Electronic Supplementary Material (ESI) for Dalton Transactions.

Highly active chromium(III) complexes based on tridentate pyrazolyl pyridyl ligands for ethylene polymerization and oligomerization

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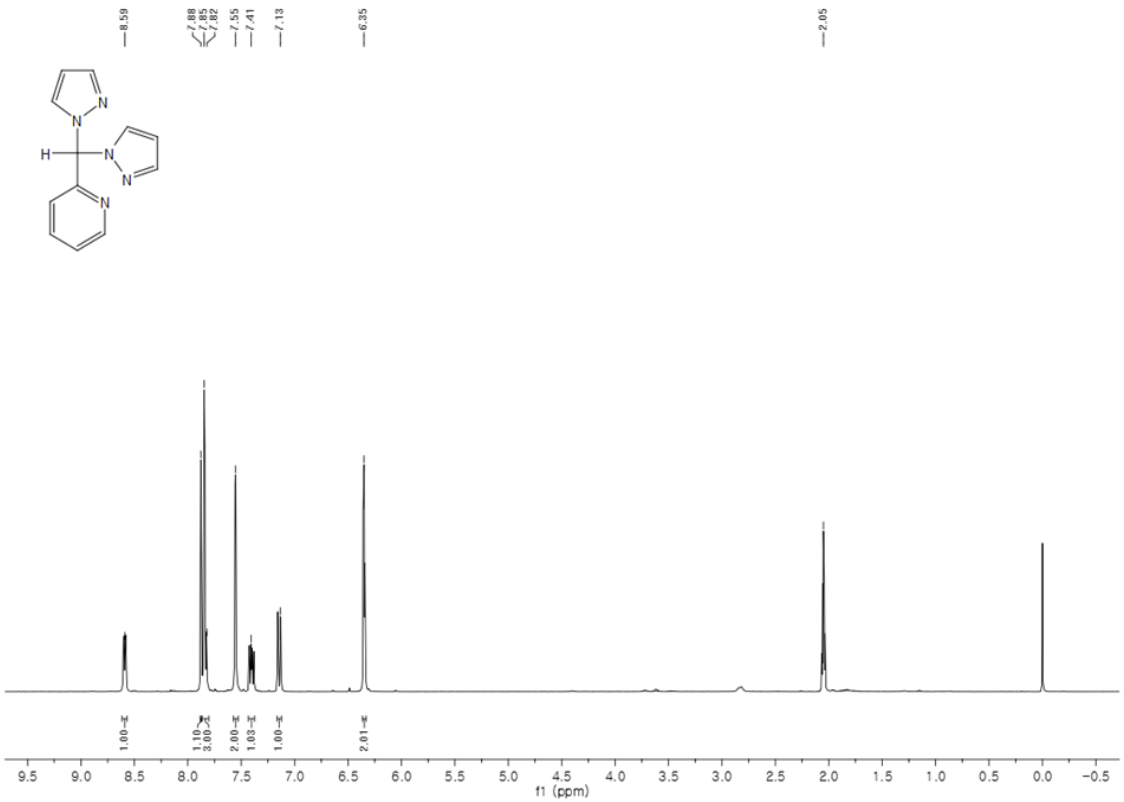

Figure S1 : ^{1}H NMR of Bis(1-pyrazolyl)(2-pyridyl)methane (L1) in Acetone-d_6

Figure S1. ^{1}H NMR of **L1** in acetone-d_6

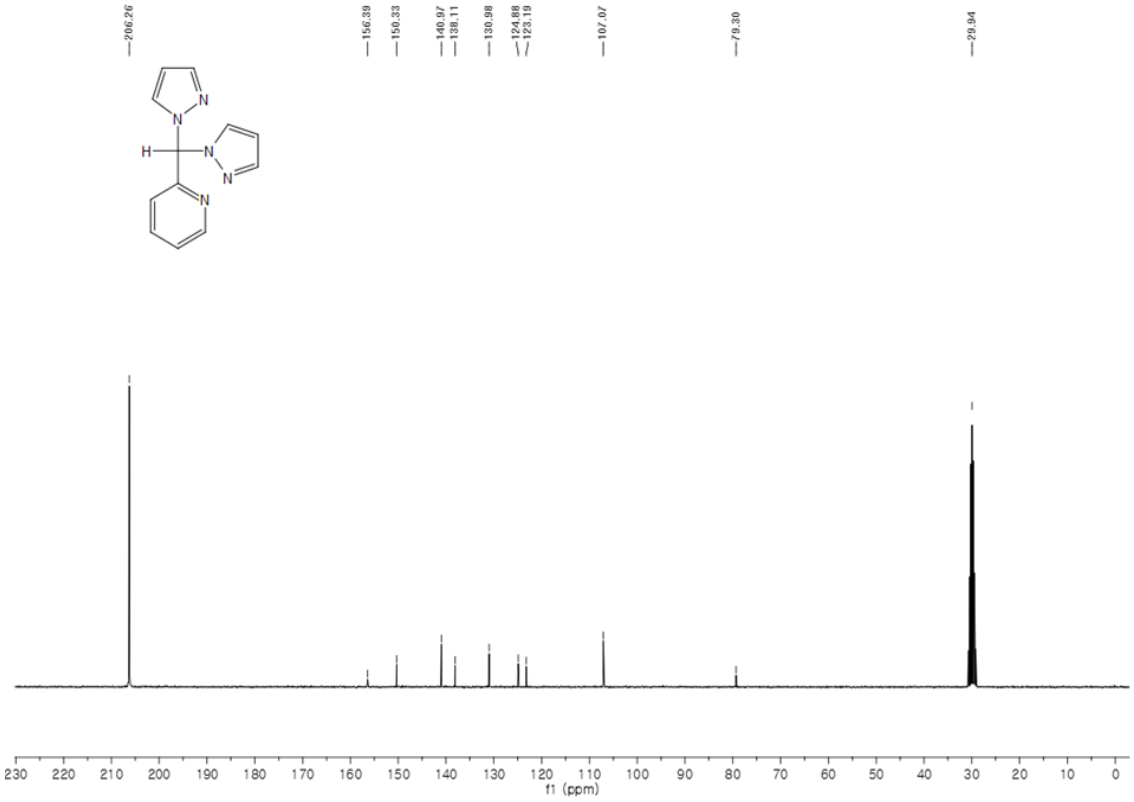

Figure S2 : ^{13}C NMR of Bis(1-pyrazolyl)(2-pyridyl)methane (L1) in Acetone-d_6

Figure S2. ^{13}C NMR of **L1** in acetone-d_6

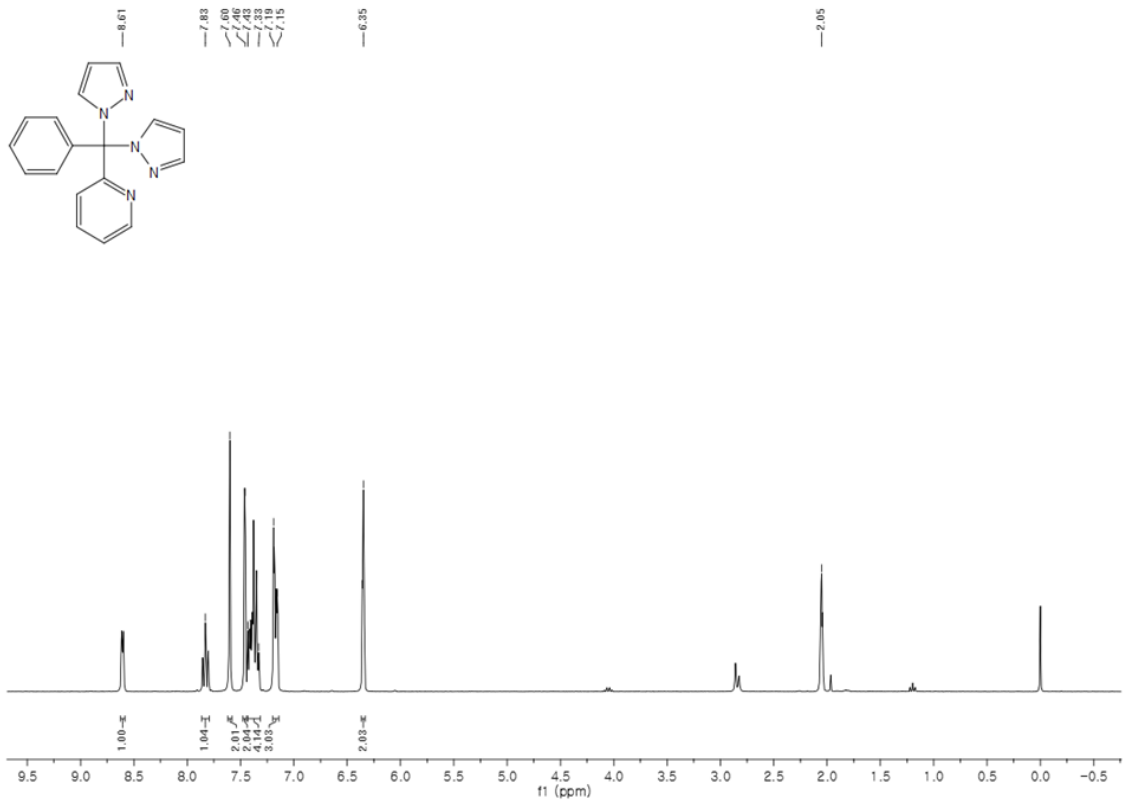

Figure S3 : ^{1}H NMR of (phenyl)bis(1-pyrazolyl)(2-pyridyl)methane (L2) in Acetone-d_6

Figure S3. ^{1}H NMR of **L2** in acetone-d_6

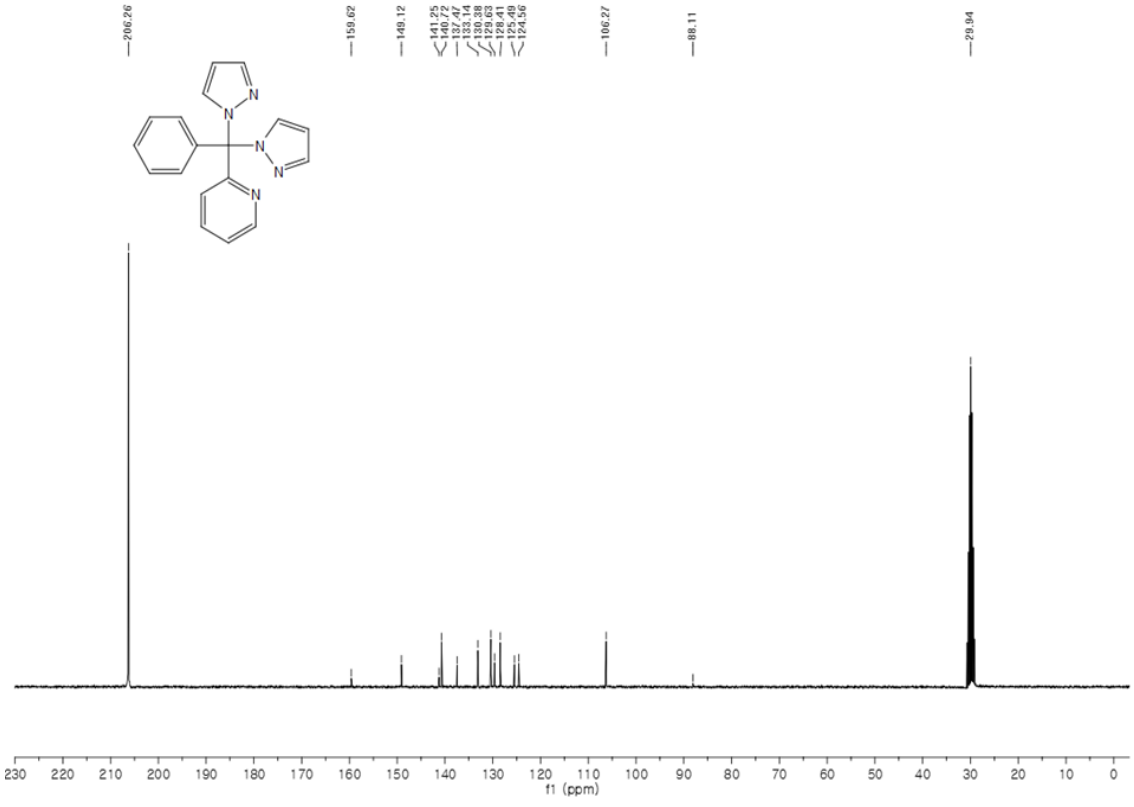

Figure S4 : ^{13}C NMR of (phenyl)bis(1-pyrazolyl)(2-pyridyl)methane (L2) in Acetone-d_6

Figure S4. ^{13}C NMR of **L2** in acetone-d_6

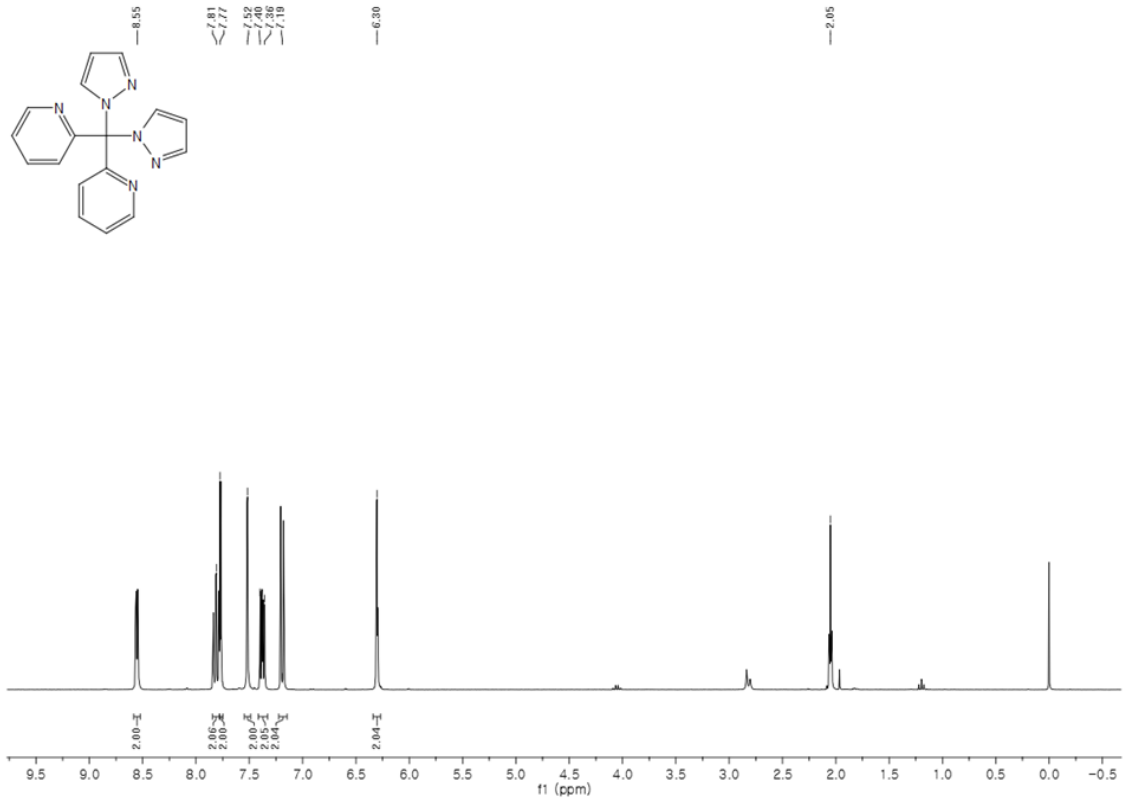

Figure S5 : ^{1}H NMR of Bis(1-pyrazolyl)-Bis(2-pyridyl)methane (L3) in Acetone-d_6

Figure S5. ^{1}H NMR of **L3** in acetone-d_6

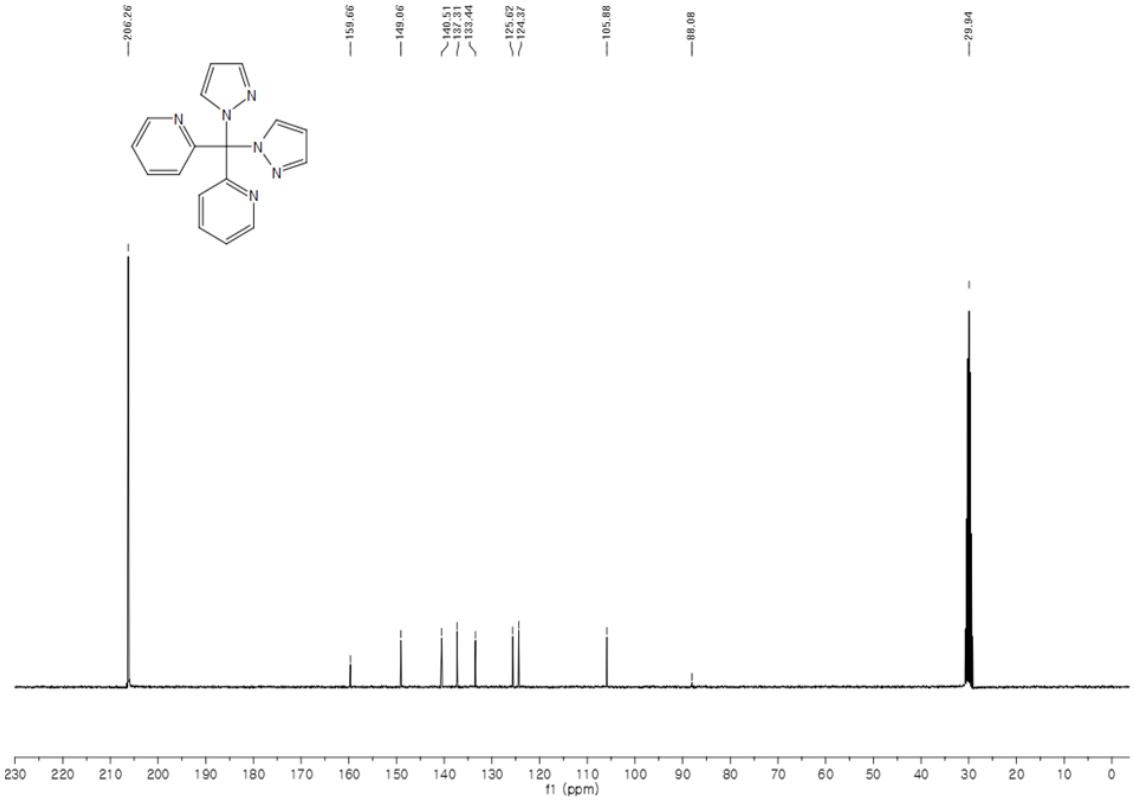

Figure S6 : ^{13}C NMR of Bis(1-pyrazolyl)-Bis(2-pyridyl)methane (L3) in Acetone-d_6

Figure S6. ^{13}C NMR of **L3** in acetone-d_6

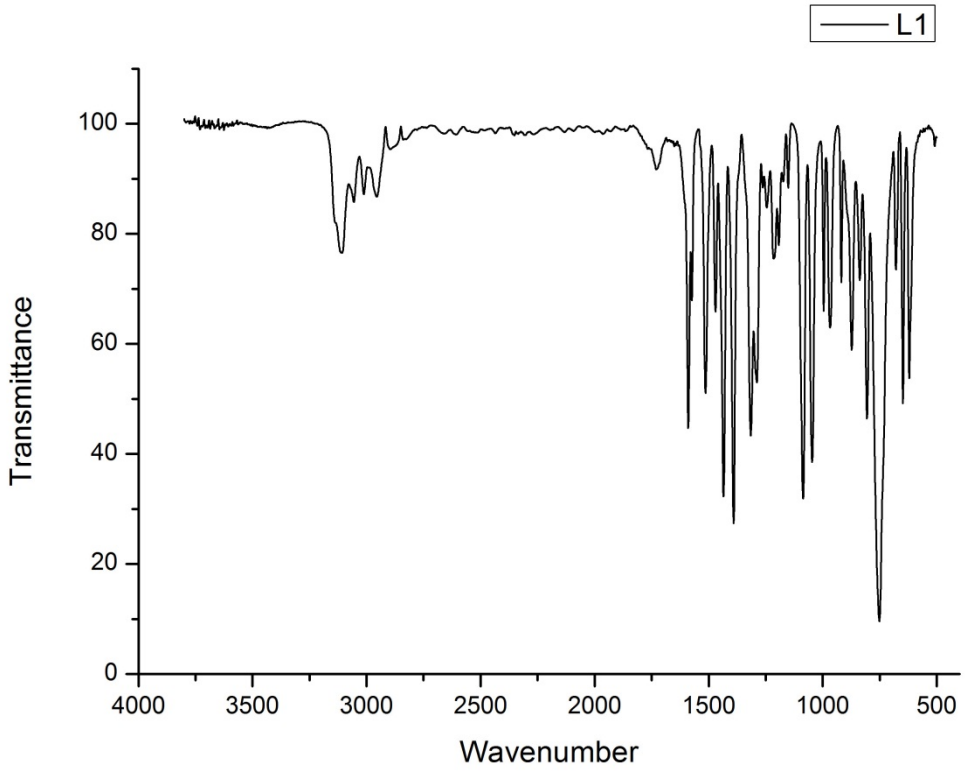

Figure S7. FT-IR spectrum of **L1**

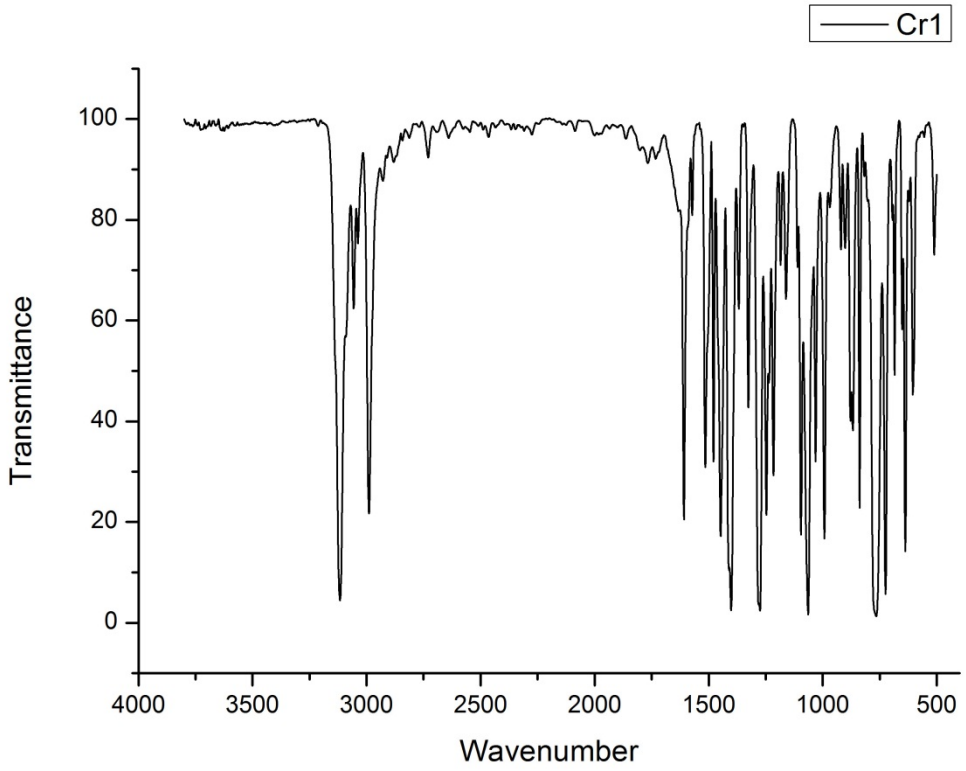

Figure S8. FT-IR spectrum of **Cr1**

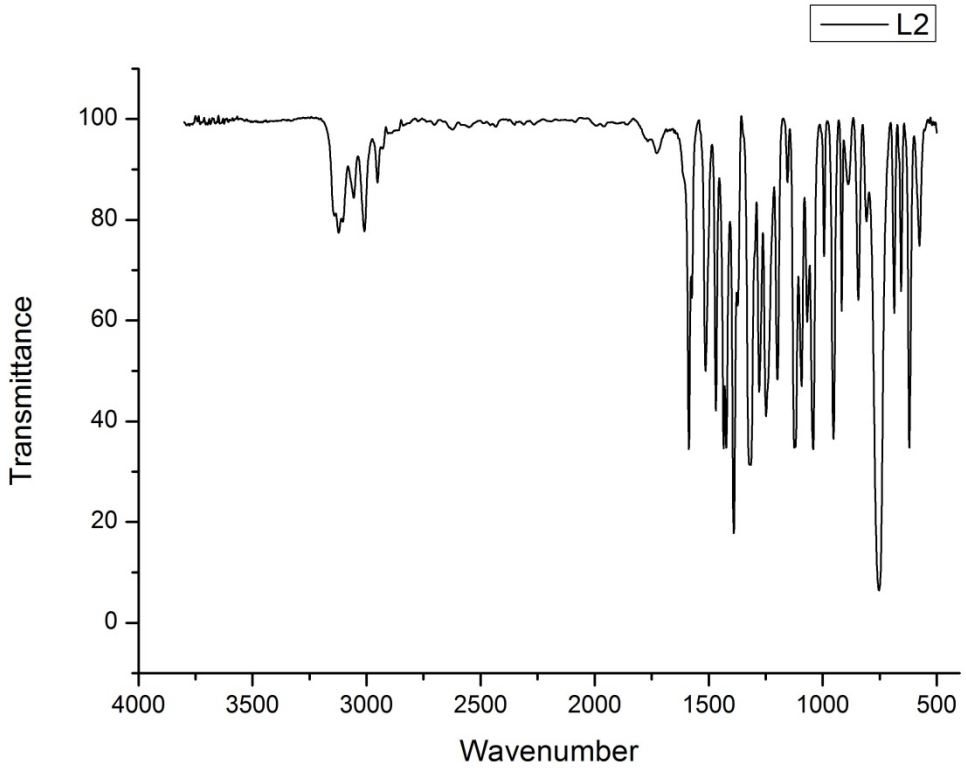

Figure S9. FT-IR spectrum of **L2**

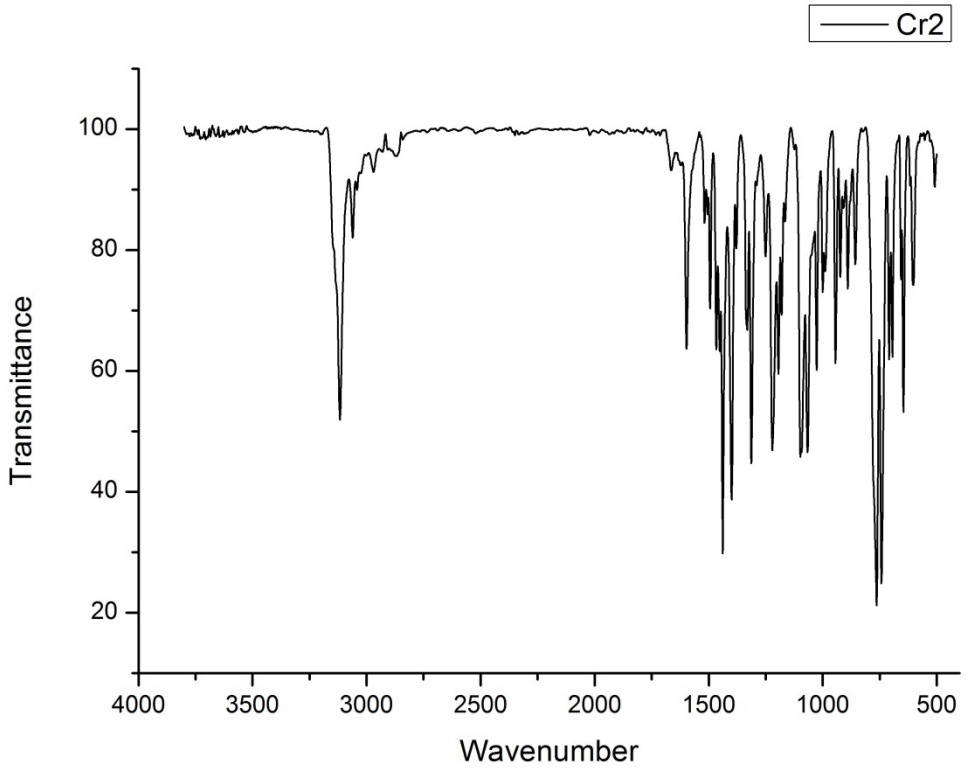

Figure S10. FT-IR spectrum of **Cr2**

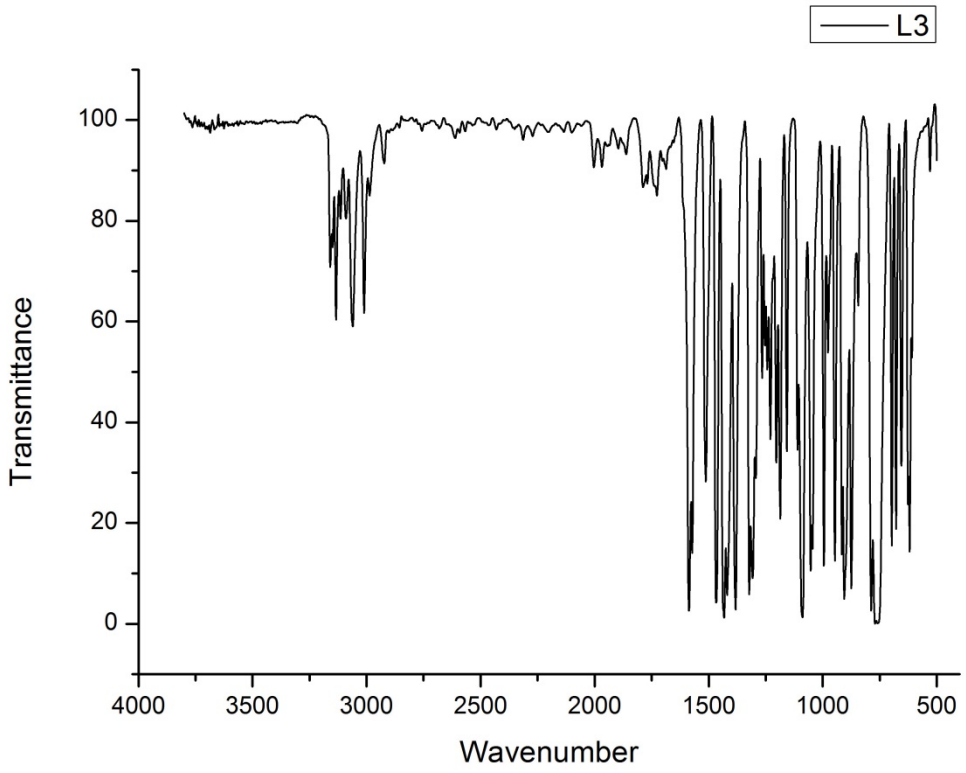

Figure S11. FT-IR spectrum of **L3**

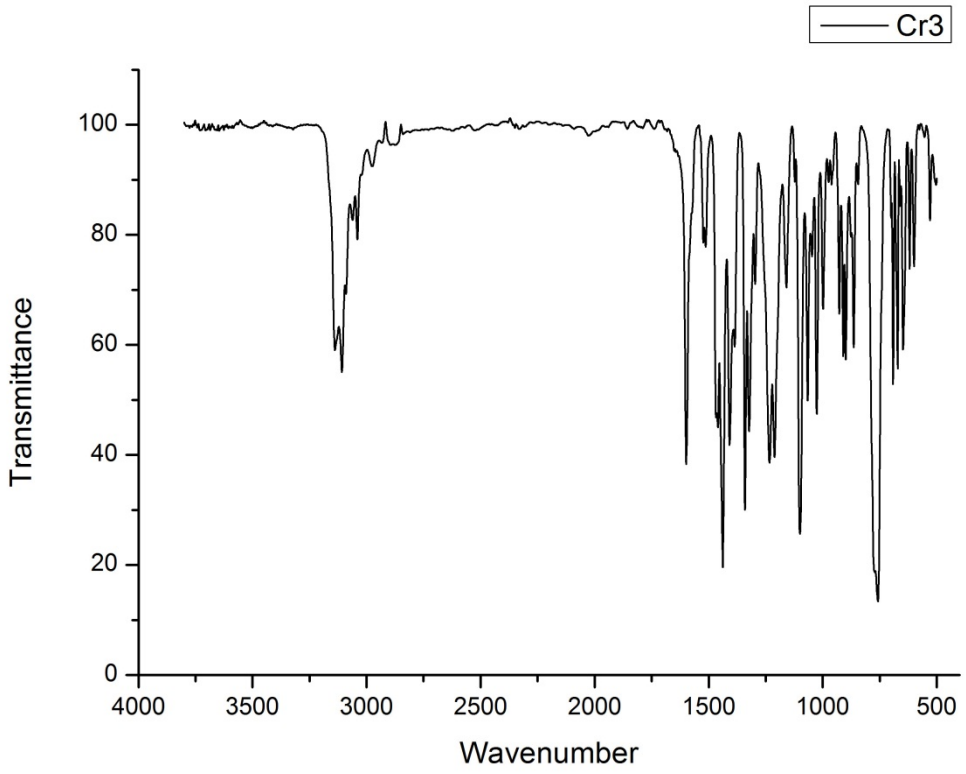

Figure S12. FT-IR spectrum of **Cr3**

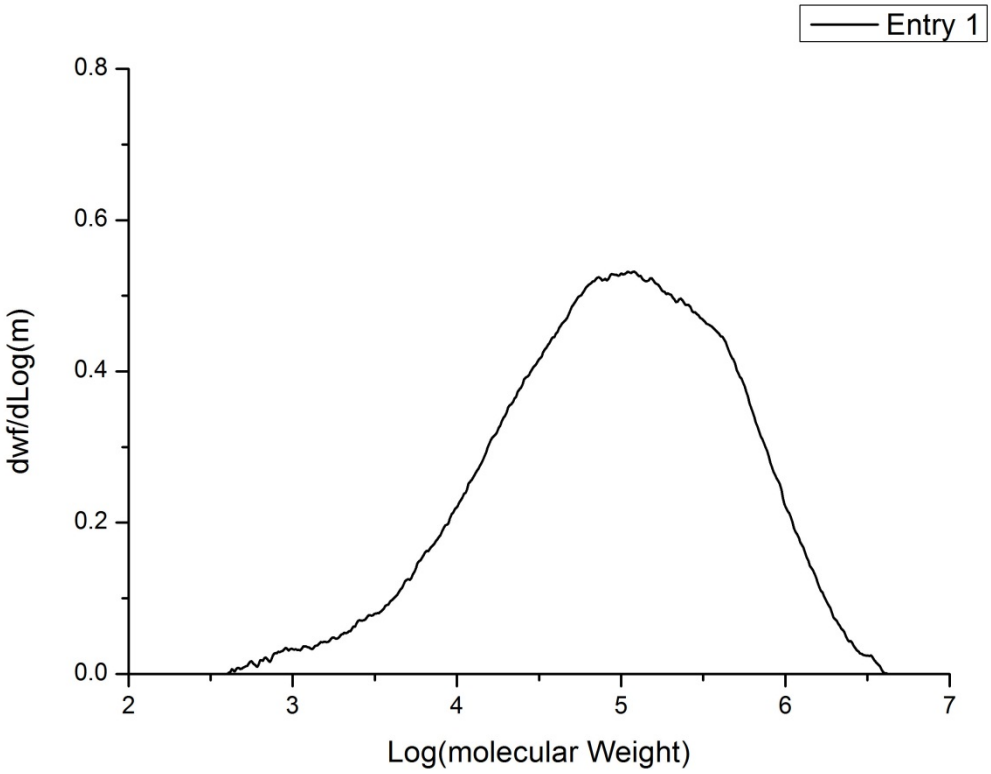

Figure S13. GPC trace of polyethylene (entry 1)

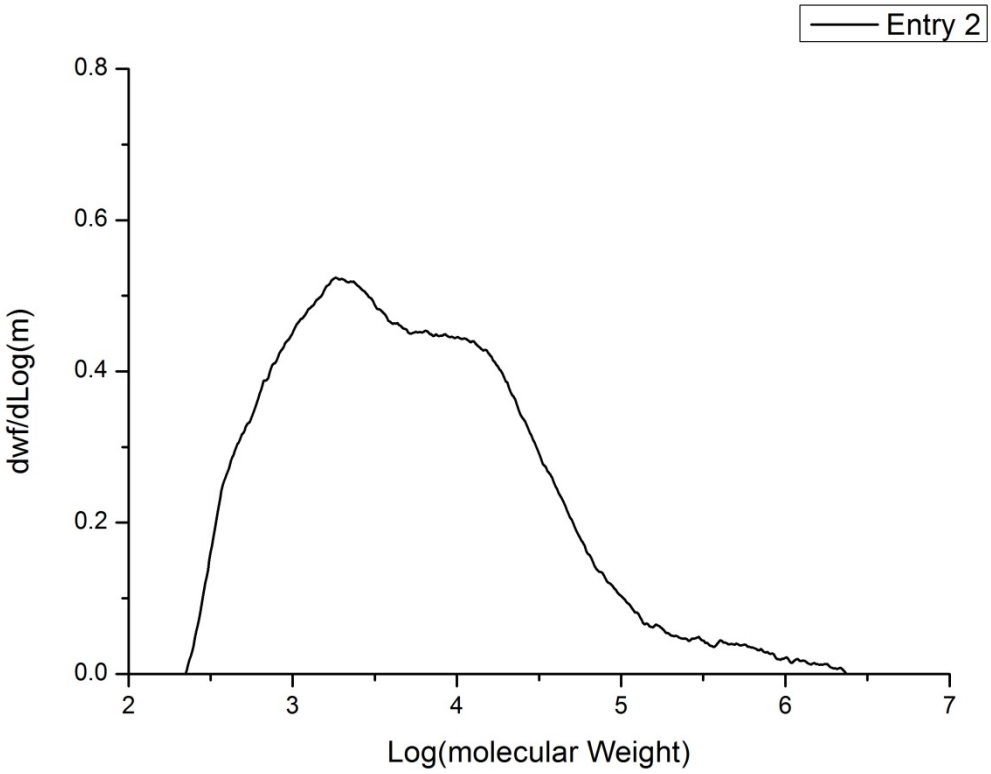

Figure S14. GPC trace of polyethylene (entry 2)

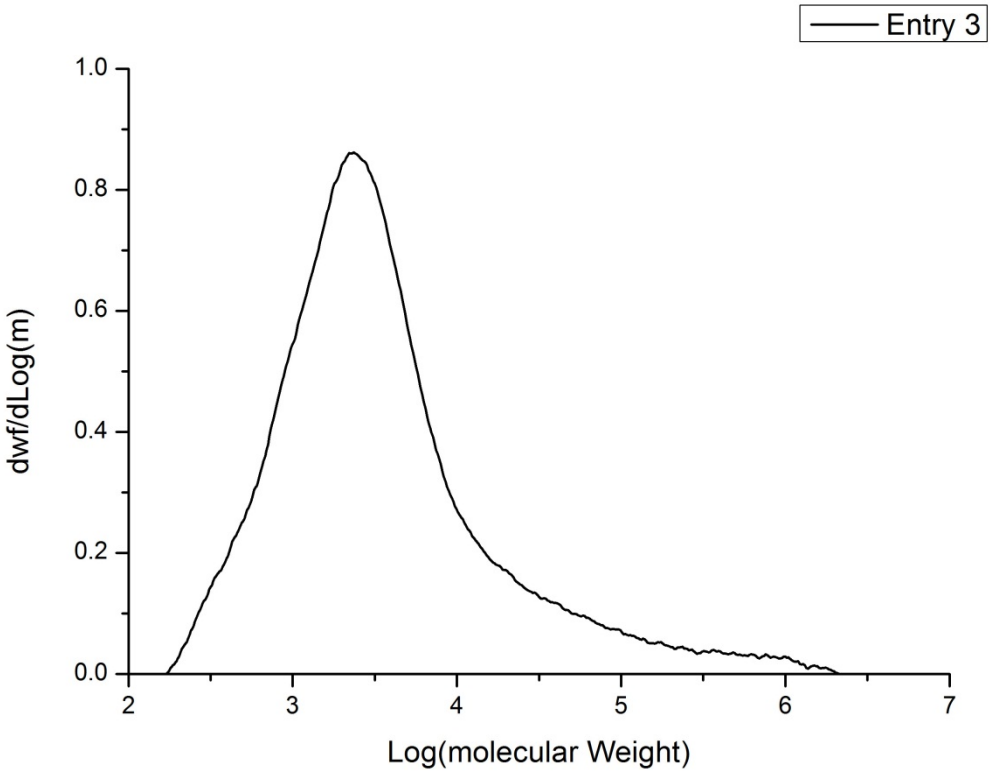

Figure S15. GPC trace of polyethylene (entry 3)

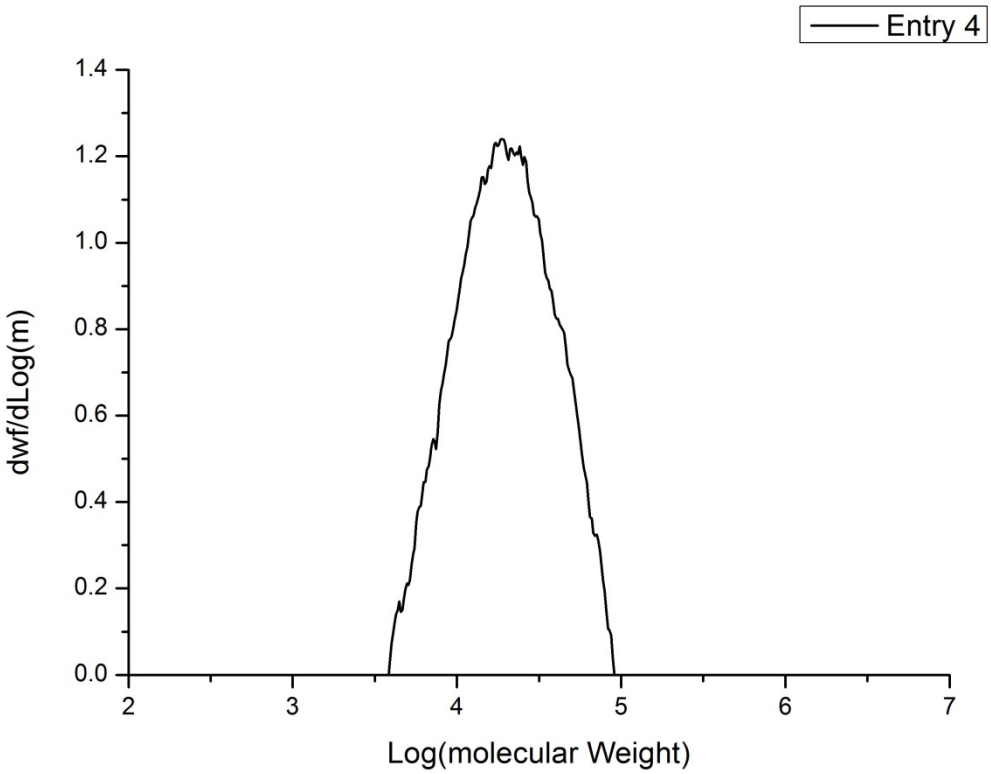

Figure S16. GPC trace of polyethylene (entry 4)

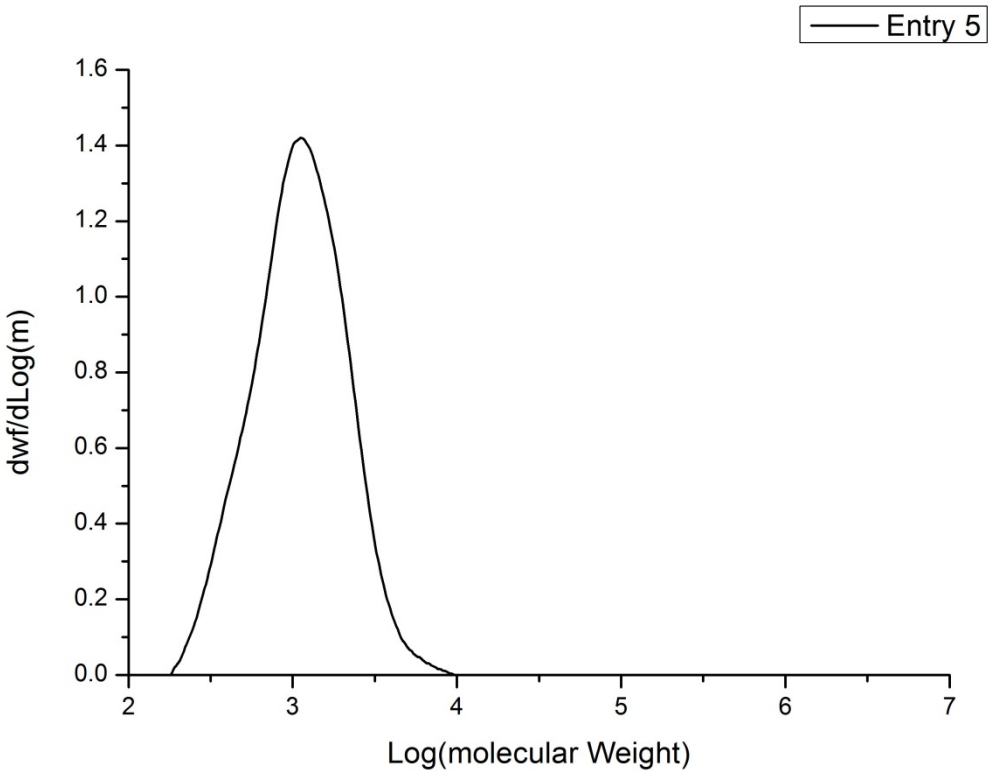

Figure S17. GPC trace of polyethylene (entry 5)

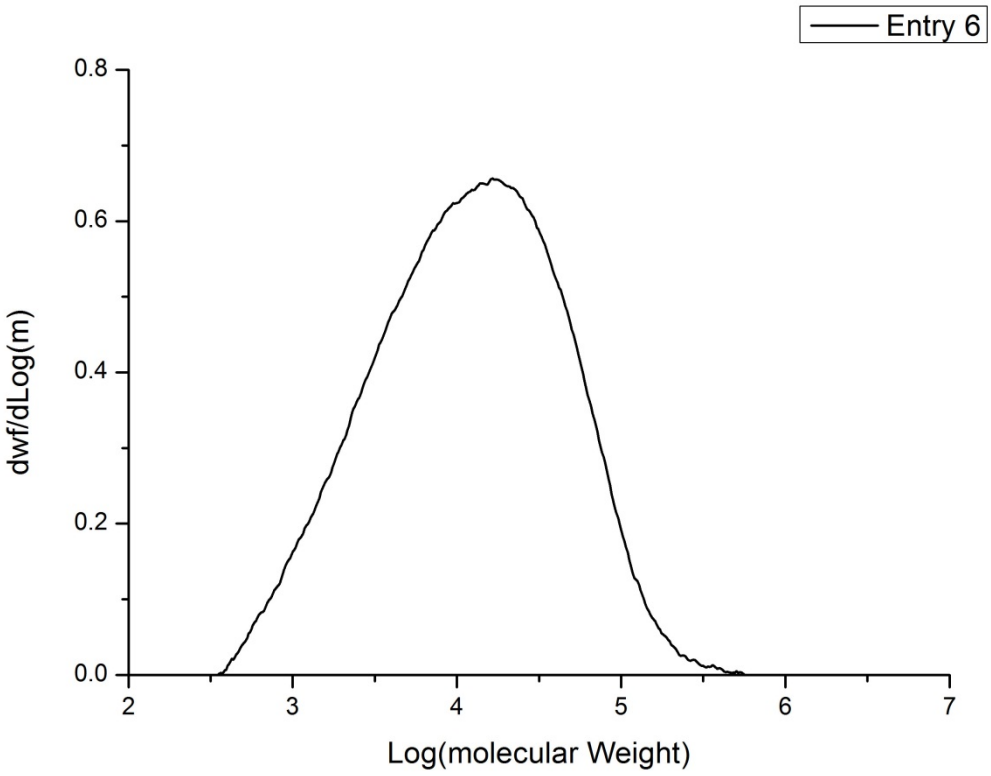

Figure S18. GPC trace of polyethylene (entry 6)

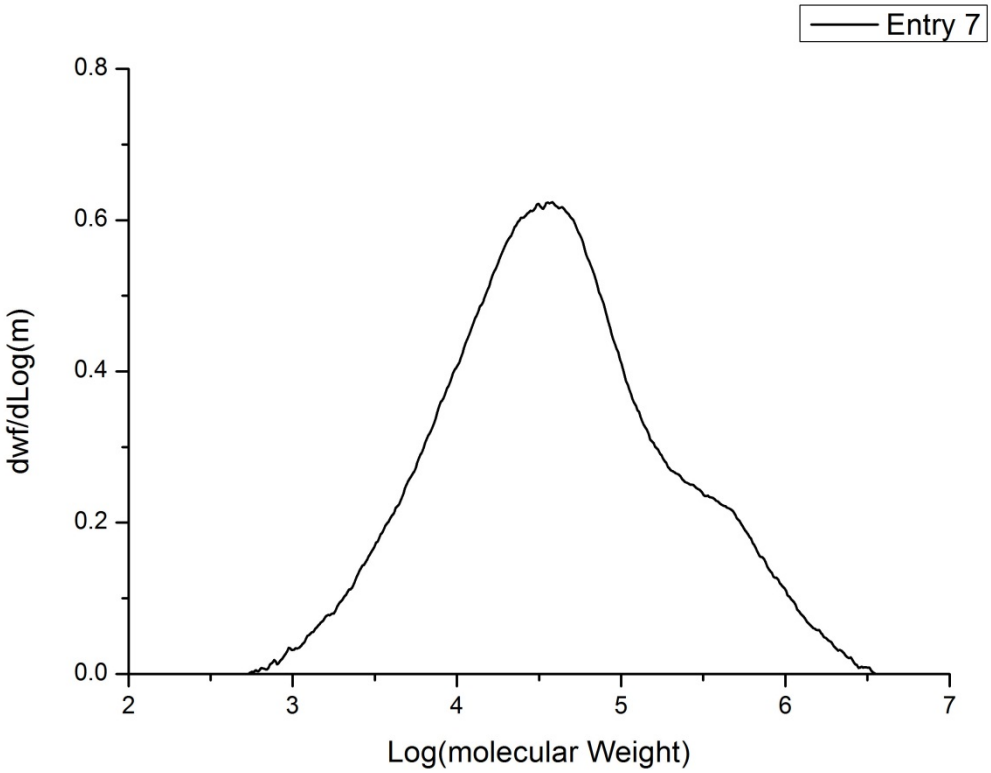

Figure S19. GPC trace of polyethylene (entry 7)

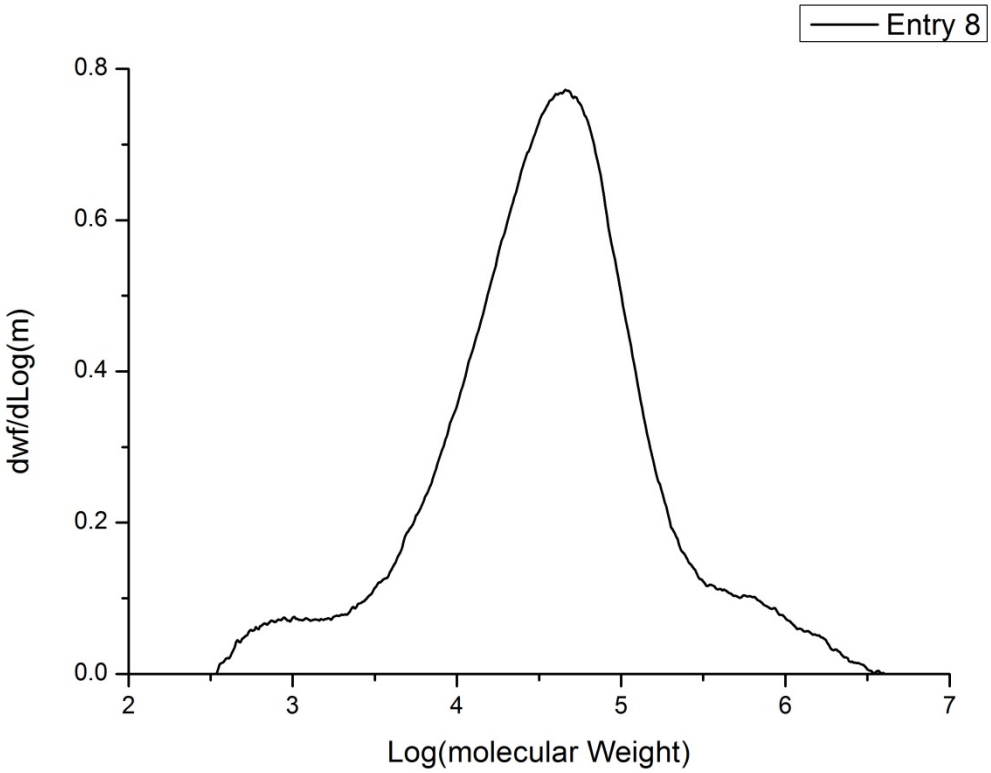

Figure S20. GPC trace of polyethylene (entry 8)

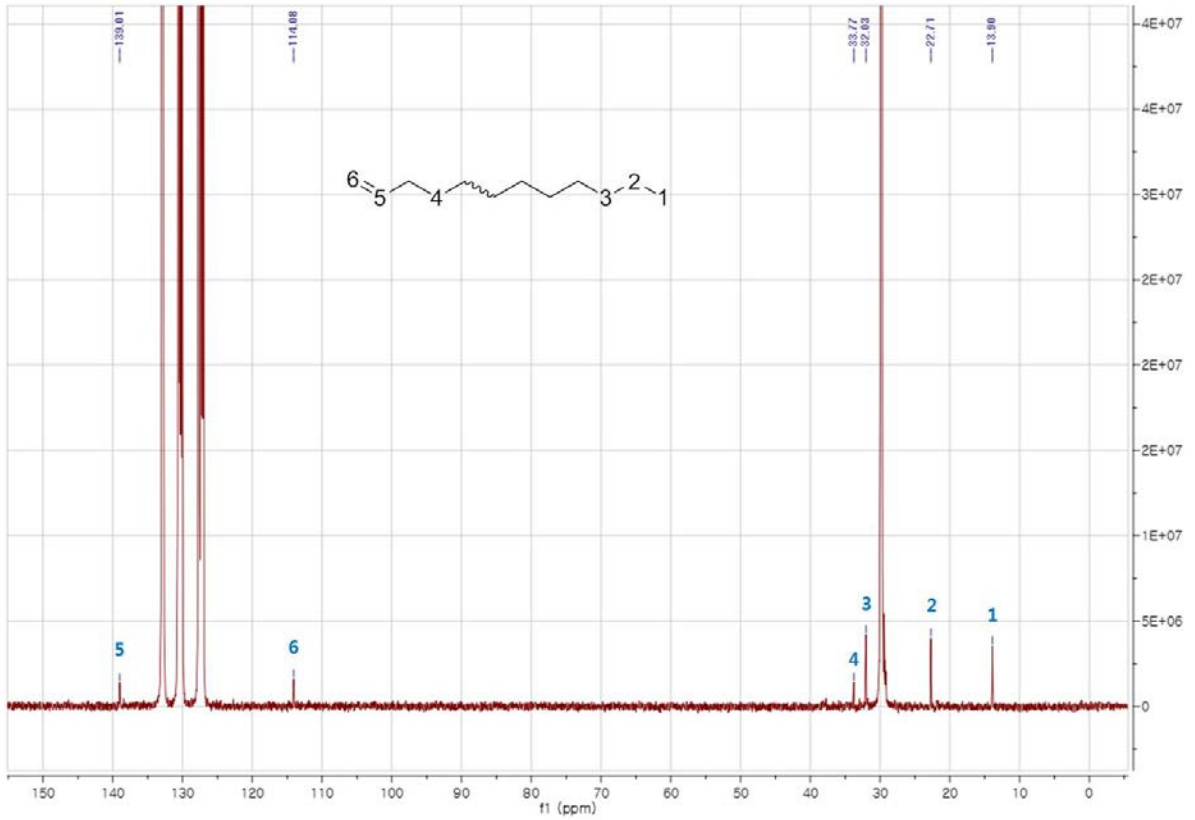

Figure S21. Representative ^{13}C NMR spectrum of polyethylene (entry 8)

Table S1. Crystal data and structure refinement for **Cr2**

Empirical formula	C_{21} H_{22} Cl_3 Cr N_6 O
Formula weight	532.79
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 9.0372(2) Å alpha = 87.5459(15)˚.
	b = 12.0050(3) Å beta = 68.1978(12)˚.
	c = 12.1284(3) Å gamma = 71.7827(13)˚.
Volume	1156.46(5) $Å^3$
Z, Calculated density	2, 1.530 Mg/m^3
Absorption coefficient	0.868 mm^{-1}
F(000)	546
Crystal size	0.20 x 0.18 x 0.05 mm
Theta range for data collection	1.792 to 28.308˚.
Limiting indices	-12<=h<=12, -16<=k<=16, -16<=l<=16
Reflections collected / unique	21213 / 5744 [R_{int} = 0.0513]
Completeness to theta = 25.242	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.947 and 0.831
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5744 / 0 / 288
Goodness-of-fit on F^2	1.045
Final R indices [I>2sigma(I)]	R_1 = 0.0493, wR_2 = 0.1187
R indices (all data)	R_1 = 0.0899, wR_2 = 0.1381
Extinction coefficient	n/a
Largest diff. peak and hole	0.694 and -0.387 e.$Å^{-3}$

Table S2. Selected bond lengths [Å] and angles [°] for **Cr2**

Cr(1)-N(5)	2.020(2)	C(17)-H(17)	0.93
Cr(1)-N(10)	2.095(3)	C(18)-C(19)	1.313(6)
Cr(1)-N(15)	2.106(2)	C(18)-H(18)	0.93
Cr(1)-Cl(2)	2.2958(9)	C(19)-C(20)	1.311(6)
Cr(1)-Cl(4)	2.2994(10)	C(19)-H(19)	0.93
Cr(1)-Cl(3)	2.3103(10)	C(20)-H(20)	0.93
N(5)-C(9)	1.325(4)	C(21)-C(22)	1.529(4)
N(5)-N(6)	1.357(3)	C(22)-C(27)	1.386(4)
N(6)-C(7)	1.359(4)	C(22)-C(23)	1.390(4)
N(6)-C(21)	1.490(4)	C(23)-C(24)	1.385(4)
C(7)-C(8)	1.370(4)	C(23)-H(23)	0.93
C(7)-H(7)	0.93	C(24)-C(25)	1.374(5)
C(8)-C(9)	1.389(5)	C(24)-H(24)	0.93
C(8)-H(8)	0.93	C(25)-C(26)	1.368(5)
C(9)-H(9)	0.93	C(25)-H(25)	0.93
N(10)-C(14)	1.326(4)	C(26)-C(27)	1.390(5)
N(10)-N(11)	1.361(3)	C(26)-H(26)	0.93
N(11)-C(12)	1.361(4)	C(27)-H(27)	0.93
N(11)-C(21)	1.496(4)	O(28)-C(29)	1.226(6)
C(12)-C(13)	1.432(6)	C(29)-N(30)	1.308(6)
C(12)-H(12)	0.93	C(29)-H(29)	0.93
C(13)-C(14)	1.458(6)	N(30)-C(32)	1.412(5)
C(13)-H(13)	0.93	N(30)-C(31)	1.456(5)
C(14)-H(14)	0.93	C(31)-H(31A)	0.96
N(15)-C(20)	1.337(4)	C(31)-H(31B)	0.96
N(15)-C(16)	1.358(4)	C(31)-H(31C)	0.96
C(16)-C(17)	1.376(4)	C(32)-H(32A)	0.96
C(16)-C(21)	1.525(4)	C(32)-H(32B)	0.96
C(17)-C(18)	1.356(5)	C(32)-H(32C)	0.96
N(5)-Cr(1)-N(10)	83.11(10)	C(16)-C(17)-H(17)	120.7
N(5)-Cr(1)-N(15)	81.74(10)	C(19)-C(18)-C(17)	122.6(4)

N(10)-Cr(1)-N(15)	83.65(10)	C(19)-C(18)-H(18)	118.7
N(5)-Cr(1)-Cl(2)	91.20(7)	C(17)-C(18)-H(18)	118.7
N(10)-Cr(1)-Cl(2)	172.46(8)	C(20)-C(19)-C(18)	116.6(4)
N(15)-Cr(1)-Cl(2)	90.66(7)	C(20)-C(19)-H(19)	121.7
N(5)-Cr(1)-Cl(4)	171.08(7)	C(18)-C(19)-H(19)	121.7
N(10)-Cr(1)-Cl(4)	90.63(8)	C(19)-C(20)-N(15)	125.5(4)
N(15)-Cr(1)-Cl(4)	91.29(7)	C(19)-C(20)-H(20)	117.3
Cl(2)-Cr(1)-Cl(4)	94.46(4)	N(15)-C(20)-H(20)	117.3
N(5)-Cr(1)-Cl(3)	90.34(7)	N(6)-C(21)-N(11)	108.6(2)
N(10)-Cr(1)-Cl(3)	90.82(8)	N(6)-C(21)-C(16)	110.2(2)
N(15)-Cr(1)-Cl(3)	170.81(7)	N(11)-C(21)-C(16)	105.1(2)
Cl(2)-Cr(1)-Cl(3)	94.16(4)	N(6)-C(21)-C(22)	104.4(2)
Cl(4)-Cr(1)-Cl(3)	96.12(4)	N(11)-C(21)-C(22)	113.2(2)
C(9)-N(5)-N(6)	106.4(2)	C(16)-C(21)-C(22)	115.4(2)
C(9)-N(5)-Cr(1)	131.9(2)	C(27)-C(22)-C(23)	118.0(3)
N(6)-N(5)-Cr(1)	121.74(18)	C(27)-C(22)-C(21)	120.9(3)
N(5)-N(6)-C(7)	110.0(2)	C(23)-C(22)-C(21)	119.9(3)
N(5)-N(6)-C(21)	121.0(2)	C(24)-C(23)-C(22)	120.9(3)
C(7)-N(6)-C(21)	129.0(2)	C(24)-C(23)-H(23)	119.5
N(6)-C(7)-C(8)	107.4(3)	C(22)-C(23)-H(23)	119.5
N(6)-C(7)-H(7)	126.3	C(25)-C(24)-C(23)	120.2(3)
C(8)-C(7)-H(7)	126.3	C(25)-C(24)-H(24)	119.9
C(7)-C(8)-C(9)	105.4(3)	C(23)-C(24)-H(24)	119.9
C(7)-C(8)-H(8)	127.3	C(26)-C(25)-C(24)	119.7(3)
C(9)-C(8)-H(8)	127.3	C(26)-C(25)-H(25)	120.2
N(5)-C(9)-C(8)	110.8(3)	C(24)-C(25)-H(25)	120.2
N(5)-C(9)-H(9)	124.6	C(25)-C(26)-C(27)	120.5(3)
C(8)-C(9)-H(9)	124.6	C(25)-C(26)-H(26)	119.7
C(14)-N(10)-N(11)	108.2(3)	C(27)-C(26)-H(26)	119.7
C(14)-N(10)-Cr(1)	127.5(2)	C(22)-C(27)-C(26)	120.6(3)
N(11)-N(10)-Cr(1)	122.93(19)	C(22)-C(27)-H(27)	119.7
N(10)-N(11)-C(12)	111.9(3)	C(26)-C(27)-H(27)	119.7
N(10)-N(11)-C(21)	117.3(2)	O(28)-C(29)-N(30)	122.6(5)

C(12)-N(11)-C(21)	129.4(3)	O(28)-C(29)-H(29)	118.7
N(11)-C(12)-C(13)	106.0(3)	N(30)-C(29)-H(29)	118.7
N(11)-C(12)-H(12)	127	C(29)-N(30)-C(32)	122.1(4)
C(13)-C(12)-H(12)	127	C(29)-N(30)-C(31)	120.5(4)
C(12)-C(13)-C(14)	104.5(3)	C(32)-N(30)-C(31)	117.3(4)
C(12)-C(13)-H(13)	127.7	N(30)-C(31)-H(31A)	109.5
C(14)-C(13)-H(13)	127.7	N(30)-C(31)-H(31B)	109.5
N(10)-C(14)-C(13)	109.1(3)	H(31A)-C(31)-H(31B)	109.5
N(10)-C(14)-H(14)	125.4	N(30)-C(31)-H(31C)	109.5
C(13)-C(14)-H(14)	125.4	H(31A)-C(31)-H(31C)	109.5
C(20)-N(15)-C(16)	117.3(3)	H(31B)-C(31)-H(31C)	109.5
C(20)-N(15)-Cr(1)	119.2(2)	N(30)-C(32)-H(32A)	109.5
C(16)-N(15)-Cr(1)	122.51(19)	N(30)-C(32)-H(32B)	109.5
N(15)-C(16)-C(17)	118.6(3)	H(32A)-C(32)-H(32B)	109.5
N(15)-C(16)-C(21)	116.6(2)	N(30)-C(32)-H(32C)	109.5
C(17)-C(16)-C(21)	124.4(3)	H(32A)-C(32)-H(32C)	109.5
C(18)-C(17)-C(16)	118.6(3)	H(32B)-C(32)-H(32C)	109.5
C(18)-C(17)-H(17)	120.7		

Table S3. Crystal data and structure refinement for Cr3

Empirical formula	$C_{23}\ H_{28}\ Cl_3\ Cr\ N_8\ O_2$
Formula weight	606.88
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21/c
Unit cell dimensions	a = 11.4170(13) Å alpha = 90°.
	b = 14.1673(15) Å beta = 98.684(2)°.
	c = 16.8852(19) Å gamma = 90°.
Volume	2699.8(5) $Å^3$
Z, Calculated density	4, 1.493 Mg/m^3
Absorption coefficient	0.758 mm^{-1}
F(000)	1252
Crystal size	0.12 x 0.10 x 0.08 mm
Theta range for data collection	1.804 to 25.499°.
Limiting indices	-13<=h<=13, -17<=k<=17, -20<=l<=20
Reflections collected / unique	21459 / 5019 [R_{int} = 0.1085]
Completeness to theta = 25.242	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.921 and 0.903
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5019 / 0 / 333
Goodness-of-fit on F^2	1.049
Final R indices [I>2sigma(I)]	R_1 = 0.0712, wR_2 = 0.1725
R indices (all data)	R_1 = 0.1238, wR_2 = 0.2055
Extinction coefficient	n/a
Largest diff. peak and hole	1.823 and -0.548 e.$Å^{-3}$

Table S4. Selected bond lengths [Å] and angles [°] for Cr3

Cr(1)-N(5)	2.036(5)	C(20)-C(21)	1.337(9)
Cr(1)-N(10)	2.106(5)	C(20)-H(20)	0.93
Cr(1)-N(16)	2.115(5)	C(21)-H(21)	0.93
Cr(1)-Cl(3)	2.2946(18)	C(22)-N(23)	1.472(7)
Cr(1)-Cl(2)	2.3026(17)	N(23)-N(24)	1.358(7)
Cr(1)-Cl(4)	2.3087(18)	N(23)-C(27)	1.375(8)
N(5)-C(9)	1.337(8)	N(24)-C(25)	1.311(8)
N(5)-N(6)	1.363(6)	C(25)-C(26)	1.496(11)
N(6)-C(7)	1.361(7)	C(25)-H(25)	0.93
N(6)-C(22)	1.510(7)	C(26)-C(27)	1.418(10)
C(7)-C(8)	1.434(10)	C(26)-H(26)	0.93
C(7)-H(7)	0.93	C(27)-H(27)	0.93
C(8)-C(9)	1.580(11)	O(28)-C(29)	1.229(10)
C(8)-H(8)	0.93	C(29)-N(30)	1.347(10)
C(9)-H(9)	0.93	C(29)-H(29)	0.93
N(10)-C(15)	1.325(8)	N(30)-C(32)	1.419(10)
N(10)-C(11)	1.366(7)	N(30)-C(31)	1.429(9)
C(11)-C(12)	1.379(8)	C(31)-H(31A)	0.96
C(11)-C(22)	1.492(8)	C(31)-H(31B)	0.96
C(12)-C(13)	1.339(10)	C(31)-H(31C)	0.96
C(12)-H(12)	0.93	C(32)-H(32A)	0.96
C(13)-C(14)	1.229(12)	C(32)-H(32B)	0.96
C(13)-H(13)	0.93	C(32)-H(32C)	0.96
C(14)-C(15)	1.301(11)	O(33)-C(34)	1.226(10)
C(14)-H(14)	0.93	C(34)-N(35)	1.319(10)
C(15)-H(15)	0.93	C(34)-H(34)	0.93
N(16)-C(21)	1.329(7)	N(35)-C(37)	1.437(11)
N(16)-C(17)	1.355(7)	N(35)-C(36)	1.445(11)
C(17)-C(18)	1.366(8)	C(36)-H(36A)	0.96

C(17)-C(22)	1.519(8)	C(36)-H(36B)	0.96
C(18)-C(19)	1.364(9)	C(36)-H(36C)	0.96
C(18)-H(18)	0.93	C(37)-H(37A)	0.96
C(19)-C(20)	1.306(10)	C(37)-H(37B)	0.96
C(19)-H(19)	0.93	C(37)-H(37C)	0.96

N(5)-Cr(1)-N(10)	83.38(18)	C(19)-C(20)-H(20)	121
N(5)-Cr(1)-N(16)	83.50(18)	C(21)-C(20)-H(20)	121
N(10)-Cr(1)-N(16)	84.29(18)	N(16)-C(21)-C(20)	124.1(6)
N(5)-Cr(1)-Cl(3)	90.53(14)	N(16)-C(21)-H(21)	118
N(10)-Cr(1)-Cl(3)	90.88(14)	C(20)-C(21)-H(21)	118
N(16)-Cr(1)-Cl(3)	172.71(14)	N(23)-C(22)-C(11)	112.2(4)
N(5)-Cr(1)-Cl(2)	91.32(14)	N(23)-C(22)-N(6)	105.0(4)
N(10)-Cr(1)-Cl(2)	172.44(14)	C(11)-C(22)-N(6)	109.8(4)
N(16)-Cr(1)-Cl(2)	89.77(13)	N(23)-C(22)-C(17)	111.4(4)
Cl(3)-Cr(1)-Cl(2)	94.56(6)	C(11)-C(22)-C(17)	106.2(4)
N(5)-Cr(1)-Cl(4)	172.33(14)	N(6)-C(22)-C(17)	112.4(4)
N(10)-Cr(1)-Cl(4)	90.61(13)	N(24)-N(23)-C(27)	112.9(5)
N(16)-Cr(1)-Cl(4)	91.19(13)	N(24)-N(23)-C(22)	117.9(5)
Cl(3)-Cr(1)-Cl(4)	94.33(7)	C(27)-N(23)-C(22)	125.4(5)
Cl(2)-Cr(1)-Cl(4)	94.20(7)	C(25)-N(24)-N(23)	107.4(5)
C(9)-N(5)-N(6)	110.2(5)	N(24)-C(25)-C(26)	110.0(6)
C(9)-N(5)-Cr(1)	129.6(4)	N(24)-C(25)-H(25)	125
N(6)-N(5)-Cr(1)	120.0(3)	C(26)-C(25)-H(25)	125
C(7)-N(6)-N(5)	113.3(5)	C(27)-C(26)-C(25)	103.4(6)
C(7)-N(6)-C(22)	126.6(5)	C(27)-C(26)-H(26)	128.3
N(5)-N(6)-C(22)	120.1(4)	C(25)-C(26)-H(26)	128.3
N(6)-C(7)-C(8)	107.4(6)	N(23)-C(27)-C(26)	106.1(6)
N(6)-C(7)-H(7)	126.3	N(23)-C(27)-H(27)	126.9
C(8)-C(7)-H(7)	126.3	C(26)-C(27)-H(27)	126.9

C(7)-C(8)-C(9)	103.2(6)	O(28)-C(29)-N(30)	124.9(8)
C(7)-C(8)-H(8)	128.4	O(28)-C(29)-H(29)	117.6
C(9)-C(8)-H(8)	128.4	N(30)-C(29)-H(29)	117.6
N(5)-C(9)-C(8)	105.9(6)	C(29)-N(30)-C(32)	120.9(7)
N(5)-C(9)-H(9)	127.1	C(29)-N(30)-C(31)	119.4(7)
C(8)-C(9)-H(9)	127.1	C(32)-N(30)-C(31)	119.7(7)
C(15)-N(10)-C(11)	114.2(5)	N(30)-C(31)-H(31A)	109.5
C(15)-N(10)-Cr(1)	122.4(4)	N(30)-C(31)-H(31B)	109.5
C(11)-N(10)-Cr(1)	122.5(4)	H(31A)-C(31)-H(31B)	109.5
N(10)-C(11)-C(12)	117.4(5)	N(30)-C(31)-H(31C)	109.5
N(10)-C(11)-C(22)	115.3(5)	H(31A)-C(31)-H(31C)	109.5
C(12)-C(11)-C(22)	127.0(5)	H(31B)-C(31)-H(31C)	109.5
C(13)-C(12)-C(11)	118.3(7)	N(30)-C(32)-H(32A)	109.5
C(13)-C(12)-H(12)	120.9	N(30)-C(32)-H(32B)	109.5
C(11)-C(12)-H(12)	120.9	H(32A)-C(32)-H(32B)	109.5
C(14)-C(13)-C(12)	126.6(10)	N(30)-C(32)-H(32C)	109.5
C(14)-C(13)-H(13)	116.7	H(32A)-C(32)-H(32C)	109.5
C(12)-C(13)-H(13)	116.7	H(32B)-C(32)-H(32C)	109.5
C(13)-C(14)-C(15)	113.2(10)	O(33)-C(34)-N(35)	125.3(8)
C(13)-C(14)-H(14)	123.4	O(33)-C(34)-H(34)	117.4
C(15)-C(14)-H(14)	123.4	N(35)-C(34)-H(34)	117.4
C(14)-C(15)-N(10)	130.1(8)	C(34)-N(35)-C(37)	121.0(8)
C(14)-C(15)-H(15)	114.9	C(34)-N(35)-C(36)	121.1(8)
N(10)-C(15)-H(15)	114.9	C(37)-N(35)-C(36)	117.9(8)
C(21)-N(16)-C(17)	117.7(5)	N(35)-C(36)-H(36A)	109.5
C(21)-N(16)-Cr(1)	119.5(4)	N(35)-C(36)-H(36B)	109.5
C(17)-N(16)-Cr(1)	122.0(4)	H(36A)-C(36)-H(36B)	109.5
N(16)-C(17)-C(18)	119.1(5)	N(35)-C(36)-H(36C)	109.5
N(16)-C(17)-C(22)	115.7(5)	H(36A)-C(36)-H(36C)	109.5
C(18)-C(17)-C(22)	124.7(5)	H(36B)-C(36)-H(36C)	109.5

C(19)-C(18)-C(17)	119.4(6)	N(35)-C(37)-H(37A)	109.5
C(19)-C(18)-H(18)	120.3	N(35)-C(37)-H(37B)	109.5
C(17)-C(18)-H(18)	120.3	H(37A)-C(37)-H(37B)	109.5
C(20)-C(19)-C(18)	121.0(7)	N(35)-C(37)-H(37C)	109.5
C(20)-C(19)-H(19)	119.5	H(37A)-C(37)-H(37C)	109.5
C(18)-C(19)-H(19)	119.5	H(37B)-C(37)-H(37C)	109.5
C(19)-C(20)-C(21)	118.0(7)		