Communications.

Electronic Supplementary Information

Regioselective magnesiation of N-heterocyclic molecules: securing insecure cyclic anions by a β-diketiminate-magnesium clamp

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Experimental Section

General remarks

All the experiments were performed under a protective argon inert atmosphere and using standard Schlenk techniques. The use of a glove-box has also been required for some manipulations. Hexane, toluene and THF were dried by heating to reflux over sodium benzophenone ketyl and distilled under nitrogen prior to use. The [(^{Dipp}Nacnac)Mg(TMP)] (^{Dipp}Nacnac = Ar*NC(Me)CHC(Me)NAr*; Ar* = 2,6-^{i}Pr$_2$-C$_6$H$_3$ and TMP = 2,2,6,6-tetramethylpiperidide) base **1** was synthesized according to a literature method.[1] All reagents were purchased from Sigma-Aldrich (pyrazine and 2-picoline), Alfa Aesar (1-methyl-1,2,4-triazole) or Fluorochem (2-(2,4-difluorophenyl)pyridine) and were dried before use where applicable. 1,5-Diphenyl-1,2,3-triazole was synthesised according to a literature method.[2]

All NMR spectra were recorded on a Bruker AV3 or AV 400 MHz, or on an AV 600 MHz spectrometer, operating at 400.13 MHz for ^{1}H, 100.61 MHz for ^{13}C and 376.40 MHz for ^{19}F. All ^{13}C NMR spectra were proton-decoupled. The NMR assignments were performed, in some cases, with the help of ^{1}H,^{13}C-HSQC, COSY, DOSY and HMBC experiments. ^{1}H and ^{13}C{^{1}H} chemical shifts are expressed in parts per million (δ, ppm) and referenced to residual solvent peaks. Elemental analyses were performed using a Perkin Elmer 2400 elemental analyzer.

X-ray crystallography

Data for samples **2**, **3** and **4** were collected on Oxford Diffraction Gemini S or Xcalibur E instruments with graphite-monochromated Mo Kα (λ = 0.71073 Å) or Cu Kα (λ = 1.54180 Å) radiation. Data for samples **5** and **6** were measured at Beamline I19 of the Diamond Light Source synchrotron radiation source using 0.6889 Å radiation and a custom-built three-circle diffractometer with Pilatus 2M detector; data collection and processing used Diamond in-house and Bruker APEX3 software. All structures were solved and refined to convergence on F^2 for all independent

reflections by the full-matrix least squares method using SHELXL-2014/7[3,4] or by the Gauss-Newton algorithm using OLEX2.[5] Selected crystallographic data are shown in Table S1 and full details in .cif format are available from the CCDC (1519748-1519752).

Table S1: Selected crystallographic and refinement parameters.

	2	**3**	**4**	**5**	**6**
Empirical formula	$C_{73}H_{96}Mg_2N_8$	$C_{93}H_{110}Mg_2N_{10}$	$C_{32}H_{45}MgN_5$	$C_{74}H_{102}Mg_2N_6O$	$C_{44}H_{55}F_2MgN_3O$
Mol. Mass	1134.2	1416.5	524.0	1140.2	704.2
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a/ Å	10.7648(8)	15.3537(5)	11.5906(4)	12.3525(7)	9.2553(9)
b/ Å	12.8654(11)	14.2772(5)	15.2013(6)	12.4080(8)	12.7671(13)
c/ Å	13.4034(12)	19.1707(8)	17.8446(7)	22.7369(14)	16.8484(16)
□	96.729(7)	90.00	90.00	101.488(3)	84.318(2)
□	109.851(8)	104.615(4)	98.976(4)	92.550(3)	82.946(2)
□	103.994(7)	90.00	90.00	93.804(3)	86.524(2)
V/ Å^3	1653.3(2)	4066.4(3)	3105.6(2)	3401.6(4)	1963.7(3)
Z	1	2	4	2	2
□□□Å	0.71073	0.71073	1.54180	0.6889	0.6889
□□mm	0.084	0.082	0.693	0.079	0.086
2□ma	54.0	58.7	145.86	51.0	51.2
Measured reflections	13766	25760	21057	42336	16112
Unique reflections	9992	10388	6086	13767	8089
R_{int}	0.0776	0.0280	0.0226	0.0635	0.0442
Observed rflns [I>2□□□	4313	7675	5378	9222	6867
GooF	1.082	1.026	1.040	1.066	1.119
R [on *F*, obs rflns only]	0.0776	0.0453	0.0419	0.0561	0.0477
□ on F^2, all data]	0.2400	0.1183	0.1150	0.1595	0.1275
Largest diff. Peak/hole. e/ Å^{-3}	0.509/-0.367	0.276/-0.238	0.269/-0.204	0.432/-0.388	0.370/-0.390

Synthesis of compounds

Synthesis of [{(^{Dipp}Nacnac)Mg($C_4H_3N_2$)}$_2$] (2)

To a solution of compound **1** (0.56 g, 1 mmol) in THF (10 mL), pyrazine (0.08 g, 1 mmol) was added. An immediate colour change from yellow to dark green was noted, and the solution was stirred for 2 hours at room temperature. The solvent was removed and 5 mL of toluene was added. The resulting suspension was heated to give a clear solution and was left to cool in a hot water bath. This yielded the title compound after 24 hours as a light brown crystalline solid that was isolated and placed in a glove-box. In order to obtain a good yield of the compound, after 4 hours of reaction the solvent was removed and 10 mL of hexane was added, giving a dark brown suspension. The resulting solid was isolated and placed in a glove-box (0.27 g, 51-%).

^{1}H NMR (400.13 MHz, C_6D_6, 298 K) δ 9.29-9.28 [d, 2H, *J* = 1.9 Hz, $C_4H_3N_2$], 8.78-8.77 [dd, 2H, *J* = 1.6 Hz, *J* = 2.9 Hz, $C_4H_3N_2$], 7.96-7.95 [d, 2H, *J* = 3.0 Hz, $C_4H_3N_2$], 7.01 [br. s, 8H, Ar* of ^{Dipp}Nacnac], 6.86-6.84 [m, 4H, Ar* of ^{Dipp}Nacnac], 4.88 [s, 2H, C*H* of ^{Dipp}Nacnac], 3.88-3.80 [sept, 4H, *J* = 6.8 Hz, C*H*, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 2.56-2.44 [m, 4H, C*H*, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 1.62 [s, 12H, CH_3 of ^{Dipp}Nacnac], 1.56-1.54 [d, 12H, *J* = 6.8 Hz, CH_3, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 1.22-1.20 [d, 12H, *J* = 6.7 Hz, CH_3, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 0.97-0.96 [d, 12H, *J* = 6.8 Hz, CH_3, ^{i}Pr, Ar* of ^{Dipp}Nacnac],-0.55--0.58 [d, 12H, *J* = 6.8 Hz, CH_3, ^{i}Pr, Ar* of ^{Dipp}Nacnac].

^{13}C NMR {^{1}H} (100.61 MHz, C_6D_6, 298 K) δ 169.5 [C_q, CH*C*(Me) of ^{Dipp}Nacnac], 158.0 [*C*H of $C_4H_3N_2$], 145.8 [C_q, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 145.1 [*C*H of $C_4H_3N_2$], 142.9 [C_q, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 142.2 [*C*H of $C_4H_3N_2$], 141.8 [C_q, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 124.3 [*C*H, Ar* of ^{Dipp}Nacnac], 124.2 [*C*H, Ar* of ^{Dipp}Nacnac], 123.4 [*C*H, Ar* of ^{Dipp}Nacnac], 94.0 [*C*H of ^{Dipp}Nacnac], 32.1 [*C*H, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 32.0 [*C*H, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 30.0 [*C*H, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 28.1 [*C*H, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 25.2 [*C*H_3, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 24.5 [*C*H_3 of ^{Dipp}Nacnac], 24.3 [*C*H_3, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 23.8 [*C*H_3,

^{i}Pr, Ar* of ^{Dipp}Nacnac], 23.5 [*C*H$_3$, ^{i}Pr, Ar* of ^{Dipp}Nacnac], (C$_q$ of *C*-Mg was not possible to assign).

Elemental analysis: (C$_{66}$H$_{88}$Mg$_2$N$_8$) *Calculated:* C: 76.07 % H: 8.51 % N: 10.75 %. *Found:* C: 75.81 % H: 8.81 % N: 9.81 %.

Reaction of [(^{Dipp}Nacnac)Mg(Bu)(THF)] with pyrazine – DOSY NMR studies

In a J. Young's NMR tube, pyrazine (20 µL of a 1.78 M solution of pyrazine in C_6D_6, 0.035 mmol) was added to a solution of [(^{Dipp}Nacnac)Mg(Bu)(THF)] (0.020 g, 0.035 mmol) in C_6D_6 (0.6 mL). The solution changed colour to brown. 5 µL of TMS (tetramethylsilane) was added in order to use as internal standard in the DOSY experiment.[6] (Table S2)

^{1}H NMR (400.13 MHz, C_6D_6, 298 K) δ 8.14 [br s, 4H, $C_4H_4N_2$], 7.16 [br s, 6H, Ar* of ^{Dipp}Nacnac], 4.86 [br s, 1H, C*H* of ^{Dipp}Nacnac], 3.18 [br s, 4H, C*H*, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 2.01-0.66 [br m, 60H, CH_3 of ^{Dipp}Nacnac and Bu], -0.29 [br s, 2H, Mg-CH_2 of Bu].

Table S2: Possible species formed in C_6D_6 and the corresponding diffusion coefficients (D), molecular weights (MW), and errors.

Compound	D	MW_{calc} (g mol^{-1})	MW_{est} (g mol^{-1})	Error (%)
pyrazine	1.373E-9	80	151	47
[(^{Dipp}Nacnac)Mg(Bu)($C_4H_4N_2$)]	5.7503E-10	579	615	6
[(^{Dipp}Nacnac)Mg(Bu)(THF)]	5.7503E-10	571	615	7

The diffusion coefficient of pyrazine indicates a molecular weight of 151 g mol^{-1}, 47% larger than free pyrazine. This result is consistent with the formation of a pyrazine adduct undergoing rapid solvation/desolvation.

Synthesis of [{(^{Dipp}Nacnac)Mg($C_{14}H_{10}N_3$)}$_2$] (3)

To a solution of **1** (0.28 g, 0.5 mmol) in THF (5 mL), 1,5-dipphenyl-1,2,3-triazole (0.11 g, 0.5 mmol) was added. The yellow solution was stirred for 3 hours at room temperature; a precipitate appeared after this time. The solvent was removed and 10 mL of toluene was added. The resulting suspension was heated to give a dark yellow solution and was left to cool in a hot water bath. After 48 hours a crop of colourless crystals was isolated and placed in a glove-box (0.15 g, 45-%).

^{1}H NMR (400.13 MHz, C_6D_6, 298 K) δ 7.50-7.48 [br. d, 4H, *J* = 7.2 Hz, $C_{14}H_{10}N_3$], 7.15-6.95 [m, 28H, $C_{14}H_{10}N_3$ + Ar* of ^{Dipp}Nacnac], 4.76 [s, 2H, C*H* of ^{Dipp}Nacnac], 3.83-3.72 [sept, 4H, *J* = 6.8 Hz, C*H*, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 3.10-3.00 [sept, 4H, *J* = 6.8 Hz, C*H*, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 1.59 [s, 12H, CH_3 of ^{Dipp}Nacnac], 1.25-1.23 [d, 12H, *J* = 6.8 Hz, CH_3, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 1.19-1.17 [d, 12H, *J* = 6.7 Hz, CH_3, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 1.00-0.98 [d, 12H, *J* = 6.8 Hz, CH_3, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 0.12-0.10 [d, 12H, *J* = 6.8 Hz, CH_3, ^{i}Pr, Ar* of ^{Dipp}Nacnac].

^{13}C NMR {^{1}H} (100.61 MHz, C_6D_6, 343 K) δ 168.3 [C_q, CH*C*(Me) of ^{Dipp}Nacnac], 147.2 [C_q, Ar], 147.0 [C_q, Ar], 143.3 [C_q, Ar], 143.0 [C_q, Ar], 138.7 [C_q, Ar], 130.4 [*C*H, $C_{14}H_{10}N_3$], 129.0 [*C*H, Ar], 128.8 [*C*H, Ar], 127.4 [*C*H, Ar], 124.7 [*C*H, Ar], 124.4 [*C*H, Ar], 123.6 [*C*H, Ar], 96.6 [*C*H of ^{Dipp}Nacnac], 28.5 [*C*H, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 27.6 [*C*H, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 25.2 [*C*H$_3$, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 25.1 [*C*H$_3$ of ^{Dipp}Nacnac], 24.8 [*C*H$_3$, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 24.7 [*C*H$_3$, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 24.5 [*C*H$_3$, of ^{Dipp}Nacnac], (C_q of *C*-Mg was not possible to assign).

Elemental analysis: ($C_{88}H_{102}Mg_2N_{10}$) *Calculated:* C: 77.99 % H: 7.76 % N: 10.58 %. *Found:* C: 78.36 % H: 7.89 % N: 10.17 %.

Synthesis of [{(^{Dipp}Nacnac)Mg($C_3H_4N_3$)}$_2$] (4)

To a solution of **1** (0.56g, 1mmol) in THF (10 mL), 1-methyl-1,2,4-triazole (0.075 mL, 1mmol) was added. The yellow solution was stirred for 2 hours at room temperature and a solid precipitated. The solvent was removed and 10 mL of toluene were added. The suspension was dissolved by gentle warming and was left in the fridge. After 48 hours a crop of colorless crystals were isolated and placed in a glove box. Single crystals suitable for X-Ray analysis were obtained by heating the solution and cooling it down in a hot water bath. In order to obtain a good yield of the compound, after 2 hours of reaction the solvent was removed and 10 mL of hexane was added, giving a suspension. The resulting solid was isolated and placed in a glove-box (0.35 g, 66-%).

^{1}H NMR (400.13 MHz, C_6D_6, 298 K) δ 8.10 [s, 2H, N(Me)NC*H*NC], 7.09-7.02 [m, 4H, Ar* of ^{Dipp}Nacnac], 7.02-7.00 [dd, 4H, *J* = 1.6 Hz, *J* = 7.7 Hz, Ar* of ^{Dipp}Nacnac], 6.91-6.86 [dd, 4H, *J* = 1.6 Hz, *J* = 7.5 Hz, Ar* of ^{Dipp}Nacnac], 4.77 [s, 2H, C*H* of ^{Dipp}Nacnac], 3.97 [s, 6H, N(C*H*$_3$)NCHNC], 3.66-3.59 [sept, 4H, *J* = 6.8 Hz, C*H*, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 2.79-2.72 [sept, 4H, *J* = 6.8 Hz, C*H*, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 1.54 [s, 12H, C*H*$_3$ of ^{Dipp}Nacnac], 1.44-1.42 [d, 12H, *J* = 7.0 Hz, C*H*$_3$, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 1.19-1.17 [m, 12H, *J* = 6.7 Hz, C*H*$_3$, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 1.03-1.01 [d, 12H, *J* = 6.9 Hz, C*H*$_3$, ^{i}Pr, Ar* of ^{Dipp}Nacnac], - 0.36- -0.38 [d, 12H, *J* = 6.8 Hz, C*H*$_3$, ^{i}Pr, Ar* of ^{Dipp}Nacnac].

^{13}C NMR {^{1}H} (100.61 MHz, C_6D_6, 298 K) δ 184.9 [C_q, C_α of *C*-Mg, *C*$_3$H$_4$N$_3$], 168.9 [C_q, CH*C*(Me) of ^{Dipp}Nacnac], 150.2 [*C*H of *C*$_3$H$_4$N$_3$], 145.5 [*C*, Ar* of ^{Dipp}Nacnac], 142.7 [of ^{Dipp}Nacnac], 141.7 [*C*, Ar* of ^{Dipp}Nacnac], 129.3 [*C*, Ar* of ^{Dipp}Nacnac] 125.3 [*C*H, Ar* of ^{Dipp}Nacnac], 124.4 [*C*H, Ar* of ^{Dipp}Nacnac], 123.4 [*C*H, Ar* of ^{Dipp}Nacnac], 94.4 [*C*H of ^{Dipp}Nacnac], 38.8 [*C*H$_3$ of *C*$_3$H$_4$N$_3$], 29.4 [*C*H, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 27.2 [*C*H, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 25.0 [*C*H$_3$, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 24.4 [*C*H$_3$, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 24.2 [*C*H$_3$ of ^{Dipp}Nacnac], 24.0 [*C*H$_3$, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 22.4 [*C*H$_3$, ^{i}Pr, Ar* of ^{Dipp}Nacnac].

Elemental analysis: *Calculated:* C: 73.34 %, H: 8.66 %, N: 13.36 %. *Found:* C: 73.59 %, H: 8.92 %, N: 13.68 %.

Synthesis of [{(^{Dipp}Nacnac)Mg(C_5H_6N)}$_2$] (5)

To a solution of compound **1** (0.56 g, 1 mmol) in THF (10 mL), 2-picoline (0.1 mL, 1 mmol) was added. The yellow solution turned a strong orange colour and was stirred for 2 hours at room temperature. The solvent was removed and 2 mL of hexane and 4 mL of THF were added. The resulting suspension was heated to give a clear solution and was cooled to -33 ^{o}C. This yielded the title compound after 24 hours as colourless crystals. In order to obtain a good yield of the compound, after 2 hours of reaction the solvent was removed and 10 mL of hexane was added. The suspension was heated and then cooled to -15 ^{o}C. The resulting solid was isolated after 2 days and placed in a glove-box (0.35 g, 67-%).

^{1}H NMR (600.13 MHz, C_6D_6, 298 K) δ 7.79-7.78 [d, 2H, *J* = 5.4 Hz, C_6H_6N], 7.28-7.17 [br. m, 2H, Ar* of ^{Dipp}Nacnac], 7.15-6.90 [br. m, 10H, Ar* of ^{Dipp}Nacnac], 6.45-6.40 [br. td, 2H, C_6H_6N], 5.88-5.84 [br. t, 2H, *J* = 6.2 Hz, C_6H_6N], 4.87-4.86 [br. d, 2H, *J* = 8.2 Hz, C_6H_6N], 4.82 [s, 2H, C*H* of ^{Dipp}Nacnac], 3.60 [br. m, 2H, C*H*, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 3.26 [br. m, 2H, C*H*, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 3.22 [br. m, 2H, C*H*, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 2.55 [br. m, 2H, C*H*, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 1.68 [br. s, 6H, CH_3 of ^{Dipp}Nacnac], 1.63 [br. s, 2H, CH_2 of C_6H_6N], 1.60 [br. s, 6H, CH_3 of ^{Dipp}Nacnac], 1.49 [br. m, 6H, CH_3, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 1.28 [br. s, 2H, CH_2 of C_6H_6N], 1.26-1.09 [br. m, 18H, CH_3, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 1.09-1.01 [br. m, 6H, CH_3, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 1.01-0.93 [br. m, 6H, CH_3, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 0.93-0.80 [br. m, 6H, CH_3, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 0.23 [br. m, 6H, CH_3, ^{i}Pr, Ar* of ^{Dipp}Nacnac].

^{13}C NMR {^{1}H} (150.90 MHz, C_6D_6, 298 K) δ 176.8 [C_q, CH*C*(Me) of ^{Dipp}Nacnac], 144.9 [*C*H of C_6H_6N], 135.5 [*C*H of C_6H_6N], 125.6 [*C*H, Ar* of ^{Dipp}Nacnac], 124.8 [*C*H, Ar* of ^{Dipp}Nacnac], 124.5 [*C*H, Ar* of ^{Dipp}Nacnac], 124.3 [*C*H, Ar* of ^{Dipp}Nacnac], 123.4 [*C*H, Ar* of ^{Dipp}Nacnac], 122.0 [*C*H of C_6H_6N], 110.8 [*C*H of C_6H_6N], 95.1 [*C*H of ^{Dipp}Nacnac], 35.5 [Mg-*C*H_2 of C_6H_6N], 29.3 [*C*H, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 28.7 [*C*H, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 28.0 [*C*H, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 25.7 [*C*H_3, ^{Dipp}Nacnac], 25.5 [*C*H_3, ^{Dipp}Nacnac], 25.4 [*C*H_3, ^{Dipp}Nacnac], 25.1 [*C*H_3, ^{Dipp}Nacnac], 24.9 [*C*H_3, ^{Dipp}Nacnac],

24.5[*C*H_3, ^{Dipp}Nacnac], 24.3 [*C*H_3, ^{Dipp}Nacnac], 23.8 [*C*H_3, ^{Dipp}Nacnac], 23.5 [*C*H_3, ^{Dipp}Nacnac], 14.34 [*C*H_3, ^{i}Pr, Ar* of ^{Dipp}Nacnac].

Elemental analysis: ($C_{66}H_{88}Mg_2N_8$) *Calculated:* C: 78.71 % H: 8.87 % N: 7.87 %. *Found:* C: 77.39 % H: 8.52 % N: 7.35 %.

Synthesis of [(^{Dipp}Nacnac)MgTHF($C_{11}H_6F_2N$)] (6)

To a solution of **1** (0.56 g, 1 mmol) in THF (5 mL), 2-(2,4-difluorophenyl)pyridine (0.2 g, 1mmol) was added. The dark yellow solution was stirred for 5 hours at room temperature. The solvent was removed and 1 mL of THF was added. The suspension was dissolved by heating and was then cooled to -30 ^{o}C. After 48 hours a crop of colourless crystals was isolated, washed with hexane, and placed in a glove-box (0.43 g, 68%). Single crystals suitable for X-ray analysis were obtained by a mixture of 1 mL of hexane and 1 mL of toluene at -30 ^{o}C. The THF in the structure was removed when the crystals were isolated *in vacuo*.

^{1}H NMR (400.13 MHz, C_6D_6, 298 K) δ 8.96-8.88 [br. dd, 1H, *J* = 0.8 Hz, *J* = 5.4 Hz, $C_{11}H_6F_2N$], 7.36-7.32 [br. dd, 1H, *J* = 1.2 Hz, *J* = 8.1, Ar* of ^{Dipp}Nacnac], 7.23-7.17 [br. m, 1H, Ar* of ^{Dipp}Nacnac], 7.14-7.00 [m, 3H, Ar* of ^{Dipp}Nacnac + 1H, $C_{11}H_6F_2N$], 6.93-6.86 [br. m, 1H, Ar* of ^{Dipp}Nacnac], 6.75-6.73 [br.d, 1H, $C_{11}H_6F_2N$], 6.62-6.54 [br. td, 1H, $C_{11}H_6F_2N$], 6.28-6.20 [br. m, 1H, $C_{11}H_6F_2N$], 6.06-6.00 [dd, 1H, *J* = 3.6 Hz, *J* = 8.0 Hz, $C_{11}H_6F_2N$], 4.98 [s, 1H, C*H* of ^{Dipp}Nacnac], 3.65-3.50 [sept, 1H, *J* = 6.4 Hz, C*H*, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 3.45-3.30 [sept, 1H, *J* = 6.7 Hz, C*H*, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 3.00-2.90 [sept, 1H, *J* = 6.7 Hz, C*H*, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 2.84-2.73 [sept, 1H, *J* = 6.4 Hz, C*H*, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 1.84 [s, 3H, CH_3 of ^{Dipp}Nacnac], 1.81 [s, 3H, CH_3 of ^{Dipp}Nacnac], 1.54-1.52 [d, 3 H, *J* = 6.8 Hz, CH_3, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 1.31-1.30 [d, 3H, *J* = 6.8 Hz, CH_3, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 1.25-1.24 [d, 3H, *J* = 6.8 Hz, CH_3, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 1.14-1.11 [br. m, 6H, CH_3, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 0.82-0.80 [d, 3H, *J* = 6.8 Hz, CH_3, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 0.53-0.51 [d, 3H, *J* = 6.7 Hz, CH_3, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 0.22-0.21 [d, 3H, *J* = 6.7 Hz, CH_3, ^{i}Pr, Ar* of ^{Dipp}Nacnac].

^{13}C NMR {^{1}H} (100.61 MHz, C_6D_6, 298 K) δ 169.3 [C_q, CH*C*(Me) of ^{Dipp}Nacnac], 168.5 [C_q, CH*C*(Me) of ^{Dipp}Nacnac], 158.9 [C_q, $C_{11}H_6F_2N$], 148.9 [$C_{11}H_6F_2N$], 146.7 [C_q, Ar* of ^{Dipp}Nacnac], 143.1 [C_q, Ar* of ^{Dipp}Nacnac], 142.9 [C_q, Ar* of ^{Dipp}Nacnac], 142.5 [C_q, Ar* of ^{Dipp}Nacnac], 141.7 [C_q, Ar* of ^{Dipp}Nacnac], 137.8 [$C_{11}H_6F_2N$], 129.3 [C_q], 128.6 [$C_{11}H_6F_2N$], 125.3 [*C*H, Ar* of ^{Dipp}Nacnac], 124.2 [*C*H, Ar* of ^{Dipp}Nacnac], 123.9 [*C*H, Ar* of ^{Dipp}Nacnac], 123.4 [$C_{11}H_6F_2N$], 123.1[*C*H, Ar* of ^{Dipp}Nacnac], 122.0 [$C_{11}H_6F_2N$],

109.5-109.1 [*C*H, d, *J* = 38.8 Hz, $C_{11}H_6F_2N$], 93.9 [*C*H of ^{Dipp}Nacnac], 30.3 [*C*H, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 29.5 [*C*H, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 28.3 [*C*H, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 28.1 [*C*H, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 25.3 [CH_3, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 25.2 [$CH_3$of ^{Dipp}Nacnac], 24.8 [CH_3, ^{i}Pr, Ar*], 24.7 [CH_3, of ^{Dipp}Nacnac], 24.6 [CH_3, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 24.5 [CH_3, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 24.0 [CH_3, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 23.8 [CH_3, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 23.5 [CH_3, ^{i}Pr, Ar* of ^{Dipp}Nacnac], 22.8 [CH_3, ^{i}Pr, Ar* of ^{Dipp}Nacnac].

^{13}C NMR {^{19}F} (100.61 MHz, C_6D_6, 298 K) δ 171.6-171.27 [C_q, dd, *J* = 12.5 Hz, *J* = 43.6 Hz, C-F of $C_{11}H_6F_2N$], 166.9-166.7 [C_q, d, *J* = 11.5 Hz, C-F of $C_{11}H_6F_2N$], 132.3 [C_q], 119.0-118.9 [C_q, d, *J* = 10 Hz, $C_{11}H_6F_2N$], (C_q of *C*-Mg was not possible to assign).

^{19}F NMR (376.40 MHz, C_6D_6, 298 K) δ -77.6 [s, $C_{11}H_6F_2N$], -82.0 [s, $C_{11}H_6F_2N$].

Elemental analysis: ($C_{37}H_{46}MgN_2O$) *Calculated:* C: 76.00 % H: 7.49 % N: 6.65 %. *Found:* C: 76.22 % H: 7.75 % N: 6.51 %.

Electrophilic Interception Studies

Synthesis of 2-(2,4-difluoro-3-iodophenyl)pyridine (7)

To a solution of **1** (0.56 g, 1 mmol) in THF (5 mL), 2-(2,4-difluorophenyl)pyridine (0.2 g, 1mmol) was added. The dark yellow solution was stirred for 5 hours at room temperature. A solution of iodine (0.51 g, 2 mmol) in THF (4 mL) was then added and the yellow solution turned to a brown suspension that was stirred overnight at room temperature. After this time the suspension was opened to air. Water (40 mL) was added and the solution was extracted with diethylether (30 ml x 2). The ether solution was washed with water (40 mL), sat. $Na_2S_2O_3$ aq (40 mL) and brine (40 mL). The solution was then dried over Na_2SO_4, and the filtrate was evaporated *in vacuo*. Ferrocene (0.019 g) was added as an internal standard and the mixture was dissolved in $CDCl_3$.

The ^{1}H NMR spectrum suggests the presence of a 65% of compound **7** since the integration versus ferrocene revealed 35% of presence of 2-(2,4-

difluorophenyl)pyridine and the signals corresponding to the iodinated product **7** are overlapping with the 2-(2,4-difluorophenyl)pyridine signals.

^{1}H NMR (400.13 MHz, $CDCl_3$, 298 K) δ 8.74-8.73 [br. d, 1H, *J* = 4 Hz, $C_{11}H_6F_2IN$], 8.14-8.00 [m, 1H, $C_{11}H_6F_2IN$], 7.80-7.69 [m, 2H, $C_{11}H_6F_2IN$], 7.27-7.10 [m, 1H, $C_{11}H_6F_2IN$], 7.06-6.98 [m, 1H, $C_{11}H_6F_2IN$].

^{19}F NMR (376.40 MHz, $CDCl_3$, 298 K) δ -90.8 [s, $C_{11}H_6F_2IN$], -93.6 [s, $C_{11}H_6F_2IN$].

Synthesis of 2-(2,4-difluoro-3-deuteriophenyl)pyridine (8)

To a solution of **6** (0. 63 g, 1 mmol) in THF (5 mL), d_4-methanol (0.06 mL, 1.5 mmol) was added. The mixture turned to a beige suspension that was stirred overnight at room temperature. The suspension was then filtered and washed with dichloromethane and the filtrate was evaporated *in vacuo*. $CHCl_3$ was then added to perform the deuterium NMR experiments. After this, the solvent was removed, ferrocene (0.019 g) was added as an internal standard and the mixture was dissolved in $CDCl_3$.

The integration versus ferrocene revealed a 72% of compound **8**.

^{1}H NMR (400.13 MHz, $CDCl_3$, 298 K) δ 8.61 [br. s, 1H, $C_{11}H_6F_2DN$], 8.04-7.09 [br. m, 1H, $C_{11}H_6F_2DN$], 7.70-7.54 [br. m, 2H, $C_{11}H_6F_2DN$], 7.16-6.95 [m, 1H, $C_{11}H_6F_2DN$], 6.96-6.87 [m, 1H, $C_{11}H_6F_2DN$].

^{19}F NMR (376.40 MHz, $CDCl_3$, 298 K) δ -109.3 [$C_{11}H_6F_2DN$], -112.8 [$C_{11}H_6F_2DN$].

NMR spectra of compounds

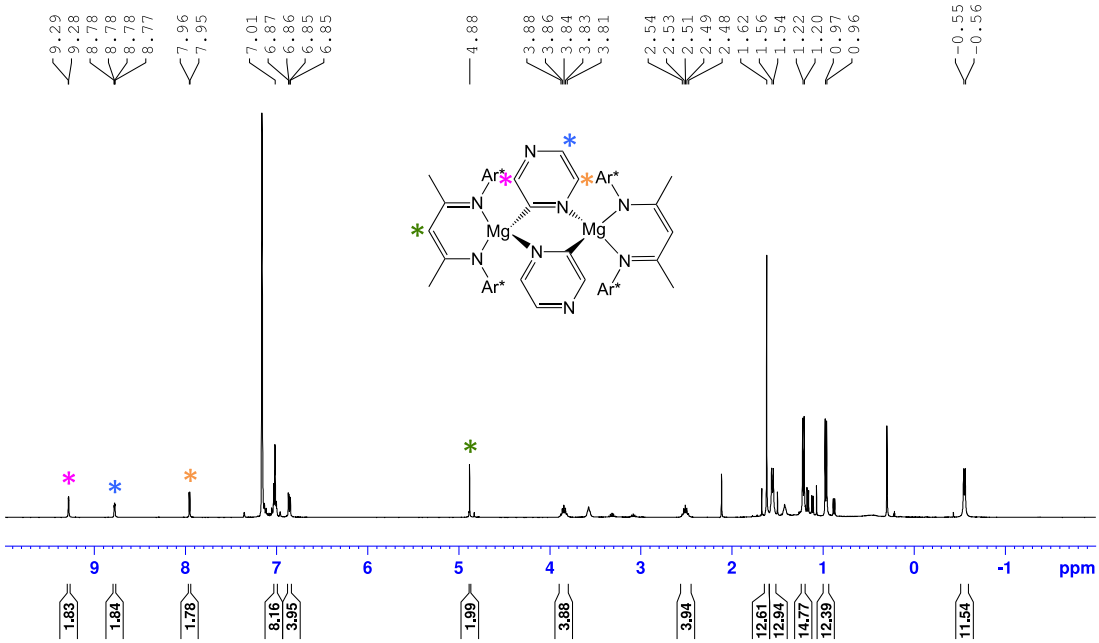

Fig S 1. ^{1}H NMR spectrum of **2** in C_6D_6.

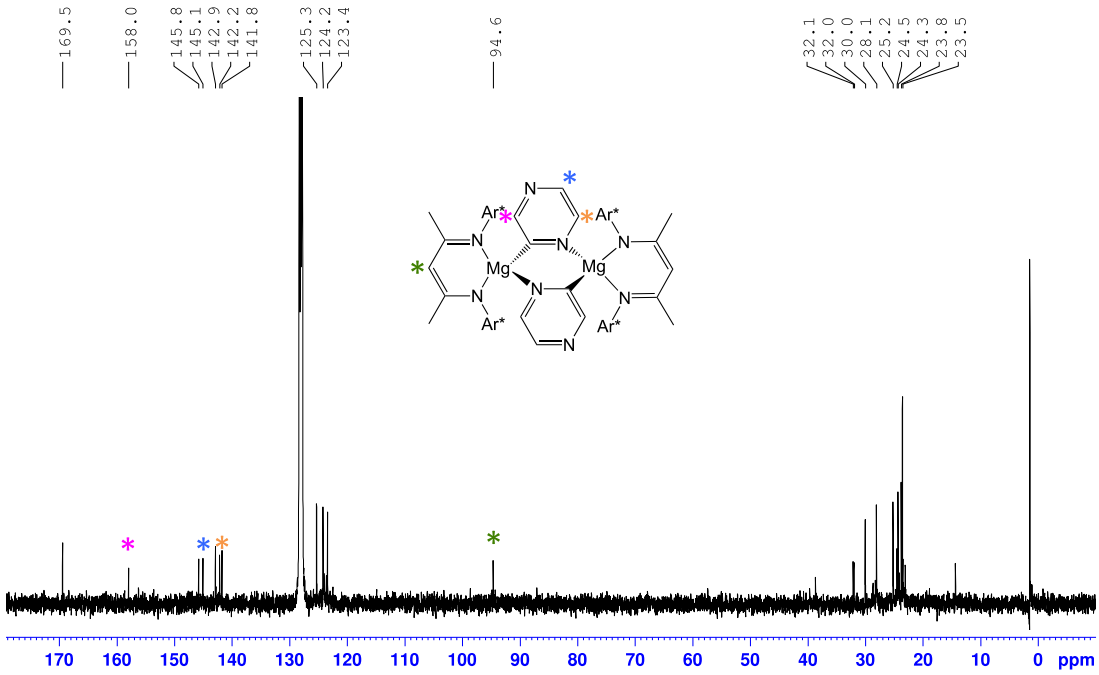

Fig S 2. ^{13}C NMR spectrum of **2** in C_6D_6.

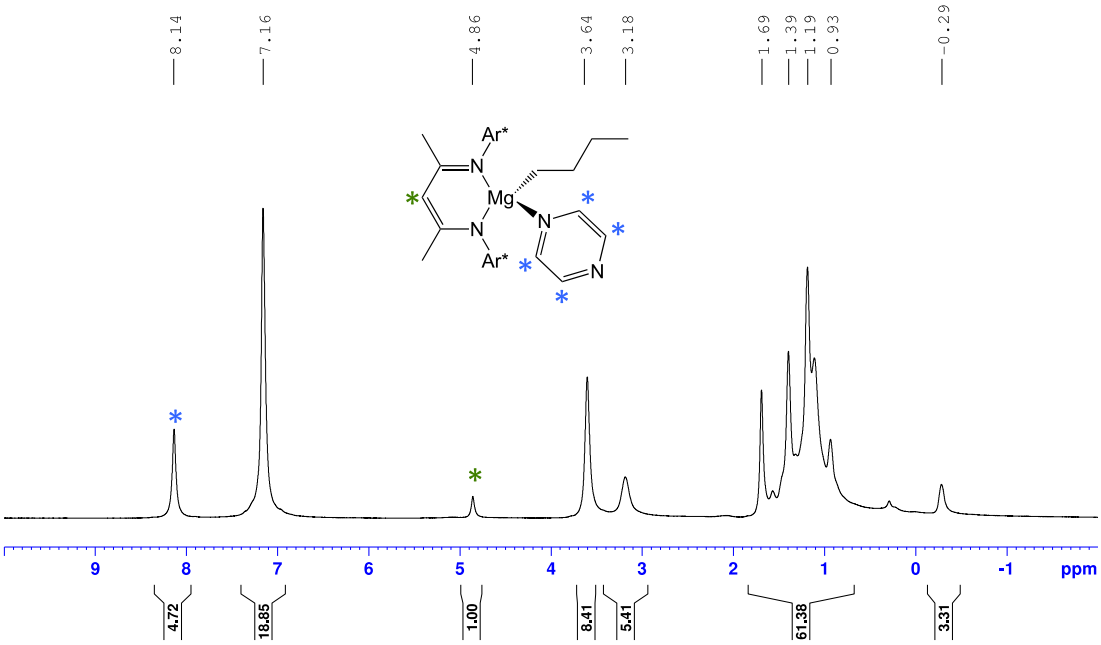

Fig S 3. ^{1}H NMR spectrum of [(^{Dipp}Nacnac)Mg(Bu)($C_4H_4N_2$)] in C_6D_6.

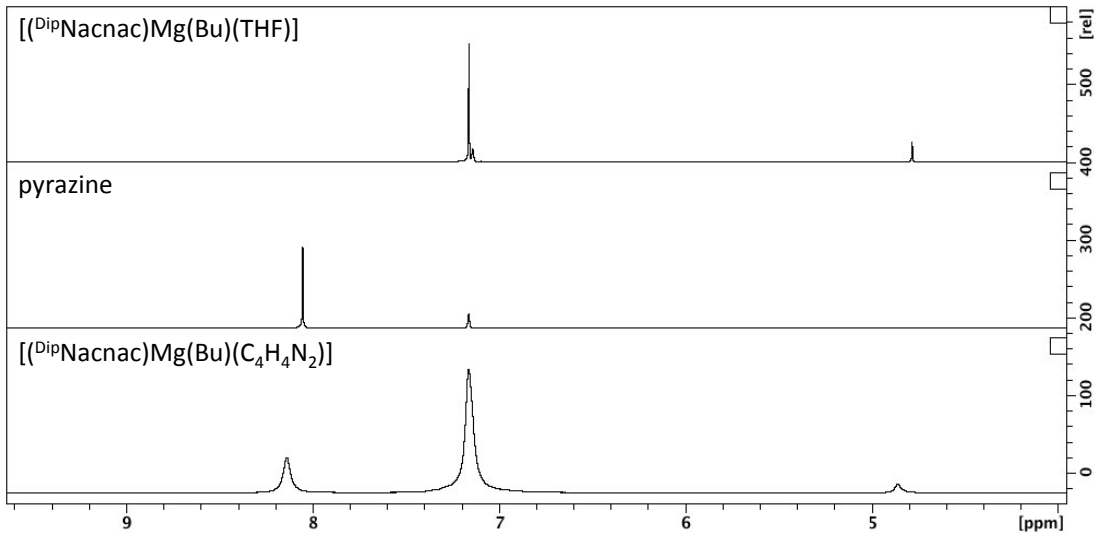

Fig S 4. Comparison of the aromatic regions of the ^{1}H NMR spectra of [(^{Dipp}Nacnac)Mg(Bu)($C_4H_4N_2$)] and the corresponding starting materials in C_6D_6.

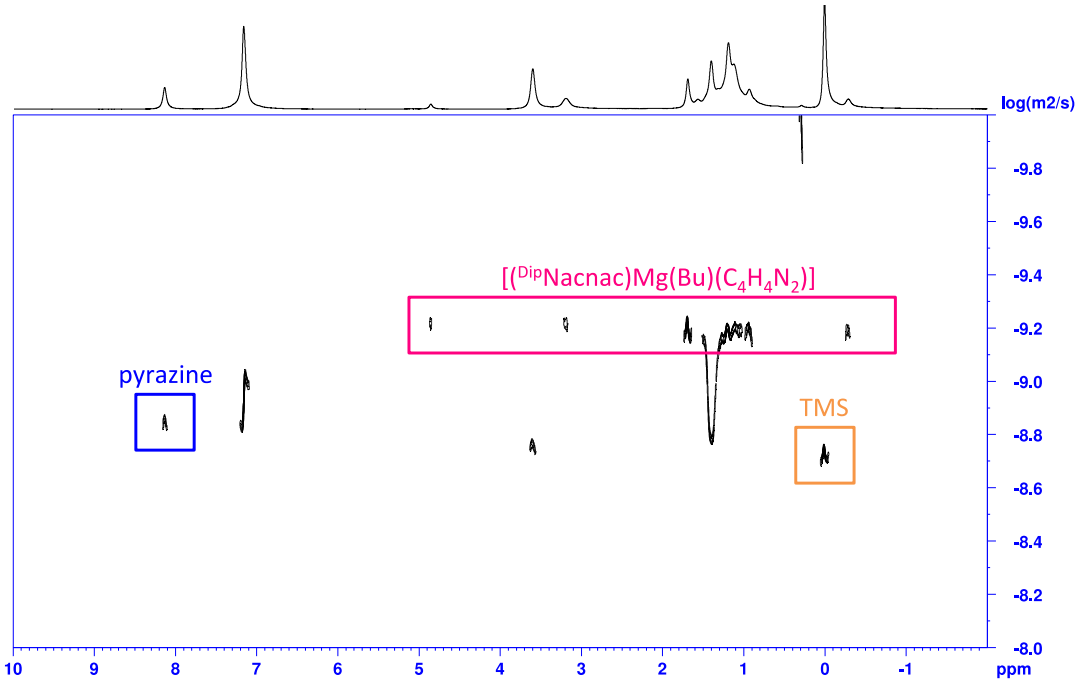

Fig S 5. ^{1}H DOSY NMR spectrum of [(^{Dipp}Nacnac)Mg(Bu)($C_4H_4N_2$)] in C_6D_6.

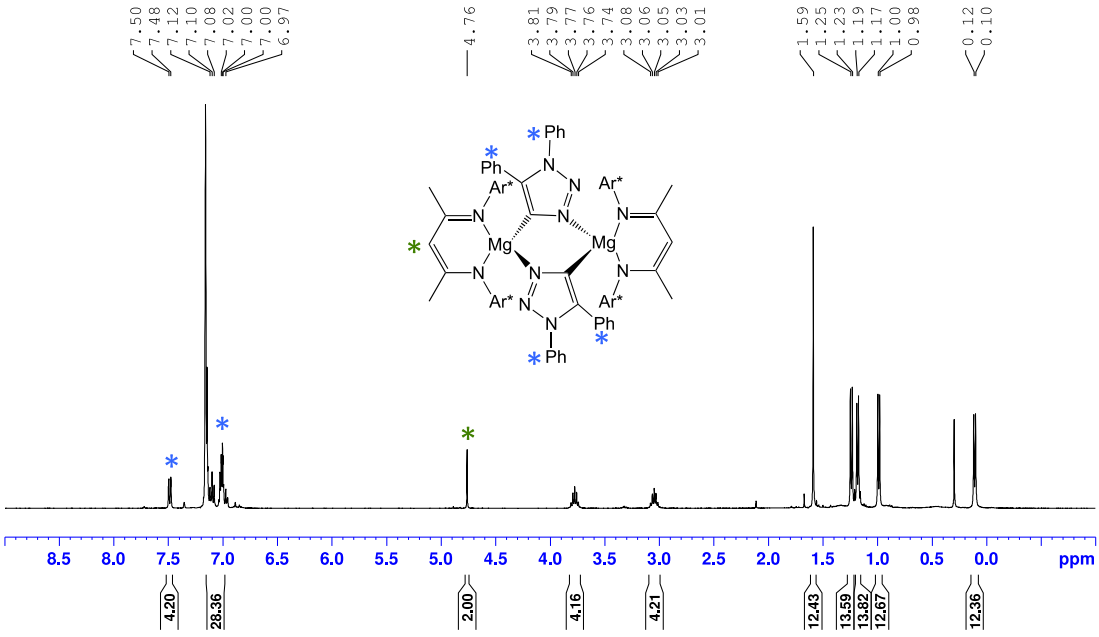

Fig S 6. ^{1}H NMR spectrum of **3** in C_6D_6.

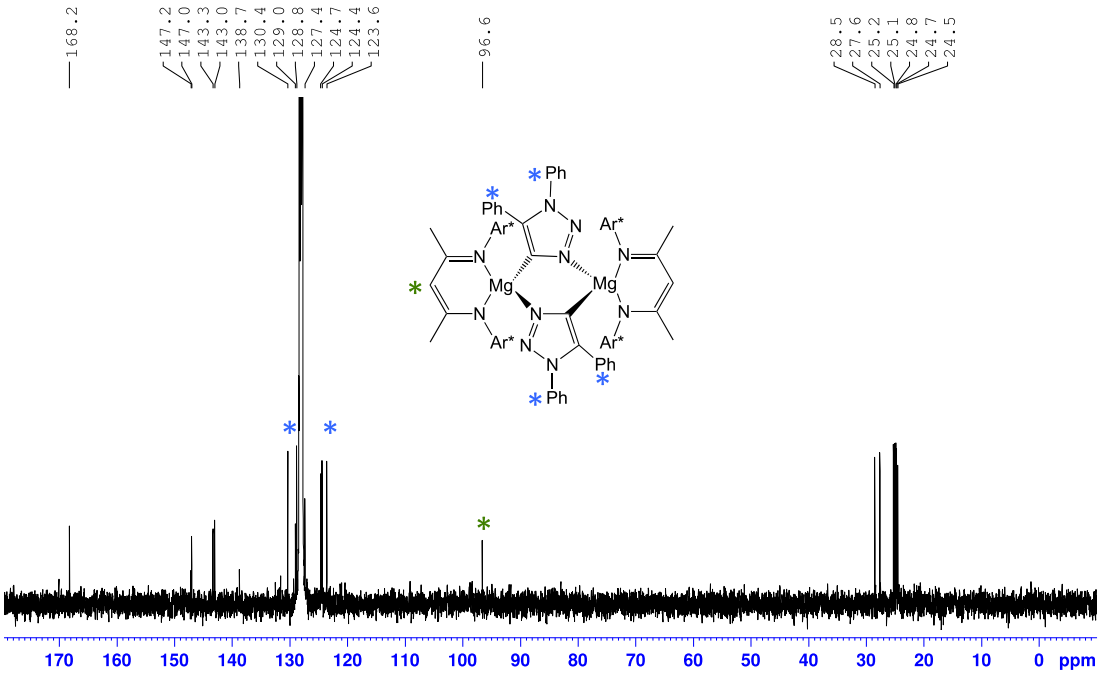

Fig S 7. ^{13}C NMR spectrum of **3** in C_6D_6.

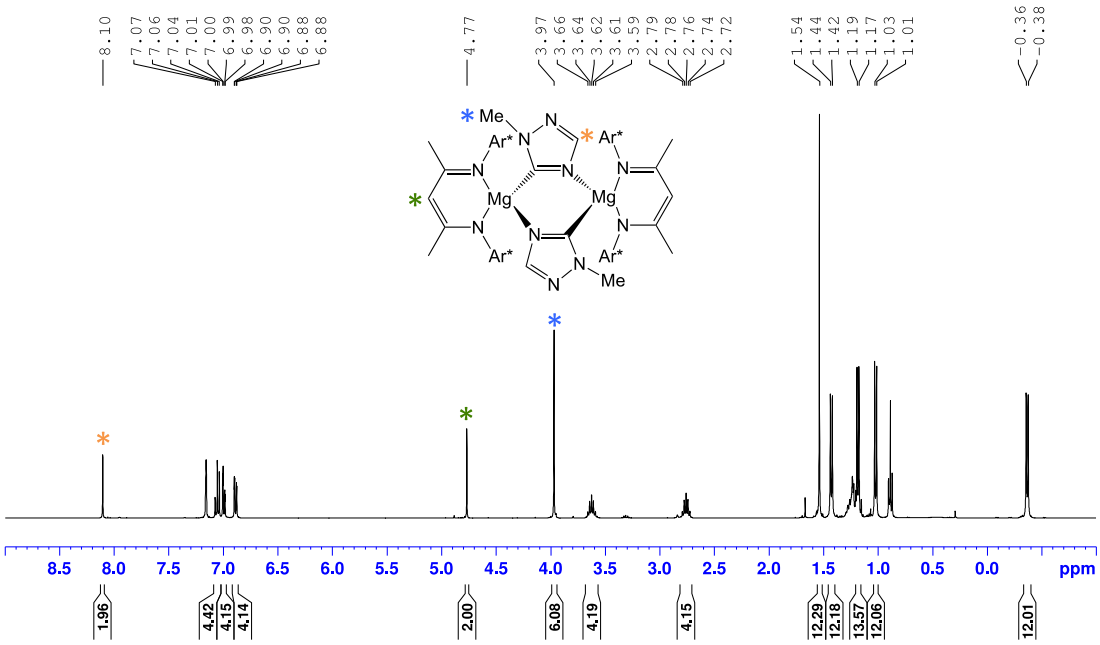

Fig S 8. ^{1}H NMR spectrum of **4** in C_6D_6.

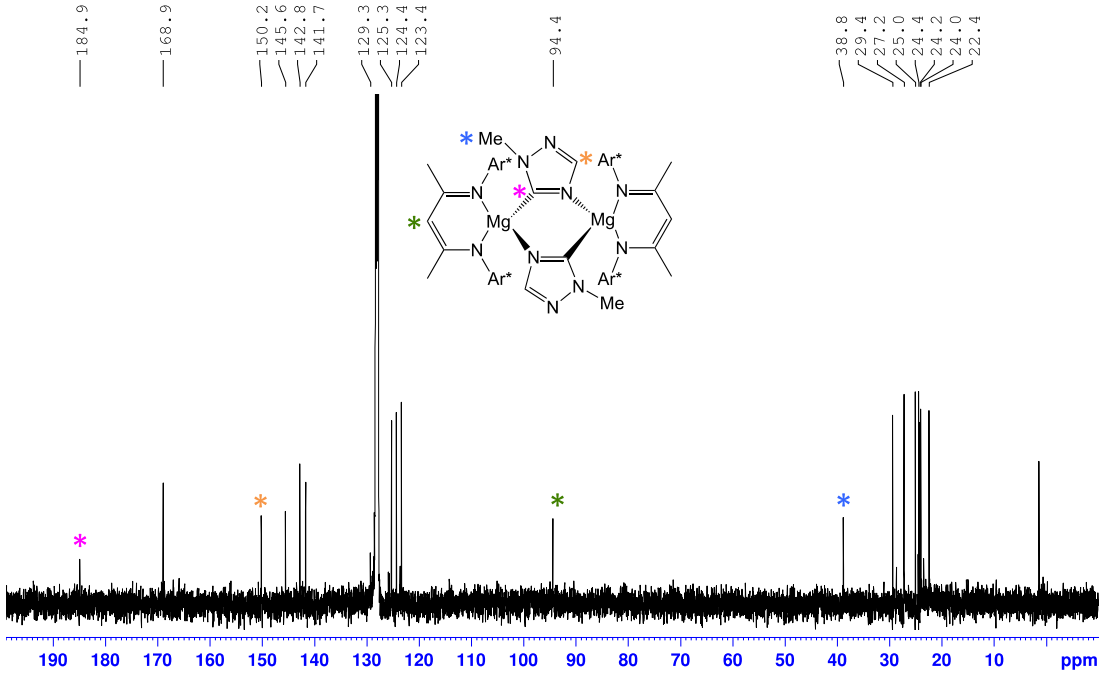

Fig S 9. ^{13}C NMR spectrum of **4** in C_6D_6.

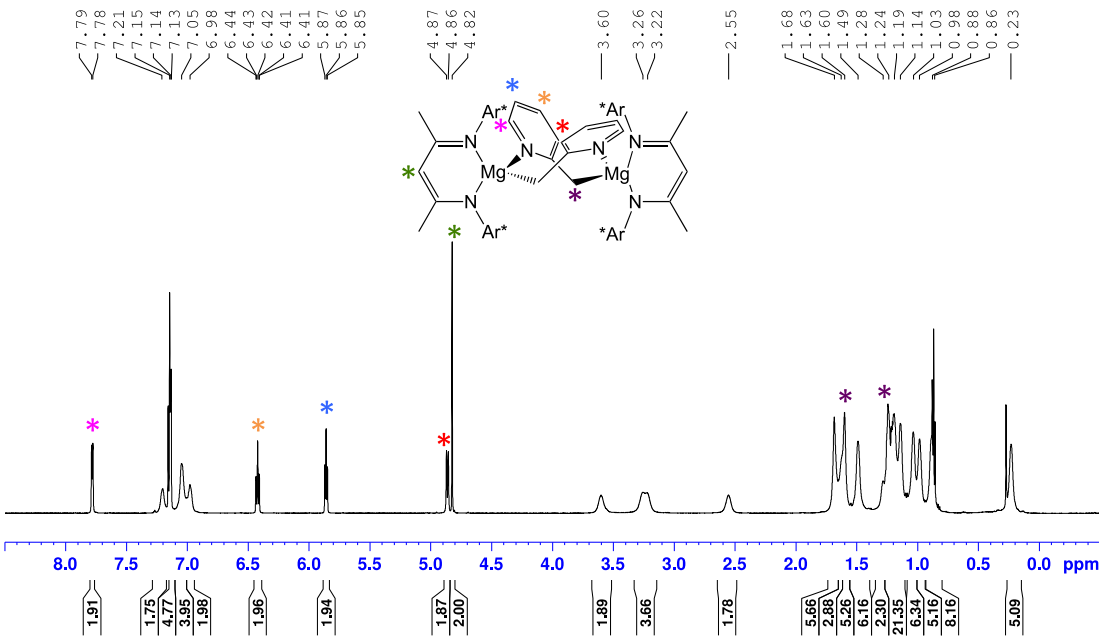

Fig S 10. ^{1}H NMR spectrum of **5** in C_6D_6.

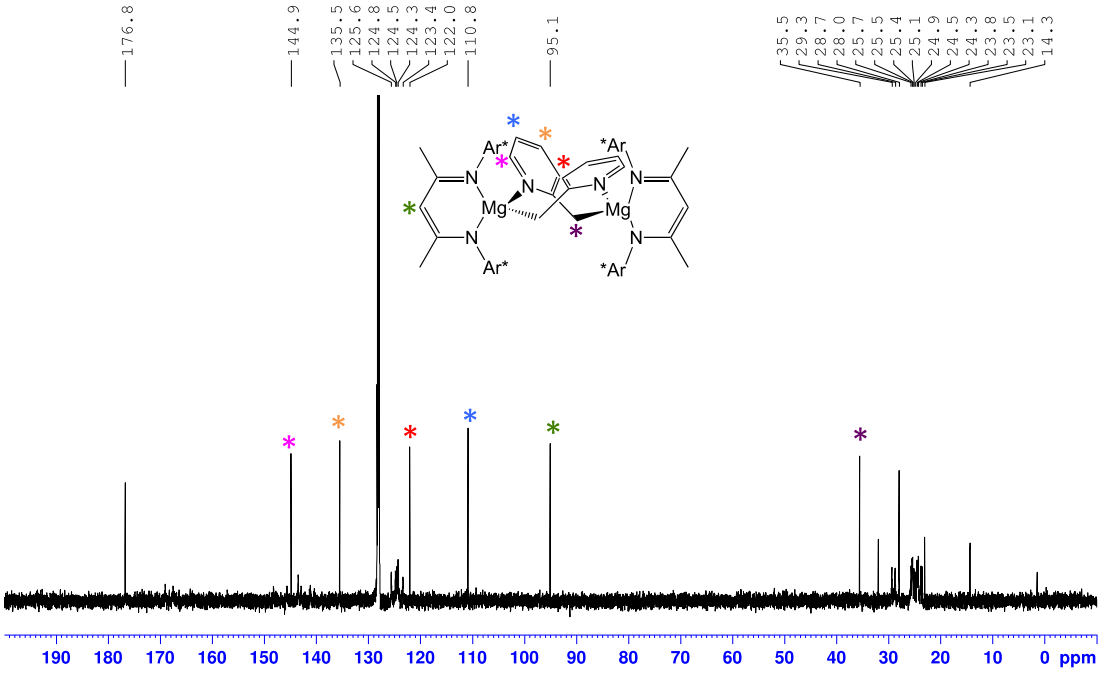

Fig S 11. ^{13}C NMR spectrum of **5** in C_6D_6.

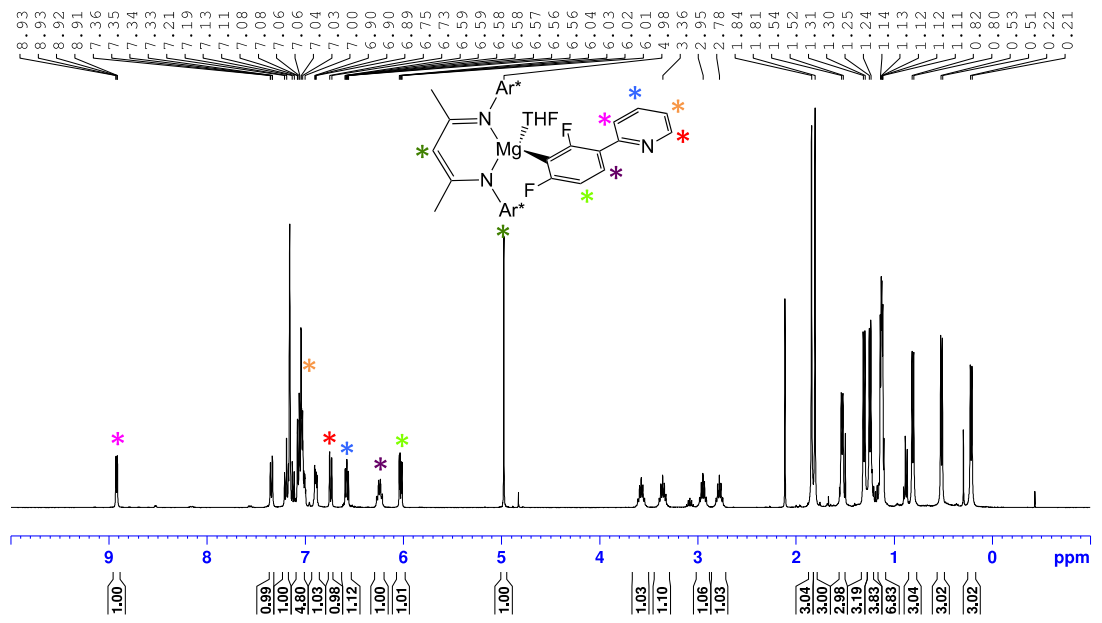

Fig S 12. ^{1}H NMR spectrum of **6** in C_6D_6.

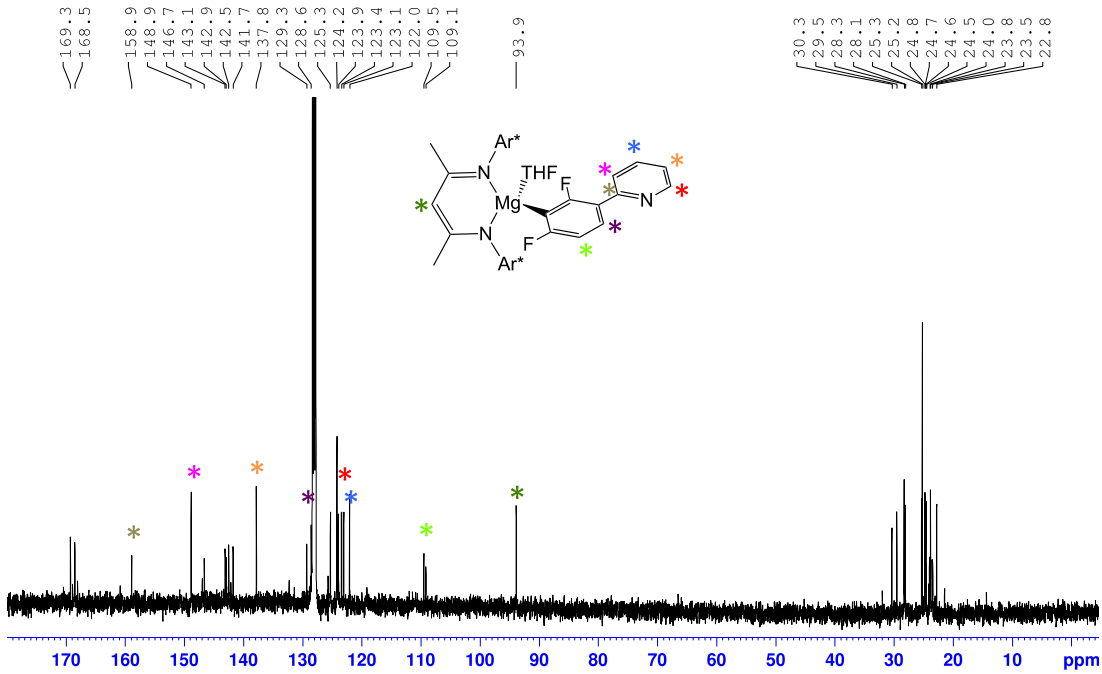

Fig S 13. ^{13}C NMR spectrum of **6** in C_6D_6.

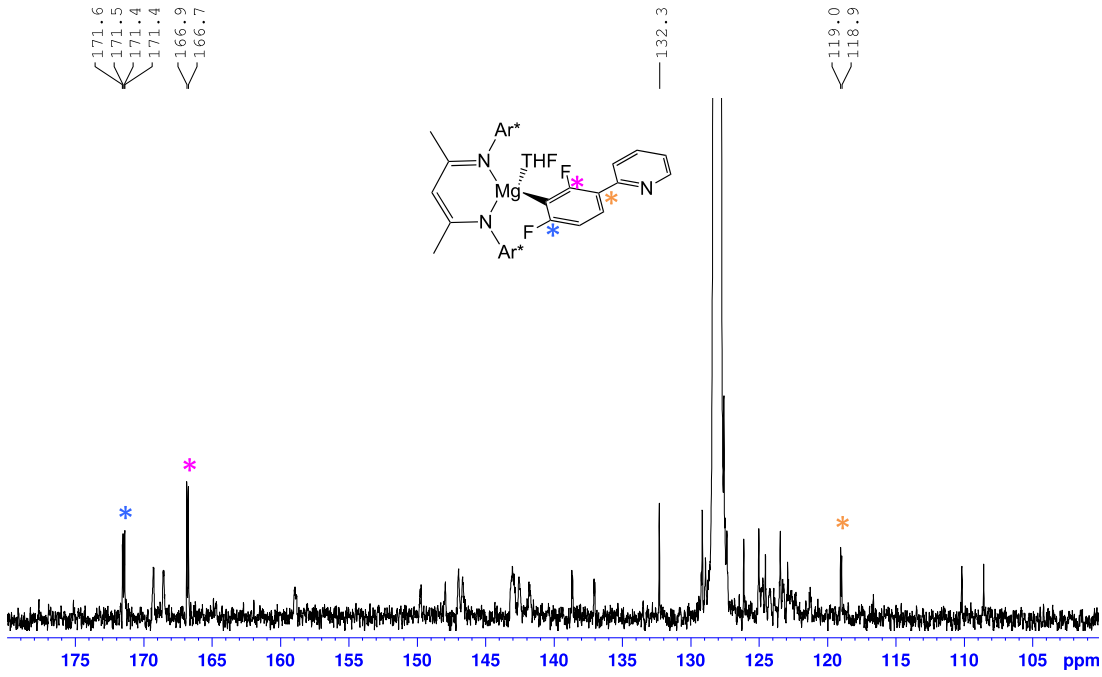

Fig S 14. ^{13}C {^{19}F} NMR spectrum of **6** in C_6D_6.

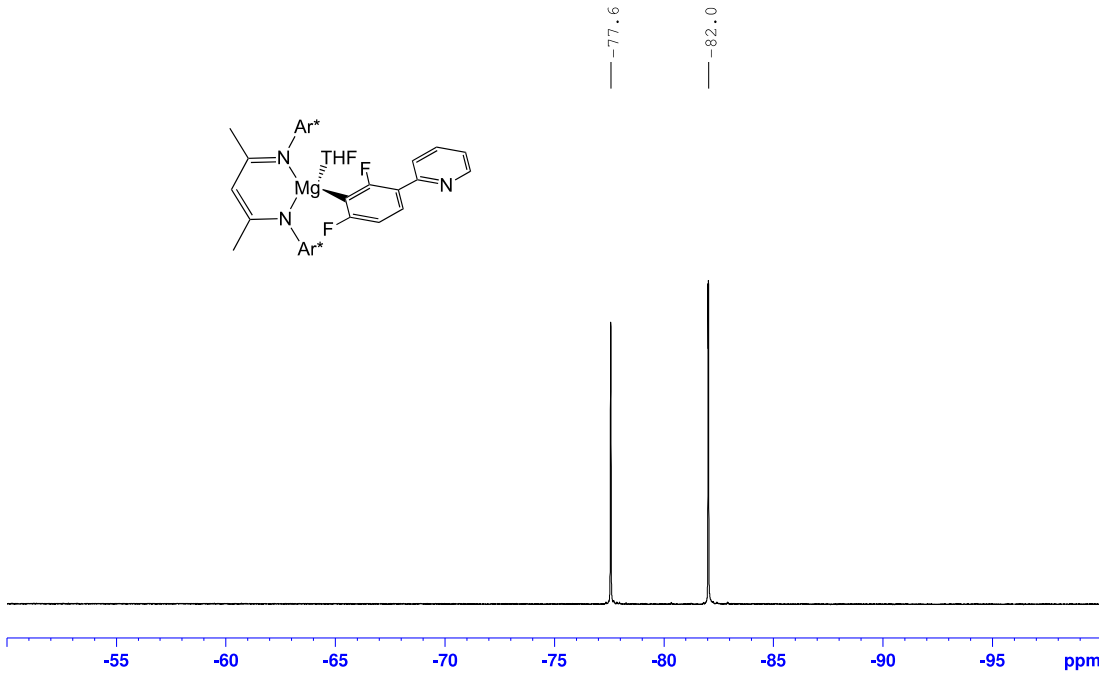

Fig S 15. ^{19}F NMR spectrum of **6** in C_6D_6.

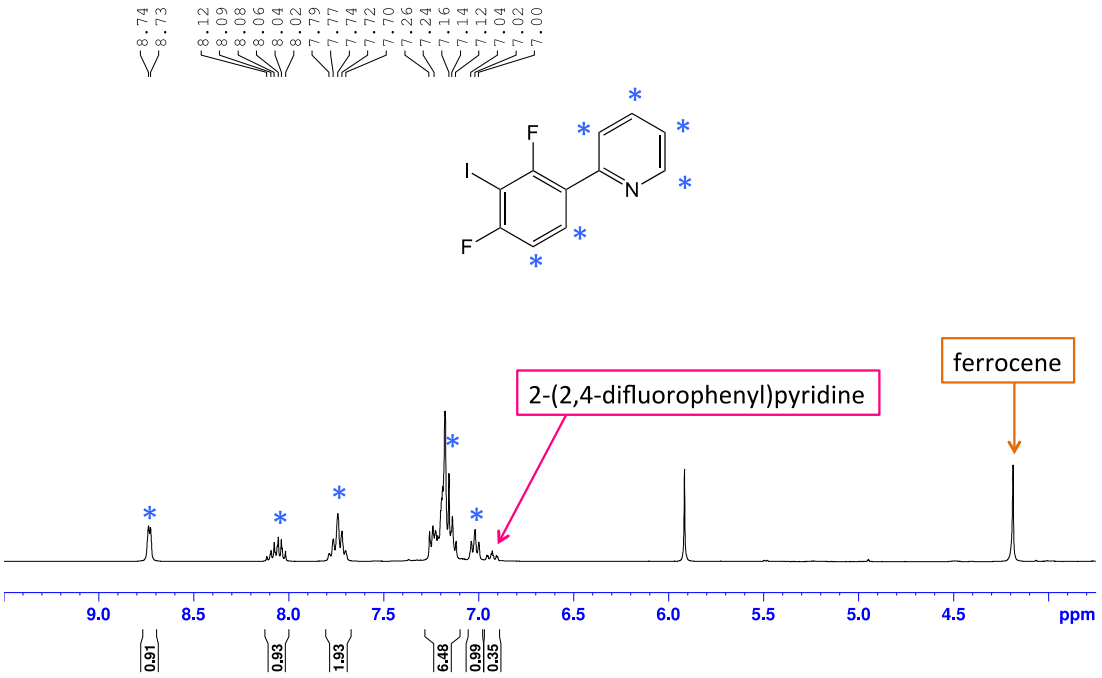

Fig S 16. ^{1}H NMR spectrum of **7** in $CDCl_3$.

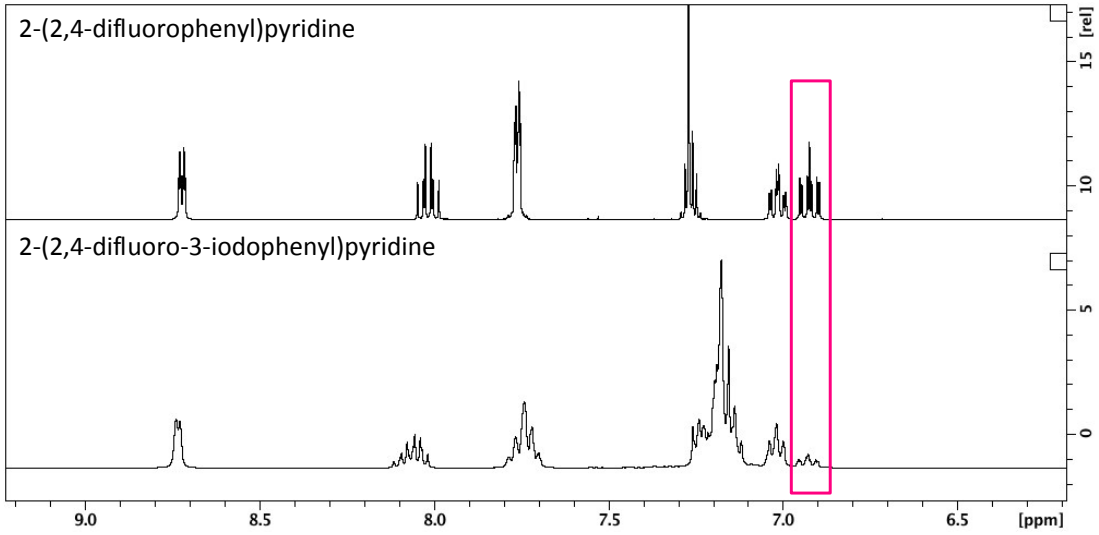

Fig S 17. Comparison of ^{1}H NMR spectra of **7** and 2-(2,4-difluorophenyl)pyridine in $CDCl_3$.

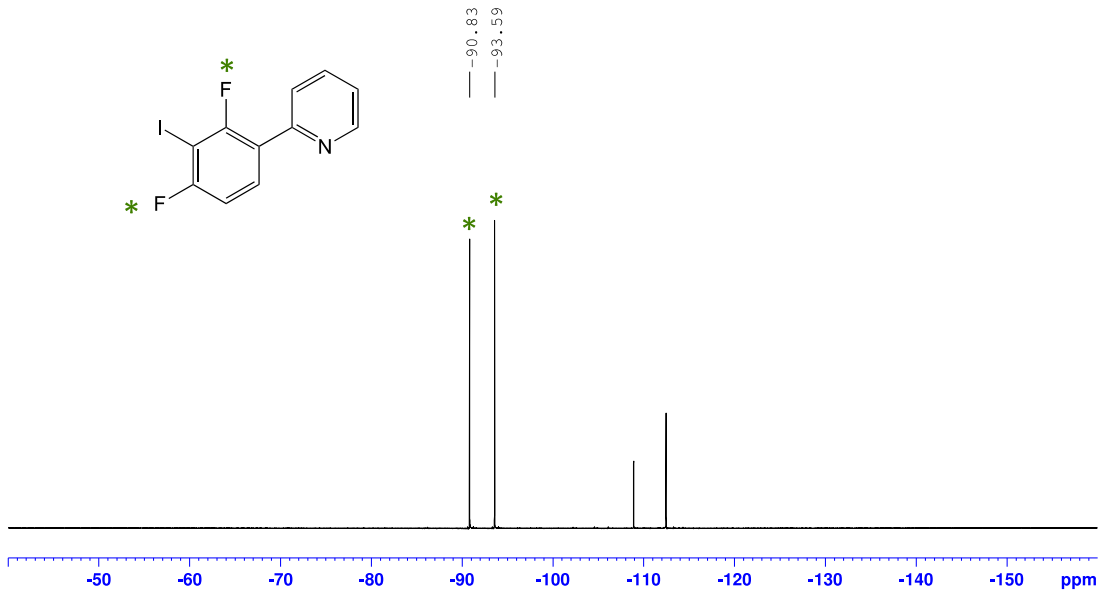

Fig S 18. ^{19}F NMR spectrum of **7** in $CDCl_3$.

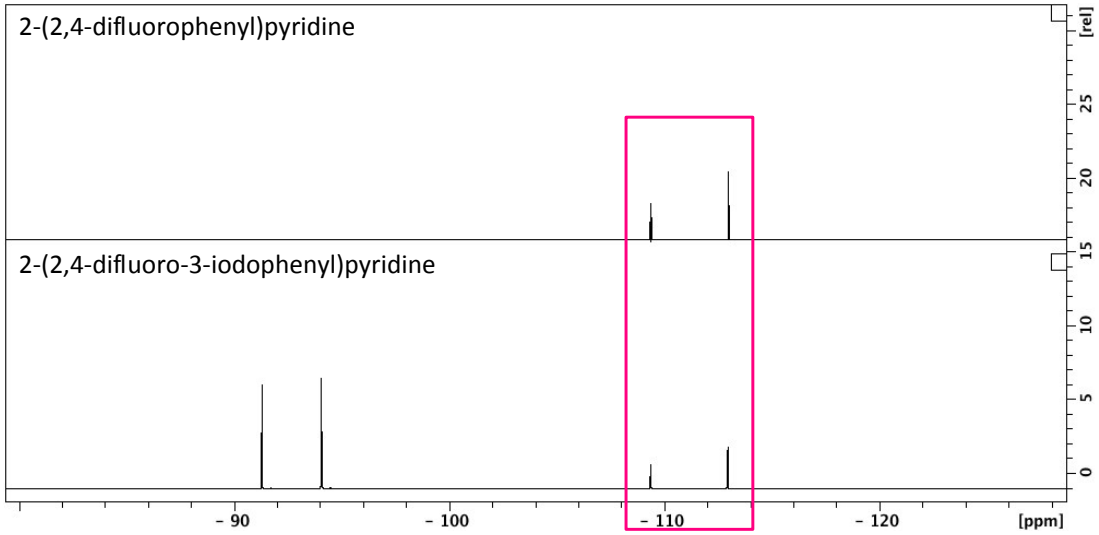

Fig S 19. Comparison of ^{19}F NMR spectra of **7** and 2-(2,4-difluorophenyl)pyridine in $CDCl_3$.

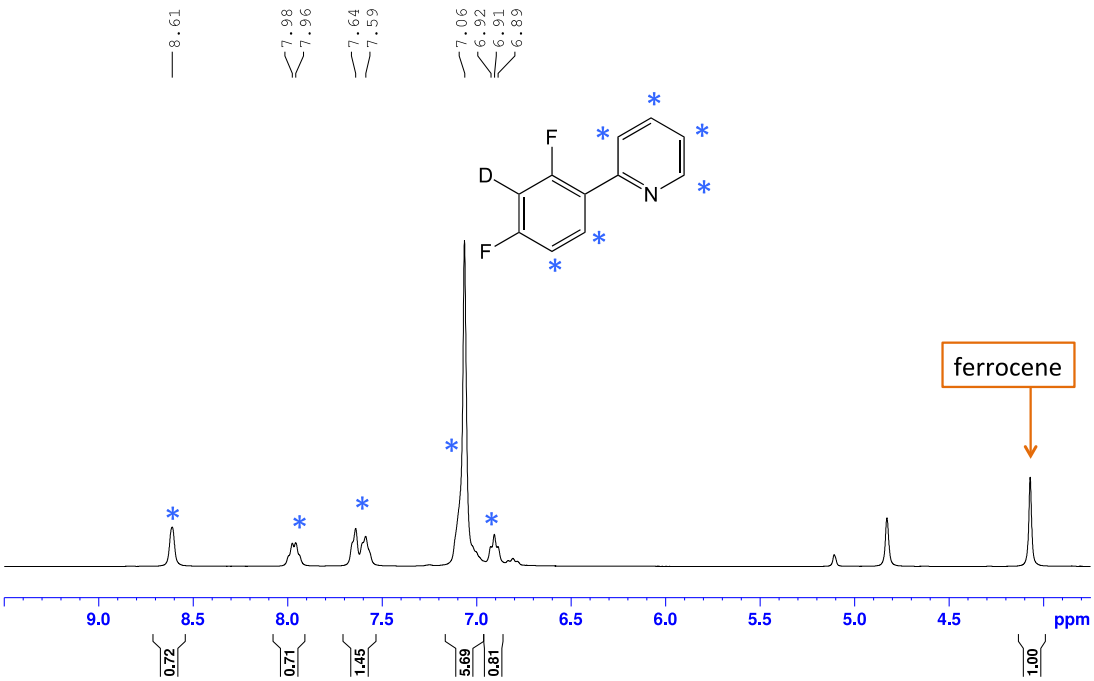

Fig S 20. ^{1}H NMR spectrum of **8** in $CDCl_3$.

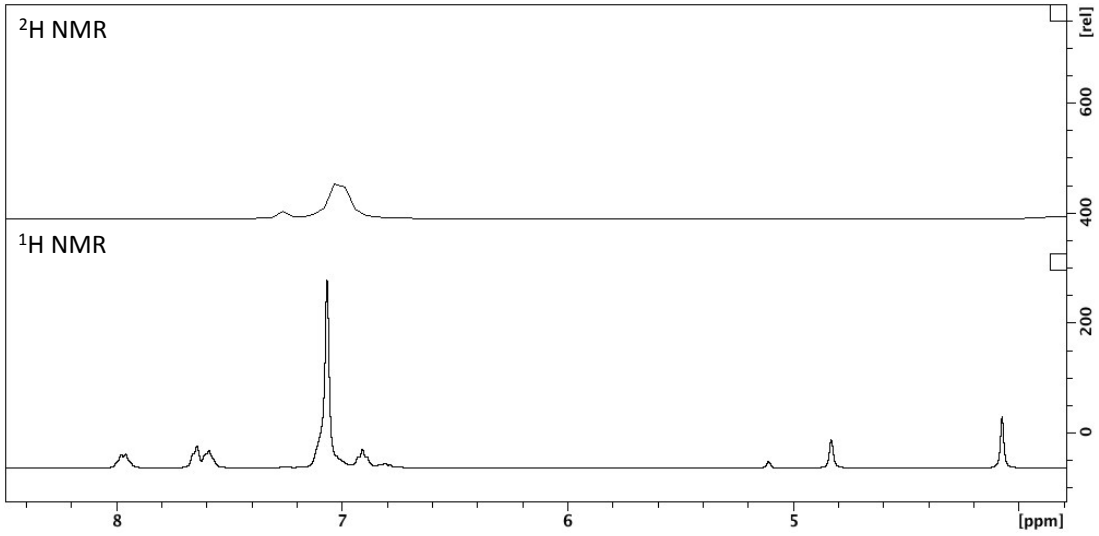

Fig S 21. Comparison of ^{1}H and ^{2}H NMR spectra of compound **8** in $CDCl_3$.

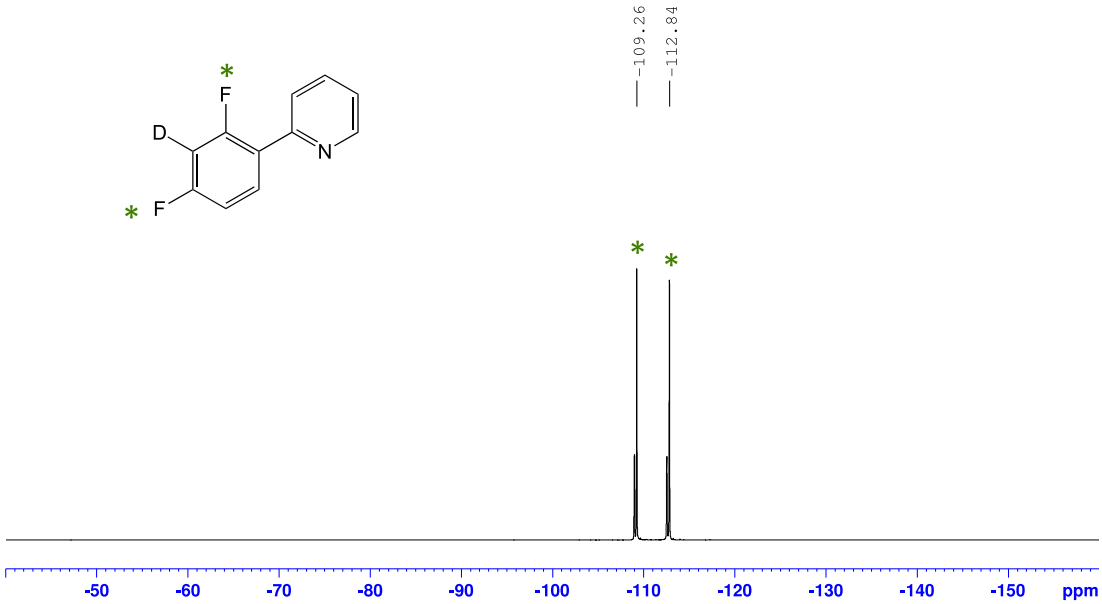

Fig S 22. ^{19}F NMR spectrum of **8** in $CDCl_3$..

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