

Probing Chloride Substitution on the Performance of a Benzhydryl-Substituted Bis(arylimino)pyridyl-Cobalt Ethylene Polymerization Catalyst

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Table S1 Crystal data and structure refinements for **Co1** and **Co2**

Identification code	Co1	Co2
CCDC number	2464596	2464597
Empirical formula	C ₁₀₀ Cl ₁₂ Co ₂ N ₆	C ₅₂ Cl ₆ CoN ₃ H ₄₅
Formula weight	1828.32	983.59
Temperature/K	102(3)	170.00(10)
Crystal system	monoclinic	monoclinic
Space group	P2 ₁ /n	I2/a
a/Å	17.8722(8)	19.3959(2)
b/Å	24.8273(8)	17.3211(2)
c/Å	21.6954(10)	30.0962(5)
α /°	90	90
β /°	99.168(4)	96.1810(10)
γ /°	90	90
Volume/Å ³	9503.7(7)	10052.3(2)
Z	4	43
ρ_{calc} /cm ³	1.278	1.259
μ /mm ⁻¹	6.217	5.906
F(000)	3600.0	3753.0
Crystal size/mm ³	0.35 × 0.2 × 0.02	0.2 × 0.07 × 0.02
Radiation	Cu K α (λ = 1.54184)	Cu K α (λ = 1.54184)
2 θ range for data collection/°	5.45 to 150.668	5.896 to 150.642
Index ranges	-21 ≤ h ≤ 22, -30 ≤ k ≤ 29, -27 ≤ l ≤ 26	
	26	≤ 36
Reflections collected	71517	34019
Independent reflections	18848 [R _{int} = 0.1681, R _{sigma} = 0.1238]	10001 [R _{int} = 0.0809, R _{sigma} = 0.0650]
Data/restraints/parameters	18848/0/1081	10001/0/564
Goodness-of-fit on F ²	1.383	1.050

Final R indexes [I>2 σ (I)]	R ₁ = 0.1607, wR ₂ = 0.3992	R ₁ = 0.0736, wR ₂ = 0.2029
Final R indexes [all data]	R ₁ = 0.2334, wR ₂ = 0.4452	R ₁ = 0.0818, wR ₂ = 0.2108
Largest diff. peak/hole / e Å ⁻³	2.43/-1.28	0.96/-0.78

CCDC-2464596 for **Co1** and 2464597 for **Co2** contain the supplementary crystallographic data for this article; these data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>.

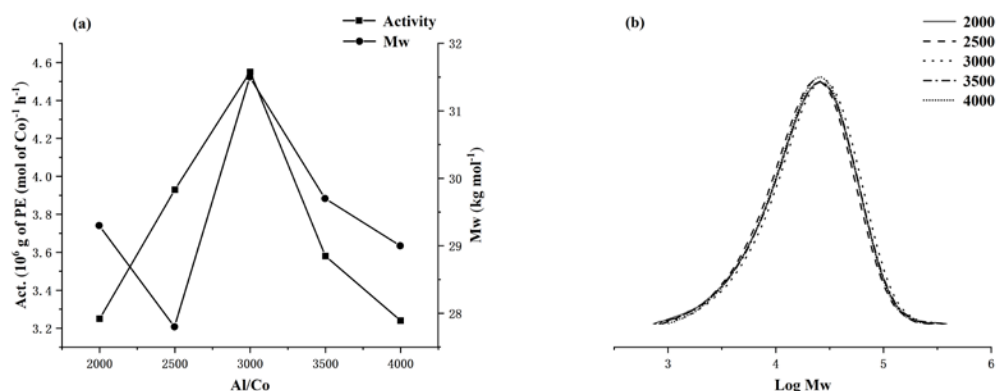


Figure S1 For **Co1**/MMAO: (a) dual plots of catalytic activity and molecular weight of the polymer as a function of the Al:Co molar ratio and (b) GPC traces showing variations of log M_w of the polymer as the molar ratio is varied (entries 2 and 6 - 9, Table 3).

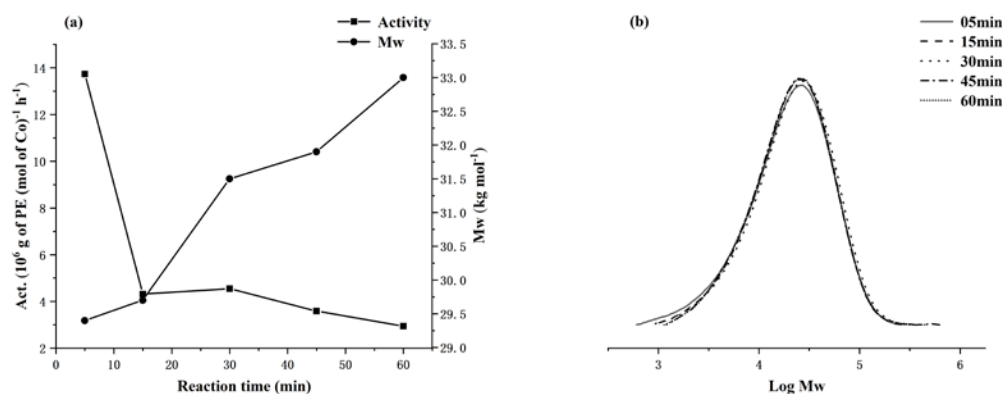


Figure S2 For **Co1**/MMAO: (a) dual plots of catalytic activity and molecular weight of the polymer as a function of reaction time and (b) GPC traces showing variations of log M_w as the

reaction time is varied (entries 7 and 10 - 13, Table 3).

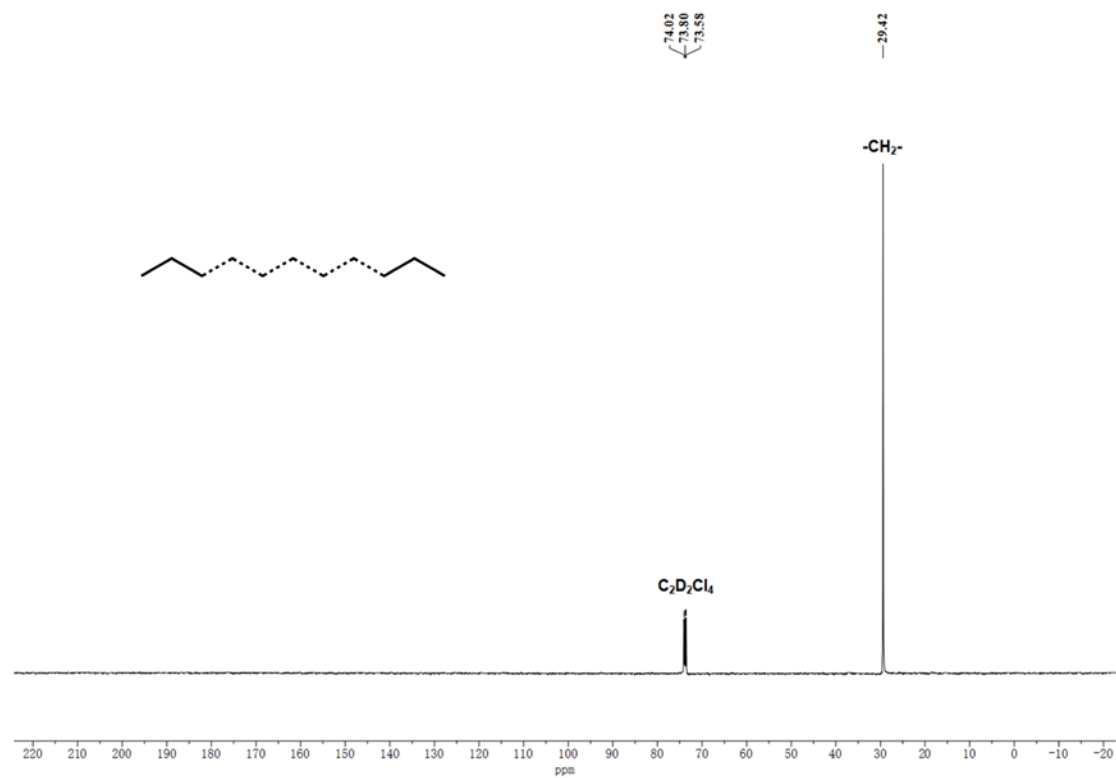


Figure S3 ^{13}C NMR spectrum of the polyethylene obtained using **Co1**/MMAO at 30 °C (entry 7, Table 3); recorded in 1,1,2,2- tetrachloroethane- d_2 at 100 °C.

MALDI, L1, 20220721

Analysis Info

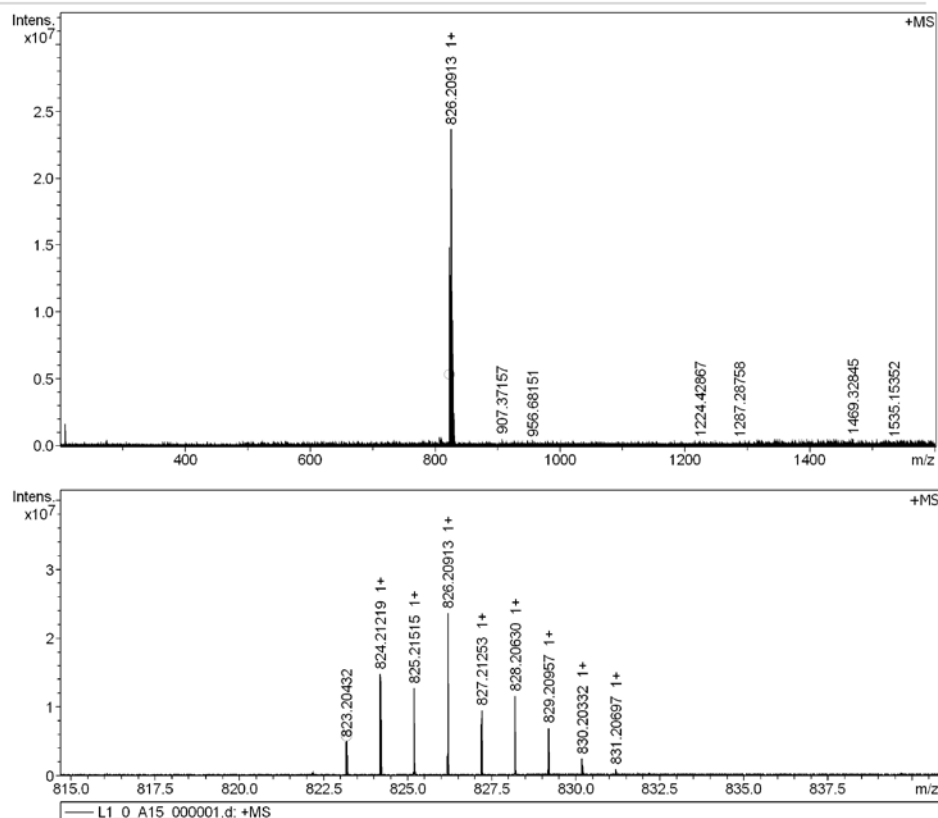
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Operator
 Instrument solarix

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Ion Accumulation Time	0.010 sec				



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823.204325	1	C50H41Cl4N3	100.00	823.204910	-0.7		1.7	136.2	30.0	odd

Figure S4 High resolution (MALDI-TOF-MS) mass spectrum of 2-{{2,4-((p-ClPh)₂CH)₂-6-MeC₆H₂}N=CMe}-6-{{(2,6-Me₂C₆H₃)N=CMe}C₅H₃N (L1).

MALDI, L2, 20220721

Analysis Info

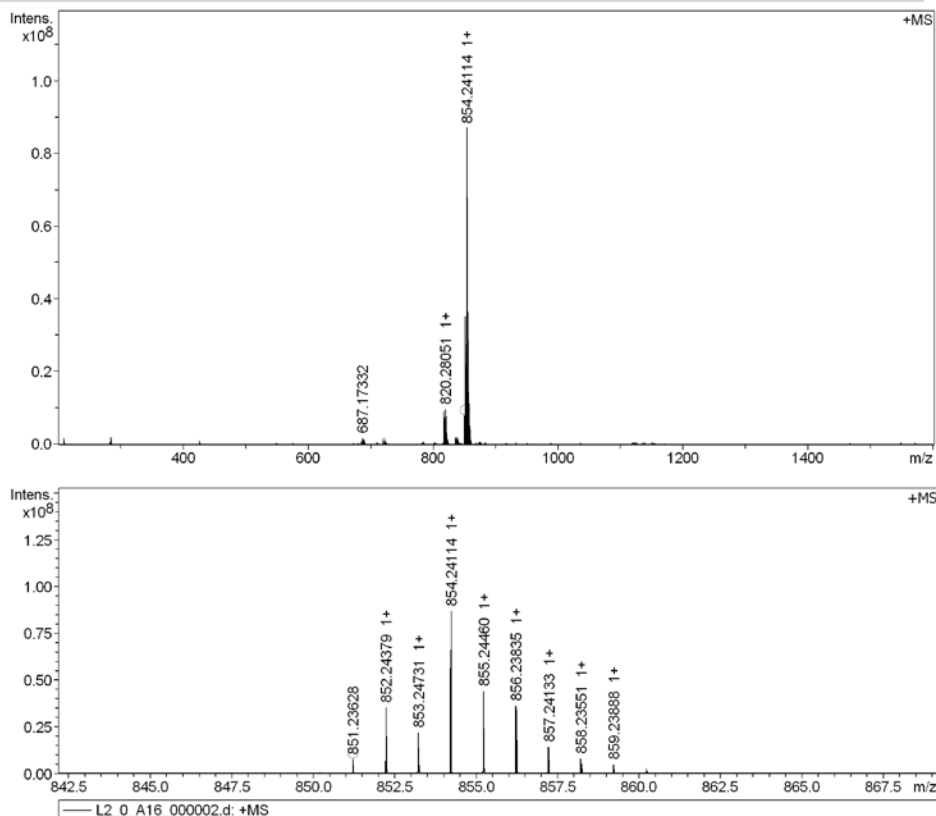
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Operator
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Broadband High Mass	1600.0 m/z	Laser Power	22.8 lp	Apodization	Sine-Bell Multiplication
Source Accumulation	0.001 sec	Laser Shot Frequency	0.020 sec		
Ion Accumulation Time	0.010 sec				



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e ⁻ Conf	N-Rule
851.236277	1	C52H45Cl4N3	100.00	851.236211	0.1	1.1	194.1	30.0	odd	ok

Figure S5 High resolution (MALDI-TOF-MS) mass spectrum of 2-{{2,4-((*p*-ClPh)₂CH)₂-6-MeC₆H₂}N=CMe}-6-{{(2,6-Et₂C₆H₃)N=CMe}C₅H₃N (L2).

MALDI, L3, 20220721

Analysis Info

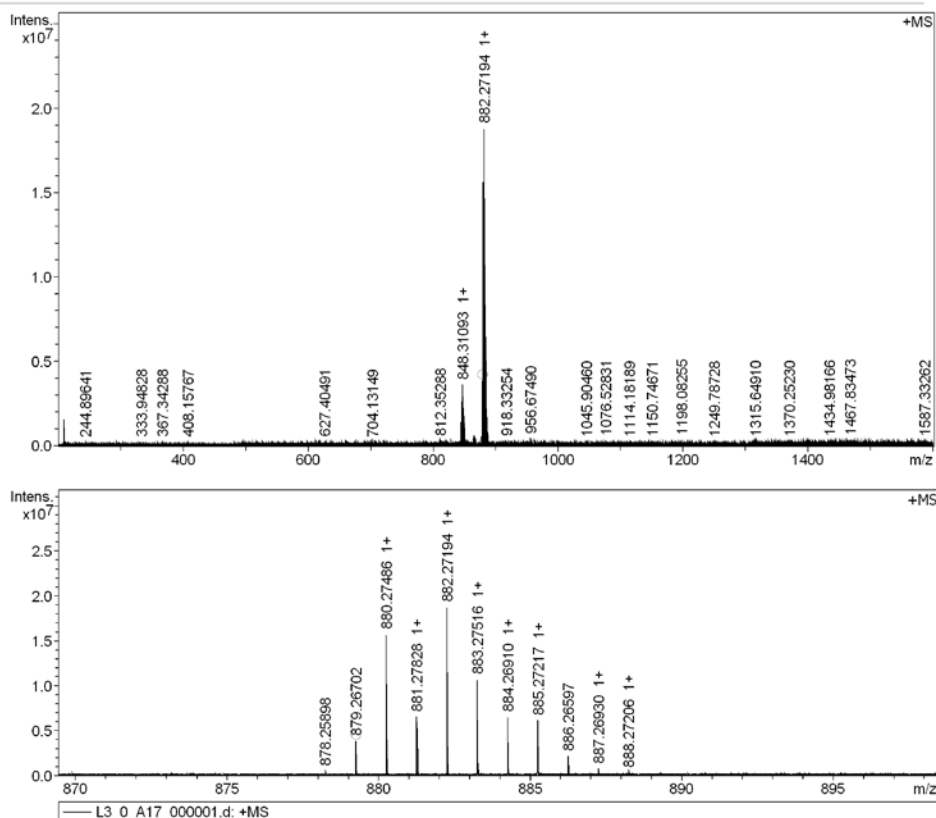
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Operator
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Acquisition Parameter

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Ion Accumulation Time	0.010 sec				



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdB	e ⁻ Conf	N-Rule
879.267025	1	C54H49Cl4N3	100.00	879.267511	0.6	1.8	167.0	30.0	odd	ok

Figure S6 High resolution (MALDI-TOF-MS) mass spectrum of 2-{{2,4-((*p*-ClPh)₂CH)₂-6-MeC₆H₂}N=CMe}-6-{{(2,6-*i*-Pr₂C₆H₃)N=CMe}C₅H₃N (L3).

MALDI, L4, 20220721

Analysis Info

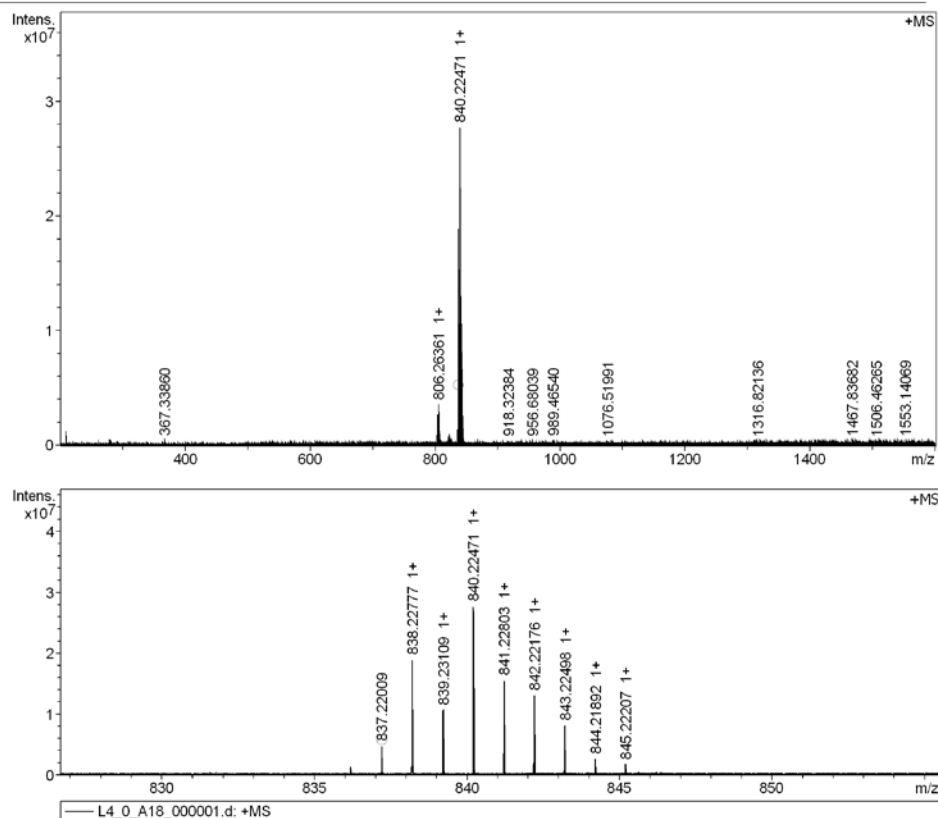
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Operator
 Instrument solariX

Acquisition Parameter

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Broadband High Mass	1600.0 m/z	Laser Power	26.8 lp	Apodization	Sine-Bell Multiplication
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Ion Accumulation Time	0.010 sec				



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e ⁻ Conf	N-Rule
837.220087	1	C51H43Cl4N3	100.00	837.220561	-0.6	1.7	152.8	30.0	odd	ok

Figure S7 High resolution (MALDI-TOF-MS) mass spectrum of 2-{{2,4-((*p*-ClPh)₂CH)₂-6-MeC₆H₂}N=CMe}-6- {(2,4,6-Me₃C₆H₂)N=CMe}C₅H₃N (**L4**).

MALDI,L5,20220721

Analysis Info

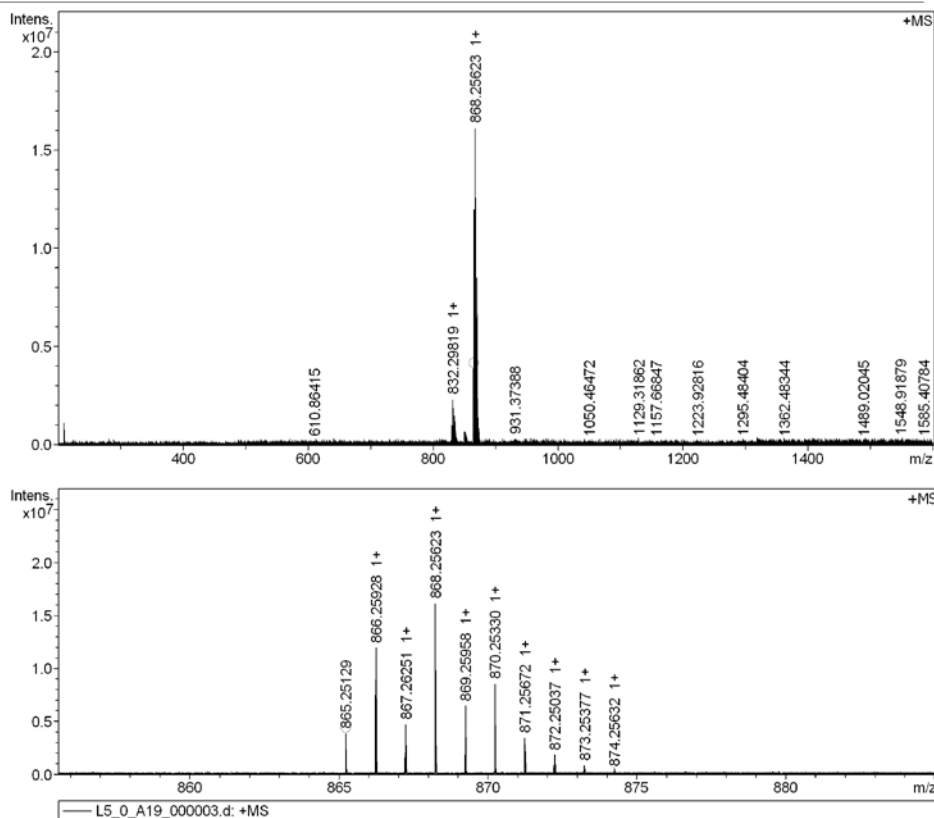
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Operator
 Instrument solariX

Acquisition Parameter

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Source Accumulation	0.001 sec	Laser Shot Frequency	0.020 sec		
Ion Accumulation Time	0.010 sec				



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e ⁻ Conf	N-Rule
865.251289	1	C ₅₃ H ₄₇ Cl ₄ N ₃	100.00	865.251861	-0.7	1.5	200.5	30.0	odd	ok

Figure S8 High resolution (MALDI-TOF-MS) mass spectrum of 2-{{2,4-((*p*-ClPh)₂CH)₂-6-MeC₆H₂}N=CMe}-6-{{2,6-Et₂-4-MeC₆H₂}N=CMe}C₅H₃N (L5).

ESI(P),Co1,20220721

Analysis Info

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Acquisition Date 7/21/2022 10:16:42 AM

Sample Name Co1

Instrument solarix

Acquisition Parameter

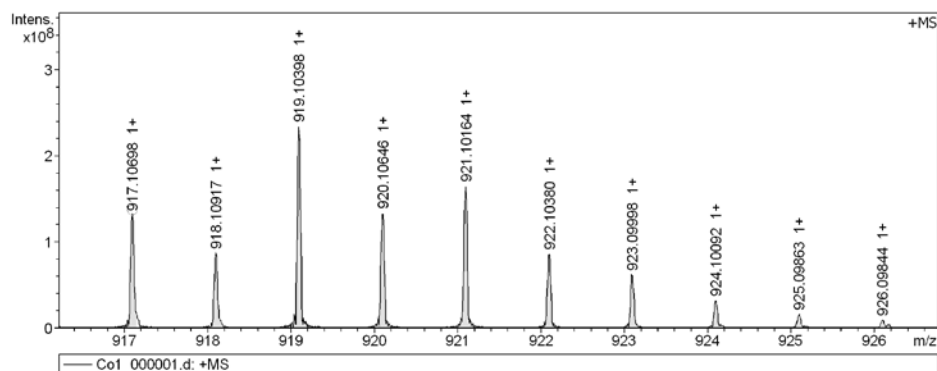
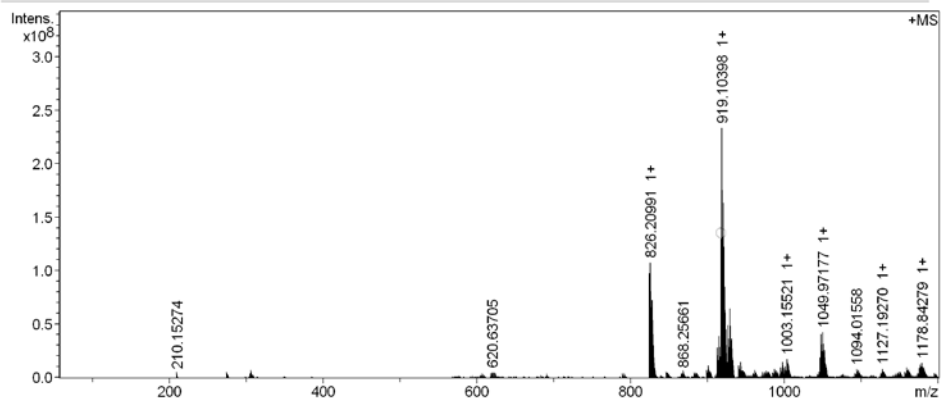
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Acquired Scans 10

Polarity Positive

Broadband Low Mass 57.7 m/z

Broadband High Mass 1200.0 m/z



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e ⁻	Conf	N-Rule
917.106984	1	C50H41Cl5CoN3	100.00	917.106958	0.0	1.1	24.5	29.5	even		-

Figure S9 High resolution (ESI-MS) mass spectrum of [2-{2,4-((*p*-ClPh)₂CH)₂-6-MeC₆H₂}N=CMe]-6-((2,6-Me₂C₆H₃)N=CMe)C₅H₃N]CoCl₂ (**Co1**).

ESI(P),Co2,20220721

Analysis Info

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Acquisition Date 7/21/2022 10:21:50 AM

Sample Name Co2

Instrument solarix

Acquisition Parameter

Acquisition Mode Single MS

Acquired Scans 10

Polarity Positive

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Broadband High Mass 1200.0 m/z

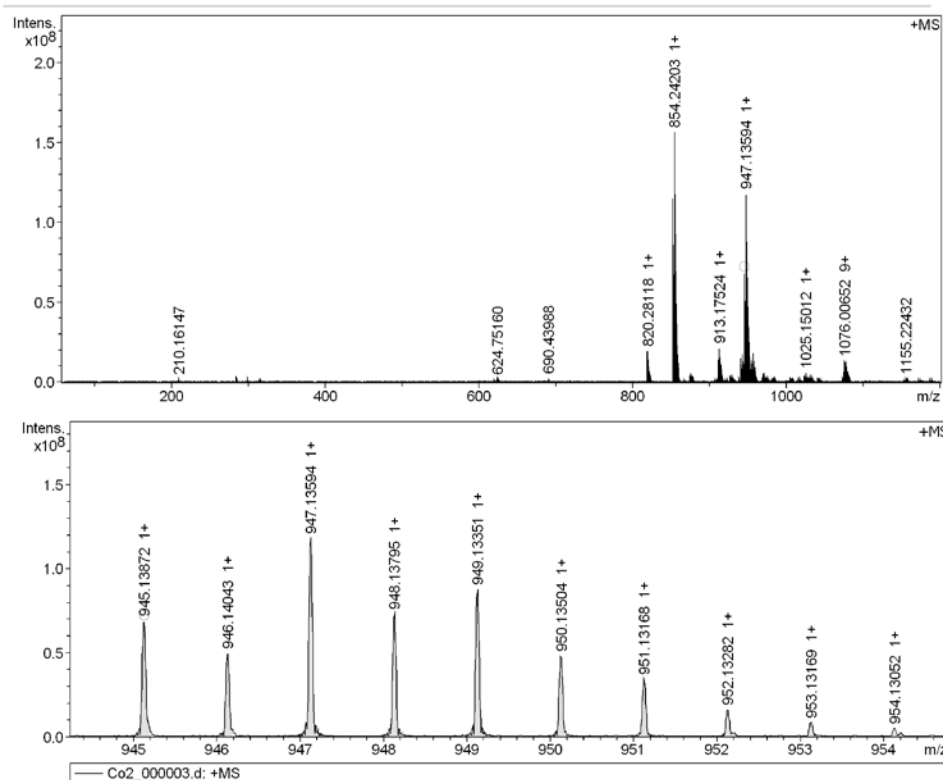


Figure S10 High resolution (ESI-MS) mass spectrum of [2-{{2,4-((*p*-ClPh)₂CH)₂-6-MeC₆H₂}N=CMe}-6-{{(2,6-Et₂C₆H₃)N=CMe}C₅H₃N}]CoCl₂ (**Co2**).

ESI(P),Co3,20220721

Analysis Info

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Acquisition Date 7/21/2022 10:26:29 AM

Sample Name Co3

Instrument solarix

Acquisition Parameter

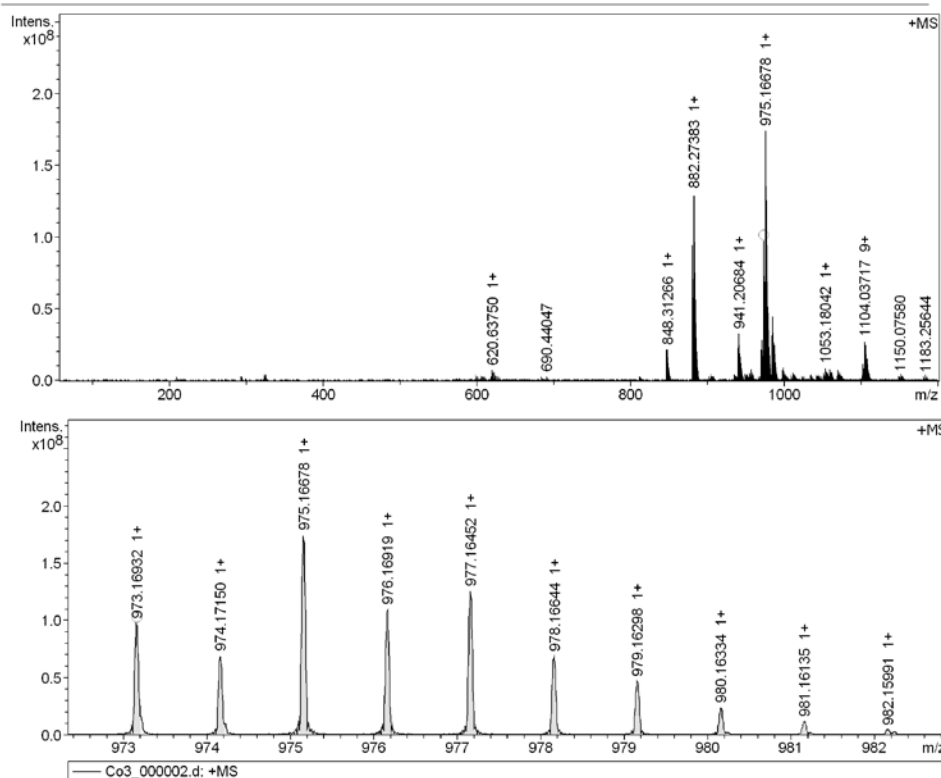
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Broadband High Mass 1200.0 m/z



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973.169320	1	C54H49Cl5CoN3	100.00	973.169558	0.2	1.0	29.2	29.5	even	-

Figure S11 High resolution (ESI-MS) mass spectrum of [2-{2,4-((*p*-ClPh)₂CH)₂-6-MeC₆H₂}N=CMe]-6-((2,6-*i*-Pr₂C₆H₃)N=CMe)C₅H₃N]CoCl₂ (**Co3**).

ESI(P),Co4,20220721

Analysis Info

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Acquisition Date 7/21/2022 10:31:11 AM

Sample Name Co4

Instrument solarix

Acquisition Parameter

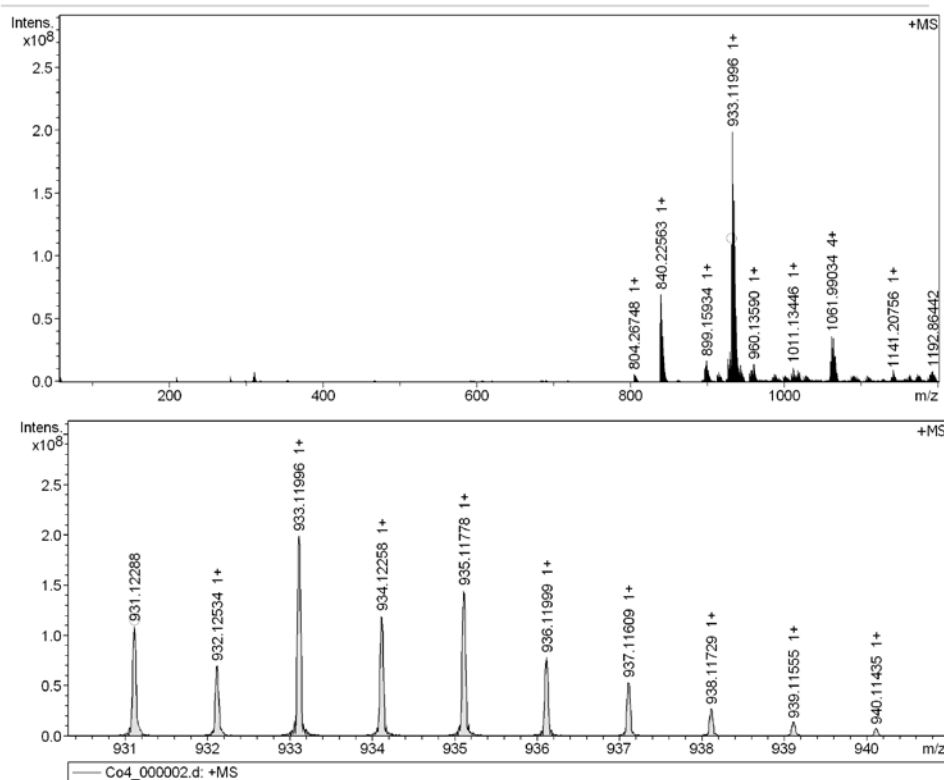
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Polarity Positive

Broadband Low Mass 57.7 m/z

Broadband High Mass 1200.0 m/z



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e ⁻ Conf	N-Rule
931.122880	1	C51H43Cl5CoN3	100.00	931.122608	-0.3	0.6	26.6	29.5	even	-

Figure S12 High resolution (ESI-MS) mass spectrum of [2-{{2,4-((*p*-ClPh)₂CH)₂-6-MeC₆H₂}N=CMe}-6-{{(2,4,6-Me₃C₆H₂}N=CMe)C₅H₃N]CoCl₂ (**Co4**).

ESI(P),Co5,20220721

Analysis Info

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Acquisition Date 7/21/2022 10:36:43 AM

Sample Name Co5

Instrument solarix

Acquisition Parameter

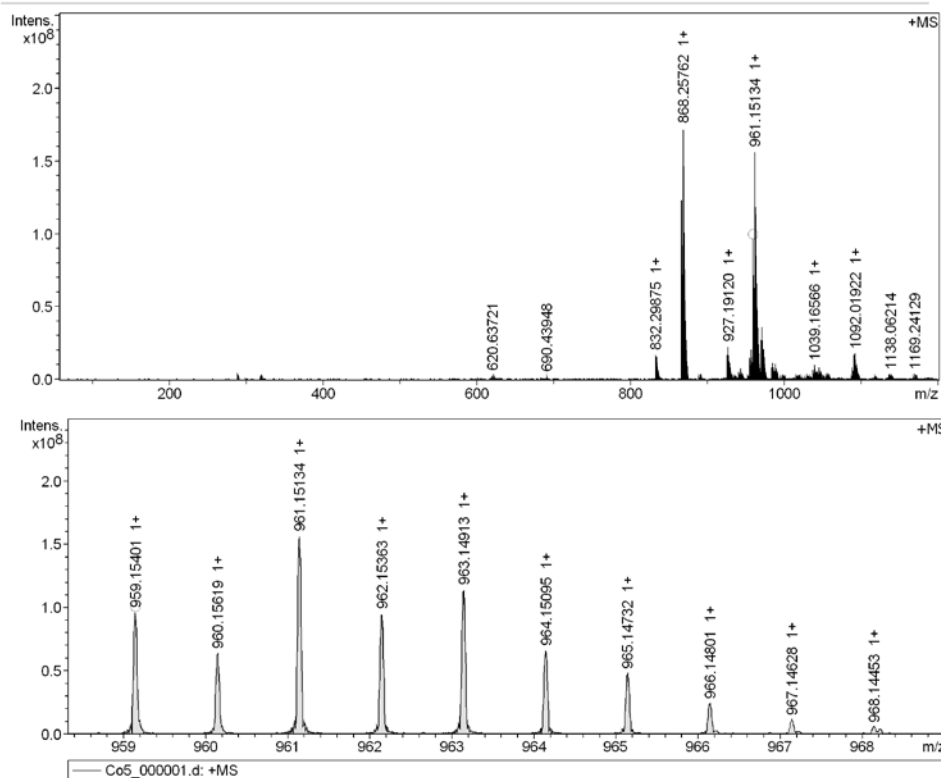
Acquisition Mode Single MS

Acquired Scans 8

Polarity Positive

Broadband Low Mass 57.7 m/z

Broadband High Mass 1200.0 m/z



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e ⁻ Conf	N-Rule
959.154011	1	C53H47Cl5CoN3	100.00	959.153908	0.1	0.8	37.6	29.5	even	-

Figure S13 High resolution (ESI-MS) mass spectrum of [2-{{2,4-((*p*-ClPh)₂CH)₂-6-MeC₆H₂}N=CMe}-6-{{(2,6-Et₂-4-MeC₆H₂)N=CMe}C₅H₃N}CoCl₂ (**Co5**).