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# Supplementary Information

# Accessible bidentate diol functionality within highly ordered composite periodic mesoporous organosilicas

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**Contents:**



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## 1. Solid-state NMR characterization of materials

### 1.1 Deprotection of solid-state MeO- and MEMO-PMOs

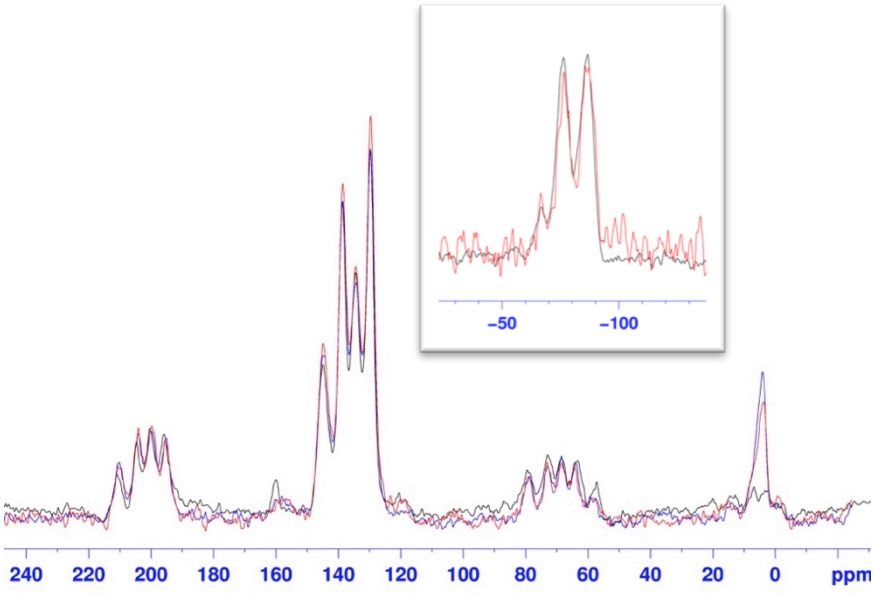



**Figure S1.** Solid-state $^{13}C$ CP MAS NMR of MeO-cPMO before deprotection (black), passivated with TMS and subsequently deprotected with boron tribromide over 24 hours at room temperature (blue), and subjected to deprotection a second time using the same conditions (red); and $^{29}Si$ NMR (inset) of MeO-cPMO material before (black) and after (red) deprotection

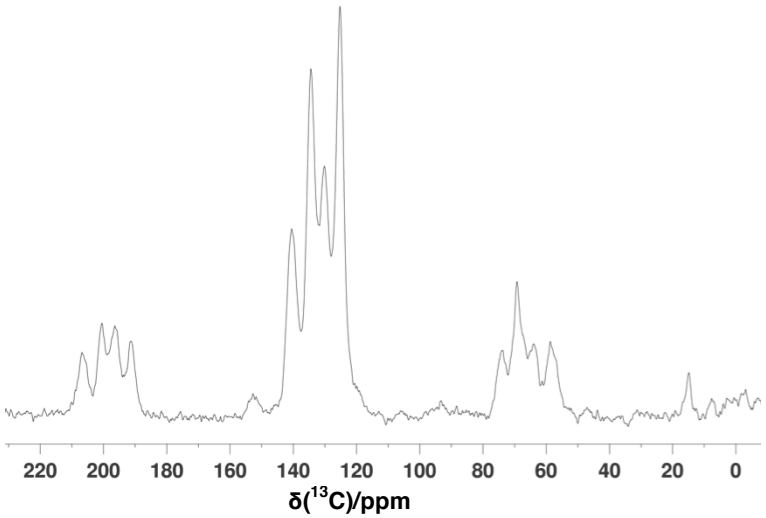



**Figure S2.** Solid-state $^{13}C$ CP MAS NMR spectra of $^{20}$MEMO-cPMO, after extraction of the surfactant with acidified ethanol

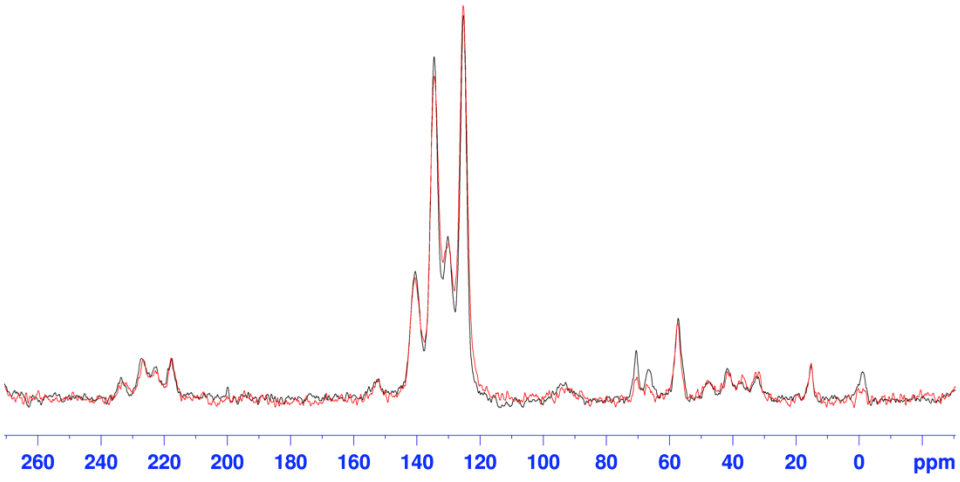



**Figure S3.** Solid-state $^{13}C$ CP MAS NMR of TMS-passivated MEMO-PMO treated with acidified ethanol at 55 $^{o}C$ for 6 hours (black) and subsequently treated for 24 hours (red) to cleave MEM groups

## 1.2 Preparation of phosphate ester materials

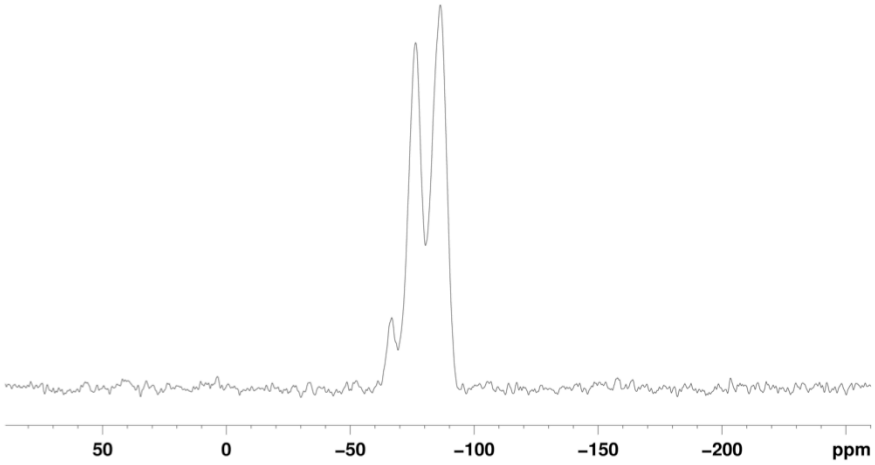



**Figure S4.** Solid-state $^{29}$Si CP MAS NMR of BTESBp PMO treated with phosphorus oxychloride

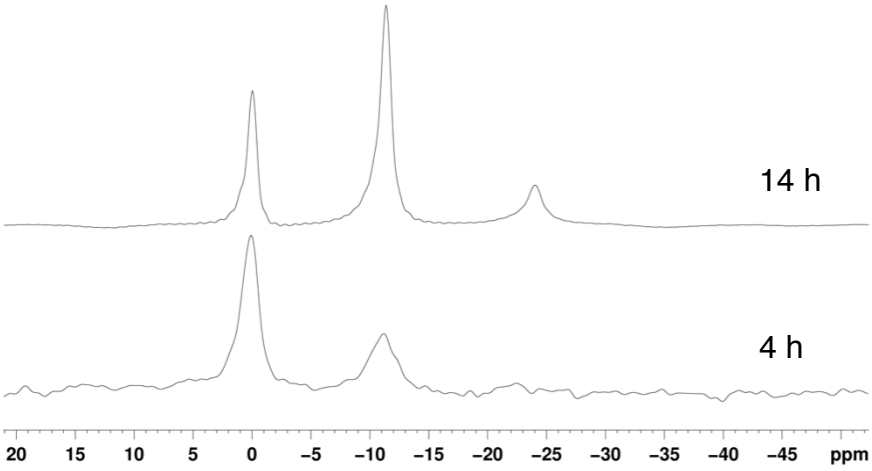



**Figure S5.** Solid-state $^{31}$P MAS NMR of MCM-41 treated with $POCl_3$ for 4 h or 14 h to prepare HOP(O)-MCM showed an increase in the -12, -22 ppm signals with longer treatment times, indicating a higher degree of $[O=P\text{-}(OSi)(OH)_2]$ and $[O=P\text{-}(OSi)_2(OH)]$ formation at longer exposures

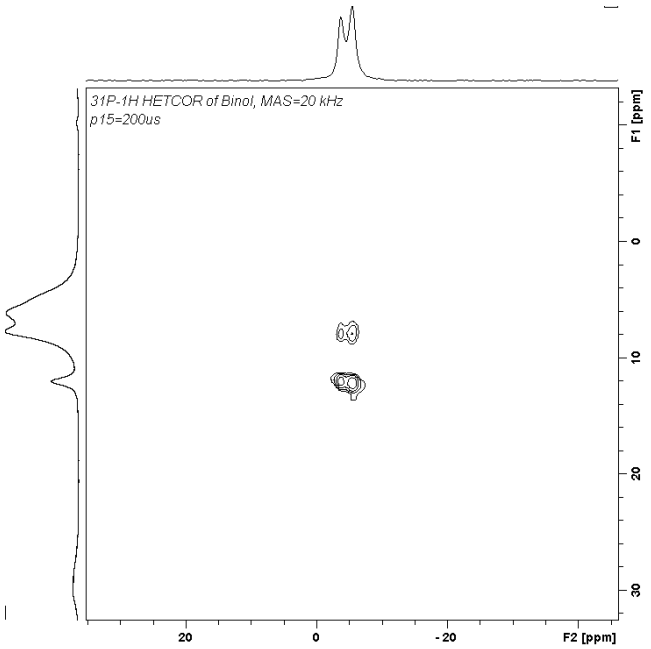
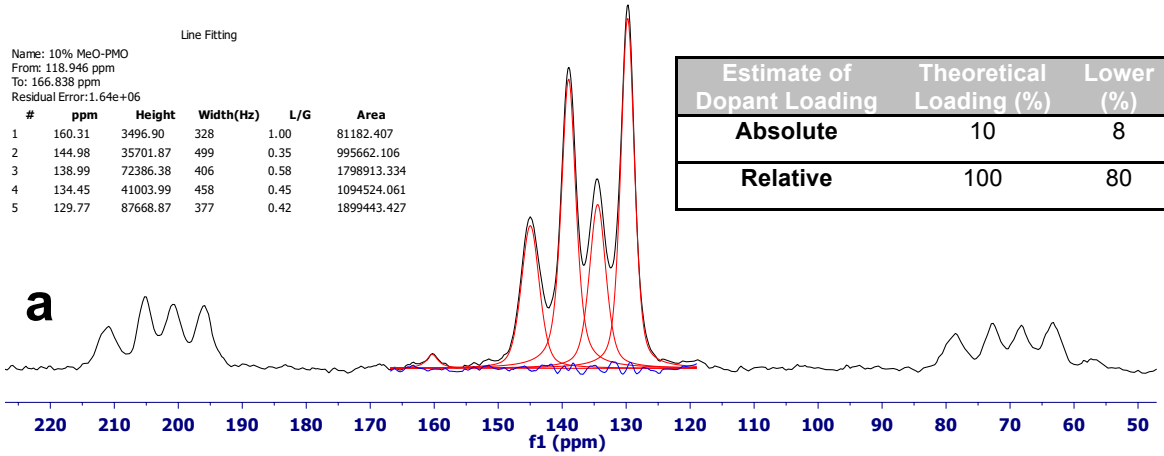



**Figure S6.** High-field solid –state $^{31}$P-$^{1}$H HETCOR spectra of BINOL hydrogen phosphate reference

## 1.3 Deconvolution and line fitting of solid-state $^{13}$C CP MAS NMR spectra




| Estimate of Dopant Loading | Theoretical Loading (%) | Lower (%) | Upper (%) |
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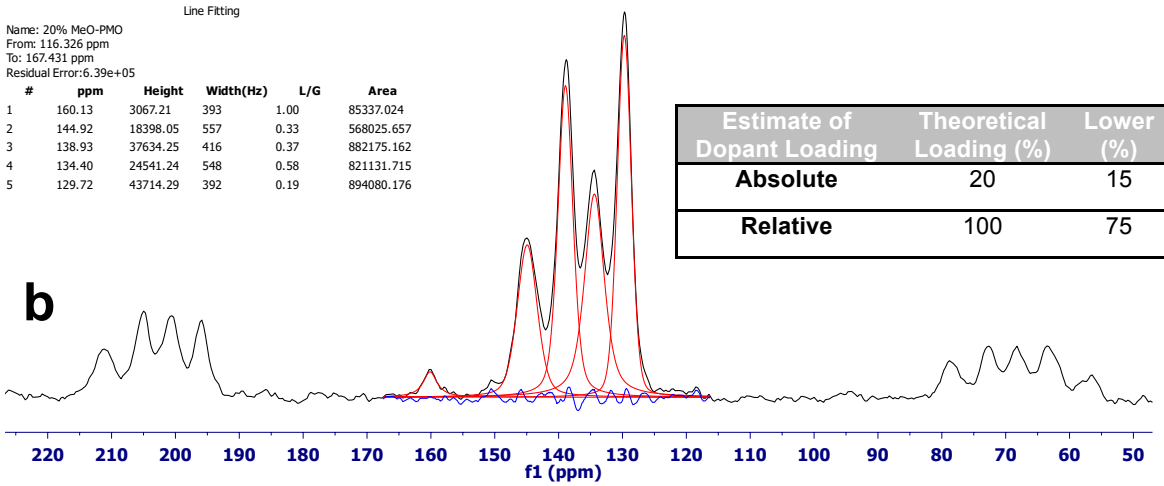
| **Absolute** | 10 | 8 | 9 |
| **Relative** | 100 | 80 | 90 |




| Estimate of Dopant Loading | Theoretical Loading (%) | Lower (%) | Upper (%) |
|---|---|---|---|
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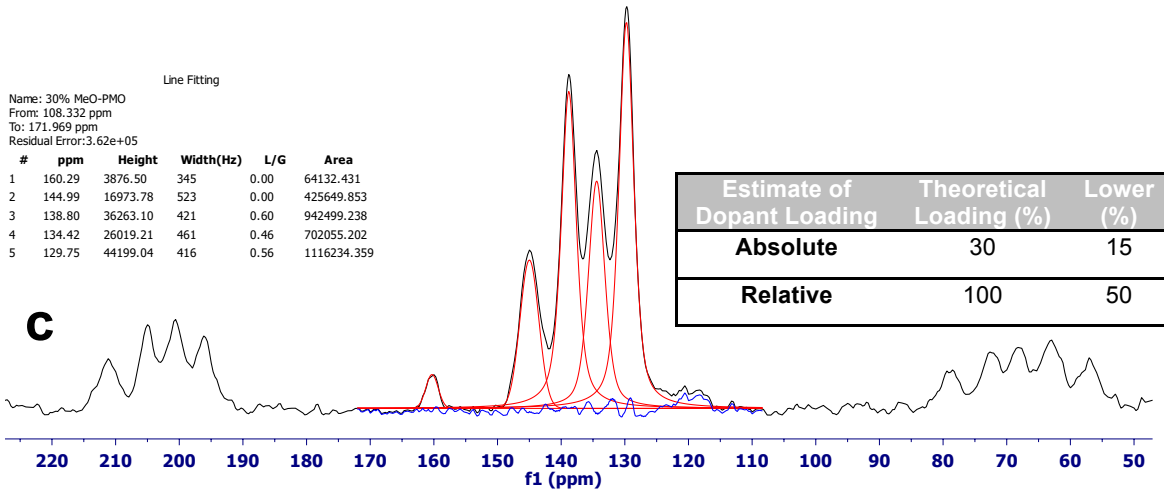
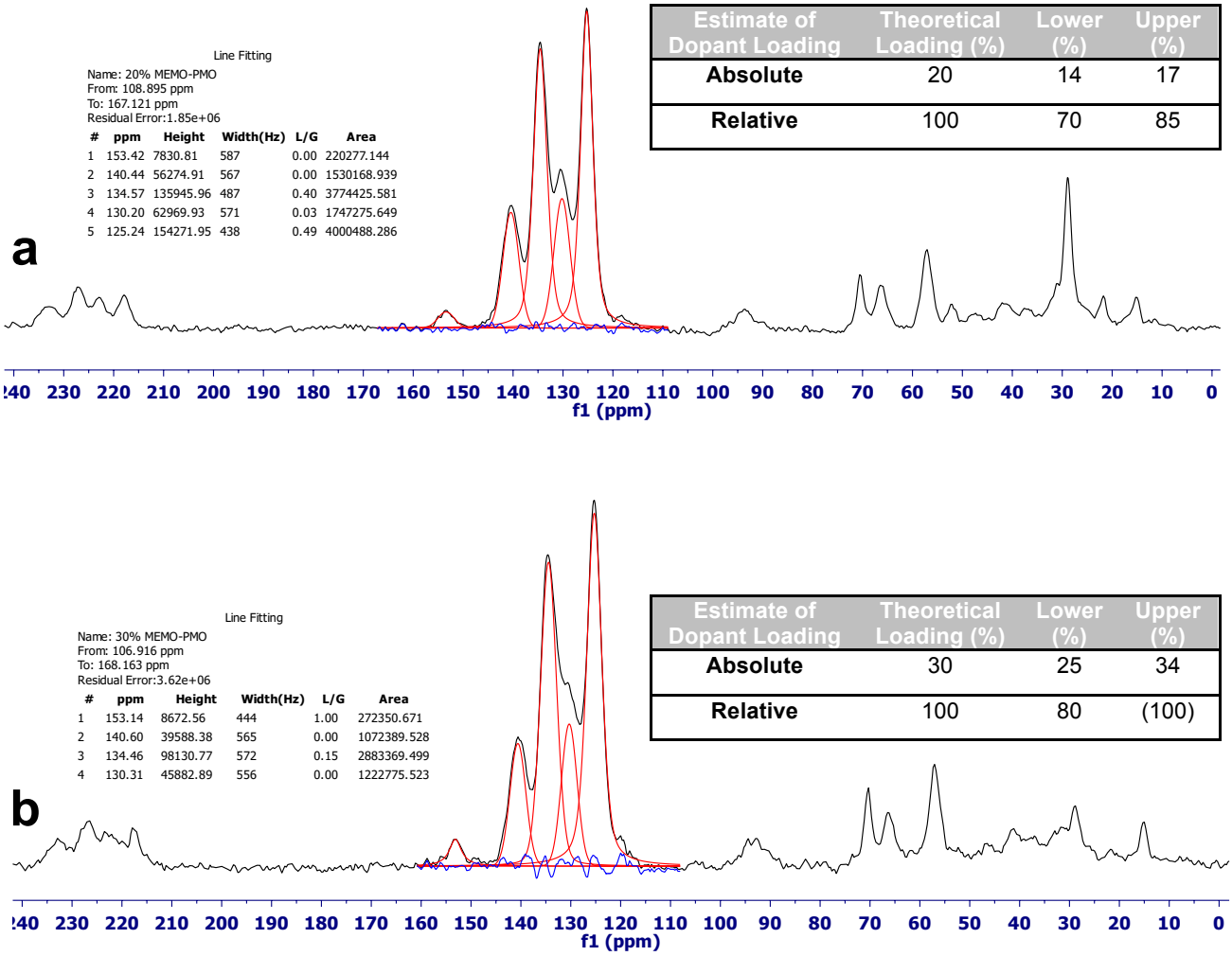
| **Relative** | 100 | 75 | 90 |




| Estimate of Dopant Loading | Theoretical Loading (%) | Lower (%) | Upper (%) |
|---|---|---|---|
| **Absolute** | 30 | 15 | 18 |
| **Relative** | 100 | 50 | 60 |

**Figure S 7.** Deconvolution and line fitting of $^{13}$C CP MAS NMR spectra of a) $^{10}$MeO-PMO, b) $^{20}$MeO-PMO and; c) $^{30}$MeO-PMO showing fitted peak area report and calculated estimates of dopant loadings relative to the theoretical loading




| Estimate of Dopant Loading | Theoretical Loading (%) | Lower (%) | Upper (%) |
|---|---|---|---|
| **Absolute** | 20 | 14 | 17 |
| **Relative** | 100 | 70 | 85 |

| Estimate of Dopant Loading | Theoretical Loading (%) | Lower (%) | Upper (%) |
|---|---|---|---|
| **Absolute** | 30 | 25 | 34 |
| **Relative** | 100 | 80 | (100) |

**Figure S 8.** Deconvolution and line fitting of $^{13}$C CP MAS NMR spectra of a) $^{20}$MEMO-PMO and; b) $^{30}$MEMO-PMO showing fitted peak area reports and calculated estimates of dopant loadings relative to the theoretical loading

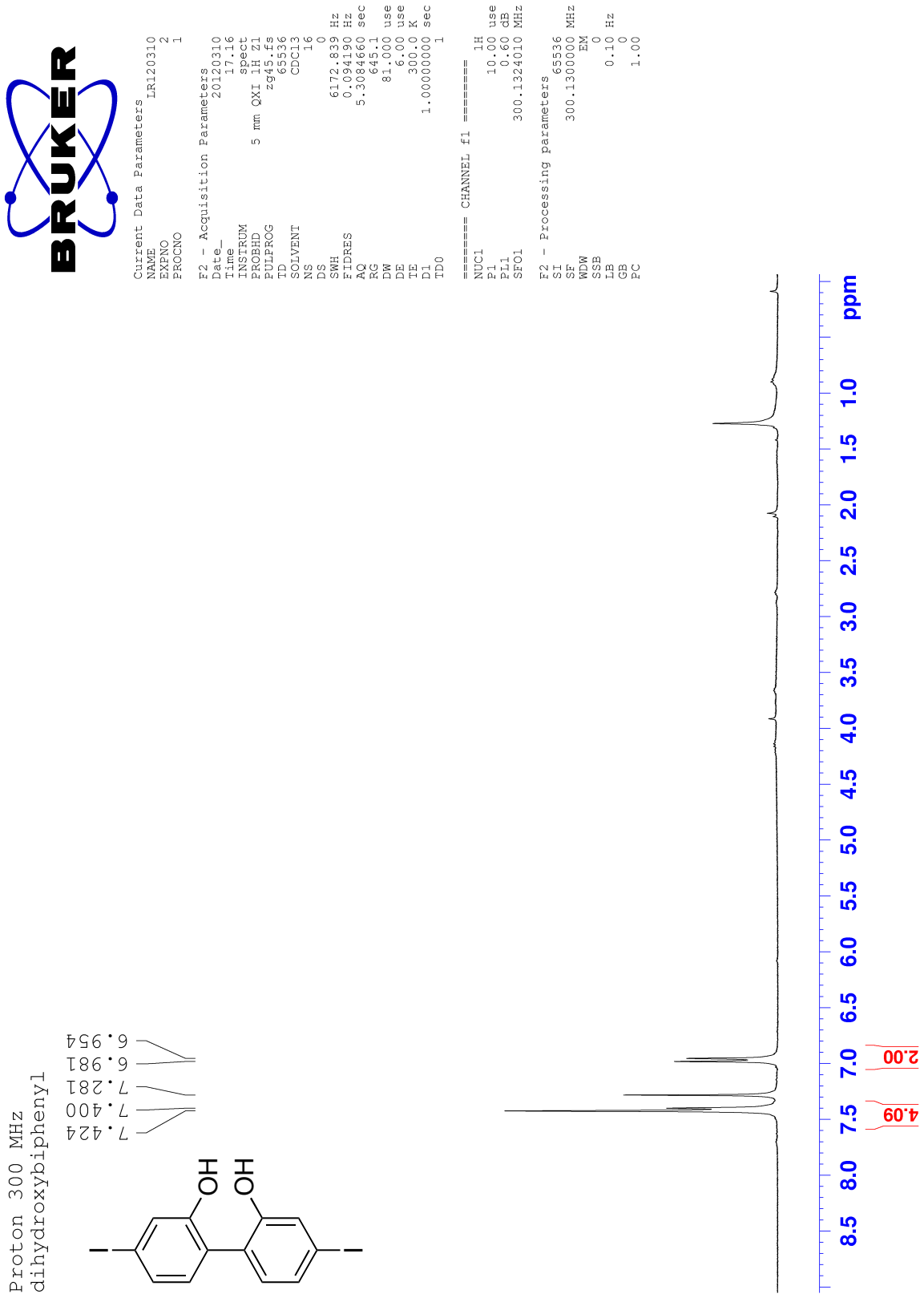
## Estimate calculations

Deconvolution was achieved using the line-fitting feature of MestRec Nova NMR processing software. Estimates were calculated based on the ratio of areas of peaks 1 and 2, representing quaternary carbon signals from (Ar)**C**-O (dopant) and (Ar)**C**-C(Ar) (bulk and dopant), respectively. The dopant (Ar)**C**-C(Ar) overlaps completely here and thus (Ar)**C**-C(Ar) (bulk) cannot be evaluated independently. Upper estimates subtract $Area_1$ of (Ar)**C**-O (dopant) from $Area_2$ (bulk + dopant overlapped with bulk). Lower limits assume $Area_1$ is negligible to $Area_2$ and the overlapped signal is not subtracted. See example calculation for $^{10}$MeO-PMO:

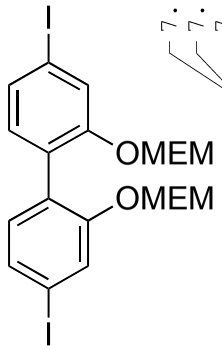
Lower estimate limit: $$\frac{mol\%\ dopant}{mol\%\ bulk} = \frac{Area_1}{Area_2} \times 100\% = \frac{81182.407}{995662.106} \times 100\% = 8\%$$

Upper estimate limit: $$\frac{mol\%\ dopant}{mol\%\ bulk} = \frac{Area_1}{(Area_2 - Area_1)} \times 100\% = \frac{81182.407}{(995662.106 - 81182.407)} \times 100\% = 9\%$$

## 2. NMR characterization of precursors



proton NMR on bbfo probe 400 MHz







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RG                            181
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DE                          6.00 usec
TE                         297.0 K
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TD0                             1

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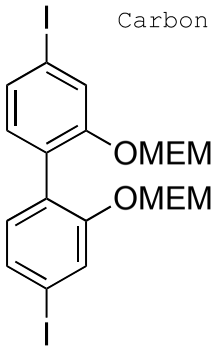
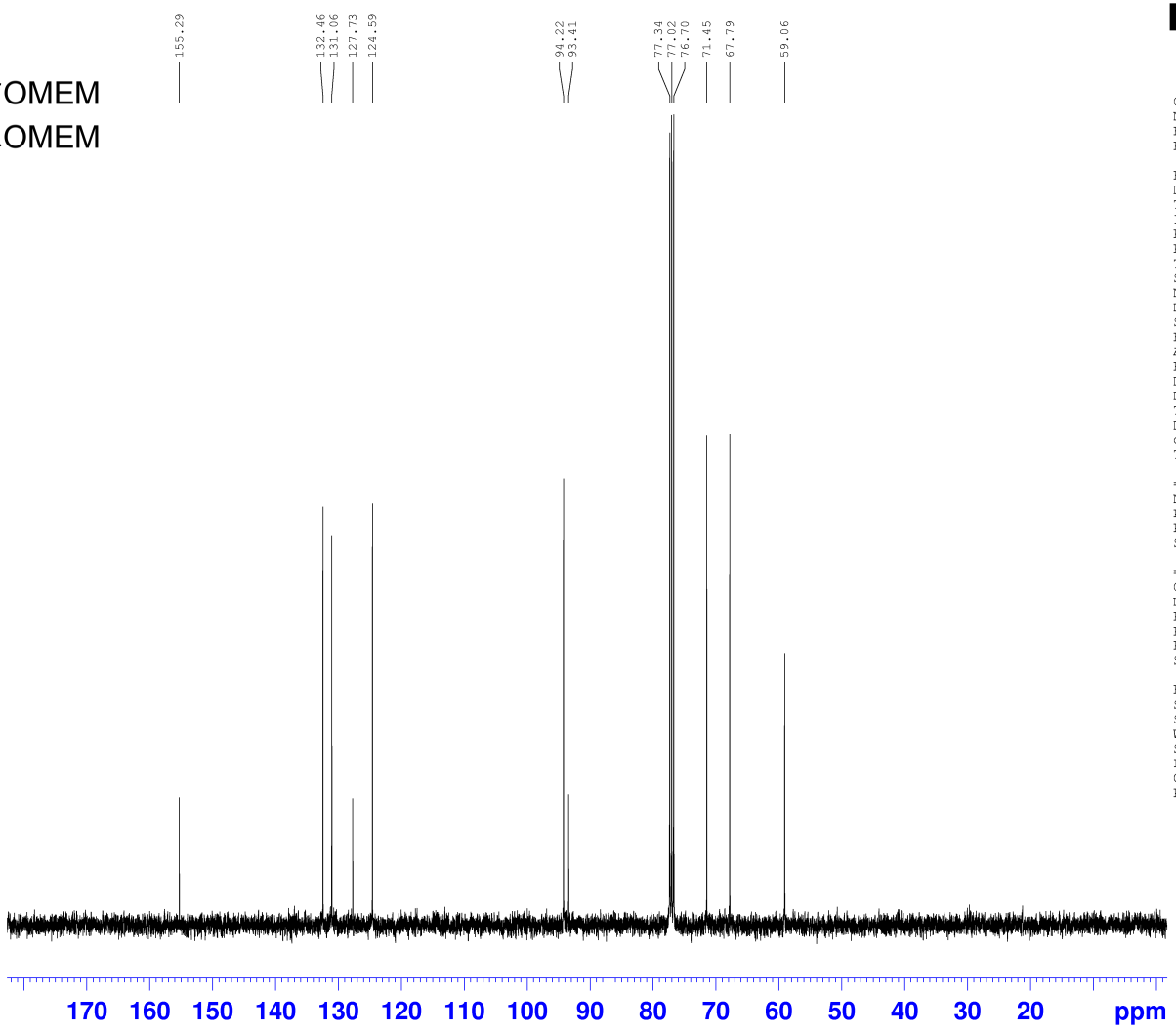
Carbon NMR on bbfo probe

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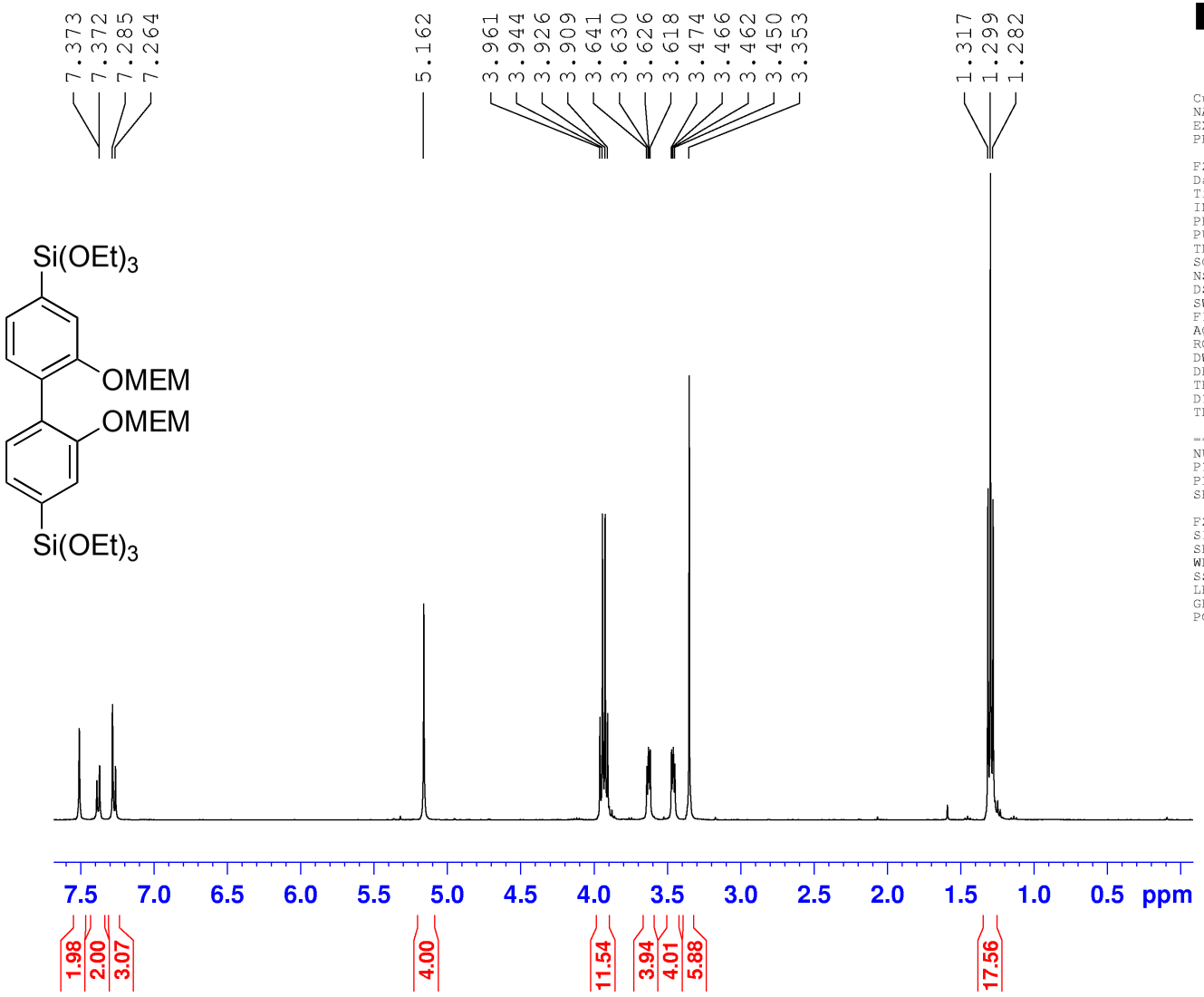
proton NMR on bbfo probe 400 MHz

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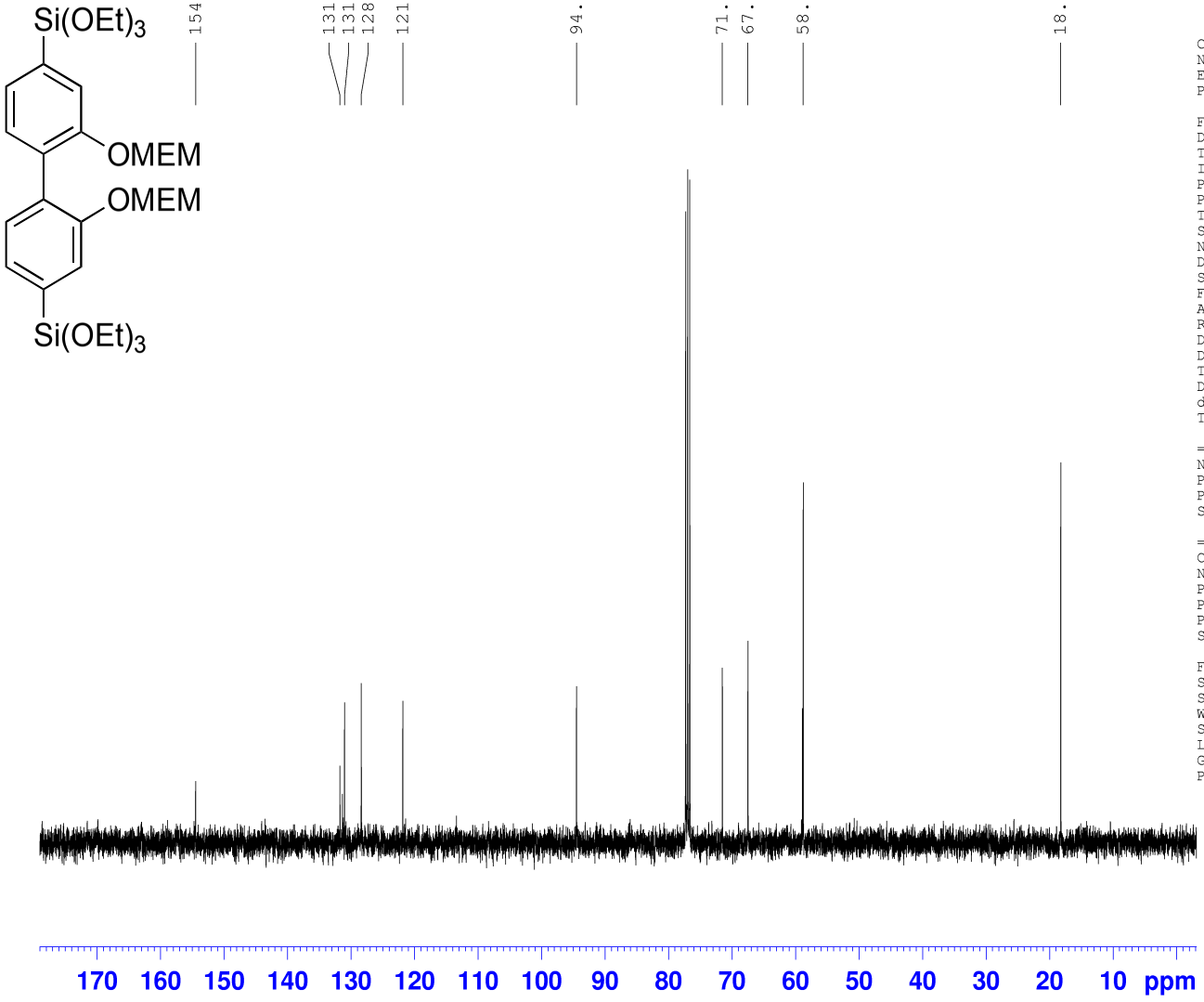


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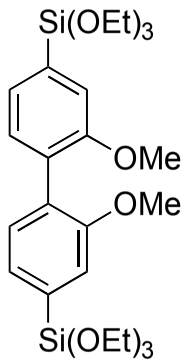
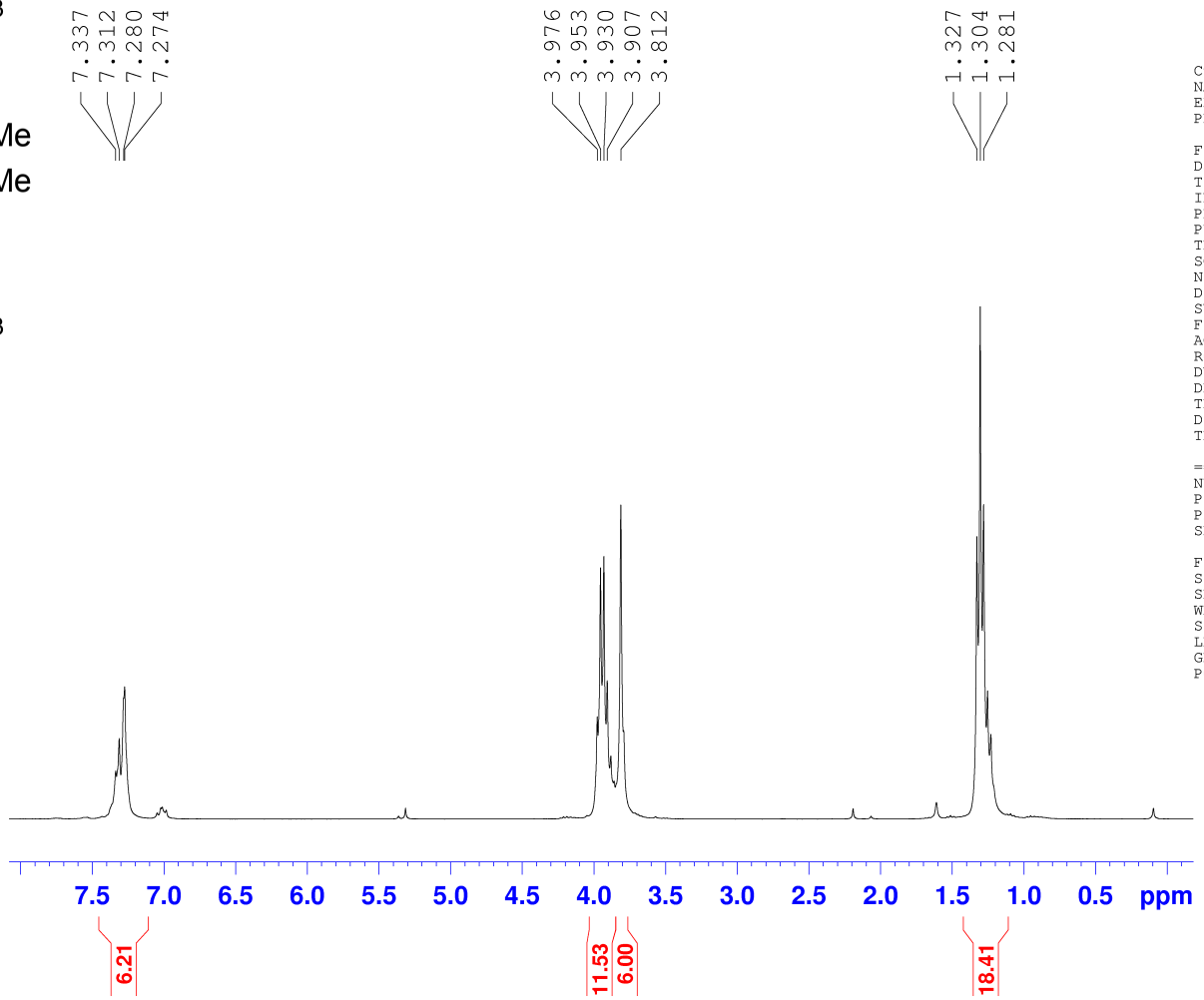
Proton 300 MHz

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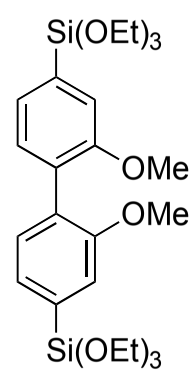
Carbon-13 {H}
75.47 MHz







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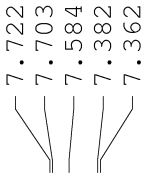
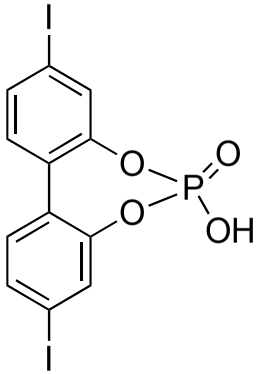
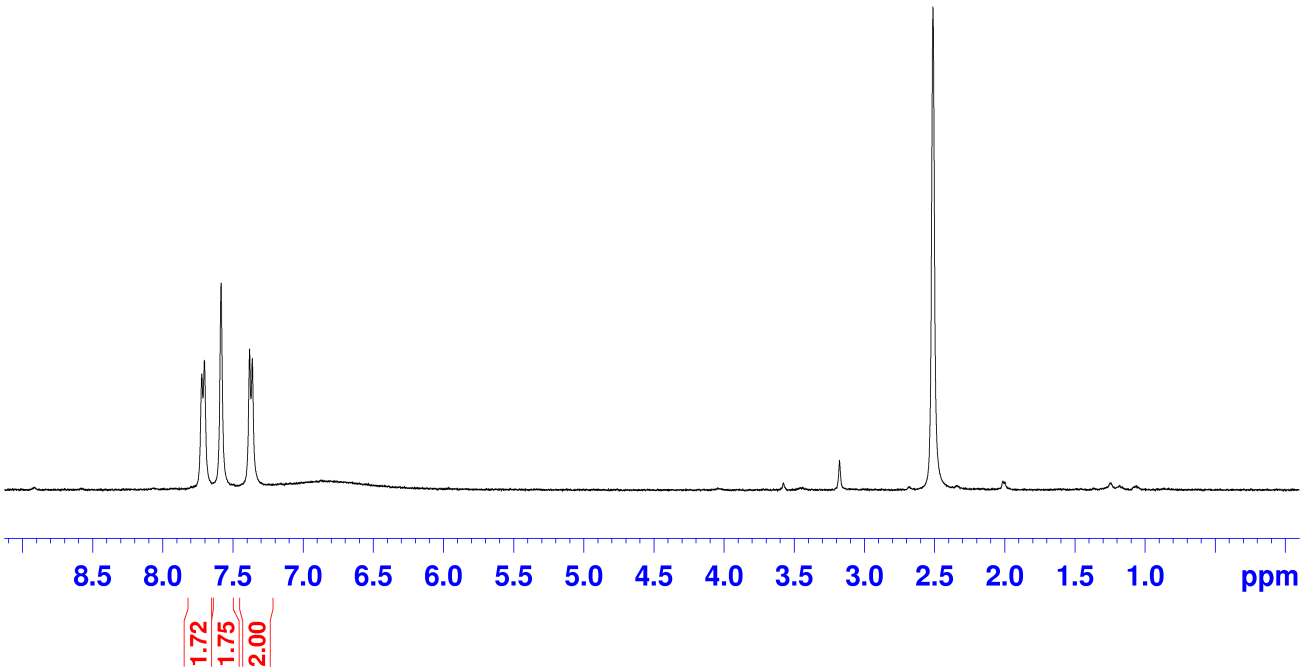
proton NMR on bbfo probe 400 MHz

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TE 295.7 K
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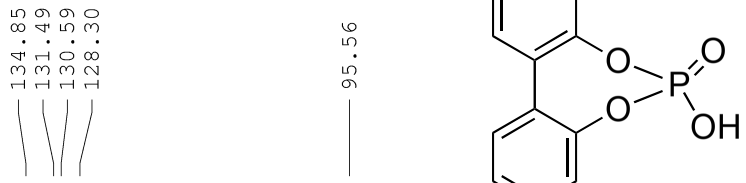
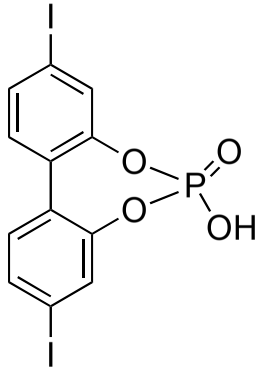
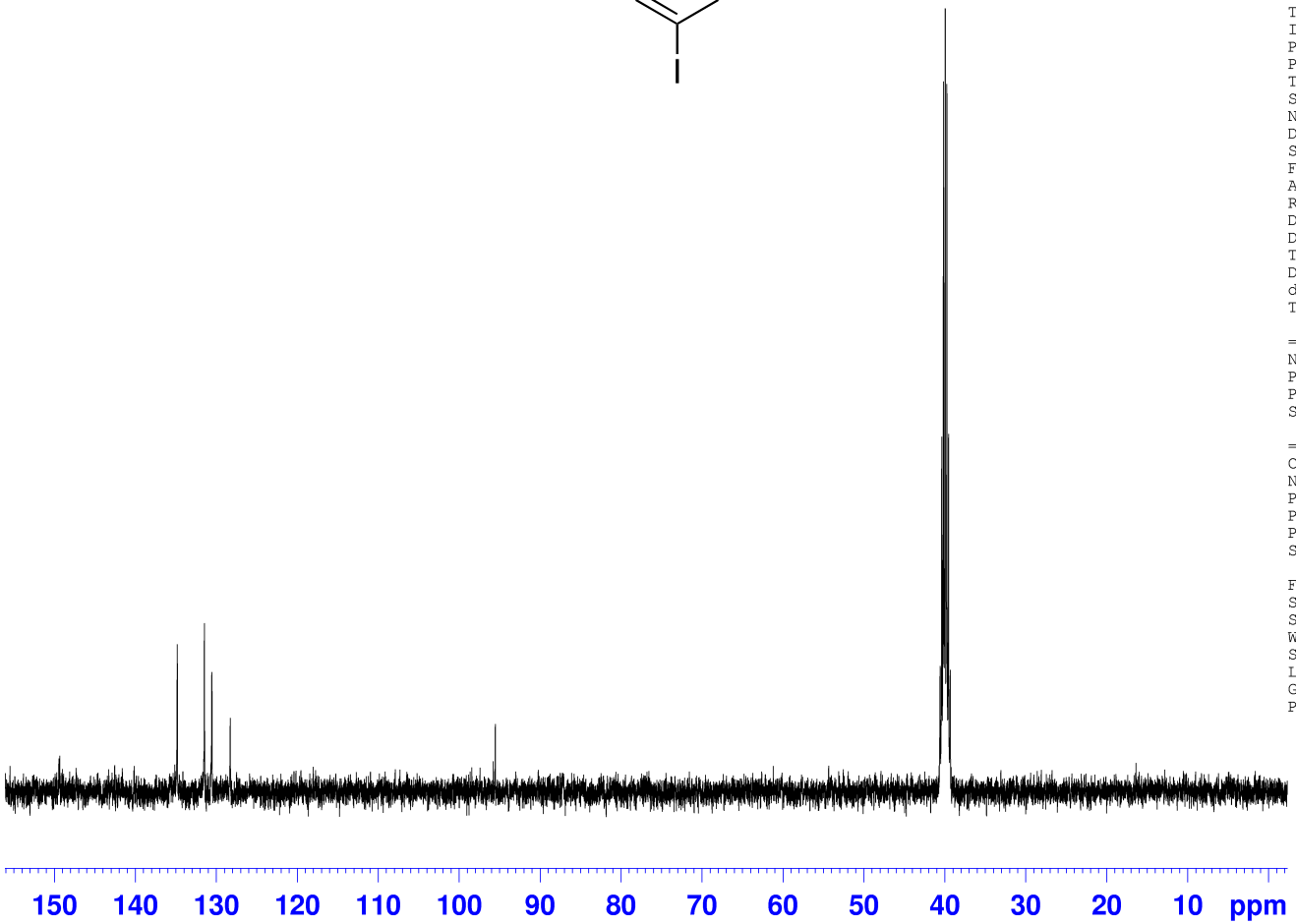
Carbon NMR on bbfo probe







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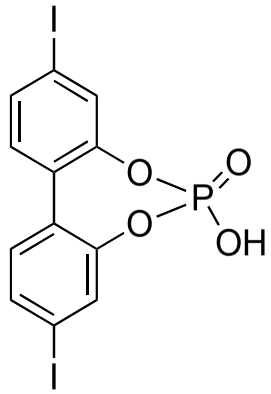
Phosphorus NMR on bbfo probe







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RG                         9195.2
DW                         19.275 use
DE                          27.54 use
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D1                     2.00000000 sec
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TD0                              1

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SFO1                  161.9753930 MHz

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PCPD2                       100.00 use
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PL12                         14.48 dB
SFO2                  400.1320007 MHz

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WDW                             EM
SSB                              0
LB                            5.00 Hz
GB                               0
PC                            1.40
```