Palladium (II)-catalyzed efficient synthesis of Wedelolactone and evaluation as potential tyrosinase inhibitor

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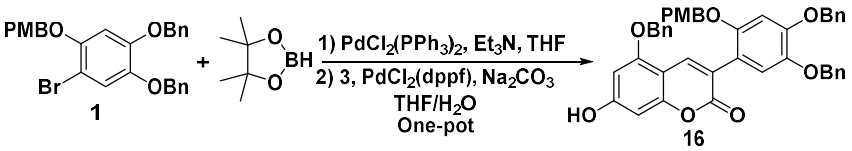
^{1}H NMR and ^{13}C NMR spectra of the products

Optimization of boronation/Suzuki-Miyaura reactions[a]



Entry	$n_1:n_3$[b]	$Pd(PPh_3)_2Cl_2$(mol%)	$Pd(dppf)Cl_2$(mol%)	THF(mL/mmol)	Yield[c] of **16** (%)
1	1.1	10	10	20	45
2	1.3	10	10	20	54
3	1.5	10	10	20	75
4	1.7	10	10	20	71
5	1.5	5	10	20	73
6	1.5	5	5	20	70
7	1.5	3	5	20	61
8[d]	1.5	5	5	20	42
9	1.5	5	5	10	72
10	1.5	5	5	5	62

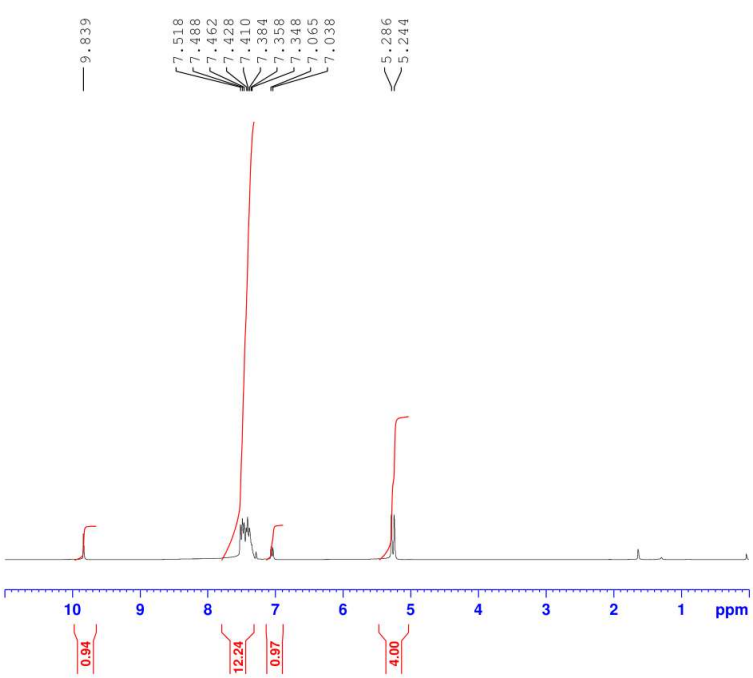
[a]Reaction conditions: **1** (1.0 mmol), pinacoborane (7.5 mmol), $Pd(PPh_3)_2Cl_2$, TEA (8.6 mmol), THF, under Ar atmosphere, stirred at 80 ℃ overnight; **3**, $Pd(dppf)Cl_2$, Na_2CO_3 (7 mmol), H_2O (2.5 mL/mmol), under Ar atmosphere, stirred at 90 ℃ for another 12 h.

[b]The ratio of bromide product **1** and bromocoumarin **3**.

[c]Isolated yield.

[d]Under air atmosphere.

^{1}H NMR and ^{13}C NMR spectra of the products

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PROCNO                  1

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TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              6009.615 Hz
FIDRES           0.183399 Hz
AQ              5.4525952 sec
RG                 158.58
DW                 83.200 usec
DE                  6.50 usec
TE                 296.1 K
D1             1.00000000 sec
TD0                     1
SFO1          300.1318533 MHz
NUC1                   1H
P1                 11.60 usec
PLW1          12.00000000 W

F2 - Processing parameters
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WDW                    EM
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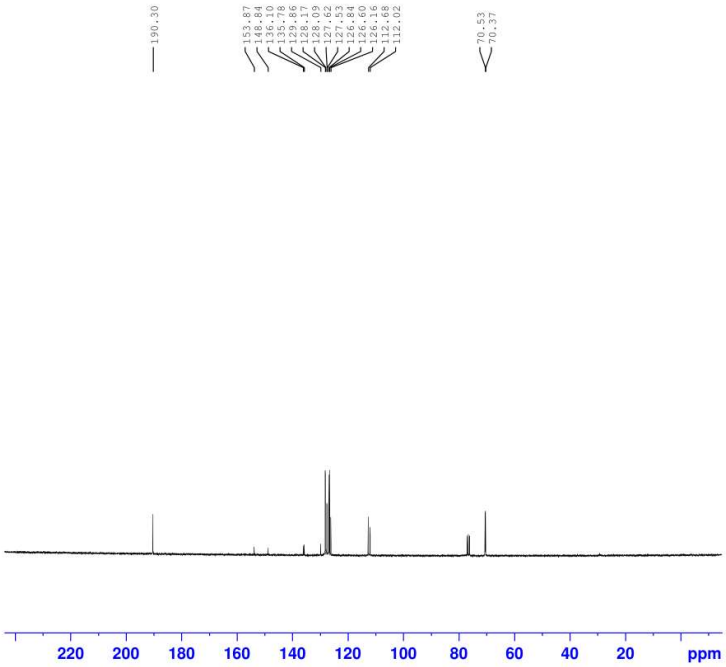
^{1}H NMR of **7**

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TD                  65536
SOLVENT             CDCl3
NS                    150
DS                      4
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FIDRES           0.298023 Hz
AQ              1.6777216 sec
RG                     64
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DE                  7.00 usec
TE                 300.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   13C
P1                 11.80 usec
PL1                 1.00 dB
PL1W          26.73651505 W
SFO1           75.4764278 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                   1H
PCPD2              80.00 usec
PL2                -1.00 dB
PL12               14.62 dB
PL2W          12.36450577 W
PL12W          0.33898211 W
SFO2          300.1312005 MHz

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LB                  1.00 Hz
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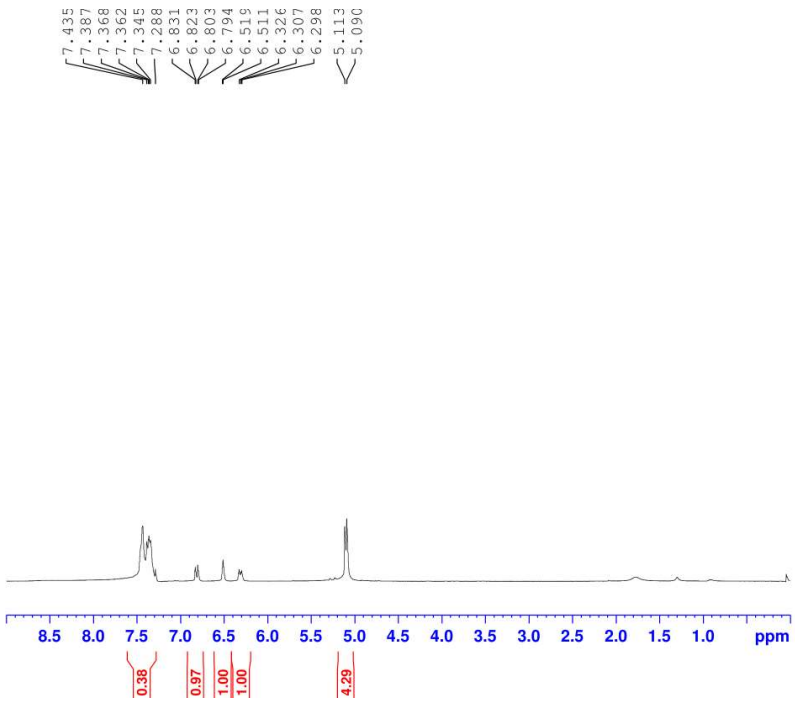
^{13}C NMR of **7**

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TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               6009.615 Hz
FIDRES            0.183399 Hz
AQ               5.4525952 sec
RG                  144.65
DW                  83.200 usec
DE                    6.50 usec
TE                   296.1 K
D1              1.00000000 sec
TD0                      1
SFO1           300.1318533 MHz
NUC1                    1H
P1                   11.60 usec
PLW1           12.00000000 W

F2 - Processing parameters
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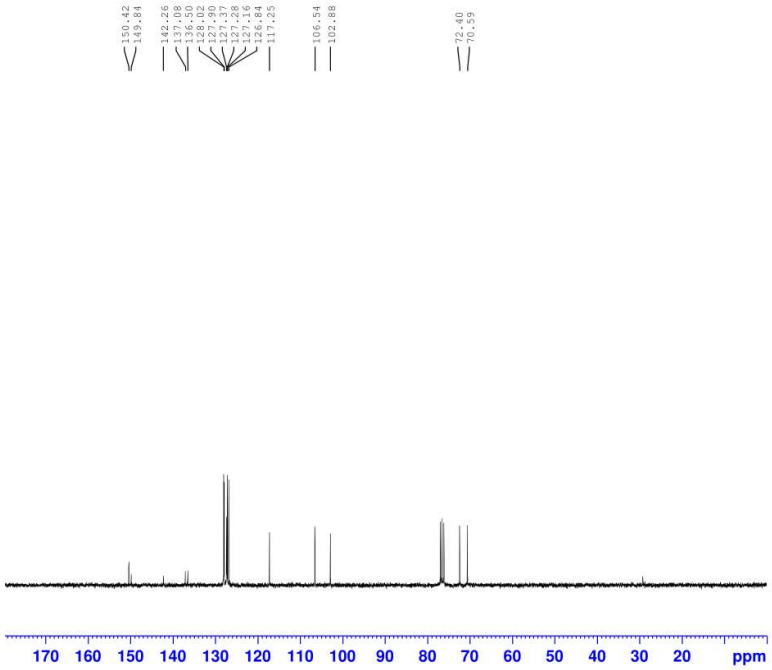
^{1}H NMR of **8**

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EXPNO                   1
PROCNO                  1

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TD                   65536
SOLVENT              CDCl3
NS                     201
DS                       4
SWH              19531.250 Hz
FIDRES            0.298023 Hz
AQ               1.6777216 sec
RG                      64
DW                  25.600 usec
DE                    7.00 usec
TE                   300.0 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    13C
P1                   11.80 usec
PL1                   1.00 dB
PL1W           26.73651505 W
SFO1            75.4764278 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                  -1.00 dB
PL12                 14.62 dB
PL2W           12.36450577 W
PL12W           0.33898211 W
SFO2           300.1312005 MHz

F2 - Processing parameters
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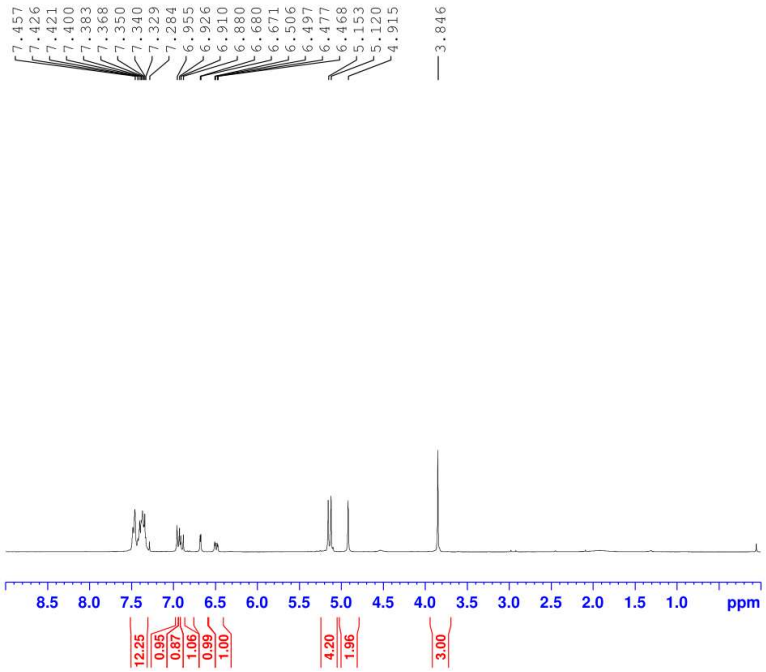
^{13}C NMR of **8**

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PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH               6009.615 Hz
FIDRES            0.183399 Hz
AQ               5.4525952 sec
RG                  128.61
DW                  83.200 usec
DE                    6.50 usec
TE                   296.5 K
D1              1.00000000 sec
TD0                     1
SFO1           300.1318533 MHz
NUC1                   1H
P1                   11.60 usec
PLW1           12.00000000 W

F2 - Processing parameters
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WDW                    no
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PC                    1.00
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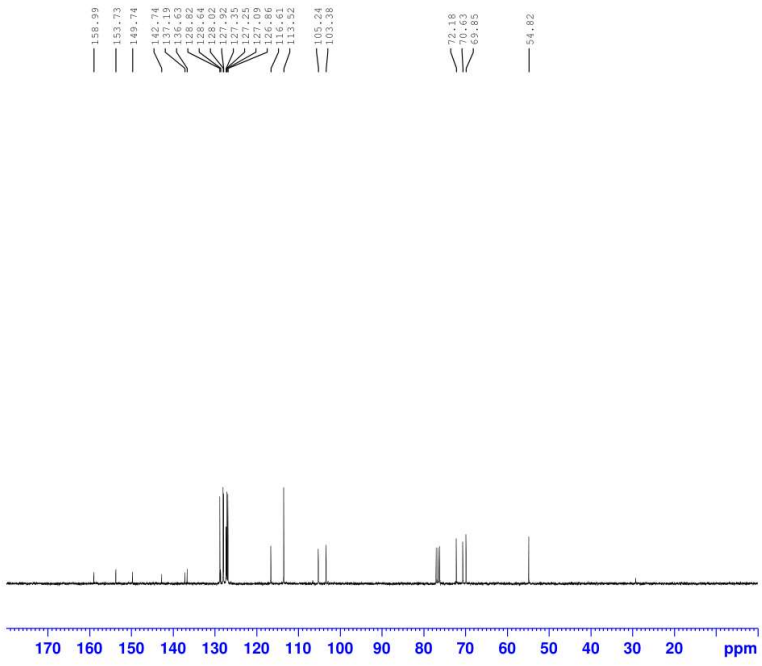
^{1}H NMR of **9**

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Current Data Parameters
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EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
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Time                 11.25
INSTRUM              spect
PROBHD   5 mm PADUL 13C
PULPROG              zgdc
TD                  65536
SOLVENT             CDCl3
NS                    167
DS                      4
SWH              19531.250 Hz
FIDRES            0.298023 Hz
AQ               1.6777216 sec
RG                     64
DW                  25.600 usec
DE                    7.00 usec
TE                   300.0 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   13C
P1                   11.80 usec
PL1                   1.00 dB
PL1W           26.73651505 W
SFO1            75.4764278 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                   1H
PCPD2                80.00 usec
PL2                  -1.00 dB
PL12                 14.62 dB
PL2W           12.36450577 W
PL12W           0.33898211 W
SFO2           300.1312005 MHz

F2 - Processing parameters
SI                  32768
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WDW                    EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.40
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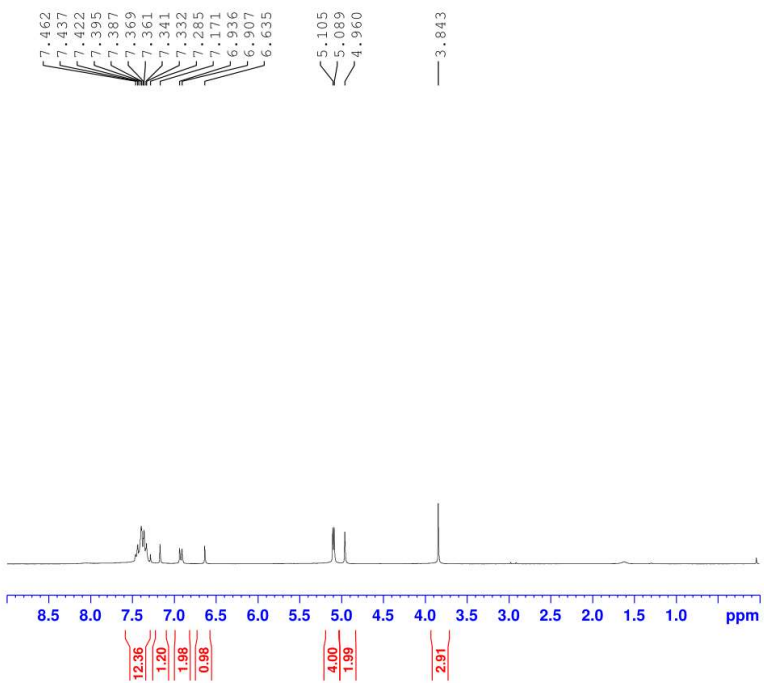
^{13}C NMR of **9**

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INSTRUM           spect
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PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            6009.615 Hz
FIDRES         0.183399 Hz
AQ             5.4525952 sec
RG               158.58
DW               83.200 usec
DE                 6.50 usec
TE                296.3 K
D1            1.00000000 sec
TD0                    1
SFO1        300.1318533 MHz
NUC1                  1H
P1                11.60 usec
PLW1        12.00000000 W

F2 - Processing parameters
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WDW                   no
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LB       0 Hz
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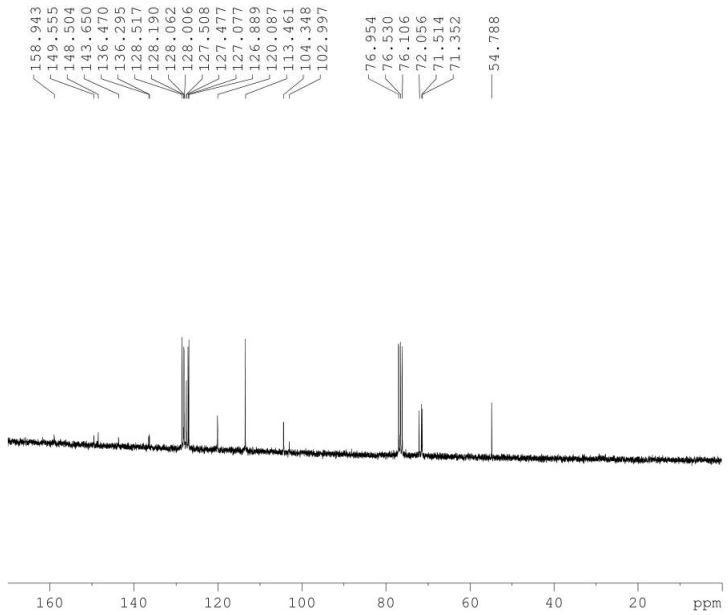
PC                  1.00
```

^{1}H NMR of **1**

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EXPNO                   1
PROCNO                  1

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INSTRUM           spect
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PULPROG             zgdc
TD                 65536
SOLVENT            CDCl3
NS                    256
DS                      4
SWH           19531.250 Hz
FIDRES         0.298023 Hz
AQ            1.6777216 sec
RG                     64
DW               25.600 usec
DE                 7.00 usec
TE                300.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                11.80 usec
PL1                1.00 dB
PL1W        26.73651505 W
SFO1         75.4764278 MHz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             80.00 usec
PL2               -1.00 dB
PL12              14.62 dB
PL2W        12.36450577 W
PL12W        0.33898211 W
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF           75.4677867 MHz
WDW                   EM
SSB      0
LB                 1.00 Hz
GB       0
PC                  1.40
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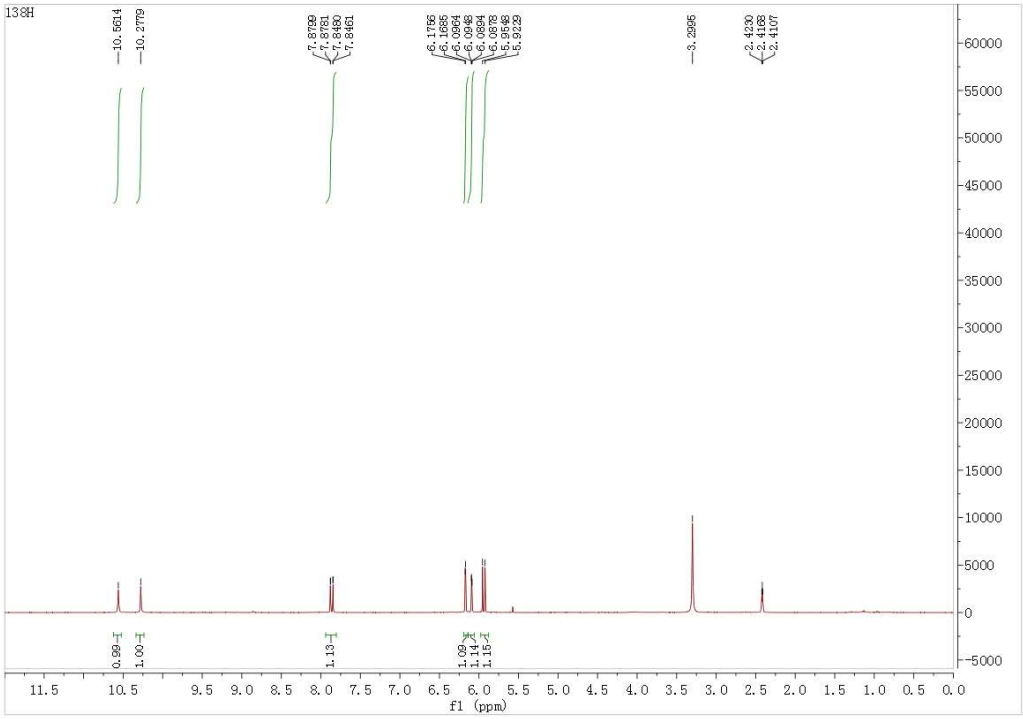
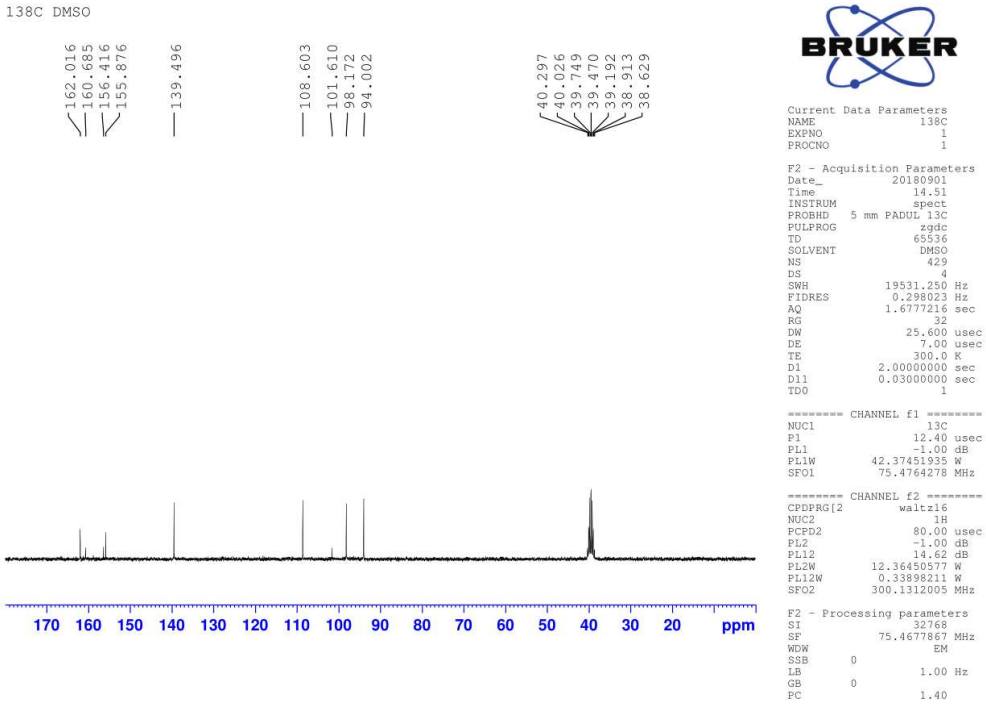
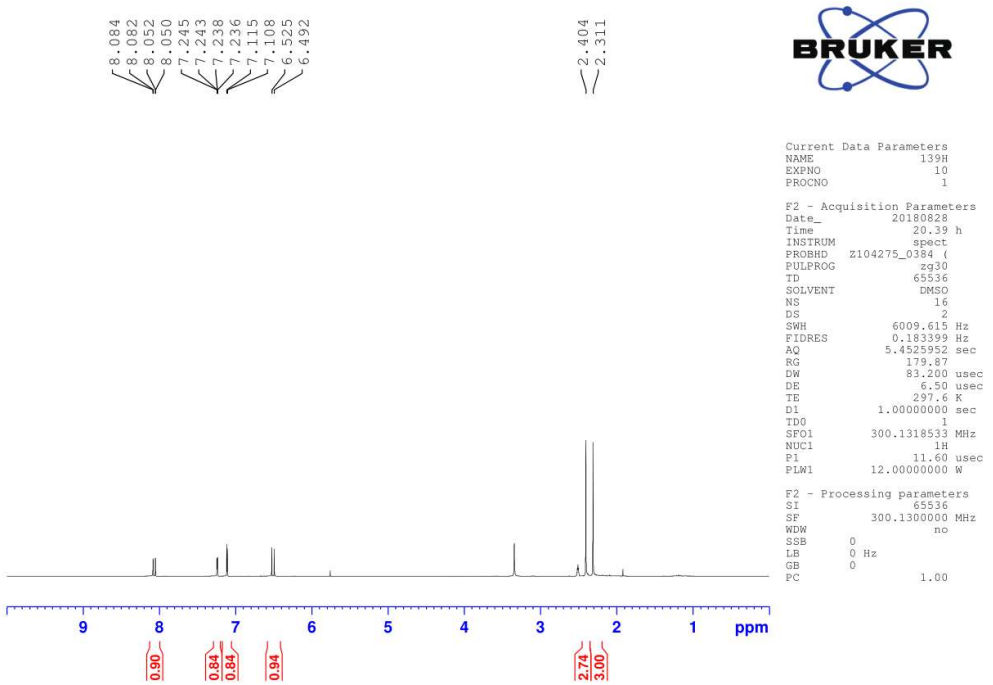
^{13}C NMR of **1**



^{1}H NMR of **11**



^{13}C NMR of **11**



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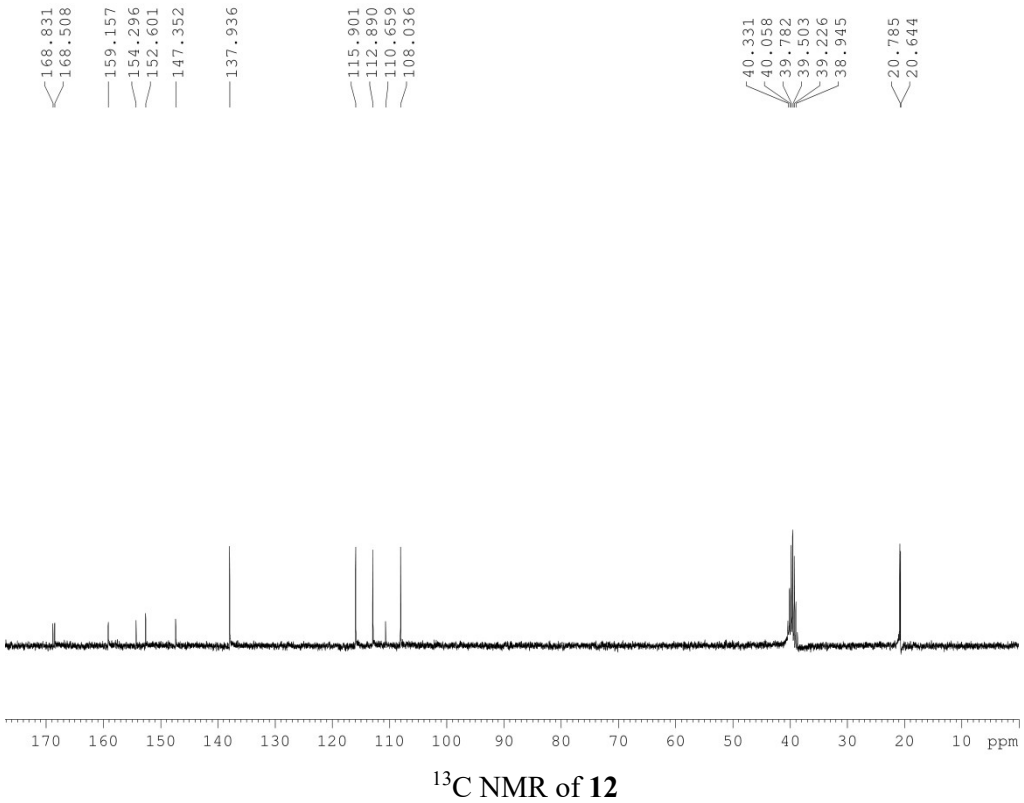
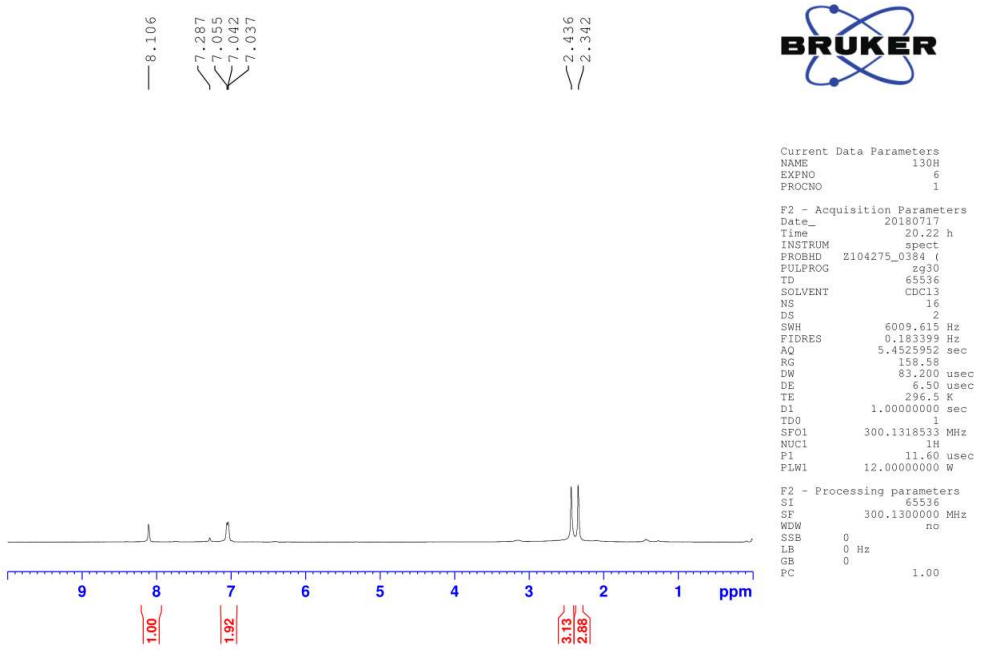


^{13}C NMR of **12**

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EXPNO                   6
PROCNO                  1

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PULPROG              zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               6009.615 Hz
FIDRES            0.183399 Hz
AQ               5.4525952 sec
RG                  158.58
DW                  83.200 usec
DE                    6.50 usec
TE                   296.5 K
D1              1.00000000 sec
TD0                      1
SFO1           300.1318533 MHz
NUC1                    1H
P1                   11.60 usec
PLW1           12.00000000 W

F2 - Processing parameters
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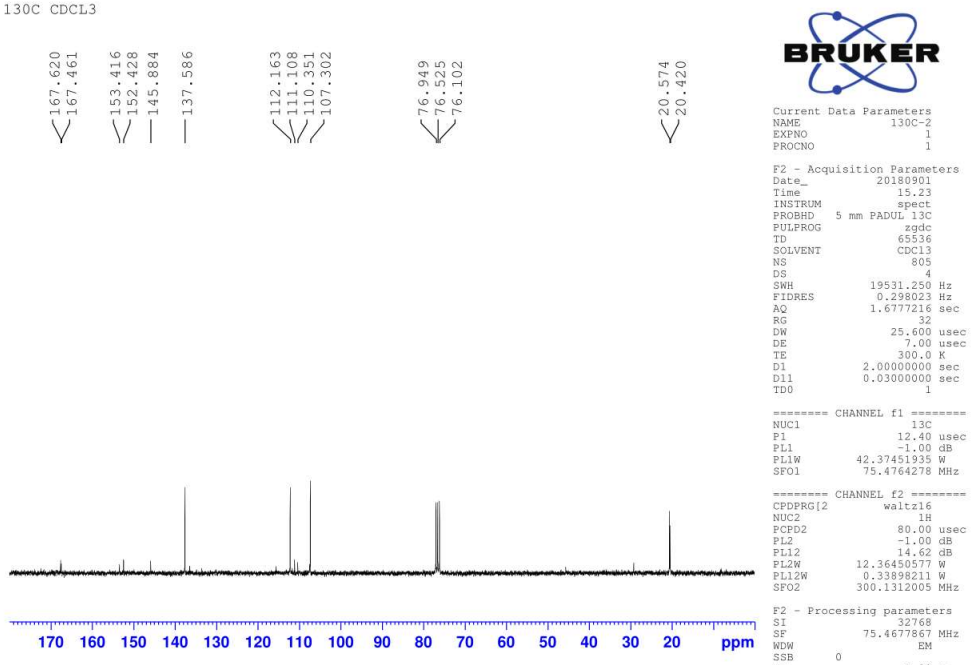
WDW                     no
SSB       0
LB        0 Hz
GB        0
PC                    1.00
```

^{1}H NMR of **13**

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PROCNO                  1

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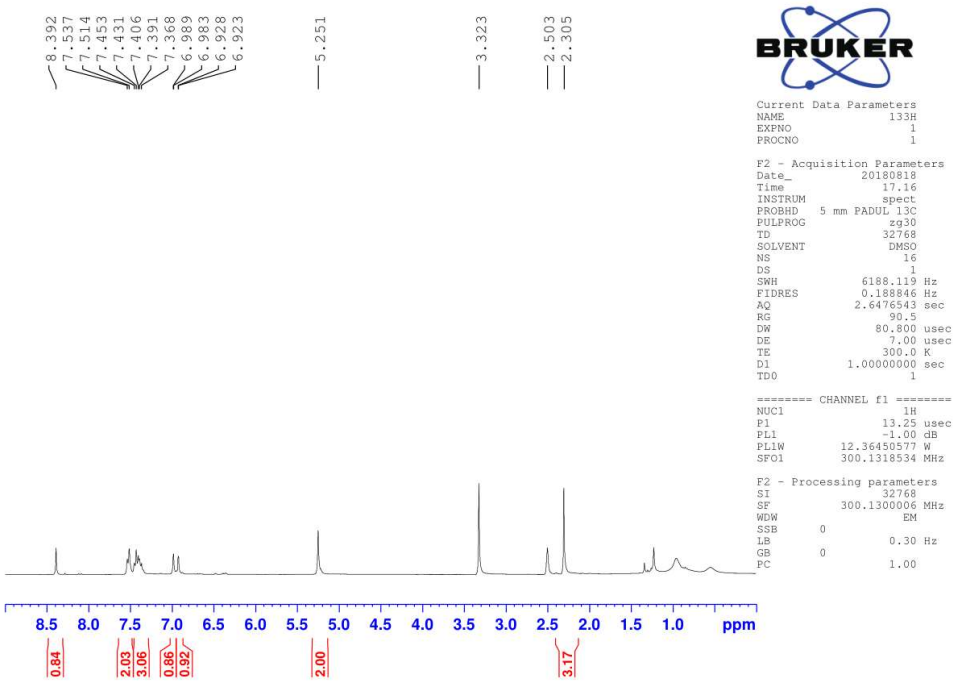
PROBHD    5 mm PADUL 13C
PULPROG              zgdc
TD                   65536
SOLVENT              CDCl3
NS                     805
DS                       4
SWH              19531.250 Hz
FIDRES            0.298023 Hz
AQ               1.6777216 sec
RG                      32
DW                  25.600 usec
DE                    7.00 usec
TE                   300.0 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    13C
P1                    12.40 usec
PL1                   -1.00 dB
PL1W           42.37451935 W
SFO1            75.4764278 MHz

======== CHANNEL f2 ========
CPDPRG[2             waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                   -1.00 dB
PL12                  14.62 dB
PL2W           12.36450577 W
PL12W           0.33898211 W
SFO2           300.1312005 MHz

F2 - Processing parameters
SI                   32768
SF             75.4677867 MHz
WDW                     EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.40
```

^{13}C NMR of **13**

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EXPNO                   1
PROCNO                  1

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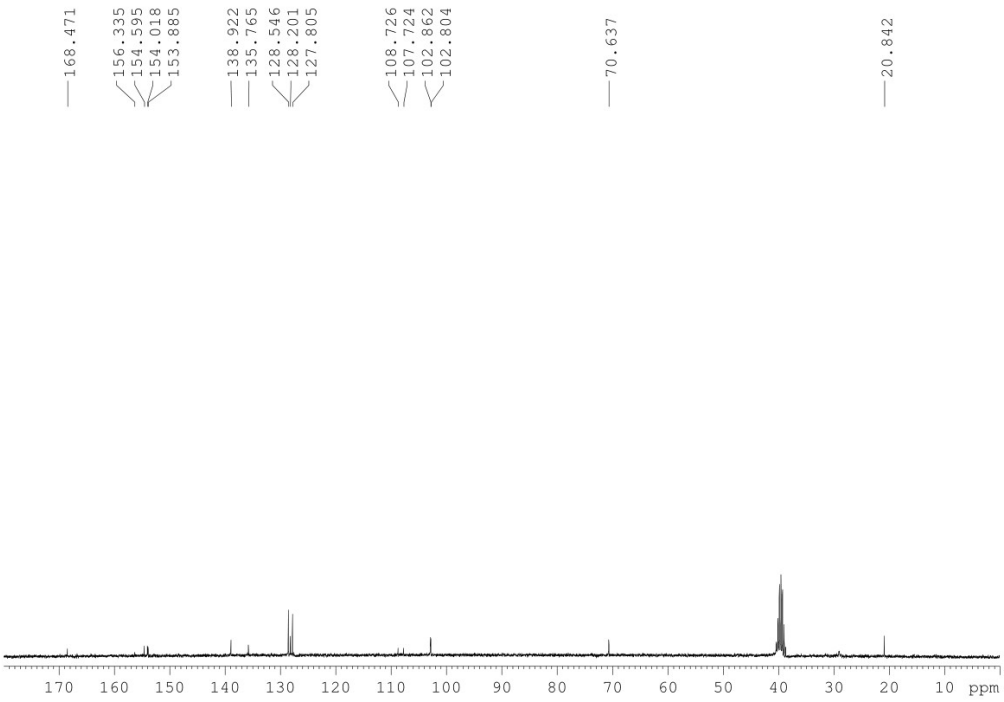
INSTRUM            spect
PROBHD   5 mm PADUL 13C
PULPROG             zg30
TD                 32768
SOLVENT             DMSO
NS                     16
DS                      1
SWH            6188.119 Hz
FIDRES         0.188846 Hz
AQ           2.6476543 sec
RG                  90.5
DW               80.800 usec
DE                 7.00 usec
TE                300.0 K
D1          1.00000000 sec
TD0                     1

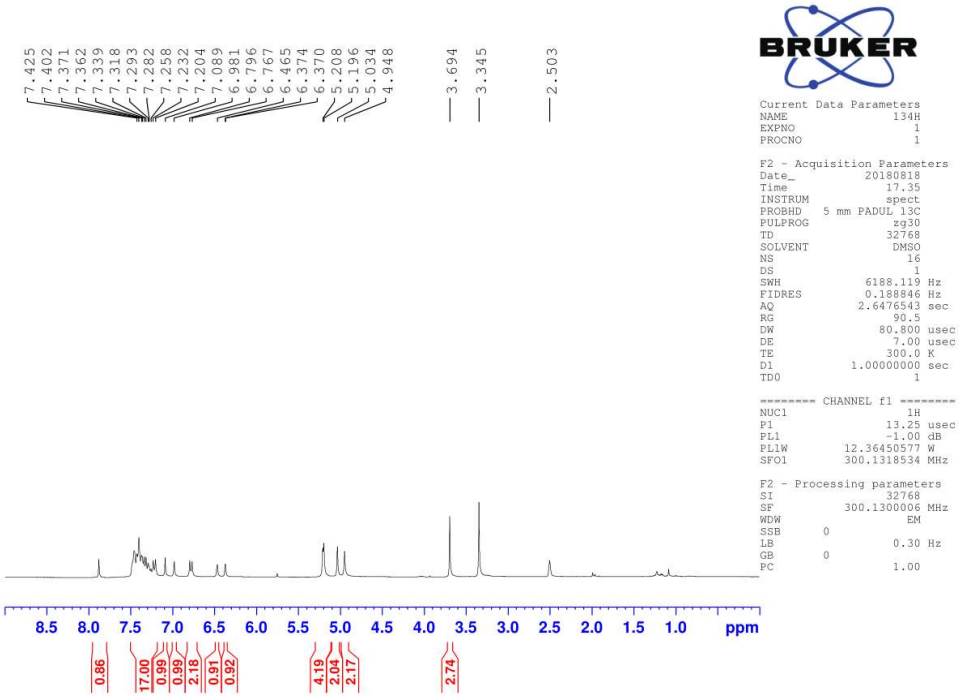
======== CHANNEL f1 =======
NUC1                   1H
P1                  13.25 usec
PL1                 -1.00 dB
PL1W        12.36450577 W
SFO1       300.1318534 MHz

F2 - Processing parameters
SI                  32768
SF          300.1300006 MHz
WDW                    EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

^{1}H NMR of **3**



^{13}C NMR of **3**



Current Data Parameters
NAME 134H
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PROCNO 1

F2 - Acquisition Parameters
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Time 17.35
INSTRUM spect
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PULPROG zg30
TD 32768
SOLVENT DMSO
NS 16
DS 1
SWH 6188.119 Hz
FIDRES 0.188846 Hz
AQ 2.6476543 sec
RG 90.5
DW 80.800 usec
DE 7.00 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 13.25 usec
PL1 -1.00 dB
PL1W 12.36450577 W
SFO1 300.1318534 MHz

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WDW EM
SSB 0
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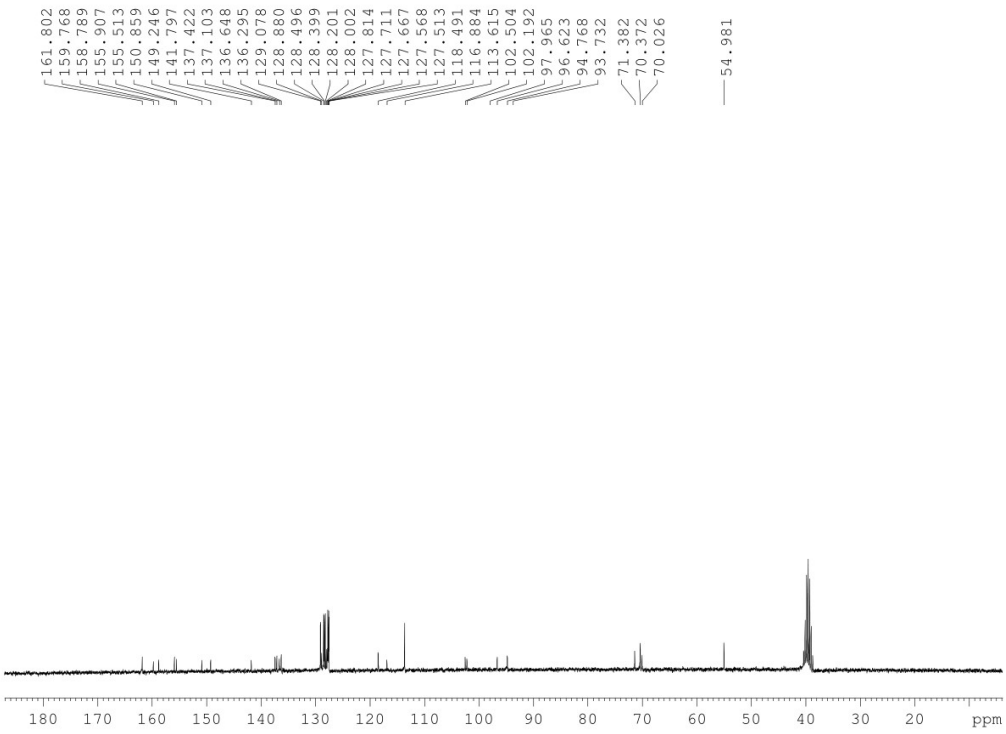
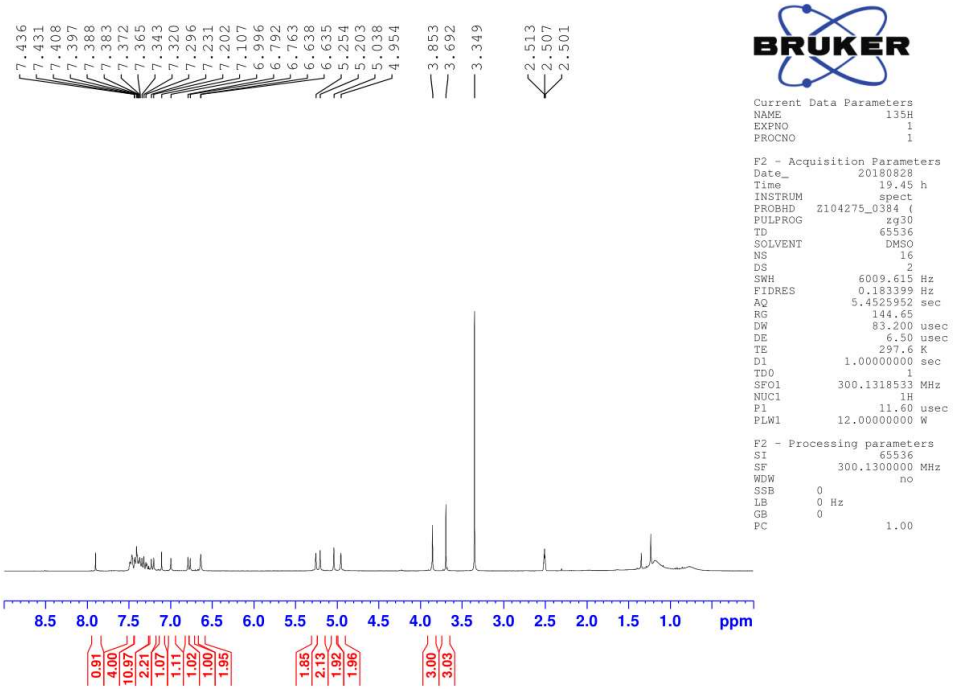
^{1}H NMR of **16**



^{13}C NMR of **16**



BRUKER

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EXPNO                   1
PROCNO                  1

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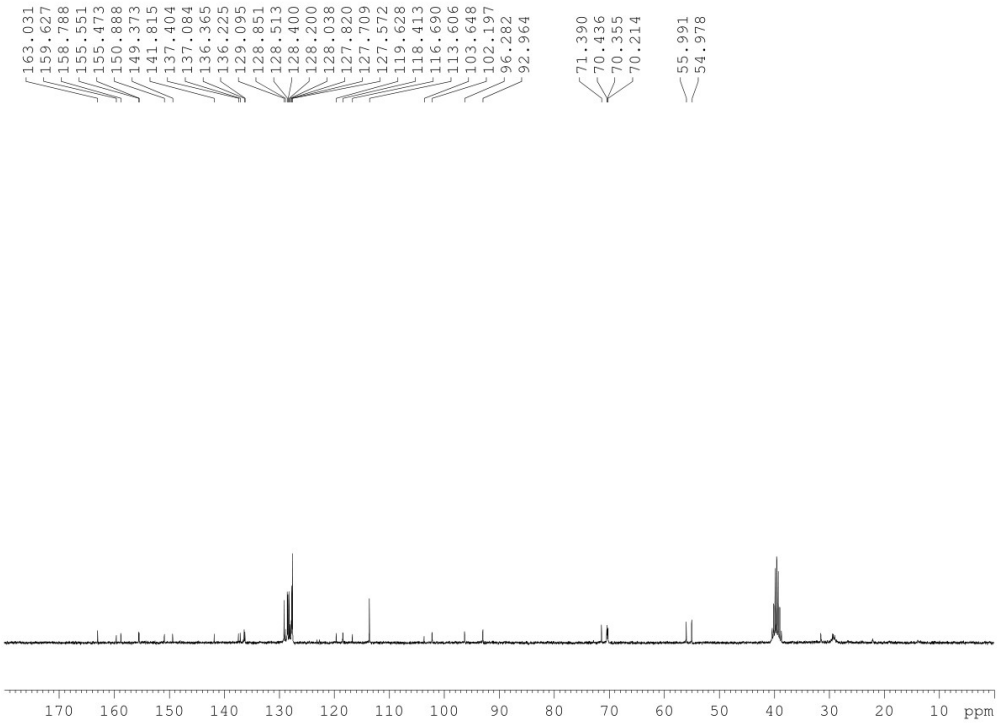
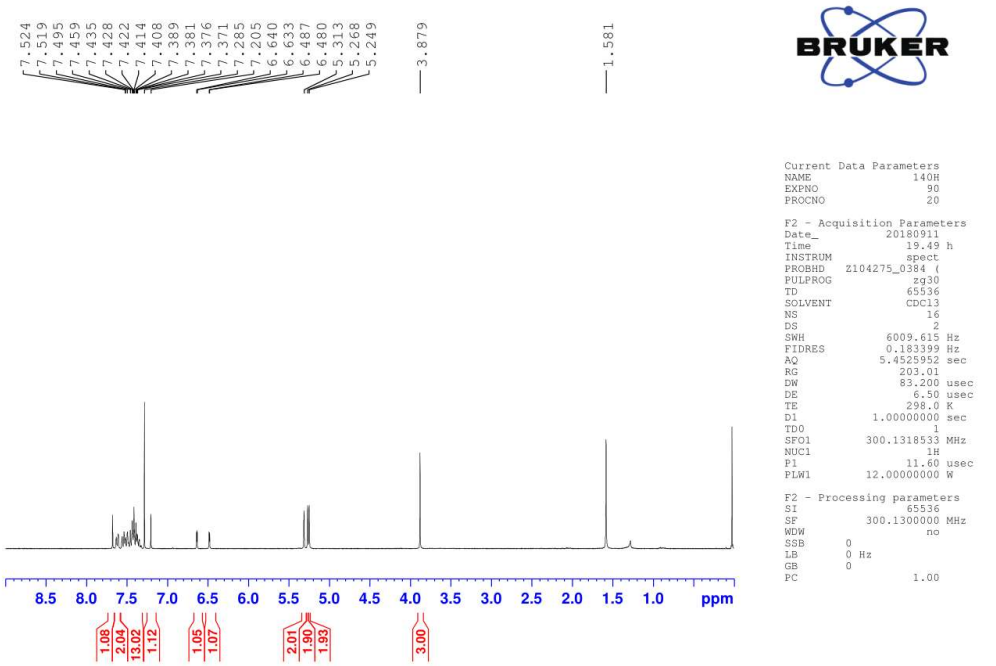
PULPROG               zg30
TD                   65536
SOLVENT               DMSO
NS                      16
DS                       2
SWH               6009.615 Hz
FIDRES            0.183399 Hz
AQ               5.4525952 sec
RG                  144.65
DW                  83.200 usec
DE                    6.50 usec
TE                   297.6 K
D1              1.00000000 sec
TD0                      1
SFO1           300.1318533 MHz
NUC1                    1H
P1                   11.60 usec
PLW1           12.00000000 W

F2 - Processing parameters
SI                   65536
SF             300.1300000 MHz
WDW                     no
SSB       0
LB        0 Hz
GB        0
PC                    1.00
```

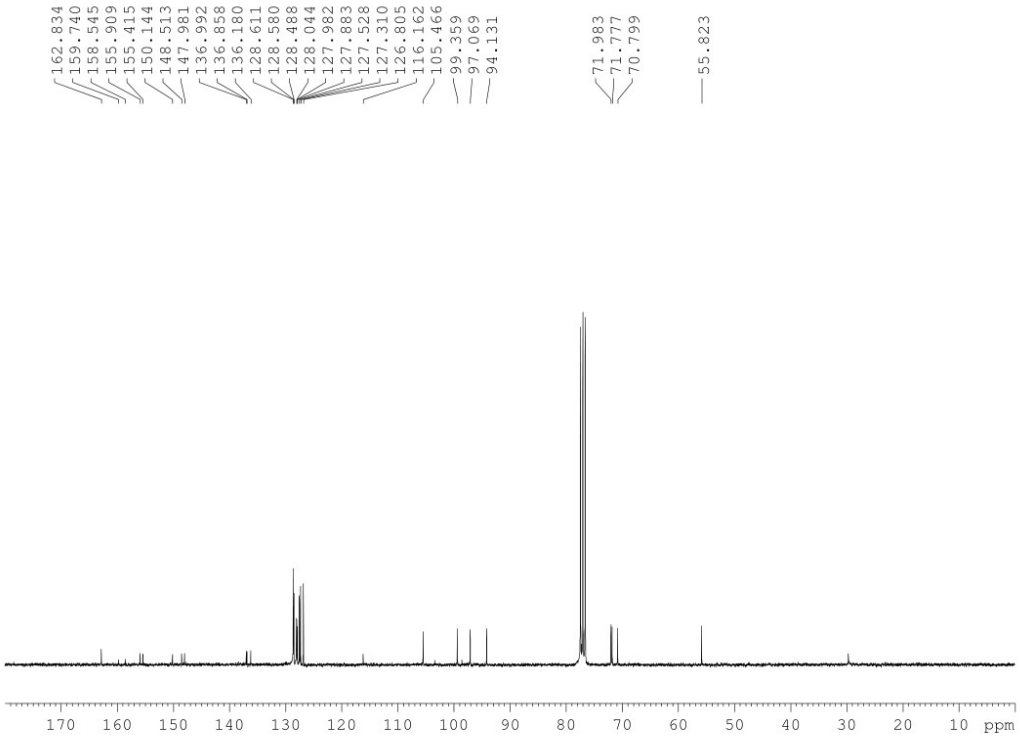
^{1}H NMR of **4**



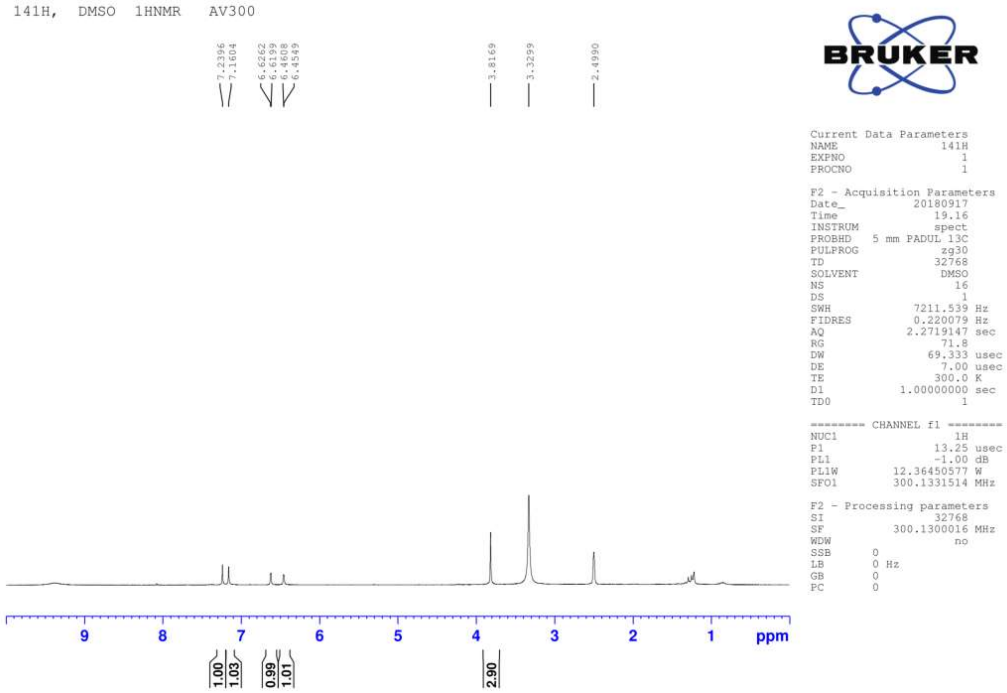
^{13}C NMR of **4**



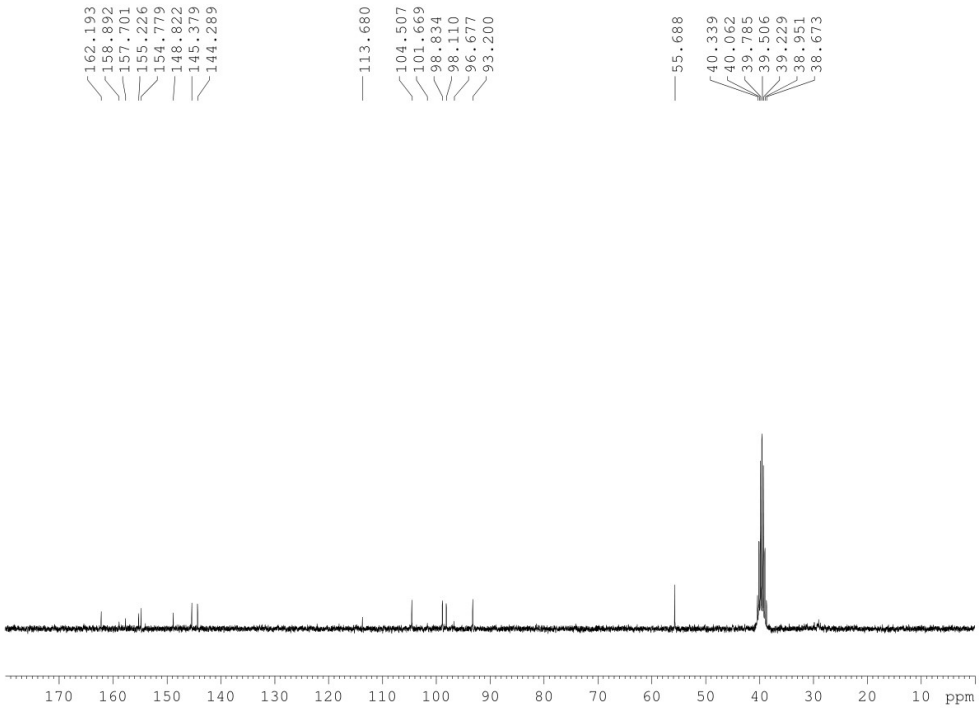
^{1}H NMR of **17**



^{13}C NMR of **17**



^{1}H NMR of **5**



^{13}C NMR of **5**