Supporting Information

Electronic and chiroptical properties of chiral cycloiridiated complexes bearing helicenic NHC ligands

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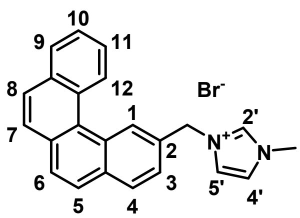
General:

Most experiments were performed using standard Schlenk techniques. Solvents were freshly distilled under argon from sodium / benzophenone (THF) or from phosphorus pentoxide (CH_2Cl_2 = DCM). Starting materials were purchased from Aldrich. Column chromatography purifications were performed in air over silica gel (Merck Geduran 60, 0.063–0.200 mm). Irradiation reactions were conducted using a Heraeus TQ 700 mercury vapor lamp. NMR spectra were recorded at room temperature on a Bruker AV III 400 MHz spectrometer equipped with a tunable BBFO probe, or a Bruker Av III HD 500 MHz fitted with a tunable BBO probe (Biosit platform - Université de Rennes 1). ^{1}H and ^{13}C chemical shifts are reported in parts per million (ppm) relative to Me_4Si as external standard. All spectra were obtained using deuterated dichloromethane or chloroform as solvents. The terms s, d, t, q, m indicate respectively singlet, doublet, triplet, quartet, multiplet; b is for broad; dd is doublet of doublets, dt – doublet of triplets, td – triplet of doublets. Assignment of proton and carbon signals is based on COSY, HSQC and HMBC experiments. ^{1}H dipolar couplings were studied using either NOESY or ROESY sequence, with a 500 ms mixing time. Mass spectrometry was performed by the CRMPO, University of Rennes 1. Specific rotations (in deg cm^2g^{-1}) were measured in a 1 dm thermostated quartz cell on a Perkin Elmer-341 polarimeter. Circular dichroism (in $M^{-1}cm^{-1}$) was measured on a Jasco J-815 Circular Dichroism Spectrometer IFR140 facility (Biosit platform - Université de Rennes 1). UV/vis spectroscopy was conducted on a Varian Cary 5000 spectrometer.

2-Bromomethyl[4]helicene (*i.e.* benzo[c]phenanthrylmethylbromide) **1a**[1] and 2-bromomethylene[6]helicene **1b**[2] were prepared according to the literature.

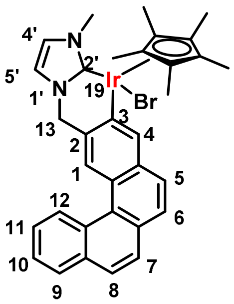
2-(1-Methylene-3-methyl-imidazolium)[4]helicene bromide salt 2a



1-Methylimidazole (62 µL; 0.78 mmol) was mixed with 2-(bromomethyl)benzo[*c*]phenanthrene **1a**[1] (400 mg; 1.25 mmol; 1.2 eq) in acetone (1 mL). The mixture was refluxed overnight. After removal of acetone under reduced pressure, the obtained solid was washed with ethyl acetate to afford the desired compound **2a** as a beige solid (225 mg; 71%; very hygroscopic).

^{1}H NMR (400 MHz, C*D*Cl$_3$): δ 10.12 (s, 1H, H$^{2'}$), 8.82 (d, 1H, *J* = 8.6 Hz, H^{12}), 8.79 (s, 1H, H^1), 7.83 (d, 1H, *J* = 8.0 Hz, H^9), 7.75 (d, 1H, *J* = 8.2 Hz), 7.71 (d, 1H, *J* = 8.6 Hz), 7.66 (t, 1H, *J* = 7.6 Hz, H^{11}), 7.60 (m, 2H), 7.58 (d, 1H, *J* = 8.5 Hz), 7.47 (t, 1H, *J* = 7.4 Hz, H^{10}), 7.42 (d, 1H, *J* = 8.2 Hz), 7.32 (d, 1H, *J* = 2.0 Hz, H$^{4'or5'}$), 7.22 (d, 1H, *J* = 1.8 Hz, H$^{4'or5'}$), 5.61 (s, 2H, *CH$_2$*), 3.77 (s, 3H, NC*H$_3$*). ^{13}C NMR (101 MHz, C*D*Cl$_3$): δ 136.92 (*C*H$^{2'}$), 133.21 (*C*x2), 131.12 (*C*), 130.71 (*C*), 129.84 (*C*), 129.77 (*C*), 129.60 (*C*H), 128.50 (*C*H), 127.89 (*C*H), 127.77 (*C*H), 127.63 (*C*H), 127.55 (*C*H), 126.99 (*C*H), 126.85 (*C*H), 126.63 (*C*), 126.51 (*C*H), 126.12 (*C*H), 125.37 (*C*H), 123.61 (*C*H$^{4'or5'}$), 121.93 (*C*H$^{4'or5'}$), 53.44 (CH_2), 36.51 (CH_3). HRMS (ESI) calculated for C^+ ($C_{23}H_{19}N_2$): m/z 323.15482, found: m/z 323.1547 (0 ppm).

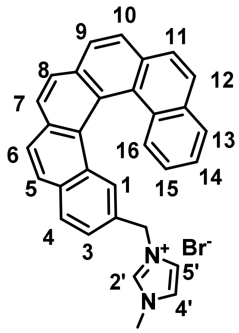
Iridium(III) complex 3a[3]



A mixture of $[Cp^*IrCl_2]_2$ (64 mg; 0.080 mmol; 0.5 eq), imidazolium salt **2a** (65 mg; 0.161 mmol), and NaOAc (20 mg; 0.241 mmol; 1.5 eq) in acetonitrile was refluxed overnight. The solution was filtered over Celite, the solvent was evaporated, and the crude solid was purified by column chromatography on silica gel using pure ethyl acetate as the eluent. A mixture of chlorido and bromo complexes was obtained as evidenced by mass spectrometry (ESI MS: calculated for $[M]^{\cdot+}$ (C_{33} H_{32} N_2 $^{35}Cl^{193}Ir$): m/z 684.18779, found: m/z 684.183). The desired pure compound **3a** was finally obtained as a yellow solid (67 mg; 57 %) after crystallization from a CH_2Cl_2 / pentane mixture.

^{1}H NMR (500 MHz, C*D*Cl$_3$): *δ* 9.20 (d, 1H, *J* = 8.5 Hz, H^{12}), 8.79 (s, 1H, H^1), 8.34 (s, 1H, H^4), 7.99 (dd, 1H, *J* = 8.0, 1.1 Hz, H^9), 7.84 (d, 1H, *J* = 8.6 Hz,), 7.78 (m, 2H), 7.69 (d, 1H, *J* = 8.5 Hz), 7.64 (ddd, 1H, *J* = 8.4, 6.9, 1.5 Hz, H^{11}), 7.58 (ddd, 1H, *J* = 7.9, 6.9, 1.2 Hz, H^{10}), 7.05 (dd, 1H, *J* = 2.0, 1.1 Hz, $H^{4' or 5'}$), 6.96 (d, 1H, *J* = 2.0 Hz, $H^{4' or 5'}$), 5.19 (d, 1H, *J* = 14.2 Hz, C*H*$_2$), 4.99 (d, 1H, *J* = 14.1 Hz, C*H*$_2$), 3.97 (s, 3H, NC*H*$_3$), 1.76 (d, 15 H, *J* = 14.5 Hz, Cp*). ^{13}C NMR (101 MHz, C*D*Cl$_3$) δ 156.23 (*C*$^{2'}$), 142.63 (*C*H), 141.34 (*C*), 138.78 (*C*), 138.68 (*C*), 134.57 (*C*), 133.54 (*C*), 130.63 (*C*), 128.63 (*C*H), 127.97 (*C*H), 127.58 (*C*H), 127.38 (*C*), 127.35 (*C*H), 126.82 (*C*), 125.89 (*C*H), 125.49 (*C*H), 125.33 (*C*H), 125.20 (*C*H), 122.29 (*C*H), 121.44 (*C*H), 120.64 (*C*H), 90.81 (*C* Cp*), 58.17 (*C*H$_2$), 38.20 (*C*H$_3$), 9.85 (*C*H$_3$ Cp*). HRMS (ESI) calculated for $[M]^{\cdot+}$ (C_{33} H_{32} N_2 $^{79}Br^{193}Ir$): m/z 728.13728, found: m/z 728.1369 (0 ppm).

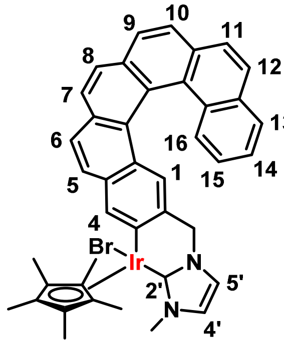
2-(1-Methylene-3-methyl-imidazolium)[6]helicene bromide salt 2b



1-Methylimidazole (38 µL; 0,48 mmol) was mixed with 2-bromomethylene[6]helicene **1b** (204 mg; 0.48 mmol) in acetone (1 mL). The mixture was refluxed overnight. After removal of acetone under reduced pressure, the solid was washed with ethyl acetate to afford the desired compound **2b** as a beige solid (161 mg; 66%).

^{1}H NMR (400 MHz, C*D*$_2$Cl$_2$): *δ* 10.17 (s, 1H, $H^{2'}$), 8.13 – 7.91 (m, 8H), 7.91 – 7.86 (m, 2H), 7.58 (d, 1H, *J* = 8.4 Hz, H^{16}), 7.56 (s, 1H, H^1), 7.36 – 7.22 (m, 2H), 7.12 (d, 1H, *J* = 1.8 Hz, $H^{4' or 5'}$), 6.71 (ddd, 1H, *J* = 8.5, 6.9, 1.5 Hz, H^{15}), 6.07 (d, 1H, *J* = 1.8 Hz, $H^{4' or 5'}$), 5.10 (d, 1H, *J* = 14.5 Hz, C*H*$_2$), 4.62 (d, 1H, *J* = 14.5 Hz, C*H*$_2$), 4.00 (s, 3H, NC*H*$_3$). ^{13}C NMR (101 MHz, C*D*$_2$Cl$_2$): *δ* 137.97 (*C*H$^{2'}$), 133.92 (*C*), 132.53 (*C*), 132.41 (*C*), 132.25 (*C*), 132.21 (*C*), 130.31 (*C*), 130.26 (*C*), 129.86 (*C*H), 129.71 (*C*), 128.65 (*C*H), 128.45 (*C*H), 128.37 (*C*H), 128.17 (*C*Hx2), 128.07 (*C*H), 128.03 (*C*Hx2), 127.91 (*C*H), 127.75 (*C*H), 127.32 (*C*H), 126.34 (*C*H), 125.94 (*C*H), 125.54 (*C*H), 124.16 (*C*), 123.54 (*C*H), 121.93 (*C*H), 53.61 (*C*H$_2$), 37.12 (*C*H$_3$). 2 quaternary carbons are not attributed. HRMS (ESI) calculated for C^+ (C_{31} H_{23} N_2): m/z 423.18612, found: m/z 423.1858 (1 ppm).

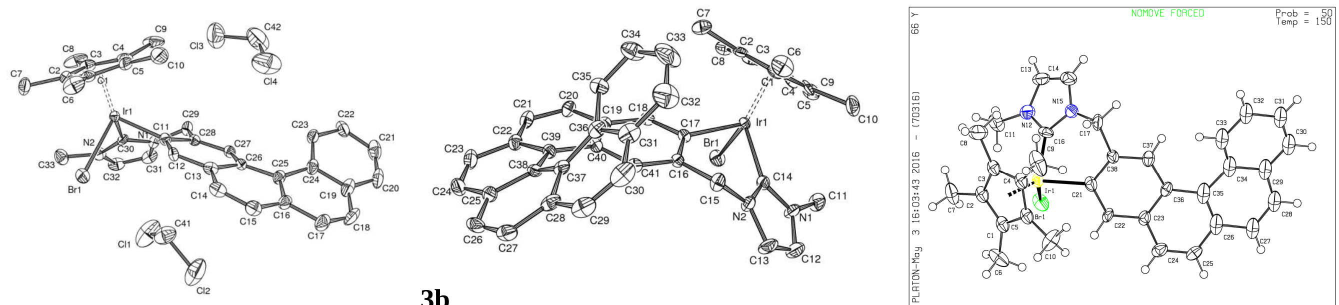
Racemic iridium(III) complex (±)-3b



A mixture of $[Cp^*IrCl_2]_2$ (122 mg; 0.153 mmol; 0.5 eq), imidazolium salt **2b** (154 mg; 0.306 mmol), and NaOAc (38 mg; 0.463 mmol; 1.5 eq) in acetonitrile was refluxed overnight. The solution was filtered over Celite, the solvent was evaporated, and the crude solid was purified by column chromatography on silica gel using pure ethyl acetate. A mixture of chlorido and bromo complexes was obtained as evidenced by mass spectrometry (ESI MS: calculated for $[M]^{\cdot+}$ (C_{41} H_{36} N_2 $^{35}Cl^{193}Ir$): m/z 784.21909, found: m/z 784.219). The desired pure racemic compound (±)-**3b** was finally obtained as a yellow solid (90 mg, 35 %) after crystallization from a CH_2Cl_2 / pentane mixture.

^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.08 (s, 1H, H^4), 8.04 (d, 1H, J = 8.2 Hz), 8.01 – 7.93 (m, 5H), 7.84 (dd, 1H, J = 8.1, 1.4 Hz, H^{16}), 7.82 (m, 2H), 7.70 (d, 1H, J = 8.7 Hz, H^{13}), 7.24 (ddd, 1H, J = 8.0, 6.9, 1.2 Hz, H^{15}), 7.15 (s, 1H, H^1), 6.80 (d, 1H, J = 2.0 Hz, $H^{4' or 5'}$), 6.73 (ddd, 1H, J = 8.4, 6.8, 1.4 Hz, H^{14}), 6.64 (d, 1H, J = 2.0 Hz, $H^{4' or 5'}$), 4.29 (dd, 1H, J = 14.3, 1.3 Hz, CH_2), 3.86 (d, 1H, J = 14.7 Hz, CH_2), 3.80 (s, 3H, NCH_3), 1.71 (s, 15H, Cp*). ^{13}C NMR (126 MHz, CD_2Cl_2): δ 156.04 ($C^{2'}$), 142.53 (*C*), 141.74 (*C*H), 138.14 (*C*), 133.51 (*C*), 133.06 (*C*), 132.28 (*C*), 131.61 (*C*), 131.17 (*C*), 131.04 (*C*), 128.67 (*C*), 128.38 (*C*), 128.30 (*C*H), 128.25 (*C*H), 128.11 (*C*H), 127.77 (*C*H), 127.76 (*C*H), 127.71 (*C*H), 126.95 (*C*H), 126.93 (*C*H), 126.26 (*C*), 125.97 (*C*H), 125.81 (*C*H), 125.13 (*C*H), 125.04 (*C*H), 124.36 (*C*), 122.55 (*C*H), 121.70 (*C*H), 120.56 (*C*H), 91.09 (*C* Cp*), 57.27 (CH_2), 38.36 (CH_3), 10.03 (CH_3 Cp*). HRMS (ESI) calculated for $[M]^{\cdot+}$ (C_{41} H_{36} N_2 $^{79}Br^{193}Ir$): m/z 828.16858, found: m/z 828.1672 (2 ppm).

X-ray crystallographic data:



3a

3b

Figure S1. ORTEP diagrams with ellipsoids at 50% probability of racemic **3a**,**b** and enantiopure (P,S_{Ir})-**3a**.

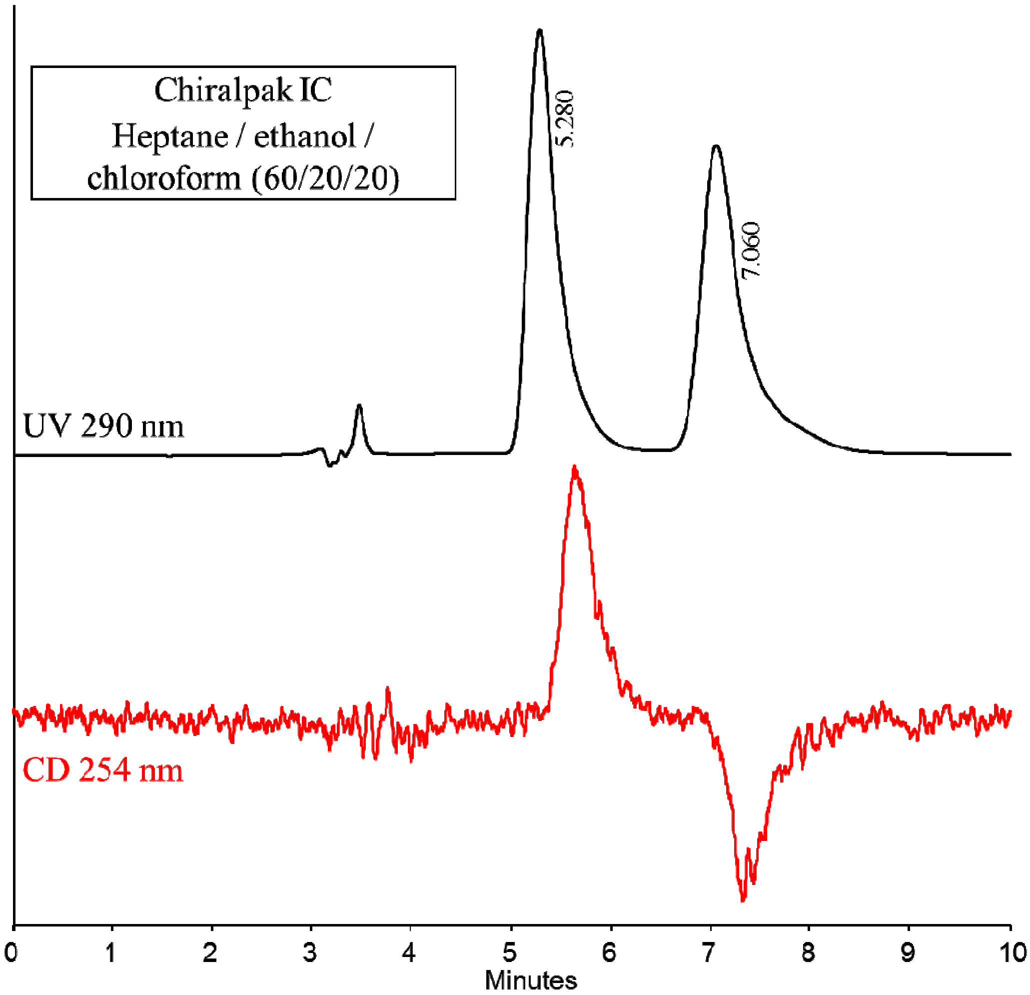
Table S1. X-ray crystallographic data of complexes **3a**,**b**.

	3a	**3b**	(P,S_{Ir})-**3a**
Empirical Formula	$C_{33}H_{32}BrIrN_2,2CH_2Cl_2$	$C_{41}H_{36}BrIrN_2$	$C_{33}H_{32}BrIrN_2$
CCDC number	1028016	1055806	1480527
Formula Weight	898.57	828.83	728.71
Temperature (K)	140(2)	150(2)	150 K
Wavelenght (Å)	0.71073	1.54184	0.71073
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Space Group	$P2_1/n$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	11.51870	13.7643(8)	9.2873(8)
b (Å)	12.8279	14.1122(7)	16.9087(16)
c (Å)	23.1283	16.9238(9)	17.4950(16) Å
α (Å)	90	90	90
β (Å)	96.5290(10)	90	90
γ (Å)	90	90	90
Volume ($Å^3$)	3395.29(8)	3287.4(3)	2747.3(4)
Z	4	4	4
Color	yellow	yellow	yellow
$\rho_{calculated}$ ($g.cm^{-3}$)	1.758	1.675	1.762
Absorption coefficient (mm^{-1})	5.452	9.522	6.339
F(000)	1760	1632	1424
Crystal size (mm)	0.210 * 0.150 * 0.057	0.202 * 0.193 * 0.091	0.120 x 0.100 x 0.050 mm
θ range for data collection (º)	3.027 to 26.998	4.079 to 71.277	3.199 to 27.481
Tmin	0.460	0.443	0.417
Tmax	0.756	1.000	0.728
limiting indices	$-14\leq h\leq 14$, $15\leq k\leq 16$, $-29\leq l\leq 29$	$-16\leq h\leq 16$, $-17\leq k\leq 17$, $-20\leq l\leq 20$	$-12\leq h\leq 12$, $-21\leq k\leq 20$, $-22\leq l\leq 22$
Data completeness	99.9% (θ = 25.242º)	100% (θ = 67.684º)	99.8%
Reflections collected	26738	62658	22563
Reflections unique	7396 [R(int) = 0.0659]	6378 [R(int) = 0.0504]	6266 [R(int) = 0.0623]
Data / restraints / parameters	7396 / 0 / 393	6378 / 0 / 413	6266 / 0 / 253
Goodness-of-fit on F^2	1.110	1.044	1.138
Flack parameter		-0.018(3)	-0.039(8)
Final R indices [I>2 σ (I)]	R1 = 0.0375, wR2 = 0.0941	R1 = 0.0202, wR2 = 0.0460	R1 = 0.0487, wR2 = 0.1137
R indices (all data)	R1 = 0.0471, wR2 = 0.1030	R1 = 0.0204, wR2 = 0.0544	R1 = 0.0681, wR2 = 0.1267
Largest diff peak and hole (e $Å^{-3}$)	2.100 and -1.515	0.831 and -1.109	2.968 and -2.452

Analytical chiral HPLC separation for complex 3a:

The sample is dissolved in dichloromethane, injected on the chiral column, and detected with a UV detector at 290 nm and circular dichroism detector at 254 nm. The flow-rate is 1 ml/min.

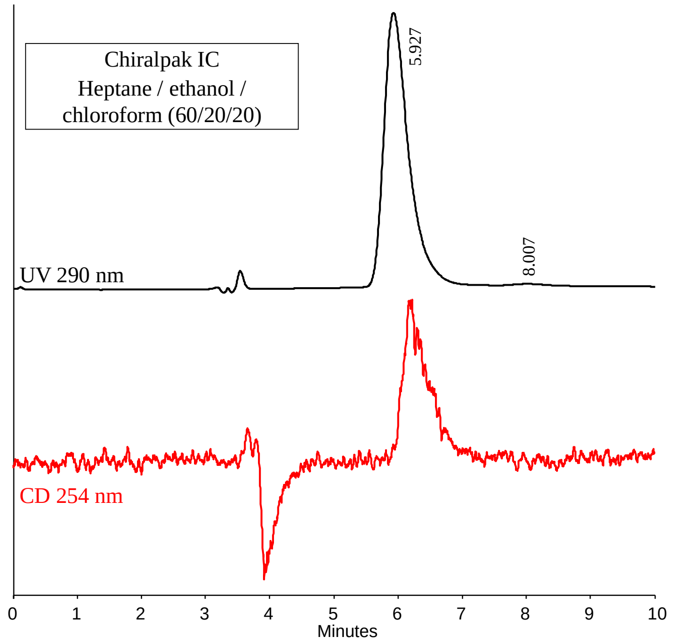
Column	Mobile Phase	t1	k1	t2	k2	α	Rs
Chiralpak IC	heptane / ethanol / chloroform (60/20/20)	5.28 (+)	0.76	7.06 (-)	1.35	1.77	2.80

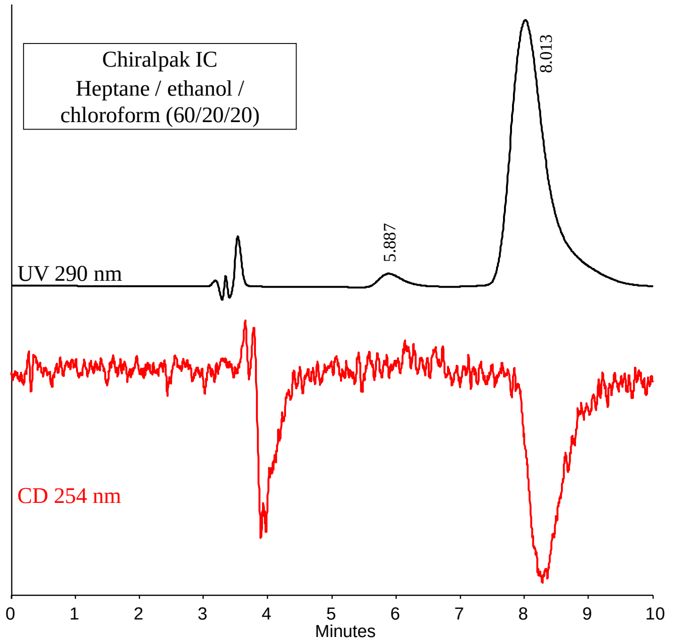


Retention time	Area	Area %
5.28	17920350	49.89
7.06	18002026	50.11

Semi-preparative separation for compound 3a:

• Sample preparation: about 29 mg of compound **3a** is dissolved in 3.4 mL of dichloromethane.
• Chromatographic conditions: Chiralpak IC (250 x 10 mm), heptane / ethanol / chloroform (60/20/20) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm.
• Injections (stacked): 23 times 150 µL, every 4.3 minutes.
• Collection: the first eluted enantiomer is collected between 4.8 and 6.2 minutes and the second one between 6.85 and 8.5 minutes.
• First fraction: 9 mg of the first eluted ((+, CD254)-enantiomer) with *ee* > 96%
• Second fraction: 7 mg of the second eluted ((-, CD254)-enantiomer) with *ee* > 93%
• Chromatograms of the collected fractions:





Retention time	Area	Area %
5.93	52144573	98.45
8.01	822338	1.55

Retention time	Area	Area %
5.89	812041	3.43
8.01	22846164	96.47

Kinetics of racemization of complex 3a in chloroform:

About 0.5 mg of a (+, CD254) enriched sample is heated in about 25 mL of chloroform at 60°C. 20 µL are taken and then injected on Chiralpak IC (60/20/20 heptane / ethanol / chloroform), 1 mL/min, UV 290 nm. The percentage decrease of the (+, CD254) enantiomer is monitored.

Time (min)	% enantiomer (+, CD254)	ln ((%t-50%)/(%(t=0)-50%))
0	91.54	0
38	82.34	-0.250351964
53	79.74	-0.334163877
70	76.77	-0.439374961
86	74.56	-0.525537715
110	71.10	-0.677383778
190	63.21	-1.1456827

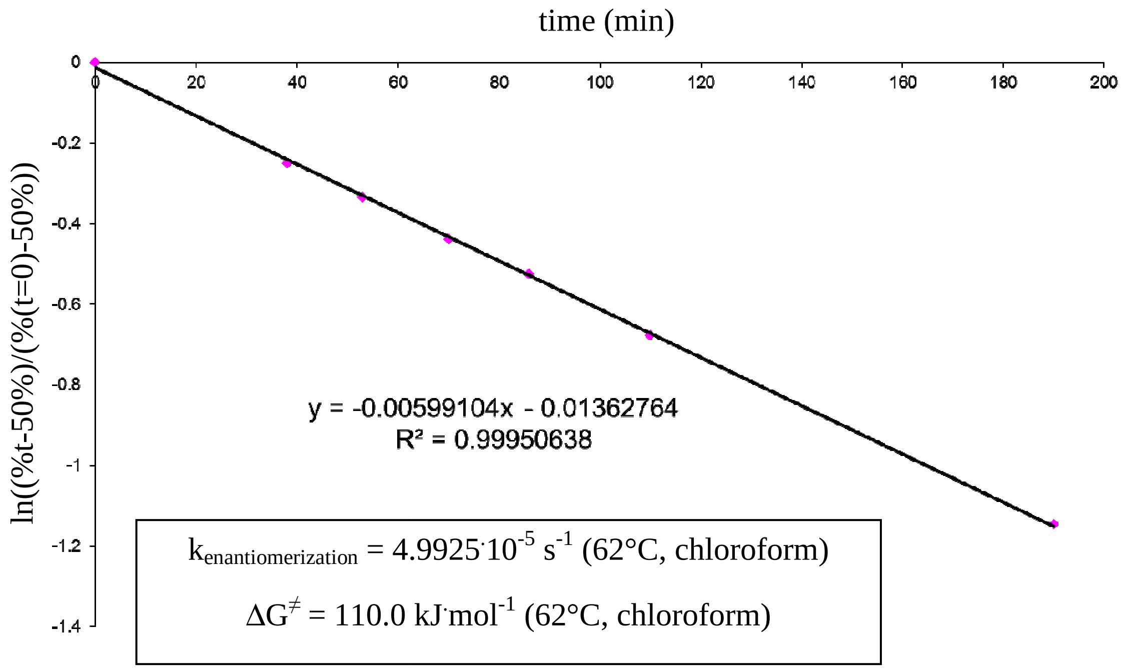


Figure S2. Kinetic evolution of the CD at 254 nm of complex 3a

$k_{enantiomerization} = 4.9925 \cdot 10^{-5}\ s^{-1}$

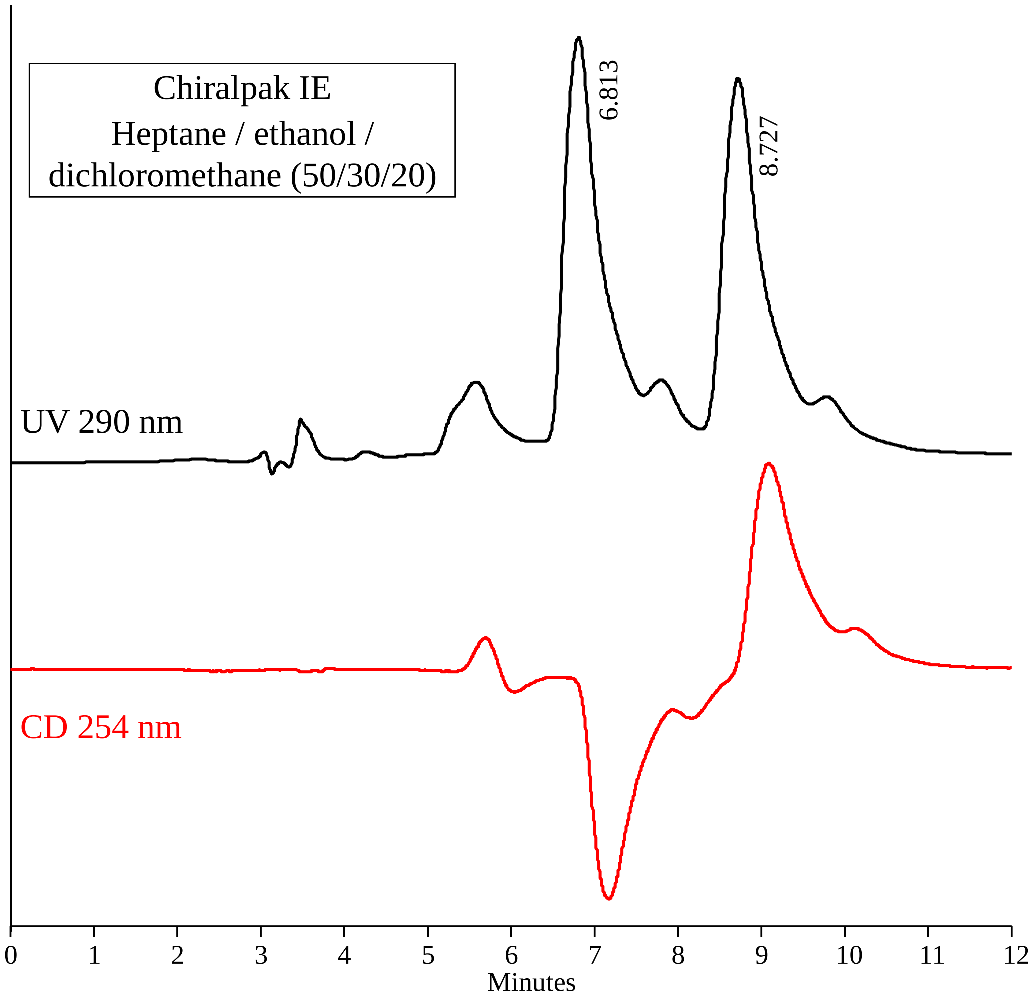
$\Delta G^{\neq} = 110.01\ kJ \cdot mol^{-1} = 26.32\ kcal \cdot mol^{-1}$

Half-life time: $t_{1/2}$ =115.70 min = 1.93 h

Analytical chiral HPLC separation for complex 3b:

The sample is dissolved in dichloromethane, injected on the chiral column, and detected with an UV detector at 290 nm and circular dichroism detector at 254 nm. The flow-rate is 1 ml/min.

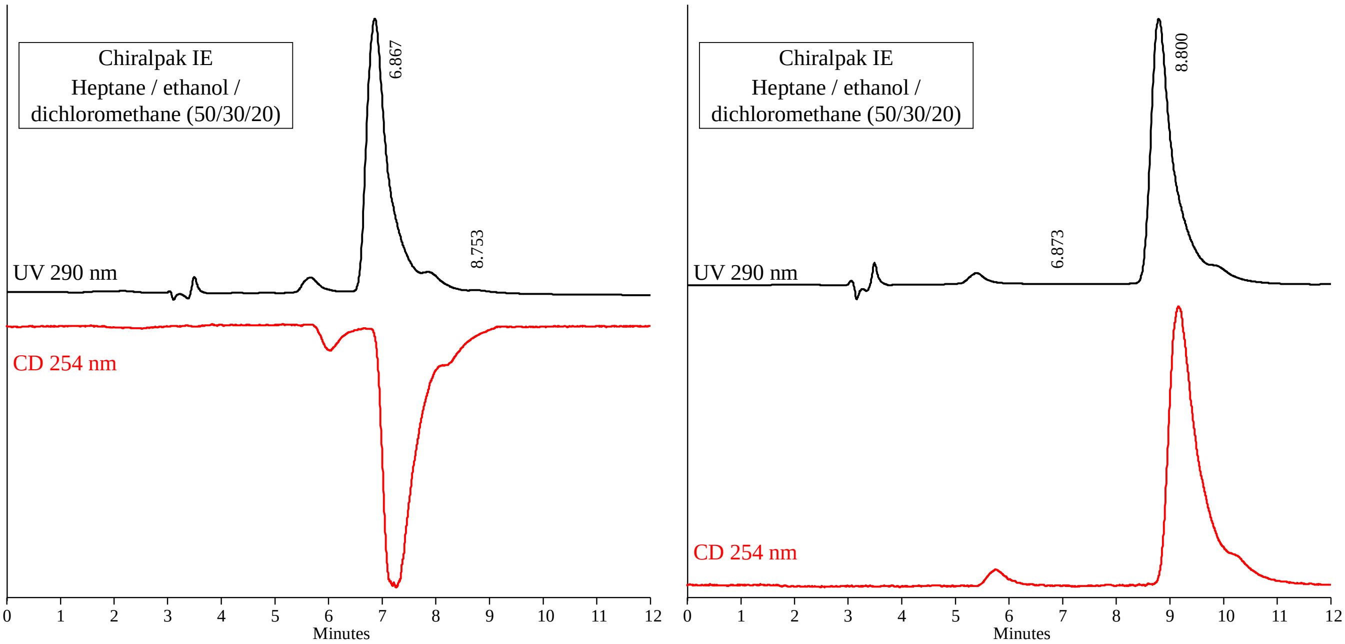
Column	Mobile Phase	t1	k1	t2	k2	α	Rs
Chiralpak IE	heptane / ethanol / dichloromethane (50/30/20)	6.81(-)	1.27	8.73(+)	1.91	1.50	1.74



Retention time	Area	Area %
6.81	21560426	50.20
8.73	21388997	49.80

Semi-preparative separation for compound 3b:

• Sample preparation: about 80 mg of compound **3b** is dissolved in 40 mL of dichloromethane.
• Chromatographic conditions: Chiralpak IE (250 x 10 mm), heptane / ethanol / dichloromethane (50/30/20) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm.
• Injections (stacked): 400 times 100 µL, every 6 minutes.
• Collection: the first eluted enantiomer is collected between 6.2 and 7.5 minutes and the second one between 8.6 and 9.5 minutes.
• First fraction: 22 mg of the first eluted ((-, CD254)-enantiomer) with *ee* > 96%
• Second fraction: 16 mg of the second eluted ((+, CD254)-enantiomer) with *ee* > 99%
• Chromatograms of the collected fractions (the minor optically active peaks do not correspond to **3b** diastereomers but to residual chlorinated complex (**4b**)IrClCp*).



Retention time	Area	Area %
6.87	63679090	98.08
8.75	1246540	1.92

Retention time	Area	Area %
7.51	40075	0.09
8.80	45991590	99.91

Experimental circular dichroism and UV/vis spectra:

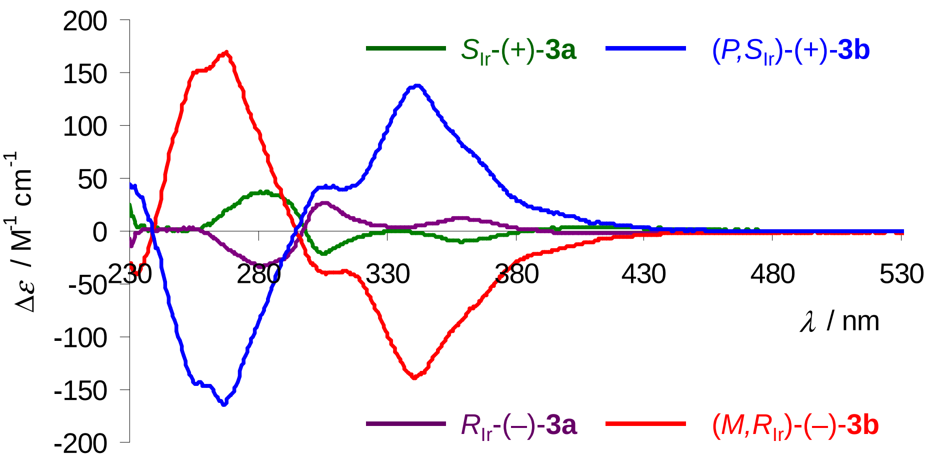


Figure S3a. CD spectra of the two enantiomeric complexes **3a** and **3b**.

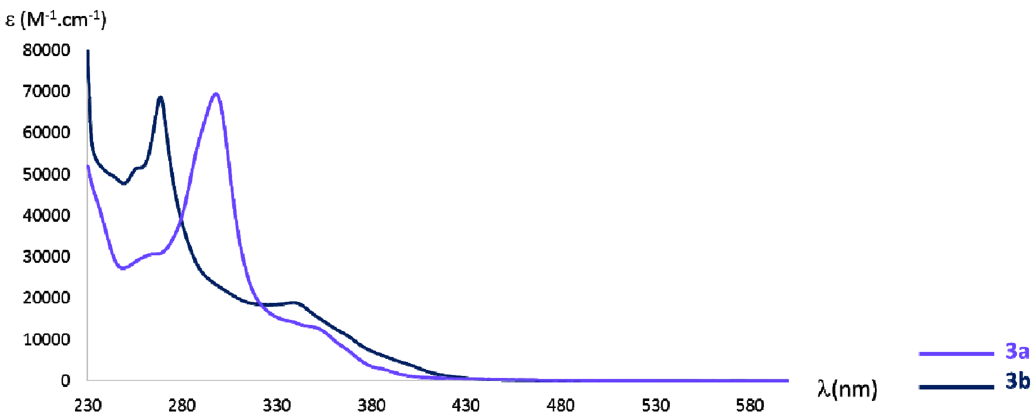


Figure S3b. UV/vis spectra of complexes **3a** and **3b** in CH_2Cl_2 (C 10^{-4}-10^{-5} M).

Experimental optical rotation values:

***R*$_{Ir}$-3a**: $[\alpha]_D^{23}$ = -24 (± 7 %), $[\phi]_D^{23}$ = -180 (CH_2Cl_2, 1.8 10^{-3} mol·L^{-1})

***S*$_{Ir}$-3a**: $[\alpha]_D^{23}$ = +32 (± 7 %), $[\phi]_D^{23}$ = +230 (CH_2Cl_2, 1.8 10^{-3} mol·L^{-1})

(*M*,*R*$_{Ir}$)-3b: $[\alpha]_D^{23}$ = -1530 (± 5 %), $[\phi]_D^{23}$ = -12680 (CH_2Cl_2, 1.1 10^{-4} mol·L^{-1})

(*P*,*S*$_{Ir}$)-3b: $[\alpha]_D^{23}$ = +1490 (± 5 %), $[\phi]_D^{23}$ = +12350 (CH_2Cl_2, 1.1 10^{-4} mol·L^{-1})

^{1}H and ^{13}C NMR spectra:

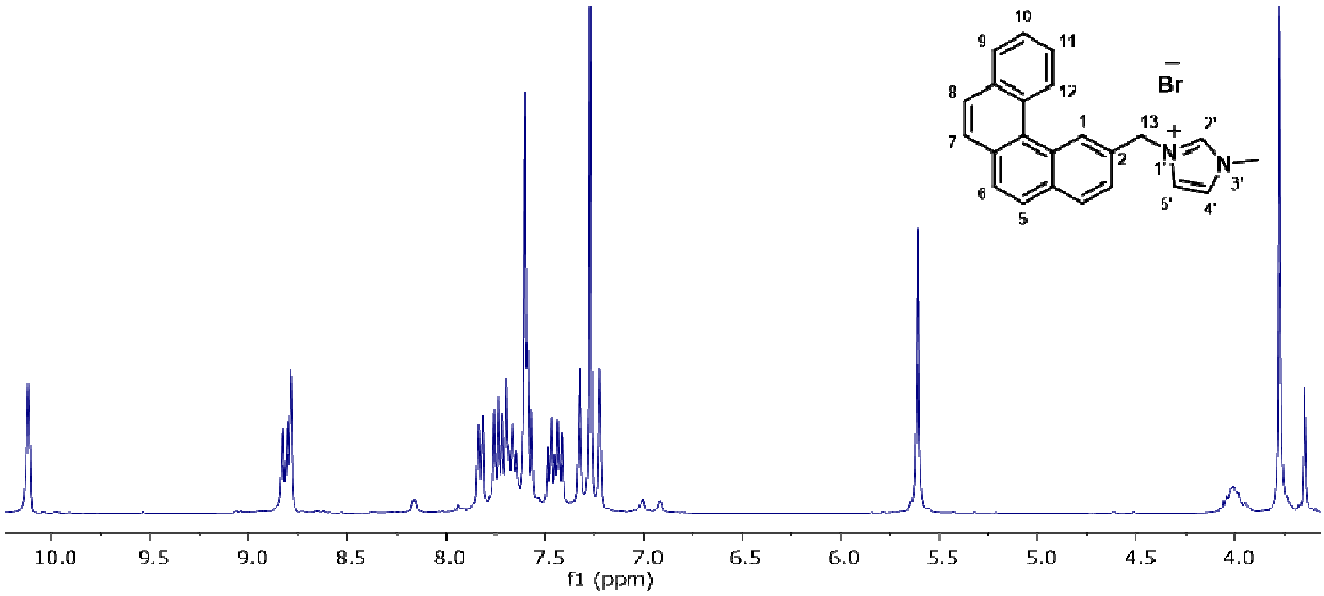


Figure S4. ^{1}H NMR spectrum (400 MHz, C*D*Cl_3) of compound **2a**.

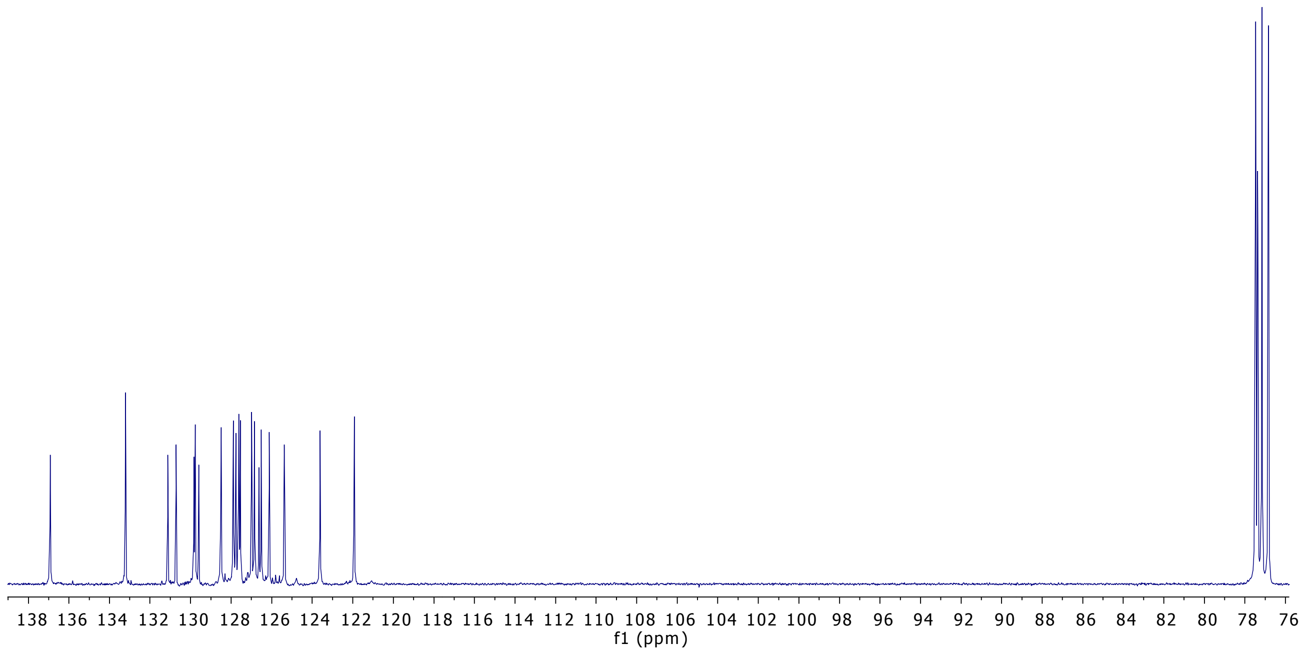


Figure S5. ^{13}C NMR spectrum (101 MHz, C*D*Cl_3) of compound **2a**.

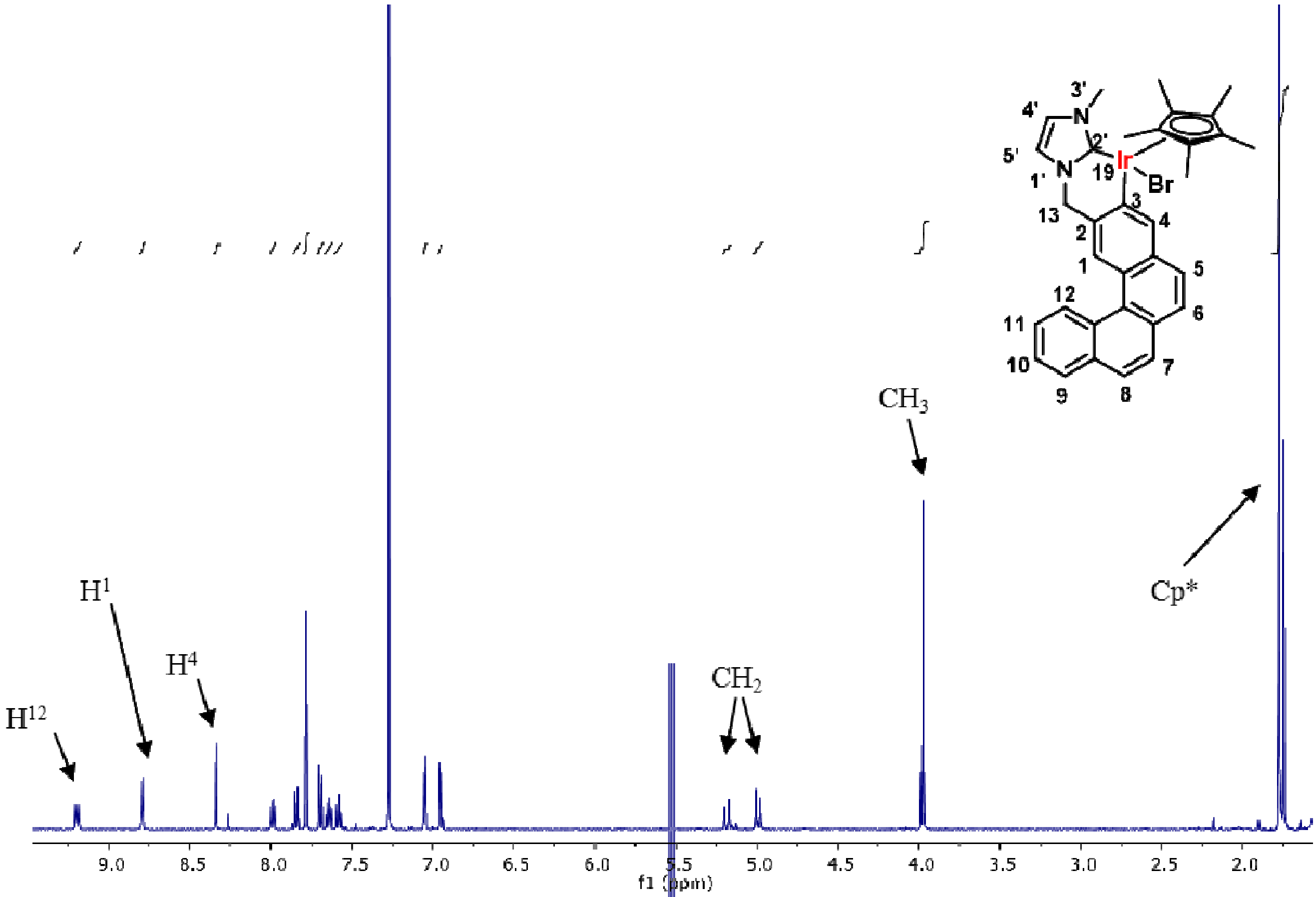


Figure S6. ^{1}H NMR spectrum (500 MHz, C*D*Cl$_3$) of complex **3a**.

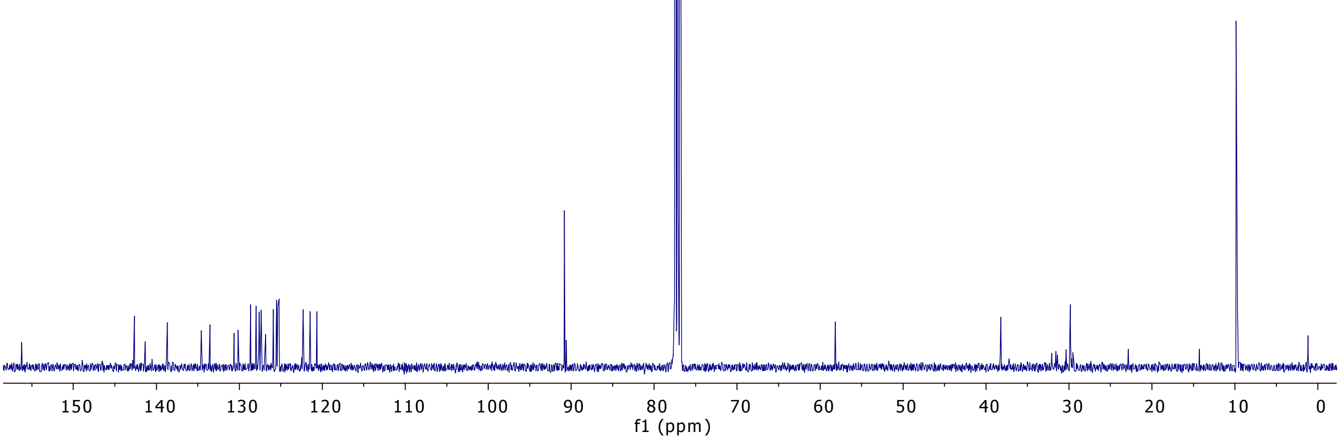


Figure S7. ^{13}C NMR spectrum (101 MHz, C*D*Cl$_3$) of complex **3a**.

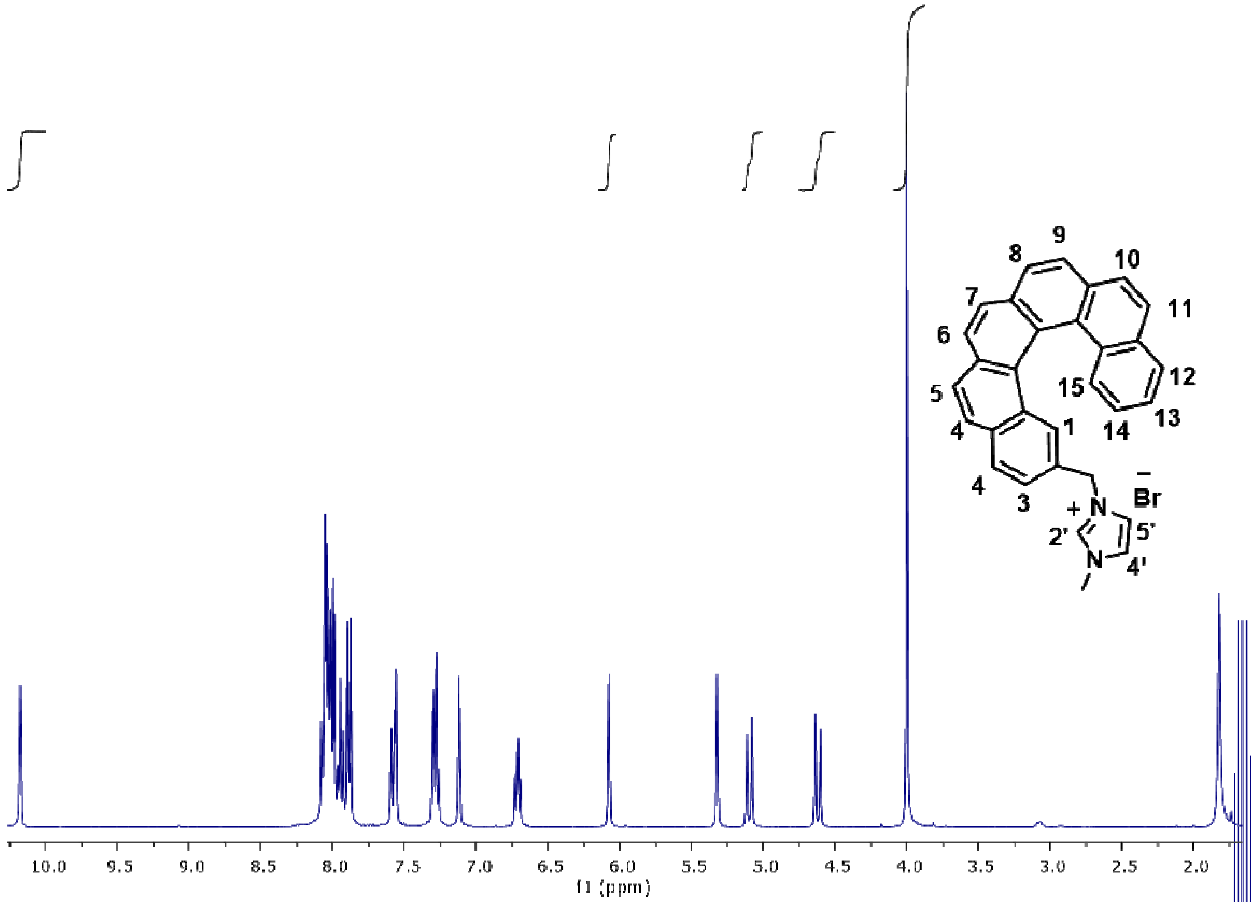


Figure S8. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of compound **2b**.

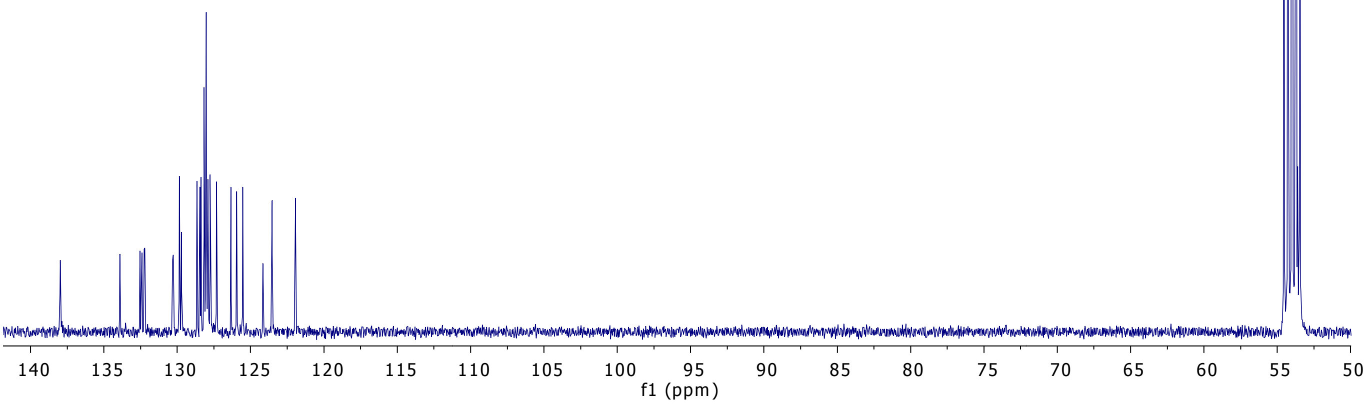


Figure S9. ^{13}C NMR spectrum (101 MHz, CD_2Cl_2) of compound **2b**.

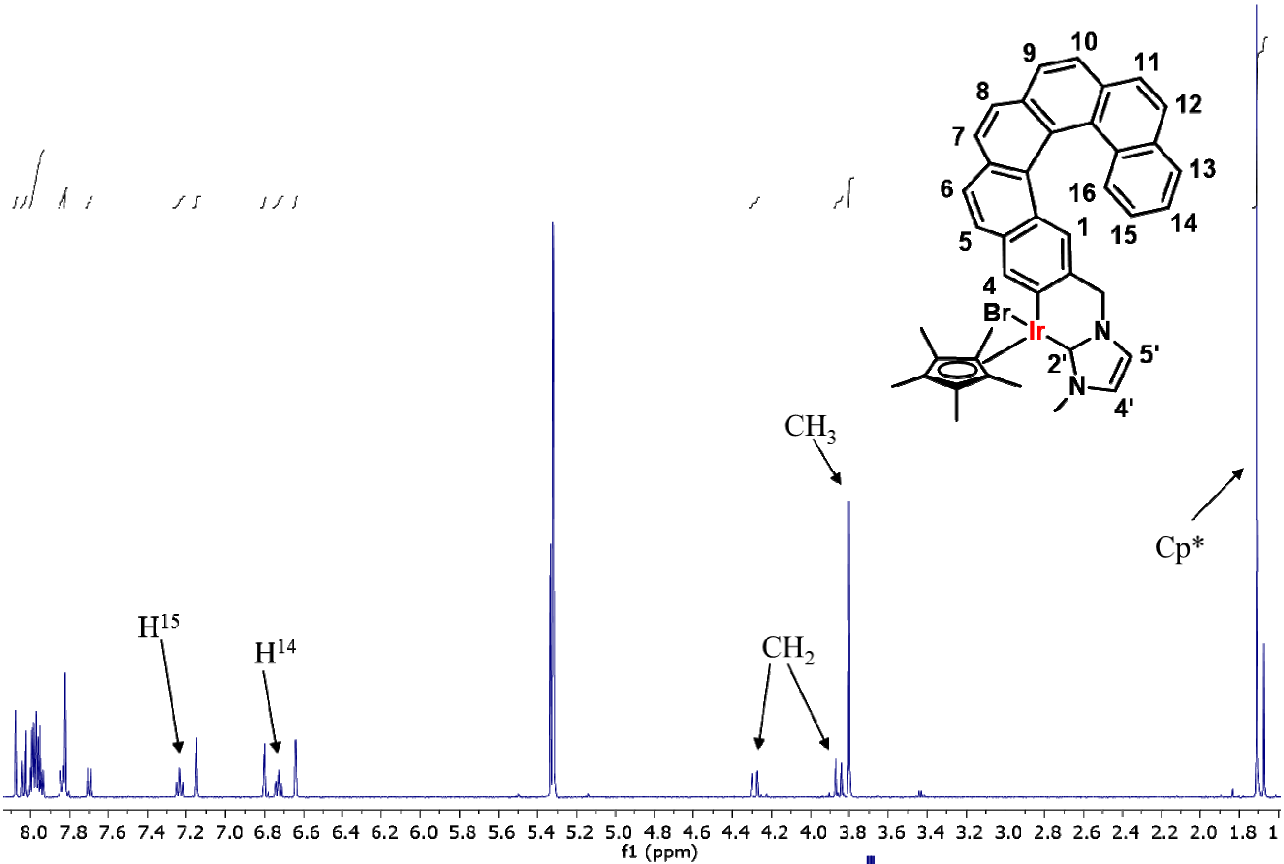


Figure S10a. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2) of complex **3b**.

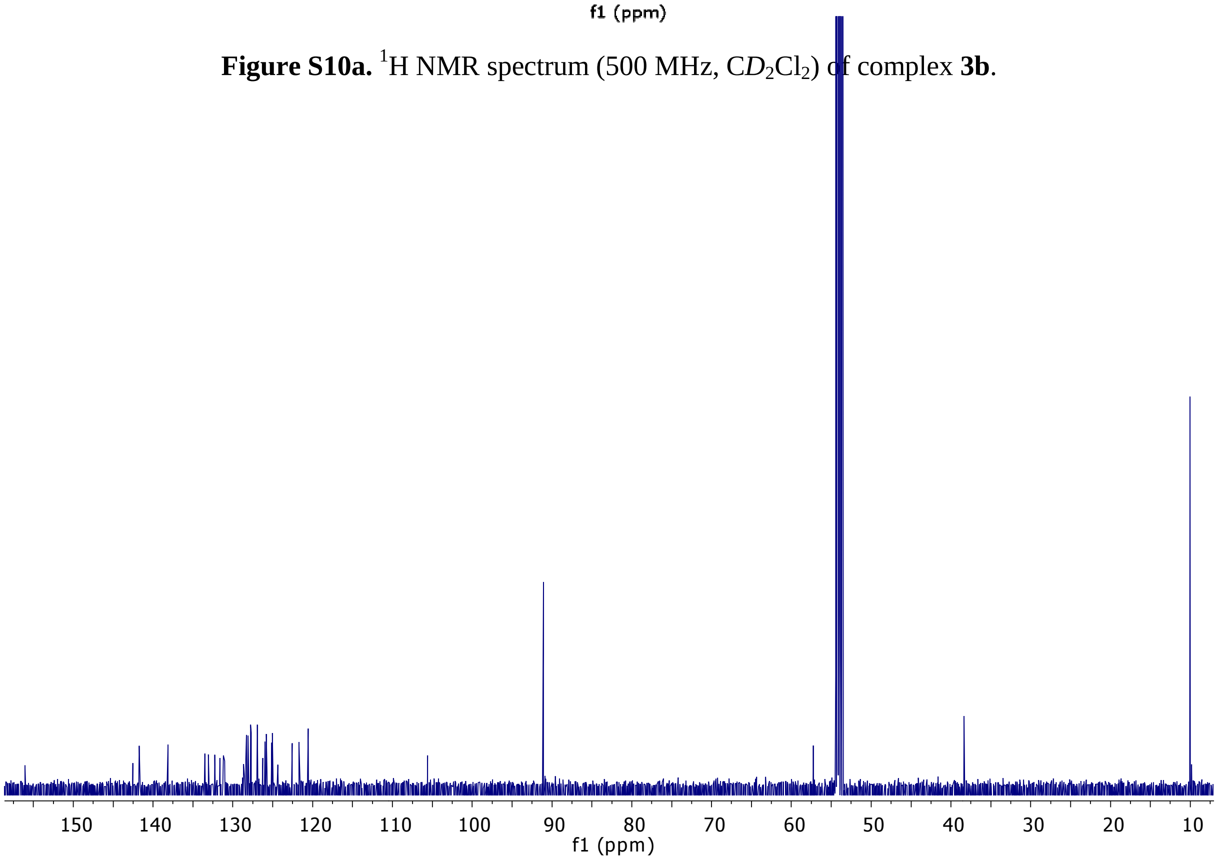


Figure S10b. ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of complex **3b**.

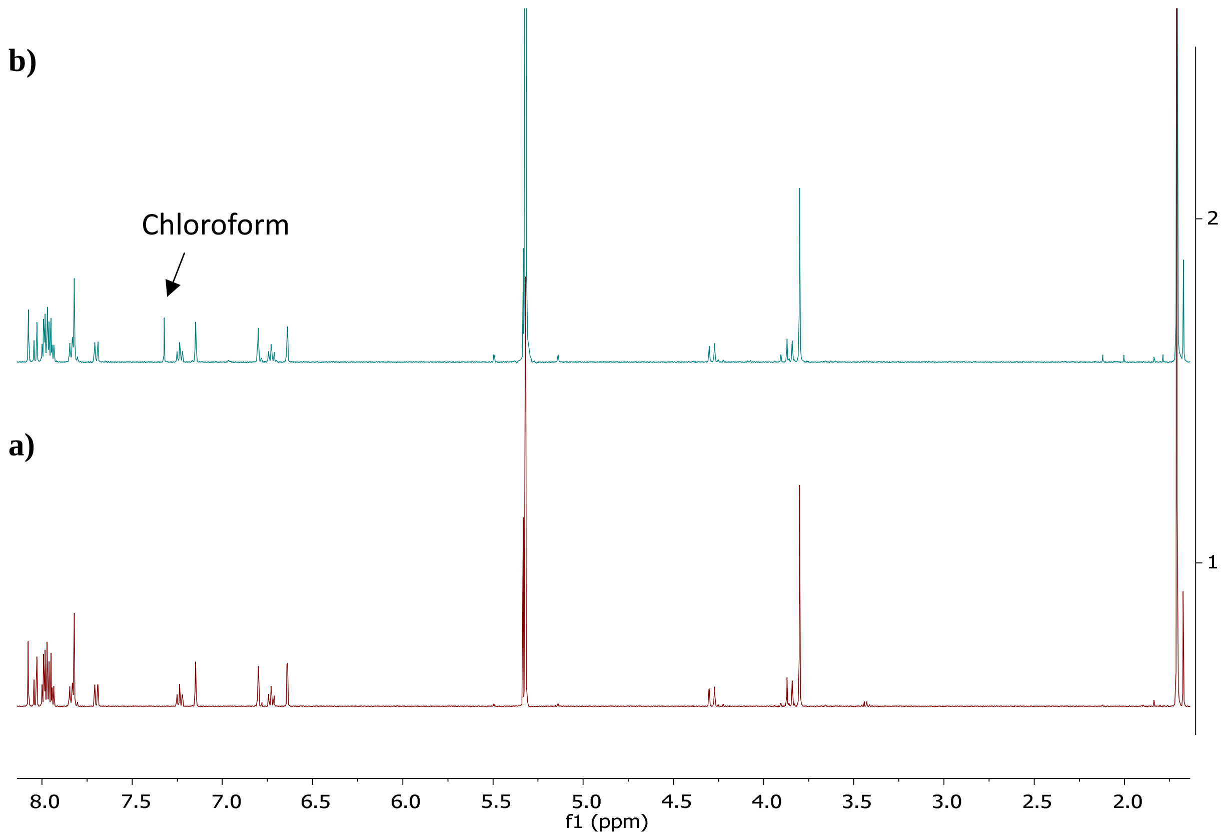
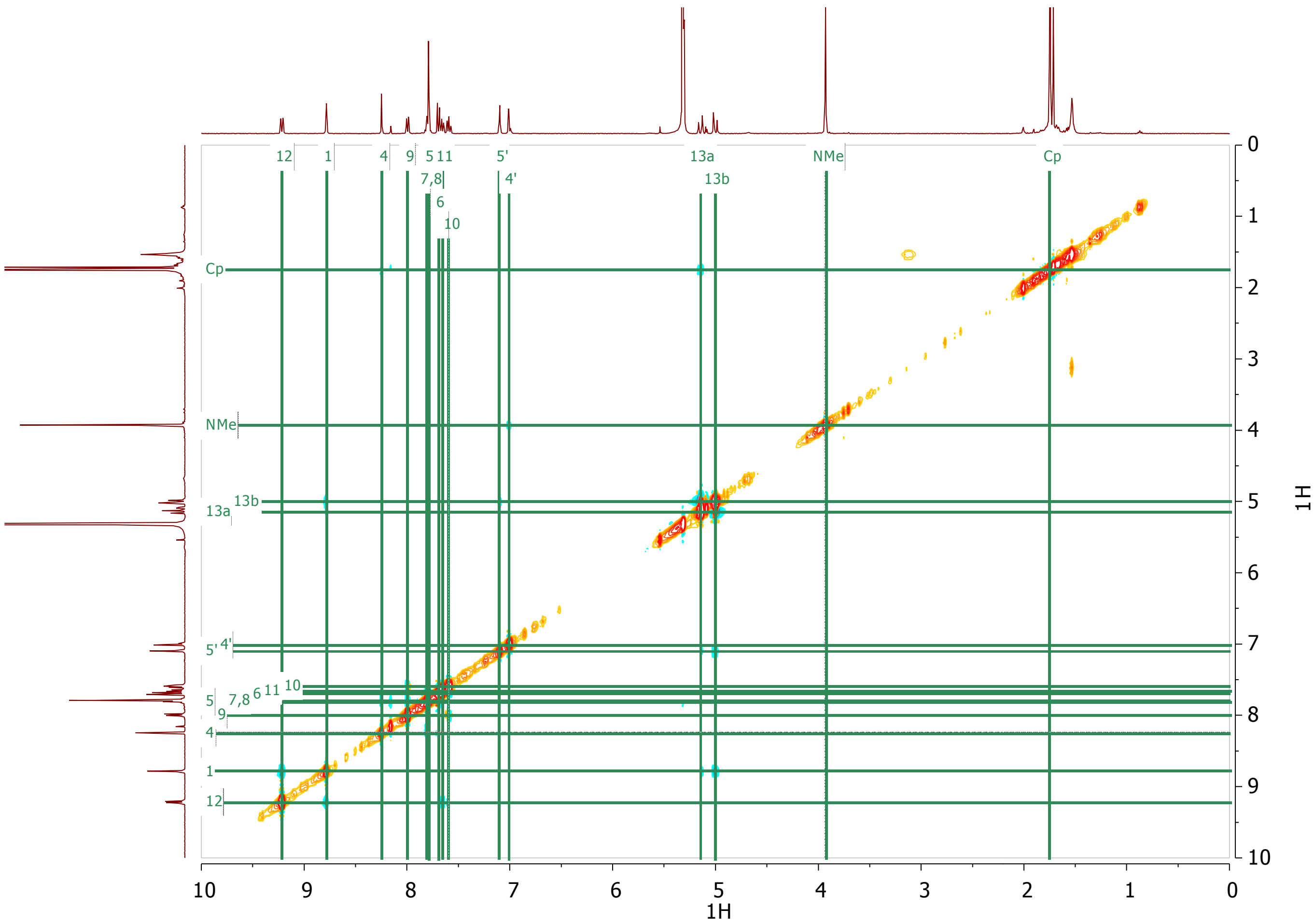


Figure S11. Comparison of [1]H NMR spectrum (500 MHz, CD_2Cl_2) of enantiopure complex (M,R_{Ir})-**3b** before (a) and after (b) heating in refluxing chloroform for 2 hrs.



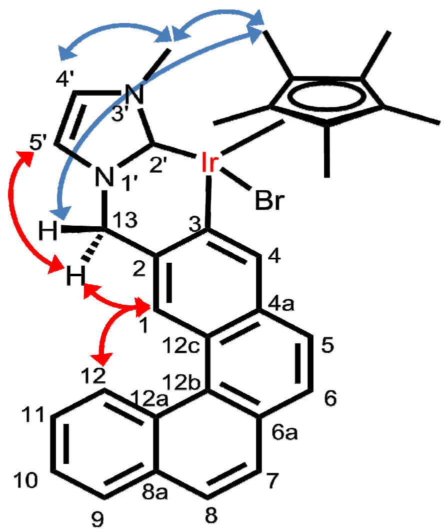
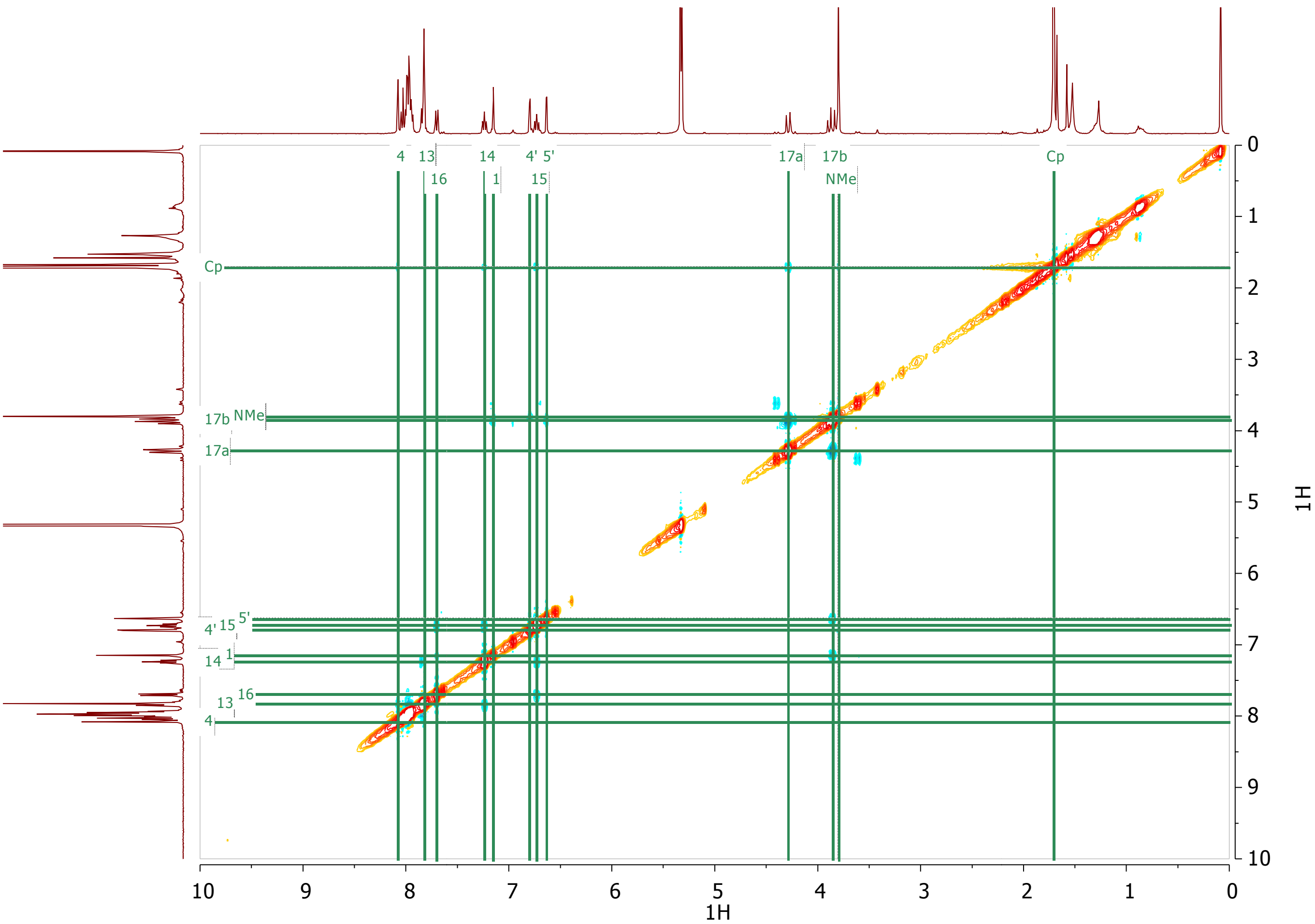


Figure S12. NOESY NMR experiment and assignment of complex **3a**.



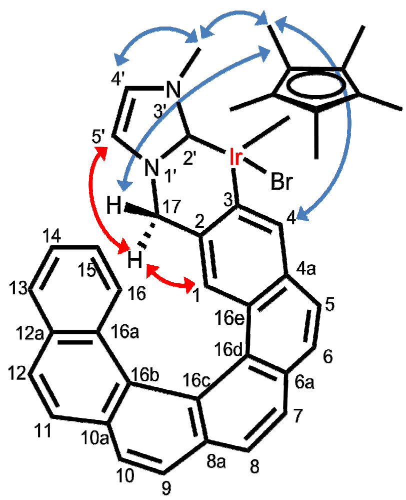


Figure S13. ROESY NMR experiment and assignment of complex **3b**.

Computational details:

Kohn-Sham density functional theory (DFT) and time-dependent DFT calculations were performed using the Turbomole package, version 6.6,[4,5,6] and - where specifically stated - with the Gaussian 09 program (G09).[7] In all calculations a split-valence basis set with one set of polarization functions for non-hydrogen atoms, abbreviated as SV(P), was used.[8,9,10] Scalar relativistic effects were treated implicitly by the use of a 60-electron relativistic effective core potential (ECP) for Ir.[11] Solvent effects for dichloromethane (DCM, ε = 8.9) were included in the calculations via the conductor-like screening model (COSMO)[12,13,14] in Turbomole and via the polarizable continuum model (PCM)[14,15,16,17] in Gaussian. In both cases, default parameters were used.

DFT geometry optimizations employed the BP exchange-correlation functional.[18,19,20] TDDFT linear response optical rotation (OR) and electronic circular dichroism (ECD) calculations utilized three well-established global hybrid functionals differing in the fraction of exact exchange (eX, listed in parentheses): B3LYP[21,22,23] (20%), PBE0[24] (25%), and BHLYP[21,25] (50%). Additionally, some calculations employed functionals with range-separated exchange and correct asymptotic behavior (long-range correction = LC) based on the PBE[26,27,28] functional: LC-PBE and LC-PBE0. The former, LC-PBE, affords 0% of eX in the short-range limit, while the latter, LC-PBE0, affords 25%. In both cases an error-function separation with a range-separation parameter γ of 0.30 a_0^{-1} – typically used in global parametrizations of LC functionals – was employed. The subset of computations with LC functionals was performed using G09.

All ECD calculations covered the 120 lowest singlet excited states (S1 to S120) for each system. The simulated spectra shown are the sums of Gaussian functions centered at the vertical excitation energies and scaled using the calculated rotatory strengths, with a parameter of σ = 0.2 eV applied for the root mean square width.[29] The optical rotation parameters were computed at the sodium line wavelength λ = 589.3 nm.

The calculations were performed for Ir-based NHC-helicene derivatives (P,S_{Ir})- and (P,R_{Ir})-**3a**, and (P,S_{Ir})- and (P,R_{Ir})-**3b**, and for the corresponding parent NHC-helicene *P*-**4b**. Chiroptical properties of (P,R_{Ir})-**3a** are analyzed with the sign opposite that of the ones calculated to match data for its optical antipode ((M,S_{Ir})-**3a**).

Additional calculated data:

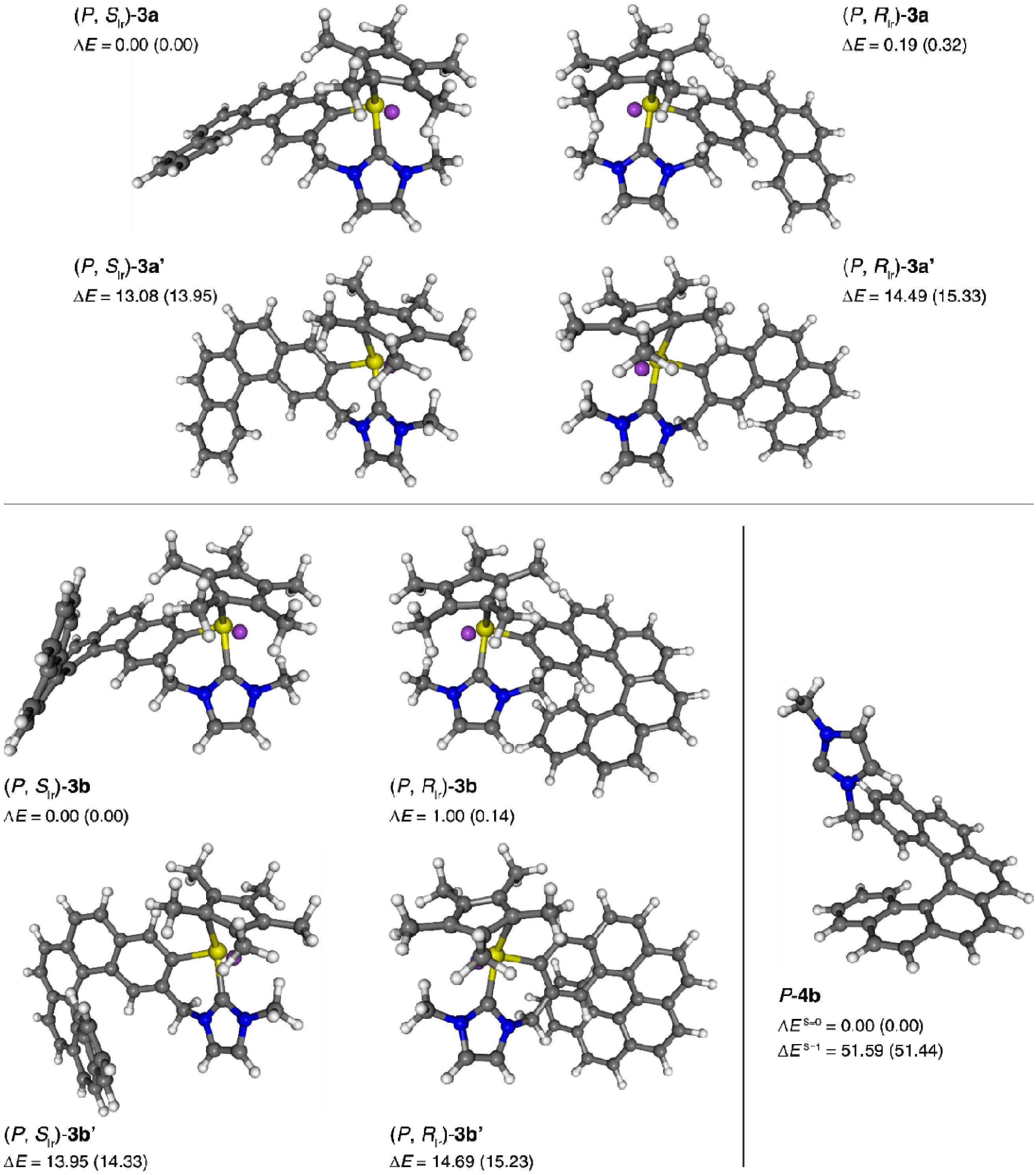


Figure S14. Molecular structures of Ir-based NHC-helicene derivatives **3a** and **3b** along with the corresponding parent ligand **4b**. Δ*E* values listed for **3a** and **3b** are relative energies in kcal/mol for geometries optimized using BP/SV(P) with continuum solvent model for CH_2Cl_2 (displayed); in parentheses are given Δ*E* for BP/SV(P) geometries optimized without the solvent model. The ligand **4b** was optimized in a closed-shell $S = 0$, $M_S = 0$ (displayed) and in an open-shell $S = 1$, $M_S = 1$ spin state. The corresponding relative energies in kcal/mol are listed for geometries optimized with and without (in parentheses) solvent effects.

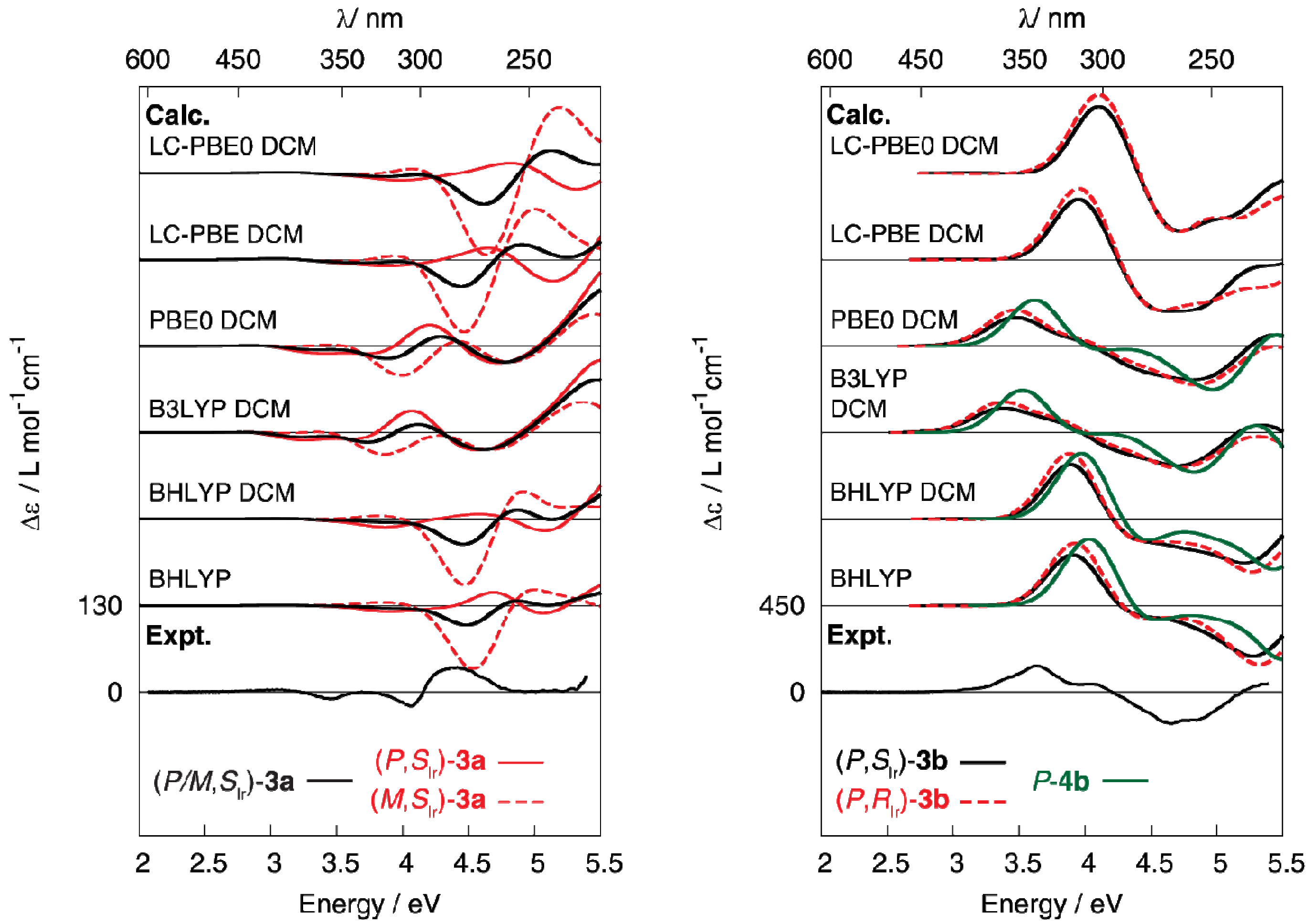


Figure S15. Comparison of the experimental and simulated TDDFT ECD spectra of Ir-based NHC-helicene complexes. No spectral shift has been applied. 'DCM': continuum solvent model (dichloromethane, ε = 8.9) calculations.

Table S2. Experimental and calculated molar rotations (in deg cm^2/dmol) for the **3a** and **3b** complexes and for the corresponding parent ligand **4b**.

System	Expt.	gas-phase	dichloromethane				
		BHLYP	BHLYP	B3LYP	PBE0	LC-PBE	LC-PBE0
(P,S_{Ir})-**3a**	-	2378	1800	1385	1426	1410	1329
(M,S_{Ir})-**3a**	-	-2115	-1794	-2245	-2068	-1790	-1694
S_{Ir}-**3a**	230	734[a]	284[a]	-147[a]	-48[a]	60[a]	54[a]
(P,S_{Ir})-**3b**	12350	14153	13409	19705	18014	10713	9562
(P,R_{Ir})-**3b**	-	15720	15158	22916	20822	12428	11165
P-**4b**	-	8058	8049	11616	10634	-	-

[a] Boltzmann-averaged value for (P,S_{Ir})-**3a** and (M,S_{Ir})-**3a**.

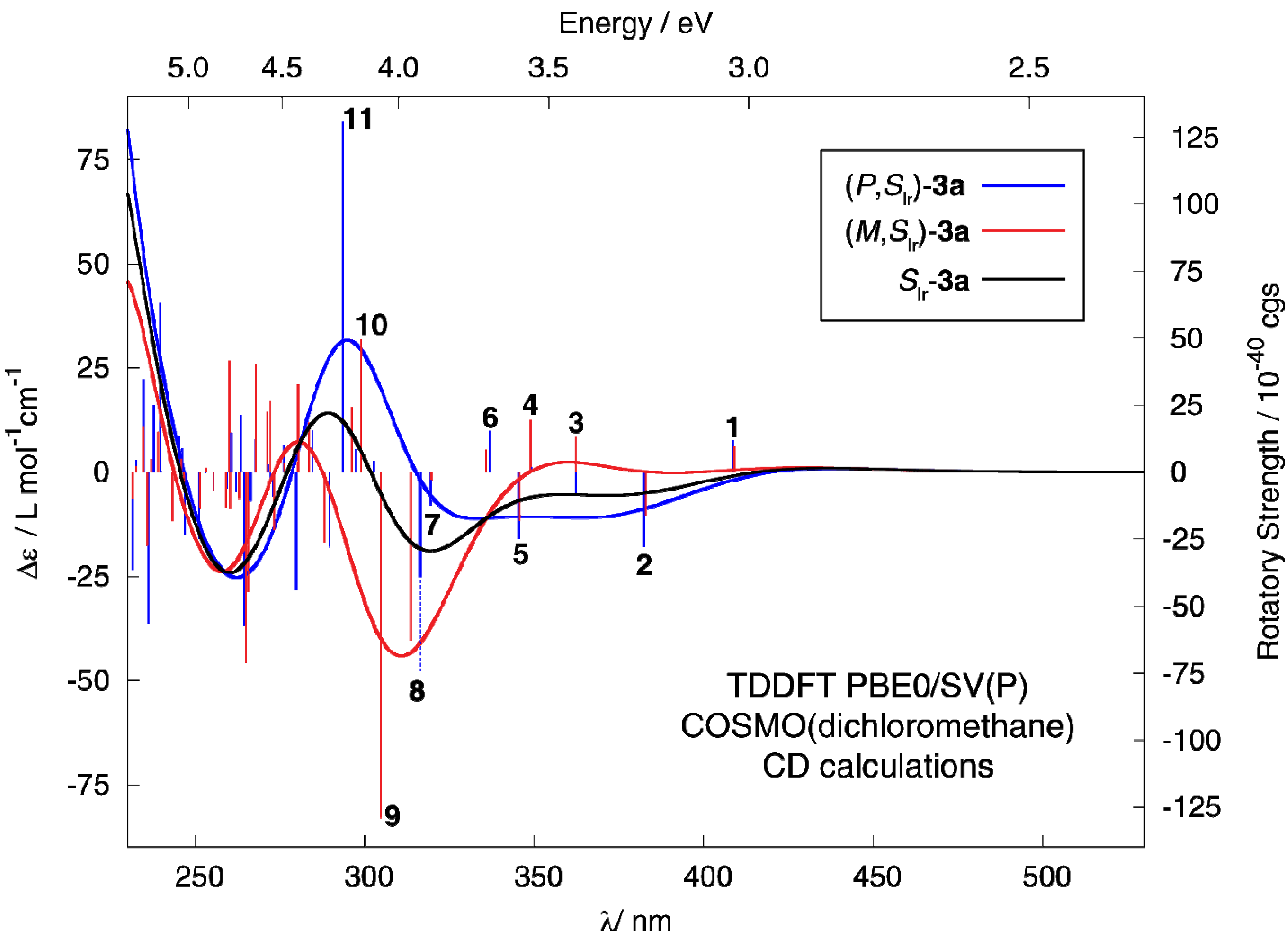


Figure S16. Comparison of the simulated ECD spectra of the Ir-based NHC-helicene complexes (*P*,S_{Ir})-**3a** (blue line) and (*M*,S_{Ir})-**3a** (red line) along with the corresponding Boltzmann-averaged spectrum for S_{Ir}-**3a** (black line). No spectral shift has been applied. Calculated excitation energies and rotatory strengths indicated as 'stick' spectra. Numbered excitations correspond to those analyzed in detail.

Table S3. Selected dominant excitations and occupied (occ) – unoccupied (unocc) MO pair contributions (greater than 10%) of the (*P*,S_{Ir})-**3a**.

Excitation	*E* / eV	λ / nm	*f*	*R* / 10^{-40} cgs	occ no.	unocc no.	%
1	3.03	409	0.011	11.90	148	151	74.0
					147	151	10.4
2	3.24	382	0.014	-27.83	147	151	44.1
					146	151	28.5
3	3.42	362	0.066	-8.40	148	149	70.6
4	3.55	349	0.032	1.91	147	149	64.8
					148	150	12.5
5	3.59	345	0.039	-24.73	148	149	20.1
					147	150	18.7
					147	149	18.6
					146	149	13.8
6	3.68	337	0.011	15.31	144	151	23.2
					146	151	19.3
					145	151	16.9
					147	151	11.4
7	3.88	319	0.016	-12.35	148	150	57.7
					147	150	28.0
8	3.92	316	0.163	-39.21	146	149	64.9
					145	149	14.2
9	4.10	303	0.584	4.06	145	149	32.9
					147	150	31.7
					146	150	15.7
10	4.17	297	0.008	8.31	144	149	46.0
					144	151	18.4
					147	151	12.9
					146	151	10.9
11	4.23	293	0.242	130.59	146	150	21.5
					144	151	21.4
					144	149	19.5
					145	149	15.1

Table S4. Selected dominant excitations and occupied (occ) – unoccupied (unocc) MO pair contributions (greater than 10%) of the (M,S_{Ir})-**3a**.

Excitation	E / eV	λ / nm	f	R / 10^{-40} cgs	occ no.	unocc no.	%
1	3.03	409	0.008	9.71	148	151	74.9
					147	151	12.0
2	3.24	383	0.013	-16.21	147	151	48.6
					146	151	25.3
3	3.42	362	0.067	13.10	148	149	73.5
4	3.55	349	0.027	19.56	147	149	70.9
					148	150	11.7
5	3.59	346	0.045	-18.30	148	149	20.2
					147	150	18.2
					148	150	14.7
					147	149	14.2
					146	149	13.2
6	3.69	336	0.017	-8.24	145	151	28.9
					144	151	28.6
					146	151	13.8
7	3.88	320	0.007	2.94	148	150	51.2
					147	150	35.8
8	3.95	314	0.144	-62.91	146	149	67.1
					145	149	16.4
9	4.08	304	0.674	-129.12	145	149	38.5
					147	150	28.8
10	4.15	299	0.029	49.63	144	149	34.8
					146	151	20.2
					144	151	17.1
					147	151	13.6
11	4.19	296	0.024	24.30	144	149	41.4
					144	151	14.1
					146	150	11.3

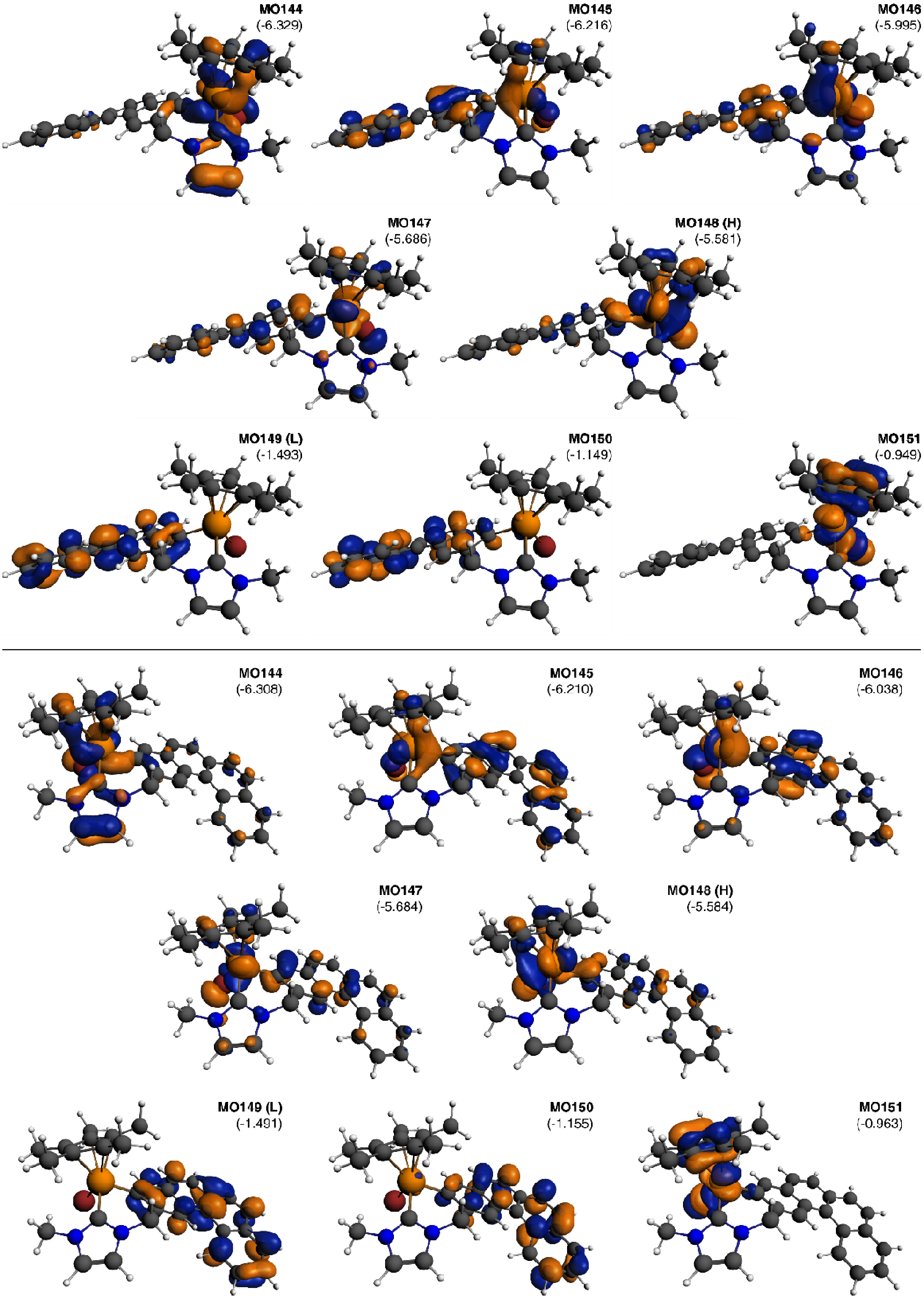


Figure S17. Isosurfaces (0.04 au) of MOs involved in selected transitions of (P,S_{Ir})-**3a** (top) and (M,S_{Ir})-**3a** (bottom). 'H' = HOMO, 'L' = LUMO. Values listed in the parentheses are the corresponding orbital energies, in eV.

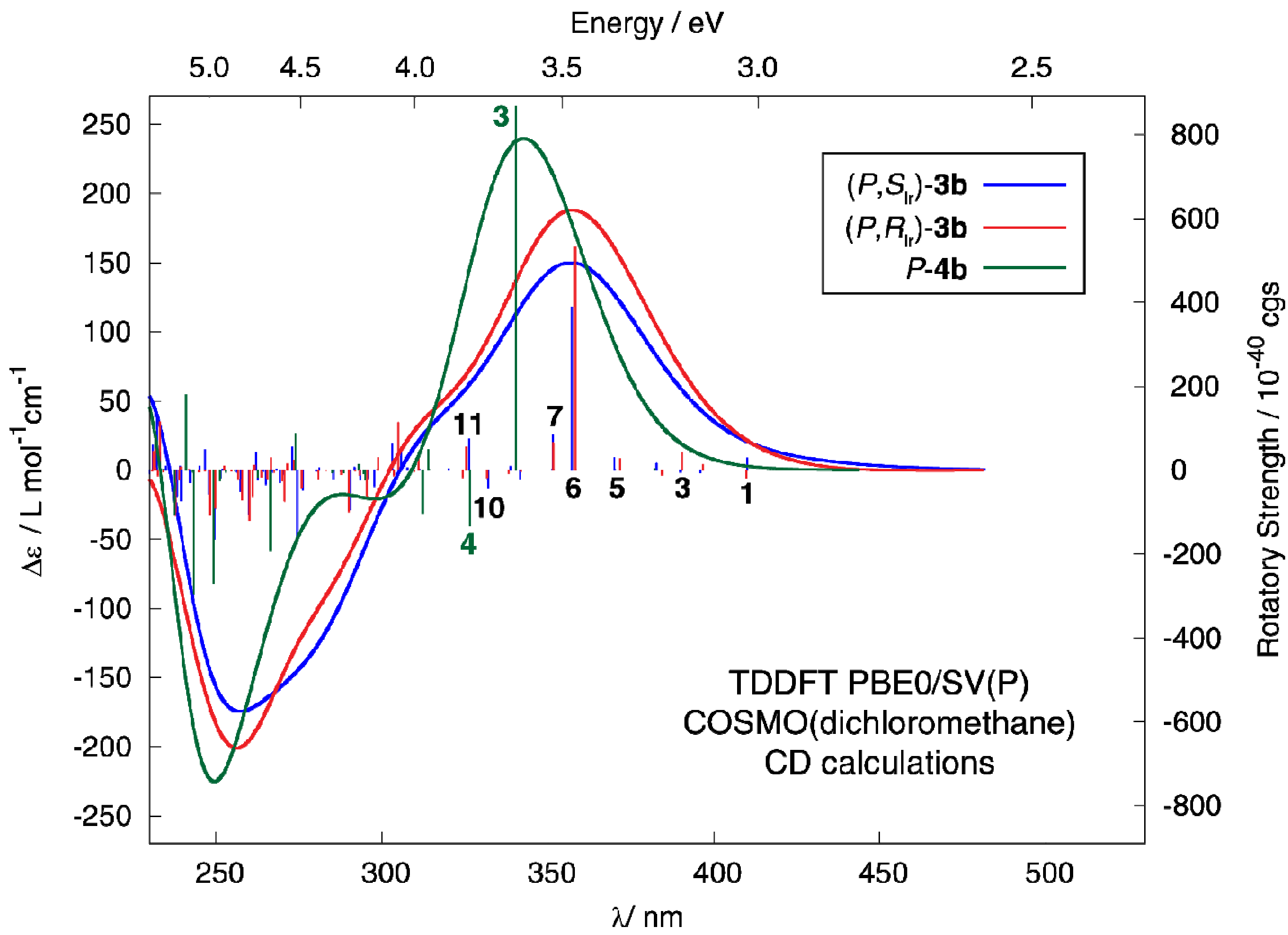


Figure S18. Comparison of the simulated ECD spectra of the Ir-based NHC-helicene complex (P,S_{Ir})-**3b** (blue line) and (P,R_{Ir})-**3b** (red line), and of its parent NHC-helicene ligand *P*-**4b** (green line). No spectral shift has been applied. Calculated excitation energies and rotatory strengths indicated as 'stick' spectra. Numbered excitations correspond to those analyzed in detail.

Table S5. Selected dominant excitations and occupied (occ) – unoccupied (unocc) MO pair contributions (greater than 10%) of the *P*-**4b**.

Excitation	*E* / eV	λ / nm	*f*	*R* / 10^{-40} cgs	occ no.	unocc no.	%
3	3.64	340	0.440	868.81	111	113	54.0
					110	112	36.0
4	3.80	327	0.084	-133.64	110	113	46.1
					111	112	17.6
					106	112	17.6

Table S6. Selected dominant excitations and occupied (occ) – unoccupied (unocc) MO pair contributions (greater than 10%) of the (P,S_{Ir})-**3b**.

Excitation	*E* / eV	λ / nm	*f*	*R* / 10^{-40} cgs	occ no.	unocc no.	%
1	3.02	410	0.017	29.45	174	177	69.7
					173	177	10.7
3	3.18	390	0.042	-5.85	173	175	25.2
					174	176	19.9
					174	175	14.7
					172	175	13.7
					173	176	11.3
5	3.35	370	0.039	30.44	173	175	58.2
					174	175	24.6
6	3.47	357	0.255	390.08	172	175	49.9
					174	176	35.7
7	3.53	351	0.054	85.11	173	176	49.4
					174	176	28.7
10	3.73	332	0.029	-43.78	171	176	21.4
					172	176	16.3
					168	175	15.4
11	3.80	326	0.058	75.75	172	176	32.1
					171	175	22.9
					171	176	21.5

Table S7. Selected dominant excitations and occupied (occ) – unoccupied (unocc) MO pair contributions (greater than 10%) of the (P,R_{Ir})-**3b**.

Excitation	*E* / eV	λ / nm	*f*	*R* / 10^{-40} cgs	occ no.	unocc no.	%
1	3.03	410	0.009	-19.76	174	177	72.5
					173	177	13.7
3	3.18	390	0.041	43.76	174	176	22.9
					173	175	19.1
					172	175	16.6
					174	175	14.9
					173	176	12.9
5	3.33	372	0.019	27.67	173	175	64.4
					174	175	24.0
6	3.47	357	0.302	532.19	172	175	49.8
					174	176	35.8
7	3.53	352	0.050	66.49	173	176	55.5
					174	176	27.0
10	3.74	332	0.038	-19.22	171	176	16.6
					168	175	16.3
					171	175	14.7
					172	176	13.0
11	3.81	325	0.064	55.48	171	175	29.3
					172	176	24.3
					171	176	21.3

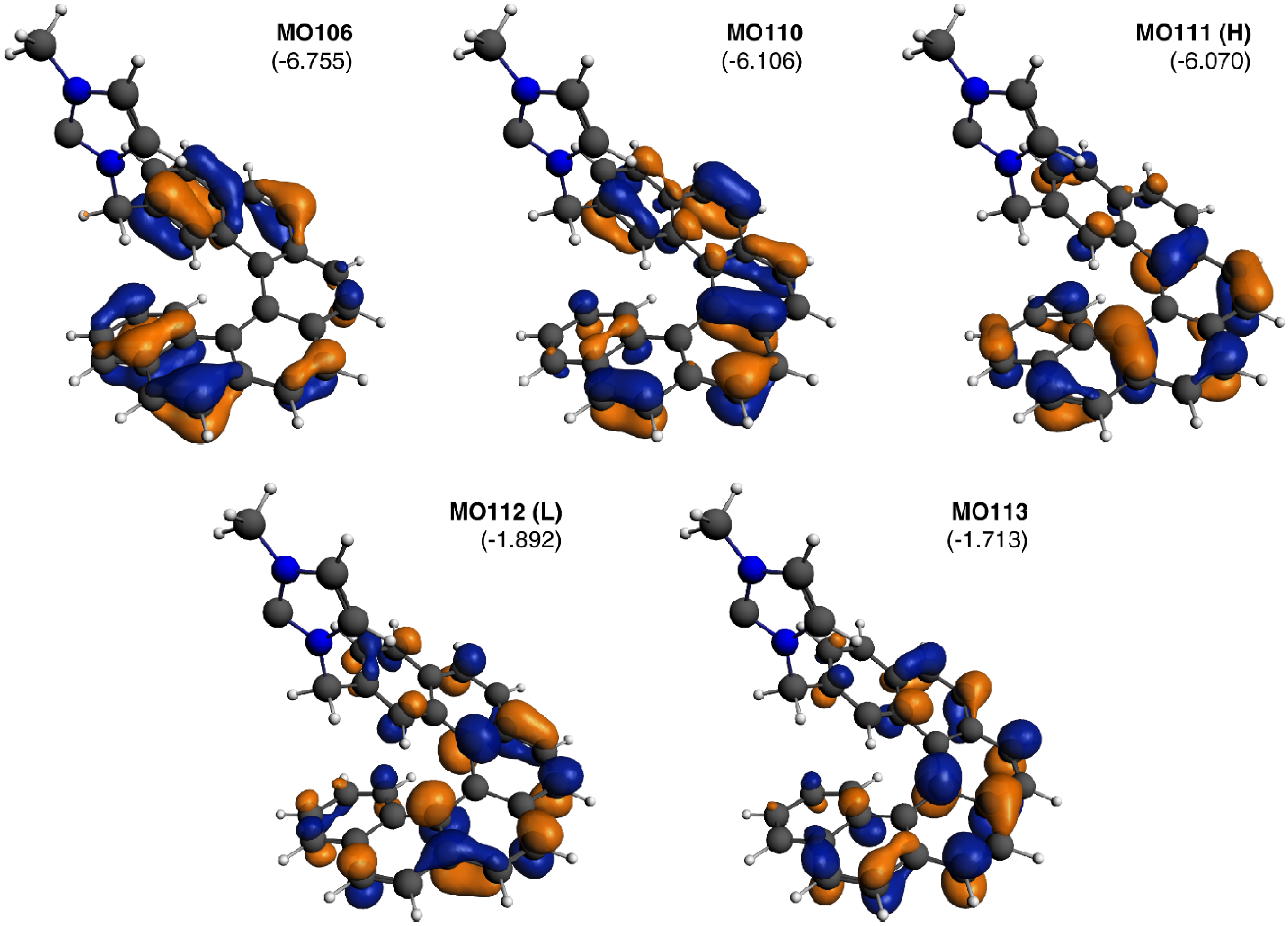


Figure S19. Isosurfaces (0.04 au) of MOs involved in selected transitions of **4b**. 'H' = HOMO, 'L' = LUMO. Values listed in the parentheses are the corresponding orbital energies, in eV.

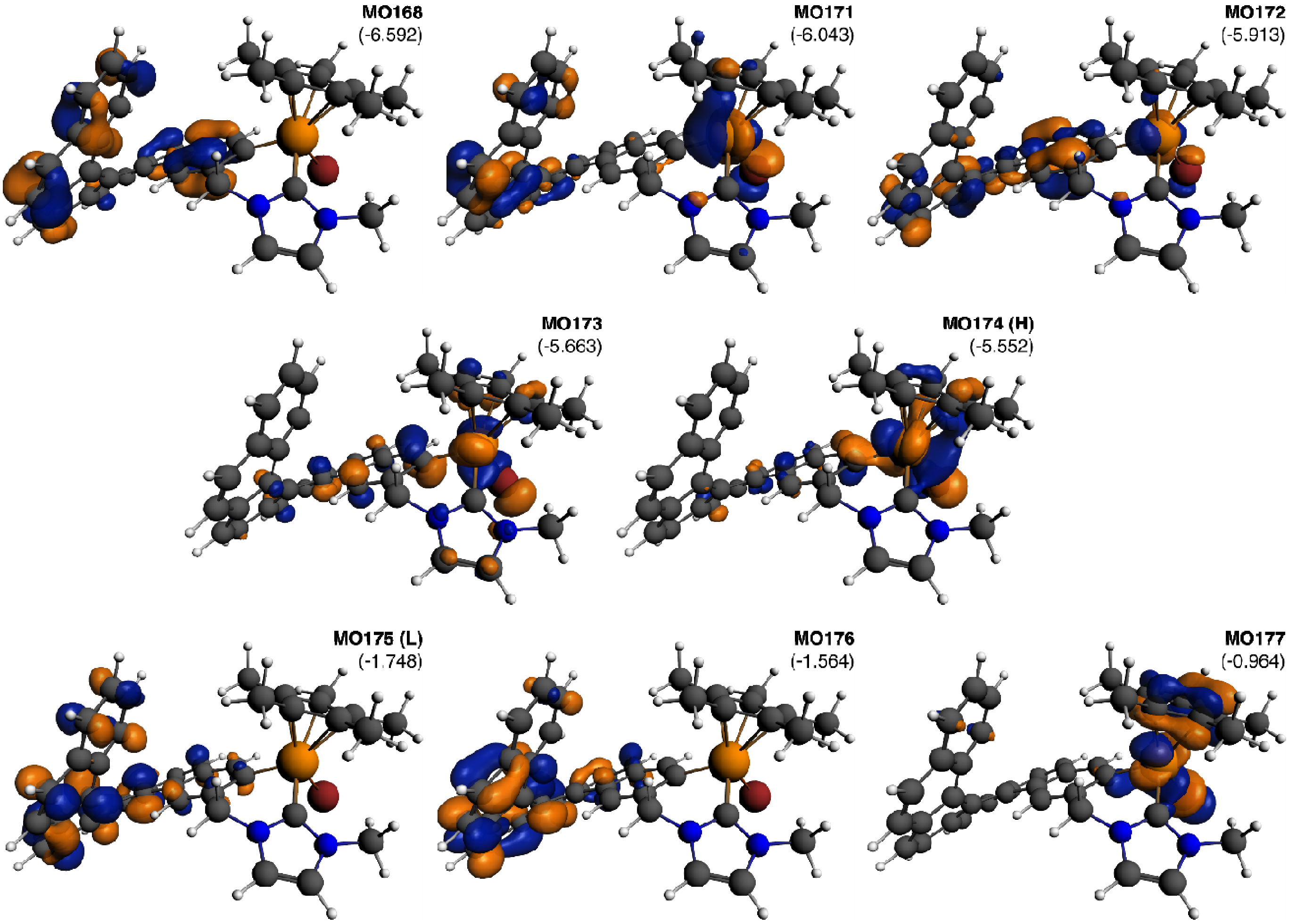


Figure S20. Isosurfaces (0.04 au) of MOs involved in selected transitions of (P,S_{Ir})-**3b**. 'H' = HOMO, 'L' = LUMO. Values listed in the parentheses are the corresponding orbital energies, in eV.

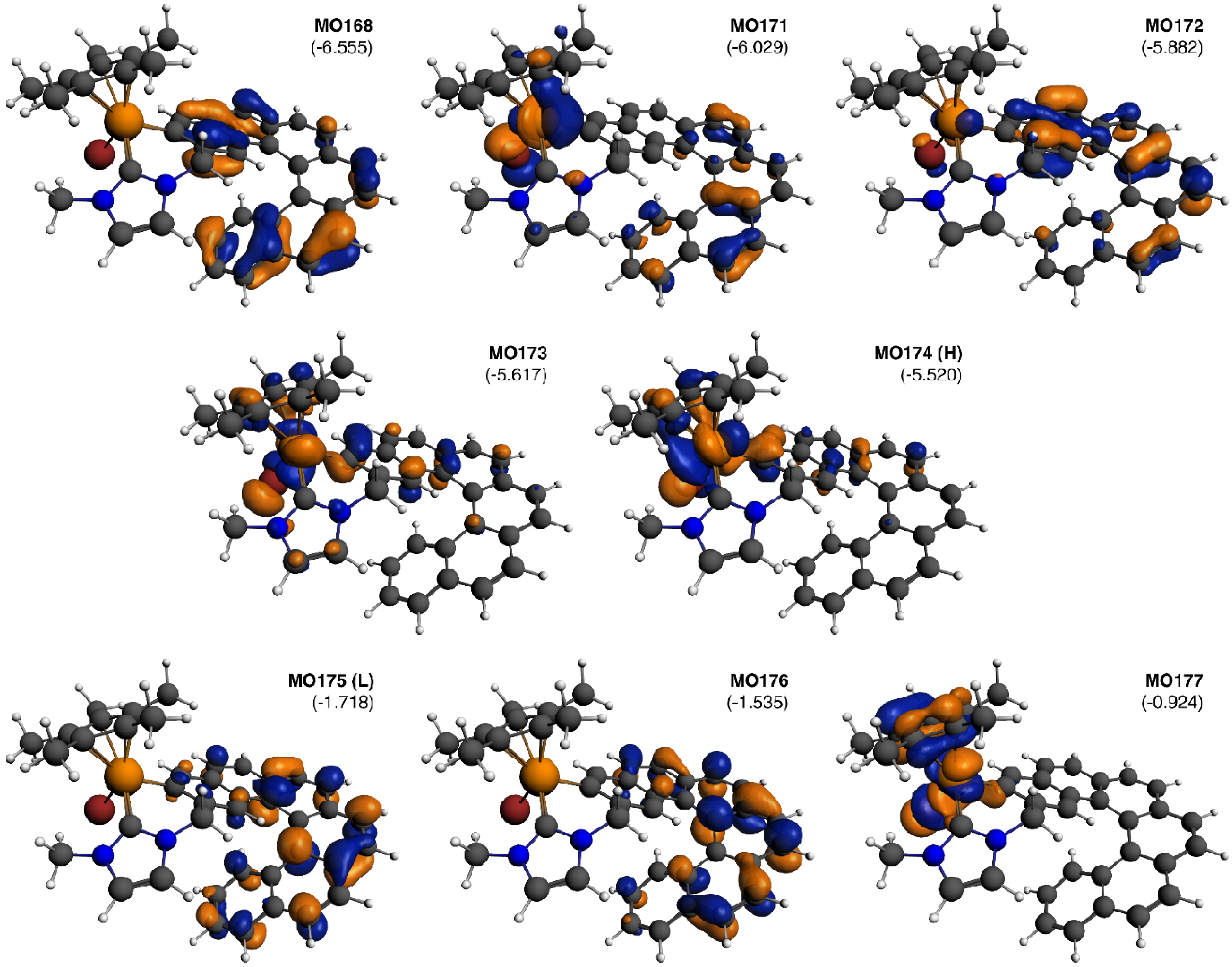


Figure S21. Isosurfaces (0.04 au) of MOs involved in selected transitions of (P,R_{Ir})-**3b**. 'H' = HOMO, 'L' = LUMO. Values listed in the parentheses are the corresponding orbital energies, in eV.

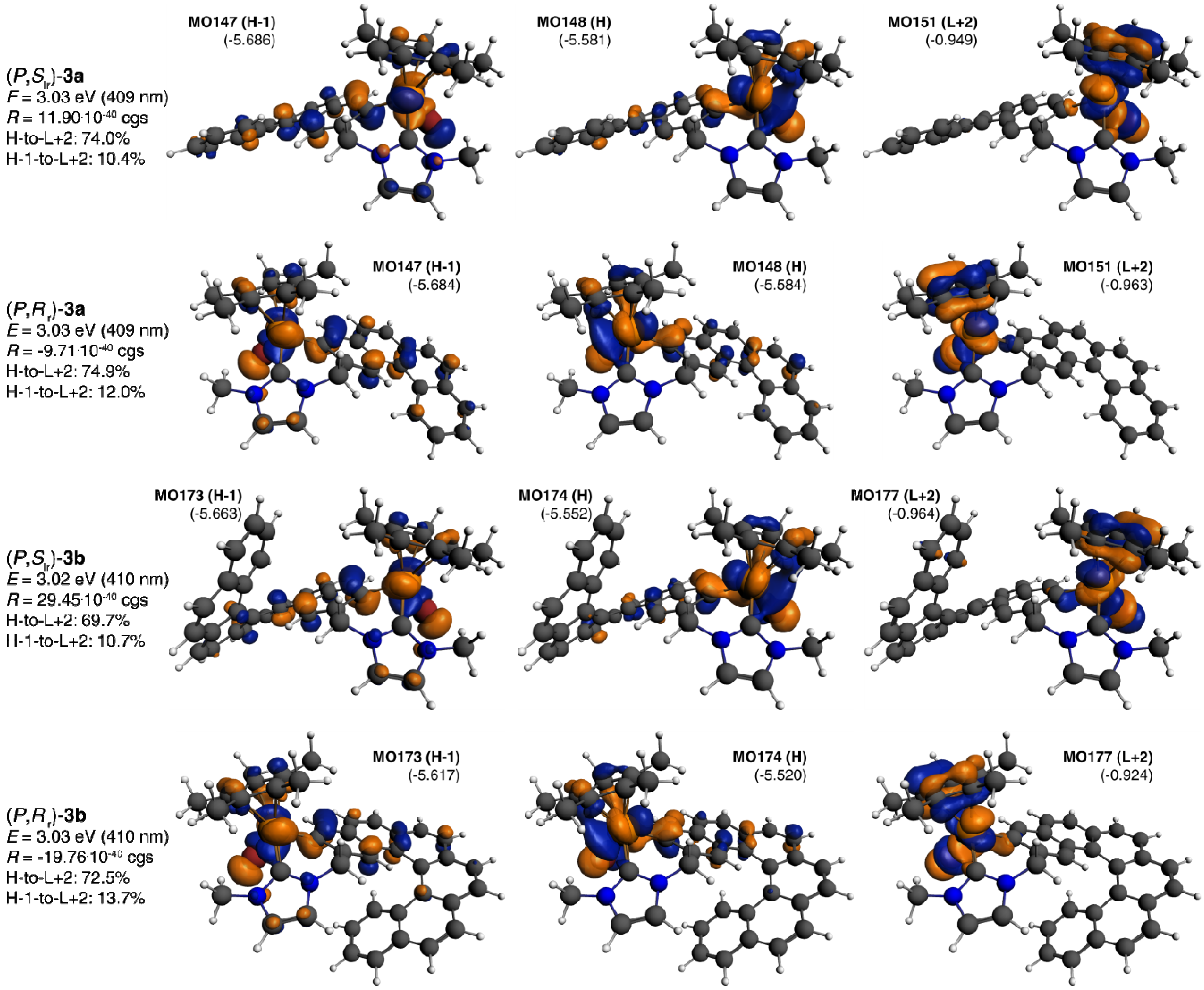


Figure S22. Characterization of the first calculated excitation in Ir-based NHC-[4]helicene and NHC-[6]helicene complexes **3a** and **3b** along with isosurfaces (0.04 au) of relevant MOs involved in the transitions. 'H' = HOMO, 'L' = LUMO. Values listed in the parentheses below MO labels are the corresponding orbital energies, in eV.

Optimized (BP/SV(P) with the continuum solvent model for CH_2Cl_2) geometries of 3a and 3b complexes and of the pristine 4b ligand along with the corresponding absolute energies:

The atomic symbol followed by three Cartesian coordinates, in Å.

(P,S_{Ir})-**3a**

Total energy = -4064.079079 au

Ir	1.1600134	1.6674059	-1.0682669
Br	3.6706820	0.9540920	-0.8279537
N	0.3494630	2.2250350	1.7782895
N	1.9990565	3.5339138	1.2489703
C	1.1418606	1.4906551	-3.3960509
C	1.4924898	2.8901101	-3.0724905
C	0.4098928	3.4639620	-2.3482622
C	-0.6089634	2.4167217	-2.1440274
C	-0.1662258	1.2280306	-2.8850940
C	1.9980224	0.5819705	-4.2297929
H	3.0445485	0.5612270	-3.8535197
H	2.0262488	0.9275969	-5.2898652
H	1.6156838	-0.4601056	-4.2260014
C	2.7561566	3.5584745	-3.5290441
H	3.6482947	2.9496637	-3.2612643
H	2.8803966	4.5641268	-3.0759259
H	2.7575806	3.6844851	-4.6371268
C	0.2491084	4.8956421	-1.9214876
H	-0.1597154	4.9786138	-0.8916084
H	-0.4632364	5.4226147	-2.5988951
H	1.2101099	5.4497295	-1.9551690
C	-2.0076533	2.6643394	-1.6503703
H	-2.0258648	3.4106233	-0.8279520
H	-2.4822187	1.7319173	-1.2782526
H	-2.6530716	3.0600564	-2.4713779
C	-0.9862458	-0.0116054	-3.0944724
H	-1.6213765	-0.2357349	-2.2121468
H	-0.3504395	-0.9014450	-3.2826364
H	-1.6607913	0.1165656	-3.9733036
C	0.6126706	-0.0555737	-0.0857282
C	1.0534333	-1.3096117	-0.5342828
H	1.7999665	-1.3632866	-1.3447126
C	0.6227750	-2.5412266	0.0364938
C	1.2114240	-3.7798222	-0.3900560
H	1.9575948	-3.7598729	-1.2025340
C	0.9015895	-4.9580043	0.2494486
H	1.4098495	-5.8973496	-0.0270372

C -0.1078140 -5.0058807 1.2716278
C -0.3772494 -6.2527047 1.9317058
H 0.2366114 -7.1287086 1.6613545
C -1.3543803 -6.3558068 2.8953381
H -1.5257405 -7.3066408 3.4273939
C -2.2185353 -5.2435257 3.1683542
C -3.3253269 -5.3969096 4.0543223
H -3.4441486 -6.3588675 4.5817358
C -4.2602632 -4.3812401 4.2266719
H -5.1163665 -4.5188668 4.9078537
C -4.1284162 -3.1874834 3.4744300
H -4.9028666 -2.4051447 3.5410475
C -3.0351497 -2.9998612 2.6292710
H -3.0027822 -2.0878081 2.0183302
C -2.0080703 -3.9842099 2.4859378
C -0.8343425 -3.8224748 1.6281002
C -0.3555196 -2.5473489 1.1001877
C -0.7089888 -1.2669059 1.6199480
H -1.3223227 -1.2016383 2.5305577
C -0.2522447 -0.0703777 1.0567921
C -0.7264993 1.2368912 1.6579237
H -1.5273047 1.6838606 1.0247717
H -1.1511350 1.0822778 2.6698775
C 1.2000169 2.5309974 0.7470147
C 0.5992561 3.0137295 2.8940396
H 0.0251793 2.9166415 3.8225058
C 1.6398337 3.8409993 2.5590684
H 2.1616672 4.6106868 3.1390278
C 3.0530061 4.2340371 0.5216088
H 3.8843856 4.4644107 1.2189561
H 3.4253730 3.5706115 -0.2837675
H 2.6670285 5.1833262 0.0915200

(P,S_{Ir})-**3a’**

Total energy = -4064.058232 au

C 3.3179833 -4.6482229 5.1131076
C 2.9345407 -3.2858729 4.9394298
C 2.3402454 -2.8563288 3.6913116
C 2.3071681 -3.8165869 2.6326394
C 2.7203232 -5.1357696 2.8172447
C 3.1974732 -5.5708871 4.0787361
C 1.9003507 -1.4692152 3.5490055
C 2.3280280 -0.5305456 4.5448522
C 2.9585590 -0.9873149 5.7516032
C 3.1980358 -2.3247091 5.9717295
C 2.1256829 0.8788650 4.3476776
C 1.5051667 1.3584753 3.2165641
C 0.9342967 0.4528207 2.2595457
C 1.0642331 -0.9677782 2.4636432
C 0.2471918 -1.7697347 1.6164182
C -0.5179980 -1.2415487 0.5714701
C -0.4960081 0.1526091 0.2220373
C 0.1995595 0.9523762 1.1458237
C -1.4812660 -2.1731606 -0.1125347
N -1.4504541 -2.0637275 -1.5674723
C -1.5072329 -0.8793872 -2.2653001
N -1.6491382 -1.2971803 -3.5792289
C -1.6563043 -2.6850531 -3.6736794
C -1.5344495 -3.1685655 -2.4016035
Ir -1.4382183 0.9910011 -1.4410024
C -1.8749915 -0.4720857 -4.7527042
C -2.1819139 3.2241795 -1.8262485
C -1.0054593 3.2460972 -0.9922663
C 0.0674907 2.6220598 -1.7523026
C -0.4634305 2.2798122 -3.0718464
C -1.8518659 2.6952381 -3.1273026
C -3.5050278 3.8239620 -1.4554074
C -0.9091690 4.0240219 0.2945839
C 1.5337738 2.6304231 -1.4251580
C 0.4192489 1.8956689 -4.2296779
C -2.7494350 2.8373481 -4.3301885
H 2.6898975 -5.8376830 1.9670833
H -2.7096100 -0.8999474 -5.3463436
H -2.1550062 0.5372948 -4.4151722
H -0.9677835 -0.4229806 -5.3904949
H -1.7506449 -3.1983266 -4.6372026
H -1.5088936 -4.1938683 -2.0156906
H -2.5189914 -1.9312724 0.2160324
H -1.2716875 -3.2302681 0.1442239
H 0.1666434 2.0445737 1.0631923
H 1.3941504 2.4445682 3.0558396
H 2.5005433 1.5733752 5.1184844
H 0.1410695 -2.8440616 1.8281889
H 3.2305147 -0.2376753 6.5140929
H 3.6451577 -2.6699557 6.9191215
H 3.7447297 -4.9526024 6.0841537
H 3.5069330 -6.6190304 4.2257286
H 2.0673015 1.7963920 -1.9267983
H 1.7283735 2.5461403 -0.3370852
H 1.9950018 3.5844586 -1.7750935
H 1.1430783 2.7185686 -4.4347204
H -0.1569136 1.7276578 -5.1608017
H 1.0142798 0.9811987 -4.0221296
H -2.9927616 3.9130855 -4.4960342
H -3.7184863 2.3045275 -4.2133602
H -2.2683817 2.4748680 -5.2620767
H -3.5197666 4.9030796 -1.7412460
H -3.6943649 3.7597990 -0.3643303
H -4.3463193 3.3240759 -1.9782426
H -1.5627851 3.6167228 1.0966154
H -1.2202282 5.0806385 0.1240351
H 0.1301156 4.0574109 0.6819839
H 2.0010848 -3.5044696 1.6250130
Br -3.7632393 0.4324223 -0.3704666

(P,R_{Ir})-**3a**

Total energy = -4064.078784 au

C -2.1855293 2.4495407 -0.1549877
C -1.6570984 3.3940917 -1.0891526
C -2.2247168 3.0902975 -2.4200532
C -3.0742167 1.9559677 -2.2963730
C -2.9997325 1.4822384 -0.9012933
Ir -0.9405740 1.2475649 -1.6511293
Br 1.2605617 2.0373457 -2.8320227
C -0.7852356 4.5811458 -0.7964026
C -1.9667167 3.9210779 -3.6427814
C -3.9764735 1.3649205 -3.3424806
C -3.9301087 0.4694273 -0.2931074
C -2.0059788 2.4547477 1.3350438
C -0.8645338 -0.5280837 -2.5927738
N -0.8490646 -0.8390443 -3.9337989
C -0.8483552 -2.2196244 -4.1190870
C -0.8550439 -2.7921130 -2.8731675
N -0.8640196 -1.7450916 -1.9607643
C -0.8726270 0.1206297 -5.0339394
C -0.9110261 -1.8790982 -0.5009113
C 0.1228864 -1.0037275 0.1773875
C 0.2316138 0.3738330 -0.2034292
C 1.1313515 1.1453314 0.5462064
C 1.9057457 0.6233349 1.6213127
C 1.8629086 -0.7877310 1.9310197
C 0.9106126 -1.5530833 1.1941401
C 2.7028398 -1.3128374 3.0052082
C 3.3210774 -0.3675293 3.8884967
C 3.3124480 1.0348225 3.5733150
C 2.6821655 1.5066628 2.4451471
C 3.9515179 -0.8075801 5.1017058
C 4.0065822 -2.1412727 5.4362044
C 3.5533744 -3.1367175 4.5076036
C 2.9618311 -2.7318420 3.2497442
C 2.7542416 -3.7621959 2.2803168
C 2.9915718 -5.1065301 2.5657534
C 3.4566929 -5.4996685 3.8452866
C 3.7505772 -4.5206200 4.7889188
H 2.8312325 -5.8638863 1.7803190
H -1.9169171 0.3295076 -5.3503616
H -0.3802929 1.0555834 -4.6991685
H -0.3129872 -0.3031432 -5.8925626
H -0.8332116 -2.6721237 -5.1170974
H -0.8488479 -3.8429587 -2.5619570
H -1.9364526 -1.6007460 -0.1669701
H -0.7587869 -2.9494528 -0.2586758
H 1.2415990 2.2203510 0.3238657
H 2.7144413 2.5795446 2.1895303
H 3.8410699 1.7261908 4.2513435
H 0.7284042 -2.6020683 1.4684155
H 4.3726881 -0.0434226 5.7769846
H 4.4520375 -2.4665513 6.3914290
H 4.1758741 -4.7999992 5.7680199
H 3.6240110 -6.5652231 4.0742717
H -2.3950950 3.4584815 -4.5562376
H -0.8743089 4.0559296 -3.8074278
H -2.4170377 4.9352954 -3.5328783
H -5.0351229 1.6583074 -3.1489150
H -3.9424819 0.2541753 -3.3418587
H -3.7170134 1.7164178 -4.3626325
H -4.9217861 0.9304258 -0.0666862
H -3.5303310 0.0637141 0.6599499
H -4.1128832 -0.3843457 -0.9797138
H -2.8517892 2.9948567 1.8214035
H -1.0649402 2.9587946 1.6380326
H -1.9816892 1.4247023 1.7478827
H -0.3515137 4.5288767 0.2241729
H -1.3678949 5.5297454 -0.8655501
H 0.0563454 4.6493070 -1.5203559
H 2.4541315 -3.4948753 1.2582730

(P,R_{Ir})-**3a’**

Total energy = -4064.055985 au

C -3.5091841 -2.0217288 -2.8991276
N -2.1307063 -2.1684957 -3.0229509
C -1.4680821 -1.6622137 -1.9173261
N -2.4920195 -1.2430210 -1.1001619
C -3.7370863 -1.4439308 -1.6826890
C -2.3573320 -0.9596468 0.3243521
C -1.1667760 -0.1256612 0.7142247
C 0.1167059 -0.3089898 0.1005219
C 1.1464490 0.4314153 0.7087079
C 0.9719798 1.3227107 1.8046688
C -0.3198203 1.4673331 2.4273776
C -1.3673891 0.7364702 1.8010584
C -0.4777407 2.3728669 3.5632884
C 0.5972194 3.2806018 3.8399305
C 1.8658423 3.1286083 3.1806006
C 2.0667669 2.1432446 2.2421383
C -1.6460265 2.4252516 4.4425854
C -1.8093900 3.5538154 5.3349220
C -0.7647865 4.5302135 5.4501545
C 0.4216956 4.3562848 4.7750844
C -2.6135973 1.3784276 4.5552911
C -3.7264330 1.4839159 5.3892628
C -3.9354857 2.6494815 6.1675924
C -2.9746971 3.6552364 6.1504097
C -1.5458687 -2.9285555 -4.1142792
Ir 0.5266732 -1.5137810 -1.5495125
Br 0.2309596 -3.5513735 0.0558688
C 2.0476537 -0.1048674 -2.4154241
H 2.1724736 0.3540008 0.3340239
H 3.0552045 2.0113992 1.7694091
H 2.6841363 3.8140650 3.4592683
H 1.2582563 5.0600731 4.9235374
H -0.9080140 5.3852503 6.1320187
H -3.0838300 4.5416579 6.7984178
H -4.8270752 2.7383892 6.8102494
H -4.4368206 0.6428408 5.4534655
H -2.4582992 0.4328895 4.0193837
H -2.4017328 0.8671412 2.1483951
H -2.2829420 -1.9444919 0.8446962
H -3.3008397 -0.4803409 0.6549112

H	-4.6687122	-1.1712753	-1.1741934
H	-4.1996622	-2.3466765	-3.6854282
H	-1.3217545	-2.2865568	-4.9915794
H	-0.6186128	-3.4039377	-3.7487744
H	-2.2631415	-3.7152938	-4.4249076
C	1.3306732	-0.7398497	-3.5196706
C	1.7419353	-2.1359319	-3.5863248
C	2.5867279	-2.3754691	-2.4512919
C	2.8284383	-1.1314721	-1.7484824
C	0.6040652	0.0290694	-4.5890088
C	1.6195785	-3.0702715	-4.7608837
C	3.2535253	-3.6747236	-2.1087413
C	3.9049225	-0.9676724	-0.7074862
C	2.1566935	1.3851290	-2.2490396
H	-0.0953450	-0.6080358	-5.1674697
H	1.3347000	0.4594767	-5.3144730
H	0.0216688	0.8729225	-4.1642058
H	0.8592780	-2.7357251	-5.4942825
H	1.3807299	-4.1149665	-4.4658598
H	2.5929000	-3.1078864	-5.3058342
H	3.2190182	-3.8689574	-1.0155210
H	4.3268842	-3.6465197	-2.4121655
H	2.7771039	-4.5345733	-2.6229536
H	3.6932092	-1.5413104	0.2213492
H	4.0551977	0.0953813	-0.4267277
H	4.8806317	-1.3337806	-1.1031883
H	2.5739133	1.6781346	-1.2655834
H	1.1719611	1.8860107	-2.3578251
H	2.8334309	1.7982748	-3.0337923

(*P*,S_{Ir})-**3b**

Total energy = -4371.142296 au

Ir	1.9335310	-1.2480820	1.7097888
Br	4.3759355	-0.5377494	1.0723351
N	2.7517183	-3.7047891	0.0170076
N	0.9803308	-2.7076642	-0.7449051
C	0.2839164	-1.6929211	3.0975795
C	0.6981644	-0.3161742	3.4004053
C	2.0486446	-0.3556011	3.8645604
C	2.4636811	-1.7711208	3.9617265
C	1.3755038	-2.5836666	3.5361276
C	-1.1261527	-2.1354554	2.8170958
H	-1.6922693	-2.2797873	3.7688831
H	-1.1526824	-3.1011747	2.2686813
H	-1.6793842	-1.3840305	2.2148126
C	-0.1817569	0.8937546	3.2822651
H	-0.8105358	1.0034724	4.1969396
H	-0.8627892	0.8208647	2.4084081
H	0.4107375	1.8245992	3.1650001
C	2.8981932	0.7987654	4.3110241
H	2.4475208	1.7732648	4.0296248
H	3.9122153	0.7493496	3.8562624
H	3.0230293	0.7915652	5.4193399
C	3.7915260	-2.2123226	4.5043089
H	3.9480366	-3.3043240	4.3816790
H	3.8693730	-1.9796941	5.5922732
H	4.6272158	-1.6873833	3.9900582
C	1.2759397	-4.0819330	3.5894196
H	2.2691416	-4.5599693	3.7195477
H	0.8099981	-4.5003518	2.6715875
H	0.6406661	-4.3955545	4.4509050
C	3.8957518	-4.0938368	0.8363597
H	4.3528703	-3.1803525	1.2670975
H	4.6376449	-4.6099884	0.1937564
H	3.5793190	-4.7828720	1.6485214
C	2.3301073	-4.4205596	-1.1011273
H	2.8670781	-5.3057241	-1.4605401
C	1.2126864	-3.7894541	-1.5837903
H	0.5749521	-4.0103890	-2.4473148
C	1.9174576	-2.6349811	0.2532541
C	-0.1454224	-1.7745280	-0.8464696
H	-0.8641004	-2.0199538	-0.0314435
H	-0.6545018	-1.9711823	-1.8106833
C	0.2956268	-0.3300110	-0.7415384
C	1.2228905	0.0559470	0.2821635
C	1.6068197	1.4055493	0.2859007
H	2.3772094	1.7491678	0.9968277
C	1.0905154	2.3662703	-0.6304178
C	1.6176120	3.7034547	-0.6573624
H	2.3669463	3.9947643	0.0982410
C	1.2603665	4.5733365	-1.6618792
H	1.7373898	5.5649114	-1.7422473
C	0.2734234	4.2125231	-2.6446122
C	0.0582397	5.0633321	-3.7763967
H	0.6329334	6.0019735	-3.8508931
C	-0.7700515	4.6605760	-4.8027483
H	-0.8424105	5.2450828	-5.7352432
C	-1.5876679	3.4935662	-4.6591879
C	-2.4201699	3.0676753	-5.7446913
H	-2.3701728	3.6229253	-6.6965052
C	-3.2319627	1.9614374	-5.6146011
H	-3.8141443	1.5825759	-6.4711695
C	-3.4171117	1.3532609	-4.3306985
C	-4.3847918	0.2999409	-4.1793069
H	-4.8678696	-0.0975701	-5.0879709
C	-4.7145504	-0.1937110	-2.9386865
H	-5.4463814	-1.0122989	-2.8333342
C	-4.1823137	0.4194469	-1.7535240
C	-4.6754815	0.0496729	-0.4679443
H	-5.4121078	-0.7693329	-0.4039045
C	-4.2754991	0.7285754	0.6788342
H	-4.6782743	0.4437729	1.6650817
C	-3.3763124	1.8184911	0.5614823
H	-3.0984055	2.4023255	1.4546150
C	-2.8475674	2.1691847	-0.6791609
H	-2.1684478	3.0305014	-0.7419495
C	-3.1973970	1.4682284	-1.8704059
C	-2.6859535	1.8331018	-3.1923299
C	-1.5704921	2.7462326	-3.4253718
C	-0.4415766	2.9719739	-2.5266918
C	0.0886636	1.9813830	-1.5927338
C	-0.2472460	0.6002013	-1.6313878
H	-0.9375685	0.2394953	-2.4086132

(*P*,S_{Ir})-**3b’**

Total energy = -4371.120059 au

C	1.6292718	-1.7392665	4.5147712
C	0.3248094	-2.3400225	4.3517417
C	0.2165388	-2.9291920	3.0416857
C	1.4408668	-2.6006854	2.3241943
C	2.3130978	-1.8718434	3.2454648
Ir	0.4525016	-0.6252554	2.7062572
C	-0.6930812	-2.4833457	5.4434941
C	-0.8655620	-3.9012696	2.6476326
C	1.9200685	-3.1913472	1.0283045
C	3.7751647	-1.6441454	2.9661550
C	2.1834633	-1.3124681	5.8498645
C	1.1902511	1.2520522	2.3849268
N	2.2858881	1.9104369	2.9218465
C	2.3975424	3.2031387	2.4197889
C	1.3498005	3.3855340	1.5621536
N	0.6313696	2.1998458	1.5597249
C	3.1840253	1.4384132	3.9608015
C	-0.6613095	2.0659208	0.8957856
C	-0.8291323	0.7502075	0.1866697
C	-0.5066618	-0.4800268	0.8556386
C	-0.9356140	-1.6285350	0.1676449
C	-1.5634888	-1.6198616	-1.1105422
C	-1.7456133	-0.3805508	-1.8158979
C	-1.3906716	0.7879742	-1.0923821
C	-2.3597569	-0.3748126	-3.1402744
C	-3.0232012	-1.5789307	-3.5589755
C	-2.8160637	-2.8065758	-2.8377982
C	-2.0707253	-2.8375146	-1.6814088
C	-3.9485247	-1.5500317	-4.6513030
C	-4.2800109	-0.3532167	-5.2507290
C	-3.5557747	0.8412924	-4.9351320
C	-2.4483349	0.7939526	-4.0114758
C	-1.5227103	1.9237009	-4.0331801
C	-1.9981324	3.1773221	-4.5466457
C	-3.2394287	3.2407185	-5.2591108
C	-3.9381450	2.0850918	-5.5343040
C	-1.2040015	4.3678658	-4.4035062
C	0.0662096	4.3194993	-3.8785181
C	0.6716472	3.0540409	-3.5696287
C	-0.1031081	1.8416834	-3.6861713
C	0.5958196	0.6065793	-3.5486742
C	1.9549560	0.5614948	-3.2457858
C	2.6885263	1.7580857	-3.0487855
C	2.0516399	2.9831411	-3.2190815
H	3.3172035	2.2374259	4.7198131
H	2.7257803	0.5603344	4.4410017
H	4.1768218	1.1694106	3.5437429
H	3.2100487	3.8729529	2.7227820
H	1.0476986	4.2518473	0.9632121
H	-1.4474544	2.1658353	1.6802291
H	-0.7608409	2.9158385	0.1920790
H	-0.8377383	-2.6172341	0.6291271
H	-1.9082364	-3.7882644	-1.1450149
H	-3.2842284	-3.7258172	-3.2290622
H	-1.6074055	1.7728454	-1.5327266
H	-4.4526521	-2.4864984	-4.9439653
H	-5.0849270	-0.2997537	-6.0028341
H	-4.8247563	2.1033592	-6.1902129
H	-3.5773554	4.2140706	-5.6523242
H	-1.6373196	5.3257449	-4.7377820
H	0.6624283	5.2397109	-3.7576667
H	2.6163244	3.9256150	-3.1165082
H	3.7600441	1.7173059	-2.7911680
H	2.4607980	-0.4148642	-3.1639083
H	0.0580487	-0.3367916	-3.7155194
H	-0.6530980	-4.3825289	1.6705607
H	-1.8703996	-3.4291735	2.5860707
H	-0.9335993	-4.7207207	3.3997998
H	2.4335473	-4.1635515	1.2202357
H	2.6455434	-2.5219494	0.5211158
H	1.0930898	-3.3860525	0.3162594
H	4.2776159	-2.6255627	2.8006646
H	4.2942091	-1.1503516	3.8110625
H	3.9426942	-1.0345919	2.0530696
H	2.1423077	-2.1632525	6.5696702
H	1.6094882	-0.4774160	6.3082599
H	3.2471463	-1.0026615	5.7858132
H	-0.6820571	-1.6152402	6.1343308
H	-0.4719655	-3.3992238	6.0424415
H	-1.7207097	-2.5830985	5.0380160
Br	-1.5905009	0.5532077	3.8540995

(*P*,R_{Ir})-**3b**

Total energy = -4371.140697 au

Ir	-0.5770764	-2.3800464	-1.4017616
C	0.1096093	-0.9827863	-2.6744914
N	-0.1226634	-0.7942746	-4.0183324
C	-0.9845356	-1.6194149	-4.8595290
H	-0.4066381	-2.4504674	-5.3177382
H	-1.8060071	-2.0245639	-4.2347716
H	-1.4114134	-0.9888965	-5.6660989
C	0.6184778	0.2826074	-4.4994168
H	0.5686432	0.6001049	-5.5471522
C	1.3251493	0.7884058	-3.4388850
H	2.0177479	1.6348618	-3.3726010
N	1.0009910	0.0035243	-2.3405883
C	1.5483110	0.1522985	-0.9878599
H	2.2720752	-0.6780411	-0.8213782
H	2.1165162	1.1030767	-0.9613334
C	0.4607203	0.1307638	0.0660872
C	-0.5394380	-0.8950234	0.0223292
C	-1.4682899	-0.8923967	1.0722667
H	-2.2556710	-1.6644584	1.1042106

C	-1.4424712	0.0538099	2.1360663
C	-2.3432795	-0.0802972	3.2477510
H	-3.1022063	-0.8809722	3.2241759
C	-2.2055141	0.7229244	4.3558839
H	-2.8325438	0.5616330	5.2493302
C	-0.4715180	1.1200805	2.1324563
H	1.2886044	1.8426318	1.0673636
C	0.4810120	1.0959612	1.0760094
C	-0.4601373	2.0964801	3.2207989
C	-1.2327391	1.7820508	4.3918176
C	-0.9950539	2.4732608	5.6231671
H	-1.5954032	2.2015109	6.5077818
C	0.0363390	3.3823704	5.7223659
H	0.3125455	3.8234517	6.6947884
C	0.7444134	3.8043147	4.5514750
C	0.3620057	3.3049316	3.2522491
C	1.8371466	4.7220450	4.6767968
H	2.1442418	5.0400469	5.6874033
C	0.8368552	4.0586491	2.0936901
C	2.5159884	5.1613331	3.5610563
H	3.4075120	5.8035277	3.6565742
C	2.0041679	4.8797316	2.2531230
C	2.6339706	5.4769167	1.1062414
H	3.5738449	6.0337273	1.2599170
C	2.0793670	5.3721332	-0.1478016
H	2.5779886	5.8186441	-1.0246266
C	0.7917978	4.7587204	-0.3184603
C	0.1265957	4.8205612	-1.5778877
H	0.6551637	5.2838674	-2.4286082
C	-1.1723487	4.3457303	-1.7292620
H	-1.6792757	4.4086949	-2.7065020
C	-1.8513062	3.8116429	-0.6057556
H	-2.8973216	3.4767345	-0.7021140
C	-1.2079048	3.7070605	0.6256884
H	-1.7661241	3.3068385	1.4831520
C	0.1389624	4.1371729	0.8092089
C	-1.0927498	-4.4731311	-0.5196106
Br	-3.0579514	-1.7167537	-1.9091154
C	-0.8985957	-4.6637188	-1.9726504
C	0.4348904	-4.2924457	-2.2998433
C	1.0822707	-3.7945721	-1.0714560
C	0.1401425	-4.0046168	0.0343718
C	-1.9505767	-5.2224153	-2.8852824
C	1.1342992	-4.4476038	-3.6206879
C	2.5580152	-3.5415472	-0.9294892
C	0.4610501	-3.8100396	1.4876650
C	-2.3442480	-4.8505403	0.2194746
H	-1.6377889	-5.1856648	-3.9497003
H	-2.9018092	-4.6524062	-2.7883663
H	-2.1680099	-6.2862157	-2.6313513
H	1.8262026	-5.3221311	-3.5907687
H	1.7484633	-3.5567212	-3.8740042
H	0.4194458	-4.6197001	-4.4521107
H	3.1152210	-4.5037116	-0.8246693
H	2.7865577	-2.9294065	-0.0318962
H	2.9719422	-3.0169644	-1.8169367
H	0.9274283	-4.7331409	1.9049452
H	-0.4466569	-3.5889043	2.0864009
H	1.1736493	-2.9728241	1.6408207
H	-2.3311334	-4.4767475	1.2647014
H	-2.4637610	-5.9589078	0.2605142
H	-3.2461807	-4.4323636	-0.2792245

(P,R_{Ir})-**3b'**

Total energy = -4371.118886 au

Ir	-0.3170485	-2.1682861	-1.6754408
C	1.1404708	-1.1601004	-2.6676446
N	1.8597433	-1.5337145	-3.7908907
C	1.5825979	-2.6609740	-4.6645578
H	2.2279790	-3.5330698	-4.4296858
H	0.5198263	-2.9369966	-4.5460627
H	1.7683978	-2.3544619	-5.7143480
C	2.8193595	-0.5803061	-4.1184825
H	3.5000891	-0.7110861	-4.9671693
C	2.6917238	0.4346930	-3.2133986
H	3.2263961	1.3860164	-3.1129728
N	1.6652493	0.0705890	-2.3507960
C	1.0287703	1.0502884	-1.4770220
H	1.7801449	1.8370516	-1.2631220
H	0.2079029	1.5256902	-2.0653996
C	0.4404918	0.5111742	-0.2019504
C	-0.2619664	-0.7391053	-0.1615687
C	-0.9394050	-0.9747922	1.0479139
H	-1.5396502	-1.8826766	1.1728953
C	-0.9007425	-0.1135210	2.1804501
C	-1.5113881	-0.5175694	3.4174657
H	-2.0933264	-1.4548755	3.4460479
C	-1.2943936	0.2066054	4.5668029
H	-1.6758136	-0.1522961	5.5378337
C	-0.1806091	1.1294471	2.1186900
H	1.0907211	2.2967917	0.7941741
C	0.4912280	1.3801512	0.8946659
C	-0.1207853	1.9995411	3.2911918
C	-0.5499342	1.4378884	4.5427561
C	-0.1839384	2.0624303	5.7780230
H	-0.5163089	1.6019608	6.7236192
C	0.6573240	3.1549030	5.7820814
H	1.0517756	3.5635781	6.7274846
C	1.0002636	3.8096255	4.5556052
C	0.4433856	3.3475871	3.3070037
C	1.8993624	4.9248066	4.5725220
H	2.3567320	5.2175955	5.5325361
C	0.4966140	4.2765778	2.1805135
C	2.2167326	5.5888258	3.4074043
H	2.9680968	6.3961225	3.4020344
C	1.4897890	5.3134898	2.2040574
C	1.7184641	6.1262213	1.0396520
H	2.5425726	6.8589435	1.0701581
C	0.9273010	6.0090823	-0.0792173
H	1.1197208	6.6248438	-0.9739861
C	-0.2213901	5.1469451	-0.0637770
C	-1.1497930	5.1647658	-1.1456705
H	-0.9245288	5.7979851	-2.0208254
C	-2.3316610	4.4327558	-1.0915051
H	-3.0460842	4.4624556	-1.9308804
C	-2.6261881	3.6754812	0.0698748
H	-3.5826323	3.1321277	0.1450488
C	-1.7169089	3.6135426	1.1235917
H	-1.9815476	3.0351792	2.0194210
C	-0.4723409	4.3081364	1.0840758
C	-1.5421760	-3.8449362	-0.5803881
Br	-2.0113391	-0.6083332	-2.8963903
C	-1.6774608	-4.1372160	-1.9919407
C	-0.3940338	-4.4624472	-2.5460646
C	0.5895695	-4.2337618	-1.4961500
C	-0.1252660	-3.9021508	-0.2646603
C	-2.9925551	-4.2284348	-2.7079476
C	-0.1959691	-5.2137354	-3.8359665
C	2.0452704	-4.6099724	-1.5453365
C	0.5026659	-3.9279306	1.1000314
C	-2.7136870	-3.7875677	0.3656432
H	-3.5138602	-5.1760785	-2.4332315
H	-2.8669203	-4.2175231	-3.8102414
H	-3.6616680	-3.3856274	-2.4324463
H	-0.5690210	-6.2588948	-3.7158441
H	0.8710221	-5.2901561	-4.1254184
H	-0.7556527	-4.7733115	-4.6895741
H	2.1810656	-5.6671943	-1.2148852
H	2.6568894	-3.9700561	-0.8759266
H	2.4674399	-4.5291837	-2.5677513
H	0.5807322	-4.9820002	1.4576478
H	-0.0846106	-3.3630786	1.8511292
H	1.5269022	-3.5004135	1.0877439
H	-2.3906268	-3.7401958	1.4261867
H	-3.3351081	-4.7075122	0.2615398
H	-3.3824440	-2.9203523	0.1710214

P-**4b**

Total energy = -1303.151674 au

C	-0.9367138	4.8021700	1.1170226
N	-0.1591671	3.6654795	1.0788678
C	1.2068551	3.9417886	1.0204410
C	1.3142961	5.3096601	1.0271854
N	0.0095932	5.8003520	1.0838285
C	-0.7197011	2.3122593	1.0687084
C	-0.5764369	1.6002472	-0.2665321
C	0.0321857	0.3468895	-0.3394231
C	0.1759213	-0.3653028	-1.5660163
C	-0.2597812	0.2989582	-2.7688428
C	-0.9127381	1.5637667	-2.6762310
C	-1.0825672	2.1996128	-1.4538408
C	0.8237451	-1.6732876	-1.6598876
C	1.2746895	-2.0880654	-2.9583549
C	0.8153687	-1.4058006	-4.1375926
C	0.0254542	-0.2827221	-4.0496658
C	2.2318805	-3.1466525	-3.0848464
C	2.7929812	-3.7101899	-1.9594532
C	2.2785038	-3.4041995	-0.6579002
C	1.1457329	-2.5230703	-0.5169016
C	2.8920080	-3.9766810	0.5028513
C	2.3915591	-3.7151372	1.7600511
C	1.1328430	-3.0476205	1.9091074
C	0.4295303	-2.5641046	0.7547479
C	0.5531561	-2.9178088	3.2189153
C	-0.7212809	-2.4298793	3.3890884
C	-1.5463951	-2.1495557	2.2471084
C	-0.9926990	-2.2591770	0.9184749
C	-2.9257514	-1.8320635	2.4170082
C	-3.7706454	-1.6867973	1.3213449
C	-3.2533664	-1.8799175	0.0158807
C	-1.9004804	-2.1526219	-0.1759094
C	-0.3209968	7.2199974	1.1171053
H	-1.4243517	7.3112179	1.1523992
H	0.0612980	7.7355822	0.2091029
H	0.1161352	7.7060989	2.0166614
H	2.1983413	5.9591185	1.0032488
H	1.9770073	3.1614681	0.9815539
H	-1.7925914	2.4345276	1.3279894
H	-0.2417650	1.7142013	1.8740953
H	-1.2622977	2.0443595	-3.6057274
H	-0.3381402	0.2244776	-4.9589569
H	1.1213471	-1.8012661	-5.1207589
H	2.5696060	-3.4396476	-4.0928976
H	3.6225236	-4.4322386	-2.0421123
H	3.7917400	-4.6006108	0.3707314
H	2.9055872	-4.0866235	2.6622383
H	1.1561958	-3.2294476	4.0883680
H	-1.1517209	-2.3160014	4.3982252
H	-3.3192748	-1.7334619	3.4430082
H	-4.8384207	-1.4531674	1.4671829
H	-3.9248189	-1.8206526	-0.8567738
H	-1.5341874	-2.3198383	-1.1982717
H	0.4404395	-0.0913595	0.5827125
H	-1.5802353	3.1827372	-1.3983585

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