Modulation of 2-imino-6,7-dihydroquinlin-8(5*H*)-imine-iron ethylene polymerization catalysts through (cyclo)alkyl, benzhydryl and halide substitution

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1. Additional catalytic data and polymer data from runs using Fe5/MAO

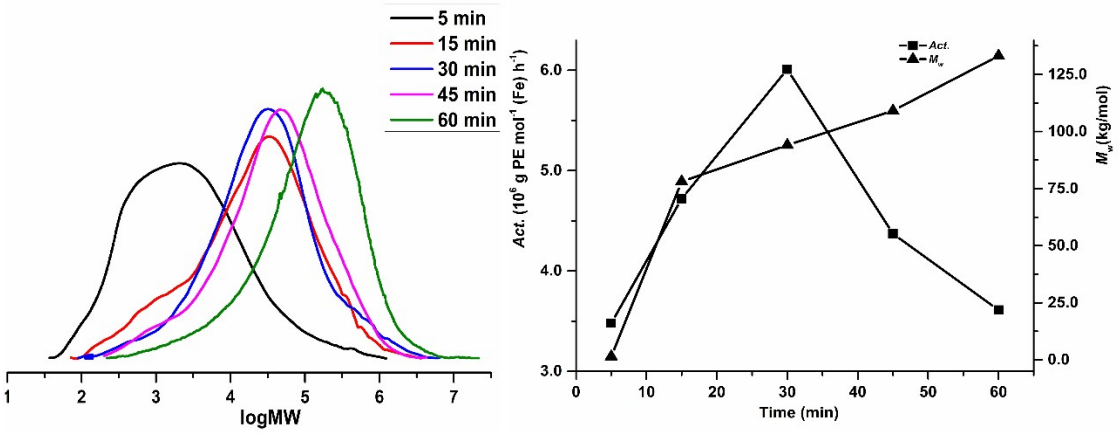

Figure S1. For **Fe5**/MAO: (a) GPC traces showing log M_w as a function of reaction time (entries 8, 11 – 14, Table 3) and (b) plots of catalytic activity and M_w of the polymer versus reaction time.

2. Additional ^{1}H and ^{13}C NMR data for the polymers

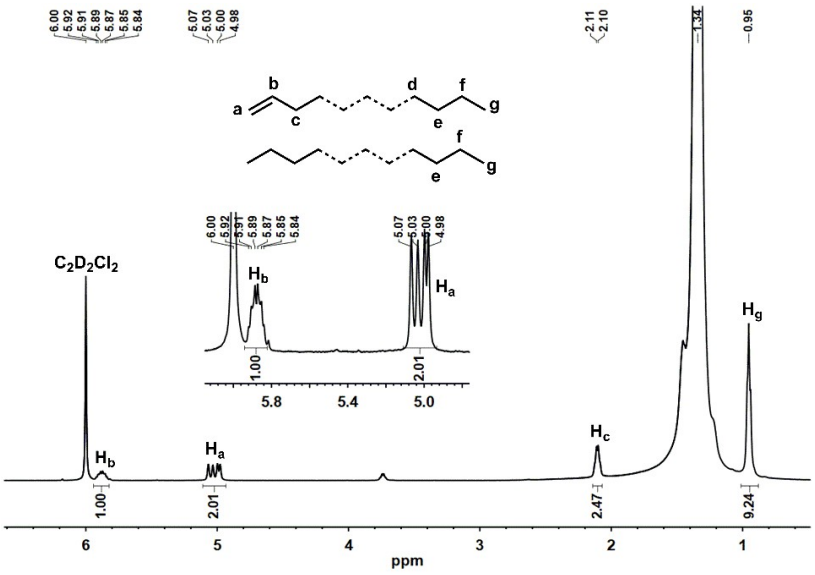

Figure S2. ^{1}H NMR spectrum of the polyethylene obtained using **Fe7**/MAO at 40 °C including an expansion of the vinylic region (entry 16, Table 4); recorded in tetrachloroethane-d_2 at 100 °C

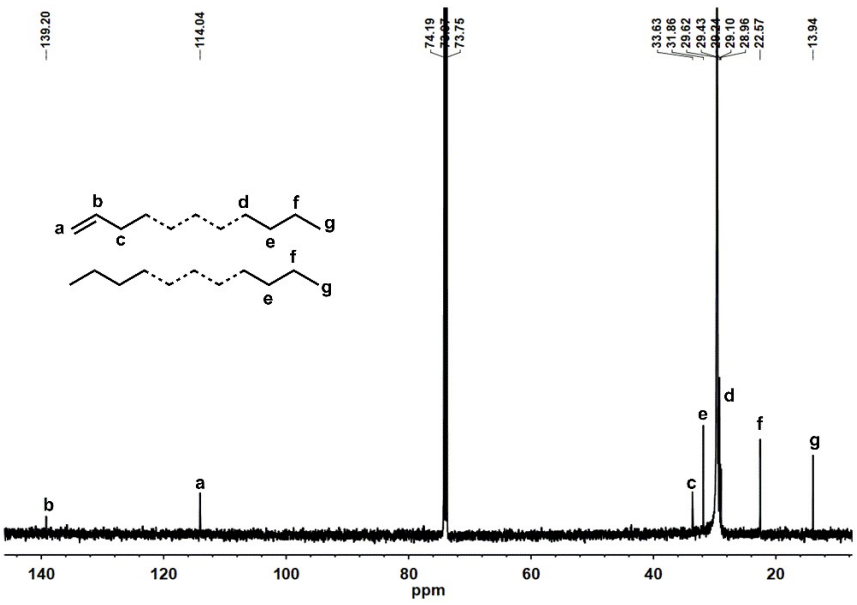

Figure S3. [13]C NMR spectrum of the polyethylene obtained using **Fe7**/MAO at 40 °C (entry 16, Table 4); recorded in tetrachloroethane-d_2 at 100 °C

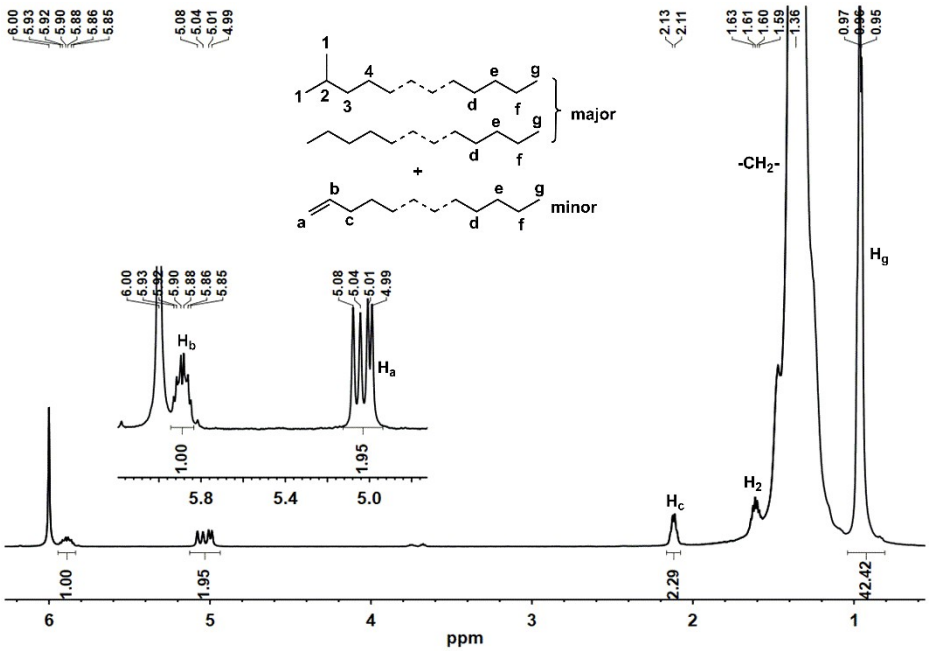

Figure S4. [1]H NMR spectrum of the polyethylene obtained using **Fe4**/MMAO at 60 °C (entry 4, Table 4); recorded in tetrachloroethane-d_2 at 100 °C

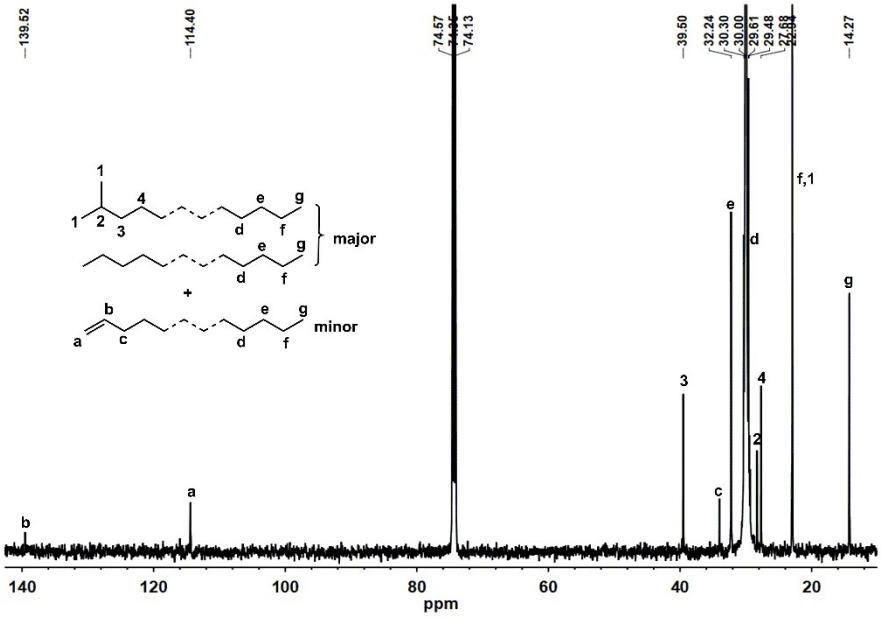

Figure S5. ^{13}C NMR spectrum of the polyethylene obtained using **Fe4**/MMAO at 60 °C (entry 4, Table 4); recorded in tetrachloroethane-d_2 at 100 °C

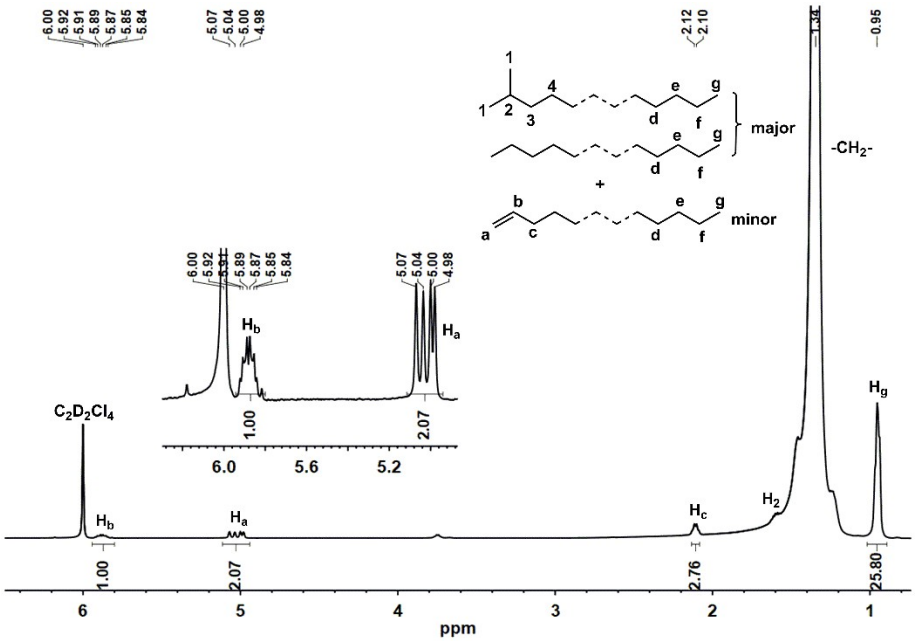

Figure S6. ^{1}H NMR spectrum of the polyethylene obtained using **Fe5**/MMAO at 60 °C including an expansion of the vinylic region (entry 5, Table 4); recorded in tetrachloroethane-d_2 at 100 °C

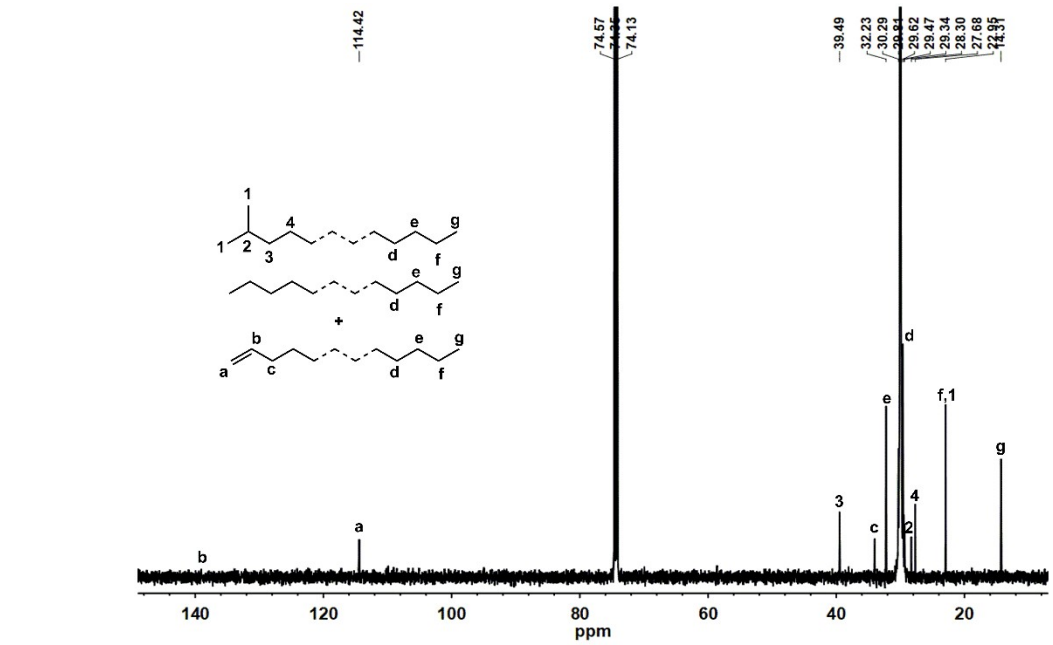

Figure S7. ^{13}C NMR spectrum of the polyethylene obtained using **Fe5**/MMAO at 60 °C (entry 5, Table 4); recorded in tetrachloroethane-d_2 at 100 °C

3. Proposed mechanistic pathways for polymer formation

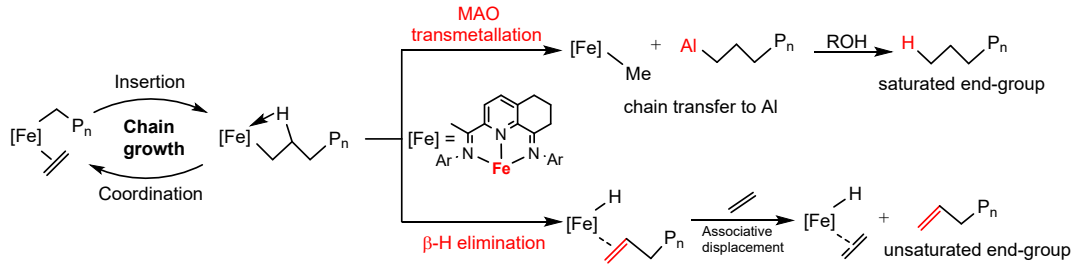

Figure S8. Proposed mechanistic pathways to account for the different polymer end groups generated by the iron catalysts.[1-4]

4. Crystallographic data

Single crystals of **Fe3** and **Fe5** suitable for the X-ray determinations were obtained by layering heptane onto a dichloromethane solution of the corresponding complex at room temperature. With graphite monochromated Cu-Kα radiation (λ = 1.54184 Å) at 170(2) K, cell parameters were obtained by global refinement of the positions of all collected reflections. The data were corrected for Lorentz and polarization effects (SAINT) and semiempirical absorption corrections based on equivalent reflections were applied (SADABS). Using Olex2,[4] the structure was solved with the SHELXT structure solution program[5] using Intrinsic Phasing and refined with the SHELXL refinement package[6] using Least Squares minimization. All hydrogen atoms were placed in calculated positions. Details of the X-ray structure determinations and refinements are provided in Table S1.

Table S1 Crystal data and structural refinements for **Fe3** and **Fe5**

	Fe3	Fe5
CCDC number	2482813	2482814
Empirical formula	$C_{63}H_{64}Cl_6FeN_3$	$C_{87}H_{81}Cl_2FeN_3$
Formula weight	1131.72	1295.29
Temperature/K	169.99(14)	170.00(16)
Wavelength/Å	1.54184	1.54184
Crystal system	triclinic	monoclinic
Space group	P-1	$P2_1/c$
a/Å	9.3002(4)	28.2417(18)
b/Å	13.7002(6)	17.0632(12)
c/Å	22.4970(7)	17.8586(12)
Alpha/°	96.212(3)	90
Beta/°	90.550(3)	101.352(6)
Gamm/°	100.482(4)	90
Volume/Å^3	2800.8(2)	8437.6(10)
Z	2	4
D_{calcd}/(g/cm^{-3})	1.342	1.020
μ/mm^{-1}	5.117	2.317
F(000)	1182.0	2736.0
Crystal size/mm^3	0.15 × 0.1 × 0.05	0.15 × 0.12 × 0.1
2θ range (°)	6.602 to 151.492	6.084 to 152.98
Limiting indices	-11 ≤ h ≤ 11, -15 ≤ k ≤ 17, -28 ≤ l ≤ 28	-34 ≤ h ≤ 35, -20 ≤ k ≤ 21, -22 ≤ l ≤ 21
No. of reflections collected	36885	66083
No. unique reflections	11095	16933
R_{int}	0.0782	0.2270
No. of parameters	634	958
Completeness to θ	0.951	0.955
Goodness of fit on F^2	1.062	0.931
Final *R* indexes [*I*>=2σ (*I*)]	R_1 = 0.0908, wR_2 = 0.2673	R_1 = 0.1060, wR_2 = 0.2488
Final *R* indexes (all data)	R_1 = 0.1222, wR_2 = 0.2973	R_1 = 0.1932, wR_2 = 0.3119
Largest diff. peak and hole/(e Å^{-3})	1.42/-0.91	0.72/-0.93

4. References

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