

## **Alkyl Potassium-Magnesiates: Synthesis, Structures and Applications in Mg-H Exchange Reactions of Aromatic and Heterocyclic Substrates**

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**General Considerations.** All reactions were performed under a protective argon atmosphere using standard Schlenk techniques. Hexane, toluene and THF were dried by heating to reflux over sodium benzophenone ketyl and distilled under nitrogen prior to use.  $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2$  was prepared from the Grignard reagent  $(\text{Me}_3\text{SiCH}_2)\text{MgCl}$  by manipulation of the Schlenk equilibrium *via* the dioxane precipitation method. The resultant off white solid was purified via sublimation at 175 °C ( $10^{-2}$  torr) to furnish pure  $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2$ .  $\text{KCH}_2\text{SiMe}_3$  was prepared according to the literature procedure by reaction of  $\text{KO}^t\text{Bu}$  with  $\text{LiCH}_2\text{SiMe}_3$  using hexane as a solvent.<sup>1</sup>  $\text{LiCH}_2\text{SiMe}_3$  was purchased from Sigma Aldrich chemicals and used as received. PMDETA and TMEDA were distilled over  $\text{CaH}_2$  prior to use. NMR spectra were recorded on a Bruker DPX400 MHz spectrometer, operating at 400.13 MHz for  $^1\text{H}$ , 100.62 MHz for  $^{13}\text{C}$  and  $^{29}\text{Si}\{^1\text{H}\}$  NMR 79.475 MHz for  $^{29}\text{Si}$ .  $^{29}\text{Si}$  NMR chemical shifts were referenced to  $\text{SiMe}_4$ . Elemental analyses were carried out using a Perkin Elmer 2400 elemental analyzer. Due to the extreme air-sensitivity of the organometallic compounds **1**, **2** and **3** satisfactory analyses could not be obtained. Melting/decomposition points were measured with a Büchi Melting Point B-545 apparatus.

**Crystal Structure Determinations of 1–3:** All measurements were made with Oxford Diffraction instruments fitted with cryogenic devices. Structures were refined to convergence against  $F^2$  using all unique reflections and the program SHELX-97.<sup>2</sup> All three structures were

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1 W. Clegg, B. Conway, P. Garcia-Alvarez, A. R. Kennedy, R. E. Mulvey, L. Russo, J. Sasmannshausen, T. Tuttle, *Chem. Eur. J.* 2009, **15**, 10702.

2 G. M. Sheldrick, *Acta Crystallogr. A*, 2008, **64**, 112.

modeled with some groups disordered over two sites. For **1** the disordered benzene ring required constraints to be placed on the C atoms' displacement ellipsoids and restraints to be placed on the C-C distances, whilst for **2** it was found necessary both to restrain C-C and N-C distances and to place constraints and restraints on the displacement ellipsoids of the disordered chelate ligands. Compound **3** also has a disordered chelate ligand.

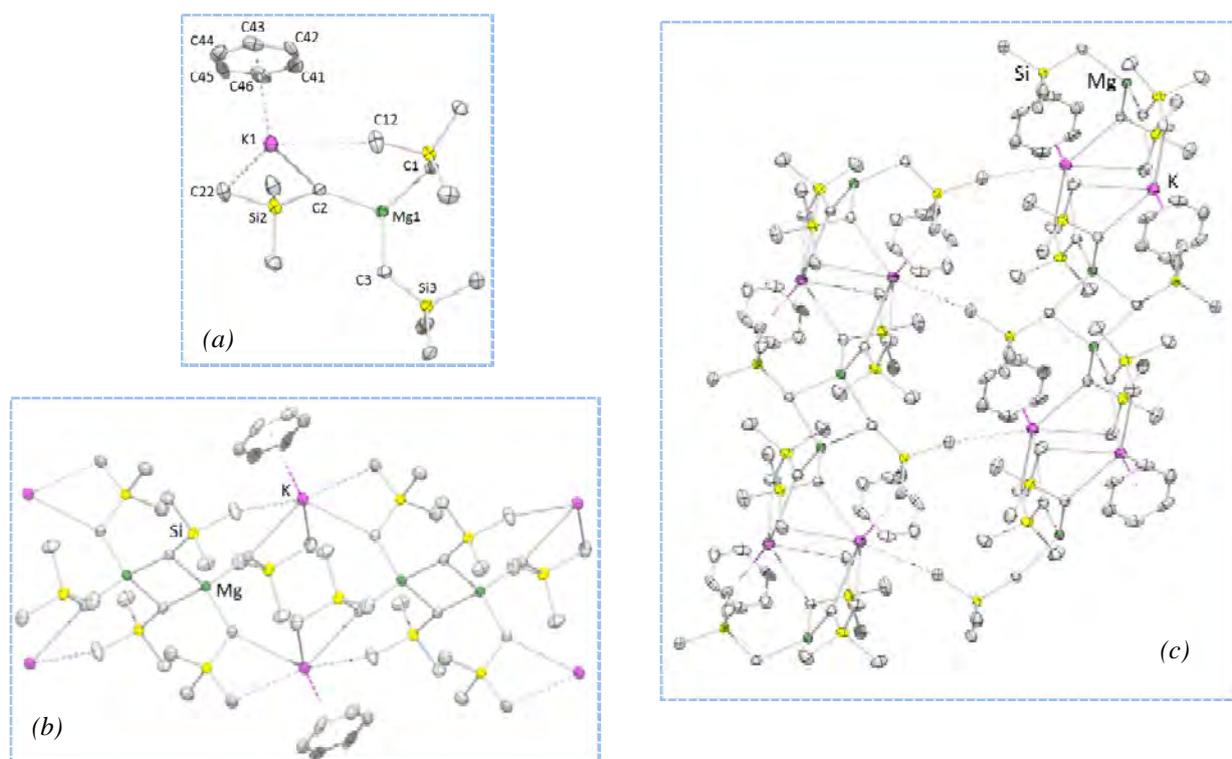
*Crystal data for 1:* C<sub>36</sub>H<sub>78</sub>K<sub>2</sub>Mg<sub>2</sub>Si<sub>6</sub>,  $M_r = 806.34$ , monoclinic, space group P2<sub>1</sub>/c,  $a = 12.0299(13)$ ,  $b = 10.6135(10)$ ,  $c = 19.8180(17)$  Å,  $\beta = 95.260(9)^\circ$ ,  $V = 2519.7(4)$  Å<sup>3</sup>,  $Z = 2$ ,  $\lambda = 0.71073$  Å,  $\mu = 0.377$  mm<sup>-1</sup>,  $T = 123(2)$  K;  $2\theta_{\max} = 54.0^\circ$ , 12822 reflections, 5506 unique,  $R_{\text{int}} = 0.0348$ ; final refinement to convergence on  $F^2$  gave  $R = 0.0329$  ( $F$ , 3596 obs. data only) and  $R_w = 0.0637$  ( $F^2$ , all data), GOF = 0.853, max and min residual electron density 0.296 and -0.217 eÅ<sup>-3</sup>.

*Crystal data for 2:* C<sub>34</sub>H<sub>90</sub>K<sub>2</sub>MgN<sub>6</sub>Si<sub>4</sub>,  $M_r = 797.99$ , orthorhombic, space group P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>,  $a = 12.2327(4)$ ,  $b = 17.0823(5)$ ,  $c = 25.0444(9)$  Å,  $V = 5233.3(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $\lambda = 0.71073$  Å,  $\mu = 0.311$  mm<sup>-1</sup>,  $T = 123(2)$  K;  $2\theta_{\max} = 58.0^\circ$ , 40219 reflections, 13880 unique,  $R_{\text{int}} = 0.0572$ ; final refinement to convergence on  $F^2$  gave  $R = 0.0418$  ( $F$ , 8778 obs. data only) and  $R_w = 0.0596$  ( $F^2$ , all data), GOF = 0.805, max and min residual electron density 0.411 and -0.246 eÅ<sup>-3</sup>. Flack = 0.17(2).

*Crystal data for 3:* C<sub>28</sub>H<sub>56</sub>K<sub>2</sub>MgN<sub>4</sub>Si<sub>4</sub>,  $M_r = 683.80$ , triclinic, space group P  $\bar{1}$ ,  $a = 11.0105(4)$ ,  $b = 14.4843(5)$ ,  $c = 14.9162(5)$  Å,  $\alpha = 85.542(3)$ ,  $\beta = 75.580(3)$ ,  $\gamma = 82.035(3)^\circ$ ,  $V = 2279.34(14)$  Å<sup>3</sup>,  $Z = 2$ ,  $\lambda = 0.71073$  Å,  $\mu = 0.347$  mm<sup>-1</sup>,  $T = 150(2)$  K;  $2\theta_{\max} = 50.0^\circ$ , 14022 reflections, 7897 unique,  $R_{\text{int}} = 0.0241$ ; final refinement to convergence on  $F^2$  gave  $R = 0.0344$  ( $F$ , 5596 obs. data only) and  $R_w = 0.0848$  ( $F^2$ , all data), GOF = 0.947, max and min residual electron density 0.326 and -0.316 eÅ<sup>-3</sup>.

CCDC reference numbers 1010341-1010343. See <http://www.rsc.org/suppdata/cc/?????????> for crystallographic data in CIF or other electronic format.

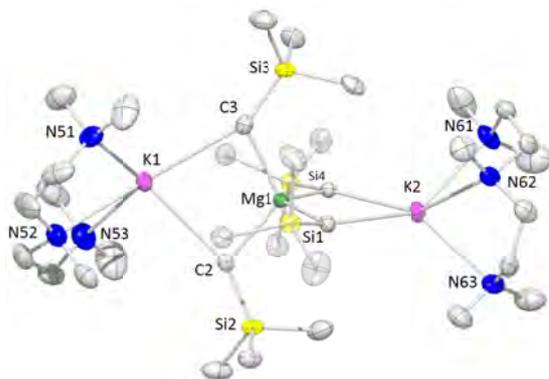
**Synthesis of  $[(C_6H_6)KMg(CH_2SiMe_3)_3]$  (**1**).** To a suspension of  $KCH_2SiMe_3$  (0.12 g, 1 mmol) in hexane (15 mL)  $Mg(CH_2SiMe_3)_2$  (0.20 g, 1 mmol) was added and the resulting suspension stirred for 1 hour. The solution was concentrated *in vacuo* (to approx. 8 mL) and benzene (4 mL) added. Gentle heating resulted in a clear colourless solution which was allowed to cool slowly to room temperature. A crop of clear colourless crystals was isolated (0.18 g, 45%). mp: 66°C.  $^1H$  NMR (400.13 MHz, 298 K,  $d_8$ -toluene)  $\delta$  -1.72 (6H, s,  $SiCH_2$ ), 0.28 (27H, s,  $Si(CH_3)_3$ ), 7.13 (2H, CH, benzene).  $^1H$  NMR (400.13 MHz, 298 K,  $C_6D_6$ )  $\delta$  (ppm) -1.67 (6H, s,  $SiCH_2$ ), 0.35 (27H, s,  $Si(CH_3)_3$ ).  $^{13}C$  { $^1H$ } NMR (100.62 MHz, 298 K,  $C_6D_6$ )  $\delta$  (ppm) 5.66 ( $Si(CH_3)_3$ ), 0.97 ( $SiCH_2$ ).  $^{29}Si$  { $^1H$ } NMR (79.475 MHz, 298K,  $C_6D_6$ )  $\delta$  -1.04



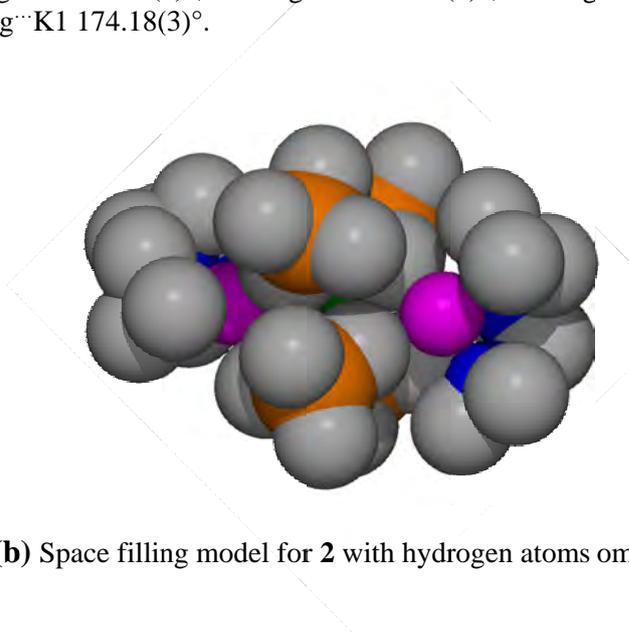
**Figure S1.** (a) Asymmetric unit of **1**. (b) Fragment of the polymeric structure of **1** along the crystallographic *b*-axis. (c) 2D network structure of **1**. In all figures displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms and disorder in benzene omitted for clarity. Dotted lines represent longer K-CH<sub>3</sub> interactions. Selected bond angles and distances, K1-C2 3.1482(17) Å, K1-C3 3.374(4) Å, K1-C22 3.294(2) Å, K1-C32#1 3.1352(18) Å, Mg1-C2 2.2076(18) Å, Mg1-C3 2.2152(18) Å, Mg1-C1 2.2513(18) Å, Mg1-C1#3 2.4296(18) Å; C2-Mg1-C3 105.88(7)°, C2-Mg1-C1 114.38(7)°, C3-Mg1-C1 117.28(8)°, C2-Mg1-C1#3 110.74(7)°, C3-Mg1-C1#3 109.28(7)°, C1-Mg1-C1#3 99.12(6)°, Mg1-C2-K1 137.70(8)°, Mg1-C3-K1#1 148.12(8)°.

**Synthesis of  $[(PMDTA)_2K_2Mg(CH_2SiMe_3)_4]$  (**2**).** To a suspension of  $KCH_2SiMe_3$  (0.12 g, 1 mmol) in hexane (15 mL)  $Mg(CH_2SiMe_3)_2$  (0.1 g, 0.5 mmol) was added and the suspension stirred for 1 hour. PMDTA (0.21 mL, 1.0 mmol) was then added giving a clear solution with a

yellow oil deposited at the bottom of the Schlenk. The Schlenk was transferred to the freezer (-28 °C) overnight. A crop of clear, colourless crystals was isolated (0.31 g, 78%). mp: 78 °C.  $^1\text{H}$  NMR (400.13 MHz, 298 K,  $\text{C}_6\text{D}_6$ )  $\delta$  -1.56 (8H, s,  $\text{SiCH}_2$ ), 0.47 (36H, s,  $\text{Si}(\text{CH}_3)_3$ ), 1.72-1.76 (16H, m,  $\text{NCH}_2$ , PMDETA), 1.83 (6H, s,  $\text{NCH}_3$ , PMDETA), 1.91 (24H, s,  $\text{N}(\text{CH}_3)_2$ , PMDETA).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100.62 MHz, 298 K,  $\text{C}_6\text{D}_6$ )  $\delta$  0.00 ( $\text{SiCH}_2$ ), 5.34 ( $\text{Si}(\text{CH}_3)_3$ ), 44.09 ( $\text{CH}_3$ , PMDETA), 46.05 ( $(\text{CH}_3)_2$ , PMDETA), 54.83 ( $\text{CH}_2$ , PMDETA), 56.63 ( $\text{CH}_2$ , PMDETA).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (79.475 MHz, 298K,  $\text{C}_6\text{D}_6$ )  $\delta$  -0.99.



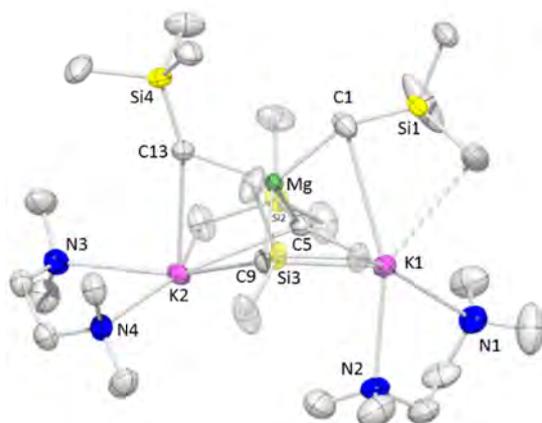
**Figure S2 (a)** Molecular structure of **2**. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms and minor disorder in PMDETA omitted for clarity. Selected bond distances and angles, K1-C2 3.002(2) Å, K1-C3 3.062(2) Å, K2-N61 2.870(4) Å, K2-N62 2.871(4) Å, K2-N63 2.877(5) Å, K2-C4 2.999(2) Å, K2-C1 3.015(2) Å, Mg-C2 2.251(2) Å, Mg-C3 2.261(2) Å, Mg-C4 2.273(2) Å, Mg-C1 2.274(2) Å; N51-K1-C3 90.72(11), N52-K1-C3 146.4(2), N53-K1-C3 149.81(7), C2-K1-C3 76.94(6), C2-Mg-C3 113.44(9)°, C2-Mg-C4 106.59(9)°, C3-Mg-C4 107.82(9)°, C2-Mg-C1 106.55(9)°, C3-Mg-C1 107.83(9)°, C4-Mg-C1 114.79(9)°, K2 $\cdots$ Mg $\cdots$ K1 174.18(3)°.



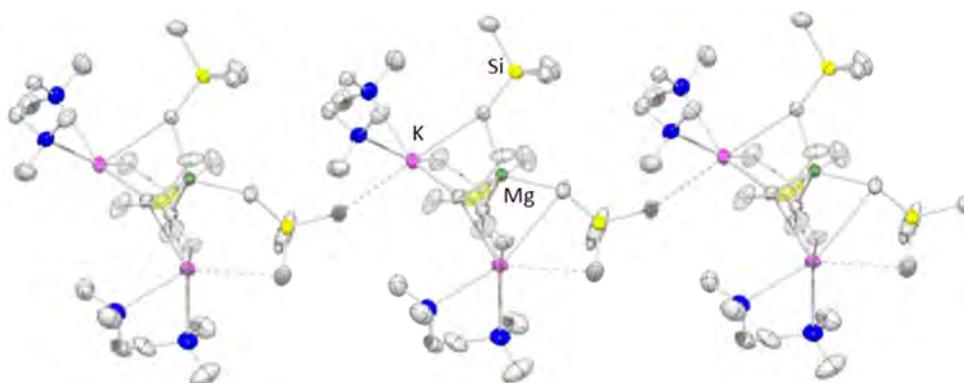
**Figure S2 (b)** Space filling model for **2** with hydrogen atoms omitted for clarity)

**Synthesis of  $[(\text{TMEDA})_2\text{K}_2\text{Mg}(\text{CH}_2\text{SiMe}_3)_4]$  (**3**).** To a suspension of  $\text{KCH}_2\text{SiMe}_3$  (0.24 g, 2 mmol) in hexane (15 mL)  $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2$  (0.20 g, 1 mmol) was added and the suspension stirred for 1 hour. TMEDA (0.30 mL, 2 mmol) was then added and the almost clear solution transferred

to the freezer (-28 °C). After 16 hours a crop of peach crystals was isolated (0.41 g, 60%). mp: 63°C (decomposition observed at 82°C).  $^1\text{H}$  NMR (400.03 MHz, 298 K,  $\text{C}_6\text{D}_6$ ) $^3$   $\delta$  -1.74 and -1.70 (2H, overlapping s,  $\text{SiCH}_2$ ), 0.40 and 0.41 (9H, overlapping s,  $\text{Si}(\text{CH}_3)_3$ ), 1.93 and 1.94 (8H, overlapping s, TMEDA).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100.62 MHz, 298 K,  $\text{C}_6\text{D}_6$ )  $\delta$  -0.03 ( $\text{SiCH}_2$ ), 1.67 ( $\text{SiCH}_2$ ), 5.64 ( $\text{Si}(\text{CH}_3)_3$ ), 45.53 ( $\text{N}(\text{CH}_3)_2$ , TMEDA), 57.31 ( $\text{NCH}_2$ , TMEDA).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (79.475 MHz, 298K,  $\text{C}_6\text{D}_6$ )  $\delta$  -0.56.



**Figure S3:** Molecular structure of **3**. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond angles and distances, Mg-C1 2.232(2) Å, Mg-C5 2.2951(18) Å, Mg-C9 2.314(2) Å, Mg-C13 2.3202(2) Å, K1-N1 2.9036(17) Å, K1-N2 2.8599(18) Å, K1-C1 3.418(2) Å, K1-C5 3.116(2) Å, K1-C9 3.006(2) Å, K2-N3 2.9016(19) Å, K2-N4 2.8466(18) Å, K2-C5 3.159(2) Å, K2-C9 3.199(2) Å, K2-C13 3.0428(18) Å; C1-Mg-C5 109.33(8)°, C1-Mg-C9 111.39(9)°, C1-Mg-C13 120.09(8)°, C5-Mg-C9 102.41(7)°, C5-Mg-C13 110.94(7)°, C9-Mg-C13 101.04(8)°, K1 $\cdots$ Mg $\cdots$ K2 100.14 (19)°.



**Figure S4.** Fragment of the polymeric structure of **3** along the crystallographic *a*-axis. Dotted lines represent longer K-CH<sub>3</sub> interactions. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms and minor disorder components have been omitted for clarity.

<sup>3</sup> For **3** it is possible to distinguish between the two different types ( $\mu_2$  and  $\mu_3$ ) R ligands, as evidenced by the two distinct set of resonances observed for the monosilyl groups in its  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra.

**Synthesis of [(TMEDA)<sub>2</sub>Na<sub>2</sub>Mg(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>4</sub>].** To a suspension of NaCH<sub>2</sub>SiMe<sub>3</sub> (0.22 g, 2 mmol) in hexane (15 mL) Mg(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub> (0.20 g, 1 mmol) was added and the suspension stirred for 1 hour. TMEDA (0.30 mL, 2 mmol) was then added and the almost clear solution transferred to the freezer (-28 °C). After 16 hours a crop of clear, colourless crystals was isolated (0.35 g, 54%). <sup>1</sup>H NMR (400.03 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>) δ -1.78 (2H, s, SiCH<sub>2</sub>), 0.47 (9H, s, Si(CH<sub>3</sub>)<sub>3</sub>), 1.67 (2H, s, NCH<sub>2</sub>, TMEDA), 1.92 (6H, s, N(CH<sub>3</sub>)<sub>2</sub>, TMEDA). <sup>13</sup>C {<sup>1</sup>H} NMR (100.62 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>) δ -3.14 (SiCH<sub>2</sub>), 5.63 (Si(CH<sub>3</sub>)<sub>3</sub>), 45.80 (N(CH<sub>3</sub>)<sub>2</sub>, TMEDA), 56.76 (NCH<sub>2</sub>, TMEDA). Isolated crystals of these compound, which according to its NMR data can be expected to be isostructural to higher order magnesiates **2** and [(TMEDA)<sub>2</sub>Li<sub>2</sub>MgR<sub>4</sub>]<sup>4</sup> were employed to test its metalating ability towards anisole (**4a**) (Table 1, entry 6).

**General procedure for metallation studies of organic substrates.** To a suspension of KCH<sub>2</sub>SiMe<sub>3</sub> (0.12 g, 1 mmol) in hexane (10 mL) Mg(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub> (0.10 g, 0.5 mmol) was added and the suspension stirred for 1 hour. PMDETA (0.21 mL, 1 mmol) was then added giving a clear peach solution. 4 equivalents of organic substrate were then introduced at temperature, T, and stirred for 1 h before I<sub>2</sub> (4 mL of a 1 M solution in THF, 4 mmol) was added and stirred for 1 hour. The reaction was quenched with NH<sub>4</sub>Cl and sodium thiosulfate then allowed to settle. An aliquot of the organic phase was diluted with Et<sub>2</sub>O and analysed by gas chromatography.

**Table S1.** Metalation of anisole (**4a**) using different variable amounts of higher order magnesiates **2** and **3**.

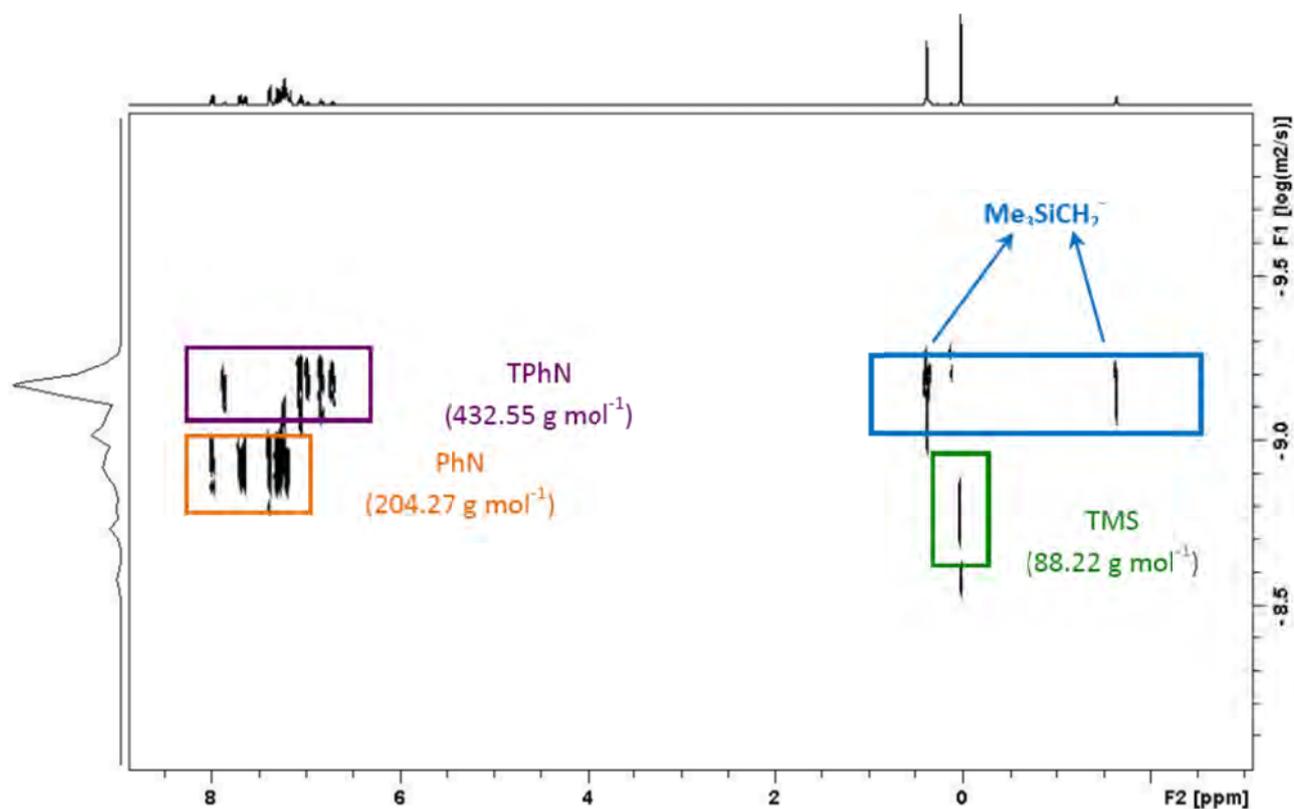
Entry	N-donor <sup>a</sup>	n equiv.	Conversion to <b>5a</b> (%) <sup>b</sup>
1	PMDETA	1	99
2	PMDETA	0.5	98
3	PMDETA	0.25	74
4	PMDETA	0.33	88
5	TMEDA	0.25	65

<sup>a</sup> Scale: 1.0 mmol of **4a**. <sup>b</sup> Conversion was determined by GC analysis of iodolysed reaction aliquots, using an internal standard (heptadecane).

**<sup>1</sup>H-DOSY NMR studies.** The Diffusion-Ordered Spectroscopy (DOSY) NMR experiment was performed on a Bruker AVANCE 400 NMR spectrometer operating at 400.13 MHz for proton resonance under TopSpin (version 2.0, Bruker Biospin, Karlsruhe) and equipped with a BBFO-z-atm probe with actively shielded z-gradient coil capable of delivering a maximum gradient strength of 54 G/cm. Diffusion ordered NMR data was acquired using the Bruker pulse program dstegp3s employing a double stimulated echo with three spoiling gradients. Sine-shaped gradient pulses were used with a duration of 3 ms together with a diffusion period of 100 ms. Gradient recovery delays of 200  $\mu$ s followed the application of each gradient pulse. Data was accumulated by linearly varying the diffusion encoding gradients over a range from 2% to 95% of maximum for 64 gradient increment values. DOSY plot was generated by use of the DOSY processing module of TopSpin. Parameters were optimized empirically to find the best quality of data for presentation purposes. Diffusion coefficients were calculated by fitting intensity data to the Stejskal-Tanner expression with estimates of errors taken from the variability in the calculated diffusion coefficients by consideration of different NMR responses for the same molecules of interest (except TMS). It has been shown that, using hydrocarbons as references, accurate estimations of formula weights of aggregates in solution can be ascertained.<sup>5</sup> We chose 1,2,3,4-tetraphenylnaphthalene (TPhN), 1-phenylnaphthalene (PhN) and tetramethylsilane (TMS) as internal standards for this study as they have good solubility in benzene with minimal overlapping signals and are inert to **1**.

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<sup>5</sup> a) D. Li, I. Keresztes, R. Hopson, P. G. Willard, *Acc. Chem. Res.* **2009**, *42*, 270; (b) A. Macchioni, G. Ciancaleoni, C. Zuccaccia, D. Zuccaccia, *Chem. Soc. Rev.* **2008**, *37*, 479; (c) I. Keresztes, P. G. Willard, *J. Am. Chem. Soc.* **2000**, *122*, 10228.

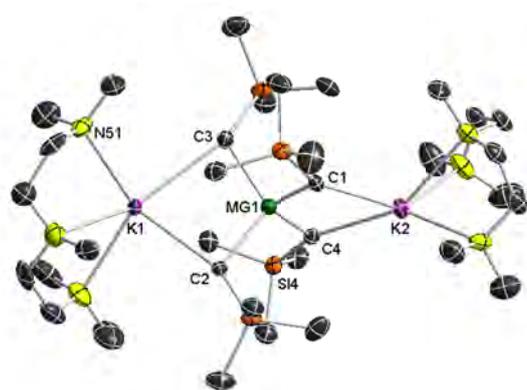


**Figure S5.** <sup>1</sup>H-DOSY NMR spectrum of [(C<sub>6</sub>H<sub>6</sub>)KMg(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>] (**1**), TPhN, PhN and TMS at 27 °C in C<sub>6</sub>D<sub>6</sub>.

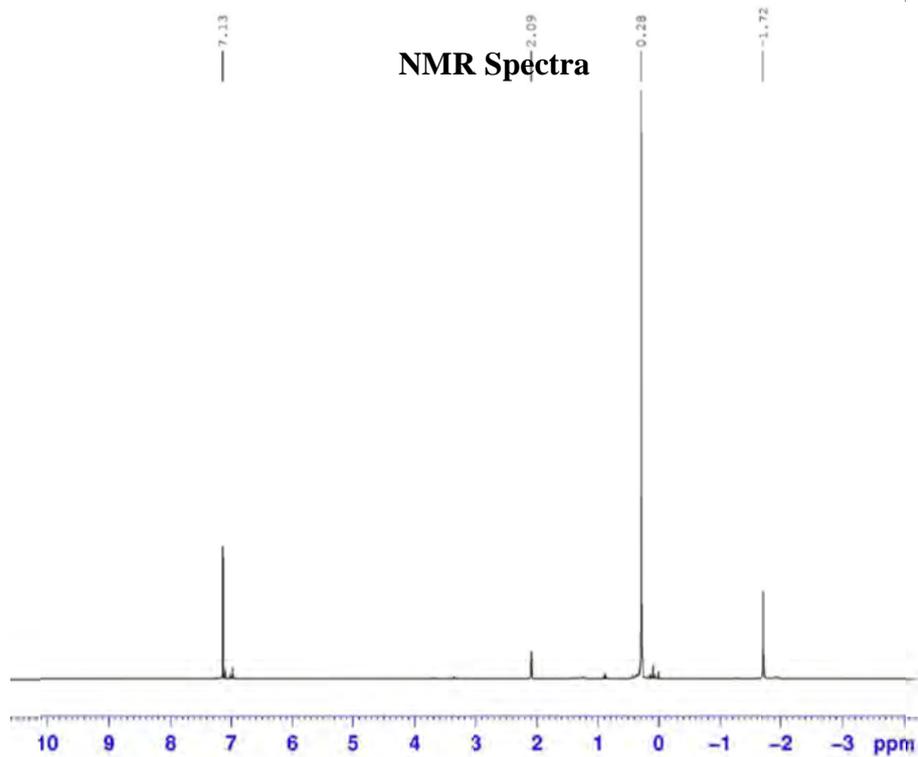
Possible species of **1** in C<sub>6</sub>D<sub>6</sub> with errors respect to the FW value predicted through the DOSY study (433 g/mol).

FW	A	[KMg(CH <sub>2</sub> SiMe <sub>3</sub> ) <sub>3</sub> ] <sub>3</sub>	975 g mol <sup>-1</sup> (56 %)	FW predicted for <b>1</b> in C <sub>6</sub> D <sub>6</sub> 433 (g mol <sup>-1</sup> )
	B	KMg(CH <sub>2</sub> SiMe <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub>	650 g mol <sup>-1</sup> (33 %)	
	C	[KMg(CH <sub>2</sub> SiMe <sub>3</sub> ) <sub>3</sub> ] · 2 C <sub>6</sub> D <sub>6</sub>	493 g mol <sup>-1</sup> (12%)	
	D	[KMg(CH <sub>2</sub> SiMe <sub>3</sub> ) <sub>3</sub> ] · C <sub>6</sub> D <sub>6</sub>	409 g mol <sup>-1</sup> (- 6%)	
	E	[KMg(CH <sub>2</sub> SiMe <sub>3</sub> ) <sub>3</sub> ]	325 g mol <sup>-1</sup> (- 33 %)	

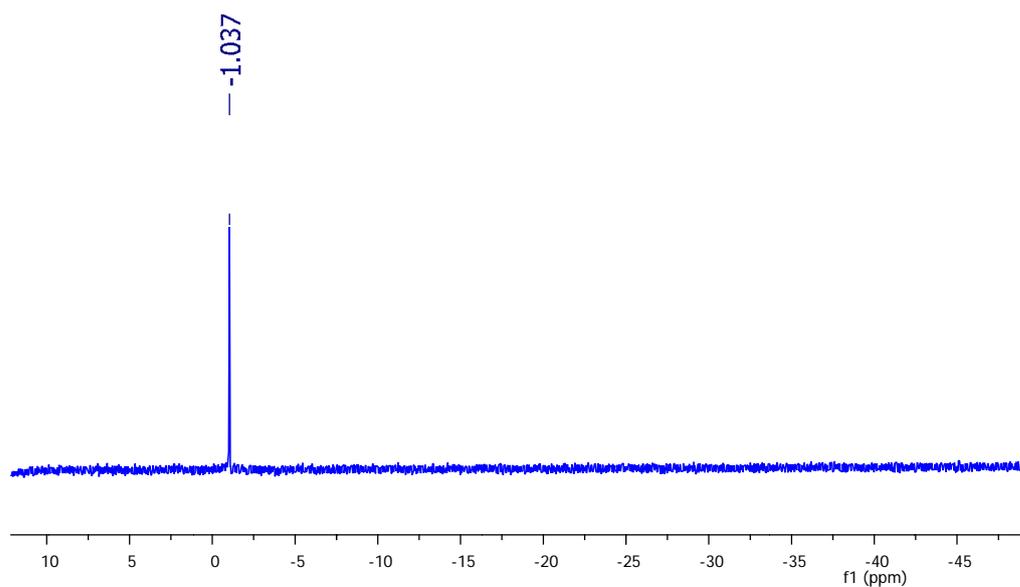
**Figure S6.** Possible species of **1** in C<sub>6</sub>D<sub>6</sub> solution with errors (in parentheses) for every consideration with respect to the estimated FW value predicted through DOSY

[(TMEDA)<sub>2</sub>Li<sub>2</sub>MgR<sub>4</sub>][(PMDETA)<sub>2</sub>K<sub>2</sub>MgR<sub>4</sub>] (2)**Table S2:** Selected bond distances (Å) and angles (°) of [(TMEDA)<sub>2</sub>Li<sub>2</sub>MgR<sub>4</sub>] and [(PMDETA)<sub>2</sub>K<sub>2</sub>MgR<sub>4</sub>]

	[(TMEDA) <sub>2</sub> Li <sub>2</sub> MgR <sub>4</sub> ]	[(PMDETA) <sub>2</sub> K <sub>2</sub> MgR <sub>4</sub> ] (2)
M <sup>I</sup> ...Mg...M <sup>I</sup>	175.2(11)	174.18(3)
M <sup>I</sup> -C (average)	2.228	3.0195
Mg-C (average)	2.268	2.265
C-Mg-C (average)	109.62	109.50



**Figure S7**  $^1\text{H}$  NMR spectrum of **1** in  $\text{d}_8$ -toluene solution



**Figure S8**  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum of **1** in  $\text{d}_8$ -toluene solution

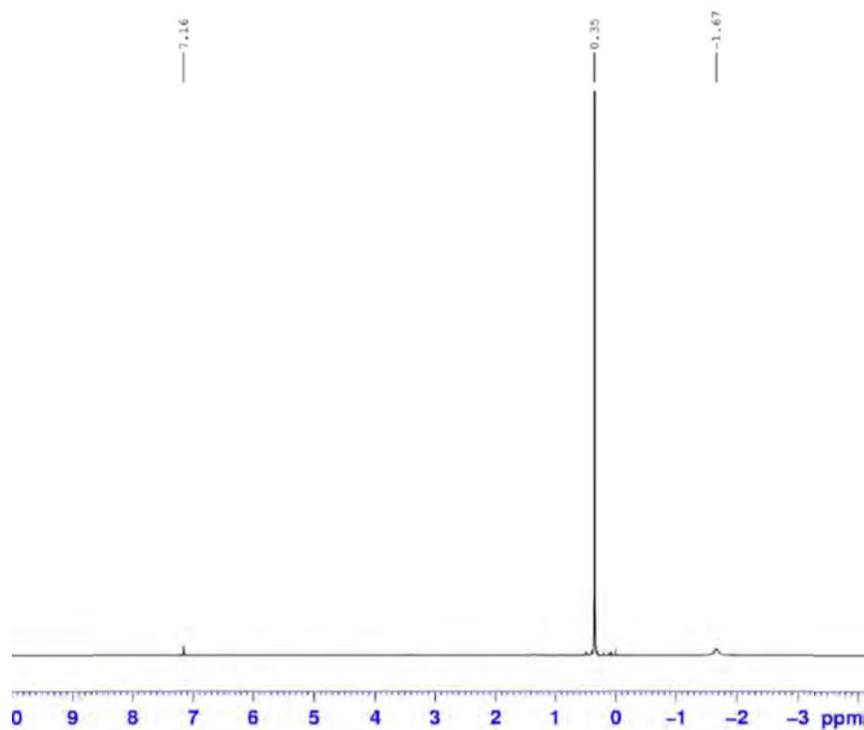


Figure S9  $^1\text{H}$  NMR spectrum of **1** in  $d_6$ -benzene solution

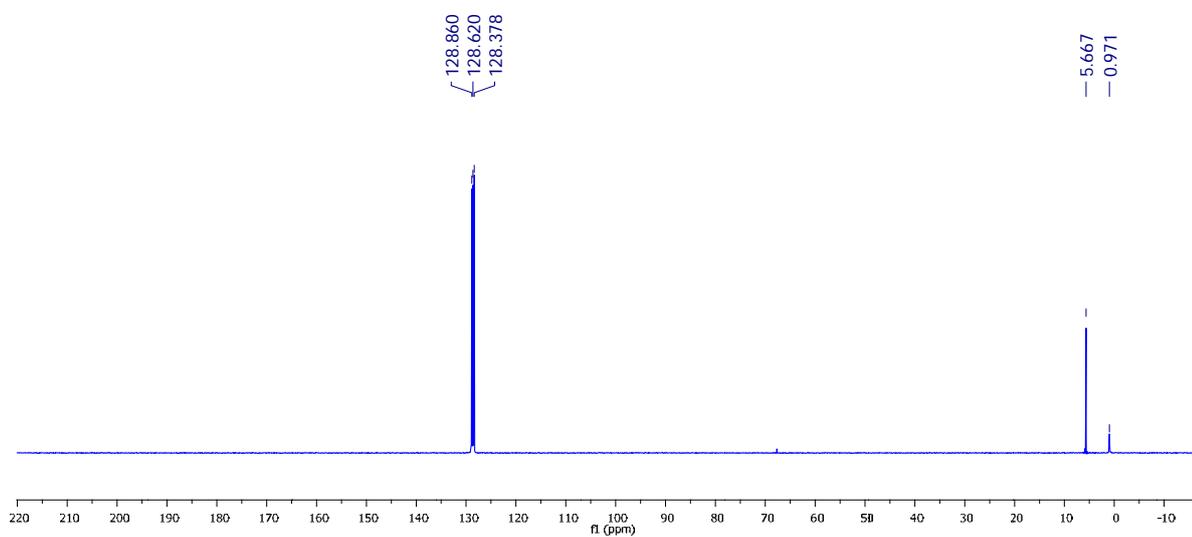


Figure S10  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **1** in  $d_6$ -benzene solution

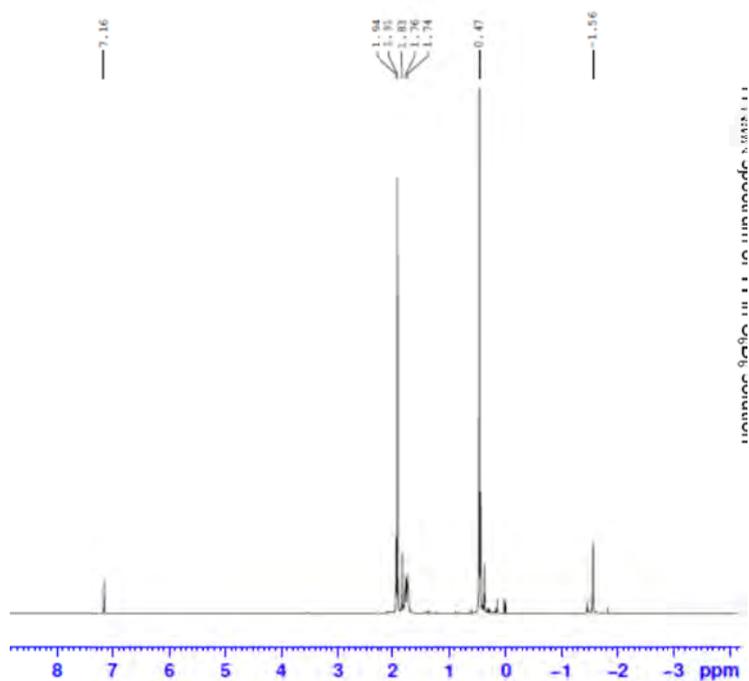


Figure S11  $^1\text{H}$  NMR spectrum of **2** in  $d_6$ -benzene solution

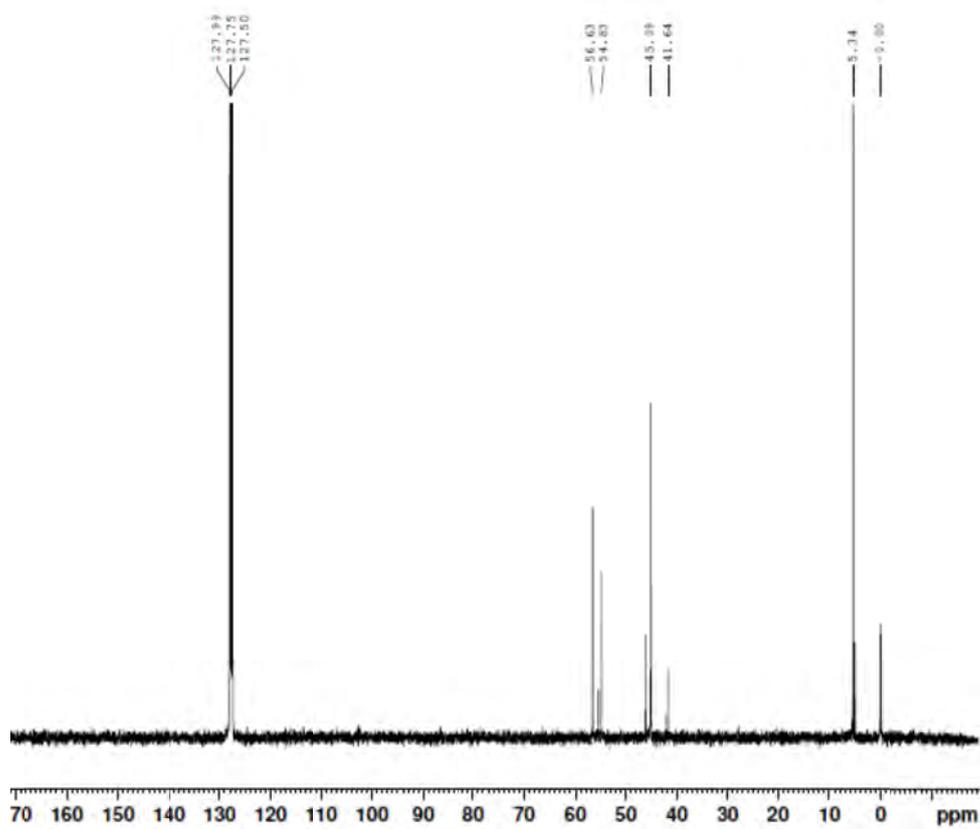


Figure S12  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **2** in  $d_6$ -benzene solution

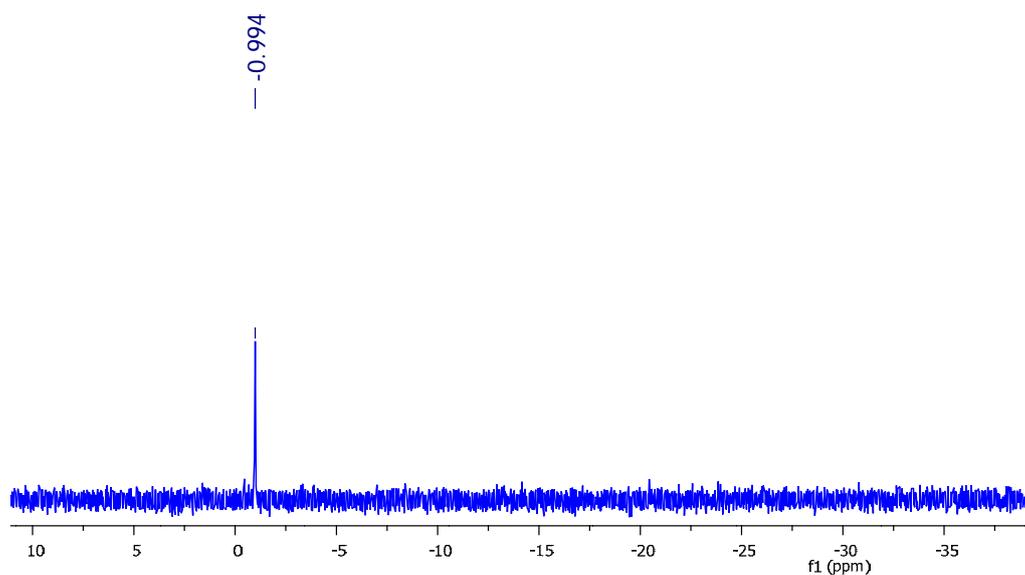


Figure S13  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum of **2** in  $\text{d}_6$ -benzene solution

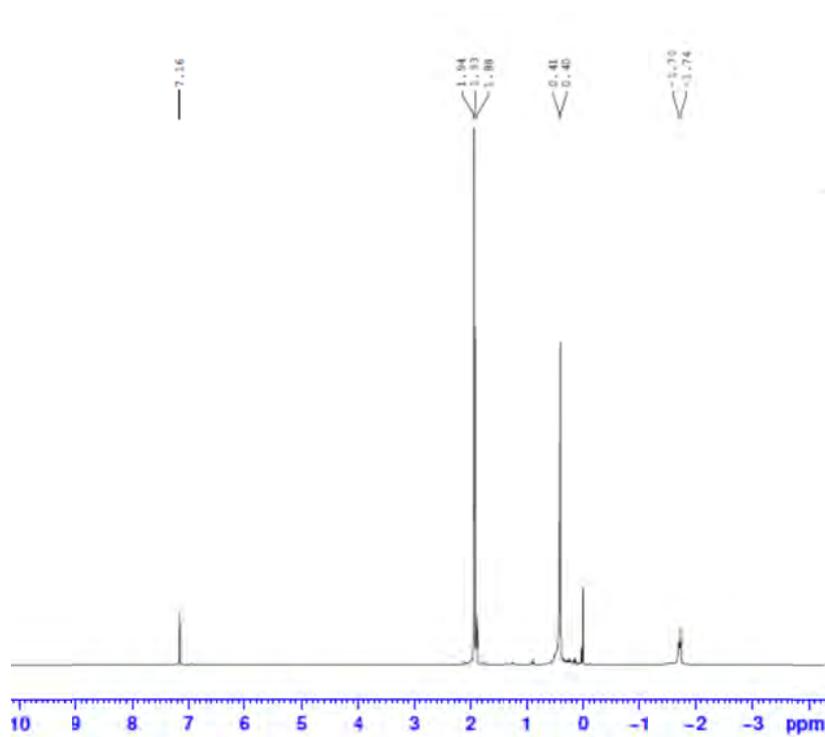


Figure S14  $^1\text{H}$  NMR spectrum of **3** in  $\text{d}_6$ -benzene solution



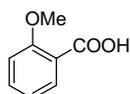
## PREPARATION AND NMR DATA OF PRODUCTS (TABLE 2)

## 2-Iodoanisole (6a)



A dry Schlenk flask was charged with  $\text{KCH}_2\text{SiMe}_3$  (126 mg, 1 mmol) and  $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2$  (99 mg, 0.5 mmol). The mixture was suspended in hexane (10 mL) and the suspension stirred for 1 h at 20 °C. PMDETA (173 mg, 1 mmol) was then added resulting in a clear solution with yellow oil deposited at the bottom of the flask. Anisole (162 mg, 1.5 mmol) was added in one portion and the mixture stirred for 1.5 h. Iodine (1 g) was added and after stirring for 1 h the excess iodine was removed using sat. aqueous  $\text{Na}_2\text{S}_2\text{O}_3$  solution. The phases were separated and the organic phase was extracted three times with DCM. The combined organic extracts were dried over  $\text{MgSO}_4$  and the solvent removed under reduced pressure. Column chromatographical purification ( $\text{SiO}_2$ , hexane/EtOAc = 10:1) afforded 2-iodoanisole **6a** as yellowish oil (274 mg, 78% yield). <sup>6</sup>**<sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ )**  $\delta$  (ppm) = 3.88 (s, 3H), 6.70-6.74 (dt,  $J$  = 7.6 Hz, 1.2 Hz, 1H), 6.82-6.84 (dd,  $J$  = 8.0 Hz, 1.2 Hz, 1H), 7.29-7.33 (ddd,  $J$  = 8.8 Hz, 7.6 Hz, 1.6 Hz, 1H), 7.77-7.79 (dd,  $J$  = 8.0 Hz, 1.6 Hz, 1H); **<sup>13</sup>C NMR (125 MHz,  $\text{CDCl}_3$ )**  $\delta$  (ppm) = 56.5, 86.2, 111.2, 122.7, 129.7, 139.7, 158.2; **MS (EI, 70 eV):**  $m/z$  (%) = 234 [ $\text{M}^+$ ] (100), 219 (22), 92 (43), 77 (31), 63 (31), 51 (23), 50 (20). The values are consistent with previously reported data in the literature.<sup>7</sup>

## 2-Methoxybenzoic acid (6a')



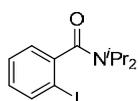
A dry Schlenk flask was charged with  $\text{KCH}_2\text{SiMe}_3$  (126 mg, 1 mmol) and  $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2$  (99 mg, 0.5 mmol). The mixture was suspended in hexane (10 mL) and the suspension stirred for 1 h at 20 °C. PMDETA (173 mg, 1 mmol) was then added resulting in a clear solution with yellow oil deposited at the bottom of the flask. Anisole (162 mg, 1.5 mmol) was added in one portion and the mixture stirred for 1.5 h before  $\text{CO}_2(\text{g})$  was constantly allowed to pass through the reaction mixture for 1h, resulting in instant precipitation of a white solid. The reaction was quenched with sat.  $\text{Na}_2\text{CO}_3$  solution, the phases separated and the aqueous phase was washed three times with DCM (3 x 1 mL). Acidification of the aqueous phase using HCl (2M in water) led to precipitation of the

<sup>6</sup> No significant changes in the isolated yield of **6a** were observed when isolated crystals of the base **3** were employed.

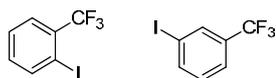
<sup>7</sup> Tilly, D.; Snégaroff, K.; Dayaker, G.; Chevallier, F.; Gros, P. C.; Mongin, F. *Tetrahedron* **2012**, *68*, 8761–8766.

carboxylic acid which was extracted using diethyl ether. The combined ether phases were dried over MgSO<sub>4</sub> and the solvent was evaporated in vacuo. 2-Methoxybenzoic acid (**6a'**) is obtained as a white solid (190 mg, 83% yield). <sup>1</sup>H NMR (500 MHz, DMSO) δ (ppm) = 3.80 (s, 3H), 6.97 (t, *J* = 7.5 Hz, 1H), 7.10 (d, *J* = 8 Hz, 1H), 7.49 (dt, *J* = 2 Hz, 7.5 Hz, 1H), 7.64 (dd, *J* = 1.5 Hz, 7.5 Hz, 1H), 12.61 (broad s, 1H); <sup>13</sup>C NMR (125 MHz, DMSO) δ (ppm) = 56.2, 112.9, 120.5, 121.8, 131.1, 133.5, 158.5, 167.8; MS (EI, 70 eV): *m/z* (%) = 151 [M<sup>+</sup>] (19), 135 (17), 123 (100), 105 (77), 79 (73), 77 (85), 63 (19); Elemental analysis (%): Calculated for C<sub>8</sub>H<sub>8</sub>O<sub>3</sub>: C, 63.15; H, 5.30. Found: C, 62.84; H, 5.05.

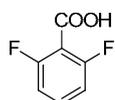
### 2-Iodo-*N,N*-diisopropylbenzamide (**6b**)



A dry Schlenk flask was charged with KCH<sub>2</sub>SiMe<sub>3</sub> (126 mg, 1 mmol) and Mg(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub> (99 mg, 0.5 mmol). The mixture was suspended in hexane (10 mL) and the suspension stirred for 1 h at 20 °C. PMDETA (173 mg, 1 mmol) was then added resulting in a clear solution with yellow oil deposited at the bottom of the flask. *N,N*-Diisopropylbenzamide (152 mg, 0.5 mmol) was added and the resulting solution allowed to stir at 0 °C for 1.5 hours. The reaction was quenched with excess of I<sub>2</sub> (1,015 g, in 5 mL THF) and allowed to stir for 1 hour. Excess iodine was removed using sat. aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution, the phases were separated and the organic phase was extracted three times with DCM. The combined organic extracts were dried over MgSO<sub>4</sub> and the solvent removed under reduced pressure. Column chromatographical purification (SiO<sub>2</sub>, hexane/EtOAc = 8:1) afforded 2-iodo-*N,N*-diisopropylbenzamide (**6b**) as colourless crystals (156 mg, 94% Yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm) = 1.05 (d, 3H), 1.27 (d, 3H), 1.60 (m, 6H), 3.56 (m, 2H), 7.02 (dt, <sup>4</sup>*J*=1.6 Hz, <sup>3</sup>*J*=7.6 Hz 1H), 7.13 (dd, <sup>4</sup>*J*=1.6 Hz, <sup>3</sup>*J*=7.6 Hz, 1H), 7.34 (dt, <sup>4</sup>*J*=1.2 Hz, <sup>3</sup>*J*=7.2 Hz, 1H), 7.8 (dd, <sup>4</sup>*J*=1 Hz, <sup>3</sup>*J*=8 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ (ppm) = 21.0, 46.3, 51.5, 92.61, 126.2, 128.5, 129.8, 139.7, 144.6, 170.1; MS (EI, 70 eV): *m/z* (%) = 330 [M<sup>+</sup>] (27), 288 (18), 231 (100), 204 (45), 203 (11); Elemental analysis (%): Calculated for C<sub>13</sub>H<sub>18</sub>INO: C, 47.14; H, 5.48; N, 4.23. Found: C, 47.16; H, 5.36; N, 4.34.

**1-Iodo-2-(trifluoromethyl)benzene (6c) + 1-Iodo-3-(trifluoromethyl)benzene (6c')**

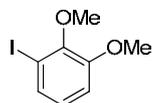
A dry Schlenk flask was charged with  $\text{KCH}_2\text{SiMe}_3$  (126 mg, 1 mmol) and  $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2$  (99 mg, 0.5 mmol). The mixture was suspended in hexane (10 mL) and the suspension stirred for 1 h at 20 °C. PMDETA (173 mg, 1 mmol) was then added resulting in a clear solution with yellow oil deposited at the bottom of the flask. Trifluoromethylbenzene (73 mg, 0.5 mmol) was added and the resulting mixture was stirred for 1.5 hours at 0 °C. The reaction was quenched with excess of  $\text{I}_2$  (1,015 g, in 5 mL THF) and allowed to stir for 1 hour. Excess iodine was removed using sat. aqueous  $\text{Na}_2\text{S}_2\text{O}_3$  solution, the phases were separated and the organic phase was extracted three times with DCM. Ferrocene was added to the solution (29.7 mg, 10 mol%). The yield obtained by integration of the corresponding signals for **6c** and **6c'** in the  $^1\text{H}$  NMR channel was 92% with 18:1 ratio of products **6c**/**6c'**.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) for **6c** = 6.45 (t,  $^3J=7$  Hz, 1H), 6.71 (t,  $^3J=8$  Hz, 1H), 7.20 (dd,  $^3J=8$  Hz,  $^4J=1.5$  Hz, 1H), 7.54 (d,  $^3J=8$  Hz, 1H).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) for **6c'** = 6.78 (t,  $^3J=8$  Hz, 1H), 7.00 (t,  $^3J=8$  Hz, 1H), 7.24 (dd,  $^3J=8$  Hz, 1H), 7.76 (s, 1H).

**2,6-Difluorobenzoic acid (6d)**

A dry Schlenk flask was charged with  $\text{KCH}_2\text{SiMe}_3$  (126 mg, 1 mmol) and  $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2$  (99 mg, 0.5 mmol). The mixture was suspended in hexane (10 mL) and the suspension stirred for 1 h at 20 °C. PMDETA (173 mg, 1 mmol) was then added resulting in a clear solution with yellow oil deposited at the bottom of the flask. 1,3-Difluorobenzene (171 mg, 1.5 mmol) was added in one portion and the mixture stirred for 1.5 h before  $\text{CO}_{2(g)}$  was constantly allowed to pass through the reaction mixture for 1 h, resulting in instant precipitation of a white solid. The reaction was quenched with sat.  $\text{Na}_2\text{CO}_3$  solution, the phases separated and the aqueous phase was washed three times with DCM (3 x 1 mL). Acidification of the aqueous phase using HCl (2M in water) led to precipitation of the carboxylic acid which was extracted using diethyl ether. The combined ether phases were dried over  $\text{MgSO}_4$  and the solvent was evaporated in vacuo. 2-Difluorobenzoic acid (**6d**) is obtained as a white solid (123 mg, 52% yield).  $^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  (ppm) = 7.20 (t,  $J=8$  Hz, 2H), 7.58 (m,  $^4J=2$  Hz, 1H), 13.94 (broad s, 1H);  $^{13}\text{C}$  NMR (125 MHz, DMSO)  $\delta$  (ppm) = 112.4 (dd,  $^4J=5$  Hz,  $^2J=20$  Hz), 133.0 (t,  $^3J=10$  Hz), 160.0 (dd,  $^1J=250$

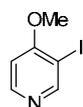
Hz,  $^3J=7$  Hz), 162.2;  $^{19}\text{F}$  NMR (376 MHz, DMSO)  $\delta$  (ppm) = -112.4; MS (EI, 70 eV):  $m/z$  (%) = 158 [ $\text{M}^+$ ] (52), 141 (100), 113 (30), 63 (20); Elemental analysis (%): Calculated for  $\text{C}_7\text{H}_4\text{F}_2\text{O}_2$ : C, 53.18; H, 2.55. Found: C, 54.60; H, 2.15.

### 1-iodo-2,3-dimethoxybenzene (6e)



A dry Schlenk flask was charged with  $\text{KCH}_2\text{SiMe}_3$  (126 mg, 1 mmol) and  $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2$  (99 mg, 0.5 mmol). The mixture was suspended in hexane (10 mL) and the suspension stirred for 1 h at 20 °C. PMDETA (173 mg, 1 mmol) was then added resulting in a clear solution with yellow oil deposited at the bottom of the flask. 1,2-Dimethoxybenzene (207 mg, 1.5 mmol) was added and the resulting mixture was stirred for 1.5 hours at 20 °C. The reaction was quenched with excess of  $\text{I}_2$  (1,015 g, in 5 mL THF) and allowed to stir for 1 hour. Excess iodine was removed using sat. aqueous  $\text{Na}_2\text{S}_2\text{O}_3$  solution, the phases were separated and the organic phase was extracted three times with DCM. The combined organic extracts were dried over  $\text{MgSO}_4$  and the solvent removed under reduced pressure. Column chromatographical purification ( $\text{SiO}_2$ , hexane/EtOAc = 20:1) afforded **6e** as yellowish oil (278 mg, 70% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) = 3.86 (s, 3H), 3.87 (s, 3H), 6.81 (t,  $J = 8.1$  Hz, 1H), 6.99 (dd,  $J = 8.1$  Hz, 1.5 Hz, 1H), 7.36 (dd,  $J = 8.1$  Hz, 1.5 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) = 55.9, 60.3, 92.4, 112.7, 125.8, 130.4, 148.9, 152.8; MS (EI, 70 eV):  $m/z$  (%) = 264 [ $\text{M}^+$ ] (100), 249 (32), 232 (2), 178 (16), 167 (5), 166 (26), 138 (69), 107 (5), 79 (2), 51 (1).

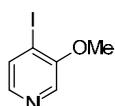
### 3-Iodo-4-methoxypyridine (6f)



A dry Schlenk flask was charged with  $\text{KCH}_2\text{SiMe}_3$  (126 mg, 1 mmol) and  $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2$  (99 mg, 0.5 mmol). The mixture was suspended in hexane (10 mL) and the suspension stirred for 1 h at 20 °C. PMDETA (173 mg, 1 mmol) was then added resulting in a clear solution with yellow oil deposited at the bottom of the flask. 4-Methoxypyridine (164 mg, 1.5 mmol) was added and the resulting green solution was stirred for 2 hours at 0 °C. The reaction was quenched with excess of  $\text{I}_2$  (1,015 g, in 5 mL THF) and allowed to stir for 1 hour. Excess iodine was removed using sat. aqueous  $\text{Na}_2\text{S}_2\text{O}_3$  solution, the phases were separated and the organic phase was extracted three times with DCM. The combined organic extracts were dried over  $\text{MgSO}_4$  and the solvent removed

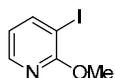
under reduced pressure. Column chromatographical purification (SiO<sub>2</sub>, hexane/DCM = 60:40) afforded 3-iodo-4-methoxypyridine (**6f**) as a yellowish solid (247 mg, 70% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) = 3.97 (s, 3H), 6.70 (d, *J*=5.6 Hz, 1H), 8.33 (d, *J*=5.6 Hz, 1H), 8.70 (s, 1H); <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>) δ (ppm) = 56.4, 85.3, 107.3, 151.2, 158.1, 164.4; MS (EI, 70 eV): *m/z* (%) = 235 [M<sup>+</sup>] (100), 93 (21), 78 (83), 51 (84), 50 (48); Elemental analysis (%): Calculated for C<sub>6</sub>H<sub>6</sub>INO: C, 30.66; H, 2.57; N, 5.96. Found: C, 30.39; H, 2.37; N, 6.40. The values are consistent with previously reported data in the literature.<sup>8</sup>

#### 4-Iodo-3-methoxypyridine (**6g**)



A dry Schlenk flask was charged with KCH<sub>2</sub>SiMe<sub>3</sub> (126 mg, 1 mmol) and Mg(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub> (99 mg, 0.5 mmol). The mixture was suspended in hexane (10 mL) and the suspension stirred for 1 h at 20 °C. PMDETA (173 mg, 1 mmol) was then added resulting in a clear solution with yellow oil deposited at the bottom of the flask. 3-Methoxypyridine (164 mg, 1.5 mmol) was added and the resulting orange solution was stirred for 2 hours at 0 °C. The reaction was quenched with excess of I<sub>2</sub> (1.015 g, in 5 mL THF) and allowed to stir for 1 hour. Excess iodine was removed using sat. aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution, the phases were separated and the organic phase was extracted three times with DCM. The combined organic extracts were dried over MgSO<sub>4</sub> and the solvent removed under reduced pressure. Column chromatographical purification (SiO<sub>2</sub>, hexane/EtOAc = 1:1) afforded 4-iodo-3-methoxypyridine (**6g**) as a white solid (204 mg, 58% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm) = 3.96 (s, 3H), 7.70 (d, *J*=5 Hz 1H), 7.86 (d, *J*=5 Hz, 1H), 8.09 (s, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ (ppm) = 57.1, 97.3, 133.3, 134.5, 143.4, 155.4; MS (EI, 70 eV): *m/z* (%) = 235 [M<sup>+</sup>] (100), 93 (27), 78 (13); Elemental analysis (%): Calculated for C<sub>6</sub>H<sub>6</sub>INO: C, 30.66; H, 2.57; N, 5.96. Found: C, 31.01; H, 2.43; N, 5.81. The values are consistent with previously reported data in the literature.<sup>9</sup>

#### 3-Iodo-2-methoxypyridine (**6h**)



<sup>8</sup> Uchiyama, M.; Naka, H.; Matsumoto, Y.; Wheatley, A. E. H.; McPartlin, M.; Morey, J. V.; Kondo, Y. *J. Am. Chem. Soc.* **2007**, *129*, 1921–30.

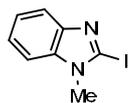
<sup>9</sup> Blair, V. L.; Blakemore, D. C.; Hay, D.; Hevia, E.; Pryde, D. C. *Tetrahedron Lett.* **2011**, *52*, 4590–4594.

A dry Schlenk flask was charged with  $\text{KCH}_2\text{SiMe}_3$  (126 mg, 1 mmol) and  $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2$  (99 mg, 0.5 mmol). The mixture was suspended in hexane (10 mL) and the suspension stirred for 1 h at 20 °C. PMDETA (173 mg, 1 mmol) was then added resulting in a clear solution with yellow oil deposited at the bottom of the flask. 2-Methoxypyridine (164 mg, 1.5 mmol) was added and the resulting orange solution was stirred for 2 hours at 0 °C. The reaction was quenched with excess of  $\text{I}_2$  (1,015 g, in 5 mL THF) and allowed to stir for 1 hour. Excess iodine was removed using sat. aqueous  $\text{Na}_2\text{S}_2\text{O}_3$  solution, the phases were separated and the organic phase was extracted three times with DCM. The combined organic extracts were dried over  $\text{MgSO}_4$  and the solvent removed under reduced pressure. Column chromatographical purification ( $\text{SiO}_2$ , hexane/DCM = 20:80) afforded 3-iodo-2-methoxypyridine (**6h**) as colorless oil (260 mg, 75% yield).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) = 3.98 (s, 3 H), 6.62-6.65 (dd,  $J=7.5$  Hz,  $J=5$  Hz, 1 H), 8.01 (dd,  $J=7.5$ , 1.5 Hz, 1 H), 8.11 (dd,  $J=5$ , 1.5 Hz, 1 H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) = 54.9, 80.1, 118.5, 146.8, 148.3, 162.2; **MS (EI, 70 eV)**:  $m/z$  (%) = 235 [ $\text{M}^+$ ] (23), 234 (72), 205 (32), 107 (18), 93 (31), 78 (42), 51 (26), 50 (48). The values are consistent with previously reported data in the literature.

### 5-Iodo-1-methyl-1H-pyrazole (**6i**)



A dry Schlenk flask was charged with  $\text{KCH}_2\text{SiMe}_3$  (126 mg, 1 mmol) and  $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2$  (99 mg, 0.5 mmol). The mixture was suspended in hexane (10 mL) and the suspension stirred for 1 h at 20 °C. PMDETA (173 mg, 1 mmol) was then added resulting in a clear solution with yellow oil deposited at the bottom of the flask. 1-Methylpyrazole (123 mg, 1.5 mmol) was added and the resulting solution was stirred for 2 hours at 0 °C. The reaction was quenched with excess of  $\text{I}_2$  (1,015 g, in 5 mL THF) and allowed to stir for 1 hour. Excess iodine was removed using sat. aqueous  $\text{Na}_2\text{S}_2\text{O}_3$  solution, the phases were separated and the organic phase was extracted three times with DCM. The combined organic extracts were dried over  $\text{MgSO}_4$  and the solvent removed under reduced pressure. Column chromatographical purification ( $\text{SiO}_2$ , hexane/EtOAc = (100:0  $\rightarrow$  0:100)) afforded 5-Iodo-1-methyl-1H-pyrazole (**6i**) as yellowish crystals (287 mg, 92% yield).  $^1\text{H NMR}$  (500 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  (ppm) = 3.34 (s, 3H), 6.16 (d,  $^3J=1.5$  Hz, 1H), 7.34 (d,  $^3J=2$  Hz, 1H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  (ppm) = 39.8, 81.2, 116.1, 141.8; **MS (EI, 70 eV)**:  $m/z$  (%) = 208 [ $\text{M}^+$ ] (100), 181 (65), 54 (16), 52 (16); **Elemental analysis (%)**: Calculated for  $\text{C}_4\text{H}_5\text{IN}_2$ : C, 23.10; H, 2.42; N, 13.47. Found: C, 24.35; H, 2.65; N, 12.98.

**2-Iodo-1-methyl-1H-benzo[d]imidazole (6k)**

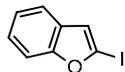
A dry Schlenk flask was charged with  $\text{KCH}_2\text{SiMe}_3$  (126 mg, 1 mmol) and  $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2$  (99 mg, 0.5 mmol). The mixture was suspended in hexane (10 mL) and the suspension stirred for 1 h at 20 °C. PMDETA (173 mg, 1 mmol) was then added resulting in a clear solution with yellow oil deposited at the bottom of the flask. 1-Methylbenzo[d]imidazole (198 mg, 1.5 mmol) was added and the resulting solution was stirred for 1.5 hours at 20 °C. The reaction was quenched with excess of  $\text{I}_2$  (1,015 g, in 5 mL THF) and allowed to stir for 1 hour. Excess iodine was removed using sat. aqueous  $\text{Na}_2\text{S}_2\text{O}_3$  solution, the phases were separated and the organic phase was extracted three times with DCM. The combined organic extracts were dried over  $\text{MgSO}_4$  and the solvent removed under reduced pressure. Column chromatographical purification ( $\text{SiO}_2$ , hexane/EtOAc = 70:30) afforded **6k** as a colourless solid (318 mg, 82% Yield).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) = 3.76 (s, 3H), 7.21-7.26 (m, 2H), 7.31-7.33 (d,  $^3J=7.5$  Hz 1H), 7.70-7.72 (d,  $^3J=7.5$  Hz, 1H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) = 34, 104.5, 109.7, 119.5, 122.5, 123.4, 136.6, 145.8; **MS (EI, 70 eV)**:  $m/z$  (%) = 260 [ $\text{M}^+$ ] (100), 133 (50), 89 (97), 63 (20); **Elemental analysis (%)**: Calculated for  $\text{C}_8\text{H}_7\text{IN}_2$ : C, 37.23; H, 2.73; N, 10.86. Found: C, 36.91; H, 2.64; N, 10.81.

**5-Iodo-1-methyl-1H-1,2,4-triazole (6l)**

A dry Schlenk flask was charged with  $\text{KCH}_2\text{SiMe}_3$  (126 mg, 1 mmol) and  $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2$  (99 mg, 0.5 mmol). The mixture was suspended in hexane (10 mL) and the suspension stirred for 1 h at 20 °C. PMDETA (173 mg, 1 mmol) was then added resulting in a clear solution with yellow oil deposited at the bottom of the flask. 1-Methyl-1,2,4-triazole (125 mg, 1.5 mmol) was added and the resulting solution was stirred for 1.5 hours at 20 °C. The reaction was quenched with excess of  $\text{I}_2$  (1,015 g, in 5 mL THF) and allowed to stir for 1 hour. Excess iodine was removed using sat. aqueous  $\text{Na}_2\text{S}_2\text{O}_3$  solution, the phases were separated and the organic phase was extracted three times with DCM. The combined organic extracts were dried over  $\text{MgSO}_4$  and the solvent removed under reduced pressure. Column chromatographical purification ( $\text{SiO}_2$ , hexane/EtOAc = 70:30) afforded **6l** as a yellowish solid (290 mg, 93% yield).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) = 3.86 (s, 3H), 7.83 (s, 1H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) = 38.1, 100.5, 154.3; **MS (EI,**

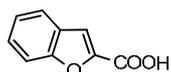
**70 eV):**  $m/z$  (%) = 209 [ $M^+$ ] (100), 182 (7), 56 (10); **Elemental analysis (%)**: Calculated for  $C_3H_4IN_3$ : C, 17.24; H, 1.93; N, 20.11 Found: C, 18.23; H, 1.88; N, 20.20.

### 2-Iodobenzofuran (6m)



A dry Schlenk flask was charged with  $KCH_2SiMe_3$  (126 mg, 1 mmol) and  $Mg(CH_2SiMe_3)_2$  (99 mg, 0.5 mmol). The mixture was suspended in hexane (10 mL) and the suspension stirred for 1 h at 20 °C. PMDETA (173 mg, 1 mmol) was then added resulting in a clear solution with yellow oil deposited at the bottom of the flask. Benzofuran (177 mg, 1.5 mmol) was added and the resulting solution was stirred for 1.5 hours at 20 °C. The reaction was quenched with excess of  $I_2$  (1,015 g, in 5 mL THF) and allowed to stir for 1 hour. Excess iodine was removed using sat. aqueous  $Na_2S_2O_3$  solution, the phases were separated and the organic phase was extracted three times with DCM. The combined organic extracts were dried over  $MgSO_4$  and the solvent removed under reduced pressure. Column chromatographical purification ( $SiO_2$ , hexane/EtOAc = 70:30) afforded **6m** as a yellowish oil (296 mg, 81% Yield).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  (ppm) = 6.98 (s, 1H), 7.25-7.27 (m, 2H), 7.52-7.77 (m, 2H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  (ppm) = 95.3, 110.0, 116.5, 118.9, 122.4, 123.5, 128.4, 132.5, 157.4; **MS (EI, 70 eV):**  $m/z$  (%) = 244 [ $M^+$ ] (65), 89 (100), 63 (30), 62 (23).

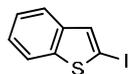
### Benzofuran-2-carboxylic acid (6m')



A dry Schlenk flask was charged with  $KCH_2SiMe_3$  (126 mg, 1 mmol) and  $Mg(CH_2SiMe_3)_2$  (99 mg, 0.5 mmol). The mixture was suspended in hexane (10 mL) and the suspension stirred for 1 h at 20 °C. PMDETA (173 mg, 1 mmol) was then added resulting in a clear solution with yellow oil deposited at the bottom of the flask. Benzofuran (177 mg, 1.5 mmol) was added in one portion and the mixture stirred for 1.5 h before  $CO_{2(g)}$  was constantly allowed to pass through the reaction mixture for 1 h, resulting in instant precipitation of a white solid. The reaction was quenched with sat.  $Na_2CO_3$  solution, the phases separated and the aqueous phase was washed three times with DCM (3 x 1 mL). Acidification of the aqueous phase using HCl (2M in water) led to precipitation of the carboxylic acid which was extracted using diethyl ether. The combined ether phases were dried over  $MgSO_4$  and the solvent was evaporated in vacuo. Benzofuran-2-carboxylic acid (**6m'**) is obtained as a white solid (231 mg, 95% yield).  $^1H$  NMR (400 MHz, DMSO)  $\delta$  (ppm) = 7.33 (t, 1H), 7.48 (t, 1H), 7.66 (s, 1H), 7.68 (d, 1H), 7.78 (d, 1H), 13.6 (broad s, 1H);  $^{13}C$  NMR (125

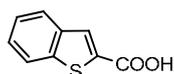
**MHz, DMSO)**  $\delta$  (ppm) = 112.0, 113.5, 123.1, 123.8, 126.9, 127.6, 146.2, 155.0, 160.1; **MS (EI, 70 eV):**  $m/z$  (%) = 162 [ $M^+$ ] (100), 145 (43), 134 (27), 89 (39), 78 (19).

### 2-Iodobenzo[b]thiophene (6n)



A dry Schlenk flask was charged with  $KCH_2SiMe_3$  (126 mg, 1 mmol) and  $Mg(CH_2SiMe_3)_2$  (99 mg, 0.5 mmol). The mixture was suspended in hexane (10 mL) and the suspension stirred for 1 h at 20 °C. PMDETA (173 mg, 1 mmol) was then added resulting in a clear solution with yellow oil deposited at the bottom of the flask. Benzothiophene (201 mg, 1.5 mmol) was added and the resulting solution was stirred for 1.5 hours at 20 °C. The reaction was quenched with excess of  $I_2$  (1,015 g, in 5 mL THF) and allowed to stir for 1 hour. Excess iodine was removed using sat. aqueous  $Na_2S_2O_3$  solution, the phases were separated and the organic phase was extracted three times with DCM. The combined organic extracts were dried over  $MgSO_4$  and the solvent removed under reduced pressure. Column chromatographical purification ( $SiO_2$ , hexane/EtOAc = 70:30) afforded **6n** as a pale yellow solid (359 mg, 92% Yield).  **$^1H$  NMR (500 MHz,  $CDCl_3$ )**  $\delta$  (ppm) = 7.30-7.32(m, 2H), 7.54 (s, 1H), 7.71-7.73 (m, 1H), 7.76-7.78 (m, 1H);  **$^{13}C$  NMR (125 MHz,  $CDCl_3$ )**  $\delta$  (ppm) = 78.7, 121.5, 122.5, 124.6, 124.7, 134.0, 141.0, 144.6; **MS (EI, 70 eV):**  $m/z$  (%) = 260 [ $M^+$ ] (100), 133 (50), 89 (97), 63 (20); **Elemental analysis (%)**: Calculated for  $C_8H_5IS$ : C, 36.94; H, 1.94. Found: C, 37.58; H, 1.91.

### Benzo[b]thiophene-2-carboxylic acid (6n')



A dry Schlenk flask was charged with  $KCH_2SiMe_3$  (126 mg, 1 mmol) and  $Mg(CH_2SiMe_3)_2$  (99 mg, 0.5 mmol). The mixture was suspended in hexane (10 mL) and the suspension stirred for 1 h at 20 °C. PMDETA (173 mg, 1 mmol) was then added resulting in a clear solution with yellow oil deposited at the bottom of the flask. Benzothiophene (201 mg, 1.5 mmol) was added in one portion and the mixture stirred for 1.5 h before  $CO_{2(g)}$  was constantly allowed to pass through the reaction mixture for 1 h, resulting in instant precipitation of a white solid. The reaction was quenched with sat.  $Na_2CO_3$  solution, the phases separated and the aqueous phase was washed three times with DCM (3 x 1 mL). Acidification of the aqueous phase using HCl (2M in water) led to precipitation of the carboxylic acid which was extracted using diethyl ether. The combined ether phases were dried over  $MgSO_4$  and the solvent was evaporated in vacuo. Benzo[b]thiophene-2-

carboxylic acid (**6n'**) is obtained as a as a yellowish solid (240 mg, 90% yield).  $^1\text{H NMR}$  (400 MHz, DMSO)  $\delta$  (ppm) = 7.48 (m, 2H), 8.00 (m, 2H), 8.10 (s, 1H);  $^{13}\text{C NMR}$  (125 MHz, DMSO)  $\delta$  (ppm) = 122.9, 125.0, 125.7, 126.9, 130.1, 134.9, 138.7, 141.3, 163.5;  $\text{MS}^*$  (EI, 70 eV):  $m/z$  (%) = 192 [ $\text{M}^+$ ] (69), 161 (100), 133 (22), 89 (31). \* The GC MS sample was prepared in methanol due to the low solubility of benzo[b]thiophene-2-carboxylic acid. The mass obtained corresponds to methyl benzo[b]thiophene-2-carboxylate the ester derivative of the carboxylic acid previously formed.

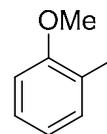
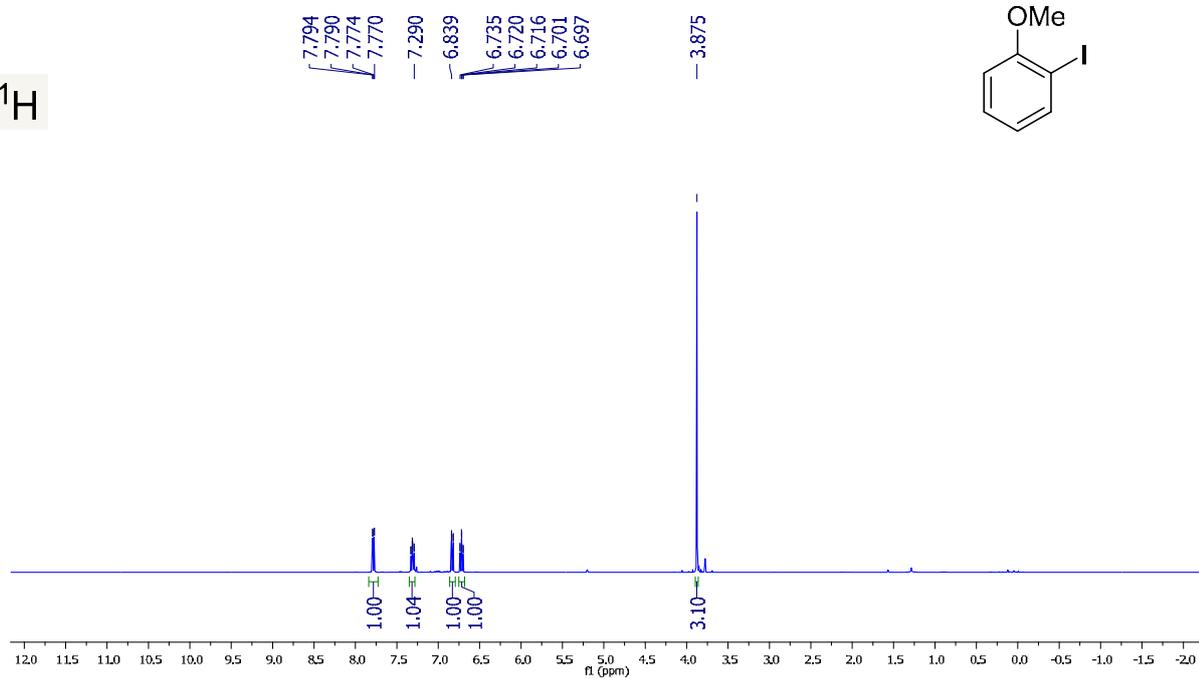
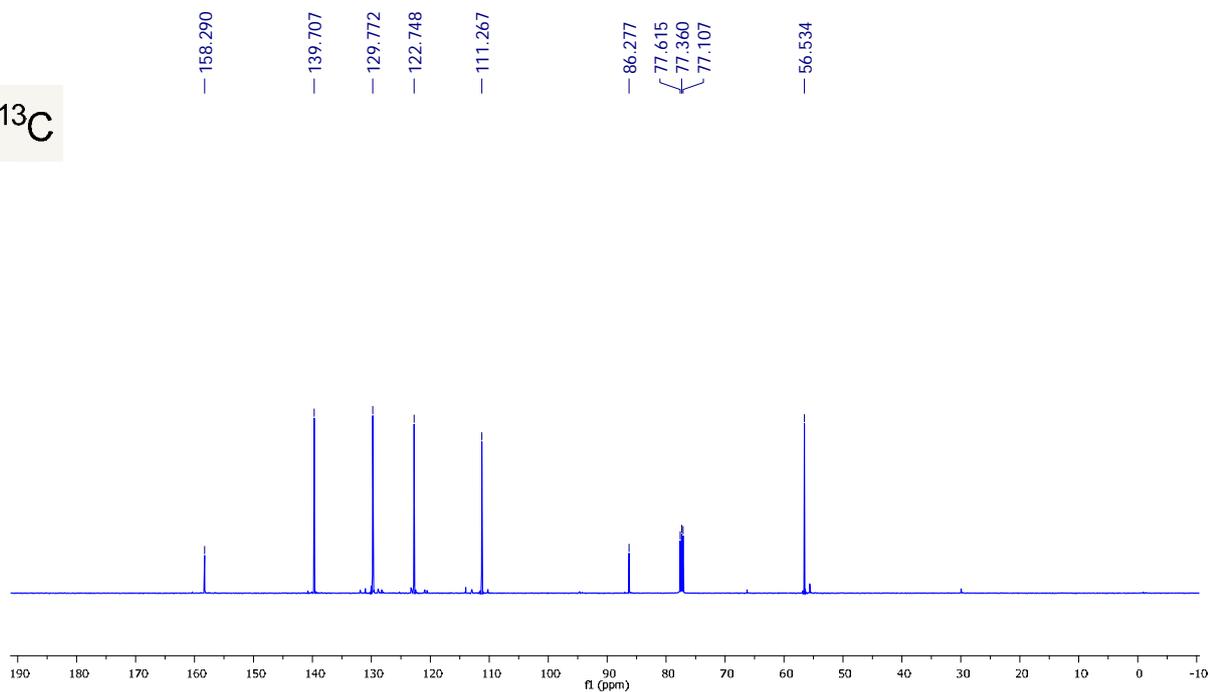
### 2-Iodothiophene (**6o**) + 3-Iodothiophene (**6o'**)



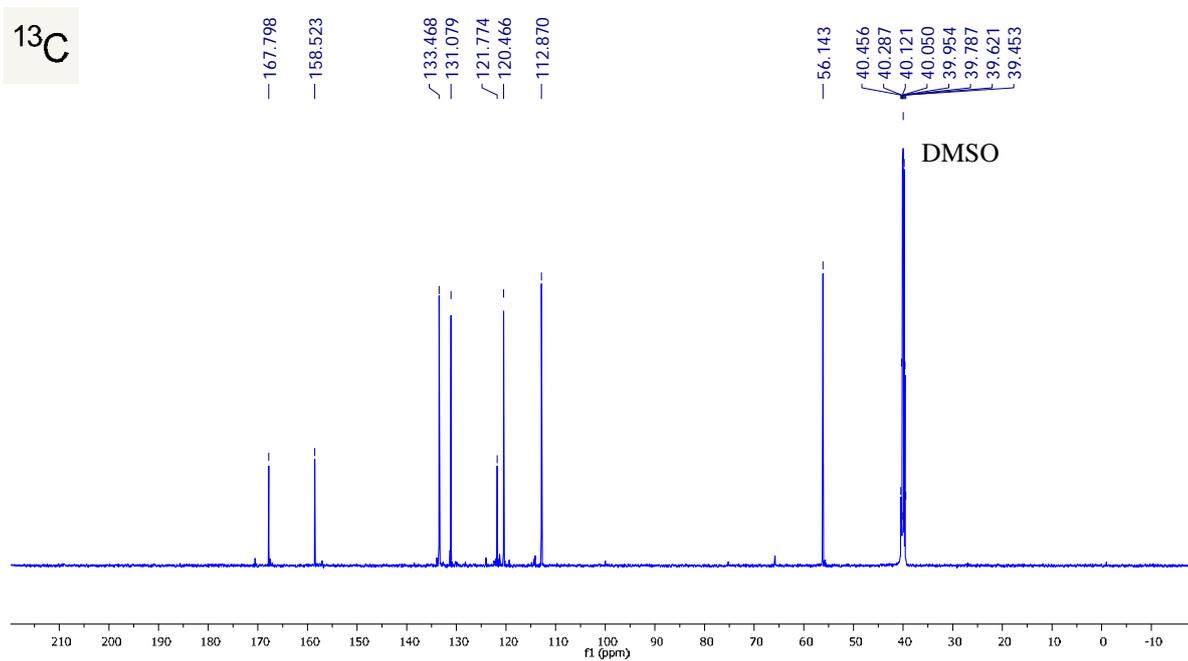
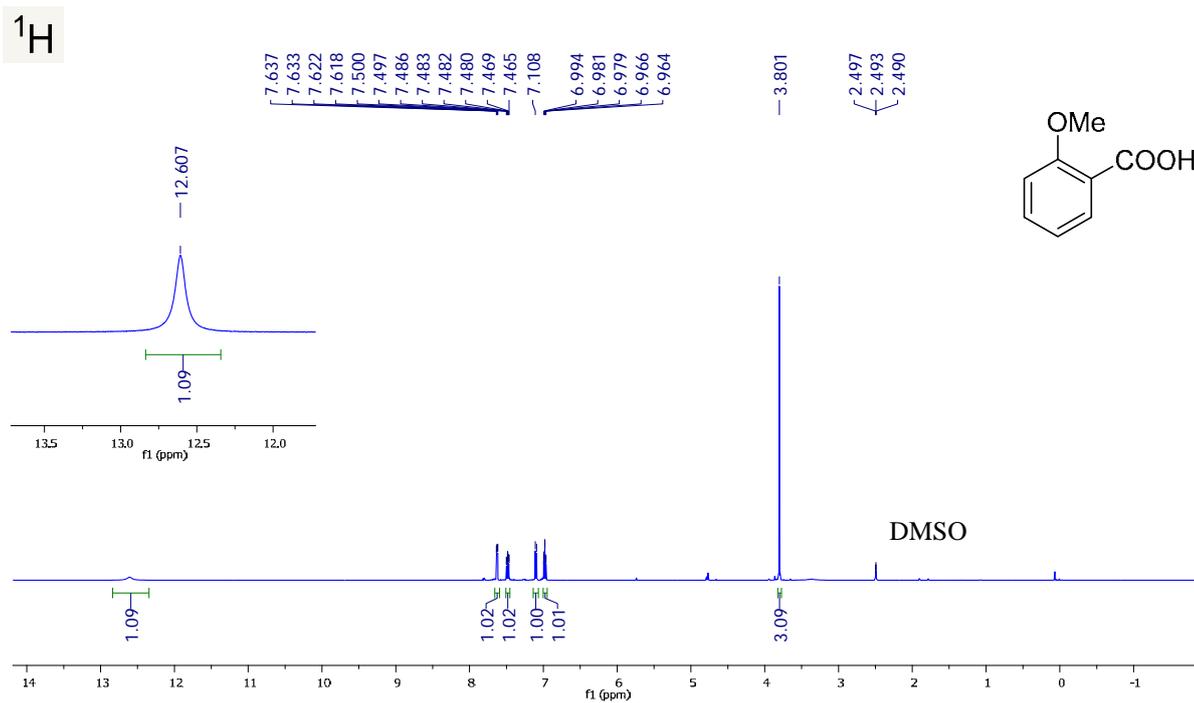
A dry Schlenk flask was charged with  $\text{KCH}_2\text{SiMe}_3$  (126 mg, 1 mmol) and  $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2$  (99 mg, 0.5 mmol). The mixture was suspended in hexane (10 mL) and the suspension stirred for 1 h at 20 °C. PMDETA (173 mg, 1 mmol) was then added resulting in a clear solution with yellow oil deposited at the bottom of the flask. Thiophene (126 mg, 1.5 mmol) was added and the resulting solution was stirred for 1.5 hours at 0 °C. The reaction was quenched with excess of  $\text{I}_2$  (1,015 g, in 5 mL THF) and allowed to stir for 1 hour. Excess iodine was removed using sat. aqueous  $\text{Na}_2\text{S}_2\text{O}_3$  solution, the phases were separated and the organic phase was extracted three times with DCM. The combined organic extracts were dried over  $\text{MgSO}_4$  and the solvent removed under reduced pressure. Ferrocene was added to the solution (29.7 mg, 10 mol%). The yield obtained by integration of the corresponding signals for **6o** and **6o'** by  $^1\text{H NMR}$  was 83% for **6o** and 8% for **6o'**.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) = 6.73 (m,  $^3J=4$  Hz,  $^4J=1.5$  Hz, 1H), 7.17 (dd,  $^3J=3.5$  Hz,  $^4J=1$  Hz, 1H), 7.28 (dd,  $^3J=5.5$  Hz,  $^4J=1$  Hz, 1H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) = 73.3, 129.0, 131.6, 137.0,  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) = 6.86 (s, 2H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) = 76.5, 138.9.

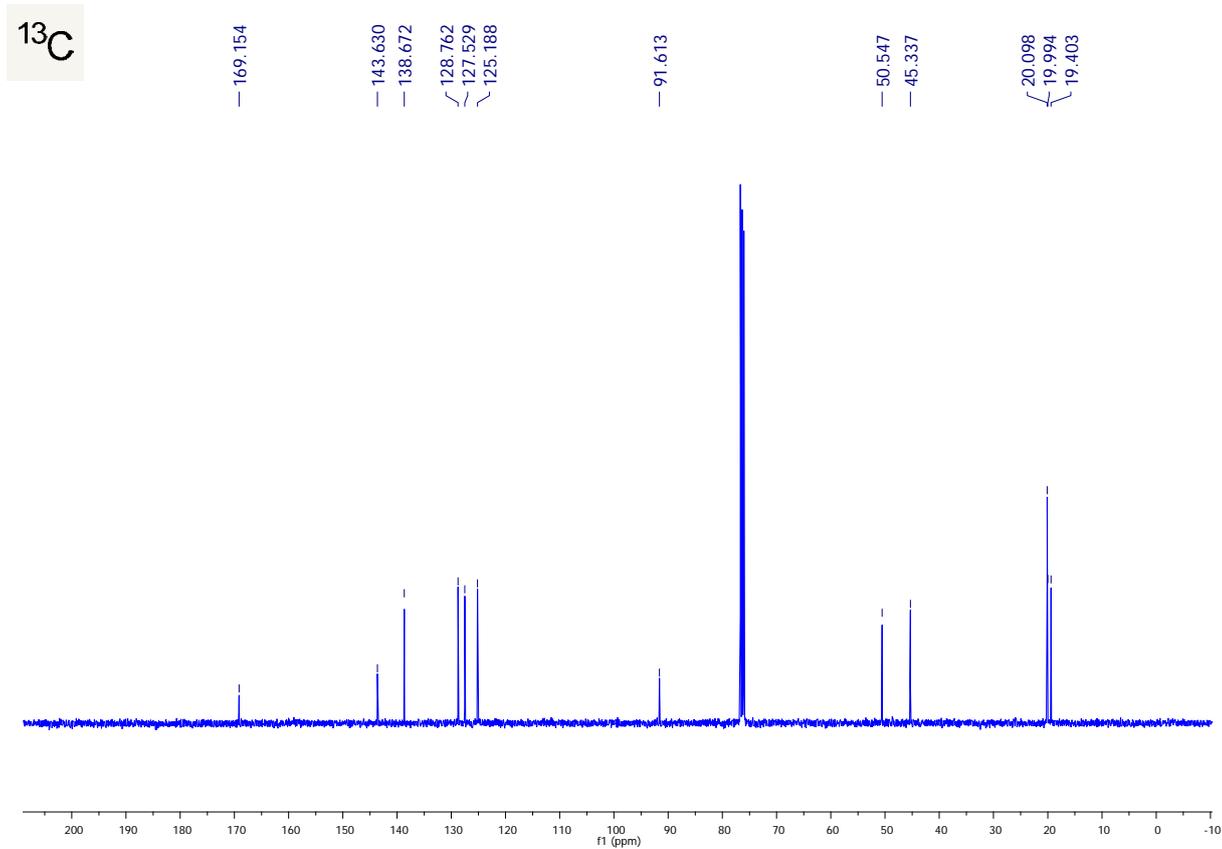
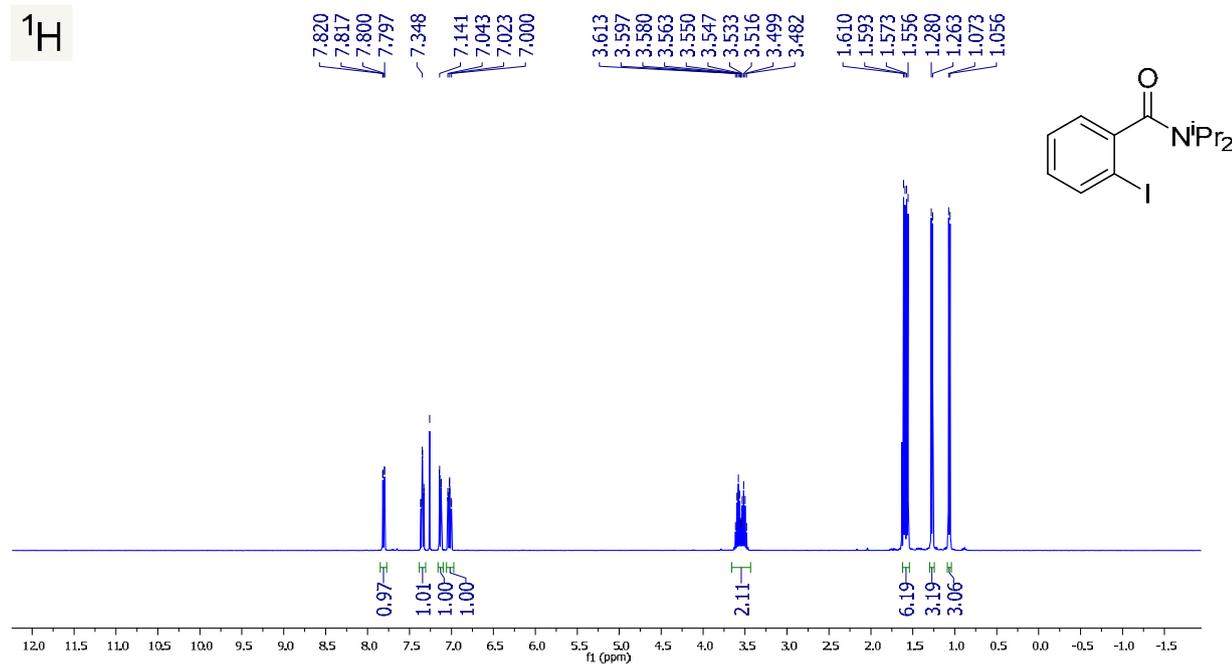
## NMR Spectra of Products (Table 2)

## 2-Iodoanisole (6a)

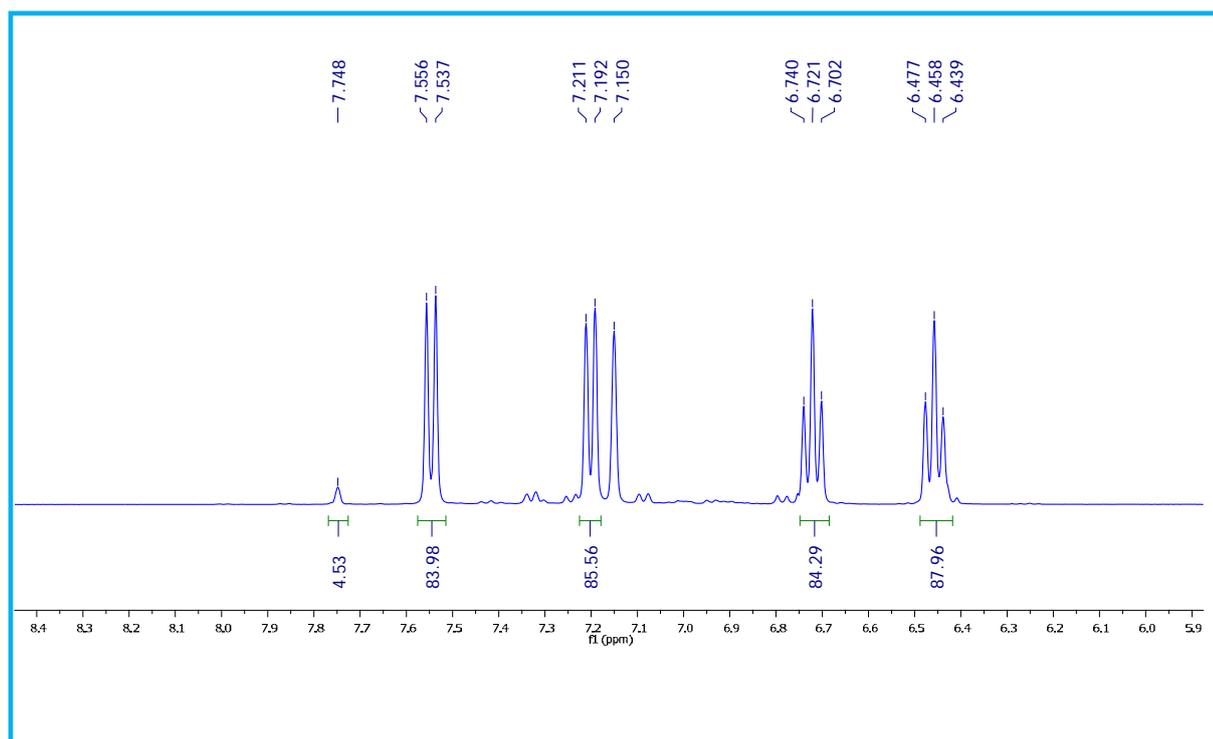
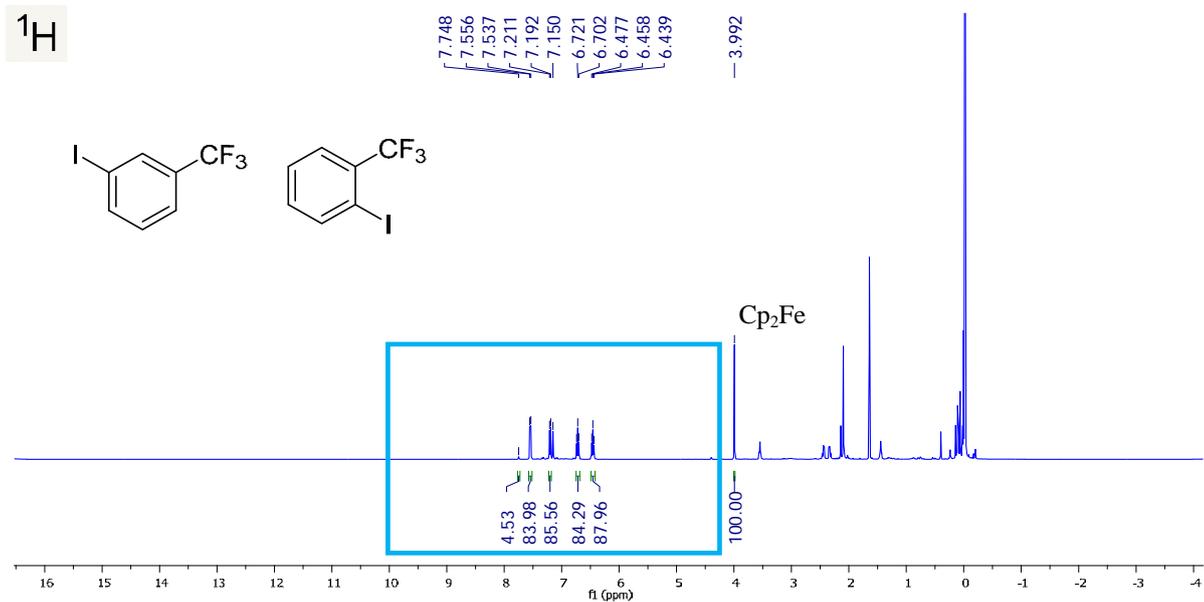
 $^1\text{H}$  $^{13}\text{C}$ 

## Methoxybenzoic acid (6a')

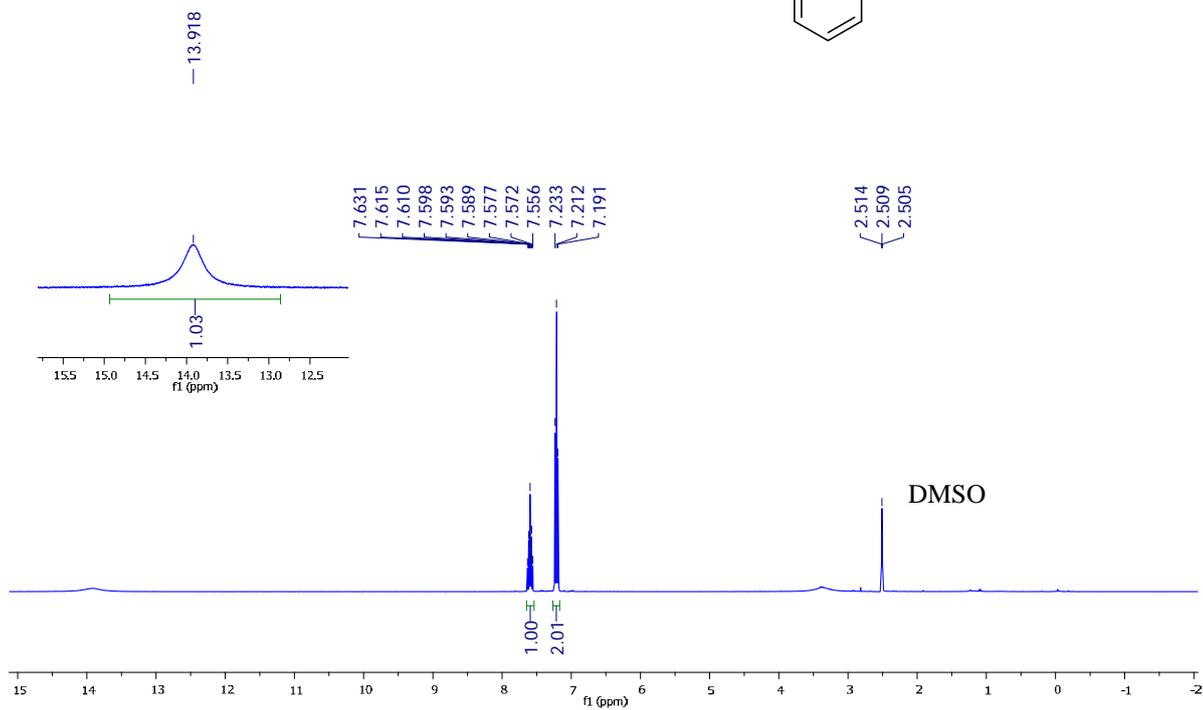
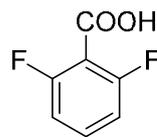
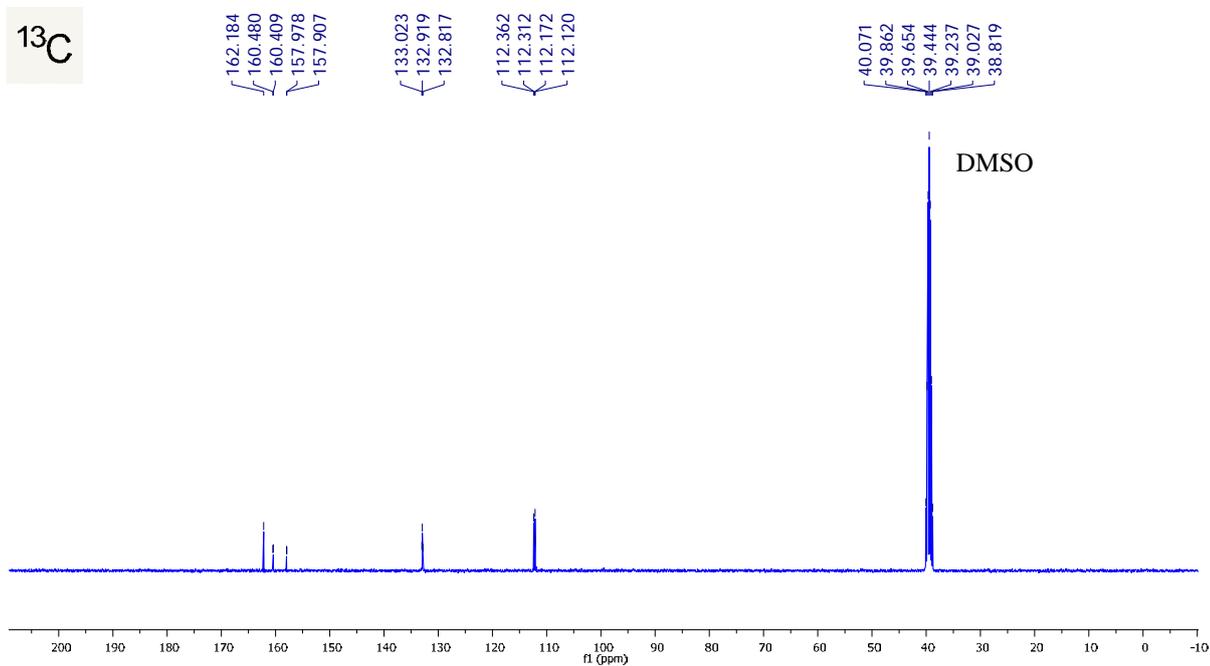


2-Iodo-*N,N*-diisopropylbenzamide (6b)

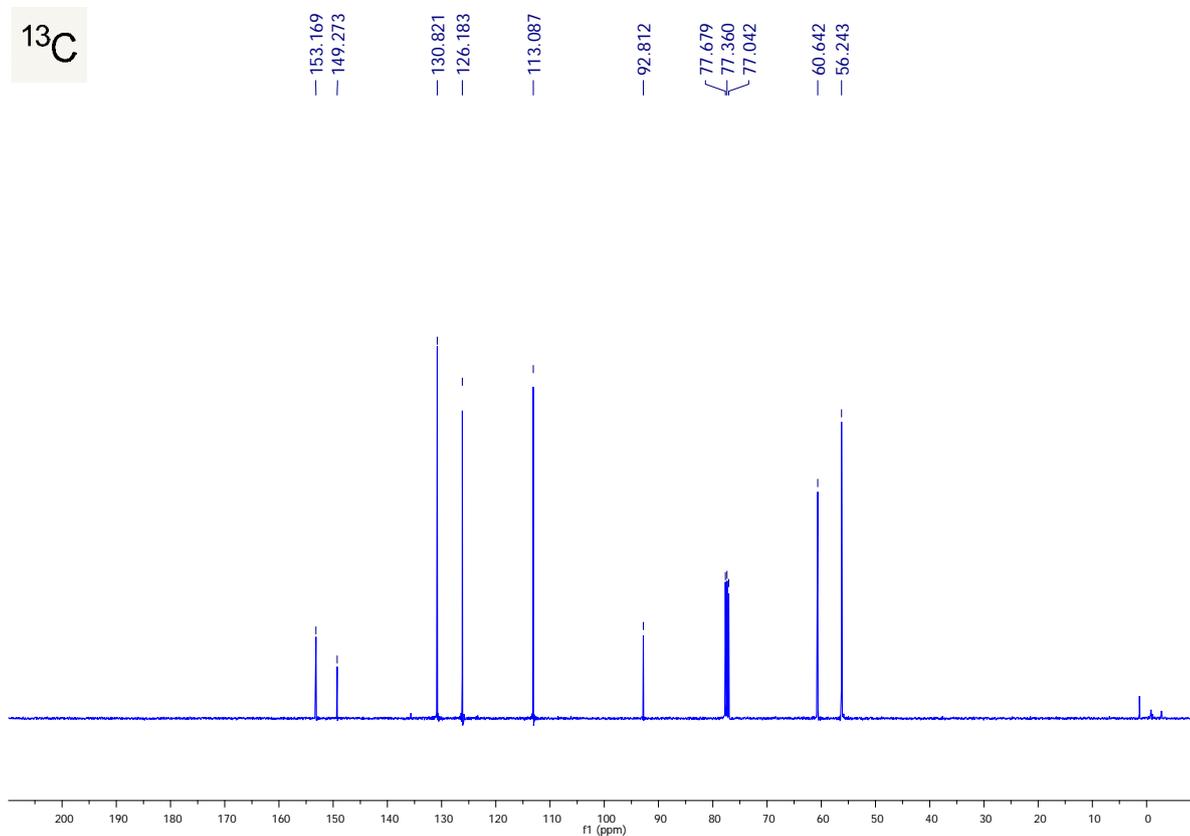
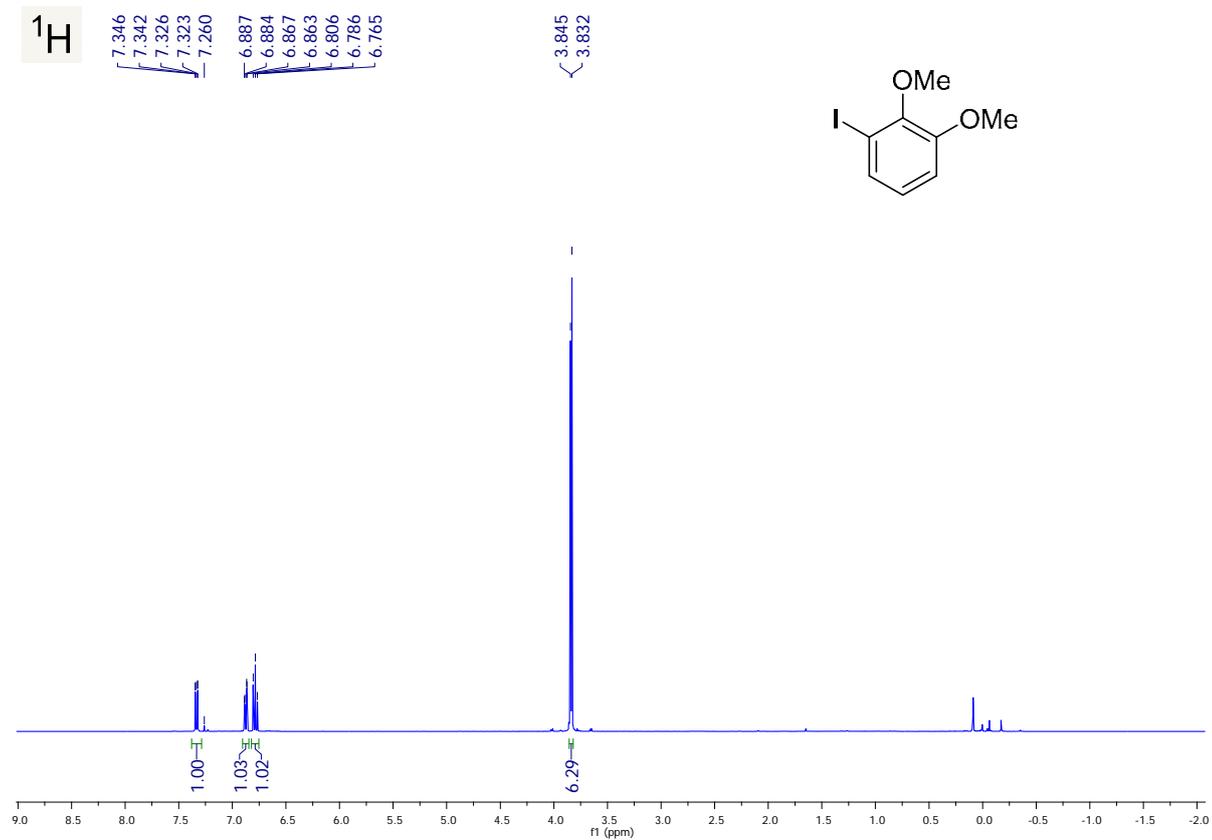
## 1-Iodo-2-(trifluoromethyl)benzene (6c) + 1-iodo-3-(trifluoromethyl)benzene (6c')



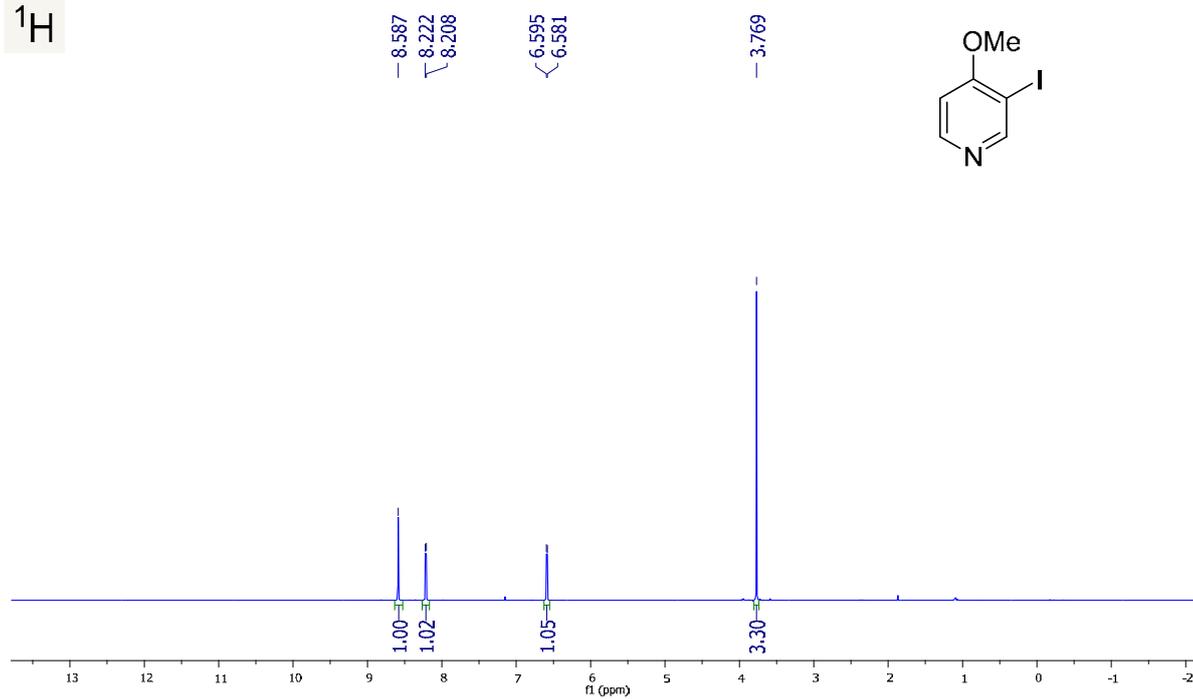
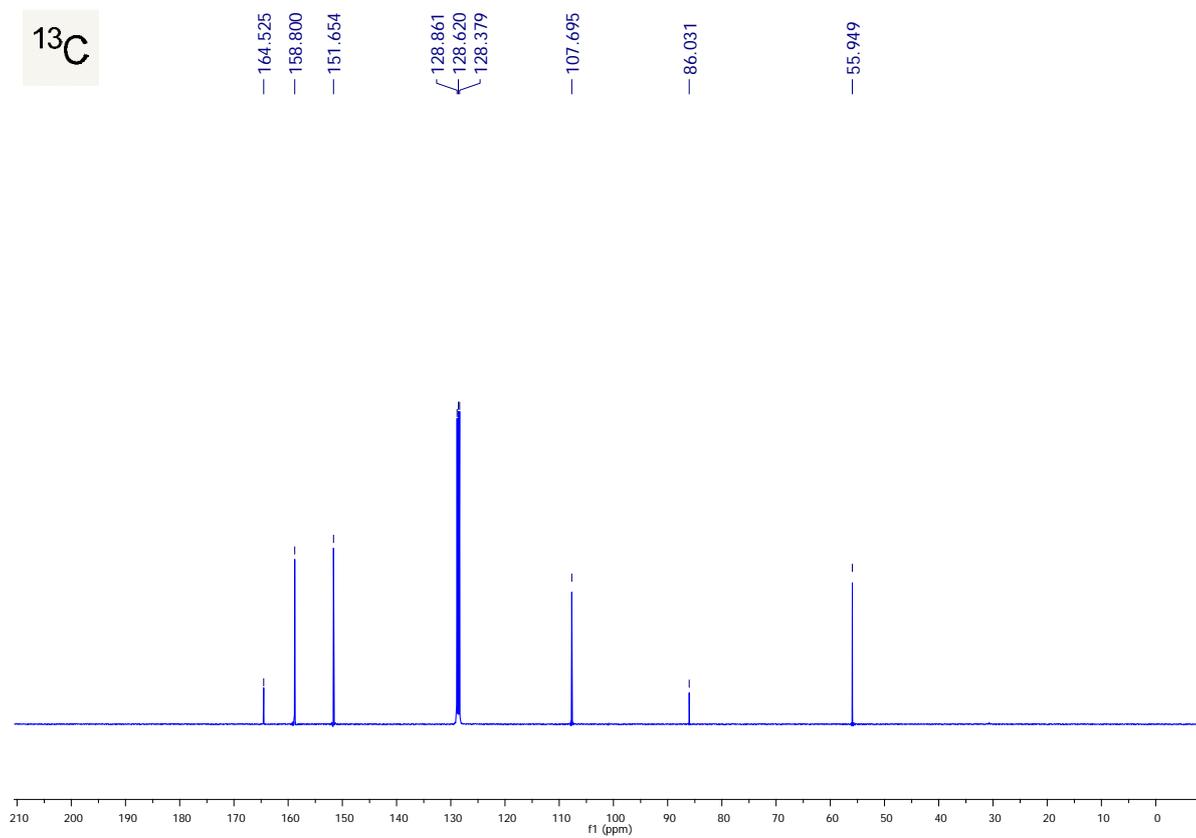
## 2,6-Difluorobenzoic acid (6d)

 $^1\text{H}$  $^{13}\text{C}$ 

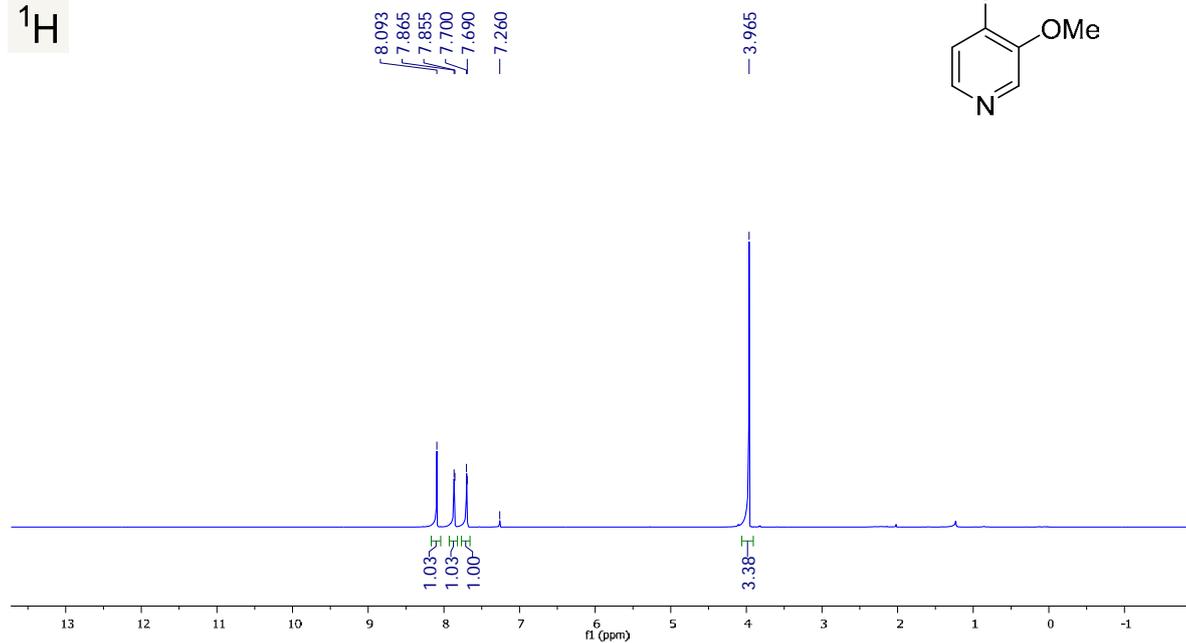
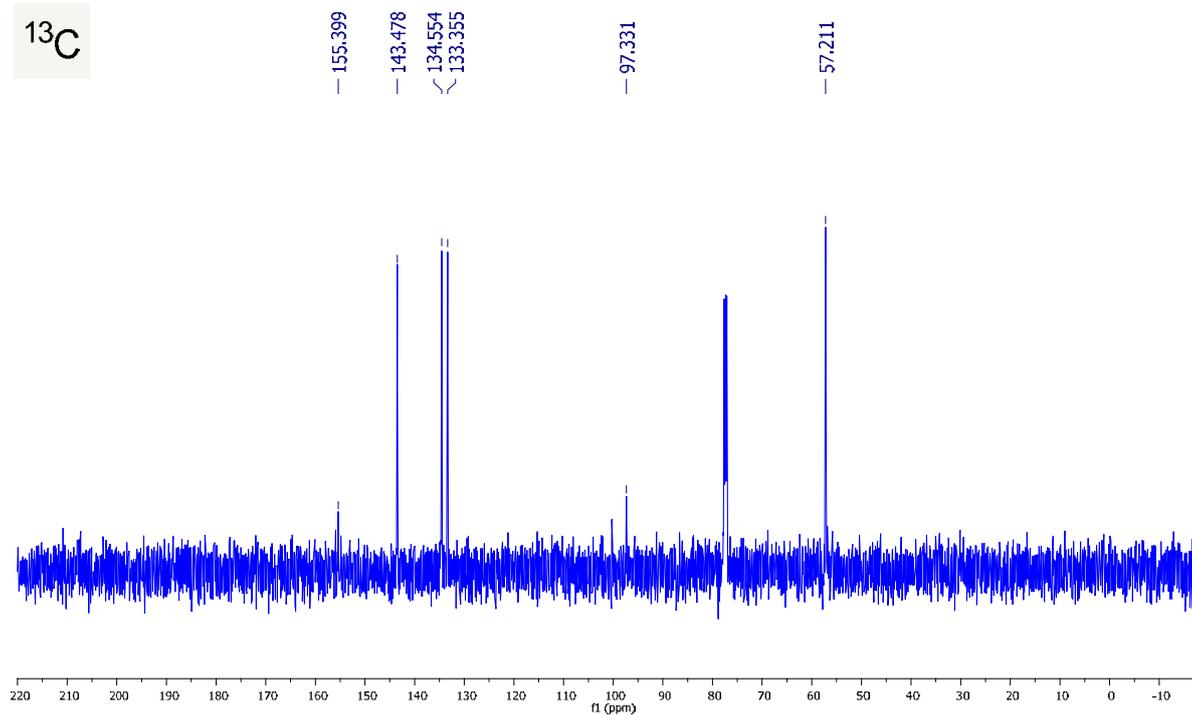
## 1-Iodo-2,3-dimethoxybenzene (6e)



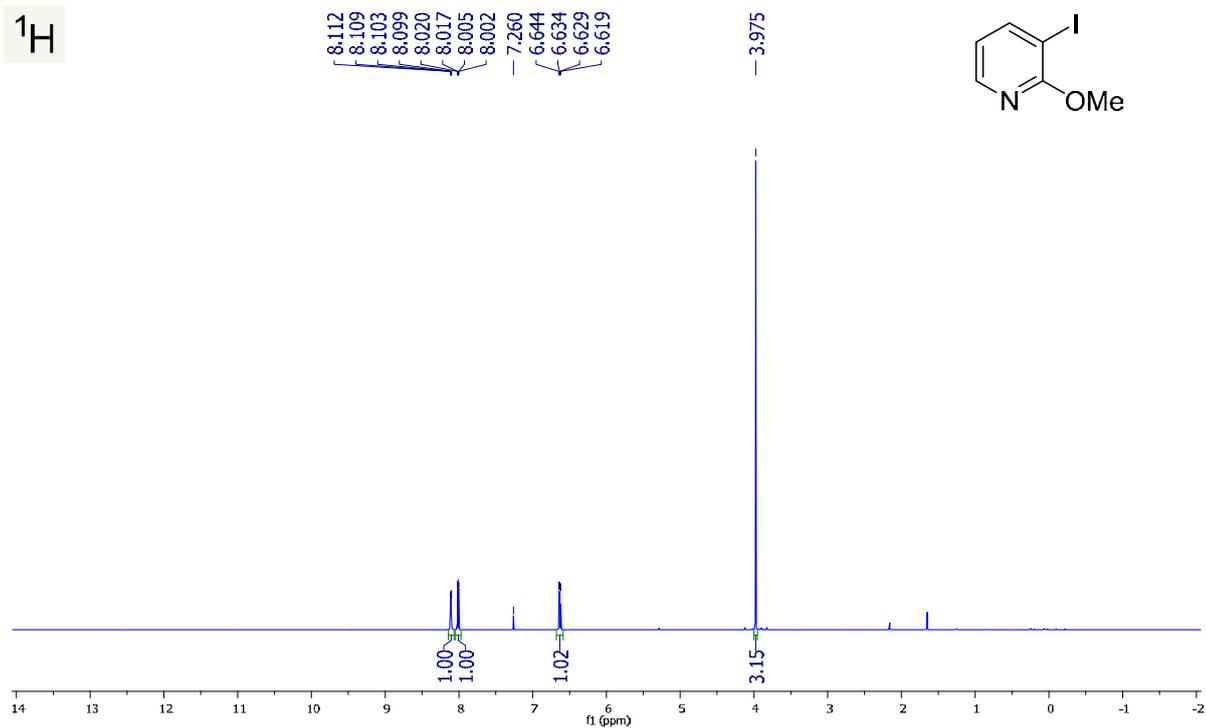
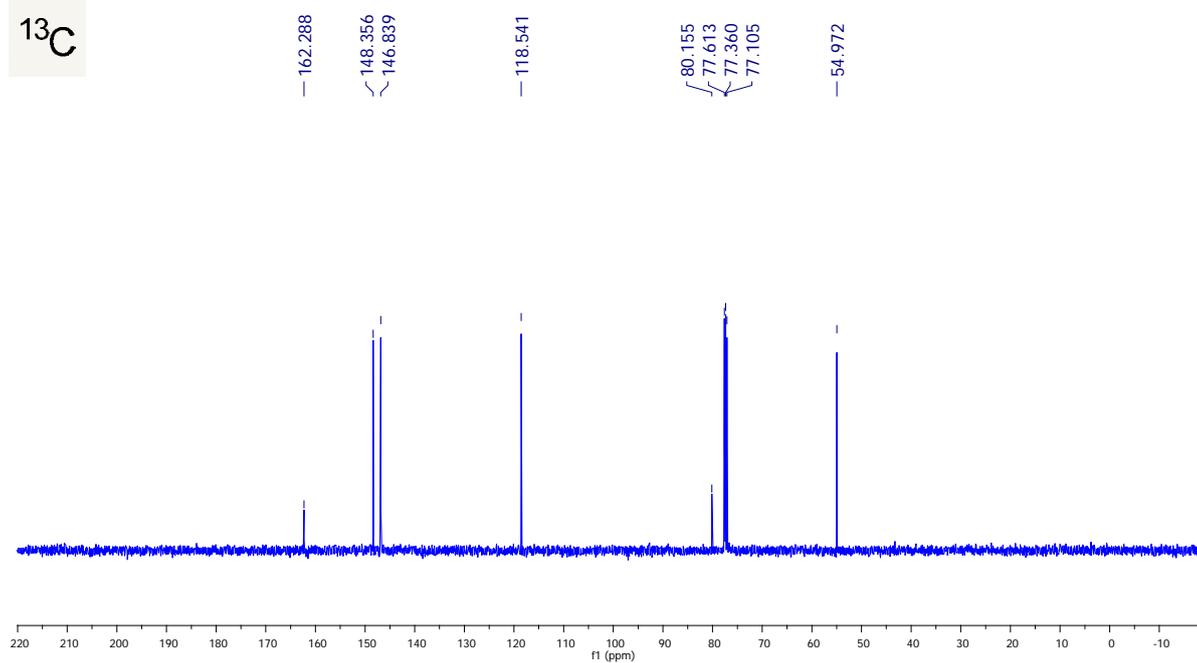
## 3-Iodo-4-methoxypyridine (6f)

 $^1\text{H}$  $^{13}\text{C}$ 

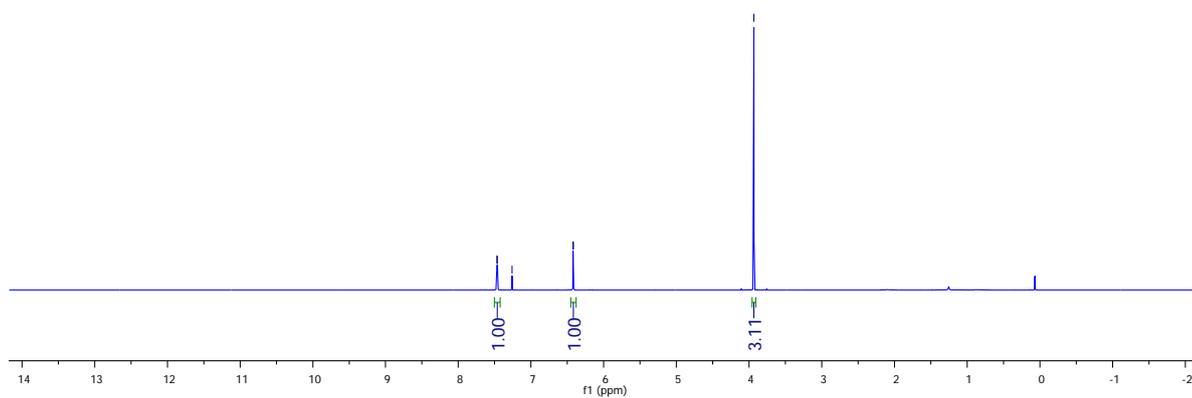
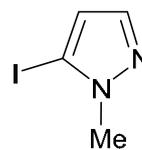
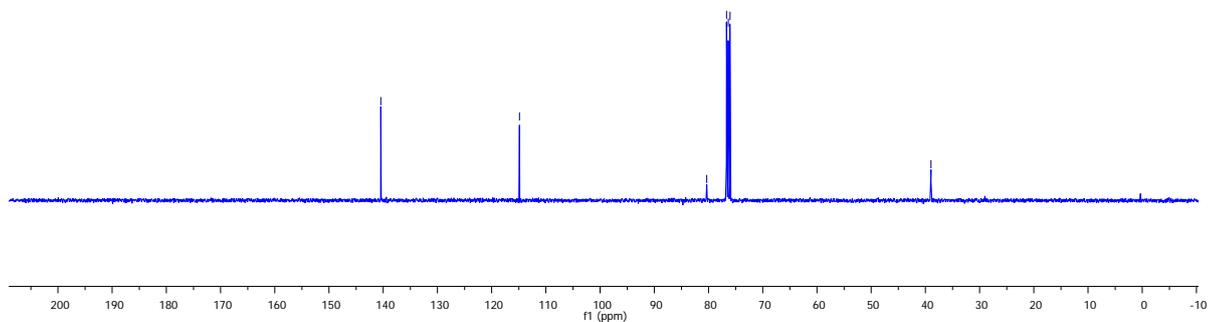
## 4-Iodo-3-methoxypyridine (6g)

 $^1\text{H}$  $^{13}\text{C}$ 

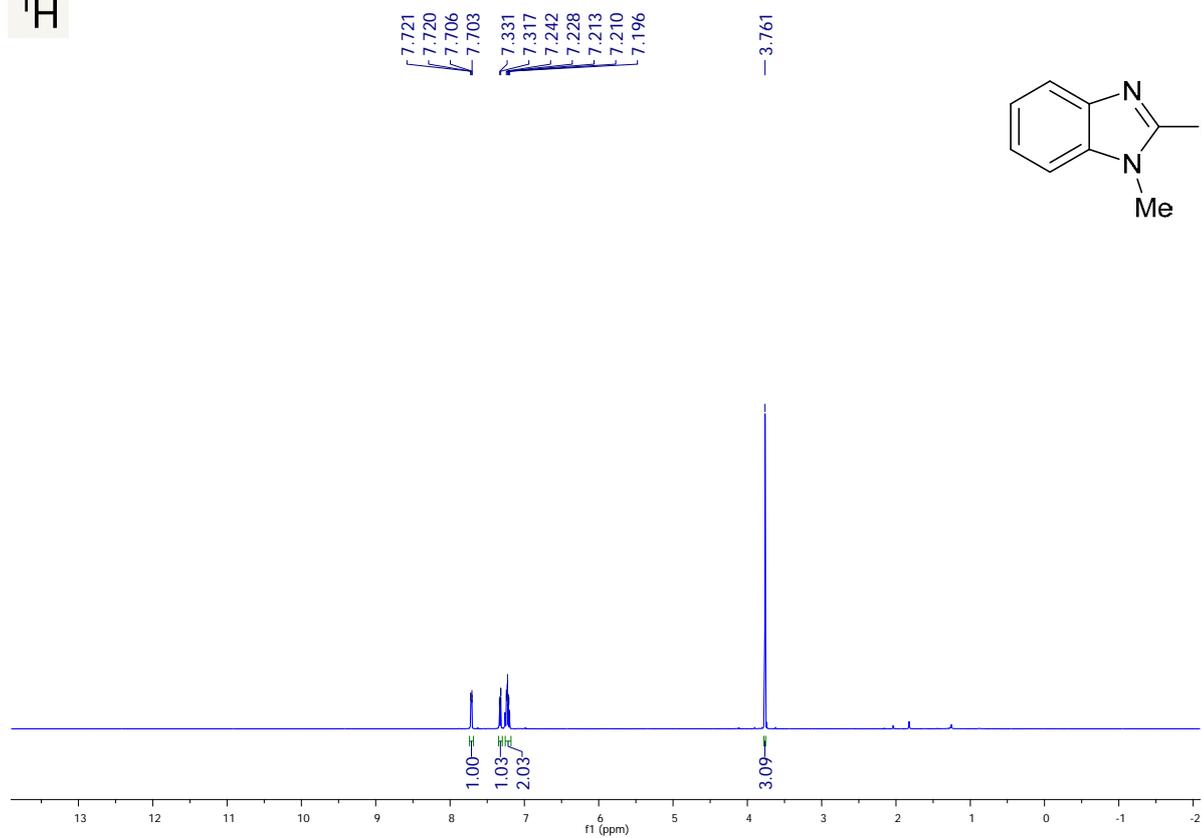
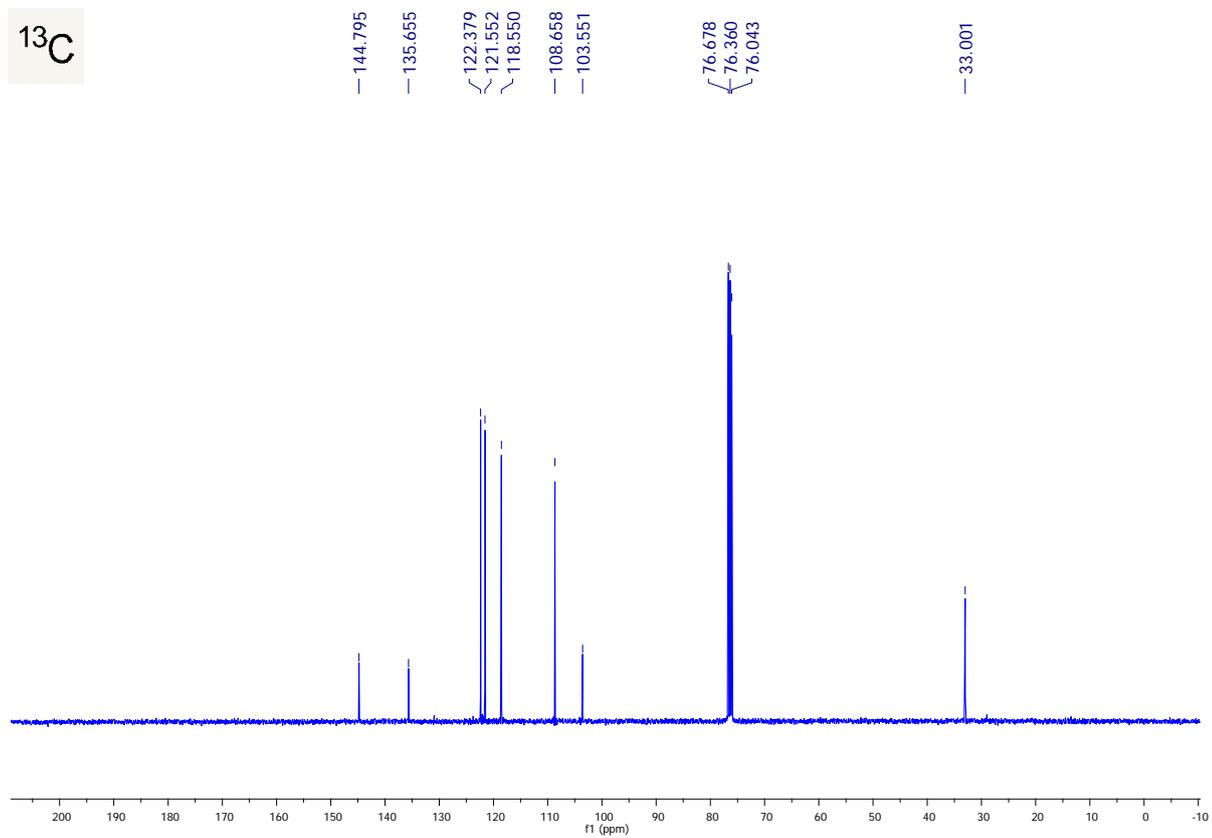
## 3-Iodo-2-methoxypyridine (6h)

 $^1\text{H}$  $^{13}\text{C}$ 

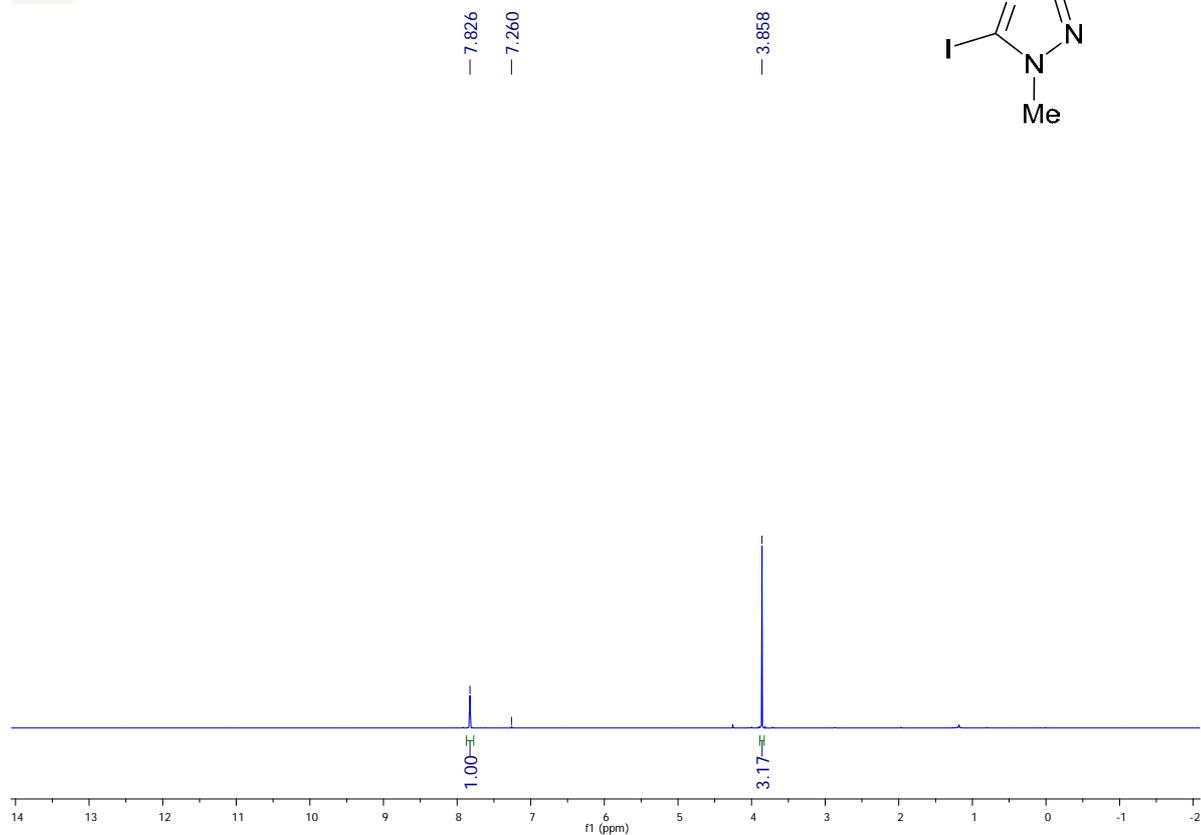
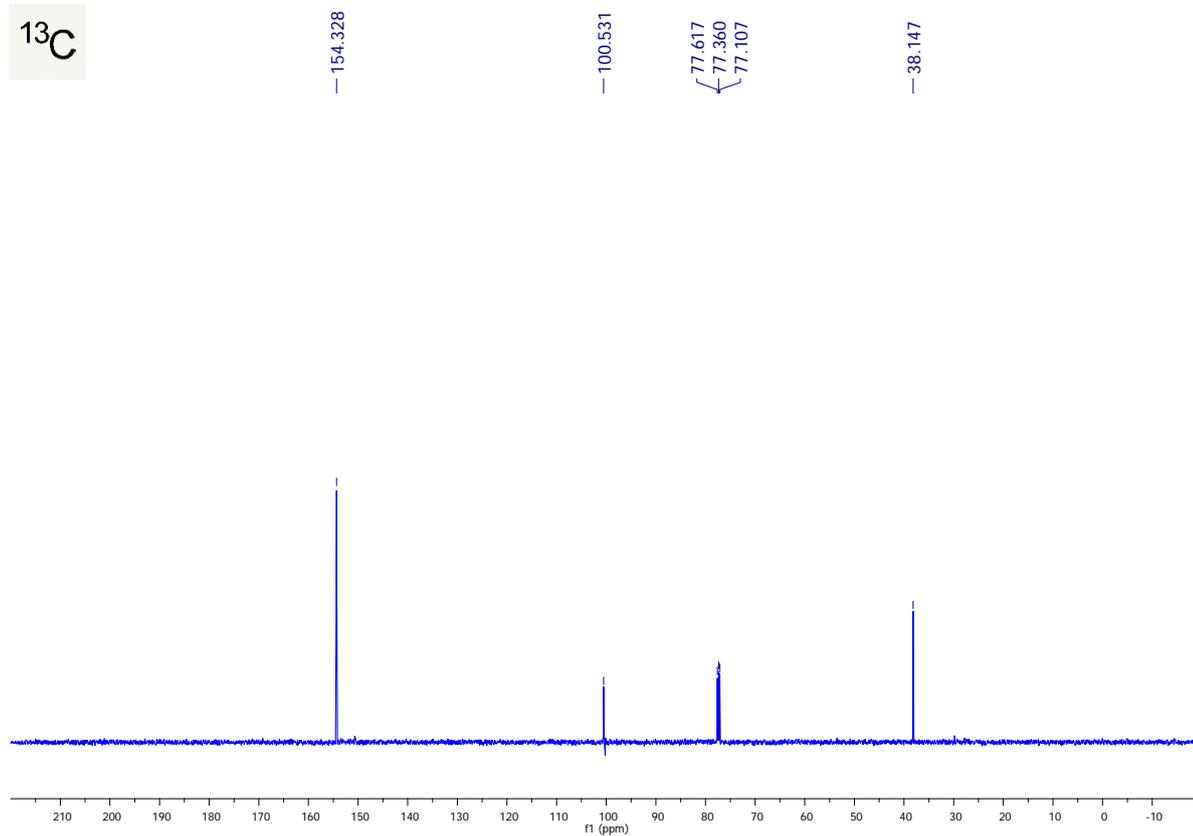
## 5-Iodo-1-methyl-1H-pyrazole (6i)

 $^1\text{H}$ 7.467  
7.462  
7.260  
6.422  
6.417  
3.934 $^{13}\text{C}$ 140.442  
114.878  
80.344  
76.677  
76.360  
76.043  
38.975

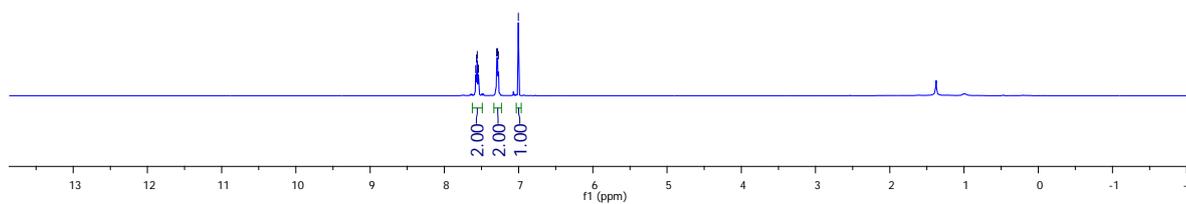
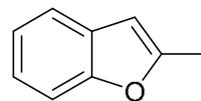
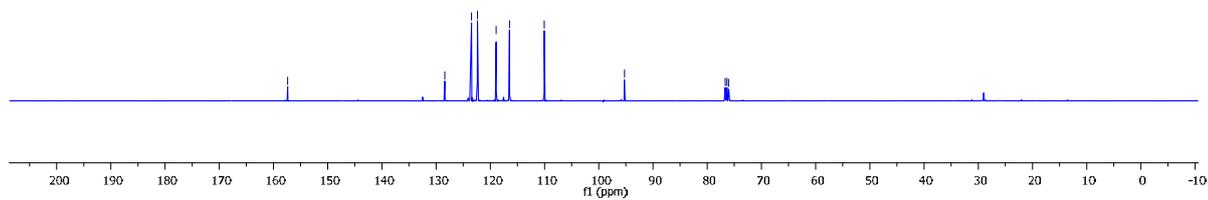
## 2-Iodo-1-methyl-1H-benzo[d]imidazole (6k)

 $^1\text{H}$  $^{13}\text{C}$ 

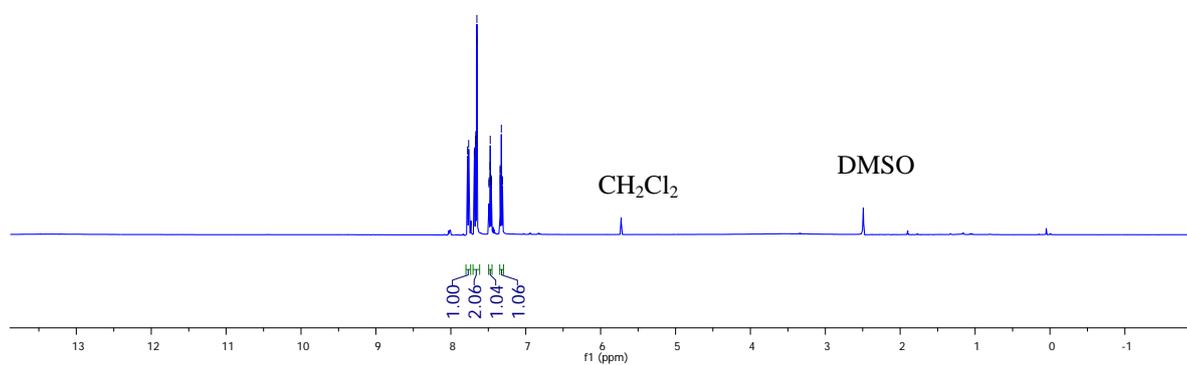
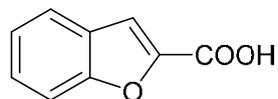
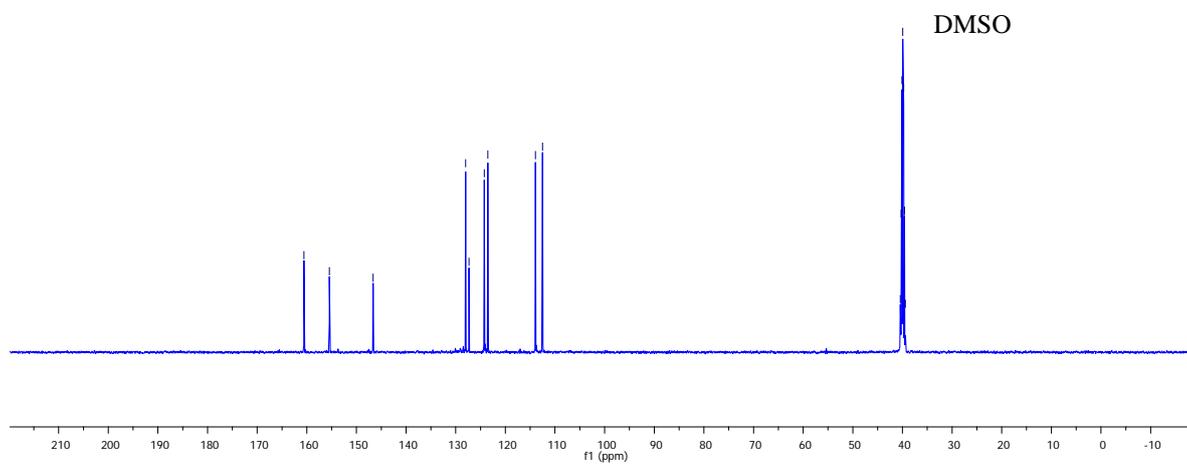
## 5-Iodo-1-methyl-1H-1,2,4-triazole (6l)

 $^1\text{H}$  $^{13}\text{C}$ 

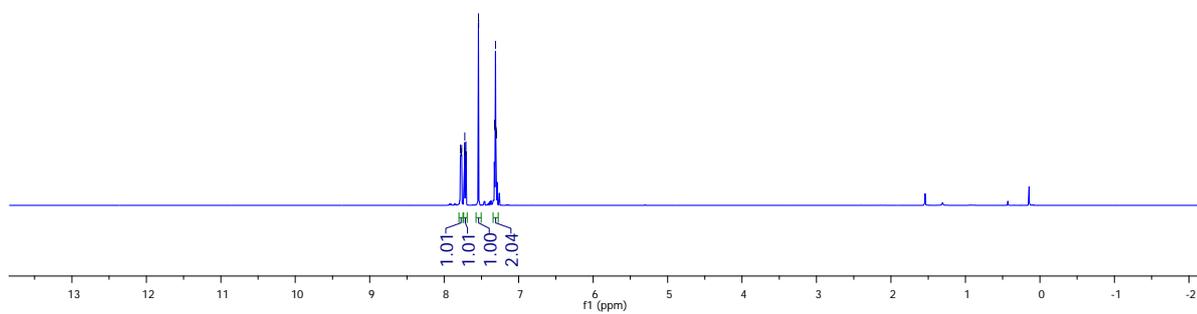
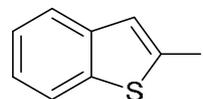
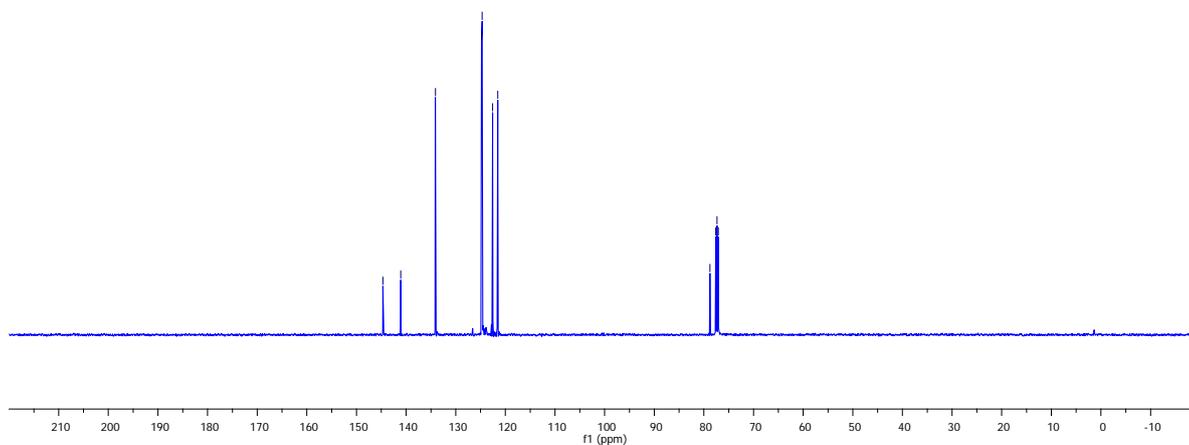
## 2-Iodobenzofuran (6m)

 $^1\text{H}$ 7.578  
7.566  
7.556  
7.541  
7.295  
7.284  
7.273  
7.003 $^{13}\text{C}$ 157.386  
128.402  
122.379  
116.465  
110.066  
95.264  
76.678  
76.360  
76.043

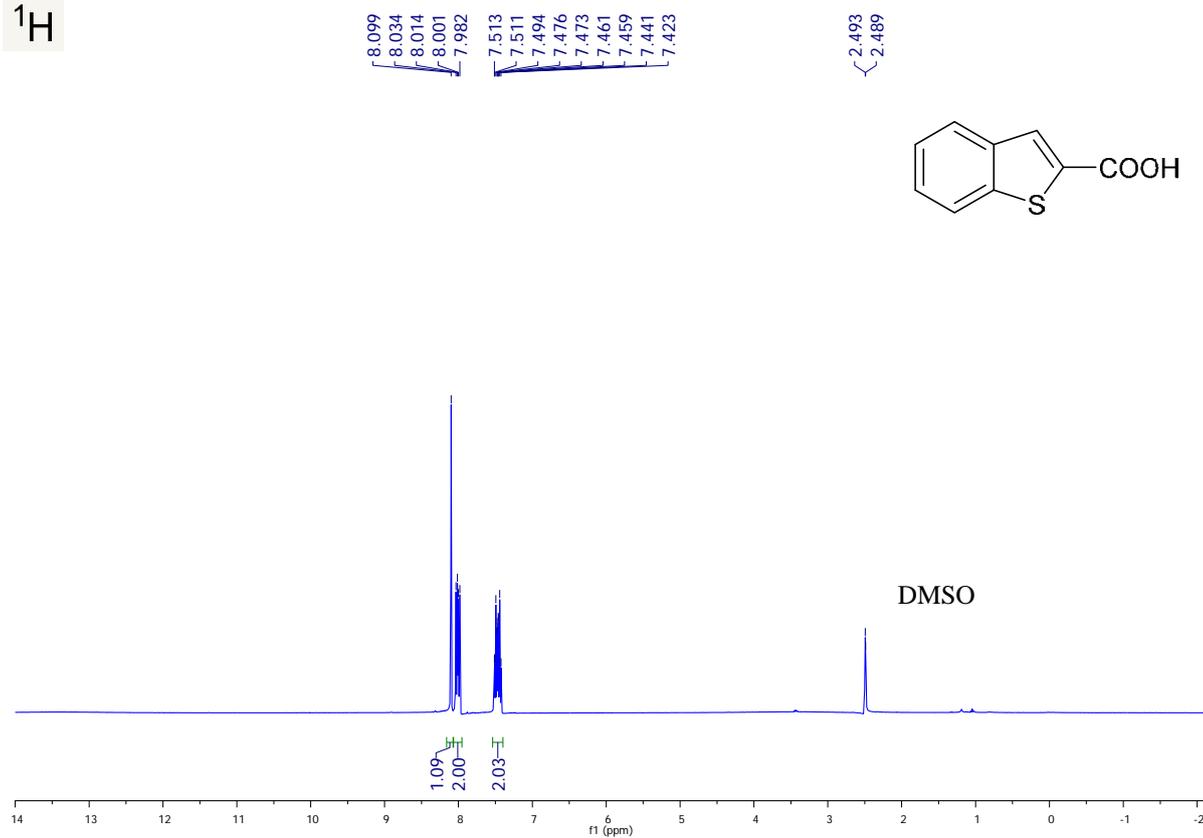
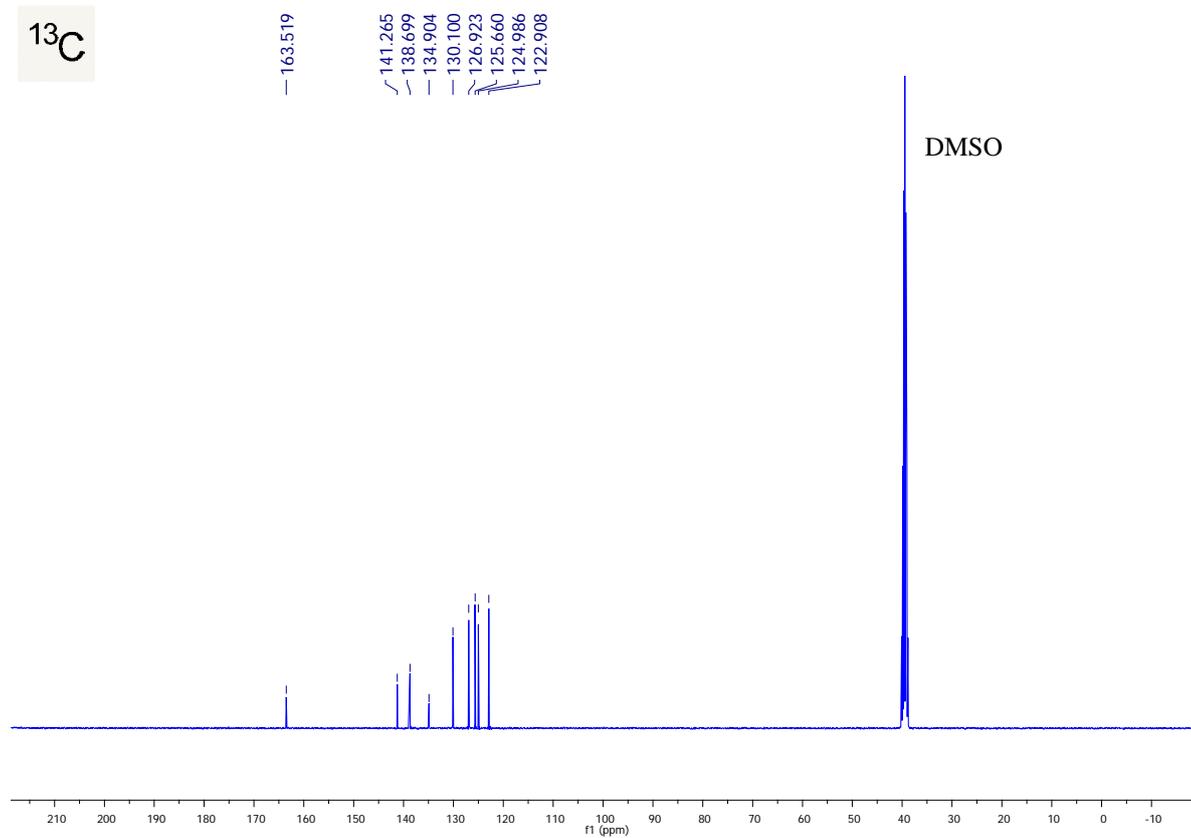
## Benzofuran-2-carboxylic acid (6m')

 $^1\text{H}$ 7.777  
7.761  
7.685  
7.684  
7.669  
7.667  
7.653  
7.651  
7.491  
7.488  
7.476  
7.474  
7.472  
7.460  
7.457  
7.341  
7.340  
7.326  
7.311  
7.310 $^{13}\text{C}$ 160.573  
155.456  
146.654  
127.997  
127.315  
124.259  
123.539  
113.949  
112.502  
40.430  
40.264  
40.096  
39.930  
39.762  
39.596  
39.429

## 2-Iodobenzo[b]thiophene (6n)

 $^1\text{H}$ 7.783  
7.781  
7.769  
7.768  
7.764  
7.727  
7.723  
7.715  
7.711  
7.710  
7.539  
7.539  
7.324  
7.321  
7.317  
7.311  
7.306  
7.301  
7.298 $^{13}\text{C}$ 144.686  
141.092  
134.096  
124.800  
124.669  
122.572  
121.531  
78.771  
77.613  
77.360  
77.107

## Benzo[b]thiophene-2-carboxylic acid (6n')

 $^1\text{H}$  $^{13}\text{C}$ 

## 2-Iodothiophene (6o) + 2,5-Diiodothiophene (6o')

 $^1\text{H}$ 7.301  
7.298  
7.290  
7.288  
7.185  
7.183  
7.178  
7.176  
6.870  
6.746  
6.738  
6.735  
6.727