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A Synthron for a 14-Electron Ir(III) Species: Catalyst for Highly Selective β -(Z) Hydrosilylation of Terminal Alkynes

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Experimental Section

General Information

All manipulations were performed using standard Schlenk techniques under an argon atmosphere, except where otherwise noted. All complexes after their formation were treated under aerobic conditions. Solvents were obtained dried from a solvent purification system from Innovative Technology Inc. All other reagents were used as received. NMR spectra were recorded on Bruker Avance 300 MHz, Bruker ARX 300 or Bruker Avance 400 MHz spectrometers. The chemical shifts are given as dimensionless δ values and are frequency referenced relative to the peak for TMS for ^1H and ^{13}C . Coupling constants J are given in hertz as positive values regardless of their real individual signs. The multiplicity of the signals is indicated as “s”, “d”, or “m” for singlet, doublet, or multiplet, respectively. Mass spectra and high-resolution mass spectra were obtained on a esquire 3000+ with ion trap detector interfaced on an Agilent 1100 HPLC analyser, in electrospray (ES) mode unless otherwise reported. Elemental analyses C/H/N were carried out in a Perkin-Elmer 2400 CHNS/O analyser.

Synthesis of Methylenebis(*N*-2-methoxyethyl)imidazolium Diiodide (1).

1-(2-methoxyethyl)-1H-imidazole (0.50 g, 4 mmol) and CH_2I_2 (161 μl , 2 mmol) were dissolved in CH_3CN (2 mL). The resulting solution was stirred under reflux for 16 h, after which time the solvent was evaporated under reduced pressure. The remaining residue was washed with diethyl ether (3×20 mL) and dried in vacuo to give 0.75 g of a white solid (73%). ^1H NMR (DMSO-d_6 , 400MHz): δ 9.47 (s, 2H, CH_{im}), 8.03 (s, 2H, CH_{im}), 7.87 (s, 2H CH_{im}), 6.70 (s, 2H, NCH_2N), 4.44 (t, 4H, $J_{\text{H-H}} = 4\text{Hz}$, NCH_2), 3.72 (t, 4H, $J_{\text{H-H}} = 4\text{Hz}$, CH_2O), 3.29 (s, 6H, CH_3O). $^{13}\text{C}\{^1\text{H}\}$ NMR (DMSO-d_6 , 20°C, 101 MHz): δ 137.8 (CH_{imid}), 123.6 (CH_{im}), 121.9 (CH_{im}), 69.8 (OCH_2), 58.0 (CH_3O), 58.0 (NCH_2N), 49.2 (CH_2N). ESI+: m/z 165.1 ($\text{M} - \text{H}^+$). Anal. Calcd. for $\text{C}_{13}\text{H}_{22}\text{I}_2\text{N}_4\text{O}_2$ (519.98): C, 30.02; H, 4.26; N, 10.77. Found: C, 30.09; H, 4.11; N, 10.77.

Synthesis of Methylenebis(*N*-2-methoxyethyl)imidazole-2-ylidene)acetato(Diiodo)Iridium(III) (**2**)

A mixture of [Ir(μ -Cl)(COD)]₂ (0.17 g, 0.25 mmol), **1** (0.80 g, 0.5 mmol), NaI (0.70 g, 5.0 mmol), KOAc (0.65 g, 6.5 mmol) and CH₃CN (15 mL) was refluxed for 2 days, after which time the solvent was evaporated under reduced pressure. The remaining residue was dissolved in CH₂Cl₂, and any insoluble impurities were filtered off. The solution was concentrated to ca. 1 mL and the product precipitated with diethyl ether. The solid was washed with diethyl ether (3 × 10 mL) and dried in vacuo to give 0.17 g of an orange solid (88%). ¹H NMR (Acetone-d₆, 400MHz): δ 7.34 (d, 2H, $J_{\text{H-H}} = 4\text{Hz}$, CH_{im}), 7.32 (d, 2H, $J_{\text{H-H}} = 4\text{Hz}$, CH_{im}), 6.38 (s, 2H, NCH₂N), 4.57 (t, 4H, $J_{\text{H-H}} = 8\text{Hz}$, NCH₂), 3.75 (t, 4H, $J_{\text{H-H}} = 8\text{Hz}$, CH₂O), 3.31 (s, 6H, CH₃O), 1.85 (s, 3H, CH₃-AcO). ¹H NMR (CDCl₃, 400MHz): δ 7.34 (d, 2H, $J_{\text{H-H}} = 4\text{Hz}$, CH_{im}), 7.31 (d, 2H, $J_{\text{H-H}} = 4\text{Hz}$, CH_{im}), 6.38 (s, 2H, NCH₂N), 4.57 (t, 4H, $J_{\text{H-H}} = 8\text{Hz}$, NCH₂), 3.75 (t, 4H, $J_{\text{H-H}} = 8\text{Hz}$, CH₂O), 3.31 (s, 6H, CH₃O), 1.85 (s, 3H, CH₃-AcO). ¹³C{¹H} NMR (CDCl₃, 101 MHz): δ 183.4 (CCOO⁻), 125.8 (NC_{im}N), 123.6 (CH_{im}), 119.6 (CH_{im}), 72.4 (OCH₂), 61.9 (NCH₂N), 58.0 (CH₃O), 49.6 (CH₂N), 25.0 (CH₃COO⁻). Anal. Calcd. for C₁₅H₂₄I₂IrN₄O₄ (770.95): C, 23.42; H, 3.01; N, 7.28. Found: C, 24.62; H, 3.01; N, 7.41.

Synthesis of Methylenebis(*N*-2-methoxyethyl- κ O, κ O')imidazole-2-ylidene)(Diiodo)Iridium(III) tetrafluoroborate (**3**)

To a solution of **2** (0.10 g, 0.20 mmol) in dry CH₂Cl₂ (20 mL) at 0 °C, HBF₄ (58 μ L, 0.2 mmol) was added dropwise under Argon, stirred for 1 h and allowed to warm to room temperature, thus affording an orange suspension. Subsequently, the solvent was evaporated under reduced pressure until a volume of ca. 1mL and precipitated with Et₂O (10 mL). The resulting residue was washed with diethyl ether (3 × 10 mL) to afford 100 mg of an orange solid (74%). ¹H NMR (Acetone-d₆, 400MHz): δ 7.43 (d, 2H, $J_{\text{H-H}} = 4\text{Hz}$, CH_{im}), 7.41 (d, 2H, $J_{\text{H-H}} = 4\text{Hz}$, CH_{im}), 6.52 (s, 2H, NCH₂N), 4.61 (m, 4H, NCH₂), 4.38 (m, 4H, CH₂O), 4.05 (s, 6H, CH₃O). ¹³C{¹H} NMR (Acetone-d₆, 101 MHz): δ 124.4 (CH_{im}), 122.1 (CH_{im}),

121.4 (NC_{im}N), 76.5 (OCH₂), 67.2 (CH₃O), 62.7 (NCH₂N), 49.6 (CH₂N). Anal. Calcd. for C₁₃H₂₀BF₄I₂IrN₄O₂ (812.96): C, 19.59; H, 2.53; N, 7.03 Found: C, 19.88; H, 2.48; N, 6.92.

Hydrosilylation of alkynes

6 mg (7.5×10^{-3} mmol) of **3** were dissolved in 0.5 mL of acetone-d₆ in an NMR tube. Subsequently, 33 μL (0.16 mmol) of diphenylmethylsilane, 0.15 mmol of the corresponding alkyne and mesitylene (21 μL, 0.15 mmol) as internal standard were added. The NMR tube was then placed in an oil bath and reacted for 5h at 50 °C. Yields and selectivities were calculated by ¹H NMR. The isomers were unambiguously identified by means of the ³J_{H-H} coupling constants of the vinylic protons.

Synthesis of (Z)-dimethyl(4-methylstyryl)(phenyl)silane

A Schlenk tube with a screw top was charged with the catalyst precursors **4** (0.075 mmol, 60 mg), acetone (5 mL), 1-ethynyl-4-methylbenzene (1.5 mmol, 190 μL), and HSiMe₂Ph (1.65 mmol, 260 μL). The solution was stirred at 50 °C for 3 h and the solvent evaporated under reduced pressure. The crude was purified by column chromatography in silica gel using hexane as eluent (rf = 0.4) to afford a colorless liquid (Z:E = 90:10, 345 mg, 91%). The α isomer was observed only in traces amounts.¹

1 M. Nagao, K. Asano, K. Umeda, H. Katayama, F. Ozawa, *J. Org. Chem.*, 2005, **70**, 10511.

X-ray Crystallography

Data Collection: Crystal data, data collection and refinement parameters for compound [Ir(L-C,C,O,O)₂]BF₄ (L = methylenebis[(N-2-methoxyethyl)imidazole-2-ylidene]) (**3**) were recorded with a Bruker Kappa APEX2 diffractometer equipped with an area detector and graphite monochromated Mo Kα radiation (0.71073 Å). Data reduction was done with the APEX2 software.² The structure was solved by direct methods and refined by full-matrix least-squares methods based on *F*² using SHELXL-97 and WinGX programs.³ Non-hydrogen atoms were refined anisotropically, while hydrogen atoms were positioned geometrically and refined with isotropic displacement parameters according to the

riding model. Distance and angle calculations were performed using the SHELXL-97 and WinGX programs.³ Crystal data of **3**: [C₁₆H₂₆BF₄I₂IrN₄O₃], orthorhombic, *Pna2(1)*, *a* = 19.5550(14) Å, *b* = 10.6594(8) Å, *c* = 11.3757(8) Å, *Z* = 4, *M_r* = 855.22 g mol⁻¹, *V* = 2371.2(3) Å³, *D_{calcd}* = 2.396 g cm⁻³, λ(Mo Kα) = 0.71073 Å, *T* = 100 K, μ = 8.291 mm⁻¹, 24968 reflections collected, 6159 observed (*R_{int}* = 0.0567), *R1(F_o)* = 0.0252 [*I* > 2σ(*I*)], *wR2(F_o²)* = 0.0650 (all data), GOF = 1.023. CCDC 883047.

2 APEX2 Bruker AXS Inc., Madison, Wisconsin, USA, 2011.

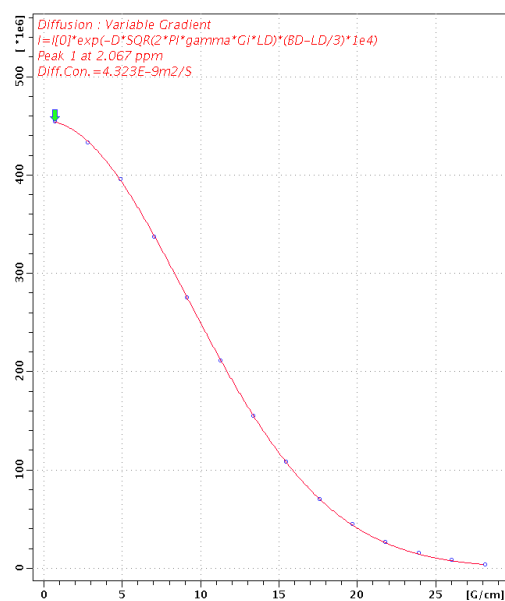
3 (a) G. M. Sheldrick, SHELXS-97 and SHELXL-97; University of Göttingen, Germany, 1997; (b) Farrugia, L. J. *WinGX*; University of Glasgow, Great Britain, 1998.

DOSY experiments

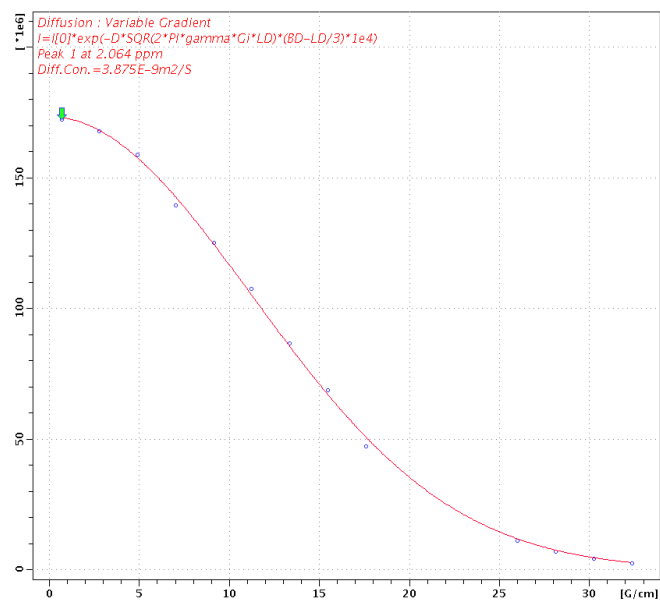
The ¹H DOSY experiments were performed on a Bruker Avance 400 MHz spectrometer. During the DOSY experiments, the temperature was set to 300 K and maintained with an air flow of 400 L h⁻¹. The experiments were acquired with the pulse program *stebpgp1s* in Bruker software with spinning of the sample to avoid convection influence. The diffusion time (D20) and gradient duration (P30) were optimised with the *stebpgp1s* sequence by observation of progressive decay of the signal intensities of the acetone residual peak for each measurement until 1 to 5% of the initial value with maximum strength (*gpz6* = 95%). The value of D20 employed in the ¹H DOSY experiments was set to 100 ms and the spoil gradient (P19) to 0.6 ms, while P30 values of 0.6 and 0.7 ms were optimised for a solution of **3** (24 mg, 0.03 mmol in 0.5 mL of acetone-d₆) and complex-free acetone-d₆, respectively. The gradient strength was varied between 2% and 95% in 16 square spaced increments. The spectral width was set to AQ = 6.4 s, the number of scans was 8, and a relaxation delay D1 = 1 s was used. The raw data was processed using the Bruker DOSY package and T1/T2 relaxation module.

The DOSY experiments on the solution of **3** in acetone-d₆ were performed using the same sample of acetone-d₆ employed for the complex-free acetone-d₆ measurement. The fitting curves for both experiments are presented below.

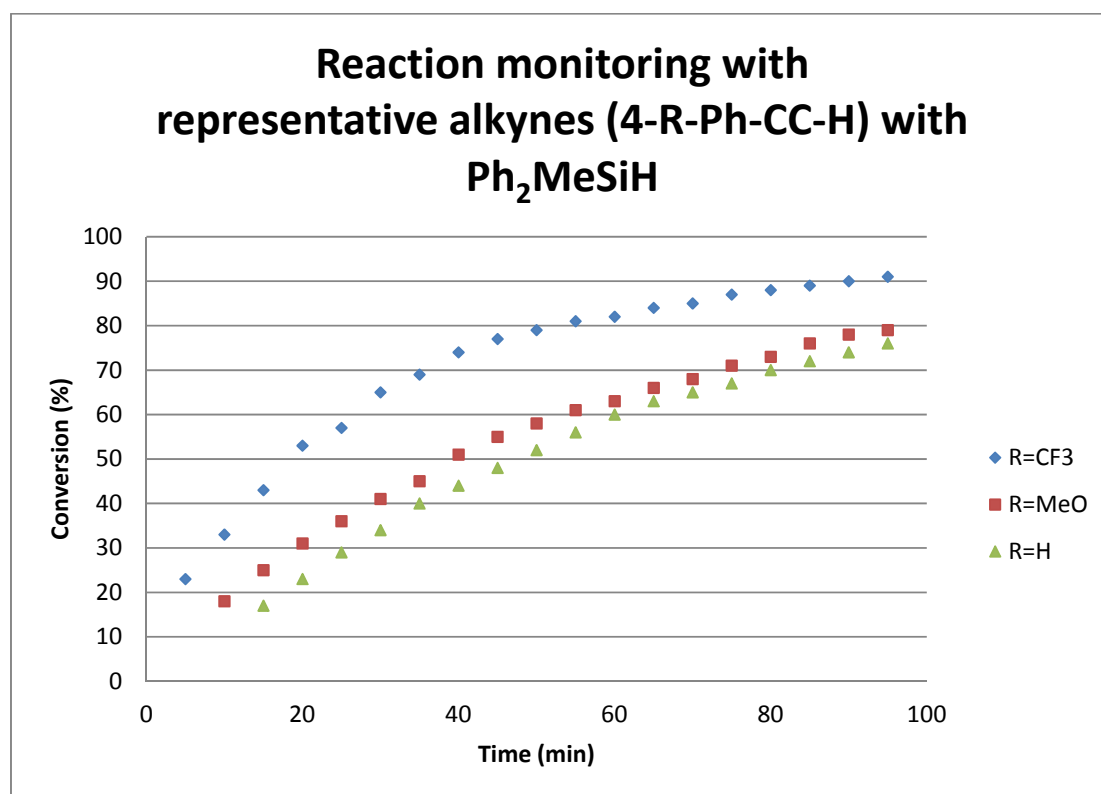
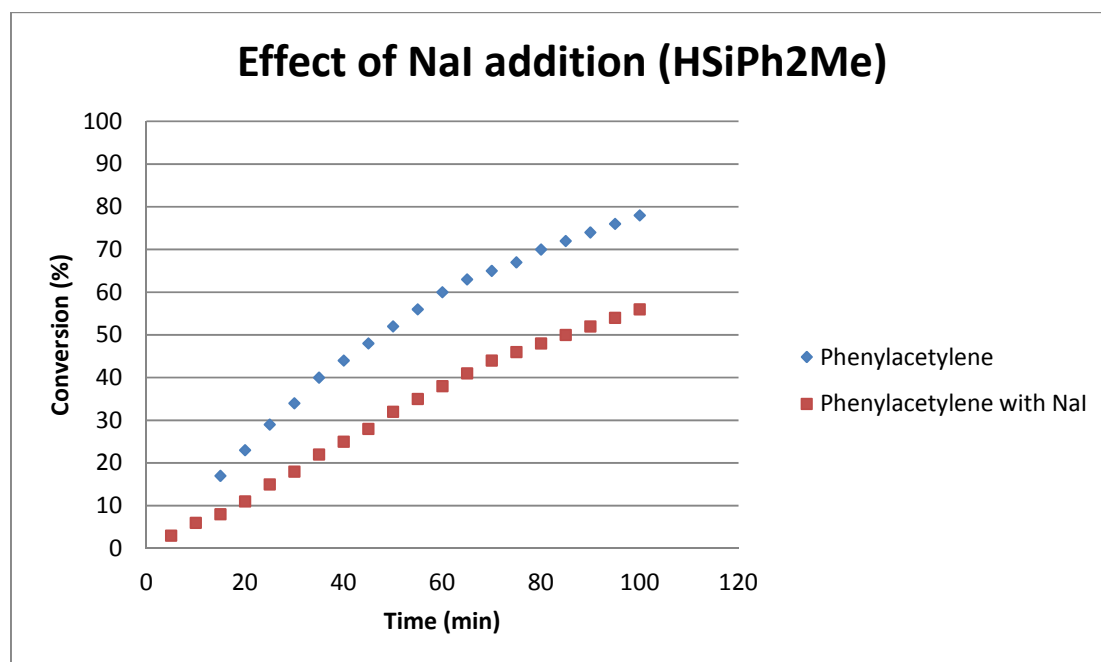
Complex-free acetone-d₆



Solution of 3 in acetone-d₆



Kinetic Experiments



Computational Details

All geometrical calculations were fully optimized with the Gaussian09 package⁴ at the DFT level using the B3LYP approach.⁵ Iridium atom was represented by the Lanl2 relativistic effective core potential and the Lanl2dz associated basis set⁶ plus a set of f-type polarization basis function.⁷ The 6-31G(d) basis set was used for all the other atoms (C, H, Si, O, N).⁸ Gibbs free energies calculated at 323.15 K and 1 atm.

References:

4 Gaussian 09, Revision A.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2009**.

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7 A. W. Ehlers, M. Böhme, S. Dapprich, A. Gobbi, A. Höllwarth, V. Jonas, K. F. Köhler, R. Stegmann, A. Veldkamp, G. Frenking, *Chem. Phys. Lett.*, **1993**, *208*, 111.

8 a) W. J. Hehre, R. Ditchfield, and J. A. Pople, *J. Chem. Phys.*, **1972**, *56*, 2257. b) M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees, and J. A. Pople, *J. Chem. Phys.* **1982**, *77*, 3654. c) P.C. Hariharan and J.A. Pople, *Theor. Chim. Acta*, **1973**, *28*, 213.

Figure S1. Graphical representation of DFT optimized structure **8a**.

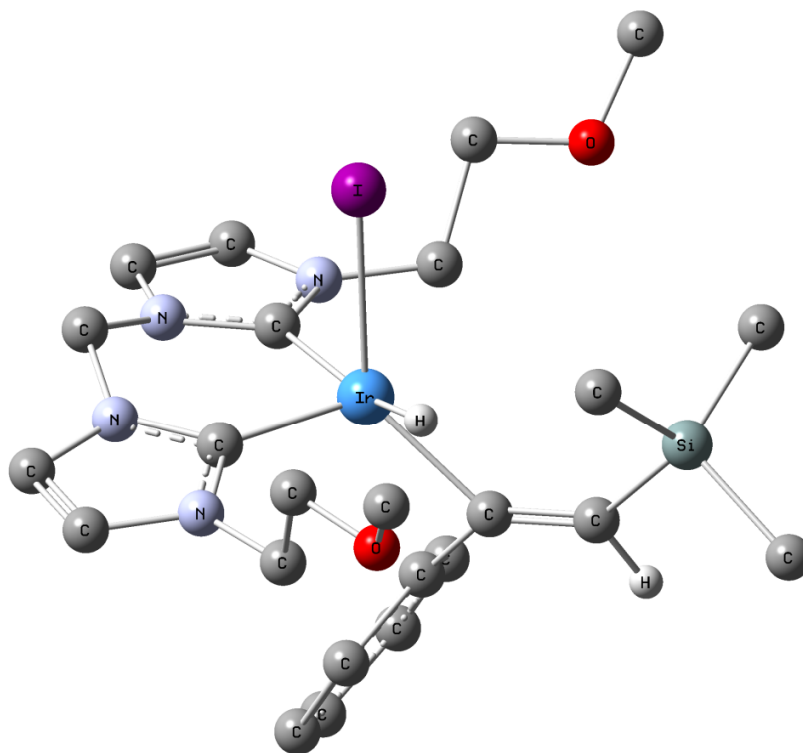


Figure S2. Graphical representation of DFT optimized structure **8b**.

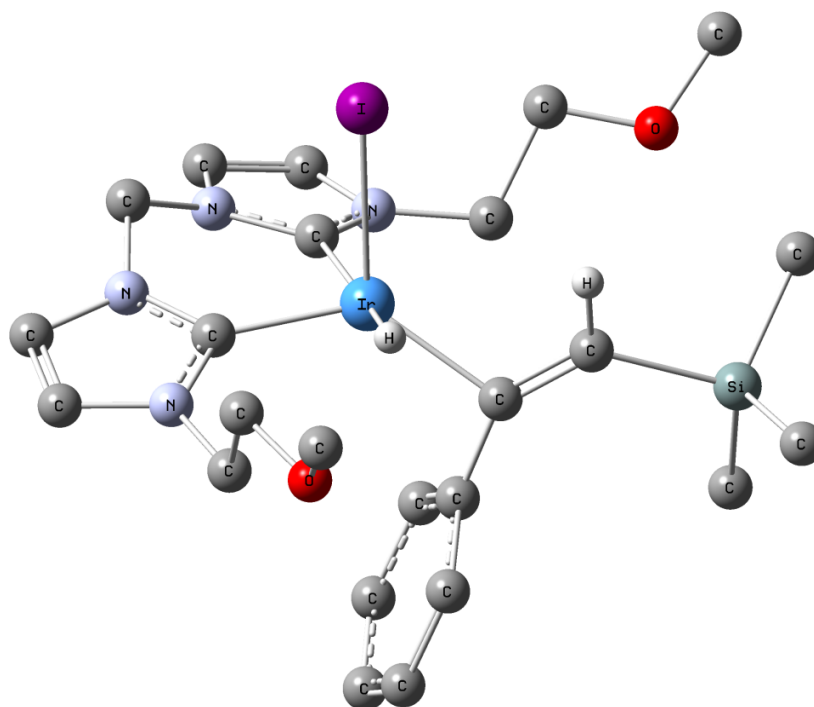


Table S1. DFT optimized Cartesian coordinates (in Å) of structures **8a** and **8b**:

8a (energy: -1710.72214936 a.u.)

77	0.096032	-0.225014	0.104242
1	-1.351578	0.466345	-0.097027
6	-0.790990	-1.943337	-0.336878
6	-2.278682	-3.615040	-0.572198
6	-1.070718	-4.107304	-0.929496
1	-3.247049	-4.089606	-0.526802
6	1.970386	-1.130532	-0.218531
6	3.543502	-2.664303	-0.770662
6	4.183472	-1.553613	-0.325739
1	3.927035	-3.608369	-1.127636
53	0.246118	0.583131	-2.455871

6 1.176443 -3.180128 -1.368143
1 1.472303 -4.229351 -1.322996
1 1.121113 -2.867697 -2.416916
1 -0.778879 -5.087562 -1.274958
1 5.236758 -1.355453 -0.198250
6 -0.660913 0.733095 1.719165
6 -1.128784 1.948231 2.004517
6 -3.253101 -1.446117 0.165940
1 -3.912681 -2.054477 0.789971
1 -2.906606 -0.603709 0.759776
6 -4.024609 -0.931520 -1.056919
1 -3.351382 -0.373228 -1.728723
1 -4.441511 -1.777263 -1.628509
6 -6.005824 0.290643 -1.491233
1 -5.545744 0.888365 -2.289491
1 -6.508890 -0.579752 -1.933304
1 -6.737259 0.898139 -0.956817
8 -5.034489 -0.117723 -0.526632
6 3.495577 0.745398 0.449801
1 2.541560 1.237842 0.655721
1 4.069356 0.706215 1.380318
6 4.247436 1.578620 -0.595551
1 3.703378 1.565020 -1.554826
1 5.252582 1.160441 -0.775306
6 5.066419 3.784448 -0.826911
1 4.621601 3.914571 -1.823178
1 5.046431 4.735908 -0.293856
1 6.107364 3.450909 -0.936826
8 4.311985 2.862453 -0.042024
6 -0.043065 -0.360971 2.505165

6 1.259202 -0.184663 3.065104
6 -0.810493 -1.491312 2.919951
6 1.760723 -1.089934 3.987694
1 1.828788 0.699254 2.799499
6 -0.295454 -2.394994 3.835288
1 -1.820427 -1.610909 2.546196
6 0.988024 -2.196965 4.368278
1 2.740215 -0.933512 4.428445
1 -0.893210 -3.239798 4.162422
1 1.379692 -2.899636 5.098251
7 -2.100310 -2.285524 -0.212819
7 -0.156282 -3.070684 -0.778212
7 2.183875 -2.385981 -0.688775
7 3.206662 -0.621763 -0.002156
14 -1.962210 3.388067 1.014519
1 -0.980885 2.210714 3.060124
6 -2.888225 2.750616 -0.493634
1 -3.430575 3.598309 -0.932996
1 -2.226437 2.362691 -1.275168
1 -3.634593 1.986831 -0.245487
6 -0.550870 4.548056 0.542838
1 0.146341 4.080369 -0.161895
1 -0.960505 5.442501 0.057272
1 0.017203 4.884043 1.417447
6 -3.132357 4.170987 2.262913
1 -2.605454 4.521278 3.158112
1 -3.625601 5.042371 1.815667
1 -3.920404 3.479022 2.581431

8b (energy: -1710.72761366 a.u.)

77 -0.321817 -0.249808 0.001294
1 -1.161187 0.824941 -0.883872
6 -2.110066 -0.966669 0.509357
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53 -0.307071 -1.492815 -2.367298
6 -1.446805 -3.379837 0.820662
1 -1.845401 -4.187538 1.435174
1 -1.411254 -3.703172 -0.224580
1 -4.098776 -3.331236 1.613150
1 2.916750 -3.815855 2.249006
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6 1.228090 2.054889 -0.813415
6 -3.613261 1.065523 0.215270
1 -4.384272 1.423115 0.901317
1 -2.723354 1.670184 0.369203
6 -4.086435 1.206171 -1.236970
1 -3.375301 0.714303 -1.921930
1 -5.066670 0.718462 -1.369306
6 -4.747052 2.936757 -2.707181
1 -4.163590 2.535739 -3.547722
1 -5.778592 2.565187 -2.775019
1 -4.752420 4.026547 -2.756968
8 -4.156473 2.588183 -1.456419
6 3.007085 -1.300201 1.058774

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6 -1.000008 2.463905 4.081961
1 0.265071 0.849114 4.742338
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7 1.857252 -2.184417 1.292622
14 2.795111 3.213831 -0.614165
6 2.244882 4.805825 -1.461414
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1	3.436193	2.524753	1.715179
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