 124.6, 64.8, 42.4, 26.6, 23.1, 21.5, 21.1, 17.3, 17.3. LC-MS calcd for $C_{18}H_{24}N_2O_2^+$ ([M]$^+$): m/z 301.19, found: m/z 301.00. (*R*)-**S1.Cl** $[\alpha]_D^{23}$ = -32 (± 5 %) ($CHCl_3$, $3.12\cdot10^{-3}$ mol·L^{-1})

2.2. Preparation of the silver-NHC complexes (S)-2 and (R)-2.

The silver-NHC complexes were prepared according to the procedure reported by our laboratory[2]: In a flame-dried 100 mL round-bottomed flask were placed the imidazolium chloride (*S*)-**S1.Cl** or (*R*)-**S1.Cl** (2 mmol, 1.0 equiv.), 3Å molecular sieves, Ag_2O (5 mmol, 2.5 equiv.) and dry DCM (23 mL). The resulting mixture under argon atmosphere was vigorously stirred at room temperature overnight in dark. Next, CH_2Cl_2 was removed under reduce pressure. Then, acetone was added, and the mixture was filtered through a celite pad using acetone as eluent. The filtered solution was concentrated and pentane was added to induce precipitation. The precipitate was washed twice with pentane. The oligo- or polymeric silver-NHC complexes (*S*)-**2** and (*R*)-**2** were obtained upon the removal of solvent residues under vacuum and stored protected from light under an inert atmosphere.

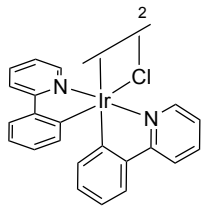


(*S*)-**2** (*R*)-**2**

In agreement with the literature[2]: (*S*)-**2** (beige solid, 99% yield), (*R*)-**2** (beige solid, 90% yield) ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.41 (br. s, 1H), 6.91 (s, 2H), 6.87 (s, 1H), 5.24 (br. s, 1H), 2.32 (s, 3H), 2.10 (br. s, 2H), 1.96 (s, 2H), 1.88 (br. s, 2H), 1.32 (br. s, 1H), 0.99 (br. s, 3H), 0.89 (d, *J*= 8 Hz, 3H).

2.3. Preparation of racemic [Ir(μ-Cl)(ppy)$_2$]$_2$ (1).

Racemic [Ir(μ-Cl)(ppy)$_2$]$_2$ **(1)** was prepared according to a reported procedure (yellow powder, 76% yield).[3] In agreement with the literature: ^{1}H NMR (400 MHz, CD_2Cl_2): δ (ppm) 9.27-9.24 (m, 4H), 7.94 (d, J = 8.2 Hz, 4H), 7.82-7.77 (m, 4H), 7.56 (dd, J = 7.9 Hz, 1.1 Hz, 4H), 6.85-6.79 (m, 8H), 6.63-6.58 (m, 4H), 5.88 (dd, J = 7.9 Hz, 1.1 Hz, 4H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ (ppm) 168.0, 151.4, 144.9, 144.0, 136.6, 130.4, 129.1, 123.7, 122.5, 121.3, 118.6.



[2] J. Thongpaen, T. E. Schmid, L. Toupet, V. Dorcet, M. Mauduit and O. Baslé, *Chem. Commun.* 2018, **54**, 8202-8205.
[3] Y. Zhou, H. Gao, X. Wang and Honglan Qi, *Inorg. Chem.* 2015, **54**, 1446-1453.

2.4. Preparation of the Iridium-NHC complexes 3 and 4

In a flamed-dried Schlenk tube, under argon atmosphere, the silver-NHC complex *(S)*-**2** (152 mg, 0.2 mmol, 1.0 equiv.), $[Ir(\mu\text{-}Cl)(ppy)_2]_2$ **1** (100 mg, 0.1 mmol, 0.5 equiv.) were dissolved in distilled dichloromethane (5 mL). The resulting mixture was warmed up to 40 °C and stirred in the dark for 16h. The resulting solution was filtered through a celite pad and concentrated under reduced pressure. The crude product with a diastereomeric ratio of about 2:1 determined by ^{1}H NMR spectroscopy (fig. S1) was purified by column chromatography on silica gel (dichloromethane/acetone: 95/5) to afford the iridium complexes Λ-(S)-**3** as a yellow solid (79 mg, 49%) and Δ-(S)-**4** as a yellow solid (42 mg, 26%).

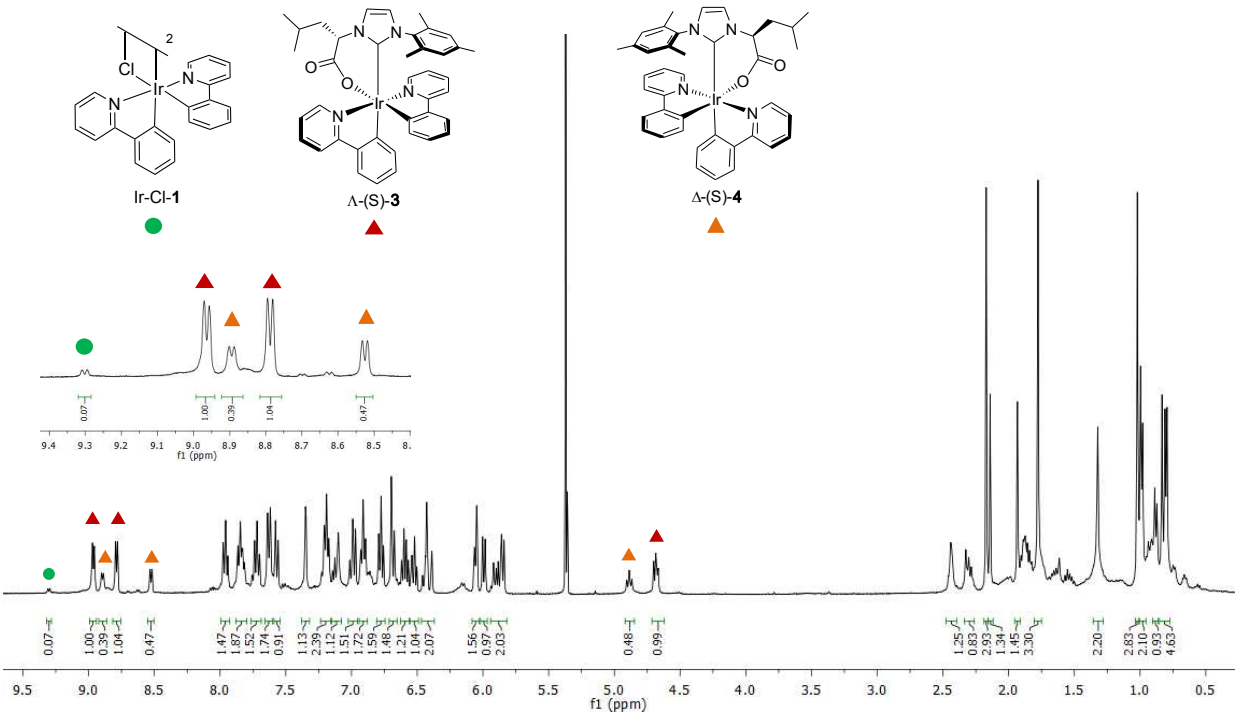
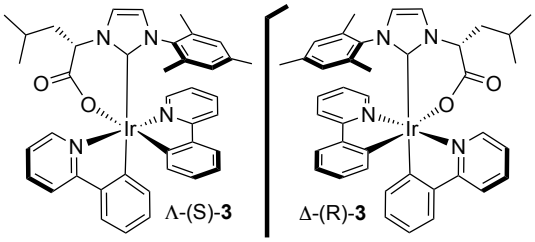
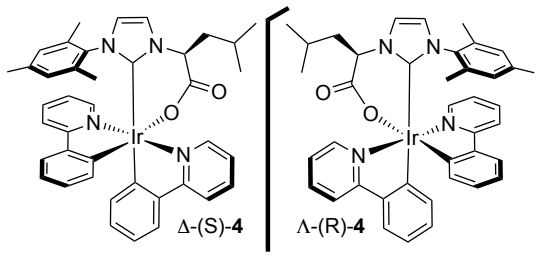


Figure S1. ^{1}H NMR spectra of the crude mixture

The same procedure has been followed for the synthesis of iridium complexes Δ-(R)-**3** and Λ-(R)-**4** that are enantiomers of Λ-(S)-**3** and Δ-(S)-**4**, respectively. The crude product with a diastereomeric ratio of about 2:1 determined by ^{1}H NMR spectroscopy was purified by column chromatography on silica gel (dichloromethane/acetone: 95/5) to afford the iridium complexes Δ-(R)-**3** as a yellow solid (75 mg, 47%) and Λ-(R)-**4** as a yellow solid (53 mg, 33%).



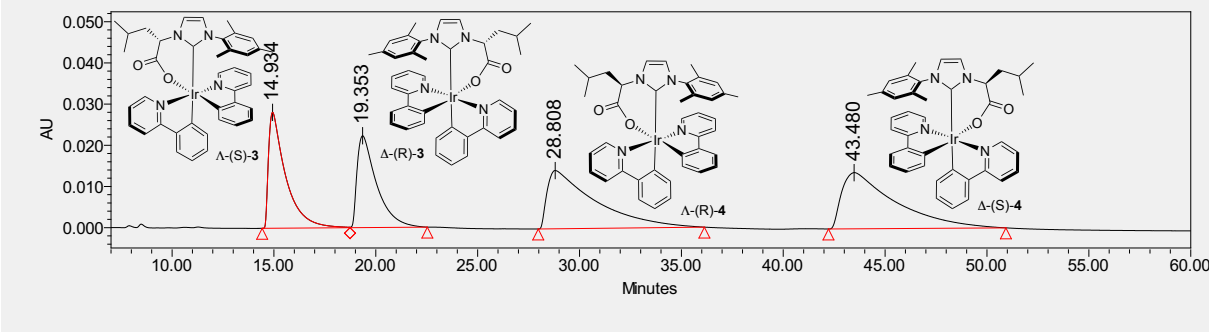
Λ-(S)-**3** and Δ-(*R*)-**3**: ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.04 (d, *J* = 5.9 Hz, 1H), 8.72 (d, *J* = 5.8 Hz, 1H), 7.89 (d, *J* = 8.3 Hz, 1H), 7.75 (t, *J* = 8.2 Hz, 1H), 7.63 (t, *J* = 8.3 Hz, 1H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.48 (d, *J* = 8.2 Hz, 1H), 7.26 (d, *J* = 2.1 Hz, 1H), 7.12 (d, *J* = 6.7 Hz, 1H), 7.08 (d, *J* = 6.6 Hz, 1H), 6.87 (d, *J* = 7.6 Hz, 1H), 6.78 (t, *J* = 7.7 Hz, 1H), 6.68 (t, *J* = 7.3 Hz, 1H), 6.58 (d, *J* = 1.9 Hz, 1H), 6.50 (t, *J* = 7.6 Hz, 1H), 6.44 (t, *J* = 7.4 Hz, 1H), 6.37 (s, 1H), 6.01 (s, 1H), 5.94 (d, *J* = 7.7 Hz, 1H), 5.78 (d, *J* = 7.6 Hz, 1H), 4.72 (dd, *J* = 8.0, 7.0 Hz, 1H), 2.39 – 2.28 (m, 1H), 2.13 (s, 3H), 1.98 – 1.85 (m, 1H,), 1.73 (s, 3H), 1.32 – 1.23 (m, 1H), 0.96 (s, 3H), 0.94 (d, *J* = 6.2 Hz, 3H), 0.82 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm): 174.5, 173.3, 171.5, 168.1, 164.7, 152.5, 149.4, 145.3, 144.1, 142.5, 138.1, 136.6, 135.8, 134.6, 134.4, 133.8, 131.1, 129.9, 129.6, 128.5, 128.2, 127.6, 123.9, 123.4, 122.6, 121.9, 121.6, 121.1, 119.9, 119.1, 118.4, 118.2, 60.9, 38.5, 25.1, 23.3, 22.7, 20.9, 18.9, 16.3. HRMS (ESI): calcd. for $C_{40}H_{39}N_4O_2Na^{193}Ir$ |M+Na]$^+$: 823.25946 m/z, found: 823.2601 (1 ppm). Anal. Calcd. for $C_{40}H_{39}IrN_4O_2.CH_3OH$: C 59.19%, H 5.21%, N 6.73%, found C 59.38%, H 5.28%, N 6.46%. CalclOptical rotation: Λ–(*S*)-**3**: $[\alpha]_D^{23}$= +58 (± 5 %) (CH_2Cl_2, 2.1·10^{-4} mol·L^{-1}); Δ–(*R*)-**3**: $[\alpha]_D^{23}$= -60 (± 5 %) (CH_2Cl_2, 2.1·10^{-4} mol·L^{-1}).



Δ-(*S*)-**4** and Λ-(*R*)-**4** : ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 8.98 (d, *J* = 5.1 Hz, 1H), 8.45 (d, *J* = 5.8 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.74 (t, *J* = 8.2 Hz, 1H), 7.64 (t, *J* = 8.2 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.14 (t, *J* = 7.4 Hz, 1H), 7.06 – 6.95 (m, 2H), 6.88 (d, *J* = 7.7 Hz, 1H), 6.77 (t, *J* = 7.3 Hz, 1H), 6.66 (t, *J* = 7.4 Hz, 1H), 6.57 (d, *J* = 1.9 Hz, 1H), 6.45 (t, *J* = 7.5 Hz, 1H), 6.40 – 6.29 (m, 2H), 6.01 (s, 1H), 5.82 (d, *J* = 7.8 Hz, 1H), 5.79 (d, *J* = 7.5 Hz, 1H), 4.94 (dd, *J* = 8.0, 7.0 Hz, 1H), 2.09 (s, 3H), 1.88 (s, 3H), 1.82 – 1.66 (m, 1H), 1.63 – 1.51 (m, 1H), 1.31 – 1.24 (m, 1H), 0.94 (d, *J* = 6.4 Hz, 3H), 0.91 (d, *J* = 6.4 Hz, 3H), 0.77 (s, 3H$_l$). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm): 173.1, 171.5, 171.1, 168.1, 164.5, 154.3, 149.3, 145.6, 144.1, 142.7, 138.3, 136.6, 135.8, 135.1, 134.4, 134.1, 130.9, 129.9, 129.2, 129.0, 128.2, 127.7, 123.9, 123.6, 122.6, 122.0, 121.7, 121.3, 119.8, 118.5, 117.9, 66.3, 45.7, 24.7, 22.6, 22.3, 21.0, 19.2, 15.7. Anal. Calcd. for $C_{40}H_{39}IrN_4O_2.CH_3OH$: C 59.19%, H 5.21%, N 6.73%, found C 59.31%, H 5.47%, N 6.57%. HRMS (ESI): calcd. for $C_{40}H_{39}N_4O_2Na^{193}Ir$ [M+Na]$^+$: 823.25946 m/z , found : 823.2604 (1 ppm). Optical rotation: Δ–*(S)*-**4**: $[\alpha]_D^{23}$= -32 (± 5 %) (CH_2Cl_2, 2.1·10^{-4} mol·L^{-1}), Λ–*(R)*-**4**: $[\alpha]_D^{23}$= +30 (± 5 %) (CH_2Cl_2, 2.1·10^{-4} mol·L^{-1}).

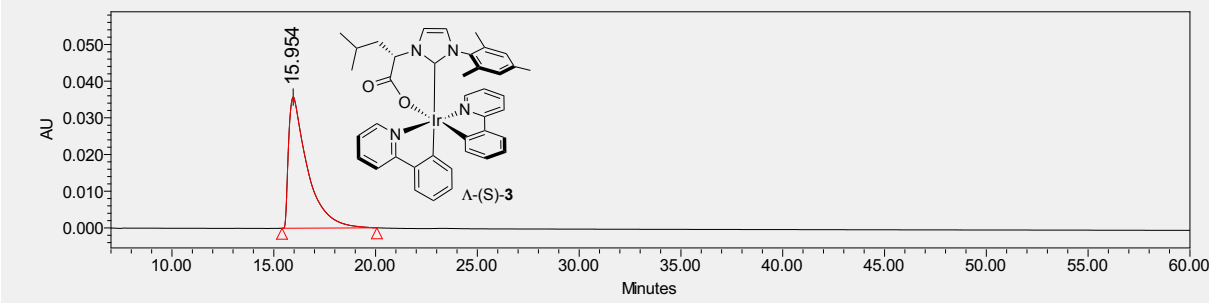
2.5. HPLC analyses for the Iridium-NHC complexes 3 and 4

The analyses were performed with a Daicel Chiralpack IA (250 x 4.6 mm) HPLC column on Waters system using a mobile phase composed of Hexane/DCM/EtOH (50/50/0.6 v/v/v). The column temperature was 20 °C and UV-absorption was measured at 254 nm.



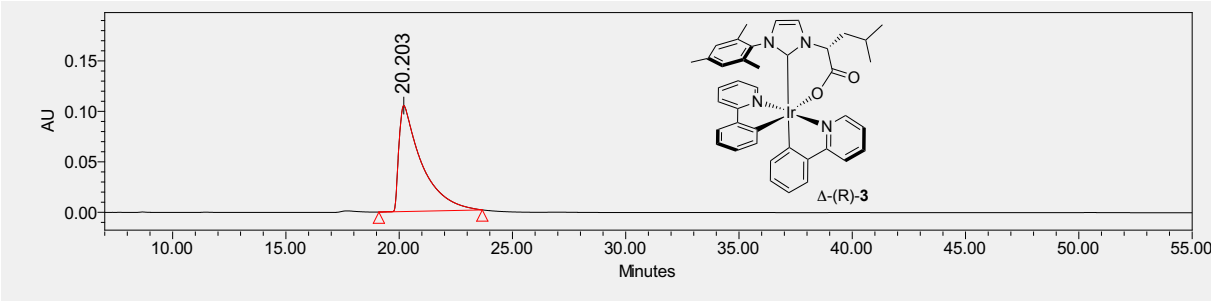
	Name	Retention Time	Area	% Area	Height
1	Λ-(S)-**3**	14.934	1651213	20.80	28167
2	Δ-(R)-**3**	19.353	1481456	18.66	22306
3	Λ-(R)-**4**	28.808	2311984	29.13	14160
4	Δ-(S)-**4**	43.480	2493060	31.41	13653

Figure S2. HPLC trace for the mixture of Λ-(*S*)-**3,** Δ-(*R*)-**3,** Λ-(*R*)-**4** and Δ-(*S*)-**4**



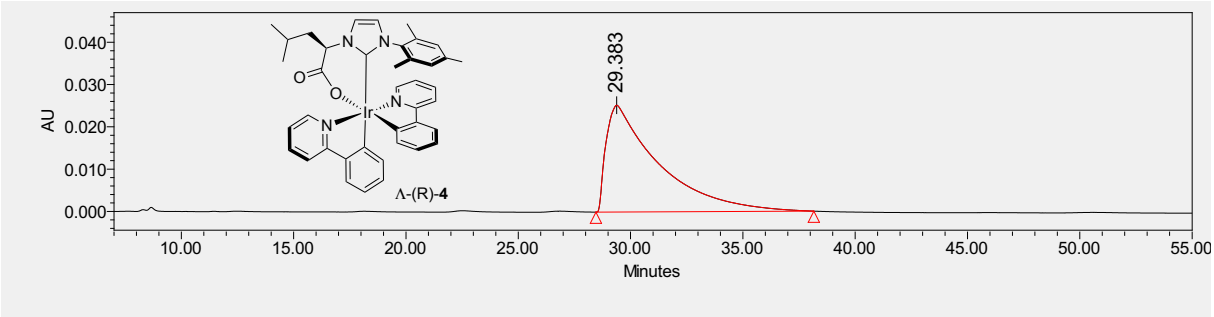
	Name	Retention Time	Area	% Area	Height
1	Λ-(S)-**3**	15.954	2306622	100.00	35774

Figure S3. HPLC trace for the isolated Λ-(*S*)-**3**



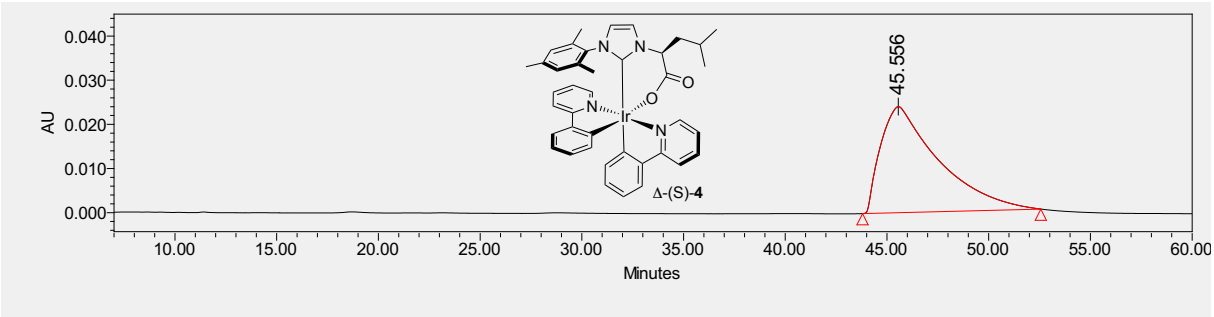
	Name	Retention Time	Area	% Area	Height
1	Δ-(R)-**3**	20.203	7779711	100.00	105913

Figure S4. HPLC trace for the isolated Δ-(*R*)-**3**



	Name	Retention Time	Area	% Area	Height
1	Λ-(R)-**4**	29.383	4096582	100.00	25270

Figure S5. HPLC trace for the isolated Λ-(R)-**4**



	Name	Retention Time	Area	% Area	Height
1	Δ-(S)-**4**	45.556	4973589	100.00	24208

Figure S6. HPLC trace for the isolated Δ-(*S*)-**4**

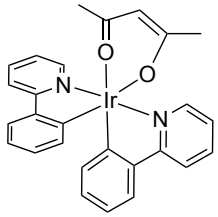
2.6. Thermal and photochemical stability of Δ-(*S*)-4.

In a NMR tube, a solution of **Δ-(*S*)-4** (10 mg, 0.012 mmol) in CD_2Cl_2 (0.5 mL) was heated at 40 °C for 2 days and no epimerization could be detected by ^{1}H NMR. The same sample was then irradiated under UV-light (365 nm) for one night and its HPLC analysis did not revealed any epimerization or structural modification.

3. Kinetic resolution studies

3.1. Preparation of racemic Ir-acac-5.

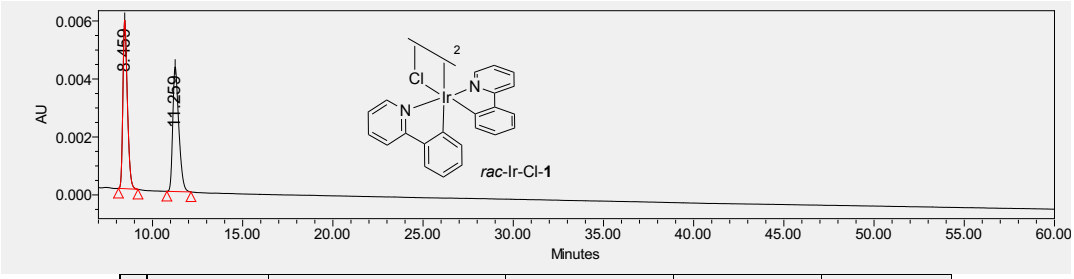
Racemic [Ir(ppy)$_2$(acac)] **(5)** was prepared according to a reported procedure (orange powder, 80% yield).[3] In agreement with the literature: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.51 (ddd, 2H, J = 6.0, 1.6, 0.8 Hz), 7.84 (dd, 2H, J = 7.2, 0.8 Hz), 7.72 (ddd, 2H, J = 8.4, 7.6, 1.6 Hz), 7.54 (dd, 2H, J = 8.0, 1.2 Hz), 7.13 (ddd, 2H, J = 7.6, 6.0, 1.6 Hz), 6.80 (dt, 2H, J = 7.6, 1.2 Hz), 6.68 (dt, 2H, J = 7.6, 1.6 Hz), 6.26 (dt, 2H, J = 8.0, 1.2 Hz), 5.21 (1H, s); 1.78 (6H, s). ^{13}C NMR (75 MHz, CD_2Cl_2): δ (ppm) 184.7,168.2, 148.2, 147.4, 145.1, 137.2, 133.2, 128.7, 123.8, 121.8, 120.8, 118.6, 100.3, 28.3.



[3] Y. Zhou, H. Gao, X. Wang and Honglan Qi, *Inorg. Chem.* 2015, 54, 1446-1453.

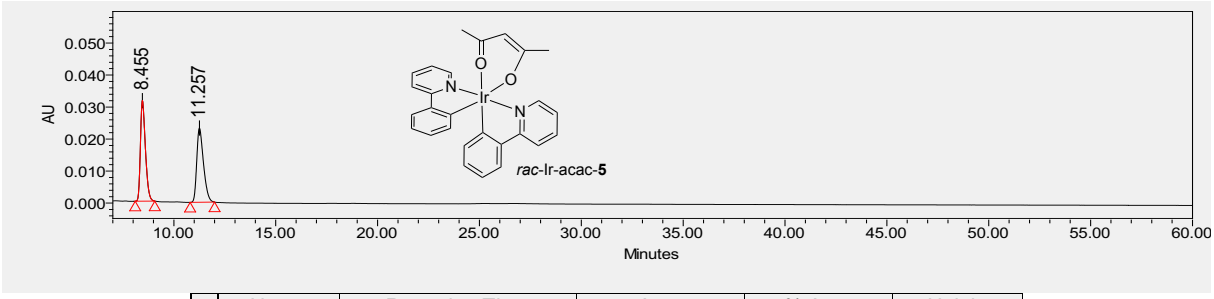
3.2. HPLC analyses for reference samples

The analyses were performed with a Daicel Chiralpack IA (250 x 4.6 mm) HPLC column on Waters system using a mobile phase composed of Hexane/DCM/EtOH (50/50/0.6 v/v/v). The column temperature was 20 °C and UV-absorption was measured at 254 nm.



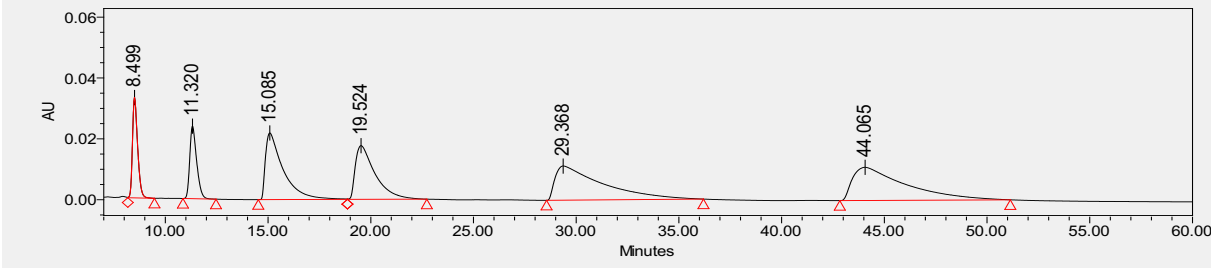
	Name	Retention Time	Area	% Area	Height
1	Λ-Cl-**1**	8.459	100437	50.13	5812
2	Δ-Cl-**1**	11.259	99906	49.87	4298

Figure S7. HPLC trace for racemic Ir-Cl-**1**



	Name	Retention Time	Area	% Area	Height
1	Λ-acac-**5**	8.455	545111	50.33	31569
2	Δ-acac-**5**	11.257	538060	49.67	23275

Figure S8. HPLC trace for racemic Ir-acac-**5**



	Name	Retention Time	Area	% Area	Height
1	Λ-acac-**5**	8.499	600487	8.13	34613
2	Δ-acac-**5**	11.320	578535	7.84	24897
3	Λ-(S)-**3**	15.085	1303525	17.66	21522
4	Δ-(R)-**3**	19.524	1177706	15.95	17415
5	Λ-(R)-**4**	29.368	1791550	24.27	11078
6	Δ-(S)-**4**	44.065	1929780	26.14	10703

Figure S9: HPLC trace for the reference mixture of **3**, **4** and **5**.

3.3. Kinetic resolution using the silver complex (*S*)-2

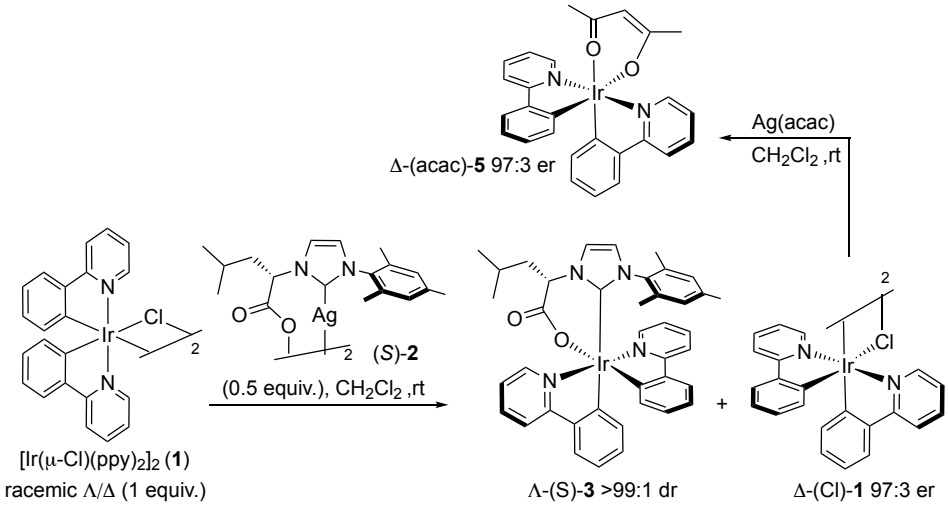
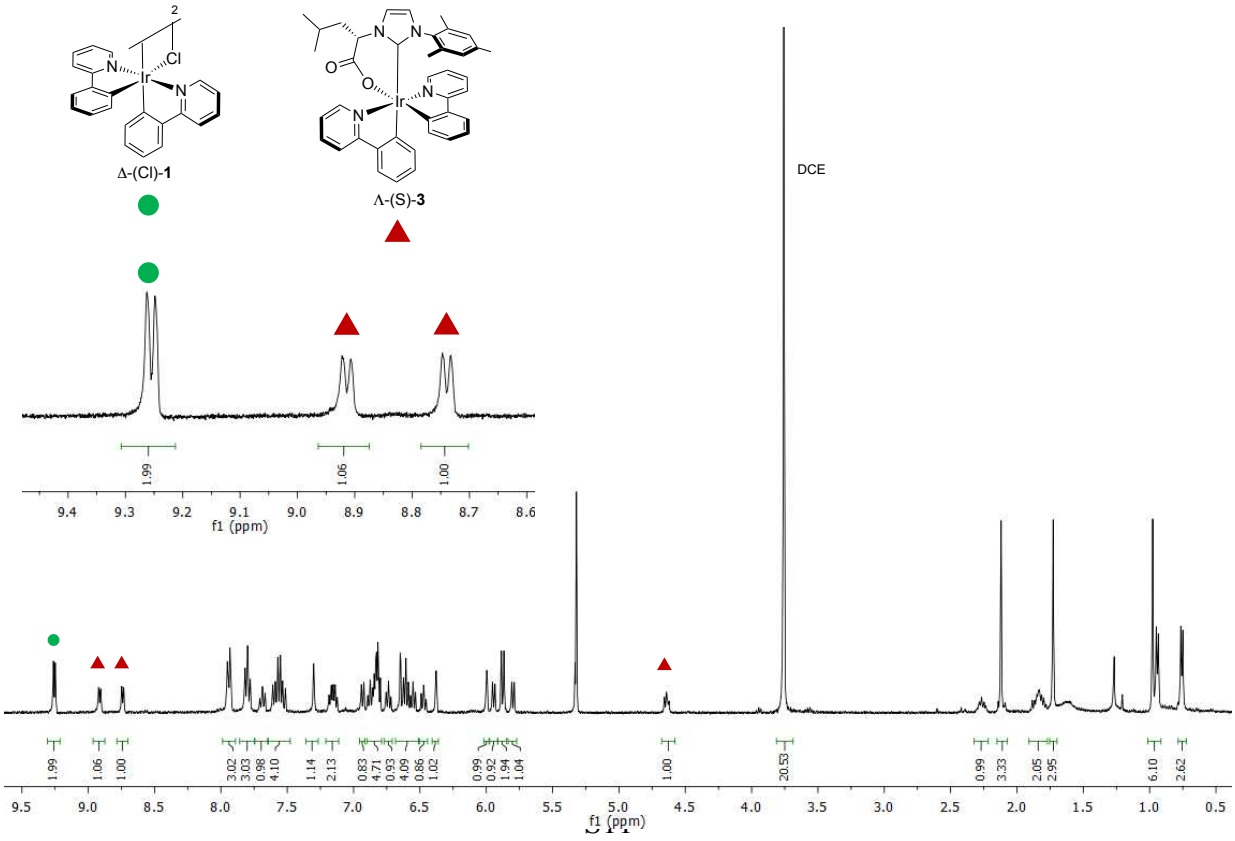


Figure S10. Synthetic route to Λ-(S)-**3** and enantioenriched Δ-Cl-**1** and Δ-acac-**5**

In a NMR tube, $[Ir(\mu\text{-Cl})(ppy)_2]_2$ **1** (20.0 mg, 0.0185 mmol, 1.0 equiv.) and **(*S*)-2** (8.2 mg, 0.01 mmol, 0.54 equiv.) were dissolved in CD_2Cl_2 (1.5 mL). The reaction was monitored by ^1H NMR using 1,2-dichloroethane as internal standard. The HPLC analysis revealed the presence of Λ–*(S)*-**3** (RT = 15.01 min) as a single diastereoismer and the enantioenriched Ir-Cl-**1** (RT = 11.22 min (Δ–Cl-**1**) and RT = 8.43 min (Λ–Cl-**1**) (Fig. S11). Then, Ag(acac) (5.7 mg, 0.028 mmol, 1.5 equiv.) was added and the reaction was monitored by 1H NMR. After full conversion, the reaction mixture was analyzed by HPLC and demonstrated the full retention of configuration at metal center (Fig. S12). The mixture of Ir(acac) and Ir(NHC) complexes were separated on silica gel using DCM/Acetone (10:0 to 9:1) as eluent to afford the Λ–(*S*)-**3** as yellow solid (13.2 mg, 44% yield) and the Δ-acac-**5** as orange solid (9.8 mg, 43% yield).



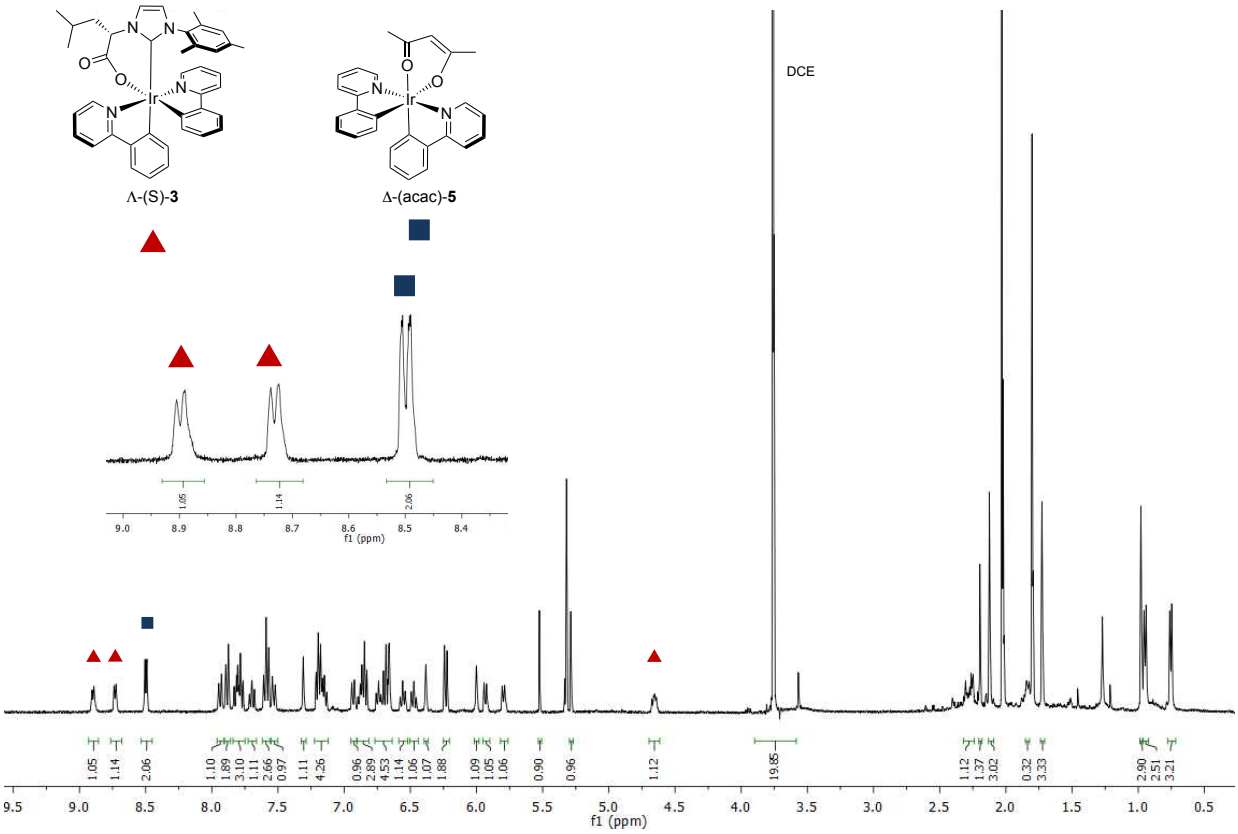
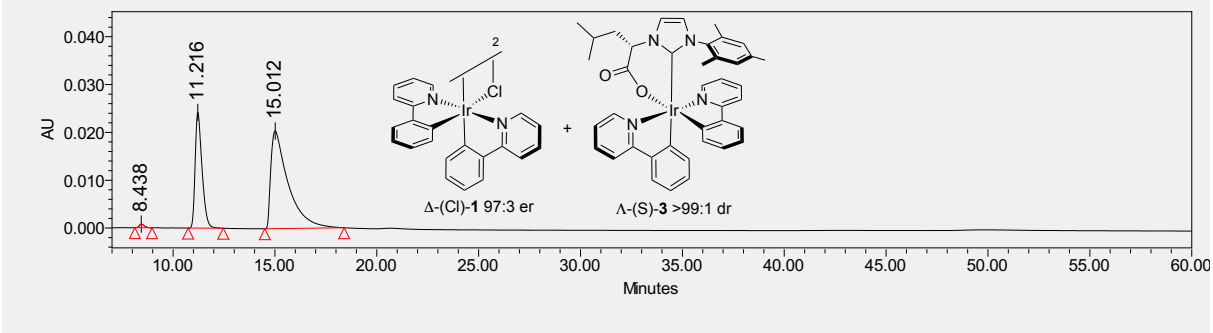


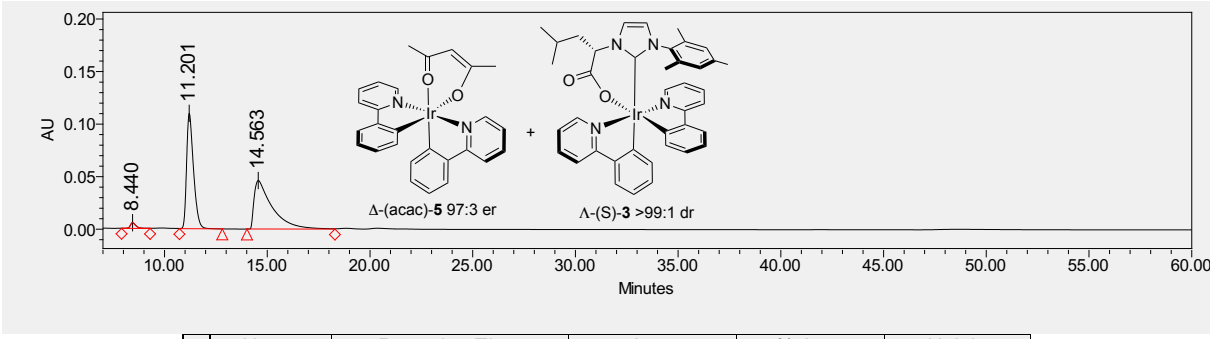
Figure S11: ^{1}H NMR analyses for the kinetic resolution using the silver complex (*S*)-**2** before (top) and after (bottom) the addition of Ag(acac).

The analyses were performed with a Daicel Chiralpack IA (250 x 4.6 mm) HPLC column on Waters system using a mobile phase composed of Hexane/DCM/EtOH (50/50/0.6 v/v/v). The column temperature was 20 °C and UV-absorption was measured at 254 nm.



	Name	Retention Time	Area	% Area	Height
1	Λ-Cl-**1**	8.438	13097	0.73	755
2	Δ-Cl-**1**	11.216	567962	31.71	24206
3	Λ-S-**3**	15.012	1209965	67.56	20418
4	Δ-S-**3**	-	-	-	-

Figure S12: HPLC trace for the kinetic resolution using silver complex (S)-**2** before Ag(acac).



	Name	Retention Time	Area	% Area	Height
1	Λ-acac-**5**	8.440	76761	1.42	4935
2	Δ-acac-**5**	11.201	2544314	47.08	109692
3	Λ-S-**3**	14.563	2783501	51.50	46214
4	Δ-S-**3**	-	-	-	-

Figure S13: HPLC trace for the kinetic resolution using silver complex (S)-**2** after Ag(acac).

3.4. Kinetic resolution using the silver complex (*R*)-2

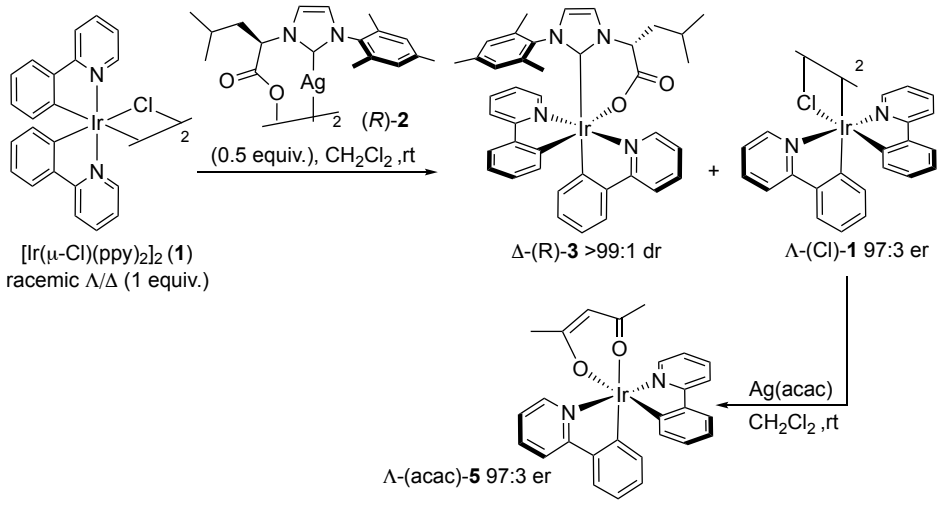
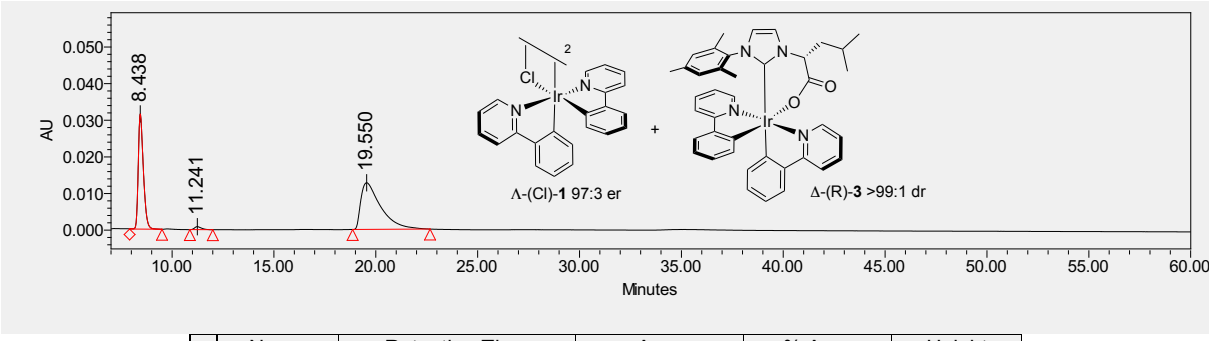


Figure S14. Synthetic route to Δ-(*R*)-**3** and enantioenriched Λ-Cl-**1** and Λ-acac-**5**

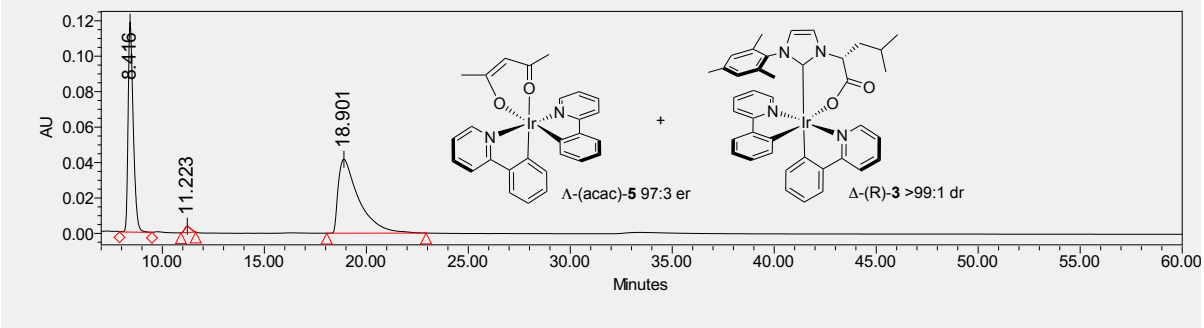
In a NMR tube, $[Ir(\mu\text{-}Cl)(ppy)_2]_2$ **1** (20.0 mg, 0.0185 mmol, 1.0 equiv.) and **(*R*)-2** (8.2 mg, 0.01 mmol, 0.54 equiv.) were dissolved in CD_2Cl_2 (1.5 mL). The reaction was monitored by ^1H NMR using 1,2-dichloroethane as internal standard. The HPLC analysis revealed the presence of **Δ–(R)-3** (RT = 19.55 min) as a single diastereoismer and the enantioenriched Ir-Cl-**1** (RT = 8.44 min (**Λ–Cl-1**) and RT = 11.24 min (Δ–Cl-**1**) (Fig. S15). Then, Ag(acac) (5.7 mg, 0.028 mmol, 1.5 equiv.) was added and the reaction was monitored by 1H NMR. After full conversion, the reaction mixture was analyzed by HPLC and demonstrated the full retention of configuration at metal center (Fig. S16). The mixture of Ir(acac) and Ir(NHC) complexes were separated on silica gel using DCM/Acetone (10:0 to 9:1) as eluent to afford the **Δ–(*R*)-3** as yellow solid (14.3 mg, 48% yield) and the **Λ-acac-5** also as orange solid (10 mg, 45% yield).

The analyses were performed with a Daicel Chiralpack IA (250 x 4.6 mm) HPLC column on Waters system using a mobile phase composed of Hexane/DCM/EtOH (50/50/0.6 v/v/v). The column temperature was 20 °C and UV-absorption was measured at 254 nm.



	Name	Retention Time	Area	% Area	Height
1	Λ-(Cl)-**1**	8.438	547978	38.16	31474
2	Δ-(Cl)-**1**	11.241	19171	1.33	826
3	Δ-(R)-**3**	19.550	868991	60.51	12742
4	Λ-(R)-**3**	-	-	-	-

Figure S15: HPLC trace for the kinetic resolution using silver complex (R)-**2** before Ag(acac).



	Name	Retention Time	Area	% Area	Height
1	Λ-(acac)-**5**	8.416	2085477	41.06	118534
2	Δ-(acac)-**5**	11.223	73549	1.45	3560
3	Δ-(R)-**3**	18.901	2919531	57.49	41707
4	Λ-(R)-**4**	-	-	-	-

Figure S16: HPLC trace for the kinetic resolution using silver complex (R)-**2** after Ag(acac).

4. (Chiro)optical properties

4.1. UV-vis absorption

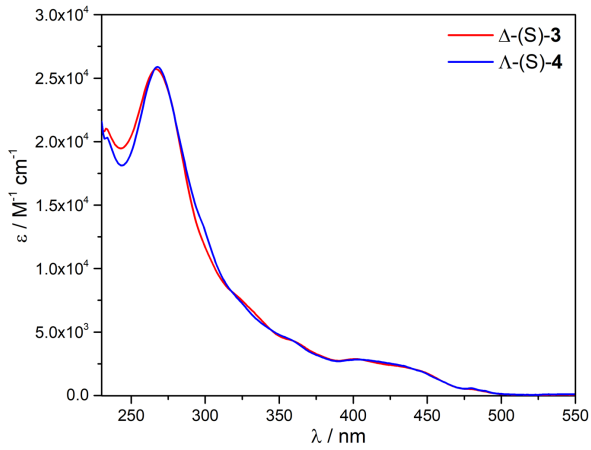


Figure S17: UV-vis absorption spectra of Λ-(*S*)-**3** (blue) and Δ-(*S*)-**4** (red) recorded in CH_2Cl_2 solution at 298 K (~10^{-5} M).

4.2. Emission spectra

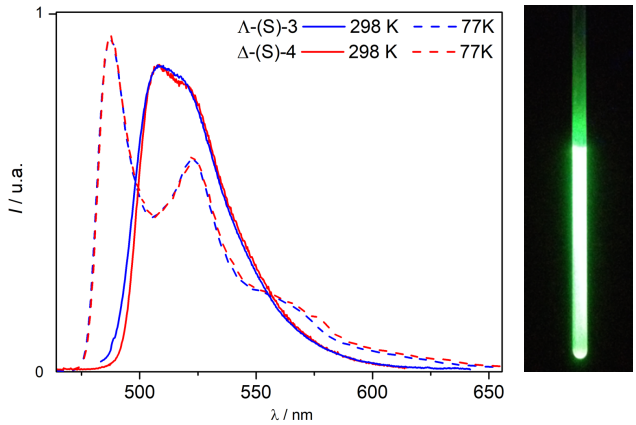


Figure S18: Luminescence spectra of Λ-(*S*)-**3** (blue) and Δ-(*S*)-**4** (red) at room temperature in CH_2Cl_2 solutions (solid lines) and in 2-MeTHF matrix at 77 K (dashed lines) and picture of the green luminescence of Λ-(*S*)-**3** at 77k excited at 365 nm (right).

Table S1. Non-polarized photophysical data including luminescence quantum yields (averaged values) and excited state lifetimes for the reported iridium complexes in degassed dichloromethane solution, at 77K and 298 K.

Compound	Absorption λ_{max} / nm (ε / M^{-1} nm^{-1})	Emission λ_{max} / nm	ϕ^a	τ / ns	Emission 77 K[b]		E^{00} eV
					λ_{max} / nm	τ / ns	
Δ-(*S*)-**4**	267 (25700), 402 (2900), 478 (520)	508, 520 (shoulder)	0.01[a]	851	487, 522, 558 (shoulder)	4400	2.55
Λ-(*S*)-**3**	267 (26100), 404 (3070), 480 (800)	508, 518(shoulder)	0.01[a]	1048	487, 522, 558 (shoulder)	4500	2.55

[a]Relative to $[Ru(bpy)_3]Cl_2$ as the standard (Φ_{lum} = 0.042) in degassed aqueous solution. [b]In 2-methyltetra-hydrofuran.

4.3. Circularly Polarized Luminescence (CPL)

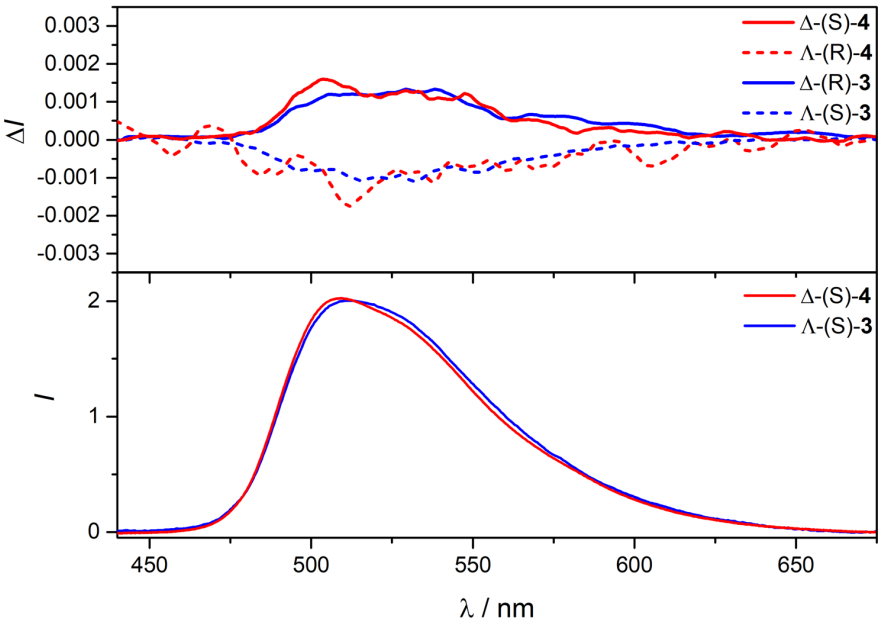


Figure S19: Top: Circularly polarized luminescence spectra of Λ-(*S*)-**3** and Δ-(*R*)-**3** (blue, dotted and solid lines, respectively) and of Δ-(*S*)-**4** and Λ-(*R*)-**4** (red, solid and dotted lines, respectively); bottom: total luminescence spectra of Λ-(*S*)-**3** (blue) and Δ-(*S*)-**4** (red) recorded in CH_2Cl_2 solution at 298 K (~10^{-5} M).

4.4. Electronic Circular Dichroism (ECD)

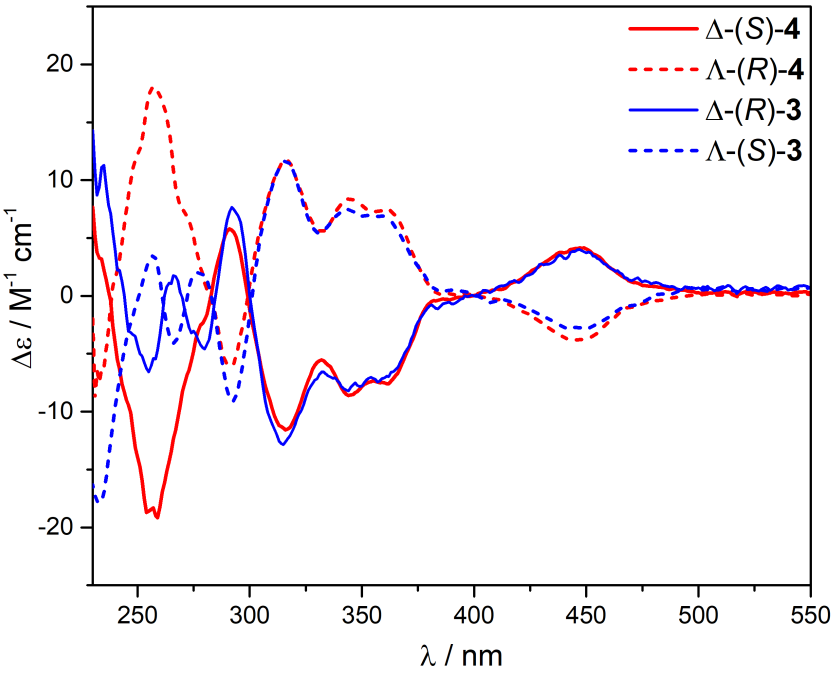


Figure S20: ECD spectra of Λ-(*S*)-**3** and Δ-(*R*)-**3** (blue, dotted and solid lines, respectively) and of Δ-(*S*)-**4** and Λ-(*R*)-**4** (red, solid and dotted lines, respectively) recorded in CH_2Cl_2 solution at 298 K (~10^{-5} M).

Calculated ECD spectra were obtained from Time-Dependent Density Functional Theory (TD-DFT) calculations carried out with Gaussian 09 program. To simulate the spectra, 60 excited states were computed.

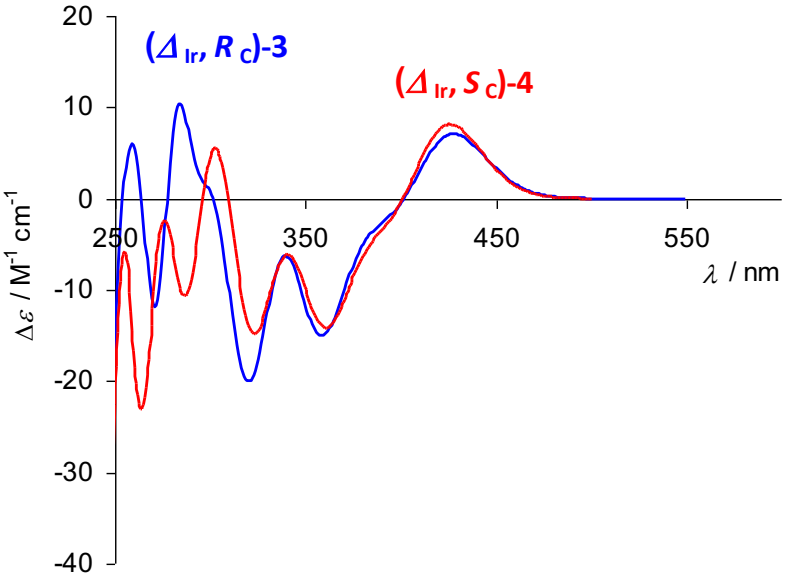
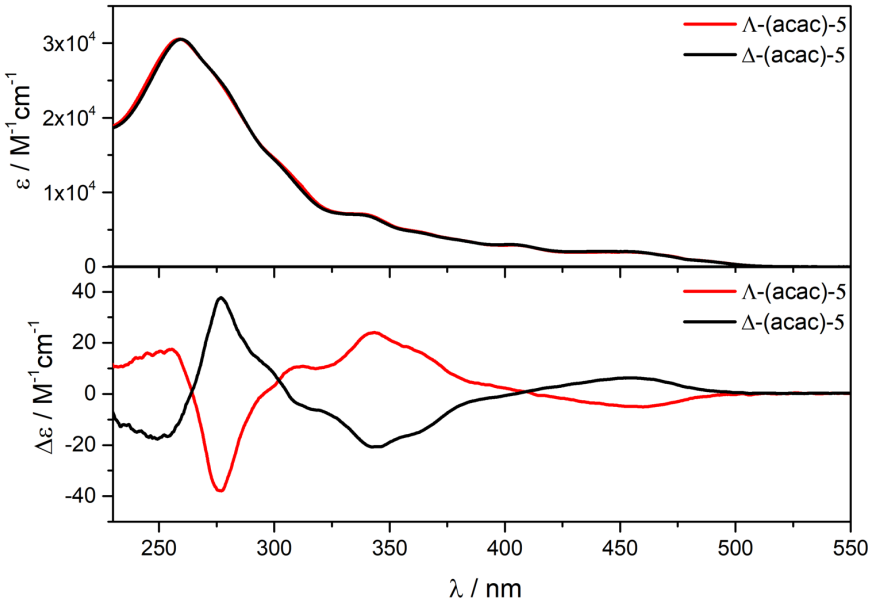


Figure S21. a) Theoretical ECD spectra of (Δ_{Ir}, R_C)-**3** and (Δ_{Ir}, S_C)-**4** computed at SMD(DCM)-B3LYP/SDD+f(Ir), 6-31G**(H,C,N,O) level of theory by taking into account solvent effect by SMD model.



Δ–(acac)-**5**: $[\alpha]_D^{23}$ = -53 (± 5 %) (CH_2Cl_2, $1.0 \cdot 10^{-4}$ mol·L^{-1})

Λ–(acac)-**5**: $[\alpha]_D^{23}$ = +52 (± 5 %) (CH_2Cl_2, $1.0 \cdot 10^{-4}$ mol·L^{-1})

Figure S22. UV-vis (top) and ECD (bottom) spectra of Λ-(acac)-**5** and Δ-(acac)-**5** (red and black solid lines, respectively) recorded in CH_2Cl_2 solution at 298 K (~10^{-5} M).

4.5. Vibrational Circular Dichroism (VCD)

IR and VCD spectra of enantiopure complexes **3** and **4** were recorded on a Jasco FSV-6000 spectrometer in CD_2Cl_2 in a 200 microns cell and at respective concentrations of 0.04 M, and 0.09 M.

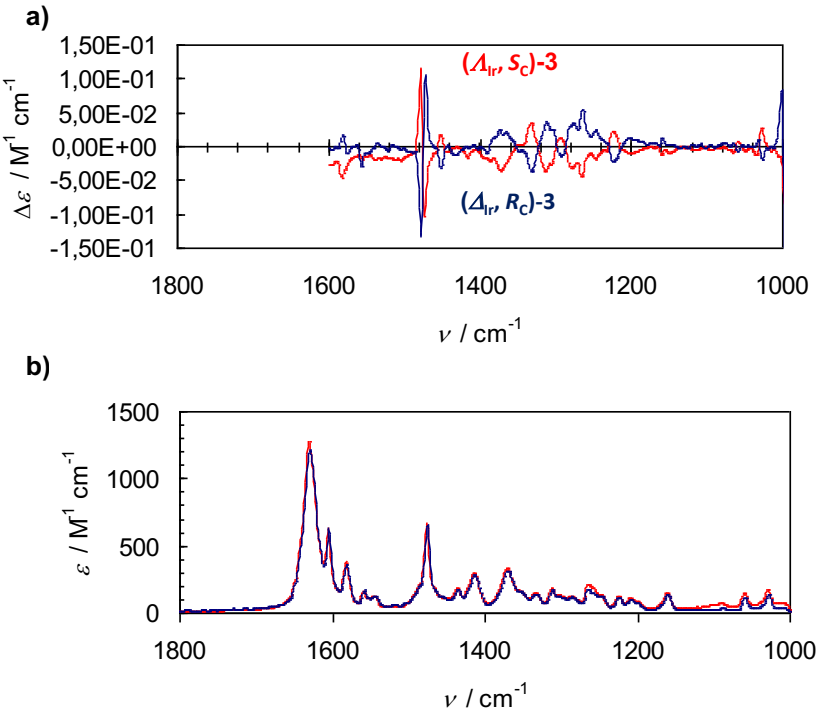


Figure S23. a) Experimental VCD and b) IR spectra of (Λlr, Sc)-**3** (red) and (Λlr, Rc)-**3** (blue) in CD_2Cl_2 (C 0.04 M, path-length 0.2 mm).

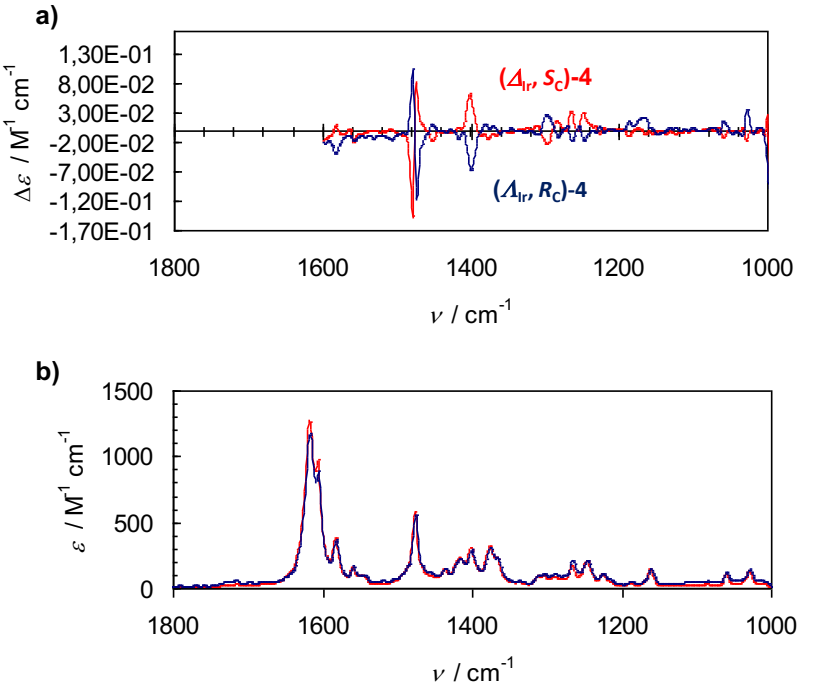


Figure S24. a) Experimental VCD and b) IR spectra of (Λlr, Sc)-4 (red) and (Λlr, Rc)-4 (blue) in CD_2Cl_2 (C 0.09 M, path-length 0.2 mm).

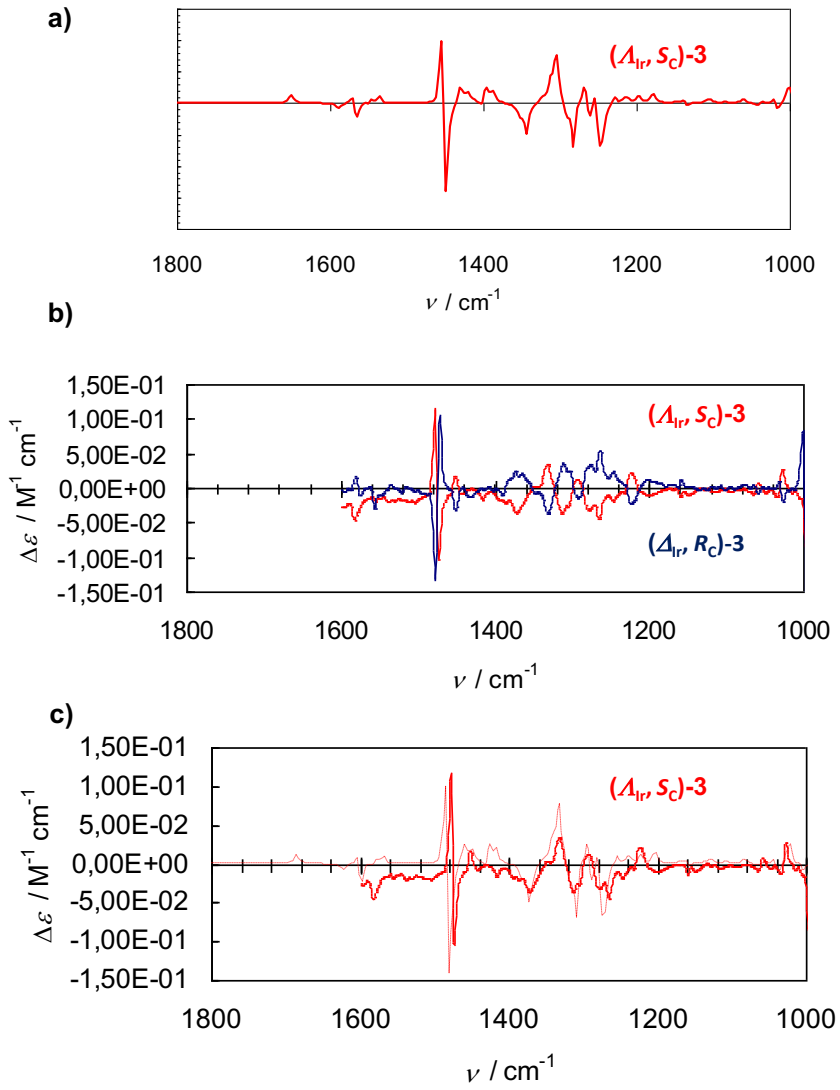


Figure S25. a) Theoretical VCD spectrum of (Λ_{Ir}, S_C)-**3** computed at SMD(CH_2Cl_2)-B3LYP/SDD+f(Ir),6-31G**(H,C,N,O) level of theory by taking into account solvent effect by SMD model. Energies have been scaled by a factor of 0.98. b) Experimental VCD of (Λ_{Ir}, S_C)-**3** (red) and (Λ_{Ir}, R_C)-3 (blue) in CD_2Cl_2 (C 0.04 M, path-length 0.2 mm). c) Superimposition of theoretical (dotted line) and experimental VCD spectra of (Λ_{Ir}, S_C)-**3**.

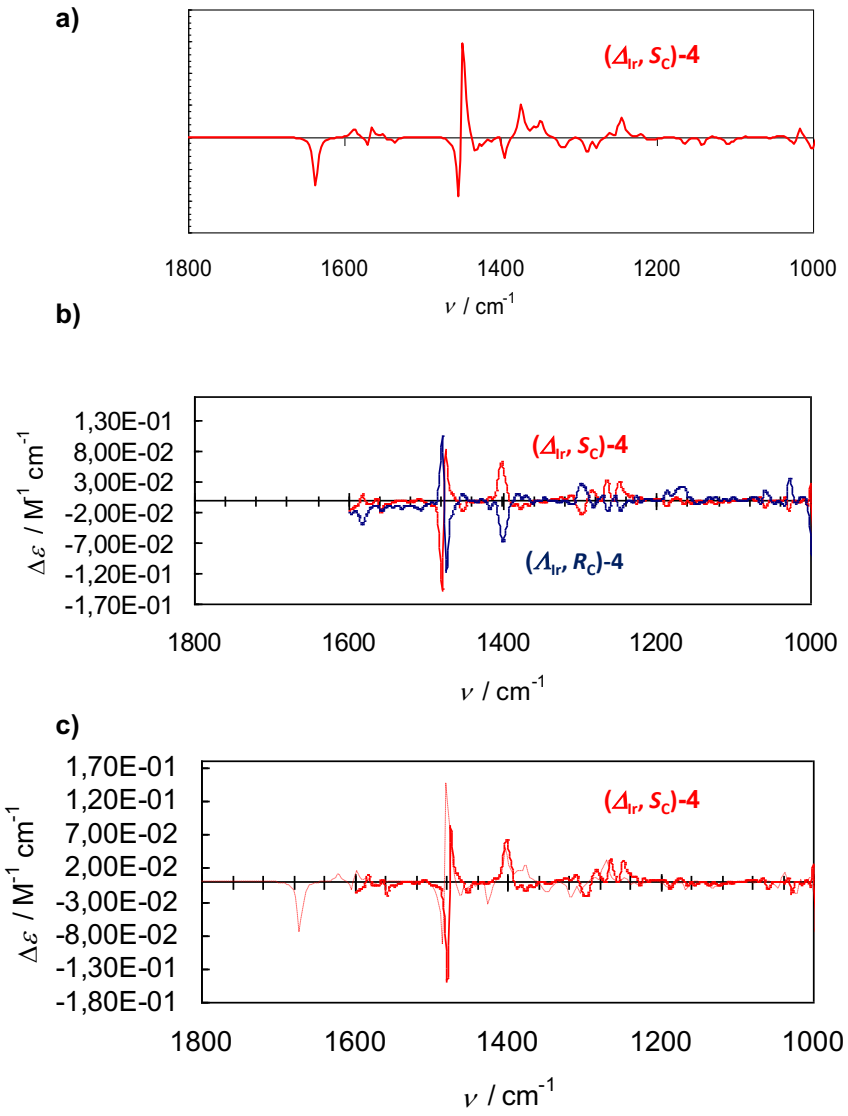


Figure S26. a) Theoretical VCD spectrum of (ΔIr, *S*C)-4 computed at SMD(CH_2Cl_2)-B3LYP/SDD+f(Ir), 6-31G**(H,C,N,O) level of theory by taking into account solvent effect by SMD model. Energies have been scaled by a factor of 0.98. b) Experimental VCD of (ΔIr, *S*C)-**4** (red) and (ΛIr, *R*C)-**4** (blue) in CD_2Cl_2 (C 0.04 M, path-length 0.2 mm). c) Superimposition of theoretical (dotted line) and experimental VCD spectra of (ΔIr, *S*C)-4.

4.6. Electrochemistry

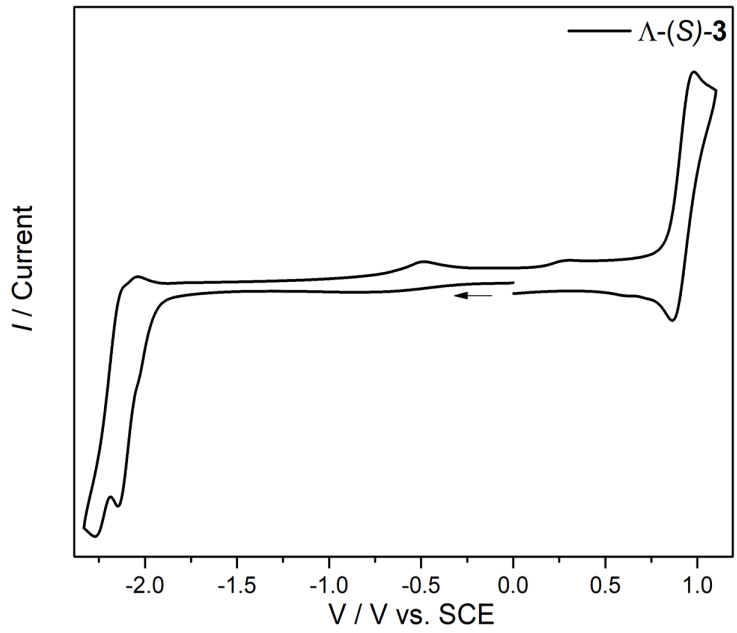
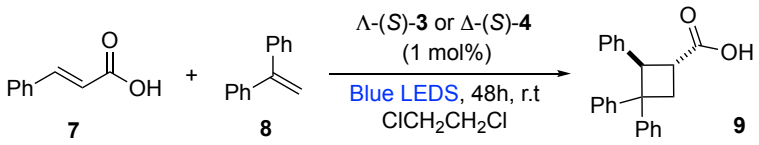


Figure S27. Cyclic voltammogram of Λ-(*S*)-**3** versus saturated calomel electrode (SCE) as the reference and 0.1 M Bu_4NPF_6 in **CH_2Cl_2** as the electrolyte.

Table S2. Oxidation potentials (E_{Ox}) of Λ-(*S*)-**3** and Δ-(*S*)-**4**, referenced *versus* saturated calomel electrode (SCE) and given in V.

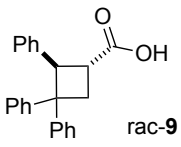
Compound	E_{Ox} Ir(IV)/Ir(III)	E_{Red} Ir(III)/Ir(II)
Λ-(*S*)-**3**	0.85	-2.10
Δ-(*S*)-**4**	0.84	-2.10

5. Visible-light induced Ir-catalyzed Intermolecular [2+2] cycloaddition



A quartz cuvette with a magnetic stir bar was charged with cinnamic acid 7 (0.2 mmol, 1.0 equiv.), 1,1-diphenylethylene 8 (1 mmol, 5.0 equiv.), catalyst (1 mol%) and dichloroethane (2 mL). The mixture was bubbled with Ar for 10 minutes, then sealed and irradiated at room temperature with 20W blue LED (λ_{max} = 460 nm) for 72 hours. The solvent was removed under reduced pressure. The desired product was purified on silica gel (DCM/MeOH 99:1 as eluent) as a white powder with 95% yield (64 mg, 0.195 mmol).

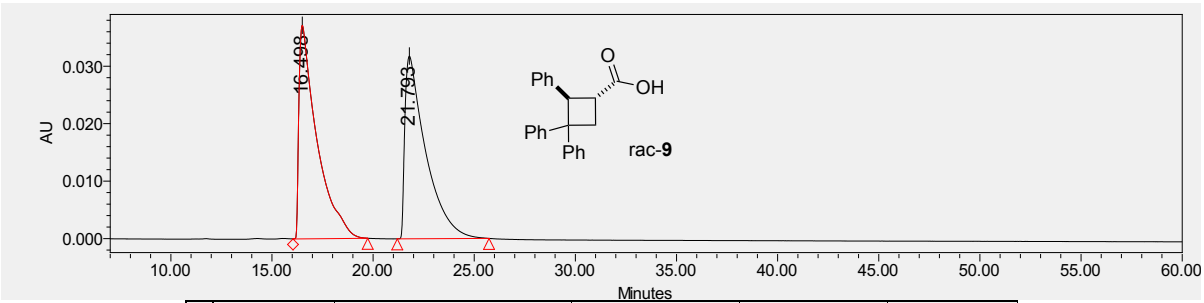
2,3,3-triphenylcyclobutane-1-carboxylic acid: (**9**)[4]



^{1}H NMR (400 MHz, CD_2Cl_2): δ(ppm): 7.39 – 7.31 (m, 4H), 7.27 – 7.12 (m, 7H), 7.03 – 6.92 (m, 4H), 4.59 (d, *J* = 10.5 Hz, 1H), 3.60 (m, 1H), 3.42 (dd, *J* = 11.6, 8.3 Hz, 1H), 2.73 (t, *J* = 11.1 Hz, 1H). **^{13}C NMR (101 MHz, CD_2Cl_2):** δ (ppm): 150.6, 141.3, 138.3, 128.4, 128.7, 128.5, 128.0, 127.9, 127.1, 126.3, 126.1, 77.36, 54.2, 53.0, 39.3. 34.4.

HPLC Analyses

The analyses were performed with a Daicel Chiralpack IA (250 x 4.6 mm) HPLC column on Waters system using a mobile phase composed of Hexane/DCM/EtOH (50/50/0.6 v/v/v). The column temperature was 20 °C and UV-absorption was measured at 254 nm.



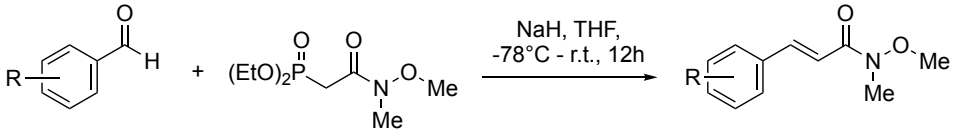
	Name	Retention Time	Area	% Area	Height
1	**9**	16.498	2290102	50.19	37159
2	**9**	21.793	2273080	49.81	31789

Figure S28. HPLC trace for *rac*-**9**

[4] T. Lei, C. Zhou, M.-Y. Huang, L.-M. Zhao, B. Yang, C. Ye, H. Xiao, Q.Y. Meng, V. Ramamurthy, C.-H. Tsung and L.-Z. Wu, *Angew. Chem. Int. Ed.* 2017, **56**, 15407–15410.

6. Friedel Craft alkylation

6.1. General procedure for the synthesis of the Weinreb Amide



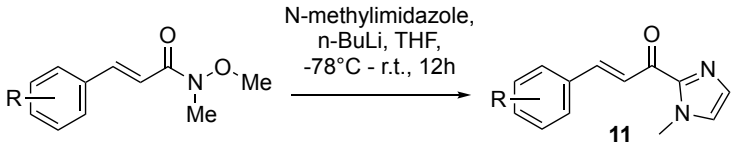
In a flame-dried round-bottomed flask, was added diethyl (2-(methoxy(methyl)amino)-2-oxoethyl)phosphonate (1.2 equiv.) in distilled THF (c = 0.4 M). At room temperature, sodium hydride (60% in oil, 1.2 equiv.) was added portionwise and the mixture was stirred under argon until the end of the bubbling. The mixture was cooled down to -78°C and the aldehyde (1.0 equiv.) in THF solution (c = 0.4 M) was added dropwise. The mixture was stirred for one hour at -78°C, then warm up to room temperature and stirred overnight under Argon. The mixture was quenched with water and layers were separated. The organic layer was washed with $NaHCO_3$ saturated solution and brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure.

(E)-3-([1,1'-biphenyl]-4-yl)-*N*-methoxy-*N*-methylacrylamide was purified by silica gel chromatography (dichloromethane) as a yellow powder with 95% yield (835 mg from 3.95 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 7.79 (d, *J* = 16.0 Hz, 1H), 7.67-7.60 (m, 6H), 7.48-7.43 (m, 2H), 7.39-7.35 (m, 1H), 7.08 (d, *J* = 16.0 Hz, 1H), 3.79 (s, 3H), 3.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm): 167.1, 143.1, 142.7, 140.4, 134.3, 129.0, 128.7, 127.9, 127.6, 127.2, 115.8, 62.1, 32.7. HRMS (ESI): m/z = 290.1151, calcd. for $C_{17}H_{17}NO_2Na$ $[M+Na]^+$: 290.1154 (1 ppm). m.p. : 125-128°C.

(E)-3-(3-isopropylphenyl)-*N*-methoxy-*N*-methylacrylamide[5] was purified by silica gel chromatography (pentane/diethyl ether 60:40) as a yellow powder with 70% yield (232 mg from 3.24 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 7.73 (d, *J* = 16.0 Hz, 1H), 7.43-7.39 (m, 1H), 7.34-7.28 (m, 1H), .726-7.22 (m, 1H), 7.02 (d, *J* = 16.0 Hz), 3.77 (s, 3H), 3.32 (s, 3H), 2.99-2.88 (sept, *J* = 6.9 Hz, 1H), 1.27 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm): 180.6, 149.5, 144.9, 134.9, 129.3, 128.8, 128.8, 127.2, 126.7, 122.4, 36.4, 34.1, 24.0.

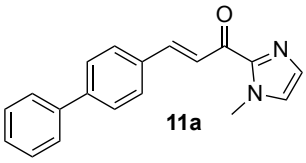
[5] S. Drissi-Amraoui, T. E. Schmid, J. Lauberteaux, C. Crévisy, O. Baslé, R. M. de Figueiredo, S. Halbert, H. Gérard, M. Mauduit, J.-M. campagne, *Adv. Synth. Catal.* 2016, **358**, 2519-2540.

6.2. General procedure for the synthesis of acylimidazoles



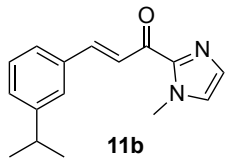
In a flame-dried schlenk, was placed *N*-methylimidazole (1.5 equiv.) in dry THF (c = 0.3 M). The solution was cooled down to -78°C and *n*-BuLi (1.6M in hexane) was added dropwise. The mixture was stirred for 20 minutes and allowed to warm up to room temperature for 10 minutes. The media was cooled down at -78°C and a solution of the weinreb amide in dry THF (c = 0.3 M) was added dropwise. The mixture was quenched by NH_4Cl saturated solution and stirred for an extra 10 minutes. The organic layer was separated and washed with $NaHCO_3$ and brine, dried over magnesium sulphate, filtered and concentrated under reduced pressure.

(E)-3-([1,1'-biphenyl]-4-yl)-N-methoxy-N-methylacrylamide: (**11a**) was purified by silica gel chromatography (pentane/diethylether 60/40) as a yellow powder with 86% yield (440 mg from 3.05 mmol).



^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.10 (d, *J* = 16.0 Hz, ^{1}H), 7.85 (d, *J* = 16.0 Hz, 1H), 7.78-7.74 (m, 2H), 7.64-7.60 (m, 4H), 7.47-7.42 (m, 2H), 7.38-7.33 (m, 1H), 7.23 (d, *J* = 1.0 Hz, 1H), 7.08 (s, 1H), 4.10 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm): 180.6, 144.2, 143.3, 143.1, 140.4, 134.1, 129.5, 129.4, 129.0, 128.0, 127.6, 127.4, 127.2, 122.8, 36.5. HRMS (ESI): m/z = 289.1335, calcd. for $C_{19}H_{17}NO_2$ $[M+H]^+$: 289.1337 (1 ppm). m.p.: 133-136 °C.

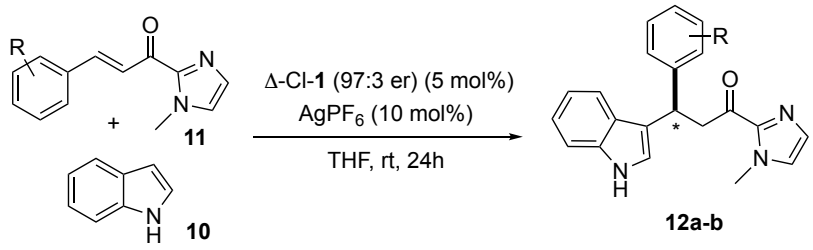
(E)-3-(3-isopropylphenyl)-1-(1-methyl-*1H*-imidazol-2-yl)prop-2-en-1-one (**11b**)[5] was purified by precipitation in pentane as a yellow powder with 82% yield (171 mg from 0.729 mmol).



^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 8.06 (d, *J* = 16.0 Hz, 1H), 7.83 (d, *J* = 16.0 Hz, 1H), 7.57-7.50 (m, 2H), 7.33-7.23 (m, 4H), 7.08 (m, 1H), 4.12 (s, 3H), 2.97-2.90 (sept, *J* = 6.9 Hz, 1H), 1.28 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm): 180.7, 149.6, 144.2, 144.0, 135.0, 129.4, 129.0, 128.9, 127.3, 126.8, 126.8, 122.5, 36.5, 34.2, 24.1.

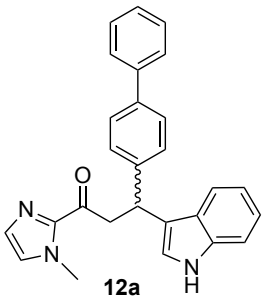
[5] S. Drissi-Amraoui, T. E. Schmid, J. Lauberteaux, C. Crévisy, O. Baslé, R. M. de Figueiredo, S. Halbert, H. Gérard, M. Mauduit, J.-M. campagne, *Adv. Synth. Catal.* 2016, **358**, 2519-2540.

6.3. Chiral Lewis-acid catalyzed Friedel Craft alkylation



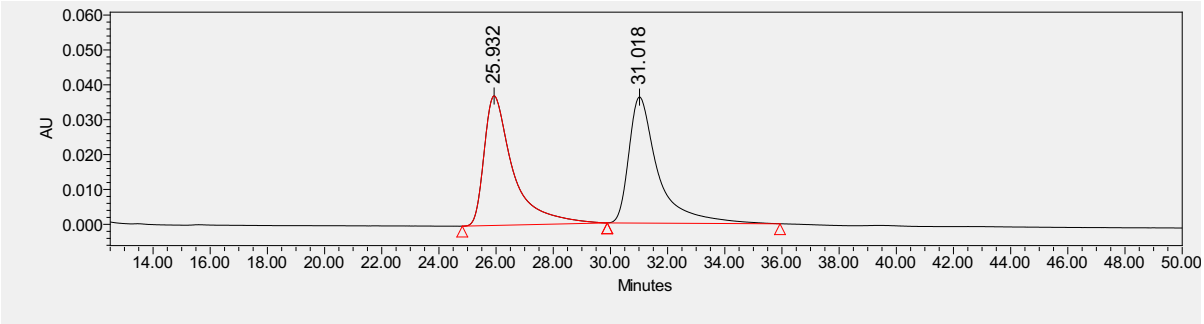
In a round-bottomed flask, to a solution of Δ-(Cl)-**1** (0.005 mmol, 5 mol%) in distilled THF (1 mL) under Argon, was added $AgPF_6$ (0.01 mmol, 10 mol%). After being stirred at room temperature for 10 minutes, 2-acyl imidazole (0.1 mmol, 1.0 equiv.) was added and the resulting mixture was also stirred for 10 minutes. Then, indole (0.25 mmol, 2.5 equiv.) was added at room temperature and the mixture was stirred overnight and monitored by TLC. The mixture was then concentrated under reduced pressure and the desired product was purified by silica gel chromatography (pentane:AcOEt 70:30).

3-([1,1'-biphenyl]-4-yl)-3-(1H-indol-3-yl)-1-(1-methyl-1H-imidazol-2-yl)propan-1-one (**12a**)



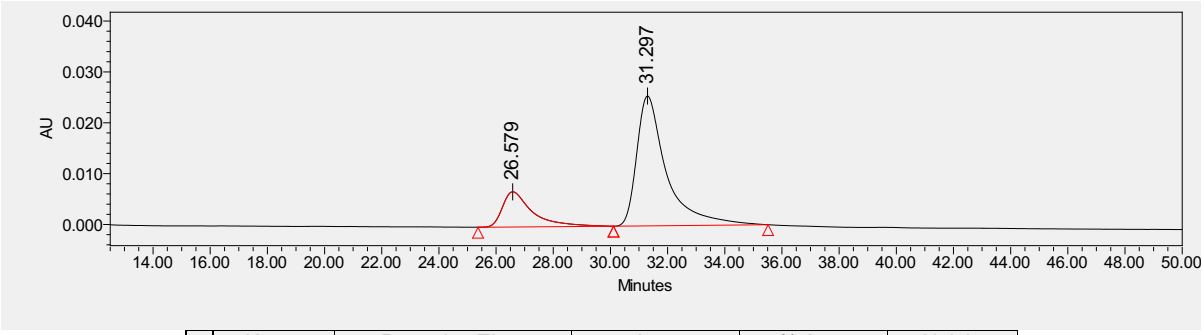
12a

Brown oil (25 mg, 68% yield).^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 (br, 1H), 7.55 – 7.51 (m, 3H), 7.46 (m, 3H), 7.41 – 7.36 (m, 2H), 7.33 – 7.27 (m, 2H), 7.18 (dd, *J* = 2.5, 0.9 Hz, 1H), 7.16 (d, *J* = 0.9 Hz, 1H), 7.14 – 7.11 (m, 1H), 7.04 – 7.00 (m, 1H), 6.99 (d, *J* = 0.9 Hz, 1H), 5.11 (td, *J* = 7.7, 0.9 Hz, 1H), 4.04 (dd, *J* = 16.5, 7.7 Hz, 1H), 3.91 (s, 3H), 3.90 (dd, *J* = 16.5, 7.7 Hz, 1H). ^{13}C NMR (101 MHz, Methylene Chloride-d_2) δ = 190.9, 144.0, 143.3, 140.9, 138.9, 136.6, 128.9, 128.7, 128.4, 127.2, 127.1, 127.0, 126.9, 126.7, 122.1, 121.6, 119.2, 119.1, 111.1, 45.1, 37.9, 36.0, 24.7. HRMS (ESI): m/z = 428.1733, calcd. for $C_{27}H_{23}N_3ONa$ [M+Na] : 428.1734 (0 ppm). Optical rotation**:** $[\alpha]_D^{20}$ = -35.0 (c = 1, $CHCl_3$).



	Name	Retention Time	Area	% Area	Height
1	**12a**	25.932	2617720	50.56	37149
2	**12a**	31.018	2559575	49.44	36138

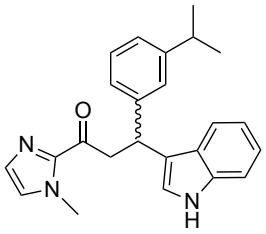
Figure S29. HPLC trace for rac-**12a**



	Name	Retention Time	Area	% Area	Height
1	**12a**	26.579	503322	21.42	6931
2	**12a**	31.297	1846316	78.58	25549

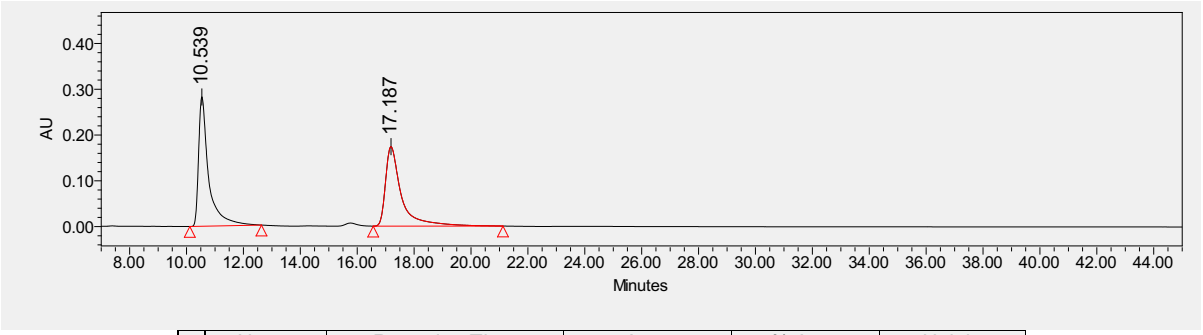
Figure S30. HPLC trace for enantioenriched **12a**

3-(1H-indol-3-yl)-3-(3-isopropylphenyl)-1-(1-methyl-1H-imidazol-2-yl)propan-1-one (**12b**)



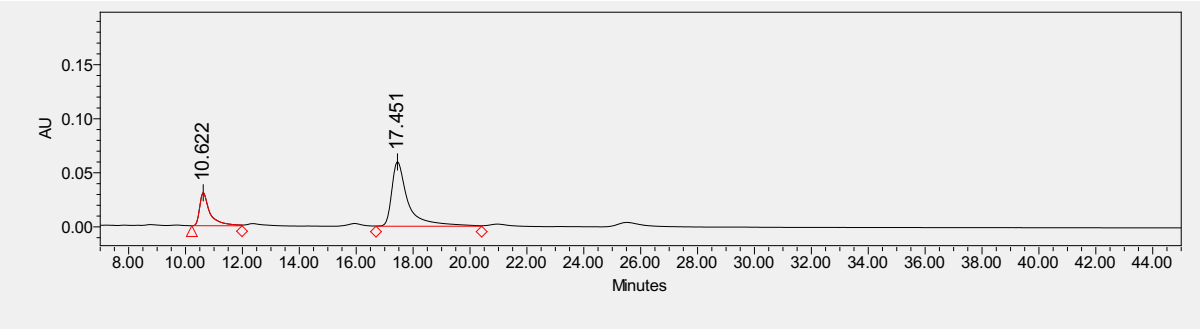
12b

Brown oil (20 mg, 55% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm): 8.16 (br, 1H), 7.51 (d, *J* = 7.9 Hz, 1H), 7.31-7.26 (m, 2H), 7.19-7.09 (m, 5H), 7.04-6.95 (m, 3H), 5.05 (t, *J* = 7.6 Hz, 1H), 4.02 (dd, *J* = 7.8, 4.1 Hz, 1H), 3.87 (s, 3H), 3.83 (dd, *J* = 7.8, 4.1 Hz, 1H), 2.82 (sept, *J* = 6.9 Hz, 1H), 1.19 (s, 3H), 1.17 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm): 191.4, 148.8, 144.4, 136.6, 129.0, 128.3, 127.0, 126.4, 125.4, 124.1, 122.0, 121.6, 119.7, 119.3, 111.0, 45.5, 38.4, 36.2, 34.2, 24.2, 24.1. HRMS (ESI): m/z = 394.1890, calcd. for $C_{24}H_{26}N_3ONa$ $[M+Na]^+$: 394.1886 (1 ppm). Optical rotation: $[\alpha]_D^{20}$ = +32.0 (c = 1, $CHCl_3$).



	Name	Retention Time	Area	% Area	Height
1	**12b**	10.539	6968473	50.78	282809
2	**12b**	17.187	6753536	49.22	173727

Figure S31. HPLC trace for rac-**12b**

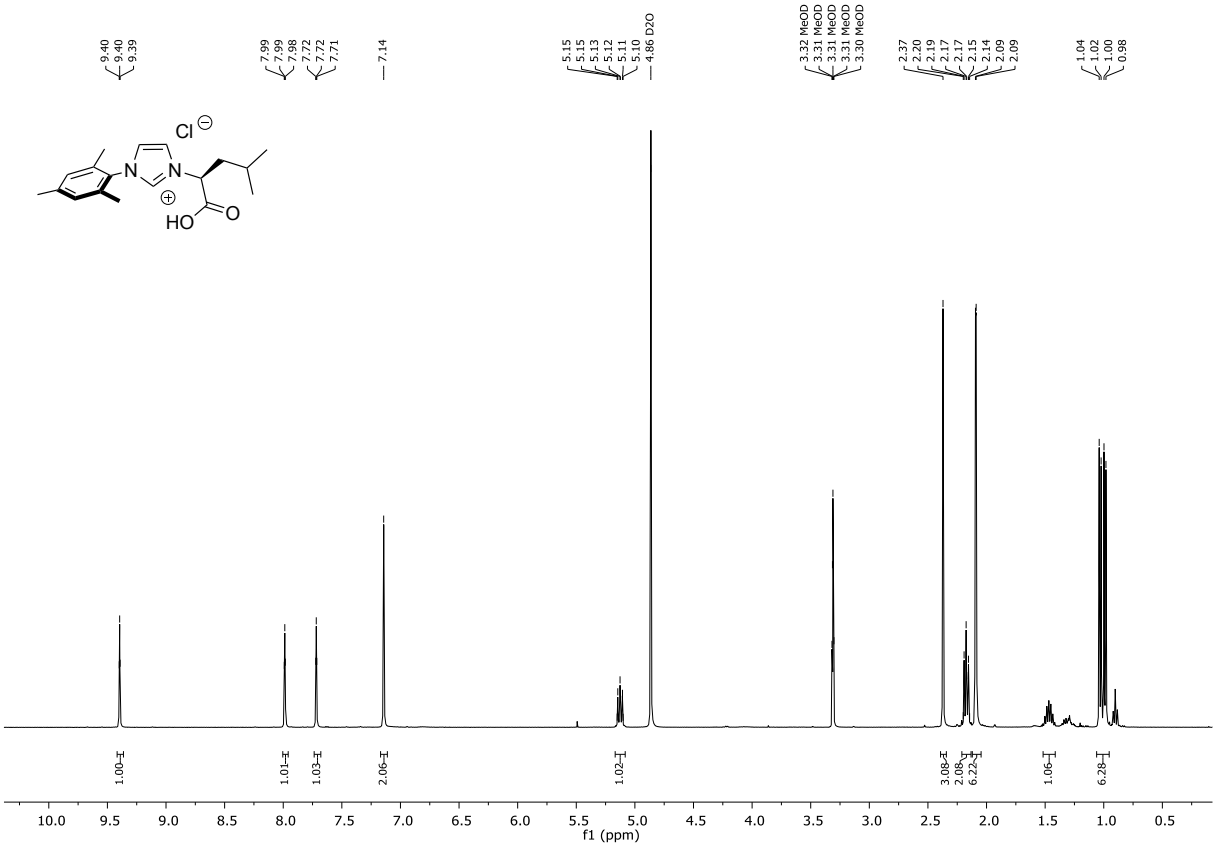


	Name	Retention Time	Area	% Area	Height
1	**12b**	10.622	775511	24.44	30491
2	**12b**	17.451	2398216	75.56	59568

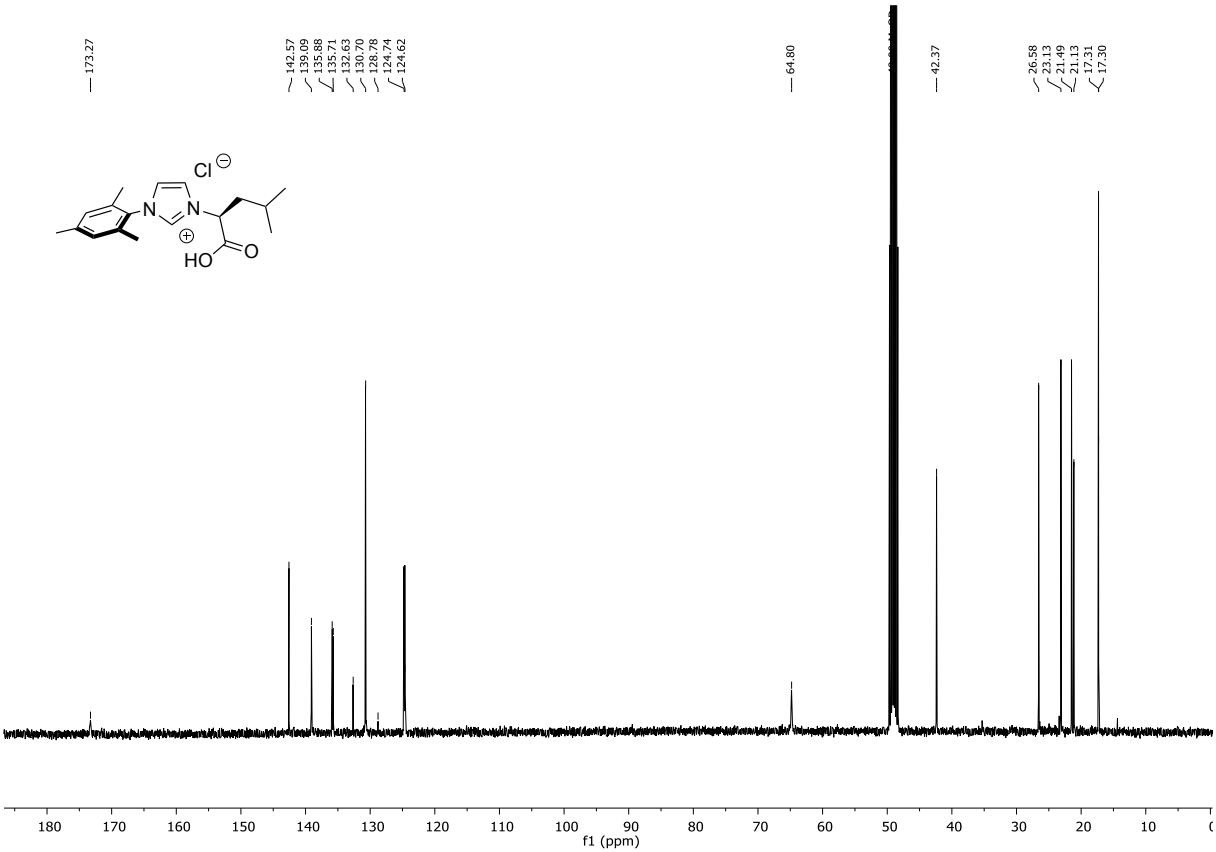
Figure S32. HPLC trace for enantioenriched **12b**

7. NMR spectra

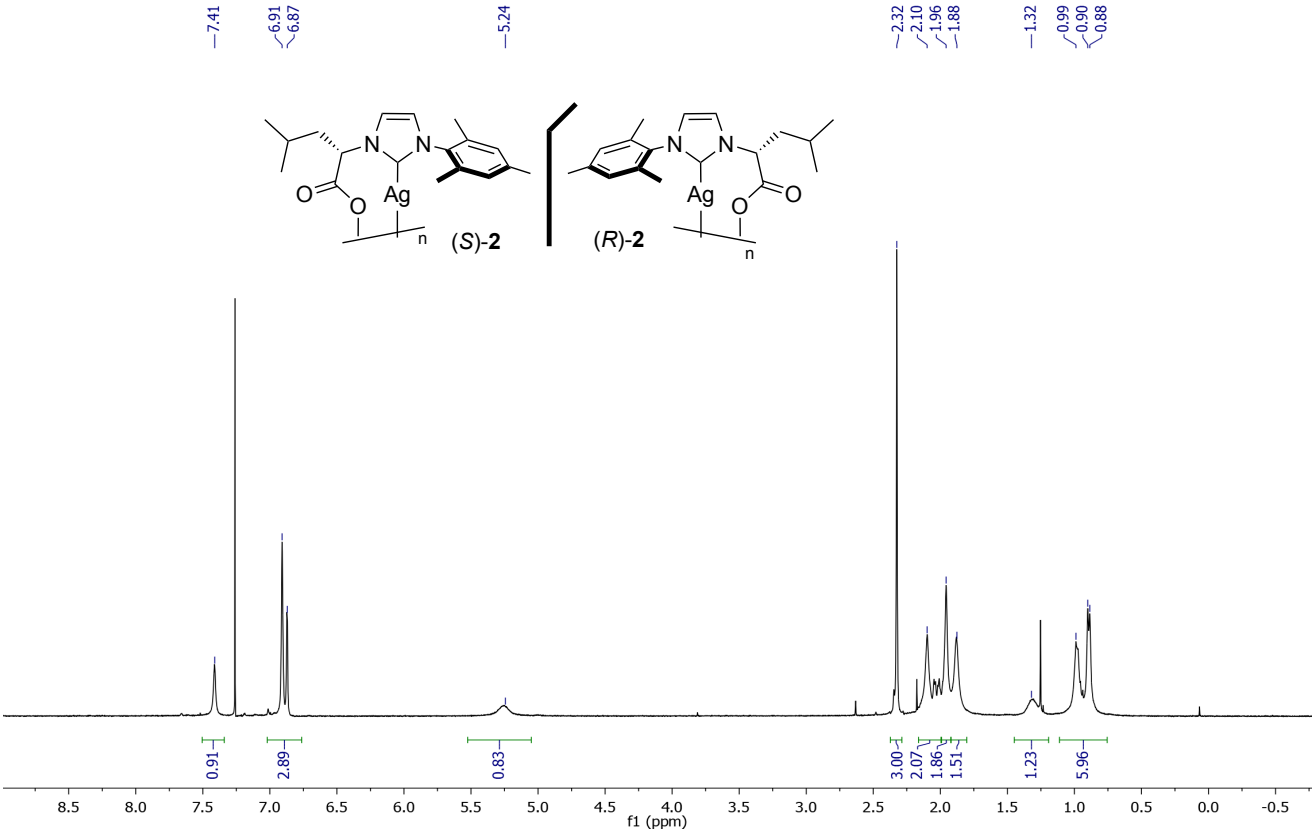
^{1}H NMR (400 MHz, MeOD):



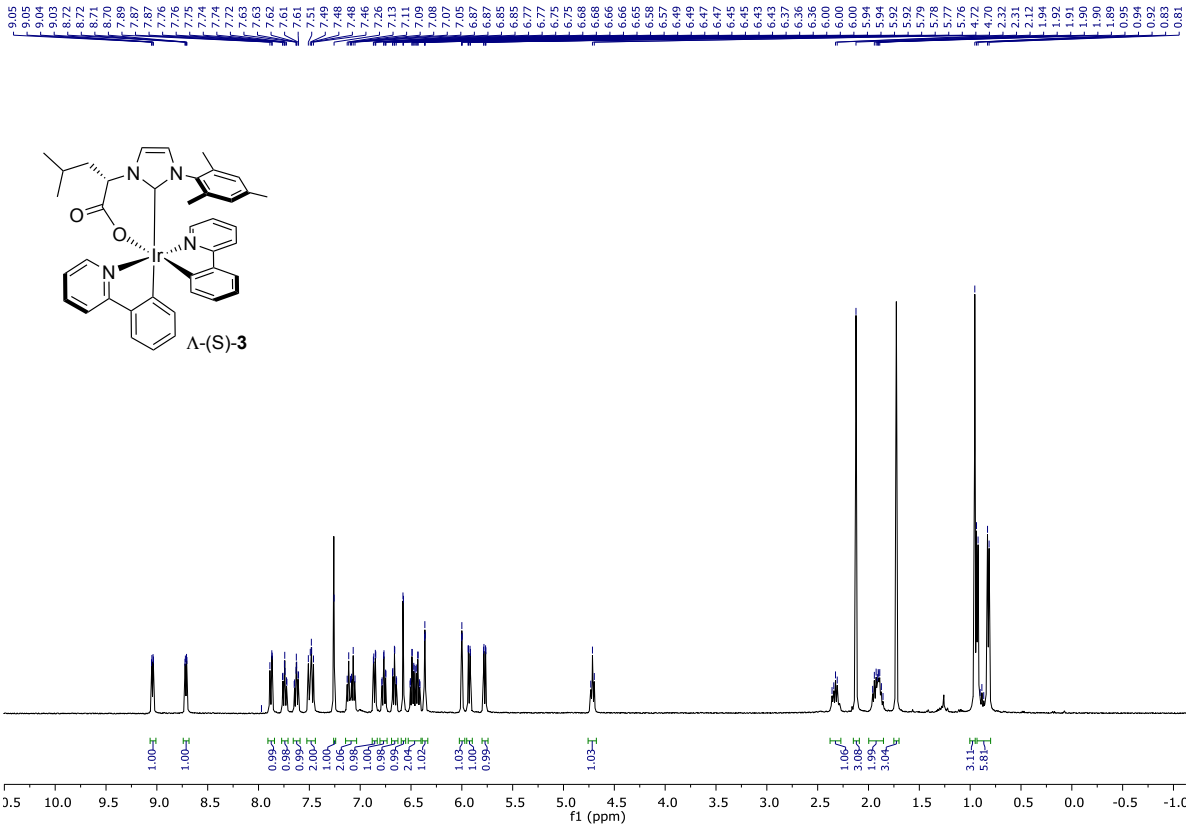
^{13}C NMR (100 MHz, MeOD):



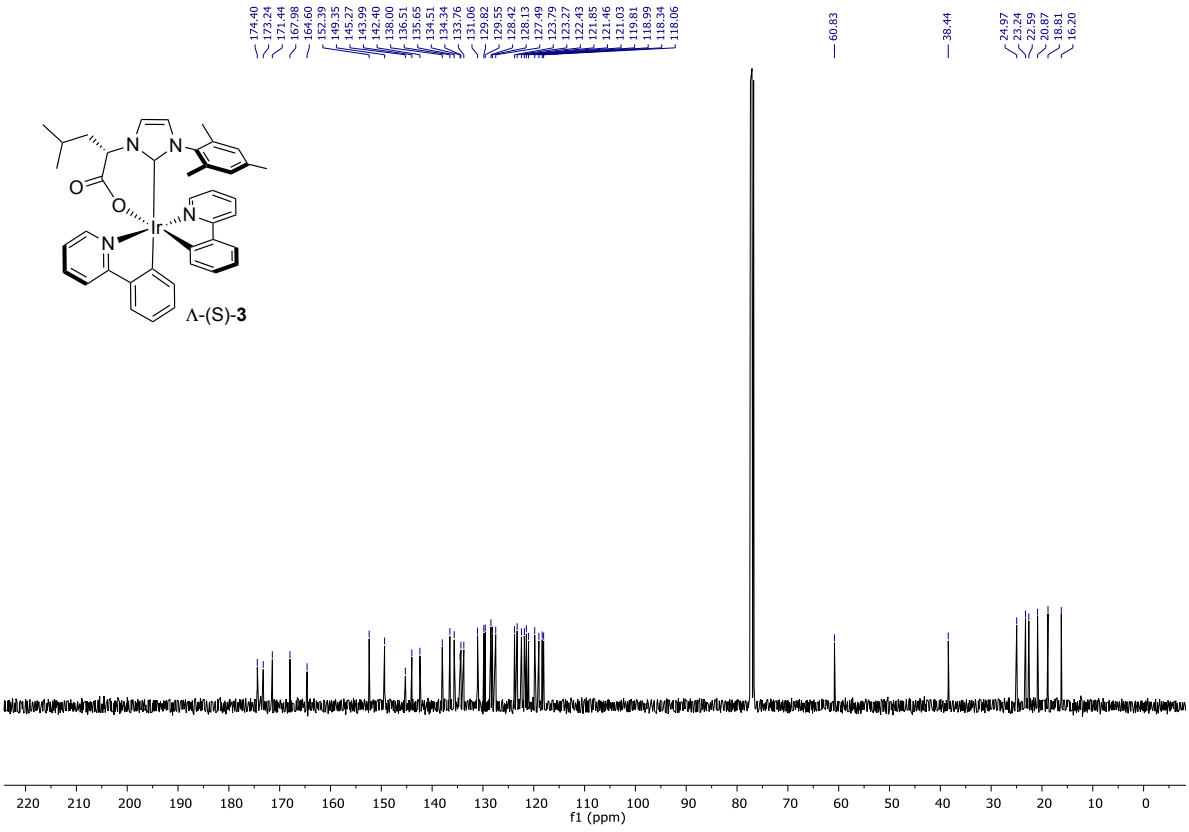
^{1}H NMR (400 MHz, $CDCl_3$):



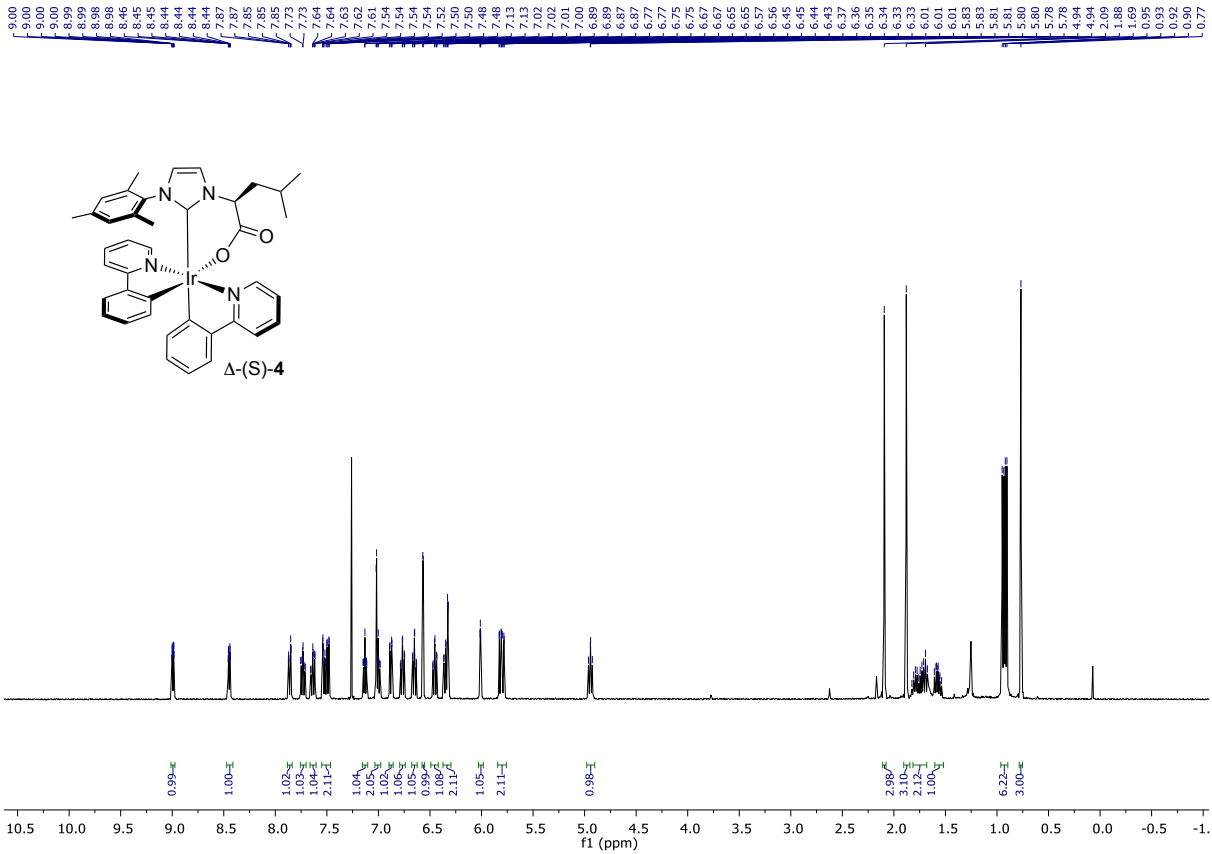
^{1}H NMR (400 MHz, $CDCl_3$):



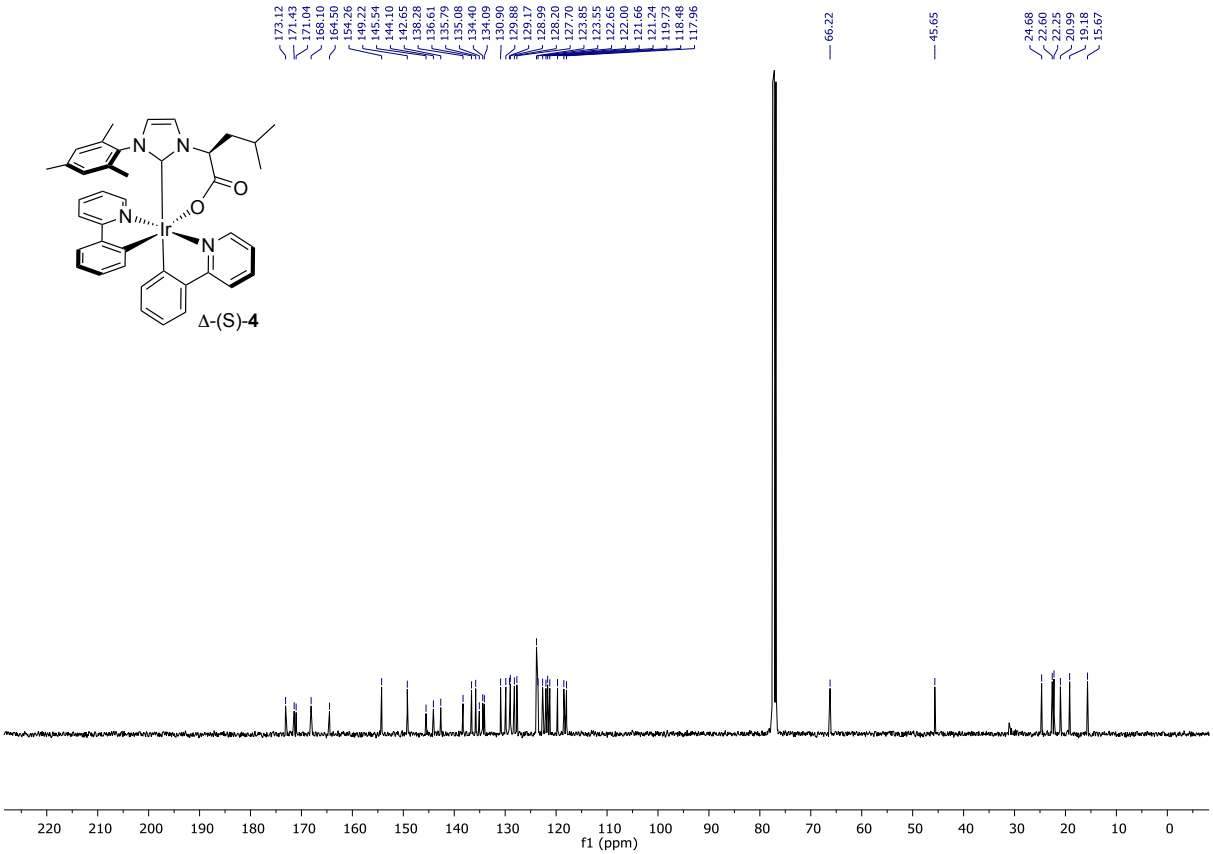
^{13}C NMR (100 MHz, $CDCl_3$):



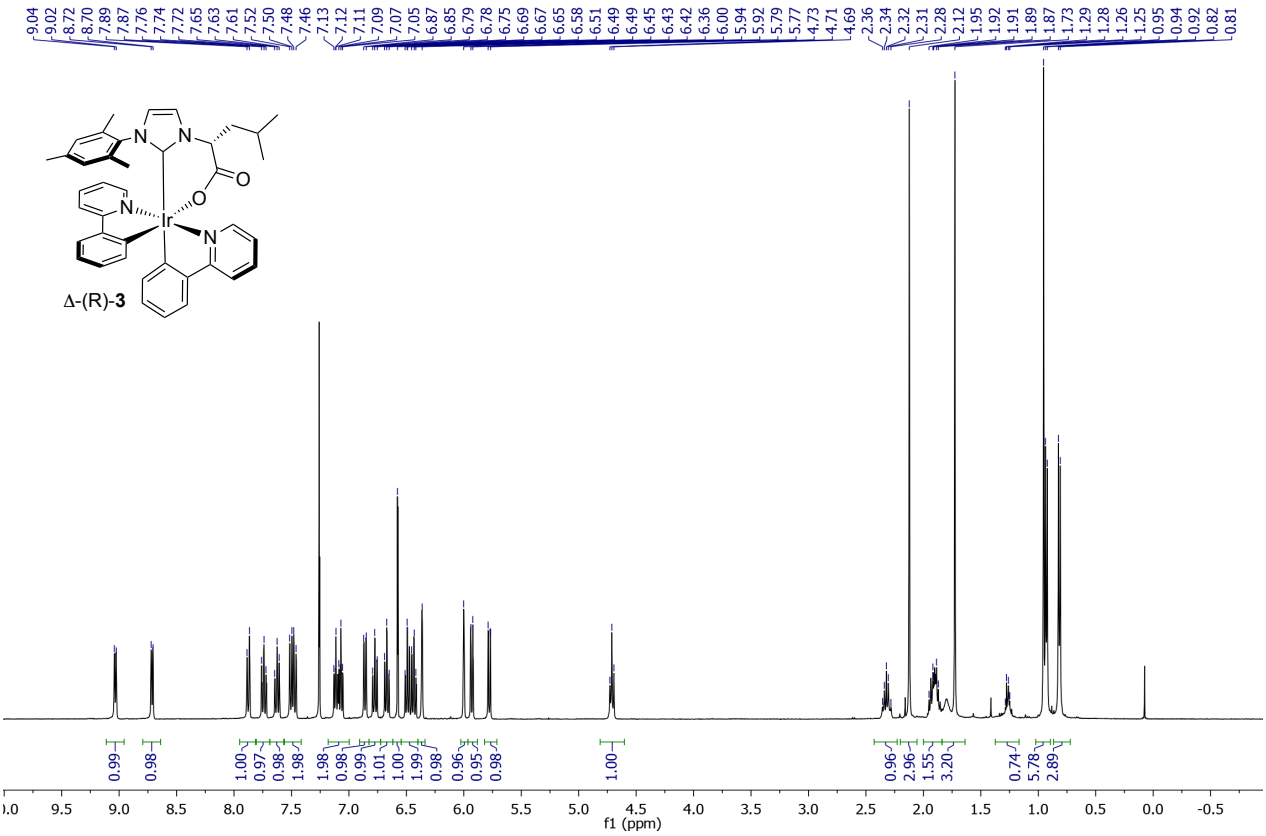
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):



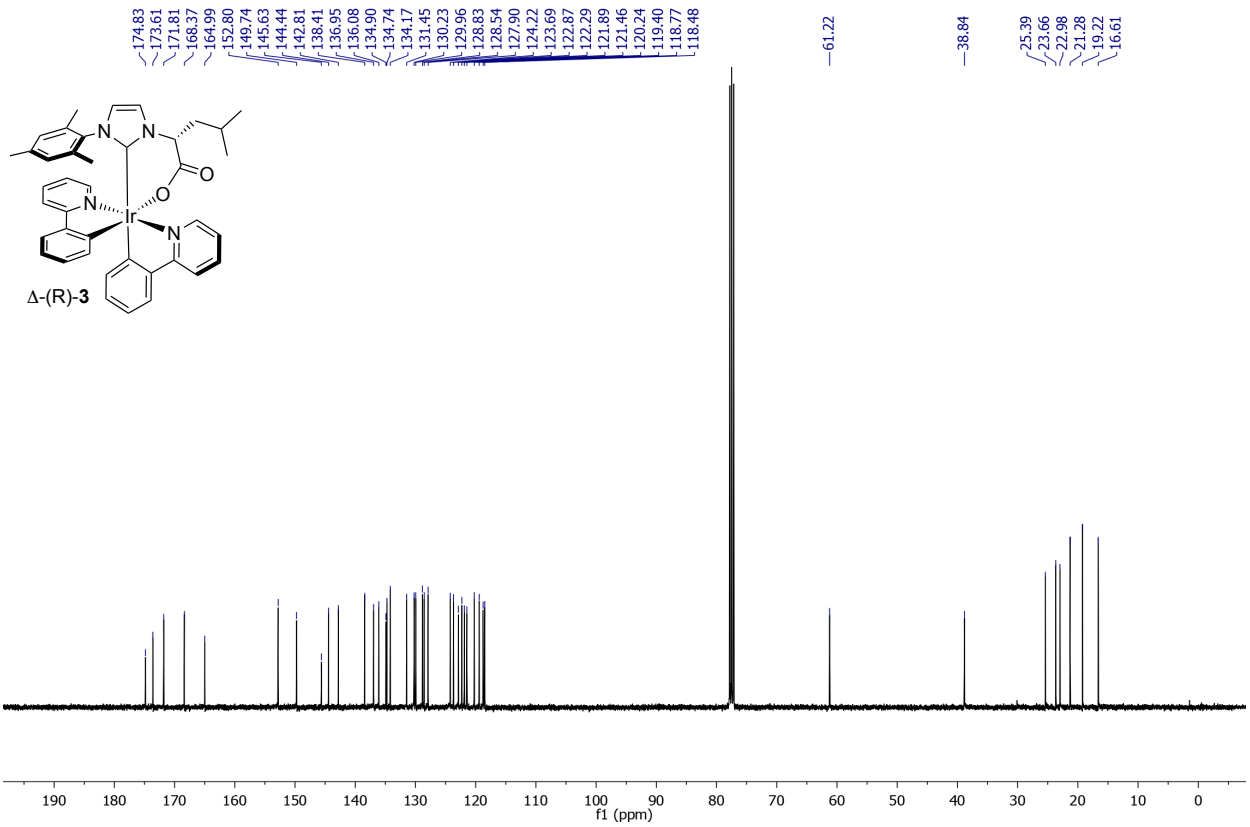
^{13}C NMR (100 MHz, $CDCl_3$):



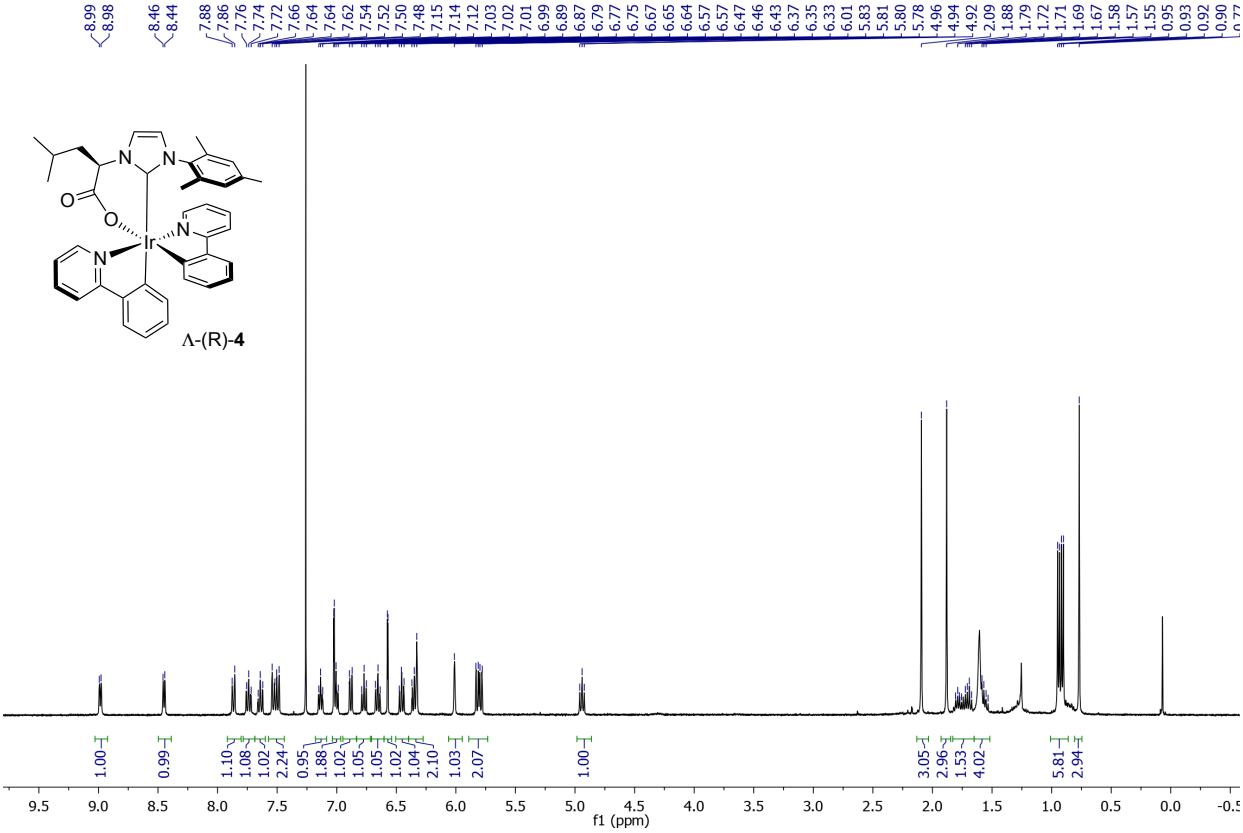
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):



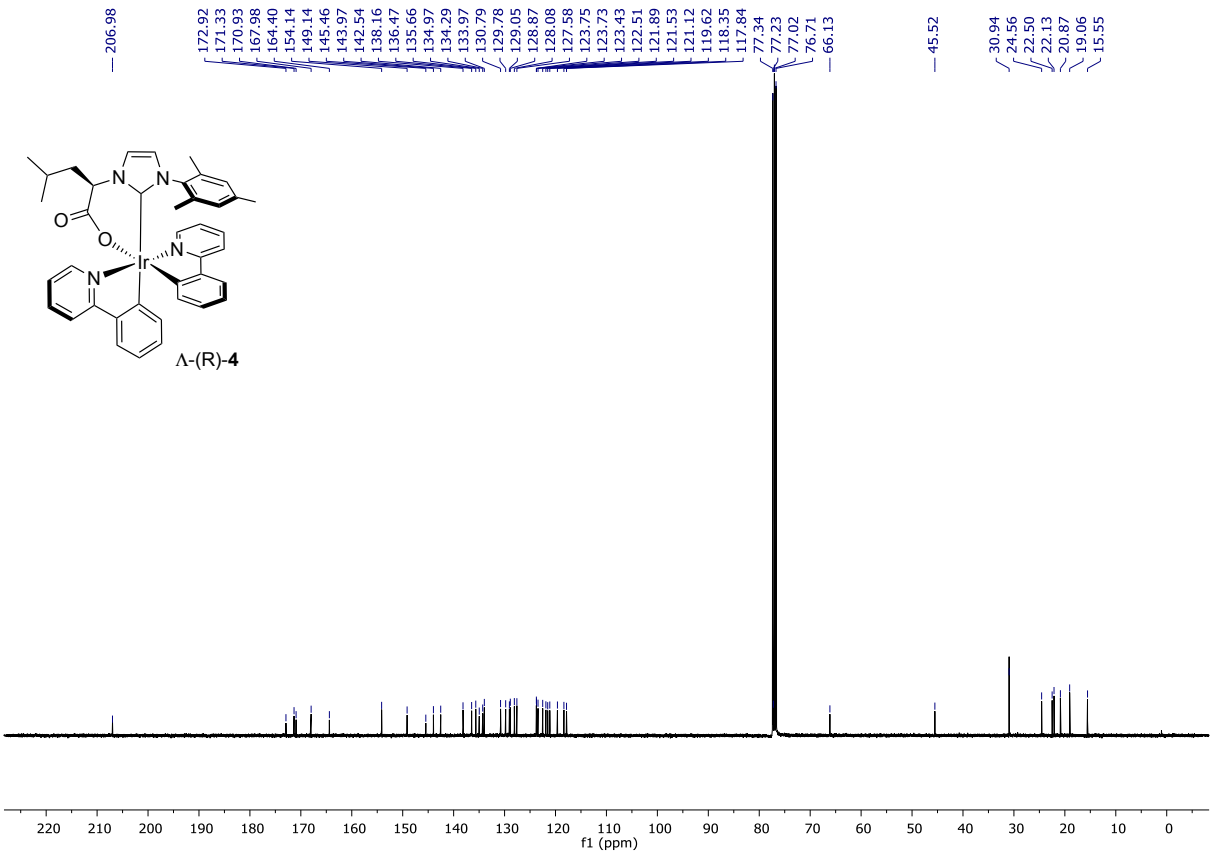
^{13}C NMR (100 MHz, $CDCl_3$):



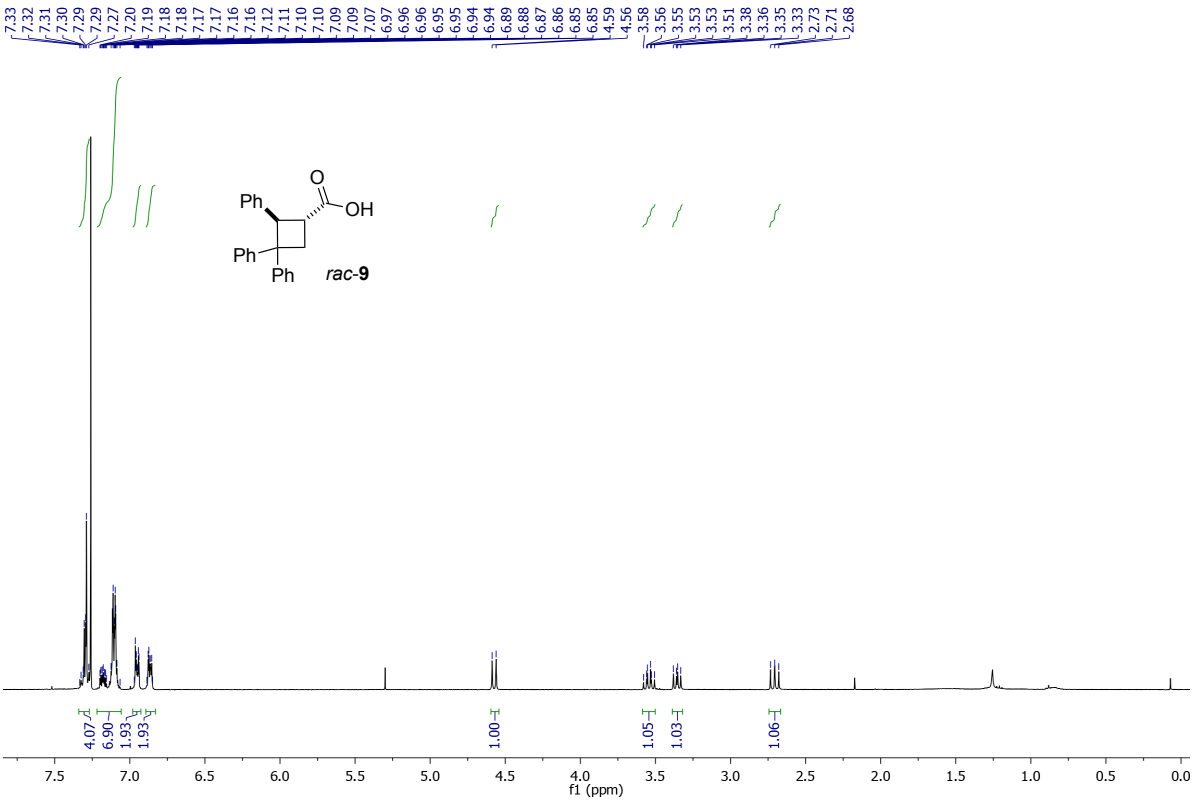
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):



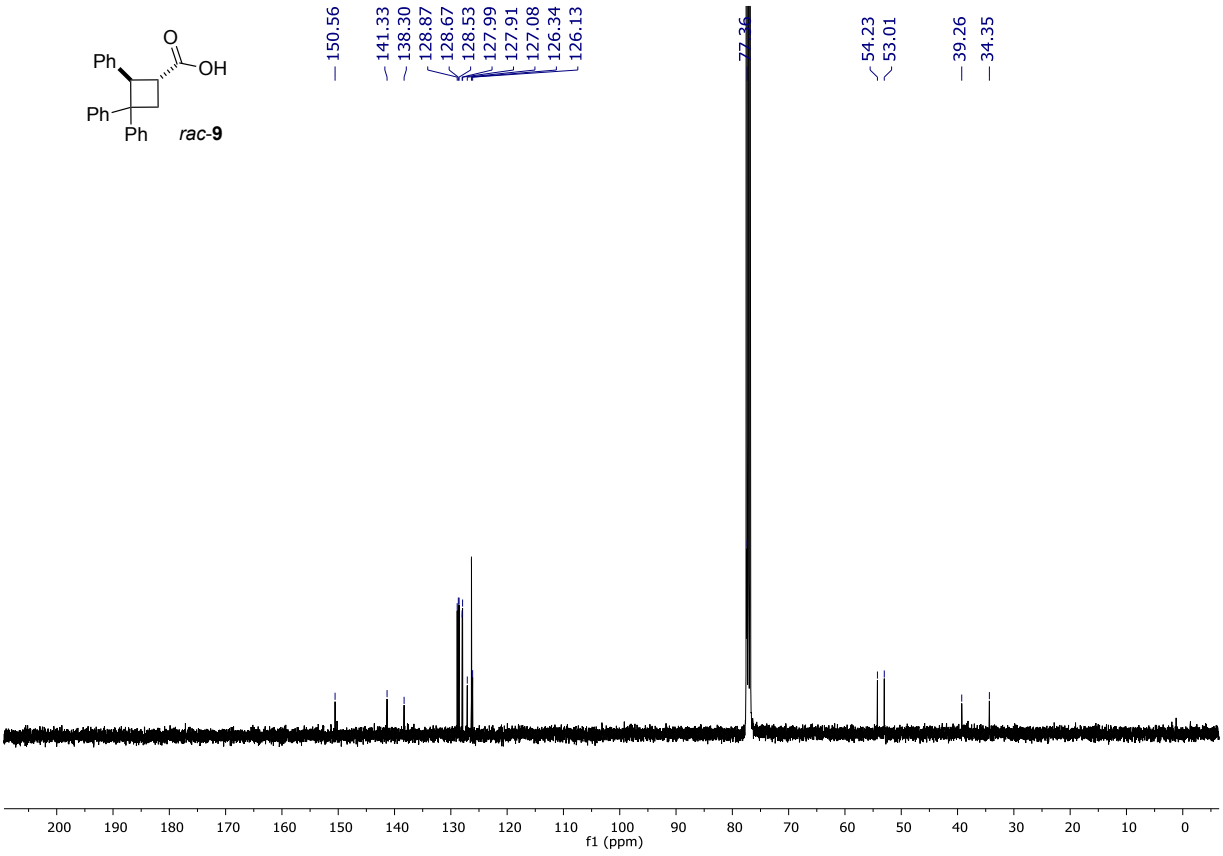
^{13}C NMR (100 MHz, $CDCl_3$):



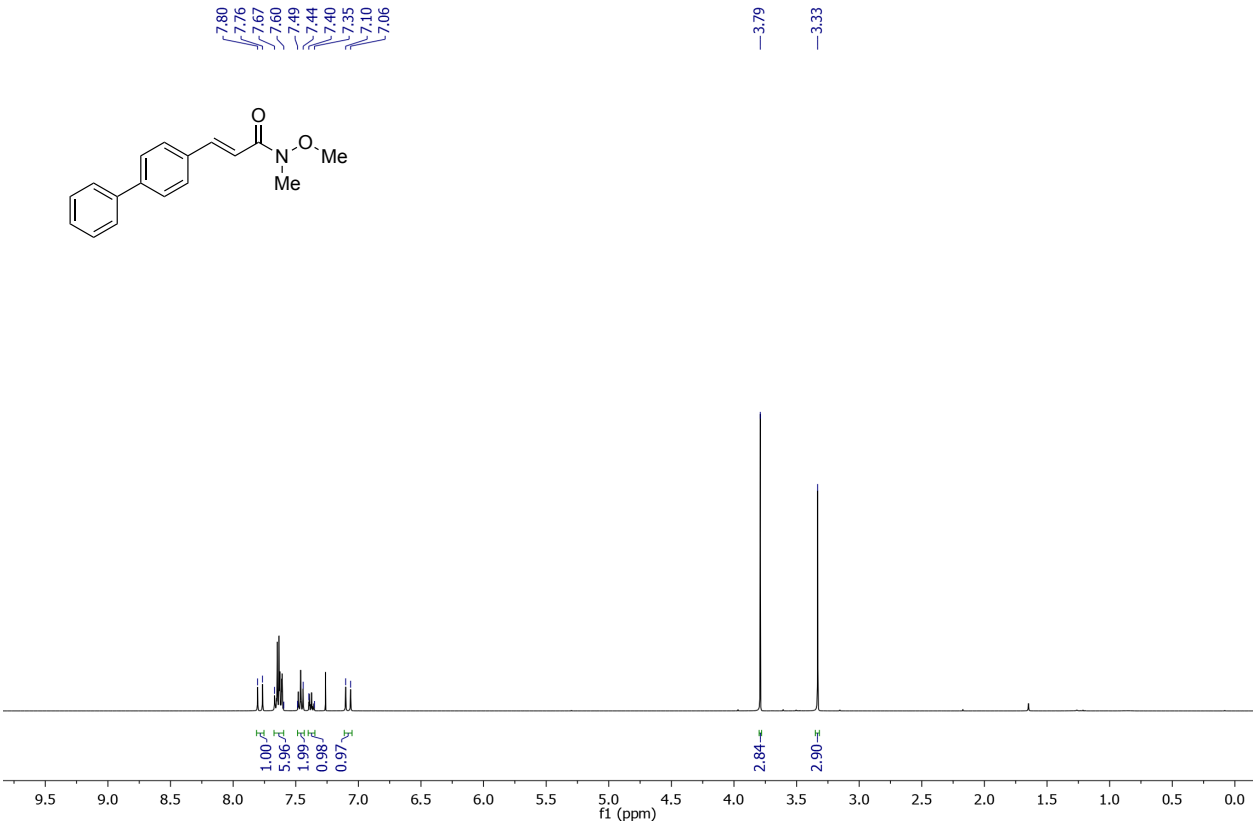
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):



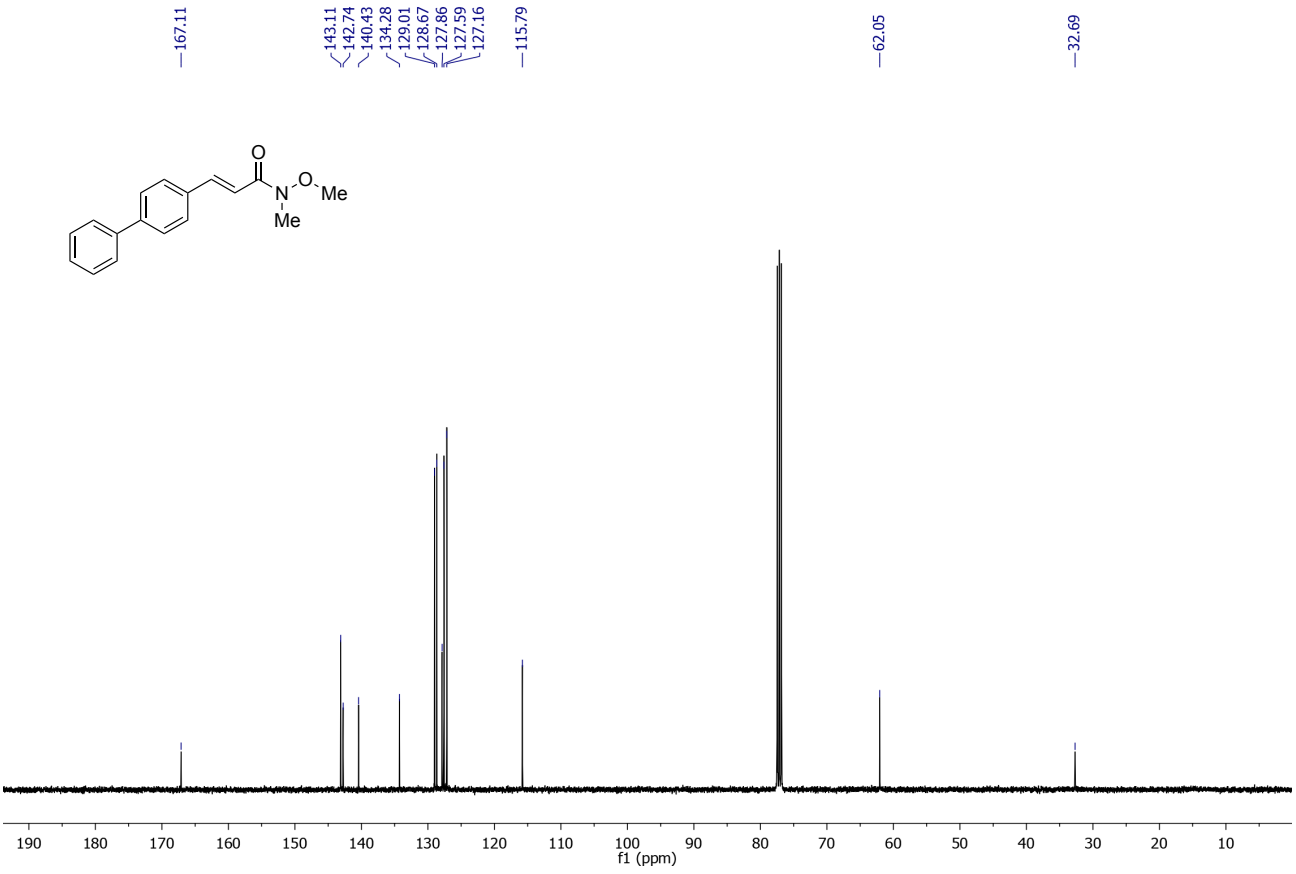
^{13}C NMR (100 MHz, $CDCl_3$):



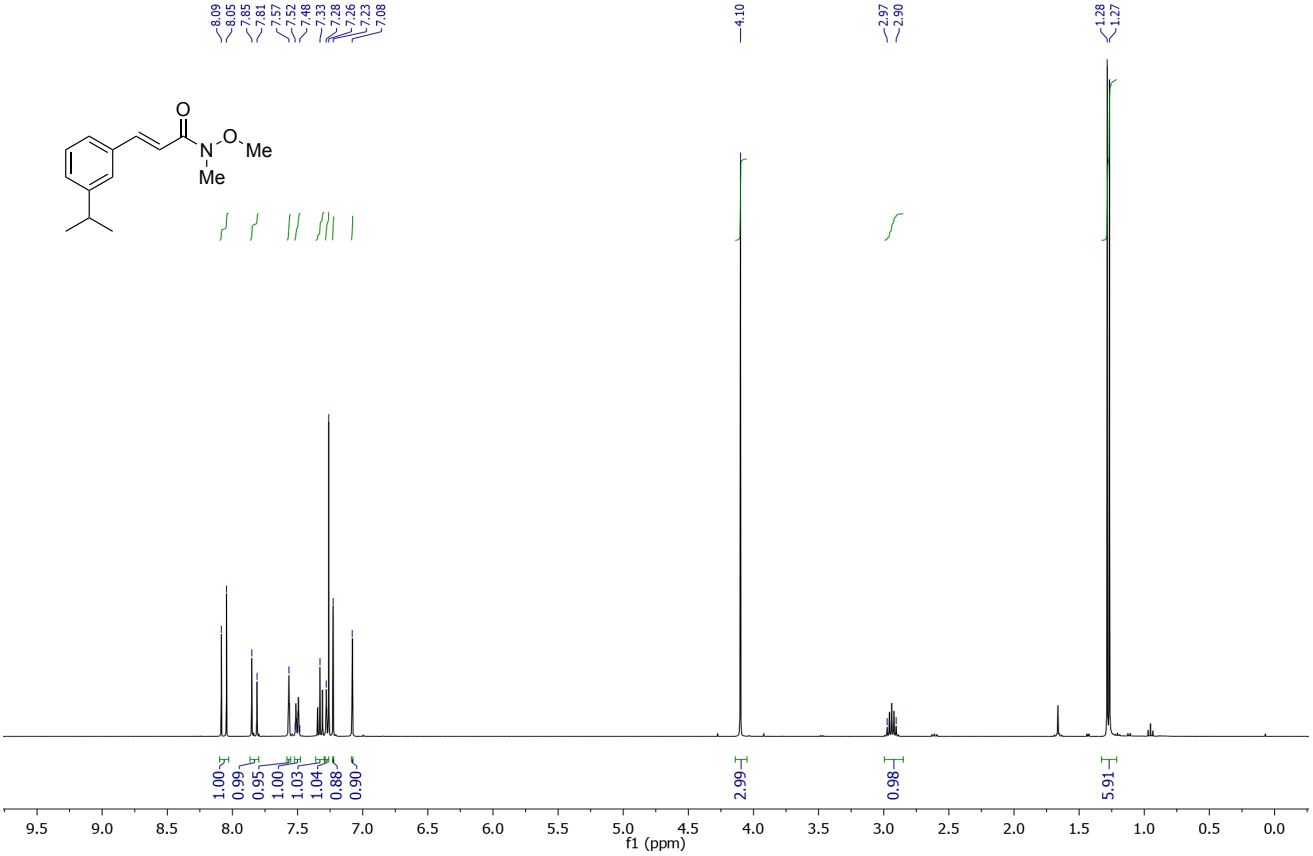
^{1}H NMR (400 MHz, $CDCl_3$):



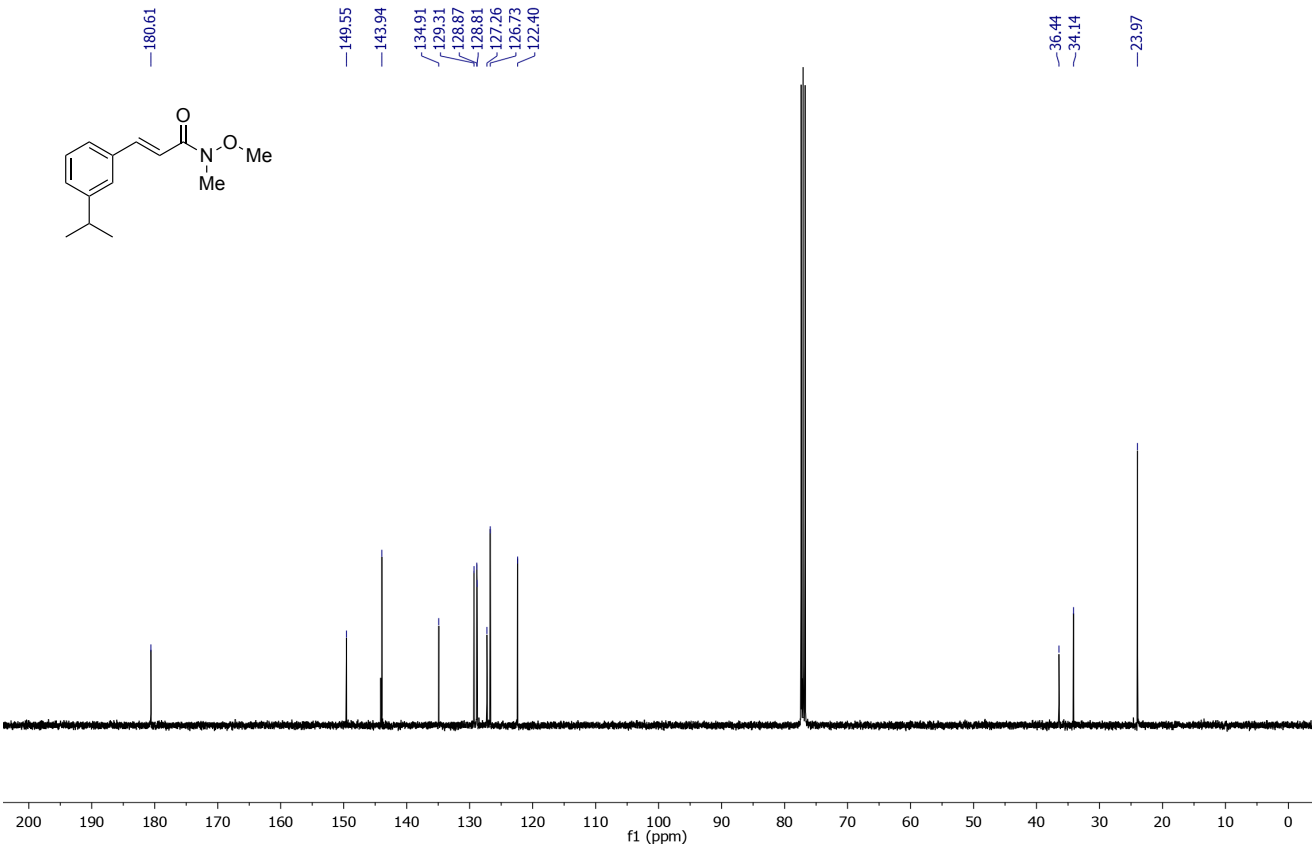
^{13}C NMR (100 MHz, $CDCl_3$):



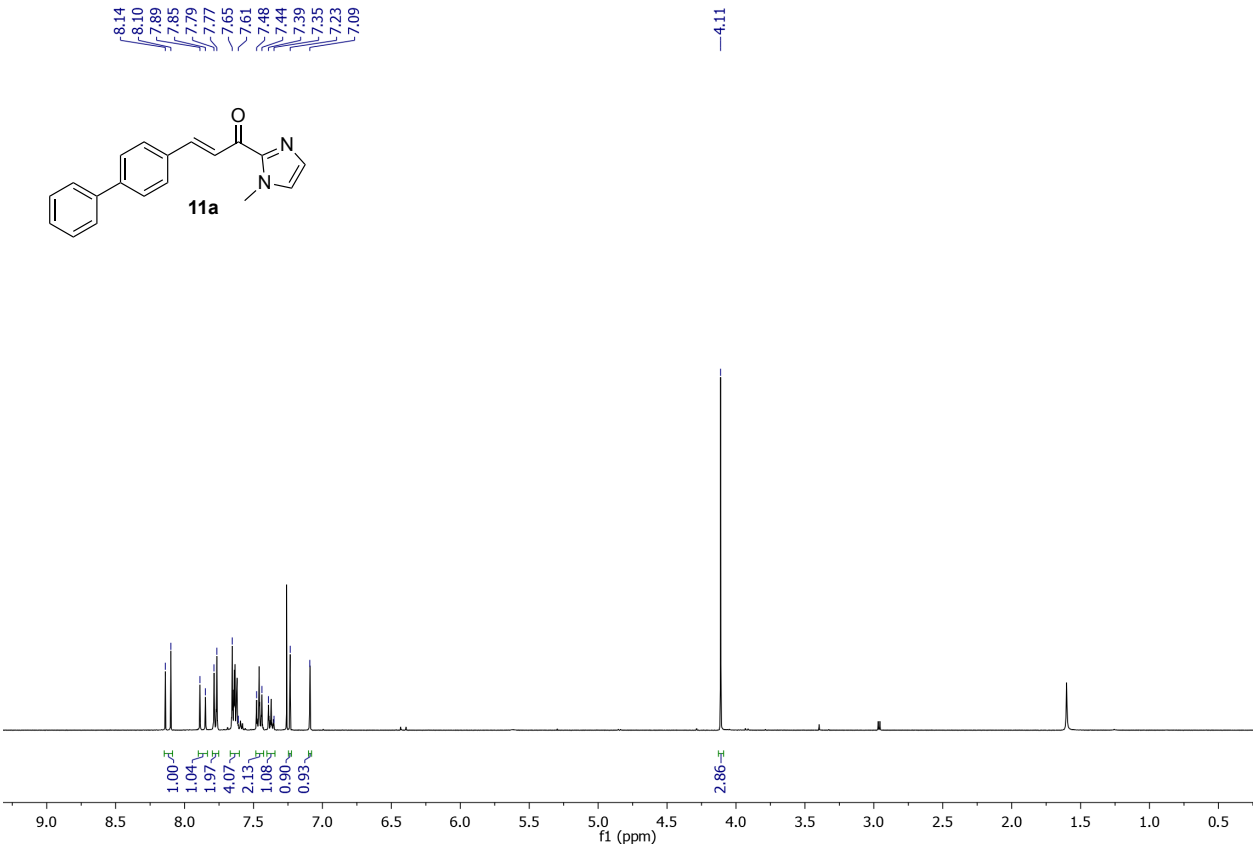
^{1}H NMR (400 MHz, $CDCl_3$):



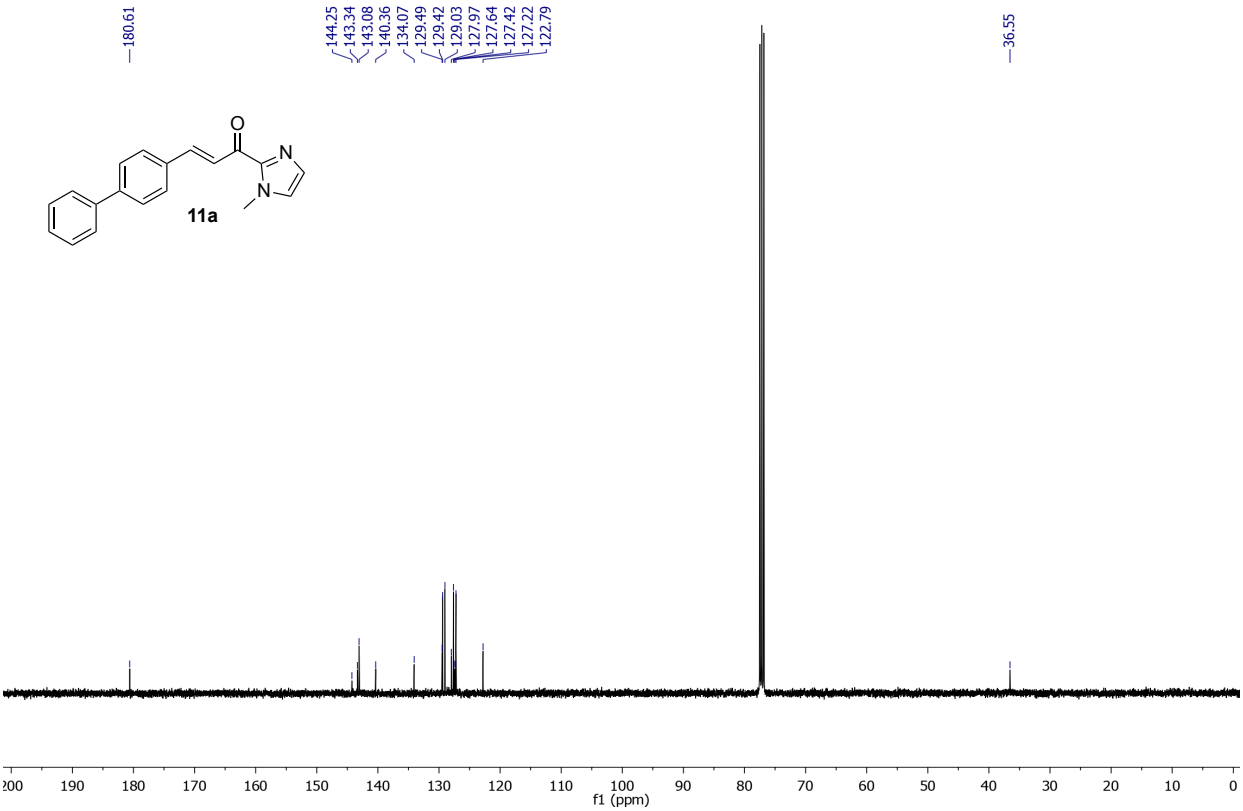
^{13}C NMR (100 MHz, $CDCl_3$):



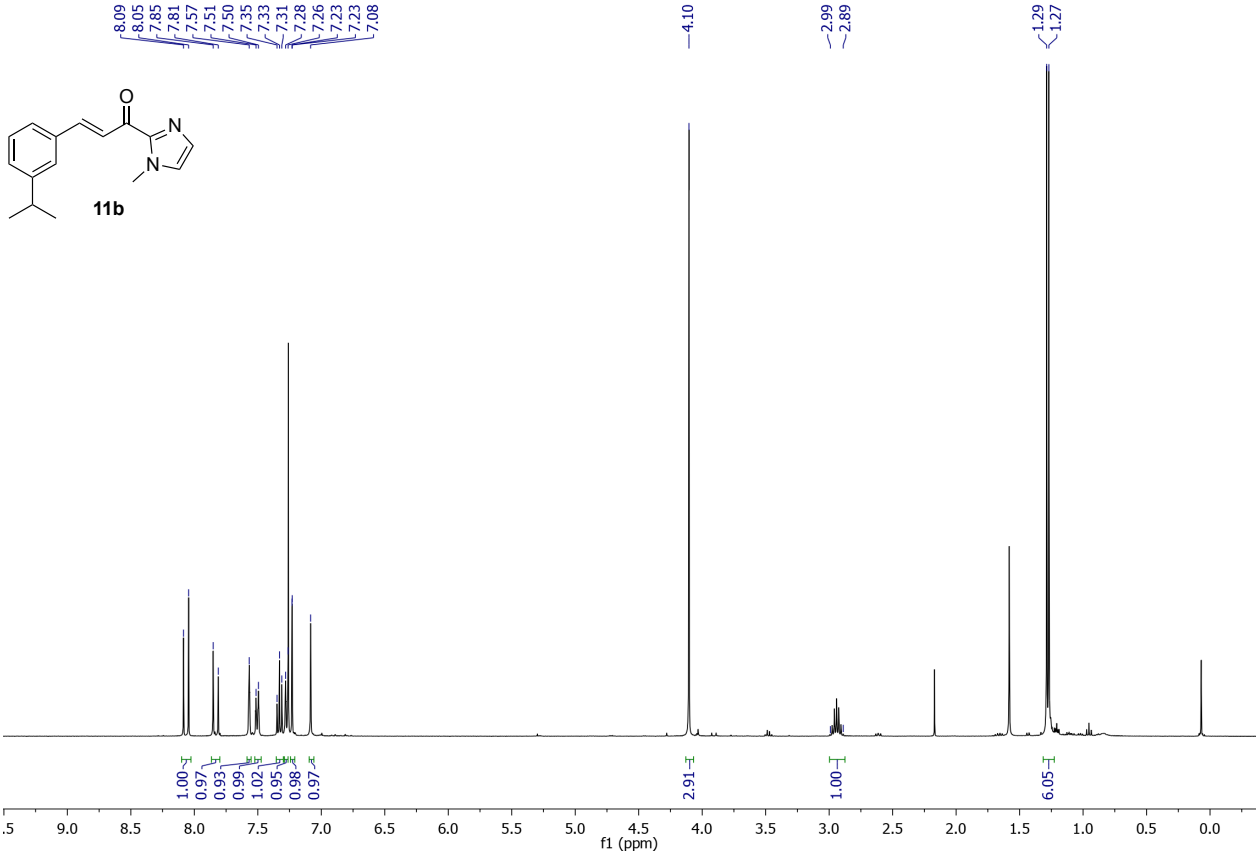
^{1}H NMR (400 MHz, $CDCl_3$):



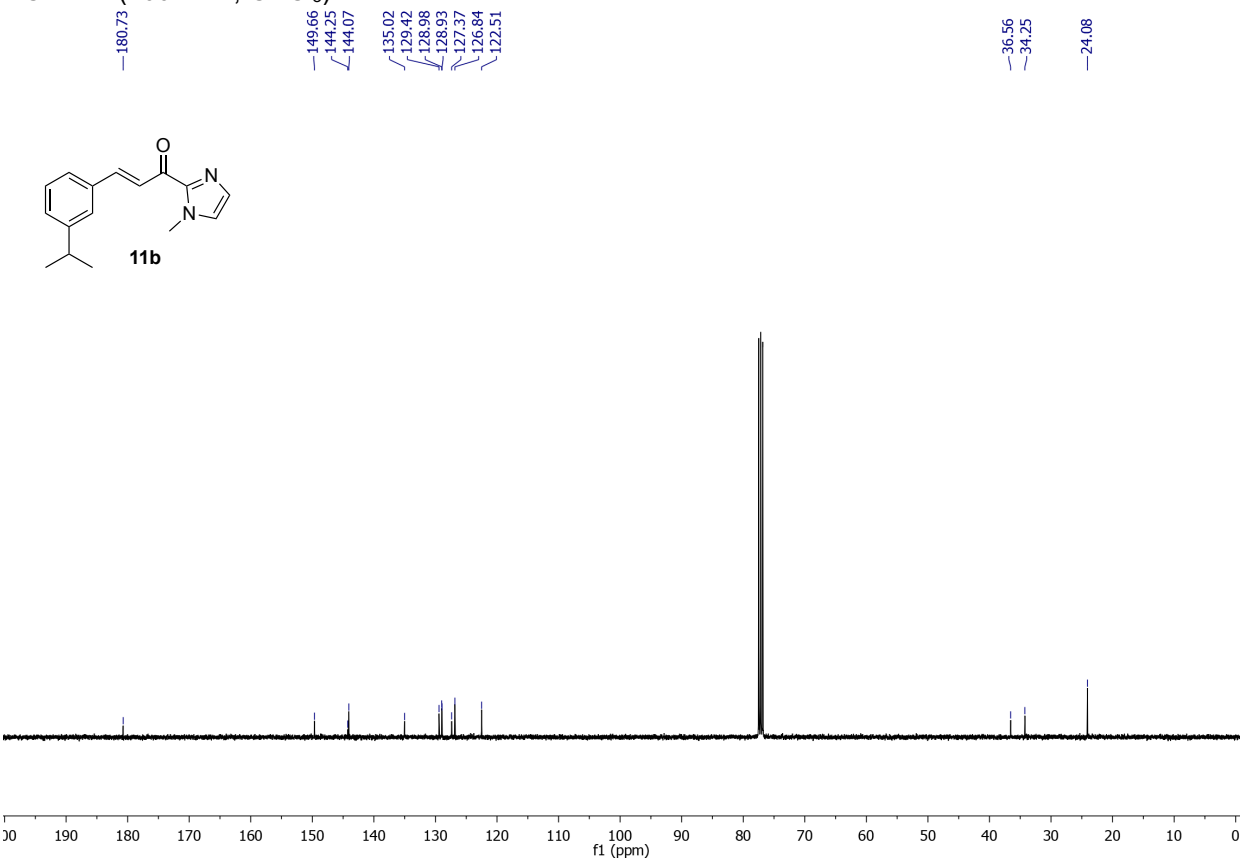
^{13}C NMR (100 MHz, $CDCl_3$):



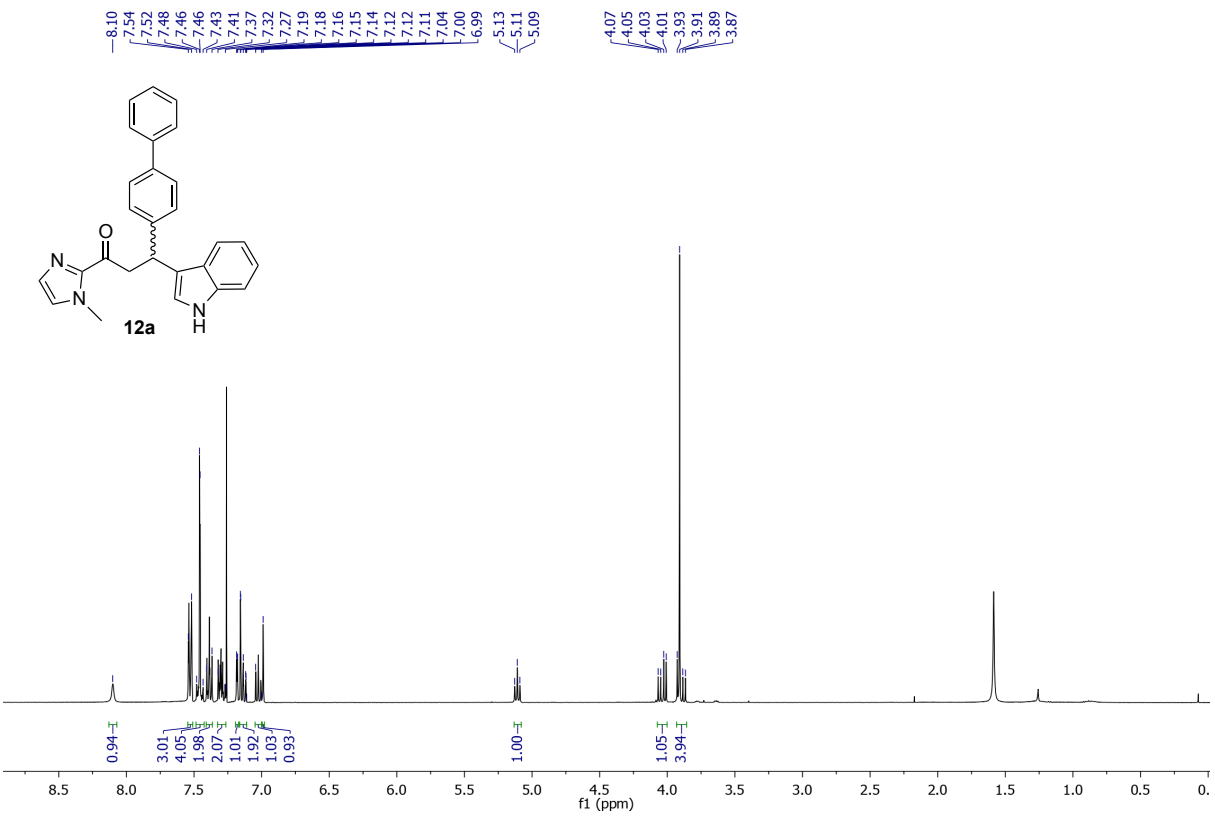
^{1}H NMR (400 MHz, $CDCl_3$):



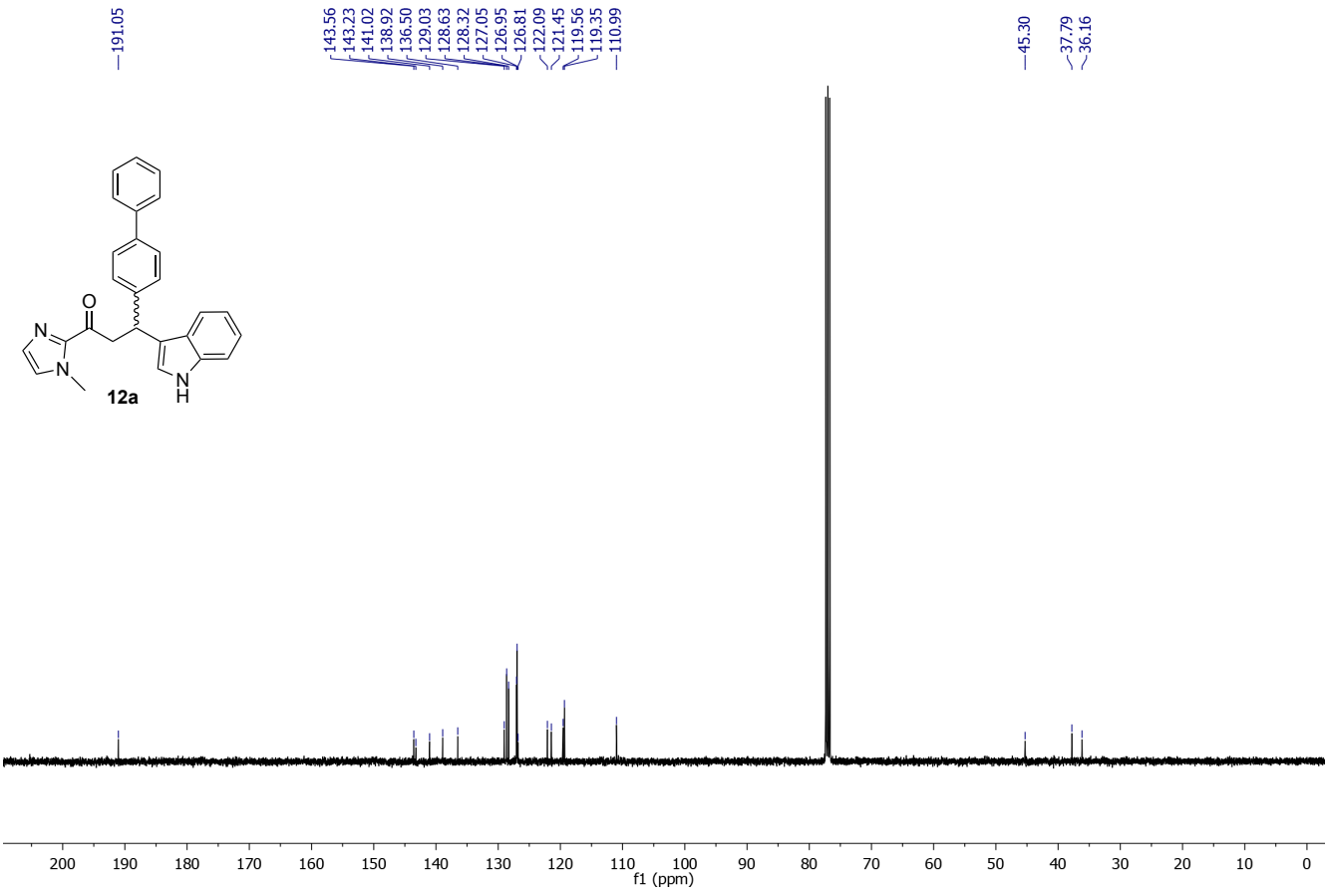
^{13}C NMR (100 MHz, $CDCl_3$):



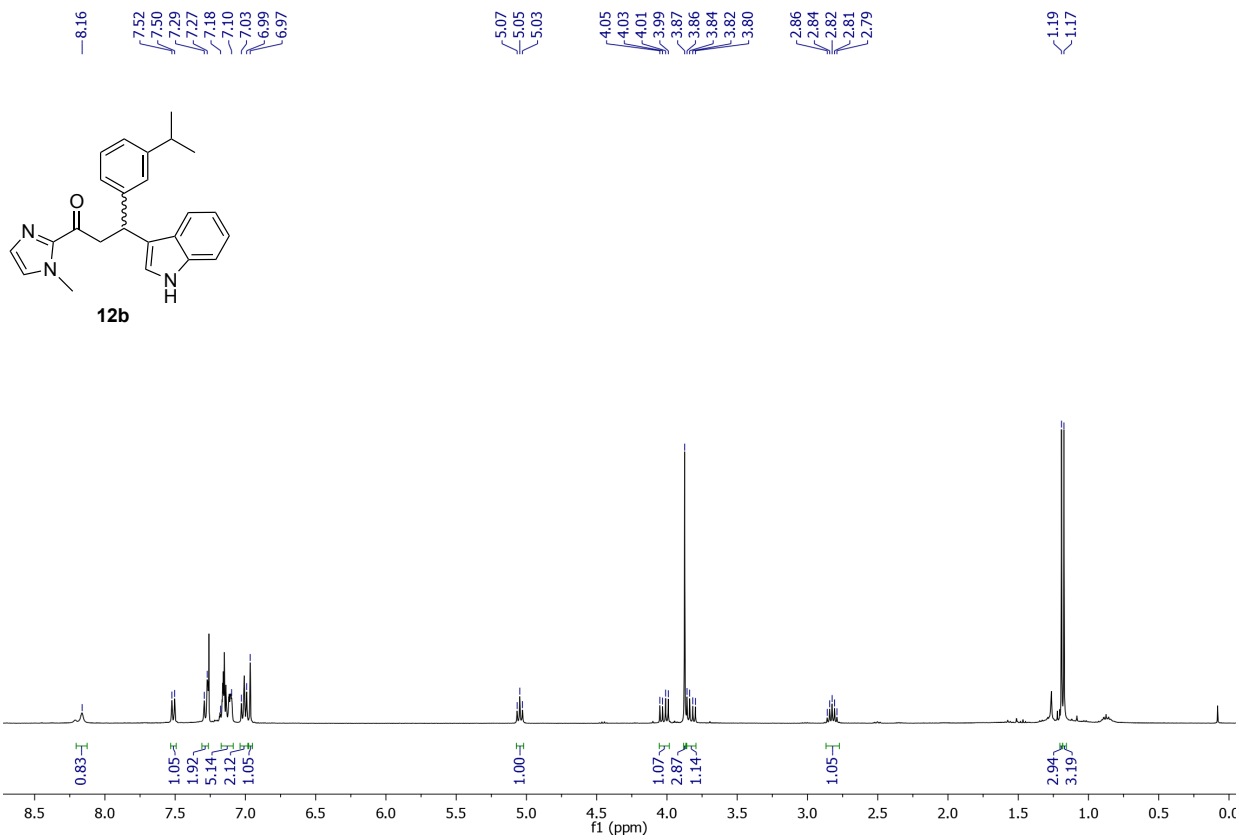
^{1}H NMR (400 MHz, $CDCl_3$):



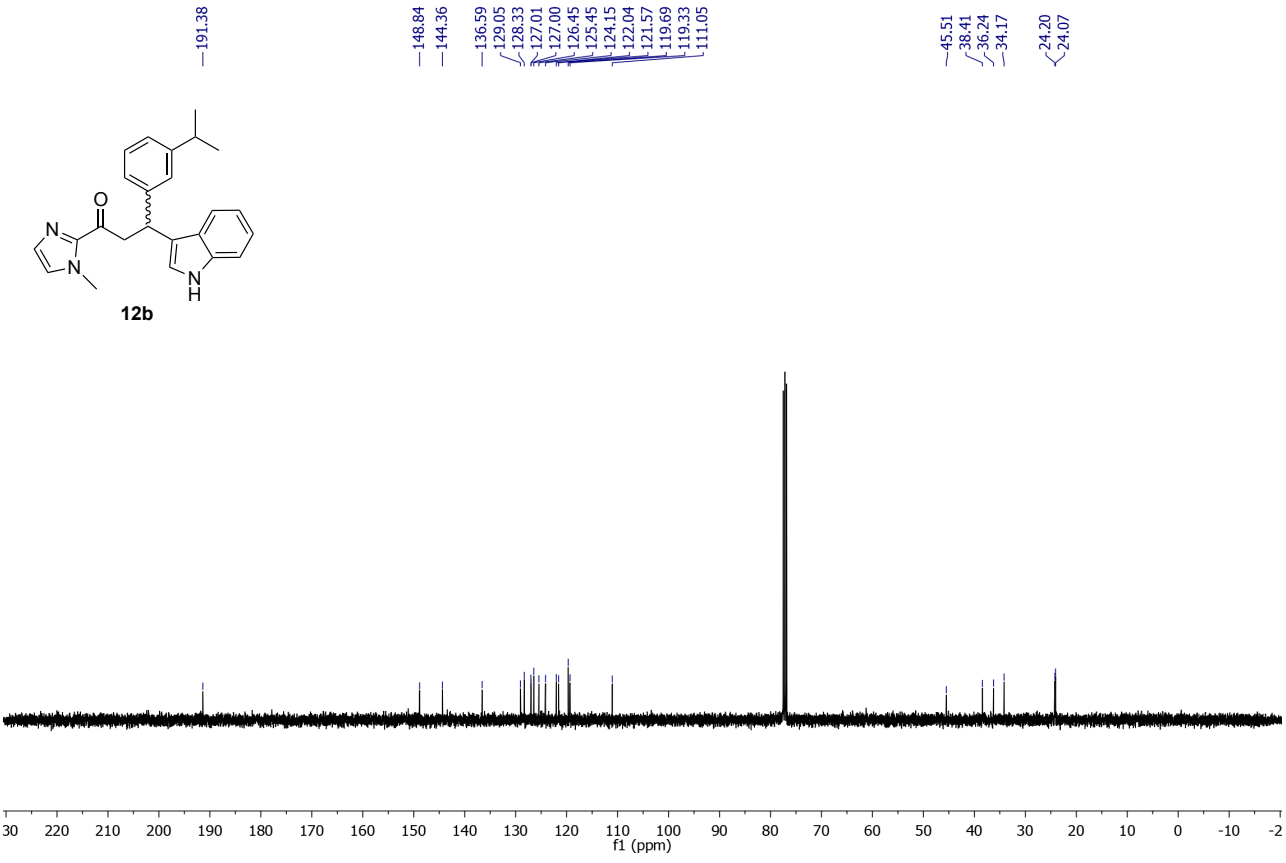
^{13}C NMR (100 MHz, $CDCl_3$):



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



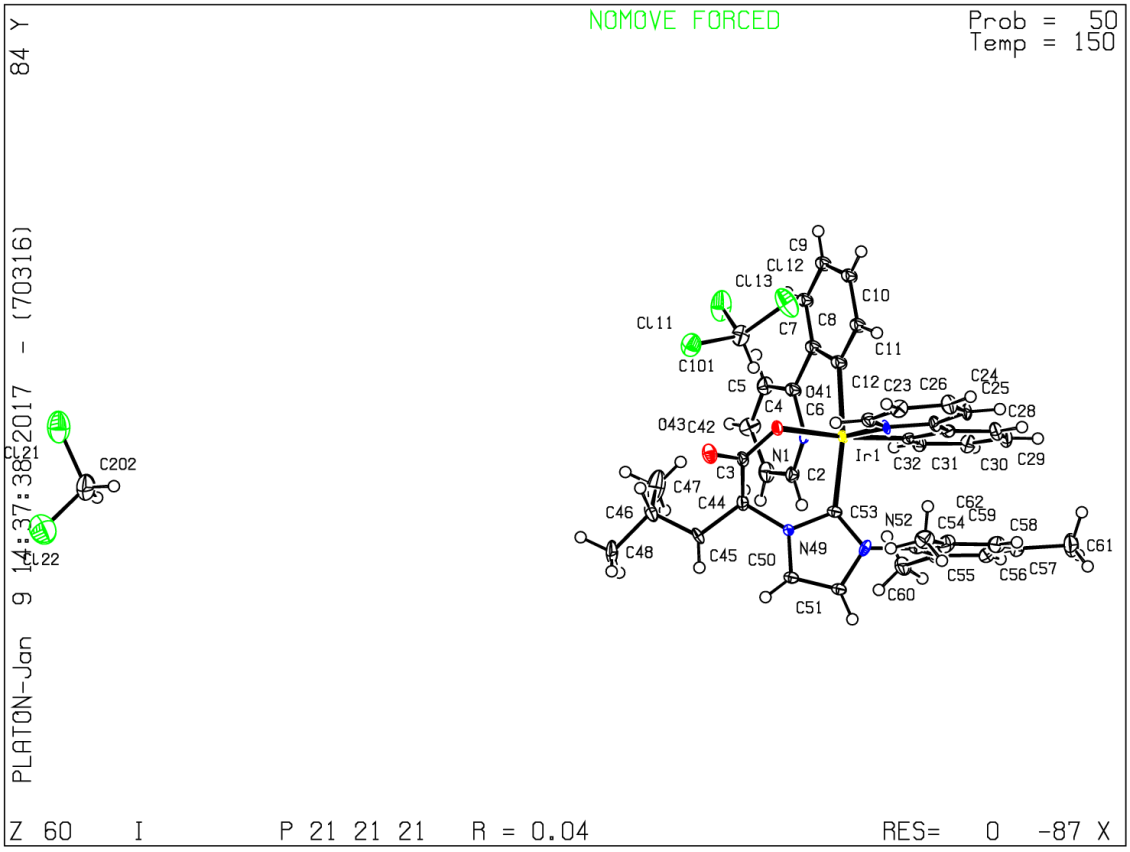
^{13}C NMR (100 MHz, $CDCl_3$):



8. X-ray crystallographic data

X-ray crystallographic study of Λ(S)-3

- ORTEP of Λ(S)-**3**; CCDC n° 1894794



($C_{40}H_{38}IrN_4O_2$, $CHCl_3$, CH_2Cl_2); M = 1003.24. D8 VENTURE Bruker AXS diffractometer [*], Mo-Kα radiation (λ = 0.71073 Å), T = 150 K; orthorhombic P 21 21 21 (I.T.#19), a = 9.3124(9), b = 16.7999(17), c = 26.446(2) Å, V = 4137.3(7) Å3. Z = 4, d = 1.611 g.cm-3, μ = 3.591 mm-1. The structure was solved by dual-space algorithm using the SHELXT program [1], and then refined with full-matrix least-square methods based on F2 (SHELXL-2014) [2]. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions. A final refinement on F2 with 9473 unique intensities and 445 parameters converged at ωR(F2) = 0.1170 (R(F) = 0.0438) for 9331 observed reflections with I > 2σ(I).

[1] G. M. Sheldrick, Acta Cryst. A71 (2015) 3-8

[2] Sheldrick G.M., Acta Cryst. C71 (2015) 3-8

Structural data

Empirical formula	C_{42} H_{41} Cl_5 Ir N_4 O_2
Extended formula	C_{40} H_{38} Ir N_4 O_2, C H Cl_3, C H_2 Cl_2
Formula weight	1003.24
Temperature	150 *K*
Wavelength	0.71073 Å
Crystal system, space group	orthorhombic, *P* 2_1 2_1 2_1
Unit cell dimensions	a = 9.3124(9) Å, α = 90 ° b = 16.7999(17) Å, β = 90 ° c = 26.446(2) Å, γ = 90 °
Volume	4137.3(7) $Å^3$
Z, Calculated density	4, 1.611 ($g.cm^{-3}$)
Absorption coefficient	3.591 mm^{-1}
F(000)	1996
Crystal size	0.510 x 0.090 x 0.060 mm
Crystal color	yellow
Theta range for data collection	2.319 to 27.535 °
h_min, h_max	-12, 12
k_min, k_max	-21, 21
l_min, l_max	-34, 32
Reflections collected / unique	35458 / 9473 [R(int)[a] = 0.0323]
Reflections [I>2σ]	9331
Completeness to theta_max	0.994
Absorption correction type	multi-scan
Max. and min. transmission	0.806 , 0.550
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9473 / 0 / 445
Flack parameter	0.026(13)
[b]S (Goodness-of-fit)	1.233
Final *R* indices [I>2σ]	*R*1[c] = 0.0438, *wR*2[d] = 0.1170
R indices (all data)	*R*1[c] = 0.0445, *wR*2[d] = 0.1174
Largest diff. peak and hole	3.811 and -3.060 $e^-.Å^{-3}$

$^a R_{int} = \sum |F_o^2 - < F_o^2>| / \sum [F_o^2]$

$^b S = \{\sum [w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$

$^c R1 = \sum | |F_o| - |F_c| | / \sum |F_o|$

$^d wR2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$

$w = 1 / [\sigma(F_o^2) + aP^2 + bP]$ where $P = [2F_c^2 + MAX(F_o^2, 0)] /3$

Atomic coordinates, site occupancy (%) and equivalent isotropic displacement parameters ($Å^2$). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	occ.	U(eq)
Ir1	0.54037(4)	0.21624(2)	0.14998(2)	1	0.01026(10)
N1	0.3432(9)	0.2345(5)	0.1842(3)	1	0.0122(18)
C2	0.2739(13)	0.1826(7)	0.2137(4)	1	0.018(2)
H2	0.316661	0.133402	0.219306	1	0.021
C3	0.1437(13)	0.1971(8)	0.2364(5)	1	0.023(3)
H3	0.097470	0.157777	0.255035	1	0.028
C4	0.0826(12)	0.2727(8)	0.2305(5)	1	0.024(3)
H4	-0.000414	0.287110	0.247775	1	0.029
C5	0.1514(13)	0.3258(7)	0.1977(5)	1	0.020(2)
H5	0.110418	0.375339	0.191723	1	0.024
C6	0.2795(13)	0.3061(7)	0.1739(4)	1	0.0178(9)
C7	0.3520(12)	0.3580(7)	0.1357(4)	1	0.0178(9)
C8	0.3062(13)	0.4305(7)	0.1211(4)	1	0.0178(9)
H8	0.220410	0.450465	0.133861	1	0.021
C9	0.3851(13)	0.4755(7)	0.0875(4)	1	0.0178(9)
H9	0.352205	0.525143	0.077063	1	0.021
C10	0.5135(12)	0.4459(7)	0.0694(4)	1	0.0178(9)
H10	0.568139	0.476281	0.047162	1	0.021
C11	0.5627(12)	0.3699(7)	0.0844(4)	1	0.0178(9)

H11	0.647132	0.349880	0.070537	1	0.021
C12	0.4881(12)	0.3248(7)	0.1191(4)	1	0.0178(9)
N21	0.7206(9)	0.2092(6)	0.1059(3)	1	0.0117(16)
C22	0.8493(12)	0.2396(7)	0.1187(4)	1	0.017(2)
H22	0.861207	0.260668	0.150954	1	0.021
C23	0.9644(14)	0.2406(6)	0.0858(4)	1	0.020(2)
H23	1.052464	0.261715	0.095544	1	0.024
C24	0.9445(13)	0.2088(8)	0.0373(4)	1	0.023(2)
H24	1.019536	0.208989	0.014130	1	0.027
C25	0.8142(13)	0.1775(7)	0.0243(4)	1	0.018(2)
H25	0.800762	0.156450	-0.007869	1	0.022
C26	0.7013(12)	0.1770(7)	0.0589(4)	1	0.015(2)
C27	0.5580(12)	0.1481(6)	0.0495(4)	1	0.0134(19)
C28	0.5138(13)	0.1099(7)	0.0053(4)	1	0.020(2)
H28	0.579977	0.100980	-0.020463	1	0.024
C29	0.3734(14)	0.0850(8)	-0.0009(4)	1	0.022(2)
H29	0.345966	0.058999	-0.030423	1	0.026
C30	0.2738(13)	0.0987(7)	0.0368(5)	1	0.020(2)
H30	0.179046	0.082724	0.032357	1	0.024
C31	0.3147(12)	0.1367(7)	0.0818(4)	1	0.017(2)
H31	0.246436	0.146131	0.106806	1	0.020
C32	0.4553(13)	0.1603(6)	0.0895(4)	1	0.0128(18)
O41	0.6612(8)	0.2843(5)	0.2071(3)	1	0.0149(14)
C42	0.6797(11)	0.2652(6)	0.2537(4)	1	0.014(2)
O43	0.7645(9)	0.3023(5)	0.2820(3)	1	0.0211(18)
C44	0.5914(12)	0.1961(6)	0.2736(4)	1	0.016(2)
H44	0.490557	0.207760	0.265996	1	0.019
C45	0.6015(14)	0.1809(7)	0.3304(4)	1	0.019(2)
H45	0.644994	0.135930	0.344037	1	0.023
C46	0.5338(16)	0.2462(7)	0.3629(4)	1	0.022(2)
H46	0.596313	0.293094	0.361942	1	0.027
C47	0.3819(15)	0.2713(11)	0.3462(7)	1	0.047(4)
H47A	0.384738	0.289655	0.311872	1	0.071
H47B	0.348108	0.313339	0.367741	1	0.071
H47C	0.318221	0.226529	0.348713	1	0.071
C48	0.526(2)	0.2160(10)	0.4177(4)	1	0.044(4)
H48A	0.452301	0.176163	0.420362	1	0.066
H48B	0.503639	0.259581	0.439830	1	0.066
H48C	0.616636	0.193355	0.427147	1	0.066
N49	0.6315(11)	0.1245(5)	0.2440(3)	1	0.0134(17)
C50	0.6978(13)	0.0567(7)	0.2636(4)	1	0.0169(13)
H50	0.729056	0.048869	0.296615	1	0.020
C51	0.7072(13)	0.0050(7)	0.2248(4)	1	0.0169(13)
H51	0.743155	-0.046630	0.226376	1	0.020
N52	0.6529(10)	0.0431(6)	0.1813(4)	1	0.0149(19)
C53	0.6023(13)	0.1158(7)	0.1926(4)	1	0.0169(13)
C54	0.6444(12)	0.0037(6)	0.1338(4)	1	0.015(2)
C55	0.5108(12)	-0.0279(6)	0.1193(4)	1	0.016(2)
C56	0.5044(13)	-0.0652(7)	0.0713(4)	1	0.021(3)
H56	0.417623	-0.086434	0.060338	1	0.025
C57	0.6238(16)	-0.0710(7)	0.0404(5)	1	0.024(3)
C58	0.7544(14)	-0.0425(7)	0.0579(5)	1	0.024(3)
H58	0.836268	-0.049423	0.038238	1	0.028
C59	0.7659(15)	-0.0039(8)	0.1043(5)	1	0.024(3)
C60	0.3814(14)	-0.0269(7)	0.1540(5)	1	0.026(2)
H60A	0.410098	-0.042365	0.187404	1	0.038
H60B	0.310423	-0.063440	0.141548	1	0.038
H60C	0.341611	0.025816	0.154902	1	0.038
C61	0.607(2)	-0.1069(10)	-0.0113(5)	1	0.038(4)
H61A	0.681304	-0.145818	-0.016584	1	0.057
H61B	0.614978	-0.065925	-0.036401	1	0.057
H61C	0.514984	-0.132059	-0.013836	1	0.057
C62	0.9110(13)	0.0269(8)	0.1226(5)	1	0.025(3)
H62A	0.905758	0.038392	0.158089	1	0.038
H62B	0.935196	0.074586	0.104443	1	0.038
H62C	0.983228	-0.012749	0.116684	1	0.038
Cl11	0.9083(4)	0.4839(2)	0.24910(14)	1	0.0348(7)
Cl12	0.8805(4)	0.4737(3)	0.14070(14)	1	0.0475(10)
C101	0.7948(14)	0.4547(8)	0.1986(5)	1	0.025(3)
H101	0.777875	0.397258	0.201279	1	0.030
Cl13	0.6299(4)	0.5031(3)	0.20245(16)	1	0.0457(10)
Cl21	0.4943(4)	0.8046(3)	0.87281(17)	1	0.0542(12)
Cl22	0.5978(6)	0.6721(3)	0.9354(2)	1	0.0629(13)
C202	0.527(2)	0.6981(9)	0.8756(5)	1	0.043(4)
H20A	0.438023	0.669570	0.869802	1	0.052
H20B	0.594469	0.683044	0.849266	1	0.052

Anisotropic displacement parameters (Å^2)

The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$.

Atom	U11	U22	U33	U23	U13	U12
Ir1	0.01125(15)	0.01207(15)	0.00747(15)	-0.00023(15)	0.00103(15)	0.00264(15)
N1	0.008(4)	0.015(5)	0.014(4)	-0.006(3)	0.003(3)	0.003(3)
C2	0.019(5)	0.018(5)	0.016(5)	-0.003(4)	0.003(4)	0.001(4)
C3	0.018(5)	0.030(7)	0.020(6)	-0.004(5)	0.006(4)	-0.003(5)
C4	0.012(5)	0.025(7)	0.035(7)	0.001(5)	-0.005(4)	0.002(4)
C5	0.016(5)	0.024(6)	0.021(6)	-0.003(5)	0.000(4)	0.007(4)
C6	0.019(2)	0.019(2)	0.016(2)	0.0029(16)	-0.0026(16)	0.0048(17)
C7	0.019(2)	0.019(2)	0.016(2)	0.0029(16)	-0.0026(16)	0.0048(17)
C8	0.019(2)	0.019(2)	0.016(2)	0.0029(16)	-0.0026(16)	0.0048(17)
C9	0.019(2)	0.019(2)	0.016(2)	0.0029(16)	-0.0026(16)	0.0048(17)
C10	0.019(2)	0.019(2)	0.016(2)	0.0029(16)	-0.0026(16)	0.0048(17)
C11	0.019(2)	0.019(2)	0.016(2)	0.0029(16)	-0.0026(16)	0.0048(17)
C12	0.019(2)	0.019(2)	0.016(2)	0.0029(16)	-0.0026(16)	0.0048(17)
N21	0.015(4)	0.016(4)	0.004(3)	-0.001(3)	0.004(3)	0.000(4)
C22	0.019(5)	0.017(5)	0.016(5)	0.002(4)	0.003(4)	0.003(4)
C23	0.014(5)	0.021(5)	0.025(5)	-0.001(4)	0.001(5)	-0.004(5)
C24	0.019(5)	0.029(6)	0.019(5)	0.000(5)	0.013(4)	0.001(6)
C25	0.025(6)	0.020(6)	0.009(5)	-0.004(4)	0.004(4)	0.006(5)
C26	0.014(5)	0.020(5)	0.010(5)	-0.001(4)	0.003(4)	0.002(4)
C27	0.014(5)	0.012(4)	0.014(4)	0.000(4)	-0.003(4)	0.000(4)
C28	0.020(6)	0.027(6)	0.012(5)	-0.002(4)	-0.001(4)	0.004(4)
C29	0.025(6)	0.026(6)	0.014(5)	-0.006(5)	-0.004(5)	0.005(5)
C30	0.017(5)	0.023(6)	0.021(6)	-0.005(5)	-0.003(4)	0.003(4)
C31	0.016(5)	0.019(5)	0.015(5)	-0.002(4)	-0.002(4)	0.001(4)
C32	0.015(5)	0.010(4)	0.013(4)	0.001(3)	0.001(4)	0.003(4)
O41	0.021(4)	0.015(3)	0.009(3)	-0.002(3)	0.000(3)	-0.004(4)
C42	0.015(5)	0.018(6)	0.010(5)	-0.001(4)	0.003(4)	0.002(4)
O43	0.019(4)	0.028(5)	0.016(4)	-0.003(3)	0.001(3)	-0.007(3)
C44	0.018(5)	0.019(6)	0.011(5)	-0.003(4)	0.001(4)	0.002(4)
C45	0.029(6)	0.023(6)	0.006(4)	0.002(4)	0.003(4)	0.000(5)
C46	0.027(6)	0.030(6)	0.010(5)	-0.001(4)	0.001(5)	-0.004(6)
C47	0.026(6)	0.065(11)	0.051(9)	-0.032(10)	0.007(7)	0.008(7)
C48	0.079(11)	0.035(7)	0.017(5)	-0.012(6)	0.015(7)	0.000(10)
N49	0.023(5)	0.010(4)	0.008(4)	0.000(3)	0.001(4)	0.004(4)
C50	0.024(3)	0.013(3)	0.014(3)	0.004(2)	0.001(2)	0.004(2)
C51	0.024(3)	0.013(3)	0.014(3)	0.004(2)	0.001(2)	0.004(2)
N52	0.015(4)	0.013(4)	0.017(5)	-0.007(4)	0.004(4)	0.002(3)
C53	0.024(3)	0.013(3)	0.014(3)	0.004(2)	0.001(2)	0.004(2)
C54	0.020(5)	0.010(5)	0.014(5)	0.004(4)	0.000(4)	0.003(4)
C55	0.018(5)	0.015(5)	0.014(5)	-0.001(4)	0.001(4)	-0.002(4)
C56	0.028(7)	0.015(5)	0.020(5)	-0.001(4)	0.000(4)	-0.003(4)
C57	0.038(7)	0.017(6)	0.018(6)	-0.003(4)	0.005(5)	0.002(5)
C58	0.026(6)	0.022(6)	0.023(6)	0.002(5)	0.012(5)	0.009(5)
C59	0.024(6)	0.021(6)	0.028(7)	-0.002(5)	0.013(5)	0.005(5)
C60	0.031(6)	0.028(6)	0.018(6)	0.001(5)	0.008(6)	0.004(5)
C61	0.057(10)	0.038(8)	0.020(7)	-0.009(6)	0.010(6)	-0.006(7)
C62	0.020(6)	0.027(6)	0.029(7)	0.001(5)	-0.001(5)	0.005(5)
Cl11	0.0320(16)	0.0378(18)	0.0345(18)	-0.0072(15)	-0.0100(14)	0.0050(14)
Cl12	0.0369(19)	0.079(3)	0.0266(19)	0.0063(18)	0.0048(15)	-0.0026(19)
C101	0.021(6)	0.028(6)	0.027(6)	-0.005(5)	0.005(5)	-0.005(5)
Cl13	0.0276(18)	0.067(3)	0.043(2)	-0.0201(19)	-0.0081(15)	0.0224(18)
Cl21	0.043(2)	0.074(3)	0.046(2)	-0.016(2)	-0.0065(16)	0.0052(19)
Cl22	0.066(3)	0.071(3)	0.052(3)	0.000(2)	-0.002(2)	-0.006(3)
C202	0.050(9)	0.047(9)	0.033(7)	-0.011(6)	0.007(7)	0.004(8)

Bond lengths [Å]

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Ir1  - C32      = 2.017(10)
Ir1  - N21      = 2.047(8)
Ir1  - C12      = 2.057(11)
Ir1  - N1       = 2.070(8)
Ir1  - C53      = 2.110(11)
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Ir1  - O41      = 2.204(7)
N1   - C2       = 1.336(15)
N1   - C6       = 1.369(14)
C2   - C3       = 1.374(16)
C2   - H2       = 0.9300
C3   - C4       = 1.401(18)
C3   - H3       = 0.9300
C4   - C5       = 1.399(18)
C4   - H4       = 0.9300
C5   - C6       = 1.389(16)
C5   - H5       = 0.9300
C6   - C7       = 1.496(16)
C7   - C8       = 1.347(16)
C7   - C12      = 1.453(16)
C8   - C9       = 1.380(16)
C8   - H8       = 0.9300
C9   - C10      = 1.380(16)
C9   - H9       = 0.9300
C10  - C11      = 1.414(15)
C10  - H10      = 0.9300
C11  - C12      = 1.377(16)
C11  - H11      = 0.9300
N21  - C22      = 1.346(14)
N21  - C26      = 1.367(13)
C22  - C23      = 1.380(16)
C22  - H22      = 0.9300
C23  - C24      = 1.402(16)
C23  - H23      = 0.9300
C24  - C25      = 1.366(17)
C24  - H24      = 0.9300
C25  - C26      = 1.394(15)
C25  - H25      = 0.9300
C26  - C27      = 1.442(15)
C27  - C28      = 1.397(15)
C27  - C32      = 1.440(15)
C28  - C29      = 1.383(17)
C28  - H28      = 0.9300
C29  - C30      = 1.382(17)
C29  - H29      = 0.9300
C30  - C31      = 1.403(16)
C30  - H30      = 0.9300
C31  - C32      = 1.383(16)
C31  - H31      = 0.9300
O41  - C42      = 1.282(13)
C42  - O43      = 1.254(13)
C42  - C44      = 1.518(15)
C44  - N49      = 1.483(13)
C44  - C45      = 1.526(15)
C44  - H44      = 0.9800
C45  - C46      = 1.529(16)
C45  - H45      = 0.9300
C46  - C48      = 1.538(16)
C46  - C47      = 1.540(19)
C46  - H46      = 0.9800
C47  - H47A     = 0.9600
C47  - H47B     = 0.9600
C47  - H47C     = 0.9600
C48  - H48A     = 0.9600
C48  - H48B     = 0.9600
C48  - H48C     = 0.9600
N49  - C50      = 1.395(14)
N49  - C53      = 1.393(14)
C50  - C51      = 1.348(16)
C50  - H50      = 0.9300
C51  - N52      = 1.411(14)
C51  - H51      = 0.9300
N52  - C53      = 1.343(14)
N52  - C54      = 1.422(14)
C54  - C59      = 1.380(17)
C54  - C55      = 1.406(15)
C55  - C56      = 1.415(15)
C55  - C60      = 1.515(16)
C56  - C57      = 1.385(17)
C56  - H56      = 0.9300
C57  - C58      = 1.387(19)
C57  - C61      = 1.501(17)
C58  - C59      = 1.392(19)
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C58  - H58      = 0.9300
C59  - C62      = 1.526(19)
C60  - H60A     = 0.9600
C60  - H60B     = 0.9600
C60  - H60C     = 0.9600
C61  - H61A     = 0.9600
C61  - H61B     = 0.9600
C61  - H61C     = 0.9600
C62  - H62A     = 0.9600
C62  - H62B     = 0.9600
C62  - H62C     = 0.9600
Cl11 - C101     = 1.772(14)
Cl12 - C101     = 1.757(13)
C101 - Cl13     = 1.740(14)
C101 - H101     = 0.9800
Cl21 - C202     = 1.817(17)
Cl22 - C202     = 1.769(17)
C202 - H20A     = 0.9700
C202 - H20B     = 0.9700
```

Angles [°]

```
C32      - Ir1      - N21      =   81.00(4)
C32      - Ir1      - C12      =   90.30(4)
N21      - Ir1      - C12      =   91.10(4)
C32      - Ir1      - N1       =   93.90(4)
N21      - Ir1      - N1       =  170.00(4)
C12      - Ir1      - N1       =   80.40(4)
C32      - Ir1      - C53      =   99.20(4)
N21      - Ir1      - C53      =   92.00(4)
C12      - Ir1      - C53      =  170.40(5)
N1       - Ir1      - C53      =   97.30(4)
C32      - Ir1      - O41      =  170.40(4)
N21      - Ir1      - O41      =   90.10(3)
C12      - Ir1      - O41      =   86.20(4)
N1       - Ir1      - O41      =   94.40(3)
C53      - Ir1      - O41      =   84.70(4)
C2       - N1       - C6       =  118.60(9)
C2       - N1       - Ir1      =  126.00(7)
C6       - N1       - Ir1      =  115.30(7)
N1       - C2       - C3       =  124.50(11)
N1       - C2       - H2       =  117.70
C3       - C2       - H2       =  117.70
C2       - C3       - C4       =  118.00(11)
C2       - C3       - H3       =  121.00
C4       - C3       - H3       =  121.00
C5       - C4       - C3       =  117.40(11)
C5       - C4       - H4       =  121.30
C3       - C4       - H4       =  121.30
C6       - C5       - C4       =  121.50(11)
C6       - C5       - H5       =  119.20
C4       - C5       - H5       =  119.20
N1       - C6       - C5       =  119.40(11)
N1       - C6       - C7       =  116.80(10)
C5       - C6       - C7       =  123.70(10)
C8       - C7       - C12      =  122.40(11)
C8       - C7       - C6       =  125.30(11)
C12      - C7       - C6       =  112.00(10)
C7       - C8       - C9       =  120.80(11)
C7       - C8       - H8       =  119.60
C9       - C8       - H8       =  119.60
C8       - C9       - C10      =  119.20(11)
C8       - C9       - H9       =  120.40
C10      - C9       - H9       =  120.40
C9       - C10      - C11      =  120.60(11)
C9       - C10      - H10      =  119.70
C11      - C10      - H10      =  119.70
C12      - C11      - C10      =  121.30(11)
C12      - C11      - H11      =  119.30
C10      - C11      - H11      =  119.30
C11      - C12      - C7       =  115.50(10)
C11      - C12      - Ir1      =  129.20(8)
C7       - C12      - Ir1      =  115.20(8)
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```
C22      - N21      - C26      =  119.70(9)
C22      - N21      - Ir1      =  124.40(7)
C26      - N21      - Ir1      =  115.60(7)
N21      - C22      - C23      =  122.50(10)
N21      - C22      - H22      =  118.70
C23      - C22      - H22      =  118.70
C22      - C23      - C24      =  118.00(11)
C22      - C23      - H23      =  121.00
C24      - C23      - H23      =  121.00
C25      - C24      - C23      =  119.70(10)
C25      - C24      - H24      =  120.20
C23      - C24      - H24      =  120.20
C24      - C25      - C26      =  120.40(10)
C24      - C25      - H25      =  119.80
C26      - C25      - H25      =  119.80
N21      - C26      - C25      =  119.70(10)
N21      - C26      - C27      =  114.30(9)
C25      - C26      - C27      =  125.90(10)
C28      - C27      - C32      =  119.00(10)
C28      - C27      - C26      =  124.90(10)
C32      - C27      - C26      =  116.10(9)
C29      - C28      - C27      =  121.10(11)
C29      - C28      - H28      =  119.50
C27      - C28      - H28      =  119.50
C30      - C29      - C28      =  119.90(11)
C30      - C29      - H29      =  120.00
C28      - C29      - H29      =  120.00
C29      - C30      - C31      =  120.40(11)
C29      - C30      - H30      =  119.80
C31      - C30      - H30      =  119.80
C32      - C31      - C30      =  120.80(11)
C32      - C31      - H31      =  119.60
C30      - C31      - H31      =  119.60
C31      - C32      - C27      =  118.70(10)
C31      - C32      - Ir1      =  128.40(8)
C27      - C32      - Ir1      =  112.80(8)
C42      - O41      - Ir1      =  126.70(7)
O43      - C42      - O41      =  122.30(10)
O43      - C42      - C44      =  120.90(10)
O41      - C42      - C44      =  116.80(9)
N49      - C44      - C42      =  107.50(9)
N49      - C44      - C45      =  111.60(9)
C42      - C44      - C45      =  115.90(9)
N49      - C44      - H44      =  107.10
C42      - C44      - H44      =  107.10
C45      - C44      - H44      =  107.10
C44      - C45      - C46      =  114.00(10)
C44      - C45      - H45      =  123.00
C46      - C45      - H45      =  123.00
C45      - C46      - C48      =  108.20(11)
C45      - C46      - C47      =  114.50(11)
C48      - C46      - C47      =  108.40(13)
C45      - C46      - H46      =  108.50
C48      - C46      - H46      =  108.50
C47      - C46      - H46      =  108.50
C46      - C47      - H47A     =  109.50
C46      - C47      - H47B     =  109.50
H47A     - C47      - H47B     =  109.50
C46      - C47      - H47C     =  109.50
H47A     - C47      - H47C     =  109.50
H47B     - C47      - H47C     =  109.50
C46      - C48      - H48A     =  109.50
C46      - C48      - H48B     =  109.50
H48A     - C48      - H48B     =  109.50
C46      - C48      - H48C     =  109.50
H48A     - C48      - H48C     =  109.50
H48B     - C48      - H48C     =  109.50
C50      - N49      - C53      =  111.30(9)
C50      - N49      - C44      =  125.30(9)
C53      - N49      - C44      =  123.40(9)
C51      - C50      - N49      =  105.80(10)
C51      - C50      - H50      =  127.10
N49      - C50      - H50      =  127.10
C50      - C51      - N52      =  107.70(10)
C50      - C51      - H51      =  126.10
N52      - C51      - H51      =  126.10
C53      - N52      - C51      =  110.90(9)
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C53      - N52      - C54      =  127.00(10)
C51      - N52      - C54      =  121.90(9)
N52      - C53      - N49      =  104.20(9)
N52      - C53      - Ir1      =  134.70(8)
N49      - C53      - Ir1      =  119.40(8)
C59      - C54      - C55      =  122.40(11)
C59      - C54      - N52      =  119.80(11)
C55      - C54      - N52      =  117.80(10)
C54      - C55      - C56      =  116.70(10)
C54      - C55      - C60      =  122.30(10)
C56      - C55      - C60      =  120.90(10)
C57      - C56      - C55      =  121.80(11)
C57      - C56      - H56      =  119.10
C55      - C56      - H56      =  119.10
C56      - C57      - C58      =  118.80(11)
C56      - C57      - C61      =  118.90(13)
C58      - C57      - C61      =  122.20(13)
C57      - C58      - C59      =  121.50(11)
C57      - C58      - H58      =  119.20
C59      - C58      - H58      =  119.20
C54      - C59      - C58      =  118.60(13)
C54      - C59      - C62      =  121.00(12)
C58      - C59      - C62      =  120.40(11)
C55      - C60      - H60A     =  109.50
C55      - C60      - H60B     =  109.50
H60A     - C60      - H60B     =  109.50
C55      - C60      - H60C     =  109.50
H60A     - C60      - H60C     =  109.50
H60B     - C60      - H60C     =  109.50
C57      - C61      - H61A     =  109.50
C57      - C61      - H61B     =  109.50
H61A     - C61      - H61B     =  109.50
C57      - C61      - H61C     =  109.50
H61A     - C61      - H61C     =  109.50
H61B     - C61      - H61C     =  109.50
C59      - C62      - H62A     =  109.50
C59      - C62      - H62B     =  109.50
H62A     - C62      - H62B     =  109.50
C59      - C62      - H62C     =  109.50
H62A     - C62      - H62C     =  109.50
H62B     - C62      - H62C     =  109.50
Cl13     - C101     - Cl12     =  111.50(8)
Cl13     - C101     - Cl11     =  110.60(7)
Cl12     - C101     - Cl11     =  109.60(7)
Cl13     - C101     - H101     =  108.30
Cl12     - C101     - H101     =  108.30
Cl11     - C101     - H101     =  108.30
Cl22     - C202     - Cl21     =  109.90(8)
Cl22     - C202     - H20A     =  109.70
Cl21     - C202     - H20A     =  109.70
Cl22     - C202     - H20B     =  109.70
Cl21     - C202     - H20B     =  109.70
H20A     - C202     - H20B     =  108.20
```

Torsion angles [°]

```
C6       - N1       - C2       - C3       =   -2.50(17)
Ir1      - N1       - C2       - C3       =  179.20(9)
N1       - C2       - C3       - C4       =   -3.70(18)
C2       - C3       - C4       - C5       =    6.40(17)
C3       - C4       - C5       - C6       =   -3.40(18)
C2       - N1       - C6       - C5       =    5.50(16)
Ir1      - N1       - C6       - C5       = -175.90(9)
C2       - N1       - C6       - C7       = -172.60(10)
Ir1      - N1       - C6       - C7       =    5.90(13)
C4       - C5       - C6       - N1       =   -2.60(18)
C4       - C5       - C6       - C7       =  175.40(11)
N1       - C6       - C7       - C8       = -179.40(11)
C5       - C6       - C7       - C8       =    2.60(19)
N1       - C6       - C7       - C12      =   -5.10(14)
C5       - C6       - C7       - C12      =  176.90(11)
C12      - C7       - C8       - C9       =    2.90(18)
C6       - C7       - C8       - C9       =  176.60(11)
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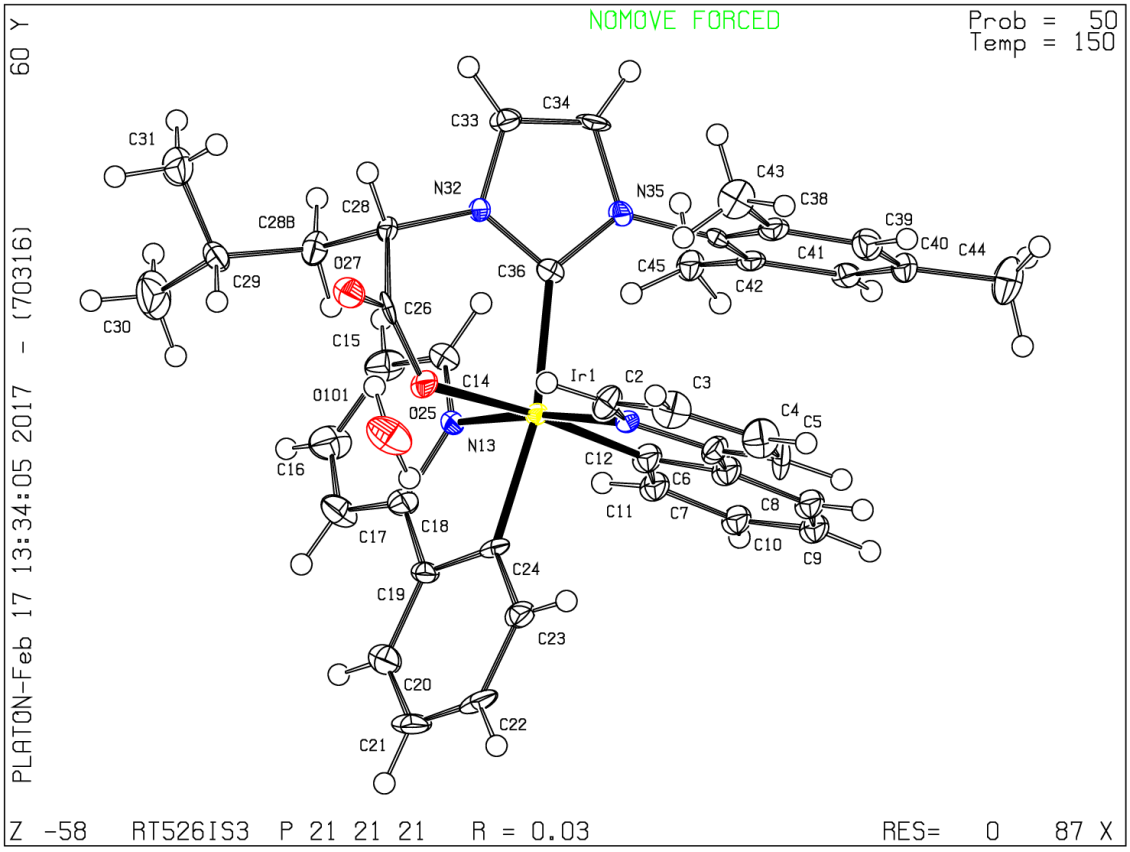
C7      - C8      - C9      - C10     =   -1.10(18)
C8      - C9      - C10     - C11     =    1.10(17)
C9      - C10     - C11     - C12     =   -3.10(17)
C10     - C11     - C12     - C7      =    4.60(16)
C10     - C11     - C12     - Ir1     = -176.40(9)
C8      - C7      - C12     - C11     =   -4.50(17)
C6      - C7      - C12     - C11     = -179.00(10)
C8      - C7      - C12     - Ir1     =  176.30(9)
C6      - C7      - C12     - Ir1     =    1.80(12)
C26     - N21     - C22     - C23     =    0.80(17)
Ir1     - N21     - C22     - C23     = -173.40(8)
N21     - C22     - C23     - C24     =    0.20(17)
C22     - C23     - C24     - C25     =   -0.60(18)
C23     - C24     - C25     - C26     =   -0.10(18)
C22     - N21     - C26     - C25     =   -1.50(16)
Ir1     - N21     - C26     - C25     =  173.20(8)
C22     - N21     - C26     - C27     = -178.80(10)
Ir1     - N21     - C26     - C27     =   -4.10(12)
C24     - C25     - C26     - N21     =    1.10(18)
C24     - C25     - C26     - C27     =  178.10(11)
N21     - C26     - C27     - C28     = -177.20(10)
C25     - C26     - C27     - C28     =    5.70(18)
N21     - C26     - C27     - C32     =    2.70(14)
C25     - C26     - C27     - C32     = -174.40(11)
C32     - C27     - C28     - C29     =    1.10(17)
C26     - C27     - C28     - C29     = -179.10(11)
C27     - C28     - C29     - C30     =    0.80(19)
C28     - C29     - C30     - C31     =   -1.00(19)
C29     - C30     - C31     - C32     =   -0.60(18)
C30     - C31     - C32     - C27     =    2.50(16)
C30     - C31     - C32     - Ir1     =  179.50(8)
C28     - C27     - C32     - C31     =   -2.70(15)
C26     - C27     - C32     - C31     =  177.40(10)
C28     - C27     - C32     - Ir1     =  179.90(8)
C26     - C27     - C32     - Ir1     =    0.00(11)
Ir1     - O41     - C42     - O43     =  171.00(7)
Ir1     - O41     - C42     - C44     =  -10.20(13)
O43     - C42     - C44     - N49     = -119.70(11)
O41     - C42     - C44     - N49     =   61.50(12)
O43     - C42     - C44     - C45     =    5.90(15)
O41     - C42     - C44     - C45     = -172.90(10)
N49     - C44     - C45     - C46     = -168.50(10)
C42     - C44     - C45     - C46     =   68.00(14)
C44     - C45     - C46     - C48     =  169.30(11)
C44     - C45     - C46     - C47     =   48.30(15)
C42     - C44     - N49     - C50     =  115.90(12)
C45     - C44     - N49     - C50     =  -12.20(15)
C42     - C44     - N49     - C53     =  -66.40(13)
C45     - C44     - N49     - C53     =  165.50(10)
C53     - N49     - C50     - C51     =   -1.30(13)
C44     - N49     - C50     - C51     =  176.60(10)
N49     - C50     - C51     - N52     =    2.80(13)
C50     - C51     - N52     - C53     =   -3.50(14)
C50     - C51     - N52     - C54     = -178.40(10)
C51     - N52     - C53     - N49     =    2.50(13)
C54     - N52     - C53     - N49     =  177.10(10)
C51     - N52     - C53     - Ir1     =  166.80(10)
C54     - N52     - C53     - Ir1     =  -18.60(19)
C50     - N49     - C53     - N52     =   -0.70(13)
C44     - N49     - C53     - N52     = -178.80(10)
C50     - N49     - C53     - Ir1     = -168.00(8)
C44     - N49     - C53     - Ir1     =   14.00(15)
C53     - N52     - C54     - C59     =  106.70(14)
C51     - N52     - C54     - C59     =  -79.20(14)
C53     - N52     - C54     - C55     =  -74.70(15)
C51     - N52     - C54     - C55     =   99.40(13)
C59     - C54     - C55     - C56     =   -2.90(17)
N52     - C54     - C55     - C56     =  178.50(10)
C59     - C54     - C55     - C60     =  173.60(11)
N52     - C54     - C55     - C60     =   -5.00(16)
C54     - C55     - C56     - C57     =    0.50(17)
C60     - C55     - C56     - C57     = -176.10(11)
C55     - C56     - C57     - C58     =    3.00(18)
C55     - C56     - C57     - C61     = -176.40(12)
C56     - C57     - C58     - C59     =   -4.20(19)
C61     - C57     - C58     - C59     =  175.00(13)
C55     - C54     - C59     - C58     =    1.70(19)
```

```
N52      - C54      - C59      - C58      = -179.80(11)
C55      - C54      - C59      - C62      = -176.50(11)
N52      - C54      - C59      - C62      =    2.10(18)
C57      - C58      - C59      - C54      =    2.00(19)
C57      - C58      - C59      - C62      = -179.80(12)
```

X-ray crystallographic study of Δ(S)-4

- ORTEP of Δ(S)-**4**; CCDC n° 1894795



(C_{40} H_{39} Ir N_4 O_2, H_2 O); *M* = 817.97. D8 VENTURE Bruker AXS diffractometer [*], Mo-Kα radiation (λ = 0.71073 Å), *T* = 150(2) K; orthorhombic *P* 2_1 2_1 2_1 (I.T.#19), a = 9.2852(6), b = 15.2175(12), c = 24.7997(19) Å, *V* = 3504.1(4) Å^3. *Z* = 4, *d* = 1.550 g.cm^{-3}, μ = 3.854 mm^{-1}. The structure was solved by dual-space algorithm using the *SHELXT* program [1], and then refined with full-matrix least-square methods based on F^2 (*SHELXL-2014*) [2]. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Except XXX linked hydrogen atoms that were introduced in the structural model through Fourier difference maps analysis, H atoms were finally included in their calculated positions. A final refinement on F^2 with 8014 unique intensities and 414 parameters converged at ω*R*(F^2) = 0.0539 (*R*(*F*) = 0.0346) for 6874 observed reflections with *I* > 2σ(*I*).

[1] G. M. Sheldrick, Acta Cryst. A71 (2015) 3-8

[2] Sheldrick G.M., Acta Cryst. C71 (2015) 3-8

Atomic coordinates, site occupancy (%) and equivalent isotropic displacement parameters (Å^2). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	occ.	U(eq)
Ir1	0.41683(3)	0.34698(2)	0.65537(2)	1	0.01136(6)
N1	0.5946(6)	0.3256(3)	0.60868(18)	1	0.0150(12)
C2	0.7190(7)	0.2896(5)	0.6260(3)	1	0.0203(17)
H2	0.727431	0.272863	0.662748	1	0.024
C3	0.8337(8)	0.2763(5)	0.5922(3)	1	0.0262(19)
H3	0.919858	0.250712	0.605607	1	0.031
C4	0.8236(8)	0.3003(5)	0.5381(3)	1	0.0284(19)
H4	0.902515	0.292077	0.514297	1	0.034
C5	0.6967(7)	0.3363(6)	0.5201(3)	1	0.0238(18)
H5	0.687026	0.352152	0.483229	1	0.029
C6	0.5821(8)	0.3497(5)	0.5555(2)	1	0.0180(12)
C7	0.4403(7)	0.3859(5)	0.5417(3)	1	0.0205(7)
C8	0.4029(9)	0.4118(4)	0.4891(3)	1	0.0205(7)
H8	0.472733	0.410152	0.461080	1	0.025
C9	0.2652(7)	0.4395(5)	0.4782(3)	1	0.0205(7)
H9	0.239066	0.457012	0.442801	1	0.025
C10	0.1648(8)	0.4416(5)	0.5195(3)	1	0.0205(7)
H10	0.069297	0.460242	0.511856	1	0.025
C11	0.2003(8)	0.4171(5)	0.5715(3)	1	0.0205(7)
H11	0.128245	0.418099	0.598649	1	0.025
C12	0.3414(8)	0.3906(5)	0.5850(3)	1	0.0205(7)
N13	0.2233(5)	0.3619(4)	0.6940(2)	1	0.0137(13)
C14	0.1752(7)	0.4380(5)	0.7157(3)	1	0.0177(16)
H14	0.232727	0.489343	0.712350	1	0.021
C15	0.0464(7)	0.4434(6)	0.7424(3)	1	0.026(2)
H15	0.013807	0.497942	0.756501	1	0.031
C16	-0.0354(8)	0.3683(6)	0.7483(3)	1	0.032(2)
H16	-0.122823	0.370097	0.768154	1	0.039
C17	0.0100(8)	0.2914(6)	0.7255(3)	1	0.0275(19)
H17	-0.046445	0.239719	0.729425	1	0.033
C18	0.1392(7)	0.2883(5)	0.6965(3)	1	0.0186(17)
C19	0.1932(7)	0.2136(5)	0.6663(3)	1	0.0162(16)
C20	0.1194(7)	0.1340(5)	0.6621(3)	1	0.0243(18)
H20	0.030921	0.126063	0.680681	1	0.029
C21	0.1740(9)	0.0671(5)	0.6312(3)	1	0.0284(19)
H21	0.123388	0.013041	0.628206	1	0.034
C22	0.3033(9)	0.0787(5)	0.6044(3)	1	0.027(2)
H22	0.342153	0.032161	0.583434	1	0.032
C23	0.3773(7)	0.1587(6)	0.6080(2)	1	0.0212(16)
H23	0.465321	0.165716	0.588924	1	0.025
C24	0.3249(7)	0.2279(5)	0.6388(2)	1	0.0150(16)
O25	0.5182(5)	0.2796(3)	0.72311(18)	1	0.0182(11)
C26	0.5811(8)	0.3114(4)	0.7637(2)	1	0.0152(14)
O27	0.6768(5)	0.2713(3)	0.78928(19)	1	0.0205(12)
C28	0.5394(7)	0.4016(5)	0.7853(3)	1	0.0138(16)
H28	0.614478	0.418929	0.812123	1	0.017
C28B	0.3971(8)	0.3946(5)	0.8156(3)	1	0.0214(17)
H00A	0.322102	0.373919	0.790209	1	0.026
H00B	0.368920	0.453998	0.827964	1	0.026
C29	0.3993(8)	0.3329(5)	0.8644(2)	1	0.0211(16)
H29	0.440046	0.275517	0.852119	1	0.025
C30	0.2475(9)	0.3157(6)	0.8842(3)	1	0.043(2)
H30A	0.202776	0.371234	0.895079	1	0.064
H30B	0.250571	0.275604	0.915093	1	0.064
H30C	0.190855	0.288981	0.855119	1	0.064
C31	0.4932(8)	0.3657(6)	0.9105(3)	1	0.031(2)
H31A	0.456862	0.422477	0.923199	1	0.046
H31B	0.592536	0.372619	0.897748	1	0.046
H31C	0.490874	0.323124	0.940092	1	0.046
N32	0.5375(5)	0.4705(4)	0.7429(2)	1	0.0130(12)
C33	0.5868(8)	0.5536(4)	0.7549(2)	1	0.0185(14)
H33	0.616848	0.574389	0.789191	1	0.022
C34	0.5843(9)	0.5993(4)	0.7089(2)	1	0.0204(15)
H34	0.610416	0.659230	0.704569	1	0.024
N35	0.5367(5)	0.5432(4)	0.66886(19)	1	0.0136(13)
C36	0.5040(6)	0.4616(5)	0.6890(3)	1	0.0131(15)
C37	0.5458(7)	0.5683(5)	0.6123(3)	1	0.0154(16)
C38	0.6801(7)	0.5595(5)	0.5874(3)	1	0.0192(16)
C39	0.6933(7)	0.5904(5)	0.5349(3)	1	0.0217(17)
H39	0.783491	0.585191	0.517065	1	0.026
C40	0.5790(9)	0.6285(4)	0.5078(2)	1	0.0217(15)

C41	0.4484(7)	0.6361(4)	0.5341(3)	1	0.0172(16)
H41	0.369898	0.662511	0.515636	1	0.021
C42	0.4270(9)	0.6065(4)	0.5870(2)	1	0.0166(14)
C43	0.8087(7)	0.5230(6)	0.6166(3)	1	0.029(2)
H43A	0.838873	0.564298	0.644728	1	0.043
H43B	0.887797	0.514297	0.590995	1	0.043
H43C	0.783159	0.466602	0.633099	1	0.043
C44	0.5995(9)	0.6643(6)	0.4511(2)	1	0.034(2)
H44A	0.701355	0.678199	0.445335	1	0.051
H44B	0.541615	0.717635	0.446603	1	0.051
H44C	0.568646	0.620040	0.424799	1	0.051
C45	0.2864(7)	0.6192(5)	0.6152(3)	1	0.0214(18)
H45A	0.266151	0.567888	0.637819	1	0.032
H45B	0.209529	0.626026	0.588402	1	0.032
H45C	0.291175	0.671937	0.637758	1	0.032
O101	0.7609(6)	0.1253(4)	0.7302(2)	1	0.0336(14)
H1W	0.740(8)	0.172(4)	0.751(3)	1	0.050
H2W	0.688(6)	0.121(6)	0.707(3)	1	0.050

Anisotropic displacement parameters (Å²)

The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$.

Atom	U11	U22	U33	U23	U13	U12
Ir1	0.01418(10)	0.00967(11)	0.01022(10)	-0.00041(12)	-0.00057(12)	0.00032(13)
N1	0.021(3)	0.012(3)	0.011(2)	-0.003(2)	0.003(3)	-0.003(3)
C2	0.022(4)	0.024(5)	0.015(4)	0.001(3)	-0.003(3)	0.006(3)
C3	0.021(4)	0.024(5)	0.033(5)	-0.003(4)	0.003(3)	0.010(3)
C4	0.034(4)	0.022(5)	0.030(4)	-0.004(4)	0.010(4)	0.011(4)
C5	0.033(4)	0.026(5)	0.012(3)	0.009(4)	0.008(3)	0.006(4)
C6	0.026(3)	0.016(3)	0.012(3)	-0.002(3)	0.001(3)	0.002(5)
C7	0.0295(17)	0.0159(17)	0.0161(15)	0.0014(13)	-0.0054(13)	0.0017(14)
C8	0.0295(17)	0.0159(17)	0.0161(15)	0.0014(13)	-0.0054(13)	0.0017(14)
C9	0.0295(17)	0.0159(17)	0.0161(15)	0.0014(13)	-0.0054(13)	0.0017(14)
C10	0.0295(17)	0.0159(17)	0.0161(15)	0.0014(13)	-0.0054(13)	0.0017(14)
C11	0.0295(17)	0.0159(17)	0.0161(15)	0.0014(13)	-0.0054(13)	0.0017(14)
C12	0.0295(17)	0.0159(17)	0.0161(15)	0.0014(13)	-0.0054(13)	0.0017(14)
N13	0.017(3)	0.011(4)	0.013(3)	0.000(2)	0.002(2)	-0.002(2)
C14	0.016(4)	0.015(4)	0.022(4)	0.001(3)	-0.001(3)	-0.001(3)
C15	0.021(4)	0.026(5)	0.030(4)	-0.011(4)	0.003(3)	0.004(4)
C16	0.018(4)	0.041(7)	0.037(5)	-0.012(4)	0.007(3)	-0.007(4)
C17	0.025(4)	0.021(5)	0.036(5)	0.001(4)	0.004(4)	-0.007(3)
C18	0.015(3)	0.022(5)	0.019(4)	0.001(3)	-0.007(3)	-0.004(3)
C19	0.020(3)	0.012(4)	0.016(4)	0.001(3)	-0.007(3)	-0.004(3)
C20	0.028(4)	0.020(5)	0.025(4)	0.007(3)	-0.012(3)	-0.005(3)
C21	0.042(5)	0.016(5)	0.028(4)	0.000(4)	-0.022(4)	-0.009(4)
C22	0.053(5)	0.010(4)	0.017(4)	-0.005(3)	-0.019(4)	0.007(4)
C23	0.034(4)	0.015(4)	0.015(3)	0.000(4)	-0.007(3)	0.000(4)
C24	0.027(4)	0.006(4)	0.012(4)	0.000(3)	-0.014(3)	0.004(3)
O25	0.028(3)	0.014(3)	0.013(2)	0.003(2)	-0.007(2)	0.001(2)
C26	0.014(3)	0.016(4)	0.016(3)	0.009(3)	0.007(4)	-0.003(4)
O27	0.020(3)	0.019(3)	0.023(3)	0.003(2)	-0.004(2)	-0.001(2)
C28	0.020(4)	0.013(4)	0.009(3)	0.002(3)	-0.001(3)	-0.001(3)
C28B	0.022(4)	0.028(5)	0.015(3)	0.002(3)	0.002(3)	0.000(4)
C29	0.027(4)	0.015(4)	0.021(3)	0.002(3)	0.006(3)	-0.005(4)
C30	0.035(5)	0.056(7)	0.037(5)	0.008(5)	0.013(4)	-0.010(5)
C31	0.045(5)	0.025(6)	0.024(4)	0.006(4)	0.001(3)	-0.001(4)
N32	0.019(3)	0.010(3)	0.010(3)	0.003(2)	-0.004(2)	-0.001(2)
C33	0.026(3)	0.013(4)	0.017(3)	-0.001(3)	-0.009(4)	0.000(4)
C34	0.027(4)	0.008(4)	0.026(4)	-0.003(3)	-0.007(4)	-0.007(4)
N35	0.018(3)	0.010(3)	0.014(3)	0.003(2)	-0.003(2)	0.000(2)
C36	0.010(3)	0.011(4)	0.018(4)	-0.003(3)	0.005(3)	0.001(3)
C37	0.028(4)	0.005(4)	0.013(3)	0.000(3)	0.001(3)	-0.005(3)
C38	0.028(4)	0.012(4)	0.017(4)	-0.004(3)	-0.003(3)	-0.001(3)
C39	0.022(4)	0.021(5)	0.022(4)	0.000(3)	0.003(3)	-0.001(3)
C40	0.033(4)	0.017(4)	0.015(3)	0.003(3)	-0.002(4)	-0.003(4)
C41	0.027(4)	0.008(4)	0.017(3)	0.002(3)	-0.008(3)	0.002(3)
C42	0.025(4)	0.010(4)	0.015(3)	-0.002(3)	-0.006(3)	-0.002(4)
C43	0.026(4)	0.032(5)	0.028(4)	0.000(4)	0.000(3)	0.006(4)
C44	0.036(4)	0.047(6)	0.020(4)	0.010(4)	-0.002(3)	0.008(5)

C45	0.028(4)	0.019(5)	0.016(4)	0.003(3)	-0.004(3)	0.000(3)
O101	0.030(3)	0.018(3)	0.053(4)	0.000(3)	0.003(3)	0.004(3)

Bond lengths [Å]

Ir1	- C12	= 1.994(7)
Ir1	- N1	= 2.042(5)
Ir1	- C24	= 2.044(7)
Ir1	- N13	= 2.049(5)
Ir1	- C36	= 2.097(7)
Ir1	- O25	= 2.181(4)
N1	- C2	= 1.349(8)
N1	- C6	= 1.374(7)
C2	- C3	= 1.369(9)
C2	- H2	= 0.9500
C3	- C4	= 1.393(10)
C3	- H3	= 0.9500
C4	- C5	= 1.373(9)
C4	- H4	= 0.9500
C5	- C6	= 1.395(9)
C5	- H5	= 0.9500
C6	- C7	= 1.468(10)
C7	- C8	= 1.406(8)
C7	- C12	= 1.416(9)
C8	- C9	= 1.372(10)
C8	- H8	= 0.9500
C9	- C10	= 1.384(9)
C9	- H9	= 0.9500
C10	- C11	= 1.382(9)
C10	- H10	= 0.9500
C11	- C12	= 1.411(10)
C11	- H11	= 0.9500
N13	- C14	= 1.353(9)
N13	- C18	= 1.367(9)
C14	- C15	= 1.370(9)
C14	- H14	= 0.9500
C15	- C16	= 1.380(10)
C15	- H15	= 0.9500
C16	- C17	= 1.366(11)
C16	- H16	= 0.9500
C17	- C18	= 1.400(9)
C17	- H17	= 0.9500
C18	- C19	= 1.450(10)
C19	- C20	= 1.397(9)
C19	- C24	= 1.418(9)
C20	- C21	= 1.371(10)
C20	- H20	= 0.9500
C21	- C22	= 1.384(11)
C21	- H21	= 0.9500
C22	- C23	= 1.400(11)
C22	- H22	= 0.9500
C23	- C24	= 1.390(10)
C23	- H23	= 0.9500
O25	- C26	= 1.260(8)
C26	- O27	= 1.251(8)
C26	- C28	= 1.523(9)
C28	- N32	= 1.484(8)
C28	- C28B	= 1.524(9)
C28	- H28	= 1.0000
C28B	- C29	= 1.532(9)
C28B	- H00A	= 0.9900
C28B	- H00B	= 0.9900
C29	- C30	= 1.516(10)
C29	- C31	= 1.521(9)
C29	- H29	= 1.0000
C30	- H30A	= 0.9800
C30	- H30B	= 0.9800
C30	- H30C	= 0.9800
C31	- H31A	= 0.9800
C31	- H31B	= 0.9800
C31	- H31C	= 0.9800
N32	- C36	= 1.378(8)
N32	- C33	= 1.378(8)
C33	- C34	= 1.335(8)
C33	- H33	= 0.9500

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C34  - N35      = 1.382(8)
C34  - H34      = 0.9500
N35  - C36      = 1.372(9)
N35  - C37      = 1.455(8)
C37  - C42      = 1.397(9)
C37  - C38      = 1.398(9)
C38  - C39      = 1.390(10)
C38  - C43      = 1.503(9)
C39  - C40      = 1.384(9)
C39  - H39      = 0.9500
C40  - C41      = 1.383(10)
C40  - C44      = 1.519(8)
C41  - C42      = 1.399(8)
C41  - H41      = 0.9500
C42  - C45      = 1.494(10)
C43  - H43A     = 0.9800
C43  - H43B     = 0.9800
C43  - H43C     = 0.9800
C44  - H44A     = 0.9800
C44  - H44B     = 0.9800
C44  - H44C     = 0.9800
C45  - H45A     = 0.9800
C45  - H45B     = 0.9800
C45  - H45C     = 0.9800
O101 - H1W      = 0.90(3)
O101 - H2W      = 0.89(3)
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Angles [°]

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C12      - Ir1      - N1       =   80.80(3)
C12      - Ir1      - C24      =   88.40(3)
N1       - Ir1      - C24      =   94.70(2)
C12      - Ir1      - N13      =   93.70(3)
N1       - Ir1      - N13      =  172.50(2)
C24      - Ir1      - N13      =   80.00(3)
C12      - Ir1      - C36      =  101.90(3)
N1       - Ir1      - C36      =   92.60(2)
C24      - Ir1      - C36      =  168.20(2)
N13      - Ir1      - C36      =   93.50(2)
C12      - Ir1      - O25      =  169.10(2)
N1       - Ir1      - O25      =   90.75(19)
C24      - Ir1      - O25      =   85.40(2)
N13      - Ir1      - O25      =   94.05(19)
C36      - Ir1      - O25      =   85.30(2)
C2       - N1       - C6       =  119.10(6)
C2       - N1       - Ir1      =  125.20(4)
C6       - N1       - Ir1      =  115.70(5)
N1       - C2       - C3       =  122.10(6)
N1       - C2       - H2       =  119.00
C3       - C2       - H2       =  119.00
C2       - C3       - C4       =  119.80(7)
C2       - C3       - H3       =  120.10
C4       - C3       - H3       =  120.10
C5       - C4       - C3       =  118.40(7)
C5       - C4       - H4       =  120.80
C3       - C4       - H4       =  120.80
C4       - C5       - C6       =  120.50(6)
C4       - C5       - H5       =  119.70
C6       - C5       - H5       =  119.70
N1       - C6       - C5       =  120.00(6)
N1       - C6       - C7       =  113.60(6)
C5       - C6       - C7       =  126.30(5)
C8       - C7       - C12      =  122.00(7)
C8       - C7       - C6       =  122.90(6)
C12      - C7       - C6       =  115.00(6)
C9       - C8       - C7       =  119.80(7)
C9       - C8       - H8       =  120.10
C7       - C8       - H8       =  120.10
C8       - C9       - C10      =  119.40(6)
C8       - C9       - H9       =  120.30
C10      - C9       - H9       =  120.30
C11      - C10      - C9       =  121.50(7)
C11      - C10      - H10      =  119.30
C9       - C10      - H10      =  119.30
C10      - C11      - C12      =  121.40(7)
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C10      - C11      - H11      =  119.30
C12      - C11      - H11      =  119.30
C11      - C12      - C7       =  115.80(6)
C11      - C12      - Ir1      =  129.00(5)
C7       - C12      - Ir1      =  114.80(5)
C14      - N13      - C18      =  119.60(6)
C14      - N13      - Ir1      =  124.80(5)
C18      - N13      - Ir1      =  115.60(5)
N13      - C14      - C15      =  122.20(7)
N13      - C14      - H14      =  118.90
C15      - C14      - H14      =  118.90
C14      - C15      - C16      =  118.80(7)
C14      - C15      - H15      =  120.60
C16      - C15      - H15      =  120.60
C17      - C16      - C15      =  119.70(7)
C17      - C16      - H16      =  120.10
C15      - C16      - H16      =  120.10
C16      - C17      - C18      =  120.40(8)
C16      - C17      - H17      =  119.80
C18      - C17      - H17      =  119.80
N13      - C18      - C17      =  119.10(7)
N13      - C18      - C19      =  114.90(6)
C17      - C18      - C19      =  126.00(7)
C20      - C19      - C24      =  121.30(7)
C20      - C19      - C18      =  123.40(6)
C24      - C19      - C18      =  115.30(6)
C21      - C20      - C19      =  120.40(7)
C21      - C20      - H20      =  119.80
C19      - C20      - H20      =  119.80
C20      - C21      - C22      =  119.60(7)
C20      - C21      - H21      =  120.20
C22      - C21      - H21      =  120.20
C21      - C22      - C23      =  120.50(7)
C21      - C22      - H22      =  119.80
C23      - C22      - H22      =  119.80
C24      - C23      - C22      =  121.50(7)
C24      - C23      - H23      =  119.30
C22      - C23      - H23      =  119.30
C23      - C24      - C19      =  116.80(6)
C23      - C24      - Ir1      =  129.60(5)
C19      - C24      - Ir1      =  113.50(5)
C26      - O25      - Ir1      =  129.40(4)
O27      - C26      - O25      =  123.10(6)
O27      - C26      - C28      =  116.30(6)
O25      - C26      - C28      =  120.50(6)
N32      - C28      - C26      =  113.00(5)
N32      - C28      - C28B     =  112.90(5)
C26      - C28      - C28B     =  109.30(6)
N32      - C28      - H28      =  107.10
C26      - C28      - H28      =  107.10
C28B     - C28      - H28      =  107.10
C28      - C28B     - C29      =  114.90(6)
C28      - C28B     - H00A     =  108.50
C29      - C28B     - H00A     =  108.50
C28      - C28B     - H00B     =  108.50
C29      - C28B     - H00B     =  108.50
H00A     - C28B     - H00B     =  107.50
C30      - C29      - C31      =  110.40(6)
C30      - C29      - C28B     =  110.40(6)
C31      - C29      - C28B     =  113.60(6)
C30      - C29      - H29      =  107.40
C31      - C29      - H29      =  107.40
C28B     - C29      - H29      =  107.40
C29      - C30      - H30A     =  109.50
C29      - C30      - H30B     =  109.50
H30A     - C30      - H30B     =  109.50
C29      - C30      - H30C     =  109.50
H30A     - C30      - H30C     =  109.50
H30B     - C30      - H30C     =  109.50
C29      - C31      - H31A     =  109.50
C29      - C31      - H31B     =  109.50
H31A     - C31      - H31B     =  109.50
C29      - C31      - H31C     =  109.50
H31A     - C31      - H31C     =  109.50
H31B     - C31      - H31C     =  109.50
C36      - N32      - C33      =  111.90(5)
C36      - N32      - C28      =  128.40(6)
```

C33	- N32	- C28	=	119.40(5)
C34	- C33	- N32	=	106.70(5)
C34	- C33	- H33	=	126.60
N32	- C33	- H33	=	126.60
C33	- C34	- N35	=	107.30(6)
C33	- C34	- H34	=	126.30
N35	- C34	- H34	=	126.30
C36	- N35	- C34	=	111.60(5)
C36	- N35	- C37	=	127.00(6)
C34	- N35	- C37	=	120.80(6)
N35	- C36	- N32	=	102.40(6)
N35	- C36	- Ir1	=	133.90(5)
N32	- C36	- Ir1	=	123.60(5)
C42	- C37	- C38	=	123.00(6)
C42	- C37	- N35	=	119.80(6)
C38	- C37	- N35	=	116.90(6)
C39	- C38	- C37	=	117.50(6)
C39	- C38	- C43	=	120.40(6)
C37	- C38	- C43	=	122.00(6)
C40	- C39	- C38	=	121.90(7)
C40	- C39	- H39	=	119.00
C38	- C39	- H39	=	119.00
C41	- C40	- C39	=	118.60(6)
C41	- C40	- C44	=	121.20(7)
C39	- C40	- C44	=	120.20(7)
C40	- C41	- C42	=	122.70(6)
C40	- C41	- H41	=	118.70
C42	- C41	- H41	=	118.70
C37	- C42	- C41	=	116.30(7)
C37	- C42	- C45	=	122.20(6)
C41	- C42	- C45	=	121.40(6)
C38	- C43	- H43A	=	109.50
C38	- C43	- H43B	=	109.50
H43A	- C43	- H43B	=	109.50
C38	- C43	- H43C	=	109.50
H43A	- C43	- H43C	=	109.50
H43B	- C43	- H43C	=	109.50
C40	- C44	- H44A	=	109.50
C40	- C44	- H44B	=	109.50
H44A	- C44	- H44B	=	109.50
C40	- C44	- H44C	=	109.50
H44A	- C44	- H44C	=	109.50
H44B	- C44	- H44C	=	109.50
C42	- C45	- H45A	=	109.50
C42	- C45	- H45B	=	109.50
H45A	- C45	- H45B	=	109.50
C42	- C45	- H45C	=	109.50
H45A	- C45	- H45C	=	109.50
H45B	- C45	- H45C	=	109.50
H1W	- O101	- H2W	=	105.00(6)

Torsion angles [°]

C6	- N1	- C2	- C3	= 0.10(11)
Ir1	- N1	- C2	- C3	= 179.30(6)
N1	- C2	- C3	- C4	= 0.00(12)
C2	- C3	- C4	- C5	= -0.60(12)
C3	- C4	- C5	- C6	= 1.10(12)
C2	- N1	- C6	- C5	= 0.40(10)
Ir1	- N1	- C6	- C5	= -178.90(6)
C2	- N1	- C6	- C7	= 178.50(6)
Ir1	- N1	- C6	- C7	= -0.80(8)
C4	- C5	- C6	- N1	= -1.10(12)
C4	- C5	- C6	- C7	= -178.90(8)
N1	- C6	- C7	- C8	= -177.70(6)
C5	- C6	- C7	- C8	= 0.20(12)
N1	- C6	- C7	- C12	= 0.50(9)
C5	- C6	- C7	- C12	= 178.40(7)
C12	- C7	- C8	- C9	= -2.60(11)
C6	- C7	- C8	- C9	= 175.50(7)
C7	- C8	- C9	- C10	= 0.10(11)
C8	- C9	- C10	- C11	= 0.50(11)
C9	- C10	- C11	- C12	= 1.30(12)
C10	- C11	- C12	- C7	= -3.60(11)
C10	- C11	- C12	- Ir1	= -176.60(6)
C8	- C7	- C12	- C11	= 4.20(11)
C6	- C7	- C12	- C11	= -174.00(7)

```
C8       - C7       - C12      - Ir1      =  178.20(6)
C6       - C7       - C12      - Ir1      =    0.00(8)
C18      - N13      - C14      - C15      =    2.70(10)
Ir1      - N13      - C14      - C15      = -178.20(5)
N13      - C14      - C15      - C16      =    1.50(11)
C14      - C15      - C16      - C17      =   -3.00(11)
C15      - C16      - C17      - C18      =    0.30(12)
C14      - N13      - C18      - C17      =   -5.40(10)
Ir1      - N13      - C18      - C17      =  175.40(5)
C14      - N13      - C18      - C19      =  172.80(6)
Ir1      - N13      - C18      - C19      =   -6.40(7)
C16      - C17      - C18      - N13      =    3.90(11)
C16      - C17      - C18      - C19      = -174.10(7)
N13      - C18      - C19      - C20      = -177.20(6)
C17      - C18      - C19      - C20      =    0.90(11)
N13      - C18      - C19      - C24      =    0.00(9)
C17      - C18      - C19      - C24      =  178.00(6)
C24      - C19      - C20      - C21      =    0.50(10)
C18      - C19      - C20      - C21      =  177.50(6)
C19      - C20      - C21      - C22      =    0.30(11)
C20      - C21      - C22      - C23      =   -1.00(11)
C21      - C22      - C23      - C24      =    0.80(11)
C22      - C23      - C24      - C19      =    0.00(9)
C22      - C23      - C24      - Ir1      =  175.00(5)
C20      - C19      - C24      - C23      =   -0.70(9)
C18      - C19      - C24      - C23      = -177.90(6)
C20      - C19      - C24      - Ir1      = -176.50(5)
C18      - C19      - C24      - Ir1      =    6.30(7)
Ir1      - O25      - C26      - O27      = -153.60(5)
Ir1      - O25      - C26      - C28      =   28.30(9)
O27      - C26      - C28      - N32      =  130.80(6)
O25      - C26      - C28      - N32      =  -51.00(8)
O27      - C26      - C28      - C28B     = -102.60(7)
O25      - C26      - C28      - C28B     =   75.60(7)
N32      - C28      - C28B     - C29      = -172.50(6)
C26      - C28      - C28B     - C29      =   60.80(7)
C28      - C28B     - C29      - C30      = -167.90(6)
C28      - C28B     - C29      - C31      =   67.50(8)
C26      - C28      - N32      - C36      =   31.90(9)
C28B     - C28      - N32      - C36      =  -92.70(7)
C26      - C28      - N32      - C33      = -141.40(7)
C28B     - C28      - N32      - C33      =   93.90(7)
C36      - N32      - C33      - C34      =    0.50(8)
C28      - N32      - C33      - C34      =  174.90(6)
N32      - C33      - C34      - N35      =   -1.40(9)
C33      - C34      - N35      - C36      =    1.90(9)
C33      - C34      - N35      - C37      = -169.10(6)
C34      - N35      - C36      - N32      =   -1.50(7)
C37      - N35      - C36      - N32      =  168.80(5)
C34      - N35      - C36      - Ir1      =  175.90(5)
C37      - N35      - C36      - Ir1      =  -13.80(9)
C33      - N32      - C36      - N35      =    0.60(7)
C28      - N32      - C36      - N35      = -173.20(5)
C33      - N32      - C36      - Ir1      = -177.20(5)
C28      - N32      - C36      - Ir1      =    9.10(8)
C36      - N35      - C37      - C42      =   95.50(8)
C34      - N35      - C37      - C42      =  -95.00(8)
C36      - N35      - C37      - C38      =  -90.00(8)
C34      - N35      - C37      - C38      =   79.50(8)
C42      - C37      - C38      - C39      =   -0.30(11)
N35      - C37      - C38      - C39      = -174.50(6)
C42      - C37      - C38      - C43      =  176.30(7)
N35      - C37      - C38      - C43      =    2.10(10)
C37      - C38      - C39      - C40      =    0.00(11)
C43      - C38      - C39      - C40      = -176.70(7)
C38      - C39      - C40      - C41      =    0.30(11)
C38      - C39      - C40      - C44      =  177.90(7)
C39      - C40      - C41      - C42      =   -0.30(10)
C44      - C40      - C41      - C42      = -177.90(7)
C38      - C37      - C42      - C41      =    0.20(10)
N35      - C37      - C42      - C41      =  174.40(6)
C38      - C37      - C42      - C45      = -177.10(6)
N35      - C37      - C42      - C45      =   -2.90(10)
C40      - C41      - C42      - C37      =    0.00(10)
C40      - C41      - C42      - C45      =  177.30(6)
```

9. Computational details.

All calculations were carried out with the Gaussian 09 package[6] and the B3LYP hybrid functional[7] on the real experimental systems. The iridium atom was described with the relativistic electron core potential SDD and associated basis set[8] augmented by a set of f-orbital polarization functions.[9] The 6-31G** basis set were employed for all other atoms. Optimizations were carried out without any symmetry restrictions taking into solvent effect (DCM : CH_2Cl_2) by means of the universal Solvation Model based on solute electron Density.[10] All stationary points involved were fully optimized. Frequency calculations were realized to confirm the nature of the *minima* (positive frequencies). CD and VCD spectra were computed for all relevant diastereomers. Time-Dependent Density Functional Theory (TD-DFT) calculations have been performed to obtain ECD spectra. The same level of theory was adopted and 60 excited states were admitted. VCD spectra were generated with Gaussview 6.0[11] by assigning 4 cm^{-1} bandwidth Lorentzian band shape to each vibrational transition and plotted with excel. Energies have been scaled by a factor of 0.98 to directly compare with the experimental spectra.

[6] Gaussian 09, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2009**.

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[10] A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* **2009**, *113*, 6378.

[11] GaussView, Version 6, R. Dennington, T- A. Keith, J- M. Millam, Semichem Inc., Shawnee Mission, KS, 2016.

In agreement with experimental data, Λ(*S*)-**3** was found slightly lower in energy than Δ(*S*)-**4** (ΔG about 1.2 kcal/mol). In the same way, Δ(*R*)-**3** was found slightly lower in energy than Λ(*R*)-**4** (ΔG around 0.6 kcal/mol).

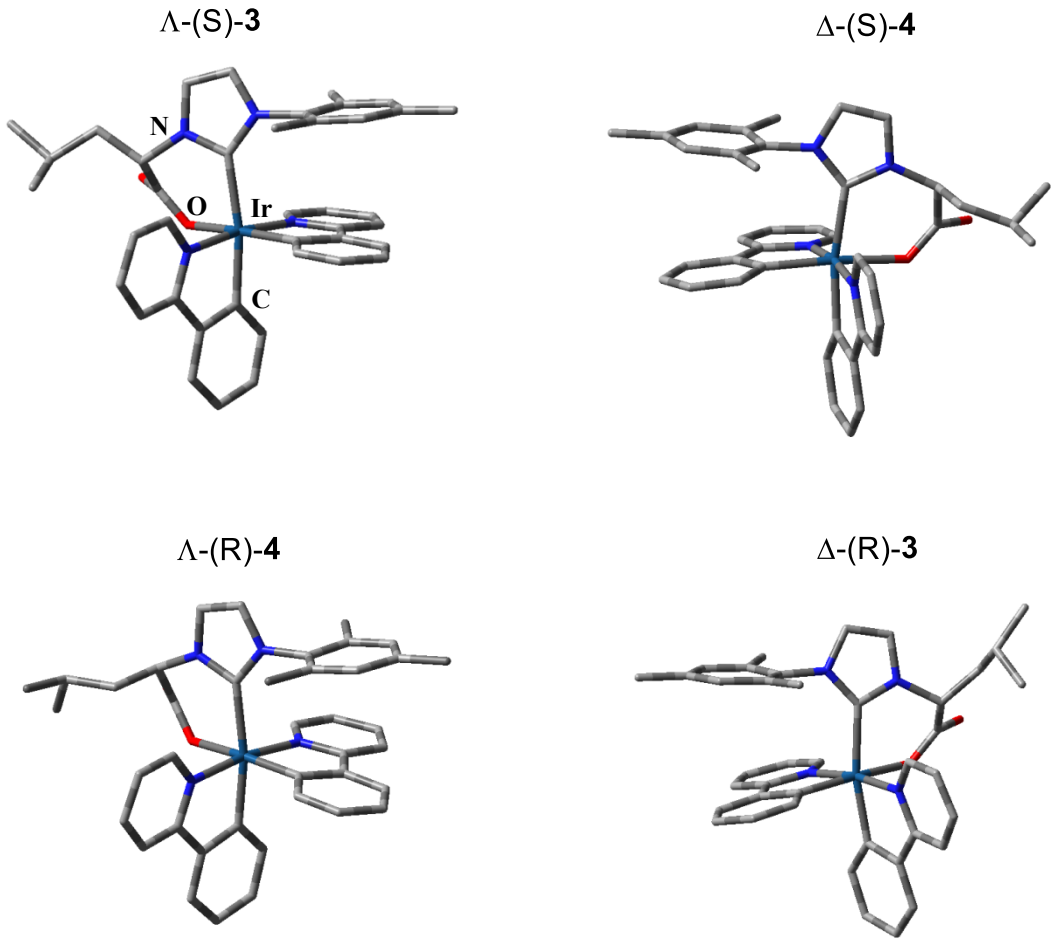

Figure S33. Structures of the different diastereomers optimized at SMD(DCM)-B3LYP/SDD+f(Ir), 6-31G**(other atoms) level of theory.

Z-matrices (energies in au)

Λ-(*R*)-4

Sum of electronic and zero-point Energies= -2021.142914
Sum of electronic and thermal Energies= -2021.100324
Sum of electronic and thermal Enthalpies= -2021.099380
Sum of electronic and thermal Free Energies= -2021.218048

Ir	0.35915400	0.50821000	-0.17876100
N	1.55108400	0.39515300	1.53301000
C	1.62880800	-0.66885500	2.36009400
H	1.04157500	-1.53108800	2.07763700
C	2.41149700	-0.68239700	3.50513000
H	2.42960700	-1.56758700	4.13094200
C	3.16431400	0.45231500	3.81196500
H	3.79624000	0.47856400	4.69427700
C	3.08792600	1.55385100	2.97162100
H	3.65371400	2.44998100	3.19593500
C	2.26519400	1.52537700	1.83588400
C	2.06165900	2.64832600	0.91566000
C	2.74143600	3.87315200	1.03988300
H	3.47609000	4.02304300	1.82601800
C	2.48195400	4.90764700	0.14623800
H	3.00822500	5.85330700	0.23897300
C	1.53807900	4.71716200	-0.86876600
H	1.32811600	5.52203600	-1.56959900
C	0.86592400	3.49767400	-0.99150100
H	0.14611600	3.38440100	-1.79780500
C	1.10654500	2.42716200	-0.11228600
N	-0.86551400	0.92777600	-1.79428800
C	-0.51072200	0.76136300	-3.08574400
H	0.47580200	0.34745400	-3.25273900
C	-1.34481100	1.11614300	-4.13574300
H	-1.01392800	0.96304000	-5.15686700
C	-2.59460800	1.66829200	-3.84262300
H	-3.27276600	1.95743500	-4.63956400
C	-2.95812200	1.84959000	-2.51552900
H	-3.91928400	2.28419100	-2.26786000
C	-2.08057400	1.47845200	-1.48564800
C	-2.32099800	1.64078400	-0.05172600
C	-3.48444000	2.22940400	0.47466800
H	-4.27574600	2.57089300	-0.18691200
C	-3.62912000	2.39037500	1.84867000
H	-4.52515200	2.85109100	2.25418700
C	-2.60419500	1.95827100	2.69982800
H	-2.70541400	2.08682800	3.77526100
C	-1.45049700	1.36723200	2.18207000
H	-0.67426600	1.04943500	2.87232700
C	-1.27061000	1.18163500	0.79672700
O	2.76988400	-1.14724800	-3.25048300
C	2.37163400	-1.02064400	-2.08401700
O	2.05398800	0.09779800	-1.53658100
C	2.29044300	-2.29350000	-1.21379600
H	2.48419800	-3.12787500	-1.88996900
C	4.74003200	-2.80568700	-0.46066600
H	4.64107400	-3.73330200	-1.04477500
C	5.48766500	-1.77858900	-1.32374400
H	4.97291400	-1.58589100	-2.26809000
H	6.49778000	-2.13438800	-1.55758900
H	5.58803700	-0.82317000	-0.79285800
C	5.54749400	-3.13355300	0.80459900
H	5.65637600	-2.24690300	1.44161400
H	6.55431000	-3.48320200	0.55035400
H	5.06306600	-3.91509300	1.40129600
N	0.90730500	-2.53103400	-0.72628000
C	0.42413400	-3.83254900	-0.69906000
H	1.02962500	-4.67315300	-0.99989400
C	-0.85269300	-3.76724100	-0.26541500
H	-1.59458900	-4.53442000	-0.11129900
N	-1.12811500	-2.42290800	-0.03115000
C	-0.03626900	-1.62654000	-0.30586900
C	-2.47224900	-2.04402000	0.34503100
C	-2.82841000	-2.01590100	1.70470400
C	-4.16630300	-1.76605700	2.02806500

H	-4.45220300	-1.73915700	3.07678000
C	-5.14249700	-1.56573500	1.04597200
C	-4.75577600	-1.64133700	-0.29561700
H	-5.50496100	-1.51774500	-1.07383000
C	-3.43127400	-1.89141000	-0.67235300
C	-1.82109000	-2.26331700	2.79915400
H	-1.20081700	-3.14101000	2.59111400
H	-2.32699100	-2.42503500	3.75465600
H	-1.15059600	-1.40710000	2.92017100
C	-6.57103000	-1.26390300	1.42702300
H	-7.26361300	-1.52049500	0.62004400
H	-6.69965000	-0.19560000	1.64274200
H	-6.87130200	-1.81210900	2.32563700
C	-3.07847300	-2.04691600	-2.13132500
H	-2.17919500	-1.48916000	-2.40130400
H	-3.89920600	-1.69955400	-2.76361900
H	-2.88971300	-3.09827400	-2.38094700
C	3.31892700	-2.35200200	-0.06054300
H	2.93175300	-3.06585000	0.67653800
H	3.37219500	-1.37833300	0.43498200

Λ-(*S*)-3

Sum of electronic and zero-point Energies= -2021.147314
Sum of electronic and thermal Energies= -2021.104779
Sum of electronic and thermal Enthalpies= -2021.103835
Sum of electronic and thermal Free Energies= -2021.222040

Ir	-0.30101700	0.57167200	0.20947800
N	-1.60954900	0.81410800	-1.40318900
C	-1.78750500	-0.07899100	-2.40183900
H	-1.21772200	-0.99583100	-2.32377700
C	-2.64340200	0.14197200	-3.46983500
H	-2.74395300	-0.61313400	-4.24136900
C	-3.35857500	1.34074700	-3.51386400
H	-4.04441100	1.54867100	-4.32909800
C	-3.17074300	2.27144600	-2.50228100
H	-3.70133600	3.21543100	-2.52780400
C	-2.27901900	2.00872100	-1.45078900
C	-1.94373100	2.94639200	-0.37438300
C	-2.55623200	4.20501400	-0.23735300
H	-3.34001100	4.51944200	-0.92056600
C	-2.16400800	5.06365400	0.78496200
H	-2.63775700	6.03516500	0.89246500
C	-1.15665800	4.66336200	1.66920800
H	-0.84276000	5.33048600	2.46890900
C	-0.55374200	3.40932200	1.53544800
H	0.21851700	3.13043000	2.24745400
C	-0.92719700	2.51149400	0.51984600
N	1.06534300	0.65873900	1.75691500
C	0.78905600	0.32222100	3.03395600
H	-0.21160900	-0.05696100	3.20320100
C	1.71335500	0.47563300	4.05669500
H	1.44343600	0.19430900	5.06846100
C	2.97538500	0.99104500	3.74816500
H	3.72482000	1.12087000	4.52288200
C	3.26056900	1.34011200	2.43509300
H	4.23160900	1.74540400	2.17620300
C	2.28978800	1.17880100	1.43511700
C	2.43873300	1.53649500	0.02421100
C	3.60575700	2.11410200	-0.50580700
H	4.46151800	2.31046000	0.13417900
C	3.67277100	2.44852500	-1.85434400
H	4.57341300	2.89804300	-2.26221000
C	2.56590700	2.20361100	-2.67622800
H	2.60830800	2.46596900	-3.73103200
C	1.40405100	1.63157400	-2.15446800
H	0.56411000	1.46203300	-2.82192900
C	1.30000000	1.27518800	-0.79529300
O	-1.87248400	0.00677900	1.68588800
C	-2.48261500	-1.12704300	1.75125600
O	-3.00812000	-1.59326900	2.76751100
C	-2.52027700	-1.92518200	0.42056900
H	-2.75648300	-1.21655400	-0.37213200
C	-5.01289500	-2.57418000	0.46918100
H	-5.10902500	-1.91775000	1.34182300

C	-5.42945300	-1.78541100	-0.78089100
H	-4.84736400	-0.86722900	-0.90936600
H	-6.48343800	-1.49226900	-0.71843200
H	-5.30791700	-2.38991000	-1.68919500
C	-5.94585200	-3.77547100	0.67886000
H	-5.88102200	-4.48154800	-0.15926200
H	-6.99013300	-3.45308300	0.75738300
H	-5.69609500	-4.32290600	1.59469300
N	-1.13966200	-2.40670600	0.14705500
C	-0.77005900	-3.74263300	0.08012300
H	-1.46584700	-4.55307600	0.21077800
C	0.55944200	-3.76447900	-0.16679300
H	1.24326700	-4.58706000	-0.30343700
N	0.98074700	-2.43958800	-0.23629200
C	-0.06535400	-1.57143200	-0.03468400
C	2.36695200	-2.14205200	-0.51110900
C	2.76537000	-1.91615600	-1.84180900
C	4.12675500	-1.72989400	-2.09677100
H	4.44605500	-1.55194700	-3.12086800
C	5.08610500	-1.78173700	-1.07763100
C	4.65369600	-2.04425700	0.22472600
H	5.38501200	-2.11098000	1.02651200
C	3.30115700	-2.24135600	0.53284200
C	1.76970300	-1.90878100	-2.97407100
H	1.17847600	-2.83145100	-2.99381300
H	2.28298200	-1.81643500	-3.93449500
H	1.06971800	-1.07300400	-2.88703900
C	6.54564600	-1.55332700	-1.38517300
H	7.18307000	-1.84926000	-0.54721500
H	6.74072200	-0.49406800	-1.59349100
H	6.86093100	-2.11634800	-2.27017900
C	2.89299100	-2.59814900	1.94105400
H	1.99454100	-2.06524000	2.25869000
H	3.69674000	-2.36509200	2.64374900
H	2.67834200	-3.67009600	2.03124200
C	-3.54718800	-3.05765600	0.41283000
H	-3.35969900	-3.70696400	1.27402600
H	-3.41616200	-3.65869600	-0.49666200

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Sum of electronic and zero-point Energies= -2021.145205
Sum of electronic and thermal Energies= -2021.102864
Sum of electronic and thermal Enthalpies= -2021.101920
Sum of electronic and thermal Free Energies= -2021.219037

Ir	0.26821700	0.69974900	0.23245600
N	-1.22437500	0.81553300	1.65787600
C	-1.02171500	0.66047100	2.98262200
H	-0.00654600	0.40834200	3.26465300
C	-2.03579300	0.83538900	3.91246000
H	-1.82340900	0.70322700	4.96750800
C	-3.31105200	1.18077400	3.45619500
H	-4.12881100	1.32456400	4.15563200
C	-3.52073000	1.34366300	2.09361700
H	-4.50063600	1.61834900	1.72126200
C	-2.46220400	1.16455400	1.19011700
C	-2.52973300	1.33687800	-0.26122200
C	-3.70130400	1.71727100	-0.93880600
H	-4.62288000	1.88859900	-0.38970000
C	-3.69064900	1.88460000	-2.31966900
H	-4.59568400	2.18155300	-2.84152500
C	-2.50059500	1.67023400	-3.02569500
H	-2.48170000	1.80391200	-4.10508000
C	-1.33458100	1.29231900	-2.35714200
H	-0.42916500	1.14257700	-2.93805600
C	-1.30698400	1.10727000	-0.96069400
N	1.67313400	0.90526800	-1.29999000
C	2.03114300	-0.07031600	-2.16340900
H	1.56436700	-1.03361800	-2.00597000
C	2.93841500	0.12653800	-3.19351300
H	3.18466800	-0.69616300	-3.85515600
C	3.51702500	1.38931000	-3.34058900
H	4.23954000	1.58103200	-4.12760100
C	3.14434900	2.40204300	-2.46912400
H	3.56669600	3.39395000	-2.57536400
C	2.20466900	2.15867800	-1.45555600

C	1.68037600	3.16992100	-0.53282400
C	2.13263100	4.50158600	-0.52044500
H	2.92124600	4.82614300	-1.19334400
C	1.57234200	5.42010200	0.36162500
H	1.92158800	6.44851900	0.37302900
C	0.55715100	5.00546900	1.23041600
H	0.11310800	5.71803700	1.92190500
C	0.11144300	3.68074900	1.21832300
H	-0.67384200	3.39547900	1.91323900
C	0.65610300	2.72240700	0.34534700
O	1.74734300	0.47456700	1.86699600
C	2.51722100	-0.53038900	2.11046300
O	3.09309700	-0.73379700	3.18346800
C	2.71700300	-1.51620400	0.92703400
N	1.40715400	-2.15852000	0.62121200
C	1.16460400	-3.52315500	0.70580000
H	1.90967700	-4.23939900	1.00342700
C	-0.12648100	-3.71263200	0.35285100
H	-0.71513400	-4.61227800	0.27083400
N	-0.65648800	-2.45871000	0.06824900
C	0.28192200	-1.46870200	0.23948600
C	-2.03099200	-2.34496200	-0.36047300
C	-3.04921000	-2.41638800	0.60432500
C	-4.37789600	-2.39822400	0.16004700
H	-5.17461100	-2.44400900	0.89853100
C	-4.70407700	-2.33868900	-1.19720200
C	-3.65909300	-2.31473700	-2.12938200
H	-3.89262500	-2.29755400	-3.19124800
C	-2.31751800	-2.32703000	-1.73848900
C	-2.74914300	-2.56672500	2.07579500
H	-2.47168800	-3.60031900	2.31778600
H	-3.62880200	-2.31743900	2.67413000
H	-1.92272300	-1.92983600	2.39769600
C	-6.14207800	-2.30091600	-1.65366300
H	-6.82699800	-2.55267000	-0.83912600
H	-6.31875600	-2.99999900	-2.47815900
H	-6.41236000	-1.30202000	-2.01779400
C	-1.22397500	-2.35905800	-2.77635000
H	-0.64136300	-1.43344200	-2.77365000
H	-1.64949500	-2.48232700	-3.77559400
H	-0.52804000	-3.18690500	-2.60059100
C	3.84246000	-2.52086700	1.18589400
H	3.52959900	-3.22930700	1.95988100
H	4.65359800	-1.94657600	1.64456000
C	4.39801500	-3.26678100	-0.04891600
H	3.55843400	-3.61923000	-0.66403700
C	5.19792400	-4.49935800	0.39708000
H	4.57263900	-5.20426800	0.95701000
H	5.61709900	-5.03424500	-0.46257800
H	6.03321000	-4.21094900	1.04748900
C	5.26777600	-2.35056900	-0.92275300
H	4.72788300	-1.45668600	-1.25195000
H	6.15640000	-2.01797800	-0.37206200
H	5.61074600	-2.87570400	-1.82140000
H	2.97196800	-0.91034900	0.05566400

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Sum of electronic and zero-point Energies= -2021.145085
Sum of electronic and thermal Energies= -2021.102448
Sum of electronic and thermal Enthalpies= -2021.101504
Sum of electronic and thermal Free Energies= -2021.220108

Ir	0.31348200	0.54955100	0.20065000
N	-0.91949800	0.84244100	1.83516600
C	-0.54773900	0.64168900	3.11660300
H	0.46165200	0.27613000	3.25791700
C	-1.39234500	0.90630500	4.18427600
H	-1.04720200	0.72968700	5.19684200
C	-2.67306300	1.39981800	3.91949000
H	-3.36147300	1.61581500	4.73066500
C	-3.05478800	1.61593600	2.60274200
H	-4.04111200	2.00330100	2.37642300
C	-2.16382500	1.33981900	1.55450200
C	-2.42246400	1.54562600	0.12962300
C	-3.61769600	2.09663500	-0.36513600
H	-4.41560600	2.38004500	0.31579700

C	-3.78506300	2.29550200	-1.73149400
H	-4.70599200	2.72664600	-2.11305500
C	-2.75036600	1.93991900	-2.60607700
H	-2.86994900	2.09801900	-3.67568300
C	-1.56335600	1.39000600	-2.11927100
H	-0.78028800	1.13497900	-2.82765400
C	-1.35806900	1.16871400	-0.74239700
N	1.49766100	0.56447500	-1.51960200
C	1.61044700	-0.45650000	-2.39517200
H	1.05570300	-1.35075200	-2.14908600
C	2.38601400	-0.38773000	-3.54326000
H	2.43317700	-1.24132500	-4.21011400
C	3.09437400	0.78767900	-3.79916800
H	3.72023600	0.87912200	-4.68136800
C	2.97881900	1.84648500	-2.90961800
H	3.50715200	2.77354700	-3.09620500
C	2.16303500	1.73511400	-1.77390900
C	1.91149200	2.80958700	-0.80874500
C	2.54076700	4.06532600	-0.87913900
H	3.27352800	4.27705400	-1.65284600
C	2.23210100	5.05175100	0.05238900
H	2.71947000	6.02111500	0.00140600
C	1.29017900	4.78269700	1.05132500
H	1.04205300	5.55047700	1.78071700
C	0.66955700	3.53199000	1.12146600
H	-0.05039900	3.35649300	1.91665800
C	0.96122700	2.50789800	0.20375500
O	2.03118900	0.18918900	1.52088300
C	2.61106400	-0.88712700	1.91388100
O	3.38182000	-0.95412000	2.88161300
C	2.42934700	-2.18530400	1.10704500
H	2.63244700	-2.99133100	1.81200000
C	3.44465500	-2.28251600	-0.05437100
H	3.26901600	-1.45249300	-0.74321600
H	3.23044800	-3.20835500	-0.60630200
C	4.93189300	-2.27988600	0.35546100
H	5.13430800	-1.34362900	0.89079600
C	5.80496000	-2.30309300	-0.90752400
H	5.65052700	-3.22766900	-1.47850900
H	6.86869000	-2.24621400	-0.65129700
H	5.57497800	-1.46034900	-1.56946900
C	5.29504300	-3.43996600	1.29343800
H	5.02414500	-4.40892500	0.85398600
H	4.79269000	-3.34659000	2.26023400
H	6.37365700	-3.45592100	1.48676400
N	1.04772900	-2.46033700	0.63661000
C	0.63621600	-3.78634400	0.58011000
H	1.29144900	-4.59901300	0.85168700
C	-0.64629500	-3.78317300	0.16052400
H	-1.34408200	-4.58761400	-0.00900900
N	-0.99973800	-2.45110600	-0.03511600
C	0.04831300	-1.60081900	0.25223200
C	-2.36349300	-2.13847000	-0.40167500
C	-3.32648500	-2.04776000	0.61944200
C	-4.66153100	-1.84886300	0.24956900
H	-5.41358600	-1.77192200	1.03102500
C	-5.05461500	-1.76627800	-1.08967300
C	-4.07390700	-1.91236600	-2.07662400
H	-4.36391300	-1.88340100	-3.12417500
C	-2.72522000	-2.10813500	-1.76026700
C	-2.96522300	-2.21937700	2.07440000
H	-2.72245600	-3.26536200	2.29894500
H	-3.80262900	-1.93077000	2.71426500
H	-2.09656600	-1.62185300	2.35809400
C	-6.49516600	-1.51674600	-1.46256900
H	-7.17390700	-1.80485900	-0.65450000
H	-6.77861200	-2.06967000	-2.36380700
H	-6.66470700	-0.45255700	-1.67014000
C	-1.71412000	-2.29741900	-2.86305800
H	-1.09733600	-1.40280500	-2.99308300
H	-2.21819000	-2.49123900	-3.81355600
H	-1.04063600	-3.13585400	-2.65935800