

# Index

<b>Table S1.</b> LC-HR-MS data for the characteristic compounds .....	1
<b>Figure S1.</b> LC-MS profiles of samples 7 (2015-70) in negative ion mode.....	2
<b>Figure S2.</b> LC-MS profiles of samples 8 (2015-71) in negative ion mode.....	4
<b>Figure S3.</b> $^1\text{H}$ NMR spectrum of <b>10</b> (measured in $\text{CDCl}_3$ , 500 MHz). ....	6
<b>Figure S4.</b> $^{13}\text{C}$ NMR spectrum of <b>10</b> (measured in $\text{CDCl}_3$ , 126 MHz). ....	7
<b>Figure S5.</b> $^1\text{H}$ - $^1\text{H}$ COSY spectrum of <b>10</b> (measured in $\text{CDCl}_3$ , 500 MHz). ....	8
<b>Figure S6.</b> HSQC spectrum of <b>10</b> (measured in $\text{CDCl}_3$ , 500 MHz). ....	9
<b>Figure S7.</b> HMBC spectrum of <b>10</b> (measured in $\text{CDCl}_3$ , 500 MHz). ....	10
<b>Figure S8.</b> NOESY spectrum of <b>10</b> (measured in $\text{CDCl}_3$ , 500 MHz). ....	11
<b>Figure S9.</b> $^1\text{H}$ NMR spectrum of <b>17</b> (measured in $\text{CDCl}_3$ , 500 MHz). ....	12
<b>Figure S10.</b> $^{13}\text{C}$ NMR spectrum of <b>17</b> (measured in $\text{CDCl}_3$ , 126 MHz). ....	13
<b>Figure S11.</b> $^1\text{H}$ - $^1\text{H}$ COSY spectrum of <b>17</b> (measured in $\text{CDCl}_3$ , 500 MHz). ....	14
<b>Figure S12.</b> HSQC spectrum of <b>17</b> (measured in $\text{CDCl}_3$ , 500 MHz). ....	15
<b>Figure S13.</b> HMBC spectrum of <b>17</b> (measured in $\text{CDCl}_3$ , 500 MHz). ....	16
<b>Figure S14.</b> NOESY spectrum of <b>17</b> (measured in $\text{CDCl}_3$ , 500 MHz). ....	17
<b>Figure S15.</b> $^1\text{H}$ NMR spectrum of <b>18</b> (measured in $\text{CDCl}_3$ , 500 MHz). ....	18
<b>Figure S16.</b> $^{13}\text{C}$ NMR spectrum of <b>18</b> (measured in $\text{CDCl}_3$ , 126 MHz). ....	19

<b>Figure S17.</b> $^1\text{H}$ - $^1\text{H}$ COSY spectrum of <b>18</b> (measured in $\text{CDCl}_3$ , 500 MHz).	20
<b>Figure S18.</b> HSQC spectrum of <b>18</b> (measured in $\text{CDCl}_3$ , 500 MHz)	21
<b>Figure S19.</b> HMBC spectrum of <b>18</b> (measured in $\text{CDCl}_3$ , 500 MHz)	22
<b>Figure S20.</b> NOESY spectrum of <b>18</b> (measured in $\text{CDCl}_3$ , 500 MHz)	23
<b>Figure S21.</b> $^1\text{H}$ NMR spectrum of <b>24</b> (measured in $\text{CDCl}_3$ , 500 MHz)	24
<b>Figure S22.</b> $^{13}\text{C}$ NMR spectrum of <b>24</b> (measured in $\text{CDCl}_3$ , 126 MHz)	25
<b>Figure S23.</b> $^1\text{H}$ - $^1\text{H}$ COSY spectrum of <b>24</b> (measured in $\text{CDCl}_3$ , 500 MHz)	26
<b>Figure S24.</b> HSQC spectrum of <b>24</b> (measured in $\text{CDCl}_3$ , 500 MHz)	27
<b>Figure S25.</b> HMBC spectrum of <b>24</b> (measured in $\text{CDCl}_3$ , 500 MHz)	28
<b>Figure S26.</b> NOESY spectrum of <b>24</b> (measured in $\text{CDCl}_3$ , 500 MHz)	29
<b>Figure S27.</b> $^1\text{H}$ NMR spectrum of <b>31</b> (measured in $\text{CDCl}_3$ , 500 MHz)	30
<b>Figure S28.</b> $^{13}\text{C}$ NMR spectrum of <b>31</b> (measured in $\text{CDCl}_3$ , 126 MHz)	31
<b>Figure S29.</b> $^1\text{H}$ - $^1\text{H}$ COSY spectrum of <b>31</b> (measured in $\text{CDCl}_3$ , 500 MHz)	32
<b>Figure S30.</b> HSQC spectrum of <b>31</b> (measured in $\text{CDCl}_3$ , 500 MHz)	33
<b>Figure S31.</b> HMBC spectrum of <b>31</b> (measured in $\text{CDCl}_3$ , 500 MHz)	34
<b>Figure S32.</b> NOESY spectrum of <b>31</b> (measured in $\text{CDCl}_3$ , 500 MHz)	35
<b>Figure S33.</b> $^1\text{H}$ NMR spectrum of <b>36</b> (measured in $\text{CDCl}_3$ , 500 MHz, 298 K)	36
<b>Figure S34.</b> $^1\text{H}$ NMR spectrum of <b>36</b> (measured in $\text{CDCl}_3$ , 400 MHz, 233 K)	37

<b>Figure S35.</b> $^{13}\text{C}$ NMR spectrum of <b>36</b> (measured in $\text{CDCl}_3$ , 100 MHz, 233 K).	38
<b>Figure S36.</b> $^1\text{H}$ - $^1\text{H}$ COSY spectrum of <b>36</b> (measured in $\text{CDCl}_3$ , 400 MHz, 233 K)	39
<b>Figure S37.</b> HSQC spectrum of <b>36</b> (measured in $\text{CDCl}_3$ , 400 MHz, 233 K)	40
<b>Figure S38.</b> HMBC spectrum of <b>36</b> (measured in $\text{CDCl}_3$ , 400 MHz, 233 K)	41
<b>Figure S39.</b> NOESY spectrum of <b>36</b> (measured in $\text{CDCl}_3$ , 400 MHz, 233 K)	42
<b>Figure S40.</b> $^1\text{H}$ NMR spectrum of <b>40</b> (measured in $\text{CDCl}_3$ , 500 MHz, 298 K)	43
<b>Figure S41.</b> $^1\text{H}$ NMR spectrum of <b>40</b> (measured in $\text{CDCl}_3$ , 400 MHz, 233 K)	44
<b>Figure S42.</b> $^1\text{H}$ - $^1\text{H}$ COSY spectrum of <b>40</b> (measured in $\text{CDCl}_3$ , 400 MHz, 233 K)	45
<b>Figure S43.</b> $^1\text{H}$ NMR spectrum of <b>45</b> (measured in $\text{CDCl}_3$ , 500 MHz)	46
<b>Figure S44.</b> $^{13}\text{C}$ NMR spectrum of <b>45</b> (measured in $\text{CDCl}_3$ , 126 MHz)	47
<b>Figure S45.</b> $^1\text{H}$ - $^1\text{H}$ COSY spectrum of <b>45</b> (measured in $\text{CDCl}_3$ , 500 MHz)	48
<b>Figure S46.</b> HSQC spectrum of <b>45</b> (measured in $\text{CDCl}_3$ , 500 MHz)	49
<b>Figure S47.</b> HMBC spectrum of <b>45</b> (measured in $\text{CDCl}_3$ , 500 MHz)	50
<b>Figure S48.</b> NOESY spectrum of <b>45</b> (measured in $\text{CDCl}_3$ , 500 MHz)	51
<b>Figure S49.</b> $^1\text{H}$ NMR spectrum of <b>50</b> (measured in $\text{CDCl}_3$ , 500 MHz)	52
<b>Figure S50.</b> $^{13}\text{C}$ NMR spectrum of <b>50</b> (measured in $\text{CDCl}_3$ , 126 MHz)	53
<b>Figure S51.</b> $^1\text{H}$ - $^1\text{H}$ COSY spectrum of <b>50</b> (measured in $\text{CDCl}_3$ , 500 MHz)	54
<b>Figure S52.</b> HSQC spectrum of <b>50</b> (measured in $\text{CDCl}_3$ , 500 MHz)	55

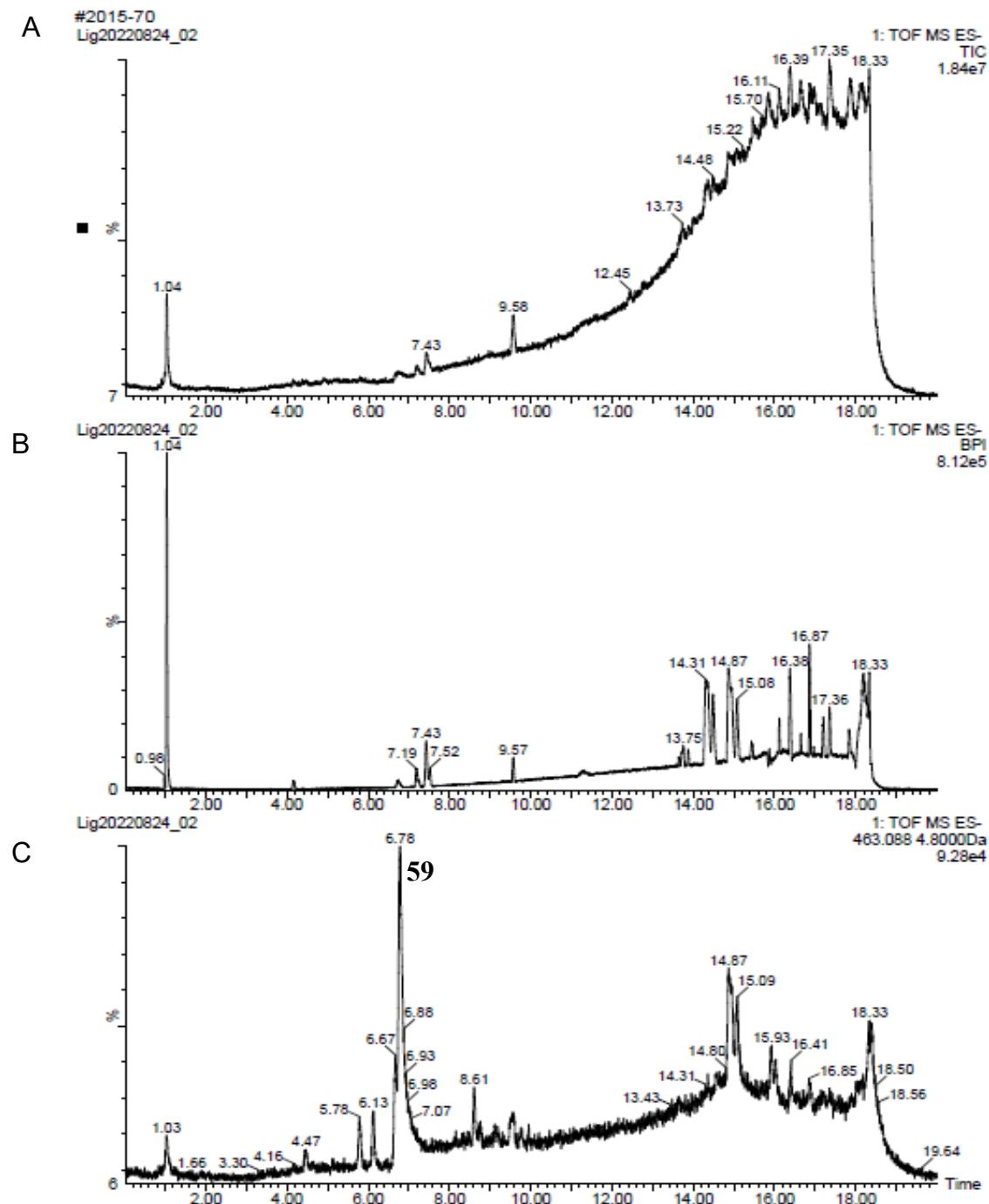
<b>Figure S53.</b> HMBC spectrum of <b>50</b> (measured in CDCl <sub>3</sub> , 500 MHz).	56
<b>Figure S54.</b> NOESY spectrum of <b>50</b> (measured in CDCl <sub>3</sub> , 500 MHz)	57
<b>Figure S55.</b> <sup>1</sup> H NMR spectrum of <b>51</b> (measured in CDCl <sub>3</sub> , 500 MHz).	58
<b>Figure S56.</b> <sup>13</sup> C NMR spectrum of <b>51</b> (measured in CDCl <sub>3</sub> , 126 MHz).	59
<b>Figure S57.</b> <sup>1</sup> H- <sup>1</sup> H COSY spectrum of <b>51</b> (measured in CDCl <sub>3</sub> , 500 MHz).	60
<b>Figure S58.</b> HSQC spectrum of <b>51</b> (measured in CDCl <sub>3</sub> , 500 MHz).	61
<b>Figure S59.</b> HMBC spectrum of <b>51</b> (measured in CDCl <sub>3</sub> , 500 MHz).	62
<b>Figure S60.</b> NOESY spectrum of <b>51</b> (measured in CDCl <sub>3</sub> , 500 MHz).	63
<b>Figure S61.</b> <sup>1</sup> H NMR spectrum of <b>53</b> (measured in CDCl <sub>3</sub> , 500 MHz).	64
<b>Figure S62.</b> <sup>13</sup> C NMR spectrum of <b>53</b> (measured in CDCl <sub>3</sub> , 126 MHz).	65
<b>Figure S63.</b> <sup>1</sup> H- <sup>1</sup> H COSY spectrum of <b>53</b> (measured in CDCl <sub>3</sub> , 500 MHz).	66
<b>Figure S64.</b> HSQC spectrum of <b>53</b> (measured in CDCl <sub>3</sub> , 500 MHz).	67
<b>Figure S65.</b> HMBC spectrum of <b>53</b> (measured in CDCl <sub>3</sub> , 500 MHz).	68
<b>Figure S66.</b> NOESY spectrum of <b>53</b> (measured in CDCl <sub>3</sub> , 500 MHz).	69
<b>Figure S67.</b> <sup>1</sup> H NMR spectrum of <b>54</b> (measured in CDCl <sub>3</sub> , 500 MHz).	70
<b>Figure S68.</b> <sup>13</sup> C NMR spectrum of <b>54</b> (measured in CDCl <sub>3</sub> , 126 MHz).	71
<b>Figure S69.</b> <sup>1</sup> H- <sup>1</sup> H COSY spectrum of <b>54</b> (measured in CDCl <sub>3</sub> , 500 MHz).	72
<b>Figure S70.</b> HSQC spectrum of <b>54</b> (measured in CDCl <sub>3</sub> , 500 MHz).	73

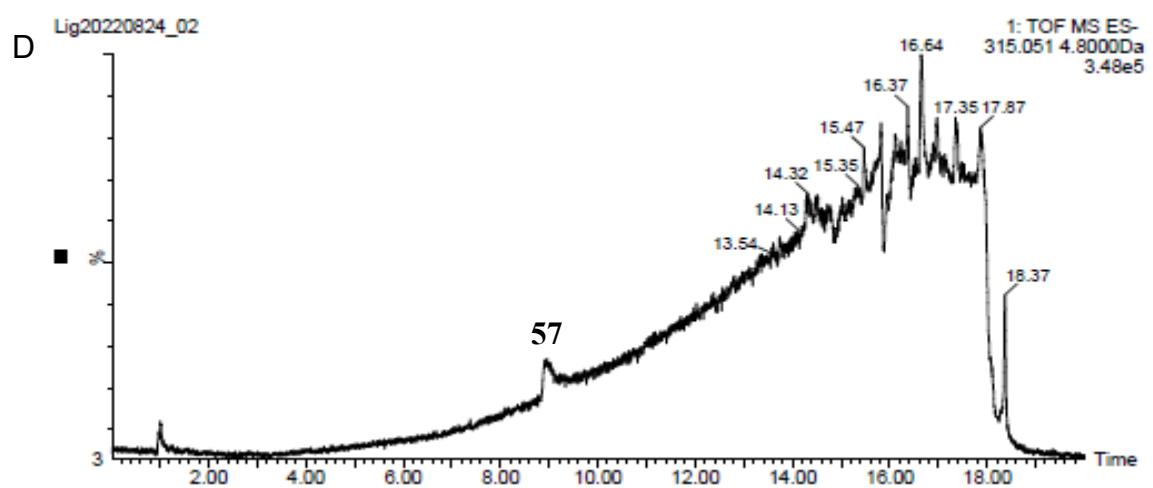
<b>Figure S71.</b> HMBC spectrum of <b>54</b> (measured in CDCl <sub>3</sub> , 500 MHz).	74
<b>Figure S72.</b> NOESY spectrum of <b>54</b> (measured in CDCl <sub>3</sub> , 500 MHz)	75
<b>Figure S73.</b> <sup>1</sup> H NMR spectrum of <b>62</b> (measured in CDCl <sub>3</sub> , 500 MHz).	76
<b>Figure S74.</b> <sup>13</sup> C NMR spectrum of <b>62</b> (measured in CDCl <sub>3</sub> , 126 MHz).	77
<b>Figure S75.</b> <sup>1</sup> H- <sup>1</sup> H COSY spectrum of <b>62</b> (measured in CDCl <sub>3</sub> , 500 MHz).	78
<b>Figure S76.</b> HSQC spectrum of <b>62</b> (measured in CDCl <sub>3</sub> , 500 MHz)	79
<b>Figure S77.</b> HMBC spectrum of <b>62</b> (measured in CDCl <sub>3</sub> , 500 MHz).	80
<b>Figure S78.</b> NOESY spectrum of <b>62</b> (measured in CDCl <sub>3</sub> , 500 MHz)	81
<b>Figure S79.</b> Experimental and calculated ECD spectra of <b>10</b> .	82

**Table S1.** LC-HR-MS data for the characteristic compounds.

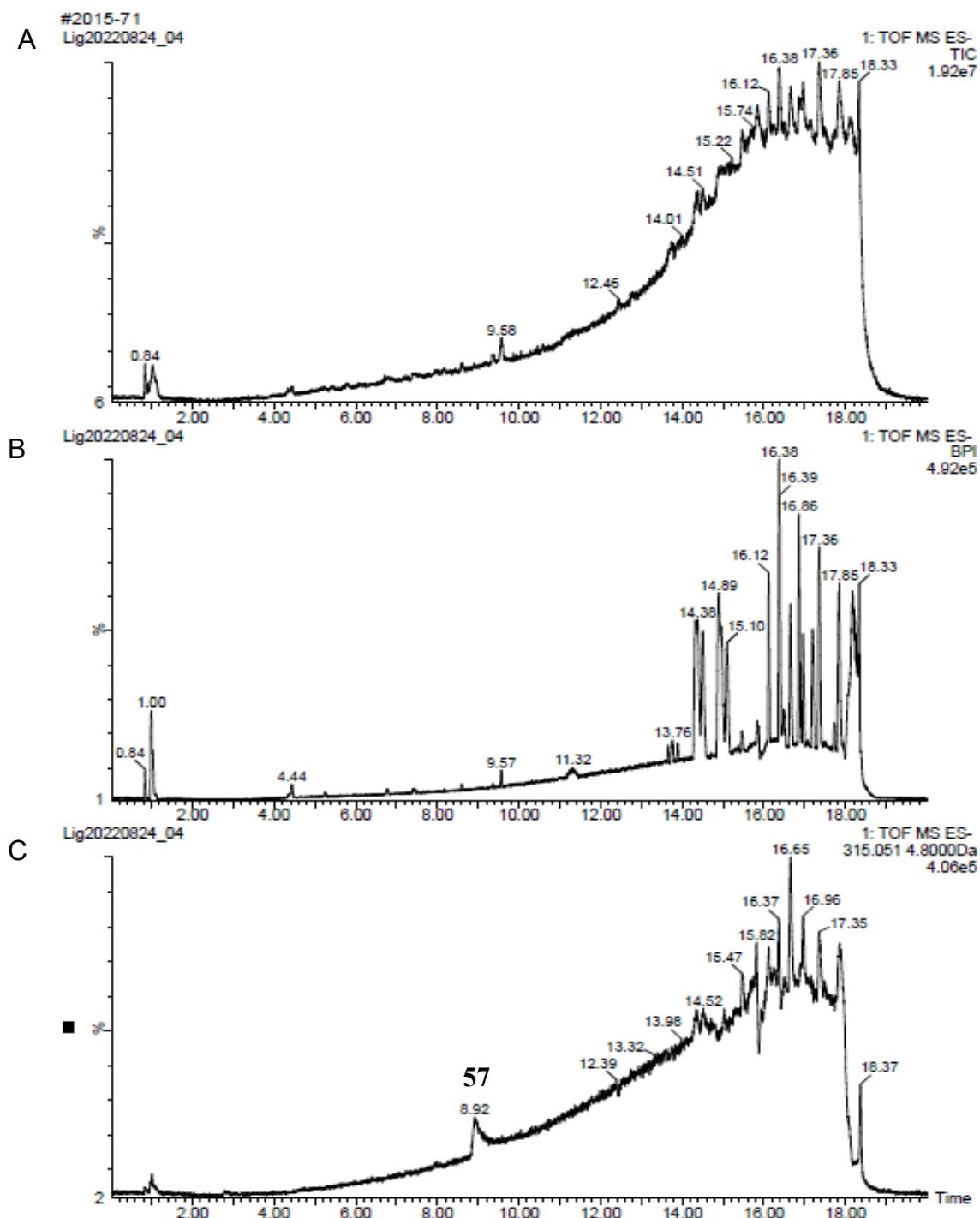
Compound	<i>t</i> <sub>R</sub> (min)	Ions mode	Formula	Detected	Calculated	Error (mDa)
<b>1</b>	8.56	[M+Na] <sup>+</sup>	C <sub>22</sub> H <sub>28</sub> O <sub>8</sub>	443.1686	443.1682	0.4
<b>2</b>	9.14	[M+Na] <sup>+</sup>	C <sub>22</sub> H <sub>28</sub> O <sub>9</sub>	443.1685	443.1682	0.3
<b>3</b>	9.65	[M+Na] <sup>+</sup>	C <sub>22</sub> H <sub>28</sub> O <sub>7</sub>	427.1732	427.1733	-0.1
<b>4</b>	10.02	[M+Na] <sup>+</sup>	C <sub>22</sub> H <sub>28</sub> O <sub>7</sub>	427.1735	427.1733	0.2
<b>11</b>	9.02	[M+Na] <sup>+</sup>	C <sub>22</sub> H <sub>26</sub> O <sub>8</sub>	441.1532	441.1525	0.7
<b>16</b>	6.11	[M+Na] <sup>+</sup>	C <sub>22</sub> H <sub>28</sub> O <sub>10</sub>	475.1572	475.1580	-0.8
<b>25</b>	10.62	[M+Na] <sup>+</sup>	C <sub>22</sub> H <sub>28</sub> O <sub>7</sub>	427.1735	427.1733	0.2
<b>26</b>	9.51	[M+Na] <sup>+</sup>	C <sub>20</sub> H <sub>26</sub> O <sub>6</sub>	385.1627	385.1627	0.0
<b>27</b>	10.88	[M+Na] <sup>+</sup>	C <sub>20</sub> H <sub>26</sub> O <sub>5</sub>	369.1687	369.1678	0.9
<b>28</b>	10.73	[M+Na] <sup>+</sup>	C <sub>20</sub> H <sub>26</sub> O <sub>5</sub>	369.1682	369.1678	0.4
<b>29</b>	10.65	[M+Na] <sup>+</sup>	C <sub>20</sub> H <sub>26</sub> O <sub>5</sub>	369.1673	369.1678	-0.5
<b>30</b>	12.67	[M+Na] <sup>+</sup>	C <sub>20</sub> H <sub>26</sub> O <sub>4</sub>	353.1736	353.1729	0.7
<b>37</b>	9.71	[M+Na] <sup>+</sup>	C <sub>24</sub> H <sub>30</sub> O <sub>9</sub>	485.1796	485.1788	0.8
<b>38</b>	7.93	[M+Na] <sup>+</sup>	C <sub>22</sub> H <sub>28</sub> O <sub>8</sub>	443.1685	443.1682	0.3
<b>44</b>	6.48	[M+Na] <sup>+</sup>	C <sub>20</sub> H <sub>26</sub> O <sub>7</sub>	401.1581	401.1576	0.5
<b>55</b>	8.70	[M+Na] <sup>+</sup>	C <sub>22</sub> H <sub>26</sub> O <sub>8</sub>	441.1524	441.1525	-0.1
<b>57</b>	8.94	[M+Na] <sup>+</sup>	C <sub>16</sub> H <sub>12</sub> O <sub>7</sub>	339.0475	339.0481	-0.6
<b>59</b>	6.77	[M+Na] <sup>+</sup>	C <sub>21</sub> H <sub>20</sub> O <sub>12</sub>	487.085	487.0852	-0.2
<b>57</b>	8.94	[M-H] <sup>-</sup>	C <sub>16</sub> H <sub>12</sub> O <sub>7</sub>	315.0505	315.0505	0.0
<b>59</b>	6.77	[M-H] <sup>-</sup>	C <sub>21</sub> H <sub>20</sub> O <sub>12</sub>	463.0877	463.0877	0.0

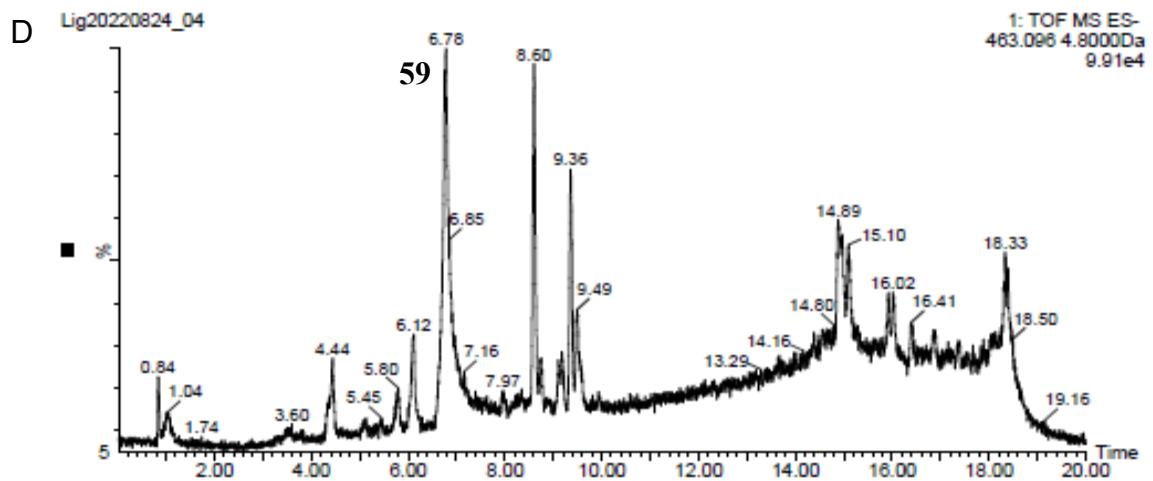
**Figure S1.** LC-MS profiles of sample 7 (2015-70) in negative ion mode for detecting flavonoidal constituents, **57** and **59**. A: total ion chromatogram; B: base peak ion chromatogram; C: extracted ion chromatogram of  $m/z$  463.09; D: extracted ion chromatogram of  $m/z$  315.05.



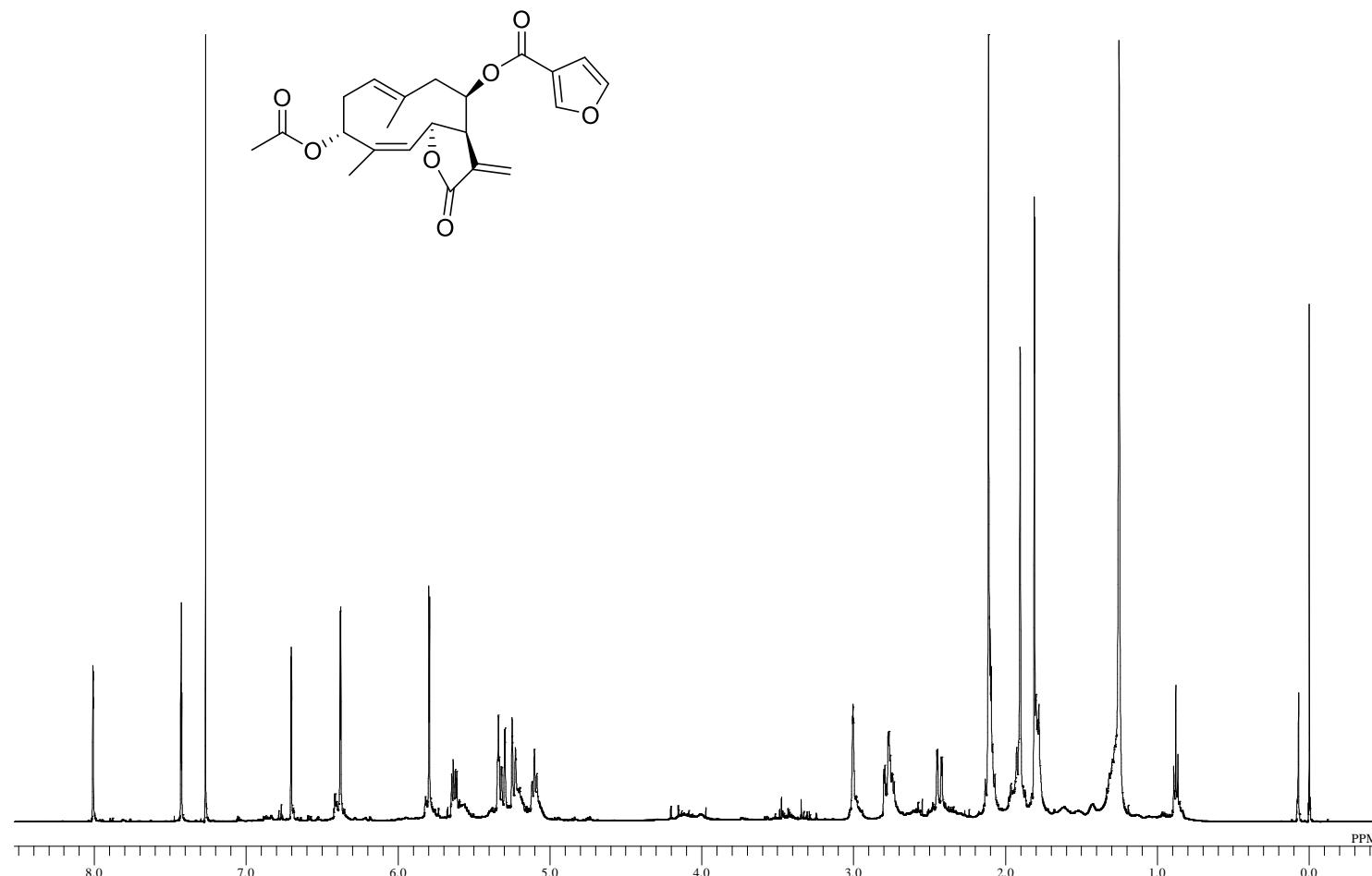


**Figure S2.** LC-MS profiles of sample 8 (2015-71) in negative ion mode for detecting flavonoidal constituents, **57** and **59**. A: total ion chromatogram; B: base peak ion chromatogram; C: extracted ion chromatogram of  $m/z$  315.05; D: extracted ion chromatogram of  $m/z$  463.09.

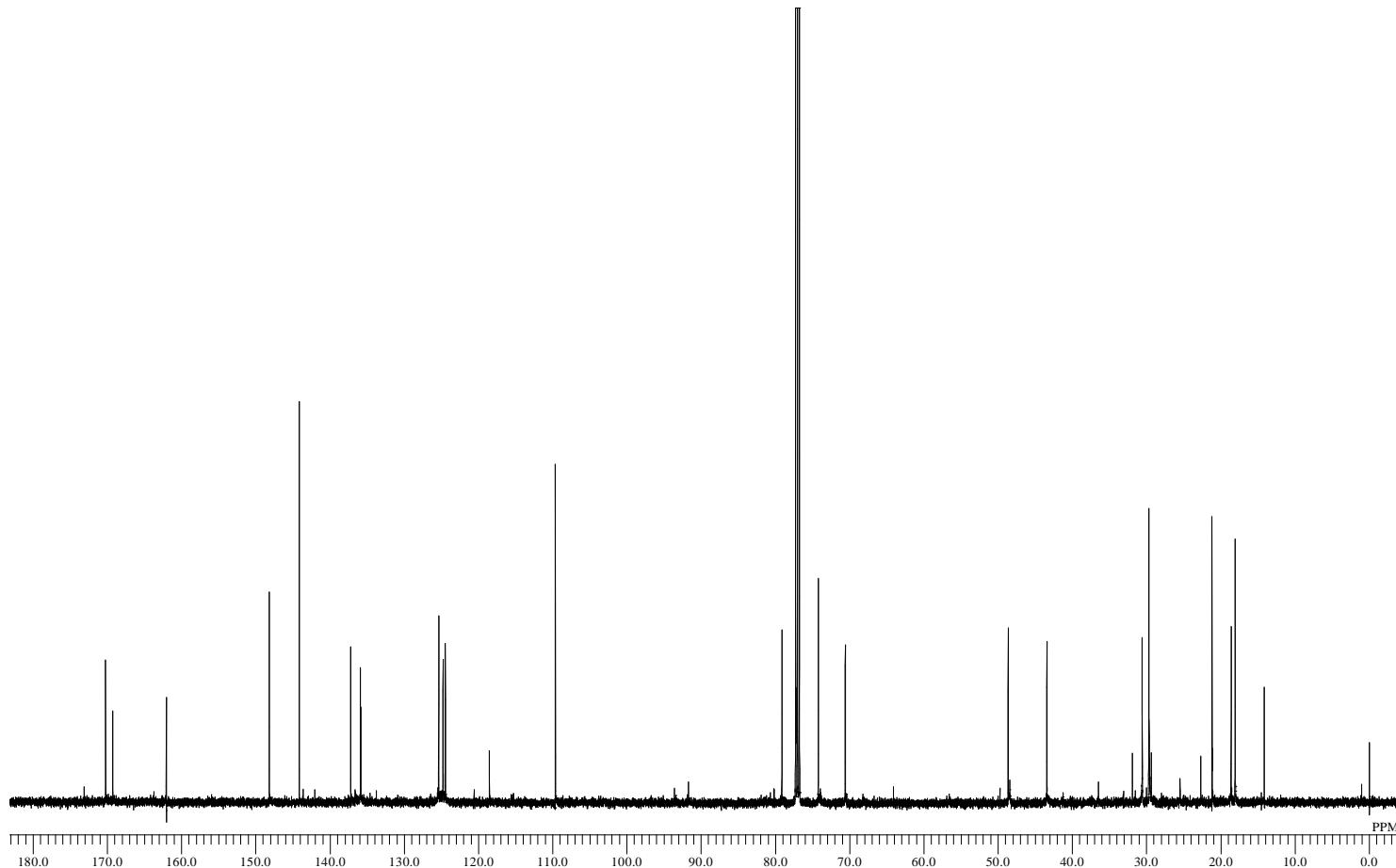




**Figure S3.**  $^1\text{H}$  NMR spectrum of **10** (measured in  $\text{CDCl}_3$ , 500 MHz).



**Figure S4.**  $^{13}\text{C}$  NMR spectrum of **10** (measured in  $\text{CDCl}_3$ , 126 MHz).



**Figure S5.**  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of **10** (measured in  $\text{CDCl}_3$ , 500 MHz).

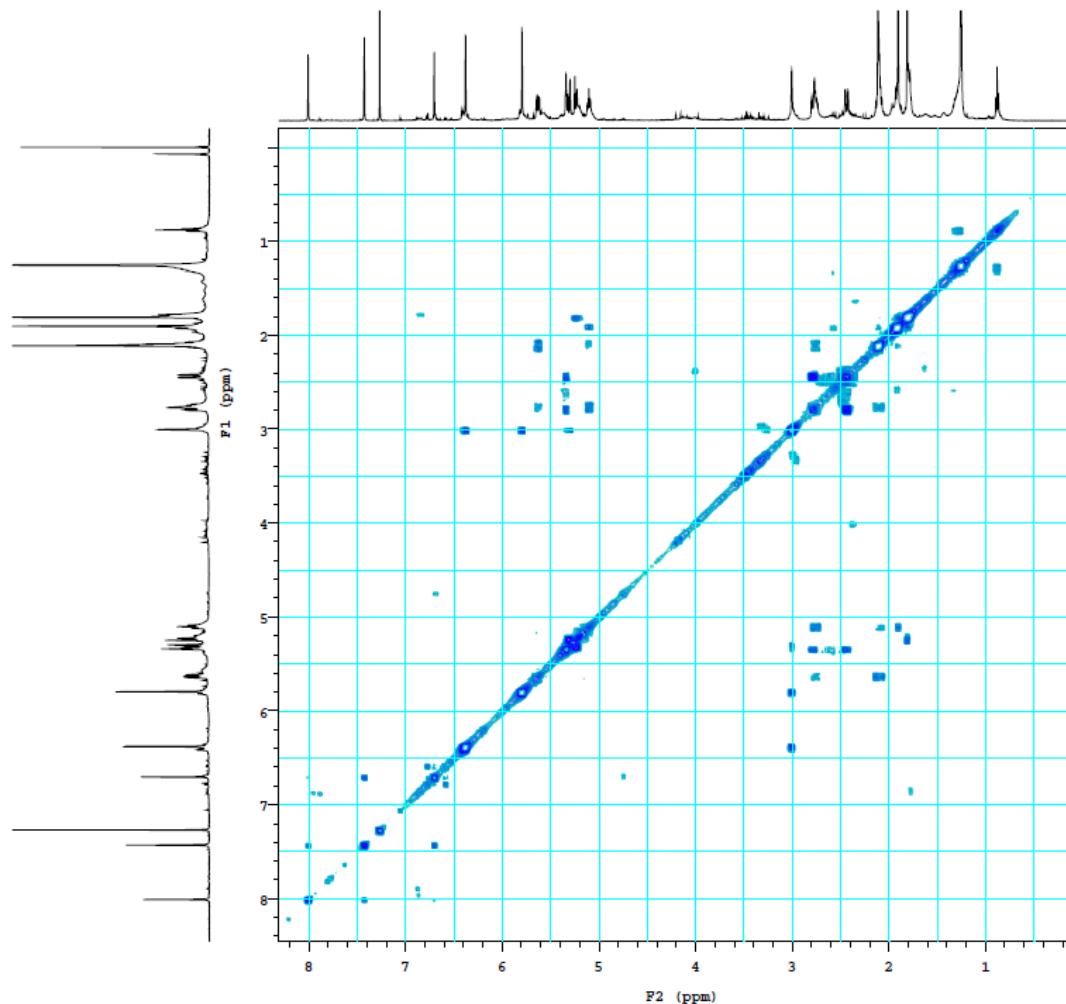
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HYM-2014-48-L-4-3-17.9mg-COSY-CDCl3
exp4 gCOSY

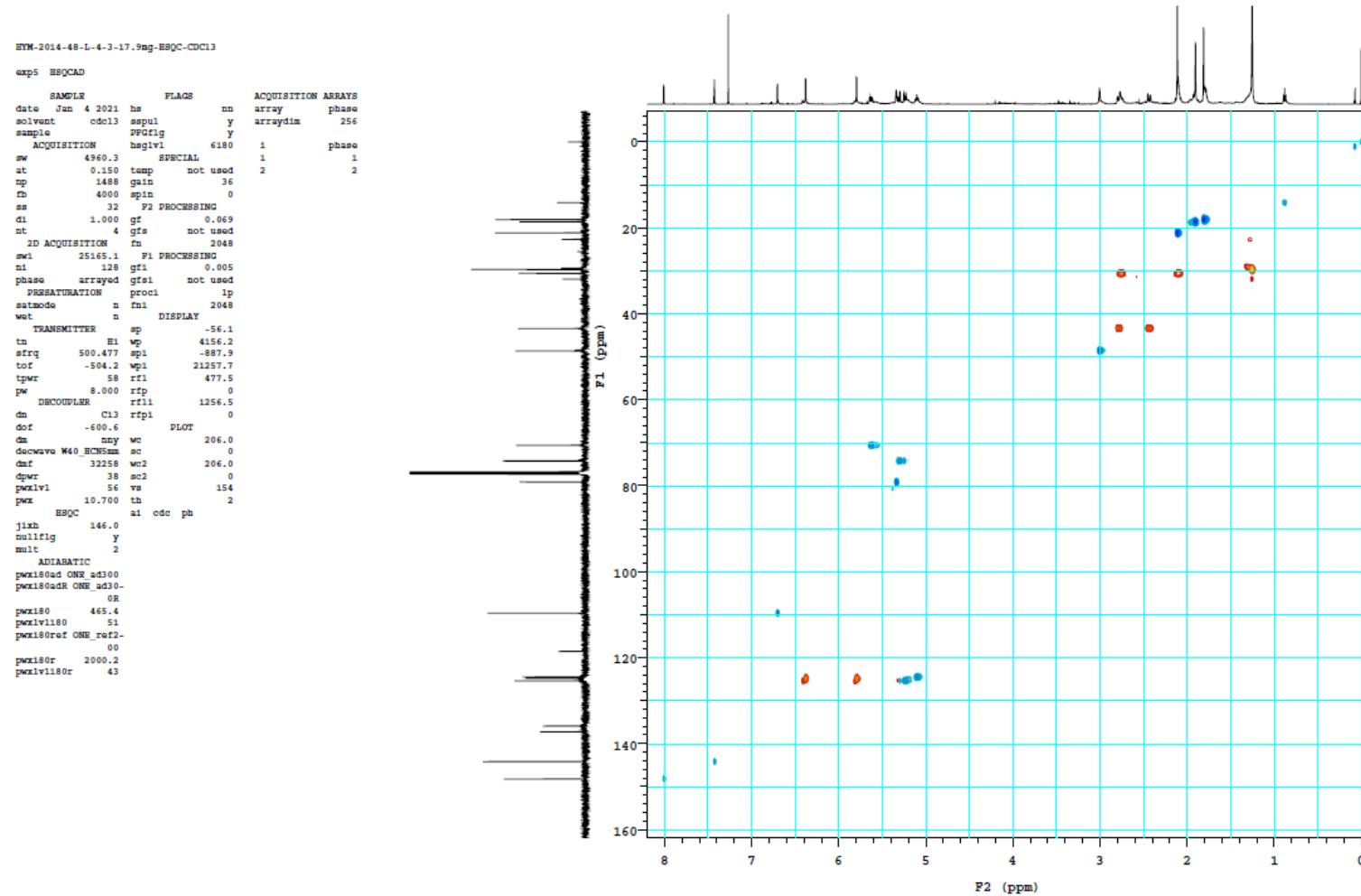
SAMPLE          FLAGS
date   Jan 4 2021 ha      nn
solvent    cdcl3 aspul     y
sample   haglv1    6180

ACQUISITION      SPECIAL
sw       4560.3  temp    not used
at        0.150  gain     36
sp        1488   spin     0
fb       4000   F2 PROCESSING
ss        32    ab     -0.075
d1      1.000   abs    not used
nt         4    f1n    2048
2D ACQUISITION  F1 PROCESSING
sw1      4560.3  sb1    -0.026
n1        128   sb1n   not used
d2         0  proc1    1p
PRESATURATION  f1n
satmode    n  DISPLAY
w1t      n  sp    -16.7
TRANSMITTER    w1      4195.0
tn        E1  sp1    -99.7
sfrq     500.477 wpi    4330.6
tot      -504.2 rfi    477.5
tpwr      58 rfp    0
pw       8.000  rfi1   477.5
GRADIENTS      rfpl    0
gr1v1R    5154   PLOT
gr2R     0.001000 wc    206.0
EDratio     1.000  ac    0
grt2b     0.000500 wc2   206.0
DECOUPLER     C13 vs    154
dn        nnn th    154
ai  odc av

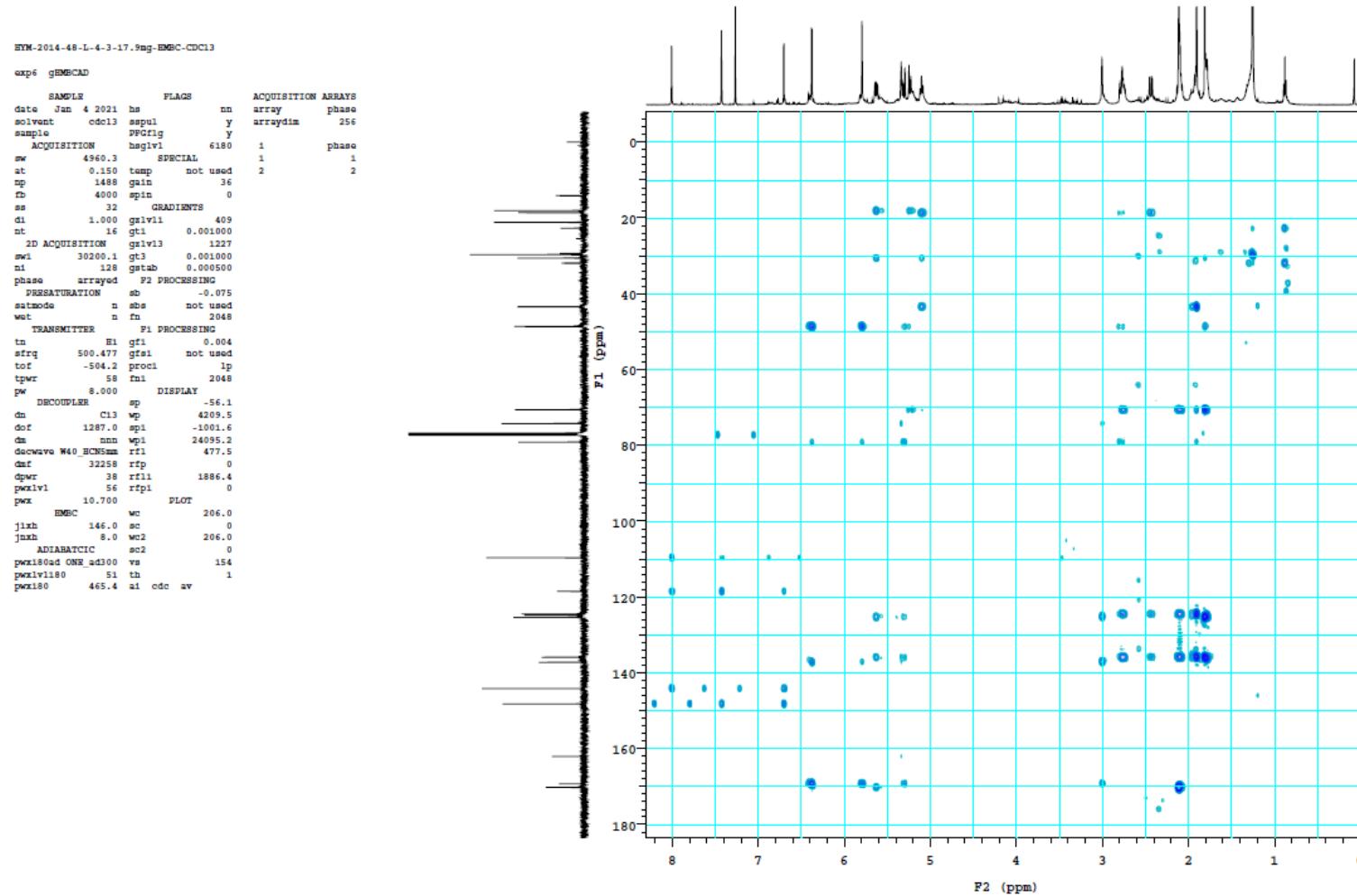
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**Figure S6.** HSQC spectrum of **10** (measured in  $\text{CDCl}_3$ , 500 MHz).

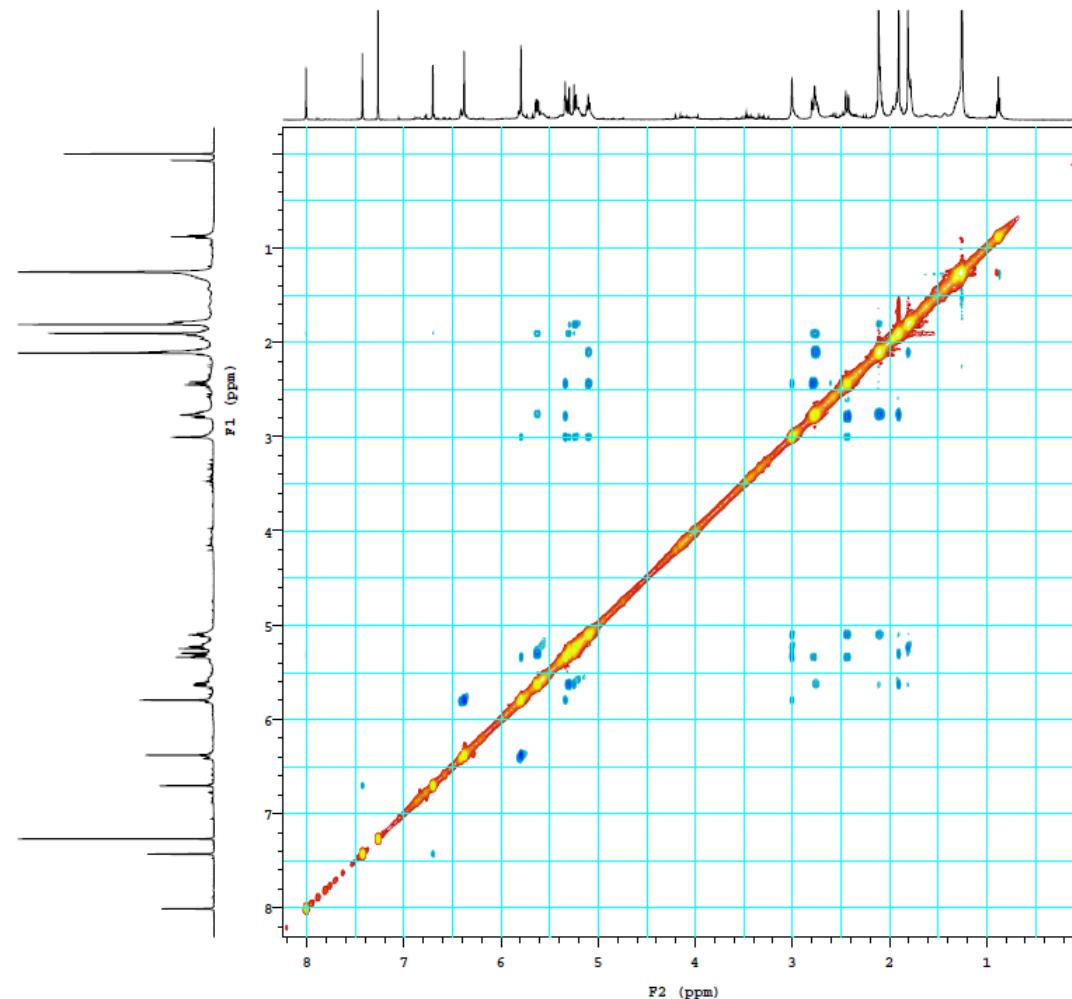


**Figure S7.** HMBC spectrum of **10** (measured in  $\text{CDCl}_3$ , 500 MHz).

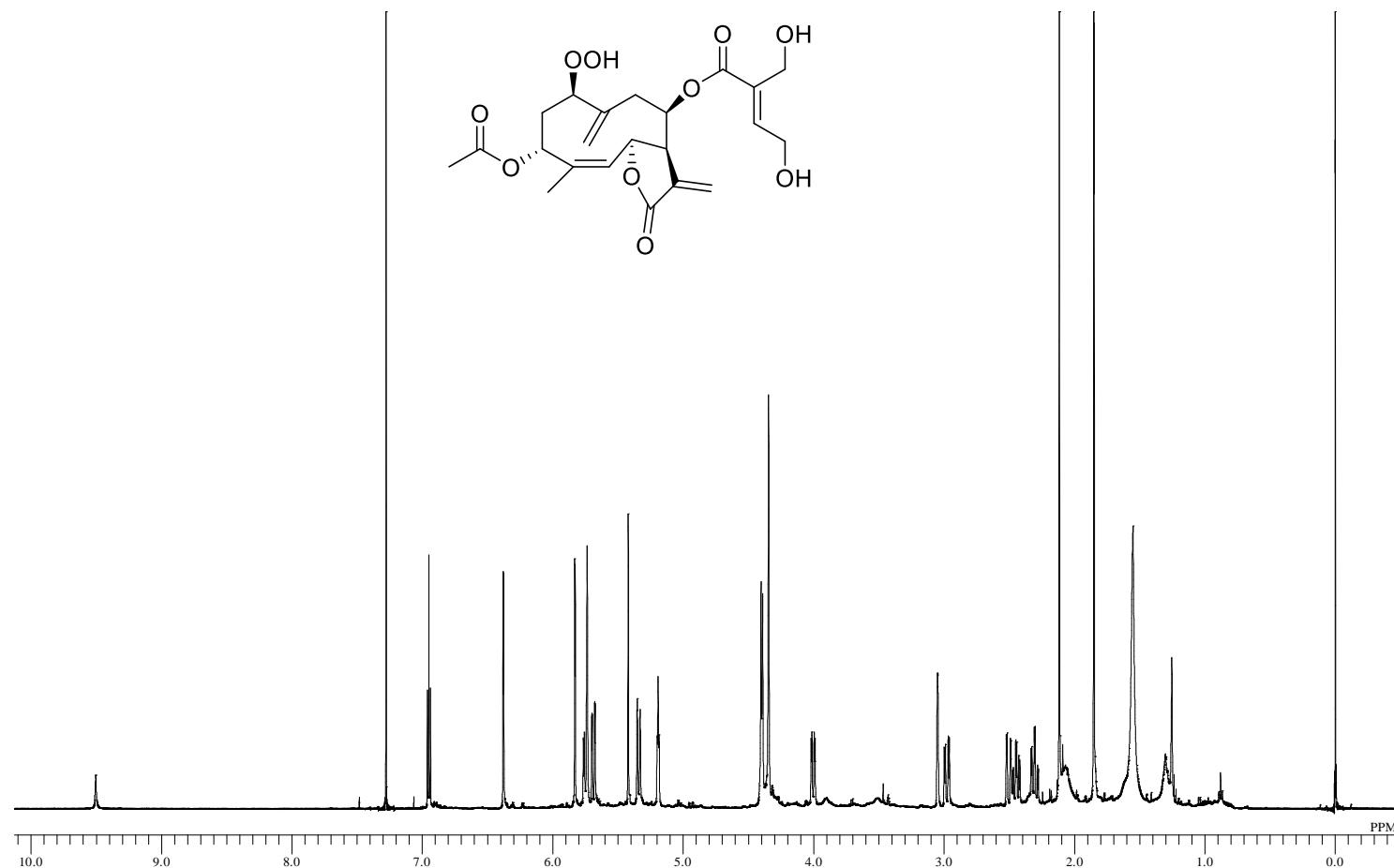


**Figure S8.** NOESY spectrum of **10** (measured in  $\text{CDCl}_3$ , 500 MHz).

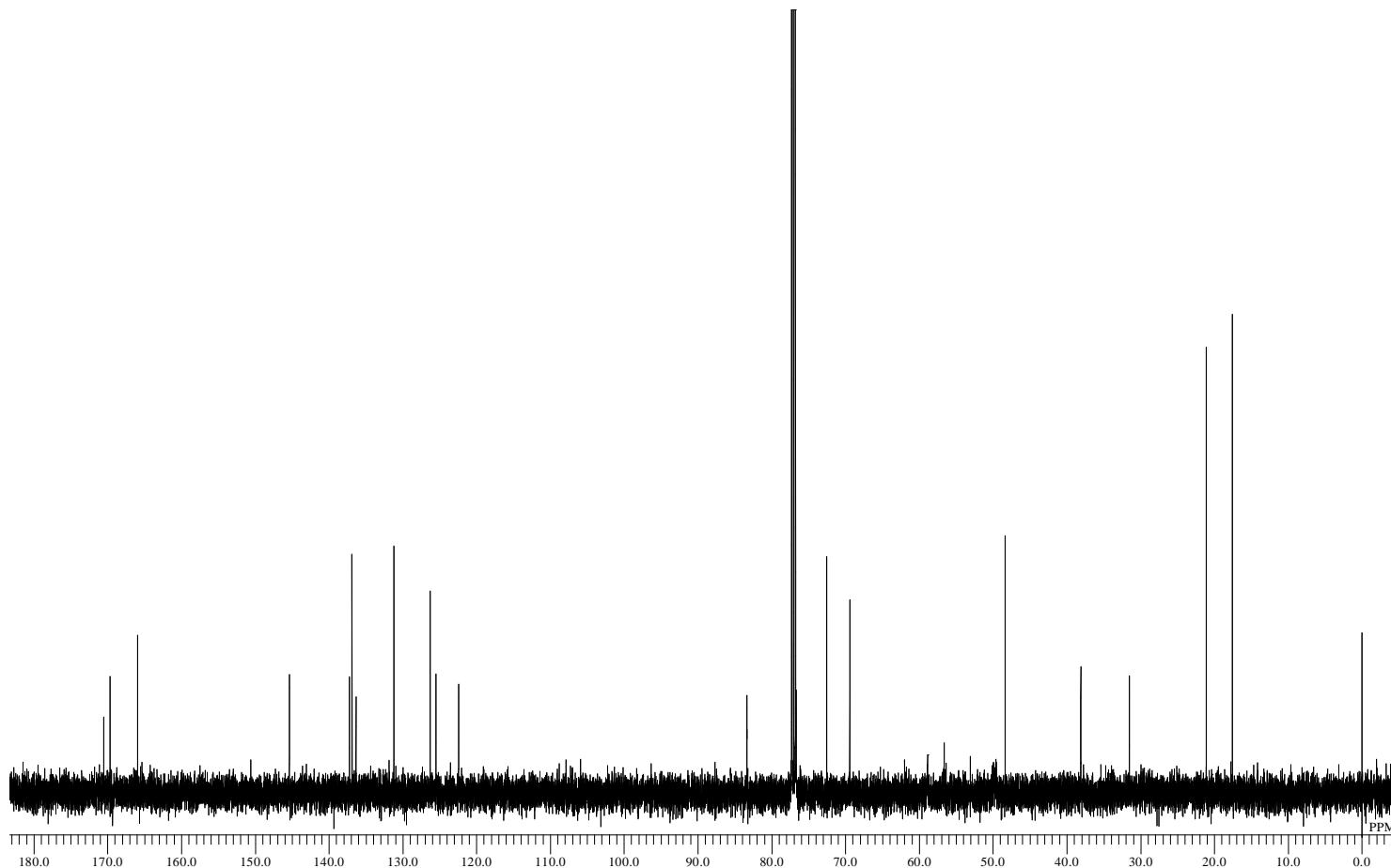
```
HYM-2014-48-L-4-3-17.9mg-NOESY-CDCl3
exp7 NOESY
      SAMPLE      PLACE
date Jan 4 2021 bs      nn
solvent cdcl3 spul      y
sample PFGgrg      y
      ACQUISITION bsgv1      6180
sw   4560.3      SPGRCL
at   0.150 temp      not used
np   1488 gain      36
fb   4000 spin      0
ss   32      P2 PROCESSING
d1   2.000 gfs      0.069
nt   8 gfs      not used
      2D ACQUISITION fn      2048
sw1  4560.3      P1 PROCESSING
ni   128 gfi      0.024
      TRANSMITTER gfa1      not used
tn   H1 procl      lp
sfrq 500.477 fml      2048
tof  -504.2      DISPLAY
tpwr 58 ap      -31.9
pw   8.000 wp      4156.2
      NOESY spi      -138.4
mixN 0.500 wpi      4296.7
PRESATURATION rfi      477.5
satmode n rfp      0
wot   n rfp1      477.5
      DCOUPLER rfp1      0
dn   C13 PLOT
dm   nnn wc      206.0
      sc      0
      wc2     206.0
      sc2     0
      vs      154
      th      1
ai   ph
```



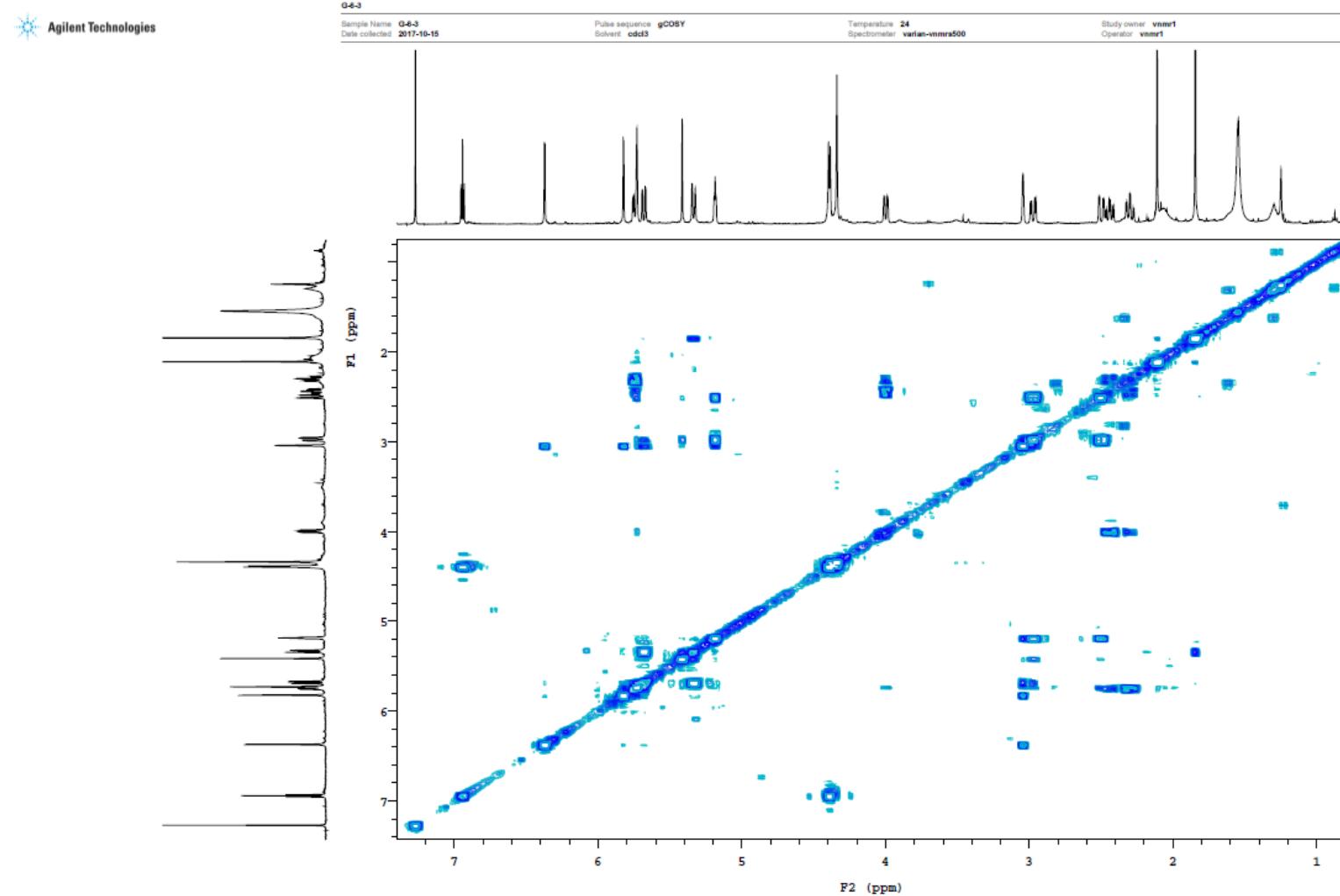
**Figure S9.**  $^1\text{H}$  NMR spectrum of **17** (measured in  $\text{CDCl}_3$ , 500 MHz).



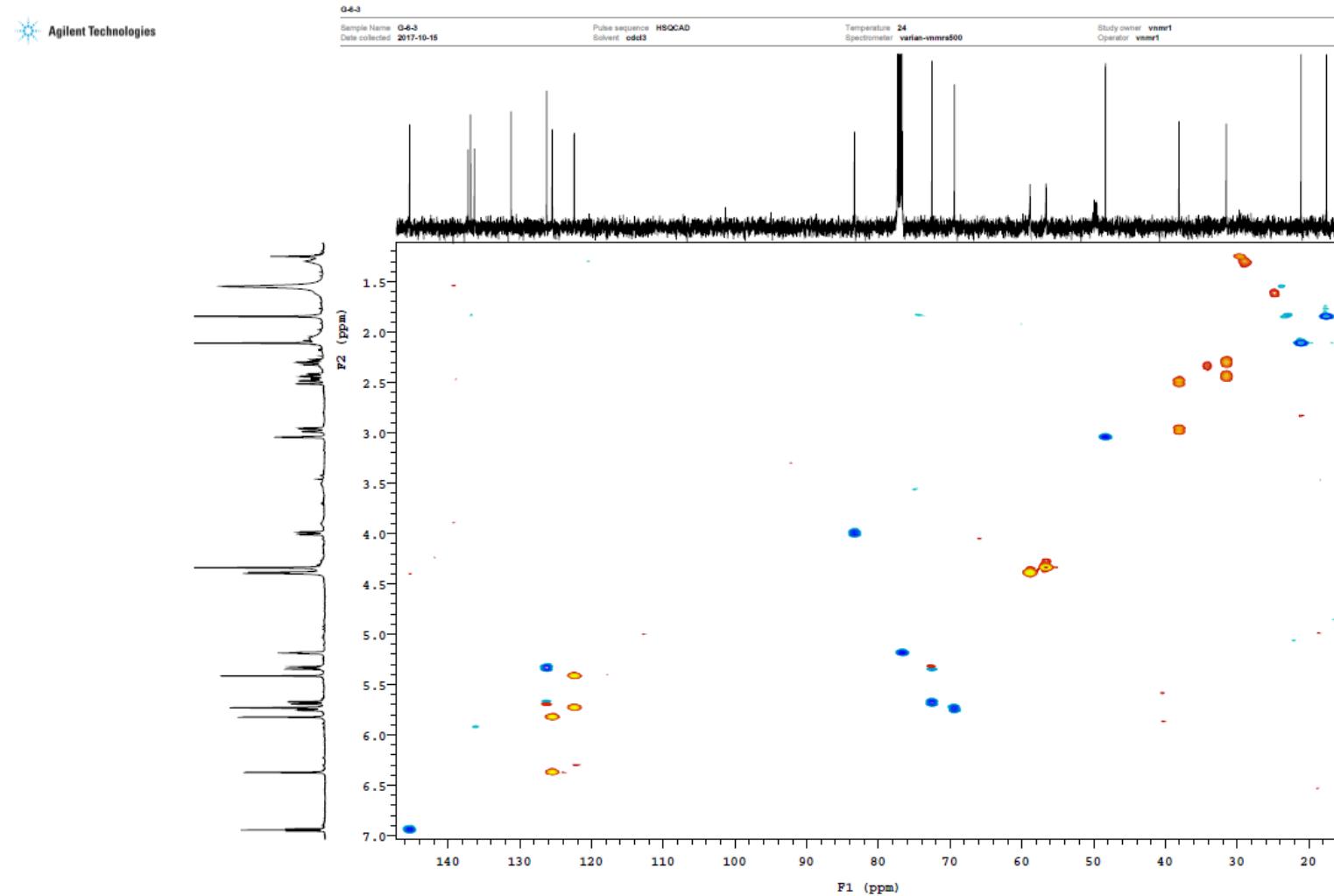
**Figure S10.**  $^{13}\text{C}$  NMR spectrum of **17** (measured in  $\text{CDCl}_3$ , 126 MHz).



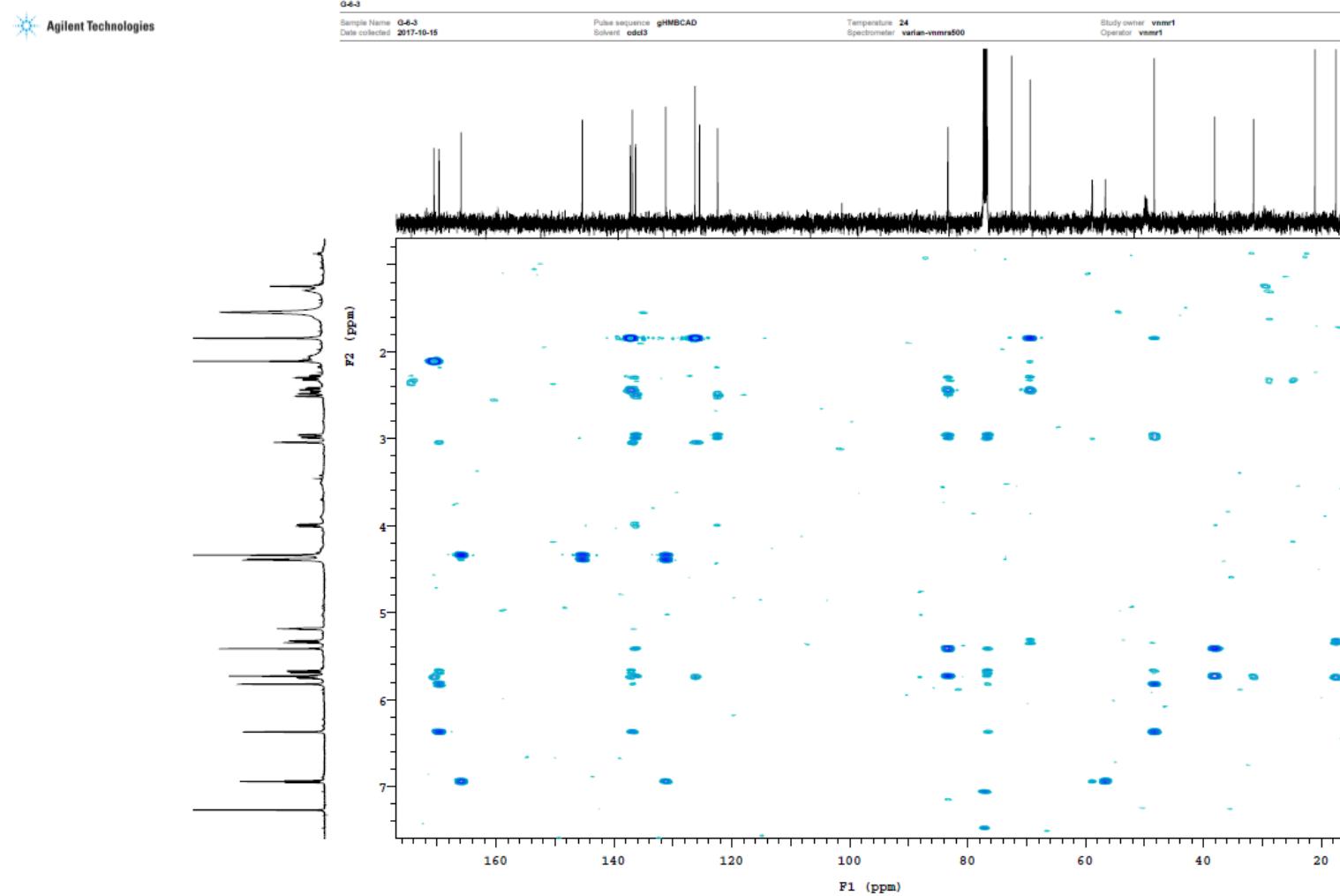
**Figure S11.**  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of **17** (measured in  $\text{CDCl}_3$ , 500 MHz).



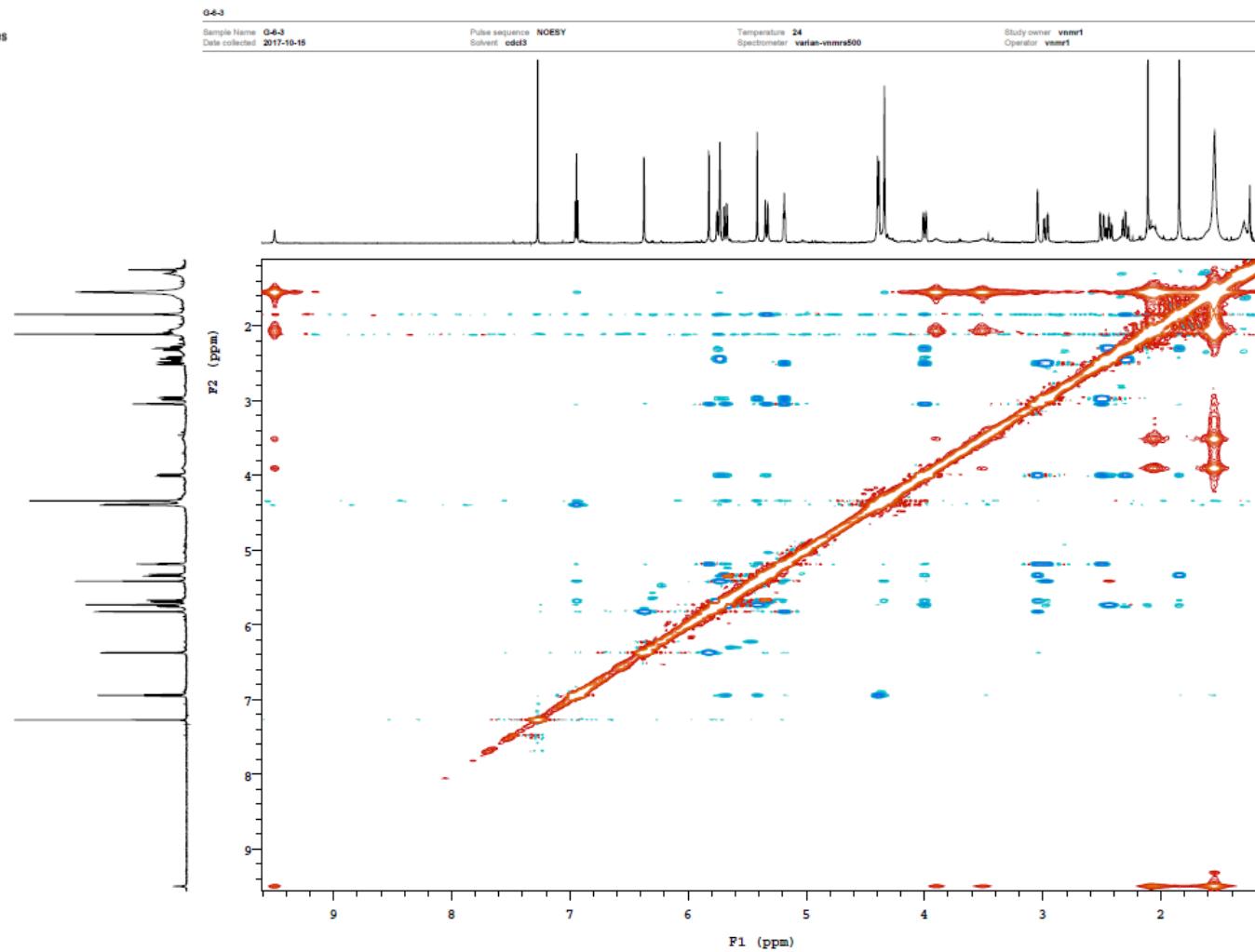
**Figure S12.** HSQC spectrum of **17** (measured in  $\text{CDCl}_3$ , 500 MHz).



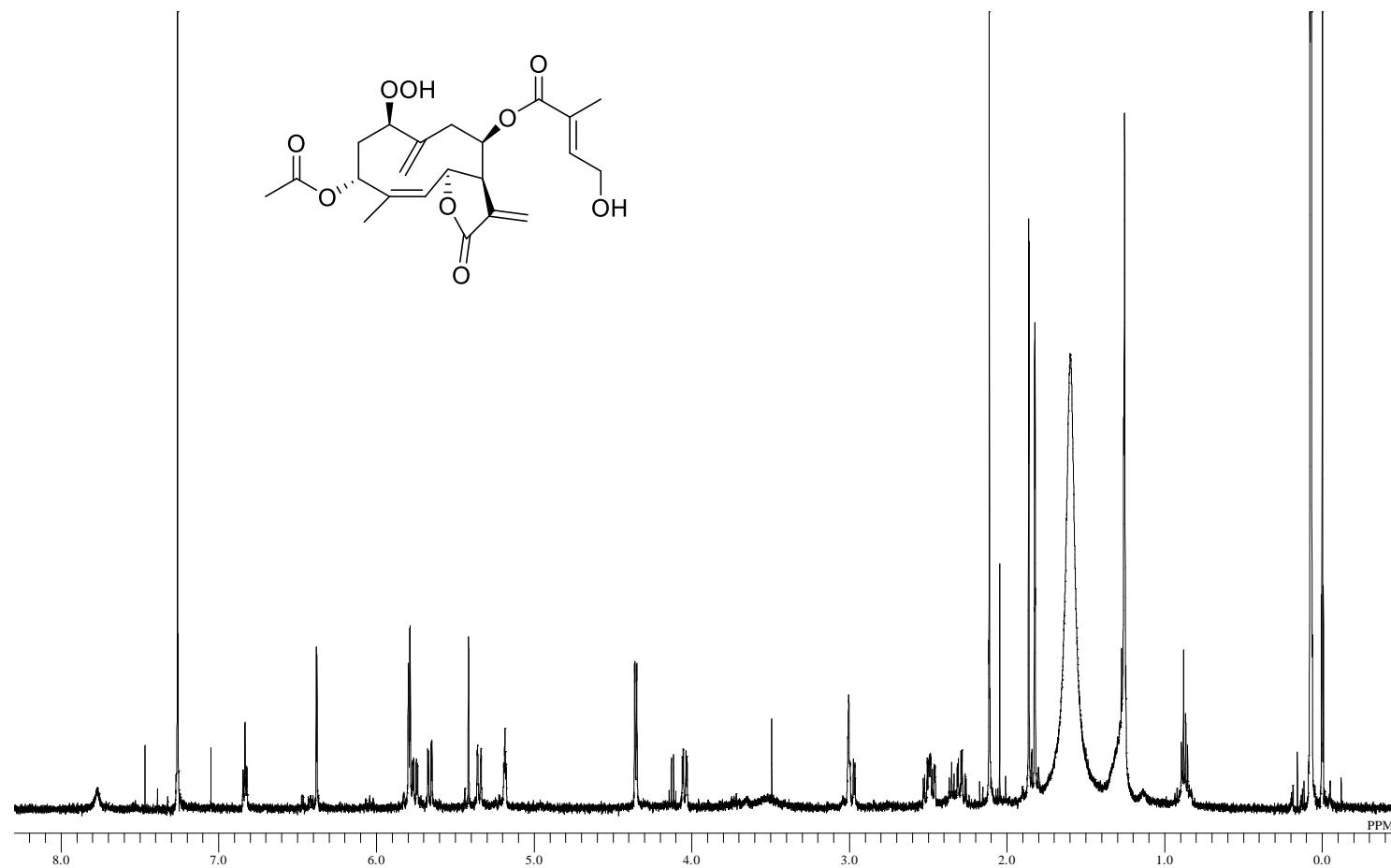
**Figure S13.** HMBC spectrum of **17** (measured in  $\text{CDCl}_3$ , 500 MHz).



**Figure S14.** NOESY spectrum of **17** (measured in  $\text{CDCl}_3$ , 500 MHz).

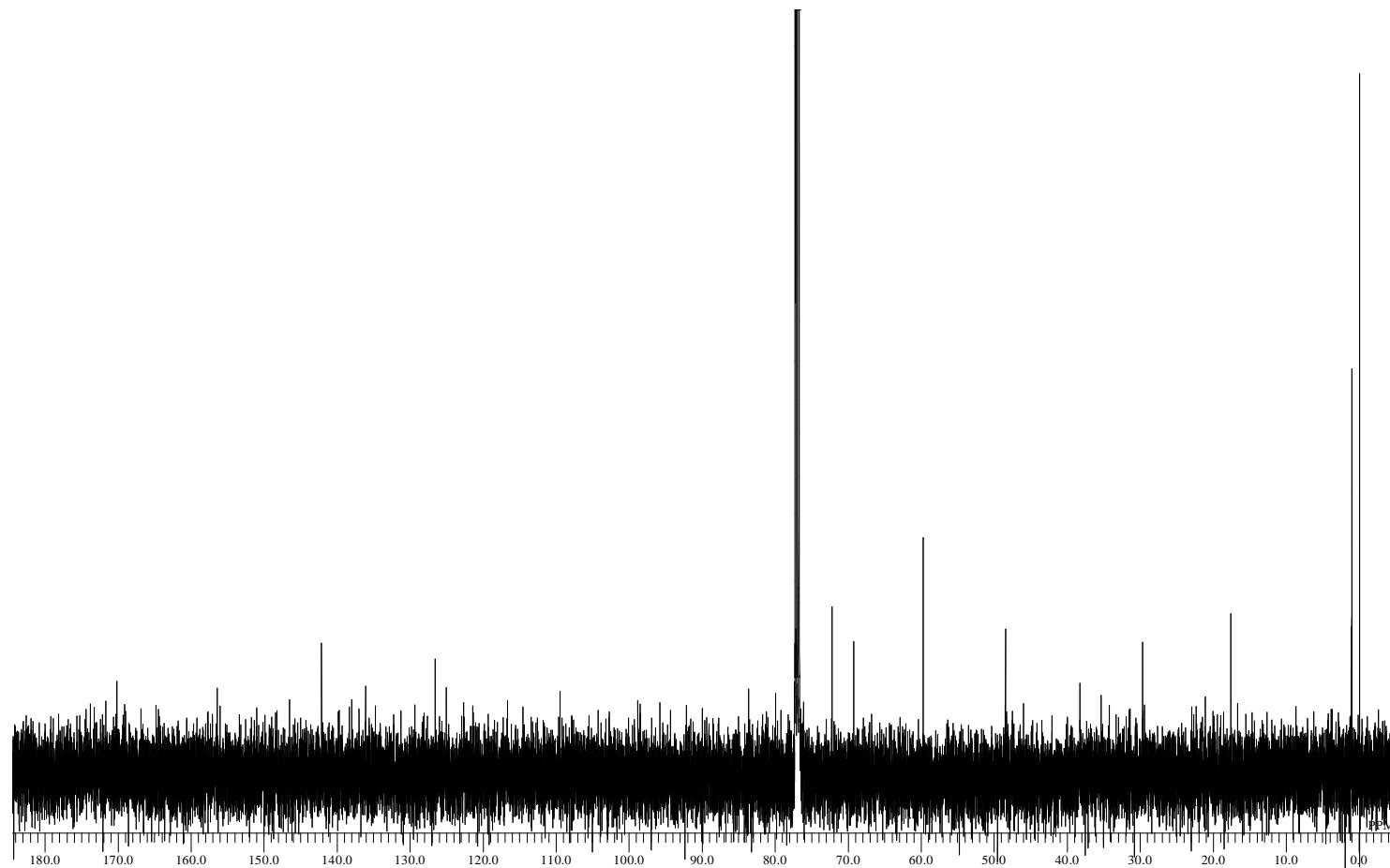


**Figure S15.**  $^1\text{H}$  NMR spectrum of **18** (measured in  $\text{CDCl}_3$ , 500 MHz).



18

**Figure S16.**  $^{13}\text{C}$  NMR spectrum of **18** (measured in  $\text{CDCl}_3$ , 126 MHz).



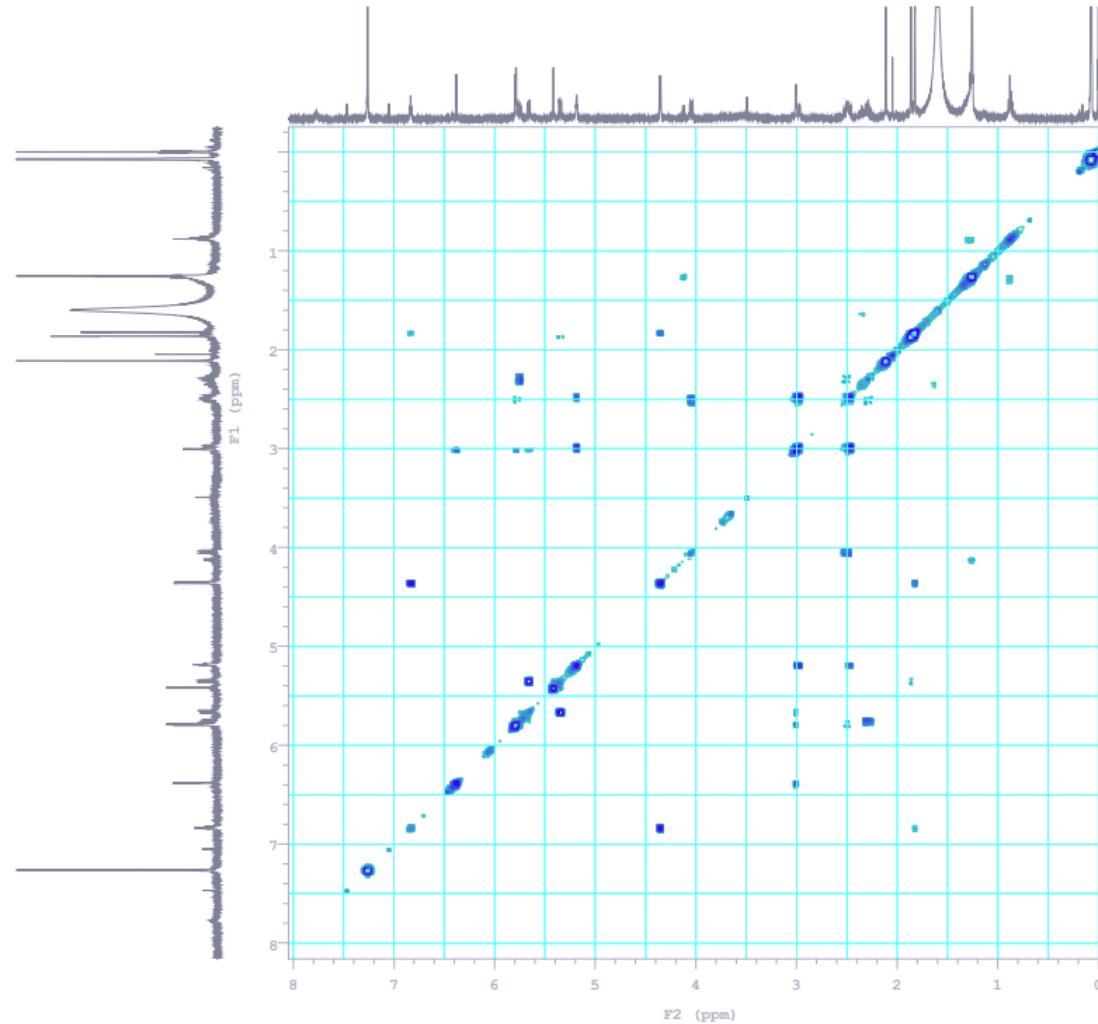
**Figure S17.**  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of **18** (measured in  $\text{CDCl}_3$ , 500 MHz).

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HYM-F-2-2-combined1.5mg-COSY_cdc13
exp6 gCOSY

SAMPLE          FLAGS
date   Jun 12 2017 hs      nn
solvent    cdc13 asspl     y
sample    hsglvl      6240
ACQUISITION    SPECIAL
sw        4464.3 ttemp   24.0
at         0.150 gain    50
np        1340 spin     0
fb        4000 F2 PROCESSING
ss         32 ab      -0.075
d1        1.000 abs     not used
nt         4 fn      2048
2D ACQUISITION   F1 PROCESSING
sw1       4464.3 ab1     -0.029
ni1        128 ab1l    not used
d2         0 proc1      1p
PRESATURATION   f1l      2048
satmode      n DISPLAY
wet         n sp      -93.8
TRANSMITTER    wp      4119.9
tn        H1 spl     -124.3
sfrq      500.483 wpl    4207.1
tof       -524.7 rf1    259.5
tpwr       58 rfP     0
pw        7.500 rf1l   259.5
GRADIENTS      rfpl    0
gslvLE      5208 PLOT
gtx       0.001000 wc    206.0
Rbratio     1.000 ac    0
gstab      0.000500 wc2   206.0
DECOUPLER      ac2    0
dn        C13 vs     889
dm        ann th      7
ai      cdc av

```



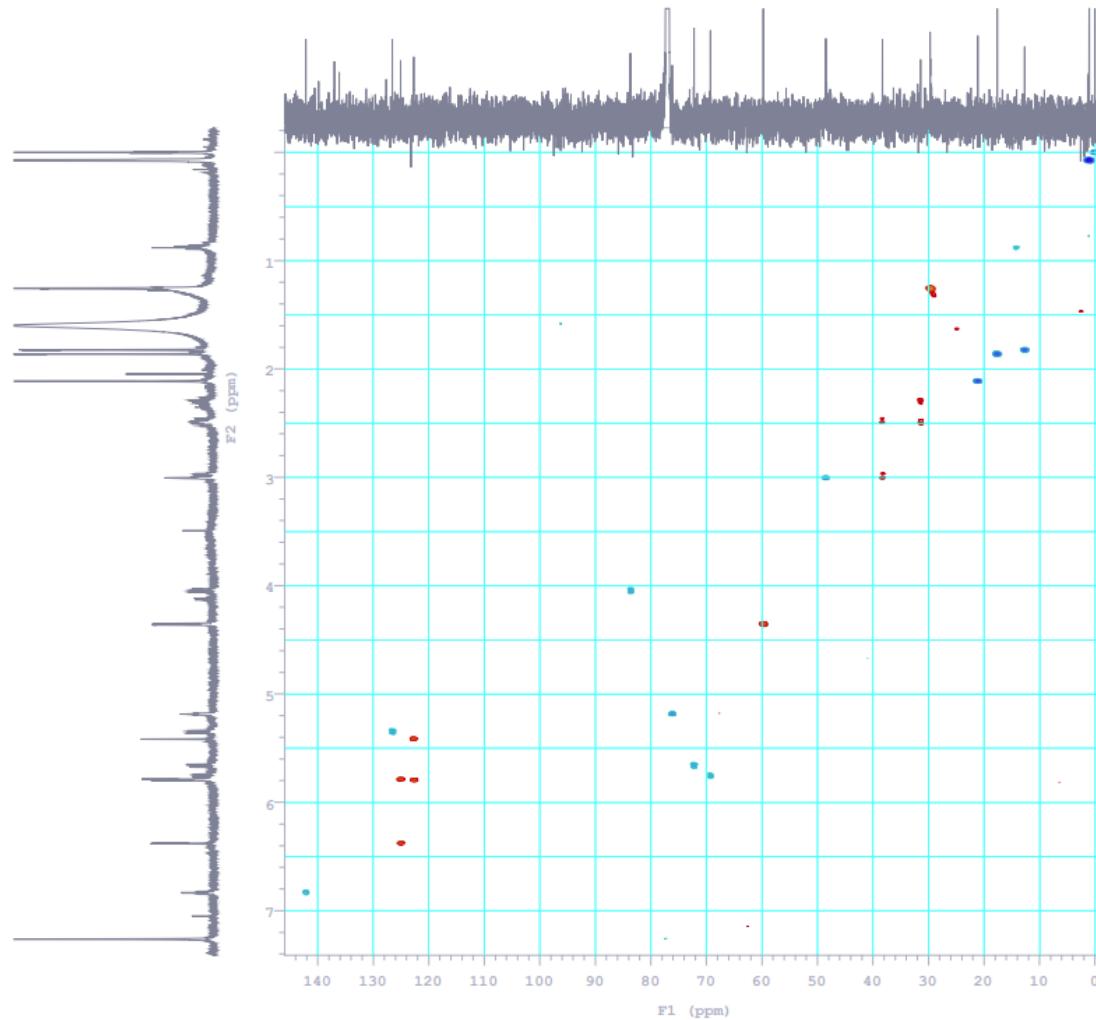
**Figure S18.** HSQC spectrum of **18** (measured in  $\text{CDCl}_3$ , 500 MHz).

```

HYM-F-2-2-combined1.5mg-HSQC_cdcl3
exp6 gHSQCAD

SAMPLE          FLAGS          ACQUISITION ARRAYS
date   Jun 12 2017 hs      nn      array    phase
solvent   cdc13  aspul   y      arraydim  256
sample    PFGF1g  hsgl1v1 6240   i      phase
ACQUISITION    hsgl1v1
sw        4464.3 SPECIAL    1      1
st        0.150  temp     24.0   2
np        1340   gain      50
fb        4000   spin      0
ss        32     GRADIENTS
dl        1.000  g1v1E    5208
nt        16     gTE      0.002000
2D ACQUISITION EDRatio   3.978
sw1      21396.1 gatab    0.000500
ni        128    F2 PROCESSING
phase    arrayed  qf      0.069
PRESATURATION qfs      not used
satmode   n      fn      2048
wet       n      F1 PROCESSING
TRANSMITTER   qf1      0.006
tn        H1      qfs1    not used
sfrq     500.483 procl    lp
tof      -524.7  fnl     2048
tpwr      58     DISPLAY
pw        7.500  ap      -111.3
DECOUPLER    wp      3819.1
dn        C13    apl     -320.0
dof      -2489.0 wpl     18679.8
dm        any    rfl     259.5
decwave W40_HCN5m rfp     0
dmf      32258  rfl1    1260.3
dpwr     38    rfpl     0
pwlvlv1  56     PLOT
pwx      10.700 wc     206.0
HSQC      ac      0
j1kh     146.0 wu2    206.0
nullflg   y      ac2     0
mult      2    vs      889
ADIABATIC   th      3
pwx180ad CNE_ad300 ai  cdc ph
pwx180adr CNE_ad30-
OR
pwx180    465.4
pwx1v180  51
pwx180ref CNE_ref2-
00
pwx180r   2000.2
pwx1v180r 43

```



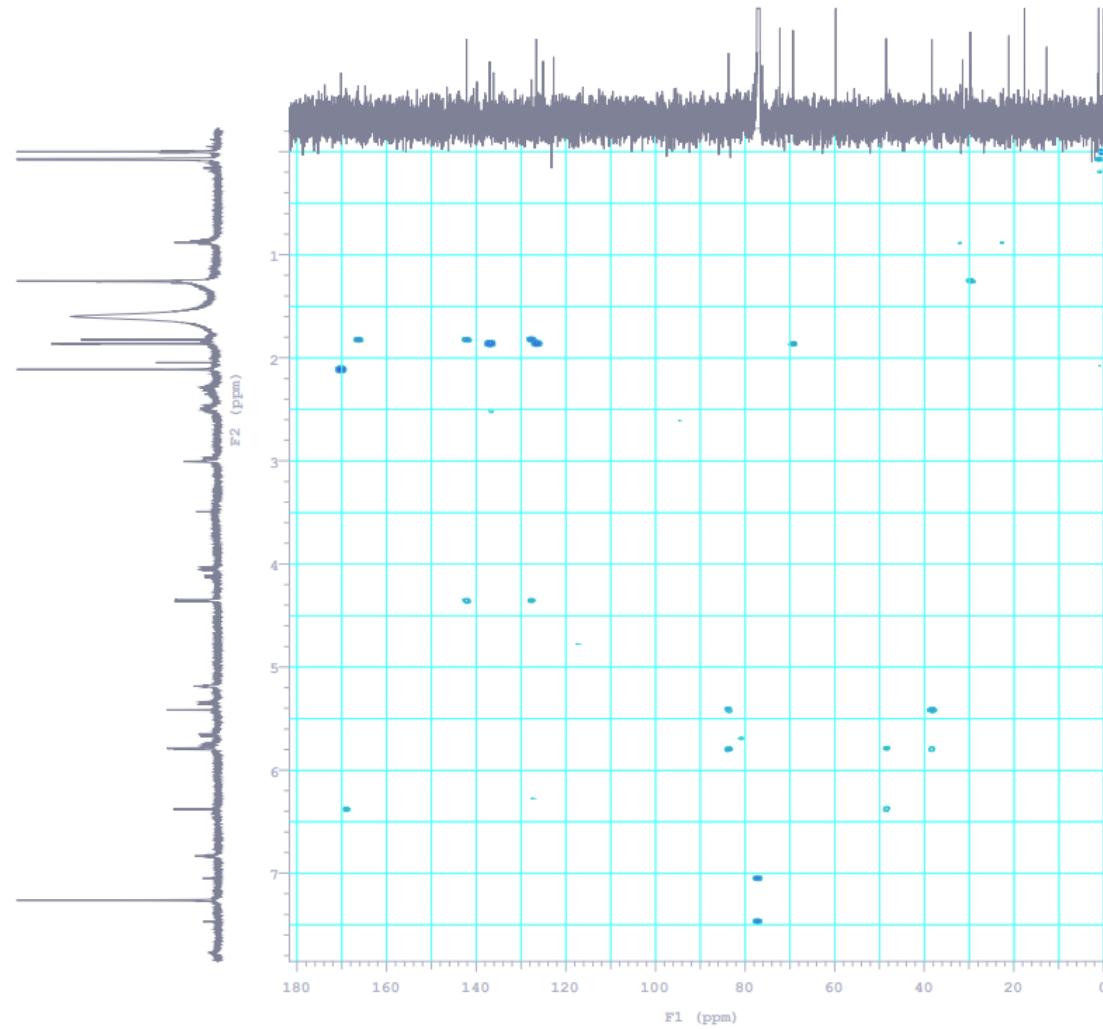
**Figure S19.** HMBC spectrum of **18** (measured in  $\text{CDCl}_3$ , 500 MHz).

```

HYM-F-2-2-combined1.5mg-HMBC_cdcl3
exp6 gHMBCAD

SAMPLE          FLAGS          ACQUISITION ARRAYS
date   Jun 12 2017 hs      nn      array    phase
solvent   cdcl3  sspl     y      arraydim  256
sample    PFPGf1g
          hsglv1  6240   i      phase
sw        4464.3  SPECIAL   1      1
at        0.150  ttmp     24.0   2      2
np        1340   gain     50
fb        4000   spin     0
ss        32     GRADIENTS
dl        1.000  gxlv11  409
nt        16     gt1      0.001000
2D ACQUISITION  gxlv13  1227
swl      30200.1  gt3      0.001000
ni        128   gxtab    0.000500
phase    arrayed  F2 PROCESSING
PRESATURATION ab      -0.075
satmode   n     abs      not used
wet       n     fn      2048
TRANSMITTER   F1 PROCESSING
tn        H1  gfl1    0.004
sfrq     500.483  gfs1    not used
tof      -524.7  proc1    lp
tpwr      58  fml     2048
pw        7.500  DISPLAY
DECOUPLER    ap      -111.3
dn        C13  wp     4041.4
dof      1287.0  apl     -441.1
dm        mnn  wpl    23298.9
decwave W40_HCN5m  rf1     259.5
dmf      32258  rfp     0
dpwr      38  rf11    1886.2
pwlvl1    56  rfpl    0
pxw      10.700  PLOT
HMBC      wc     206.0
j1xh     146.0  ac      0
j1xh     8.0    wc2    206.0
ADIABATICCIC ac2      0
pxw180ad ONE_ad300  vs     889
pxw1180    51  th      5
pxw180    465.4  ai  edc  av

```



**Figure S20.** NOESY spectrum of **18** (measured in  $\text{CDCl}_3$ , 500 MHz).

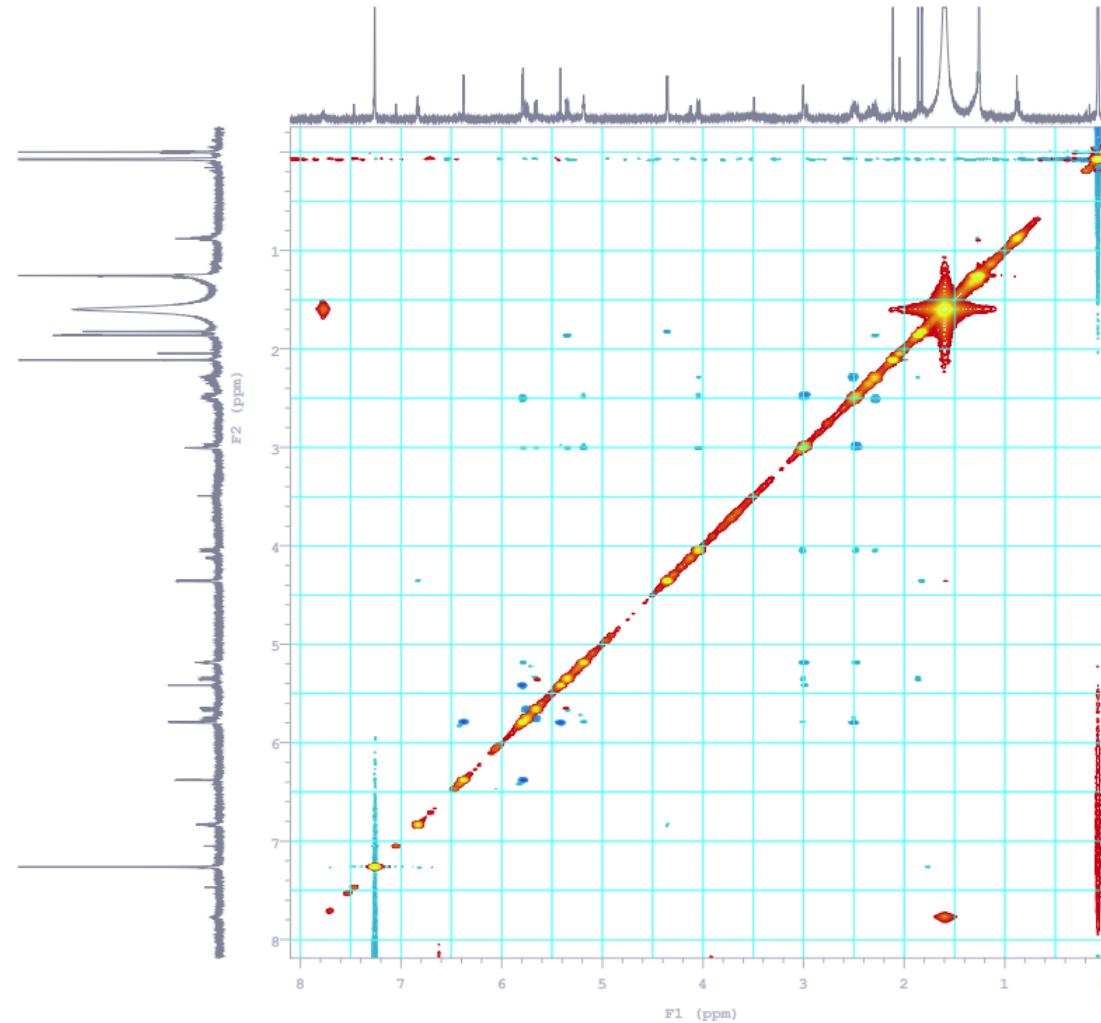
```

HYM-F-2-2-combined1.Smg-NOESY_cdc13

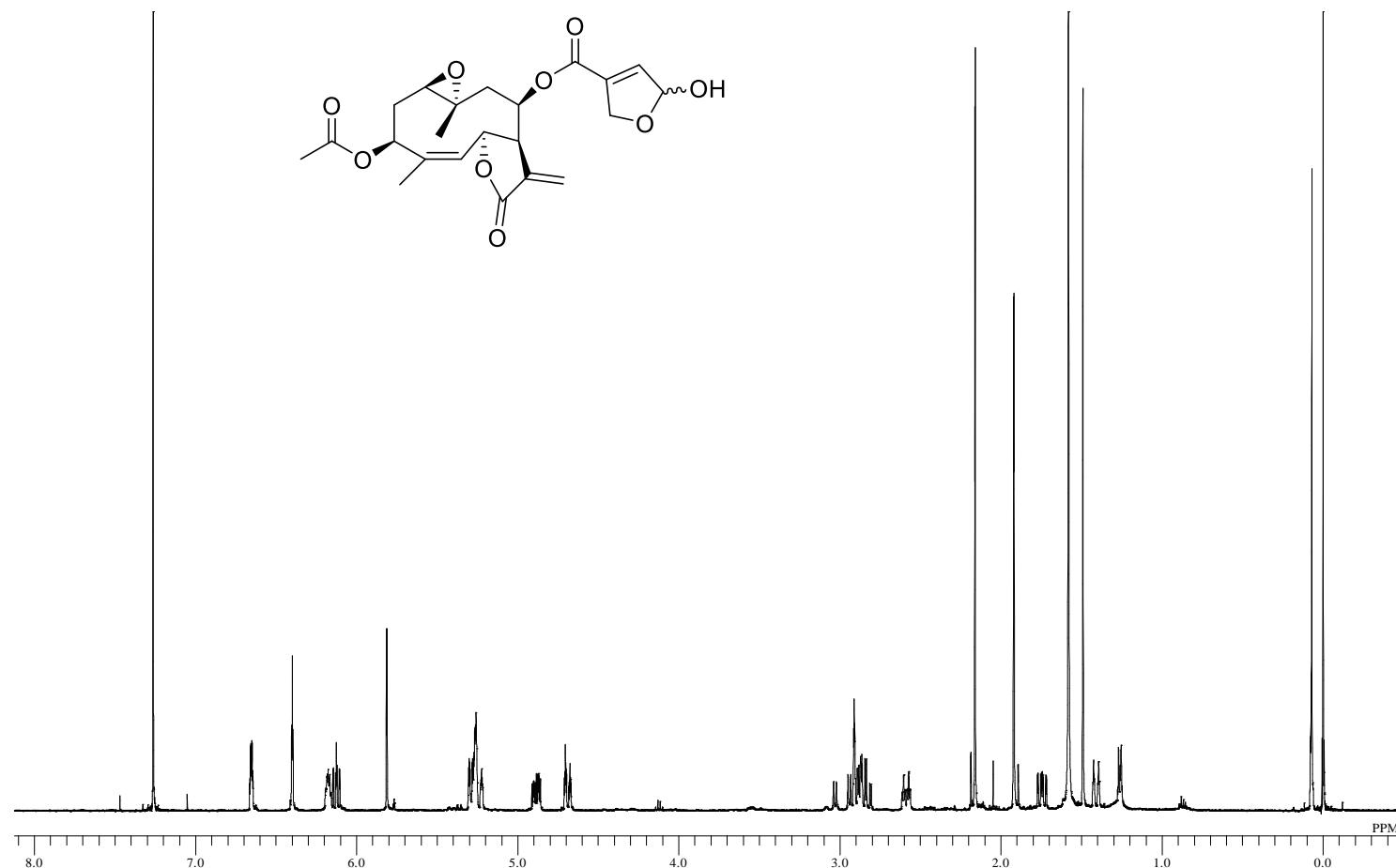
exp6 NOESY

SAMPLE          FLAGS
date   Jun 12 2017 hs      nn
solvent    cdc13 sepal     y
sample    PPGf1g   y
ACQUISITION haglv1  6240
sw        4464.3 SPECIAL
at       0.150 temp     24.0
np       1340  gain     50
fb       4000  spin      0
ss       32   F2 PROCESSING
dt       2.000  gfs     0.069
nt       4   gfs      not used
2D ACQUISITION fn      2048
sw1      4464.3 F1 PROCESSING
ni       128  gfs1    0.026
TRANSMITTER H1 proc1   1p
afrq     500.483 f1l
t0f      -524.7 DISPLAY
tpwr      58 sp      -124.3
pw       7.500 wp     4220.1
NOEST     0.500 wpl    4115.5
mixN      0.500 wpl    4115.5
PRESATURATION rfl1   259.5
satmode   n rfp      0
wet       n rfl1   259.5
DECOUPLER rfp1
dn       C13 PLOT
dm      nnn wc     206.0
      sc      0
      wc2   206.0
      sc2      0
      vs     889
      th      1
      ai ph

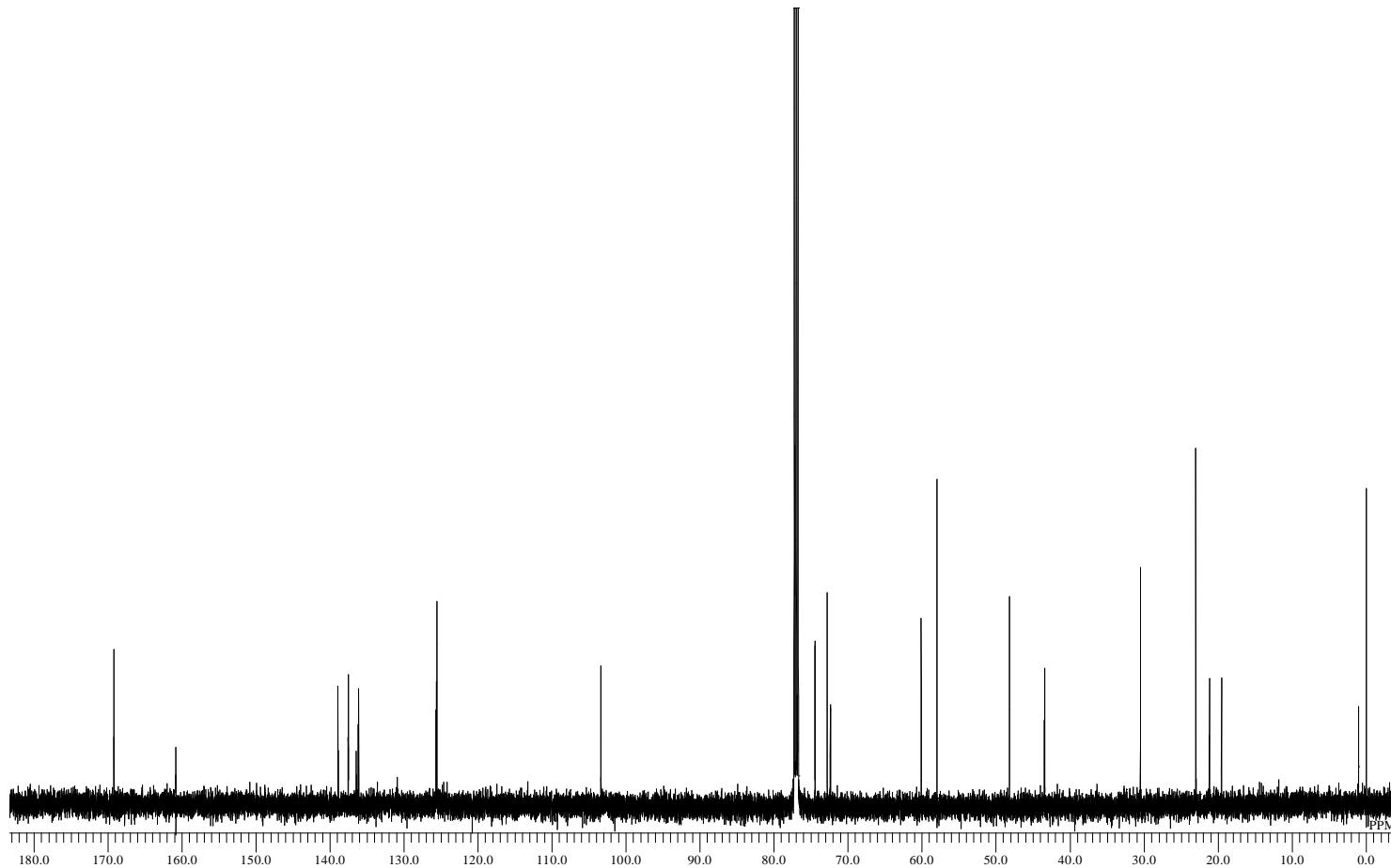
```



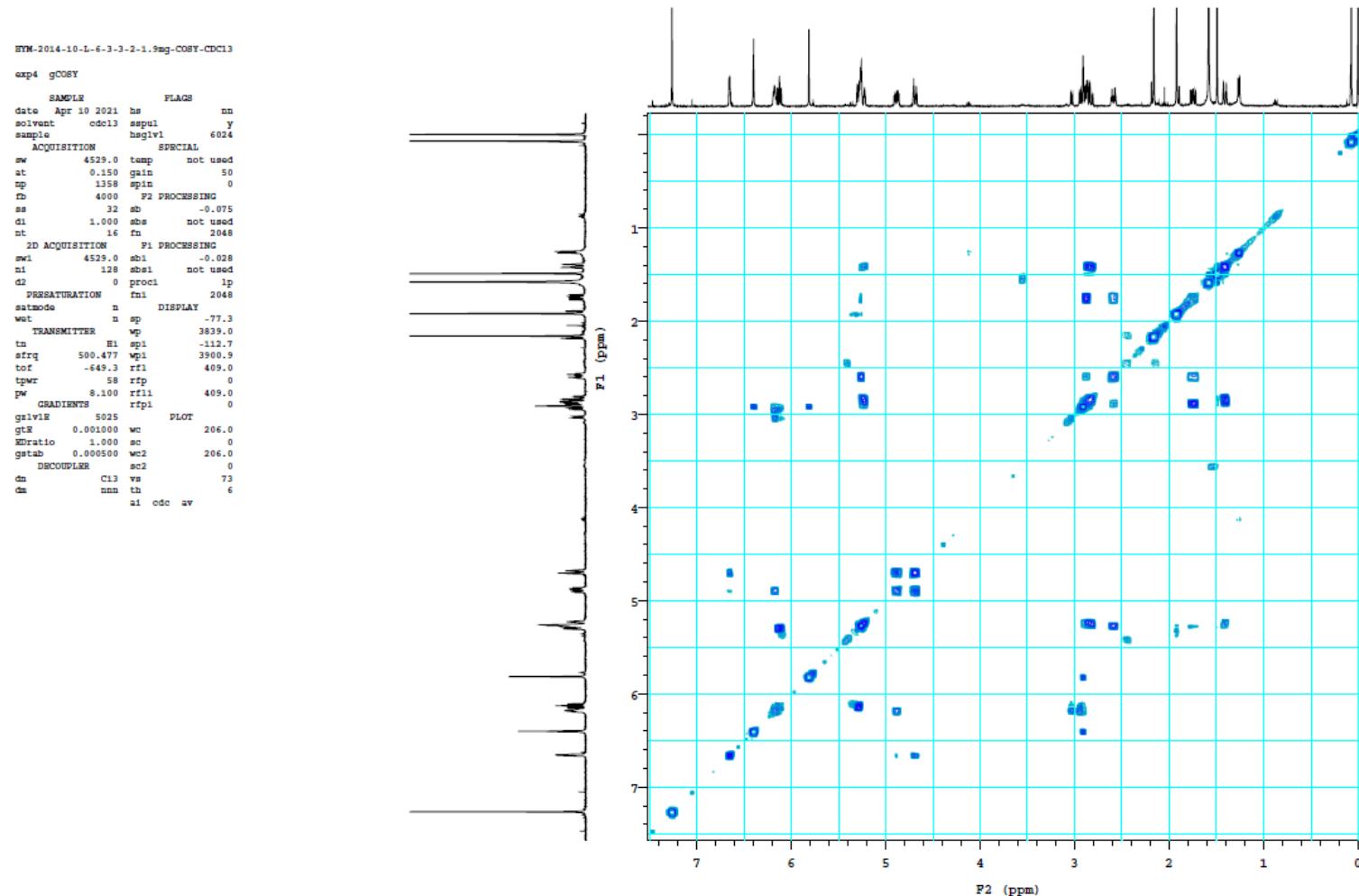
**Figure S21.**  $^1\text{H}$  NMR spectrum of **24** (measured in  $\text{CDCl}_3$ , 500 MHz).



**Figure S22.**  $^{13}\text{C}$  NMR spectrum of **24** (measured in  $\text{CDCl}_3$ , 126 MHz).



**Figure S23.**  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of **24** (measured in  $\text{CDCl}_3$ , 500 MHz).



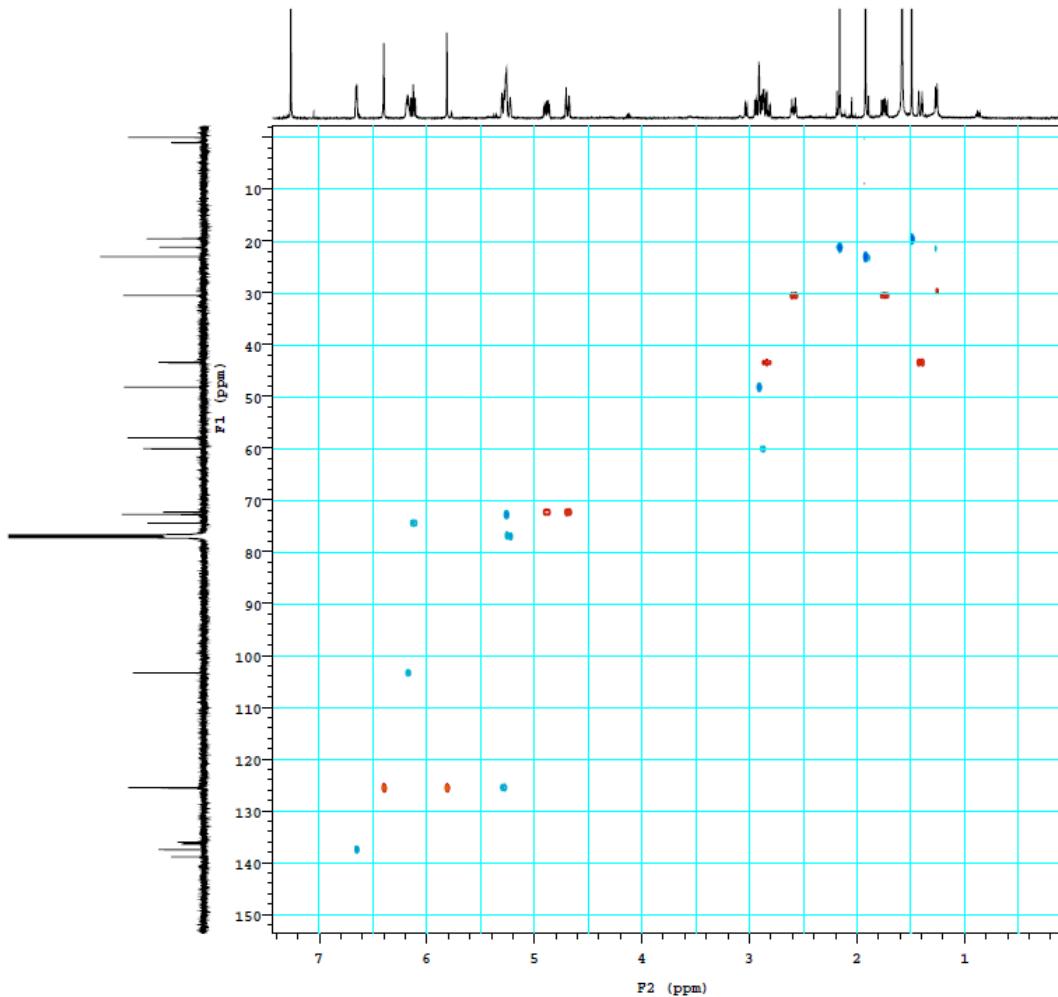
**Figure S24.** HSQC spectrum of **24** (measured in  $\text{CDCl}_3$ , 500 MHz).

```

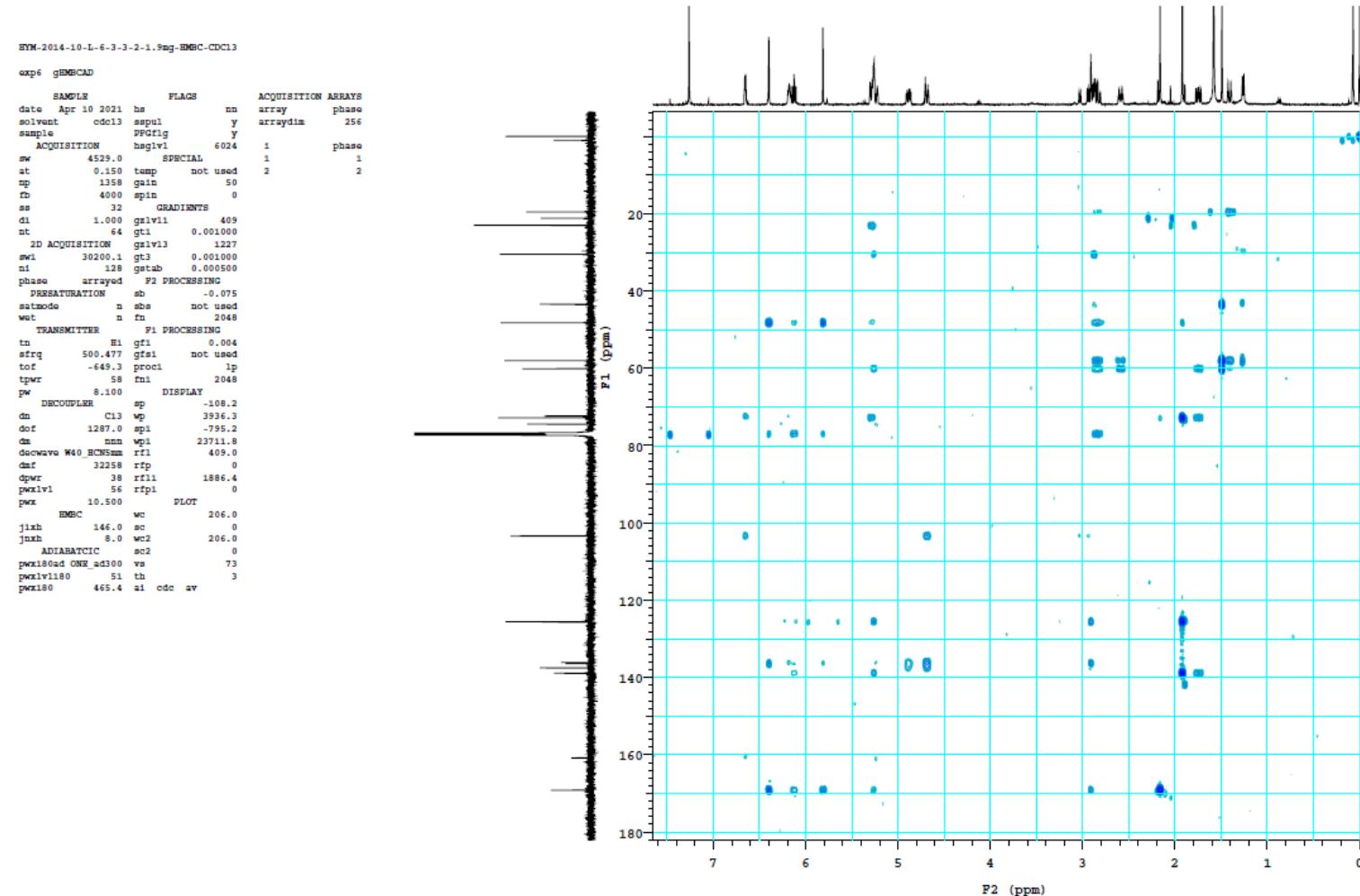
HTM-2014-10-L-6-3-3-2-1.7mg-HSQC-CDCl3
exp5 HSQCAD

SAMPLE      PFLAGS      ACQUISITION ARRAYS
date Apr 10 2021 hs      nn      array      phase
solvent   cdcl3 asspl     y      arraydim    256
sample    DPGdig   y
ACQUISITION hsg1v1 6024 1      phase
sw        4529.0   SPECIAL 1      1
at        0.150 temp  not used 2      2
np        1358 gain  50
fb        4000 spin   0
ss        32 P2 PROCESSING
di        1.000 gfs  0.069
nt        16 gfts  not used
2D ACQUISITION fn      2048
sw1      25165.1   F1 PROCESSING
ni        128 gfs1  0.005
phase    arrayed gfs1  not used
PRESATURATION proc1 1p
satmode  n fns1 2048
wt       n          DISPLAY
TRANSMITTER sp      -24.2
tn        H1 wp     3741.7
stfgrq   500.477 sp1   -273.5
t0f      -649.3 wpi    19611.1
tpwr     58 rf1    409.0
pw       8.100 rfp   0
DECOUPLER rf1    1256.5
dn        C13 rf1   0
dof      -600.6   PLOT
dm       nny w0    206.0
decwave W40_HCN5m sc     0
dmf      32258 w02   206.0
dpwr     38 sc2   0
pxw1v1   56 vs    73
pwr      10.500 th    3
pwc      HSQC ai cdc ph
j1xb     146.0
nullfig  y
nult     2
ADIABATIC
pxw180ad ONR_ad100
pxw180adR ONR_ad430
OR
pxw180    465.4
pxw1v180  51
pxw180ref ONR_rf2-
00
pxw180r   2000.2
pxw1v180r 43

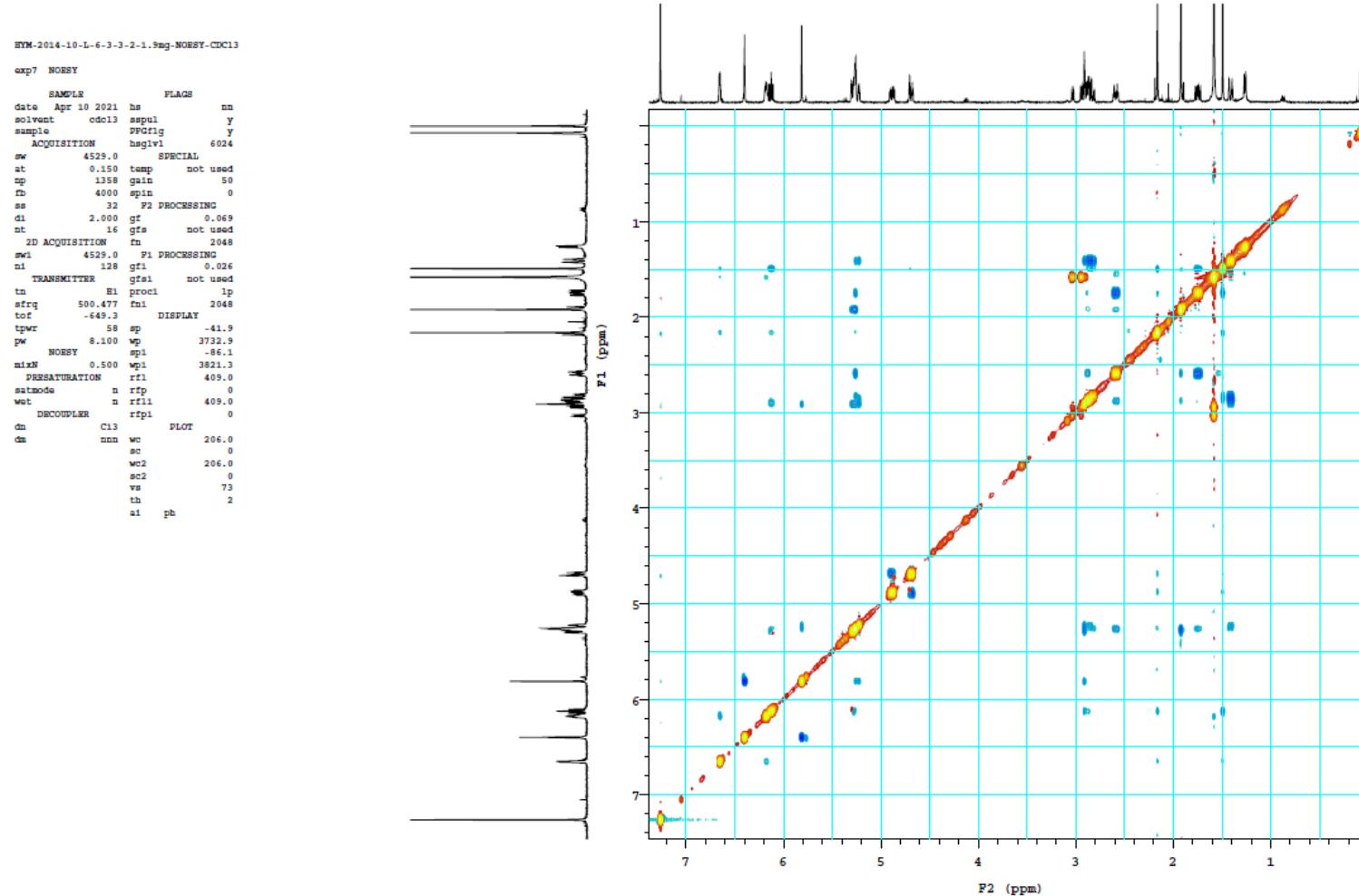
```



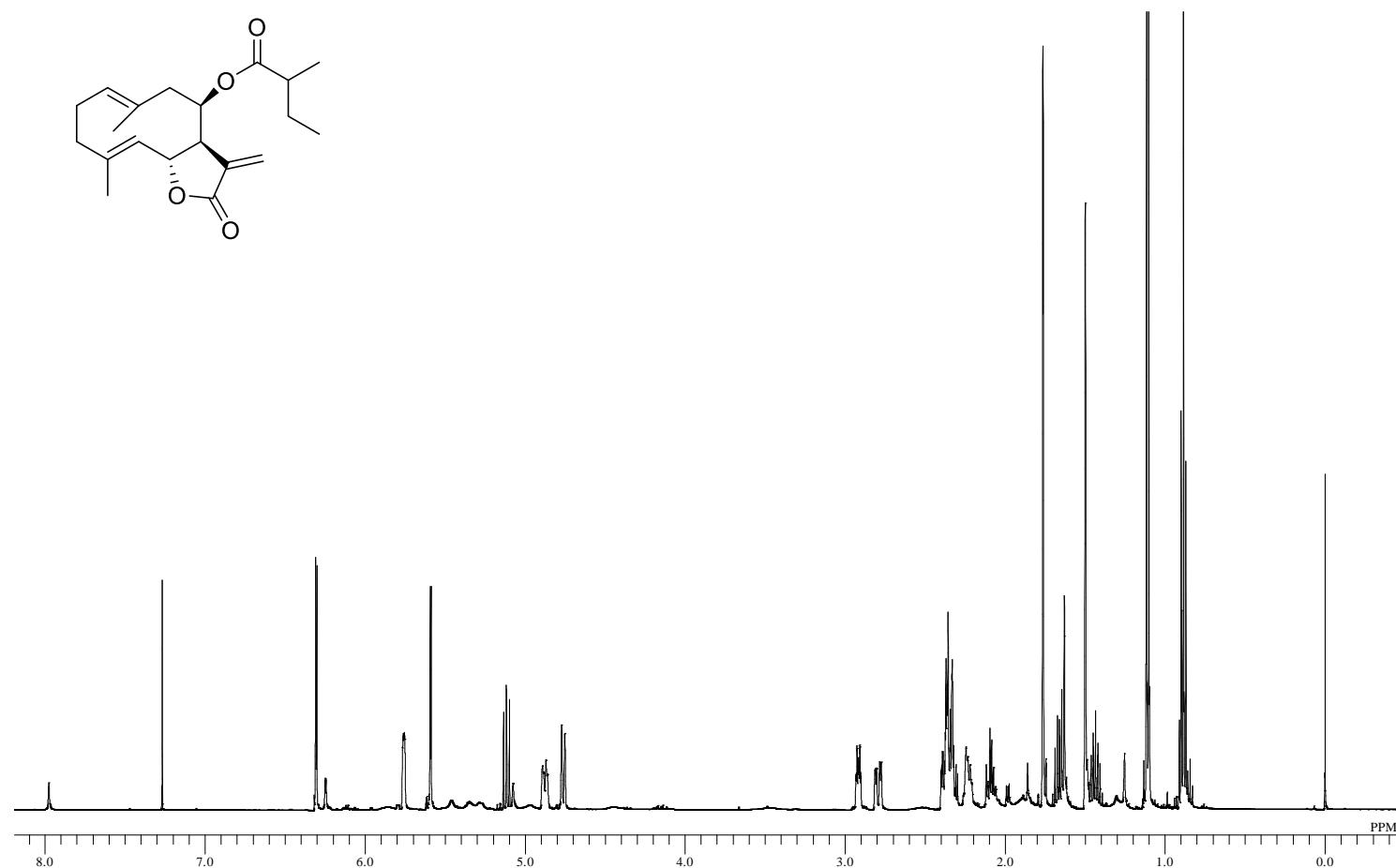
**Figure S25.** HMBC spectrum of **24** (measured in  $\text{CDCl}_3$ , 500 MHz).



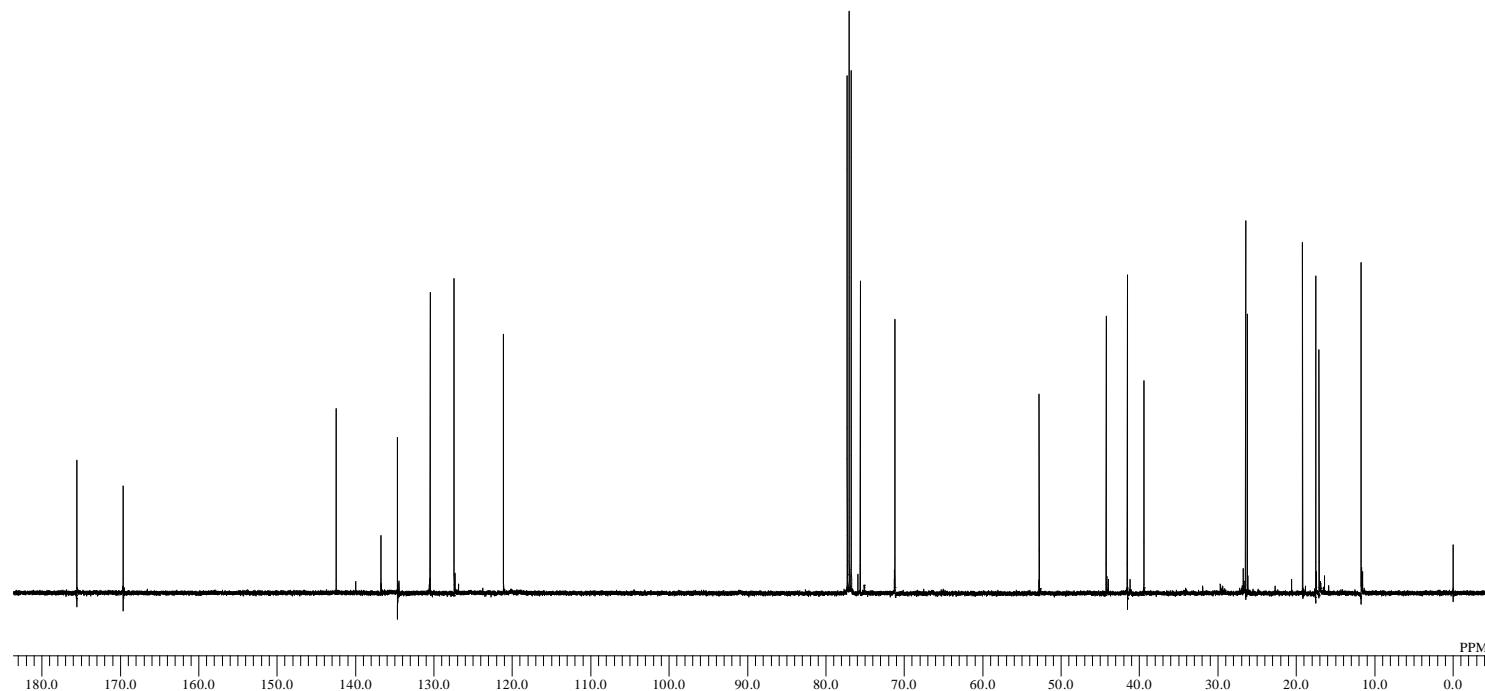
**Figure S26.** NOESY spectrum of **24** (measured in  $\text{CDCl}_3$ , 500 MHz).



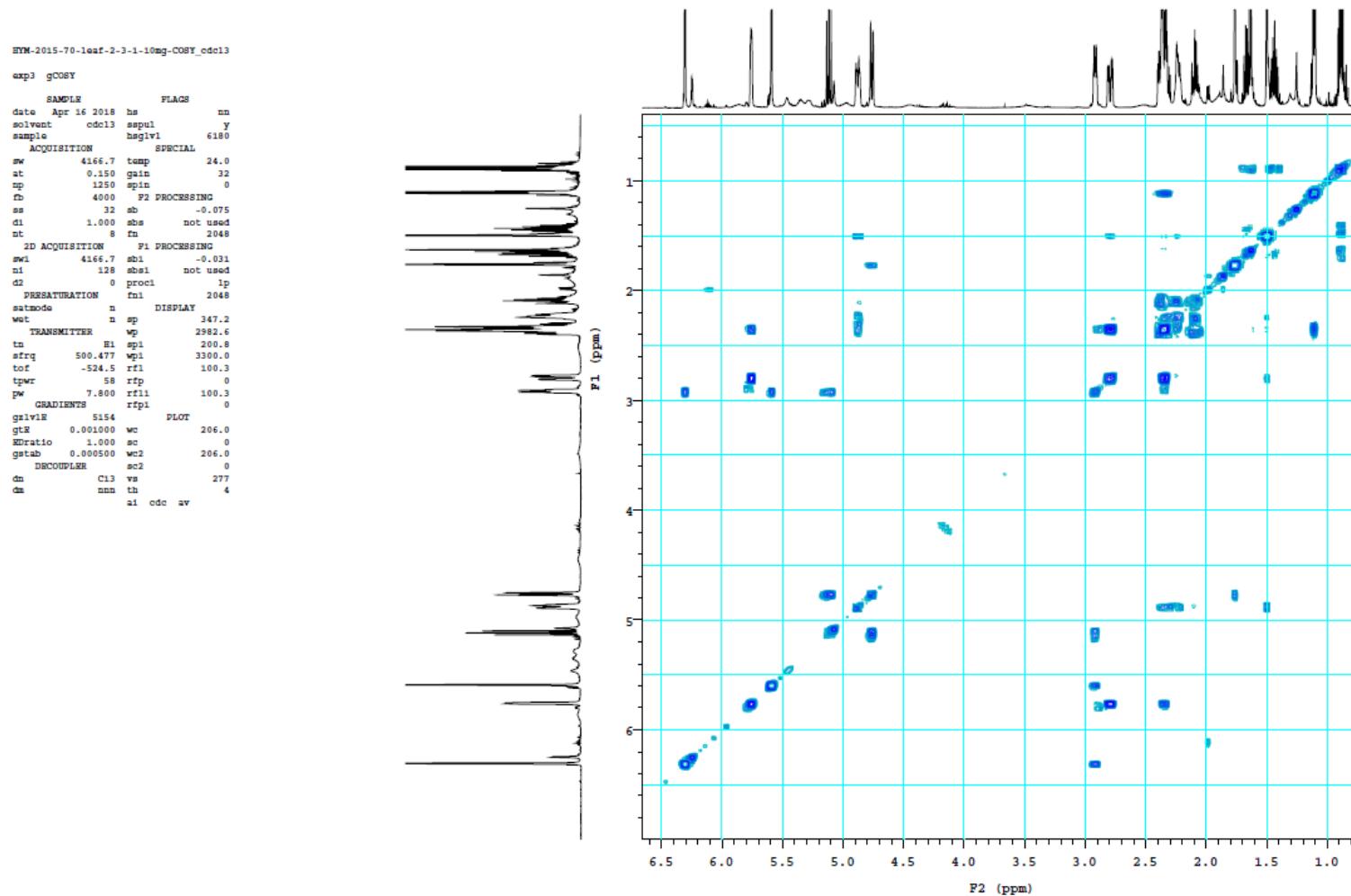
**Figure S27.**  $^1\text{H}$  NMR spectrum of **31** (measured in  $\text{CDCl}_3$ , 500 MHz).



**Figure S28.**  $^{13}\text{C}$  NMR spectrum of **31** (measured in  $\text{CDCl}_3$ , 126 MHz).



**Figure S29.**  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of **31** (measured in  $\text{CDCl}_3$ , 500 MHz).



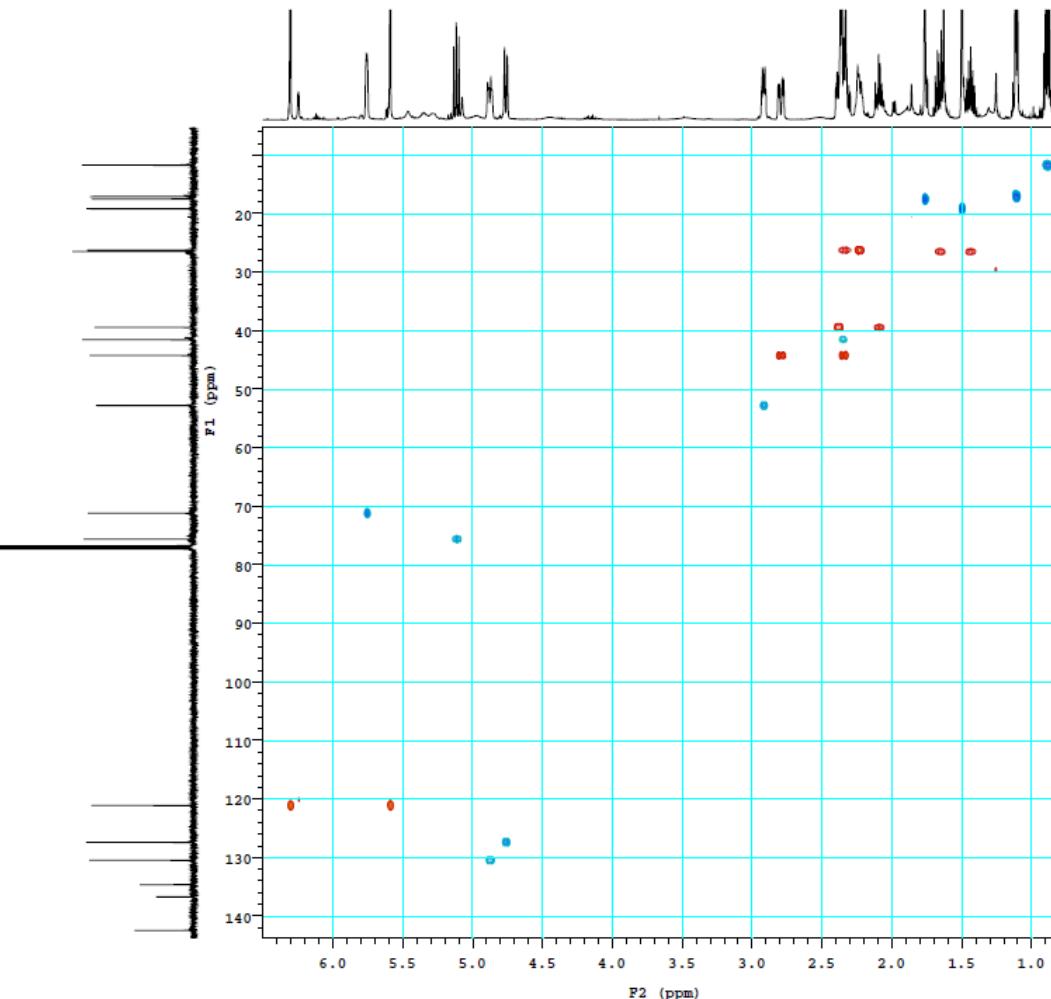
**Figure S30.** HSQC spectrum of **31** (measured in  $\text{CDCl}_3$ , 500 MHz).

```

HYM-2015-70-leaf-2-3-1-10mg-HSQC_odec13
exp5 HSQCAD

SAMPLE          FLAGS      ACQUISITION ARRAYS
date Apr 16 2018 hs        nn      array    phase
solvent odec13 ssqul      y       arraydim 256
sample          PPGcig     y
ACQUISITION    hsgv1l    6180  1      phase
sw   4166.7   SPECIAL   1      1
at   0.150   temp      24.0   2
np   1250    gain      32
fb   4000    spin      0
ss   32      P2 PROCESSING
di   1.000   gf      0.069
nt   8       gfs      not used
2D ACQUISITION fn      2048
sw1  21390.4   PI PROCESSING
n1   128      gfs      0.005
phase arrayed gfs1      not used
DESATURATION   proc1     lp
satmode n      fni      2048
wut   n      DISPLAY
TRANSMITTER    sp      359.5
tn   H1      wp      2893.1
afrq 500.477  sp1      666.2
tof   -524.5  wpi      17421.5
tpwr 58      rf1      100.3
pw   7.800   rfp1     0
DECOUPLER      C13     rfpl     1255.6
dn   -2487.0  PLOT
dm   nny   w0      206.0
decwave W40_HCNHm ad      0
dmt   32258  wct2     206.0
dpwr 38      sc2      0
pwx1v1 56      vs      277
pwx1v1 10.600 th      1
pwx1v1 10.600 th      1
HSQC           ai      odc ph
j1xh 146.0
nullfig Y
nullk 2
ADABATIC
pwx180ad GNR ad300
pwx180adH GNR ad30-
OR
pwx180 465.4
pwx1v180 51
pwx180ref GNR ref2-
00
pwx180r 2000.2
pwx1v180r 43

```



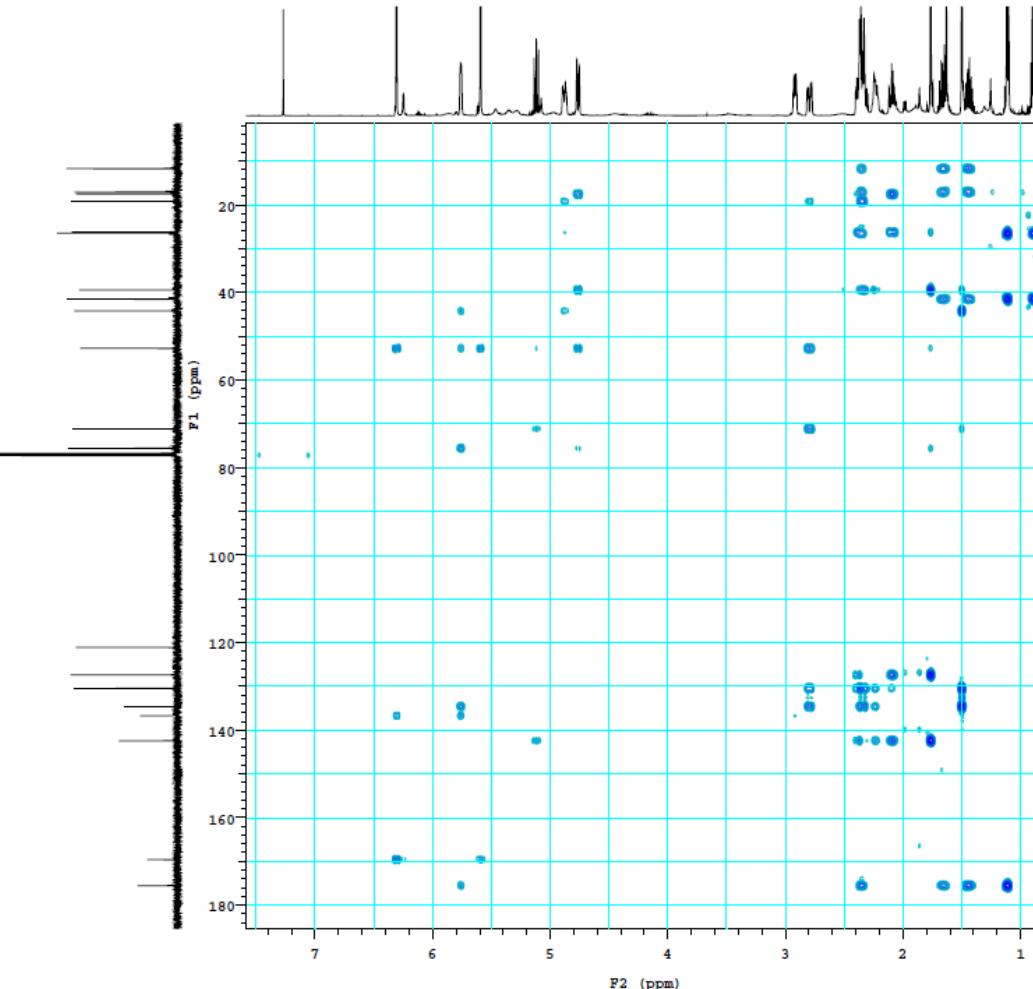
**Figure S31.** HMBC spectrum of **31** (measured in  $\text{CDCl}_3$ , 500 MHz).

```

HM-2015-70-leaf-2-3-1-10mg-HMBC_cdc13
exp6 gHMBCAD

SAMPLE          PLATES      ACQUISITION ARRAYS
date   Apr 16 2018 hs        nn      array    phase
solvent   cdc13  sspl       y      arraydim  256
sample    DPGfrg          y
ACQUISITION   b4glv1    6180  1      phase
sw      4166.7  SPGRCL    1      1
at      0.150  temp      24.0   2
np      1250   gain      32
fb      4000   spin      0
ss      32     GRADIENTS
dt      1.000  gr1v11   409
nt      16     gr1v11  0.001000
2D ACQUISITION gr1v13  1227
sw1    30200.1  gt3     0.001000
ni      128   gtab     0.000500
phase   arrayed   P2 PROCESSING
PRESATURATION ab     -0.075
satmode nabs    not used
wet     nfn     2048
TRANSMITTER   P1 PROCESSING
tn      H1   gfi     0.004
sfrq   500.477 gfs1    not used
t0f     -524.5  proc1   1p
tpwr    58   fmi    2048
pw      7.800  DISPLAY
DECOUPLER    sp     375.8
dn      C13   wp     3413.9
dof     1287.0  sp1     178.1
dm      mnm   wp1    23151.4
Decwvav W40_HCNSP1  rfi1  100.3
dmr    32258  rfp     0
dpwr    38   rfp11  1886.4
pwxlv1  56   rfp1   0
pwx    10.600  PLOT
HMBC      ws     206.0
j1xb   146.0  ws     0
j2xb    8.0   ws2    206.0
ADIABATICIC  ws2     0
pwx180ad ONE_ad300  ws     277
pwx1180      51   th     1
pwx180     465.4  ai   cdc av

```



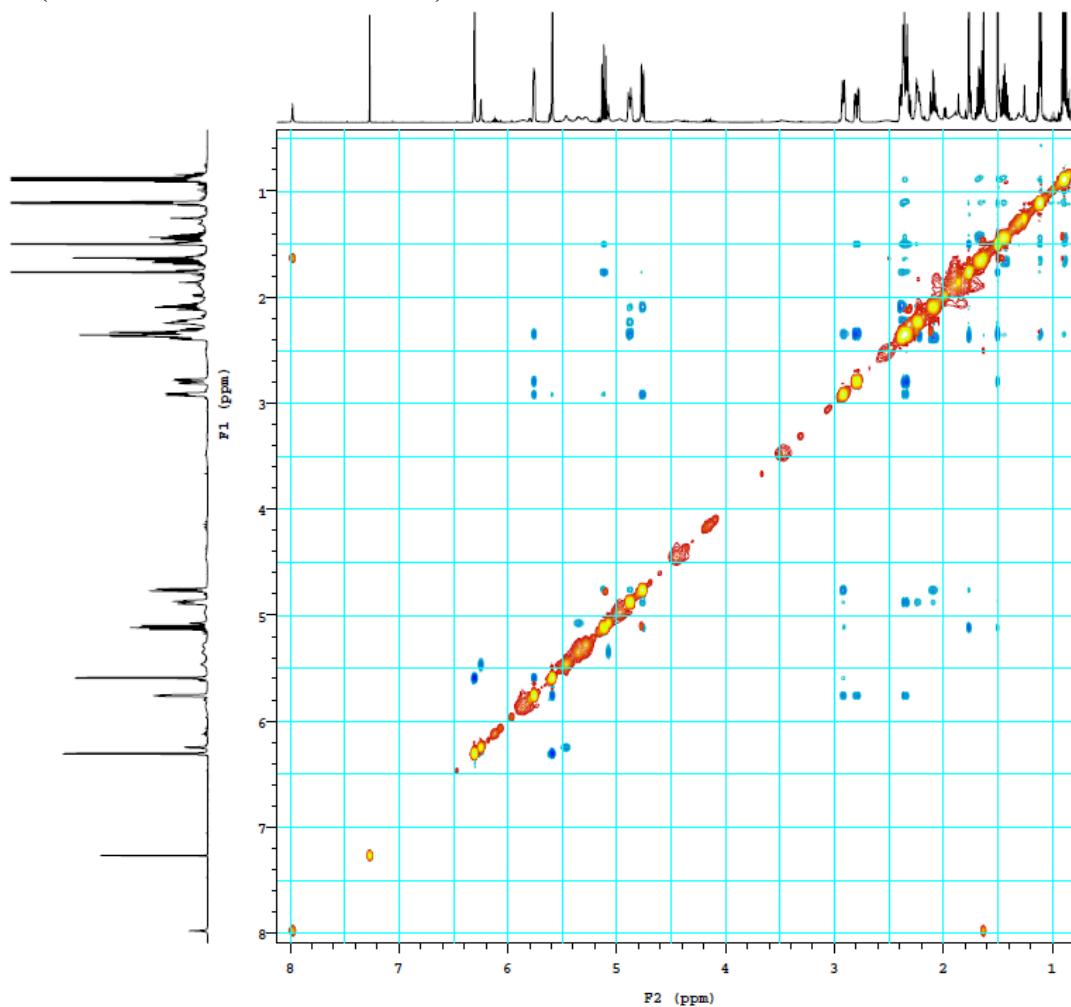
**Figure S32.** NOESY spectrum of **31** (measured in  $\text{CDCl}_3$ , 500 MHz).

```

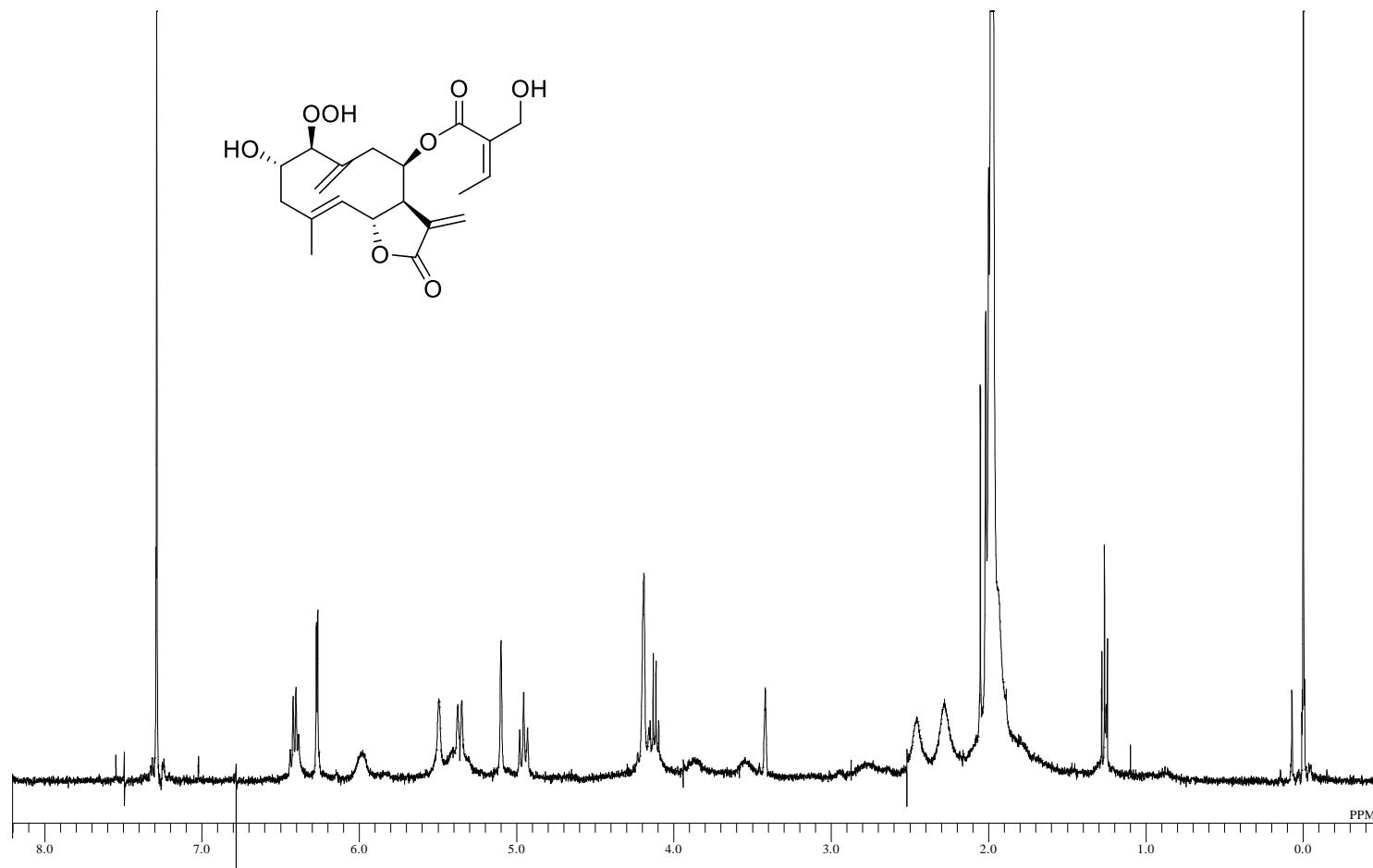
HYM-2015-70-leaf-2-3-1-10mg-NOESY_cdc13
exp7 NOESY

SAMPLE          FLAGS
date   Apr 16 2018 hs      nn
solvent    cdc13 ssqul     y
sample    PPGfig    PPGfig  y
ACQUISITION   hsgv1l    6180
sw       4166.7   SPECIAL
at        0.150   temp     24.0
tp        1250    gain     32
fb        4000    spin     0
ss        32      P2 PROCESSING
d1       2.000    g1        0.069
nt        8       gfts      not used
2D ACQUISITION fn      2048
sw1      4166.7   P1 PROCESSING
ni        128     gft1     0.028
TRANSMITTER   gft1     not used
tn       H1      proc1    1p
afrq     500.477  fml      2048
tof      -524.5   DISPLAY
tppr     58      ap       339.1
pw       7.800    ap       3723.1
NOESY      0.500  wpl      3837.1
mixN     0.500  wpl      3837.1
PRESATURATION rfl      100.3
satmode   n      rfp      0
wet      n      rfll     100.3
DECOUPLER    rfp1     0
dn       C13      PLOT
dm      nnn ws     206.0
sc      0
wc2     206.0
sc2     0
vs      277
th      1
ai      ph

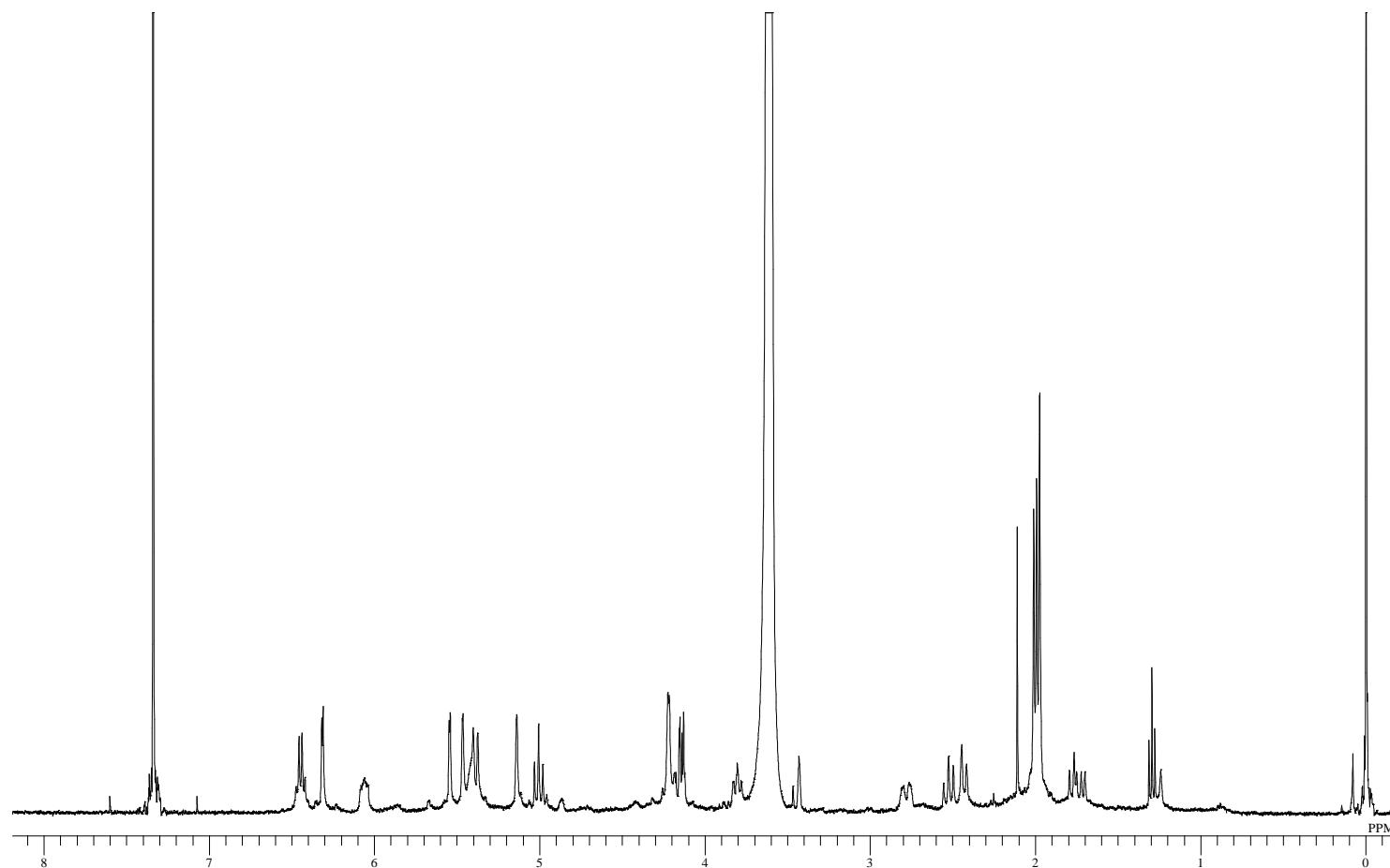
```



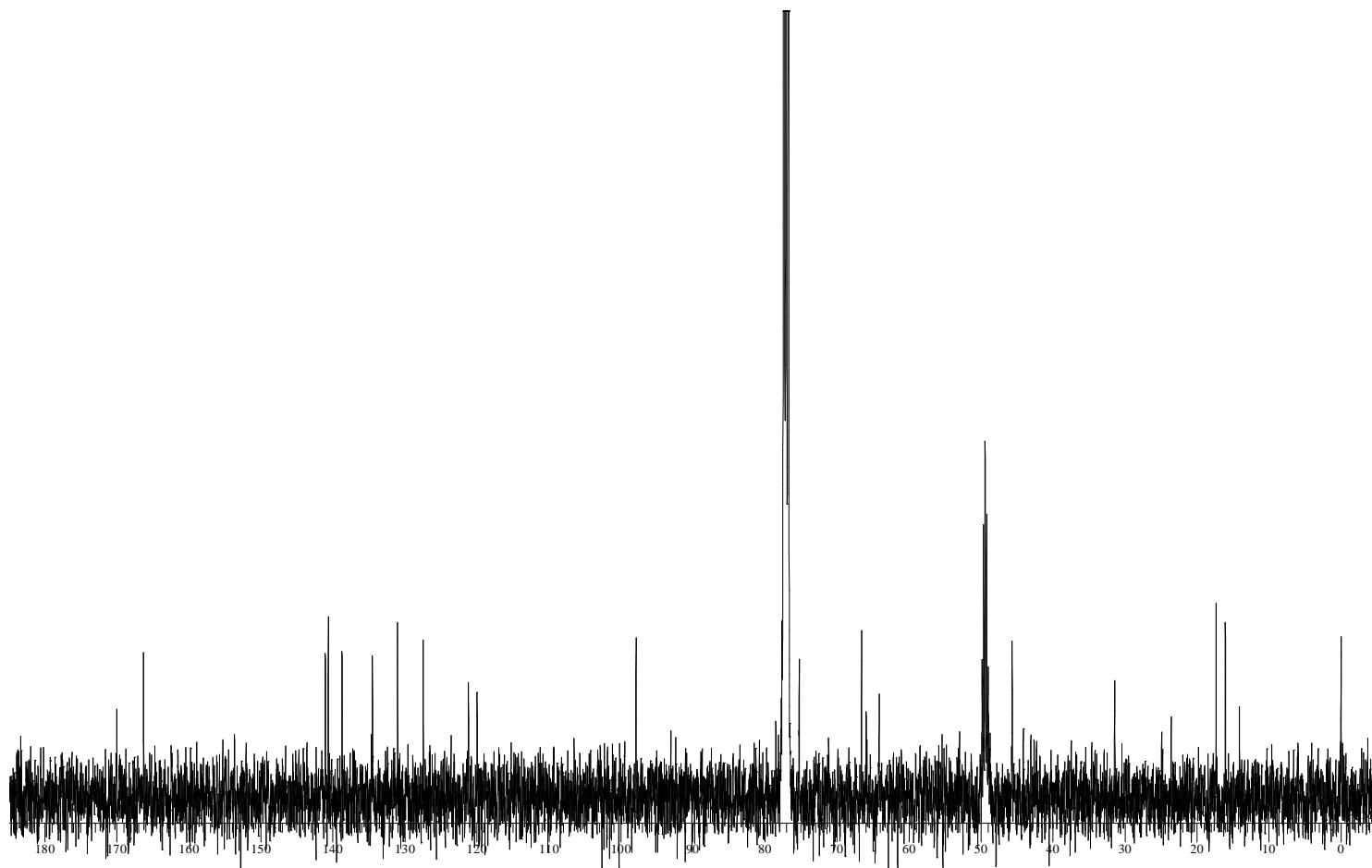
**Figure S33.**  $^1\text{H}$  NMR spectrum of **36** (measured in  $\text{CDCl}_3$ , 500 MHz, 298 K).



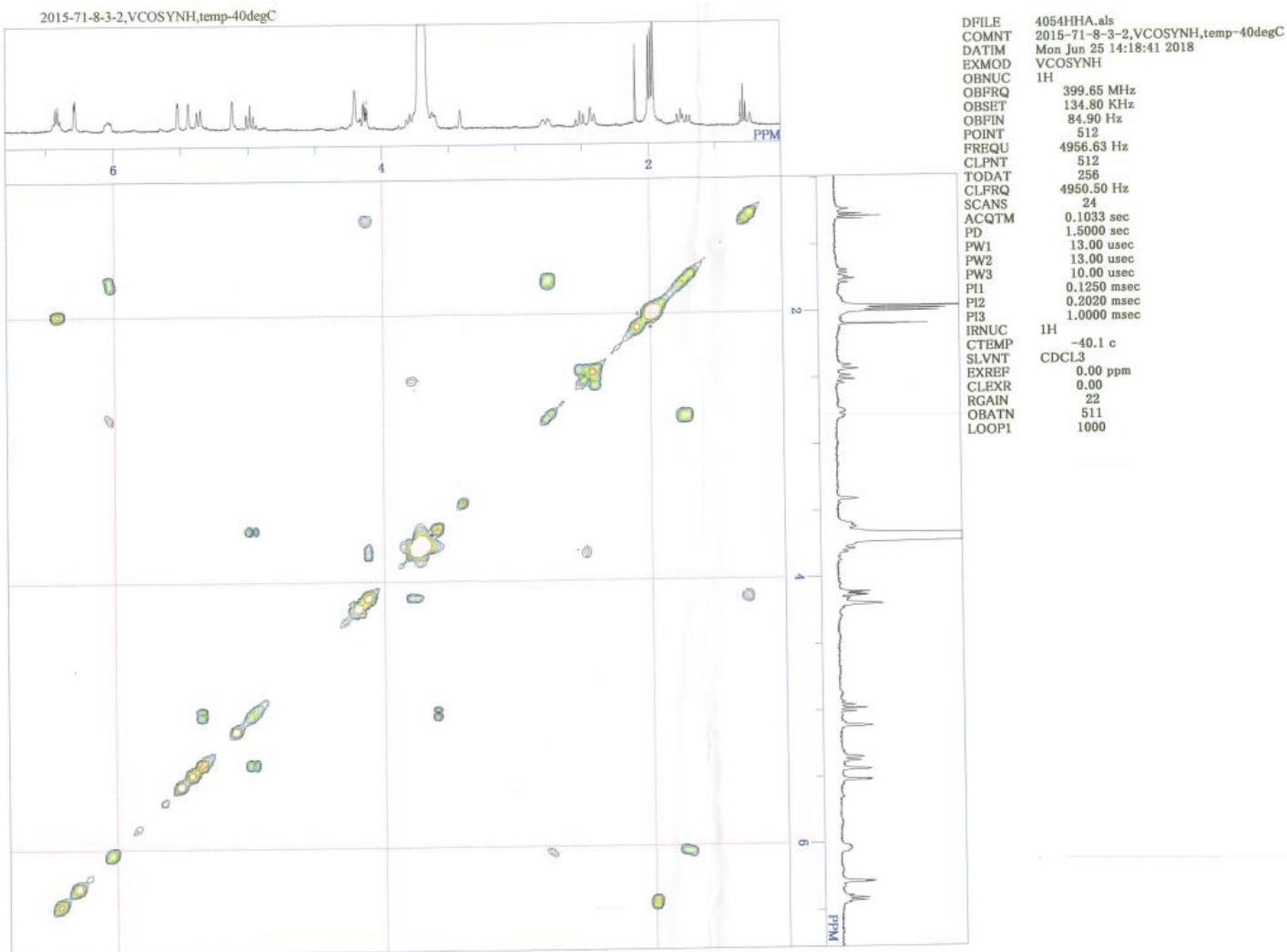
**Figure S34.**  $^1\text{H}$  NMR spectrum of **36** (measured in  $\text{CDCl}_3$ , 400 MHz, 233 K).



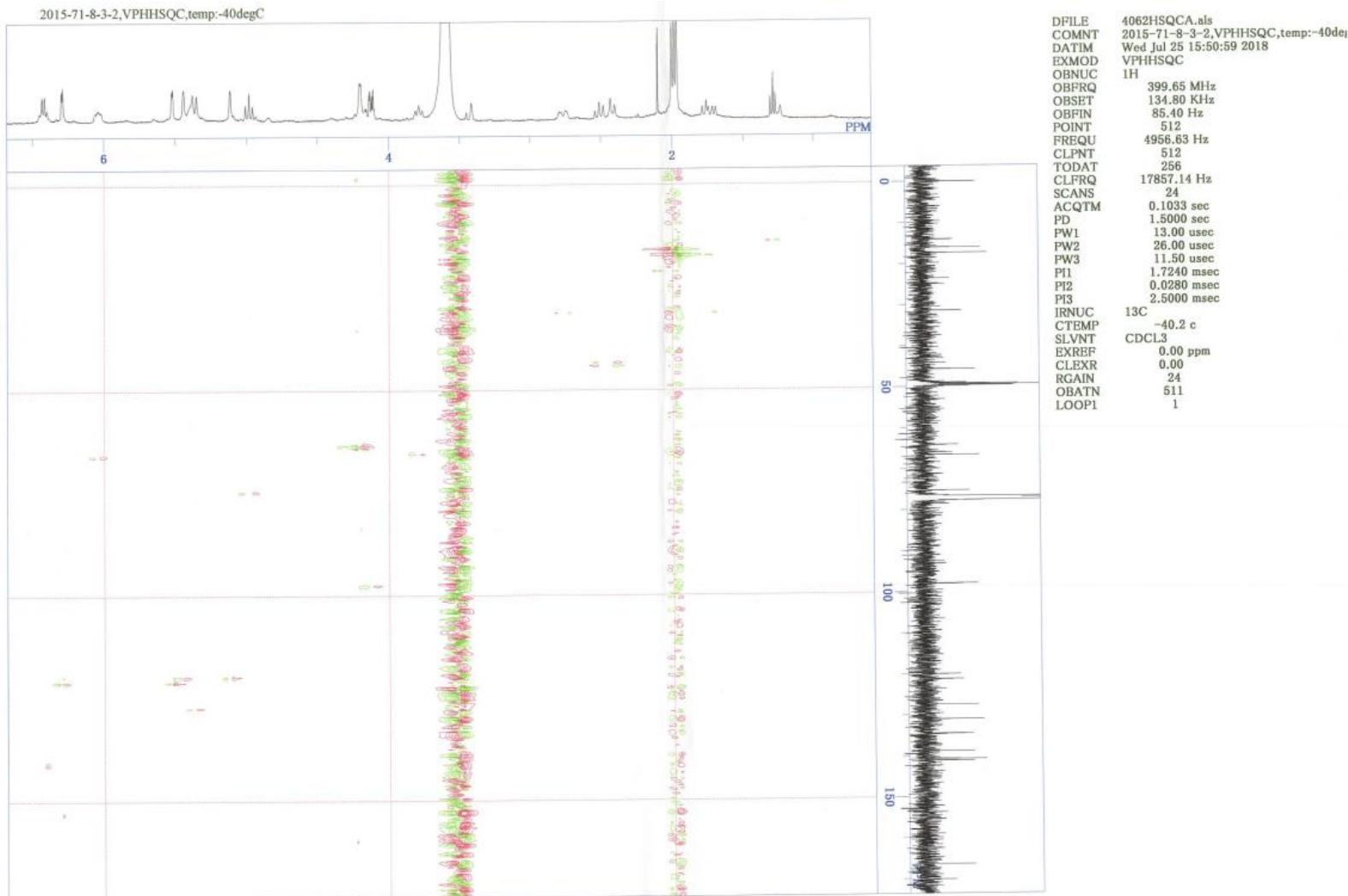
**Figure S35.**  $^{13}\text{C}$  NMR spectrum of **36** (measured in  $\text{CDCl}_3$ , 100 MHz, 233 K).



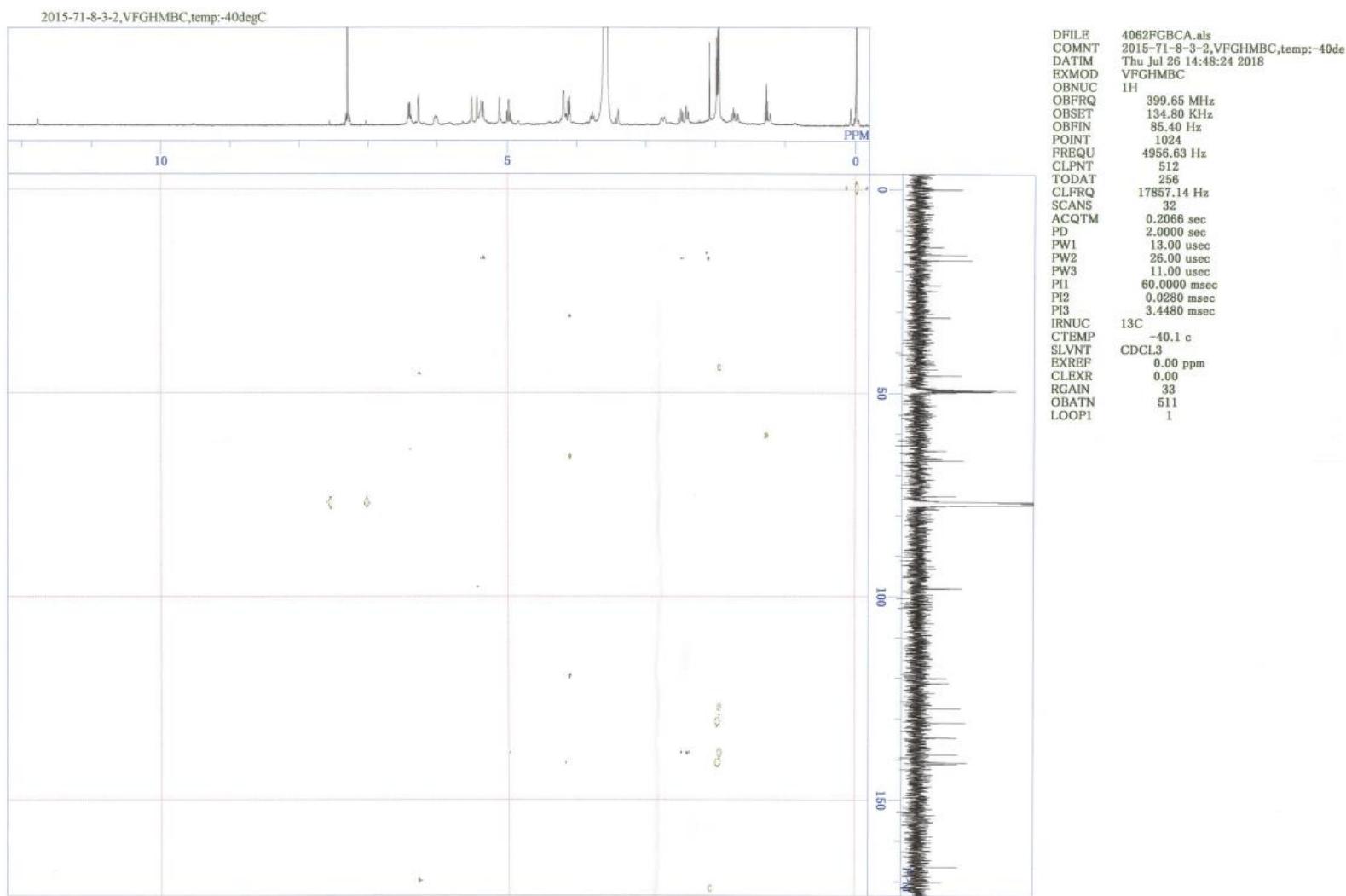
**Figure S36.**  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of **36** (measured in  $\text{CDCl}_3$ , 400 MHz, 233 K).



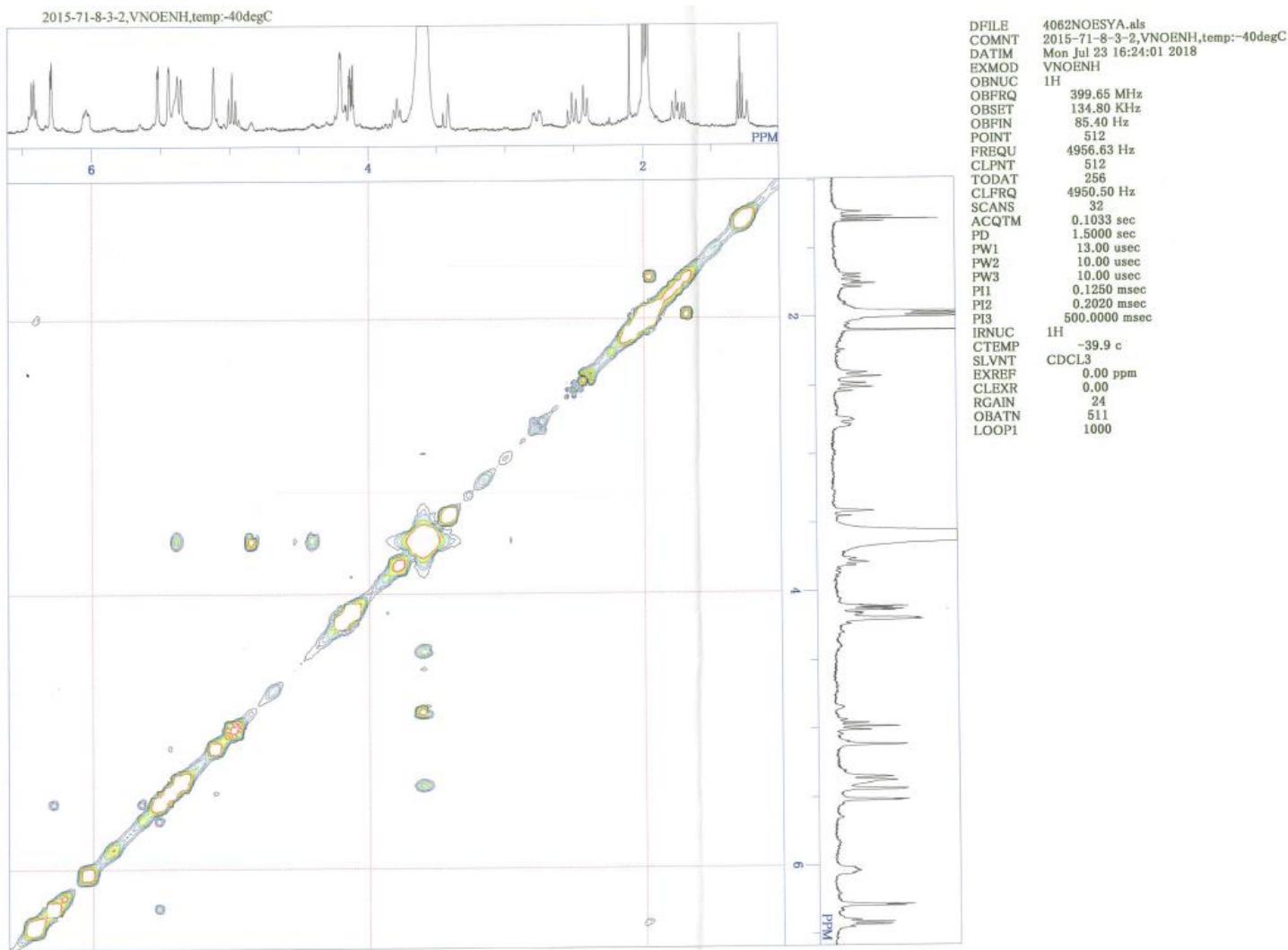
**Figure S37.** HSQC spectrum of **36** (measured in  $\text{CDCl}_3$ , 400 MHz, 233 K).



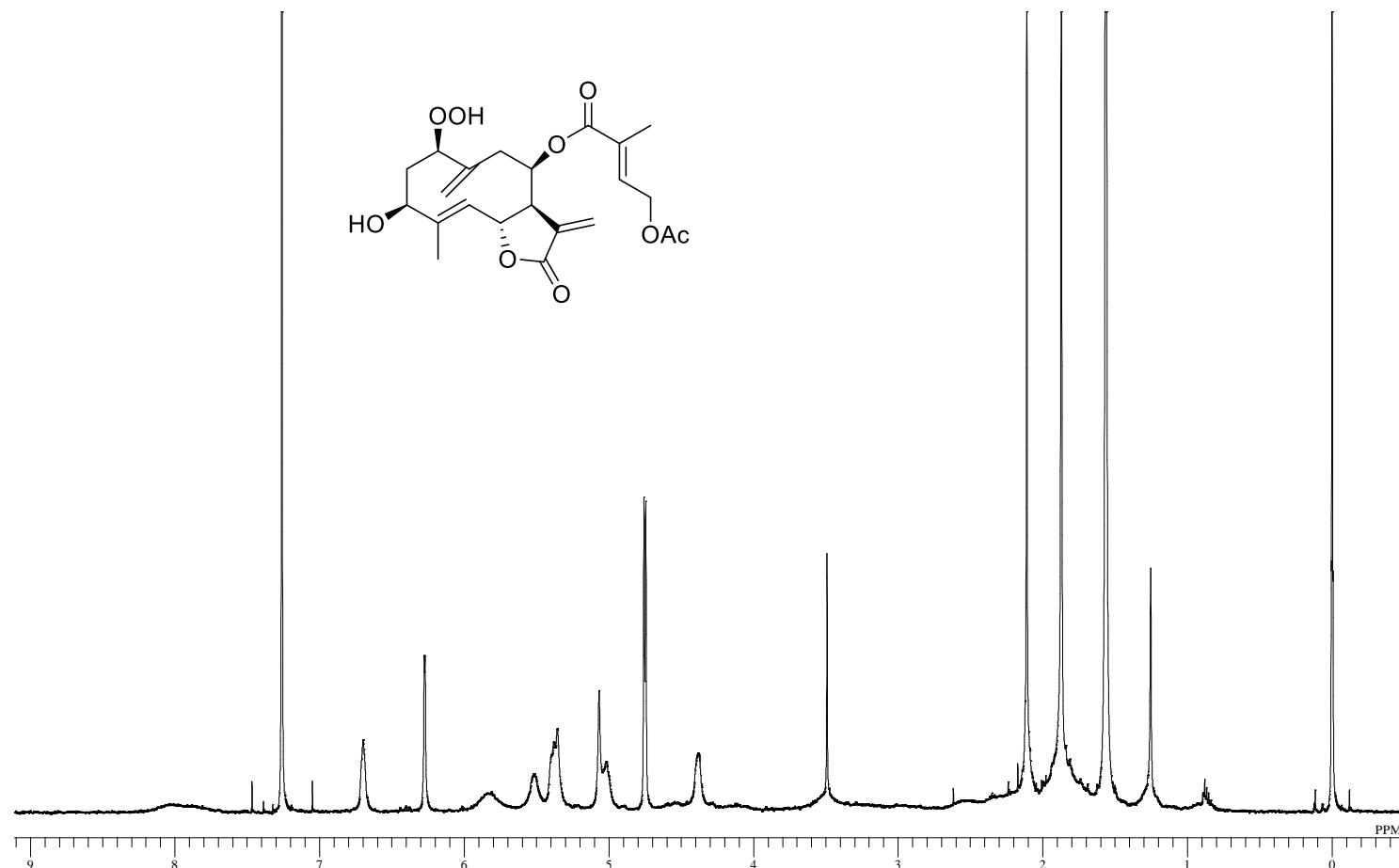
**Figure S38.** HMBC spectrum of **36** (measured in  $\text{CDCl}_3$ , 400 MHz, 233 K).



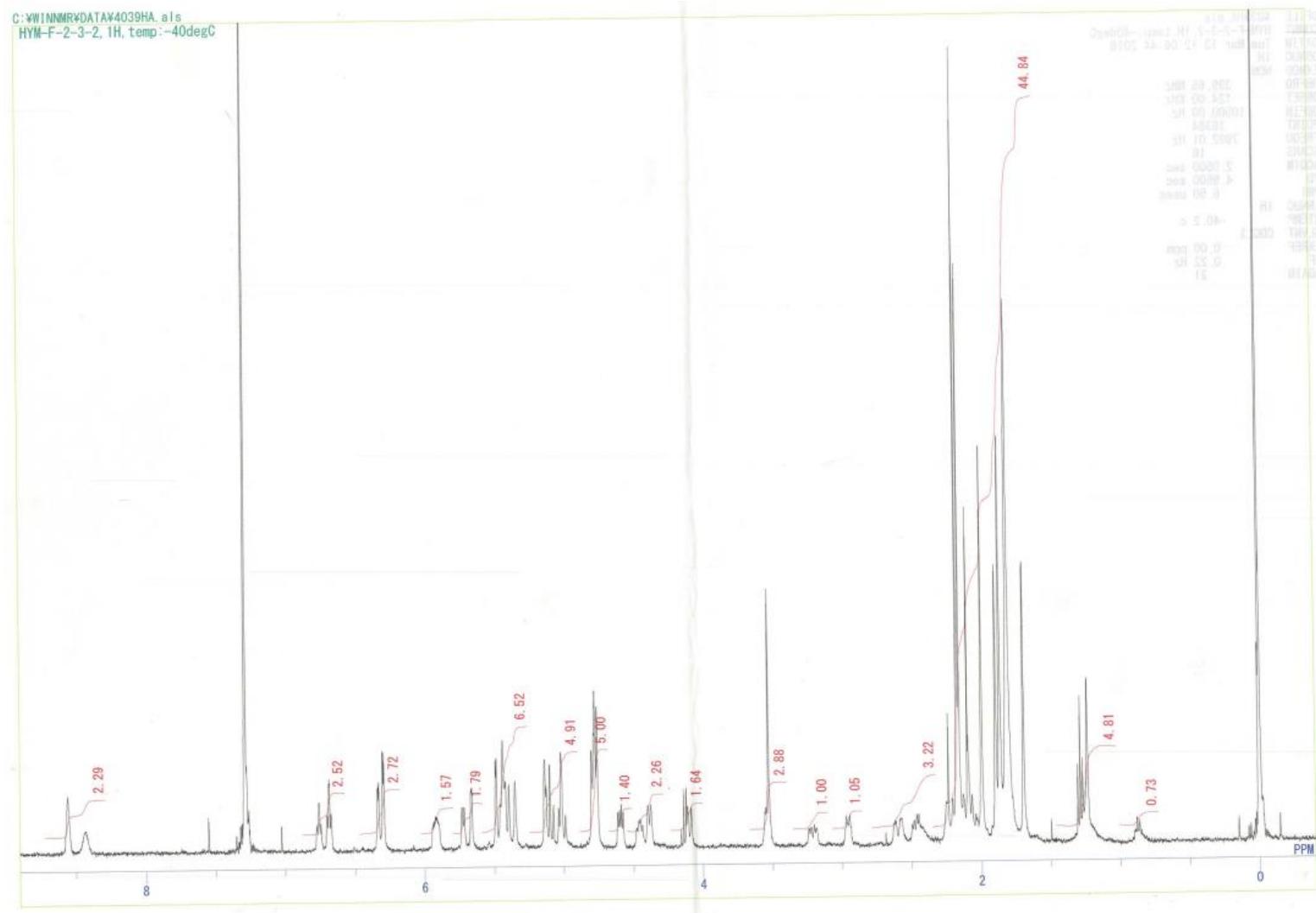
**Figure S39.** NOESY spectrum of **36** (measured in  $\text{CDCl}_3$ , 400 MHz, 233 K).



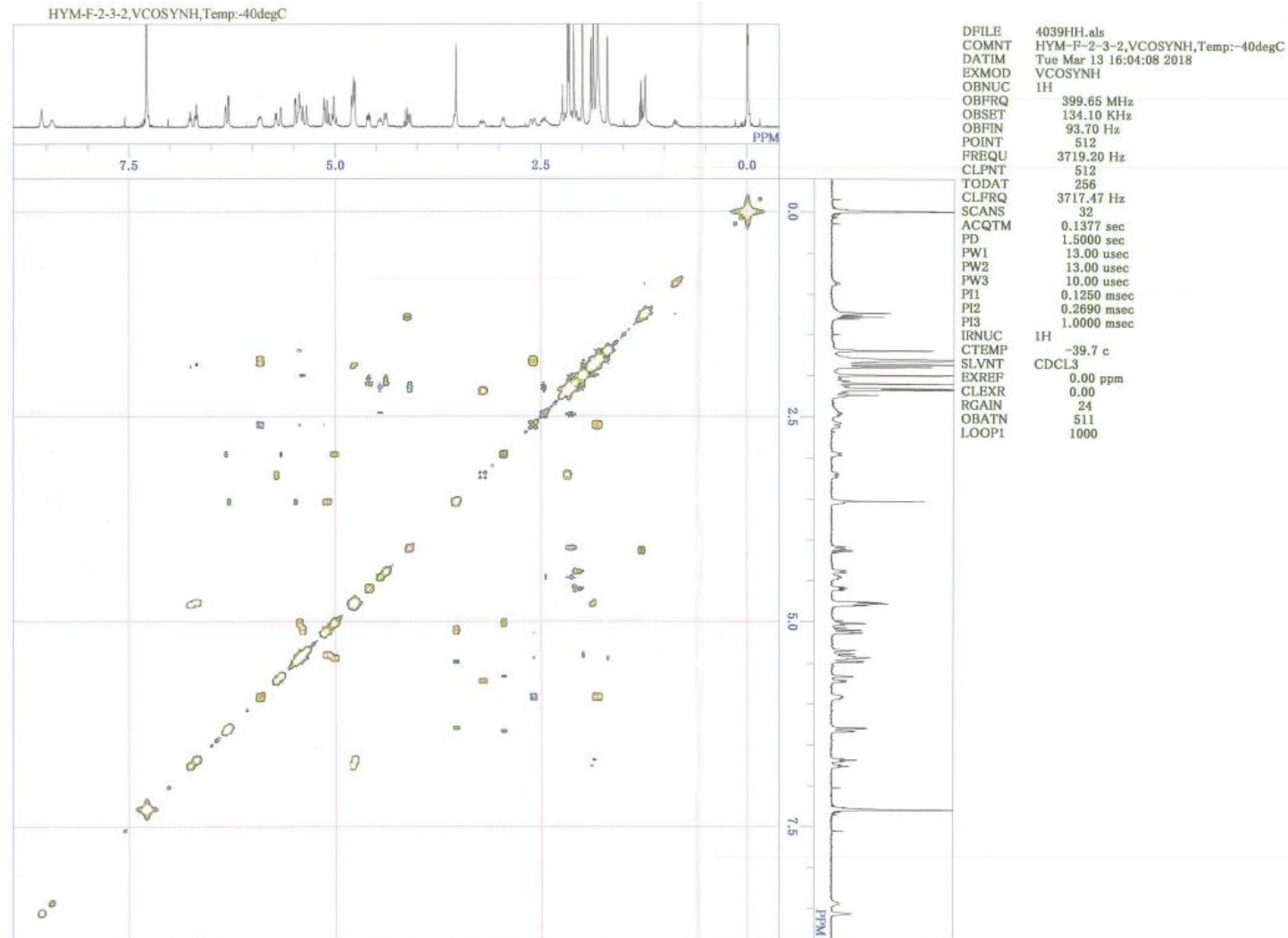
**Figure S40.**  $^1\text{H}$  NMR spectrum of **40** (measured in  $\text{CDCl}_3$ , 500 MHz, 298 K).



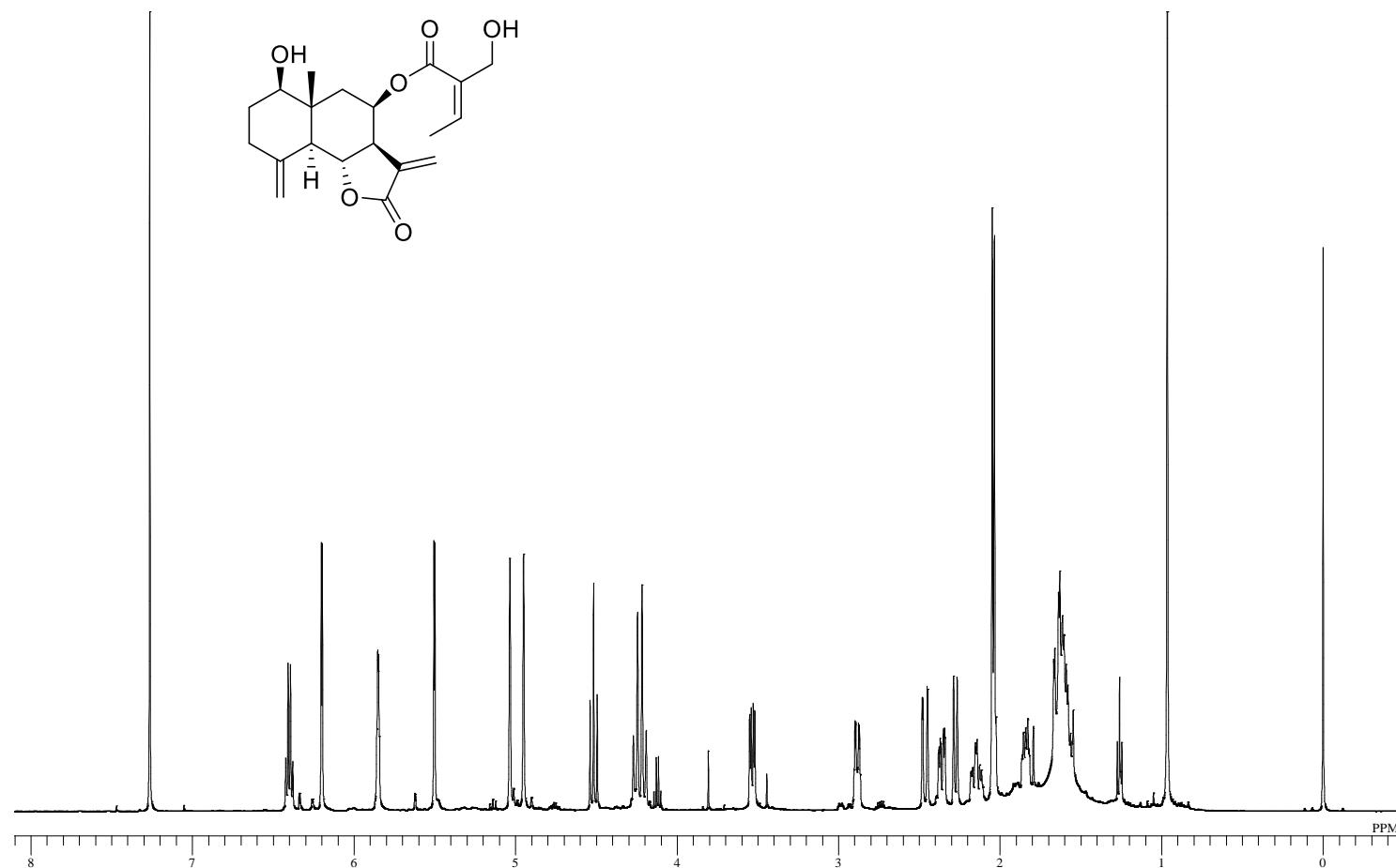
**Figure S41.**  $^1\text{H}$  NMR spectrum of **40** (measured in  $\text{CDCl}_3$ , 400 MHz, 233 K).



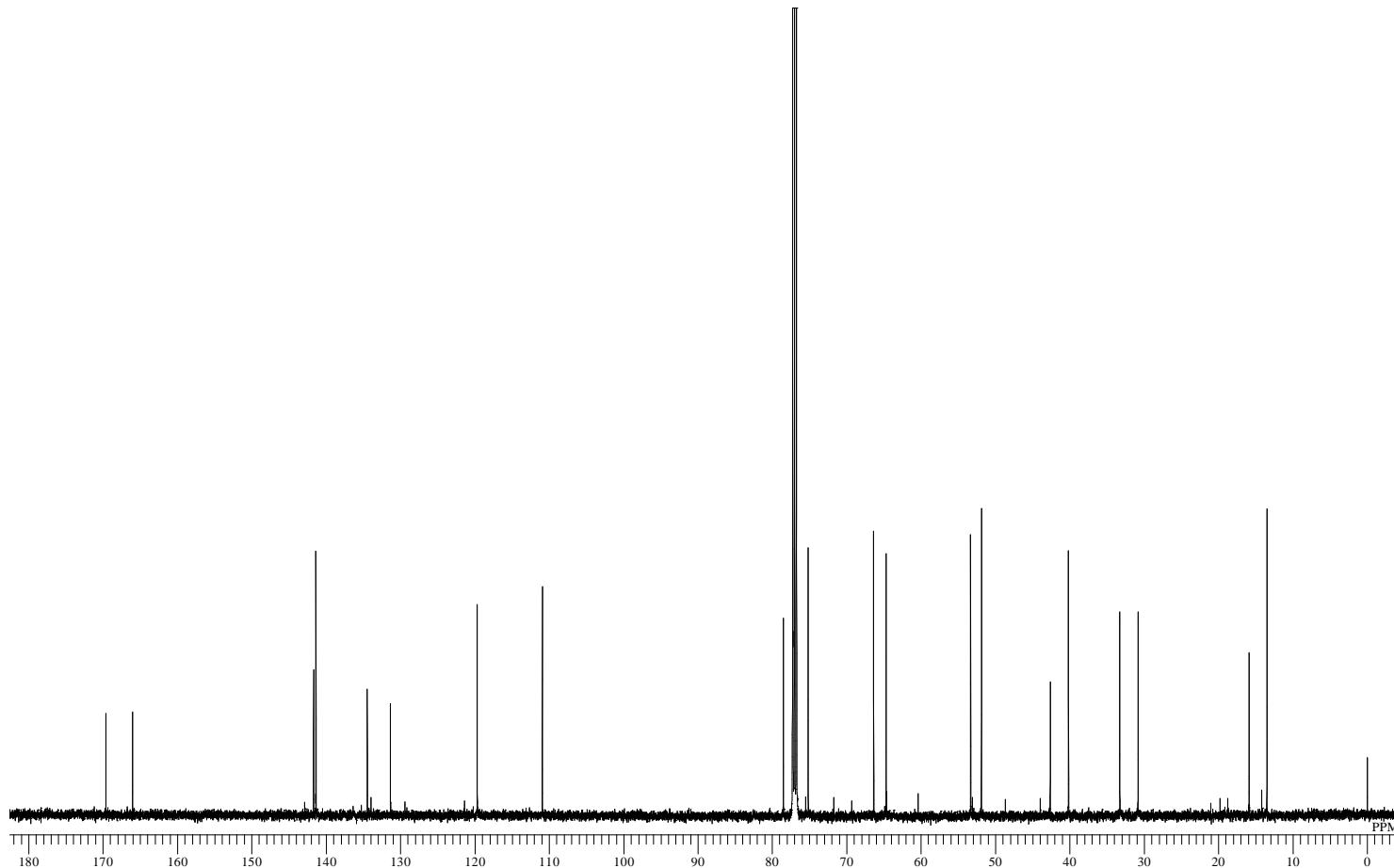
**Figure S42.**  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of **40** (measured in  $\text{CDCl}_3$ , 400 MHz, 233 K).



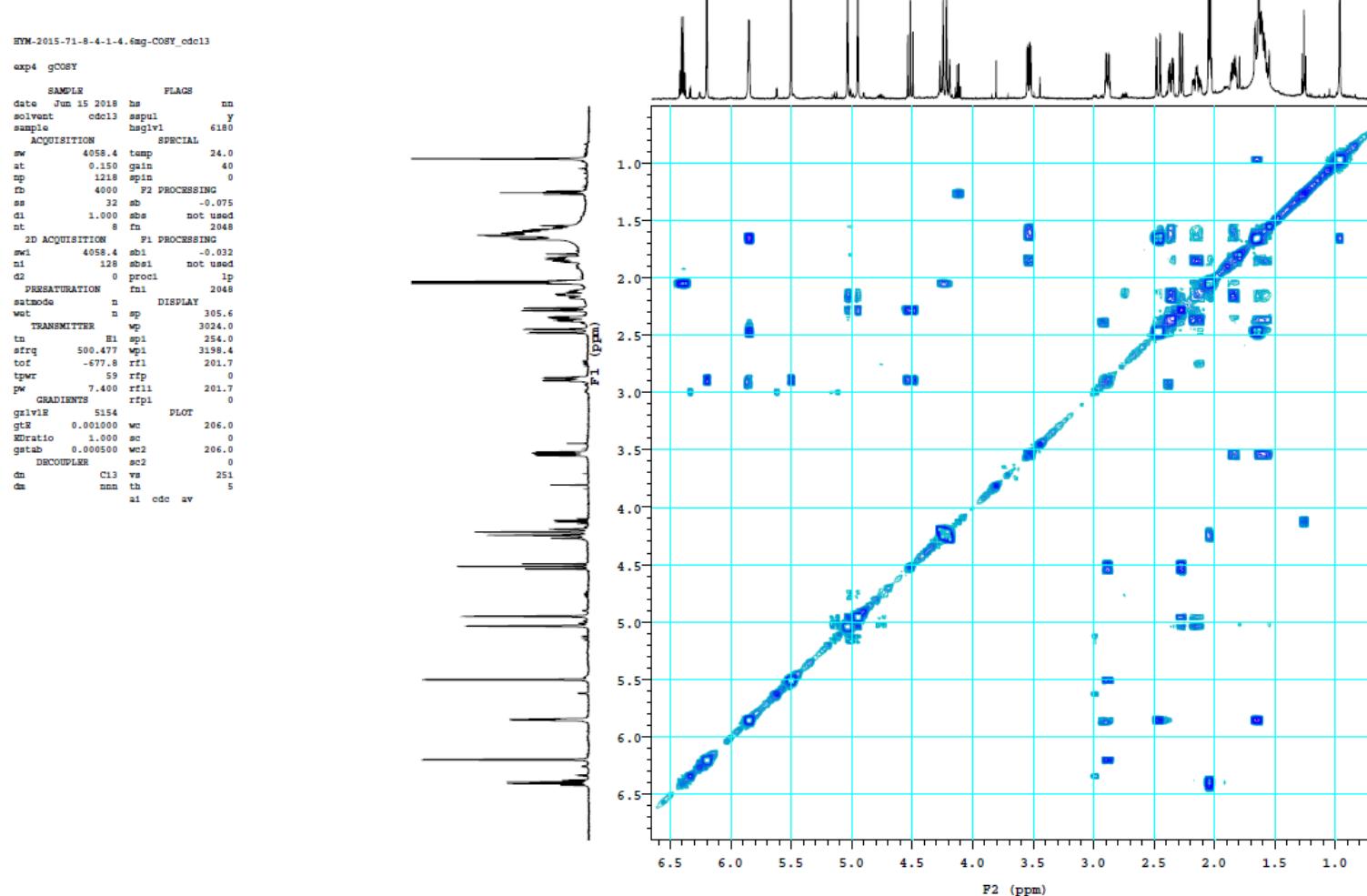
**Figure S43.**  $^1\text{H}$  NMR spectrum of **45** (measured in  $\text{CDCl}_3$ , 500 MHz).



**Figure S44.**  $^{13}\text{C}$  NMR spectrum of **45** (measured in  $\text{CDCl}_3$ , 126 MHz).



**Figure S45.**  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of **45** (measured in  $\text{CDCl}_3$ , 500 MHz).



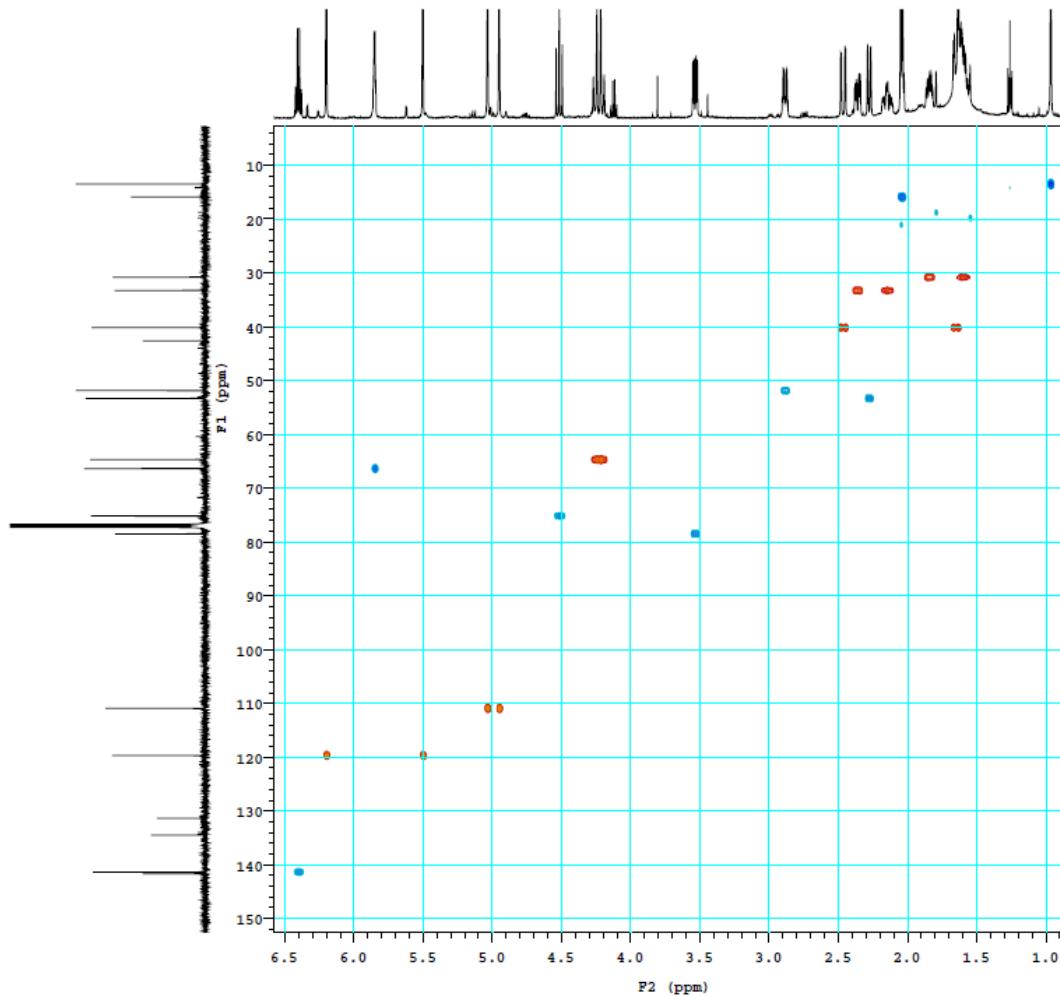
**Figure S46.** HSQC spectrum of **45** (measured in  $\text{CDCl}_3$ , 500 MHz).

```

HTM-2015-71-8-4-1-4.4mg-HSQC_cdc13
exp5 HSQCAD

SAMPLE          FLAGS      ACQUISITION ARRAYS
date   Jun 15 2018  hs       nn      array      phase
solvent    cdc13  aspol     y      arraydim    256
sample    DPCGig    y
ACQUISITION   hsg1v1    6180    1      phase
sw        4058.4  SPPECIAL   1      1
at         0.150  temp      24.0    2
np        1218   gain       40
fb        4000   spin       0
ss         32    F2 PROCESSING
d1        1.000  gfs      0.069
nt         8    gfts      not used
2D ACQUISITION   fn      2048
sw1      21390.4  F1 PROCESSING
nt1        128  gft1     0.006
phase      arrayed  gft1      not used
PRESATURATION   proc1    1p
satmode    n      fn1     2048
wet        n      DISPLAY
TRANSMITTER    sp      384.8
tn        H1  wpt     2905.1
stfgrq  500.477  sp1      352.9
t0f      -677.8  wpt1    18841.9
tpwr      59  rf1      201.7
pw       7.400  rfp      0
DECOUPLER      rf11    1255.6
dn        C13  rfpl      0
dof      -2487.0  PLOT
dm        nny  wc      206.0
decwave W40_HCN5m sc      0
dmf      32258  wct2    206.0
dpwr      38  sc2      0
pxv1v1    56  vs      251
pwr      11.000  th      2
HSQC          ai  cdc  ph
j1xb      146.0
nullfig     y
mult       2
ADIABATIC
pxv180ad ONH ad300
pxv180adr ONH ad30-
OR
pxv180      465.4
pxv1v180      51
pxv180ref ONH ref2-
00
pxv180r     2000.2
pxv1v180r     43

```



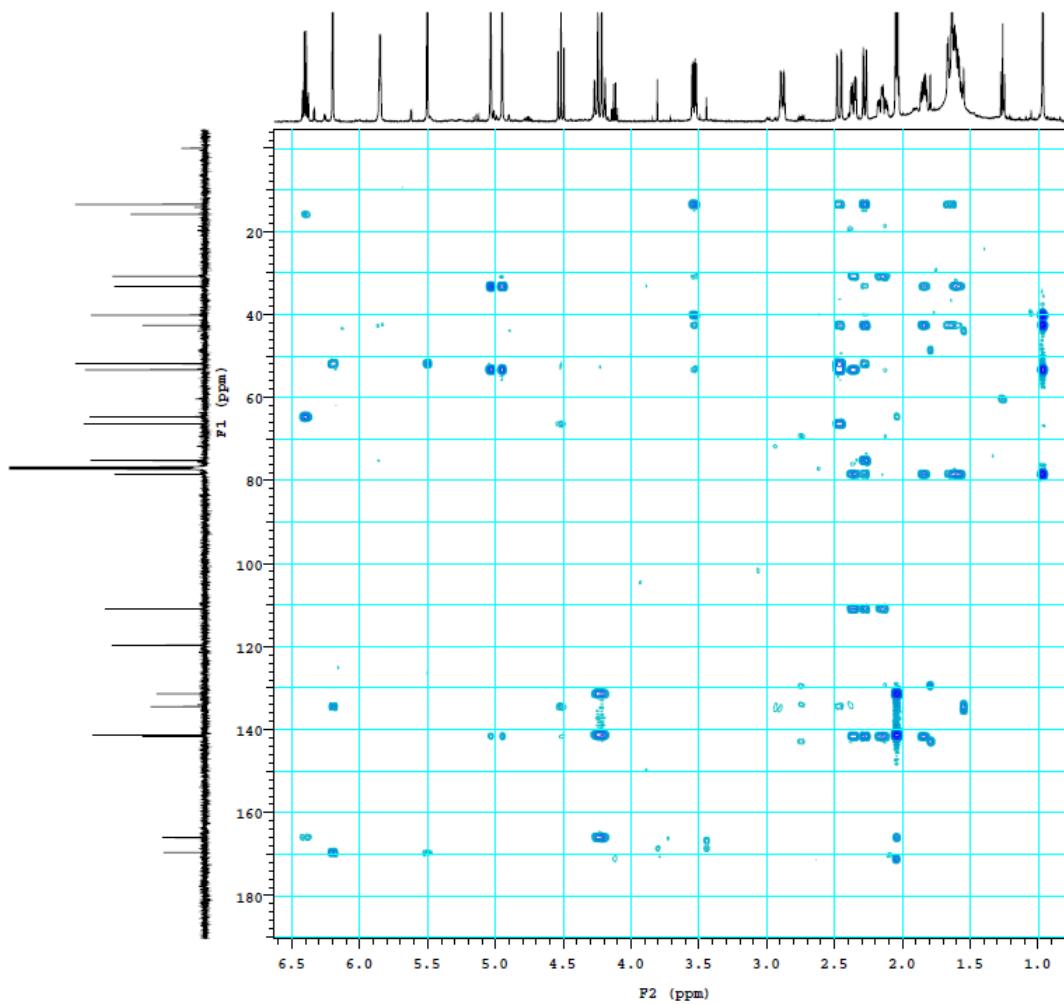
**Figure S47.** HMBC spectrum of **45** (measured in  $\text{CDCl}_3$ , 500 MHz).

```

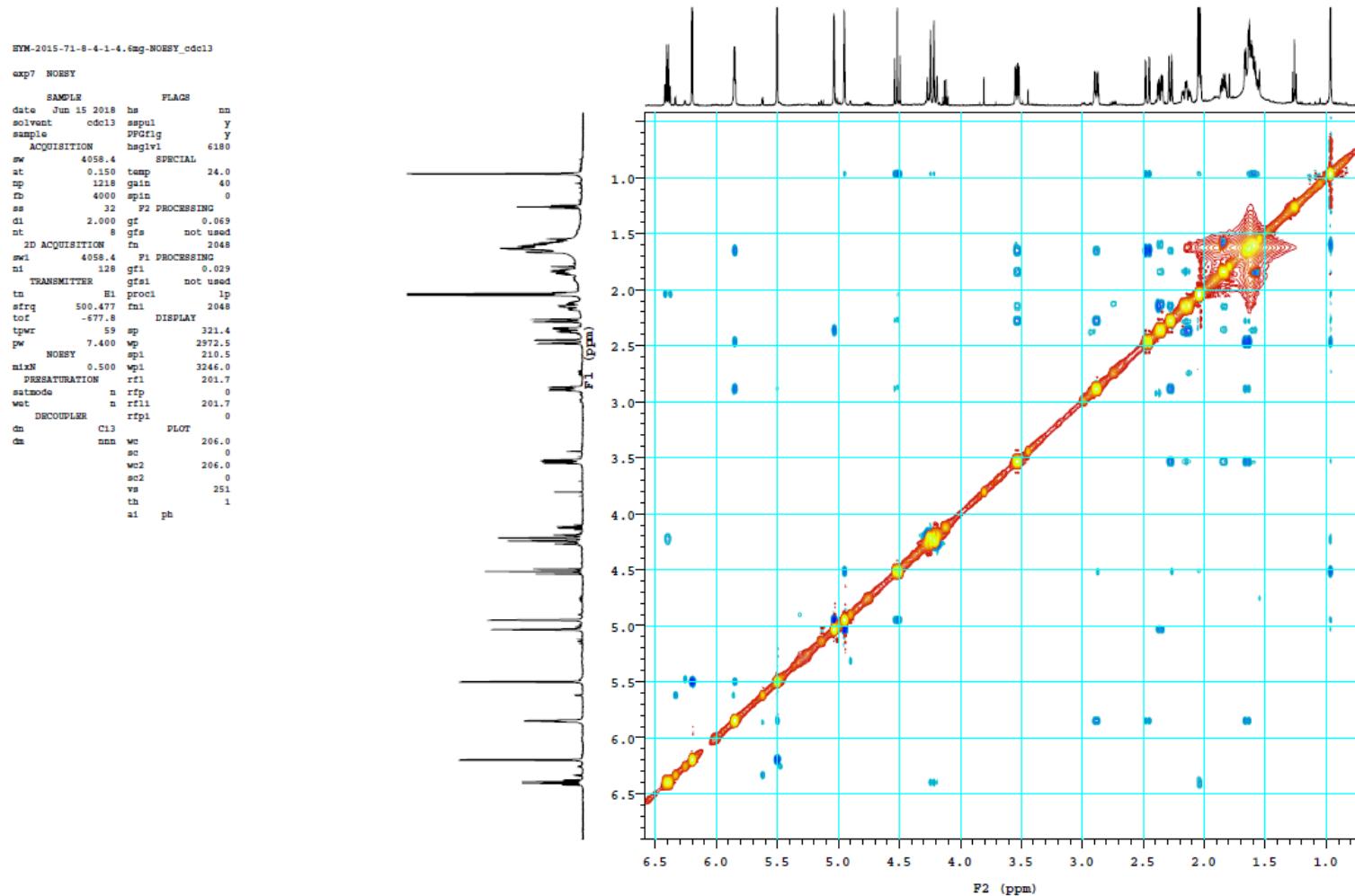
HYM-2015-71-8-4-1-4.fmg-HMBC_cdc13
exp6 gHMBCAD

SAMPLE          FLAGS      ACQUISITION ARRAYS
date   Jun 15 2018    hs        nn      array    phase
solvent   cdc13    ssppul     y      arraydim  256
sample          PPGfig     y
ACQUISITION    hsgv1l    6180    1      phase
sw       4058.4    SPECIAL   1        1
at       0.150    temp     24.0    2
np       1218     gain      40
fb       4000    spin      0
ss        32    GRADIENTS
di       1.000    gr1v1l   409
nt       16      gt1      0.001000
2D ACQUISITION  gr1v1l3  1227
sw1      30200.1   gt3      0.001000
ni        128    gtab      0.000500
phase      arrayed    F2 PROCESSING
PRESATURATION    sb      -0.075
satmode      nabs    not used
wet        nfn      2048
TRANSMITTER      F1 PROCESSING
tn        61      gfc      0.004
stsq      500.477   gr1s    not used
tof      -677.8    proc1      1p
tpwr      59    fmi      2048
pw       7.400    DISPLAY
DECOUPLER      sp      345.2
dm        C13    wp      2972.5
dof      1287.0   spi      -559.3
dm        nnn    wpi     24508.1
decwave W40_HCN5ms rfl1    201.7
dmf      32258    rfp      0
dpwr      38    rf1l    1886.4
pxv1vl     56    rfpl      0
pmx      11.000    PLOT
HMBC      wc      206.0
j1xh     146.0    sc      0
j2xh      8.0    wc2     206.0
ADIABATICCIC    sc2      0
pxv180ad ONE_ad300    vs      251
pxv1vl180     51    th      3
pxv180      465.4   ai    cdc    av

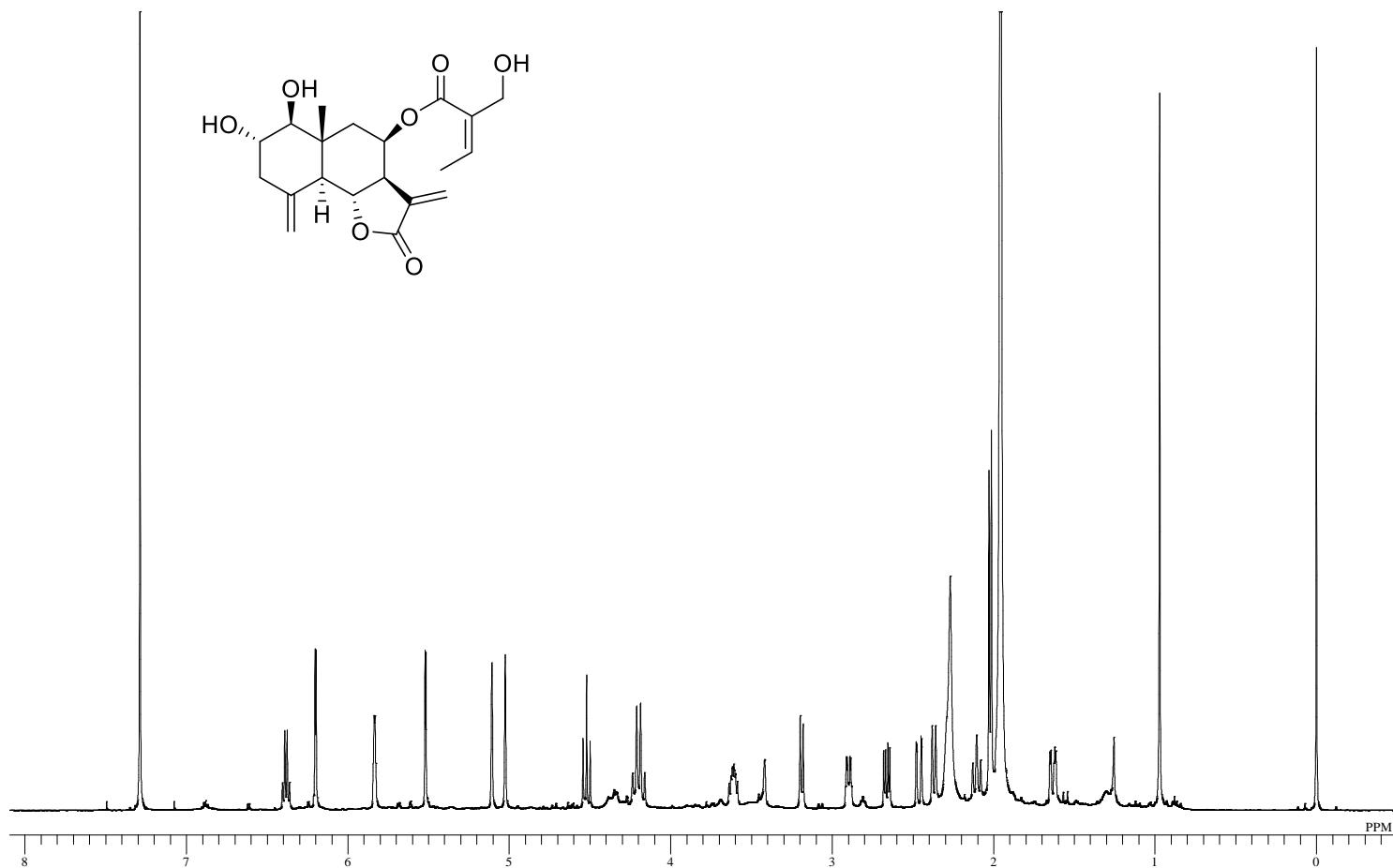
```



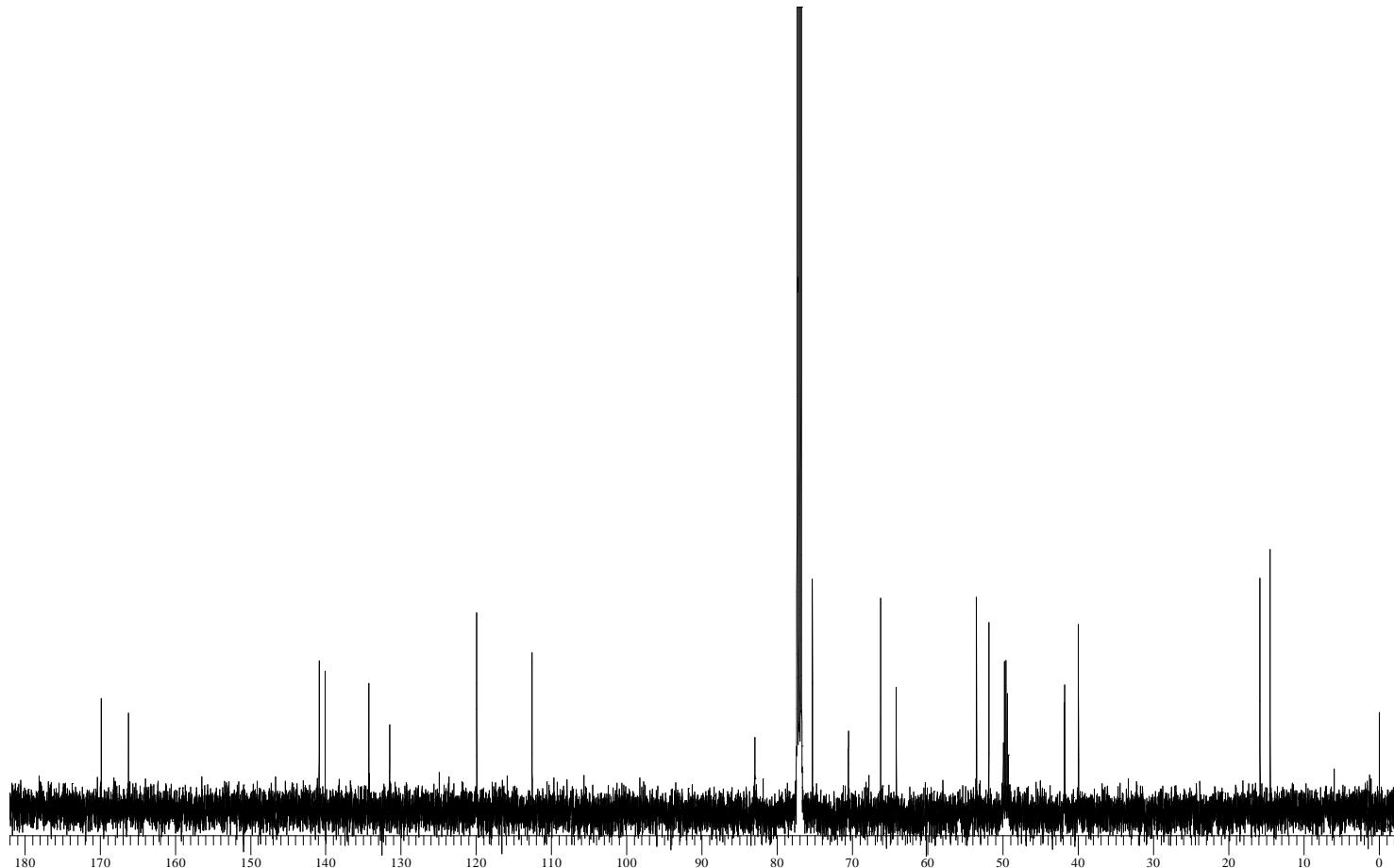
**Figure S48.** NOESY spectrum of **45** (measured in  $\text{CDCl}_3$ , 500 MHz).



**Figure S49.**  $^1\text{H}$  NMR spectrum of **50** (measured in  $\text{CDCl}_3$ , 500 MHz).



**Figure S50.**  $^{13}\text{C}$  NMR spectrum of **50** (measured in  $\text{CDCl}_3$ , 126 MHz).



**Figure S51.**  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of **50** (measured in  $\text{CDCl}_3$ , 500 MHz).

```

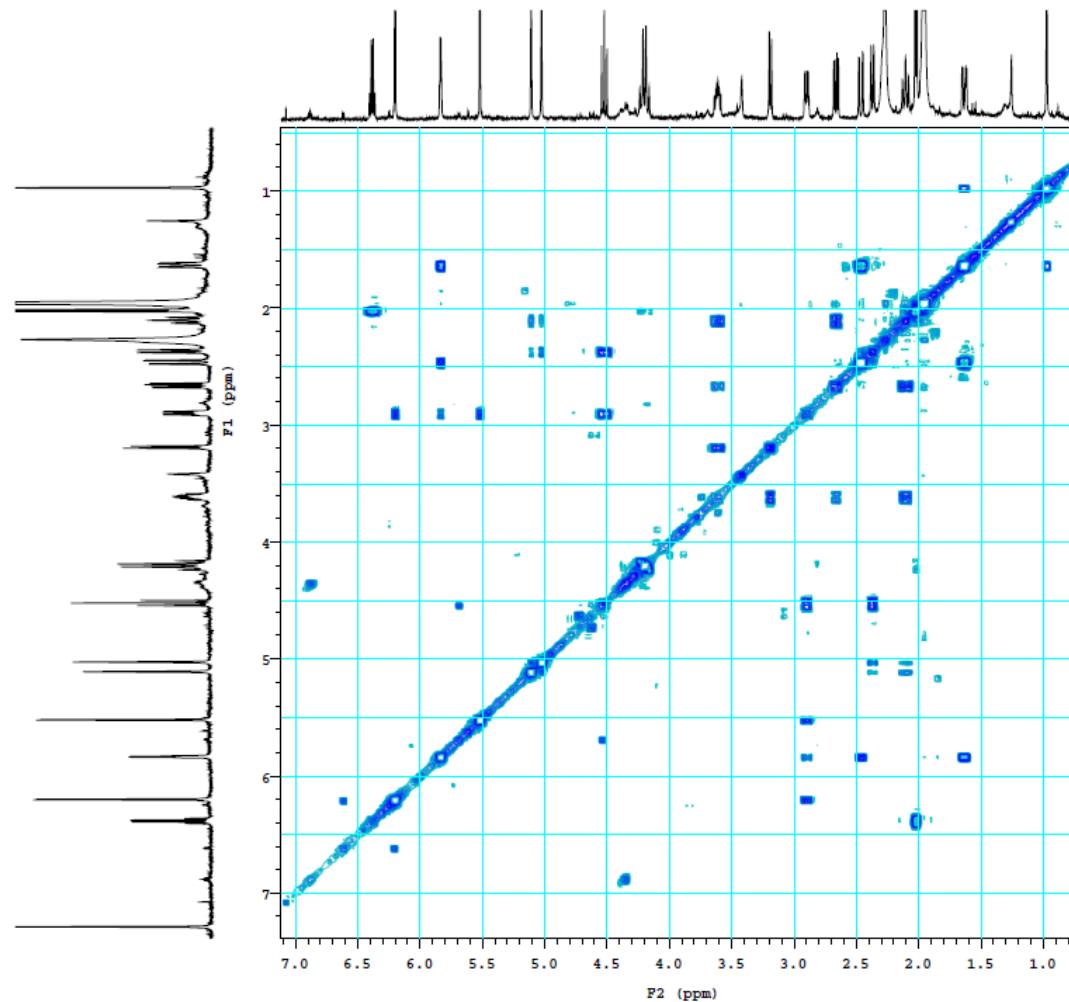
SYN-2015-71-9-4-1-1-1.4mg-COSY_cdcl3+av
exp4 gCOSY

SAMPLE          PLATE
date Jul 2 2018 hs      nn
solvent   cdcl3  spul     y
sample    hmg1v1 6180

ACQUISITION      SPECIAL
sw        4006.4 temp  not used
at         0.150 gain   44
sp        12.02 spin    0
fb        4000   P2 PROCESSING
ss         32 ab   -0.075
d1        1.000 sbs   not used
d1t       16 fm    2048
nt          2048

2D ACQUISITION   P1 PROCESSING
sw1       4006.4 ab1  -0.032
ni        128 ab1  not used
d2         0 proc1 lp
PRESATURATION   f1i   2048
satmode      n DISPLAY
wot        n sp    316.8
TRANSMITTER    wP    3243.5
tn         H1 sp1   230.8
sfrq      500.477 wpi   3466.5
tof        -674.8 rfi1  160.5
tpwr       59 rfp   0
pw        7.400 rfi1  160.5
GRADIENTS
g1v1R      5154  PLOT
gtR       0.001000 wc   206.0
EDratio     1.000 sc   0
gstab      0.000500 wc2  206.0
DECOPPLER   sc2   0
dn        C13 vs    142
dm        mnz tb     5
ai      odc av

```



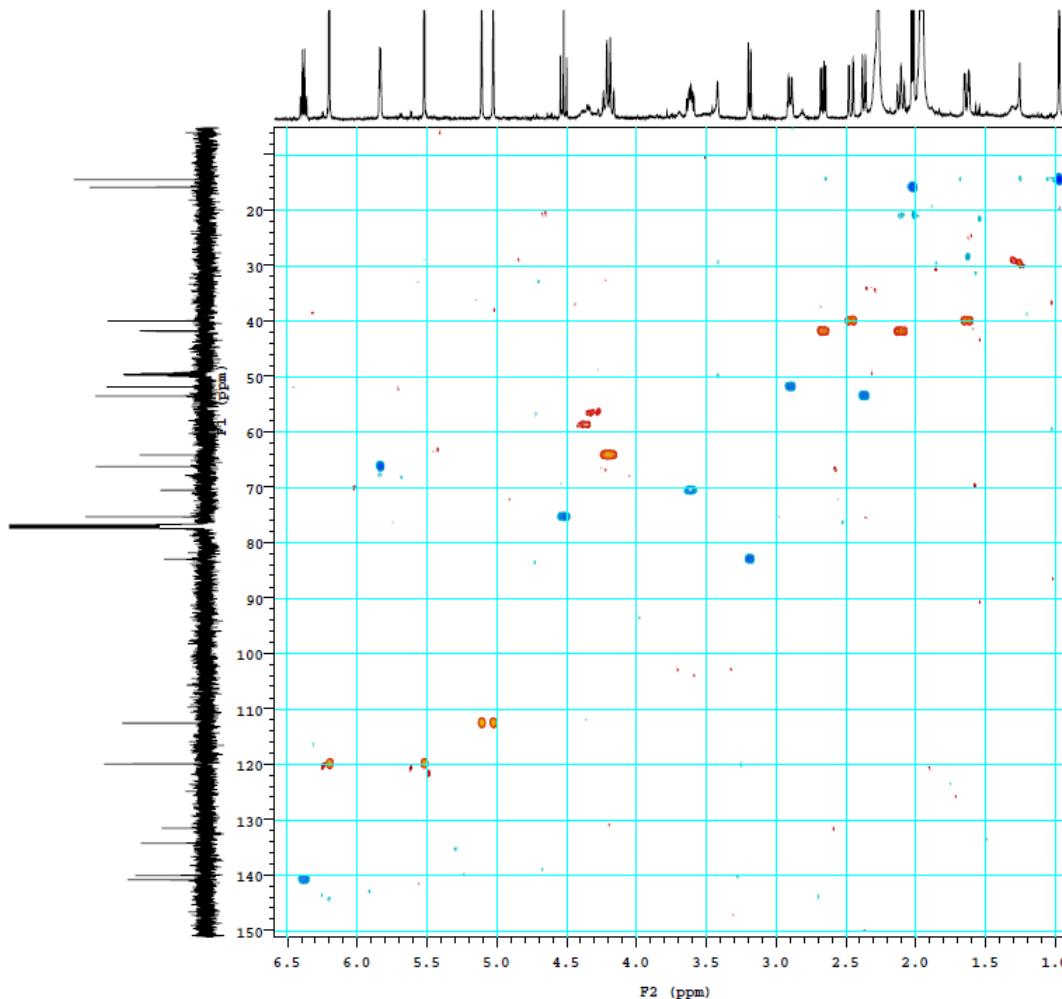
**Figure S52.** HSQC spectrum of **50** (measured in  $\text{CDCl}_3$ , 500 MHz).

```

HYM-2015-71-9-4-1-1-1.4mg-HSQC_cdc134m
exp5 HSQCAD

SAMPLE          PLATES      ACQUISITION ARRAYS
date Jul 2 2018 hs        nn      array    phase
solvent   odc13  seppul     y      arraydim 256
sample    PPCrlg          y
ACQUISITION    hagl1v       6180   1      phase
sw        4006.4   SPECIAL   1      1
at        0.150  temp    not used  2      2
np        1202   gain      44
fb        4000   spin      0
ss        32      P2 PROCESSING
di        1.000  gf      0.069
nt        16      gfs    not used
2D ACQUISITION fm      2048
sw1      21390.4  P1 PROCESSING
ni        128   gfi      0.006
phase    arrayed gfs1    not used
PRESATURATION proc1    1p
satmode   n   fni      2048
wet      n      DISPLAY
TRANSMITTER    sp      406.8
tn        H1   wpt     2891.3
strq    500.477  sp1      645.3
t0f      -674.8  wpt1    18382.4
tpwr     59   rf1      160.5
pw        7.400  rfp      0
DECOUPLER     C13  rfpi    1255.6
dn        -2487.0  PLOT
dof      146.0
dm        nny  wc      206.0
decwave W40_HCN5mm sc      0
dmt      32258  wc2    206.0
dpwr     38   sc2      0
pxiv1v1  56   vs      142
pxv     11.000  th      3
HSQC          ai  cdc ph
j1xb     146.0
nullflg    y
nullt      2
ADiABATIC
pxiv80ad GME ad300
pxiv80adR GME ad30-
OR
pxiv80     465.4
pxiv1v180   51
pxiv80ref CNR_rf2-
00
pxiv80r    2000.2
pxiv1v180r  43

```



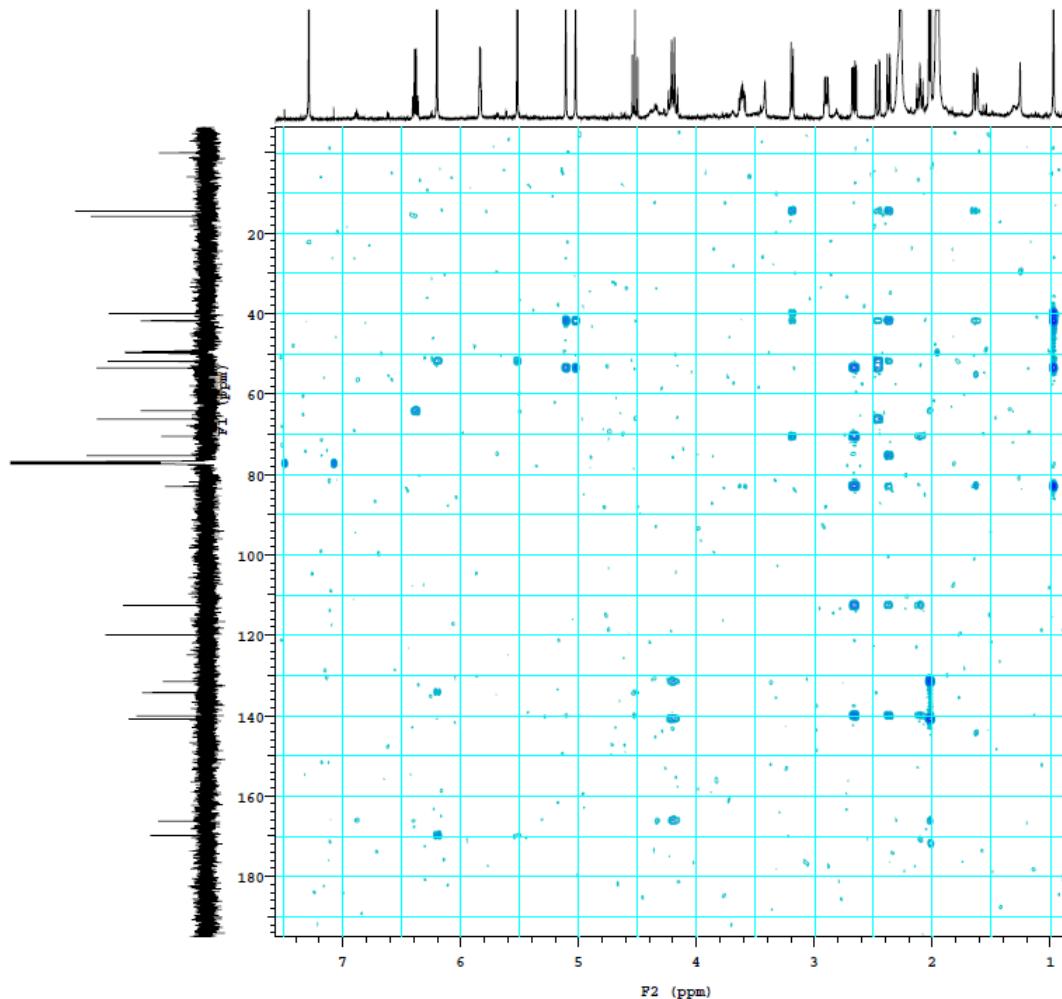
**Figure S53.** HMBC spectrum of **50** (measured in  $\text{CDCl}_3$ , 500 MHz).

```

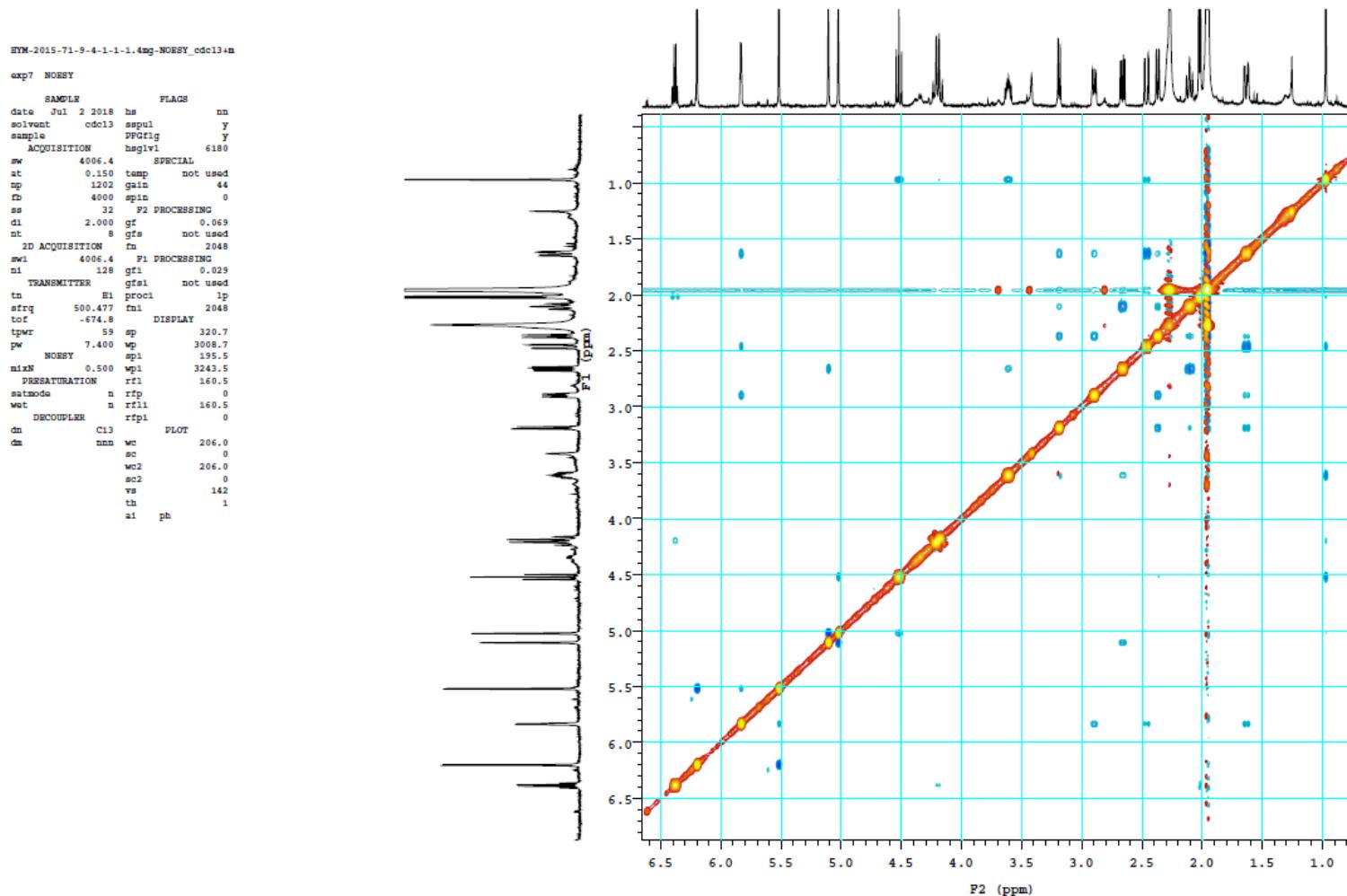
HYM-2015-71-9-4-1-1-1.4mg-HMBC_cdc13+av
exp6 gHMBCAD

SAMPLE          FLAGS      ACQUISITION ARRAYS
date   Jul 2 2018 hs      nn      array    phase
solvent   cdc13  aspul     y      arraydim  256
sample    PPGrig     y
ACQUISITION   hsgv1       6180   1      phase
sw      4006.4  SPGR1L    1      1
at      0.150  temp      not used  2      2
np      1202   gain      44
fb      4000   spin      0
ss      32     GRADIENTS
di      1.000  gr1v1l   409
nt      32     gt1       0.001000
2D ACQUISITION gr1v13   1227
sw1     30200.1 gt3       0.001000
ni      128    getab     0.000500
phase    arrayed   P2 PROCESSING
DESATURATION   ab       -0.075
satmode   nabs      not used
wet      nfn       2048
TRANSMITTER   P1 PROCESSING
tn      H1   gt1       0.004
afrq    500.477 gfs1     not used
t0f     -674.8  proc1     lp
tpwr     59   fmi      2048
pw      7.400  DISPLAY
DECOUPLER    sp      363.8
dn      C13   wp      3423.4
dof     1287.0  sp1      -795.2
dm      mnm   wpl     25333.9
decwave W0_HCNSMM rfi      160.5
dmr     32258  rfp      0
dpwr     38   rfi1     1886.4
pwxlv1  56   rfp1      0
pwx     11.000  PLOT
HMBC      ws      206.0
j1xb    146.0  ws2      206.0
j2xb     8.0   ws2      0
ADABATIC1C   ws2      0
pwx180ad ONR_ad300 vs      142
pwx1v1180  51   th      4
pwx180   465.4  ai cdc av

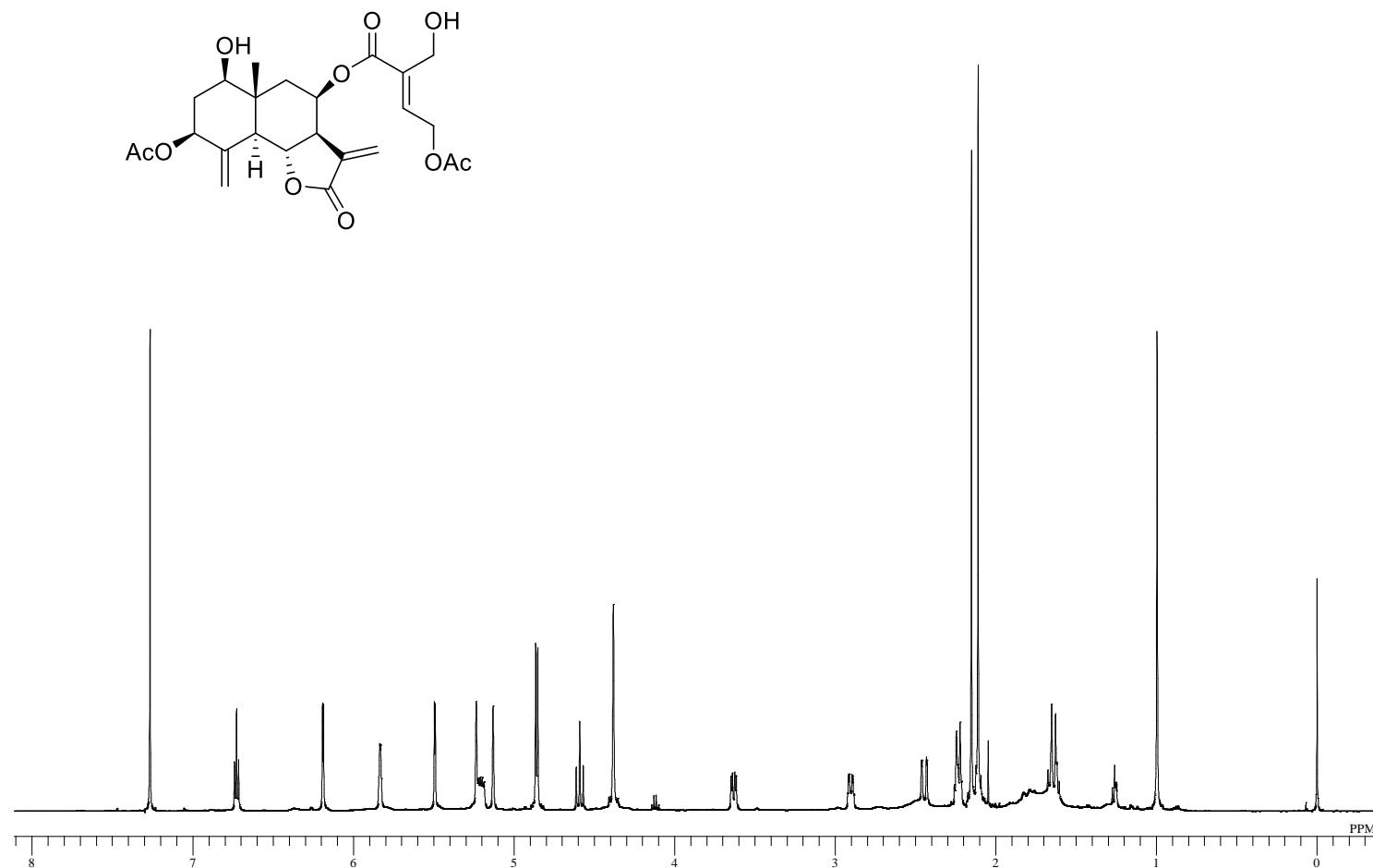
```



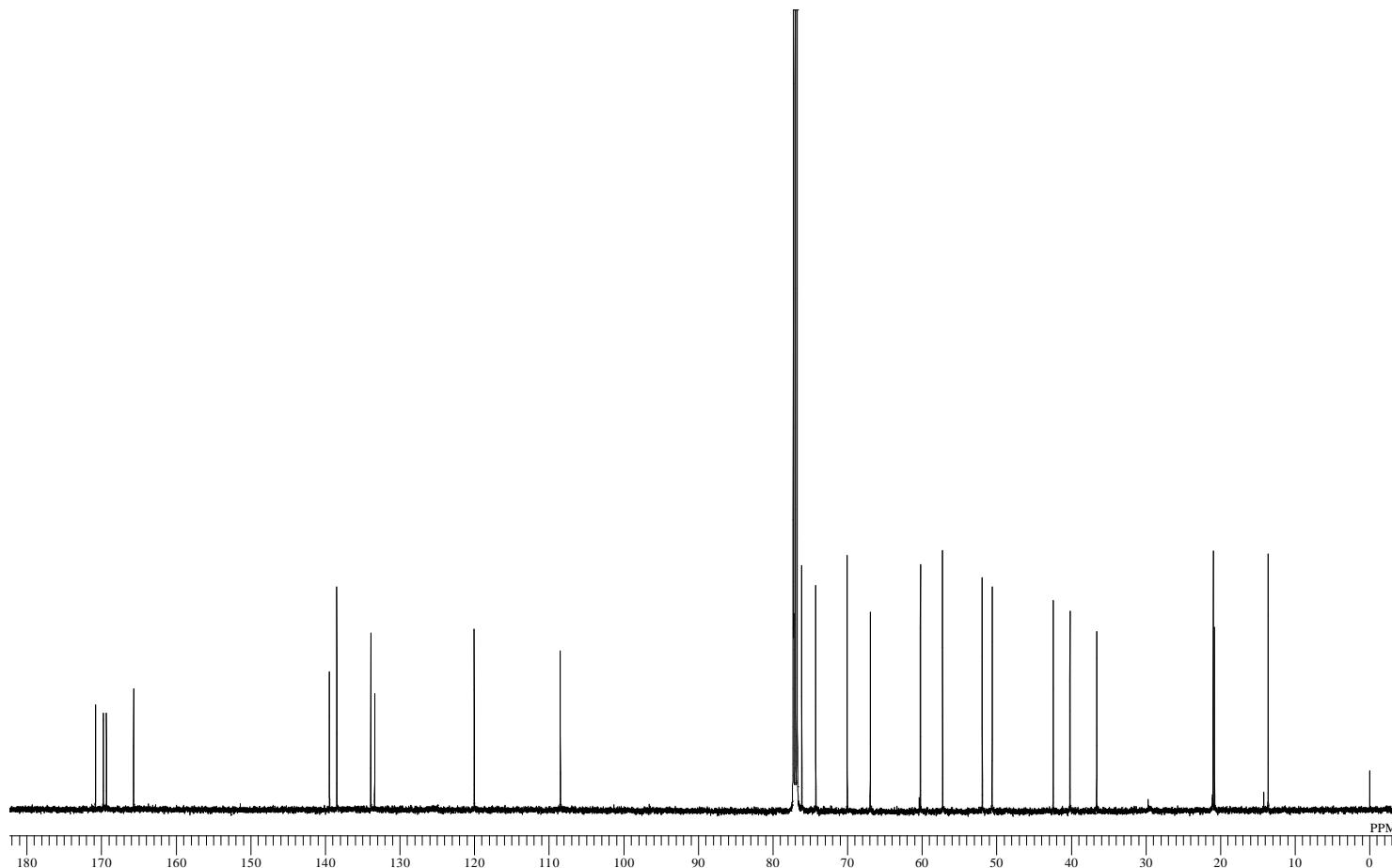
**Figure S54.** NOESY spectrum of **50** (measured in  $\text{CDCl}_3$ , 500 MHz).



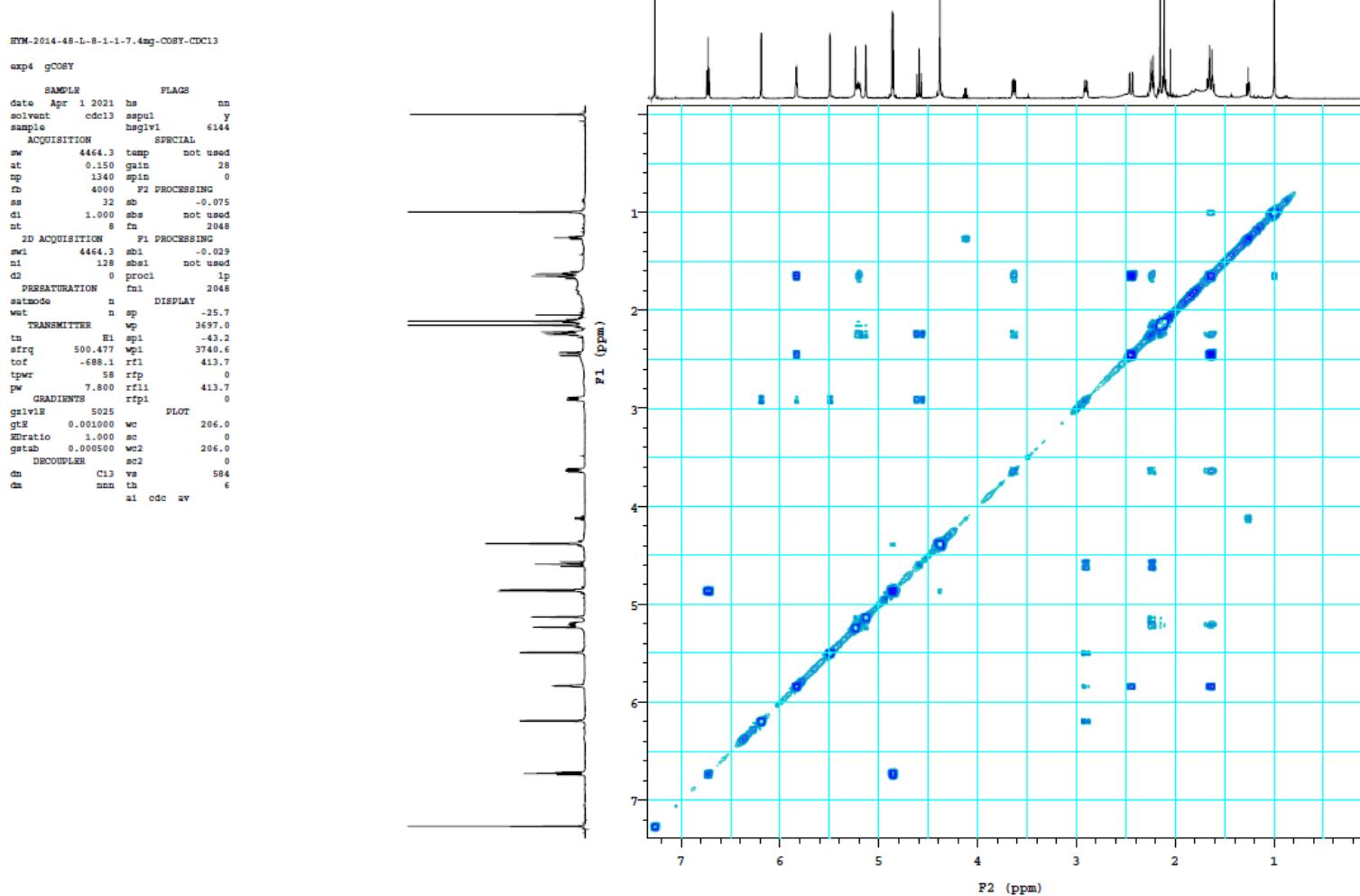
**Figure S55.**  $^1\text{H}$  NMR spectrum of **51** (measured in  $\text{CDCl}_3$ , 500 MHz).



**Figure S56.**  $^{13}\text{C}$  NMR spectrum of **51** (measured in  $\text{CDCl}_3$ , 126 MHz).



**Figure S57.**  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of **51** (measured in  $\text{CDCl}_3$ , 500 MHz).



**Figure S58.** HSQC spectrum of **51** (measured in  $\text{CDCl}_3$ , 500 MHz).

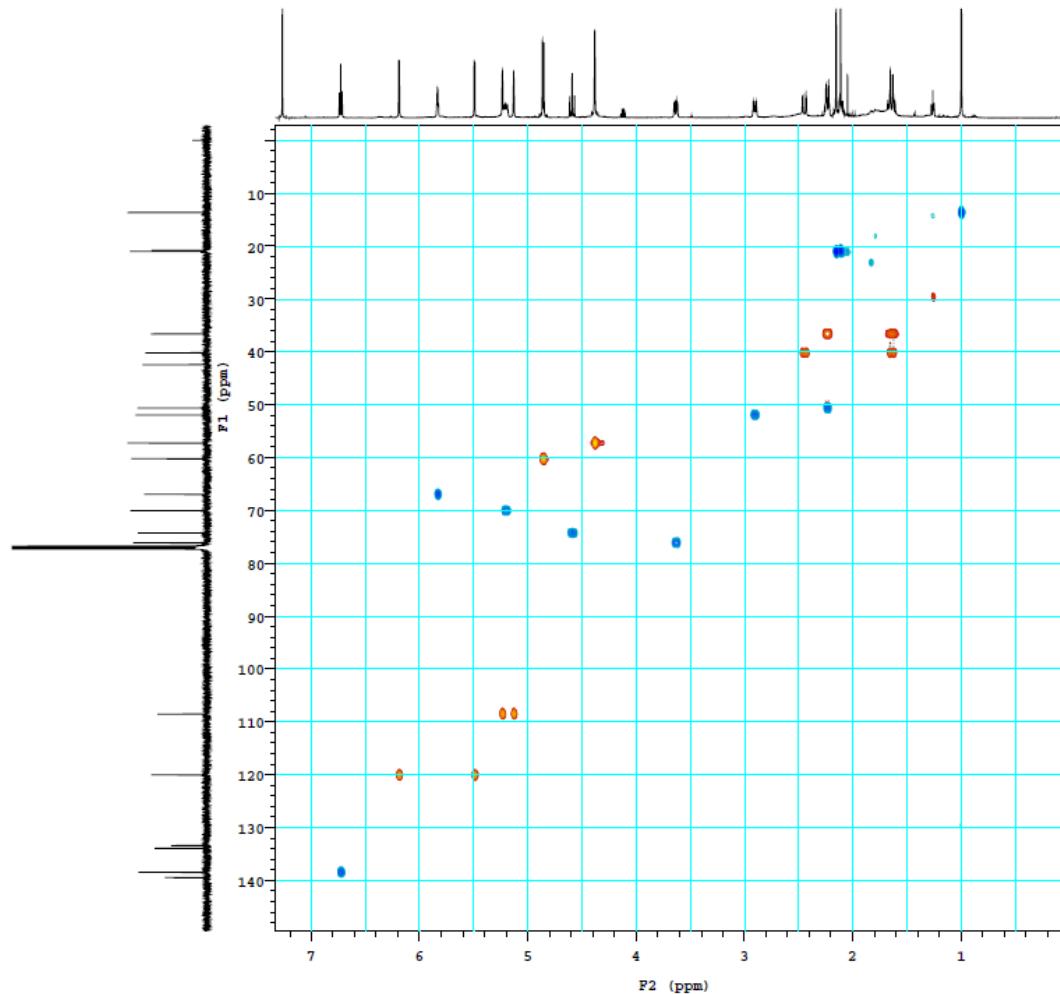
HYM-2014-48-L-8-1-1-7.4mg-HSQC-CDCl3

exp5 HSQCAD

```

SAMPLE          FLAGS      ACQUISITION ARRAYS
date   Apr 1 2021 hs        nn      array    phase
solvent   dcdl3  ssppul     y      arraydim 256
sample    PPGfig    y
ACQUISITION   hsgv1l   6144    1      phase
sw       4464.3  SPECIAL   1        1
at       0.150  temp    not used  2        2
np       1340   gain      28
fb       4000   spin      0
ss        32    F2 PROCESSING
di       1.000  gf      0.069
nt       16    gfs    not used
2D ACQUISITION fn      2048
sw1      25165.1  F1 PROCESSING
ni       128   gfs1    0.005
phase    arrayed gfs1    not used
PRESATURATION proc1    1p
satmode   n   fni    2048
wot      n   DISPLAY
TRANSMITTER sp      -38.8
tn       B1 wpt    3765.7
sirq    500.477  sp1      -347.3
tof      -688.1  wpt    15168.8
tpwr     58 rfi     413.7
pw       7.800  rfp      0
DECOUPLER   rfc1    1256.5
dm       C13 rfp1    0
dof      -600.6  PLOT
dm       nny w2     206.0
decwave W40_BCN5mm sc     0
dmf     32258  wc2     206.0
dpwr     38 sc2     0
pxxvl1  56 vs      584
pxx    10.500  th      1
HSQC      ai odc ph
jxh     146.0
nullflg   y
mult      2
ADIABATIC
pxx180ad ONE ad300
pxx180adn ONE ad30-
OR
pxx180     465.4
pxx1v1180    51
pxx180ref ONE ref2-
00
pxx180r   2000.2
pxx1v1180r   43

```



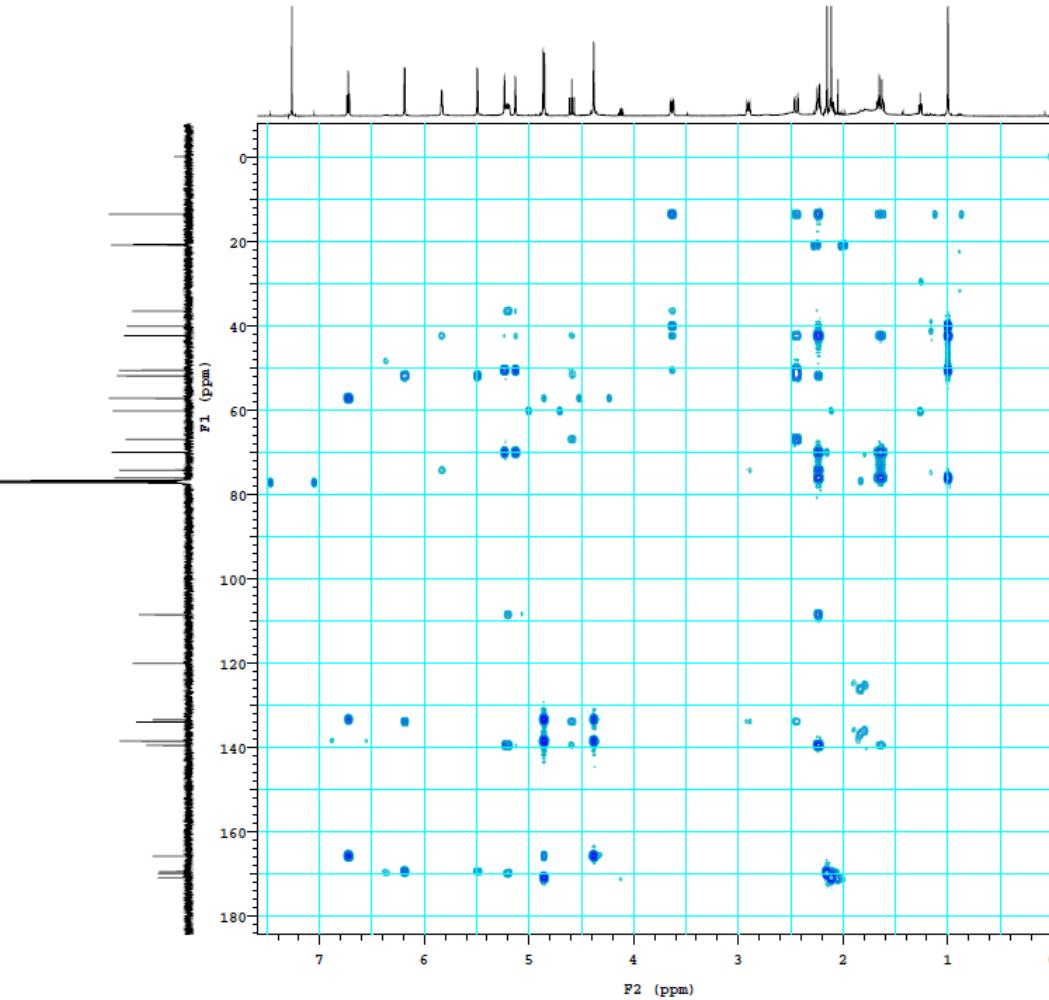
**Figure S59.** HMBC spectrum of **51** (measured in  $\text{CDCl}_3$ , 500 MHz).

```

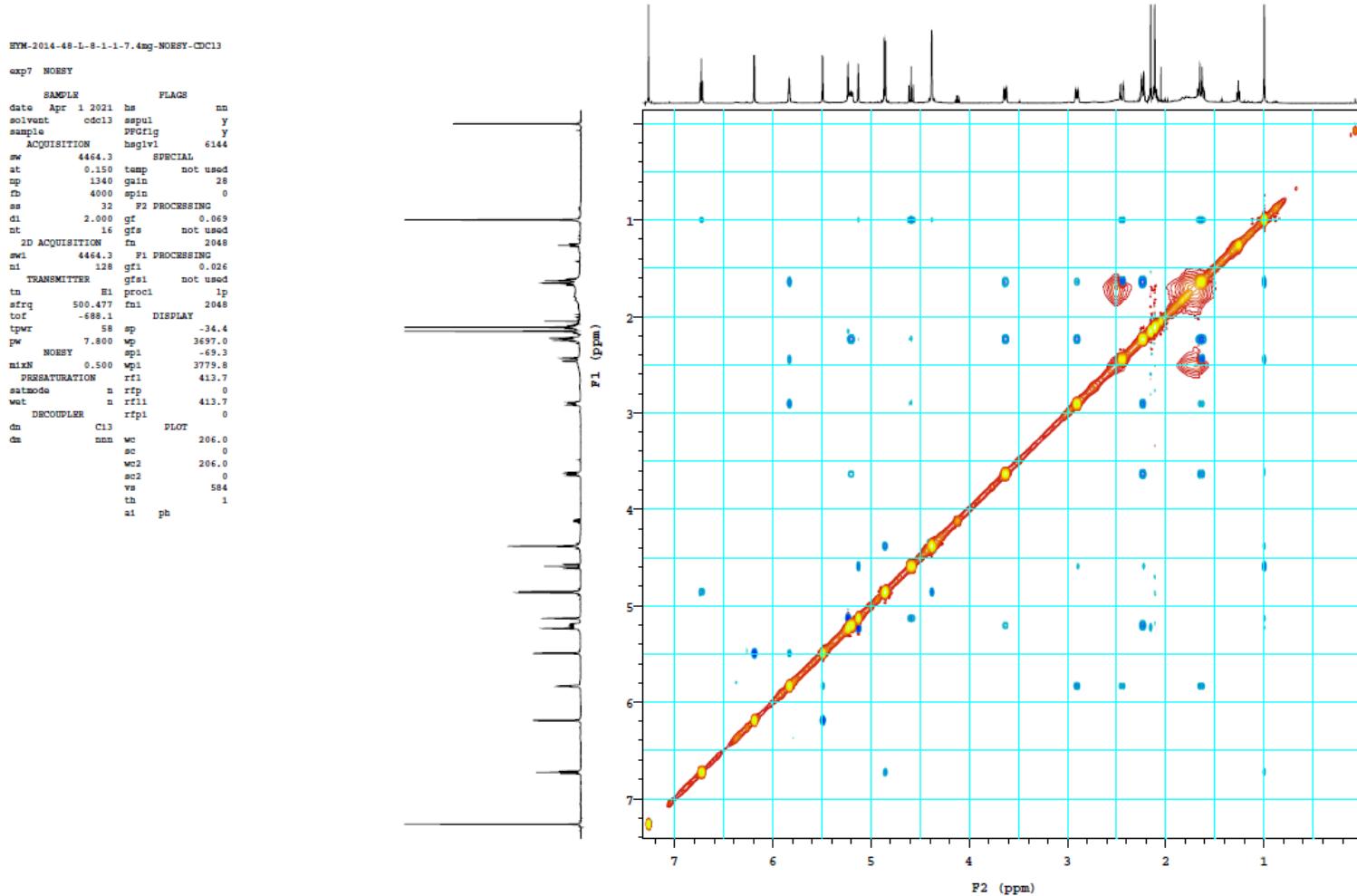
HYM-2014-48-L-8-1-1-7.4ng-HMBC-CDCl3
exp6 gHMBCAD

SAMPLE          PLATES      ACQUISITION ARRAYS
date   Apr 1 2021    hs        nn      array phase
solvent   cdc13    sepu1      y      arraydim 256
sample   PFGrlg      y
ACQUISITION   hsgv1l     6144     1      phase
sw       4464.3    SPECIAL    1        1
at       0.150    temp    not used  2        2
np       1340     gain      28
fb       4000     spin      0
ss       32       GRADIENTS
d1       1.000    gr1v1l    409
nt       64       gti      0.001000
2D ACQUISITION gr1v13    1227
sw1      30200.1   gt3      0.001000
ni       128      gstab     0.000500
phase    arrayed   F2 PROCESSING
PRESATURATION sb      -0.075
satmode   n      abs      not used
wst      n      fn      2048
TRANSMITTER   F1 PROCESSING
tn       H1      gfi      0.004
sfreq   500.477   gfs1     not used
tot      -688.1    proc1    1p
tpmr     58      fml      2048
pw       7.800    DISPLAY
DECODUCER    sp      -65.0
dn       C13      wp      3862.7
dot      1287.0   spi      -972.1
daa     nnn      wpi      24154.2
decwave W4_0_HCN5mm rft1    413.7
dmf     32258    rfp      0
dpw     38      rf11     1886.4
pw1v1l  56      rfp1     0
pwx    10.500    PLOT
HMBC      wc      206.0
j1xh    146.0    sc      0
jnxh    8.0      wc2     206.0
ADIABATIC1C sc2      0
pwx180ad ONK_ad300 vs      584
pwx1v1180 s1      th      1
pwx180    465.4   ai      cdc  av

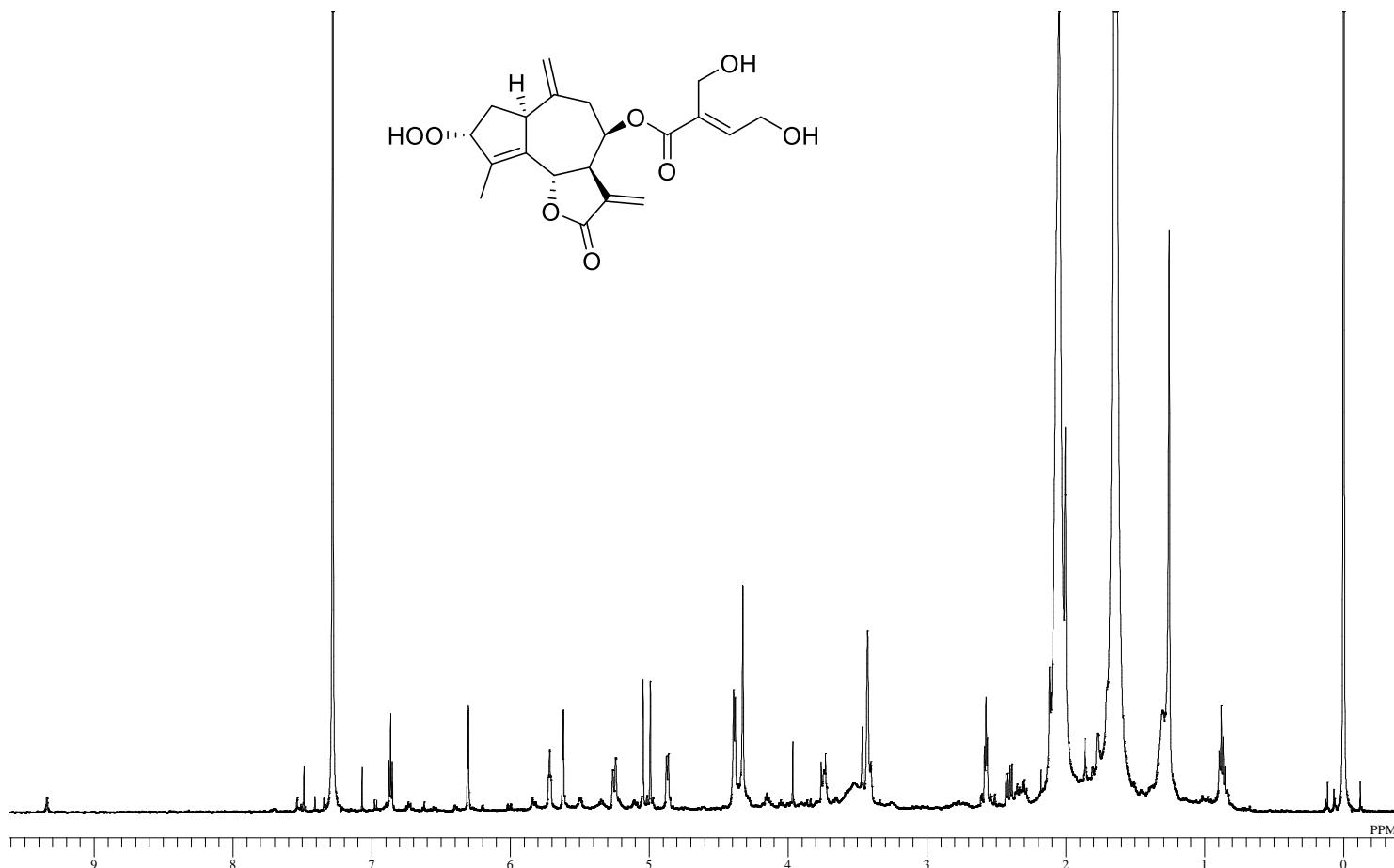
```



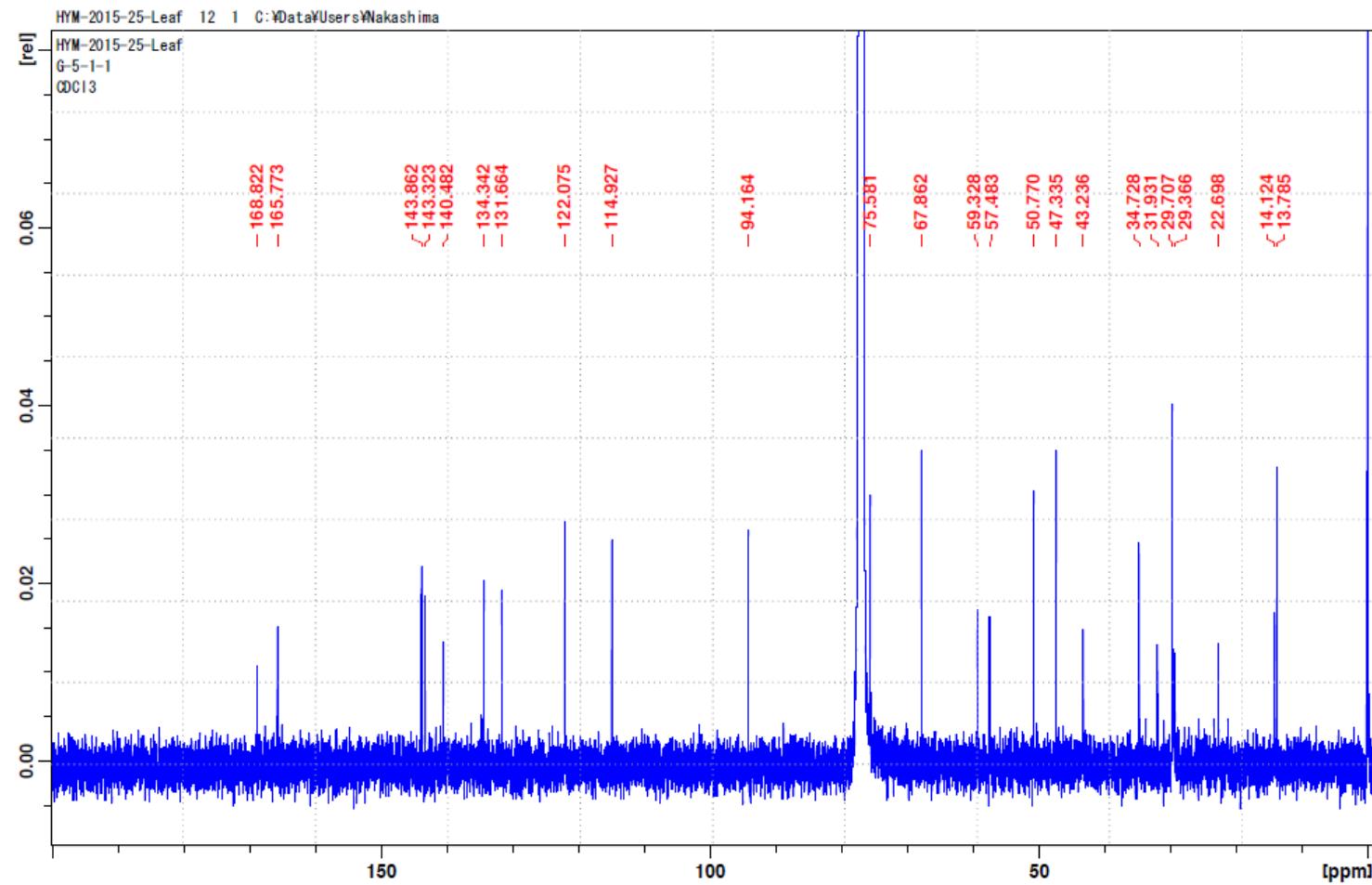
**Figure S60.** NOESY spectrum of **51** (measured in  $\text{CDCl}_3$ , 500 MHz).



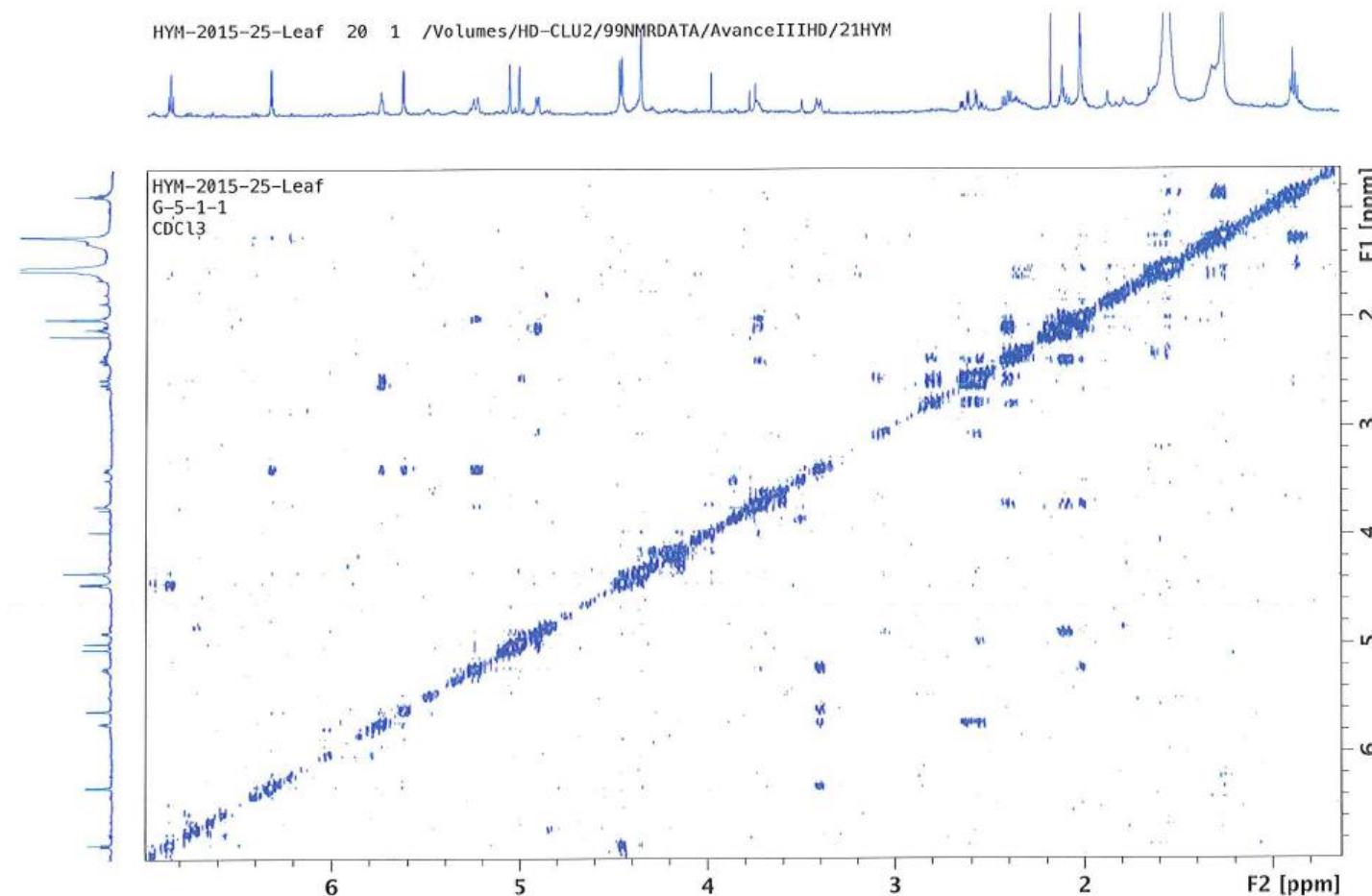
**Figure S61.**  $^1\text{H}$  NMR spectrum of **53** (measured in  $\text{CDCl}_3$ , 500 MHz).



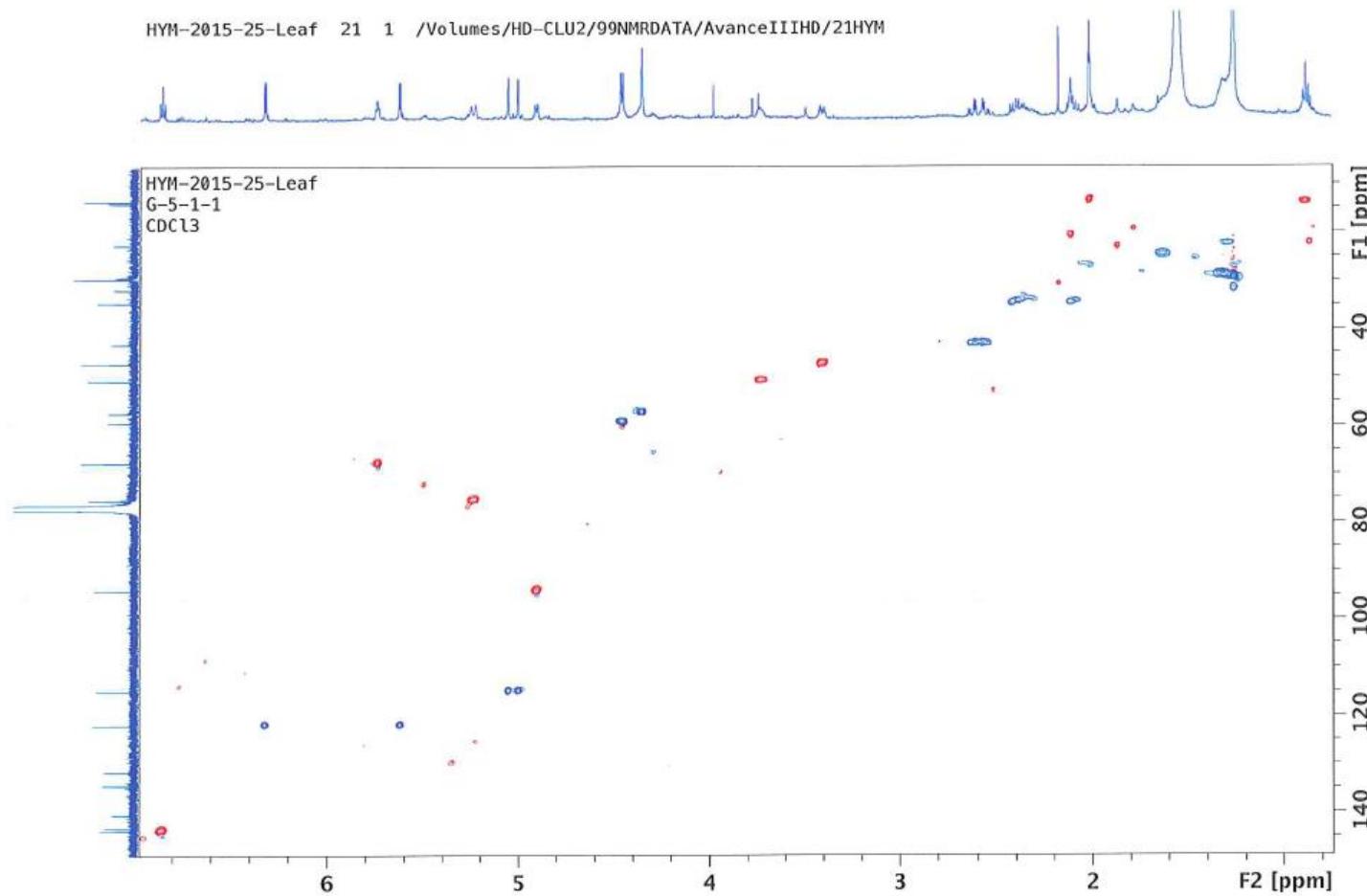
**Figure S62.**  $^{13}\text{C}$  NMR spectrum of **53** (measured in  $\text{CDCl}_3$ , 126 MHz).



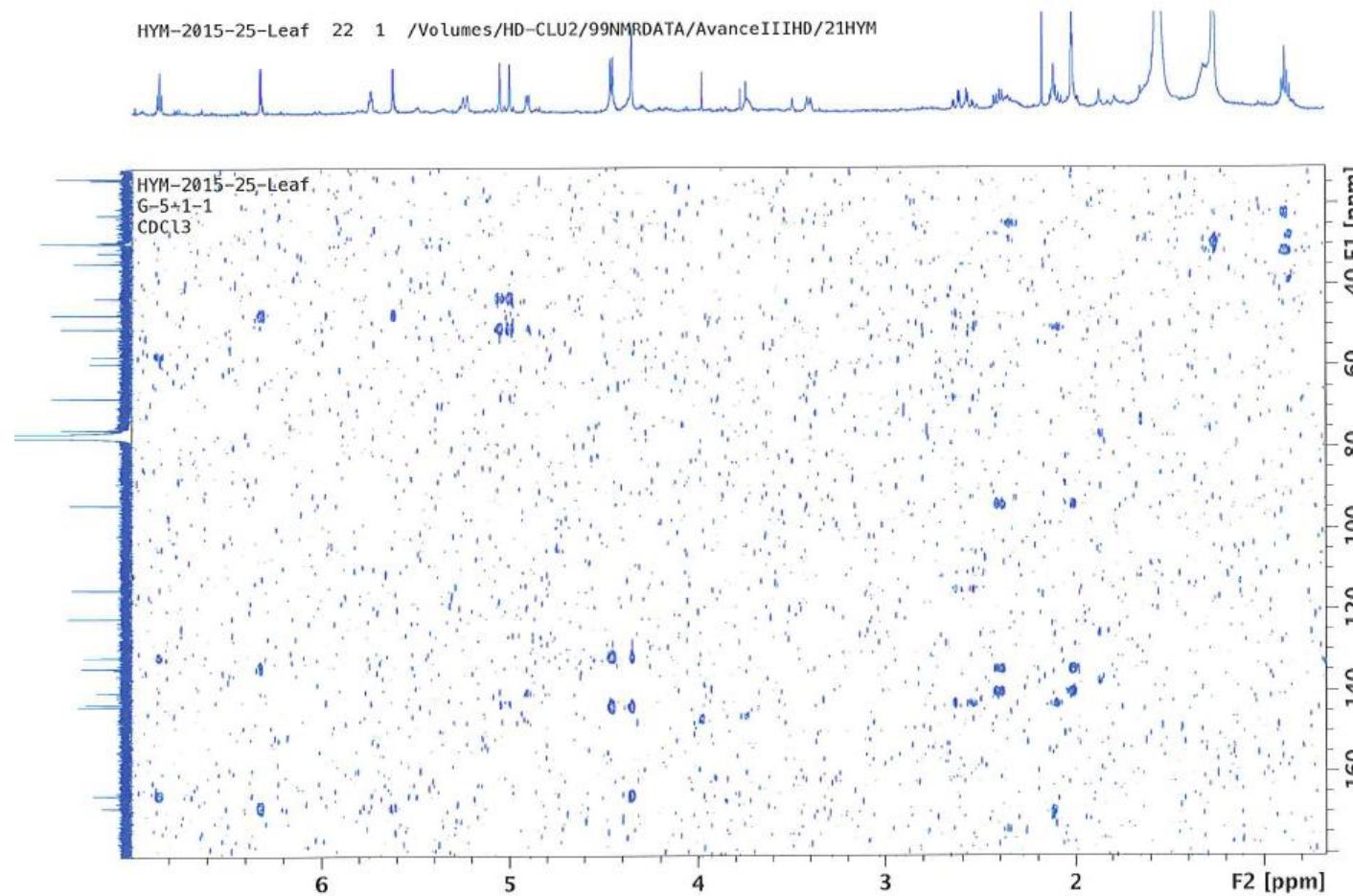
**Figure S63.**  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of **53** (measured in  $\text{CDCl}_3$ , 500 MHz).



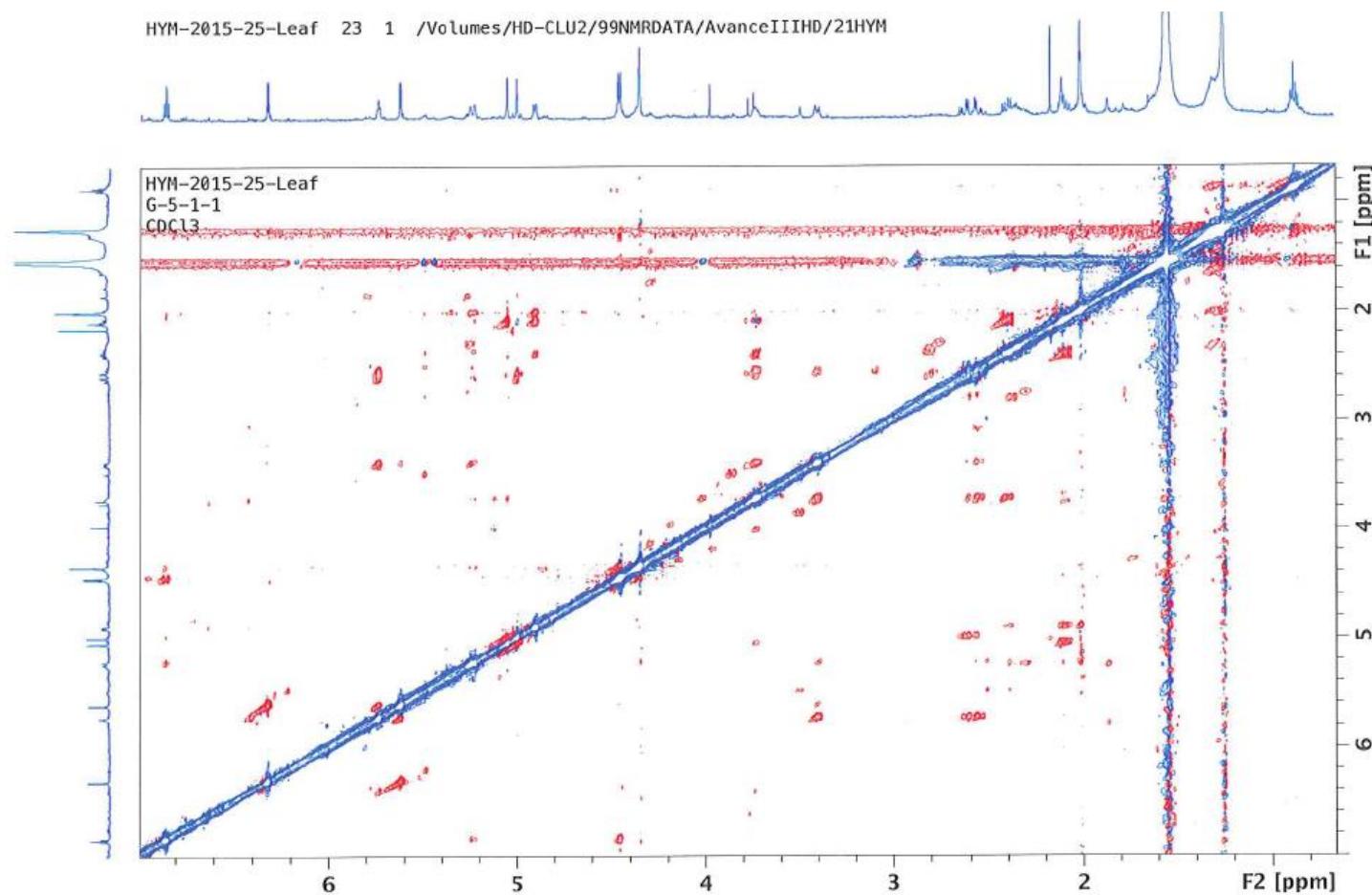
**Figure S64.** HSQC spectrum of **53** (measured in  $\text{CDCl}_3$ , 500 MHz).



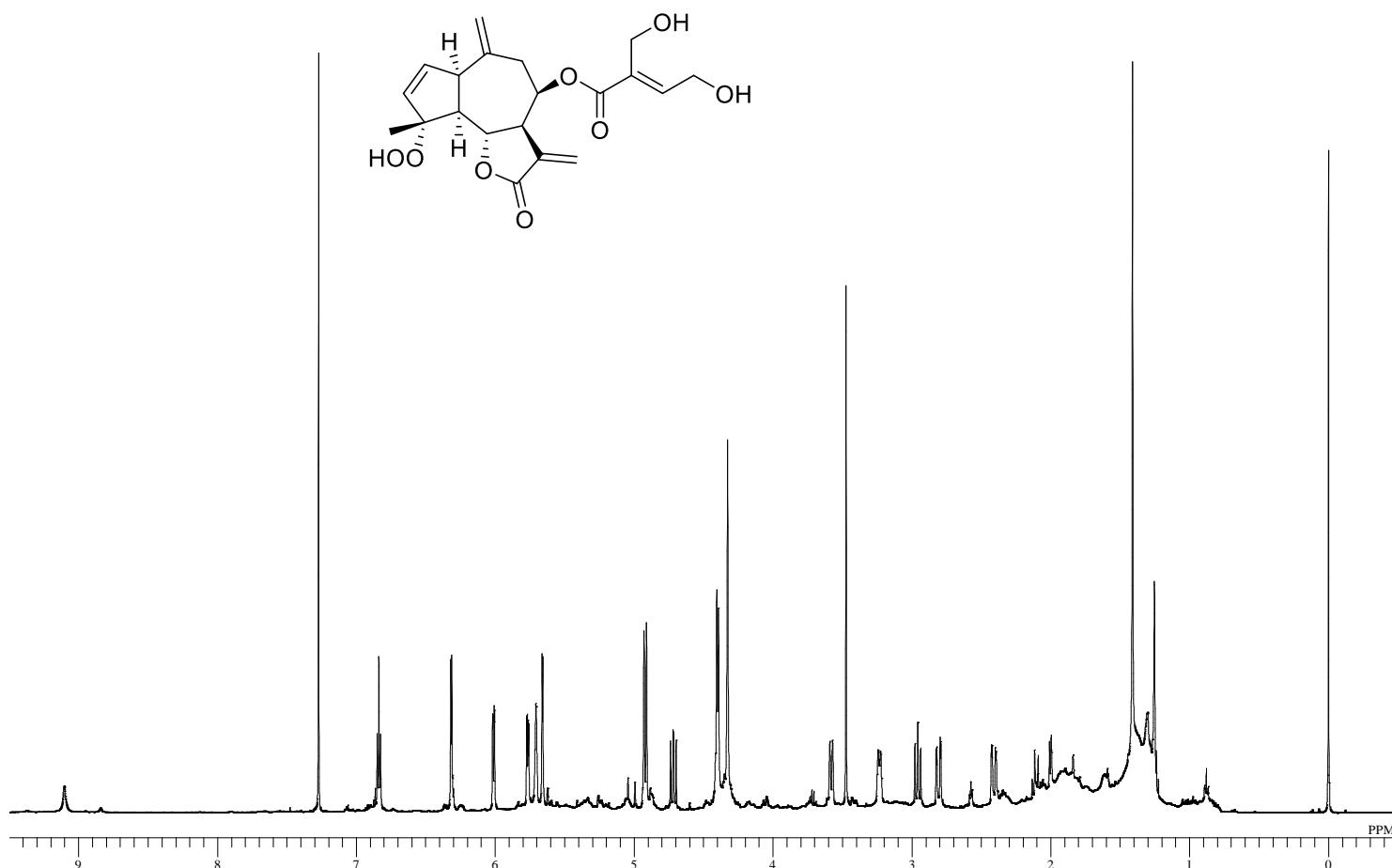
**Figure S65.** HMBC spectrum of **53** (measured in  $\text{CDCl}_3$ , 500 MHz).



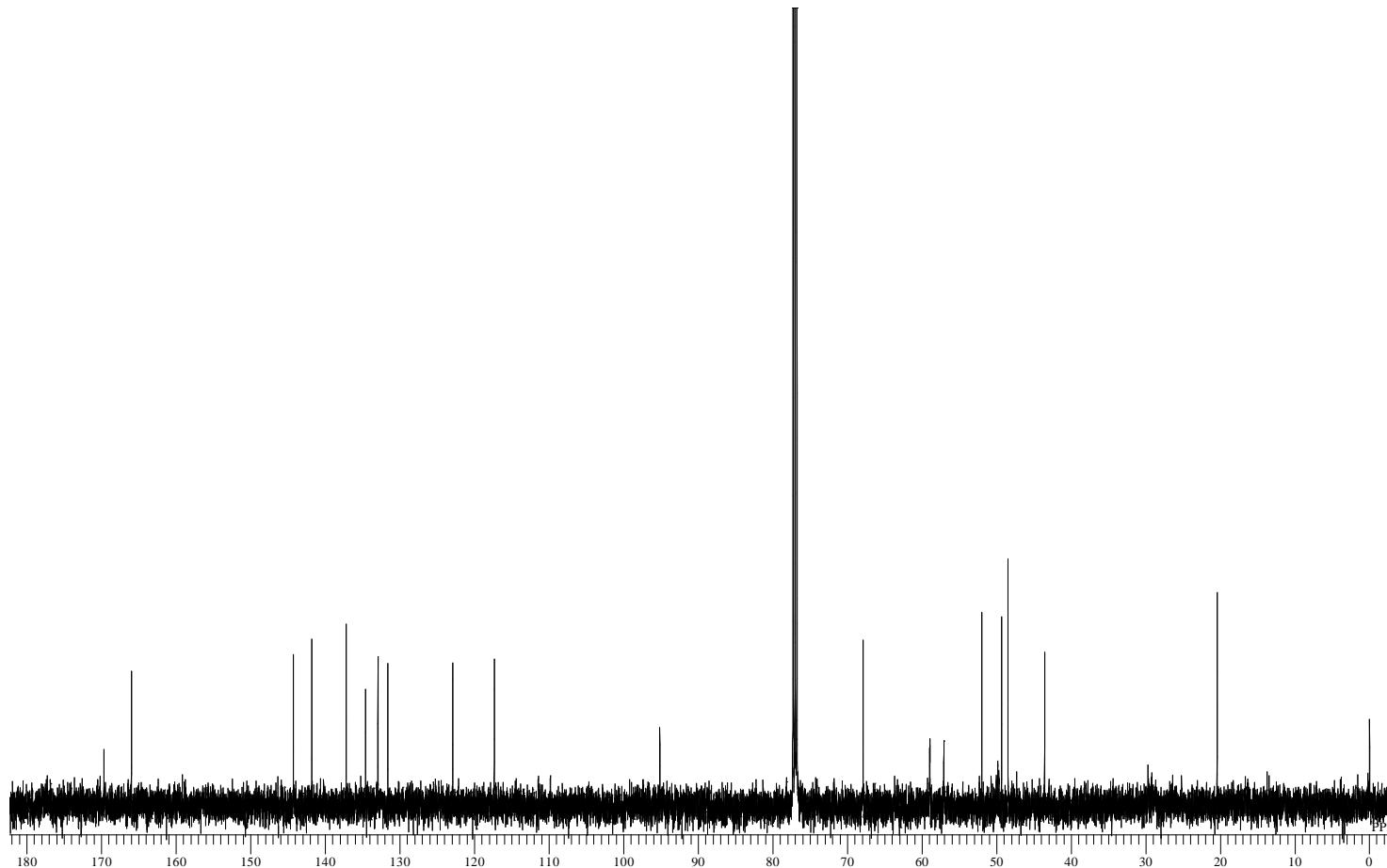
**Figure S66.** NOESY spectrum of **53** (measured in  $\text{CDCl}_3$ , 500 MHz).



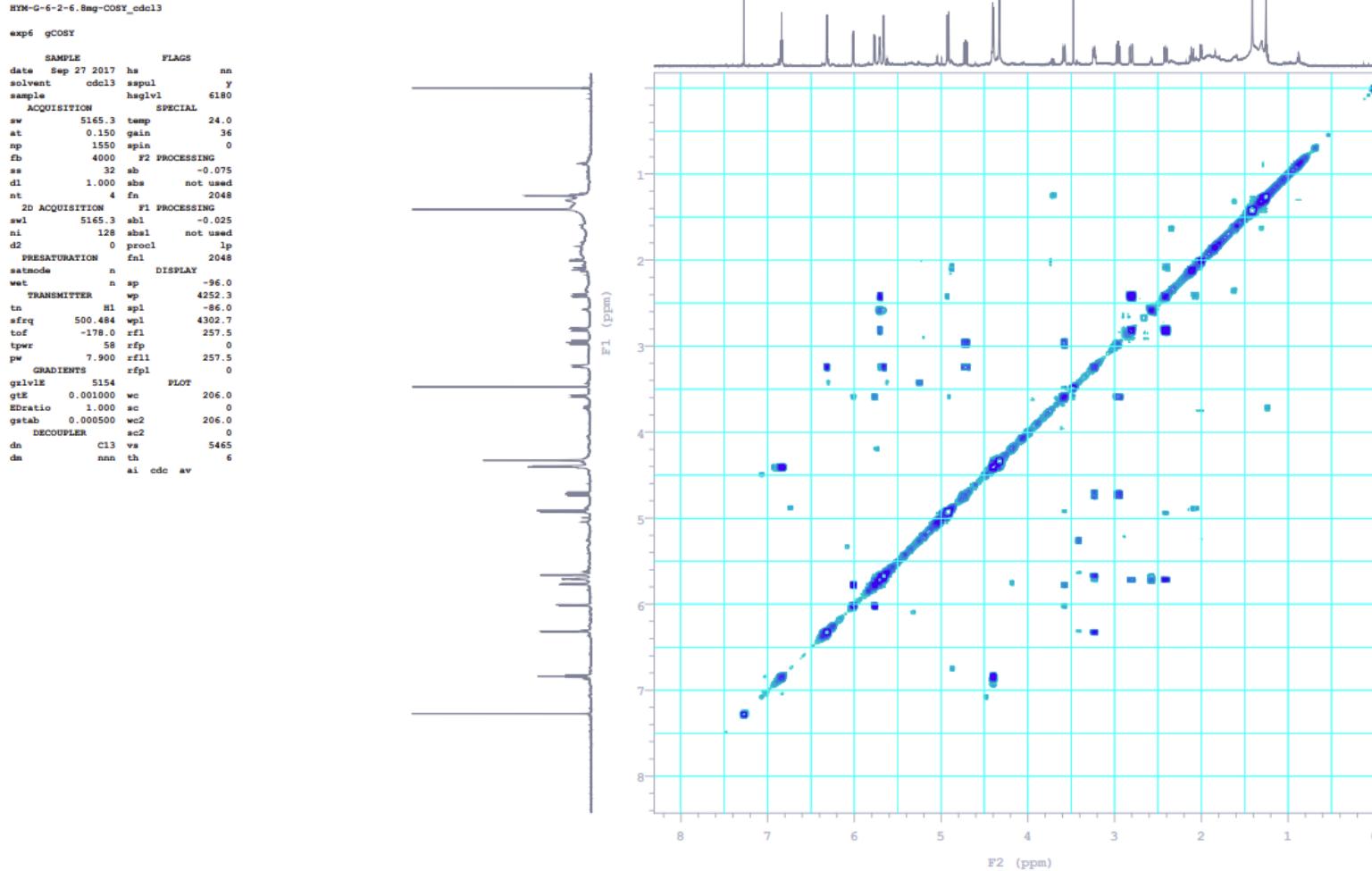
**Figure S67.**  $^1\text{H}$  NMR spectrum of **54** (measured in  $\text{CDCl}_3$ , 500 MHz).



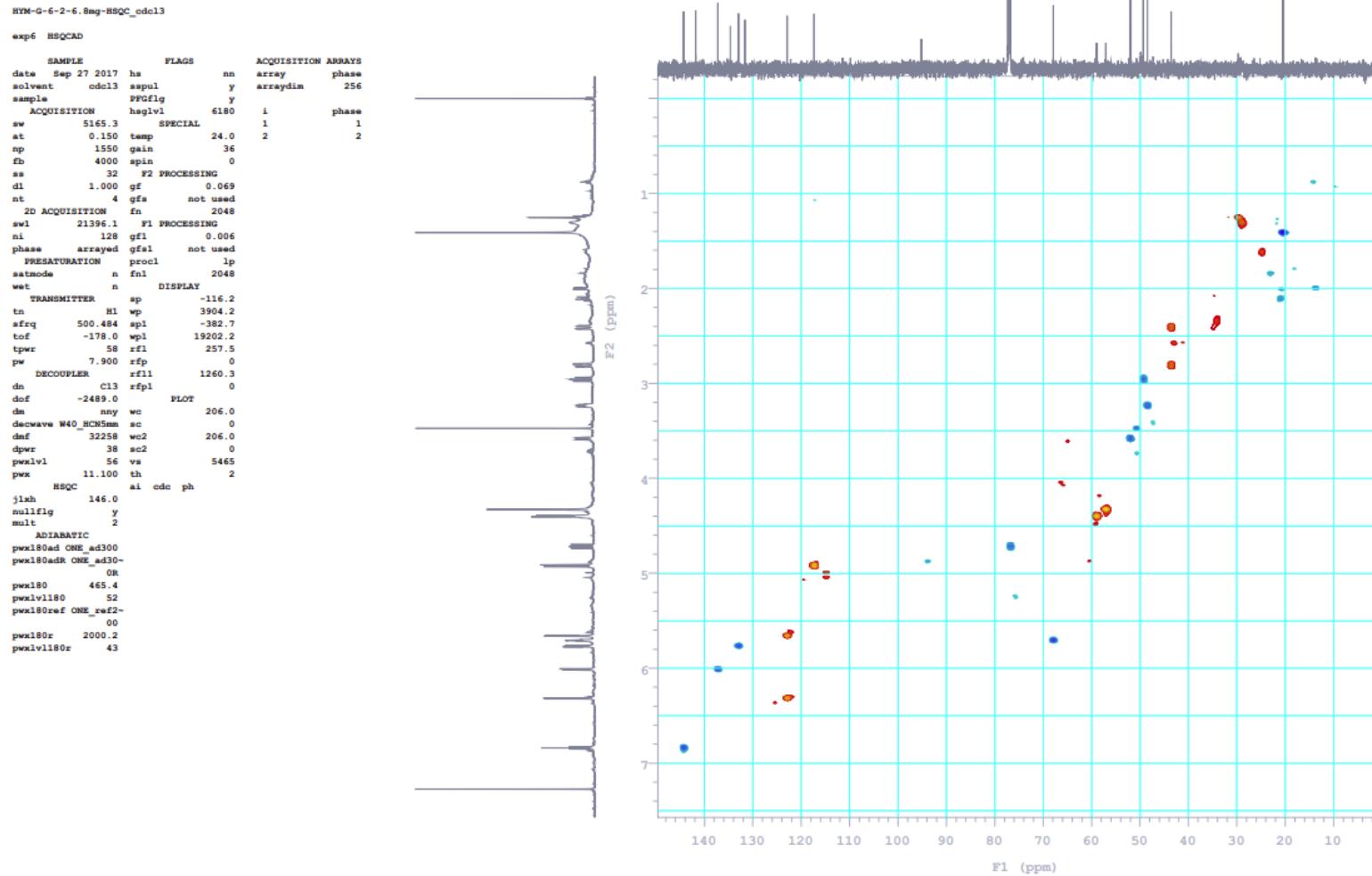
**Figure S68.**  $^{13}\text{C}$  NMR spectrum of **54** (measured in  $\text{CDCl}_3$ , 126 MHz).



**Figure S69.**  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of **54** (measured in  $\text{CDCl}_3$ , 500 MHz).



**Figure S70.** HSQC spectrum of **54** (measured in  $\text{CDCl}_3$ , 500 MHz).



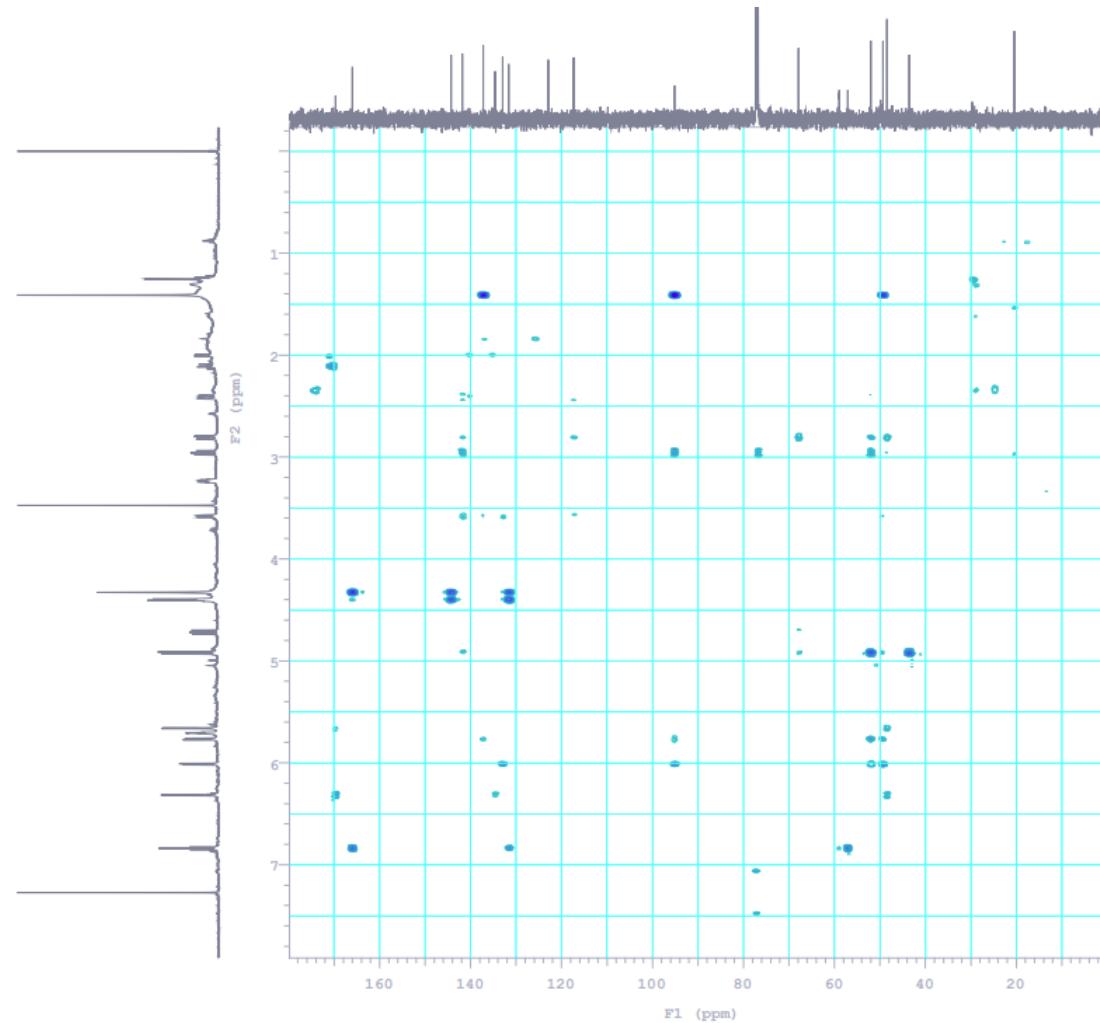
**Figure S71.** HMBC spectrum of **54** (measured in  $\text{CDCl}_3$ , 500 MHz).

```

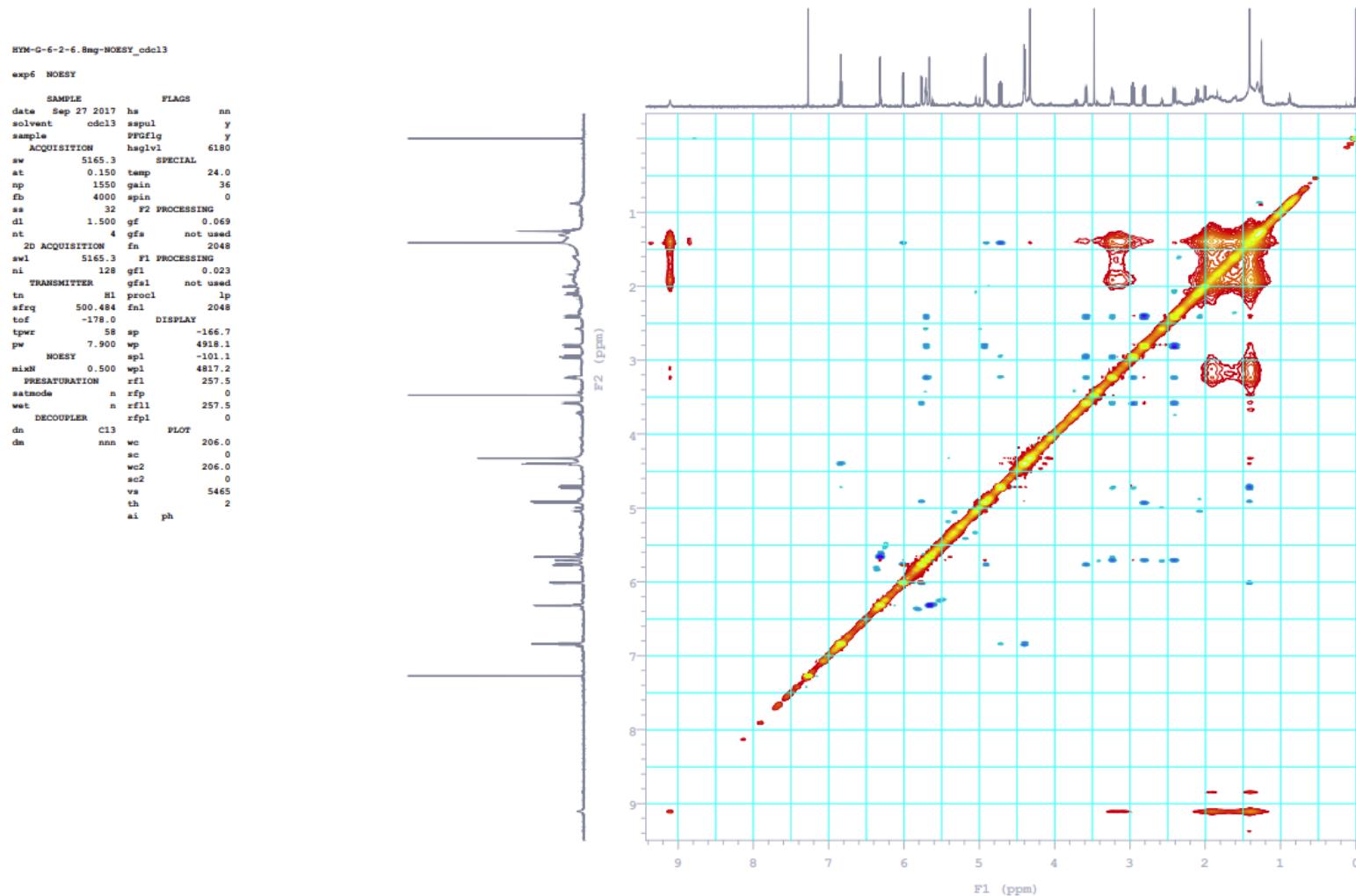
HYM-G-6-2-6.8mg-HMBC_cdcl3
exp6 qHMBCD

SAMPLE          FLAGS      ACQUISITION ARRAYS
date  Sep 27 2017 hs        nn      array    phase
solvent   cdcl3 ssful      y       arraydim  256
sample    PFGf1g      y
ACQUISITION hsgv13     6180 i      phase
sw      5165.3 SPECIAL    1       1
at       0.150 temp       24.0    2       2
np      1550 gain        36
fb      4000 spin        0
ss      32 GRADIENTS
dl      1.000 gxlv11     409
nt       4 gtl      0.001000
2D ACQUISITION gxlv13     1227
sw1    30200.1 gt3      0.001000
ni      128 gatab     0.000500
phase   arrayed  F2 PROCESSING
PRESATURATION ab      -0.075
satnode  n abs      not used
wet      n fn      2048
TRANSMITTER   F1 PROCESSING
tn      H1 qf1      0.004
sfrq   500.484 qfsl      not used
tof     -178.0 procl    lp
tpwr    58 fnl      2048
pw      7.900 DISPLAY
DECOUPLER    ap      -116.2
dn      C13 wp      4075.7
dof     1287.0 spl     -293.7
dm      nnn wpl     22915.5
decwave W40_HCNSm wfl      257.5
dnf     32258 rfp      0
dpwr    38 rfll     1886.2
pwlvl   56 rfpl     0
pwx    11.100 PLOT
HMBC      wc      206.0
j1kh    146.0 sc      0
jnxh    8.0  wc2     206.0
ADIABATICCIC sc2      0
pwx180ad CNE ad300 vs      5465
pwxlv1180      52 th      4
pwx180    465.4 ai cdc av

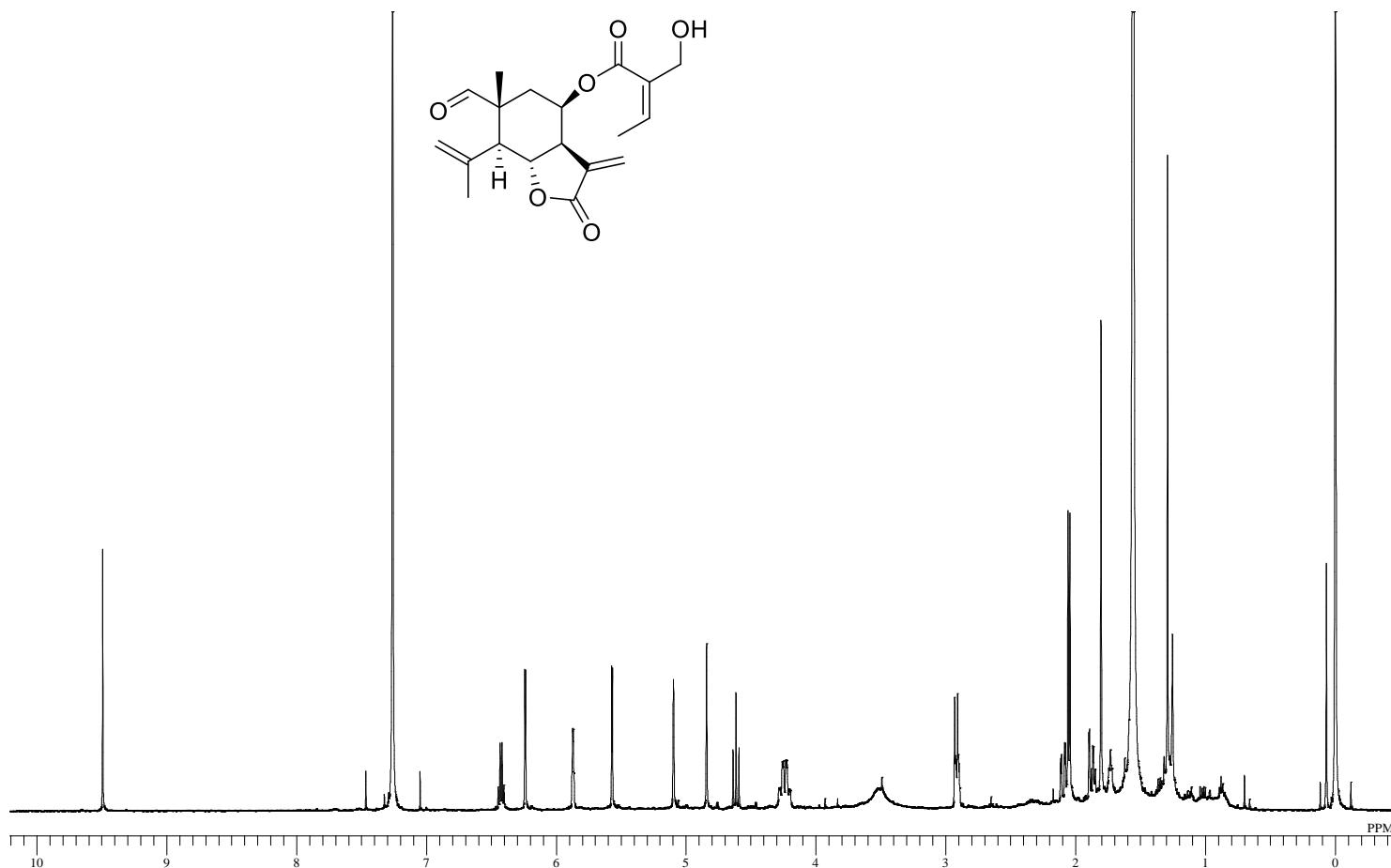
```



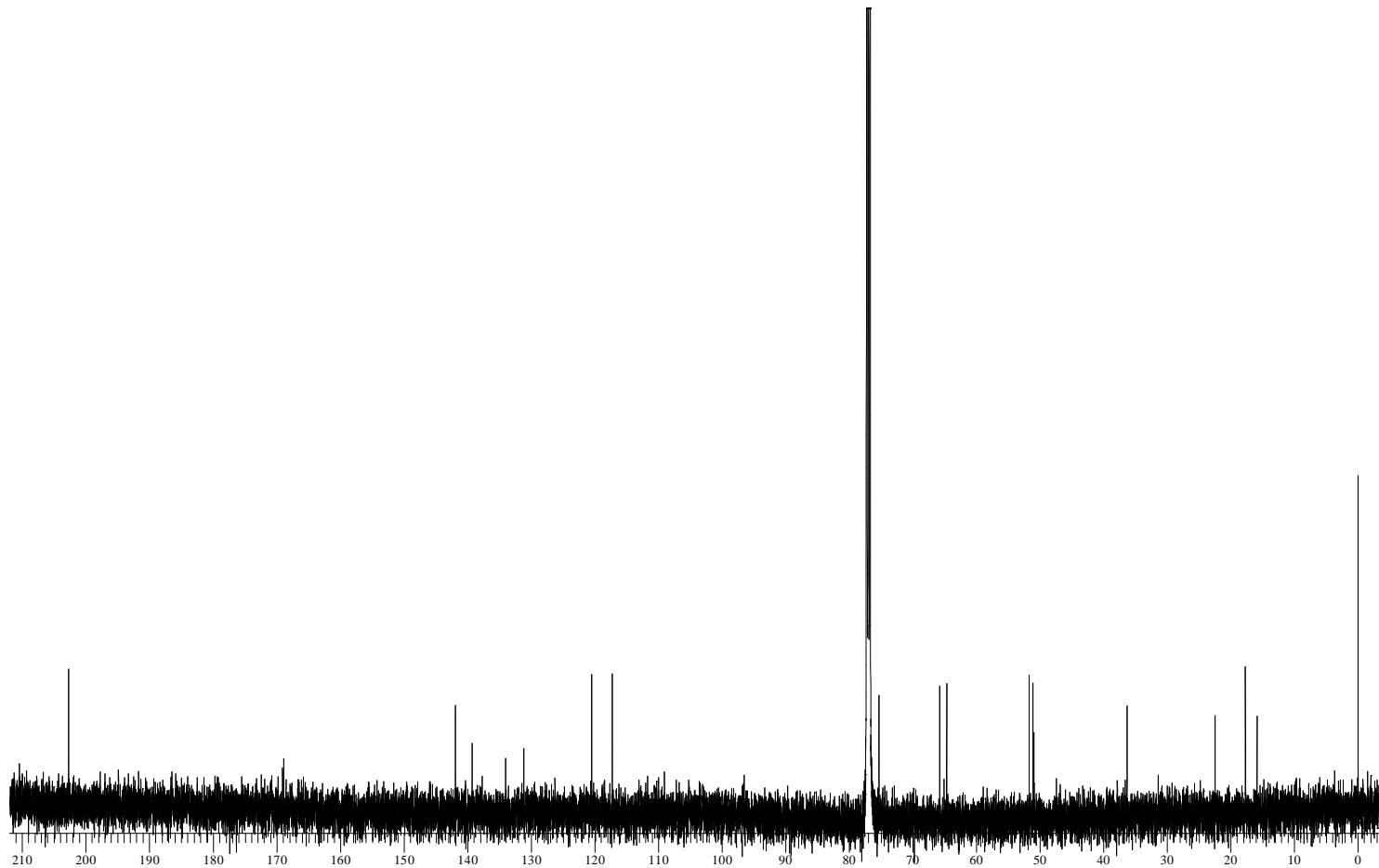
**Figure S72.** NOESY spectrum of **54** (measured in  $\text{CDCl}_3$ , 500 MHz).



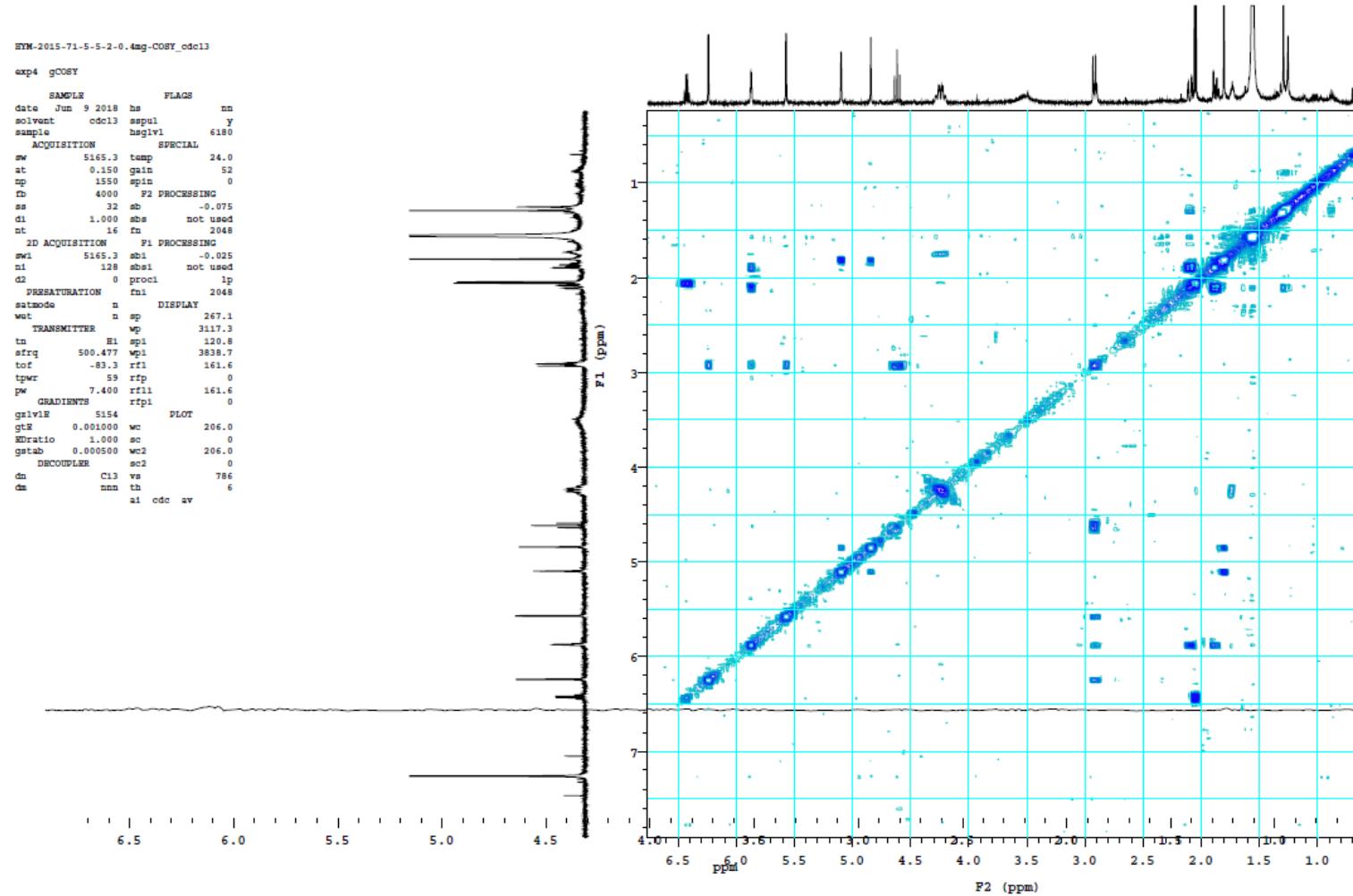
**Figure S73.**  $^1\text{H}$  NMR spectrum of **62** (measured in  $\text{CDCl}_3$ , 500 MHz).



**Figure S74.**  $^{13}\text{C}$  NMR spectrum of **62** (measured in  $\text{CDCl}_3$ , 126 MHz).



**Figure S75.**  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of **62** (measured in  $\text{CDCl}_3$ , 500 MHz).

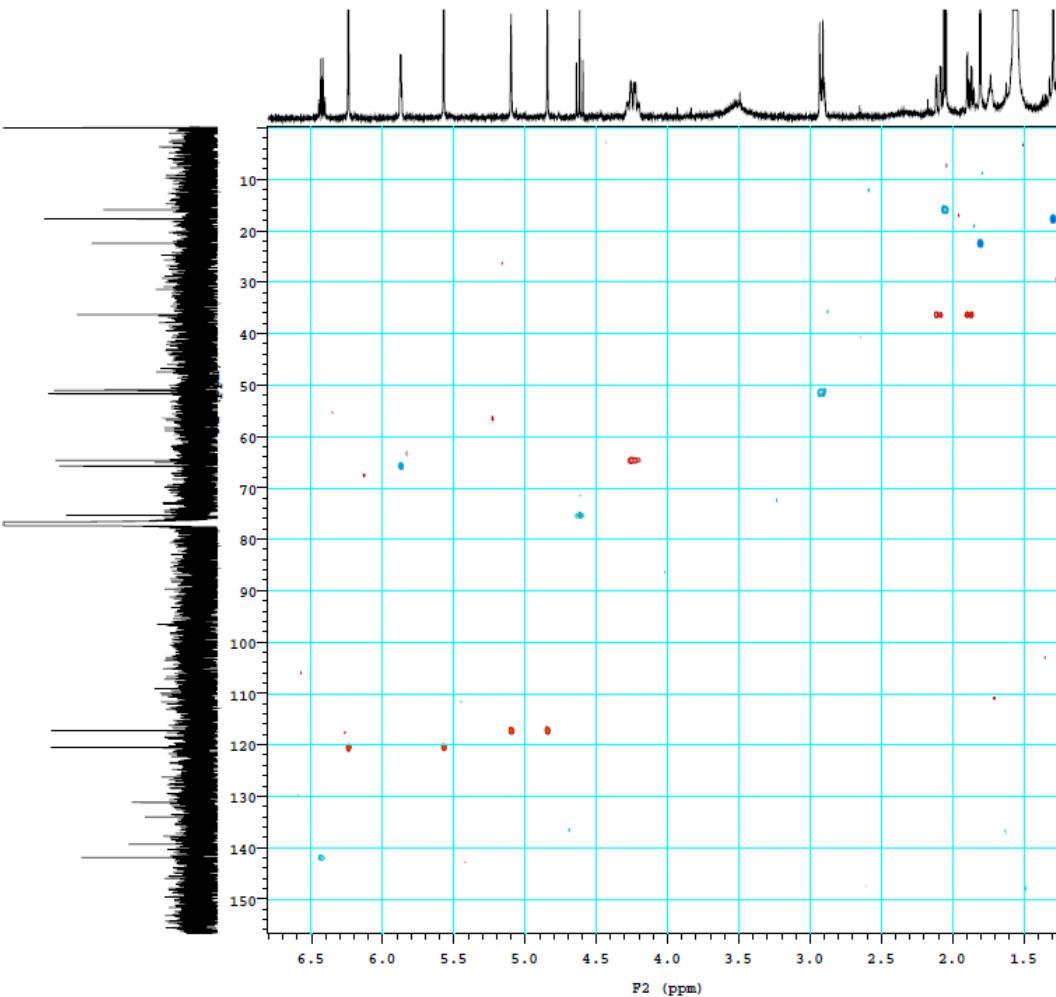


**Figure S76.** HSQC spectrum of **62** (measured in  $\text{CDCl}_3$ , 500 MHz).

HTM-2015-71-5-5-2-0.4mg-HSQC\_cdc13

exp5 HSQCAD

SAMPLE	FLAGS	ACQUISITION ARRAYS
date Jun 25 2018	hs	nn array
solvent cdc13	asgul	y arraydim
sample PPGfig		256
ACQUISITION hsg1v1		6180 1 phase
sw 4921.3	SPECIAL	1 1
at 0.150	temp	24.0 2
np 1476	gain	52
fb 4000	spin	0
ss 32	P2 PROCESSING	
dt 1.000	gf	0.069
nt 16	gfs	not used
2D ACQUISITION fn		2048
sw1 21390.4	PI PROCESSING	
ni 128	gf1	0.006
phase arrayed	gfsl	not used
PRESATURATION procl		1p
satmode n	fni	2048
wst n		DISPLAY
TRANSMITTER sp		579.7
tn H1 wp		2825.9
sfrq 500.477	sp1	-23.1
tof -136.8	wpi	19740.1
tpwr 59	rfl	93.1
PW 7.400	rtp	0
DECOUPLER rfill		1255.6
dn C13 rtp1		0
dof -2487.0		PLOT
dm nny wo		206.0
dcwave W40_HCNsm	sc	0
dmt 32258	wc2	206.0
dpwr 38	sc2	0
pwx1v1 56	vs	1000
pwx 11.000	th	5
HSQC	ai cdc ph	
j1xb 146.0		
nullfig	y	
mult 2		
ADIABATIC		
pwx180ad ONR_ad100		
pwx180adR ONR_ad100-		
OR		
pwx180 465.4		
pwx1v1180 51		
pwx180ref ONR_ref2-		
00		
pwx180r 2000.2		
pwx1v1180r 43		



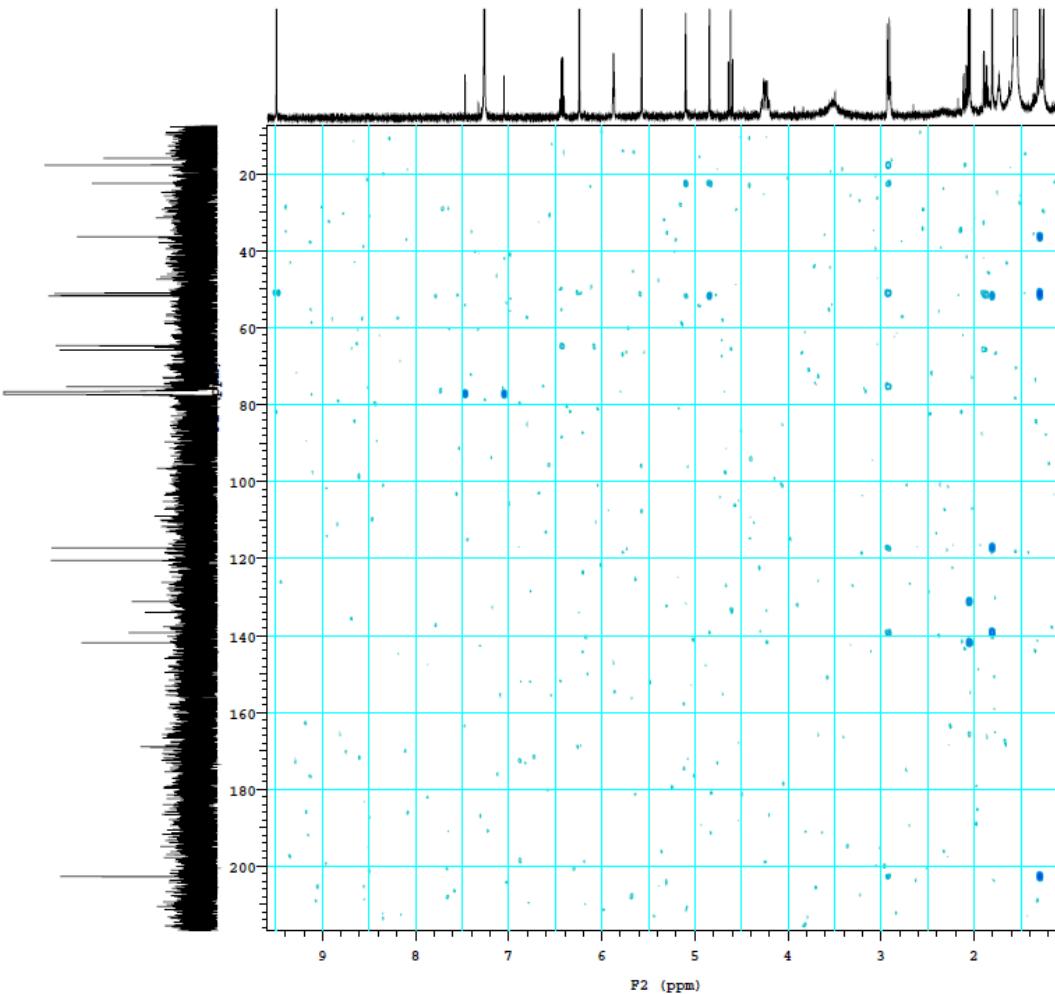
**Figure S77.** HMBC spectrum of **62** (measured in  $\text{CDCl}_3$ , 500 MHz).

```

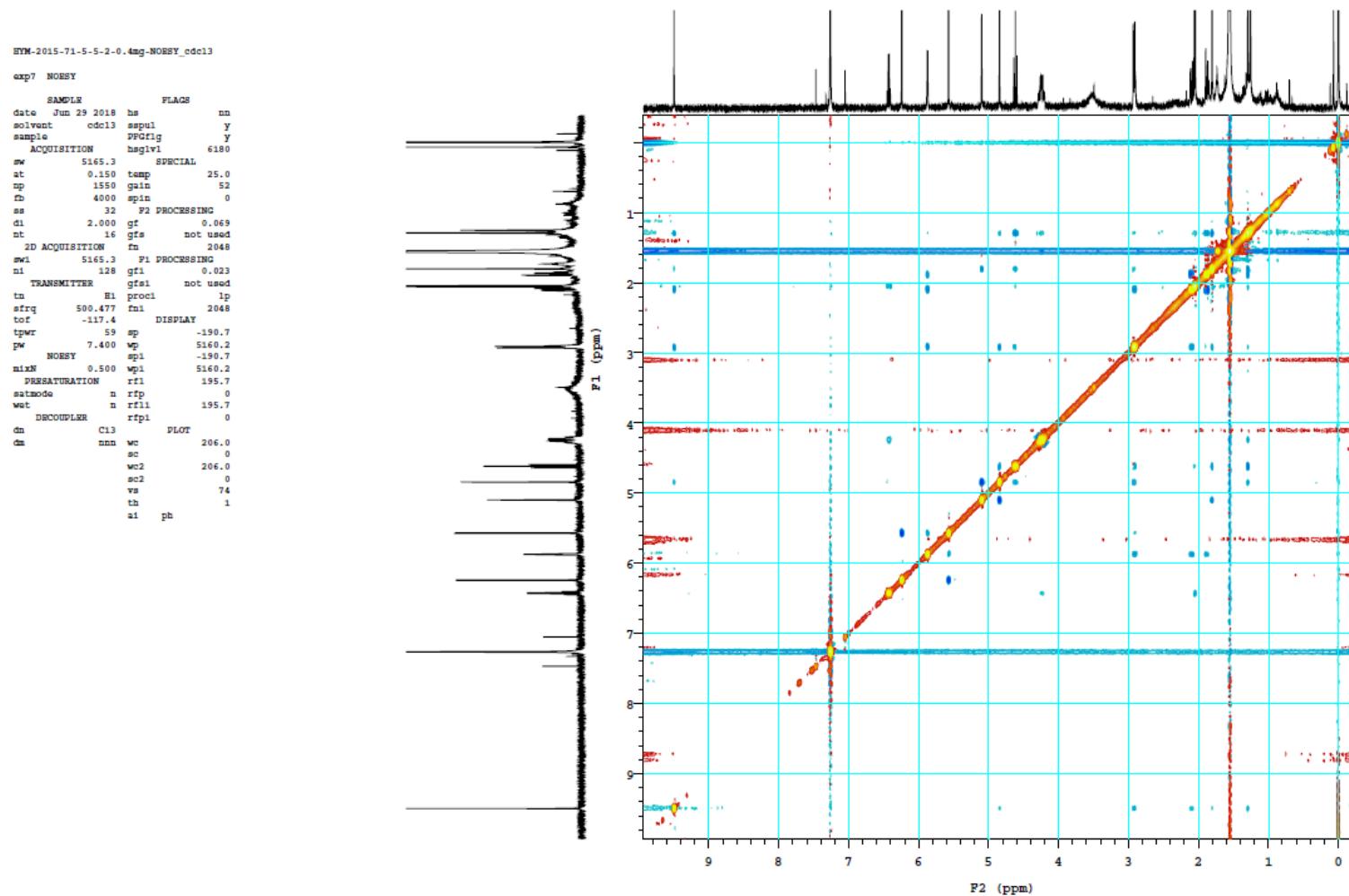
HM-2015-71-5-5-2-0.4mg_HMBC_cdc13
exp6 gHMBCAD

SAMPLE          FLAGS      ACQUISITION ARRAYS
date   Jun 25 2018    bs        nn      array    phase
solvent   cdc13    sepu1      y      arraydim  256
sample      PPGflg      y
ACQUISITION   bag1v1     6180    1      phase
sw       4321.3    SPECIAL    1        1
at        0.150    temp     24.0      2
np        1476     gain      52
fb        4000     spin      0
ss         32      GRADIENTS
d1       1.000    g1v1l     409
nt        64      gti      0.001000
2D_ACQUISITION   g1v1l3    1227
sw1      30200.1    gt3      0.001000
ni        128     gstab     0.000500
phase      arrayed    F2 PROCESSING
PRESATURATION   sb      -0.075
satmode      n     abs      not used
wet         n      fn      2048
TRANSMITTER      F1 PROCESSING
tn        81      gfi      0.004
sfrq     500.477    gfs1      not used
tof      -136.8    proc1     1p
tpmr      59      fml      2048
pw       7.400    DISPLAY
DECODER          sp      488.4
dn        C13     wp      4310.9
dof      1287.0    spi      944.9
dm        mnn     wpi     26336.6
decwave W4_1HNSnm rfi      93.1
dmf      32258    rfp      0
dpwr      38     rf11     1886.4
pw1v1l     56     rf11      0
pw1x     11.000    PLOT
HMBC          wc      206.0
j1xh     145.0    ac      0
j1xh      8.0     wc2     206.0
ADABATIC1C      wc2      0
pw180ad ONE_sd300    vs      1000
pw1v1l180     51     th      5
pw1x180     465.4    ai     cdc     sv

```



**Figure S78.** NOESY spectrum of **62** (measured in  $\text{CDCl}_3$ , 500 MHz).



**Figure S79.** Experimental and calculated ECD spectra of **10**.

