Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Metallaaromatic Biaryl Atropisomers

*M. Talavera, A. Peña-Gallego, J. L. Alonso-Gómez, S. Bolaño**

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Experimental Section

General Procedures, Methods and Materials

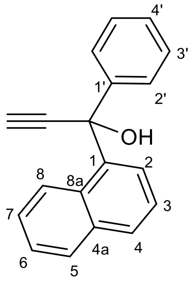
All experiments were carried out under an atmosphere of argon by Schlenk techniques. Solvents were dried by the usual procedures[1] and, prior to use, distilled under argon. All reagents were obtained from commercial sources except for the di(1-naphtyl)-ketone which was synthesized as described in the literature.[2] The starting material $[IrCp^{*}Cl(NCMe)(PMe_3)]PF_6$ [3] was prepared as described in the literature while the propargylic alcohols were synthesized following the method described by Mantovani *et al.*[4] Unless stated, NMR spectra were recorded in $(CD_3)_2CO$ (organometallic complexes) or $CDCl_3$ (organic compounds) at room temperature on Bruker ARX–400 instrument, with resonating frequencies of 400 MHz (^1H), 161 MHz ($^{31}P\{^1H\}$), and 100 MHz ($^{13}C\{^1H\}$) using the solvent as the internal lock. ^1H and $^{13}C\{^1H\}$ signals are referred to internal TMS and those of $^{31}P\{^1H\}$ to 85% H_3PO_4; downfield shifts (expressed in ppm) are considered positive. ^1H and $^{13}C\{^1H\}$ NMR (or JMOD) signal assignments were confirmed by ^1H, ^1H COSY, ^1H, ^1H NOESY, ^1H,^{13}C HSQC, ^1H,^{13}C HMBC and DEPT NMR experiments. Coupling constants are given in hertz. Ratios of all mixtures have been calculated by ^1H NMR and $^{31}P\{^1H\}$ NMR using relaxation delays of 10s in this case. Infrared spectra were run on a Jasco FT/IR–6100 spectrometer using KBr pellets. C, H, and N analyses were carried out with a Carlo Erba 1108 analyzer. Mass spectra are referred to the most abundant isotopes and they were acquired using an Apex–Qe spectrometer by high resolution electrospray technique for organometallic complexes and high resolution electron impact technique for organic compounds.

General Procedure for Preparation of Propargylic Alcohols

To a solution of trimethylsilylacetilene (360 µL, 2.5 mmol) in dry THF (25 mL) at around 203 K, n-buthyllithium 2.5 M in hexanes (1 mL, 2.5 mmol) was added dropwise and the reaction mixture was stirred for one hour. After that, the corresponding ketone (2.27 mmol) was added and the mixture was stirred at room temperature until the ketone had completely reacted. Then, a methanolic solution of KOH was added (6 mL, 0.5 M) at 273 K and the mixture was stirred again for 15 min. Finally, glacial acetic acid was added until pH≈7 followed by water addition. The organic phase, which was extracted with ethylacetate, was dried with Na_2SO_4 and concentrated under vacuum.

Synthesis of 1-(1-naphthalenyl)-1-phenyl-2-propyn-1-ol (I)

After 4 hours, the reaction finished and the propargylic alcohol was extracted dried and the ethylacetate removed. No further purification was necessary. Yield: 531 mg (96%).



$C_{19}H_{14}O$: 258.32 g/mol. **HR-EI-MS** (m/z): calculated: 258.1045 [M]; experimental: 258.1042 [M], 240.09 [M–H_2O] 181.07 [M–Ph]. **IR** (cm^{-1}): ν (C≡C) 2110 (w); (H–C≡) 3288 (s) and (OH) 3538 (m). **^{1}H NMR:** δ 8.30–8.26 (m, 1H, C^2H); 8.26–8.21 (m, 1H, C^8H); 8.02–7.95 (m, 2H, C^4H + C^5H); 7.76–7.70 (m, 2H, $C^{2'}H$); 7.69–7.36 (m, 1H, C^3H); 7.56–7.49 (m, 1H, C^6H); 7.49–7.37 (m, 4H, C^7H + $C^{3'}H$ + $C^{4'}H$); 3.07 (d, 1H, J_{HH} = 0.3 Hz, HC≡) ppm. **^{13}C{^{1}H} NMR:** δ 144.2 (s, $C^{1'}$); 138.4 (s, C^1); 134.6 (s, C^{4a}); 129.9 (s, C^{8a}); 129.6 and 128.6 (both s, C^4 and C^5); 128.5 (s, 2C $C^{3'}$); 128.0 (s, C^8); 126.8 (s, C^7); 126.4 (s, 2C $C^{2'}$); 125.44 (s, C^6); 125.37 (s, $C^{4'}$); 124.8 (s, C^2); 124.7 (s, C^3); 86.3 (s, HC≡C); 76.5 (s, HC≡C); 74.2 (s, C–OH) ppm.

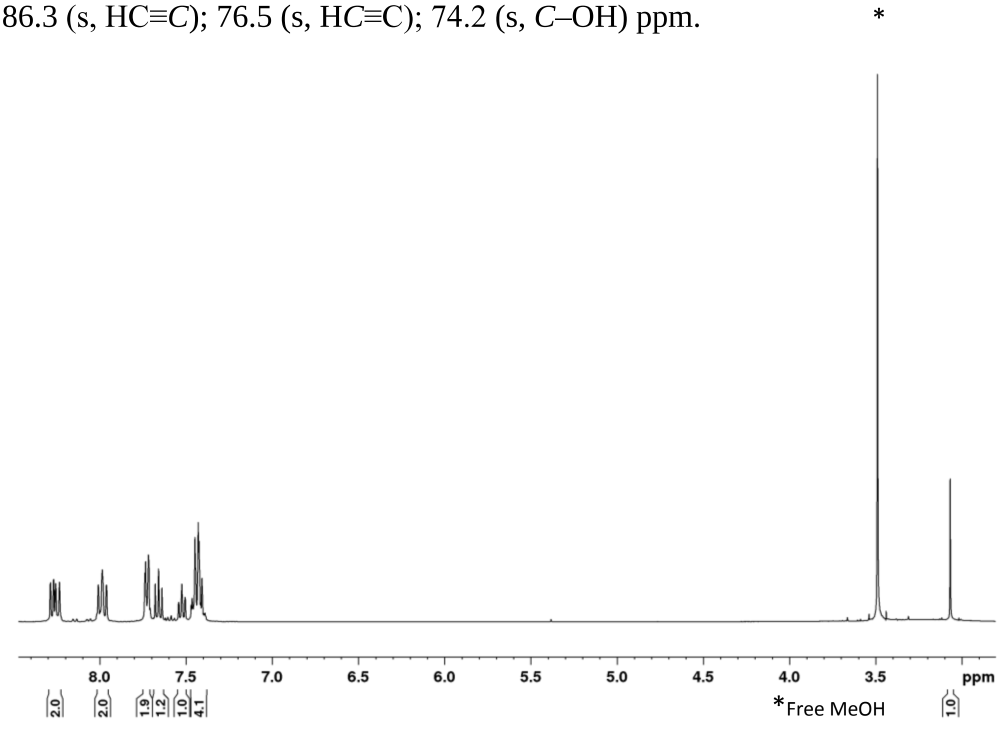
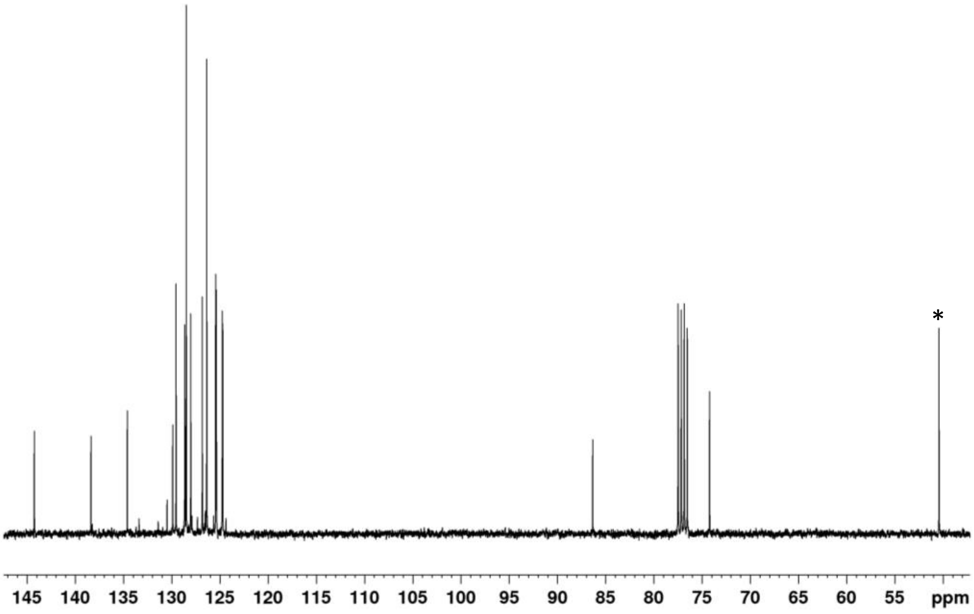


Figure S1. ^{1}H NMR spectrum of **I**.



*Free MeOH

Figure S2. ^{13}C{^{1}H} NMR spectrum of **I**.

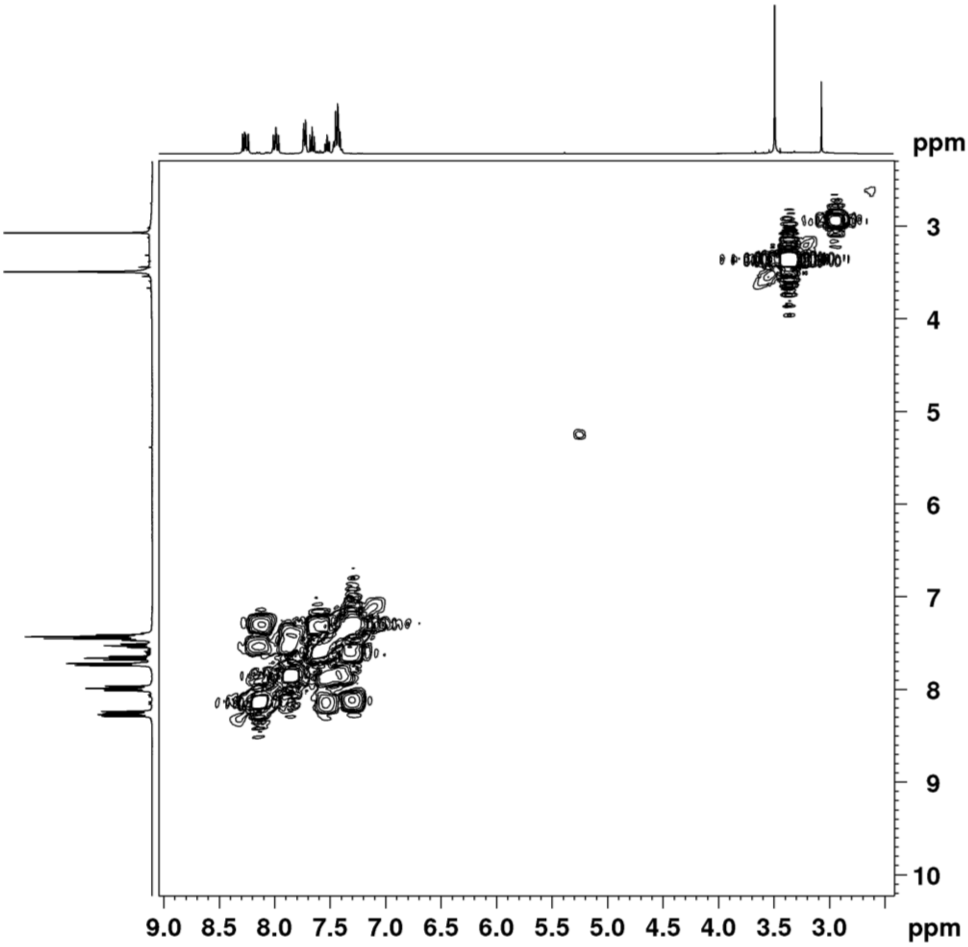


Figure S3. ^{1}H, ^{1}H COSY NMR spectrum of **I**.

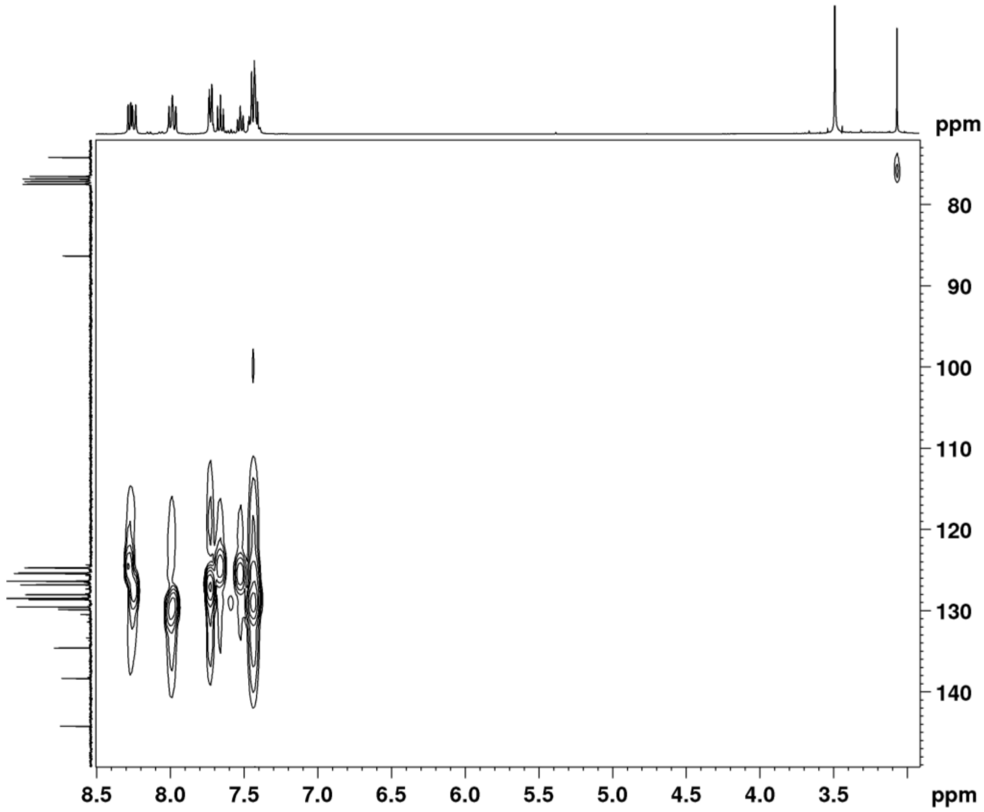


Figure S4. ^{1}H, ^{13}C HSQC NMR spectrum of **I**.

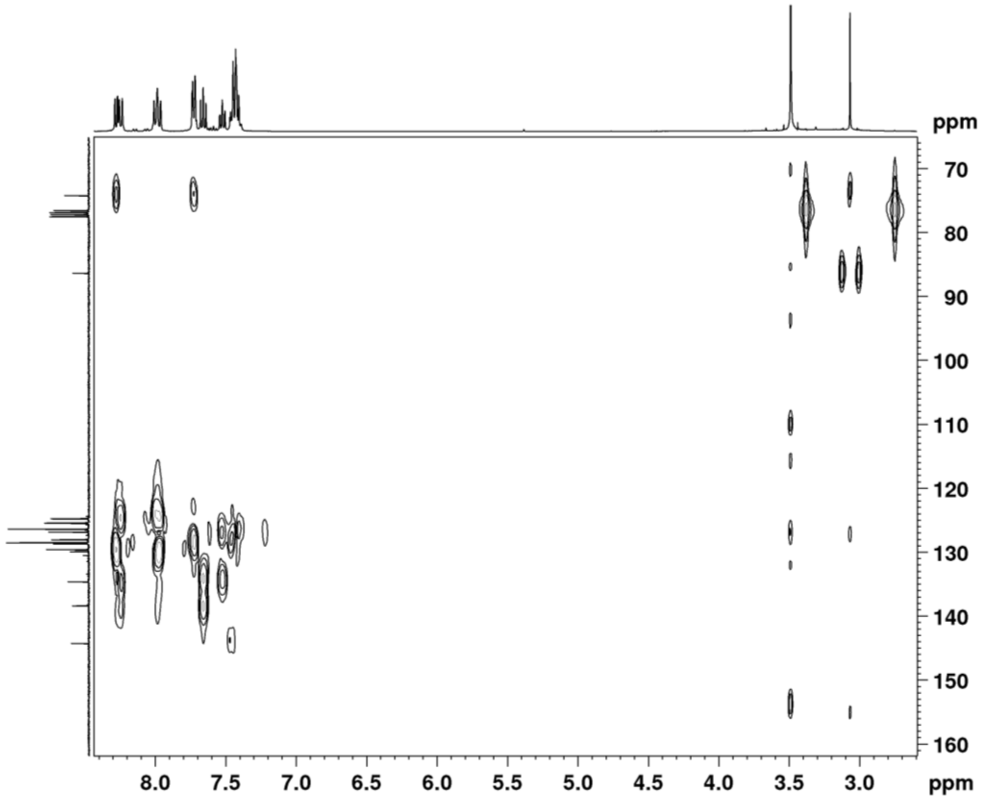


Figure S5. ^{1}H, ^{13}C HMBC NMR spectrum of **I**.

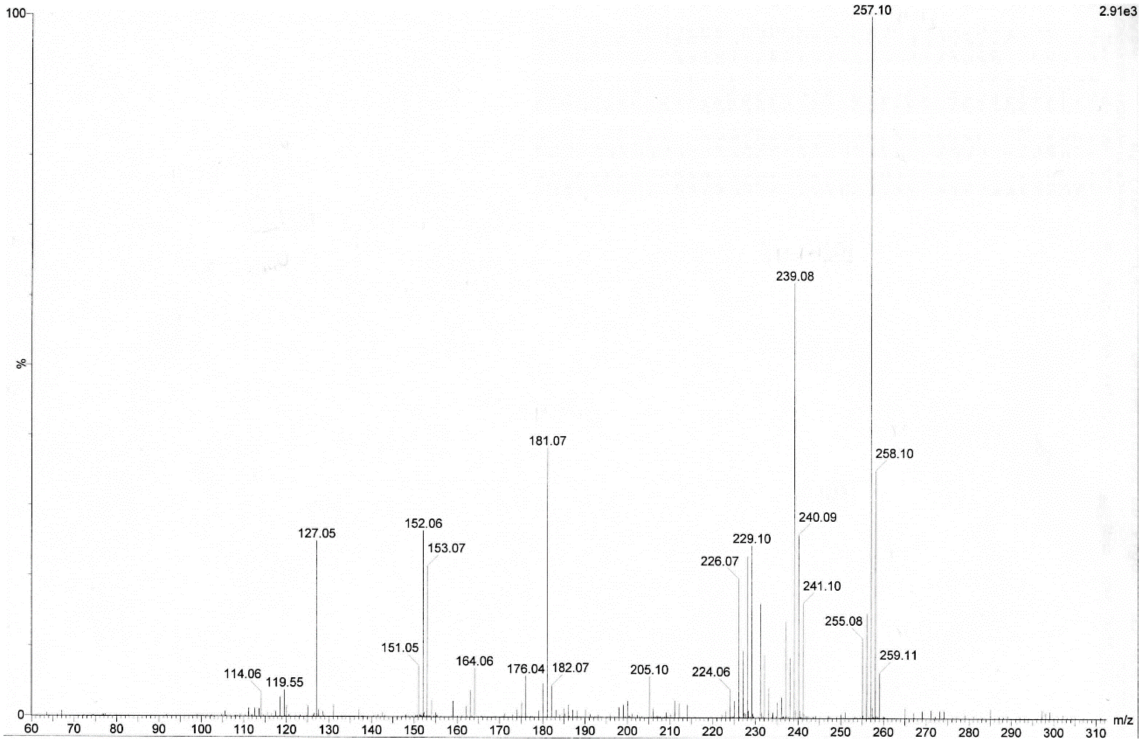
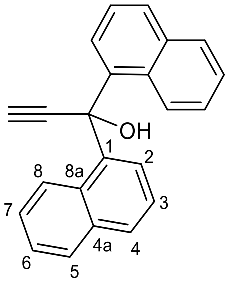


Figure S6. HR-EI-MS spectrum of **I**.

Synthesis of bis-(1-(1-naphthalenyl))-2-propyn-1-ol (II)

After 4 hours, the reaction finished and the propargylic alcohol was extracted and further purified through a silica column using hexane/AcOEt (9:2) as eluent. Yield: 672 mg (69%).



$C_{23}H_{16}O$: 308.38 g/mol. **HR-EI-MS** (m/z): calculated: 308.1201 [M]; experimental: 308.1200 [M], 290.12 [M–H_2O], 181.06 [M–$C_{10}H_7$]. **IR** (cm^{-1}): ν (C≡C) 2111 (w); (H–C≡) 3268 (s) and (OH) 3526 (m). **^{1}H NMR:** δ 8.53–8.44 (m, 2H, C^8H); 8.01–7.93 (m, 2H, C^2H); 7.90–7.81 (m, 4H, C^4H + C^5H); 7.49–7.38 (m, 4H, C^3H + C^6H); 7.38–7.29 (m, 2H, C^7H); 3.28 (s br, 1H, O*H*); 3.02 (s, 1H, *H*C≡) ppm. **^{13}C{^{1}H} NMR:** δ 138.4 (s, 2C C^1); 134.9 (s, 2C C^{4a}); 130.6 (s, 2C C^{8a}); 129.9 (s, 2C C^5); 128.9 (s, 2C C^4); 127.1 (s, 2C C^8); 126.1 (s, 2C C^2); 125.7 (s, 2C C^3); 125.6 (s, 2C C^7); 124.9 (s, 2C C^6); 86.6 (s, HC≡*C*); 77.8 (s, H*C*≡C); 75.8 (s, *C*–OH) ppm.

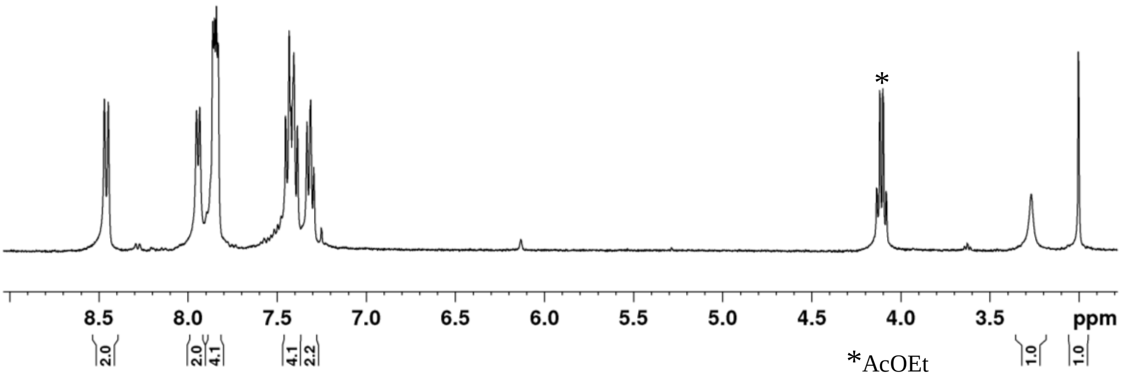


Figure S7. ^1H NMR spectrum of **II**.

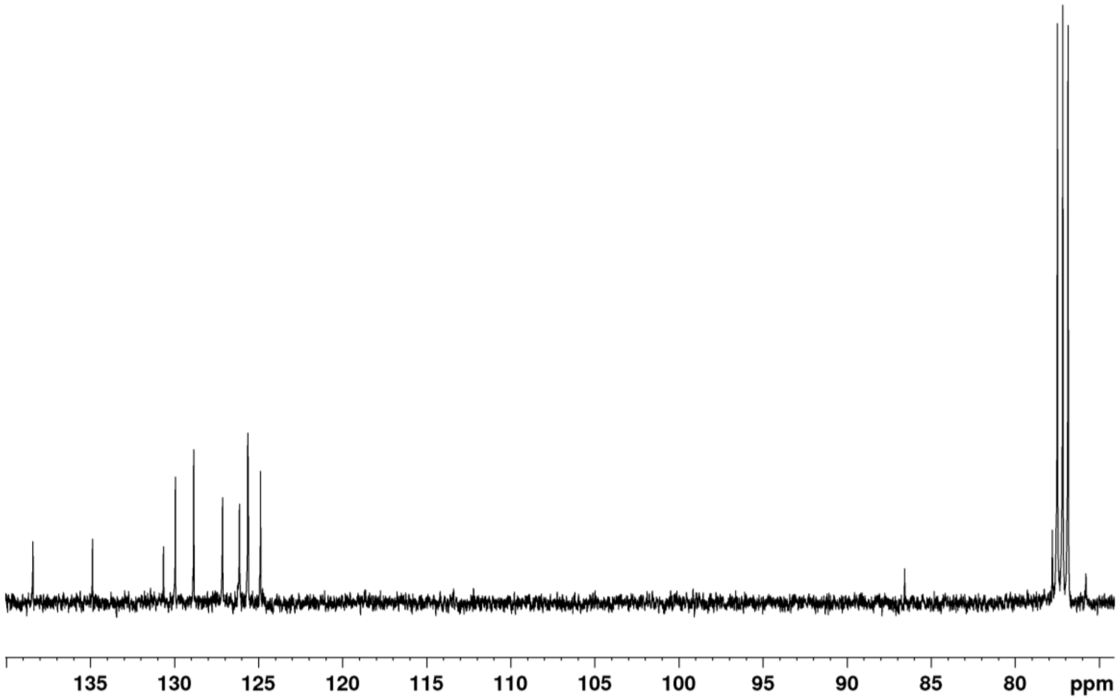


Figure S8. $^{13}C\{^1H\}$ NMR spectrum of **II**.

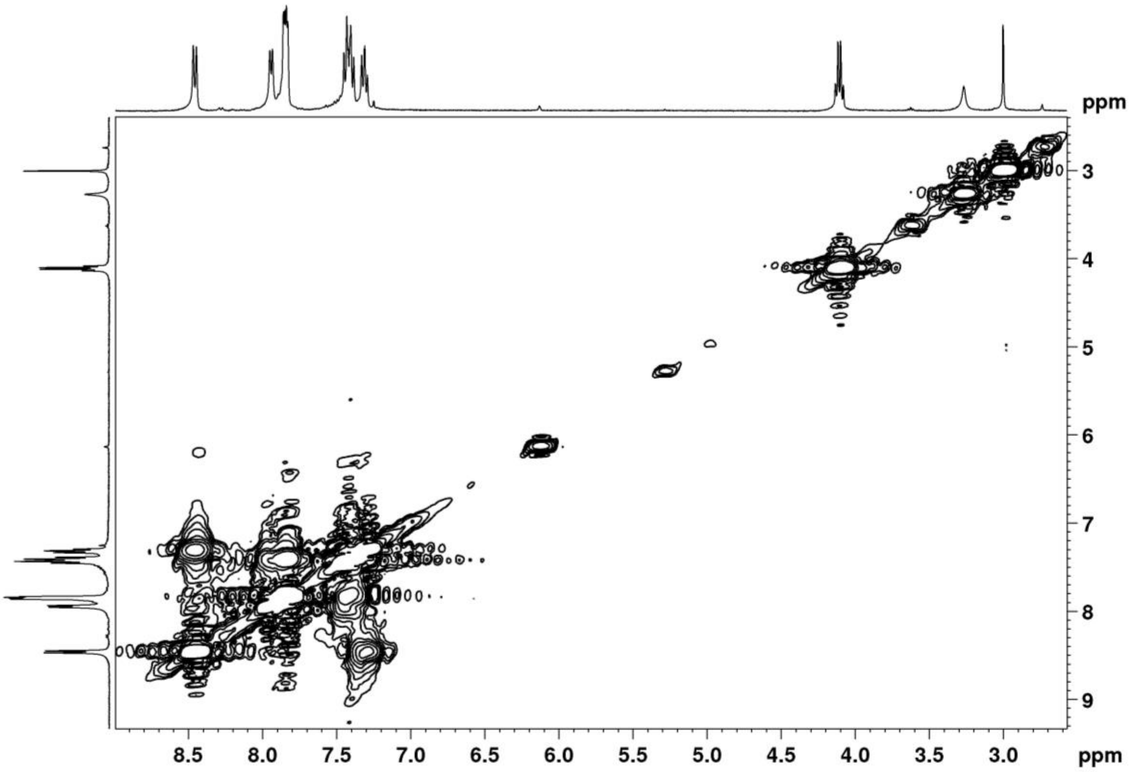


Figure S9. ^{1}H, ^{1}H COSY NMR spectrum of **II**.

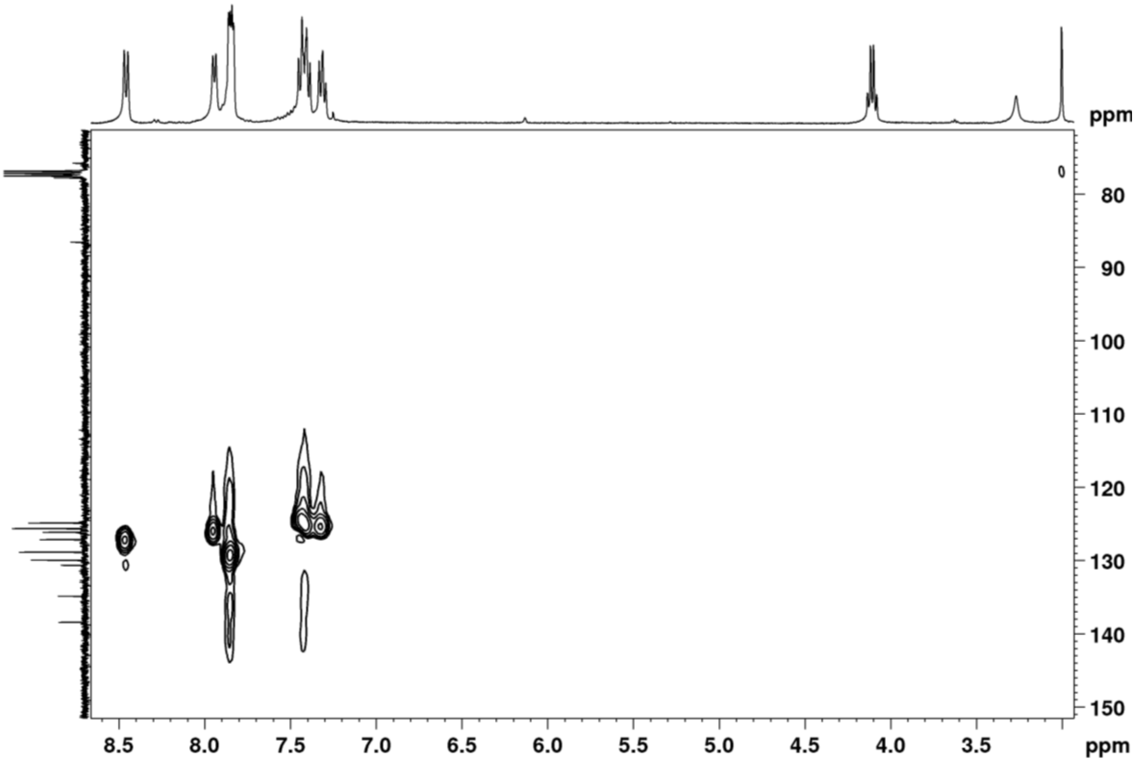


Figure S10. ^{1}H, ^{13}C HSQC NMR spectrum of **II**.

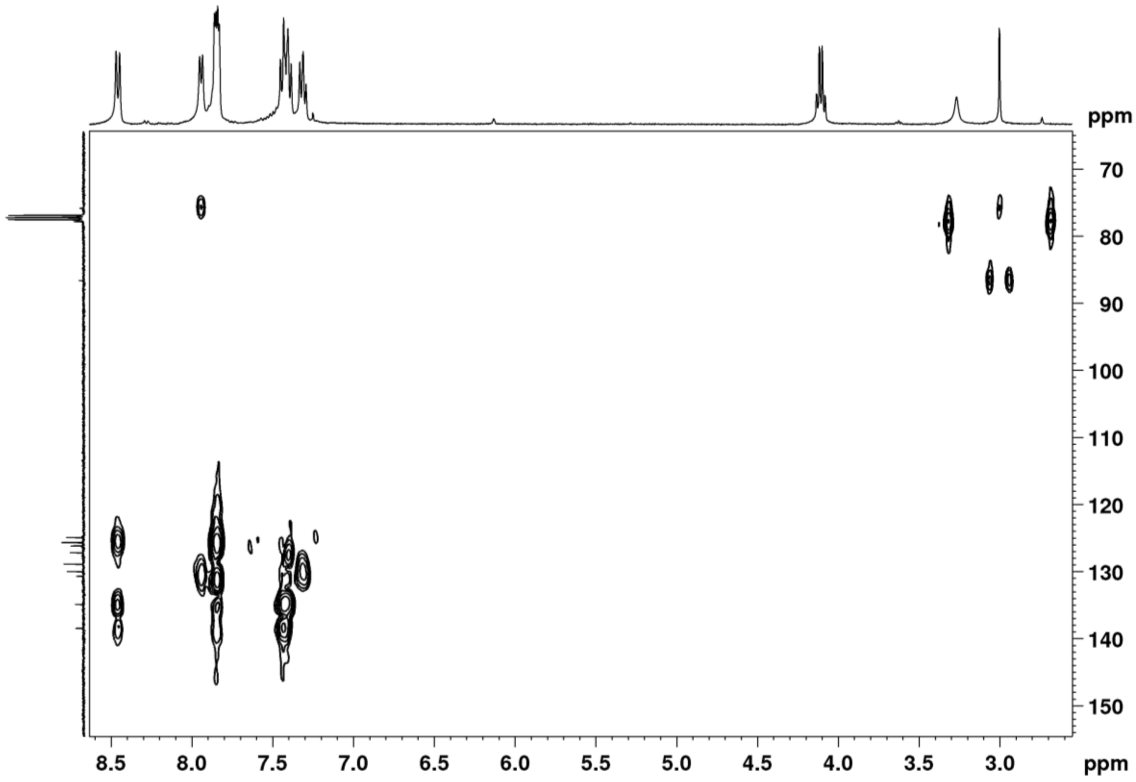


Figure S11. ^{1}H, ^{13}C HMBC NMR spectrum of **II**.

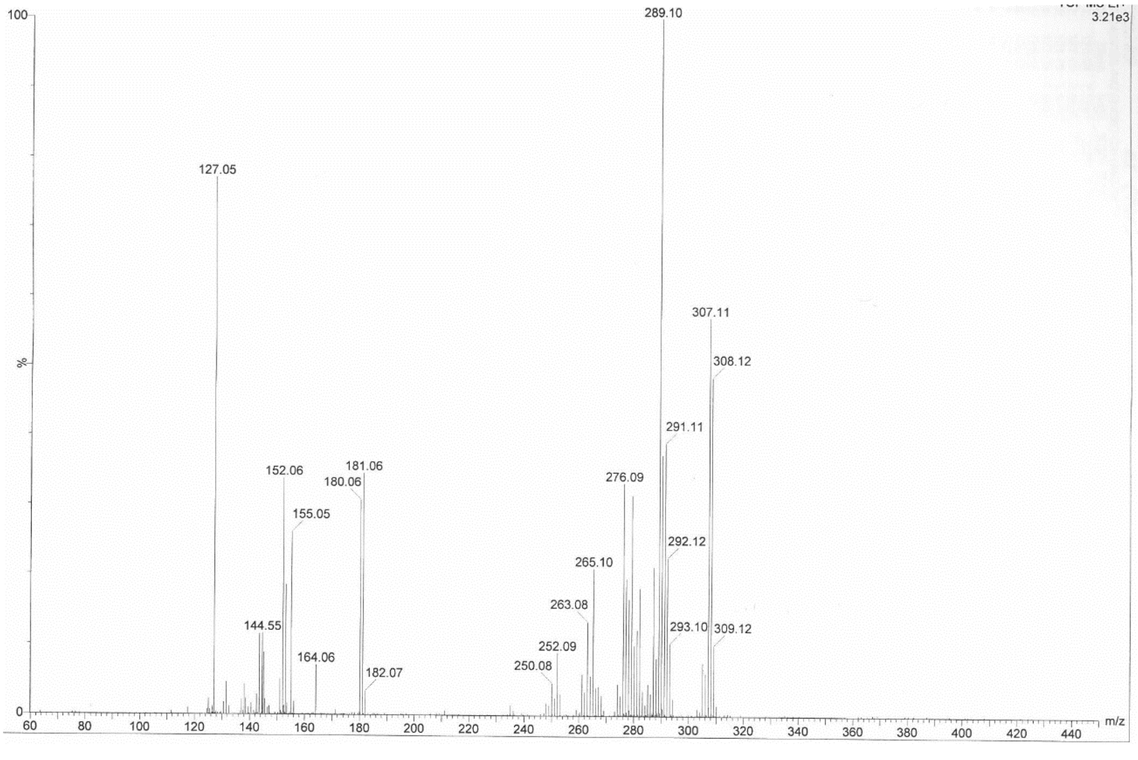
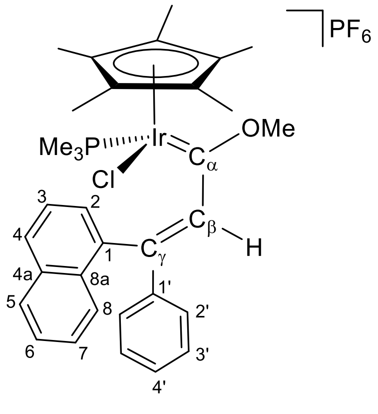


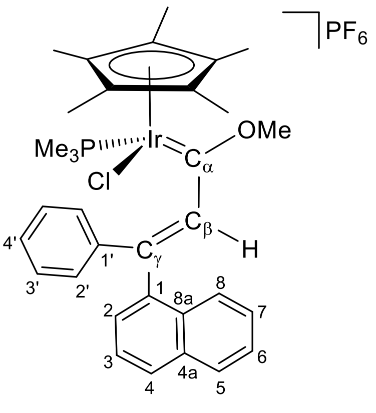
Figure S12. HR-EI-MS spectrum of **II**.

Synthesis of *Z*-,*E*-[IrCp*Cl{=C(OMe)–CH=C(1–$C_{10}H_7$)(Ph)}(PMe_3)]PF_6 (1a, 1b)

To a yellow solution of [IrCp*Cl(NCMe)(PMe_3)]PF_6 (150 mg, 0.24 mmol) in methanol (10 mL), 1-(1-naphthalenyl)-1-phenyl-2-propyn-1-ol (62 mg, 0.24 mmol) was added and the mixture was stirred for 25 min. The dark red solution obtained was vacuum-concentrated yielding a dark red solid that was stirred in *n*-pentane (3 × 5 mL) and the solvent removed by decantation. Finally, the mixture of **1a** (*Z*) and **1b** (*E*) isomers (~27:73 mole ratio estimated by NMR, respectively) was dried under vacuum. Yield: 185 mg (90% isolated mixture).



1a



1b

Anal. Calcd for $C_{33}H_{40}OClF_6IrP_2$ (856.29 g/mol): C 46.29, H 4.71; found: C 46.63, H 4.82. **HR-ESI-MS** (m/z): calculated: 711.21347 $[M]^+$; experimental: 711.21148 $[M]^+$. **IR** (cm^{-1}): ν (PF_6) 836 (s).

Analytical data for **1a** isomer: **^{1}H NMR:** δ 4.01 (s, 3H, OCH_3); 1.73 (d, 9H, $^2J_{HP}$ = 12.9 Hz, P(CH_3)$_3$) ppm. **^{31}P{^{1}H} NMR:** δ –30.73 (s, $P(CH_3)_3$); –143.91 (sept, $^1J_{PF}$ = 710.7 Hz, PF_6) ppm. **^{13}C{^{1}H} NMR:** δ 264.0 (observed by ^{1}H, ^{13}C HMBC NMR spectrum, C_α); 99.2 (d, $^2J_{CP}$ = 2.2 Hz, $C_5(CH_3)_5$); 69.5 (s, OCH_3); 15.1 (d, $^1J_{CP}$ = 40.6 Hz, P(CH_3)$_3$); 9.1 (s, $C_5(CH_3)_5$) ppm. Rest of the signals cannot be identify due to their overlapping with **1b** isomer resonances.

Analytical data for **1b** isomer: **^{1}H NMR:** δ 8.06–8.02 (m, 1H, C^4H); 8.02–7.97 (m, 1H, C^5H); 7.97–7.93 (m, 1H, C^8H); 7.70–7.67 (m, 1H, C^2H); 7.61–7.56 (m, 1H, C^3H); 7.55–7.50 (m, 1H, C^6H); 7.48–7.43 (m, 2H, C^7H + $C^{4'}H$); 7.43–7.39 (m, 2H, $C^{3'}H$); 7.30–7.25 (m, 2H, $C^{2'}H$); 6.75 (s, $C_\beta H$); 4.51 (s, 3H, OCH_3); 1.83 (d, 15H, $^4J_{HP}$ = 2.4 Hz, $C_5(CH_3)_5$); 1.82 (d, 9H, $^2J_{HP}$ = 10.4 Hz, P(CH_3)$_3$) ppm. **^{31}P{^{1}H} NMR:** δ –28.84 (s, $P(CH_3)_3$); –143.91 (sept, $^1J_{PF}$ = 707.7 Hz, PF_6) ppm. **^{13}C{^{1}H} NMR:** δ 265.8 (observed by ^{1}H, ^{13}C HMBC NMR spectrum, C_α); 150.6 (observed by ^{1}H, ^{13}C HMBC NMR spectrum, C_γ); 141.6 (s, C_β); 140.9 (s, $C^{1'}$); 140.2 (s, C^1); 135.0 (s, C^{4a}); 131.7 (s, C^{8a}); 130.8 (s, C^4); 130.6 (s, $C^{4'}$); 129.64 (s, 4C $C^{2'}$ + $C^{3'}$); 129.58 (s, C^5); 129.0 (s, C^2); 127.6 (s, C^7); 127.2 (s, C^6); 126.6 (s, C^8); 126.2 (s, C^3); 100.6 (d, $^2J_{CP}$ = 2.0 Hz $C_5(CH_3)_5$); 69.5 (s, OCH$_3$); 14.8 (d, $^1J_{CP}$ = 40.9 Hz, P(CH$_3$)$_3$); 9.1 (s, C$_5$(CH$_3$)$_5$) ppm.

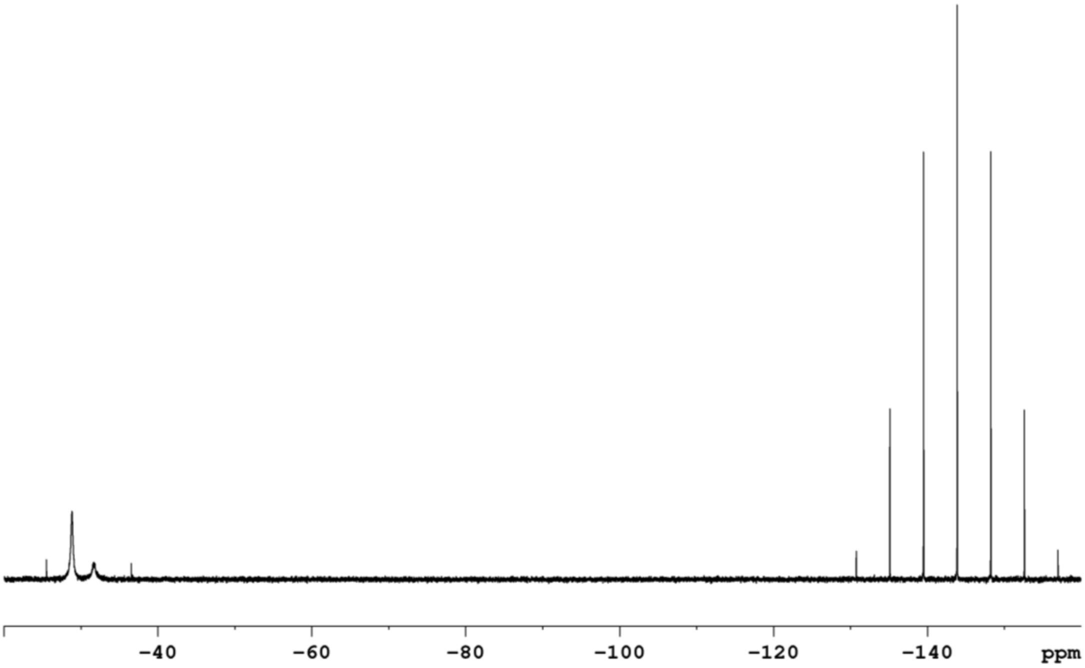


Figure S13. $^{31}P\{^1H\}$ NMR spectrum of **1a**,**1b** mixture.

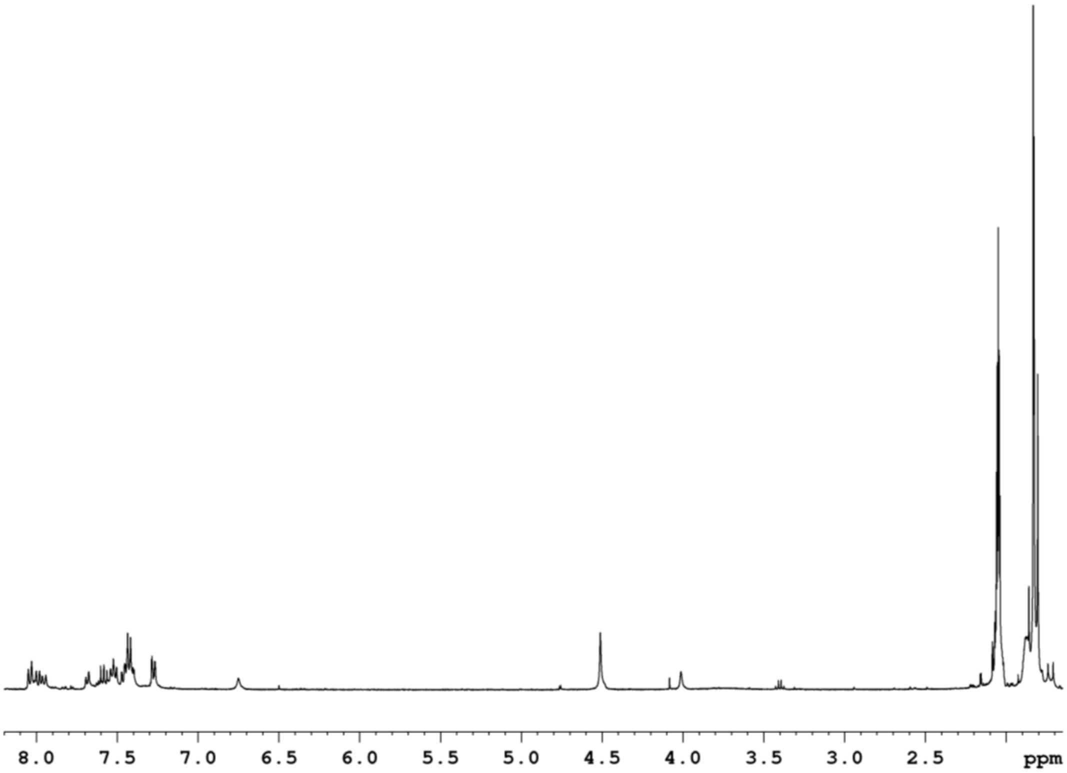


Figure S14. ^1H NMR spectrum of **1a**,**1b** mixture.

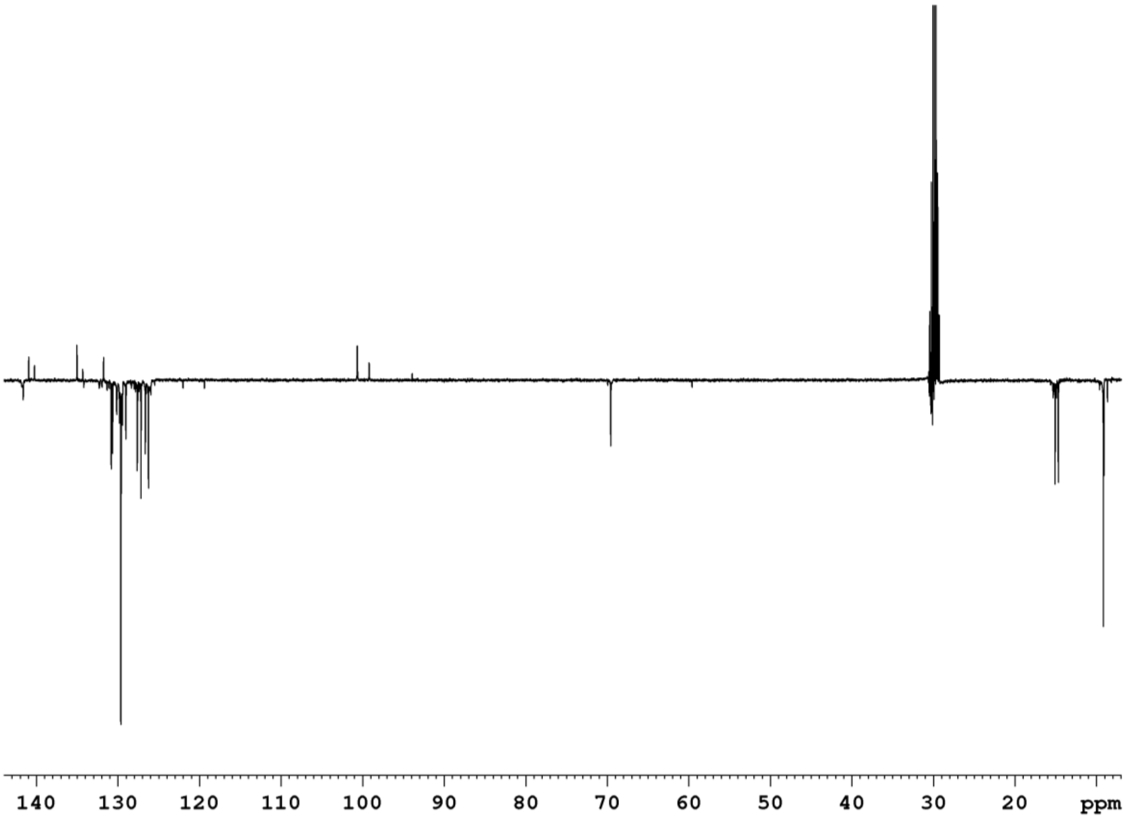


Figure S15. JMOD NMR spectrum of **1a**,**1b** mixture.

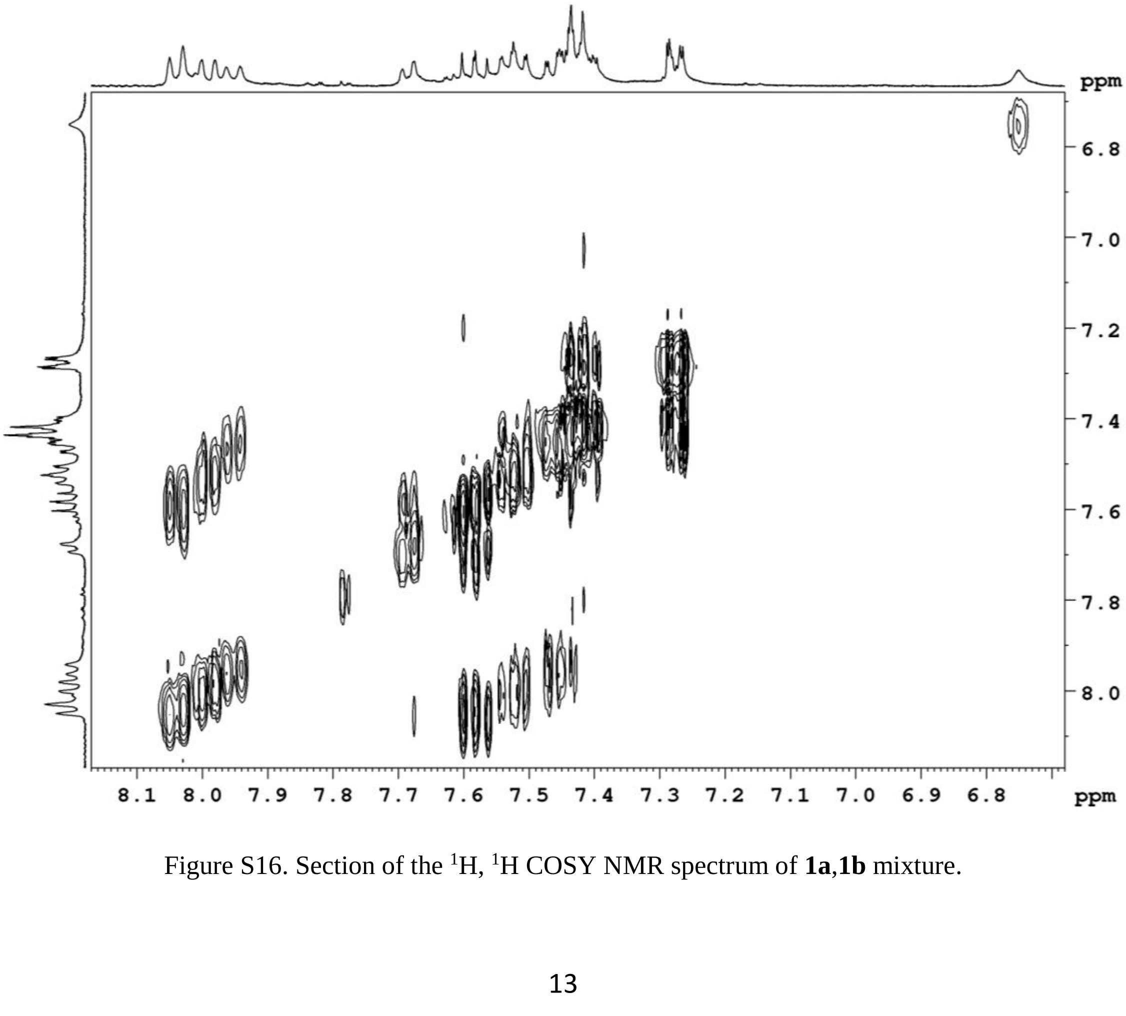


Figure S16. Section of the ^{1}H, ^{1}H COSY NMR spectrum of **1a**,**1b** mixture.

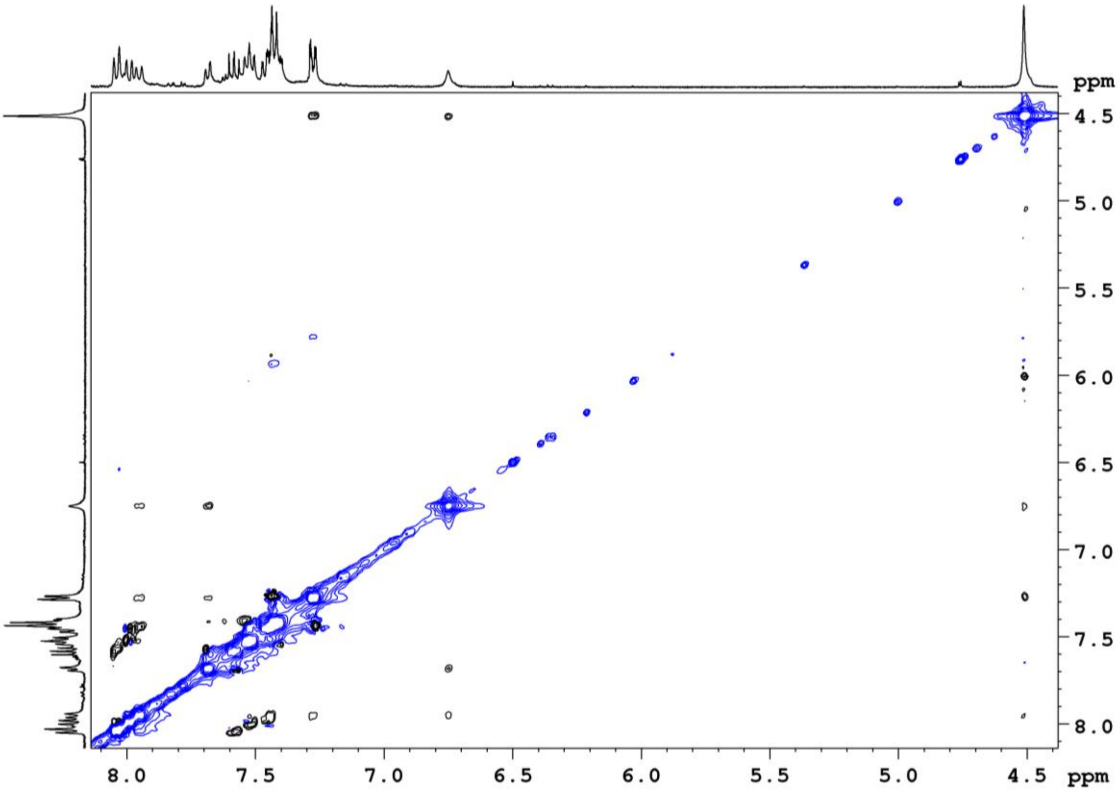


Figure S17. Section of the ^{1}H, ^{1}H NOESY NMR spectrum of **1a**,**1b** mixture.

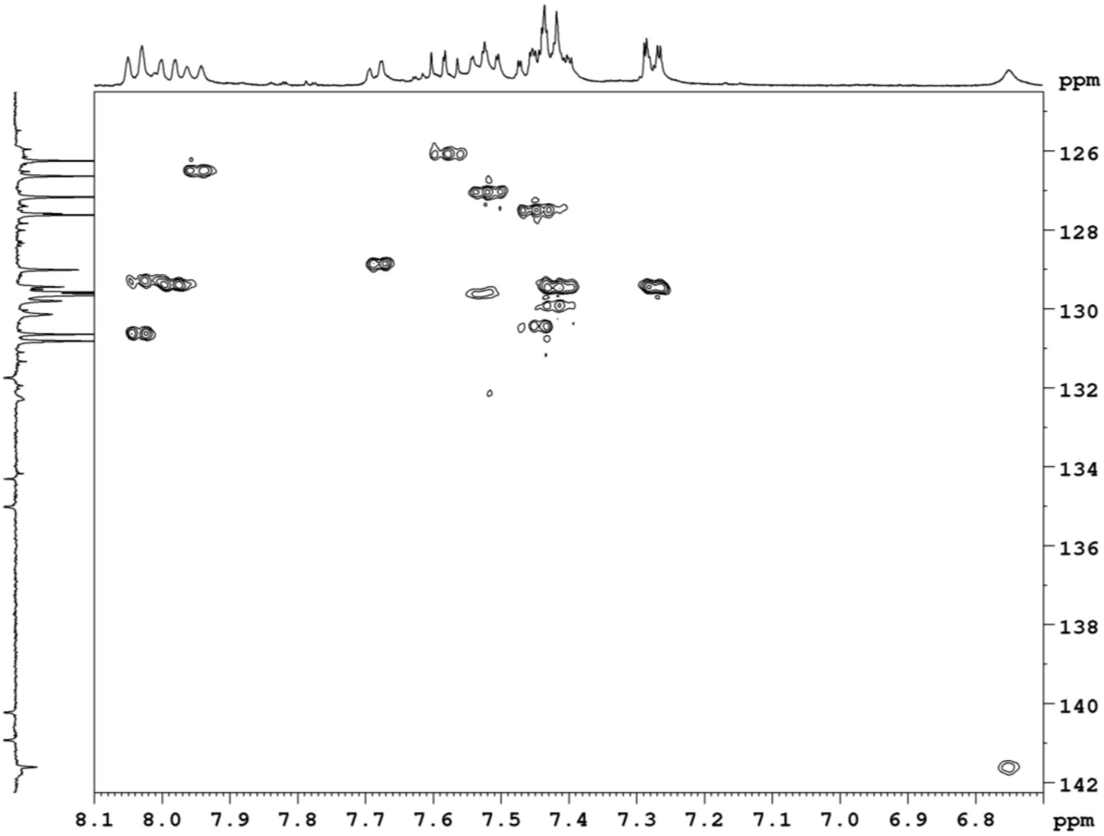


Figure S18. Section of the ^{1}H, ^{13}C HSQC NMR spectrum of **1a**,**1b** mixture.

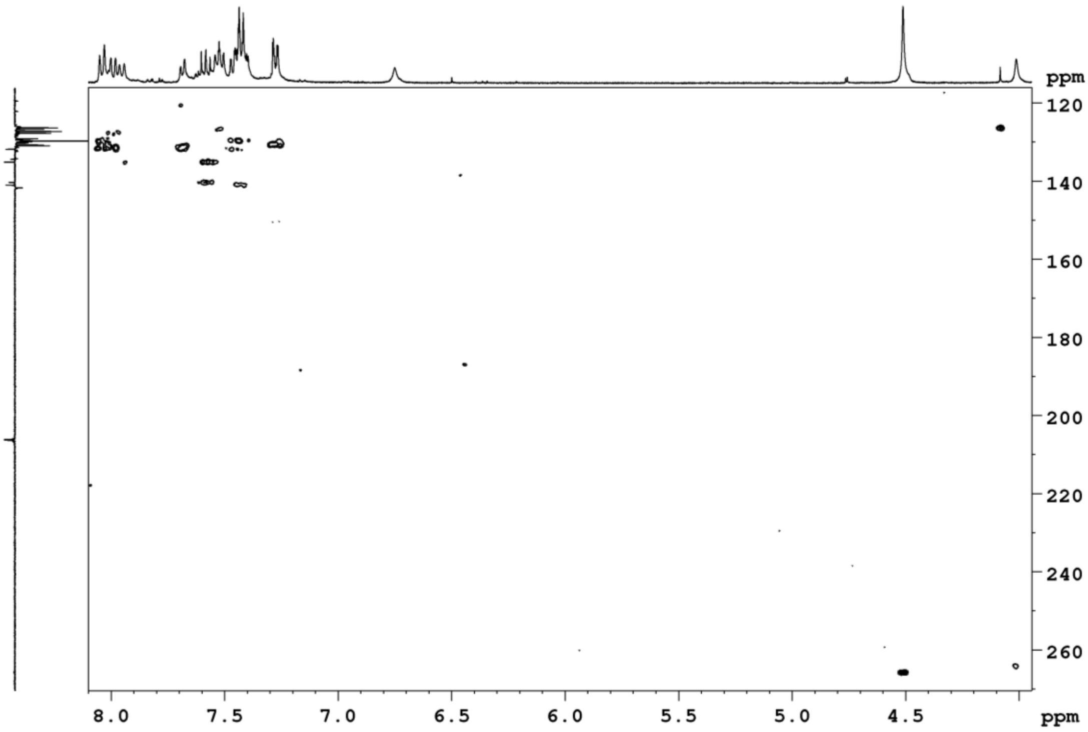


Figure S19. Section of the ^{1}H, ^{13}C HMBC NMR spectrum of **1a,1b** mixture.

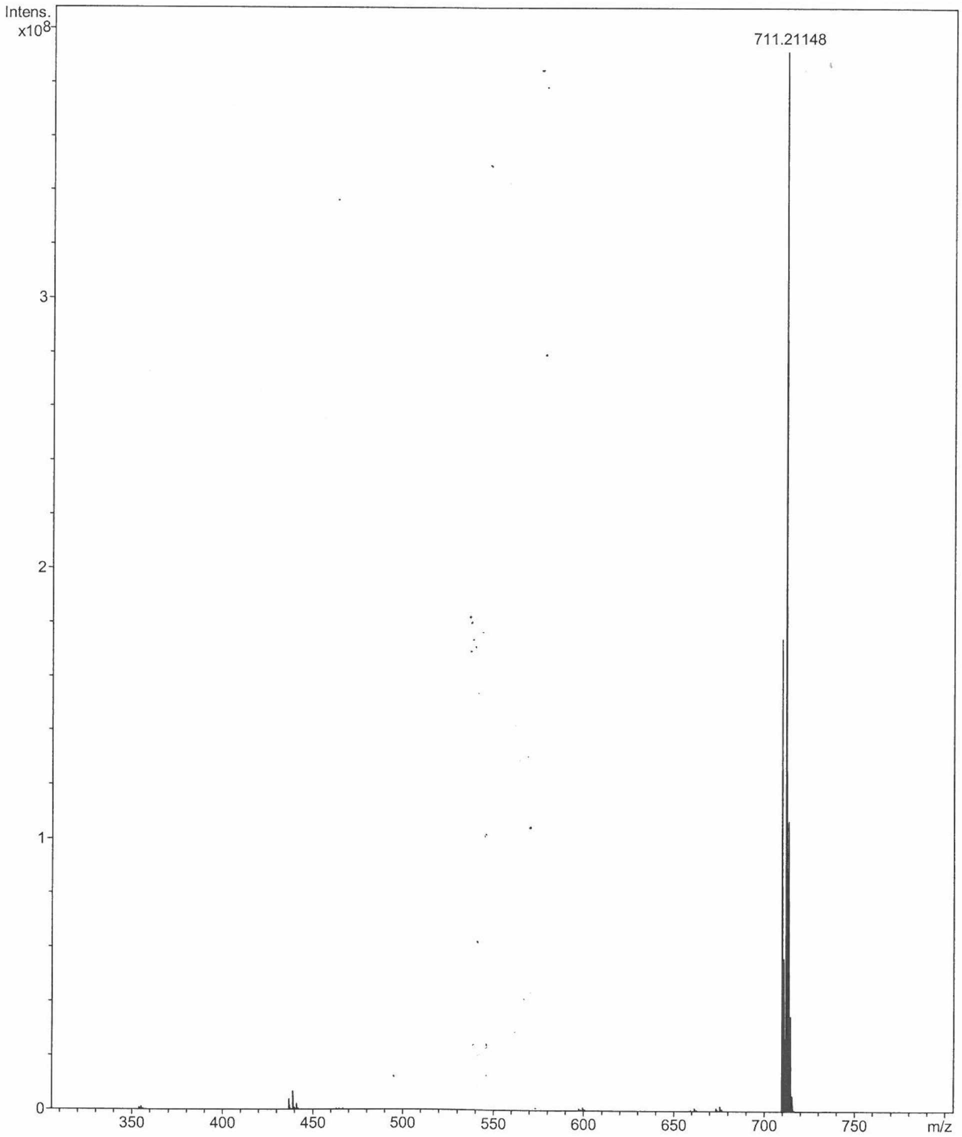
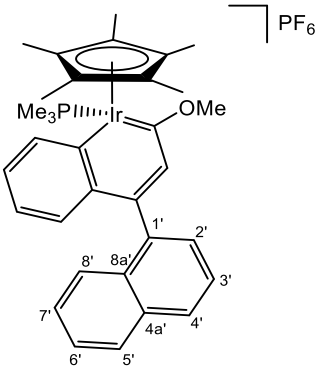


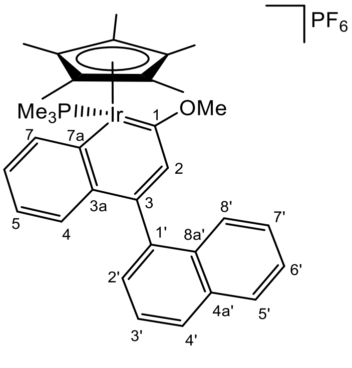
Figure S20. HR-ESI-MS spectrum of **1a,1b** mixture.

Synthesis of $[\overline{\mathrm{IrCp^*\{=C(OMe)–CH=C(}\mathit{o}\mathrm{–C}}\mathrm{_6H_4)(1–C_{10}H_7)\}(PMe_3)]PF_6}$ (2b) and $\mathrm{[IrCp^*\{=C(OMe)–CH=C(}\eta^2\mathrm{–1–C_{10}H_7)(Ph)\}(PMe_3)](PF_6)_2}$

A red solution of the mixture **1a** and **1b** (185 mg, 0.22 mmol) in 8 mL of dichloromethane was treated with $AgPF_6$ (64 mg, 0.24 mmol). The red solution was stirred 5 min at room temperature obtaining a brown solution. The solution was filtered through Celite® and the solution obtained vacuum-concentrated giving a brown solid which correspond to the mixture of two iridanaphthalene atropisomer complexes ***(S,M)*-2b** and ***(S,P)*-2b** and a ***η*² complex** (~53:28:19 mole ratio, respectively). The mixture was stirred in *n*-pentane (3 × 5 mL) and the solvent removed by decantation. Finally, the solid was dried under vacuum. Yield: 115 mg (isolated mixture, ~69% for **2b** calculated on *E*- isomer and ~40% for ***η*² complex** calculated on *Z*- isomer).



(S,M)-2b



(S,P)-2b

HR-ESI-MS (m/z): calculated: 675.2368 $[M]^+$; experimental: 675.23591 $[M]^+$. **IR** (cm^{-1}): ν (PF_6) 839 (s).

Analytic data for ***(S,M)*-2b** isomer: **^{1}H NMR:** δ 8.14–8.02 (m, 3H, $C^{4'}H$ + $C^{5'}H$ + C^7H); 7.71–7.63 (m, 1H, $C^{3'}H$); 7.63–7.53 (m, 2H, $C^{2'}H$ + $C^{8'}H$); 7.49–7.40 (m, 2H, $C^{6'}H$ + $C^{7'}H$); 7.33–7.24 (m, 1H, C^4H); 7.19–7.10 (m, 1H, C^6H); 7.06–6.96 (m, 1H, C^5H); 7.04 (s, 1H, C^2H); 4.64 (s, 3H, OCH_3); 1.98 (d, $^4J_{HP}$ = 1.6 Hz, 15H, $C_5(CH_3)_5$); 1.40 (d, $^2J_{HP}$ = 11.2 Hz, 9H, $P(CH_3)_3$) ppm. **^{31}P{^{1}H} NMR:** δ –34.32 (s, $P(CH_3)_3$); –143.92 (sept, $^1J_{PF}$ = 708.8 Hz, PF_6) ppm. **^{13}C{^{1}H} NMR:** δ 249.7 (d, $^2J_{CP}$ = 10.2 Hz, C^1); 177.0 (s, C^3); 155.8 (d, $^2J_{CP}$ = 10.4 Hz, C^{7a}); 143.9 (d, $^3J_{CP}$ = 4.9 Hz, C^7); 140.3 (s, $C^{1'}$); 137.3 (s, C^4); 135.6 (s, C^{3a}); 134.3 (s, $C^{4a'}$); 132.2 (s, $C^{8a'}$); 132.0 (s, C^6); 130.1 (s, $C^{4'}$); 129.5 (s, $C^{5'}$); 127.6 and 126.8 (both s, $C^{6'}$ and $C^{7'}$); 127.2 (s, $C^{8'}$); 126.9 (s, $C^{2'}$); 126.4 (s, $C^{3'}$); 124.0 (s, C^5); 120.5 (d, $^3J_{CP}$ = 2.2 Hz, C^2); 100.8 (d, $^2J_{CP}$ = 2.0 Hz, $C_5(CH_3)_5$); 64.7 (s, OCH_3); 13.7 (d, $^1J_{CP}$ = 41.3 Hz, $P(CH_3)_3$); 9.9 (s, $C_5(CH_3)_5$) ppm.

Analytic data for ***(S,P)*-2b** isomer: **^{1}H NMR:** δ 8.14–8.02 (m, 3H, $C^{4'}H$ + $C^{5'}H$ + C^7H); 7.71–7.63 (m, 1H, $C^{3'}H$); 7.63–7.53 (m, 2H, $C^{6'}H$ + $C^{7'}H$); 7.49–7.40 (m, 2H, $C^{2'}H$ + $C^{8'}H$); 7.33–7.24 (m, 1H, C^4H); 7.19–7.10 (m, 1H, C^6H); 7.06–6.96 (m, 1H, C^5H); 6.97 (s, 1H, C^2H); 4.56 (s, 3H, OCH_3); 1.90 (d, $^4J_{HP}$ = 1.6 Hz, 15H, $C_5(CH_3)_5$); 1.52 (d, $^2J_{HP}$ = 11.1 Hz, 9H, $P(CH_3)_3$) ppm. **^{31}P{^{1}H} NMR:** δ –33.41 (s, $P(CH_3)_3$); –143.92 (sept, $^1J_{PF}$ = 708.8 Hz, PF_6) ppm. **^{13}C{^{1}H} NMR:** δ 251.2 (d, $^2J_{CP}$ = 10.3 Hz, C^1); 177.3 (s, C^3); 157.6 (d, $^2J_{CP}$ = 10.1 Hz, C^{7a}); 143.9 (d, $^3J_{CP}$ = 5.0 Hz, C^7); 140.3 (s, $C^{1'}$); 137.5 (s, C^4); 135.5 (s, C^{3a}); 134.5 (s, $C^{4a'}$); 132.2 (s, $C^{8a'}$); 131.9 (s, C^6); 129.8 (s, $C^{4'}$); 129.4 (s, $C^{5'}$); 128.0 (s, $C^{8'}$); 127.4 and 126.4 (both s, $C^{6'}$ and $C^{7'}$); 127.0 (s, $C^{2'}$); 126.2 (s, $C^{3'}$); 124.1 (s, C^5); 120.5 (d, $^3J_{CP}$ = 2.2 Hz, C^2); 100.4 (d, $^2J_{CP}$ = 2.0 Hz, $C_5(CH_3)_5$); 64.8 (s, OCH_3); 14.3 (d, $^1J_{CP}$ = 40.8 Hz, $P(CH_3)_3$); 9.7 (s, $C_5(CH_3)_5$) ppm.

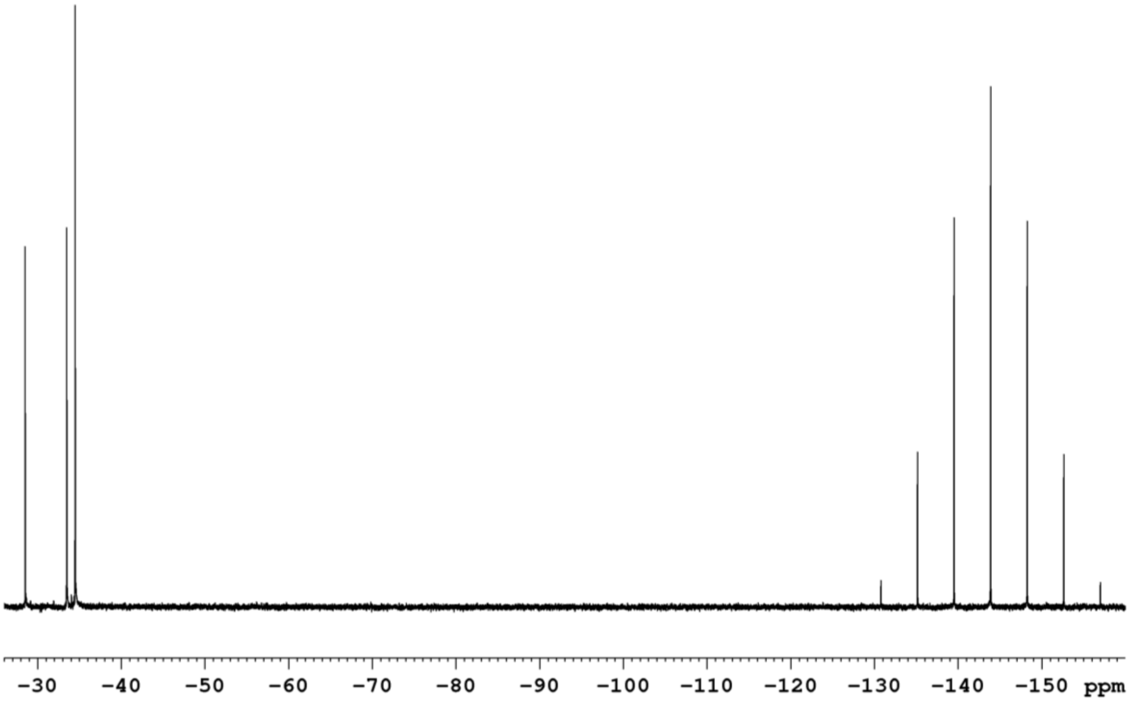


Figure S21. $^{31}P\{^{1}H\}$ NMR spectrum of ***(S,M)*-2b**, ***(S,P)*-2b** and ***η²* complex** mixture.

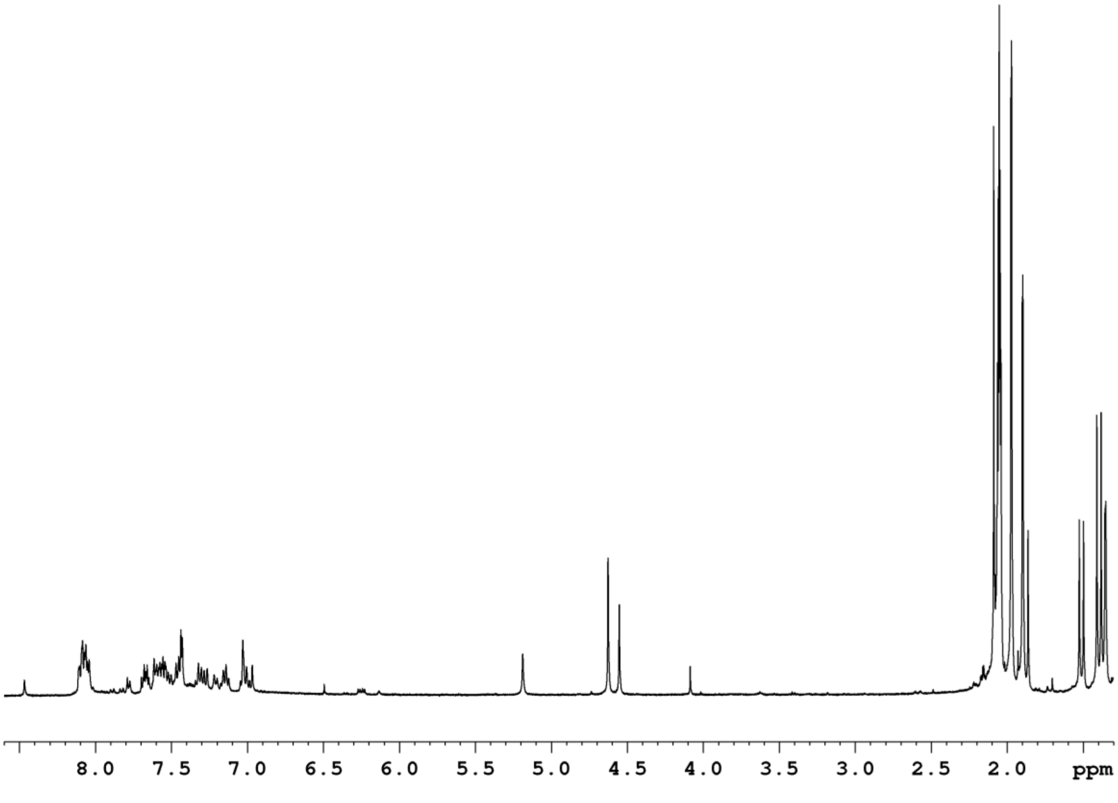


Figure S22. ^{1}H NMR spectrum of ***(S,M)*-2b**, ***(S,P)*-2b** and ***η²* complex** mixture.

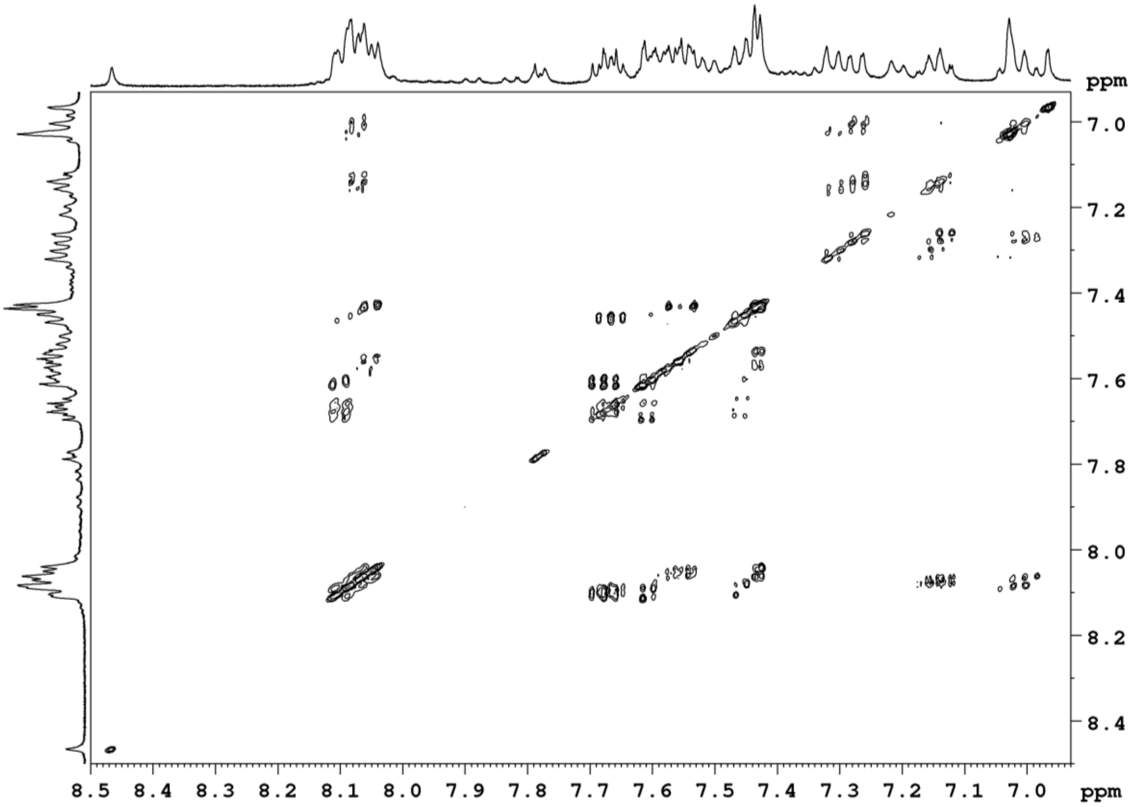


Figure S23. Section of the ^{1}H, ^{1}H COSY NMR spectrum of ***(S,M)*-2b**, ***(S,P)*-2b** and ***η*^{2} complex** mixture.

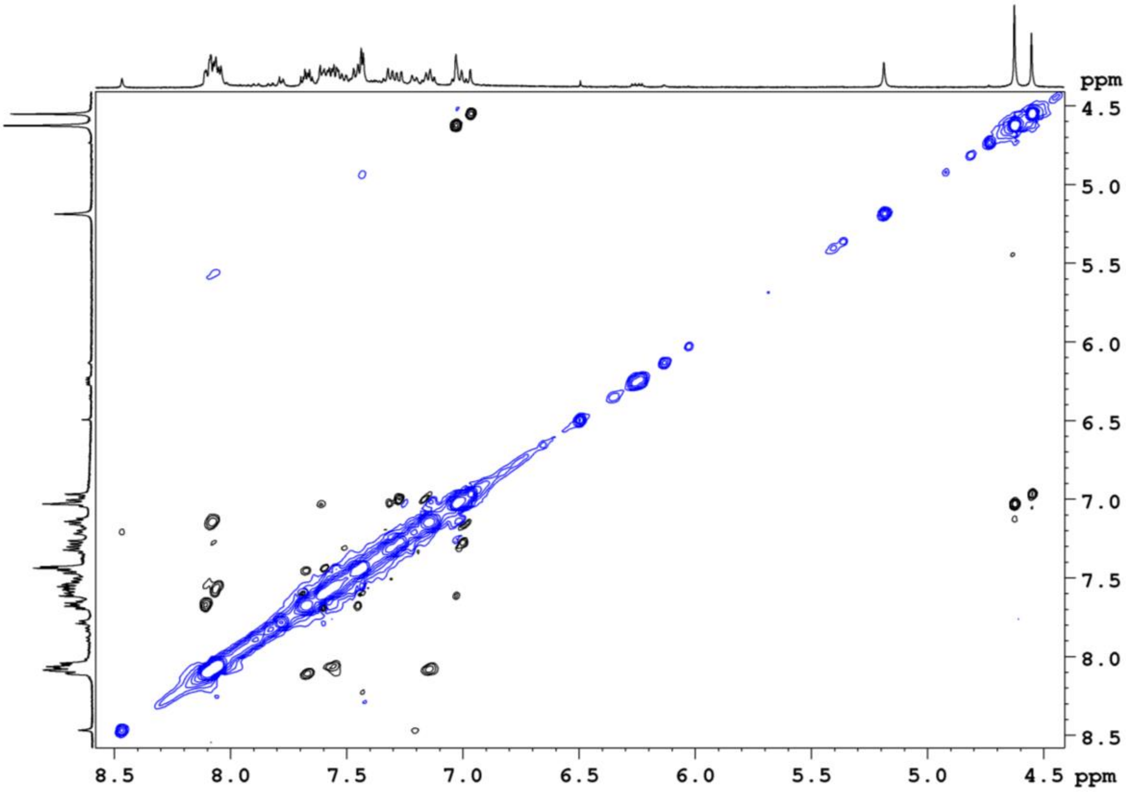


Figure S24. Section of the ^{1}H, ^{1}H NOESY NMR spectrum of ***(S,M)*-2b**, ***(S,P)*-2b** and ***η*^{2} complex** mixture.

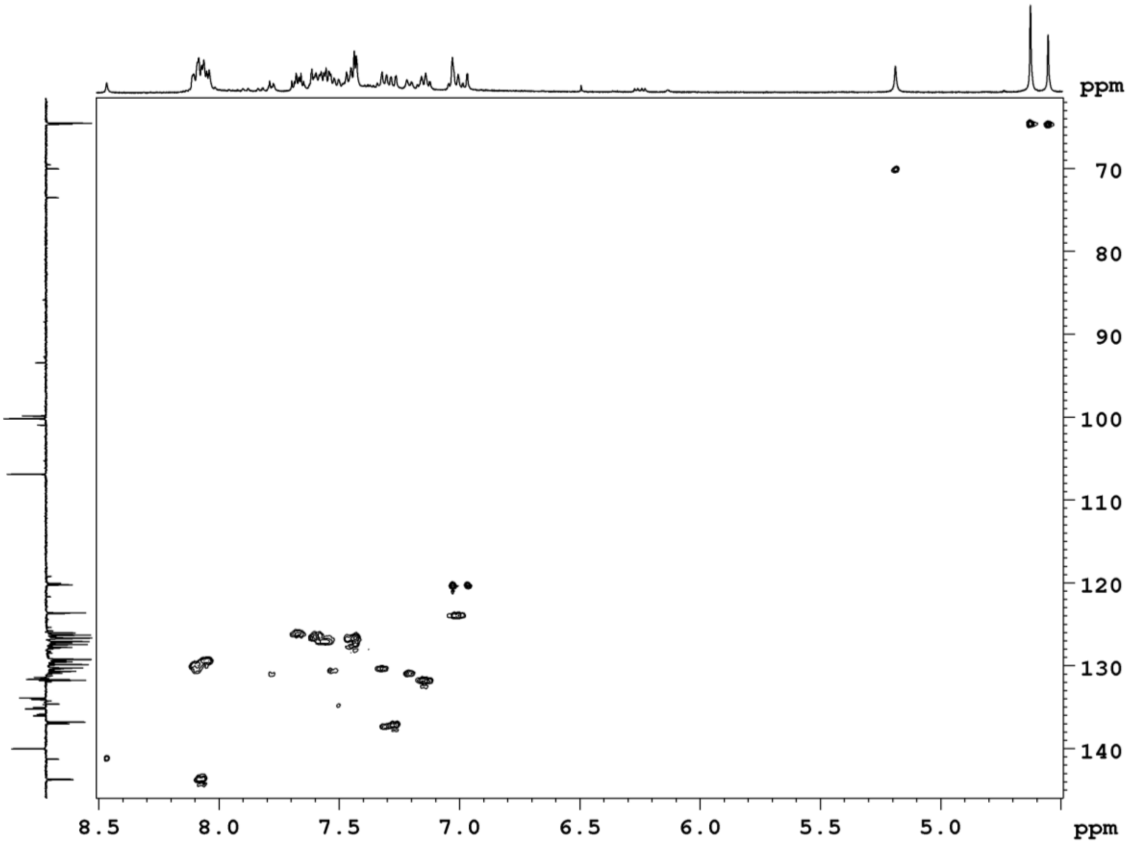


Figure S25. Section of the ^{1}H, ^{13}C HSQC NMR spectrum of ***(S,M)*-2b**, ***(S,P)*-2b** and ***η*^{2} complex** mixture.

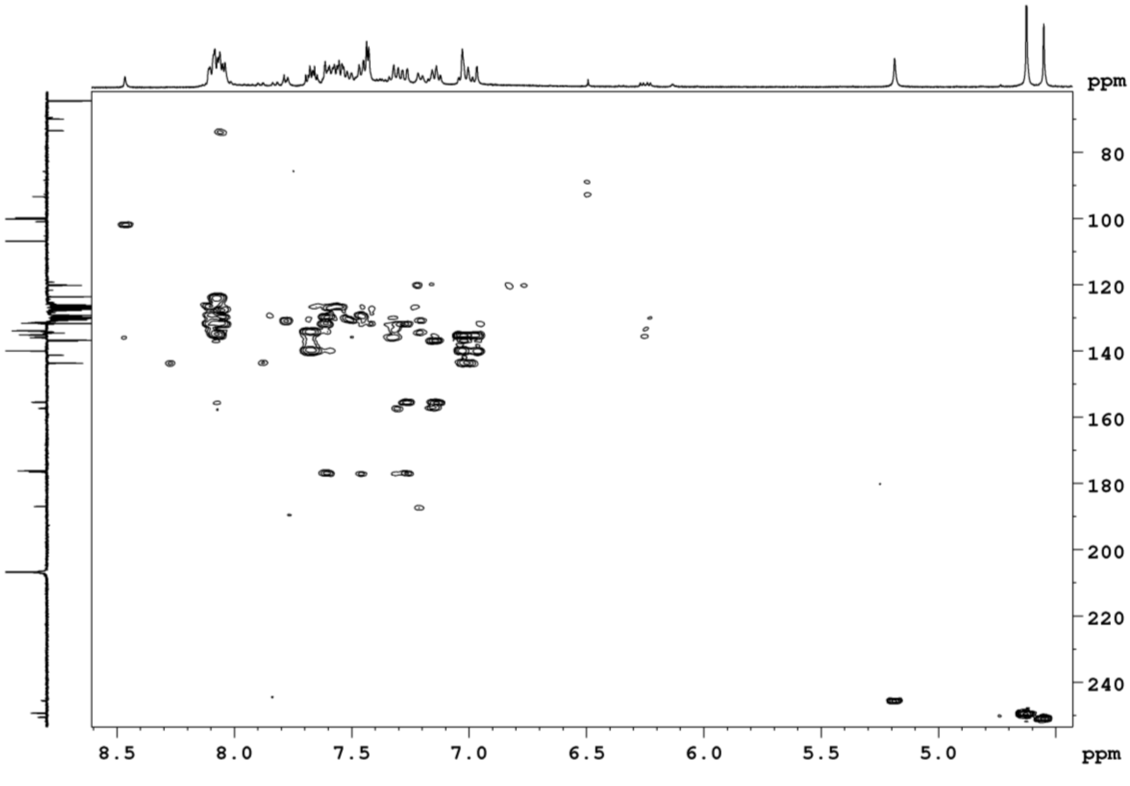


Figure S26. Section of the ^{1}H, ^{13}C HMBC NMR spectrum of ***(S,M)*-2b**, ***(S,P)*-2b** and ***η*^{2} complex** mixture.

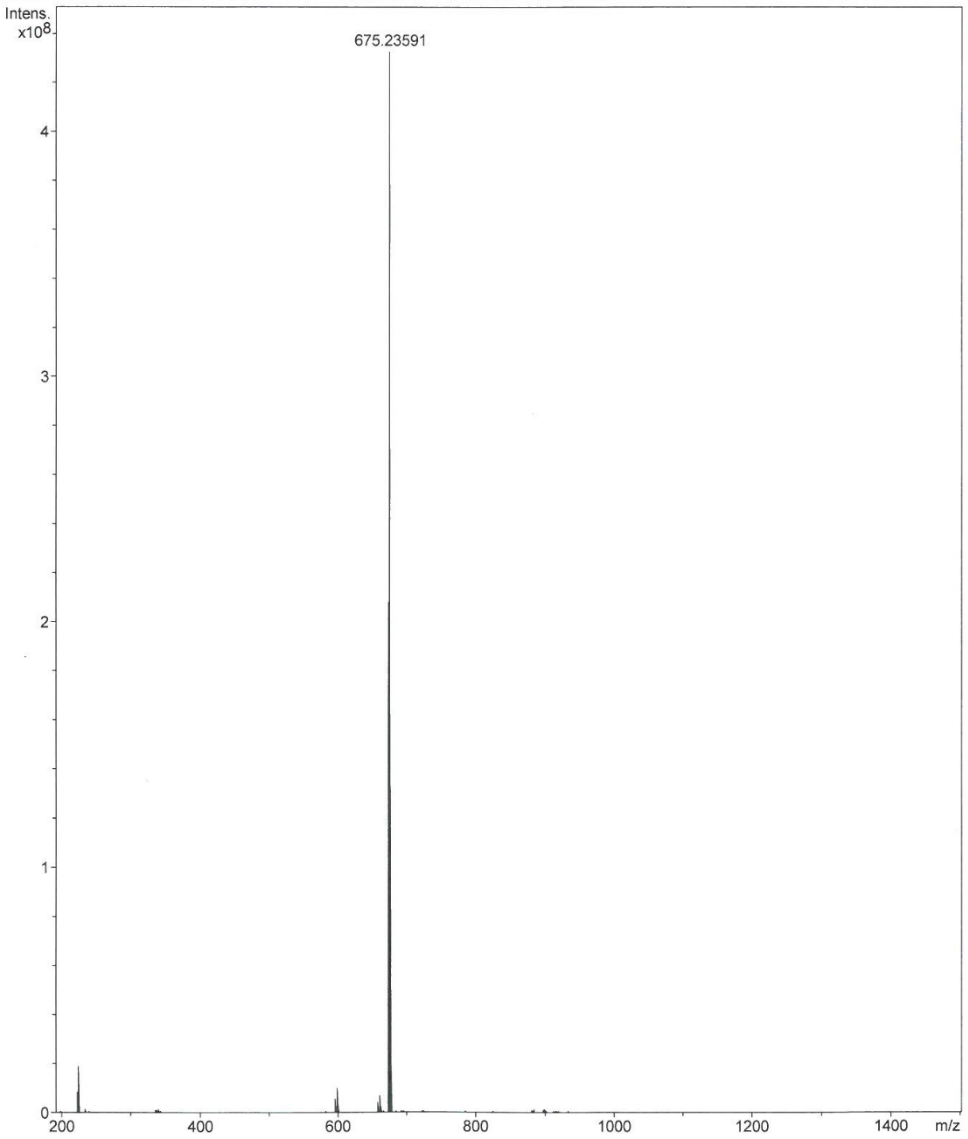
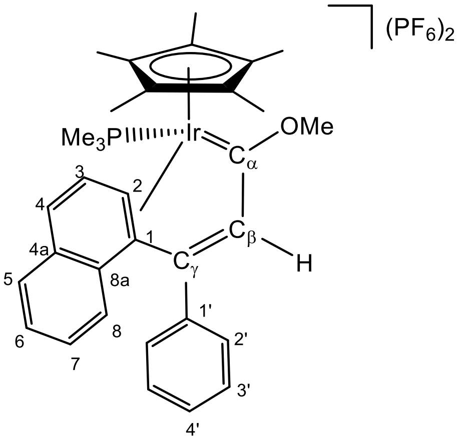


Figure S27. HR-ESI-MS spectrum of ***(S,M)*-2b**, ***(S,P)*-2b** mixture.

In order to characterize the ***η*^{2}** intermediate, the NMR experiments were recorded at lower temperature which avoid the evolution to the phenantrene derivative.



η^2-complex

Analytic data for ***η*^{2} complex**: **^{1}H NMR** (253 K): *δ* 8.49 (s, 1H, C$_β$*H*); 8.09–8.00 (m, 1H, C^4*H*); 7.42–7.36 (m, 1H, C^3*H*); 7.27–7.21 (m, 1H, C$^{2'}$*H*); 6.26 (dd, 1H, $^3J_{HH}$ = 11.8 Hz, $^3J_{HP}$ = 4.8 Hz, C^2*H*); 5.19 (s, 3H, OC*H$_3$*); 2.07 (d, $^2J_{HP}$ = 11.7 Hz, 9H, P(C*H$_3$*)$_3$); 1.32 (s br, 15H, C$_5$(C*H$_3$*)$_5$) ppm. **^{31}P{^{1}H} NMR** (253 K): *δ* –27.86 (s, *P*(CH$_3$)$_3$); –144.03 (sept, $^1J_{PF}$ = 708.8 Hz, *P*F$_6$) ppm. **^{13}C{^{1}H} NMR** (253 K): *δ* 245.6 (d, $^2J_{CP}$ = 12.8 Hz, *C$_α$*); 186.9 (s, *C$_γ$*); 141.2 (s, *C$_β$*); 136.0 (s, *C$^{1'}$*); 135.8 (s, *C^{8a}*); 131.4 (s, *C^{4a}*); 100.9 (s, *C^1*); 100.9 (s, *C^1*); 100.7 (d, $^2J_{CP}$ = 2.0 Hz, *C*$_5$(CH$_3$)$_5$); 73.5 (s, *C^2*); 70.0 (s, O*C*H$_3$); 14.6 (d, $^1J_{CP}$ = 42.7 Hz, P(*C*H$_3$)$_3$); 7.5 (s, C$_5$(*C*H$_3$)$_5$) ppm. Rest of signals are overlapped with main products or could not be assigned.

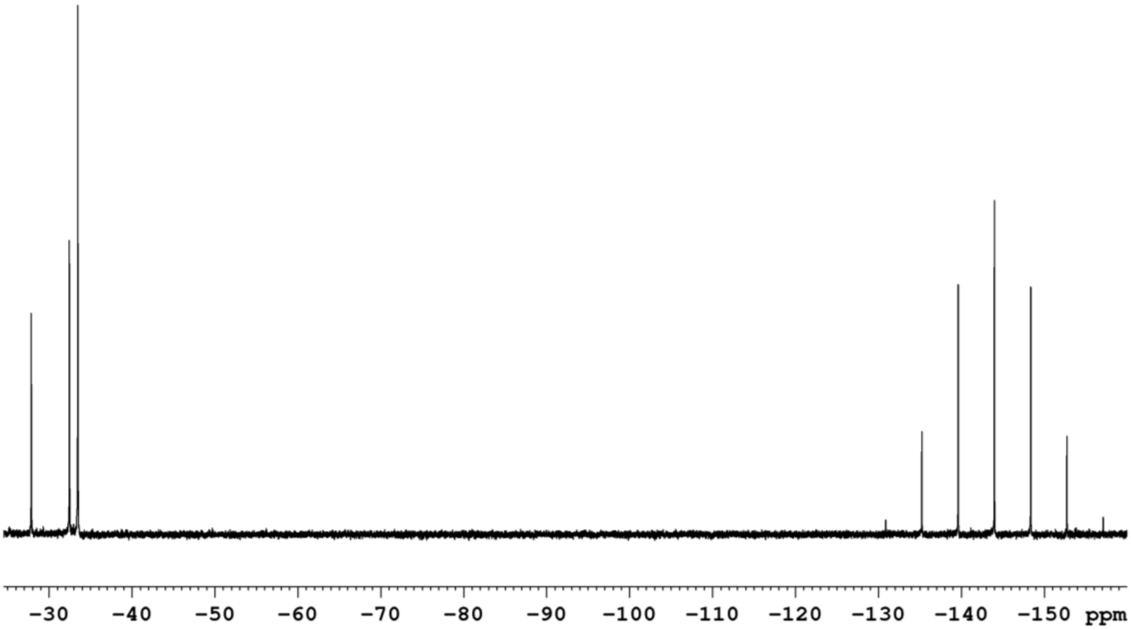


Figure S28. ^{31}P{^{1}H} NMR spectrum of ***(S,M)*-2b**, ***(S,P)*-2b** and ***η*^{2} complex** mixture at 253K.

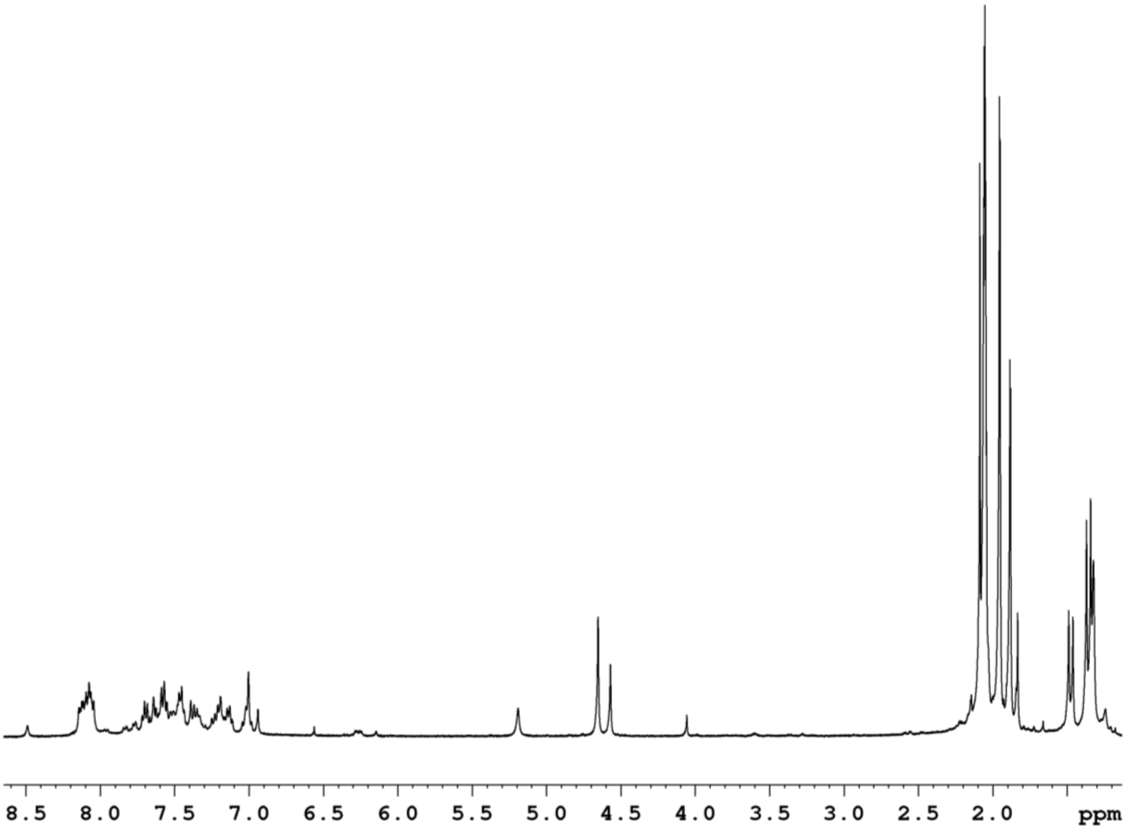


Figure S29. ^{1}H NMR spectrum of ***(S,M)*-2b**, ***(S,P)*-2b** and ***η*^{2} complex** mixture at 253K.

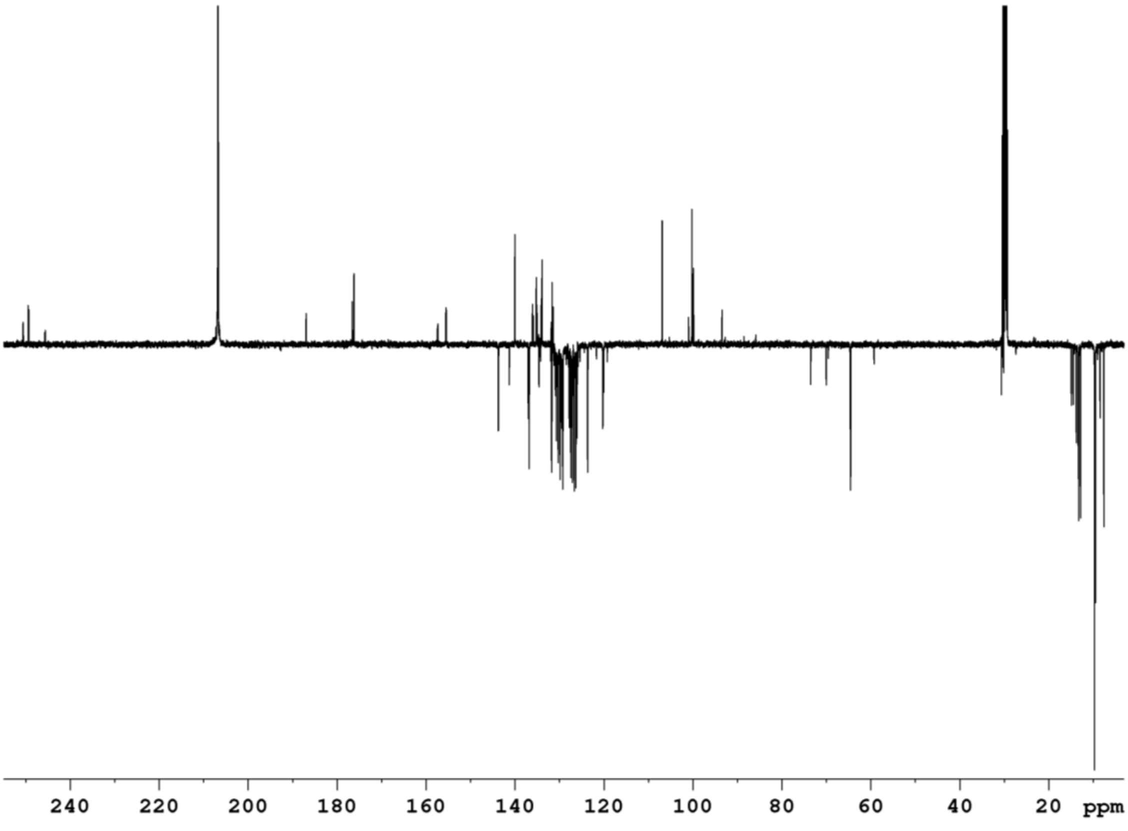
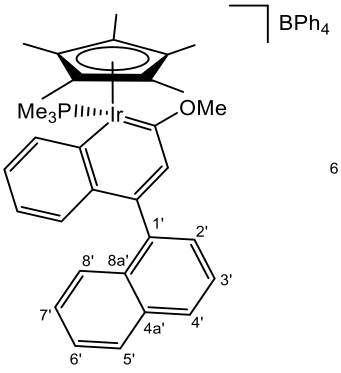


Figure S30. JMOD NMR spectrum of ***(S,M)*-2b**, ***(S,P)*-2b** and ***η*^{2} complex** mixture at 253K.

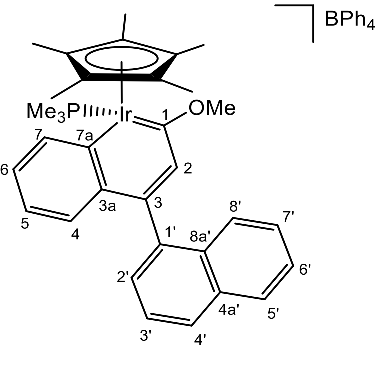
Synthesis of $[\overline{\mathrm{IrCp^*\{=C(OMe)–CH=C(}\mathit{o}\mathrm{–C}}\mathrm{_6H_4)(1–C_{10}H_7)\}(PMe_3)]BPh_4}$ (2b·BPh$_4$)

In an attempt to crystallize the atropisomers, a counteranion exchange is performed. Their characterization supports the previous characterization.

A brown solution of the mixture **2b** and ***η*^{2} complex** (75 mg, ~0.089 mmol; ~0.074 mmol of **2b**) in 10 mL of dichloromethane was treated with NaBPh$_4$ (34.2 mg, 0.1 mmol) and the mixture was stirred for 20 min at room temperature. The suspension was decanted and filtered with a cannula to obtain a brown solution that was vacuum-concentrated yielding the mixture of **(S,M)-2b·BPh$_4$** and **(S,P)-2b·BPh$_4$** and the phenantrene complex (**2a·BPh$_4$**) (~57:35:8 mole ratio, respectively) as a brown oil. The mixture was treated with *n*-pentane (5 mL) to obtain a solid which was stirred in *n*-pentane (3 × 5 mL) and the solvent removed by decantation. The final solid was dried under vacuum. Yield: 72 mg (isolated mixture, ~93% calculated on the mixture **2b**).



***(S,M)*-2b**



***(S,P)*-2b**

HR-ESI-MS (m/z): calculated: 675.2368 [M]$^+$; experimental: 675.23536 [M]$^+$.

Analytic data for ***(S,M)*-2b·BPh$_4$** isomer: **^{1}H NMR:** δ 8.13–8.02 (m, 3H, C$^{4'}$*H* + C$^{5'}$*H* + C^7*H*); 7.70–7.63 (m, 1H, C$^{3'}$*H*); 7.60–7.50 (m, 2H, C$^{2'}$*H* + C$^{8'}$*H*); 7.50–7.39 (m, 2H, C$^{6'}$*H* + C$^{7'}$*H*); 7.38–7.31 (m, 8H, B*Ph$_4$*); 7.31–7.24 (m, 1H, C^4*H*); 7.18–7.10 (m, 1H, C^6*H*); 7.06–6.97 (m, 1H, C^5*H*); 7.00 (s, 1H, C^2*H*); 6.97–6.87 (m, 8H, B*Ph$_4$*); 6.81–6.73 (m, 4H, B*Ph$_4$*); 4.57 (s, 3H, OC*H$_3$*); 1.95 (d, $^4J_{\mathrm{HP}}$ = 1.8 Hz, 15H, C$_5$(C*H$_3$*)$_5$); 1.36 (d, $^2J_{\mathrm{HP}}$ = 11.1 Hz, 9H, P(C*H$_3$*)$_3$) ppm. **^{31}P{^{1}H} NMR:** δ –34.38 (s, *P*(CH$_3$)$_3$) ppm. **^{13}C{^{1}H} NMR:** δ 249.6 (d, $^2J_{\mathrm{CP}}$ = 10.1 Hz, *C^1*); 177.0 (s, *C^3*); 155.7 (d, $^2J_{\mathrm{CP}}$ = 10.5 Hz, *C^{7a}*); 143.8 (d, $^3J_{\mathrm{CP}}$ = 4.5 Hz, *C^7*); 140.2 (s, *C$^{1'}$*); 137.3 (s, *C^4*); 135.4 (s, *C^{3a}*); 134.3 (s, *C$^{4a'}$*); 132.0 (s, *C$^{8a'}$*); 132.0 (s, *C^6*); 130.0 (s, *C$^{4'}$*); 129.4 (s, *C$^{5'}$*); 128.4–126.7 (all s, *C$^{2'}$*, *C$^{6'}$*, *C$^{7'}$* and *C$^{8'}$*); 126.3 (s, *C$^{3'}$*); 124.0 (s, *C^5*); 120.4 (d, $^3J_{\mathrm{CP}}$ = 2.2 Hz, *C^2*); 100.7 (d, $^2J_{\mathrm{CP}}$ = 2.0 Hz, *C$_5$*(CH$_3$)$_5$); 64.6 (s, O*C*H$_3$); 13.7 (d, $^1J_{\mathrm{CP}}$ = 41.2 Hz, P(*C*H$_3$)$_3$); 9.9 (s, C$_5$(*C*H$_3$)$_5$) ppm.

Analytic data for ***(S,P)*-2b·BPh$_4$** isomer: **^{1}H NMR:** δ 8.13–8.02 (m, 3H, C$^{4'}$*H* + C$^{5'}$*H* + C^{7}*H*); 7.70–7.63 (m, 1H, C$^{3'}$*H*); 7.50–7.39 (m, 4H, C$^{2'}$*H* + C$^{6'}$*H* + C$^{7'}$*H* + C$^{8'}$*H*); 7.38–7.31 (m, 8H, BPh_4); 7.31–7.24 (m, 1H, C^{4}*H*); 7.18–7.10 (m, 1H, C^{6}*H*); 7.06–6.97 (m, 1H, C^{5}*H*); 6.94 (s, 1H, C^{2}*H*); 6.97–6.87 (m, 8H, BPh_4); 6.81–6.73 (m, 4H, BPh_4); 4.49 (s, 3H, OCH_3); 1.88 (d, $^4J_{\mathrm{HP}}$ = 1.7 Hz, 15H, C$_5$(CH_3)$_5$); 1.48 (d, $^2J_{\mathrm{HP}}$ = 11.1 Hz, 9H, P(CH_3)$_3$) ppm. **^{31}P{^{1}H} NMR:** δ –33.37 (s, *P*(CH$_3$)$_3$) ppm. ^{13}C{^{1}H} NMR: δ 251.1 (d, $^2J_{\mathrm{CP}}$ = 10.4 Hz, C^{1}); 177.3 (s, C^{3}); 157.5 (d, $^2J_{\mathrm{CP}}$ = 10.2 Hz, C^{7a}); 143.8 (d, $^3J_{\mathrm{CP}}$ = 4.5 Hz, C^{7}); 140.2 (s, $C^{1'}$); 137.5 (s, C^{4}); 135.5 (s, C^{3a}); 134.4 (s, $C^{4a'}$); 132.1 (s, $C^{8a'}$); 131.9 (s, C^{6}); 129.8 (s, $C^{4'}$); 129.4 (s, $C^{5'}$); 128.4–126.7 (all s, $C^{2'}$, $C^{6'}$, $C^{7'}$ and $C^{8'}$); 126.3 (s, $C^{3'}$); 124.1 (s, C^{5}); 120.4 (d, $^3J_{\mathrm{CP}}$ = 2.0 Hz, C^{2}); 100.3 (d, $^2J_{\mathrm{CP}}$ = 2.1 Hz, C_5(CH$_3$)$_5$); 64.7 (s, O*C*H$_3$); 14.3 (d, $^1J_{\mathrm{CP}}$ = 40.7 Hz, P(*C*H$_3$)$_3$); 9.7 (s, C$_5$(*C*H$_3$)$_5$) ppm.

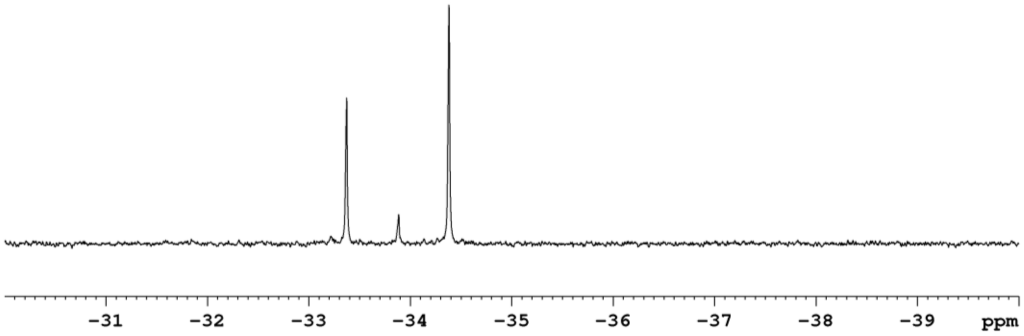


Figure S31. ^{31}P{^{1}H} NMR spectrum of ***(S,M)*-2b**, ***(S,P)*-2b·BPh$_4$** mixture.

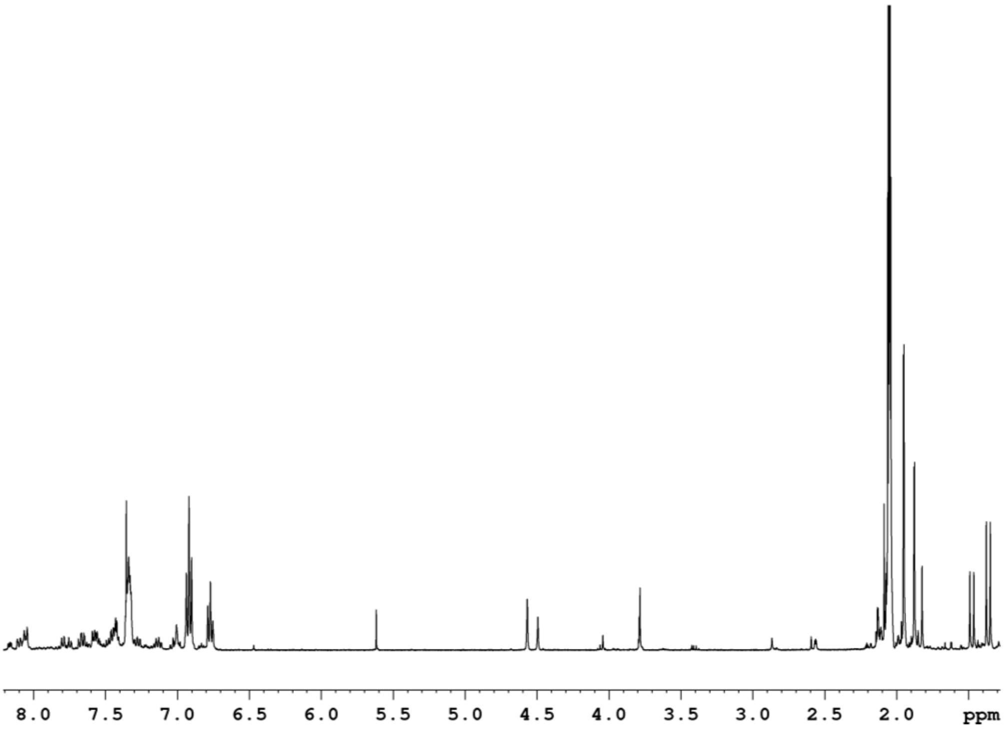


Figure S32. ^{1}H NMR spectrum of ***(S,M)*-2b**, ***(S,P)*-2b·BPh$_4$** mixture.

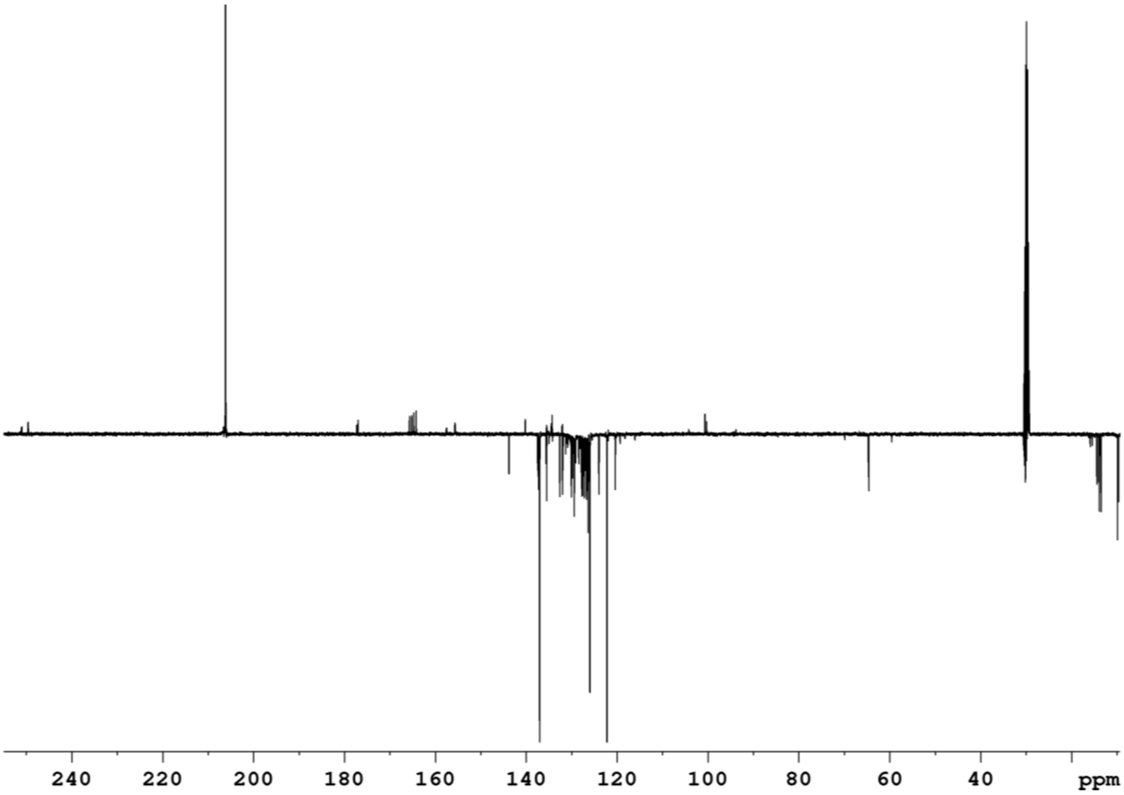


Figure S33. JMOD NMR spectrum of ***(S,M)*-2b**, ***(S,P)*-2b·BPh$_4$** mixture.

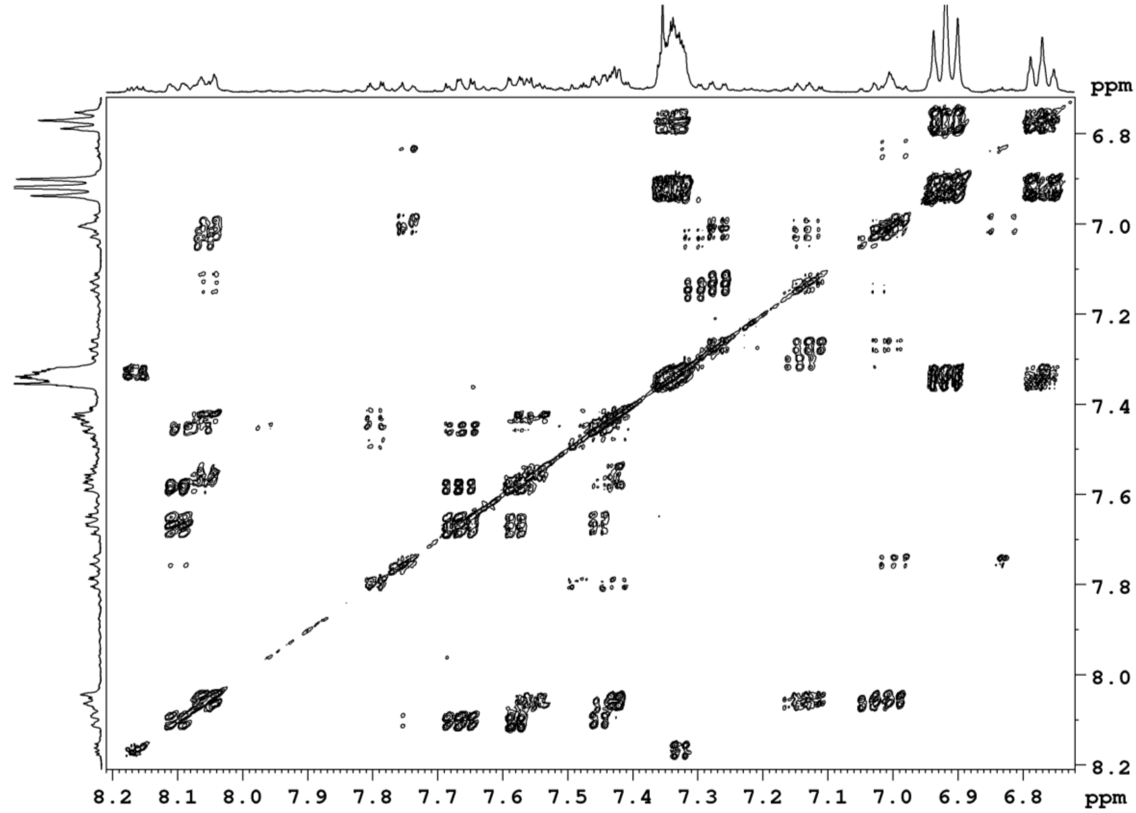


Figure S34. Section of the ^{1}H, ^{1}H COSY NMR spectrum of ***(S,M)*-2b**, ***(S,P)*-2b·BPh$_4$** mixture.

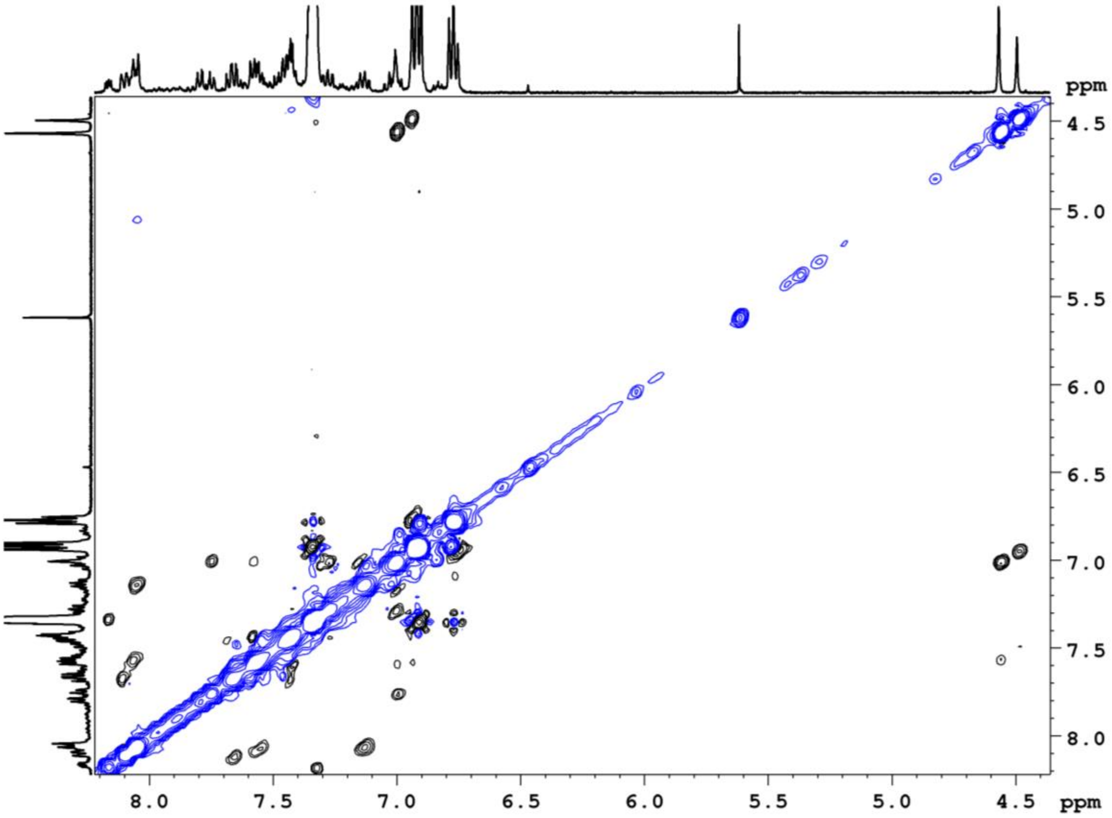


Figure S35. Section of the ^{1}H, ^{1}H NOESY NMR spectrum of ***(S,M)*-2b**, ***(S,P)*-2b·BPh$_4$** mixture.

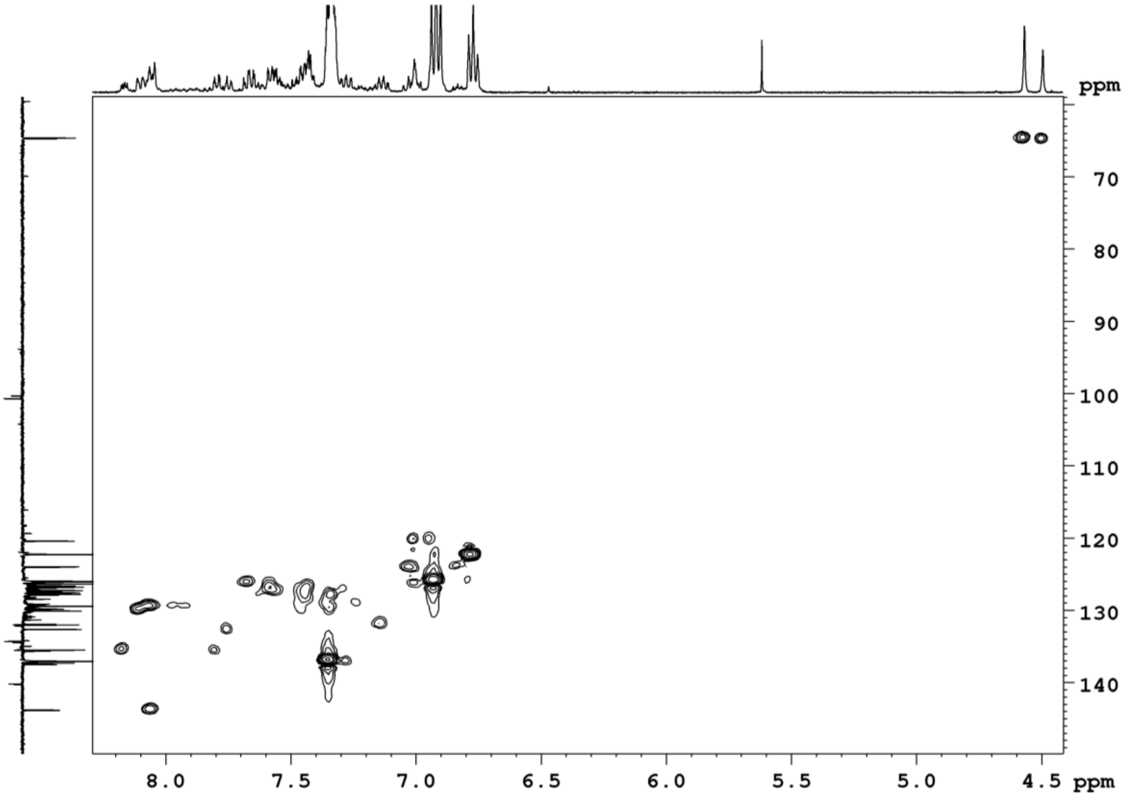


Figure S36. Section of the ^{1}H, ^{13}C HSQC NMR spectrum of ***(S,M)*-2b**, ***(S,P)*-2b·BPh$_4$** mixture.

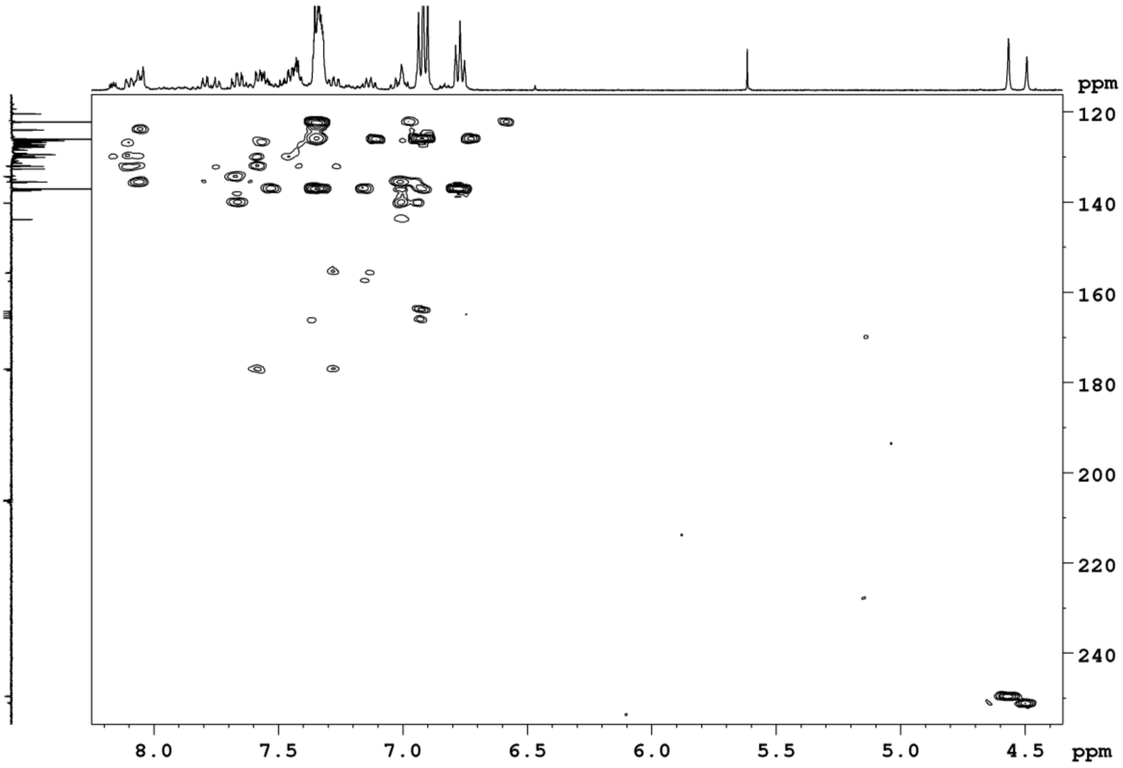


Figure S37. Section of the ^{1}H, ^{13}C HMBC NMR spectrum of ***(S,M)*-2b**, ***(S,P)*-2b·BPh$_4$** mixture.

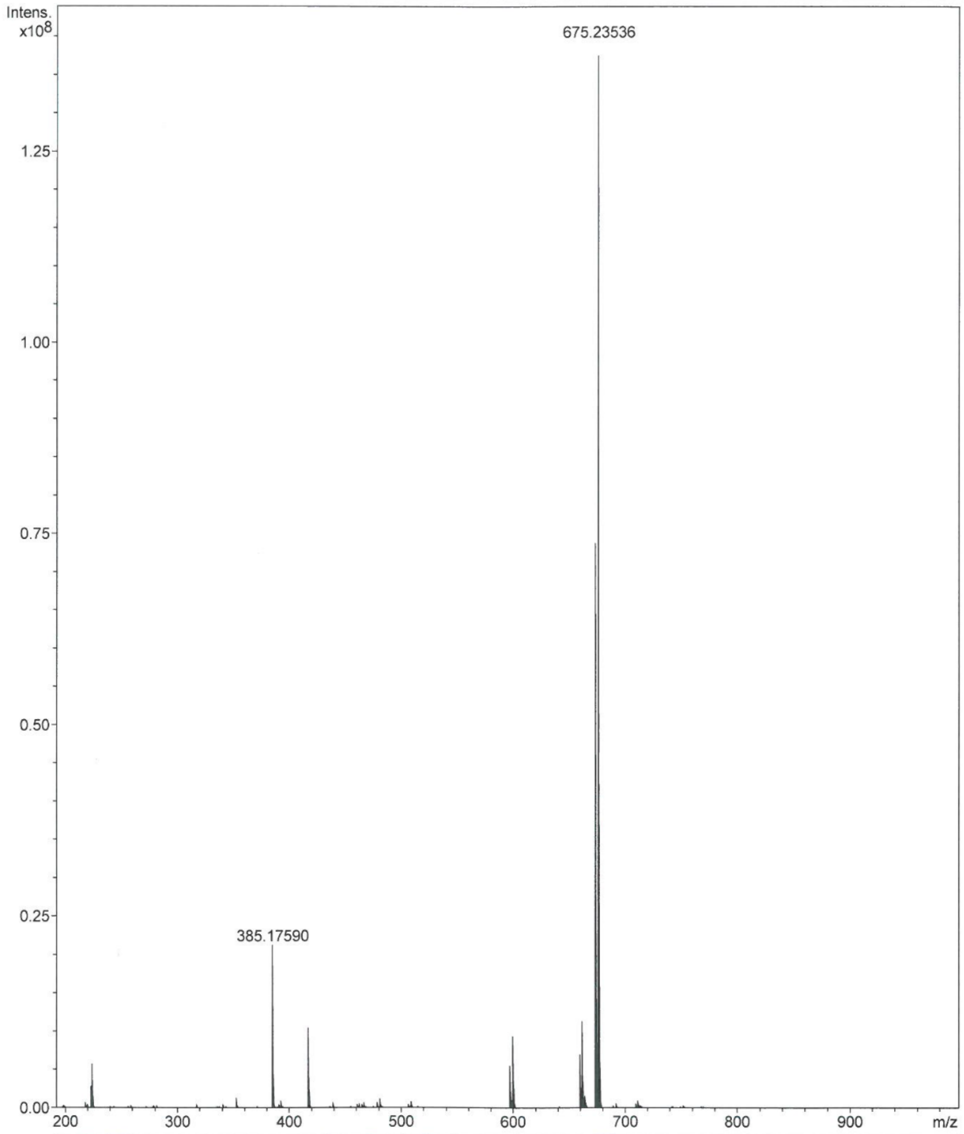
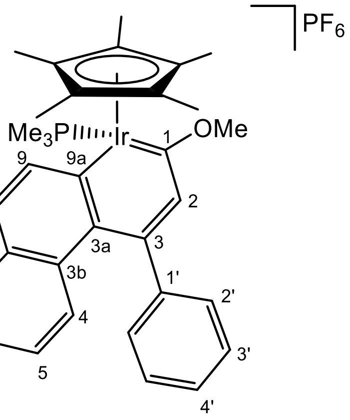


Figure S38. HR-ESI-MS spectrum of ***(S,M)*-2b**, ***(S,P)*-2b·BPh$_4$** mixture

Synthesis of [IrCp*{=C(OMe)–CH=C(*o*–1–$C_{10}H_6$)(Ph)}(PMe_3)]PF_6 (2a)

A brown solution of the mixture mixture **2b** and ***η*^{2} complex** (75 mg, ~0.015 mmol of *η*^{2} complex) in 10 mL of dichloromethane was stirred 24 h at room temperature obtaining a brown solution. The solution was vacuum-concentrated giving a brown solid which corresponds to the mixture of ***(S,M)*-2b** and ***(S,P)*-2b** unaltered and new phenantrene complex **2a** (~53:30:17 mole ratio, respectively). The mixture was stirred in *n*-pentane (3 × 5 mL), the solvent removed by decantation and the solid dried under vacuum. Yield: 72 mg (isolated mixture, ~86% calculated on *η*^{2} complex).



$C_{33}H_{39}OF_6IrP_2$ (819.82 g/mol). **HR-ESI-MS** (m/z): calculated: 675.2368 $[M]^+$; experimental: 675.23567 $[M]^+$. **IR** (cm^{-1}): ν (PF_6) 840 (s). **^{1}H NMR:** δ 8.14–8.02 (m, 1H, C^9*H*); 7.86–7.80 (m, 1H, C^7*H*); 7.80–7.76 (m, 1H, C^8*H*); 7.24–7.19 (m, 1H, C^6*H*); 7.00 (s, 1H, C^2*H*); 4.75 (s, 3H, OCH_3); 1.87 (s br, 15H, $C_5(CH_3)_5$); 1.33 (d, $^2J_{HP}$ = 11.1 Hz, 9H, $P(CH_3)_3$) ppm. **$^{31}P\{^1H\}$ NMR:** δ –33.97 (s, $P(CH_3)_3$); –143.92 (sept, $^1J_{PF}$ = 708.8 Hz, PF_6) ppm. **$^{13}C\{^1H\}$ NMR:** δ 250.7 (d, $^2J_{CP}$ = 10.7 Hz, C^1); 175.0 (s, C^3); 164.2 (d, $^2J_{CP}$ = 10.4 Hz, C^{9a}); 141.5 (d, $^3J_{CP}$ = 4.9 Hz, C^9); 146.4 (s, $C^{1'}$); 136.4 (s, C^{3b}); 120.5 (d, $^3J_{CP}$ = 2.2 Hz, C^2); 100.7 (d, $^2J_{CP}$ = 2.0 Hz, $C_5(CH_3)_5$); 65.1 (s, OCH_3); 14.3 (d, $^1J_{CP}$ = 40.8 Hz, $P(CH_3)_3$); 9.8 (s, $C_5(CH_3)_5$) ppm. Rest of signals are overlapped by main products or could not be assigned.

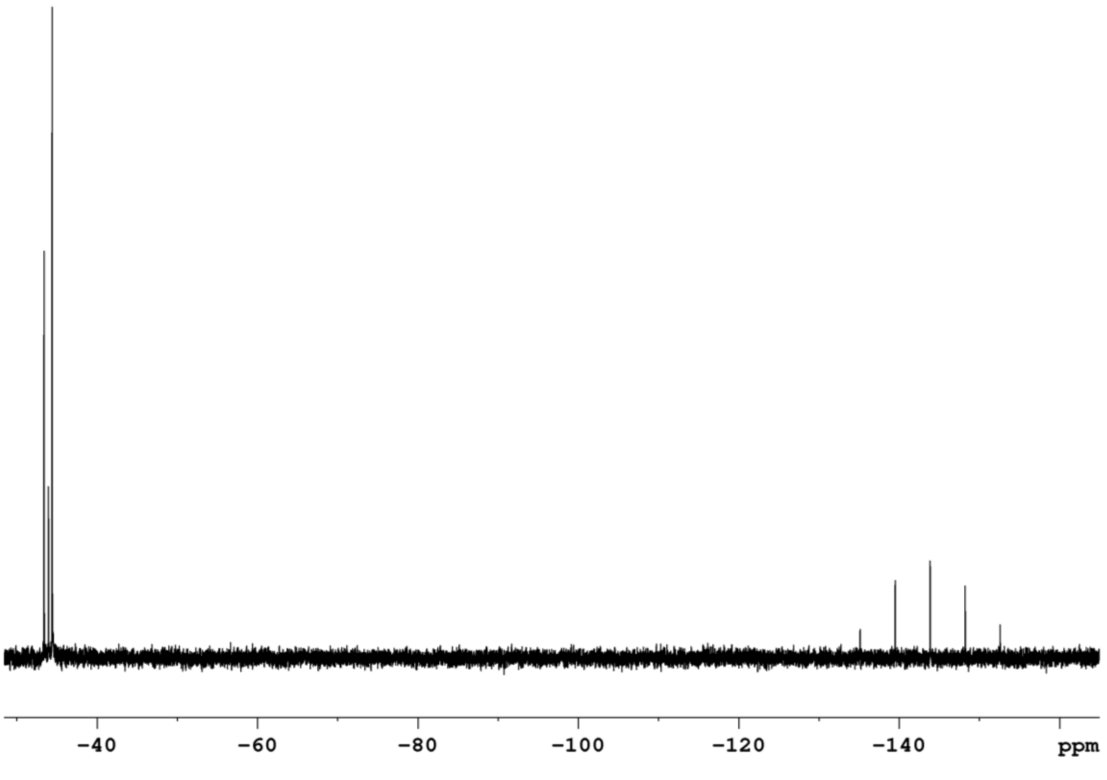


Figure S39. $^{31}P\{^1H\}$ NMR spectrum of **2a** and ***(S,M)*-2b**, ***(S,P)*-2b** mixture.

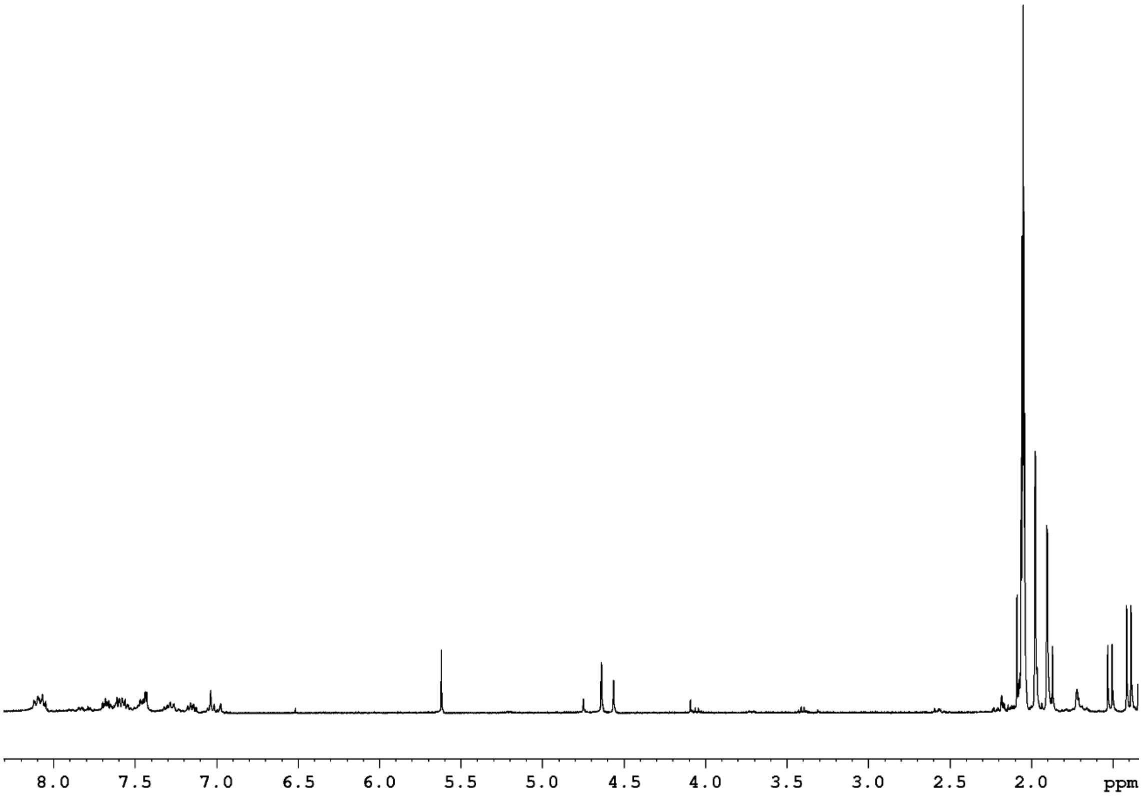


Figure S40. ^{1}H NMR spectrum of **2a** and ***(S,M)*-2b**, ***(S,P)*-2b** mixture.

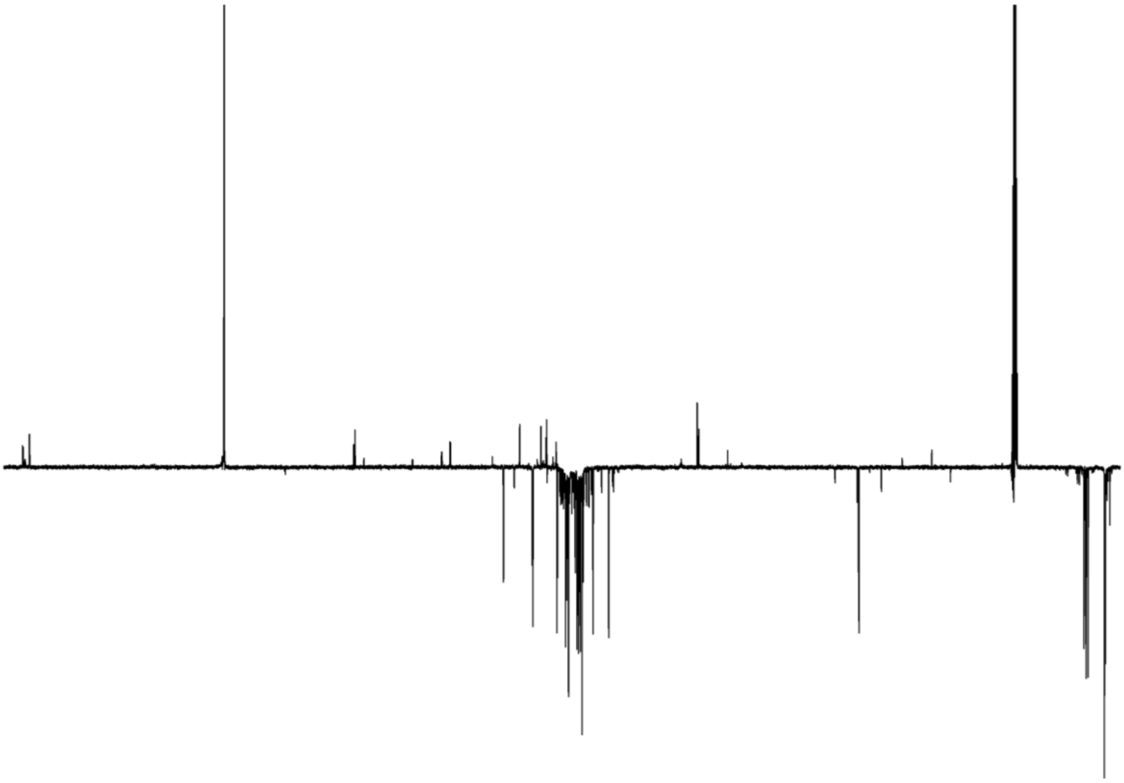


Figure S41. JMOD NMR spectrum of **2a** and ***(S,M)*-2b**, ***(S,P)*-2b** mixture.

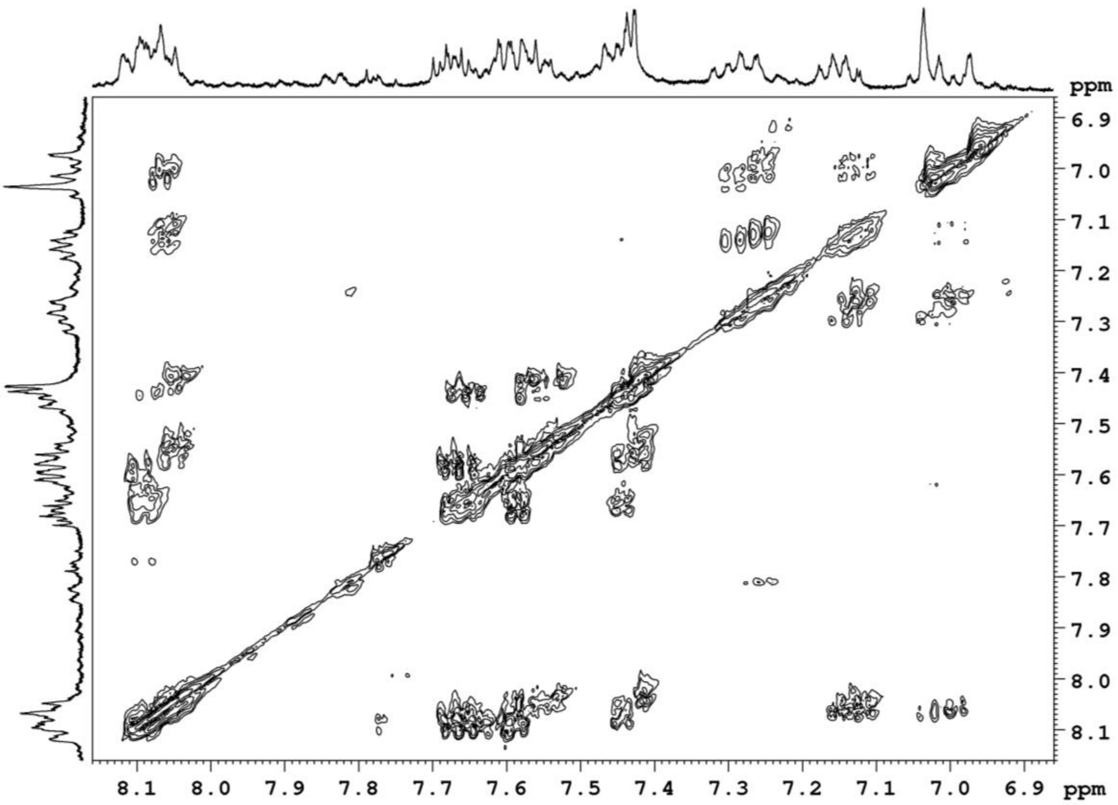


Figure S42. Section of the ^{1}H, ^{1}H COSY NMR spectrum of **2a** and ***(S,M)*-2b**, ***(S,P)*-2b** mixture.

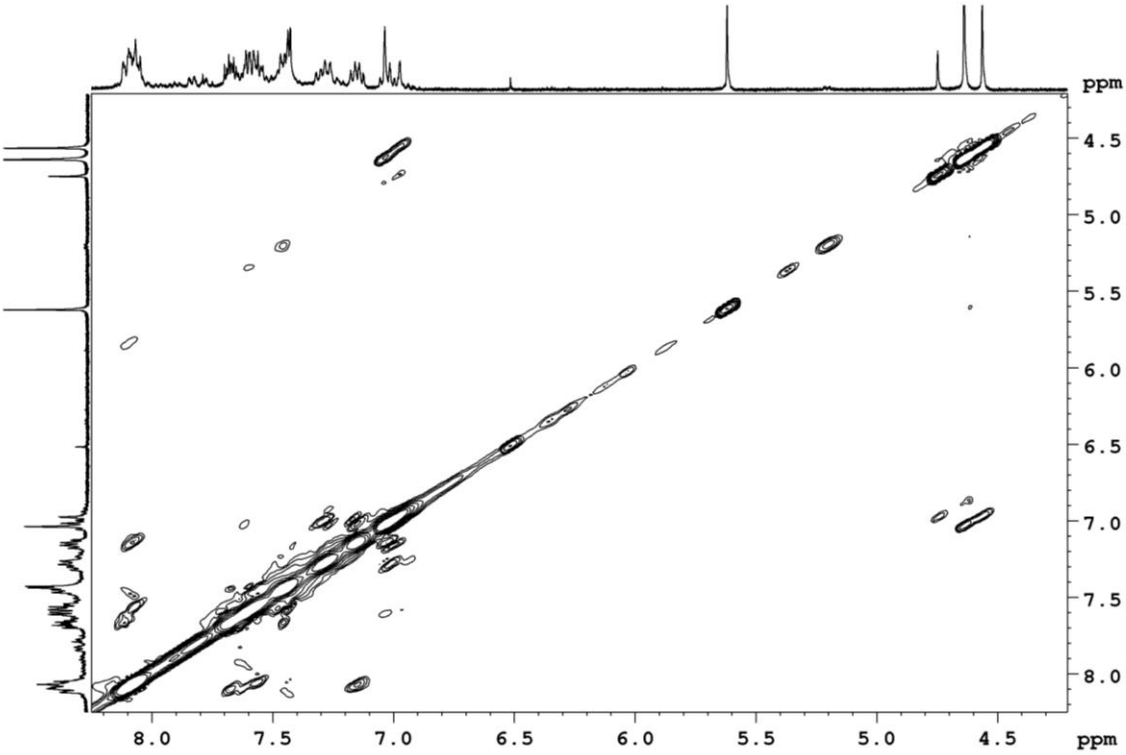


Figure S43. Section of the ^{1}H, ^{1}H NOESY NMR spectrum of **2a** and ***(S,M)*-2b**, ***(S,P)*-2b** mixture.

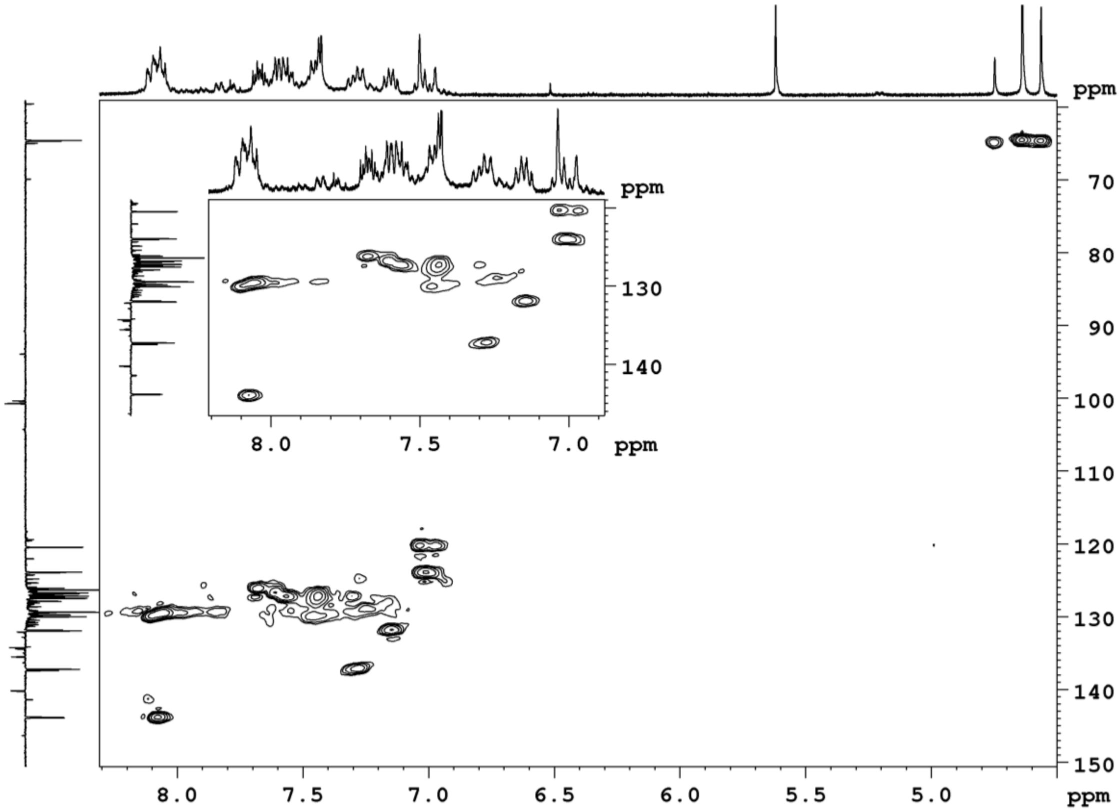


Figure S44. Section of the ^{1}H, ^{13}C HSQC NMR spectrum of **2a** and ***(S,M)*-2b**, ***(S,P)*-2b** mixture.

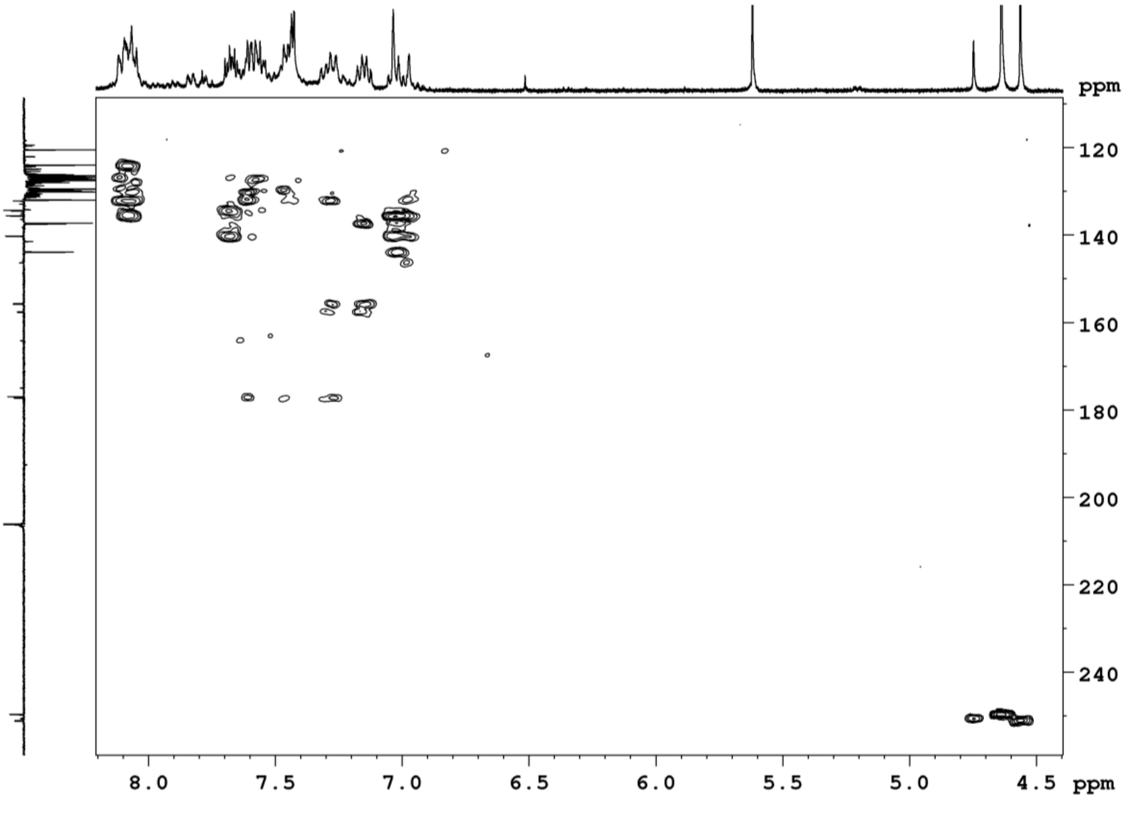


Figure S45. Section of the ^{1}H, ^{13}C HMBC NMR spectrum of **2a** and ***(S,M)*-2b**, ***(S,P)*-2b** mixture.

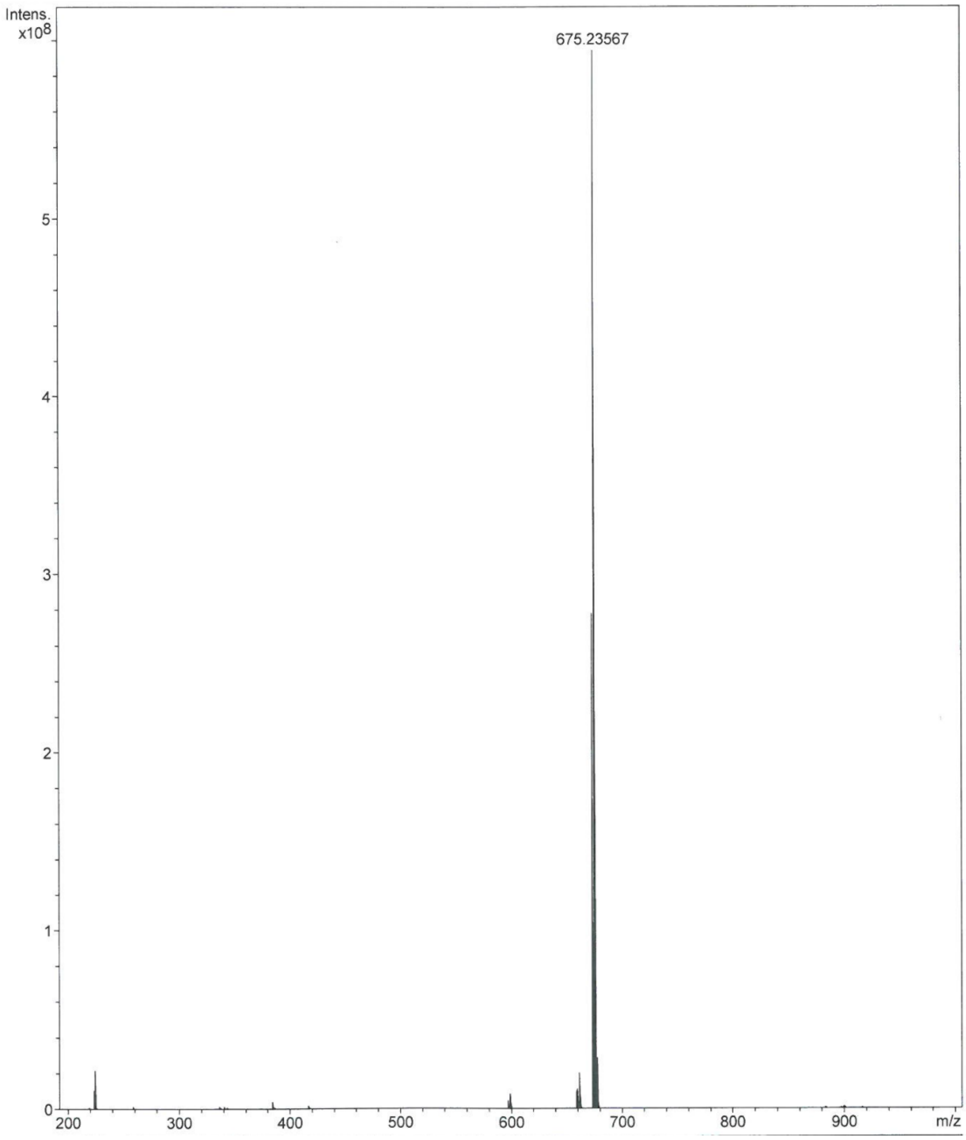
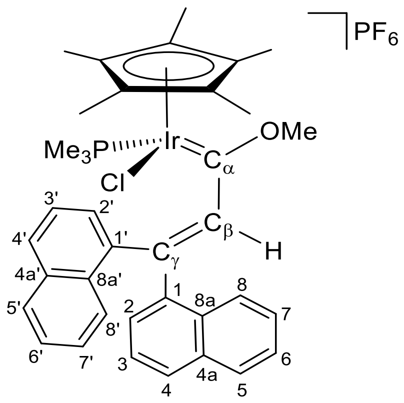


Figure S46. HR-ESI-MS spectrum of **2a** and ***(S,M)*-2b**, ***(S,P)*-2b** mixture

Synthesis of [IrCp*Cl{=C(OMe)–CH=C(1–$C_{10}H_7$)$_2$}(PMe_3)]PF_6 (1c)

To a yellow solution of [IrCp*Cl(NCMe)(PMe_3)]PF_6 (100 mg, 0.16 mmol) in methanol (10 mL), bis(1-(1-naphthalenyl))-2-propyn-1-ol (53 mg, 0.18 mmol) was added and the mixture was stirred for 20 min. The dark solution obtained was vacuum-concentrated yielding a dark red solid that was stirred in *n*-pentane (3 × 5 mL) and the solvent removed by decantation. Finally, the solid was dried under vacuum. Yield: 130 mg (90%).



Anal. Calcd for $C_{37}H_{42}OClF_6IrP_2$ (906.35 g/mol): C 49.03, H 4.67; found: C 49.35, H 4.75. **HR-ESI-MS** (m/z): calculated: 761.22912 $[M]^+$; experimental: 761.22760 $[M]^+$. **IR** (cm^{-1}): ν (PF_6) 839 (s). **^{1}H NMR:** δ 8.70 (d, J_{HH} = 8.3 Hz, 1H, C^8H); 8.07–8.04 (m, 2H, $C^{4'}H$ + C^5H); 8.01–7.98 (m, 2H, C^4H + $C^{5'}H$); 7.82 (d, J_{HH} = 8.3 Hz, 1H, $C^{8'}H$); 7.74–7.69 (m, 1H, C^7H); 7.70–7.66 (br, 1H, $C_\beta H$); 7.66–7.60 (m, 2H, $C^{3'}H$ + C^6H); 7.53–7.47 (m, 2H, $C^{2'}H$ + $C^{6'}H$); 7.43–7.38 (m, 2H, C^2H + C^3H); 7.38–7.33 (m, 1H, $C^{7'}H$); 4.17 (s, 3H, OCH_3); 1.83 (d, 15H, $^4J_{HP}$ = 2.0 Hz, $C_5(CH_3)_5$); 1.78 (d, 9H, $^2J_{HP}$ = 11.2 Hz, $P(CH_3)_3$) ppm. **^{31}P{^{1}H} NMR:** δ –30.73 (s, $P(CH_3)_3$); –143.91 (sept, $^1J_{PF}$ = 707.7 Hz, PF_6) ppm. **^{13}C{^{1}H} NMR:** δ 265.4 (observed by ^{1}H, ^{13}C HMBC NMR spectrum, C_α); 151.1 (s, C_γ); 146.4 (s, C_β); 139.9 (s, C^1); 139.3 (s, $C^{1'}$); 135.4 (s, C^{4a}); 134.7 (s, $C^{4a'}$); 131.5 (s, C^{8a}); 131.4 (s, C^4); 130.8 (s, $C^{8a'}$); 130.5 and 130.1 (both s, $C^{4'}$ and C^5); 129.6 (s, 2C $C^{5'}$ + C^2); 128.3 (s, C^7); 127.9 (s, $C^{7'}$); 127.8 (s, $C^{2'}$); 127.5 (s, C^6); 127.2 (s, $C^{6'}$); 126.6 (s, $C^{8'}$); 126.3 (s, C^8); 126.08 (s, $C^{3'}$); 126.07 (s, C^3); 99.6 (d, $^2J_{CP}$ = 2.1 Hz, $C_5(CH_3)_5$); 69.9 (s, OCH_3); 15.1 (d, $^1J_{CP}$ = 40.6 Hz, $P(CH_3)_3$); 9.1 (s, $C_5(CH_3)_5$) ppm.

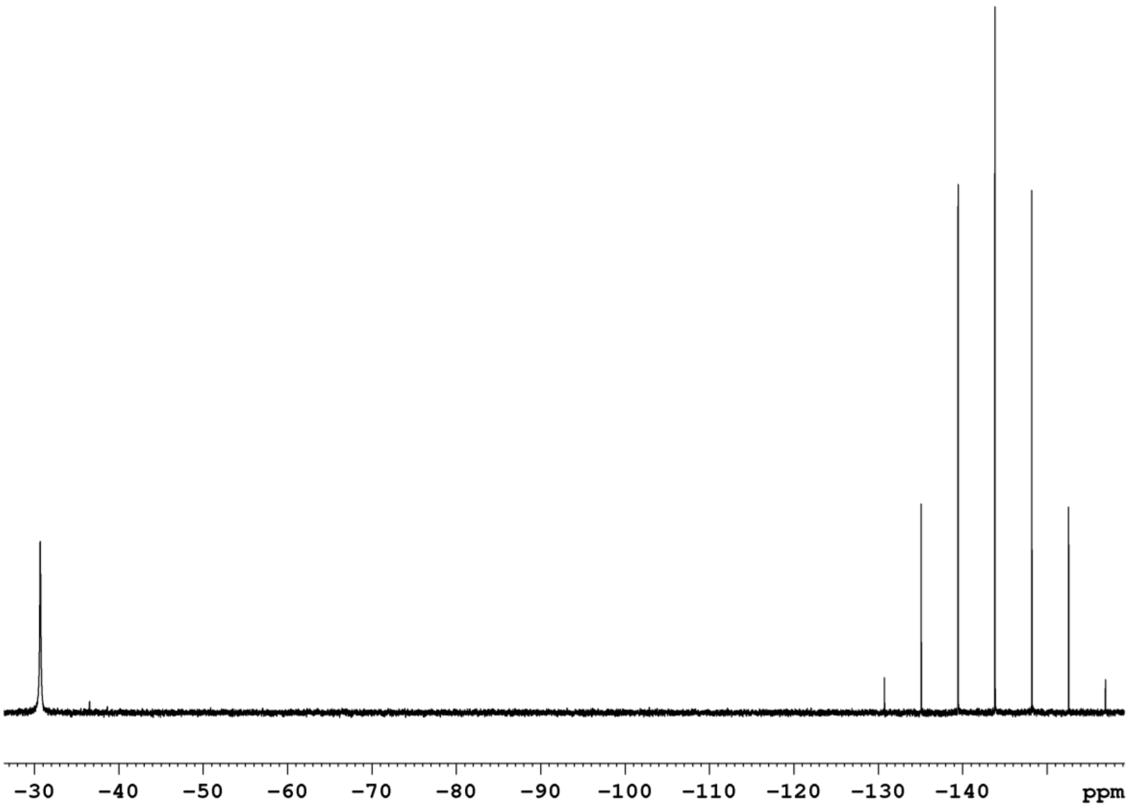


Figure S47. $^{31}P\{^{1}H\}$ NMR spectrum of **1c**.

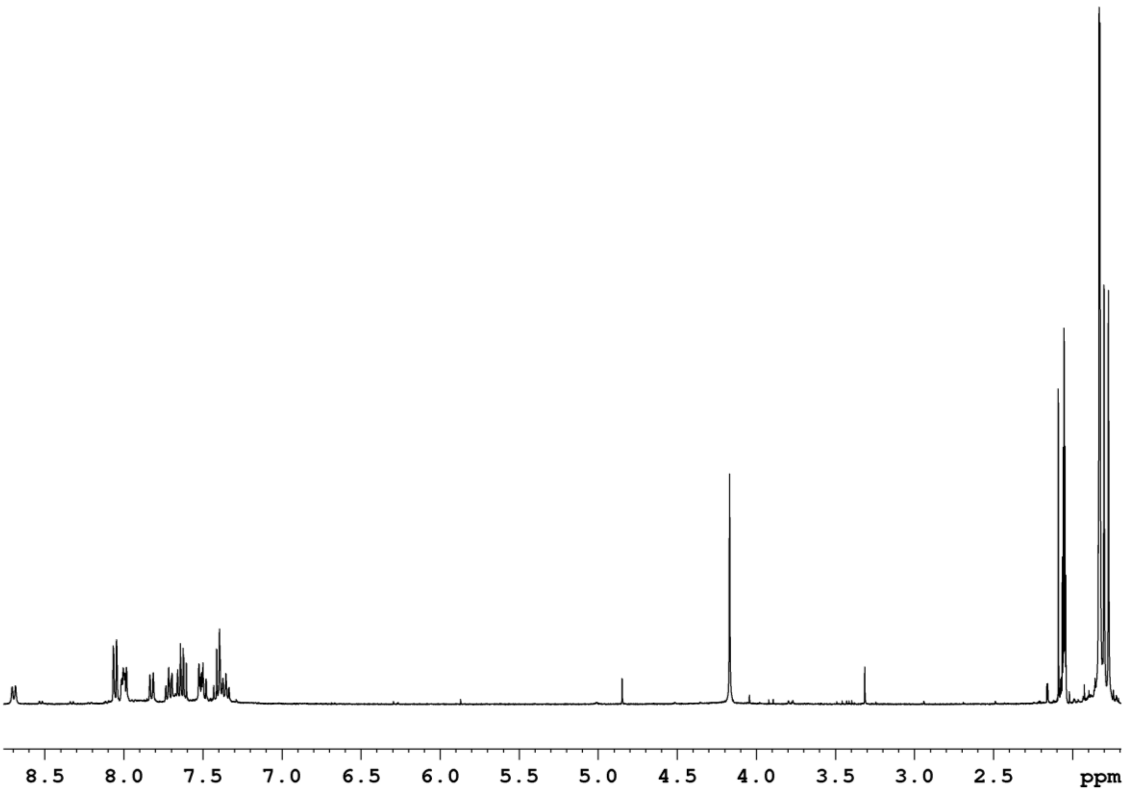


Figure S48. ^{1}H NMR spectrum of **1c**.

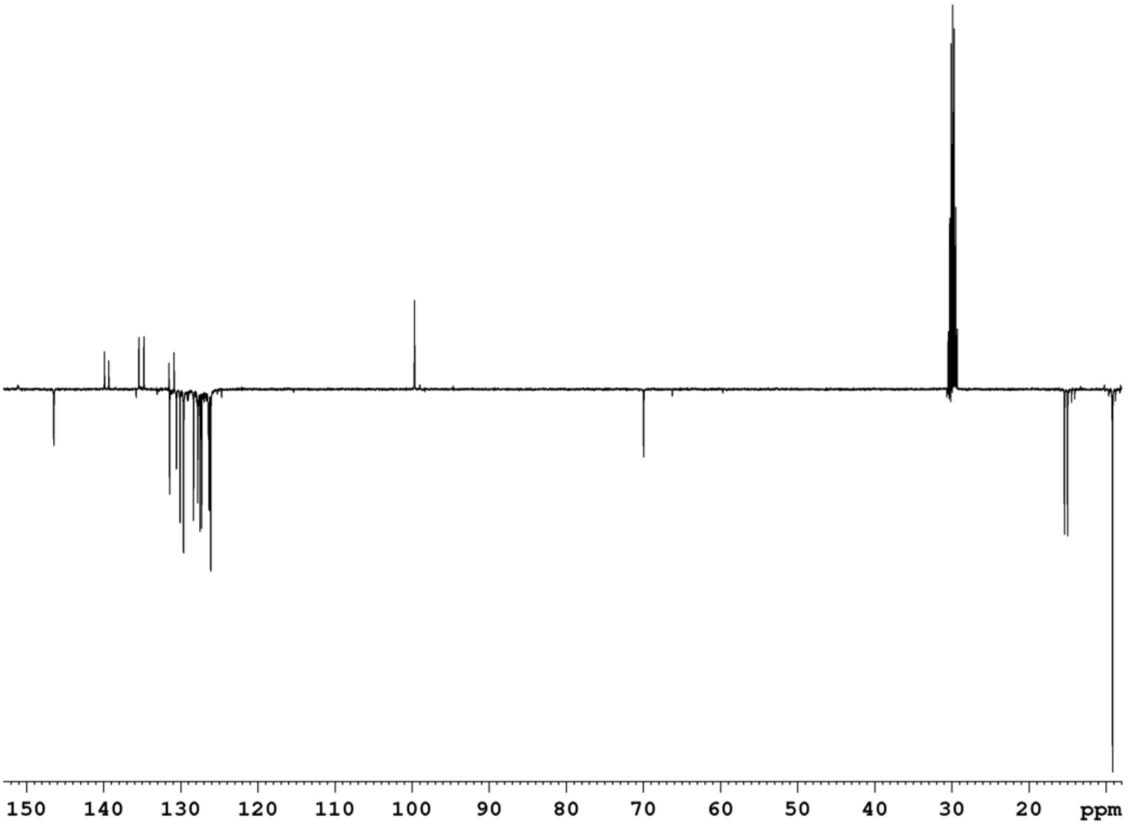


Figure S49. JMOD NMR spectrum of **1c**.

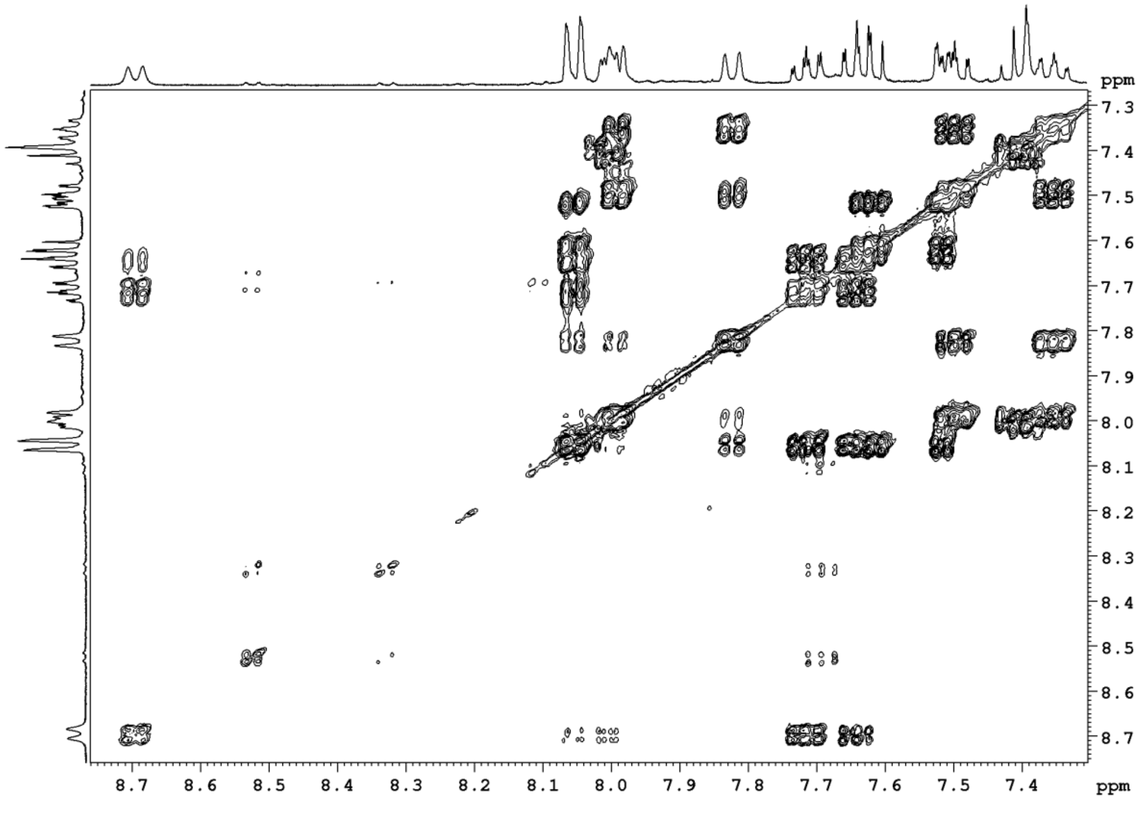


Figure S50. Section of the ^{1}H, ^{1}H COSY NMR spectrum of **1c**.

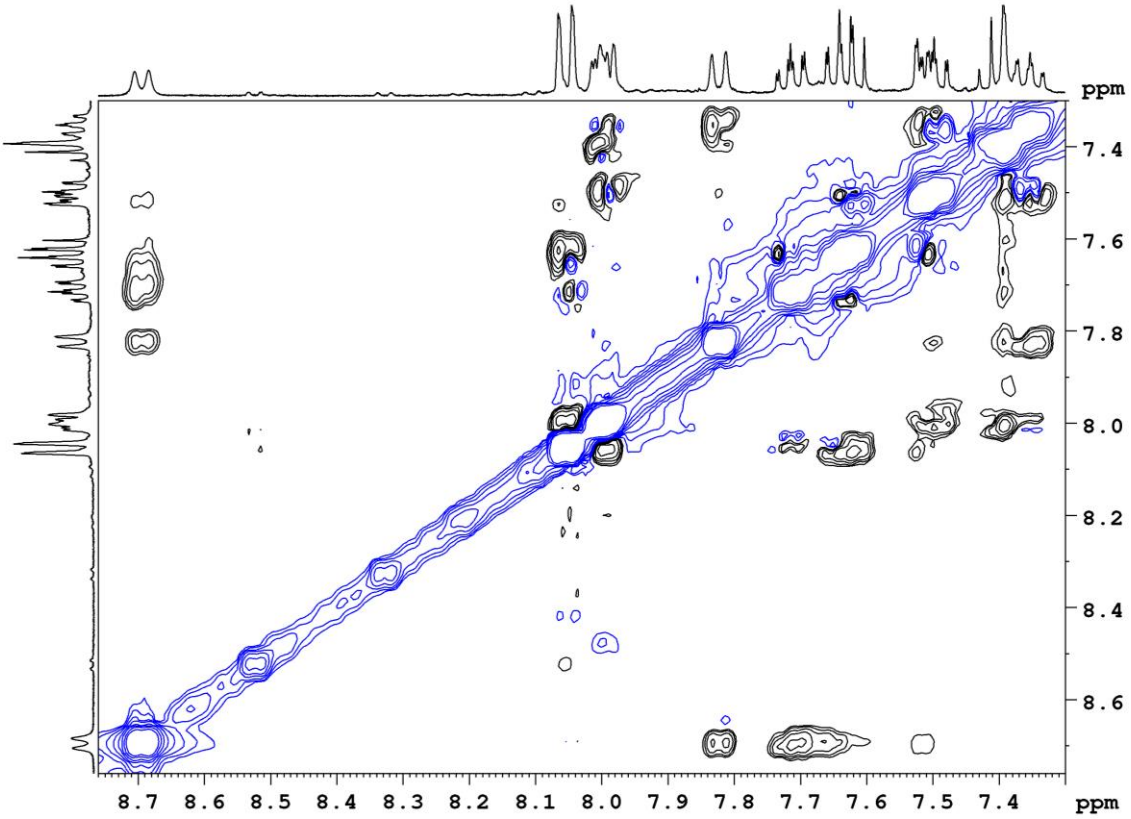


Figure S51. Section of the ^1H, ^1H NOESY NMR spectrum of **1c**.

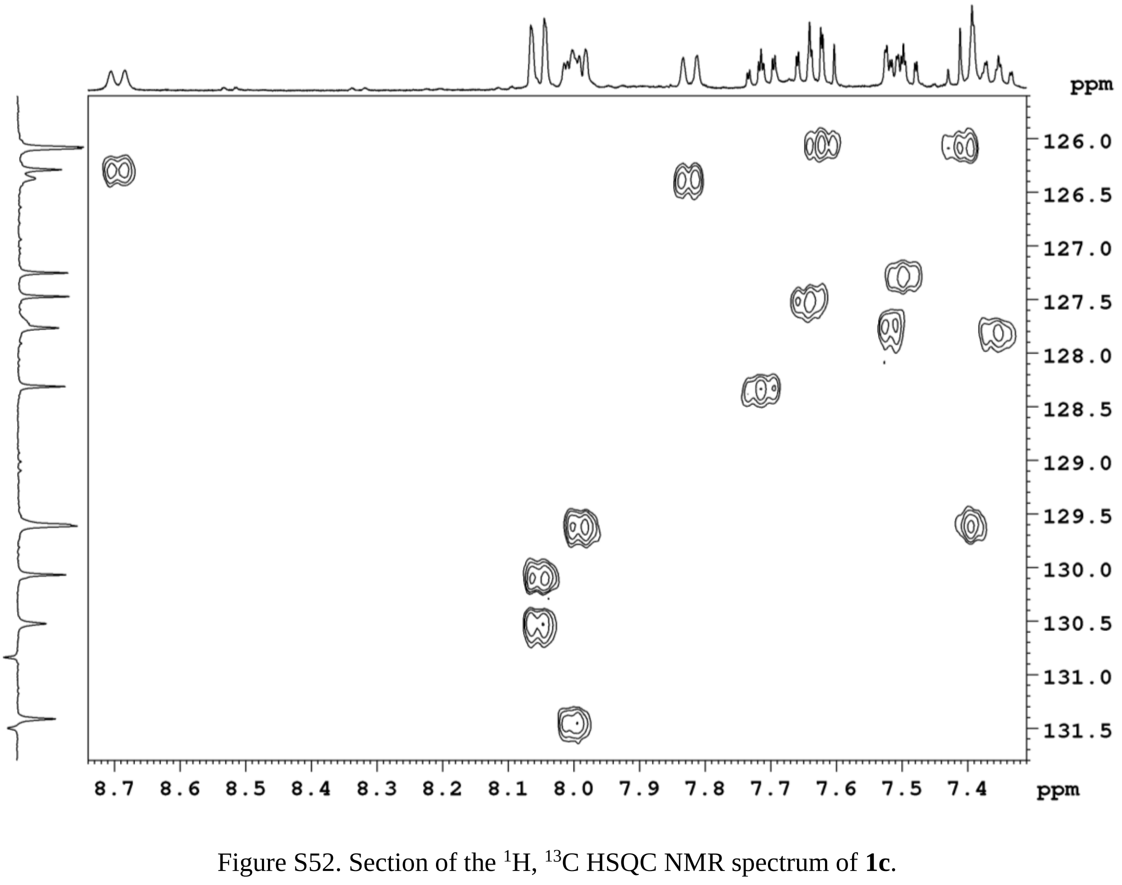


Figure S52. Section of the ^1H, ^{13}C HSQC NMR spectrum of **1c**.

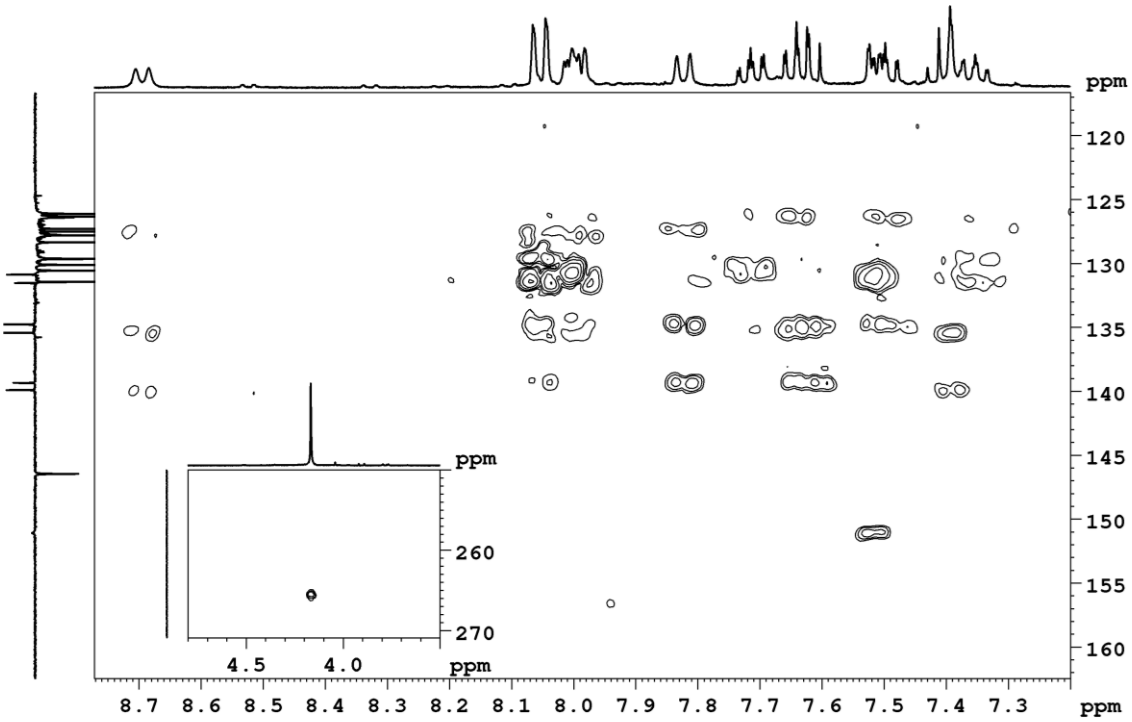


Figure S53. Section of the ^{1}H, ^{13}C HMBC NMR spectrum of **1c**.

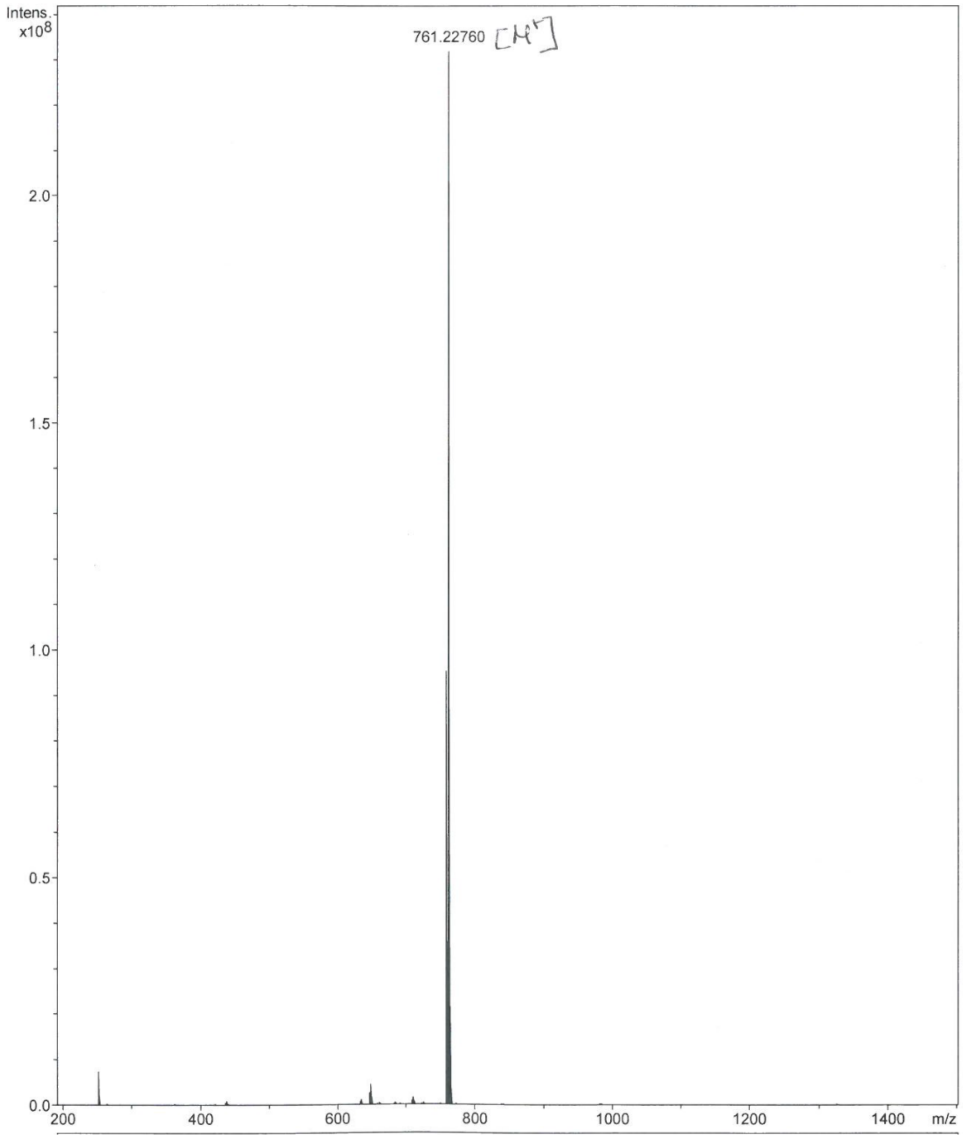
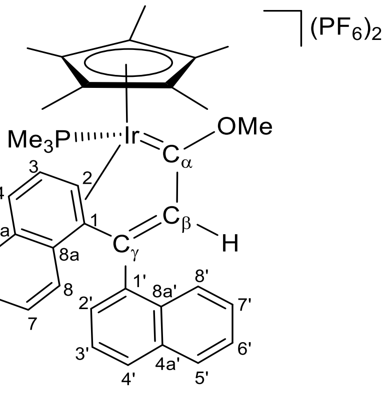


Figure S54. HR-ESI-MS spectrum of **1c.**

Synthesis of [IrCp*{=C(OMe)–CH=C(η^2–1–C$_{10}$H$_7$)(1–C$_{10}$H$_7$)}(PMe$_3$)](PF$_6$)$_2$

A red solution of **1c** (352 mg, 0.36 mmol) in 25 mL of dichloromethane was treated with AgPF$_6$ (102 mg, 0.39 mmol). The red solution was stirred 5 min at room temperature obtaining a brown solution. The volatiles were removed under vacuum and the brown residue was dissolved and extracted with acetone by filtration with Celite®. The volatiles were removed again under vacuum yielding a brown solid that was stirred in *n*-pentane (3 × 7 mL) and the solvent removed by decantation. Finally, the solid was dried under vacuum. Yield: 300 mg (82%).



***η^2*-complex**

In order to properly characterize the **η^2 complex**, NMR spectra were recorded at low temperature avoiding the evolution to the phenantrene derivative.

$C_{37}H_{42}OF_{12}IrP_3$ (1015.85 g/mol). **IR** (cm^{-1}): *ν* (PF_6) 840 (s). **^{1}H NMR:** *δ* 8.84–8.77 (m, 1H, $C^{8'}H$); 8.26 (s, 1H, $C_\beta H$); 8.04–7.98 (m, 4H, $C^4H + C^{4'}H + C^5H + C^{5'}H$); 7.96–7.93 (m, 1H, C^8H); 7.82–7.76 (m, 1H, $C^{7'}H$); 7.69–7.64 (m, 1H, $C^{6'}H$); 7.49–7.35 (m, 3H, $C^3H + C^6H + C^7H$); 7.31–7.24 (m, 1H, $C^{3'}H$); 6.93–6.87 (m, 1H, $C^{2'}H$); 6.51 (dd, 1H, $^3J_{HH}$ = 12.5 Hz, $^3J_{HP}$ = 5.4 Hz, C^2H); 5.22 (s, 3H, OCH_3); 2.10 (d, 9H, $^2J_{HP}$ = 10.8 Hz, $P(CH_3)_3$); 1.36 (d, 15H, $^4J_{HP}$ = 2.2 Hz, $C_5(CH_3)_5$) ppm. **^{31}P{^{1}H} NMR:** *δ* –28.67 (s, $P(CH_3)_3$); –143.90 (sept, $^1J_{PF}$ = 708.1 Hz, PF_6) ppm. **^{13}C{^{1}H} NMR** (253 K): *δ* 246.8 (d, $^2J_{CP}$ = 13.1 Hz, C_α); 186.8 (s, C_γ); 144.6 (s, C_β); 135.5 (s, $C^{1'}$); 135.4 (s, C^{8a}); 134.8 (s, $C^{4a'}$); 134.5 (s, C^4); 131.8 (s, C^{4a}); 131.3 (s, $C^{8a'}$); 130.5 (s, C^6); 130.46 (s, C^8); 130.3 (s, C^5); 130.1 (s, C^7); 129.9 and 129.8 (both s, $C^{4'}$ and $C^{5'}$); 129.7 (s, $C^{7'}$); 128.7 (s, $C^{2'}$); 128.1 (s, C^3); 127.9 (s, $C^{6'}$); 125.9 (s, $C^{3'}$); 125.7 (s, $C^{8'}$); 103.9 (s, C^1); 73.6 (s, C^2); 106.8 (d, $^2J_{CP}$ = 1.0 Hz, $C_5(CH_3)_5$); 70.2 (s, OCH_3); 14.6 (d, $^1J_{CP}$ = 42.4 Hz, $P(CH_3)_3$); 7.7 (s, $C_5(CH_3)_5$) ppm.

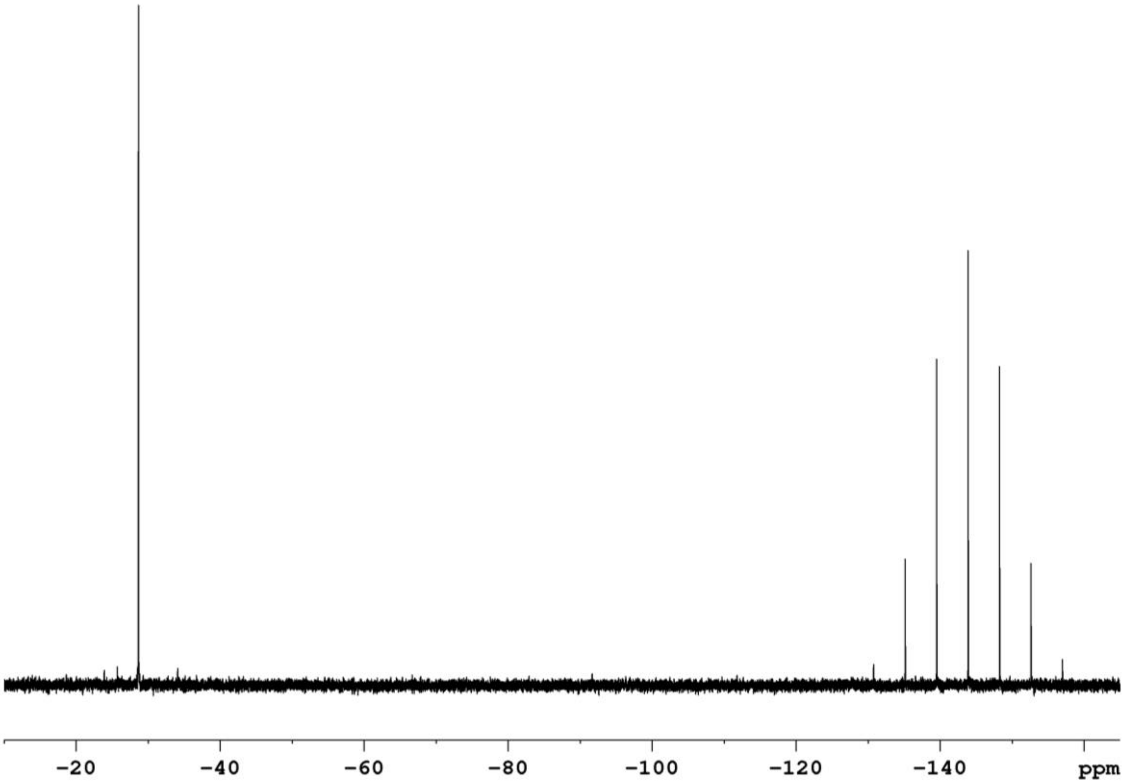


Figure S55. $^{31}P\{^{1}H\}$ NMR spectrum of ***η*²** **complex**.

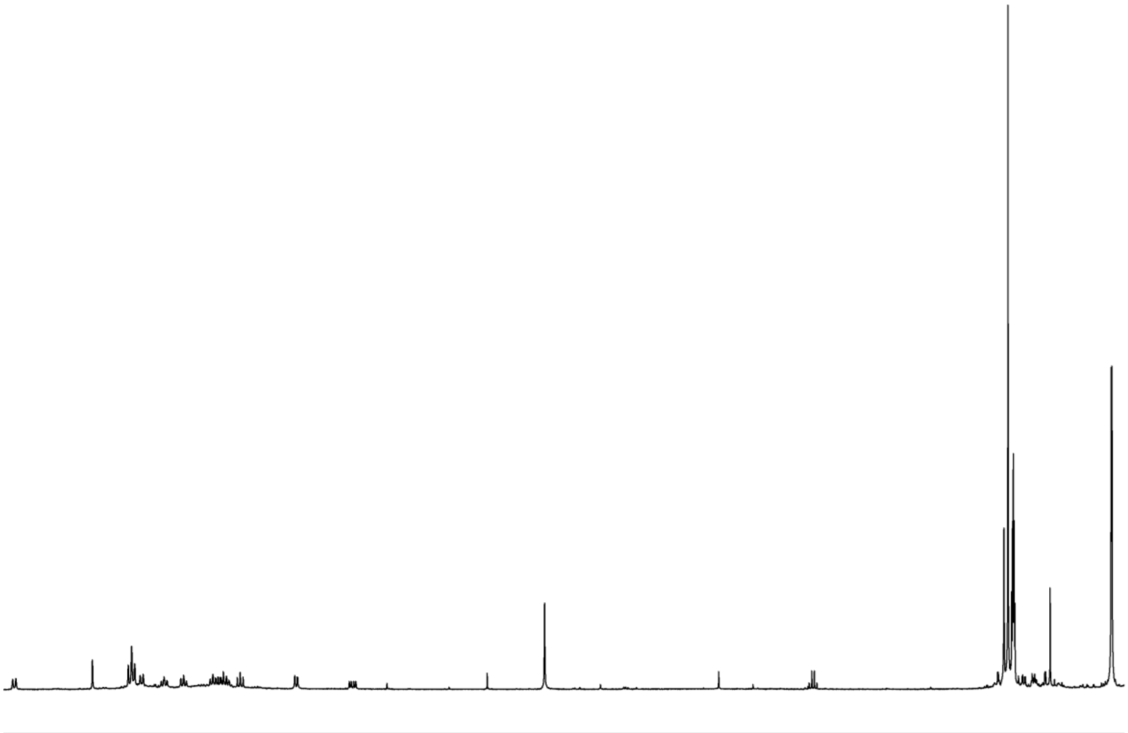


Figure S56. ^{1}H NMR spectrum of ***η*²** **complex**.

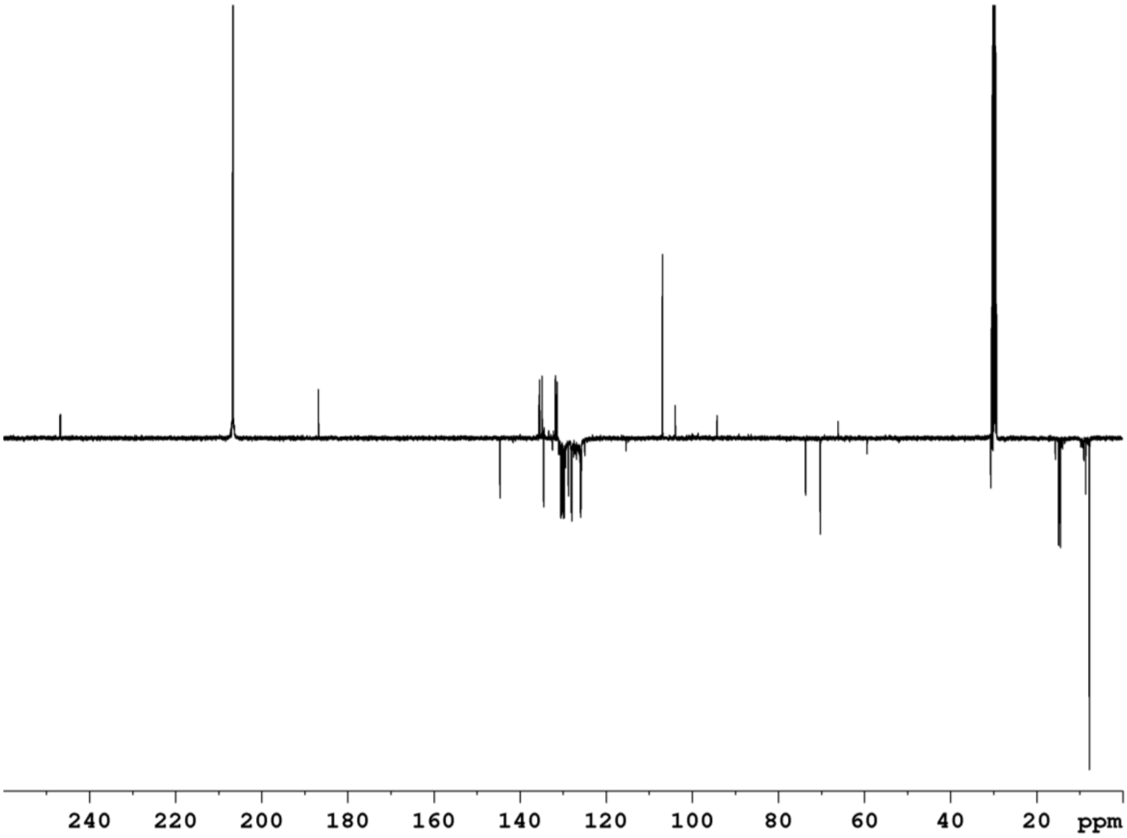


Figure S57. JMOD NMR spectrum of ***η^2* complex**.

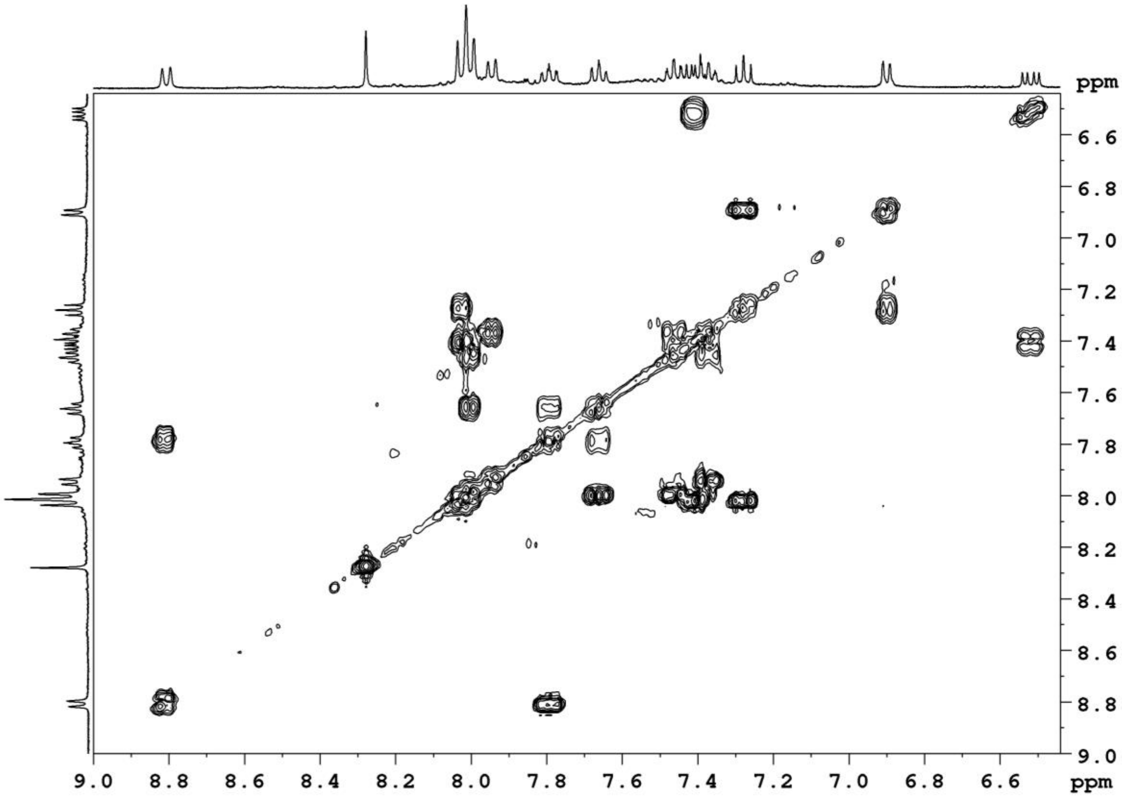


Figure S58. Section of the ^{1}H, ^{1}H COSY NMR spectrum of ***η^2* complex**.

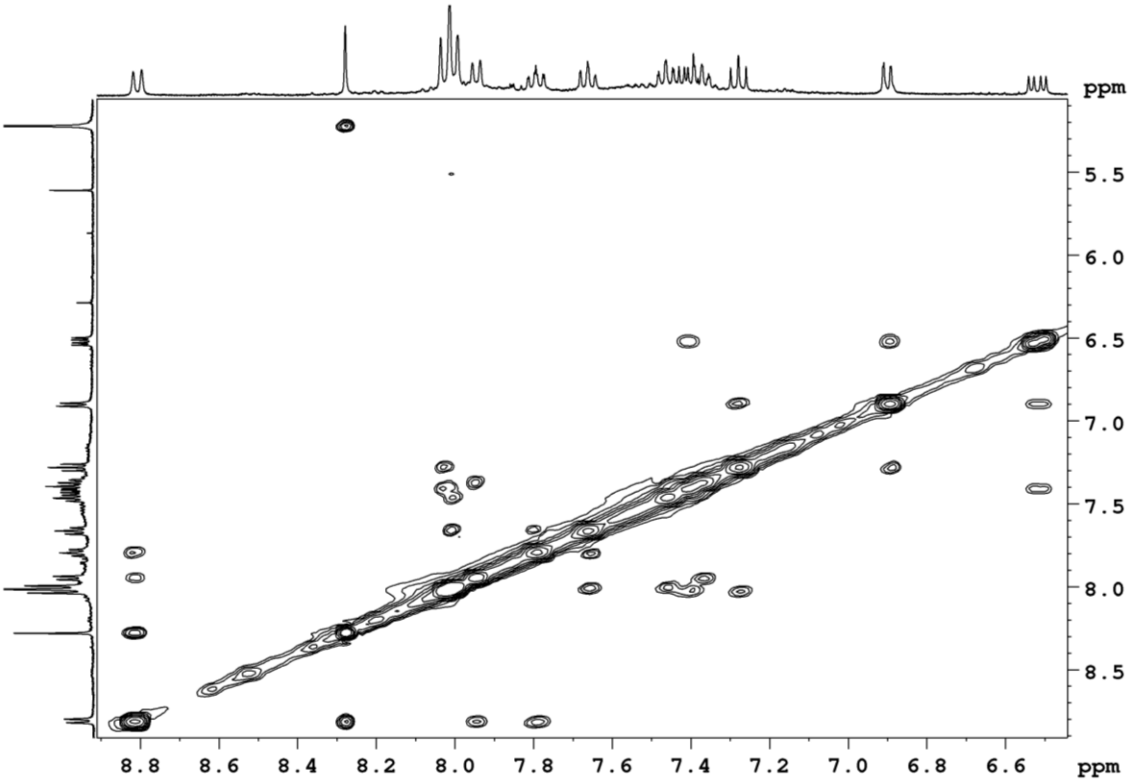


Figure S59. Section of the ^{1}H, ^{1}H NOESY NMR spectrum of ***η*^{2} complex**.

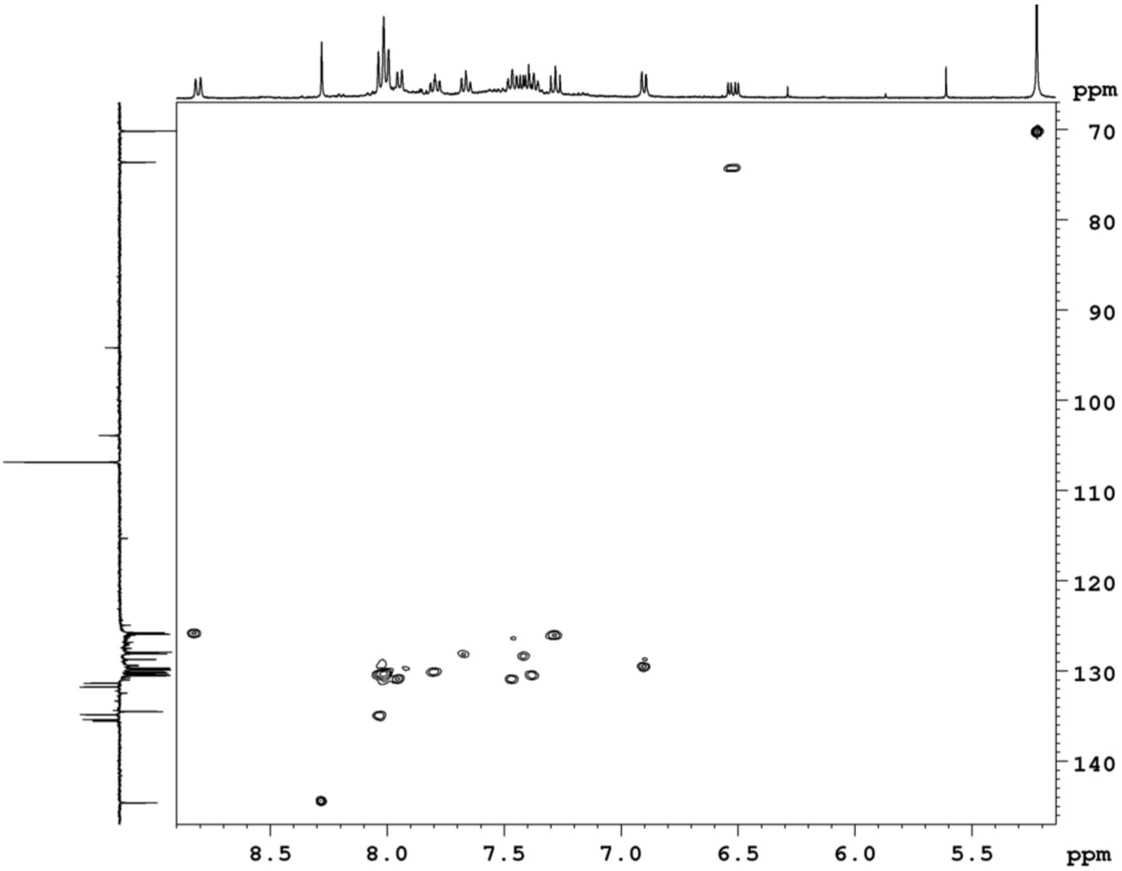


Figure S60. Section of the ^{1}H, ^{13}C HSQC NMR spectrum of ***η*^{2} complex**.

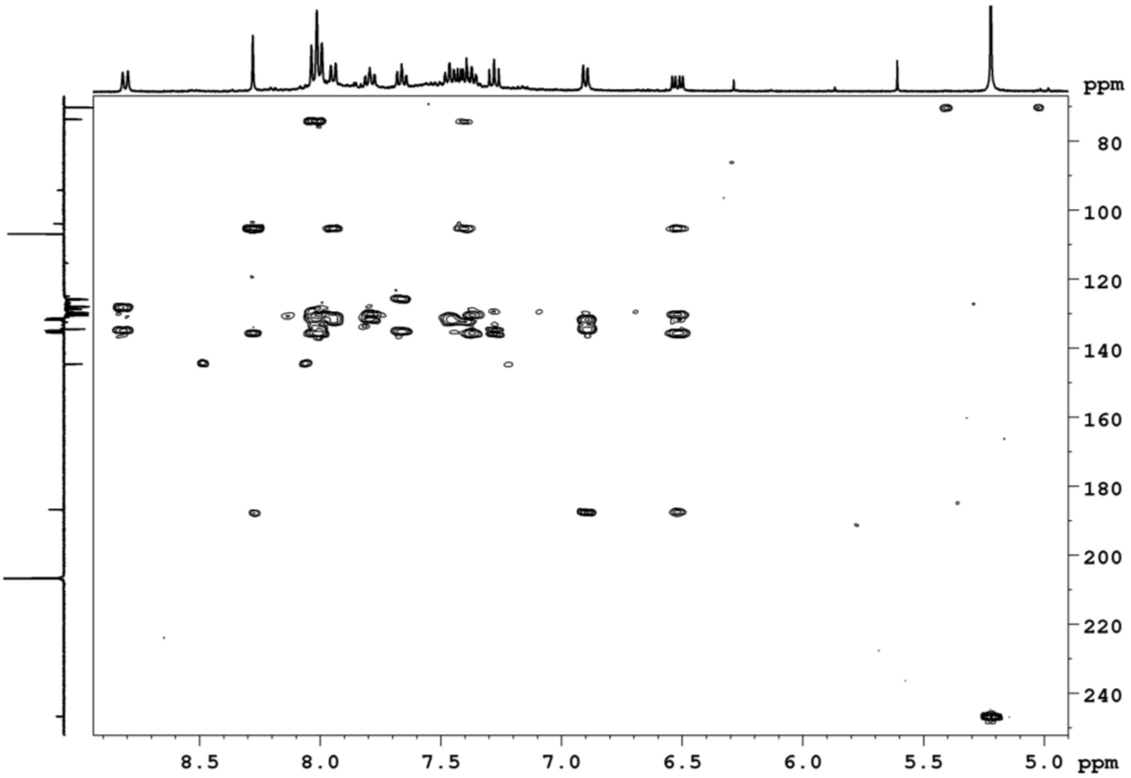
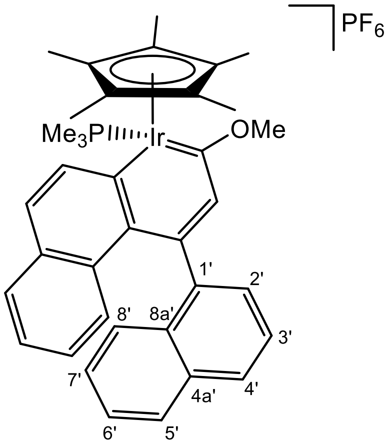


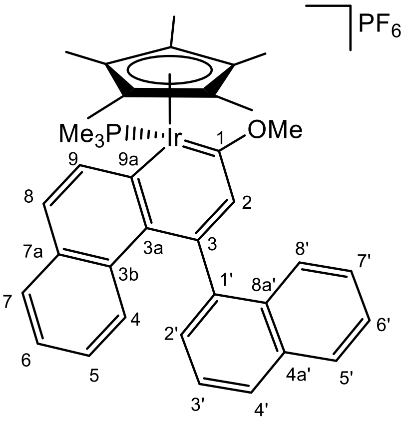
Figure S61. Section of the ^{1}H, ^{13}C HMBC NMR spectrum of ***η*^{2} complex**.

Synthesis of [IrCp*{=C(OMe)–CH=C(*o*–1–$C_{10}H_6$)(1–$C_{10}H_7$)}(PMe_3)]PF_6 (2c)

A brown solution of [IrCp*{=C(OMe)–CH=C(η^2–1–$C_{10}H_7$)(1–$C_{10}H_7$)}(PMe_3)]$(PF_6)_2$ **(*η*^{2} complex)** (100 mg, 0.098 mmol) in 15 mL of dichloromethane was stirred 16 h at room temperature obtaining a dark brown solution that was filtered through Celite® and vacuum-concentrated giving a dark brown solid that was stirred in *n*-pentane (3 × 4 mL) and the solvent removed by decantation. Finally, the solid was dried under vacuum yielding a mixture of isomers ***(S,M)*-2c** and ***(S,P)*-2c** (~56:44 mole ratio, respectively). Yield: 70 mg (82% isolated mixture).



***(S,M)*-2c**



***(S,P)*-2c**

Anal. Calcd for $\mathrm{C_{37}H_{41}OF_6IrP_2}$ (869.87 g/mol): C 51.09, H 4.75; found: C 51.31, H 4.80. **HR-ESI-MS** (m/z): calculated: 725.25245 [M]$^+$; experimental: 725.25142 [M]$^+$. **IR** (cm^{-1}): *ν* (PF$_6$) 842 (s).

Analytical data for ***(S,M)*-2c** isomer: **^{1}H NMR:** *δ* 8.27–8.17 (m, 1H, C^9*H*); 8.08–8.03 (m, 1H, C$^{4'}$*H*); 7.97–7.91 (m, 1H, C$^{5'}$*H*); 7.77–7.72 (m, 1H, C^7*H*); 7.72–7.56 (m, 3H, C$^{2'}$*H* + C$^{3'}$*H* + C^8*H*); 7.49–7.39 (m, 2H, C$^{6'}$*H* + C$^{8'}$*H*); 7.39–7.32 (m, 1H, C^4*H*); 7.27–7.20 (m, 1H, C$^{7'}$*H*); 7.20–7.10 (m, 1H, C^6*H*); 7.07 (s, 1H, C^2*H*); 6.73–6.63 (m, 1H, C^5*H*); 4.69 (s, 3H, OC*H*$_3$); 1.96 (d, 15H, $^4J_{\mathrm{HP}}$ = 0.5 Hz, C$_5$(C*H*$_3$)$_5$); 1.37 (d, 9H, $^2J_{\mathrm{HP}}$ = 11.2 Hz, P(C*H*$_3$)$_3$) ppm. **^{31}P{^{1}H} NMR:** *δ* –33.97 (s, *P*(CH$_3$)$_3$); –143.99 (sept, $^1J_{\mathrm{PF}}$ = 711.3 Hz, *P*F$_6$) ppm. **^{13}C{^{1}H} NMR:** *δ* 247.7 (d, $^2J_{\mathrm{CP}}$ = 10.0 Hz, C^1); 173.5 (s, C^3); 166.6 (d, $^2J_{\mathrm{CP}}$ = 9.3 Hz, C^{9a}); 142.0 (d, $^3J_{\mathrm{CP}}$ = 4.5 Hz, C^9); 144.6 (s, $C^{1'}$); 136.8 (s, C^{3b}); 134.8 (s, $C^{4a'}$); 132.9 (s, C^{7a}); 132.7 (s, C^{3a}); 132.0 (s, C^8); 131.1 (s, $C^{8a'}$); 130.5 (s, $C^{4'}$); 129.6 (s, C^7); 129.5 (s, $C^{5'}$); 127.5 (s, $C^{2'}$); 127.3 (s, $C^{7'}$); 127.2 (s, $C^{6'}$); 126.8 (s, C^4); 126.7 (s, $C^{3'}$); 125.9 (s, C^5); 125.7 (s, $C^{8'}$); 125.0 (s, C^6); 123.9 (s, C^2); 101.1 (d, $^2J_{\mathrm{CP}}$ = 1.8 Hz, *C*$_5$(CH$_3$)$_5$); 64.5 (s, O*C*H$_3$); 13.9 (d, $^1J_{\mathrm{CP}}$ = 41.1 Hz, P(*C*H$_3$)$_3$); 9.8 (s, C$_5$(*C*H$_3$)$_5$) ppm.

Analytical data for ***(S,P)*-2c** isomer: **^{1}H NMR:** *δ* 8.27–8.17 (m, 2H, C$^{8'}$*H* + C^9*H*); 8.08–8.03 (m, 1H, C$^{5'}$*H*); 8.03–7.98 (m, 1H, C$^{4'}$*H*); 7.82–7.77 (m, 1H, C^7*H*); 7.72–7.56 (m, 2H, C$^{6'}$*H* + C^8*H*); 7.56–7.49 (m, 1H, C$^{7'}$*H*); 7.49–7.39 (m, 1H, C$^{3'}$*H*); 7.37–7.32 (m, 1H, C^4*H*); 7.20–7.10 (m, 2H, C$^{2'}$*H* + C^6*H*); 7.02 (s, 1H, C^2*H*); 6.73–6.63 (m, 1H, C^5*H*); 4.66 (s, 3H, OC*H*$_3$); 1.91 (d, 15H, $^4J_{\mathrm{HP}}$ = 0.6 Hz, C$_5$(C*H*$_3$)$_5$); 1.42 (d, 9H, $^2J_{\mathrm{HP}}$ = 11.1 Hz, P(C*H*$_3$)$_3$) ppm. **^{31}P{^{1}H} NMR:** *δ* –34.16 (s, *P*(CH$_3$)$_3$); –143.99 (sept, $^1J_{\mathrm{PF}}$ = 711.3 Hz, *P*F$_6$) ppm. **^{13}C{^{1}H} NMR:** *δ* 249.7 (d, $^2J_{\mathrm{CP}}$ = 10.5 Hz, C^1); 173.8 (s, C^3); 167.8 (d, $^2J_{\mathrm{CP}}$ = 8.5 Hz, C^{9a}); 144.5 (s, $C^{1'}$); 142.0 (d, $^3J_{\mathrm{CP}}$ = 5.0 Hz, C^9); 136.8 (s, C^{3b}); 135.3 (s, $C^{4a'}$); 132.74 (s, C^{7a}); 132.66 (s, C^{3a}); 131.6 (s, C^8); 131.1 (s, $C^{8a'}$); 130.1 (s, $C^{4'}$); 129.8 (s, $C^{5'}$); 129.7 (s, C^7); 128.1 (s, $C^{7'}$); 127.7 (s, $C^{2'}$); 127.4 (s, 2C C^4 + $C^{6'}$); 126.4 (s, $C^{3'}$); 126.2 (s, $C^{8'}$); 125.9 (s, C^5); 125.0 (s, C^6); 124.5 (s, C^2); 100.6 (d, $^2J_{\mathrm{CP}}$ = 1.9 Hz, *C*$_5$(CH$_3$)$_5$); 64.8 (s, O*C*H$_3$); 14.3 (d, $^1J_{\mathrm{CP}}$ = 40.7 Hz, P(*C*H$_3$)$_3$); 9.7 (s, C$_5$(*C*H$_3$)$_5$) ppm.

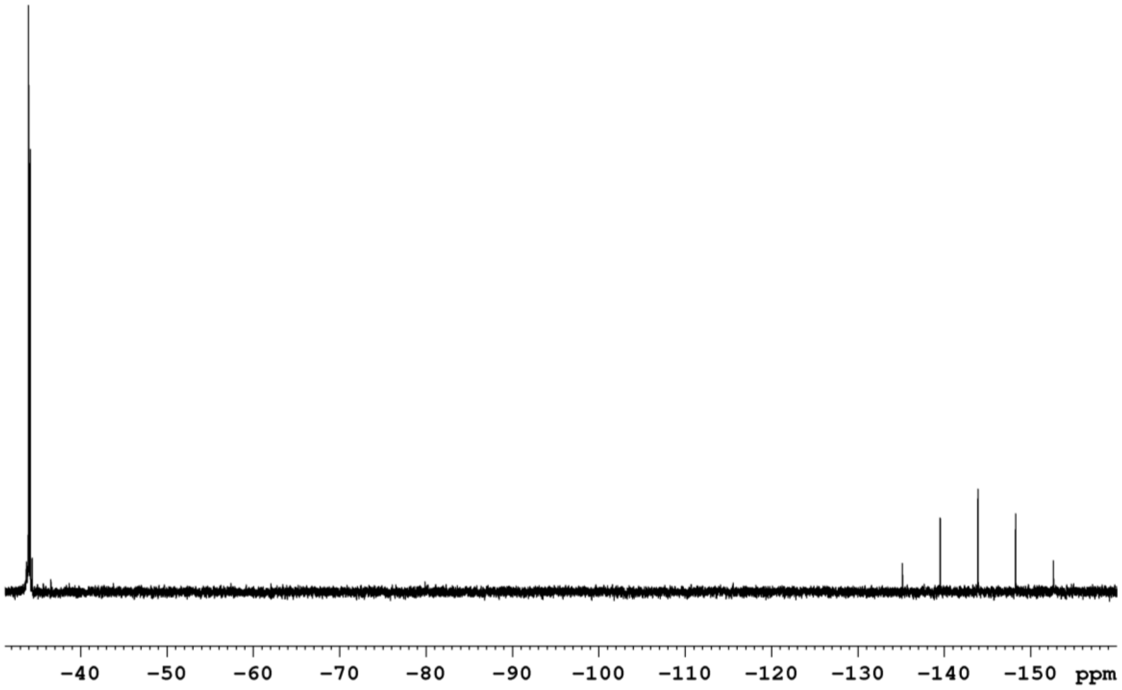


Figure S62. $^{31}P\{^{1}H\}$ NMR spectrum of ***(S,M)*-2c**, ***(S,P)*-2c** mixture.

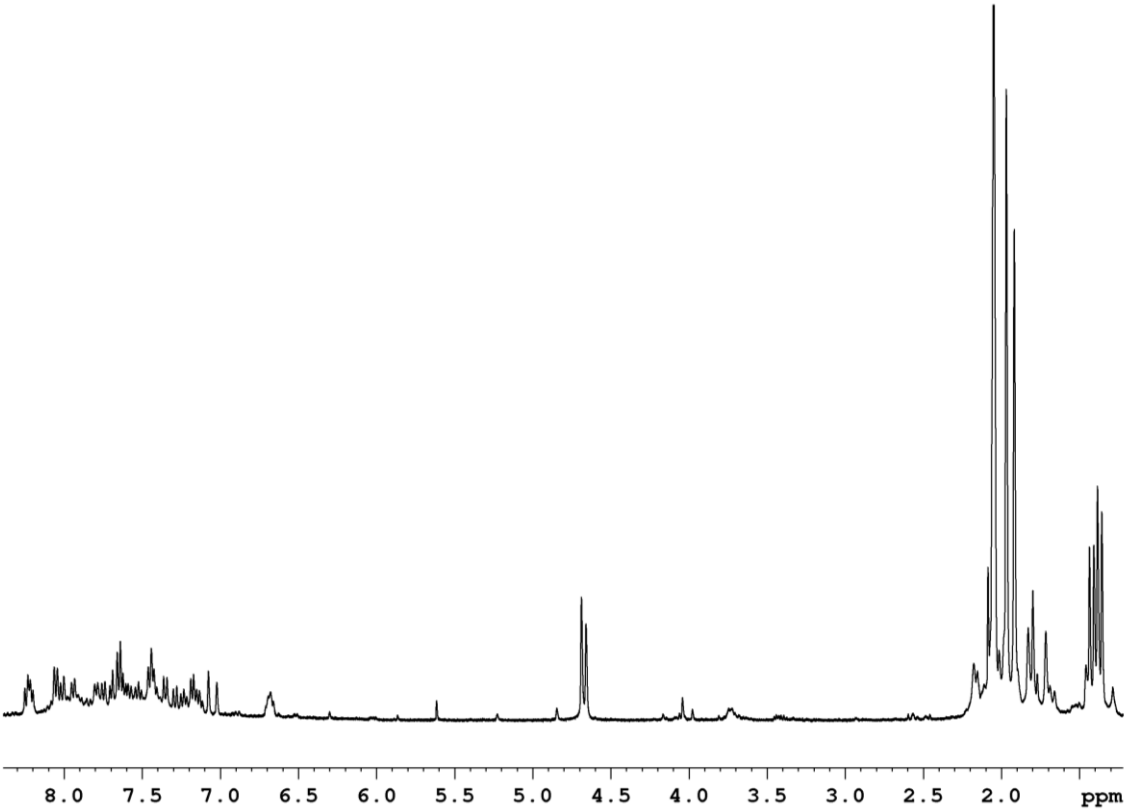


Figure S63. ^{1}H NMR spectrum of ***(S,M)*-2c**, ***(S,P)*-2c** mixture.

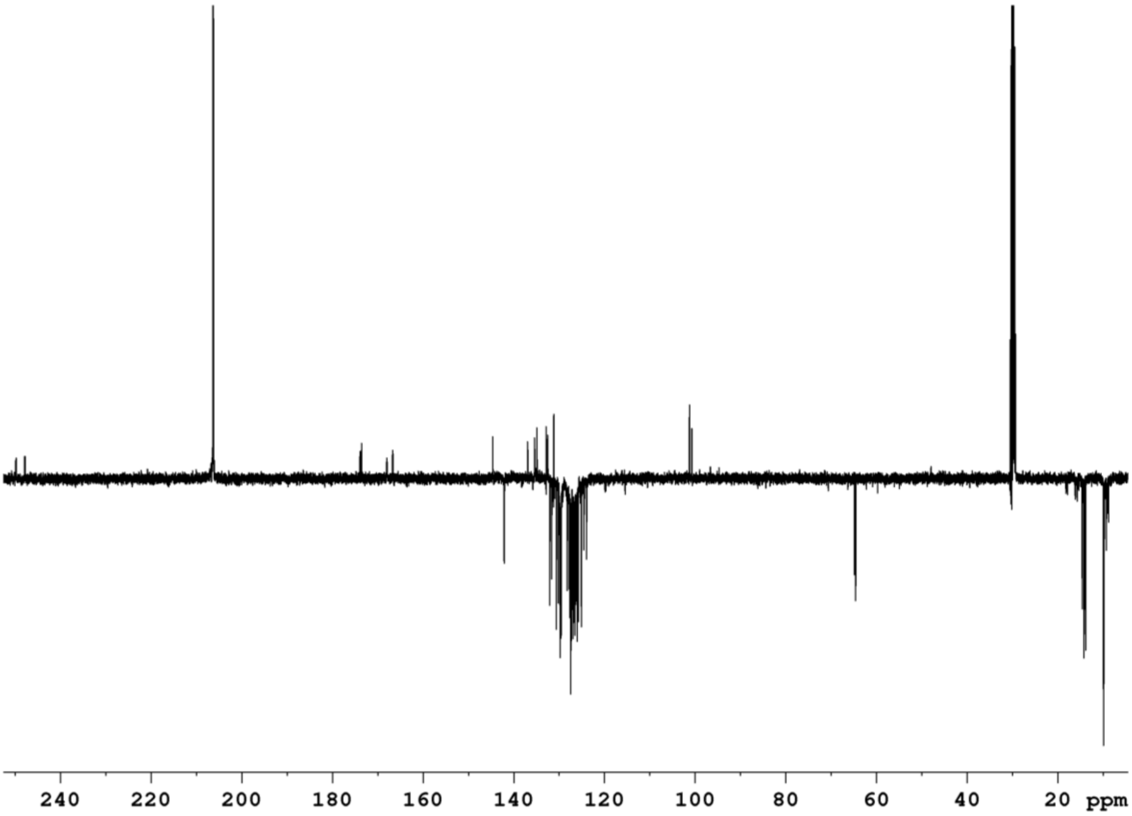


Figure S64. JMOD NMR spectrum of ***(S,M)*-2c**, ***(S,P)*-2c** mixture.

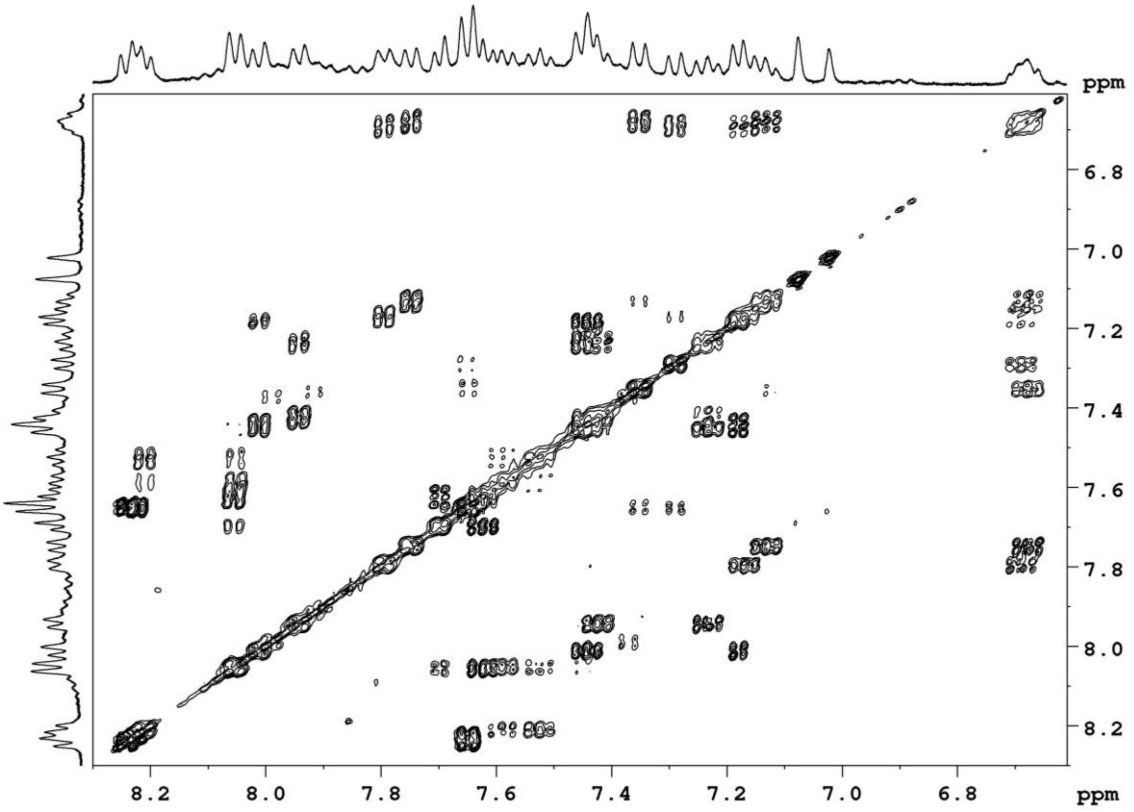


Figure S65. Section of the ^{1}H, ^{1}H COSY NMR spectrum of ***(S,M)*-2c**, ***(S,P)*-2c** mixture.

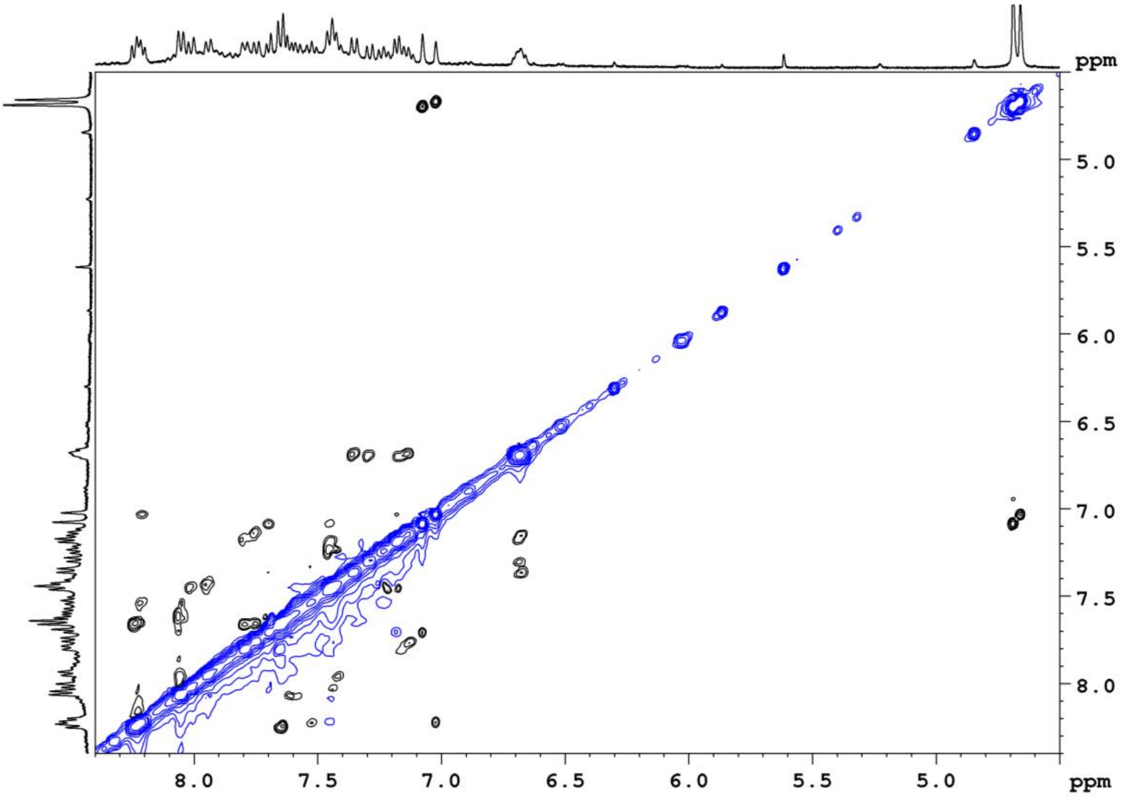


Figure S66. Section of the ^{1}H, ^{1}H NOESY NMR spectrum of ***(S,M)*-2c**, ***(S,P)*-2c** mixture.

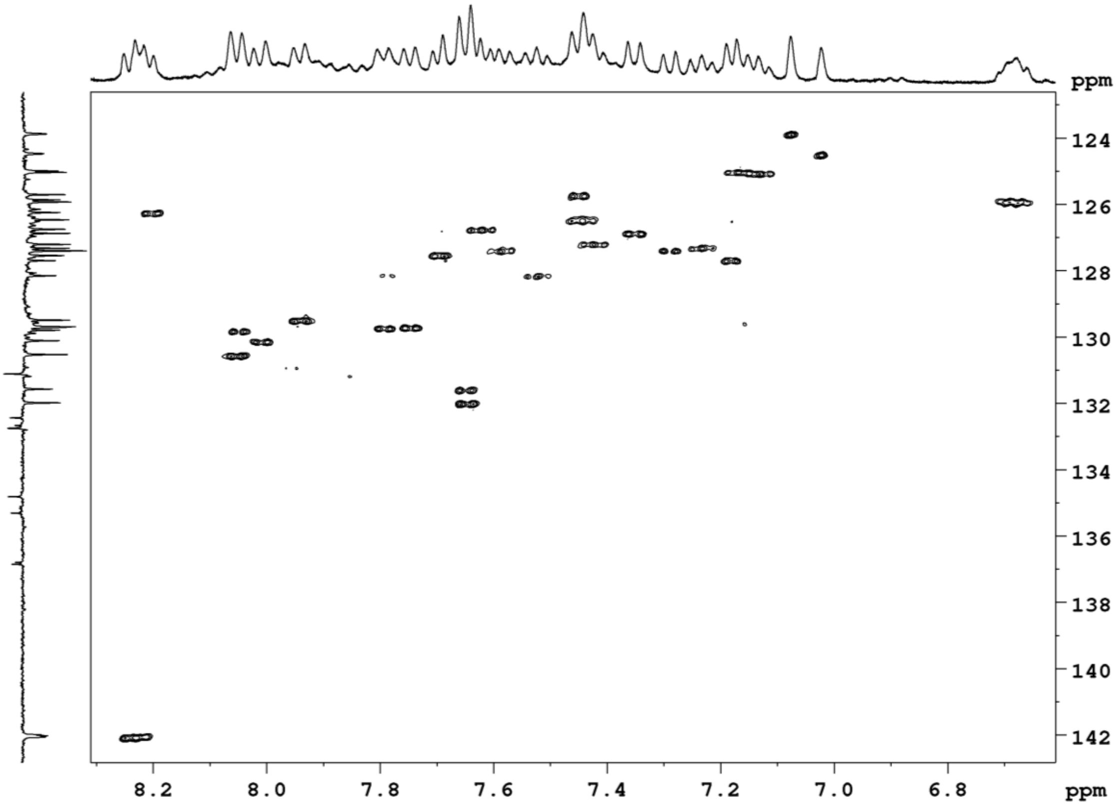


Figure S67. Section of the ^{1}H, ^{13}C HSQC NMR spectrum of ***(S,M)*-2c**, ***(S,P)*-2c** mixture.

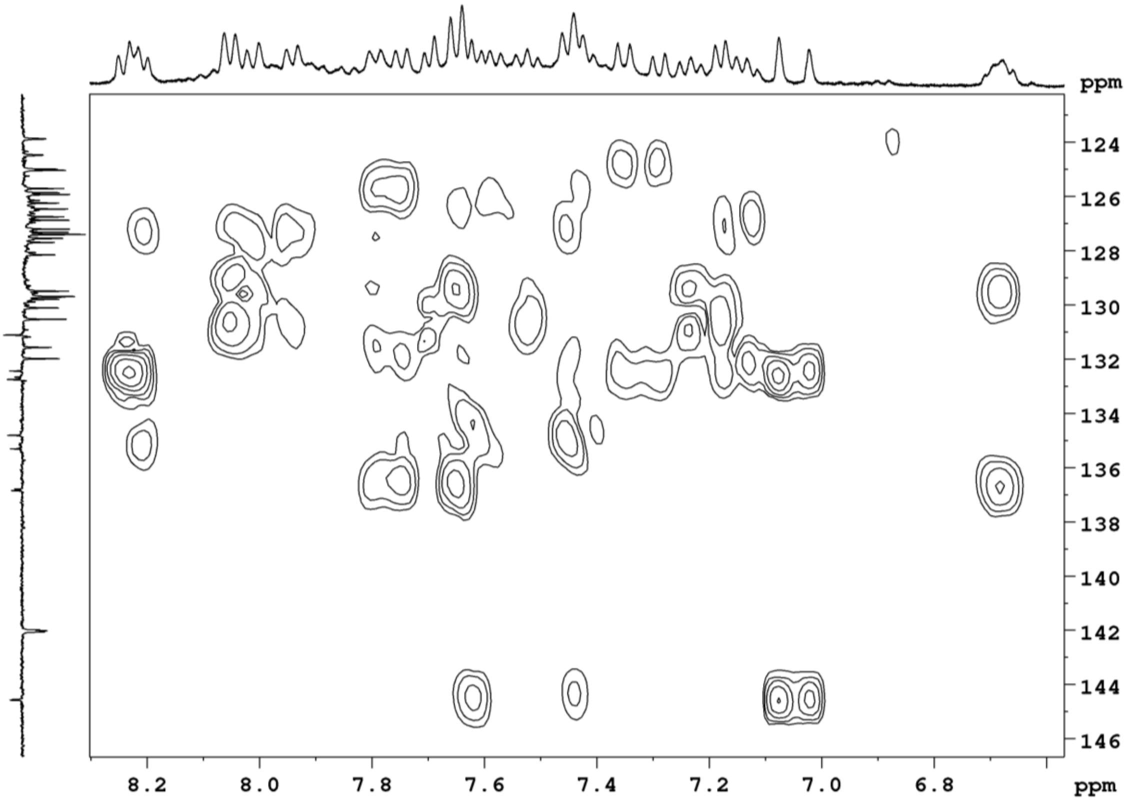


Figure S68. Section of the ^{1}H, ^{13}C HMBC NMR spectrum of ***(S,M)*-2c**, ***(S,P)*-2c** mixture.

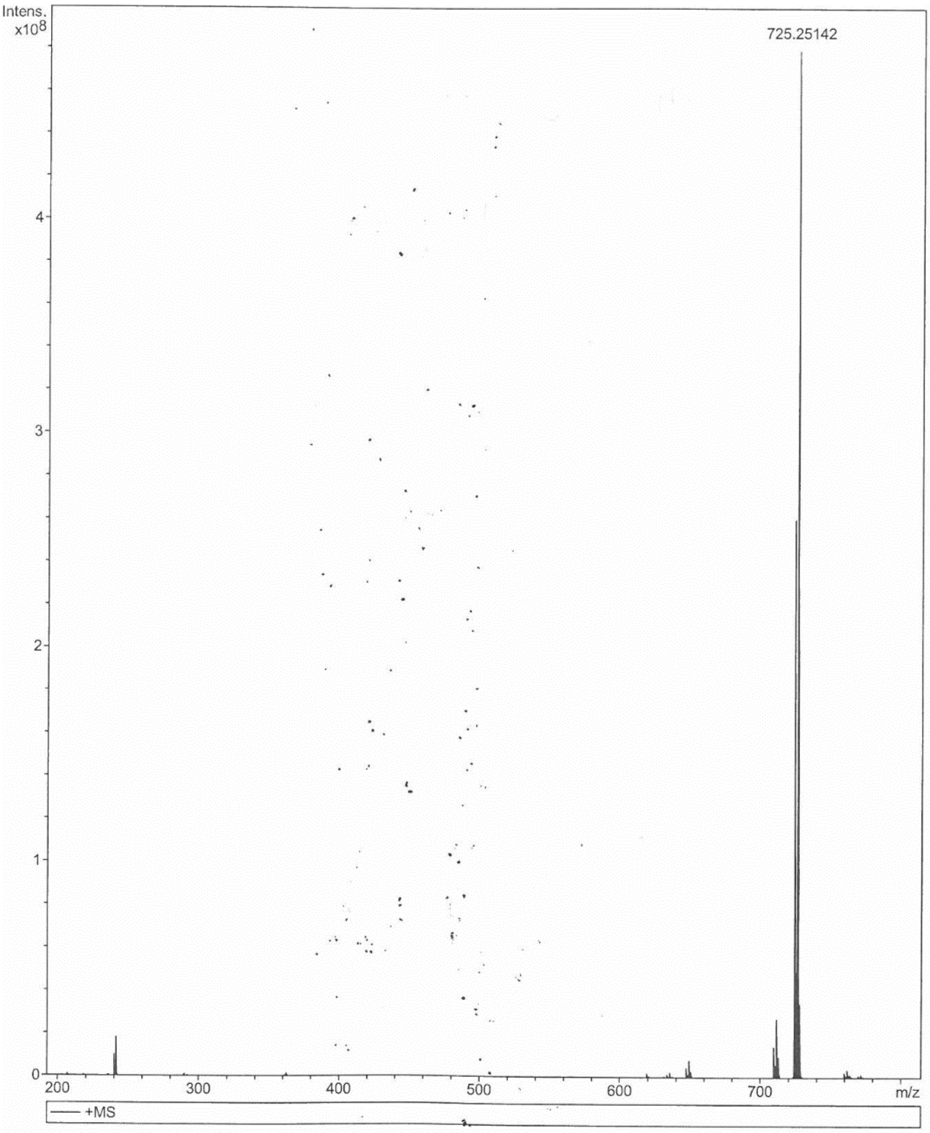


Figure S69. HR-ESI-MS spectrum of ***(S,M)*-2c**, ***(S,P)*-2c** mixture.

Computational Details

General Procedure and Analysis of Data

All calculations were carried out with the GAUSSIAN 09 program package. Structures were optimized at the B3LYP level employing the lanl2dz for iridium atom and 6-31G(d) basis set for other elements in gas phase. Harmonic frequency calculations were performed at the same level to confirm them as local minimums and to obtain energy corrections.

Punctual calculations at MP2 level with the same basis set were performed in order to improve the results. Cartesian coordinates (in Armstrong) and energies (in Hartree) of the optimized structures of the atropisomers are shown below.

With the results obtained, the ΔG between atropisomers is calculated:

Reaction 1. Complexes **2b**: 0.92 kcal mol^{-1} (this value leads to a 78:22 isomer ratio at room temperature)

Reaction 2. Complexes **2c**: 0.35 kcal mol^{-1} (this value leads to a 56:44 isomer ratio at room temperature)

Calculated Anisotropy of the Current-Induced Density (ACID) Figures and CIV values

The ACID figures of the atropisomers are depicted here. Their CIV values have been also calculated. Therefore, isomers **(S,P)-2b** and **(S,M)-2b** present values of 0.052 and 0.050, respectively, while the CIV values of complexes **(S,P)-2c** and **(S,M)-2c** are 0.052 and 0.044, respectively. In addition, the CIV value of complex **2a** is 0.060.

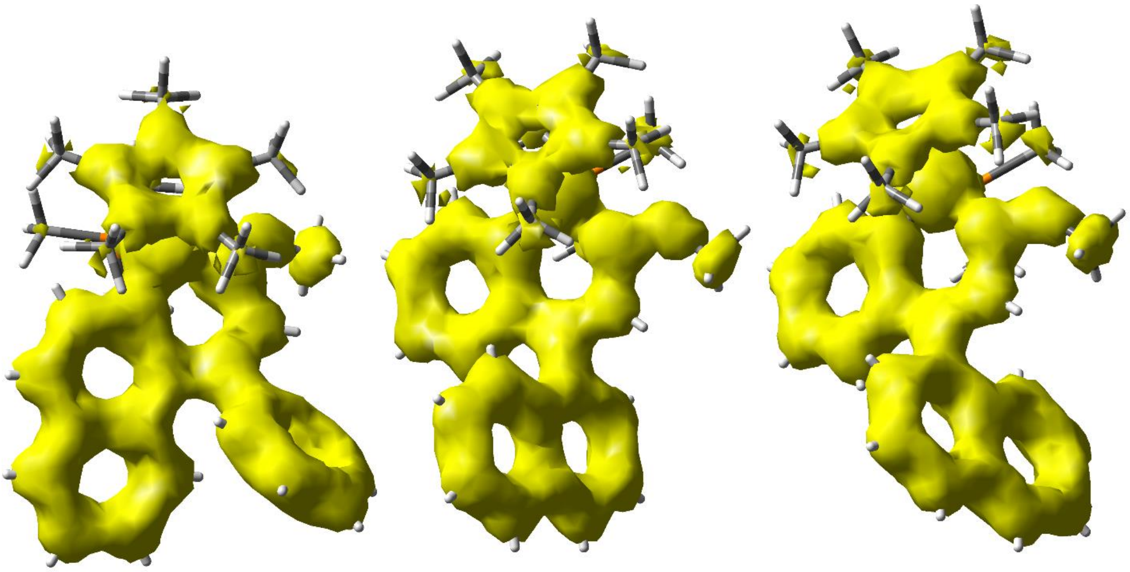


Figure S70. ACID representation for **2a** (left) ***(S,P)*-2b** (middle) and ***(S,M)*-2b** (right).

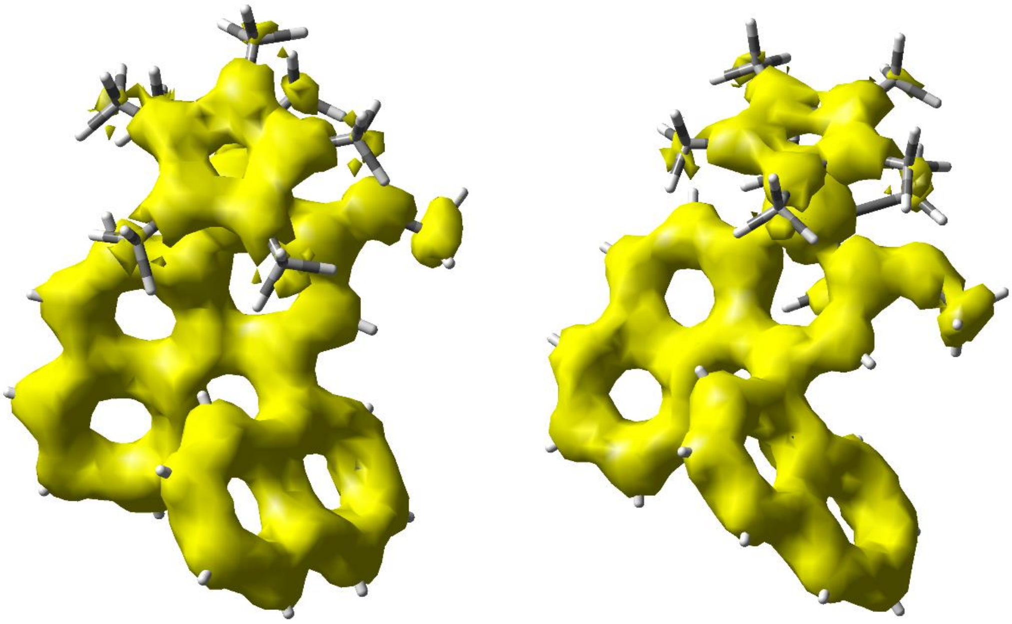


Figure S71. ACID representation for ***(S,P)*-2c** (left) and ***(S,M)*-2c** (right).

The ACID figure for an Iridabenzene presented as example of an aromatic compound by Herges *et al*.[6] with a CIV value of 0.047 and the corresponding figure for 1,1’-binaphthalene (CIV value of 0.071) are also included:

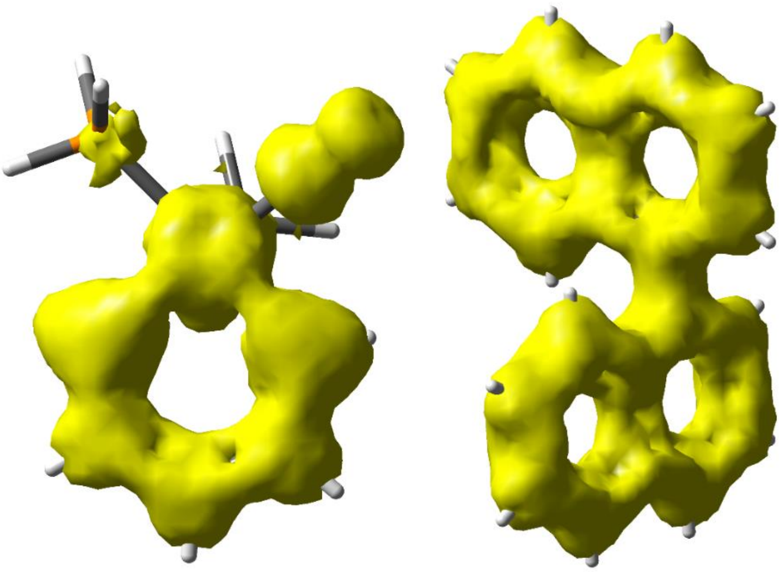


Figure S72. ACID representation for an iridabenzene (left) and 1,1`-binaphthalene (right).

Scan Details

In order to get insight into the barriers between atropisomers, scans at HF level were obtained. As comparison, complete scan for 1,1’-binaphtalene is shown while for **2b** and **2c**, only the smaller barrier is presented. The barriers for **2b** and **2c** are very similar. The lower value in the case of **2c** could be associated to a greater adaptability of the biaryl bond due to the larger aromatic system as compared with **2b**.

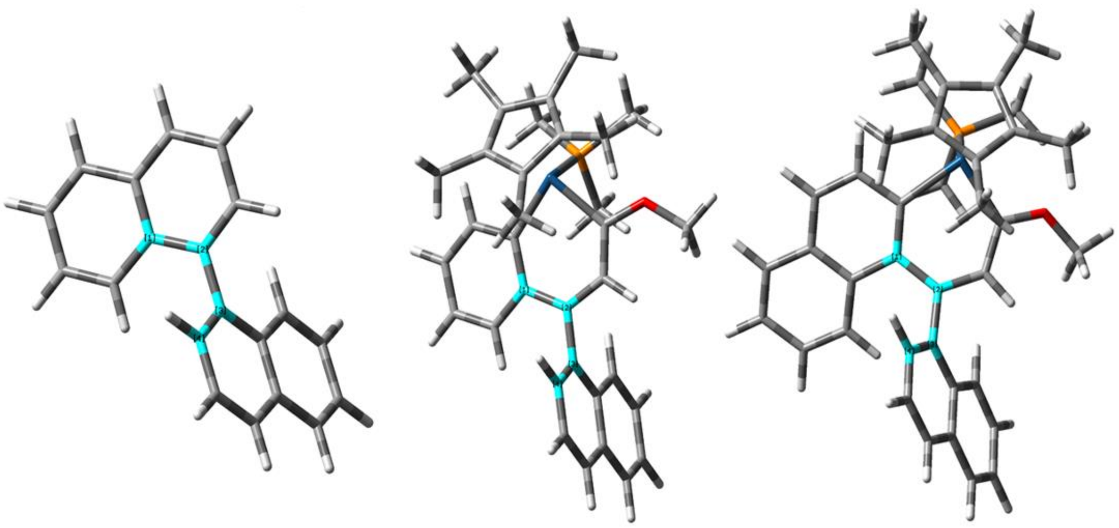


Figure S73. Structures of 1,1’,-binaphtnalene (left), **2b** (center) and **2c** (right) showing the dihedral angle varied during the scan calculation.

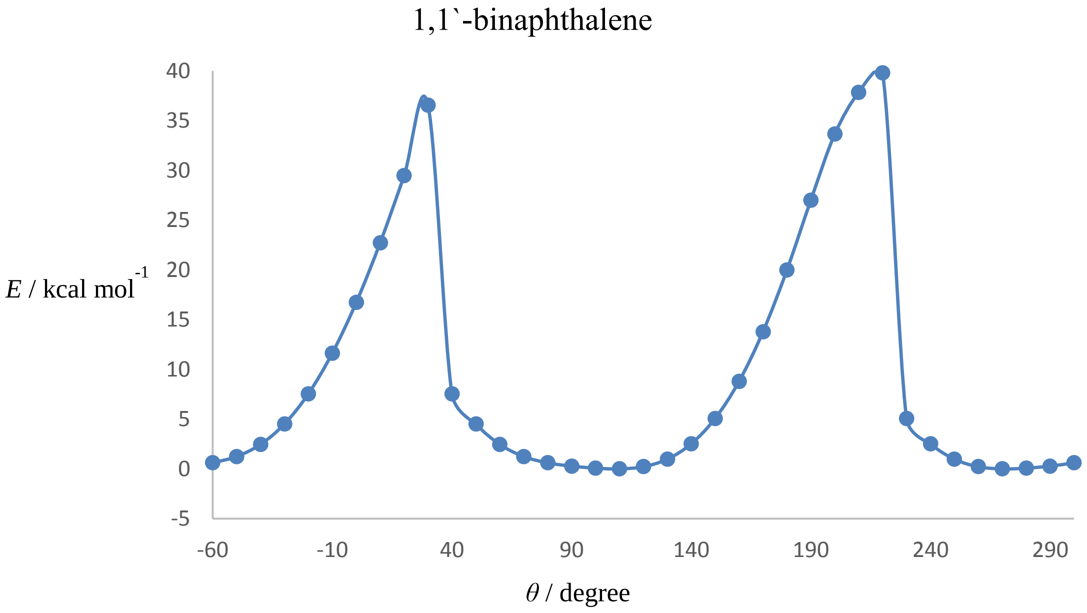


Figure S74. Graphical representation of the energy vs. the dihedral angle for 1,1’,-binaphthalene.

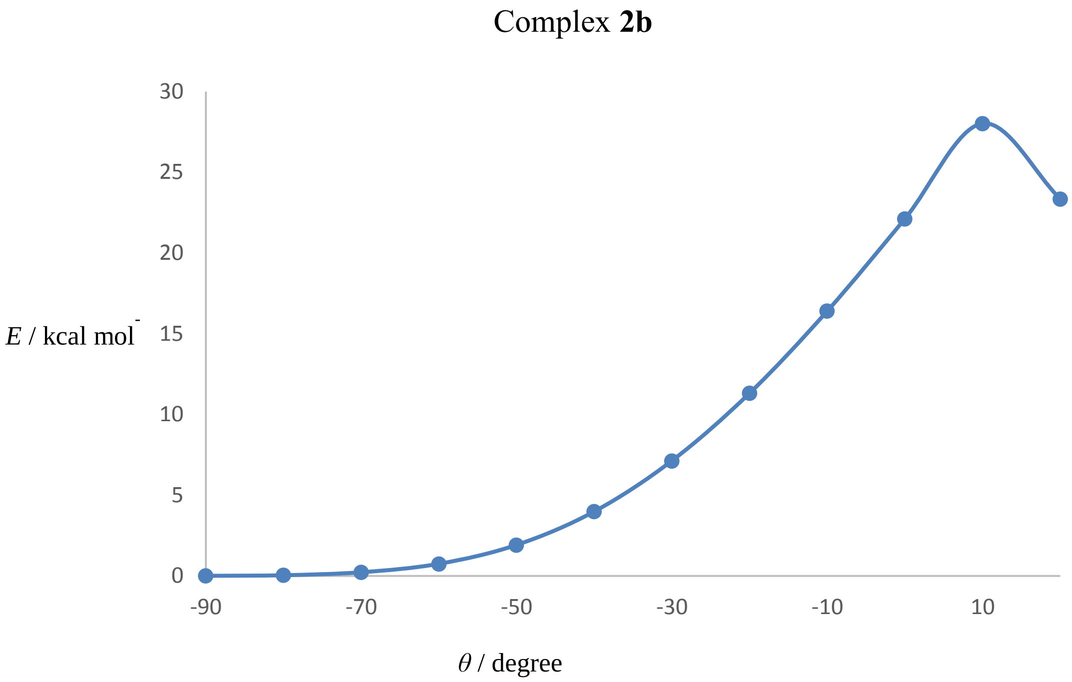


Figure S75. Graphical representation of the energy vs. the torsion angle for **2b**.

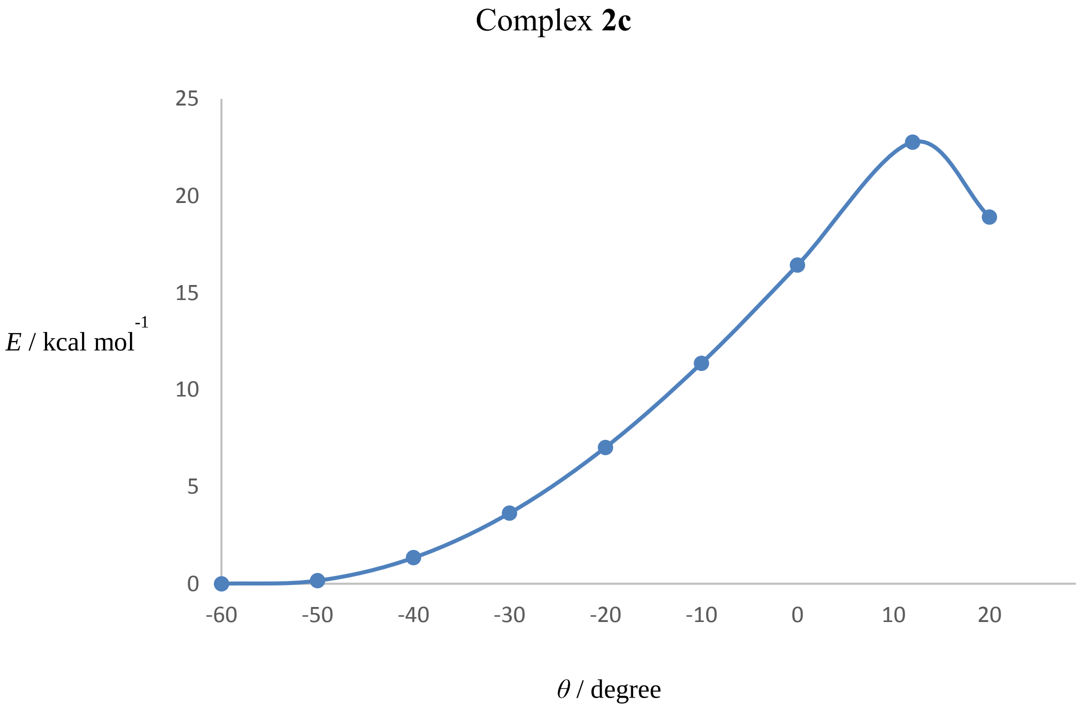


Figure S76. Graphical representation of the energy vs. the torsion angle for **2c**.

XYZ Coordinates and Energy of Atropisomers of 2b and 2c.

Reaction 1, structure **(*S*,*P*)-2b**:

B3LYP Energy=-1802.19414955H

MP2 Energy=-1796.7119632H

C	-2.86420700	-1.65002600	-1.46612200
C	-3.84390500	-0.96869200	-0.70056100
C	-3.78279700	0.45425700	-1.04588800
C	-2.76525900	0.62263300	-2.01896000
C	-2.12262000	-0.66112700	-2.23232900
C	-2.69150300	-3.13647000	-1.56199500
H	-2.91887600	-3.63503500	-0.61818500
H	-1.67426400	-3.40816600	-1.85121800
H	-3.36697000	-3.53885000	-2.32722000
C	-4.91751800	-1.61534800	0.12586900
H	-5.77758500	-1.87523300	-0.50438200
H	-5.28964800	-0.95203200	0.91077700
H	-4.56608000	-2.53670300	0.59580000
C	-4.79371600	1.48674300	-0.63470300
H	-5.20848500	1.28482900	0.35572200
H	-5.63694600	1.49431100	-1.33701400
H	-4.37303200	2.49519100	-0.62397100
C	-2.46718000	1.86473500	-2.80349000
H	-2.84630200	2.76422700	-2.31510900
H	-2.94999400	1.79810100	-3.78658500
H	-1.39630600	1.99752400	-2.97062100
C	-1.12061500	-0.95666700	-3.31205100
H	-0.52091800	-1.83888000	-3.07745100
H	-0.43446900	-0.11977400	-3.46049700
H	-1.62562200	-1.14462400	-4.26811600
C	1.18786700	1.11938000	0.00470200
C	1.76801500	-0.20485400	-0.12786100
C	-0.22357800	1.27795900	-0.03910800
C	1.08285100	-1.38866600	0.13441000
C	3.13966900	-0.40750100	-0.68584500
Ir	-1.67334700	-0.17990000	-0.05470000
C	-0.29218500	-1.51080900	0.39187400
C	3.39146800	0.10897500	-1.94880800
C	4.14277700	-1.20806600	-0.03488200
C	4.58991700	-0.17694600	-2.63596700
C	5.36164000	-1.48774800	-0.74099300
C	5.55053700	-0.96750800	-2.04884500
P	-1.99410300	0.24631000	2.23569700
C	-2.84354700	-1.10342500	3.15523000
H	-2.29781300	-2.03723400	3.00432900
H	-2.88264100	-0.87106000	4.22380100
H	-3.86179300	-1.23411300	2.78355400
C	-2.97428000	1.74620300	2.66310000
H	-3.03631300	1.85996600	3.74974200
H	-2.48974000	2.62848900	2.23842700
H	-3.98538300	1.67192700	2.25736200
C	-0.44925800	0.49125700	3.20498500
H	0.19553800	-0.38458700	3.10348100

H	0.08943000	1.36232100	2.82767900
H	-0.68584700	0.64143300	4.26227200
C	-0.73464200	2.60809700	-0.10578300
C	2.04748800	2.29787100	0.17812900
C	1.47284800	3.60378700	0.06774700
C	0.07045100	3.71910700	-0.10603300
H	-0.36671600	4.71140100	-0.19168700
H	-1.80833800	2.74588200	-0.17225900
H	1.66921600	-2.29717000	0.05128700
O	-0.77035400	-2.68965900	0.82515700
C	0.09845900	-3.80381600	1.12630200
H	-0.54517100	-4.55453100	1.58369300
H	0.54173100	-4.20941200	0.21224900
H	0.88708000	-3.50968300	1.82372100
H	6.47417700	-1.19546100	-2.57344200
C	4.02386400	-1.67975100	1.30308300
C	6.36859100	-2.26668400	-0.10880500
C	6.20643100	-2.73030400	1.17624400
H	6.98631700	-3.31900500	1.64903200
C	5.02629700	-2.42024400	1.89146800
H	4.91458500	-2.76119000	2.91655400
H	7.28082600	-2.47935500	-0.65925700
H	3.13491900	-1.43493900	1.87455000
H	2.63800900	0.72590600	-2.42822500
H	4.74287800	0.22616000	-3.63205300
C	2.27529300	4.76568500	0.20207500
C	3.41829400	2.24315000	0.54415300
C	4.17674500	3.38876500	0.69657500
C	3.61559400	4.66612600	0.49872300
H	4.22704000	5.55613200	0.60785500
H	1.80219200	5.73749400	0.09013700
H	5.22055100	3.29792400	0.98199200
H	3.89314200	1.29222800	0.73465000

Structure **(*S,M*)-2b**:

B3LYP Energy=-1802.19393197H

MP2 Energy=-1796.7102541H

1 1

C	2.89549000	-1.88217000	1.02560600
C	3.73301300	-0.73777900	1.07486300
C	3.10116400	0.26296100	1.93258000
C	1.88163500	-0.29058400	2.41302000
C	1.70109000	-1.59266200	1.80612900
C	3.22891100	-3.20427300	0.39954100
H	3.85378100	-3.08959000	-0.48833500
H	2.33050700	-3.74966600	0.10500400
H	3.77423900	-3.83219400	1.11514400
C	5.12960900	-0.64074700	0.53339700
H	5.85151200	-0.92210900	1.31060700
H	5.38397000	0.37543200	0.21990300

H	5.28728400	-1.31273600	-0.31297500
C	3.76288200	1.51615600	2.43229100
H	4.41325400	1.96866400	1.67986700
H	4.38880300	1.29615600	3.30659100
H	3.03445100	2.26981400	2.74142200
C	0.97963800	0.30568500	3.45126000
H	1.02339500	1.39605500	3.46104500
H	1.28148400	-0.04712600	4.44539900
H	-0.06148800	0.01386000	3.29962700
C	0.63802600	-2.58589900	2.18123700
H	0.47823400	-3.32547100	1.39339700
H	-0.32096900	-2.10080000	2.37690600
H	0.92575300	-3.13073100	3.08924700
C	-1.32241000	0.84354800	-0.34679500
C	-1.64706600	-0.47116700	-0.87811400
C	-0.01746700	1.09118600	0.15873200
C	-0.69526400	-1.36307600	-1.36606200
C	-3.03862600	-1.01415100	-0.92508300
Ir	1.64339000	-0.11938800	0.06405800
C	0.70032600	-1.23506500	-1.25946700
C	-3.52796100	-1.50620200	-2.12904700
C	-3.84515300	-1.12796700	0.26313500
C	-4.81971400	-2.06339100	-2.23412600
C	-5.15047000	-1.71593400	0.14799600
C	-5.61612600	-2.16177500	-1.11727300
P	2.44411900	1.25756100	-1.65957900
C	3.68004800	0.43771000	-2.74970600
H	3.24497900	-0.47367000	-3.16419800
H	3.97835100	1.10597800	-3.56313100
H	4.56365400	0.16474200	-2.16949800
C	3.28795700	2.81372500	-1.15421900
H	3.61760100	3.36738600	-2.03858500
H	2.59916900	3.43691500	-0.57991300
H	4.15821900	2.58685700	-0.53464600
C	1.16596000	1.84739800	-2.84273800
H	0.62849600	0.99111600	-3.25685100
H	0.44892200	2.48500800	-2.32243700
H	1.63040100	2.41148900	-3.65673900
C	0.19793400	2.31671900	0.85721400
C	-2.32799900	1.91414400	-0.31734400
C	-2.05306200	3.11085200	0.41864800
C	-0.78049300	3.26324200	1.02460800
H	-0.57462800	4.16941100	1.58992900
H	1.17715100	2.50499700	1.28426400
H	-1.09037700	-2.27818400	-1.79469900
O	1.48404300	-2.06203600	-1.96962100
C	0.94119400	-2.99846400	-2.92651300
H	1.80505400	-3.41537500	-3.44309500
H	0.39614500	-3.80010700	-2.41977400
H	0.28419300	-2.49272200	-3.63907700
H	-6.61234100	-2.58973000	-1.18585000
C	-3.40516300	-0.73013300	1.55565000
C	-5.95733300	-1.85592500	1.30977600
C	-5.50295700	-1.44806500	2.54190800
H	-6.12831300	-1.56147100	3.42193700
C	-4.21174800	-0.88402800	2.66206300

H	-3.85380400	-0.56809800	3.63751600
H	-6.94336900	-2.30001200	1.20493500
H	-2.42106900	-0.29120900	1.67034100
H	-2.91974500	-1.41413100	-3.02411700
H	-5.17757000	-2.40750200	-3.19934900
C	-3.00790300	4.15646800	0.49261500
C	-3.54896500	1.88966500	-1.04072900
C	-4.45705200	2.93038600	-0.97286500
H	-5.37626100	2.86772200	-1.54765600
C	-4.20438600	4.06825600	-0.18228800
H	-4.93176400	4.87197500	-0.12904300
H	-2.76421600	5.03974100	1.07675200
H	-3.78359900	1.05321700	-1.68105100

Reaction 2, structure **(*S*,*P*)-2c**:

B3LYP Energy=-1955.82643201H

MP2 Energy=-1949.8766205H

1 1

C	-2.86420700	-1.65002600	-1.46612200
C	-3.84390500	-0.96869200	-0.70056100
C	-3.78279700	0.45425700	-1.04588800
C	-2.76525900	0.62263300	-2.01896000
C	-2.12262000	-0.66112700	-2.23232900
C	-2.69150300	-3.13647000	-1.56199500
H	-2.91887600	-3.63503500	-0.61818500
H	-1.67426400	-3.40816600	-1.85121800
H	-3.36697000	-3.53885000	-2.32722000
C	-4.91751800	-1.61534800	0.12586900
H	-5.77758500	-1.87523300	-0.50438200
H	-5.28964800	-0.95203200	0.91077700
H	-4.56608000	-2.53670300	0.59580000
C	-4.79371600	1.48674300	-0.63470300
H	-5.20848500	1.28482900	0.35572200
H	-5.63694600	1.49431100	-1.33701400
H	-4.37303200	2.49519100	-0.62397100
C	-2.46718000	1.86473500	-2.80349000
H	-2.84630200	2.76422700	-2.31510900
H	-2.94999400	1.79810100	-3.78658500
H	-1.39630600	1.99752400	-2.97062100
C	-1.12061500	-0.95666700	-3.31205100
H	-0.52091800	-1.83888000	-3.07745100
H	-0.43446900	-0.11977400	-3.46049700
H	-1.62562200	-1.14462400	-4.26811600
C	1.18786700	1.11938000	0.00470200
C	1.76801500	-0.20485400	-0.12786100
C	-0.22357800	1.27795900	-0.03910800
C	1.08285100	-1.38866600	0.13441000
C	3.13966900	-0.40750100	-0.68584500
Ir	-1.67334700	-0.17990000	-0.05470000
C	-0.29218500	-1.51080900	0.39187400

C	3.39146800	0.10897500	-1.94880800
C	4.14277700	-1.20806600	-0.03488200
C	4.58991700	-0.17694600	-2.63596700
C	5.36164000	-1.48774800	-0.74099300
C	5.55053700	-0.96750800	-2.04884500
P	-1.99410300	0.24631000	2.23569700
C	-2.84354700	-1.10342500	3.15523000
H	-2.29781300	-2.03723400	3.00432900
H	-2.88264100	-0.87106000	4.22380100
H	-3.86179300	-1.23411300	2.78355400
C	-2.97428000	1.74620300	2.66310000
H	-3.03631300	1.85996600	3.74974200
H	-2.48974000	2.62848900	2.23842700
H	-3.98538300	1.67192700	2.25736200
C	-0.44925800	0.49125700	3.20498500
H	0.19553800	-0.38458700	3.10348100
H	0.08943000	1.36232100	2.82767900
H	-0.68584700	0.64143300	4.26227200
C	-0.73464200	2.60809700	-0.10578300
C	2.04748800	2.29787100	0.17812900
C	1.47284800	3.60378700	0.06774700
C	0.07045100	3.71910700	-0.10603300
H	-0.36671600	4.71140100	-0.19168700
H	-1.80833800	2.74588200	-0.17225900
H	1.66921600	-2.29717000	0.05128700
O	-0.77035400	-2.68965900	0.82515700
C	0.09845900	-3.80381600	1.12630200
H	-0.54517100	-4.55453100	1.58369300
H	0.54173100	-4.20941200	0.21224900
H	0.88708000	-3.50968300	1.82372100
H	6.47417700	-1.19546100	-2.57344200
C	4.02386400	-1.67975100	1.30308300
C	6.36859100	-2.26668400	-0.10880500
C	6.20643100	-2.73030400	1.17624400
H	6.98631700	-3.31900500	1.64903200
C	5.02629700	-2.42024400	1.89146800
H	4.91458500	-2.76119000	2.91655400
H	7.28082600	-2.47935500	-0.65925700
H	3.13491900	-1.43493900	1.87455000
H	2.63800900	0.72590600	-2.42822500
H	4.74287800	0.22616000	-3.63205300
C	2.27529300	4.76568500	0.20207500
C	3.41829400	2.24315000	0.54415300
C	4.17674500	3.38876500	0.69657500
C	3.61559400	4.66612600	0.49872300
H	4.22704000	5.55613200	0.60785500
H	1.80219200	5.73749400	0.09013700
H	5.22055100	3.29792400	0.98199200
H	3.89314200	1.29222800	0.73465000

(*S*,*M*)-2c:

B3LYP Energy=-1802,19414955H

MP2 Energy=-1796,7119632H

1 1

C	2.89549000	-1.88217000	1.02560600
C	3.73301300	-0.73777900	1.07486300
C	3.10116400	0.26296100	1.93258000
C	1.88163500	-0.29058400	2.41302000
C	1.70109000	-1.59266200	1.80612900
C	3.22891100	-3.20427300	0.39954100
H	3.85378100	-3.08959000	-0.48833500
H	2.33050700	-3.74966600	0.10500400
H	3.77423900	-3.83219400	1.11514400
C	5.12960900	-0.64074700	0.53339700
H	5.85151200	-0.92210900	1.31060700
H	5.38397000	0.37543200	0.21990300
H	5.28728400	-1.31273600	-0.31297500
C	3.76288200	1.51615600	2.43229100
H	4.41325400	1.96866400	1.67986700
H	4.38880300	1.29615600	3.30659100
H	3.03445100	2.26981400	2.74142200
C	0.97963800	0.30568500	3.45126000
H	1.02339500	1.39605500	3.46104500
H	1.28148400	-0.04712600	4.44539900
H	-0.06148800	0.01386000	3.29962700
C	0.63802600	-2.58589900	2.18123700
H	0.47823400	-3.32547100	1.39339700
H	-0.32096900	-2.10080000	2.37690600
H	0.92575300	-3.13073100	3.08924700
C	-1.32241000	0.84354800	-0.34679500
C	-1.64706600	-0.47116700	-0.87811400
C	-0.01746700	1.09118600	0.15873200
C	-0.69526400	-1.36307600	-1.36606200
C	-3.03862600	-1.01415100	-0.92508300
Ir	1.64339000	-0.11938800	0.06405800
C	0.70032600	-1.23506500	-1.25946700
C	-3.52796100	-1.50620200	-2.12904700
C	-3.84515300	-1.12796700	0.26313500
C	-4.81971400	-2.06339100	-2.23412600
C	-5.15047000	-1.71593400	0.14799600
C	-5.61612600	-2.16177500	-1.11727300
P	2.44411900	1.25756100	-1.65957900
C	3.68004800	0.43771000	-2.74970600
H	3.24497900	-0.47367000	-3.16419800
H	3.97835100	1.10597800	-3.56313100
H	4.56365400	0.16474200	-2.16949800
C	3.28795700	2.81372500	-1.15421900
H	3.61760100	3.36738600	-2.03858500
H	2.59916900	3.43691500	-0.57991300
H	4.15821900	2.58685700	-0.53464600
C	1.16596000	1.84739800	-2.84273800
H	0.62849600	0.99111600	-3.25685100

H	0.44892200	2.48500800	-2.32243700
H	1.63040100	2.41148900	-3.65673900
C	0.19793400	2.31671900	0.85721400
C	-2.32799900	1.91414400	-0.31734400
C	-2.05306200	3.11085200	0.41864800
C	-0.78049300	3.26324200	1.02460800
H	-0.57462800	4.16941100	1.58992900
H	1.17715100	2.50499700	1.28426400
H	-1.09037700	-2.27818400	-1.79469900
O	1.48404300	-2.06203600	-1.96962100
C	0.94119400	-2.99846400	-2.92651300
H	1.80505400	-3.41537500	-3.44309500
H	0.39614500	-3.80010700	-2.41977400
H	0.28419300	-2.49272200	-3.63907700
H	-6.61234100	-2.58973000	-1.18585000
C	-3.40516300	-0.73013300	1.55565000
C	-5.95733300	-1.85592500	1.30977600
C	-5.50295700	-1.44806500	2.54190800
H	-6.12831300	-1.56147100	3.42193700
C	-4.21174800	-0.88402800	2.66206300
H	-3.85380400	-0.56809800	3.63751600
H	-6.94336900	-2.30001200	1.20493500
H	-2.42106900	-0.29120900	1.67034100
H	-2.91974500	-1.41413100	-3.02411700
H	-5.17757000	-2.40750200	-3.19934900
C	-3.00790300	4.15646800	0.49261500
C	-3.54896500	1.88966500	-1.04072900
C	-4.45705200	2.93038600	-0.97286500
H	-5.37626100	2.86772200	-1.54765600
C	-4.20438600	4.06825600	-0.18228800
H	-4.93176400	4.87197500	-0.12904300
H	-2.76421600	5.03974100	1.07675200
H	-3.78359900	1.05321700	-1.68105100

References

[1] D. D. Perrin, W. L. F. Armarego, *Purification of Laboratory Chemicals*, Butterworth/Heinemann, London/Oxford, *3rd ed*, **1988**.

[2] S. Tartaglia, F. Pace, P. Scafato, C. Rosini, *Org. Lett.*, **2008**, *10*, 3421–3424.

[3] M. Talavera, S. Bolaño, J. Bravo, J. Castro, S. García–Fontán, J. M. Hermida–Ramón, *Organometallics*, **2013**, *32*, 4058–4060.

[4] N. Mantovani, M. Bragnati, L. Gonsalvi, E. Grigiotti, F. Laschi, L. Marvelli, M. Peruzzini, G. Reginato, R. Rossi, P. Zanello, *Organometallics* **2005**, *24*, 405–418.

[5] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, 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, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox *Gaussian 09*, Gaussian, Inc.: Wallingford CT, 2016.

[6] D. Geuenich, K. Hess, F. Köhler, R. Herges, *Chem. Rev.* **2005**, *105*, 3758−3772.