Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Electronic Supplementary Information

Lewis acid triggered *N*-alkylation of sulfoximines through nucleophilic ring-opening of donor-acceptor cyclopropanes: synthesis of γ-sulfoximino malonic diesters

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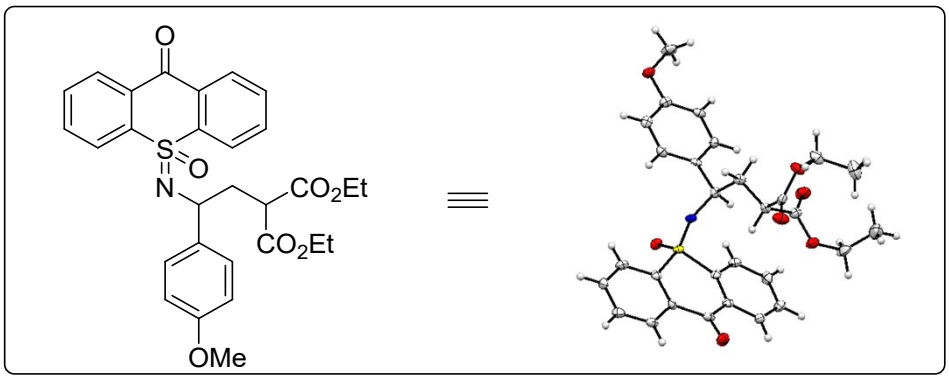
1. X-Ray crystallography data of compound (3q)

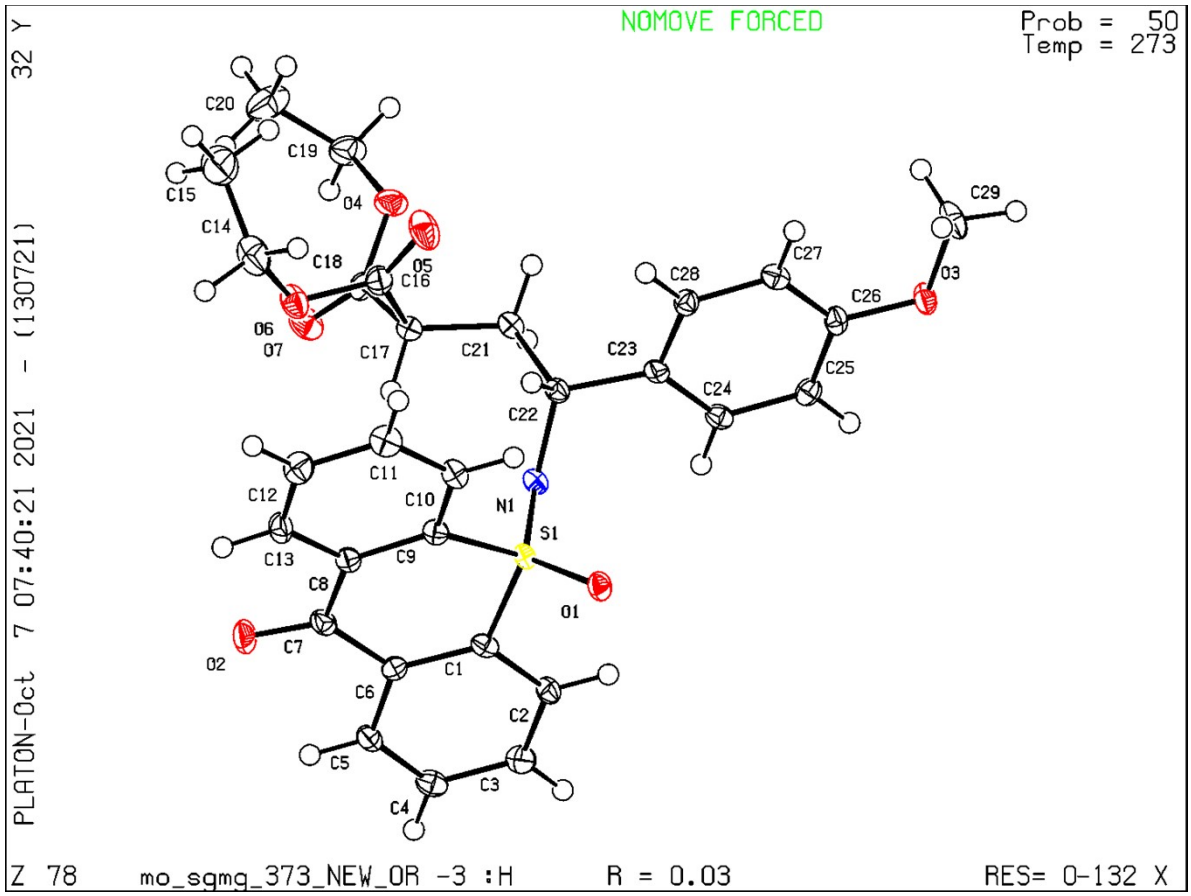


(CCDC Deposition No.- 2114333)

Single-crystal diffraction analysis data were collected at 100 K with a BRUKER KAPPA APEX II CCD Duo diffractometer (operated at 1500 W power: 50 kV, 30 mA) using graphite monochromatic Mo Kα radiation (λ = 0.71073 Å). In case of disordered solvent molecules, the contributions to the scattering arising from the disordered solvents in the crystal were removed by use of the utility SQUEEZE in the PLATON software package.

Sample preparation method for crystal growth

The 10 mg compound (**3q**) was taken in a 2 ml glass vial, 1ml Methanol solvent was added, and the vail was closed with the cotton plug. Kept it for 4 to 5 days for growing of crystal. Slow evaporation at room temperature in a dark place till crystals formed.



The thermal ellipsoid was drawn at the 50% probability level

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) mo_sgmg_373_NEW_0m_a

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: mo_sgmg_373_NEW_0m_a

```
Bond precision:   C-C = 0.0032 A          Wavelength=0.71073

Cell:              a=41.083(6)      b=41.083(6)      c=8.1322(10)
                   alpha=90         beta=90          gamma=120
Temperature:       273 K

                 Calculated                Reported
Volume           11887(4)                  11887(4)
Space group      R -3                      R -3 :H
Hall group       -R 3                      -R 3
Moiety formula   C29 H29 N O7 S            ?
Sum formula      C29 H29 N O7 S            C29 H29 N O7 S
Mr               535.59                    535.59
Dx,g cm-3        1.347                     1.347
Z                18                        18
Mu (mm-1)        0.171                     0.171
F000             5076.0                    5076.0
F000'            5080.79
h,k,lmax         45,45,9                   45,45,9
Nref             3839                      3835
Tmin,Tmax        0.950,0.966
Tmin'            0.950

Correction method= Not given

Data completeness= 0.999           Theta(max)= 23.363

R(reflections)= 0.0323( 3390)                    wR2(reflections)=
                                                 0.0742( 3835)
S = 0.603                Npar= 347
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2. HPLC Data

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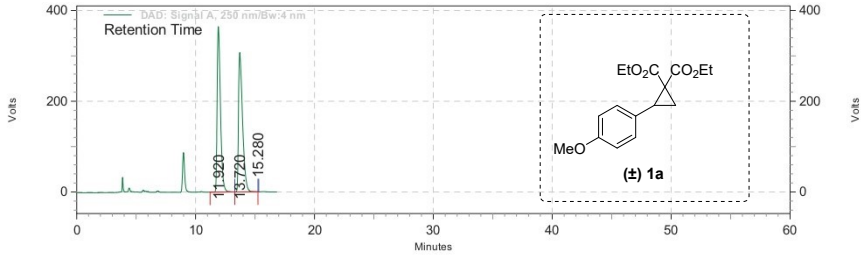

DAD: Signal A,
250 nm/Bw:4 nm
Results

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13.720	15276360	50.70	643785	45.72
15.280	83	0.00	26	0.00
Totals	30128601	100.00	1408058	100.00

2) HPLC of Chiral (1a)

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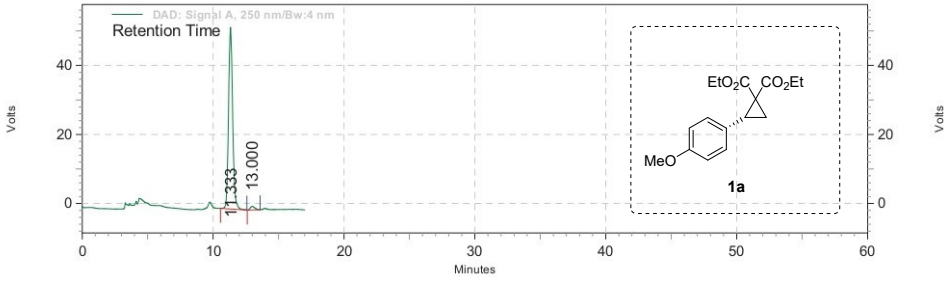

DAD: Signal A,
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Results

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HPLC of (3a)

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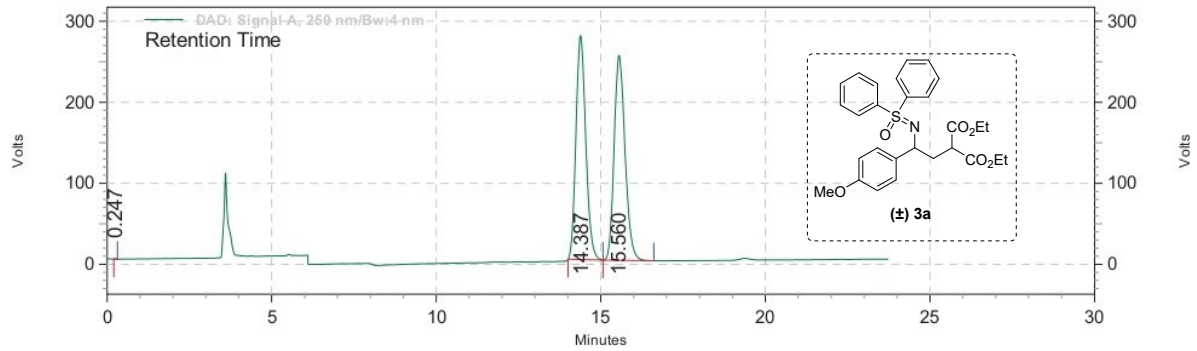

DAD: Signal A,
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Results

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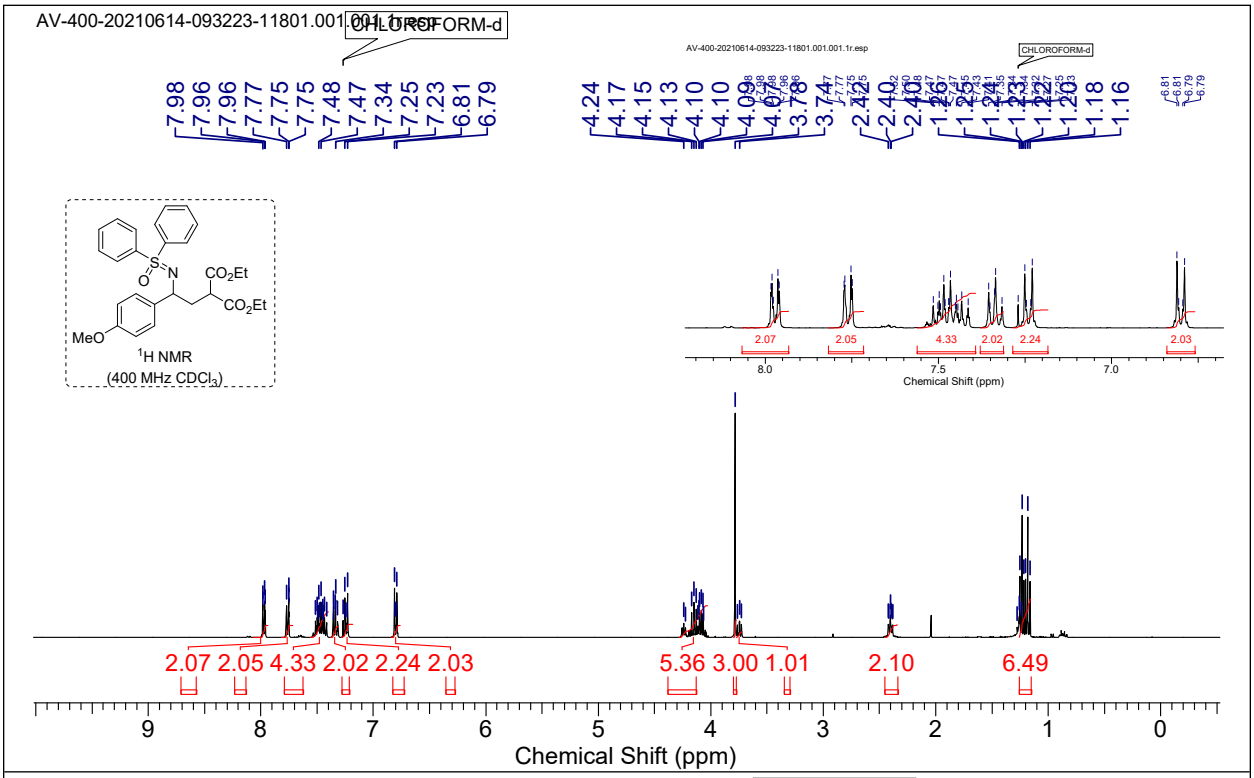
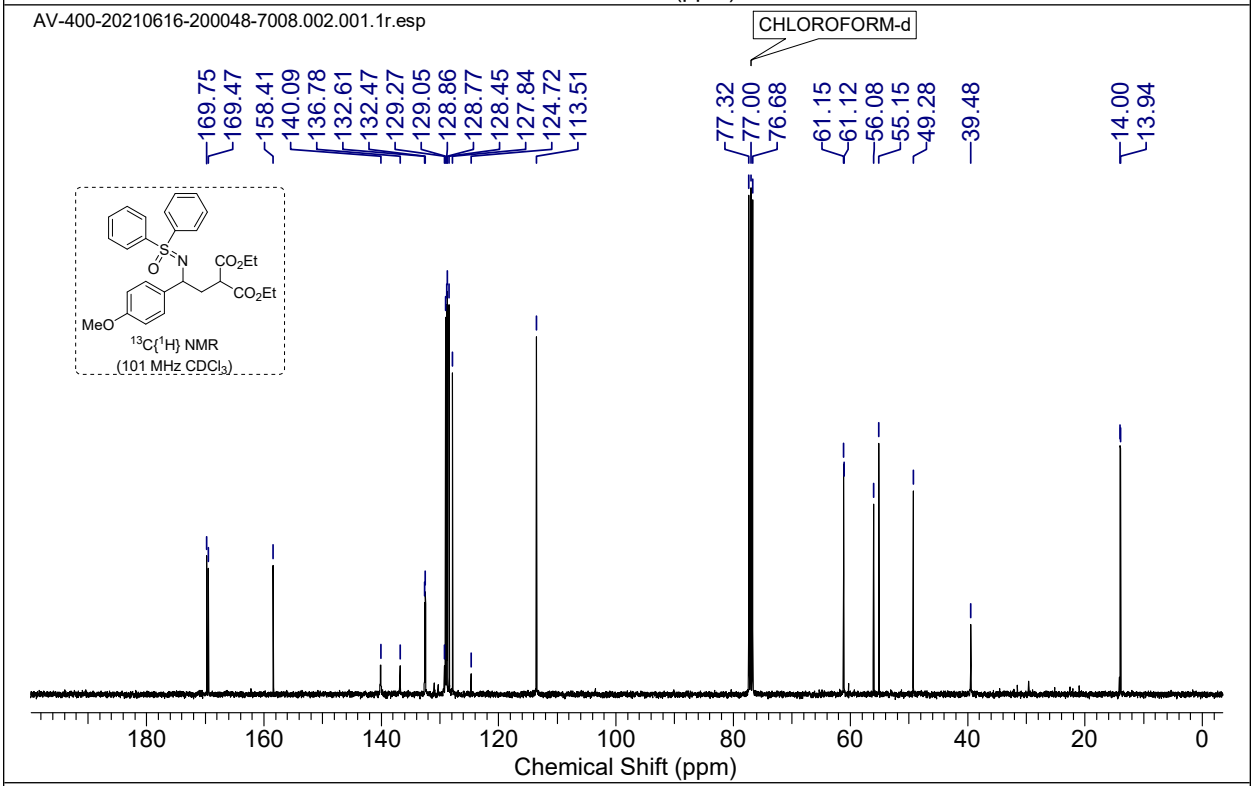
14.387	12060902	49.59	578977	52.14
15.560	12256585	50.40	530080	47.74

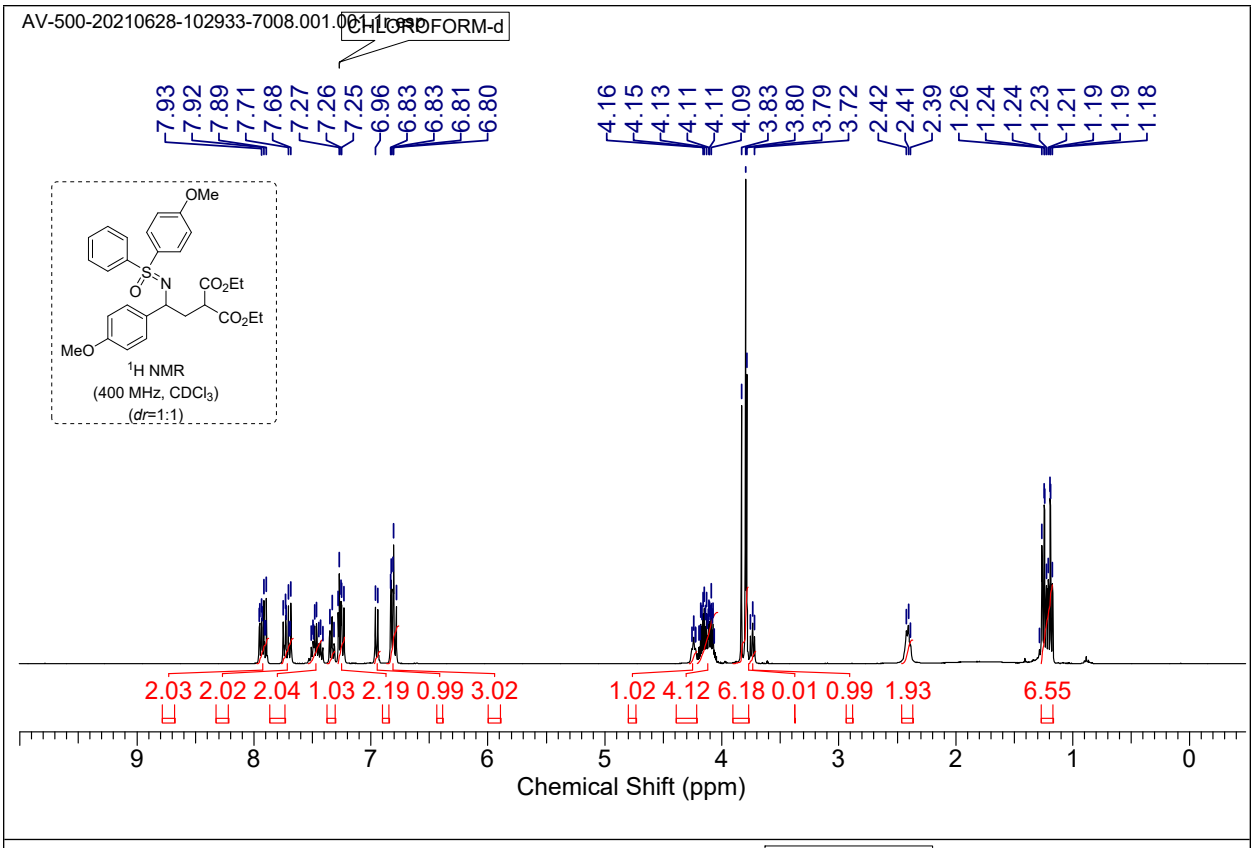
Totals	24320606	100.00	1110364	100.00

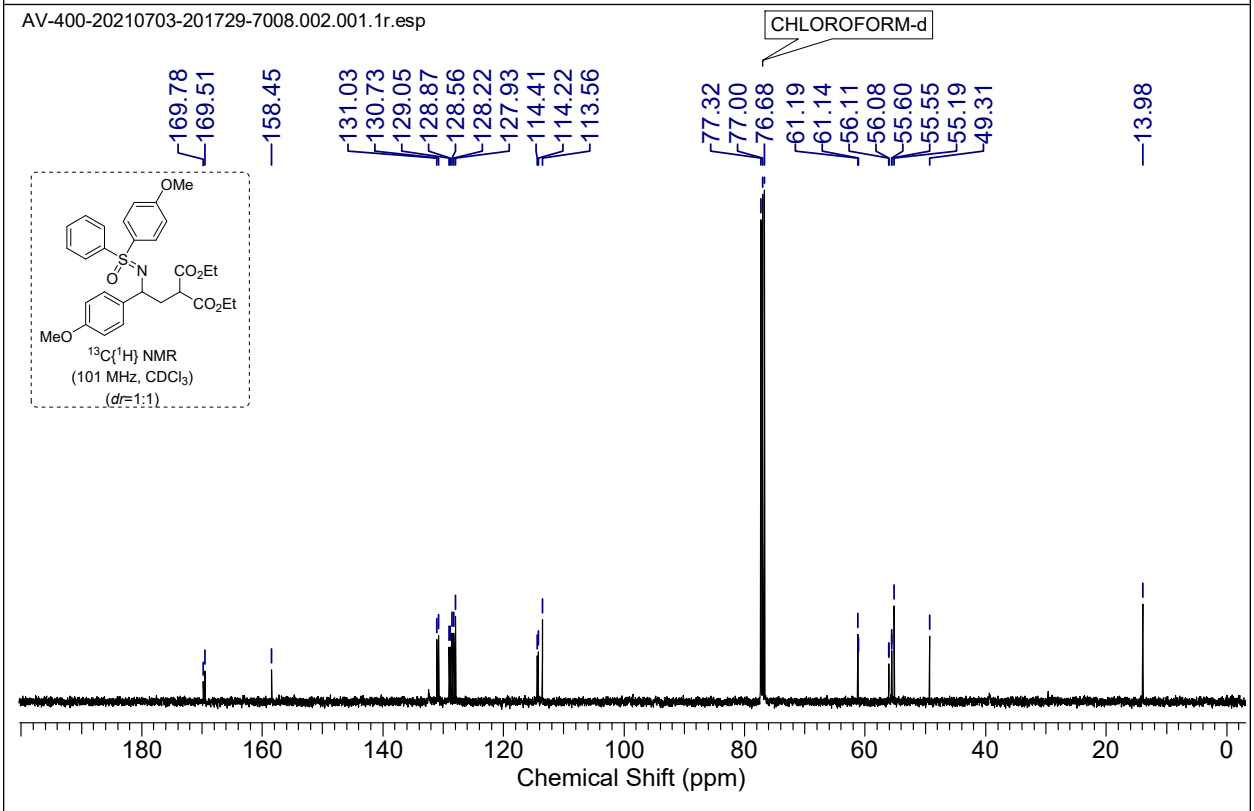
3. ^{1}H, ^{13}C, and ^{19}F NMR Spectra of products





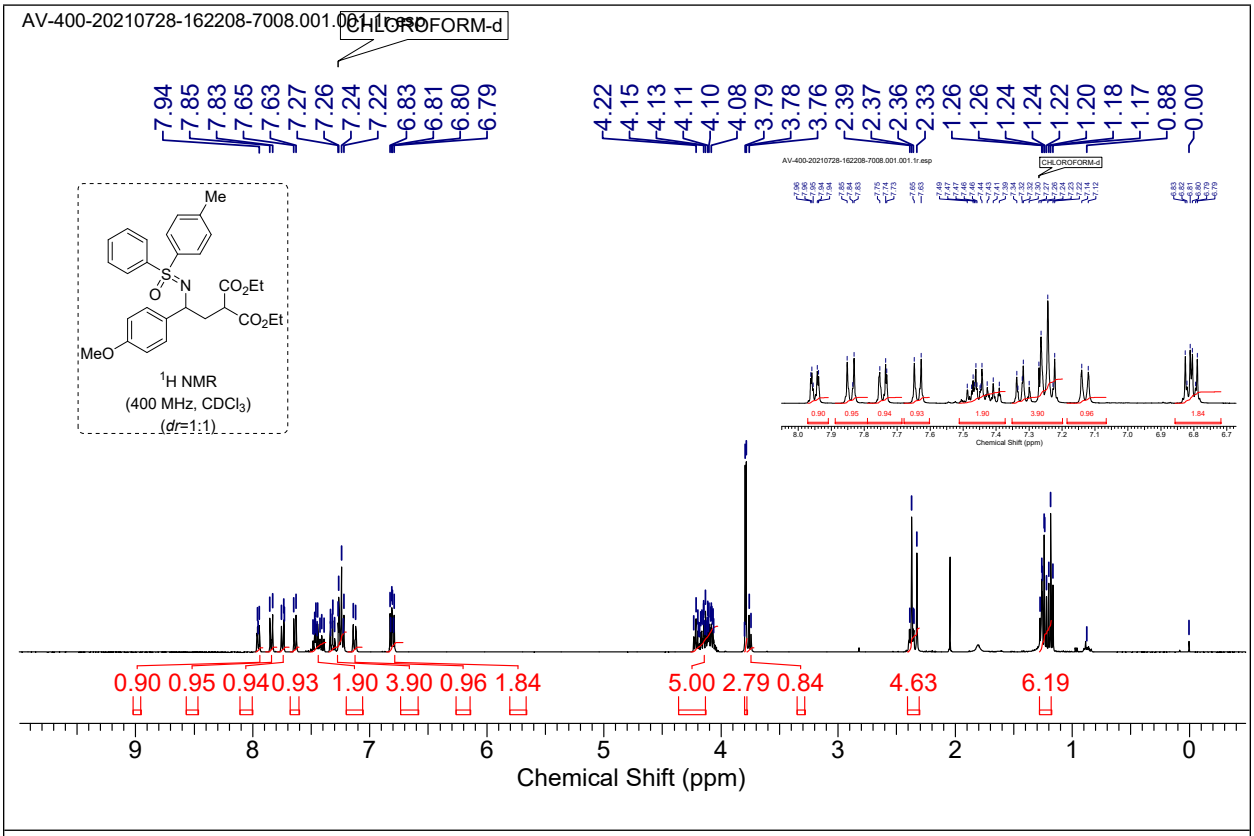
Diethyl 2-(2-(4-methoxyphenyl)-2-((oxodiphenyl-l6-sulfaneylidene) amino) ethyl) malonate (3a)

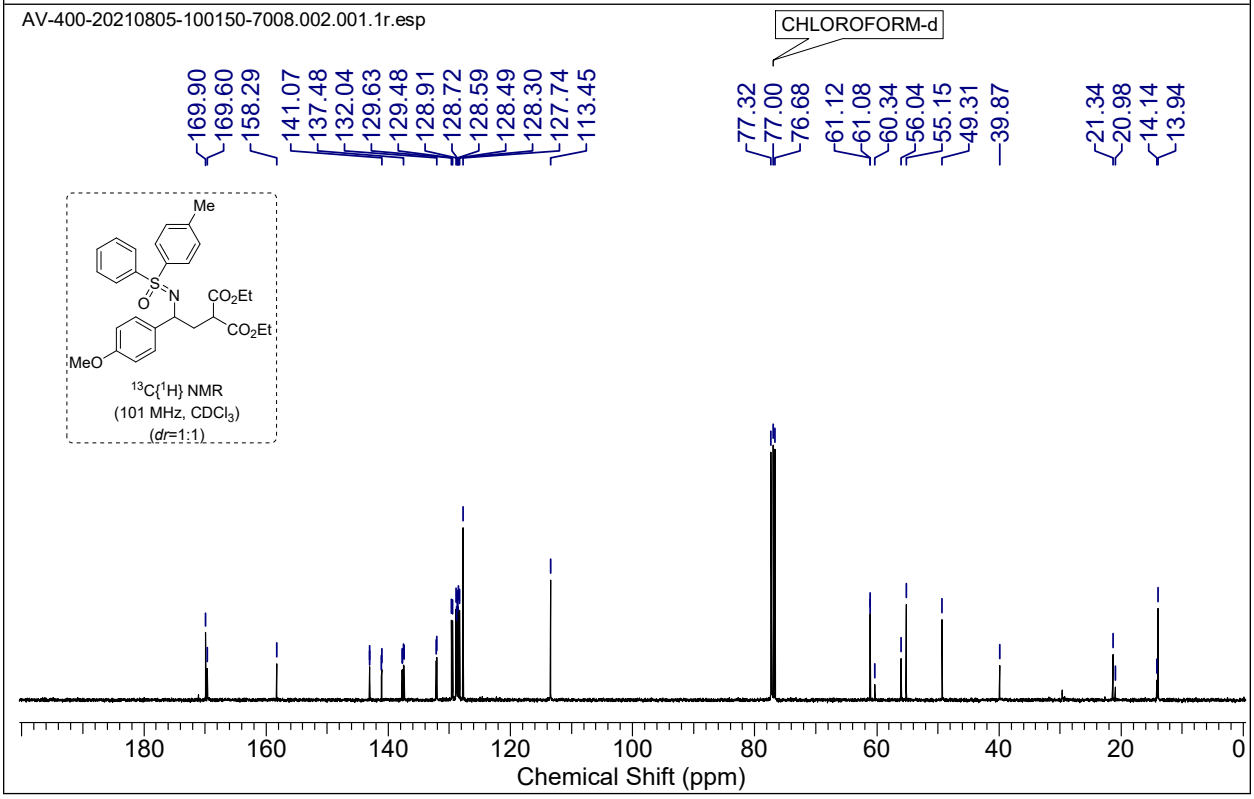




Diethyl 2-(2-(4-methoxyphenyl)-2-(((4-methoxyphenyl) (oxo)(phenyl)-l6-sulfaneylidene)

amino) ethyl) malonate (3b)





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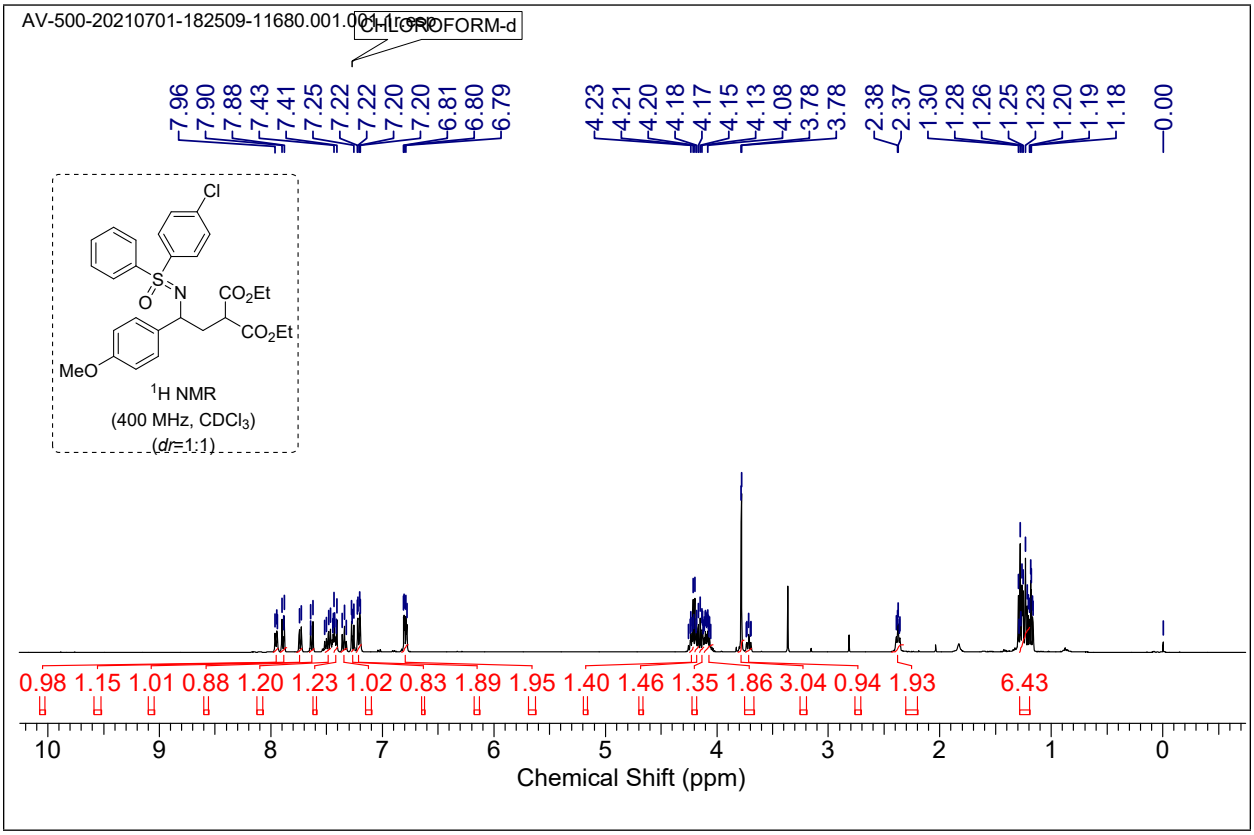
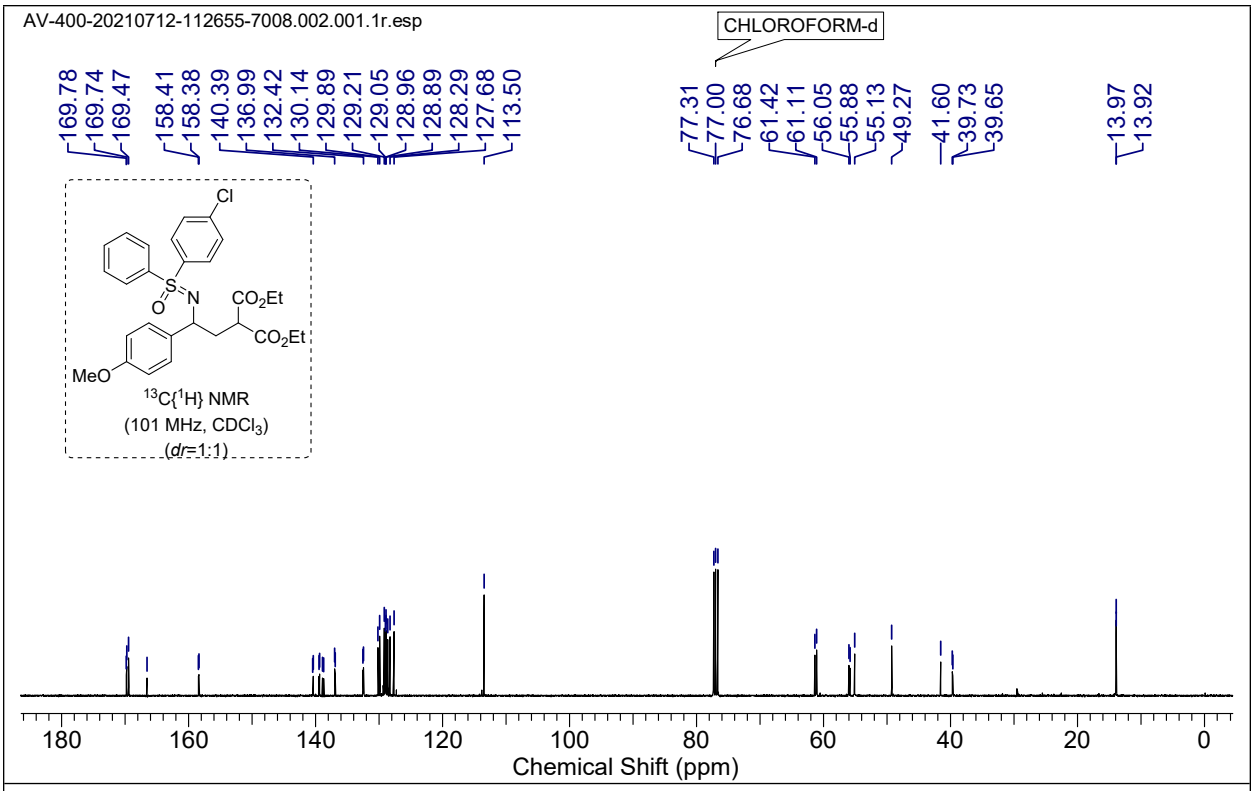
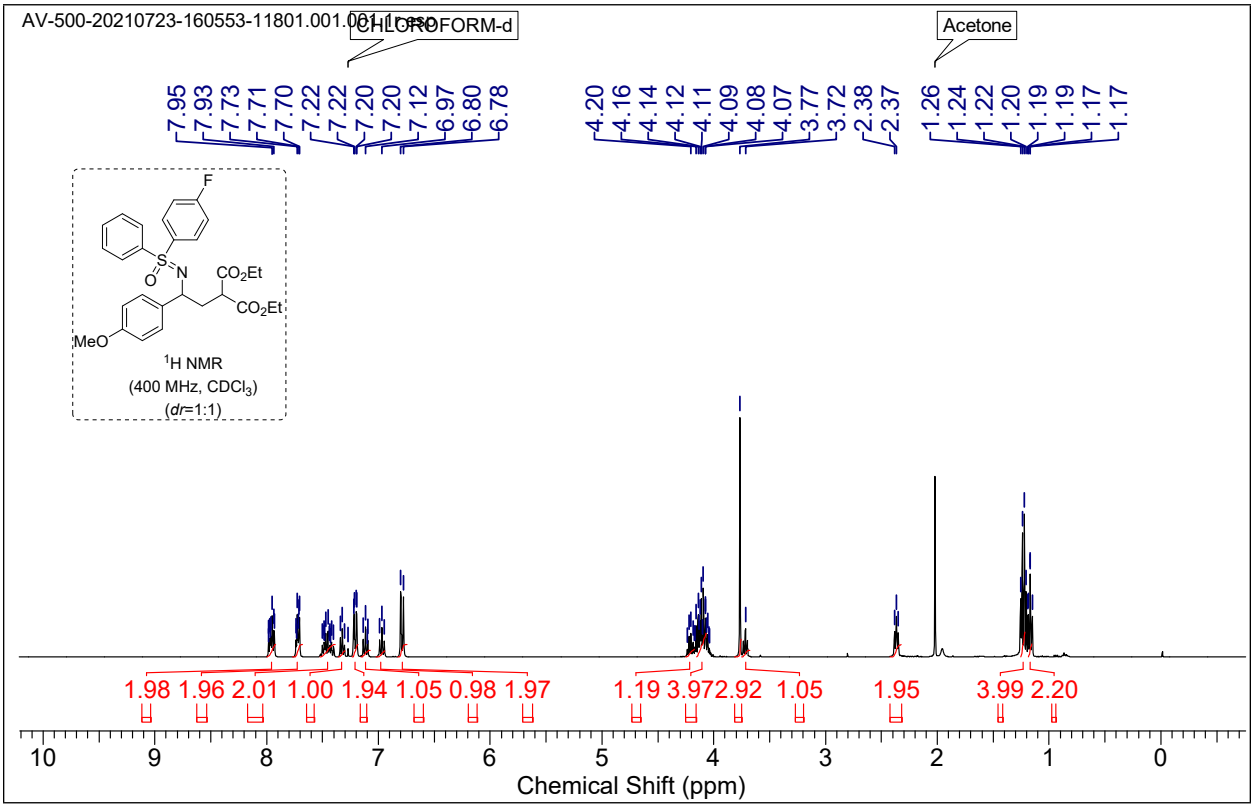
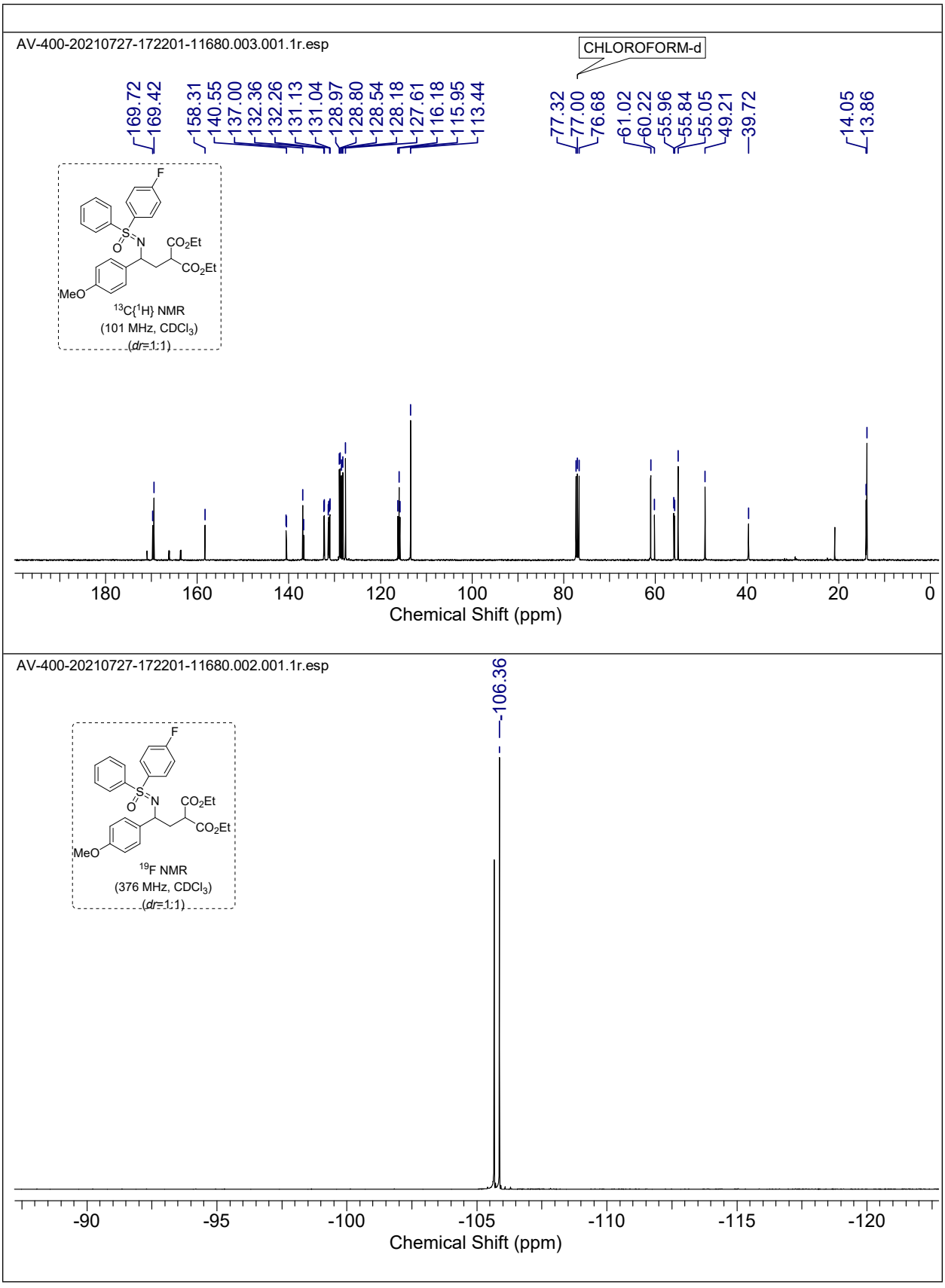




Diethyl 2-(2-(((4-chlorophenyl) (oxo)(phenyl)-l6-sulfaneylidene) amino)-2-(4-methoxyphenyl) ethyl) malonate (3d)

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132.26
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128.80
128.54
128.18
127.61
116.18
115.95
113.44
77.32
77.00
76.68
61.02
60.22
55.96
55.84
55.05
49.21
39.72
14.05
13.86
F
S
O
N
CO2Et
CO2Et
MeO
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(101 MHz, CDCl3)
(dr=1:1)
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160
140
120
100
80
60
40
20
0
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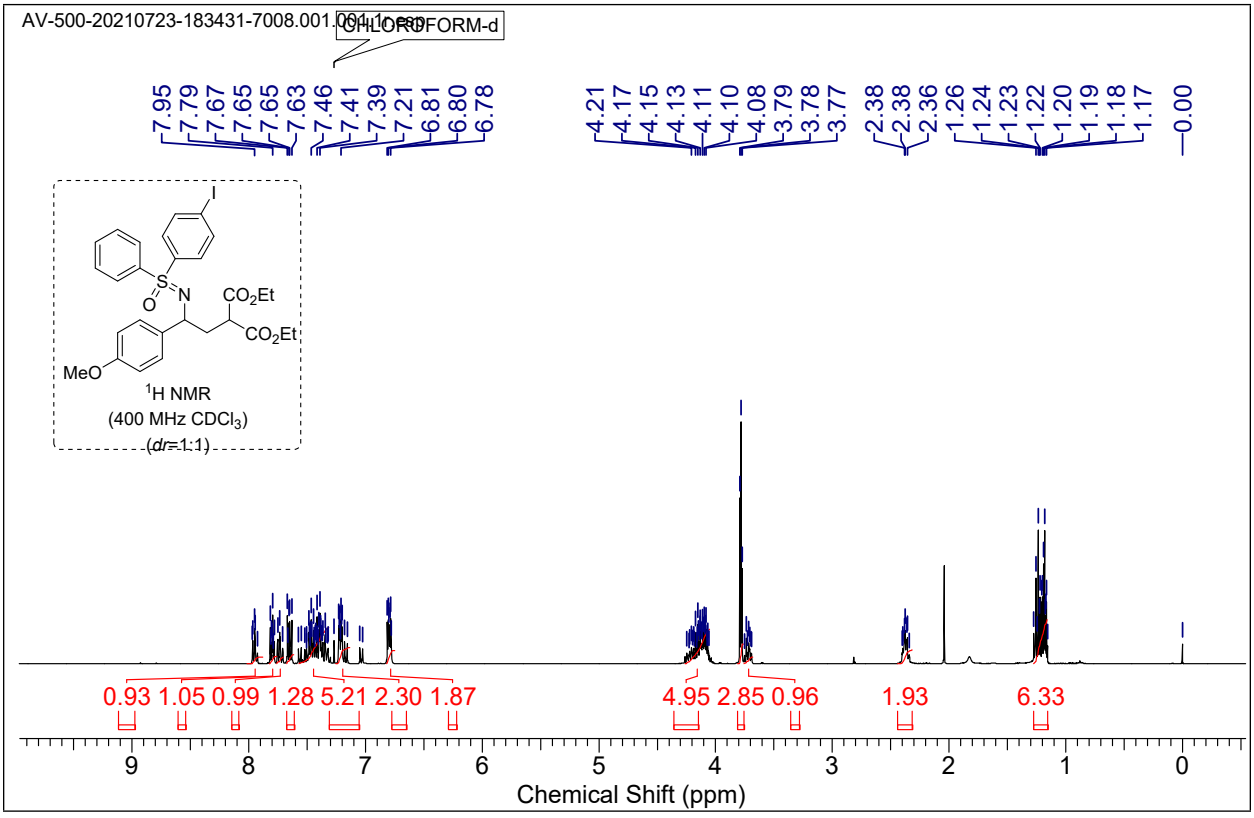
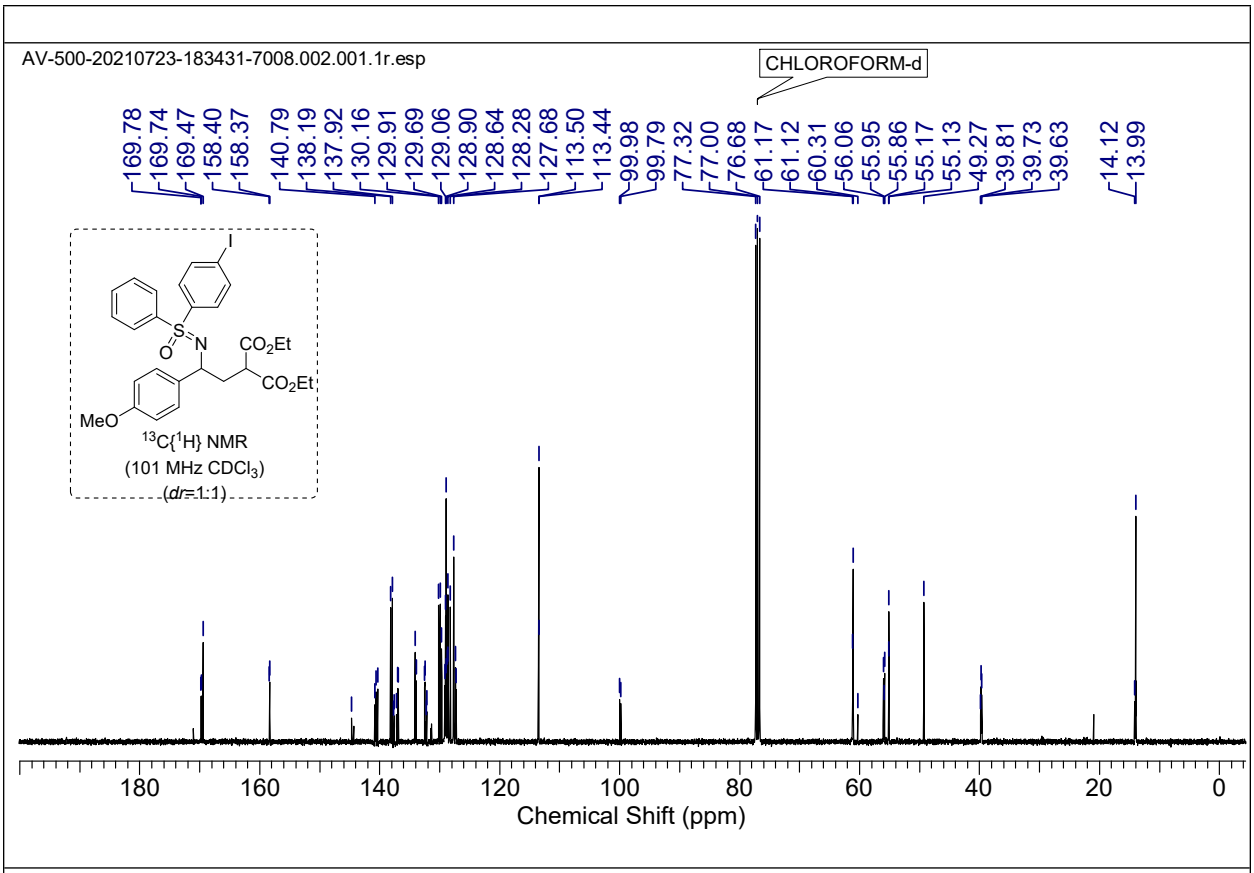
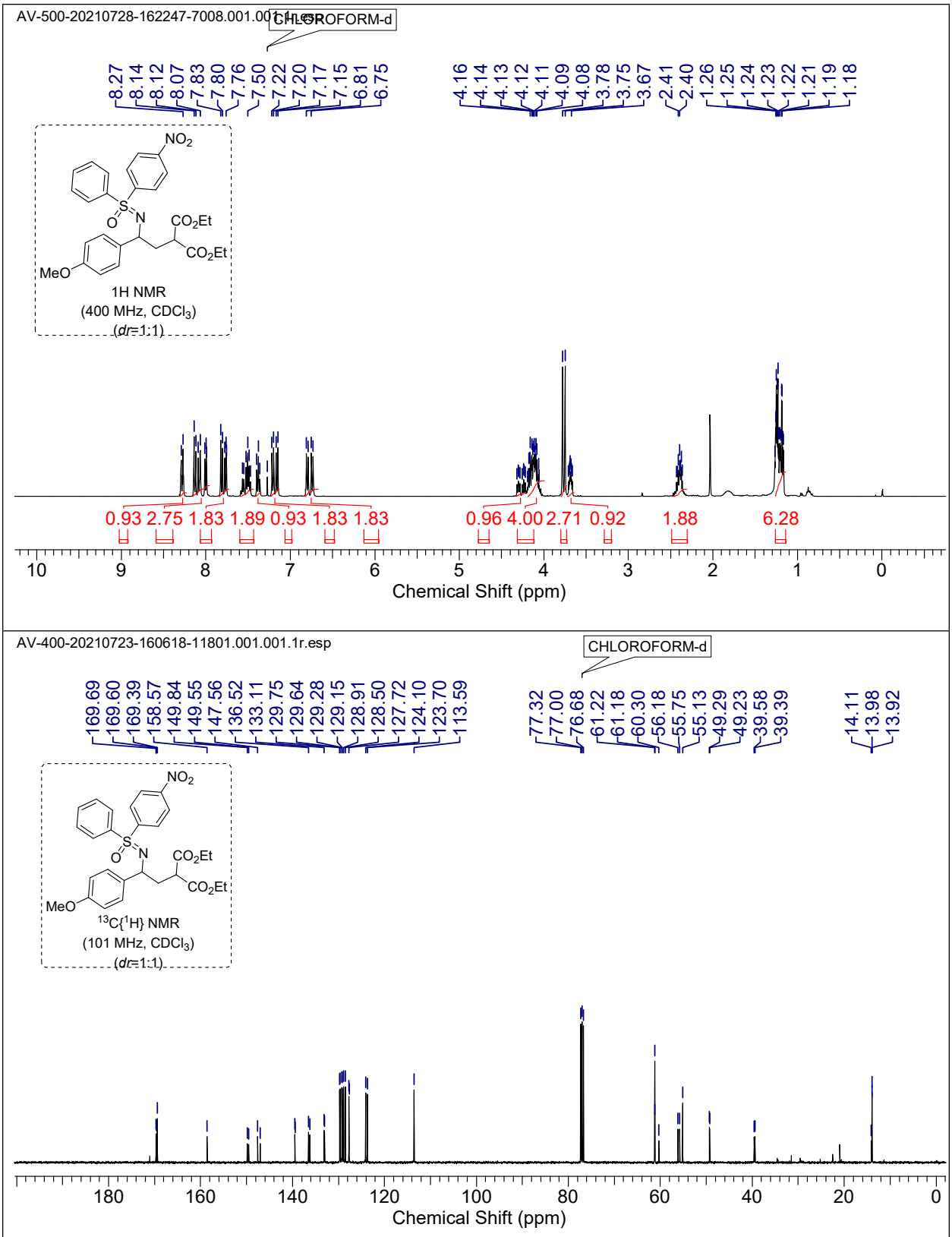




Diethyl 2-(2-(((4-iodophenyl) (oxo)(phenyl)-l6-sulfaneylidene) amino)-2-(4-methoxyphenyl) ethyl) malonate (3f)



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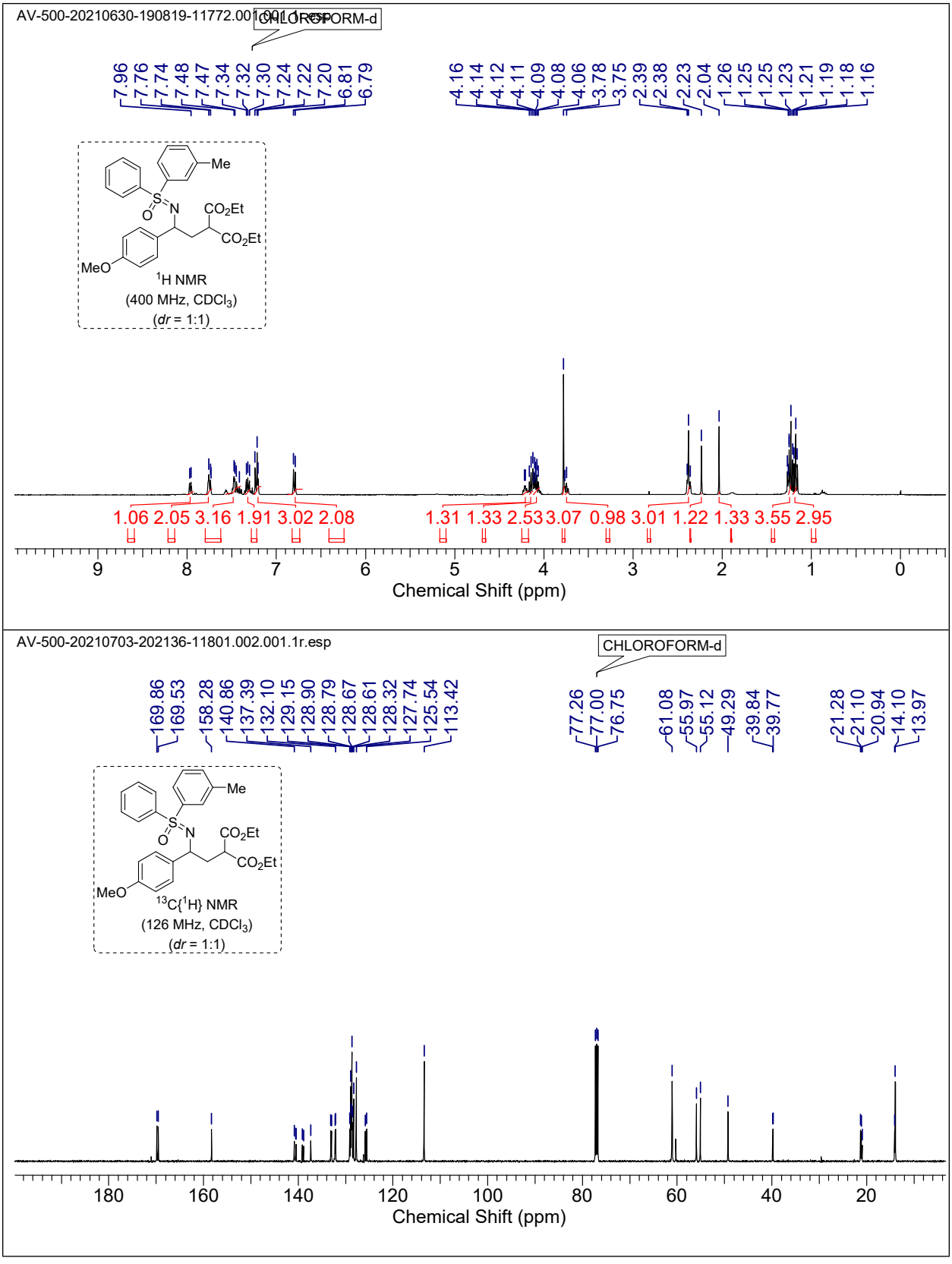
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4.16 4.14 4.12 4.11 4.09 4.08 4.06 3.78 3.75 2.39 2.38 2.23 2.04 1.26 1.25 1.25 1.23 1.21 1.19 1.18 1.16
Me
S
O
N
CO2Et
CO2Et
MeO
1H NMR
(400 MHz, CDCl3)
(dr = 1:1)
1.06 2.05 3.16 1.91 3.02 2.08
1.31 1.33 2.53 3.07 0.98 3.01 1.22 1.33 3.55 2.95
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Me
S
O
N
CO2Et
CO2Et
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(dr = 1:1)
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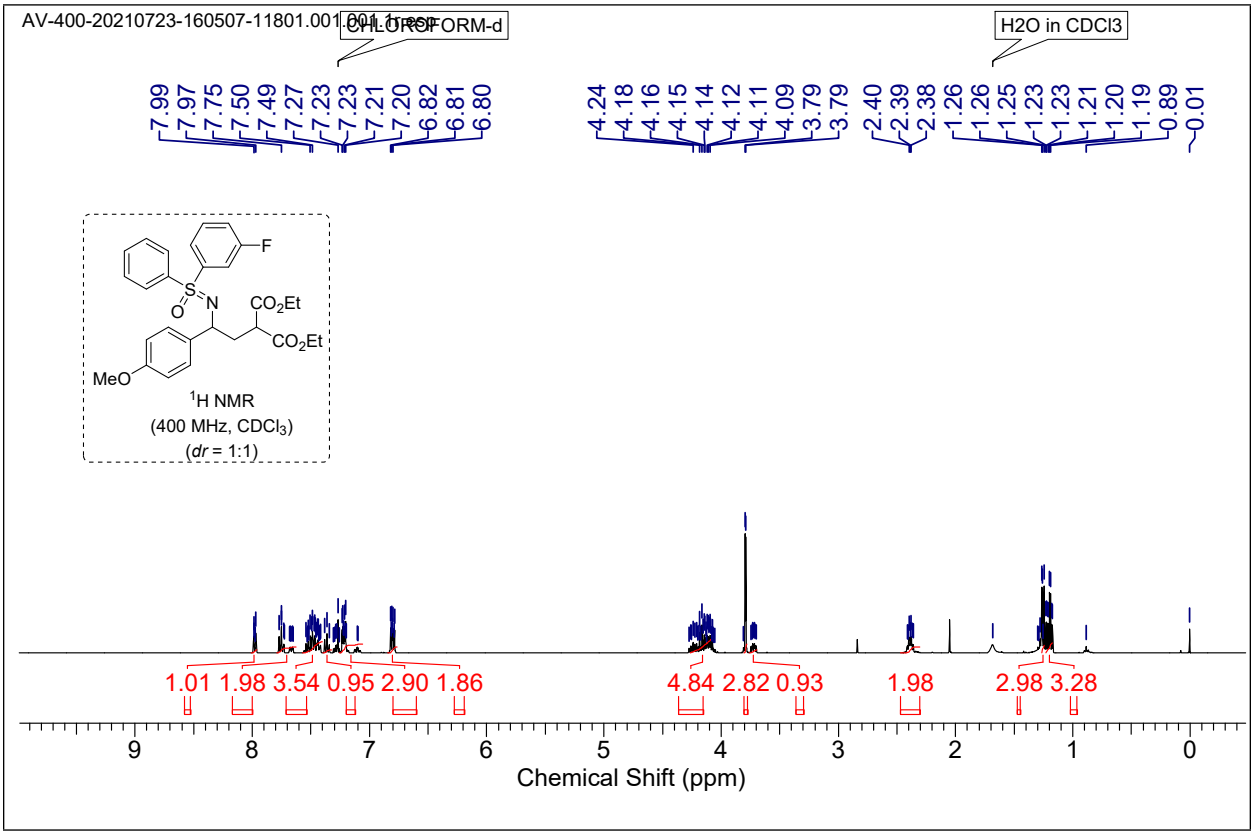

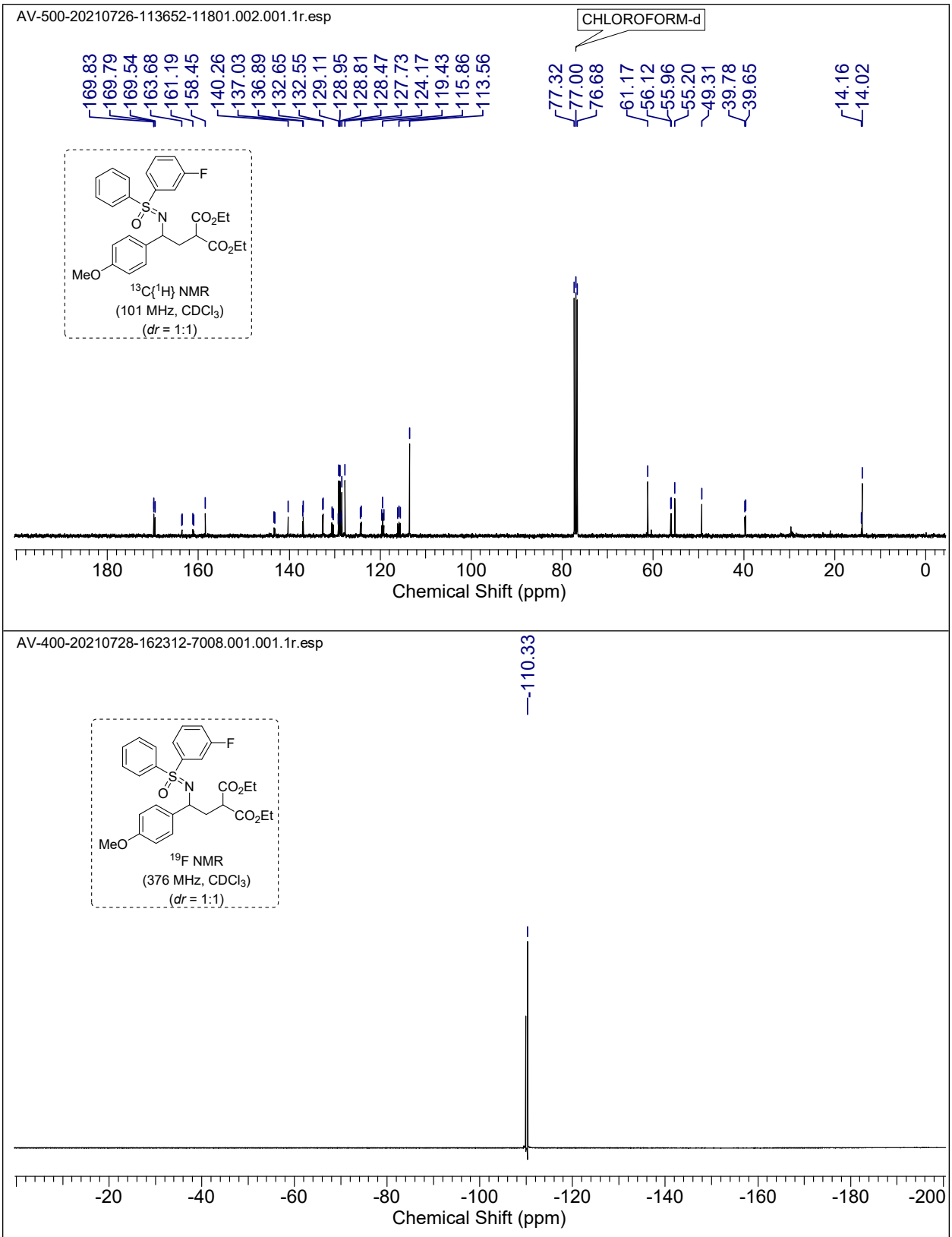

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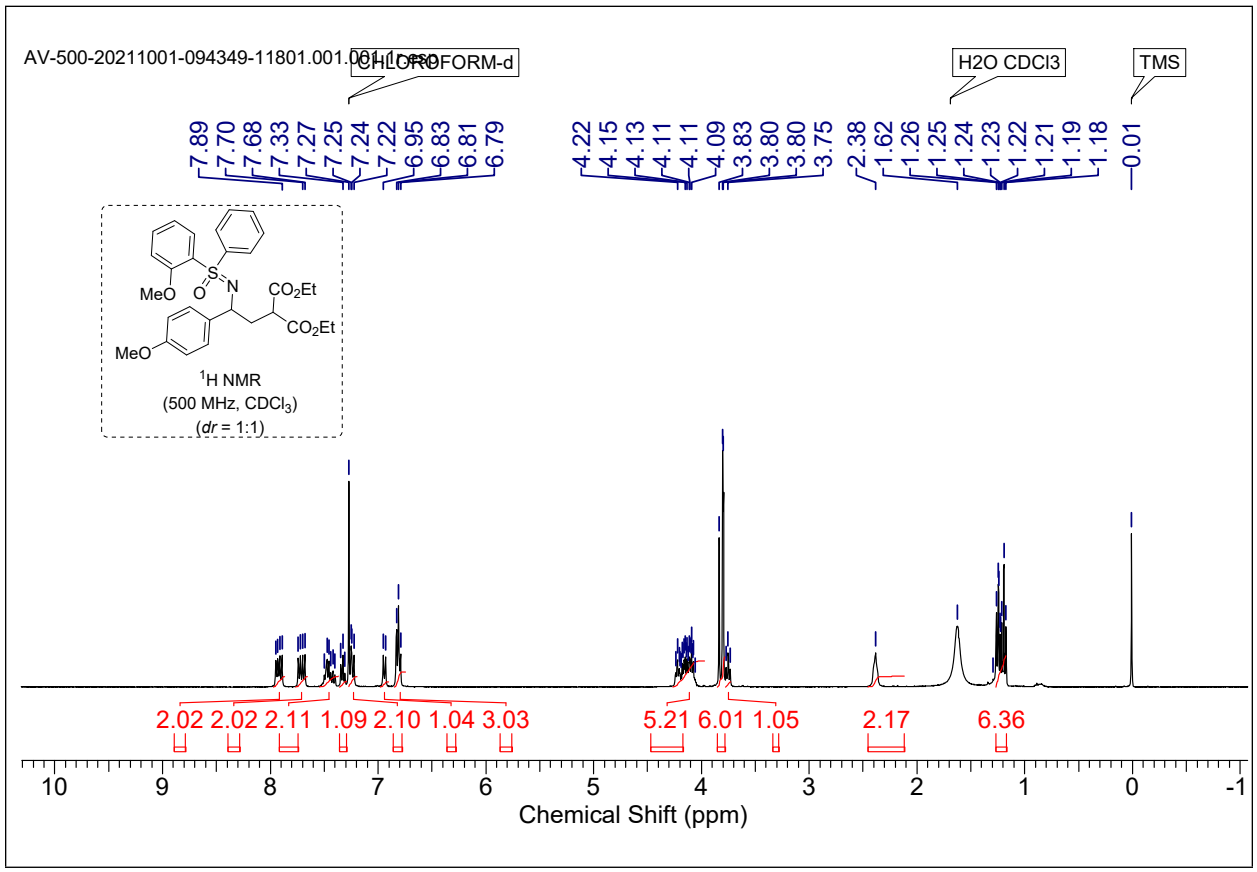
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MeO
O
S
N
CO2Et
CO2Et
MeO
1H NMR
(500 MHz, CDCl3)
(dr = 1:1)
2.02 2.02 2.11 1.09 2.10 1.04 3.03
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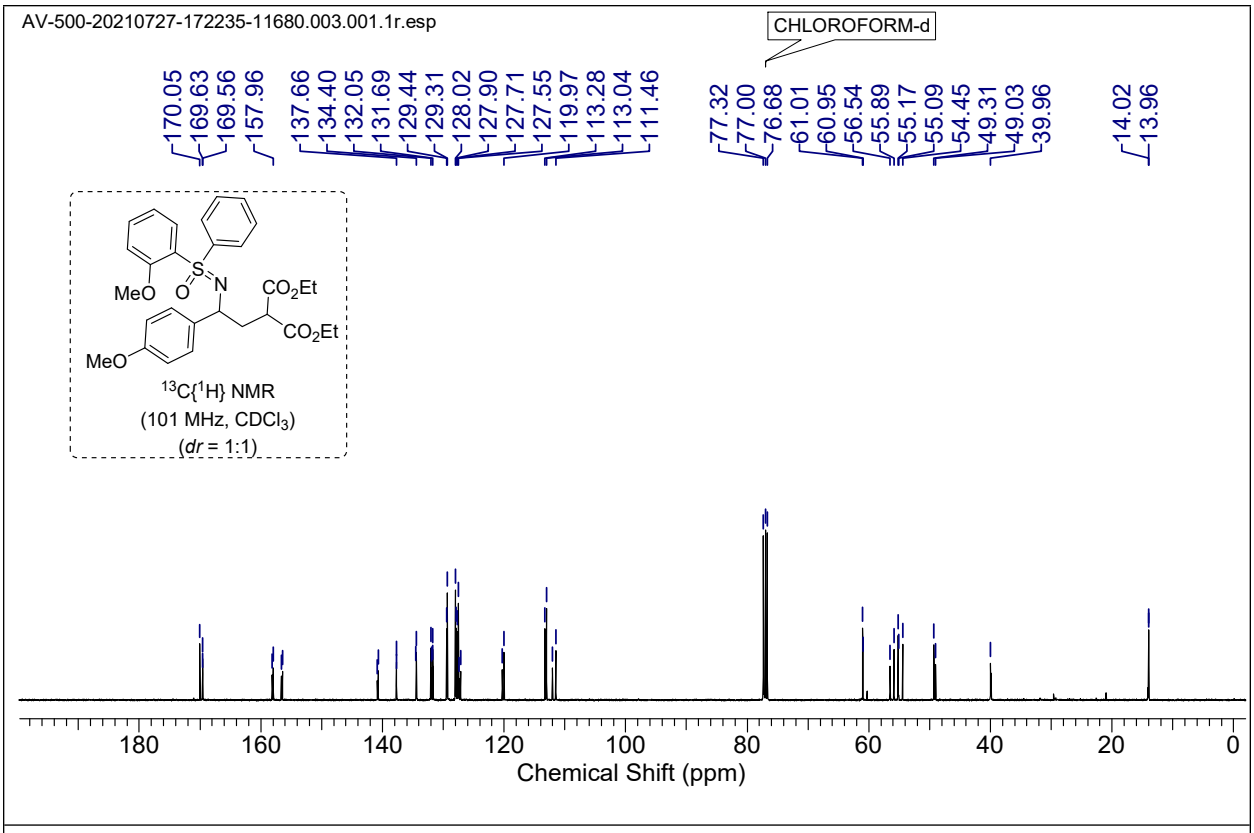
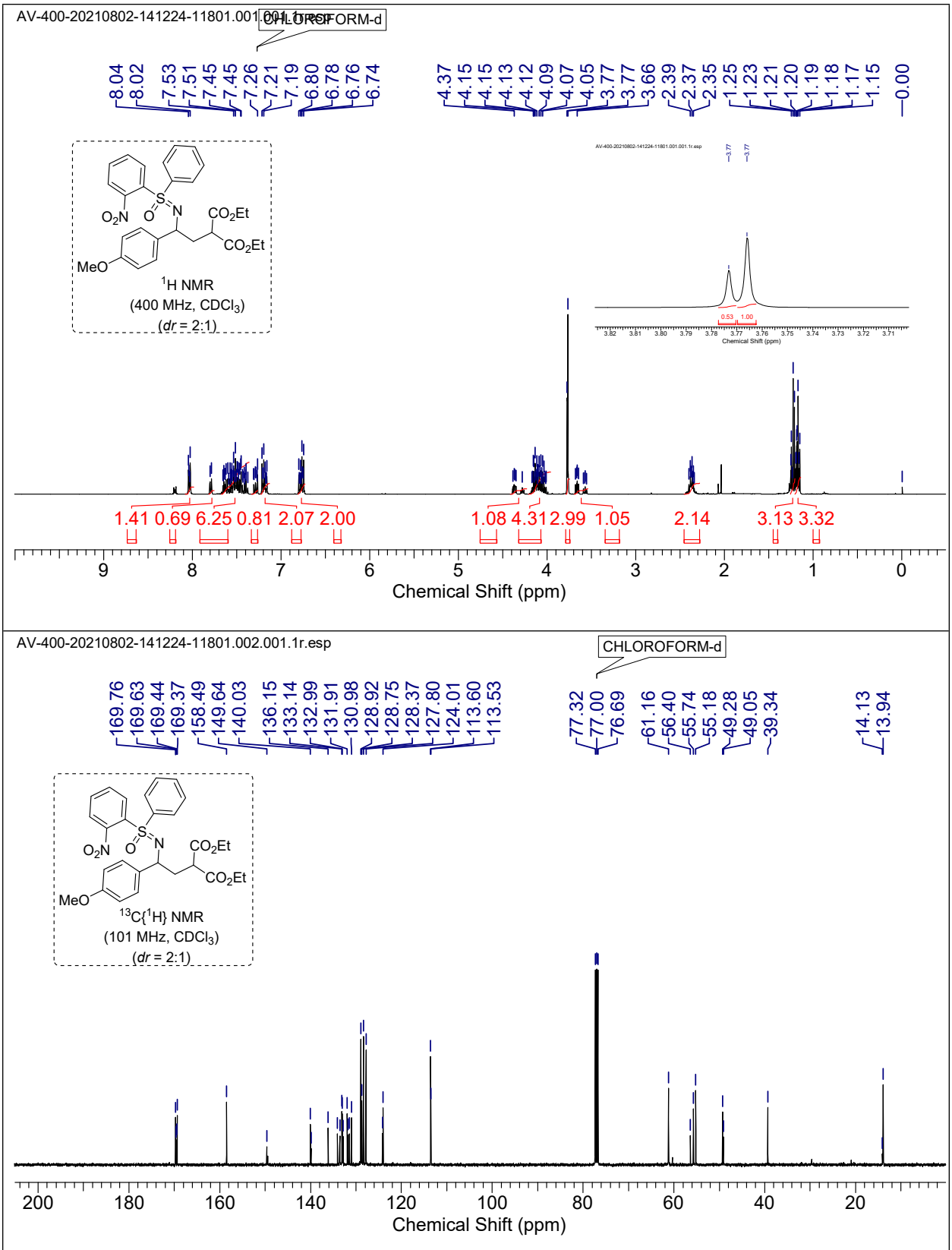


Diethyl 2-(2-(4-methoxyphenyl)-2-(((2-methoxyphenyl) (oxo)(phenyl)-l6-sulfaneylidene) amino) ethyl) malonate (3j)



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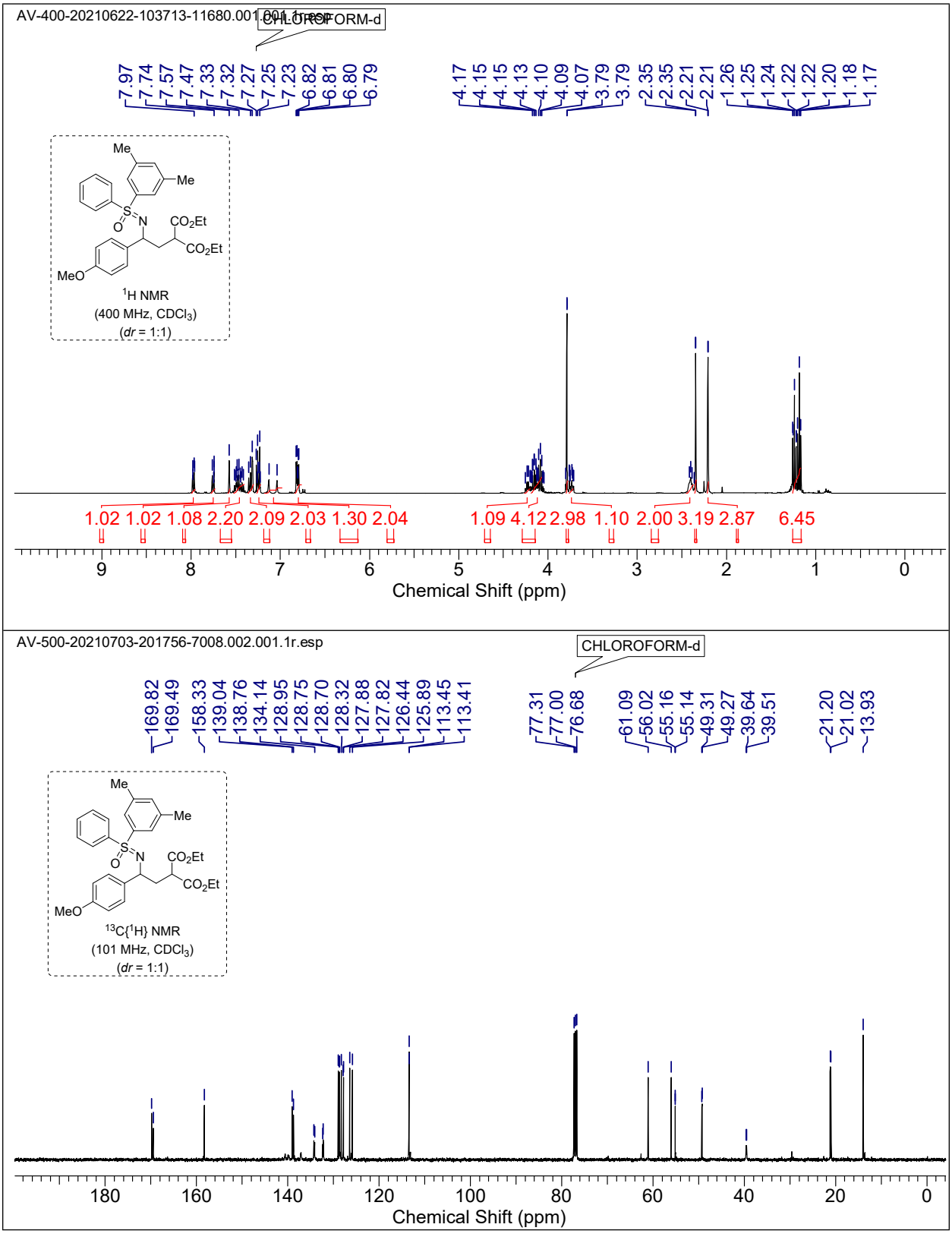
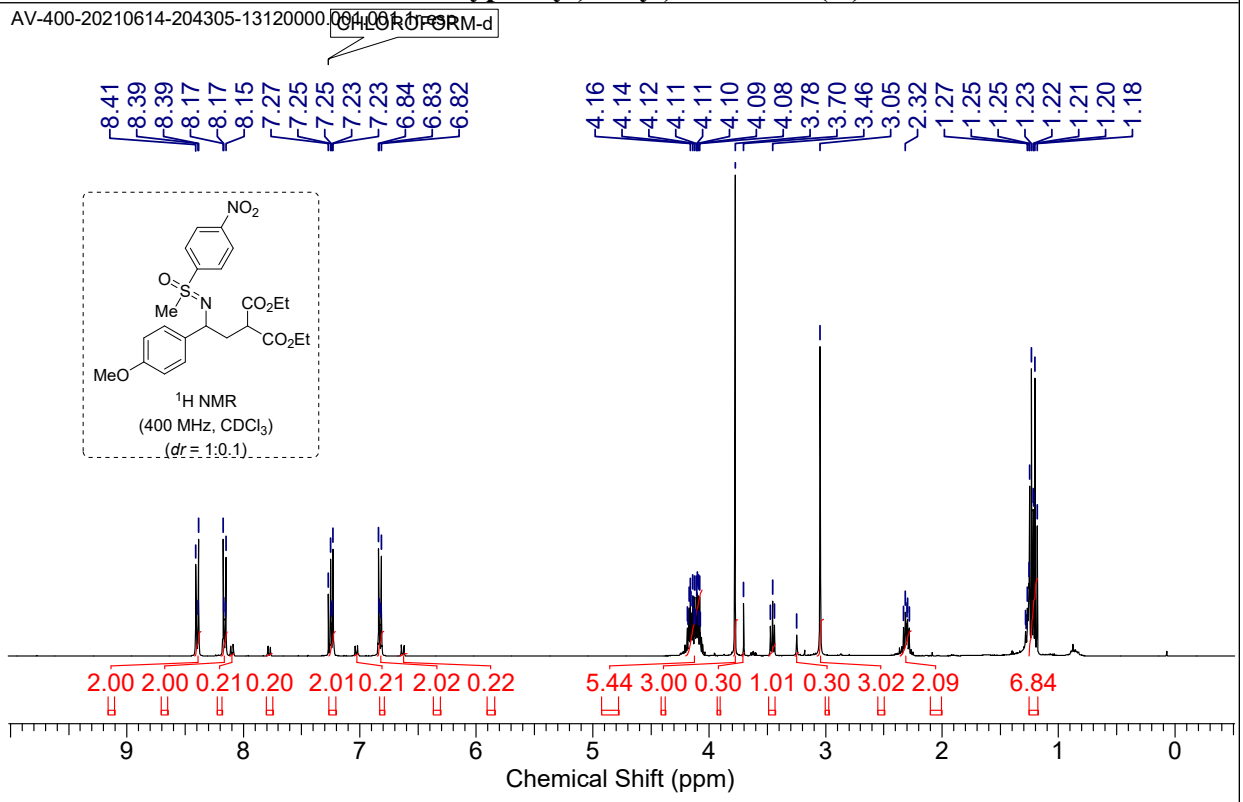
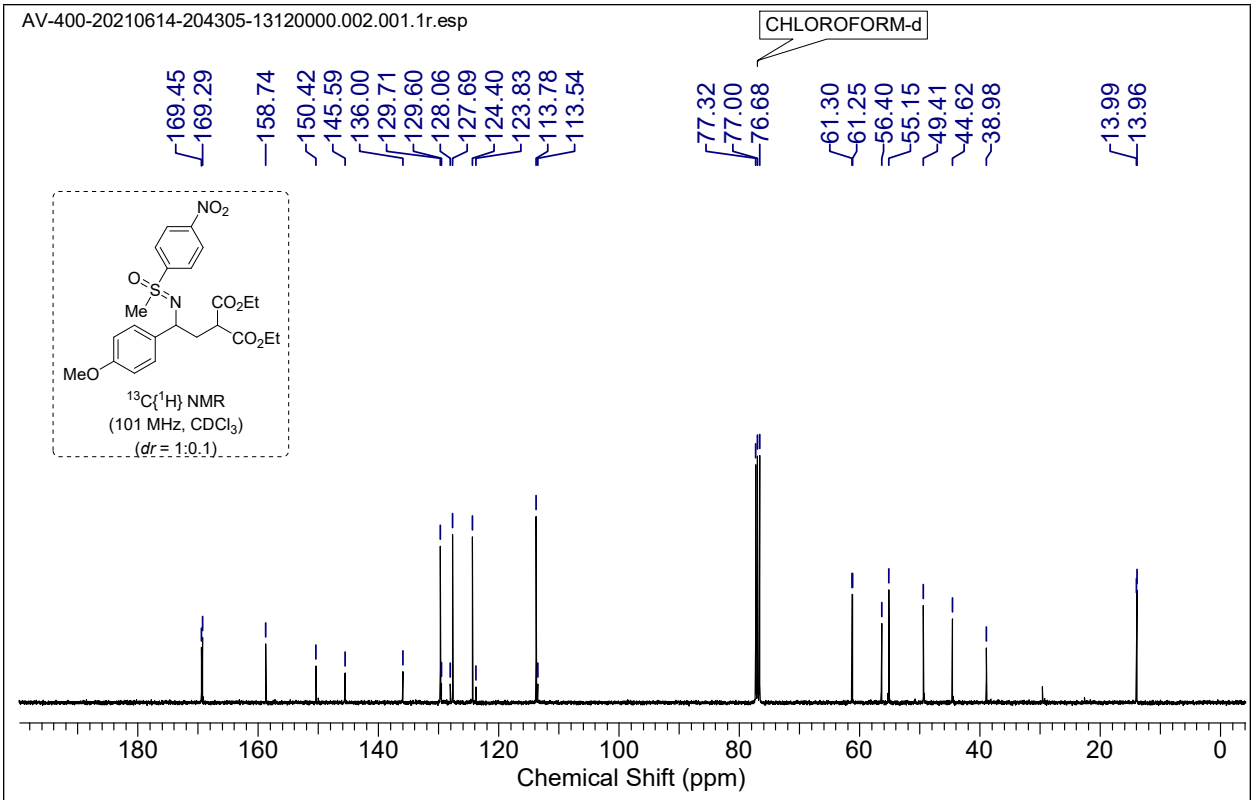
amino) ethyl) malonate (3k)

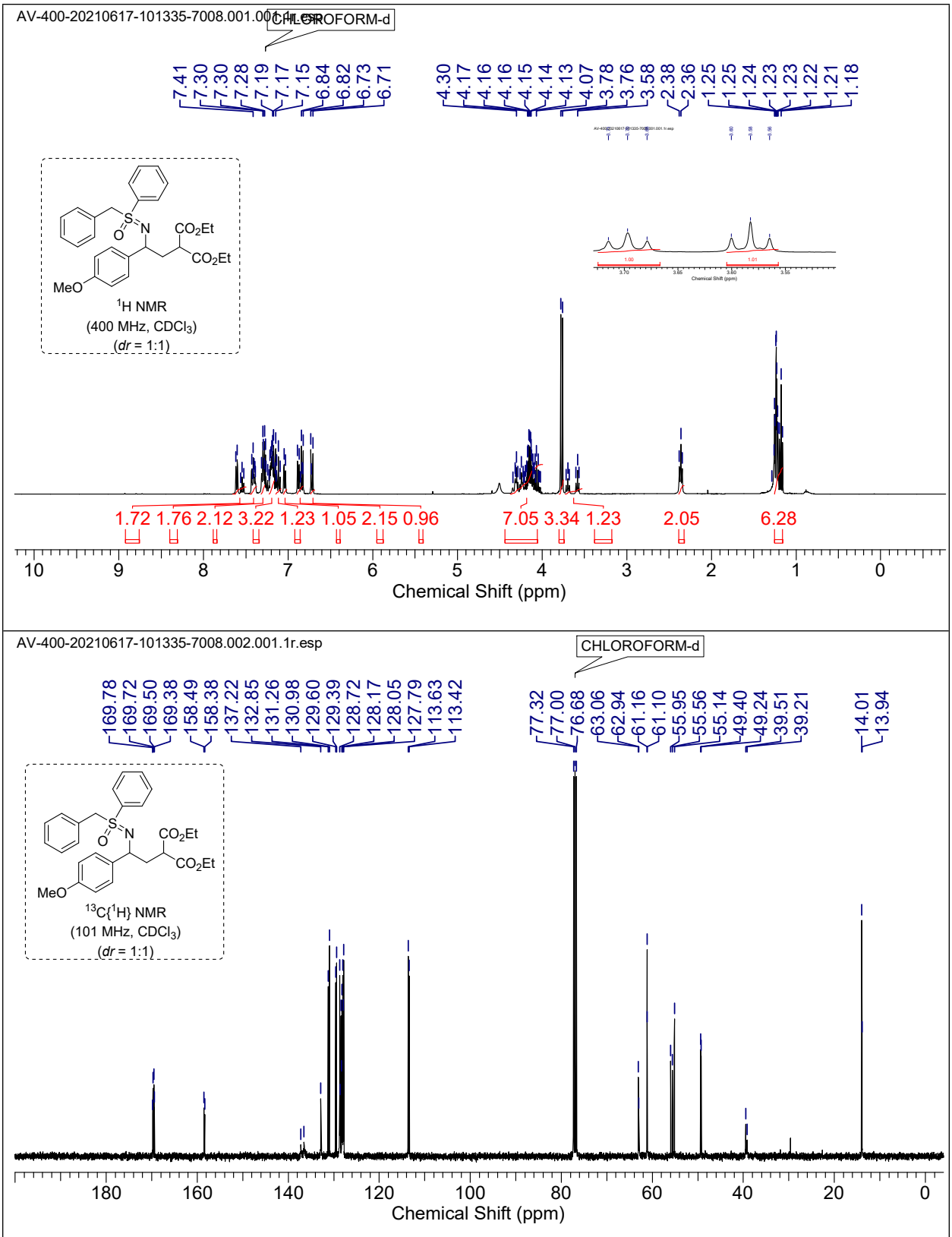


Diethyl 2-(2-(((3,5-dimethylphenyl) (oxo)(phenyl)-l6-sulfaneylidene) amino)-2-(4-methoxyphenyl) ethyl) malonate (3l)





Diethyl 2-(2-(4-methoxyphenyl)-2-((methyl(4-nitrophenyl) (oxo)-l6-sulfaneylidene) amino) ethyl) malonate (3m)



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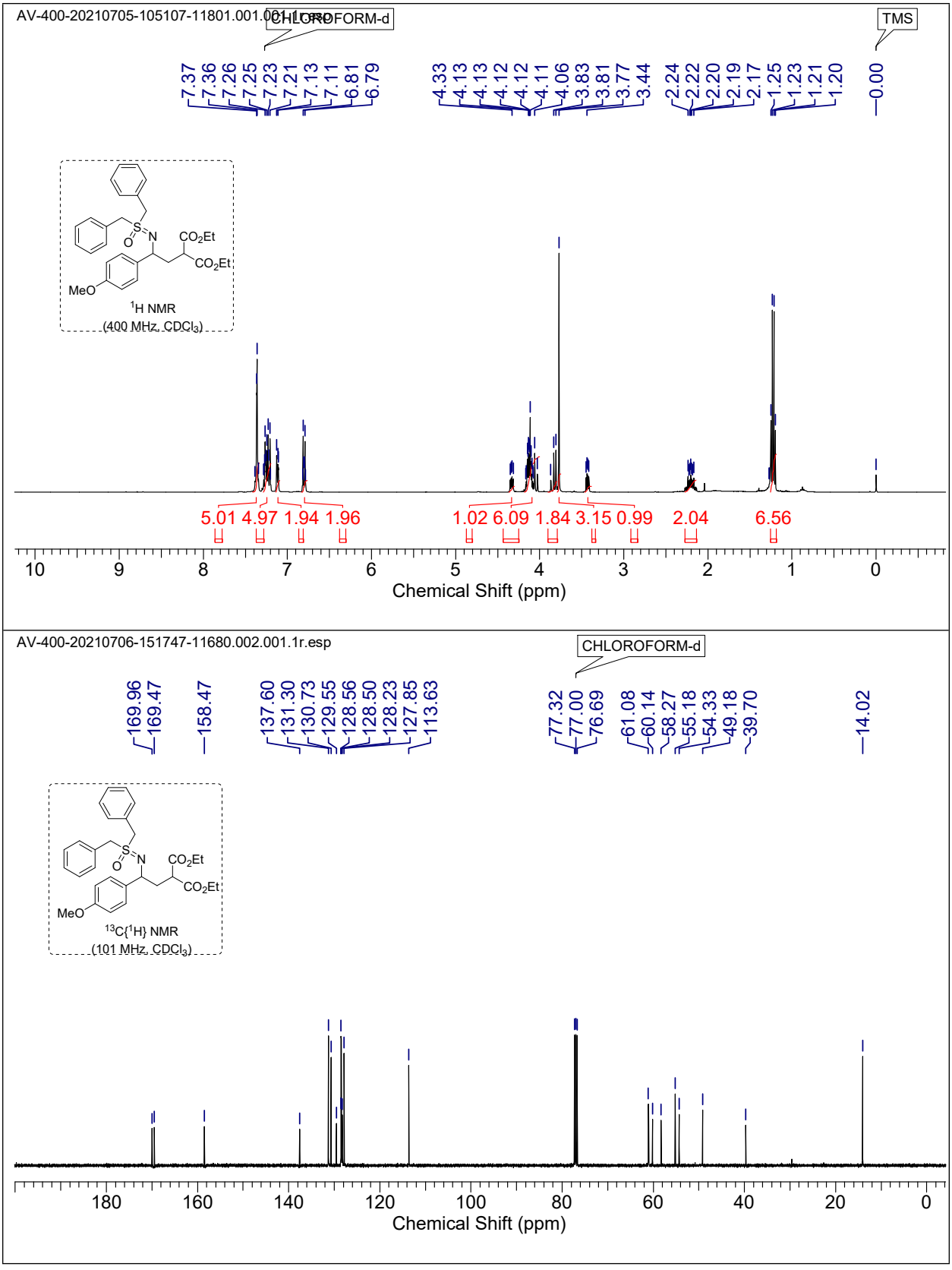
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4.33 4.13 4.13 4.12 4.12 4.11 4.06 3.83 3.81 3.77 3.44
2.24 2.22 2.20 2.19 2.17
1.25 1.23 1.21 1.20
0.00
MeO
CO2Et
CO2Et
1H NMR
(400 MHz, CDCl3)
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1.02 6.09 1.84 3.15 0.99
2.04
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14.02
MeO
CO2Et
CO2Et
13C{1H} NMR
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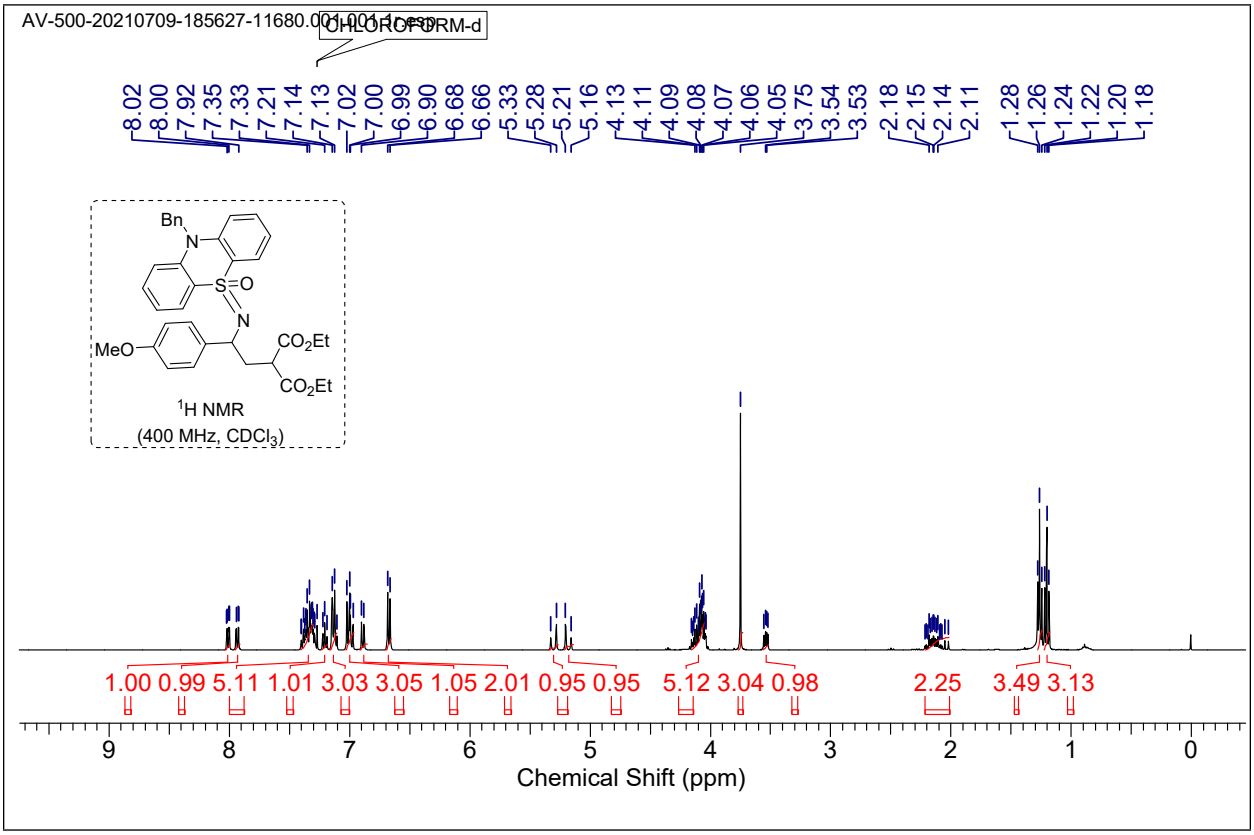
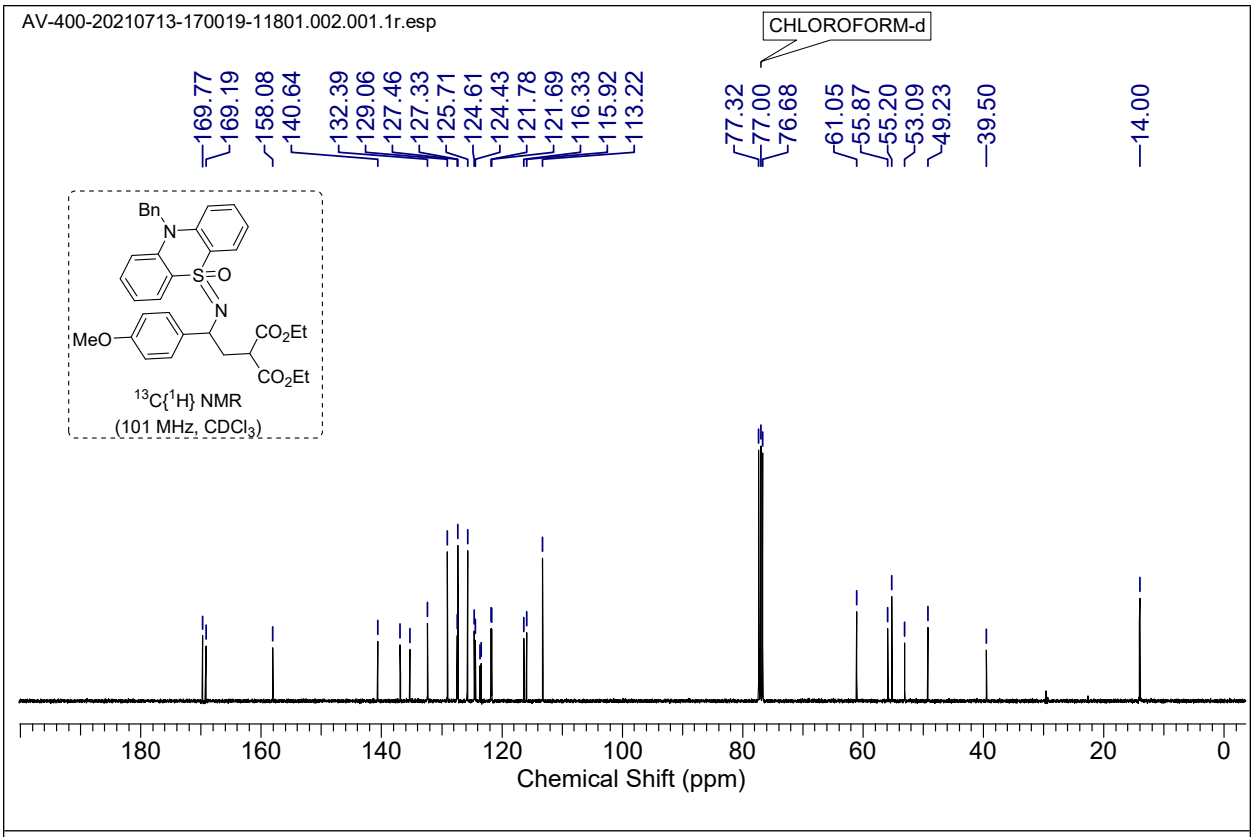
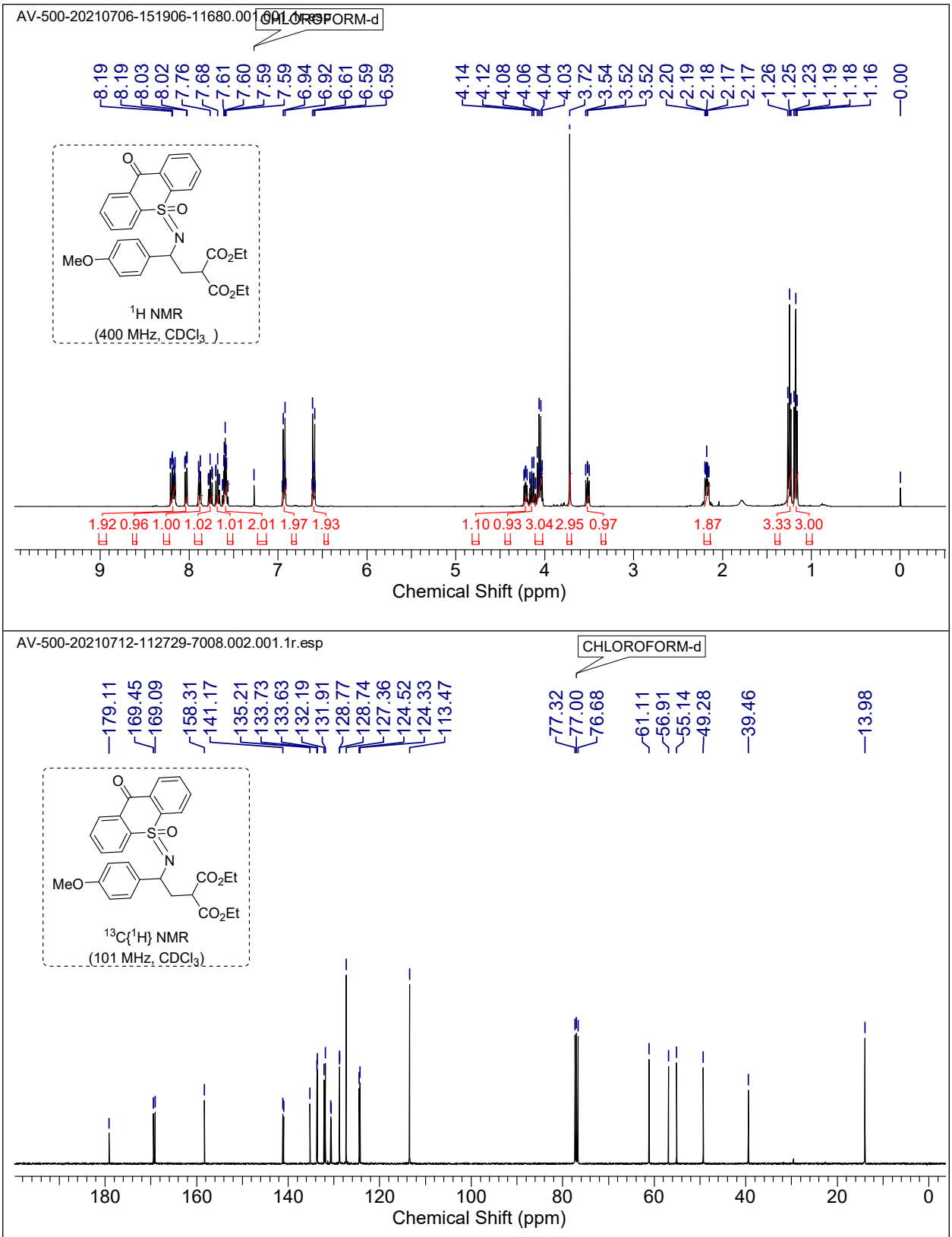
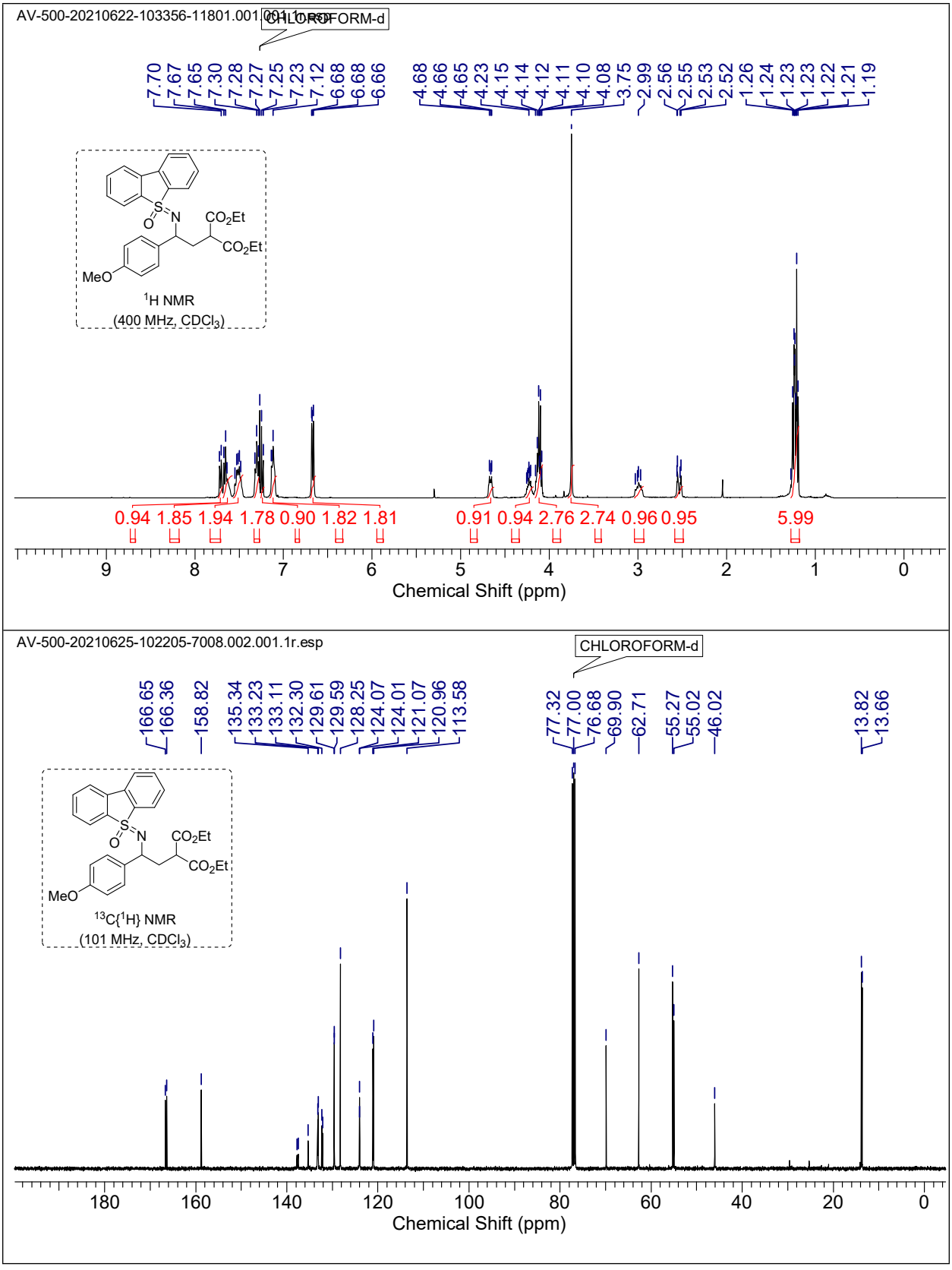




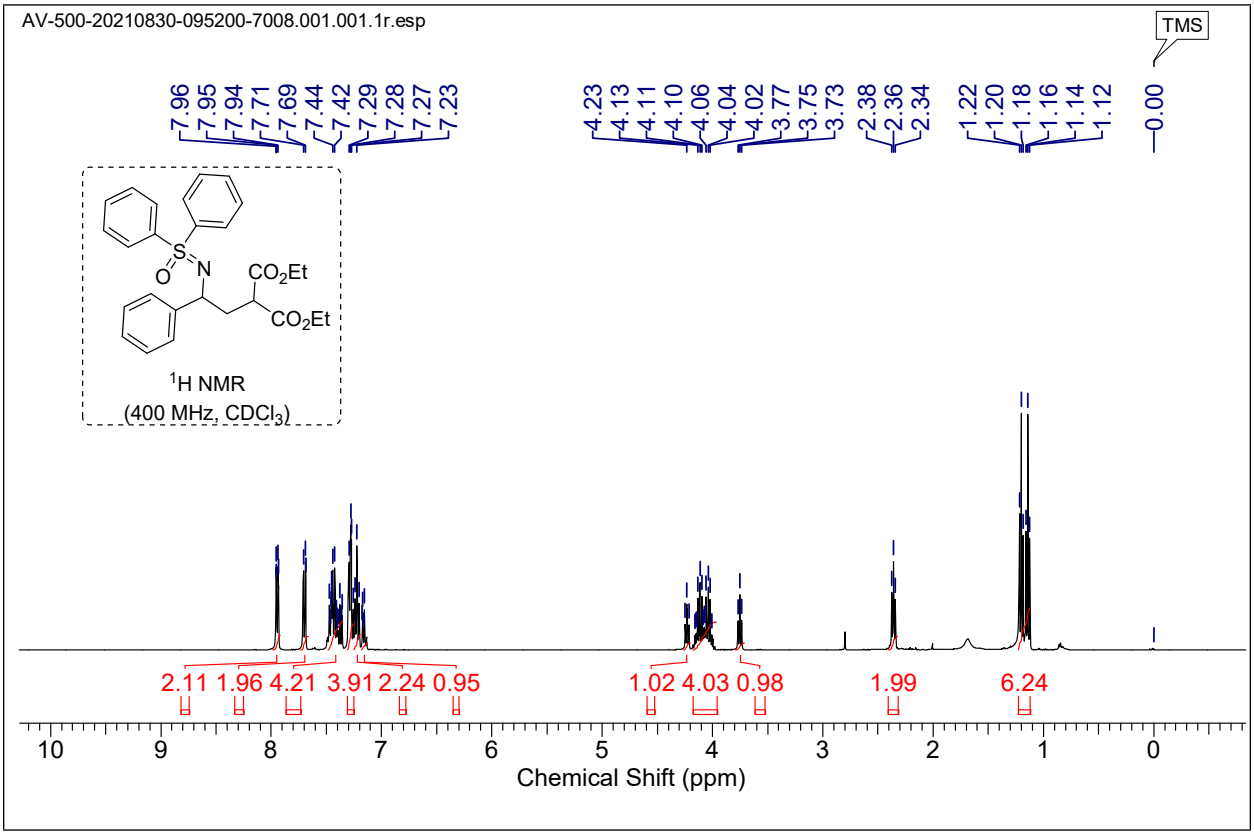
Diethyl 2-(2-((10-benzyl-5-oxido-10H-5l4-phenothiazin-5-ylidene) amino)-2-(4-methoxyphenyl) ethyl) malonate (3p)

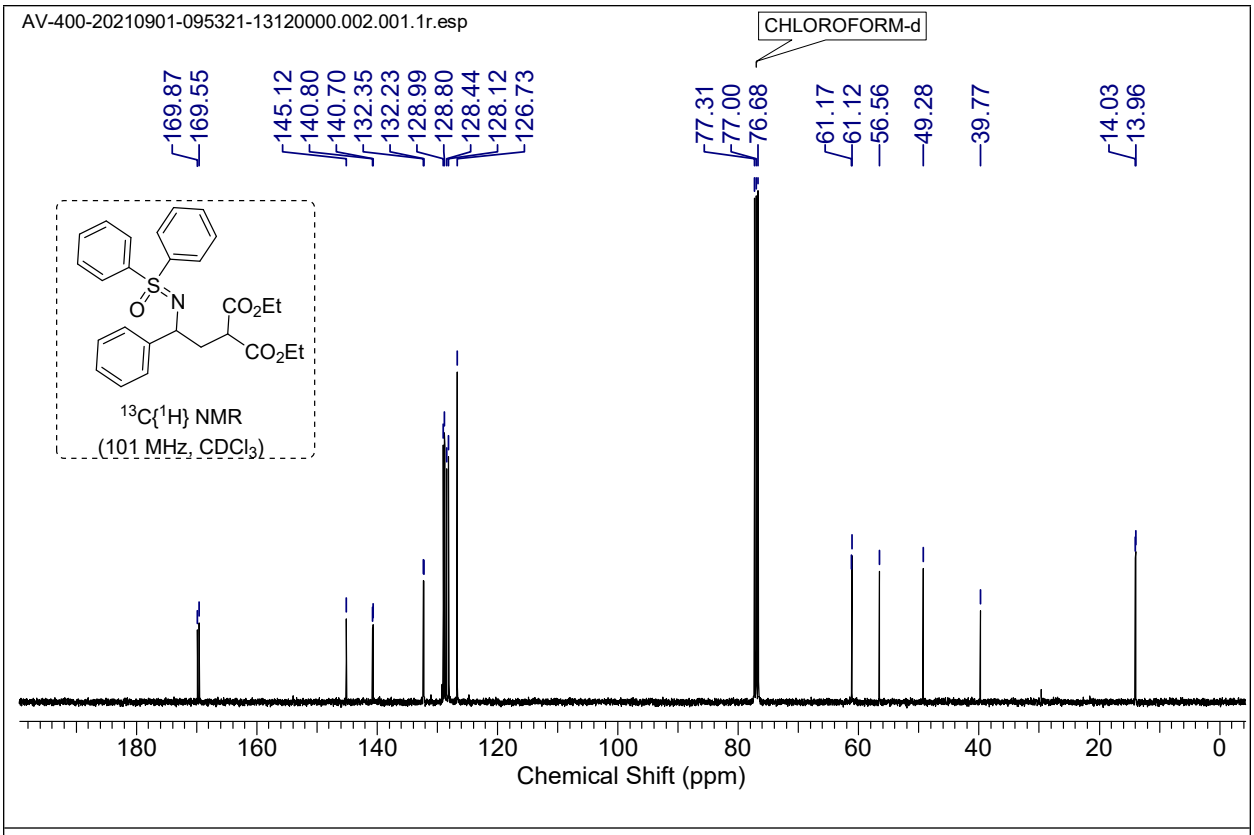


Diethyl 2-(2-(4-methoxyphenyl)-2-((10-oxido-9-oxo-9H-10l4-thioxanthen-10-ylidene) amino) ethyl) malonate (3q)

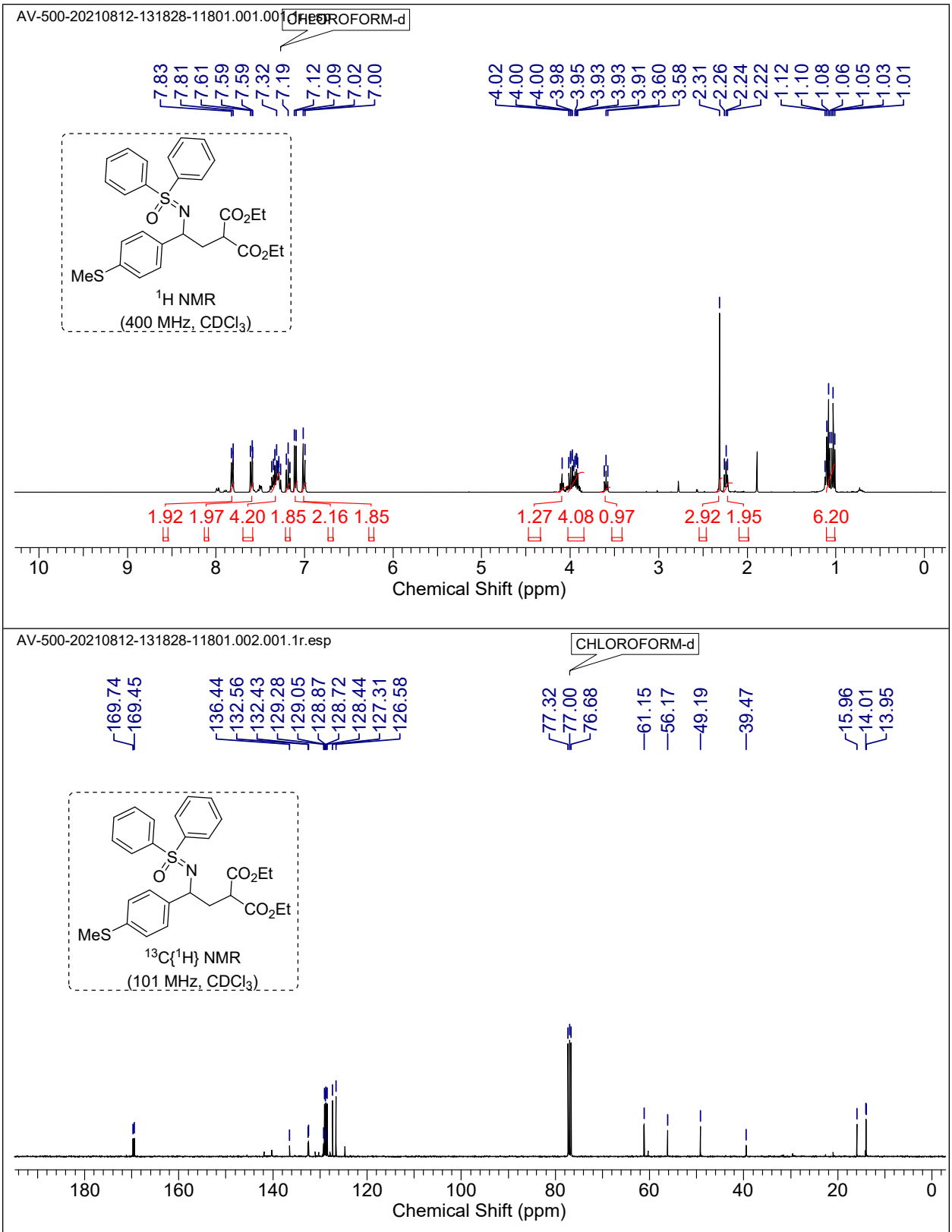

AV-500-20210622-103356-11801.001.001.1r.esp
CHLOROFORM-d
7.70 7.67 7.65 7.30 7.28 7.27 7.25 7.23 7.12 6.68 6.68 6.66
4.68 4.66 4.65 4.23 4.15 4.14 4.12 4.11 4.10 4.08 3.75 2.99 2.56 2.55 2.53 2.52 1.26 1.24 1.23 1.23 1.22 1.21 1.19
CO2Et
CO2Et
MeO
1H NMR
(400 MHz, CDCl3)
0.94 1.85 1.94 1.78 0.90 1.82 1.81
0.91 0.94 2.76 2.74 0.96 0.95
5.99
Chemical Shift (ppm)
AV-500-20210625-102205-7008.002.001.1r.esp
CHLOROFORM-d
166.65 166.36 158.82 135.34 133.23 133.11 132.30 129.61 129.59 128.25 124.07 124.01 121.07 120.96 113.58
77.32 77.00 76.68 69.90 62.71 55.27 55.02 46.02
13.82 13.66
CO2Et
CO2Et
MeO
13C{1H} NMR
(101 MHz, CDCl3)
Chemical Shift (ppm)

Diethyl 2-(2-(4-methoxyphenyl)-2-((5-oxido-5l4-dibenzo [b, d] thiophen-5-ylidene) amino) ethyl) malonate (3r)

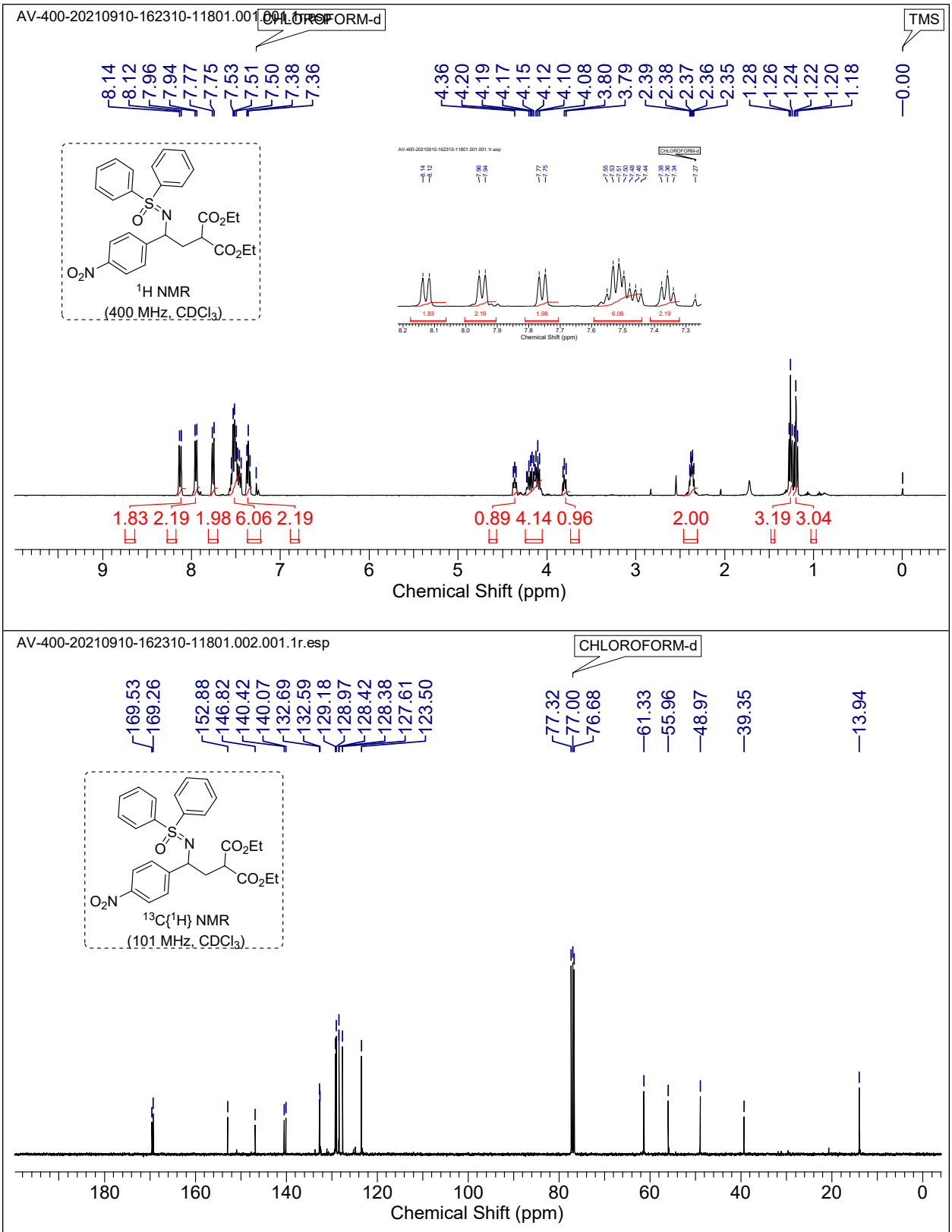




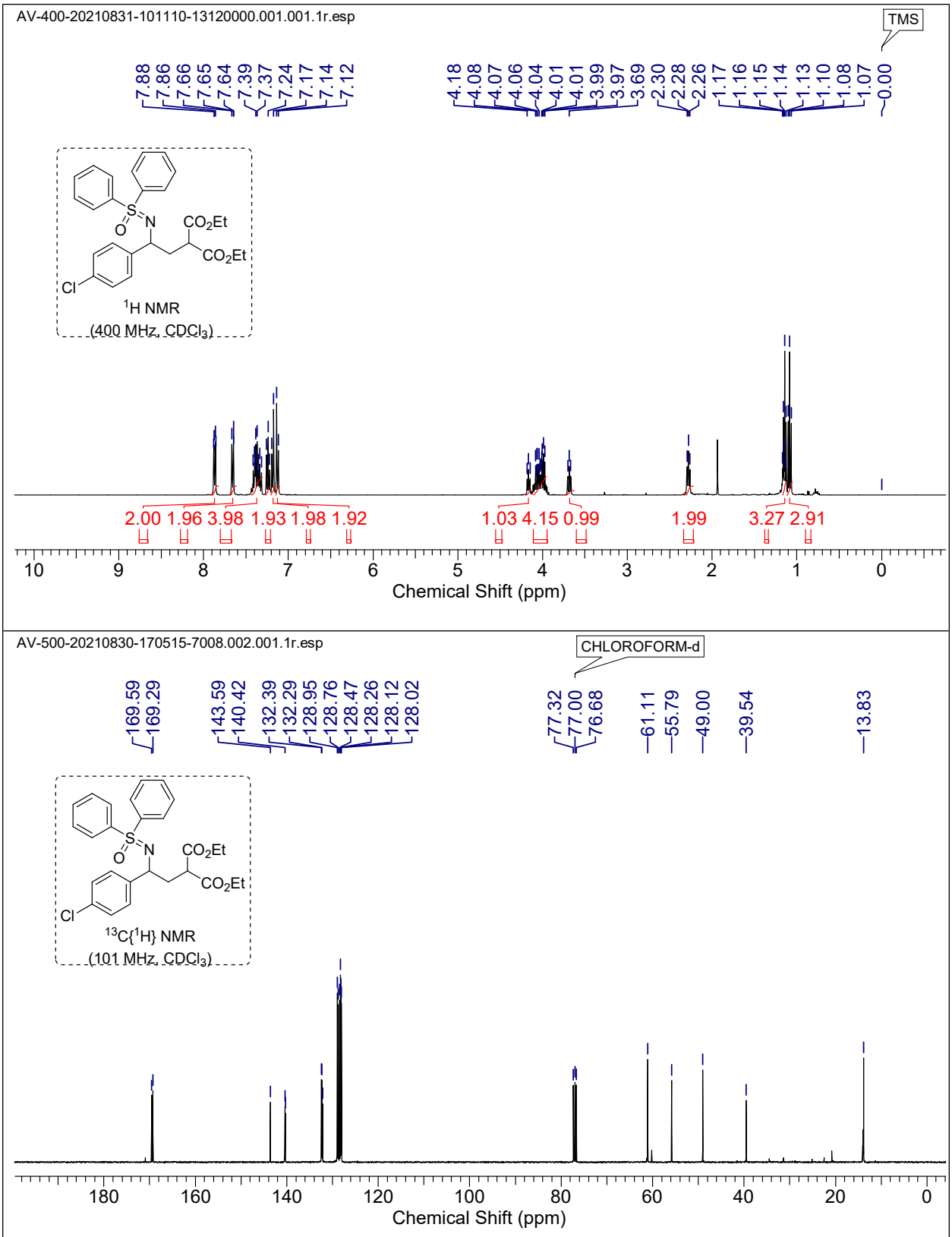
Diethyl 2-(2-((oxodiphenyl-l6-sulfaneylidene) amino)-2-phenylethyl) malonate (5a)



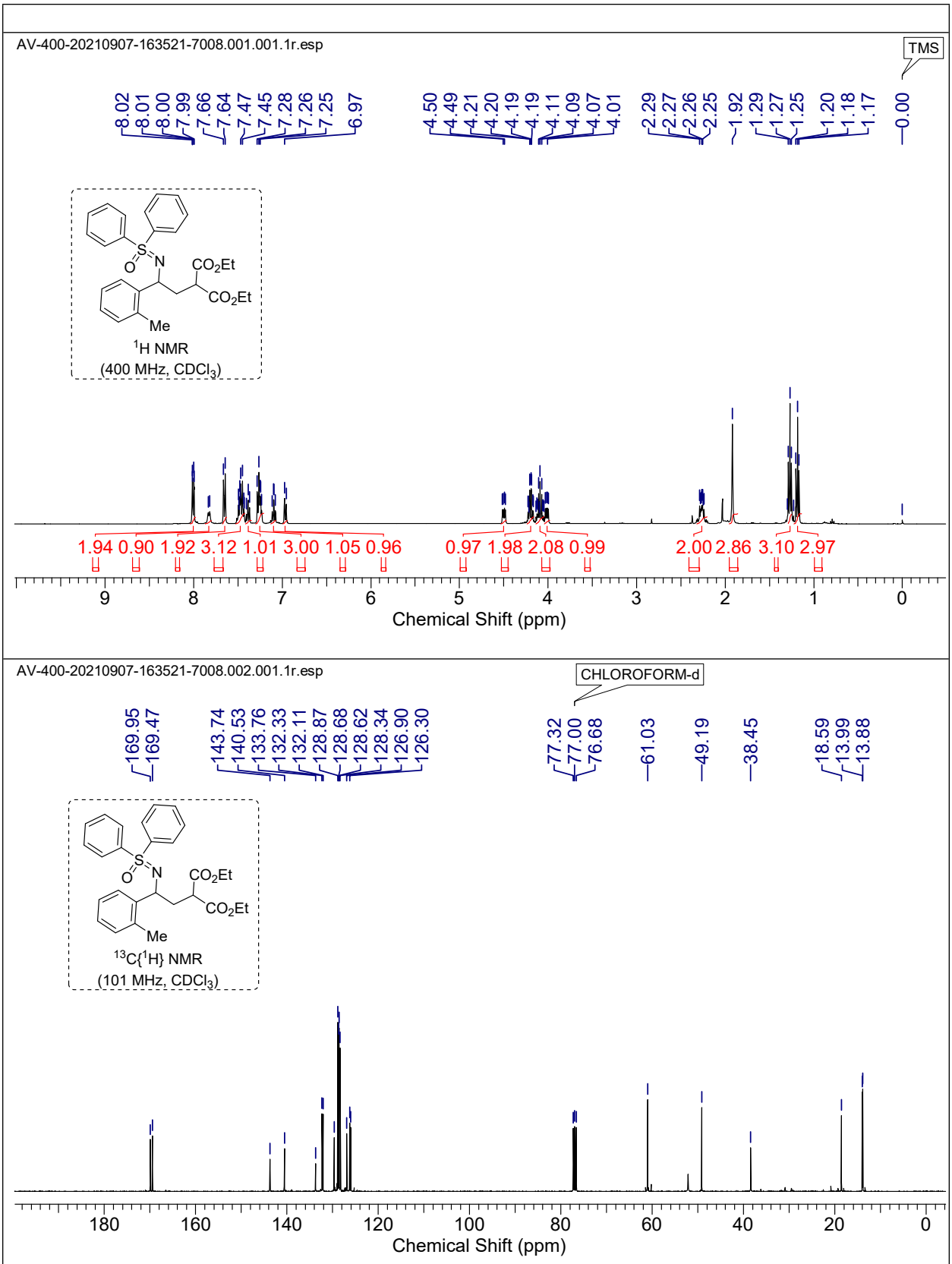
Diethyl 2-(2-(4-(methylthio) phenyl)-2-((oxodiphenyl-l6-sulfaneylidene) amino) ethyl) malonate (5b)



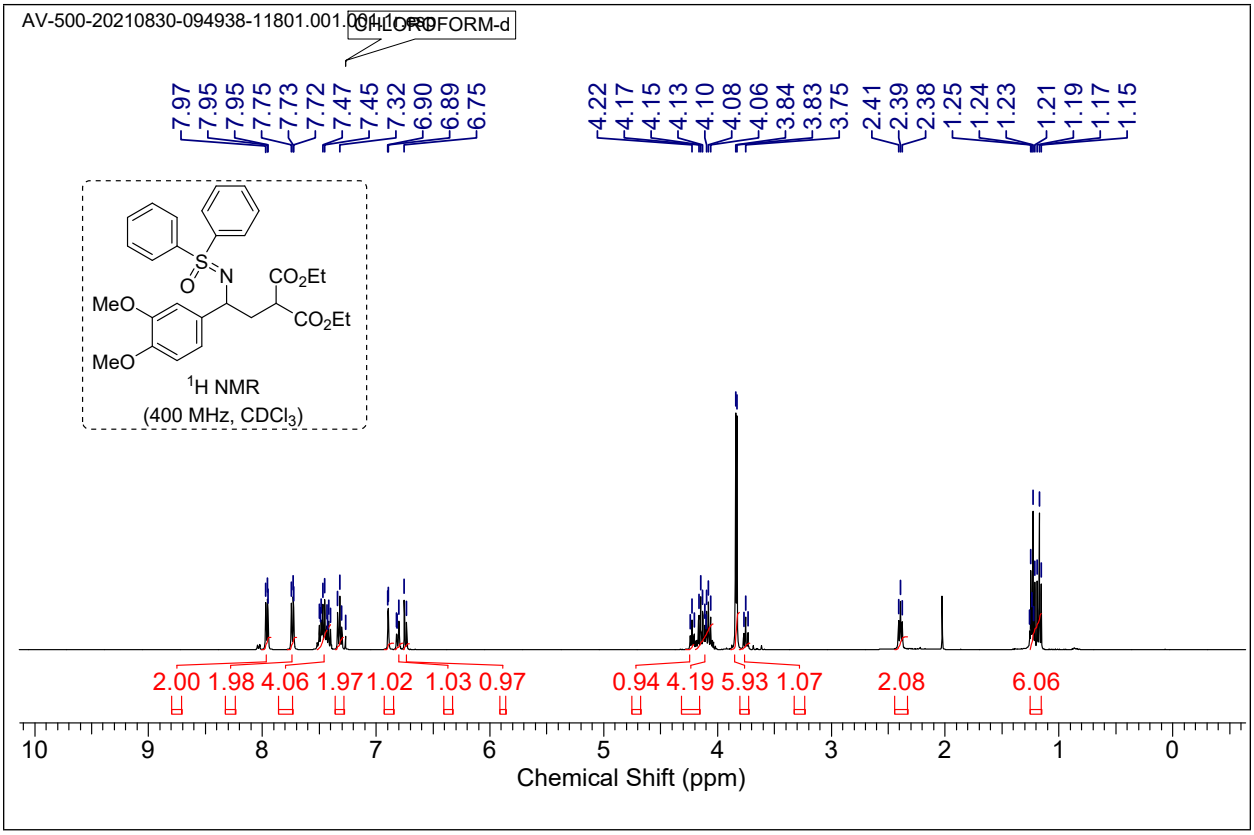
Diethyl 2-(2-(4-nitrophenyl)-2-((oxodiphenyl-l6-sulfaneylidene) amino) ethyl) malonate (5c)



Diethyl 2-(2-(4-chlorophenyl)-2-((oxodiphenyl-l6-sulfaneylidene) amino) ethyl) malonate (5d)



Diethyl 2-(2-((oxodiphenyl-l6-sulfaneylidene) amino)-2-(*o*-tolyl) ethyl) malonate (5e)


AV-500-20210830-094938-11801.001.001.1.1H.1.PROTON
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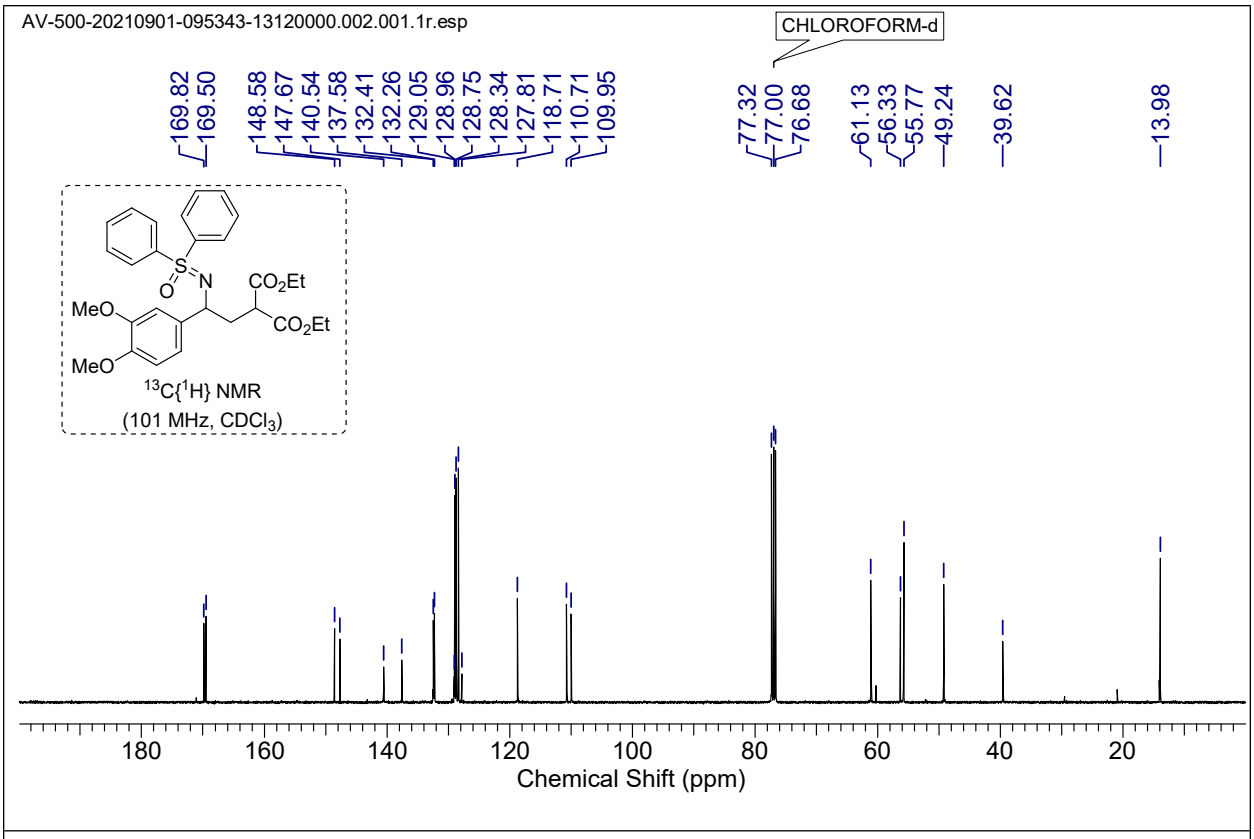
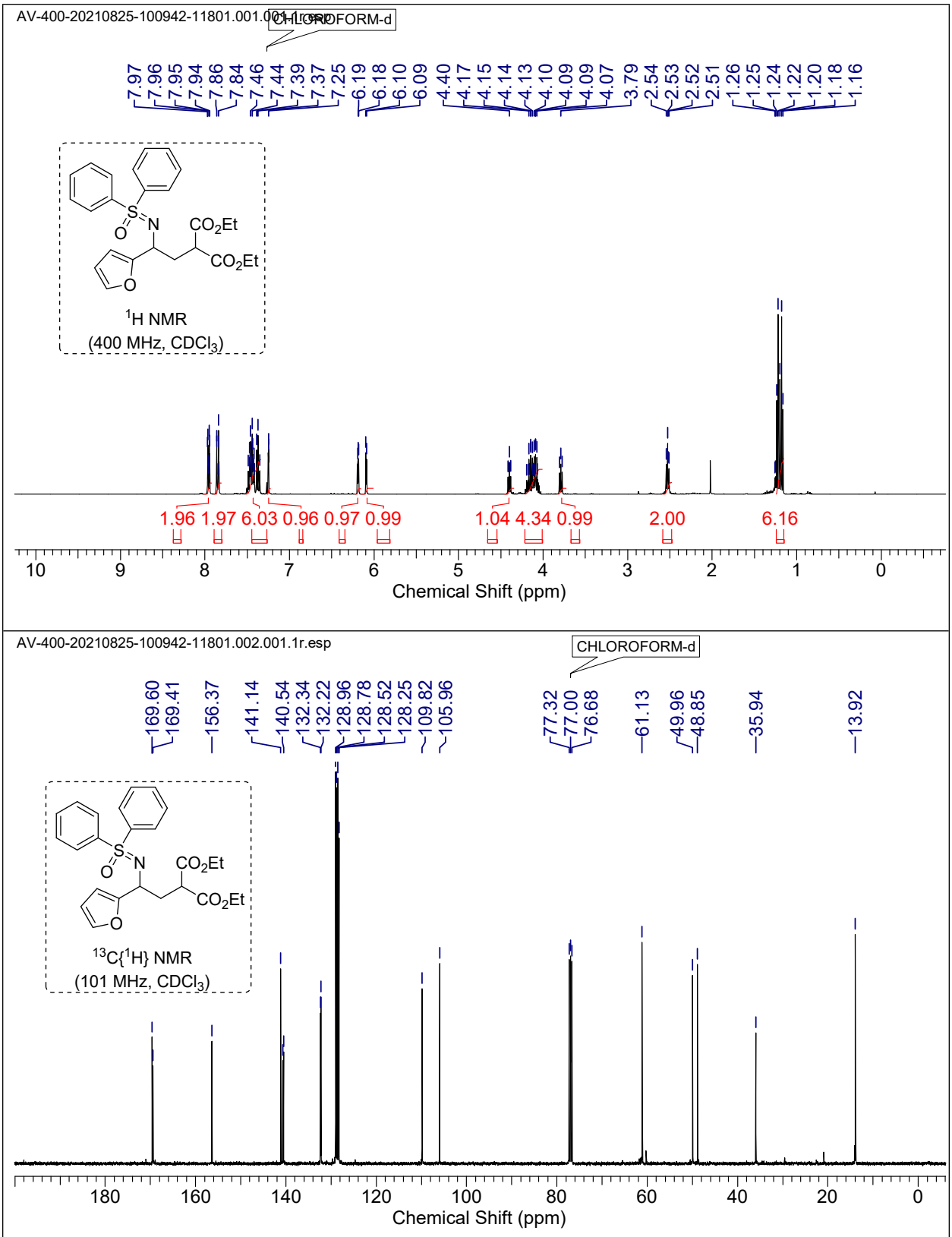
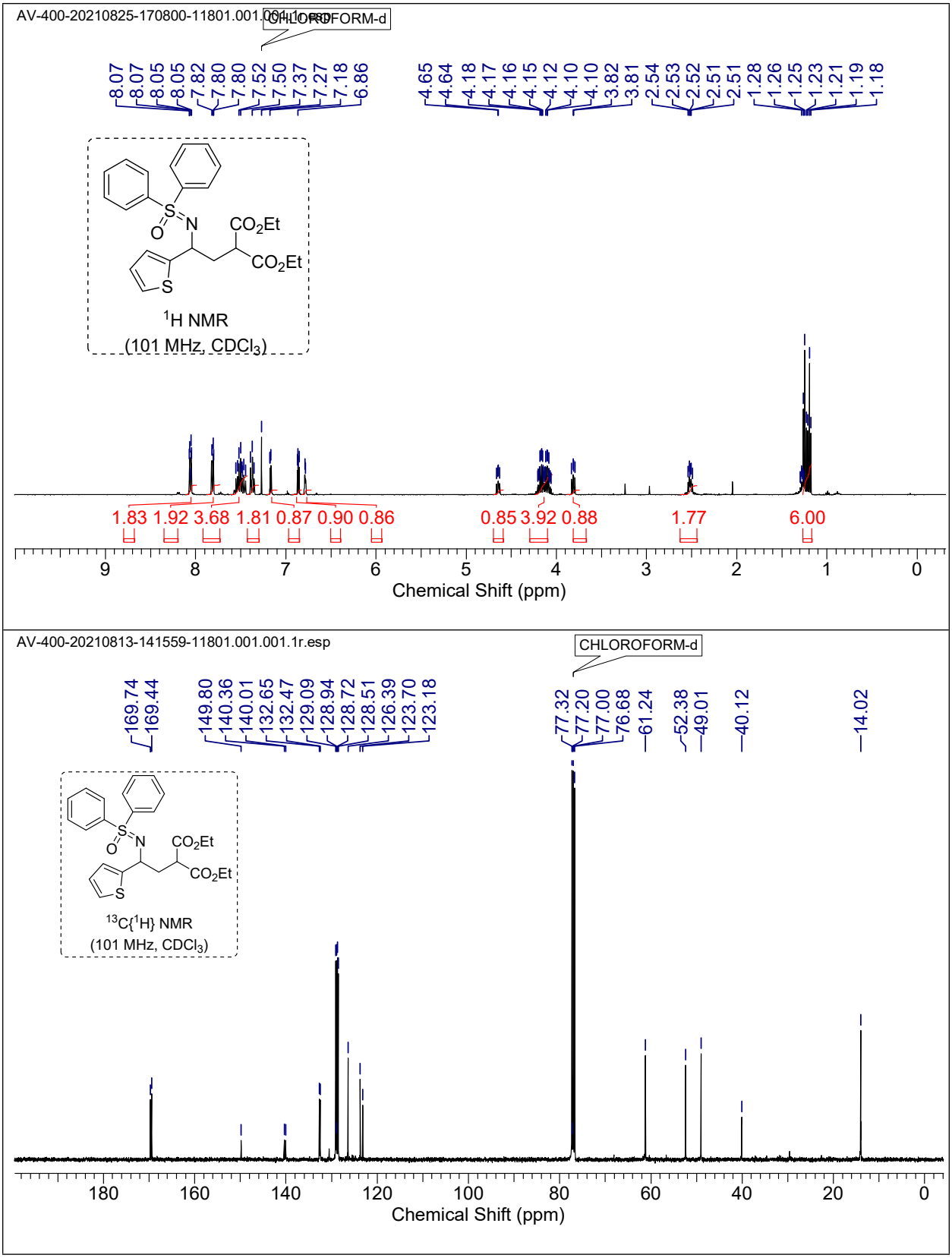
7.72
7.47
7.45
7.32
6.90
6.89
6.75
4.22
4.17
4.15
4.13
4.10
4.08
4.06
3.84
3.83
3.75
2.41
2.39
2.38
1.25
1.24
1.23
1.21
1.19
1.17
1.15
MeO
MeO
CO2Et
CO2Et
1H NMR
(400 MHz, CDCl3)
2.00 1.98 4.06 1.97 1.02 1.03 0.97
0.94 4.19 5.93 1.07
2.08
6.06
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)



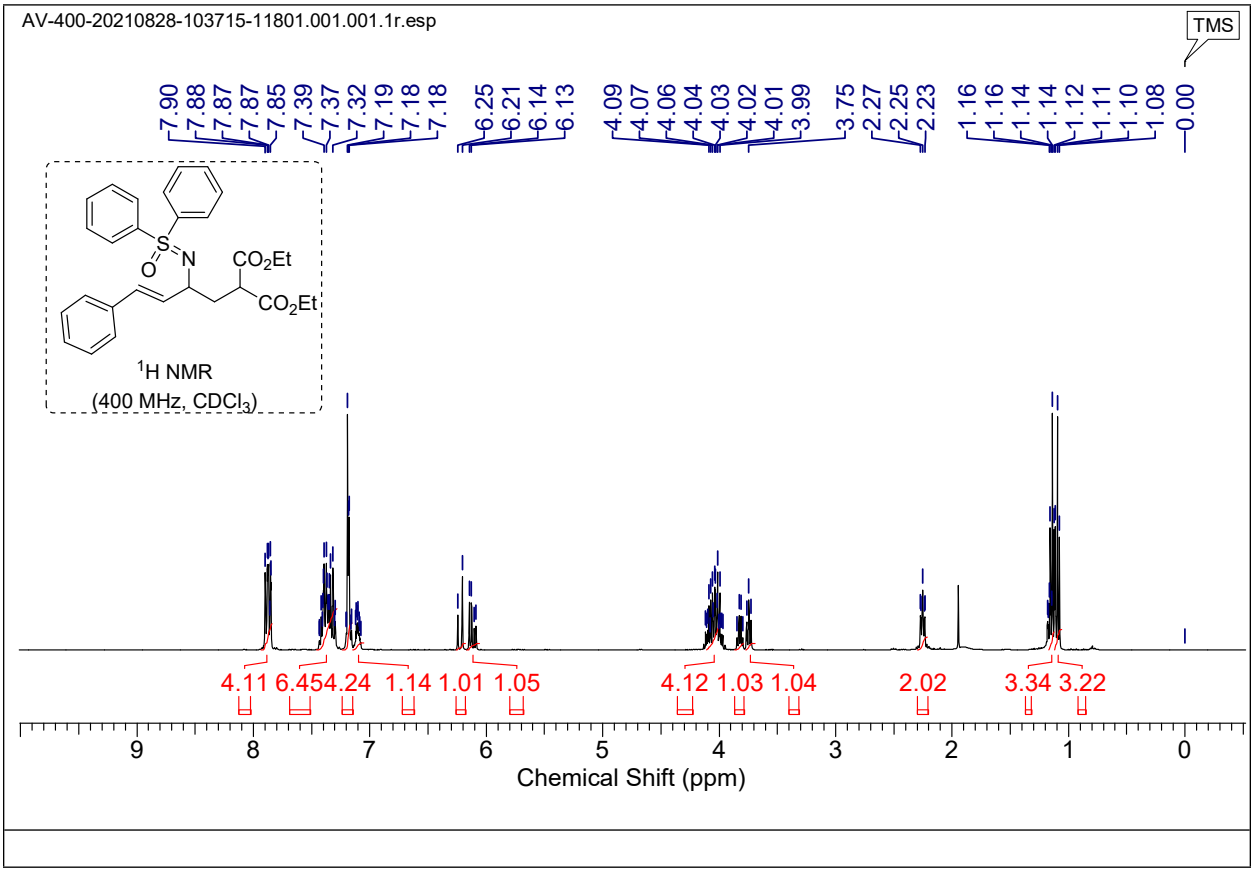
Diethyl 2-(2-(3,4-dimethoxyphenyl)-2-((oxodiphenyl-l6-sulfaneylidene) amino) ethyl) malonate (5f)

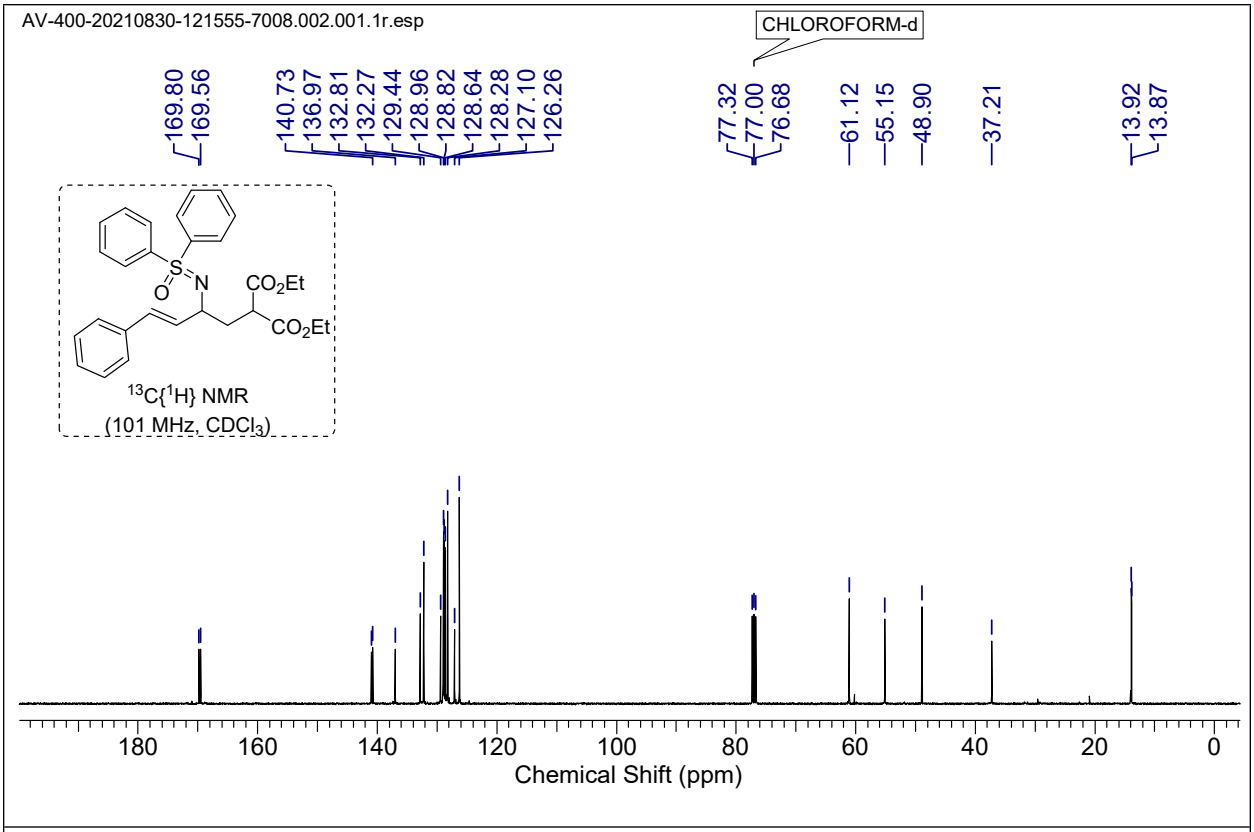


Diethyl 2-(2-(furan-2-yl)-2-((oxodiphenyl-l6-sulfaneylidene) amino) ethyl) malonate (5g)


AV-400-20210825-170800-11801.001.001.1r.esp
CHLOROFORM-d
8.07 8.07 8.05 8.05 7.82 7.80 7.80 7.52 7.50 7.37 7.27 7.18 6.86
4.65 4.64 4.18 4.17 4.16 4.15 4.12 4.10 4.10 3.82 3.81 2.54 2.53 2.52 2.51 2.51 1.28 1.26 1.25 1.23 1.21 1.19 1.18
CO2Et
CO2Et
1H NMR
(101 MHz, CDCl3)
1.83 1.92 3.68 1.81 0.87 0.90 0.86 0.85 3.92 0.88 1.77 6.00
Chemical Shift (ppm)
AV-400-20210813-141559-11801.001.001.1r.esp
CHLOROFORM-d
169.74 169.44 149.80 140.36 140.01 132.65 132.47 129.09 128.94 128.72 128.51 126.39 123.70 123.18
77.32 77.20 77.00 76.68 61.24 52.38 49.01 40.12 14.02
13C{1H} NMR
(101 MHz, CDCl3)
Chemical Shift (ppm)

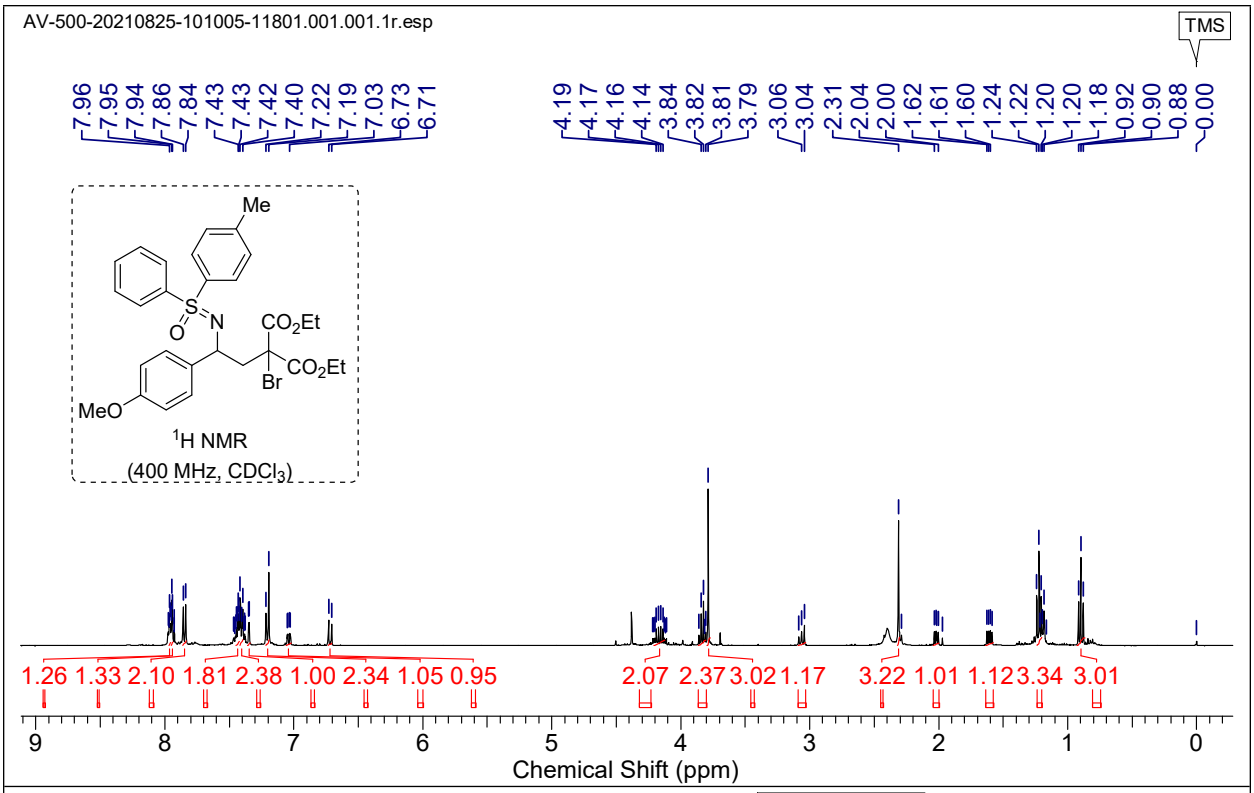
Diethyl 2-(2-((oxodiphenyl-l6-sulfaneylidene) amino)-2-(thiophen-2-yl) ethyl) malonate (5h)

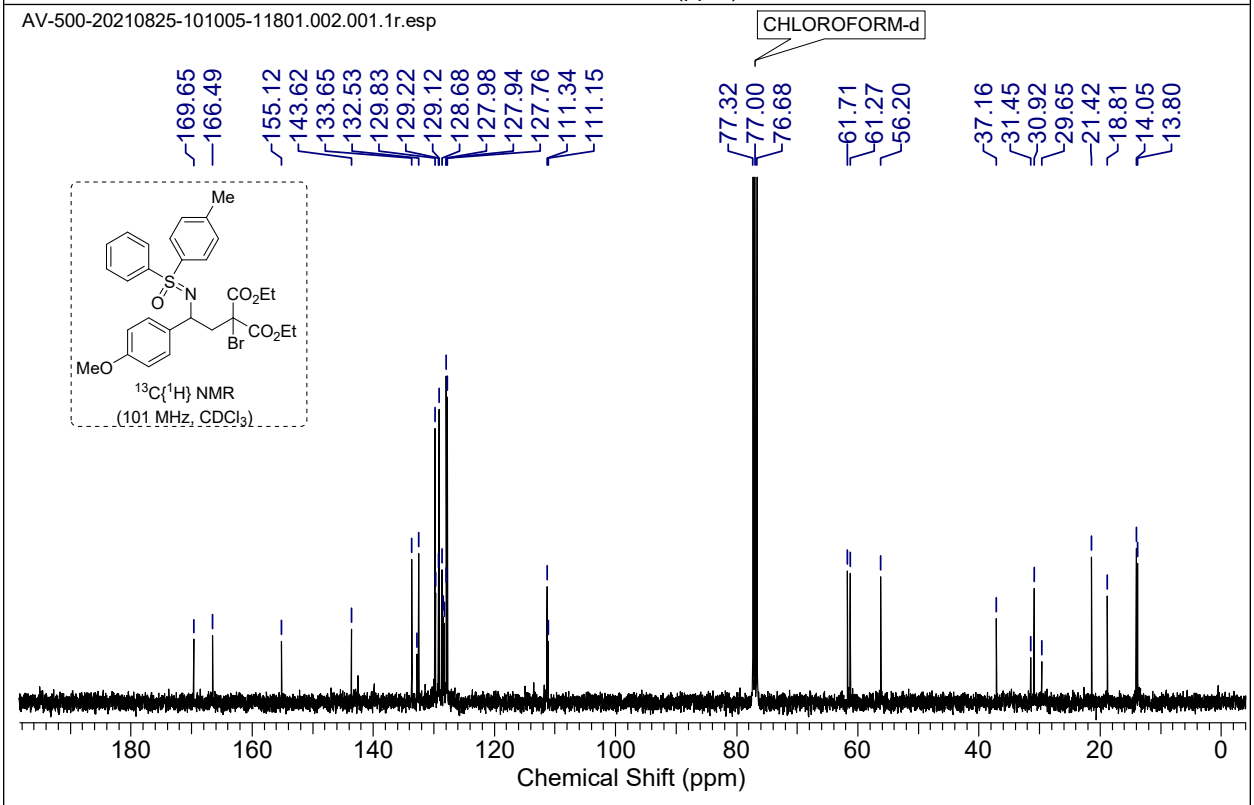




Diethyl (E)-2-(2-((oxodiphenyl-l6-sulfaneylidene) amino)-4-phenylbut-3-en-1-yl) malonate (5i)

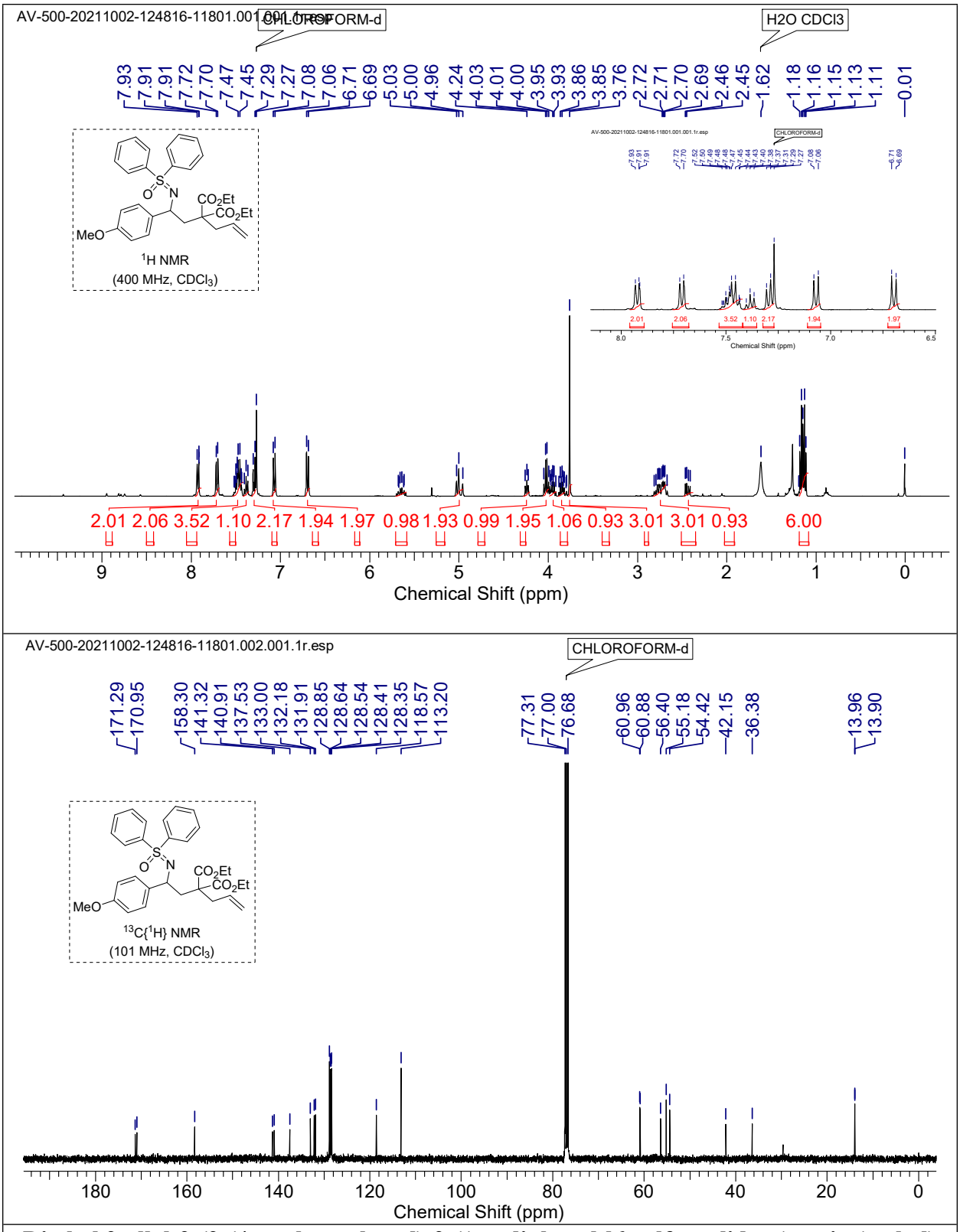
4. ^{1}H, and ^{13}C NMR spectrum of *γ*-sulfoximino, *α*- bromo malonic diester (6)





Diethyl 2-bromo-2-(2-(4-methoxyphenyl)-2-((oxo(phenyl)(*p*-tolyl)-l6-sulfaneylidene) amino) ethyl) malonate (6)

5. ^{1}H, and ^{13}C NMR spectrum of synthetic utility of product 3a (7)



Diethyl 2-allyl-2-(2-(4-methoxyphenyl)-2-((oxodiphenyl-l6-sulfaneylidene) amino) ethyl) malonate (7)