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Supporting Information

Unimodal polyethylenes of high linearity and narrow dispersity by using *ortho*-4,4'-dichlorobenzhydryl-modified bis(imino)pyridyl-iron catalysts

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Table S1. Crystal data and structure refinements for **Fe2** and **Fe5**

Identification code	Fe2	Fe5
CCDC number	2231616	2231617
Empirical formula	C ₅₂ H ₄₆ Cl ₆ FeN ₃	C ₅₃ H ₄₉ Cl ₈ FeN ₄
Formula weight	981.47	1081.41
Temperature/K	169.99(11)	100.00(10)
Crystal system	monoclinic	monoclinic
Space group	P2 ₁ /n	P2 ₁ /n
a/Å	9.5593(3)	9.6074(2)
b/Å	35.4325(9)	35.6770(10)
c/Å	14.4482(4)	15.0592(6)
α/°	90	90
β/°	106.610(3)	97.548(3)
γ/°	90	90
Volume/Å ³	4689.5(2)	5117.0(3)
Z	4	4
ρ _{calc} /cm ³	1.390	1.404
μ/mm ⁻¹	6.027	6.520
F(000)	2028.0	2228.0
Crystal size/mm ³	0.2 × 0.15 × 0.02	0.25 × 0.1 × 0.03
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2θ range for data collection/°	4.988 to 150.804	4.954 to 151.43
Index ranges	-11 ≤ h ≤ 11, -33 ≤ k ≤ 44, -18 ≤ l ≤ 17	-11 ≤ h ≤ 11, -44 ≤ k ≤ 43, -18 ≤ l ≤ 18
Reflections collected	35062	34363
Independent reflections	9297 [R _{int} = 0.0792, R _{sigma} = 0.0643]	10142 [R _{int} = 0.0706, R _{sigma} = 0.0614]
Data/restraints/parameters	9297/0/564	10142/0/568
Goodness-of-fit on F ²	1.053	1.062
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0745, wR ₂ = 0.1975	R ₁ = 0.0859, wR ₂ = 0.2402
Final R indexes [all data]	R ₁ = 0.0955, wR ₂ = 0.2123	R ₁ = 0.1059, wR ₂ = 0.2648
Largest diff. peak/hole / e Å ⁻³	1.12/-0.58	1.54/-1.44

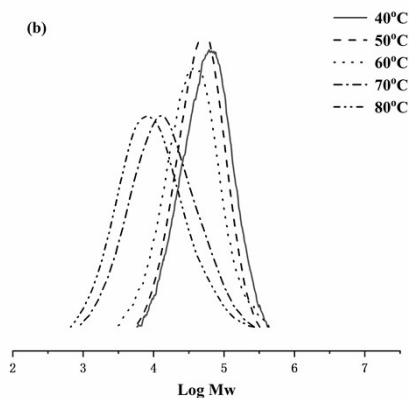


Fig. S1 For Fe1/MAO: GPC traces of the polymer molecular weight as a function of temperature (entries 1 - 5, Table 2).

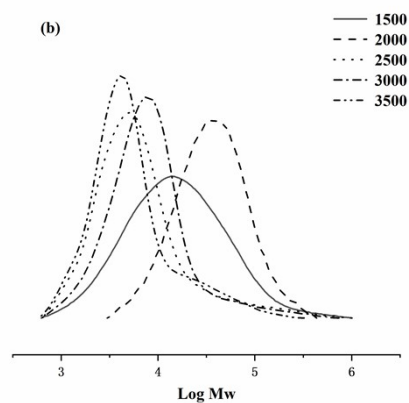


Fig. S2 For Fe1/MAO: GPC traces of the polymer molecular weight as a function of the molar ratio (entries 3 and 6 - 9, Table 2).

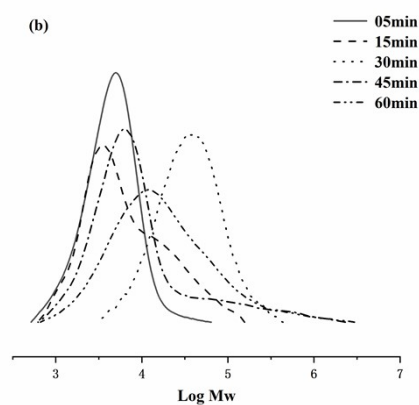


Fig. S3 For Fe1/MAO: GPC traces of the polymer molecular weight as a function of reaction time (entries 7 and 10 - 13, Table 2).

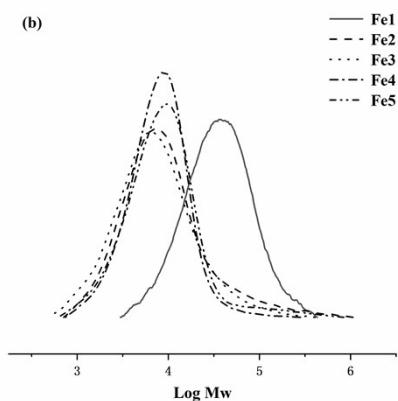


Fig. S4 For **Fe1 – Fe5** using MAO as co-catalyst: GPC traces of the polymer molecular weight as a function of the iron precatalyst (entries 7 and 16 - 20, Table 2).

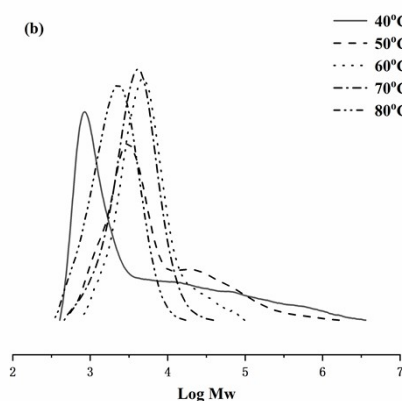


Fig. S5 For **Fe1/MMAO**: GPC traces of the polymer as a function of temperature (entries 1 - 5, Table 3).

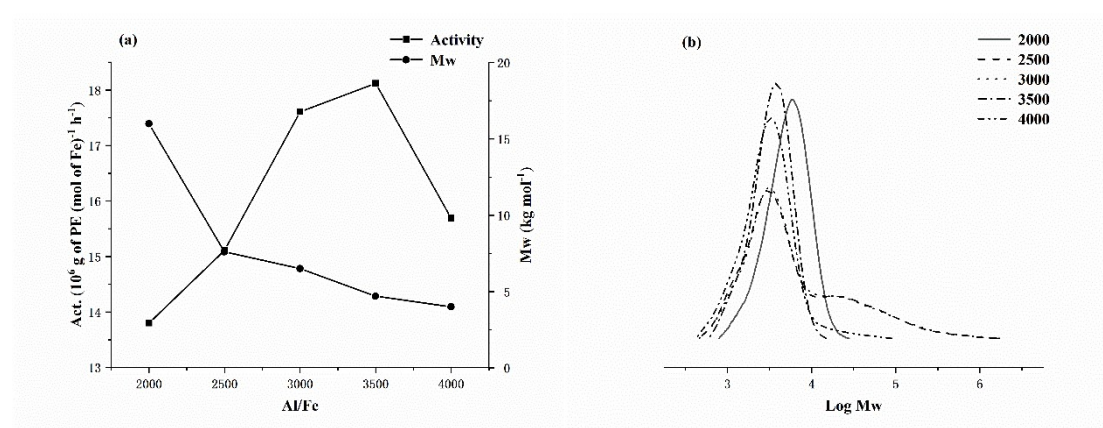


Fig. S6 For **Fe1/MMAO**: (a) plots of catalytic activity and molecular weight of the polymer versus Al:Co molar ratio and (b) GPC traces of the polymer molecular weight as a function of the molar ratio (entries 2 and 6 - 9, Table 3).

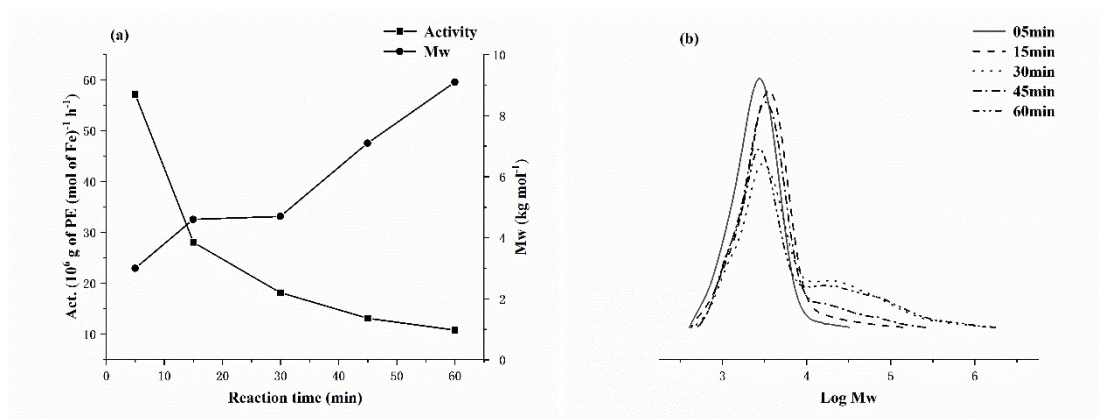


Fig. S7 For **Fe1/MMAO**: (a) plots of catalytic activity and molecular weight of the polymer versus reaction time and (b) GPC traces of the polymer molecular weight as a function of reaction time (entries 8 and 10 - 13, Table 3).

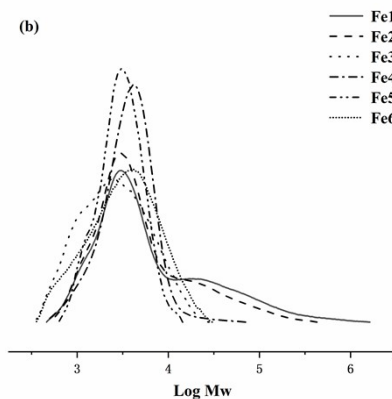


Fig. S8 For **Fe1 – Fe6** with MAO as co-catalyst: GPC traces of the polymer as a function of the iron precatalyst (entries 8 and 16 - 20, Table 3).

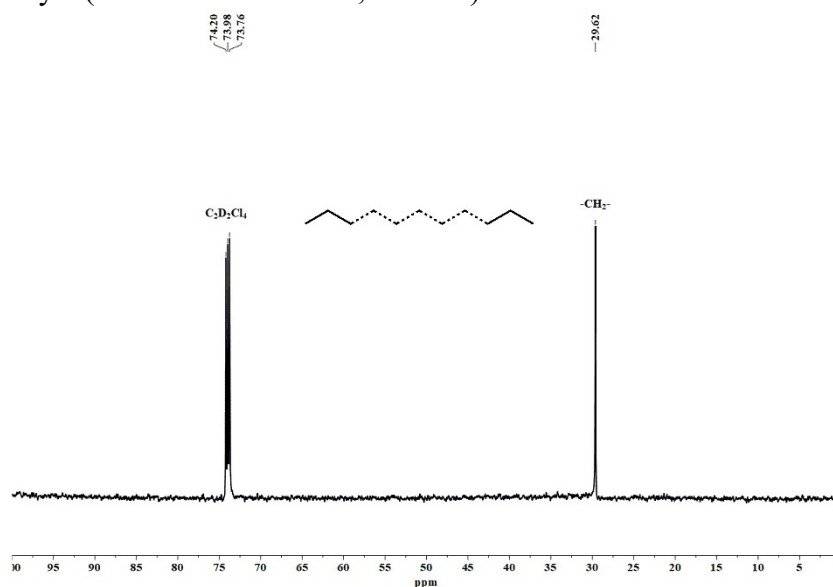
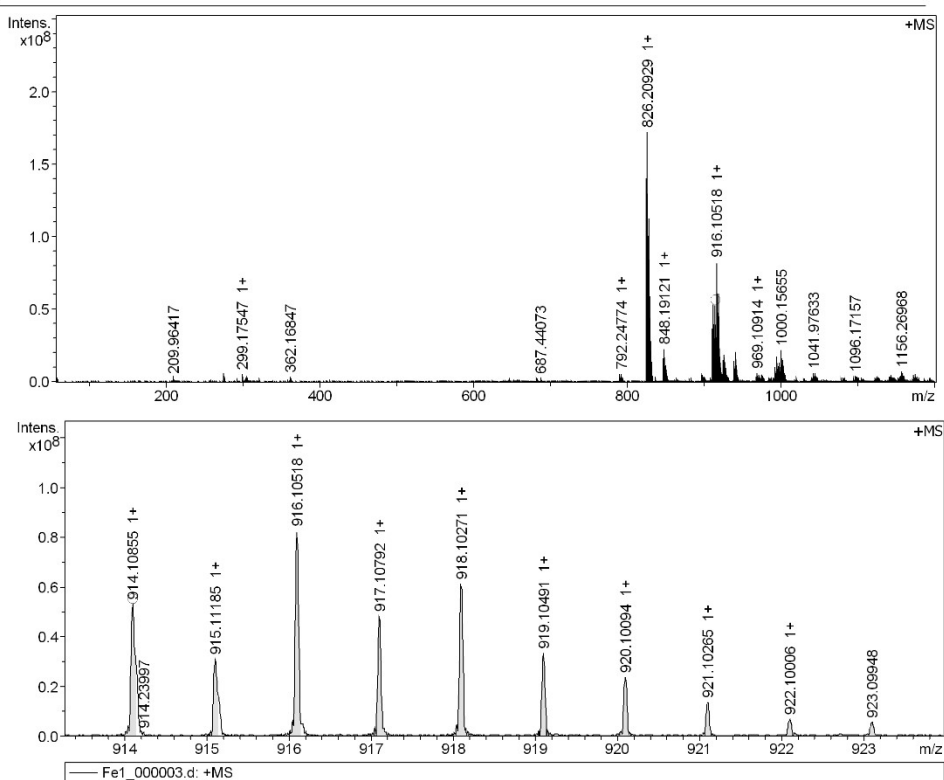


Fig. S9 ^{13}C NMR spectrum of the polyethylene obtained using **Fe1/MMAO** at $50\text{ }^\circ\text{C}$ (entry 8, Table 3); recorded in 1,1,2,2- tetrachloroethane- d_2 at $100\text{ }^\circ\text{C}$.

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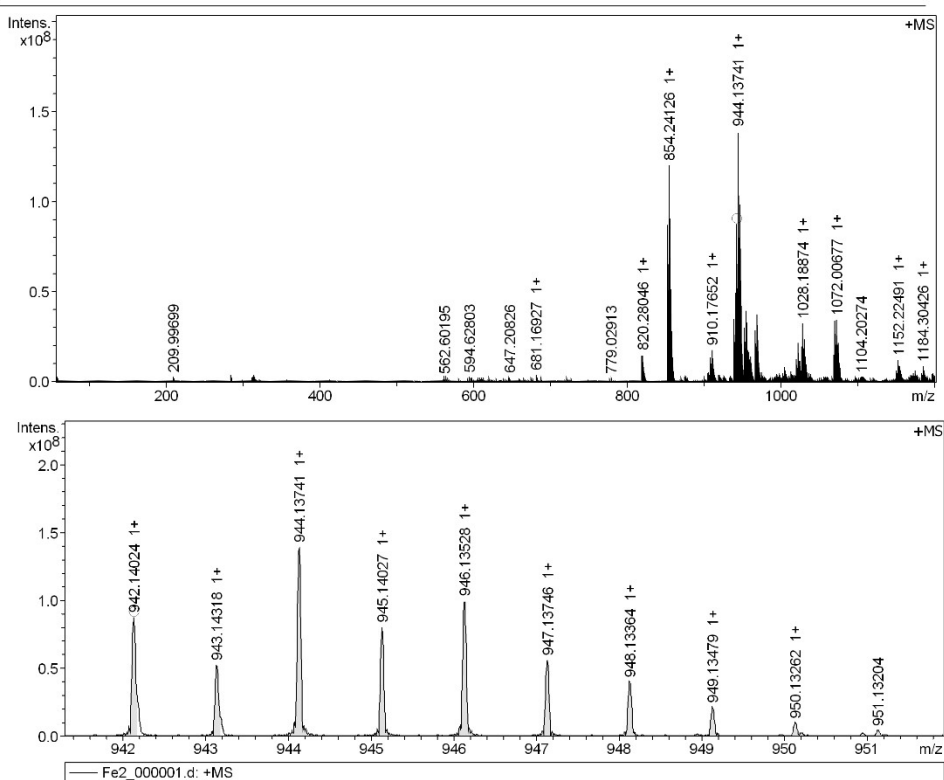
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914.108550	1	C50H41Cl5FeN3	100.00	914.108956	0.4		1.7	30.5	29.5	even	ok

Fig. S10 High resolution (ESI-MS) mass spectrum for [2-{{2,6-((p-ClPh)₂CH)₂-4-MeC₆H₂}N=CMe}-6-{{(2,6-Me₂C₆H₃)N=CMe}C₅H₃N]FeCl₂ (**Fe1**).

ESI(P),Fe2,20220721

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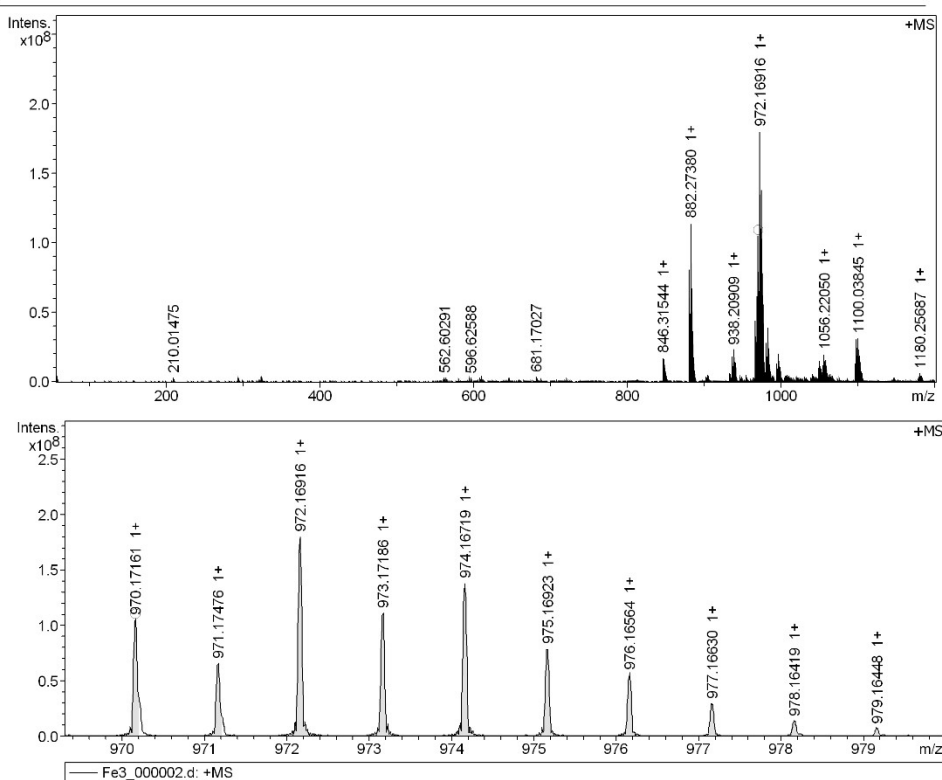
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942.140242	1	C52H45Cl5FeN3	100.00	942.140264	0.0	0.7	18.7	29.5	even	ok

Fig. S11 High resolution (ESI-MS) mass spectrum for [2-{{2,6-((p-ClPh)₂CH)₂-4-MeC₆H₂}N=CMe}-6-{{(2,6-Et₂C₆H₃)N=CMe};C₃H₃N]FeCl₂ (**Fe2**).

ESI(P),Fe3,20220721

Analysis Info Acquisition Date 7/21/2022 9:38:09 AM
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 Broadband Low Mass 57.7 m/z



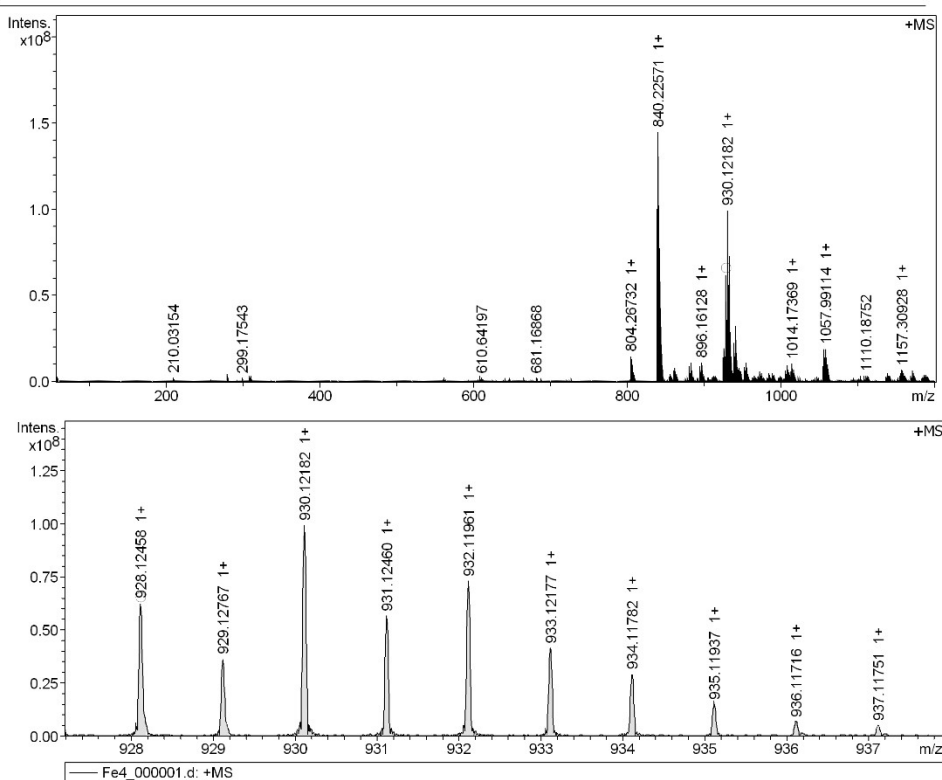
Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e ⁻ Conf	N-Rule
970.171610	1	C54H49Cl5FeN3	100.00	970.171572	-0.0	0.6	25.1	29.5	even	ok

Fig. S12 High resolution (ESI-MS) mass spectrum for [2-{{2,6-((p-ClPh)₂CH)₂-4-MeC₆H₂}N=CMe}-6-{{(2,6-*i*-Pr₂C₆H₃)N=CMe}C₅H₃N]FeCl₂ (**Fe3**).

ESI(P),Fe4,20220721

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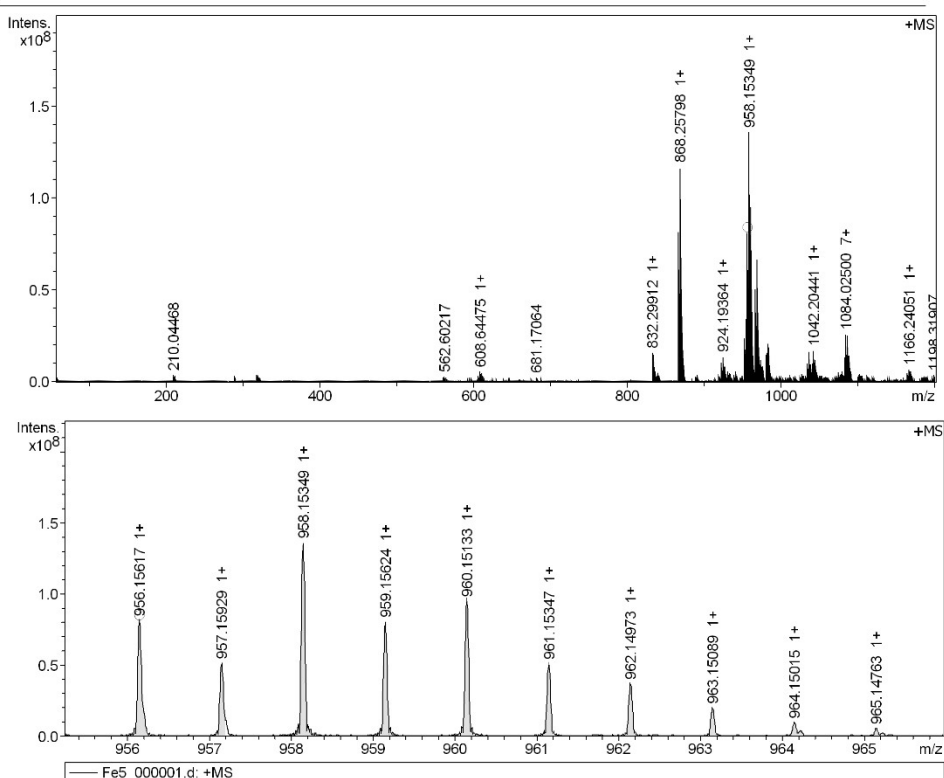
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928.124576	1	C51H43Cl5FeN3	100.00	928.124610	-0.0	0.5	25.8	29.5	even	ok

Fig. S13 High resolution (ESI-MS) mass spectrum for [2-{{2,6-((p-ClPh)₂CH)₂-4-MeC₆H₂}N=CMe}-6-{{(2,4,6-Me₃C₆H₂}N=CMe}C₅H₃N]FeCl₂ (**Fe4**).

ESI(P),Fe5,20220721

Analysis Info Acquisition Date 7/21/2022 9:48:09 AM
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 Sample Name Fe5 Instrument solariX

Acquisition Parameter
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 Broadband Low Mass 57.7 m/z



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956.156174	1	C53H47C15FeN3	100.00	956.155918	0.3	0.2	17.8	29.5	even	ok

Fig. S14 High resolution (ESI-MS) mass spectrum for [2-{{2,6-((p-ClPh)₂CH)₂-4-MeC₆H₂}N=CMe}-6-{{(2,6-Et₂-4-MeC₆H₂)N=CMe}C₃H₃N]FeCl₂ (**Fe5**).