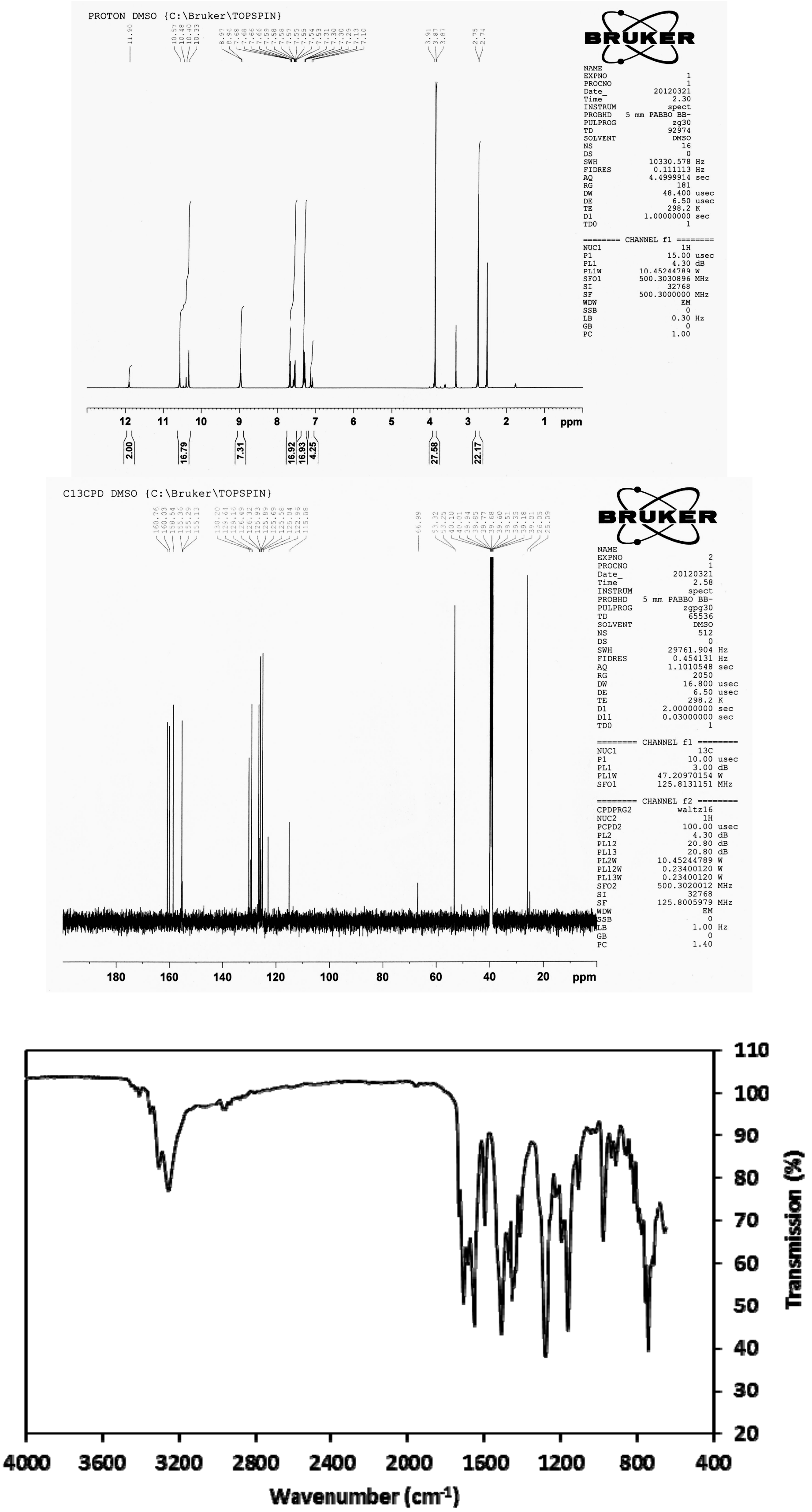
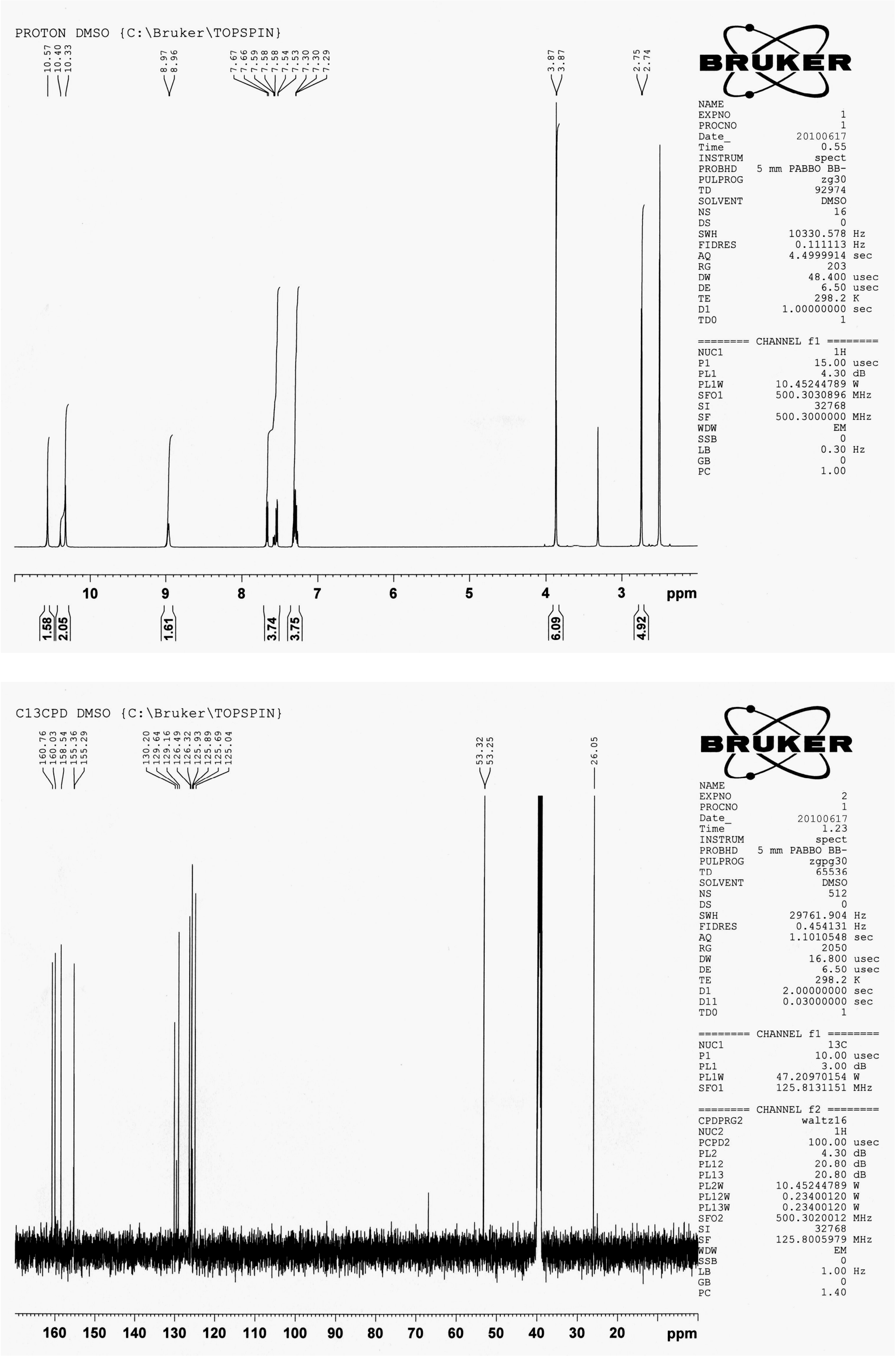


Fig. S1. ^1H (above), ^{13}C NMR (middle) and IR spectra (down) of the material obtained from the reaction of opbaH$_2$Et$_2$ with MeNH$_2$ in MeOH, referred to as crude.



```
NAME
EXPNO                    1
PROCNO                   1
Date_             20100617
Time                  0.55
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG               zg30
TD                   92974
SOLVENT               DMSO
NS                      16
DS                       0
SWH             10330.578 Hz
FIDRES           0.111113 Hz
AQ              4.4999914 sec
RG                     203
DW                  48.400 usec
DE                    6.50 usec
TE                   298.2 K
D1             1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   15.00 usec
PL1                   4.30 dB
PL1W           10.45244789 W
SFO1           500.3030896 MHz
SI                   32768
SF             500.3000000 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

```
NAME
EXPNO                    2
PROCNO                   1
Date_             20100617
Time                  1.23
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT               DMSO
NS                     512
DS                       0
SWH             29761.904 Hz
FIDRES           0.454131 Hz
AQ              1.1010548 sec
RG                    2050
DW                  16.800 usec
DE                    6.50 usec
TE                   298.2 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                   10.00 usec
PL1                   3.00 dB
PL1W           47.20970154 W
SFO1           125.8131151 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2               100.00 usec
PL2                   4.30 dB
PL12                 20.80 dB
PL13                 20.80 dB
PL2W           10.45244789 W
PL12W           0.23400120 W
PL13W           0.23400120 W
SFO2           500.3020012 MHz
SI                   32768
SF             125.8005979 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

Fig. S2. ^{1}H (above) and ^{13}C NMR spectra (below) of the recrystallized crude from MeOH and MeOH:THF (1:1), repectively.

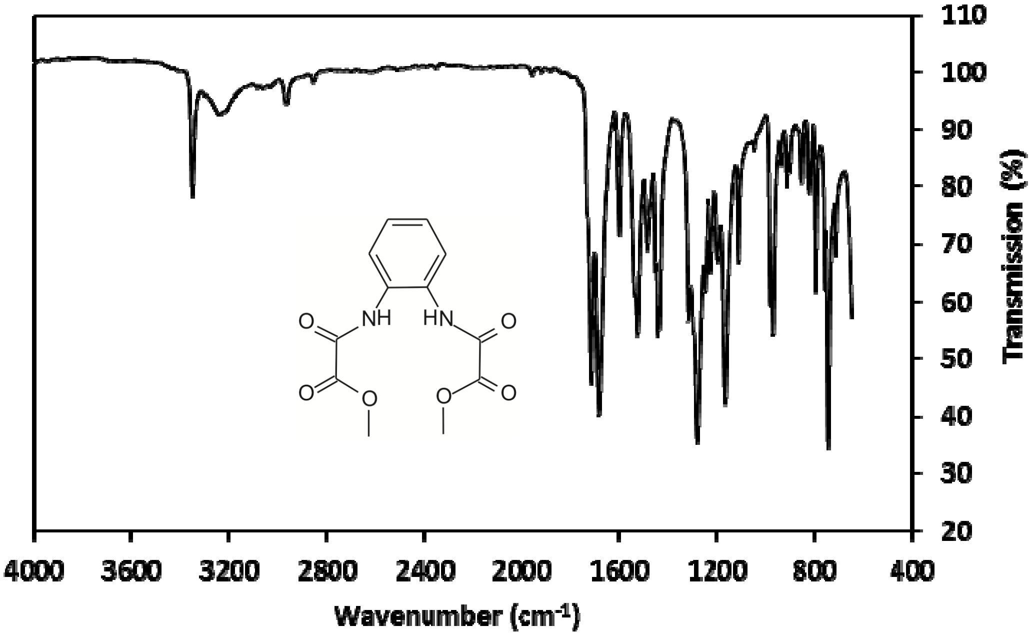
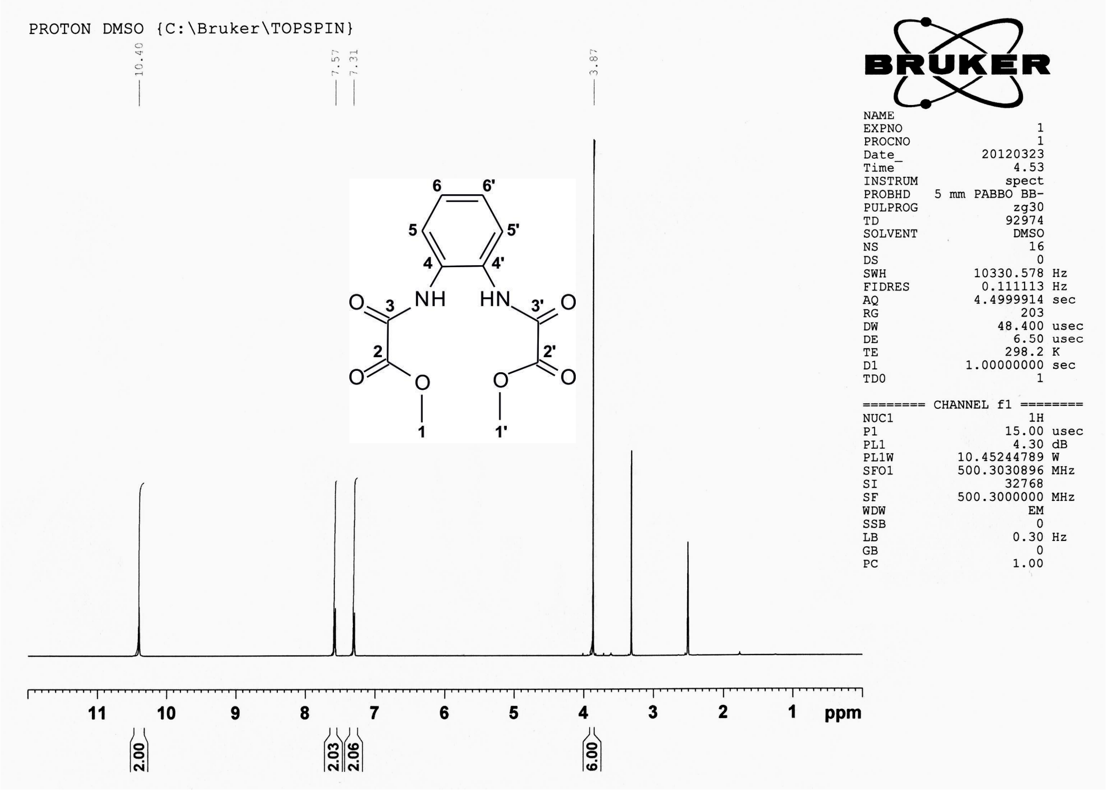
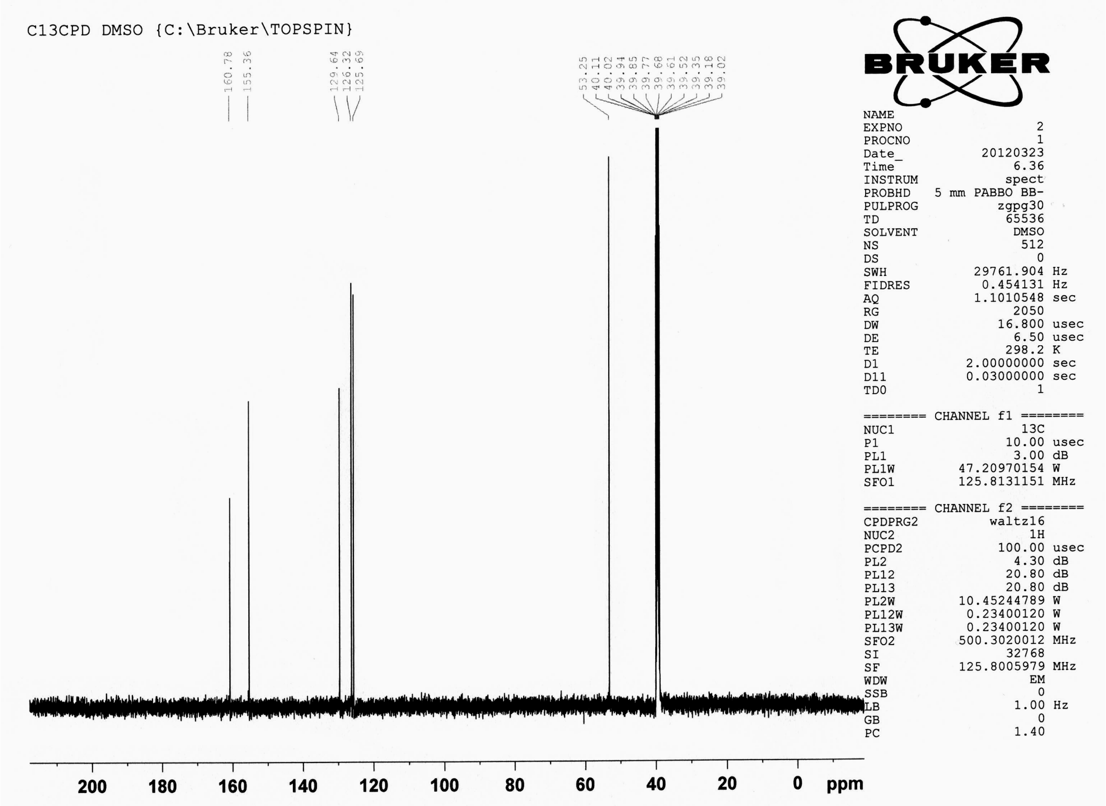


Fig. S3. IR spectrum of opbaH_2Me_2 (**2**).



```
PROTON DMSO {C:\Bruker\TOPSPIN}
```

```
NAME
EXPNO                     1
PROCNO                    1
Date_              20120323
Time                   4.53
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    92974
SOLVENT                DMSO
NS                       16
DS                        0
SWH           10330.578 Hz
FIDRES         0.111113 Hz
AQ            4.4999914 sec
RG                      203
DW               48.400 usec
DE                 6.50 usec
TE                298.2 K
D1           1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                15.00 usec
PL1                4.30 dB
PL1W        10.45244789 W
SFO1        500.3030896 MHz
SI                    32768
SF          500.3000000 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```



```
C13CPD DMSO {C:\Bruker\TOPSPIN}
```

```
NAME
EXPNO                     2
PROCNO                    1
Date_              20120323
Time                   6.36
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT                DMSO
NS                      512
DS                        0
SWH           29761.904 Hz
FIDRES         0.454131 Hz
AQ            1.1010548 sec
RG                     2050
DW               16.800 usec
DE                 6.50 usec
TE                298.2 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                10.00 usec
PL1                3.00 dB
PL1W        47.20970154 W
SFO1        125.8131151 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2            100.00 usec
PL2                4.30 dB
PL12              20.80 dB
PL13              20.80 dB
PL2W        10.45244789 W
PL12W        0.23400120 W
PL13W        0.23400120 W
SFO2        500.3020012 MHz
SI                    32768
SF          125.8005979 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```

Fig. S4. ^{1}H (above) and ^{13}C NMR spectra (below) of opbaH$_2$Me$_2$ (**2**).

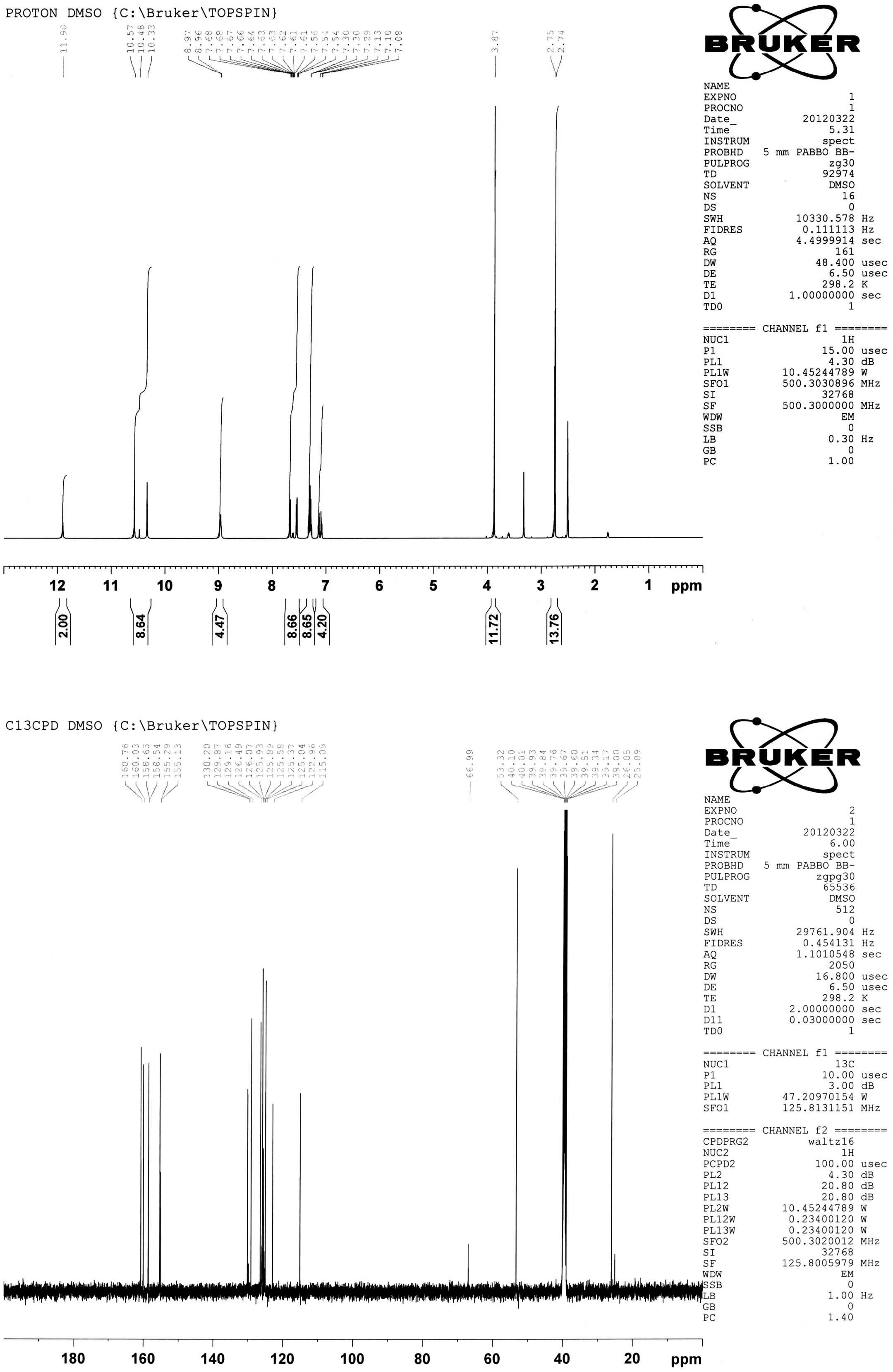


Fig. S5. ^{1}H (above) and ^{13}C NMR spectra (below) of the residue **B**.

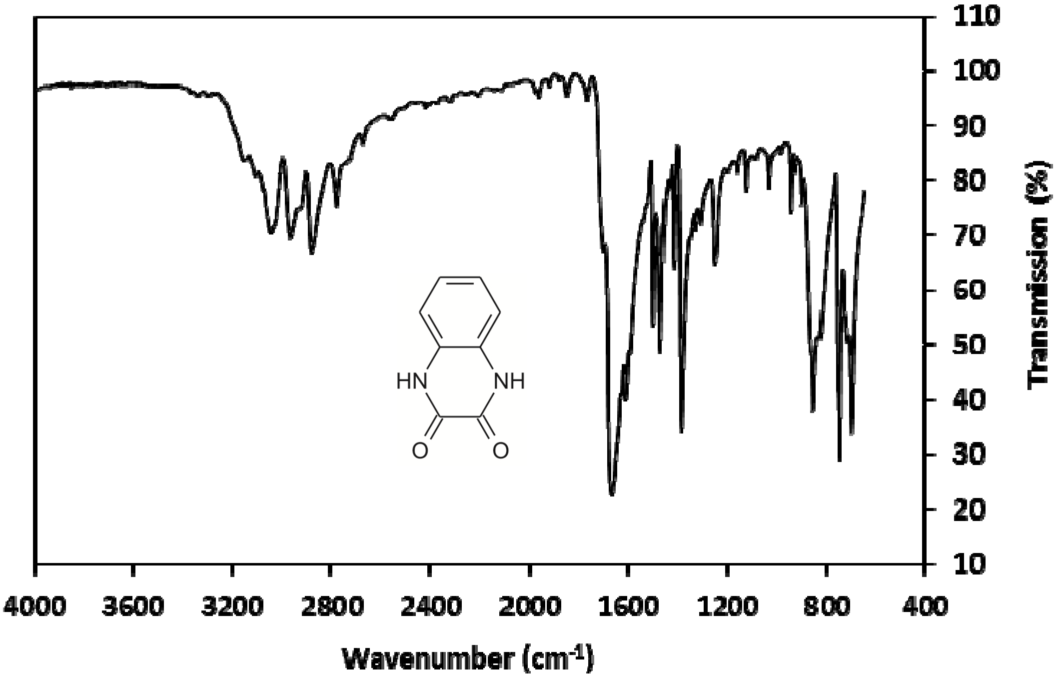
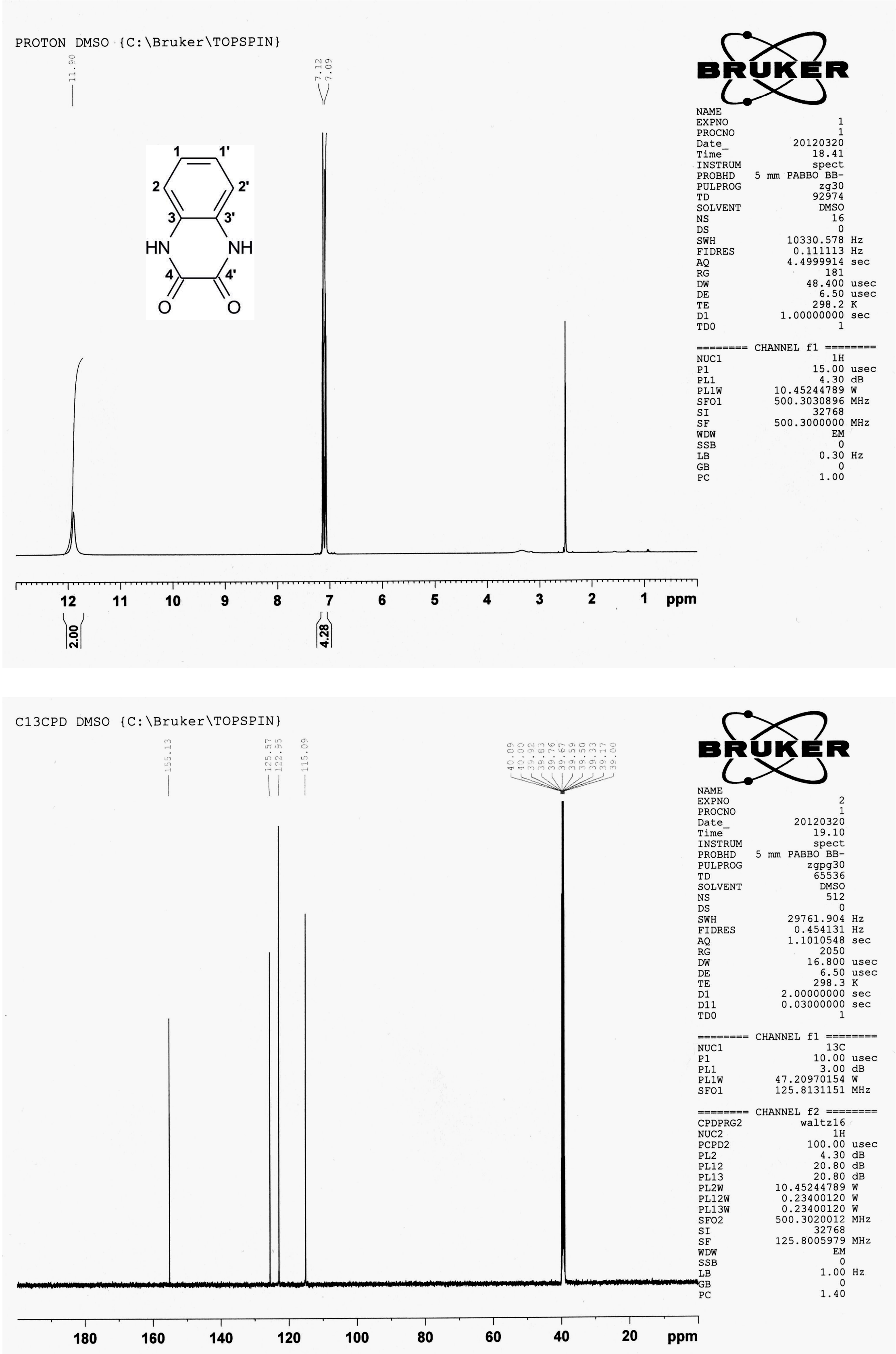


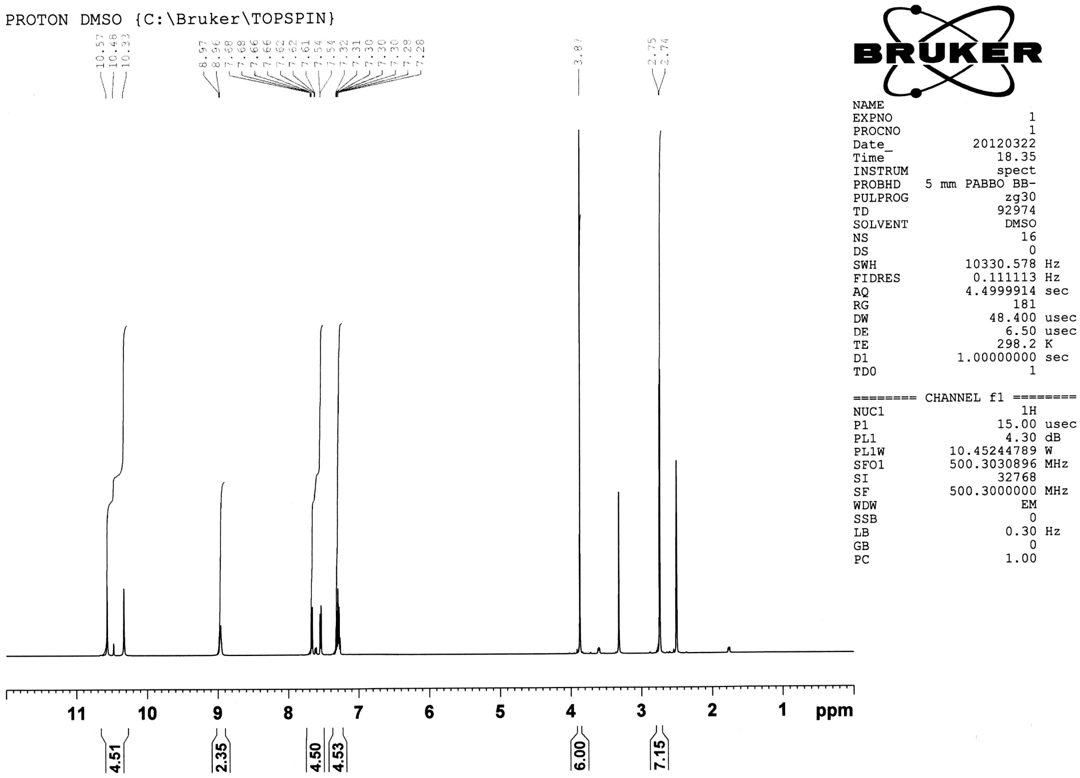
Fig. S6. IR spectrum of 1,4-dihydro-2,3-quinoxalinedione (**3**).



```
NAME
EXPNO                   1
PROCNO                  1
Date_            20120320
Time                18.41
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  92974
SOLVENT              DMSO
NS                     16
DS                      0
SWH             10330.578 Hz
FIDRES           0.111113 Hz
AQ              4.4999914 sec
RG                    181
DW                 48.400 usec
DE                   6.50 usec
TE                  298.2 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  15.00 usec
PL1                  4.30 dB
PL1W          10.45244789 W
SFO1        500.3030896 MHz
SI                  32768
SF          500.3000000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

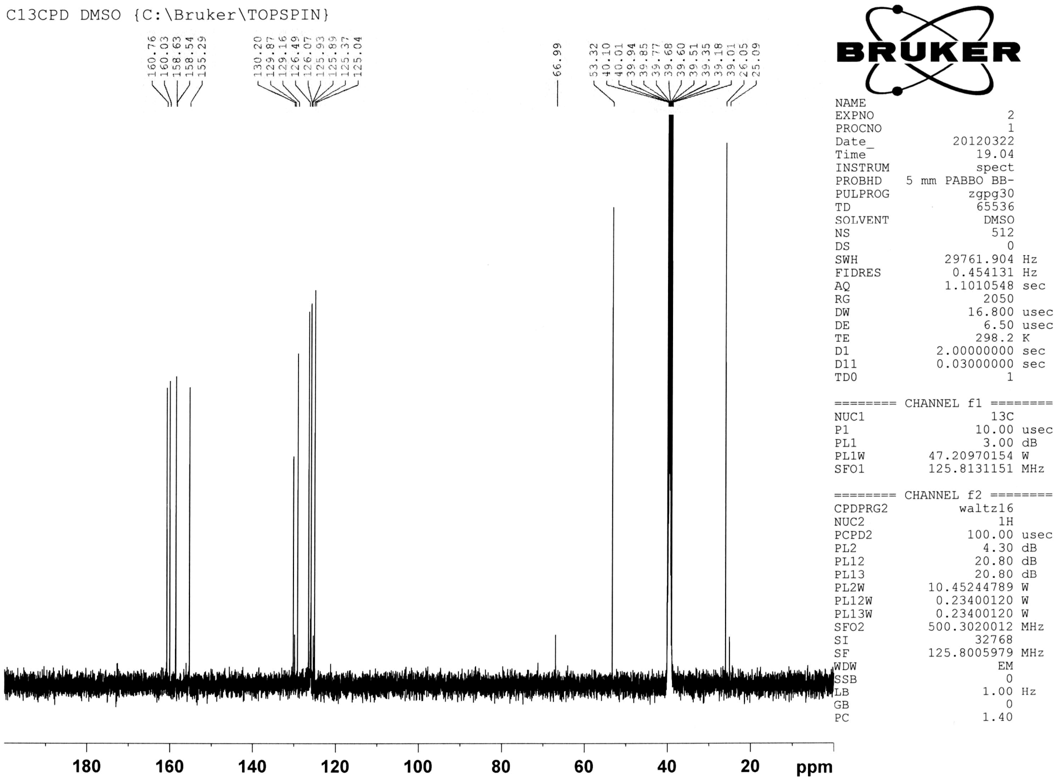
```
NAME
EXPNO                   2
PROCNO                  1
Date_            20120320
Time                19.10
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                  65536
SOLVENT              DMSO
NS                    512
DS                      0
SWH             29761.904 Hz
FIDRES           0.454131 Hz
AQ              1.1010548 sec
RG                   2050
DW                 16.800 usec
DE                   6.50 usec
TE                  298.3 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                  10.00 usec
PL1                  3.00 dB
PL1W          47.20970154 W
SFO1        125.8131151 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  4.30 dB
PL12                20.80 dB
PL13                20.80 dB
PL2W          10.45244789 W
PL12W          0.23400120 W
PL13W          0.23400120 W
SFO2        500.3020012 MHz
SI                  32768
SF          125.8005979 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

Fig. S7: ^{1}H (above) and ^{13}C NMR spectra (below) of 1,4-dihydro-2,3-quinoxalinedione (**3**).



```
PROTON DMSO {C:\Bruker\TOPSPIN}
```

```
NAME
EXPNO                    1
PROCNO                   1
Date_             20120322
Time                 18.35
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG               zg30
TD                   92974
SOLVENT               DMSO
NS                      16
DS                       0
SWH             10330.578 Hz
FIDRES           0.111113 Hz
AQ              4.4999914 sec
RG                     181
DW                  48.400 usec
DE                    6.50 usec
TE                   298.2 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   15.00 usec
PL1                   4.30 dB
PL1W           10.45244789 W
SFO1           500.3030896 MHz
SI                   32768
SF             500.3000000 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```



```
C13CPD DMSO {C:\Bruker\TOPSPIN}
```

```
NAME
EXPNO                    2
PROCNO                   1
Date_             20120322
Time                 19.04
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT               DMSO
NS                     512
DS                       0
SWH             29761.904 Hz
FIDRES           0.454131 Hz
AQ              1.1010548 sec
RG                    2050
DW                  16.800 usec
DE                    6.50 usec
TE                   298.2 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                   10.00 usec
PL1                   3.00 dB
PL1W           47.20970154 W
SFO1           125.8131151 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2               100.00 usec
PL2                   4.30 dB
PL12                 20.80 dB
PL13                 20.80 dB
PL2W           10.45244789 W
PL12W           0.23400120 W
PL13W           0.23400120 W
SFO2           500.3020012 MHz
SI                   32768
SF             125.8005979 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

Fig. S8: ^{1}H (above) and ^{13}C NMR spectra (below) of **C**.

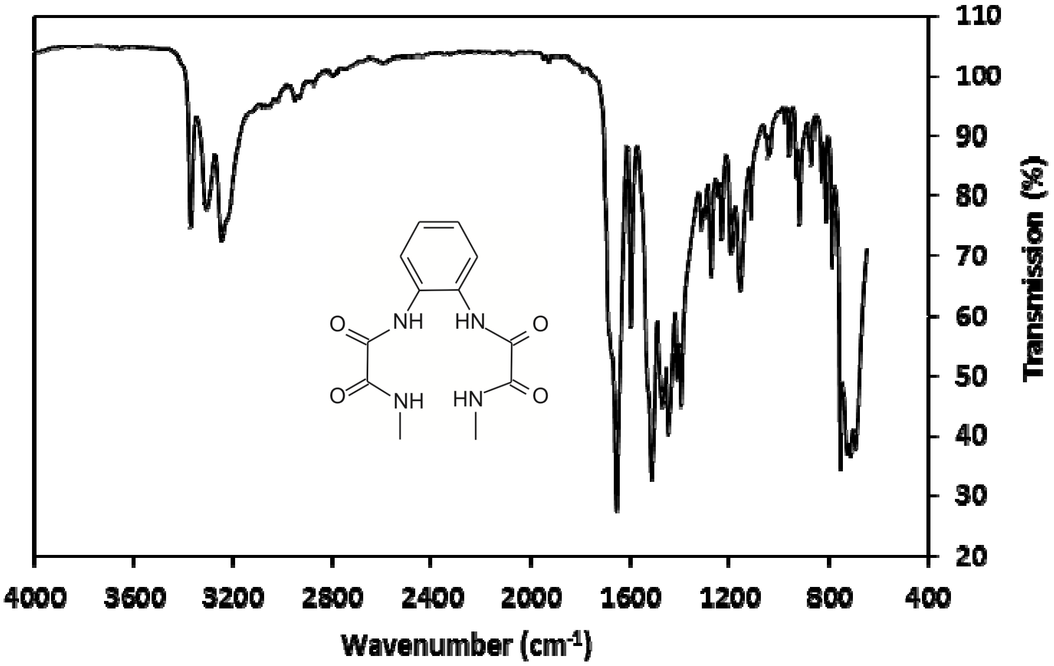


Fig. S9. IR spectrum of opboH_4Me_2 (**4**).

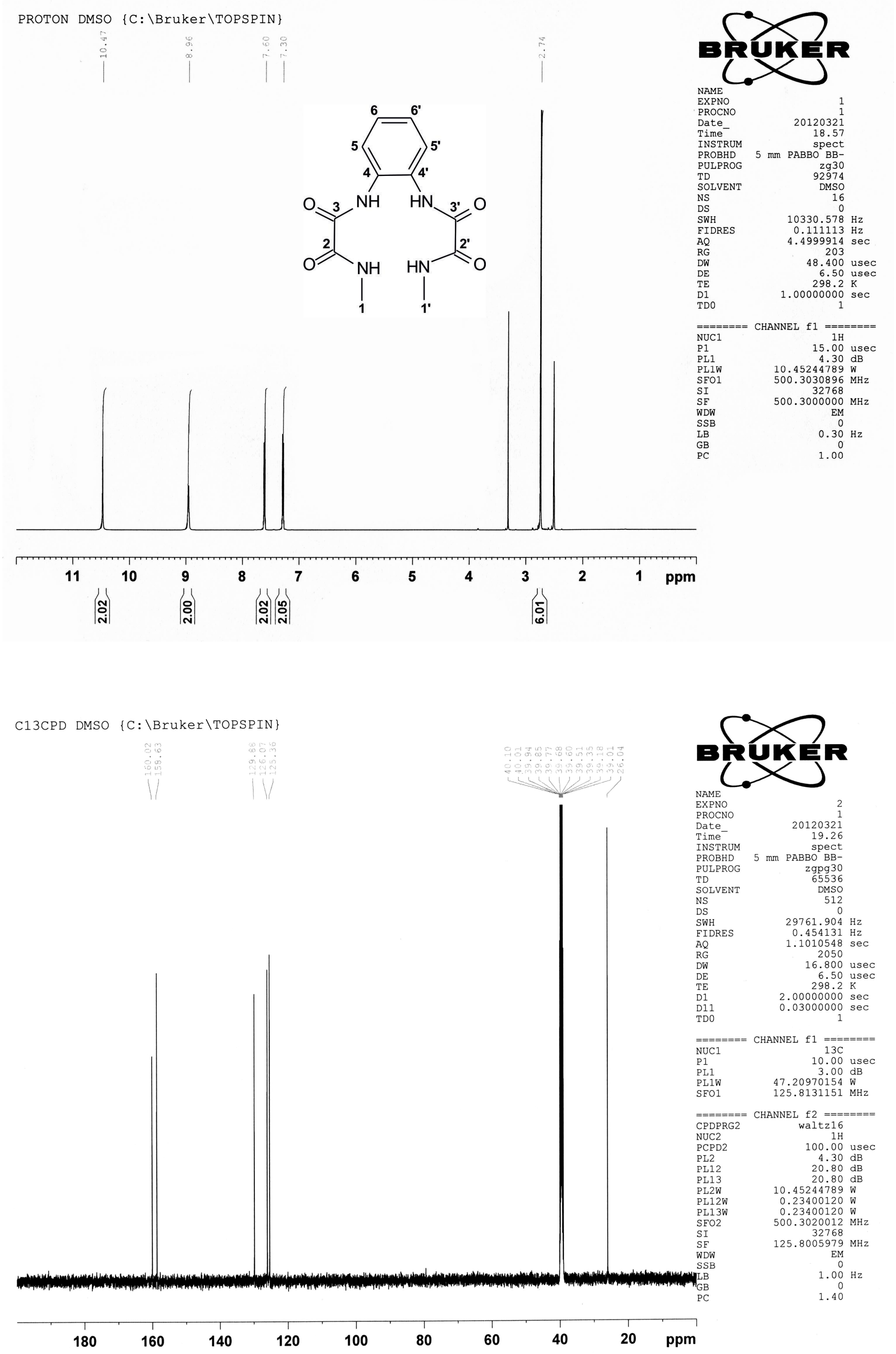


Fig. S10: ^{1}H (above) and ^{13}C NMR spectra (below) of opboH$_4$Me$_2$ (**4**).

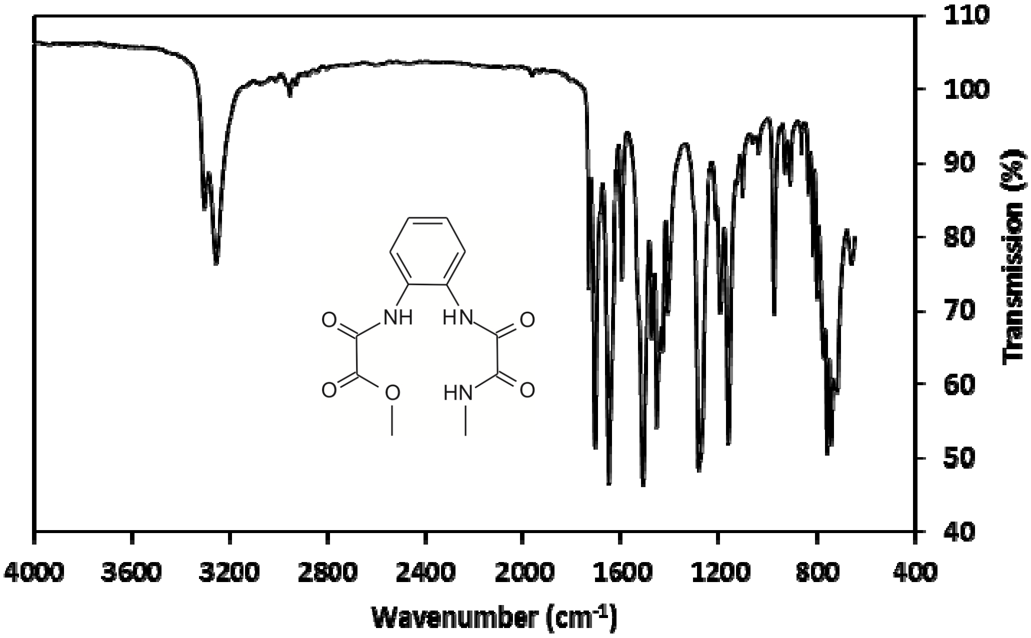
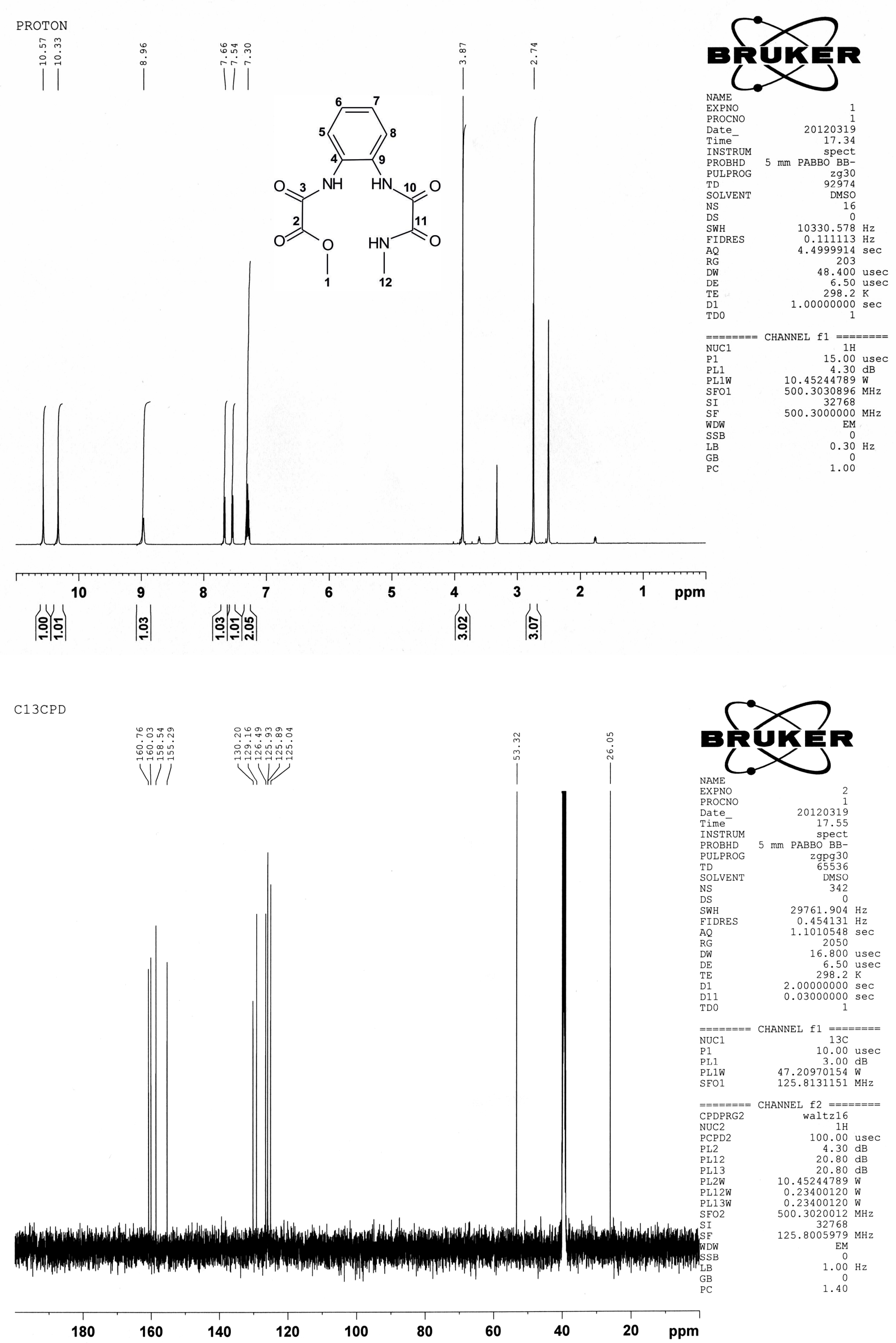


Fig. S11. The IR spectrum of opooH$_3$Me$_2$ (**1**).



```
NAME
EXPNO                   1
PROCNO                  1
Date_            20120319
Time                17.34
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  92974
SOLVENT              DMSO
NS                     16
DS                      0
SWH             10330.578 Hz
FIDRES           0.111113 Hz
AQ              4.4999914 sec
RG                    203
DW                 48.400 usec
DE                   6.50 usec
TE                  298.2 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  15.00 usec
PL1                  4.30 dB
PL1W          10.45244789 W
SFO1          500.3030896 MHz
SI                  32768
SF            500.3000000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

```
NAME
EXPNO                   2
PROCNO                  1
Date_            20120319
Time                17.55
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                  65536
SOLVENT              DMSO
NS                    342
DS                      0
SWH             29761.904 Hz
FIDRES           0.454131 Hz
AQ              1.1010548 sec
RG                   2050
DW                 16.800 usec
DE                   6.50 usec
TE                  298.2 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                  10.00 usec
PL1                  3.00 dB
PL1W          47.20970154 W
SFO1          125.8131151 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  4.30 dB
PL12                20.80 dB
PL13                20.80 dB
PL2W          10.45244789 W
PL12W          0.23400120 W
PL13W          0.23400120 W
SFO2          500.3020012 MHz
SI                  32768
SF            125.8005979 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

Fig. S12: ^{1}H (above) and ^{13}C NMR spectra (below) of opooH$_3$Me$_2$ (**1**).

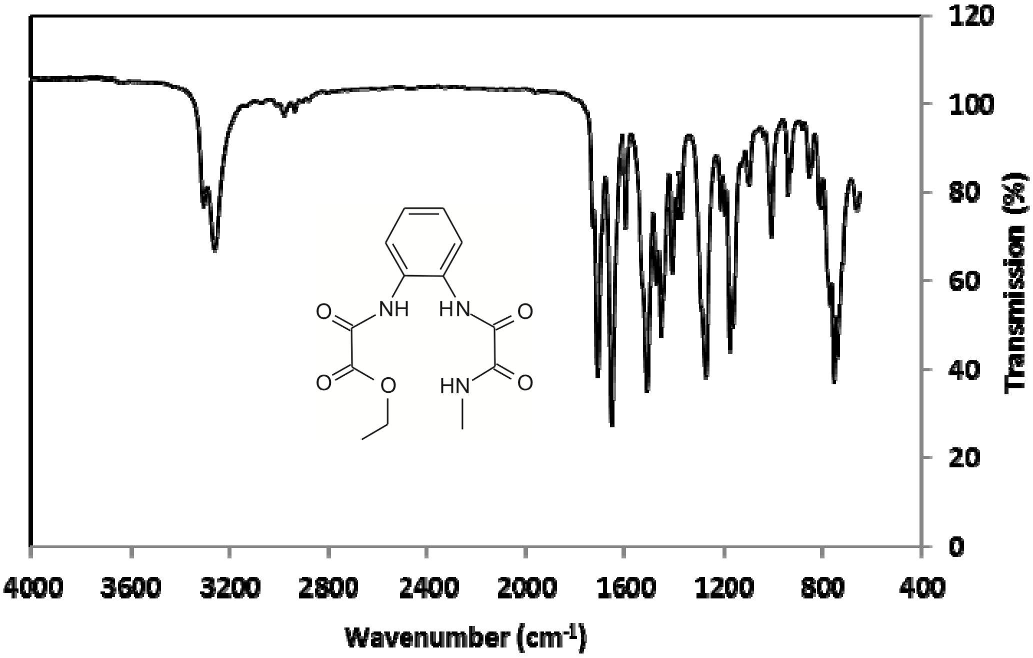
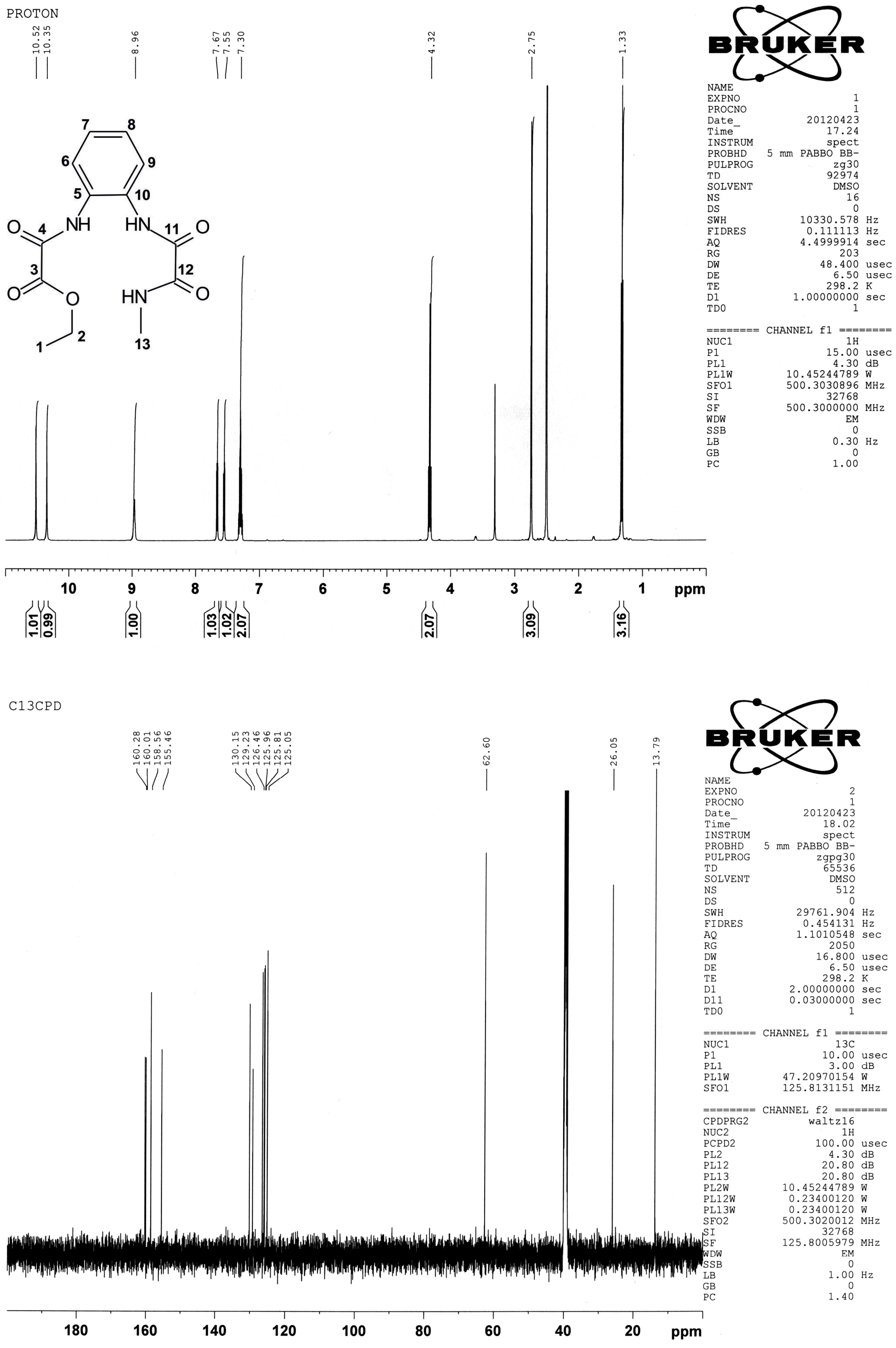


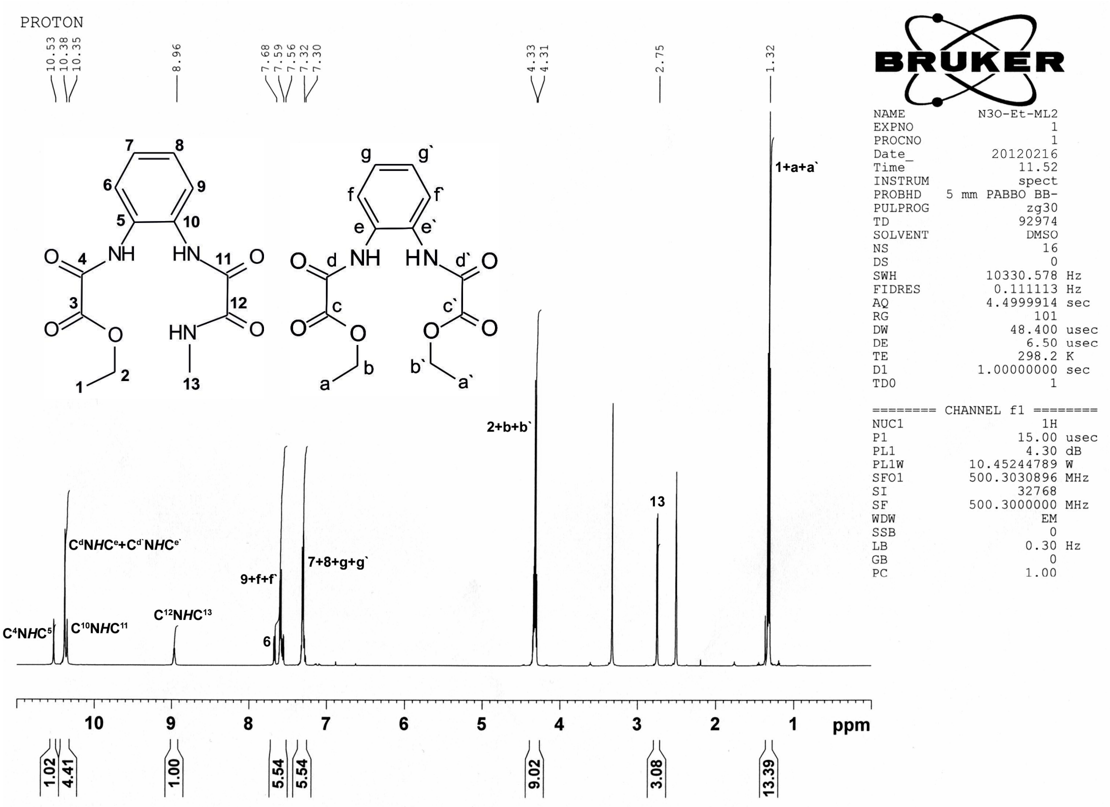
Fig. S13. The IR spectrum of opooH$_3$EtMe (**9**).



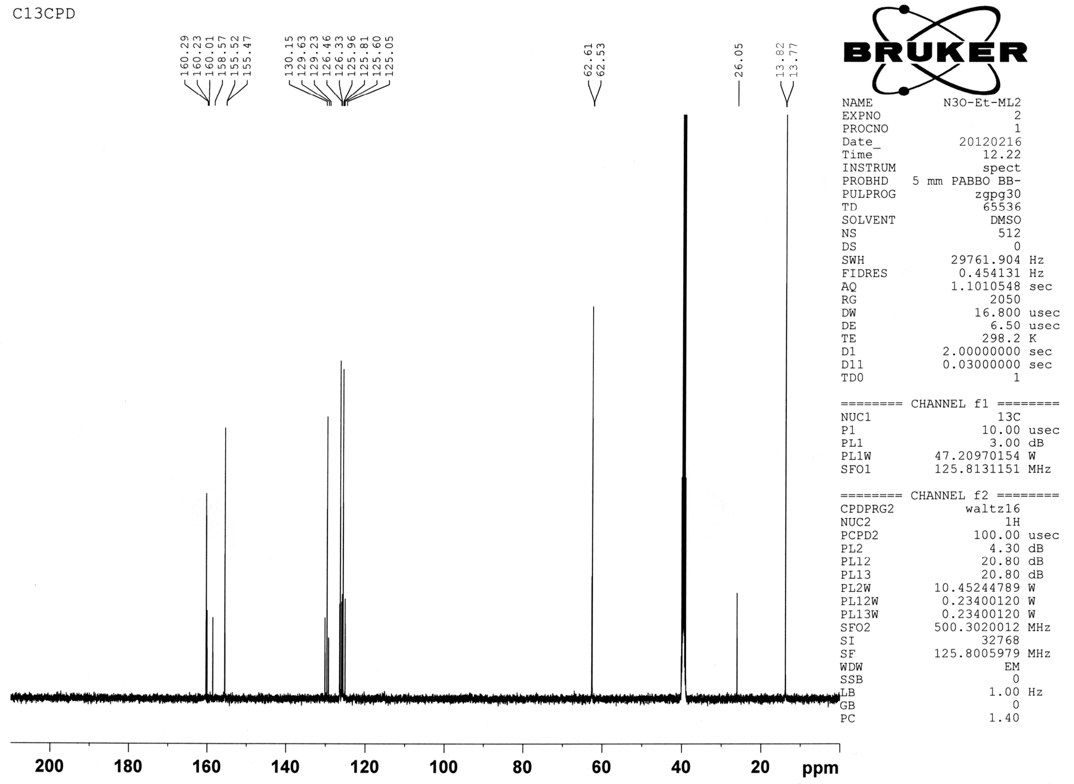
```
NAME
EXPNO                   1
PROCNO                  1
Date_            20120423
Time                17.24
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  92974
SOLVENT              DMSO
NS                     16
DS                      0
SWH             10330.578 Hz
FIDRES           0.111113 Hz
AQ              4.4999914 sec
RG                    203
DW                 48.400 usec
DE                   6.50 usec
TE                  298.2 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  15.00 usec
PL1                  4.30 dB
PL1W          10.45244789 W
SFO1          500.3030896 MHz
SI                  32768
SF            500.3000000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

```
NAME
EXPNO                   2
PROCNO                  1
Date_            20120423
Time                18.02
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                  65536
SOLVENT              DMSO
NS                    512
DS                      0
SWH             29761.904 Hz
FIDRES           0.454131 Hz
AQ              1.1010548 sec
RG                   2050
DW                 16.800 usec
DE                   6.50 usec
TE                  298.2 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                  10.00 usec
PL1                  3.00 dB
PL1W          47.20970154 W
SFO1          125.8131151 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  4.30 dB
PL12                20.80 dB
PL13                20.80 dB
PL2W          10.45244789 W
PL12W          0.23400120 W
PL13W          0.23400120 W
SFO2          500.3020012 MHz
SI                  32768
SF            125.8005979 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

Fig. S14. ^{1}H (above) and ^{13}C NMR spectra (below) of opooH$_3$EtMe (**9**).



```
NAME             N30-Et-ML2
EXPNO                     1
PROCNO                    1
Date_              20120216
Time                  11.52
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    92974
SOLVENT                DMSO
NS                       16
DS                        0
SWH              10330.578 Hz
FIDRES            0.111113 Hz
AQ               4.4999914 sec
RG                      101
DW                   48.400 usec
DE                     6.50 usec
TE                    298.2 K
D1               1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                    15.00 usec
PL1                    4.30 dB
PL1W           10.45244789 W
SFO1           500.3030896 MHz
SI                    32768
SF             500.3000000 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```



```
NAME             N30-Et-ML2
EXPNO                     2
PROCNO                    1
Date_              20120216
Time                  12.22
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG              zgpg30
TD                    65536
SOLVENT                DMSO
NS                      512
DS                        0
SWH              29761.904 Hz
FIDRES            0.454131 Hz
AQ               1.1010548 sec
RG                     2050
DW                   16.800 usec
DE                     6.50 usec
TE                    298.2 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                    10.00 usec
PL1                    3.00 dB
PL1W           47.20970154 W
SFO1           125.8131151 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                100.00 usec
PL2                    4.30 dB
PL12                  20.80 dB
PL13                  20.80 dB
PL2W           10.45244789 W
PL12W           0.23400120 W
PL13W           0.23400120 W
SFO2           500.3020012 MHz
SI                    32768
SF             125.8005979 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```

Fig. S15. ^{1}H (above) and ^{13}C NMR spectra (below) of the residue obtained from the filtrate of the reaction of opbaH$_2$Et$_2$ with 5/6 equivalent of MeNH$_2$ in EtOH.

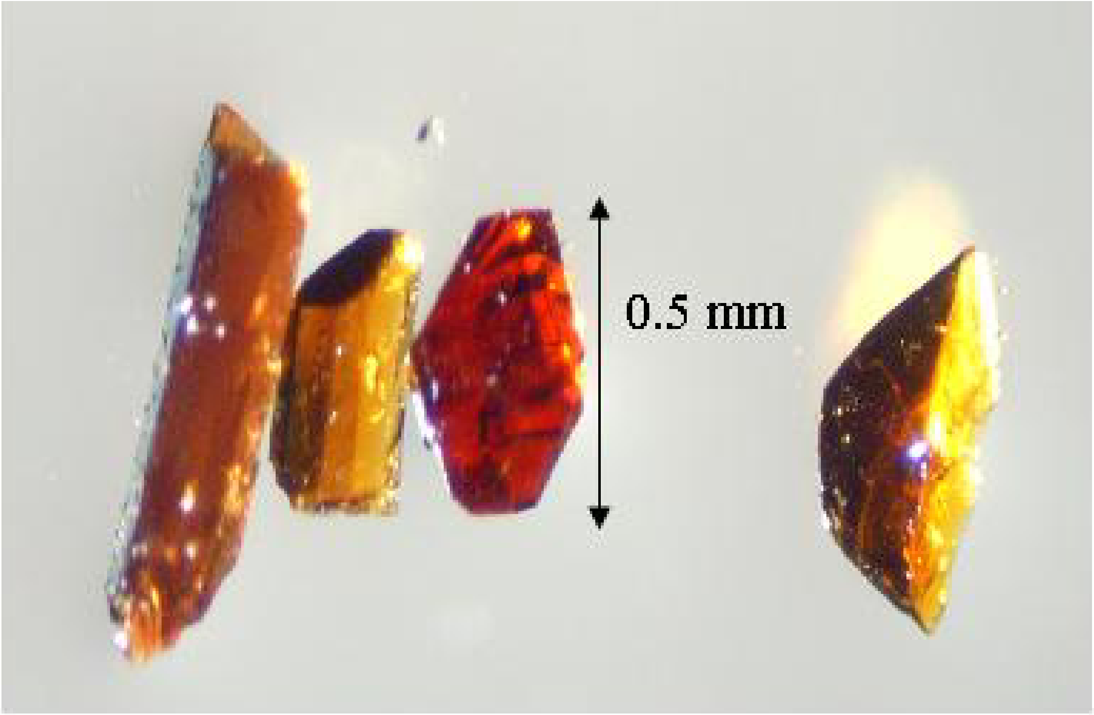


Fig. S16. Optical photography of single crystals of **7**@**5** (the three crystals on the left side) and **8**@**6** (right). Crystals on the left side have even optically well recognizeable crystals faces, their different colours are due to the use of an optical polarisation filter. Crystal faces of the crystal shown on the right side are less well formed.

Remark I: The identities of the single crystals shown here have been verified by unit cell measurements. It should be noted again, that the differently shaped crystals were collected from one and the same crystallization of 99% of the orange together with 1% of the purple coloured powder.

Remark II: It is mentioned within the manuscript that from the crystallization of the orange powder containing **5** and **6** or the crystallization of the purple powder containing **7** and **8** the crystals formed were optically distinguishable. Their respective different shapes refer approximately to the shapes shown here.

Obviously, the formation of compounds **1** and **2** is due to a transesterification reaction[1-3] of opbaH_2Et_2 with MeOH in the presence of $MeNH_2$ which, in addition to its role as nucleophile in the amide formation reaction, may further catalyze the transesterification reaction. Transesterification reactions are well known and have been studied by achieving the reaction using a variety of alcohols to react with different esters catalyzed by Lewis acids,[4] bases,[5,6] were performed under neutral conditions[7-9] and by addition of other catalysts.[10-17] Nevertheless, all the transesterification reactions carried out to-date were performed under reflux and call for somewhat long time. Interestingly, the reaction understudy had gone to end at 60 °C in 30 min, which makes it a good candidate catalytic reaction for related transesterification reactions in future. For example, it seems to be interesting to study the use of tertiary amines as catalysts.

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