Supporting Information

Identifying and Rationalizing the Conditions for the Isomerization of 1,5-Cyclooctadiene in Iridium Complexes by Experimental and Theoretical Mechanistic Studies

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Contents

1. NMR spectra

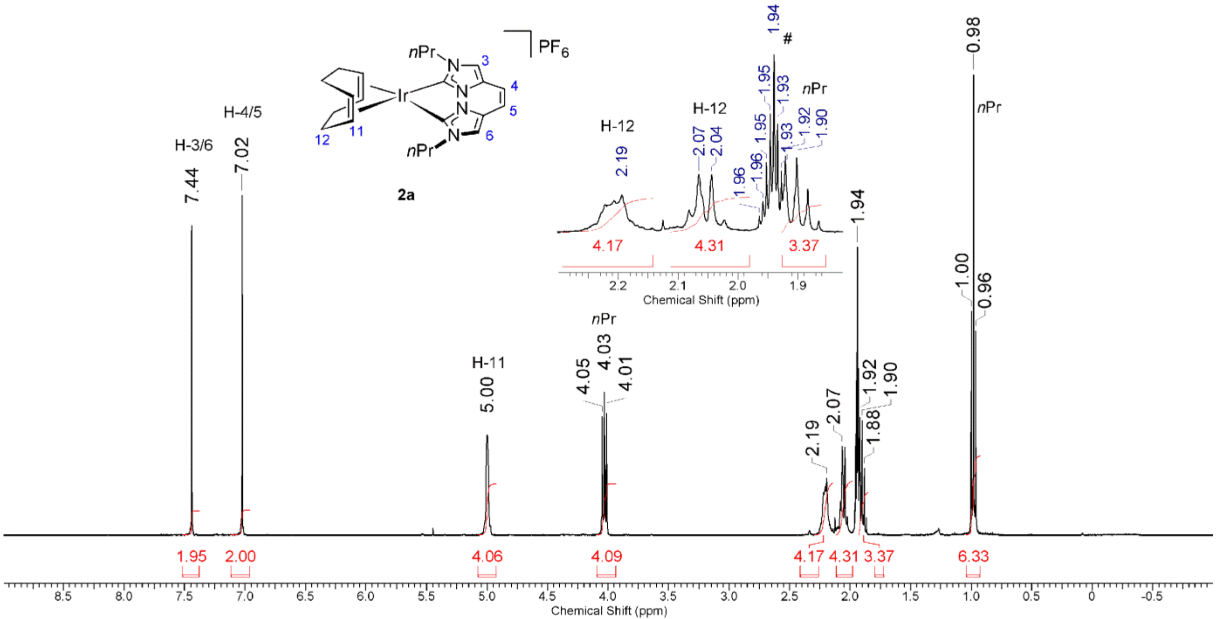

Figure S1. ^{1}H NMR spectrum (400.11 MHz, CD_3CN) of complex **2a** (# solvent).

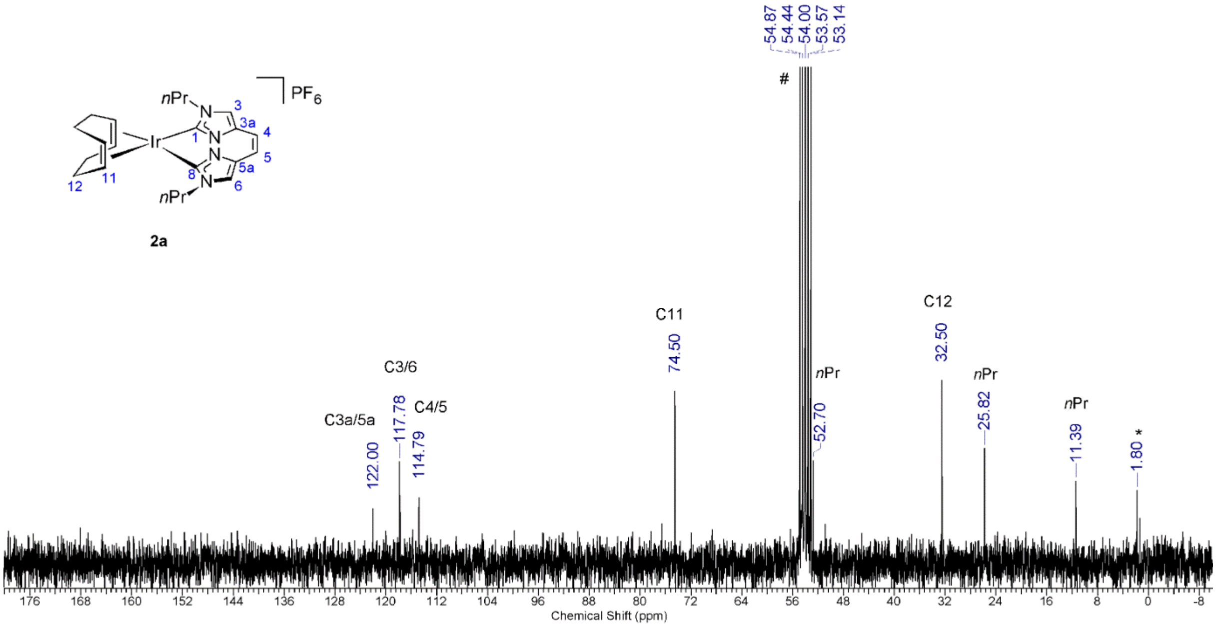

Figure S2. $^{13}C\{^1H\}$ NMR spectrum (62.90 MHz, CD_2Cl_2) of complex **2a** (# solvent). C1/8 was detected by a HMBC experiment (Figure S3).

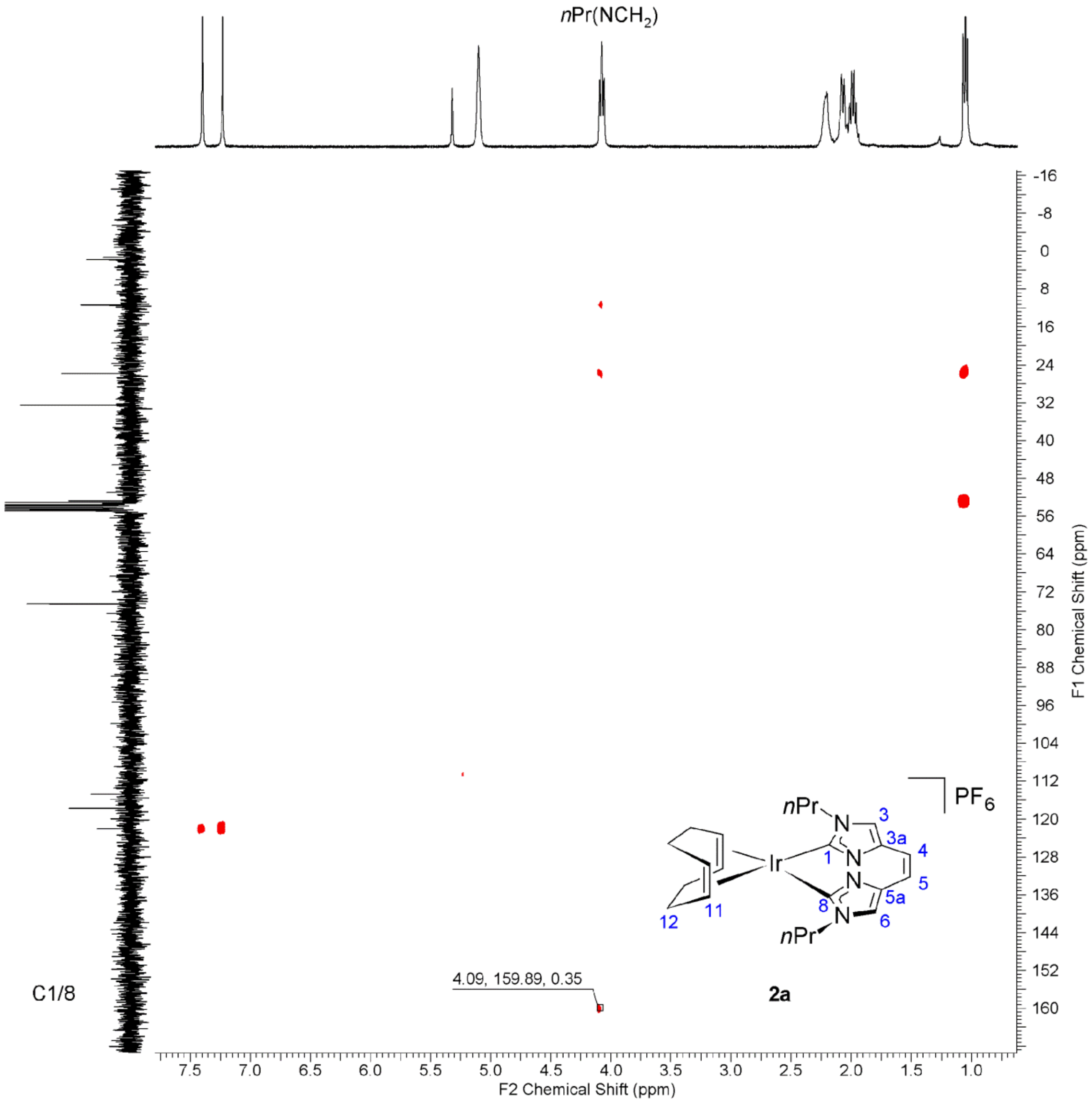

Figure S3. ^{1}H-^{13}C-HMBC NMR spectrum (400.11 MHz/100.62 MHz, CD_2Cl_2) of complex **2a** for detection of C1/8.

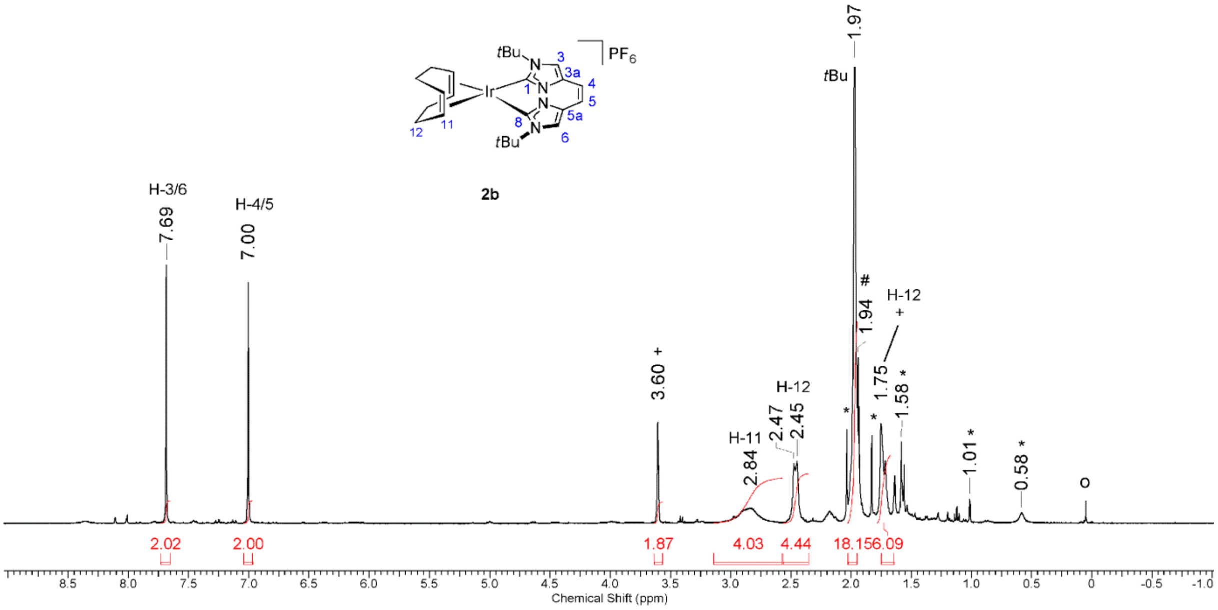

Figure S4. ^{1}H NMR spectrum (400.11 MHz, CD_3CN) of complex **2b** generated *in situ* from vegi^{tBu}·$2HPF_6$ (**1b**), *n*BuLi and $[Ir(\mu\text{-}Cl)(1,5\text{-}cod)]_2$ (# solvent, + thf, o grease, * unknown impurity).

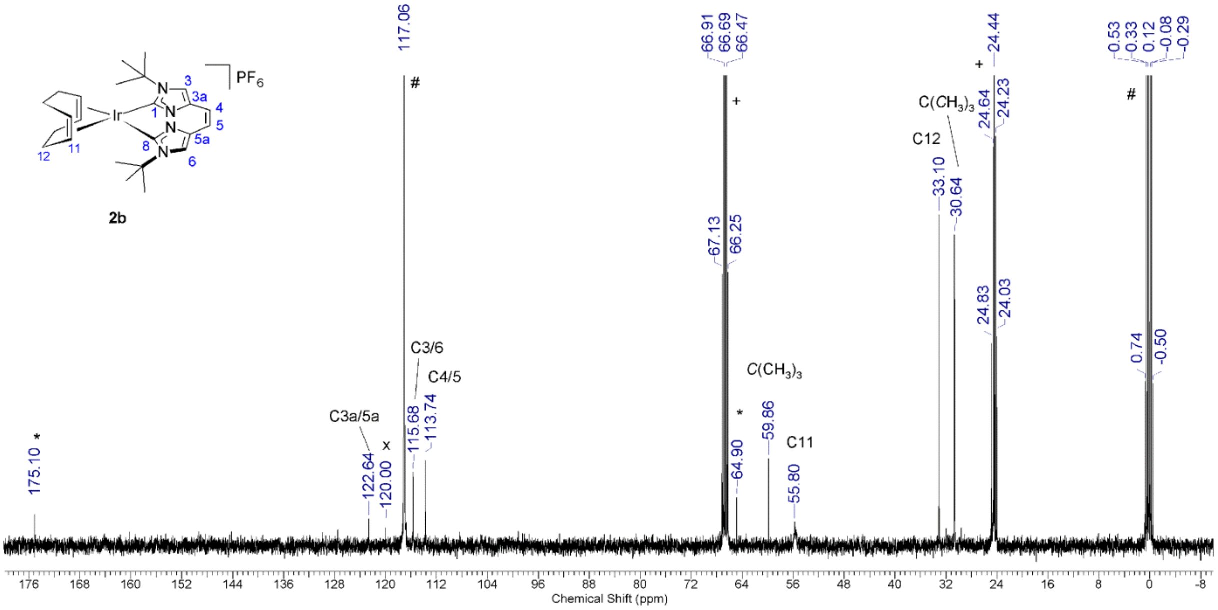

Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum (100.61 MHz, CD_3CN) of complex **2b** generated *in situ* from vegi^{tBu}·$2HPF_6$ (**1b**), *n*BuLi and $[Ir(\mu\text{-}Cl)(1,5\text{-}cod)]_2$ (# solvent, + thf-d_8, ^{x} offset, * unknown impurity). C1/8 could not be detected.

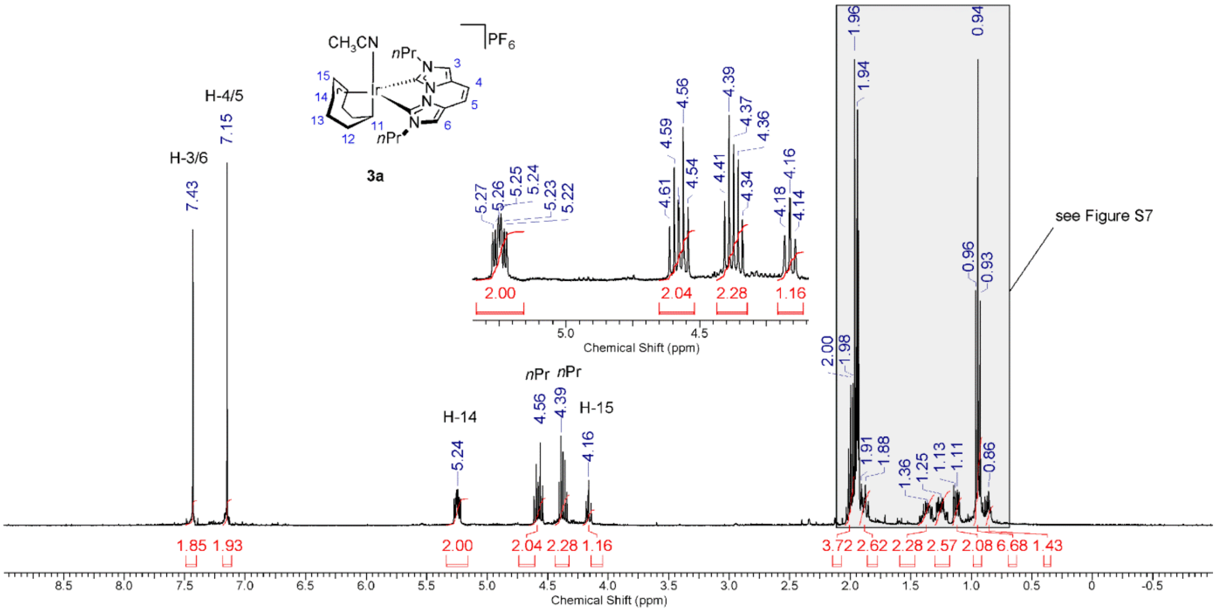

Figure S6. ^{1}H NMR spectrum (400.11 MHz, CD_3CN) of complex **3a**.

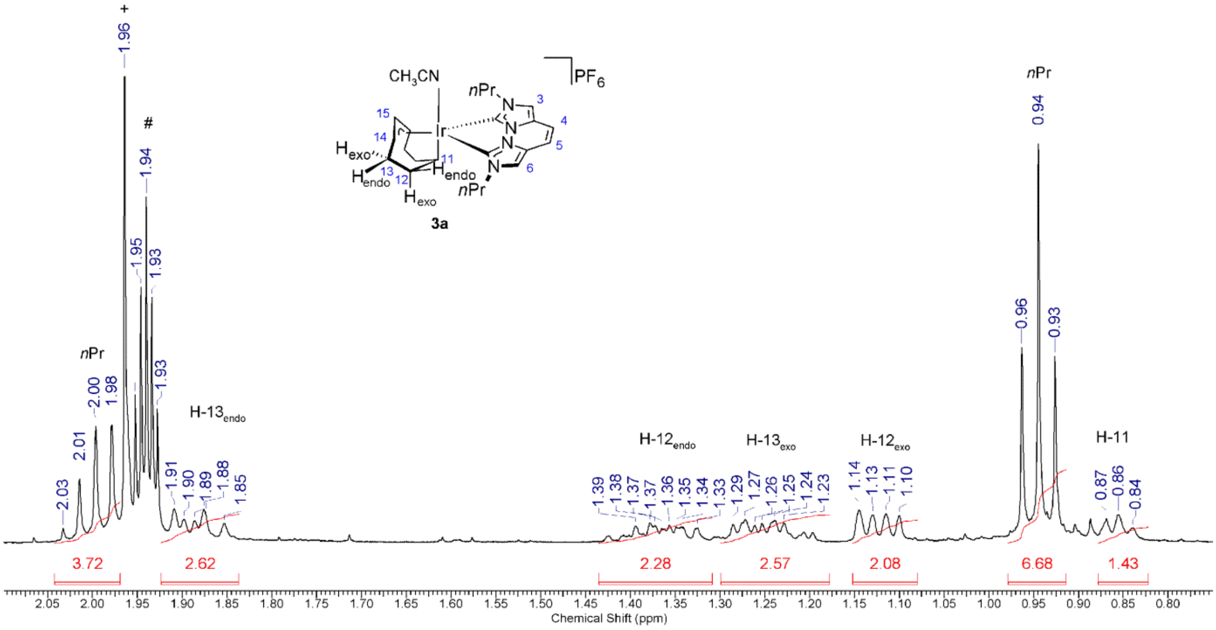

Figure S7. Excerpt from the ^{1}H NMR spectrum (400.11 MHz, CD_3CN) of complex **3a** highlighted in Figure S6 (# solvent, + CH_3CN). Endo and exo positions were distinguished by coupling patterns and the Karplus equation. The assignment was verified by simulation of the spectrum with MestReNova[1]. Coordinated acetonitrile could not be detected due to its exchange with the deuterated solvent.

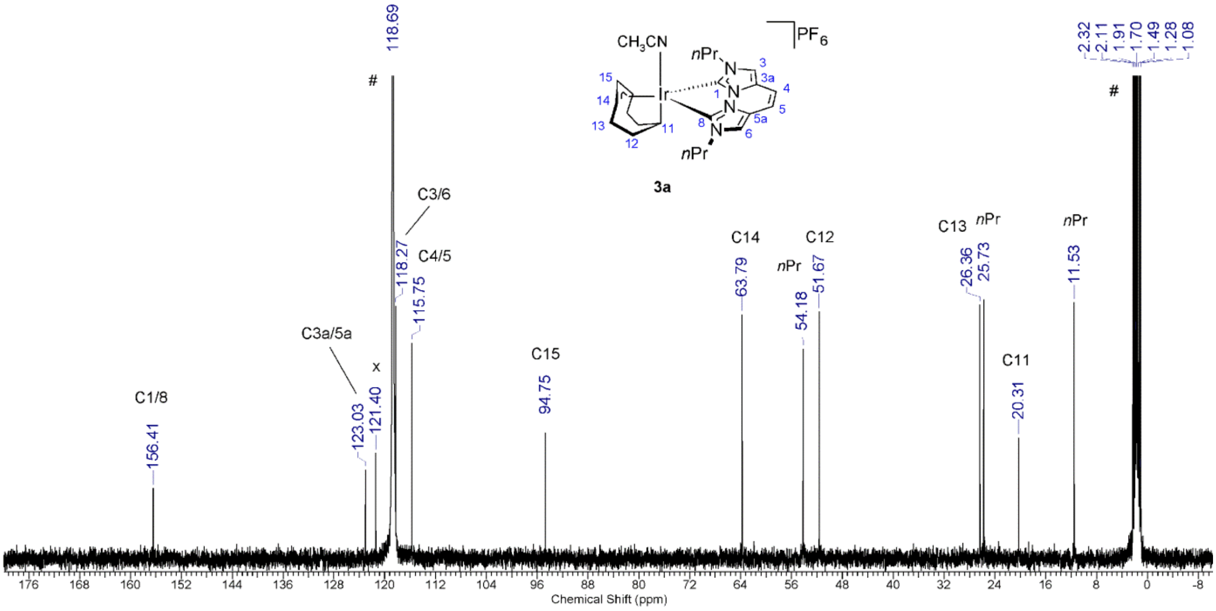

Figure S8. $^{13}C\{^1H\}$ NMR spectrum (100.61 MHz, CD_3CN) of complex **3a** (# solvent, ^{x} offset). Coordinated acetonitrile could not be detected.

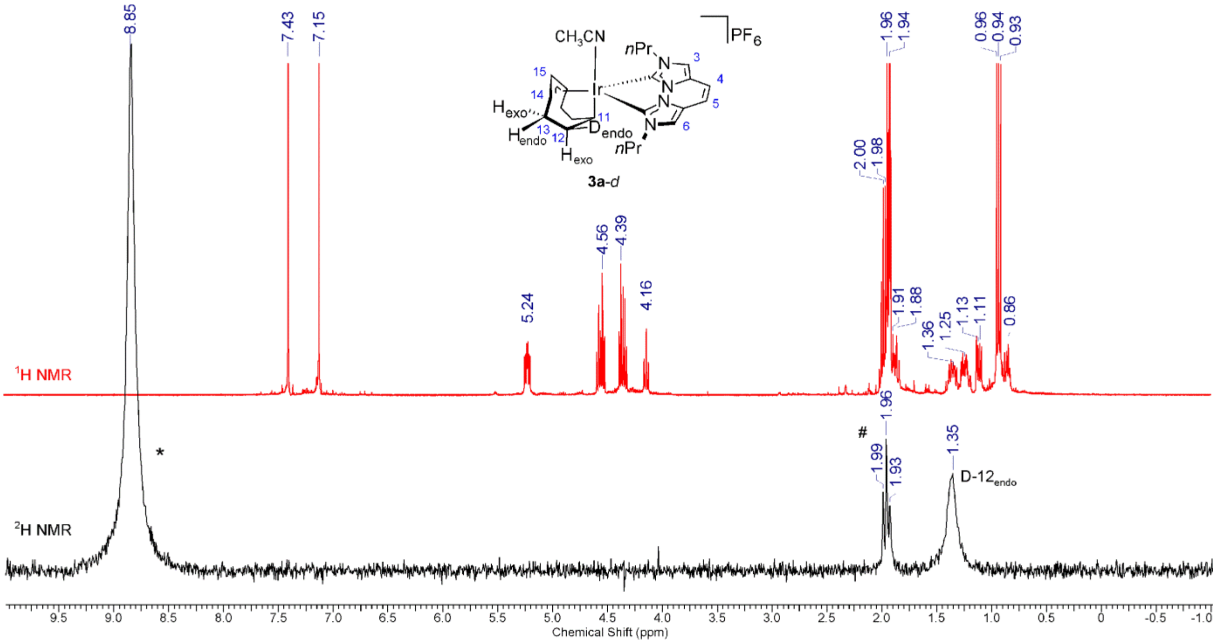

Figure S9. ^2H NMR spectrum (76.77 MHz, CH_3CN) of complex **3a**-*d* (black), synthesized *in situ* from **2a** and stoichiometric amounts of acetic acid-d_1 in CH_3CN (# solvent (CH_2DCN, natural abundance ^2H), * CH_3CO_2D), in direct comparison with the ^1H NMR spectrum of isolated **3a** (red).

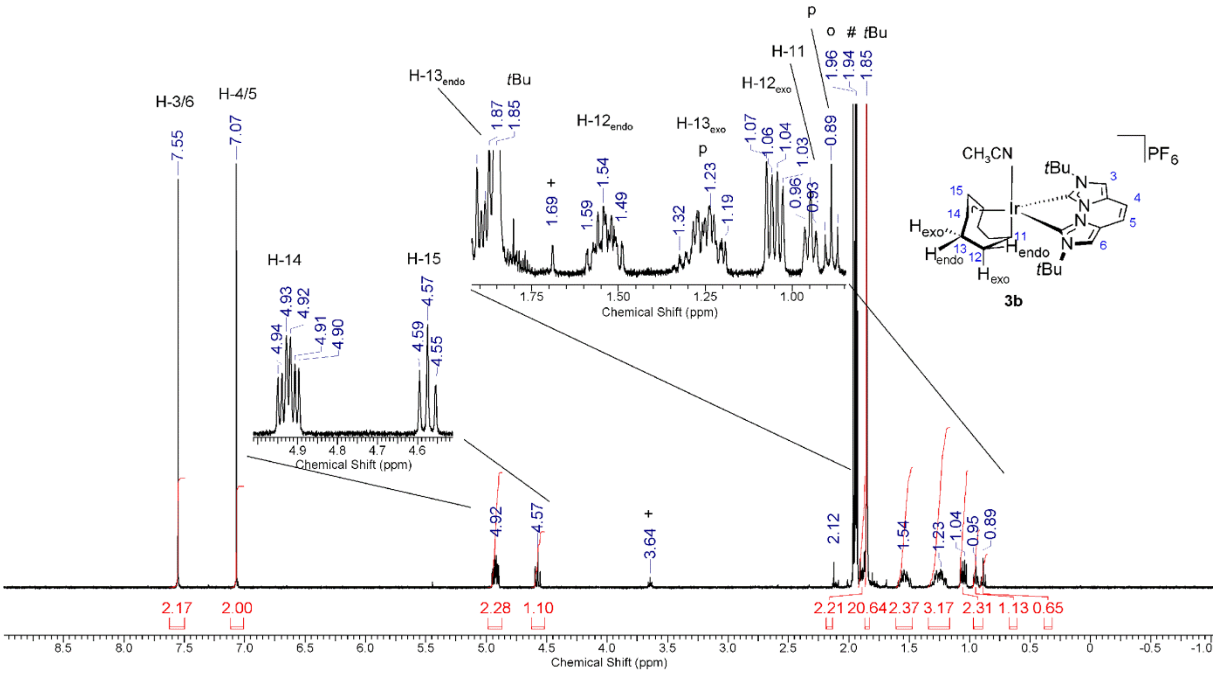

Figure S10. ^{1}H NMR spectrum (400.11 MHz, CD_3CN) of complex **3b** (# solvent, o CH_3CN, + thf, p pentane). Coordinated acetonitrile could not be detected.

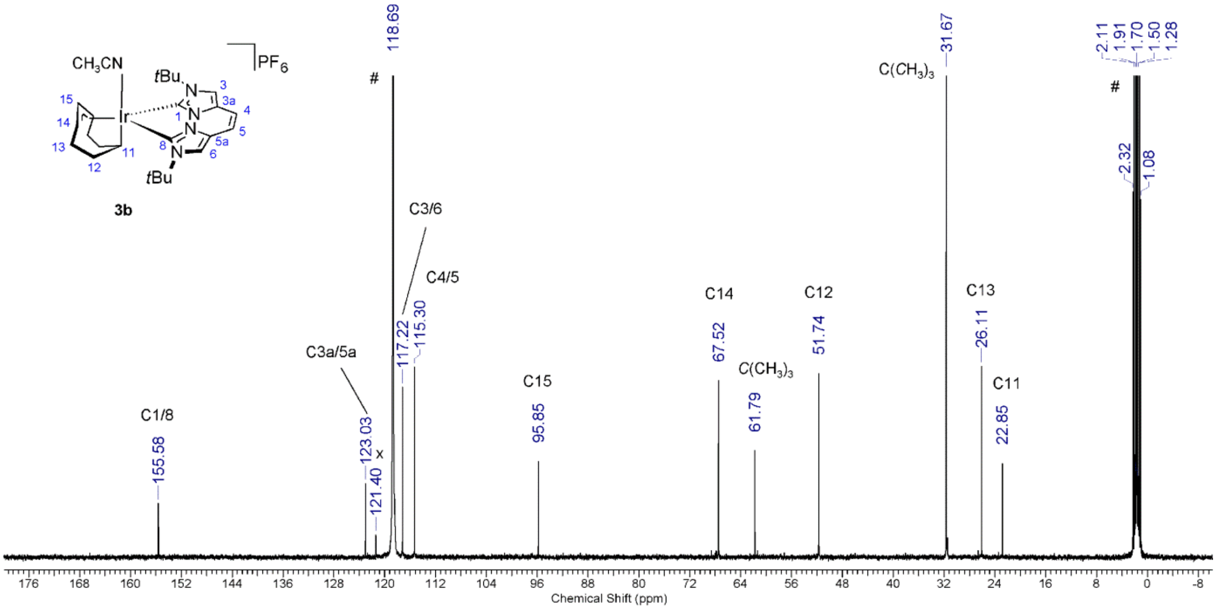

Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum (100.61 MHz, CD_3CN) of complex **3b** (# solvent, ^{x} offset). Coordinated acetonitrile could not be detected.

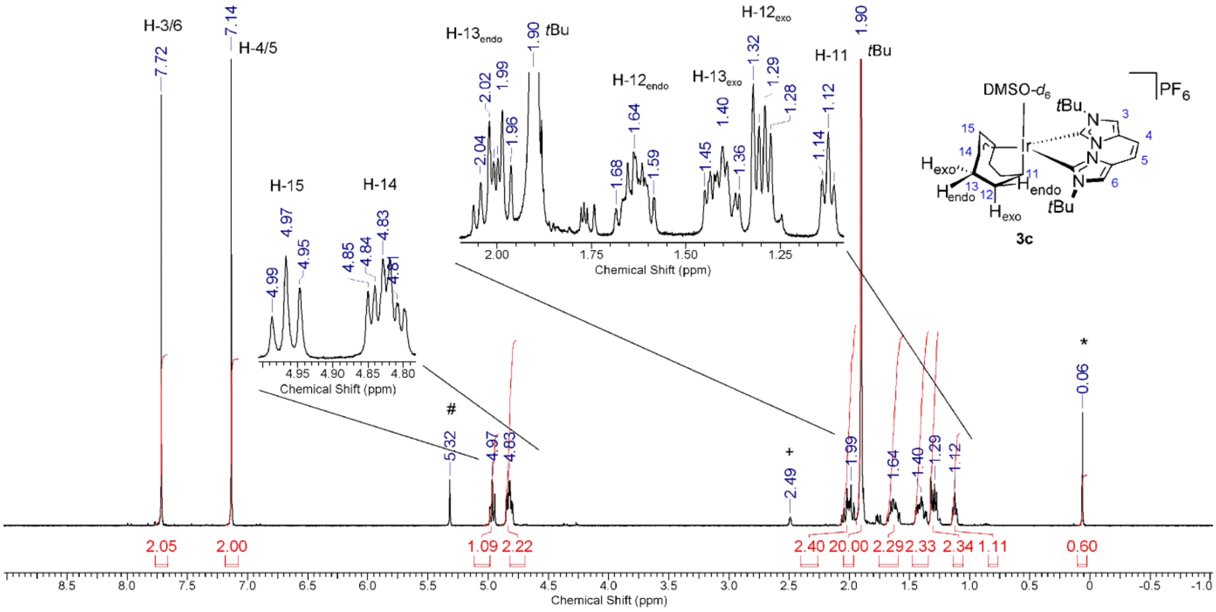

Figure S12. ^{1}H NMR spectrum (400.11 MHz, CD_2Cl_2) of complex **3c** (# solvent, + DMSO-d_6, * grease).

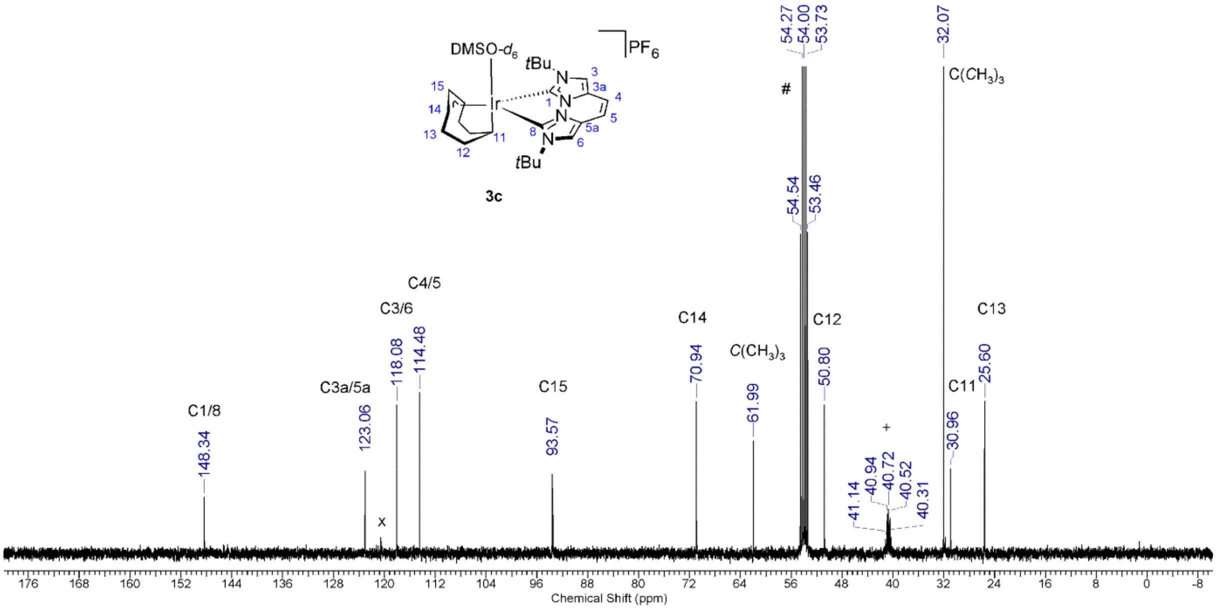

Figure S13. $^{13}C\{^1H\}$ NMR spectrum (100.61 MHz, CD_2Cl_2) of complex **3c** (# solvent, ^{x} offset, + DMSO-d_6).

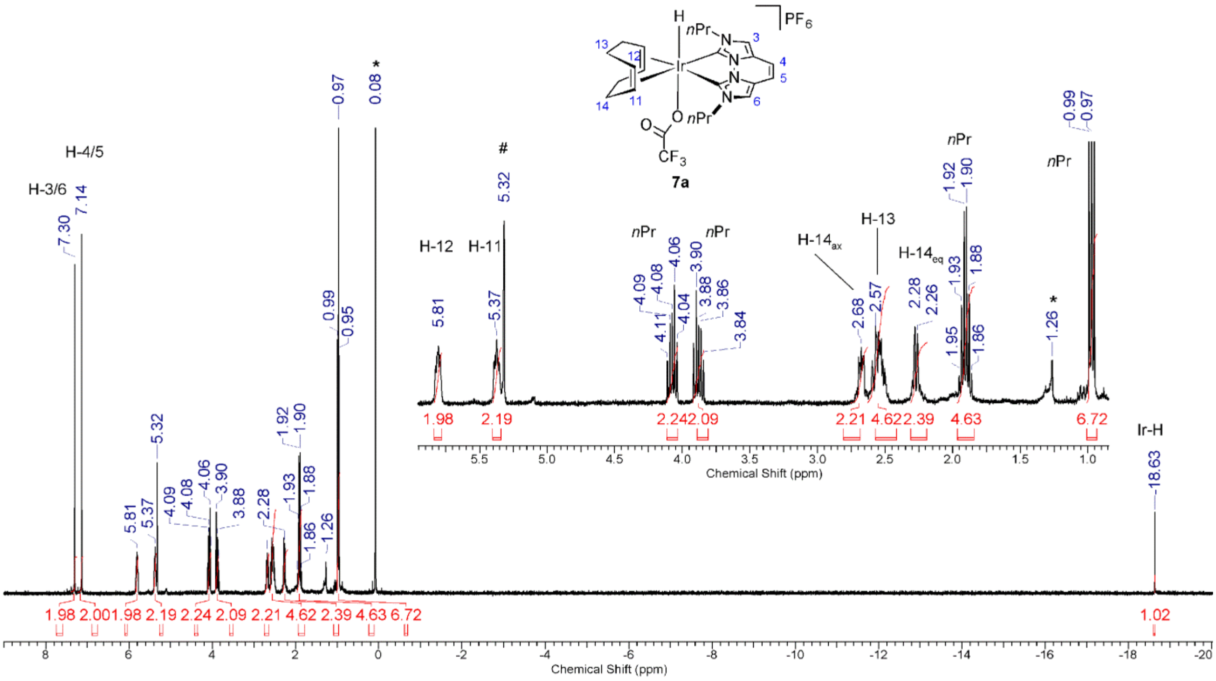

Figure S14. ^{1}H NMR spectrum (400.11 MHz, CD_2Cl_2) of complex **7a** (# solvent, * grease). H-12 and H-13 were assigned by observing an NOE between Ir-H and H-12/H-13 in a ^{1}H NOESY experiment (Figure S16). H-14$_{ax}$ and H-14$_{eq}$ were distinguished by observing an NOE between H-11 and H-14$_{ax}$ but not between H-11 and H-14$_{eq}$ (Figure S17).

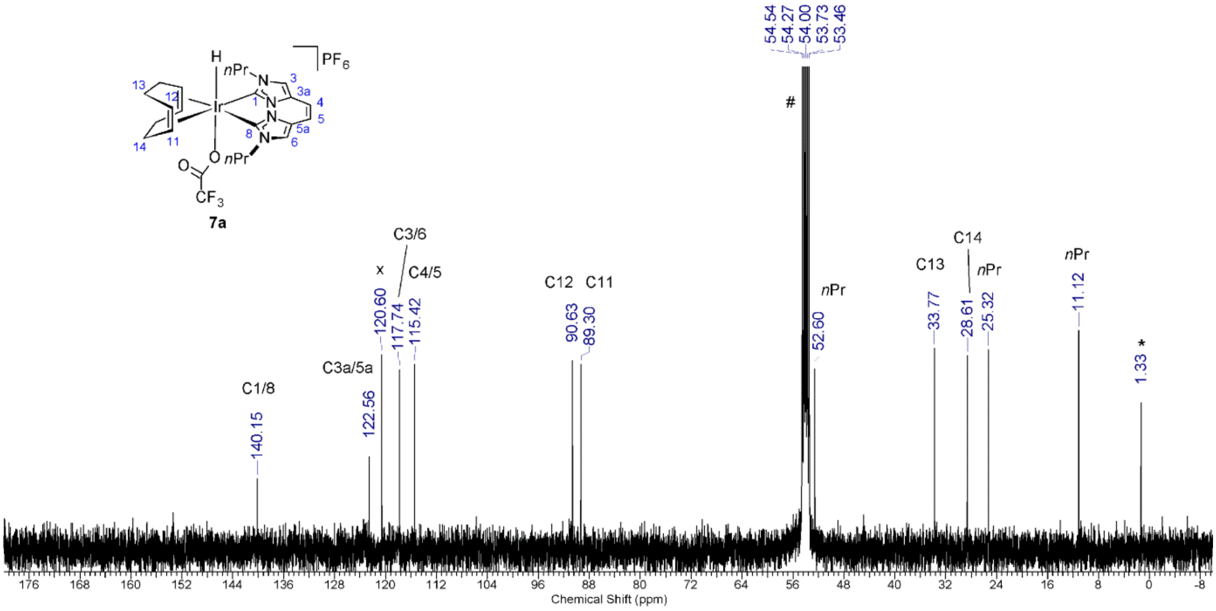

Figure S15. $^{13}C\{^1H\}$ NMR spectrum (100.61 MHz, CD_2Cl_2) of complex **7a** (# solvent, ^{x} offset, * grease).

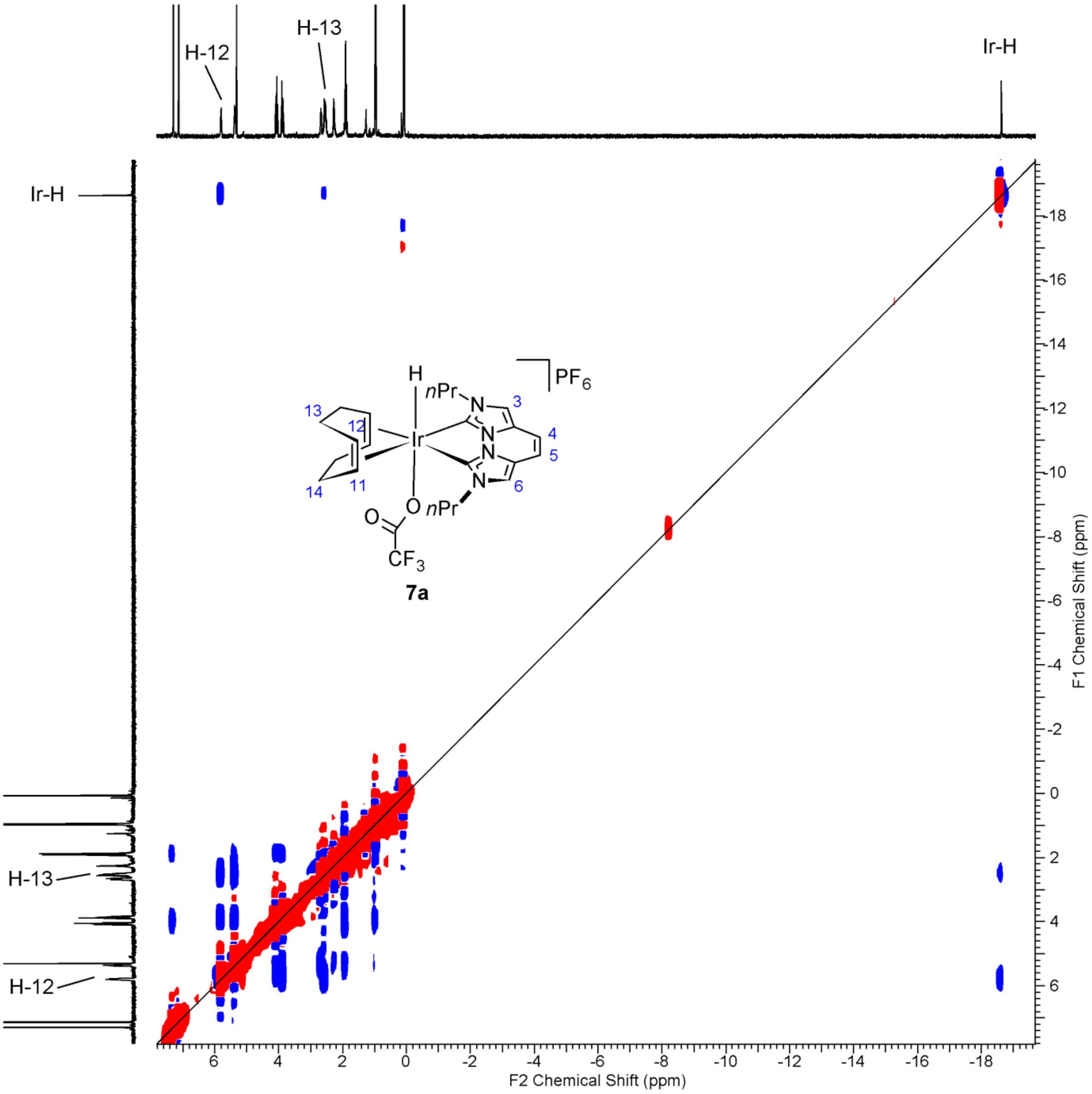

Figure S16. ^{1}H,^{1}H NOESY spectrum (400.11 MHz, CD_2Cl_2) of complex **7a** for distinguishing H-12 and H-11 (Figure S14).

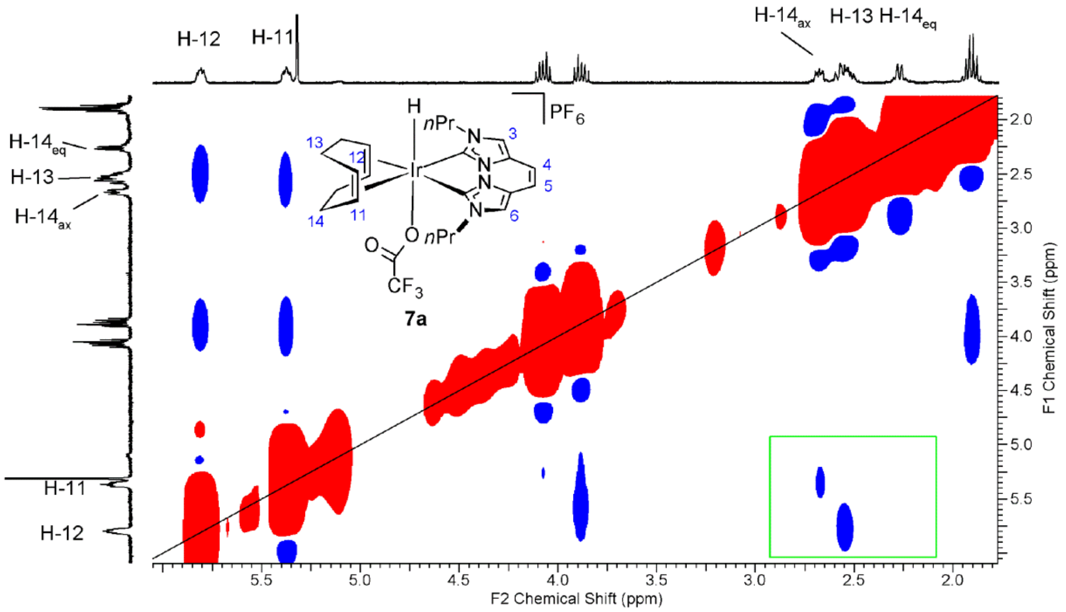

Figure S17. Excerpt from the $^1H,^1H$ NOESY spectrum (400.11 MHz, CD_2Cl_2) of complex **7a** (Figure S16). As shown in the green area, there is a non-scalar coupling between H-11 and H-14_{ax}, but not between H-11 and H-14_{eq}. The molecular structure from X-ray diffraction shows mean distances of 2.312 Å (H-11—H-14_{ax}) and 2.691 Å (H-11—H-14_{eq}).

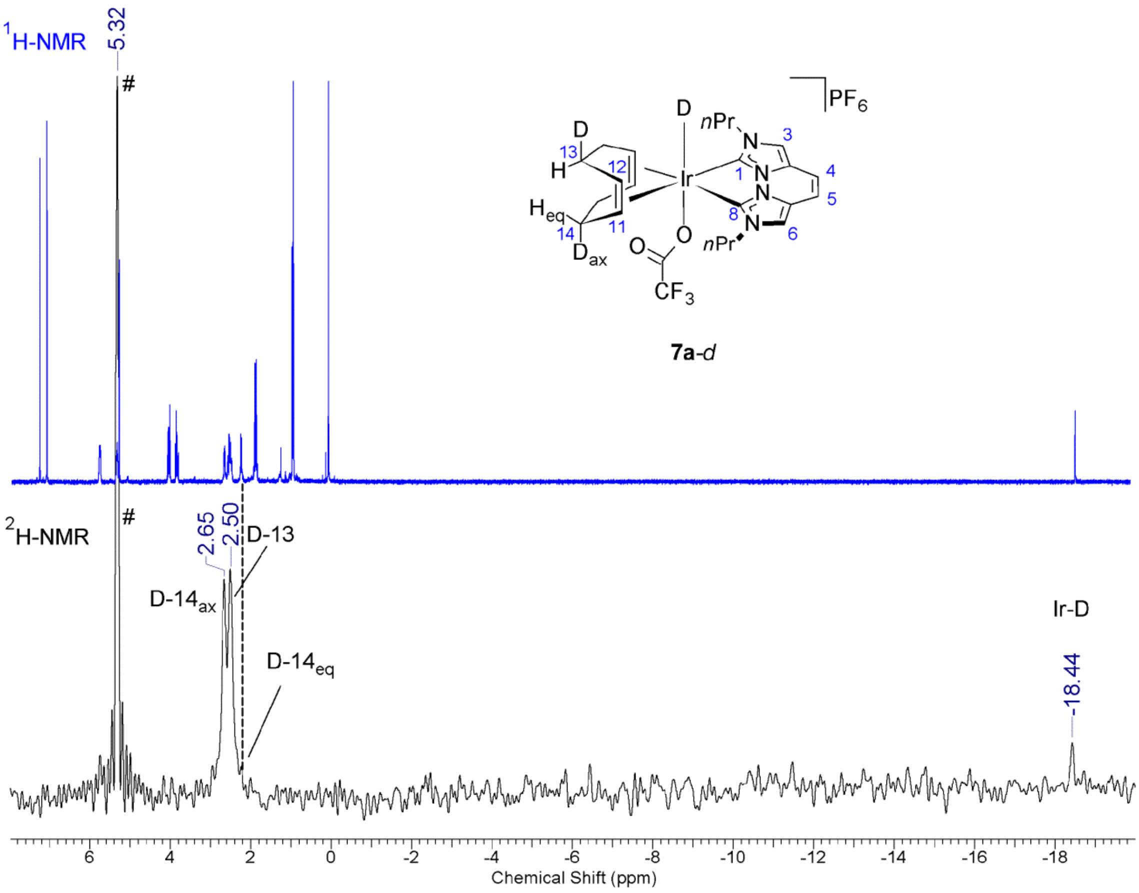

Figure S18. ^2H NMR spectrum (76.77 MHz, CH_2Cl_2) of complex **7a**-*d* (black; # solvent/natural abundance of ^2H), synthesized *in situ* from **2a** and stoichiometric amounts of trifluoroacetic acid-d_1 in CH_2Cl_2, in direct comparison to the ^1H NMR spectrum of non-deuterated **7a** (blue, see Figure S14).

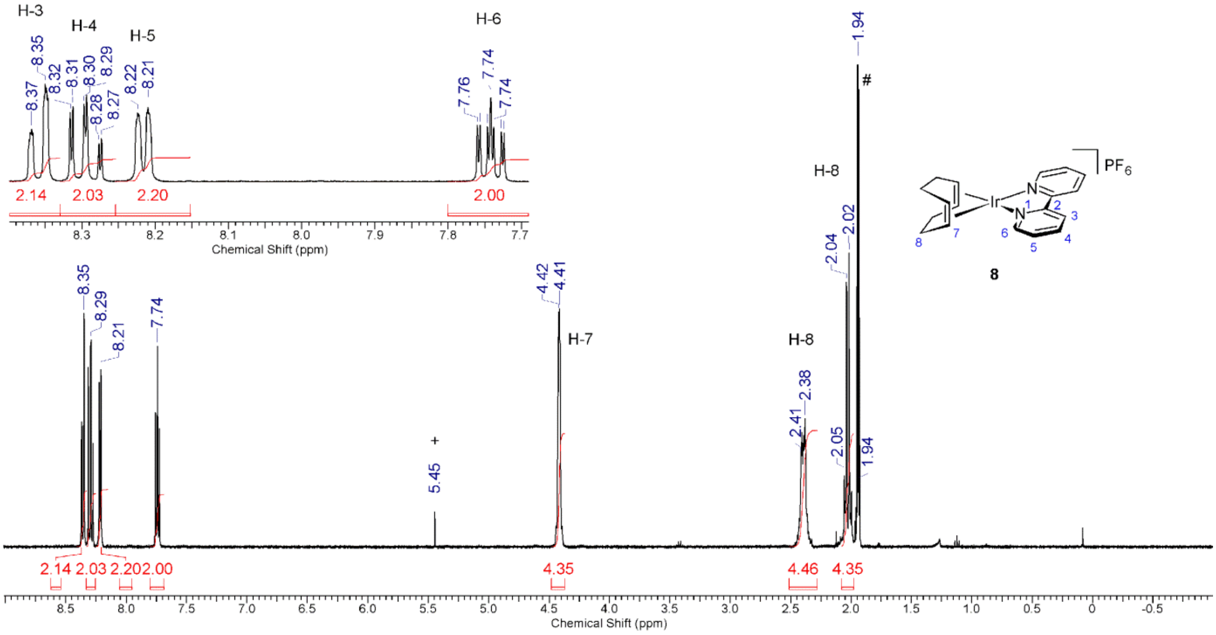

Figure S19. ^{1}H NMR spectrum (400.11 MHz, CD_3CN) of complex **8** (# solvent, + CH_2Cl_2).

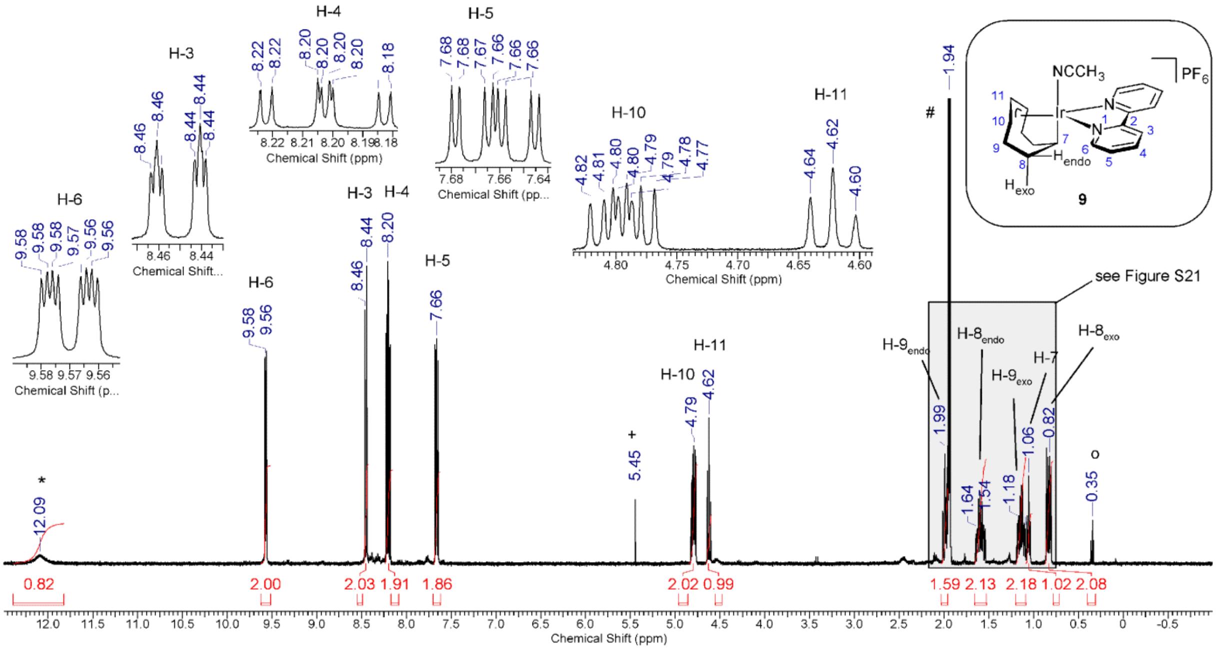

Figure S20. ^{1}H NMR spectrum (400.11 MHz, CD_3CN) of complex **9** (# solvent, * TFA, $^+$ CH_2Cl_2, ^{o} impurity from TFA). Endo and exo positions were distinguished by the Karplus equation referring to the spectra of **3a**, **3b** and **3c** (Figures S6, S10, S12). For enlargement of the highlighted area see Figure S21. Coordinated acetonitrile could not be detected.

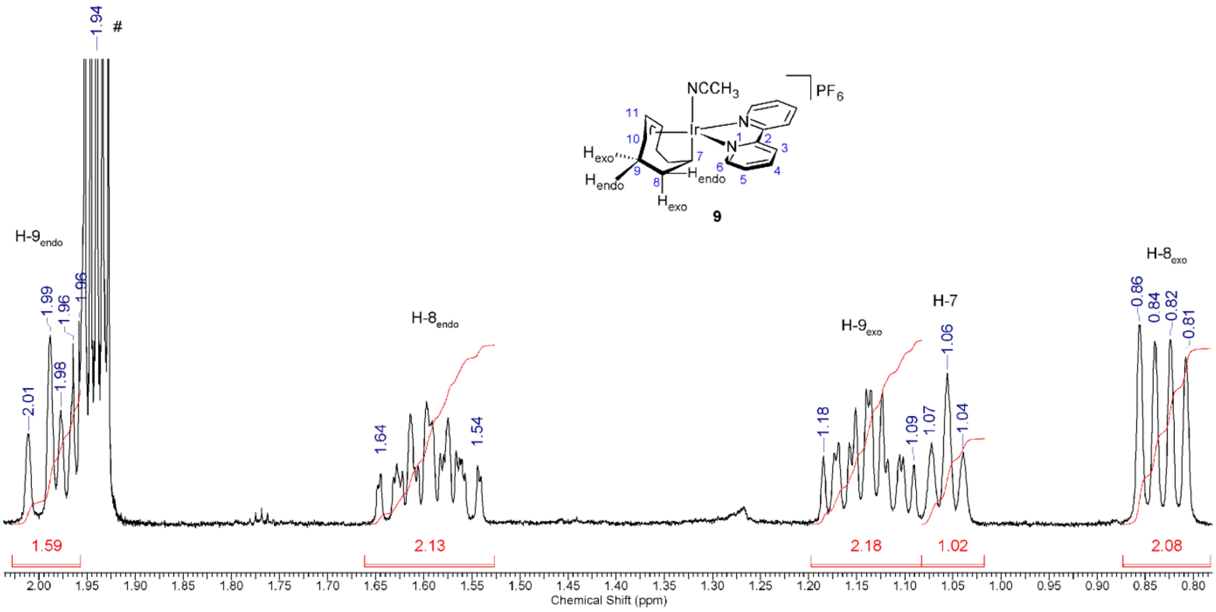

Figure S21. Excerpt from the ^{1}H NMR spectrum (400.11 MHz, CD_3CN) of complex **9** highlighted in Figure S20 (# solvent). Endo and exo positions were distinguished by the Karplus equation referring to the spectra of **3a**, **3b** and **3c** (Figures S6, S10, S12). Coordinated acetonitrile could not be detected.

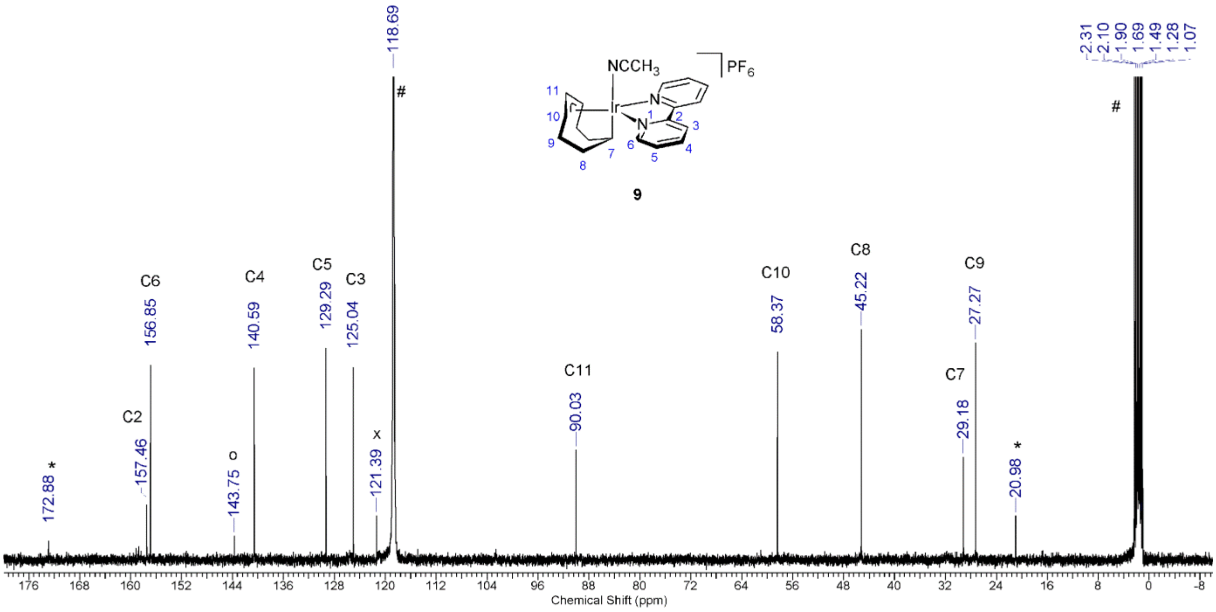

Figure S22. $^{13}C\{^{1}H\}$ NMR spectrum (100.61 MHz, CD_3CN) of complex **9**, synthesized *in situ* from [Ir(2,2'-bipyridine-κ^2N,N')(η^4-cod)](PF_6) (**8**) in CD_3CN by addition of an acetic acid-trifluoroacetic acid mixture (# solvent, ^{x} offset, * AcOH, ^{o} unknown impurity). Coordinated acetonitrile could not be detected.

2. Cartesian coordinates and absolute energies

The supplemental file *Computational_data.xyz* contains the computed Cartesian coordinates of all calculated molecules reported in this study. The file may be opened as a text file to read the coordinates, or opened directly by a molecular modelling program or Mercury (version 3.3 or later, http://www.ccdc.cam.ac.uk/pages/Home.aspx) for visualization and analysis.

3. Figures of the geometrically optimized structures

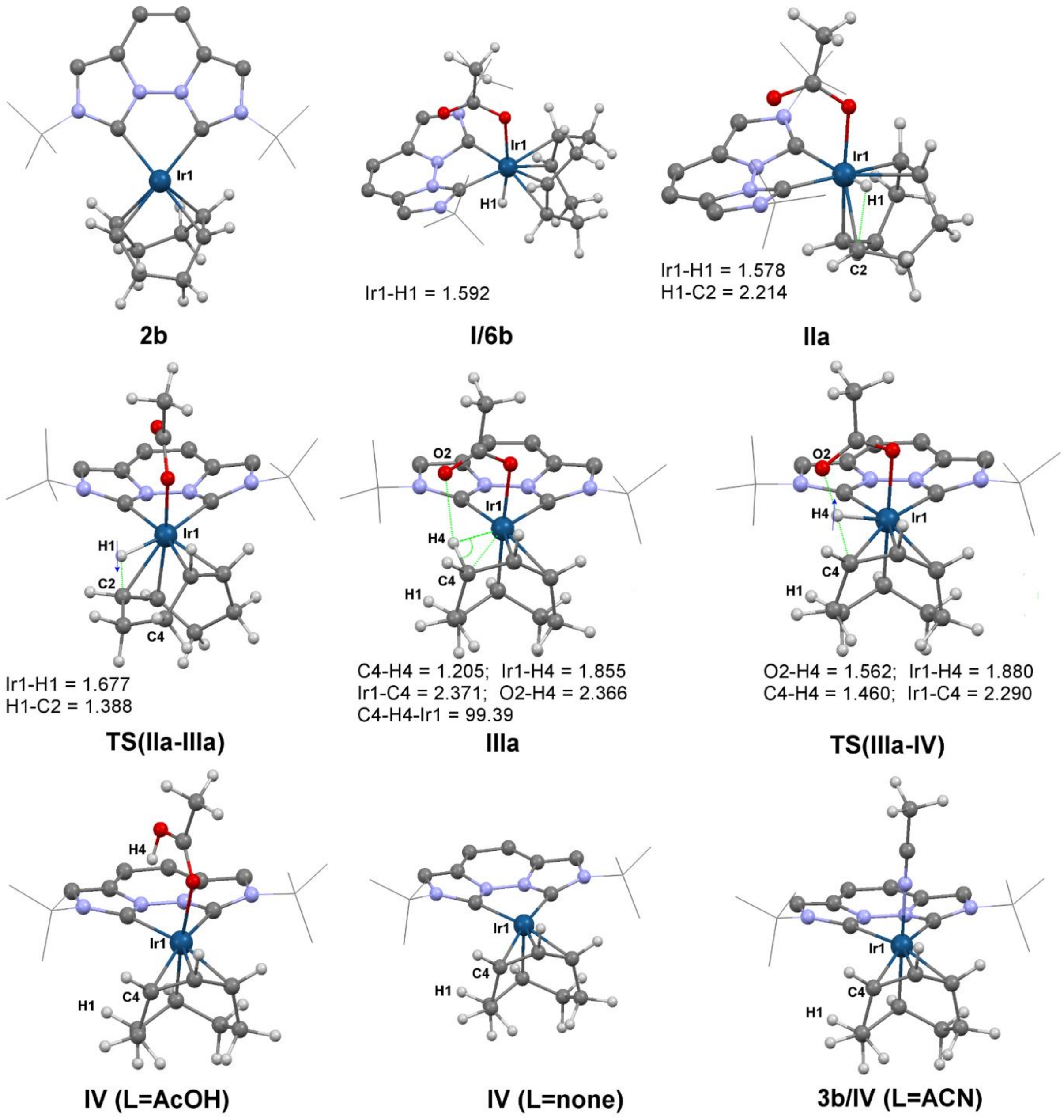

Figure S23. Geometrically optimized structures of intermediates and transition states examined in this study (Part 1; for Part 2 see Figure S24). Hydrogen atoms of the vegi^{tBu}-ligand are not shown for clarity. Bond lengths are given in [Å] and angles in [°]. Blue arrows in transition states indicate the normal mode with an imaginary frequency.

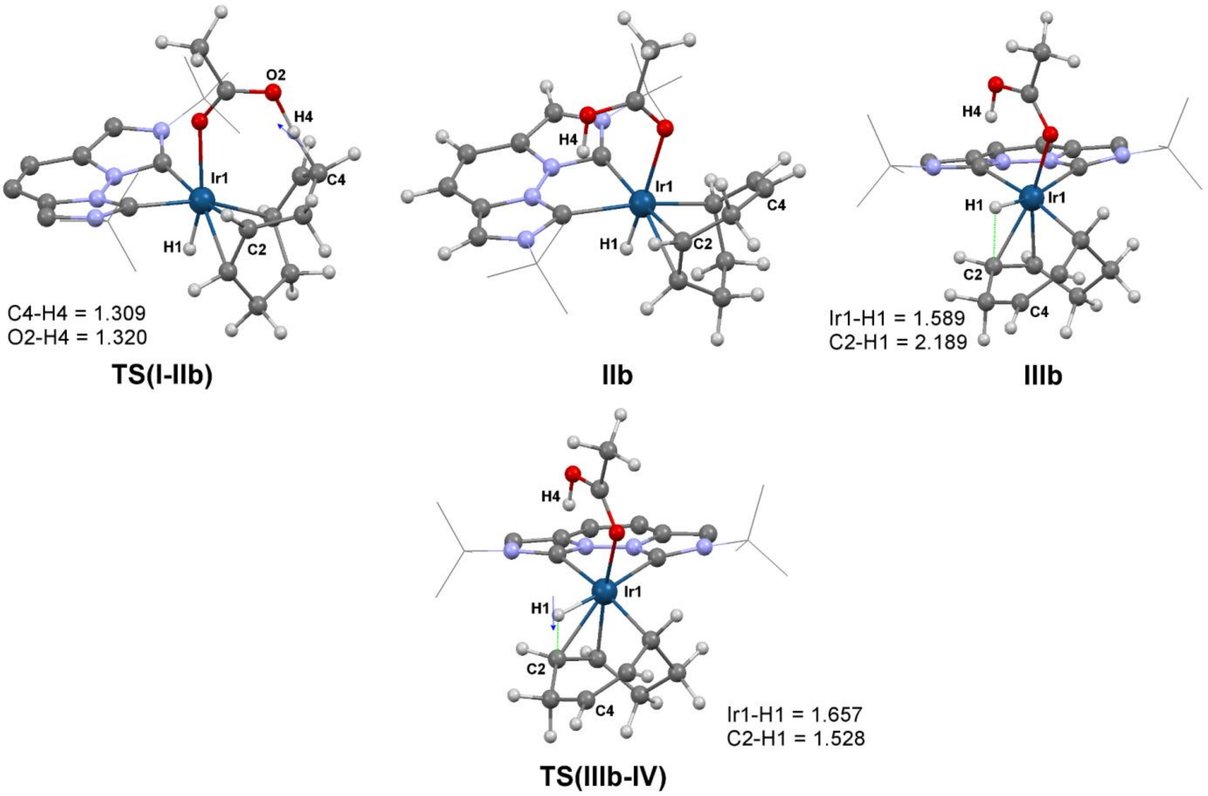

Figure S24. Geometrically optimized structures of intermediates and transition states examined in this study (Part 2; for Part 1 see Figure S23). Hydrogen atoms of the vegi^{tBu}-ligand are not shown for clarity. Bond lengths are given in [Å] and angles in [°]. Blue arrows in transition states indicate the normal mode with an imaginary frequency.

REFERECES

[1] *MestReNova*, version 10.0.1; Mestrelab Research S.L.: Santiago de Compostela, Spain, **2015**; available from http://www.mestrelab.com.