Supporting Information

Protonolysis of a Ruthenium-Carbene Bond and Applications in Olefin Metathesis

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General Information.

All reactions were carried out in dry glassware under an argon atmosphere using standard Schlenk line techniques or in a Vacuum Atmospheres Glovebox under a nitrogen atmosphere unless otherwise specified. All solvents were purified by passage through solvent purification columns and further degassed with argon.\(^1\) NMR solvents were dried over CaH\(_2\) and vacuum transferred to a dry Schlenk flask and subsequently degassed with argon. Commercially available reagents were used as received unless otherwise noted.

1D-NMR experiments were conducted on a Varian 600 MHz spectrometer equipped with a Triax (\(^1\)H, \(^{13}\)C, \(^{15}\)N) probe or a Varian Inova 400 Mhz spectrometer, while VT and kinetic experiments were conducted on a Varian 500 MHz spectrometer equipped with an AutoX probe. Accurate temperature measurements of the NMR probe were obtained using a thermocouple connected to a multimeter with the probe immersed in an NMR tube containing a minimal amount of toluene. Experiments and pulse sequences from Varian’s Chempack 4 software were used without modification except for changes in the number of FIDs and scans per FID. Reaction conversions were obtained by comparing the integral values of starting material and product, no internal standard was used. Chemical shifts are reported in ppm downfield from Me\(_4\)Si by using the residual solvent peak as an internal standard. Spectra were analyzed and processed using MestReNova Ver. 6.2.0 – 7163.\(^2\)

High-resolution mass spectrometry (HRMS) data was obtained on a JEOL MSRoute mass spectrometer using FAB+ ionization. ESI-MS Analyses were performed on a Finnigan LCQ classic mass spectrometer using the following conditions: spray voltage, 41 kV; sheath-gas

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(2) www.mestrelab.com
flow rate, 20; cap. voltage, 5 V; cap. temp., 190 °C; tube lens voltage, 8 V; spectrum averaging, 10. In the daughter mode collision energy of 30 V was employed using He as the collision gas.

1,3-Bis(2,6-diisopropylphenyl)-1H-1,2,3-triazol-5-ylidene (2). Anhydrous THF (10 mL) is added to a stirred mixture of triazolium salt 2·HPF_6 (268 mg, 0.5 mmol) and potassium tert-butoxide (112 mg, 1.0 mmol) at 0°C. The reaction mixture is stirred for 30 min at 0°C, then warmed to room temperature while stirring for an additional 30 min. Volatiles are evaporated under reduced pressure, and dry benzene (20 mL) is added. The mixture is triturated for 15-30 min, and filtered through a filter cannula. Evaporation of the solvents under reduced pressure affords the solid 2 (156 mg, 80%) as a pale yellow solid. M.p.: 141–143°C (dec). Note: The NMR spectra of 2 present some concentration-dependent broadening / coalescence, attributed to the exchange of protons at the C4/C5 position. At low concentration in the presence of ~1 eq. residual PhMe, the spectra of 2 is clearly asymmetric, but shows some peak broadening, indicative of slow proton exchange at C4/C5 with respect to the NMR timescale. At higher concentrations, the exchange accelerates and the spectra of 2 becomes symmetric, and displays resonances at the expected mid-point chemical shifts of the low [2] resonances. Low [2]: ^1^H NMR (C_6D_3, 300 MHz): δ = 7.53 (br s, 1H), 7.32 (br m, 1H), 7.20 (br m, 1H), 7.14-7.10 (m, 2H), 7.07-7.00 (m, 2H), 2.94 (br m, 2H), 2.47 (br m, 2H), 1.28 (br m, 6H), 1.23 (br m, 6H), 1.05 (br m, 12H). ^13^C NMR (C_6D_6, 75 MHz): δ = 201.9 (C), 146.0 (C), 145.9 (C), 139.9 (C), 138.4 (CH), 133.9 (C), 131.4 (CH), 130.2 (CH), 124.4 (CH), 124.1 (CH), 29.2 (2 CH), 25.0 (CH_3), 24.8 (CH_3), 24.4 (CH_3), 24.2 (CH_3)

High [2]: ^1^H NMR (C_6D_3, 300 MHz): δ = 7.56 (br s, 1H), 7.27 (t, J = 7.6 Hz, 2H), 7.10 (d, J = 7.7 Hz, 4H), 2.70 (br sept, J = 6.8 Hz, 4H), 2.47 (br m, 2H), 1.15 (d, J = 6.8 Hz, 12H), 1.11 (d, J
= 6.8 Hz, 12H). $^{13}$C NMR (C$_6$D$_6$, 75 MHz): $\delta = \sim 170$ (br, C/CH), 145.9 (C), 136.8 (C), 130.8 (CH), 124.3 (CH), 29.2 (CH), 24.9 (CH), 24.2 (CH).

**Synthesis of 5.**

In a glovebox, a 20 mL scintillation vial was charged with MIC $^2$ (208 mg, 0.535 mmol), $^4$ (300 mg, 0.412 mmol), and C$_6$H$_6$ (7 mL). The brown solution was stirred for one hour and concentrated *in vacuo* to a brown residue which was washed with cold pentane until the washes were colorless. The remaining brown solid was dried to give 5 (375 mg, 95%) which was subsequently lyophilized from C$_6$H$_6$. $^1$H NMR (400 MHz, CD$_2$Cl$_2$) $\delta$ 18.52 (s, 1H), 7.53 (m, 3H), 7.33 (s, 1H), 7.31 (s, 1H), 7.20 (tt, $J = 7.6$, 0.8 Hz, 1H), 6.97 – 6.81 (m, 5H), 6.76 (d, $J = 7.8$ Hz, 2H), 6.59 (s, 1H), 6.28 (br s, 1H), 4.03 – 3.86 (m, 4H), 2.57 (s, 6H), 2.47 (sept, $J = 6.8$ Hz, 2H), 2.23 (sept, $J = 6.8$ Hz, 2H), 2.14 (br s, 6H), 2.00 (s, 3H), 1.93 (s, 3H), 1.17 (d, $J = 6.8$ Hz, 6H), 1.09 (d, $J = 6.9$ Hz, 6H), 1.05 (d, $J = 6.6$ Hz, 6H), 0.77 (d, $J = 6.9$ Hz, 6H). $^{13}$C NMR (101 MHz, CD$_2$Cl$_2$) $\delta$ 225.91, 183.63, 150.56, 146.18, 145.84, 140.71, 137.07, 136.19, 134.23, 132.51, 131.98, 130.65, 130.44, 129.69, 129.31, 128.85, 127.53, 126.99, 125.39, 124.57, 123.32, 52.03, 51.79, 28.78, 28.60, 26.65, 25.38, 24.06, 22.22, 20.83, 18.62. HRMS (FAB+): Calculated – 958.3896, Found – 958.3917.

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Polymerization Reactions.

Scheme S1. ROMP of COD (top) and COE (bottom) with 5. Reactions conditions are outlined in Table S1.

Table S1. Polymerization Results with catalyst 5.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Monomer</th>
<th>Acid</th>
<th>[Monomer] (M)</th>
<th>[5] (M)</th>
<th>[Acid] (M)a</th>
<th>Mn (g/mol)b</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhH</td>
<td>COE</td>
<td>TFA</td>
<td>0.26</td>
<td>0.003</td>
<td>0.04</td>
<td>12,000</td>
<td>1.42</td>
</tr>
<tr>
<td>PhH</td>
<td>COE</td>
<td>MSA</td>
<td>0.26</td>
<td>0.003</td>
<td>0.04</td>
<td>19,000</td>
<td>1.53</td>
</tr>
<tr>
<td>PhH</td>
<td>COE</td>
<td>HCl</td>
<td>0.5</td>
<td>0.0005</td>
<td>0.059</td>
<td>42,000</td>
<td>1.48</td>
</tr>
<tr>
<td>PhH</td>
<td>COE</td>
<td>HCl</td>
<td>0.5</td>
<td>0.0005</td>
<td>0.08</td>
<td>29,500</td>
<td>1.65</td>
</tr>
<tr>
<td>PhH</td>
<td>COD</td>
<td>HCl</td>
<td>0.5</td>
<td>0.001</td>
<td>0.059</td>
<td>50,000</td>
<td>1.48</td>
</tr>
<tr>
<td>PhCH₃</td>
<td>COD</td>
<td>HCl</td>
<td>0.5</td>
<td>0.001</td>
<td>0.059</td>
<td>31,000</td>
<td>1.47</td>
</tr>
</tbody>
</table>

a HCl was added as a 1M solution in Et₂O. b Molecular weights measured by MALLs GPC.

Figure S1. Representative GPC trace from ROMP of COD.

Representative Procedure for RCM of 7 with 5 and HCl.

In a glovebox, a 1 mL volumetric flask was charged with 5 (5.6 mg, 0.0058 mmol) and filled to the 1 mL line with C₆D₆. A portion of the stock solution (140 µL, 0.0008 mmol 5) was
added to an NMR tube and diluted with C₆D₆ (660 µL). Compound 7 (19.3 µL, 0.08 mmol) was added and the NMR tube was capped with a rubber septum, removed from the glovebox, and placed inside the spectrometer. The tube was ejected and HCl (1M in Et₂O) (25 µL, 31 eq.) was injected after which the tube was quickly inverted once and placed back inside the spectrometer. An array of ¹H spectra were collected using the ‘pad’ function in vNMRj and processed according to the General Information.

Representative Procedure and Kinetic Plots for Reaction of 5 with HCl in C₆H₆.

In a glovebox, a 1 mL volumetric flask was charged with 5 (11.5 mg, 0.012 mmol) and filled to the 1 mL line with C₆D₆ to form a stock solution of catalyst. A portion (0.25 mL) of the stock solution above was transferred to an NMR tube and diluted with C₆D₆ (0.35 mL) such that the final concentration of 5 was ca. 0.005 M. The NMR tube was capped with a rubber septum, removed from the glovebox, and placed inside the spectrometer. After equilibration at the desired temperature for 10 min, HCl in Et₂O (between 5 and 50 uL) was injected through the rubber septum and the tube was quickly inverted once and placed back inside the spectrometer. An array of 1D ¹H spectra were collected using the ‘pad’ function in vNMRj.
Figure S2. First order plots of benzylidene disappearance at varying [HCl].
Figure S3. Plot of observed rate constant versus [HCl] in C₆D₆. Conditions were 5 (0.003 mmol), C₆D₆ (0.6 mL) with varying amounts of HCl (0.0083 M – 0.077 M).

**Representative Procedure and Kinetic Plots for Reaction of 5 with HCl in C₆H₆ with olefin 14.**

Inside a glovebox, an NMR tube with stock catalyst solution (0.25 mL) and C₆D₆ (0.35 mL) was prepared as above. Olefin 14 (1.6 uL, 0.009 mmol) was added along with anthracene (35 uL of a 0.086 M solution) as an internal standard and the tube was capped with a rubber septum and removed from the box. After equilibrating in the spectrometer, HCl (50 uL, 1 M in Et₂O) was added through the rubber septum and data was collected as above. Completion of the reaction was characterized by a change in color from yellow/brown to green and the formation of a white precipitate. The precipitate was collected by filtration and identified as 13 by ¹H NMR spectroscopy and HRMS (FAB+: C – 390.2909, F – 390.2898). The green filtrate was concentrated and identified as 6 by HRMS (FAB+: C – 626.1405, F – 626.1397) and ¹H NMR spectroscopy by comparison with authentic samples.
Figure S4. First order plots of \( \ln([P]_\infty - [P]) \) versus time for varying concentrations of olefin 14.

Figure S5. Plot of observed rate constant versus [Olefin] in \( C_6D_6 \). Conditions were 5 (0.003 mmol) and HCl (1 M in Et\(_2\)O, 0.077 M) in \( C_6D_6 \) (0.6 mL) with varying amounts of 14 (0.014 M – 0.14 M).
Eyring Plot Procedure.

In a glovebox, a 2 mL volumetric flask was charged with 5 (23 mg, 0.024 mmol) and filled to the line with d₈-toluene. A portion (0.25 mL) of the catalyst stock solution was added to an NMR tube and diluted with d₈-toluene (0.35 mL). The NMR tube was capped with a rubber septum, removed from the glovebox, and placed in the spectrometer at the desired temperature and allowed to equilibrate for ca. 10 min. The exact temperature of the NMR probe was determined as described in the General Information. After equilibrating, the tube was ejected and HCl (50 uL, 1 M in Et₂O) was added, after which the tube was inverted once and quickly placed back inside the spectrometer. Data was collected with the vNMRj array function as above. All reactions showed clean first order kinetics over period of at least three half-lives and \( k_{\text{obs}} \) was determined from a plot of \( \ln(C/C_0) \) versus time.

According to the Activated Complex Theory of Henry Eyring,

\[
k = \left( \frac{h \Delta S^\ddagger / R}{k_b} \right) e^{\Delta H^\ddagger / RT}
\]

where \( k \) is the rate in s⁻¹, \( k_b \) is Boltzmann’s constant, \( h \) is Planck’s constant, \( R \) is the gas constant, and \( T \) is the temperature in Kelvin. Eq. 3 can be re-worked to yield a linear equation which gives \( \Delta H^\ddagger \) as the slope and \( \Delta S^\ddagger \) as the intercept (Eq. 4).

\[
R \ln \frac{h \Delta S^\ddagger}{k_b T} = \Delta S^\ddagger + \left( \frac{\Delta H^\ddagger}{T} \right)
\]

(2)

The uncertainty in the slope and intercept was determined directly from the output provided by the linear regression function of OriginPro 8.1.⁵ The uncertainty in \( \Delta G^\ddagger \) can be calculated using

the error in the slope, intercept, and the off-diagonal component of the variance-covariance matrix (because $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are correlated) created by OriginPro.6

![Graph](image)

**Figure S6.** Eyring Plot for activation of 5.

**Mass Spectrometry Study of Reaction Mechanism.**

![Scheme](image)

**Scheme S2.** Mass spectrometry study of activation of 5.

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A 1 mM solution of 5 in C₆H₆ was prepared and TFA (5 uL) was added. The solution was loaded into a syringe and placed on a syringe pump connected to a mass spectrometer running on continuous electrospray ionization. Masses corresponding to SM and protonated SM were obtained (Figure S7). Parent and CID daughter peaks were collected according to the General Information.

Figure S7. Mass spec (ESI) of 5 immediately following addition of TFA.
**Representative Procedure and Kinetic Plots for Reaction of 5 with TFA in C₆H₆.**

In a glovebox, a 1 mL volumetric flask was charged with 5 (13 mg, 0.0134 mmol) and filled to 1 mL with C₆D₆ to form a stock solution of catalyst. A portion of the stock solution (0.225 mL, 0.003 mmol 5) was added to an NMR tube and diluted with C₆D₆ (0.375 mL). The NMR tube was capped with a rubber septum, removed from the glovebox, and placed inside the spectrometer. TFA (0.026 mmol – 0.091 mmol) was injected, the tube was inverted once, and placed back inside the spectrometer. Data was collected as above.
**Figure S9.** First order plots for reaction of 5 with TFA in C₆D₆.

**Table S2.** Linear fit parameters for first order plots in Figure S9. Reaction conditions were as above.

<table>
<thead>
<tr>
<th>[TFA] (mmol)</th>
<th>Slope</th>
<th>Slope Error</th>
<th>Intercept</th>
<th>Intercept Error</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.026</td>
<td>-0.00144</td>
<td>1.29E-05</td>
<td>0.0513</td>
<td>0.013</td>
<td>0.99</td>
</tr>
<tr>
<td>0.039</td>
<td>-0.0056</td>
<td>7.19E-05</td>
<td>0.365</td>
<td>0.018</td>
<td>0.99</td>
</tr>
<tr>
<td>0.060</td>
<td>-0.016</td>
<td>2.39E-04</td>
<td>0.499</td>
<td>0.029</td>
<td>0.99</td>
</tr>
<tr>
<td>0.078</td>
<td>-0.036</td>
<td>0.001</td>
<td>1.0422</td>
<td>0.074</td>
<td>0.99</td>
</tr>
<tr>
<td>0.091</td>
<td>-0.053</td>
<td>0.002</td>
<td>1.38</td>
<td>0.106</td>
<td>0.98</td>
</tr>
</tbody>
</table>

**Figure S10.** Observed rate constant versus [TFA] showing 2nd order dependence on [TFA]. Values of k_{obs} are from Table S2.
Representative Procedure and Kinetic Plots for Reaction of 5 with TFA in CD$_3$CN at constant pH.

In a glovebox, a 1 mL volumetric flask was charged with potassium trifluoroacetate (KTFA) (15 mg, 0.0986 mmol) which had been dried under vacuum at 70 °C for 12h, and the flask was filled to the line with CD$_3$CN. A portion of the stock solution (from 30.4 µL, 0.003 mmol) was added to a vial containing 5 (2.9 mg, 0.003 mmol) and CD$_3$CN (0.570 mL). The resulting fine suspension was shaken and quickly transferred to an NMR tube which was capped with a rubber septum. (Note : Over prolonged periods of time (hours), 5 would decompose in the presence of CD$_3$CN, therefore, all samples for kinetic runs were prepared immediately prior to use). The NMR tube was removed from the glovebox and placed inside the spectrometer. TFA (3.4 µL, 0.045 mmol) was injected through the rubber septum and the tube was quickly inverted before being placed back inside the spectrometer. NMR spectra were recorded as described previously.

Table S3. First order fit parameters for reaction of 5 with TFA in CD$_3$CN at constant pH. Reaction conditions were as above.

<table>
<thead>
<tr>
<th>[TFA] (M)</th>
<th>[KTFA] (M)</th>
<th>Slope</th>
<th>Slope Error</th>
<th>Intercept</th>
<th>Intercept Error</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.075</td>
<td>0.0050</td>
<td>-0.008</td>
<td>1.90E-04</td>
<td>0.654</td>
<td>0.05</td>
<td>0.99</td>
</tr>
<tr>
<td>0.1</td>
<td>0.0067</td>
<td>-0.0122</td>
<td>2.42E-04</td>
<td>0.833</td>
<td>0.05</td>
<td>0.99</td>
</tr>
<tr>
<td>0.125</td>
<td>0.0083</td>
<td>-0.017</td>
<td>5.09E-04</td>
<td>0.969</td>
<td>0.06</td>
<td>0.99</td>
</tr>
<tr>
<td>0.15</td>
<td>0.0100</td>
<td>0.02</td>
<td>2.72E-04</td>
<td>0.685</td>
<td>0.02</td>
<td>0.99</td>
</tr>
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</table>
Figure S11. First order plots for reaction of 5 with TFA in CD$_3$CN at constant pH.

Figure S12. Observed rate constant versus TFA concentration in CD$_3$CN at RT and constant pH. Conditions were 5 (0.003 mmol), potassium trifluoroacetate (0.003-0.006 mmol), TFA (0.045-0.09 mmol), in CD$_3$CN (0.6 mL).

Representative Procedure for Brønsted Plot

In a glovebox, a 1 mL volumetric flask was charged with 5 (9.7 mg, 0.01 mmol) and filled to the line with CD$_3$CN to make a 0.01 M stock solution. An aliquot of the stock solution
(300 uL) was added to an NMR tube and diluted with CD$_3$CN (300 uL). The NMR tube was capped with a rubber septum, removed from the glovebox, and placed inside the spectrometer. TFA (3.5 µL, 0.045 mmol, 15 eq.) was injected after which the tube was inverted once and placed back inside the spectrometer. Spectra were recorded periodically as described above. The same procedure was repeated for the following acids: Methane-sulfonic acid (3 µL, 0.045 mmol), Dichloroacetic acid (3.7 µL, 0.045 mmol), and Acetic acid (2.6 µL, 0.045 mmol). Acid dissociation constants in acetonitrile were estimated from Eq. 3 using pK$_a$ values in DMSO.$^8$

$$pK_a(AN) = b + a pK_a(DMSO)$$

$$b = 11.80 \quad a = 0.884$$

Figure S13. First order plots for reaction of 5 with different acids in CD$_3$CN.

Table S4. First order fit parameters for Figure S13.

<table>
<thead>
<tr>
<th>Acid</th>
<th>Slope</th>
<th>Slope Error</th>
<th>Intercept</th>
<th>Intercept Error</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSA</td>
<td>-0.041</td>
<td>1.15E-03</td>
<td>1.52</td>
<td>0.07</td>
<td>0.99</td>
</tr>
<tr>
<td>TFA</td>
<td>-0.007</td>
<td>1.88E-04</td>
<td>0.45</td>
<td>0.04</td>
<td>0.99</td>
</tr>
<tr>
<td>Cl2CHCOOH</td>
<td>-0.0018</td>
<td>3.33E-05</td>
<td>-0.0023</td>
<td>0.017</td>
<td>0.99</td>
</tr>
<tr>
<td>Acetic</td>
<td>-1.69E-04</td>
<td>1.91E-06</td>
<td>0.097</td>
<td>0.01</td>
<td>0.99</td>
</tr>
</tbody>
</table>

Representative Procedure and Kinetic Plots for Reaction of 5 with TFA in CD$_3$CN containing varying amounts of KTFA (variable pH).

A 1 mL volumetric flask was charged with KTFA (13.6 mg, 0.0907 mmol) and filled to the line with CD$_3$CN. A portion of the KTFA stock solution (55 uL, 0.005 mmol) was transferred to a vial containing 5 (2.9 mg, 0.003 mmol) and CD$_3$CN (550 uL). The resulting suspension was quickly shaken and transferred to an NMR tube and capped with a rubber septa. TFA (3.4 uL, 0.045 mmol) was injected and the tube was quickly inverted and placed inside the spectrometer. Spectra were recorded as above.

Table S5. First order fit parameters for reaction of 5 with TFA at varying pH. Reaction conditions were as above.

<table>
<thead>
<tr>
<th>TFA (mmol)</th>
<th>KTFA (mmol)</th>
<th>Slope</th>
<th>Slope Error</th>
<th>Intercept</th>
<th>Intercept Error</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.045</td>
<td>0.0000</td>
<td>-0.00994</td>
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<td>7.39E-05</td>
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Figure S14. First order plots for reaction of 5 with TFA in CD$_3$CN at varying pH. Reaction conditions were as above.

Figure S15. Log($k_{obs}$) versus pH for reaction of 5 with TFA in CD3CN.
Representative Procedure and Kinetic Plots for Reaction of 5 with HCl (1 M in Et$_2$O) in CD$_3$CN.

In a glovebox, a 4 mL vial was charged with 5 (2.9 mg, 0.003 mmol) and CD$_3$CN (0.6 mL). The fine suspension was transferred to an NMR tube which was capped with a rubber septum and removed from the box. The NMR tube was placed inside the spectrometer and equilibrated at 25 °C after which it was ejected and HCl (1 M in Et$_2$O, 5 µL) was added via syringe. After inverting once, the tube was placed back inside the spectrometer and data was collected as above. Note that in the case of a small amount of HCl (5 µL), pseudo first order conditions are not applicable. Therefore, only the first few minutes of the reaction were used to obtain $k_{obs}$. All other amounts of HCl displayed good first order behavior until completion of the reaction.

<table>
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<tr>
<th>HCl (mmol)</th>
<th>Intercept</th>
<th>Intercept Error</th>
<th>Slope</th>
<th>Slope Error</th>
<th>$R^2$</th>
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<tr>
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Figure S16. First order plots for reaction of 5 with HCl in CD$_3$CN.

Figure S17. Plot of $k_{obs}$ versus [HCl] for reaction of 5 with HCl in CD$_3$CN.
Figure S18. $^1$H NMR spectrum of 2 (low conc.) in C$_6$D$_6$.

Figure S19. $^{13}$C NMR spectrum of 2 (low conc.) in C$_6$D$_6$. 
Figure S20. $^1$H NMR (400 MHz) spectrum of 5 in CD$_2$Cl$_2$. 
Figure S21. $^{13}$C NMR spectrum of 5 in CD$_2$Cl$_2$. 

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