

Supporting Information for:

**Heterometallic Samarium(III) and Titanium(IV) Complex with
Bifunctional Catalytic Property**

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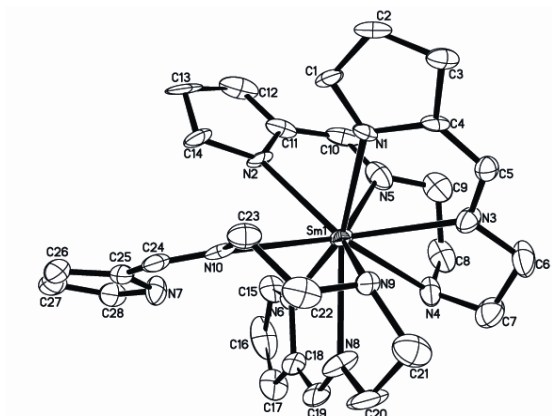
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1. Structural Data for [Sm(Hbptd)(H₂bptd)] (**1**)

(a)



(b)

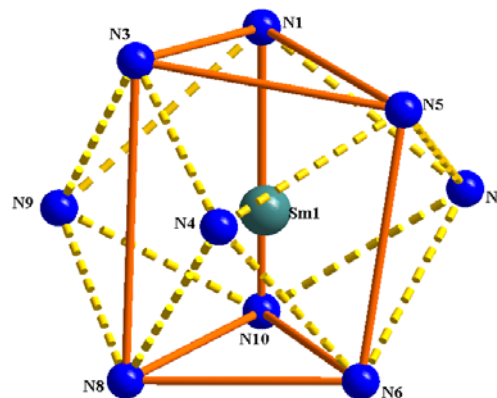


Figure S1. (a) Molecular structure of complex **1**. H atoms have been omitted for clarity. Selected bond lengths and angles are given in the Supporting Information. (b) View of the coordination polyhedron of samarium atom in **1**.

Table S1-1. Crystal data and structure refinement for **1**.

Complex	1
Empirical formula	C ₂₈ H ₃₅ N ₁₀ Sm
Formula weight(g mol ⁻¹)	662.01
Temperature	293(2) K
Wavelength	0.71073
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions	<i>a</i> = 9.390(1) Å
	<i>b</i> = 23.924(2) Å
	<i>c</i> = 13.7190(14) Å
	α = 90°
	β = 113.470(2)°
	γ = 90°
Volume (Å ³)	2827.0(5)
<i>Z</i>	4
ρ (g cm ⁻³)	1.556
<i>F</i> (000)	1340
Crystal size(mm ³)	0.24 x 0.26 x 0.48
Theta range for data collection	2.359° to 26.662°
Limiting indices	-11 ≤ <i>h</i> ≤ 10
	-28 ≤ <i>k</i> ≤ 28
	-16 ≤ <i>l</i> ≤ 14
Reflections collected / unique	12555 / 4713
Data / restraints / parameters	4713 / 0 / 352
GOF	1.080
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0980
	<i>wR</i> ₂ = 0.2163
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	<i>R</i> ₁ = 0.1434
	<i>wR</i> ₂ = 0.2436
Largest diff. peak and hole (e Å ⁻³)	0.352 and -4.036

Table S1-1. Bond lengths [Å] and angles [°] for **1**.

Sm(1)-N(2)	2.498(10)
Sm(1)-N(5)	2.502(15)
Sm(1)-N(1)	2.503(11)
Sm(1)-N(6)	2.526(11)
Sm(1)-N(3)	2.555(13)
Sm(1)-N(8)	2.609(14)
Sm(1)-N(9)	2.671(12)
Sm(1)-N(4)	2.714(12)
Sm(1)-N(10)	2.829(12)
N(1)-C(1)	1.342(17)
N(1)-C(4)	1.394(18)
N(2)-C(11)	1.342(19)
N(2)-C(14)	1.357(19)
N(3)-C(5)	1.30(2)
N(3)-C(6)	1.48(2)
N(4)-C(8)	1.47(3)
N(4)-C(7)	1.47(2)
N(4)-H(4)	0.9100
N(5)-C(10)	1.26(2)
N(5)-C(9)	1.44(2)
N(6)-C(15)	1.31(2)
N(6)-C(18)	1.42(2)
N(7)-C(28)	1.35(2)
N(7)-C(25)	1.35(2)
N(7)-H(7)	0.8600
N(8)-C(19)	1.28(2)
N(8)-C(20)	1.46(2)
N(9)-C(22)	1.47(2)
N(9)-C(21)	1.50(2)
N(9)-H(9)	0.9100
N(10)-C(24)	1.25(2)
N(10)-C(23)	1.50(2)
C(1)-C(2)	1.38(2)
C(1)-H(1)	0.9300
C(2)-C(3)	1.37(2)
C(2)-H(2)	0.9300
C(3)-C(4)	1.411(19)
C(3)-H(3)	0.9300
C(4)-C(5)	1.405(19)
C(5)-H(5)	0.9300
C(6)-C(7)	1.51(3)
C(6)-H(6A)	0.9700

C(6)-H(6B)	0.9700
C(7)-H(7A)	0.9700
C(7)-H(7B)	0.9700
C(8)-C(9)	1.56(3)
C(8)-H(8A)	0.9700
C(8)-H(8B)	0.9700
C(9)-H(9A)	0.9700
C(9)-H(9B)	0.9700
C(10)-C(11)	1.43(3)
C(10)-H(10)	0.9300
C(11)-C(12)	1.34(3)
C(12)-C(13)	1.39(3)
C(12)-H(12)	0.9300
C(13)-C(14)	1.42(2)
C(13)-H(13)	0.9300
C(14)-H(14)	0.9300
C(15)-C(16)	1.36(3)
C(15)-H(15)	0.9300
C(16)-C(17)	1.34(4)
C(16)-H(16)	0.9300
C(17)-C(18)	1.42(3)
C(17)-H(17)	0.9300
C(18)-C(19)	1.39(3)
C(19)-H(19)	0.9300
C(20)-C(21)	1.54(3)
C(20)-H(20A)	0.9700
C(20)-H(20B)	0.9700
C(21)-H(21A)	0.9700
C(21)-H(21B)	0.9700
C(22)-C(23)	1.51(2)
C(22)-H(22A)	0.9700
C(22)-H(22B)	0.9700
C(23)-H(23A)	0.9700
C(23)-H(23B)	0.9700
C(24)-C(25)	1.45(2)
C(24)-H(24)	0.9300
C(25)-C(26)	1.31(2)
C(26)-C(27)	1.41(3)
C(26)-H(26)	0.9300
C(27)-C(28)	1.33(2)
C(27)-H(27)	0.9300
C(28)-H(28)	0.9300
N(2)-Sm(1)-N(5)	66.4(5)
N(2)-Sm(1)-N(1)	74.7(4)

N(5)-Sm(1)-N(1)	84.1(4)
N(2)-Sm(1)-N(6)	80.7(4)
N(5)-Sm(1)-N(6)	81.8(5)
N(1)-Sm(1)-N(6)	155.0(5)
N(2)-Sm(1)-N(3)	128.6(4)
N(5)-Sm(1)-N(3)	77.3(5)
N(1)-Sm(1)-N(3)	66.3(4)
N(6)-Sm(1)-N(3)	129.5(4)
N(2)-Sm(1)-N(8)	134.7(4)
N(5)-Sm(1)-N(8)	131.5(5)
N(1)-Sm(1)-N(8)	137.8(4)
N(6)-Sm(1)-N(8)	65.3(4)
N(3)-Sm(1)-N(8)	96.6(5)
N(2)-Sm(1)-N(9)	129.5(4)
N(5)-Sm(1)-N(9)	147.1(4)
N(1)-Sm(1)-N(9)	75.3(4)
N(6)-Sm(1)-N(9)	125.7(4)
N(3)-Sm(1)-N(9)	71.1(4)
N(8)-Sm(1)-N(9)	62.5(4)
N(2)-Sm(1)-N(4)	124.0(5)
N(5)-Sm(1)-N(4)	64.1(5)
N(1)-Sm(1)-N(4)	123.0(4)
N(6)-Sm(1)-N(4)	68.1(4)
N(3)-Sm(1)-N(4)	61.5(4)
N(8)-Sm(1)-N(4)	70.7(5)
N(9)-Sm(1)-N(4)	106.4(5)
N(2)-Sm(1)-N(10)	73.3(4)
N(5)-Sm(1)-N(10)	139.7(5)
N(1)-Sm(1)-N(10)	85.2(3)
N(6)-Sm(1)-N(10)	92.2(4)
N(3)-Sm(1)-N(10)	131.9(4)
N(8)-Sm(1)-N(10)	78.9(4)
N(9)-Sm(1)-N(10)	64.5(4)
N(4)-Sm(1)-N(10)	148.6(4)
C(1)-N(1)-C(4)	104.1(12)
C(1)-N(1)-Sm(1)	139.3(10)
C(4)-N(1)-Sm(1)	115.7(8)
C(11)-N(2)-C(14)	106.1(13)
C(11)-N(2)-Sm(1)	115.0(10)
C(14)-N(2)-Sm(1)	138.9(10)
C(5)-N(3)-C(6)	117.6(14)
C(5)-N(3)-Sm(1)	116.2(10)
C(6)-N(3)-Sm(1)	126.1(11)
C(8)-N(4)-C(7)	115.1(14)

C(8)-N(4)-Sm(1)	114.0(12)
C(7)-N(4)-Sm(1)	109.7(11)
C(8)-N(4)-H(4)	105.7
C(7)-N(4)-H(4)	105.7
Sm(1)-N(4)-H(4)	105.7
C(10)-N(5)-C(9)	119.3(17)
C(10)-N(5)-Sm(1)	118.6(11)
C(9)-N(5)-Sm(1)	122.0(14)
C(15)-N(6)-C(18)	104.1(14)
C(15)-N(6)-Sm(1)	139.2(11)
C(18)-N(6)-Sm(1)	115.8(11)
C(28)-N(7)-C(25)	106.6(13)
C(28)-N(7)-H(7)	126.7
C(25)-N(7)-H(7)	126.7
C(19)-N(8)-C(20)	121.8(17)
C(19)-N(8)-Sm(1)	117.2(13)
C(20)-N(8)-Sm(1)	121.0(11)
C(22)-N(9)-C(21)	110.0(13)
C(22)-N(9)-Sm(1)	116.3(9)
C(21)-N(9)-Sm(1)	111.7(10)
C(22)-N(9)-H(9)	106.0
C(21)-N(9)-H(9)	106.0
Sm(1)-N(9)-H(9)	106.0
C(24)-N(10)-C(23)	114.8(13)
C(24)-N(10)-Sm(1)	142.5(12)
C(23)-N(10)-Sm(1)	102.6(9)
N(1)-C(1)-C(2)	113.2(14)
N(1)-C(1)-H(1)	123.4
C(2)-C(1)-H(1)	123.4
C(3)-C(2)-C(1)	106.2(13)
C(3)-C(2)-H(2)	126.9
C(1)-C(2)-H(2)	126.9
C(2)-C(3)-C(4)	106.7(14)
C(2)-C(3)-H(3)	126.6
C(4)-C(3)-H(3)	126.6
N(1)-C(4)-C(5)	118.8(12)
N(1)-C(4)-C(3)	109.6(12)
C(5)-C(4)-C(3)	131.1(14)
N(3)-C(5)-C(4)	121.7(13)
N(3)-C(5)-H(5)	119.2
C(4)-C(5)-H(5)	119.2
N(3)-C(6)-C(7)	107.3(14)
N(3)-C(6)-H(6A)	110.3
C(7)-C(6)-H(6A)	110.3

N(3)-C(6)-H(6B)	110.3
C(7)-C(6)-H(6B)	110.3
H(6A)-C(6)-H(6B)	108.5
N(4)-C(7)-C(6)	112.5(18)
N(4)-C(7)-H(7A)	109.1
C(6)-C(7)-H(7A)	109.1
N(4)-C(7)-H(7B)	109.1
C(6)-C(7)-H(7B)	109.1
H(7A)-C(7)-H(7B)	107.8
N(4)-C(8)-C(9)	112.3(14)
N(4)-C(8)-H(8A)	109.1
C(9)-C(8)-H(8A)	109.1
N(4)-C(8)-H(8B)	109.1
C(9)-C(8)-H(8B)	109.1
H(8A)-C(8)-H(8B)	107.9
N(5)-C(9)-C(8)	106.5(15)
N(5)-C(9)-H(9A)	110.4
C(8)-C(9)-H(9A)	110.4
N(5)-C(9)-H(9B)	110.4
C(8)-C(9)-H(9B)	110.4
H(9A)-C(9)-H(9B)	108.6
N(5)-C(10)-C(11)	119.2(14)
N(5)-C(10)-H(10)	120.4
C(11)-C(10)-H(10)	120.4
N(2)-C(11)-C(12)	110.4(17)
N(2)-C(11)-C(10)	120.8(15)
C(12)-C(11)-C(10)	128.4(16)
C(11)-C(12)-C(13)	110.3(15)
C(11)-C(12)-H(12)	124.9
C(13)-C(12)-H(12)	124.9
C(12)-C(13)-C(14)	101.9(16)
C(12)-C(13)-H(13)	129.1
C(14)-C(13)-H(13)	129.1
N(2)-C(14)-C(13)	111.2(16)
N(2)-C(14)-H(14)	124.4
C(13)-C(14)-H(14)	124.4
N(6)-C(15)-C(16)	114(2)
N(6)-C(15)-H(15)	123.1
C(16)-C(15)-H(15)	123.1
C(17)-C(16)-C(15)	108(2)
C(17)-C(16)-H(16)	126.2
C(15)-C(16)-H(16)	126.2
C(16)-C(17)-C(18)	106.6(19)
C(16)-C(17)-H(17)	126.7

C(18)-C(17)-H(17)	126.7
C(19)-C(18)-N(6)	119.6(14)
C(19)-C(18)-C(17)	132.6(19)
N(6)-C(18)-C(17)	108(2)
N(8)-C(19)-C(18)	121.8(17)
N(8)-C(19)-H(19)	119.1
C(18)-C(19)-H(19)	119.1
N(8)-C(20)-C(21)	112.6(16)
N(8)-C(20)-H(20A)	109.1
C(21)-C(20)-H(20A)	109.1
N(8)-C(20)-H(20B)	109.1
C(21)-C(20)-H(20B)	109.1
H(20A)-C(20)-H(20B)	107.8
N(9)-C(21)-C(20)	106.5(16)
N(9)-C(21)-H(21A)	110.4
C(20)-C(21)-H(21A)	110.4
N(9)-C(21)-H(21B)	110.4
C(20)-C(21)-H(21B)	110.4
H(21A)-C(21)-H(21B)	108.6
N(9)-C(22)-C(23)	110.2(13)
N(9)-C(22)-H(22A)	109.6
C(23)-C(22)-H(22A)	109.6
N(9)-C(22)-H(22B)	109.6
C(23)-C(22)-H(22B)	109.6
H(22A)-C(22)-H(22B)	108.1
N(10)-C(23)-C(22)	108.6(13)
N(10)-C(23)-H(23A)	110.0
C(22)-C(23)-H(23A)	110.0
N(10)-C(23)-H(23B)	110.0
C(22)-C(23)-H(23B)	110.0
H(23A)-C(23)-H(23B)	108.4
N(10)-C(24)-C(25)	127.6(15)
N(10)-C(24)-H(24)	116.2
C(25)-C(24)-H(24)	116.2
C(26)-C(25)-N(7)	110.2(18)
C(26)-C(25)-C(24)	127.3(18)
N(7)-C(25)-C(24)	122.4(13)
C(25)-C(26)-C(27)	107.4(16)
C(25)-C(26)-H(26)	126.3
C(27)-C(26)-H(26)	126.3
C(28)-C(27)-C(26)	105.7(17)
C(28)-C(27)-H(27)	127.1
C(26)-C(27)-H(27)	127.1
C(27)-C(28)-N(7)	110.0(17)

C(27)-C(28)-H(28)	125.0
N(7)-C(28)-H(28)	125.0

2. Structural Data for [Sm(Hbptd)(THF)(bptd)Ti(NMe₂)₂] (**2**)

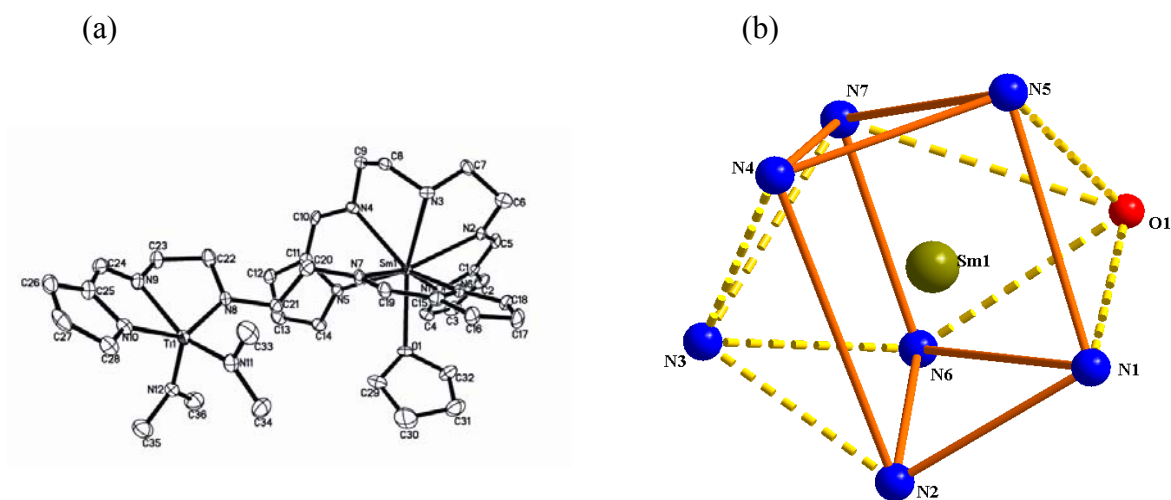


Figure S2. (a) Molecular structure of complex **2**. H atoms have been omitted for clarity. Selected bond lengths and angles are given in the Supporting Information. (b) View of the coordination polyhedron of samarium atom in **2**.

Table S2-1. Crystal data and structure refinement for **2**.

Complex	2
Empirical formula	C ₃₆ H ₅₃ N ₁₂ OSmTi (C ₄ O) _{0.8}
Formula weight(g mol ⁻¹)	919.37
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	<i>P</i> -1
Unit cell dimensions	<i>a</i> = 10.580(2) Å
	<i>b</i> = 13.715(3) Å
	<i>c</i> = 15.855(3) Å
	α = 102.19(3)°
	β = 101.24(3)°
	γ = 95.28(3)°
Volume (Å ³)	2184.2(8)
<i>Z</i>	2
ρ (g cm ⁻³)	1.398
<i>F</i> (000)	941
Crystal size(mm ³)	0.20 x 0.16 x 0.08
Theta range for data collection	1.79° to 20.60°
Limiting indices	-10 ≤ <i>h</i> ≤ 10
	-12 ≤ <i>k</i> ≤ 13
	-15 ≤ <i>l</i> ≤ 15
Reflections collected / unique	11119 / 4402
Data / restraints / parameters	4402 / 41 / 513
GOF	1.062
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0515
	<i>wR</i> ₂ = 0.1230
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	<i>R</i> ₁ = 0.0699
	<i>wR</i> ₂ = 0.1332
Largest diff. peak and hole (e Å ³)	2.594 and -0.953

Table S2-2. Bond lengths [Å] and angles [°] for **2**.

Sm(1)-N(1)	2.4893(15)
Sm(1)-N(6)	2.4939(15)
Sm(1)-O(1)	2.5029(14)
Sm(1)-N(5)	2.5037(17)
Sm(1)-N(4)	2.5180(17)
Sm(1)-N(2)	2.5257(16)
Sm(1)-N(7)	2.6016(16)
Sm(1)-N(3)	2.6956(17)
Ti(1)-N(12)	1.8871(17)
Ti(1)-N(11)	1.9015(17)
Ti(1)-N(8)	1.9329(15)
Ti(1)-N(10)	2.1072(16)
Ti(1)-N(9)	2.1666(17)
N(9)-C(24)	1.270(3)
N(9)-C(23)	1.460(2)
N(7)-C(19)	1.282(2)
N(7)-C(20)	1.473(3)
N(1)-C(4)	1.345(2)
N(1)-C(1)	1.358(2)
N(4)-C(10)	1.280(3)
N(4)-C(9)	1.464(2)
N(6)-C(18)	1.345(3)
N(6)-C(15)	1.385(2)
N(3)-C(8)	1.472(2)
N(3)-C(7)	1.487(2)
N(3)-HN1	0.995(6)
O(1)-C(29)	1.420(2)
O(1)-C(32)	1.448(3)
N(10)-C(28)	1.359(2)
N(10)-C(25)	1.389(3)
N(2)-C(5)	1.290(2)
N(2)-C(6)	1.467(3)
C(19)-C(15)	1.428(3)
C(19)-H(19)	0.9300
C(10)-C(11)	1.412(3)
C(10)-H(10)	0.9300
C(8)-C(9)	1.519(2)
C(8)-H(8A)	0.9700
C(8)-H(8B)	0.9700
N(5)-C(14)	1.339(2)
N(5)-C(11)	1.380(2)

C(9)-H(9A)	0.9700
C(9)-H(9B)	0.9700
C(1)-C(2)	1.383(2)
C(1)-C(5)	1.415(3)
C(17)-C(16)	1.377(3)
C(17)-C(18)	1.403(2)
C(17)-H(17)	0.9300
C(20)-C(21)	1.519(3)
C(20)-H(20A)	0.9700
C(20)-H(20B)	0.9700
C(15)-C(16)	1.391(3)
C(14)-C(13)	1.377(3)
C(14)-H(14)	0.9300
C(32)-C(31)	1.509(3)
C(32)-H(32A)	0.9700
C(32)-H(32B)	0.9700
C(22)-N(8)	1.462(2)
C(22)-C(23)	1.497(3)
C(22)-H(22A)	0.9700
C(22)-H(22B)	0.9700
C(24)-C(25)	1.436(2)
C(24)-H(24)	0.9300
C(27)-C(26)	1.391(3)
C(27)-C(28)	1.395(3)
C(27)-H(27)	0.9300
N(11)-C(33)	1.429(3)
N(11)-C(34)	1.467(3)
C(16)-H(16)	0.9300
C(2)-C(3)	1.376(3)
C(2)-H(2)	0.9300
C(29)-C(30)	1.421(3)
C(29)-H(29A)	0.9700
C(29)-H(29B)	0.9700
C(18)-H(18)	0.9300
C(21)-N(8)	1.458(3)
C(21)-H(21A)	0.9700
C(21)-H(21B)	0.9700
C(34)-H(34A)	0.9600
C(34)-H(34B)	0.9600
C(34)-H(34C)	0.9600
C(26)-C(25)	1.369(3)
C(26)-H(26)	0.9300
C(12)-C(13)	1.370(3)
C(12)-C(11)	1.387(3)

C(12)-H(12)	0.9300
C(28)-H(28)	0.9300
C(4)-C(3)	1.398(3)
C(4)-H(4)	0.9300
C(6)-C(7)	1.510(3)
C(6)-H(6A)	0.9700
C(6)-H(6B)	0.9700
C(3)-H(3)	0.9300
C(36)-N(12)	1.453(2)
C(36)-H(36A)	0.9600
C(36)-H(36B)	0.9600
C(36)-H(36C)	0.9600
C(31)-C(30)	1.492(4)
C(31)-H(31A)	0.9700
C(31)-H(31B)	0.9700
C(33)-H(33A)	0.9600
C(33)-H(33B)	0.9600
C(33)-H(33C)	0.9600
C(13)-H(13)	0.9300
C(23)-H(23A)	0.9700
C(23)-H(23B)	0.9700
C(7)-H(7A)	0.9700
C(7)-H(7B)	0.9700
C(5)-H(5)	0.9300
C(30)-H(30A)	0.9700
C(30)-H(30B)	0.9700
N(12)-C(35)	1.454(2)
C(35)-H(35A)	0.9600
C(35)-H(35B)	0.9600
C(35)-H(35C)	0.9600
C(39)-C(38)	1.232(5)
C(39)-C(40)	1.354(4)
O(2)-C(40)	1.387(4)
O(2)-C(37)	1.399(4)
C(37)-C(38)	1.639(5)
N(1)-Sm(1)-N(6)	112.09(6)
N(1)-Sm(1)-O(1)	76.49(5)
N(6)-Sm(1)-O(1)	74.32(5)
N(1)-Sm(1)-N(5)	81.78(6)
N(6)-Sm(1)-N(5)	141.97(5)
O(1)-Sm(1)-N(5)	75.12(5)
N(1)-Sm(1)-N(4)	110.55(5)
N(6)-Sm(1)-N(4)	131.35(5)
O(1)-Sm(1)-N(4)	138.81(5)

N(5)-Sm(1)-N(4)	66.35(5)
N(1)-Sm(1)-N(2)	65.10(5)
N(6)-Sm(1)-N(2)	77.05(5)
O(1)-Sm(1)-N(2)	117.57(5)
N(5)-Sm(1)-N(2)	138.25(5)
N(4)-Sm(1)-N(2)	101.13(5)
N(1)-Sm(1)-N(7)	158.31(5)
N(6)-Sm(1)-N(7)	67.27(6)
O(1)-Sm(1)-N(7)	82.76(5)
N(5)-Sm(1)-N(7)	86.93(5)
N(4)-Sm(1)-N(7)	81.25(5)
N(2)-Sm(1)-N(7)	132.18(5)
N(1)-Sm(1)-N(3)	125.88(5)
N(6)-Sm(1)-N(3)	72.39(5)
O(1)-Sm(1)-N(3)	145.21(4)
N(5)-Sm(1)-N(3)	129.19(5)
N(4)-Sm(1)-N(3)	64.10(5)
N(2)-Sm(1)-N(3)	63.87(5)
N(7)-Sm(1)-N(3)	75.39(5)
N(12)-Ti(1)-N(11)	101.75(7)
N(12)-Ti(1)-N(8)	104.25(6)
N(11)-Ti(1)-N(8)	100.45(7)
N(12)-Ti(1)-N(10)	112.54(7)
N(11)-Ti(1)-N(10)	93.85(7)
N(8)-Ti(1)-N(10)	136.67(7)
N(12)-Ti(1)-N(9)	107.39(7)
N(11)-Ti(1)-N(9)	150.76(7)
N(8)-Ti(1)-N(9)	74.88(7)
N(10)-Ti(1)-N(9)	72.97(6)
C(24)-N(9)-C(23)	124.64(16)
C(24)-N(9)-Ti(1)	119.11(11)
C(23)-N(9)-Ti(1)	115.31(12)
C(19)-N(7)-C(20)	116.62(14)
C(19)-N(7)-Sm(1)	113.35(12)
C(20)-N(7)-Sm(1)	130.01(10)
C(4)-N(1)-C(1)	105.53(14)
C(4)-N(1)-Sm(1)	136.48(12)
C(1)-N(1)-Sm(1)	117.41(11)
C(10)-N(4)-C(9)	119.80(16)
C(10)-N(4)-Sm(1)	116.86(12)
C(9)-N(4)-Sm(1)	122.64(12)
C(18)-N(6)-C(15)	105.01(14)
C(18)-N(6)-Sm(1)	138.62(11)
C(15)-N(6)-Sm(1)	116.10(12)

C(8)-N(3)-C(7)	111.93(14)
C(8)-N(3)-Sm(1)	111.33(11)
C(7)-N(3)-Sm(1)	114.75(10)
C(8)-N(3)-HN1	102.1(5)
C(7)-N(3)-HN1	117.0(6)
Sm(1)-N(3)-HN1	98.4(6)
C(29)-O(1)-C(32)	107.16(15)
C(29)-O(1)-Sm(1)	130.06(13)
C(32)-O(1)-Sm(1)	116.10(11)
C(28)-N(10)-C(25)	104.14(16)
C(28)-N(10)-Ti(1)	137.09(14)
C(25)-N(10)-Ti(1)	118.71(10)
C(5)-N(2)-C(6)	120.33(16)
C(5)-N(2)-Sm(1)	118.79(13)
C(6)-N(2)-Sm(1)	120.49(10)
N(7)-C(19)-C(15)	124.30(16)
N(7)-C(19)-H(19)	117.9
C(15)-C(19)-H(19)	117.9
N(4)-C(10)-C(11)	122.25(17)
N(4)-C(10)-H(10)	118.9
C(11)-C(10)-H(10)	118.9
N(3)-C(8)-C(9)	110.24(14)
N(3)-C(8)-H(8A)	109.6
C(9)-C(8)-H(8A)	109.6
N(3)-C(8)-H(8B)	109.6
C(9)-C(8)-H(8B)	109.6
H(8A)-C(8)-H(8B)	108.1
C(14)-N(5)-C(11)	105.11(16)
C(14)-N(5)-Sm(1)	138.35(13)
C(11)-N(5)-Sm(1)	115.92(12)
N(4)-C(9)-C(8)	107.39(14)
N(4)-C(9)-H(9A)	110.2
C(8)-C(9)-H(9A)	110.2
N(4)-C(9)-H(9B)	110.2
C(8)-C(9)-H(9B)	110.2
H(9A)-C(9)-H(9B)	108.5
N(1)-C(1)-C(2)	110.93(17)
N(1)-C(1)-C(5)	119.08(15)
C(2)-C(1)-C(5)	129.98(18)
C(16)-C(17)-C(18)	106.18(17)
C(16)-C(17)-H(17)	126.9
C(18)-C(17)-H(17)	126.9
N(7)-C(20)-C(21)	113.15(16)
N(7)-C(20)-H(20A)	108.9

C(21)-C(20)-H(20A)	108.9
N(7)-C(20)-H(20B)	108.9
C(21)-C(20)-H(20B)	108.9
H(20A)-C(20)-H(20B)	107.8
N(6)-C(15)-C(16)	110.59(17)
N(6)-C(15)-C(19)	118.88(15)
C(16)-C(15)-C(19)	130.51(16)
N(5)-C(14)-C(13)	112.06(18)
N(5)-C(14)-H(14)	124.0
C(13)-C(14)-H(14)	124.0
O(1)-C(32)-C(31)	105.41(16)
O(1)-C(32)-H(32A)	110.7
C(31)-C(32)-H(32A)	110.7
O(1)-C(32)-H(32B)	110.7
C(31)-C(32)-H(32B)	110.7
H(32A)-C(32)-H(32B)	108.8
N(8)-C(22)-C(23)	109.65(15)
N(8)-C(22)-H(22A)	109.7
C(23)-C(22)-H(22A)	109.7
N(8)-C(22)-H(22B)	109.7
C(23)-C(22)-H(22B)	109.7
H(22A)-C(22)-H(22B)	108.2
N(9)-C(24)-C(25)	116.61(18)
N(9)-C(24)-H(24)	121.7
C(25)-C(24)-H(24)	121.7
C(26)-C(27)-C(28)	106.05(16)
C(26)-C(27)-H(27)	127.0
C(28)-C(27)-H(27)	127.0
C(33)-N(11)-C(34)	111.72(17)
C(33)-N(11)-Ti(1)	119.04(14)
C(34)-N(11)-Ti(1)	128.73(13)
C(17)-C(16)-C(15)	106.64(15)
C(17)-C(16)-H(16)	126.7
C(15)-C(16)-H(16)	126.7
C(3)-C(2)-C(1)	106.63(17)
C(3)-C(2)-H(2)	126.7
C(1)-C(2)-H(2)	126.7
C(30)-C(29)-O(1)	109.2(2)
C(30)-C(29)-H(29A)	109.8
O(1)-C(29)-H(29A)	109.8
C(30)-C(29)-H(29B)	109.8
O(1)-C(29)-H(29B)	109.8
H(29A)-C(29)-H(29B)	108.3
N(6)-C(18)-C(17)	111.57(16)

N(6)-C(18)-H(18)	124.2
C(17)-C(18)-H(18)	124.2
N(8)-C(21)-C(20)	113.21(16)
N(8)-C(21)-H(21A)	108.9
C(20)-C(21)-H(21A)	108.9
N(8)-C(21)-H(21B)	108.9
C(20)-C(21)-H(21B)	108.9
H(21A)-C(21)-H(21B)	107.7
N(11)-C(34)-H(34A)	109.5
N(11)-C(34)-H(34B)	109.5
H(34A)-C(34)-H(34B)	109.5
N(11)-C(34)-H(34C)	109.5
H(34A)-C(34)-H(34C)	109.5
H(34B)-C(34)-H(34C)	109.5
C(25)-C(26)-C(27)	106.58(19)
C(25)-C(26)-H(26)	126.7
C(27)-C(26)-H(26)	126.7
C(13)-C(12)-C(11)	107.00(18)
C(13)-C(12)-H(12)	126.5
C(11)-C(12)-H(12)	126.5
N(10)-C(28)-C(27)	111.62(18)
N(10)-C(28)-H(28)	124.2
C(27)-C(28)-H(28)	124.2
N(1)-C(4)-C(3)	111.12(18)
N(1)-C(4)-H(4)	124.4
C(3)-C(4)-H(4)	124.4
N(2)-C(6)-C(7)	108.48(17)
N(2)-C(6)-H(6A)	110.0
C(7)-C(6)-H(6A)	110.0
N(2)-C(6)-H(6B)	110.0
C(7)-C(6)-H(6B)	110.0
H(6A)-C(6)-H(6B)	108.4
C(2)-C(3)-C(4)	105.77(17)
C(2)-C(3)-H(3)	127.1
C(4)-C(3)-H(3)	127.1
N(12)-C(36)-H(36A)	109.5
N(12)-C(36)-H(36B)	109.5
H(36A)-C(36)-H(36B)	109.5
N(12)-C(36)-H(36C)	109.5
H(36A)-C(36)-H(36C)	109.5
H(36B)-C(36)-H(36C)	109.5
C(30)-C(31)-C(32)	102.59(18)
C(30)-C(31)-H(31A)	111.2
C(32)-C(31)-H(31A)	111.2

C(30)-C(31)-H(31B)	111.2
C(32)-C(31)-H(31B)	111.2
H(31A)-C(31)-H(31B)	109.2
N(11)-C(33)-H(33A)	109.5
N(11)-C(33)-H(33B)	109.5
H(33A)-C(33)-H(33B)	109.5
N(11)-C(33)-H(33C)	109.5
H(33A)-C(33)-H(33C)	109.5
H(33B)-C(33)-H(33C)	109.5
C(12)-C(13)-C(14)	106.17(19)
C(12)-C(13)-H(13)	126.9
C(14)-C(13)-H(13)	126.9
N(9)-C(23)-C(22)	104.49(14)
N(9)-C(23)-H(23A)	110.9
C(22)-C(23)-H(23A)	110.9
N(9)-C(23)-H(23B)	110.9
C(22)-C(23)-H(23B)	110.9
H(23A)-C(23)-H(23B)	108.9
N(3)-C(7)-C(6)	109.49(15)
N(3)-C(7)-H(7A)	109.8
C(6)-C(7)-H(7A)	109.8
N(3)-C(7)-H(7B)	109.8
C(6)-C(7)-H(7B)	109.8
H(7A)-C(7)-H(7B)	108.2
N(2)-C(5)-C(1)	118.86(17)
N(2)-C(5)-H(5)	120.6
C(1)-C(5)-H(5)	120.6
N(5)-C(11)-C(12)	109.65(16)
N(5)-C(11)-C(10)	118.06(17)
C(12)-C(11)-C(10)	132.29(18)
C(29)-C(30)-C(31)	108.03(19)
C(29)-C(30)-H(30A)	110.1
C(31)-C(30)-H(30A)	110.1
C(29)-C(30)-H(30B)	110.1
C(31)-C(30)-H(30B)	110.1
H(30A)-C(30)-H(30B)	108.4
C(26)-C(25)-N(10)	111.60(15)
C(26)-C(25)-C(24)	135.7(2)
N(10)-C(25)-C(24)	112.51(16)
C(35)-N(12)-C(36)	112.19(16)
C(35)-N(12)-Ti(1)	116.69(12)
C(36)-N(12)-Ti(1)	129.92(13)
N(12)-C(35)-H(35A)	109.5
N(12)-C(35)-H(35B)	109.5

H(35A)-C(35)-H(35B)	109.5
N(12)-C(35)-H(35C)	109.5
H(35A)-C(35)-H(35C)	109.5
H(35B)-C(35)-H(35C)	109.5
C(21)-N(8)-C(22)	112.44(13)
C(21)-N(8)-Ti(1)	124.00(11)
C(22)-N(8)-Ti(1)	123.27(13)
C(38)-C(39)-C(40)	111.4(3)
C(40)-O(2)-C(37)	113.3(2)
O(2)-C(37)-C(38)	95.3(3)
C(39)-C(40)-O(2)	108.0(3)
C(39)-C(38)-C(37)	109.7(3)

3. Syntheses of **1** and **2**

General Considerations. All manipulations of air-sensitive compounds were carried out in an MBraun drybox under a purified nitrogen atmosphere. Hexane, toluene and THF were purchased from commercial suppliers and dried over purple sodium benzophenone ketyl. Deuterated solvent was dried over phosphoric anhydride (CDCl_3) and distilled under a nitrogen atmosphere. Elemental analyses (C, H, N) were performed with a Carlo-Erba EA 1110 CHNO-S microanalyzer.

X-ray Crystallography. Crystals grown from concentrated solutions at room temperature were quickly selected and mounted on a glass fiber in wax. The data collections were carried out with a Bruker SMART APEX II CCD diffractometer equipped with graphite-monochromated Mo- $K\alpha$ radiation by using the θ/ω scan technique at room temperature. The structures were solved by direct methods with SHELXS-97. The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by use of geometrical restraints. A full-matrix least-squares refinement on F^2 was carried out using SHELXL-97. CCDC-668001 (**1**) and CCDC-753285 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Centre, 12 Union Road, Cambridge CB21EZ, UK; Fax: +44-1223-336-033; or deposit@ccdc.cam.ac.uk).

Synthesis of [Sm(Hbptd)(H₂bptd)] (1**).** To a solution of $\text{Sm}[\text{N}(\text{SiMe}_3)_2]_3$ (0.423 g, 0.67 mmol) in THF (5 mL) was added frozen H_3bptd (0.344 g, 1.34 mmol) in THF (5 mL) dropwise. The reaction mixture was stirred overnight at room temperature. After which time, the solvent was removed to give a yellow powder. The resulting powder was crystallized from THF at -35°C to afford yellow crystalline solid. Yield: 0.337 g (76%). Elemental analysis: calcd. for $\text{C}_{28}\text{H}_{35}\text{N}_{10}\text{Sm}$: C 50.80; H 5.33; N 21.16 %; found: C 51.39; H 5.19; N 20.54%.

Synthesis of [Sm(Hbptd)(THF)(bptd)Ti(NMe₂)₂] (2**).** To a solution of **1** (0.830 g, 1.25 mmol)

in THF (5 mL) was added frozen $\text{Ti}(\text{NMe}_2)_4$ (0.281 g, 1.25 mmol) in THF (5 mL) dropwise. The reaction mixture was stirred overnight at room temperature. After which time, the solvent was removed to give a brown powder. The resulting powder was crystallized from THF at -35°C to afford orange crystalline solid. Yield: 0.757 g (66%). Elemental analysis: calcd. for $\text{C}_{36}\text{H}_{52}\text{N}_{12}\text{OSmTi}$: C 49.81; H 6.15; N 19.36%; found: C 49.62; H 6.03; N 18.94 %.

Synthesis of $[\text{Ti}(\text{bptd})(\text{NMe}_2)]$ (3). To a solution of H_3bptd (0.515 g, 2.00 mmol) in THF (5 mL) was added frozen $\text{Ti}(\text{NMe}_2)_4$ (0.448 g, 2.00 mmol) in THF (5 mL) dropwise. The reaction mixture was stirred overnight at room temperature. After which time, the solvent was removed to give a red-brown powder. Yield: 0.671 g (93%). $^1\text{H NMR}$ (400 MHz, C_6D_6): $\delta = 7.30$ (s, 2 H, $-\text{HC}=\text{N}$), 7.02 (s, 2 H, $-\text{C}_4\text{H}_3\text{N}$), $\delta = 6.70$ (m, 2 H, $4-\text{C}_4\text{H}_3\text{N}$), $\delta = 6.44$ (s, 2 H, $-\text{C}_4\text{H}_3\text{N}$), $\delta = 3.62\text{--}3.56$ (m, 5 H, $-\text{CH}_2\text{--HN--CH}_2$), $\delta = 3.19$ (m, 4 H, $-\text{CH}_2\text{--(H)C}=\text{N}$), $\delta = 3.00$ (s, 6 H, $\text{TiN}(\text{CH}_3)_2$); Elemental analysis: calcd. for $\text{C}_{20}\text{H}_{30}\text{N}_6\text{OTi}$ (**3**·THF): C 57.42; H 7.23; N 20.09%; found: C 57.02; H 7.31; N 21.08 %.

4. General Procedure for the Hydroamination Reaction

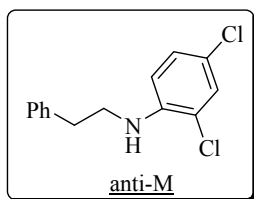
To a 35 mL pressure tube were added 0.1 mmol of catalyst **2**, 2,4-dichloroaniline (0.279 g, 3 mmol) phenylacetylene (0.204 g, 1 mmol) and toluene (2 mL). A stirring bar was added in the pressure tube, which was then fitted with a Teflon stopper. The tube was heated with stirring at 80°C . The reaction progress was typically checked every 0.5 h, which was continued until no phenylacetylene was detected or production of the product ceased as determined by TLC analysis (8 h). Then at 0°C , the reaction solution was carefully added to a suspension of LiAlH_4 (0.115 g, 3 mmol) in THF (10 mL) and the mixture was refluxed for 3 h. After cooling the solution to 0°C the excess LiAlH_4 was hydrolyzed with iced water and the precipitate was dissolved by dropwise addition of aqueous NaOH solution (2.0 mol L^{-1}). The mixture was then extracted with CH_2Cl_2 ($3 \times 15\text{ mL}$). The combined organic layers were dried with MgSO_4 and concentrated under vacuum. Column chromatography of the residue on silica gel (petroleum ether/ethyl acetate = 100/1, V/V) gave a mixture of the regioisomer products.

5. General Procedure for the Polymerization Reaction

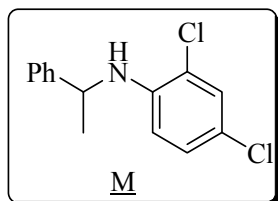
A DME solution of complex **1** (0.0332 g, 0.05 mmol) and ϵ -caprolactone (1.14 g, 10 mmol) was added to a 100 mL Schlenk flask equipped with a magnetic stirring bar in a glovebox. Afterwards, the Schlenk flask was taken out from the glovebox. The reaction mixture was heated to 60 °C for 2 h and afterwards terminated by addition of a mixture of conc. HCl/EtOH(1:5 V/V) (2 mL). Petroleum ether (20 mL) was added to give yellow solids. The solids were dissolved in THF (20 mL), column chromatography on Al₂O₃ to give a white solid. Yield: 1.025g (92%).

A DME solution of complex **2** (0.0434g, 0.05 mmol) and ϵ -caprolactone (1.14 g, 10 mmol) was added to a 100 mL Schlenk flask equipped with a magnetic stirring bar in a glovebox. Afterwards, the Schlenk flask was taken out from the glovebox. The reaction mixture was stirred at room temperature for 2 h and afterwards terminated by addition of a mixture of conc. HCl/EtOH(1:5 V/V) (2 mL). Petroleum ether (20 mL) was added to give yellow solids. The solids were dissolved in THF (20 mL), column chromatography on Al₂O₃ to give a white solid. Yield: 1.102g (97%).

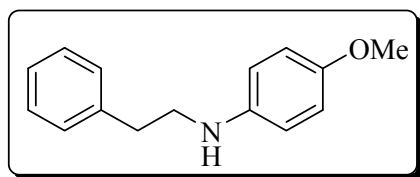
6. Characterization Data for the Hydroamination Products



¹H NMR (400 MHz, CDCl₃): δ 7.20-7.23 (m, 2H, -C₆H₃Cl₂), 7.09-7.15 (m, 4H, -C₆H₅), 6.98-7.00 (dd, *J* = 8.8, 2.4 Hz, 1H, -C₆H₃Cl₂), 6.46-6.48 (d, 1H, *J* = 8.8 Hz, -C₆H₅), 4.21 (s, 1H, NH), 3.25-3.3 (m, 2H, CH₂), 2.80-2.83 (t, 2H, *J* = 6.8 Hz, -CH₂Ph); ¹³C NMR (100 MHz, CDCl₃): δ 143.48, 139.68, 129.78, 129.71, 129.68, 128.70, 127.61, 122.02, 120.43, 120.70, 45.90, 36.22.

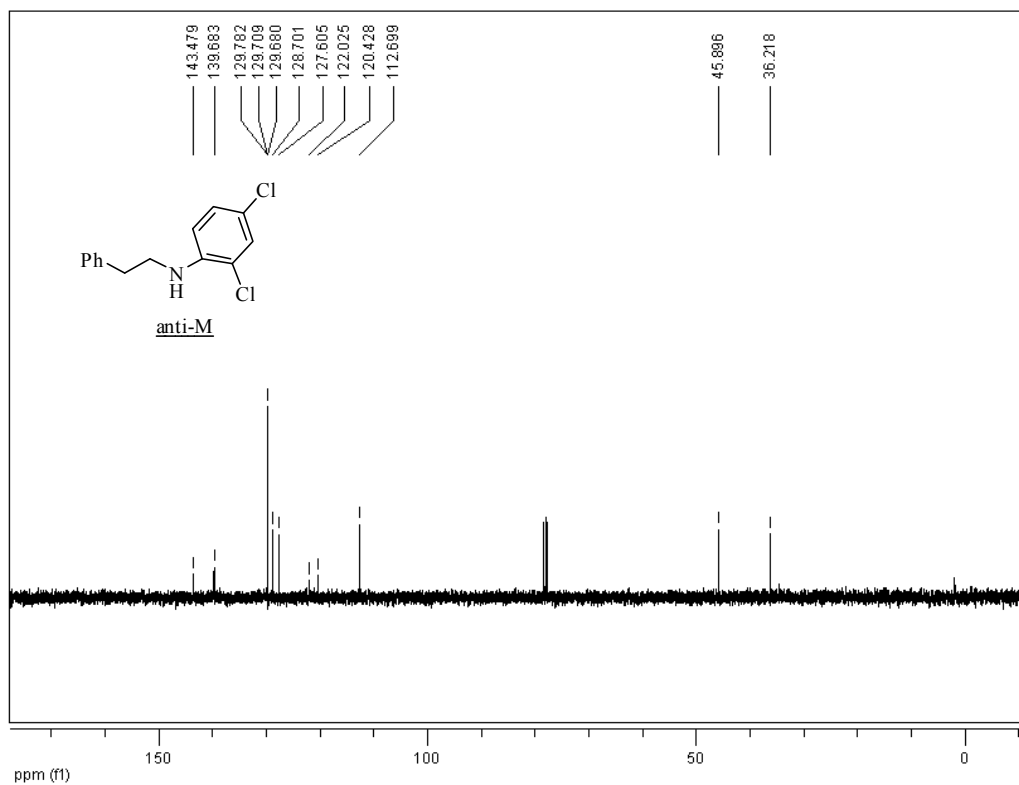
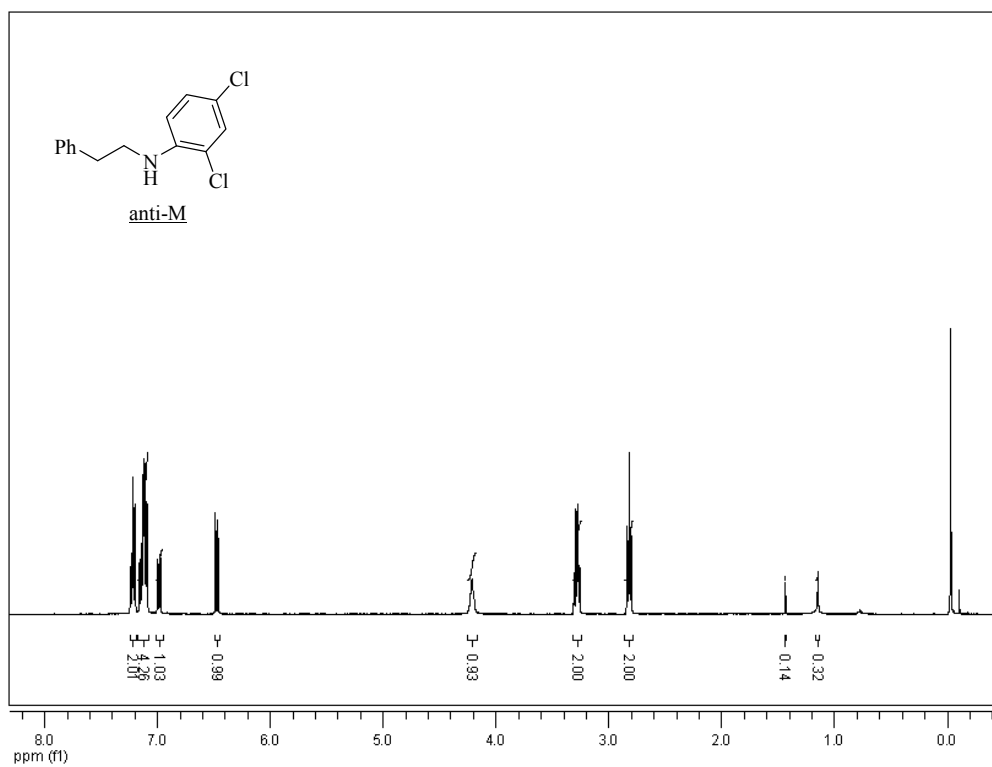


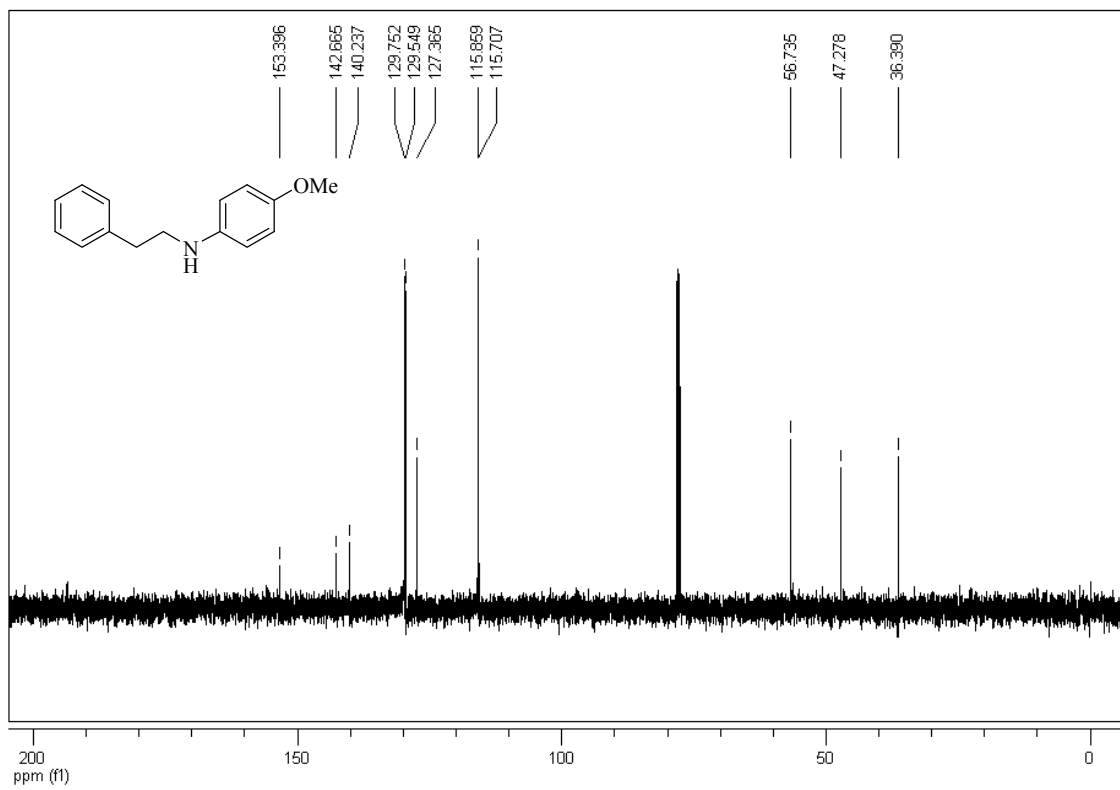
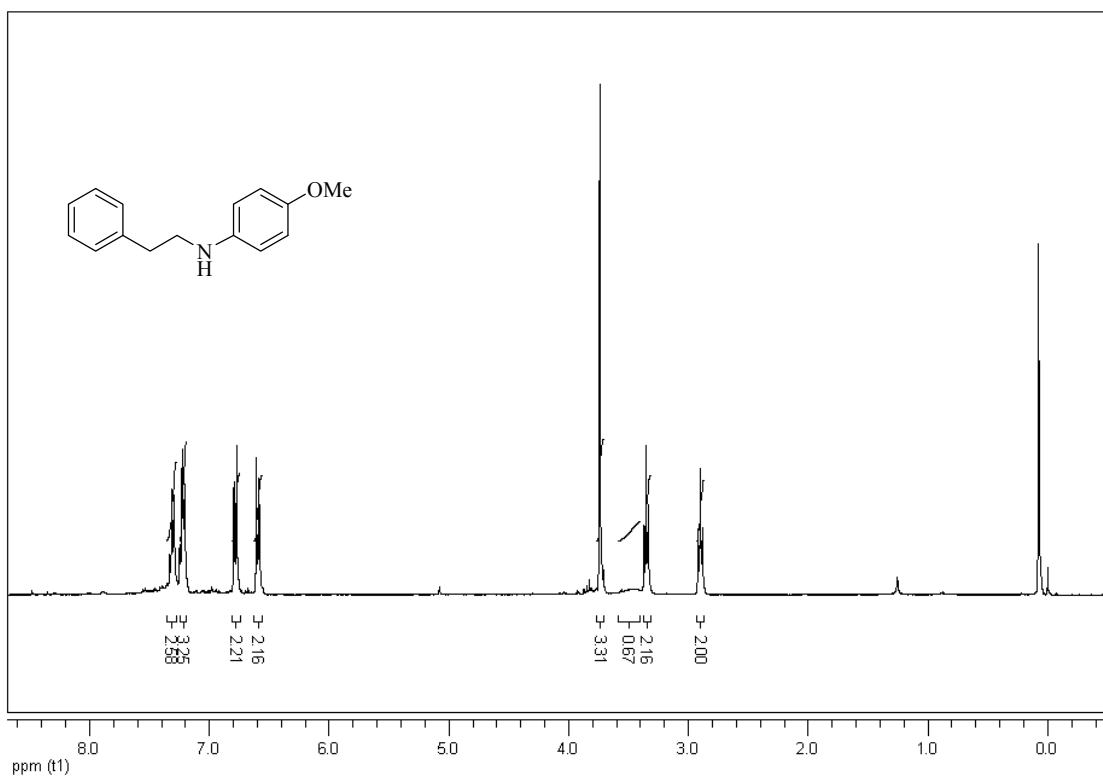
¹H NMR (400 MHz, CDCl₃): δ 7.21 (m, 4H, -C₆H₅), 7.14 (m, 2H, -C₆H₃Cl₂), 6.79-6.80 (dd, 1H, *J* = 8.8, 2.0 Hz, -C₆H₅), 6.18-6.20 (d, 1H, *J* = 8.2, -C₆H₃Cl₂), 4.56-4.58 (s, 1H, NH), 4.34-4.40 (m, 1H, CH), 1.48 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 145.04, 142.67, 129.81, 129.52, 128.56, 128.28, 126.60, 122.11, 120.13, 114.04, 54.44, 26.11.



¹H NMR (400 MHz, CDCl₃): δ 7.29-7.33 (m, 2H, -C₆H₅), 7.21-7.25 (m, 3H, -C₆H₅), 6.80-6.77 (m, 2H, -C₆H₄OMe), 6.59-6.61 (m, 2H, -C₆H₄OMe), 3.74 (s, 3H, -OMe), 3.40-3.58 (s, 1H, -NH), 3.33-3.37 (t, 2H, *J* = 7.2 Hz, -CH₂CH₂-), 2.88-2.92 (t, 2H, *J* = 6.8 Hz, -CH₂Ph). ¹³C NMR (100 MHz, CDCl₃): δ 153.40, 142.67, 140.24, 129.75, 129.55, 127.37, 115.86, 115.71, 56.74, 47.28, 36.39.

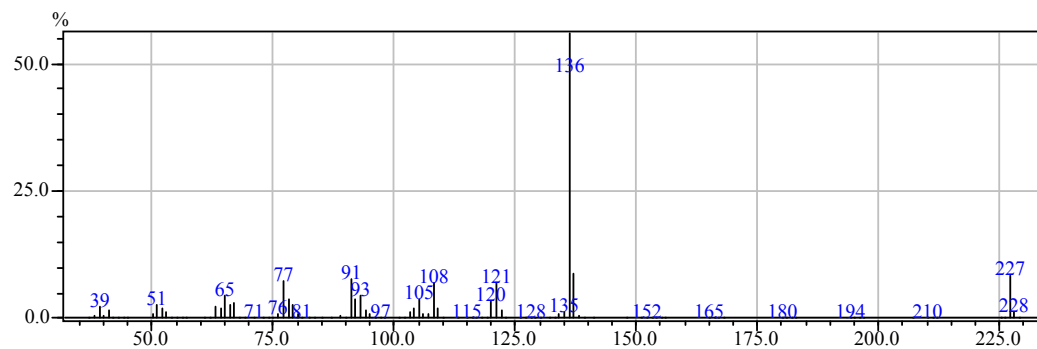
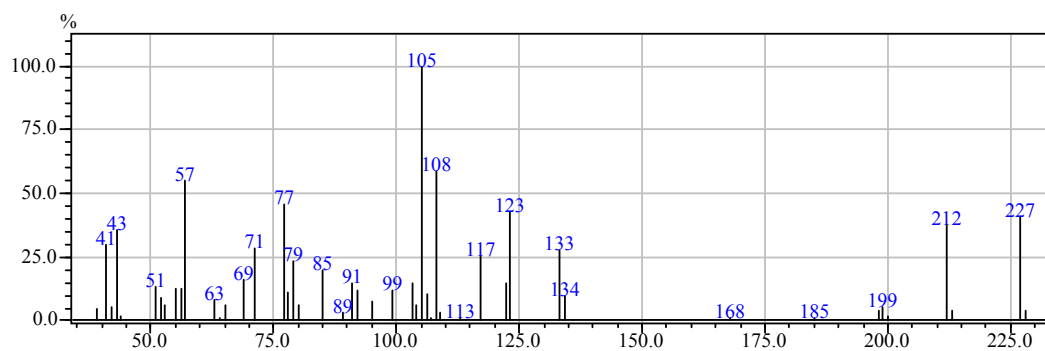
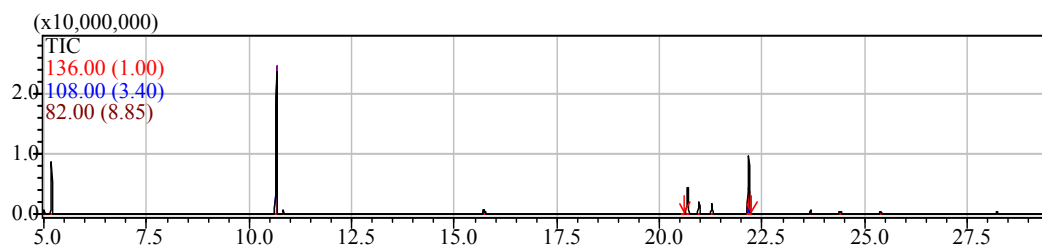
7. ^1H NMR and ^{13}C NMR Spectra for the Hydroamination Products





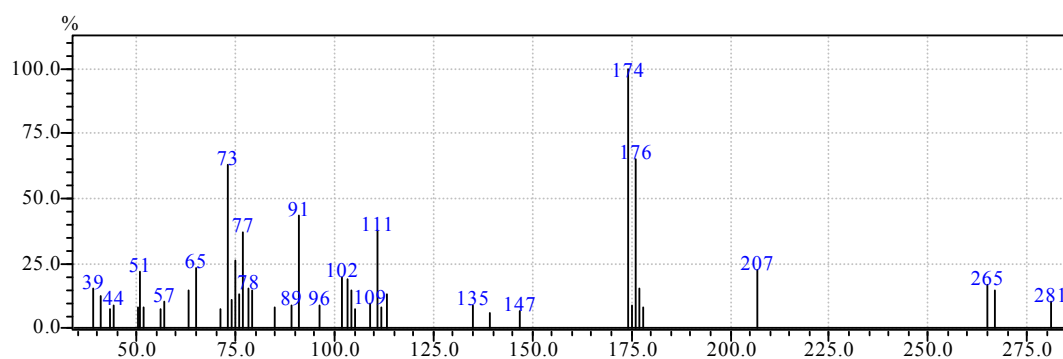
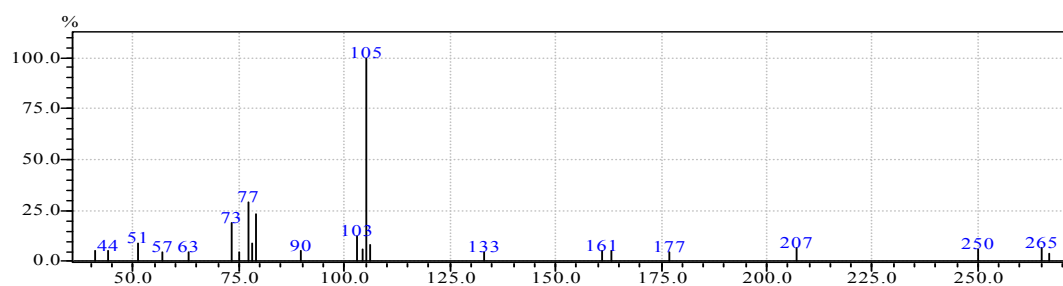
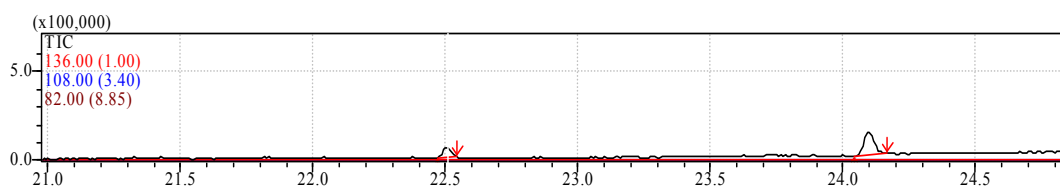
8. GC-MS data for the Hydroamination Reactions

8.1 GC-MS data for 2 catalyzed hydroamination of phenylacetylene by 4-methoxyaniline



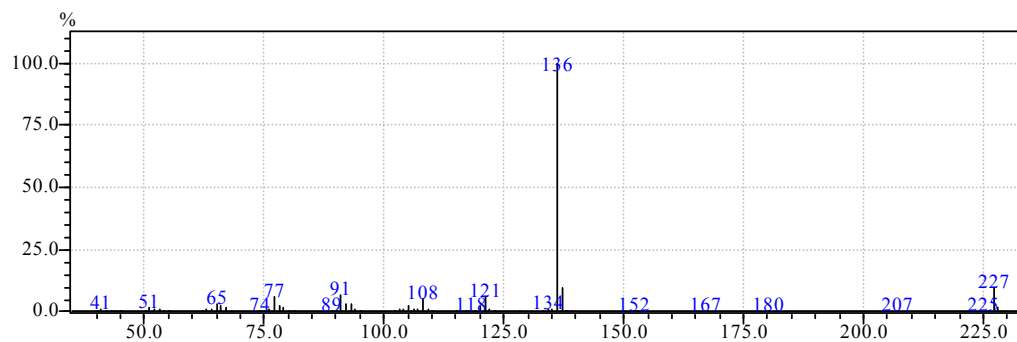
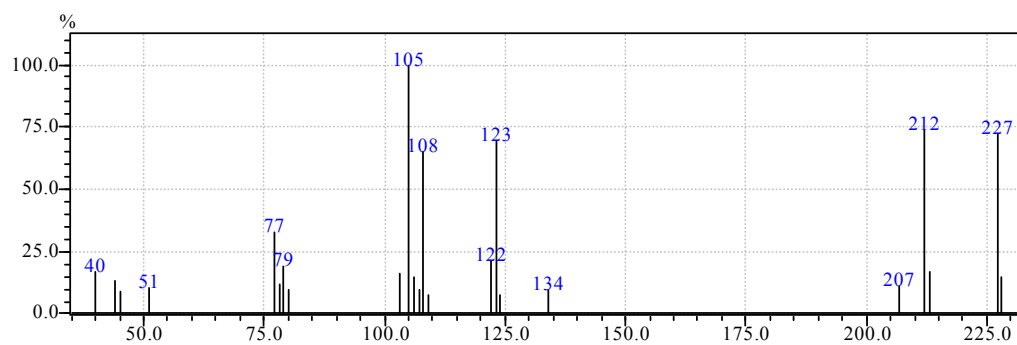
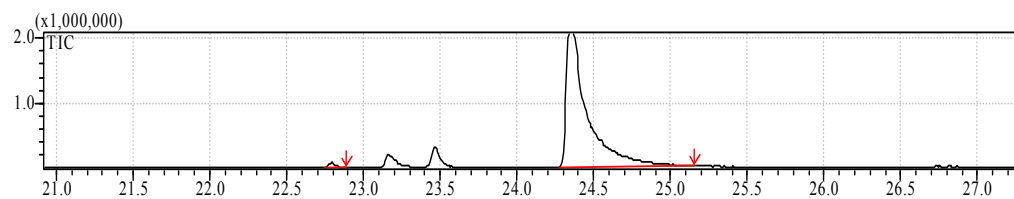
Ret. Time	Start Tm	End Tm	m/z	Area	Area%	Height	Height%	A/H	Mark
20.583	20.533	20.617	TIC	180511	0.76	83451	0.85	2.16	MI
22.175	22.092	22.275	TIC	23639023	99.24	9685656	99.15	2.44	MI

8.2 GC-MS data for **2** catalyzed hydroamination of phenylacetylene by 2,4-dichloroaniline



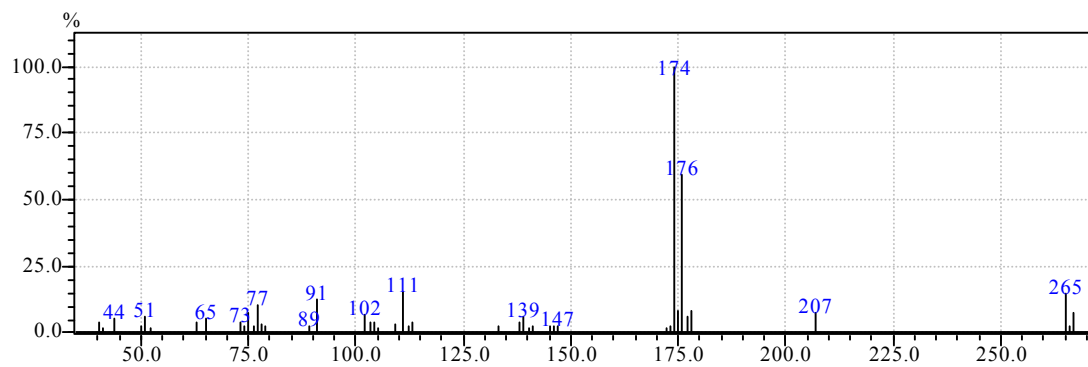
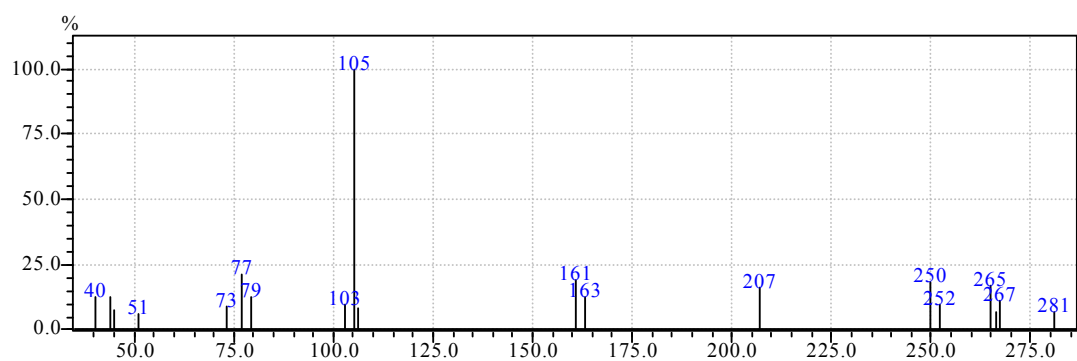
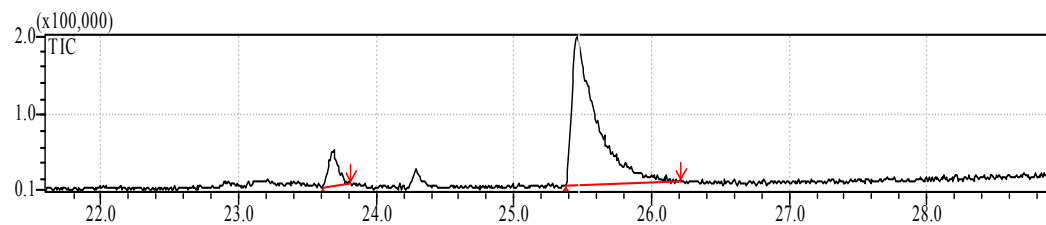
Ret. Time	Start Tm	End Tm	m/z	Area	Area%	Height	Height%	A/H	Mark
22.508	22.467	22.542	TIC	126019	25.89	55140	30.28	2.29	MI
24.100	24.042	24.167	TIC	360770	74.11	126939	69.72	2.84	MI

8.3 GC-MS data for **3** catalyzed hydroamination of phenylacetylene by 4-methoxyaniline



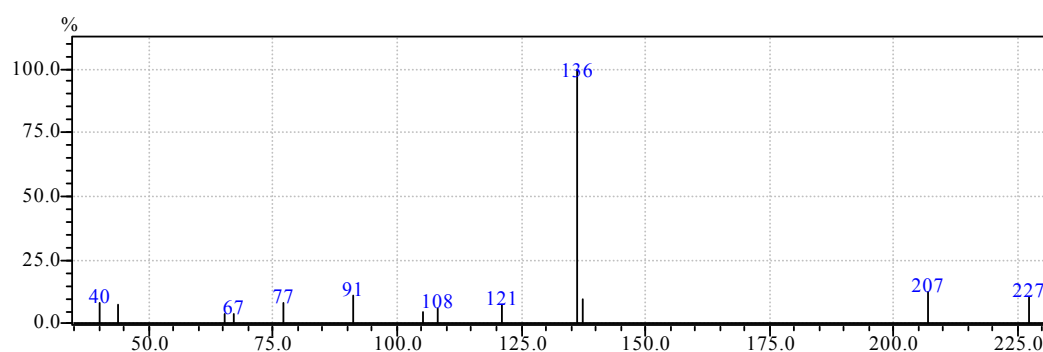
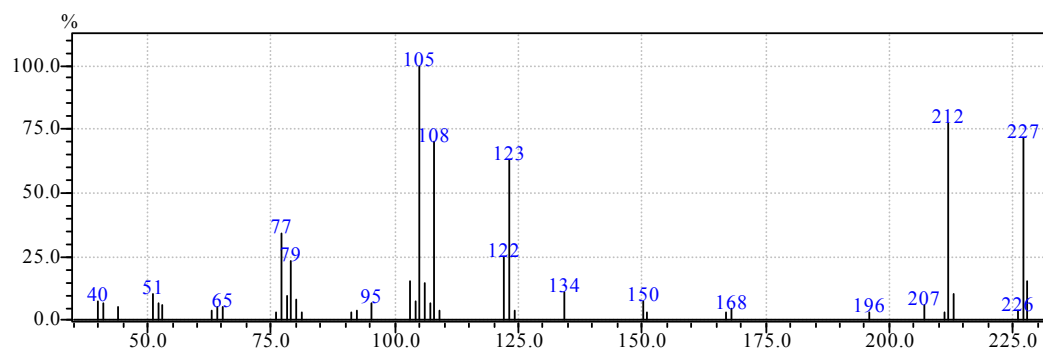
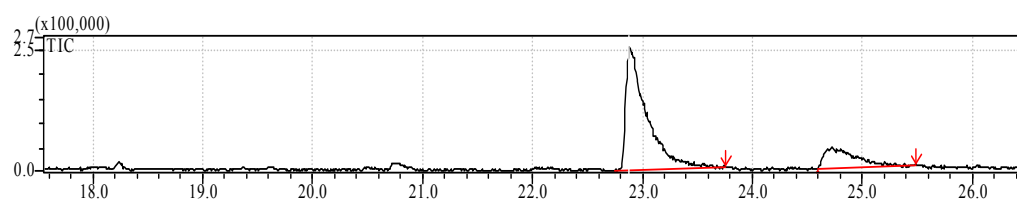
Ret. Time	Start Tm	End Tm	m/z	Area	Area%	Height	Height%	A/H	Mark
22.792	22.750	22.892	TIC	237026	1.13	73403	3.04	3.23	MI
24.350	24.275	25.150	TIC	20689843	98.87	2339891	96.96	8.84	MI

8.4 GC-MS data for **3** catalyzed hydroamination of phenylacetylene by 2,4-dichloroaniline



Ret. Time	Start Tm	End Tm	m/z	Area	Area%	Height	Height%	A/H	Mark
23.692	23.608	23.808	TIC	216463	8.68	43495	19.03	4.98	MI
25.458	25.375	26.217	TIC	2277241	91.32	185118	80.97	12.30	MI

8.5 GC-MS data for **4** catalyzed hydroamination of phenylacetylene by 4-methoxyaniline



Ret. Time	Start Tm	End Tm	m/z	Area	Area%	Height	Height%	A/H	Mark
22.883	22.742	23.758	TIC	3234502	78.38	247413	84.81	13.07	MI
24.725	24.592	25.492	TIC	892278	21.62	44303	15.19	20.14	MI

9. ^1H NMR Spectrum for **3**.

