Electronic Supplementary Material (ESI) for RSC Advances

# Supporting Information

# Ring Transformation of (4-Chloro-5*H*-1,2,3-dithiazol-5-ylidene)acetonitriles to 3-Haloisothiazole-5-carbonitriles

Andreas S. Kalogirou, Irene C. Christoforou, Heraklidia A. Ioannidou, Manolis J. Manos
and Panayiotis A. Koutentis *

*Department of Chemistry, University of Cyprus, P.O. Box 20537, 1678 Nicosia, Cyprus*

koutenti@ucy.ac.cy

# Supporting Information

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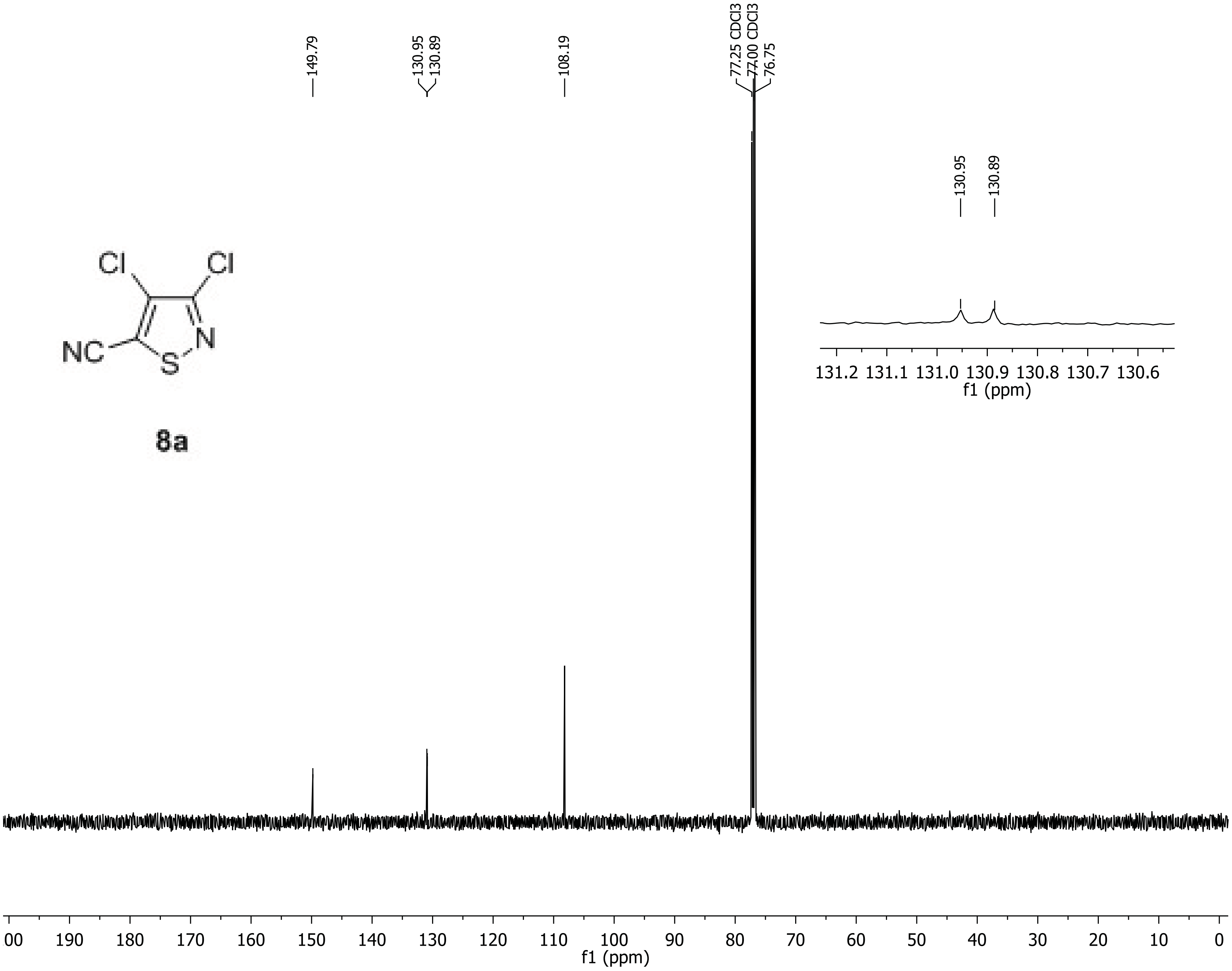
# SECTION A

3,4-Dichloroisothiazole-5-carbonitrile (**8a**)

**8a**



| | |
|---|---|
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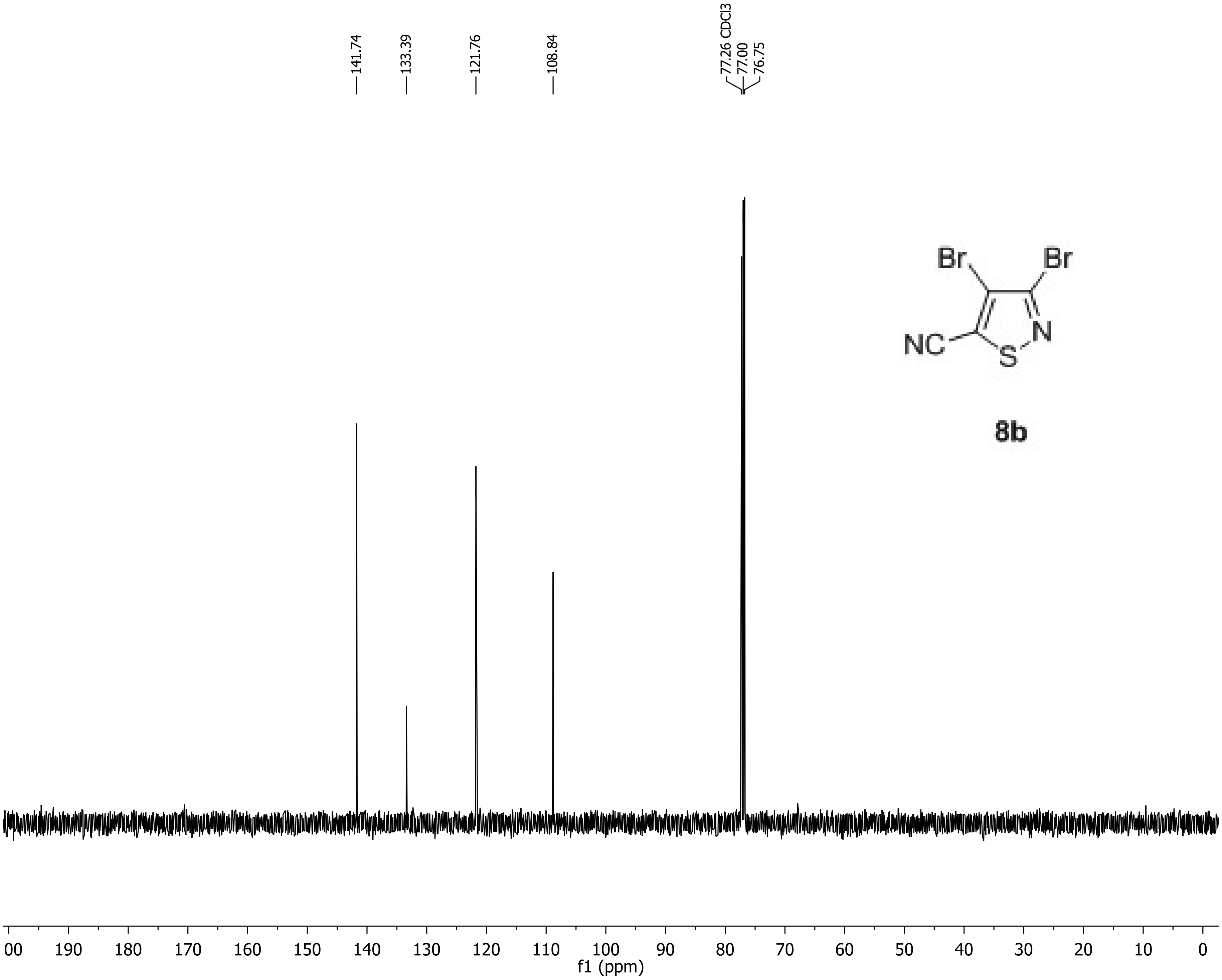
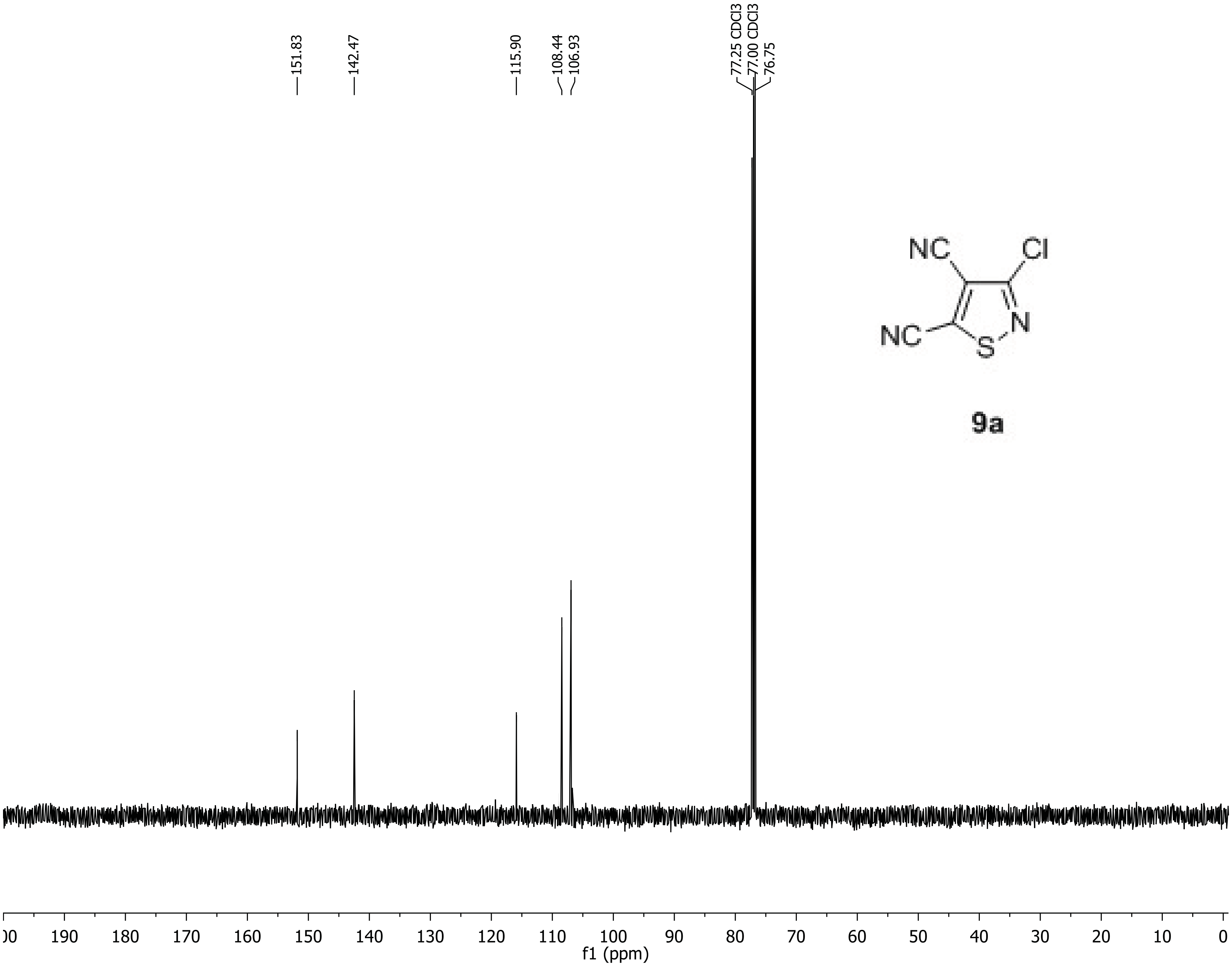
| NAME | Andreas Kalogirou |
| EXPNO | 133 |
| PROCNO | 1 |
| F2 - Acquisition Parameters | |
| Date_ | 20130409 |
| Time | 16.12 |
| INSTRUM | spect |
| PROBHD | 5 mm PABBO BB- |
| PULPROG | jmod |
| TD | 65536 |
| SOLVENT | CDCl3 |
| NS | 2825 |
| DS | 4 |
| SWH | 29761.904 Hz |
| FIDRES | 0.454131 Hz |
| AQ | 1.1010048 sec |
| RG | 2050 |
| DW | 16.800 usec |
| DE | 6.50 usec |
| TE | 295.7 K |
| CNST2 | 145.0000000 |
| CNST11 | 1.0000000 |
| D1 | 2.00000000 sec |
| D20 | 0.00689655 sec |
| TD0 | 1 |
| CHANNEL f1 | |
| SFO1 | 125.7459782 MHz |
| NUC1 | 13C |
| P1 | 8.70 usec |
| P2 | 17.40 usec |
| PLW1 | 138.00000000 W |
| CHANNEL f2 | |
| SFO2 | 500.0350280 MHz |
| NUC2 | 1H |
| CPDPRG[2 | waltz16 |
| PCPD2 | 80.00 usec |
| PLW2 | 15.41699982 W |
| PLW12 | 0.33258000 W |
| F2 - Processing parameters | |
| SI | 32768 |
| SF | 125.7334091 MHz |
| WDW | EM |
| SSB | 0 |
| LB | 1.00 Hz |
| GB | 0 |
| PC | 1.40 |

3,4-Dibromoisothiazole-5-carbonitrile (**8b**)



Current Data Parameters
NAME Andreas Kalogirou
EXPNO 54
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130218
Time 22.30
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG jmod
TD 65536
SOLVENT CDCl3
NS 512
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 2050
DW 16.800 usec
DE 6.50 usec
TE 297.0 K
CNST2 145.0000000
CNST11 1.0000000
D1 2.00000000 sec
D20 0.00689655 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7459782 MHz
NUC1 13C
P1 8.70 usec
P2 17.40 usec
PLW1 138.00000000 W
======== CHANNEL f2 ========
SFO2 500.0350280 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 15.41699982 W
PLW12 0.33258000 W
F2 - Processing parameters
SI 32768
SF 125.7334109 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

# 3-Chloroisothiazole-4,5-dicarbonitrile (**9a**)



```
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NAME    Andreas Kalogirou
EXPNO              126
PROCNO               1
F2 - Acquisition Parameters
Date_          20130407
Time             14.27
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG           jmod
TD               65536
SOLVENT           CDCl3
NS                 800
DS                   4
SWH         29761.904 Hz
FIDRES       0.454131 Hz
AQ          1.1010048 sec
RG                2050
DW             16.800 usec
DE               6.50 usec
TE              296.7 K
CNST2     145.0000000
CNST11      1.0000000
D1        2.00000000 sec
D20       0.00689655 sec
TD0                  1
======== CHANNEL f1 ========
SFO1      125.7459782 MHz
NUC1               13C
P1                8.70 usec
P2               17.40 usec
PLW1      138.00000000 W
======== CHANNEL f2 ========
SFO2      500.0350280 MHz
NUC2                1H
CPDPRG[2       waltz16
PCPD2            80.00 usec
PLW2       15.41699982 W
PLW12       0.33258000 W
F2 - Processing parameters
SI               32768
SF        125.7334111 MHz
WDW                 EM
SSB    0
LB                1.00 Hz
GB     0
PC                1.40
```
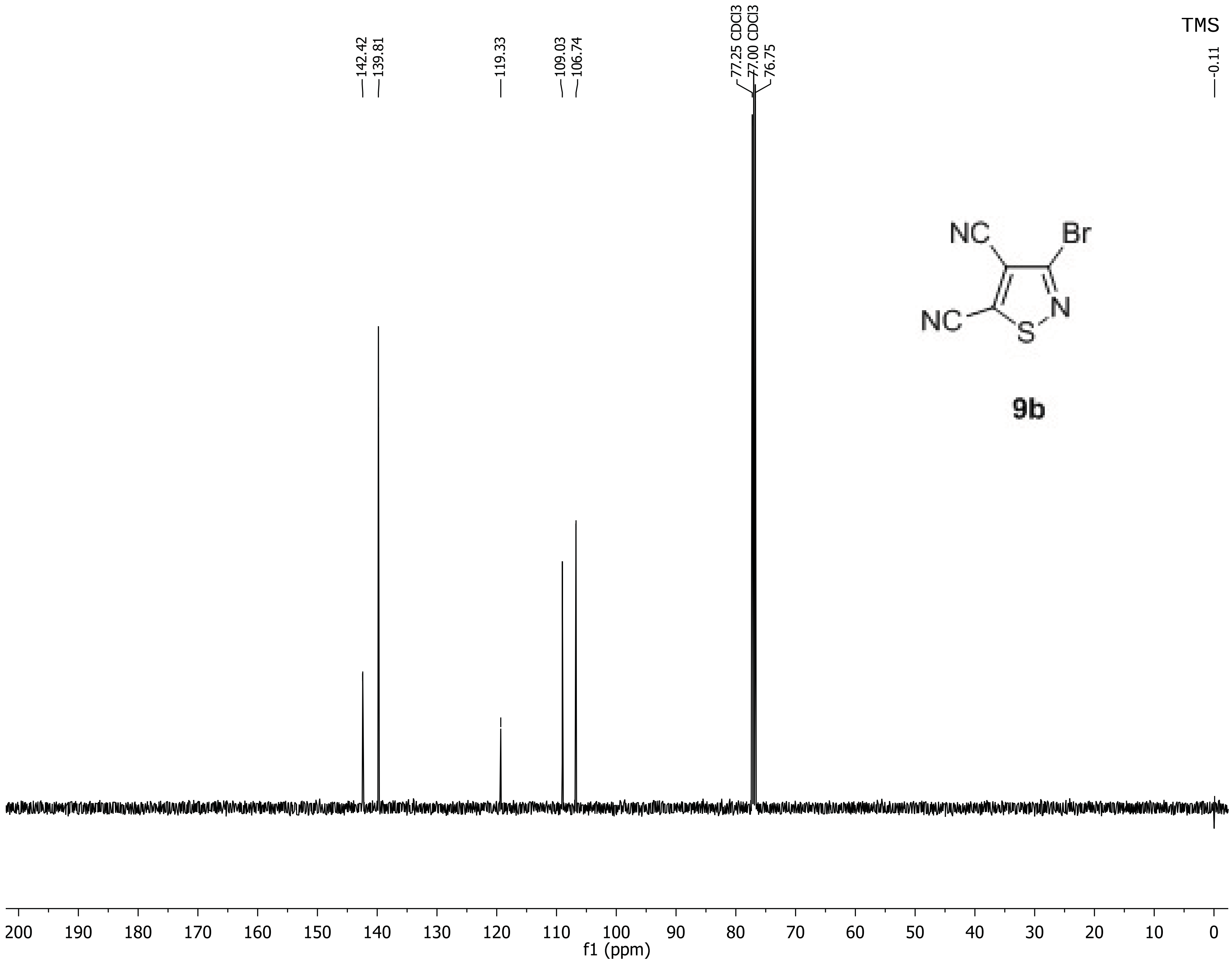
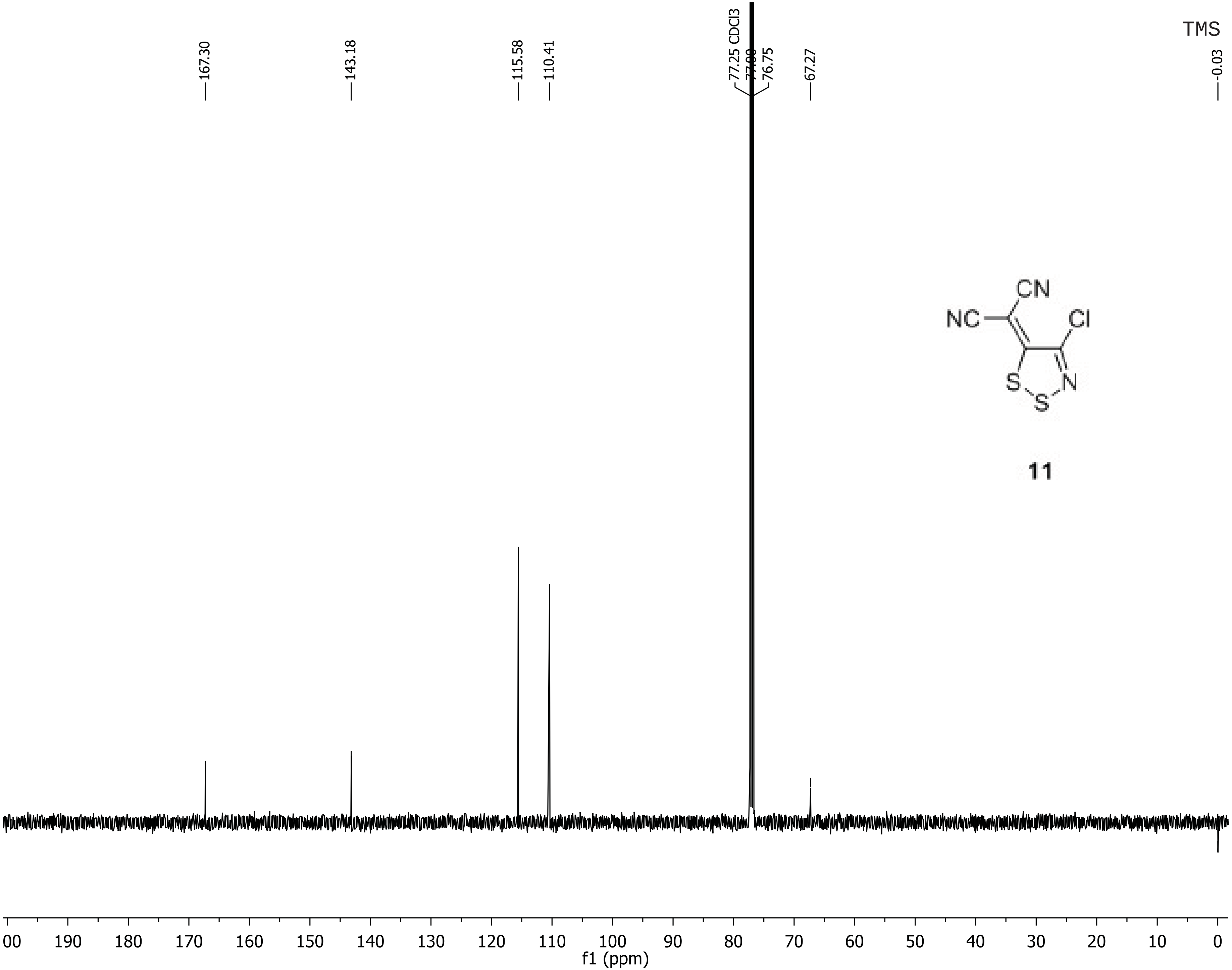

3-Bromoisothiazole-4,5-dicarbonitrile (**9b**)



**9b**

| Current Data Parameters | |
|---|---|
| NAME | Andreas Kalogirou |
| EXPNO | 365 |
| PROCNO | 1 |
| F2 - Acquisition Parameters | |
| Date_ | 20130830 |
| Time | 13.14 |
| INSTRUM | spect |
| PROBHD | 5 mm PABBO BB- |
| PULPROG | jmod |
| TD | 65536 |
| SOLVENT | CDCl3 |
| NS | 2600 |
| DS | 4 |
| SWH | 29761.904 Hz |
| FIDRES | 0.454131 Hz |
| AQ | 1.1010048 sec |
| RG | 2050 |
| DW | 16.800 usec |
| DE | 6.50 usec |
| TE | 298.5 K |
| CNST2 | 145.0000000 |
| CNST11 | 1.0000000 |
| D1 | 2.00000000 sec |
| D20 | 0.00689655 sec |
| TD0 | 1 |
| ======== CHANNEL f1 ======== | |
| SFO1 | 125.7459782 MHz |
| NUC1 | 13C |
| P1 | 8.70 usec |
| P2 | 17.40 usec |
| PLW1 | 138.00000000 W |
| ======== CHANNEL f2 ======== | |
| SFO2 | 500.0350280 MHz |
| NUC2 | 1H |
| CPDPRG[2 | waltz16 |
| PCPD2 | 80.00 usec |
| PLW2 | 15.41699982 W |
| PLW12 | 0.33258000 W |
| F2 - Processing parameters | |
| SI | 32768 |
| SF | 125.7334050 MHz |
| WDW | EM |
| SSB | 0 |
| LB | 1.00 Hz |
| GB | 0 |
| PC | 1.40 |

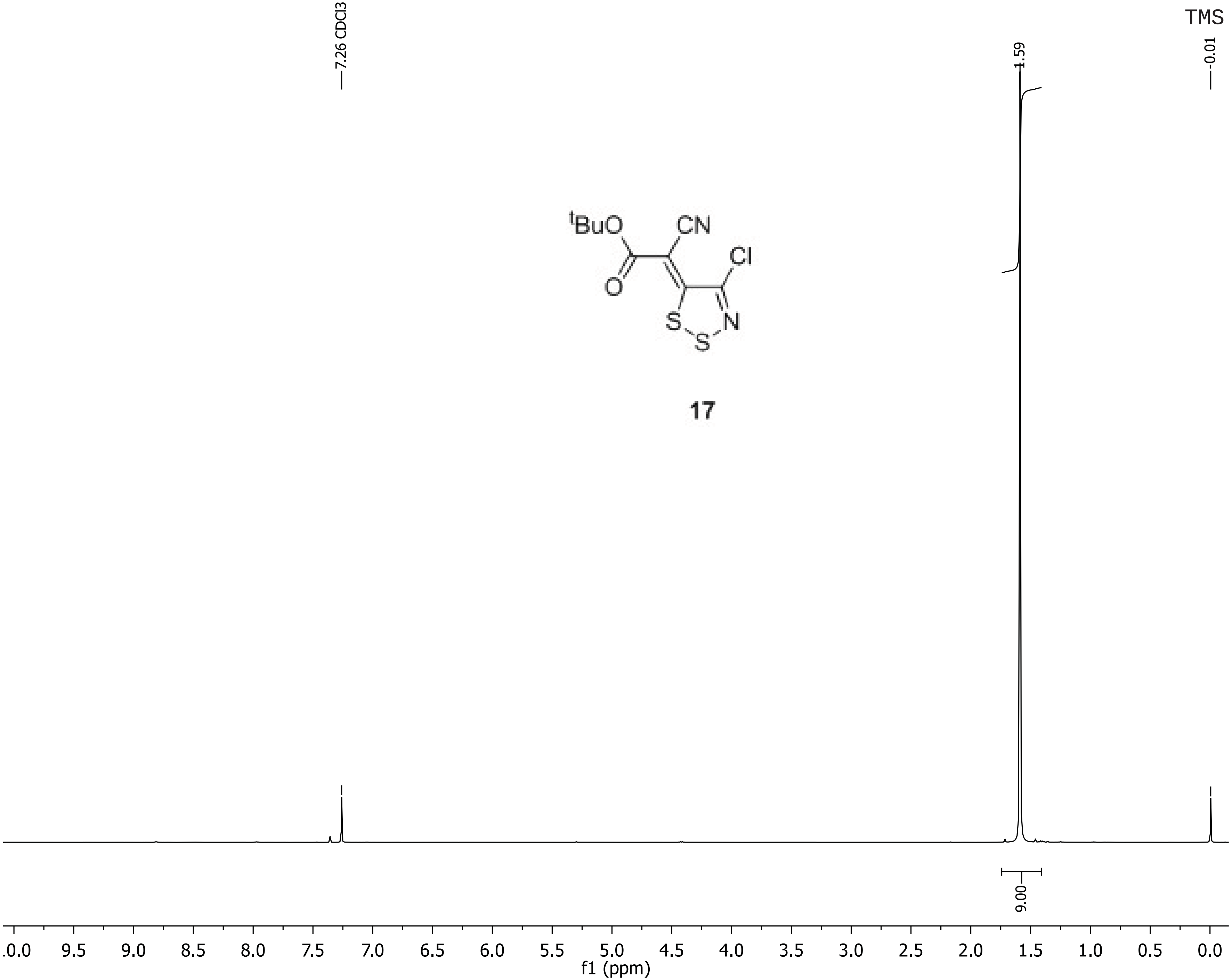
2-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)malononitrile (**11**)



11

| | |
|---|---|
| Current Data Parameters | |
| NAME | Andreas Kalogirou |
| EXPNO | 364 |
| PROCNO | 1 |
| F2 - Acquisition Parameters | |
| Date_ | 20130829 |
| Time | 9.39 |
| INSTRUM | spect |
| PROBHD | 5 mm PABBO BB- |
| PULPROG | jmod |
| TD | 65536 |
| SOLVENT | CDCl3 |
| NS | 11000 |
| DS | 4 |
| SWH | 29761.904 Hz |
| FIDRES | 0.454131 Hz |
| AQ | 1.1010048 sec |
| RG | 1820 |
| DW | 16.800 usec |
| DE | 6.50 usec |
| TE | 298.0 K |
| CNST2 | 145.0000000 |
| CNST11 | 1.0000000 |
| D1 | 2.00000000 sec |
| D20 | 0.00689655 sec |
| TD0 | 1 |
| ======== CHANNEL f1 ======== | |
| SFO1 | 125.7459782 MHz |
| NUC1 | 13C |
| P1 | 8.70 usec |
| P2 | 17.40 usec |
| PLW1 | 138.00000000 W |
| ======== CHANNEL f2 ======== | |
| SFO2 | 500.0350280 MHz |
| NUC2 | 1H |
| CPDPRG[2 | waltz16 |
| PCPD2 | 80.00 usec |
| PLW2 | 15.41699982 W |
| PLW12 | 0.33258000 W |
| F2 - Processing parameters | |
| SI | 32768 |
| SF | 125.7334050 MHz |
| WDW | EM |
| SSB | 0 |
| LB | 1.00 Hz |
| GB | 0 |
| PC | 1.40 |

(*Z*)-*tert*-Butyl 2-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-2-cyanoacetate (**17**)



Current Data Parameters

| | |
|---|---|
| NAME | Andreas Kalogirou |
| EXPNO | 315 |
| PROCNO | 1 |

F2 - Acquisition Parameters

| | |
|---|---|
| Date_ | 20130805 |
| Time | 16.14 |
| INSTRUM | spect |
| PROBHD | 5 mm PABBO BB- |
| PULPROG | zg30 |
| TD | 65536 |
| SOLVENT | CDCl3 |
| NS | 16 |
| DS | 2 |
| SWH | 10330.578 Hz |
| FIDRES | 0.157632 Hz |
| AQ | 3.1719425 sec |
| RG | 128 |
| DW | 48.400 usec |
| DE | 6.50 usec |
| TE | 295.8 K |
| D1 | 1.00000000 sec |
| TD0 | 1 |

CHANNEL f1

| | |
|---|---|
| SFO1 | 500.0361158 MHz |
| NUC1 | 1H |
| P1 | 11.75 usec |
| PLW1 | 15.41699982 W |

F2 - Processing parameters

| | |
|---|---|
| SI | 65536 |
| SF | 500.0330399 MHz |
| WDW | EM |
| SSB | 0 |
| LB | 0.30 Hz |
| GB | 0 |
| PC | 1.00 |

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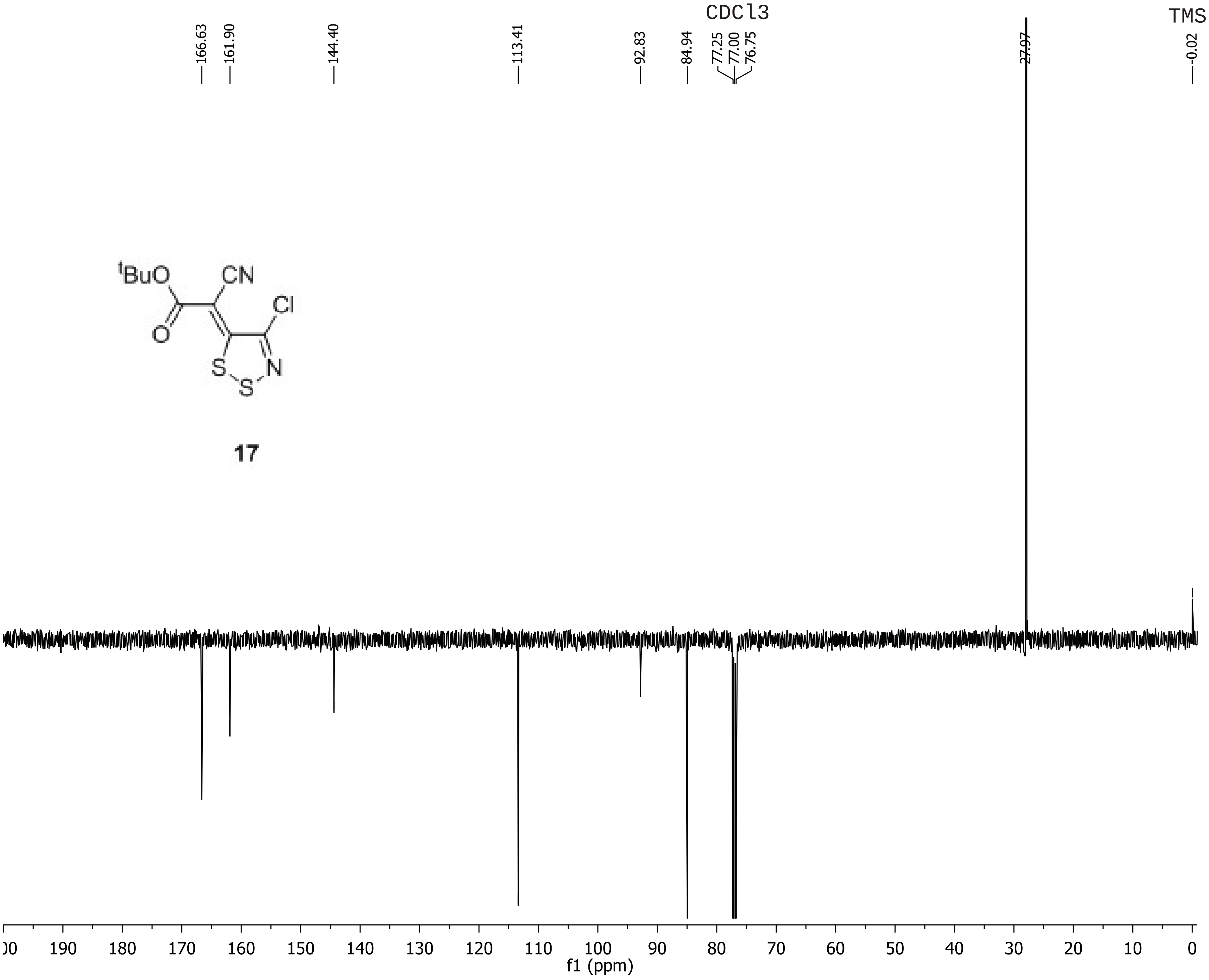
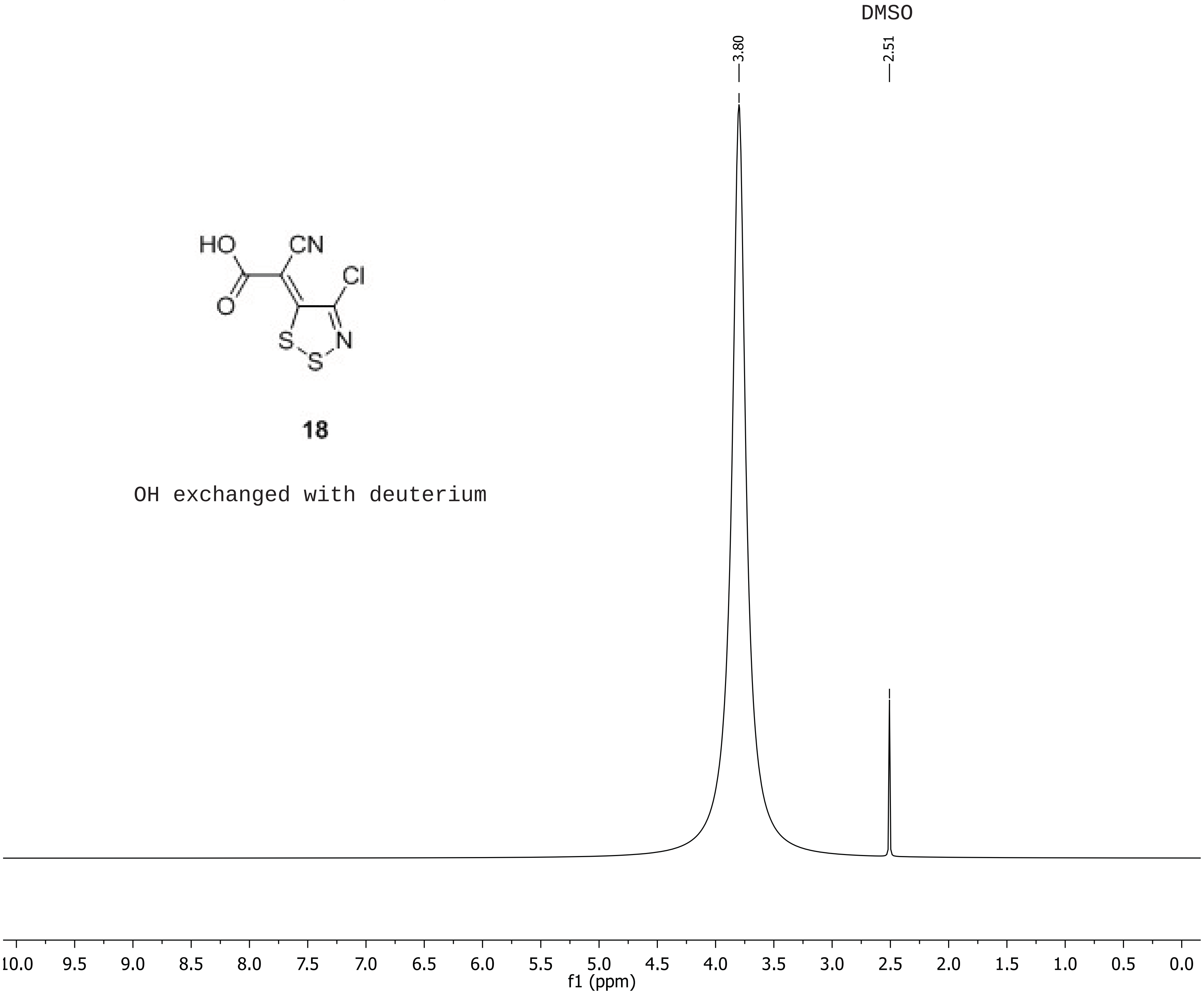
## (*Z*)-*tert*-Butyl 2-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-2-cyanoacetate (**17**)



| | |
|---|---|
| Current Data Parameters | |
| NAME | Andreas Kalogirou |
| EXPNO | 316 |
| PROCNO | 1 |
| F2 - Acquisition Parameters | |
| Date_ | 20130805 |
| Time | 16.55 |
| INSTRUM | spect |
| PROBHD | 5 mm PABBO BB- |
| PULPROG | jmod |
| TD | 65536 |
| SOLVENT | CDCl3 |
| NS | 4000 |
| DS | 4 |
| SWH | 29761.904 Hz |
| FIDRES | 0.454131 Hz |
| AQ | 1.1010048 sec |
| RG | 2050 |
| DW | 16.800 usec |
| DE | 6.50 usec |
| TE | 297.1 K |
| CNST2 | 145.0000000 |
| CNST11 | 1.0000000 |
| D1 | 2.00000000 sec |
| D20 | 0.00689655 sec |
| TD0 | 1 |
| CHANNEL f1 | |
| SFO1 | 125.7459782 MHz |
| NUC1 | 13C |
| P1 | 8.70 usec |
| P2 | 17.40 usec |
| PLW1 | 138.00000000 W |
| CHANNEL f2 | |
| SFO2 | 500.0350280 MHz |
| NUC2 | 1H |
| CPDPRG[2 | waltz16 |
| PCPD2 | 80.00 usec |
| PLW2 | 15.41699982 W |
| PLW12 | 0.33258000 W |
| F2 - Processing parameters | |
| SI | 32768 |
| SF | 125.7334050 MHz |
| WDW | EM |
| SSB | 0 |
| LB | 1.00 Hz |
| GB | 0 |
| PC | 1.40 |

# (*Z*)-2-(4-Chloro-5*H*-1,2,3-dithiazol-5-ylidene)-2-cyanoacetic acid (**18**)



Current Data Parameters

| | |
|---|---|
| NAME | Andreas Kalogirou |
| EXPNO | 322 |
| PROCNO | 1 |

F2 - Acquisition Parameters

| | |
|---|---|
| Date_ | 20130807 |
| Time | 2.25 |
| INSTRUM | spect |
| PROBHD | 5 mm PABBO BB- |
| PULPROG | zg30 |
| TD | 65536 |
| SOLVENT | DMSO |
| NS | 16 |
| DS | 2 |
| SWH | 10330.578 Hz |
| FIDRES | 0.157632 Hz |
| AQ | 3.1719425 sec |
| RG | 32 |
| DW | 48.400 usec |
| DE | 6.50 usec |
| TE | 297.1 K |
| D1 | 1.00000000 sec |
| TD0 | 1 |

CHANNEL f1

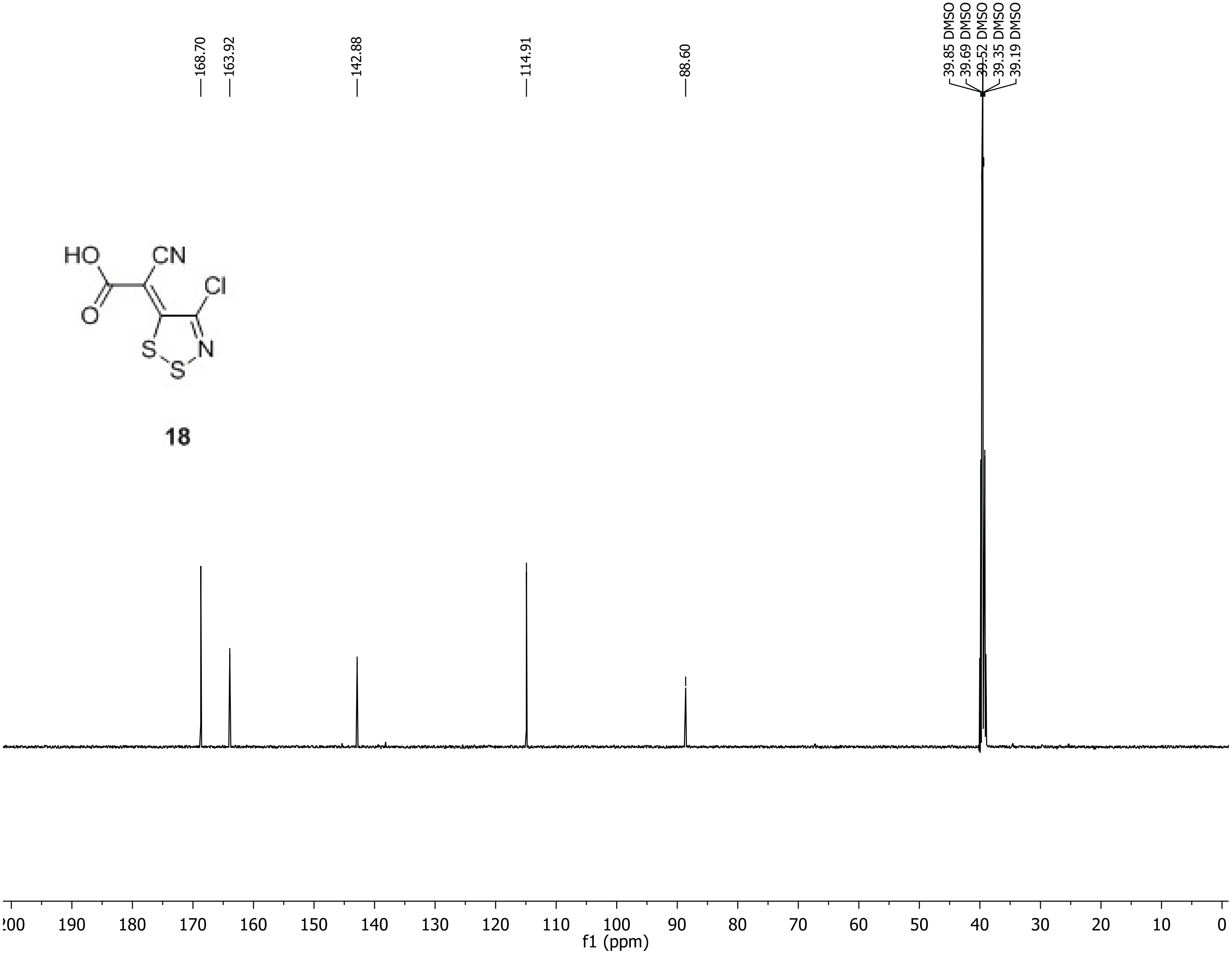
| | |
|---|---|
| SFO1 | 500.0361158 MHz |
| NUC1 | 1H |
| P1 | 11.75 usec |
| PLW1 | 15.41699982 W |

F2 - Processing parameters

| | |
|---|---|
| SI | 65536 |
| SF | 500.0330280 MHz |
| WDW | EM |
| SSB | 0 |
| LB | 0.30 Hz |
| GB | 0 |
| PC | 1.00 |

# (*Z*)-2-(4-Chloro-5*H*-1,2,3-dithiazol-5-ylidene)-2-cyanoacetic acid (**18**)

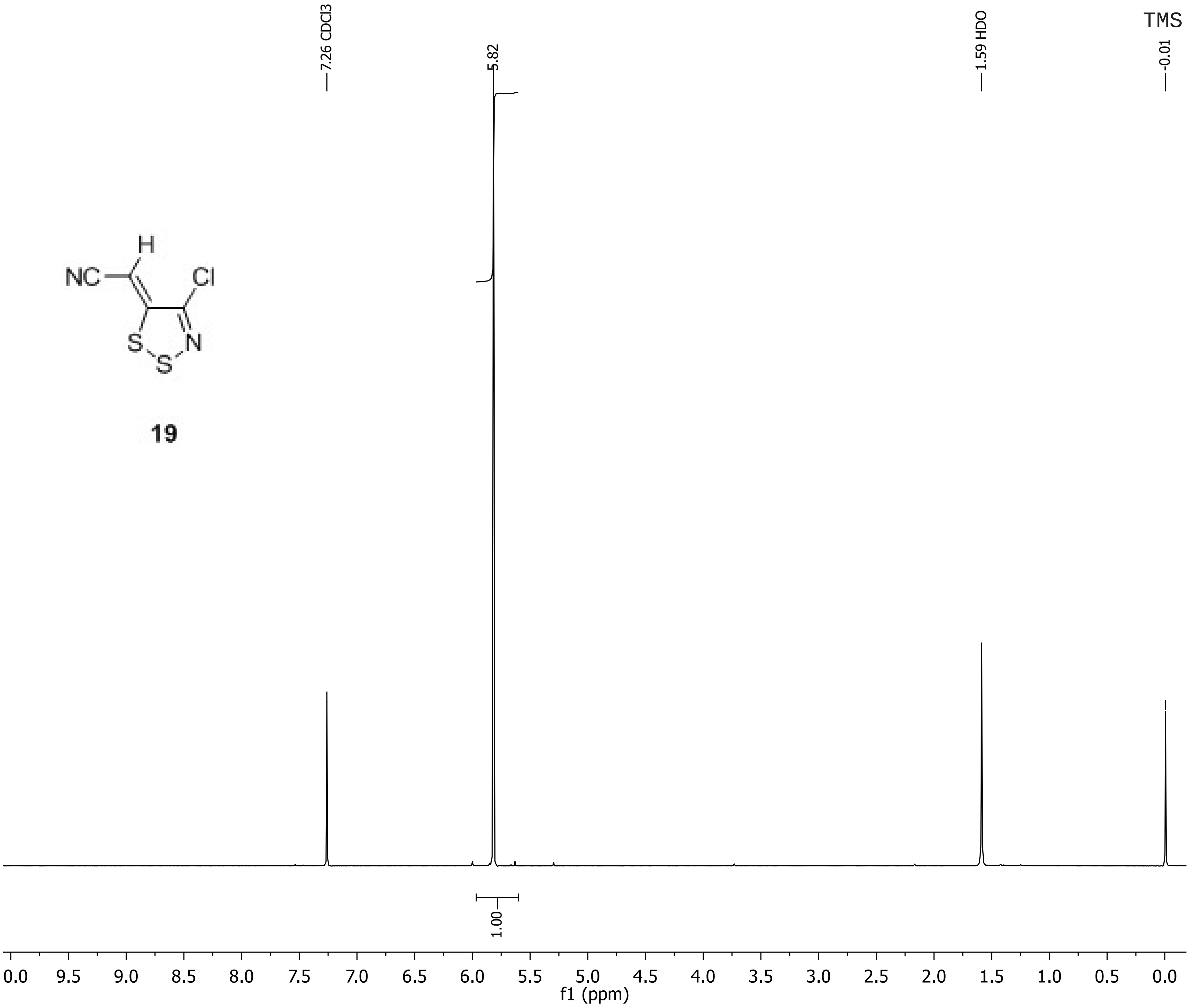
**18**



| | |
|---|---|
| Current Data Parameters | |
| NAME | Andreas Kalogirou |
| EXPNO | 323 |
| PROCNO | 1 |
| F2 - Acquisition Parameters | |
| Date_ | 20130807 |
| Time | 5.56 |
| INSTRUM | spect |
| PROBHD | 5 mm PABBO BB- |
| PULPROG | jmod |
| TD | 65536 |
| SOLVENT | DMSO |
| NS | 4000 |
| DS | 4 |
| SWH | 29761.904 Hz |
| FIDRES | 0.454131 Hz |
| AQ | 1.1010048 sec |
| RG | 2050 |
| DW | 16.800 usec |
| DE | 6.50 usec |
| TE | 297.4 K |
| CNST2 | 145.0000000 |
| CNST11 | 1.0000000 |
| D1 | 2.00000000 sec |
| D20 | 0.00689655 sec |
| TD0 | 1 |
| ======== CHANNEL f1 ======== | |
| SFO1 | 125.7459782 MHz |
| NUC1 | 13C |
| P1 | 8.70 usec |
| P2 | 17.40 usec |
| PLW1 | 138.00000000 W |
| ======== CHANNEL f2 ======== | |
| SFO2 | 500.0350280 MHz |
| NUC2 | 1H |
| CPDPRG[2 | waltz16 |
| PCPD2 | 80.00 usec |
| PLW2 | 15.41699982 W |
| PLW12 | 0.33258000 W |
| F2 - Processing parameters | |
| SI | 32768 |
| SF | 125.7334050 MHz |
| WDW | EM |
| SSB | 0 |
| LB | 1.00 Hz |
| GB | 0 |
| PC | 1.40 |

# (*Z*)-2-(4-Chloro-5*H*-1,2,3-dithiazol-5-ylidene)acetonitrile (**19**)

**19**



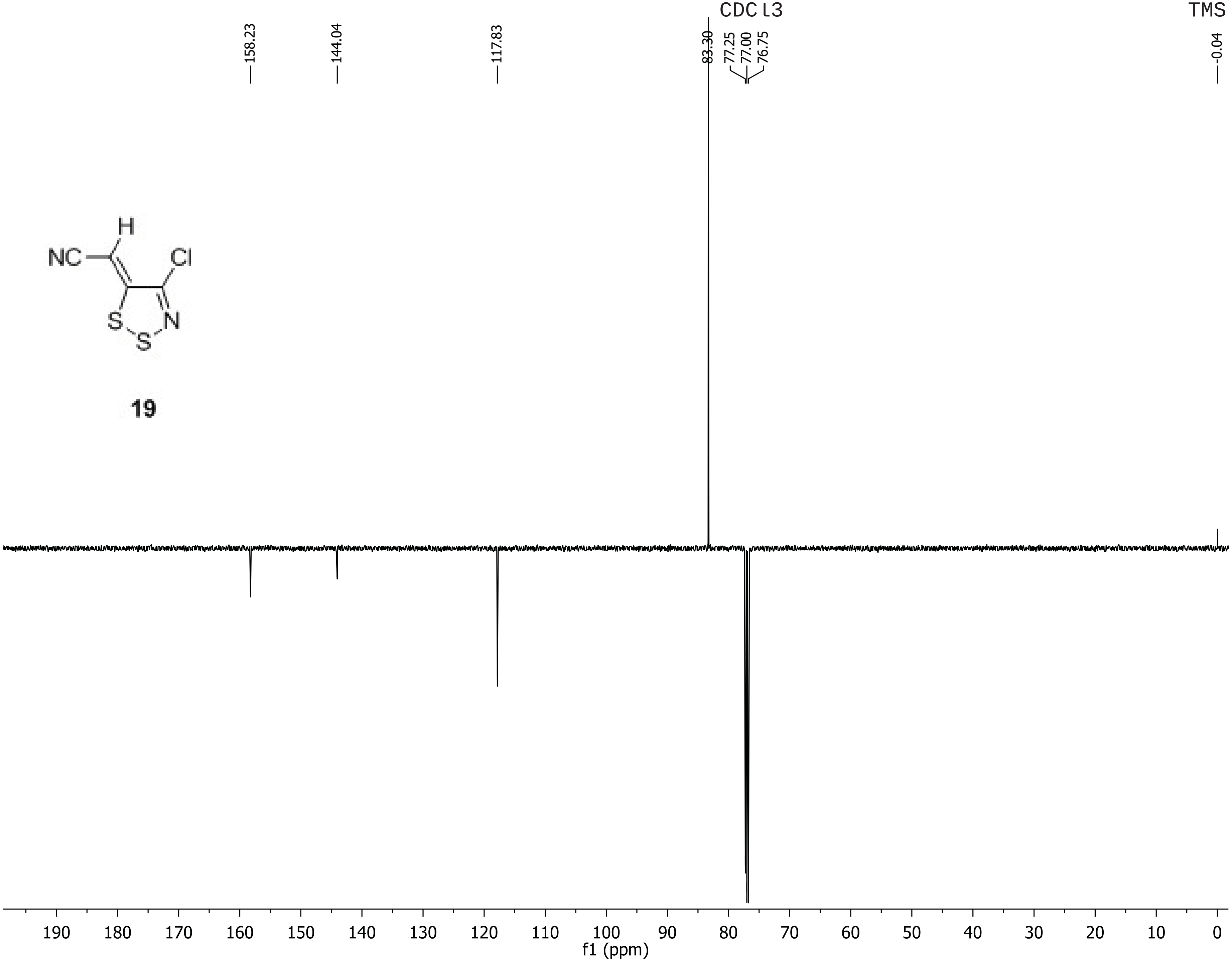
Current Data Parameters
NAME Andreas Kalogirou
EXPNO 320
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130806
Time 22.50
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719425 sec
RG 181
DW 48.400 usec
DE 6.50 usec
TE 296.9 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 500.0361158 MHz
NUC1 1H
P1 11.75 usec
PLW1 15.41699982 W

F2 - Processing parameters
SI 65536
SF 500.0330369 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

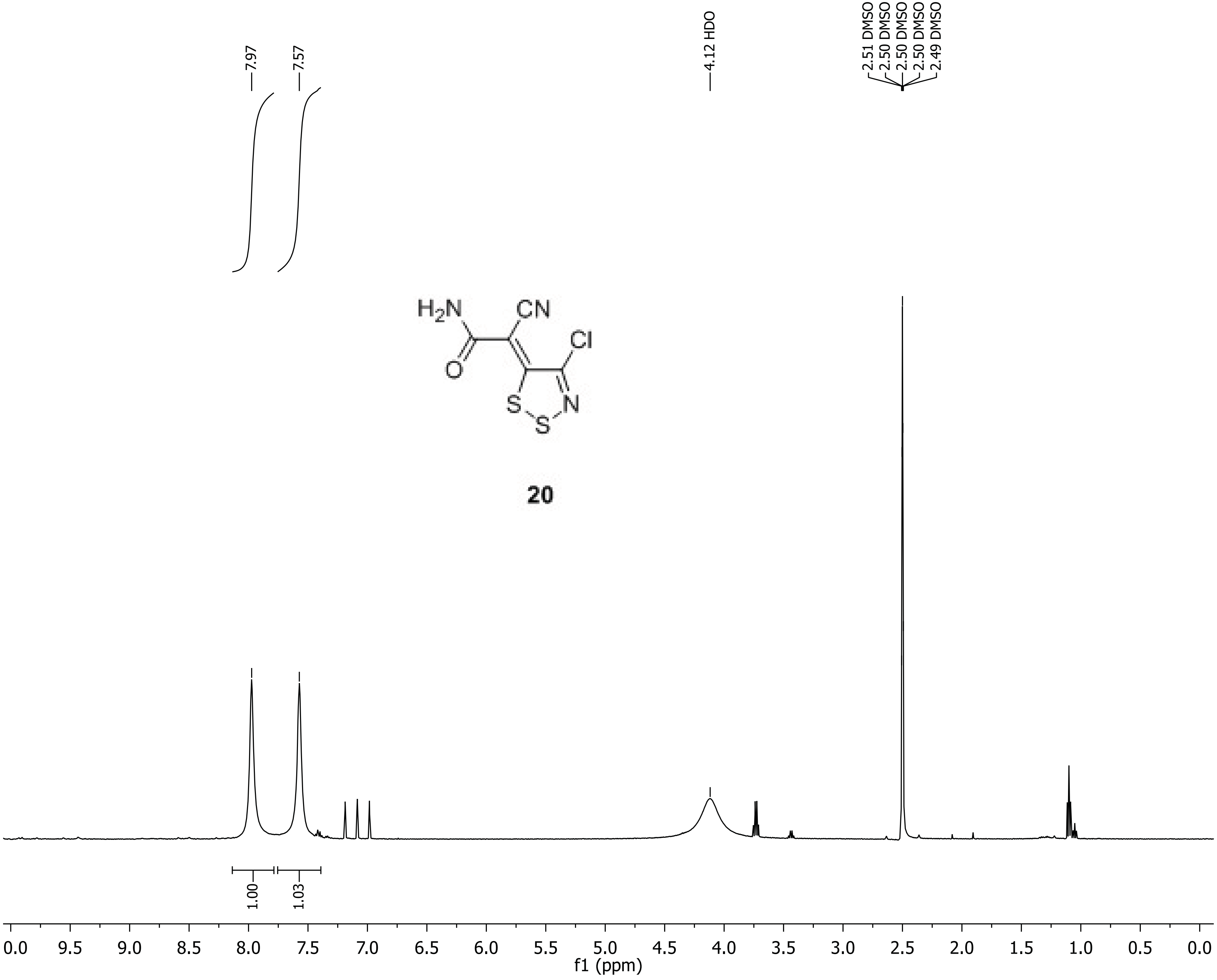
(*Z*)-2-(4-Chloro-5*H*-1,2,3-dithiazol-5-ylidene)acetonitrile (**19**)



**19**

| | |
|---|---|
| Current Data Parameters | |
| NAME | Andreas Kalogirou |
| EXPNO | 321 |
| PROCNO | 1 |
| F2 - Acquisition Parameters | |
| Date_ | 20130807 |
| Time | 2.21 |
| INSTRUM | spect |
| PROBHD | 5 mm PABBO BB- |
| PULPROG | jmod |
| TD | 65536 |
| SOLVENT | CDCl3 |
| NS | 4000 |
| DS | 4 |
| SWH | 29761.904 Hz |
| FIDRES | 0.454131 Hz |
| AQ | 1.1010048 sec |
| RG | 2050 |
| DW | 16.800 usec |
| DE | 6.50 usec |
| TE | 298.1 K |
| CNST2 | 145.0000000 |
| CNST11 | 1.0000000 |
| D1 | 2.00000000 sec |
| D20 | 0.00689655 sec |
| TD0 | 1 |
| ======== CHANNEL f1 ======== | |
| SFO1 | 125.7459782 MHz |
| NUC1 | 13C |
| P1 | 8.70 usec |
| P2 | 17.40 usec |
| PLW1 | 138.00000000 W |
| ======== CHANNEL f2 ======== | |
| SFO2 | 500.0350280 MHz |
| NUC2 | 1H |
| CPDPRG[2 | waltz16 |
| PCPD2 | 80.00 usec |
| PLW2 | 15.41699982 W |
| PLW12 | 0.33258000 W |
| F2 - Processing parameters | |
| SI | 32768 |
| SF | 125.7334050 MHz |
| WDW | EM |
| SSB | 0 |
| LB | 1.00 Hz |
| GB | 0 |
| PC | 1.40 |

# (*E*)-2-(4-Chloro-5*H*-1,2,3-dithiazol-5-ylidene)-2-cyanoacetamide (**20**)



**20**

Current Data Parameters

| | |
|---|---|
| NAME | Herc |
| EXPNO | 560 |
| PROCNO | 1 |

F2 - Acquisition Parameters

| | |
|---|---|
| Date_ | 20111101 |
| Time | 14.23 |
| INSTRUM | spect |
| PROBHD | 5 mm PABBO BB- |
| PULPROG | zg30 |
| TD | 65536 |
| SOLVENT | DMSO |
| NS | 16 |
| DS | 2 |
| SWH | 10330.578 Hz |
| FIDRES | 0.157632 Hz |
| AQ | 3.1719923 sec |
| RG | 161 |
| DW | 48.400 usec |
| DE | 6.50 usec |
| TE | 297.3 K |
| D1 | 1.00000000 sec |
| TD0 | 1 |

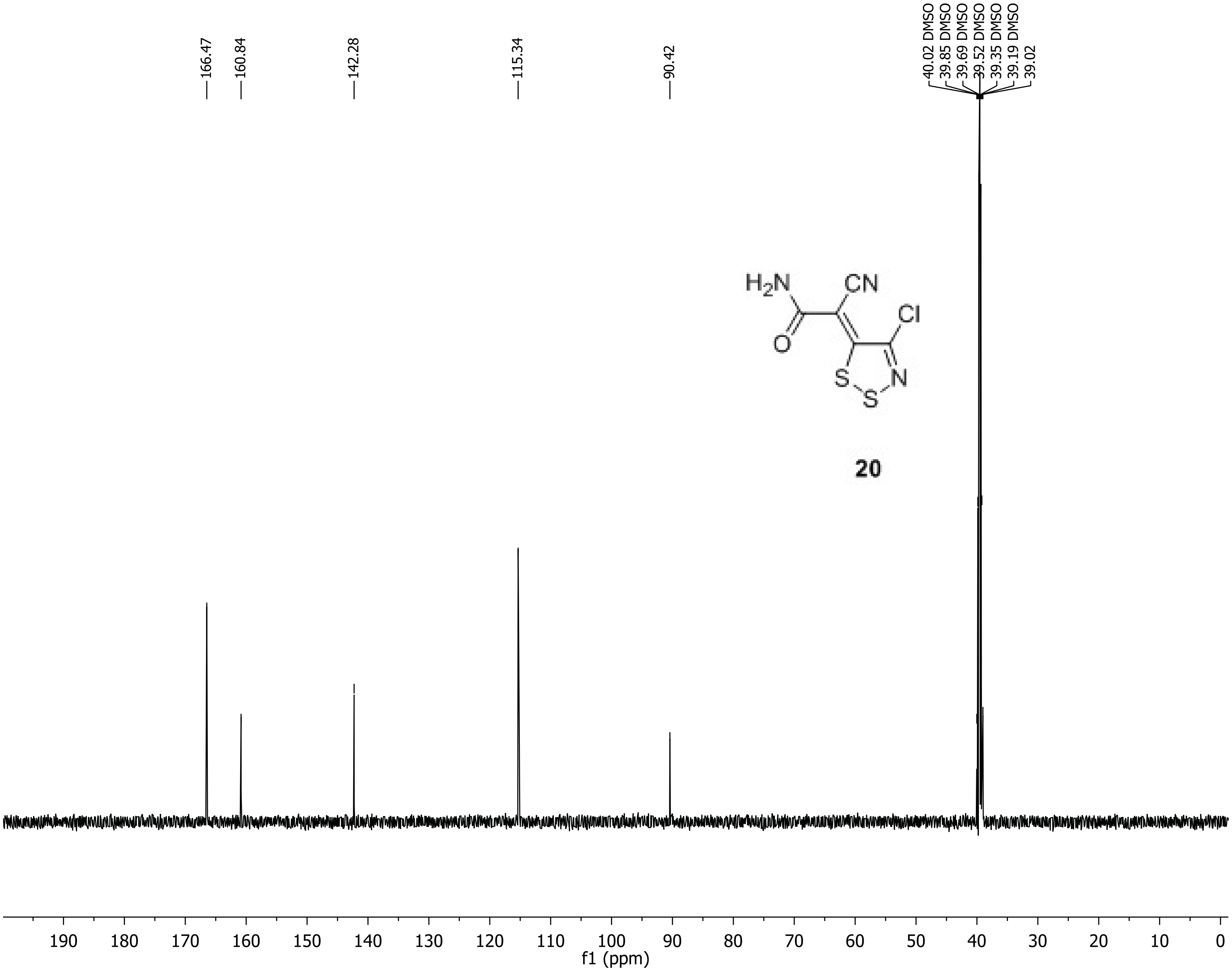
======== CHANNEL f1 ========

| | |
|---|---|
| NUC1 | 1H |
| P1 | 11.75 usec |
| PLW1 | 15.41699982 W |
| SFO1 | 500.0361158 MHz |

F2 - Processing parameters

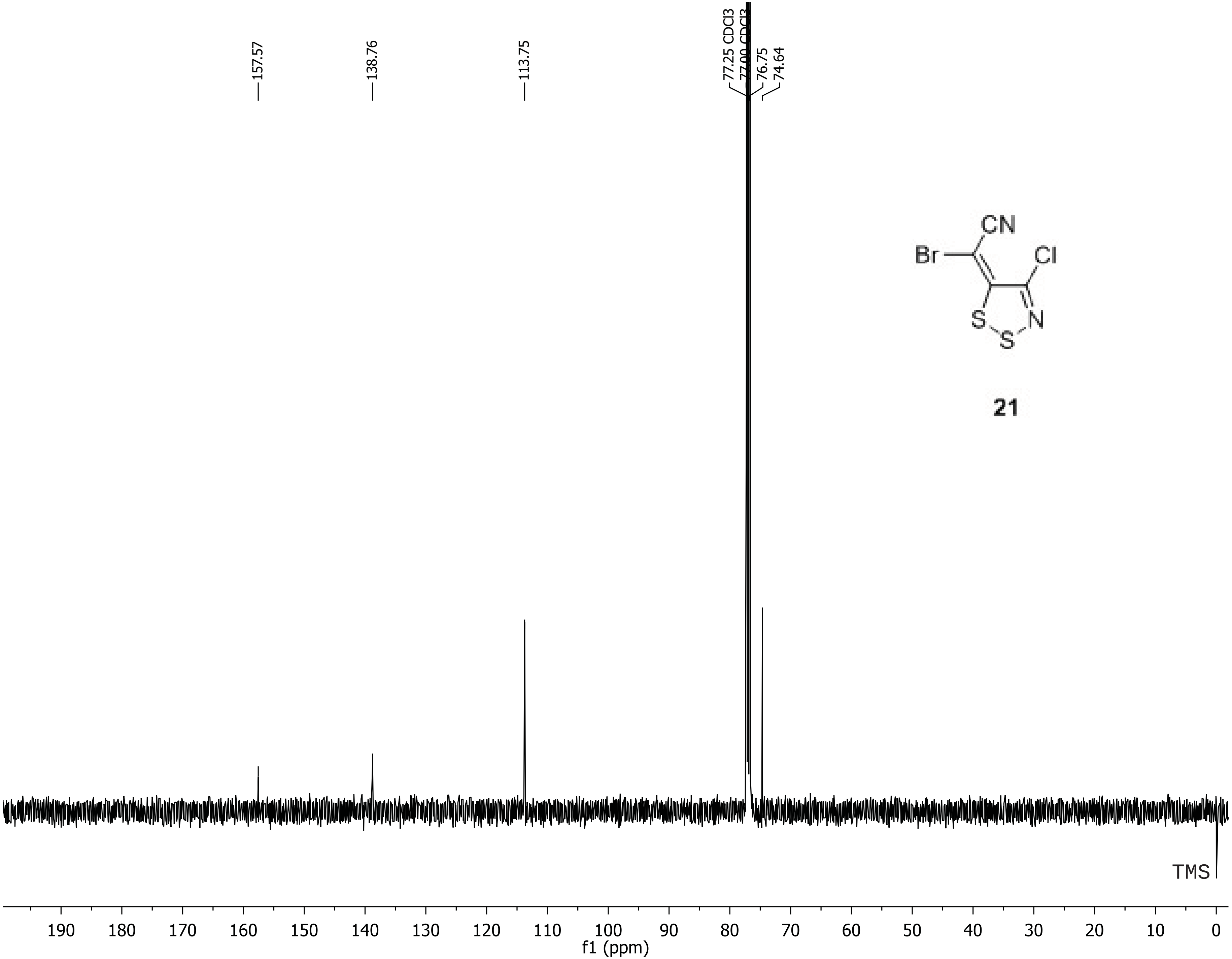
| | |
|---|---|
| SI | 65536 |
| SF | 500.0330316 MHz |
| WDW | EM |
| SSB | 0 |
| LB | 0.30 Hz |
| GB | 0 |
| PC | 1.00 |

# (*E*)-2-(4-Chloro-5*H*-1,2,3-dithiazol-5-ylidene)-2-cyanoacetamide (**20**)



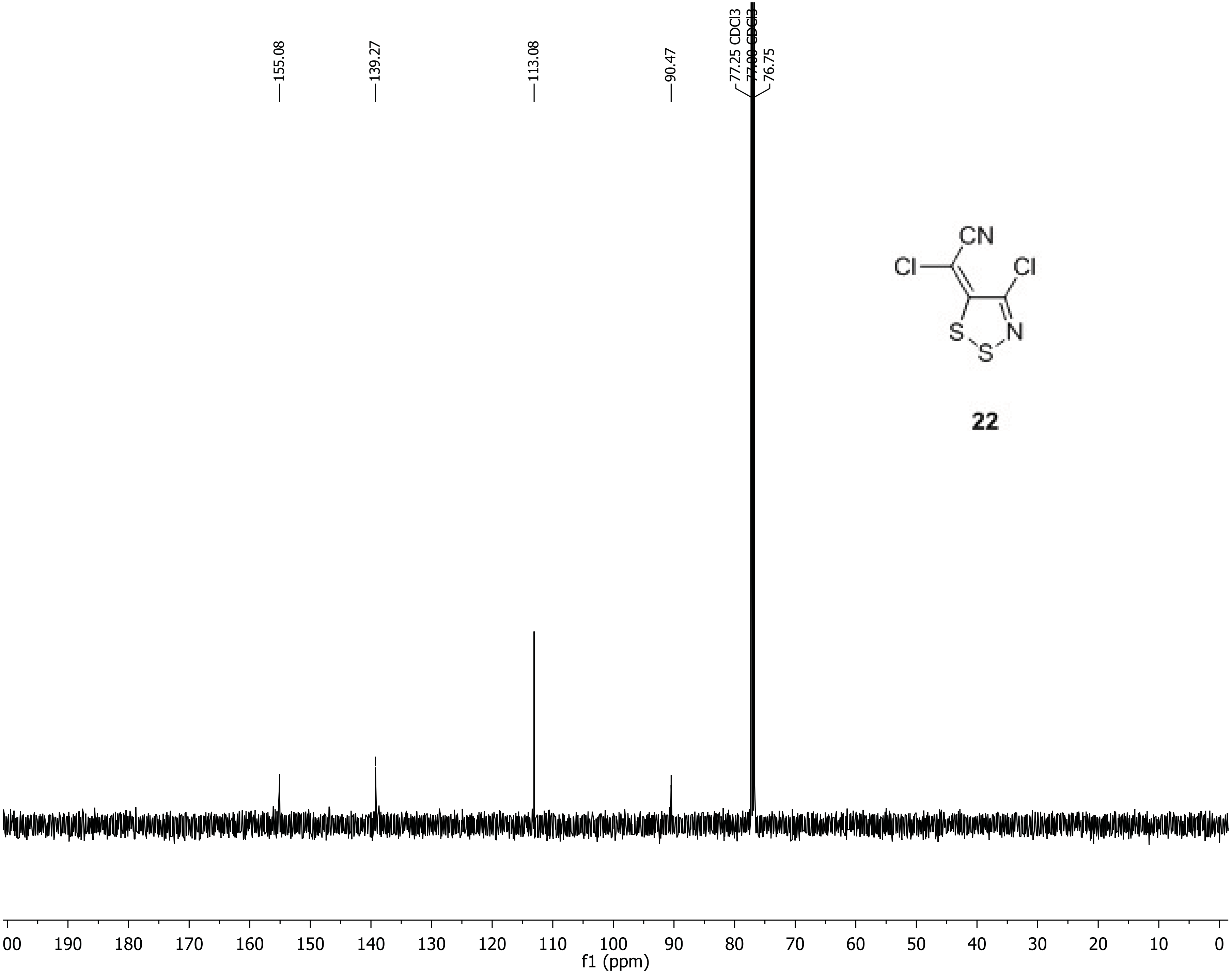
| | |
|---|---|
| Current Data Parameters | |
| NAME | Herc |
| EXPNO | 561 |
| PROCNO | 1 |
| F2 - Acquisition Parameters | |
| Date_ | 20111101 |
| Time | 14.51 |
| INSTRUM | spect |
| PROBHD | 5 mm PABBO BB- |
| PULPROG | jmod |
| TD | 65536 |
| SOLVENT | DMSO |
| NS | 512 |
| DS | 4 |
| SWH | 29761.904 Hz |
| FIDRES | 0.454131 Hz |
| AQ | 1.1010548 sec |
| RG | 2050 |
| DW | 16.800 usec |
| DE | 6.50 usec |
| TE | 298.2 K |
| CNST2 | 145.0000000 |
| CNST11 | 1.0000000 |
| D1 | 2.00000000 sec |
| D20 | 0.00689655 sec |
| TD0 | 1 |
| ======== CHANNEL f1 ======== | |
| NUC1 | 13C |
| P1 | 8.38 usec |
| P2 | 16.76 usec |
| PLW1 | 138.00000000 W |
| SFO1 | 125.7459782 MHz |
| ======== CHANNEL f2 ======== | |
| CPDPRG2 | waltz16 |
| NUC2 | 1H |
| PCPD2 | 80.00 usec |
| PLW2 | 15.41699982 W |
| PLW12 | 0.33258000 W |
| SFO2 | 500.0350280 MHz |
| F2 - Processing parameters | |
| SI | 32768 |
| SF | 125.7334747 MHz |
| WDW | EM |
| SSB | 0 |
| LB | 1.00 Hz |
| GB | 0 |
| PC | 1.40 |

# (*Z*)-2-Bromo-2-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)acetonitrile (**21**)



| | |
|---|---|
| Current Data Parameters | |
| NAME | Andreas Kalogirou |
| EXPNO | 319 |
| PROCNO | 1 |
| F2 - Acquisition Parameters | |
| Date_ | 20130806 |
| Time | 19.17 |
| INSTRUM | spect |
| PROBHD | 5 mm PABBO BB- |
| PULPROG | jmod |
| TD | 65536 |
| SOLVENT | CDCl3 |
| NS | 4000 |
| DS | 4 |
| SWH | 29761.904 Hz |
| FIDRES | 0.454131 Hz |
| AQ | 1.1010048 sec |
| RG | 1820 |
| DW | 16.800 usec |
| DE | 6.50 usec |
| TE | 296.6 K |
| CNST2 | 145.0000000 |
| CNST11 | 1.0000000 |
| D1 | 2.00000000 sec |
| D20 | 0.00689655 sec |
| TD0 | 1 |
| ======== CHANNEL f1 ======== | |
| SFO1 | 125.7459782 MHz |
| NUC1 | 13C |
| P1 | 8.70 usec |
| P2 | 17.40 usec |
| PLW1 | 138.00000000 W |
| ======== CHANNEL f2 ======== | |
| SFO2 | 500.0350280 MHz |
| NUC2 | 1H |
| CPDPRG[2 | waltz16 |
| PCPD2 | 80.00 usec |
| PLW2 | 15.41699982 W |
| PLW12 | 0.33258000 W |
| F2 - Processing parameters | |
| SI | 32768 |
| SF | 125.7334050 MHz |
| WDW | EM |
| SSB | 0 |
| LB | 1.00 Hz |
| GB | 0 |
| PC | 1.40 |

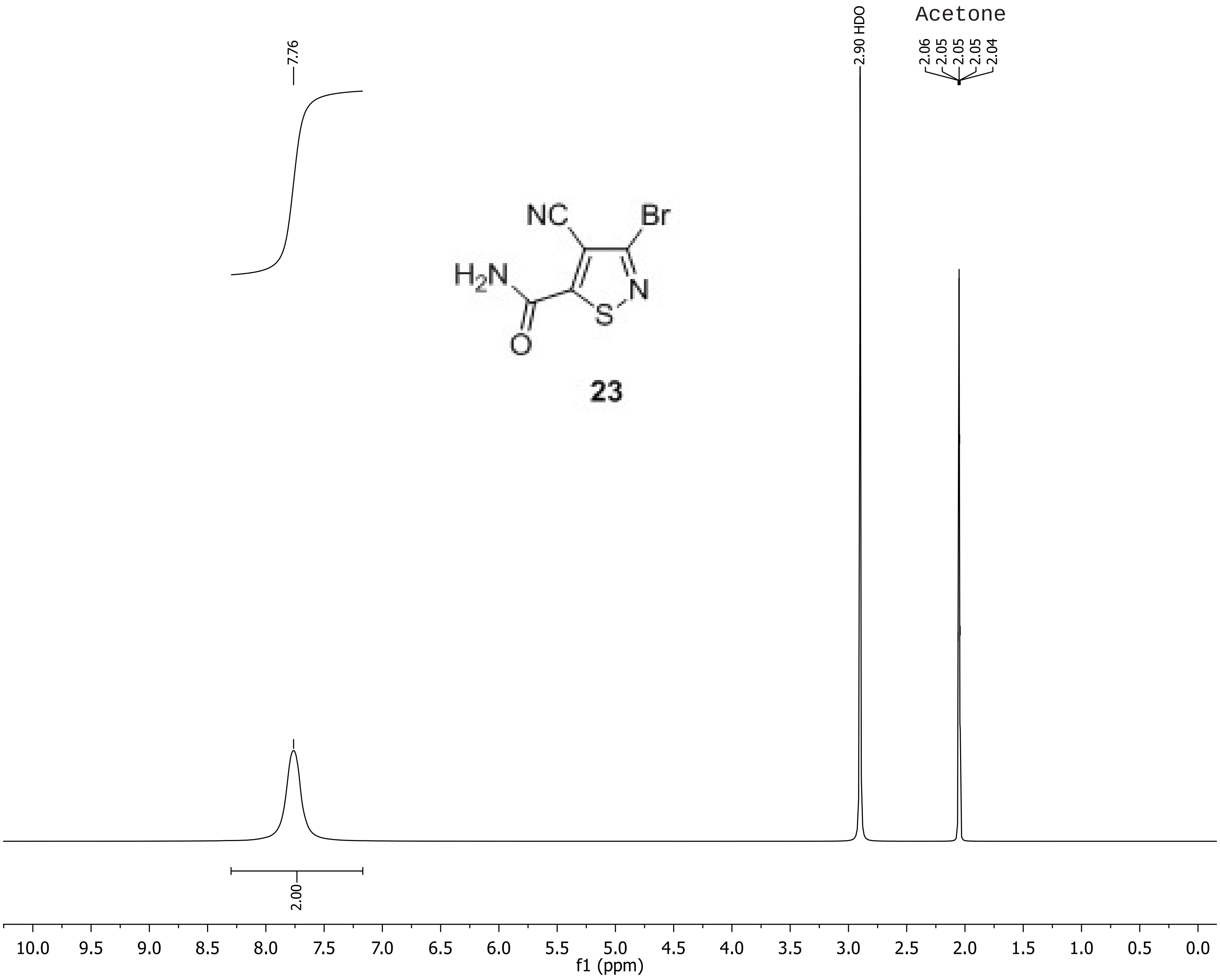
# 2-Chloro-2-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)acetonitrile (**22**)



**22**

| | |
|---|---|
| Current Data Parameters | |
| NAME | Andreas Kalogirou |
| EXPNO | 363 |
| PROCNO | 1 |
| F2 - Acquisition Parameters | |
| Date_ | 20130828 |
| Time | 23.48 |
| INSTRUM | spect |
| PROBHD | 5 mm PABBO BB- |
| PULPROG | jmod |
| TD | 65536 |
| SOLVENT | CDCl3 |
| NS | 2000 |
| DS | 4 |
| SWH | 29761.904 Hz |
| FIDRES | 0.454131 Hz |
| AQ | 1.1010048 sec |
| RG | 2050 |
| DW | 16.800 usec |
| DE | 6.50 usec |
| TE | 299.2 K |
| CNST2 | 145.0000000 |
| CNST11 | 1.0000000 |
| D1 | 2.00000000 sec |
| D20 | 0.00689655 sec |
| TD0 | 1 |
| ======== CHANNEL f1 ======== | |
| SFO1 | 125.7459782 MHz |
| NUC1 | 13C |
| P1 | 8.70 usec |
| P2 | 17.40 usec |
| PLW1 | 138.00000000 W |
| ======== CHANNEL f2 ======== | |
| SFO2 | 500.0350280 MHz |
| NUC2 | 1H |
| CPDPRG[2 | waltz16 |
| PCPD2 | 80.00 usec |
| PLW2 | 15.41699982 W |
| PLW12 | 0.33258000 W |
| F2 - Processing parameters | |
| SI | 32768 |
| SF | 125.7334050 MHz |
| WDW | EM |
| SSB | 0 |
| LB | 1.00 Hz |
| GB | 0 |
| PC | 1.40 |

3-Bromo-4-cyanoisothiazole-5-carboxamide (**23**)



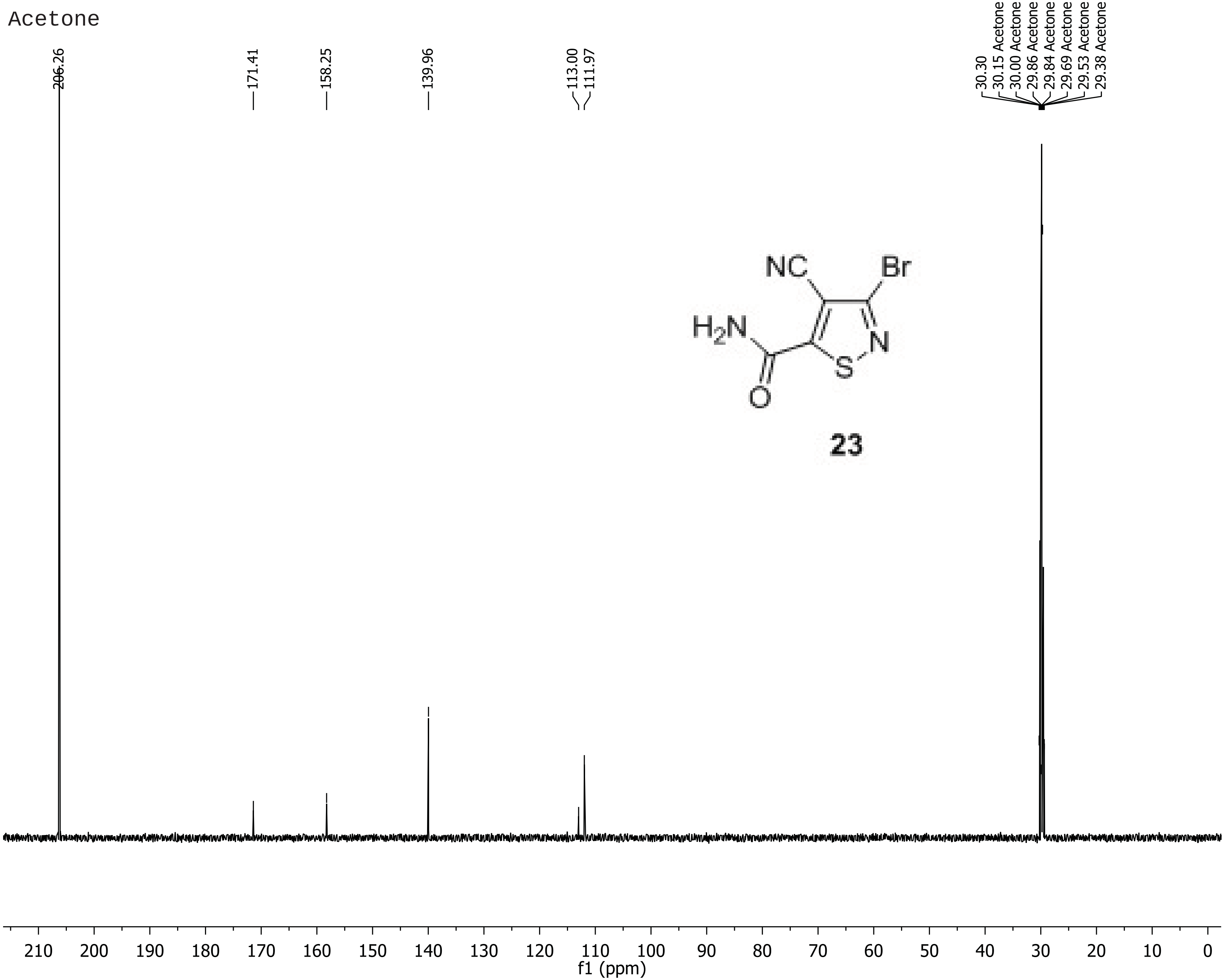
Current Data Parameters
NAME Andreas Kalogirou
EXPNO 37
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130211
Time 14.11
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT Acetone
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719425 sec
RG 144
DW 48.400 usec
DE 6.50 usec
TE 295.6 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 500.0361158 MHz
NUC1 1H
P1 11.75 usec
PLW1 15.41699982 W

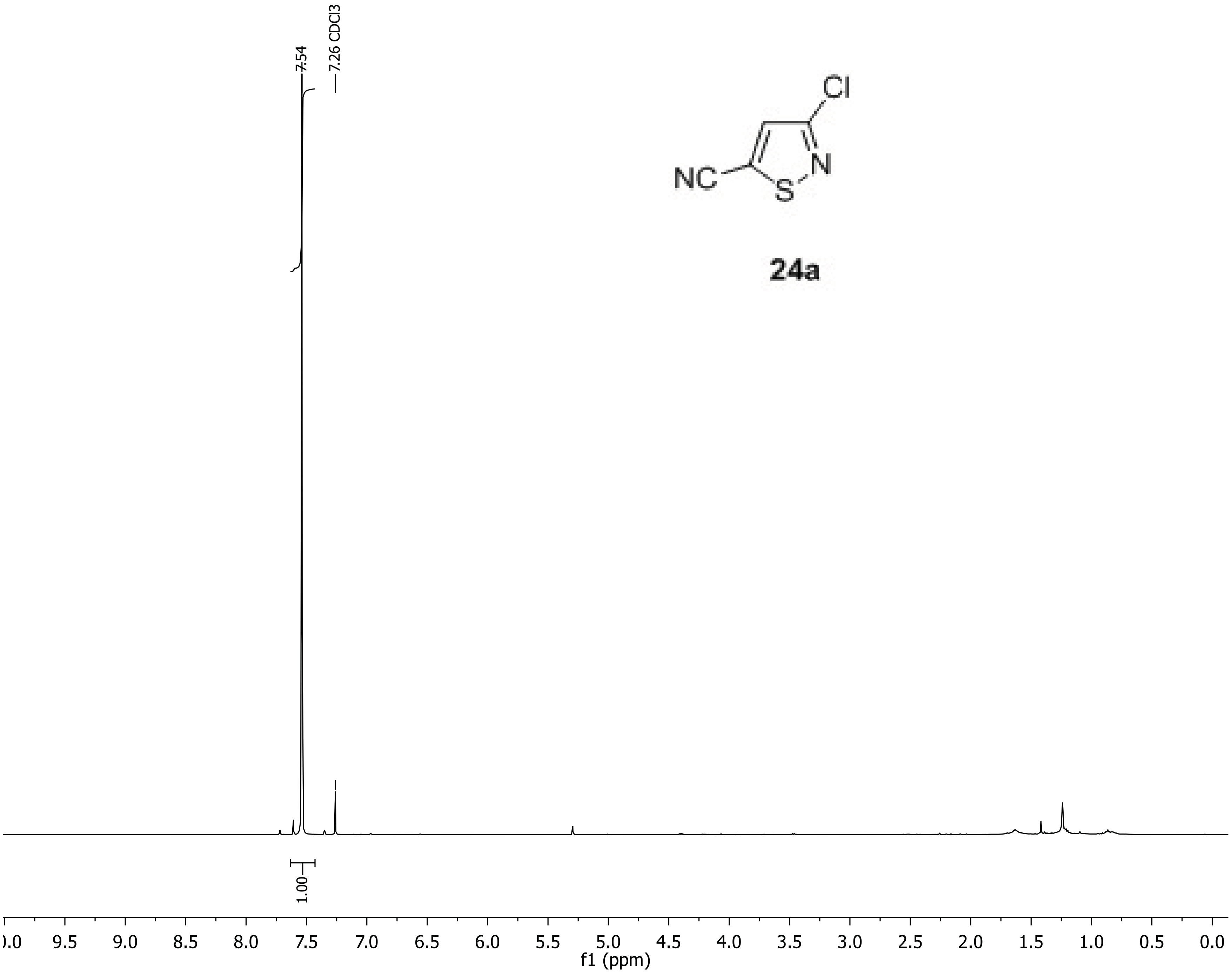
F2 - Processing parameters
SI 65536
SF 500.0330364 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

# 3-Bromo-4-cyanoisothiazole-5-carboxamide (**23**)



Current Data Parameters
NAME Andreas Kalogirou
EXPNO 36
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130209
Time 20.00
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG jmod
TD 65536
SOLVENT Acetone
NS 600
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 1820
DW 16.800 usec
DE 6.50 usec
TE 297.0 K
CNST2 145.0000000
CNST11 1.0000000
D1 2.00000000 sec
D20 0.00689655 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7459782 MHz
NUC1 13C
P1 8.70 usec
P2 17.40 usec
PLW1 138.00000000 W
======== CHANNEL f2 ========
SFO2 500.0350280 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 15.41699982 W
PLW12 0.33258000 W
F2 - Processing parameters
SI 32768
SF 125.7332989 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

# 3-Chloroisothiazole-5-carbonitrile (**24a**)



**24a**

Current Data Parameters

| | |
|---|---|
| NAME | Andreas Kalogirou |
| EXPNO | 119 |
| PROCNO | 1 |

F2 - Acquisition Parameters

| | |
|---|---|
| Date_ | 20130319 |
| Time | 14.48 |
| INSTRUM | spect |
| PROBHD | 5 mm PABBO BB- |
| PULPROG | zg30 |
| TD | 65536 |
| SOLVENT | CDCl3 |
| NS | 16 |
| DS | 2 |
| SWH | 10330.578 Hz |
| FIDRES | 0.157632 Hz |
| AQ | 3.1719425 sec |
| RG | 128 |
| DW | 48.400 usec |
| DE | 6.50 usec |
| TE | 295.4 K |
| D1 | 1.00000000 sec |
| TD0 | 1 |

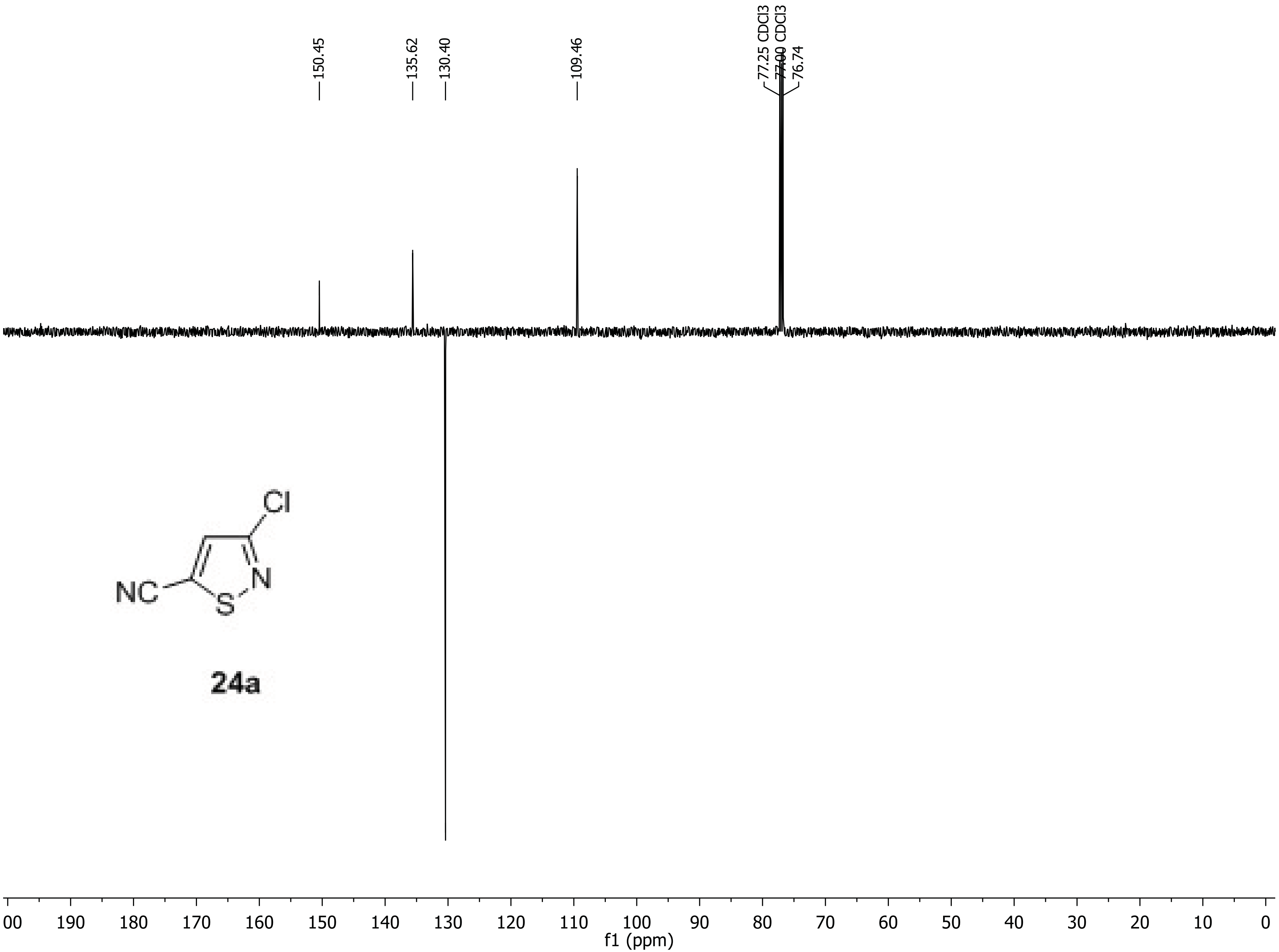
======== CHANNEL f1 ========

| | |
|---|---|
| SFO1 | 500.0361158 MHz |
| NUC1 | 1H |
| P1 | 11.75 usec |
| PLW1 | 15.41699982 W |

F2 - Processing parameters

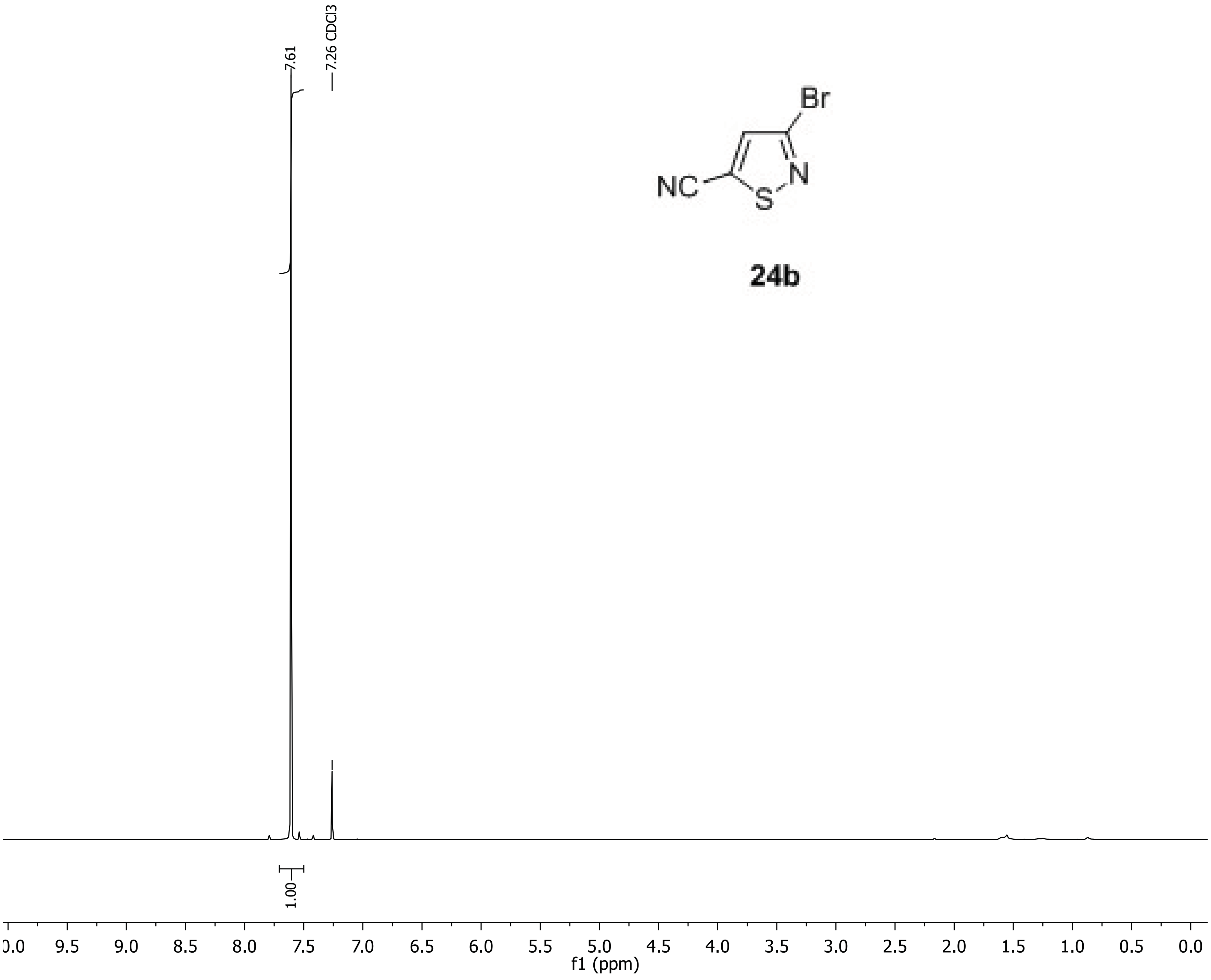
| | |
|---|---|
| SI | 65536 |
| SF | 500.0330401 MHz |
| WDW | EM |
| SSB | 0 |
| LB | 0.30 Hz |
| GB | 0 |
| PC | 1.00 |

# 3-Chloroisothiazole-5-carbonitrile (**24a**)



| | |
|---|---|
| Current Data Parameters | |
| NAME | Andreas Kalogirou |
| EXPNO | 128 |
| PROCNO | 1 |
| F2 - Acquisition Parameters | |
| Date_ | 20130407 |
| Time | 13.40 |
| INSTRUM | spect |
| PROBHD | 5 mm PABBO BB- |
| PULPROG | jmod |
| TD | 65536 |
| SOLVENT | CDCl3 |
| NS | 600 |
| DS | 4 |
| SWH | 29761.904 Hz |
| FIDRES | 0.454131 Hz |
| AQ | 1.1010048 sec |
| RG | 2050 |
| DW | 16.800 usec |
| DE | 6.50 usec |
| TE | 296.8 K |
| CNST2 | 145.0000000 |
| CNST11 | 1.0000000 |
| D1 | 2.00000000 sec |
| D20 | 0.00689655 sec |
| TD0 | 1 |
| ======== CHANNEL f1 ======== | |
| SFO1 | 125.7459782 MHz |
| NUC1 | 13C |
| P1 | 8.70 usec |
| P2 | 17.40 usec |
| PLW1 | 138.00000000 W |
| ======== CHANNEL f2 ======== | |
| SFO2 | 500.0350280 MHz |
| NUC2 | 1H |
| CPDPRG[2 | waltz16 |
| PCPD2 | 80.00 usec |
| PLW2 | 15.41699982 W |
| PLW12 | 0.33258000 W |
| F2 - Processing parameters | |
| SI | 32768 |
| SF | 125.7334118 MHz |
| WDW | EM |
| SSB | 0 |
| LB | 1.00 Hz |
| GB | 0 |
| PC | 1.40 |

3-Bromoisothiazole-5-carbonitrile (**24b**)



Current Data Parameters

| | |
|---|---|
| NAME | Andreas Kalogirou |
| EXPNO | 62 |
| PROCNO | 1 |

F2 - Acquisition Parameters

| | |
|---|---|
| Date_ | 20130219 |
| Time | 20.30 |
| INSTRUM | spect |
| PROBHD | 5 mm PABBO BB- |
| PULPROG | zg30 |
| TD | 65536 |
| SOLVENT | CDCl3 |
| NS | 16 |
| DS | 2 |
| SWH | 10330.578 Hz |
| FIDRES | 0.157632 Hz |
| AQ | 3.1719425 sec |
| RG | 161 |
| DW | 48.400 usec |
| DE | 6.50 usec |
| TE | 296.0 K |
| D1 | 1.00000000 sec |
| TD0 | 1 |

======== CHANNEL f1 ========

| | |
|---|---|
| SFO1 | 500.0361158 MHz |
| NUC1 | 1H |
| P1 | 11.75 usec |
| PLW1 | 15.41699982 W |

F2 - Processing parameters

| | |
|---|---|
| SI | 65536 |
| SF | 500.0330398 MHz |
| WDW | EM |
| SSB | 0 |
| LB | 0.30 Hz |
| GB | 0 |
| PC | 1.00 |

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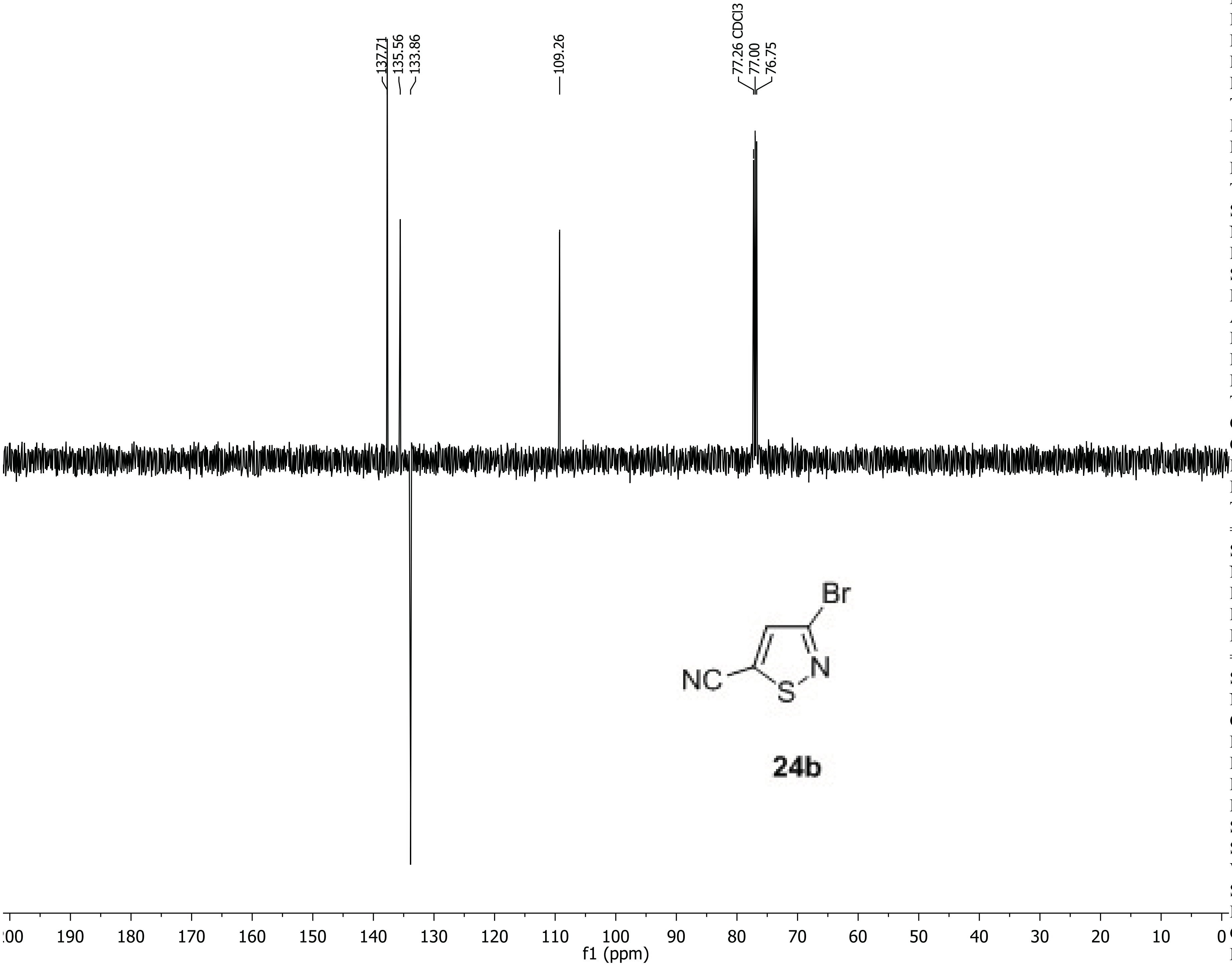
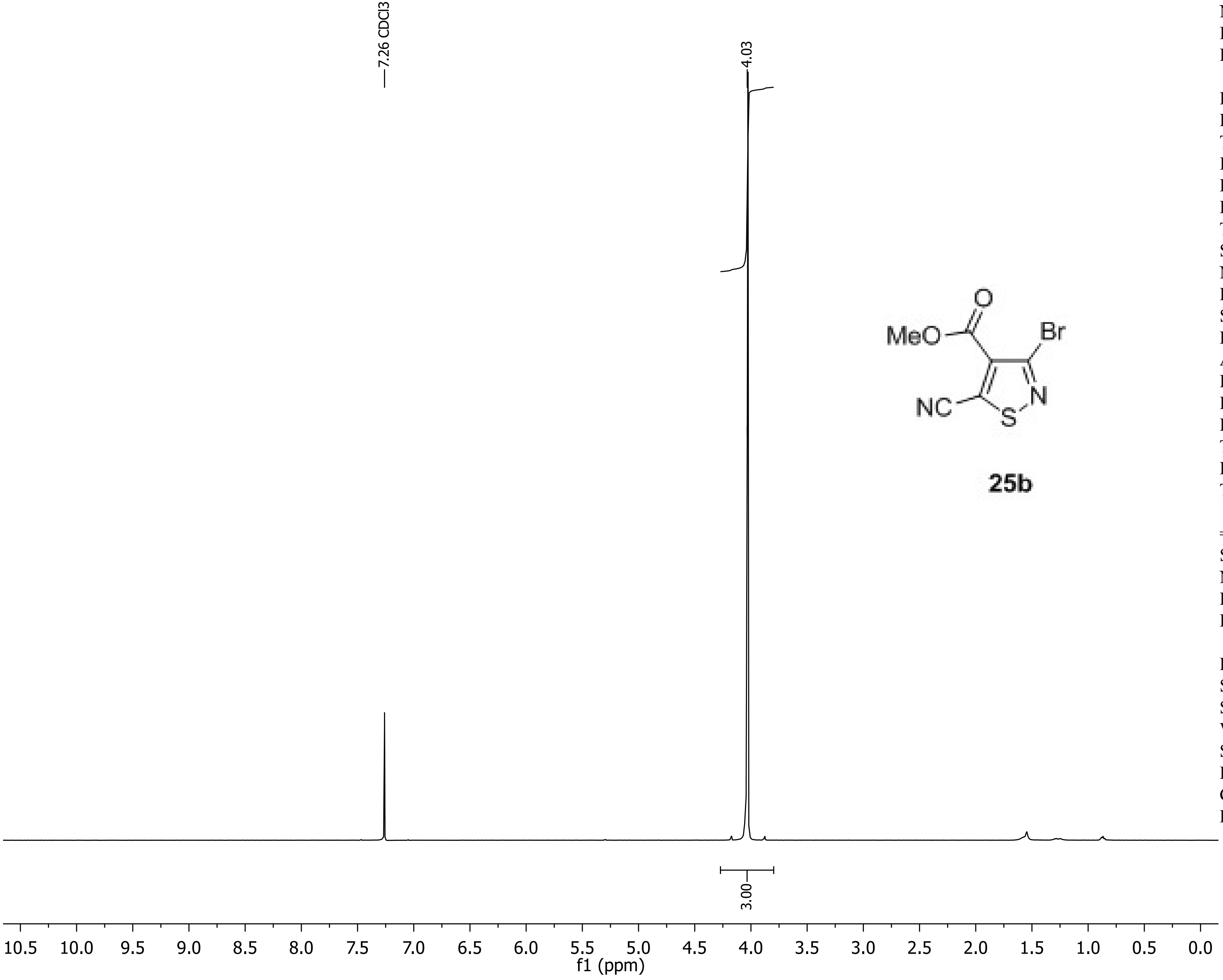
# 3-Bromoisothiazole-5-carbonitrile (**24b**)



| | |
|---|---|
| Current Data Parameters | |
| NAME | Andreas Kalogirou |
| EXPNO | 63 |
| PROCNO | 1 |
| F2 - Acquisition Parameters | |
| Date_ | 20130219 |
| Time | 20.57 |
| INSTRUM | spect |
| PROBHD | 5 mm PABBO BB- |
| PULPROG | jmod |
| TD | 65536 |
| SOLVENT | CDCl3 |
| NS | 500 |
| DS | 4 |
| SWH | 29761.904 Hz |
| FIDRES | 0.454131 Hz |
| AQ | 1.1010048 sec |
| RG | 2050 |
| DW | 16.800 usec |
| DE | 6.50 usec |
| TE | 296.9 K |
| CNST2 | 145.0000000 |
| CNST11 | 1.0000000 |
| D1 | 2.00000000 sec |
| D20 | 0.00689655 sec |
| TD0 | 1 |
| ======== CHANNEL f1 ======== | |
| SFO1 | 125.7459782 MHz |
| NUC1 | 13C |
| P1 | 8.70 usec |
| P2 | 17.40 usec |
| PLW1 | 138.00000000 W |
| ======== CHANNEL f2 ======== | |
| SFO2 | 500.0350280 MHz |
| NUC2 | 1H |
| CPDPRG[2 | waltz16 |
| PCPD2 | 80.00 usec |
| PLW2 | 15.41699982 W |
| PLW12 | 0.33258000 W |
| F2 - Processing parameters | |
| SI | 32768 |
| SF | 125.7334119 MHz |
| WDW | EM |
| SSB | 0 |
| LB | 1.00 Hz |
| GB | 0 |
| PC | 1.40 |

# Methyl 3-Bromo-5-cyanoisothiazole-4-carboxylate (**25b**)



**25b**

Current Data Parameters

| | |
|---|---|
| NAME | Andreas Kalogirou |
| EXPNO | 56 |
| PROCNO | 1 |

F2 - Acquisition Parameters

| | |
|---|---|
| Date_ | 20130219 |
| Time | 18.53 |
| INSTRUM | spect |
| PROBHD | 5 mm PABBO BB- |
| PULPROG | zg30 |
| TD | 65536 |
| SOLVENT | CDCl3 |
| NS | 16 |
| DS | 2 |
| SWH | 10330.578 Hz |
| FIDRES | 0.157632 Hz |
| AQ | 3.1719425 sec |
| RG | 161 |
| DW | 48.400 usec |
| DE | 6.50 usec |
| TE | 295.7 K |
| D1 | 1.00000000 sec |
| TD0 | 1 |

======== CHANNEL f1 ========

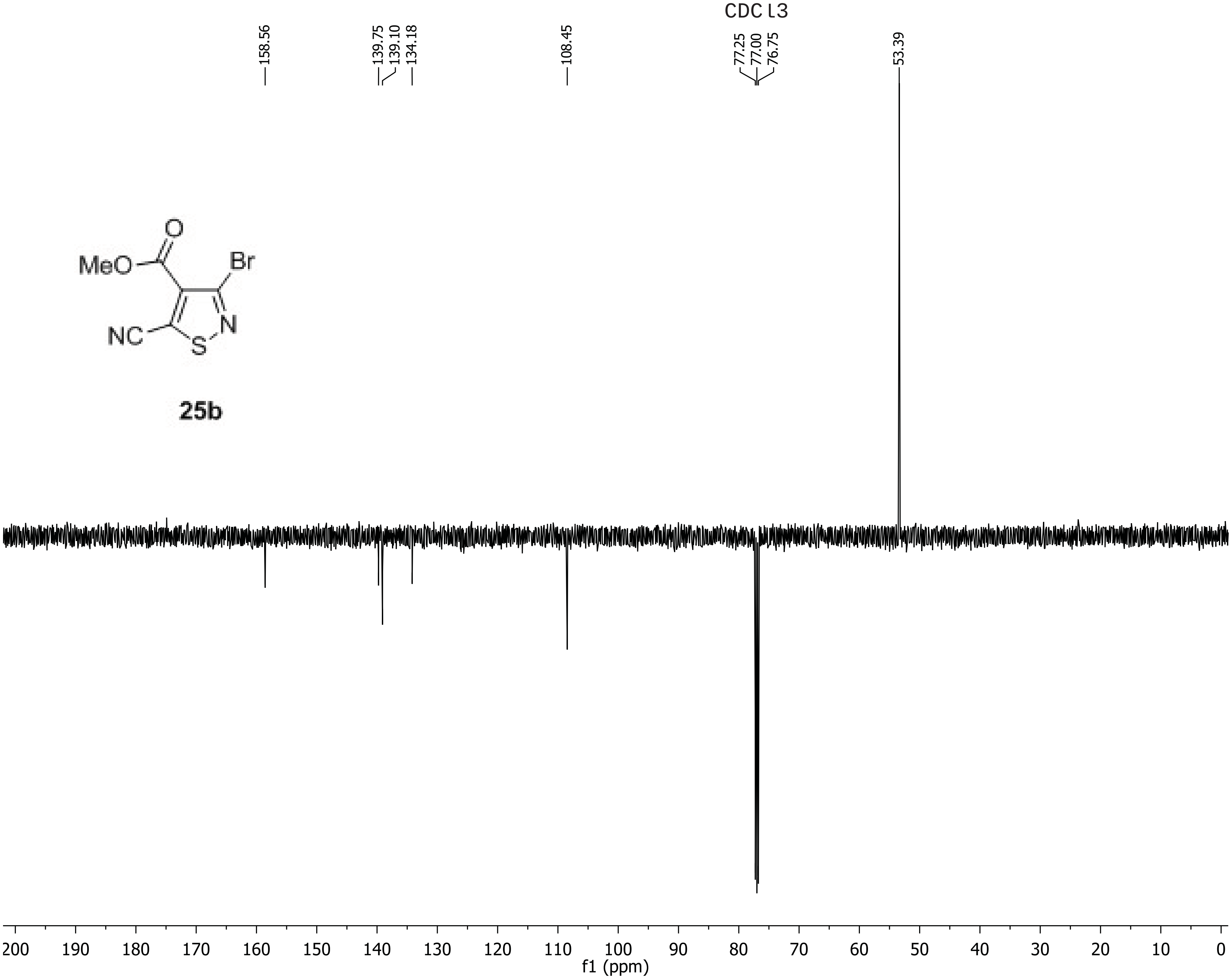
| | |
|---|---|
| SFO1 | 500.0361158 MHz |
| NUC1 | 1H |
| P1 | 11.75 usec |
| PLW1 | 15.41699982 W |

F2 - Processing parameters

| | |
|---|---|
| SI | 65536 |
| SF | 500.0330400 MHz |
| WDW | EM |
| SSB | 0 |
| LB | 0.30 Hz |
| GB | 0 |
| PC | 1.00 |

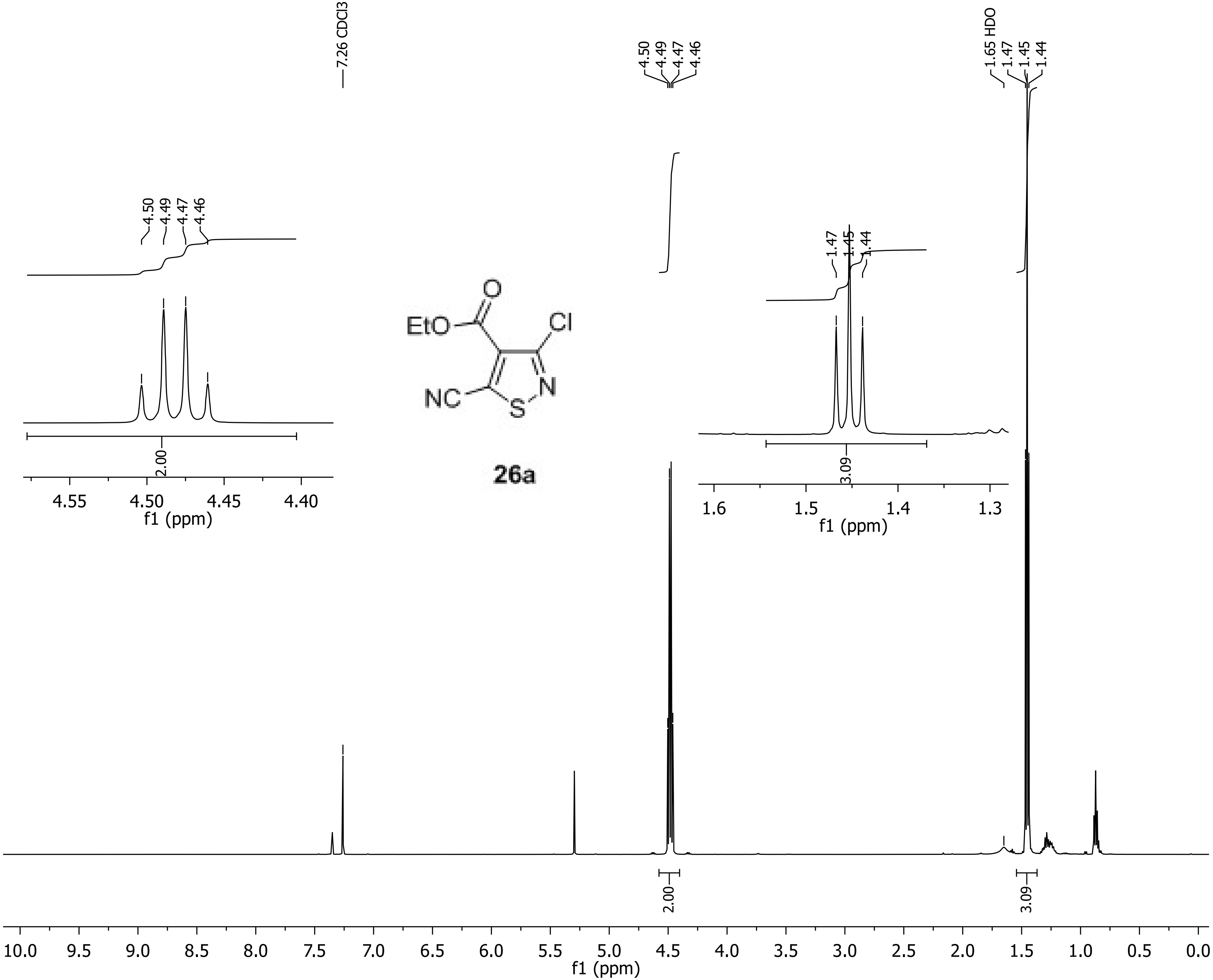
Methyl 3-Bromo-5-cyanoisothiazole-4-carboxylate (**25b**)

**25b**



Current Data Parameters
NAME Andreas Kalogirou
EXPNO 57
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130219
Time 18.54
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG jmod
TD 65536
SOLVENT CDCl3
NS 520
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 2050
DW 16.800 usec
DE 6.50 usec
TE 295.9 K
CNST2 145.0000000
CNST11 1.0000000
D1 2.00000000 sec
D20 0.00689655 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7459782 MHz
NUC1 13C
P1 8.70 usec
P2 17.40 usec
PLW1 138.00000000 W
======== CHANNEL f2 ========
SFO2 500.0350280 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 15.41699982 W
PLW12 0.33258000 W
F2 - Processing parameters
SI 32768
SF 125.7334109 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Ethyl 3-chloro-5-cyanoisothiazole-4-carboxylate (**26a**)



Current Data Parameters

| | |
|---|---|
| NAME | Andreas Kalogirou |
| EXPNO | 142 |
| PROCNO | 1 |

F2 - Acquisition Parameters

| | |
|---|---|
| Date_ | 20130422 |
| Time | 0.04 |
| INSTRUM | spect |
| PROBHD | 5 mm PABBO BB- |
| PULPROG | zg30 |
| TD | 65536 |
| SOLVENT | CDCl3 |
| NS | 16 |
| DS | 2 |
| SWH | 10330.578 Hz |
| FIDRES | 0.157632 Hz |
| AQ | 3.1719425 sec |
| RG | 114 |
| DW | 48.400 usec |
| DE | 6.50 usec |
| TE | 295.9 K |
| D1 | 1.00000000 sec |
| TD0 | 1 |

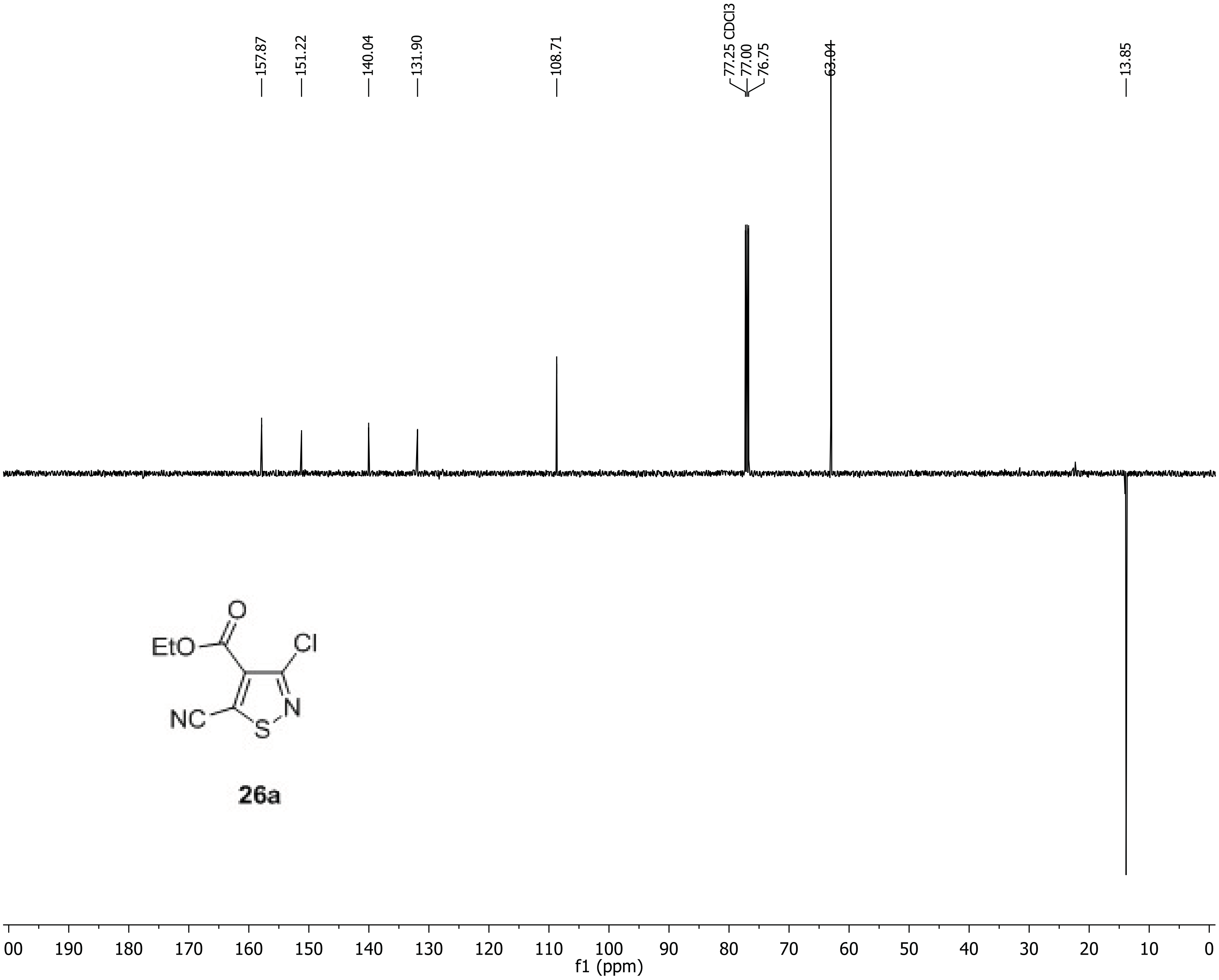
======== CHANNEL f1 ========

| | |
|---|---|
| SFO1 | 500.0361158 MHz |
| NUC1 | 1H |
| P1 | 11.75 usec |
| PLW1 | 15.41699982 W |

F2 - Processing parameters

| | |
|---|---|
| SI | 65536 |
| SF | 500.0330403 MHz |
| WDW | EM |
| SSB | 0 |
| LB | 0.30 Hz |
| GB | 0 |
| PC | 1.00 |

# Ethyl 3-chloro-5-cyanoisothiazole-4-carboxylate (**26a**)



| | |
|---|---|
| Current Data Parameters | |
| NAME | Andreas Kalogirou |
| EXPNO | 143 |
| PROCNO | 1 |
| F2 - Acquisition Parameters | |
| Date_ | 20130422 |
| Time | 1.08 |
| INSTRUM | spect |
| PROBHD | 5 mm PABBO BB- |
| PULPROG | jmod |
| TD | 65536 |
| SOLVENT | CDCl3 |
| NS | 1200 |
| DS | 4 |
| SWH | 29761.904 Hz |
| FIDRES | 0.454131 Hz |
| AQ | 1.1010048 sec |
| RG | 2050 |
| DW | 16.800 usec |
| DE | 6.50 usec |
| TE | 296.8 K |
| CNST2 | 145.0000000 |
| CNST11 | 1.0000000 |
| D1 | 2.00000000 sec |
| D20 | 0.00689655 sec |
| TD0 | 1 |
| ======== CHANNEL f1 ======== | |
| SFO1 | 125.7459782 MHz |
| NUC1 | 13C |
| P1 | 8.70 usec |
| P2 | 17.40 usec |
| PLW1 | 138.00000000 W |
| ======== CHANNEL f2 ======== | |
| SFO2 | 500.0350280 MHz |
| NUC2 | 1H |
| CPDPRG[2 | waltz16 |
| PCPD2 | 80.00 usec |
| PLW2 | 15.41699982 W |
| PLW12 | 0.33258000 W |
| F2 - Processing parameters | |
| SI | 32768 |
| SF | 125.7334102 MHz |
| WDW | EM |
| SSB | 0 |
| LB | 1.00 Hz |
| GB | 0 |
| PC | 1.40 |

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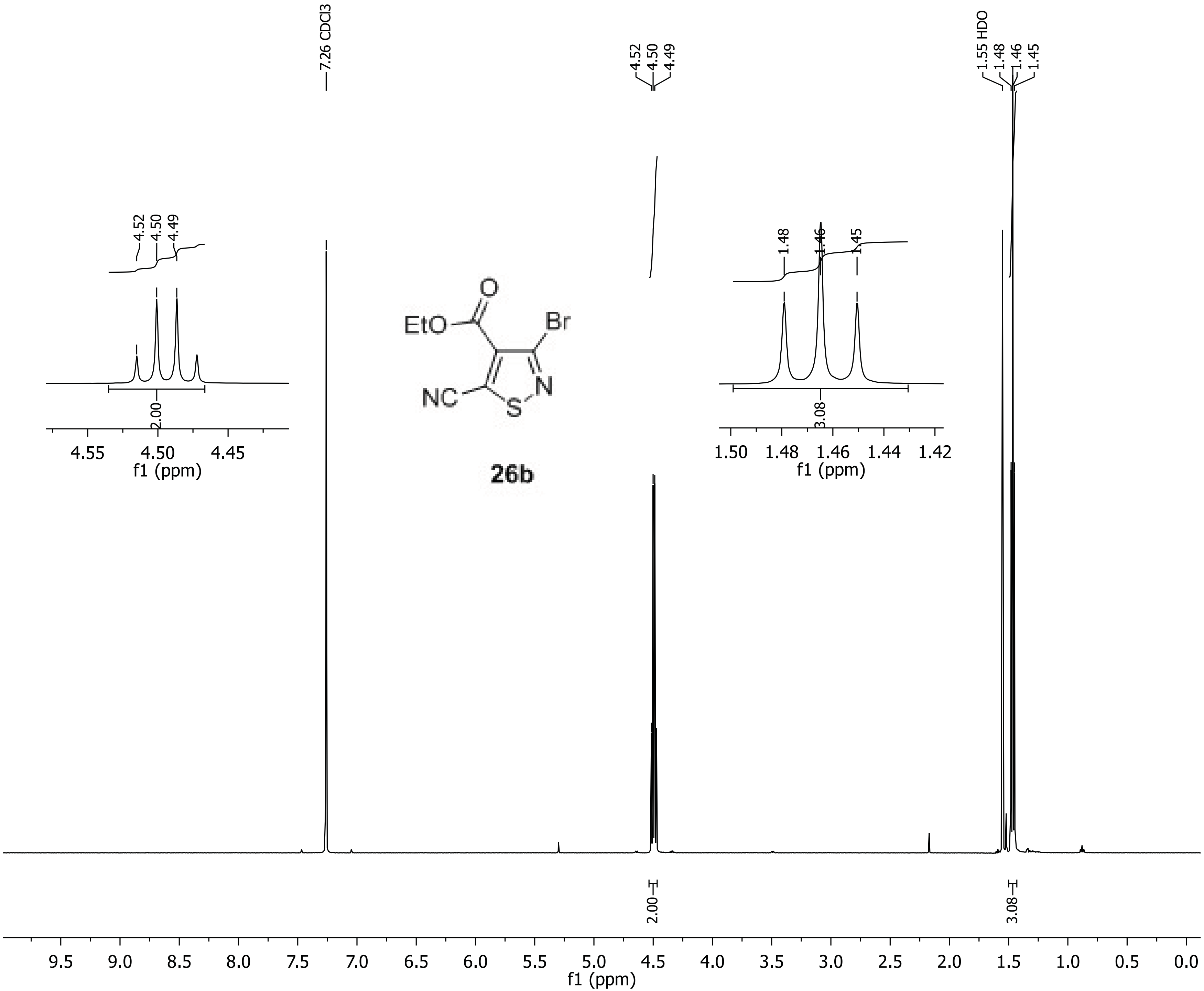
# Ethyl 3-Bromo-5-cyanoisothiazole-4-carboxylate (**26b**)



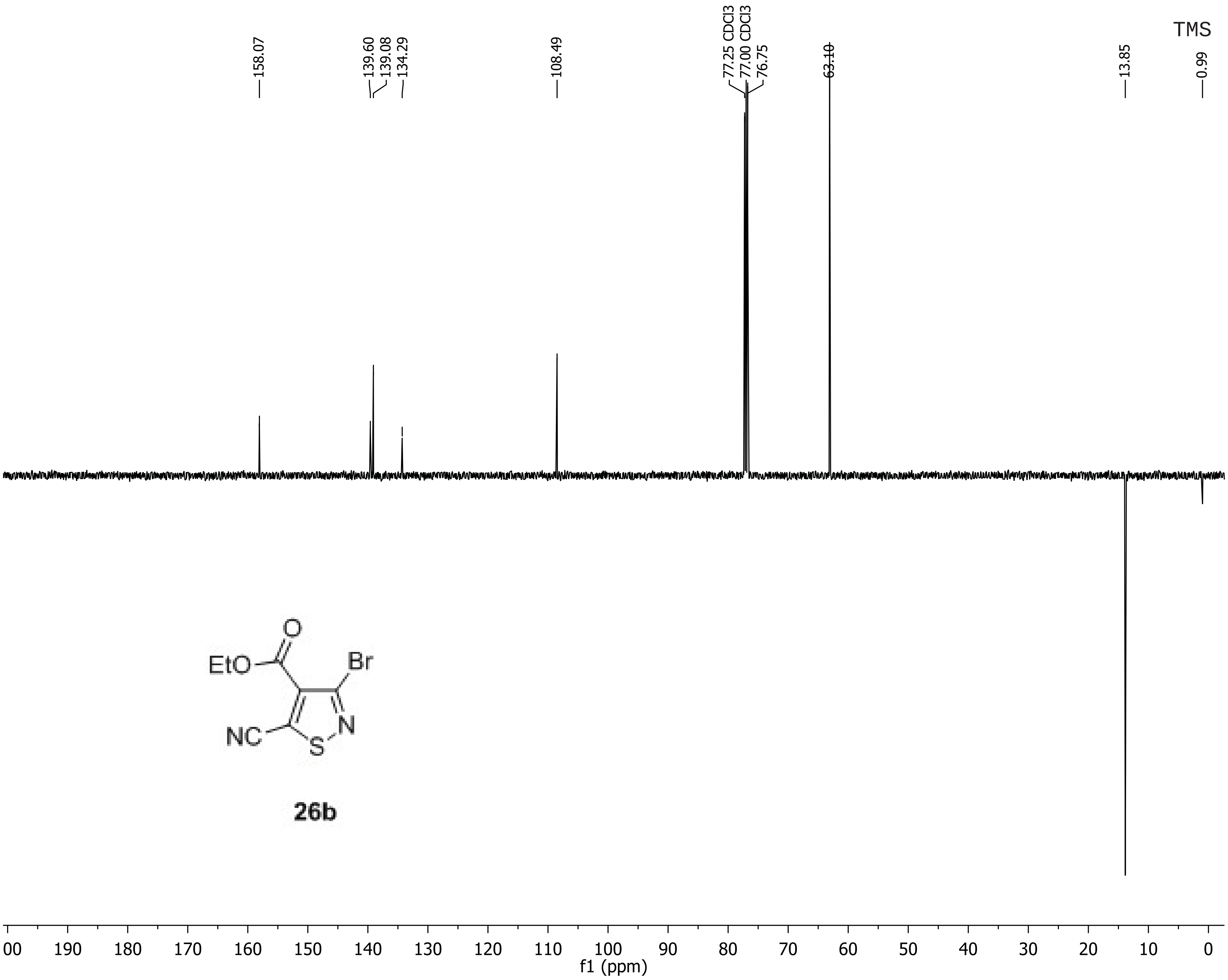
Current Data Parameters
NAME Herc
EXPNO 568
PROCNO 1

F2 - Acquisition Parameters
Date_ 20111121
Time 16.37
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 181
DW 48.400 usec
DE 6.50 usec
TE 297.6 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 11.75 usec
PLW1 15.41699982 W
SFO1 500.0361158 MHz

F2 - Processing parameters
SI 65536
SF 500.0330402 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

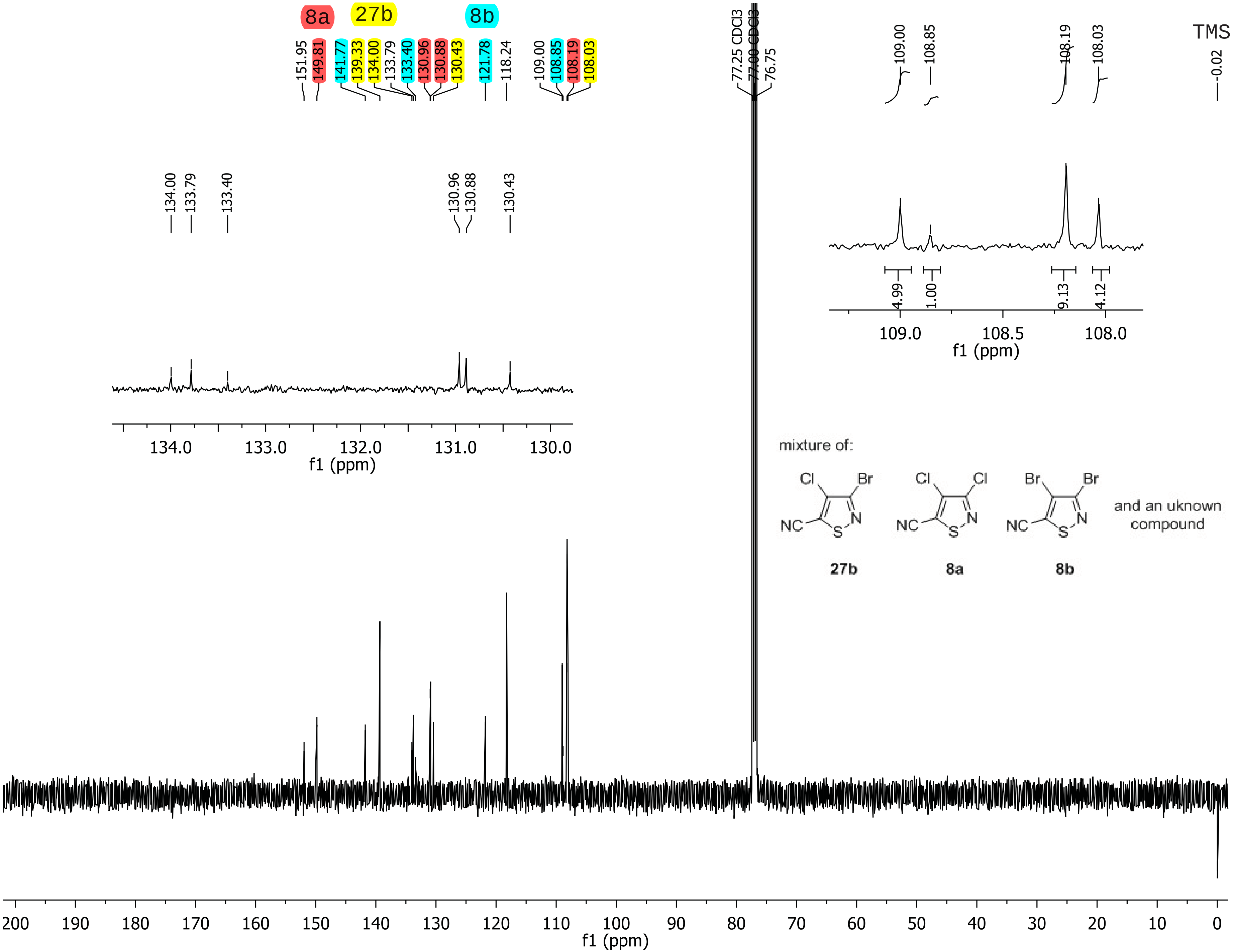
# Ethyl 3-Bromo-5-cyanoisothiazole-4-carboxylate (**26b**)



Current Data Parameters
NAME Herc
EXPNO 653
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120208
Time 12.22
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG jmod
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010548 sec
RG 2050
DW 16.800 usec
DE 6.50 usec
TE 294.9 K
CNST2 145.0000000
CNST11 1.0000000
D1 2.00000000 sec
D20 0.00689655 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.38 usec
P2 16.76 usec
PLW1 138.00000000 W
SFO1 125.7459782 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 15.41699982 W
PLW12 0.33258000 W
SFO2 500.0350280 MHz
F2 - Processing parameters
SI 32768
SF 125.7334099 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

# SECTION B

4.3.10. Reaction of (*Z*)-2-bromo-2-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)acetonitrile (**21**) with HCl in $Et_2O$; Table 1, entry 7.



Current Data Parameters

| | |
|---|---|
| NAME | Andreas |
| EXPNO | 1363 |
| PROCNO | 1 |

F2 - Acquisition Parameters

| | |
|---|---|
| Date_ | 20130908 |
| Time | 10.10 |
| INSTRUM | spect |
| PROBHD | 5 mm PABBO BB- |
| PULPROG | jmod |
| TD | 65536 |
| SOLVENT | CDCl3 |
| NS | 5000 |
| DS | 4 |
| SWH | 29761.904 Hz |
| FIDRES | 0.454131 Hz |
| AQ | 1.1010048 sec |
| RG | 2050 |
| DW | 16.800 usec |
| DE | 6.50 usec |
| TE | 296.4 K |
| CNST2 | 145.0000000 |
| CNST11 | 1.0000000 |
| D1 | 6.00000000 sec |
| D20 | 0.00689655 sec |
| TD0 | 1 |

======== CHANNEL f1 ========

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| SFO1 | 125.7459782 MHz |
| NUC1 | 13C |
| P1 | 8.70 usec |
| P2 | 17.40 usec |
| PLW1 | 138.00000000 W |

======== CHANNEL f2 ========

| | |
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| SFO2 | 500.0350280 MHz |
| NUC2 | 1H |
| CPDPRG[2 | waltz16 |
| PCPD2 | 80.00 usec |
| PLW2 | 15.41699982 W |
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F2 - Processing parameters

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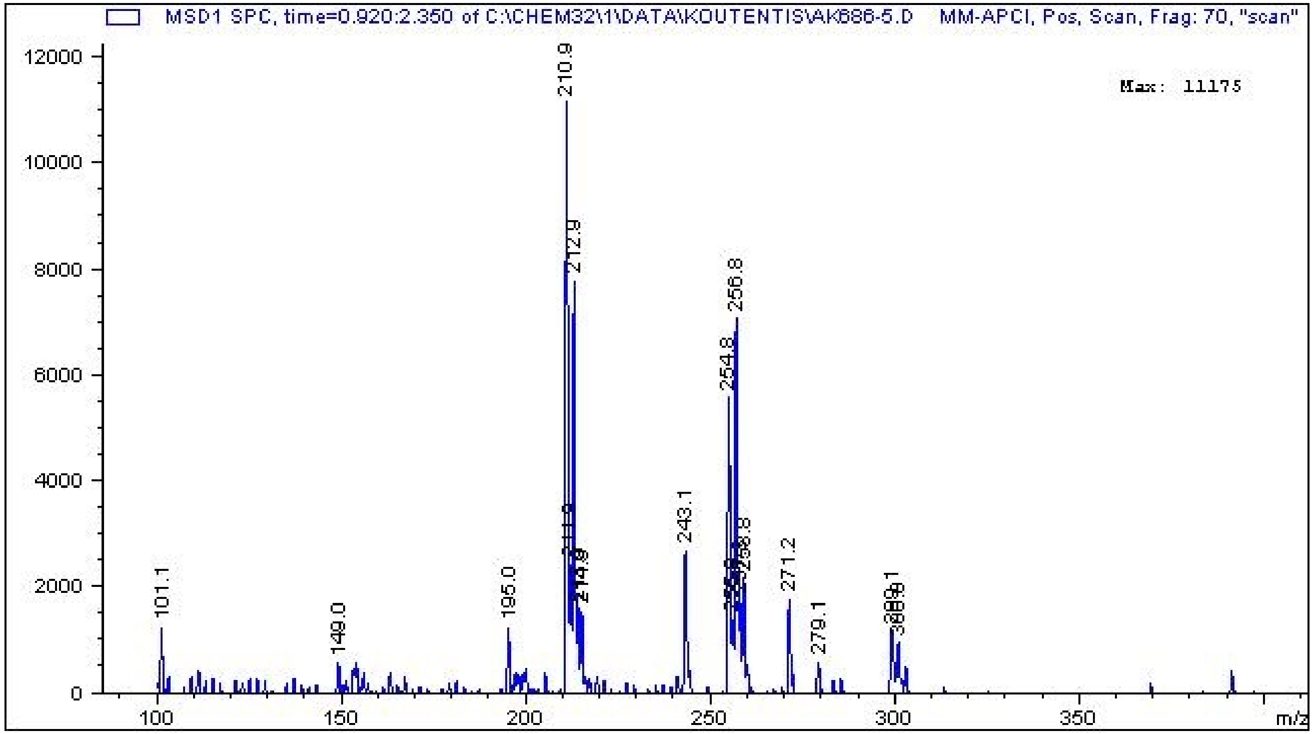
| SI | 32768 |
| SF | 125.7334067 MHz |
| WDW | EM |
| SSB | 0 |
| LB | 1.00 Hz |
| GB | 0 |
| PC | 1.40 |

### 4.3.10. Reaction of (*Z*)-2-bromo-2-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)acetonitrile (**21**) with HCl in $Et_2O$; Table 1, entry 7.

**Products:** mixture of 3,4-dichloroisothiazole-5-carbonitrile (**8a**), 3,4-dibromoisothiazole-5-carbonitrile (**8b**), 3-bromo-4-chloroisothiazole-5-carbonitrile (**27b**) and an unknown compound (**8a:uknown:27b:8b** = 9:5:4:1 by $^{13}$C NMR).



*m*/*z* (ESI-APCI+) 302.8 [**8b**, $(M+H+MeOH+4)^+$, 6%], 300.8 [**8b**, $(M+H+MeOH+2)^+$, 8%], 299.1 [**8b**, $(M+H+MeOH)^+$, 5%], 258.8 [**27b**, $(M+H+MeOH+4)^+$, 13%], 256.8 [**27b**, $(M+H+MeOH+2)^+$, 55%], 254.8 [**27b**, $(MH+MeOH)^+$, 46%], 214.9 [**8a**, $(M+H+MeOH+4)^+$, 25%], 212.9 [**8a**, $(M+H+MeOH+2)^+$, 76], 210.9 [**8a**, $(M+H+MeOH)^+$, 100%]

Electronic Supplementary Material (ESI) for RSC Advances
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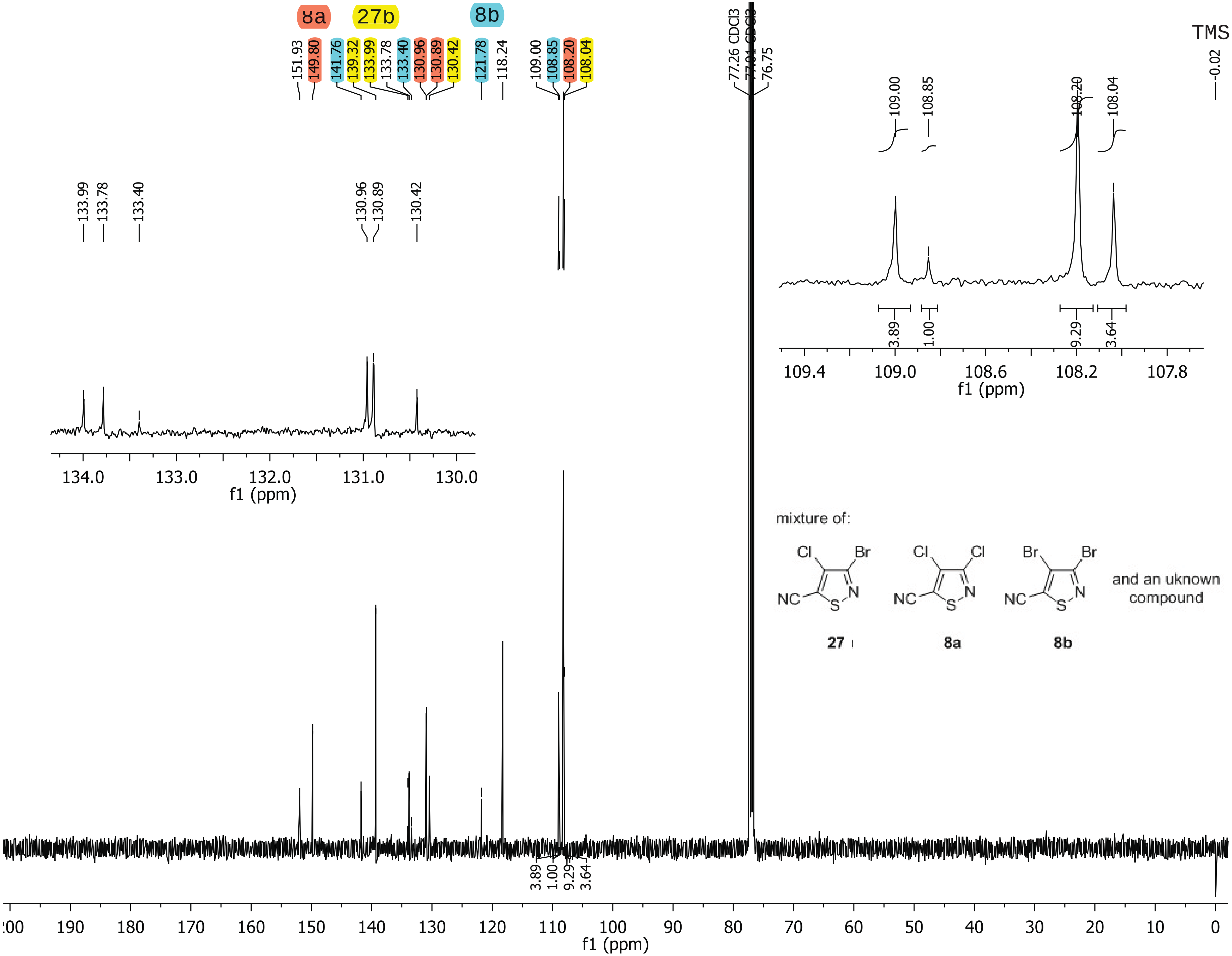
### 4.3.11. Reaction of (*Z*)-2-bromo-2-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)acetonitrile (**21**) with HCl in THF; Table 1, entry 8.



mixture of:

**27** **8a** **8b**

and an uknown compound

| | |
|---|---|
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| PROCNO | 1 |
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| SOLVENT | CDCl3 |
| NS | 5000 |
| DS | 4 |
| SWH | 29761.904 Hz |
| FIDRES | 0.454131 Hz |
| AQ | 1.1010048 sec |
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| TE | 296.4 K |
| CNST2 | 145.0000000 |
| CNST11 | 1.0000000 |
| D1 | 6.00000000 sec |
| D20 | 0.00689655 sec |
| TD0 | 1 |
| ======== CHANNEL f1 ======== | |
| SFO1 | 125.7459782 MHz |
| NUC1 | 13C |
| P1 | 8.70 usec |
| P2 | 17.40 usec |
| PLW1 | 138.00000000 W |
| ======== CHANNEL f2 ======== | |
| SFO2 | 500.0350280 MHz |
| NUC2 | 1H |
| CPDPRG[2 | waltz16 |
| PCPD2 | 80.00 usec |
| PLW2 | 15.41699982 W |
| PLW12 | 0.33258000 W |
| F2 - Processing parameters | |
| SI | 32768 |
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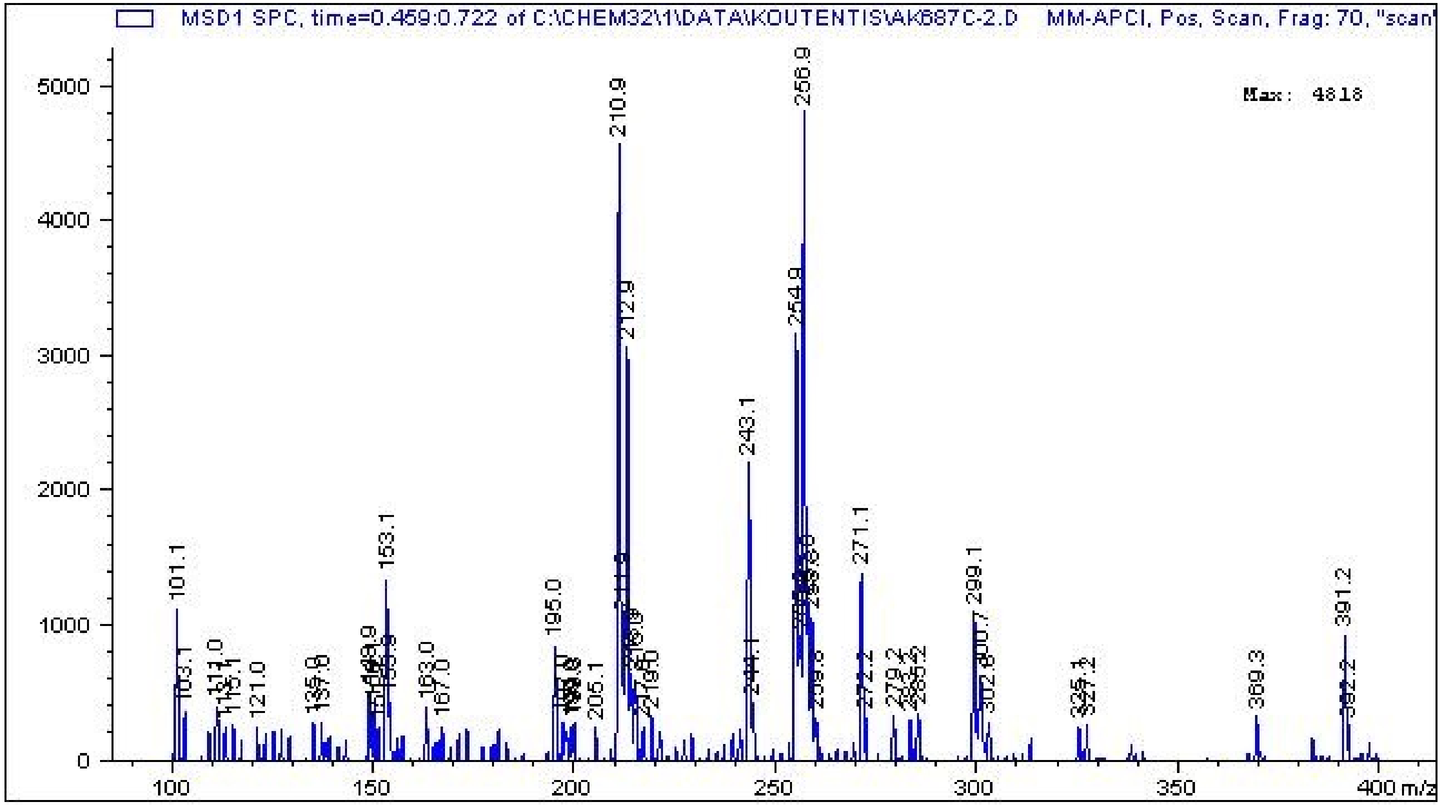
| WDW | EM |
| SSB | 0 |
| LB | 1.00 Hz |
| GB | 0 |
| PC | 1.40 |

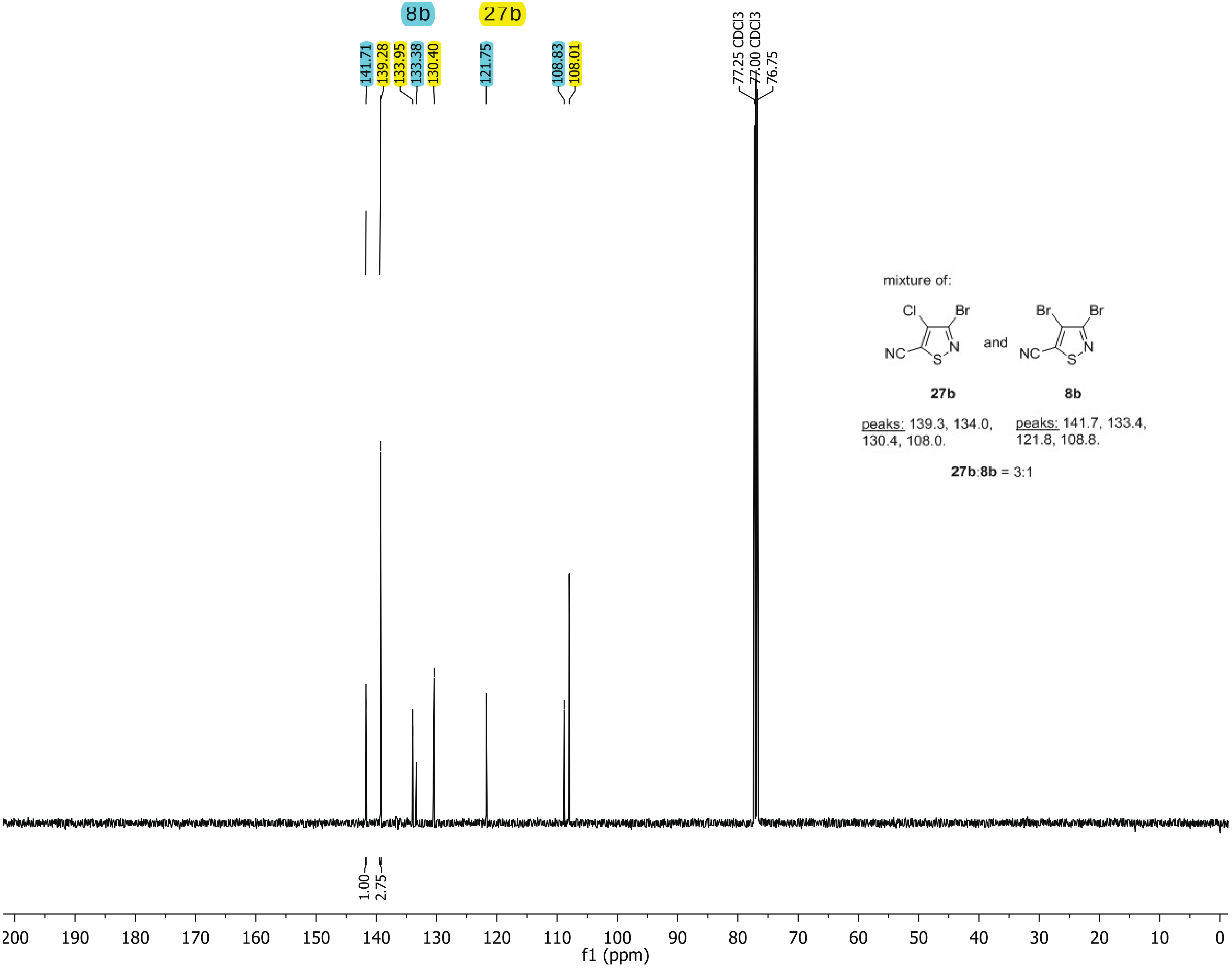
4.3.11. Reaction of (*Z*)-2-bromo-2-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)acetonitrile (**21**) with HCl in THF; Table 1, entry 8.

**Products:** mixture of 3,4-dichloroisothiazole-5-carbonitrile (**8a**), 3,4-dibromoisothiazole-5-carbonitrile (**8b**), 3-bromo-4-chloroisothiazole-5-carbonitrile (**27b**) and an unknown compound (**8a:uknown:27b:8b** = 9.3:3.9:3.6:1 by $^{13}$C NMR).



*m*/*z* (ESI-APCI+) 302.8 [**8b**, (M+H+MeOH+4)$^{+}$, 6%], 300.8 [**8b**, (M+H+MeOH+2)$^{+}$, 8%], 299.1 [**8b**, (M+H+MeOH)$^{+}$, 5%], 258.9 [**27b**, (M+H+MeOH+4)$^{+}$, 27%], 256.8 [**27b**, (M+H+MeOH+2)$^{+}$, 65%], 254.9 [**27b**, (MH+MeOH)$^{+}$, 51%], 214.9 [**8a**, (M+H+MeOH+4)$^{+}$, 18%], 212.9 [**8a**, (M+H+MeOH+2)$^{+}$, 47], 210.9 [**8a**, (M+H+MeOH)$^{+}$, 65%]

## 4.3.12. Reaction of 2-chloro-2-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)acetonitrile (**22**) with HBr in $Et_2O$; Table 1, entry 9.



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PROCNO 1
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TD 65536
SOLVENT CDCl3
NS 1000
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 2050
DW 16.800 usec
DE 6.50 usec
TE 297.0 K
CNST2 145.0000000
CNST11 1.0000000
D1 6.00000000 sec
D20 0.00689655 sec
TD0 1
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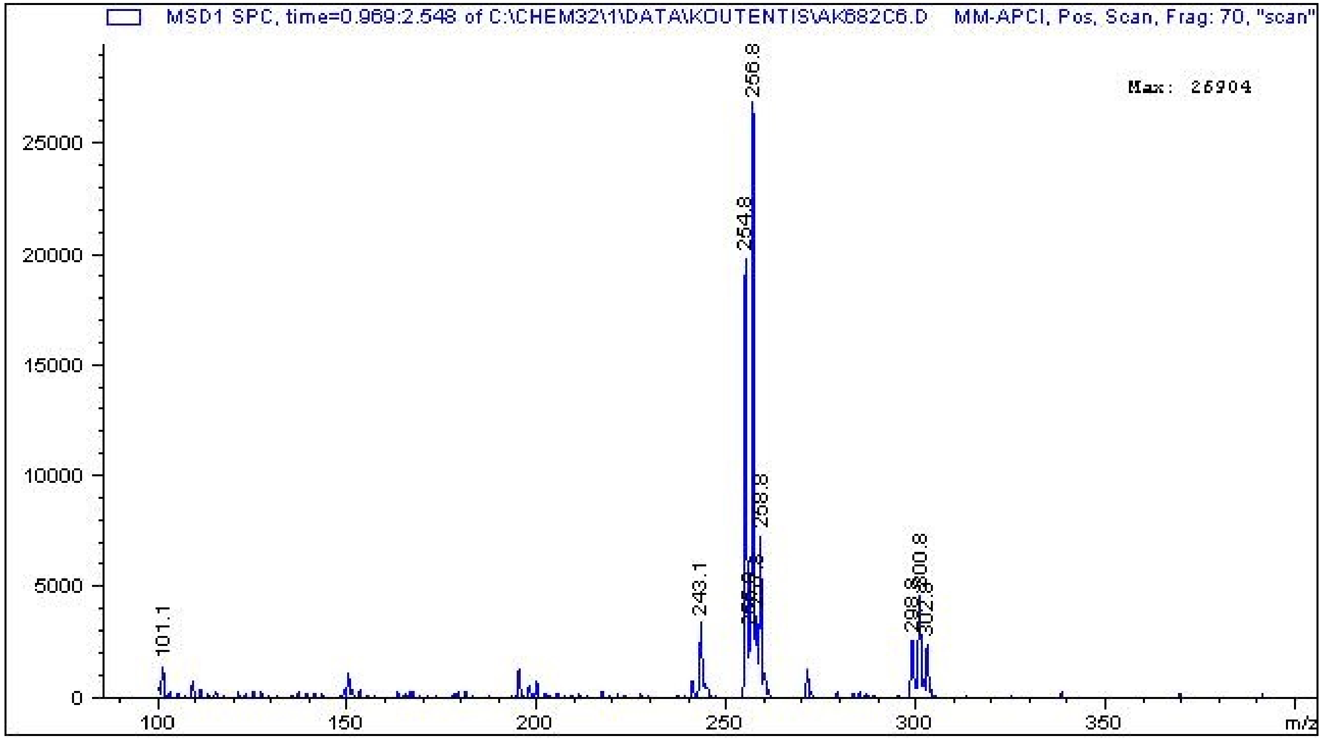
SFO1 125.7459782 MHz
NUC1 13C
P1 8.70 usec
P2 17.40 usec
PLW1 138.00000000 W
======== CHANNEL f2 ========
SFO2 500.0350280 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 15.41699982 W
PLW12 0.33258000 W
F2 - Processing parameters
SI 32768
SF 125.7334123 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

4.3.12. Reaction of 2-chloro-2-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)acetonitrile (**22**) with HBr in $Et_2O$; Table 1, entry 9.

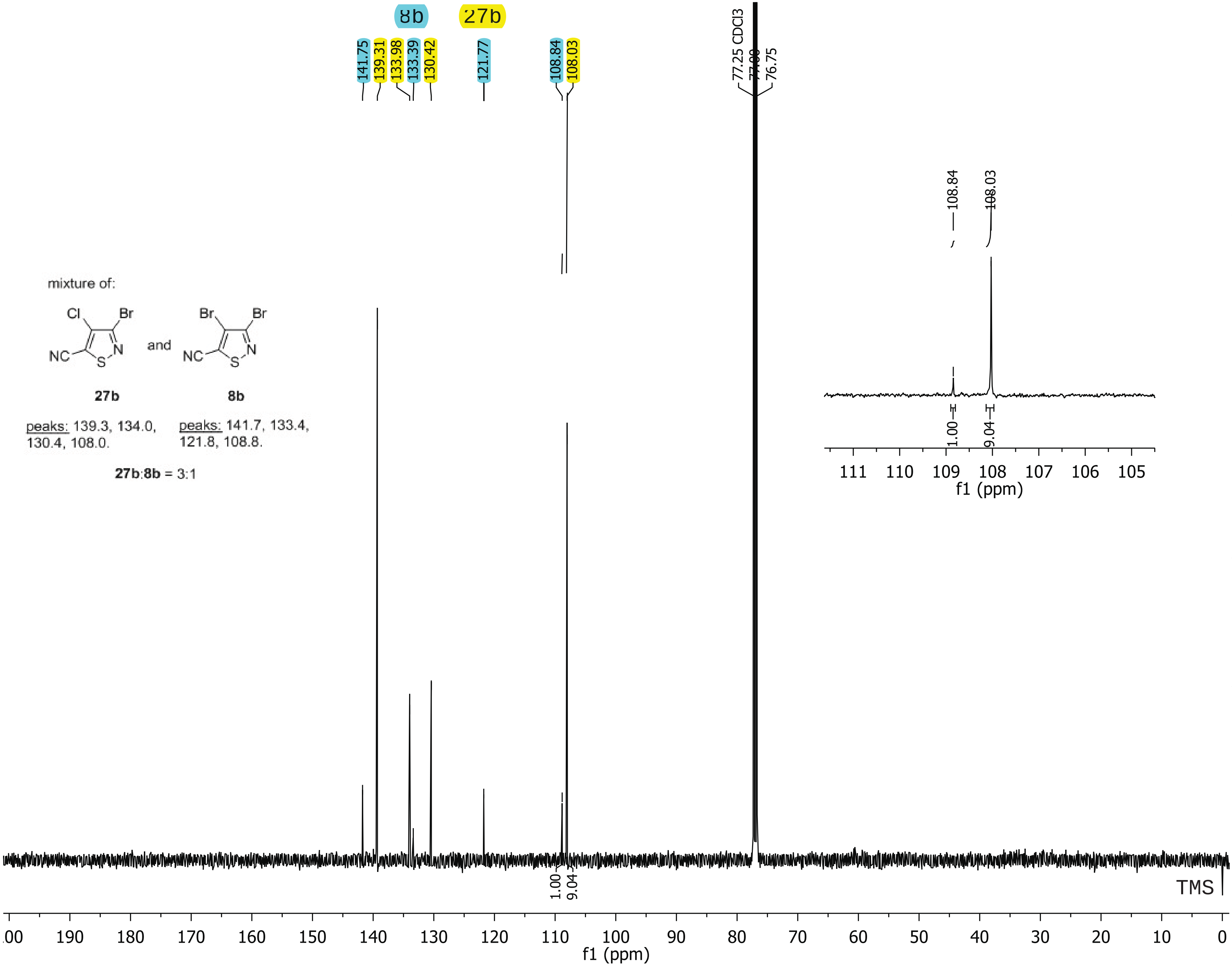
**Products:** mixture of 3-bromo-4-chloroisothiazole-5-carbonitrile (**27b**) and 3,4-dibromoisothiazole-5-carbonitrile (**8b**) (**27b**:**8b** = 3:1 by $^{13}C$ NMR).

Both ESI-APCI+ and GC-MS were run on this sample. For GC-MS data see supporting information part C.



ESI results: *m*/*z* (ESI-APCI+) 302.8 [**8b**, $(M+H+MeOH+4)^+$, 9%], 300.8 [**8b**, $(M+H+MeOH+2)^+$, 12%], 298.8 [**8b**, $(M+H+MeOH)^+$, 10%], 258.8 [**27b**, $(M+H+MeOH+4)^+$, 33%], 256.8 [**27b**, $(M+H+MeOH+2)^+$, 100%], 254.8 [**27b**, $(MH+MeOH)^+$, 72%].

4.3.13. Reaction of 2-chloro-2-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)acetonitrile (**22**) with HBr in THF; Table 1, entry 10.



peaks: 139.3, 134.0, 130.4, 108.0.

peaks: 141.7, 133.4, 121.8, 108.8.

**27b**:**8b** = 3:1

| | |
|---|---|
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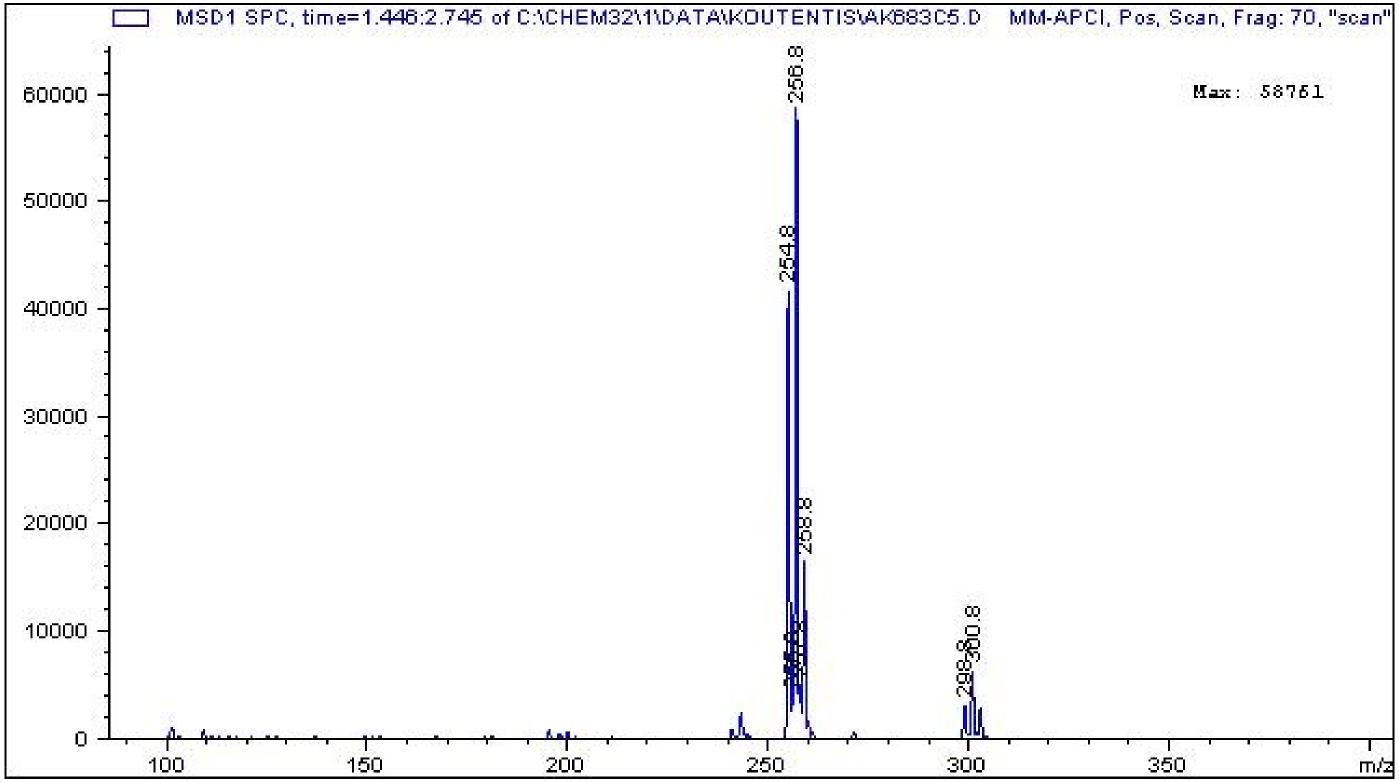
| PULPROG | jmod |
| TD | 65536 |
| SOLVENT | CDCl3 |
| NS | 3500 |
| DS | 4 |
| SWH | 29761.904 Hz |
| FIDRES | 0.454131 Hz |
| AQ | 1.1010048 sec |
| RG | 2050 |
| DW | 16.800 usec |
| DE | 6.50 usec |
| TE | 296.4 K |
| CNST2 | 145.0000000 |
| CNST11 | 1.0000000 |
| D1 | 6.00000000 sec |
| D20 | 0.00689655 sec |
| TD0 | 1 |
| ======== CHANNEL f1 ======== | |
| SFO1 | 125.7459782 MHz |
| NUC1 | 13C |
| P1 | 8.70 usec |
| P2 | 17.40 usec |
| PLW1 | 138.00000000 W |
| ======== CHANNEL f2 ======== | |
| SFO2 | 500.0350280 MHz |
| NUC2 | 1H |
| CPDPRG[2 | waltz16 |
| PCPD2 | 80.00 usec |
| PLW2 | 15.41699982 W |
| PLW12 | 0.33258000 W |
| F2 - Processing parameters | |
| SI | 32768 |
| SF | 125.7334093 MHz |
| WDW | EM |
| SSB | 0 |
| LB | 1.00 Hz |
| GB | 0 |
| PC | 1.40 |

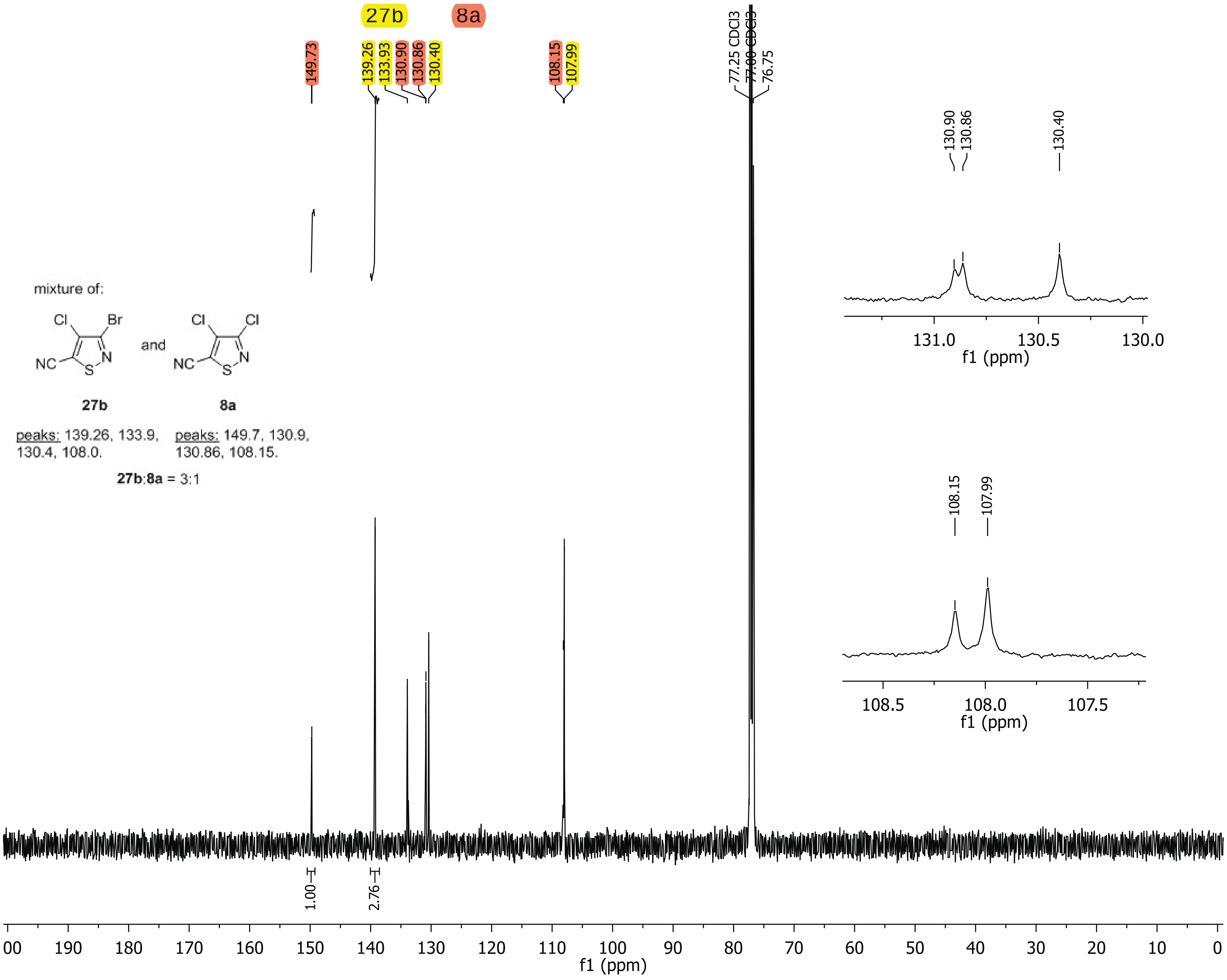
4.3.13. Reaction of 2-chloro-2-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)acetonitrile (**22**) with HBr in THF; Table 1, entry 10.

**Products:** isothiazole **24b** isolated by chromatography and mixture of 3-bromo-4-chloroisothiazole-5-carbonitrile (**27b**) and 3,4-dibromoisothiazole-5-carbonitrile (**8b**) (**27b**:**8b** = 9:1 by $^{13}$C NMR).



*m*/*z* (ESI-APCI+) 302.8 [**8b**, (M+H+MeOH+4)$^+$, 9%], 300.8 [**8b**, (M+H+MeOH+2)$^+$, 12%], 298.8 [**8b**, (M+H+MeOH)$^+$, 10%], 258.8 [**27b**, (M+H+MeOH+4)$^+$, 33%], 256.8 [**27b**, (M+H+MeOH+2)$^+$, 100%], 254.8 [**27b**, (MH+MeOH)$^+$, 72%].

### 4.5.1. Reaction of (*Z*)-2-bromo-2-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)acetonitrile (**21**) with benzyltriethylammonium chloride; Table 2, entry 2.



peaks: 139.26, 133.9, 130.4, 108.0.

peaks: 149.7, 130.9, 130.86, 108.15.

**27b**:**8a** = 3:1

Current Data Parameters

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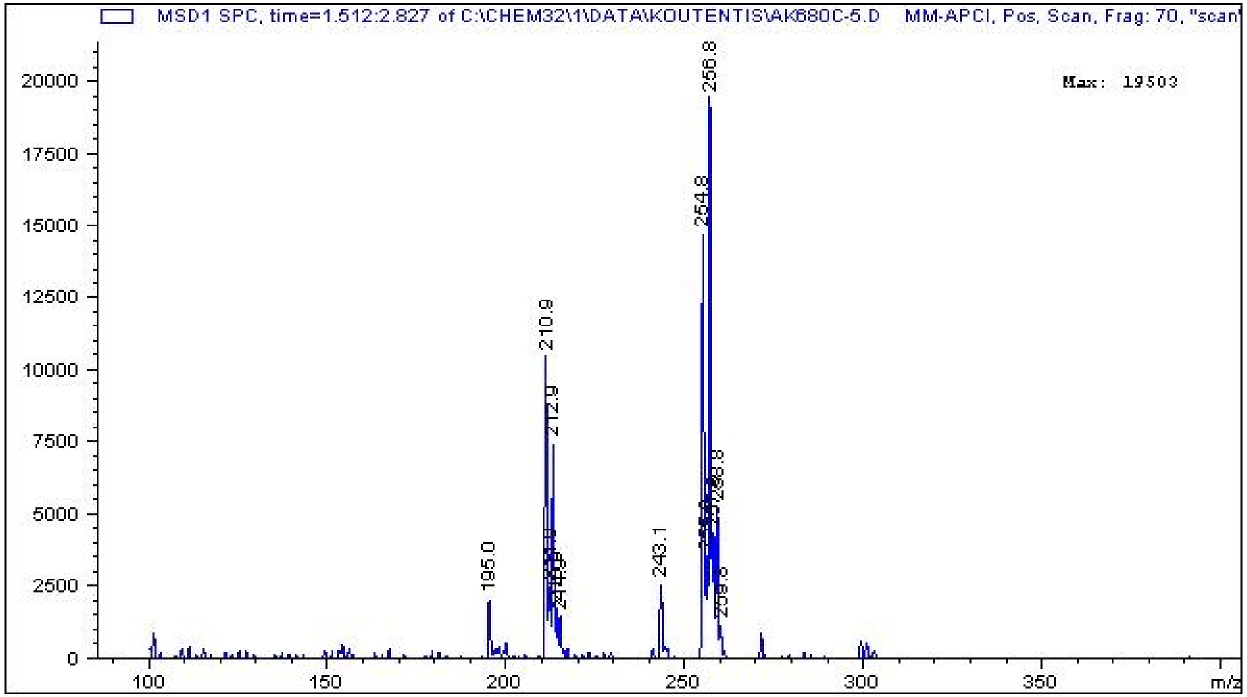
| PULPROG | jmod |
| TD | 65536 |
| SOLVENT | CDCl3 |
| NS | 1000 |
| DS | 4 |
| SWH | 29761.904 Hz |
| FIDRES | 0.454131 Hz |
| AQ | 1.1010048 sec |
| RG | 2050 |
| DW | 16.800 usec |
| DE | 6.50 usec |
| TE | 298.6 K |
| CNST2 | 145.0000000 |
| CNST11 | 1.0000000 |
| D1 | 6.00000000 sec |
| D20 | 0.00689655 sec |
| TD0 | 1 |
| ======== CHANNEL f1 ======== | |
| SFO1 | 125.7459782 MHz |
| NUC1 | 13C |
| P1 | 8.70 usec |
| P2 | 17.40 usec |
| PLW1 | 138.00000000 W |
| ======== CHANNEL f2 ======== | |
| SFO2 | 500.0350280 MHz |
| NUC2 | 1H |
| CPDPRG[2 | waltz16 |
| PCPD2 | 80.00 usec |
| PLW2 | 15.41699982 W |
| PLW12 | 0.33258000 W |
| F2 - Processing parameters | |
| SI | 32768 |
| SF | 125.7334172 MHz |
| WDW | EM |
| SSB | 0 |
| LB | 1.00 Hz |
| GB | 0 |
| PC | 1.40 |

### 4.5.1. Reaction of (*Z*)-2-bromo-2-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)acetonitrile (**21**) with benzyltriethylammonium chloride; Table 2, entry 2.

**Products:** mixture of tentatively 3-bromo-4-chloroisothiazole-5-carbonitrile (**27b**) and 3,4-dichloroisothiazole-5-carbonitrile (**8a**) (**27b**:**8a** = 3:1 by $^{13}$C NMR).



*m/z* (ESI-APCI+) 258.8 [**27b**, (M+H+MeOH+4)$^+$, 31%], 256.8 [**27b**, (M+H+MeOH+2)$^+$, 100%], 254.8 [**27b**, (MH+MeOH)$^+$, 75], 210.9 [**8a**, (M+H+MeOH+2)$^+$, 50%], 212.9 [**8a**, (M+H+MeOH)$^+$, 45]

# SECTION C

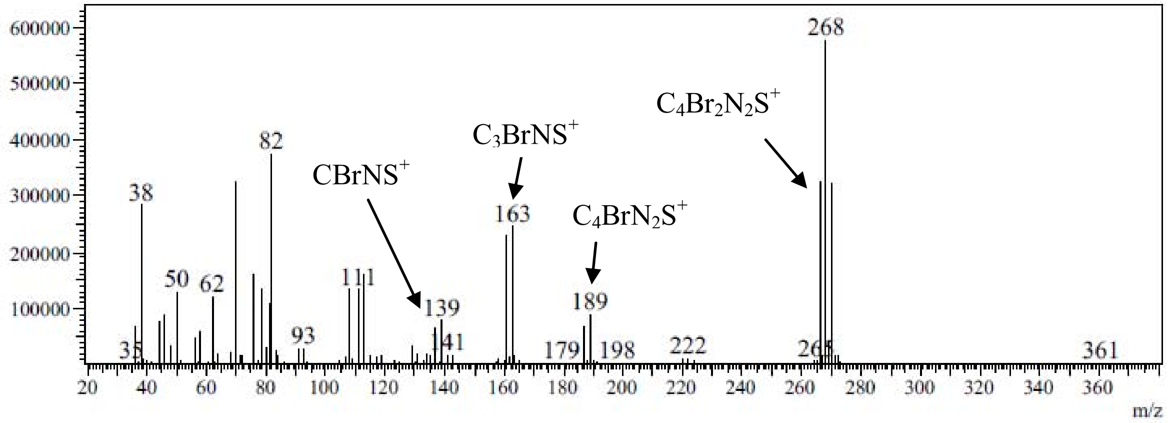
## Structure elucidation of 3-bromo-4-chloroisothiazole-5-carbonitrile (27b)

Reaction of 2-chloro-2-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)acetonitrile (**22**) with HBr in $Et_2O$, (Table 1, entry 9) gave an inseparable mixture of 3,4-dibromoisothiazole-5-carbonitrile (**8b**) and 3-bromo-4-chloroisothiazole-5-carbonitrile (**27b**) (88% overall yield, **8b**:**27b** = 1:3 by $^{13}C$ NMR). Since **8b** is a known compound, the peaks corresponding to **27b** in the $^{13}C$ NMR can be easily detected. The compound shows four quaternary carbon resonances at 139.3, 134.0, 130.4 and 108.0 ppm. The peak at 108.0 ppm is typical of a nitrile group, while the other three are similar to the isothiazole resonances of similar systems.

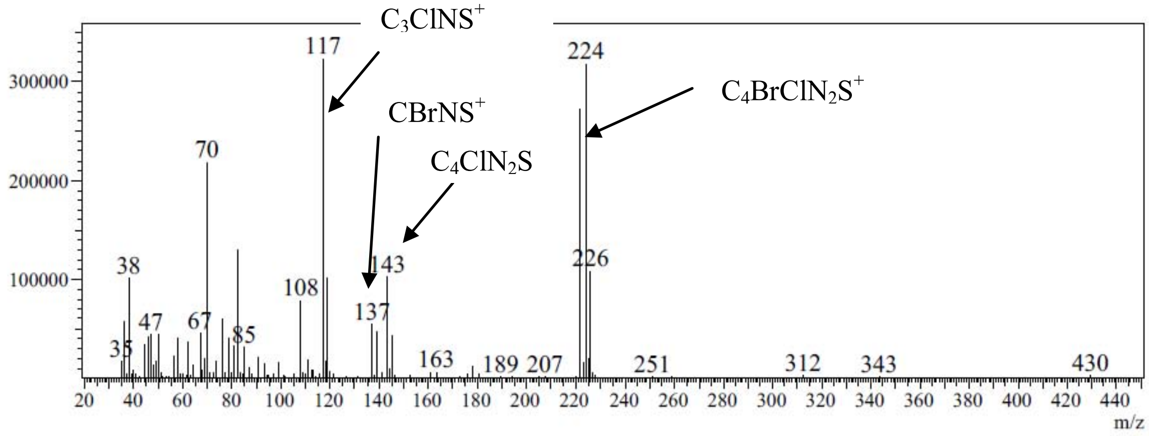
Analysis of pure **8b** be GC-MS showed a molecular ion peak at *m/z* 266 ($C_4Br_2N_2S$) with an isotope pattern corresponding to the presence of two bromine atoms. Three more fragments were identified at *m/z* 187, 161 and 137, all of them showing an isotope pattern corresponding to the presence of one bromine atom (Scheme S1). The fragment at *m/z* 187 presumably corresponds to the loss of one bromide from the isothiazole **8b**. The fragment at *m/z* 161 corresponds to $C_3BrNS$, therefore a tentative loss of cyanogen bromide, while the one at *m/z* 137 corresponds to CBrNS, by a tentative loss of 3-bromopropiolonitrile.

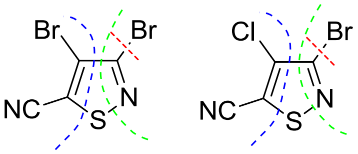
Analysis of the mixture of **8b** and **27b** obtained from the above reaction by GC-MS showed the separation of the two compounds by this technique (retention times 7.20 and 6.53 min, respectively). The major signal corresponded, as expected, to **27b** with a molecular ion peak at *m/z* 222 ($C_4BrClN_2S$) and an isotope pattern corresponding to the presence of one bromine and one chlorine atom. The compound showed a similar fragmentation pattern to **8b** giving three more fragments at *m/z* 143, 137 and 117. The fragment at *m/z* 137 showed an isotope pattern corresponding to one bromine atom and is tentatively the same fragment seen before in **8b** corresponding to CBrNS, by loss of 3-bromopropiolonitrile. The fragment at *m/z* 117 showed an isotope pattern of one chlorine atom and presumably corresponds to $C_3ClNS$ (Scheme S1) by loss of cyanogen bromide. Finally the fragment at *m/z* 143 showed an isotope pattern of one chlorine atom and presumable corresponds to the loss of one bromide from the isothiazole **27b**. These information supports the presence of a C-3 bromo and a C-4 chloro substituent and confirms the proposed structure for **27b**.

GC-MS of **8b**



GC-MS of **27b**





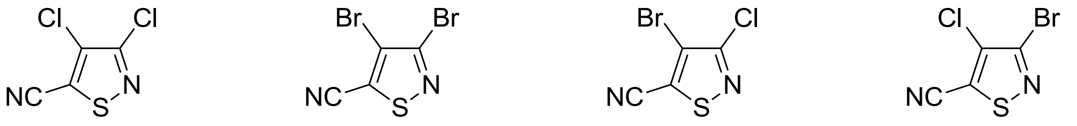
**8b** **27b**

**Scheme S1.** Tentative fragment analysis of mass spectra of compounds **8b** and **27b**.

## Identity of unknown compound

The reactions of (*Z*)-2-bromo-2-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)acetonitrile (**21**) with HCl, both in $Et_2O$ and in THF gave a mixture of four compounds (Table 1, entry 7 and 8), 3,4-dichloroisothiazole-5-carbonitrile (**8a**), 3,4-dibromoisothiazole-5-carbonitrile (**8b**), 3-bromo-4-chloroisothiazole-5-carbonitrile (**27b**) and an unknown compound.

Since the rest are previously observed compounds, the peaks corresponding to the **unknown** in the $^{13}$C NMR can be easily detected. The compound shows four quaternary carbon resonances at 151.9, 133.8, 118.2, 109.0 ppm. The peak at 109.0 ppm is typical of a nitrile group, while the other three are similar to the isothiazole resonances of similar systems. By comparison with the $^{13}$C NMR data of the known dihaloisothiazole-5-carbonitriles **8a**, **8b** and **27b** we very tentatively suspect that the unknown is 4-bromo-3-chloroisothiazole-5-carbonitrile (**27a**), however, in the absence sufficient data this assignment must remain highly speculative (Scheme S2). The formation of this product, however, is in agreement with our proposed mechanism (Scheme 10).



| **8a** | **8b** | **27a** | **27b** |
|---|---|---|---|
| **$^{13}$C NMR peaks (ppm)** | **$^{13}$C NMR peaks (ppm)** | **$^{13}$C NMR peaks (ppm)** | **$^{13}$C NMR peaks (ppm)** |
| 149.8 | 141.7 | 151.9 | 139.3 |
| 131.0 | 133.4 | 133.8 | 134.0 |
| 130.9 | 121.8 | 118.2 | 130.4 |
| 108.2 (nitrile) | 108.8 (nitrile) | 109.0 (nitrile) | 108.0 (nitrile) |

**Scheme S2**. Highly tentative structure assignment of unknown compound based on a comparison of $^{13}$C NMR data of known 3,4-dihaloisothiazole-5-carbonitriles.