Supplementary Material

E versus Z Diazeniumdiolation of Acetoacetate-Derived Carbanions

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Title **Page**

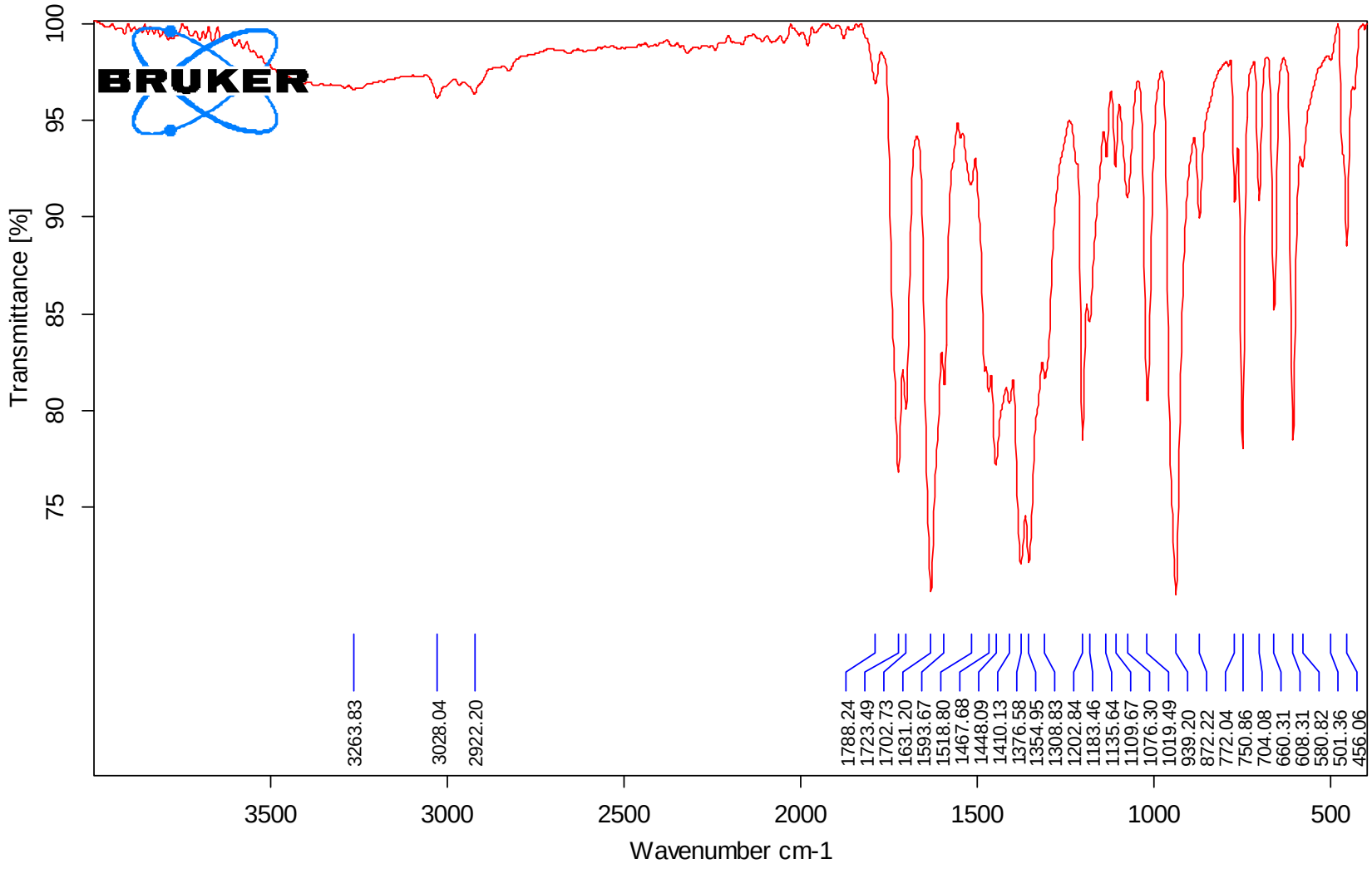


Figure S1. IR spectrum for $CH_3COC_2N_2O_3K$ (**K1**).

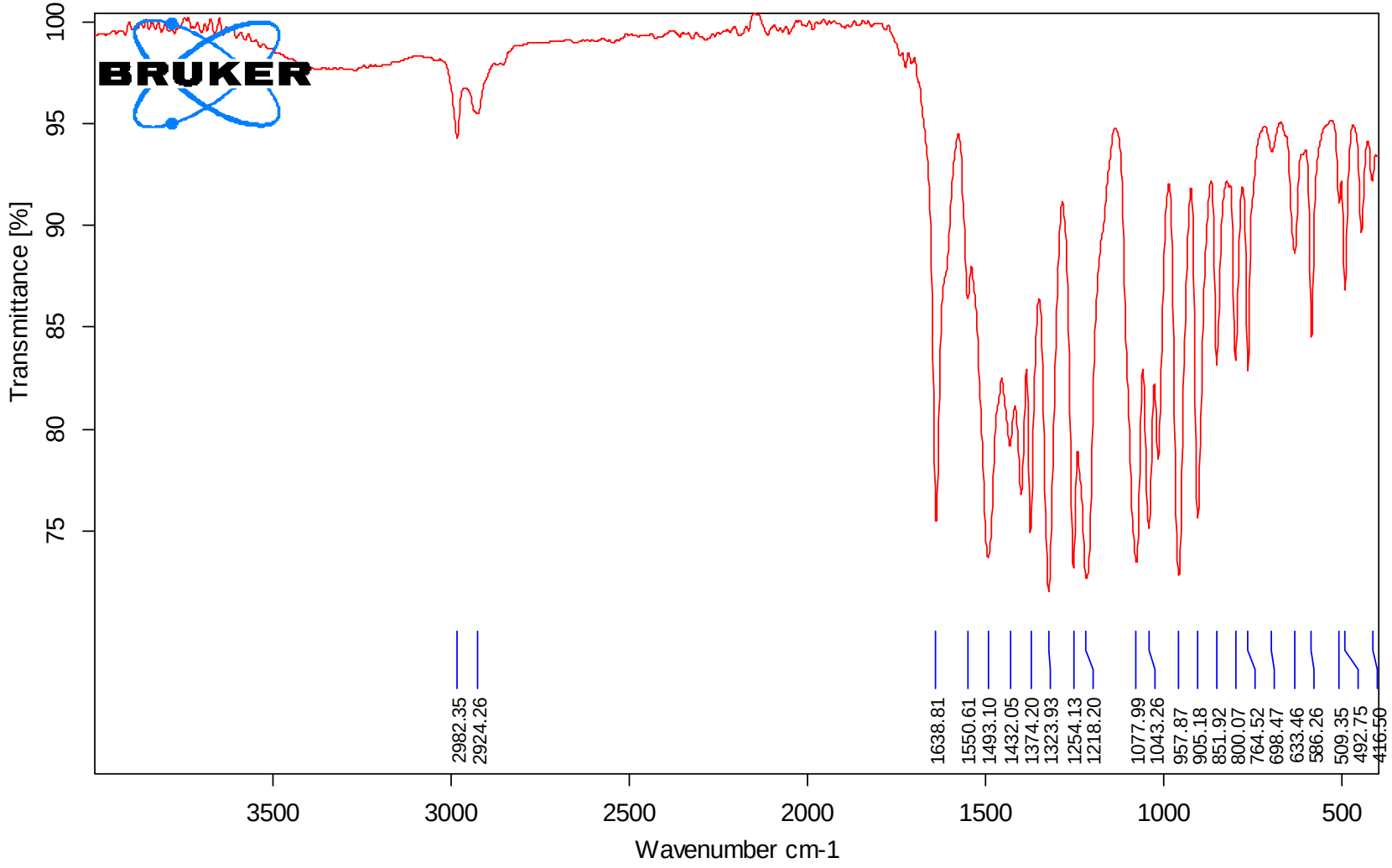


Figure S2. IR spectrum for $CH_2(N_2O_2K)CO_2K{\cdot}H_2O$ (**$K_2$2·H_2O**).

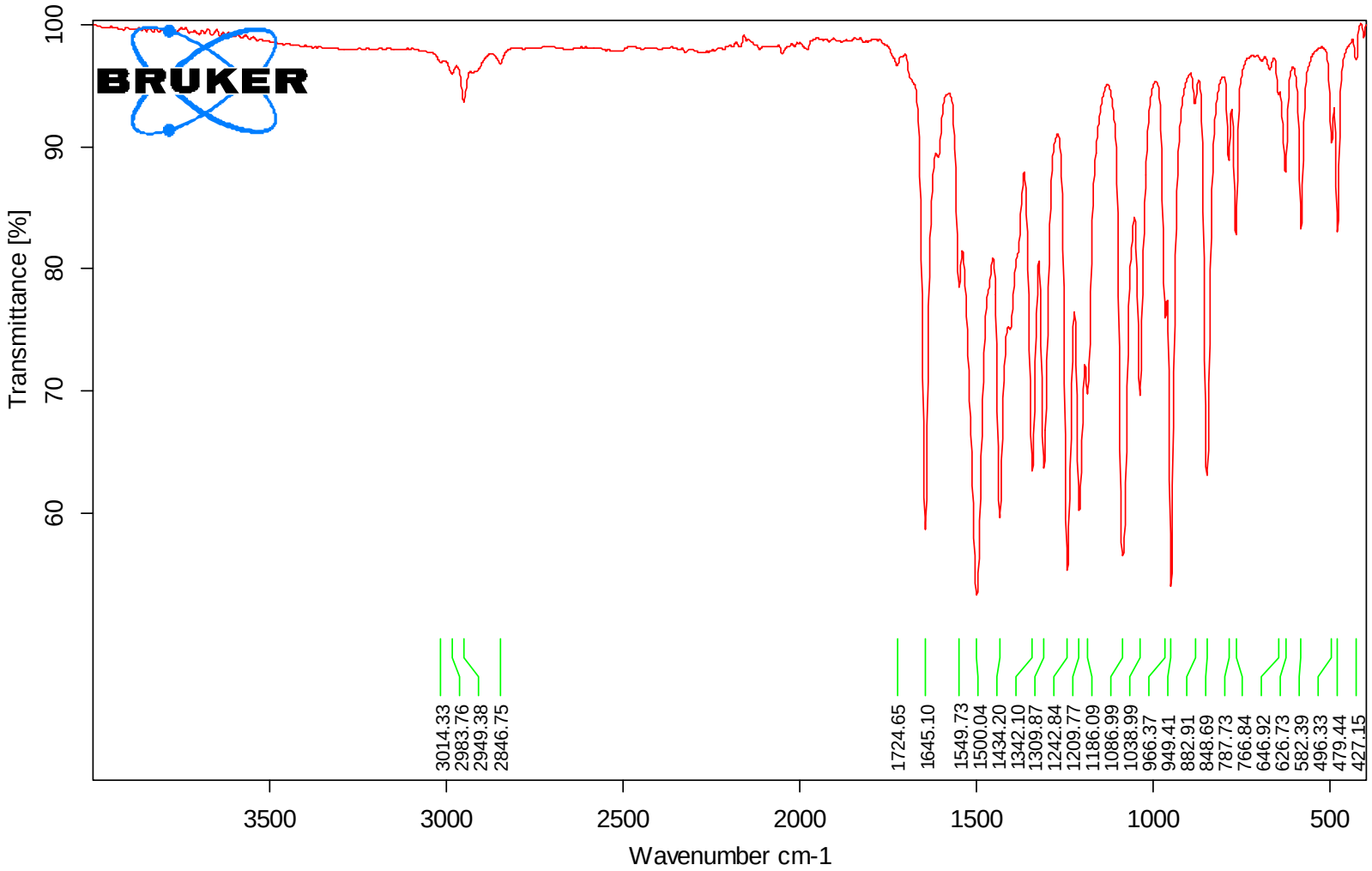


Figure S3. IR spectrum for MeC(OK)C(N_2O_2K)CO_2Me (**$K_2$3**).

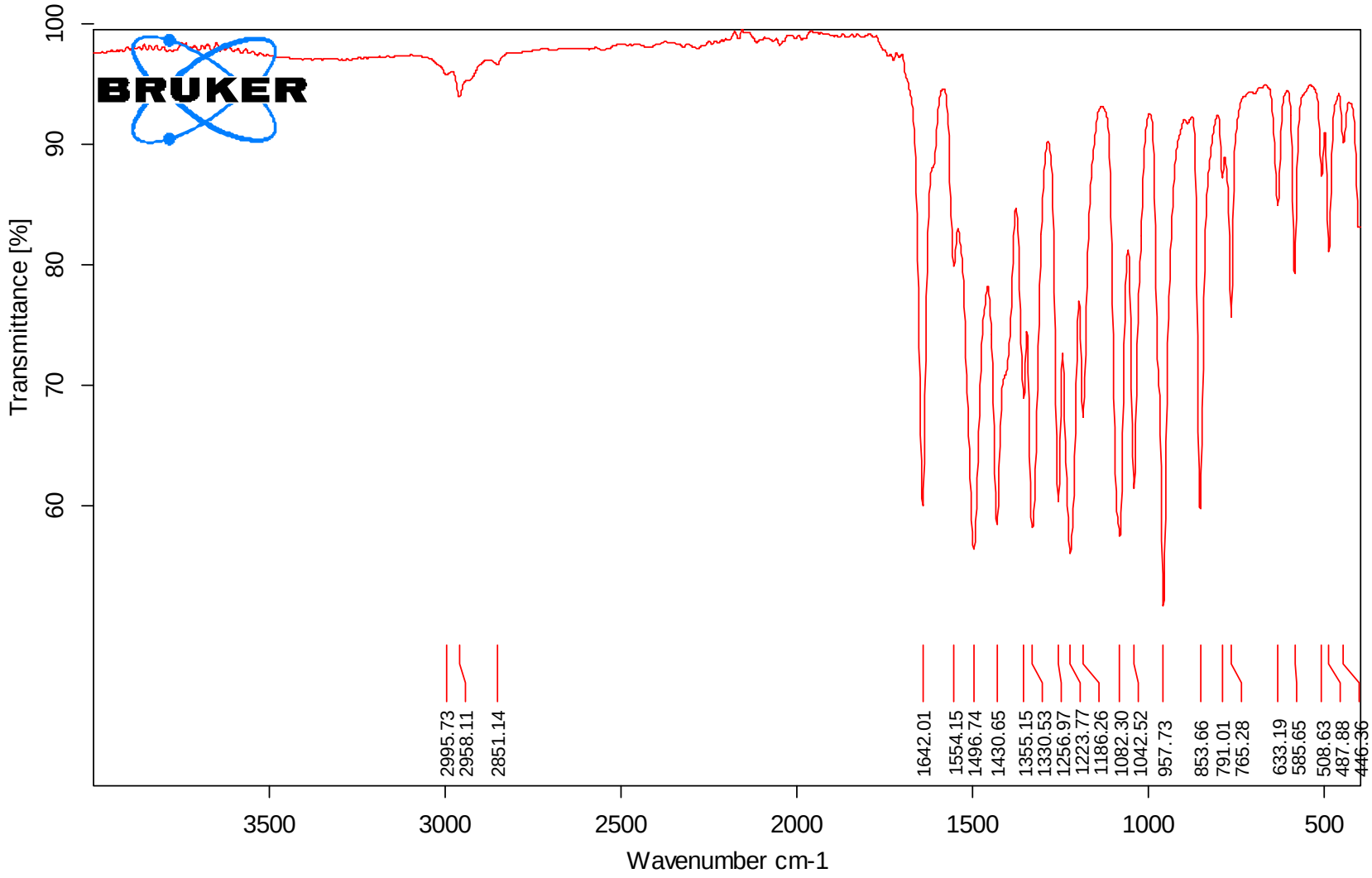


Figure S4. IR spectrum for MeC(ONa)C(N_2O_2Na)CO_2Me (**$Na_2$3**).

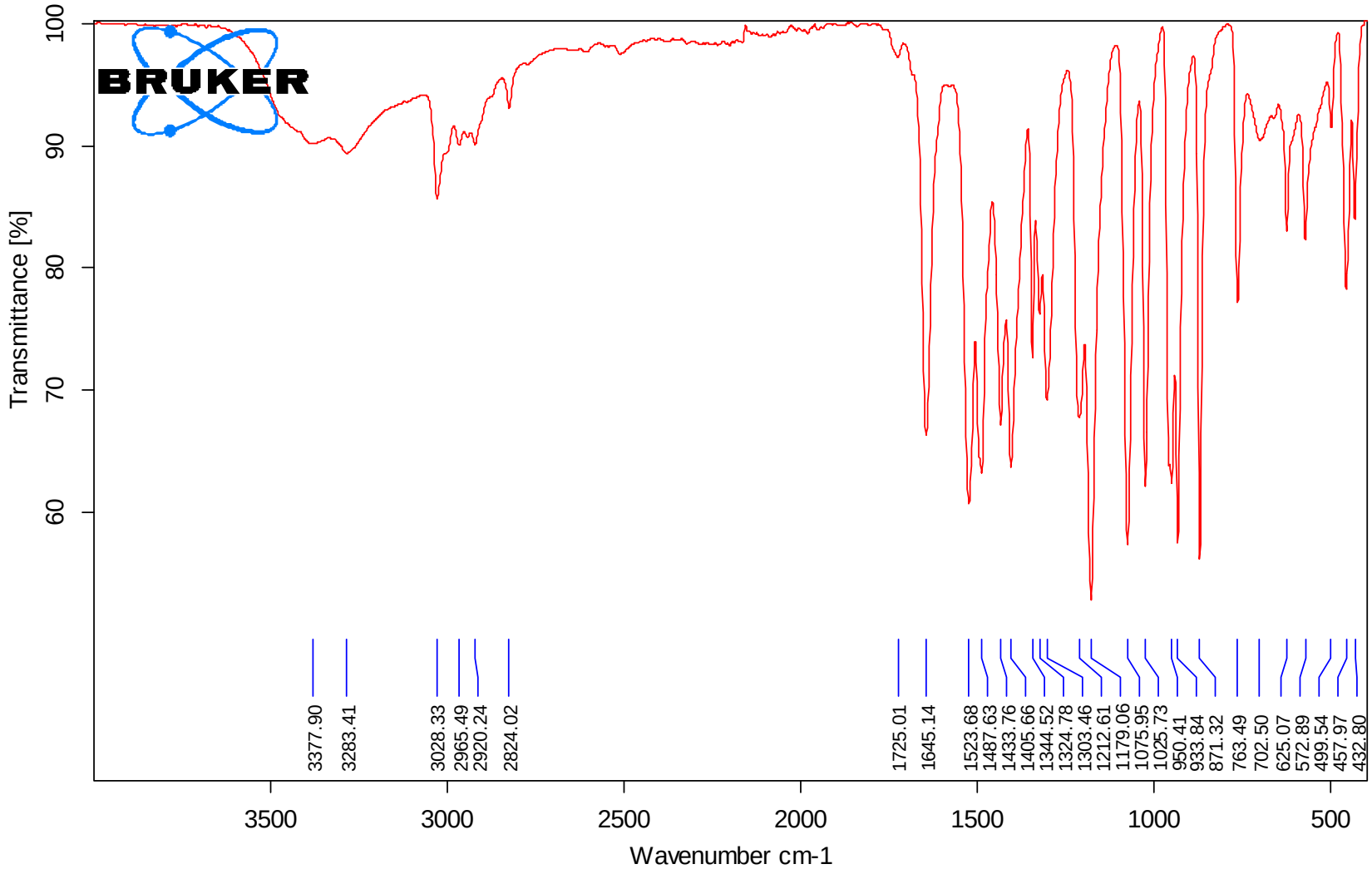


Figure S5. IR spectrum for MeC(OLi)C(N_2O_2Li)CO_2Me (**$Li_2$3·⅔MeOH·⅓H_2O**).

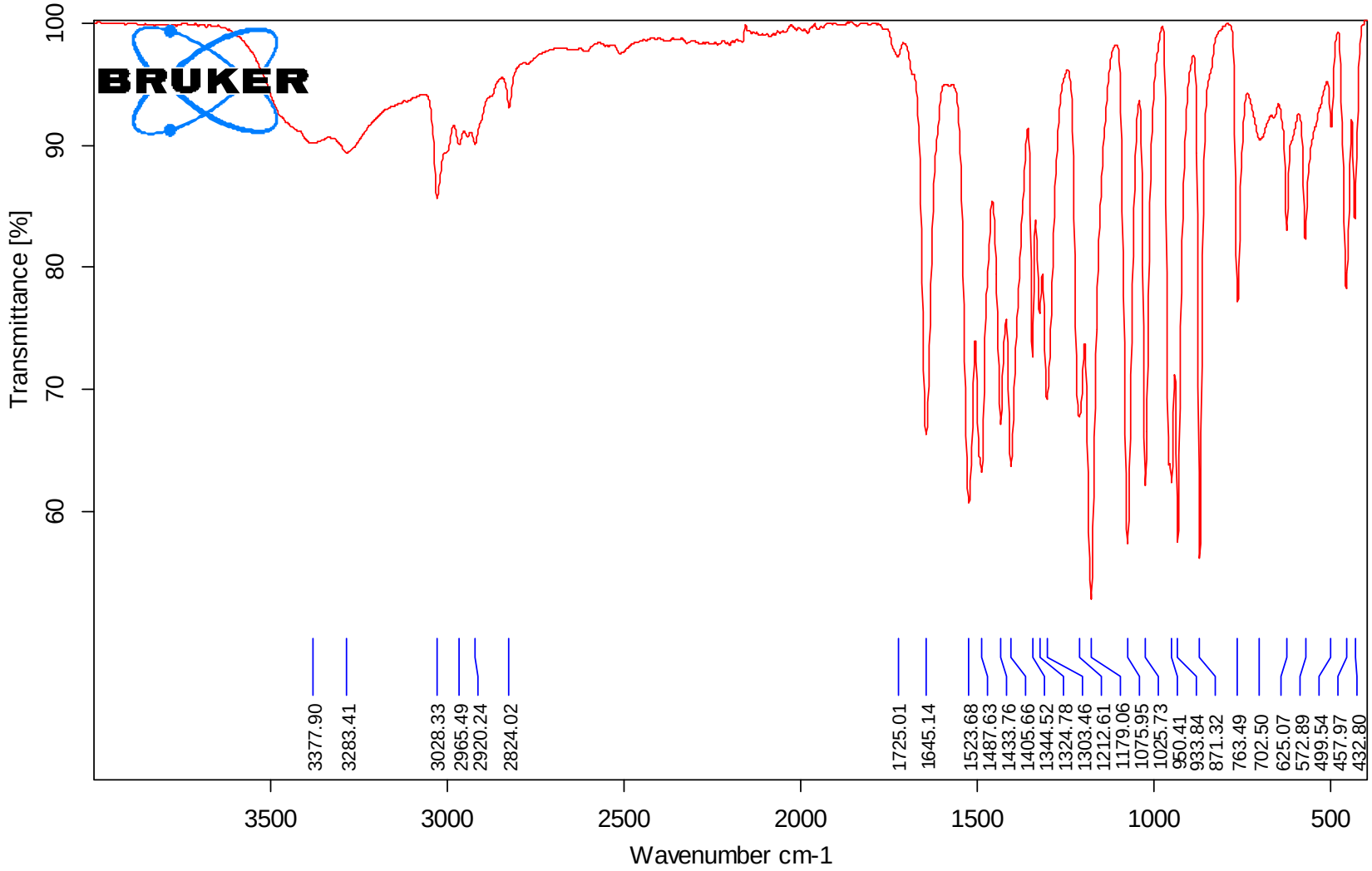


Figure S6. IR spectrum for $[NMe_4]_2[MeC(O^-)C(N_2O_2^-)CO_2Me]$ (**$[NMe_4]_2$3**).

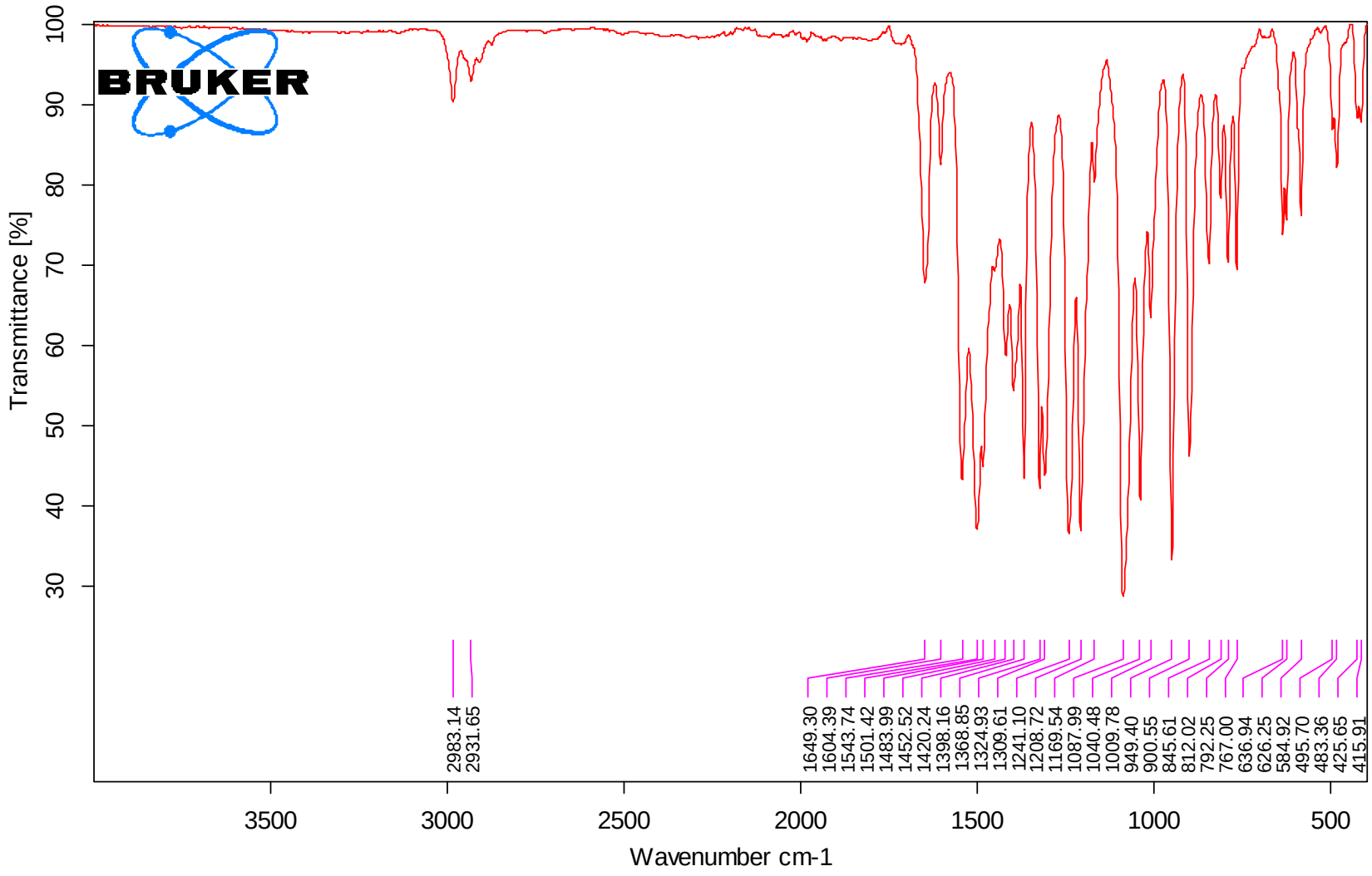


Figure S7. IR spectrum for MeC(OK)C(N_2O_2K)CO_2Et (**$K_2$4**).

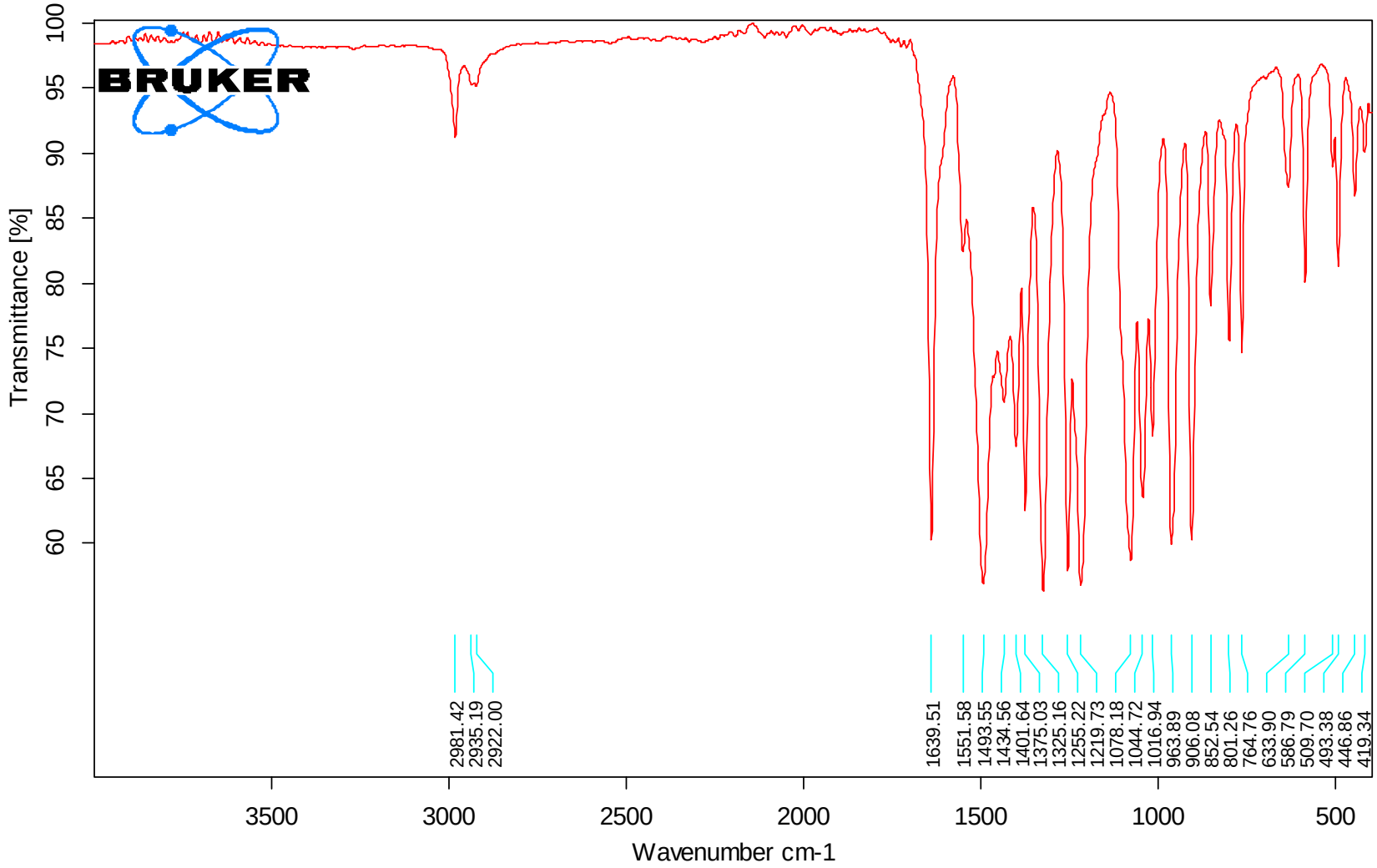
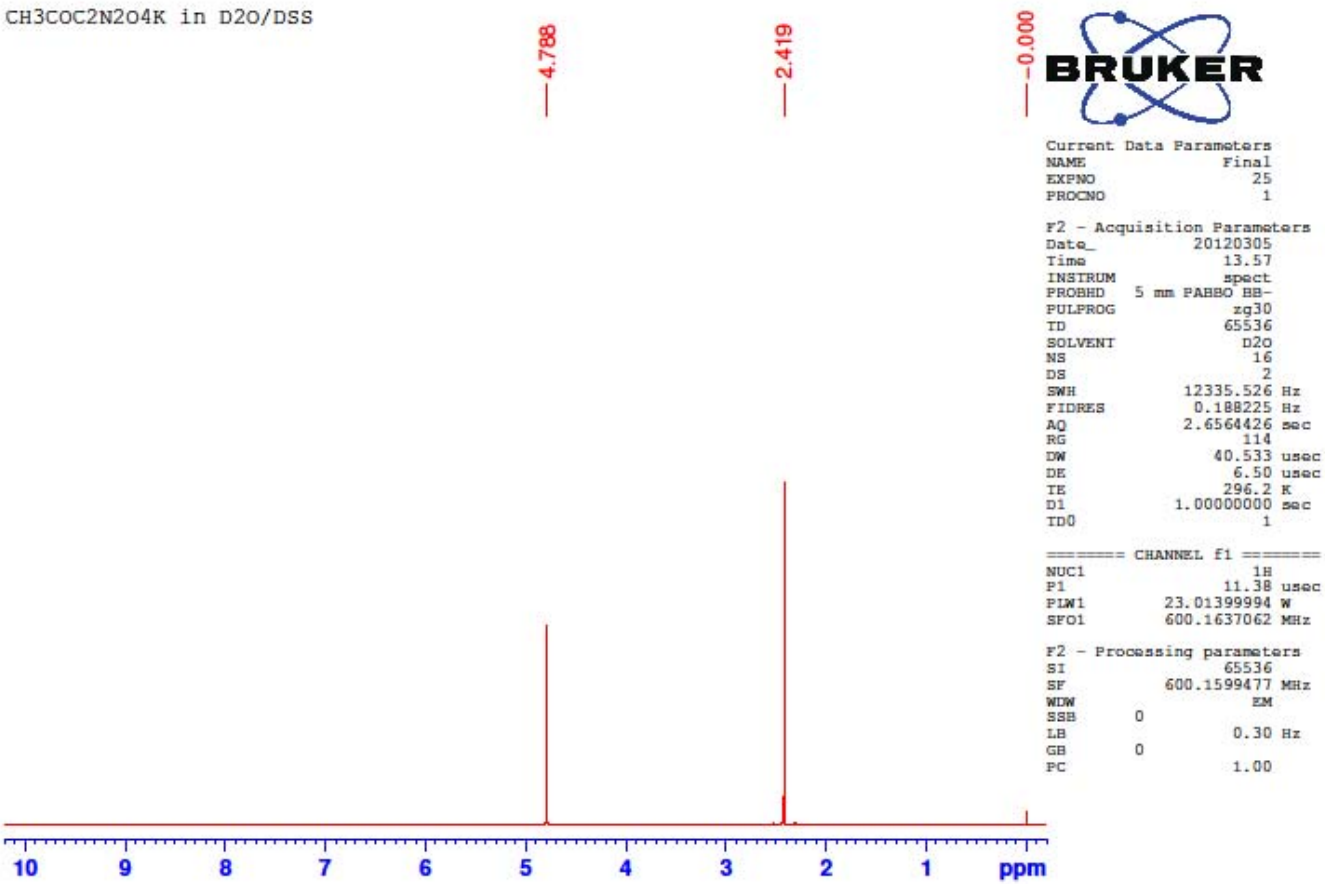


Figure S8. IR spectrum for MeC(ONa)C(N_2O_2Na)CO_2Et (**$Na_2$4**).

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DW                 40.533 usec
DE                   6.50 usec
TE                  296.2 K
D1             1.00000000 sec
TD0                      1

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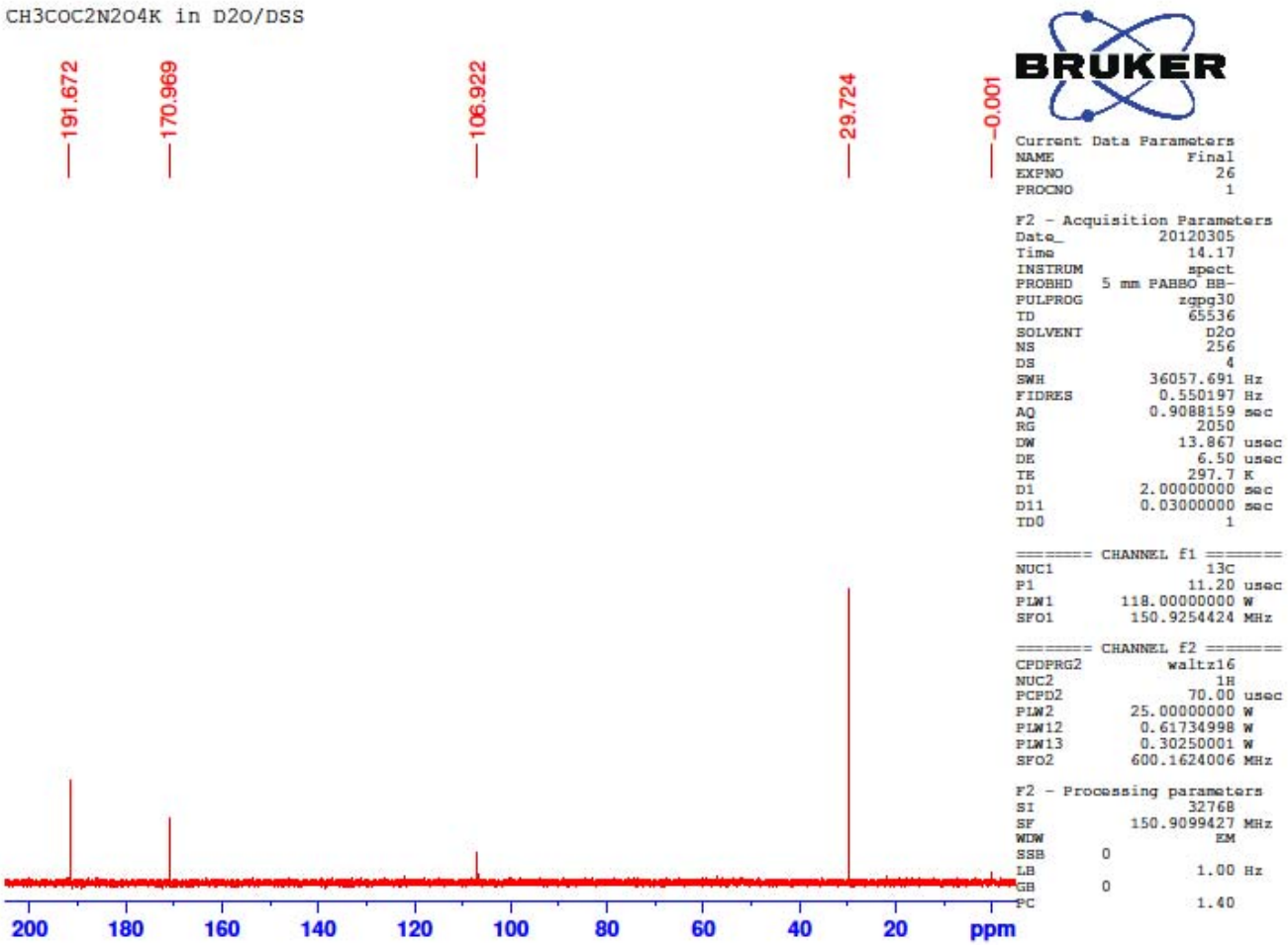
Figure S9. ^{1}H NMR spectrum for $CH_3COC_2N_2O_3K$ (**K1**) in D_2O.

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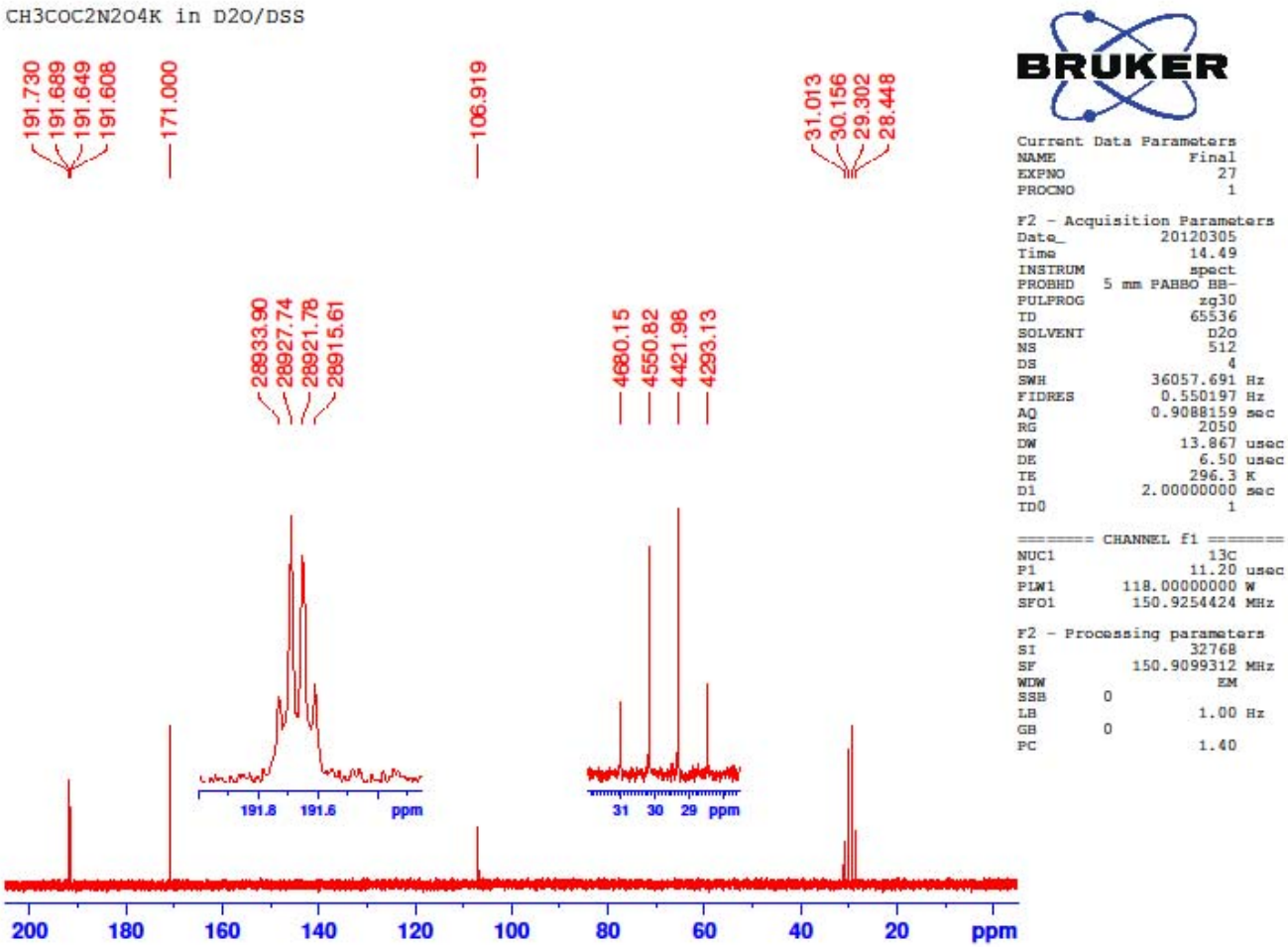
TD                   65536
SOLVENT                D2O
NS                     256
DS                       4
SWH             36057.691 Hz
FIDRES           0.550197 Hz
AQ              0.9088159 sec
RG                    2050
DW                  13.867 usec
DE                    6.50 usec
TE                   297.7 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    13C
P1                    11.20 usec
PLW1         118.00000000 W
SFO1          150.9254424 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                     1H
PCPD2                 70.00 usec
PLW2          25.00000000 W
PLW12          0.61734998 W
PLW13          0.30250001 W
SFO2         600.1624006 MHz

F2 - Processing parameters
SI                    32768
SF            150.9099427 MHz
WDW                      EM
SSB       0
LB                     1.00 Hz
GB        0
PC                     1.40
```

Figure S10. Proton decoupled ^{13}C NMR spectrum for $CH_3COC_2N_2O_3K$ (**K1**) in D_2O.

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TD                   65536
SOLVENT                D2O
NS                     512
DS                       4
SWH             36057.691 Hz
FIDRES           0.550197 Hz
AQ              0.9088159 sec
RG                    2050
DW                  13.867 usec
DE                    6.50 usec
TE                   296.3 K
D1             2.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                   11.20 usec
PLW1         118.00000000 W
SFO1          150.9254424 MHz

F2 - Processing parameters
SI                   32768
SF            150.9099312 MHz
WDW                     EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.40
```

Figure S11b. Proton coupled ^{13}C NMR spectrum for $CH_3COC_2N_2O_3K$ (**K1**) in D_2O.

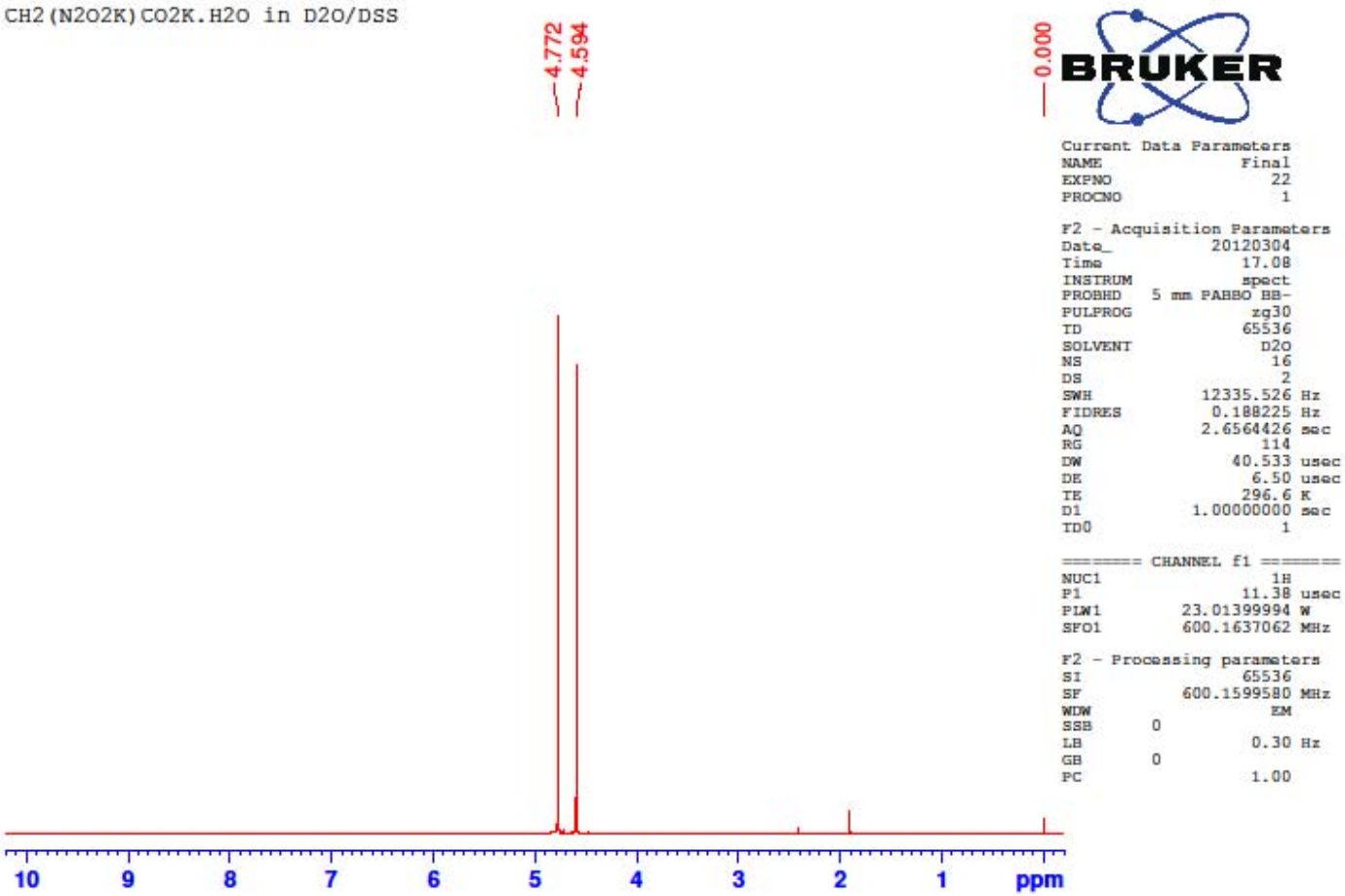


Figure S12. ^{1}H NMR spectrum for $CH_2(N_2O_2K)CO_2K{\cdot}H_2O$ (**$K_2$2·H_2O**)in D_2O.

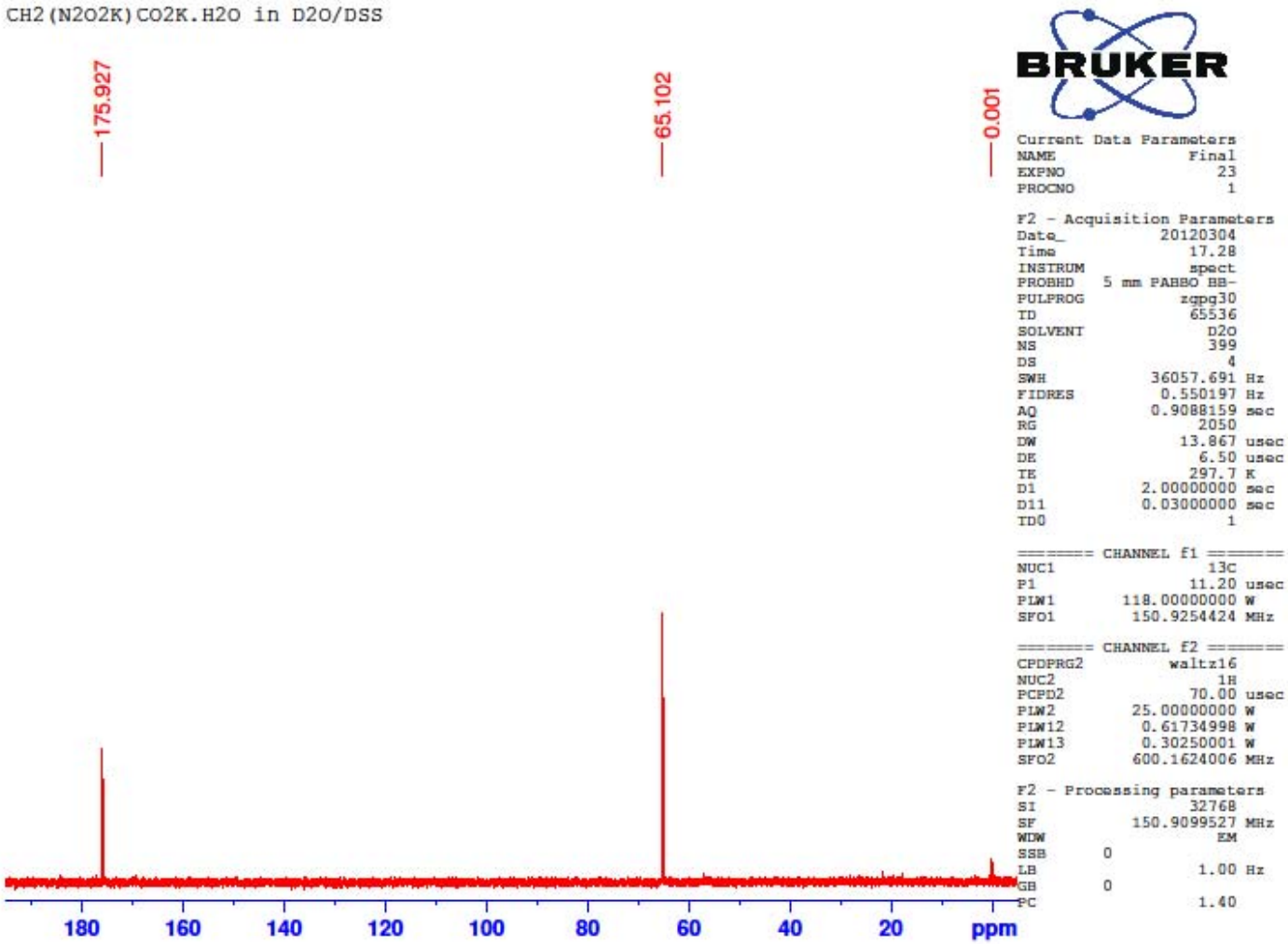
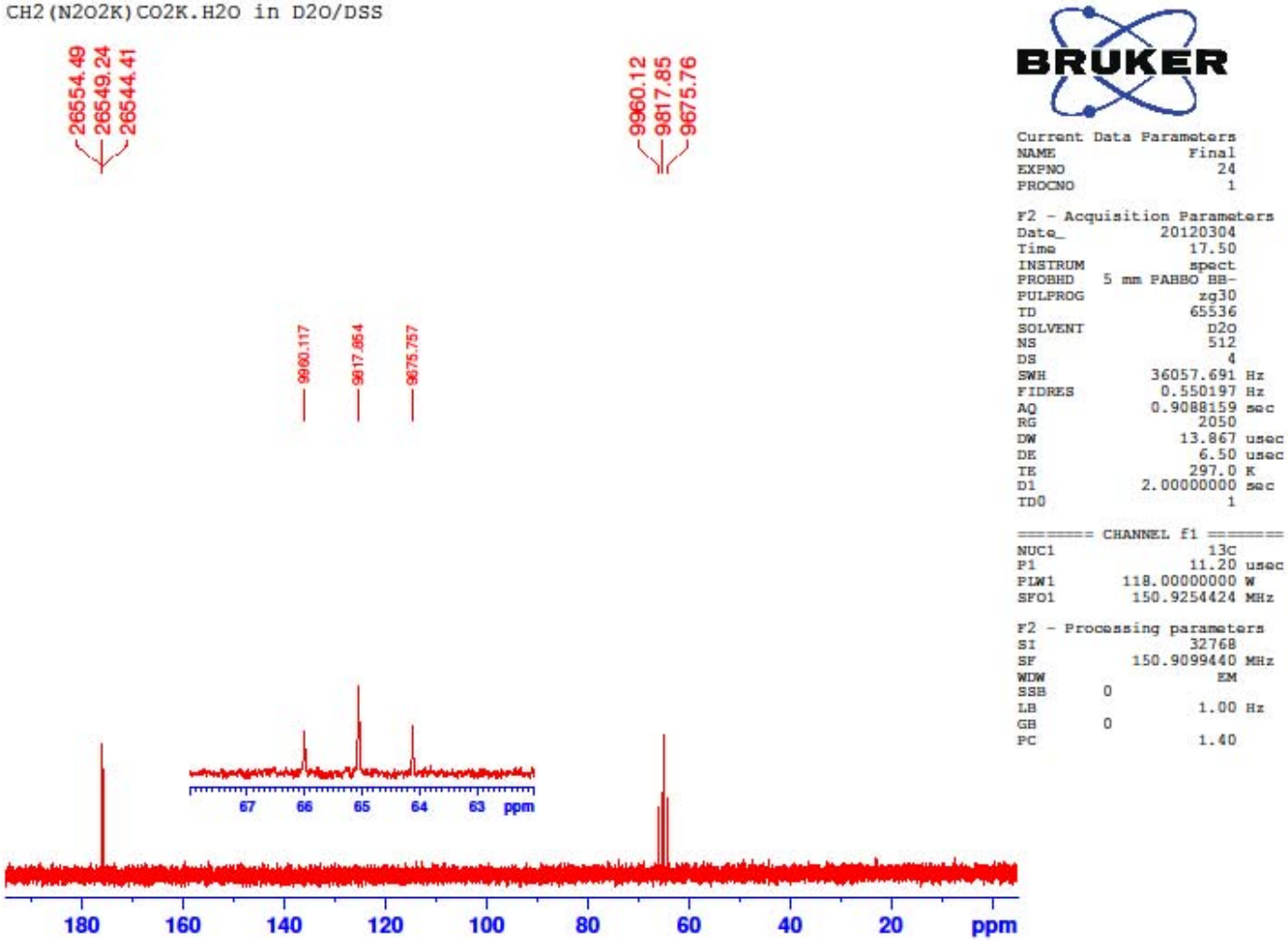


Figure S13. Proton decoupled ^{13}C NMR spectrum for $CH_2(N_2O_2K)CO_2K{\cdot}H_2O$ (**$K_2$2·H_2O**) in D_2O.

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DS                       4
SWH              36057.691 Hz
FIDRES            0.550197 Hz
AQ               0.9088159 sec
RG                    2050
DW                  13.867 usec
DE                    6.50 usec
TE                   297.0 K
D1               2.00000000 sec
TD0                      1

======== CHANNEL f1 =======
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P1                   11.20 usec
PLW1         118.00000000 W
SFO1          150.9254424 MHz

F2 - Processing parameters
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WDW                     EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.40
```

Figure S14. Proton coupled ^{13}C NMR spectrum for $CH_2(N_2O_2K)CO_2K{\cdot}H_2O$ (**$K_2$2·H_2O**) in D_2O.

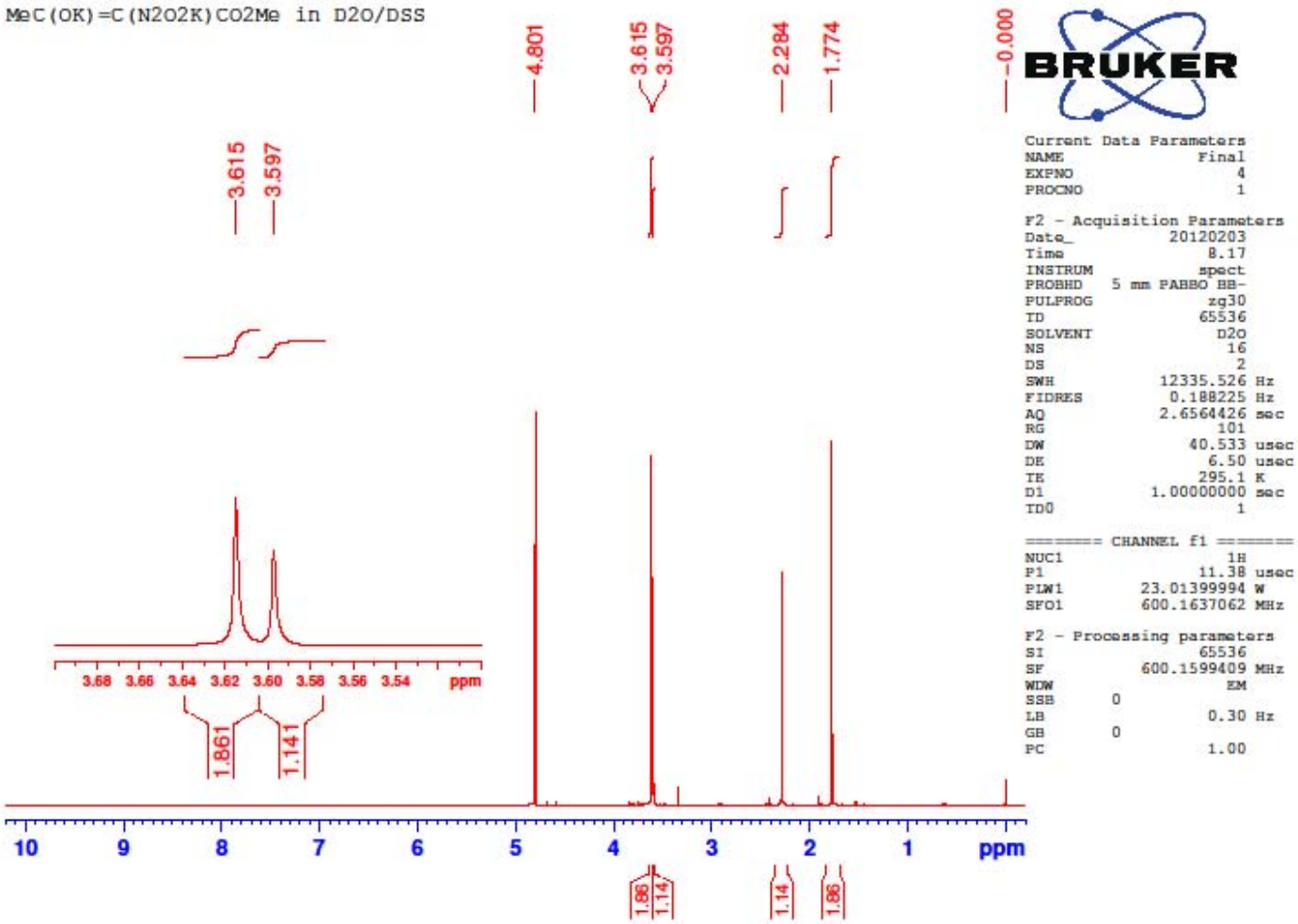


Figure S15. ^{1}H NMR spectrum for MeC(OK)C(N_2O_2K)CO_2Me (**$K_2$3**) in D_2O.

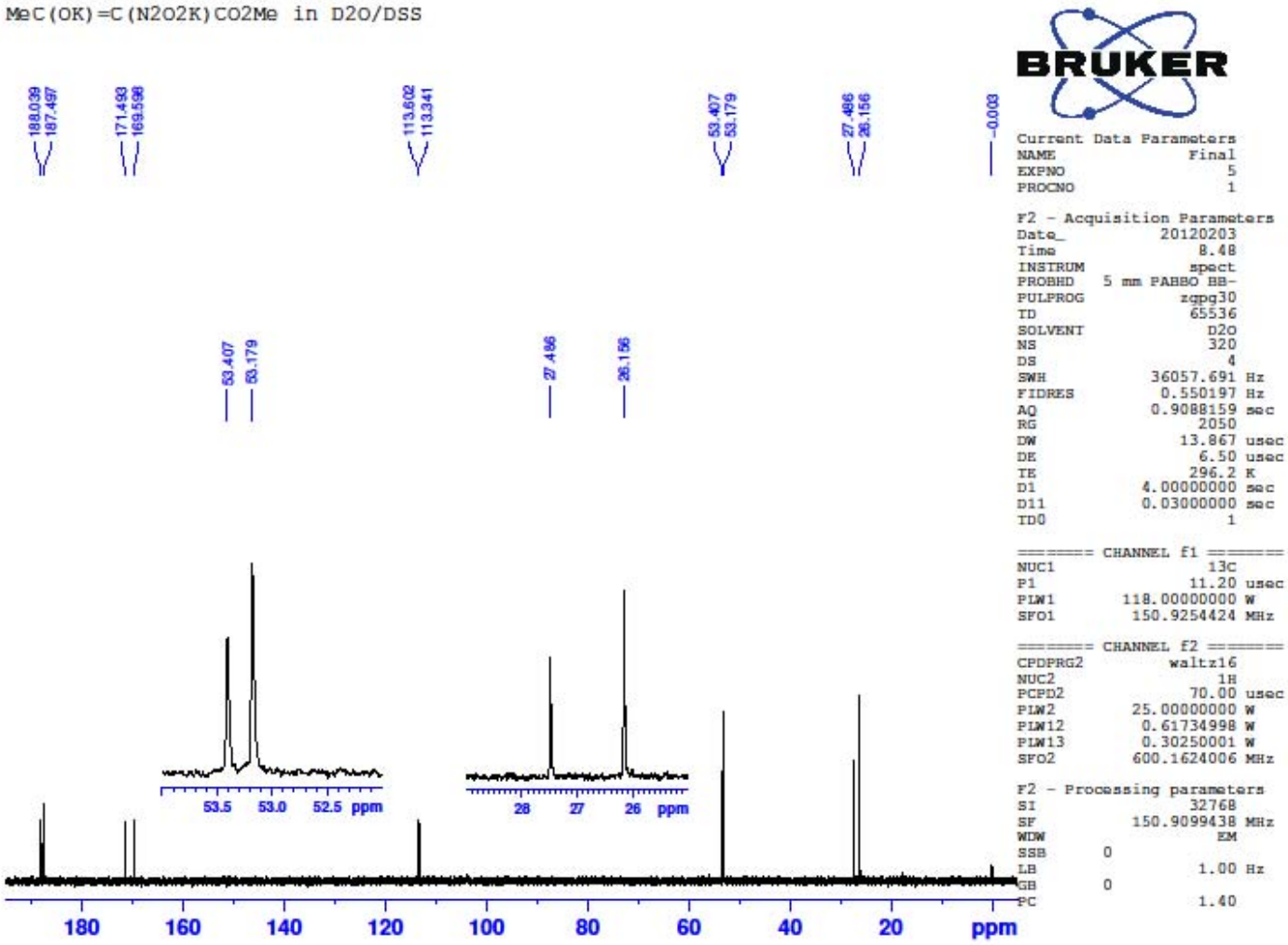
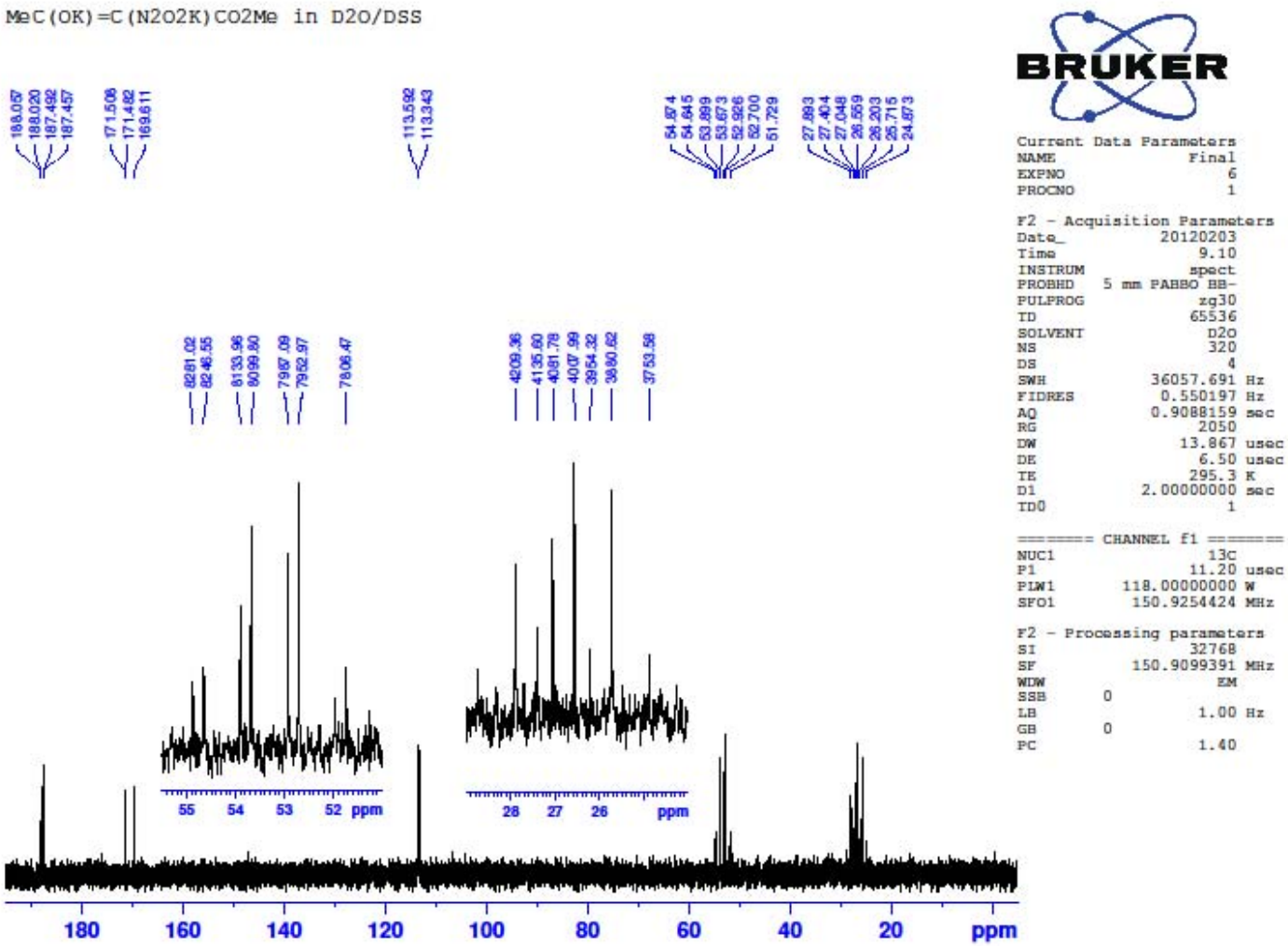


Figure S16. Proton decoupled ^{13}C NMR spectrum for $MeC(OK)C(N_2O_2K)CO_2Me$ (**$K_2$3**) in D_2O.

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FIDRES            0.550197 Hz
AQ               0.9088159 sec
RG                    2050
DW                  13.867 usec
DE                    6.50 usec
TE                   295.3 K
D1               2.00000000 sec
TD0                      1

======== CHANNEL f1 =======
NUC1                   13C
P1                   11.20 usec
PLW1         118.00000000 W
SFO1          150.9254424 MHz

F2 - Processing parameters
SI                   32768
SF            150.9099391 MHz
WDW                     EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.40
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Figure S17. Proton coupled ^{13}C NMR spectrum for MeC(OK)C(N_2O_2K)CO_2Me (**$K_2$3**) in D_2O.

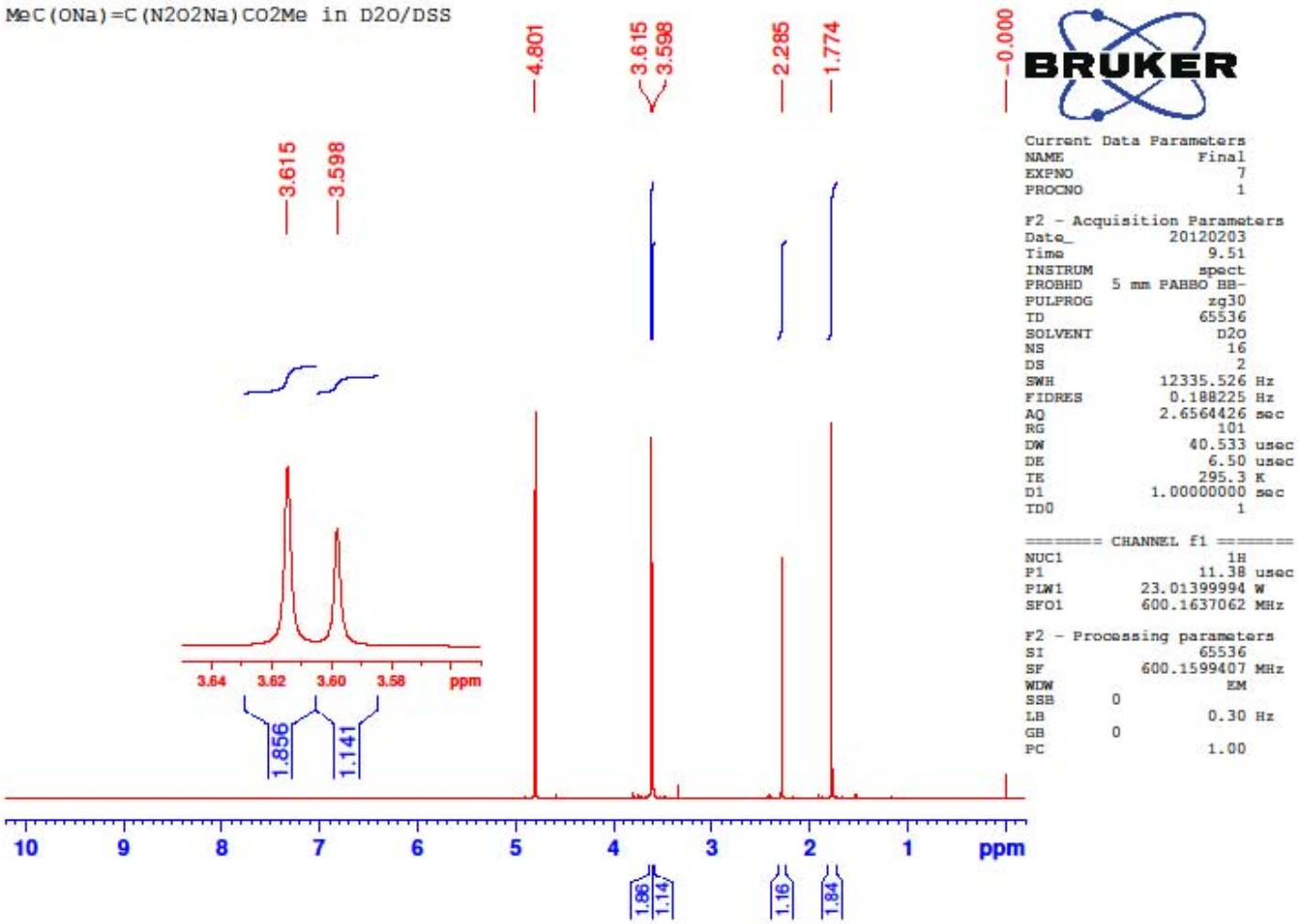


Figure S18. ^{1}H NMR spectrum for MeC(ONa)C(N_2O_2Na)CO_2Me (**$Na_2$3**) in D_2O.

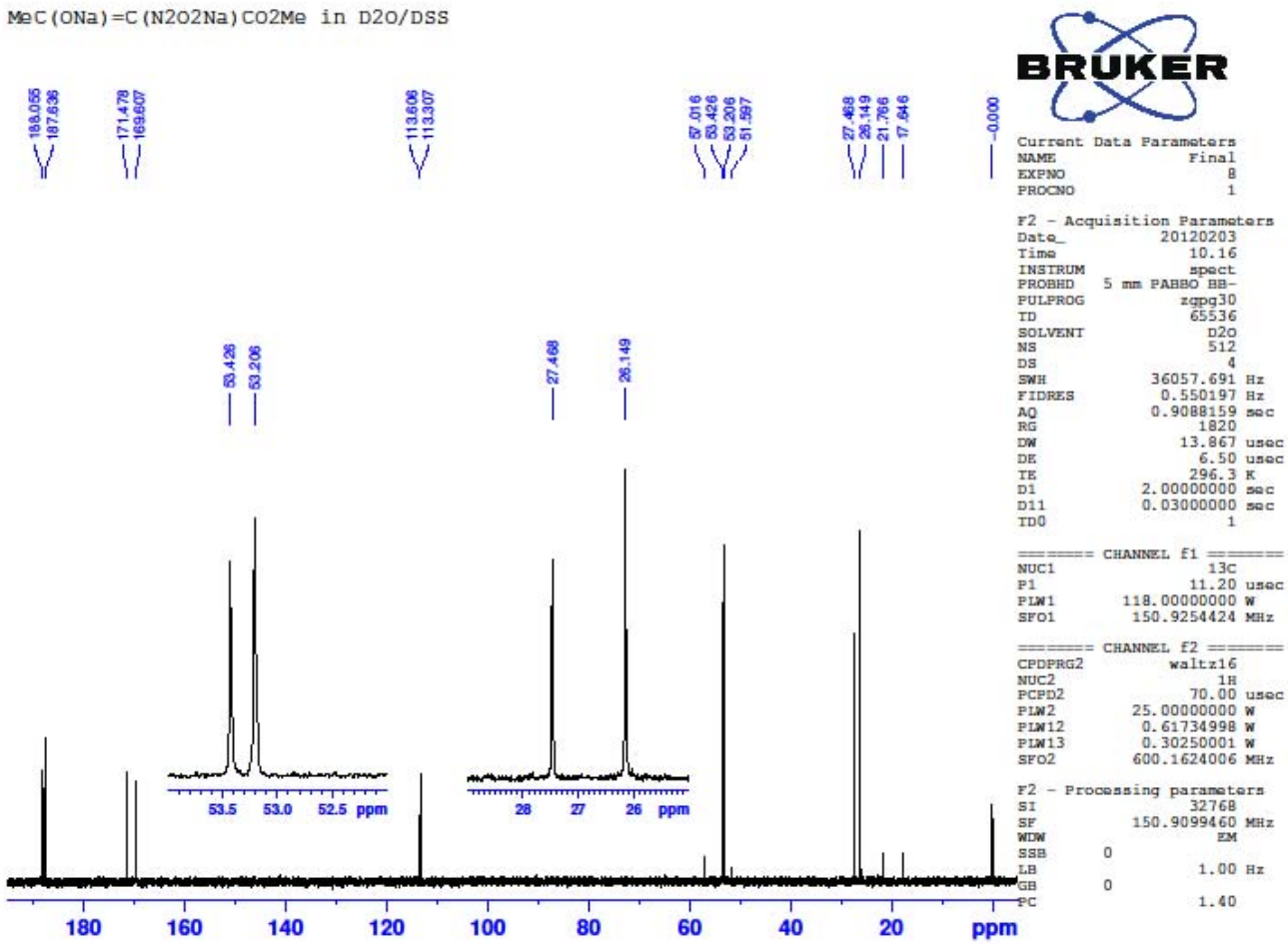
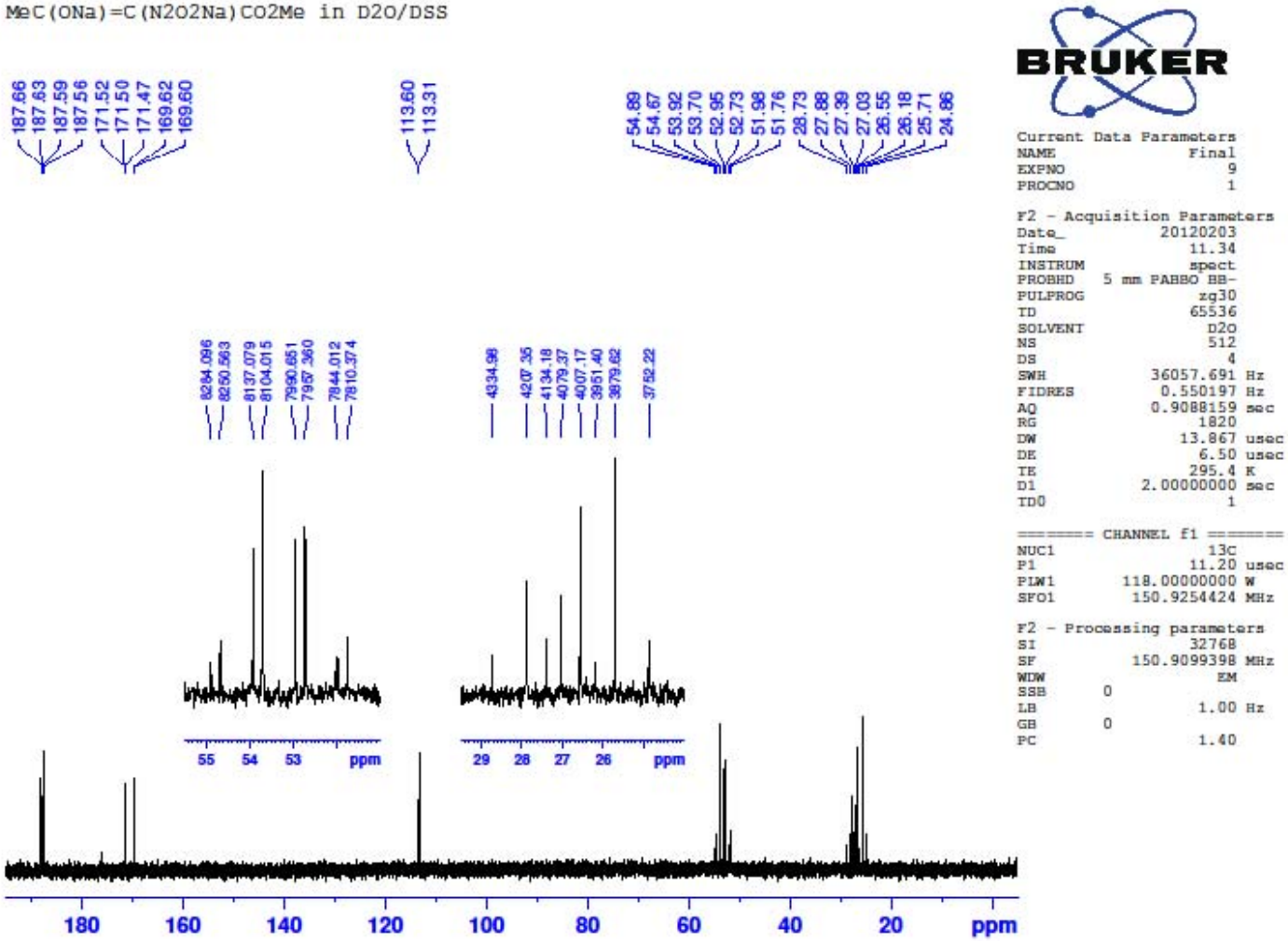


Figure S19. Proton decoupled ^{13}C NMR spectrum for MeC(ONa)C(N_2O_2Na)CO_2Me (**$Na_2$3**) in D_2O.

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SOLVENT                D2O
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DS                         4
SWH              36057.691 Hz
FIDRES            0.550197 Hz
AQ               0.9088159 sec
RG                    1820
DW                  13.867 usec
DE                    6.50 usec
TE                   295.4 K
D1               2.00000000 sec
TD0                      1

======== CHANNEL f1 =======
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P1                    11.20 usec
PLW1         118.00000000 W
SFO1          150.9254424 MHz

F2 - Processing parameters
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SF            150.9099398 MHz
WDW                      EM
SSB       0
LB                     1.00 Hz
GB        0
PC                     1.40
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Figure S20. Proton decoupled ^{13}C NMR spectrum for MeC(ONa)C(N_2O_2Na)CO_2Me (**$Na_2$3**) in D_2O.

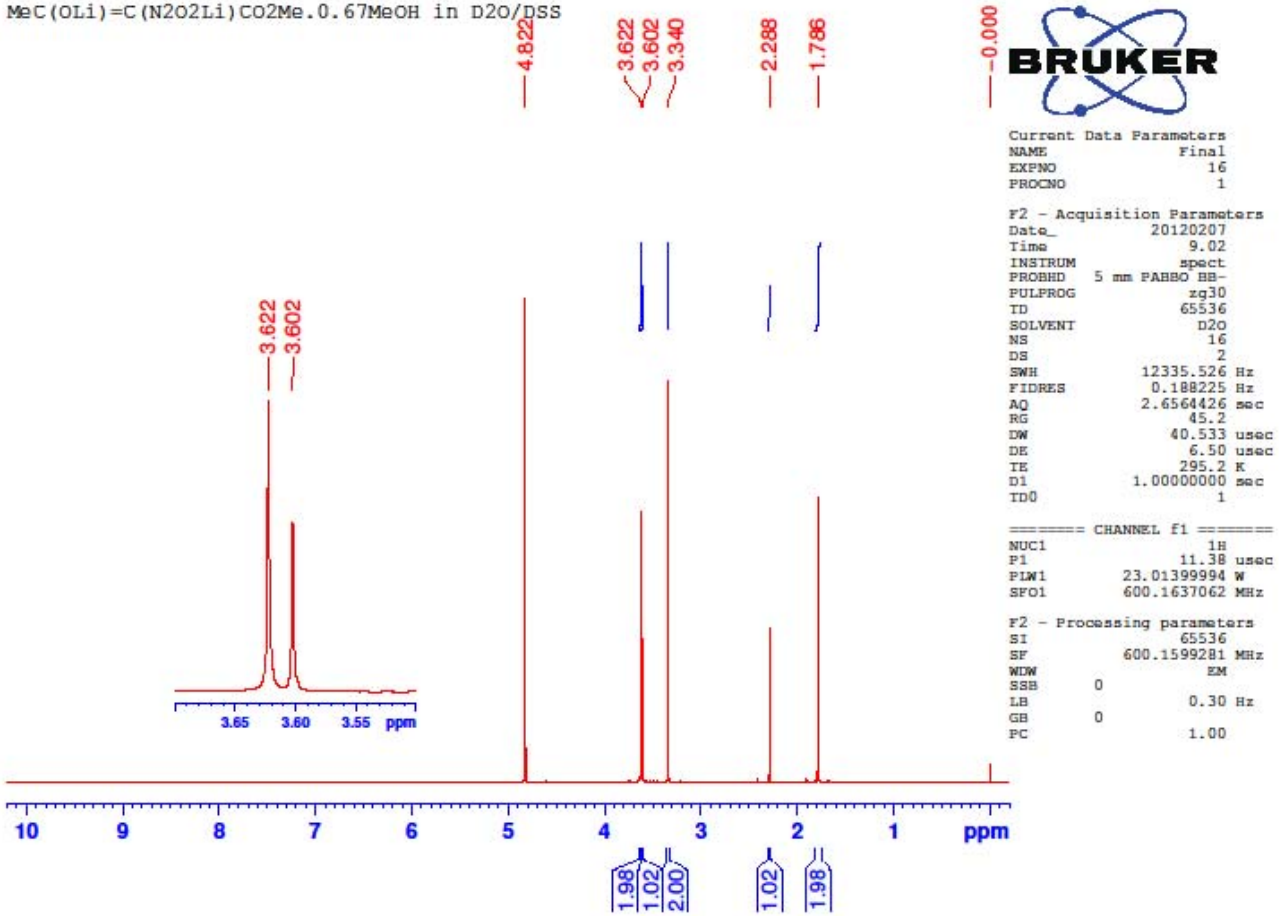


Figure S21. ^{1}H NMR spectrum for MeC(OLi)C(N_2O_2Li)CO_2Me (**$Li_2$3·⅔MeOH·⅓H_2O**) in D_2O.

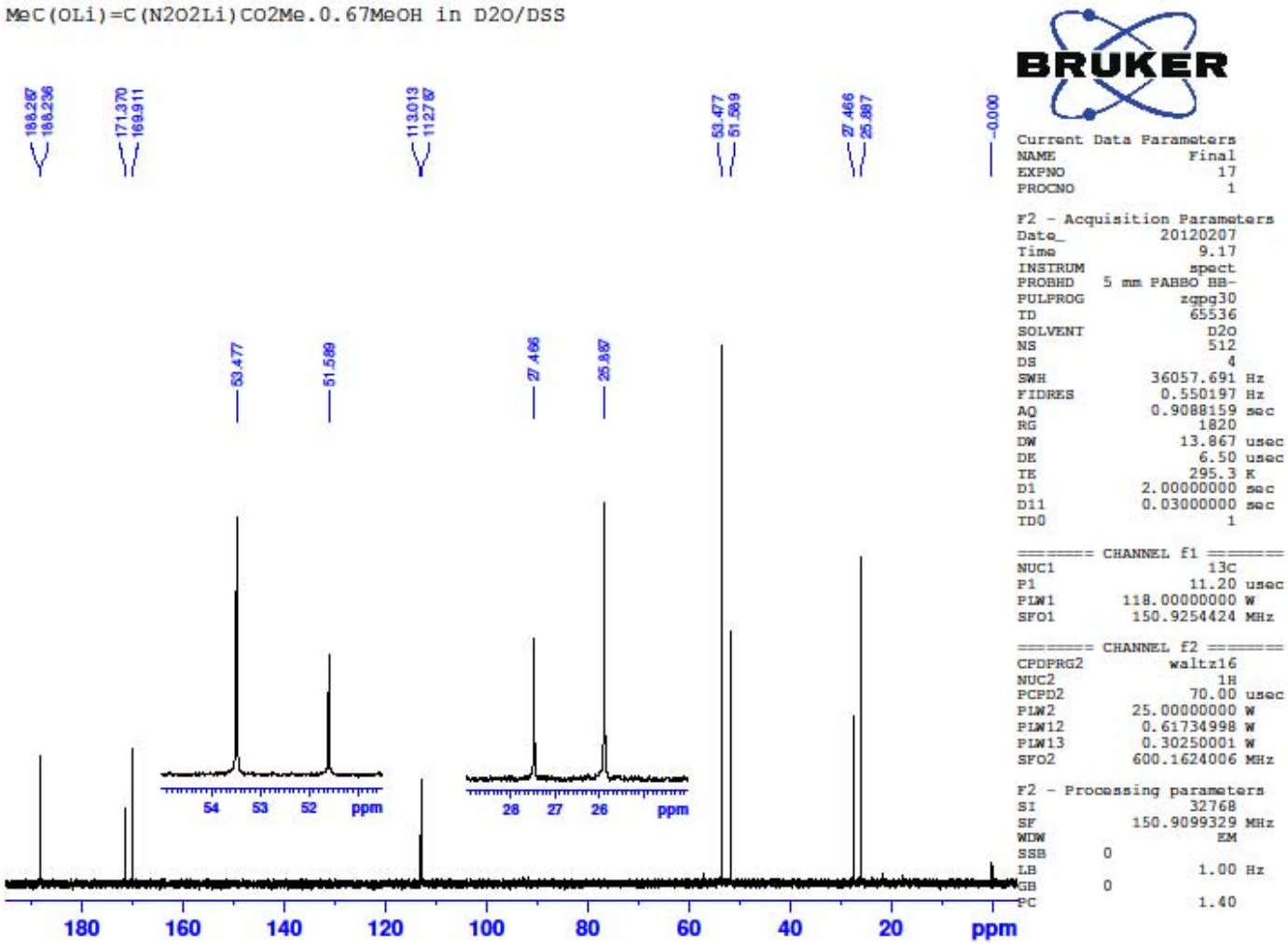
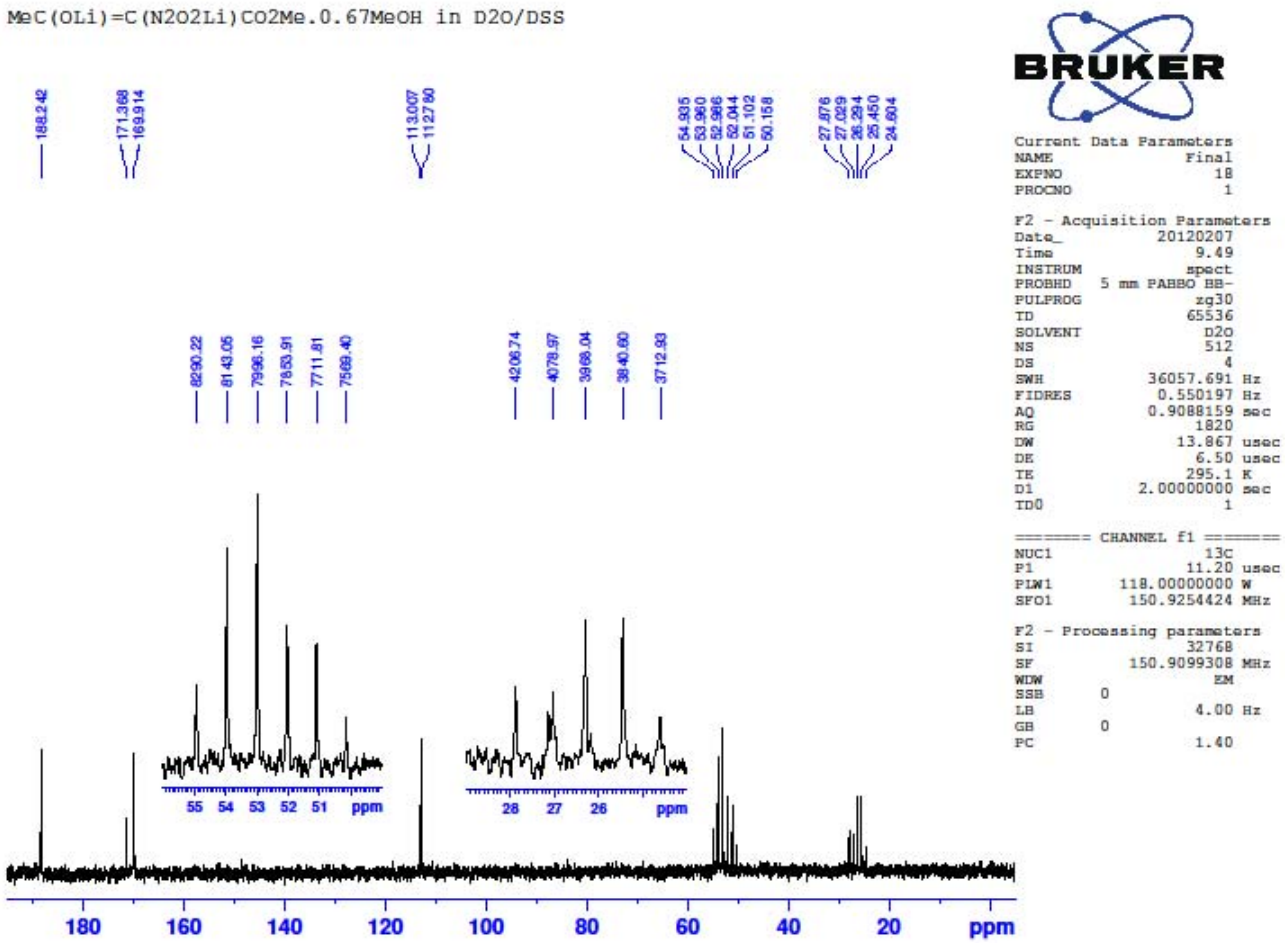


Figure S22. Proton decoupled ^{13}C NMR spectrum for $MeC(OLi)C(N_2O_2Li)CO_2Me$ (**$Li_2$3·⅔MeOH·⅓H_2O**) in D_2O.

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SOLVENT                D2O
NS                     512
DS                       4
SWH              36057.691 Hz
FIDRES            0.550197 Hz
AQ               0.9088159 sec
RG                    1820
DW                  13.867 usec
DE                    6.50 usec
TE                   295.1 K
D1              2.00000000 sec
TD0                      1

======== CHANNEL f1 =======
NUC1                   13C
P1                   11.20 usec
PLW1        118.00000000 W
SFO1         150.9254424 MHz

F2 - Processing parameters
SI                   32768
SF            150.9099308 MHz
WDW                     EM
SSB       0
LB                    4.00 Hz
GB        0
PC                    1.40
```

Figure S23. Proton coupled ^{13}C NMR spectrum for MeC(OLi)C(N_2O_2Li)CO_2Me (**$Li_2$3·⅔MeOH·⅓H_2O**) in D_2O.

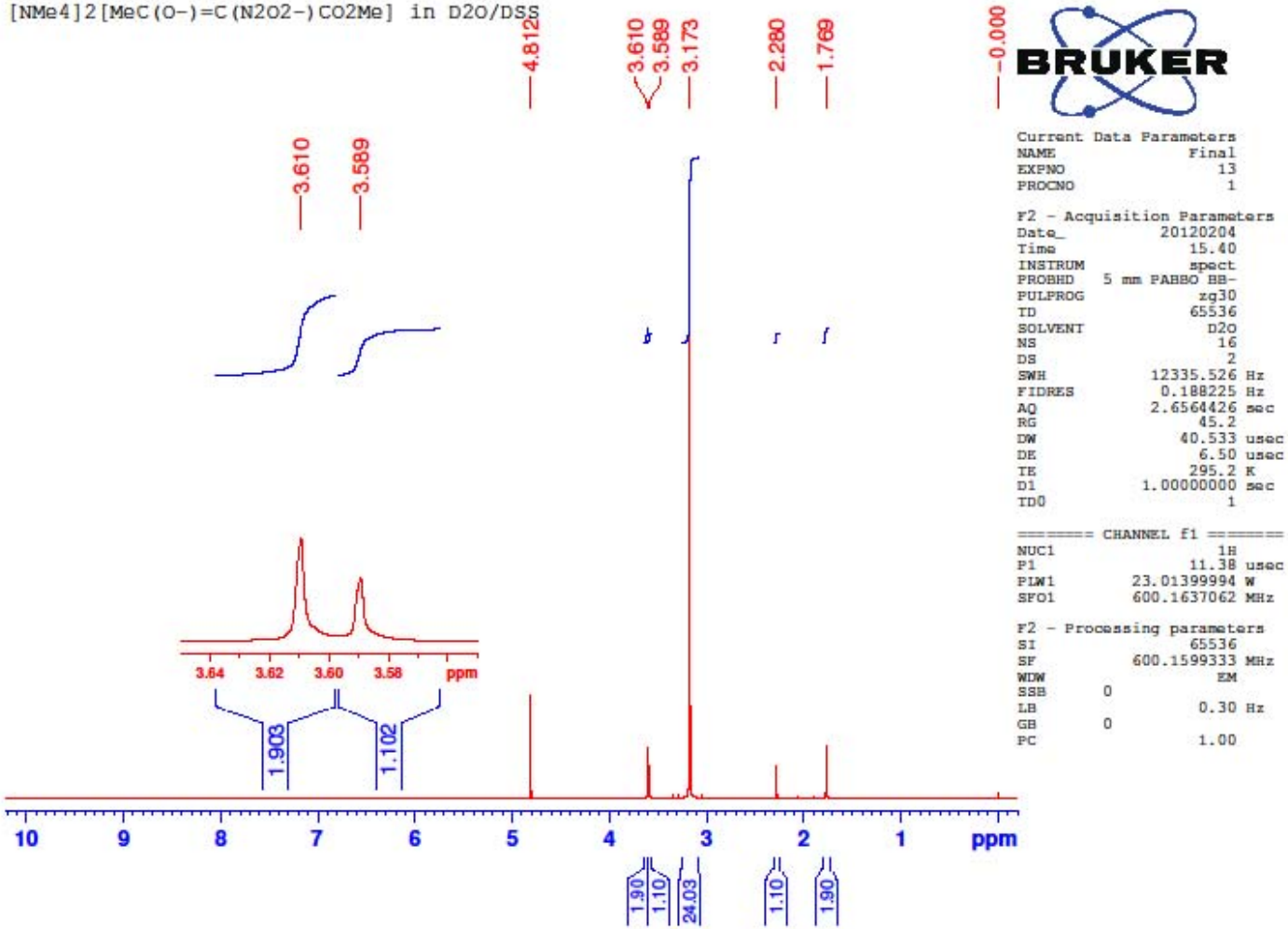


Figure S24. ^{1}H NMR spectrum for $[NMe_4]_2[MeC(O^-)C(N_2O_2^-)CO_2Me]$ (**$[NMe_4]_2$3**) in D_2O.

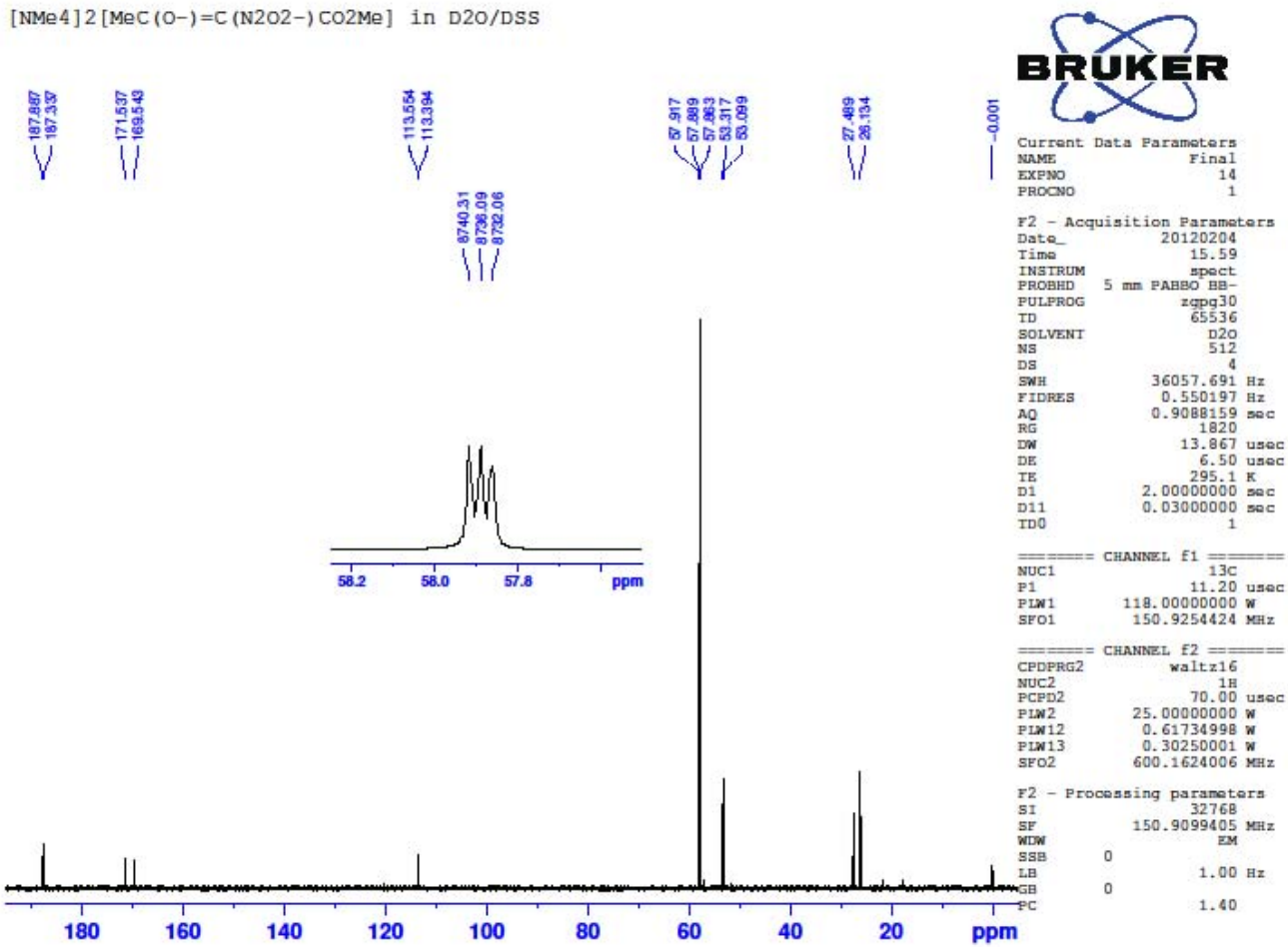


Figure S25. Proton decoupled ^{13}C NMR spectrum for $[NMe_4]_2[MeC(O^-)C(N_2O_2^-)CO_2Me]$ (**$[NMe_4]_2$3**) in D_2O.

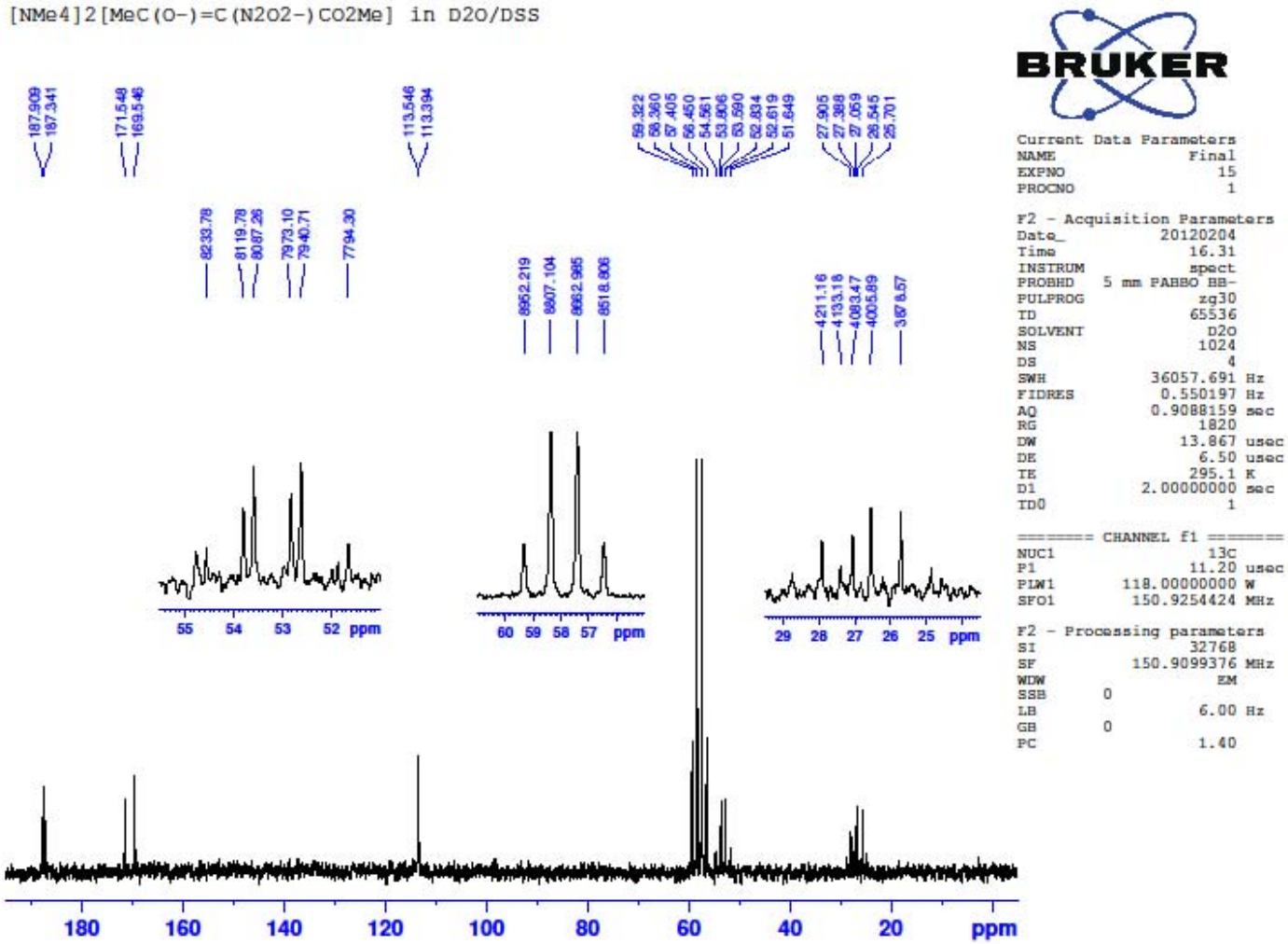
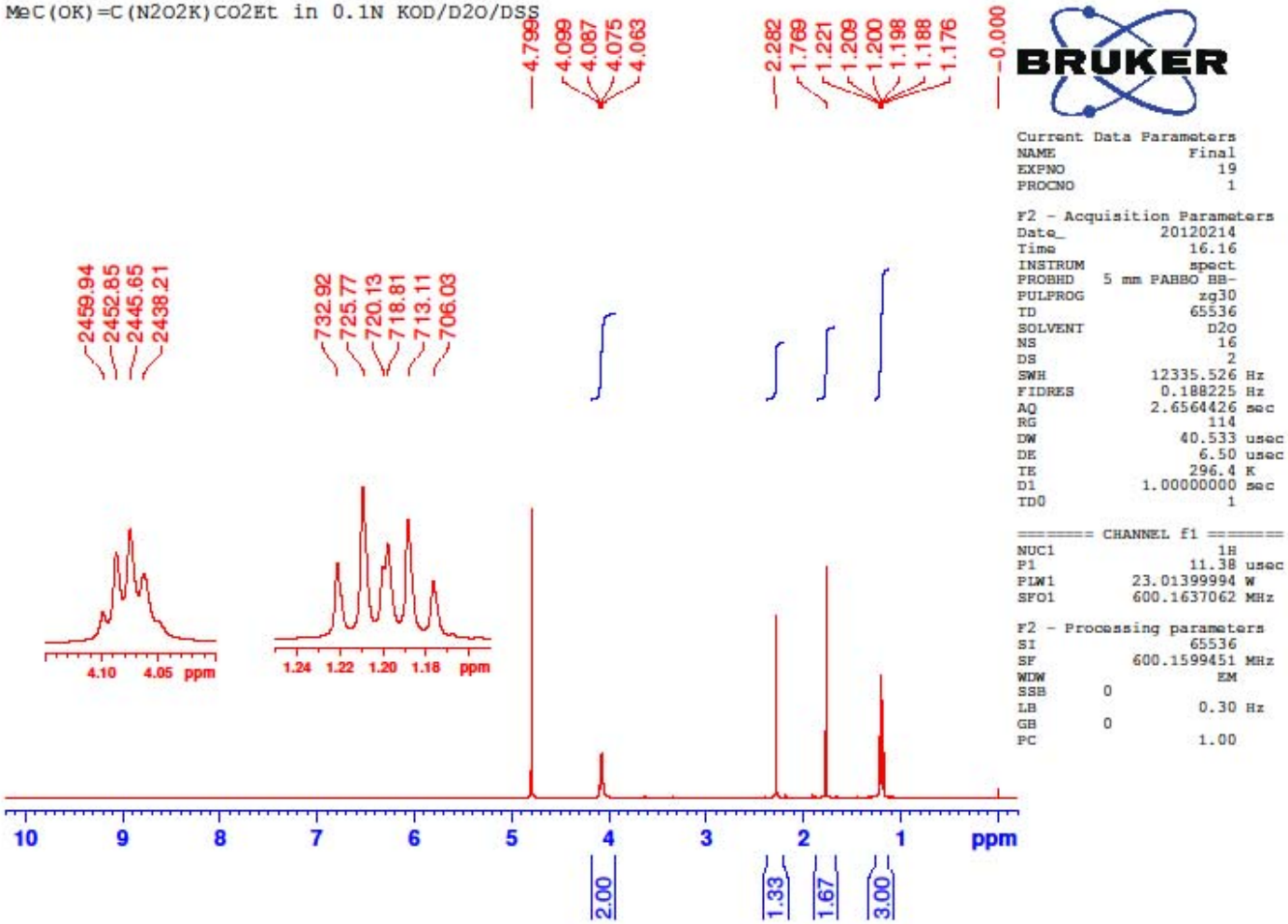


Figure S26. Proton coupled ^{13}C NMR spectrum for $[NMe_4]_2[MeC(O^-)C(N_2O_2^-)CO_2Me]$ (**$[NMe_4]_2$3**) in D_2O.

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SWH              12335.526 Hz
FIDRES            0.188225 Hz
AQ               2.6564426 sec
RG                     114
DW                  40.533 usec
DE                    6.50 usec
TE                   296.4 K
D1               1.00000000 sec
TD0                      1

======== CHANNEL f1 =======
NUC1                    1H
P1                   11.38 usec
PLW1          23.01399994 W
SFO1          600.1637062 MHz

F2 - Processing parameters
SI                   65536
SF            600.1599451 MHz
WDW                     EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.00
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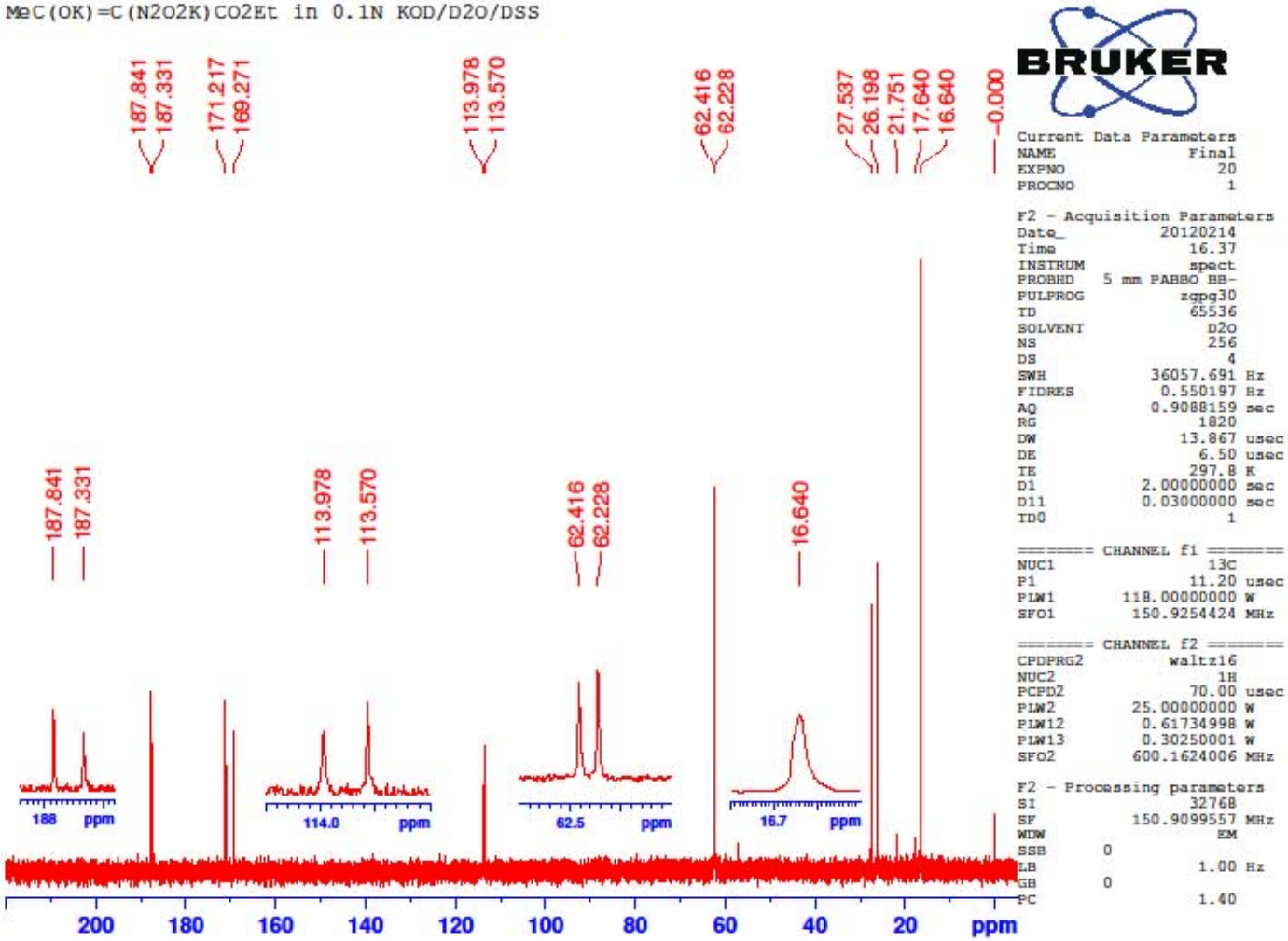
Figure S27. ^{1}H NMR spectrum for MeC(OK)C(N_2O_2K)CO_2Et (**$K_2$4**) in 0.1 N KOD (D_2O).

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TD                   65536
SOLVENT                D2O
NS                     256
DS                       4
SWH              36057.691 Hz
FIDRES            0.550197 Hz
AQ               0.9088159 sec
RG                    1820
DW                  13.867 usec
DE                    6.50 usec
TE                   297.8 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                      1

======== CHANNEL f1 =======
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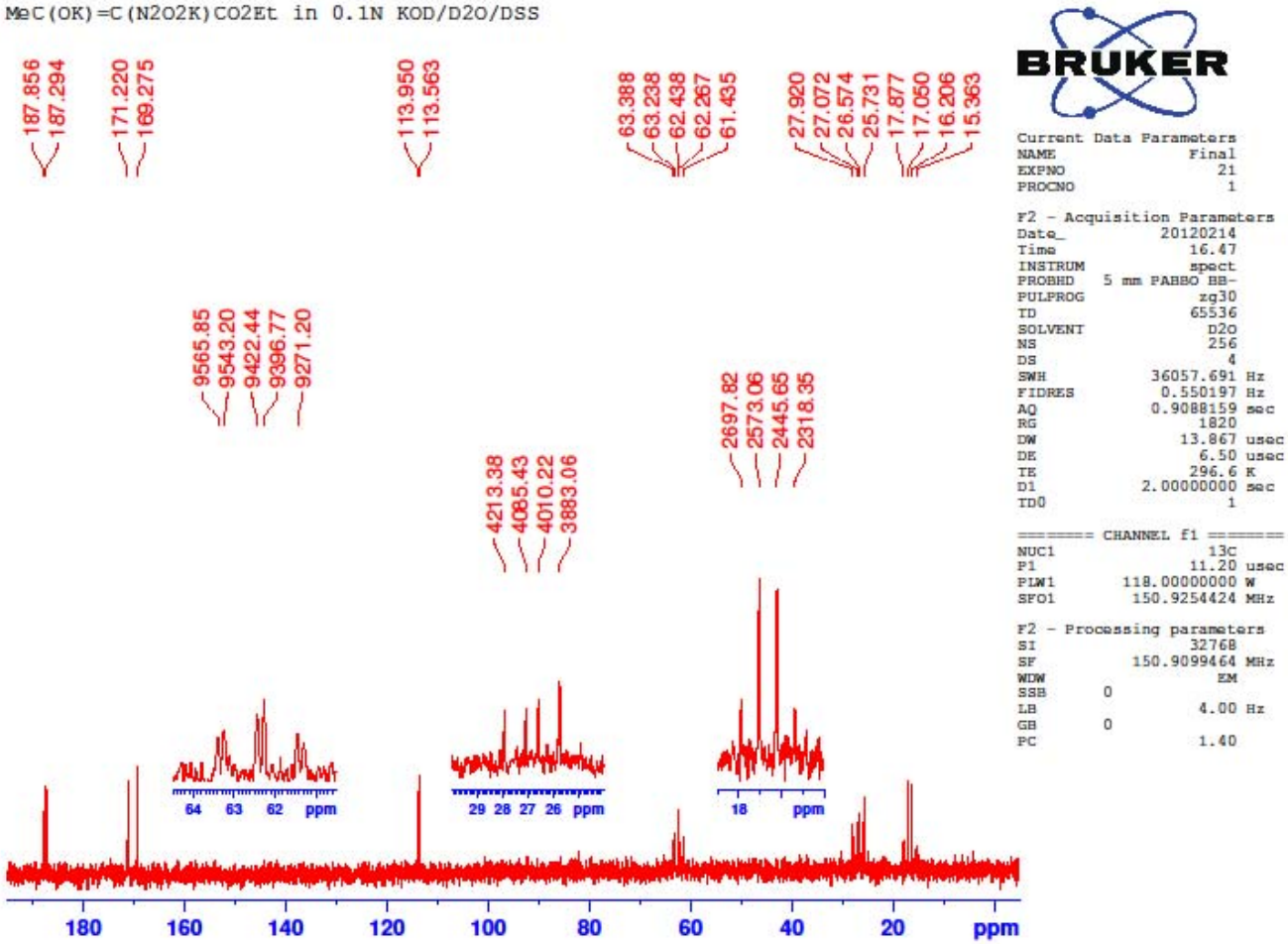
P1                   11.20 usec
PLW1          118.00000000 W
SFO1           150.9254424 MHz

======== CHANNEL f2 =======
CPDPRG2            waltz16
NUC2                    1H
PCPD2                70.00 usec
PLW2           25.00000000 W
PLW12           0.61734998 W
PLW13           0.30250001 W
SFO2          600.1624006 MHz

F2 - Processing parameters
SI                   32768
SF             150.9099557 MHz
WDW                     EM
SSB        0
LB                    1.00 Hz
GB         0
PC                    1.40
```


Figure S28. Proton decoupled ^{13}C NMR spectrum for MeC(OK)C(N_2O_2K)CO_2Et (**$K_2$4**) in 0.1 N KOD (D_2O).

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PULPROG               zg30
TD                   65536
SOLVENT                D2O
NS                     256
DS                       4
SWH              36057.691 Hz
FIDRES            0.550197 Hz
AQ               0.9088159 sec
RG                    1820
DW                  13.867 usec
DE                    6.50 usec
TE                   296.6 K
D1               2.00000000 sec
TD0                       1

======== CHANNEL f1 =======
NUC1                    13C
P1                    11.20 usec
PLW1          118.00000000 W
SFO1           150.9254424 MHz

F2 - Processing parameters
SI                    32768
SF            150.9099464 MHz
WDW                      EM
SSB        0
LB                     4.00 Hz
GB         0
PC                     1.40
```

Figure S29. Proton coupled ^{13}C NMR spectrum for MeC(OK)C(N_2O_2K)CO_2Et (**$K_2$4**) in 0.1 N KOD (D_2O).

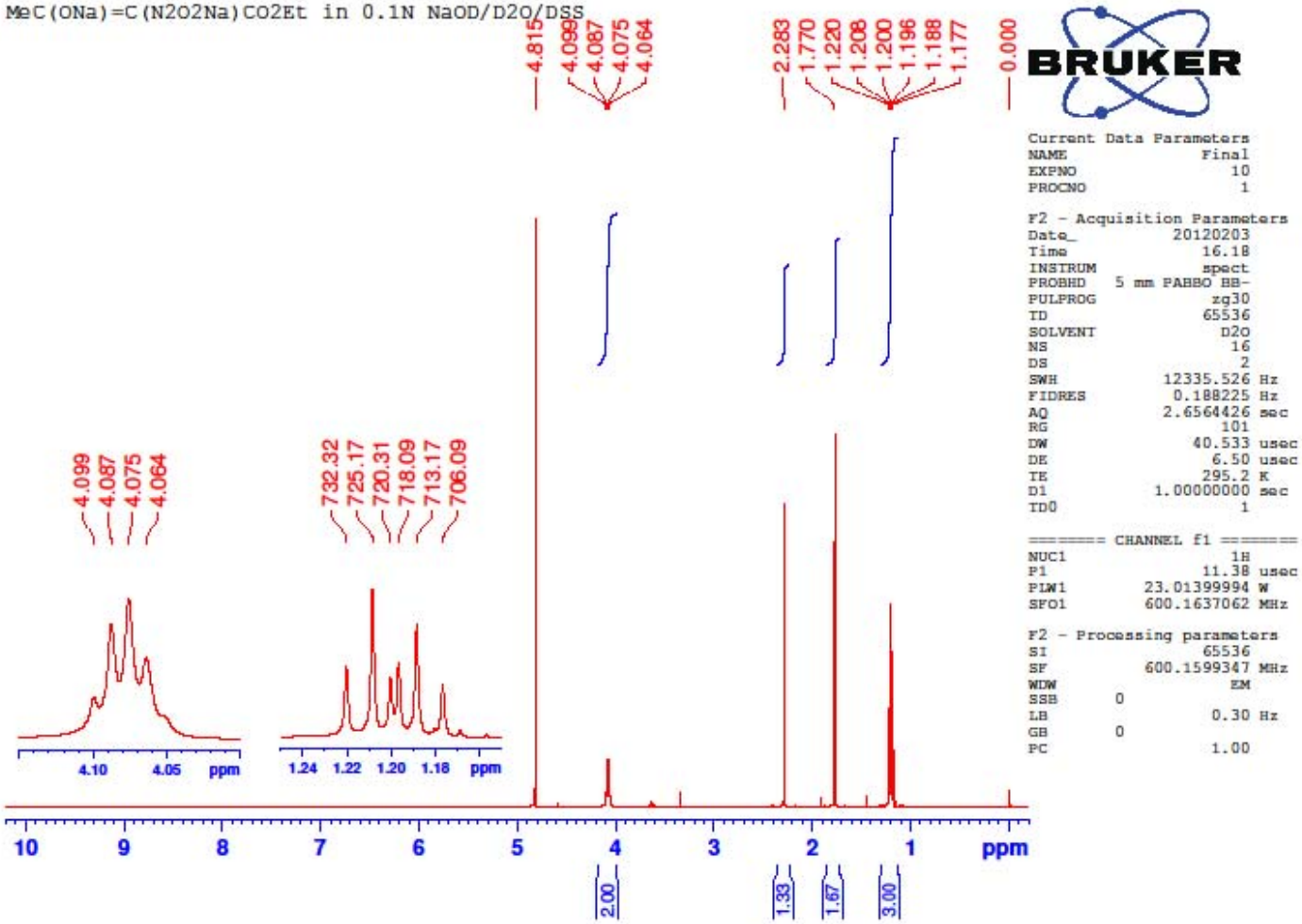
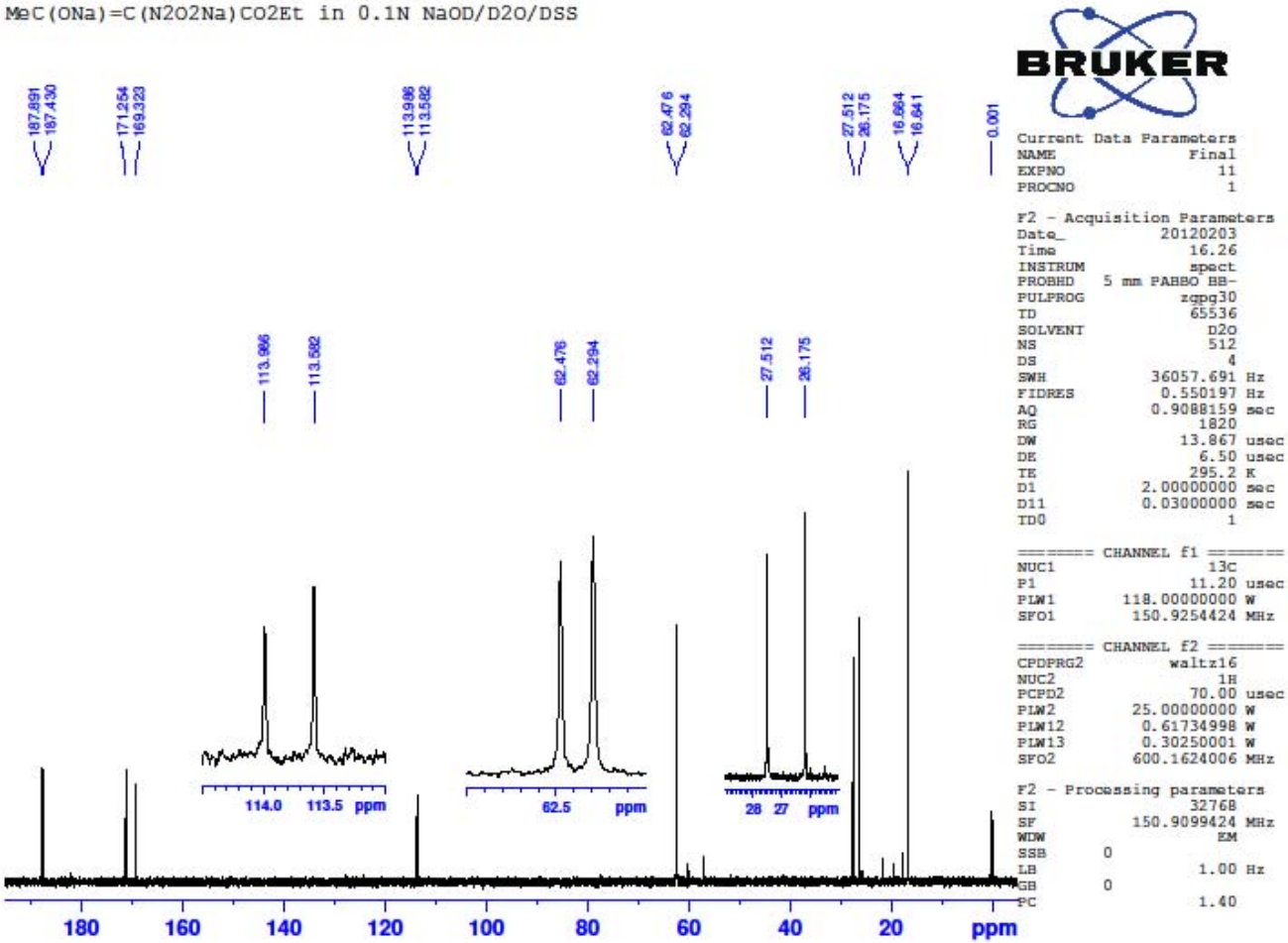
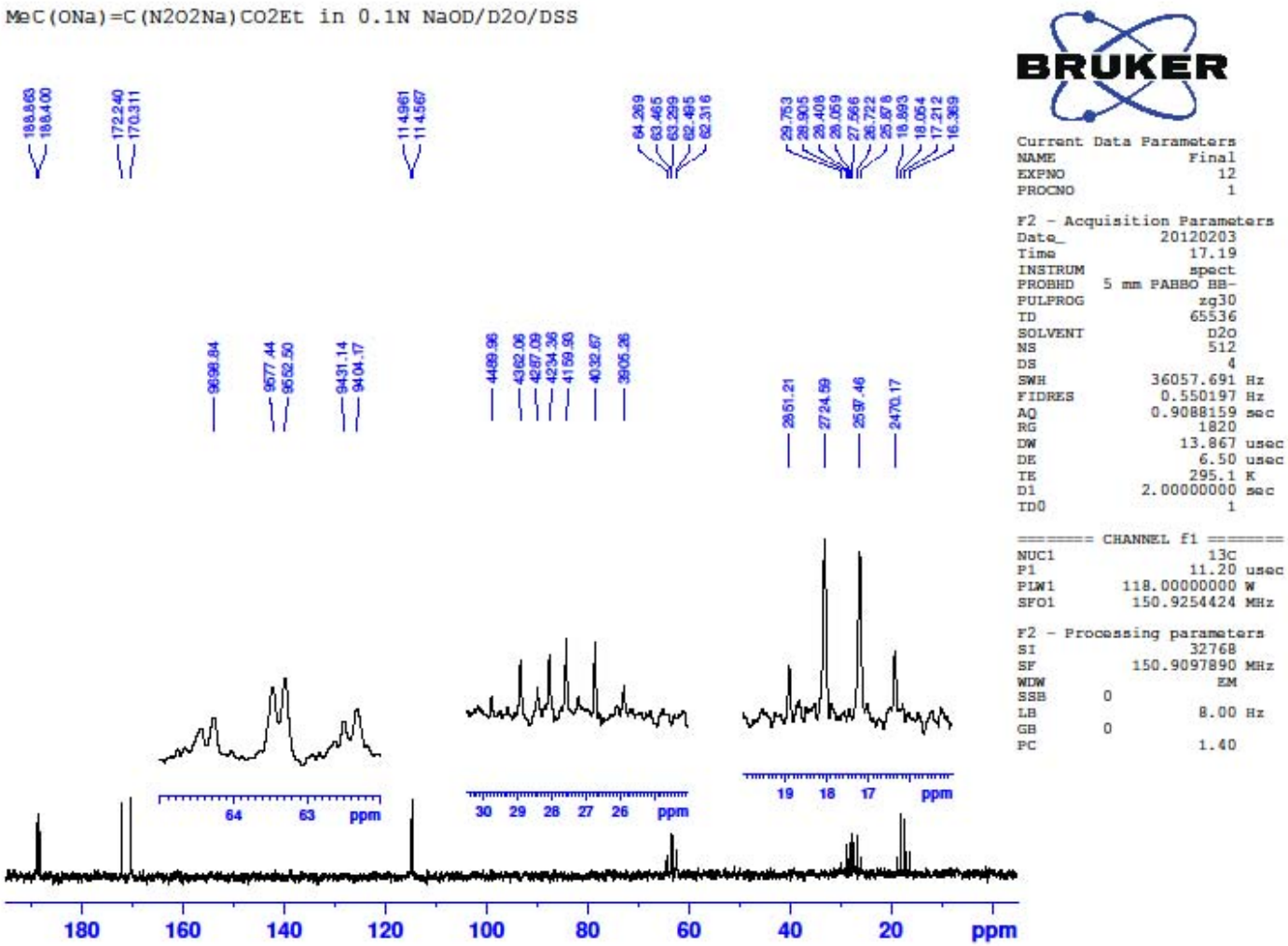


Figure S30. ^{1}H NMR spectrum for MeC(ONa)C(N_2O_2Na)CO_2Et (**$Na_2$4**) in 0.1 N KOD (D_2O).




```
Current Data Parameters
NAME                 Final
EXPNO                   11
PROCNO                   1

F2 - Acquisition Parameters
Date_             20120203
Time                 16.26
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                   65536
SOLVENT                D2O
NS                     512
DS                       4
SWH              36057.691 Hz
FIDRES            0.550197 Hz
AQ               0.9088159 sec
RG                    1820
DW                  13.867 usec
DE                    6.50 usec
TE                   295.2 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    13C
P1                    11.20 usec
PLW1         118.00000000 W
SFO1          150.9254424 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                     1H
PCPD2                 70.00 usec
PLW2          25.00000000 W
PLW12          0.61734998 W
PLW13          0.30250001 W
SFO2          600.1624006 MHz

F2 - Processing parameters
SI                    32768
SF            150.9099424 MHz
WDW                      EM
SSB       0
LB                     1.00 Hz
GB        0
PC                     1.40
```

Figure S31. Proton decoupled ^{13}C NMR for MeC(ONa)C(N_2O_2Na)CO_2Et (**$Na_2$4**) in 0.1 N KOD (D_2O).




```
Current Data Parameters
NAME                 Final
EXPNO                   12
PROCNO                   1

F2 - Acquisition Parameters
Date_             20120203
Time                 17.19
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT               D2O
NS                    512
DS                      4
SWH             36057.691 Hz
FIDRES           0.550197 Hz
AQ              0.9088159 sec
RG                   1820
DW                 13.867 usec
DE                   6.50 usec
TE                  295.1 K
D1             2.00000000 sec
TD0                     1

======== CHANNEL f1 =======
NUC1                  13C
P1                  11.20 usec
PLW1        118.00000000 W
SFO1         150.9254424 MHz

F2 - Processing parameters
SI                  32768
SF            150.9097890 MHz
WDW                    EM
SSB       0
LB                   8.00 Hz
GB        0
PC                   1.40
```

Figure S32. Proton decoupled ^{13}C NMR for MeC(ONa)C(N_2O_2Na)CO_2Et (**$Na_2$4**) in 0.1 N KOD (D_2O).

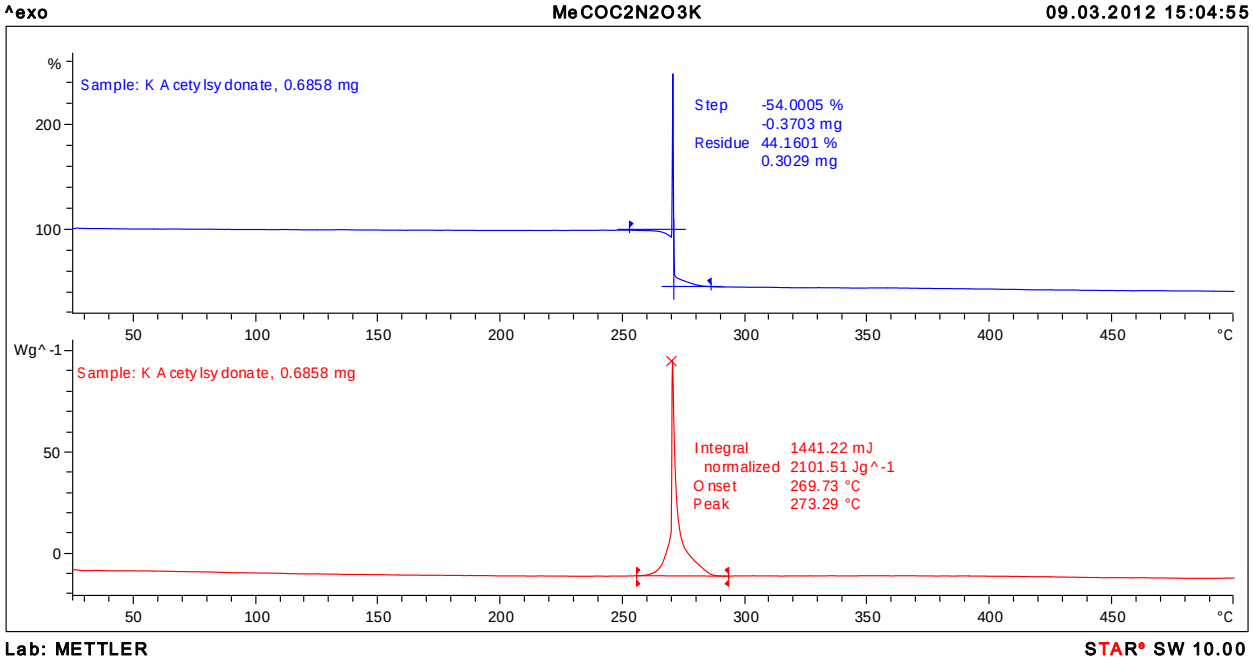


Figure S33. DSC and TGA plots for $CH_3COC_2N_2O_3K$ (**K1**).

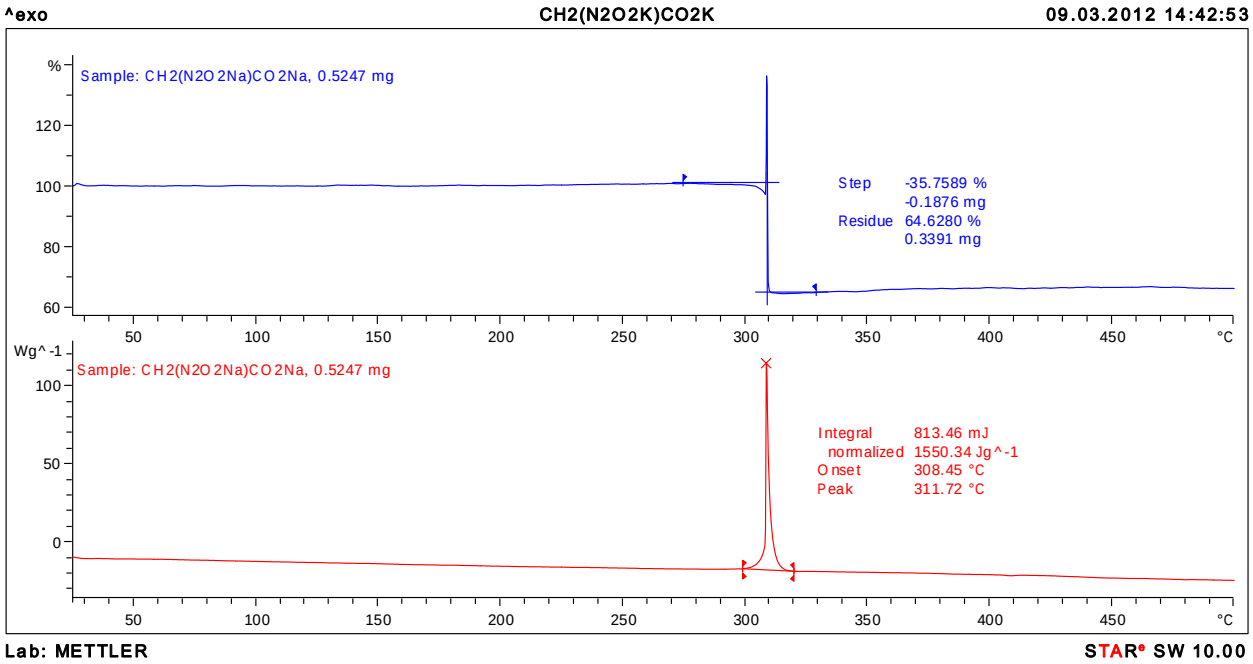


Figure S34. DSC and TGA plots for $CH_2(N_2O_2K)CO_2K{\cdot}H_2O$ (**$K_2$2·H_2O**).

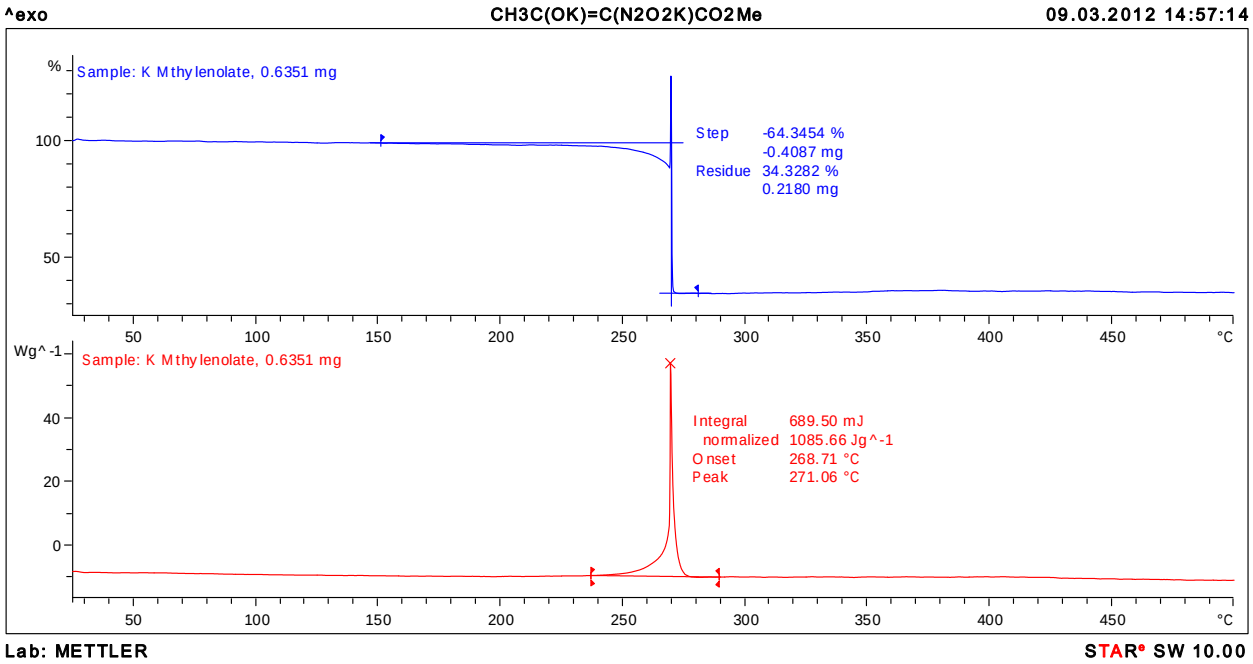


Figure S35. DSC and TGA plots for MeC(OK)C(N_2O_2K)CO_2Me (**$K_2$3**).

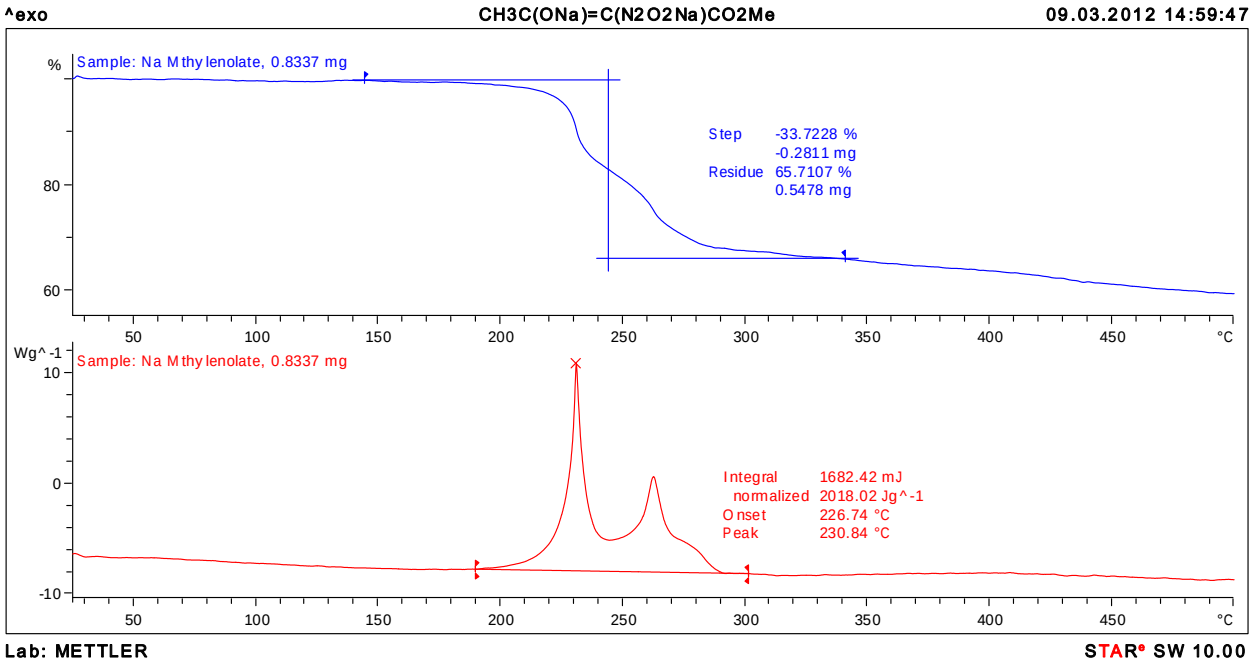


Figure S36. DSC and TGA plots for MeC(ONa)C(N_2O_2Na)CO_2Me (**$Na_2$3**).

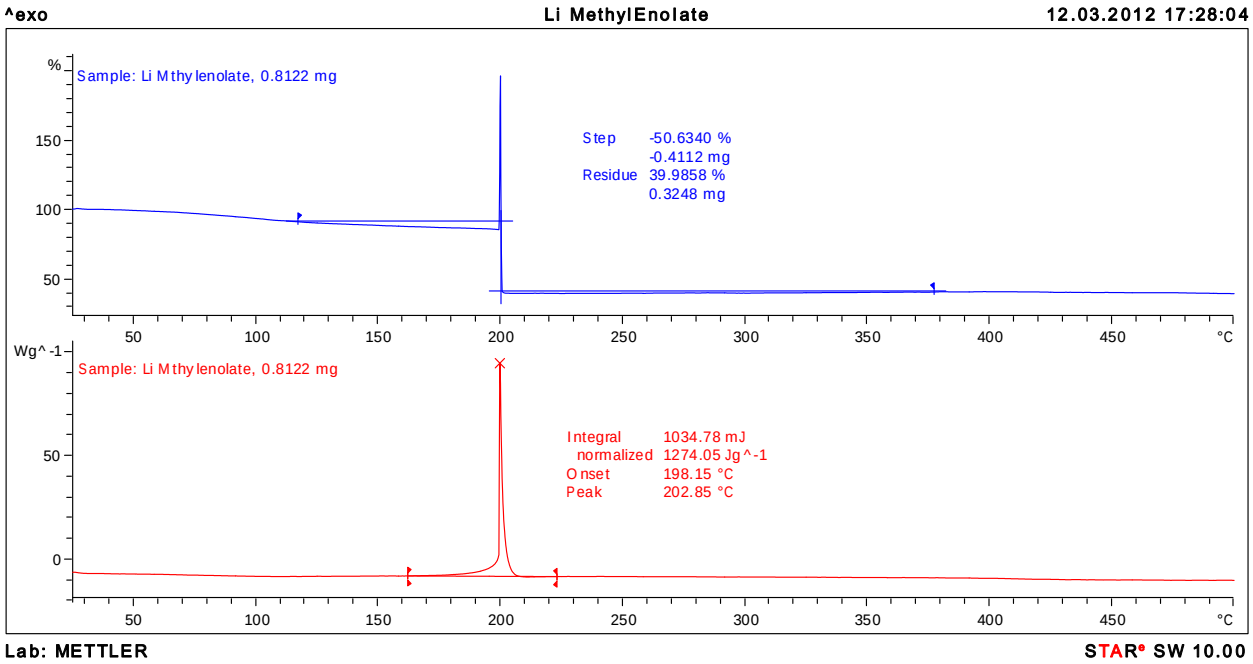


Figure S37. DSC and TGA plots for MeC(OLi)C(N_2O_2Li)CO_2Me (**$Li_2$3·⅔MeOH·⅓H_2O**).

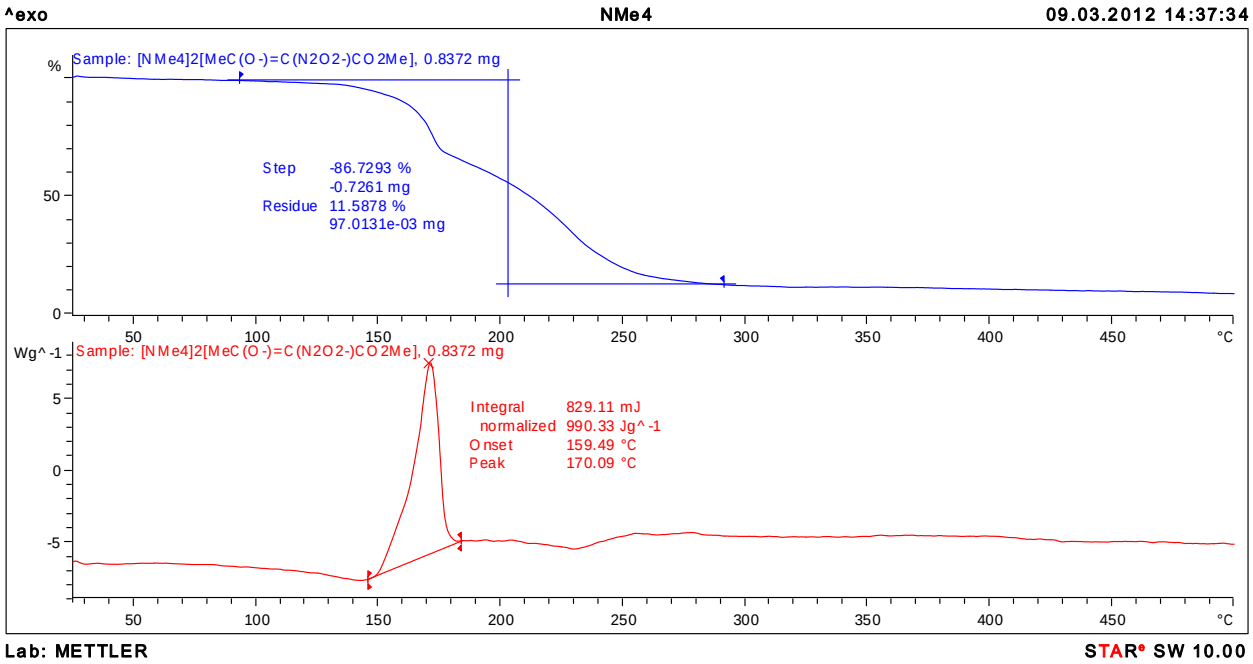


Figure S38. DSC and TGA plots for MeC(OK)C(N_2O_2K)CO_2Et (**$K_2$4**).

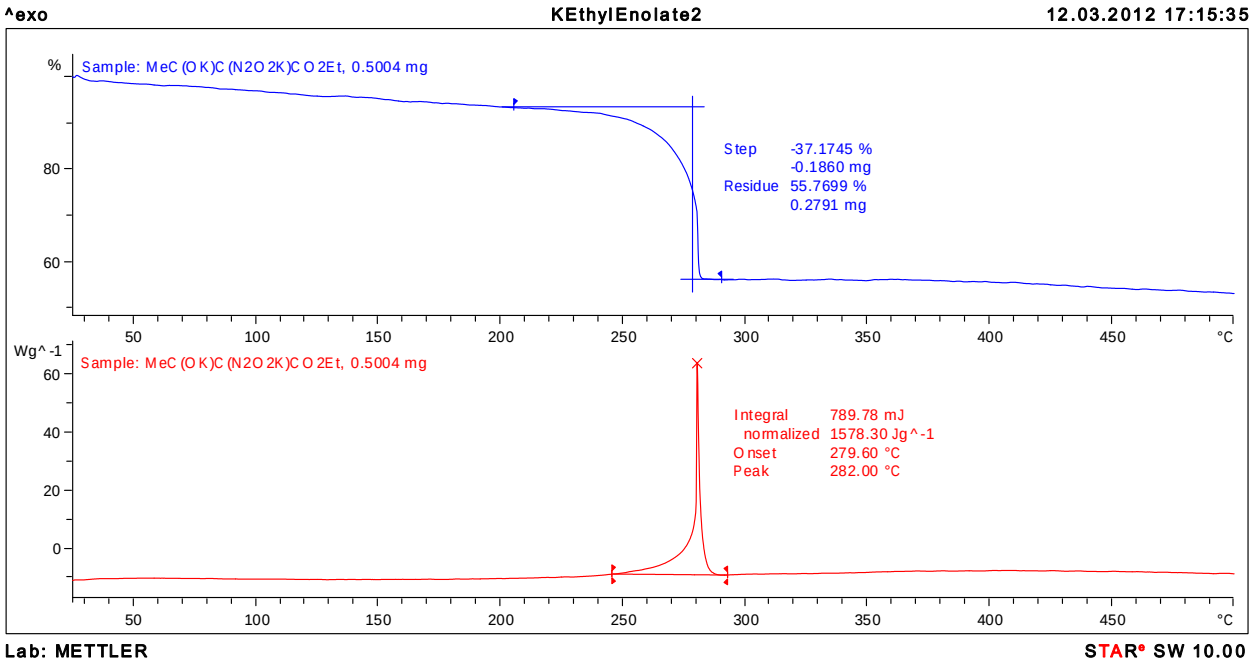


Figure S39. DSC and TGA plots for MeC(OK)C(N_2O_2K)CO_2Et (**$K_2$4**).

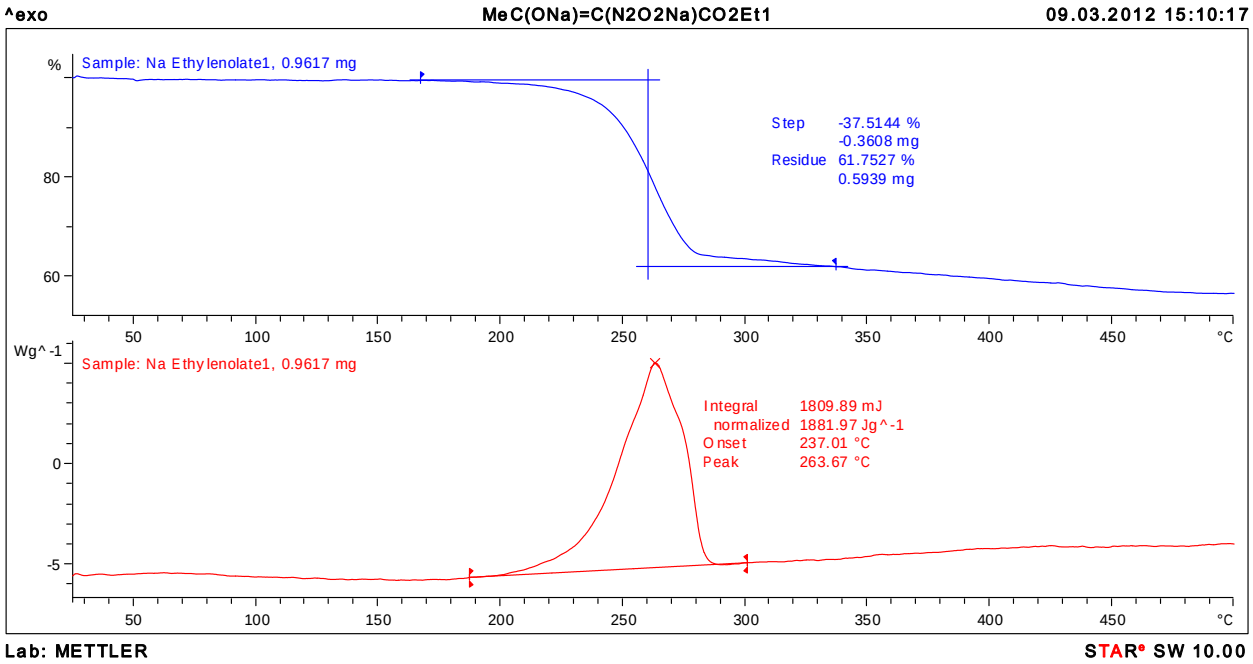
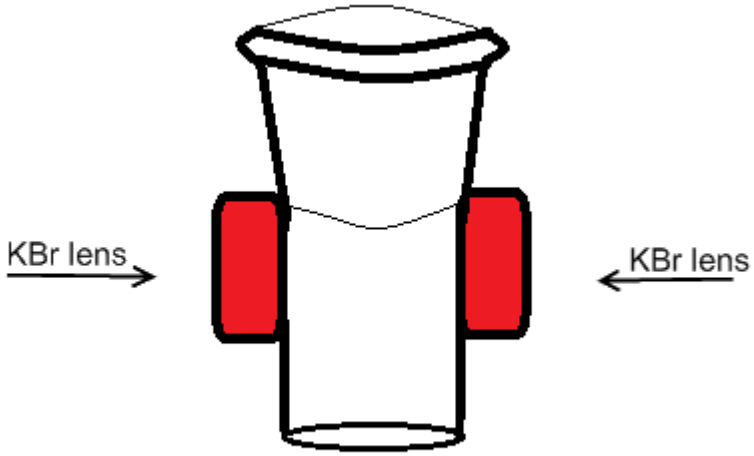


Figure S40. DSC and TGA plots for MeC(ONa)C(N_2O_2Na)CO_2Et (**$Na_2$4**).

Gas phase IR cell



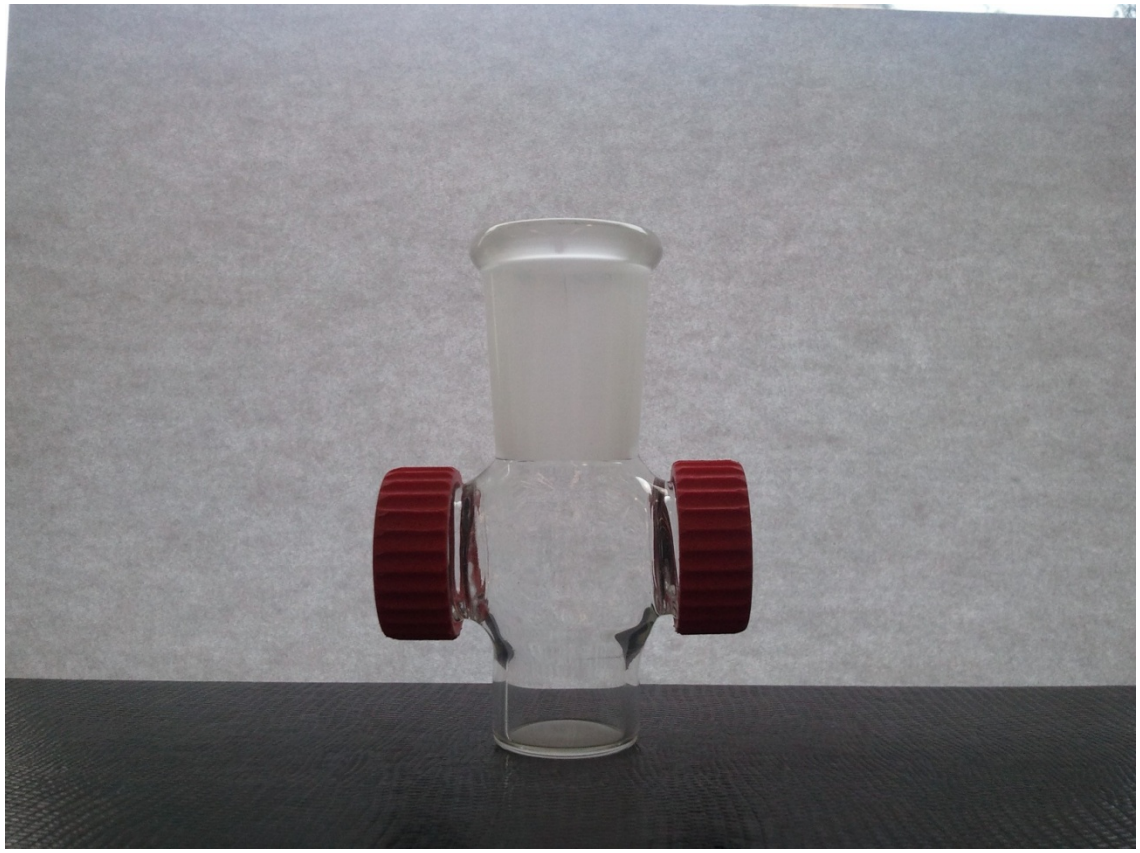


Figure S41 Sketch and picture of Gas Cell used from detection of Nitrous oxide.