

Electronically Tunable *N*-Heterocyclic Carbene Ligands: 1,3-Diaryl vs. 4,5-Diaryl Substitution

James W. Ogle and Stephen A. Miller*

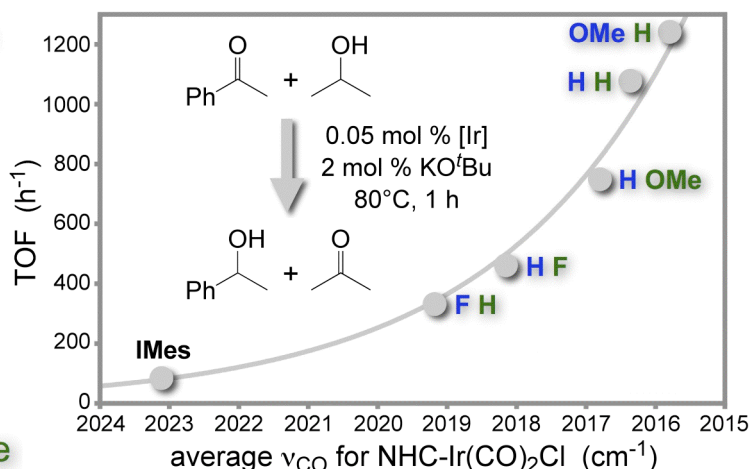
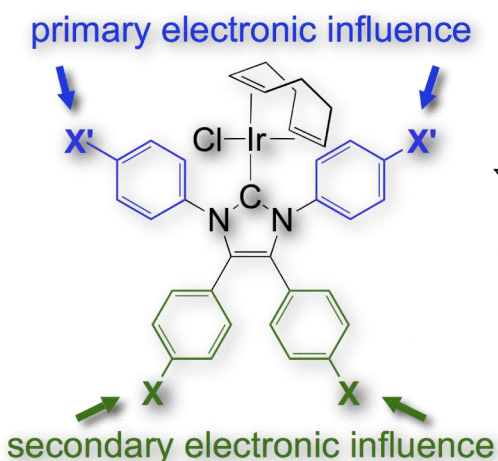
*The George and Josephine Butler Laboratory for Polymer Research, Department of Chemistry, University of Florida
Gainesville, Florida 32611-7200, USA*

Electronic Supplementary Information

Supporting Information Available: Synthetic details, NMR spectra, infrared data, transfer hydrogenation data, and Hammett correlation data.

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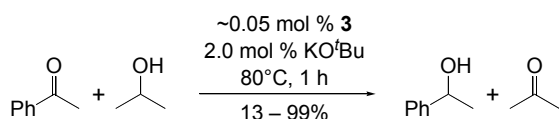


General Methods and Instrumentation. All air sensitive reactions were carried out in oven-dried glassware and procedures were performed under an atmosphere of dinitrogen in a glovebox or using standard Schlenk techniques. All solvents and reagents were used as received from commercial sources unless otherwise stated. Dichloromethane used in NHC carbene synthesis was dried using activated alumina columns (MBraun SPS). Hexanes were distilled from CaH₂. CDCl₃ was stored over 4Å molecular sieves. Acetophenone and isopropanol were dried over MgSO₄ and degassed prior to use. Iridium 1,5-cyclooctadiene chloride dimer was prepared by the procedure described in the literature by reaction of iridium trichloride hydrate (Pressure Chemical Co.) with 1,5-cyclooctadiene.¹ Imidazolium salts **2** were prepared by our previously published method.² ¹H and ¹³C NMR measurements were performed on a Varian Mercury 300 or 400 MHz spectrometer and referenced to resonances due to residual protons in the deuterated solvents or the ¹³C resonances of the deuterated solvents. Infrared spectra were taken on a PerkinElmer Spectrum One FT-IR Spectrometer.

Synthesis of [1,5-cyclooctadiene][1,3-Ar'-2,4,5-Ar₂-2-imidazolyliene]IrCl (3a-e**).** The complexes **3** were synthesized using the method developed in the literature.³ Imidazolium chloride (1.0 eq, 0.5 mmol) was dissolved in THF. To this red solution, iridium cyclooctadiene chloride dimer (0.6 eq, 0.3 mmol, 202 mg) was added, followed by potassium *tert*-butoxide (1.2 eq, 0.6 mmol, 68 mg). The solution immediately turned a dark brown color, and was allowed to stir for 30 minutes, after which it was dissolved in 10 mL of CH₂Cl₂, washed twice with water (20 mL), dried over MgSO₄, filtered, and concentrated *in vacuo*, producing dark yellow-brown flakes. NMR analysis indicated that the complexes were pure at this stage.

Synthesis of [1,3-Ar'-2,4,5-Ar₂-2-imidazolyliene]IrCl(CO)₂ (4a-e**).** The [COD][NHC]IrCl complexes (**3a-e**, 0.02 mmol) were dissolved in 10 mL of CH₂Cl₂, and CO gas was added via a submerged needle that was attached to a cylinder. Importantly, the CO gas was allowed to bubble through the solution slightly above atmospheric pressure for only **3 seconds** with vigorous stirring. A noticeable color change from dark yellow to lighter yellow was observed, after which solvent was removed *in vacuo*. NMR analysis indicated that, although the compounds were only approximately 80% pure, no starting material remained, and the solutions would be pure enough for use in the IR studies, as no interference would occur in the CO stretching region. The IR measurements were conducted using a thin film made from a CH₂Cl₂ solution of **4**, heated to 50 °C, and each compound was analyzed by IR four times except for **4b**, which was only measured three times. Ambient moisture appeared to have an influence on the IR CO stretch; thus, extra care was taken in removing the dichloromethane and multiple IR measurements were taken. The carbonyl complexes **4** were not stable under conditions required to obtain HRMS data.

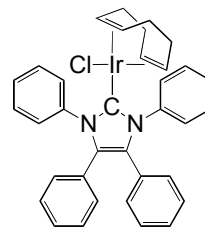
Transfer Hydrogenation Studies of Complexes **3a-e**.



A standard solution of complex **3** (~0.050 mol %, 5.0 to 10.0 mg) in 1.0 mL dichloromethane was added to a 100 mL flask fitted with a 45° Schlenk adapter in a glove box. The solvent was evacuated at room temperature on an external high vacuum line, and the sealed flask was returned to the glove box. Acetophenone (1.00 eq, ~16.6 mmol, ~2.00 g), a solution of potassium *tert*-butoxide in isopropanol (2.0 mol %, 8 mg, 0.33 mmol), and isopropanol (excess, 8 mL) were added in a glovebox, in order, to the flask, and the flask was equipped with a magnetic stirring bar and resealed. The flask was taken quickly to a vacuum line equipped with an 80 °C oil bath and stirrer, at which time a stopwatch was started, and after flushing the Schlenk adapter three times with nitrogen and vacuum over 10 seconds, the flask was opened to a nitrogen-filled bubbler. After the stopwatch reached 1.0 h, the flask was removed from the oil bath and vacuum line, and samples of about 0.1 mL of the reaction mixture were immediately diluted with 1.5 mL CDCl₃ in an NMR tube for immediate NMR analysis to measure the reaction conversion. The doublet from 1-phenylethanol at δ 1.5 ppm was integrated against the singlet from acetophenone at δ 2.6 ppm to determine conversion from each ¹H NMR spectrum. Each reaction was performed twice in this manner to obtain two sets of data for Figure 1 in the main text (see Table S1 below).

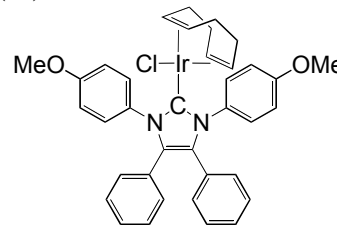
Summary of ¹H, ¹³C, ¹⁹F NMR, and MS Data

[1,5-cyclooctadiene][1,3,4,5-tetraphenyl-2-imidazolyliene]IrCl (**3a**).



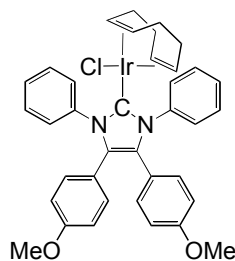
Yield 68%. ¹H (CDCl₃): δ 7.68 (m, 4H), 7.31 (m, 6H), 7.10 (m, 10H), 4.31 (m, 2H), 2.62 (m, 2H), 1.68 (m, 2H), 1.40 – 1.20 (m, 6H). ¹³C{¹H} (CDCl₃): δ 181.9, 162.3, 138.6, 132.2, 130.9, 129.0, 128.5, 128.4, 128.3, 128.2, 83.2, 51.8, 33.2, 29.2. LRMS: calculated 708.1889; found 708.19.

[1,5-cyclooctadiene][1,3-dianisyl-4,5-diphenyl-2-imidazolyliene]IrCl (**3b**).



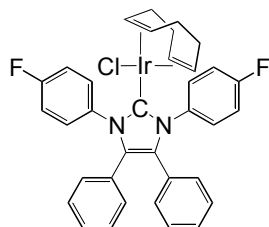
Yield 93%. ¹H (CDCl₃): δ 7.56 (d, 4H, *J* = 8.8 Hz), 7.09 (m, 10H), 5.82 (d, 4H, *J* = 9.1 Hz), 4.30 (m, 2H), 3.75 (s, 6H), 2.08 (m, 2H), 1.72 (m, 2H), 1.59 – 1.14 (m, 6H). ¹³C{¹H} (CDCl₃): δ 181.6, 159.1, 130.8, 130.0, 128.8, 128.4, 128.3, 128.2, 128.1, 114.1, 82.7, 55.5, 51.6, 33.2, 29.1. HRMS: calculated [M+H]⁺ 769.2161; found 769.2158.

[1,5-cyclooctadiene][4,5-dianisyl-1,3-diphenyl-2-imidazolylidene]IrCl (3c).



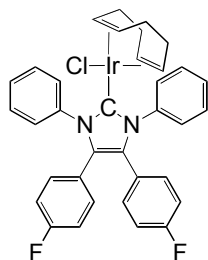
Yield 94%. ^1H (CDCl_3): δ 7.68 (m, 4H), 7.32 (m, 6H), 6.97 (d, 4H, $J = 8.8$ Hz), 6.66 (d, 4H, $J = 8.8$ Hz), 4.31 (m, 2H), 3.64 (s, 6H), 2.55 (m, 2H), 1.65 (m, 2H), 1.38 (m, 4H), 1.17 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ (CDCl_3): δ 181.2, 159.5, 138.8, 132.2, 131.7, 129.1, 128.2, 128.0, 120.7, 113.8, 82.9, 55.3, 51.7, 33.2, 29.2. HRMS: calculated $[\text{M}+\text{H}]^+$ 769.2161; found 769.2154.

[1,5-cyclooctadiene][4,5-diphenyl-1,3-di-(4-fluorophenyl)-2-imidazolylidene]IrCl (3d).



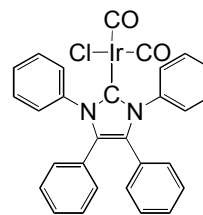
Quantitative yield. ^1H (CDCl_3): δ 7.67 (m, 4H), 7.15 (m, 6H), 7.02 (m, 8H), 4.36 (m, 2H), 2.60 (m, 2H), 1.85 – 1.65 (m, 2H), 1.55 – 1.35 (m, 4H), 1.30 – 1.19 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ (CDCl_3): δ 182.3, 164.3, 161.0, 138.3, 138.8 (d, $J = 8.3$ Hz), 131.3, 129.0, 128.4, 115.9, 115.6, 83.5, 51.9, 33.2, 29.2. ^{19}F (CDCl_3): δ -113.4. HRMS: calculated $[\text{M}+\text{H}]^+$ 745.1761; found 745.1756.

[1,5-cyclooctadiene][1,3-diphenyl-4,5-di-(4-fluorophenyl)-2-imidazolylidene]IrCl (3e).



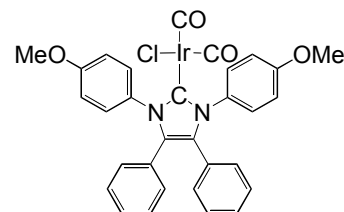
Yield 88%. ^1H (CDCl_3): δ 7.64 (dd, 4H, $J = 3.9, 4.7$ Hz), 7.15 (m, 6H), 7.0 (m, 8H), 4.34 (m, 2H), 2.56 (m, 2H), 1.72 (m, 2H), 1.55 – 1.34 (m, 4H), 1.22 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ (CDCl_3): δ 182.1, 163.8, 160.5, 134.6 (d, $J = 3.1$ Hz), 132.3, 130.9, 128.8, 128.5, 115.4, 115.1, 84.0, 52.0, 33.2, 29.2. ^{19}F (CDCl_3): δ -113.3. HRMS: calculated $[\text{M}+\text{H}]^+$ 745.1761; found 745.1740.

[1,3,4,5-tetraphenyl-2-imidazolylidene]IrCl(CO) $_2$ (4a).



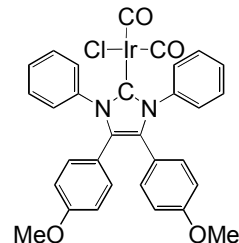
^1H (CDCl_3): δ 7.48 (m, 4 H), 7.39 (m, 6H) 7.25 - 7.11 (m, 6 H), 6.93 (d, $J = 7.1$ Hz, 4 H). $^{13}\text{C}\{^1\text{H}\}$ (CDCl_3): δ 180.8, 174.3, 168.1, 137.8, 130.7, 129.9, 129.3, 129.0, 128.9, 128.6, 128.3, 127.5.

[1,3-dianisyl-4,5-diphenyl-2-imidazolylidene]IrCl(CO) $_2$ (4b).



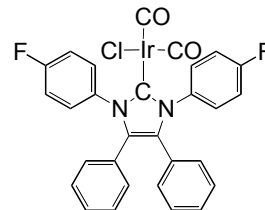
^1H (CDCl_3): δ 7.37 (d, $J = 8.8$ Hz, 4 H), 7.26 - 7.12 (m, 6 H), 6.99 (m, 4H) 6.88 (d, $J = 8.8$ Hz, 4 H), 3.38 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ (CDCl_3): δ 181.1, 174.4, 168.3, 159.9, 132.7, 130.7, 130.6, 130.0, 128.8, 128.6, 127.7, 114.08, 55.6.

[4,5-dianisyl-1,3-diphenyl-2-imidazolylidene]IrCl(CO) $_2$ (4c).



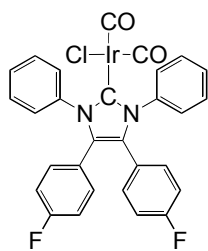
^1H (CDCl_3): δ 7.57 – 7.31 (m, 10 H), 6.87 (d, $J = 8.5$ Hz, 4 H), 6.67 (d, $J = 8.7$ Hz, 4 H), 3.72 (s, 6 H). $^{13}\text{C}\{^1\text{H}\}$ (CDCl_3): δ 181.7, 174.3, 169.0, 160.5, 138.7, 132.9, 132.8, 129.9, 129.8, 129.7, 120.5, 114.9, 56.1.

[4,5-diphenyl-1,3-di-(4-fluorophenyl)-2-imidazolylidene]IrCl(CO) $_2$ (4d).



^1H (CDCl_3): δ 7.46 (m, 4 H), 7.30 – 7.04 (m, 10 H), 6.97 (d, $J = 7.1$ Hz, 4 H). $^{13}\text{C}\{^1\text{H}\}$ (CDCl_3): δ 180.6, 174.8, 168.0, 164.4, 161.1, 133.7, 132.9, 130.7, 129.2, 128.8, 127.1, 116.3 (d, $J = 23.2$ Hz). ^{19}F (CDCl_3): δ -111.38.

[1,3-diphenyl-4,5-di-(4-fluorophenyl)-2-imidazolylidene]
IrCl(CO)₂ (4e).



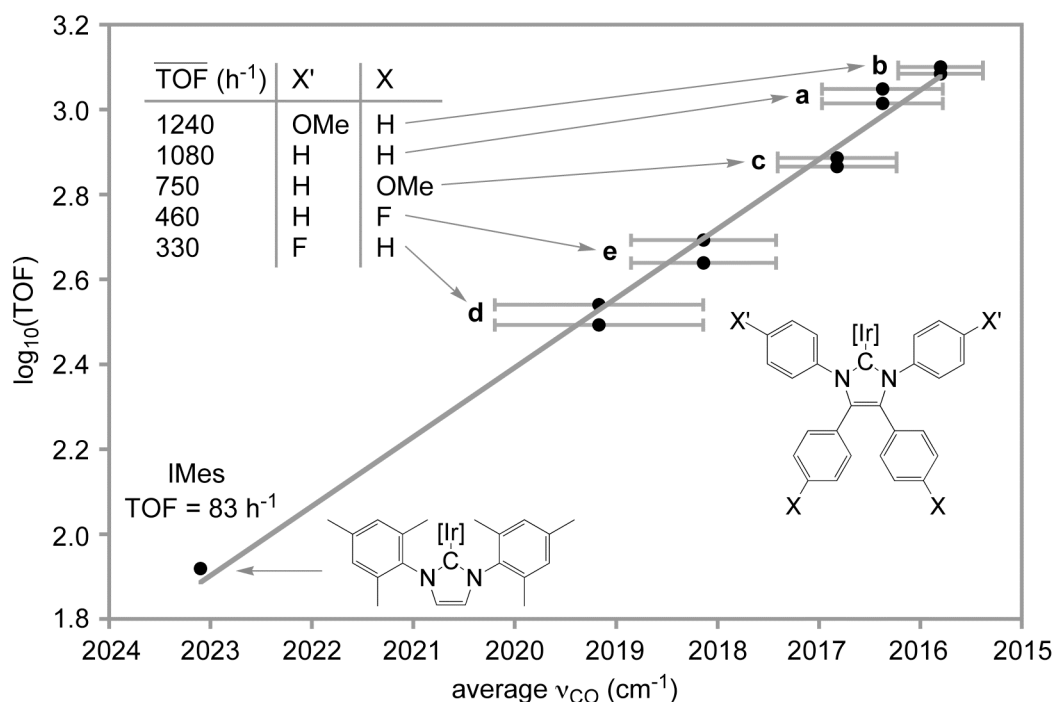
¹H (CDCl₃): δ 7.43 (m, 10H), 6.92 (m, 8H). ¹³C{¹H} (CDCl₃):
δ 180.7, 174.7, 168.1, 164.6, 161.3, 137.5, 132.6, 132.5,
129.5, 129.2, 123.4, 116.3 (d, *J* = 21.9 Hz). ¹⁹F (CDCl₃): δ -
111.30.

Infrared Data

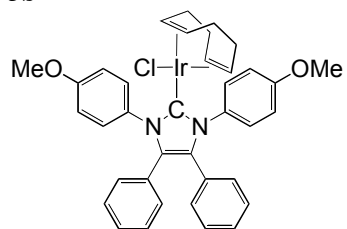
Figure 1 was prepared according to the following carbonyl stretching frequencies (from the corresponding complexes **4a** – **4e**) and TOF values (from complexes **3a** – **3e**).

entry	1,3-substitution	4,5-substitution	IR (unsym + sym)/2 (cm ⁻¹)	average IR (cm ⁻¹)	st. dev	TOF (h ⁻¹)	log ₁₀ (TOF)
IMes ^a	2,4,6-Me ₃ C ₆ H ₂	H	2023.1	2023.1		83	1.9191
3a	C ₆ H ₅	C ₆ H ₅	2015.605 2016.04 2017.16 2016.69	2016.374	0.59594	1119 1034	3.0488 3.0145
3b	<i>p</i> -C ₆ H ₄ OMe	C ₆ H ₅	wet 2015.07 2015.79 2016.54	2015.800	0.41861	1260 1215	3.1004 3.0846
3c	C ₆ H ₅	<i>p</i> -C ₆ H ₄ OMe	2016.355 2016.125 2017.415 2017.39	2016.821	0.58698	734 769	2.8657 2.8859
3d	<i>p</i> -C ₆ H ₄ F	C ₆ H ₅	2020.14 2019.675 2017.445 2019.42	2019.170	1.02884	311 347	2.4928 2.5403
3e	C ₆ H ₅	<i>p</i> -C ₆ H ₄ F	2018.605 2018.795 2016.96 2018.19	2018.138	0.71416	493 435	2.6928 2.6385

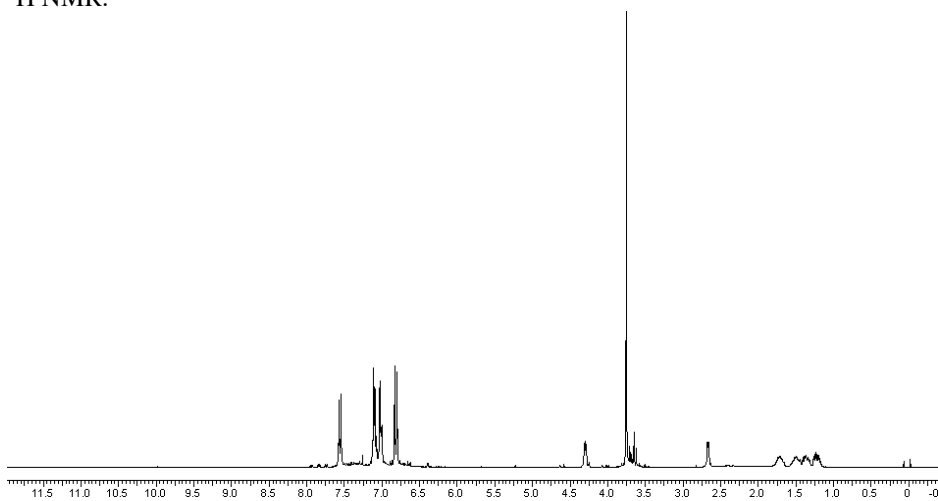
^aIR values for IMes are obtained from references 4 and 5.



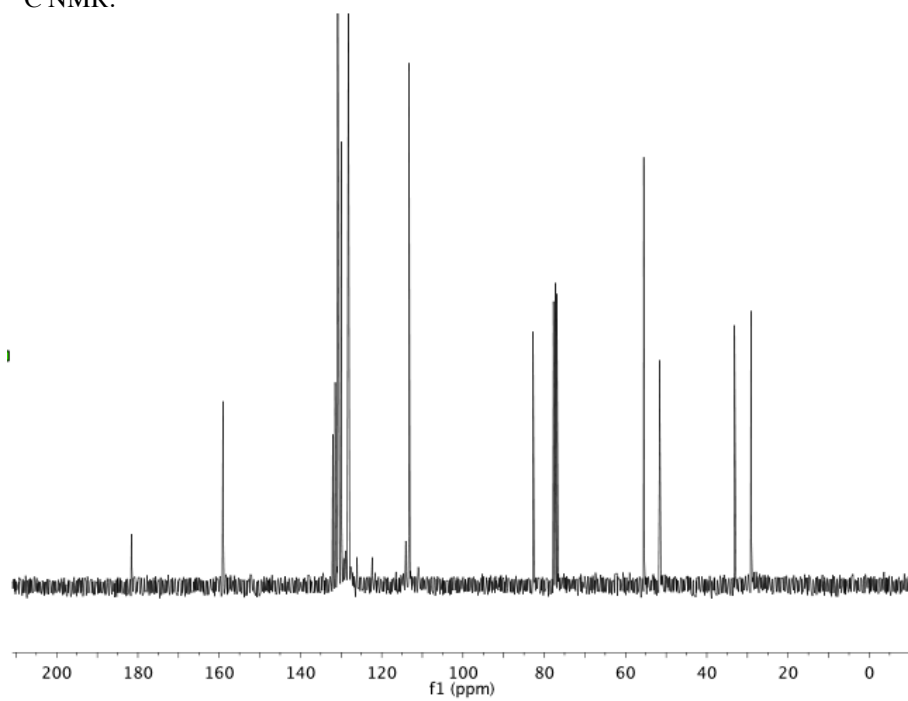
3b



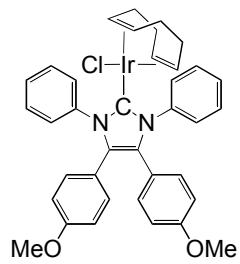
^1H NMR:



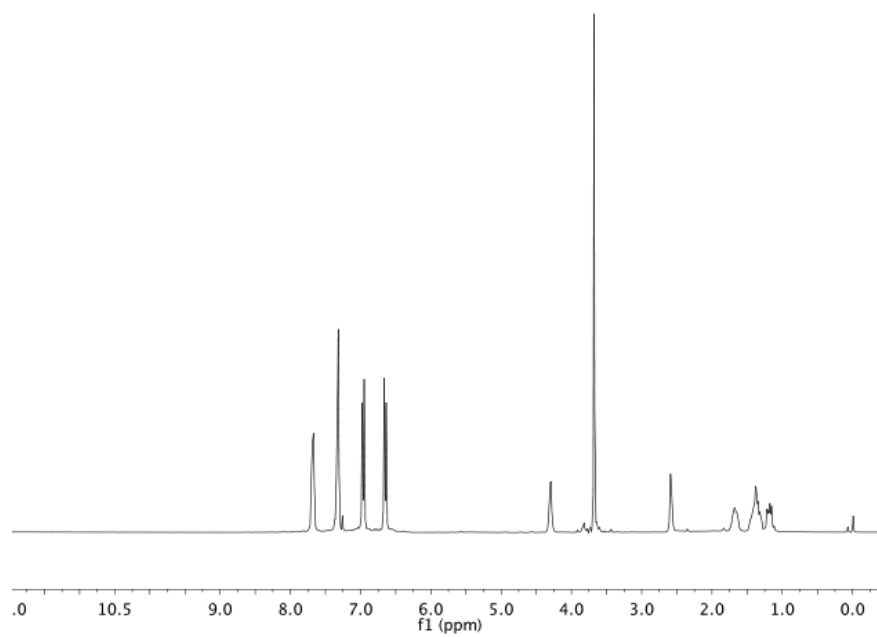
^{13}C NMR:



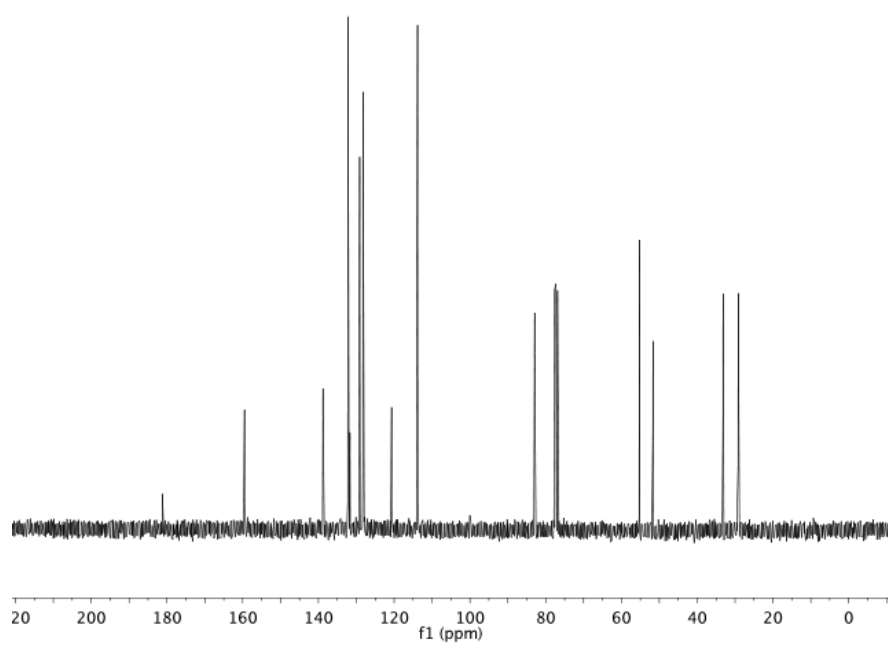
3c



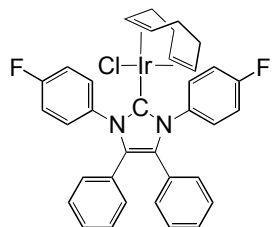
^1H NMR:



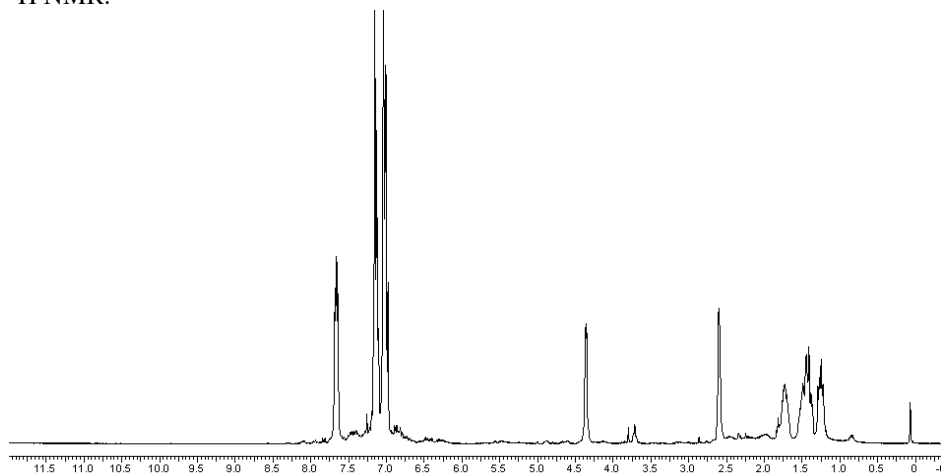
^{13}C NMR:



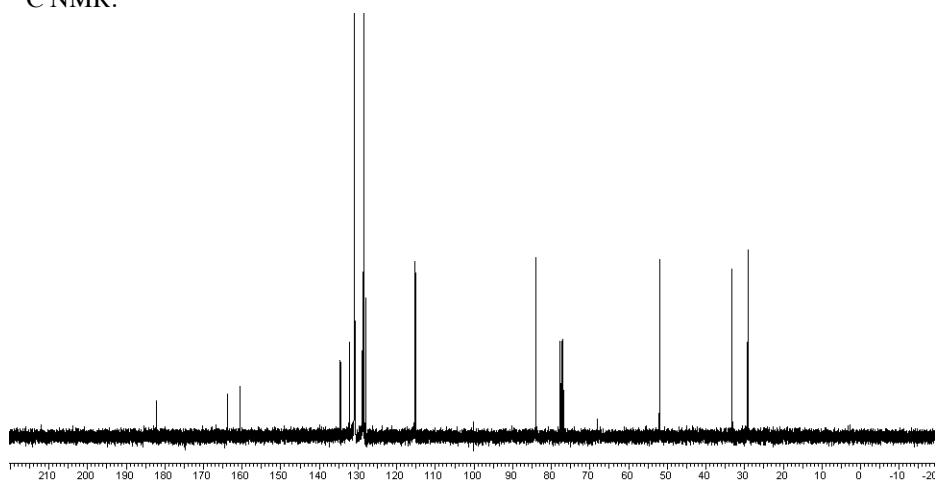
3d



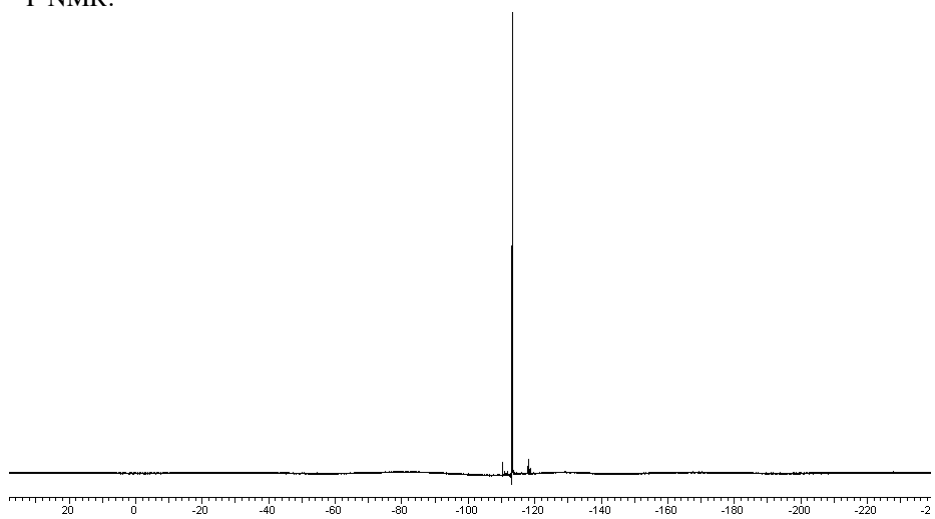
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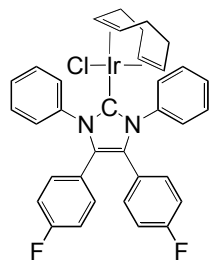
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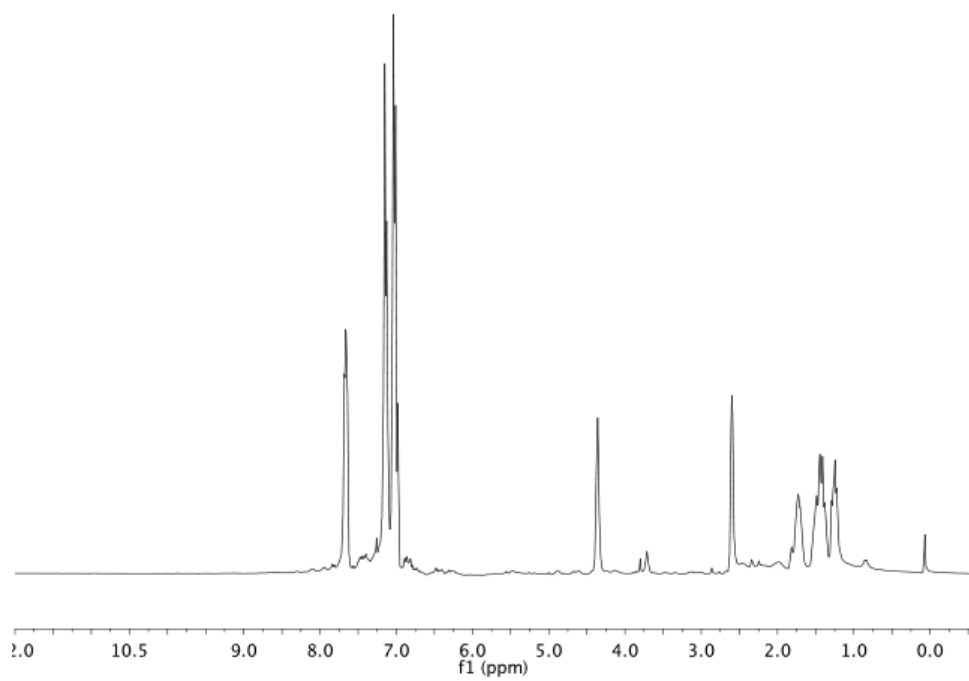
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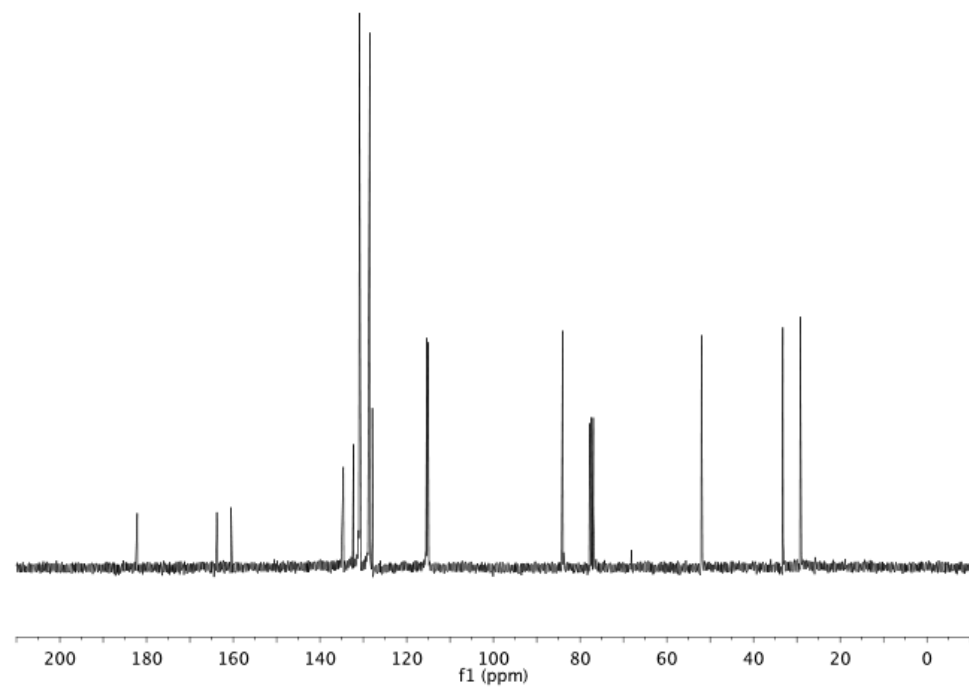
3e



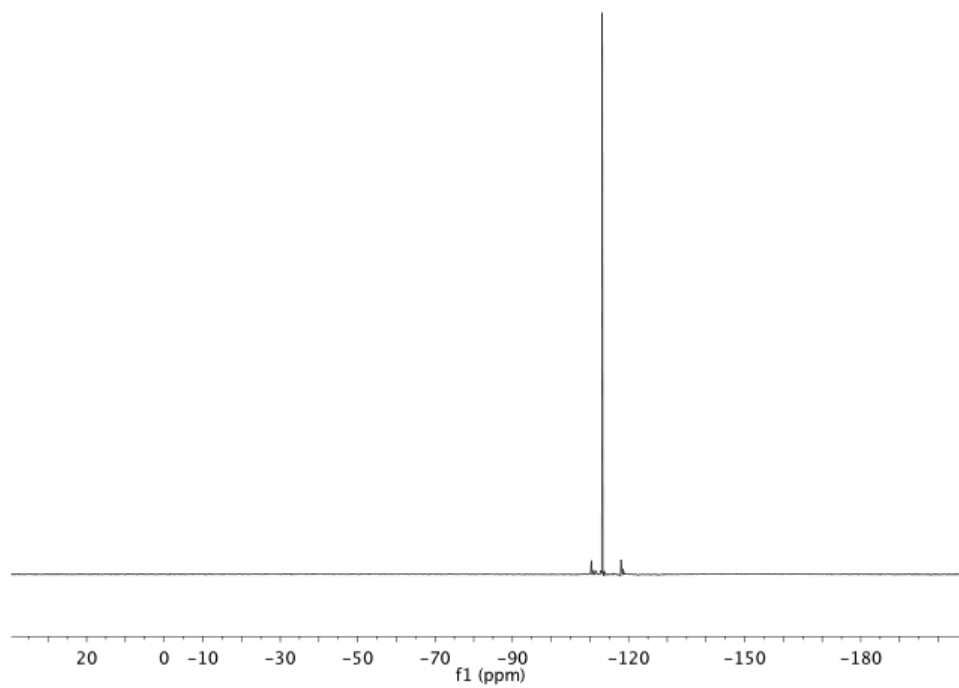
^1H NMR:



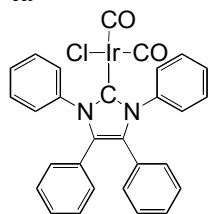
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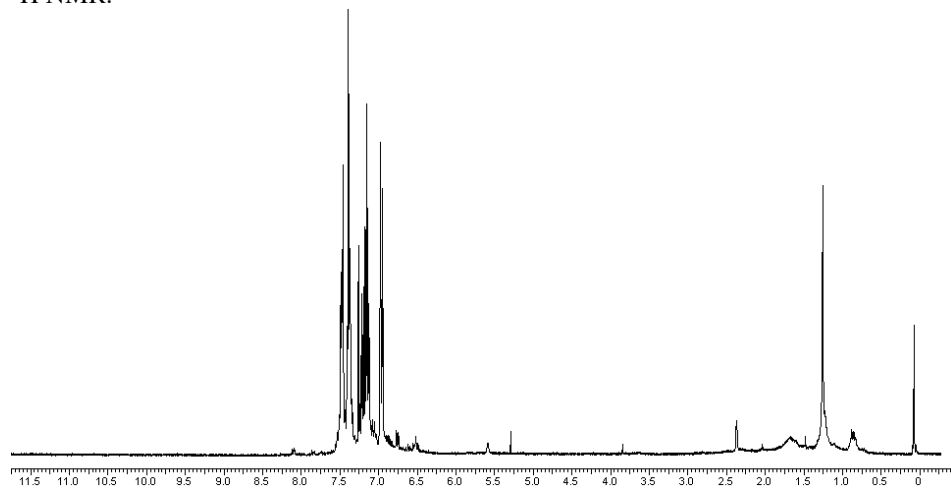
^{19}F NMR:



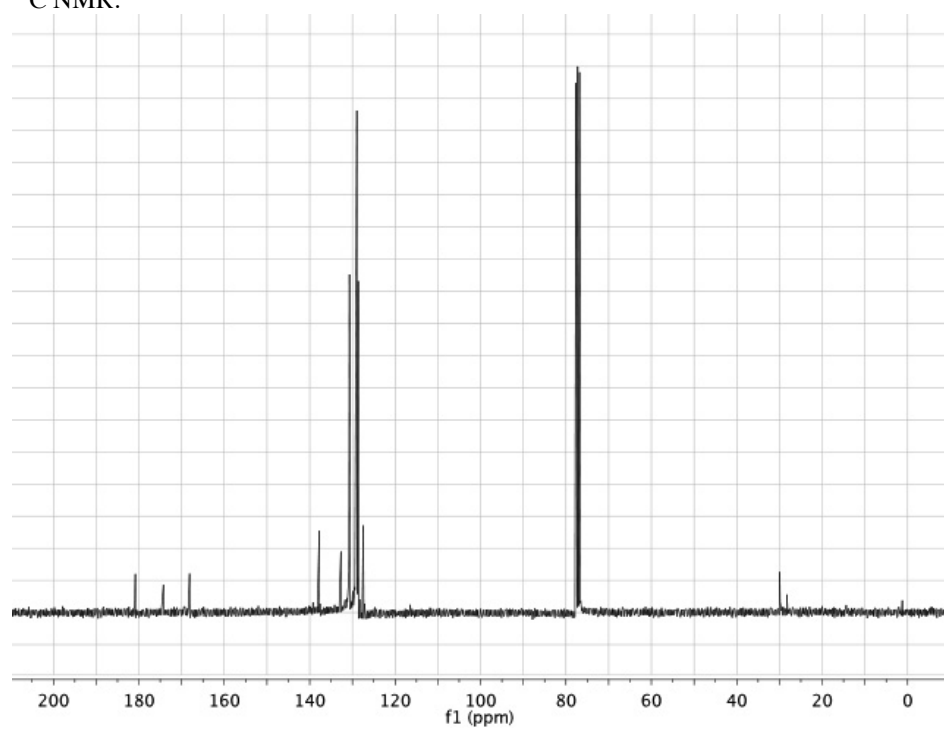
4a



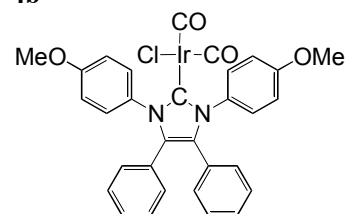
¹H NMR:



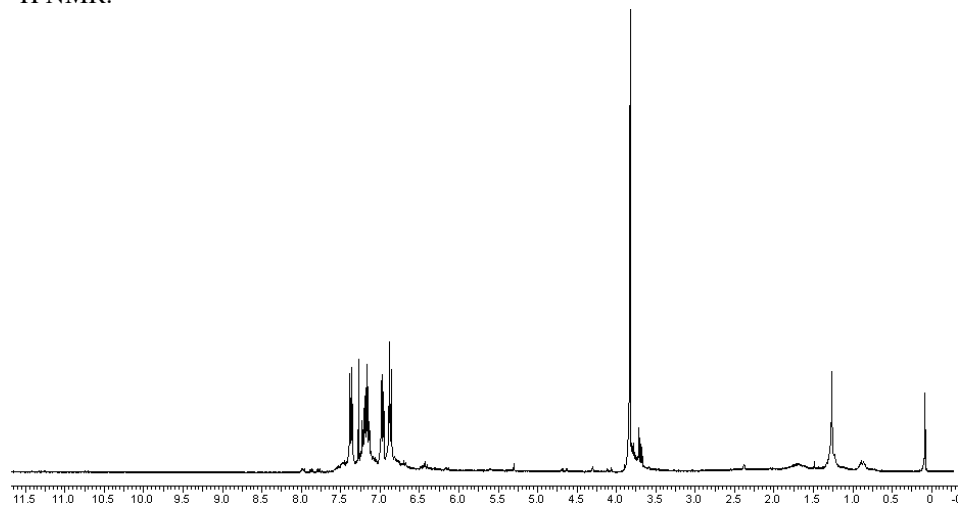
¹³C NMR:



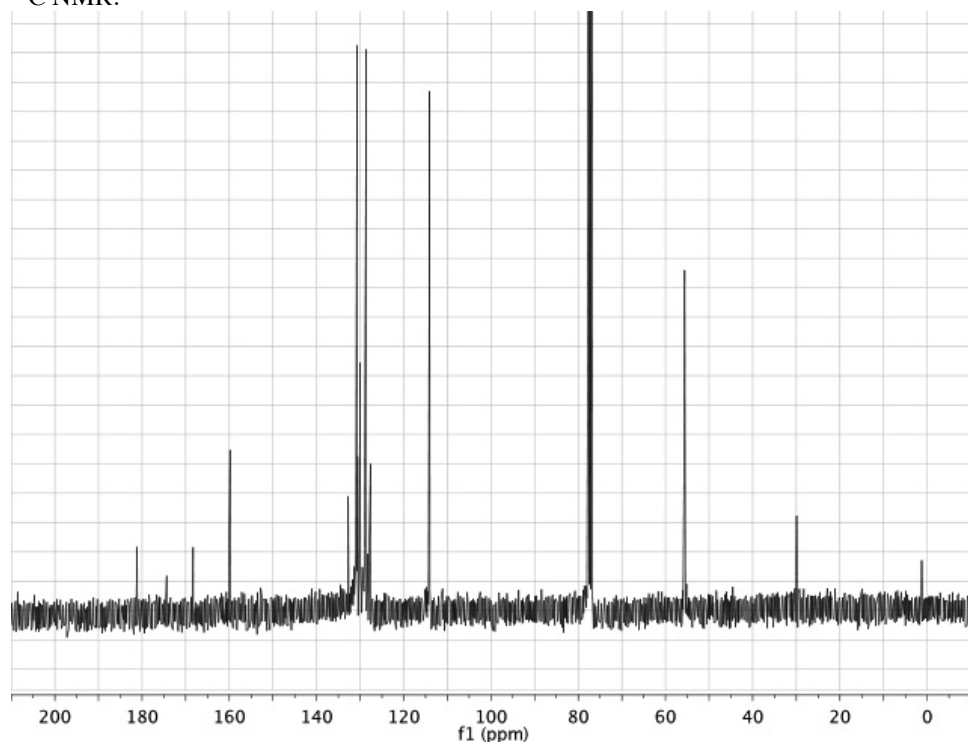
4b



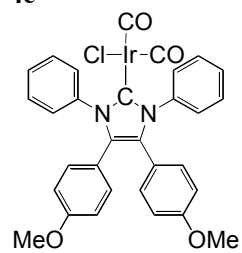
^1H NMR:



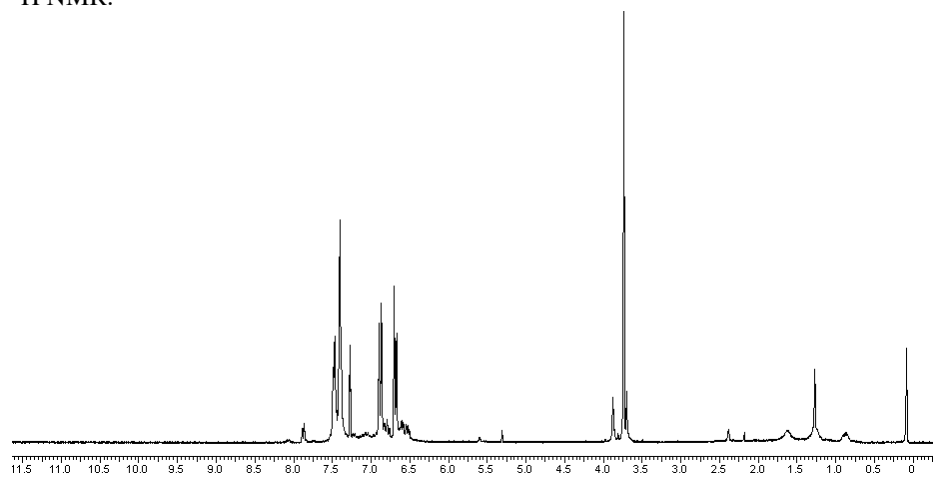
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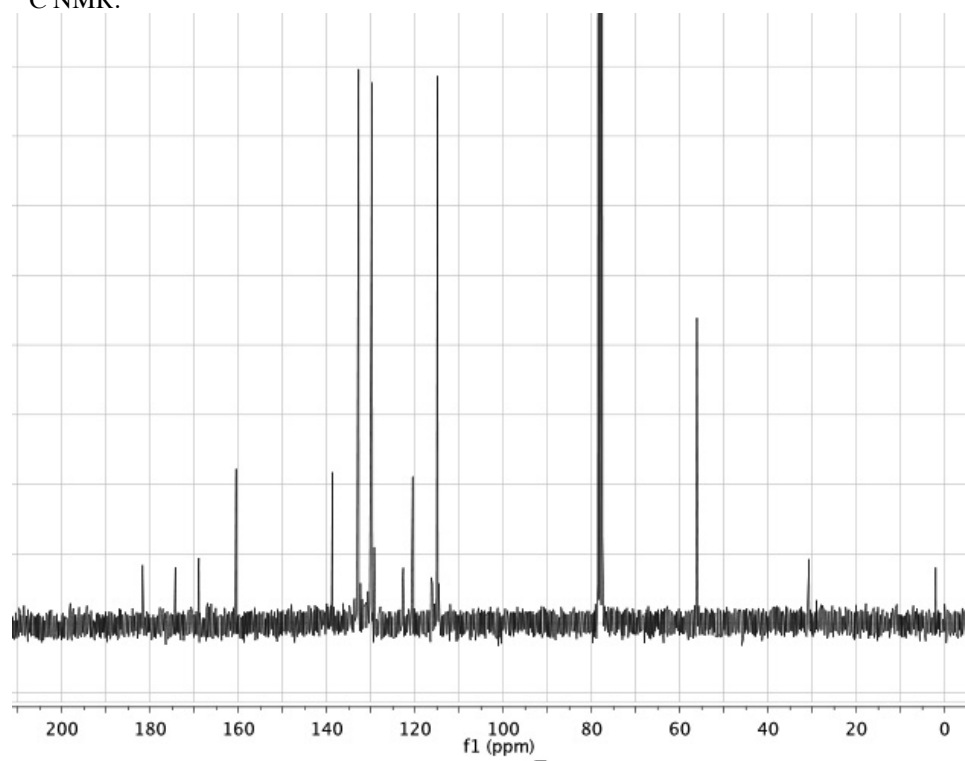
4c



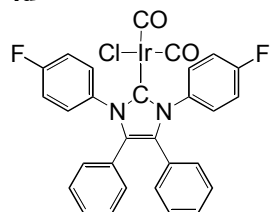
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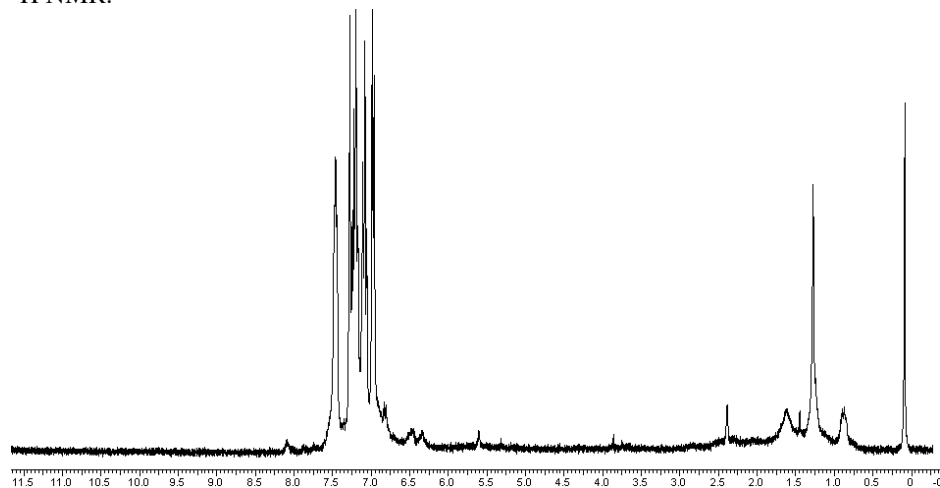
^{13}C NMR:



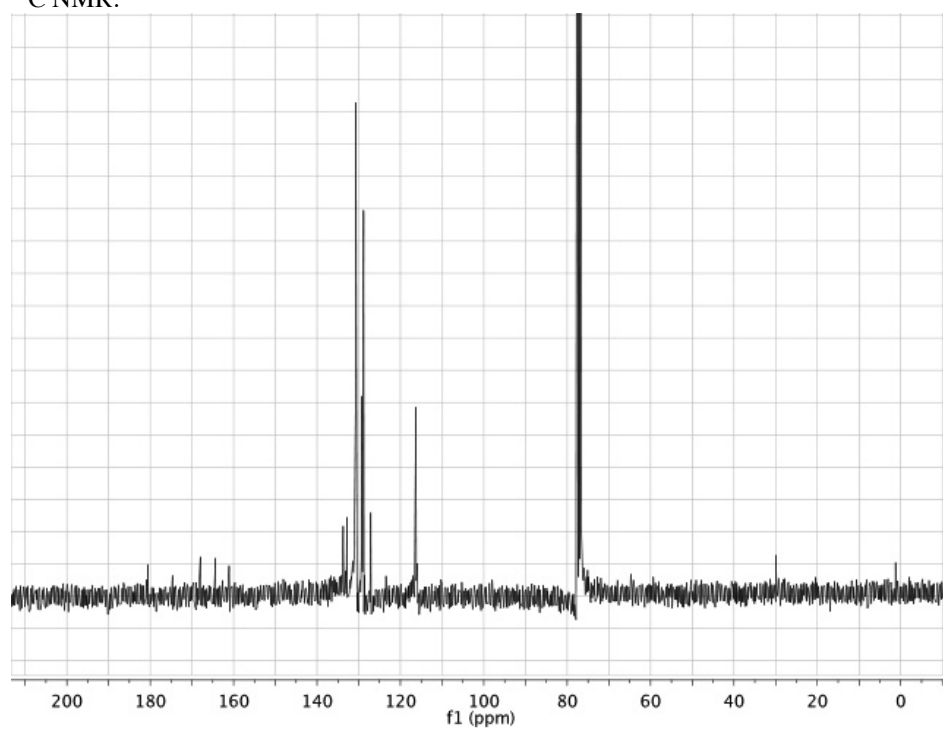
4d



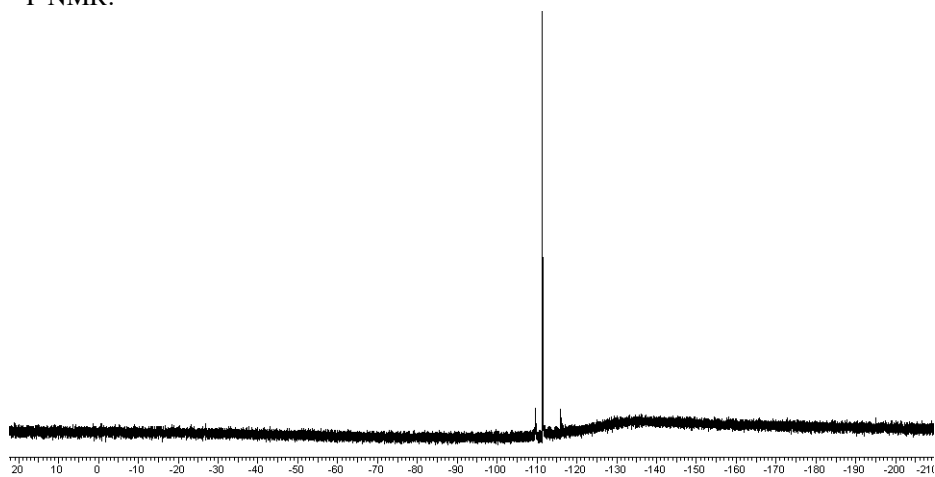
^1H NMR:



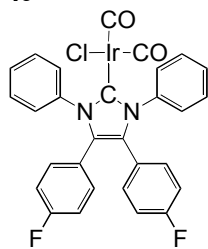
^{13}C NMR:



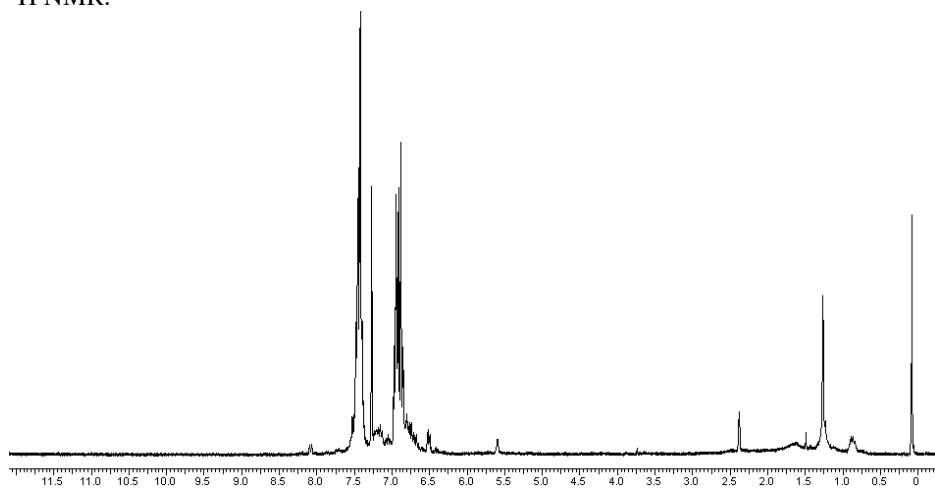
^{19}F NMR:



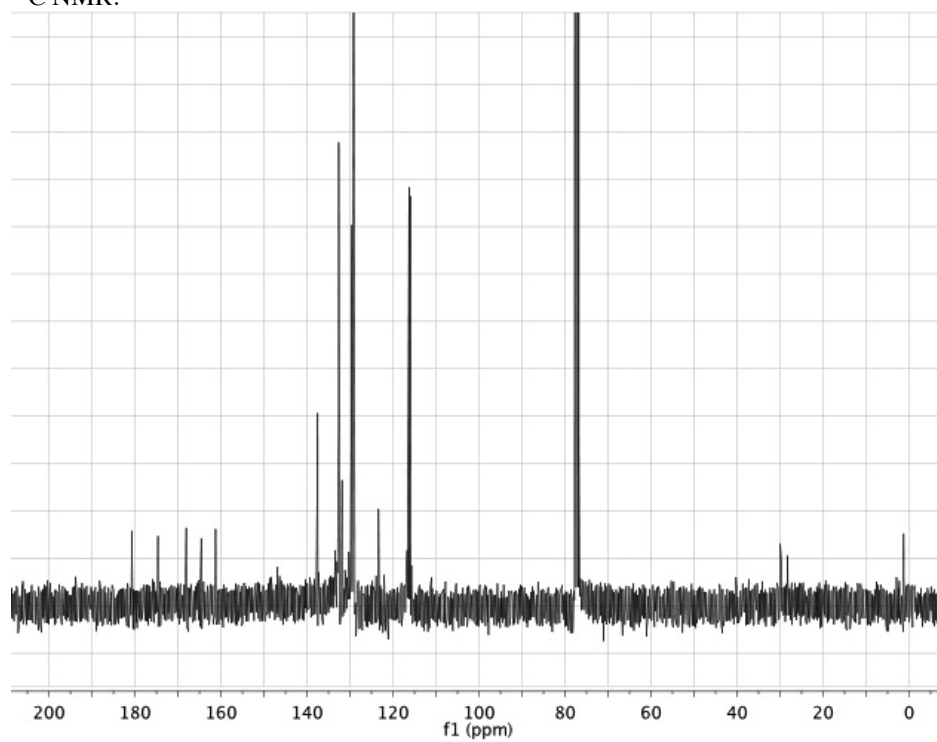
4e



^1H NMR:



^{13}C NMR:



^{19}F NMR:

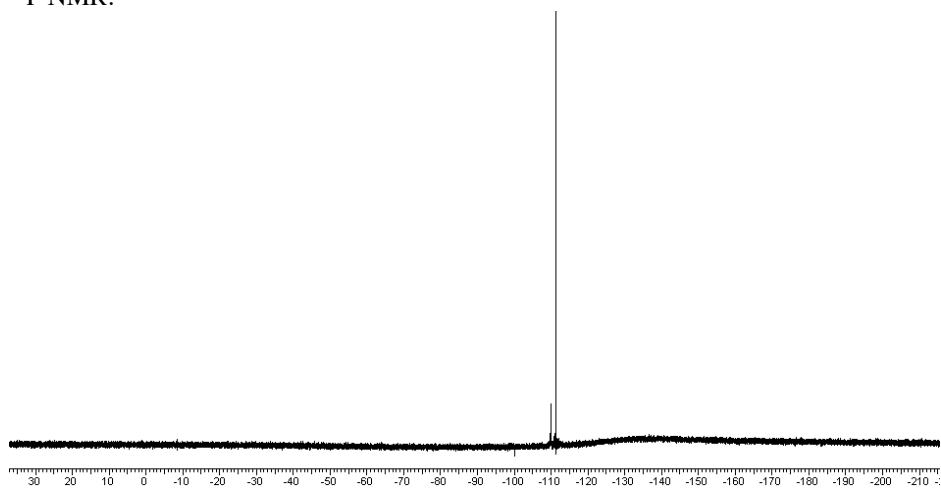
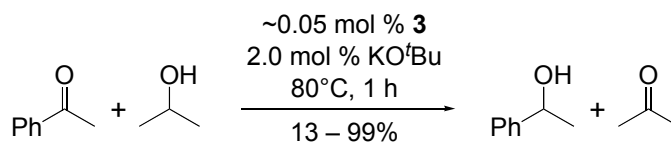


Table S1. Acetophenone Transfer Hydrogenations



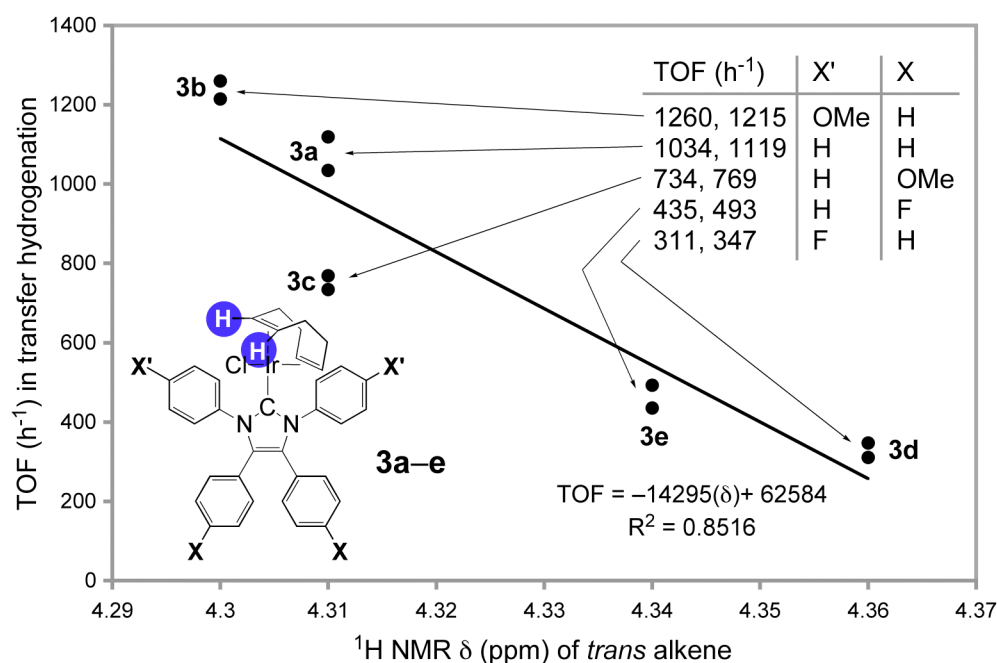
entry	1,3-substitution	4,5-substitution	catalyst loading (mol %)	¹ H NMR conversion (%) ^{a,b}	turnovers
3a.1	C ₆ H ₅	C ₆ H ₅	0.032	34	1034
3a.2	C ₆ H ₅	C ₆ H ₅	0.034	39	1119
3b.1	<i>p</i> -C ₆ H ₄ OMe	C ₆ H ₅	0.064	86	1260
3b.2	<i>p</i> -C ₆ H ₄ OMe	C ₆ H ₅	0.059	71	1210
3c.1	C ₆ H ₅	<i>p</i> -C ₆ H ₄ OMe	0.065	50	769
3c.2	C ₆ H ₅	<i>p</i> -C ₆ H ₄ OMe	0.038	27	734
3d.1	<i>p</i> -C ₆ H ₄ F	C ₆ H ₅	0.042	13	311
3d.2	<i>p</i> -C ₆ H ₄ F	C ₆ H ₅	0.040	14	346
3e.1	C ₆ H ₅	<i>p</i> -C ₆ H ₄ F	0.170	85	493
3e.2	C ₆ H ₅	<i>p</i> -C ₆ H ₄ F	0.230	99	435

^aDetermined by integration of the methyl 1-phenylethanol doublet vs. the methyl acetophenone singlet.

^b2.0 grams +/- 0.1 grams of acetophenone were employed in these reactions. In each instance, the precise amount was measured to the nearest mg in order to obtain accurate turnover measurements.

¹H NMR Correlation to Transfer Hydrogenation Turnover Frequency

A plot of the turnover frequency (for 1 hour transfer hydrogenation reactions with **3a-e**; see Table S1) versus the ¹H NMR chemical shift of the vinylic hydrogens *trans* to the *N*-heterocyclic carbene is approximately linear.



Hammett Correlations

Hammett plots for the transfer hydrogenation of acetophenone by **3a–e**. Rates are determined by ^1H NMR conversion at $t = 1.0$ hour (average of two reactions; see Table S1) and are plotted as $\log_{10}(k/k_{\text{H}})$ vs. σ_{para} , σ_{meta} or σ_{I} . The Hammett parameters for σ_{para} and σ_{meta} are taken from reference 6 and the Hammett parameters for σ_{I} are taken from reference 7. Rates are assumed to be proportional to the turnover frequency; thus $\log_{10}(k/k_{\text{H}})$ is assumed to be equal to $\log_{10}(\text{TOF}/\text{TOF}_{\text{H}})$. All linear fits include the point at 0,0 and the R^2 values are given.

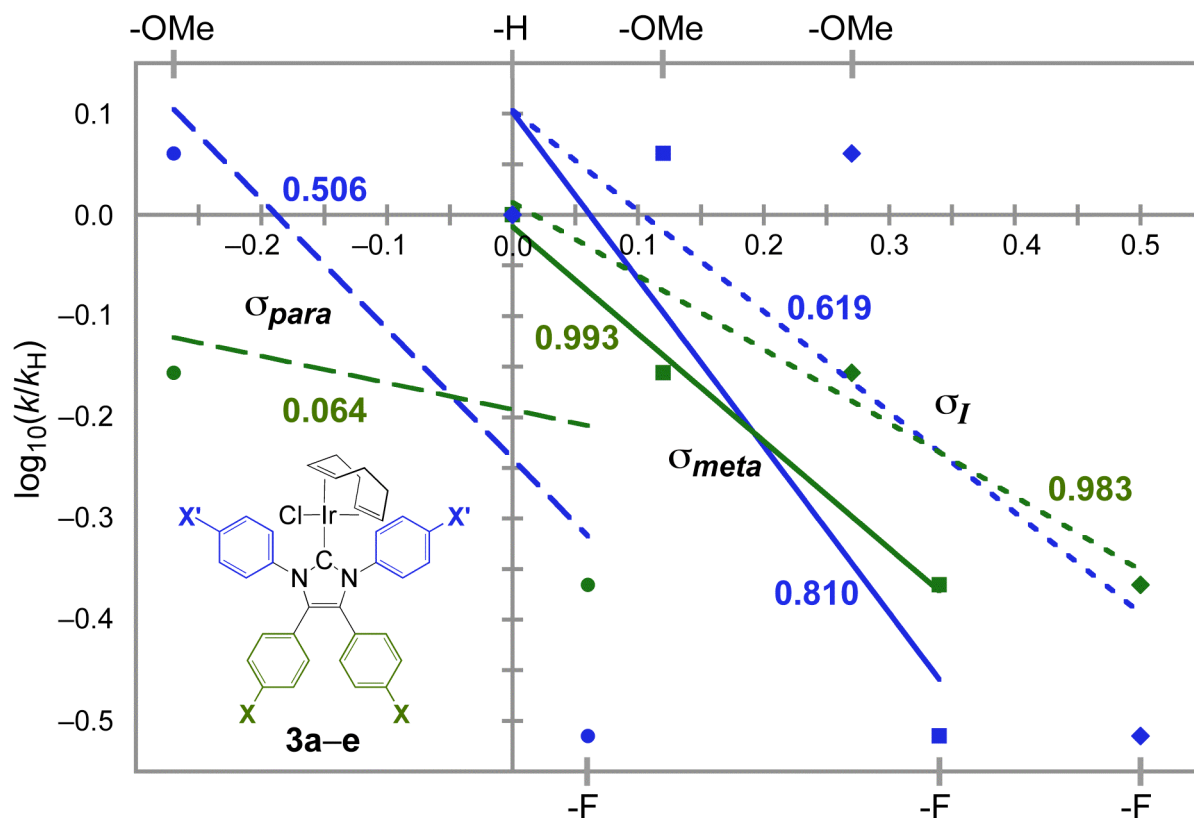


Table S2. Hammett Correlation Data

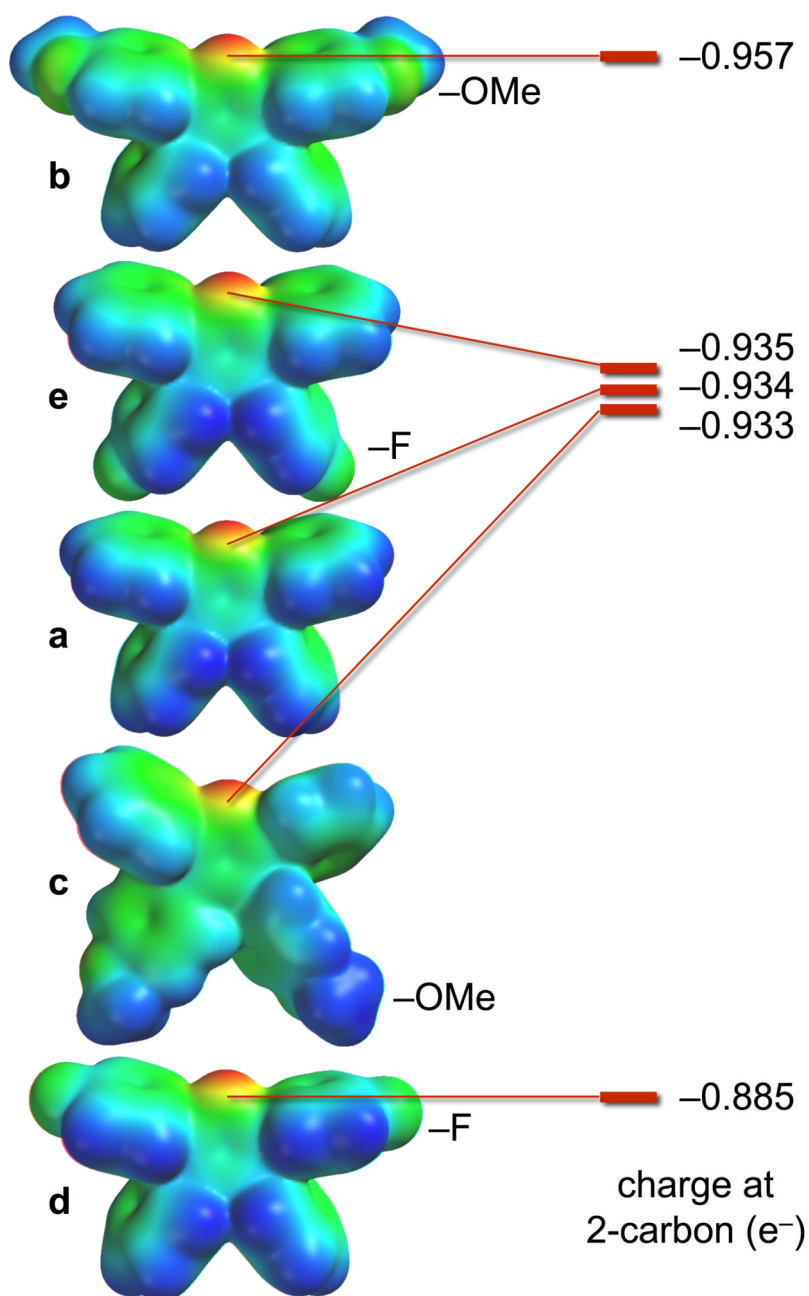
entry	1,3-substitution	4,5-substitution	average TOF (h^{-1})	$\log_{10}(\text{TOF}/\text{TOF}_{\text{H}})$	σ_{para}	σ_{meta}	σ_{I}	R^2
●	C_6H_5	C_6H_5	1076.5	0.00000	0.00			
●	<i>p</i> - $\text{C}_6\text{H}_4\text{OMe}$	C_6H_5	1237.5	0.06053	-0.27			0.5056
●	<i>p</i> - $\text{C}_6\text{H}_4\text{F}$	C_6H_5	329.0	-0.51482	0.06			
●	C_6H_5	C_6H_5	1076.5	0.00000	0.00			
●	C_6H_5	<i>p</i> - $\text{C}_6\text{H}_4\text{OMe}$	751.5	-0.15609	-0.27			0.0639
●	C_6H_5	<i>p</i> - $\text{C}_6\text{H}_4\text{F}$	464.0	-0.36550	0.06			
■	C_6H_5	C_6H_5	1076.5	0.00000		0.00		
■	<i>p</i> - $\text{C}_6\text{H}_4\text{OMe}$	C_6H_5	1237.5	0.06053		0.12		0.8098
■	<i>p</i> - $\text{C}_6\text{H}_4\text{F}$	C_6H_5	329.0	-0.51482		0.34		
■	C_6H_5	C_6H_5	1076.5	0.00000		0.00		
■	C_6H_5	<i>p</i> - $\text{C}_6\text{H}_4\text{OMe}$	751.5	-0.15609		0.12		0.9929
■	C_6H_5	<i>p</i> - $\text{C}_6\text{H}_4\text{F}$	464.0	-0.36550		0.34		
◆	C_6H_5	C_6H_5	1076.5	0.00000			0.00	
◆	<i>p</i> - $\text{C}_6\text{H}_4\text{OMe}$	C_6H_5	1237.5	0.06053			0.27	0.6186
◆	<i>p</i> - $\text{C}_6\text{H}_4\text{F}$	C_6H_5	329.0	-0.51482			0.50	
◆	C_6H_5	C_6H_5	1076.5	0.00000			0.00	
◆	C_6H_5	<i>p</i> - $\text{C}_6\text{H}_4\text{OMe}$	751.5	-0.15609			0.27	0.9831
◆	C_6H_5	<i>p</i> - $\text{C}_6\text{H}_4\text{F}$	464.0	-0.36550			0.50	

Computational Study

All calculations were performed using Spartan '06 for Macintosh, version 1.0.3.⁸ The five carbene structures employed were generated by removal of the silver and chlorine atoms from the published² X-ray crystal structures, correlated as follows:

This work	Reference 2	Computed charge (e^-) on 2-carbon of 5a-e
5a	4a	-0.934372
5b	4h	-0.957340
5c	4e	-0.933040
5d	4f	-0.885186
5e	4c	-0.935327

Geometry optimization was not performed primarily because of the assumption that the AgCl and Ir(L)_n moieties enforce similar conformations of the NHC. Thus, the electronics are probably better represented by the static carbene structures derived directly from the NHC-AgCl complexes. The Atomic Electrostatic Charges (ESP) were determined on the static carbene structures using Density Function Theory (DFT) employing Becke's 3-parameter hybrid functional (B3)⁹ with the correlation functional of Lee, Yang, and Parr (LYP)^{10,11} and the Pople style basis set 6-31G*.



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