Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information for

Rigid NON-Donor Pincer Ligand Complexes of Lutetium and Lanthanum: Synthesis and Hydroamination Catalysis

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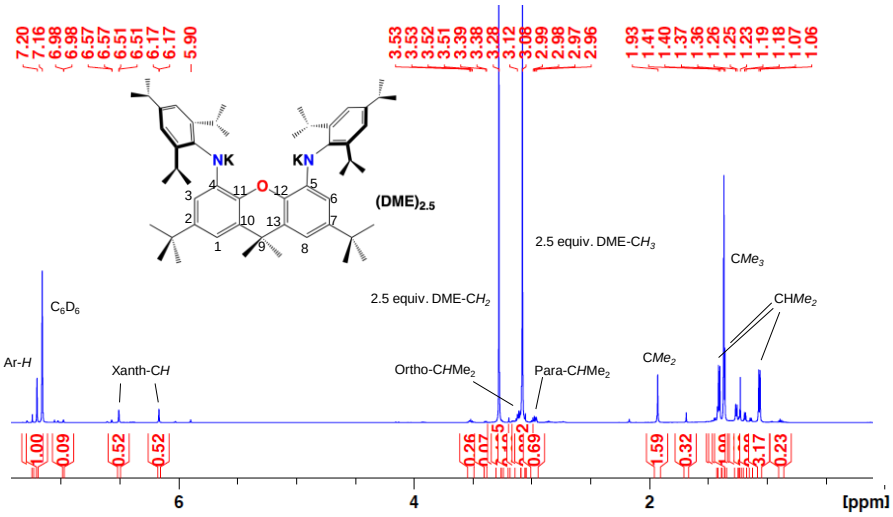


Figure S1 - ^{1}H NMR Spectrum of $[K_2(XN_2)(dme)_{2.5}]$ (600 MHz, C_6D_6)

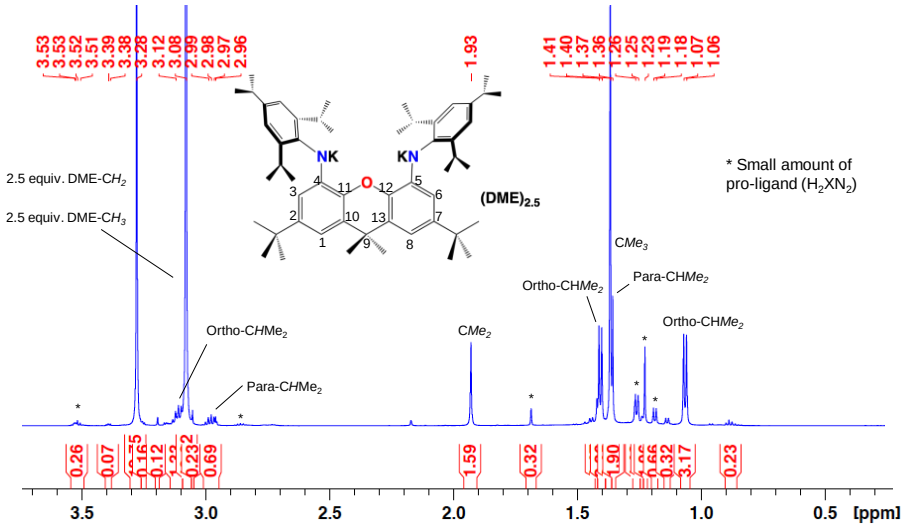


Figure S2 - Expanded Region of the ^{1}H NMR Spectrum of $[K_2(XN_2)(dme)_{2.5}]$ (600 MHz, C_6D_6)

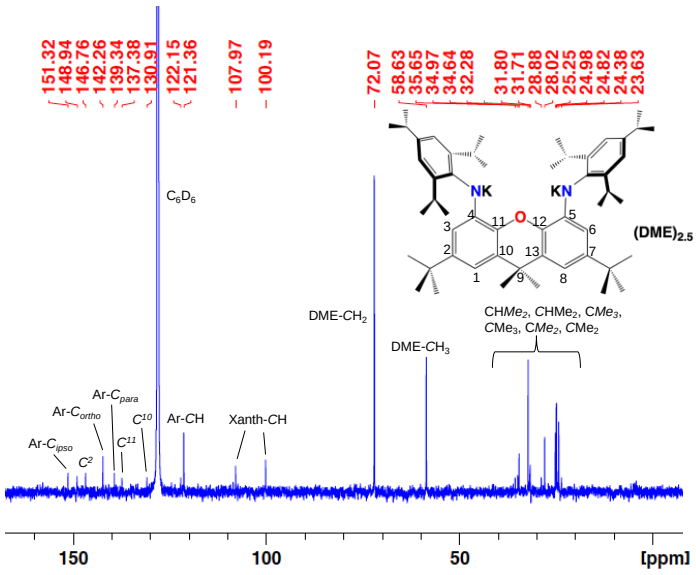


Figure S3 - ^{13}C NMR Spectrum of $[K_2(XN_2)(dme)_{2.5}]$ (126 MHz, C_6D_6)

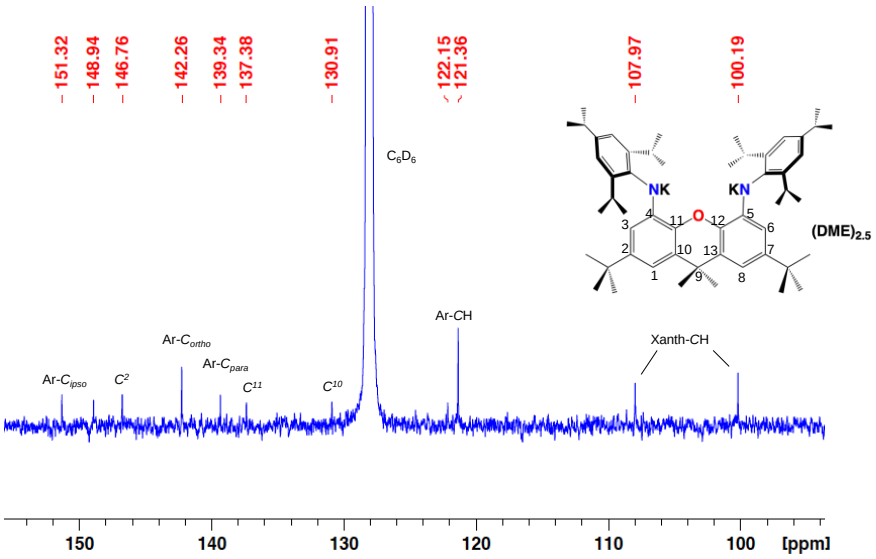


Figure S4 - Expanded Region of the ^{13}C NMR Spectrum of $[K_2(XN_2)(dme)_{2.5}]$ (126 MHz, C_6D_6)

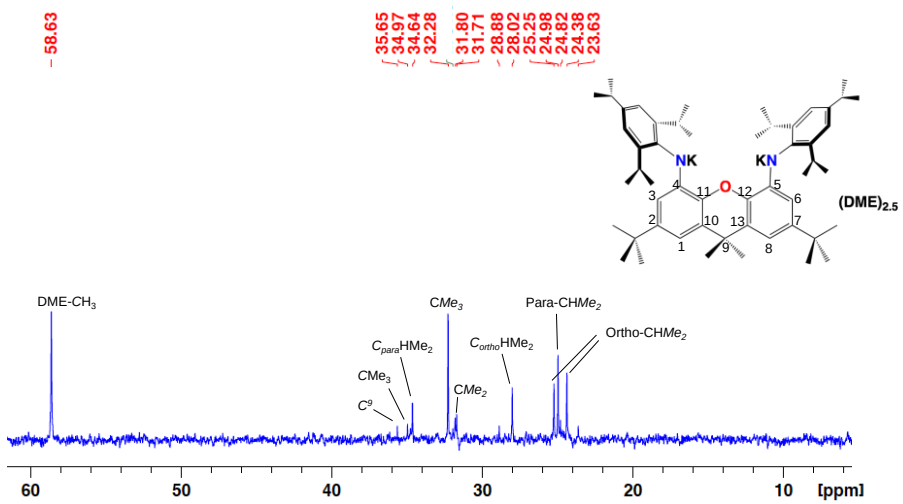


Figure S5 - Expanded Region of the ^{13}C NMR Spectrum of $[K_2(XN_2)(dme)_{2.5}]$ (126 MHz, C_6D_6)

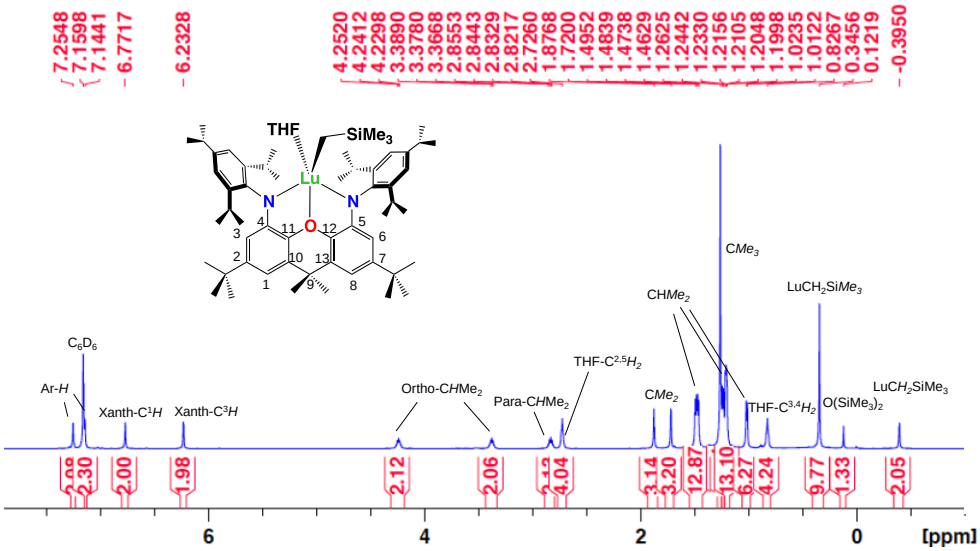


Figure S6 - ^1H NMR Spectrum of $[(XN_2)LuCH_2SiMe_3(THF)]$ (**1**) (600 MHz, C_6D_6)

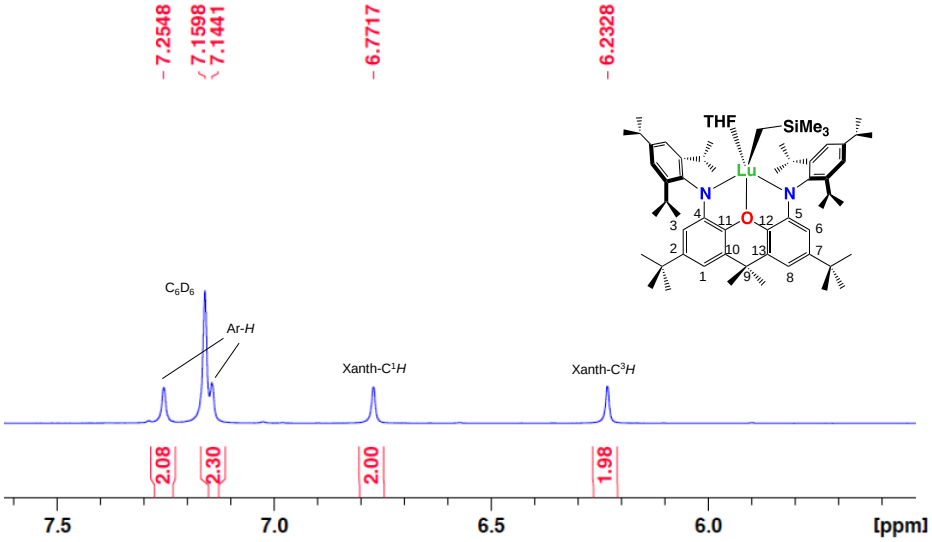


Figure S7 - Expanded Region of the ^{1}H NMR Spectrum of $[(XN_2)LuCH_2SiMe_3(THF)]$ (**1**) (600 MHz, C_6D_6)

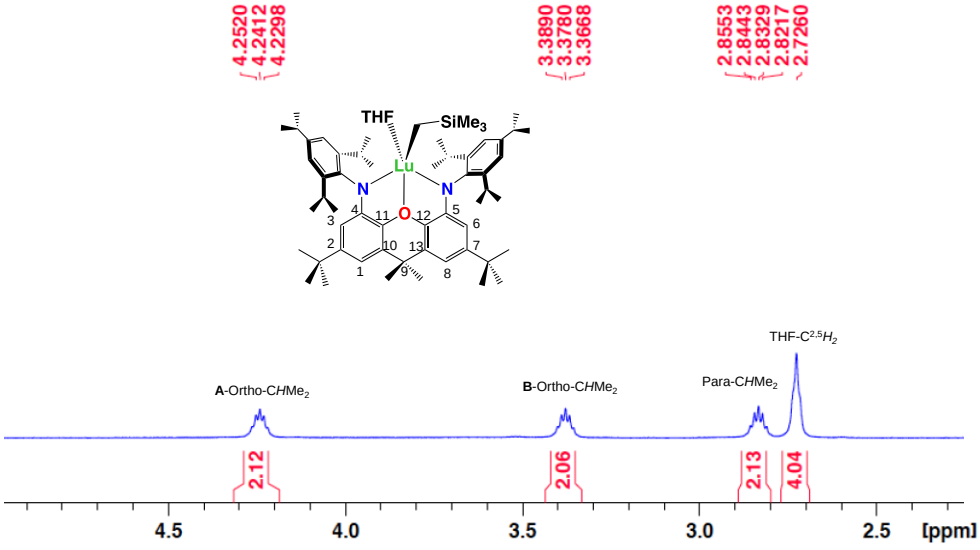


Figure S8 - Expanded Region of the ^{1}H NMR Spectrum of $[(XN_2)LuCH_2SiMe_3(THF)]$ (**1**) (600 MHz, C_6D_6)

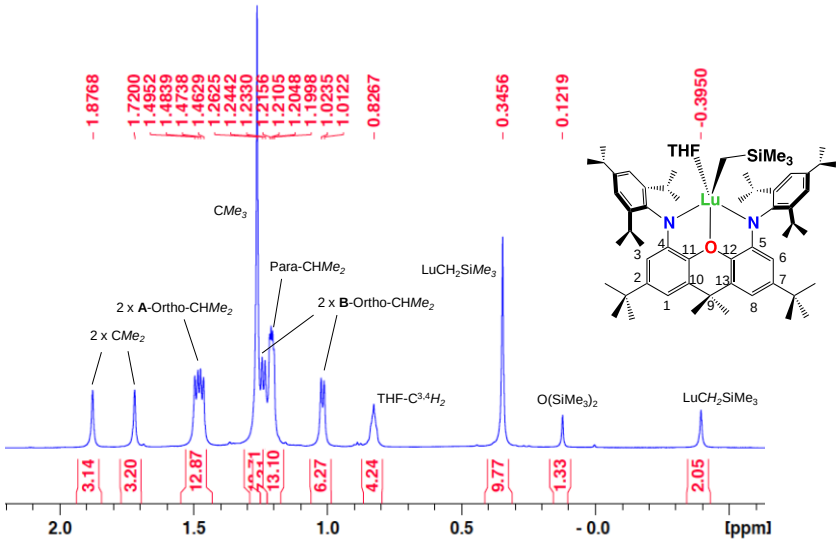


Figure S9 - Expanded Region of the ^{1}H NMR Spectrum of $[(XN_2)LuCH_2SiMe_3(THF)]$ (**1**) (600 MHz, C_6D_6)

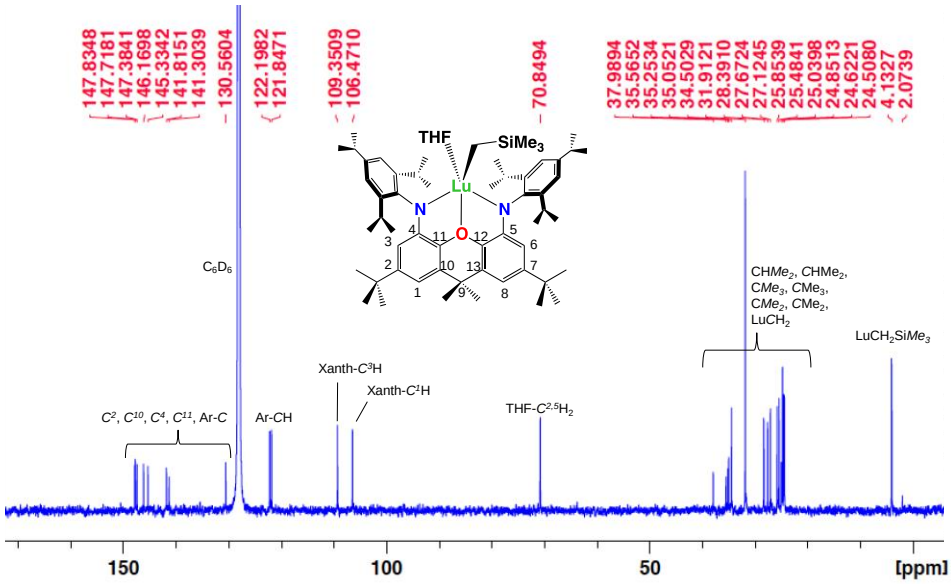


Figure S10 - ^{13}C NMR Spectrum of $[(XN_2)LuCH_2SiMe_3(THF)]$ (**1**) (126 MHz, C_6D_6)

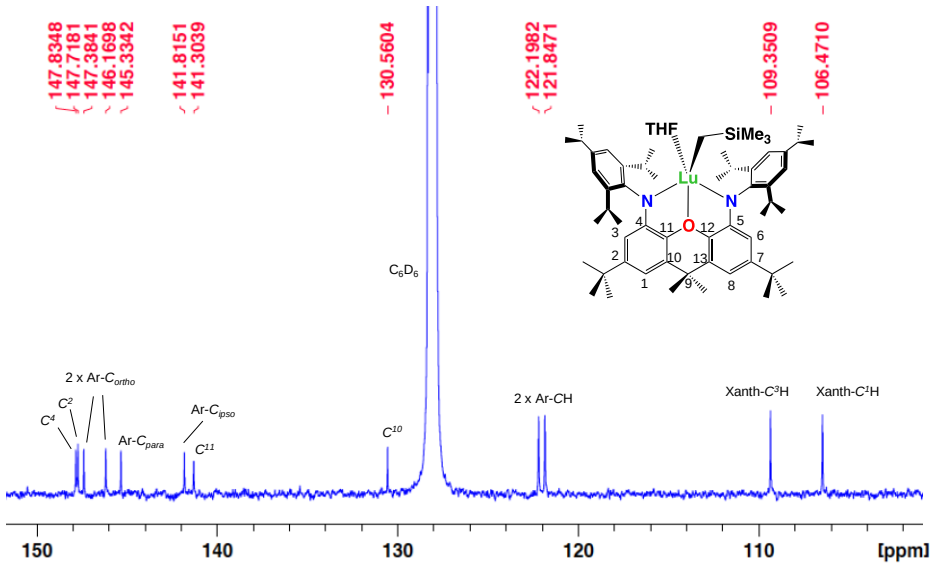


Figure S11 - Expanded Region of the ^{13}C NMR Spectrum of $[(XN_2)LuCH_2SiMe_3(THF)]$ (**1**) (126 MHz, C_6D_6)

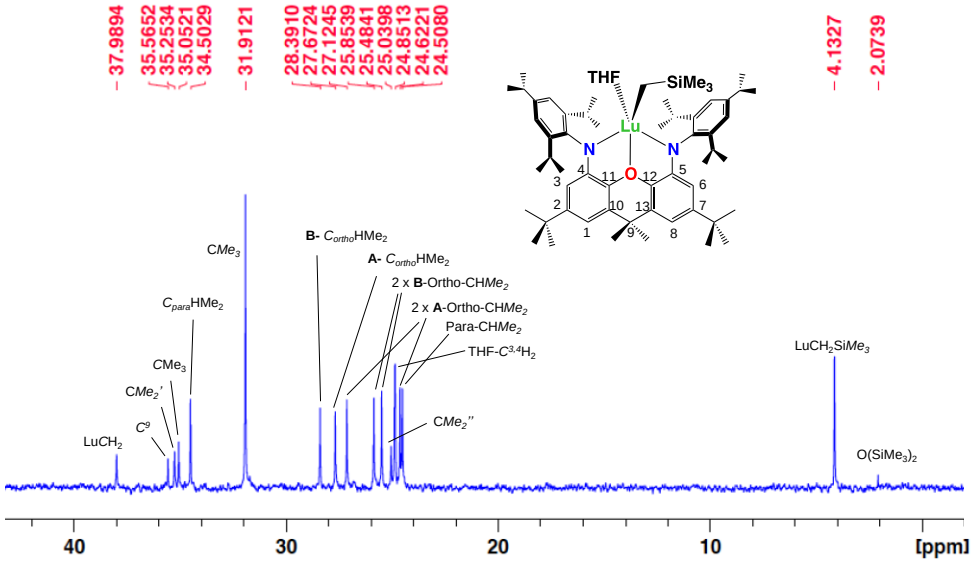


Figure S12 - Expanded Region of the ^{13}C NMR Spectrum of $[(XN_2)LuCH_2SiMe_3(THF)]$ (**1**) (126 MHz, C_6D_6)

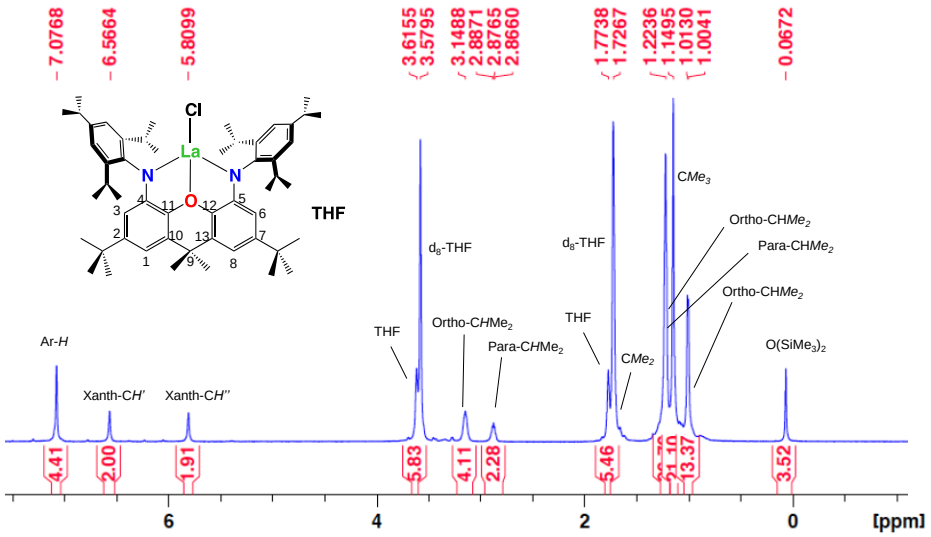


Figure S13 - ^{1}H NMR Spectrum of [{$(XN_2)LaCl(THF)\}_x$] (x = 1 or 2) (**2**) (600 MHz, d_8-THF)

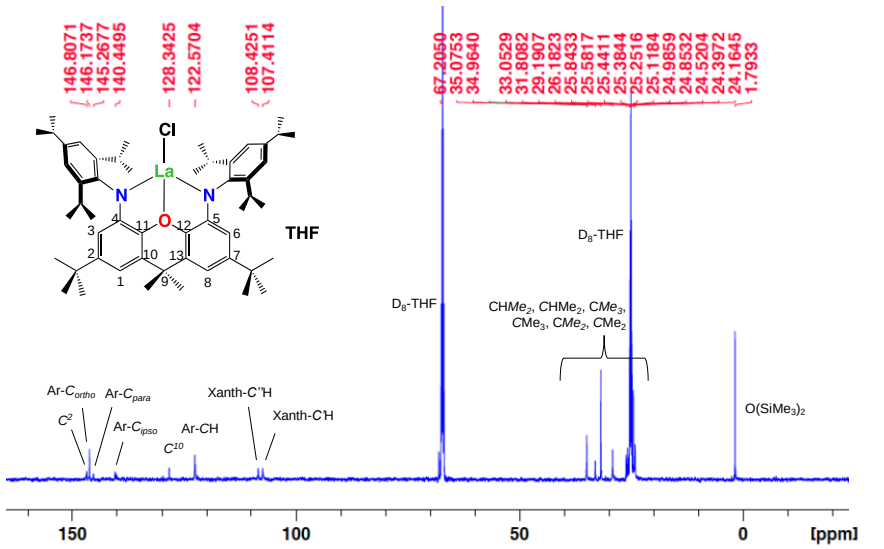


Figure S14 - ^{13}C NMR Spectrum of [{$(XN_2)LaCl(THF)\}_x$] (x = 1 or 2) (**2**) (126 MHz, d_8-THF)

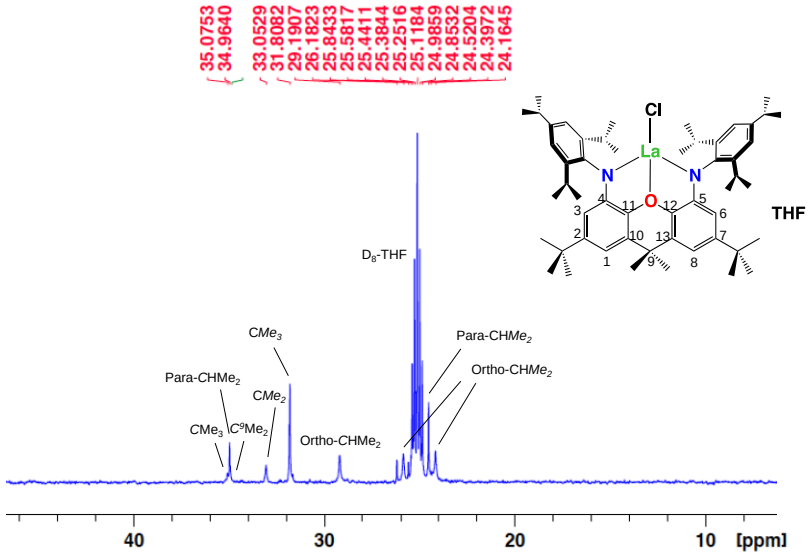


Figure S15 - Expanded Region of the ^{13}C NMR Spectrum of $[\{(XN_2)LaCl(THF)\}_x]$ ($x = 1$ or 2) (**2**) (126 MHz, d_8-THF)

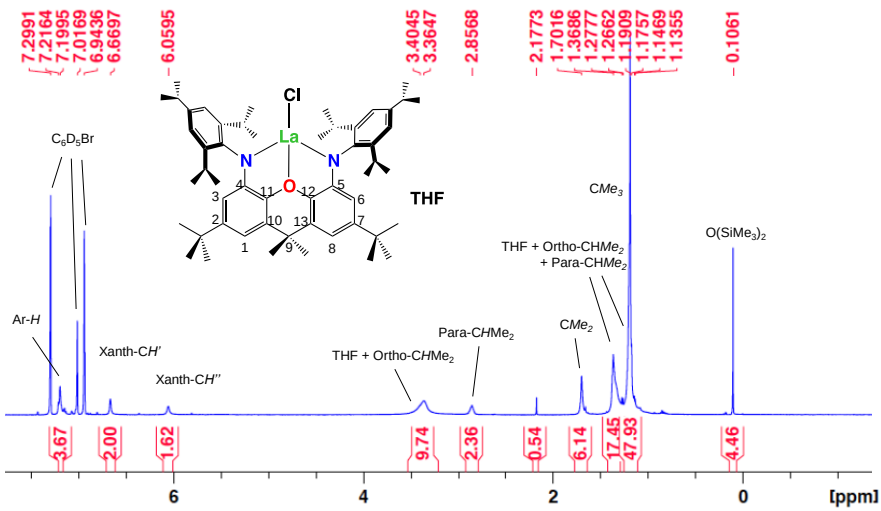


Figure S16 - ^1H NMR Spectrum of $[\{(XN_2)LaCl(THF)\}_x]$ ($x = 1$ or 2) (**2**) (600 MHz, C_6D_5Br)

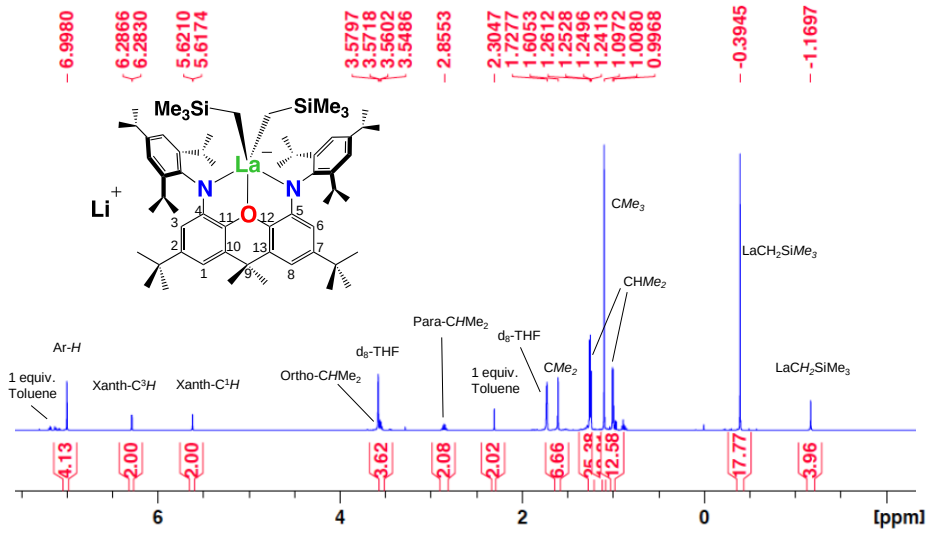


Figure S17 - ^{1}H NMR Spectrum of $[Li(THF)_x]^+[(XN_2)La(CH_2SiMe_3)_2]^-\cdot(Tol)$ **(3)** (600 MHz, d_8-THF)

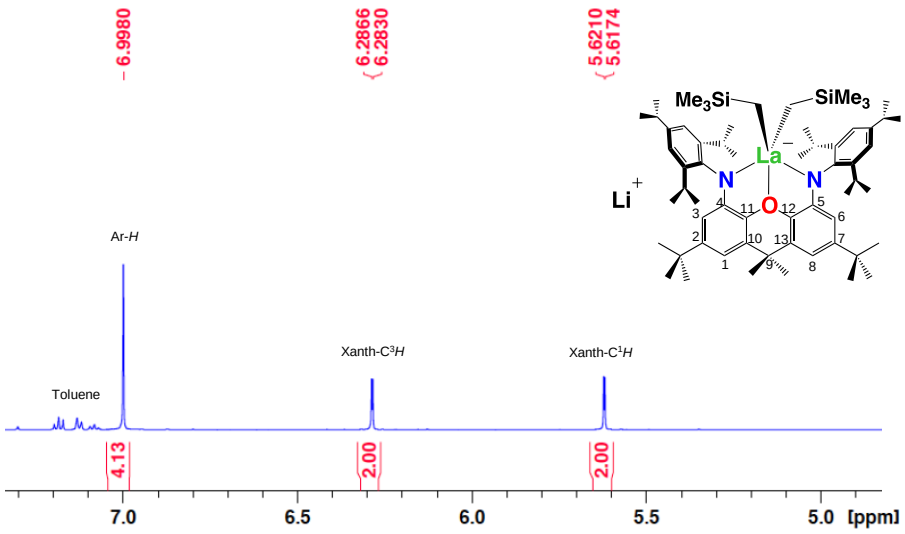


Figure S18 - Expanded Region of the ^{1}H NMR Spectrum of $[Li(THF)_x]^+[(XN_2)La(CH_2SiMe_3)_2]^-\cdot(Tol)$ **(3)** (600 MHz, d_8-THF)

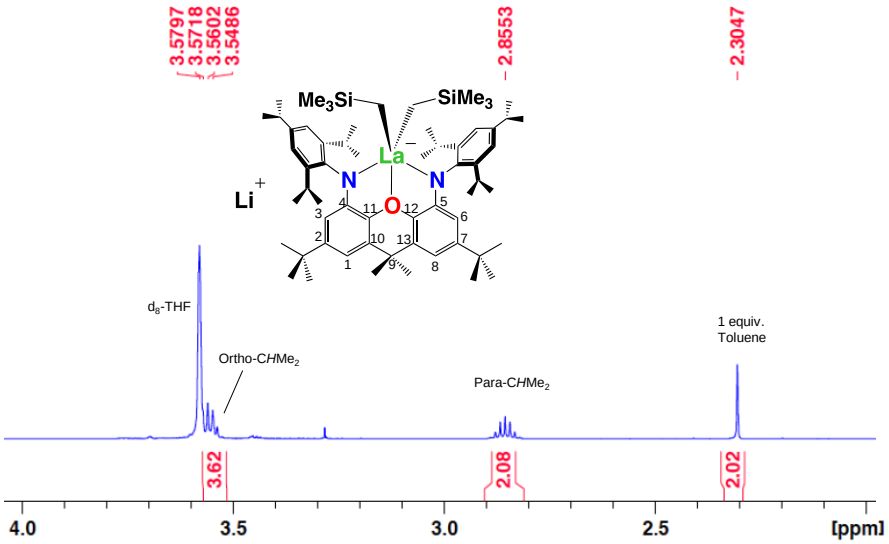


Figure S19 - Expanded Region of the ^{1}H NMR Spectrum of $[Li(THF)_x]^+[(XN_2)La(CH_2SiMe_3)_2]^-\cdot(Tol)$ (**3**) (600 MHz, d_8-THF)

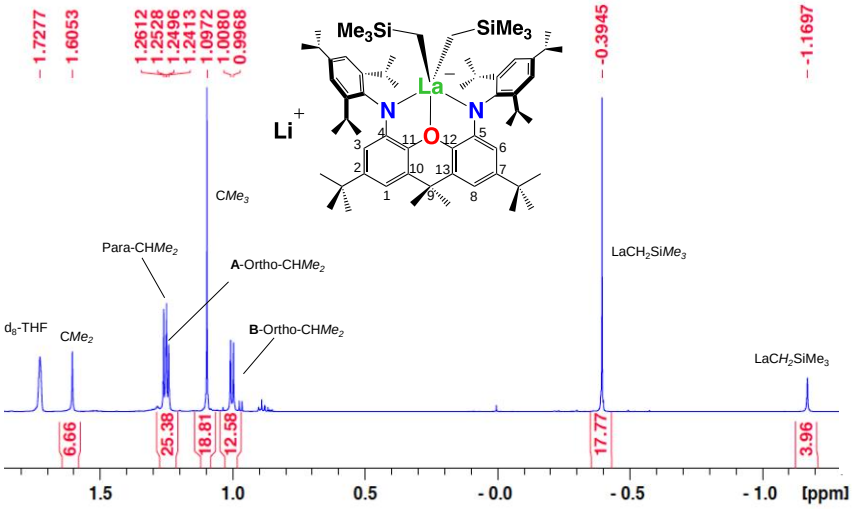


Figure S20 - Expanded Region of the ^{1}H NMR Spectrum of $[Li(THF)_x]^+[(XN_2)La(CH_2SiMe_3)_2]^-\cdot(Tol)$ (**3**) (600 MHz, d_8-THF)

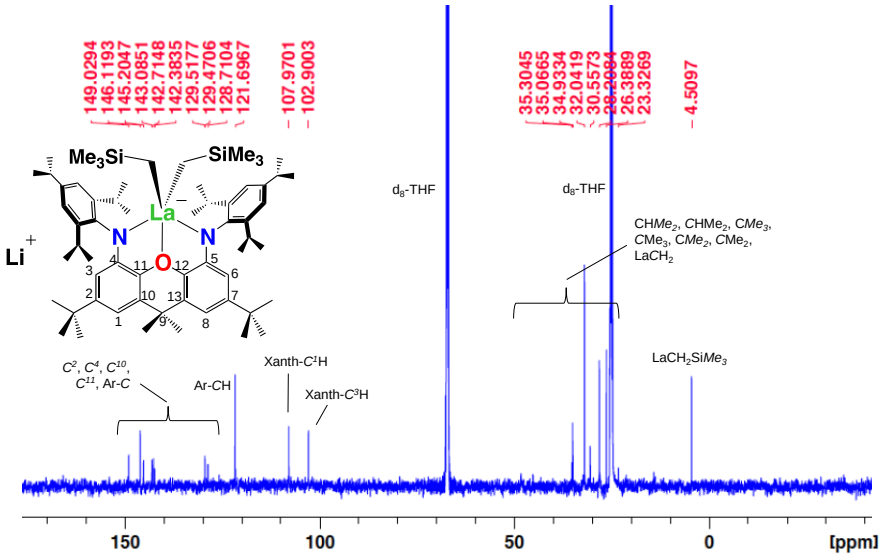


Figure S21 - ^{13}C NMR Spectrum of $[Li(THF)_x]^+[(XN_2)La(CH_2SiMe_3)_2]^-\cdot(Tol)$ **(3)** (600 MHz, d_8-THF)

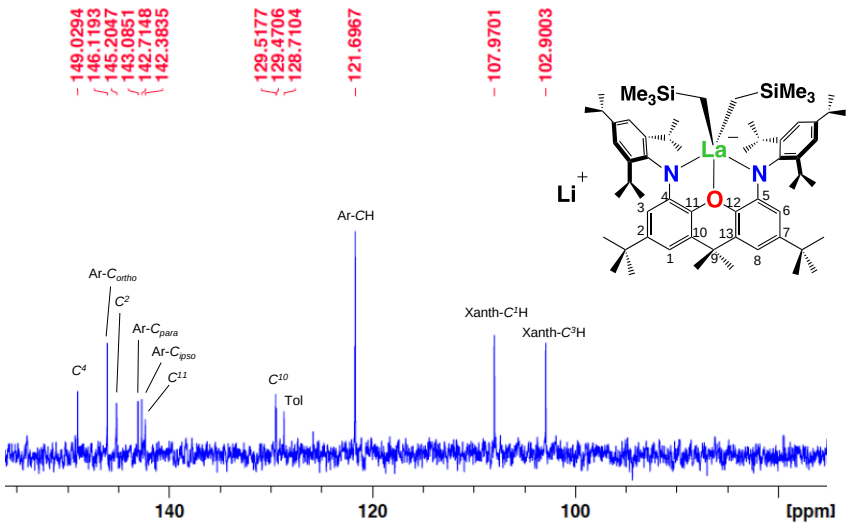


Figure S22 - Expanded Region of the ^{13}C NMR Spectrum of $[Li(THF)_x]^+[(XN_2)La(CH_2SiMe_3)_2]^-\cdot(Tol)$ **(3)** (600 MHz, d_8-THF)

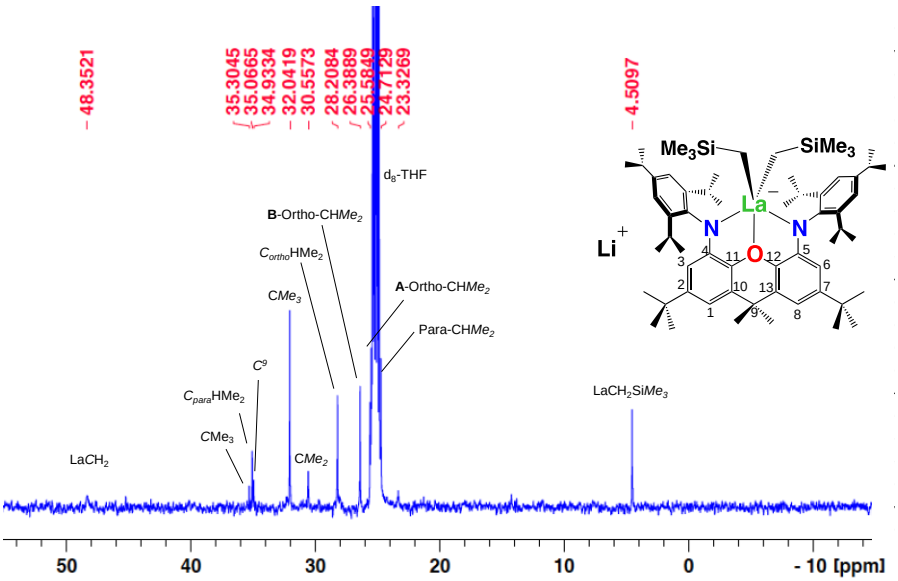


Figure S23 - Expanded Region of the ^{13}C NMR Spectrum of $[Li(THF)_x]^+[(XN_2)La(CH_2SiMe_3)_2]^-\cdot(Tol)$ (**3**) (600 MHz, d_8-THF)

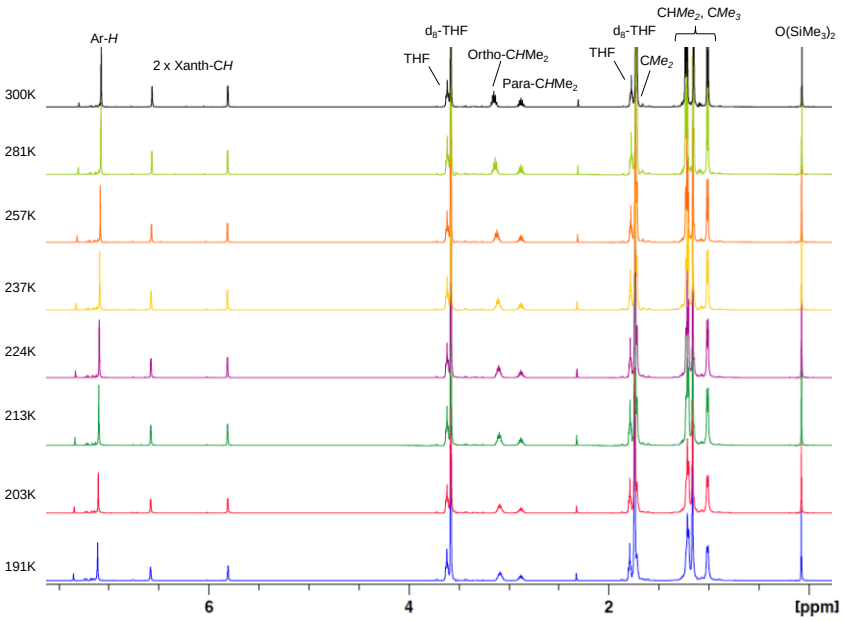


Figure S24 - Variable Temperature ^1H NMR Spectrum of $[\{(XN_2)LaCl(THF)\}_x]$ ($x = 1$ or 2) (**2**) (500 MHz, d_8-THF)

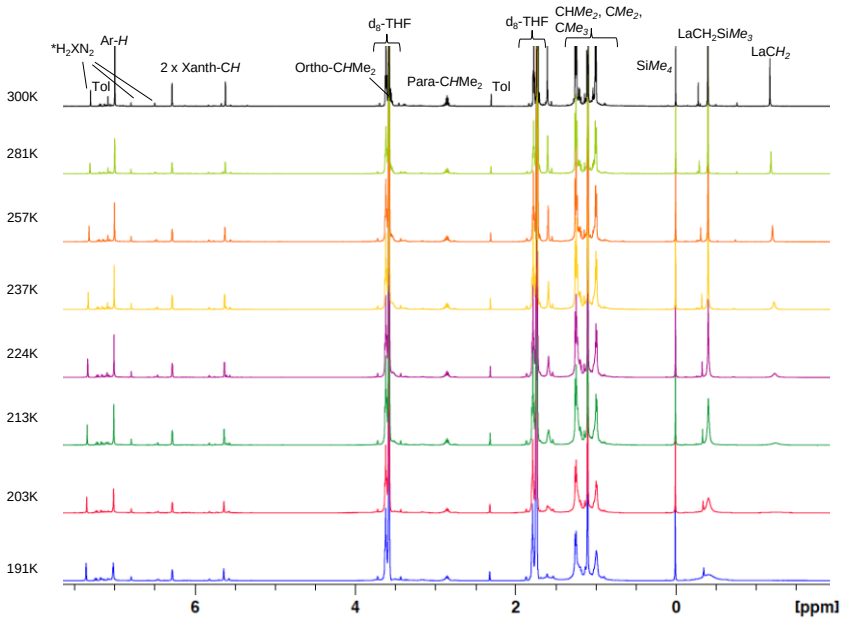


Figure S25 - Variable Temperature ^{1}H NMR Spectrum of $[Li(THF)_3]^+[(XN_2)La(CH_2SiMe_3)_2]^-\cdot(Tol)$ **(3)** (500 MHz, d_8-THF)

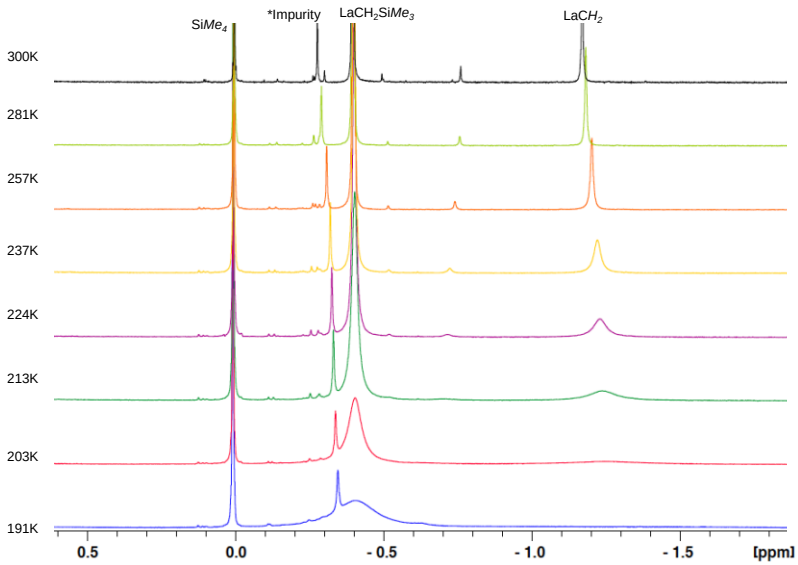


Figure S26 – Expanded Reagion of the Variable Temperature ^{1}H NMR Spectrum of $[Li(THF)_3]^+[(XN_2)La(CH_2SiMe_3)_2]^-\cdot(Tol)$ **(3)** (500 MHz, d_8-THF)

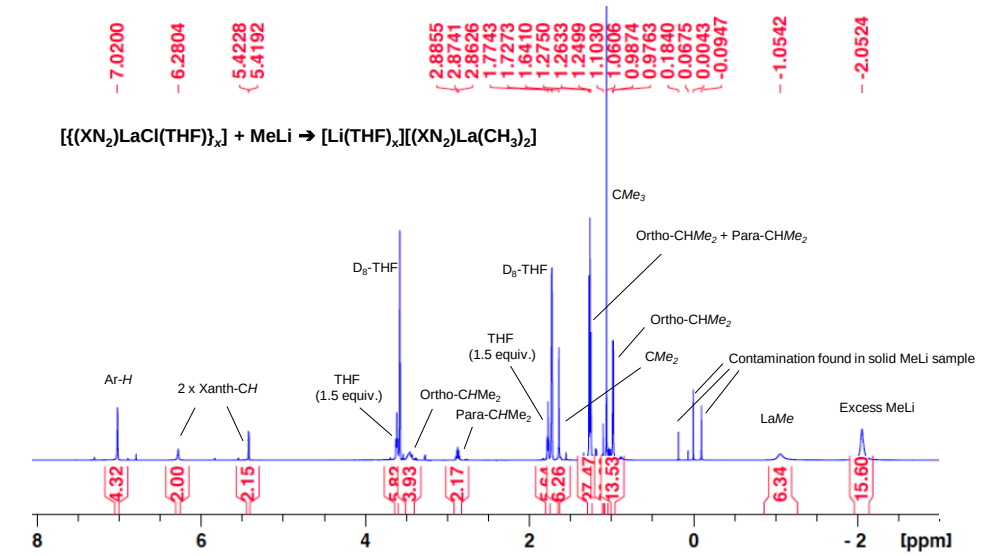


Figure S27 - *In Situ* ^{1}H NMR Spectrum of $[(XN_2)LaCl(THF)_{1.5}]$ (**2**) with excess MeLi after 20 min at 24 °C (600 MHz, d_8-THF)

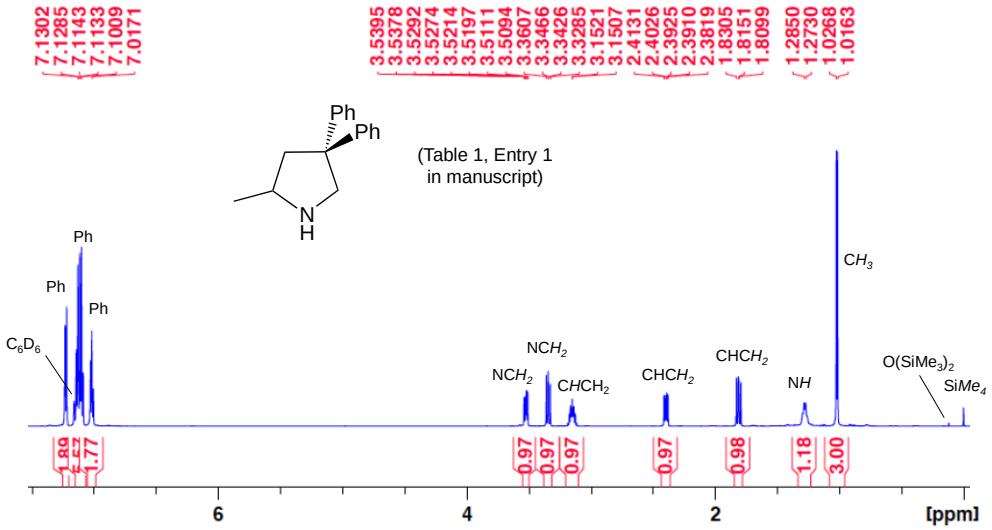


Figure S28 - *In Situ* ^{1}H NMR Spectrum of the Intramolecular Hydroamination of 1 mol % (**1**) with 1-Amino-2,2-diphenylpent-4-ene after ~10 min at 24 °C (600 MHz, C_6D_6)

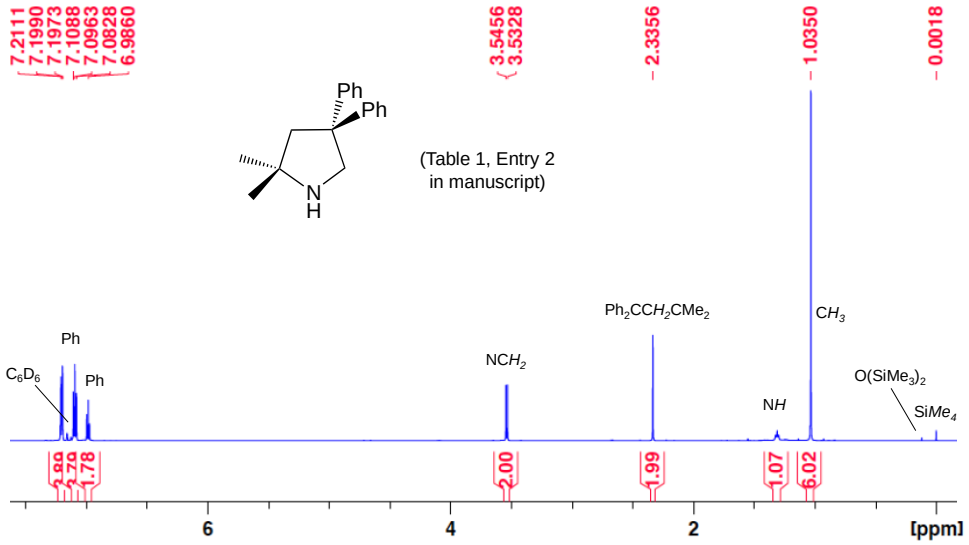


Figure S29 - *In Situ* ^{1}H NMR Spectrum of the Intramolecular Hydroamination of 1 mol % (**1**) with 1-Amino-2,2-diphenyl-4-methylpent-4-ene after ~2.75 h at 24 °C (600 MHz, C_6D_6)

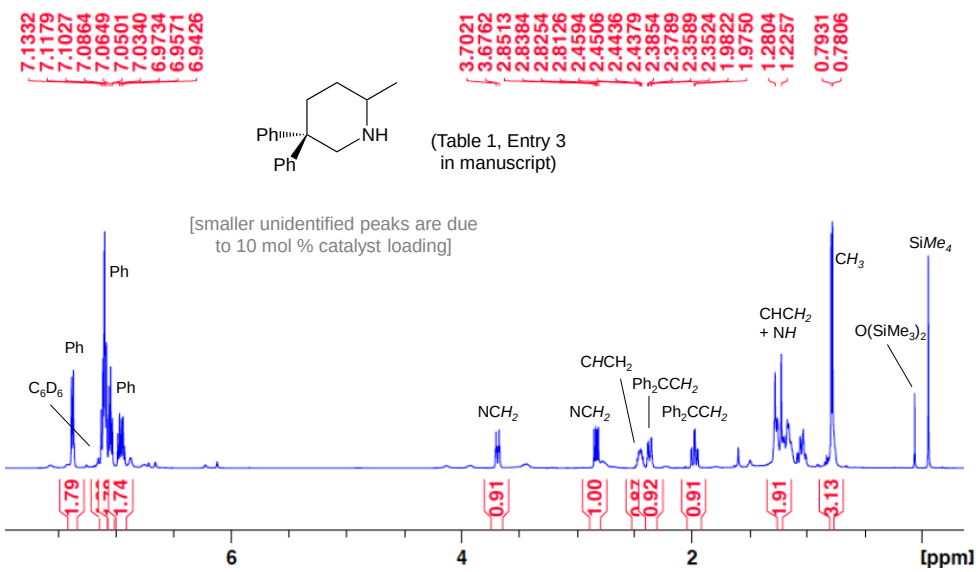


Figure S30 - *In Situ* ^{1}H NMR Spectrum of the Intramolecular Hydroamination of 10 mol % (**1**) with 1-Amino-2,2-diphenylhex-5-ene after ~20 min at 24 °C (600 MHz, C_6D_6)

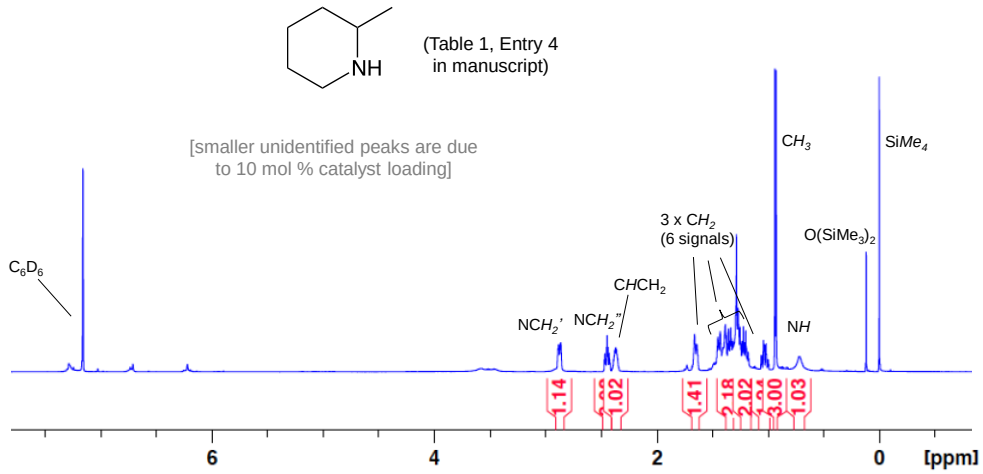


Figure S31 - *In Situ* ^{1}H NMR Spectrum of the Intramolecular Hydroamination of 10 mol % (**1**) with 1-Amino-hexene after ~48 h at 24 °C (600 MHz, C_6D_6)

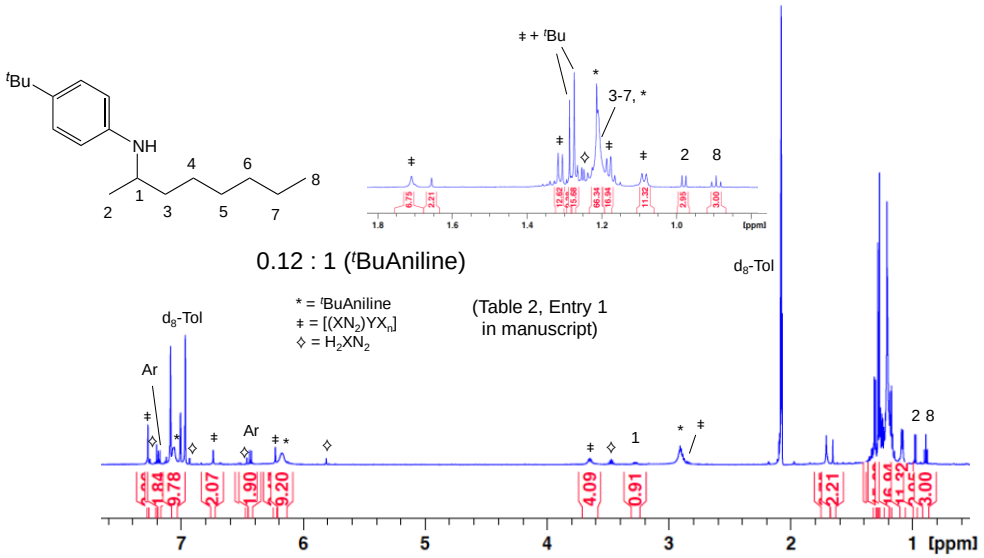


Figure S32 - *In Situ* ^{1}H NMR Spectrum of the *In Situ* Intermolecular Hydroamination of (**1**) with ^{t}BuAniline and 1-octene. Evaporated to dryness *in vacuo* to remove excess 1-octene before NMR (600 MHz, d_8-Tol)

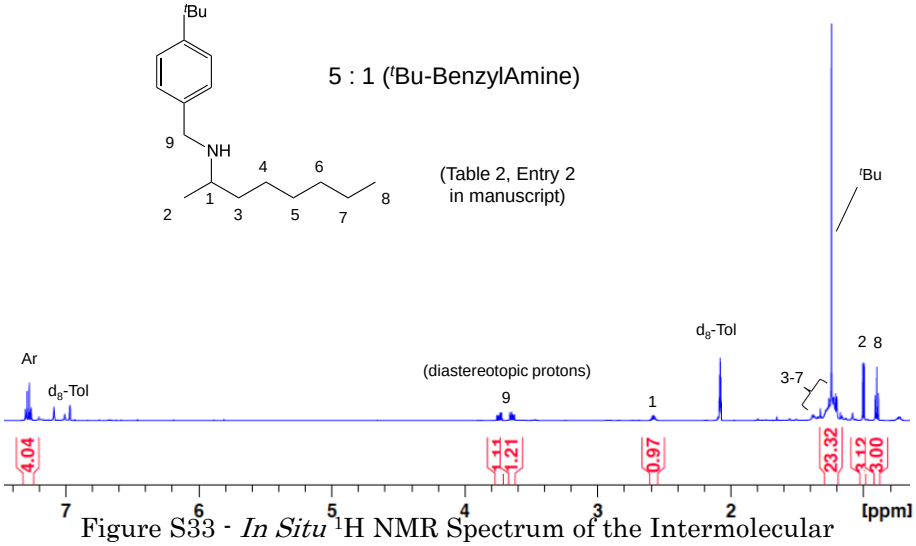


Figure S33 - *In Situ* ^{1}H NMR Spectrum of the Intermolecular Hydroamination of (**1**) with ^{t}Bu-BenzylAmine and 1-octene. Evaporated to dryness *in vacuo* to remove excess 1-octene before NMR (600 MHz, d_8-Tol)

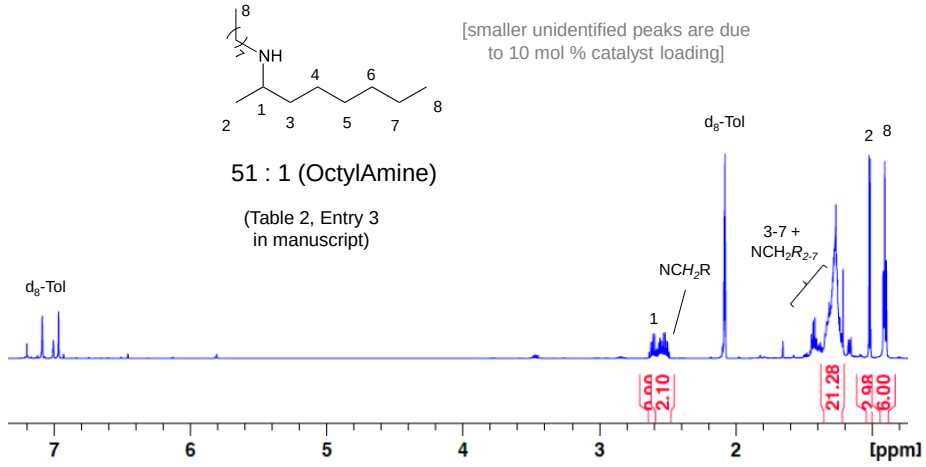


Figure S34 - *In Situ* ^{1}H NMR Spectrum of the Intermolecular Hydroamination of (**1**) with Octyl-Amine and 1-octene. Evaporated to dryness *in vacuo* to remove excess 1-octene before NMR (600 MHz, d_8-Tol)

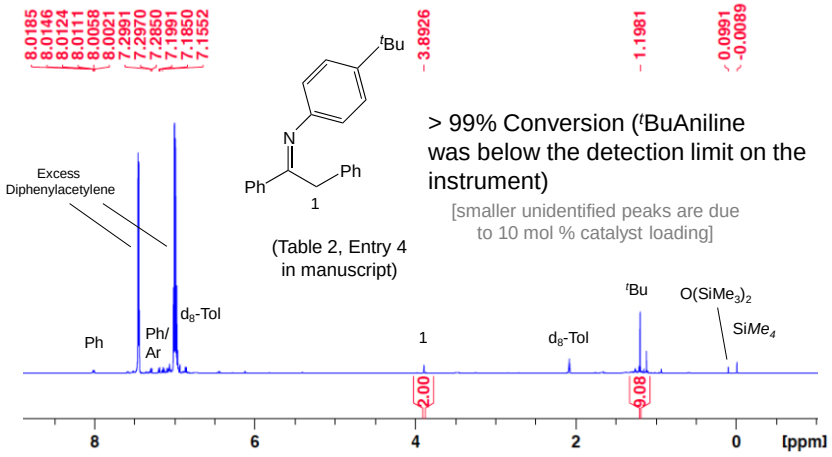


Figure S35 - *In Situ* ^{1}H NMR Spectrum of the Intermolecular Hydroamination of (**1**) with ^{t}Bu-Aniline and Diphenylacetylene (600 MHz, d_8-Tol)

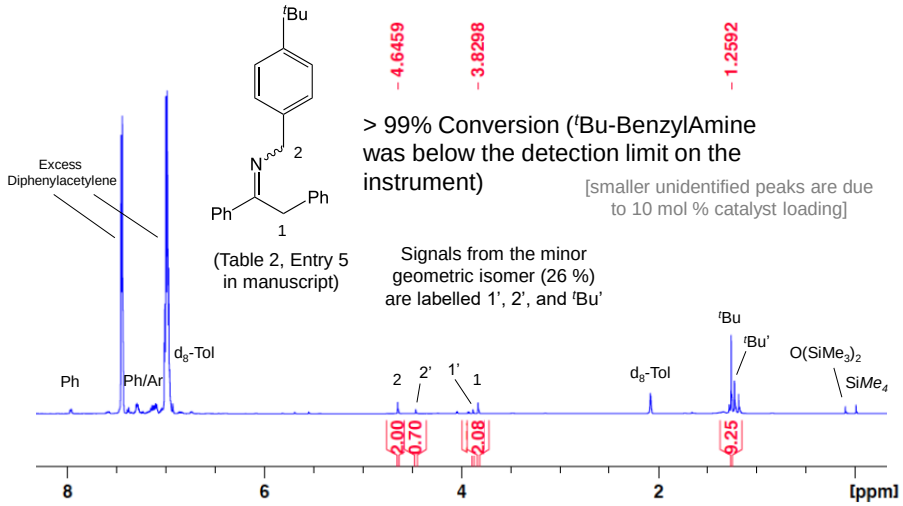


Figure S36 - *In Situ* ^{1}H NMR Spectrum of the Intermolecular Hydroamination of (**1**) with ^{t}Bu-BenzylAmine and Diphenylacetylene (600 MHz, d_8-Tol)

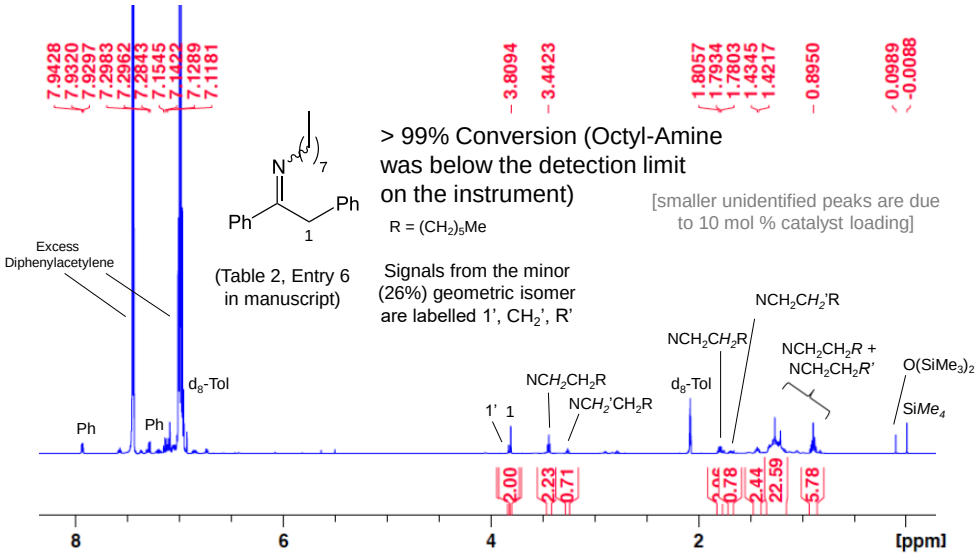


Figure S37 - *In Situ* ^{1}H NMR Spectrum of the Intermolecular Hydroamination of (**1**) with Octyl-Amine and Diphenylacetylene (600 MHz, d_8-Tol)

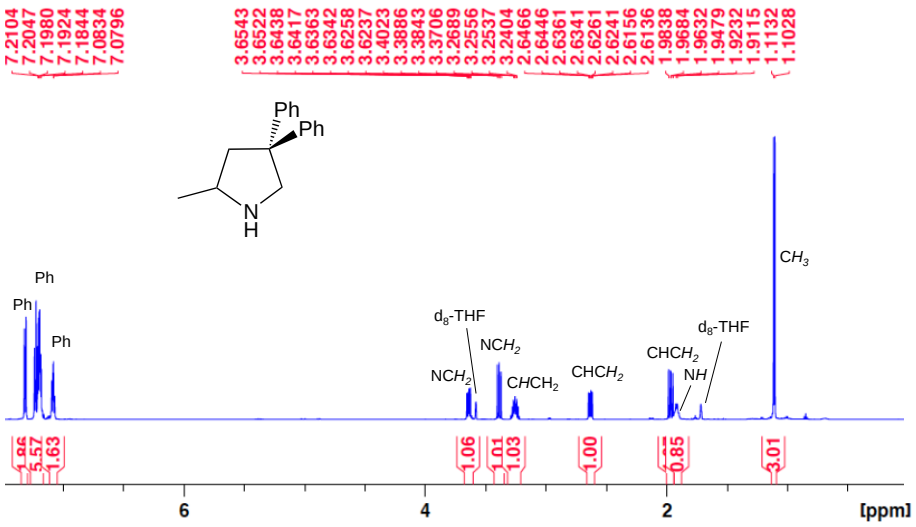


Figure S38 - *In Situ* ^{1}H NMR Spectrum of the Intramolecular Hydroamination of 1 mol % (**3**) with 1-Amino-2,2-diphenylpent-4-ene after ~45 h at 24 °C (600 MHz, d_8-THF)

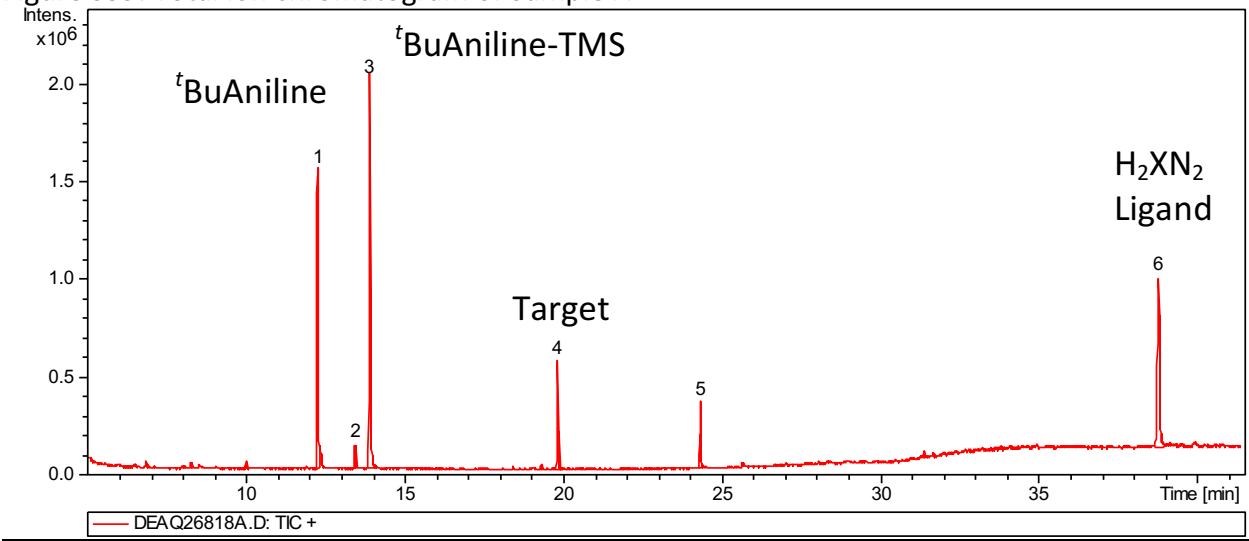
GC-MS Data for Intermolecular Hydroamination Reactions

Note: MSTFA (N-methyl-N-(trimethylsilyl)trifluoroacetamide) is a common derivatizing reagent and was used for the following GC-MS studies. It will silylate OH, COOH, NH_2 groups by replacing one or two hydrogen atoms with a trimethylsilyl, (TMS / $Si(CH_3)_3$) group, to make it less polar and therefore more amendable for GC separation. This is particular important for the starting reagents as they would not otherwise be detected using the chosen GC column without derivatization. The product of the reaction between octylamine and 1-octene was partially derivatized, while all other products did not get derivatized in the process (possibly the result of steric hinderance).
Anthrancenemethanol was used as a quality control to check if the derivatization did occur since both its underivatized and derivatized form can be detected with GC-MS.

Mass Spec. Results for the reaction of 10 mol % of 1 with ^{t}BuAniline and 1-octene after 24 h at 110 °C (Table 2, Entry 1 in Manuscript)

Sample A was diluted 10 fold in toluene and then derivatized 1:4 with MSTFA. Sample B was used to determine the selectivity for Markovnikov product formation and was pumped down prior to obtaining the ^{1}H NMR spectra and submitting for GC-MS. Sample B was diluted 10 fold in toluene, and then derivatized 1:1 with MSTFA. Samples were analyzed with Agilent GCMS on DB-5MS column after an one hour incubation at 60 °C.

Figure S39: Total ion chromatogram of Sample A



#	RT [min]	Area	
1	12.3	4112569	MW 149
2	13.5	230584	
3	13.9	5586487	MW 149-TMS
4	19.8	1204724	MW 261 (Target)
5	24.3	702492	
6	38.7	4200216	H_2XN_2 proligand

Figure S40: Mass spectra for compound 4 (target) in the TIC
m/z 246 (-CH_3), m/z 176 (-C_6H_{13})

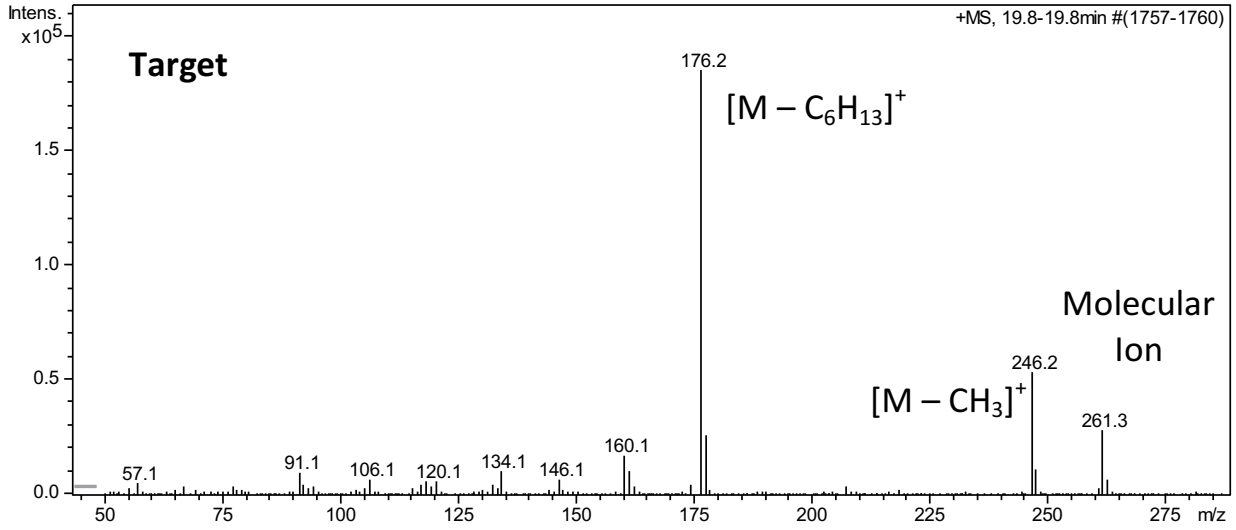
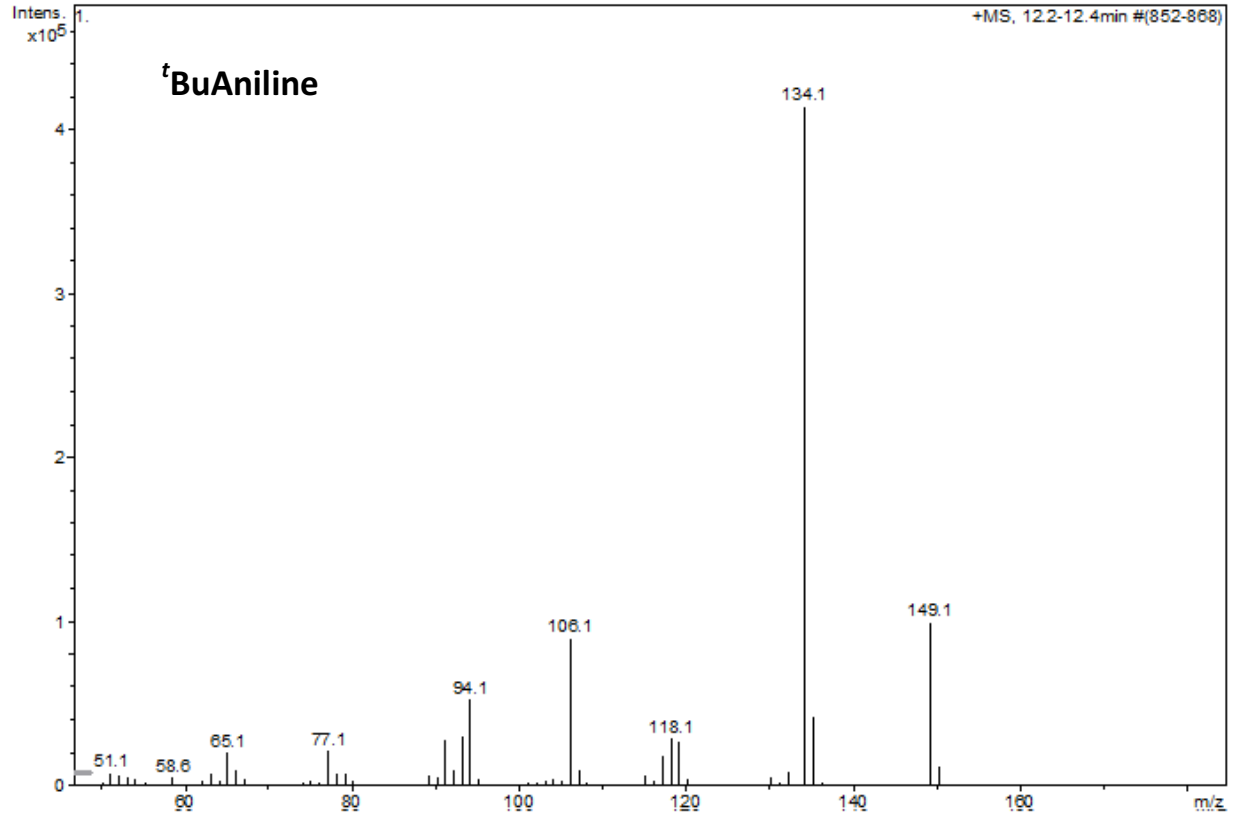


Figure S41: Mass spectra for compound 1 in the TIC and library mass spectra



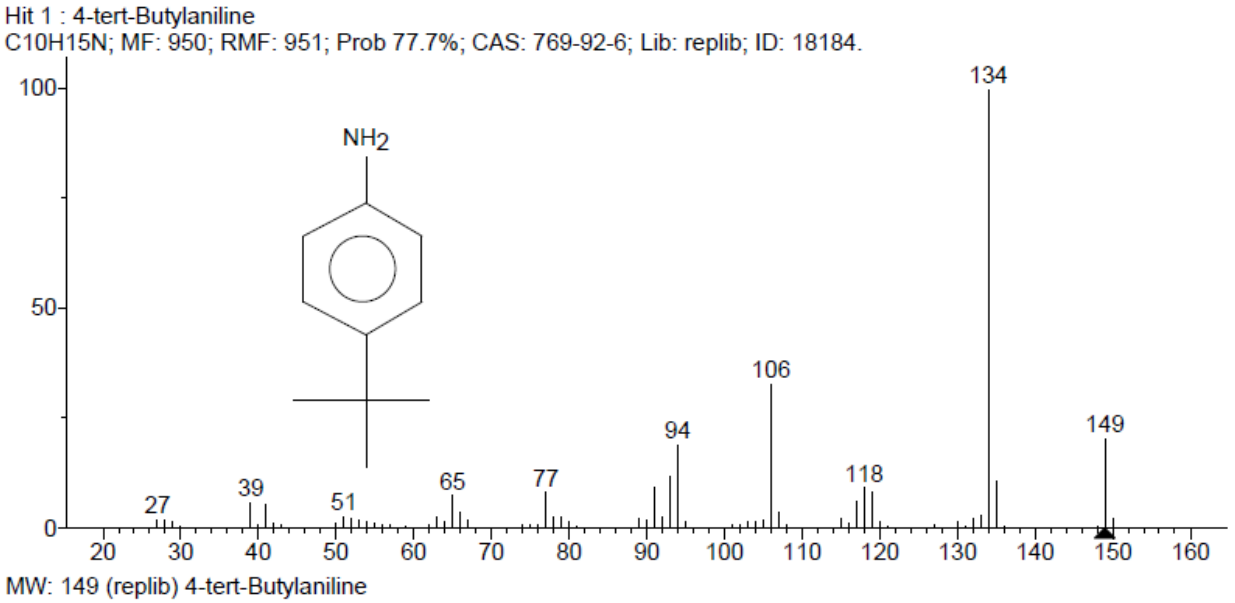


Figure S42: Mass spectra for compound 2 in the TIC

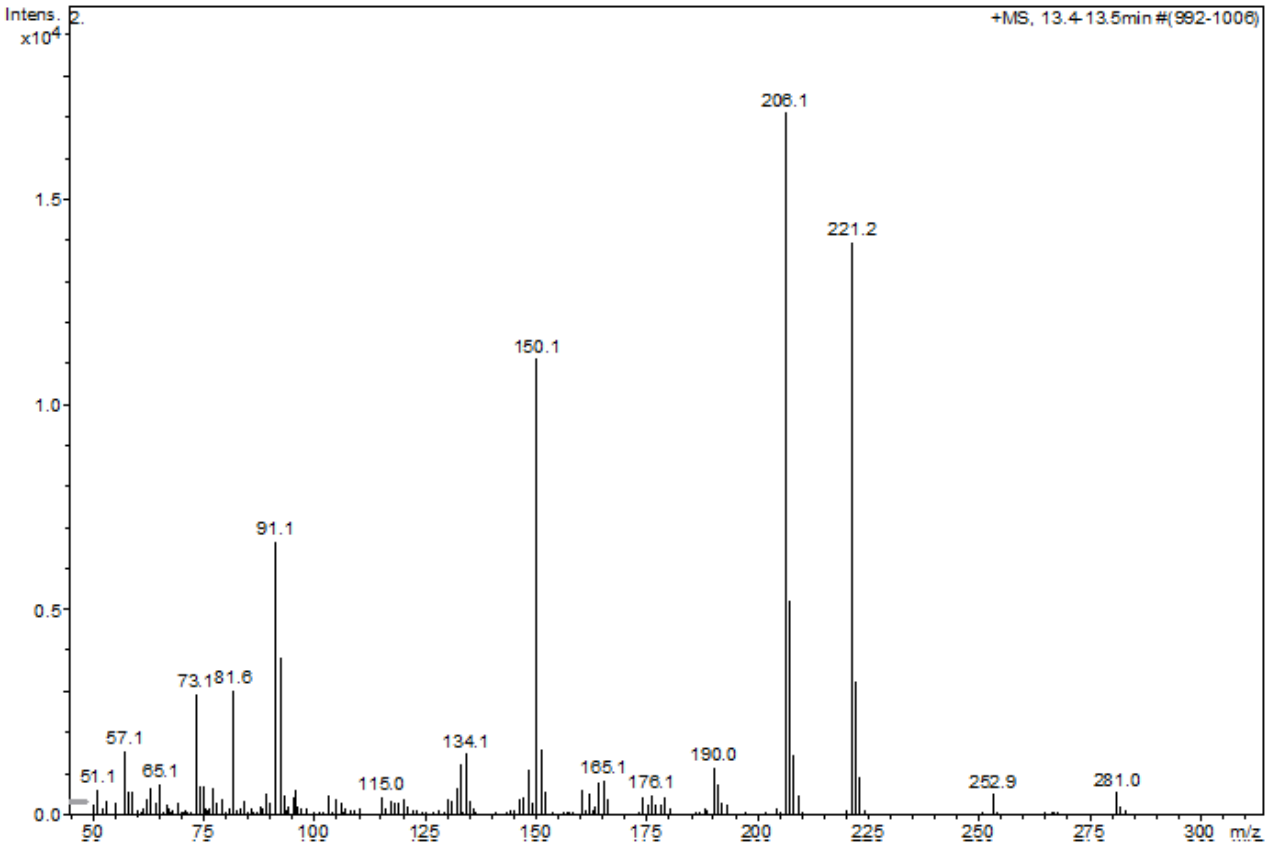


Figure S43: Mass spectra for compound 3 (MW 149-TMS) in the TIC

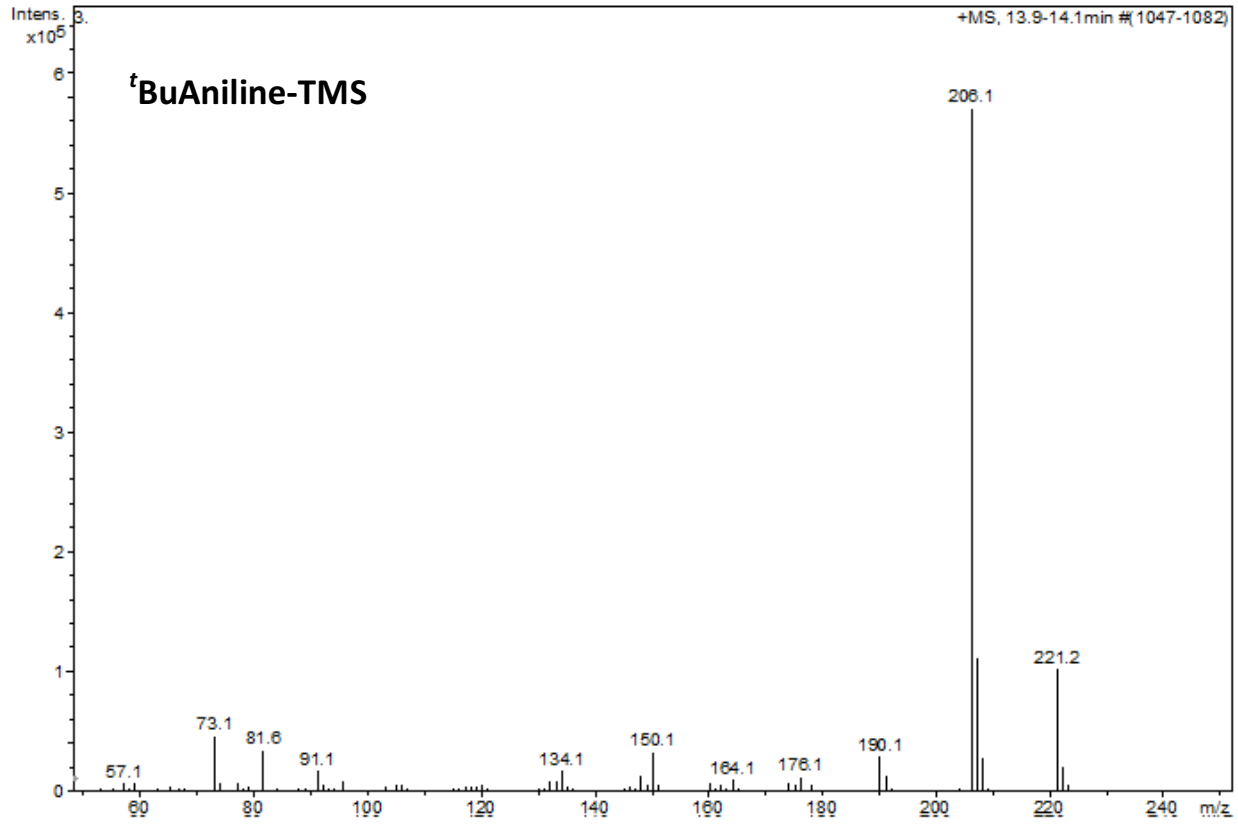


Figure S44: Mass spectra for compound 5 in the TIC

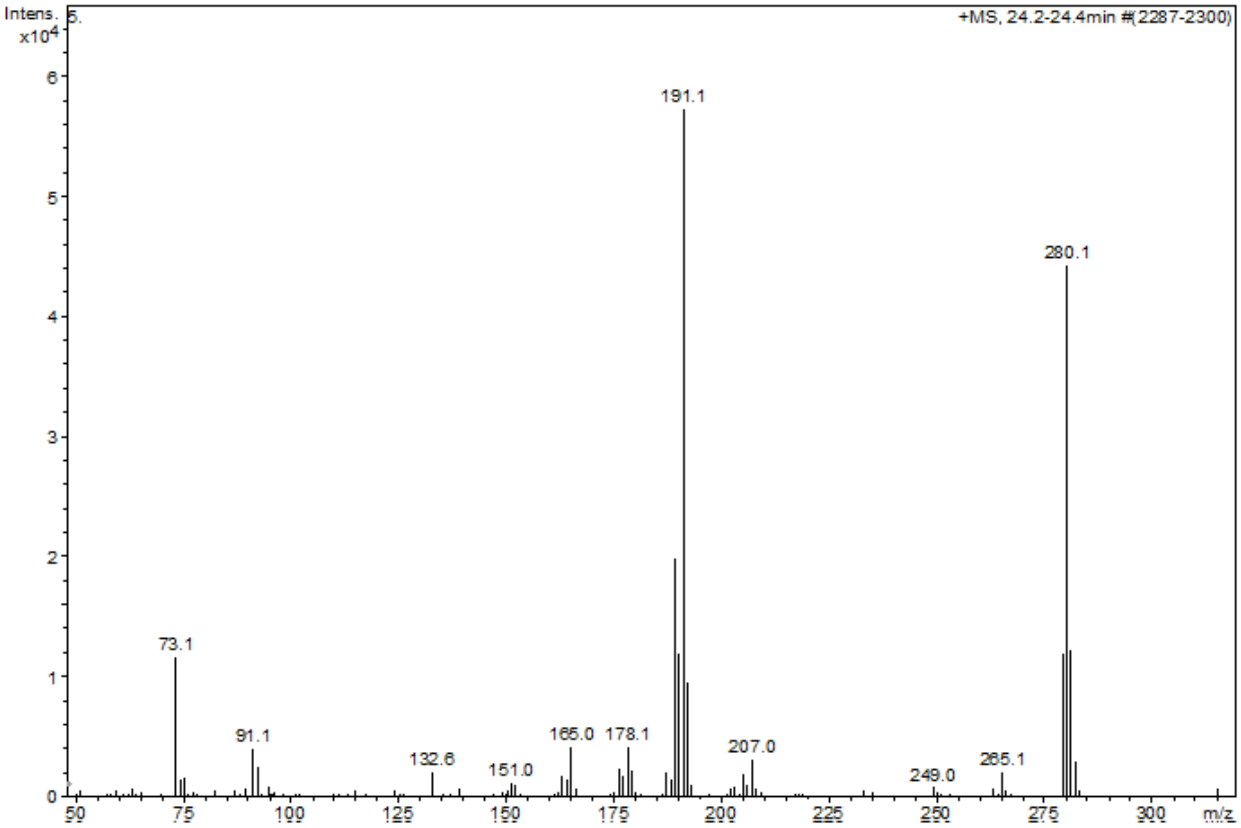


Figure S45: Mass spectra for compound 6 (H_2XN_2 proligand) in the TIC

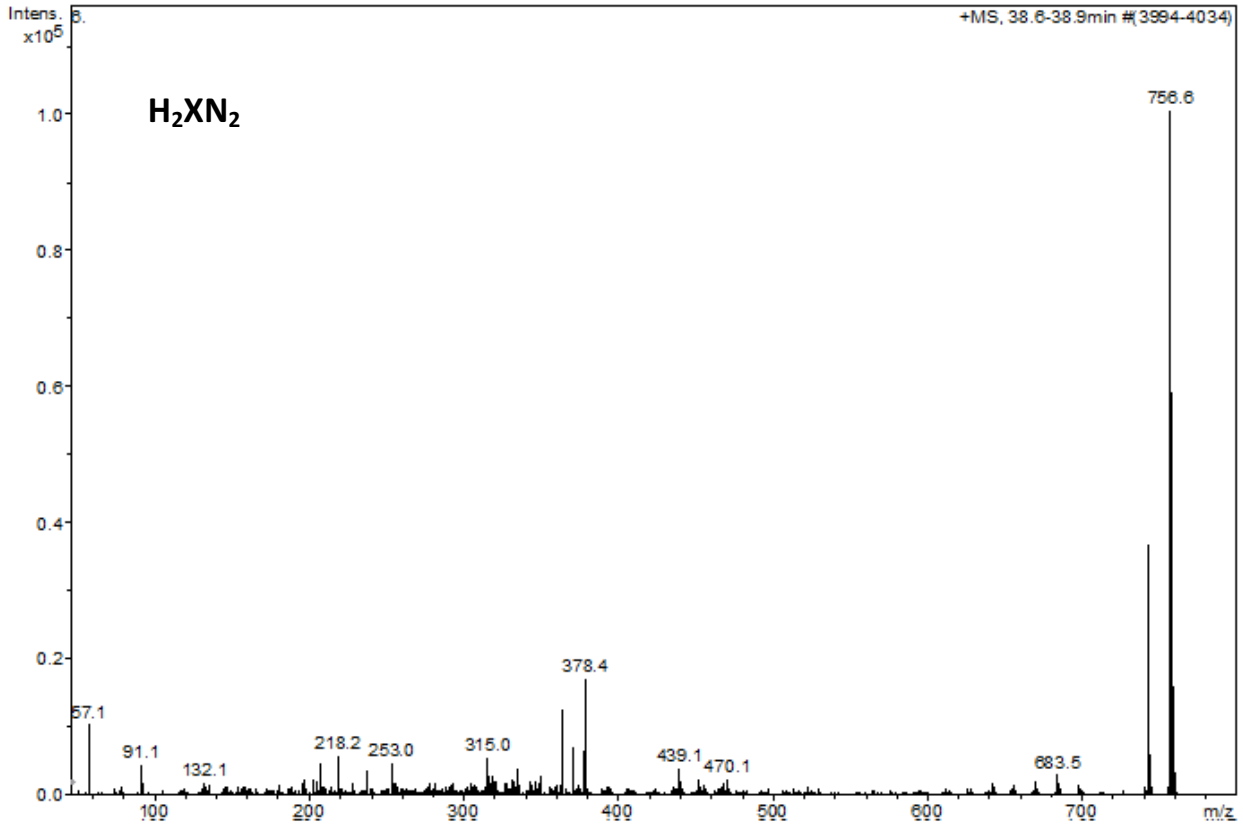
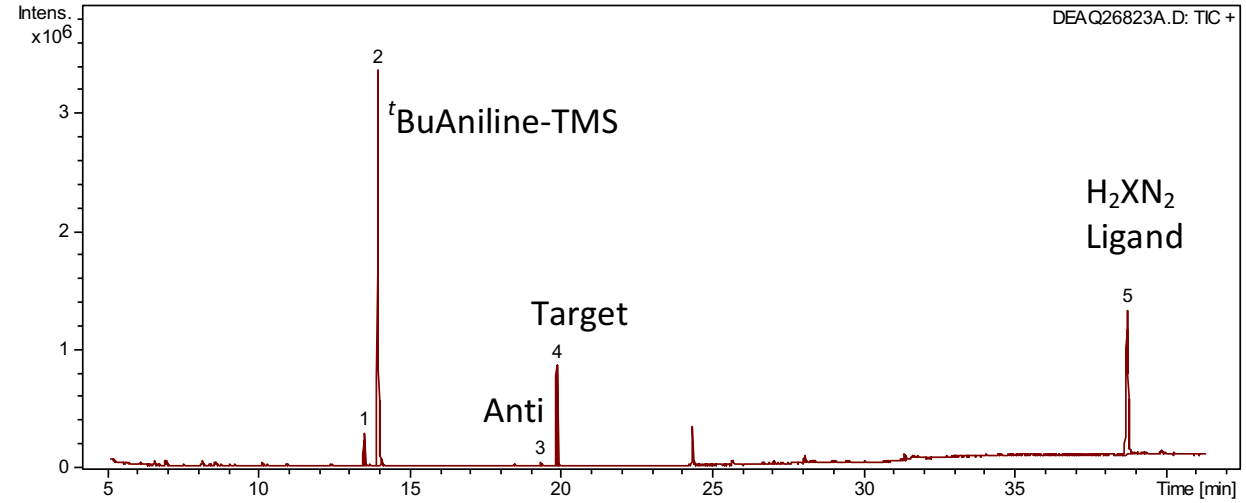


Figure S46: Total ion chromatogram of Sample B



#	RT [min]	Area	
1	13.5	486724	
2	13.9	8855853	^{t}BuAniline-TMS
3	19.3	61945	Anti
4	19.8	1741581	Target
5	38.7	5963258	H_2XN_2 proligand

Figure S47: Mass spectra for compound 3 (Anti) in the TIC for sample B

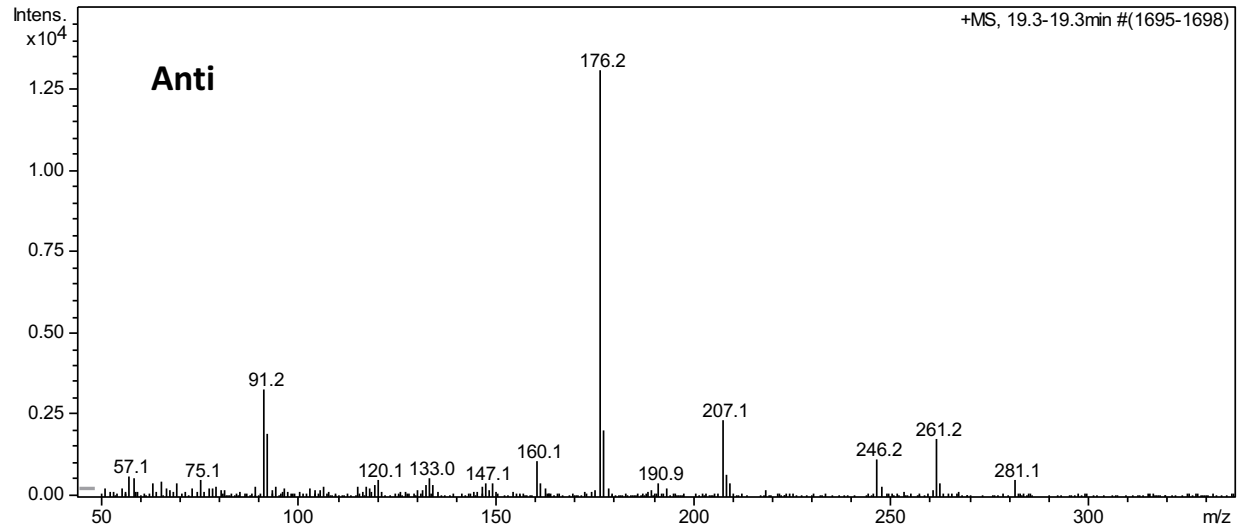


Figure S48: Mass spectra for compound 4 (Target) in the TIC for sample B

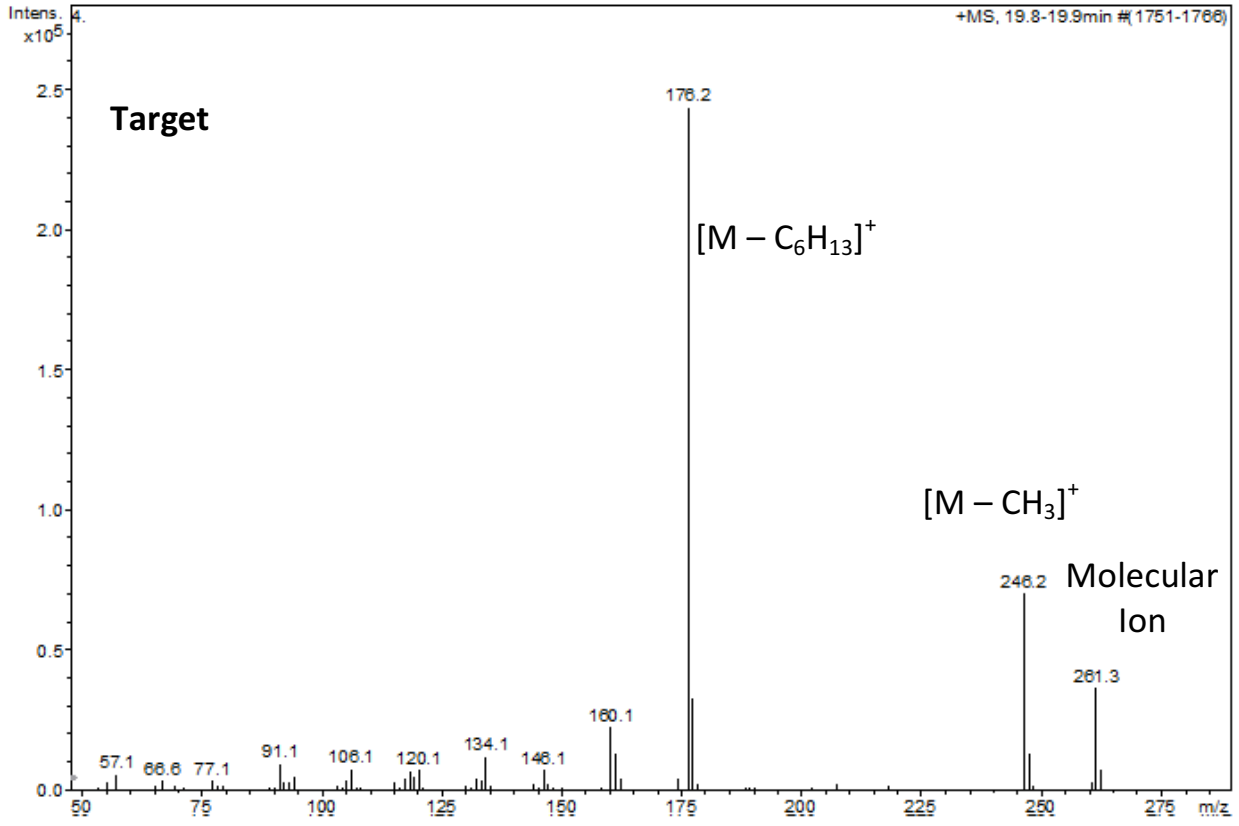


Figure S49: Mass spectra for compound 1 in the TIC for sample B

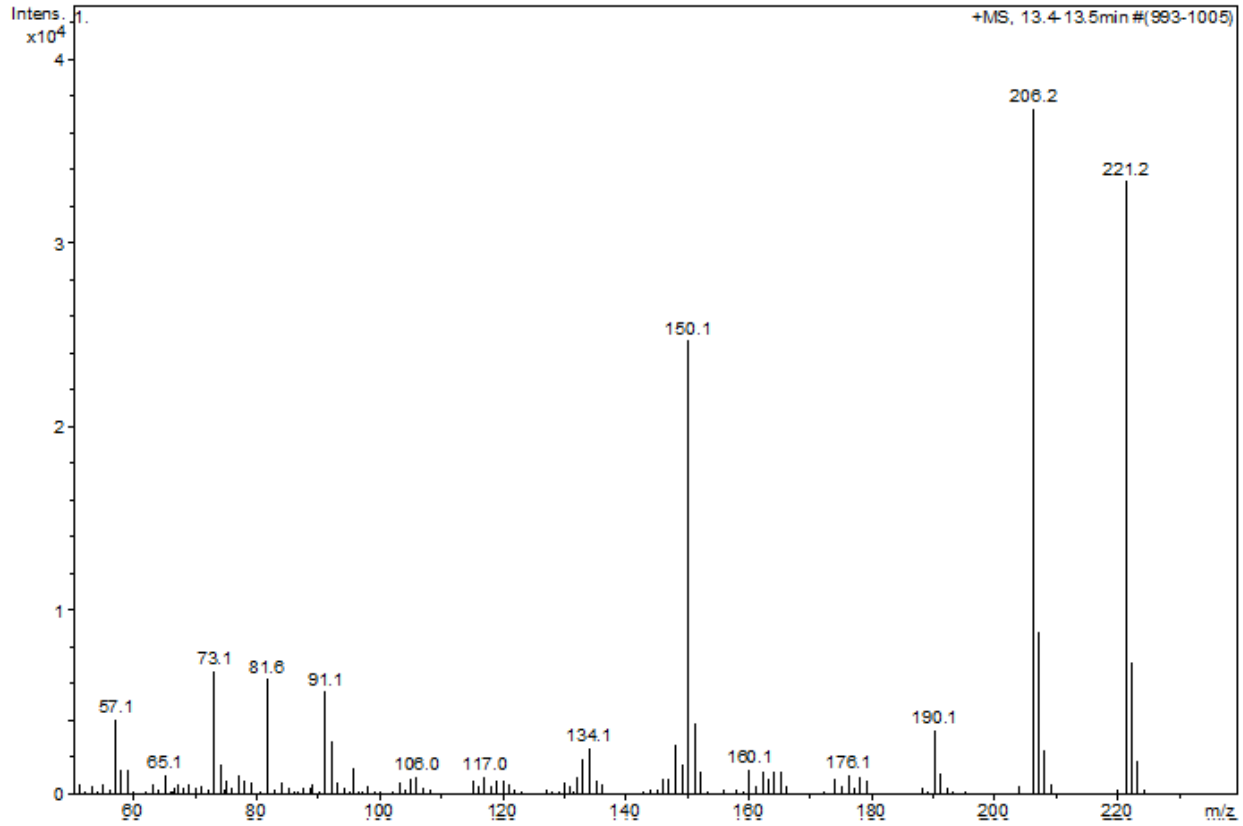


Figure S50: Mass spectra for compound 2 in the TIC for sample B

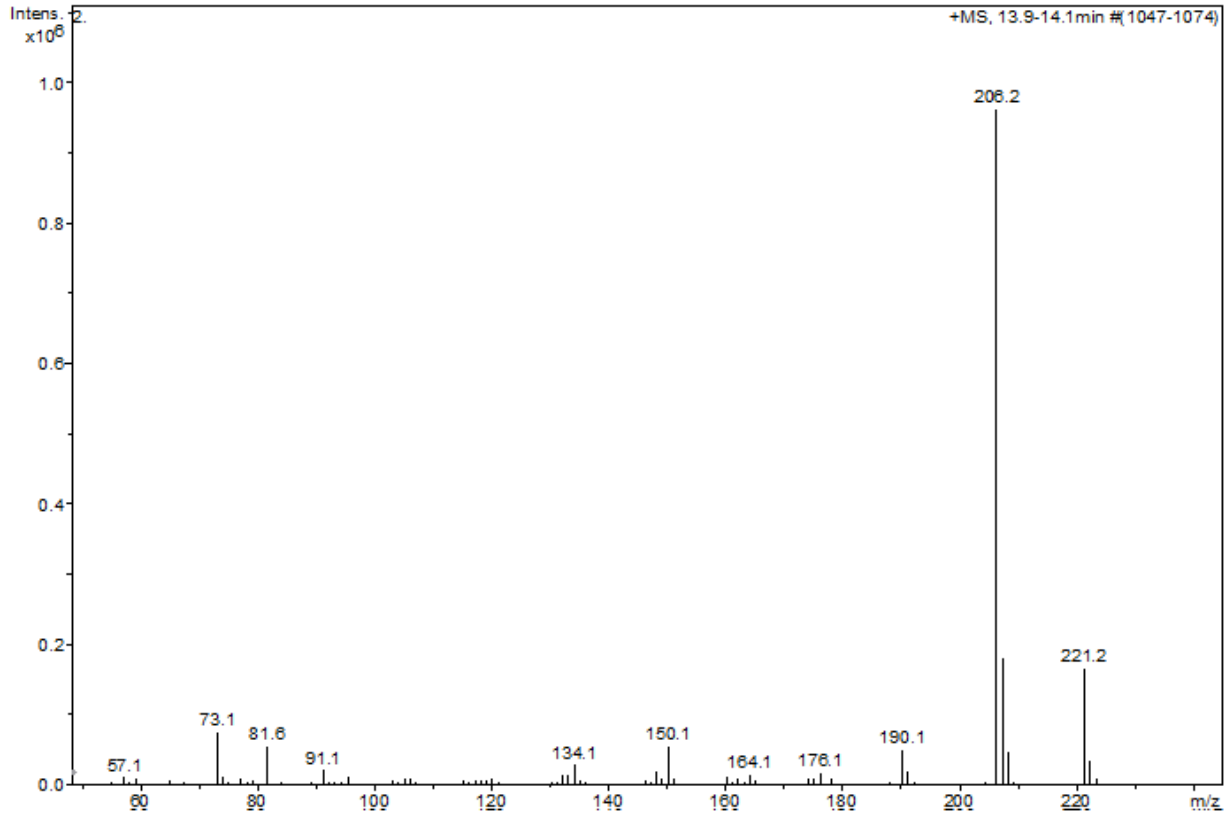
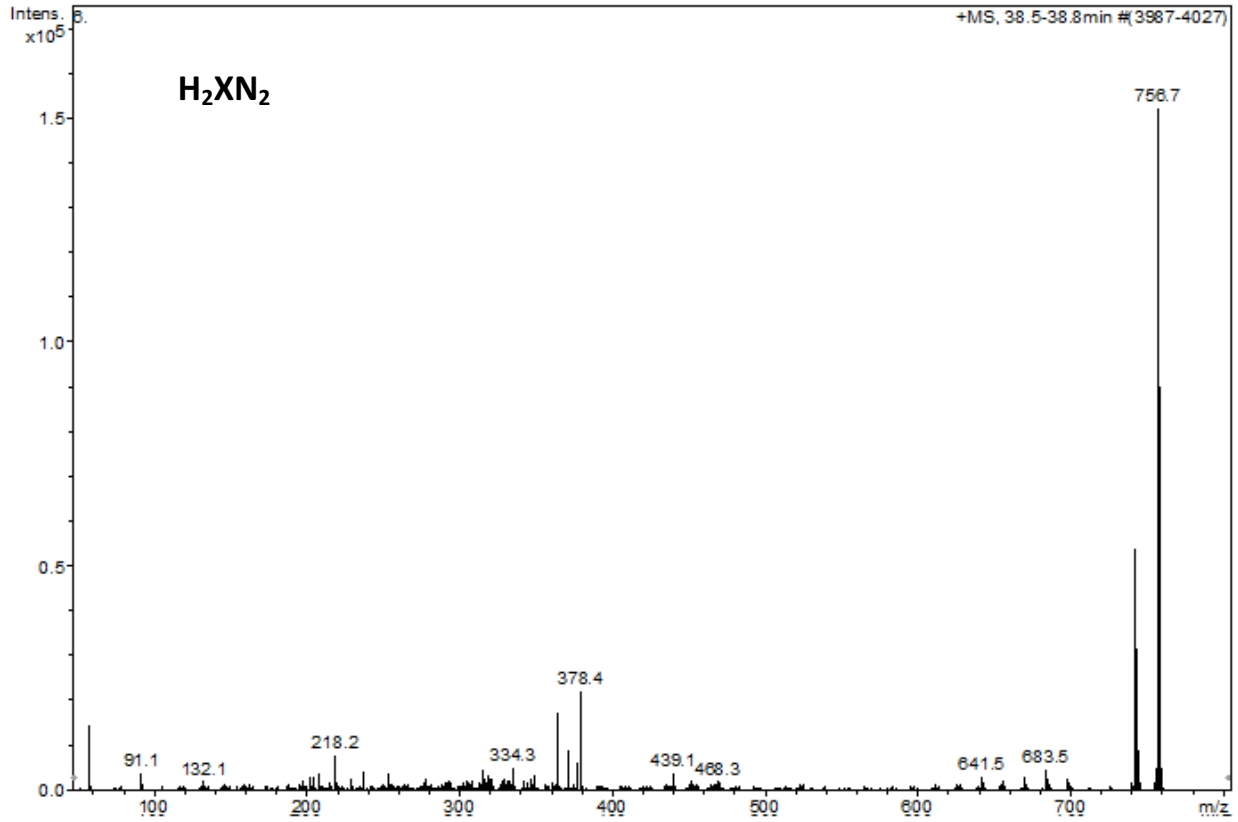


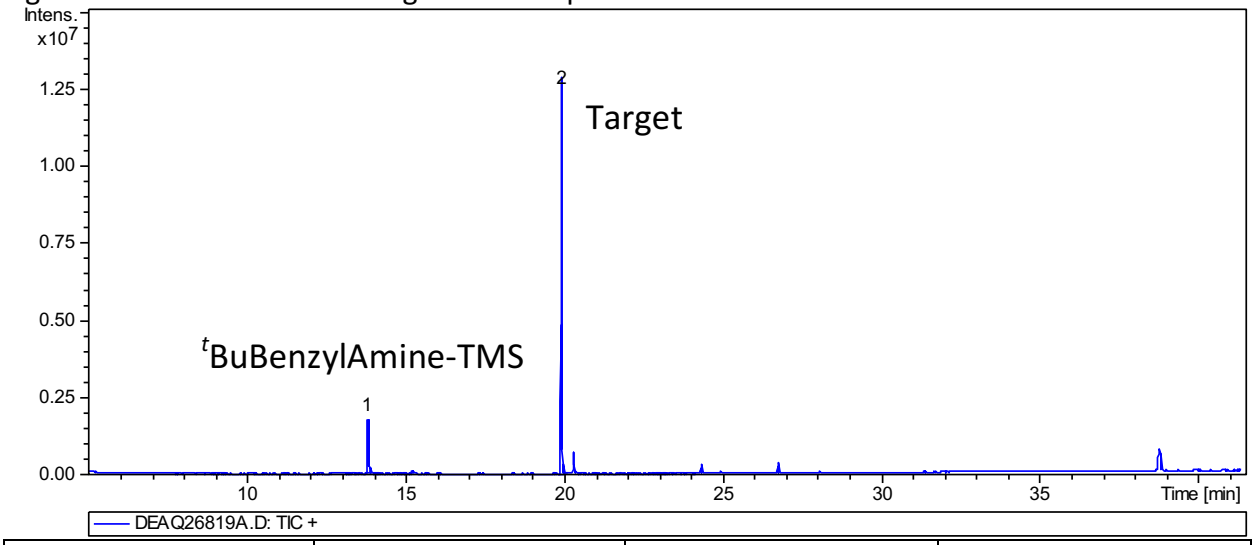
Figure S51: Mass spectra for compound 5 (H_2XN_2 proligand) in the TIC for sample B



Mass Spec. Results for the reaction of 10 mol % of 1 with ^{t}BuBenzylAmine and 1-octene after 24 h at 110 °C (Table 2, Entry 2 in Manuscript)

Sample A was diluted 10 fold in toluene, and then derivatized 1:1 with MSTFA. Sample B was used to determine the selectivity for Markovnikov product formation and was pumped down prior to obtaining the ^{1}H NMR spectra and submitting for GC-MS. Sample B was diluted 10 fold in toluene and then derivatized 1:4 with MSTFA. Samples were analyzed with Agilent GCMS on DB-5MS column after an one hour incubation at 60 °C.

Figure S52: Total ion chromatogram of Sample A



#	RT [min]	Area	
1	13.8	5126566	MW163 - TMS
2	19.9	27190104	MW 275 (Target)

Figure S53: Mass spectra for compound 2 (Target) in the TIC

m/z 260 (-CH_3), m/z 190 (-C_6H_{13}, -CH_3)

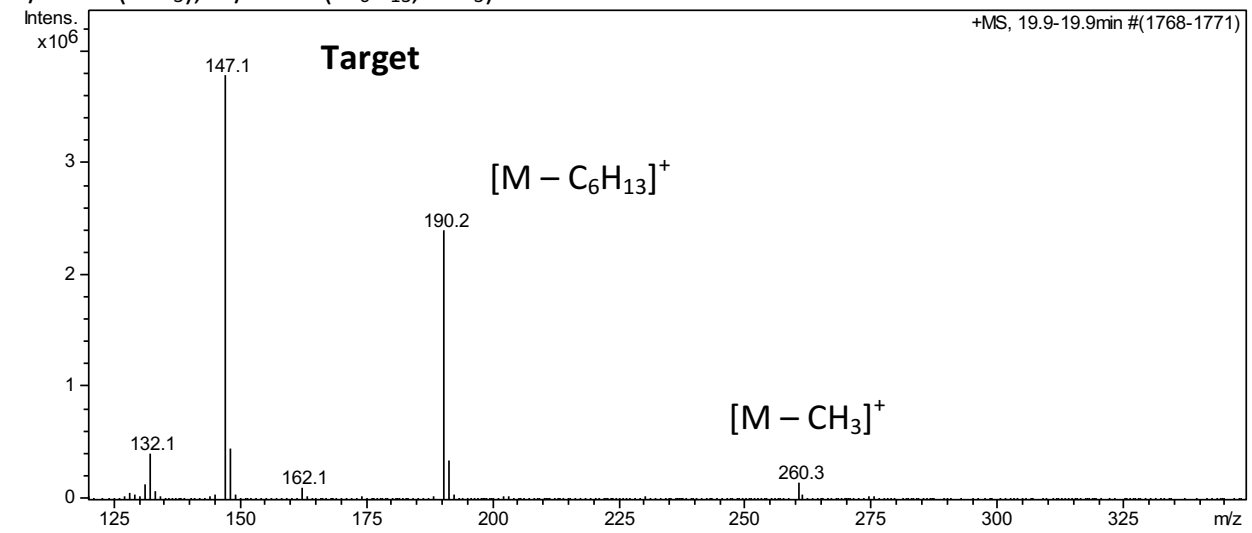


Figure S54: Mass Spectra for compound 1 in the TIC

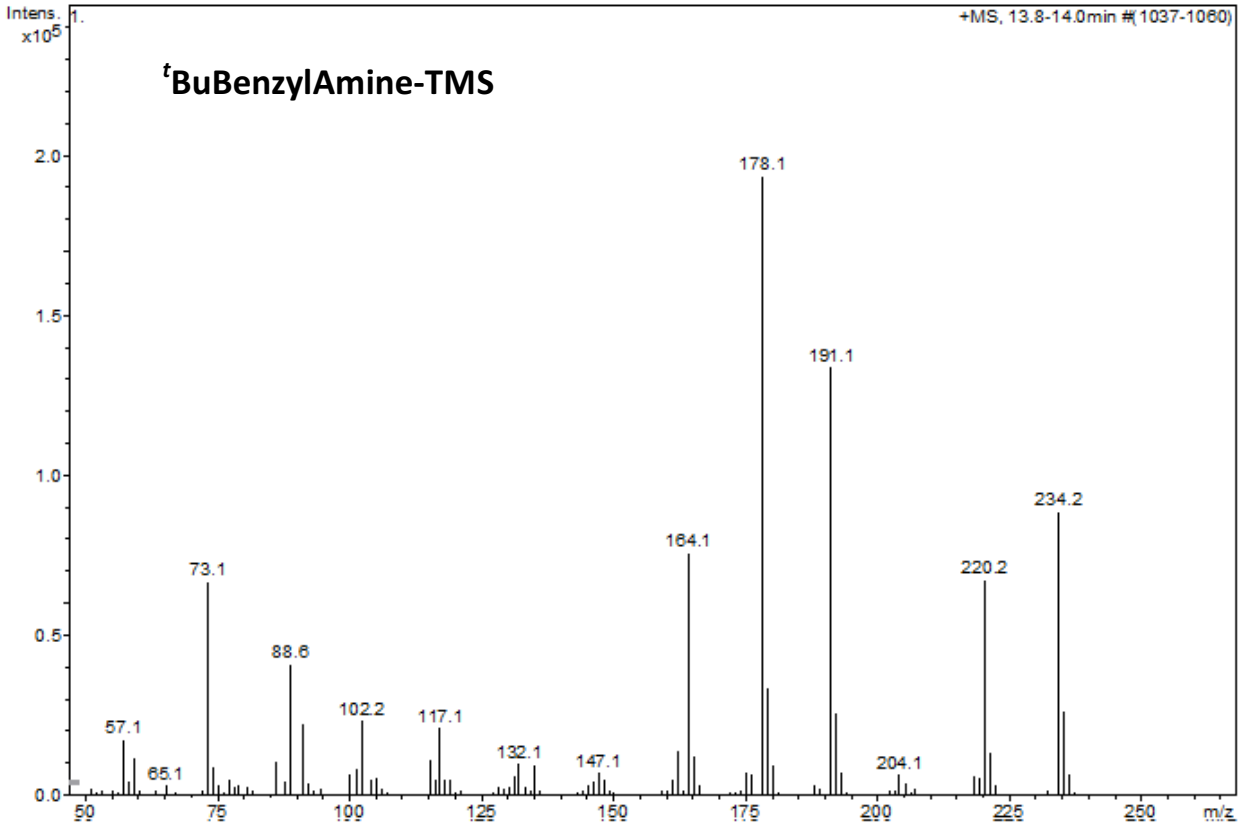
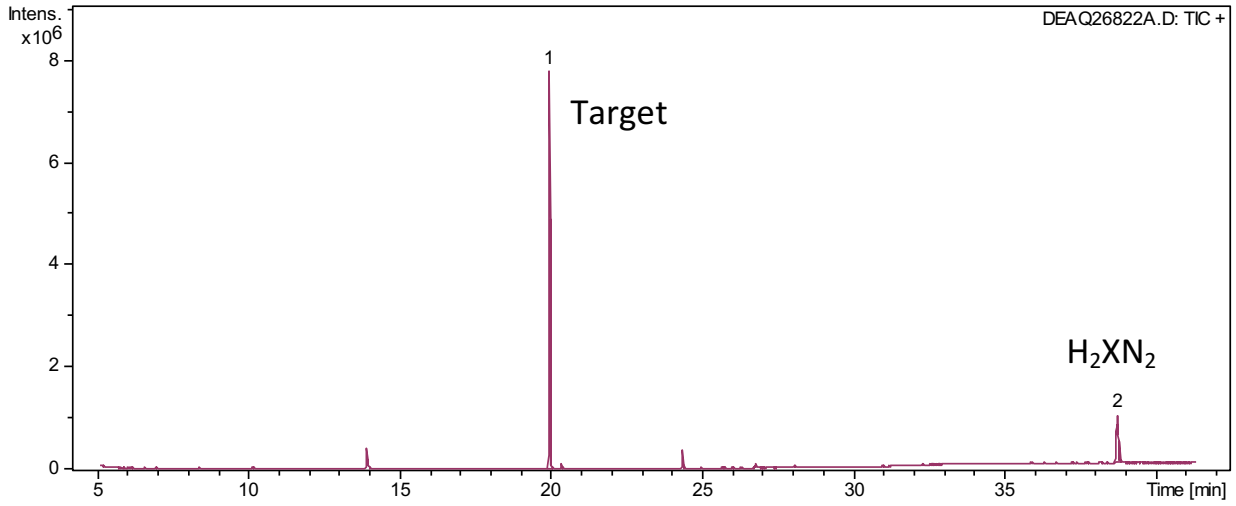


Figure S55: Total ion chromatogram of Sample B
Did not detect anti of target



#	RT [min]	Area	
1	19.9	17003864	Target
2	38.7	4221453	H_2XN_2 proligand

Figure S56: Mass spectra for compound 1 (Target) in the TIC for Sample B
m/z 260 (-CH_3), m/z 190 (-C_6H_{13}, -CH_3)

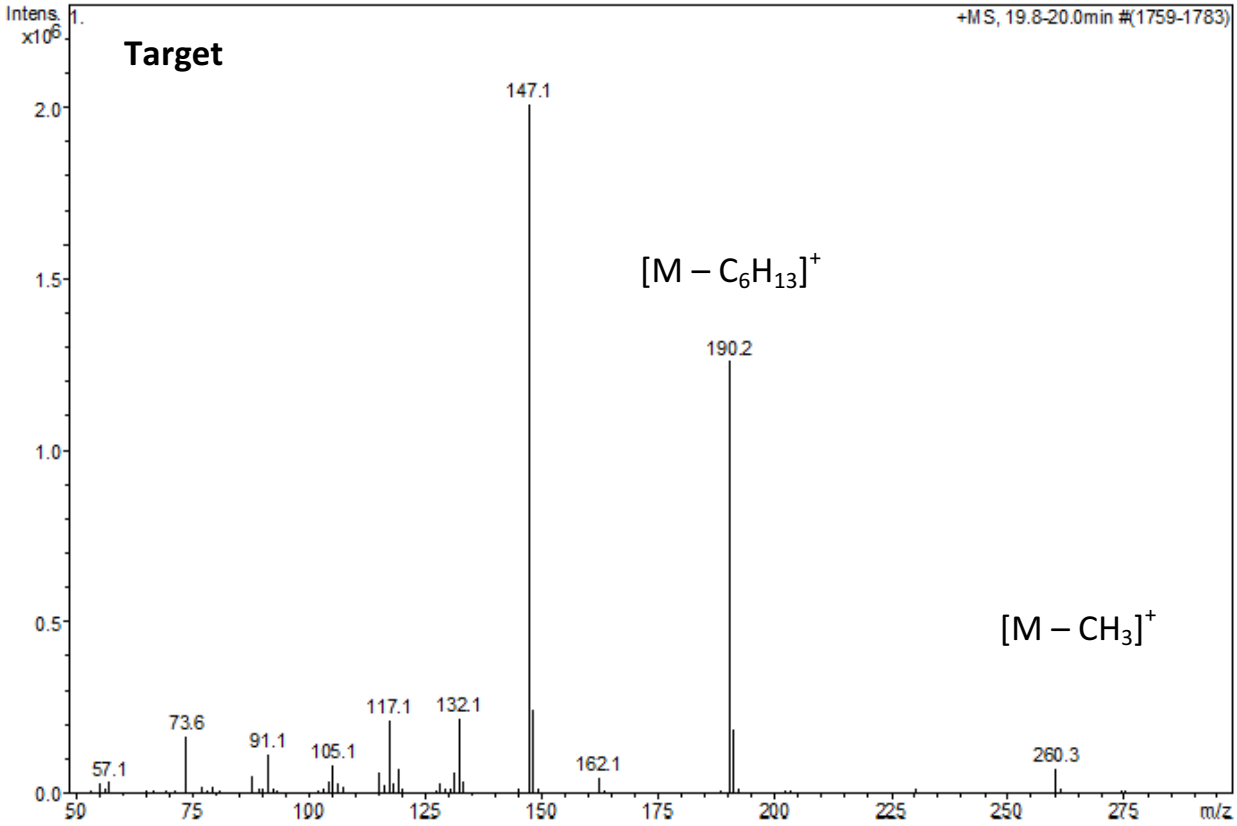
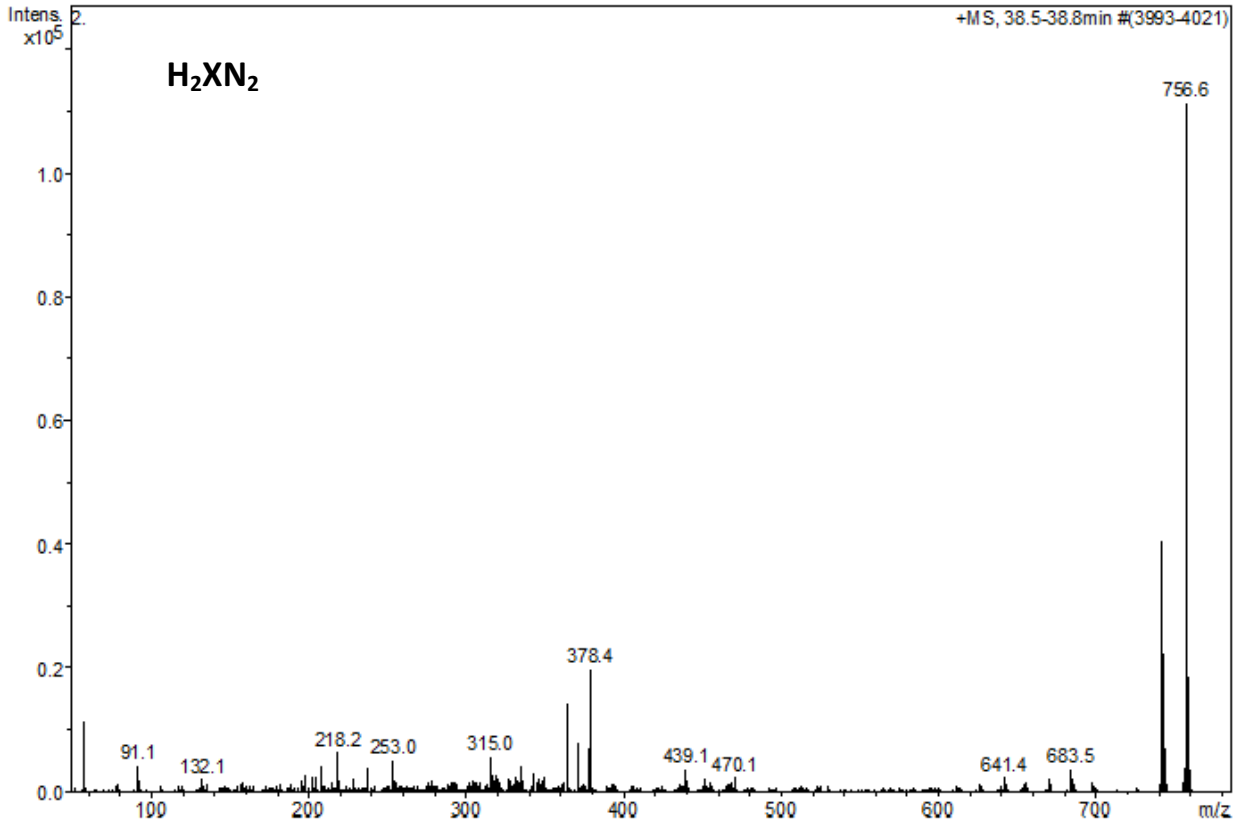


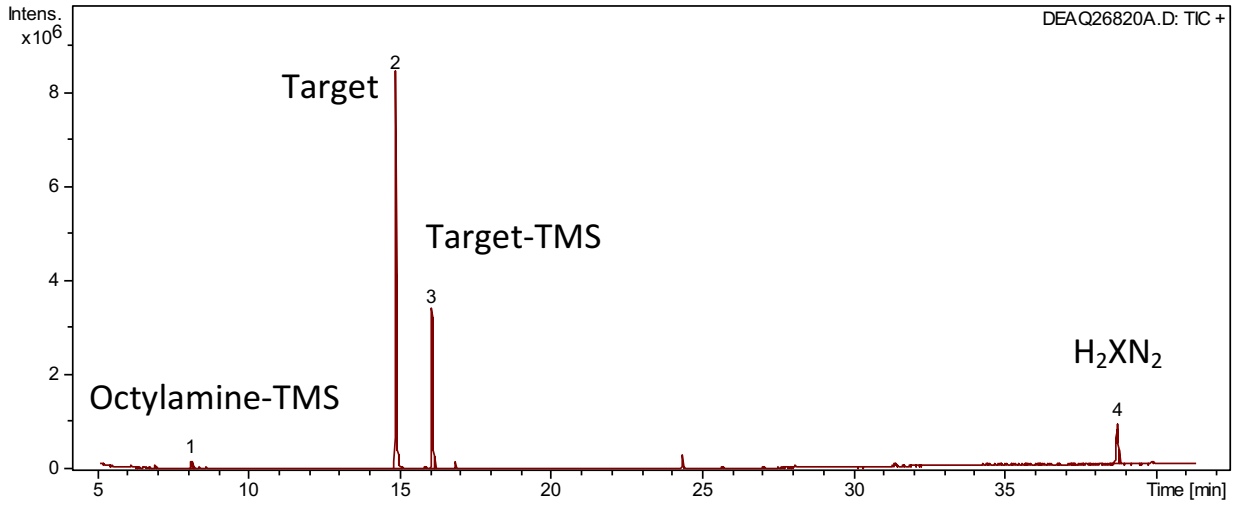
Figure S57: Mass spectra for compound 2 (H_2XN_2 proligand) in the TIC for Sample B



Mass Spec. Results for the reaction of 10 mol % of 1 with OctylAmine and 1-octene after 24 h at 110 °C (Table 2, Entry 3 in Manuscript)

Samples A and B were diluted 10 fold in toluene, and then derivatized 1:1 with MSTFA. Sample B was used to determine the selectivity for Markovnikov product formation and was pumped down prior to obtaining the ^{1}H NMR spectra and submitting for GC-MS. Samples were analyzed with Agilent GCMS on DB-5MS column after an one hour incubation at 60 °C.

Figure S58: Total ion chromatogram of Sample A



#	RT [min]	Area	
1	8.1	655964	MW 129-TMS
2	14.8	23309753	MW 241 (Target)
3	16.0	10063755	Target-TMS
4	38.7	3976270	H_2XN_2 proligand

Figure S59: Mass spectra for compound 2 (Target) in the TIC

m/z 226 (-CH3), m/z 156 (-C_6H_{13})

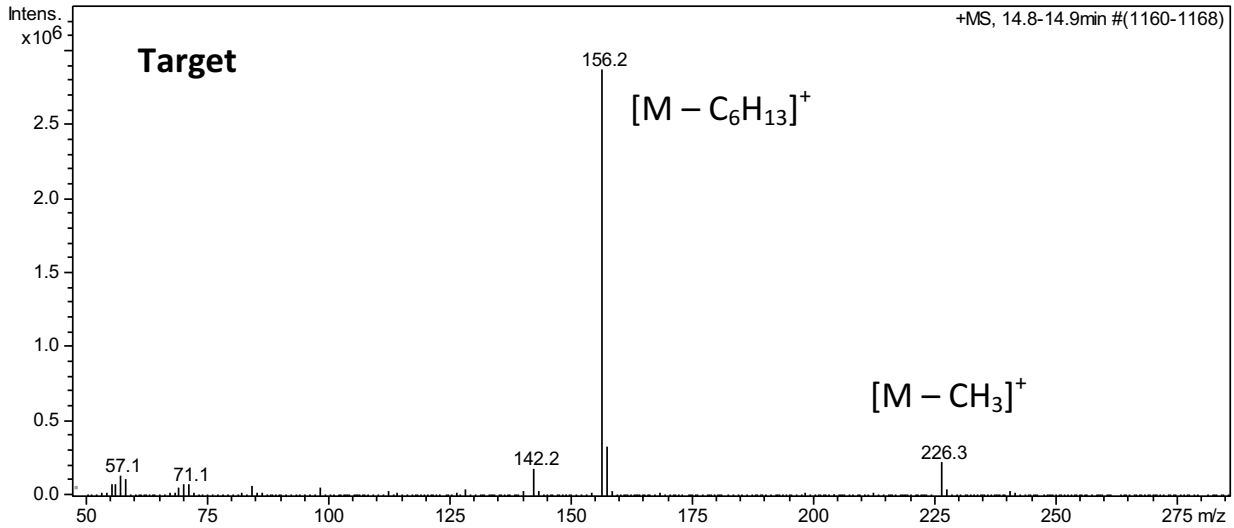


Figure S60: Mass spectra for compound 1 in the TIC

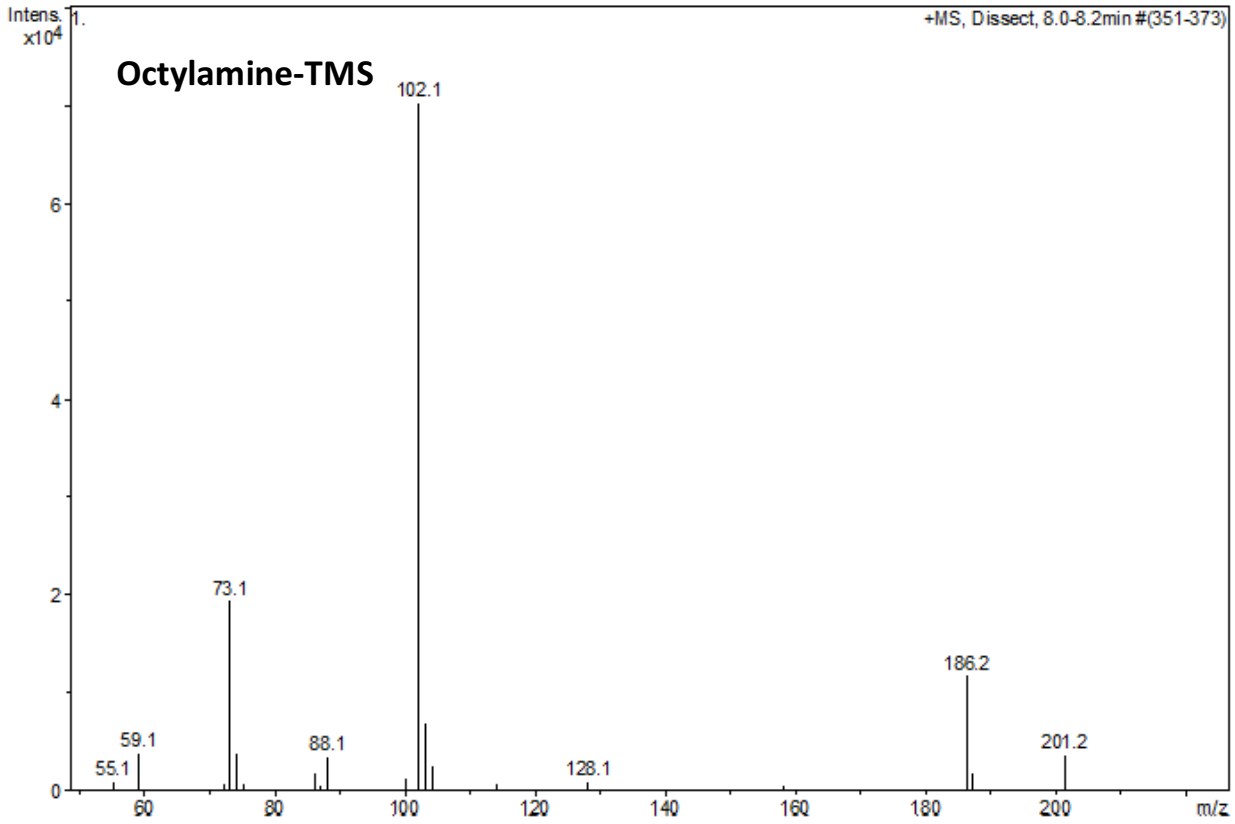


Figure S61: Mass spectra for compound 3 in the TIC

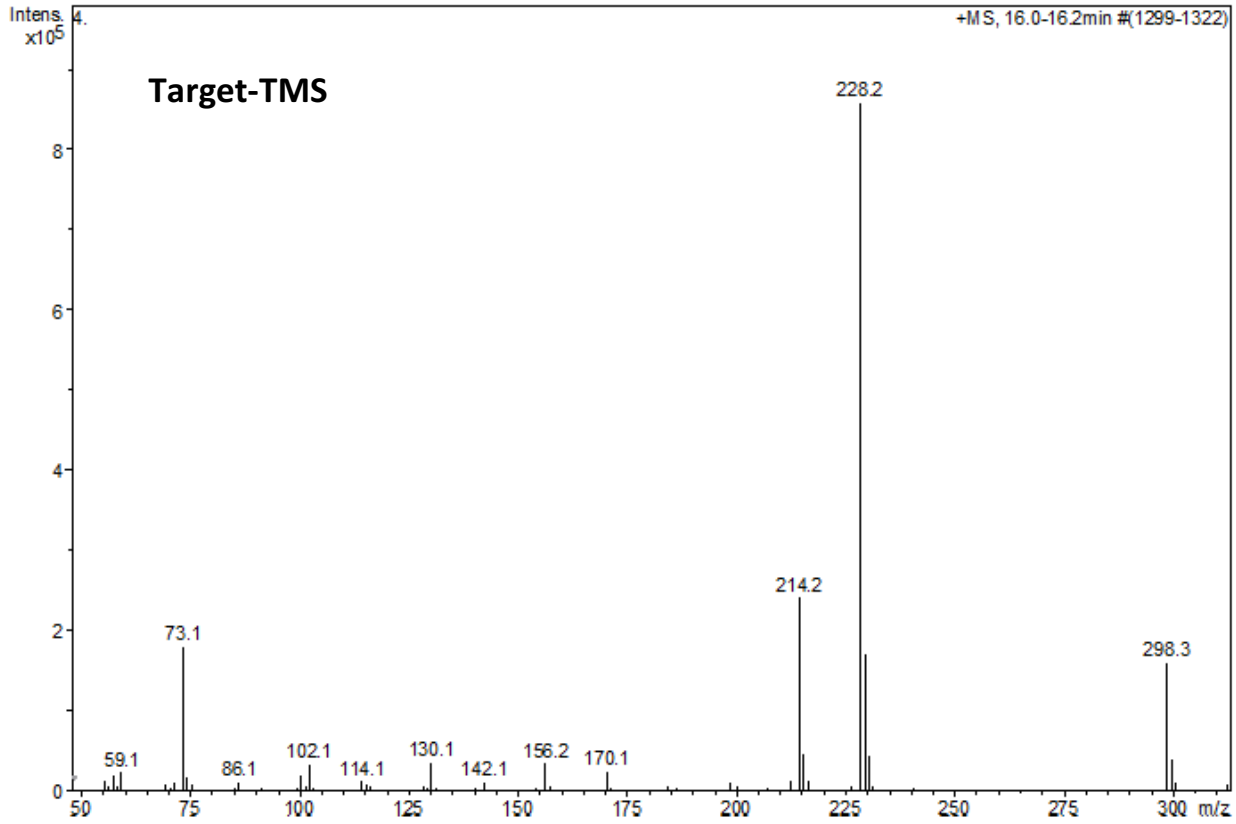


Figure S62: Mass spectra for compound 4 (H_2XN_2 pro-ligand) in the TIC

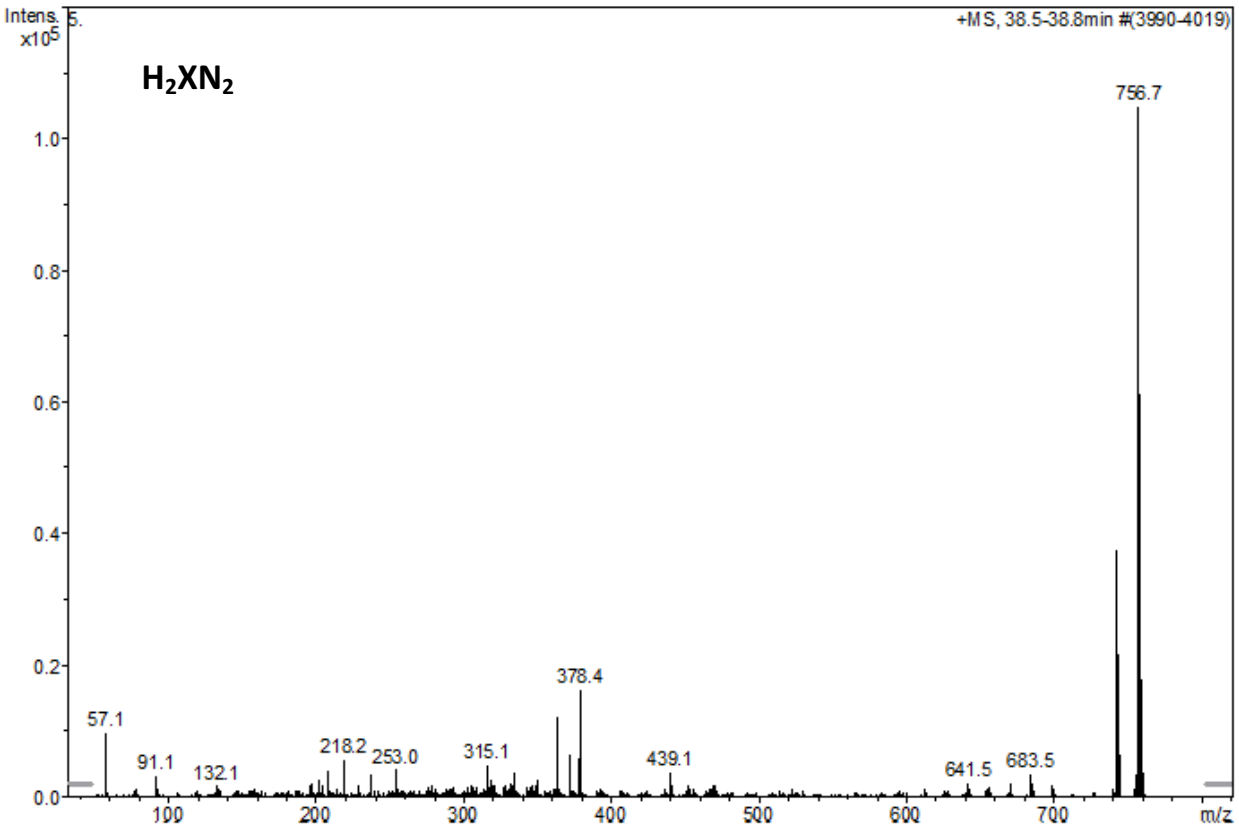
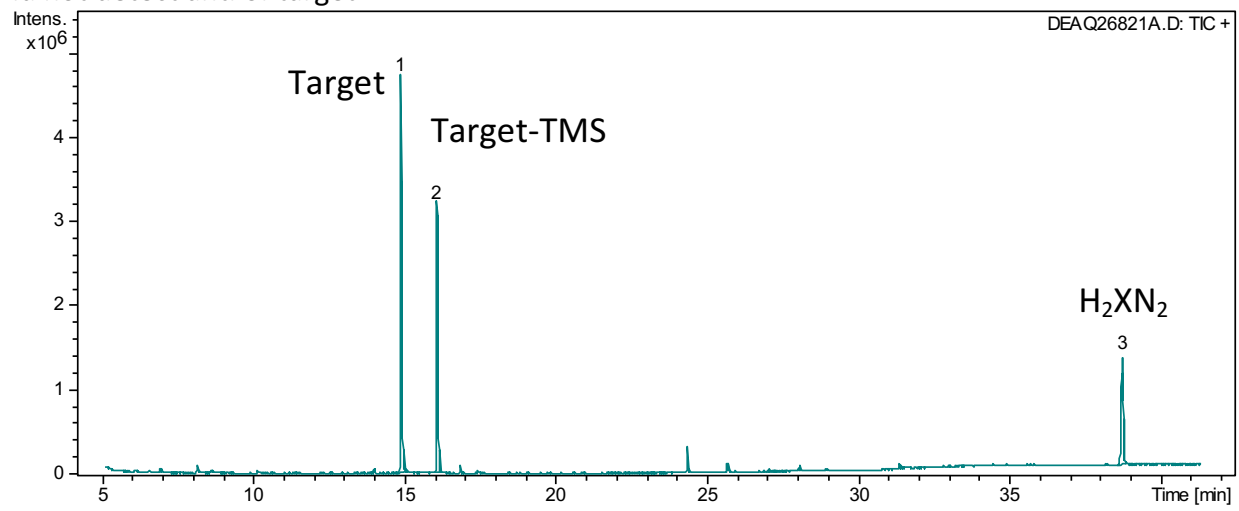


Figure S63: Total ion chromatogram of Sample B
Did not detect anti of target



#	RT [min]	Area	
1	14.8	13826204	Target
2	16.0	9599033	Target-TMS
3	38.7	6199069	H_2XN_2 proligand

Figure S64: Mass spectra for compound 1 (Target) in the TIC for sample B

m/z 226 (-CH3), m/z 156 (-C_6H_{13})

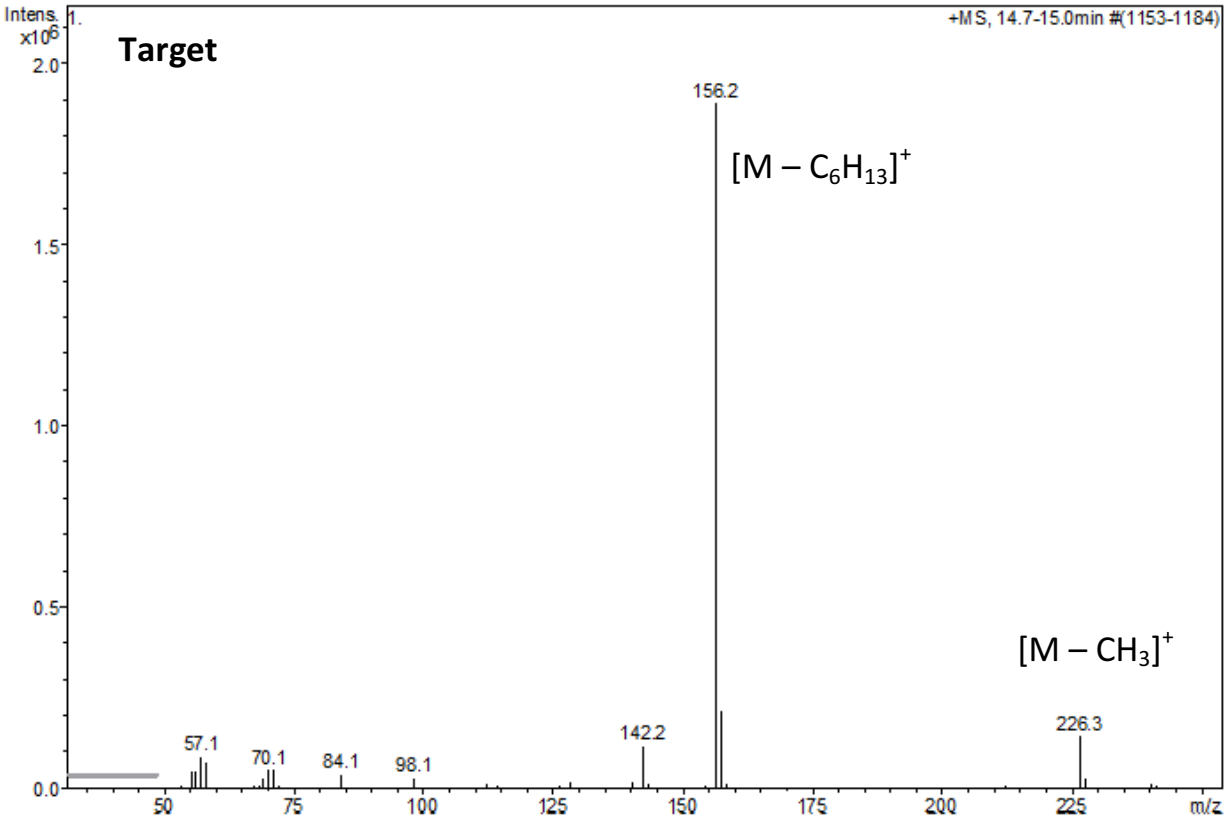


Figure S65: Mass spectra for compound 2 in the TIC for sample B

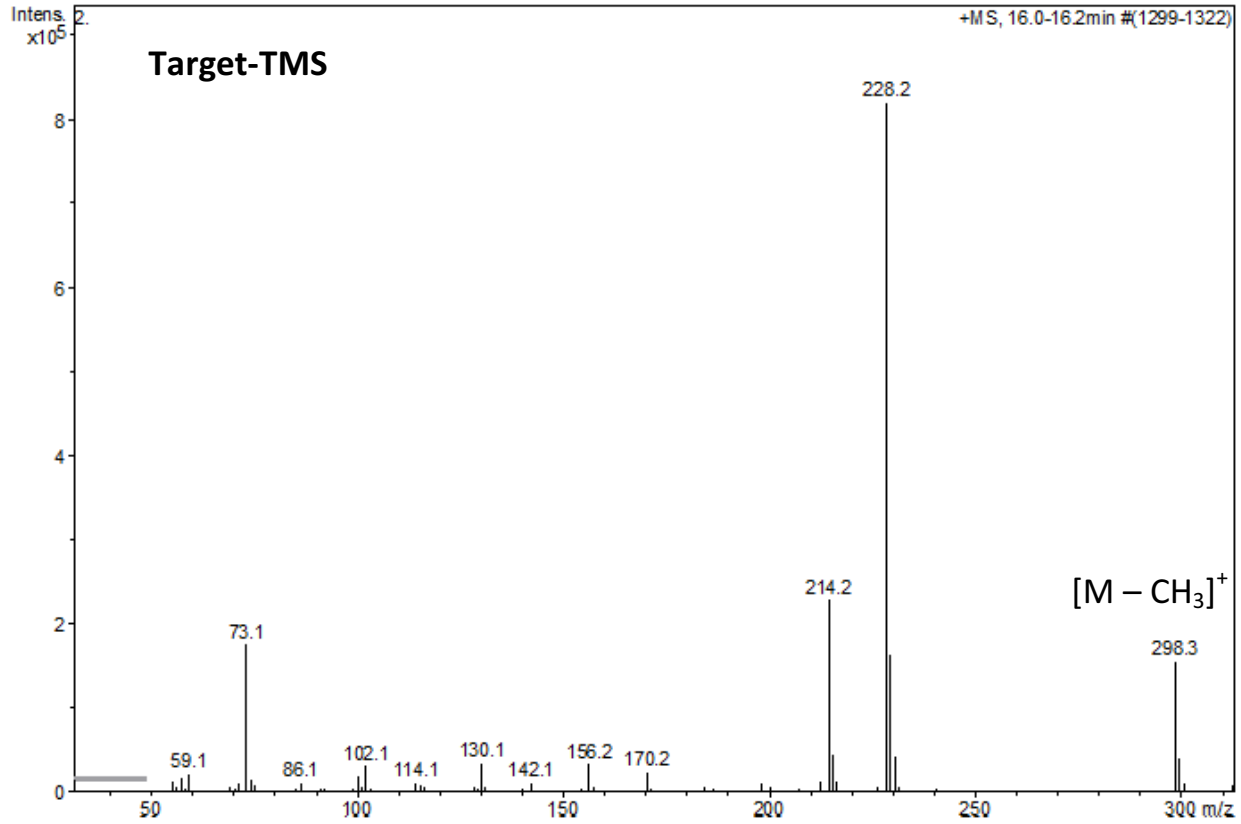
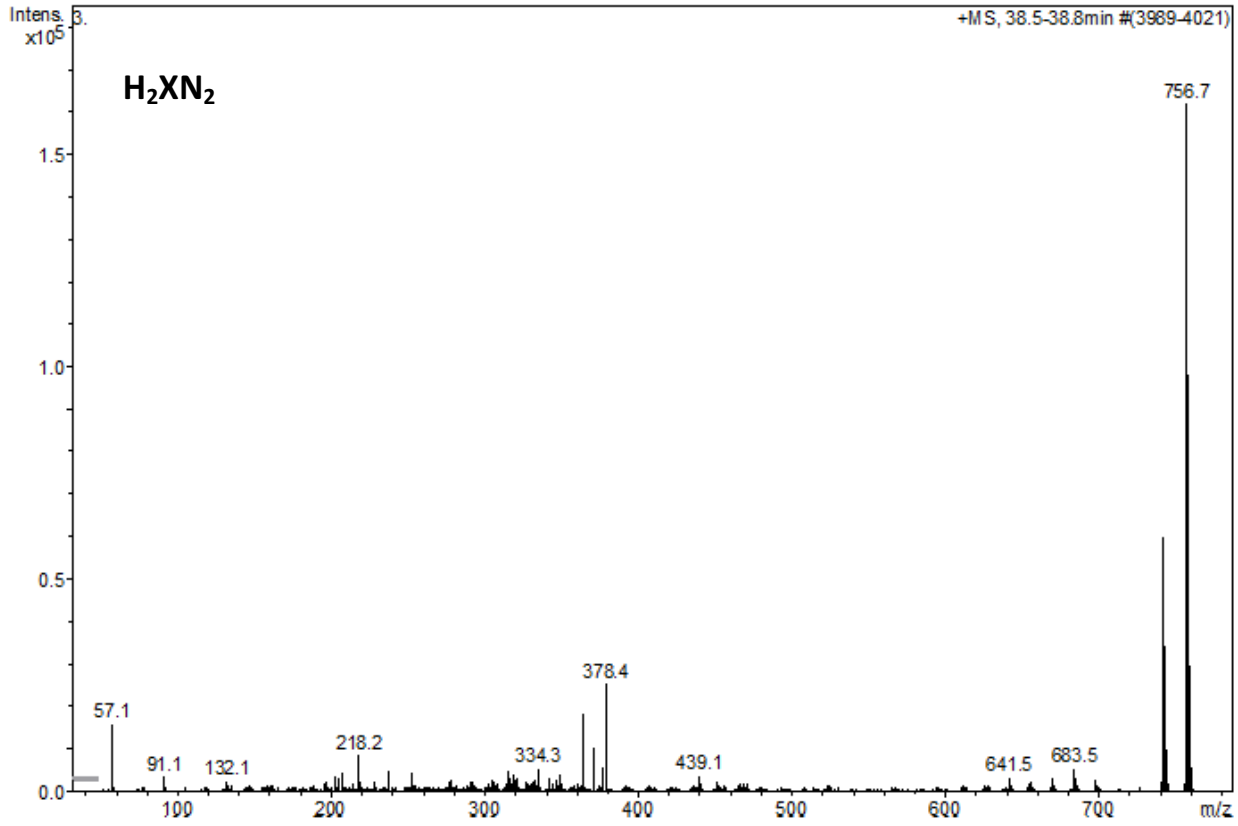


Figure S66: Mass spectra for compound 3 (H_2XN_2 proligand) in the TIC for sample B

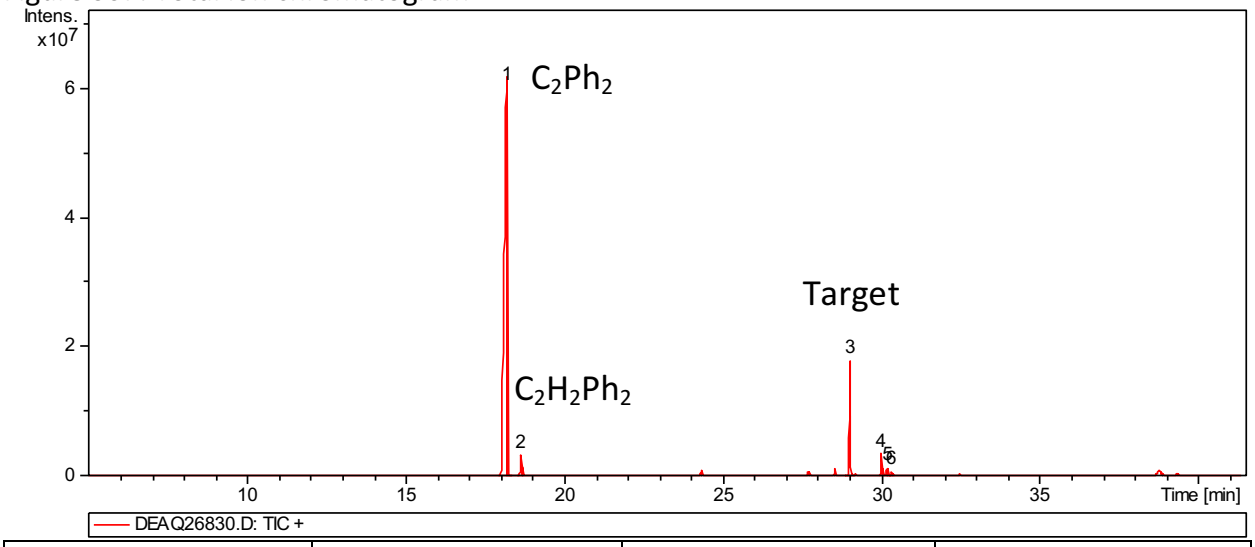


Mass Spec. Results for the reaction of 10 mol % of 1 with ^{t}BuAniline and Diphenylacetylene after 24 h at 110 °C (Table 2, Entry 4 in Manuscript)

The sample was diluted 10 fold in toluene, and then derivatized 1:1 with MSTFA. The sample was analyzed with Agilent GCMS on DB-5MS column after an one hour incubation at 60 °C.

Did not detect starting reagent ^{t}BuAniline (MW 149). The target is not included in the library. Compound 3 is assigned to be the target since the observed mass spectrum is most consistent with the target structure.

Figure S67: Total ion chromatogram



#	RT [min]	Area	
1	18.2	342622567	MW 178 Diphenylacetylene
2	18.6	7347449	Stilbene
3	29.0	38987527	Target
4	29.9	6338416	
5	30.1	2137846	
6	30.3	736699	

Figure S68: Mass spectra for compound 3 (likely the product) in the TIC
m/z 312 (-CH_3), m/z 236 (-C_7H_7, characteristic for alkyl benzene)

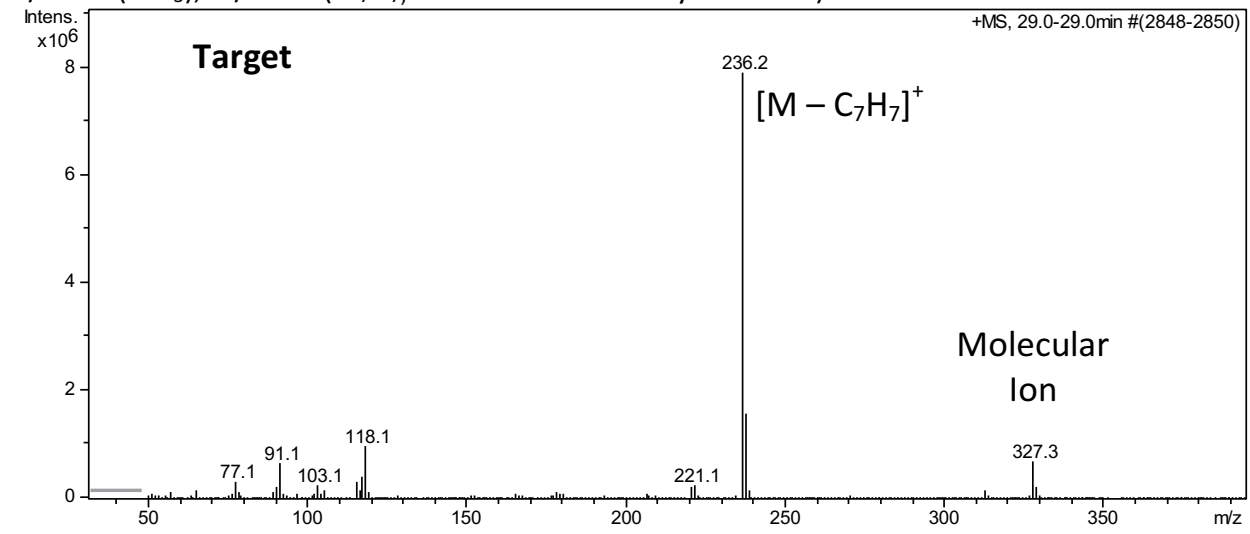


Figure S69: Mass spectra for compound 1 in the TIC and library mass spectra

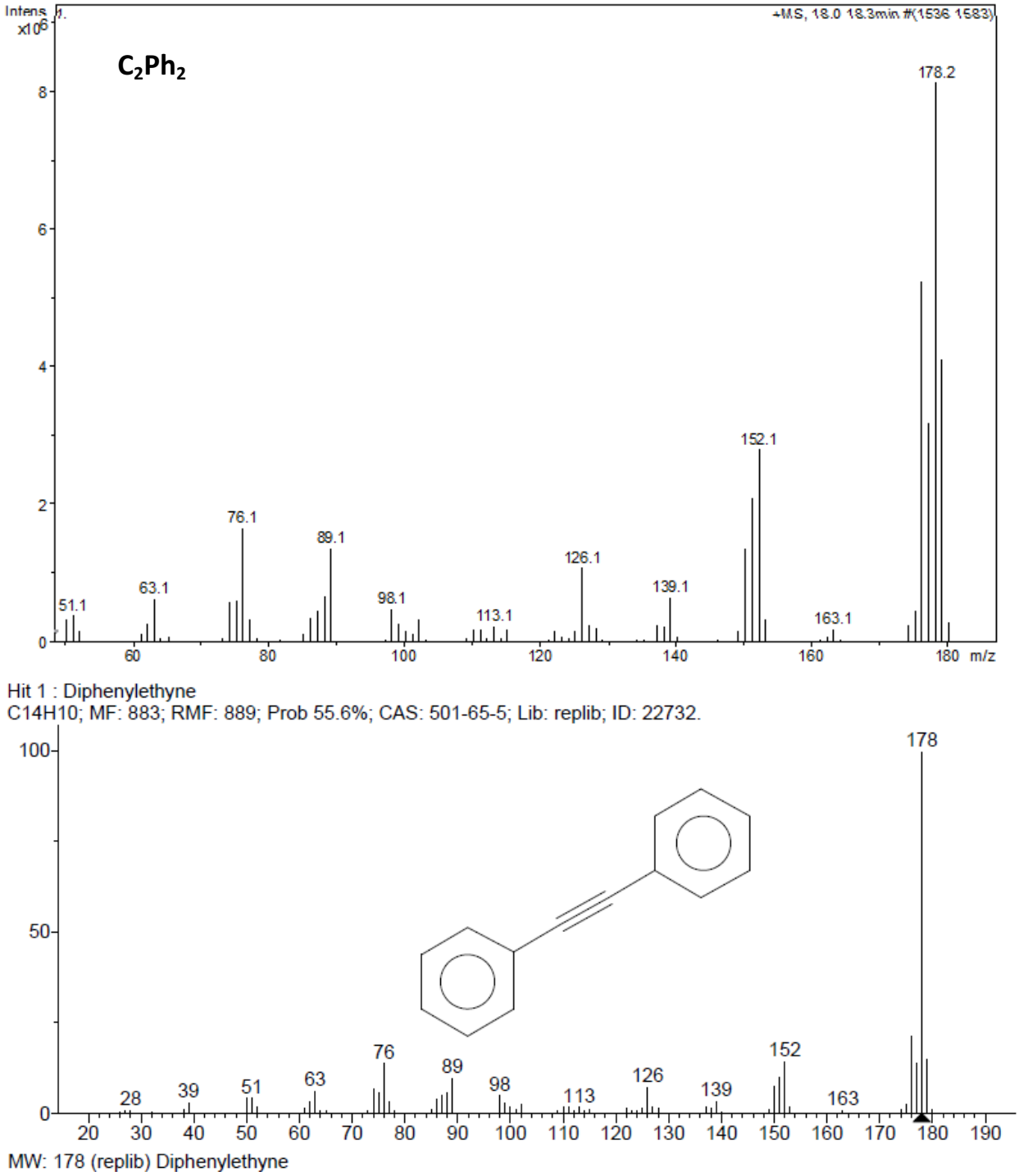


Figure S70: Mass spectra for compound 2 in the TIC and library mass spectra

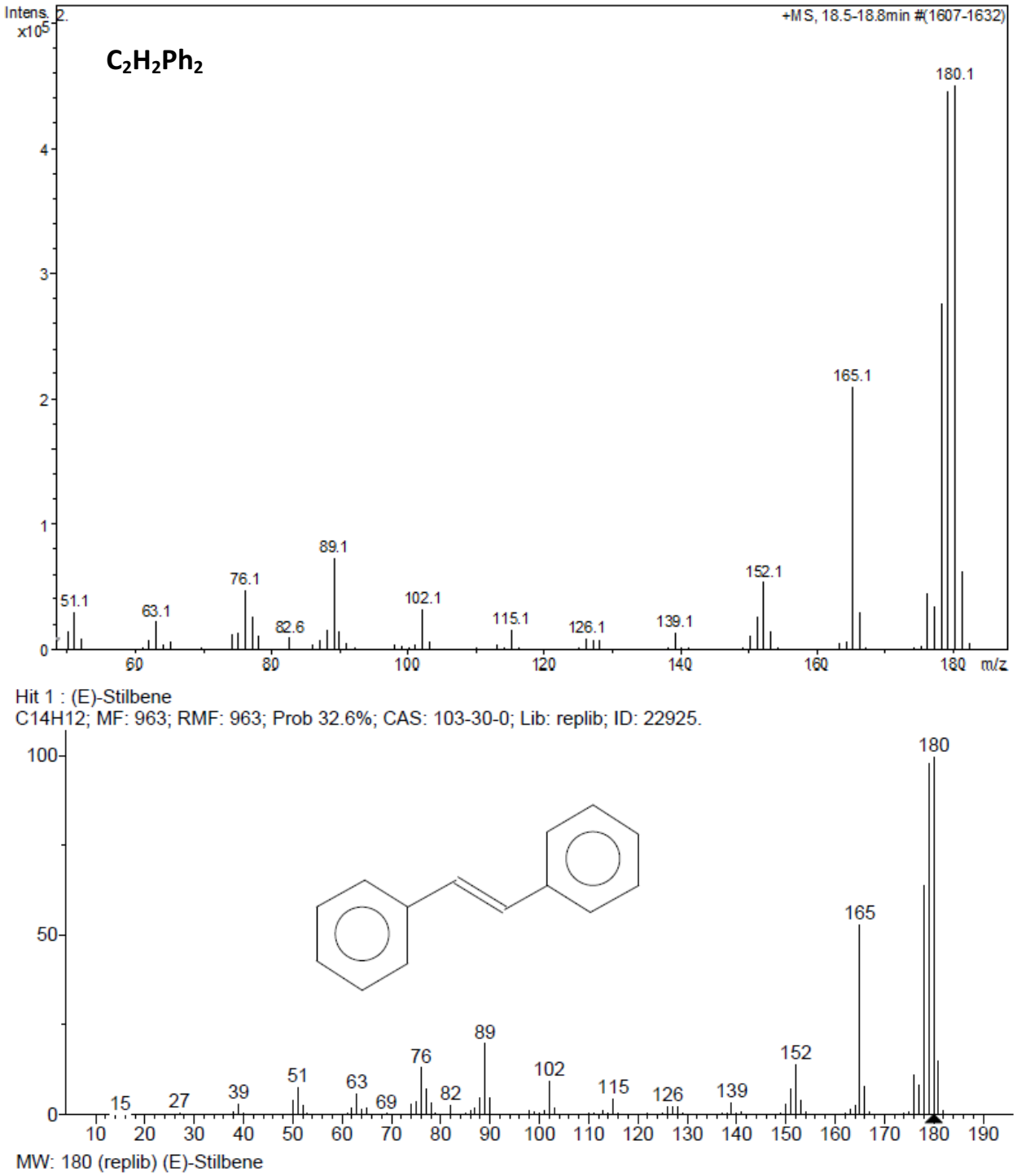


Figure S71: Mass spectra for compound 4 in the TIC
m/z 312 ($-CH_3$), m/z 270 ($-C_4H_9$)

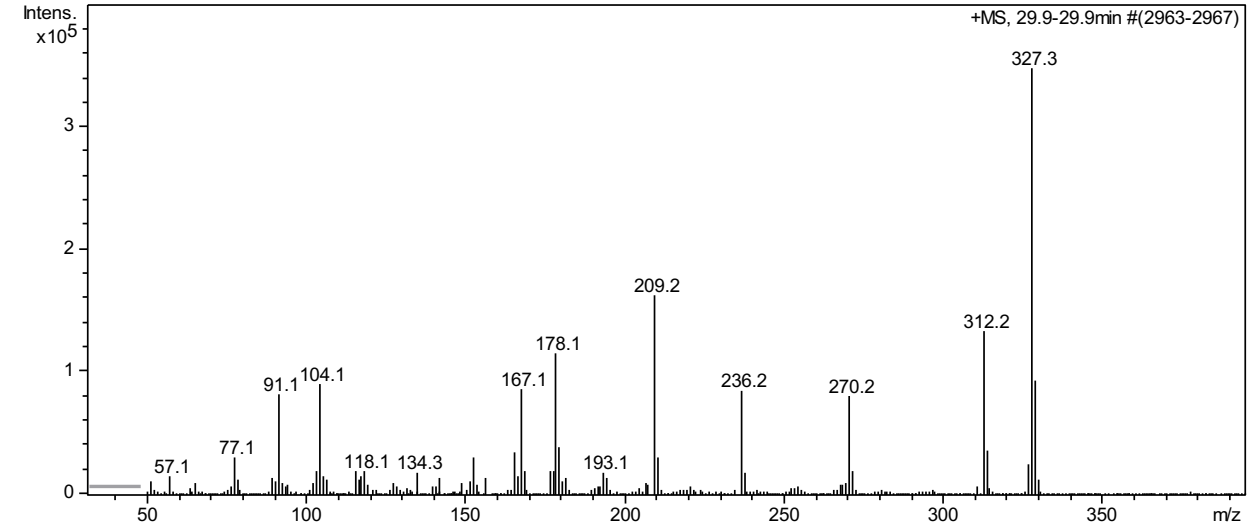


Figure S72: Mass spectra for compound 5 in the TIC

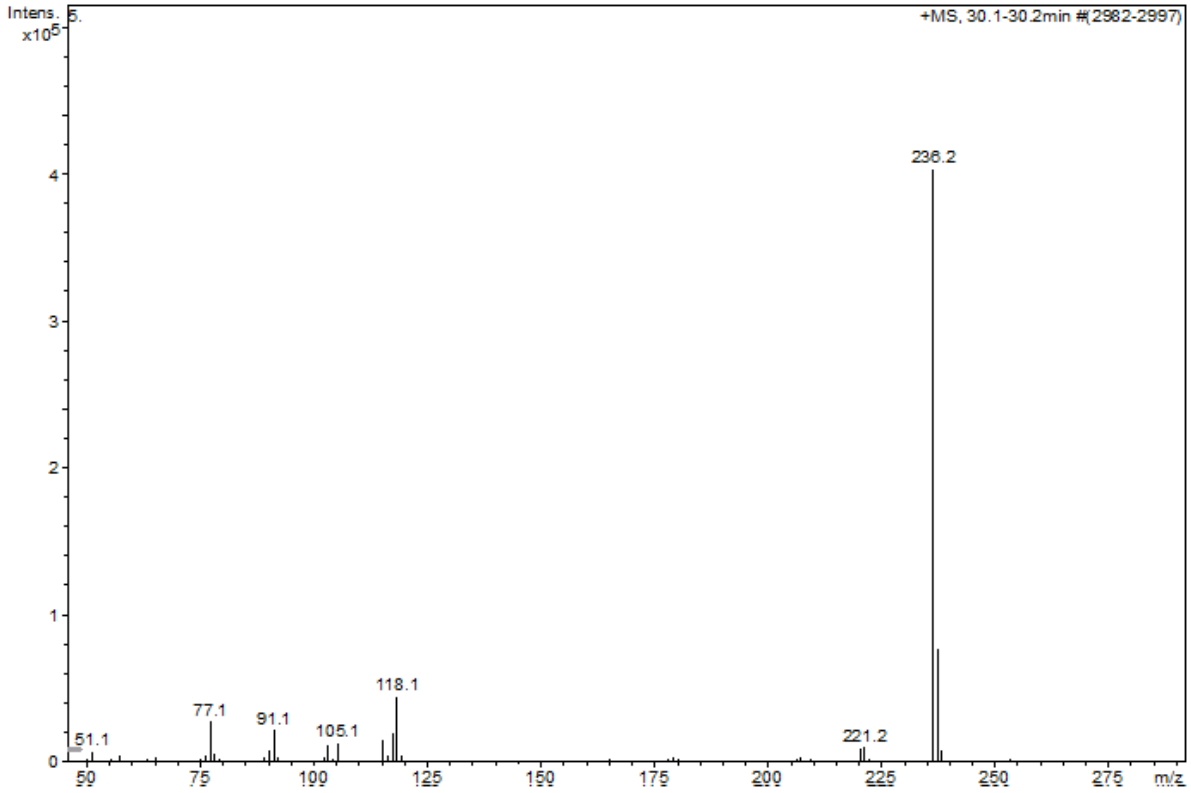
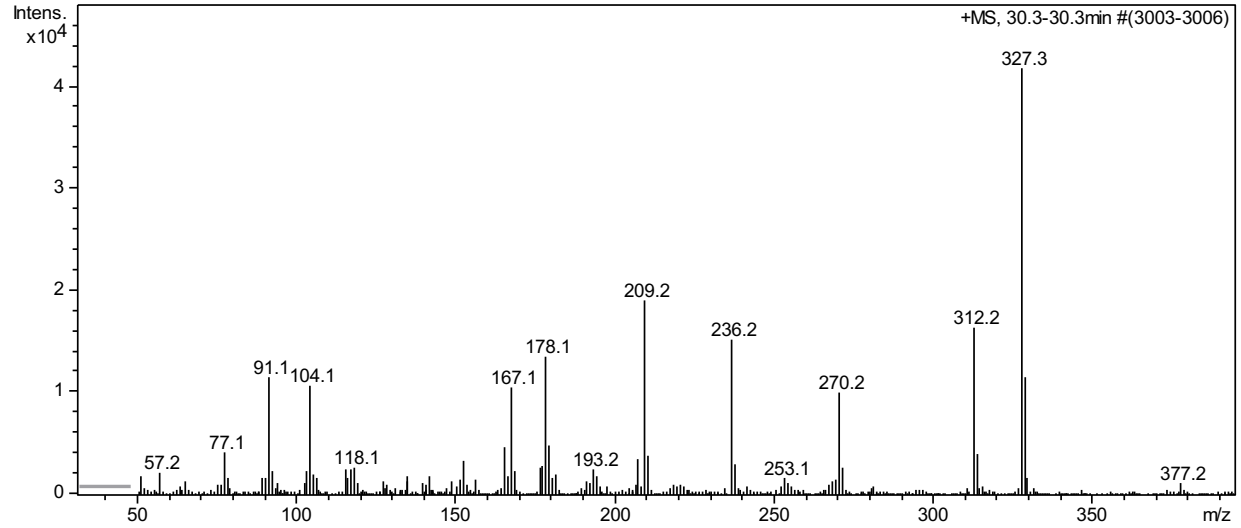


Figure S73: Mass spectra for compound 6 in the TIC
m/z 312 (-CH_3), m/z 270 (-C_4H_9)

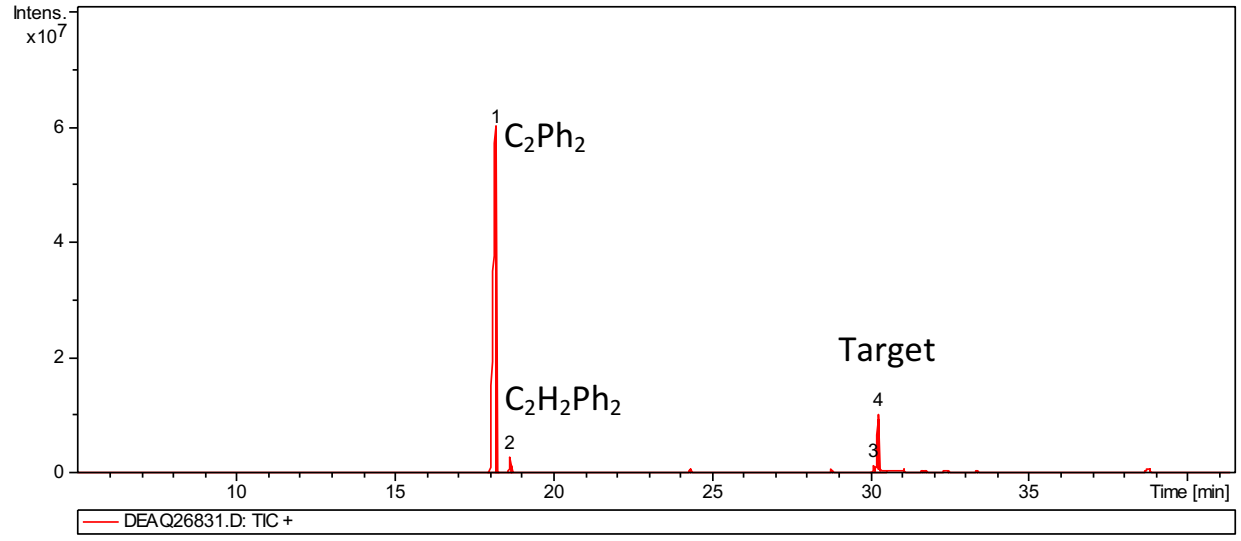


Mass Spec. Results for the reaction of 10 mol % of 1 with ^{t}BuBenzylAmine and Diphenylacetylene after 24 h at 110 °C (Table 2, Entry 5 in Manuscript)

The sample was diluted 10 fold in toluene, and then derivatized 1:1 with MSTFA. The sample was analyzed with Agilent GCMS on DB-5MS column after an one hour incubation at 60 °C.

Did not detect starting reagent ^{t}BuBenzylAmine (MW 163). The target is not included in the library. Compound 4 is assigned to be the target since the observed mass spectrum is most consistent with the target structure.

Figure S74: Total ion chromatogram



	RT [min]	Area	
1	18.2	329695471	MW 178 Diphenylacetylene
2	18.6	6945087	Stilbene
3	30.0	3269646	
4	30.2	30017498	Target

Figure S75: Mass spectra for compound 4 (Target) in the TIC
m/z 250 (-C_7H_7, characteristic for alkyl benzene), m/z 147 (-$C_{14}H_{12}N$)

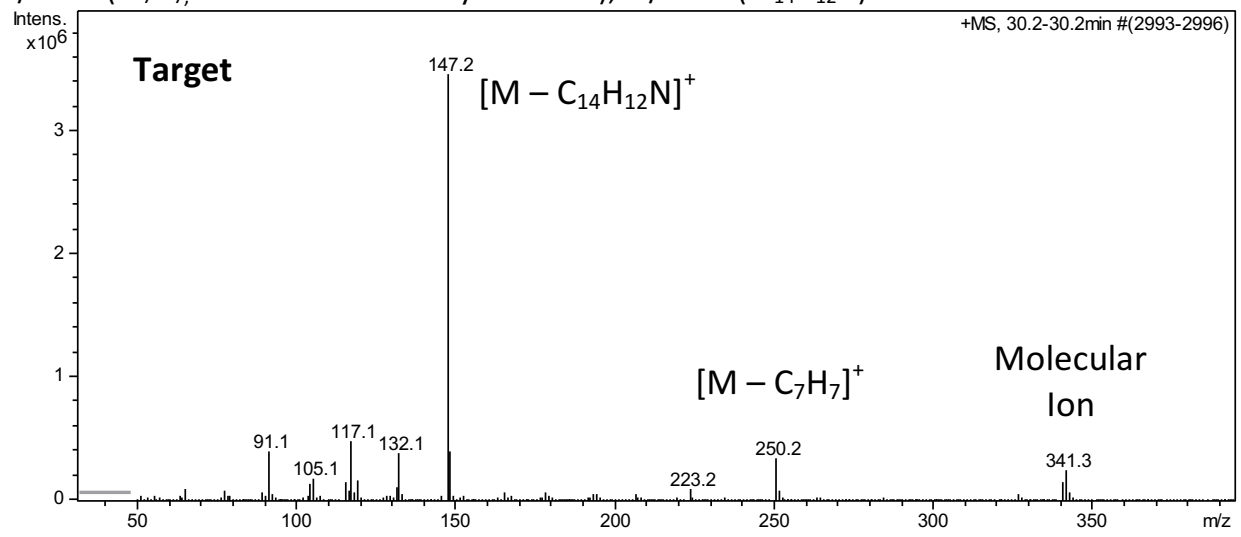


Figure S76: Mass spectra for compound 1 in the TIC and library mass spectra

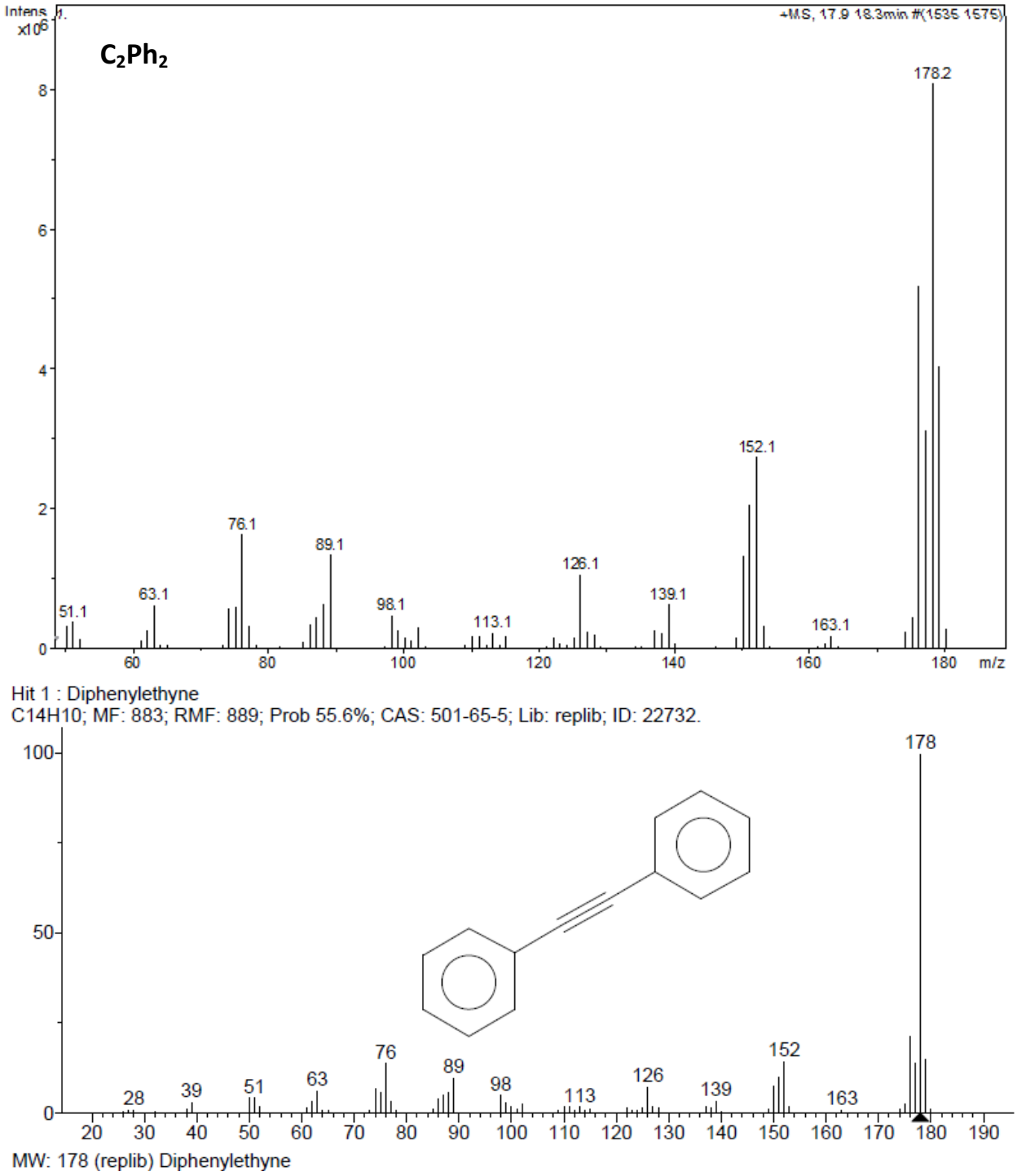


Figure S77: Mass spectra for compound 2 in the TIC and library mass spectra

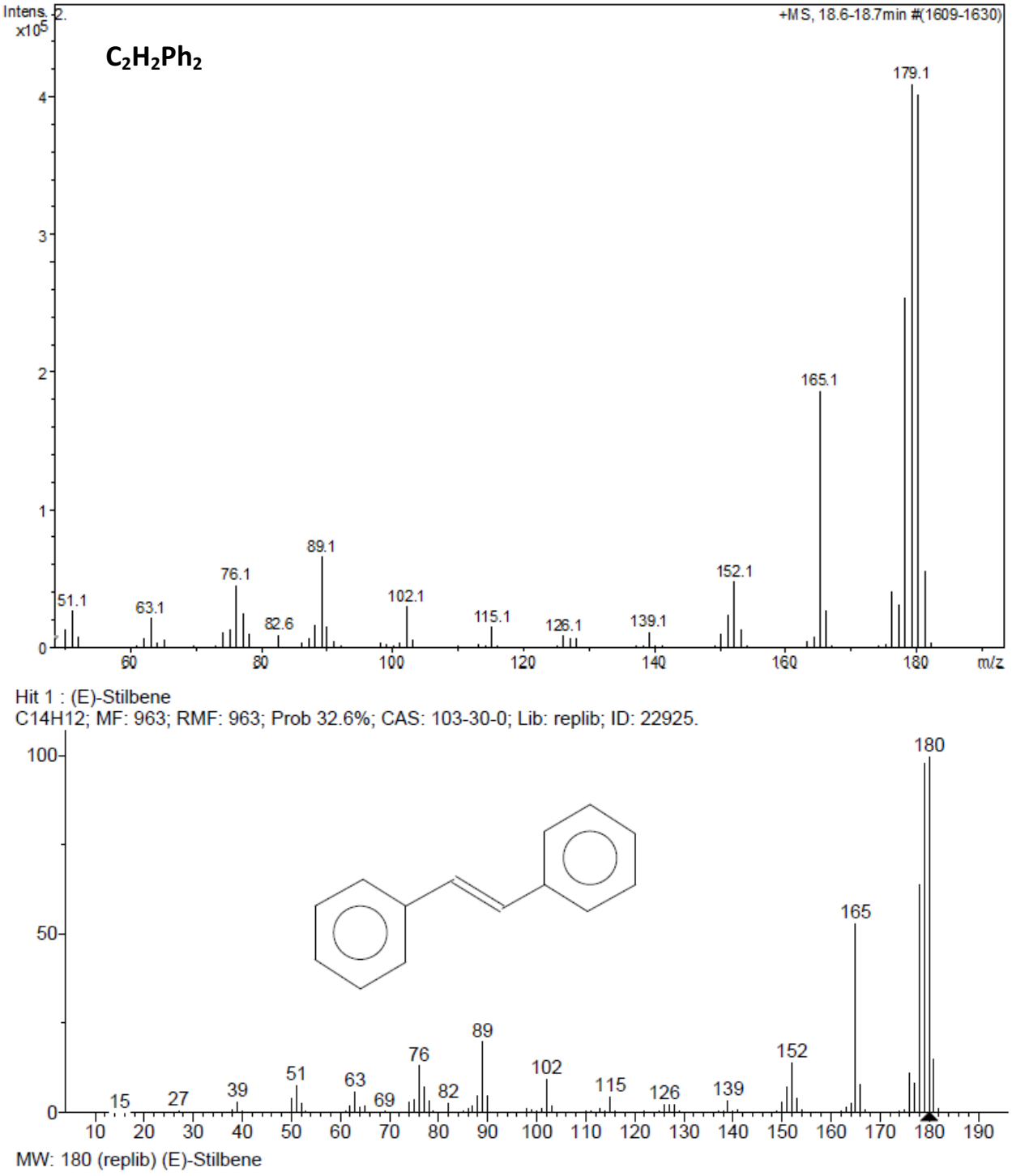
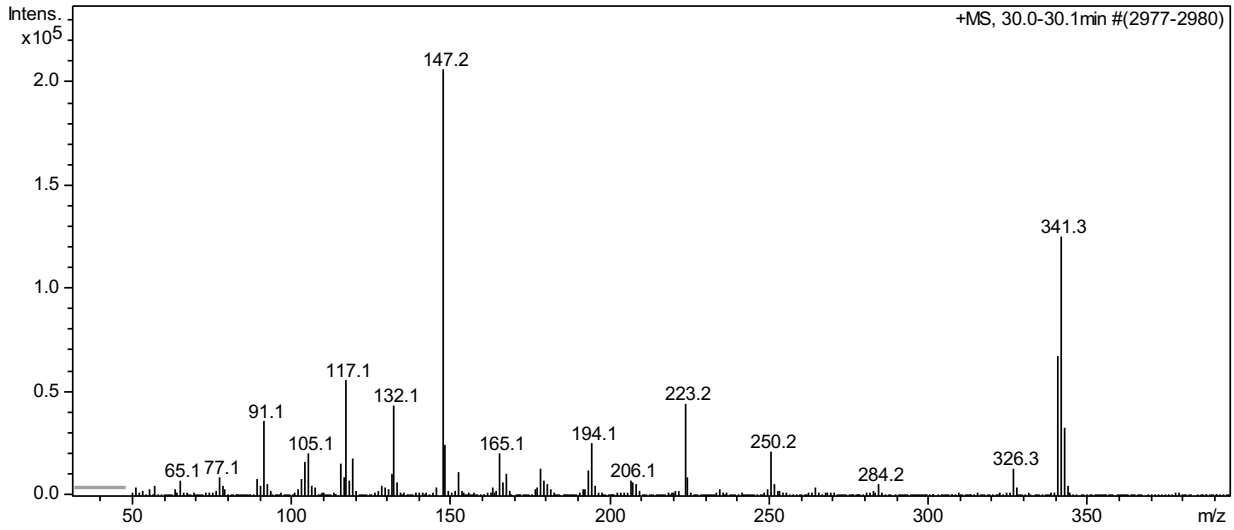
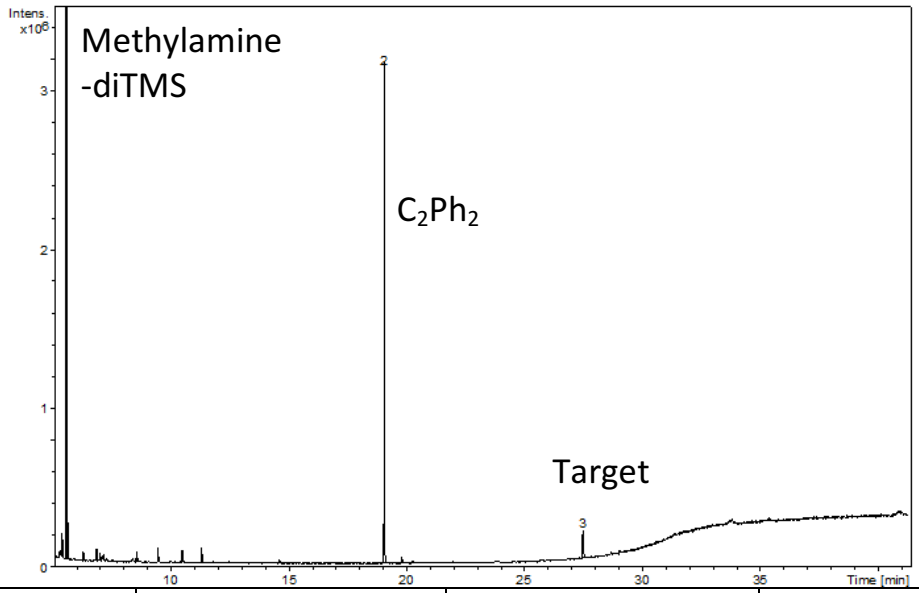


Figure S78: Mass spectra for compound 3 in the TIC
m/z 326 (-CH_3), m/z 147 (-$C_{14}H_{12}N$)



Mass Spec. Results for the reaction of 10 mol % of 1 with OctylAmine and Diphenylacetylene after 24 h at 110 °C (Table 2, Entry 6 in Manuscript)

The sample was diluted 500 fold in toluene, and then derivatized 1:1 with MSTFA. The sample was analyzed with Agilent GCMS on DB-5MS column after an one hour incubation at 60 °C. Did not detect starting reagent OctylAmine (MW 129).
Figure S79: Total ion chromatogram



#	RT [min]	Area	ID
1	5.6	17962416	Methylamine-diTMS
2	19.1	6661638	Diphenylacetylene
3	27.5	351046	MW307 - Target

Figure S80: Mass spectra for compound 3 (Target) in the TIC

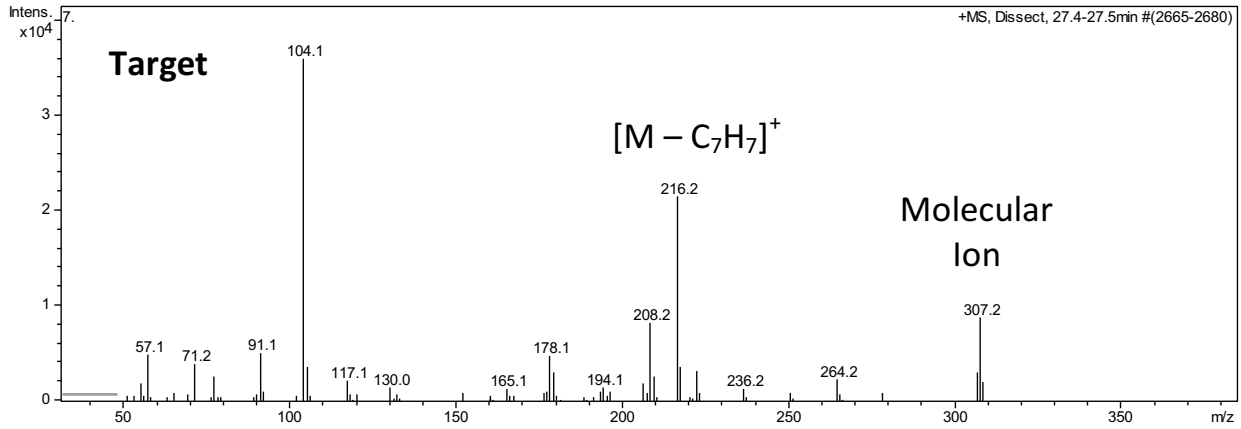


Figure S81: Mass spectra for compound 1 in the TIC

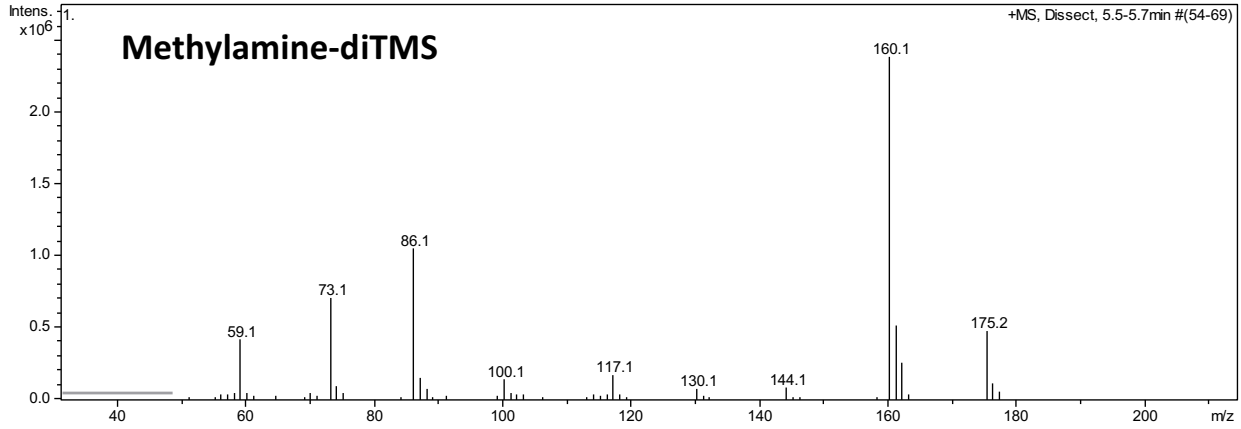
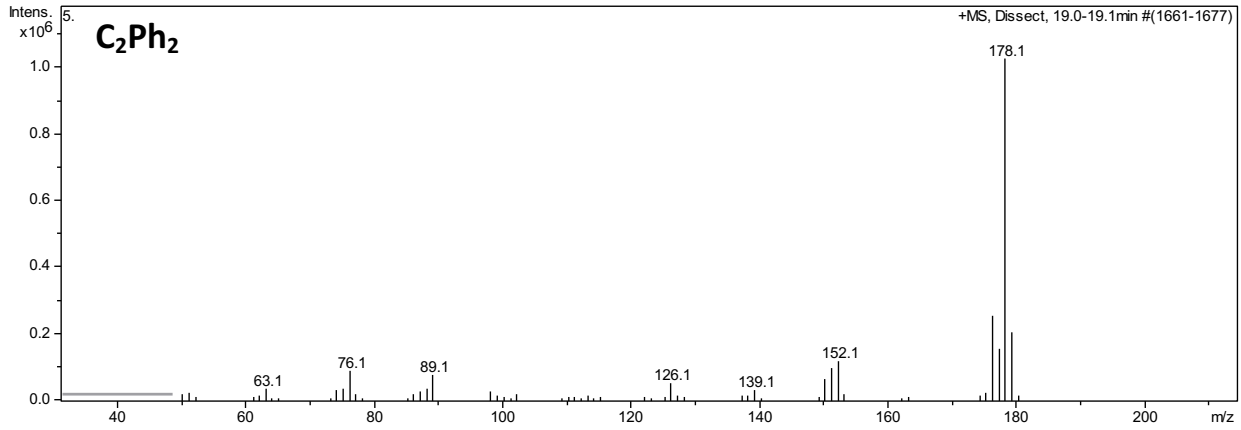
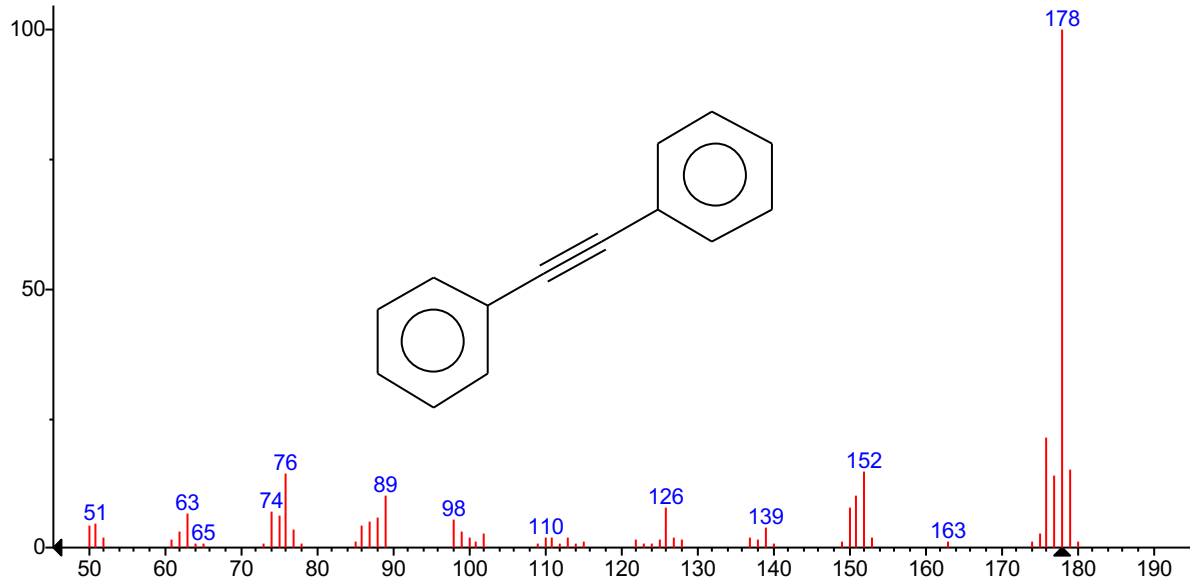


Figure S82: Mass spectra for compound 2 in the TIC and library mass spectra





MW: 178 (replib) Diphenylethyne