Supporting Information

Iron-Mediated C-H Bond Amination by Organic Azides on a Tripodal Bis(anilido)iminophosphorane Platform

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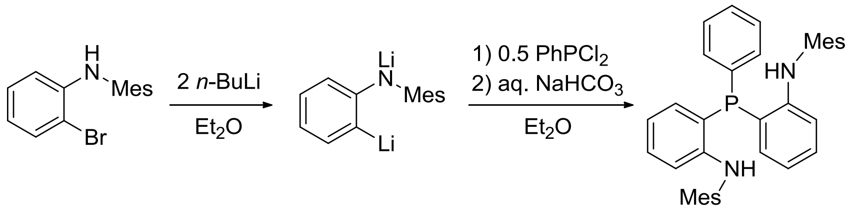
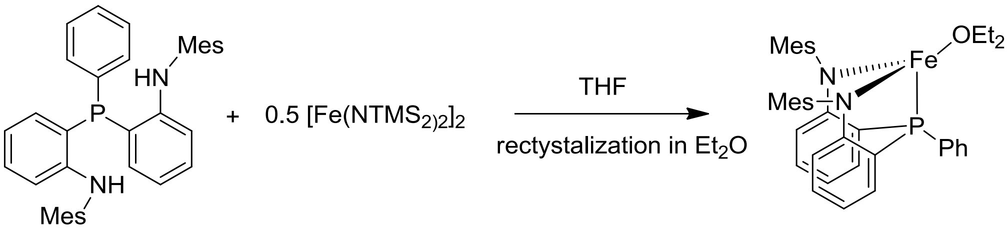
1. Experimental Section

General Procedures. All experiments were performed under an atmosphere of dry dinitrogen with the rigid exclusion of air and moisture using standard Schlenk or cannula techniques, or in a glovebox. All organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. $[Fe(NTMS_2)_2]_2$,[1] *N*-(2-bromophenyl)-2,4,6-trimethylphenylamine,[2] *n*-octyl azide,[3] 3,5-dimethylphenyl azide,[4] phenyl azide,[4] 2,6-dichlorophenyl azide[4] and adamantly azide[5] were prepared according to literature methods. All chemicals were purchased from either Strem or J&K Chemical Co. and used as received unless otherwise noted. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a VARIAN Mercury 300 MHz or 400 MHz spectrometer. All chemical shifts were reported in δ units with references to the residual protons of the deuterated solvents for proton chemical shifts, the ^{13}C of deuterated solvents for carbon chemical shifts, and the ^{31}P of the 85% H_3PO_4. MALDI/DHB Mass spectra were recorded with an IonSpec 4.7 Tesla FTMS spectrometer. GC/MS was performed on a Shimadzu GCMS-QP2010 Plus spectrometer. Elemental analysis was performed by the Analytical Laboratory of Shanghai Institute of Organic Chemistry (CAS). Magnetic moments were measured at 23°C by the method originally described by Evans with stock and experimental solutions containing a known amount of a $(CH_3)_3SiOSi(CH_3)_3$ standard.[6,7] Infrared spectra were obtained from KBr pellets prepared in the glovebox on a Perkin-Elmer 1600 Fourier transform spectrometer.



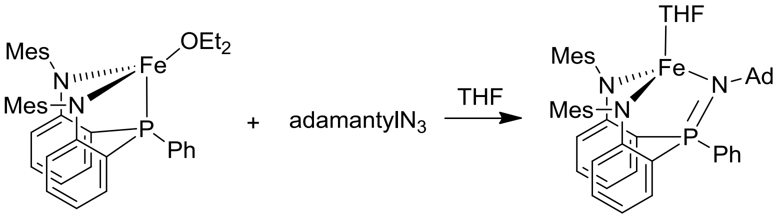
$H_2(^{Mes}N_2P)$

Preparation of Bis(*N*-mesityl-2-amidophenyl)phenylphosphine ($H_2(^{Mes}N_2P)$). To a Et_2O (20 mL) solution of *N*-(2-bromophenyl)-2,4,6-trimethylbenzenamine (1.49 g, 5.14 mmol) was added *n*-BuLi (6.4 mL, 1.6 M in *n*-hexane, 10.3 mmol) slowly at -78℃. The resulting mixture was allowed warm to room temperature and stirred for five hours. To this solution a Et_2O solution (10 mL) of $PhPCl_2$ (0.35 mL, 0.46 g, 2.57 mmol) was transferred at -78℃. The resulting mixture was allowed warm to room temperature and stirred for 16 hours. The mixture was quenched with a saturated $NaHCO_3$ aqueous solution and extracted with diethyl ether. The extracts were combined, dried with anhydrous $MgSO_4$, and concentrated to dryness under reduced pressure to afford a yellow oil. This crude product was purified via flash column chromatography (SiO_2, 200-300 mesh, CH_2Cl_2/*n*-hexanes, 1:25, as elutent) to give the ligand as a white solid (0.87 g, 64% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.96 (s, 6H, *o*-C*H*$_3$), 2.00 (s, 6H, *o*-C*H*$_3$), 2.29 (s, 6H, *p*-C*H*$_3$), 5.83 (d, $J_{\text{H-P}}$ = 5.4 H$_Z$, 2H, N*H*), 6.18-6.22 (m, 2H, C*H*), 6.68-6.71 (m, 2H, C*H*), 6.89 (s, 4H, C*H*(mesityl)), 7.05-7.16 (m, 4H, C*H*), 7.41-7.42 (m, 3H, C*H*), 7.52-7.58 (m, 2H, C*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.28, 21.10, 111.96 (d, $J_{\text{C-P}}$ = 2.6 H$_Z$), 117.18 (d, $J_{\text{C-P}}$ = 6.0 H$_Z$), 118.32 (d, $J_{\text{C-P}}$ = 3.2 H$_Z$), 128.92 (d, $J_{\text{C-P}}$ = 7.2 H$_Z$), 129.27, 130.78, 133.07 (d, $J_{\text{C-P}}$ = 5.3 H$_Z$), 134.31, 134.49, 134.56, 135.47, 135.64 (d, $J_{\text{C-P}}$ = 1.5 H$_Z$), 135.96 (d, $J_{\text{C-P}}$ = 1.5 H$_Z$), 149.33 (d, $J_{\text{C-P}}$ = 8.3 H$_Z$). ^{31}P NMR (162 MHz, $CDCl_3$): δ -32.9. HRMS-TOF (*m/z*): $[M+H]^+$ calcd for $C_{36}H_{38}N_2P$, 529.2773; found: 529.2763.



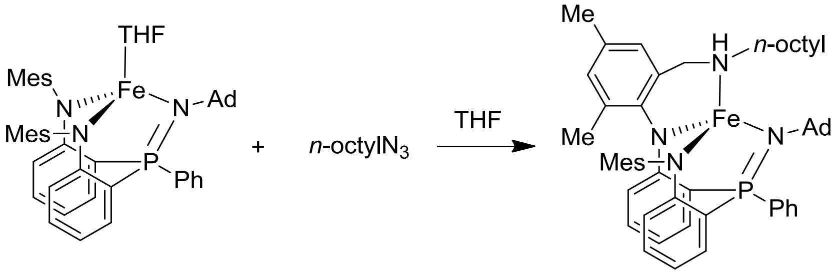
1

Preparation of [($^{\text{Mes}}$N$_2$P)Fe(OEt$_2$)] (1). Bis(*N*-mesityl-2-amidophenyl)phenylphosphine (52.9 mg, 0.10 mmol) was dissolved in THF (15 mL). To this solution was added $[Fe(NTMS_2)_2]_2$ (38 mg, 0.05 mmol) at room temperature. The reaction mixture was stirred overnight providing a red solution. After filtration, the filtrate was concentrated to dryness under reduced pressure to afford a red solid. This solid was dissolved in diethyl ether (6 mL) and then *n*-hexane (1 mL) was added. Slow evaporation of diethyl ether afforded **1** as a red crystalline solid (0.038 g, 58% yield). The ^{1}H NMR spectrum of this paramagnetic complex displayed 12 characteristic peaks in the range -150 to +150 ppm in d$_8$-THF. ^{1}H NMR (300 MHz, d$_8$-THF): δ -57.59, -42.70, -33.83, -3.17, 14.64, 20.18, 31.87, 35.05, 39.13, 40.56, 49.79, 50.53. Dissolution of **1** in C_6D_6 also gave a red solution which showed similar ^{1}H NMR spectrum as that of **1** in d$_8$-THF. ^{1}H NMR (300 MHz, C_6D_6): δ -58.60, -44.16, -35.69, -4.62, 13.30, 16.66, 18.50, 35.10, 39.54, 43.98, 54.21, 55.84. Magnetic susceptibility (C_6D_6): μ_{eff} = 4.9(1) μ_B. Anal. Calcd for $C_{40}H_{45}FeN_2OP$: C, 73.17; H, 6.91; N, 4.27. Found: C, 73.07; H, 7.34; N, 4.26%. IR (KBr, cm^{-1}): ν = 2970.6 (w), 2914.1 (w), 2855.1 (w), 1583.8 (m), 1539.2 (w), 1454.3 (m), 1432.0 (s), 1378.7 (w), 1311.8 (m), 1273.0 (m), 1199.6 (w), 1152.7 (w), 1119.3 (m), 1072.8 (w), 1033.2 (w), 875.2 (w), 857.9 (w), 746.0 (m), 694.6 (w).



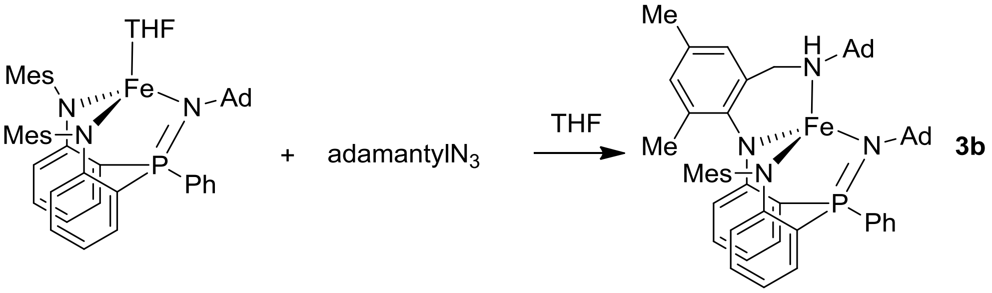
2

Preparation of [($^{Mes}N_2PN^{Ad}$)Fe(THF)] (2). Solid **1** (65.7 mg, 0.10 mmol) was dissolved in THF (15 mL). To this red solution was added AdN_3 (18 mg, 0.1 mmol) with N_2 gas evolution at room temperature. The resulting mixture was stirred overnight providing a yellow-brown solution. After filtration, the filtrate was concentrated to dryness under reduced pressure to afford a yellow-brown solid. This solid was washed by diethyl ether (15 mL) to produce **2** as a yellow solid (0.062 g, 77%). Single-crystals suitable for X-ray diffraction study were obtained standing its saturated THF solution at room temperature for 2 days. ^1H NMR (300 MHz, C_6D_6): δ -54.49, -21.00, -6.13, -4.79, -3.82, -3.17, -2.72, -1.28, 5.46, 35.36, 37.99, 45.94, 49.20, 81.53. Magnetic susceptibility (d_8-THF): μ_{eff} = 5.0(2) μ_B. Anal. Calcd for $C_{50}H_{58}FeN_3OP$: C, 74.71; H, 7.27; N, 5.23. Found: C, 74.30; H, 7.34; N, 5.04%. IR (KBr, cm^{-1}): ν = 2904.9 (s), 2848.0 (m), 2111.6 (w), 1585.8 (s), 1540.3 (w), 1462.4 (s), 1429.1 (s), 1373.3 (w), 1320.8 (m), 1302.7 (m), 1276.6 (m), 1203.8 (w), 1163.7 (w), 1151.6 (m), 1097.5 (m), 1067.9 (m), 1024.7 (w), 936.3 (w), 877.2 (w), 856.1 (w), 775.1 (w), 745.6 (s), 715.9 (w), 697.3 (w), 648.0 (w), 632.3 (w).



3a

Preparation of 3a. Solid **2** (80.4 mg, 0.10 mmol) was dissolved in THF (15 mL). To this yellow solution was added *n*-octyl azide (16 mg, 0.10 mmol) with N_2 gas evolution at the room temperature. The resulting mixture was stirred for five hours providing a brown solution. After filtration, the filtrate was concentrated to dryness under reduced pressure to afford a brown solid. This solid was washed with diethyl ether (10 mL) to produce some yellow solid. This yellow solid was dissolved in THF (6 mL) and toluene (1 mL) was added. Slow evaporation of THF afforded **3a** as a yellow crystalline solid (0.050 g, 58% yield). ^1H NMR (400 MHz, d_8-THF): δ. -47.35, -44.61, -9.40, -6.13, -5.40, -3.60, -1.45, -0.40, -0.18, 0.09, 2.3, 2.59, 3.24, 4.97, 7.16, 7.74, 8.27, 10.44, 13.74, 15.58, 21.51, 24.91, 27.31, 32.87, 35.91, 37.39, 38.13, 39.74, 59.29. Magnetic susceptibility (d_8-THF): μ_{eff} = 5.1(2) μ_B。 Anal. Calcd for $C_{54}H_{67}FeN_4P$: C, 75.51; H, 7.86; N, 6.52. Found: C, 75.53; H, 7.98; N, 5.87%. IR (KBr, cm^{-1}): ν = 3254.6 (w), 2907.3 (s), 2849.0 (m), 1584.0 (m), 1535.4 (w), 1461.1 (s), 1431.1 (s), 1376.3 (w), 1330.8 (m), 1299.8 (w), 1260.1 (w), 1205.0 (w), 1152.4 (m), 1097.8 (m), 1061.3 (w), 1025.2 (m), 939.7 (w), 871.7 (m), 847.6 (w), 813.6 (w), 745.2 (m), 712.0 (w), 624.3 (w).



Preparation of 3b. Solid **2** (80.4 mg, 0.10 mmol) was dissolved in THF (15 mL). To this yellow solution was added AdN_3 (18 mg, 0.1 mmol) at the room temperature. The resulting mixture was stirred for one day providing a brown solution, no obvious N_2 gas evolution was observed. After filtration, the filtrate was concentrated to dryness under reduced pressure to afford a brown oil. This oil was extracted with diethyl ether and filtered. The filtrate was collected. Slow evaporation of diethyl ether afforded the product as a yellow brown crystalline solid (0.022 g, 25% yield). ^{1}H NMR (400 MHz, C_6D_6): δ -71.73, -48.83, -47.72, -44.86, -40.75, -39.90, -22.62, -20.21, -16.67, -10.42, -10.35, -9.50, -7.45, -5.89, -5.22, -3.75, -2.64, -1.02, 1.60, 1.99, 2.14, 2.46, 3.07, 4.32, 4.44, 8.74, 9.67, 10.90, 14.23, 21.44, 23.70, 25.55, 26.64, 27.61, 29.15, 30.08, 30.93, 31.82, 32.73, 35.09, 36.64, 38.86, 39.21, 41.99, 44.72, 45.55, 49.19, 49.73, 61.33, 117.13, 121.95. Magnetic susceptibility (C_6D_6): μ_{eff} = 5.0(3) μ_B。Anal. Calcd for $C_{56}H_{65}FeN_4P$: C, 76.35; H, 7.44; N, 6.36. Found: C, 75.51; H, 7.61; N, 5.88%. IR (KBr, cm^{-1}): ν = 3234.0 (w), 2908.2 (s), 2847.5 (m), 2087.0 (w), 1584.3 (m), 1536.0 (w), 1469.9 (s), 1428.5 (s), 1373.9 (w), 1335.9 (m), 1316.8 (m), 1306.1 (m), 1282.6 (m), 1260.3 (m), 1208.7 (w), 1186.1 (w), 1154.9 (w), 1117.3 (m), 1094.3 (m), 1064.9 (w), 1018.6 (m), 970.4 (w), 938.0 (w), 900.8 (w), 873.3 (w), 856.4 (w), 813.8 (w), 745.9 (m), 713.1 (w), 702.0 (w), 674.5 (w), 621.6 (w).

X-ray Structure Determination. All single crystals were immersed in Paraton-N oil and sealed under N_2 in thin-walled glass capillaries. Data were collected at 140 K on a Bruker AXSD8 X-ray diffractometer using Mo-Kα radiation. An empirical absorption correction was applied using the SADABS program.[8] All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least squares calculations on F^2 using the SHELXTL program package.[9] All hydrogen atoms were geometrically fixed using the riding model. Crystal data and details of data collection and structure refinements for the four complexes (CCDC 920392-920395) are given in Table S1.

2. References

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(8) G. M. Sheldrick, SADABS: Program for Empirical Absorption Correction of Area Detector Data. University of Göttingen: Germany, 1996.

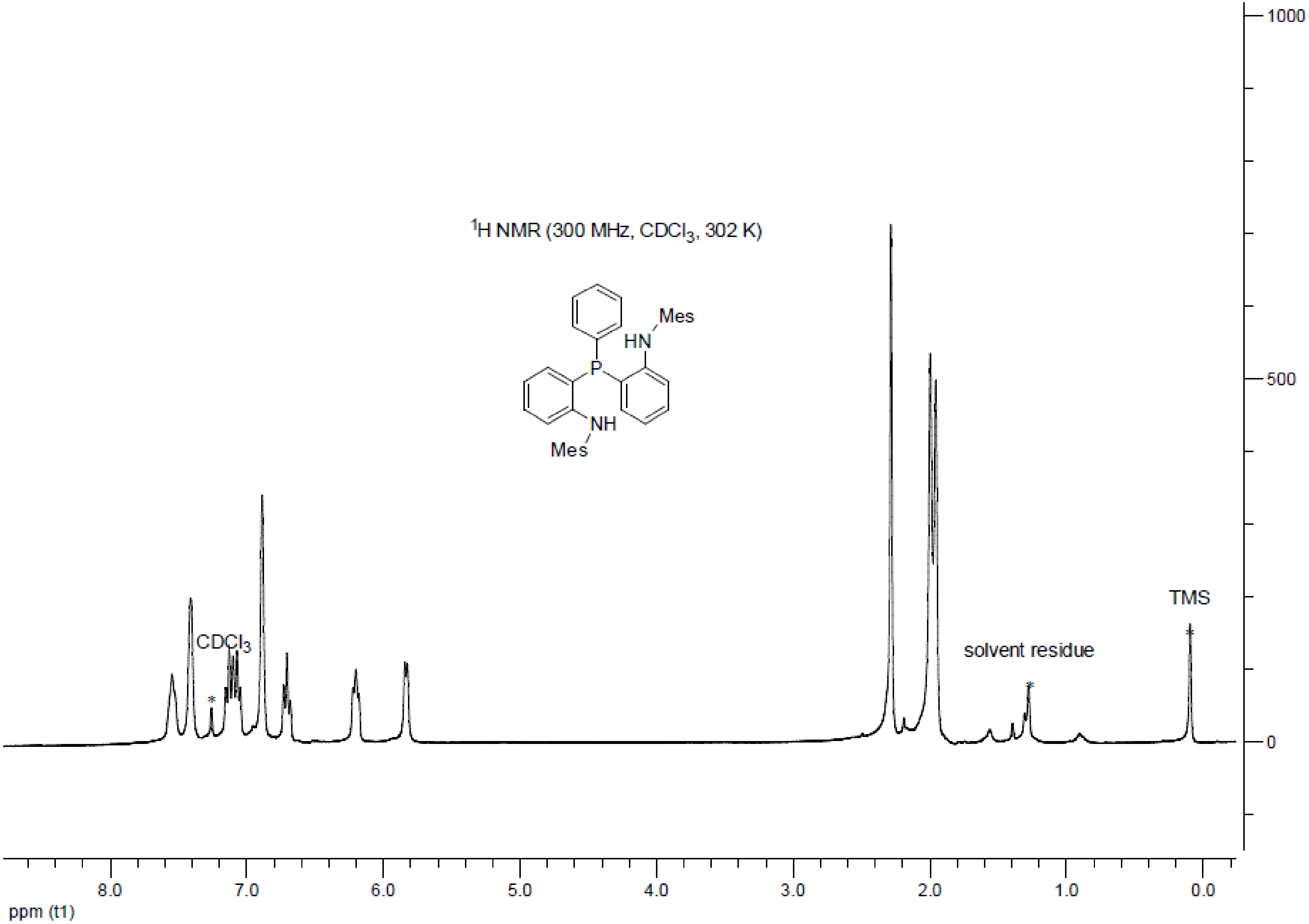
(9) G. M. Sheldrick, SHELXTL 5.10 for Windows NT: Structure Determination Software Programs. Bruker Analytical X-ray systems, Inc.: Madison, Wisconsin, USA, 1997.

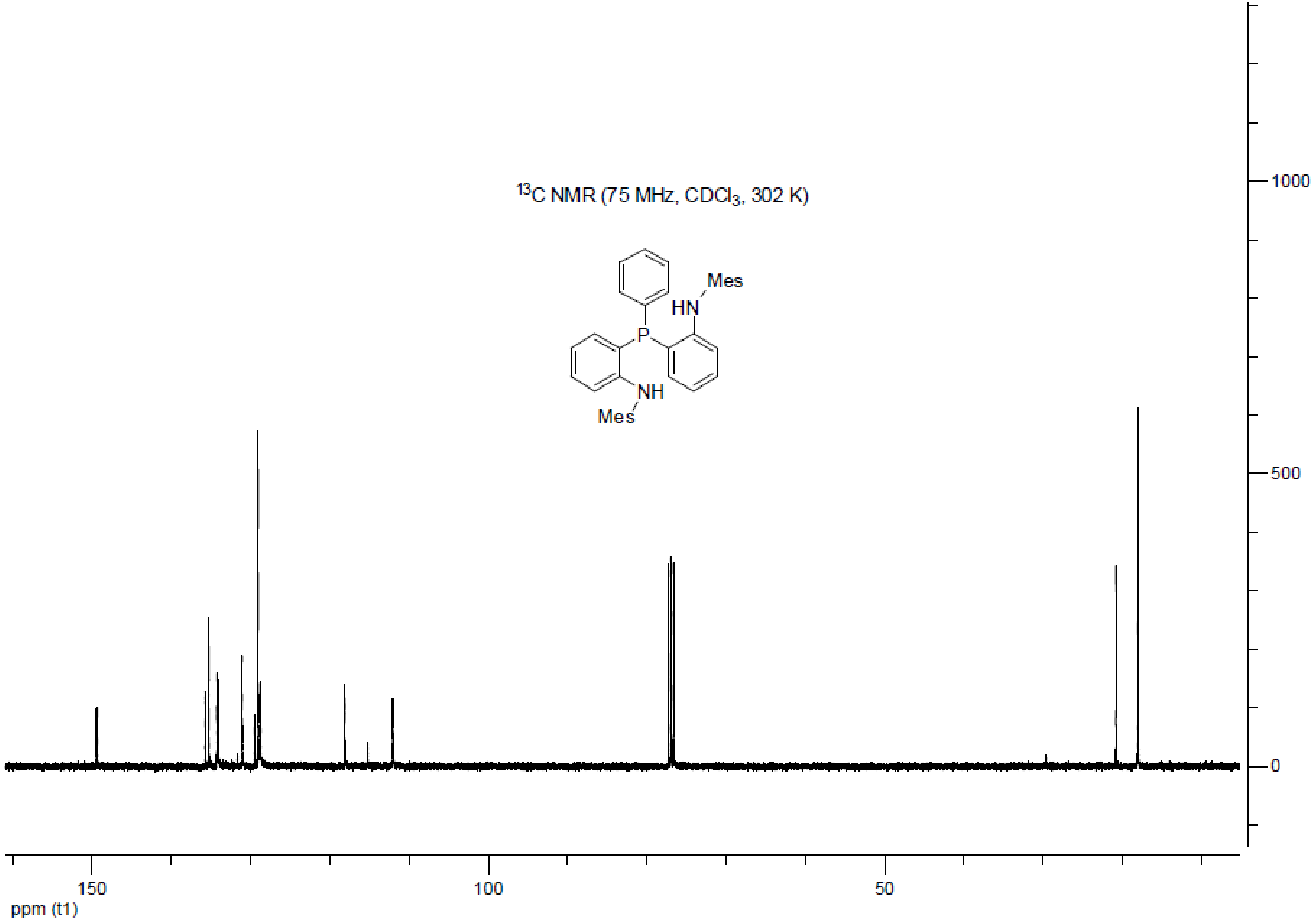
3. Table S1. Crystal Data and Summary of Data Collection and Refinement for 1-3b [a,b]

	1	**2**	**3a**	**3b**
formula	$C_{40}H_{45}FeN_2OP$	$C_{50}H_{58}FeN_3OP$	$C_{54}H_{67}FeN_4P$	$C_{56}H_{65}FeN_4P$
fw	656.60	803.81	858.94	880.94
crystal system	Triclinic	monoclinic	Triclinic	monoclinic
space group	*P*-1	*P*2(1)/n	*P*-1	*P*2(1)/n
a, Å	9.408(3)	9.7956(2)	10.748(3)	12.817(3)
b, Å	12.257(4)	17.045(3)	15.275(4)	16.341(3)
c, Å	16.542(5)	24.724(4)	16.494(4)	22.588(5)
α, deg	83.632(5)	90	93.069(5)	90
β, deg	85.283(5)	96.057(3)	105.735(4)	101.303(4)
γ, deg	72.234(5)	90	106.566(5)	90
V, Å^3	1802.9(1)	4104.9(1)	2473.1(1)	4639.3(2)
Z	2	4	2	4
d_{calcd}, g/cm^3	1.209	1.301	1.153	1.261
2θ range, deg	2.5 to 50.1	4.1-61.4	4.1-54.0	3.1-54.0
GOF (F^2)	1.061	0.962	1.017	0.971
R1^{b}	0.0456,^{d} 0.0535^{e}	0.0559,^{d} 0.1116^{e}	0.0648,^{d} 0.1139^{e}	0.0583,^{d} 0.1139^{e}
*W*R2^{c}	0.1427,^{d} 0.1655^{e}	0.1256,^{d} 0.1489^{e}	0.1565,^{d} 0.1823^{e}	0.1183,^{d} 0.1387^{e}

[a] Collected using Mo Kα radiation ($\lambda = 0.71073$ Å). [b] $R1 = \Sigma[(F_o - F_c)] / \Sigma(F_o)$. [c] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2 / \Sigma[w(F_o^2)^2]]^{1/2}$. [d] $I > 2\sigma(I)$. [e] All data.

4. NMR Spectra of the Bis(anilido)phosphine Ligand and Complexes 1-3b

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NH
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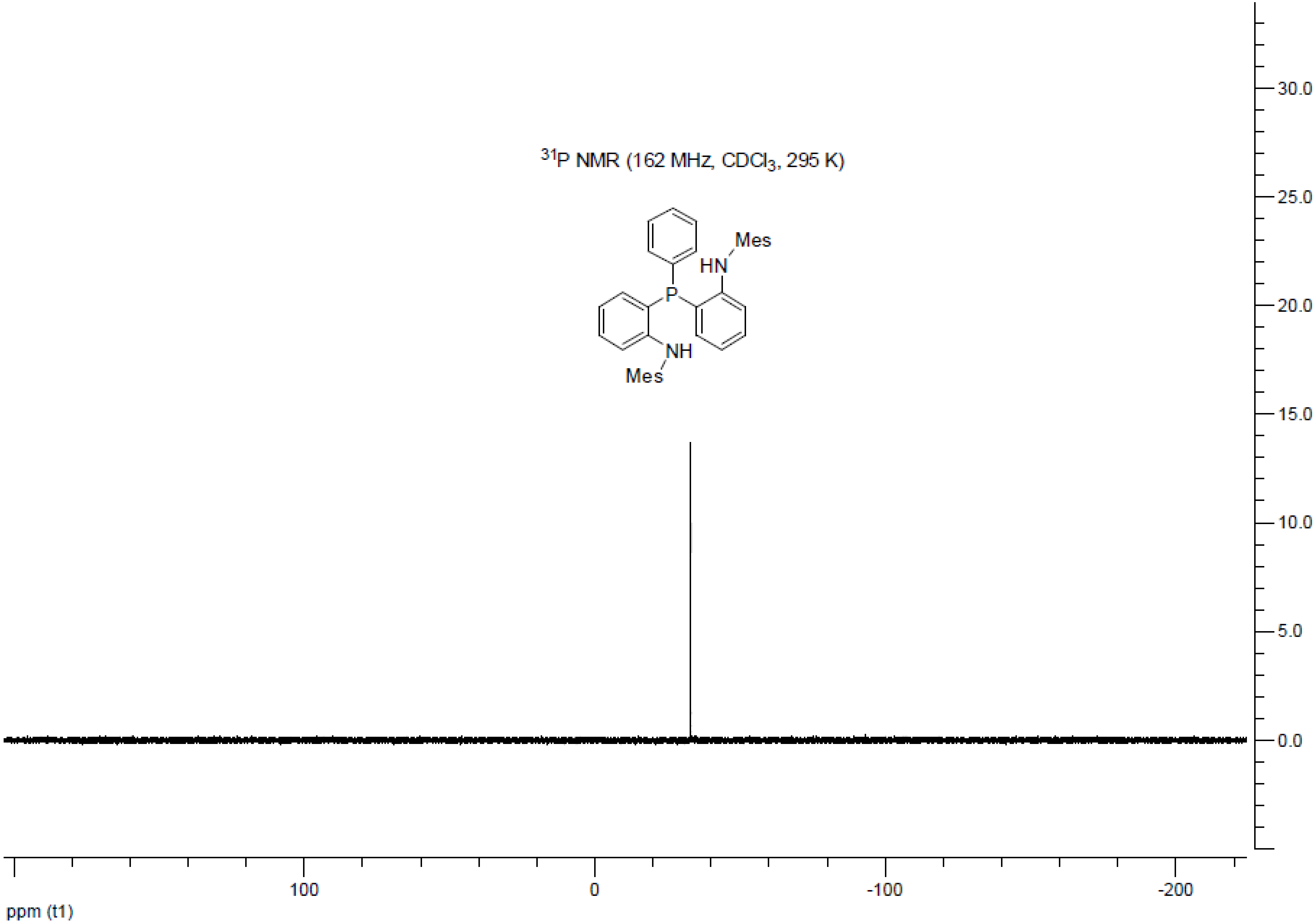
100
50
ppm (t1)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NH
Mes
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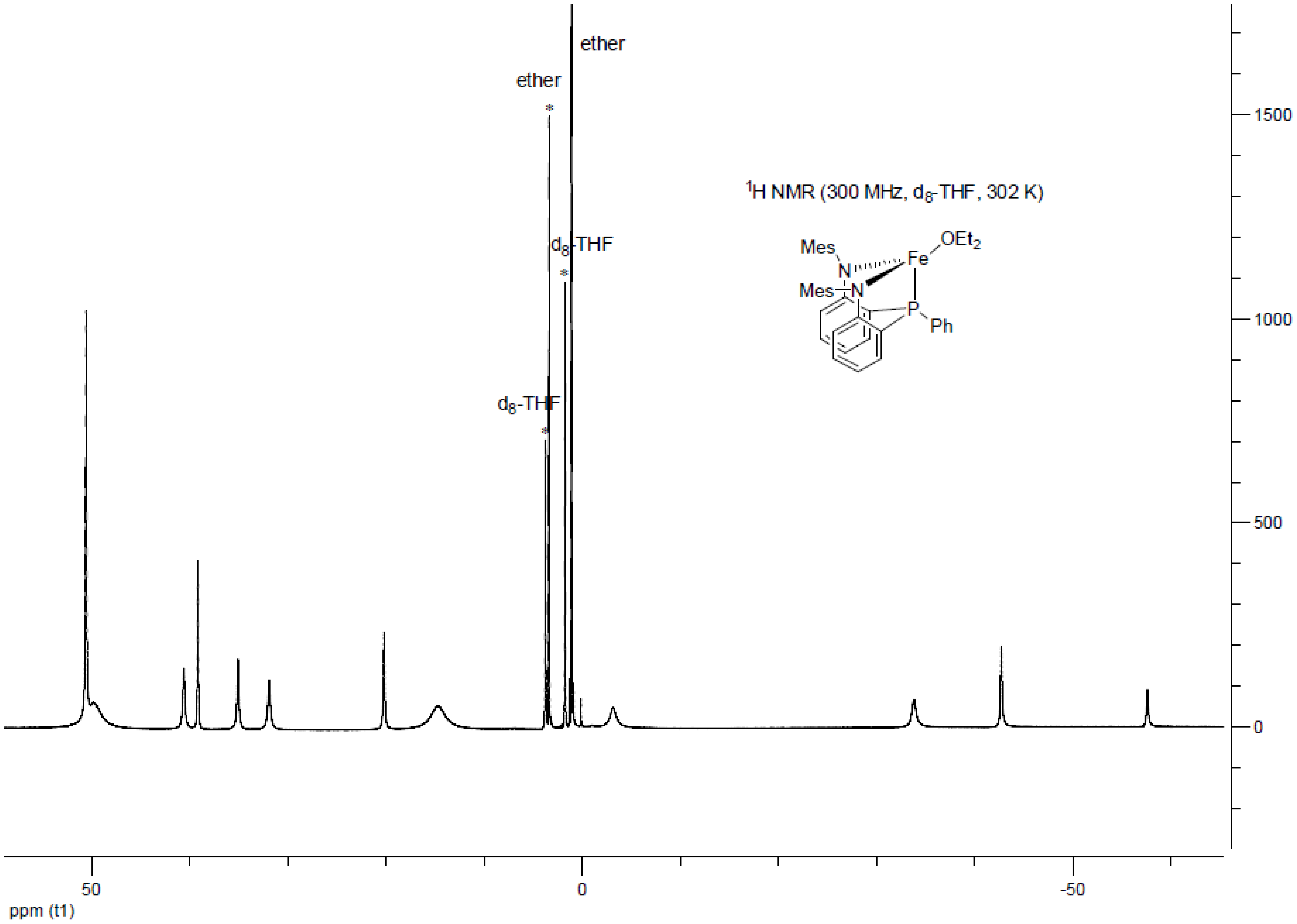
100
0
-100
-200
ppm (t1)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d8-THF
*
d8-THF
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0
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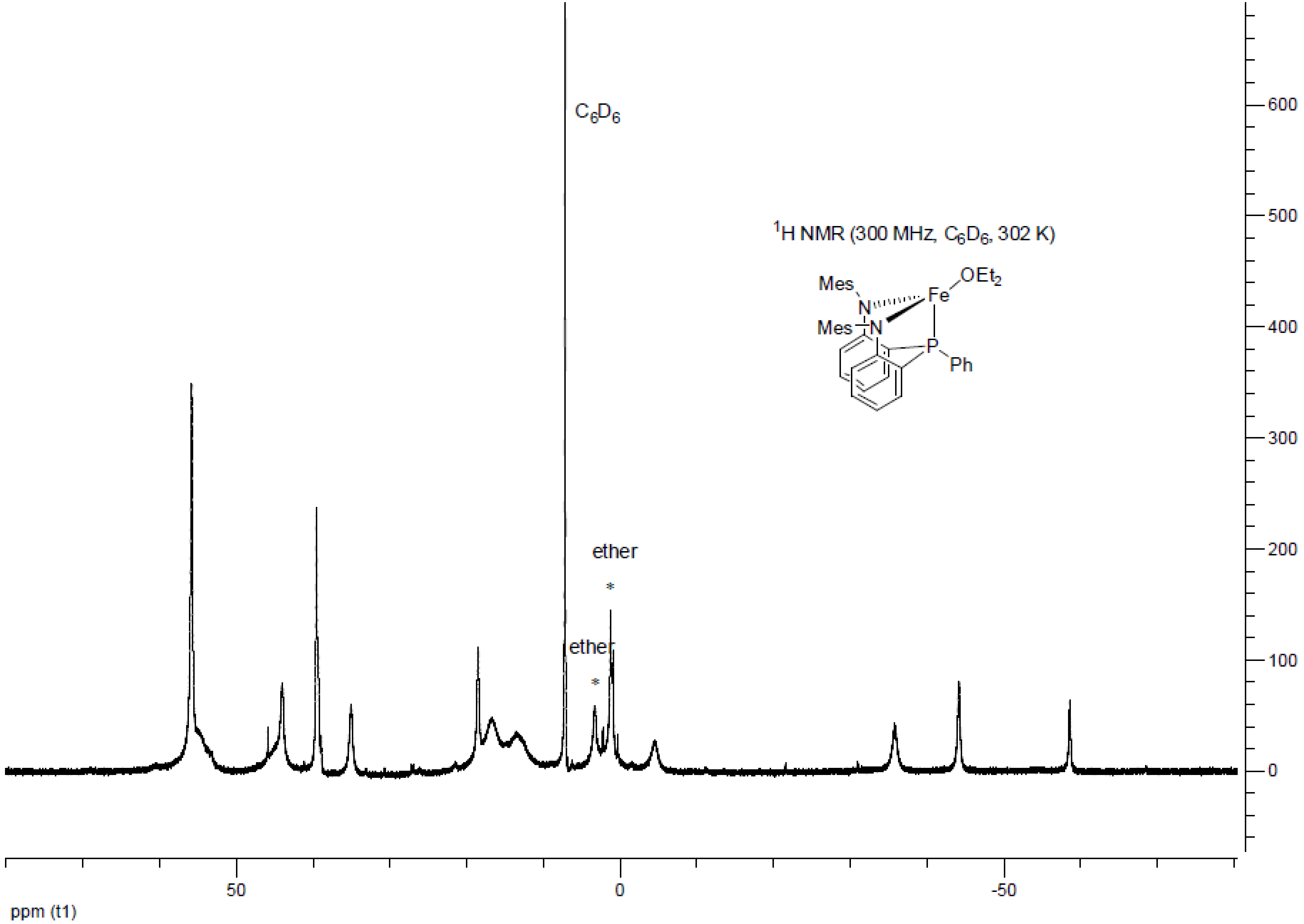
ppm (t1)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Fe
OEt2
Mes
N
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ether
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400
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0
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0
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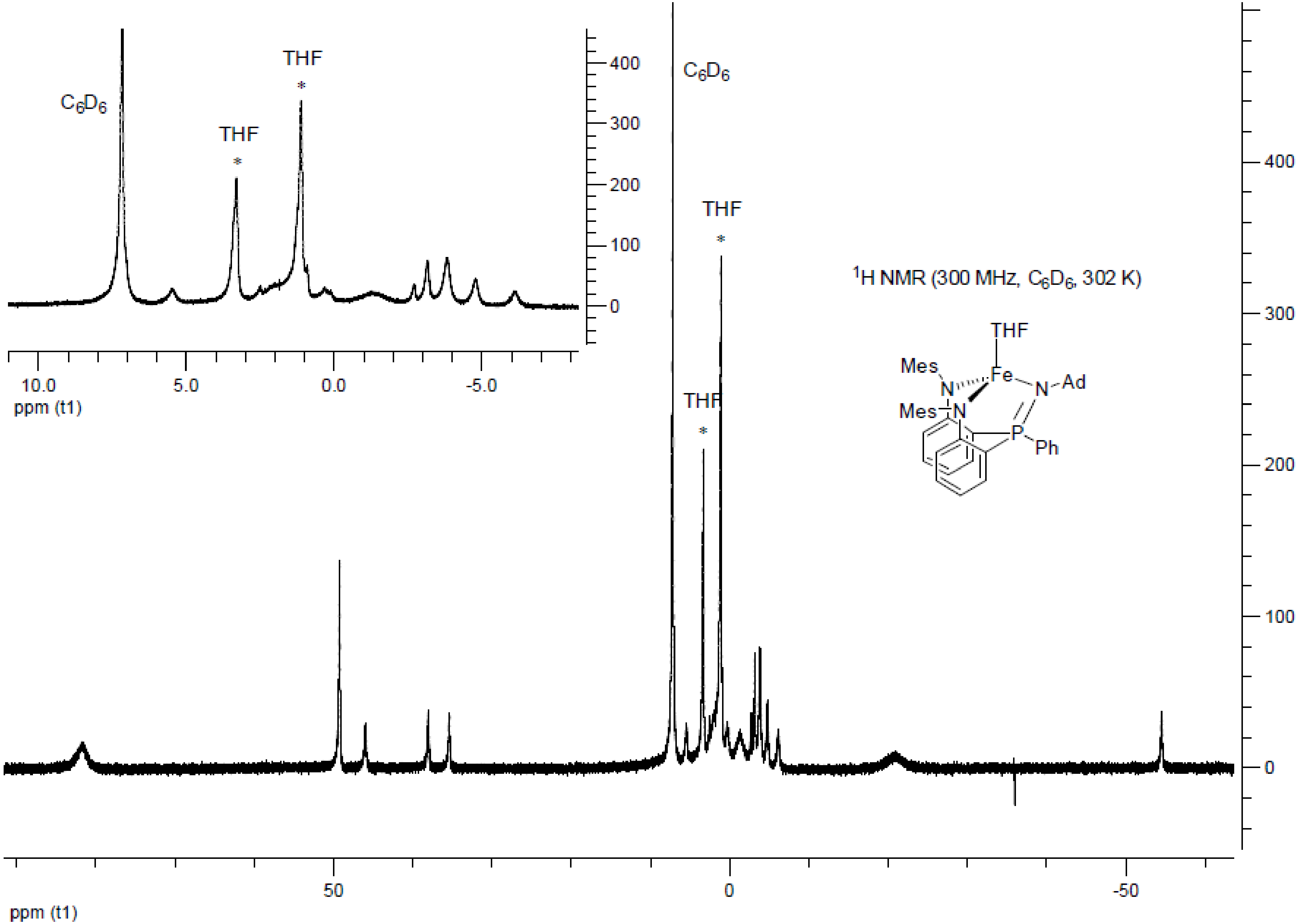
ppm (t1)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THF
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ppm (t1)
C$_6$D$_6$
THF
*
THF
*
^{1}H NMR (300 MHz, C$_6$D$_6$, 302 K)
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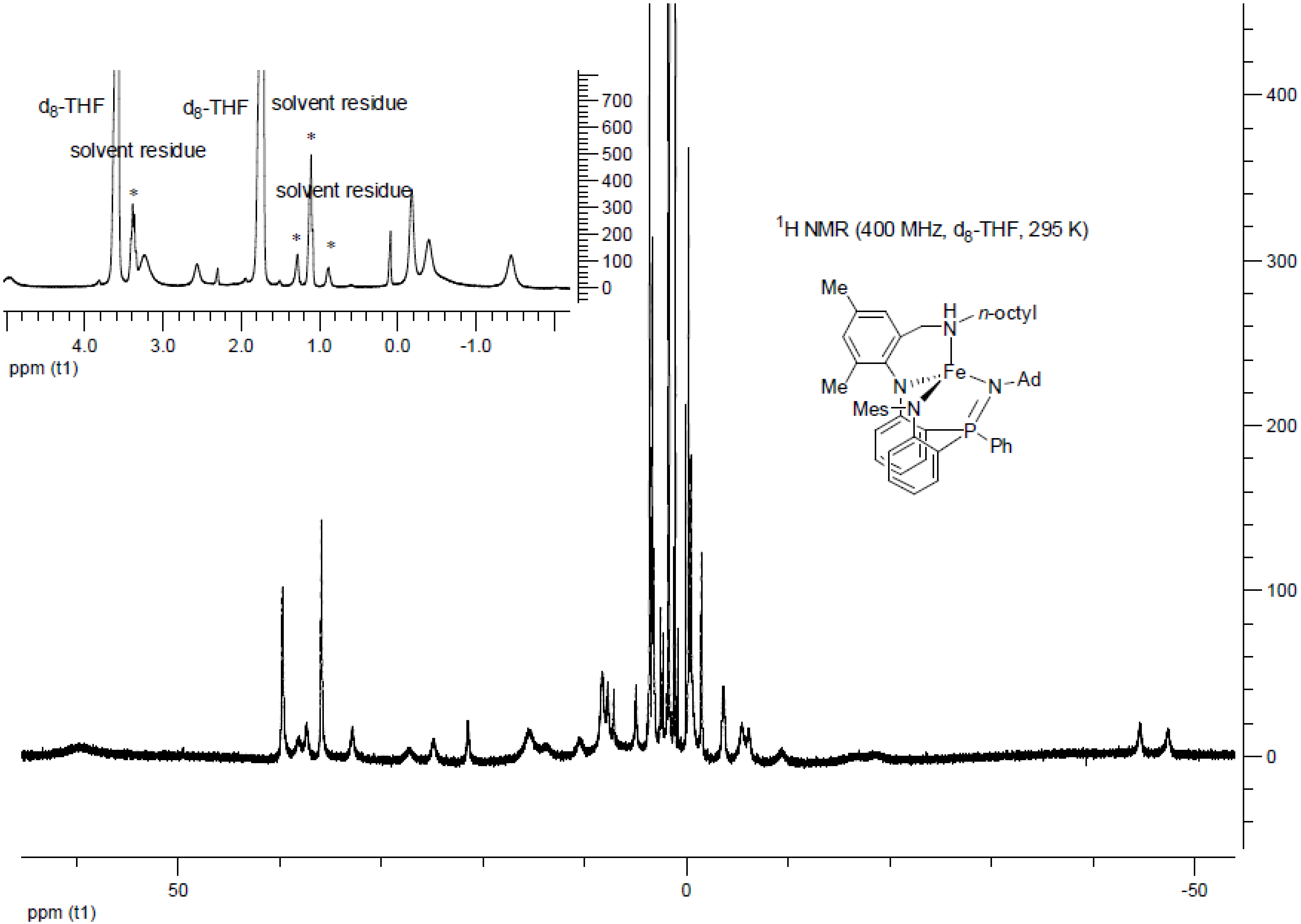
ppm (t1)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d8-THF
solvent residue
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*
*
solvent residue
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ppm (t1)
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Me
H
N
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Fe
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Ad
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Mes
N
P
Ph
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200
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0
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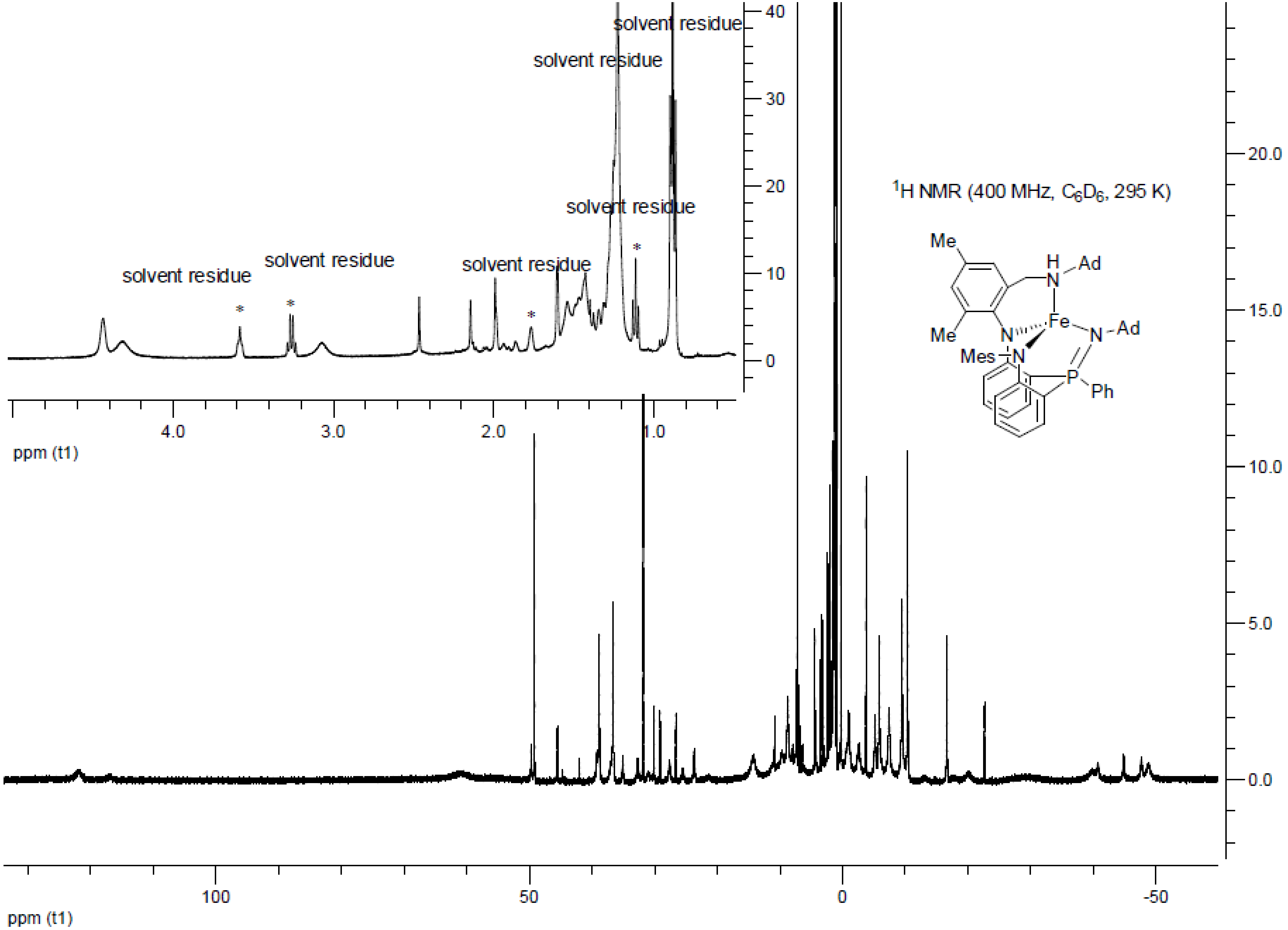
ppm (t1)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solvent residue
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solvent residue
solvent residue
solvent residue
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2.0
1.0
ppm (t1)
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Me
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N
Ad
Fe
N
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Mes
N
P
Ph
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15.0
10.0
5.0
0.0
100
50
0
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ppm (t1)