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Supporting Information

A Triflamide-Tethered N-Heterocyclic Carbene–Rhodium(I) Catalyst for Hydroalkoxylation Reactions: Ligand-Promoted Nucleophilic Activation of Alcohols

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1. Experimental Section

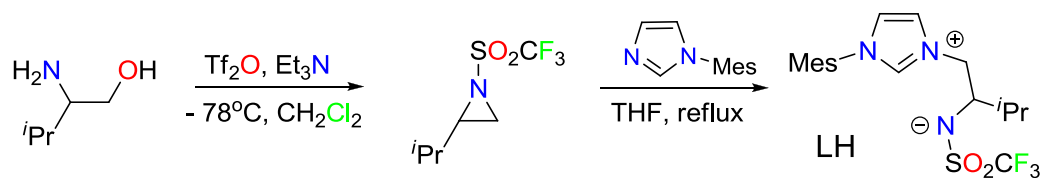
1.1. General procedures

All reactions with metal complexes were carried out under an atmosphere of purified nitrogen using standard Schlenk–vessel and vacuum line techniques. Glasswares were flame–dried under vacuum prior to use. NMR spectra were obtained on JEOL JNM–LA 400MHz and 500MHz spectrometer. ^1H NMR chemical shifts were referenced to the residual hydrogen signal of the deuterated solvents. The chemical shift is given as dimensionless δ values and is frequency referenced relative to TMS for ^1H and ^{13}C NMR spectroscopy. Elemental analyses were performed on a Thermoquest EA1110 CHNS/O analyzer. The crystallized compounds were powdered, washed several times with dry petroleum ether, and dried in vacuum for at least 48h prior to elemental analyses. Infrared spectra were recorded in the range $4000\text{--}400\text{ cm}^{-1}$ on a Vertex 70 Bruker spectrophotometer on KBr pellets. ESI–MS were recorded on a Waters Micromass Quattro Micro triple–quadrupole mass spectrometer. The GC–MS experiments were performed by using an Agilent 7890 A GC and 5975C MS system.

Materials

Solvents were dried by conventional methods, distilled under nitrogen and deoxygenated prior to use. $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ was purchased from Arora Matthey, India. All other chemicals were purchased from Sigma–Aldrich. $[\text{Rh}(\mu\text{--Cl})(\text{COD})]_2$,¹ $[\text{Rh}(\mu\text{--Cl})(\text{CO})_2]_2$,² $[\text{RhL}'(\text{COD})\text{Cl}]^3$ ($\text{L}' = N,N'$ –dimethylimidazoline–2–ylidene) were prepared from literature procedures.

1.2. Synthesis of LH:



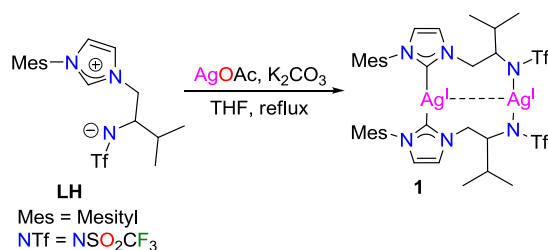
Scheme S1. Schematic representation for synthesis of **LH**.

An oven-dried, 250 mL, round-bottomed flask was equipped with a Teflon-coated magnetic stirring bar and sealed with a rubber septum containing a needle adapter to a

nitrogen source. The flask was charged with (*S*)-valinol (4.15 g, 40.25 mmol), triethylamine (13.1 mL, 94.5 mmol) and dichloromethane (70 mL). The flask was placed in a -78°C and, to the well-stirred solution; trifluoromethanesulfonic anhydride (15.9 mL, 94.5 mmol) was added via syringe. The resulting reaction mixture was held at -78°C for 5h. The reaction mixture was transferred to a 250 mL separatory funnel containing 100 mL of 0.1 N HCl and the mixture was thoroughly shaken and the layers were separated. The organic portion was washed successively with one portion of 0.1 M HCl (100 mL), two portions of saturated aqueous NaHCO_3 (100 mL each) and one portion of brine (100 mL). The organic portion was dried over anhydrous magnesium sulphate, filtered and concentrated under reduced pressure on a rotary evaporator to afford 8.5 g (97%) of *N*-trifluoromethylsulfonyl-2-isopropylaziridine as pale yellow oil. The (*S*)-*N*-trifluoromethylsulfonyl-2-isopropylaziridine was used in the next transformation without further purification.

N-trifluoromethylsulfonyl-2-isopropylaziridine (1.75 g, 8.05 mmol) was refluxed with 1.49 g (8.05 mmol) 1-mesitylimidazole in 10 mL tetrahydrofuran for 24h. The solvent was evaporated under vacuum and 20 mL of cold diethyl ether was added to furnish **LH** as the final product. The compound was filtered and washed with cold diethyl ether (3 X 10 mL) then dried under vacuum for 2h and stored under nitrogen. X-ray quality crystals were grown by slow diffusion of petroleum ether into a saturated dichloromethane solution of **LH** at room temperature. Yield: 2.9 g (90%). Mp: $>200^{\circ}\text{C}$. ESI-MS, m/z : 404.162, ($z=1$), $[\text{M}+\text{H}]^+$.

1.3. Synthesis of 1:

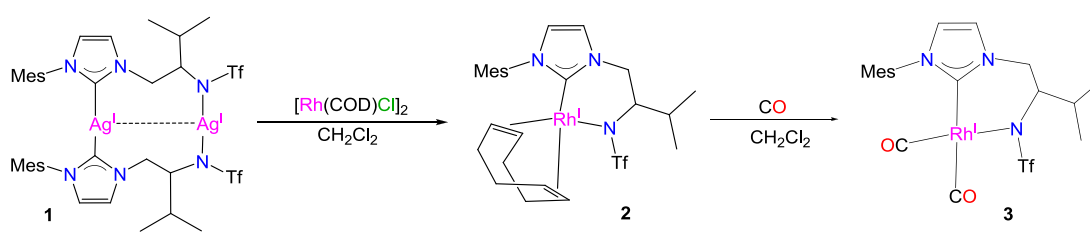


Scheme S2. Schematic representation of synthesis of 1.

A suspension of 0.1 g (0.25 mmol) of **LH**, 0.041 g (0.25 mmol) of AgOAc , and 0.041 g (0.3 mmol) of K_2CO_3 in 15 mL of THF was stirred for 16h at 60°C in dark. The reaction

was cooled to room temperature and filtered through celite. The colorless filtrate was concentrated under reduced pressure and diethyl ether was added to induce precipitation. The solid obtained was washed with 15 mL of diethyl ether and dried under vacuum. X-ray quality crystals were grown by slow diffusion of petroleum ether into a saturated dichloromethane solution of **1** at -20°C . Yield: 0.207 g (82%). Mp: $>200^{\circ}\text{C}$. Anal Calcd. for $\text{Ag}_2\text{S}_2\text{F}_6\text{C}_{36}\text{N}_6\text{O}_4\text{H}_{46}$: C, 42.43; H, 4.55; N, 8.25. Found: C, 42.39; H, 4.57; N, 8.19. ESI-MS, m/z : 915.229, ($z=1$), $[\text{AgL}_2+\text{H}]^+$.

1.4. Synthesis of **2** and **3**:



Scheme S3. Schematic representation of synthesis of **2**, **3**.

0.048 g (0.098 mmol) Chloro(1,5-cyclooctadiene)rhodium(I) dimer was added to a dichloromethane solution containing 0.01 g (0.098 mmol) **1**. The resulting mixture was stirred for 24h in dark and subsequently filtered through a pad of celite to remove precipitated silver halide. The resulting orange solution was concentrated under reduced pressure and petroleum ether was added to induce precipitation. The solid obtained was washed with 15 mL of petroleum ether and dried under vacuum. Crystals suitable for X-ray diffraction were grown by slow diffusion of petroleum ether into a saturated dichloromethane solution of **2**. Yield: 0.060 g (90%). Mp: $>200^{\circ}\text{C}$. Anal Calcd. for $\text{Rh}_1\text{S}_1\text{F}_3\text{N}_3\text{O}_2\text{C}_{26}\text{H}_{35}$: C, 50.89; H, 5.75; N, 6.85 Found: C, 50.44; H, 5.59; N, 6.58. ESI-MS, m/z : 613.146, ($z=1$), $[\text{M}+\text{H}]^+$.

0.061 g (1 mmol) **2** was dissolved in 10 mL dichloromethane and CO gas was bubbled through it for 30 minutes. The resulting pale yellow solution was concentrated under reduced pressure and petroleum ether was added to induce precipitation. The solid obtained was washed with 15 mL of petroleum ether and dried under vacuum. Yield: 0.050 g (90%). Mp: $>200^{\circ}\text{C}$. Anal Calcd. for $\text{Rh}_1\text{S}_1\text{F}_3\text{N}_3\text{O}_4\text{C}_{19}\text{H}_{23}$: C, 42.78; H, 4.13; N, 7.49 Found: C, 42.54; H, 3.89; N, 7.21. ESI-MS, m/z : 562.041, ($z=1$), $[\text{M}+\text{H}]^+$.

2. X-Ray Data Collection and Refinements:

Single-crystal X-ray studies were performed on a CCD Bruker SMART APEX diffractometer equipped with an Oxford Instruments low-temperature attachment. All data were collected at 100(2) K using graphite-monochromated Mo-K α radiation ($\lambda_{\alpha} = 0.71073$ Å). The frames were indexed, integrated, and scaled using the SMART and SAINT software packages,⁴ and the data were corrected for absorption using the SADABS program.⁵ The structures were solved and refined with the SHELX suite of programs.⁶ All non hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms of ligands were included into geometrically calculated positions in the final stages of the refinement and were refined according to 'riding model'. SQUEEZE option in PLATON program was used to remove the disordered water and solvent molecules from the overall intensity data of compounds wherever necessary.⁷ Diamond 3.1e software was used to produce the diagrams.⁸ CCDC numbers 1020182, 1020183, 1519782 contain the supplementary crystallographic data for compounds **LH**, **1** and **2**. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

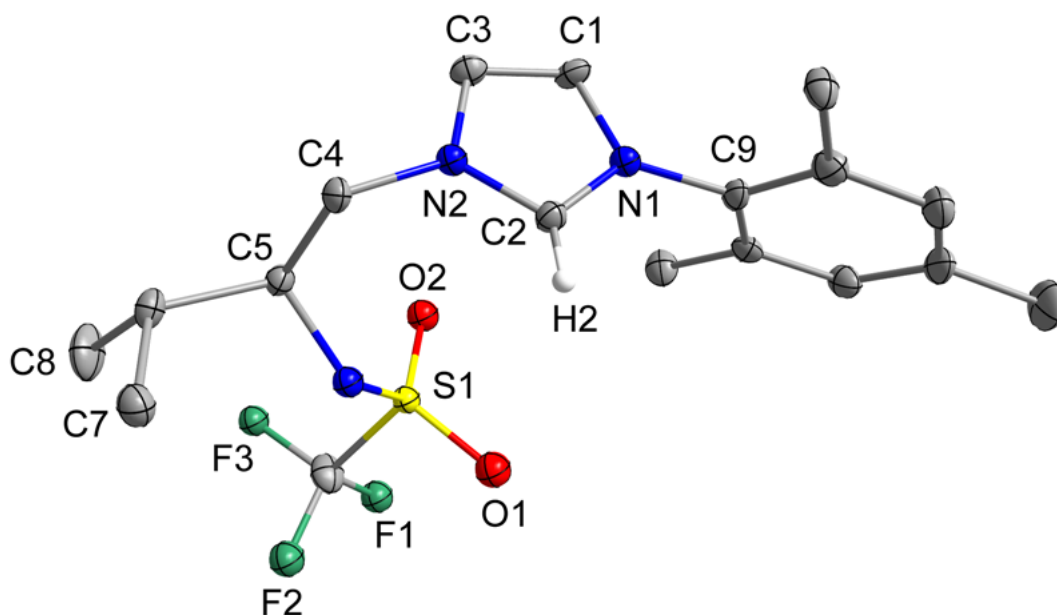


Figure S1. Molecular structure (50% probability thermal ellipsoids) of **LH** with important atoms labeled. Hydrogen atoms except H2 are omitted for the sake of clarity.

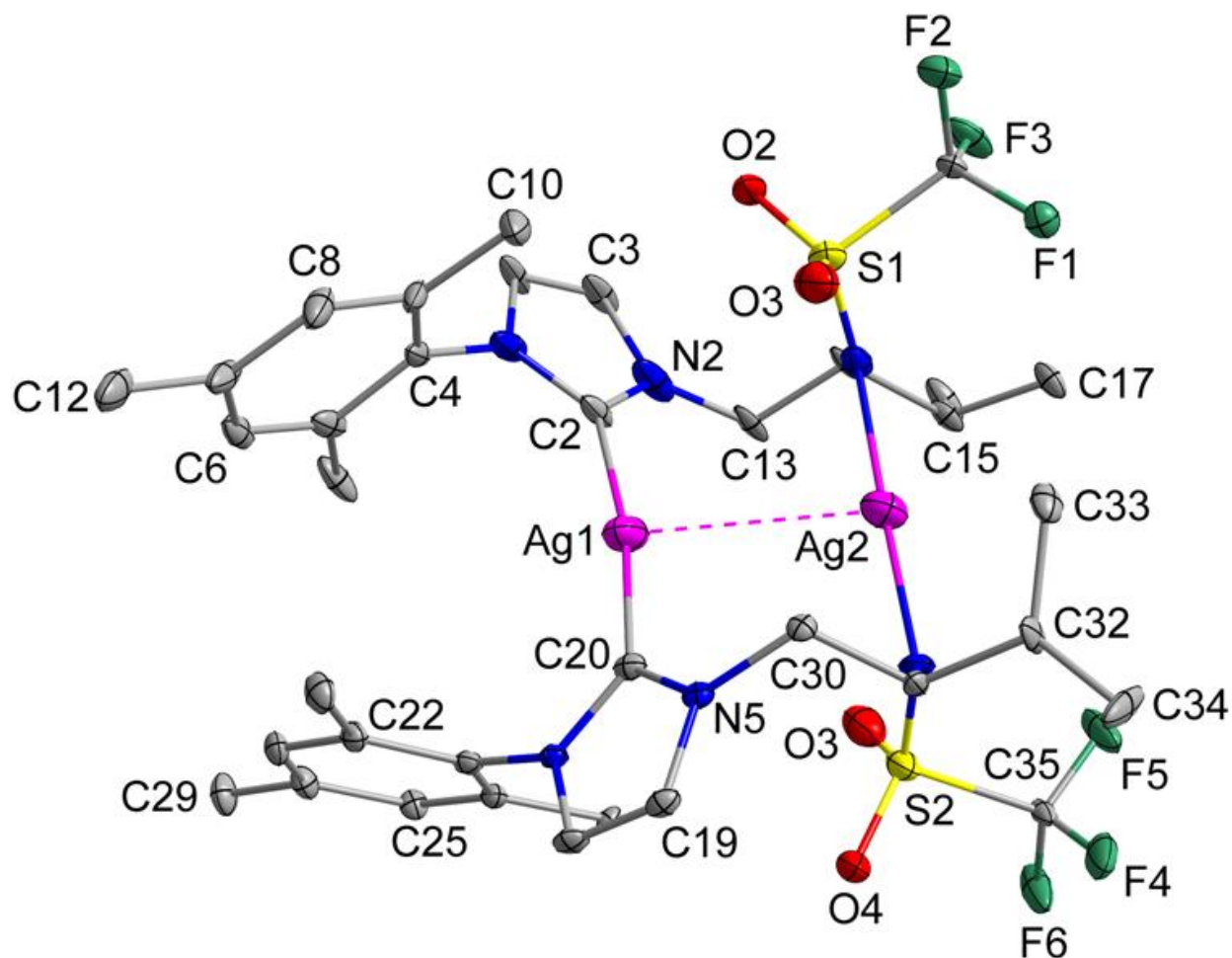


Figure S2. X-ray structure (50% probability thermal ellipsoids) of compound 1. Hydrogen atoms are omitted for the sake of clarity. Selected bond lengths (Å) and angles (deg): Ag2–Ag1 3.1184(7), Ag1–C2 2.071(7), Ag1–C20 2.066(6), Ag2–N3 2.071(5), Ag2–N6 2.094(5), S2–O3 1.422(7), S2–N6 1.536(6). C20–Ag1–C2 171.5(3), N3–Ag2–N6 178.6(2), N6–Ag2–Ag1 94.31(16), N3–Ag2–Ag1 87.08(15), C20–Ag1–Ag2 91.67(17), C2–Ag1–Ag2 96.8(2), O3–S2–O4 118.4(4), O2–S1–O1 121.0(5), N5–C20–N4 104.1(5), N2–C2–N1 106.4(7).

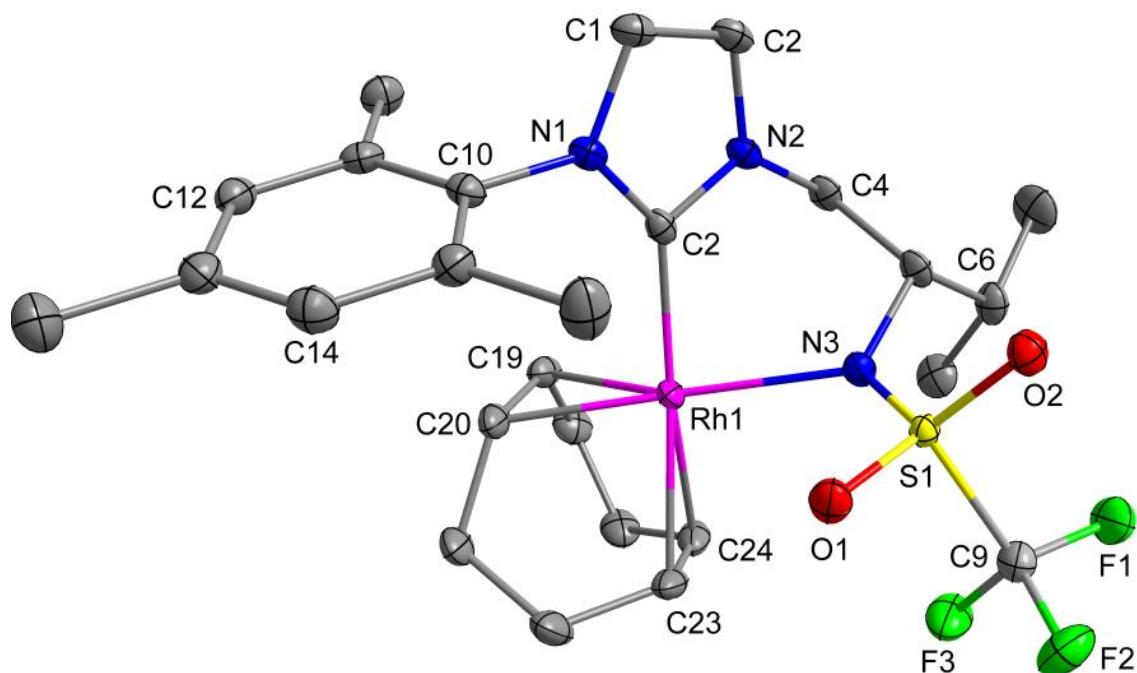


Figure S3. X-ray structure (50% probability thermal ellipsoids) of compound **2**. Hydrogen atoms are omitted for the sake of clarity. Selected bond lengths (Å) and angles (deg): Rh1–C2 2.012(2), Rh1–C19 2.097(2), Rh1–C20 2.120(3), Rh1–C23 2.214(2), Rh1–N3 2.227(2), Rh1–C24 2.241(3), N1–C2 1.363(3), N1–C1 1.384(3), N1–C10 1.436(3), S1–O1 1.4344(19), S1–O2 1.4423(18), S1–N3 1.552(2), S1–C9 1.854(3). C2–N1–C1 110.8(2), C2–N1–C10 125.6(2), C1–N1–C10 123.5(2), O1–S1–O2 118.44(11), O1–S1–N3 110.30(11), O2–S1–N3 115.59(11), O1–S1–C9 100.38(11), O2–S1–C9 101.89(11), N3–S1–C9 108.11(12), C2–Rh1–C19 92.13(10), C2–Rh1–C20 96.29(10), C19–Rh1–C20 38.85(10), C2–Rh1–C23 161.24(10), C19–Rh1–C23 97.18(10), C20–Rh1–C23 81.19(10), C2–Rh1–N3 82.42(9).

Table S1. Crystallographic data and pertinent refinement parameters for **LH, 1, 2.**

	LH	1	2
Empirical Formula	C ₁₈ H ₂₄ F ₃ N ₃ O ₂ S	C ₃₆ H ₄₆ Ag ₂ F ₆ N ₆ O ₄ S ₂	C ₂₆ H ₃₅ F ₃ N ₃ O ₂ RhS
Formula Weight	403.46	1020.65	613.54
Crystal System	Monoclinic	Orthorhombic	Orthorhombic
Space Group	<i>P2</i> ₁	<i>P2</i> ₁ <i>2</i> ₁ <i>2</i> ₁	<i>P2</i> ₁ <i>2</i> ₁ <i>2</i> ₁
a (Å)	10.6474(13)	8.3827(9)	10.1441(5)
b (Å)	7.2736(9)	21.062(2)	12.9810(6)
c (Å)	12.9621(16)	24.562(3)	20.3247(9)
α (deg)	90.00	90.00	90.00
β (deg)	90.557(4)	90.00	90.00
γ (deg)	90.00	90.00	90.00
V (Å ³)	1003.8(2)	4336.7(8)	2676.4(2)
Z	2	4	4
ρ _{calcd} (g cm ⁻³)	1.335	1.563	1.523
μ (mm ⁻¹)	0.206	1.068	0.765
F(000)	424	2064	1264
Reflections			
Collected	7334	42069	33094
Independent	3673	8305	6642
Observed [I > 2σ(I)]	3123	7817	6387
No. of variables	249	515	330
GooF	1.071	1.102	1.061
R _{int}	0.0457	0.0420	0.0268
Final R indices	R1 = 0.0408 wR2 = 0.0893	R1 = 0.0479 wR2 = 0.1179	R1 = 0.0217 wR2 = 0.0481
[I > 2σ(I)] ^a			
R indices (all data) ^a	R1 = 0.0553 wR2 = 0.1085	R1 = 0.0512 wR2 = 0.1196	R1 = 0.0545 wR2 = 0.0487

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} \text{ with } F_o^2 > 2\sigma(F_o^2). \quad wR_2 = \left[\frac{\sum w(|F_o^2| - |F_c^2|)^2}{\sum |F_o^2|} \right]^{1/2}$$

3. Catalytic Studies:

3.1. General procedure for intermolecular hydroalkoxylation: Alkyne (1 mmol), mesitylene (internal standard, 1 mmol) and MeOH (1 mL) were sequentially added to a 1 mL DMAc solution of the catalyst **3** (0.02 mmol) and the closed reaction vessel was heated at 70°C for 24h. After completion of reaction, the solutions were diluted to 10 mL with Et₂O and washed with LiCl solution (0.1 M, 2×10 mL). The organic phase was dried with saturated brine solution (20 mL) and Na₂SO₄, and the solvent was removed in vacuo. Products were analyzed using GC–MS and ¹H NMR spectroscopy.

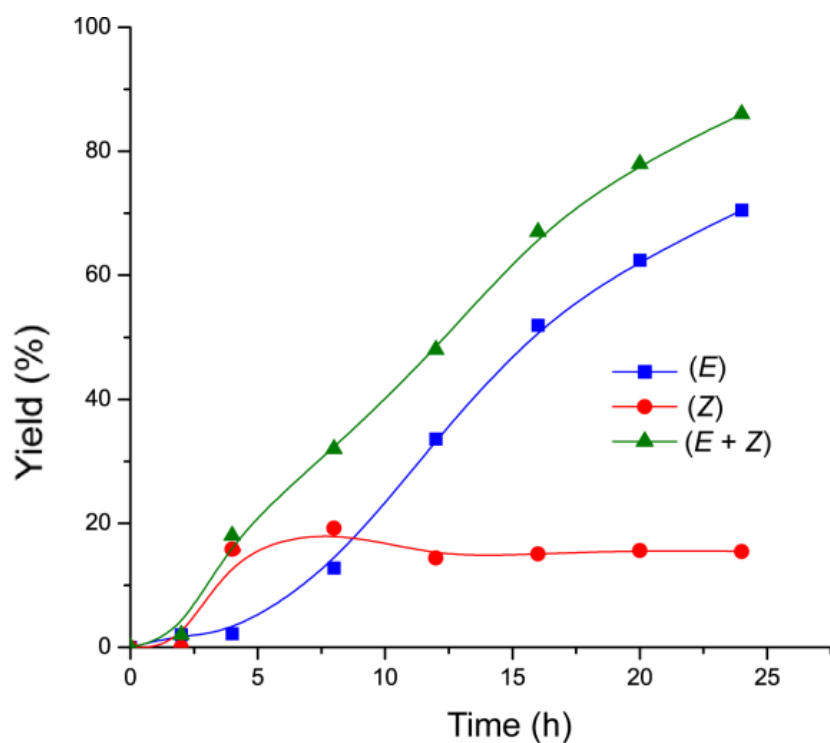


Figure S4. Reaction profile and E-Z ratios of products at different time intervals. During the initial part of the reaction (till overall yield is ca. 20%), Z product is the major (kinetically stable). However, as the reaction proceeds, E product increases (thermodynamic product).

Table S2. Screening of catalysts^a

$\text{Ph}-\text{C}\equiv\text{C} + \text{MeOH} \xrightarrow[70^\circ\text{C}]{\text{Cat.}} \text{Ph}-\text{C}(\text{H})=\text{C}(\text{OMe})$				
Entry	Catalyst	Loading (%)	Time (h)	Yield (%) ^b
1	[Rh(μ -Cl)(COD)] ₂	5	24	-
2	[Rh(μ -Cl)(CO) ₂] ₂	5	24	-
3	[RhL'(COD)Cl] ^c	5	24	-
4	2	2	24	<5
5	3	2	24	41

^aPhenylacetylene (1 mmol) and MeOH (1 mL) were sequentially added to catalyst and the closed reaction vessel was heated at 70°C for the stipulated time. ^bGC yields are reported in presence of internal standard mesitylene (1 mmol). ^cL'=N,N'-dimethylimidazoline-2-ylidene

Table S3. Screening of solvents^a

$\text{Ph}-\text{C}\equiv\text{C} + \text{MeOH} \xrightarrow[70^\circ\text{C}]{2 \text{ mol}\% \text{ 3}} \text{Ph}-\text{C}(\text{H})=\text{C}(\text{OMe})$			
Entry	Co-Solvent (1mL)	Time (h)	Yield (%) ^b
1	Toluene	24	41
2	THF	24	39
3	Acetonitrile	24	24
4	1,4 Dioxane	24	51
5	DMSO	24	44
6	DMF	24	59
7	DMAc	24	86
8	DMAc	48	99
9	Et ₃ N	24	43
10	Pyridine	24	23
11	DMAc	24	12 ^c
12	–	24	<10

^aPhenylacetylene (1 mmol) and MeOH (1 mL) were sequentially added to a 1 mL co-solvent solution of the catalyst **3** (0.02 mmol) and the closed reaction vessel was heated at 70°C for the stipulated time. ^bGC yields are reported in presence of internal standard mesitylene (1 mmol). ^cReaction vessel exposed to air.

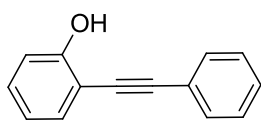
3.2. Addition of benzoic acid to terminal alkyne:

Benzoic acid (1.1 mmol), phenylacetylene (1 mmol) were sequentially added to a 2 mL chloroform solution of the catalyst **3** (0.02 mmol) and the closed reaction vessel was heated at 70°C for 24h. GC yields using 1 mmol dodecane as internal standard showed 97:3 ratio of 1-phenylvinyl benzoate: styryl benzoate. After completion of reaction, the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel (eluent: hexane: ethyl acetate = 10:1) to give 1-phenylvinyl benzoate in 90% isolated yield. ¹H NMR (CDCl₃, 500 MHz): δ 5.21 (d, *J* = 2.2 Hz, 1H), 5.63 (d, *J* = 2.3 Hz, 1H), 7.33-7.41 (m, 3H), 7.51-7.56 (m, 2H), 7.56-7.60 (m, 2H), 7.62-7.68 (m, 1H), 8.21-8.27 (m, 2H). ¹³C NMR (CDCl₃, 125 MHz): δ 102.4, 125.0, 128.68, 128.74, 129.1, 129.6, 130.3, 133.7, 134.4, 153.3, 164.9.

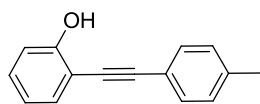
3.3. Acidification Reaction:

Phenylacetylene (1 mmol), HCl in ether (0.1 mL) was added to a 2 mL methanolic solution of the catalyst **3** (0.02 mmol) and the closed reaction vessel was heated at 70°C for 24h. GC yields using 1 mmol dodecane as internal standard showed complete conversion to acetophenone.

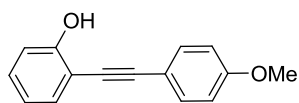
3.4. Substrate preparation for Intramolecular Hydroalkoxylation:



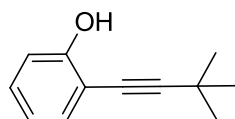
To a mixture of PdCl₂(PPh₃)₂ (70.2 mg, 0.1 mmol), CuI (38.0 mg, 0.2 mmol) and 2-iodophenol (2.2 g, 10 mmol) in 60 mL of THF was added phenylacetylene (1.3 mL, 12 mmol) at room temperature. A 0.5 M solution of aqueous ammonia (40 mL, 20 mmol) was then added dropwise and stirring was continued for 10h at room temperature. The reaction mixture was extracted with ethyl acetate, and dried over anhydrous Na₂SO₄. The solvent was evaporated and the residue was purified by chromatography on silica gel (eluent: hexane: ethyl acetate = 10:1) to afford 2-(phenylethynyl)phenol. Yield (1.88 g, 97%), brown solid. ¹H NMR (400 MHz, CDCl₃): δ 5.84 (s, 1H), 6.91 (td, *J* = 7.2, 1.2 Hz, 1H), 6.98 (m, 1H), 7.25-7.30 (m, 1H), 7.36-7.39 (m, 3H), 7.43 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.53-7.56 (m, 1H).



To a solution of 2-iodophenol (3.00 g, 13.6 mmol) in THF/Et₃N (250 mL, 4:1) was added PdCl₂(PPh₃)₂ (0.19 g, 0.27 mmol), CuI (0.11 g, 0.55 mmol) and 1-ethynyl-4-methylbenzene (3.16 g, 27.3 mmol) and the mixture was stirred at 25°C for 18h. A saturated aqueous solution of NH₄Cl was added and the mixture was extracted with DCM. The combined organic layers were dried over anhydrous Na₂SO₄ and the solvent was evaporated. The residue was purified by chromatography on silica gel (eluent: hexane: ethyl acetate = 95:5) to afford 2.82 g (99%) of 2-(*p*-tolylethynyl)phenol as a yellow solid. ¹H-NMR (400 MHz, CDCl₃): δ 7.37-7.32 (m, 3H), 7.20 (t, *J* = 6.9 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 7.7 Hz, 1H), 6.82 (t, *J* = 9.0 Hz, 1H), 5.76 (s, 1H), 2.29 (s, 3H).

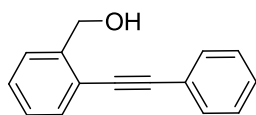


2-((4-methoxyphenyl)ethynyl)phenol was prepared similar to the procedure followed for 2-(*p*-tolylethynyl)phenol and using 1-ethynyl-4-methoxybenzene as the alkyne substrate. ¹H NMR (400 MHz, CDCl₃): δ 3.83 (s, 3H), 5.88 (s, 1H), 6.88-6.92 (m, 3H), 6.96-6.99 (m, 1H), 7.23-7.27 (m, 1H), 7.40 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.46-7.49 (m, 2H).



Imidazole (1.5 equiv, 15 mmol) was added to a mixture of 2-iodophenol (1.0 equiv, 10 mmol) and *tert*-butyldimethylsilyl chloride (1.1 equiv, 11 mmol) in DCM (15 mL) at room temperature. The mixture was stirred for about 1h (determined by TLC). Then the solvent was evaporated under vacuum, and the residue was purified by column chromatography on silica gel using hexane as the eluent to give pure *tert*-butyl(2-iodophenoxy)dimethylsilane as a colorless oil. PdCl₂(PPh₃)₂ (0.01 equiv, 0.05 mmol) and CuI (0.03 equiv, 0.15 mmol) were added to solution of *tert*-butyl(2-iodophenoxy)dimethylsilane (1.0 equiv, 5 mmol) and 3,3-dimethylbut-1-yne (1.2 equiv, 6 mmol) in *N,N*-diisopropylethylamine (15 mL). The mixture was stirred at 60°C until the reaction was complete as determined by TLC. Then the mixture was filtered through a pad of celite. Removal of solvent under reduced pressure afforded a residue, which is purified by chromatography on silica gel (eluent: hexane: ethyl acetate = 10:1) to afford the corresponding TBDMS-protected 2-alkynylphenol. The TBDMS-protected 2-alkynylphenol was dissolved in DCM, and then tetrabutylammonium fluoride in DCM (1 mol/L) was added. The resulting mixture was

stirred at room temperature for 5 minutes. Removal of solvent under reduced pressure afforded residue, which is purified by chromatography on silica gel (eluent: hexane: ethyl acetate = 4:1) to afford the corresponding 2-(3,3-dimethylbut-1-ynyl)phenol. Yield: 30%. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 1.34 (s, 9H), 5.79 (br, 1H), 6.82 (dd, 1H, $J_1=J_2 = 7.6$ Hz), 6.92 (d, 1H, $J = 8.4$ Hz), 7.17 (dd, 1H, $J_1=J_2= 7.2$ Hz), 7.27 (d, 1H, $J = 7.6$ Hz). Adapted from Q. Wang, Y. Jiang, R. Sun, X.-Y. Tang and M. Shi, *Chem. Eur. J.*, 2016, **22**, 14739.



To a mixture of phenylacetylene (10 mmol) and *o*-iodobenzyl alcohol 1 (10 mmol) in piperidine (20 mL) were added $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (70.2 mg, 0.1 mmol). The mixture was stirred at 70°C under argon for 12h. After that cold water (30 mL) was then added to the mixture, and the resulting aqueous mixture was extracted with ether (20 mL \times 3). The combined organic extract was washed with hydrochloric acid (20 mL \times 3), sat. NaHCO_3 (20 mL) and then dried (Na_2SO_4). The solvent was removed in vacuo. The red residual oil was purified by silica gel chromatography using eluent: hexane: ethyl acetate = 10:1 as eluent to give pure (2-(phenylethynyl)phenyl)methanol. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.55-7.40 (m, 4H), 7.38-7.19 (m, 5H), 4.87 (s, 2H), 2.60 (br s, 1H).

3.3. General procedure for intramolecular hydroalkoxylation: Alkynol (1 mmol), mesitylene (internal standard, 1 mmol) and Cs_2CO_3 (0.05 mmol) were sequentially added to a 2 mL chloroform solution of the catalyst **3** (0.02 mmol) and the closed reaction vessel was heated at 70°C for 24h. After completion of reaction, the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel (eluent: hexane: ethyl acetate = 10:1) to give desired product.

4. Computational Studies:

Calculations were performed using density functional theory (DFT) with Becke's three-parameter hybrid exchange functional⁹ and the Perdew and Wang correlation functional (PW91).¹⁰ Geometry-optimized structures were characterized fully via analytical frequency calculations as minima on the potential energy surface. The double- ζ basis set of Hay and Wadt (LanL2DZ) with a small core (1s2s2p3s3p3d4s4p4d) effective core potential (ECP)¹¹ was used for Ru. The ligand atoms H, N, C, O, S and F atoms were described using the 6-31+G(d,p) basis sets, were employed.¹² Phenylacetylene was chosen as the model substrate and *N,N*-dimethylacetamide as the solvent. The mesityl group of the ligand was replaced by methyl, the isopropyl group removed to reduce the computational cost. All optimization calculations were performed with the Gaussian 09 (G09) suite of programs.¹³ Solvent effects were accounted using *N,N*-dimethylacetamide ($\epsilon = 37.78$) with a SMD model.¹⁴ Gas phase optimized structures were taken as the initial geometries for optimization in solution.¹⁵ All transition states reported were found to have a single imaginary frequency.

4.2. Energy profile for the reaction:

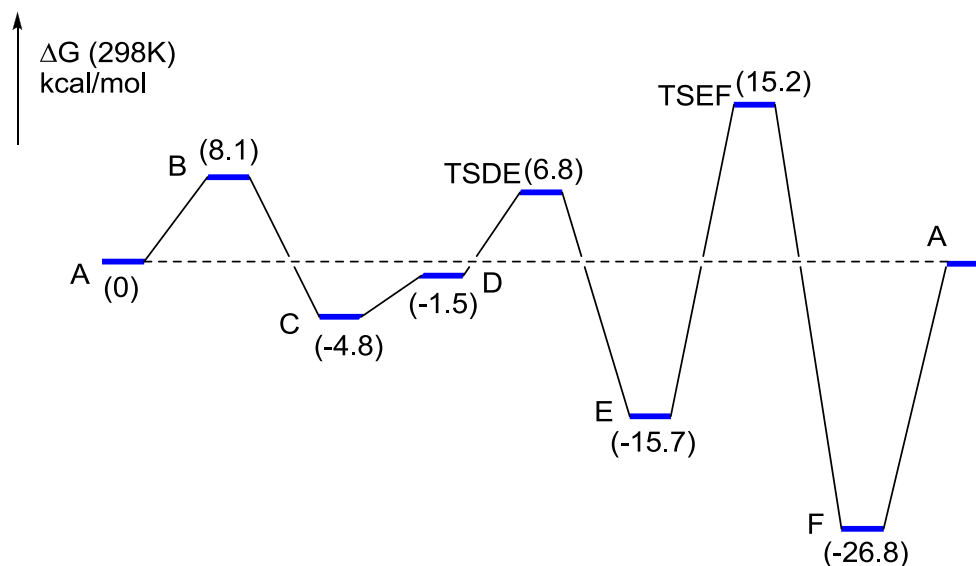
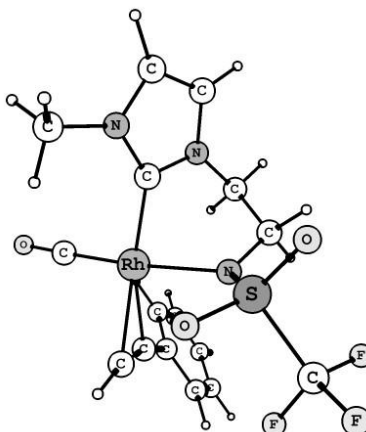


Figure S5. Computed reaction profile for intermolecular hydroalkoxylation catalyzed by **3**. Energies are shown in kcal/mol.

4.3. Cartesian coordinates for intermediates and transition states:

Intermediate A



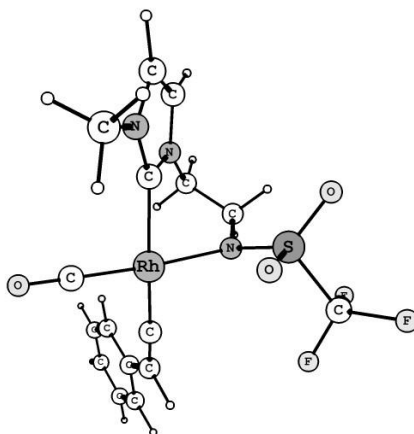
Energy = -1815.83865697 Hartree (in DMAc)

XYZ coordinates

N	3.269019000	-1.635952000	0.118162000
S	1.029173000	2.148961000	-0.205226000
Rh	0.305697000	-0.957123000	-0.653740000
F	0.194694000	4.670499000	-0.719001000
O	2.138162000	2.755642000	0.581328000
C	3.262574000	-1.257713000	2.305573000
H	3.484077000	-1.120205000	3.358738000
N	1.988543000	-1.086512000	1.779077000
O	1.203244000	1.851413000	-1.649761000
C	-0.295852000	3.527862000	-0.184414000
F	-0.682275000	3.787200000	1.096564000
C	0.791795000	-0.591964000	2.465002000
H	0.979839000	-0.596718000	3.548720000
H	-0.028964000	-1.292188000	2.244575000
N	0.306536000	0.881984000	0.523510000
F	-1.397233000	3.167891000	-0.888846000
C	1.978929000	-1.307617000	0.429604000
C	4.071129000	-1.609458000	1.257640000
H	5.132567000	-1.831287000	1.223946000
C	0.420471000	0.827881000	1.990356000
H	1.177904000	1.542372000	2.353740000
C	0.329281000	-2.603651000	-1.459741000
C	3.762887000	-1.912977000	-1.231252000
H	4.600418000	-1.240450000	-1.464585000
H	2.947571000	-1.722948000	-1.938234000
H	4.091232000	-2.959746000	-1.312558000
H	-0.546555000	1.081958000	2.463218000
O	0.348660000	-3.671867000	-1.945555000

C	-1.160618000	-0.109449000	-2.072719000
C	-1.891999000	-0.557478000	-1.160130000
H	-0.811664000	0.352014000	-2.981496000
C	-2.993944000	-0.881987000	-0.295919000
C	-4.097450000	0.005945000	-0.222760000
C	-3.018514000	-2.074888000	0.465932000
C	-5.196199000	-0.302927000	0.588226000
H	-4.077122000	0.930720000	-0.802693000
C	-4.124289000	-2.374857000	1.271520000
H	-2.165856000	-2.754834000	0.411348000
C	-5.215248000	-1.491628000	1.337940000
H	-6.040311000	0.389756000	0.636861000
H	-4.134701000	-3.302485000	1.849712000
H	-6.075182000	-1.727839000	1.969690000

Intermediate B



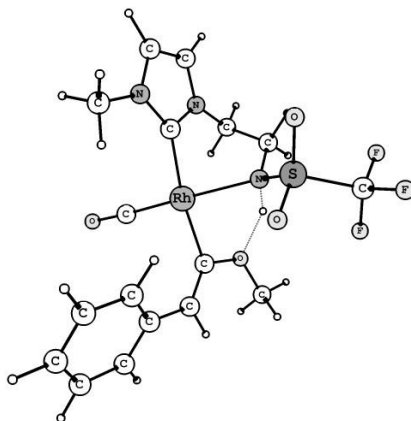
Energy = -1815.82573601 Hartree (in DMAC)

XYZ coordinates

N	2.790912000	-2.501456000	-0.103805000
S	1.987176000	1.633040000	-0.051410000
Rh	0.092011000	-0.808074000	-0.643813000
F	2.175750000	4.230384000	-0.770852000
O	3.191858000	1.836624000	0.798172000
C	2.996123000	-2.300577000	2.094990000
H	3.293534000	-2.316305000	3.138334000
N	1.821018000	-1.702907000	1.659645000
O	2.115129000	1.174823000	-1.462068000
C	1.269995000	3.394919000	-0.211006000
F	0.946161000	3.875918000	1.019643000
C	0.860826000	-0.938325000	2.461421000
H	1.089517000	-1.094329000	3.526030000
H	-0.139757000	-1.346909000	2.252762000
N	0.802899000	0.780668000	0.667433000
F	0.151977000	3.400574000	-0.976087000
C	1.683695000	-1.811618000	0.302530000
C	3.609389000	-2.808795000	0.980228000
H	4.546112000	-3.344586000	0.867766000
C	0.896307000	0.569693000	2.114760000

H	1.822421000	1.017559000	2.511488000
C	-0.461960000	-2.243110000	-1.669699000
C	3.119679000	-2.812521000	-1.495862000
H	4.083925000	-2.356756000	-1.761495000
H	2.342021000	-2.386594000	-2.138727000
H	3.168286000	-3.901584000	-1.641858000
H	0.037205000	1.039622000	2.628597000
O	-0.803578000	-3.158129000	-2.310158000
C	-1.554850000	0.056644000	-0.921114000
C	-2.766373000	0.586854000	-0.958319000
H	-2.831953000	1.445108000	-1.647340000
C	-3.989036000	0.223328000	-0.218419000
C	-5.167006000	0.982467000	-0.403354000
C	-4.026030000	-0.877189000	0.671450000
C	-6.345654000	0.653418000	0.281295000
H	-5.155000000	1.835235000	-1.087962000
C	-5.205173000	-1.202311000	1.351266000
H	-3.124378000	-1.477143000	0.819162000
C	-6.371693000	-0.439567000	1.161816000
H	-7.245755000	1.253642000	0.124393000

Intermediate C



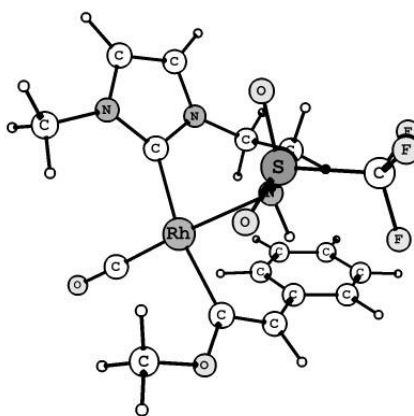
Energy = -1931.56860778 Hartree (in DMAc)

XYZ coordinates

N	0.593361000	3.481755000	0.738771000
S	1.954265000	-1.018315000	1.089488000
Rh	-0.405443000	0.723251000	-0.534653000
F	3.364314000	-3.139722000	1.928693000
O	2.769289000	-0.029096000	1.817503000
C	2.528452000	3.762241000	-0.311868000
H	3.488172000	4.091700000	-0.697184000
N	1.887655000	2.608405000	-0.755700000
O	0.713814000	-1.602959000	1.609948000
C	3.118291000	-2.516002000	0.764681000
F	4.290384000	-2.098168000	0.227026000
C	2.360914000	1.663836000	-1.763992000
H	3.231414000	2.101889000	-2.276835000
H	1.549164000	1.513468000	-2.494121000

N	1.628402000	-0.387300000	-0.496014000
F	2.532492000	-3.379187000	-0.094938000
C	0.686435000	2.408233000	-0.110918000
C	1.703607000	4.317452000	0.629403000
H	1.814215000	5.221150000	1.220072000
C	2.776463000	0.313731000	-1.154417000
H	3.559553000	0.485071000	-0.402921000
C	-1.924386000	1.603221000	-1.004717000
C	-0.522431000	3.701962000	1.657193000
H	-0.153328000	3.769508000	2.691227000
H	-1.201261000	2.845404000	1.568083000
H	-1.059488000	4.625889000	1.395190000
H	3.187153000	-0.329764000	-1.948702000
O	-2.854605000	2.225672000	-1.359347000
C	-1.206385000	-1.102095000	-1.117867000
C	-2.390979000	-1.742732000	-0.894666000
H	1.170749000	-1.130103000	-1.096141000
C	-0.452138000	-3.048627000	-2.467078000
H	0.465922000	-3.327722000	-3.002557000
H	-0.653401000	-3.772582000	-1.659052000
H	-1.298401000	-3.040513000	-3.174191000
O	-0.221458000	-1.729479000	-1.939157000
H	-2.612638000	-2.683493000	-1.413527000
C	-3.468042000	-1.289148000	-0.003803000
C	-4.806132000	-1.675179000	-0.273236000
C	-3.233799000	-0.517877000	1.163094000
C	-5.863078000	-1.279998000	0.557168000
H	-5.013990000	-2.282761000	-1.159930000
C	-4.292239000	-0.117902000	1.990536000
H	-2.203219000	-0.259583000	1.420415000
C	-5.614258000	-0.491040000	1.693715000
H	-6.884885000	-1.587446000	0.316226000
H	-4.081312000	0.471777000	2.887951000
H	-6.436466000	-0.185053000	2.346174000

Intermediate D

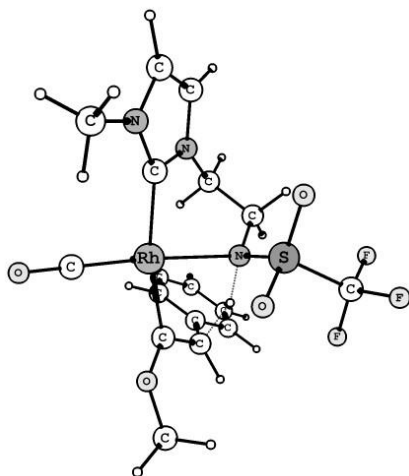


Energy = -1931.56334036 Hartree (in DMAc)

XYZ coordinates

N	-3.459360000	0.675786000	-1.074600000
S	0.560867000	2.250730000	0.258629000
Rh	-1.073800000	-0.650580000	0.602638000
F	2.450729000	4.106315000	0.622510000
O	-0.209333000	3.070679000	-0.693334000
C	-2.557424000	0.785897000	-3.098853000
H	-2.315609000	0.941787000	-4.145356000
N	-1.684736000	0.175332000	-2.203169000
O	0.282022000	2.192593000	1.698710000
C	2.383159000	2.856627000	0.131363000
F	2.791804000	2.862486000	-1.159799000
C	-0.346514000	-0.338298000	-2.483166000
H	-0.195027000	-0.357224000	-3.573187000
H	-0.285301000	-1.368575000	-2.101071000
N	0.616196000	0.620383000	-0.357959000
F	3.189627000	2.045374000	0.842772000
C	-2.221929000	0.099591000	-0.937100000
C	-3.683422000	1.095823000	-2.384325000
H	-4.606707000	1.575060000	-2.693435000
C	0.770438000	0.507447000	-1.847192000
H	0.758939000	1.515752000	-2.282973000
C	-2.293656000	-1.798722000	1.299295000
C	-4.409338000	0.848295000	0.022759000
H	-4.727504000	1.899364000	0.081452000
H	-3.898467000	0.571052000	0.952476000
H	-5.289188000	0.203234000	-0.121564000
H	1.739704000	0.033721000	-2.062168000
O	-3.103356000	-2.546504000	1.712131000
C	0.430002000	-1.206276000	1.933449000
H	1.317827000	0.069076000	0.201817000
C	-0.746108000	-0.309773000	3.846496000
H	-0.440600000	0.029255000	4.846895000
H	-1.574561000	-1.031084000	3.943086000
H	-1.069335000	0.547359000	3.236628000
C	1.679313000	-1.632989000	1.501736000
O	0.410441000	-0.942368000	3.279796000
H	2.498084000	-1.569262000	2.232758000
C	2.026222000	-2.270376000	0.227338000
C	3.369307000	-2.216639000	-0.243844000
C	1.098881000	-3.013086000	-0.556521000
C	3.755078000	-2.835708000	-1.439753000
H	4.114756000	-1.679272000	0.351296000
C	1.488137000	-3.628911000	-1.755807000
H	0.077526000	-3.129374000	-0.184877000
C	2.814790000	-3.541114000	-2.213675000
H	4.797090000	-2.773720000	-1.767248000
H	0.753968000	-4.210617000	-2.322212000
H	3.117592000	-4.036118000	-3.140000000

Transition State **TSDE**



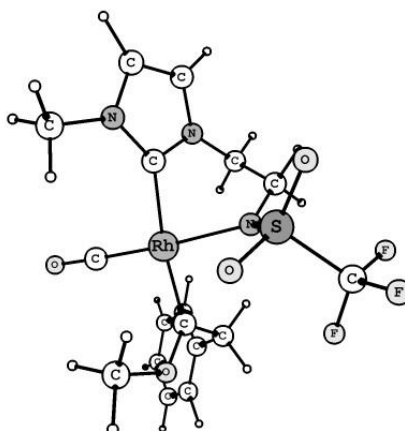
Energy = -1931.55009204 Hartree (in DMAc)

XYZ coordinates

N	-3.708065000	-0.340901000	-0.608100000
S	-0.216427000	2.237388000	0.316880000
Rh	-0.821355000	-0.938383000	0.667535000
F	1.010664000	4.609457000	0.547603000
O	-1.340487000	2.858710000	-0.419282000
C	-3.153942000	0.053845000	-2.719640000
H	-3.108166000	0.290605000	-3.777756000
N	-2.034554000	-0.304578000	-1.976895000
O	-0.217740000	2.075020000	1.781981000
C	1.268047000	3.410961000	-0.013926000
F	1.468397000	3.589249000	-1.345444000
C	-0.648975000	-0.379540000	-2.438952000
H	-0.641755000	-0.328619000	-3.538506000
H	-0.240293000	-1.354366000	-2.129941000
N	0.263511000	0.766118000	-0.380886000
F	2.405037000	2.909766000	0.523731000
C	-2.354490000	-0.546835000	-0.662367000
C	-4.214507000	0.024185000	-1.853745000
H	-5.266717000	0.233593000	-2.016627000
C	0.229489000	0.754120000	-1.876336000
H	-0.143565000	1.716779000	-2.256352000
C	-1.566429000	-2.333976000	1.574838000
C	-4.509378000	-0.444727000	0.610148000
H	-5.045798000	0.498805000	0.787318000
H	-3.827369000	-0.633065000	1.447131000
H	-5.231119000	-1.271308000	0.527621000
H	1.255834000	0.606339000	-2.248003000
O	-2.048166000	-3.225194000	2.169886000
C	0.926838000	-0.984339000	1.698607000
H	1.321844000	0.292640000	0.244645000
C	2.096038000	-0.667626000	3.812881000
H	2.893011000	-1.363236000	3.508499000

H	1.803966000	-0.854895000	4.853395000
H	2.434480000	0.374292000	3.706075000
C	2.118795000	-0.684117000	0.964410000
O	0.888088000	-0.890081000	3.036329000
H	2.963741000	-0.248537000	1.516212000
C	2.571064000	-1.437357000	-0.245041000
C	3.748894000	-1.011945000	-0.909252000
C	1.894303000	-2.566919000	-0.765362000
C	4.225432000	-1.678116000	-2.046543000
H	4.297535000	-0.148604000	-0.519431000
C	2.370354000	-3.229149000	-1.908359000
H	0.999732000	-2.928370000	-0.251554000
C	3.534767000	-2.790078000	-2.559792000
H	5.140723000	-1.328492000	-2.532515000
H	1.834769000	-4.108051000	-2.279396000
H	3.908502000	-3.315182000	-3.442554000

Intermediate E



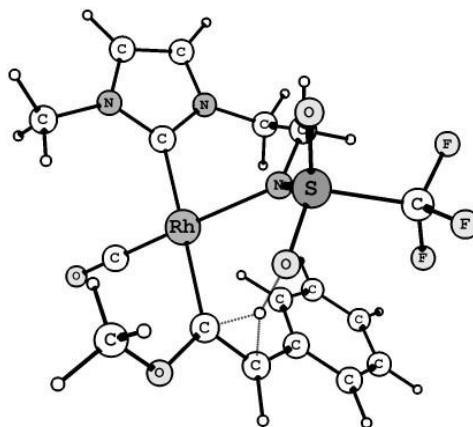
Energy = -1931.58588545 Hartree (in DMAc)

XYZ coordinates

N	-2.117978000	-3.128034000	0.382604000
S	-2.221281000	1.432786000	0.281855000
Rh	0.099463000	-0.817611000	0.358410000
F	-2.772579000	4.072493000	0.538776000
O	-3.668167000	1.228606000	-0.001268000
C	-2.934835000	-3.003970000	-1.675030000
H	-3.483978000	-3.100358000	-2.605997000
N	-1.875498000	-2.120273000	-1.513342000
O	-1.710222000	1.369419000	1.676139000
C	-1.961650000	3.268887000	-0.186563000
F	-2.236674000	3.465482000	-1.507281000
C	-1.390043000	-1.130015000	-2.474083000
H	-1.829040000	-1.348945000	-3.458913000
H	-0.296556000	-1.243950000	-2.541350000
N	-1.217449000	0.610511000	-0.701401000
F	-0.676647000	3.654206000	0.031928000
C	-1.361804000	-2.172495000	-0.244905000

C	-3.083152000	-3.649179000	-0.475623000
H	-3.786597000	-4.414861000	-0.165226000
C	-1.750632000	0.302881000	-2.042093000
H	-2.847107000	0.421466000	-2.067910000
C	1.176620000	-2.098857000	1.108397000
C	-1.964000000	-3.523574000	1.782058000
H	-2.940330000	-3.489789000	2.286132000
H	-1.286729000	-2.808778000	2.262917000
H	-1.543975000	-4.538094000	1.854755000
H	-1.318042000	0.986242000	-2.797681000
O	1.850143000	-2.946558000	1.565562000
C	1.391871000	0.658825000	0.733109000
H	1.448305000	1.344642000	-1.282618000
C	1.220390000	0.605340000	3.122052000
H	1.454026000	1.346418000	3.896096000
H	1.721280000	-0.347994000	3.337336000
H	0.138276000	0.473970000	3.002898000
C	2.084386000	1.415415000	-0.389633000
O	1.773388000	1.159263000	1.888706000
H	2.188054000	2.477122000	-0.110979000
C	3.461458000	0.813807000	-0.662480000
C	4.615046000	1.376424000	-0.081425000
C	3.600991000	-0.321860000	-1.484815000
C	5.881770000	0.823426000	-0.326638000
H	4.520588000	2.256990000	0.560213000
C	4.866188000	-0.876948000	-1.729587000
H	2.709523000	-0.774560000	-1.927461000
C	6.011302000	-0.305823000	-1.151114000
H	6.767633000	1.277784000	0.125100000
H	4.956893000	-1.757291000	-2.371493000
H	6.997410000	-0.736704000	-1.342647000

Transition State TSEF



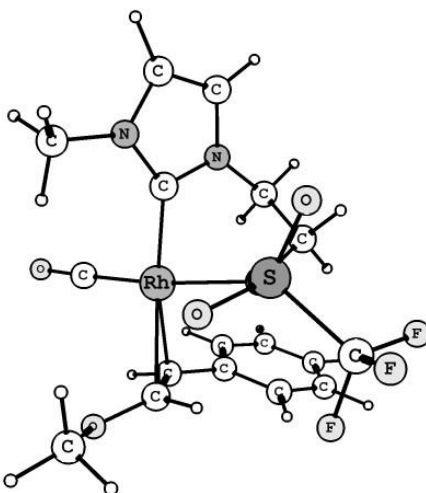
Energy = -1931.53664829 Hartree (in DMAC)

XYZ coordinates

N	-3.907001000	0.461708000	-0.559142000
S	0.815250000	1.972393000	0.916984000

Rh	-1.102324000	-0.672628000	0.310779000
F	3.236715000	3.072714000	1.364261000
O	0.152376000	3.281440000	1.147694000
C	-3.451277000	1.524172000	-2.451960000
H	-3.448918000	2.104334000	-3.368993000
N	-2.309757000	0.916478000	-1.942216000
O	1.129140000	1.093916000	2.090335000
C	2.575843000	2.490588000	0.339311000
F	2.517953000	3.380596000	-0.689171000
C	-0.951163000	1.017137000	-2.472884000
H	-0.999416000	1.530395000	-3.444611000
H	-0.563460000	-0.001417000	-2.628810000
N	0.194710000	1.047432000	-0.265454000
F	3.289967000	1.414199000	-0.075778000
C	-2.563243000	0.258871000	-0.767335000
C	-4.464335000	1.227909000	-1.580255000
H	-5.514473000	1.500587000	-1.595228000
C	-0.031452000	1.792745000	-1.526929000
H	-0.464787000	2.792996000	-1.343907000
C	-2.113529000	-2.170326000	0.543296000
C	-4.660781000	-0.029199000	0.593751000
H	-5.329899000	0.763133000	0.957800000
H	-3.945160000	-0.290244000	1.381591000
H	-5.251691000	-0.918010000	0.326130000
H	0.923818000	1.932503000	-2.065316000
O	-2.757593000	-3.149696000	0.643930000
C	0.406752000	-1.603616000	1.509067000
H	1.180328000	-0.630691000	1.411486000
C	-0.745836000	-1.115701000	3.574146000
H	-1.053099000	-1.720173000	4.438601000
H	-1.616067000	-0.853865000	2.949718000
H	-0.246951000	-0.192978000	3.907224000
C	1.680723000	-2.072969000	1.108178000
O	0.176986000	-1.934826000	2.829515000
H	2.323216000	-2.440871000	1.922407000
C	2.247110000	-2.157216000	-0.237396000
C	3.651681000	-2.293722000	-0.372207000
C	1.446267000	-2.188815000	-1.405334000
C	4.240448000	-2.427904000	-1.634654000
H	4.278491000	-2.285011000	0.524172000
C	2.038910000	-2.328479000	-2.665449000
H	0.358551000	-2.111576000	-1.294787000
C	3.435158000	-2.444710000	-2.786518000
H	5.325454000	-2.524856000	-1.721641000
H	1.409904000	-2.367883000	-3.559078000
H	3.892457000	-2.562585000	-3.772449000

Intermediate F



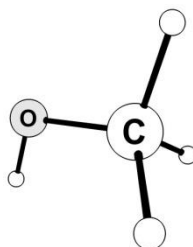
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XYZ coordinates

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S	-0.477124000	2.149011000	0.118420000
Rh	-0.534437000	-1.062075000	0.375282000
F	0.565047000	4.524904000	0.877418000
O	-1.370818000	2.920507000	-0.788849000
C	-3.042100000	-0.011456000	-2.812519000
H	-3.067297000	0.278334000	-3.857707000
N	-1.866779000	-0.355272000	-2.158228000
O	-0.898515000	1.845156000	1.510957000
C	0.992179000	3.349418000	0.363946000
F	1.614248000	3.599748000	-0.820068000
C	-0.497380000	-0.303678000	-2.673838000
H	-0.535622000	-0.162660000	-3.764263000
H	-0.025713000	-1.274717000	-2.458102000
N	0.199975000	0.815066000	-0.538807000
F	1.915653000	2.827058000	1.217769000
C	-2.103801000	-0.660224000	-0.845438000
C	-4.046593000	-0.118914000	-1.887533000
H	-5.112668000	0.062652000	-1.974227000
C	0.315359000	0.835130000	-2.011353000
H	-0.025027000	1.799325000	-2.421225000
C	-1.254646000	-2.639594000	0.960873000
C	-4.174739000	-0.691489000	0.570037000
H	-4.726413000	0.227877000	0.812516000
H	-3.436555000	-0.882594000	1.356992000
H	-4.872955000	-1.538693000	0.499463000
H	1.371696000	0.688335000	-2.295746000
O	-1.736094000	-3.654617000	1.302581000
C	1.077867000	-0.811623000	2.024881000
H	1.300328000	0.253014000	1.894302000
C	0.017198000	-0.165326000	4.048468000
H	-0.149761000	-0.605599000	5.039475000

H	-0.937474000	0.126929000	3.587334000
H	0.664188000	0.722920000	4.137617000
C	1.513031000	-1.793380000	1.127713000
O	0.665116000	-1.192641000	3.269040000
H	1.385159000	-2.826297000	1.466088000
C	2.480197000	-1.620956000	0.021677000
C	2.716091000	-2.717422000	-0.844270000
C	3.234728000	-0.440875000	-0.182026000
C	3.653989000	-2.634961000	-1.881970000
H	2.152227000	-3.642882000	-0.694186000
C	4.171126000	-0.359025000	-1.221476000
H	3.098544000	0.413284000	0.482326000
C	4.385521000	-1.451669000	-2.079526000
H	3.818649000	-3.498009000	-2.532833000
H	4.747171000	0.560990000	-1.352994000
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MeOH



Energy = -115.7222352 Hartree (in DMAc)

XYZ coordinates

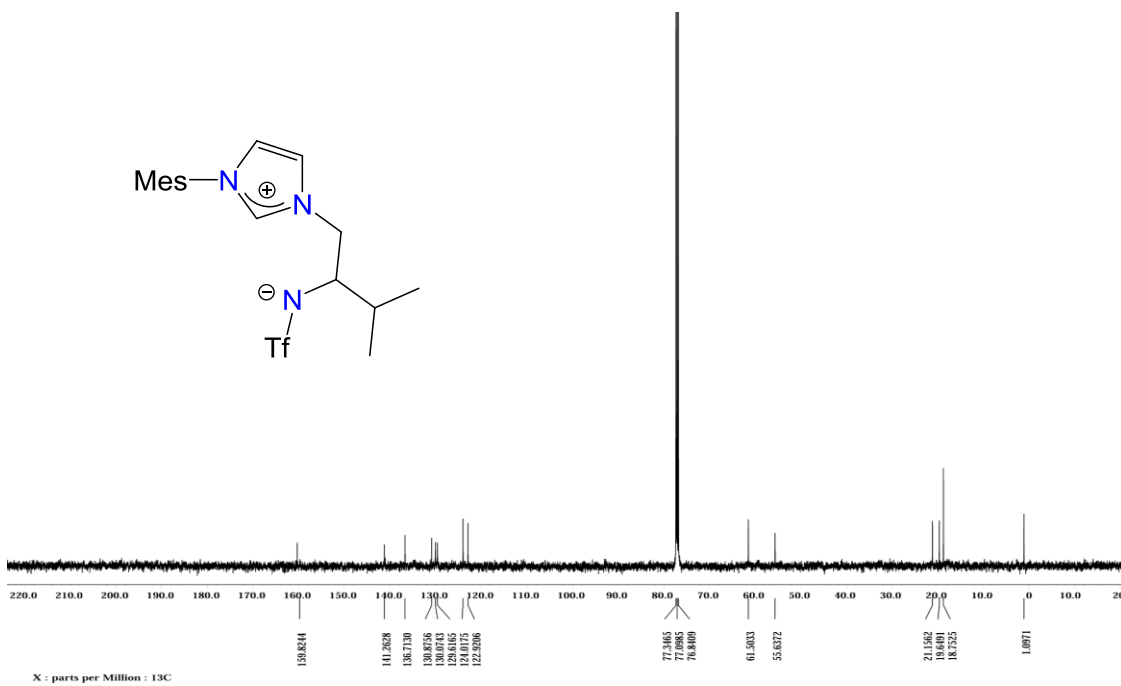
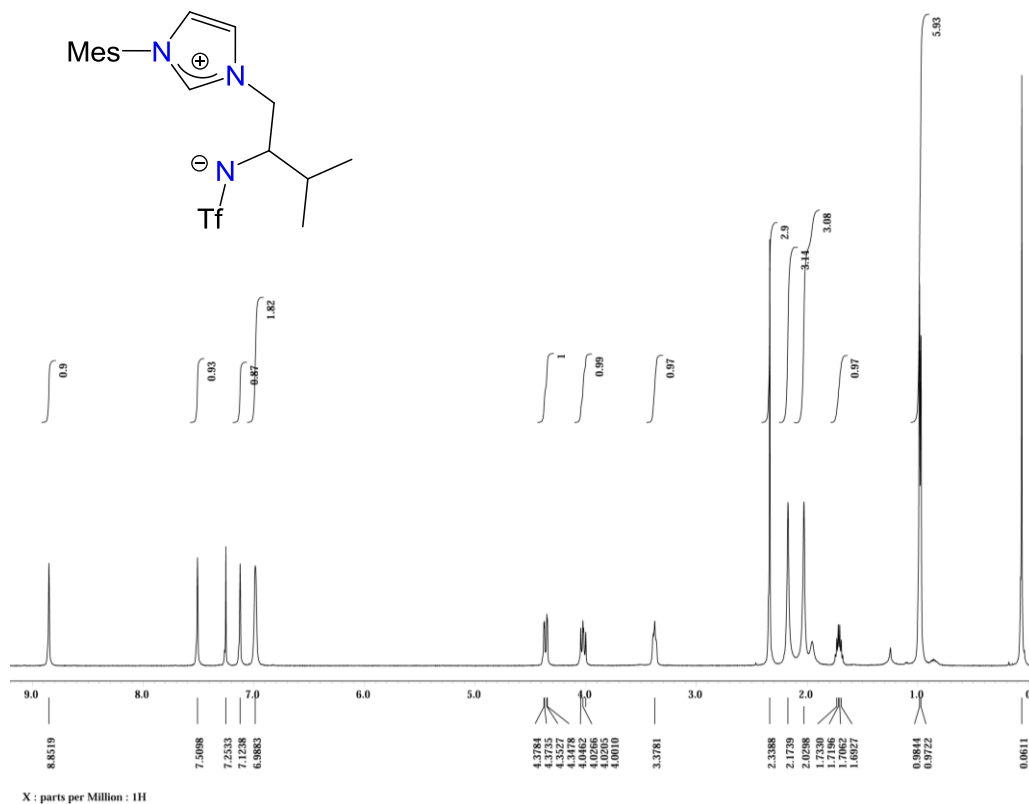
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H	1.150934000	-0.767307000	0.000318000
H	-1.041233000	-0.548578000	-0.901356000
O	0.755458000	0.123254000	-0.000034000

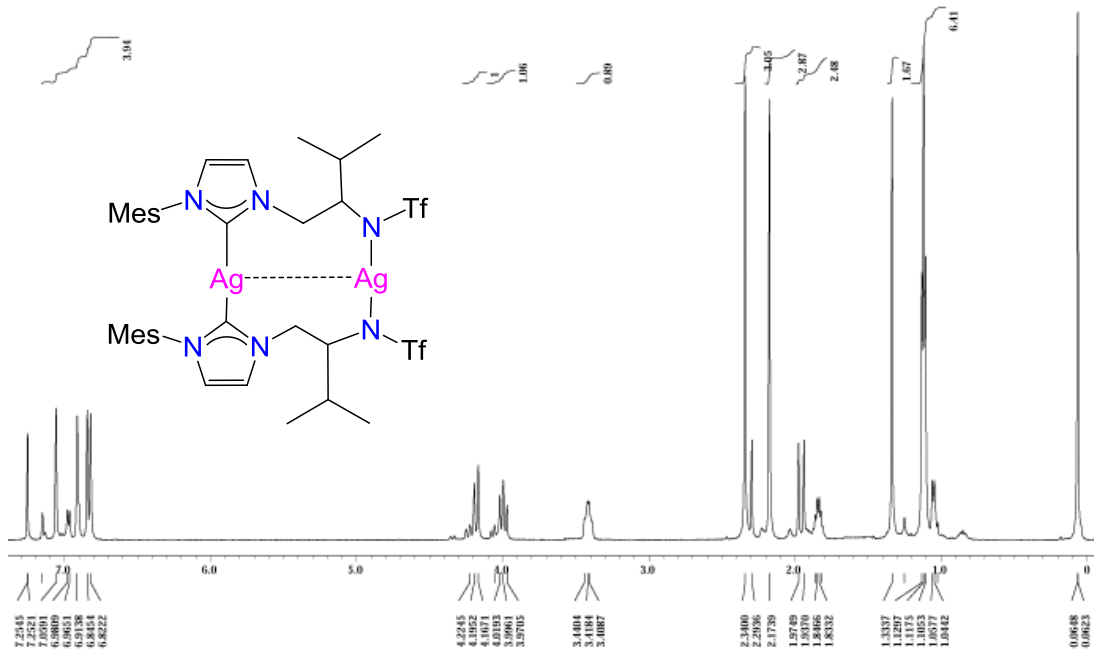
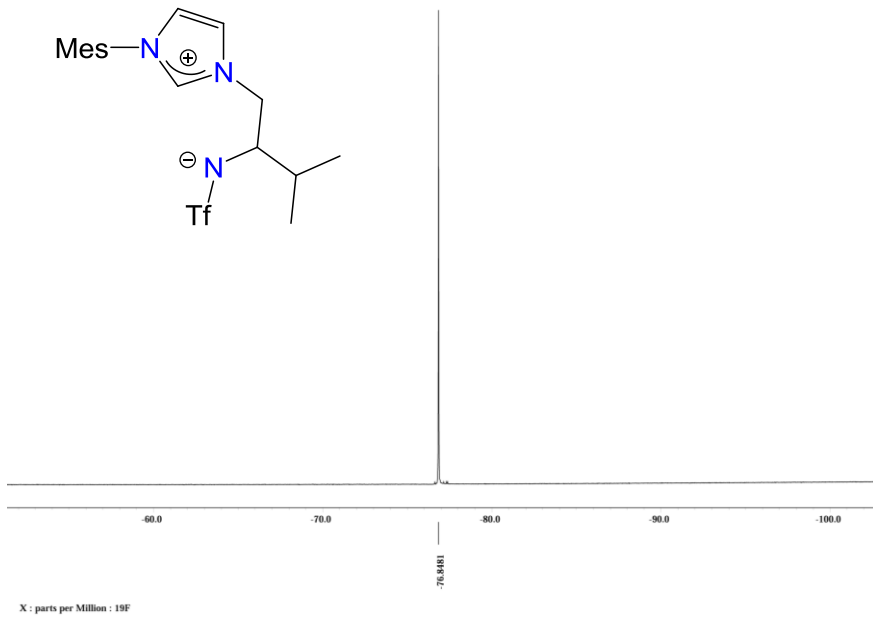
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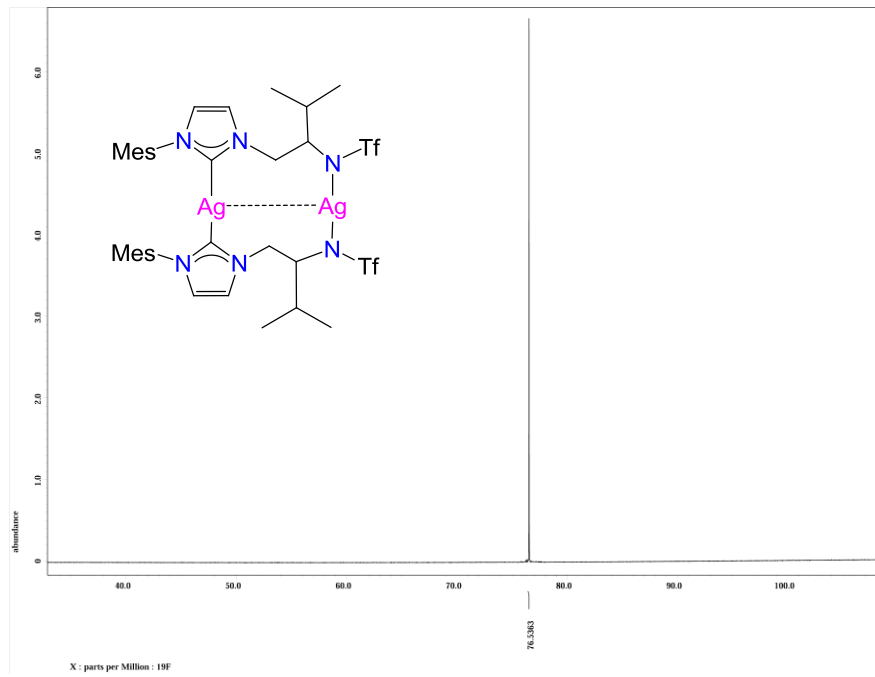
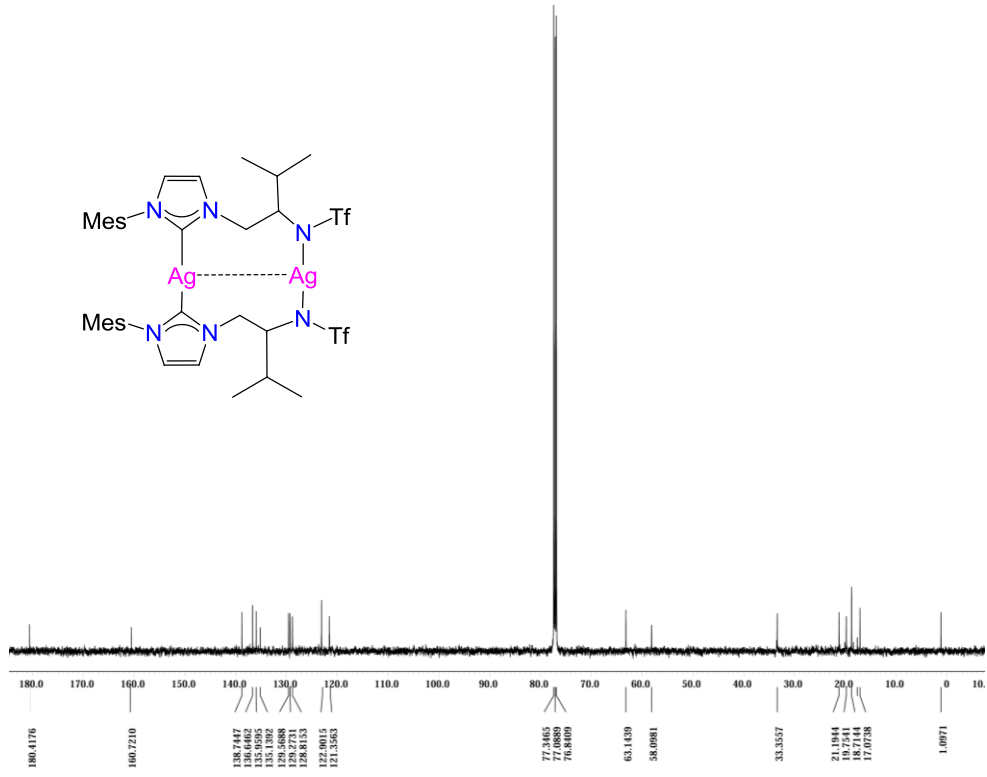
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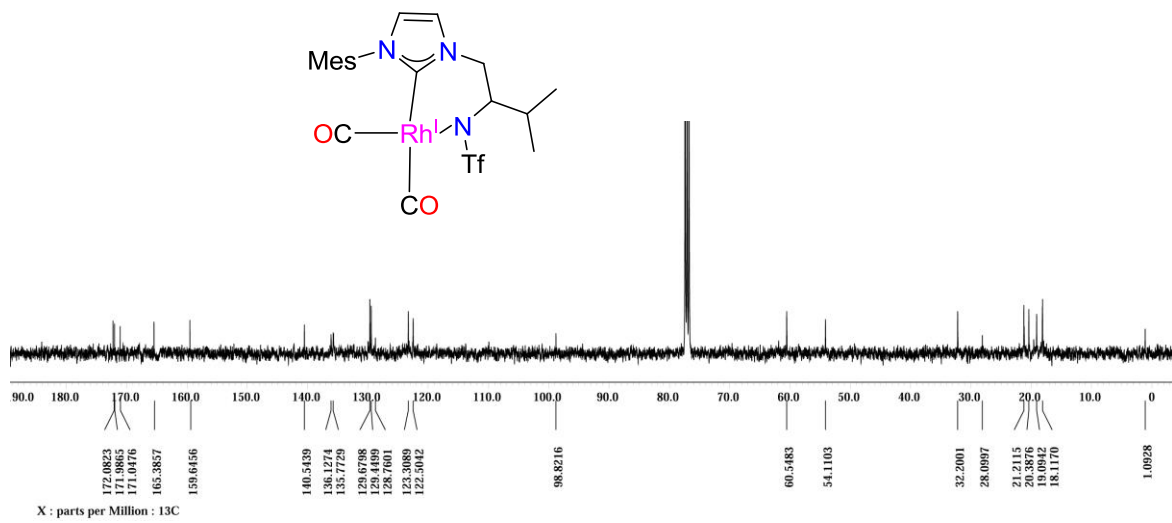
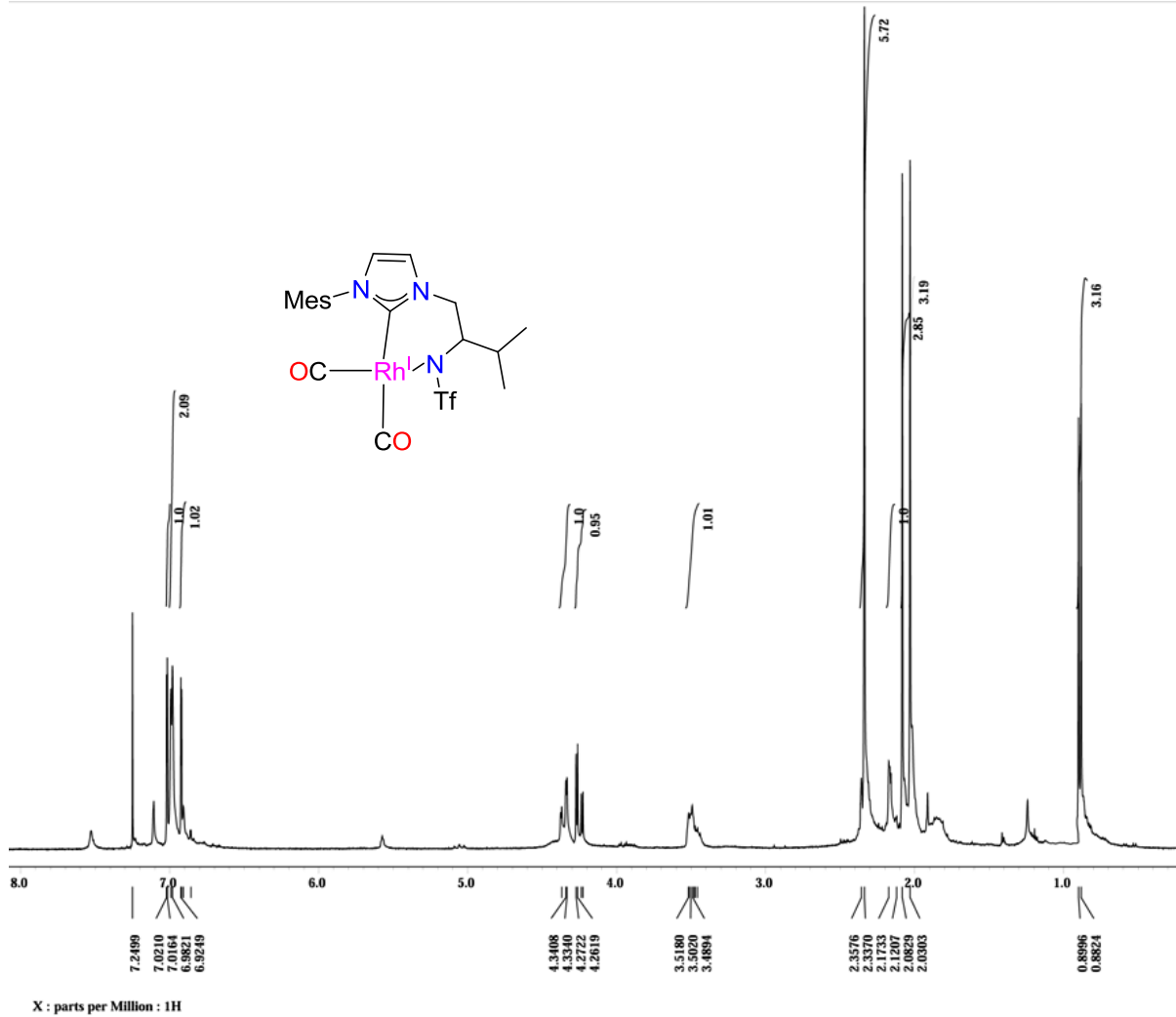
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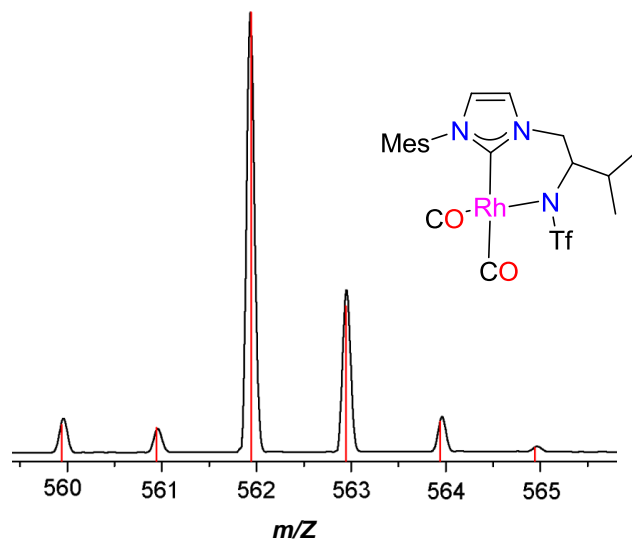
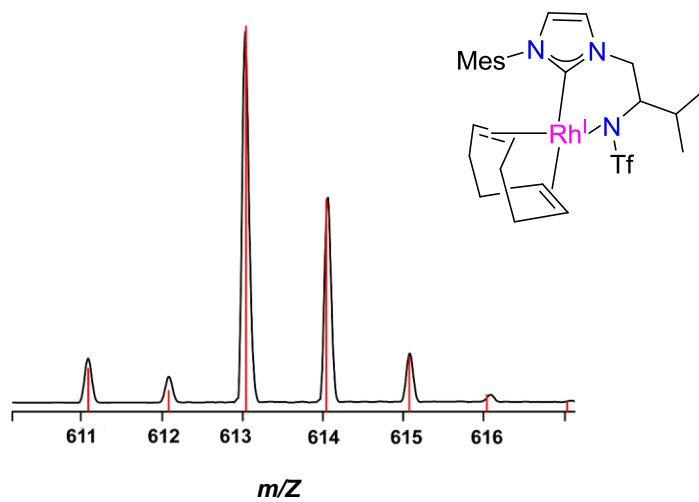
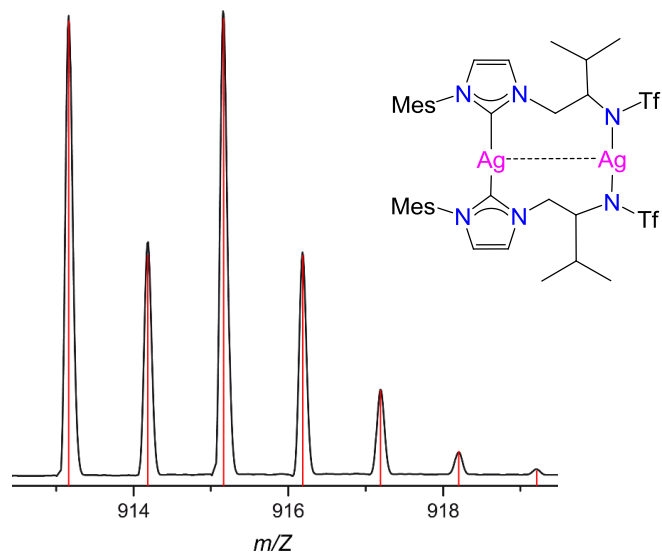
6. Spectroscopic Characterization

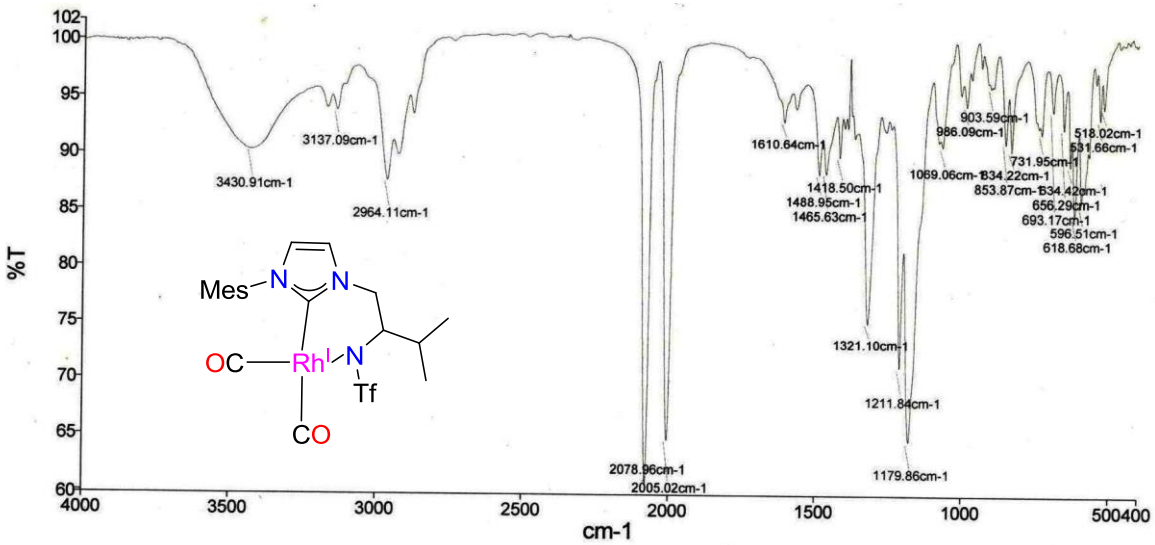
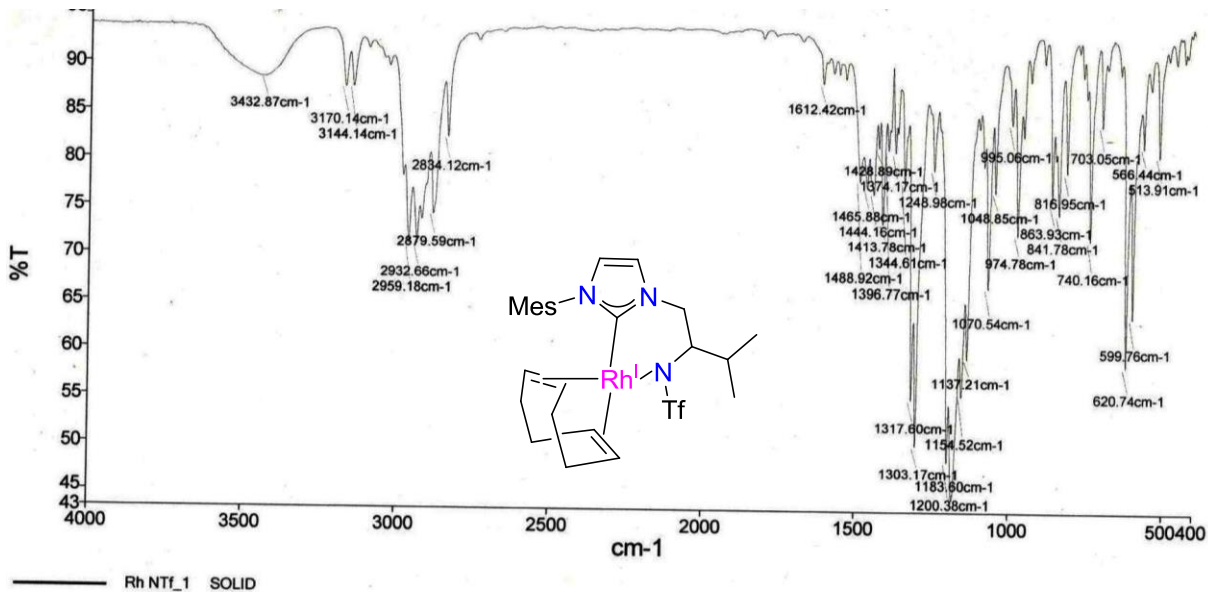


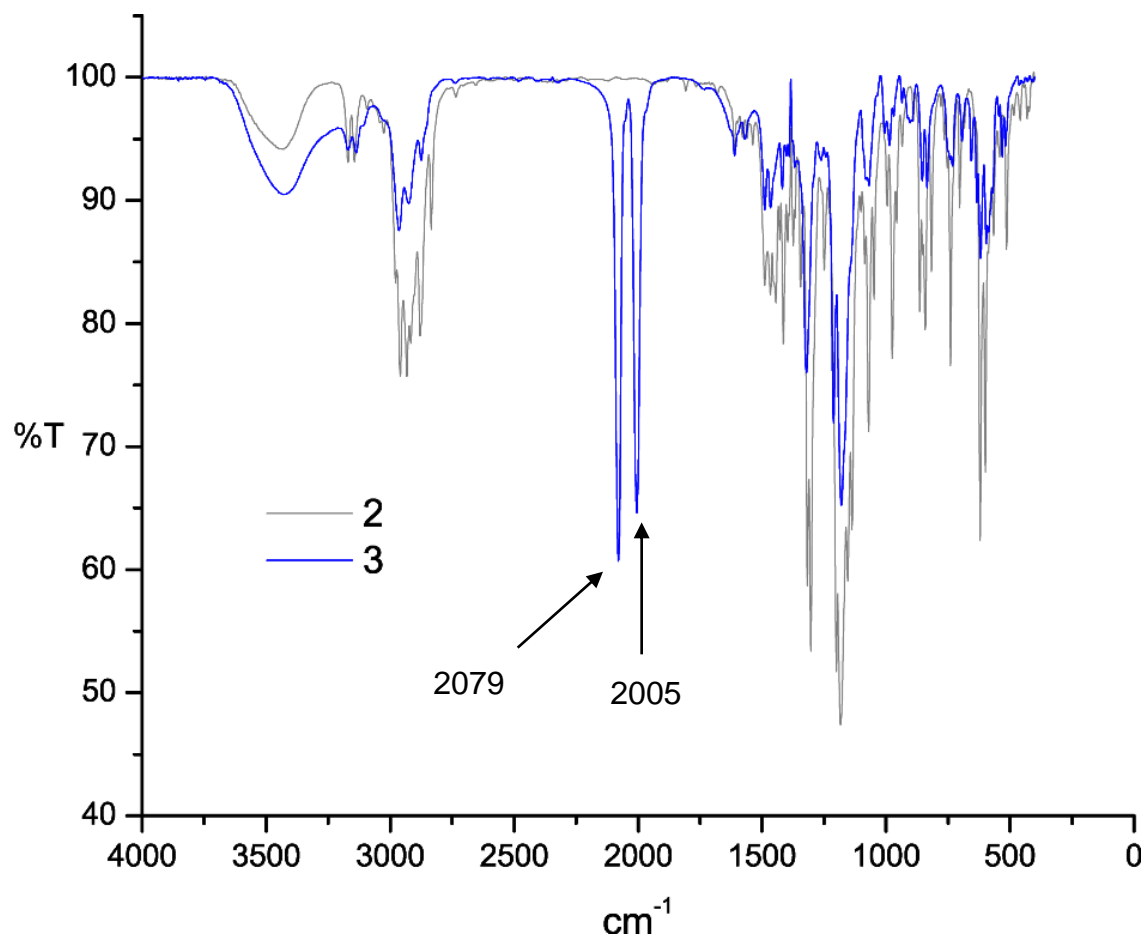


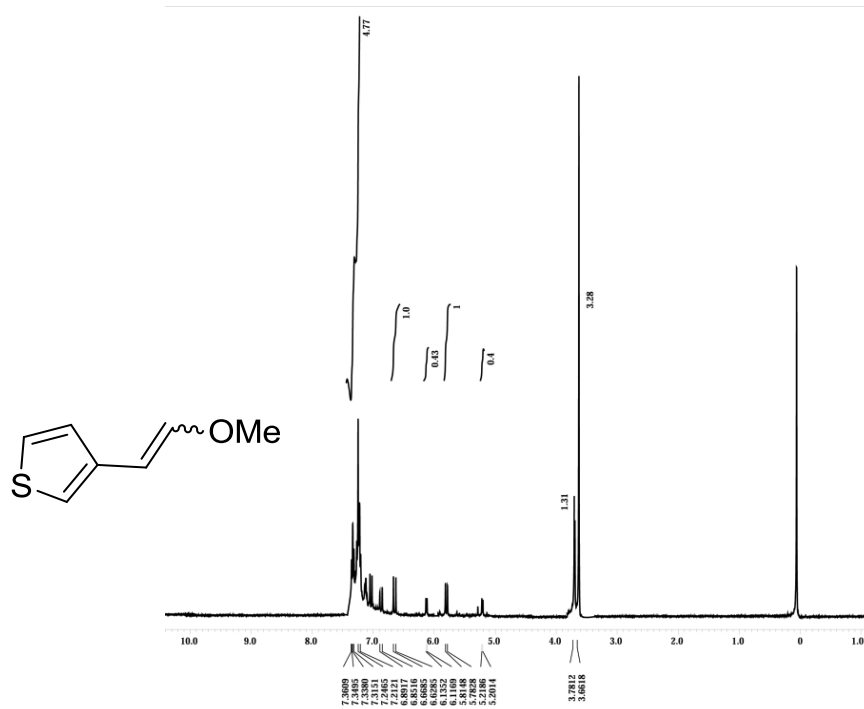
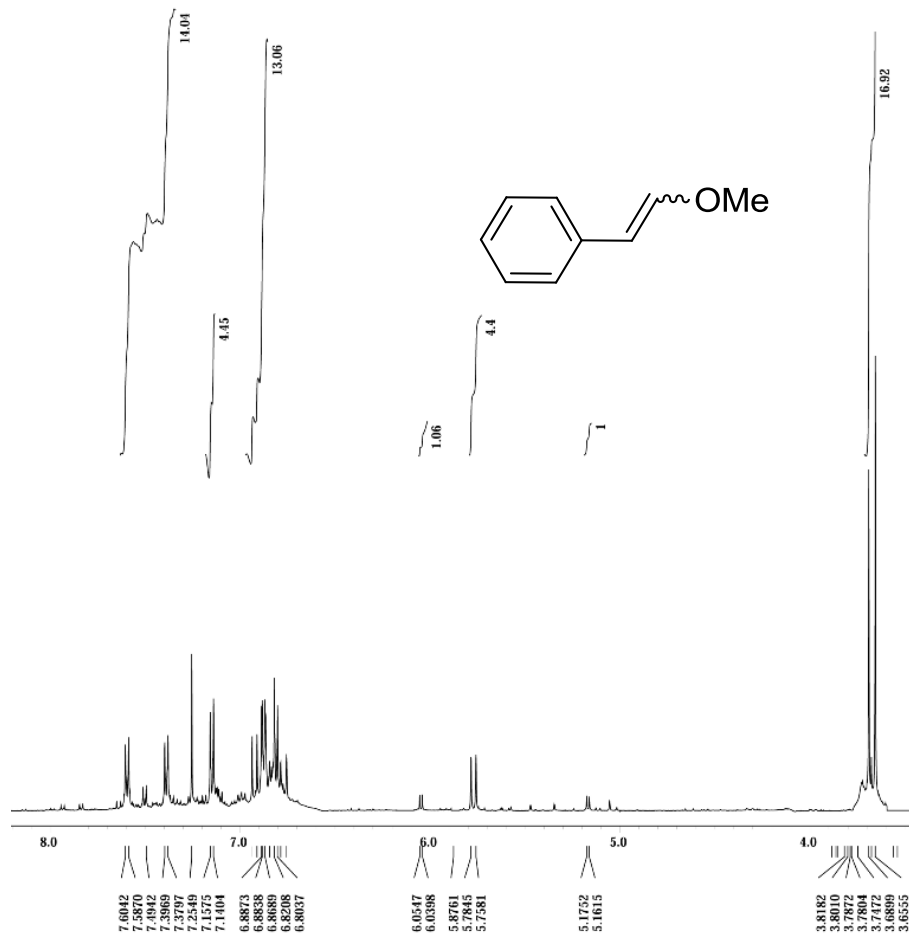


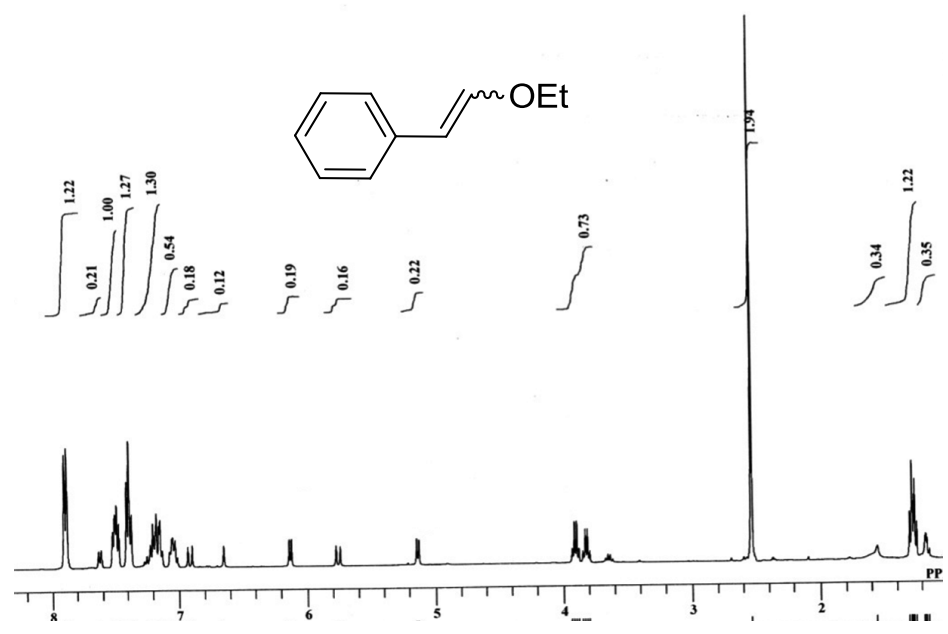
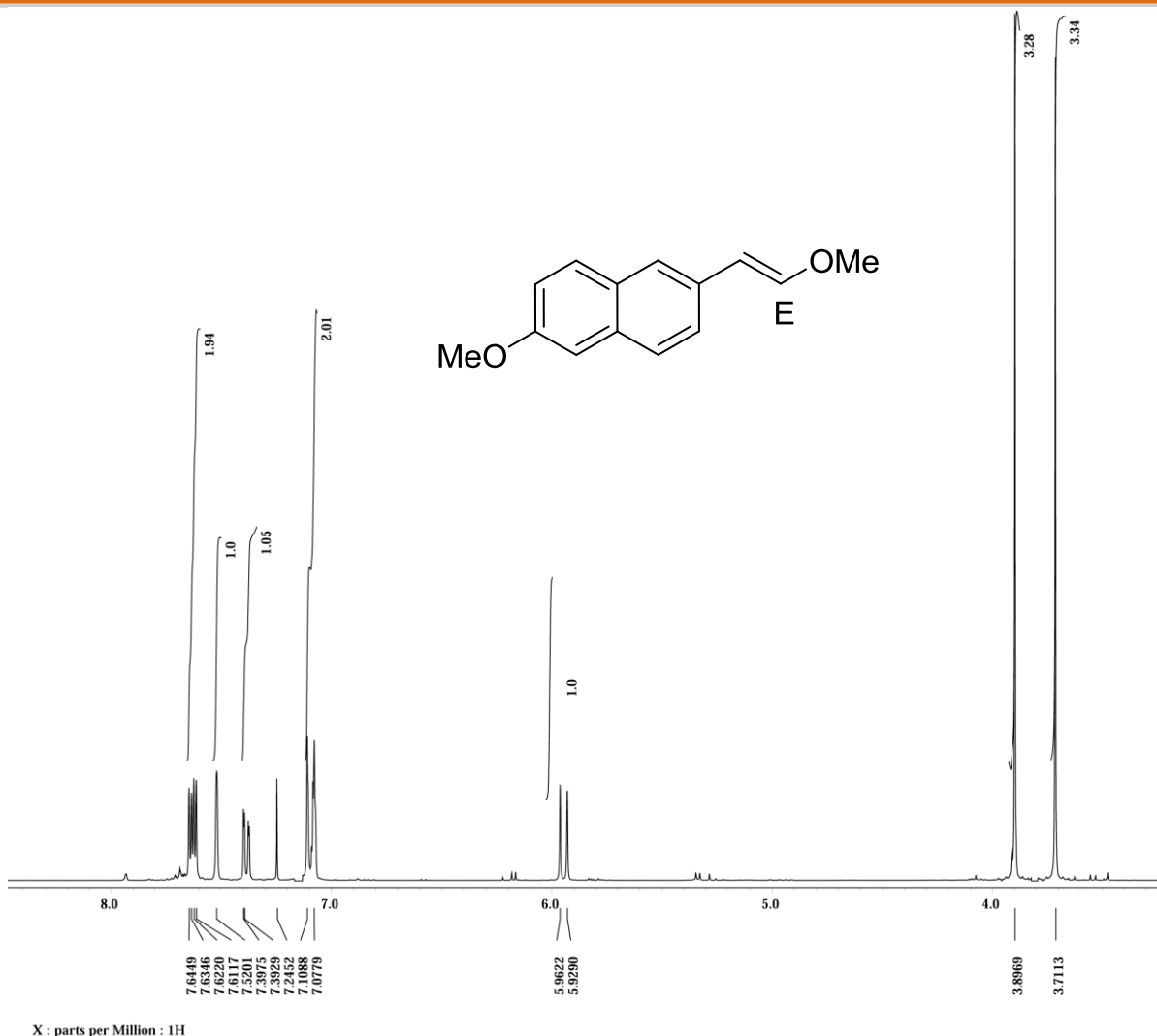


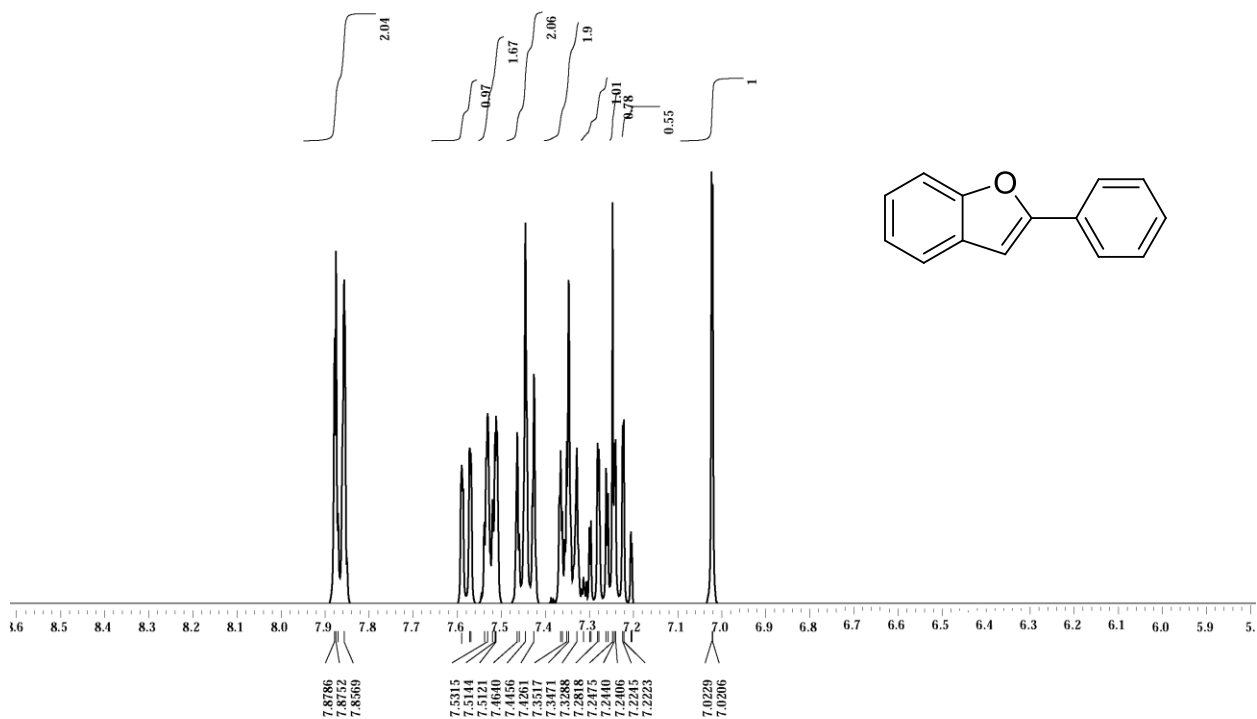




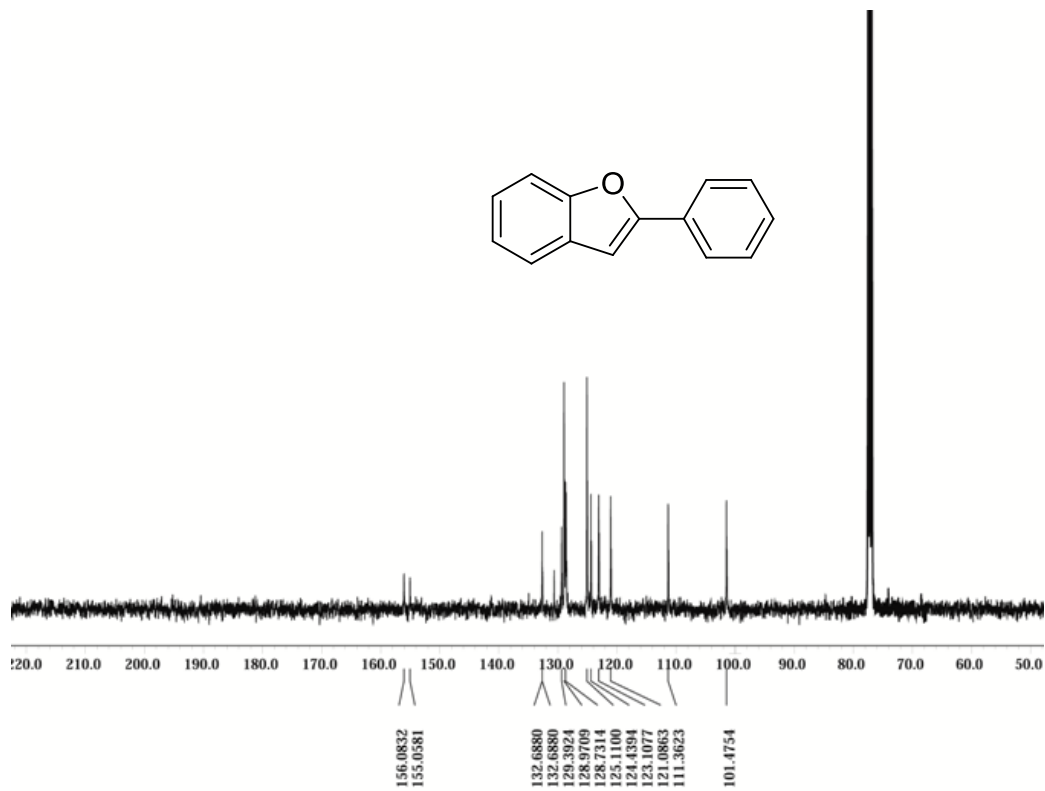




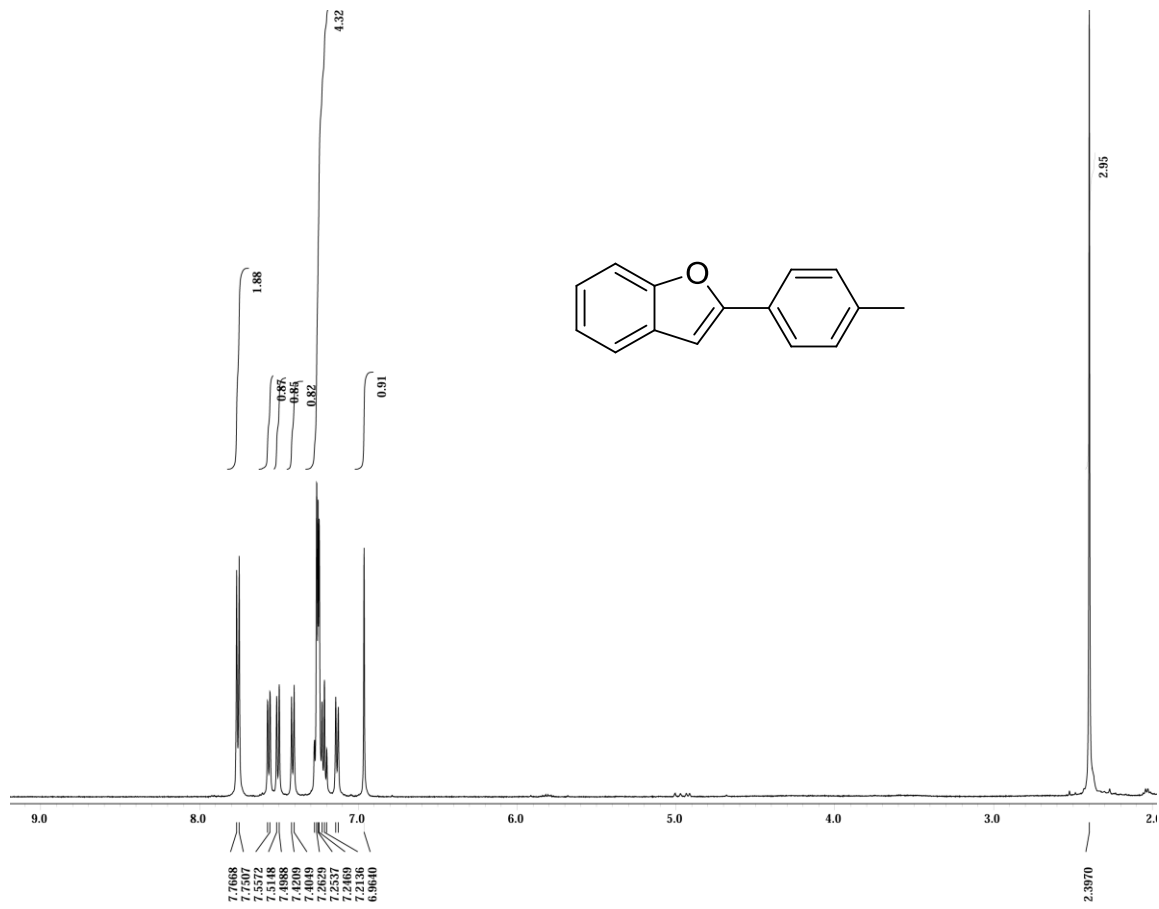




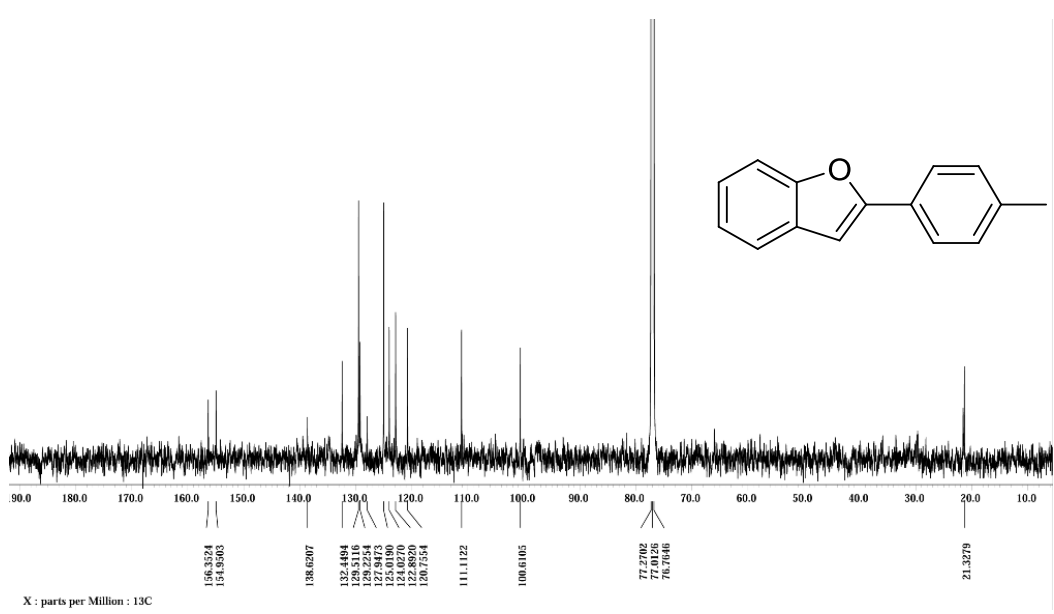
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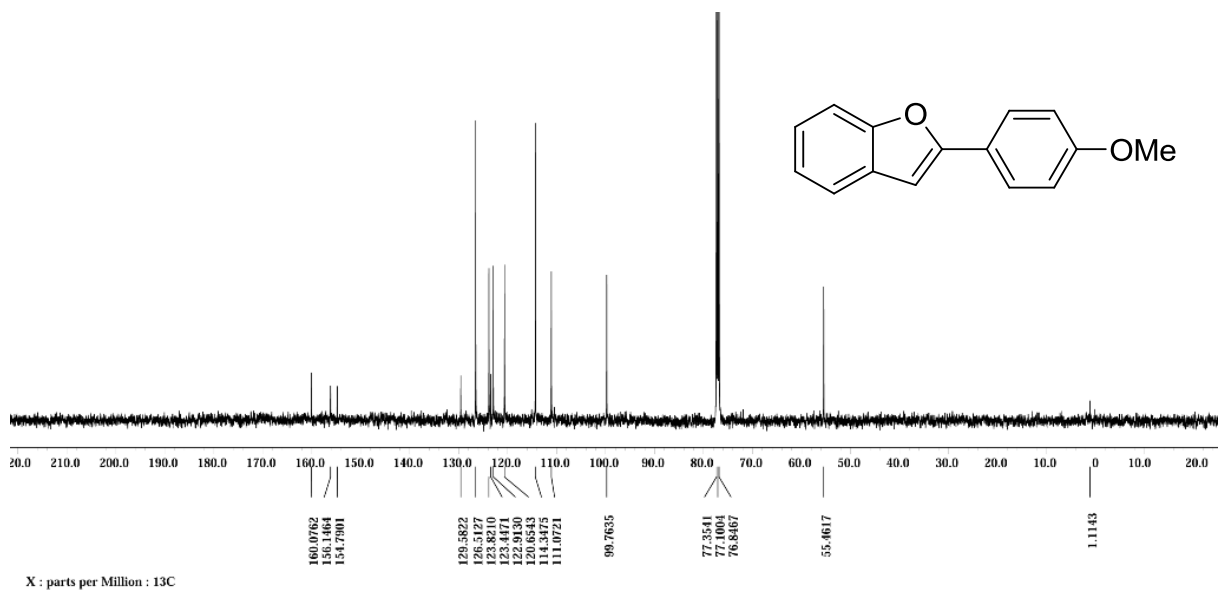
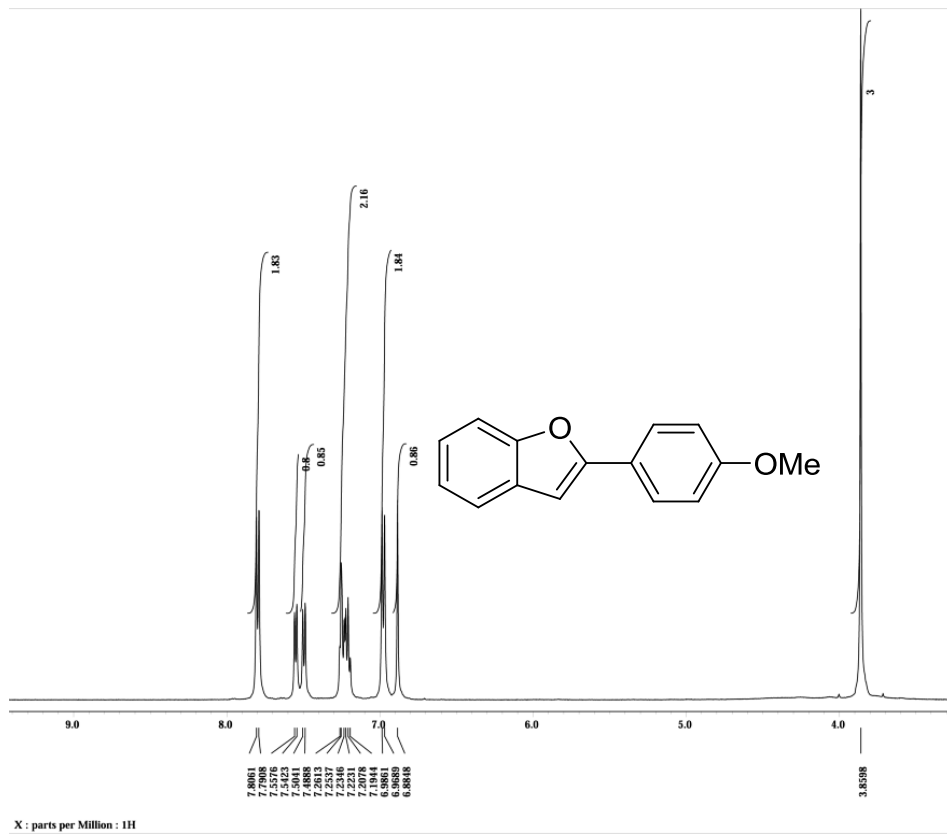
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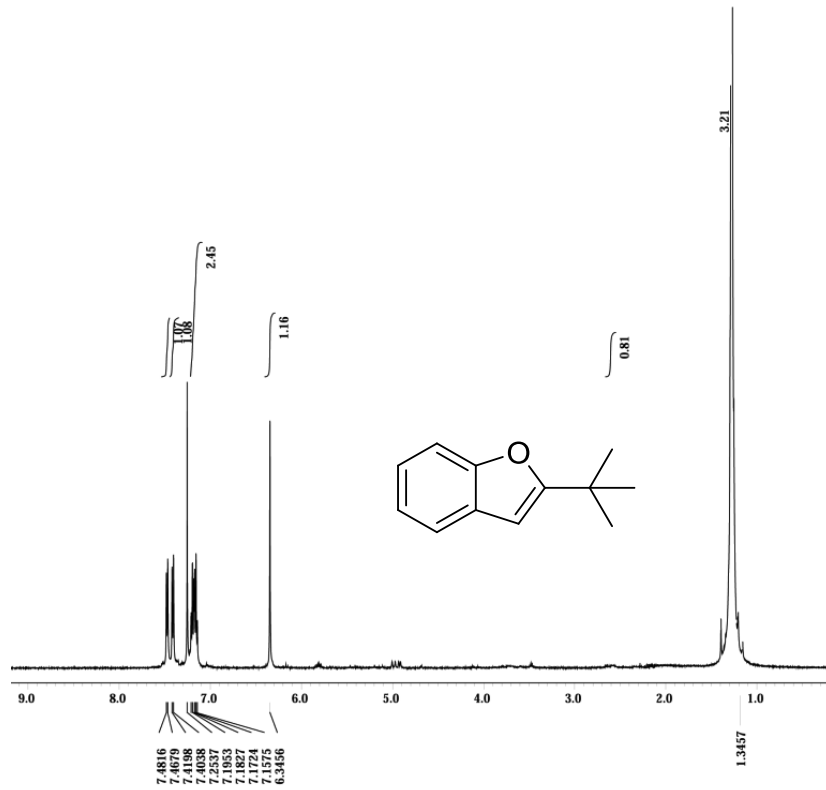


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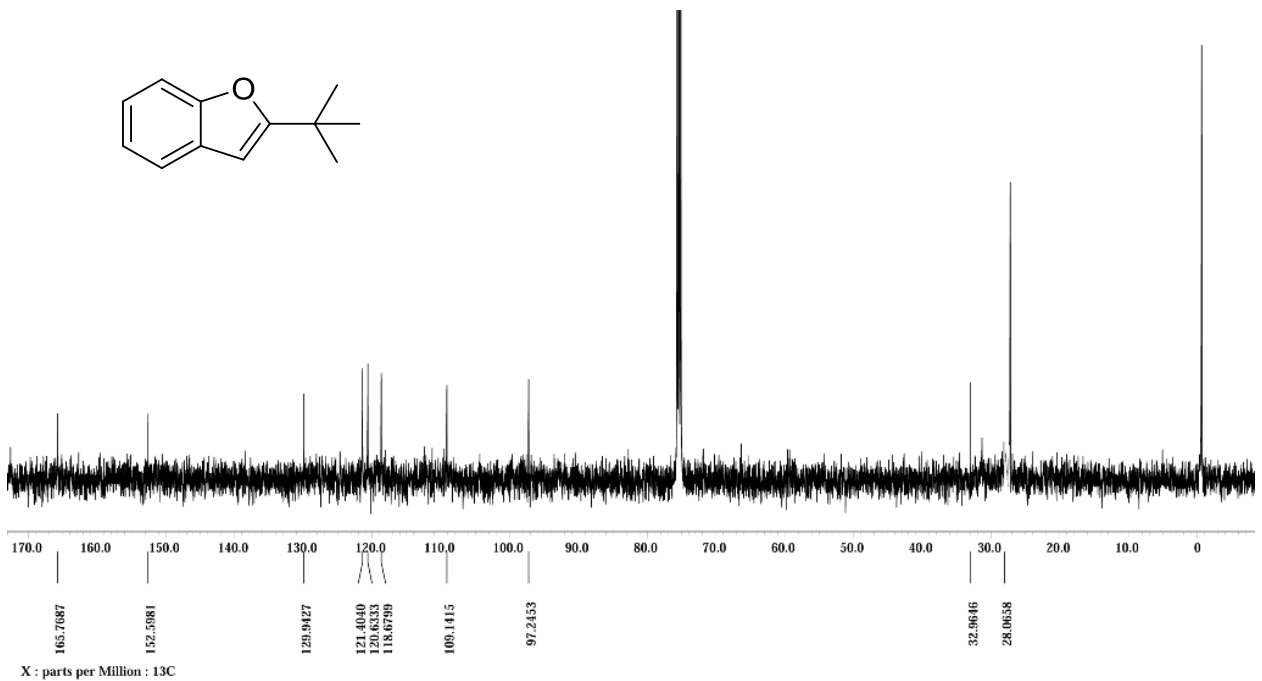


X : parts per Million : 13C





1H



X : parts per Million : 13C

