Supporting Information

Titanium complexes supported by imidazo[1,5-*a*]pyridine-containing pyrrolyl ligand as catalysts for hydroamination and polymerization reactions, and as antitumor reagent

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1. Crystallography data for 2 and 3

1.1 Crystal data and structure refinements for **2** and **3**

Table 1 Crystal data and structure refinements for **2** and **3**

Complex	**2**	**3**
Empirical formula	$C_{30}H_{36}N_8Ti$	$C_{28}H_{30}N_6O_2Ti$
Formula weight	556.54	530.45
Temperature	296(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	C 2/c
Unit cell dimensions	a = 23.010(9)Å	a = 8.7336(17)Å
	b =13.712(5)Å	b =16.212(6)Å
	c = 21.228(9) Å	c = 18.952(4) Å
	α = 90°	α = 90°
	β =115.456(7)°	β =92.30(3) °
	γ = 90°	γ = 90°
Volume	6048(4) A^3	2681.2(13) A^3
Z	8	4
ρ(mg•m^{-3})	1.222	1.314
F(000)	2352	1112
Crystal size(mm^3)	0.60 x 0.40 x 0.40	0.60 x 0.40 x 0.40
The range for data collection	1.78° to 26.22°	3.31° to 27.49°
Limiting indices	-28 ≤ h ≤ 23	-9 ≤ h ≤ 11
	-25 ≤ l ≤ 26	-20 ≤ k ≤ 20
	-16 ≤ k ≤ 17	-24 ≤ l ≤ 24
Reflections collected/ unique	35810 / 12166	12023 / 3070
Data / restraints / parameters	12094 / 0 / 711	3048 / 0 / 170
GOF	0.950	1.076
R1,wR2[I□2σ(I)]	R1 = 0.0507,wR2 = 0.1111	R1 = 0.0456, wR2 = 0.1289
R1,wR2(all data)	R1 = 0.1290, wR2 = 0.1438	R1 = 0.0578, wR2 = 0.1365
Largest diff. peak and hole(e•Å^3)	0.276 and -0.249	0.369 and -0.271

Table 2 Bond lengths (Å) and angles (°) for **2**

Ti(1)-N(6)	1.910(3)
Ti(1)-N(5)	1.912(3)

Ti(1)-N(4)	2.123(3)
Ti(1)-N(2)	2.148(3)
Ti(1)-N(1)	2.236(3)
Ti(1)-N(3)	2.277(2)
N(1)-C(7)	1.344(3)
N(1)-C(1)	1.373(4)
N(3)-C(18)	1.341(3)
N(3)-C(12)	1.377(4)
N(2)-C(11)	1.363(4)
N(2)-C(8)	1.390(4)
C(8)-C(9)	1.383(4)
C(8)-C(7)	1.439(4)
N(8)-C(18)	1.372(4)
N(8)-C(17)	1.395(4)
N(8)-C(13)	1.426(4)
N(7)-C(7)	1.363(4)
N(7)-C(6)	1.402(4)
N(7)-C(2)	1.416(4)
N(6)-C(29)	1.477(4)
N(6)-C(27)	1.485(4)
N(4)-C(22)	1.362(4)
N(4)-C(19)	1.392(4)
C(18)-C(19)	1.442(4)
C(19)-C(20)	1.384(4)
C(2)-C(1)	1.377(4)
C(2)-C(3)	1.420(4)
C(11)-C(10)	1.383(4)
C(12)-C(13)	1.377(4)
N(5)-C(23)	1.474(4)
N(5)-C(25)	1.478(4)
C(22)-C(21)	1.380(4)
C(3)-C(4)	1.356(5)
C(17)-C(16)	1.345(5)
C(6)-C(5)	1.347(5)
C(21)-C(20)	1.407(4)
C(10)-C(9)	1.396(5)
C(14)-C(15)	1.354(5)
C(14)-C(13)	1.425(4)
C(5)-C(4)	1.414(5)
C(27)-C(28)	1.527(4)
C(23)-C(24)	1.509(5)
C(15)-C(16)	1.430(5)
Ti(2)-N(14)	1.912(3)
Ti(2)-N(13)	1.916(3)

Ti(2)-N(12)	2.121(3)
Ti(2)-N(10)	2.135(3)
Ti(2)-N(9)	2.252(3)
Ti(2)-N(11)	2.279(3)
N(16)-C(48)	1.371(4)
N(16)-C(47)	1.397(4)
N(16)-C(43)	1.420(4)
N(12)-C(52)	1.369(4)
N(12)-C(49)	1.393(4)
N(11)-C(48)	1.342(4)
N(11)-C(42)	1.379(4)
N(9)-C(37)	1.341(4)
N(9)-C(31)	1.376(4)
N(10)-C(41)	1.365(4)
N(10)-C(38)	1.388(4)
C(37)-N(15)	1.369(4)
C(37)-C(38)	1.439(5)
C(48)-C(49)	1.444(4)
N(14)-C(53)	1.470(4)
N(14)-C(55)	1.479(4)
N(13)-C(59)	1.473(4)
N(13)-C(57)	1.480(4)
N(15)-C(36)	1.405(4)
N(15)-C(32)	1.406(4)
C(55)-C(56)	1.538(4)
C(49)-C(50)	1.380(4)
C(42)-C(43)	1.367(4)
C(52)-C(51)	1.379(5)
C(38)-C(39)	1.393(4)
C(43)-C(44)	1.426(5)
C(53)-C(54)	1.530(4)
C(31)-C(32)	1.382(4)
C(40)-C(41)	1.379(5)
C(40)-C(39)	1.399(5)
C(32)-C(33)	1.430(5)
C(44)-C(45)	1.360(5)
C(57)-C(58)	1.519(5)
C(47)-C(46)	1.345(5)
C(50)-C(51)	1.406(5)
C(46)-C(45)	1.432(5)
C(33)-C(34)	1.367(6)
C(59)-C(60)	1.503(5)
C(36)-C(35)	1.341(6)
C(29)-C(30)	1.518(5)

C(25)-C(26)	1.519(6)
C(34)-C(35)	1.409(7)
N(6)-Ti(1)-N(5)	102.32(12)
N(6)-Ti(1)-N(4)	99.70(11)
N(5)-Ti(1)-N(4)	96.26(11)
N(6)-Ti(1)-N(2)	97.57(11)
N(5)-Ti(1)-N(2)	97.53(11)
N(4)-Ti(1)-N(2)	155.02(10)
N(6)-Ti(1)-N(1)	162.79(10)
N(5)-Ti(1)-N(1)	93.69(11)
N(4)-Ti(1)-N(1)	84.61(9)
N(2)-Ti(1)-N(1)	73.82(10)
N(6)-Ti(1)-N(3)	88.51(10)
N(5)-Ti(1)-N(3)	167.17(11)
N(4)-Ti(1)-N(3)	74.90(10)
N(2)-Ti(1)-N(3)	87.69(10)
N(1)-Ti(1)-N(3)	76.45(9)
C(7)-N(1)-C(1)	107.8(3)
C(7)-N(1)-Ti(1)	115.1(2)
C(1)-N(1)-Ti(1)	137.0(2)
C(18)-N(3)-C(12)	107.4(3)
C(18)-N(3)-Ti(1)	112.18(19)
C(12)-N(3)-Ti(1)	140.1(2)
C(11)-N(2)-C(8)	105.9(3)
C(11)-N(2)-Ti(1)	134.7(2)
C(8)-N(2)-Ti(1)	119.14(19)
C(9)-C(8)-N(2)	110.2(3)
C(9)-C(8)-C(7)	136.2(3)
N(2)-C(8)-C(7)	113.5(3)
C(18)-N(8)-C(17)	131.3(3)
C(18)-N(8)-C(13)	107.5(2)
C(17)-N(8)-C(13)	121.2(3)
C(7)-N(7)-C(6)	131.0(3)
C(7)-N(7)-C(2)	107.8(2)
C(6)-N(7)-C(2)	121.1(3)
C(29)-N(6)-C(27)	114.1(3)
C(29)-N(6)-Ti(1)	127.6(2)
C(27)-N(6)-Ti(1)	116.5(2)
C(22)-N(4)-C(19)	105.6(3)
C(22)-N(4)-Ti(1)	135.2(2)
C(19)-N(4)-Ti(1)	118.82(19)
N(3)-C(18)-N(8)	110.0(3)
N(3)-C(18)-C(19)	119.9(3)
N(8)-C(18)-C(19)	130.1(3)

C(20)-C(19)-N(4)	110.5(3)
C(20)-C(19)-C(18)	135.9(3)
N(4)-C(19)-C(18)	113.7(3)
C(1)-C(2)-N(7)	105.2(3)
C(1)-C(2)-C(3)	136.8(3)
N(7)-C(2)-C(3)	118.0(3)
N(2)-C(11)-C(10)	110.3(3)
N(3)-C(12)-C(13)	110.4(3)
C(23)-N(5)-C(25)	113.4(3)
C(23)-N(5)-Ti(1)	124.2(2)
C(25)-N(5)-Ti(1)	121.0(2)
N(1)-C(1)-C(2)	109.6(3)
N(1)-C(7)-N(7)	109.5(3)
N(1)-C(7)-C(8)	118.4(3)
N(7)-C(7)-C(8)	132.1(3)
N(4)-C(22)-C(21)	110.8(3)
C(4)-C(3)-C(2)	119.9(4)
C(16)-C(17)-N(8)	119.5(4)
C(5)-C(6)-N(7)	118.8(3)
C(22)-C(21)-C(20)	107.3(3)
C(11)-C(10)-C(9)	107.4(3)
C(8)-C(9)-C(10)	106.3(3)
C(15)-C(14)-C(13)	119.7(4)
C(6)-C(5)-C(4)	121.6(3)
C(19)-C(20)-C(21)	105.9(3)
N(6)-C(27)-C(28)	114.2(3)
C(3)-C(4)-C(5)	120.5(4)
N(5)-C(23)-C(24)	114.7(3)
C(14)-C(15)-C(16)	121.0(4)
C(17)-C(16)-C(15)	120.8(4)
N(14)-Ti(2)-N(13)	104.39(11)
N(14)-Ti(2)-N(12)	97.78(10)
N(13)-Ti(2)-N(12)	94.76(11)
N(14)-Ti(2)-N(10)	94.38(11)
N(13)-Ti(2)-N(10)	98.40(11)
N(12)-Ti(2)-N(10)	159.28(10)
N(14)-Ti(2)-N(9)	160.18(10)
N(13)-Ti(2)-N(9)	93.54(11)
N(12)-Ti(2)-N(9)	88.91(10)
N(10)-Ti(2)-N(9)	74.41(10)
N(14)-Ti(2)-N(11)	87.77(10)
N(13)-Ti(2)-N(11)	164.82(10)
N(12)-Ti(2)-N(11)	74.31(10)
N(10)-Ti(2)-N(11)	89.53(10)

N(9)-Ti(2)-N(11)	76.06(9)
C(48)-N(16)-C(47)	130.8(3)
C(48)-N(16)-C(43)	107.4(3)
C(47)-N(16)-C(43)	121.8(3)
C(52)-N(12)-C(49)	105.5(3)
C(52)-N(12)-Ti(2)	134.3(2)
C(49)-N(12)-Ti(2)	119.7(2)
C(48)-N(11)-C(42)	107.5(3)
C(48)-N(11)-Ti(2)	112.8(2)
C(42)-N(11)-Ti(2)	139.6(2)
C(37)-N(9)-C(31)	107.7(3)
C(37)-N(9)-Ti(2)	113.1(2)
C(31)-N(9)-Ti(2)	139.1(2)
C(41)-N(10)-C(38)	105.3(3)
C(41)-N(10)-Ti(2)	135.1(2)
C(38)-N(10)-Ti(2)	119.5(2)
N(9)-C(37)-N(15)	109.5(3)
N(9)-C(37)-C(38)	120.3(3)
N(15)-C(37)-C(38)	130.1(3)
N(11)-C(48)-N(16)	109.7(3)
N(11)-C(48)-C(49)	119.6(3)
N(16)-C(48)-C(49)	130.7(3)
C(53)-N(14)-C(55)	114.3(2)
C(53)-N(14)-Ti(2)	125.1(2)
C(55)-N(14)-Ti(2)	118.2(2)
C(59)-N(13)-C(57)	113.6(3)
C(59)-N(13)-Ti(2)	122.5(2)
C(57)-N(13)-Ti(2)	122.9(2)
C(37)-N(15)-C(36)	130.0(4)
C(37)-N(15)-C(32)	108.0(3)
C(36)-N(15)-C(32)	122.0(3)
N(14)-C(55)-C(56)	114.6(3)
C(50)-C(49)-N(12)	110.3(3)
C(50)-C(49)-C(48)	136.3(3)
N(12)-C(49)-C(48)	113.3(3)
C(43)-C(42)-N(11)	110.0(3)
N(12)-C(52)-C(51)	110.8(3)
N(10)-C(38)-C(39)	110.0(3)
N(10)-C(38)-C(37)	112.7(3)
C(39)-C(38)-C(37)	137.1(3)
C(42)-C(43)-N(16)	105.4(3)
C(42)-C(43)-C(44)	136.9(4)
N(16)-C(43)-C(44)	117.7(3)
N(14)-C(53)-C(54)	115.5(3)

N(9)-C(31)-C(32)	109.5(3)
C(41)-C(40)-C(39)	106.4(3)
C(31)-C(32)-N(15)	105.3(3)
C(31)-C(32)-C(33)	136.8(4)
N(15)-C(32)-C(33)	117.9(4)
C(45)-C(44)-C(43)	119.8(4)
N(10)-C(41)-C(40)	111.6(3)
N(13)-C(57)-C(58)	114.0(3)
C(38)-C(39)-C(40)	106.7(3)
C(46)-C(47)-N(16)	119.0(4)
C(49)-C(50)-C(51)	106.4(3)
C(52)-C(51)-C(50)	107.0(3)
C(47)-C(46)-C(45)	121.2(4)
C(34)-C(33)-C(32)	119.1(5)
N(13)-C(59)-C(60)	116.3(3)
C(44)-C(45)-C(46)	120.6(4)
C(35)-C(36)-N(15)	118.1(5)
N(6)-C(29)-C(30)	114.8(3)
N(5)-C(25)-C(26)	115.7(4)
C(12)-C(13)-N(8)	104.8(3)
C(12)-C(13)-C(14)	137.3(3)
N(8)-C(13)-C(14)	117.9(3)
C(33)-C(34)-C(35)	120.7(5)
C(36)-C(35)-C(34)	122.2(5)

Table 3 Bond lengths (Å) and angles (°) for **3**

Ti(1)-O(1A)	1.7798(13)
Ti(1)-O(1)	1.7799(13)

Ti(1)-N(2)	2.1003(16)
Ti(1)-N(2A)	2.1004(16)
Ti(1)-N(1A)	2.2209(15)
Ti(1)-N(1)	2.2209(16)
O(1)-C(12)	1.418(2)
N(3)-C(7)	1.362(2)
N(3)-C(6)	1.397(2)
N(3)-C(2)	1.404(3)
N(2)-C(11)	1.369(3)
N(2)-C(8)	1.377(2)
N(1)-C(7)	1.332(2)
N(1)-C(1)	1.365(2)
C(7)-C(8)	1.432(2)
C(2)-C(1)	1.371(3)
C(2)-C(3)	1.419(3)
C(8)-C(9)	1.378(3)
C(4)-C(3)	1.352(3)
C(4)-C(5)	1.420(4)
C(4)-H(4)	0.9300
C(12)-C(13)	1.486(3)
C(12)-C(14)	1.497(4)
C(12)-H(12)	0.9800
C(1)-H(1)	0.9300
C(6)-C(5)	1.334(3)
C(6)-H(6)	0.9300
C(14)-H(14A)	0.9600
C(14)-H(14B)	0.9600
C(14)-H(14C)	0.9600
C(11)-C(10)	1.364(3)
C(11)-H(11)	0.9300
C(3)-H(3)	0.9300
C(5)-H(5)	0.9300
C(10)-C(9)	1.393(4)
C(10)-H(10)	0.9300
C(9)-H(9)	0.9300
C(13)-H(13A)	0.9600
C(13)-H(13B)	0.9600
C(13)-H(13C)	0.9600
O(1A)-Ti(1)-O(1)	100.41(9)
O(1A)-Ti(1)-N(2)	95.96(6)
O(1)-Ti(1)-N(2)	103.11(6)
O(1A)-Ti(1)-N(2A)	103.11(6)
O(1)-Ti(1)-N(2A)	95.96(6)
N(2)-Ti(1)-N(2A)	150.07(9)

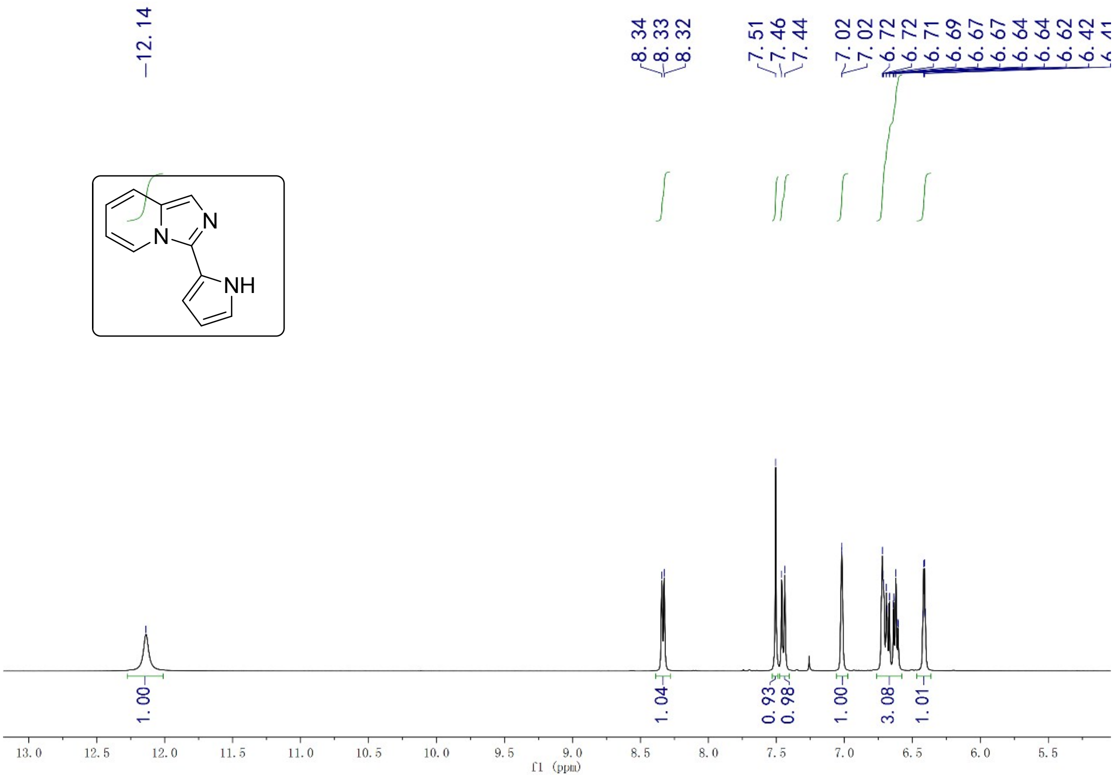
O(1)A-Ti(1)-N(1A)	90.02(6)
O(1)-Ti(1)-N(1A)	167.20(6)
N(2)-Ti(1)-N(1A)	82.96(6)
N(2A)-Ti(1)-N(1A)	74.28(6)
O(1A)-Ti(1)-N(1)	167.20(6)
O(1)-Ti(1)-N(1)	90.02(6)
N(2)-Ti(1)-N(1)	74.28(6)
N(2A)-Ti(1)-N(1)	82.96(6)
N(1A)-Ti(1)-N(1)	80.70(8)
C(12)-O(1)-Ti(1)	147.87(12)
C(7)-N(3)-C(6)	130.78(18)
C(7)-N(3)-C(2)	107.49(15)
C(6)-N(3)-C(2)	121.72(17)
C(11)-N(2)-C(8)	106.06(16)
C(11)-N(2)-Ti(1)	133.12(14)
C(8)-N(2)-Ti(1)	119.83(12)
C(7)-N(1)-C(1)	108.13(15)
C(7)-N(1)-Ti(1)	114.08(11)
C(1)-N(1)-Ti(1)	137.78(12)
N(1)-C(7)-N(3)	109.51(15)
N(1)-C(7)-C(8)	118.87(15)
N(3)-C(7)-C(8)	131.58(16)
C(1)-C(2)-N(3)	105.68(16)
C(1)-C(2)-C(3)	136.4(2)
N(3)-C(2)-C(3)	117.79(19)
N(2)-C(8)-C(9)	109.94(17)
N(2)-C(8)-C(7)	112.75(15)
C(9)-C(8)-C(7)	137.00(18)
C(3)-C(4)-C(5)	120.4(2)
C(3)-C(4)-H(4)	119.8
C(5)-C(4)-H(4)	119.8
O(1)-C(12)-C(13)	109.26(19)
O(1)-C(12)-C(14)	109.4(2)
C(13)-C(12)-C(14)	113.0(2)
O(1)-C(12)-H(12)	108.4
C(13)-C(12)-H(12)	108.4
C(14)-C(12)-H(12)	108.4
N(1)-C(1)-C(2)	109.18(17)
N(1)-C(1)-H(1)	125.4
C(2)-C(1)-H(1)	125.4
C(5)-C(6)-N(3)	118.7(2)
C(5)-C(6)-H(6)	120.6
N(3)-C(6)-H(6)	120.6
C(12)-C(14)-H(14A)	109.5

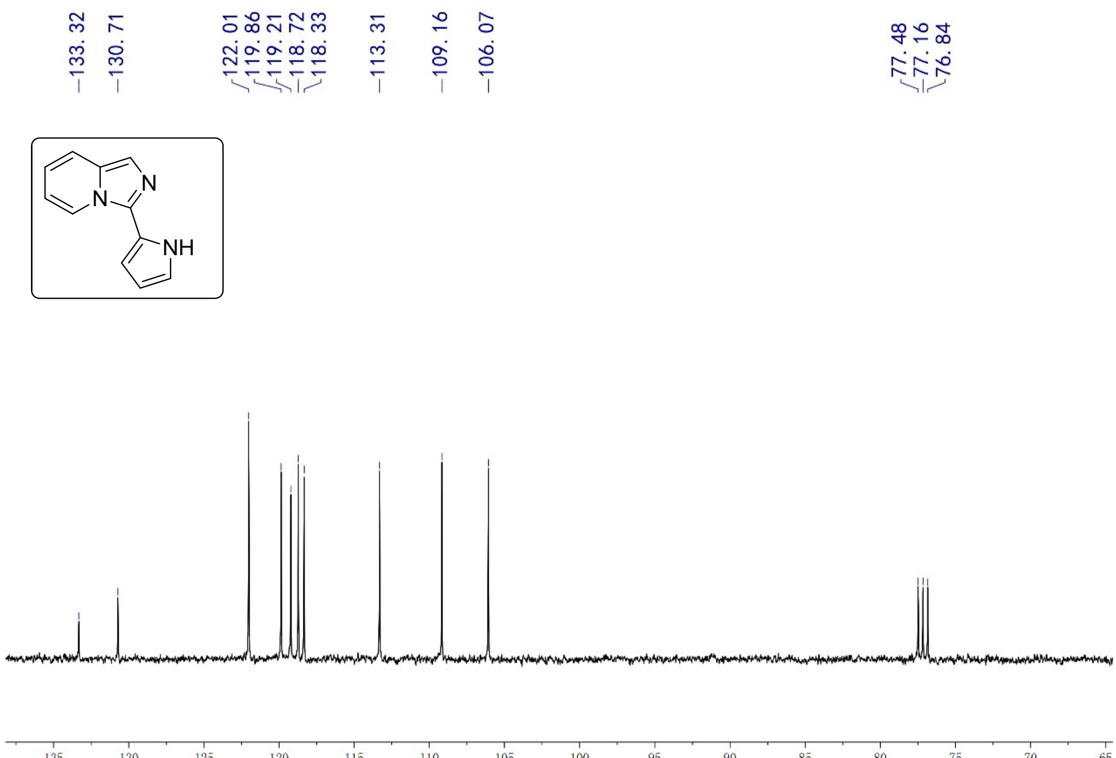
C(12)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(12)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(10)-C(11)-N(2)	110.0(2)
C(10)-C(11)-H(11)	125.0
N(2)-C(11)-H(11)	125.0
C(4)-C(3)-C(2)	119.8(2)
C(4)-C(3)-H(3)	120.1
C(2)-C(3)-H(3)	120.1
C(6)-C(5)-C(4)	121.5(2)
C(6)-C(5)-H(5)	119.2
C(4)-C(5)-H(5)	119.2
C(11)-C(10)-C(9)	107.6(2)
C(11)-C(10)-H(10)	126.2
C(9)-C(10)-H(10)	126.2
C(8)-C(9)-C(10)	106.3(2)
C(8)-C(9)-H(9)	126.8
C(10)-C(9)-H(9)	126.8
C(12)-C(13)-H(13A)	109.5
C(12)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(12)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5

2. ^{1}H and ^{13}C NMR spectra for the complexes

2.1 ^{1}H and ^{13}C NMR spectra for HL

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.14 (s, 1H), 8.39 – 8.28 (m, 1H), 7.51 (s, 1H), 7.45 (d, 1H), 7.02 (d, 1H), 6.76 – 6.58 (m, 3H), 6.41 (dd, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.32, 130.71, 122.01, 119.86, 119.21, 118.72, 118.33, 113.31, 109.16, 106.07.

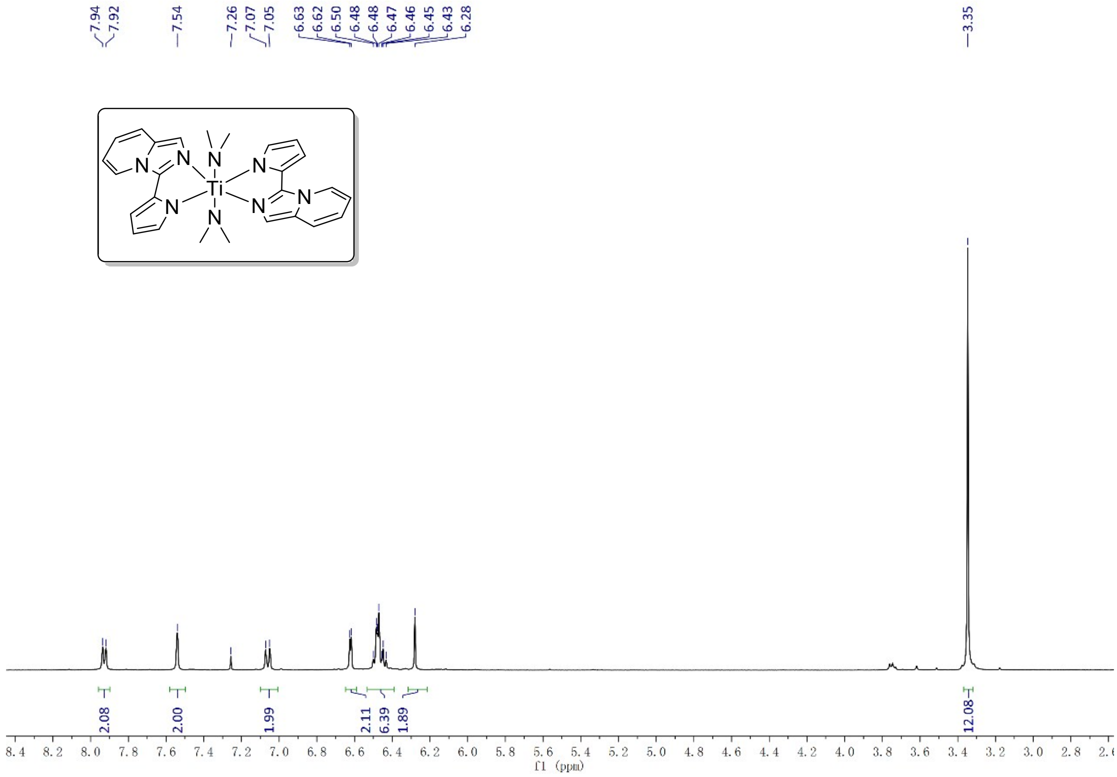


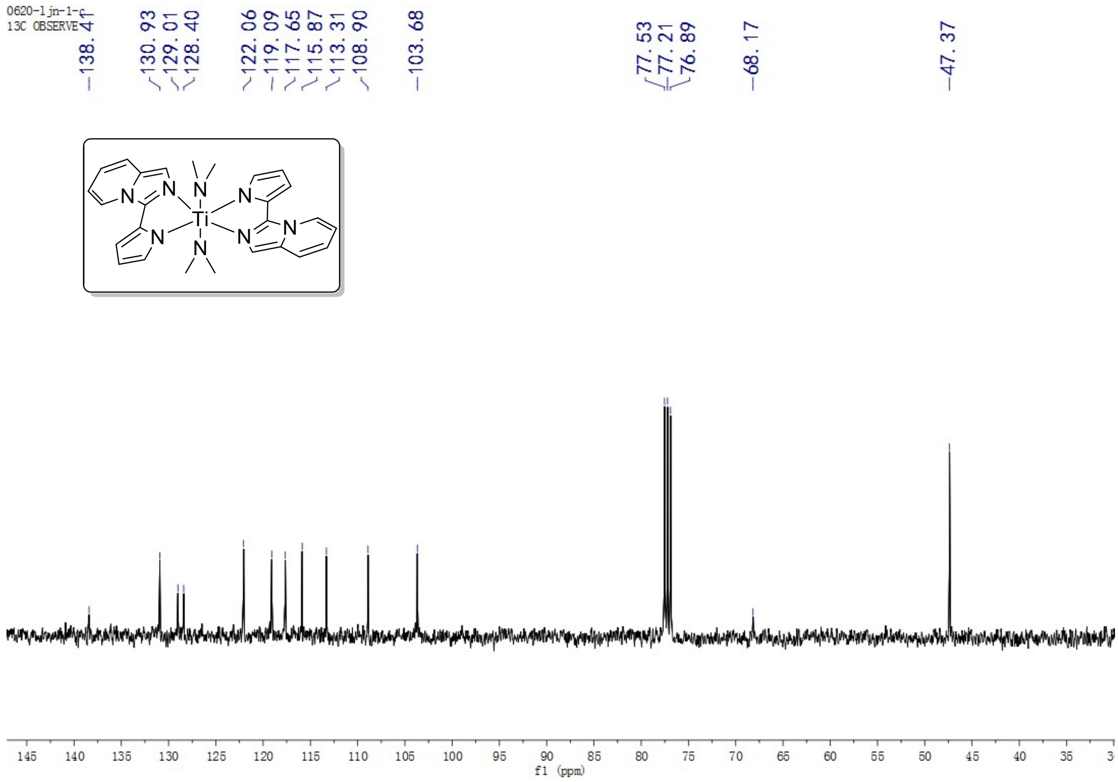


2.2 ^{1}H and ^{13}C NMR spectra for **1**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, 2H, $C_7H_5N_2$), 7.54 (s, 2H, $C_7H_5N_2$), 7.06 (d,, 2H, $C_7H_5N_2$), 6.62 (d, 2H, pyrrole-H), 6.53 – 6.39 (m, 6H, $C_7H_5N_2$ + pyrrole-H), 6.28 (s, 2H, pyrrole-H), 3.35 (s, 12H, CH_3). ^{13} C NMR

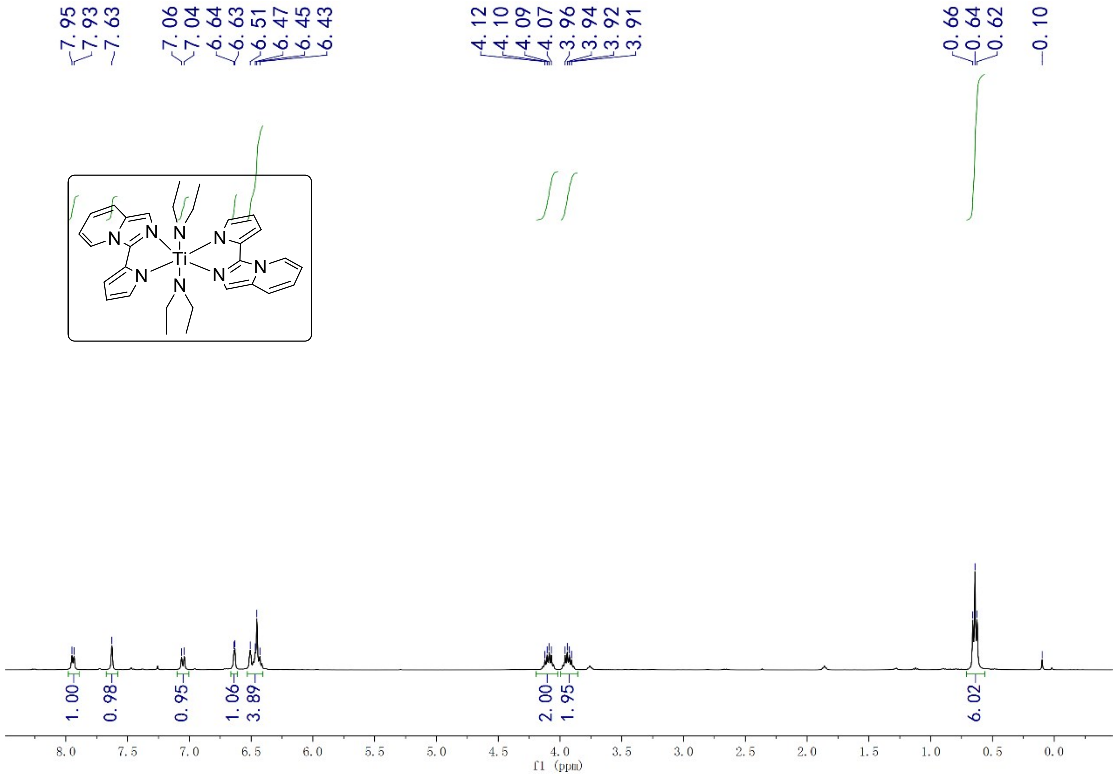
(100 MHz, $CDCl_3$) δ 138.41, 130.93, 129.01, 128.70, 122.06, 119.09, 117.65, 115.87, 113.31, 108.90, 103.68, 68.17, 47.37.

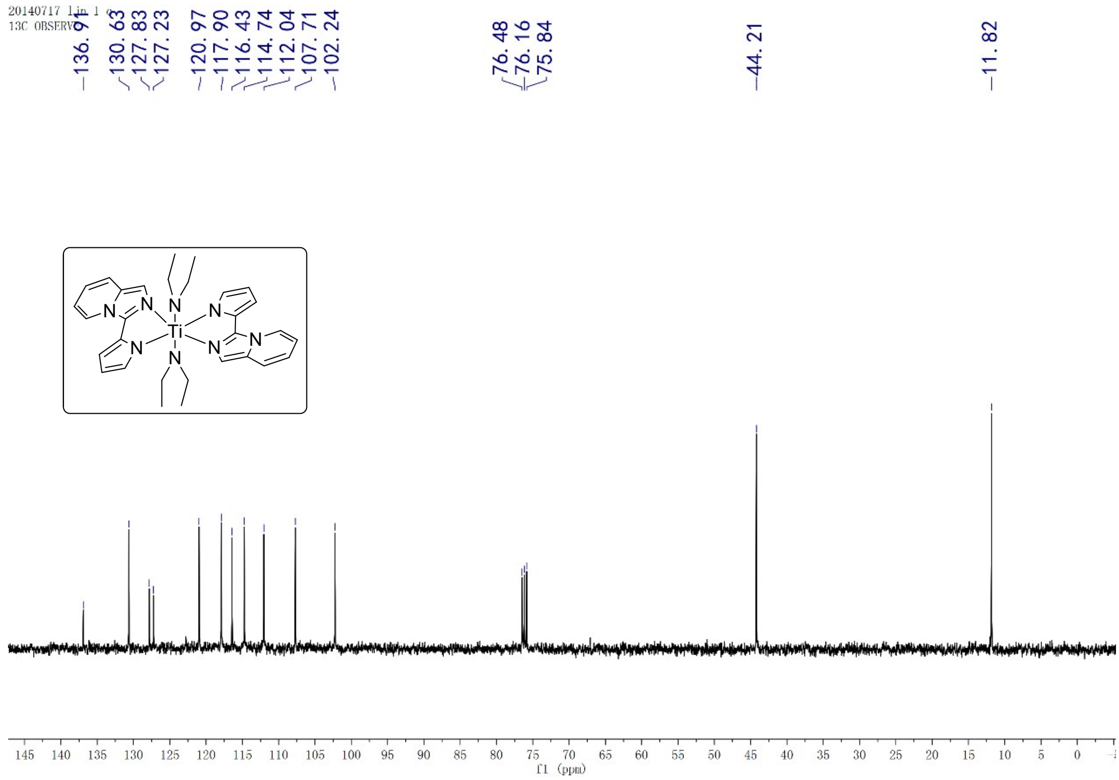




2.3 ^{1}H and ^{13}C NMR spectra for **2**

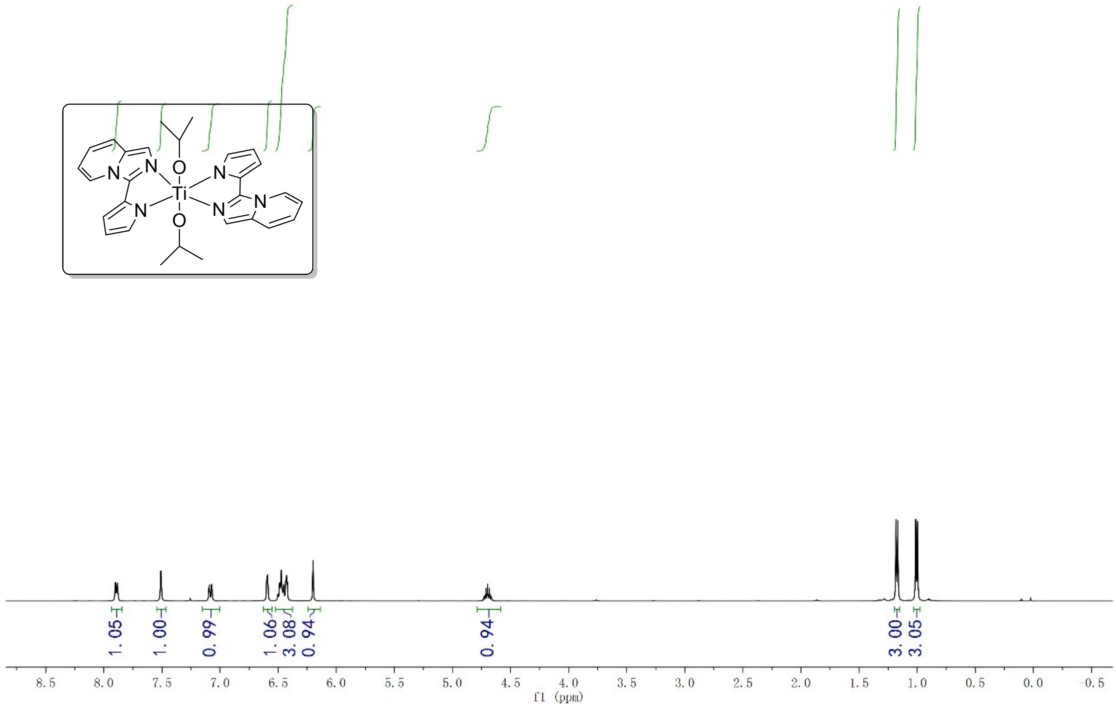
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, 2H, $C_7H_5N_2$), 7.61 (s, 2H, $C_7H_5N_2$), 7.06 (d, 2H, $C_7H_5N_2$), 6.62 (d, 2H, pyrrole-H), 6.47 (dd, 8H, $C_7H_5N_2$ + pyrrole-H), 4.22 – 3.74 (m, 8H, CH_2), 0.62 (t, 12H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.92, 131.65, 128.84, 128.25, 121.99, 118.92, 117.44, 115.76, 113.05, 108.71, 103.24, 45.21, 12.82.

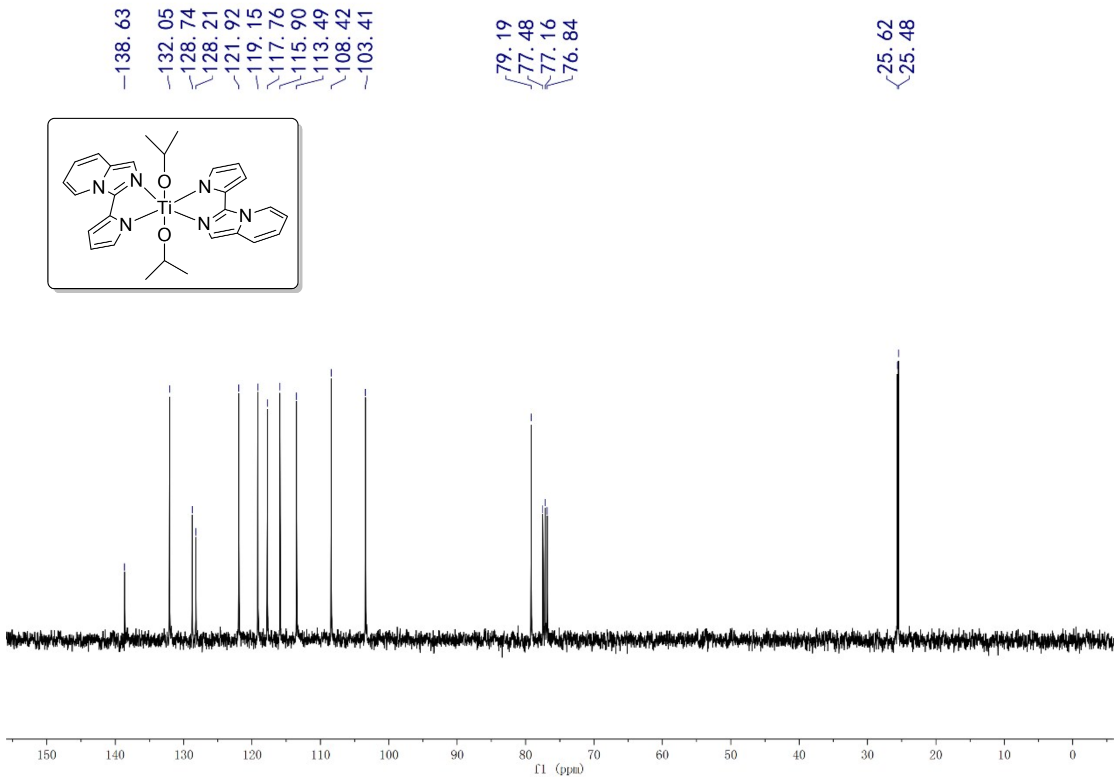




2.4 ^{1}H and ^{13}C NMR spectra for **3**

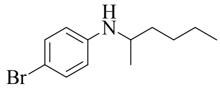
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, 2H, $C_7H_5N_2$), 7.51 (d, 2H, $C_7H_5N_2$), 7.15 – 7.00 (m, 2H, $C_7H_5N_2$), 6.59 (d, 2H, pyrrole-H), 6.52 – 6.38 (m, 6H, $C_7H_5N_2$ + pyrrole-H), 6.20 (s, 2H, pyrrole-H), 4.79 – 4.58 (m, 2H, CH), 1.17 (d, 6H, CH_3), 1.00 (d, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.63, 132.05, 128.74, 128.21, 121.92, 119.15, 117.76, 115.90, 113.49, 108.42, 103.41, 79.19, 25.55.



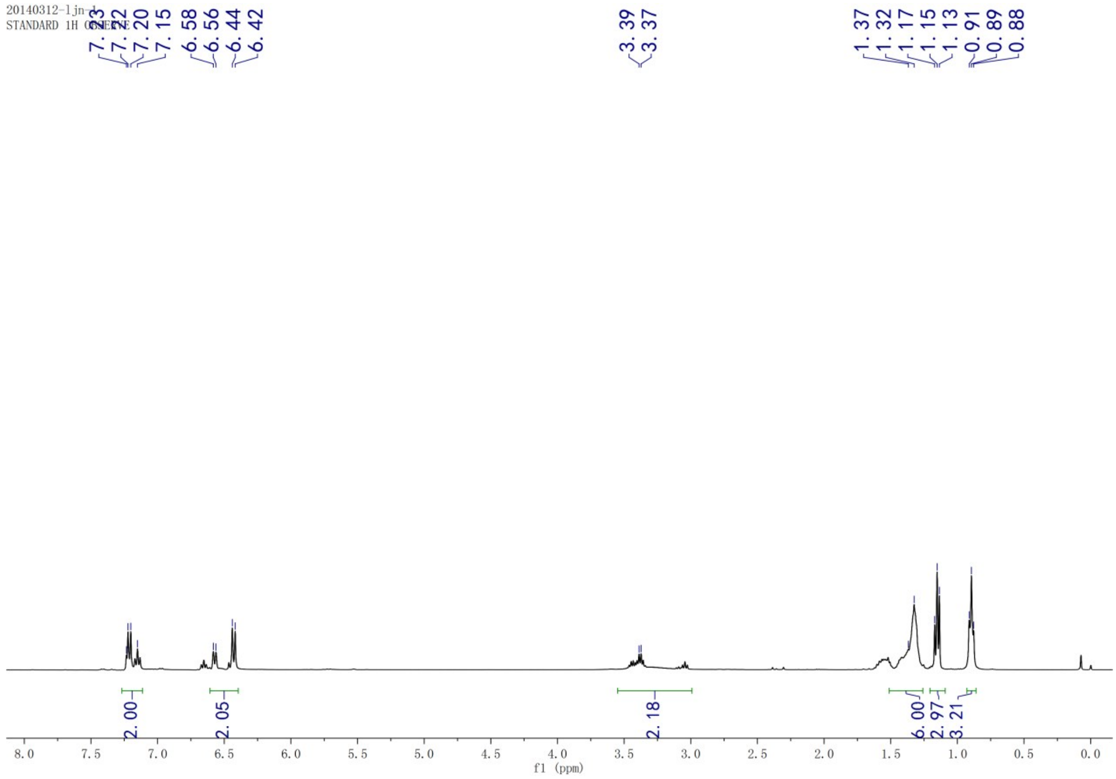


3.^{13}H NMR spectra for the hydroamination products

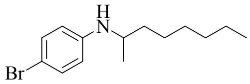
3.1 4-bromo-N-(hexan-2-yl)aniline



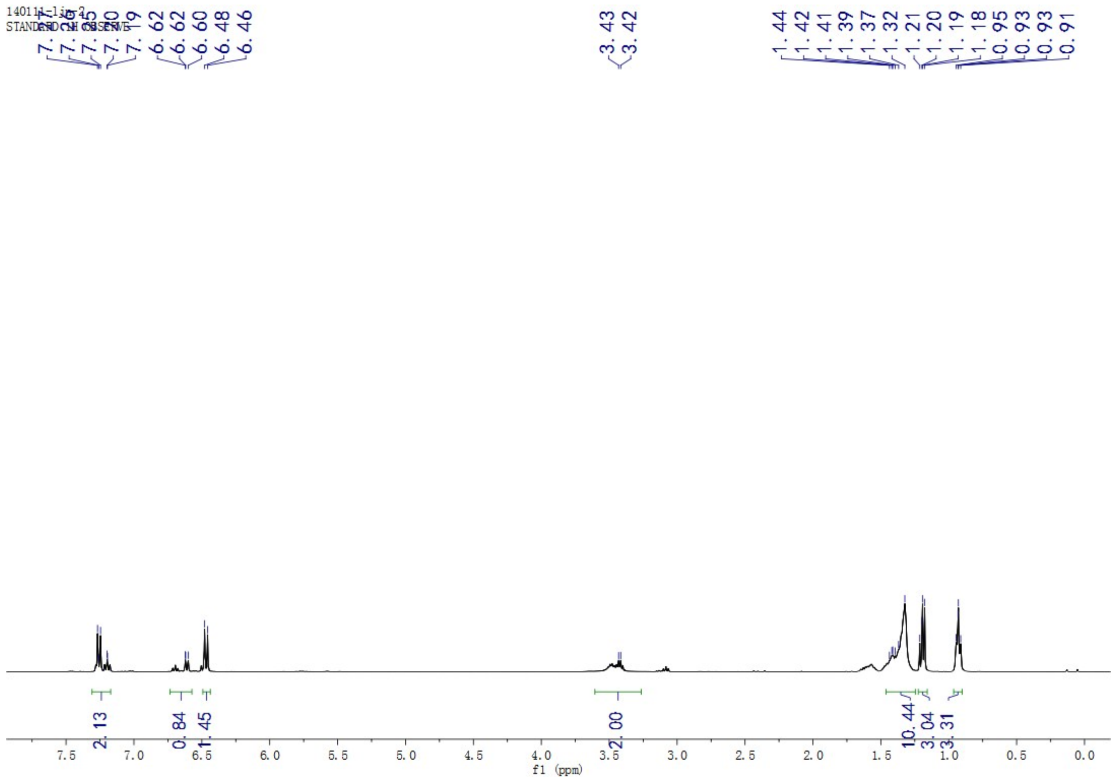
[1]H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, 2H, *m*-C_6H_4), 6.50 (d, 2H, *o*-C_6H_4), 3.38 (dd, 2H, -NCH-, -NH-), 1.49 – 3H,CH_3), 0.89 (t, 3H, CH_3).



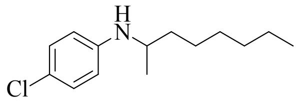
3.2 4-bromo-N-(octan-2-yl)aniline



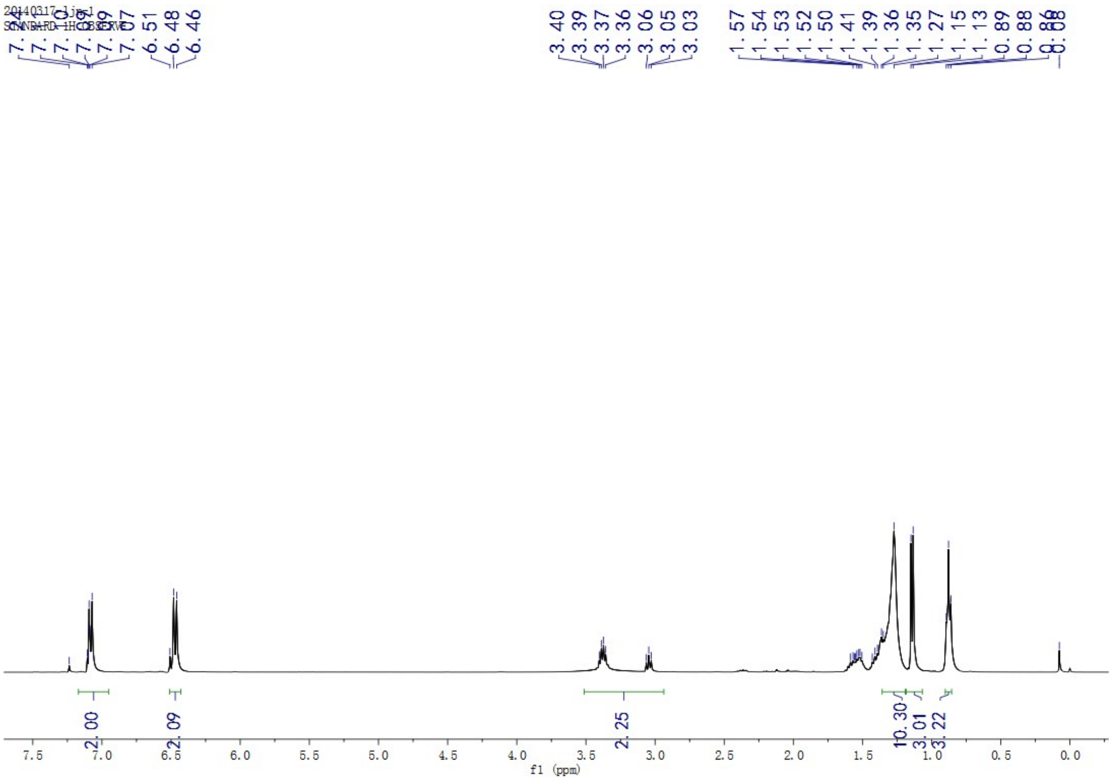
[1]H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.17 (m, 2H, Ar-H), 6.73 – 6.57 (m, 1H, Ar-H), 6.47 (d, 1H, Ar-H), 3.42 (d, 2H, NH, CH), 1.46 – 1.25 (m, 10H, CH_2), 1.20 (d, 3H, CH_3), 0.93 (d,3H, CH_3).



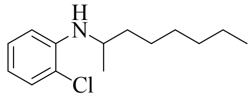
3.3 4-chloro-N-(octan-2-yl)aniline



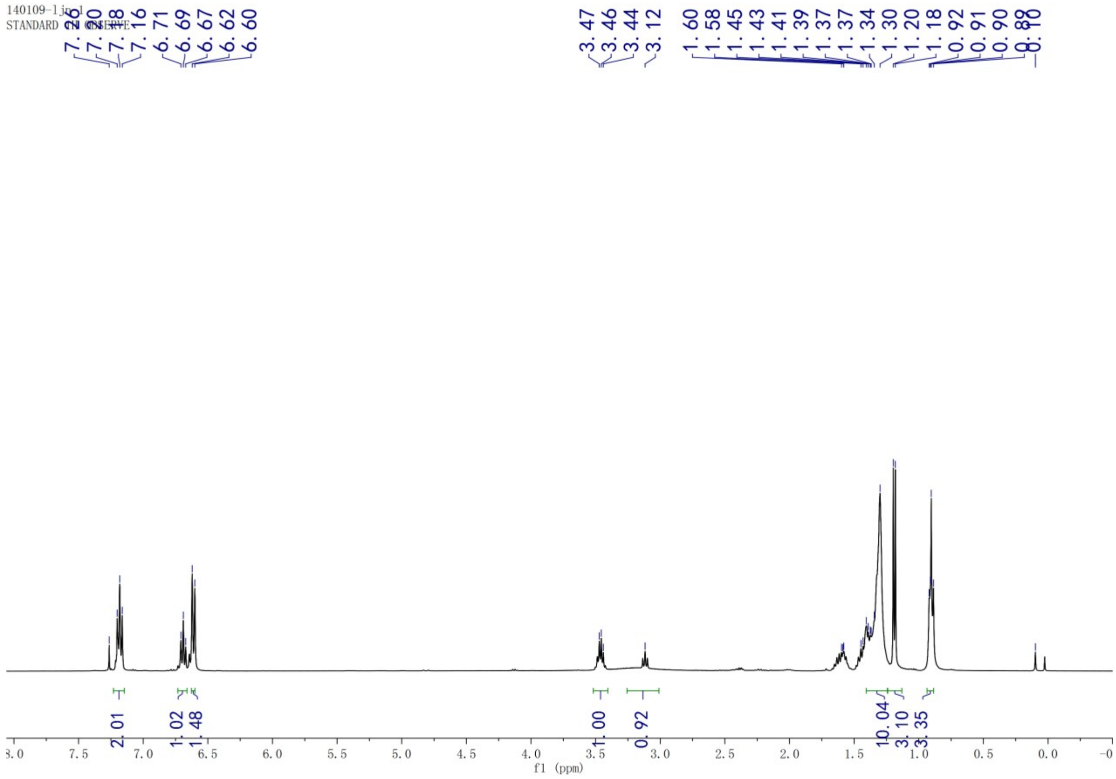
[1]H NMR (400 MHz, $CDCl_3$) δ 7.17 – 6.95 (m, 2H, Ar-H), 6.48 (t, 2H, Ar-H), 3.58 – 2.92 (m, 2H, NH, CH), 1.31 (d, 10H, CH_2), 1.14 (d, 3H, CH_3), 0.88 (t, 3H, CH_3).



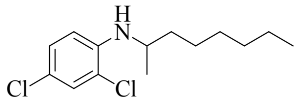
3.4 2-chloro-N-(octan-2-yl)aniline



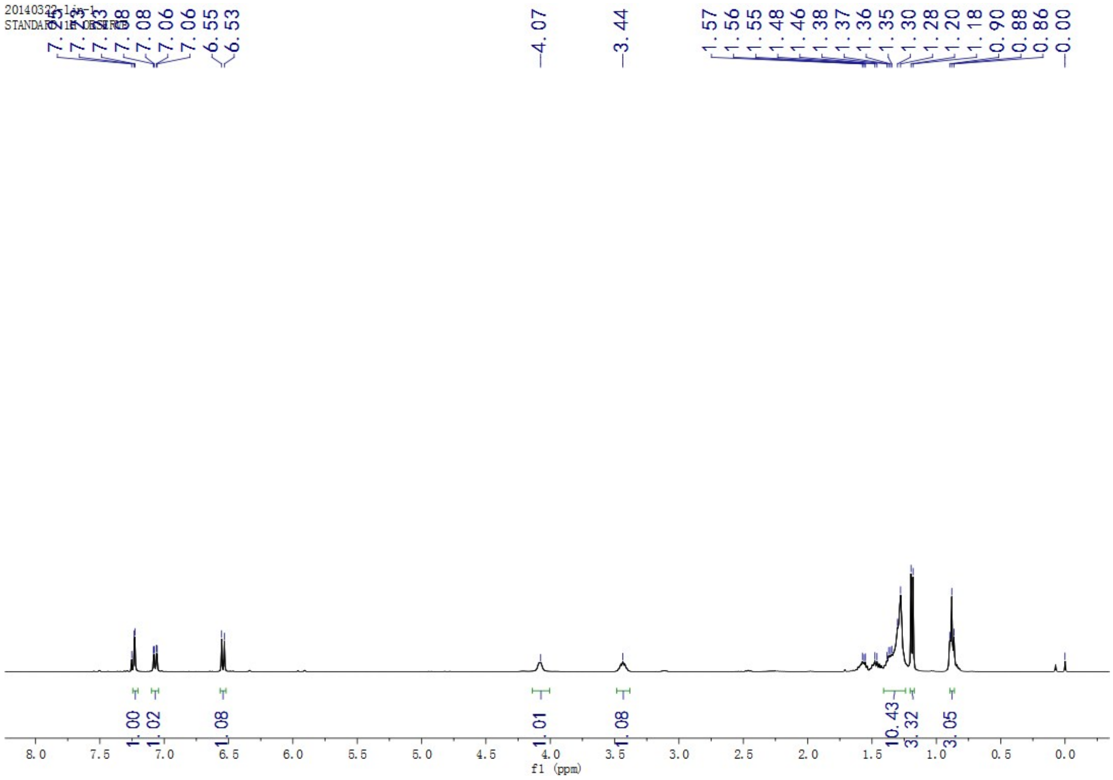
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 – 6.95 (m, 2H, Ar-H), 6.48 (t, 2H, Ar-H), 3.58 – 2.92 (m, 2H, NH, CH), 1.31 (d, 10H, CH_2), 1.14 (d, 3H, CH_2), 0.88 (t, 3H, CH_3).



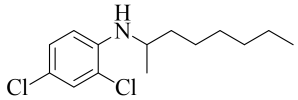
3.5 N-(2-Octyl)-2,4-dichloroaniline



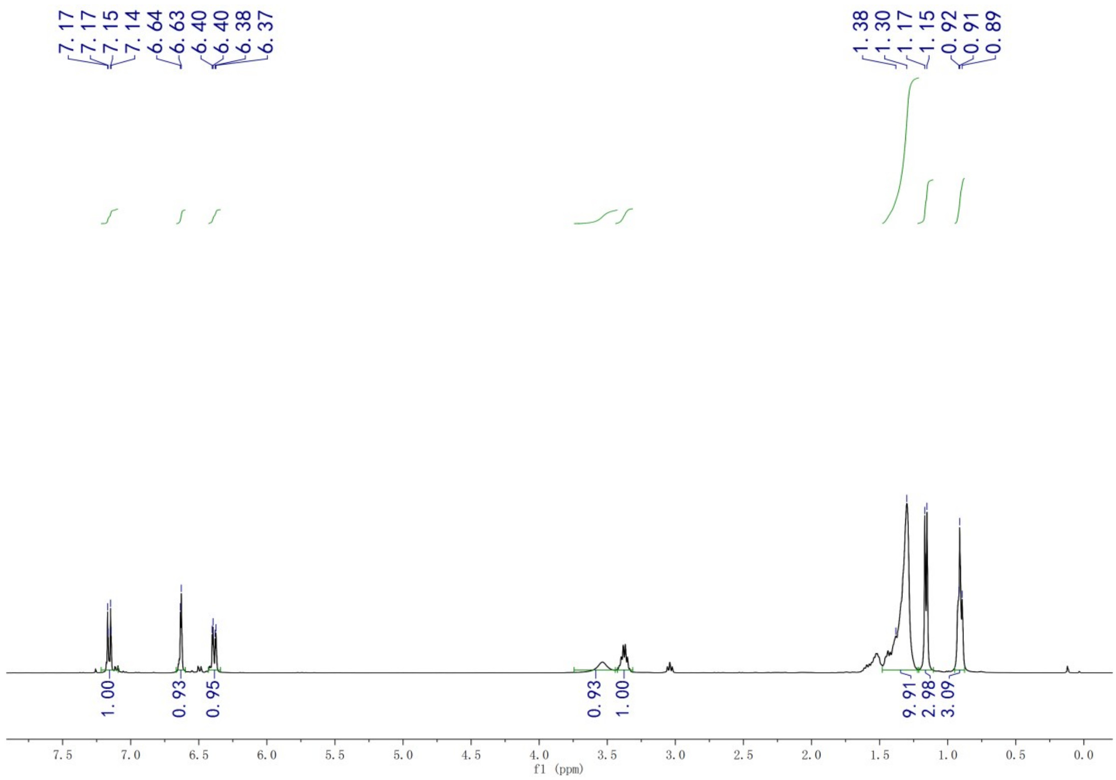
[1]H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, 1H, Ar-H), 7.07 (dd, 1H, Ar-H), 6.54 (d, 1H, Ar-H), 4.07 (s, 1H, NH), 3.44 (s, 1H, CH), 1.41 – 1.24 (m, 10H, CH_2), 1.19 (d, 3H, CH_3), 0.87 (d, 3H, CH_3).



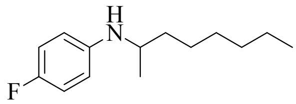
3.6 N-(2-Octyl)-3,4-dichloroaniline



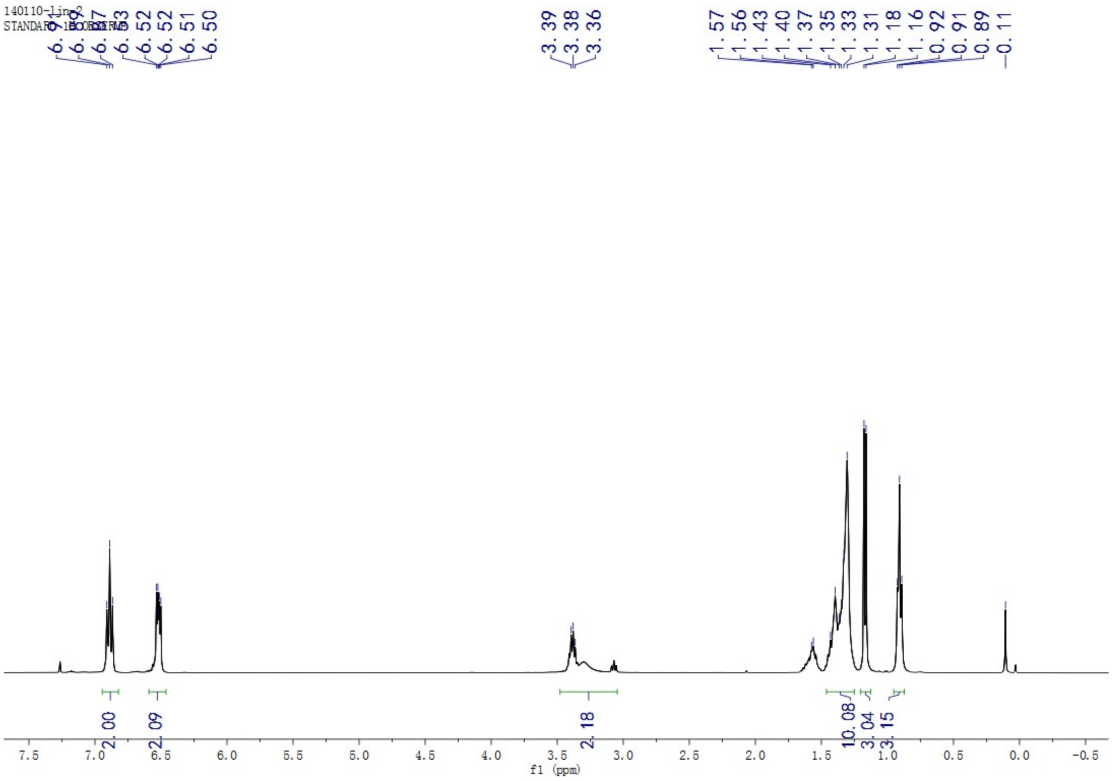
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (dd, 1H, Ar-H), 6.63 (d, 1H, Ar-H), 6.39 (dd, 1H,)Ar-H, 3.74 – 3.42 (m, 1H, NH), 3.44 – 3.31 (m, 1H, CH), 1.34 (d, 10H, CH_2), 1.16 (d, 3H, CH_3), 0.91 (t, 3H, CH_3).



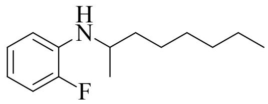
3.7 N-(2-Octyl)-4-fluoroaniline



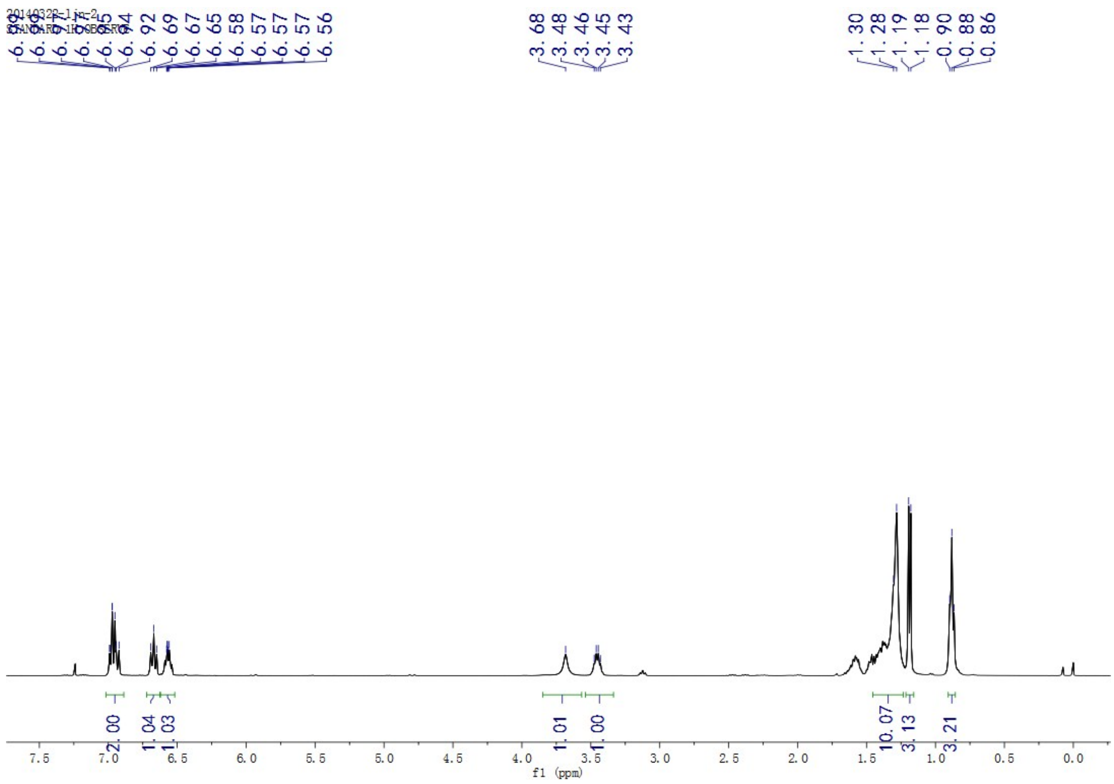
[1]H NMR (400 MHz, $CDCl_3$) δ 6.89 (t, 2H, Ar-H), 6.59 – 6.46 (m, 2H, Ar-H), 3.48 – 3.05 (m, 2H, NH, CH), 1.46 – 1.25 (m, 10H, CH_2), 1.17 (d, 3H, CH_3), 0.91 (t, 3H, CH_3).



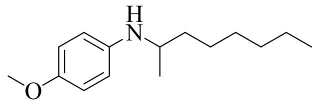
3.8 N-(2-Octyl)-2-fluoroaniline



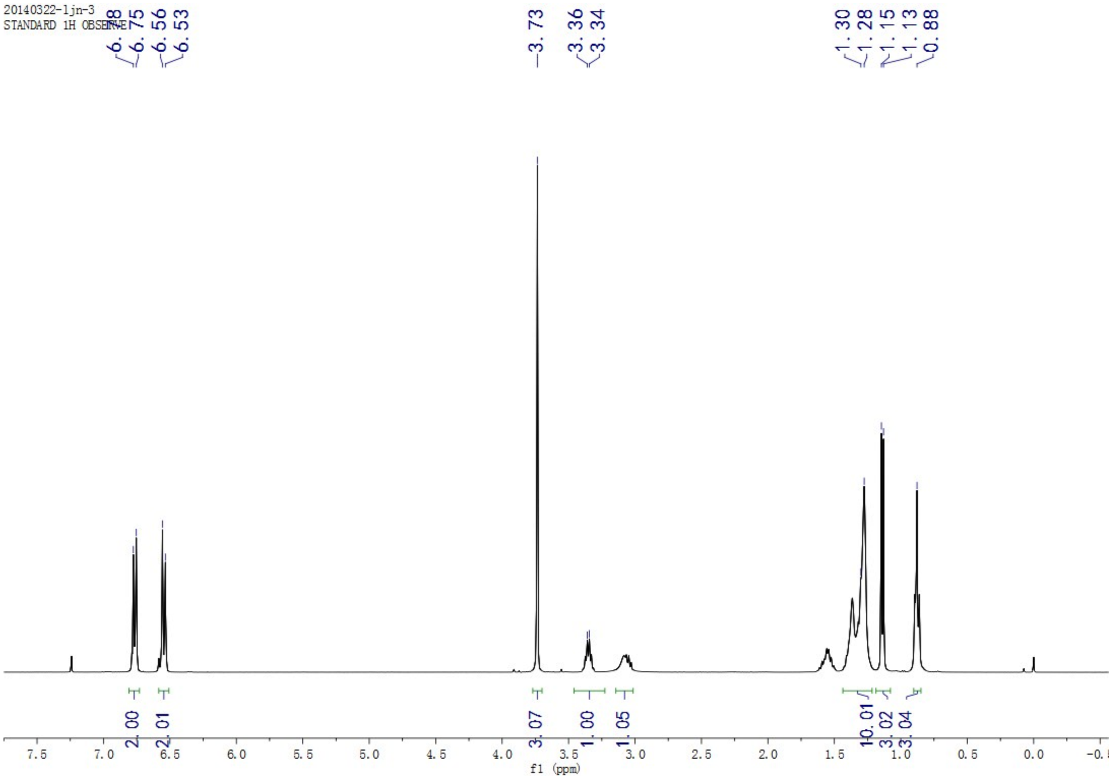
[1]H NMR (400 MHz, $CDCl_3$) δ 7.02 – 6.89 (m, 2H, Ar-H), 6.67 (t, 1H, Ar-H), 6.62 – 6.52 (m, 1H, Ar-H), 3.68 (s, 1H, NH), 3.45 (dd, 1H, CH), 1.29 (d, 10H, CH_2), 1.19 (d, 3H, CH_3), 0.88 (t, 3H, CH_3).



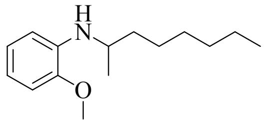
3.9 N-(2-Octyl)-4-methoxyaniline



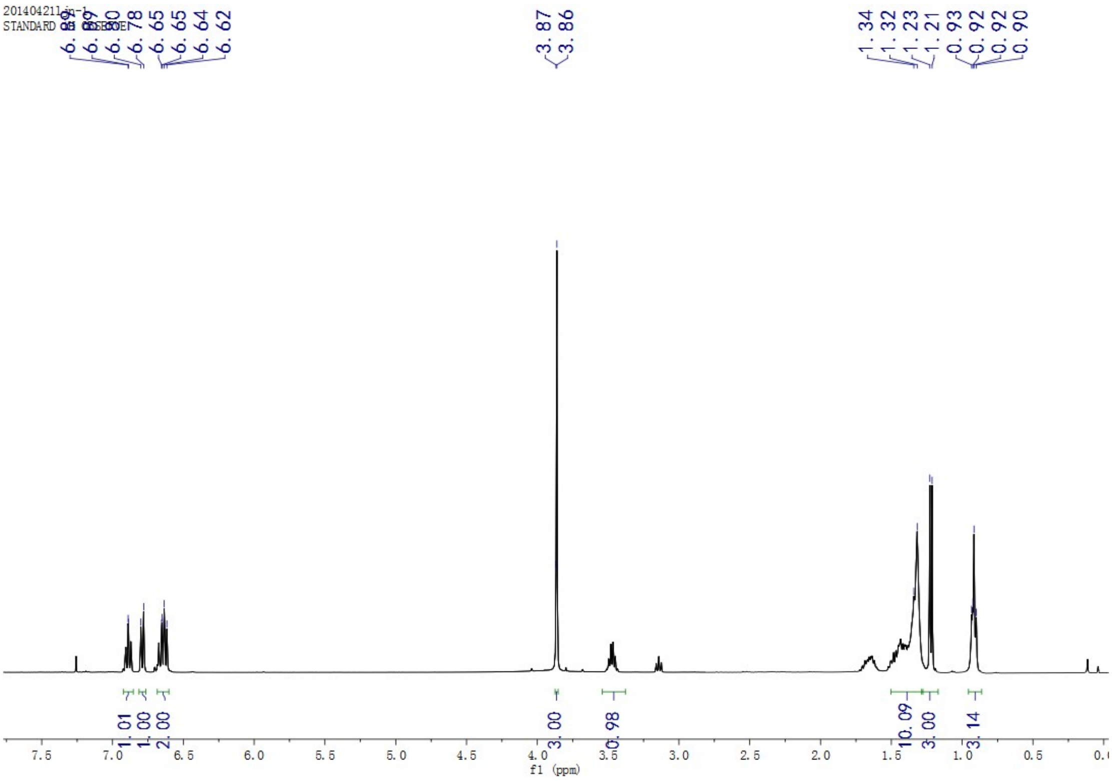
[1]H NMR (400 MHz, $CDCl_3$) δ 6.76 (d, 2H, Ar-H), 6.55 (d, 2H, Ar-H), 3.73 (s, 3H, OCH_3), 3.35 (d, 1H, NH), 3.06 (dd, 1H, CH), 1.29 (d, 10H, CH_2), 1.14 (d, 3H, CH_3), 0.88 (s, 3H, CH_3).



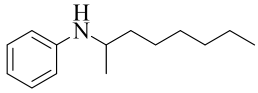
3.10 N-(2-Octyl)-2-methoxyaniline



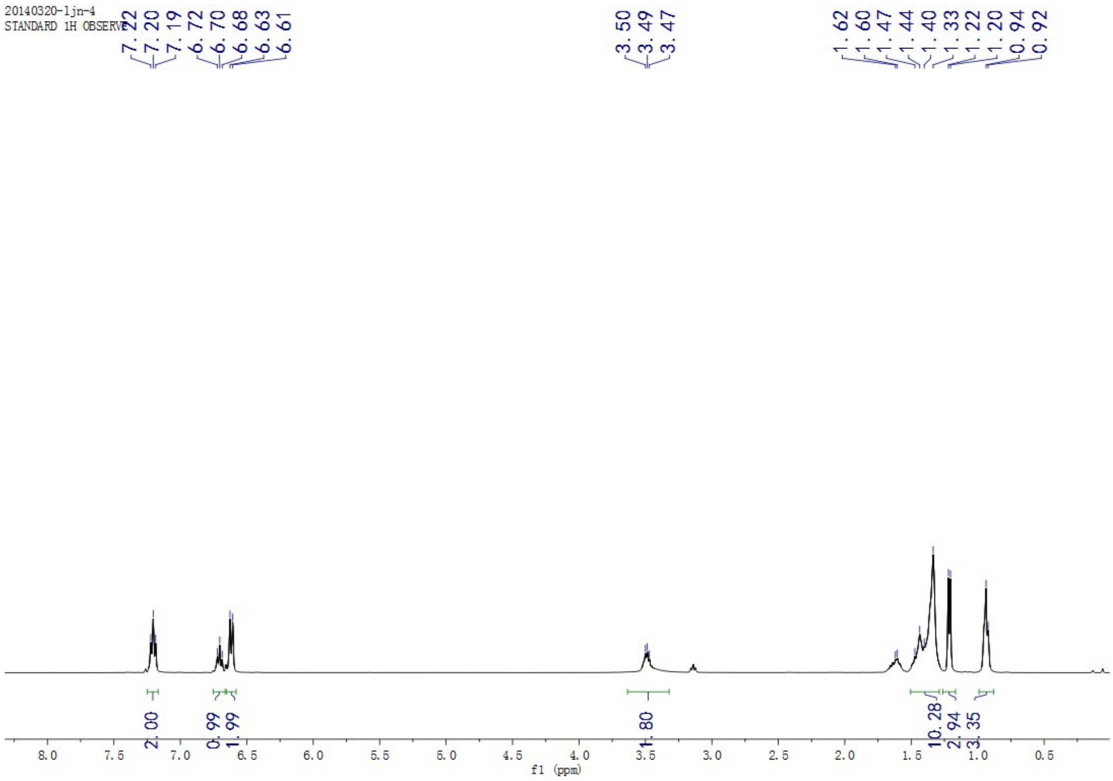
[1]H NMR (400 MHz, $CDCl_3$) δ 6.89 (d, 1H, Ar-H), 6.79 (d, 1H, Ar-H), 6.64 (dd, 2H, Ar-H), 3.87 (d, 3H, OCH_3), 3.53 – 3.37 (m, 1H, CH), 1.33 (d, 10H, CH_2), 1.22 (d, 3H, CH_3,), 0.92 (dd, 3H, CH_3).



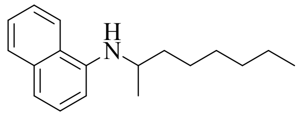
3.11 N-(2-Octyl)aniline



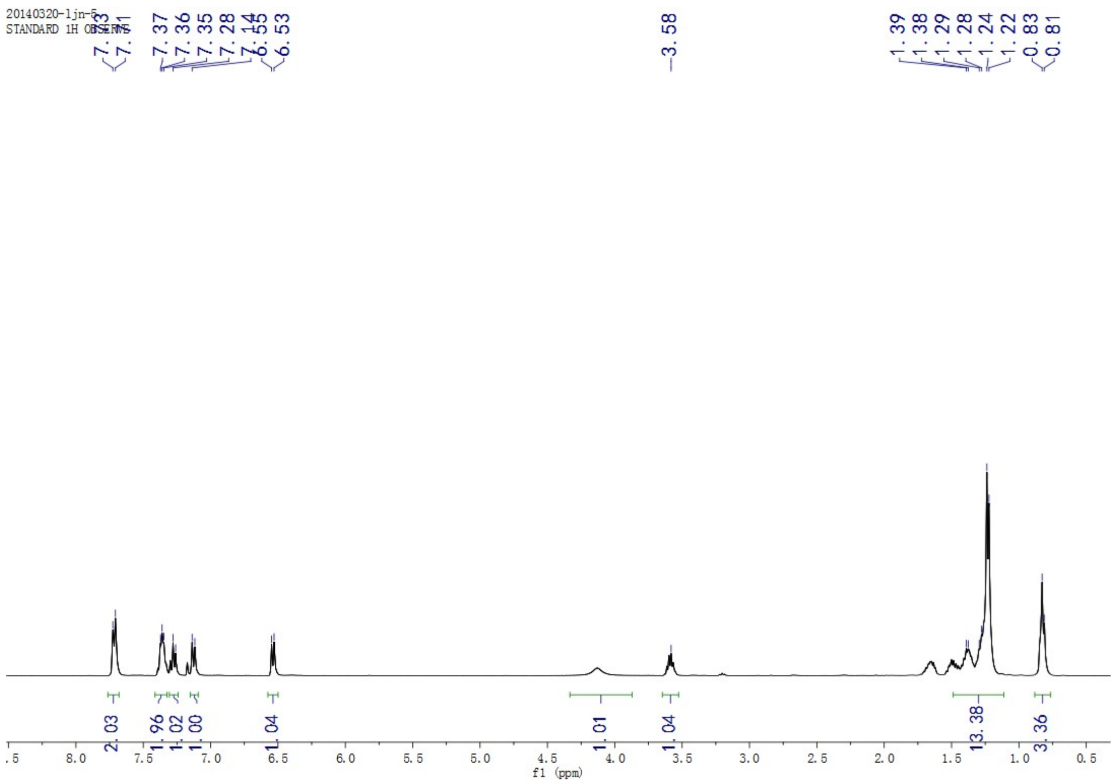
[1]H NMR (400 MHz, $CDCl_3$) δ 7.20 (t, 2H, Ar-H), 6.70 (t, 1H, Ar-H), 6.62 (d, 2H, Ar-H), 3.64 – 3.32 (m, 2H, NH, CH), 1.50 – 1.29 (m, 10H, CH_2), 1.21 (d, 3H, CH_3), 0.93 (d, 3H, CH_3).



3.12 N-(2-Octyl)naphthalen-2-amine



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, 2H, Ar-H), 7.41 – 7.32 (m, 2H, Ar-H), 7.27 (d,1H, Ar-H), 7.13 (d, 1H, Ar-H), 6.54 (d, 1H, Ar-H), 4.13 (s, 1H, NH), 3.58 (s, 1H, NH), 1.49 – 1.11 (m, 13H, CH_2, CH_3), 0.82 (d, 3H, CH_3).



4. Ring-opening polymerization of ε-caprolactone by complex 3

Table S4 Polymerization ε-caprolactone initiated by **3**

Entry	Initiator	solvent	[M]/[I]	t/h	Yield/%[a]	T/℃	Mn(calc)[b](10^4)	Mn[c](10^4)	Mn(obsd)[d](10^4)	PDI	Efficiency/%
1	**3**	DME	200	24	82	80	1.87	2.05	1.15	1.53	90.1
2	**3**	DME	200	36	55	60	1.25	2.17	1.21	1.46	57.8
3	**3**	THF	200	24	90	80	2.05	3.19	1.79	1.59	64.3
4	**3**	THF	200	36	70	60	1.60	2.00	1.12	1.31	79.6
5	**3**	Tol	200	24	84	80	1.91	2.25	1.26	1.53	81.1
6	**3**	Tol	200	36	72	60	1.64	3.09	1.73	1.57	53.1

[a]Yield: weight of polymer obtained/weight of monomer used. [b]Mn(calc) = M_{mono}*[M]/[I] *Conv. [c]Measured by GPC relative to polystyrene standards. [d] Measured by GPC relative to standards with Mark-Houwink corrections for Mn (obsd) = 0.56 Mn (GPC) for ε-caprolactone.