

Iron(III) amine-bis(phenolate) complexes as catalysts for coupling of alkyl halides with aryl Grignard reagents

SUPPORTING INFORMATION

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Experimental details, crystallographic data for L1H₂ and 1, characterization data (GC and NMR) for cross-coupled products.

General experimental conditions: Unless otherwise stated, all manipulations were performed under an atmosphere of dry oxygen-free nitrogen by means of standard Schlenk or glove box techniques. Anhydrous diethyl ether and THF was stored over sieves and distilled from sodium benzophenone ketyl under nitrogen. Reagents were purchased either from Aldrich or Alfa Aesar and used without further purification. Grignard reagents were titrated prior to use, and were also analyzed by GC-MS after being quenched with dilute HCl(aq) to quantify biaryl complexes or other impurities present prior to their use in catalyst runs. High purity anhydrous FeCl₃ (99.99+%) was purchased in ampoules from Aldrich.

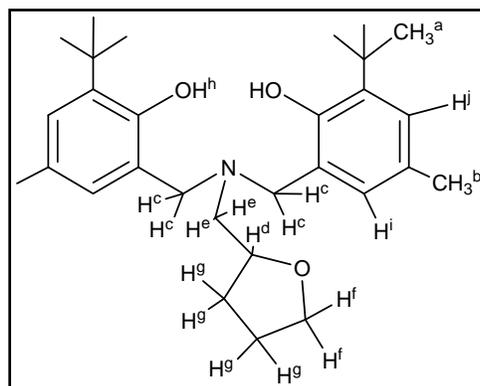
Instrumentation: NMR spectra were recorded in CDCl₃ on a Bruker Avance-500. MALDI-TOF MS spectra were recorded on an Applied Biosystems Voyager DE-PRO equipped with a reflectron, delayed ion extraction and high performance nitrogen laser (337 nm). Samples were prepared at a concentration of 0.03 mg L⁻¹ in methanol. Anthracene was used as the matrix, which was mixed at a concentration of 0.03 mg L⁻¹. FTIR spectra were recorded on a Bruker TENSOR 27 spectrometer fitted with a MIRacle ATR with a zinc selenide crystal on which the samples are placed. UV-vis spectra were recorded on an Agilent 8453 spectrophotometer. Elemental analyses were carried out by Guelph Chemical

Laboratories, Guelph, ON, Canada. Crystal structures were solved on a AFC8-Saturn 70 single crystal X-ray diffractometer from Rigaku/MSK, equipped with an X-stream 2000 low temperature system. Gas chromatography mass spectrometry (GC-MS) analyses were performed using an Agilent Technologies 6890N Network GC system coupled to an Agilent Technologies 5973 mass selective detector (MSD). The chromatograph is equipped with electronic pressure control, split/splitless and on-column injectors (7683 Series), and a DB5-MS column. All catalytic reactions were performed on a Radleys Carousel Reactor™. Twelve 45 mL reaction tubes were fitted with threaded Teflon caps equipped with valves for connection to the inert gas or vacuum supply of Schlenk apparatus, and septa for the introduction of reagents.

$\text{H}_2[\text{O}_2\text{NO}]^{\text{BuMeFur}}$ (**L1H₂**):

A solution of 2-*t*-butyl,4-methylphenol (20.236 g, 0.1232 mol), tetrahydrofurfurylamine (6.563 g, 0.0616 mol), and 37% aqueous formaldehyde (9.17 mL, 0.1232 mol) in methanol (50 mL) was stirred and refluxed for 72 h. Upon cooling, the reaction mixture separated into two phases. The upper phase was decanted, and the remaining oily residue was triturated with cold methanol to give a pure, white powder (15.37 g, 55% yield). The methanol washings were combined with the decanted upper phase from the reaction and concentrated *in vacuo* until a further 7.00 g of product precipitated from solution. A total yield of ca. 80% was thus obtained. Large single crystals suitable for X-ray diffraction studies were obtained by cooling of a hot diethyl ether solution.

^1H NMR (500 MHz, CDCl_3 , δ): 8.29 (s, 2H, $-\text{OH}^{\text{h}}$); 7.03 (s, ArH^{j} , 2H,); 6.74 (s, ArH^{i} , 2H,); 4.23 (m, CH^{d} , 1H,); 4.00 (m, CH_2^{f} , 2H,); 3.73 (s, CH_2^{c} , 4H); 2.60 (m, CH_2^{e} , 2H,); 2.26 (s, CH_3^{b} , 6H); 1.92 (m, CH_2^{g} , 4H); 1.43 (s, CH_3^{a} , 18H,). IR (cm^{-1}): 3350 (OH); 2955 (C-H); 1603 (C=C, phenyl ring). Anal. Calcd for $\text{C}_{29}\text{H}_{43}\text{NO}_3$: C, 76.78; H, 9.55; N, 3.09. Found C, 76.80; H, 9.59; N, 3.10. M.p. = 170 °C.



Representative synthesis of complexes **1** to **8** – $\text{FeCl}[\text{O}_2\text{NO}]^{\text{BuMeFur}}$ (**1**):

To a methanolic slurry of recrystallized $\text{H}_2[\text{O}_2\text{NO}]^{\text{BuMeFur}}$, **L1H₂**, (2.003 g, 4.41 mmol) was added a solution of anhydrous FeCl_3 (0.715 g, 4.41 mmol) in methanol resulting in an intense blue solution. To this solution was added triethylamine (890 mg, 8.82 mmol) and the resulting mixture was stirred for 4 h. Solvent was removed under vacuum, the residue was extracted with toluene and filtered

through Celite. Removal of solvent under vacuum yielded a waxy dark-blue product, which was triturated with pentane. Removal of solvents yielded 1.89 g (79%) of analytically pure product. Crystals suitable for X-ray diffraction were obtained by slow evaporation of an acetonitrile solution.

Anal. Calcd for $C_{29}H_{41}ClFeNO_3$: C, 64.15; H, 7.61; N, 2.58. Found C, 64.35; H, 7.82; N, 2.88. MS (MALDI-TOF) m/z (% ion): 542.0 (100, $[M]^+$), 507.1 (73, $[M-Cl]^+$). UV-vis (CH₃OH) λ_{max} , nm (ϵ): 616 (1670), 350 (1750). μ_{eff} (solid, 25 °C) 5.9 μ_B . Synthesis and characterization details of complexes **2** – **8** are reported elsewhere.¹

General method for cross-coupling catalysis runs:

Catalyst **1** (0.1 mmol, 5.0 mol%) in CH₂Cl₂ (3 mL) was added to the reaction flask followed by removal of the solvent *in vacuo*. To the catalyst were added Et₂O (5 mL), alkyl halide (2.0 mmol) and dodecane (2.0 mmol as internal standard) and the solution was stirred at room temperature. Aryl Grignard (4.0 mmol) was added and the resulting mixture was stirred for 30 minutes. The reaction was quenched with HCl (aq., 2 M, 5 mL) and the organic phase was extracted with Et₂O (1 x 5 mL) and dried over MgSO₄. The mixture was analyzed by GC-MS and quantified using ¹H NMR and/or GC. NMR samples were prepared by careful removal of solvent under vacuum and dissolving the residue in CDCl₃.

1-Cyclohexyl-4-methylbenzene. ¹H NMR (500 MHz, CDCl₃, δ): 7.08 (m, 4H); 2.45 (m, 1H, CH); 2.30 (s, 3H, CH₃); 1.81 (m, 5H CH₂); 1.27 (m, 5H CH₂). MS (EI) m/z (% ion): 174 (80).

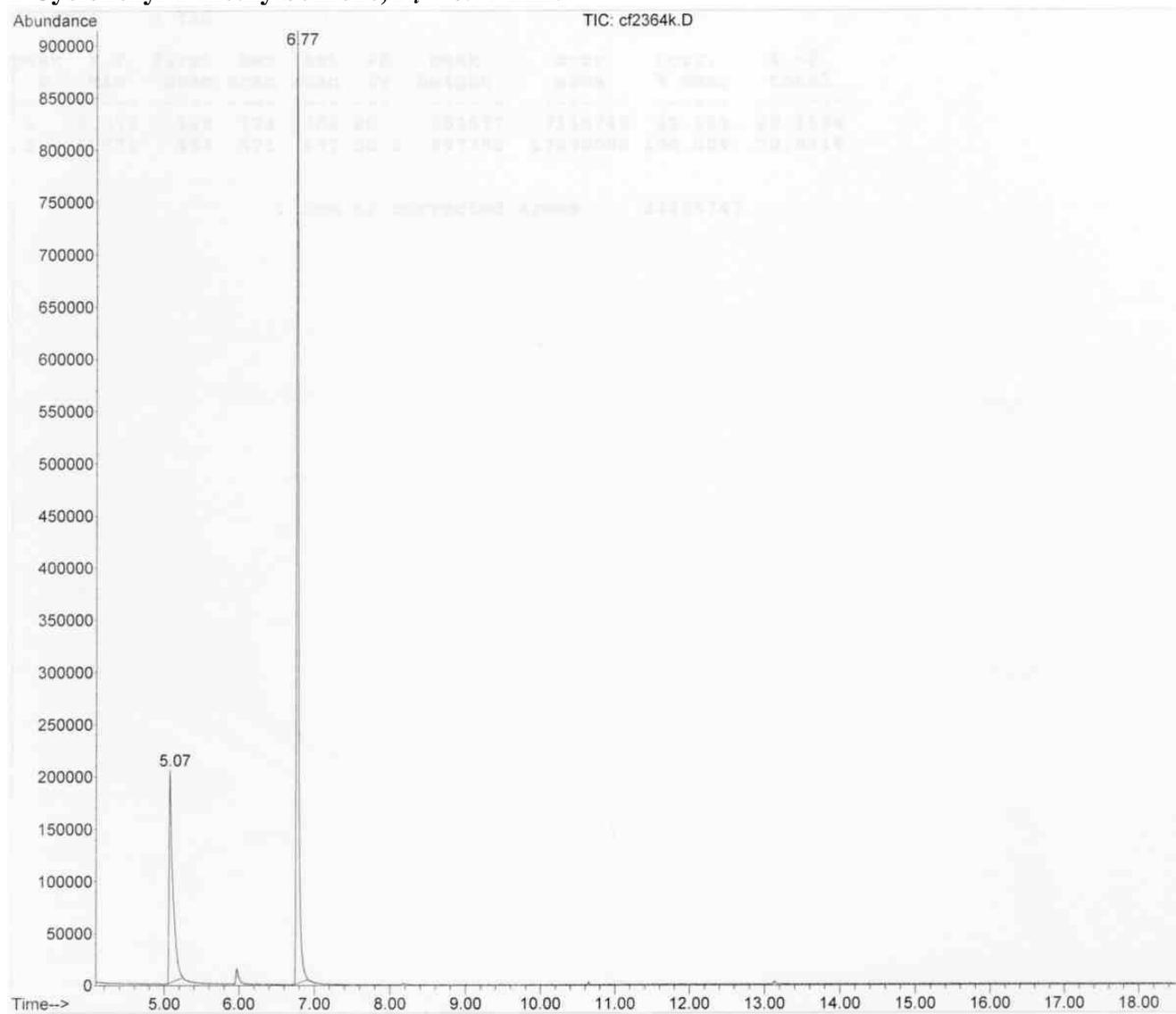
1-Cyclohexyl-4-methoxybenzene. ¹H NMR (500 MHz, CDCl₃, δ): 7.13 (d, 2H); 6.84 (d, 2H); 3.79 (s, 3H, OCH₃); 2.44 (m, 1H, CH); 1.81 (m, 5H, CH₂); 1.30 (m, 5H, CH₂). MS (EI) m/z (% ion): 190 (70).

1-Cyclohexyl-2-methylbenzene. ¹H NMR (500 MHz, CDCl₃, δ): 7.14 (m, 4H, ArH); 2.70 (m, 1H, CH); 2.33 (s, 3H, CH₃); 2.15 (m, 5H, CH₂); 1.53 (m, 2H, CH₂); 1.39 (m, 3H, CH₂). MS (EI) m/z (% ion): 174 (80).

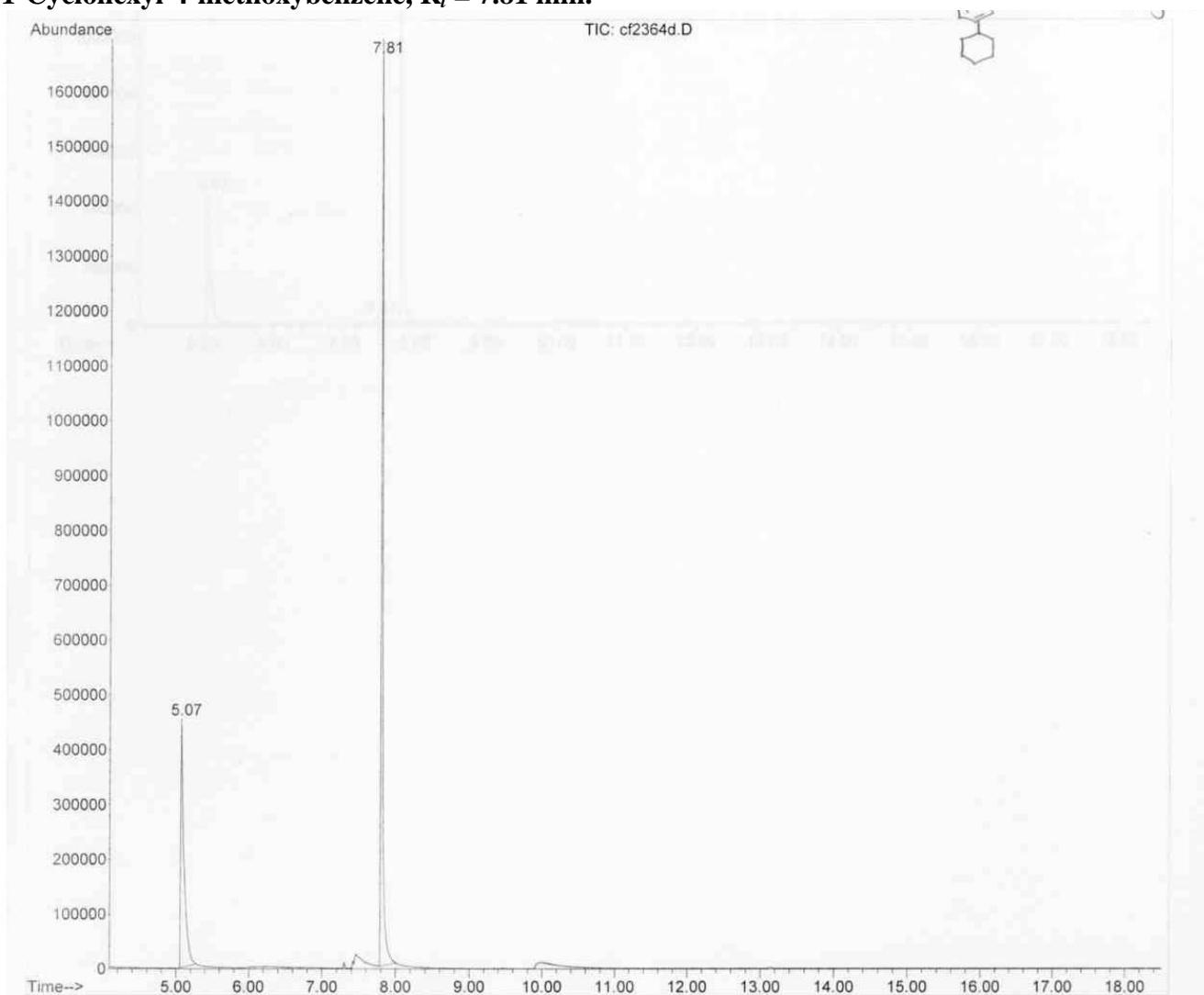
1-Methyl-4-octylbenzene. ¹H NMR (500 MHz, CDCl₃, δ): 7.41 (s, br, 4H, ArH); 2.71 (t, 2H, ArCH₂); 2.45 (s, 3H, ArCH₃); 1.74 (m, 2H, CH₂CH₃); 1.44 (m, 10H, CH₂); 1.03 (t, 3H, CH₂CH₃). MS (EI) m/z (% ion): 204 (40).

GC traces of selected cross-coupling products (dodecane internal standard $R_t = 5.07$ min):

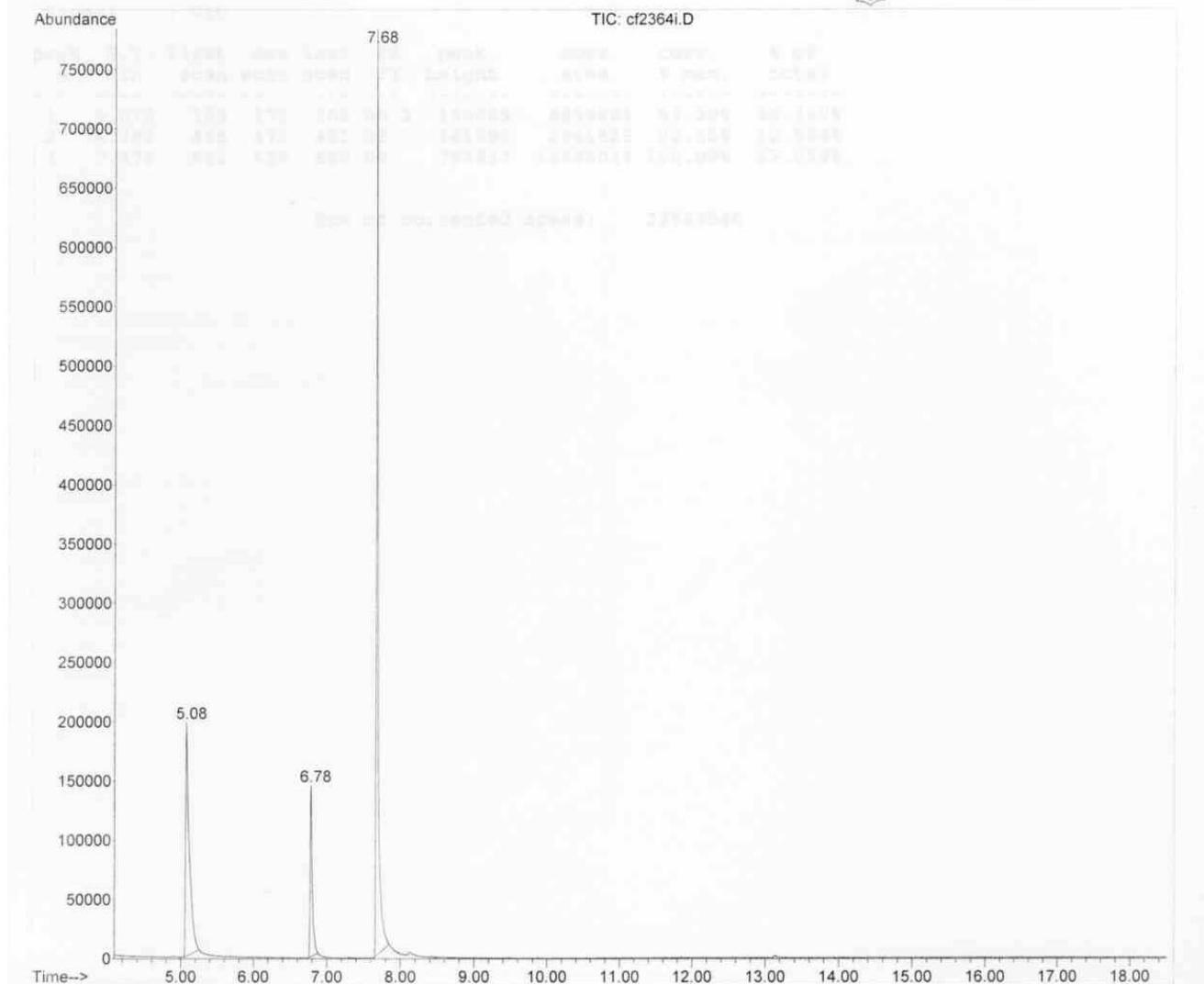
1-Cyclohexyl-2-methylbenzene, $R_t = 6.77$ min.



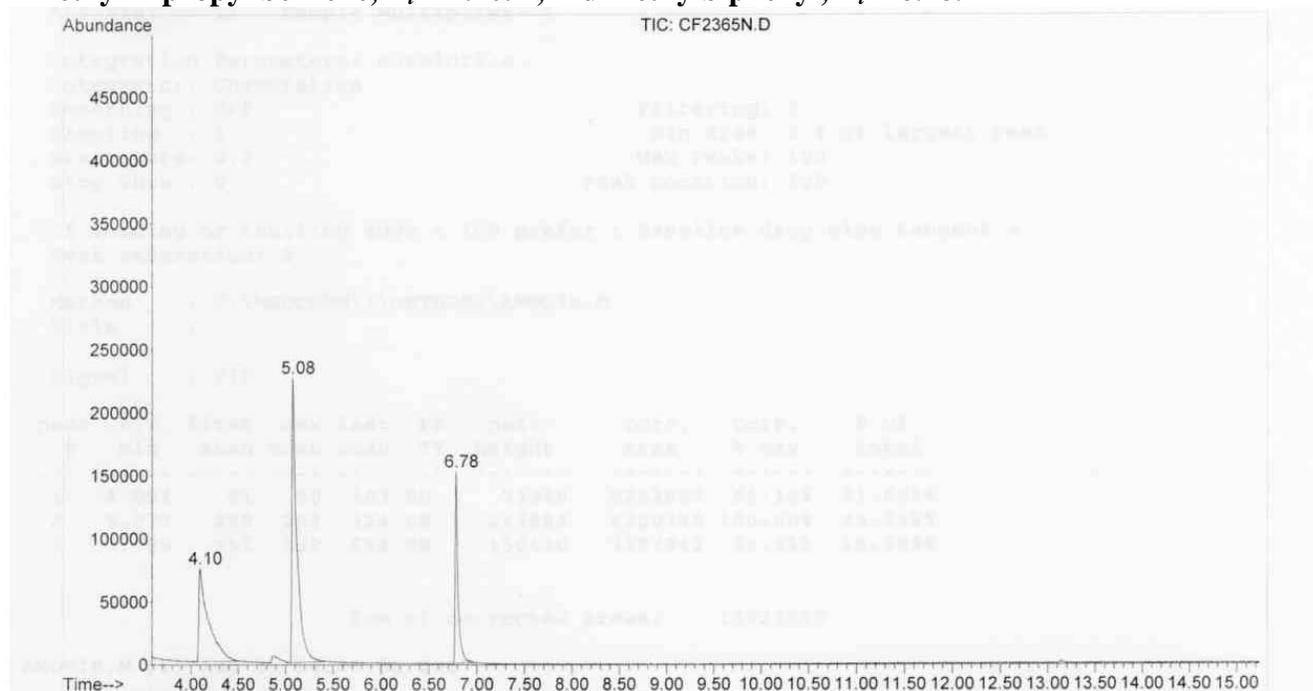
1-Cyclohexyl-4-methoxybenzene, $R_t = 7.81$ min.



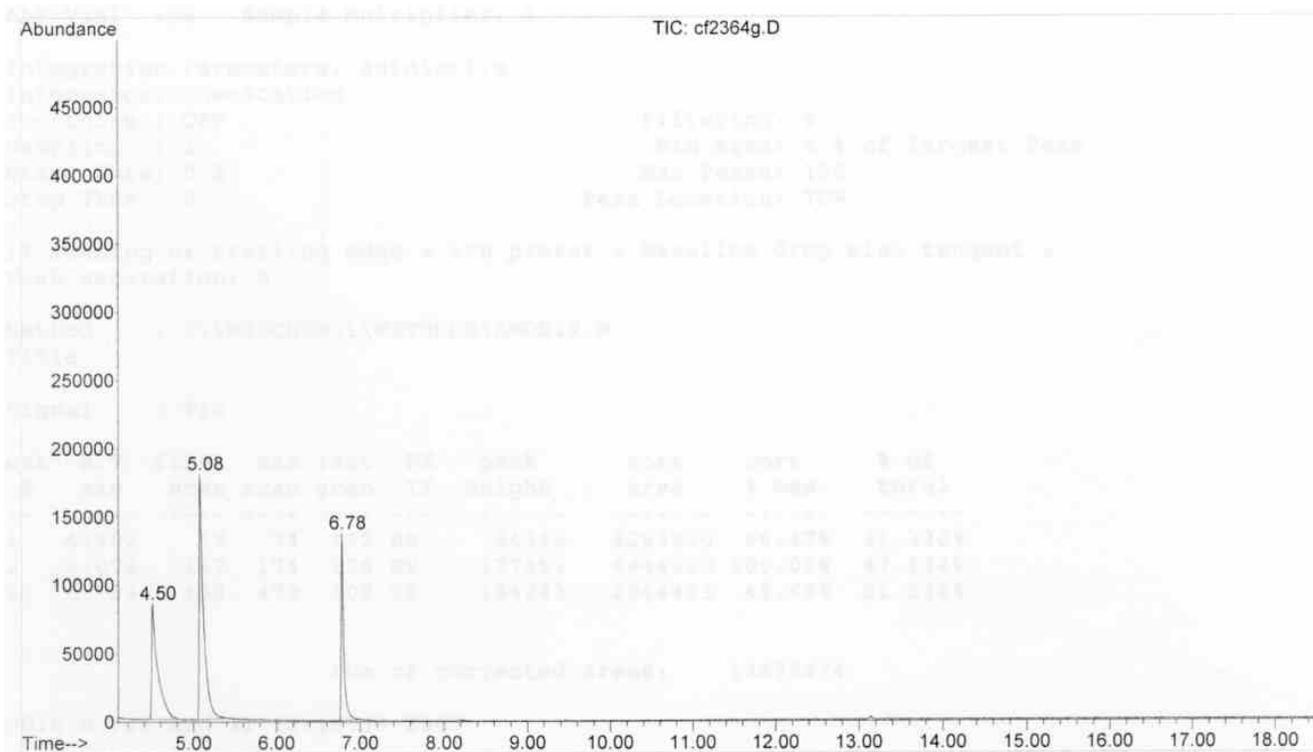
1-Methyl-2-octylbenzene, $R_t = 7.68$. 2,2'-dimethylbiphenyl, $R_t = 6.78$.



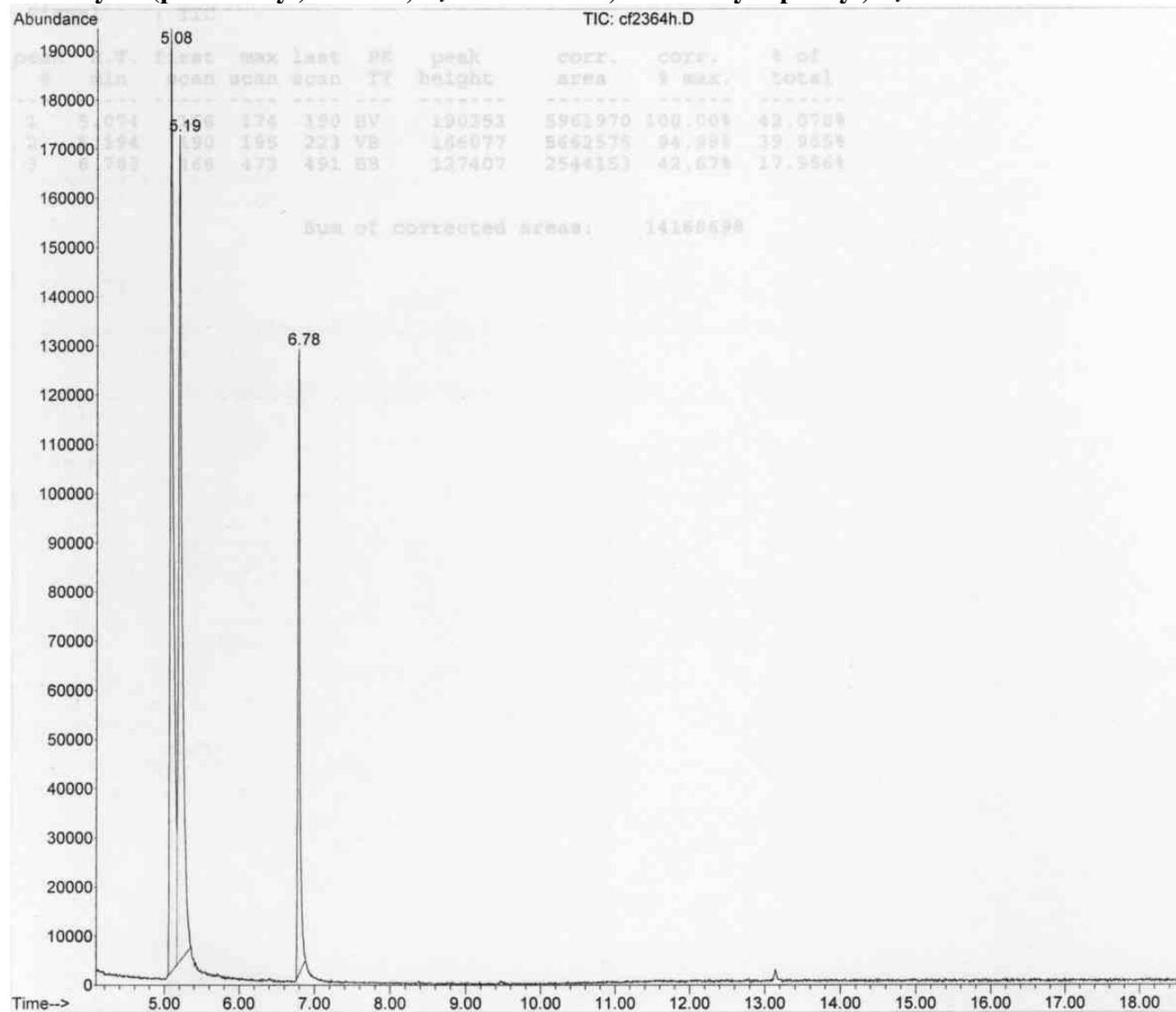
1-methyl-2-propyl benzene, $R_t = 4.10$. 2,2'-dimethylbiphenyl, $R_t = 6.78$.



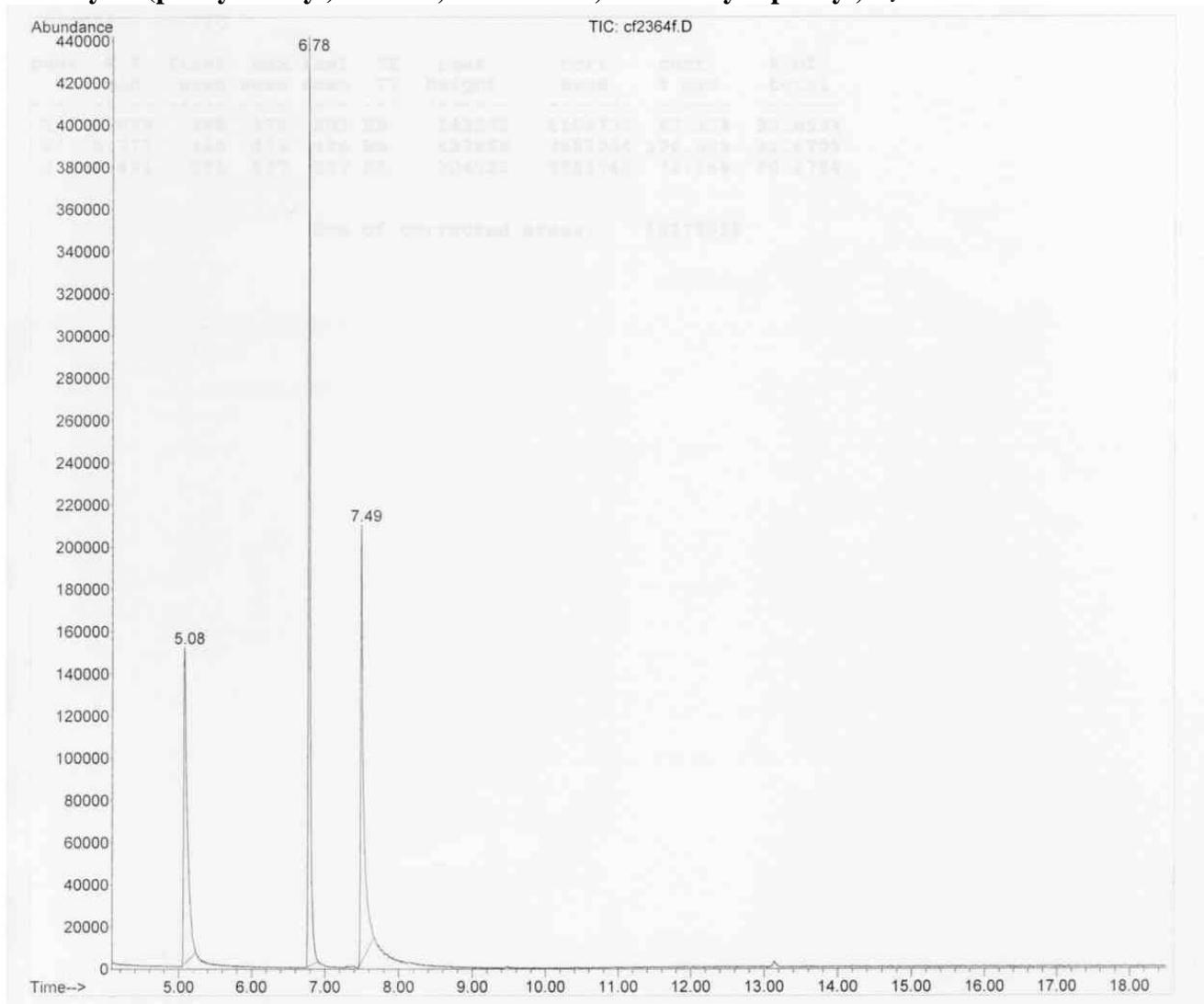
1-sec-butyl-2-methylbenzene, $R_t = 4.50$. 2,2'-dimethylbiphenyl, $R_t = 6.78$.



1-methyl-2-(pentan-3-yl)benzene, $R_t = 5.19$ min. 2,2'-dimethylbiphenyl, $R_t = 6.78$.



1-methyl-2-(phenylmethyl)benzene, $R_t = 7.49$. 2,2'-dimethylbiphenyl, $R_t = 6.78$.



Crystallographic Experimental: Suitable crystals of **L1H₂** and **1** were selected and mounted on glass fibers using Paratone-N oil and freezing to $-120\text{ }^{\circ}\text{C}$. Crystallographic data, bond lengths and bond angles for **L1H₂** and **1** are given below. All measurements were made on a Rigaku Saturn CCD area detector with graphite monochromated Mo-K α radiation. In each case the data were processed² and corrected for Lorentz and polarization effects and absorption.³ Neutral atom scattering factors for all non-hydrogen atoms were taken from the *International Tables for X-ray Crystallography*.⁴ All structures were solved by direct methods⁵ and expanded using Fourier techniques.⁶ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. Anomalous dispersion effects were included in Fcalc;⁷ the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.⁸ The values for the mass attenuation coefficients are those of Creagh and Hubbell.⁹ All calculations were performed using the CrystalStructure^{10,11} crystallographic software package except for refinement, which was performed using SHELXL-97¹².

Crystallographic data for L1H₂: C₂₉H₄₃NO₃, $M = 453.66$, $T = 153\text{ K}$, colourless, prism, triclinic, P-1 (#2), $a = 10.453(4)\text{ \AA}$, $b = 11.703(4)\text{ \AA}$, $c = 12.508(4)\text{ \AA}$, $\alpha = 101.931(6)^{\circ}$, $\beta = 107.410(5)^{\circ}$, $\gamma = 104.170(7)^{\circ}$, $V = 1349.3(8)\text{ \AA}^3$, $Z = 2$, $D_c = 1.117\text{ g cm}^{-3}$, $\mu(\text{MoK}\alpha) = 0.707\text{ cm}^{-1}$, 13994 total reflections, 6808 unique reflections, $R_{\text{int}} = 0.019$, $R [I > 2\sigma(I)] = 0.0600$, $wR2 = 0.1659$.

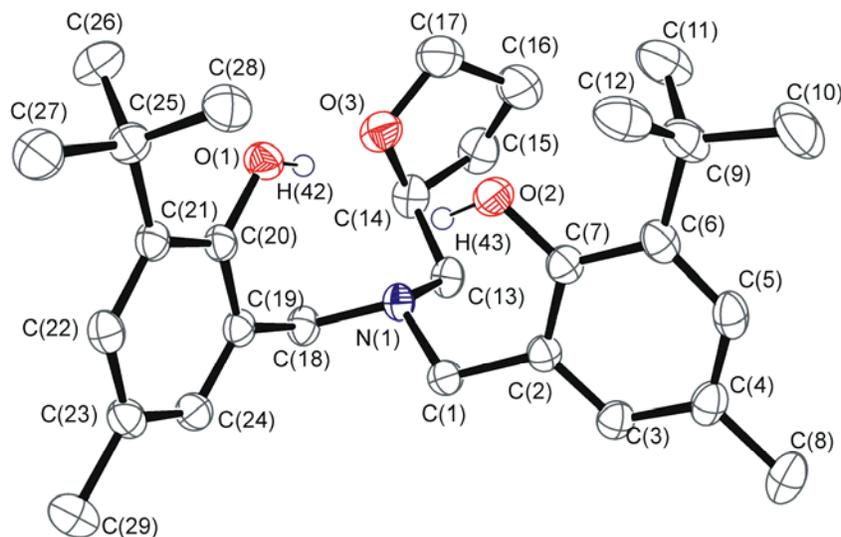


Fig. S1 Molecular structure (ORTEP) and numbering scheme of **L1H₂**. Ellipsoids are shown at 50 % probability. Except for H(42) and H(43), all hydrogen atoms have been removed.

Table S1 Bond Lengths for (Å) **L1H₂**:

O2	C7	1.3734(17)	C9	C11	1.541(2)
O3	C17	1.434(2)	C13	C14	1.527(2)
O3	C14	1.4447(19)	C14	C15	1.527(2)
N1	C13	1.4666(17)	C15	C16	1.512(3)
N1	C1	1.4744(17)	C16	C17	1.522(3)
N1	C18	1.4781(16)	C18	C19	1.5072(18)
C1	C2	1.5199(18)	C19	C24	1.3929(19)
C2	C3	1.3921(19)	C19	C20	1.4066(18)
C2	C7	1.4025(18)	C20	C21	1.4106(18)
C3	C4	1.389(2)	C21	C22	1.4008(19)
C4	C5	1.391(2)	C21	C25	1.5391(19)
C4	C8	1.513(2)	C22	C23	1.395(2)
C5	C6	1.401(2)	C23	C24	1.3919(19)
C6	C7	1.4137(19)	C23	C29	1.512(2)
C6	C9	1.539(2)	C25	C27	1.537(2)
C9	C10	1.537(2)	C25	C26	1.539(2)
C9	C12	1.537(3)	C25	C28	1.540(2)

Table S2 Bond Angles (°) for **L1H₂**:

C17	O3	C14	110.45(12)	O3	C14	C13	109.89(11)
C13	N1	C1	111.72(11)	C15	C14	C13	112.35(13)
C13	N1	C18	112.02(10)	C16	C15	C14	102.83(14)
C1	N1	C18	110.64(10)	C15	C16	C17	101.88(15)
N1	C1	C2	113.53(10)	O3	C17	C16	105.83(14)
C3	C2	C7	119.47(12)	N1	C18	C19	112.64(10)
C3	C2	C1	119.23(12)	C24	C19	C20	119.43(12)
C7	C2	C1	121.19(12)	C24	C19	C18	120.41(12)
C4	C3	C2	121.31(13)	C20	C19	C18	120.14(12)
C3	C4	C5	118.11(13)	O1	C20	C19	121.39(11)
C3	C4	C8	120.53(14)	O1	C20	C21	117.88(11)
C5	C4	C8	121.36(13)	C19	C20	C21	120.73(12)
C4	C5	C6	123.32(13)	C22	C21	C20	117.12(12)
C5	C6	C7	116.76(13)	C22	C21	C25	121.39(12)
C5	C6	C9	122.00(12)	C20	C21	C25	121.46(12)
C7	C6	C9	121.23(13)	C23	C22	C21	123.50(12)
O2	C7	C2	119.94(12)	C24	C23	C22	117.53(12)
O2	C7	C6	119.03(12)	C24	C23	C29	121.00(13)
C2	C7	C6	121.02(12)	C22	C23	C29	121.47(13)
C10	C9	C12	107.51(14)	C23	C24	C19	121.67(12)
C10	C9	C6	112.10(15)	C27	C25	C26	106.91(13)
C12	C9	C6	109.77(13)	C27	C25	C21	111.76(12)
C10	C9	C11	107.10(14)	C26	C25	C21	111.26(12)
C12	C9	C11	110.00(15)	C27	C25	C28	107.85(12)
C6	C9	C11	110.28(13)	C26	C25	C28	109.69(13)

N1	C13	C14	112.95(11)	C21	C25	C28	109.29(11)
O3	C14	C15	104.72(13)				

Crystallographic data for 1: $C_{29}H_{41}ClFeNO_3$, $M = 542.95$, black prism, monoclinic, $P2_1/n$ (#14) $a = 9.7824(8)$ Å, $b = 25.0778(19)$ Å, $c = 12.3276(9)$ Å, $\beta = 95.0780(19)^\circ$, $V = 3012.4(4)$ Å³, $T = 153$ K, $Z = 4$, $\mu(\text{MoK}\alpha) = 6.160$ cm⁻¹, $D_c = 1.197$ g cm⁻³, 27790 reflections measured, 8185 unique reflections ($R_{\text{int}} = 0.049$), $R [I > 2\sigma(I)] = 0.0836$, $wR2 = 0.2400$.

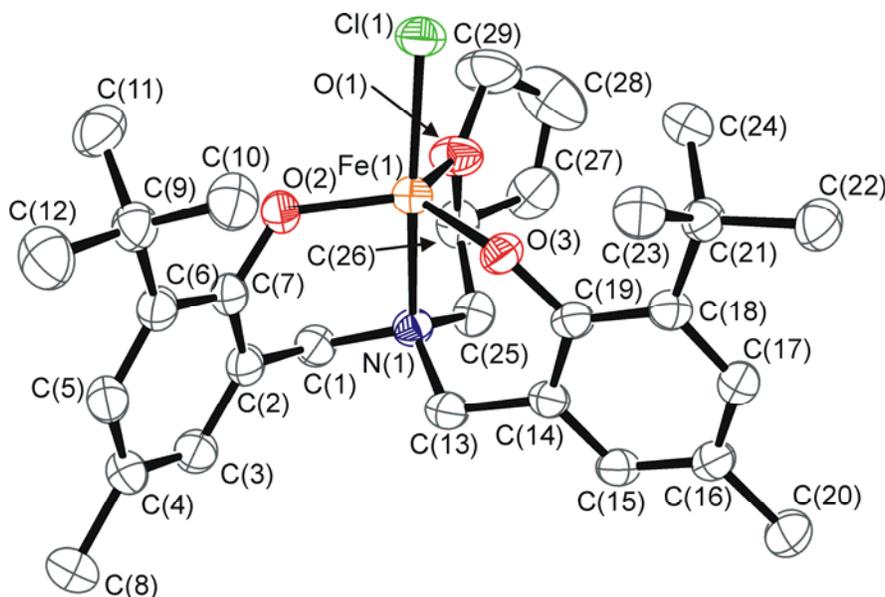


Fig. S2 Molecular structure (ORTEP) and numbering scheme of **1**. Ellipsoids are shown at 50 % probability. All hydrogen atoms have been removed.

Table S3 Bond Lengths for (Å) **1**:

Fe1	O3	1.850(2)	C6	C9	1.526(5)
Fe1	O2	1.854(2)	C9	C12	1.531(5)
Fe1	O1	2.074(3)	C9	C10	1.543(5)
Fe1	N1	2.223(3)	C9	C11	1.548(6)
Fe1	C11	2.2739(10)	C13	C14	1.507(5)
O1	C29	1.452(5)	C14	C15	1.395(4)
O1	C26	1.468(5)	C14	C19	1.398(4)
O2	C7	1.346(4)	C15	C16	1.388(5)
O3	C19	1.352(4)	C16	C17	1.389(5)
N1	C25	1.480(4)	C16	C20	1.508(4)
N1	C13	1.488(4)	C17	C18	1.409(4)
N1	C1	1.500(4)	C18	C19	1.405(4)

C1	C2	1.509(5)	C18	C21	1.530(5)
C2	C3	1.398(5)	C21	C24	1.534(5)
C2	C7	1.402(5)	C21	C22	1.540(5)
C3	C4	1.387(5)	C21	C23	1.543(5)
C4	C5	1.388(5)	C25	C26	1.493(5)
C4	C8	1.513(5)	C26	C27	1.530(5)
C5	C6	1.398(5)	C27	C28	1.499(7)
C6	C7	1.417(5)	C28	C29	1.448(7)

Table S4 Bond Angles (°) for **1**:

O3	Fe1	O2	118.39(10)	C2	C7	C6	120.7(3)
O3	Fe1	O1	119.00(11)	C6	C9	C12	112.0(3)
O2	Fe1	O1	119.60(11)	C6	C9	C10	110.8(3)
O3	Fe1	N1	87.62(10)	C12	C9	C10	107.5(3)
O2	Fe1	N1	89.37(10)	C6	C9	C11	109.5(3)
O1	Fe1	N1	75.79(10)	C12	C9	C11	107.5(3)
O3	Fe1	C11	100.81(8)	C10	C9	C11	109.5(3)
O2	Fe1	C11	96.60(8)	N1	C13	C14	113.4(3)
O1	Fe1	C11	89.98(8)	C15	C14	C19	121.0(3)
N1	Fe1	C11	165.69(8)	C15	C14	C13	120.3(3)
C29	O1	C26	106.2(3)	C19	C14	C13	118.7(3)
C29	O1	Fe1	133.6(3)	C16	C15	C14	120.5(3)
C26	O1	Fe1	120.2(2)	C15	C16	C17	117.8(3)
C7	O2	Fe1	129.3(2)	C15	C16	C20	121.2(3)
C19	O3	Fe1	132.0(2)	C17	C16	C20	121.0(3)
C25	N1	C13	109.1(3)	C16	C17	C18	123.7(3)
C25	N1	C1	110.3(3)	C19	C18	C17	117.0(3)
C13	N1	C1	108.9(2)	C19	C18	C21	121.8(3)
C25	N1	Fe1	109.1(2)	C17	C18	C21	121.2(3)
C13	N1	Fe1	111.0(2)	O3	C19	C14	118.9(3)
C1	N1	Fe1	108.41(19)	O3	C19	C18	121.1(3)
N1	C1	C2	112.4(3)	C14	C19	C18	120.0(3)
C3	C2	C7	119.8(3)	C18	C21	C24	109.7(3)
C3	C2	C1	121.1(3)	C18	C21	C22	112.1(3)
C7	C2	C1	119.1(3)	C24	C21	C22	107.4(3)
C4	C3	C2	121.2(3)	C18	C21	C23	110.5(3)
C3	C4	C5	117.6(3)	C24	C21	C23	110.0(3)
C3	C4	C8	120.8(3)	C22	C21	C23	107.2(3)
C5	C4	C8	121.6(3)	N1	C25	C26	110.1(3)
C4	C5	C6	124.3(3)	O1	C26	C25	105.9(3)
C5	C6	C7	116.4(3)	O1	C26	C27	105.0(3)
C5	C6	C9	122.1(3)	C25	C26	C27	114.4(3)
C7	C6	C9	121.5(3)	C28	C27	C26	104.5(4)
O2	C7	C2	118.4(3)	C29	C28	C27	108.0(4)
O2	C7	C6	120.9(3)	C28	C29	O1	106.1(4)

References:

- (1) Kwong, P., Fowler, C., Hasan, K., Roy Chowdhury, R., Crane, A. K., Trudel, S., Leznoff, D. B., and Kozak, C. M. *Manuscript in preparation*.
- (2) CrystalClear: Rigaku Corporation, 1999. CrystalClear Software User's Guide, Molecular Structure Corporation, (c) 2000. J.W. Pflugrath (1999) *Acta Cryst. D* 55, 1718-1725.
- (3) Larson, A.C. (1970), *Crystallographic Computing*, 291-294. F.R. Ahmed, ed. Munksgaard, Copenhagen (equation 22, with V replaced by the cell volume).
- (4) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).
- (5) SIR92: Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M., Polidori, G., and Camalli, M. (1994) *J. Appl. Cryst.*, 27, 435.
- (6) DIRDIF99: Beurskens, P.T., Admiraal, G., Beurskens, G., Bosman, W.P., de Gelder, R., Israel, R. and Smits, J.M.M. (1999). The DIRDIF-99 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.
- (7) Ibers, J. A. & Hamilton, W. C.; *Acta Crystallogr.*, 17, 781 (1964).
- (8) Creagh, D. C. & McAuley, W.J. ; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).
- (9) Creagh, D. C. & Hubbell, J.H.; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).
- (10) CrystalStructure 3.7.0: Crystal Structure Analysis Package, Rigaku and Rigaku/MSK (2000-2005). 9009 New Trails Dr. The Woodlands TX 77381 USA.
- (11) CRYSTALS Issue 10: Watkin, D.J., Prout, C.K. Carruthers, J.R. & Betteridge, P.W. Chemical Crystallography Laboratory, Oxford, UK. (1996)
- (12) SHELX97: Sheldrick, G.M. (1997).