Electronic Supplementary Material (ESI) for RSC Advances

Supporting Information

Title: Titanium and zirconium amido complexes supported by imidazole-containing ligands: syntheses, characterizations and catalytic activities

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1. Crystallography data for **2** and **6**·THF.
2. ^{1}H and ^{13}C NMR spectra for the complexes and ligand HL4.
3. ^{1}H and ^{13}C NMR spectra, IR and HRMS data for the hydroamination products.

1. Crystallography data for **2** and **6**·THF.

1.1 Crystal data and structure refinements for and **2** and **6**·THF

Table 1 Crystal data and structure refinements for **2** and **6**·THF

Complex	**2**	**6**·THF
Empirical formula	$C_{26}H_{30}Cl_2N_6Ti$	$C_{44}H_{36}Cl_4N_8Ti$
Formula weight	545.36	866.51
Temperature	223(2) K	223(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Orthorhombic	Triclinic
Space group	$P\,2_12_12_1$	P -1
a/Å	11.829(2)	8.9628(18)
b/Å	12.517(3)	13.517(3)
c/Å	18.391(4)	19.262(4)
α/°	90.00	73.96(3)
β/°	90.00	87.86(3)
γ/°	90.00	74.76(3)
Volume/Å^3	2723.2(9)	2162.3(8)
ρ/g cm^{-3}	1.330	1.331
Z	4	2
F(000)	1136	892
Crystal size/mm	0.20 x 0.15 x 0.15	0.40 x 0.20 x 0.20
θ/°	3.24 to 25.30	3.08 to 25.00
Limiting indices	-12<h<13	-8<h<10
	-10<k<15	-16<k<15
	-20<l<22	-22<l<22
Reflections collected / unique	8641 / 4561	17888 / 7536
Data/ restraints/ parameters	4561 / 0 / 323	7536 / 7 / 518
GOF	0.999	1.099
R_1, wR_2	R_1 = 0.0406	R_1 = 0.0879
[I>2σ(I)]	wR_2 = 0.0871	wR_2 = 0.1709
R_1, wR_2	R_1 = 0.0452	R_1 = 0.1400
(all data)	wR_2 = 0.0906	wR_2 = 0.1971
Largest diff. peak and hole /e. Å^3	0.222 and -0.231	0.269 and -0.390

1.2 Bond lengths (Å) and angles (°) for **2**.

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

Ti(1)-N(4)	1.880(3)
Ti(1)-N(6)	1.902(3)
Ti(1)-N(5)	1.914(3)
Ti(1)-N(2)	2.142(2)
Ti(1)-N(1)	2.292(2)
Cl(2)-C(18)	1.738(3)
N(2)-C(6)	1.368(3)
N(2)-C(7)	1.385(3)
Cl(1)-C(12)	1.737(3)
N(1)-C(1)	1.339(4)
N(1)-C(5)	1.355(4)
C(7)-C(8)	1.400(4)
C(7)-C(9)	1.463(4)
C(6)-N(3)	1.330(4)
C(6)-C(5)	1.446(4)
C(8)-N(3)	1.380(4)
C(8)-C(15)	1.464(4)
C(15)-C(20)	1.390(4)
C(15)-C(16)	1.391(4)
C(20)-C(19)	1.385(5)
N(6)-C(23)	1.446(5)
N(6)-C(24)	1.470(5)
C(4)-C(3)	1.379(5)
C(4)-C(5)	1.385(4)
C(1)-C(2)	1.369(5)
C(18)-C(17)	1.368(4)
C(18)-C(19)	1.391(5)
C(13)-C(12)	1.372(5)
C(13)-C(14)	1.385(4)
N(5)-C(21)	1.450(5)
N(5)-C(22)	1.469(4)
C(14)-C(9)	1.390(4)
C(9)-C(10)	1.388(4)
C(10)-C(11)	1.387(4)
C(3)-C(2)	1.379(5)
C(17)-C(16)	1.387(4)
N(4)-C(25)	1.439(5)
N(4)-C(26)	1.451(5)
C(11)-C(12)	1.372(5)

N(4)-Ti(1)-N(6)	98.21(13)
N(4)-Ti(1)-N(5)	110.46(12)
N(6)-Ti(1)-N(5)	95.24(13)
N(4)-Ti(1)-N(2)	124.57(11)
N(6)-Ti(1)-N(2)	96.20(10)
N(5)-Ti(1)-N(2)	121.06(11)
N(4)-Ti(1)-N(1)	91.29(11)
N(6)-Ti(1)-N(1)	168.59(10)
N(5)-Ti(1)-N(1)	87.28(11)
N(2)-Ti(1)-N(1)	73.08(8)
C(6)-N(2)-C(7)	103.9(2)
C(6)-N(2)-Ti(1)	115.02(18)
C(7)-N(2)-Ti(1)	138.04(18)
C(1)-N(1)-C(5)	118.2(3)
C(1)-N(1)-Ti(1)	126.8(2)
C(5)-N(1)-Ti(1)	113.90(19)
N(2)-C(7)-C(8)	107.4(2)
N(2)-C(7)-C(9)	124.0(2)
C(8)-C(7)-C(9)	128.5(2)
N(3)-C(6)-N(2)	115.2(3)
N(3)-C(6)-C(5)	125.8(3)
N(2)-C(6)-C(5)	118.9(3)
N(3)-C(8)-C(7)	109.6(2)
N(3)-C(8)-C(15)	120.6(2)
C(7)-C(8)-C(15)	129.8(3)
C(20)-C(15)-C(16)	117.3(3)
C(20)-C(15)-C(8)	120.0(3)
C(16)-C(15)-C(8)	122.7(3)
C(19)-C(20)-C(15)	121.9(3)
C(23)-N(6)-C(24)	109.7(4)
C(23)-N(6)-Ti(1)	130.6(3)
C(24)-N(6)-Ti(1)	119.6(3)
C(3)-C(4)-C(5)	119.2(3)
N(1)-C(1)-C(2)	122.9(3)
C(6)-N(3)-C(8)	103.8(2)
C(17)-C(18)-C(19)	121.0(3)
C(17)-C(18)-Cl(2)	119.9(2)
C(19)-C(18)-Cl(2)	119.1(2)
C(12)-C(13)-C(14)	119.2(3)
N(1)-C(5)-C(4)	121.6(3)
N(1)-C(5)-C(6)	113.2(3)
C(4)-C(5)-C(6)	125.2(3)
C(21)-N(5)-C(22)	108.9(3)

C(21)-N(5)-Ti(1)	128.4(2)
C(22)-N(5)-Ti(1)	122.4(3)
C(13)-C(14)-C(9)	121.1(3)
C(14)-C(9)-C(10)	118.5(3)
C(14)-C(9)-C(7)	119.8(3)
C(10)-C(9)-C(7)	121.7(3)
C(11)-C(10)-C(9)	120.3(3)
C(4)-C(3)-C(2)	119.0(3)
C(18)-C(17)-C(16)	119.2(3)
C(25)-N(4)-C(26)	112.4(3)
C(25)-N(4)-Ti(1)	115.6(2)
C(26)-N(4)-Ti(1)	132.0(3)
C(17)-C(16)-C(15)	121.8(3)
C(20)-C(19)-C(18)	118.7(3)
C(12)-C(11)-C(10)	120.0(3)
C(11)-C(12)-C(13)	120.8(3)
C(11)-C(12)-Cl(1)	120.0(3)
C(13)-C(12)-Cl(1)	119.2(3)
C(1)-C(2)-C(3)	119.1(3)

Table 3 Bond lengths (Å) and angles (°) for **6**·THF**.**

Cl(1)-C(12)	1.744(6)
N(1)-C(6)	1.370(6)
N(1)-C(8)	1.394(6)
N(1)-Ti(2)	2.124(4)
C(1)-N(3)	1.347(6)
C(1)-C(2)	1.379(7)
C(1)-C(6)	1.448(7)
Ti(2)-N(8)	1.880(5)
Ti(2)-N(7)	1.902(4)
Ti(2)-N(4)	2.152(4)
Ti(2)-N(3)	2.308(4)
Ti(2)-N(6)	2.314(5)
Cl(2)-C(18)	1.734(6)
N(2)-C(6)	1.326(6)
N(2)-C(7)	1.370(6)
C(2)-C(3)	1.373(8)
C(2)-H(2)	0.9400
Cl(3)-C(32)	1.741(5)
N(3)-C(5)	1.360(6)
C(3)-C(4)	1.388(8)

C(3)-H(3)	0.9400
Cl(4)-C(38)	1.741(6)
N(4)-C(26)	1.364(6)
N(4)-C(28)	1.392(6)
C(4)-C(5)	1.368(8)
C(4)-H(4)	0.9400
N(5)-C(26)	1.350(6)
N(5)-C(27)	1.365(6)
C(5)-H(5)	0.9400
N(6)-C(25)	1.343(7)
N(6)-C(21)	1.359(6)
N(7)-C(41)	1.475(7)
N(7)-C(42)	1.476(7)
C(7)-C(8)	1.387(7)
C(7)-C(9)	1.484(7)
N(8)-C(44)	1.469(7)
N(8)-C(43)	1.477(7)
C(8)-C(15)	1.476(7)
C(9)-C(10)	1.387(7)
C(9)-C(14)	1.393(7)
C(10)-C(11)	1.402(7)
C(10)-H(10)	0.9400
C(11)-C(12)	1.362(8)
C(11)-H(11)	0.9400
C(12)-C(13)	1.378(8)
C(13)-C(14)	1.374(8)
C(13)-H(13)	0.9400
C(14)-H(14)	0.9400
C(15)-C(20)	1.388(7)
C(15)-C(16)	1.388(7)
C(16)-C(17)	1.390(8)
C(16)-H(16)	0.9400
C(17)-C(18)	1.379(9)
C(17)-H(17)	0.9400
C(18)-C(19)	1.368(9)
C(19)-C(20)	1.380(8)
C(19)-H(19)	0.9400
C(20)-H(20)	0.9400
C(21)-C(22)	1.378(7)
C(21)-C(26)	1.446(7)
C(22)-C(23)	1.366(7)
C(22)-H(22)	0.9400
C(23)-C(24)	1.390(7)
C(23)-H(23)	0.9400

C(24)-C(25)	1.380(7)
C(24)-H(24)	0.9400
C(25)-H(25)	0.9400
C(27)-C(28)	1.386(7)
C(27)-C(29)	1.484(7)
C(28)-C(35)	1.477(7)
C(29)-C(30)	1.380(7)
C(29)-C(34)	1.390(7)
C(30)-C(31)	1.383(7)
C(30)-H(30)	0.9400
C(31)-C(32)	1.368(8)
C(31)-H(31)	0.9400
C(32)-C(33)	1.368(8)
C(33)-C(34)	1.372(7)
C(33)-H(33)	0.9400
C(34)-H(34)	0.9400
C(35)-C(36)	1.386(7)
C(35)-C(40)	1.387(7)
C(36)-C(37)	1.380(8)
C(36)-H(36)	0.9400
C(37)-C(38)	1.392(8)
C(37)-H(37)	0.9400
C(38)-C(39)	1.392(8)
C(39)-C(40)	1.377(8)
C(39)-H(39)	0.9400
C(40)-H(40)	0.9400
C(41)-H(41A)	0.9700
C(41)-H(41B)	0.9700
C(41)-H(41C)	0.9700
C(42)-H(42A)	0.9700
C(42)-H(42B)	0.9700
C(42)-H(42C)	0.9700
C(43)-H(43A)	0.9700
C(43)-H(43B)	0.9700
C(43)-H(43C)	0.9700
C(44)-H(44A)	0.9700
C(44)-H(44B)	0.9700
C(44)-H(44C)	0.9700

C(6)-N(1)-C(8)	103.4(4)
C(6)-N(1)-Ti(2)	115.9(3)
C(8)-N(1)-Ti(2)	140.1(3)
N(3)-C(1)-C(2)	122.0(5)
N(3)-C(1)-C(6)	115.2(4)

C(2)-C(1)-C(6)	122.7(5)
N(8)-Ti(2)-N(7)	104.9(2)
N(8)-Ti(2)-N(1)	97.18(18)
N(7)-Ti(2)-N(1)	100.82(18)
N(8)-Ti(2)-N(4)	100.11(18)
N(7)-Ti(2)-N(4)	96.49(17)
N(1)-Ti(2)-N(4)	151.44(16)
N(8)-Ti(2)-N(3)	87.00(17)
N(7)-Ti(2)-N(3)	167.93(18)
N(1)-Ti(2)-N(3)	75.20(15)
N(4)-Ti(2)-N(3)	83.16(15)
N(8)-Ti(2)-N(6)	160.54(17)
N(7)-Ti(2)-N(6)	94.23(18)
N(1)-Ti(2)-N(6)	82.41(16)
N(4)-Ti(2)-N(6)	73.77(16)
N(3)-Ti(2)-N(6)	74.04(15)
C(6)-N(2)-C(7)	103.6(4)
C(3)-C(2)-C(1)	120.2(6)
C(3)-C(2)-H(2)	119.9
C(1)-C(2)-H(2)	119.9
C(1)-N(3)-C(5)	117.1(5)
C(1)-N(3)-Ti(2)	113.3(3)
C(5)-N(3)-Ti(2)	129.7(4)
C(2)-C(3)-C(4)	118.6(6)
C(2)-C(3)-H(3)	120.7
C(4)-C(3)-H(3)	120.7
C(26)-N(4)-C(28)	103.5(4)
C(26)-N(4)-Ti(2)	115.6(3)
C(28)-N(4)-Ti(2)	139.6(4)
C(5)-C(4)-C(3)	118.5(6)
C(5)-C(4)-H(4)	120.7
C(3)-C(4)-H(4)	120.7
C(26)-N(5)-C(27)	103.3(4)
N(3)-C(5)-C(4)	123.6(5)
N(3)-C(5)-H(5)	118.2
C(4)-C(5)-H(5)	118.2
C(25)-N(6)-C(21)	117.5(5)
C(25)-N(6)-Ti(2)	127.9(4)
C(21)-N(6)-Ti(2)	114.3(3)
N(2)-C(6)-N(1)	115.3(4)
N(2)-C(6)-C(1)	124.8(5)
N(1)-C(6)-C(1)	119.9(4)
C(41)-N(7)-C(42)	107.7(5)
C(41)-N(7)-Ti(2)	127.4(4)

C(42)-N(7)-Ti(2)	124.6(4)
N(2)-C(7)-C(8)	110.6(4)
N(2)-C(7)-C(9)	119.4(4)
C(8)-C(7)-C(9)	129.8(5)
C(44)-N(8)-C(43)	110.2(5)
C(44)-N(8)-Ti(2)	129.8(4)
C(43)-N(8)-Ti(2)	118.7(4)
C(7)-C(8)-N(1)	107.1(4)
C(7)-C(8)-C(15)	130.8(5)
N(1)-C(8)-C(15)	121.8(4)
C(10)-C(9)-C(14)	116.9(5)
C(10)-C(9)-C(7)	118.0(5)
C(14)-C(9)-C(7)	125.0(5)
C(9)-C(10)-C(11)	121.6(5)
C(9)-C(10)-H(10)	119.2
C(11)-C(10)-H(10)	119.2
C(12)-C(11)-C(10)	119.2(5)
C(12)-C(11)-H(11)	120.4
C(10)-C(11)-H(11)	120.4
C(11)-C(12)-C(13)	120.7(5)
C(11)-C(12)-Cl(1)	119.0(4)
C(13)-C(12)-Cl(1)	120.3(5)
C(14)-C(13)-C(12)	119.6(5)
C(14)-C(13)-H(13)	120.2
C(12)-C(13)-H(13)	120.2
C(13)-C(14)-C(9)	122.0(5)
C(13)-C(14)-H(14)	119.0
C(9)-C(14)-H(14)	119.0
C(20)-C(15)-C(16)	117.5(5)
C(20)-C(15)-C(8)	122.8(5)
C(16)-C(15)-C(8)	119.7(5)
C(15)-C(16)-C(17)	121.7(6)
C(15)-C(16)-H(16)	119.2
C(17)-C(16)-H(16)	119.2
C(18)-C(17)-C(16)	118.4(6)
C(18)-C(17)-H(17)	120.8
C(16)-C(17)-H(17)	120.8
C(19)-C(18)-C(17)	121.6(5)
C(19)-C(18)-Cl(2)	119.4(5)
C(17)-C(18)-Cl(2)	118.9(5)
C(18)-C(19)-C(20)	118.9(6)
C(18)-C(19)-H(19)	120.6
C(20)-C(19)-H(19)	120.6
C(19)-C(20)-C(15)	121.9(6)

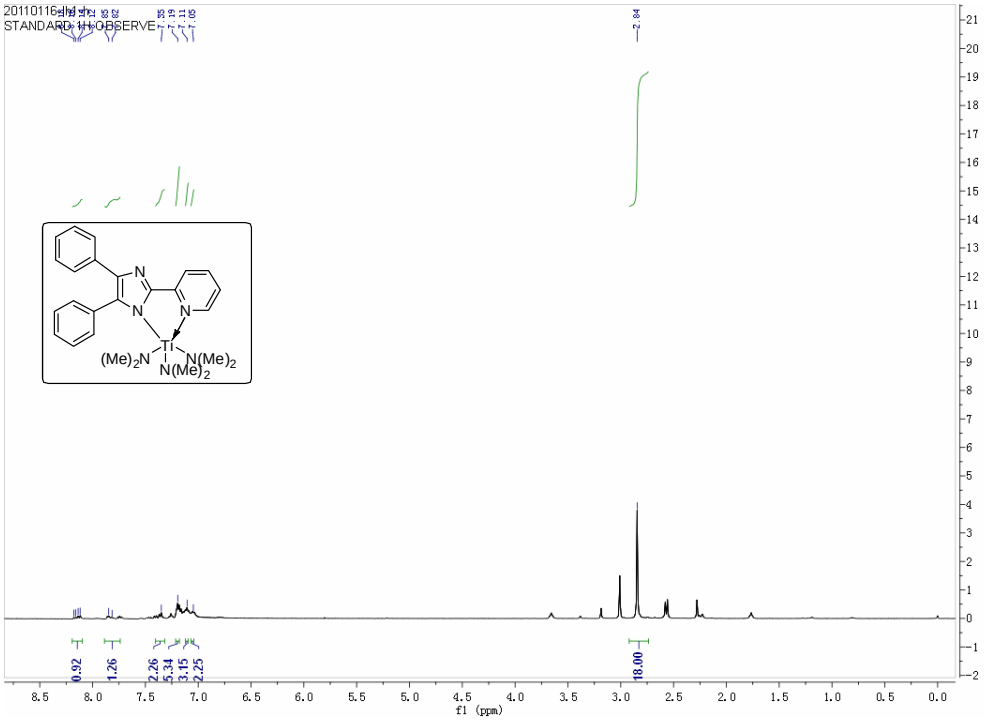
C(19)-C(20)-H(20)	119.1
C(15)-C(20)-H(20)	119.1
N(6)-C(21)-C(22)	122.9(5)
N(6)-C(21)-C(26)	113.7(5)
C(22)-C(21)-C(26)	123.4(5)
C(23)-C(22)-C(21)	118.1(5)
C(23)-C(22)-H(22)	121.0
C(21)-C(22)-H(22)	121.0
C(22)-C(23)-C(24)	120.7(5)
C(22)-C(23)-H(23)	119.6
C(24)-C(23)-H(23)	119.6
C(25)-C(24)-C(23)	117.6(5)
C(25)-C(24)-H(24)	121.2
C(23)-C(24)-H(24)	121.2
N(6)-C(25)-C(24)	123.2(5)
N(6)-C(25)-H(25)	118.4
C(24)-C(25)-H(25)	118.4
N(5)-C(26)-N(4)	114.9(5)
N(5)-C(26)-C(21)	124.7(5)
N(4)-C(26)-C(21)	120.4(4)
N(5)-C(27)-C(28)	110.6(4)
N(5)-C(27)-C(29)	119.2(5)
C(28)-C(27)-C(29)	130.1(5)
C(27)-C(28)-N(4)	107.6(4)
C(27)-C(28)-C(35)	130.1(5)
N(4)-C(28)-C(35)	122.2(4)
C(30)-C(29)-C(34)	118.0(5)
C(30)-C(29)-C(27)	120.8(5)
C(34)-C(29)-C(27)	121.2(5)
C(29)-C(30)-C(31)	120.9(5)
C(29)-C(30)-H(30)	119.5
C(31)-C(30)-H(30)	119.5
C(32)-C(31)-C(30)	119.8(5)
C(32)-C(31)-H(31)	120.1
C(30)-C(31)-H(31)	120.1
C(33)-C(32)-C(31)	120.3(5)
C(33)-C(32)-Cl(3)	119.0(5)
C(31)-C(32)-Cl(3)	120.7(4)
C(32)-C(33)-C(34)	120.0(5)
C(32)-C(33)-H(33)	120.0
C(34)-C(33)-H(33)	120.0
C(33)-C(34)-C(29)	121.0(5)
C(33)-C(34)-H(34)	119.5
C(29)-C(34)-H(34)	119.5

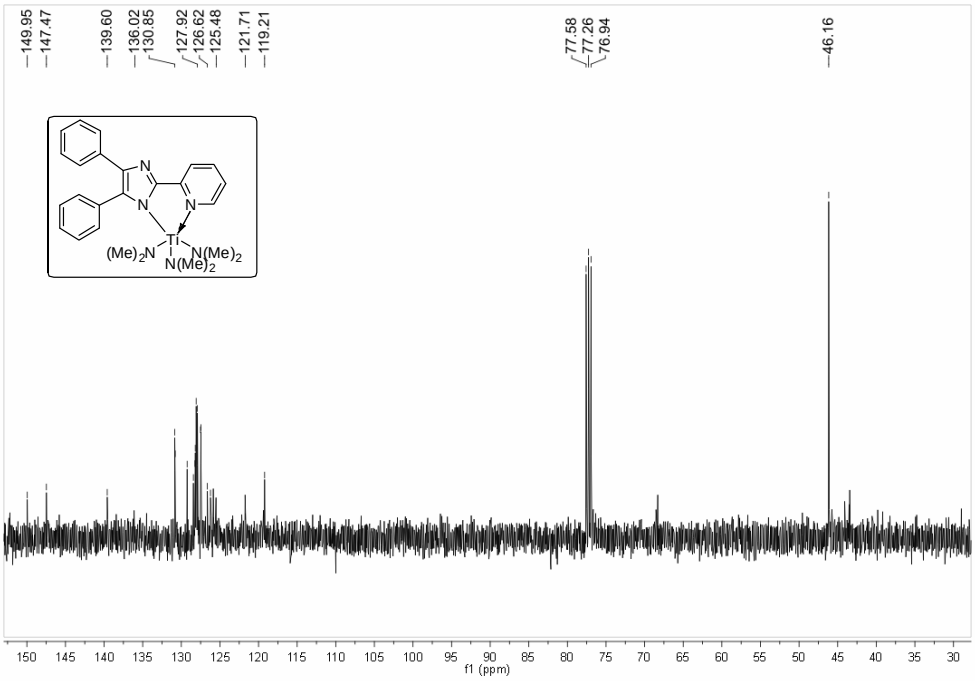
C(36)-C(35)-C(40)	117.9(5)
C(36)-C(35)-C(28)	122.0(5)
C(40)-C(35)-C(28)	120.0(5)
C(37)-C(36)-C(35)	121.6(6)
C(37)-C(36)-H(36)	119.2
C(35)-C(36)-H(36)	119.2
C(36)-C(37)-C(38)	119.3(6)
C(36)-C(37)-H(37)	120.4
C(38)-C(37)-H(37)	120.4
C(37)-C(38)-C(39)	120.2(6)
C(37)-C(38)-Cl(4)	120.2(5)
C(39)-C(38)-Cl(4)	119.5(5)
C(40)-C(39)-C(38)	119.0(6)
C(40)-C(39)-H(39)	120.5
C(38)-C(39)-H(39)	120.5
C(39)-C(40)-C(35)	122.0(6)
C(39)-C(40)-H(40)	119.0
C(35)-C(40)-H(40)	119.0
N(7)-C(41)-H(41A)	109.5
N(7)-C(41)-H(41B)	109.5
H(41A)-C(41)-H(41B)	109.5
N(7)-C(41)-H(41C)	109.5
H(41A)-C(41)-H(41C)	109.5
H(41B)-C(41)-H(41C)	109.5
N(7)-C(42)-H(42A)	109.5
N(7)-C(42)-H(42B)	109.5
H(42A)-C(42)-H(42B)	109.5
N(7)-C(42)-H(42C)	109.5
H(42A)-C(42)-H(42C)	109.5
H(42B)-C(42)-H(42C)	109.5
N(8)-C(43)-H(43A)	109.5
N(8)-C(43)-H(43B)	109.5
H(43A)-C(43)-H(43B)	109.5
N(8)-C(43)-H(43C)	109.5
H(43A)-C(43)-H(43C)	109.5
H(43B)-C(43)-H(43C)	109.5
N(8)-C(44)-H(44A)	109.5
N(8)-C(44)-H(44B)	109.5
H(44A)-C(44)-H(44B)	109.5
N(8)-C(44)-H(44C)	109.5
H(44A)-C(44)-H(44C)	109.5
H(44B)-C(44)-H(44C)	109.5

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

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

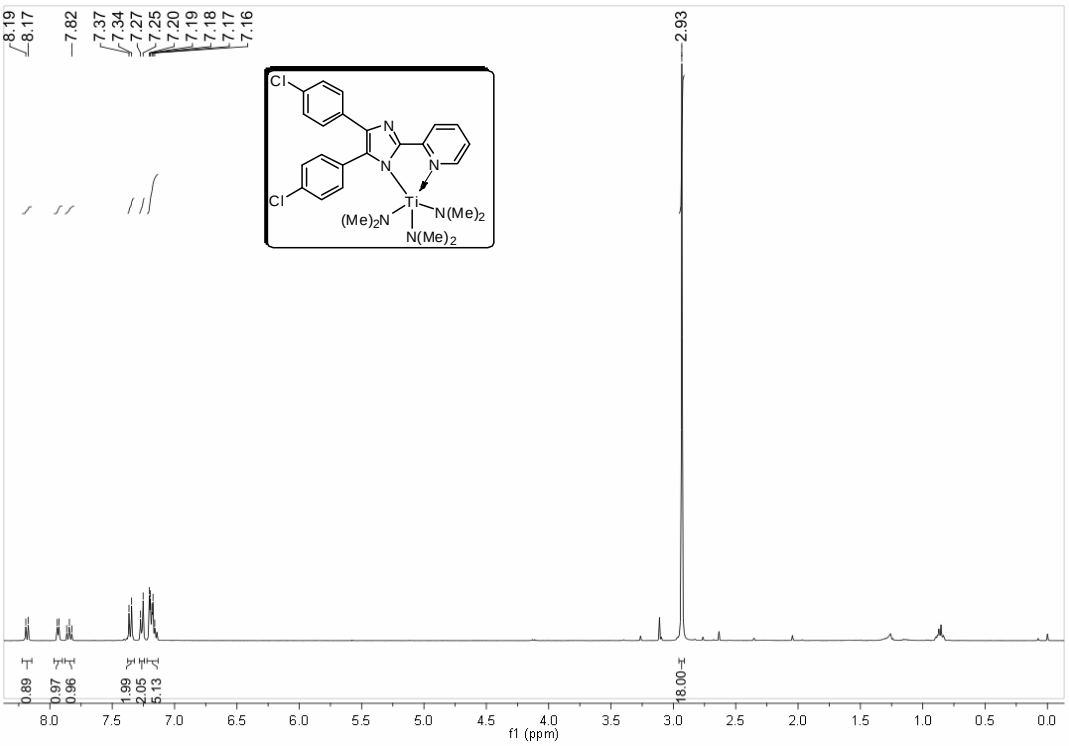
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15(d, 1H), 7.83 (d, 1H), 7.35 (m, 2H), 7.19 (m, 5H), 7.11 (m, 3H), 7.05 (m, 2H), 2.84 (s, 18H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 153.70, 149.95, 147.47, 139.60, 136.02, 130.85, 130.79, 129.25, 128.44, 128.23, 128.19, 128.08, 127.92, 127.51, 127.46, 126.62, 126.22, 125.82, 125.48, 121.71, 119.21, 46.16

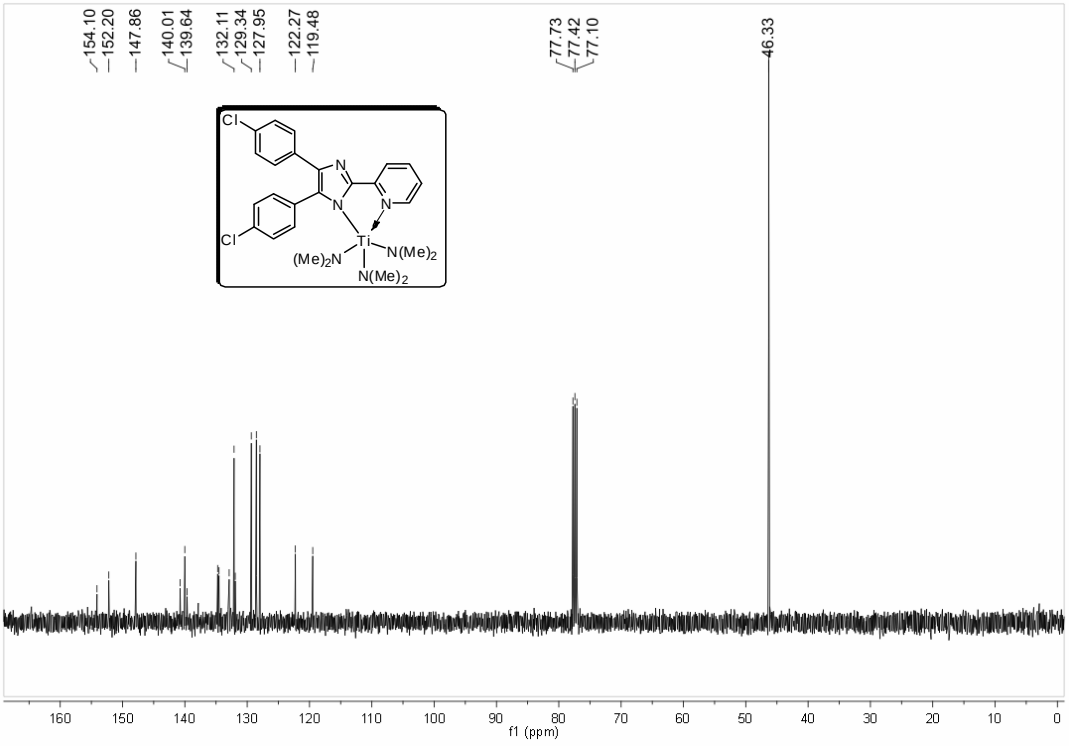




2.2 ^{1}H and ^{13}C NMR spectra for **2**

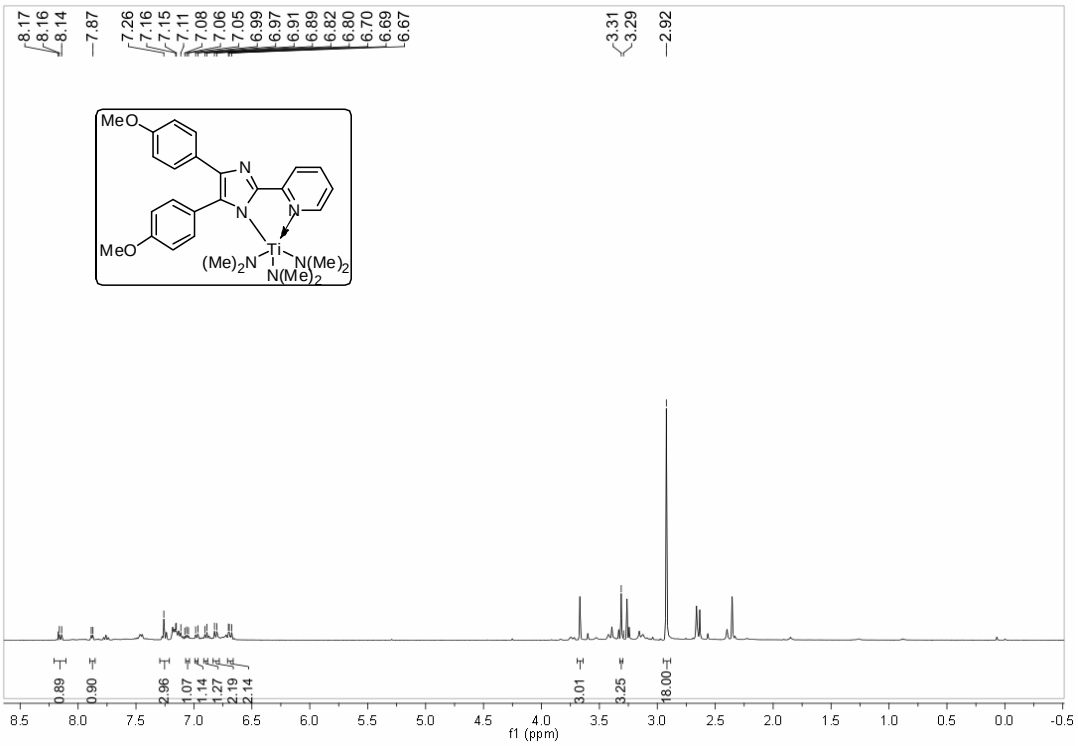
^{1}HNMR (400 MHz, $CDCl_3$) δ = 8.18 (d, 1H), 7.93 (d, 1H), 7.84 (t, 1H), 7.36 (d, 2H), 7.27-7.25 (d, 2H), 7.22–7.13 (m, 5H), 2.93 (s, 18H). **^{13}CNMR(100MHz, $CDCl_3$)** δ = 154.10, 152.20, 147.86, 140.76, 140.01, 139.64, 134.74, 134.52, 132.89, 132.11, 131.92, 129.34, 128.53, 127.95, 122.27, 119.48, 46.33.

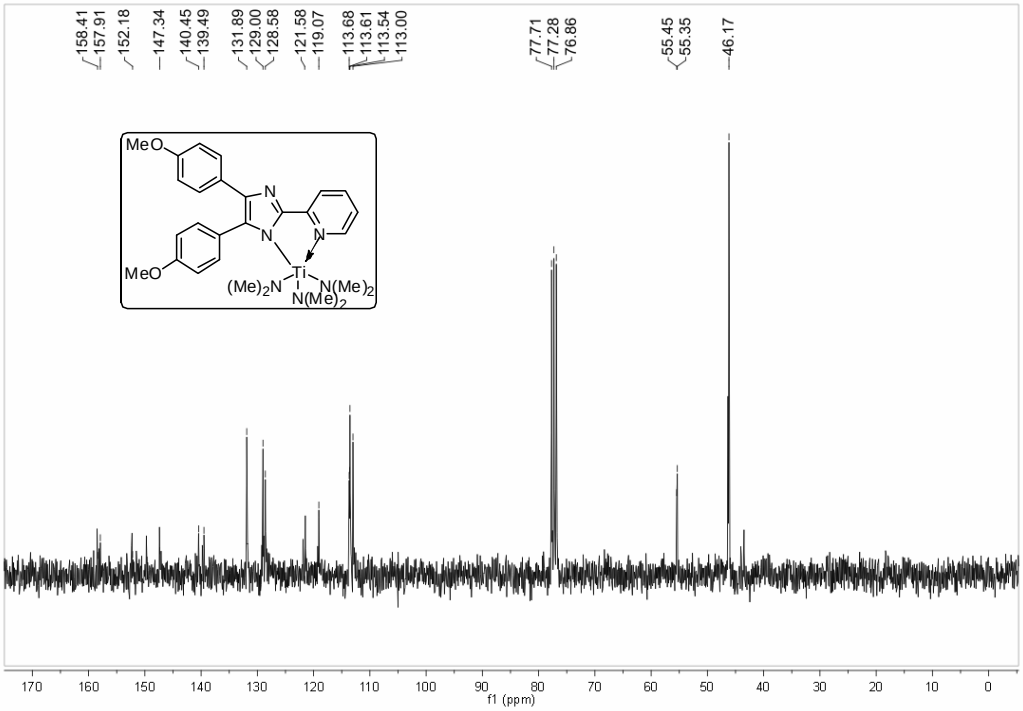




2.3 ^{1}H and ^{13}C NMR spectra for **3**

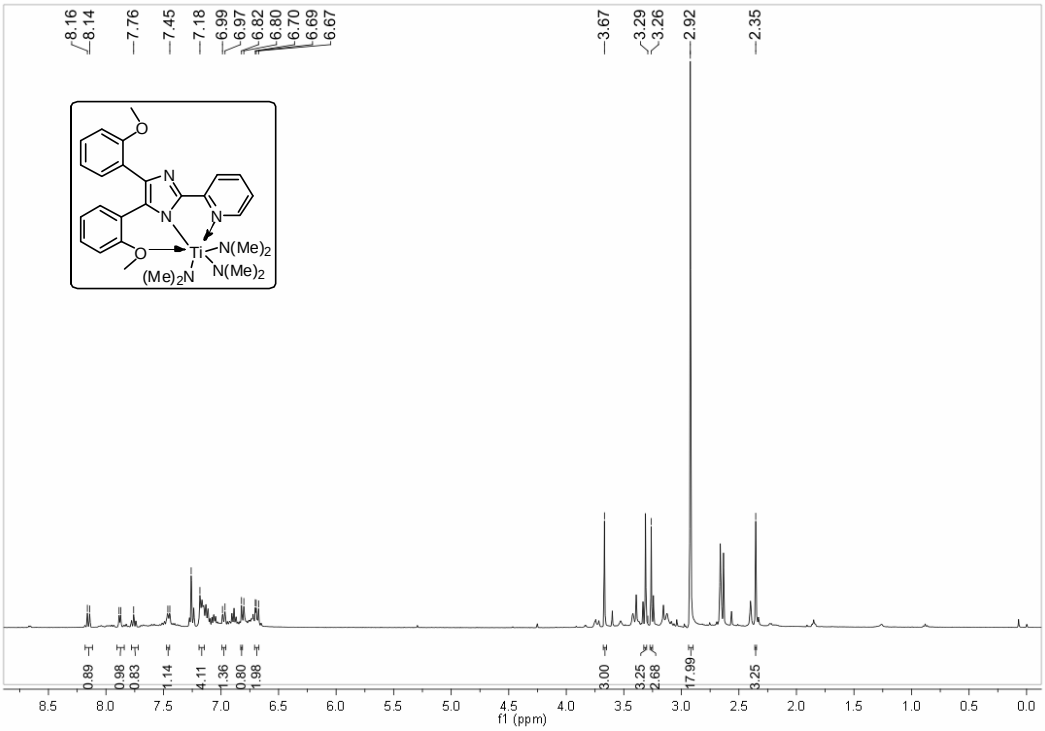
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (t, 1H), 7.88 (d, 1H), 7.26 (s, 3H), 7.06 (s, 1H), 6.98 (d, 1H), 6.90 (d, 1H), 6.81 (d, 2H), 6.71– 6.66 (m, 2H), 3.67 (s, 3H), 3.31 (s, 3H), 2.92 (s, 18H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 158.41, 157.91, 152.18, 149.61, 147.34, 140.45, 139.49, 131.89, 129.00, 128.58, 121.58, 119.07, 113.68, 113.61, 113.54, 113.00, 55.45, 55.35, 46.17.

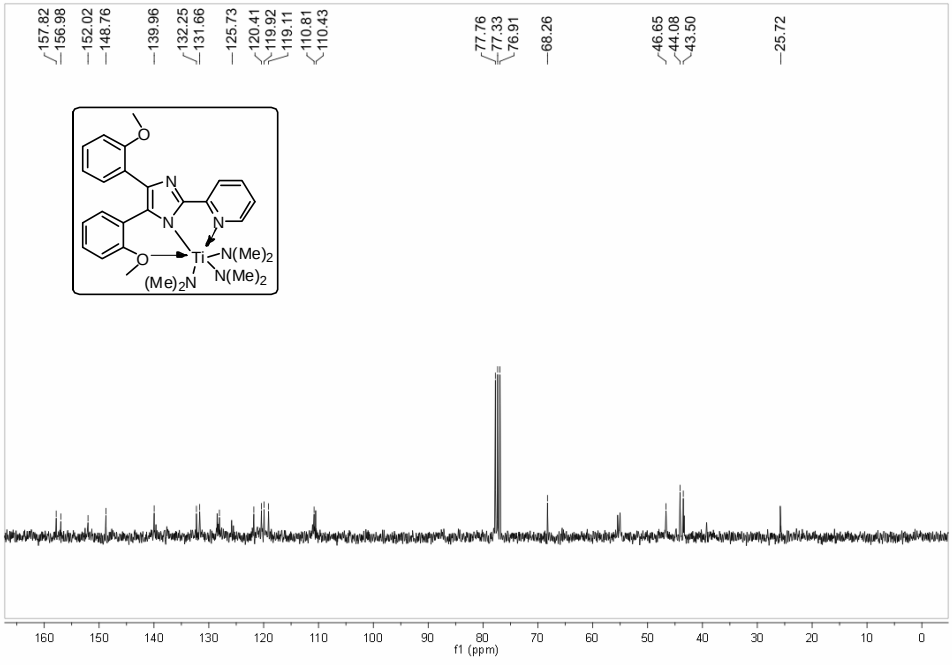




2.4 ^{1}H and ^{13}C NMR spectra for **4**·THF

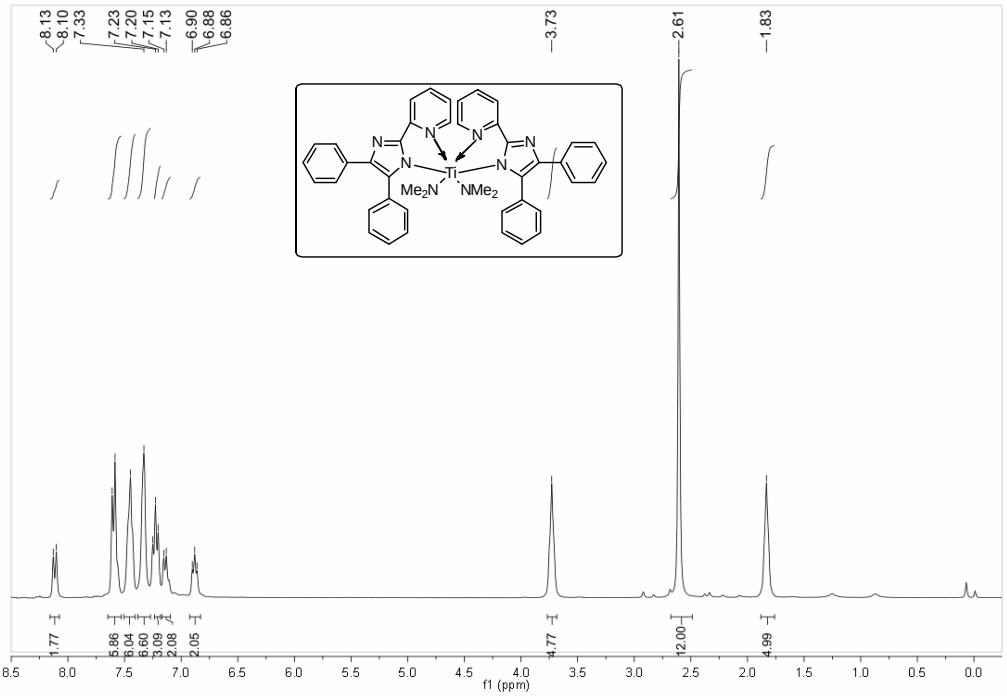
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, 1H), 7.88 (d, 1H), 7.76 (s, 1H), 7.46 (s, 1H), 7.18 (s, 4H), 6.98 (d, 1H), 6.82 (m, 1H), 6.71– 6.67 (m, 2H), 3.67 (s, 3H), 3.31 (s, 3H), 3.26 (s, 3H)2.92 (s, 18H) 2.35 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 157.82, 156.98, 152.02, 148.76, 139.96, 132.25, 131.66, 128.43, 128.06, 125.73, 121.79, 120.41, 119.92, 119.11, 110.81, 110.43, 68.26, 46.65，44.08, 43.50, 25.72.

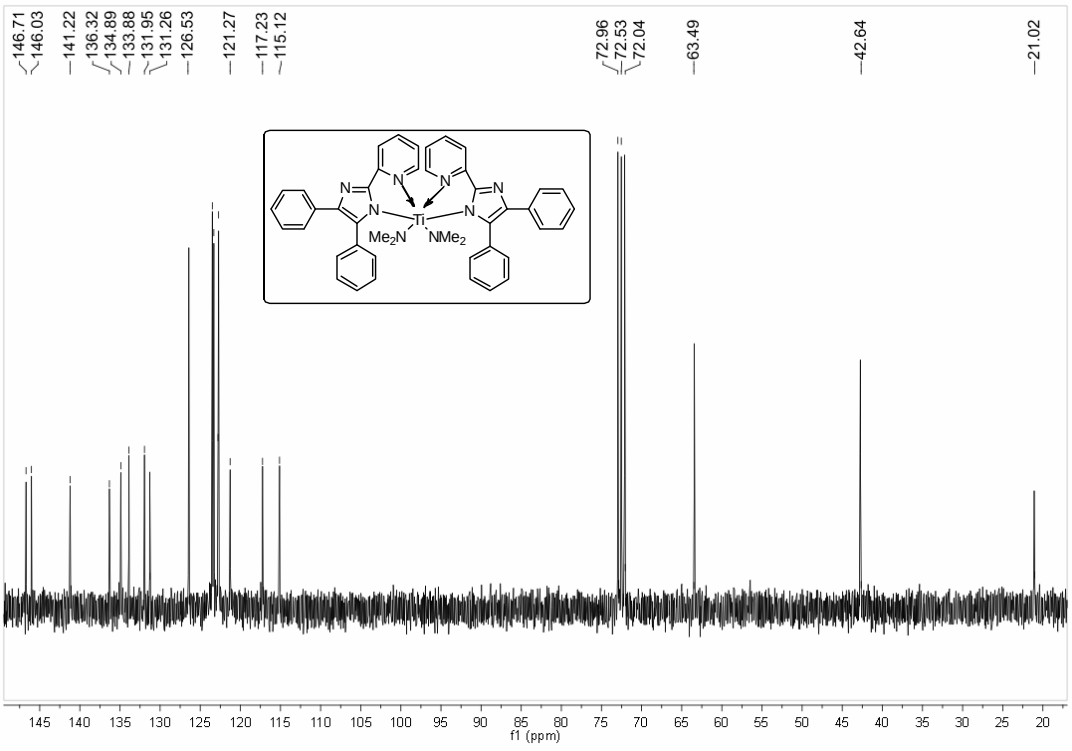




2.5 ^{1}H and ^{13}C NMR spectra for **5**·THF

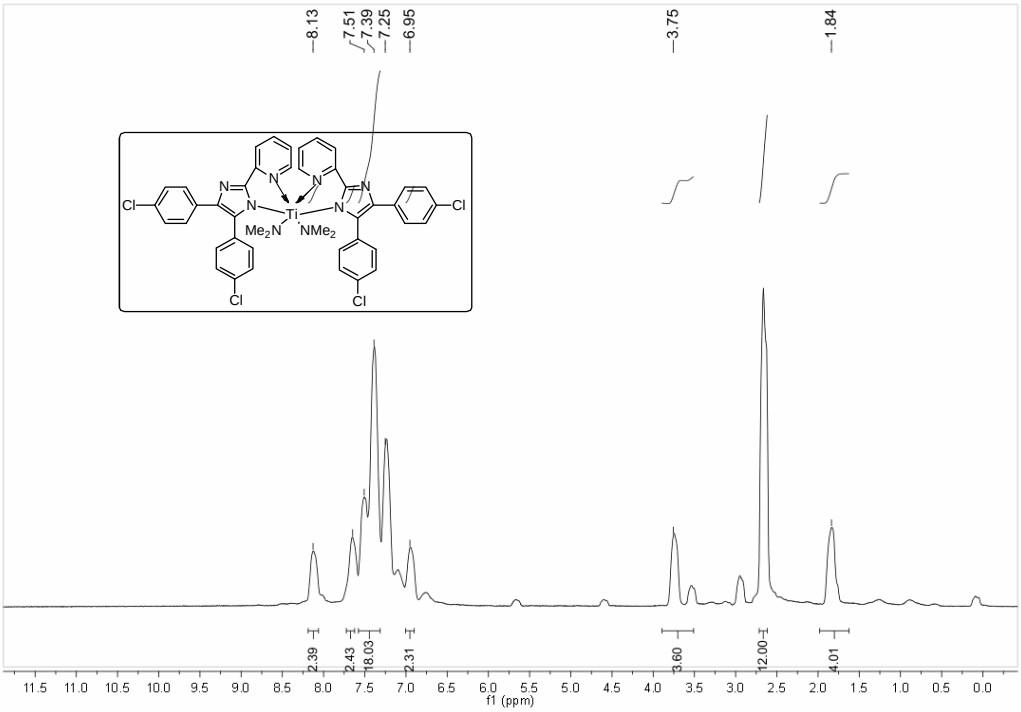
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (d, 2H), 7.60 (d, 6H), 7.45 (s, 6H), 7.33 (s, 7H), 7.22 (d, 3H), 7.14 (d, 2H), 6.88 (t, 2H), 3.73 (s, 5H), 2.61 (s, 12H), 1.83 (s, 5H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ 146.71, 146.03, 141.22, 136.32, 134.89, 133.88, 131.95, 131.26, 126.53, 123.49, 123.30, 122.78, 122.71, 121.27, 117.23, 115.12, 63.49, 42.64, 21.02.

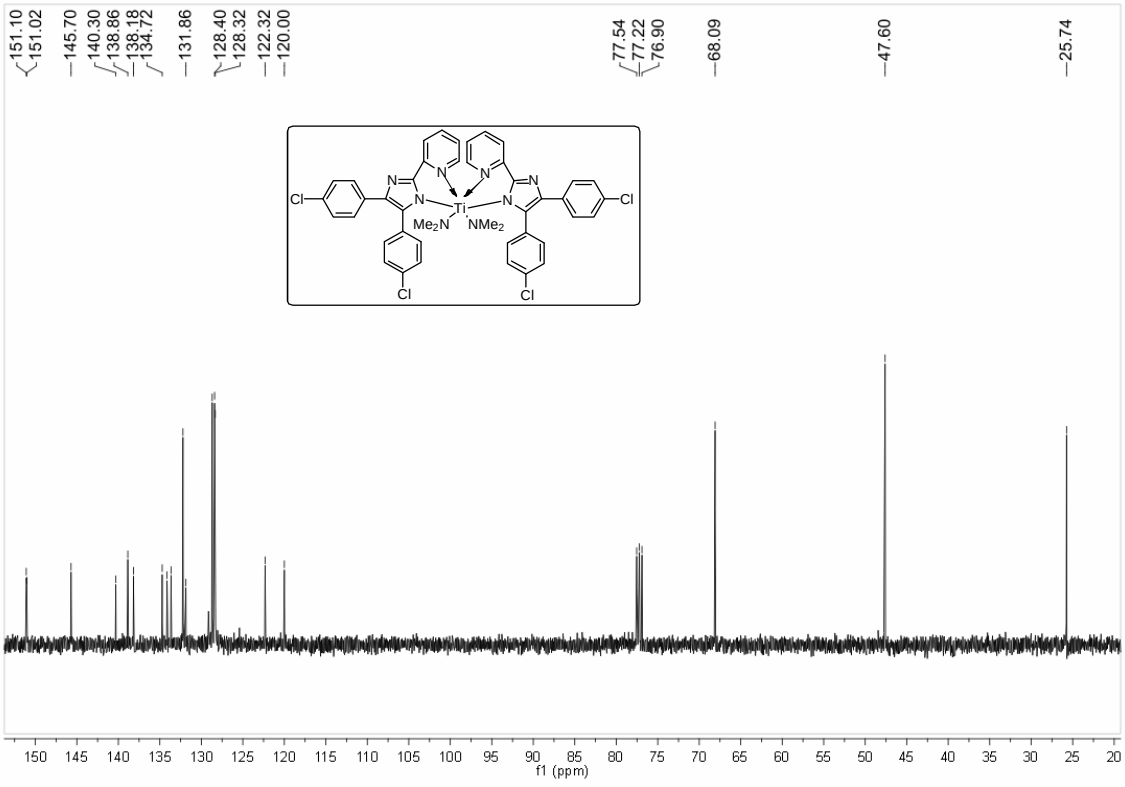




2.6 ^{1}H and ^{13}C NMR spectra for **6**·THF

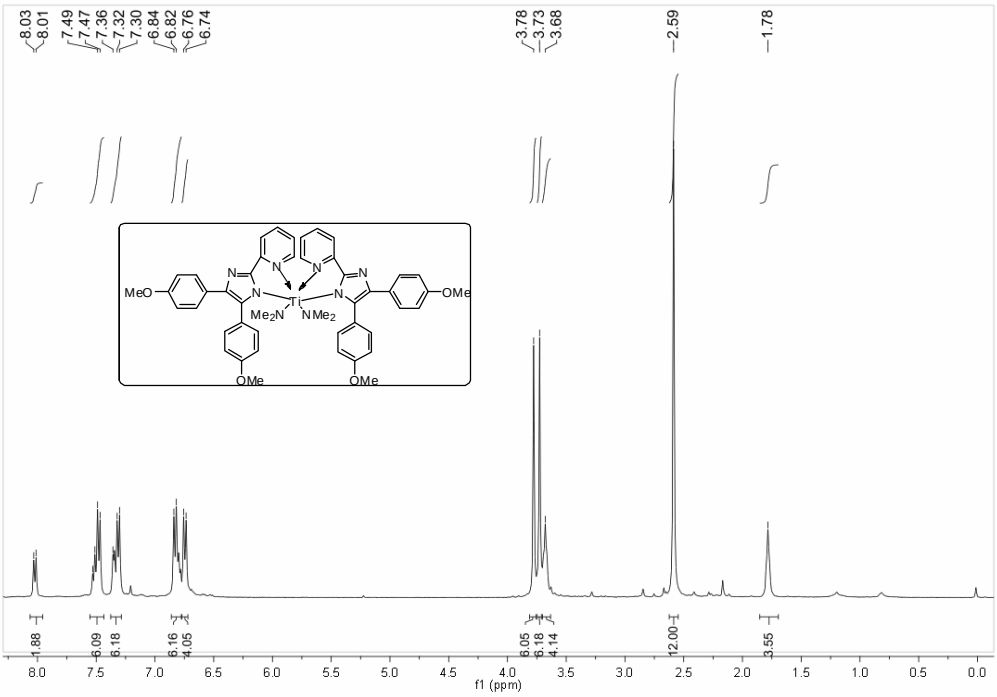
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (s, 2 H), 7.65 (s, 2 H), 7.45 (d, 18 H), 6.95 (s, 2 H), 3.75 (s, 4 H), 2.66 (s, 12 H), 1.84 (s, 4 H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ = 151.10, 151.02, 145.70, 140.30, 138.86, 138.18, 134.72, 134.13, 133.65, 132.21, 131.86, 128.69, 128.40, 128.32, 122.32, 120.00, 68.09, 47.60, 25.74.

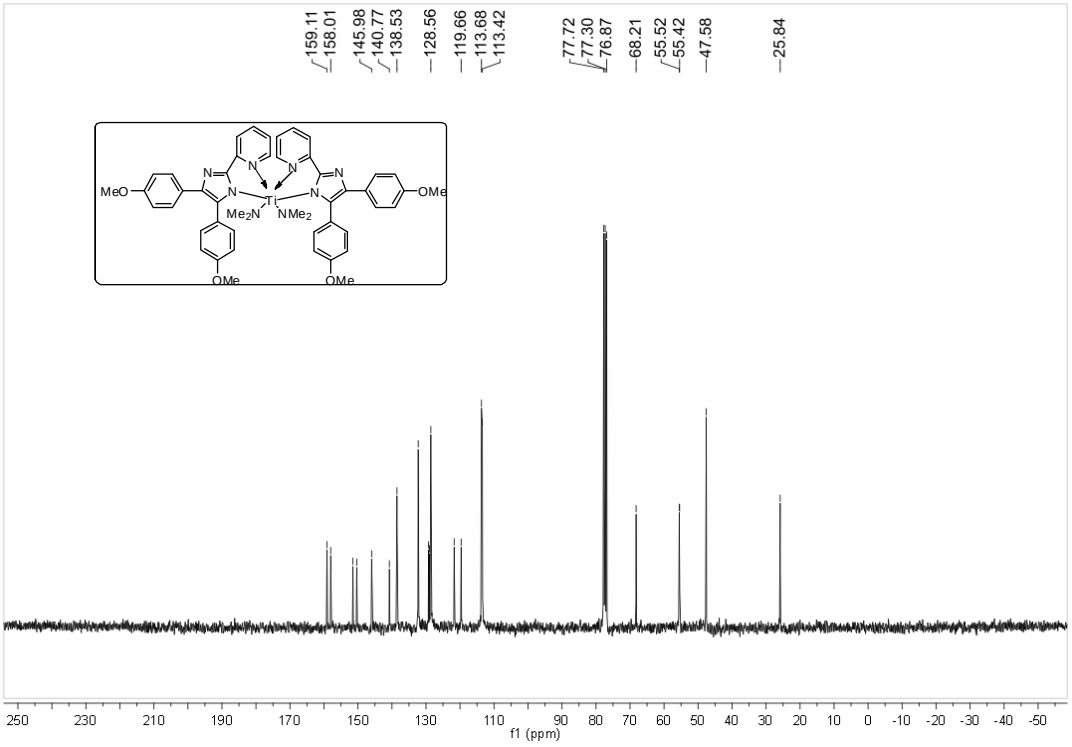




2.7 ^{1}H and ^{13}C NMR spectra for **7**·THF

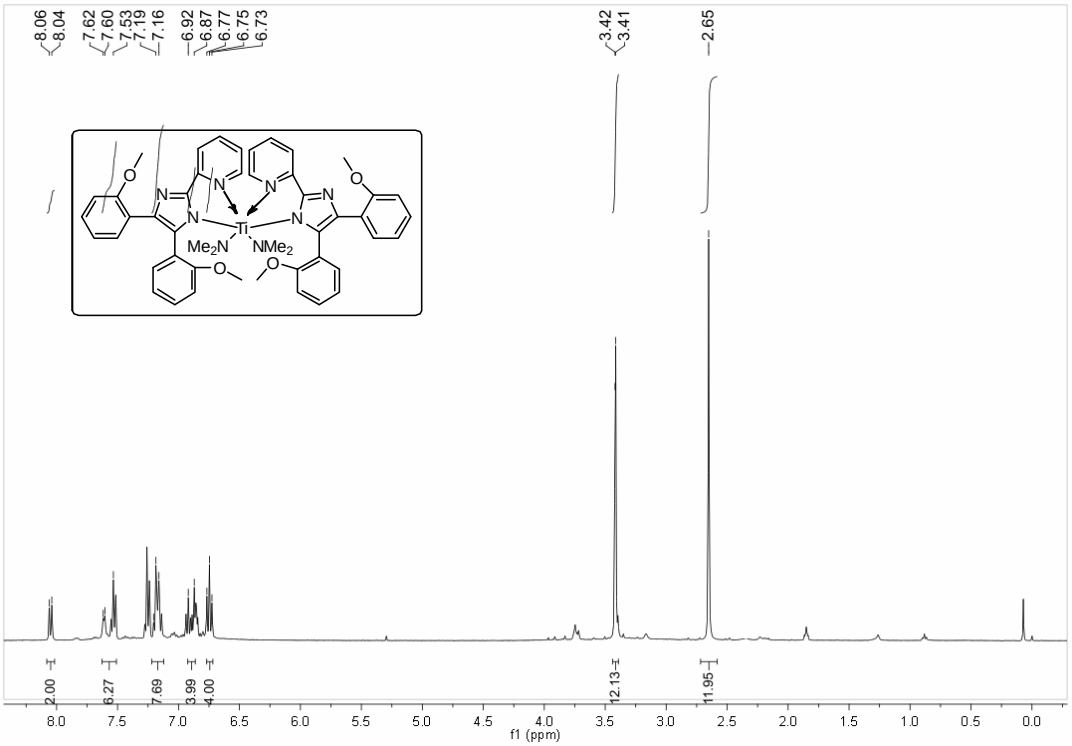
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, 2H), 7.50 (dd, 6H), 7.38–7.29 (m, 6H), 6.83 (d, 6H), 6.75 (d, 4H), 3.78 (s, 6H), 3.73 (s, 6H), 3.68 (s, 4H), 2.59 (s, 12H), 1.78 (s, 4H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ 159.11, 158.01, 151.48, 150.36, 145.98, 140.77, 138.53, 132.28, 129.26, 129.00, 128.56, 121.71, 119.66, 113.68, 113.42, 68.21, 55.52, 55.42, 47.58, 25.84.

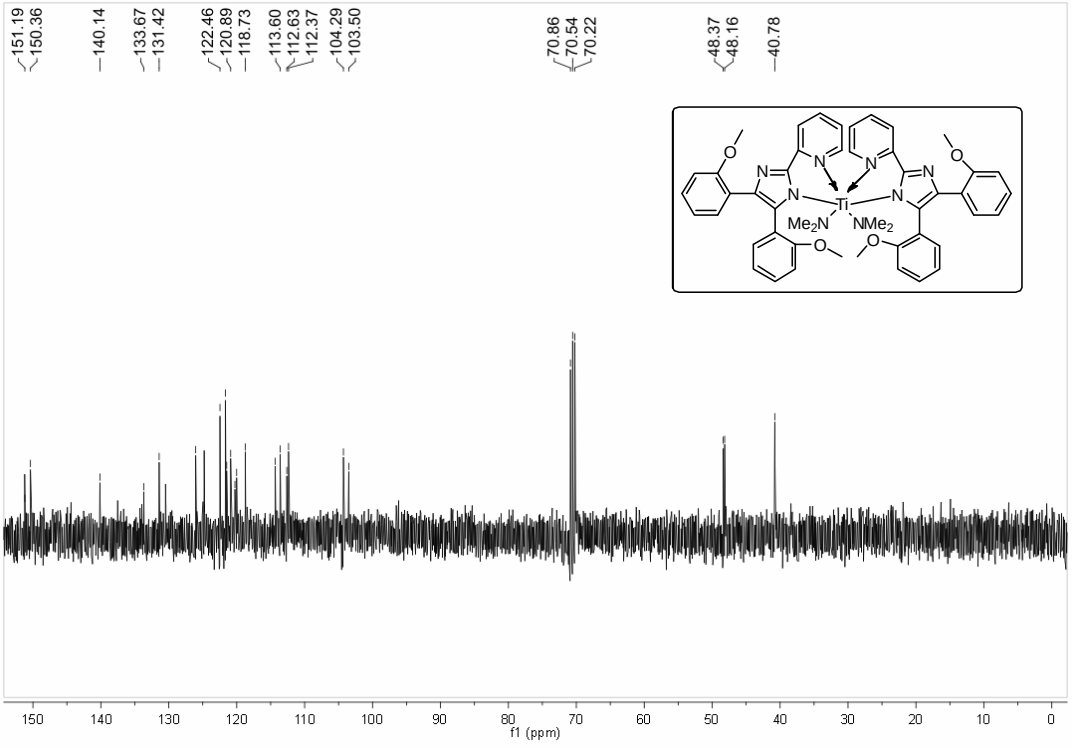




2.8 ^{1}H and ^{13}C NMR spectra for **8**

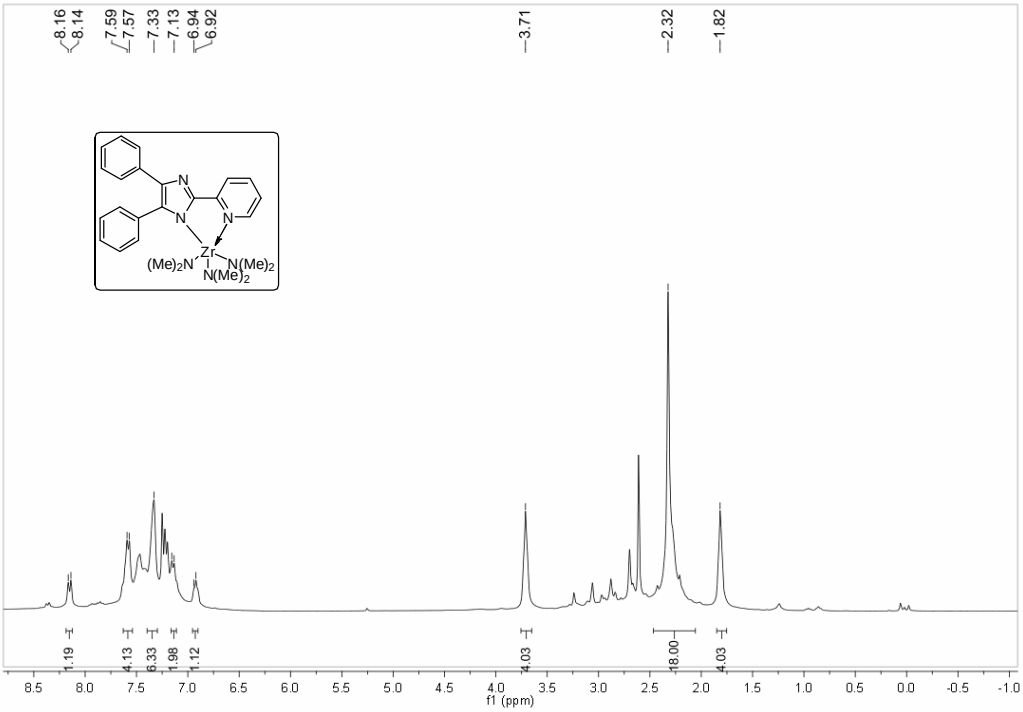
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, 2H), 7.63–7.51 (m, 6H), 7.18 (t, 8H), 6.90 (d, 4H), 6.75 (t, 4H), 3.42 (d, 12H), 2.65 (s, 12H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 151.19, 150.36, 140.14, 133.67, 131.42, 126.04, 124.75, 122.46, 121.66, 121.47, 120.89, 120.26, 120.01, 118.73, 114.33, 113.60, 112.63, 112.37, 104.29, 103.50, 48.37, 48.16, 40.78.

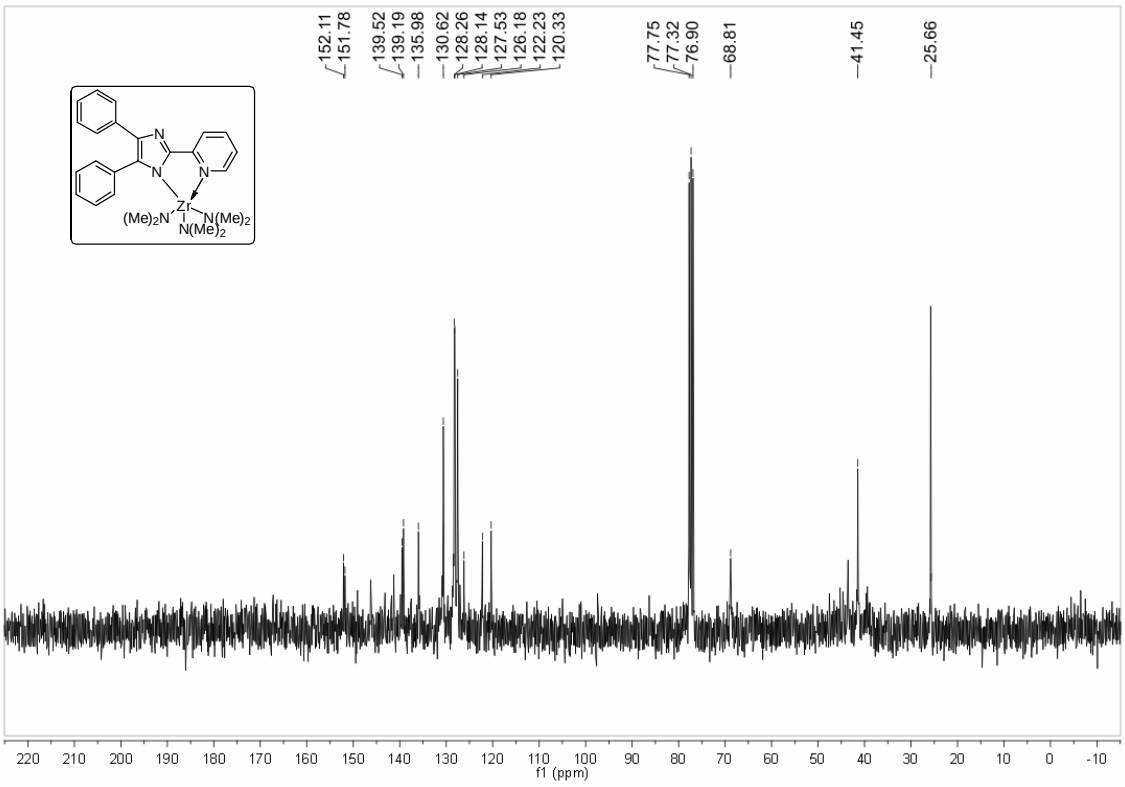




2.9 ^{1}H and ^{13}C NMR spectra for **9**

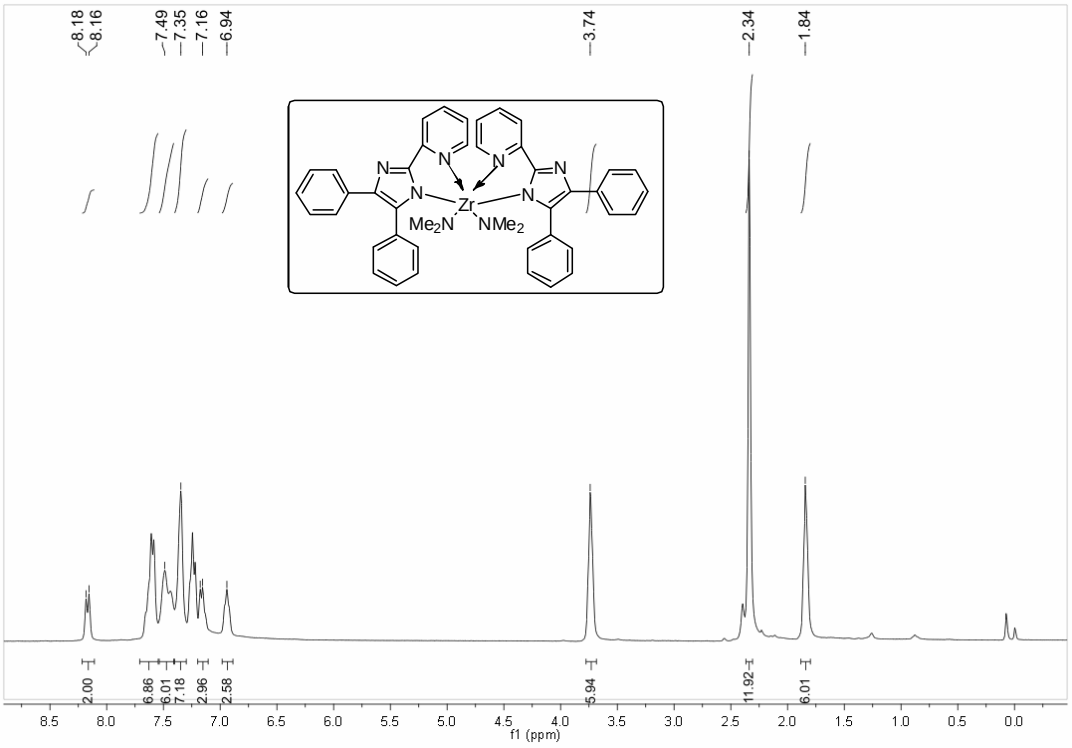
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (d, 1H), 7.58 (d, 4H), 7.33 (s, 6H), 7.14 (d, 2H), 6.93 (d, 1H), 3.71 (s, 4H), 2.32 (s, 18H), 1.82 (s, 4H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 152.11, 151.78, 139.52, 139.19, 135.98, 130.62, 128.26, 128.14, 127.53, 126.18, 122.23, 120.33, 68.81, 41.45, 25.66.

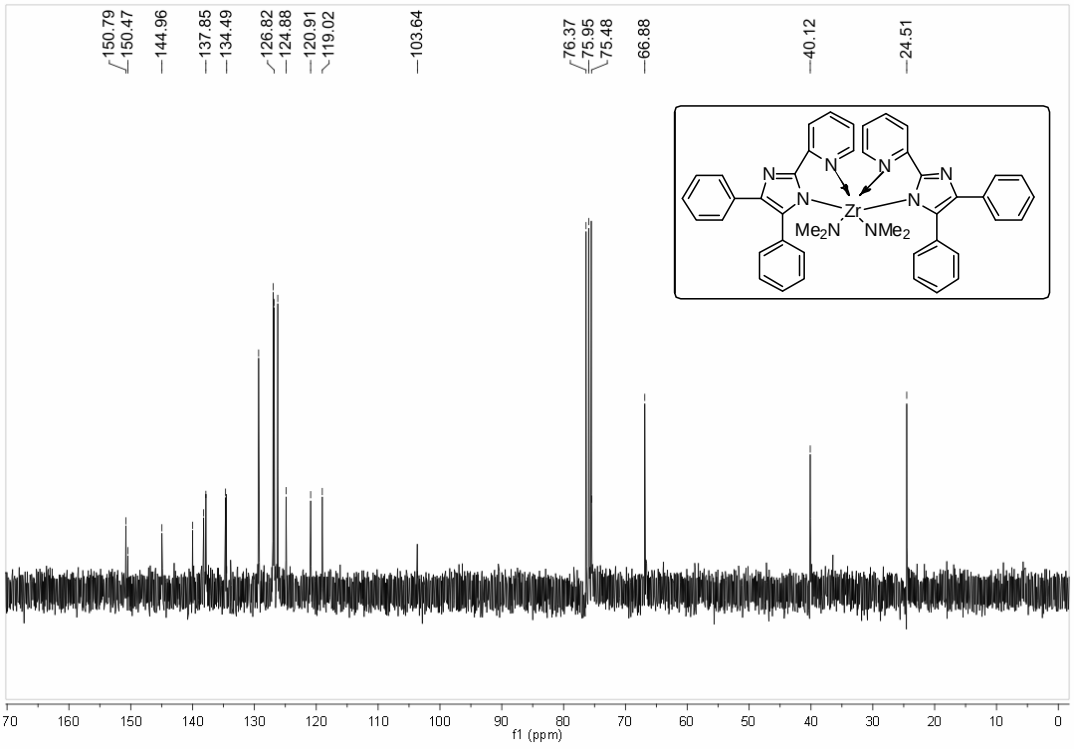




2.10 ^{1}H and ^{13}C NMR spectra for **10**·1.5THF

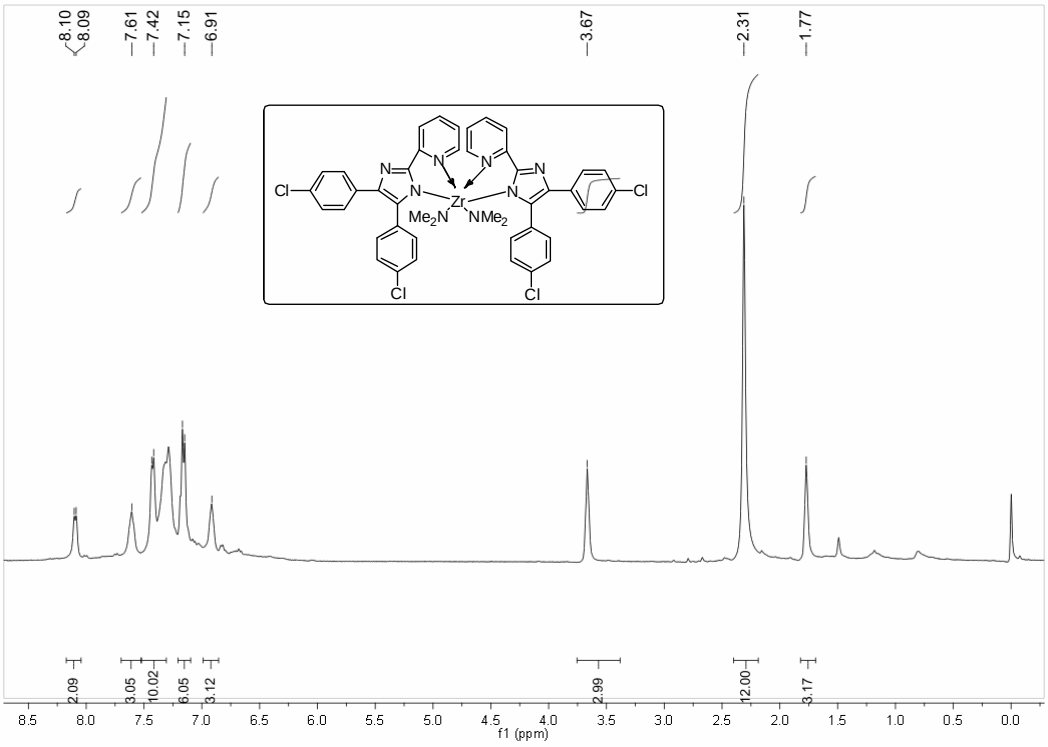
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (d, 2H), 7.60 (d, 7H), 7.49 (s, 6H), 7.35 (s, 7H), 7.17 (d, 3H), 6.94 (s, 3H), 3.74 (s, 6H), 2.34 (s, 12H), 1.84 (s, 6H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ 150.79, 150.47, 144.96, 140.00, 138.21, 137.85, 134.66, 134.49, 129.31, 126.96, 126.82, 126.22, 124.88, 120.91, 119.02, 103.64, 66.88, 40.12, 24.51.

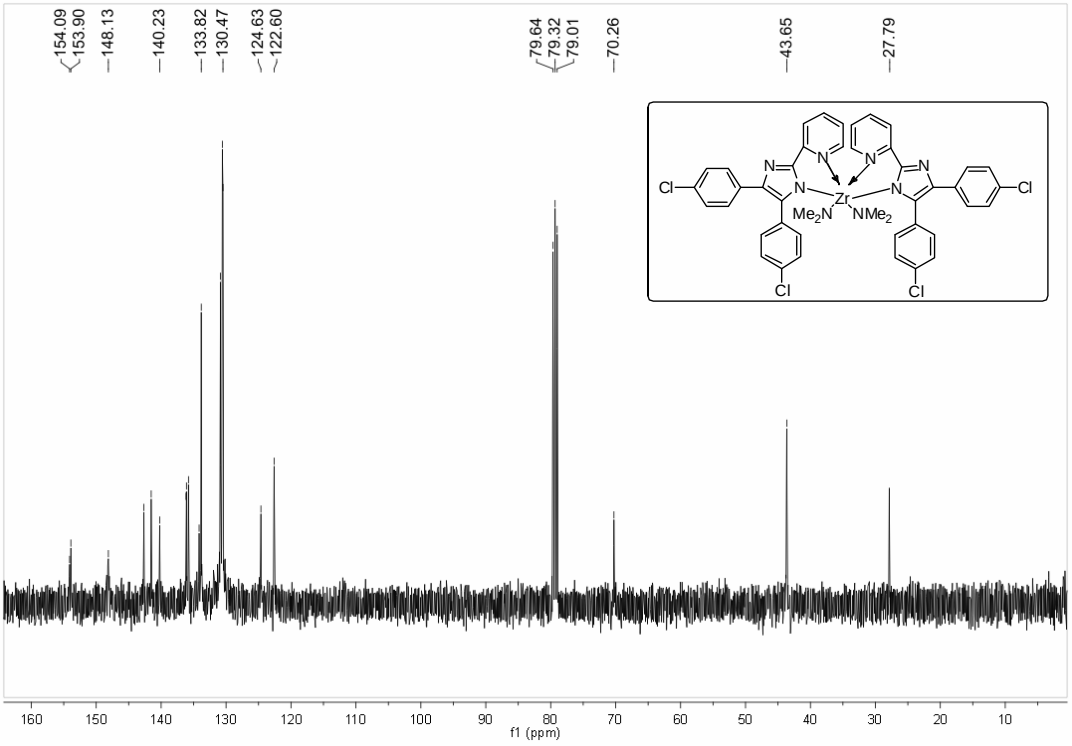




2.11 ^{1}H and ^{13}C NMR spectra for **11**·0.5THF

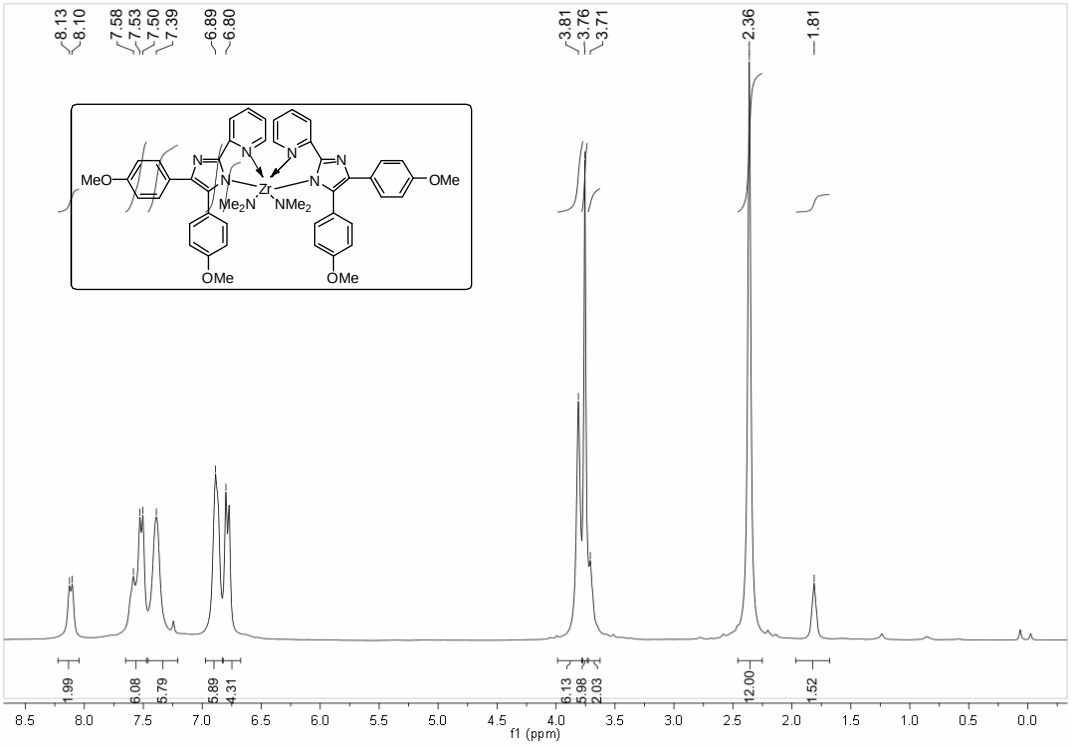
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, 2H), 7.61 (s, 3H), 7.42 (m, 10H), 7.16 (d, 6H), 6.91 (s, 3H), 3.67 (s, 3H), 2.31 (s, 12H), 1.77 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.09, 153.90, 148.13, 142.65, 141.53, 140.23, 136.17, 136.10, 135.79, 134.15, 133.82, 130.86, 130.57, 130.47, 124.63, 122.60, 70.26, 43.65, 27.79

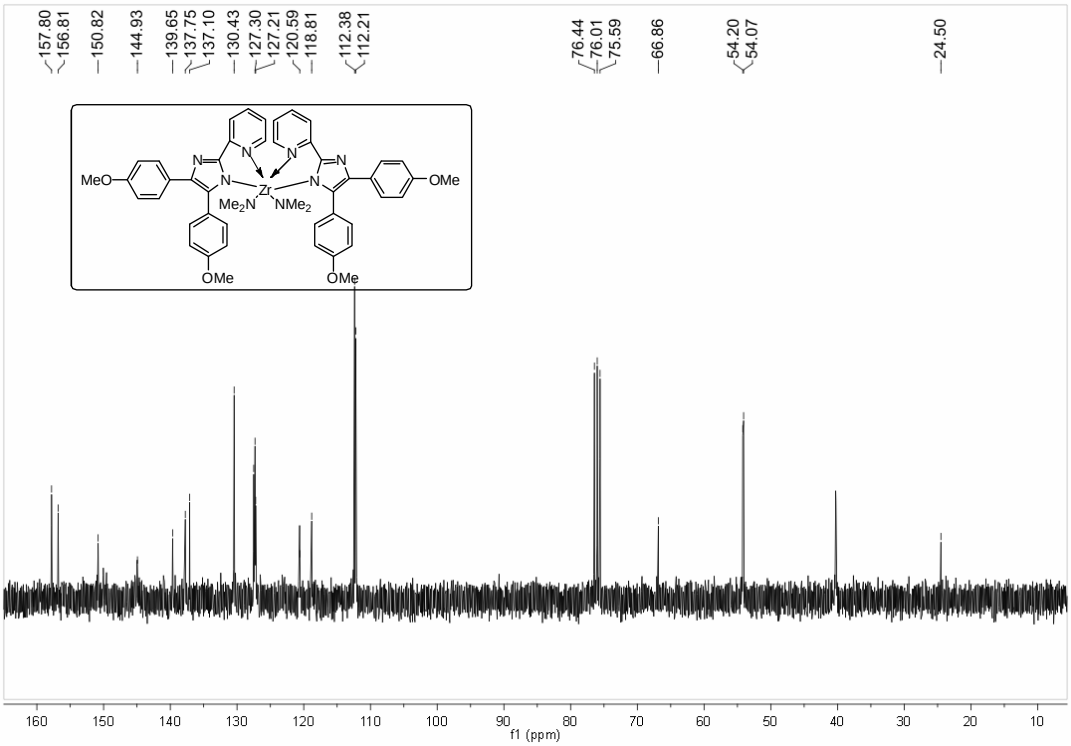




2.12 ^{1}H and ^{13}C NMR spectra for **12**·0.5THF

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (d, 2H), 7.65–7.47 (m, 6H), 7.39 (s, 6H), 6.89 (s, 6H), 6.80 (s, 4H), 3.81 (s, 6H), 3.76 (s, 6H), 3.71 (s, 2H), 2.36 (s, 12H), 1.81 (s, 2H);
^{13}C NMR (75 MHz, $CDCl_3$) δ 157.80, 156.81, 150.82, 144.93, 139.65, 137.75, 137.10, 130.43, 127.50, 127.30, 127.21, 120.59, 118.81, 112.38, 112.21, 66.86, 54.20, 54.07, 24.50

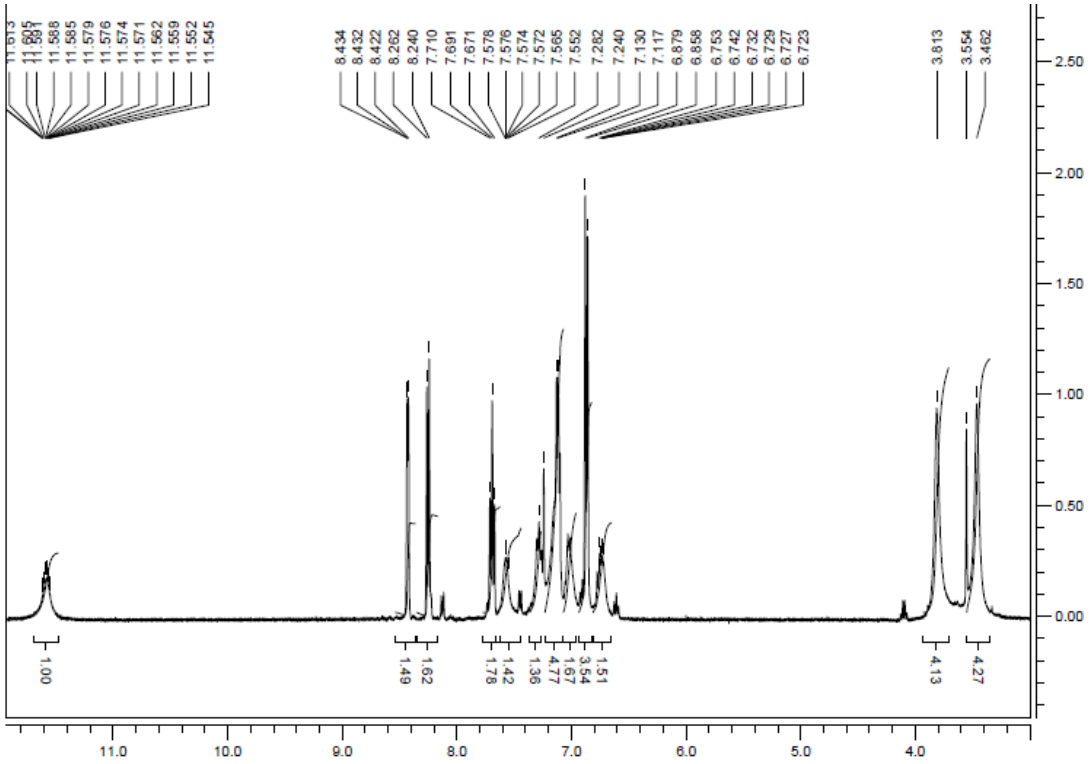




2.13 ^{1}H and ^{13}C NMR spectra for the ligand HL4

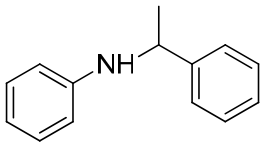
2.13 ^{1}H NMR spectrum for the HL4 ligand

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.57 (s, 1H), 8.43 (d, 1H), 8.26 (d, 1H), 7.69 (s, 1H), 7.57 (s, 1H), 7.28 (s, 4H), 7.11 (d, 1H), 6.87 (m, 1H), 6.73 (m, 2H), 3.81(s, 3H), 3.48 (s, 3H).



3. ^{1}H and ^{13}C NMR spectra, IR and HRMS data for the hydroamination products.

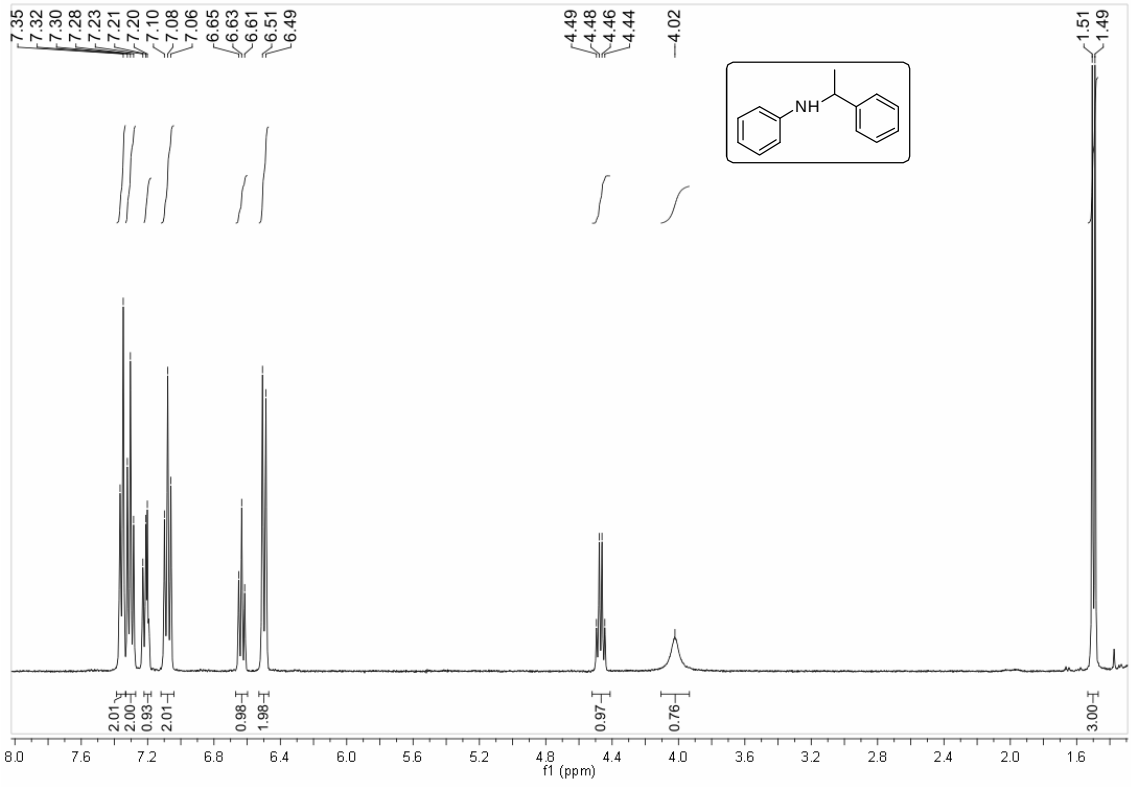
3.1 N-(1-Phenylethyl) aniline

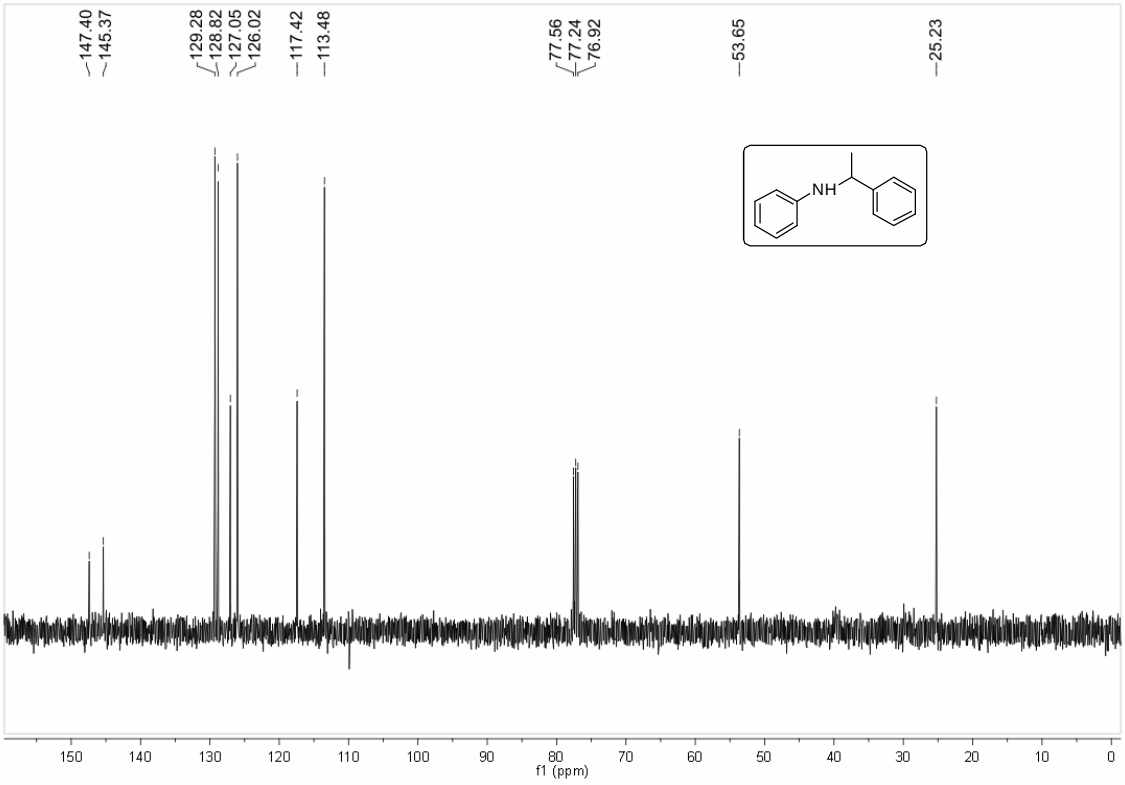


Colorless oil.**^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 7.36 (d, 2H, Ar-H), 7.30 (t, 2H, Ar-H), 7.21 (d, 1H, Ar-H), 7.08 (t, 2H, Ar-H), 6.63 (t, 1H, Ar-H), 6.50 (d, 2H, Ar-H), 4.47 (q, 1H, -NCH-), 4.02 (s, 1H, -NH), 1.50 (d, 3H, $-CH_3$). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ = 147.40, 145.37, 129.28, 128.82, 127.05, 126.02, 117.42, 113.48, 53.65, 25.23.

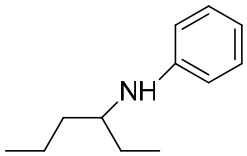
IR (KBr, cm^{-1}): 3411, 3052, 3022, 2965, 2923, 2866, 2572, 1601, 1504, 1449, 1372, 1317, 1257, 1179, 1139, 1076, 868, 748, 700, 608, 545, 510.

HRMS Calcd. for $C_{14}H_{15}N$: 197.1204. Found:197.1204





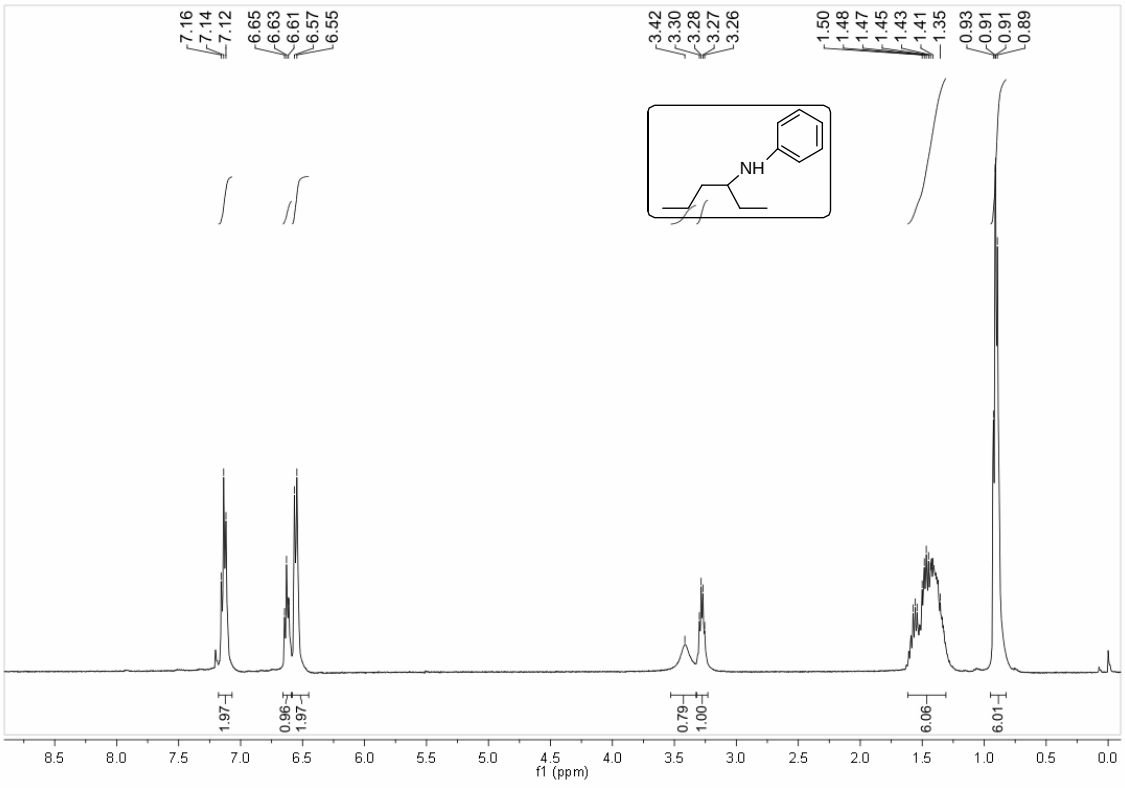
3.2 N-(Hexan-3-yl)aniline

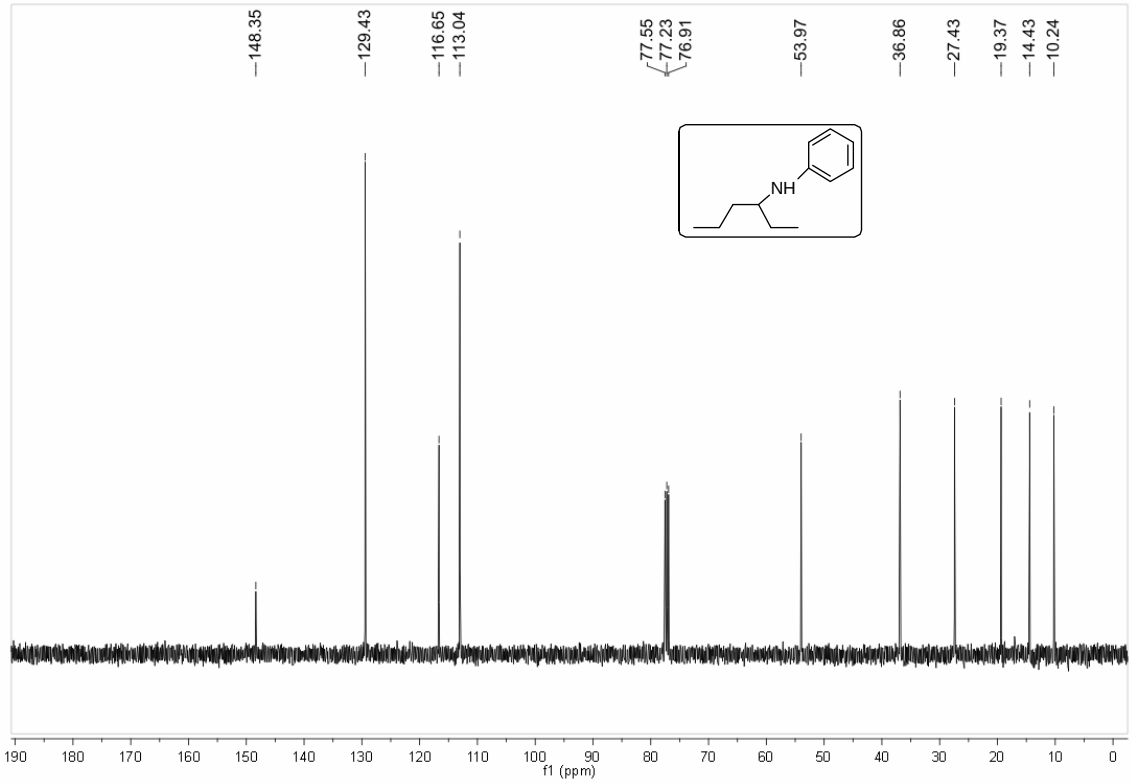


Light yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 7.14 (t, 2H, Ar-H), 6.63 (t, H, Ar-H), 6.56 (d, 2H, Ar-H), 3.42 (s, 1H, -NH), 3.28 (q, 1H, -NCH-), 1.48-1.35 (tdd, 6H, $-CH_2-$), 0.91 (dd, 6H, $-CH_3$). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ = 148.35, 129.43, 116.65, 113.04, 53.97, 36.86, 27.43, 19.37, 14.43, 10.24.

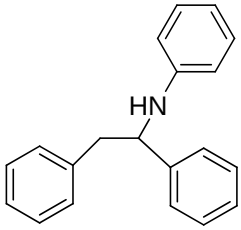
IR(KBr, cm^{-1}):3406, 3084, 3052, 3019, 2959, 2931, 2872, 2571, 1912, 1602, 1505, 1462, 1428, 1380, 1320, 1274, 1154, 1032, 865, 746, 691, 507.

HRMS Calcd. for $C_{12}H_{19}N$: 177.1517.Found：177.1514





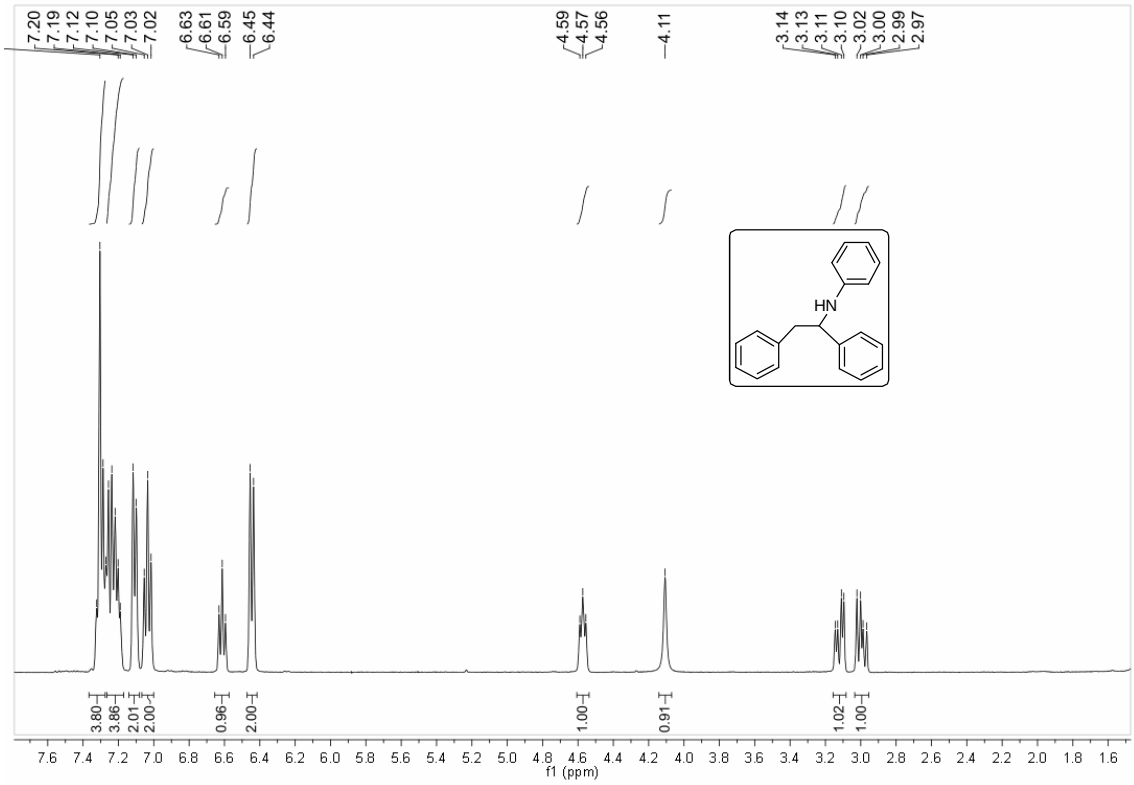
3. 3 N-(1,2-Diphenylethyl)aniline

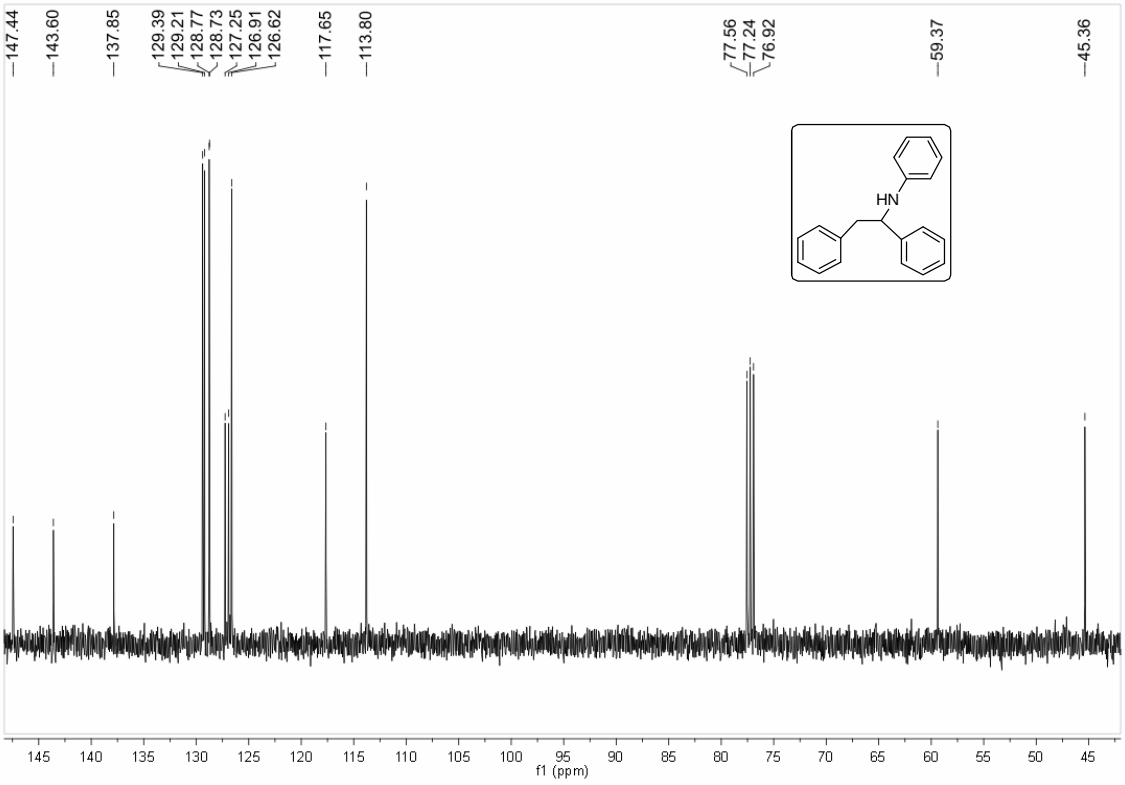


Colorless oil.**^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 7.30 (t, 4H, Ar-H), 7.27–7.17 (m, 4H, Ar-H), 7.11 (d, 2H, Ar-H), 7.03 (t, 2H, Ar-H), 6.61 (t, 1H, Ar-H), 6.44 (d, 2H, Ar-H), 4.57 (t, 1H, -NCH-), 4.11 (s, 1H, -NH), 3.12 (dd, 1H, -CH_2-), 2.99 (dd, 1H, -CH_2-). **^{13}C NMR (100MHz, $CDCl_3$)**: δ = 147.44, 143.60, 137.85, 129.39, 129.21, 128.77, 128.73, 127.25, 126.91, 126.62, 117.65, 113.80, 59.37, 45.36.

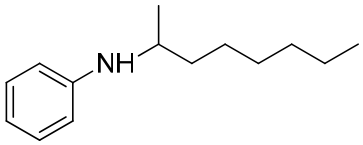
IR (KBr, cm^{-1}): 3410, 3024, 2931, 2907, 2849, 1608, 1504, 1427, 1398, 1319, 1182, 1079, 1028, 868, 749, 697, 584, 514。

HRMS Calcd. for $C_{20}H_{19}N$: 273.1517. Found:273.1521





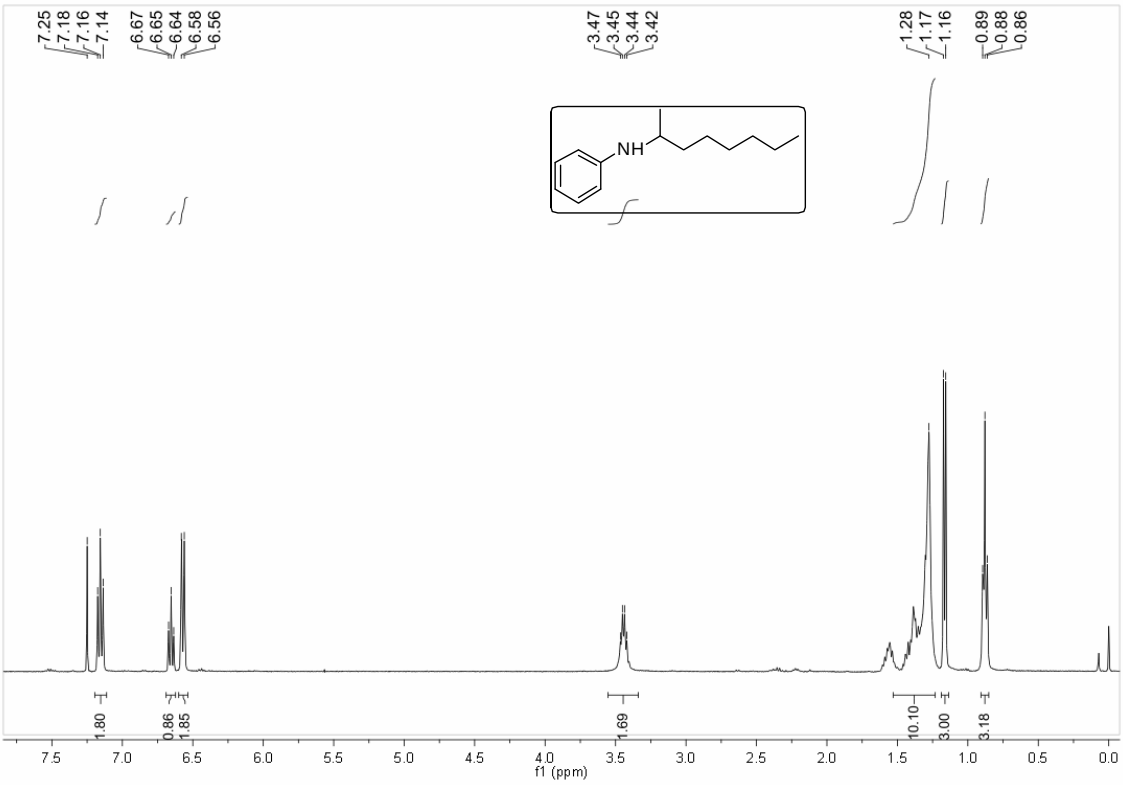
3. 4 N-(2-Octyl)aniline

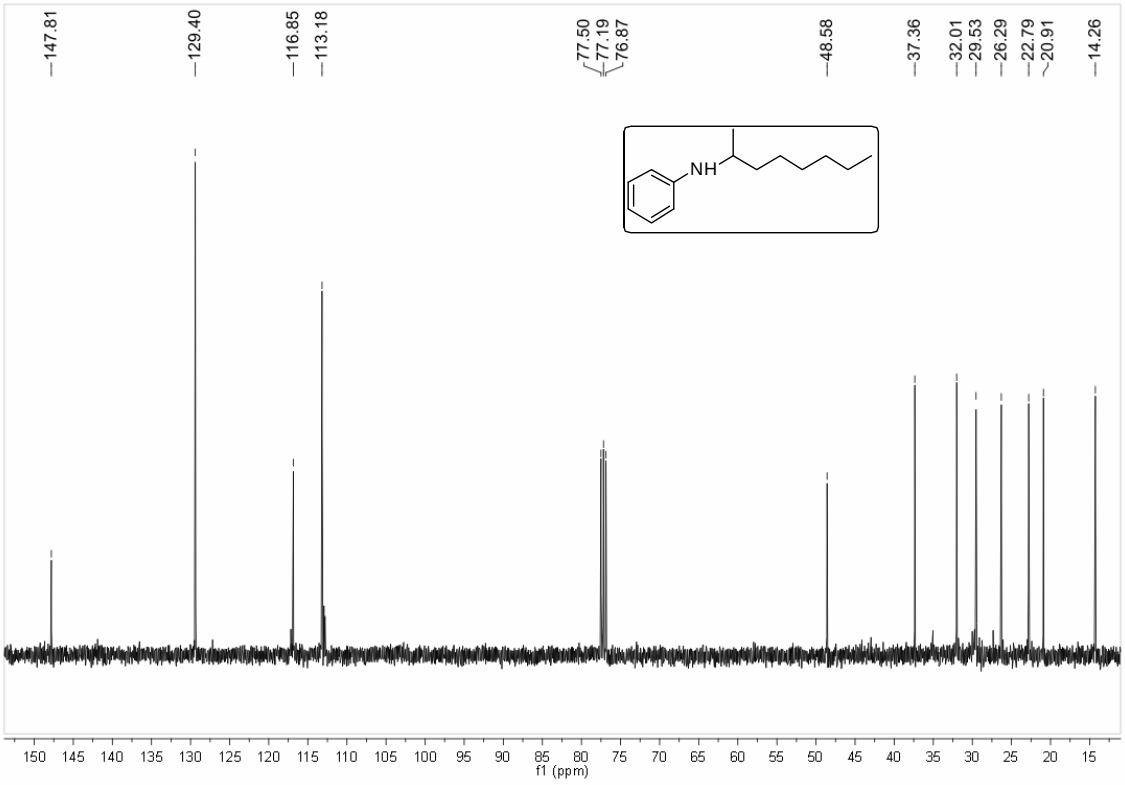


Light yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 7.16 (t, 2H, Ar-H), 6.65 (t, 1H, Ar-H), 6.57 (d, 2H, Ar-H), 3.44 (dd, 2H, -NCH- and -NH), 1.54-1.28 (m, 10H, $-(CH_2)_5-$), 1.16 (d, 3H, CH_3), 0.88 (t, 3H, CH_3). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ = 147.81, 129.40, 116.85, 113.18, 48.58, 37.36, 32.01, 29.53, 26.29, 22.79, 20.91, 14.26.

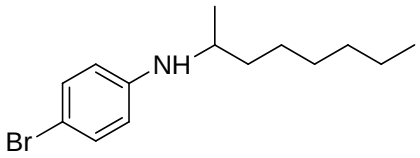
IR (KBr, cm^{-1}): 3410, 3085, 3052, 3019, 2957, 2927, 2855, 2389, 2284, 1913, 1602, 1505, 1319, 1030, 993, 865, 746, 691, 507。

HRMS Calcd. for $C_{14}H_{23}N$: 205.1830. Found: 205.1830





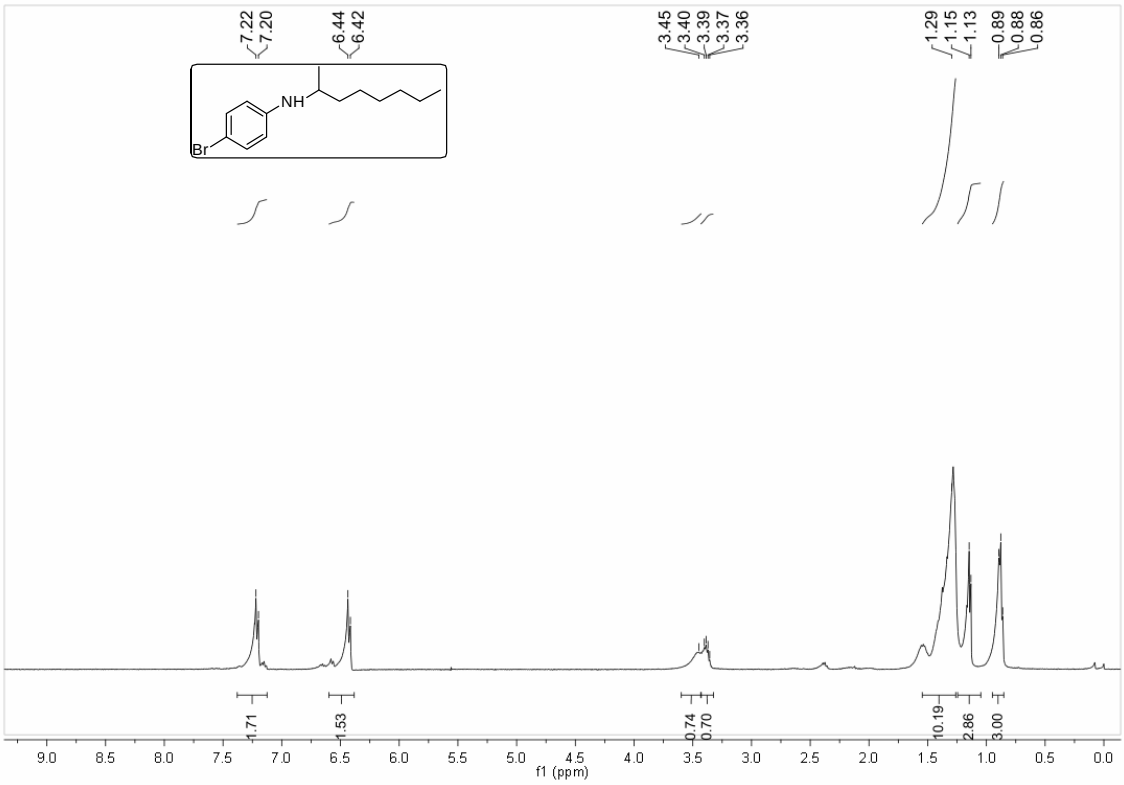
3.5 4-bromo-N-(octan-2-yl)aniline

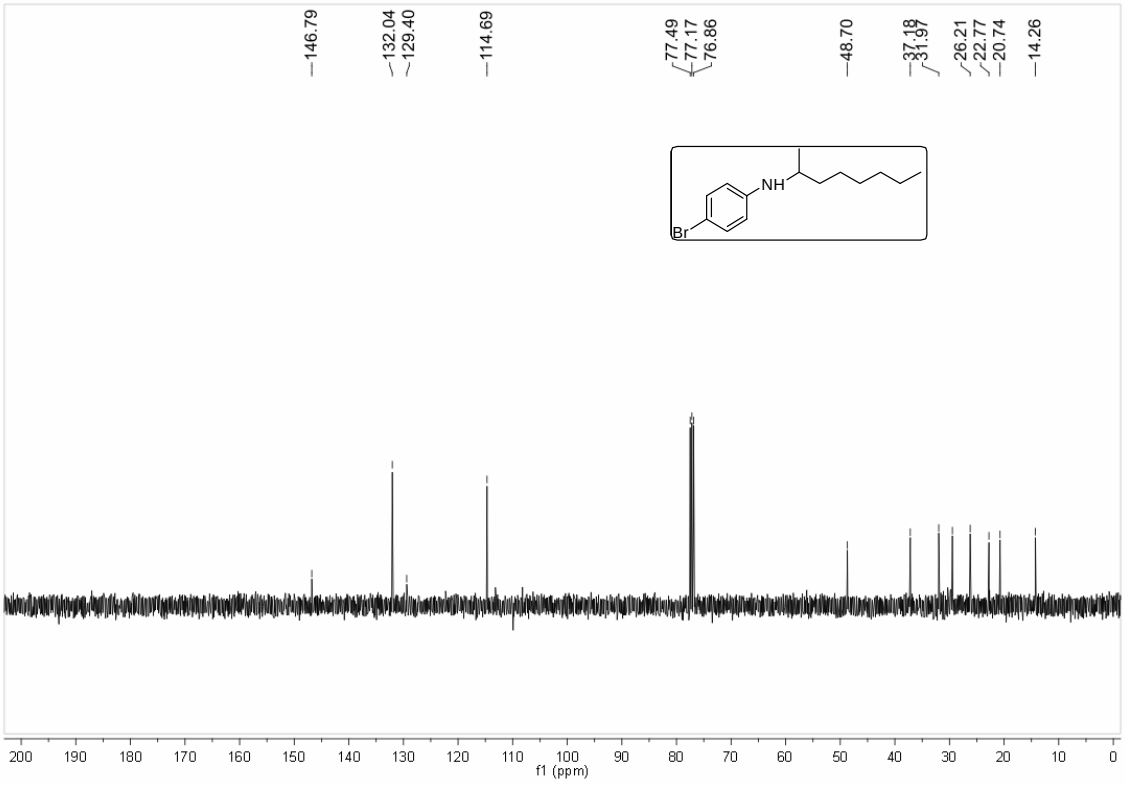


Colorless oil .**^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 7.21 (d, 2H， Ar-H), 6.43 (d, 2H, Ar-H,), 3.45 (s, 1H, -NH-), 3.38 (dd, 1H, -NCH-), 1.55-1.29 (m, 10H, -$(CH_2)_5$-), 1.14 (d, 3H, -CH_3), 0.88 (t, 3H, -CH_3). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ = 146.79, 132.04, 129.40, 114.69, 48.70, 37.18, 31.97, 29.47, 26.21, 22.77, 20.74, 14.26.

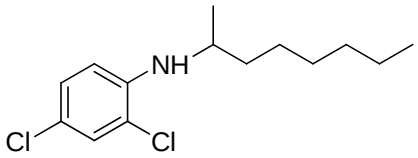
IR (KBr, cm^{-1}): 3410, 2923, 2855, 1594, 1500, 1465, 1398, 1257, 1178, 1158, 1114, 1074, 999, 968, 811, 747, 692, 646, 502.

HRMS Calcd. for $C_{14}H_{22}BrN$: 283.0936. Found:283.0938





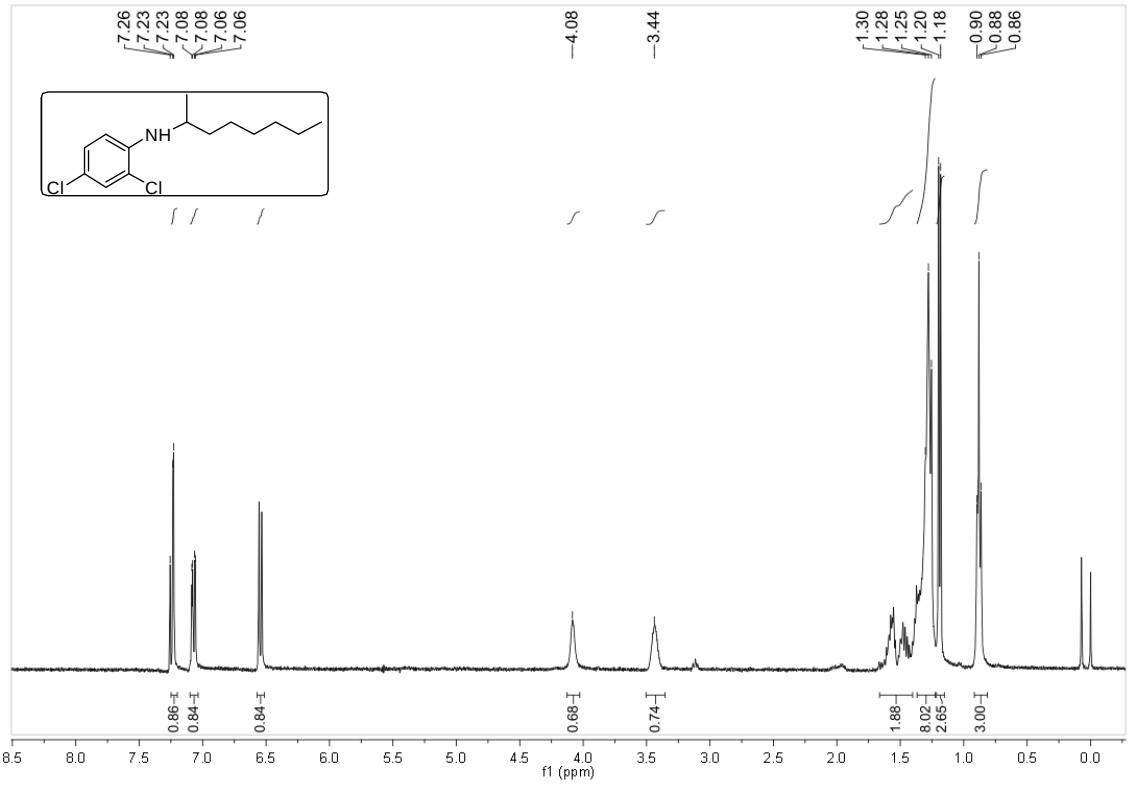
3.6 N-(2-Octyl)-2,4-dichloroaniline

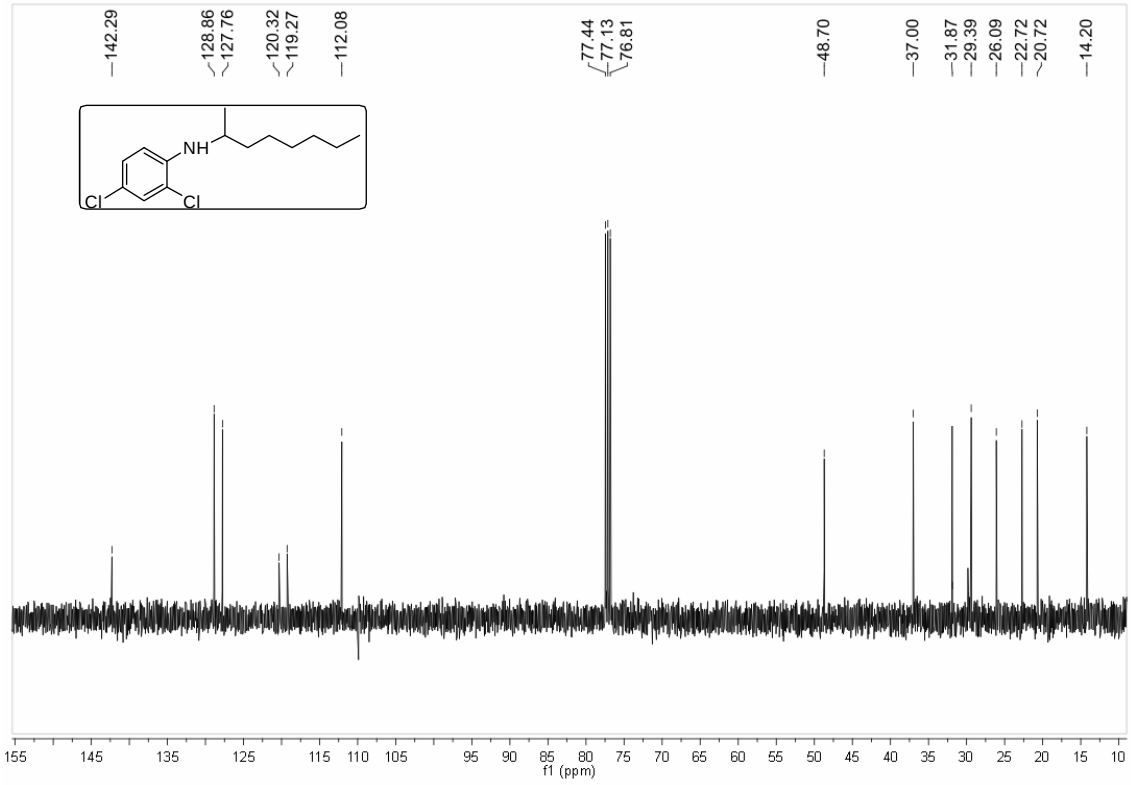


Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 7.23 (d, 1H, Ar-H), 7.07 (dd, 1H, Ar-H), 6.54 (d, 1H, Ar-H), 4.08 (s, 1H, -NH), 3.44 (s, 1H, -NCH), 1.66-1.40 (m, 2H, $-CH_2$), 1.37-1.25 (m, 8H, $-(CH_2)_4-$), 1.19 (d, 3H, $-CH_3$), 0.88 (t, 3H, $-CH_3$). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ = 142.29, 128.86, 127.76, 120.32, 119.27, 112.08, 48.70, 37.00, 31.87, 29.39, 26.09, 22.72, 20.72, 14.20.

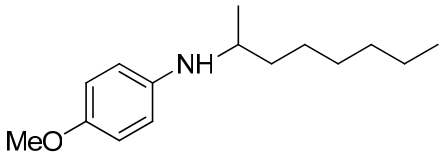
IR (KBr, cm^{-1}): 3420, 3074, 2958, 2928, 2856, 2296, 1853, 1596, 1504, 1460, 1322, 1264, 1162, 1045, 866, 800, 751, 655, 550, 437。

HRMS Calcd. for $C_{14}H_{21}Cl_2N$: 273.1051.Found:273.1049





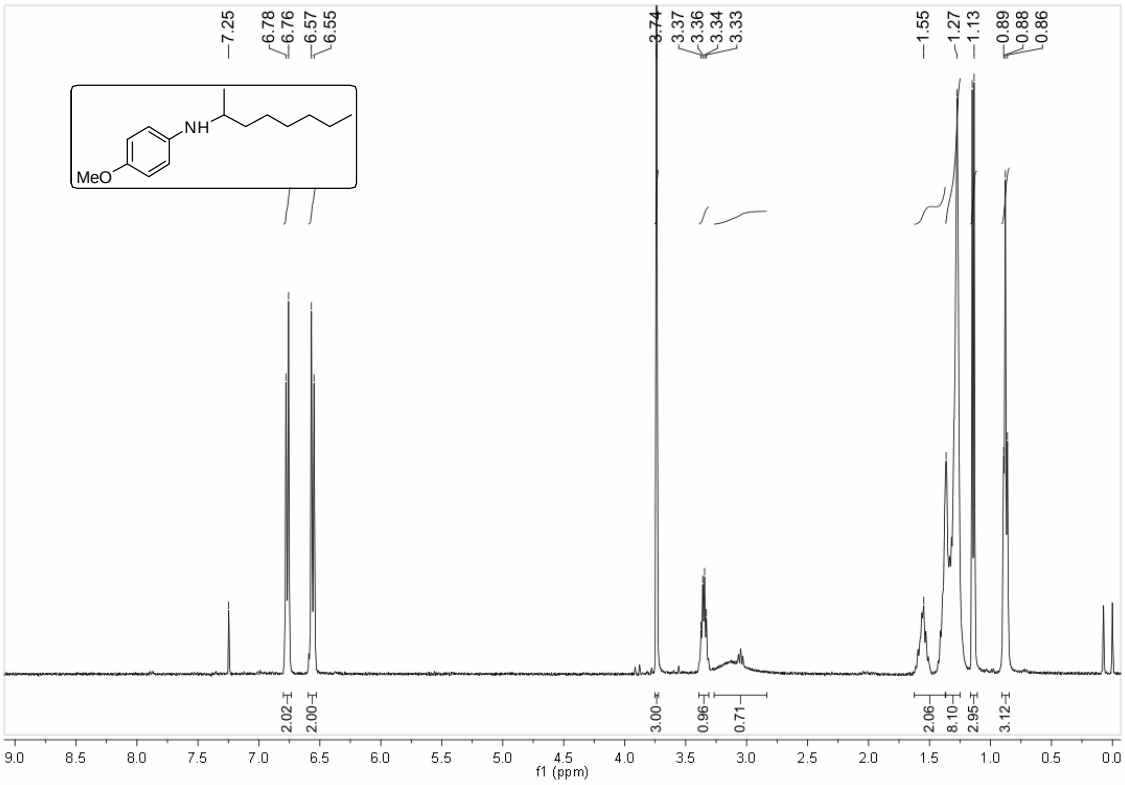
3.7 N-(2-Octyl)-4-methoxyaniline

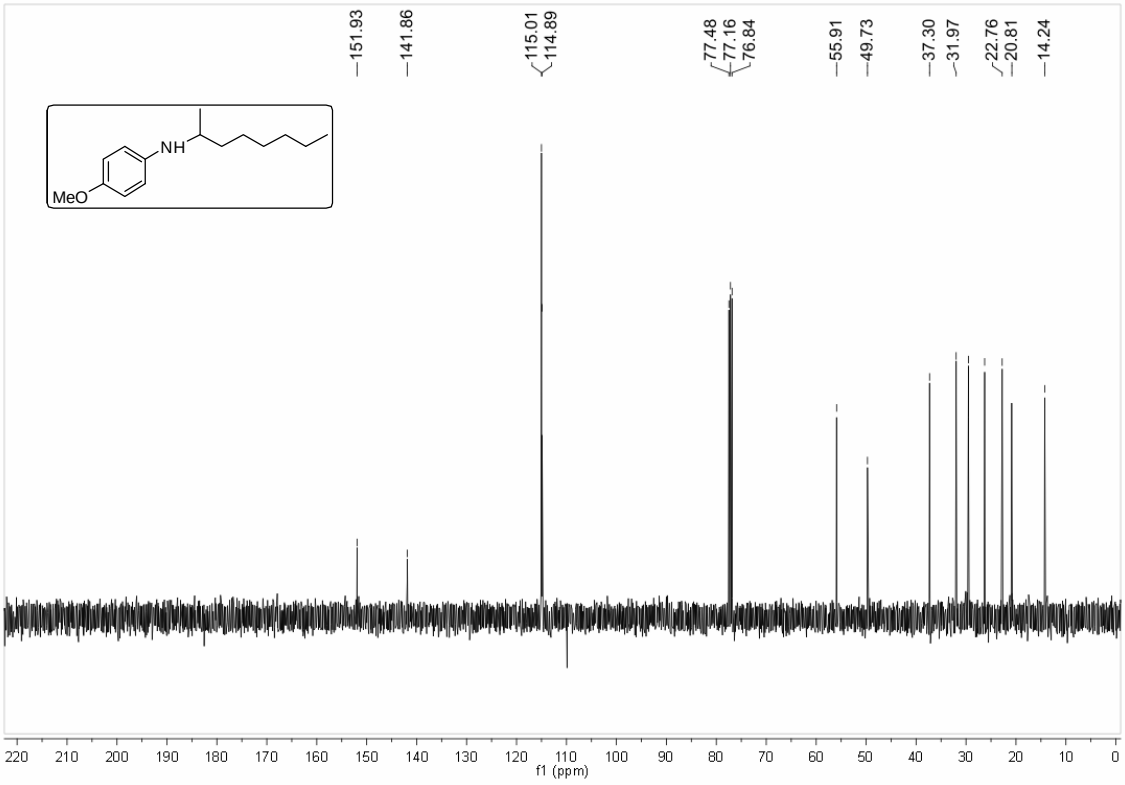


Llight yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 6.77 (d, 2H, Ar-H), 6.56 (d, 2H, Ar-H), 3.74 (s, 3H, -OCH_3), 3.35 (dd, 1H, -NCH-), 3.27–2.83 (s, 1H, -NH), 1.55 (m, 2H, -CH_2), 1.37-1.25 (d, 8H, -$(CH_2)_4$-), 1.14 (d, 3H, -CH_3), 0.88 (t, 3H, -CH_3). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ = 151.93, 141.86, 15.01, 114.89, 55.91, 49.73, 37.30, 31.97, 29.51, 26.27, 22.76, 20.81, 14.24.

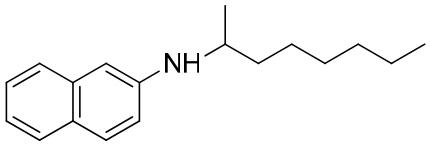
IR(KBr, cm^{-1}): 3397, 2928, 2855, 2074, 1843, 1618, 1513, 1465, 1376, 1234, 1179, 1041, 818, 757, 518.

HRMS Calcd. for $C_{15}H_{25}NO$: 235.1936. Found:235.1942.





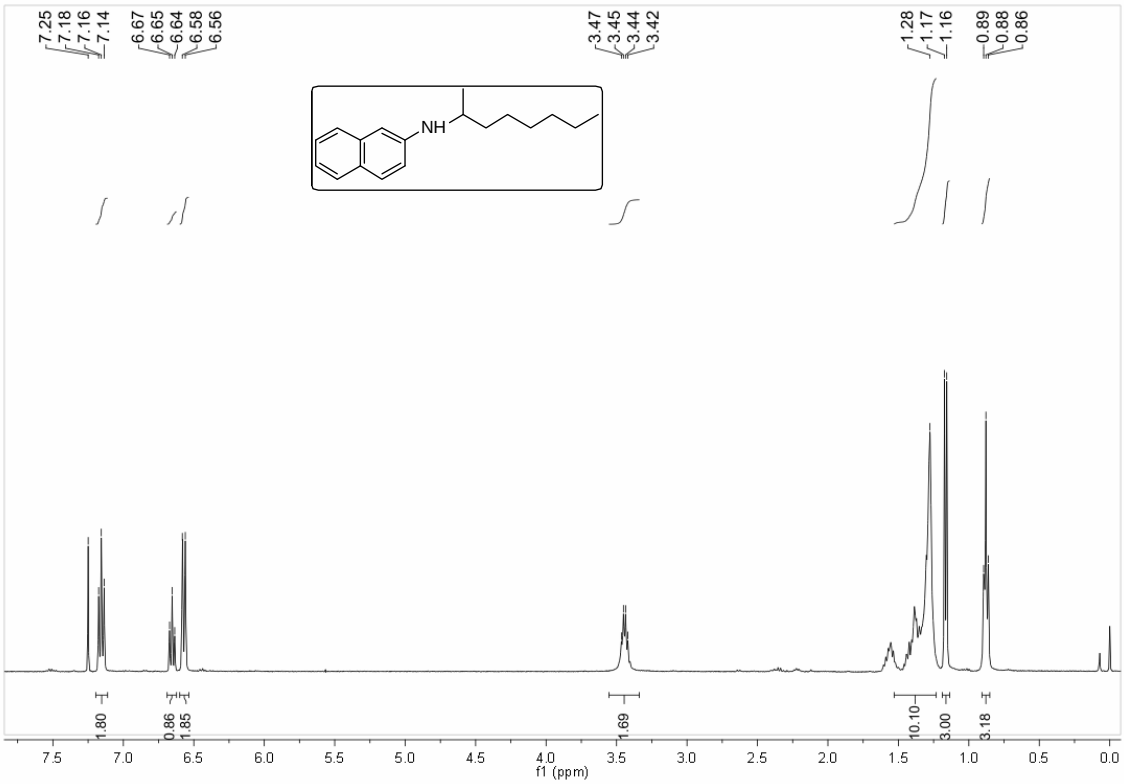
3. 8 N-(2-Octyl)naphthalen-2-amine

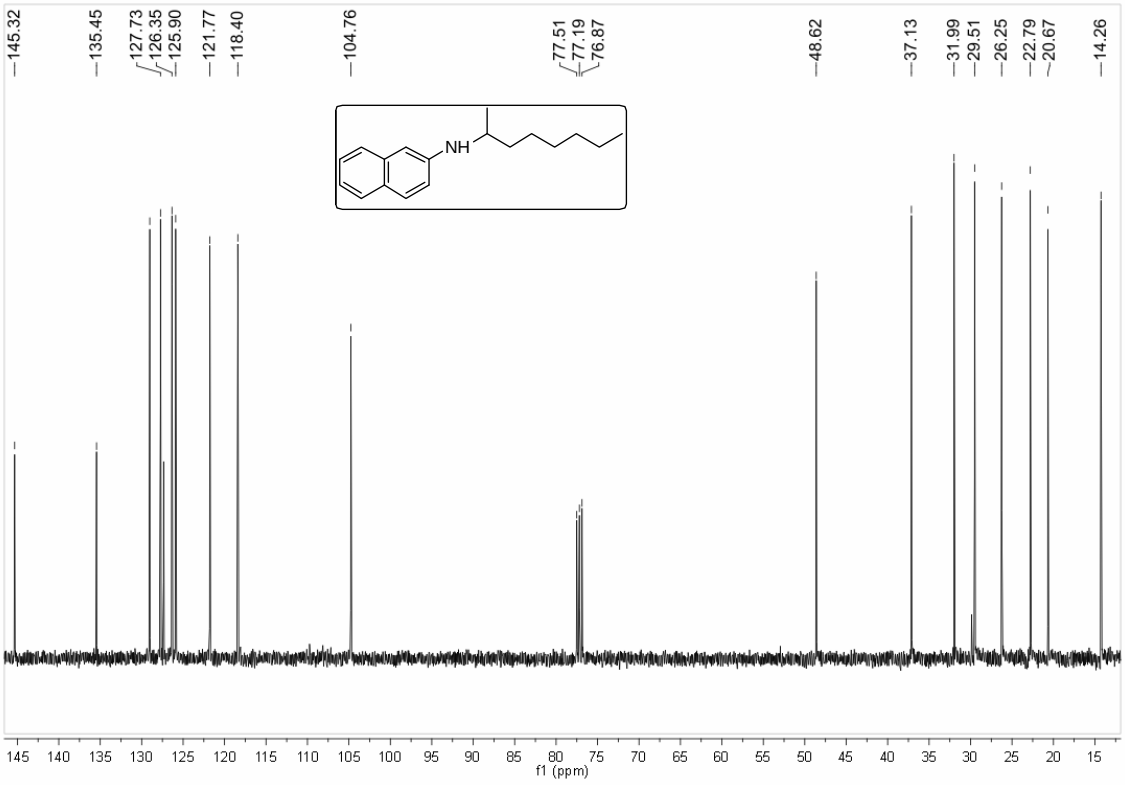


Light yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 7.61 (d, 1H, Ar-H), 7.56 (d, 2H, Ar-H), 7.31 (t, 1H, Ar-H), 7.14 (t, 1H, Ar-H), 6.80 – 6.69 (m, 2H, Ar-H), 3.52 (dd, 2H,-NCH-and-NH), 1.43-1.26 (m, 10H, -$(CH_2)_5$-), 1.17 (d, 3H, CH_3), 0.87 (t, 3H, CH_3). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ = 145.32, 135.45, 129.02, 127.73, 126.35, 125.90, 121.77, 118.40, 104.76, 48.62, 37.13, 31.99, 29.51, 26.25, 22.79, 20.67, 14.26.

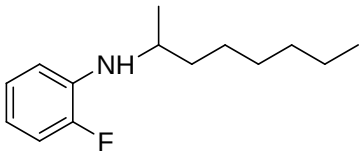
IR (KBr, cm^{-1}): 3407, 3051, 2957, 2931, 2855, 1901, 1629, 1603, 1522, 1484, 1398, 1263, 1224, 1189, 1145, 1018, 827, 743, 622, 470.

HRMS Calcd. for $C_{18}H_{25}N$: 255.1987. Found: 255.1985





3.9 N-(2-Octyl)-2-fluoroaniline



Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 7.00 (dd, 2H, Ar-H), 6.71 (t, 1H, Ar-H), 6.61 (dd, 1H, Ar-H), 3.72 (s, 1H-NH), 3.50 (d, 1H, -NCH), 1.62-1.33 (m, 10H, -$(CH_2)_5$-), 1.23 (d, 3H, -CH_3), 0.92 (d, 3H, -CH_3). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ = 143.58, 129.35, 127.86, 119.10, 116.54, 111.60, 48.54, 37.18, 31.97, 29.48, 26.21, 22.79, 20.89, 14.27.

IR(KBr, cm^{-1}): 3420,3073,2959,2928,2856,1598,1512,1463,1324,1163,1033,739,439.

HRMS Calcd. for $C_{14}H_{22}FN$: 223.1736. Found: 223.1736.