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## Supporting Information

### Experimental Details

#### General

All reactions were carried out using standard Schlenk and glove box techniques under an inert atmosphere of argon. Solvents (THF, hexane and toluene) were dried by heating to reflux over sodium benzophenone ketyl and distilled under nitrogen prior to use – THF was collected and stored over 4 Å molecular sieves for minimum 24 h prior to use, under argon atmosphere. NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer, operating at 400.13 MHz for  $^1\text{H}$ , 376.49 MHz for  $^{19}\text{F}$  and 100.62 MHz for  $^{13}\text{C}\{^1\text{H}\}$ . Elemental analyses were obtained using a Carlo Erba 1108 Elemental Analyser at London Metropolitan University by Stephen Boyer. Di-*n*-butylamine, piperidine, morpholine, pyrrolidine, diphenylamine, benzotriazole, 2-(2,4-difluorophenyl)pyridine, 2-fluoropyridine, hexafluorobenzene, fluorobenzene and octafluorotoluene were purchased from Sigma Aldrich and Fluorochem. All amine reagents were dried over  $\text{CaH}_2$  prior to use and stored over 4 Å molecular sieves. 2-(2,4-difluorophenyl)pyridine (**ppf**) was stored in a -30 °C fridge inside a glovebox under argon atmosphere.  $^{\text{Dipp}}\text{NacnacMgTMP}$  (**1**) ( $^{\text{Dipp}}\text{Nacnac} = \text{Ar}^*\text{NC}(\text{Me})\text{CHC}(\text{Me})\text{NAr}^*$ ;  $\text{Ar}^* = 2,6\text{-}^i\text{Pr}_2\text{-C}_6\text{H}_3$ ;  $\text{TMP} = 2,2,6,6\text{-tetramethylpiperidide}$ ) and **6** [ $(^{\text{Dipp}}\text{Nacnac})\text{Mg}(\text{NC}_4\text{H}_8)_2$ ] were synthesised according to literature methods.<sup>1, 2</sup> All DOSY NMR experiments were conducted using the External Calibration Curve (ECC) method as described by Stalke<sup>3</sup> using 1, 2, 3, 4-tetraphenylnaphthalene (TPhN) as a reference standard. All GC spectra were obtained using an Agilent Technologies 7890A GC System, Agilent Technologies 5975C Inert XL EI/CI MSD with Triple-Axis Detector, Agilent Technologies 7693 Autosampler and Restek GC Column (30 m, 0.25 mm i.d., 0.25  $\mu\text{m}$ ). All HRMS data was obtained using a Bruker UltrafleXtreme MALDI TOF/TOF at the University of Edinburgh. All microwave reactions were carried out in 4 mL microwave vials in a CEM Activent, Discover v2.17.

#### X-Ray Crystallography

Crystallographic data were measured at 123 K for compounds **4** and **10**, and at 193 K for compounds **3** and **9** with Oxford Diffraction Gemini S or Xcalibur E instruments and with graphite-monochromated Cu ( $\lambda=1.54180$  Å) or Mo ( $\lambda=0.71073$  Å) radiation, respectively. All structures were refined to convergence on F 2 using all unique reflections and programs from the SHELX family.<sup>4</sup> The final structures of **3**, **4** and **10** were subjected to displacement parameters that were required to model the disorder of one THF molecule for **3** and one toluene molecule each for compounds **4** and **10**. Selected crystallographic data are displayed in **Table S 1**.

**Table S 1 Selected crystallographic and refinement parameters for 3, 4, 9 and 10**

	<b>3</b>	<b>4</b>	<b>9</b>	<b>10</b>
<b>Empirical formula</b>	C <sub>41</sub> H <sub>63</sub> MgN <sub>3</sub> O	C <sub>75</sub> H <sub>110</sub> Mg <sub>2</sub> N <sub>6</sub>	C <sub>41</sub> H <sub>51</sub> MgN <sub>3</sub>	C <sub>77</sub> H <sub>98</sub> Mg <sub>2</sub> N <sub>10</sub>
<b>Mol. Mass</b>	642.28	1144.30	610.15	1212.27
<b>Crystal system</b>	Triclinic	Monoclinic	Monoclinic	Monoclinic
<b>a/Å</b>	9.3179(4)	19.7360(11)	18.4812(9)	13.0738(4)
<b>b/Å</b>	12.5656(6)	20.5218(8)	18.3287(10)	14.2398(5)
<b>c/Å</b>	18.0807(8)	17.9367(1)	10.6762(5)	19.0456(6)
<b>α/°</b>	70.915(4)	90	90	90
<b>β/°</b>	81.783(4)	112.105(5)	90.832(4)	92.872(3)
<b>γ/°</b>	85.771(4)	90	90	90

<b>V/Å<sup>3</sup></b>	1979.25(16)	6730.7(3)	3616.0(3)	3541.2(2)
<b>Z</b>	2	4	4	2
<b>λ/Å</b>	0.71073	1.54180	0.71073	0.71073
<b>Measured reflections</b>	18074	14090	35713	18999
<b>Unique reflections</b>	8627	6671	8708	9058
<b>R<sub>int</sub></b>	0.0273	0.0212	0.0382	0.0249
<b>Observed rflns [I &gt; 2σ(I)]</b>	6187	5648	6222	6862
<b>Goof</b>	1.022	1.025	1.032	1.019
<b>R [on F, obs rflns only]</b>	0.0658	0.0503	0.0474	0.0497
<b>ωR [on F<sup>2</sup>, all data]</b>	0.1862	0.1421	0.1224	0.1297
<b>Largest diff. peak/hole e/Å<sup>-3</sup></b>	0.748/-0.313	0.578/-0.275	0.243/-0.244	0.617/-0.371

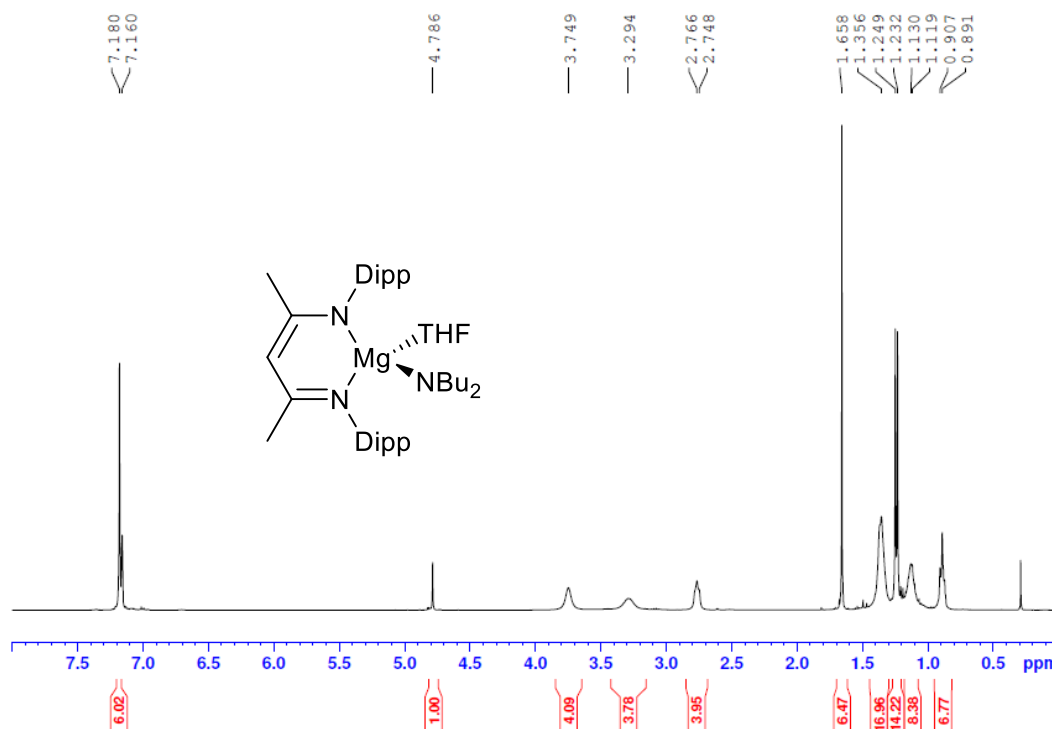
# Synthesis of <sup>Dipp</sup>Nacnac-Magnesium-Amide Compounds

## Synthesis of Compound 3

To a solution of **1** (0.291 g, 0.5 mmol) in 5 mL of THF, 85  $\mu$ L (0.5 mmol) of di-*n*-butylamine was added affording a yellow solution which was stirred at room temperature for 3 h. Then, the solution was concentrated *in vacuo*, resulting in a yellow suspension. Gentle heating of this mixture and slow cooling to room temperature produced a crop of colourless crystals, compound **3**, in a 16% yield (0.116 g). In order to obtain a good yield the reaction was repeated on a 1 mmol scale and after 3 h of reaction time, all THF was removed under vacuum and the compound was suspended in 10 mL of hexane. The resulting solid was isolated via filtration and stored in the glove box (0.368 g, 57%). Due to the inherent air-sensitive nature of this compound, no satisfactory CHN analysis could be obtained despite several attempts.

**<sup>1</sup>H NMR (400.1 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K):**  $\delta$  ~ 7.18 (br. s, 6H, Ar(C)-H of <sup>Dipp</sup>Nacnac), 4.79 (s, 1H, CH of <sup>Dipp</sup>Nacnac), 3.75 (br. m, 4H, CH<sub>2</sub>O of THF), 3.29 (br. m, 4H, C(H)(CH<sub>3</sub>)<sub>2</sub> of <sup>i</sup>Pr), 2.75 (br. m, 4H, -N(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 1.66 (s, 6H, CH<sub>3</sub> of <sup>Dipp</sup>Nacnac), 1.36 (br. m, 16H, C(H)(CH<sub>3</sub>)<sub>2</sub> of <sup>i</sup>Pr and CH<sub>2</sub> of THF), 1.23 (br. d, 12H, C(H)(CH<sub>3</sub>)<sub>2</sub> of <sup>i</sup>Pr), 1.10 (br. m, 8H, N(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 0.86 (br. t, 6H, N(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>) ppm

**<sup>13</sup>C{<sup>1</sup>H} NMR (100.62 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K):**  $\delta$  ~ 168.38 (C(CH<sub>3</sub>) of <sup>Dipp</sup>Nacnac), 146.72 (C<sub>q</sub> of Ar), 142.44 (C<sub>q</sub>(<sup>i</sup>Pr) of Ar), 125.26 (Ar-CH<sub>meta</sub>), 123.96 (Ar-C-H<sub>para</sub>), 94.6 (C-H of <sup>Dipp</sup>Nacnac), 69.9 (CH<sub>2</sub>O of THF), 56.3 (N(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 36.14 (N(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 28.29 (C(H)(CH<sub>3</sub>)<sub>2</sub> of <sup>i</sup>Pr), 25.40 (CH<sub>2</sub> of THF), 24.87 (C(H)(CH<sub>3</sub>)<sub>2</sub> of <sup>i</sup>Pr), 24.71 (C(H)(CH<sub>3</sub>)<sub>2</sub> of <sup>i</sup>Pr), 24.51 (CH<sub>3</sub> of <sup>Dipp</sup>Nacnac), 21.60 (N(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 14.98 (N(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>) ppm.



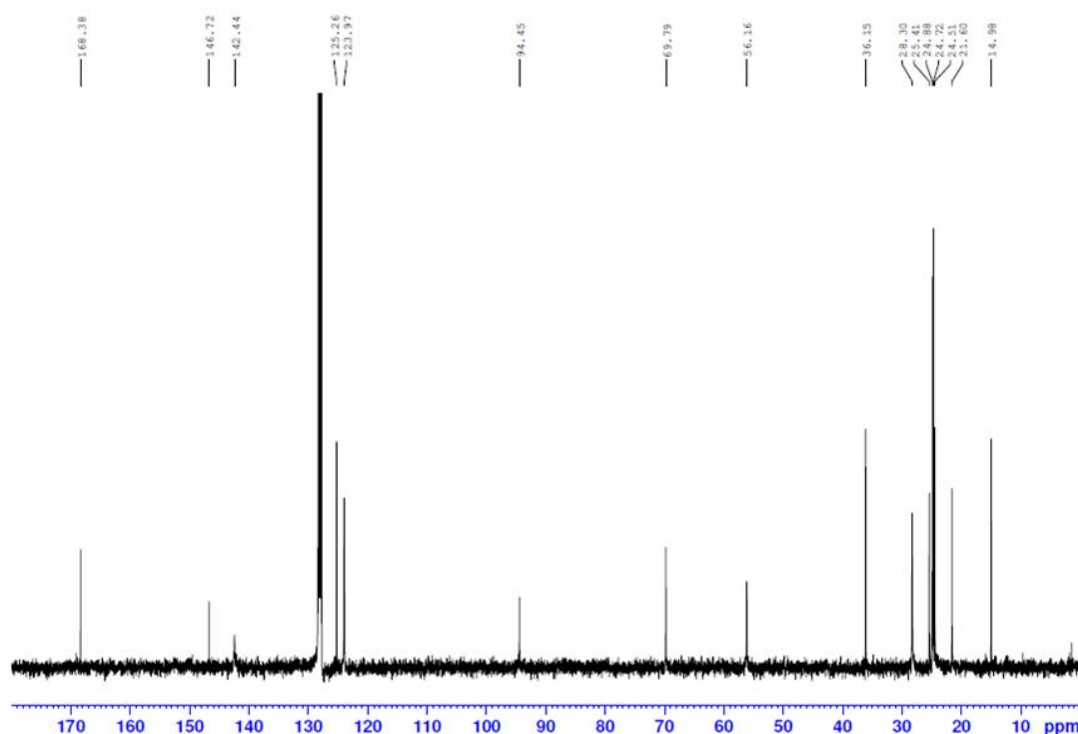


Figure S 2  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound 3

## Synthesis of Compound 4

To a Schlenk flask, 1.25 g (3 mmol) of  $\text{DippNacnacH}$  was added and the flask was purged with argon to as to ensure an inert atmosphere. The compound was then dissolved in 30 mL of toluene and 3.1 mL (3.1 mmol) of a 1.0 M solution of di-*n*-butylmagnesium was added – this mixture was heated at 50°C for 1 hour, affording a colourless solution of  $\text{DippNacnacMgBu}$ . Once cooled to room temperature, 0.3 mL (3 mmol) of piperidine was added, resulting in a yellow suspension. This suspension was stirred at room temperature for 3 hours after which, gentle heating gave a yellow solution and slow cooling to room temperature afforded a crop of yellow crystals (1.12 g, 32.7%). Anal. Calcd. for  $\text{C}_{75}\text{H}_{110}\text{Mg}_2\text{N}_6$ : C, 77.62; H, 9.77; N, 7.99. Found: C, 74.50; H, 9.46; N, 7.23

**$^1\text{H}$  NMR (400.1 MHz,  $\text{D}_8\text{-THF}$ , 300 K):**  $\delta$  ~ 7.08 (br. m, 12H, Ar(C)-H of  $\text{DippNacnac}$ ), 4.82 (s, 2H, CH of  $\text{DippNacnac}$ ), 3.19 (br. m, 8H, C(H)(CH<sub>3</sub>)<sub>2</sub> of  $^i\text{Pr}$ ), 2.38 (t, 8H, -N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub> of piperidine), 1.64 (s, 12H, CH<sub>3</sub> of  $\text{DippNacnac}$ ), 1.24 (d, 24H, C(H)(CH<sub>3</sub>)<sub>2</sub> of  $^i\text{Pr}$ ), 1.18 (d, 24H, C(H)(CH<sub>3</sub>)<sub>2</sub> of  $^i\text{Pr}$ ), 0.87 (m, 12H, -N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub> of piperidine) ppm

**$^{13}\text{C}\{^1\text{H}\}$  NMR (100.62 MHz,  $\text{D}_8\text{-THF}$ , 300 K):**  $\delta$  ~ 168.81 (C(CH<sub>3</sub>) of  $\text{DippNacnac}$ ), 146.28 (C<sub>q</sub> of Ar), 142.78 (C<sub>q</sub>( $^i\text{Pr}$ ) of Ar), 125.23 (Ar-CH<sub>meta</sub>), 123.54 (Ar-C-H<sub>para</sub>), 94.47 (C-H of  $\text{DippNacnac}$ ), 54.44 (-N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub> of piperidine), 31.35 (-N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub> of piperidine), 28.49 (C(H)(CH<sub>3</sub>)<sub>2</sub> of  $^i\text{Pr}$ ), 24.08 (C(H)(CH<sub>3</sub>)<sub>2</sub> of  $^i\text{Pr}$ ), 25.12 (CH<sub>3</sub> of  $\text{DippNacnac}$ ), 24.37 (CH<sub>3</sub> of  $\text{DippNacnac}$ ) ppm

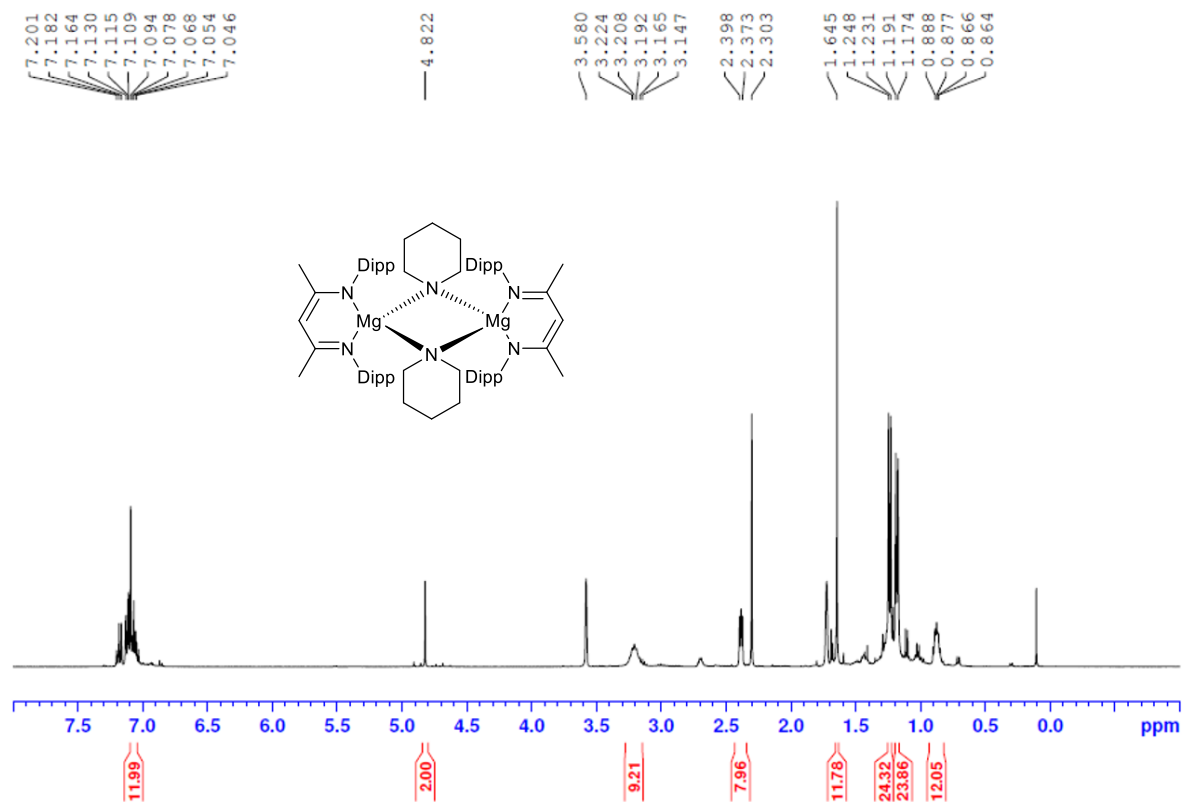


Figure S 3 <sup>1</sup>H NMR spectrum of compound 4

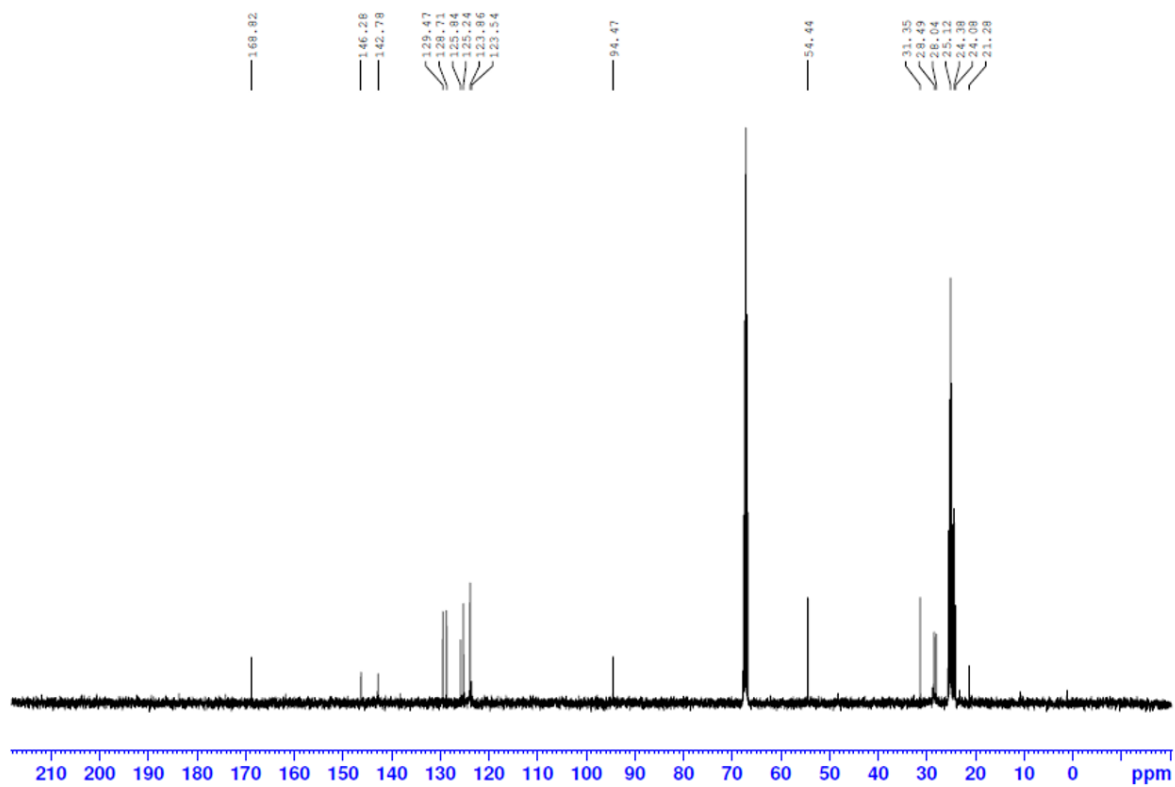


Figure S 4 <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of compound 4



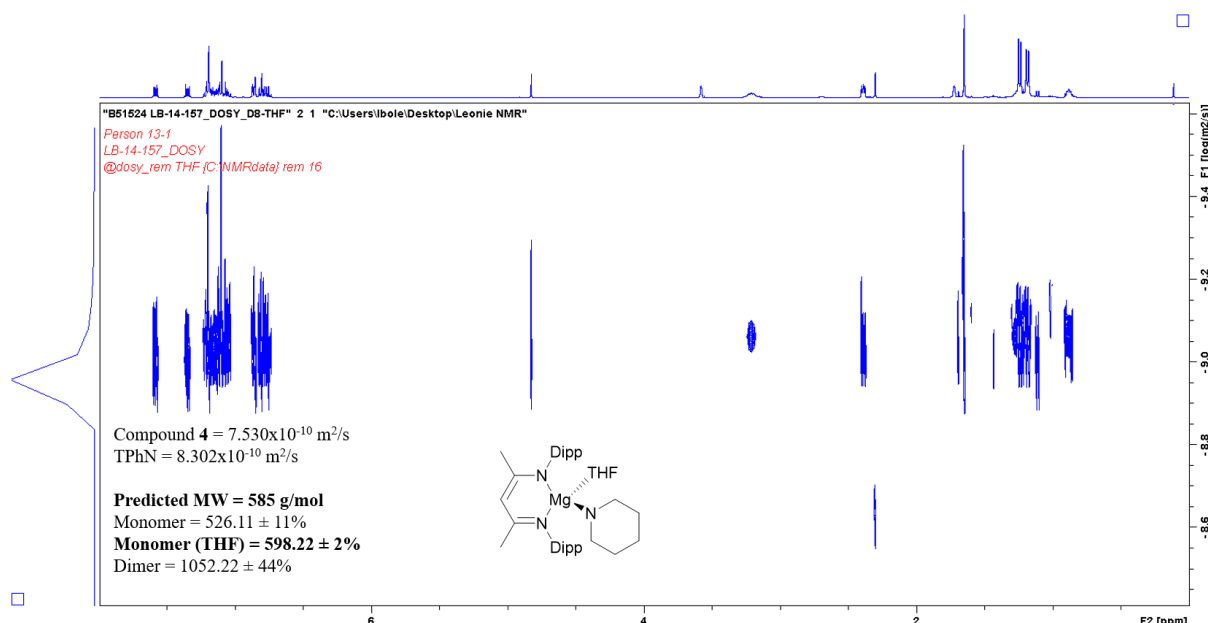


Figure S 5  $^1\text{H}$  DOSY NMR of compound **4** with TPhN as a reference standard

## Synthesis of Compound **5**

A solution of **2** (0.291 g, 0.5 mmol) in 5 mL of THF was prepared in a Schlenk flask, to which 43  $\mu\text{L}$  (0.5 mmol) of morpholine was added and stirred at room temperature for 3 g. The resulting mixture gave a pale yellow solution which was concentrated *in vacuo* and cooled down to  $-30^\circ\text{C}$ . After 24 h, a crop of colourless crystals was obtained, which upon X-ray crystallographic analysis proved to be compound **5** although the quality of data obtained does not allow for discussion of structural parameters. In order to obtain a good yield of this species, the reaction was repeated on a 1 mmol scale and, after stirring at room temperature, all THF was removed and the resulting white solid was suspended in 10 mL of hexane, isolated by filtration and stored inside the glovebox (0.439 g, 73%).  $^1\text{H}$  DOSY NMR analysis has proven compound **5** to be a non-solvated monomer in  $\text{D}_8$ -THF solvent. Due to the inherent air-sensitive nature of this compound, no satisfactory CHN analysis could be obtained despite several attempts.

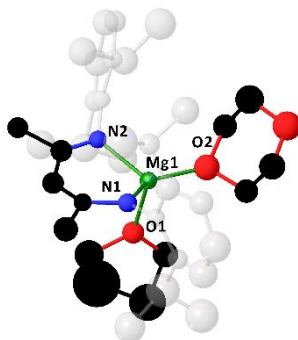


Figure S 6 Structure of compound **5** with displacement ellipsoids at 50% probability and all hydrogen atoms omitted for clarity. Structure appropriate only for general connectivity

**$^1\text{H}$  NMR (400.1 MHz,  $\text{D}_8\text{-THF}$ , 300 K):**  $\delta \sim 7.07$  (m, 6H, Ar(C)-H of  $\text{DippNacnac}$ ), 4.84 (s, 2H, CH of  $\text{DippNacnac}$ ), 3.21 (br. m, 4H, C(H)(CH<sub>3</sub>)<sub>2</sub> of  $i\text{Pr}$ ), 2.94 (m, 4H, -N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>O), 2.31 (m, 4H, -N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>O), 1.66 (s, 6H, CH<sub>3</sub> of  $\text{DippNacnac}$ ), 1.24 (d, 12H, C(H)(CH<sub>3</sub>)<sub>2</sub> of  $i\text{Pr}$ ), 1.18 (d, 12H, C(H)(CH<sub>3</sub>)<sub>2</sub> of  $i\text{Pr}$ ) ppm

**$^{13}\text{C}\{^1\text{H}\}$  NMR (100.62 MHz,  $\text{D}_8\text{-THF}$ , 300 K):**  $\delta \sim 168.99$  (C(CH<sub>3</sub>) of  $\text{DippNacnac}$ ), 146.09 (C<sub>q</sub> of Ar), 142.76 (C<sub>q</sub>( $i\text{Pr}$ ) of Ar), 125.34 (Ar-CH<sub>meta</sub>), 123.93 (Ar-C-H<sub>para</sub>), 94.51 (C-H of  $\text{DippNacnac}$ ), 71.05 (-N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>O), 53.43 (-N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>O), 28.50 (C(H)(CH<sub>3</sub>)<sub>2</sub> of  $i\text{Pr}$ ), 24.05 (C(H)(CH<sub>3</sub>)<sub>2</sub> of  $i\text{Pr}$ ), 25.11 (CH<sub>3</sub> of  $\text{DippNacnac}$ ), 24.36 (CH<sub>3</sub> of  $\text{DippNacnac}$ ) ppm

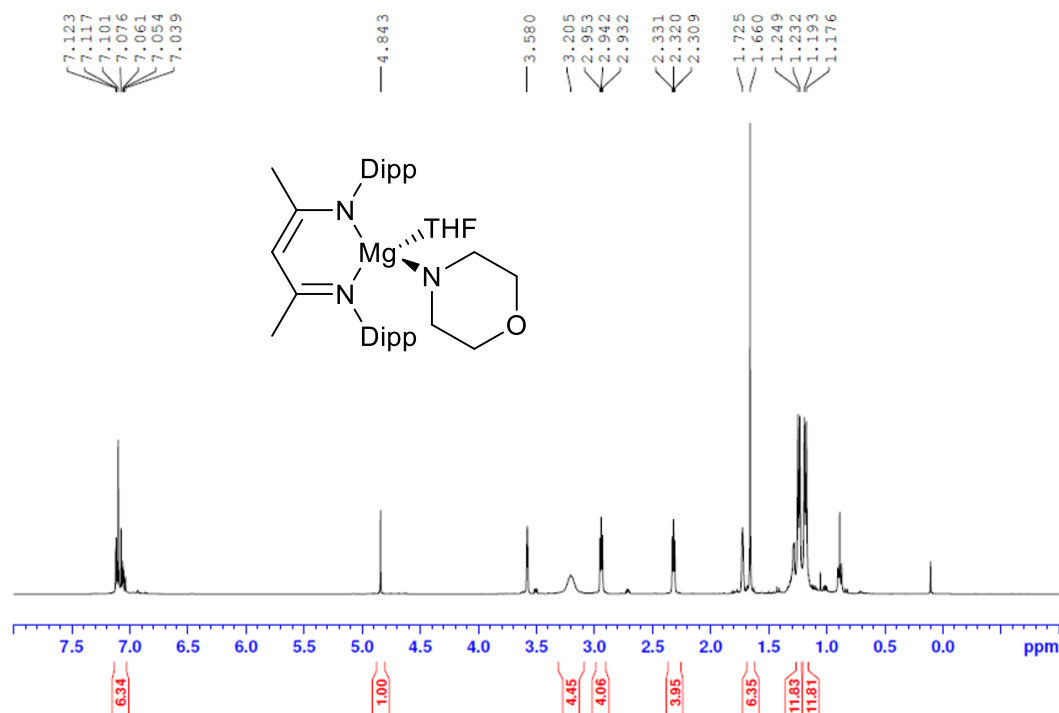


Figure S 7  $^1\text{H}$  NMR spectrum of compound 5

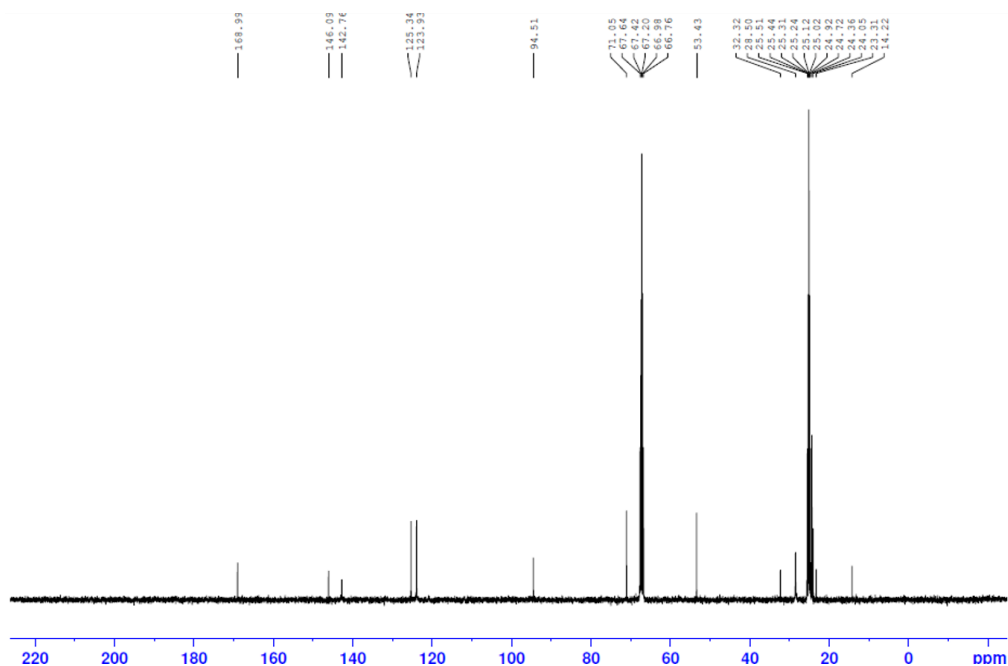


Figure S 8  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound 5

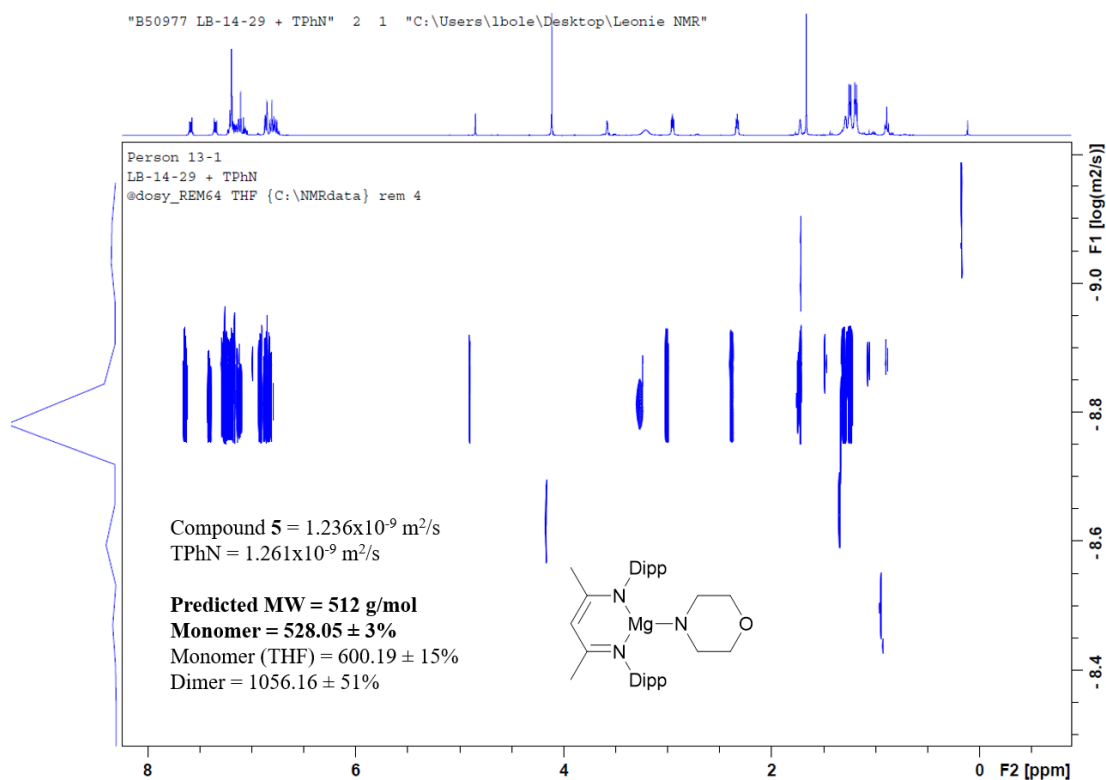


Figure S 9  $^1\text{H}$  DOSY of compound 5 in  $\text{D}_8\text{-THF}$  showing non-solvated monomer

## Synthesis of Compound 6

The synthesis of compound **6** was carried out according to the reported method.<sup>2</sup> To a Schlenk flask, 1.25 g (3 mmol) of <sup>Dipp</sup>NacnacH was added and the flask was purged with argon to as to ensure an inert atmosphere. The compound was then dissolved in 30 mL of toluene and 3.1 mL (3.1 mmol) of a 1.0 M solution of di-*n*-butylmagnesium was added – this mixture was heated at 50°C for 1 hour, affording a colourless solution of <sup>Dipp</sup>NacnacMgBu. Once cooled to room temperature, 0.26 mL (3.1 mmol) of pyrrolidine was added, resulting in a yellow suspension. This suspension was stirred at room temperature for 3 hours after which, gentle heating gave a yellow solution and slow cooling to room temperature afforded a crop of yellow crystals (0.277 g, 9%).

NMR analysis was performed in D<sub>8</sub>-THF with gentle heating required in order to solubilise the compound.

**<sup>1</sup>H NMR (400.1 MHz, D<sub>8</sub>-THF, 300 K):** δ ~ 7.10 (m, 12H, Ar(C)-H of <sup>Dipp</sup>Nacnac), 4.82 (s, 2H, CH of <sup>Dipp</sup>Nacnac), 3.22 (br. m, 4H, C(H)(CH<sub>3</sub>)<sub>2</sub> of <sup>i</sup>Pr), 2.26 (m, 8H, N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>), 1.65 (s, 12H, CH<sub>3</sub> of <sup>Dipp</sup>Nacnac), 1.18 (m, 48H, C(H)(CH<sub>3</sub>)<sub>2</sub> of <sup>i</sup>Pr), 1.02 (m, 8H, N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>) ppm

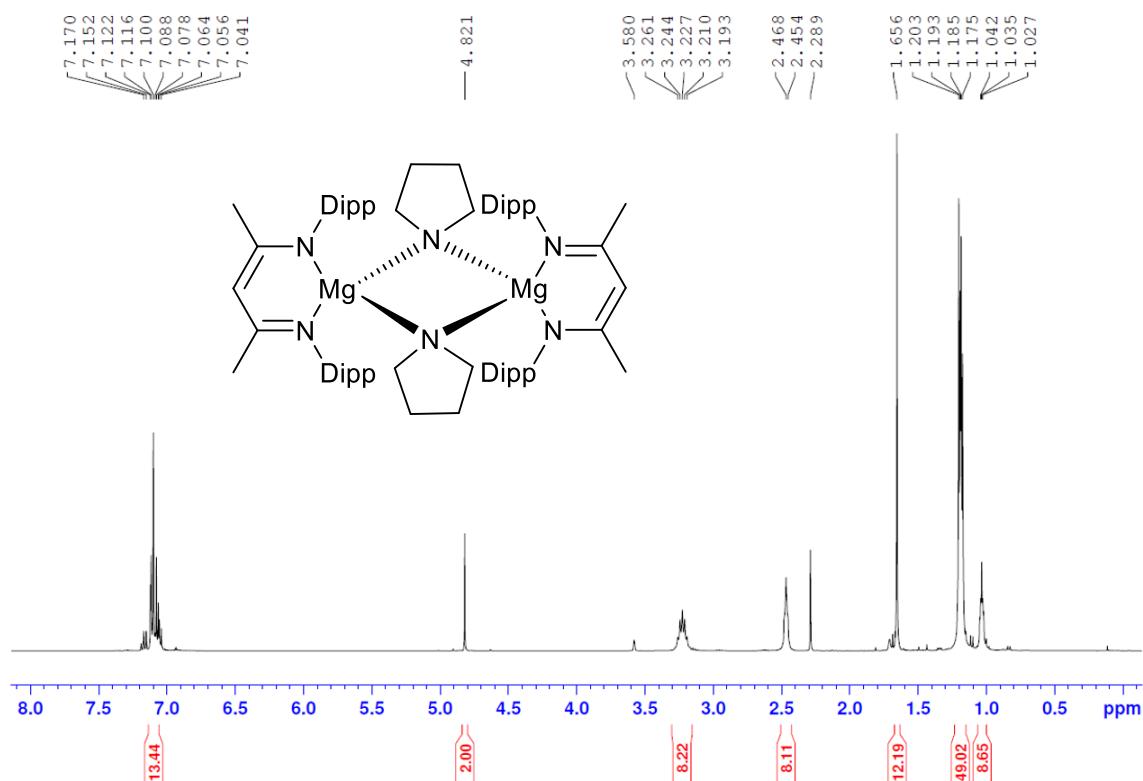


Figure S 10 <sup>1</sup>H NMR of compound **6**

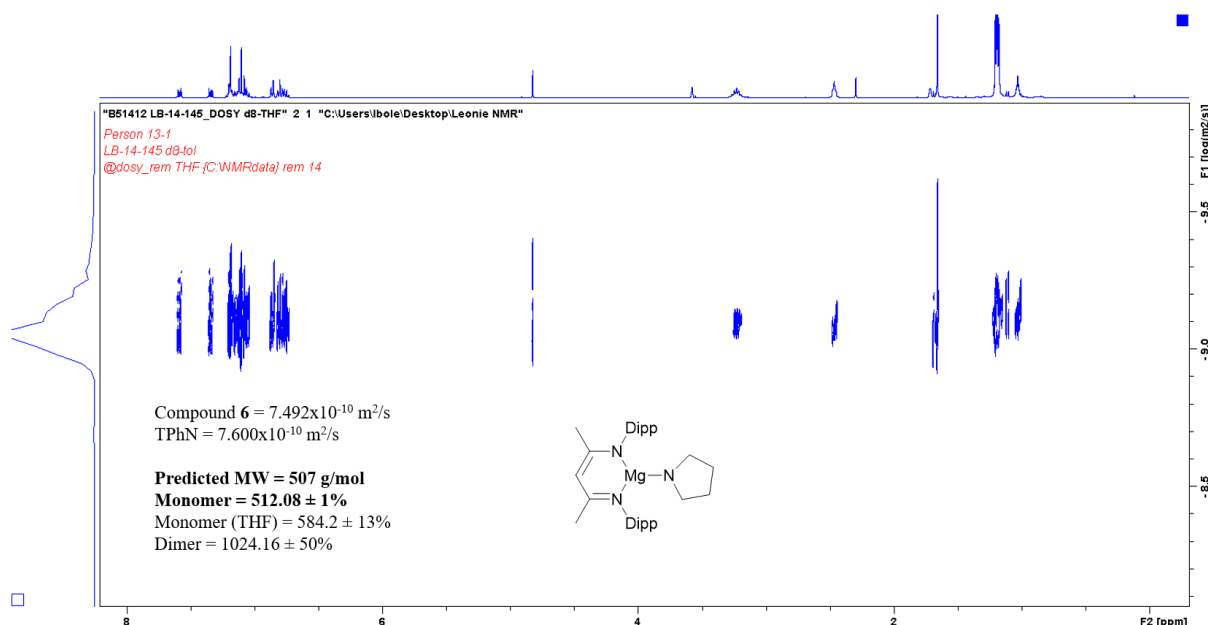


Figure S 11  $^1\text{H}$  DOSY NMR spectrum of compound **6** in  $\text{D}_8\text{-THF}$  with TPhN as reference standard

## Synthesis of Compound **9**

To an argon-flushed Schlenk flask, 1 mL of a 1.0 M solution of di-*n*-butylmagnesium was added to 10 mL of dried hexane. Then, 0.169 g (1 mmol) of diphenylamine was added giving a white suspension – this mixture was refluxed at  $70^\circ\text{C}$  for 1 hour. After this, 1 mmol (0.416 g) of  $\text{DippNacnacH}$  was added via a solid addition tube and the white suspension was heated to reflux for a further 2 hours. Once cooled to room temperature, all of the hexane was removed under vacuum and 7 mL of toluene was added. Gentle heating afforded a pale green solution and slow cooling to room temperature overnight gave a crop of green crystals (compound **6** in 0.348 g, 57% yield). Anal. Calcd. for  $\text{C}_{41}\text{H}_{51}\text{MgN}_3$ : C, 80.71; H, 8.42; N, 6.98. Found C, 80.61; H, 8.57; N, 6.79

**$^1\text{H}$  NMR (400.1 MHz,  $\text{C}_6\text{D}_6$ , 300 K):**  $\delta$  ~ 7.05 (m, 6H, Ar(C)-*H* of  $\text{DippNacnac}$ ), 6.49 (t, 4H, Ar(C)-*H*<sub>meta</sub> of diphenylamine), 6.62 (t, 2H, Ar(C)-*H*<sub>para</sub> of diphenylamine), 6.45 (d, 4H, Ar(C)-*H*<sub>ortho</sub> of diphenylamine), 4.93 (s, 2H, CH of  $\text{DippNacnac}$ ), 3.09 (sept., 4H, C(H)(CH<sub>3</sub>)<sub>2</sub> of *i*Pr), 1.65 (s, 6H, CH<sub>3</sub> of  $\text{DippNacnac}$ ), 1.14 (d, 12H, C(H)(CH<sub>3</sub>)<sub>2</sub> of *i*Pr), 1.04 (d, 12H, C(H)(CH<sub>3</sub>)<sub>2</sub> of *i*Pr) ppm

**$^{13}\text{C}\{^1\text{H}\}$  NMR (100.62 MHz,  $\text{C}_6\text{D}_6$ , 300 K):**  $\delta$  ~ 171.18 (C(CH<sub>3</sub>) of  $\text{DippNacnac}$ ), 154.63 (Ar(C)<sub>ipso</sub> of diphenylamine), 143.44 (C<sub>q</sub> of Ar), 142.21 (C<sub>q</sub>(*i*Pr) of Ar), 130.03 (Ar-CH<sub>meta</sub> of diphenylamine), 126.35 (Ar-CH<sub>meta</sub>), 124.39 (Ar-C-H<sub>para</sub>), 120.36 (Ar-CH<sub>ortho</sub> of diphenylamine), 118.11 (Ar-CH<sub>para</sub> of diphenylamine), 95.94 (C-H of  $\text{DippNacnac}$ ), 29.08 (C(H)(CH<sub>3</sub>)<sub>2</sub> of *i*Pr), 24.25 (CH<sub>3</sub> of  $\text{DippNacnac}$ ), 24.18 (CH<sub>3</sub> of  $\text{DippNacnac}$ ), 23.99 (C(H)(CH<sub>3</sub>)<sub>2</sub> of *i*Pr), ppm

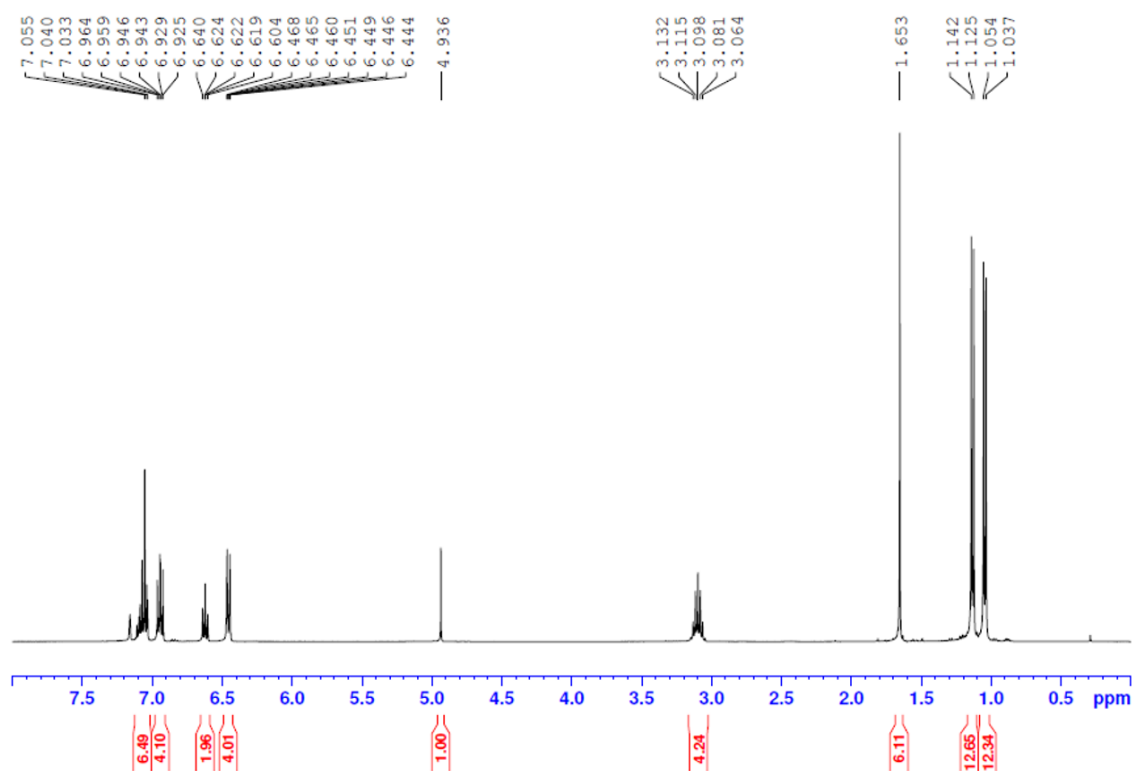


Figure S 12 <sup>1</sup>H NMR spectrum of compound 9

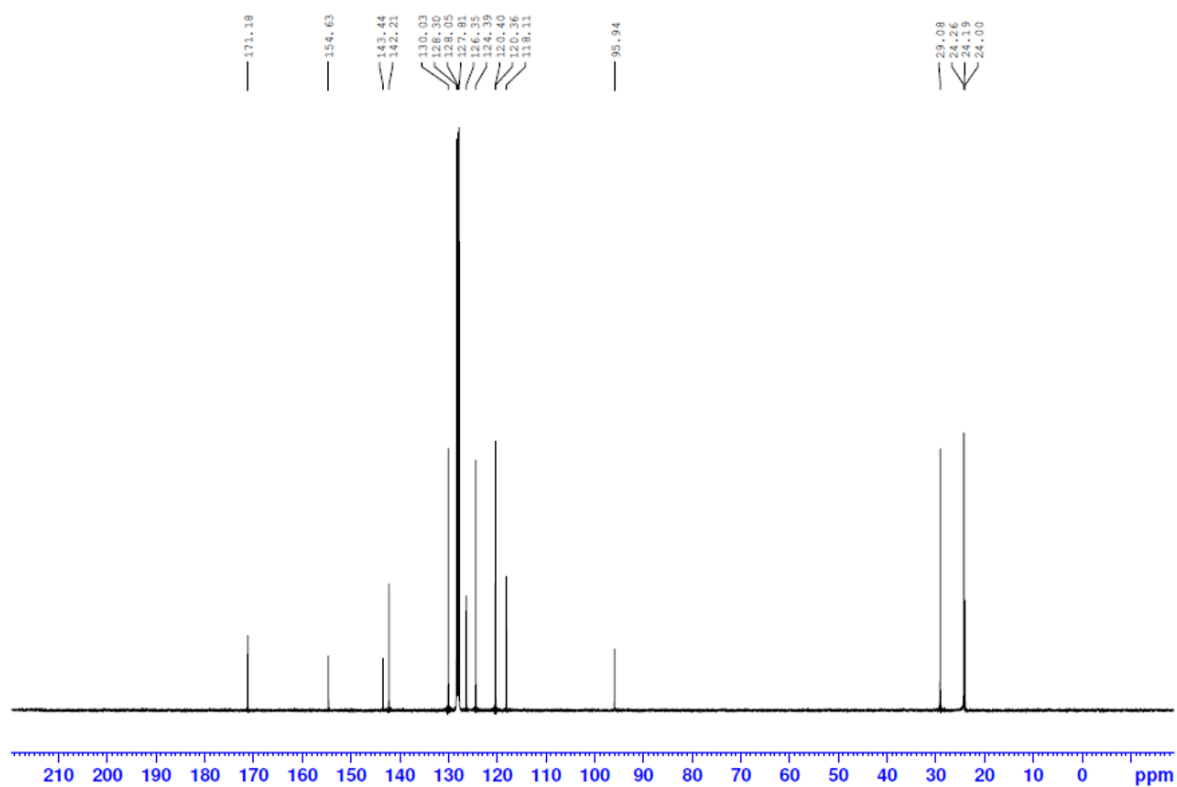


Figure S 13 <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of compound 9

## Synthesis of Compound 10

To a solution of **1** (0.56 g, 1 mmol) in THF (5 mL), benzotriazole (0.120 g, 1 mmol) was added, giving rise to a yellow solution. This was stirred for 4 hours at room temperature and resulted in the formation of a yellow suspension. Removal of all THF and addition of 10 mL of toluene gave a yellow suspension which was filtered and, from the filtrate, colourless crystals obtained. 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 obtaining a suspension. The resulting solid was isolated via filtration and placed in a glovebox (0.31 g, 55%). Due to the inherent air-sensitive nature of this compound, no satisfactory CHN analysis could be obtained despite several attempts.

**<sup>1</sup>H NMR (400.13 MHz, D<sub>5</sub>-pyr, 300 K)**  $\delta$  7.51-7.48 (br. m, 4H, C<sub>6</sub>H<sub>4</sub>N<sub>3</sub>), 7.36-7.24 (br.m, 16H, C<sub>6</sub>H<sub>4</sub>N<sub>3</sub> + Ar(C)-H of DippNacnac), 5.20 (s, 2H, CH of DippNacnac), 3.26-3.17 (m, 8H, CH, C(H)(CH<sub>3</sub>)<sub>2</sub> of <sup>*i*</sup>Pr), 1.89 (s, 12H, CH<sub>3</sub> of DippNacnac), 1.17-1.15 (d, 24H, CH<sub>3</sub>, C(H)(CH<sub>3</sub>)<sub>2</sub> of <sup>*i*</sup>Pr), 0.66-0.64 (d, 24H, CH<sub>3</sub>, C(H)(CH<sub>3</sub>)<sub>2</sub> of <sup>*i*</sup>Pr) ppm

**<sup>13</sup>C{<sup>1</sup>H} NMR (100.61 MHz, D<sub>5</sub>-pyr, 343 K)**  $\delta$  170.3 (C(CH<sub>3</sub>) of DippNacnac), 145.8 (C<sub>q</sub>, Ar), 145.7 (C<sub>q</sub> of Ar), 143.3 (C<sub>q</sub> of Ar), 125.9 (CH, C<sub>6</sub>H<sub>4</sub>N<sub>3</sub>), 124.5 (Ar-CH<sub>meta</sub>), 123.5 (Ar-C-H<sub>para</sub>), 117.2 (CH, C<sub>6</sub>H<sub>4</sub>N<sub>3</sub>), 95.3 (CH of DippNacnac), 38.9 (C(H)(CH<sub>3</sub>)<sub>2</sub> of <sup>*i*</sup>Pr), 32.4 (CH<sub>3</sub> of DippNacnac), 32.2 (CH<sub>3</sub> of DippNacnac), 29.0 (C(H)(CH<sub>3</sub>)<sub>2</sub> of <sup>*i*</sup>Pr), 26.3 (C(H)(CH<sub>3</sub>)<sub>2</sub> of <sup>*i*</sup>Pr) ppm

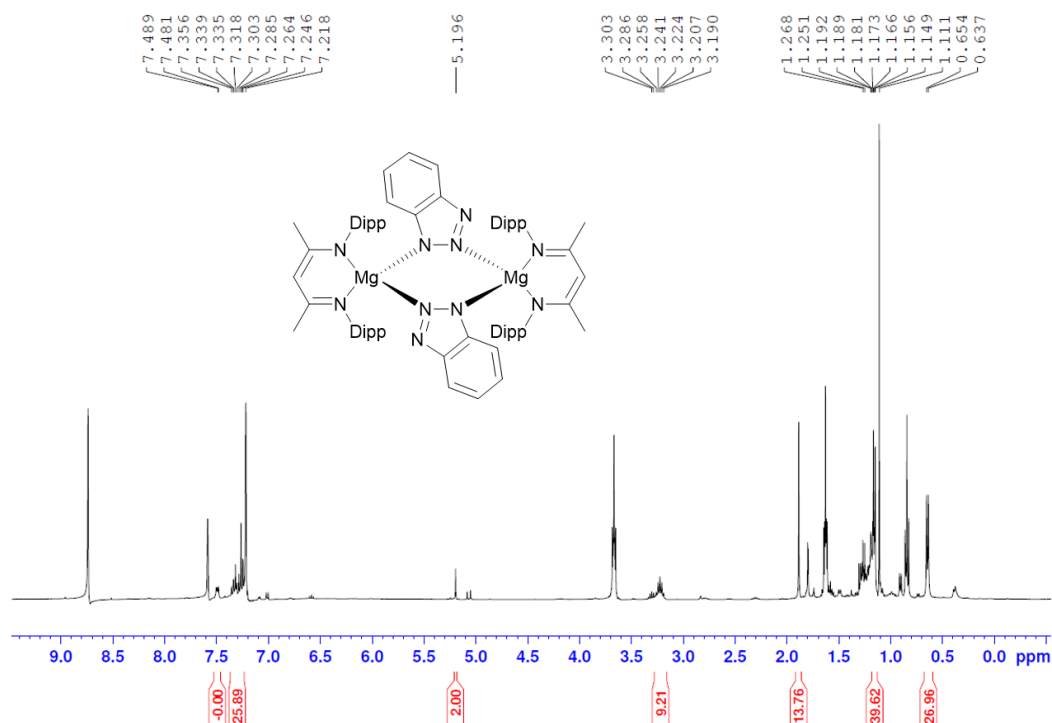


Figure S 14 <sup>1</sup>H NMR spectrum of compound 10

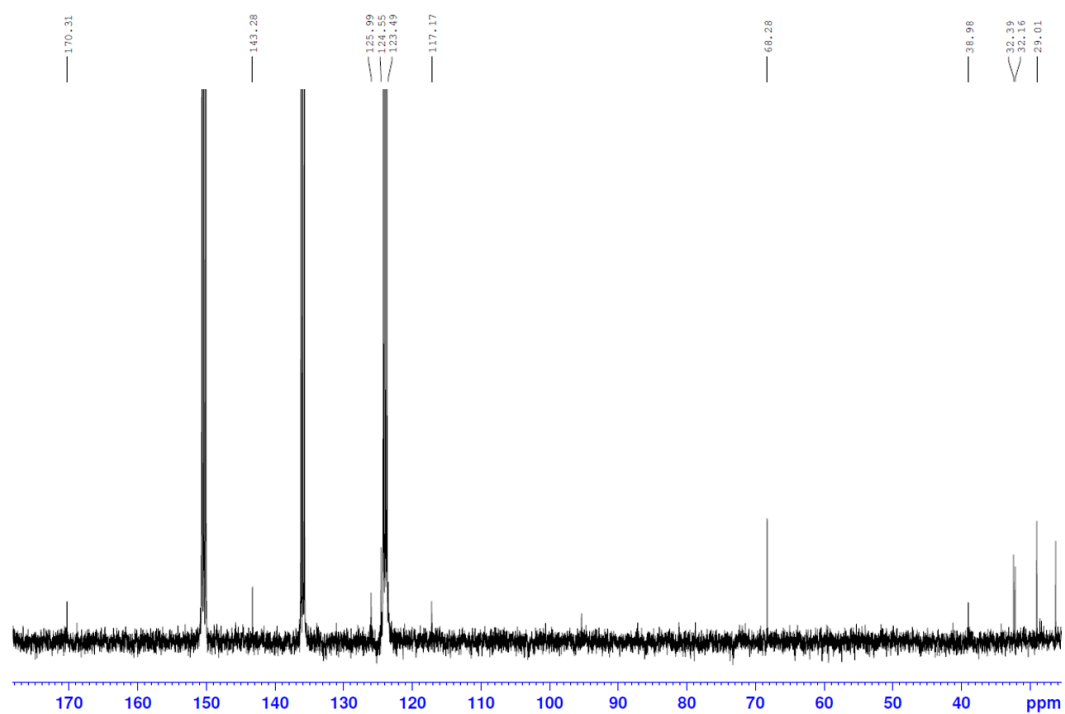


Figure S 15  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound 10



## Synthesis of Aminofluoroarenes (7a-7i, 11a-11i)

### Synthesis of Compound 7a

To a J. Young's NMR tube, 0.146 g (0.25 mmol) of **1** was added and dissolved in 0.5 mL of D<sub>8</sub>-THF alongside 46  $\mu$ L (0.25 mmol) of di-*n*-butylamine. After 1 h, di-*n*-butylamine had been quantitatively deprotonated, forming compound **3** in solution – confirmed by NMR spectroscopy. Then, 0.25 mmol (48 mg) of 2-(2,4-difluorophenyl)pyridine was added and immediate precipitation of **8** ( $[(^{\text{Dipp}}\text{NacnacMg}(\mu\text{-F})(\text{THF}))_2]$ ) was observed. Analysis of the resulting mixture, after filtration, by <sup>1</sup>H NMR revealed quantitative C-F activation giving rise to compound **7a** (>99%) with the yield determined against 20 mol% ferrocene (9 mg) as an internal standard.

For purification, 0.640 (1.1 mmol) of **1** was added to a Schlenk flask prepared inside a glovebox and then dissolved in 5 mL of THF giving a yellow solution. Then, 0.9 mL of a 1.0 M solution of 2-(2,4-difluorophenyl)pyridine in THF was added to the reaction mixture resulting in the immediate precipitation of a yellow solid. The reaction mixture was stirred at room temperature overnight. Following a filtration and washing with THF, the filtrate was evaporated to dryness resulting in a cloudy yellow oil. Reverse-phase HPLC purification of compound **7a** was conducted using a Gilson preparative HPLC system of 322 pumps coupled to a 151 UV/Vis 163 spectrometer, 234 Autoinjector and a GX-271 liquid handler using an Agilent Zorbax SB-C18, 21.2 x 150 mm, 5  $\mu$ m column at room temperature. Purification was performed using a gradient method ranging from 5-90% MeCN (1% trifluoroacetic acid (TFA)) in H<sub>2</sub>O (1% TFA) over 25 minutes at a flow rate of 5 mL/min, with UV monitoring at 254 nm. Analysis was conducted using Gilson Trilution software. Compound **7a** was thus isolated as the TFA salt. Washing with 2 M NaOH solution and extracting with DCM resulted in the purified compound as a yellow oil, 93 mg, 34%.

**<sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>, 300 K):**  $\delta$  ~ 8.67 (m, 1H, Ar-*H* of py), 7.77 (dt, 1H, Ar-*H* of py), 7.64 (td, 1H, Ar-*H* of py), 7.48 (m, 1H, Ar-*H*), 7.17 (m, 1H, Ar-*H* of py), 6.75 (m, 2H, Ar-*H*), 2.81 (t, 4H, -N(CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 1.36 (m, 4H, -N(CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 1.13 (-N(CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 0.81 (t, 6H, -N(CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), ppm

**<sup>19</sup>F{<sup>1</sup>H} NMR (376.5 MHz, CDCl<sub>3</sub>, 300 K):**  $\delta$  ~ -112.92 (s, Ar-*F*)

**<sup>13</sup>C{<sup>1</sup>H} NMR (100.62 MHz, CDCl<sub>3</sub>, 300 K):**  $\delta$  ~ 164.7 (Ar(C<sub>q</sub>) of py), 162.2 (Ar(C<sub>q</sub>)), 158.9 (Ar(C<sub>q</sub>)-di-*n*-butylamine), 151.6 (d, Ar(C)-F), 149.8 (Ar(C)-H), 135.7 (Ar(C)-H), 133.0 (d, Ar(C)-H), 124.5 (Ar(C)-H), 121.5 (Ar(C)-H), 108.6 (d, Ar(C)-H), 107.4 (d, Ar(C)-H), 52.7 (-N(CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 29.0 (-N(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 20.5 (-N(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 14.0 (-N(CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>) ppm

LRMS (GC/ESI) *m/z*: 301.2 [M+H]<sup>+</sup>

HRMS (TOF) Calc. for, C<sub>19</sub>H<sub>25</sub>N<sub>2</sub>F 300.2002; Found, 300.1999 (error 1.29 ppm)



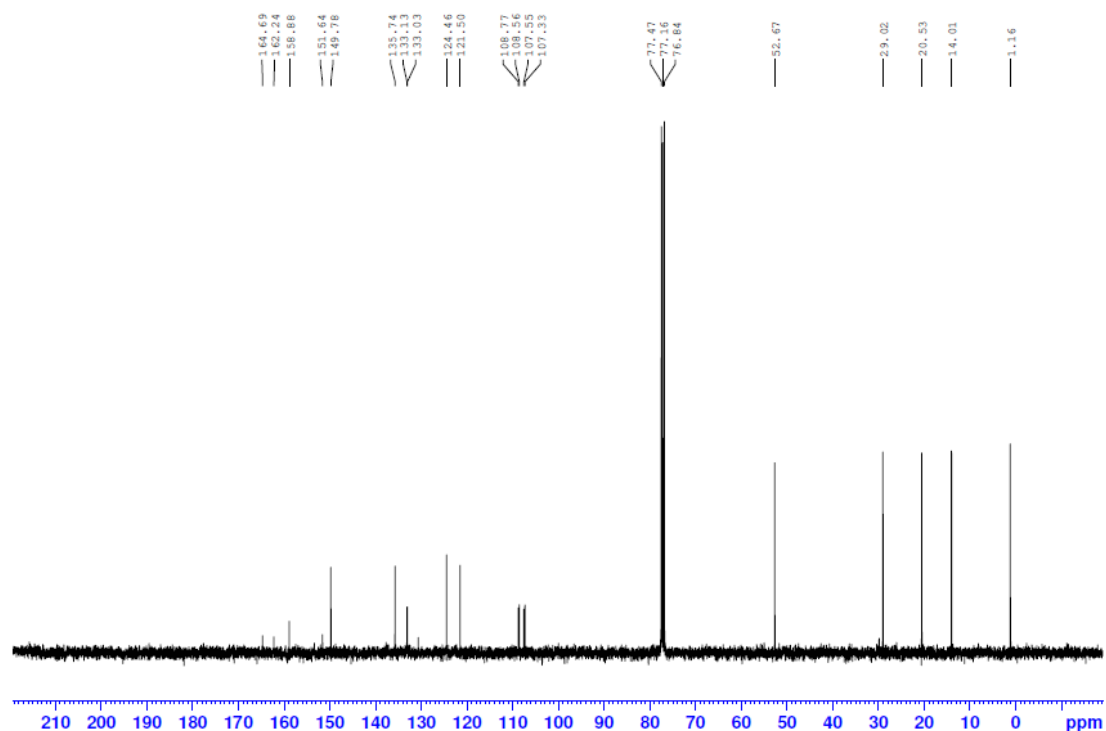


Figure S 18  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **7a**

## Synthesis of Compound **7b**

To a J. Young's NMR tube, 0.146 g (0.25 mmol) of **1** was added and dissolved in 0.5 mL of  $\text{D}_8$ -THF alongside 25  $\mu\text{L}$  (0.25 mmol) of piperidine. After 1 h, piperidine had been quantitatively deprotonated, forming compound **4** in solution – confirmed by NMR spectroscopy. Then, 0.25 mmol (48 mg) of 2-(2,4-difluorophenyl)pyridine was added and immediate precipitation of **8** ( $[(^{\text{Dipp}}\text{NacnacMg}(\mu\text{-F})(\text{THF}))_2]$ ) was observed. Analysis of the resulting mixture, after filtration, by  $^1\text{H}$  NMR revealed quantitative C-F activation giving rise to compound **7b** (>99%) with the yield determined against 20 mol% ferrocene (9 mg) as an internal standard.

For purification, 0.640 (1.1 mmol) of **1** was added to a Schlenk flask prepared inside a glovebox and then dissolved in 5 mL of THF giving a yellow solution. To this, 0.11 mL (1.1 mmol) of piperidine was added with the yellow solution persisting – this was stirred at room temperature for 6 h. Then, 0.9 mL of a 1.0 M solution of 2-(2,4-difluorophenyl)pyridine in THF was added to the reaction mixture resulting in the immediate precipitation of a yellow solid. The reaction mixture was stirred at room temperature overnight. Following a filtration and washing with THF, the filtrate was evaporated to dryness resulting in a cloudy yellow oil. Reverse-phase HPLC purification of compound **7b** was conducted using a Gilson preparative HPLC system of 322 pumps coupled to a 151 UV/Vis 163 spectrometer, 234 Autoinjector and a GX-271 liquid handler using an Agilent Zorbax SB-C18, 21.2 x 150 mm, 5  $\mu\text{m}$  column at room temperature. Purification was performed using a gradient method ranging from 5-90% MeCN (1% trifluoroacetic acid (TFA)) in  $\text{H}_2\text{O}$  (1% TFA) over 25 minutes at a flow rate of 5 mL/min, with UV monitoring at 254 nm. Analysis was conducted using Gilson Trilution software. Compound **7b** was thus isolated as the TFA salt. Washing with 2 M NaOH solution and extracting with DCM resulted in the purified compound as a yellow oil, 92 mg, 40%.

**<sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>, 300 K):** δ ~ 8.68 (m, 1H, Ar-*H* of py), 7.99 (dt, 1H, Ar-*H* of py), 7.66 (td, 1H, Ar-*H* of py), 7.54 (m, 1H, Ar-*H*), 7.16 (qd, 1H, Ar-*H* of py), 6.75 (m, 2H, Ar-*H* x 2), 2.78 (m, 4H, -N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>), 1.48 (m, 6H, -N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>) ppm

**<sup>19</sup>F NMR (376.5 MHz, CDCl<sub>3</sub>, 300 K):** δ ~ -112.15 (m, Ar-*F*)

**<sup>13</sup>C{<sup>1</sup>H} NMR (100.62 MHz, CDCl<sub>3</sub>, 300 K):** δ ~ 164.9 (Ar(C<sub>q</sub>) of py), 162.5 (Ar(C<sub>q</sub>)), 158.5 (Ar(C<sub>q</sub>)-Piperidine), 153.7 (d, Ar(C)-F), 149.9 (Ar(C)-H), 135.6 (Ar(C)-H), 133.0 (d, Ar(C)-H), 124.2 (Ar(C)-H), 121.6 (Ar(C)-H), 108.8 (d, Ar(C)-H), 105.7 (d, Ar(C)-H), 53.2 (-N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>), 26.0 (-N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>), 24.1 (-N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>) ppm

LRMS (GC/ESI) *m/z*: 257 [M+H]<sup>+</sup>

HRMS (TOF): Calc. for C<sub>16</sub>H<sub>7</sub>FN<sub>2</sub>, 256.1376; Found, 256.1370 (error 0.49 ppm)

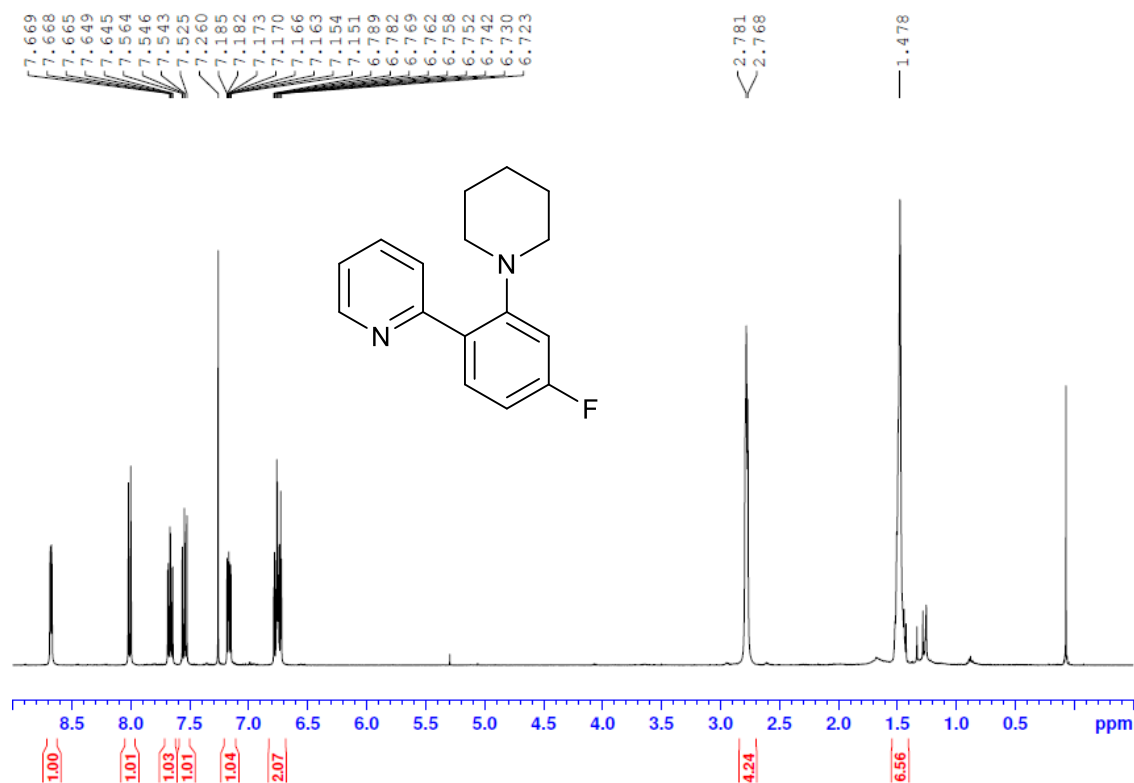


Figure S 19 <sup>1</sup>H NMR spectrum of compound 7b

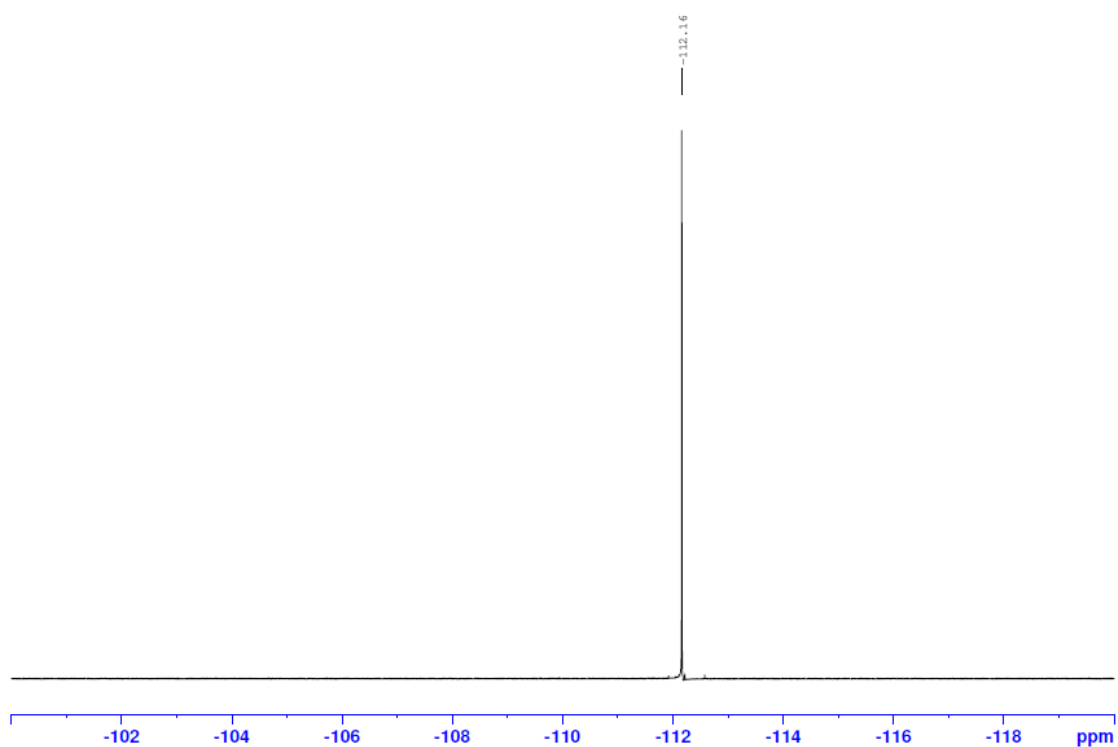


Figure S 20  $^{19}\text{F}$  NMR spectrum of compound 7b

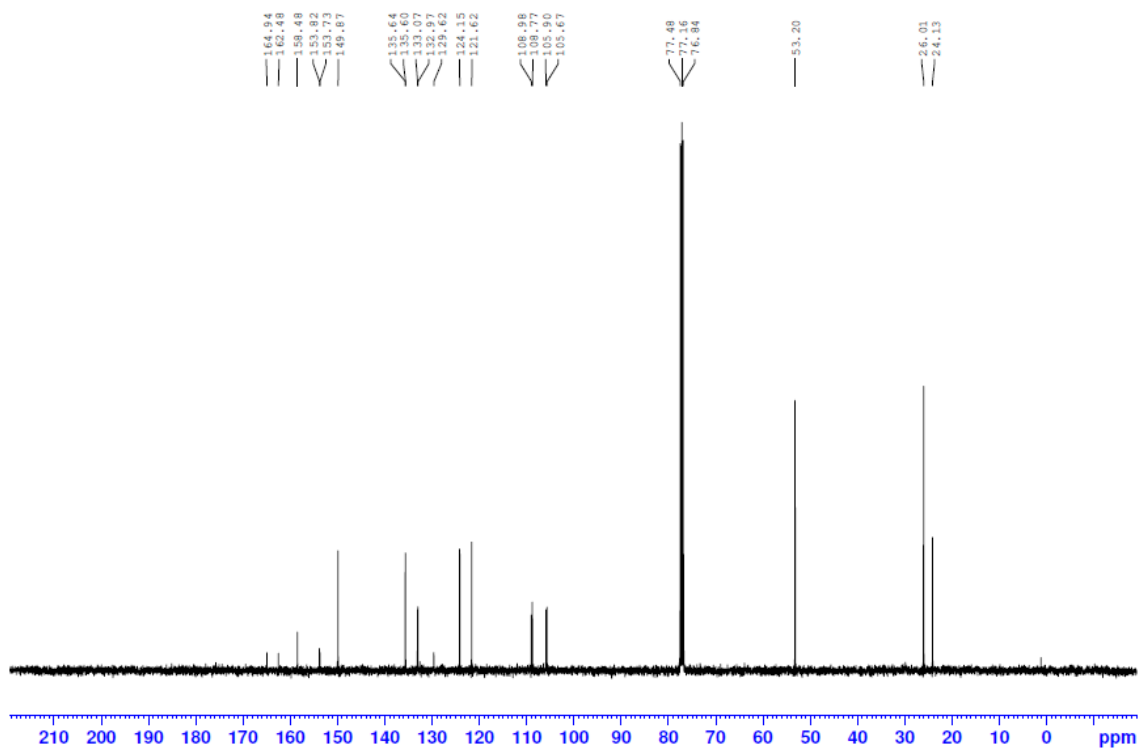


Figure S 21  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound 7b

## Synthesis of Compound 7c

To a J. Young's NMR tube, 0.146 g (0.25 mmol) of **1** was added and dissolved in 0.5 mL of D<sub>8</sub>-THF alongside 22  $\mu$ L (0.25 mmol) of morpholine. After 1 h, morpholine had been quantitatively deprotonated, forming compound **5** in solution – confirmed by NMR spectroscopy. Then, 0.25 mmol (48 mg) of 2-(2,4-difluorophenyl)pyridine was added and immediate precipitation of **8** ( $[(^{\text{Dipp}}\text{NacnacMg}(\mu\text{-F})(\text{THF}))_2]$ ) was observed. Analysis of the resulting mixture, after filtration, by <sup>1</sup>H NMR revealed quantitative C-F activation giving rise to compound **7c** (>99%) with the yield determined against 20 mol% ferrocene (9 mg) as an internal standard.

For isolation of the final organic product, this procedure was repeated on a 1 mmol scale inside a Schlenk flask under argon atmosphere. Once precipitation of **8** occurred, the solid was removed via cannula filtration and all THF solvent removed from the resulting filtrate. The oil obtained from the filtrate was then purified by alumina-flash column chromatography (100:5:10 pentane: trimethylamine:ethyl acetate) to give the target compound as a brown, crystalline solid in 81% (204 mg) yield.

**<sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>, 300 K):**  $\delta$  ~ 8.67 (m, 1H, Ar-*H* of py), 7.94 (dt, 1H, Ar-*H* of py), 7.67 (m, 1H, Ar-*H* of py), 7.53 (m, 1H, Ar-*H*), 7.18 (m, 1H, Ar-*H* of py), 6.80 (td, 1H, Ar-*H*), 6.73 (dd, 1H, Ar-*H*), 3.61 (t, 4H, -N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>O), 2.81 (t, 4H, -N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>O) ppm

**<sup>19</sup>F NMR (376.5 MHz, CDCl<sub>3</sub>, 300 K):**  $\delta$  ~ -111.50 (m, Ar-*F*)

**<sup>13</sup>C{<sup>1</sup>H} NMR (100.62 MHz, CDCl<sub>3</sub>, 300 K):**  $\delta$  ~ 164.87 (Ar(C<sub>q</sub>)-N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>O), 162.4 (Ar(C<sub>q</sub>) of py), 152.06 (d, Ar(C)-F), 149.4 (Ar(C)-H of py), 135.8 (Ar(C)-H of py), 133.4 (Ar(C)-H), 129.6 (Ar(C<sub>q</sub>) of Ph), 124.2 (Ar(C)-H of py), 122.0 (Ar(C)-H of py), 109.6 (Ar(C)-H), 105.5 (Ar(C)-H), 66.79 (-N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>O), 51.9 (-N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>O) ppm

LRMS (GC/ESI) *m/z*: 259.1 [M+H]<sup>+</sup>

HRMS (TOF): Calc. for C<sub>15</sub>H<sub>15</sub>FN<sub>2</sub>O, 258.1168; Found, 258.1163 (error 0.26 ppm)



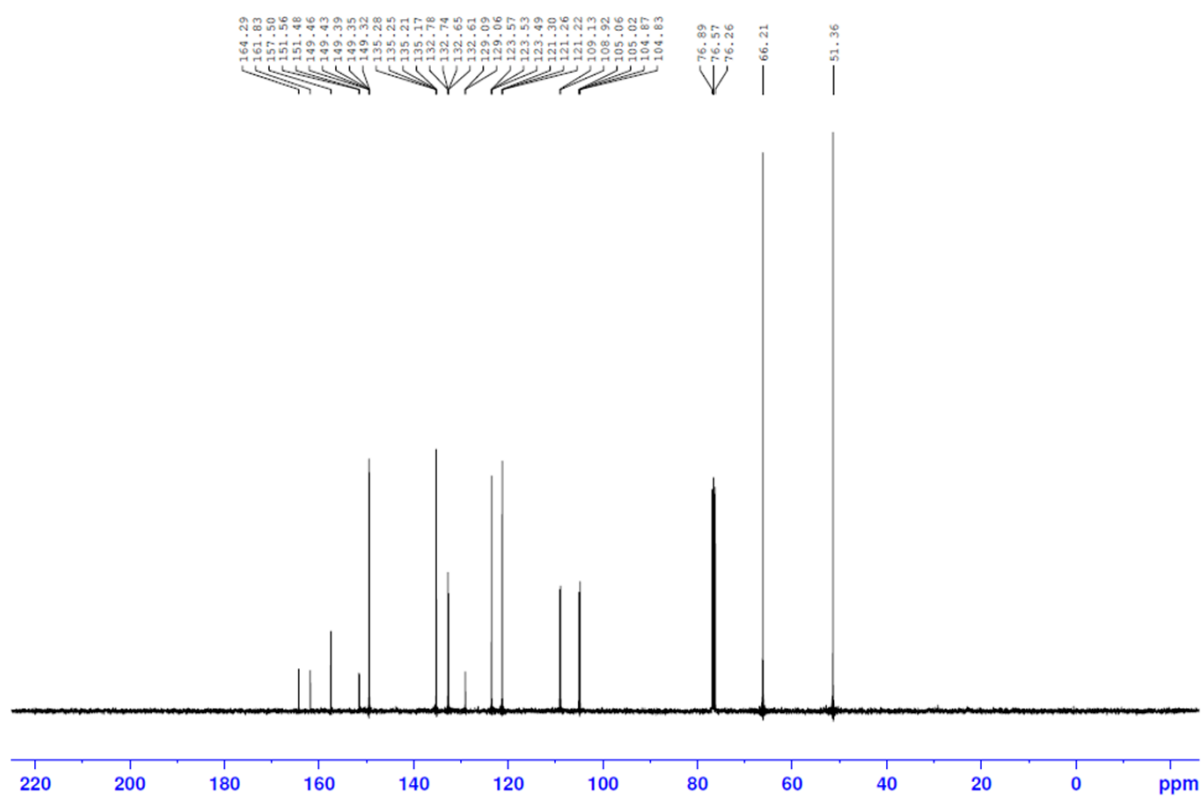


Figure S 24  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound 7c



## Synthesis of Compound 7d

To a J. Young's NMR tube, 0.146 g (0.25 mmol) of **1** was added and dissolved in 0.5 mL of D<sub>8</sub>-THF alongside 21  $\mu$ L (0.25 mmol) of pyrrolidine. After 1 h, pyrrolidine had been quantitatively deprotonated, forming compound **6** as a THF-solvated monomer (supported by DOSY NMR studies - **Figure S 11**) in solution – confirmed by NMR spectroscopy (**Figure S 26**). Then, 0.25 mmol (48 mg) of 2-(2,4-difluorophenyl)pyridine was added and immediate precipitation of **8** ( $[(^{\text{Dipp}}\text{NacnacMg}(\mu\text{-F})(\text{THF}))_2]$ ) was observed. Analysis of the resulting mixture, after filtration, by <sup>1</sup>H NMR revealed quantitative C-F activation giving rise to compound **7d** (>99%) with the yield determined against 20 mol% ferrocene (9 mg) as an internal standard. The general procedure depicted in (**Figure S 25-Figure S 29**) was carried for compounds **7a-7i** in order to determine NMR yields of these compounds.

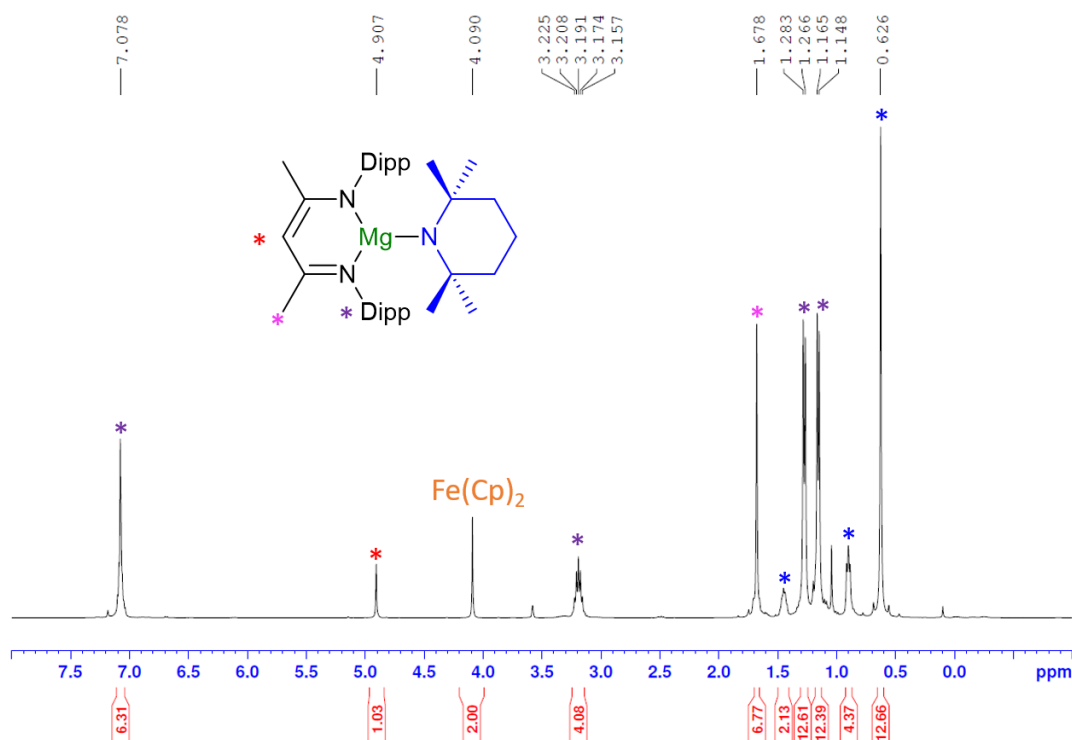


Figure S 25 <sup>1</sup>H NMR spectrum of compound **1** with 20 mol% Fe(Cp)<sub>2</sub> in D<sub>8</sub>-THF

**<sup>1</sup>H NMR (400.1 MHz, D<sub>8</sub>-THF, 300 K):**  $\delta$  ~ 7.08 (br. s, 6H, Ar-*H* of Dipp), 4.91 (s, 1H, C-*H* of <sup>Dipp</sup>Nacnac backbone), 4.90 (s, 2H, 20 mol% Fe(Cp)<sub>2</sub>), 3.19 (sept., 4H, C-*H* of <sup>i</sup>Pr), 1.67 (s, 6H, CH<sub>3</sub> x2 of <sup>Dipp</sup>Nacnac backbone), 1.28 (br. m, 2H,  $\gamma$ -CH<sub>2</sub> of TMP), 1.26 (d, 12H, CH<sub>3</sub> of <sup>i</sup>Pr), 1.15 (d, 12H, CH<sub>3</sub> of <sup>i</sup>Pr), 0.9 (br. m, 4H,  $\beta$ -CH<sub>2</sub> of TMP), 0.63 (s, 12H, CH<sub>3</sub> of TMP) ppm

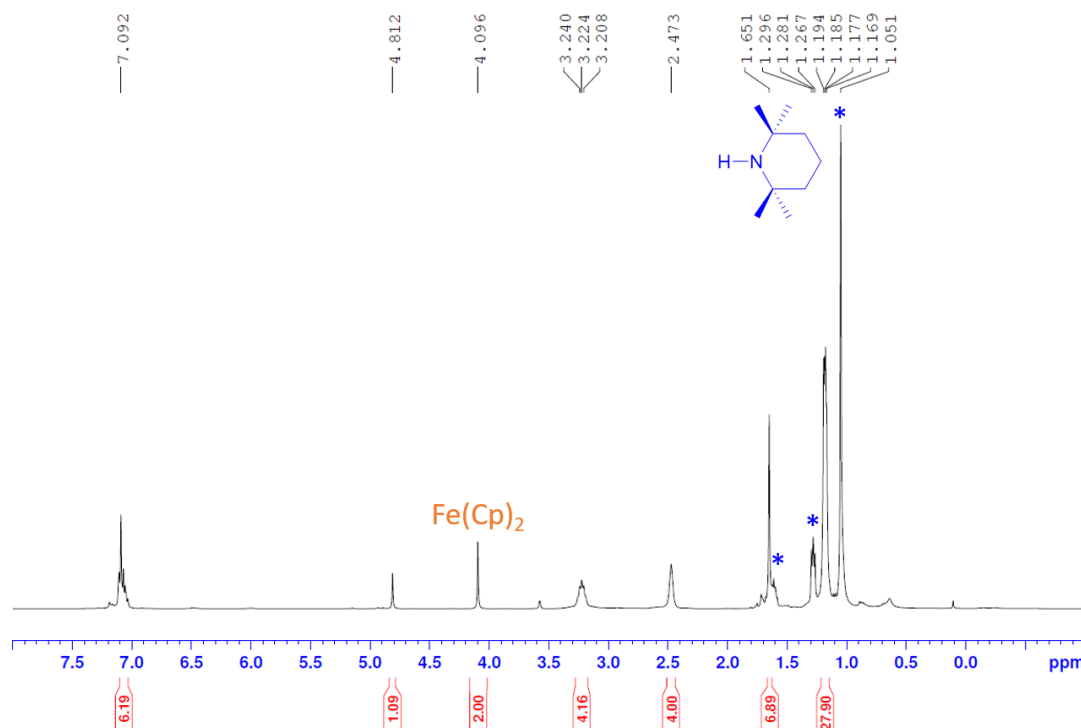


Figure S 26  $^1\text{H}$  NMR of in situ deprotonation of pyrrolidine, forming compound **6**, against 20 mol%  $\text{Fe}(\text{Cp})_2$  in  $\text{D}_8\text{-THF}$

$^1\text{H}$  NMR (400.1 MHz,  $\text{D}_8\text{-THF}$ , 300 K):  $\delta \sim 7.09$  (m, 12H, Ar(C)-H of  $\text{DippNacnac}$ ), 4.81 (s, 2H, CH of  $\text{DippNacnac}$ ), 4.09 (s, 2H,  $\text{Fe}(\text{Cp})_2$ ), 3.22 (br. m, 4H, C(H)(CH<sub>3</sub>)<sub>2</sub> of  $i\text{Pr}$ ), 2.47 (m, 4H, N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub> of compound **6**), 1.18 (br. m, 28H, CH<sub>3</sub> of  $\text{DippNacnac} \times 2$  + N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub> of compound **6**) ppm

Addition of **ppf** results in the precipitation of **8** ( $[(\text{DippNacnacMg}(\mu\text{-F})(\text{THF}))_2]$ ), leading to very broad and poorly resolved spectra due to the highly insoluble nature of this compound.

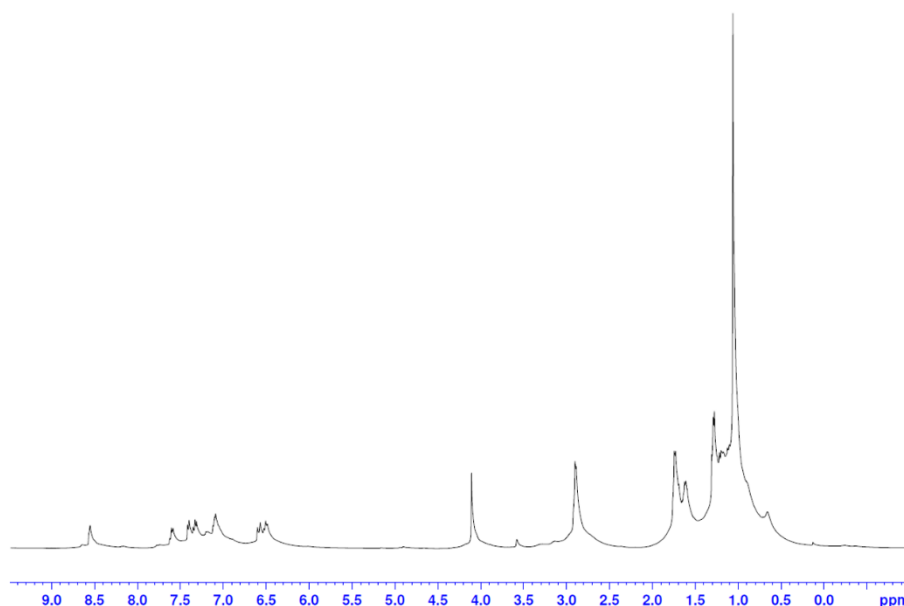


Figure S 27  $^1\text{H}$  NMR spectrum after addition of **ppf** to compound **6** in  $\text{D}_8\text{-THF}$ . Precipitation of compound **8** leads to broad and poorly resolved spectra

Filtering the reaction mixture allowed for the removal of insoluble **8** and obtainment of a well-defined spectrum displaying the formation of compound **7d**, the yield of which can be determined against  $\text{Fe}(\text{Cp})_2$ .

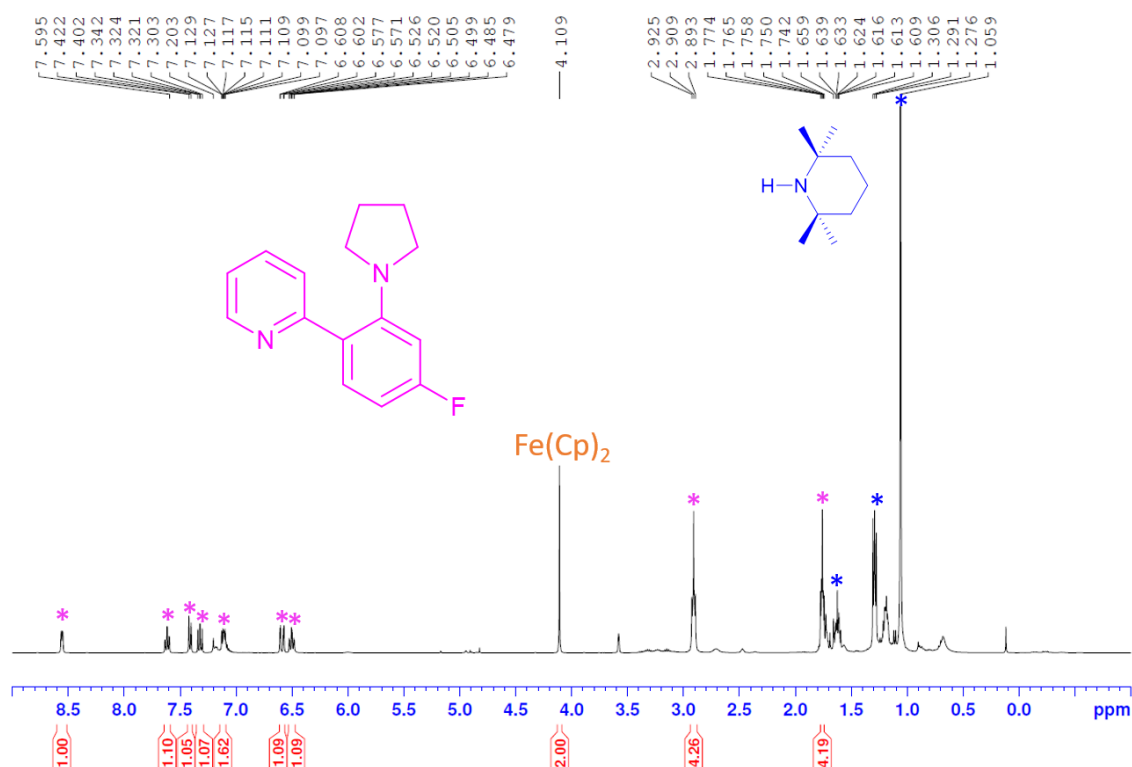


Figure S 28  $^1\text{H}$  NMR of compound **7d** in  $\text{D}_8$ -THF formed from C-F activation of ppf by in-situ formed compound **6**

$^1\text{H}$  NMR (400.1 MHz,  $\text{D}_8$ -THF, 300 K):  $\delta$  ~ 7.59 (m, 1H, Ar-*H* of py), 7.62 (dt, 1H, Ar-*H* of py), 7.40 (br. d, 1H, Ar-*H* of py), 7.30 (br. t, 1H, Ar-*H*), 7.09 (m, 1H, Ar-*H* of py + residual **8** ( $[(^{\text{Dipp}}\text{NacnacMg}(\mu\text{-F})(\text{THF}))_2]$  which is sparingly soluble in  $\text{D}_8$ -THF), 6.57 (dd, 1H, Ar-*H*), 6.48 (td, 1H, Ar-*H*), 2.91 (br. t, 4H,  $-\text{N}(\text{CH}_2)_2(\text{CH}_2)_2$ ), 1.75 (br. m, 4H,  $-\text{N}(\text{CH}_2)_2(\text{CH}_2)_2$ ) ppm

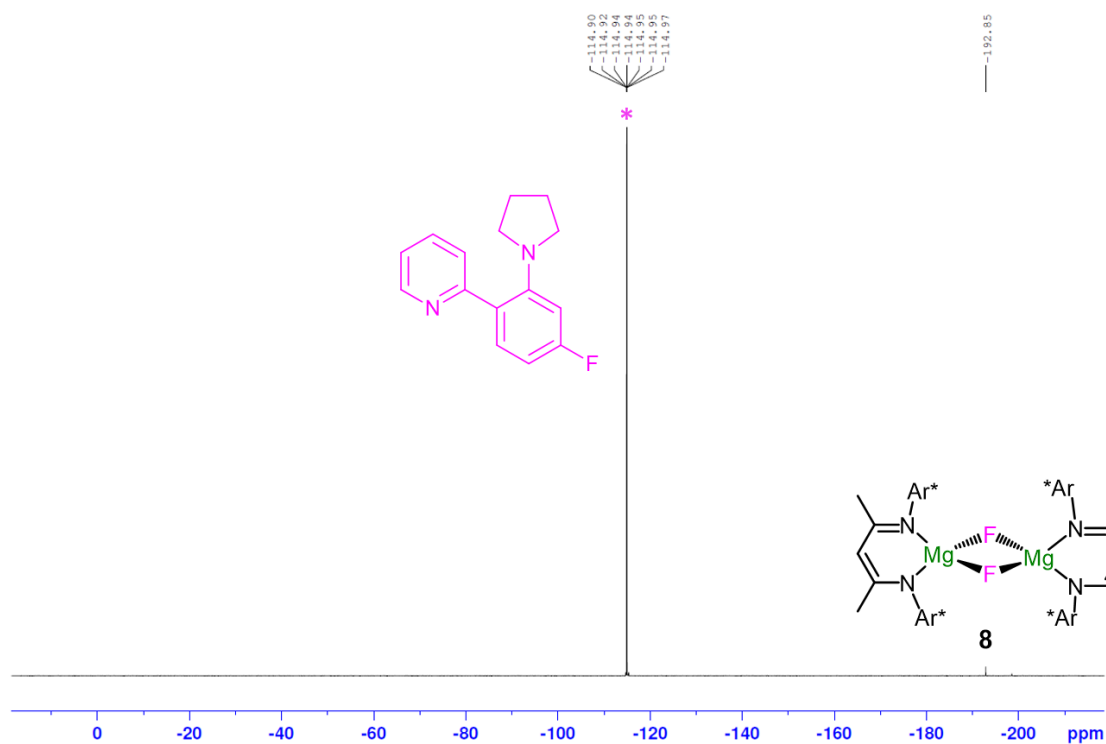


Figure S 29  $^{19}\text{F}$  NMR spectrum of compound 7d in  $\text{D}_8\text{-THF}$  formed from the C-F activation of ppf by compound 6

$^{19}\text{F}$  NMR (376.5 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta \sim -114.9$  (m, Ar-F), -192.8 (**8** ( $[(^{\text{Dipp}}\text{NacnacMg}(\mu\text{-F})(\text{THF}))_2]$ )) ppm

For purification, 0.640 (1.1 mmol) of **1** was added to a Schlenk flask prepared inside a glovebox and then dissolved in 5 mL of THF giving a yellow solution. To this, 0.11 mL (1.1 mmol) of pyrrolidine was added with a bright yellow solution persisting – this was stirred at room temperature for 2 h. Then, 0.9 mL of a 1.0 M solution of 2-(2,4-difluorophenyl)pyridine in THF was added to the reaction mixture resulting in the immediate precipitation of a yellow solid. The reaction mixture was stirred at room temperature overnight. Following a filtration and washing with THF, the filtrate was evaporated to dryness resulting in a cloudy yellow oil. Reverse-phase HPLC purification of compound **7d** was conducted using a Gilson preparative HPLC system of 322 pumps coupled to a 151 UV/Vis 163 spectrometer, 234 Autoinjector and a GX-271 liquid handler using an Agilent Zorbax SB-C18, 21.2 x 150 mm, 5  $\mu$ m column at room temperature. Purification was performed using a gradient method ranging from 5-90% MeCN (1% trifluoroacetic acid (TFA)) in H<sub>2</sub>O (1% TFA) over 25 minutes at a flow rate of 5 mL/min, with UV monitoring at 254 nm. Analysis was conducted using Gilson Trilution software. Compound **7d** was thus isolated as the TFA salt. Washing with 2 M NaOH solution and extracting with DCM resulted in the purified compound as a yellow oil, 93 mg, 39%.

**<sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>, 300 K):**  $\delta$  ~ 8.63 (m, 1H, Ar-*H* of py), 7.65 (dt, 1H, Ar-*H* of py), 7.42 (br. d, 1H, Ar-*H* of py), 7.27 (br. t, 1H, Ar-*H*), 7.16 (m, 1H, Ar-*H* of py), 6.54 (m, 2H, Ar-*H*), 2.92 (br. t, 4H, -N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>), 1.78 (br. m, 4H, -N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>) ppm

**<sup>19</sup>F NMR (376.5 MHz, CDCl<sub>3</sub>, 300 K):**  $\delta$  ~ -113.40 (m, Ar-*F*)

**<sup>13</sup>C{<sup>1</sup>H} NMR (100.62 MHz, CDCl<sub>3</sub>, 300 K):**  $\delta$  ~ 164.9 (Ar(C<sub>q</sub>)-N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>), 162.5 (Ar(C<sub>q</sub>) of py), 160.7 (Ar(C<sub>q</sub>) of Ph), 149.2 (d, Ar(C)-F), 149.0 (Ar(C)-H of py), 135.9 (Ar(C)-H of py), 133.8 (Ar(C)-H), 133.7 (Ar(C)-H) 124.2 (Ar(C)-H of py), 122.1 (Ar(C)-H of py), 104.1 (d, Ar(C)-H of Ph), 101.1 (d, Ar(C)-H of Ph), 51.3 (-N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>), 25.7 (-N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>) ppm

LRMS (GC/ESI) *m/z*: 243.3 [M+H]<sup>+</sup>

HRMS (TOF): Calc. for C<sub>15</sub>H<sub>15</sub>FN<sub>2</sub>, 242.1219; Found, 242.1214 (error 0.42 ppm)

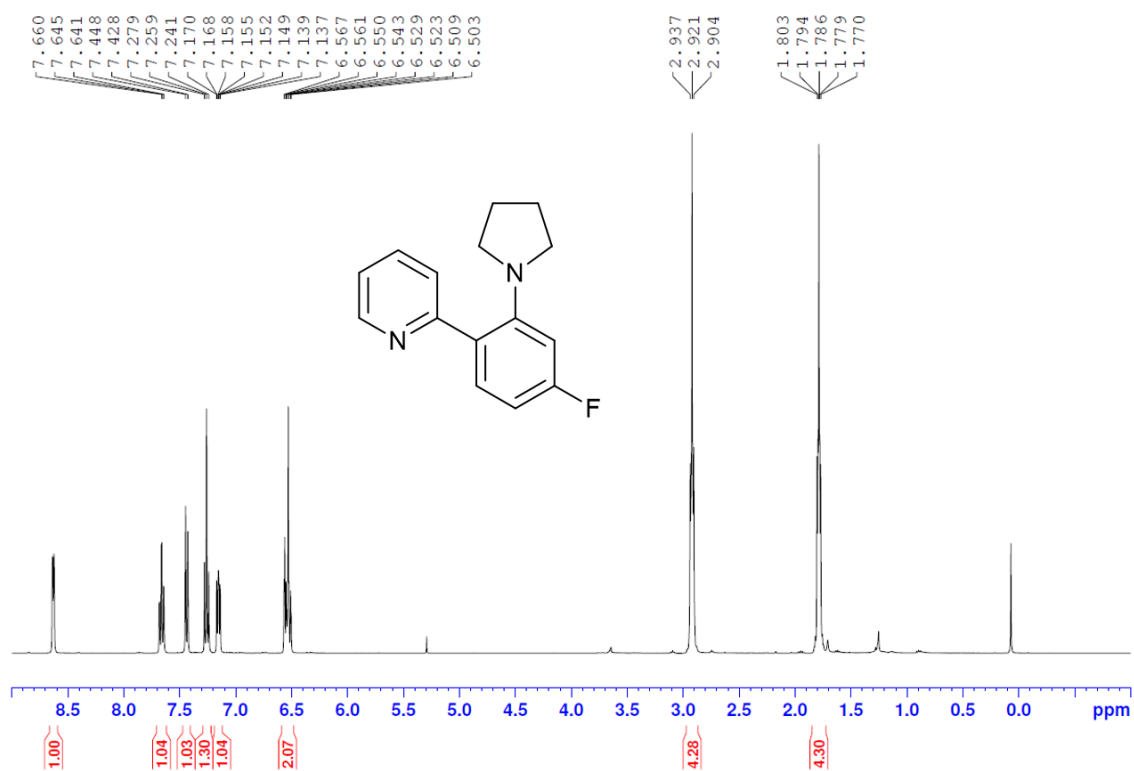


Figure S 30 <sup>1</sup>H NMR spectrum of compound 7d

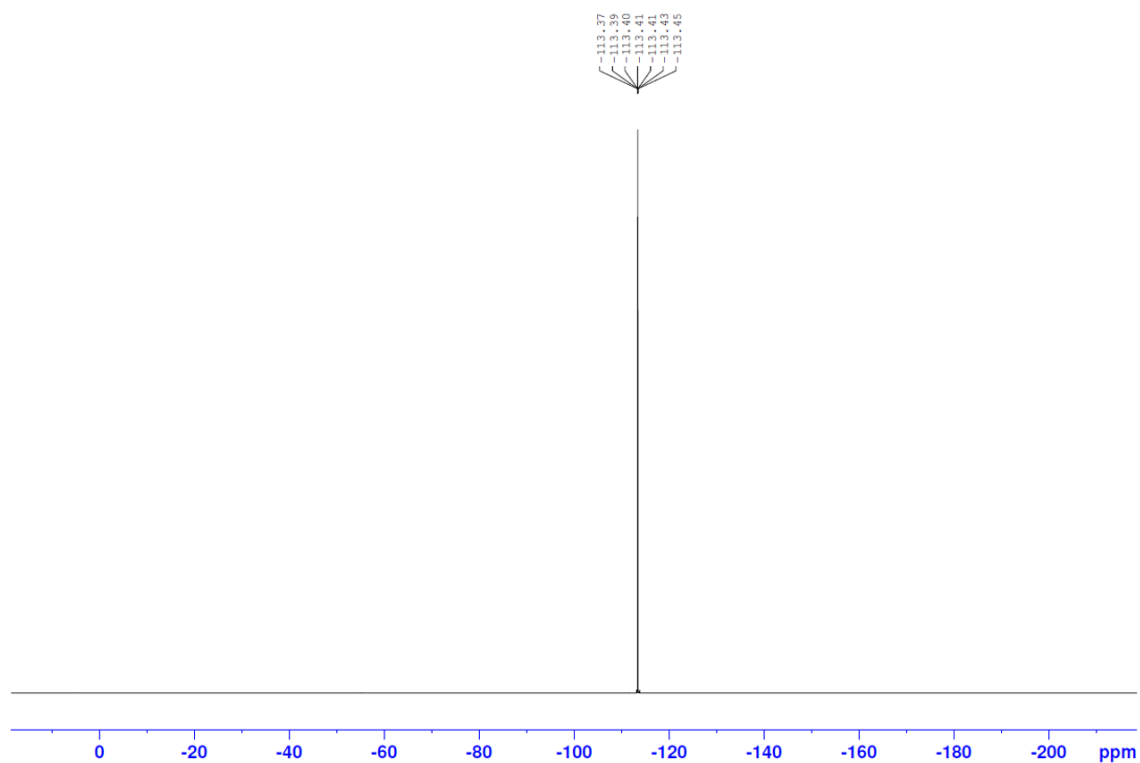


Figure S 31  $^{19}\text{F}$  NMR spectrum of compound 7d

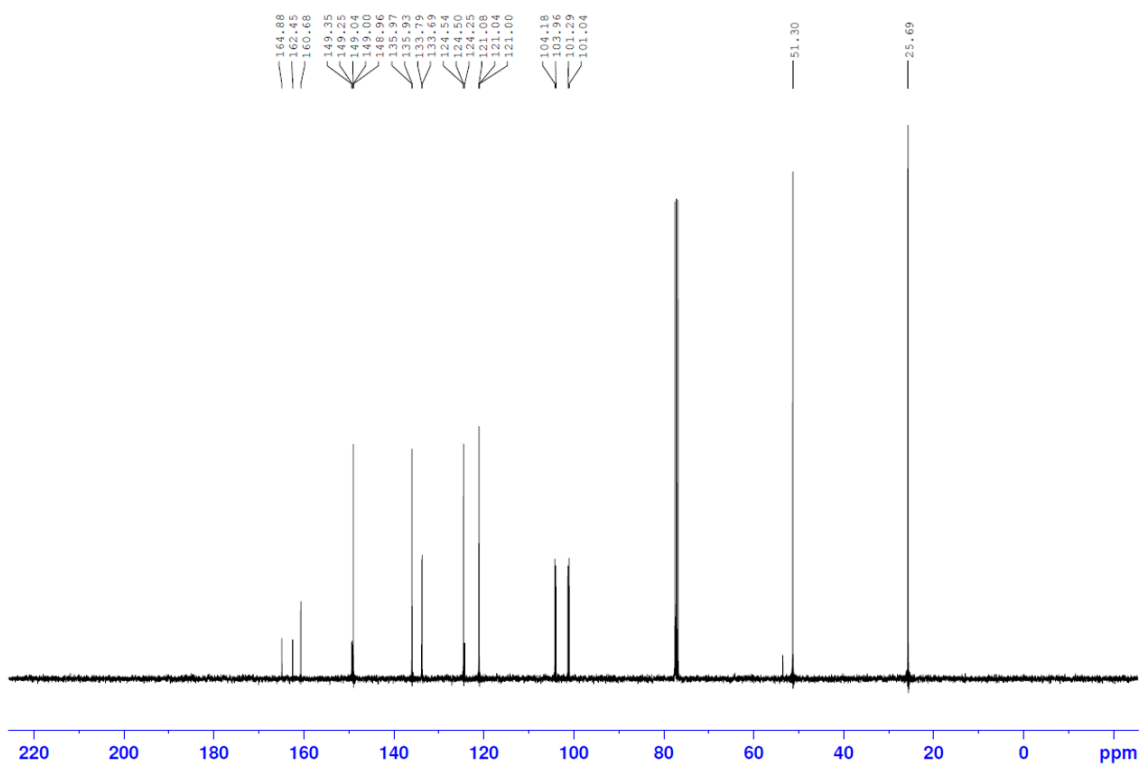


Figure S 32  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound 7d

## Synthesis of Compound 7f

Inside the glovebox, 0.146 (0.25 mmol) of **1** was added to a J. Young's NMR tube and dissolved in 0.5 ml of D<sub>8</sub>-THF and to this, 46  $\mu$ L (0.25 mmol) of di-*n*-butylamine was added and the deprotonation monitored by NMR spectroscopy. After quantitative transamination had occurred forming **3** in solution, 22  $\mu$ L of 2-fluoropyridine was introduced resulting in the immediate precipitation of ([<sup>D</sup>ippNacnacMg( $\mu$ -F)(THF)]<sub>2</sub>) (**8**). NMR analysis, after filtration, confirmed C-F activation had occurred, generating compound **7f** in an 84% yield against 17 mol% ferrocene (8 mg) as an internal standard. The values obtained for this compound are consistent with that which are reported in the literature – compound verified in CDCl<sub>3</sub> solvent.<sup>5</sup>

**<sup>1</sup>H NMR (400.1 MHz, D<sub>8</sub>-THF, 300 K):**  $\delta$  ~ 8.02 (d, 1H, Ar-*H*), 7.31 (t, 1H, Ar-*H*), 6.42 (d, 1H, Ar-*H*), 6.32 (t, 1H, Ar-*H*), 4.10 (Fe(Cp)<sub>2</sub>), 3.43 (t, 4H, -N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 1.56 (m, 6H, -N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub> +  $\gamma$ -CH<sub>2</sub> of TMP(H)), 1.30 (m, 8H, -N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub> +  $\beta$ -CH<sub>2</sub> of TMP(H)), 1.06 (s, 12H, CH<sub>3</sub> of TMP(H)) 0.94 (t, 6H, -N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub> of compound **3** and di-*n*-butylamine) ppm

**<sup>19</sup>F{<sup>1</sup>H} NMR (376.5 MHz, D<sub>8</sub>-THF, 300 K):**  $\delta$  ~ -68.35 (s, 2-fluoropyridine), -184.64 (compound **8**)

**<sup>13</sup>C{<sup>1</sup>H} NMR (100.62 MHz, D<sub>8</sub>-THF, 300 K):**  $\delta$  ~ 168.73 (Ar(C)<sub>q</sub>), 148.6 (Ar(C)-H), 137.0 (Ar(C)-H), 111.5 (Ar(C)-H), 105.7 (Ar(C)-H), 48.83 (-N(CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 30. (-N(CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 20.9 (-N(CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 14.2 (-N(CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>) ppm

**<sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>, 300 K):**  $\delta$  ~ 8.17 (m, 1H, Ar-*H*), 7.43 (m, 1H, Ar-*H*), 6.63 (m, 2H, Ar-*H*), 3.43 (t, 4H, -N(CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 1.57 (m, 4H, -N(CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 1.36 (m, 4H, -N(CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 0.95 (t, 6H, -N(CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>) ppm

**<sup>13</sup>C{<sup>1</sup>H} NMR (100.62 MHz, CDCl<sub>3</sub>, 300 K):**  $\delta$  ~ 158.1 (Ar(C)<sub>q</sub>), 148.2 (Ar(C)-H), 136.9 (Ar(C)-H), 110.8 (Ar(C)-H), 105.6 (Ar(C)-H), 48.5 (-N(CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 29.9 (-N(CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 20.5 (-N(CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 14.2 (-N(CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>) ppm

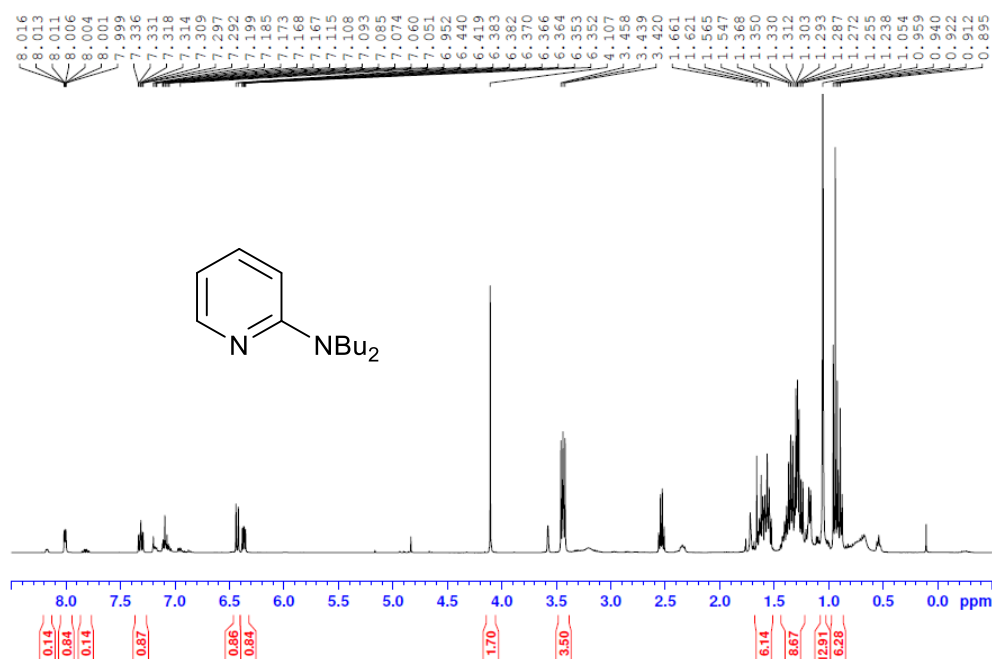


Figure S 33 <sup>1</sup>H NMR spectrum of compound 7f with ferrocene as an internal standard in D<sub>8</sub>-THF



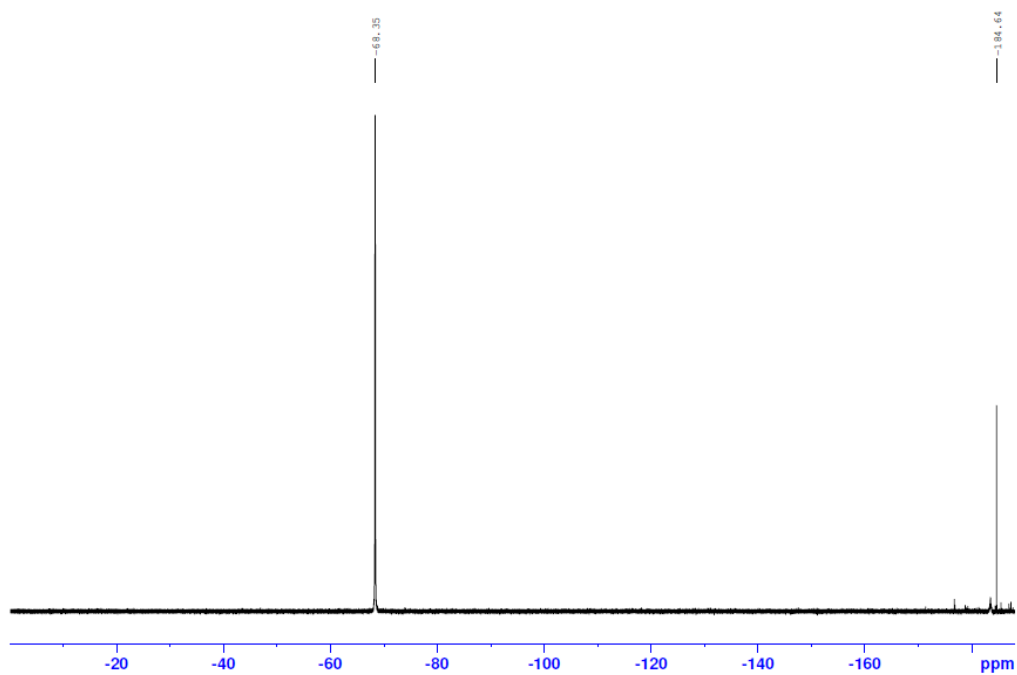


Figure S 34 <sup>19</sup>F NMR spectrum of compound 7f in D<sub>8</sub>-THF

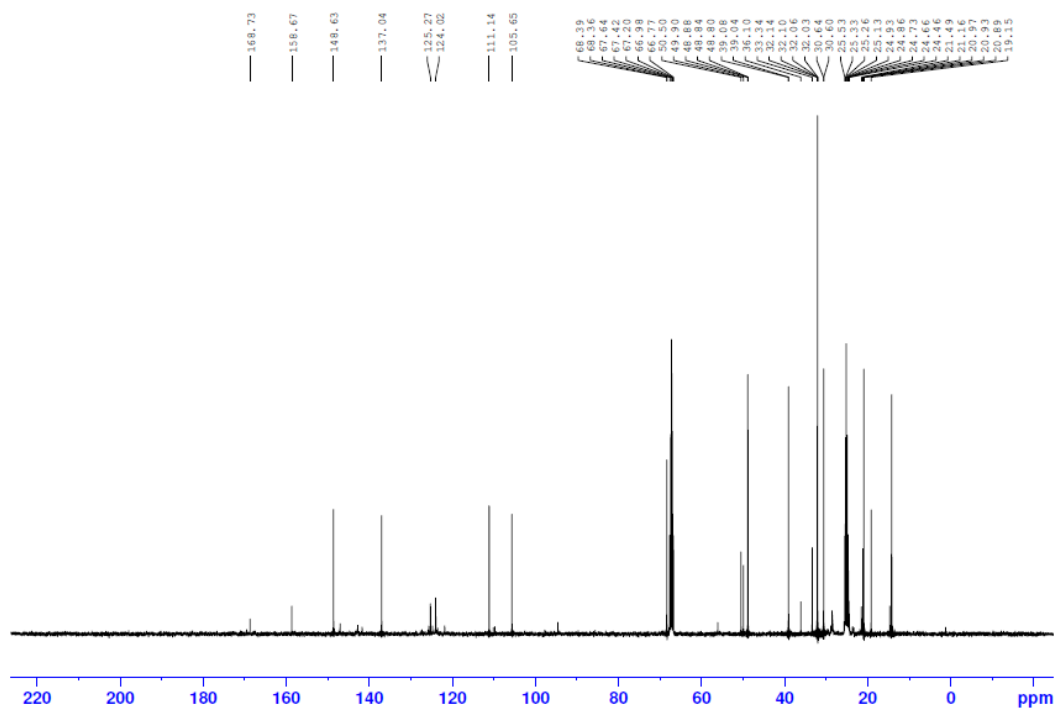


Figure S 35 <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of compound 7f in D<sub>8</sub>-THF

## Synthesis of Compound 7g

Inside the glovebox, 0.146 (0.25 mmol) of **1** was added to a J. Young's NMR tube and dissolved in 0.5 ml of D<sub>8</sub>-THF and to this, 25  $\mu$ L (0.25 mmol) of piperidine was added and the deprotonation monitored by NMR spectroscopy. After quantitative transamination had occurred forming **4** in solution, 22  $\mu$ L of 2-fluoropyridine was introduced resulting in the immediate precipitation of  $[(^{\text{Dipp}}\text{NacnacMg}(\mu\text{-F})(\text{THF}))_2]$  (**8**). NMR analysis, after filtration, confirmed C-F activation had occurred, generating compound **7g** in an 80% yield against 20 mol% ferrocene (9 mg) as an internal standard. The values obtained for this compound are consistent with that which are reported in the literature – compound verified in CDCl<sub>3</sub> solvent.<sup>6</sup>

**<sup>1</sup>H NMR (400.1 MHz, D<sub>8</sub>-THF, 300 K):**  $\delta$  ~ 8.04 (d, 1H, Ar-*H*), 7.35 (t, 1H, Ar-*H*), 6.63 (d, 1H, Ar-*H*), 6.45 (t, 1H, Ar-*H*), 3.52 (t, 4H, -N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>), 1.60 (m, 6H, -N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>) ppm

**<sup>13</sup>C{<sup>1</sup>H} NMR (100.62 MHz, D<sub>8</sub>-THF, 300 K):**  $\delta$  ~ 160.3 (Ar(C)<sub>q</sub>), 148.4 (Ar(C)-H), 137.4 (Ar(C)-H), 112.5 (Ar(C)-H), 107.0 (Ar(C)-H), 46.6 (-N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 39.0 (-N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>), 32.0 (-N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>) ppm

**<sup>19</sup>F{<sup>1</sup>H} NMR (376.5 MHz, D<sub>8</sub>-THF, 300 K):**  $\delta$  ~ -68.35 (s, 2-fluoropyridine), -184.64 (compound **8**)

**<sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>, 300 K):**  $\delta$  ~ 8.17 (m, 1H, Ar-*H*), 7.43 (m, 1H, Ar-*H*), 6.64 (d, 1H, Ar-*H*), 6.55 (ddd, 1H, Ar-*H*), 3.51 (m, 4H, -N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>), 1.64 (m, 6H, -N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>) ppm

**<sup>13</sup>C{<sup>1</sup>H} NMR (100.62 MHz, CDCl<sub>3</sub>, 300 K):**  $\delta$  ~ 159.8 (Ar(C)<sub>q</sub>), 147.9 (Ar(C)-H), 137.3 (Ar(C)-H), 112.4 (Ar(C)-H), 107.1 (Ar(C)-H), 46.3 (-N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>), 25.5 (-N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>), 24.7 (-N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>) ppm

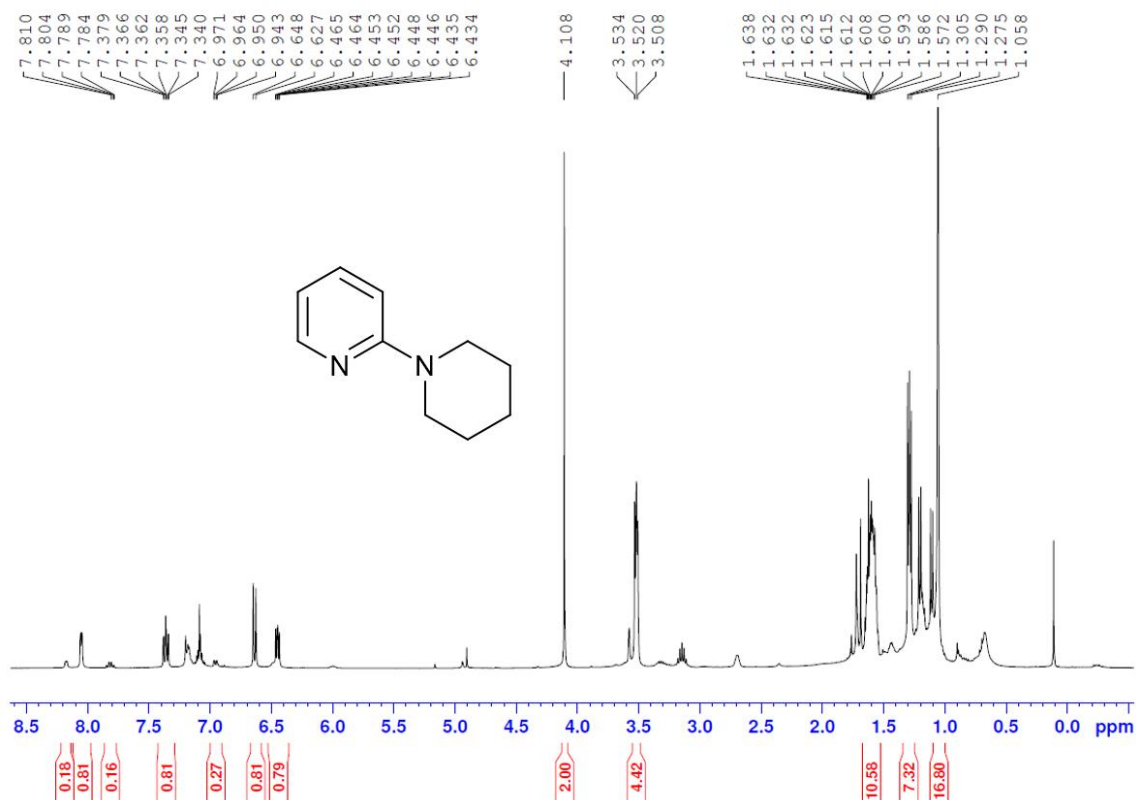


Figure S 36 <sup>1</sup>H NMR spectrum of compound **7g** in D<sub>8</sub>-THF

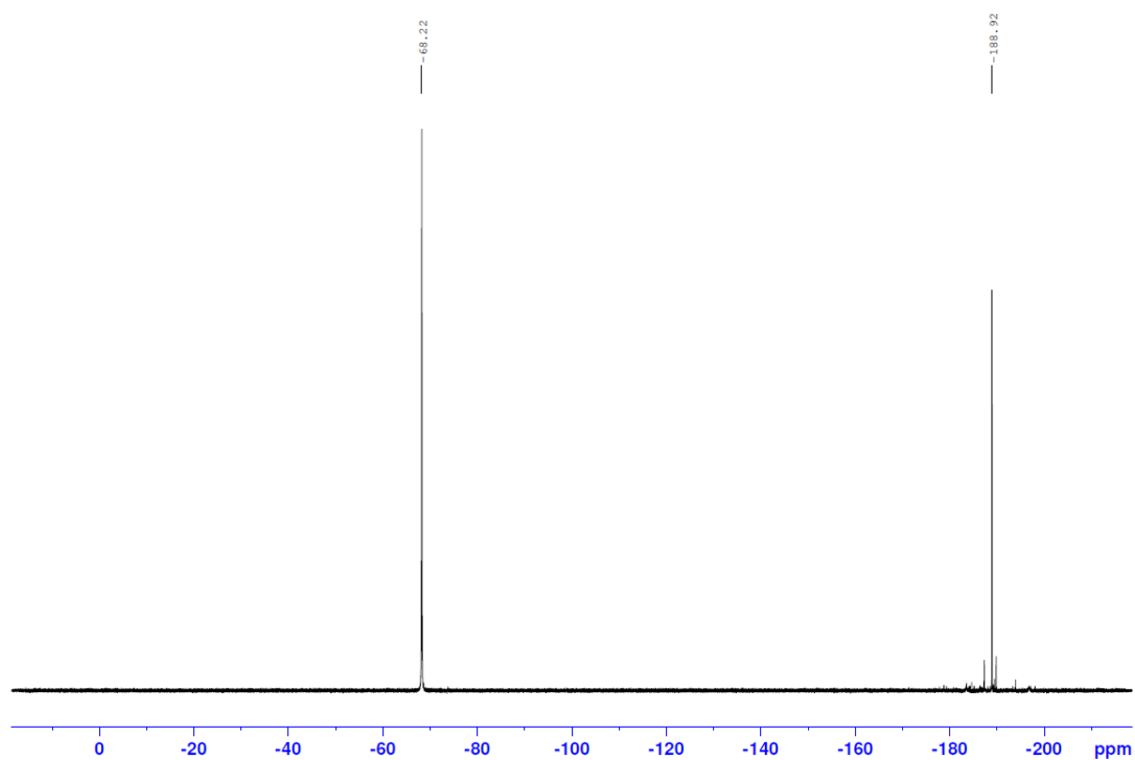


Figure S 37 <sup>19</sup>F NMR spectrum of compound 7g in D<sub>8</sub>-THF

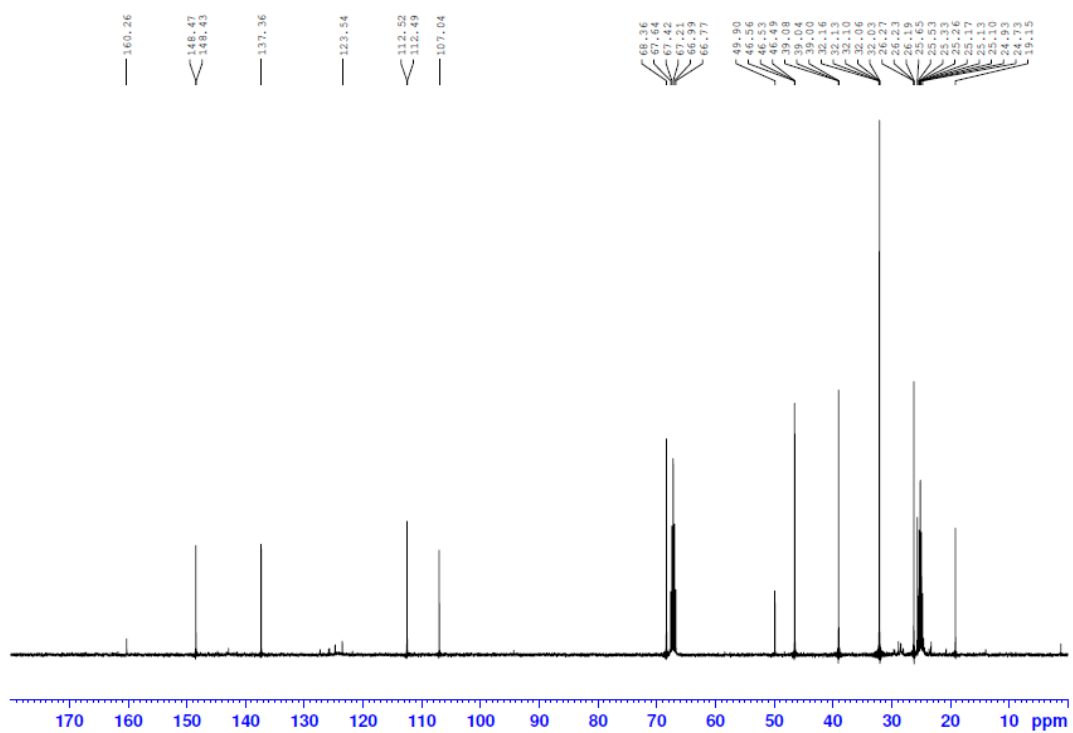


Figure S 38 <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of compound 7g in D<sub>8</sub>-THF

## Synthesis of Compound 7h

Inside the glovebox, 0.146 (0.25 mmol) of **1** was added to a J. Young's NMR tube and dissolved in 0.5 ml of D<sub>8</sub>-THF and to this, 22  $\mu$ L (0.25 mmol) of morpholine was added and the deprotonation monitored by NMR spectroscopy. After quantitative transamination had occurred forming **5** in solution, 22  $\mu$ L of 2-fluoropyridine was introduced resulting in the immediate precipitation of ([<sup>Dipp</sup>NacnacMg( $\mu$ -F)(THF)]<sub>2</sub>) (**8**). NMR analysis, after filtration, confirmed C-F activation had occurred, generating compound **7h** in an 80% yield against 20 mol% ferrocene (9 mg) as an internal standard. The values obtained for this compound are consistent with that which are reported in the literature – compound verified in CDCl<sub>3</sub> solvent.<sup>5</sup>

**<sup>1</sup>H NMR (400.1 MHz, D<sub>8</sub>-THF, 300 K):**  $\delta$  ~ 8.01 (d, 1H, Ar-*H*), 7.43 (t, 1H, Ar-*H*), 6.86 (d, 1H, Ar-*H*), 6.56 (t, 1H, Ar-*H*), 3.69 (t, 4H, -N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>O), 3.44 (t, 4H, -N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>O) ppm

**<sup>13</sup>C{<sup>1</sup>H} NMR (100.62 MHz, D<sub>8</sub>-THF, 300 K):**  $\delta$  ~ 160.4 (Ar(C)<sub>q</sub>), 148.5 (Ar(C)-H), 137.6 (Ar(C)-H), 113.8 (Ar(C)-H), 107.1 (Ar(C)-H), 67.3 (-N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>O), 46.2 (-N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>O) ppm

**<sup>19</sup>F{<sup>1</sup>H} NMR (376.5 MHz, D<sub>8</sub>-THF, 300 K):**  $\delta$  ~ -68.35 (s, 2-fluoropyridine), -184.86 (compound **8**)

**<sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>, 300 K):**  $\delta$  ~ 8.20 (m, 1H, Ar-*H*), 7.45 (t, 1H, Ar-*H*), 6.65 (m, 2H, Ar-*H* x2), 3.82 (t, 4H, -N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>O), 3.49 (t, 4H, -N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>O) ppm

**<sup>13</sup>C{<sup>1</sup>H} NMR (100.62 MHz, CDCl<sub>3</sub>, 300 K):**  $\delta$  ~ 159.8 (Ar(C)<sub>q</sub>), 148.1 (Ar(C)-H), 137.6 (Ar(C)-H), 113.9 (Ar(C)-H), 107.0 (Ar(C)-H), 66.8 (-N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>O), 45.7(-N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>O) ppm

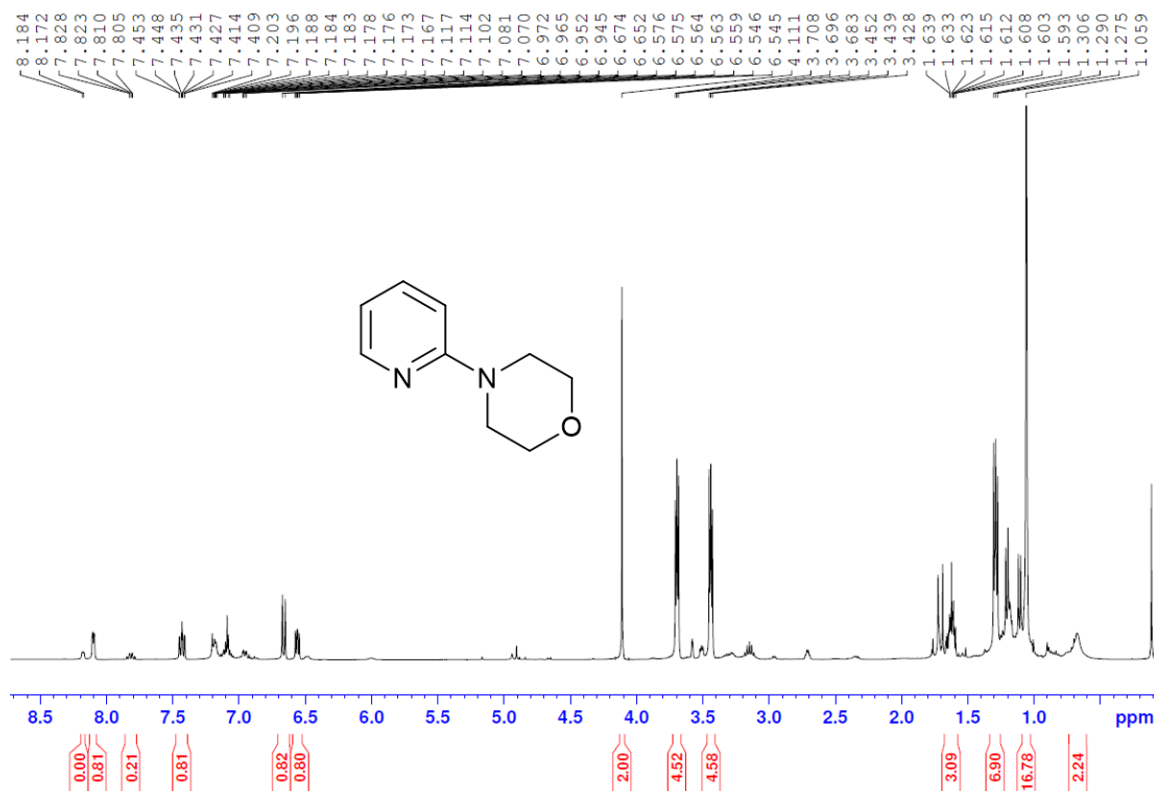
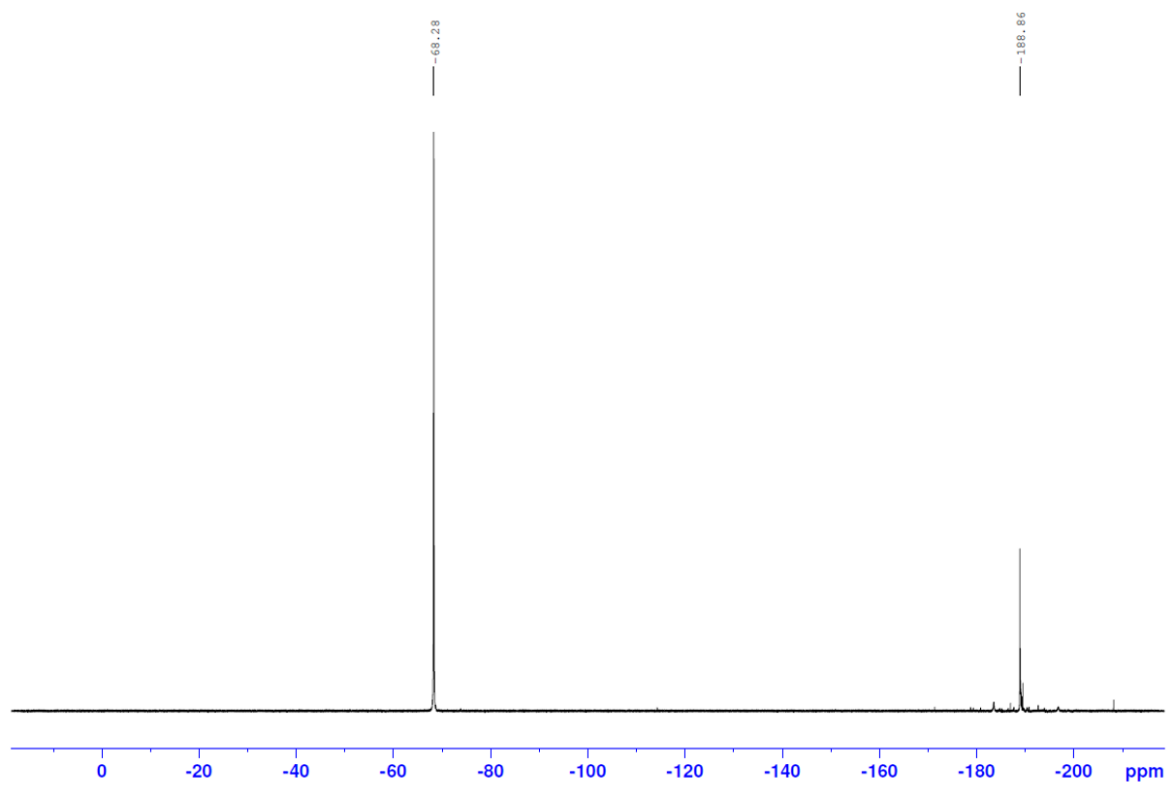


Figure S 39 <sup>1</sup>H NMR spectrum of compound 7h in D<sub>8</sub>-THF



**Figure S 40**  $^{19}\text{F}$  NMR spectrum of compound 7h in  $\text{D}_8\text{-THF}$

## Synthesis of Compound 7i

Inside the glovebox, 0.146 (0.25 mmol) of **1** was added to a J. Young's NMR tube and dissolved in 0.5 ml of D<sub>8</sub>-THF and to this, 21  $\mu$ L (0.25 mmol) of pyrrolidine was added and the deprotonation monitored by NMR spectroscopy. After quantitative transamination had occurred forming **6** in solution, 22  $\mu$ L of 2-fluoropyridine was introduced resulting in the immediate precipitation of ([<sup>Dipp</sup>NacnacMg( $\mu$ -F)(THF)]<sub>2</sub>) (**8**). NMR analysis, after filtration, confirmed C-F activation had occurred, generating compound **7i** in an 87% yield against 15 mol% ferrocene (7 mg) as an internal standard. The values obtained for this compound are consistent with that which are reported in the literature – compound verified in CDCl<sub>3</sub> solvent.<sup>7</sup>

**<sup>1</sup>H NMR (400.1 MHz, D<sub>8</sub>-THF, 300 K):**  $\delta$  ~ 8.02 (d, 1H, Ar-*H*), 7.33 (td, 1H, Ar-*H*), 6.40 (m, 1H, Ar-*H*), 6.20 (br. m, 1H, Ar-*H*), 3.39 (br. t, 4H, -N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>), 1.93 (m, 4H, -N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>) ppm

**<sup>13</sup>C{<sup>1</sup>H} NMR (100.62 MHz, D<sub>8</sub>-THF, 300 K):**  $\delta$  ~ 158.3 (Ar(C)<sub>q</sub>), 148.8 (Ar(C)-H), 136.8 (Ar(C)-H), 111.4 (Ar(C)-H), 106.4 (Ar(C)-H), 46.6 (-N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>), 39.0 (-N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>) ppm

**<sup>19</sup>F{<sup>1</sup>H} NMR (376.5 MHz, D<sub>8</sub>-THF, 300 K):**  $\delta$  ~ -68.35 (s, 2-fluoropyridine), -184.64 (compound **8**)

**<sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>, 300 K):**  $\delta$  ~ 8.11 (br. d, 1H, Ar-*H*), 7.39 (m, 1H, Ar-*H*), 6.47 (br. t, 1H, Ar-*H*), 6.33 (br. d, 1H, Ar-*H*), 3.42 (m, 4H, -N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>), 1.97 (m, 6H, -N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>) ppm

**<sup>13</sup>C{<sup>1</sup>H} NMR (100.62 MHz, CDCl<sub>3</sub>, 300 K):**  $\delta$  ~ 157.5 (Ar(C)<sub>q</sub>), 148.3 (Ar(C)-H), 137.1 (Ar(C)-H), 111.2 (Ar(C)-H), 106.7 (Ar(C)-H), 46.8 (-N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>), 25.7 (-N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>), 24.7 (-N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>) ppm

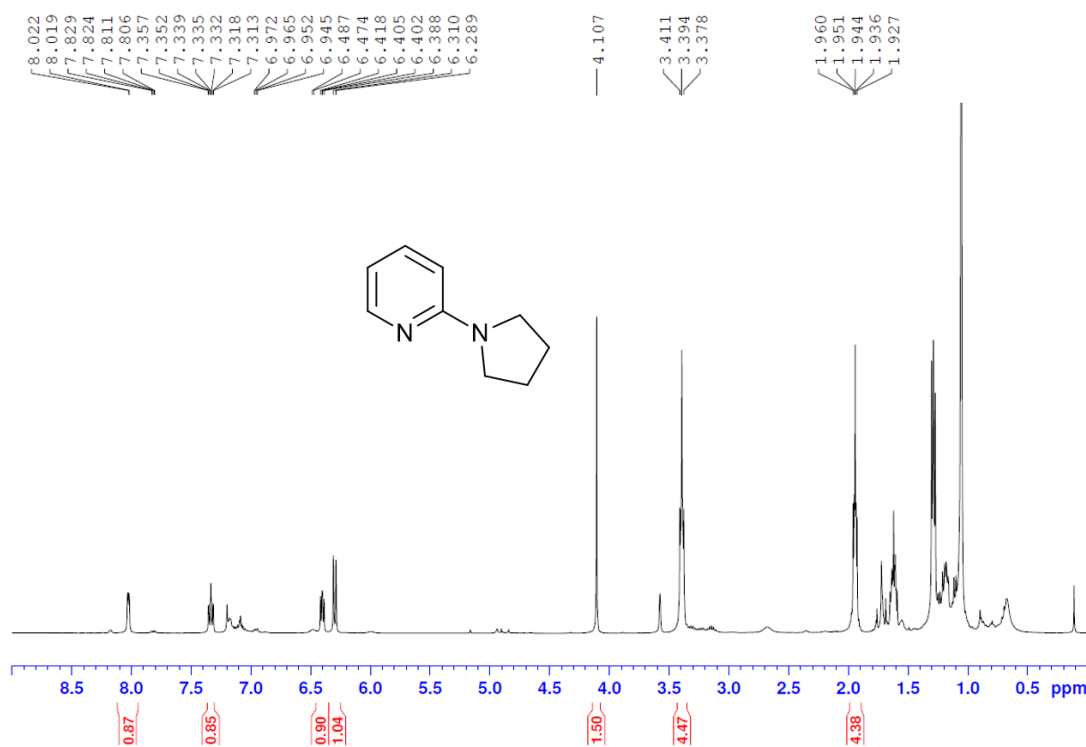


Figure S 41 <sup>1</sup>H NMR spectrum of compound **7i** in D<sub>8</sub>-THF

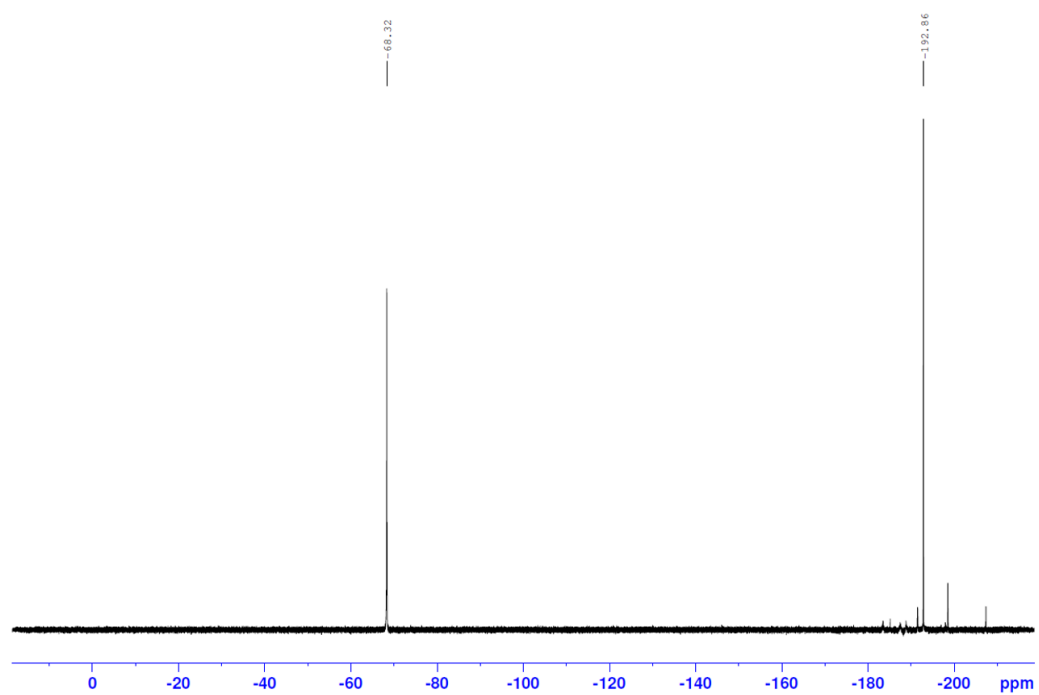


Figure S 42  $^{19}\text{F}$  NMR spectrum of compound 7i in  $\text{D}_8\text{-THF}$

## Synthesis of Compound 11a

Inside the glovebox, 1 mmol (0.582 g) of **1** was weighed into a microwave vial and then dissolved in 2 mL of THF whilst exposed to argon gas on a Schlenk line. To this, 0.1 mL (1 mmol) of piperidine was added followed by 0.12 mL (1 mmol) of hexafluorobenzene, accompanied by a yellow to dark pink colour change. The vial was then placed in a microwave reactor for 20 minutes at 125°C, resulting in a yellow suspension – precipitate indicated the formation of  $[(^{\text{Dipp}}\text{NacnacMg}(\mu\text{-F})(\text{THF}))_2]$  (**8**). This suspension was then hydrolysed in air, filtered through a plug of celite and glass wool and washed thoroughly with THF. All THF solvent was then removed under reduced pressure and the formation of compound **11a** was determined to be 80% against 10 mol% ferrocene (18 mg) as an internal standard. The compound was then purified by SiO<sub>2</sub> column chromatography with 100:1 hexane:EtOAc resulting in a colourless oil, 162 mg (65%).

**<sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>, 300 K):**  $\delta$  ~ 3.12 (m, 4H, N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>), 1.66 (m, 4H, N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>), 1.56 (m, 2H, N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>) ppm

**<sup>19</sup>F NMR (376.5 MHz, CDCl<sub>3</sub>, 300 K):**  $\delta$  ~ -150.66 (dt, 2F, *o*-F), -164.38 (tt, 2F, *m*-F), -164.91 (tt, 1F, *p*-F) ppm

**<sup>13</sup>C{<sup>1</sup>H} NMR (100.62 MHz, CDCl<sub>3</sub>, 300 K):**  $\delta$  ~ 144.7 (m, Ar(C)<sub>ortho</sub>-F), 142.7 (m, Ar(C)<sub>ortho</sub>-F), 139.4 (m, Ar(C)<sub>meta</sub>-F), 137.1 (m, Ar(C)<sub>meta</sub>-F), 135.7 (m, Ar(C)<sub>para</sub>-F), 127.5 (Ar(C) -N), 52.6 (N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>), 26.7 (N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>), 24.1 (N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>) ppm

LRMS (GC/ESI) *m/z*: 252.0 [M+H]<sup>+</sup>

HRMS (TOF): Calc. for C<sub>11</sub>H<sub>10</sub>F<sub>5</sub>N, 251.0733; Found, 251.0728 (error 2.05 ppm)





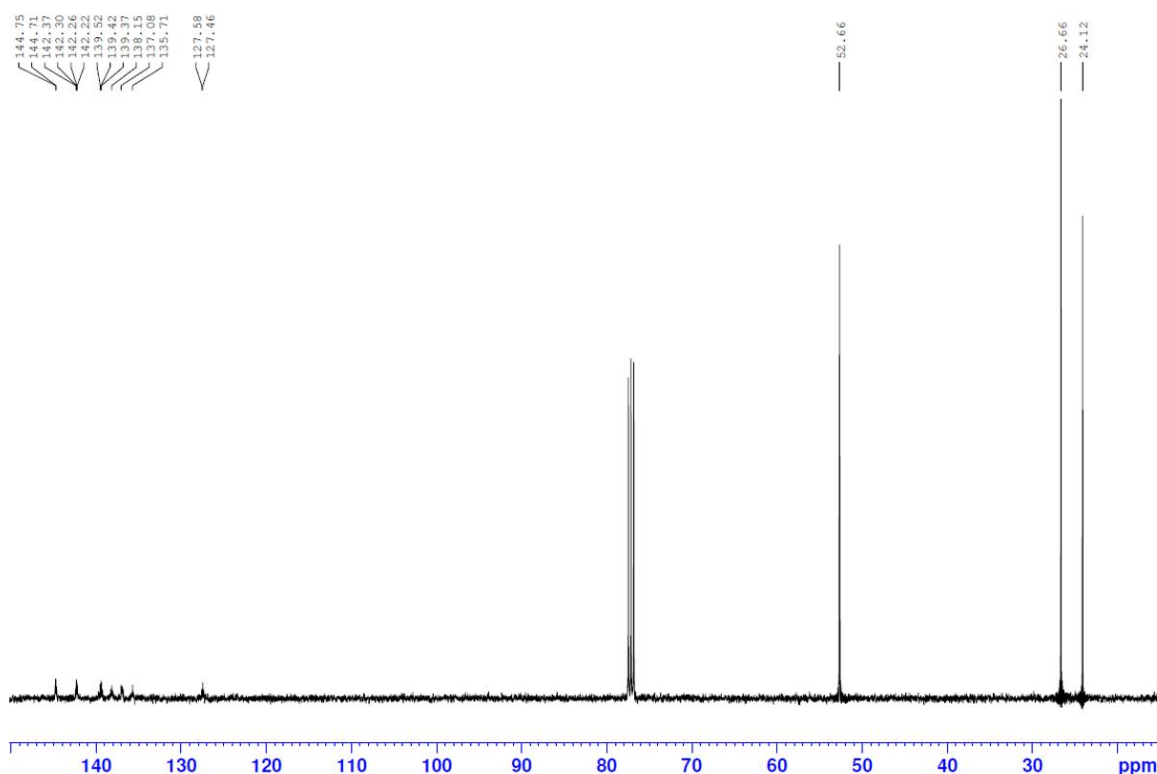


Figure S 45  $^{13}\text{C}$  NMR spectrum of compound 11a

## Synthesis of Compound 11b

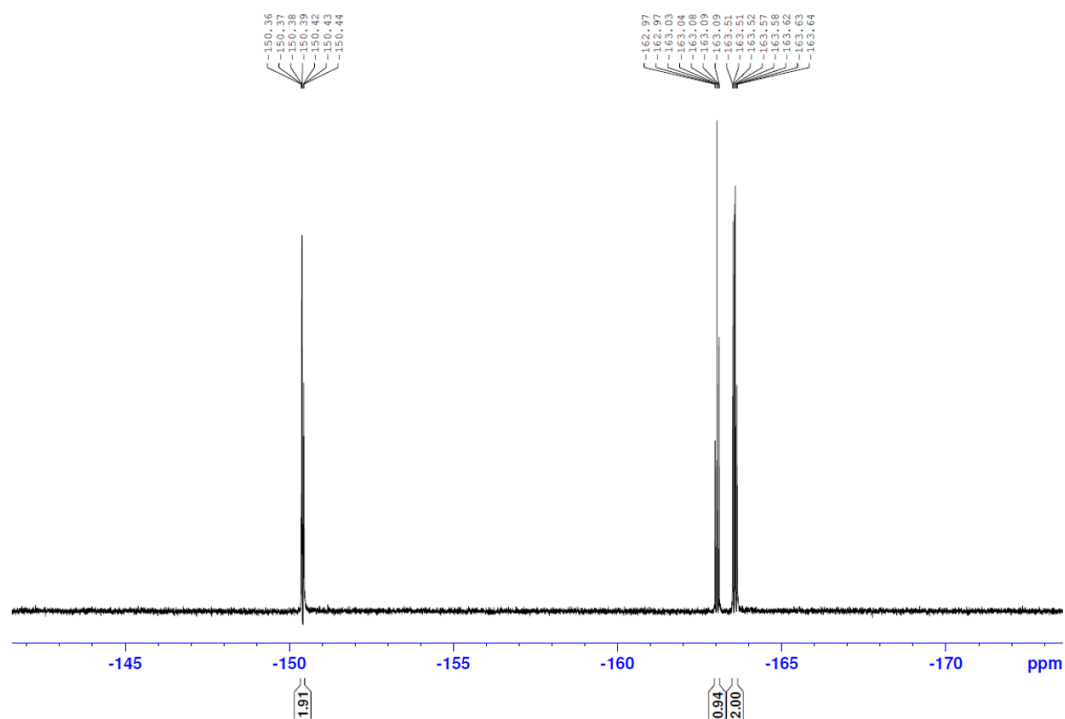
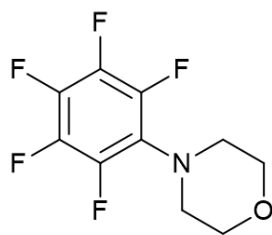
Inside the glovebox, 1 mmol (0.582 g) of **1** was weighed into a microwave vial and then dissolved in 2 mL of THF whilst exposed to argon gas on a Schlenk line. To this, 90  $\mu\text{L}$  (1 mmol) of morpholine was added followed by 0.12 mL (1 mmol) of hexafluorobenzene, accompanied by a yellow to dark pink colour change. The vial was then placed in a microwave reactor for 30 minutes at  $125^\circ\text{C}$ , resulting in a brown suspension – precipitate indicated the formation of  $([(^{\text{Dipp}}\text{NacnacMg}(\mu\text{-F})(\text{THF}))_2]_2)$  (**8**). This suspension was then hydrolysed in air, filtered through a plug of celite and glass wool and washed thoroughly with THF. All THF solvent was then removed under reduced pressure and the formation of compound **11b** was determined to be 78% against 10 mol% ferrocene (18 mg) as an internal standard. The compound was then purified by  $\text{SiO}_2$  column chromatography with 100:5 hexane: $\text{Et}_3\text{N}$  resulting in **11b** being isolated as a yellow oil (169 mg, 67%).

$^1\text{H}$  NMR (400.1 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta \sim 3.80$  (br. t, 4H,  $(\text{N}(\text{CH}_2)_2(\text{CH}_2)_2\text{O})$ ), 3.19 (br. m, 4H,  $(\text{N}(\text{CH}_2)_2(\text{CH}_2)_2\text{O})$ ) ppm

$^{19}\text{F}$  NMR (376.5 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta \sim -150.39$  (dt, 2F, *o*-F), -163.03 (m, 2F, *m*-F), -163.58 (m, 1F, *p*-F) ppm

$^{13}\text{C}\{^1\text{H}\}$  NMR (100.62 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta \sim 144.6$  (m,  $\text{Ar}(\text{C})_{\text{ortho-F}}$ ), 142.2 (m,  $\text{Ar}(\text{C})_{\text{ortho-F}}$ ), 139.3 (m,  $\text{Ar}(\text{C})_{\text{meta-F}}$ ), 136.9 (m,  $\text{Ar}(\text{C})_{\text{meta-F}}$ ), 136.2 (m,  $\text{Ar}(\text{C})_{\text{para-F}}$ ), 125.8 (m,  $\text{Ar}(\text{C})_{\text{-N}}$ ), 67.2 ( $\text{N}(\text{CH}_2)_2(\text{CH}_2)_2\text{O}$ ), 51.2 ( $\text{N}(\text{CH}_2)_2(\text{CH}_2)_2\text{O}$ ) ppm

LRMS (GC/ESI)  $m/z$ : 254.0  $[\text{M}+\text{H}]^+$  HRMS (TOF): Calc. for  $\text{C}_{10}\text{H}_8\text{F}_5\text{NO}$ , 253.0526; Found, 253.0521 (error 2.00 ppm)



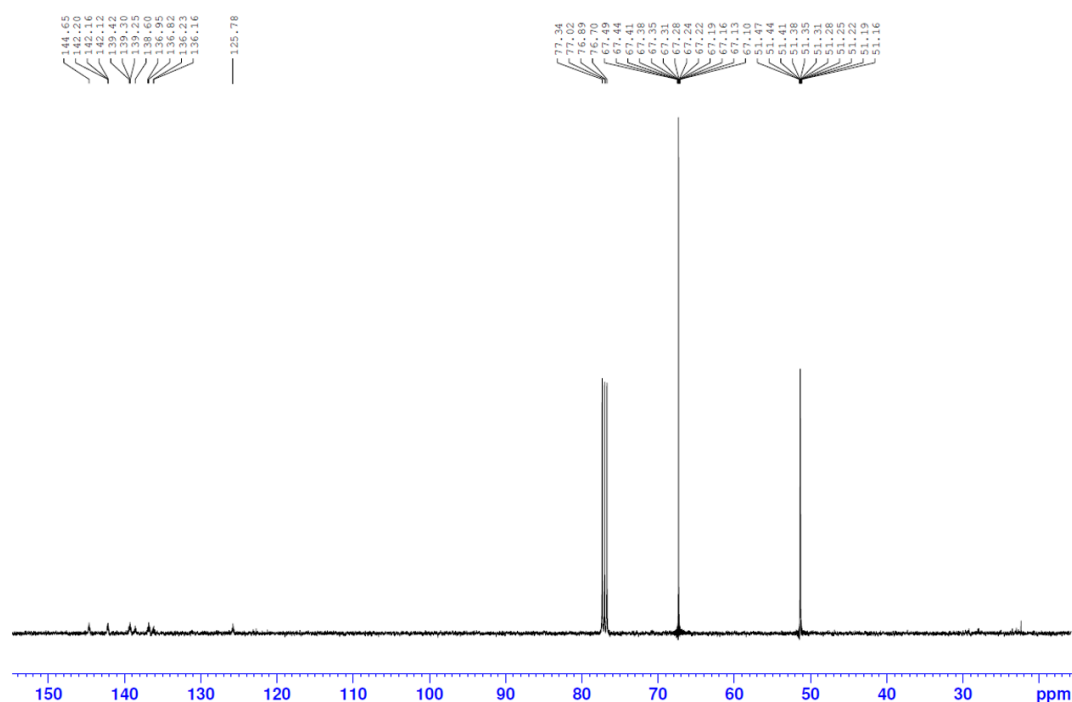


Figure S 48  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound 11b

## Synthesis of Compound 11c

Inside the glovebox, 1 mmol (0.582 g) of **1** was weighed into a microwave vial and then dissolved in 2 mL of THF whilst exposed to argon gas on a Schlenk line. To this, 80  $\mu\text{L}$  (1 mmol) of pyrrolidine was added followed by 0.12 mL (1 mmol) of hexafluorobenzene, accompanied by a yellow to peach colour change. The vial was then placed in a microwave reactor for 20 minutes at 125°C, resulting in an orange suspension – precipitate indicated the formation of  $([\text{D}^{\text{ipp}}\text{NacnacMg}(\mu\text{-F})(\text{THF})]_2)$  (**8**). This suspension was then hydrolysed in air, filtered through a plug of celite and glass wool and washed thoroughly with THF. All THF solvent was then removed under reduced pressure and the formation of compound **11c** was determined to be 87% against 10 mol% ferrocene (18 mg) as an internal standard. The compound was then purified by  $\text{SiO}_2$  column chromatography with 100:1 hexane:EtOAc resulting in a colourless oil. Yield 173 mg, 73%.

**$^1\text{H}$  NMR (400.1 MHz,  $\text{CDCl}_3$ , 300 K):**  $\delta$  ~ 3.50 (br. m, 4H,  $(\text{N}(\text{CH}_2)_2(\text{CH}_2)_2)$ ), 1.92 (br. m, 4H,  $(\text{N}(\text{CH}_2)_2(\text{CH}_2)_2)$ ) ppm

**$^{19}\text{F}$  NMR (376.5 MHz,  $\text{CDCl}_3$ , 300 K):**  $\delta$  ~ -155.86 (br. d, 2F, *o*-F), -164.97 (br. t, 2F, *m*-F), -171.55 (m, 1F, *p*-F) ppm

**$^{13}\text{C}\{^1\text{H}\}$  NMR (100.62 MHz,  $\text{CDCl}_3$ , 300 K):**  $\delta$  ~ 140.5 (m,  $\text{Ar}(\text{C})_{\text{ortho-F}}$ ), 139.1 (m,  $\text{Ar}(\text{C})_{\text{ortho-F}}$ ), 138.1 (m,  $\text{Ar}(\text{C})_{\text{meta-F}}$ ), 136.5 (m,  $\text{Ar}(\text{C})_{\text{meta-F}}$ ), 134.1 (m,  $\text{Ar}(\text{C})_{\text{para-F}}$ ), 124.0 (t,  $\text{Ar}(\text{C})_{\text{-N}}$ ), 50.5 (t,  $\text{N}(\text{CH}_2)_2(\text{CH}_2)_2$ ), 25.1 ( $\text{N}(\text{CH}_2)_2(\text{CH}_2)_2$ ) ppm

LRMS (GC/ESI)  $m/z$ : 238.1  $[\text{M}+\text{H}]^+$

HRMS (TOF): Calc. for  $\text{C}_{10}\text{H}_8\text{F}_5\text{N}$ , 237.0577; Found, 237.0571 (error 0.58 ppm)

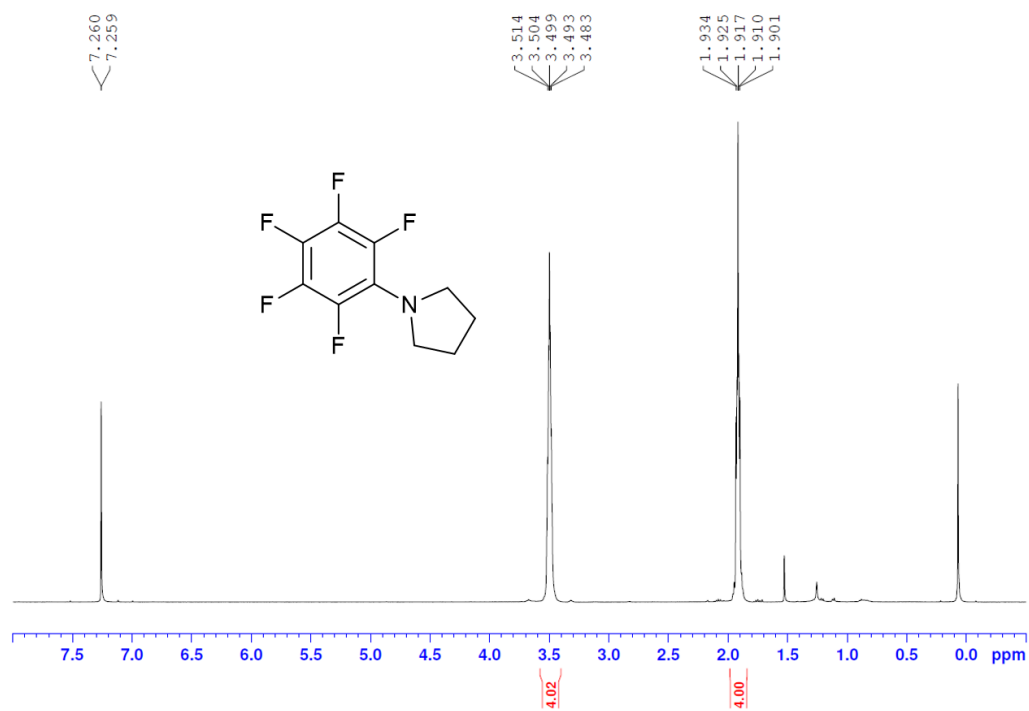


Figure S 49 <sup>1</sup>H NMR spectrum of compound 11c

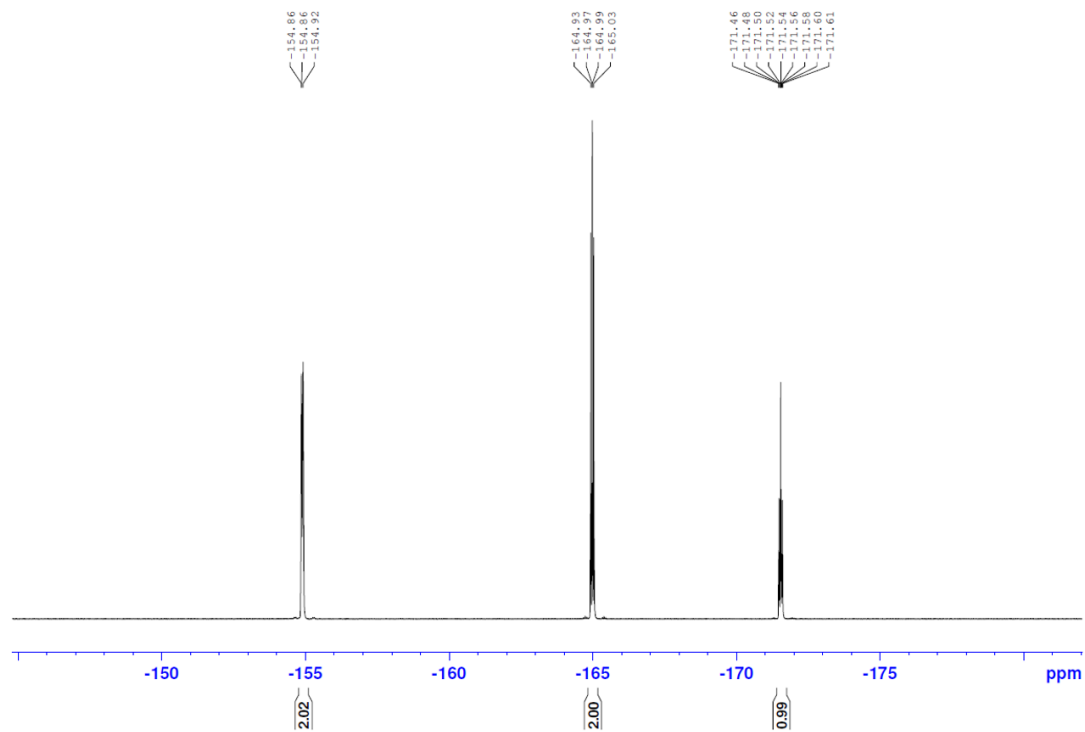
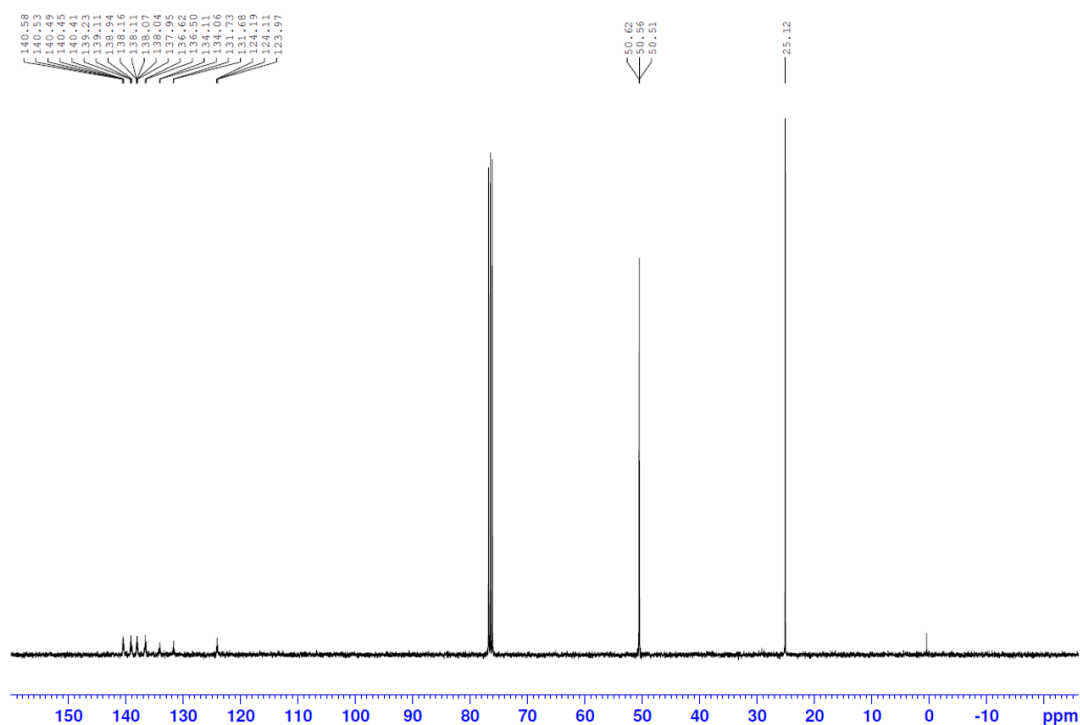


Figure S 50 <sup>19</sup>F NMR spectrum of compound 11c



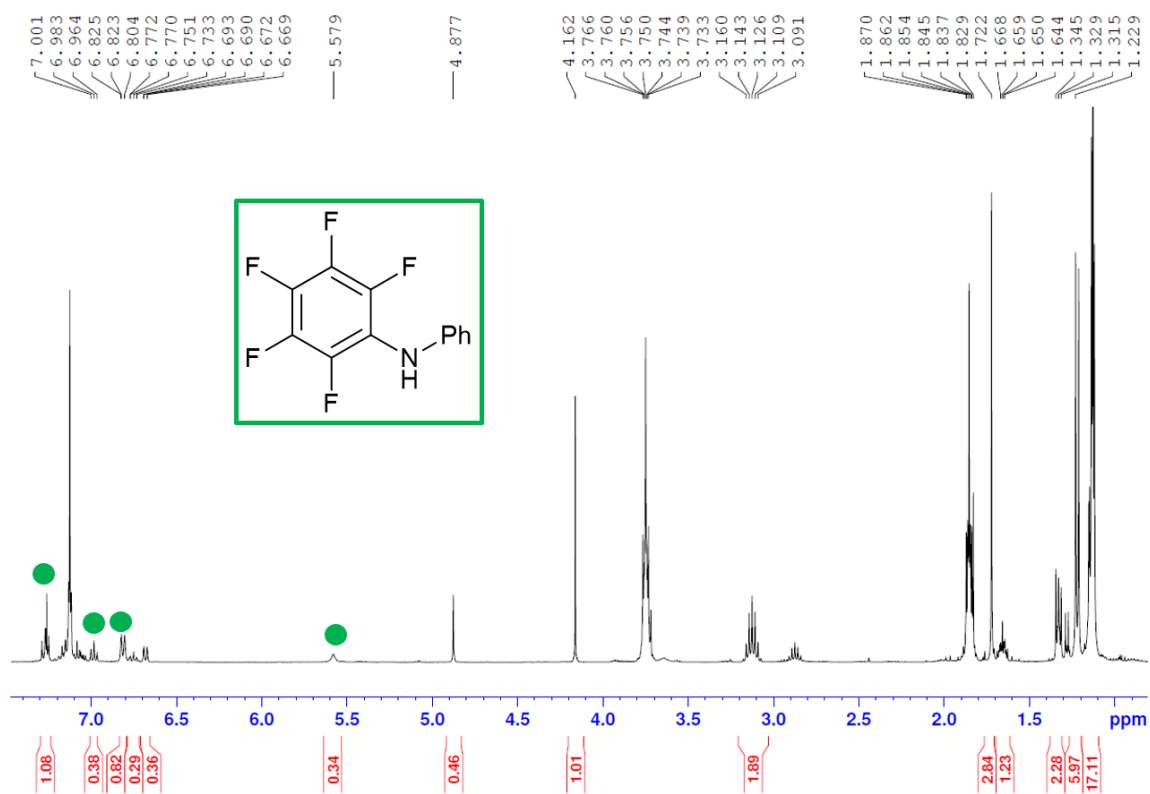


Figure S 52 <sup>1</sup>H NMR spectrum of compound 11e

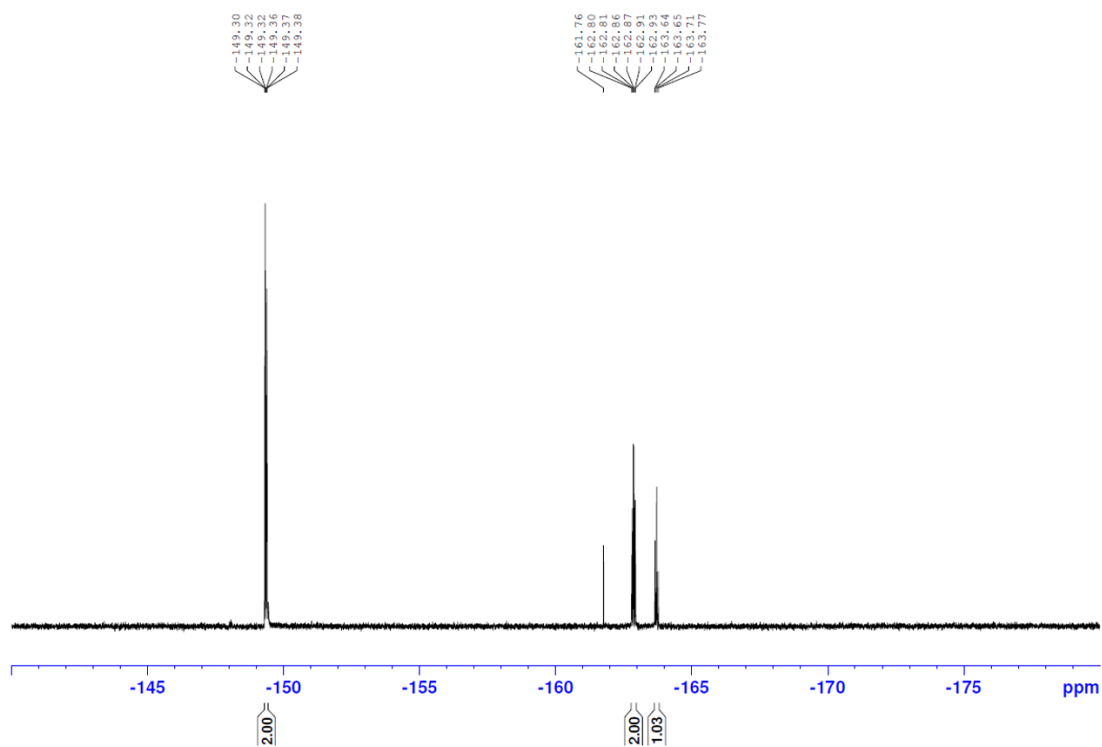


Figure S 53 <sup>19</sup>F NMR spectrum of compound 11e

## Synthesis of Compound 11e

Inside the glovebox, 1 mmol (0.582 g) of **1** was weighed into a microwave vial and then dissolved in 2 mL of THF whilst exposed to argon gas on a Schlenk line. To this, 0.17 mL (1 mmol) of di-*n*-butylamine was added followed by 0.12 mL (1 mmol) of hexafluorobenzene, giving a yellow solution. The vial was then placed in a microwave reactor for 1 h at 125°C, resulting in a light brown suspension. This reaction mixture was then hydrolysed in air, filtered through a plug of cellite and glass wool and washed thoroughly with THF. All THF solvent was then removed under reduced pressure and the formation of compound **11e** was determined to be 18% against ferrocene (13 mg) as an internal standard. Presence of compound confirmed by LRMS.

**<sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>, 300 K):** δ ~ 7.10 (m, Ar-*H* of <sup>Dipp</sup>NacnacH), 4.87 (s, C-*H* backbone of <sup>Dipp</sup>NacnacH), 4.14 (Fe(Cp)<sub>2</sub>), 3.72 (THF), 3.06 (m, C-*H* x4 of <sup>i</sup>Pr of <sup>Dipp</sup>NacnacH + 4H (N((CH<sub>2</sub>)(CH<sub>2</sub>)(CH<sub>2</sub>)CH<sub>3</sub>)<sub>2</sub> compound 11e), 2.58 (CH<sub>2</sub> x2 di-*n*-butylamine), 1.84 (THF), 1.64 (br. m, γ-CH<sub>2</sub> of TMP(H)), 1.30 (br. m, 8H (N((CH<sub>2</sub>)(CH<sub>2</sub>)(CH<sub>2</sub>)CH<sub>3</sub>)<sub>2</sub> compound 11e + 4H β-CH<sub>2</sub> of TMP(H) + CH<sub>2</sub> x2 di-*n*-butylamine), 1.20 (d, CH<sub>3</sub> x4 <sup>i</sup>Pr), 1.11 (m, CH<sub>3</sub> x4 <sup>i</sup>Pr + α-CH<sub>3</sub> of TMP(H)), 0.87 (6H (N((CH<sub>2</sub>)(CH<sub>2</sub>)(CH<sub>2</sub>)CH<sub>3</sub>)<sub>2</sub> compound 11e + CH<sub>3</sub> x2 of di-*n*-butylamine) ppm

**<sup>19</sup>F NMR (376.5 MHz, CDCl<sub>3</sub>, 300 K):** δ ~ -148.16 (dt, 2F, *o*-F), -161.76 (residual C<sub>6</sub>F<sub>6</sub>), -162.84 (br. t, 1F, *p*-F), -164.17 (br. dt, 2F, *m*-F) ppm

LRMS (GC/ESI) *m/z*: 296.1 [M+H]<sup>+</sup>

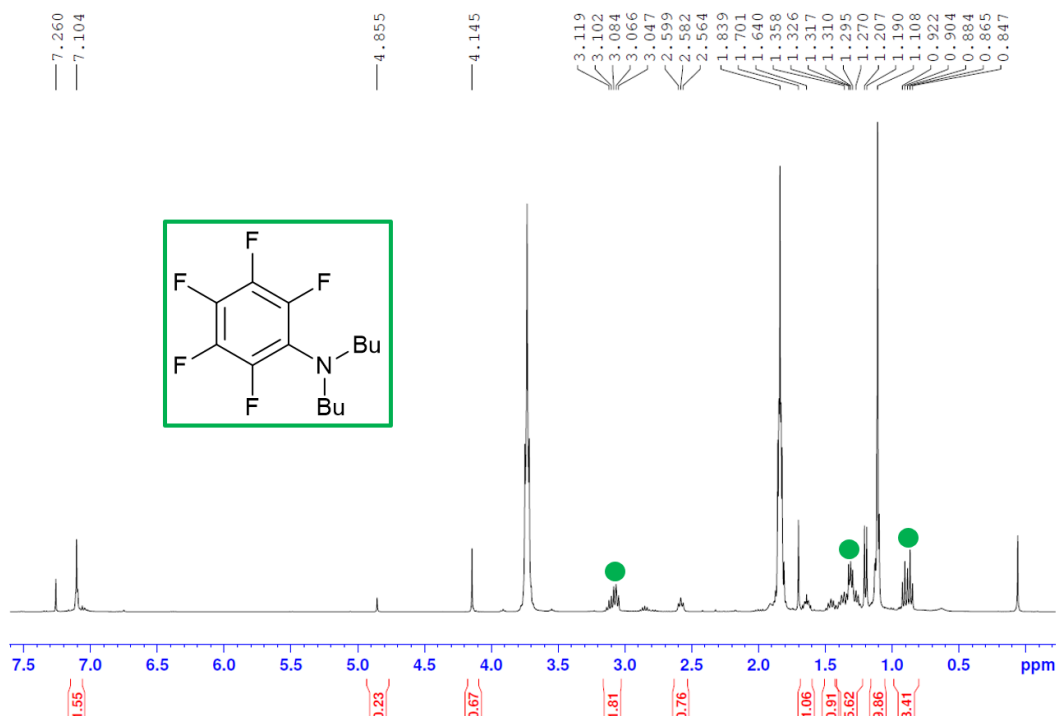


Figure S 54 <sup>1</sup>H NMR spectrum of compound 11e



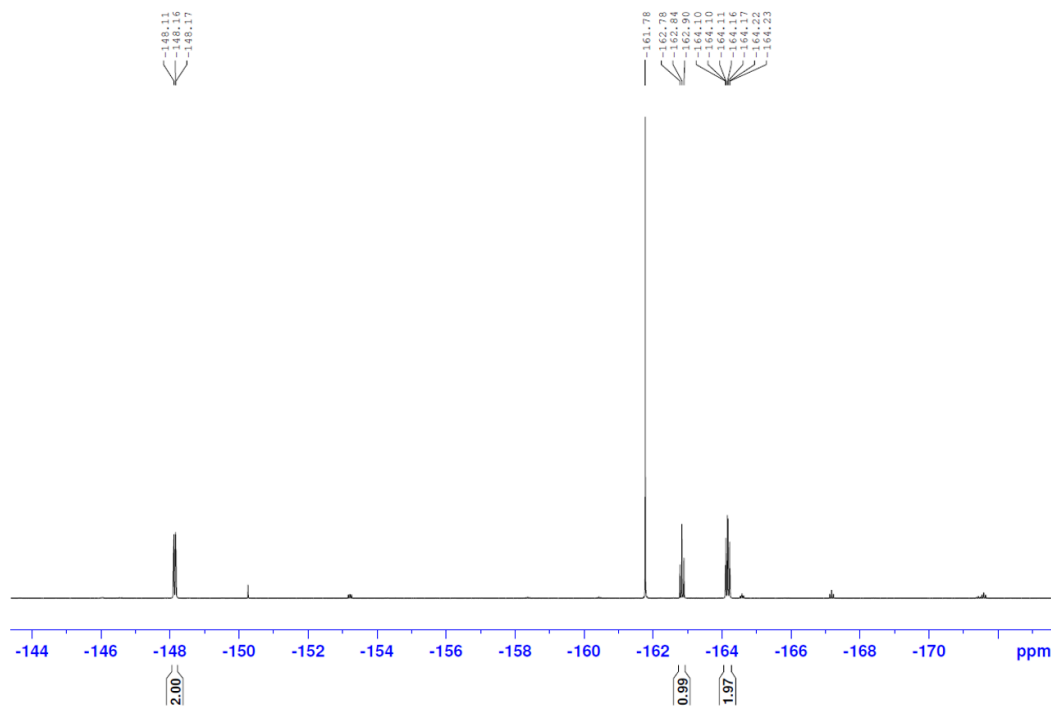


Figure S 55  $^{19}\text{F}$  NMR spectrum of compound **11e**

## Synthesis of Compound **11f**

In an argon-flushed Schlenk flask, 1 mmol (0.582 g) of **1** was dissolved in 5 mL of THF giving a yellow solution. To this, 0.1 mL (1 mmol) of piperidine and an equimolar amount of octafluorotoluene (0.14 mL, 1 mmol) was added, immediately affording a bright red suspension –solid presumed to be **8** ( $[(^{\text{Dipp}}\text{NacnacMg}(\mu\text{-F})(\text{THF}))_2]$ ). The reaction was allowed to stir at room temperature for 1 h before a cannula filtration was performed and **8** was washed with 3x5 mL of fresh THF in order to isolate the organic product. The filtrate was then hydrolysed in air and transferred into a round bottomed flask before all solvent was removed under reduced pressure to give a yellow, waxy solid. Analysis of this solid by NMR showed the formation of **11f** in a 91% yield against 10 mol% ferrocene (18 mg) as an internal standard. The crude product was then subjected to  $\text{SiO}_2$  column chromatography using 100:1 pentane:EtOAc leading to purified **11f**. White solid, 233 mg (77%).

**$^1\text{H}$  NMR (400.1 MHz,  $\text{CDCl}_3$ , 300 K):**  $\delta$  ~ 3.29 (m, 4H,  $\text{N}(\text{CH}_2)_2(\text{CH}_2)_2\text{CH}_2$ ), 1.67 (m, 6H,  $\text{N}(\text{CH}_2)_2(\text{CH}_2)_2\text{CH}_2 + \text{N}(\text{CH}_2)_2(\text{CH}_2)_2\text{CH}_2$ ) ppm

**$^{19}\text{F}$  NMR (376.5 MHz,  $\text{CDCl}_3$ , 300 K):**  $\delta$  ~ -55.41 (t, 3F,  $\text{CF}_3$ ), -143.21 (m, 2F, *m*-F), -150.94 (m, 2F, *o*-F) ppm

**$^{13}\text{C}\{^1\text{H}\}$  NMR (100.62 MHz,  $\text{CDCl}_3$ , 300 K):**  $\delta$  ~ 146.5 (m,  $\text{Ar}(\text{C})_{\text{meta-F}}$ ), 143.9 (m,  $\text{Ar}(\text{C})_{\text{meta-F}}$ ), 142.7 (m,  $\text{Ar}(\text{C})_{\text{ortho-F}}$ ), 140.4 (m,  $\text{Ar}(\text{C})_{\text{ortho-F}}$ ), 134.9 (m,  $\text{Ar}(\text{C})\text{-N}$ ), 125.7-118.0 (q,  $-\text{CF}_3$ ,  $J = 271.7$  MHz), 100.4 ( $\text{Ar}(\text{C})_{\text{q}}$ ), 52.2 ( $\text{N}(\text{CH}_2)_2(\text{CH}_2)_2\text{CH}_2$ ), 26.5 ( $\text{N}(\text{CH}_2)_2(\text{CH}_2)_2\text{CH}_2$ ), 21.1 ( $\text{N}(\text{CH}_2)_2(\text{CH}_2)_2\text{CH}_2$ ) ppm

LRMS (GC/ESI)  $m/z$ : 302.0  $[\text{M}+\text{H}]^+$

HRMS (TOF): Calc. for C<sub>12</sub>H<sub>10</sub>F<sub>7</sub>N, 301.0701; Found, 301.0696 (error 0.45 ppm)

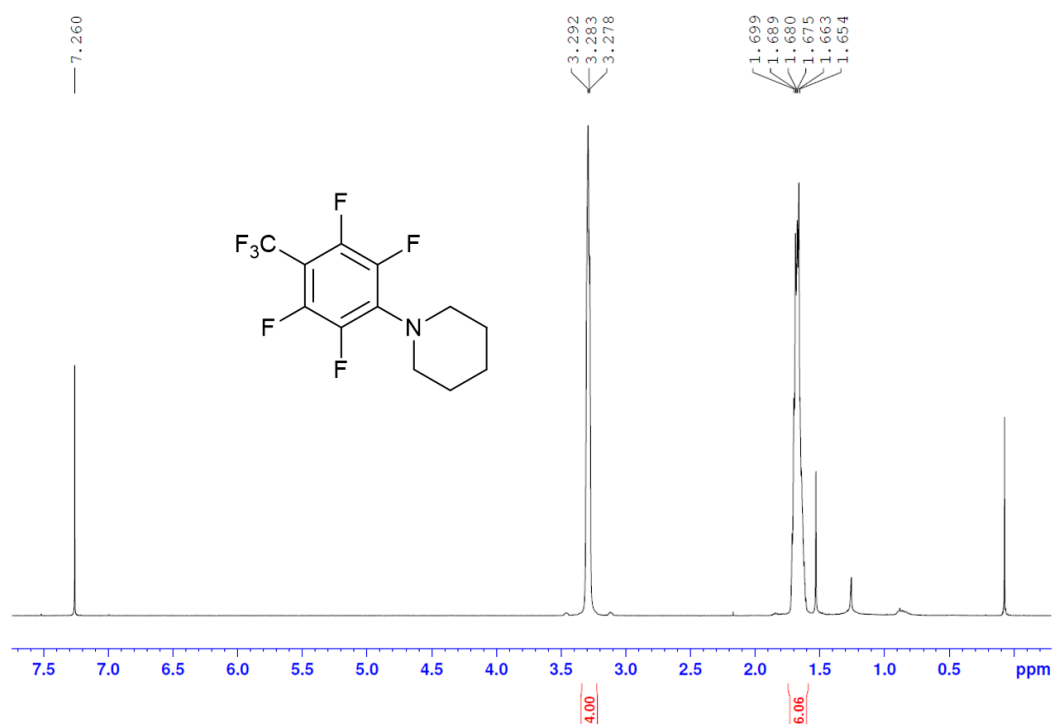


Figure S 56 <sup>1</sup>H NMR spectrum of compound 11f

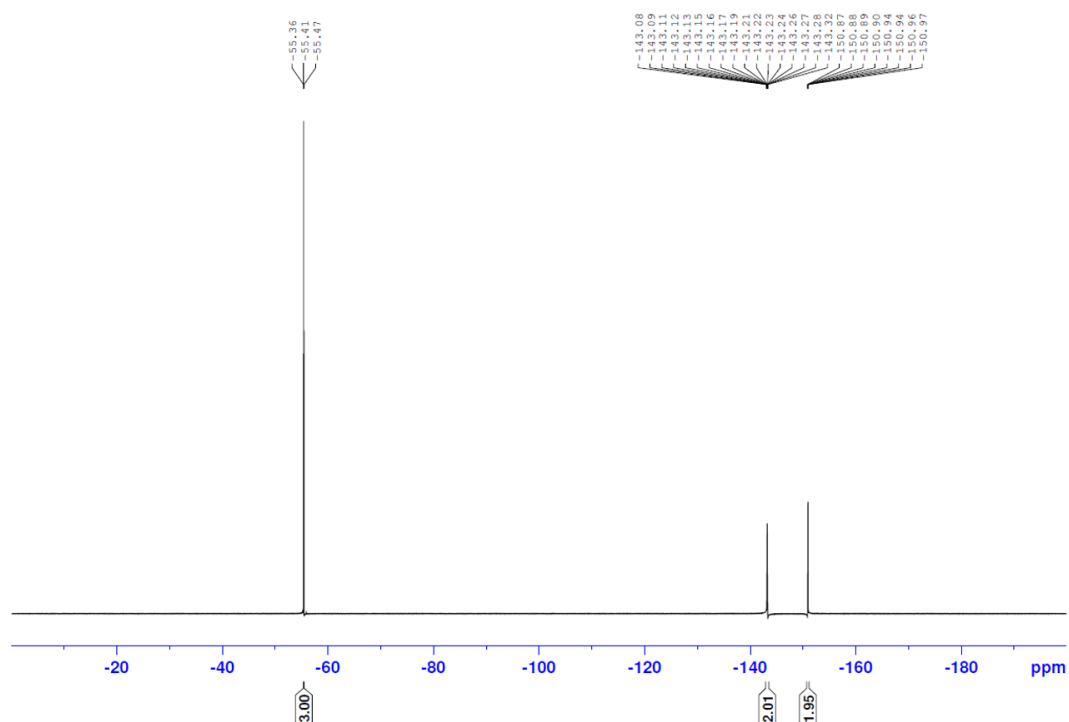


Figure S 57 <sup>19</sup>F NMR spectrum of compound 11f

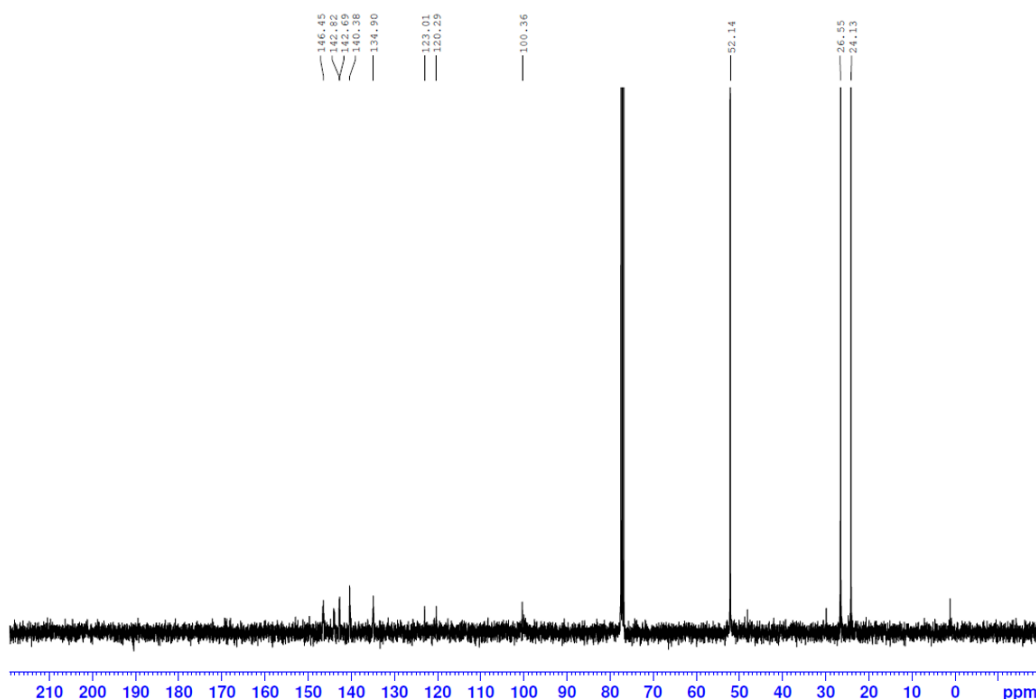


Figure S 58  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **11f**

## Synthesis of Compound **11g**

In an argon-flushed Schlenk flask, 1 mmol (0.582 g) of **1** was dissolved in 5 mL of THF giving a yellow solution. To this, 90  $\mu\text{L}$  (1 mmol) of morpholine and an equimolar amount of octafluorotoluene (0.14 mL, 1 mmol) was added, forming a red/brown suspension after approximately 15 minutes – solid presumed to be **8** ( $[(^{\text{Dipp}}\text{NacnacMg}(\mu\text{-F})(\text{THF}))_2]$ ). The reaction was allowed to stir at room temperature for 1 h before a cannula filtration was performed and **8** was washed with 3x5 mL of fresh THF in order to isolate the organic product. The filtrate was then hydrolysed in air and transferred into a round bottomed flask before all solvent was removed under reduced pressure to give a red, waxy solid. Analysis of this solid by NMR showed the formation of **11g** in an 88% yield against ferrocene (19 mg) as an internal standard. The crude product was then subjected to  $\text{SiO}_2$  column chromatography using 100:1 pentane:EtOAc leading to purified **11g**. Off-white solid, 184 mg (60%).

**$^1\text{H}$  NMR (400.1 MHz,  $\text{CDCl}_3$ , 300 K):**  $\delta$  ~ 3.82 (br. t, 4H,  $\text{N}(\text{CH}_2)_2(\text{CH}_2)_2\text{O}$ ), 3.36 (m, 4H,  $\text{N}(\text{CH}_2)_2(\text{CH}_2)_2\text{O}$ ) ppm

**$^{19}\text{F}$  NMR (376.5 MHz,  $\text{CDCl}_3$ , 300 K):**  $\delta$  ~ -55.61 (t, 3F,  $\text{CF}_3$ ), -142.48 (m, 2F, *m*-F), -150.64 (m, 2F, *o*-F) ppm

**$^{13}\text{C}\{^1\text{H}\}$  NMR (100.62 MHz,  $\text{CDCl}_3$ , 300 K):**  $\delta \sim 146.4$  (m,  $\text{Ar}(\text{C})_{\text{meta-F}}$ ), 143.8 (m,  $\text{Ar}(\text{C})_{\text{meta-F}}$ ), 142.8 (m,  $\text{Ar}(\text{C})_{\text{ortho-F}}$ ), 140.4 (m,  $\text{Ar}(\text{C})_{\text{ortho-F}}$ ), 133.6 (m,  $\text{Ar}(\text{C})_{\text{-N}}$ ), 125.4-119.0 (q,  $-\text{CF}_3$ ,  $J = 273.8$  MHz), 101.7 ( $\text{Ar}(\text{C})_{\text{q}}$ ), 67.3 ( $\text{N}(\text{CH}_2)_2(\text{CH}_2)_2\text{O}$ ), 51.0 ( $\text{N}(\text{CH}_2)_2(\text{CH}_2)_2\text{O}$ ) ppm

LRMS (GC/ESI)  $m/z$ : 304.0  $[\text{M}+\text{H}]^+$

HRMS (TOF): Calc. for  $\text{C}_{11}\text{H}_8\text{F}_7\text{NO}$ , 303.0494; Found, 303.0489 (error 0.20 ppm)

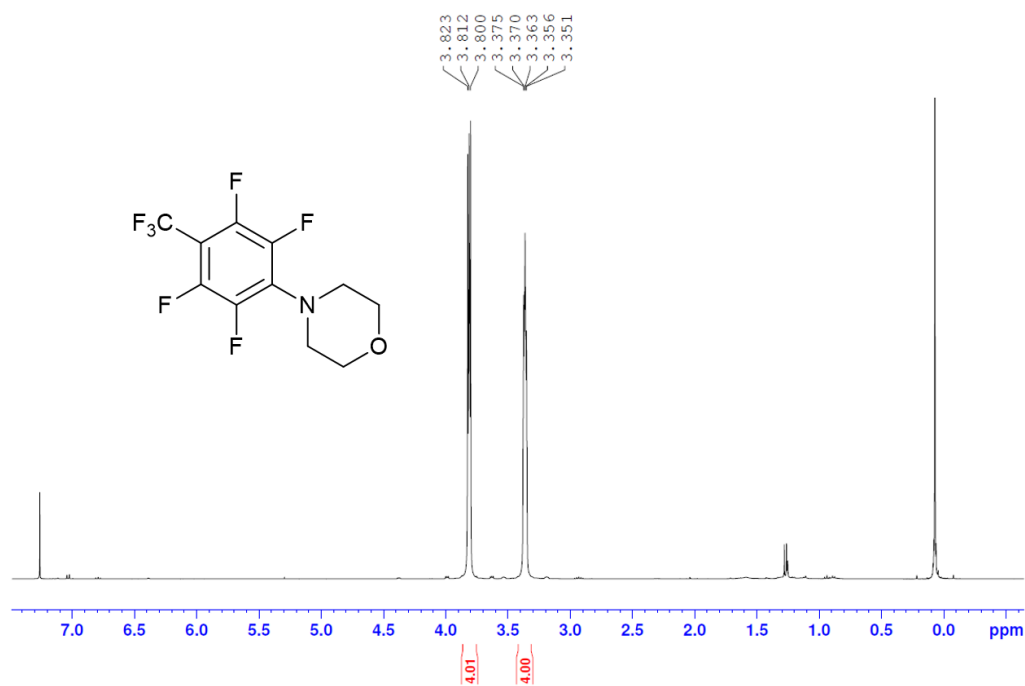


Figure S 59  $^1\text{H}$  NMR spectrum of compound 11g

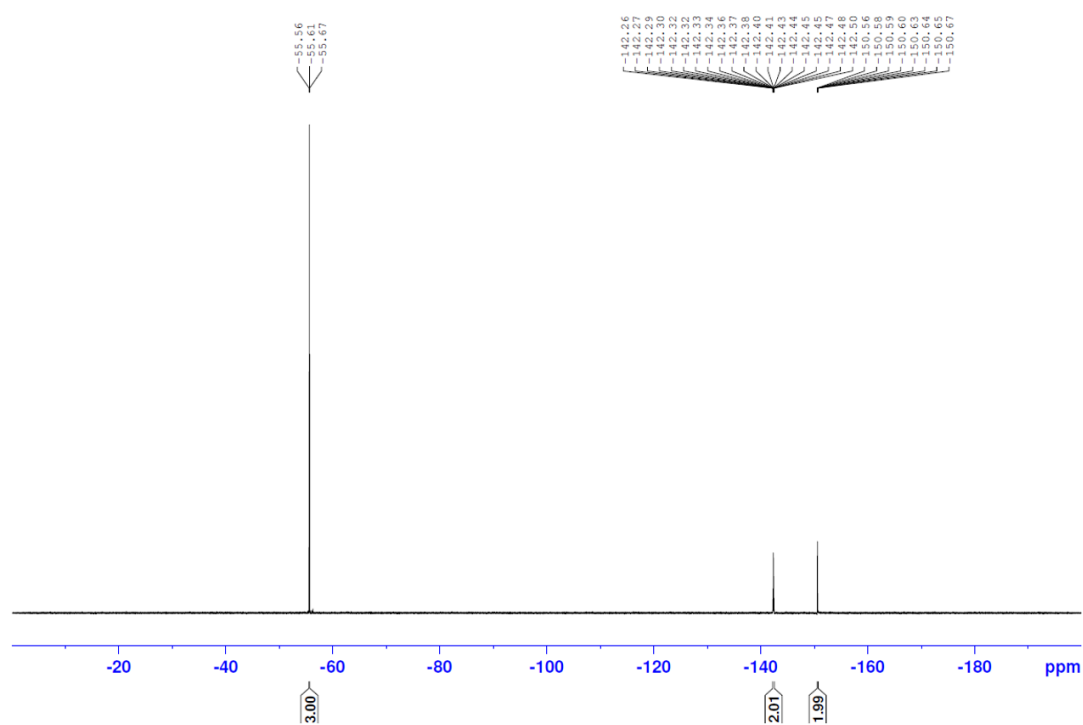


Figure S 60  $^{19}\text{F}$  NMR spectrum of compound 11g

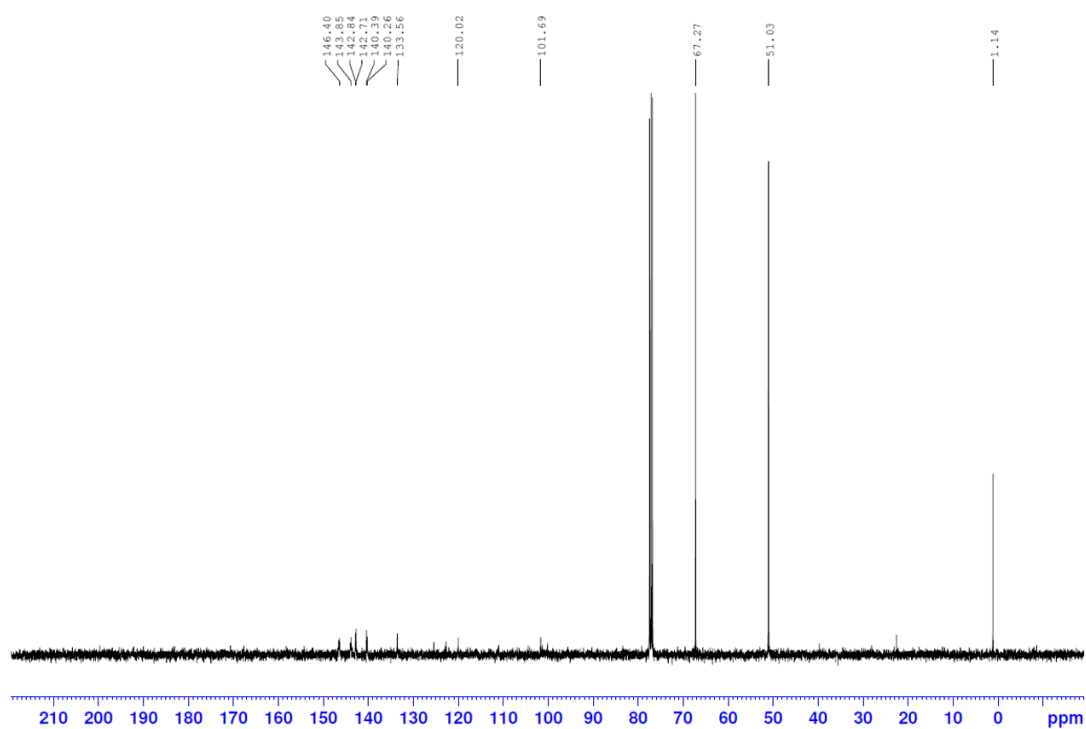


Figure S 61  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound 11g

## Synthesis of Compound 11h

In an argon-flushed Schlenk flask, 1 mmol (0.582 g) of **1** was dissolved in 5 mL of THF giving a yellow solution. To this, 0.17 mL (1 mmol) of di-*n*-butylamine and an equimolar amount of octafluorotoluene (0.14 mL, 1 mmol) was added, immediately forming a red suspension – solid presumed to be **8** ( $[(^{\text{Dipp}}\text{NacnacMg}(\mu\text{-F})(\text{THF}))_2]$ ). The reaction was allowed to stir at room temperature for 1 h before a cannula filtration was performed and **8** was washed with 3x5 mL of fresh THF in order to isolate the organic product. The filtrate was then hydrolysed in air and transferred into a round bottomed flask before all solvent was removed under reduced pressure to give a yellow, waxy solid. Analysis of this solid by NMR showed the formation of **11h** in an 85% yield against ferrocene (22 mg) as an internal standard. The crude product was then subjected to SiO<sub>2</sub> column chromatography using 100:1 hexane:EtOAc leading to purified **11h**. Colourless oil, 237 mg (69%).

**<sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>, 300 K):**  $\delta$  ~ 3.26 (t, 4H, N((CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)(CH<sub>2</sub>)CH<sub>3</sub>)<sub>2</sub>), 1.49 (quin., 4H, N((CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)(CH<sub>2</sub>)CH<sub>3</sub>)<sub>2</sub>), 1.27 (sext., 4H, N((CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)(CH<sub>2</sub>)CH<sub>3</sub>)<sub>2</sub>), 0.90 (t, 6H, N((CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)(CH<sub>2</sub>)CH<sub>3</sub>)<sub>2</sub>) ppm

**<sup>19</sup>F NMR (376.5 MHz, CDCl<sub>3</sub>, 300 K):**  $\delta$  ~ -55.42 (t, 3F, CF<sub>3</sub>), -143.25 (m, 2F, *m*-F), -149.59 (m, 2F, *o*-F) ppm

**<sup>13</sup>C{<sup>1</sup>H} NMR (100.62 MHz, CDCl<sub>3</sub>, 300 K):**  $\delta$  ~ 145.9 (m, Ar(C)<sub>meta</sub>-F), 144.3 (m, Ar(C)<sub>meta</sub>-F), 143.1 (m, Ar(C)<sub>ortho</sub>-F), 141.5, 133.6 (m, Ar(C)-N), 124.3-128.9 (q, -CF<sub>3</sub>, J = 277.13 MHz), 100.3 (Ar(C)<sub>q</sub>), 52.6 (N((CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)(CH<sub>2</sub>)CH<sub>3</sub>)<sub>2</sub>), 30.5 (N((CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)(CH<sub>2</sub>)CH<sub>3</sub>)<sub>2</sub>), 20.1 (N((CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)(CH<sub>2</sub>)CH<sub>3</sub>)<sub>2</sub>), 13.9 (N((CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)(CH<sub>2</sub>)CH<sub>3</sub>)<sub>2</sub>) ppm

LRMS (GC/ESI) *m/z*: 346 [M+H]<sup>+</sup>

HRMS (TOF): Calc. for C<sub>15</sub>H<sub>18</sub>F<sub>7</sub>N, 345.1327; Found, 345.1322 (error 0.26 ppm)

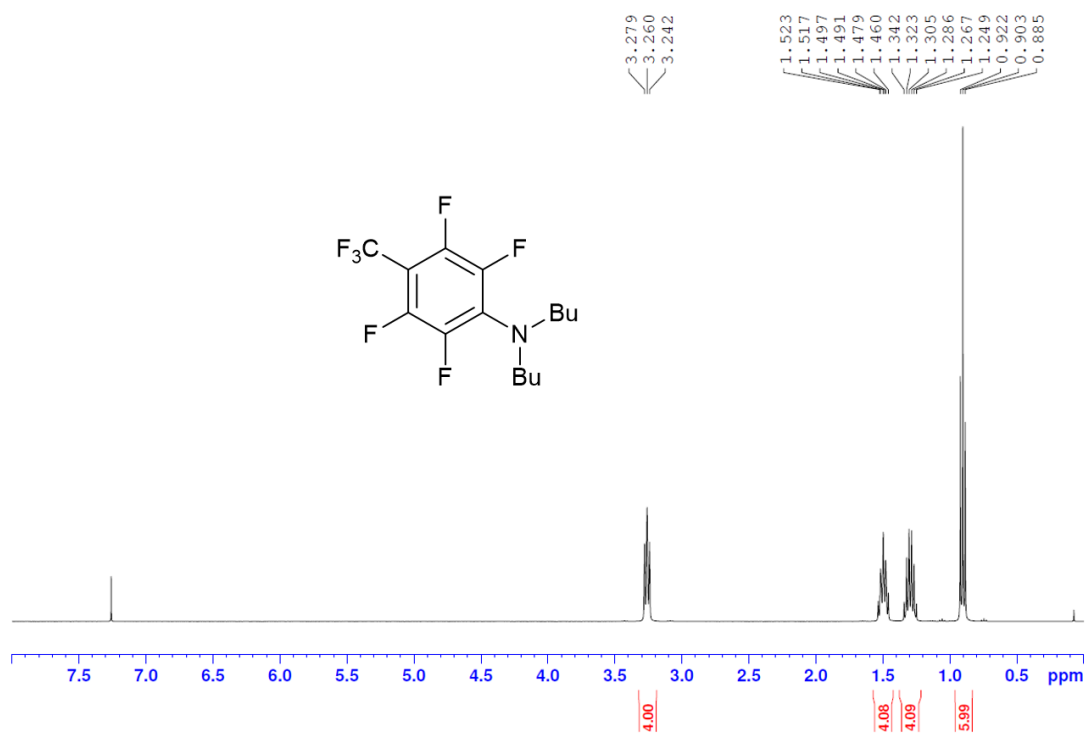


Figure S 62 <sup>1</sup>H NMR spectrum of compound 11h

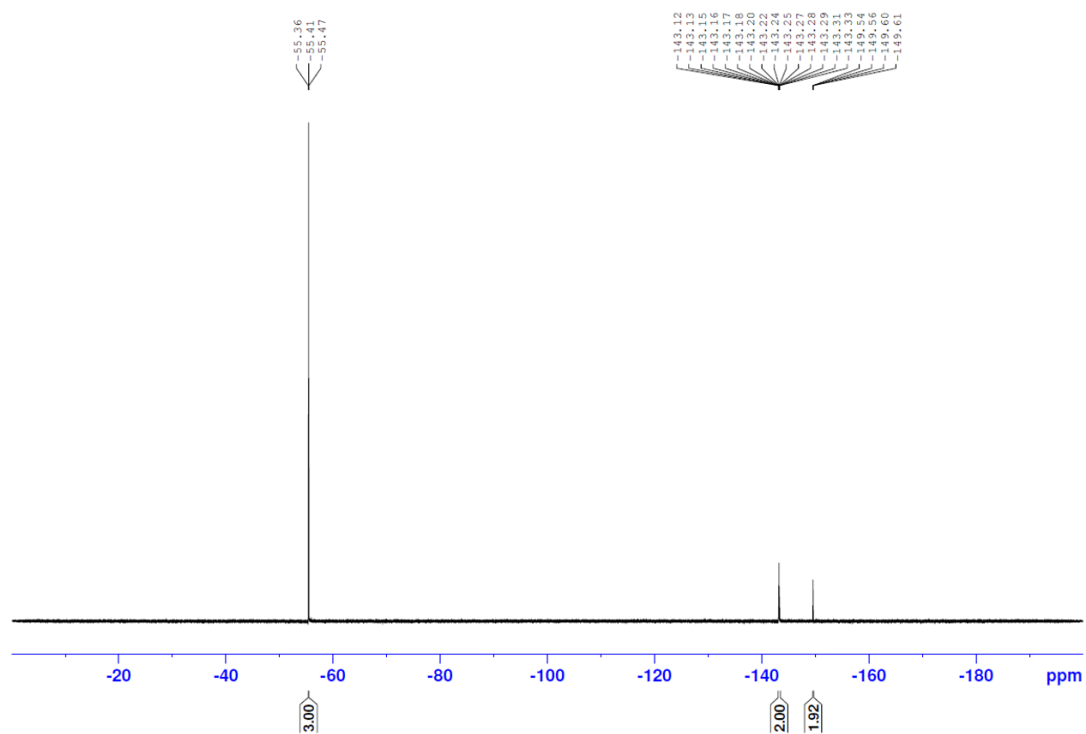


Figure S 63 <sup>19</sup>F NMR spectrum of compound 11h

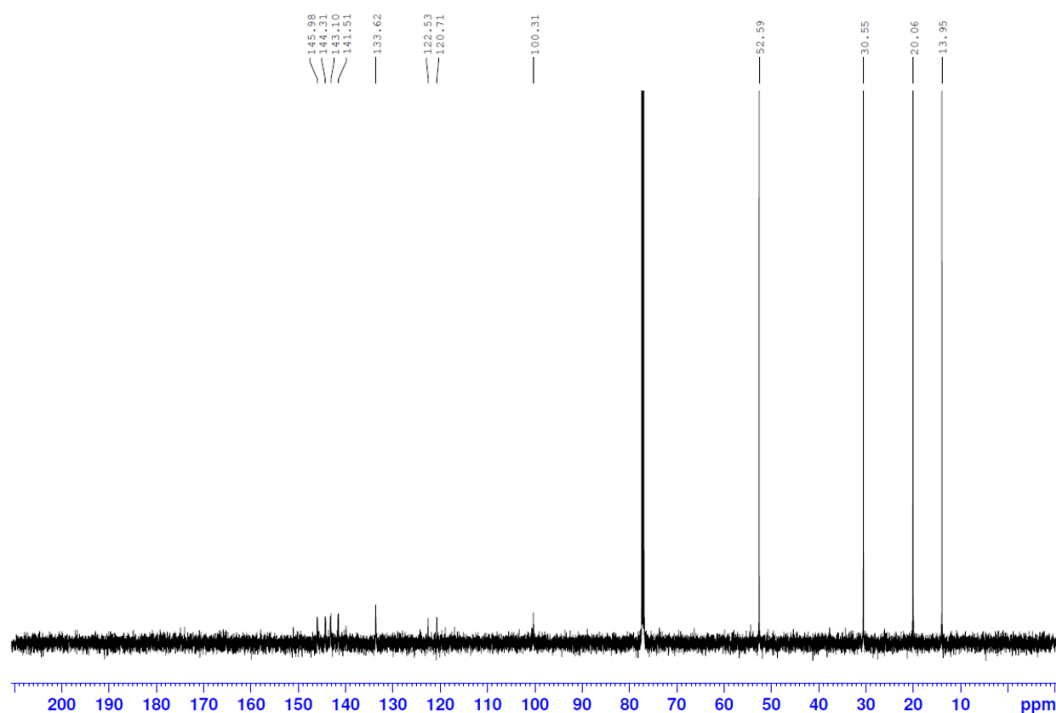


Figure S 64  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound 11h

## Synthesis of Compound 11i

In an argon-flushed Schlenk flask, 1 mmol (0.582 g) of **1** was dissolved in 5 mL of THF giving a yellow solution. To this, 80  $\mu\text{L}$  (1 mmol) of pyrrolidine and an equimolar amount of octafluorotoluene (0.14 mL, 1 mmol) was added, immediately forming a bright red suspension – solid presumed to be **8** ( $[(^{\text{Dipp}}\text{NacnacMg}(\mu\text{-F})(\text{THF}))_2]$ ). The reaction was allowed to stir at room temperature for 1 h before a cannula filtration was performed and **8** was washed with 3x5 mL of fresh THF in order to isolate the organic product. The filtrate was then hydrolysed in air and transferred into a round bottomed flask before all solvent was removed under reduced pressure to give a yellow, waxy solid. Analysis of this solid by NMR showed the formation of **11i** in a 99% yield against 10 mol% ferrocene (19 mg) as an internal standard. The crude product was then subjected to  $\text{SiO}_2$  column chromatography using 100:1 hexane:EtOAc leading to purified **11g** as large, colourless crystals (261 mg, 91%).

**$^1\text{H}$  NMR (400.1 MHz,  $\text{CDCl}_3$ , 300 K):**  $\delta$  ~ 3.68 (br. m, 4H,  $\text{N}(\text{CH}_2)_2(\text{CH}_2)_2$ ), 1.93 (br. m, 4H,  $\text{N}(\text{CH}_2)_2(\text{CH}_2)_2$ ) ppm

**$^{19}\text{F}$  NMR (376.5 MHz,  $\text{CDCl}_3$ , 300 K):**  $\delta$  ~ -54.90 (t, 3F,  $\text{CF}_3$ ), -144.32 (m, 2F, *m*-F), -156.62 (m, 2F, *o*-F) ppm

**$^{13}\text{C}\{^1\text{H}\}$  NMR (100.62 MHz,  $\text{CDCl}_3$ , 300 K):**  $\delta$  ~ 146.9 (m,  $\text{Ar}(\text{C})_{\text{meta-F}}$ ), 144.5 (m,  $\text{Ar}(\text{C})_{\text{meta-F}}$ ), 139.1 (m,  $\text{Ar}(\text{C})_{\text{ortho-F}}$ ), 136.5 (m,  $\text{Ar}(\text{C})_{\text{ortho-F}}$ ), 131.9 (m,  $\text{Ar}(\text{C})_{\text{-N}}$ ), 124.5-119.0 (q,  $-\text{CF}_3$ ,  $J = 273.9$  MHz), 95.3 (m,  $\text{Ar}(\text{C})_{\text{q}}$ ), 51.5 ( $\text{N}(\text{CH}_2)_2(\text{CH}_2)_2$ ), 25.8 ( $\text{N}(\text{CH}_2)_2(\text{CH}_2)_2$ ) ppm



LRMS (GC/ESI)  $m/z$ : 288.05  $[M+H]^+$

HRMS (TOF): Calc. for  $C_{11}H_8F_7N$  287.0545; Found, 287.0539 (error 1.16 ppm)

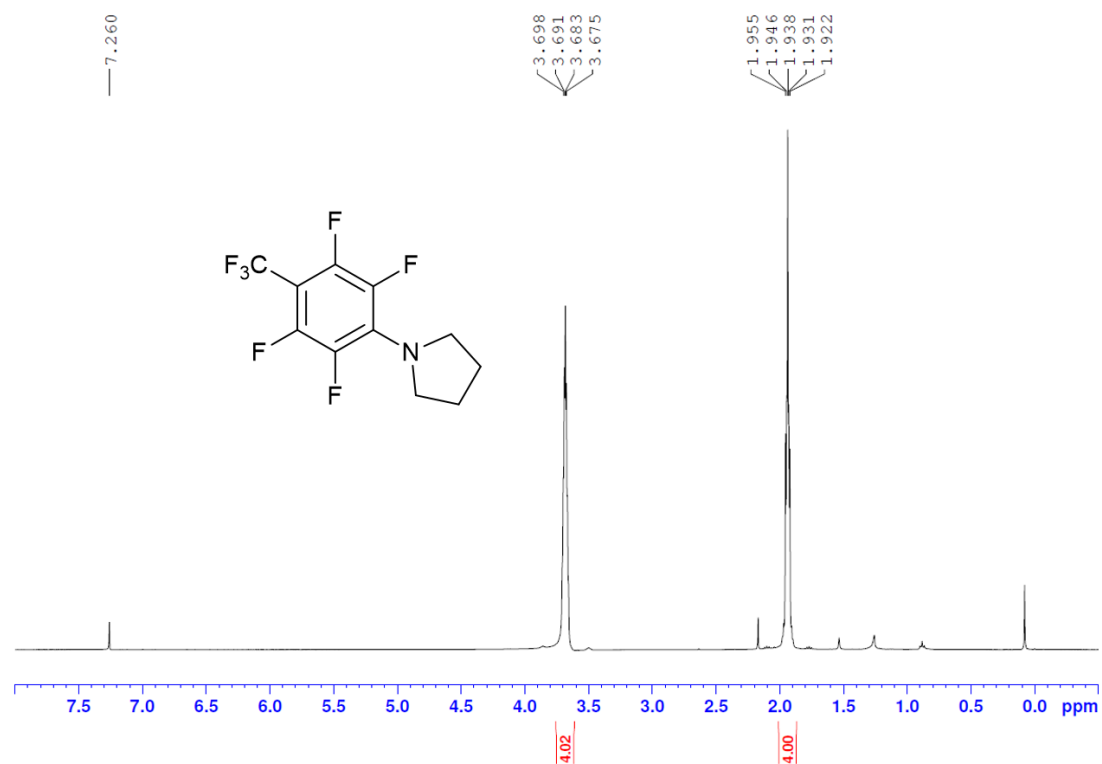


Figure S 65  $^1H$  NMR spectrum of compound 11i

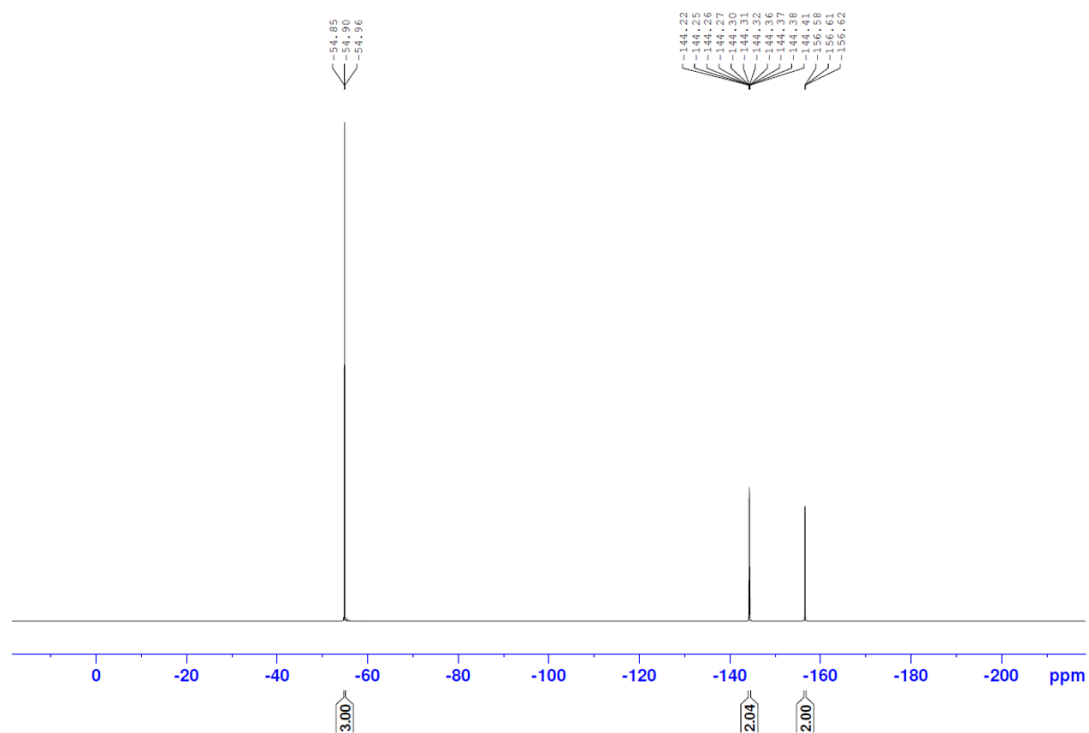


Figure S 66 <sup>19</sup>F NMR spectrum of compound 11i

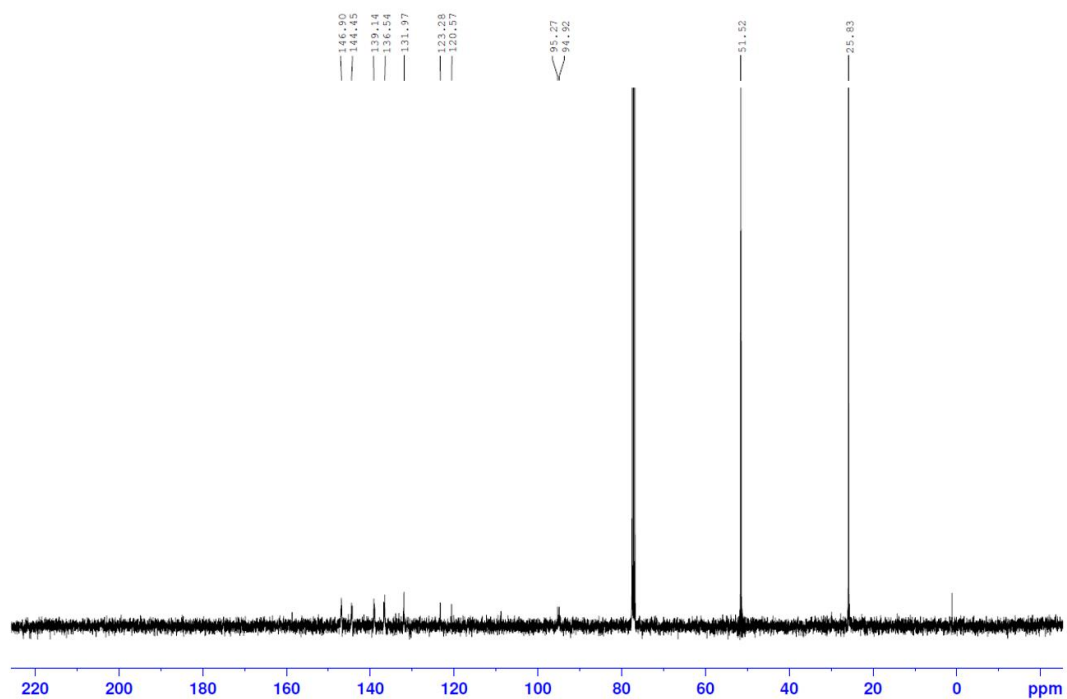


Figure S 67 <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of compound 11i

## Reactivity Studies of **4**, **9** and **10** with **ppf** and $C_6F_6$

### DOSY NMR of **9** with **ppf** at room temperature

In a J. Young's NMR tube, 76 mg (0.125 mmol) of **9** was dissolved, with heating, in 0.5 mL of  $D_8$ -Tol. To this, 24 mg (0.125 mmol) of **ppf** was added and the reaction monitored at room temperature by NMR.  $^1H$  NMR spectrum reveals a prominent broadening of the signals corresponding to compound **9** and to **ppf** – this indicated that a coordination adduct was forming between these 2 species (peak at  $\delta \sim 3.90$  ppm is  $Fe(Cp)_2$ ). This proposal is highlighted by the broad peaks observed in the  $^{19}F$  NMR and it should also be noted that these peaks are shifted compared to free, uncoordinated **ppf**. Additionally, performing a DOSY NMR of the sample at room temperature revealed that the 2 species diffuse together, providing more evidence that they have engaged in a coordination adduct at room temperature.

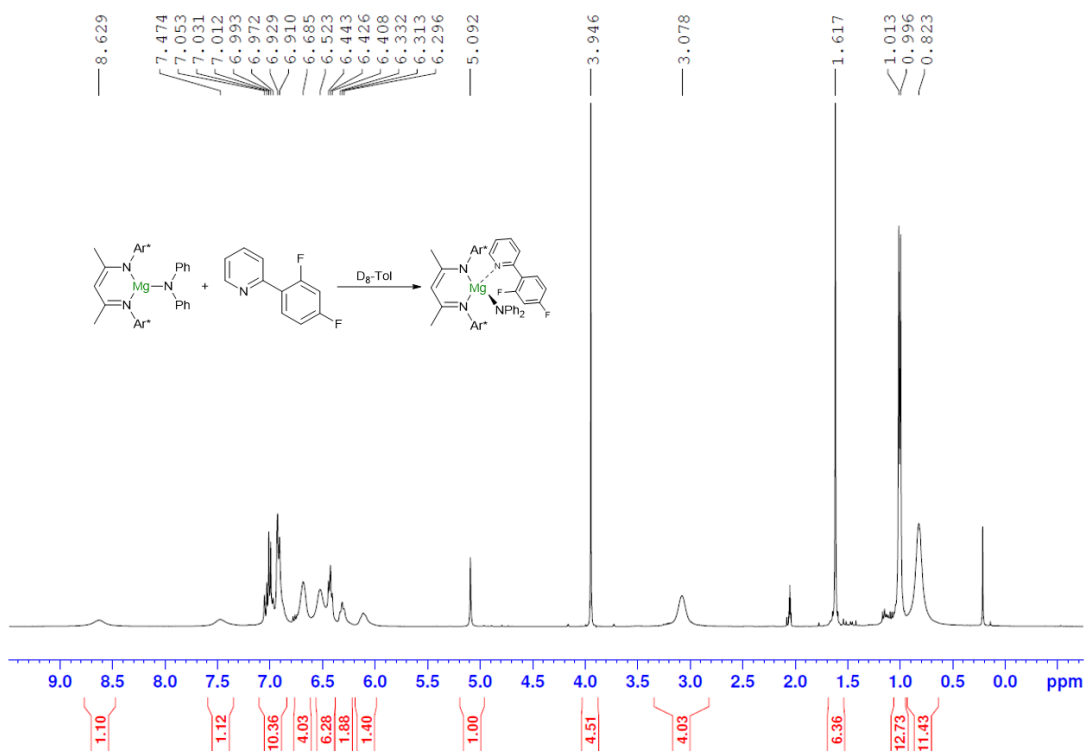


Figure S 68  $^1H$  NMR spectrum displaying coordination between compound **9** and **ppf** at 300 K in  $D_8$ -Tol

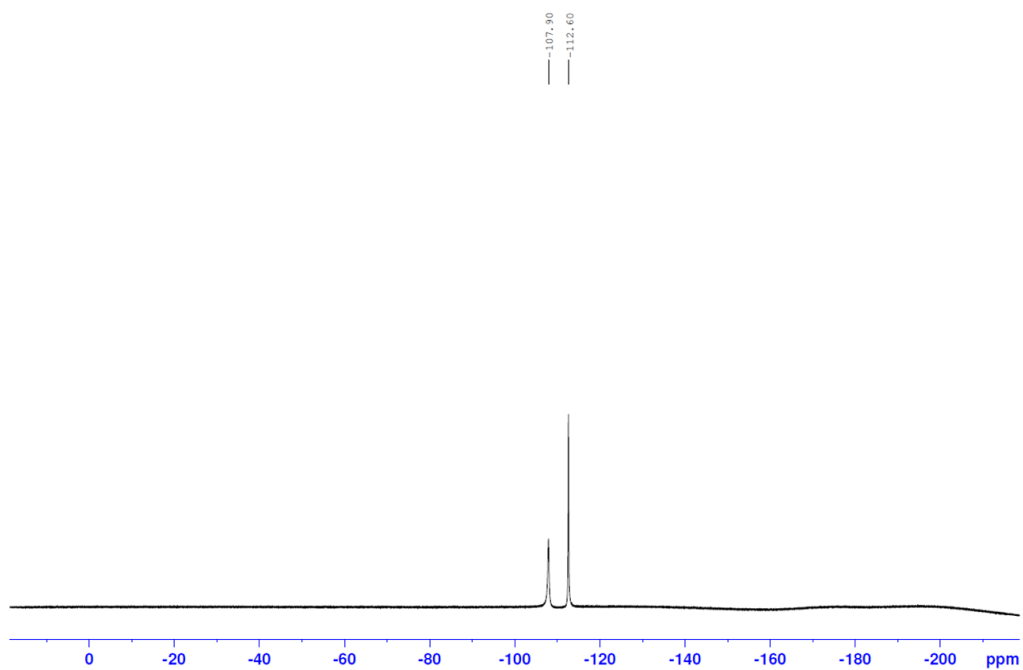


Figure S 69  $^{19}\text{F}$  NMR spectrum displaying coordination between compound 9 and ppf at 300 K in  $\text{D}_8\text{-Tol}$

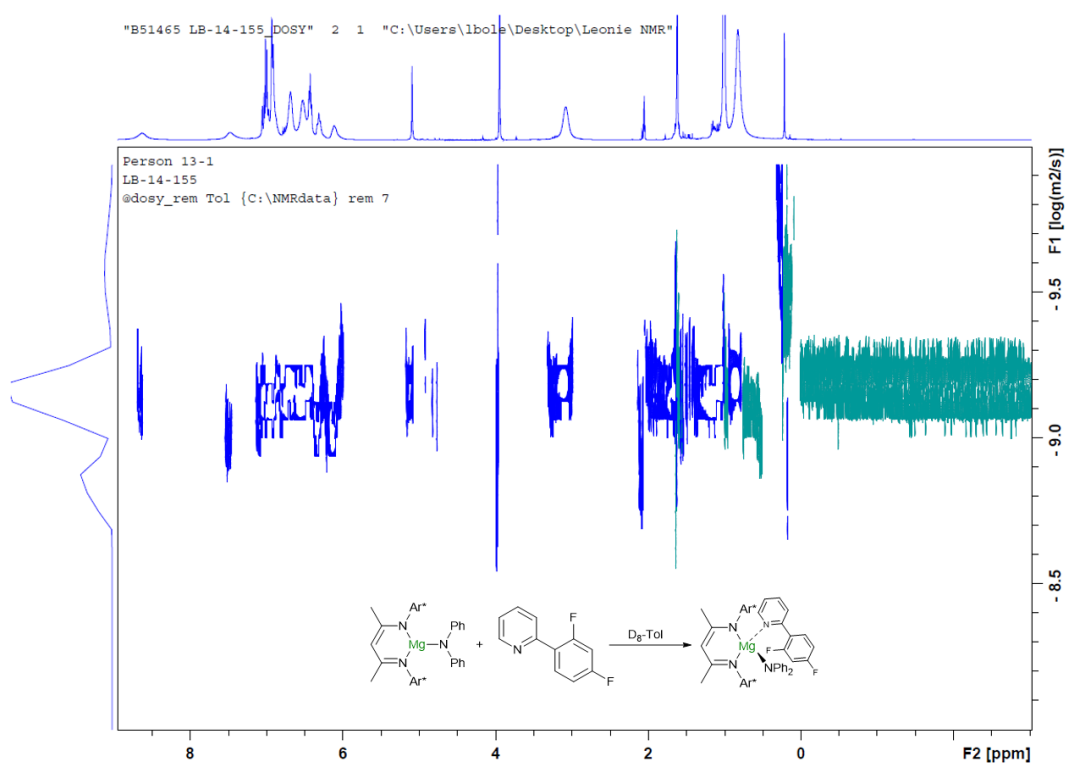


Figure S 70  $^1\text{H}$  DOSY NMR spectrum displaying co-diffusion of compound 9 and ppf in  $\text{D}_8\text{-Tol}$  at 300 K

## Reactivity between Compound **9** and ppf at Elevated Temperature

In a J. Young's NMR tube, 76 mg (0.125 mmol) of **9** was dissolved, with heating, in 0.5 mL of D<sub>8</sub>-Tol. To this, 24 mg (0.125 mmol) of **ppf** was added and the reaction examined at room temperature by NMR, depicting a coordination adduct forming between the two species, giving insight into the mechanism that we have proposed (**Scheme 3**). The tube was then heated at 70°C for 2 h, at which point, a minor amount of C-F activation of ppf (product **7e**) could be observed – 11% against Fe(Cp)<sub>2</sub> (11 mg) as an internal standard. Heating for a further (9 h in total) results in a 75% yield of **7e** against ferrocene. Unfortunately, all signals for this product cannot be definitively assigned as they are present underneath the more prominent peaks for the coordination adduct. The nature of this C-F activation occurs in the same manner as with compounds **7a-7d**. We propose that harsher conditions are required due to the reduced nucleophilicity of **9** compared to **3-6**. By <sup>19</sup>F NMR, we can observe the formation of the new aminofluoroarene, alongside coordinated **ppf** and the incident formation of Mg-F species at δ -188 (**8**) -199 ppm.

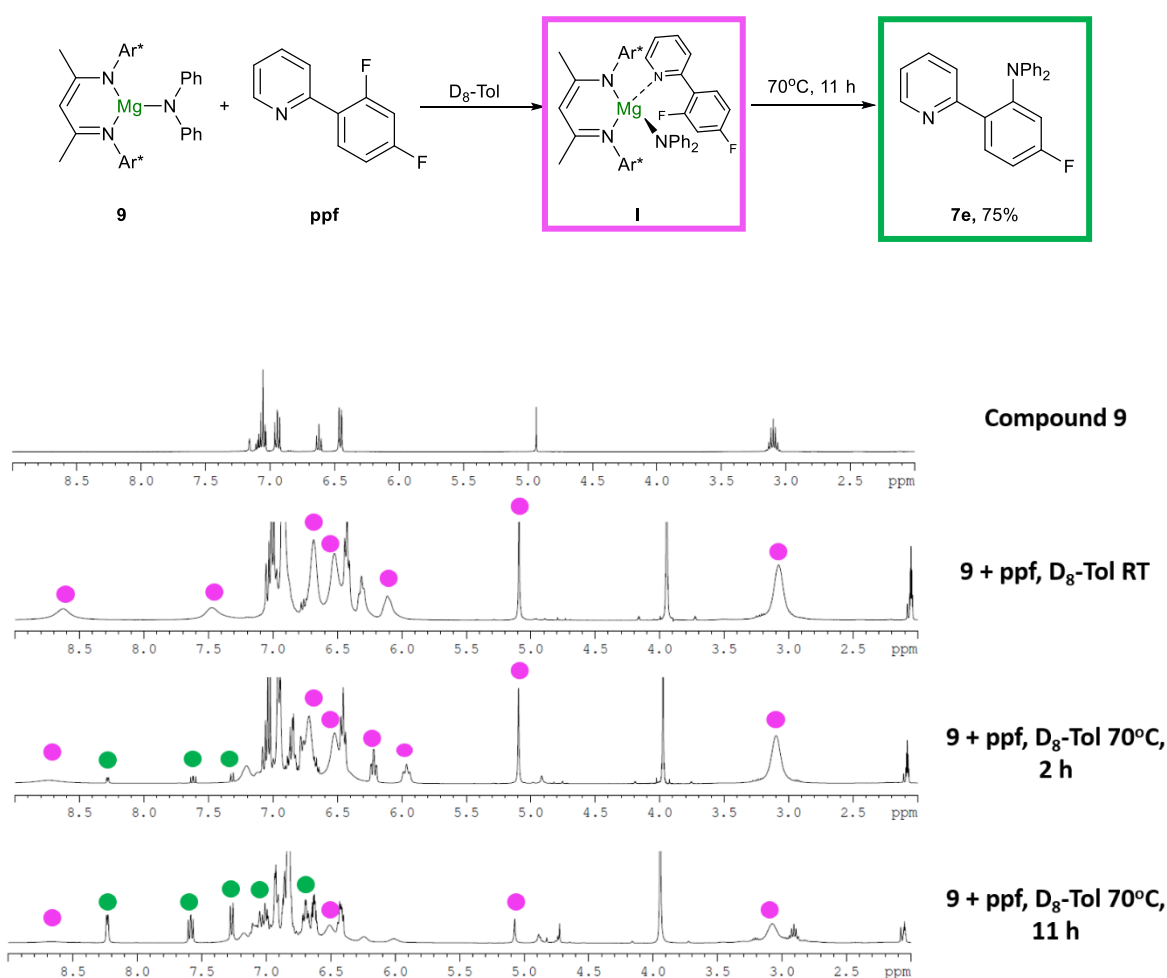


Figure S 71 <sup>1</sup>H NMR spectrum depiction of compound **9** reacting with ppf over various conditions in D<sub>8</sub>-Tol

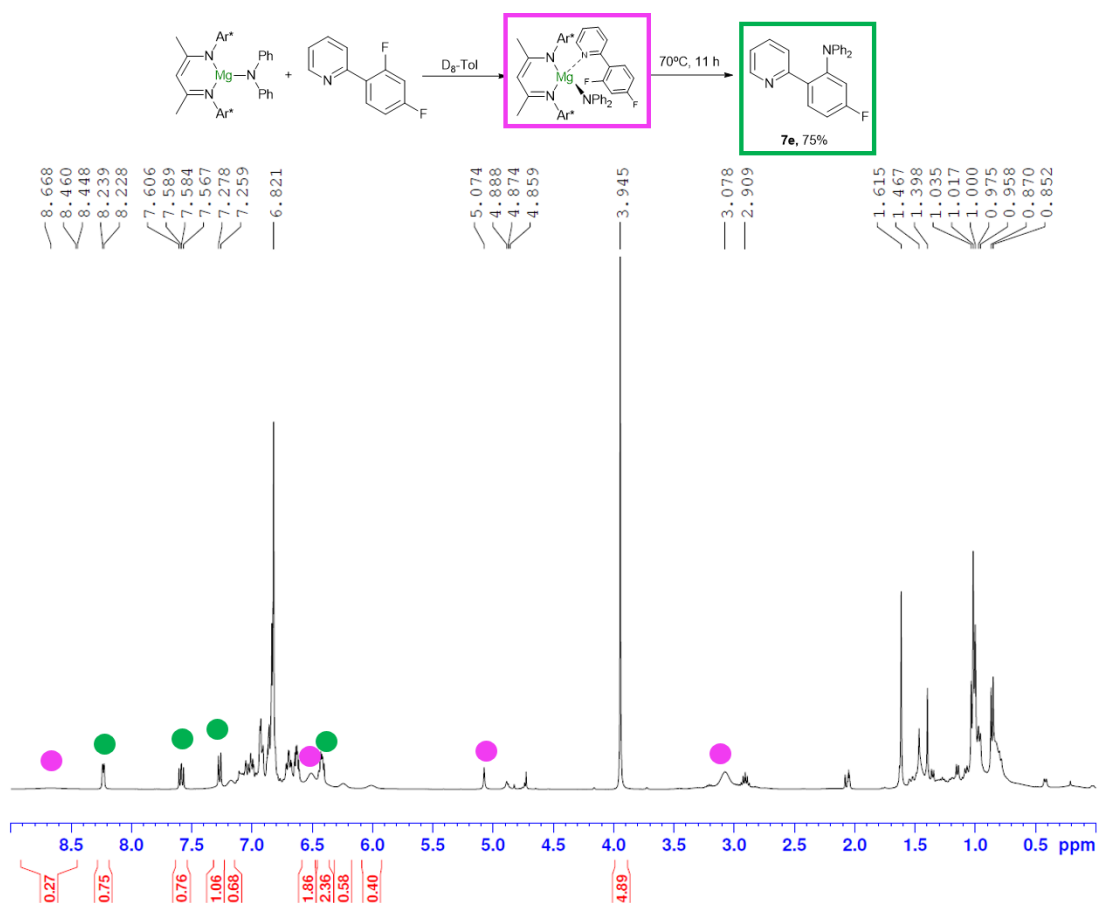


Figure S 72  $^1\text{H}$  NMR spectrum of compound **9** and ppf after 11 h at 70°C in  $D_8$ -Tol showing the formation of **7e** via C-F activation of ppf

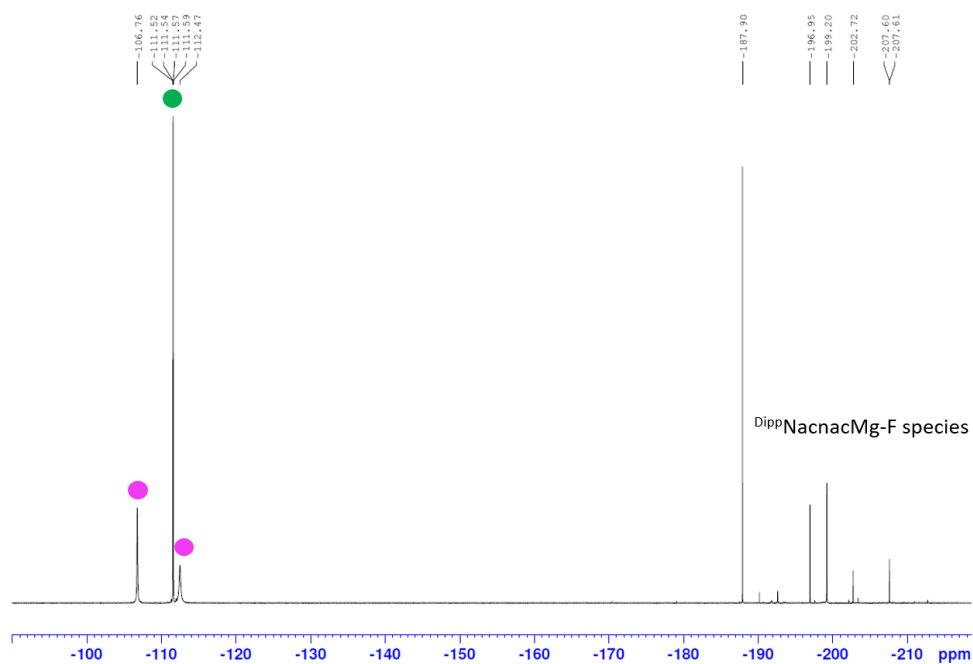


Figure S 73  $^{19}\text{F}$  NMR spectrum of compound **9** and ppf after 11 h at 70°C in  $D_8$ -Tol showing the formation of **7e** via C-F activation of ppf and the formation of  $\text{DippNacnacMg-F}$  species

## Reactivity between Compound **10** and ppf at Elevated Temperature

In a Schlenk flask, 0.125 mmol (0.14 g) of compound **10** was weighed alongside 4 mL of toluene and 0.125 mmol (0.024 g) of **ppf**. Once it was evident that no reaction was occurring at room temperature, the mixture was exposed to higher temperature of 110°C for a total of 14 h, at which point it NMR analysis revealed that both **ppf** and compound **9** remained completely intact and no C-F activation was occurring. We propose that this could be due to two factors: the decreased nucleophilicity of the benzotriazolyl anion and also the dimeric framework of compound **9** which exhibits notably poor solubility in all NMR solvents that we tested.

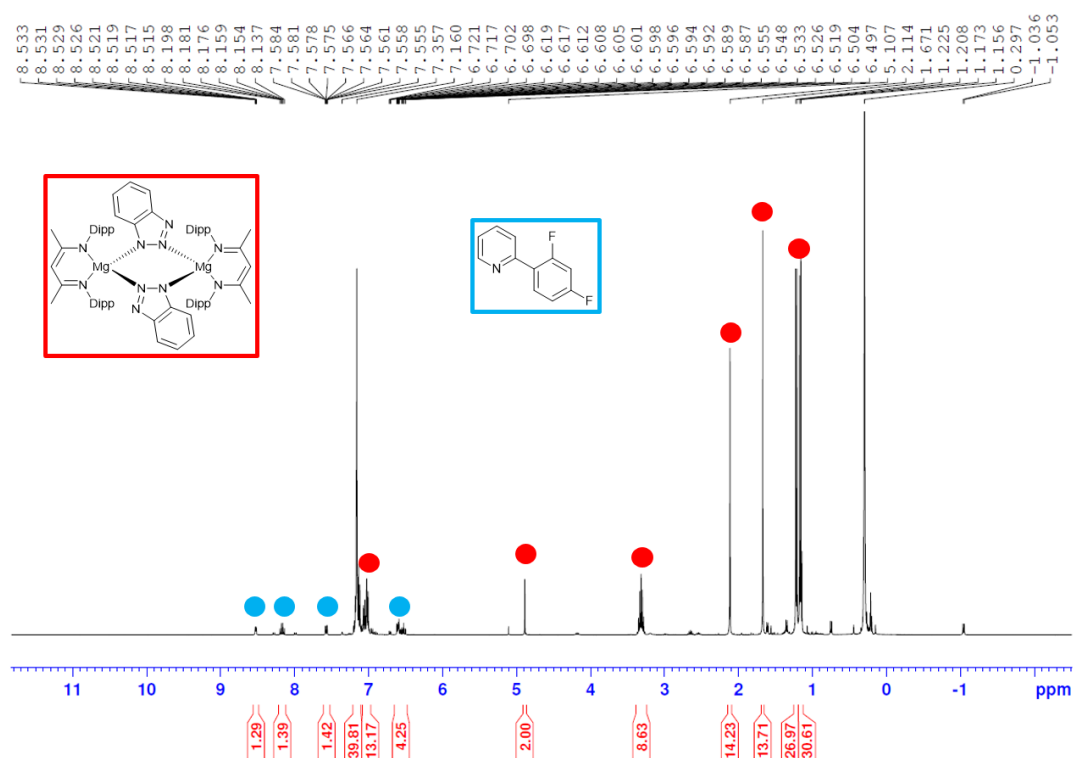


Figure S 74  $^1\text{H}$  NMR spectrum of reaction between compound **10** and ppf in  $\text{C}_6\text{D}_6$

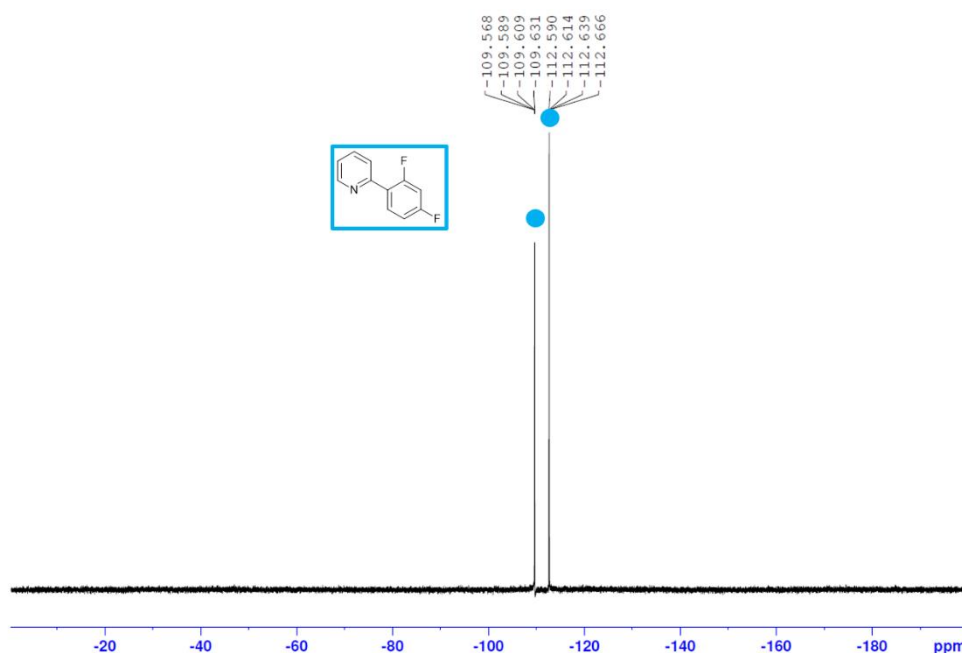


Figure S 75 <sup>19</sup>F NMR spectrum of reaction between compound 10 and ppf, showing unreacted ppf (C<sub>6</sub>D<sub>6</sub>)

## Reactivity between Compound 4 and Fluorobenzene

Inside the glovebox, 1 mmol (0.582 g) of **1** was weighed into a microwave vial and then dissolved in 2 mL of THF whilst exposed to argon gas on a Schlenk line. To this, 0.1 mL (1 mmol) of piperidine was added (forming compound **4** in situ) followed by 94  $\mu$ L (1 mmol) of fluorobenzene, giving a yellow solution. The vial was then placed in a microwave reactor for 1 h at 125°C, resulting in a green suspension. This reaction mixture was then hydrolysed in air, filtered through a plug of celite and glass wool and washed thoroughly with THF. All THF solvent was then removed under reduced pressure and the formation of compound **11j** was determined to be 20% against 10 mol% ferrocene (19 mg) as an internal standard and signals are consistent with those previously reported in the literature.<sup>9</sup>

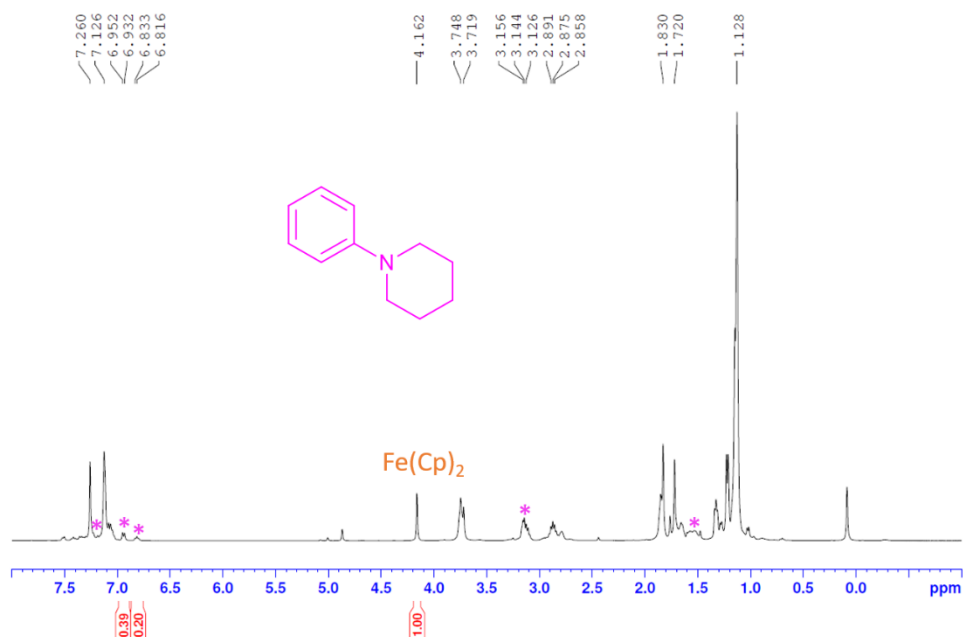
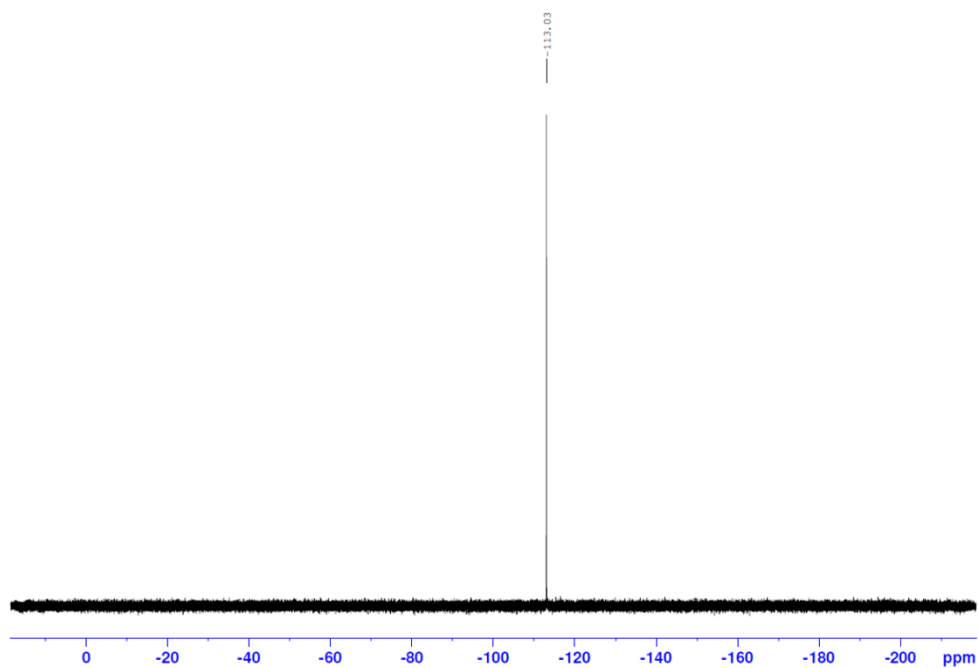


Figure S 76 <sup>1</sup>H NMR spectrum of compound 11j in CDCl<sub>3</sub>





**Figure S 77  $^{19}\text{F}$  NMR spectrum of reaction between compound 4 and fluorobenzene displaying unreacted fluorobenzene**

### Reactivity between Compound 9 and C<sub>6</sub>F<sub>6</sub>

Inside the glovebox, 1 mmol (0.582 g) of **1** was weighed into a microwave vial alongside 0.169 g (1 mmol) of diphenylamine and then dissolved in 2 mL of THF on the bench. 0.12 mL (1 mmol) of C<sub>6</sub>F<sub>6</sub> and exposed to microwave radiation for 1 h at 125°C, giving a dark brown solution. <sup>19</sup>F NMR analysis revealed that <1% C-F activation of C<sub>6</sub>F<sub>6</sub> had occurred, even after exposed to these harsh conditions.

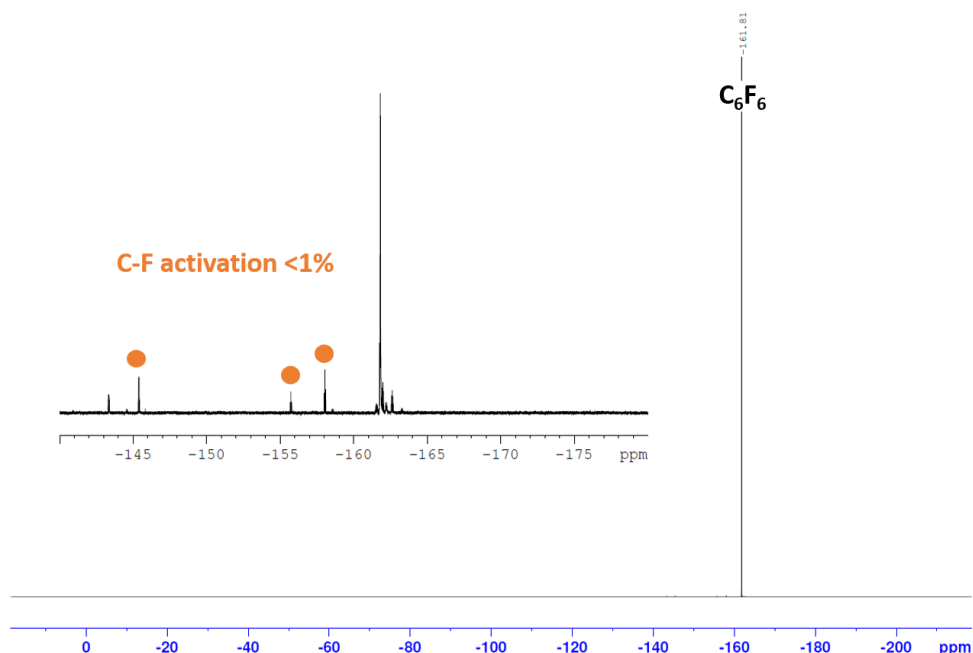


Figure S 78 <sup>19</sup>F NMR spectrum of reaction between compound 9 and C<sub>6</sub>F<sub>6</sub> showing negligible reactivity (CDCl<sub>3</sub>)

### Reactivity between Compound 10 and C<sub>6</sub>F<sub>6</sub>

Inside the glovebox, 0.560 g (0.5 mmol) of **10** was weighed into a microwave vial and then suspended in 2 mL of THF on the bench. To this 0.12 mL (1 mmol) was then added forming a cream suspension. This mixture was heated at 125°C in a microwave reactor for 1 h, giving no obvious change in the appearance of the reaction mixture. The suspension was then hydrolysed in air and filtered through a plug of cellite and glasswool to give a yellow solution. <sup>1</sup>H NMR analysis reveals the presence of only <sup>Dipp</sup>NacnacH resulting from hydrolysis of the amide. Note, that although <sup>19</sup>F NMR appears to show peaks which could correspond to C<sub>6</sub>F<sub>5</sub>-benzotriazolyl, this particular reaction had all solvent removed before <sup>19</sup>F NMR analysis of the crude product. The volatility of C<sub>6</sub>F<sub>6</sub> insinuates C-F activation to a minor degree, however, in conjunction with the <sup>1</sup>H NMR only showing the presence of <sup>Dipp</sup>NacnacH, we can deduce that the degree of C-F activation occurring is negligible.

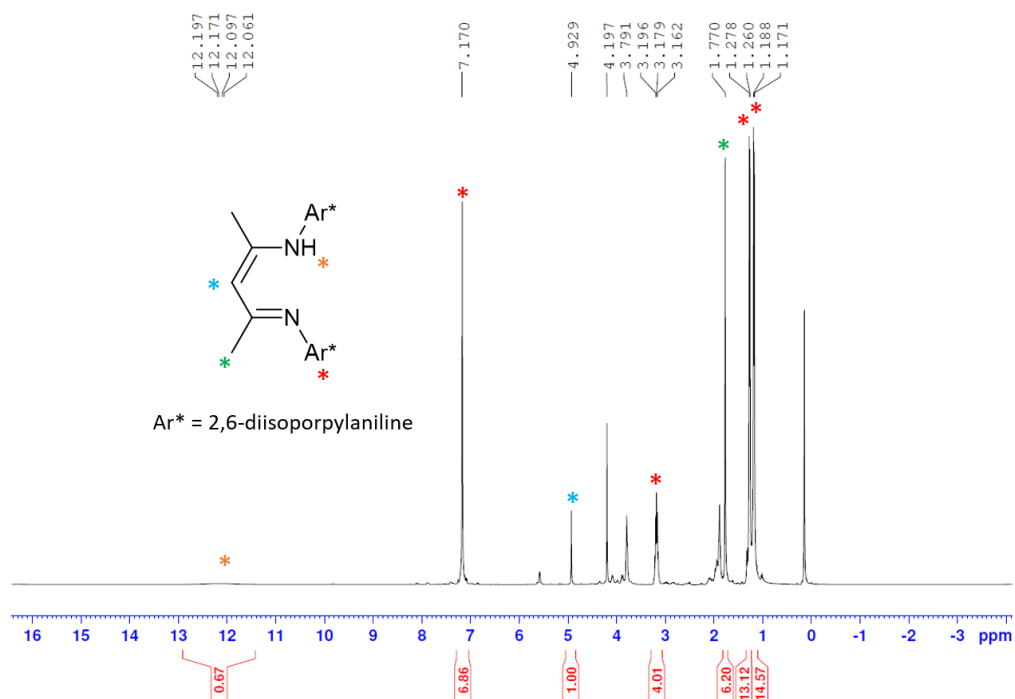


Figure S 79  $^1\text{H}$  NMR spectrum in CDCl<sub>3</sub> of reaction between compound 10 and C<sub>6</sub>F<sub>6</sub> under microwave conditions

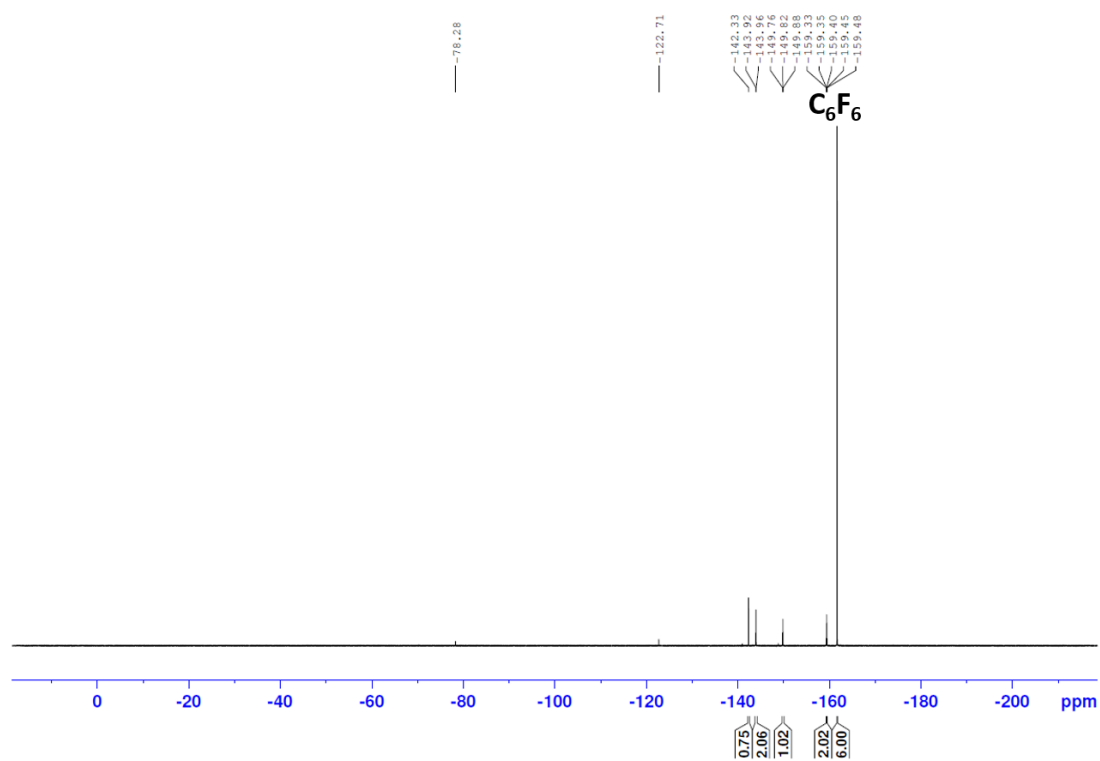


Figure S 80  $^{19}\text{F}$  NMR spectrum in  $\text{CDCl}_3$  of reaction between compound 10 and  $\text{C}_6\text{F}_6$  under microwave conditions

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