One-pot synthesis of 2-oxa-7-azaspiro[4.4]nonane-8,9-diones using Mn(III)-based oxidation of 4-acylpyrrolidine-2,3-diones

Thanh-Truc Huynh,[a] Van-Ha Nguyen,[b] and Hiroshi Nishino[c*]

[a]*Department of Chemistry, Graduate School of Science and Technology, Kumamoto University, Kurokami, Kumamoto 860-8555, Japan*
[b]*Department of Chemistry, Dalat University, 1 Phu Dong Thien Vuong St., Dalat, Vietnam*
[c]*Department of Chemistry, Faculty of Science, Kumamoto University, Kurokami 2-39-1, Chûou-Ku, Kumamoto 860-8555, Japan*

Supplementary data

Spectroscopic data of the products **3ba**, **3ca**, **3da**, **3ea**, **3ab**, and the copies of ^{1}H NMR, ^{13}C NMR, DEPT, COSY, NOESY, HMQC, and HMBC spectra for the new compounds **3** and **4**.

* Corresponding author. Tel.: +81-96-342-3374; fax: +81-96-342-3374; e-mail: nishino@sci.kumamoto-u.ac.jp

Manganese(III)-based reaction of a mixture of 1,1-diarylethenes 1a-e and 2,3-pyrrolidinediones 2a-e in glacial acetic acid. 1,1-Diarylethene **1** (1 mmol) was weighed into a 50 mL flask equipped with a magnetic stirrer. Glacial acetic acid (15 mL) and pyrrolidine-2,3-dione **2** (1.5-3 mmol) were added to the flask. The flask was placed in an oil bath and fitted with a reflux condenser. The mixture was stirred in air and heated just before refluxing, and manganese (III) acetate dihydrate (3-5 mmol) was then added. The reaction was heated under reflux until the reaction mixture turned colorless or yellow (normally for 3 min). The solvent was removed *in vacuo*, and the residue was triturated with water. The aqueous mixture was extracted with chloroform (15 mL **x** 3). The extracts were combined and dried over anhydrous sodium sulfate, filtered and then concentrated to dryness. The products were separated on silica gel TLC (Wakogel B-10, B-5F, or Merck Kieselgel 60 F_{254}) with methanol/dichloromethane (1:99 v/v) as the developing solvent. The solid products were further recrystallized by indicated solvent.

7-Benzyl-3,3-diphenyl-1-(propan-2-ylidene)-2-oxa-7-azaspiro[4.4]nonane-8,9-dione (3ba): yellowish cubes (from chloroform/hexane); mp 157-158 °C; IR ($CHCl_3$) 1762.8 (–CO–), 1714.6 (–CON–); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.19 (13H, m, arom H), 7.13-7.11 (2H, m, arom H), 4.53 (2H, s, CH_2), 3.03 (1H, d, J = 11.8 Hz, H_a-6), 2.87 (1H, d, J = 12.3 Hz, H_a-4), 2.86 (1H, d, J = 12.3 Hz, H_b-4), 2.81 (1H, d, J = 11.8 Hz, H_b-6), 1.83 (3H, s, Me-12), 1.16 (3H, s, Me-11); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.4 (C-9), 158.3 (C-8), 148.9 (C-1), 143.6, 143.0, 134.1 (arom C), 128.9 (2C), 128.53 (2C), 128.51 (2C), 128.4, 128.3 (2C), 127.6, 127.5, 125.7 (2C), 125.4 (2C) (arom CH), 103.0 (C-10), 88.2 (C-3), 53.6 (C-6), 53.1 (C-4), 51.4 (C-5), 48.3 (CH_2), 18.9 (Me), 17.5 (Me). Anal Calcd for $C_{29}H_{27}NO_3$: C, 79.61; H, 6.22; N, 3.20. Found: C, 79.35; H, 6.24; N, 3.16.

7-Benzyl-3,3-bis(4-fluorophenyl)-1-(propan-2-ylidene)-2-oxa-7-azaspiro[4.4]nonane-8,9-dione (3ca): colorless needles (from chloroform/hexane); mp 179-180 °C; IR ($CHCl_3$) 1762.8 (–CO–), 1720.4 (–CON–); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.33 (3H, m, arom H), 7.30-7.26 (2H, m, arom H), 7.21-7.19 (2H, m, arom H), 7.16-7.14 (2H, m, arom H), 6.99-6.94 (4H, m, arom H), 4.60 (1H, d, J = 14.2 Hz, $\underline{H}_a$-CH), 4.53 (1H, d, J = 14.2 Hz, HC-$\underline{H}_b$), 3.05 (1H, d, J = 11.7 Hz, H_a-6), 2.84 (1H, d, J = 12.3 Hz, H_a-4), 2.79 (1H, d, J = 11.7 Hz, H_b-6), 2.77 (1H, d, J = 12.3 Hz, H_b-4), 1.81 (3H, s, Me-12), 1.17 (3H, s, Me-11); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.2 (C-9), 162.1 (1C, d, ^1J = 245.8 Hz), 162.0 (1C, d, ^1J = 246.0 Hz), 158.2 (C-8), 148.9 (C-1), 139.1 (1C, ^4J = 3.8 Hz), 138.6 (1C, ^4J = 3.8 Hz), 134.0 (arom C), 129.0 (2C), 128.6 (2C), 128.4, 127.6 (2C, ^3J = 8.1 Hz), 127.5 (2C, ^3J = 7.9 Hz), 115.5 (2C, ^2J = 21.4 Hz), 115.2 (2C, ^2J = 21.5 Hz) (arom CH), 103.6 (C-10), 87.4 (C-3), 53.6 (C-6), 53.3 (C-4), 51.5 (C-5), 48.4 (CH_2), 18.9 (Me), 17.6 (Me). Anal Calcd for $C_{29}H_{25}F_2NO_3$: C, 73.56; H, 5.32; N, 2.96. Found: C, 73.55; H, 5.20; N, 3.05.

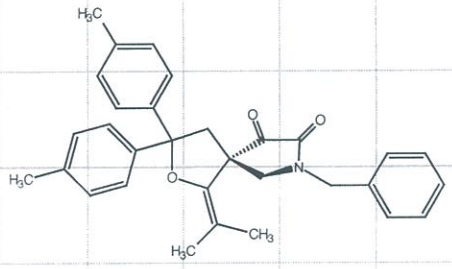
7-Benzyl-3,3-bis(4-chlorophenyl)-1-(propan-2-ylidene)-2-oxa-7-azaspiro[4.4]nonane-8,9-dione (3da): yellowish needles (from chloroform/diethyl ether); mp 184.5-185.5 °C; IR ($CHCl_3$) 1762.8 (–CO–), 1714.6 (–CON–); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.34 (3H, m, arom H), 7.25-7.22 (6H, m, arom H), 7.17-7.14 (4H, m, arom H), 4.58 (1H, d, J = 14.2 Hz, H_a–CH), 4.53 (1H, d, J = 14.2 Hz, HC–H_b), 3.07 (1H, d, J = 11.7 Hz, H_a-6), 2.82 (1H, d, J = 12.5 Hz, H_a-4), 2.81 (1H, d, J = 11.7 Hz, H_b-6), 2.79 (1H, d, J = 12.5 Hz, H_b-4), 1.80 (3H, s, Me-12), 1.17 (3H, s, Me-11); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.0 (C-9), 158.1 (C-8), 148.4 (C-1), 141.4, 141.2, 133.9, 133.8, 133.7 (arom C), 129.0 (2C), 128.3 (2C), 128.6 (2C), 128.53, (2C), 128.48, 127.0 (2C), 126.8 (2C) (arom CH), 103.8 (C-10), 87.3 (C-3), 53.6 (C-6), 52.8 (C-4), 51.3 (C-5), 48.3 (CH_2), 18.9 (Me), 17.5 (Me). Anal Calcd for $C_{29}H_{25}Cl_2NO_3 \bullet 1/2H_2O$: C, 67.58; H, 5.08; N, 2.72. Found: C, 67.83; H, 4.99; N, 2.72.

7-Benzyl-3,3-bis(4-methoxylphenyl)-1-(propan-2-ylidene)-2-oxa-7-azaspiro[4.4]nonane-8,9-dione (3ea): yellowish needles (from chloroform/diethyl ether); mp 155-156 °C; IR ($CHCl_3$) 1760.9 (–CO–), 1714.6 (–CON–); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34-7.31 (3H, m, arom H), 7.25-7.21 (2H, m, arom H), 7.15-7.12 (4H, m, arom H), 6.80-6.77 (4H, m, arom H), 4.54 (1H, d, J = 15.1 Hz, H_a-CH), 4.53 (1H, d, J = 15.1 Hz, HC-H_b), 3.80 (3H, s, OMe), 3.74 (3H, s, OMe), 3.05 (1H, d, J = 11.8

Hz, H_a-6), 2.85 (1H, d, J = 11.8 Hz, H_b-6), 2.83 (1H, d, J = 12.3 Hz, H_a-4), 2.76 (1H, d, J = 12.4 Hz, H_b-4), 1.79 (3H, s, Me-12), 1.15 (3H, s, Me-11); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.6 (C-9), 158.9 (C-8), 149.0 (C-1), 158.7, 158.4, 135.7, 134.9, 134.1 (arom C), 128.9 (2C), 128.5, 128.3 (2C), 127.2 (2C), 126.8 (2C), 113.8 (2C), 113.5 (2C) (arom CH), 102.7 (C-10), 87.9 (C-3), 55.21, 55.19 (OMe), 53.7 (C-6), 53.4 (C-4), 51.8 (C-5), 48.3 (CH_2), 18.9 (Me-12), 17.5 (Me-11). Anal Calcd for $C_{31}H_{31}NO_5$•1/4H_2O: C, 74.16; H, 6.32; N, 2.79. Found: C, 74.16; H, 6.37; N, 2.73.

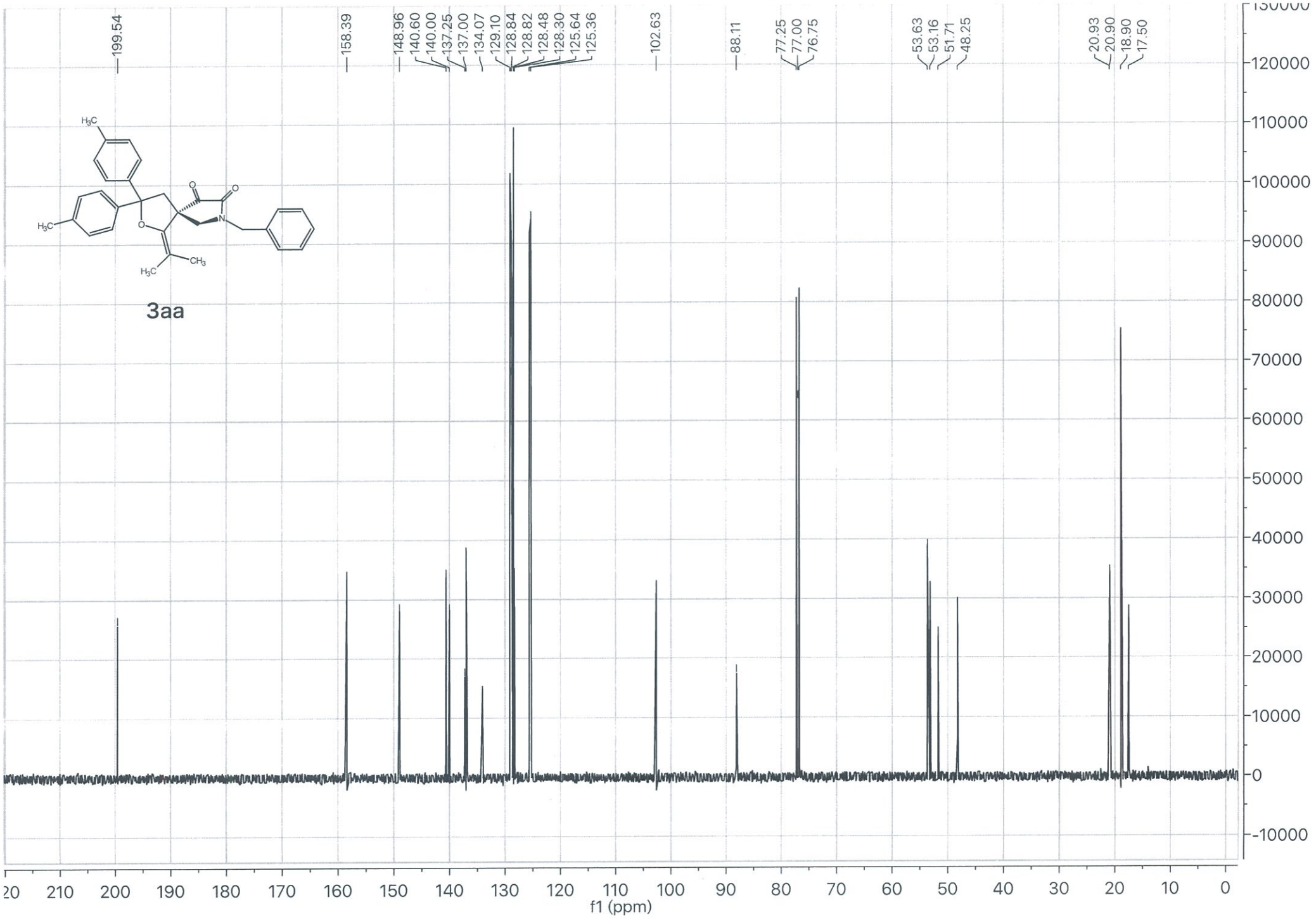
7-Benzyl-1-ethylidene-3,3-bis(4-methylphenyl)-2-oxa-7-azaspiro[4.4]nonane-8,9-dione (3ab): colorless needles (from chloroform/hexane); mp 184-185 °C; IR ($CHCl_3$) 1766.7 (–CO–), 1714.6 (–CON–); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.32 (3H, m, arom H), 7.25-7.23 (2H, m, arom H), 7.20-7.151 (4H, m, arom H), 7.107-7.08 (4H, m, arom H), 4.68 (1H, d, J = 14.3 Hz, H_a-CH), 4.45 (1H, d, J = 14.3 Hz, HC-H_b), 4.03 (1H, q, J = 6.8 Hz, H-10), 3.13 (1H, d, J = 12.8 Hz, H_a-4), 3.05 (1H, d, J = 11.0 Hz, H_a-6), 3.03 (1H, d, J = 11.0 Hz, H_a-6), 2.76 (1H, d, J = 12.8 Hz, H_b-4), 2.33 (3H, s, Me), 2.29 (3H, s, Me), 1.68 (3H, d, J = 6.8 Hz, Me-11); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.1 (C-9), 158.6 (C-8), 156.5 (C-1), 140.8, 140.60, 137.4, 137.2, 134.2 (arom C), 129.2 (2C), 128.9 (2C), 128.8 (2C), 128.5 (2C), 128.3, 125.8 (2C), 125.4 (2C) (arom CH), 94.3 (C-10), 89.4 (C-3), 55.9 (C-6), 52.4 (C-5), 48.6 (CH_2), 48.4 (C-4), 20.99 (Me), 20.98 (Me), 10.7 (Me-11). Anal Calcd for $C_{30}H_{29}NO_3$•1/2H_2O: C, 78.23; H, 6.57; N, 3.04. Found: C, 78.38; H, 6.42; N, 3.07.

S#296535
single_pulse



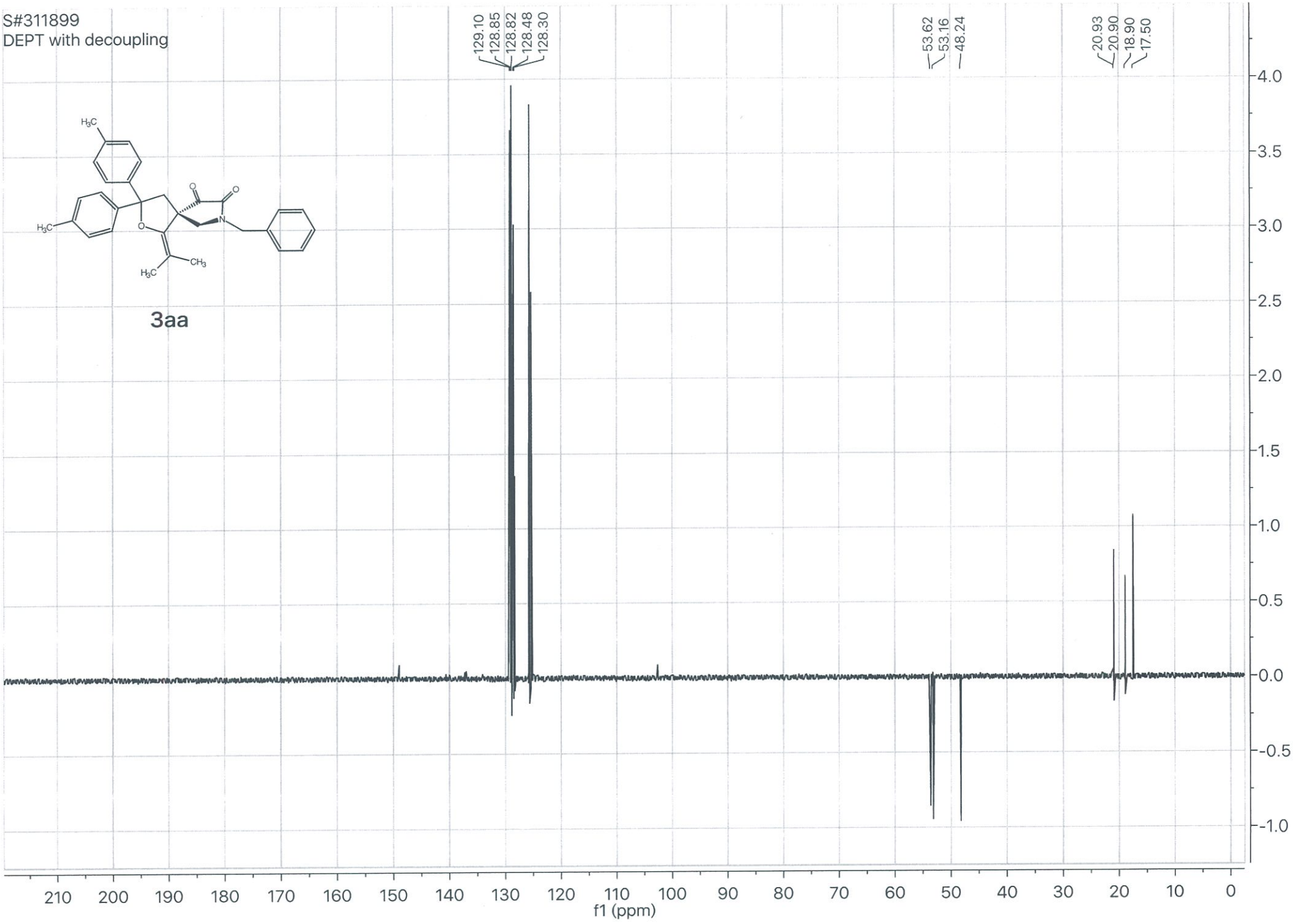
3aa

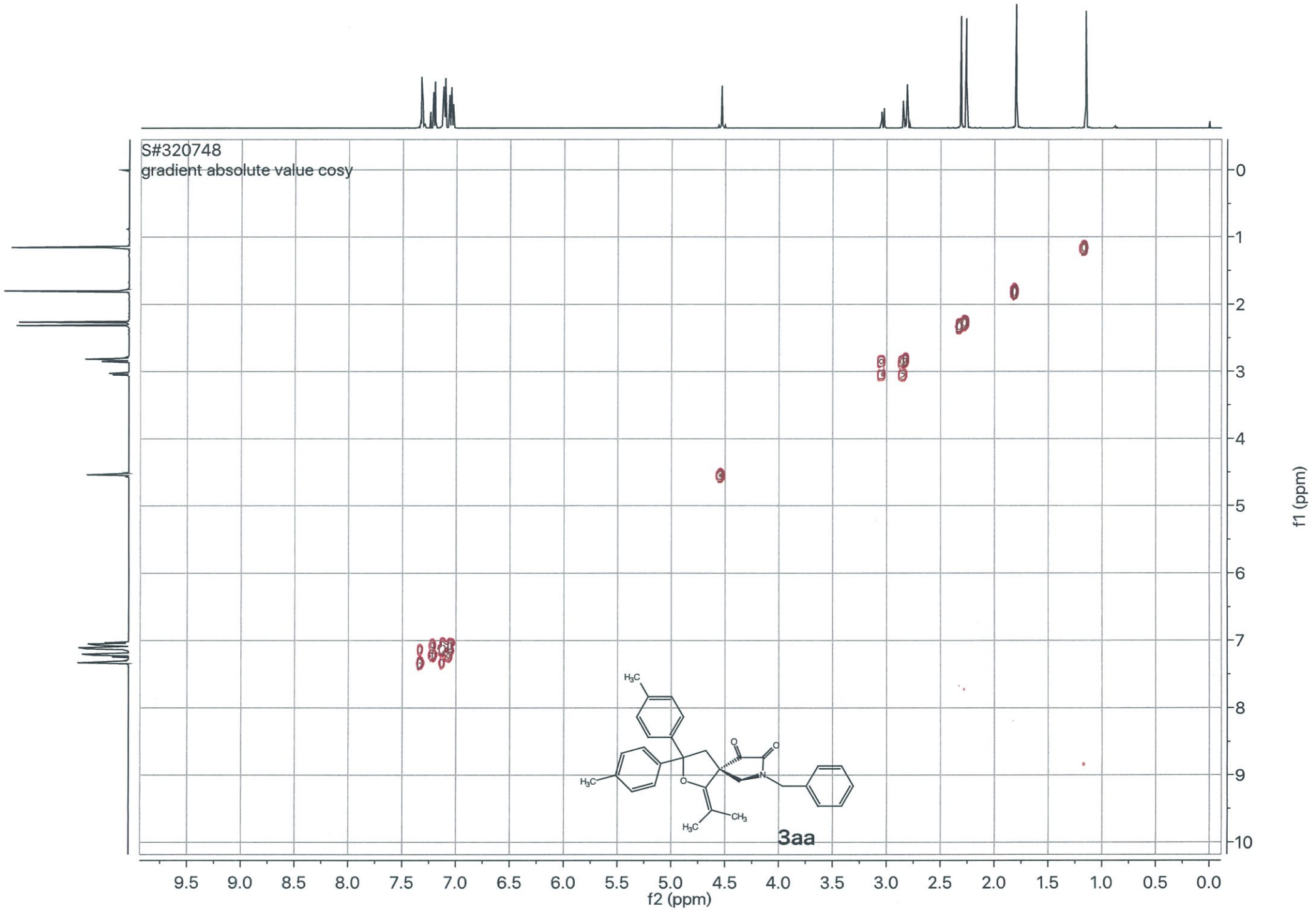
f1 (ppm)

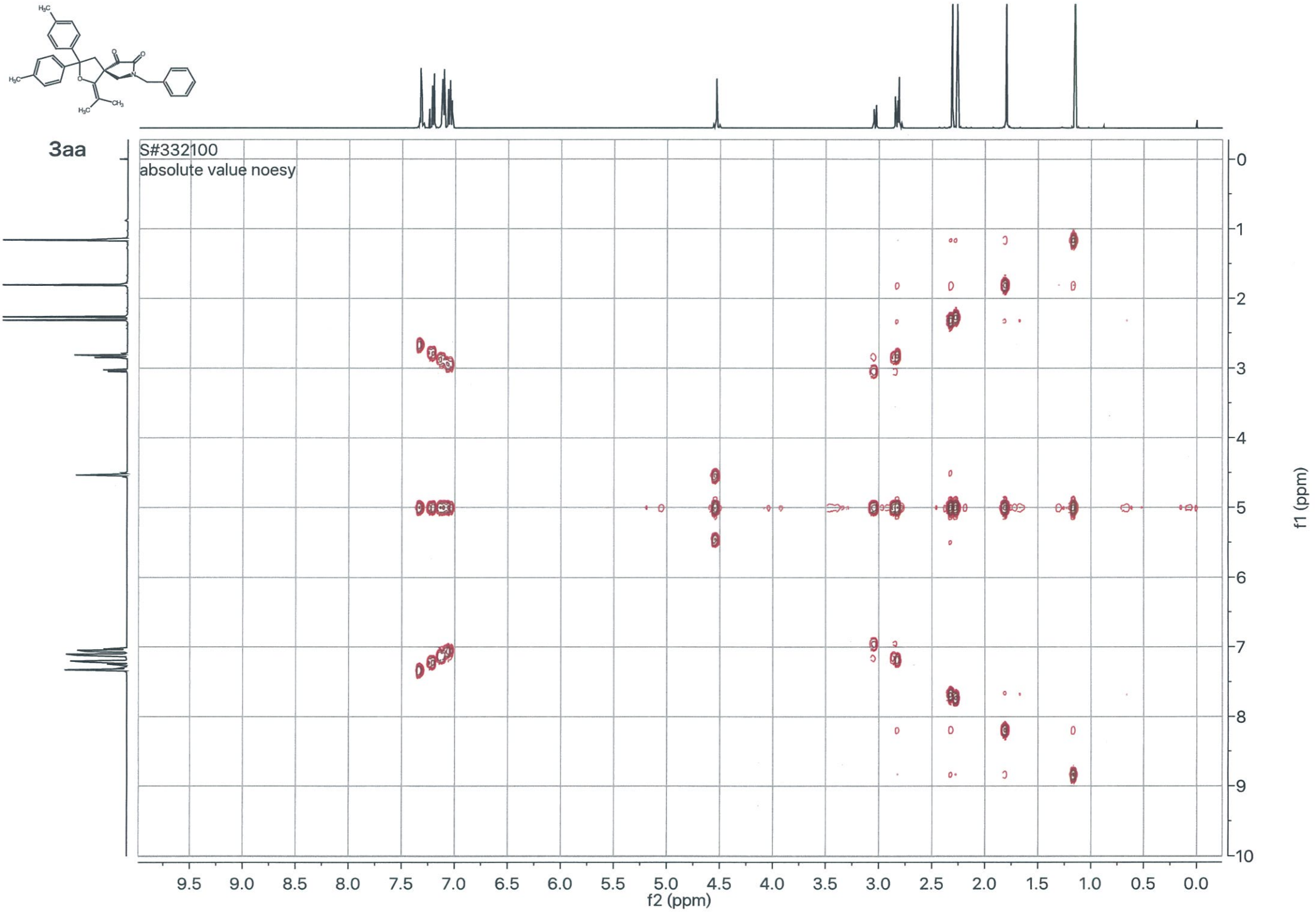

199.54
158.39
148.96
140.60
140.00
137.25
137.00
134.07
129.10
128.84
128.82
128.48
128.30
125.64
125.36
102.63
88.11
77.25
77.00
76.75
53.63
53.16
51.71
48.25
20.93
20.90
18.90
17.50
3aa
f1 (ppm)

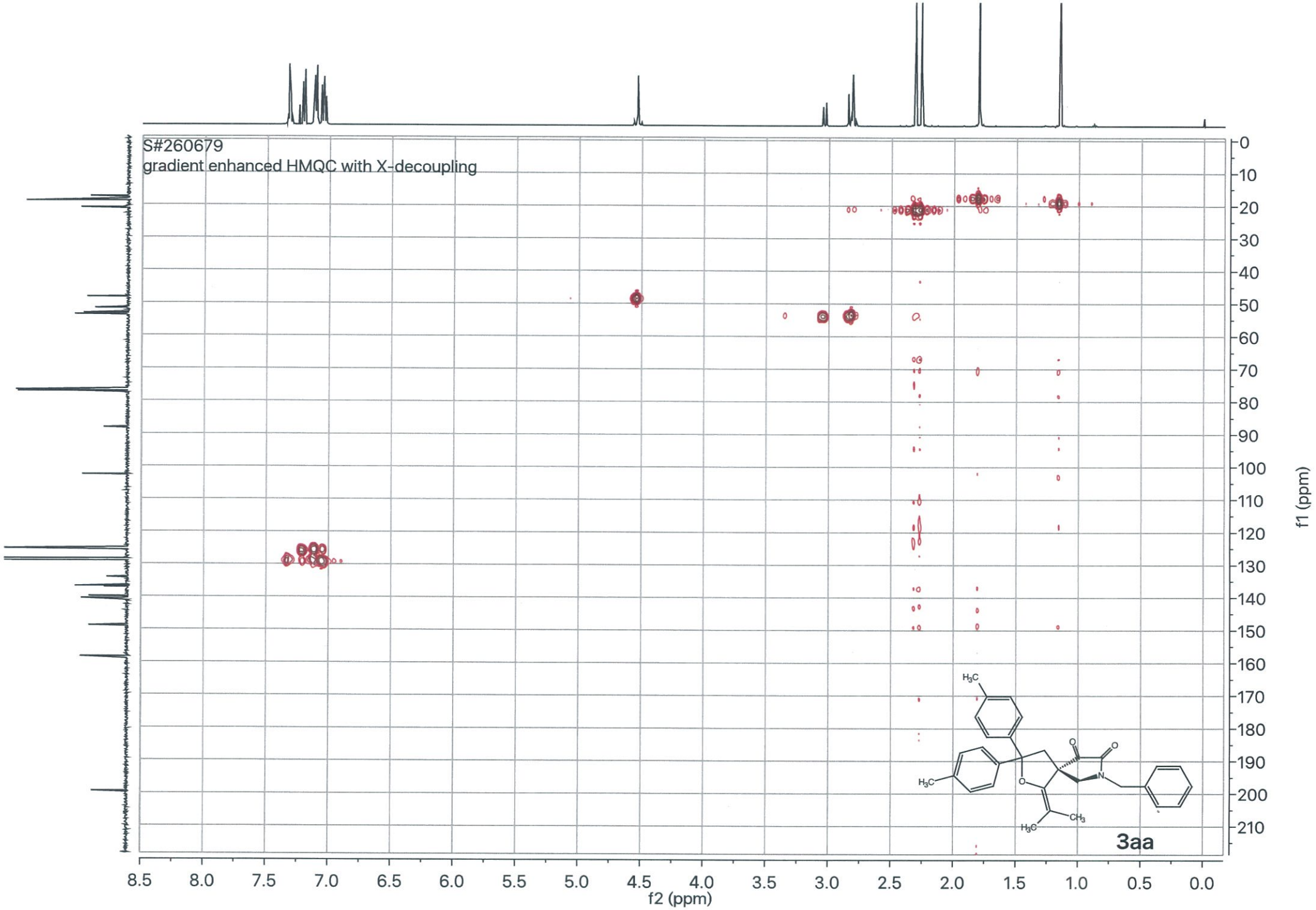
S#311899
DEPT with decoupling

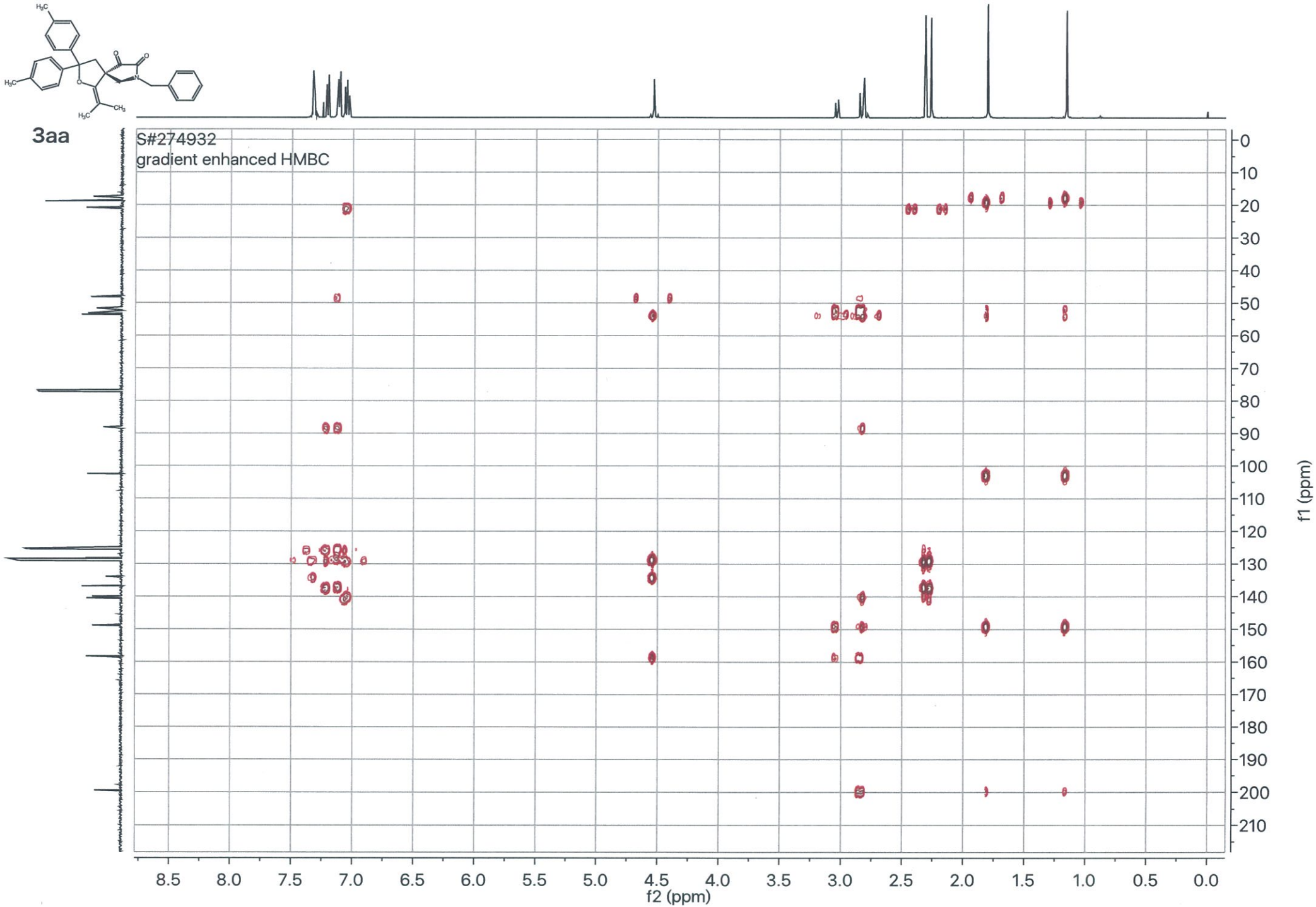
3aa

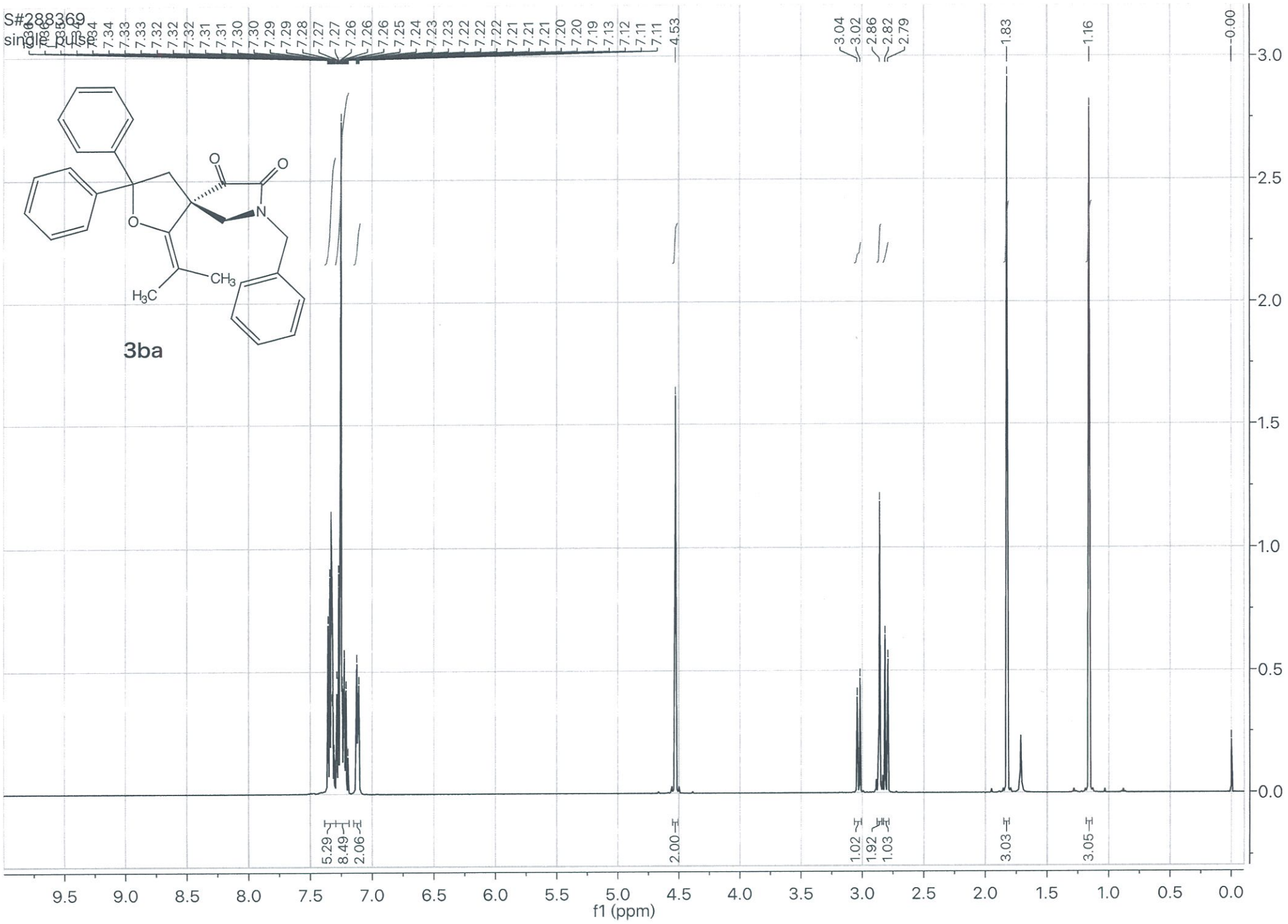



S#320748
gradient absolute value cosy
f2 (ppm)
f1 (ppm)
3aa


3aa
S#332100
absolute value noesy
f2 (ppm)
f1 (ppm)

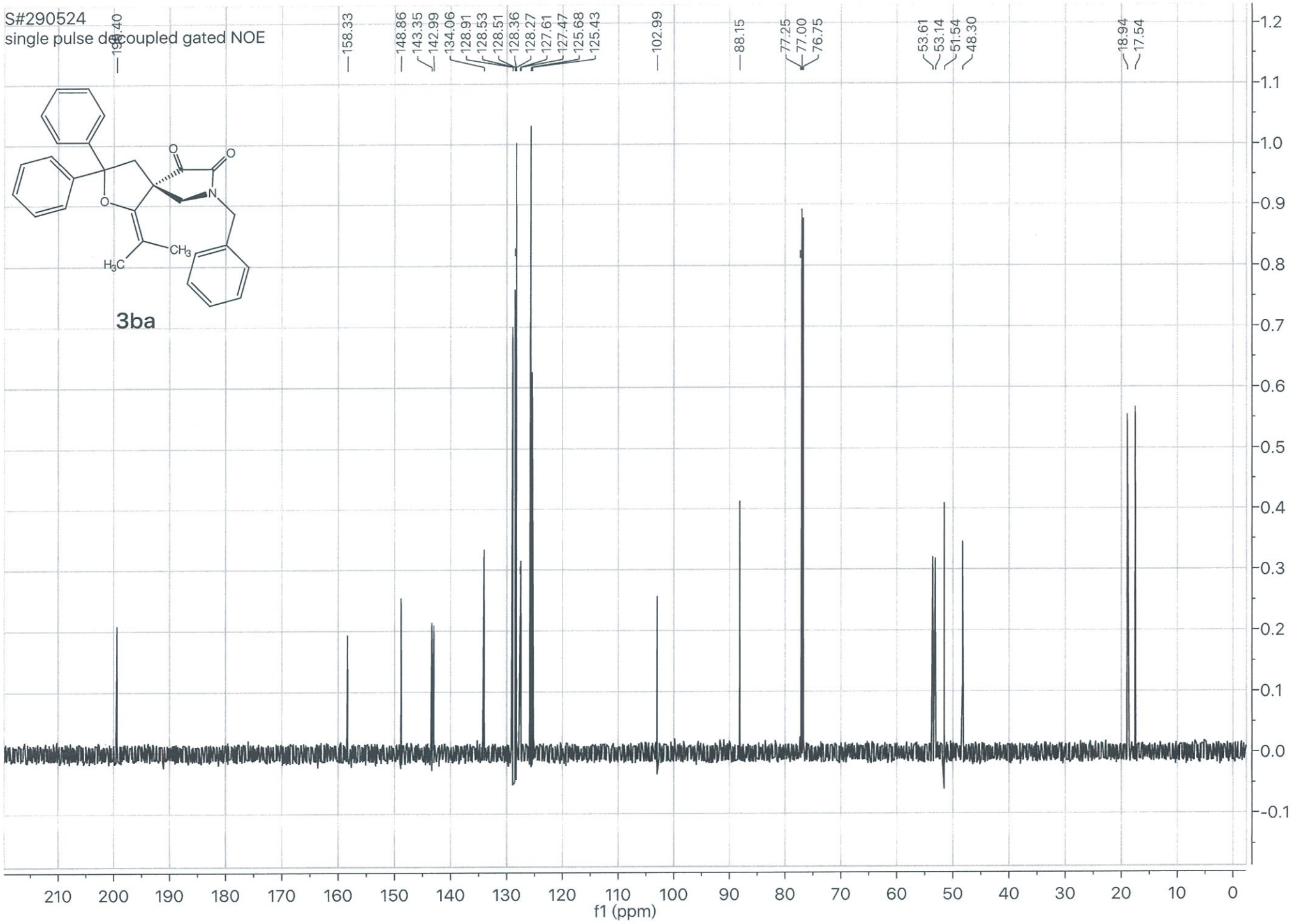

S#260679
gradient enhanced HMQC with X-decoupling
f2 (ppm)
f1 (ppm)
3aa


3aa
S#274932
gradient enhanced HMBC
f2 (ppm)
f1 (ppm)

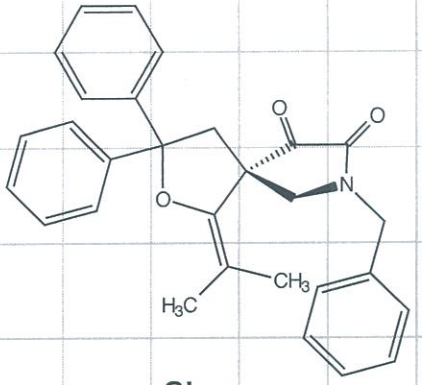

S#288369
single_pulse
7.34 7.33 7.33 7.32 7.32 7.32 7.31 7.31 7.30 7.30 7.29 7.29 7.28 7.27 7.27 7.26 7.26 7.26 7.25 7.24 7.23 7.23 7.22 7.22 7.22 7.21 7.21 7.21 7.20 7.20 7.19 7.13 7.12 7.11 7.11
4.53
3.04 3.02 2.86 2.82 2.79
1.83
1.16
0.00
O
O
O
N
CH3
H3C
3ba
5.29
8.49
2.06
2.00
1.02
1.92
1.03
3.03
3.05
f1 (ppm)

S#290524
single pulse decoupled gated NOE

3ba



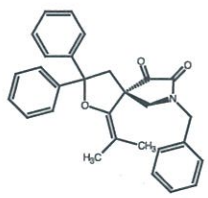
S#294577
DEPT with decoupling



3ba

128.91
128.52
128.50
128.36
128.27
127.61
127.47
125.68
125.42
53.61
53.14
48.30
18.93
17.54

f1 (ppm)

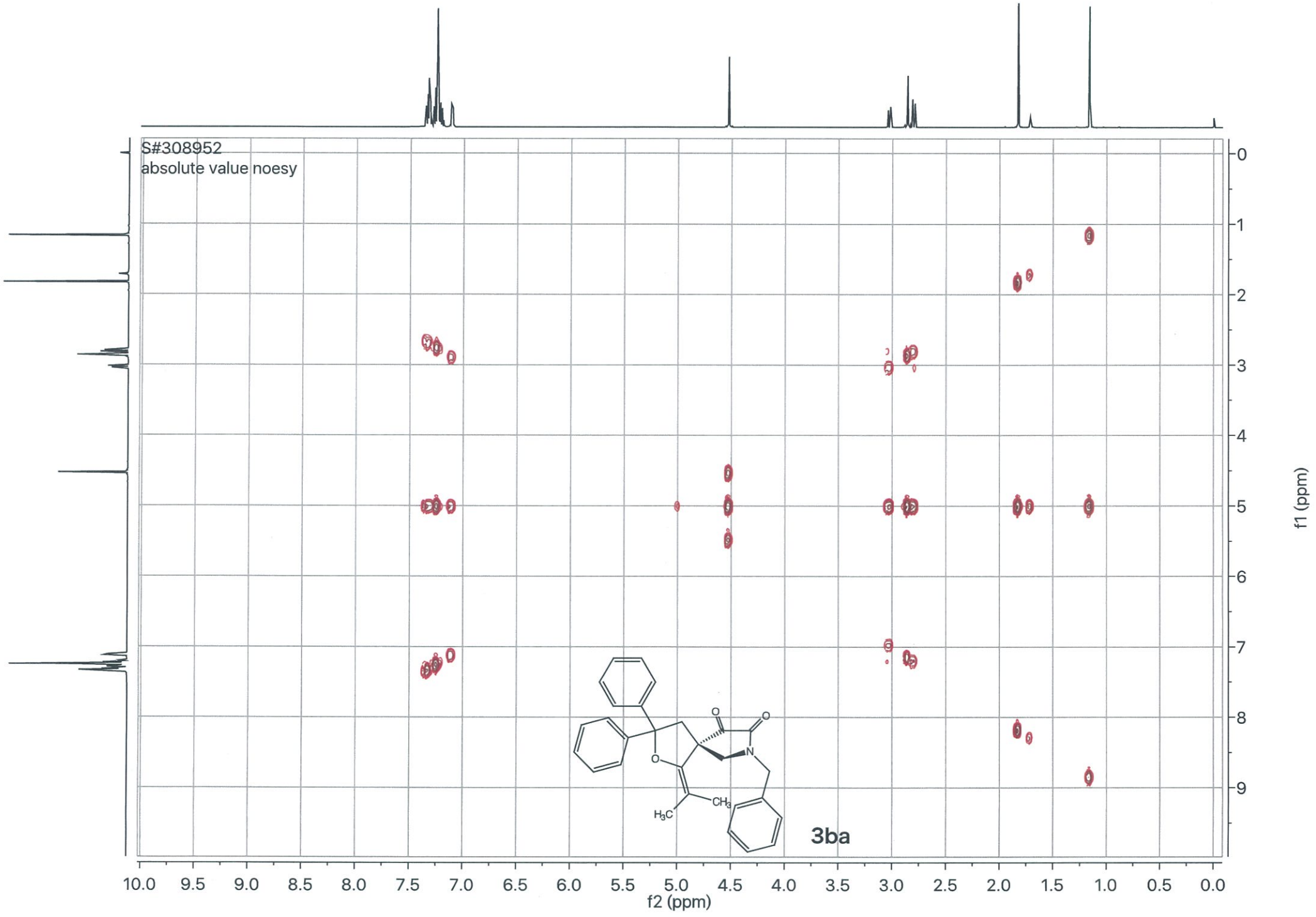


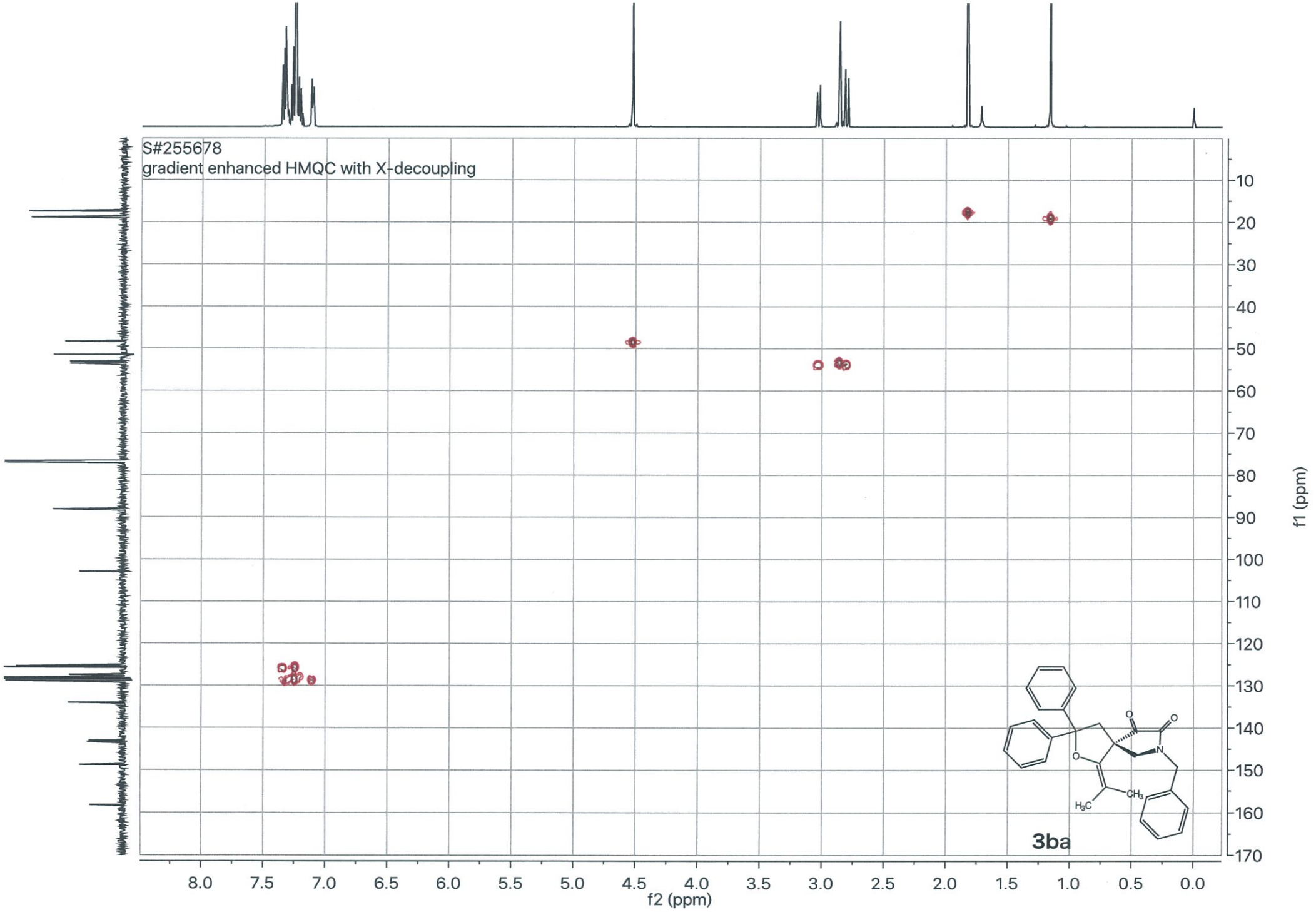
3ba

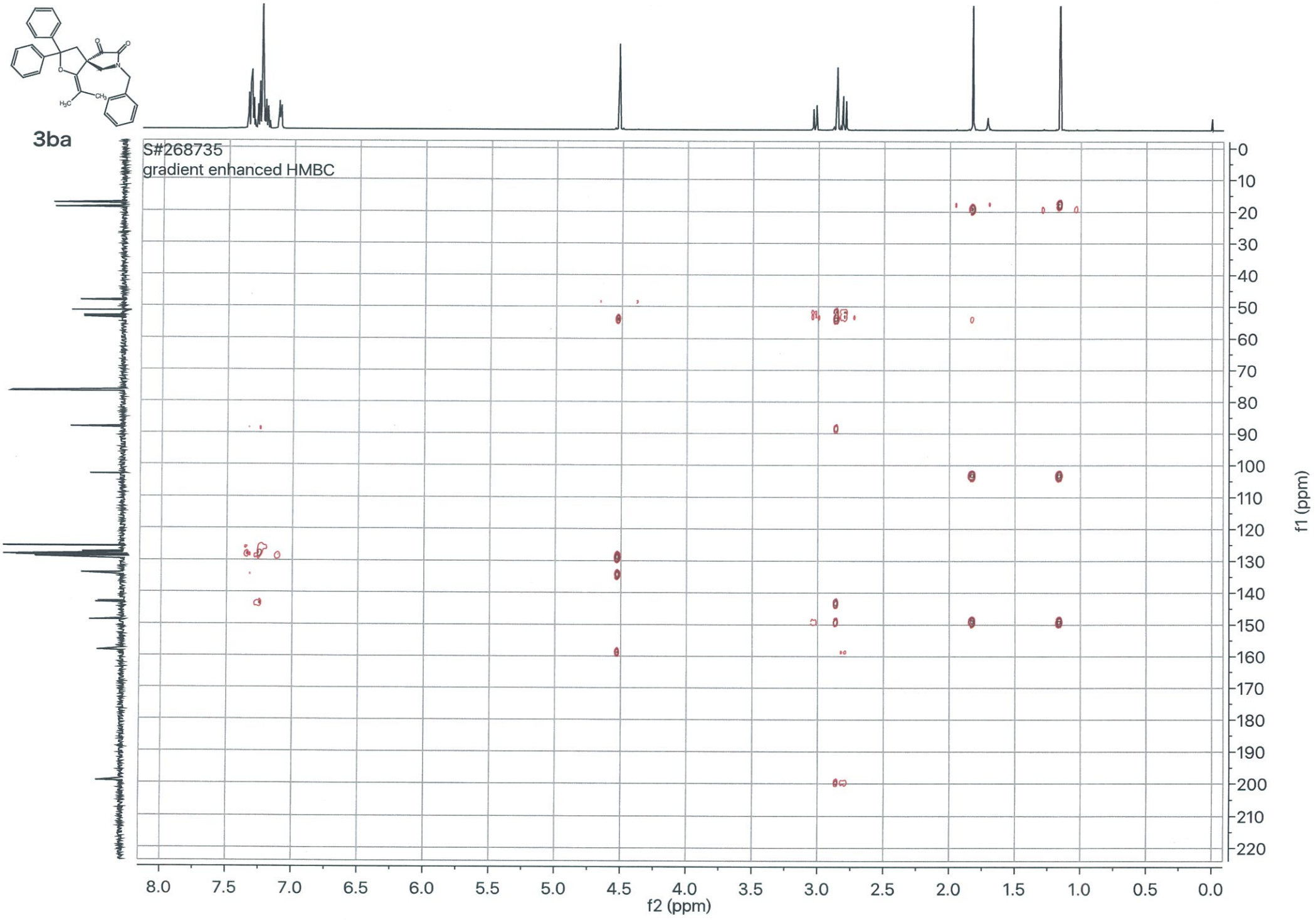
S#299169
gradient absolute value cosy

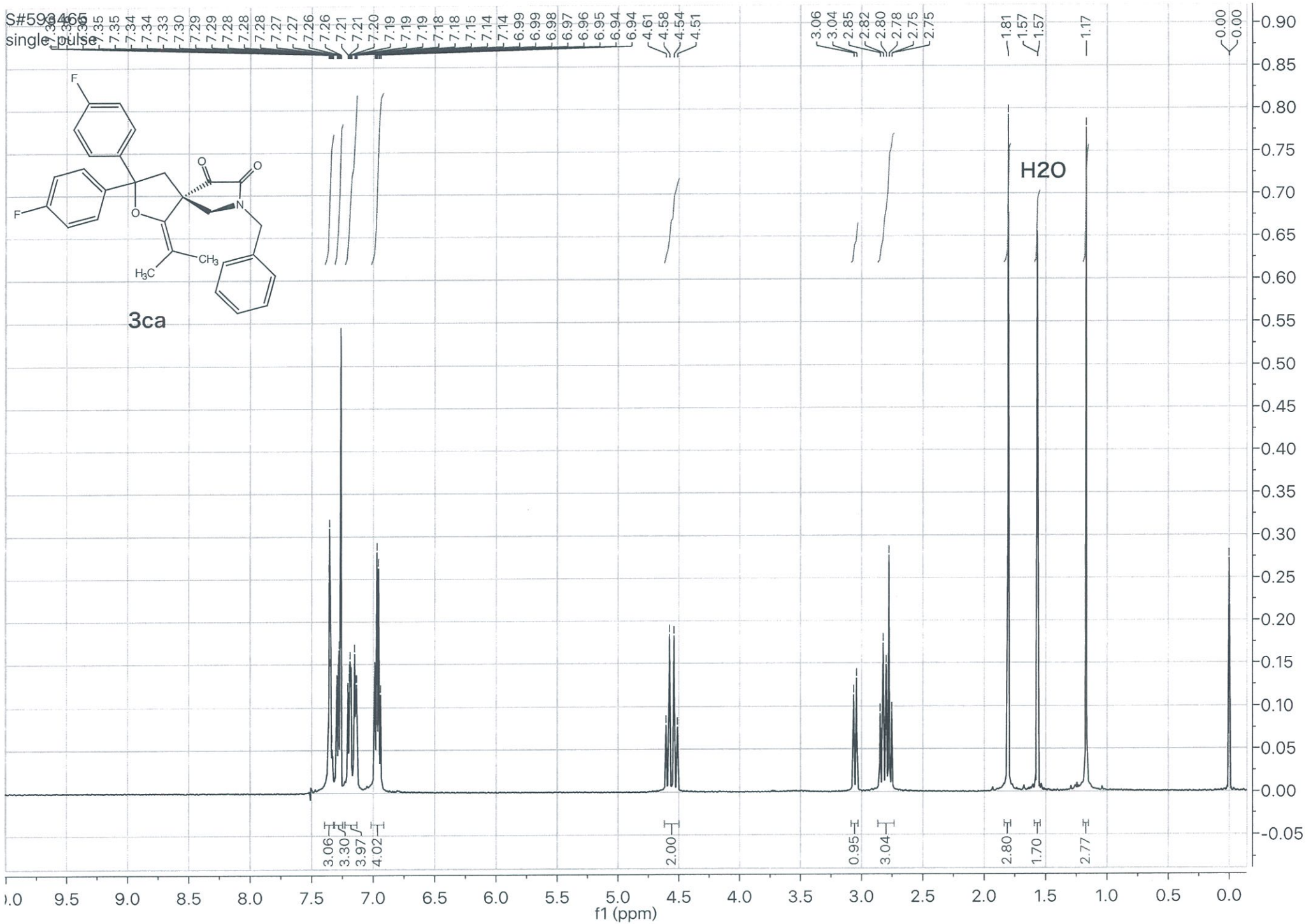
f2 (ppm)

f1 (ppm)

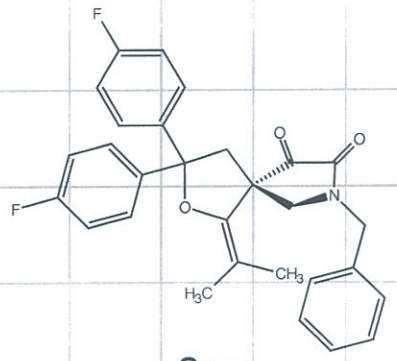

S#308952
absolute value noesy
f2 (ppm)
f1 (ppm)
3ba


S#255678
gradient enhanced HMQC with X-decoupling
f2 (ppm)
f1 (ppm)
3ba


3ba
S#268735
gradient enhanced HMBC
f2 (ppm)
f1 (ppm)


S#593465
single_pulse
F
F
O
O
O
N
H3C
CH3
3ca
H2O
f1 (ppm)

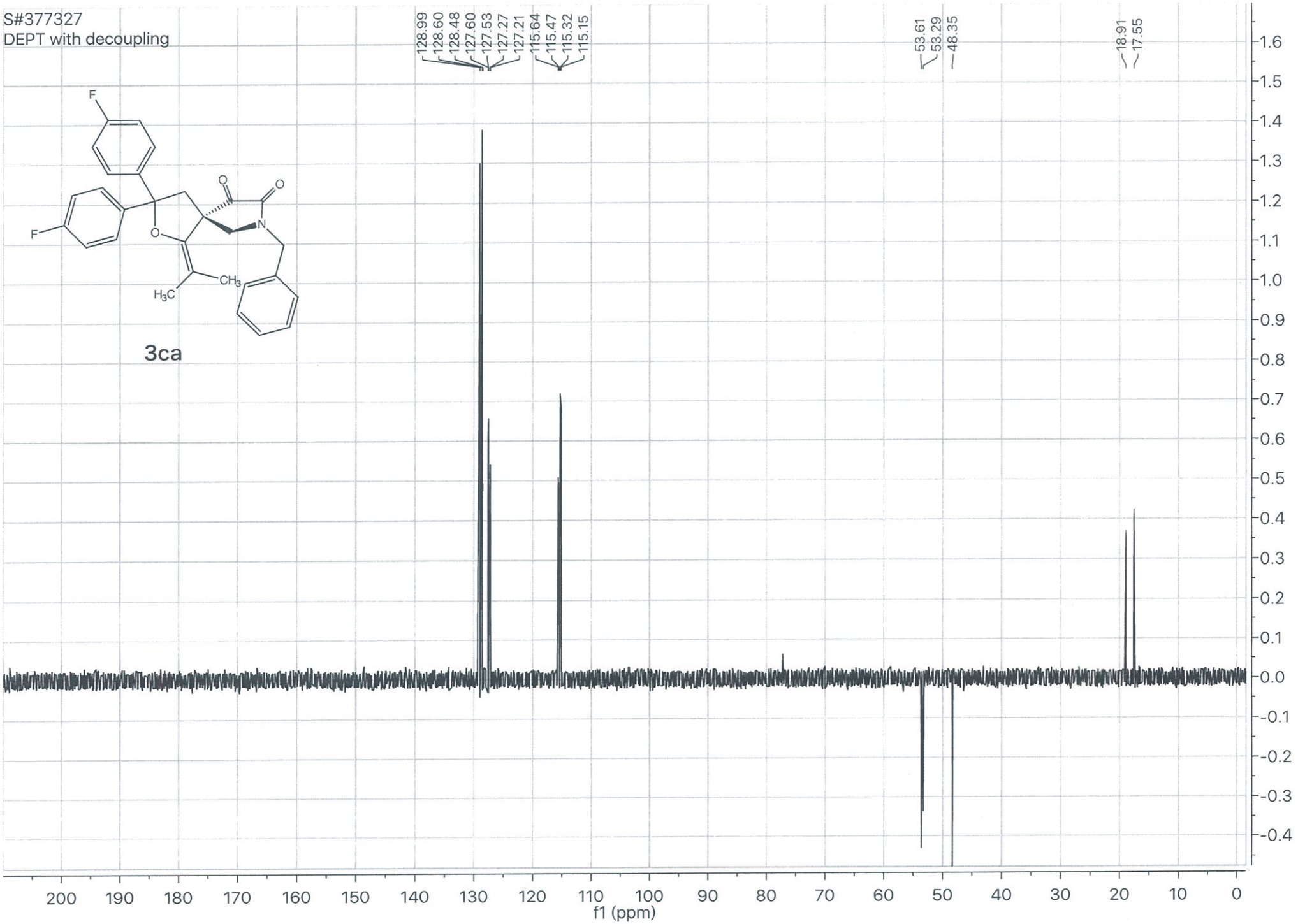
S#373815
single pulse decoupled gated NOE

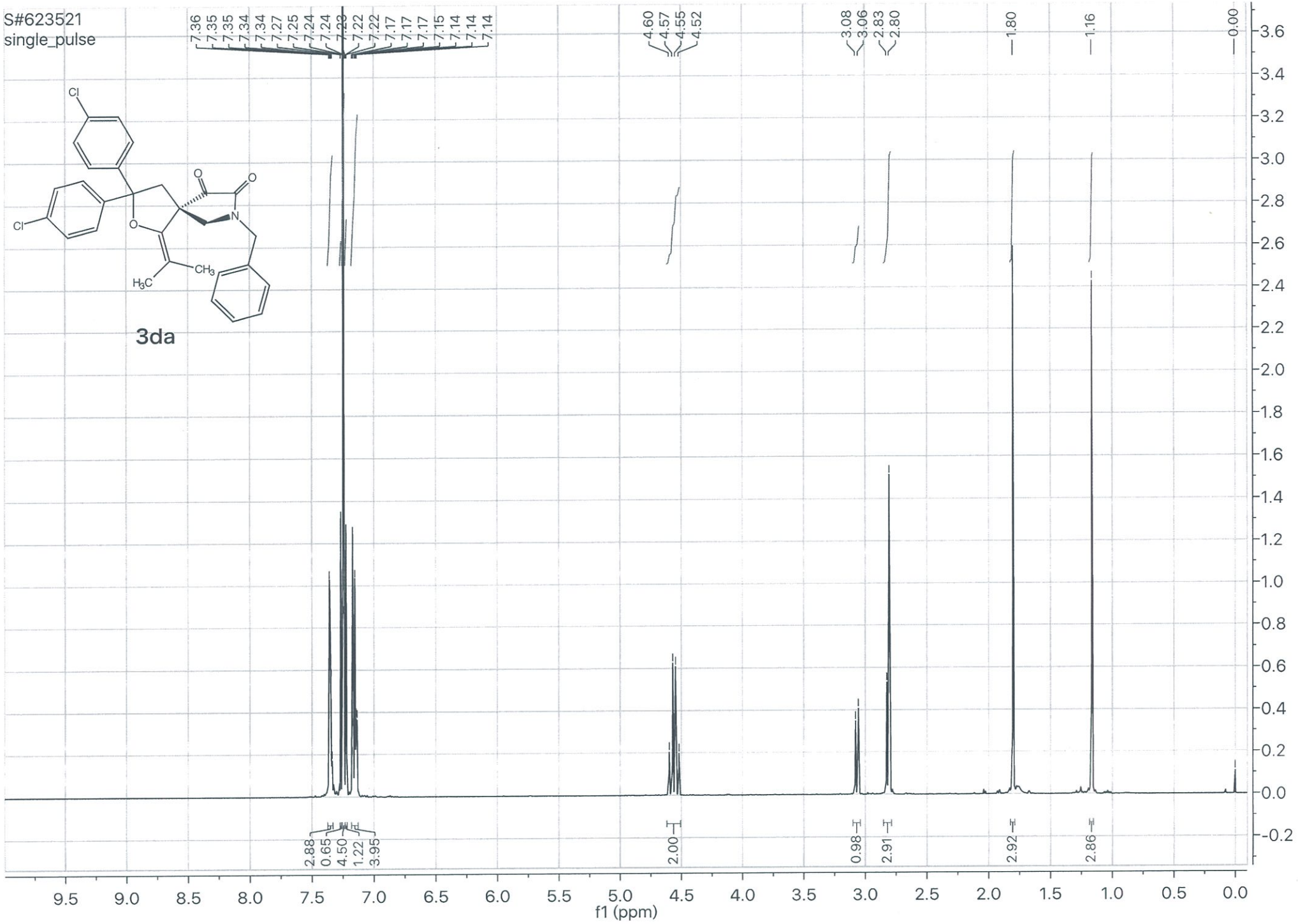


3ca

S#377327
DEPT with decoupling

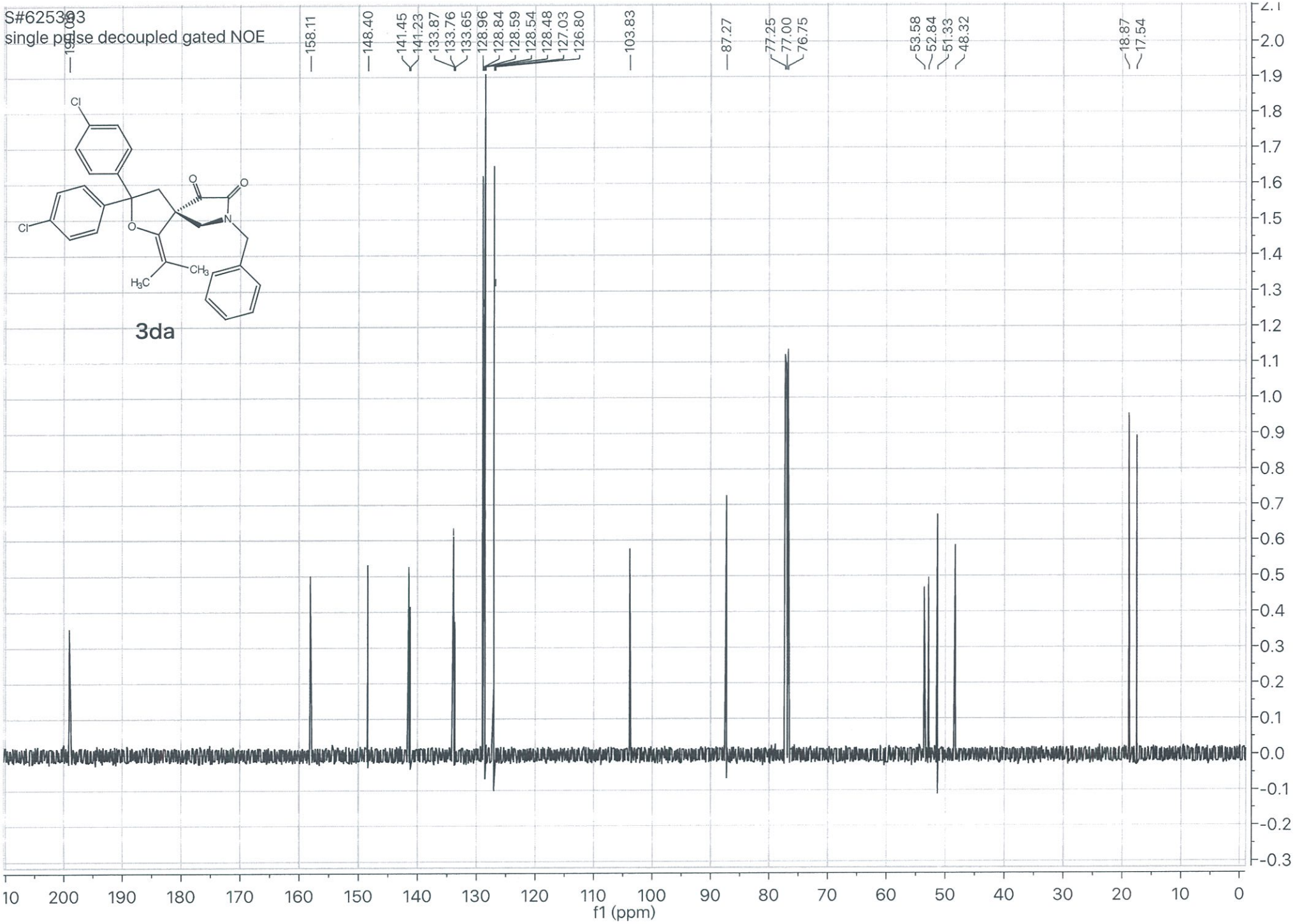
3ca




S#623521
single_pulse
7.36
7.35
7.35
7.34
7.34
7.27
7.25
7.24
7.24
7.23
7.22
7.22
7.17
7.17
7.17
7.15
7.14
7.14
7.14
4.60
4.57
4.55
4.52
3.08
3.06
2.83
2.80
1.80
1.16
0.00
Cl
Cl
O
O
O
N
H3C
CH3
3da
2.88
0.65
4.50
1.22
3.95
2.00
0.98
2.91
2.92
2.86
f1 (ppm)

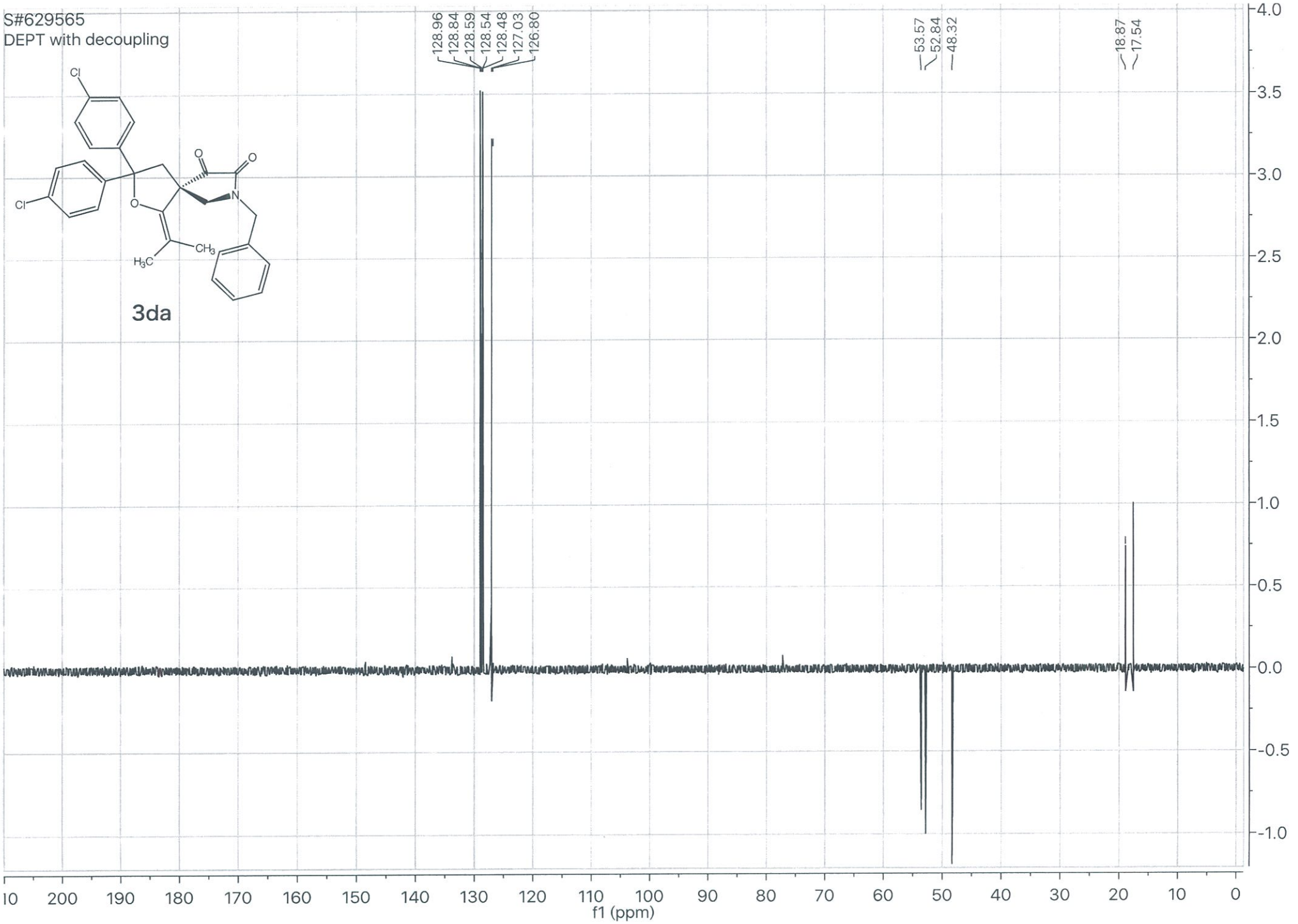
S#625393
single pulse decoupled gated NOE

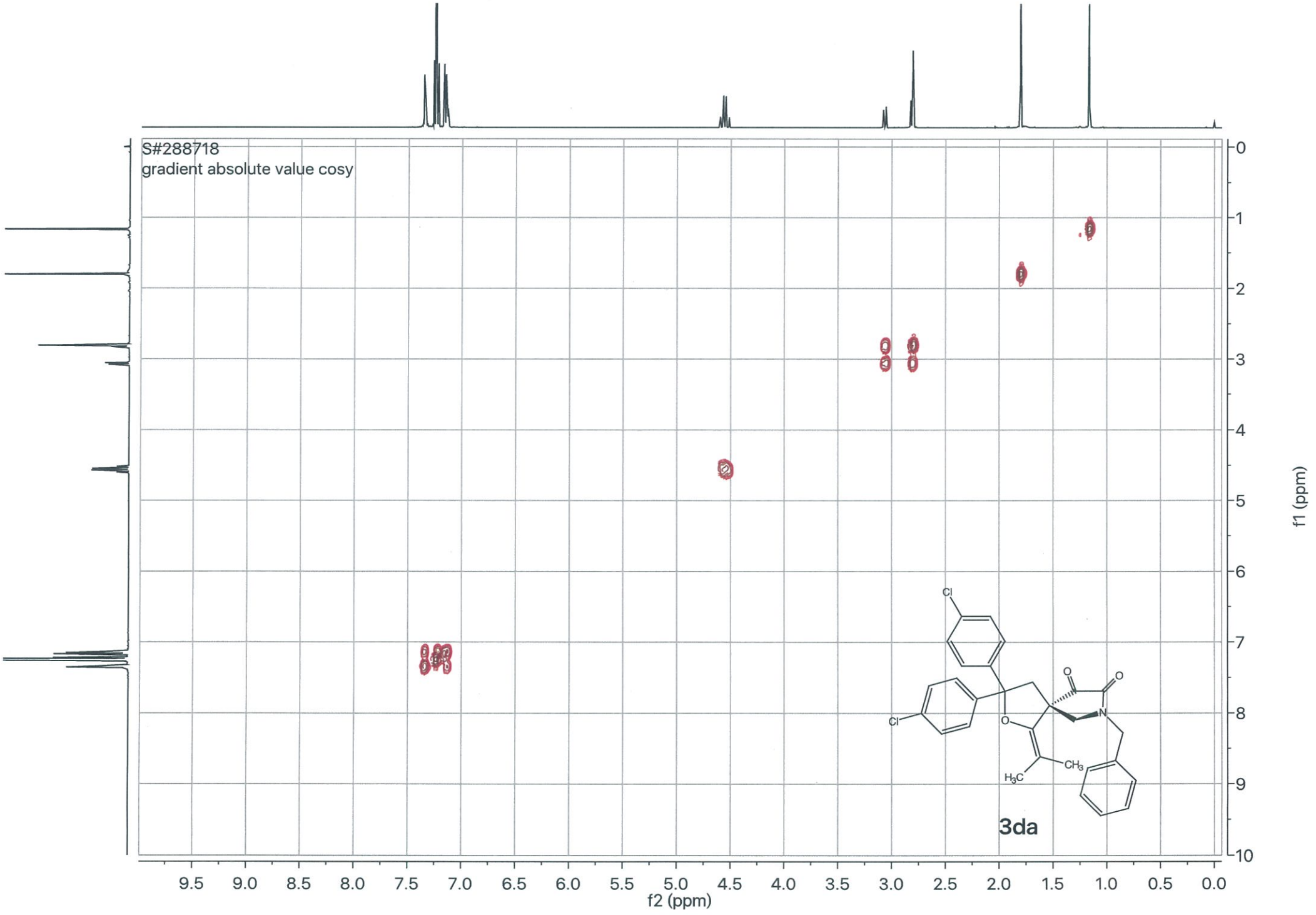
3da

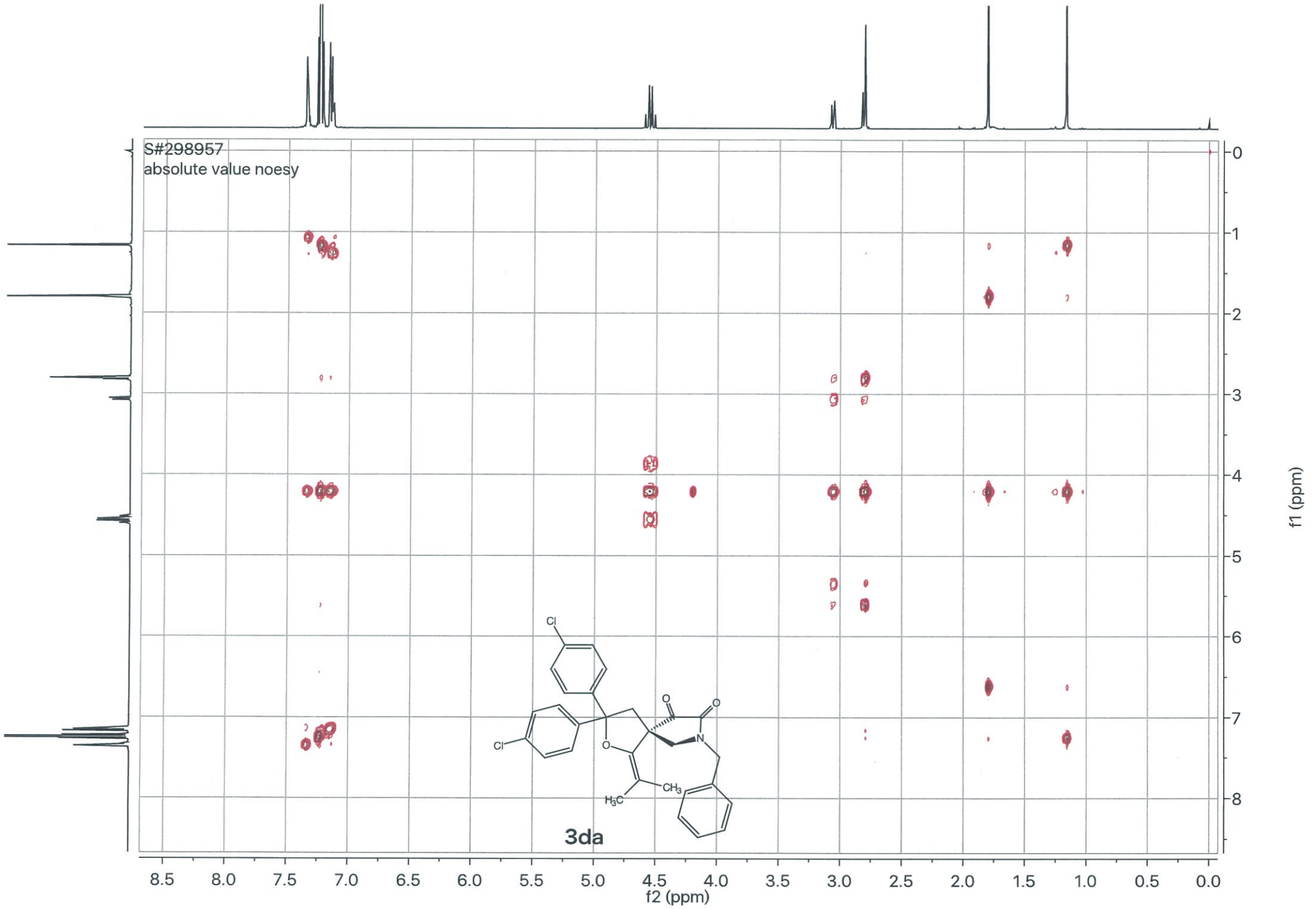


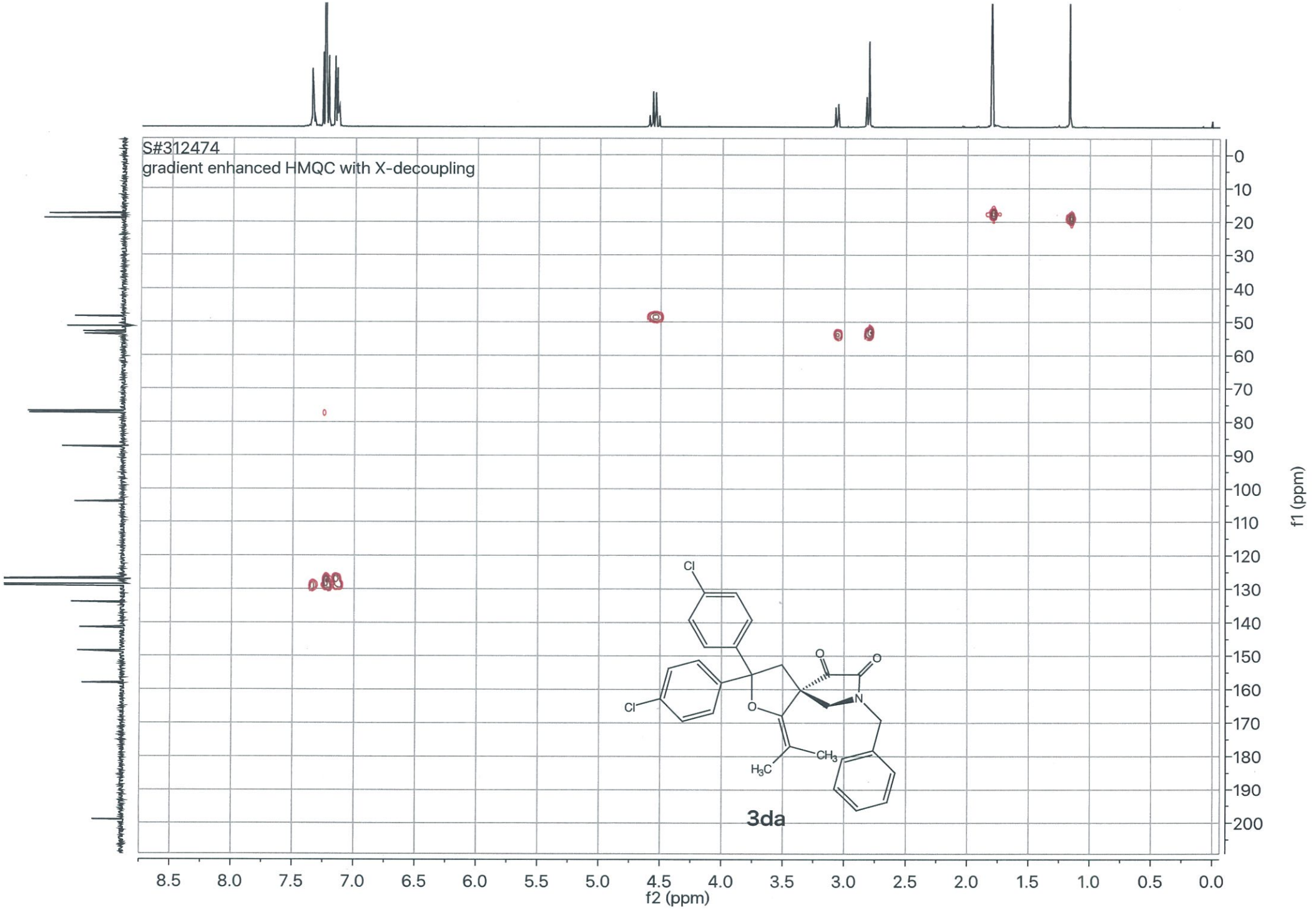
S#629565
DEPT with decoupling

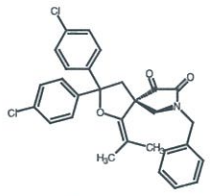
3da




S#288718
gradient absolute value cosy
f2 (ppm)
f1 (ppm)
3da


S#298957
absolute value noesy
f2 (ppm)
f1 (ppm)
3da


S#312474
gradient enhanced HMQC with X-decoupling
f2 (ppm)
f1 (ppm)
3da



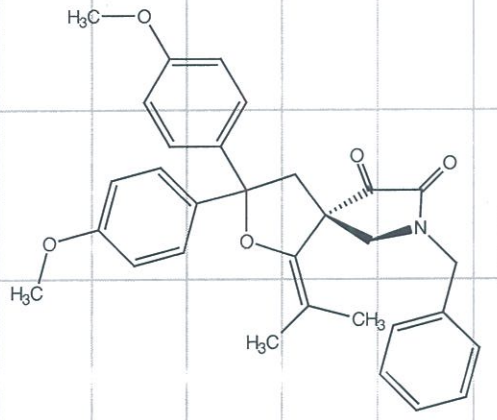
3da

S#323097
gradient enhanced HMBC

f2 (ppm)

f1 (ppm)

S#593066
single_pulse



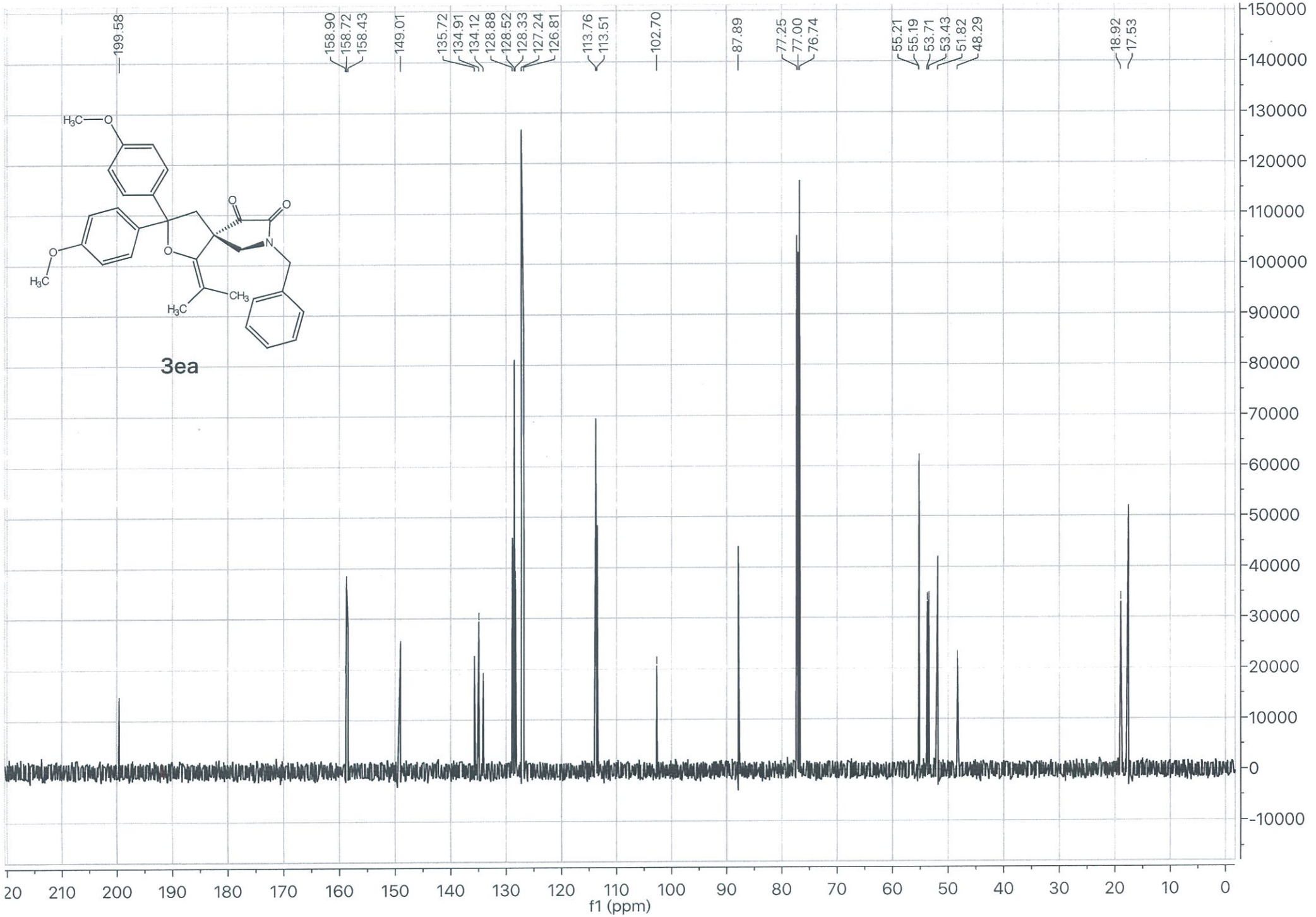
3ea

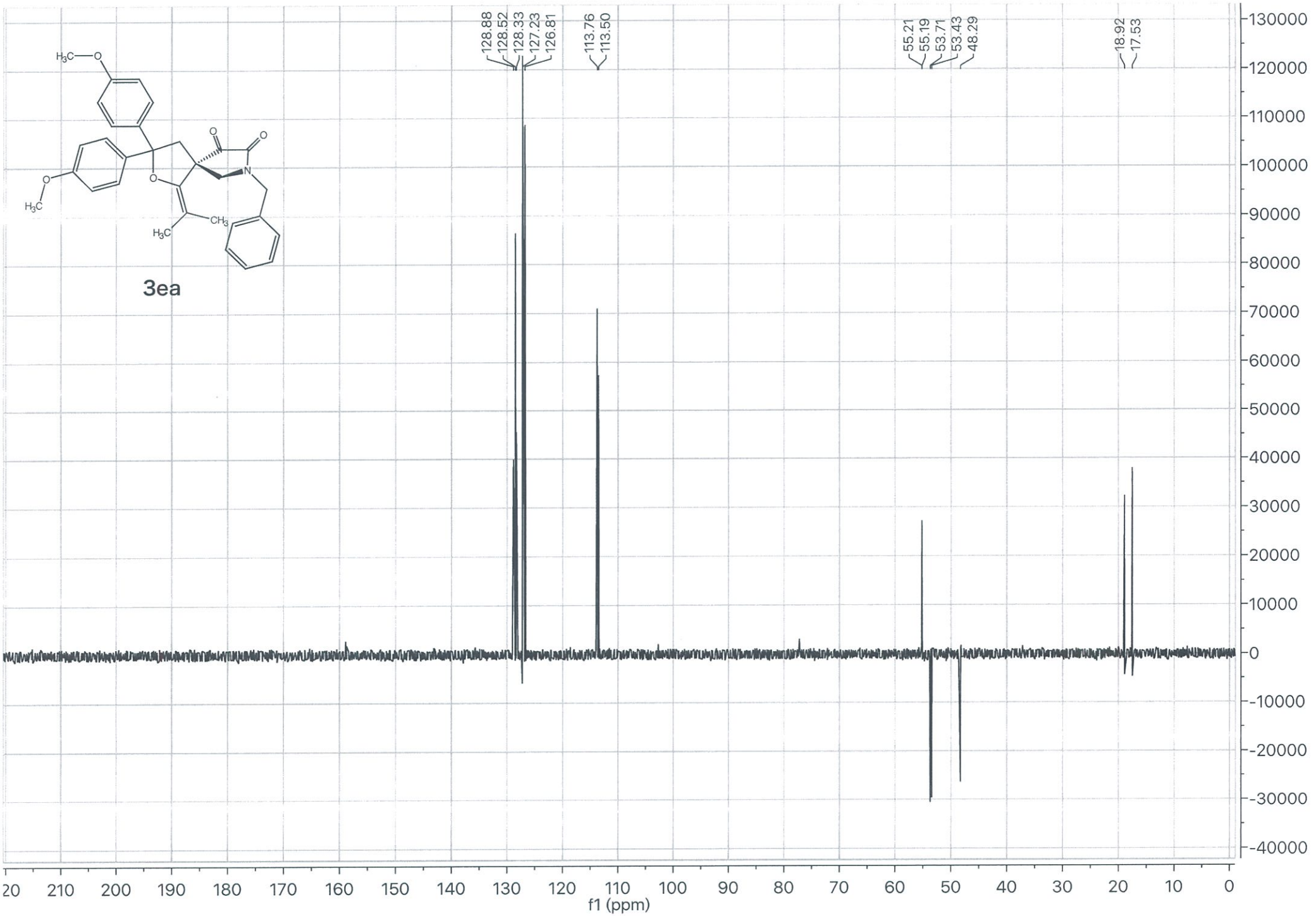
7.33 7.33 7.33 7.32 7.31 7.26 7.25 7.24 7.23 7.23 7.22 7.21 7.21 7.15 7.15 7.14 7.13 7.12 7.12 6.79 6.78 6.78 6.78 6.77

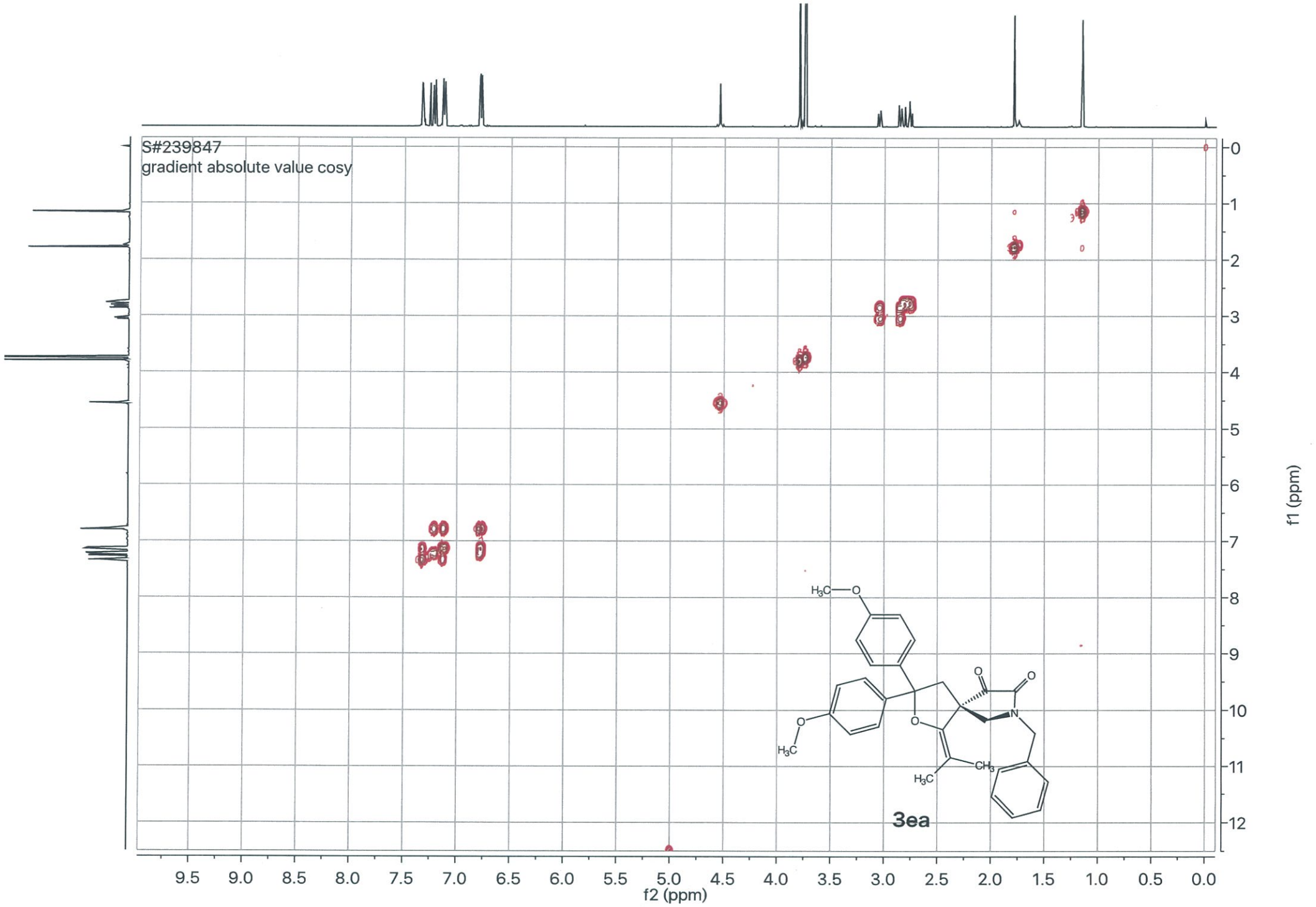
4.57 4.54 4.52 3.80 3.74 3.06 3.04 2.87 2.84 2.84 2.81 2.77 2.75 1.79 1.15 0.00

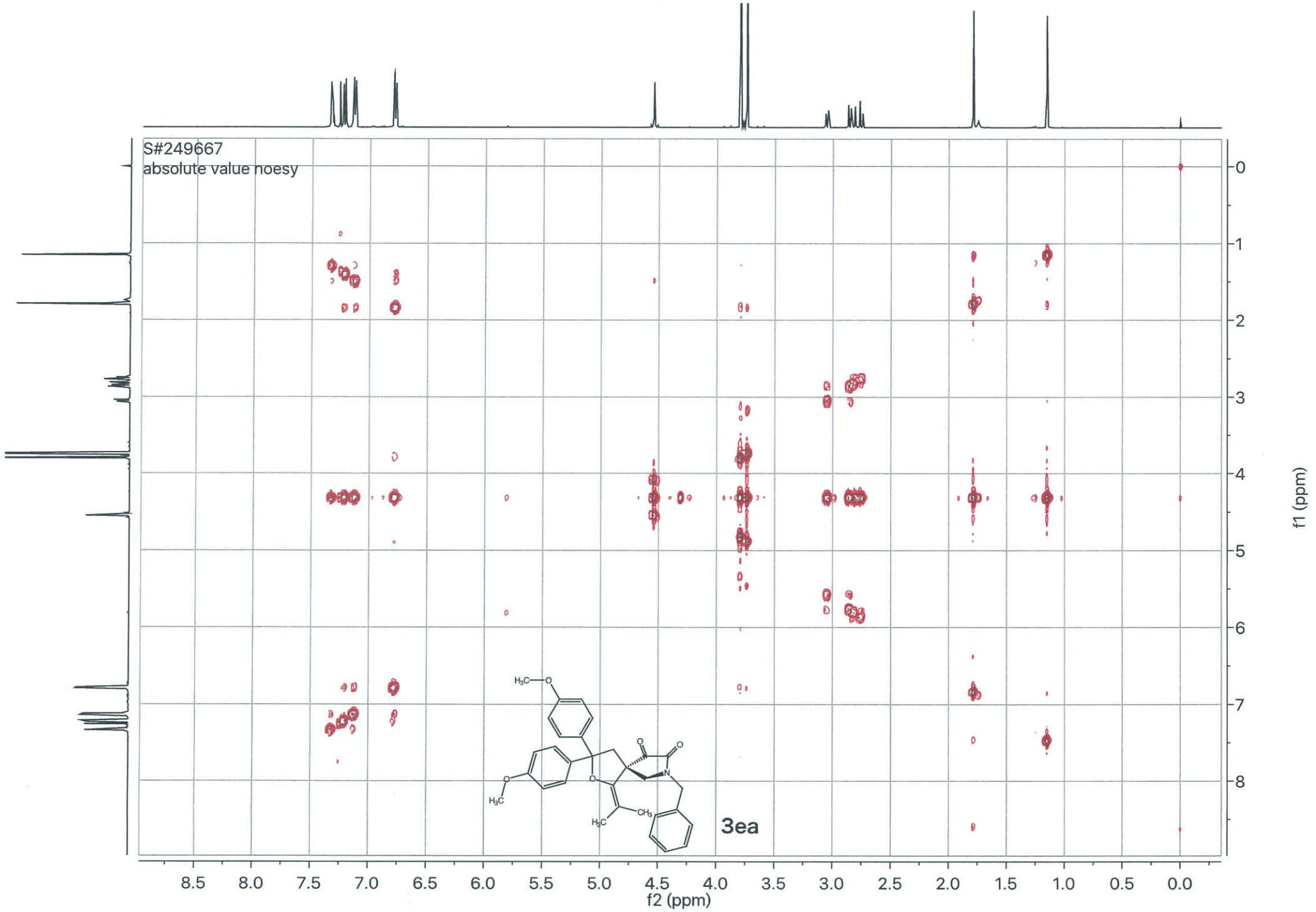
3.11 0.52 2.11 4.06 4.10 2.04 2.95 0.21 2.98 1.00 2.03 0.99 3.01 3.00

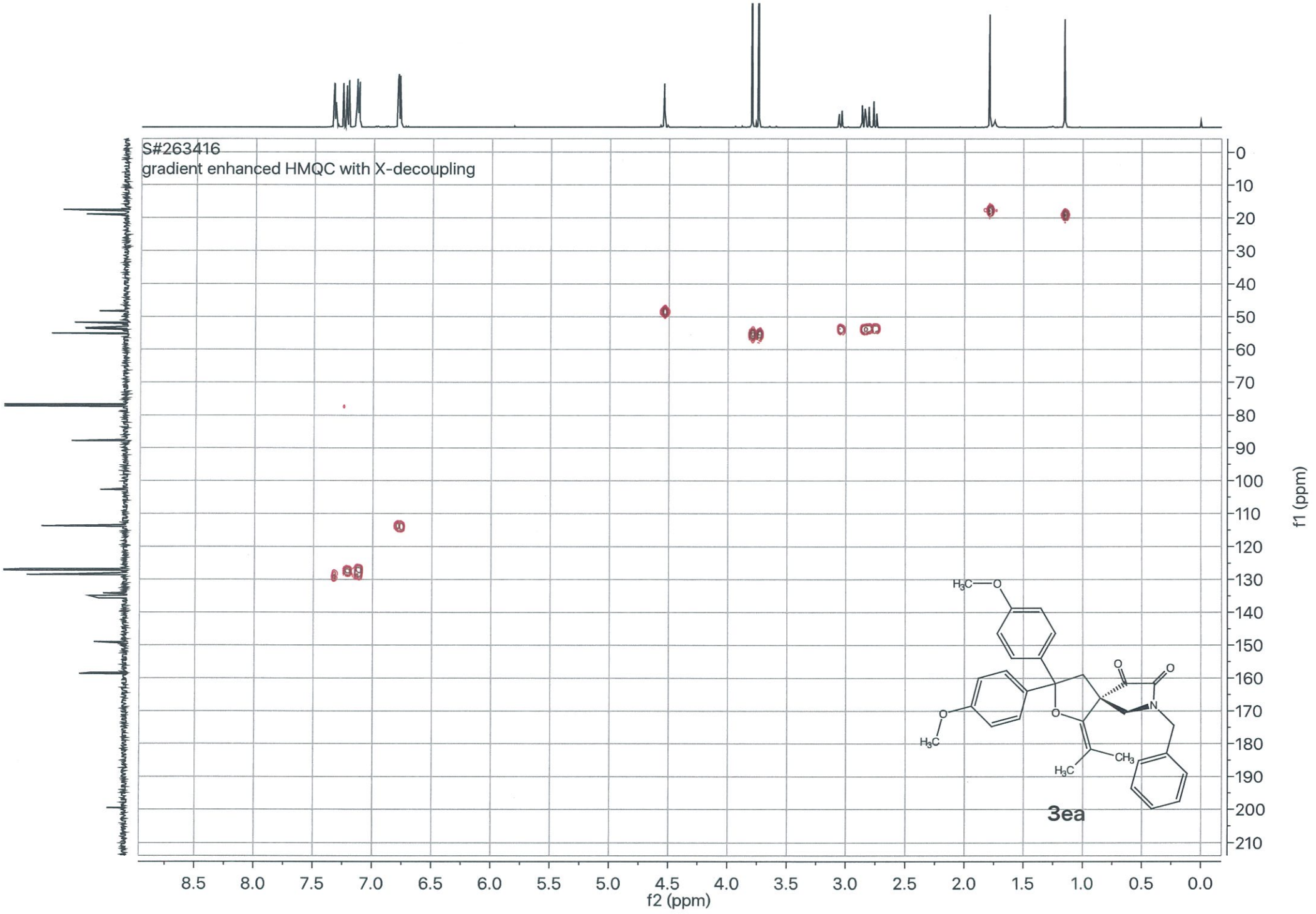
f1 (ppm)

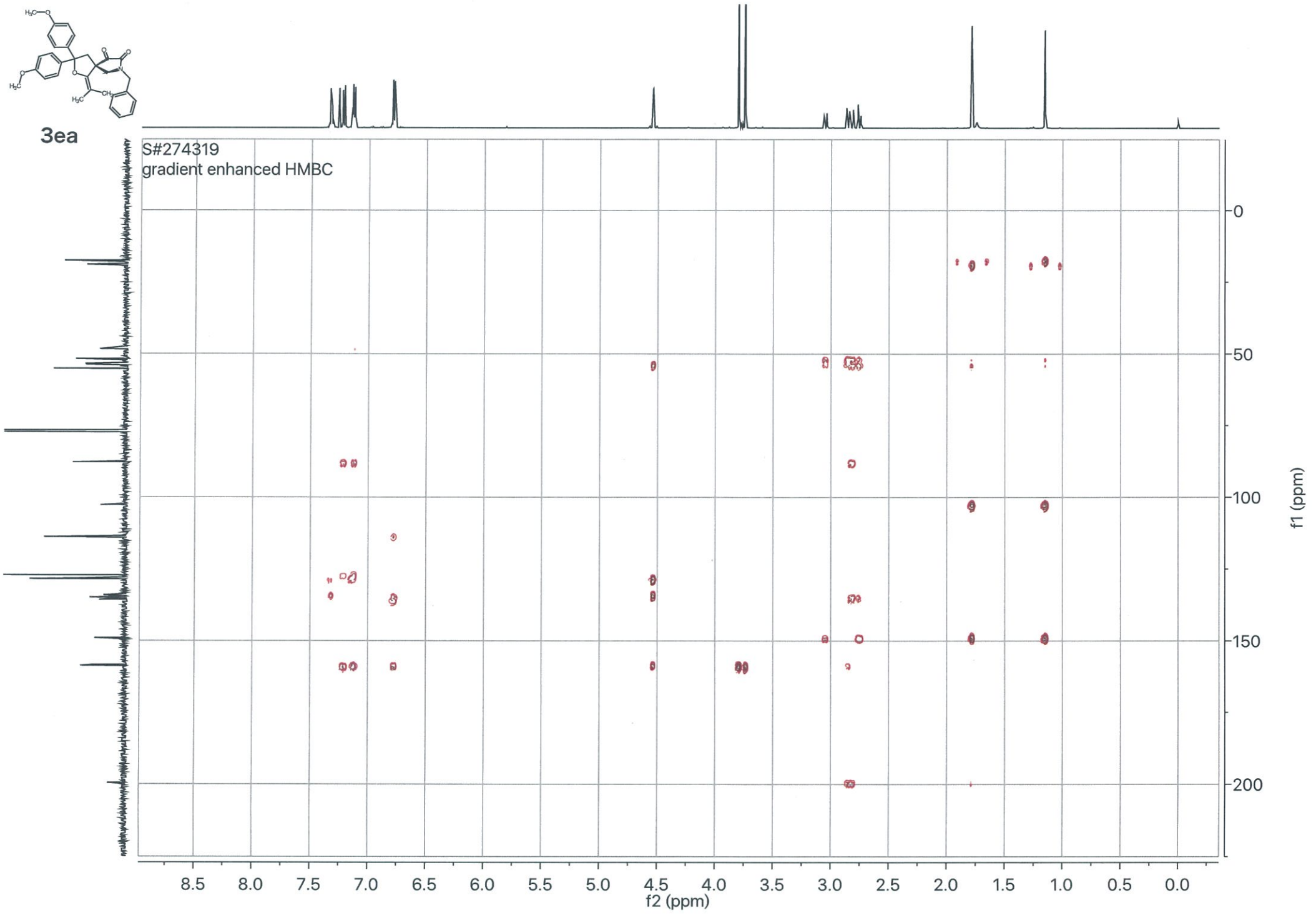

199.58
158.90
158.72
158.43
149.01
135.72
134.91
134.12
128.88
128.52
128.33
127.24
126.81
113.76
113.51
102.70
87.89
77.25
77.00
76.74
55.21
55.19
53.71
53.43
51.82
48.29
18.92
17.53
H3C—O
O
O
O
N
O
H3C
CH3
H3C
3ea
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


128.88
128.52
128.33
127.23
126.81
113.76
113.50
55.21
55.19
53.71
53.43
48.29
18.92
17.53
3ea
f1 (ppm)

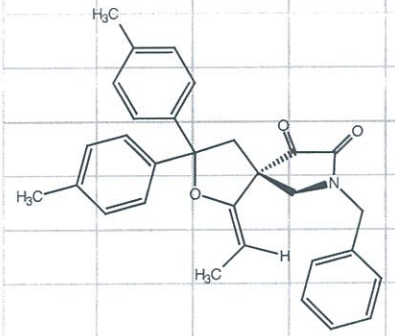

S#239847
gradient absolute value cosy
f2 (ppm)
f1 (ppm)
3ea


S#249667
absolute value noesy
f2 (ppm)
f1 (ppm)
3ea


S#263416
gradient enhanced HMQC with X-decoupling
f2 (ppm)
f1 (ppm)
3ea


3ea
S#274319
gradient enhanced HMBC
f2 (ppm)
f1 (ppm)

S#406225
single_pulse

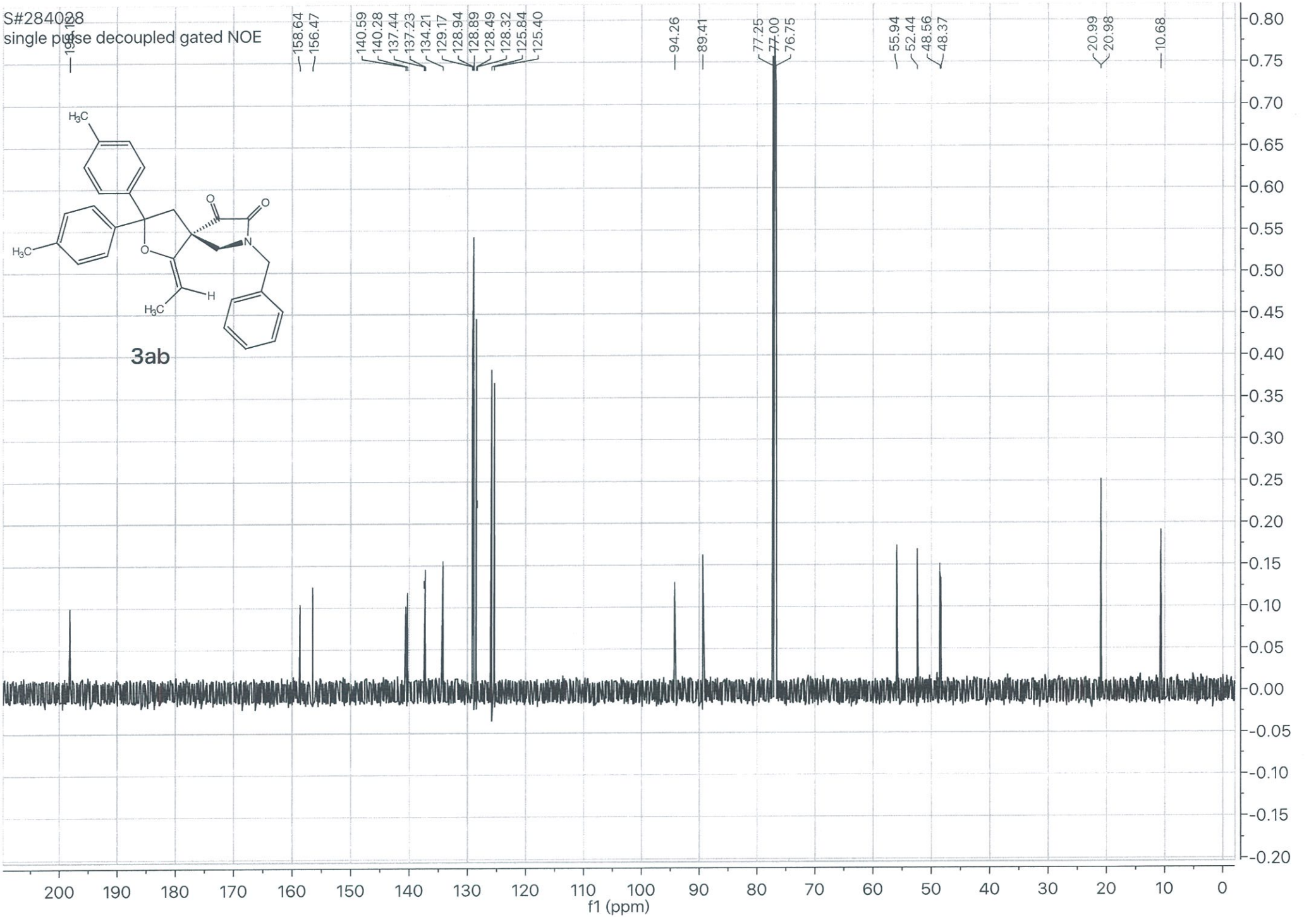


3ab

f1 (ppm)

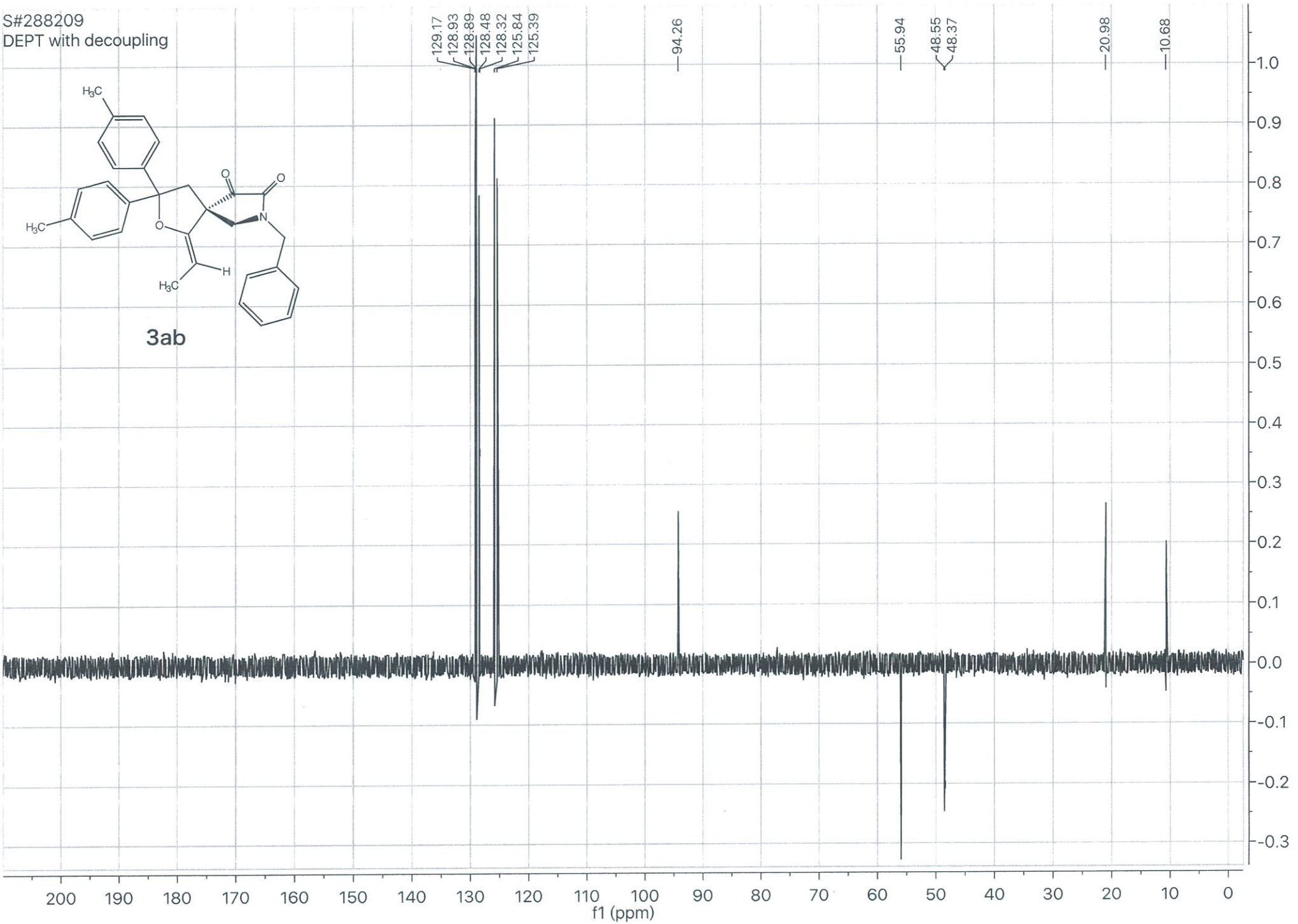
S#284028
single pulse decoupled gated NOE

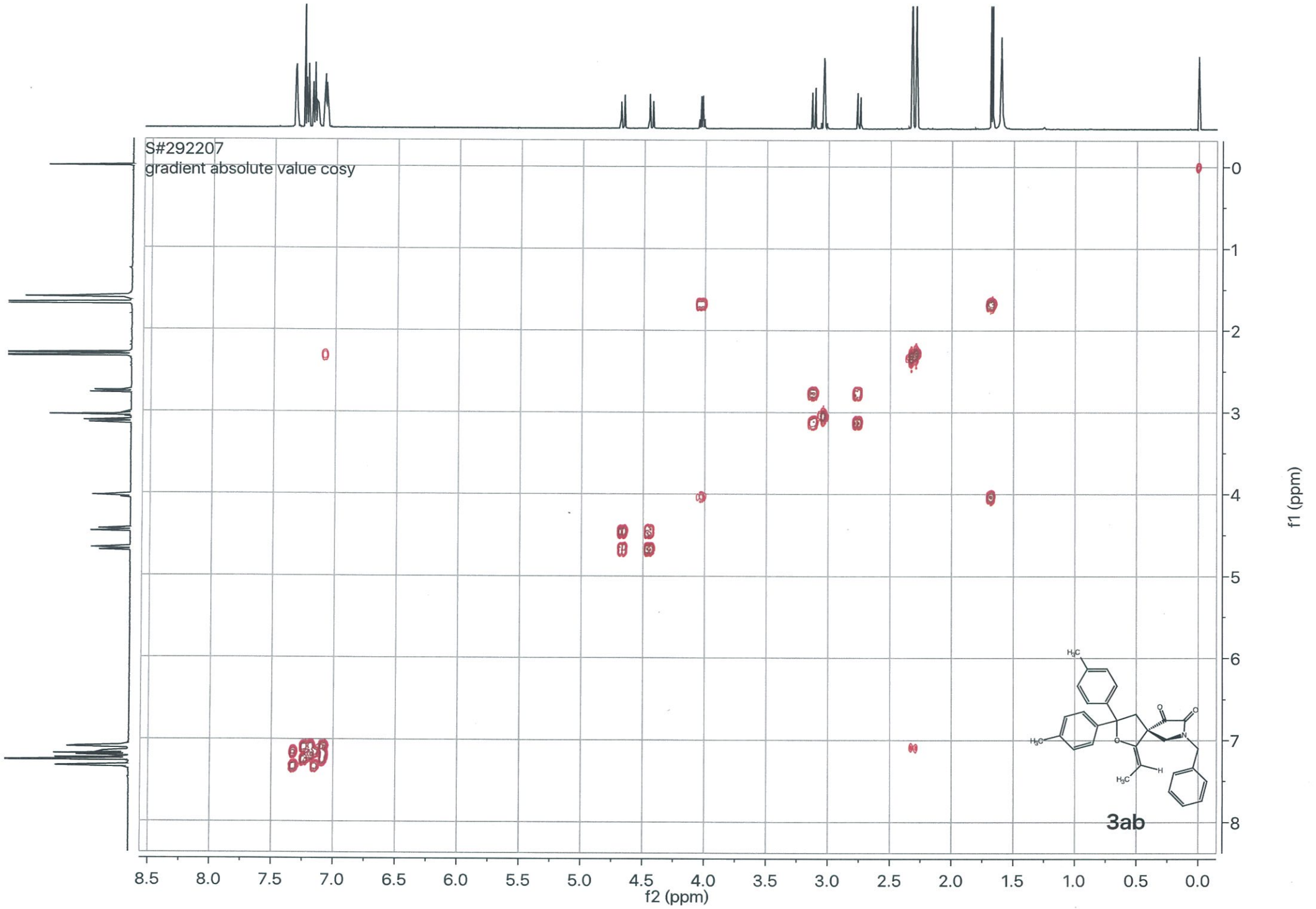
3ab

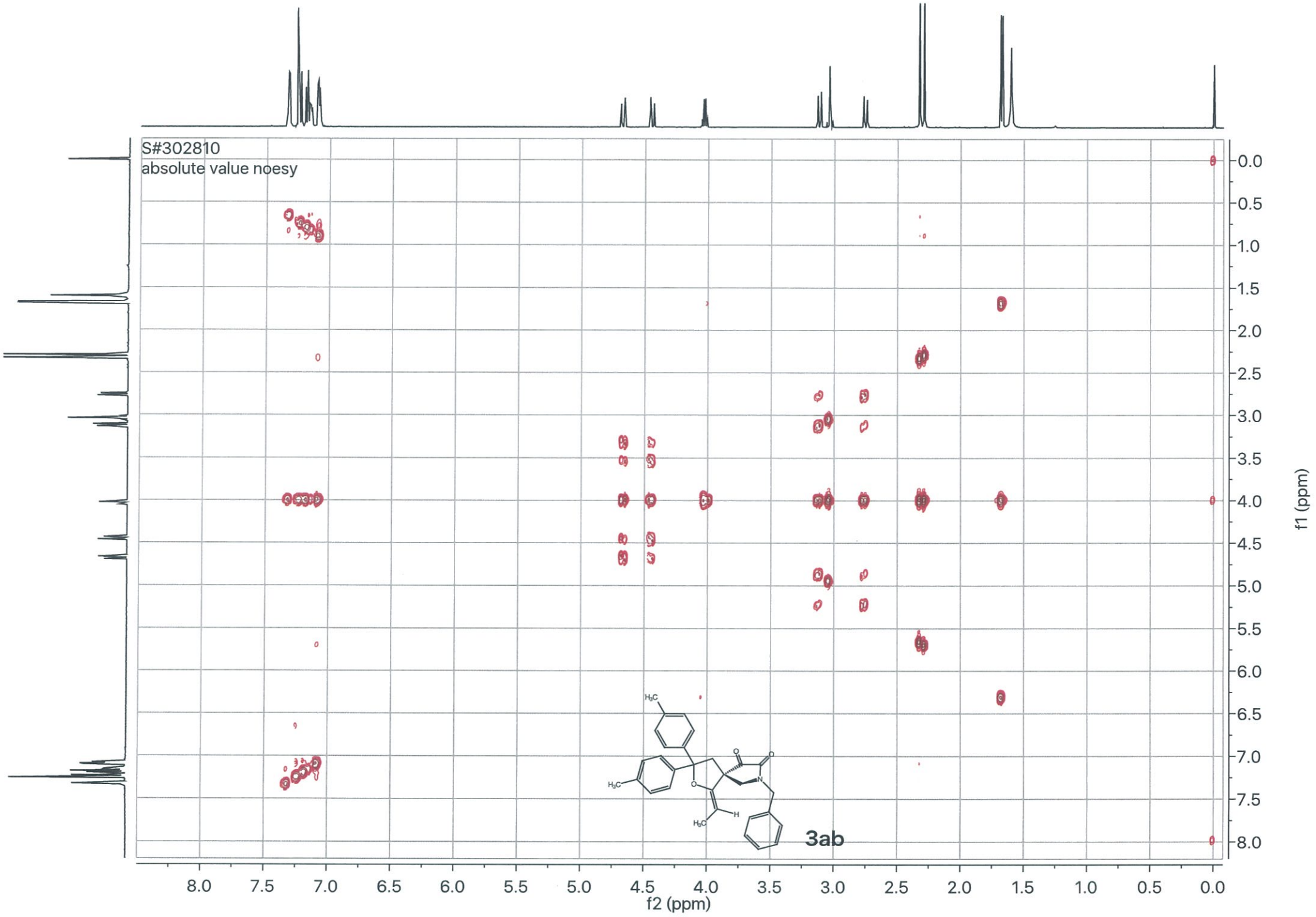


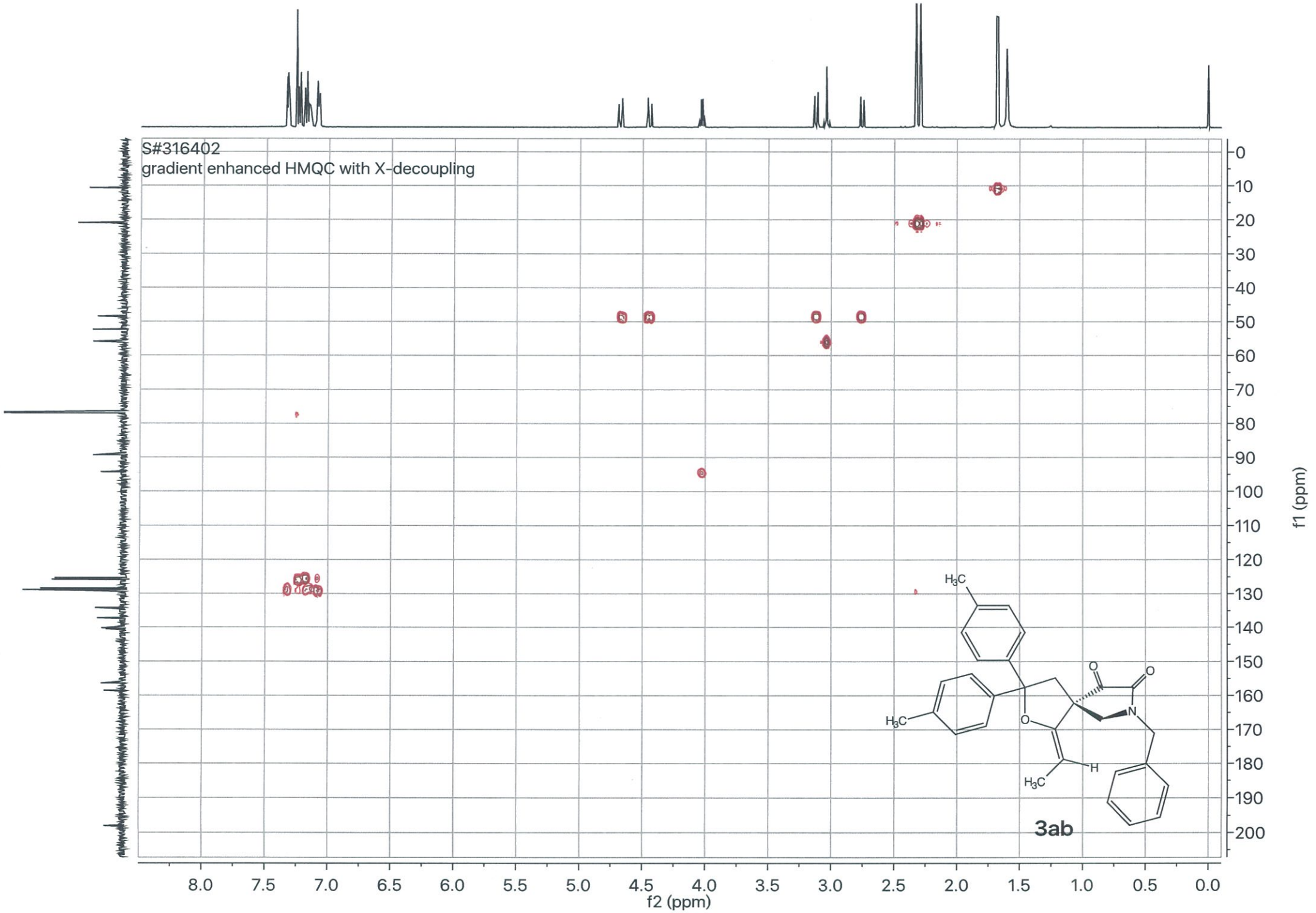
S#288209
DEPT with decoupling

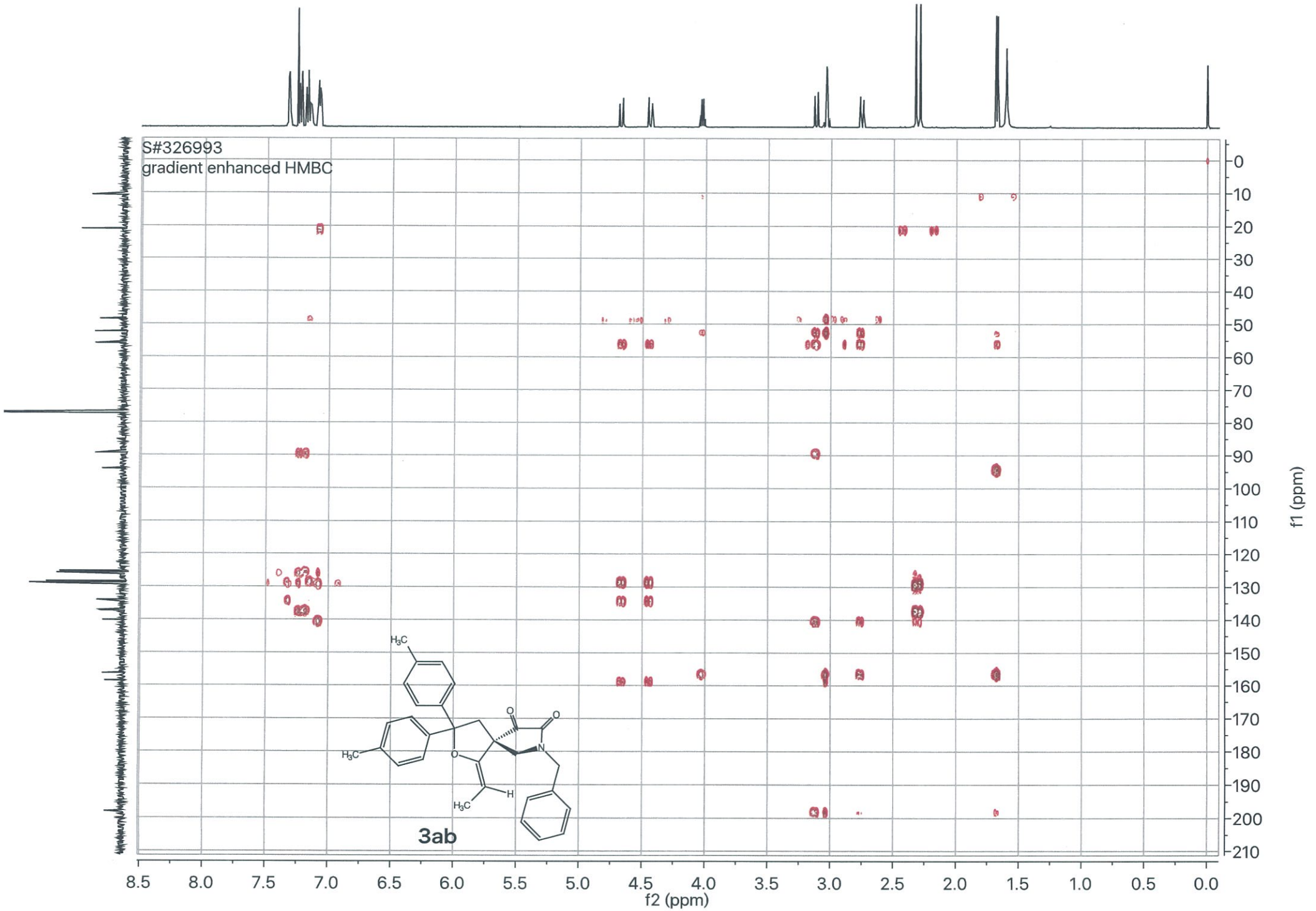
3ab



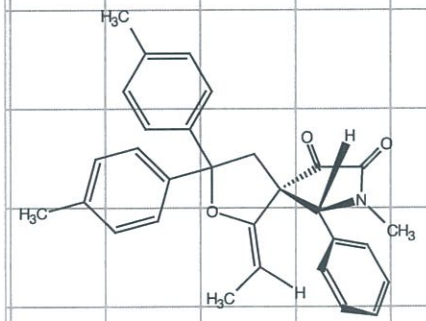

S#292207
gradient absolute value cosy
f2 (ppm)
f1 (ppm)
3ab


S#302810
absolute value noesy
f2 (ppm)
f1 (ppm)
3ab


S#316402
gradient enhanced HMQC with X-decoupling
f2 (ppm)
f1 (ppm)
3ab


S#326993
gradient enhanced HMBC
3ab
f2 (ppm)
f1 (ppm)

S#339423
single_pulse

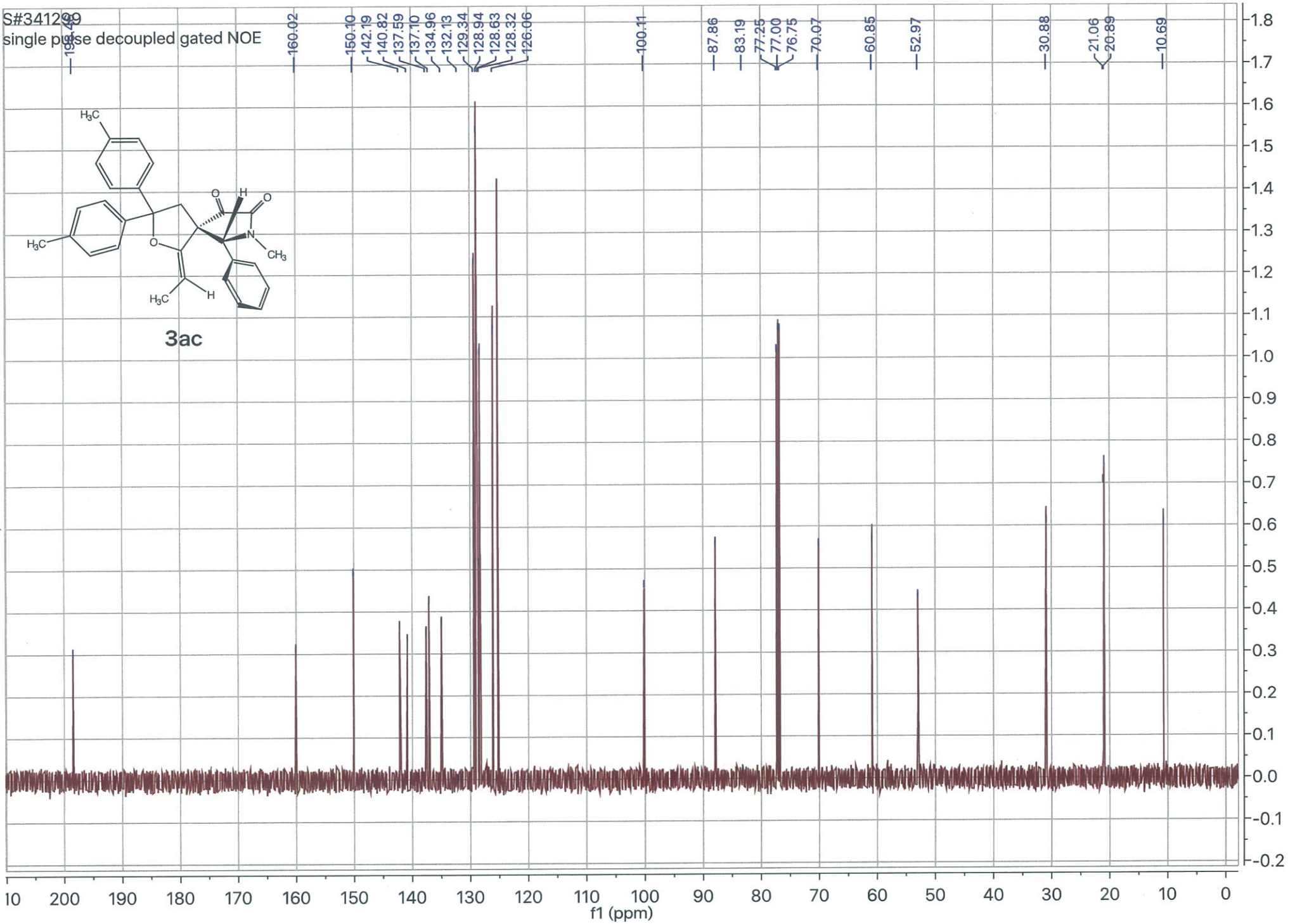


3ac

f1 (ppm)

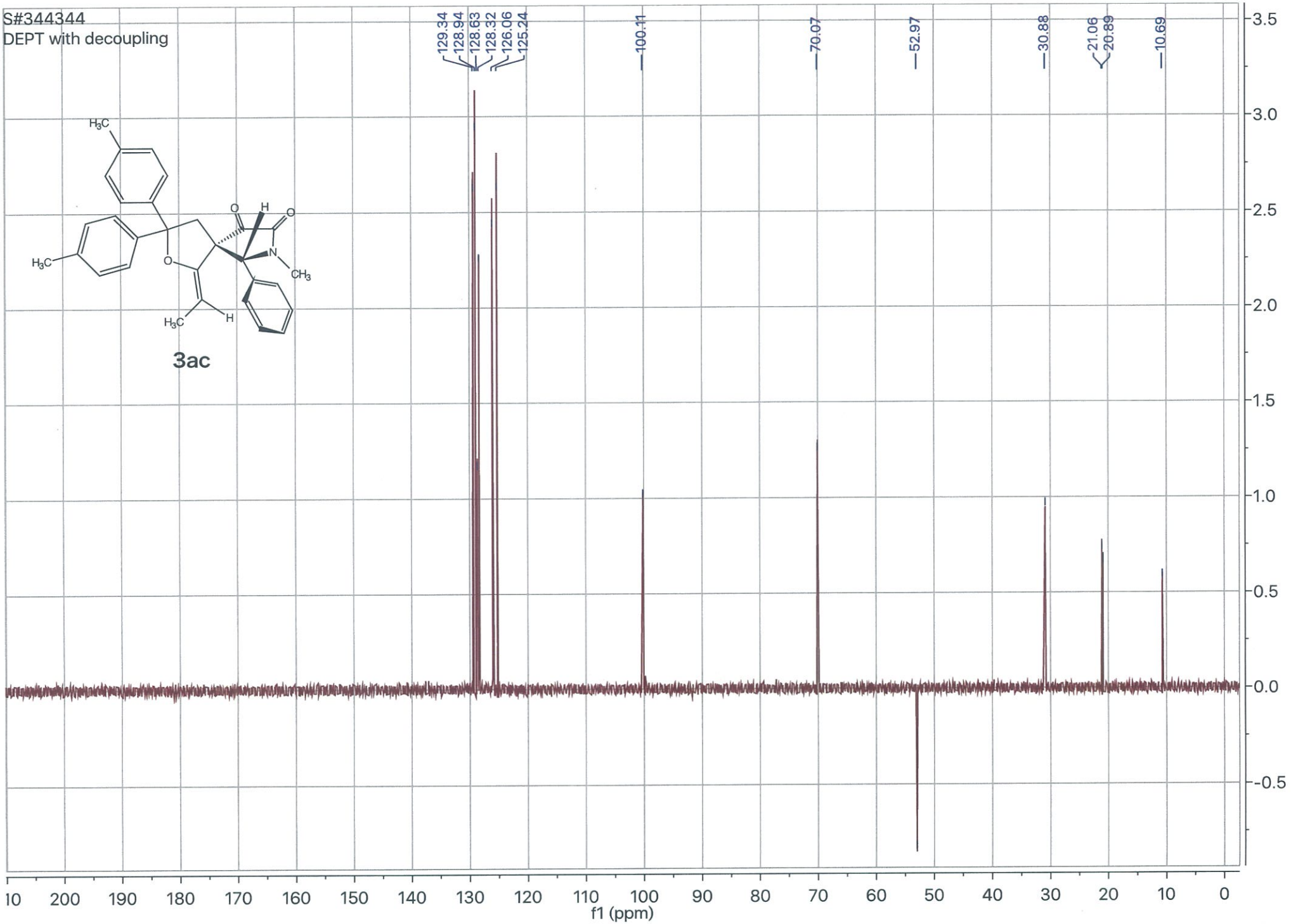
S#341299
single pulse decoupled gated NOE

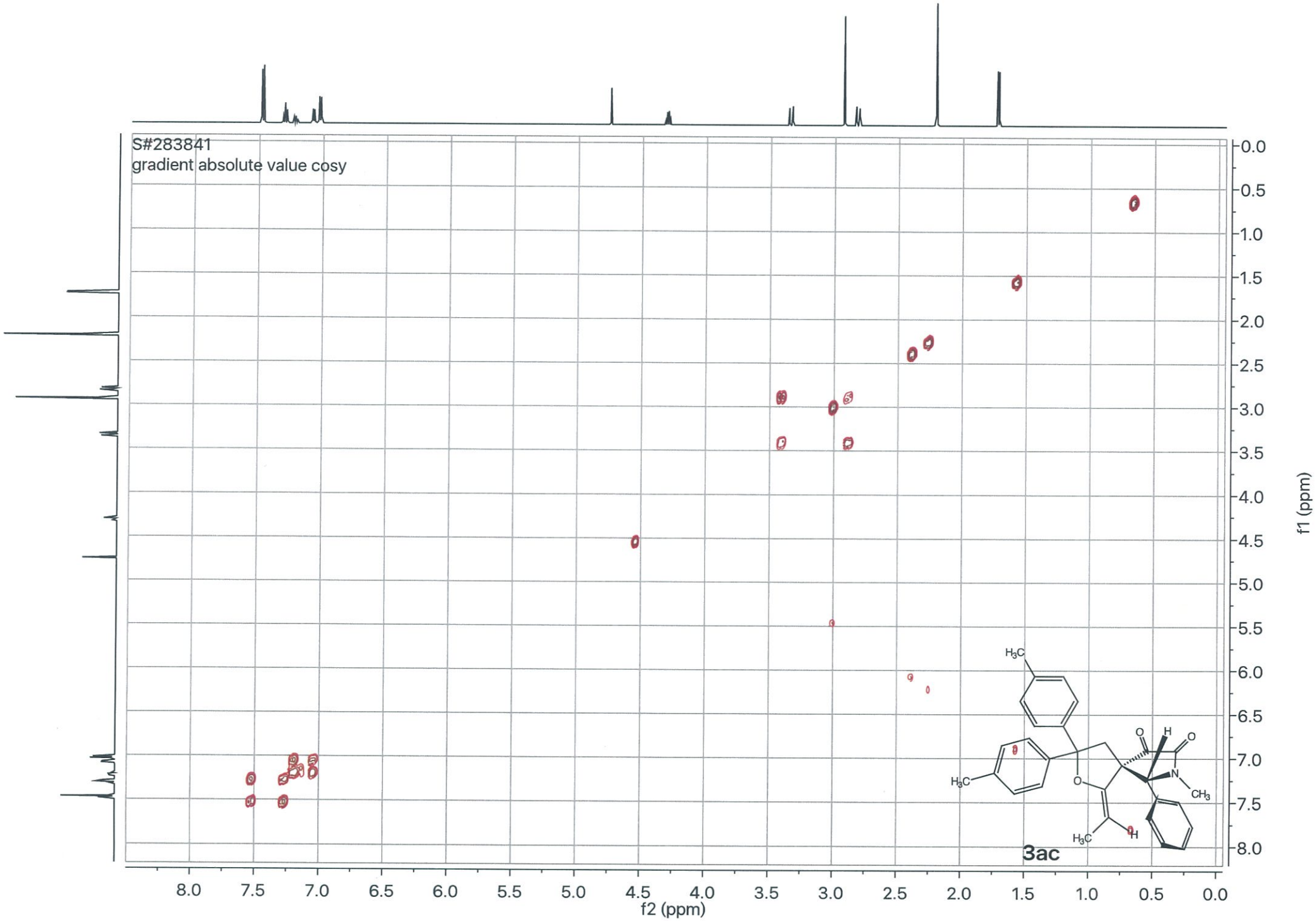
3ac

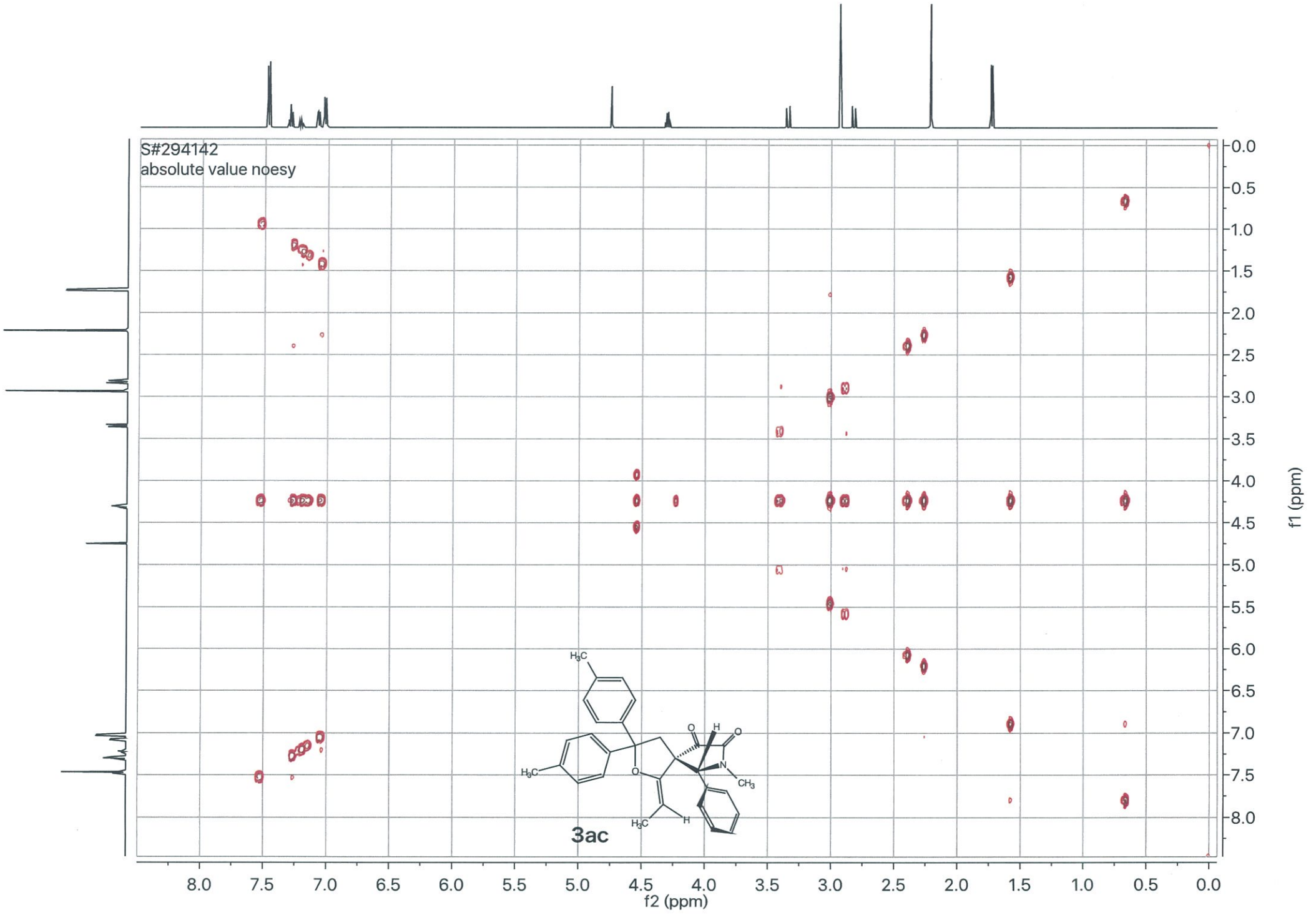


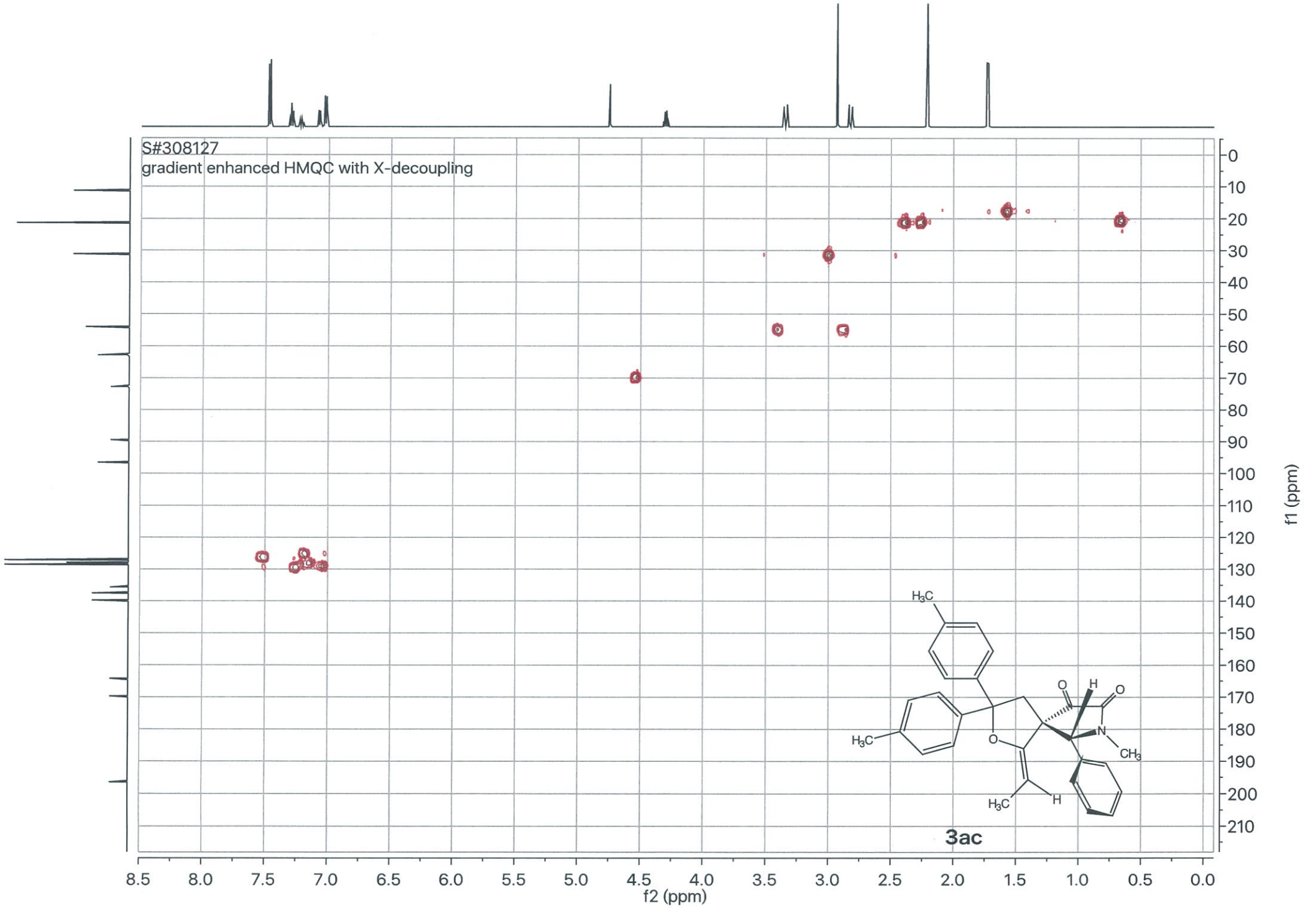
S#344344
DEPT with decoupling

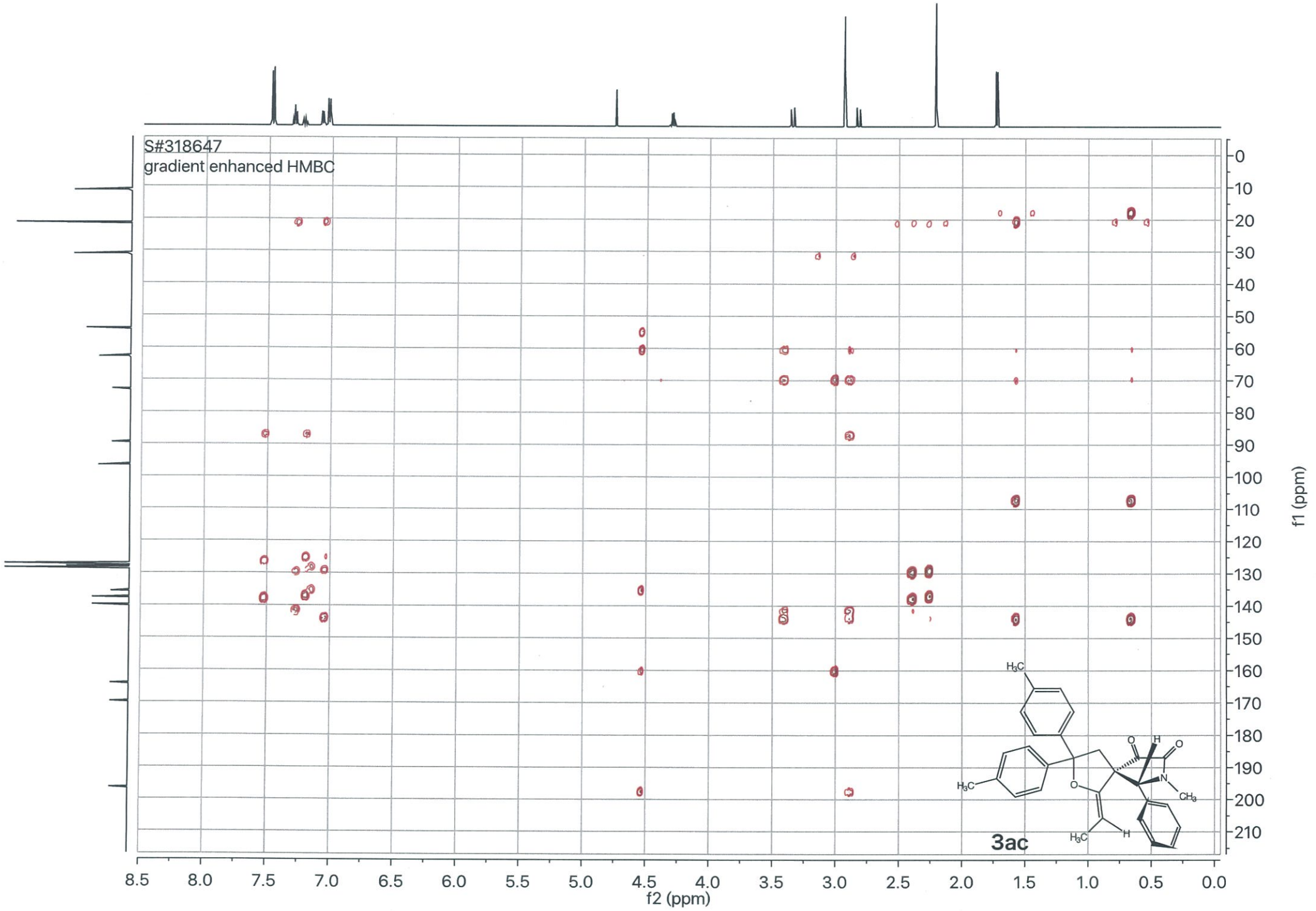
3ac



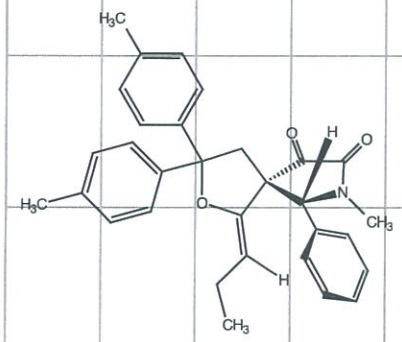

S#283841
gradient absolute value cosy
f2 (ppm)
f1 (ppm)
3ac


S#294142
absolute value noesy
f2 (ppm)
f1 (ppm)
3ac


S#308127
gradient enhanced HMQC with X-decoupling
f2 (ppm)
f1 (ppm)
3ac


S#318647
gradient enhanced HMBC
f2 (ppm)
f1 (ppm)
3ac

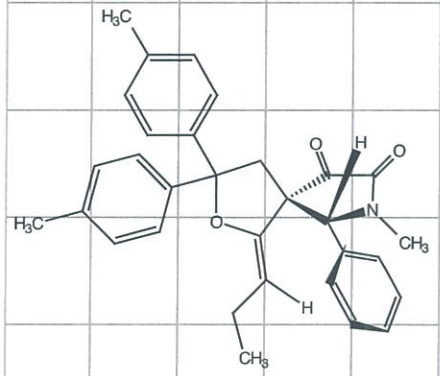
S#741238
single_pulse



3ad

f1 (ppm)

S#769685
single pulse decoupled gated NOE

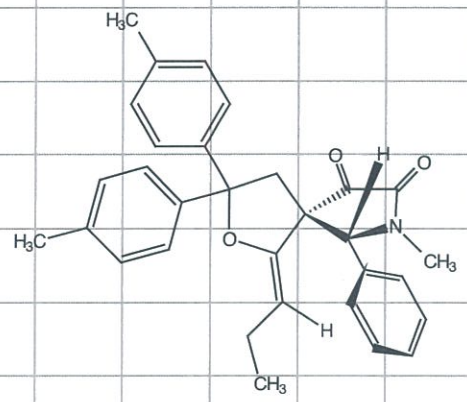


3ad

198.50
159.93
149.08
142.20
140.78
137.53
136.97
134.89
129.27
128.85
128.53
128.28
126.02
125.14
107.52
87.89
77.25
77.00
76.74
70.08
60.59
52.82
30.81
20.98
20.81
18.65
13.70

f1 (ppm)

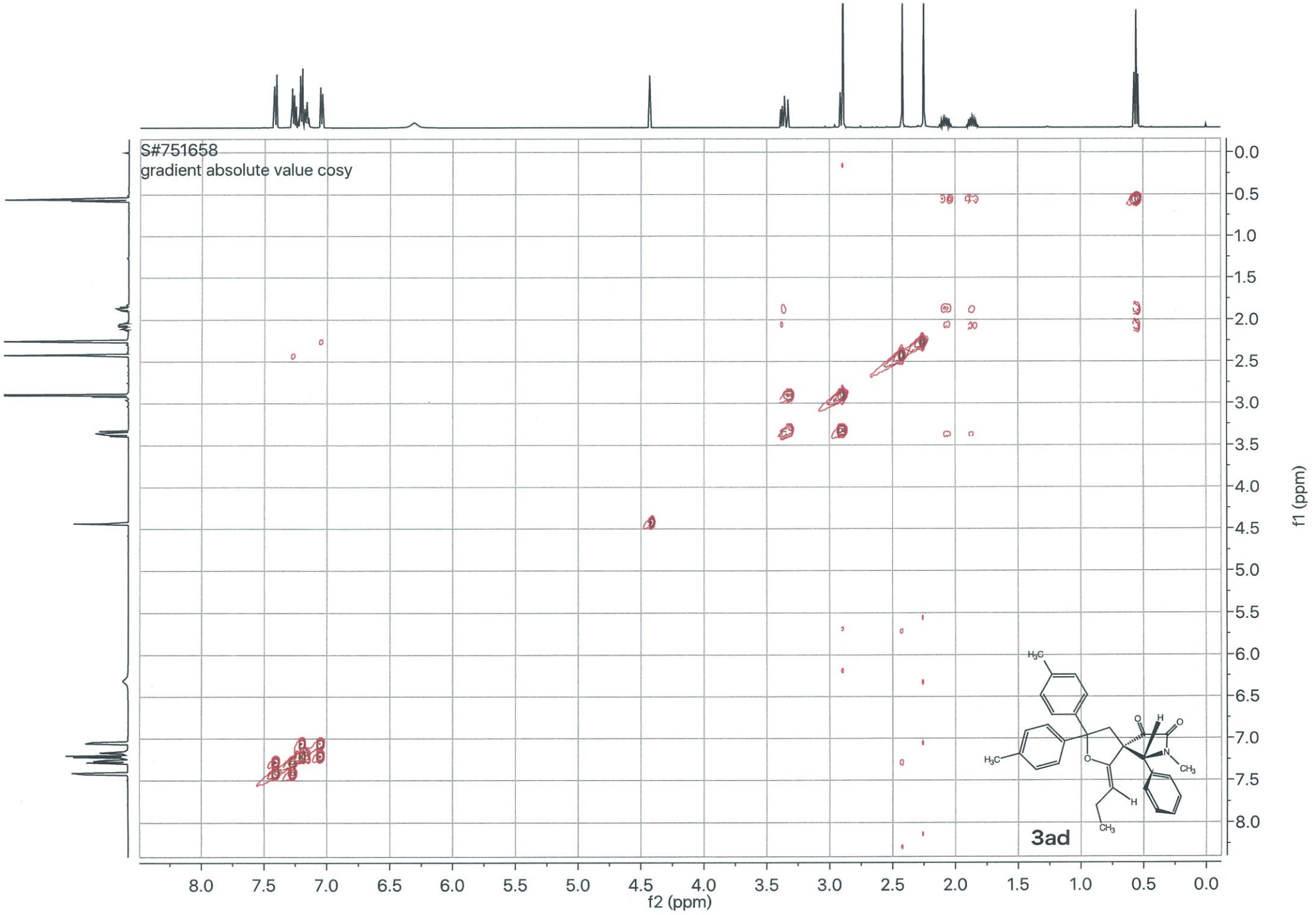
S#773744
DEPT with decoupling

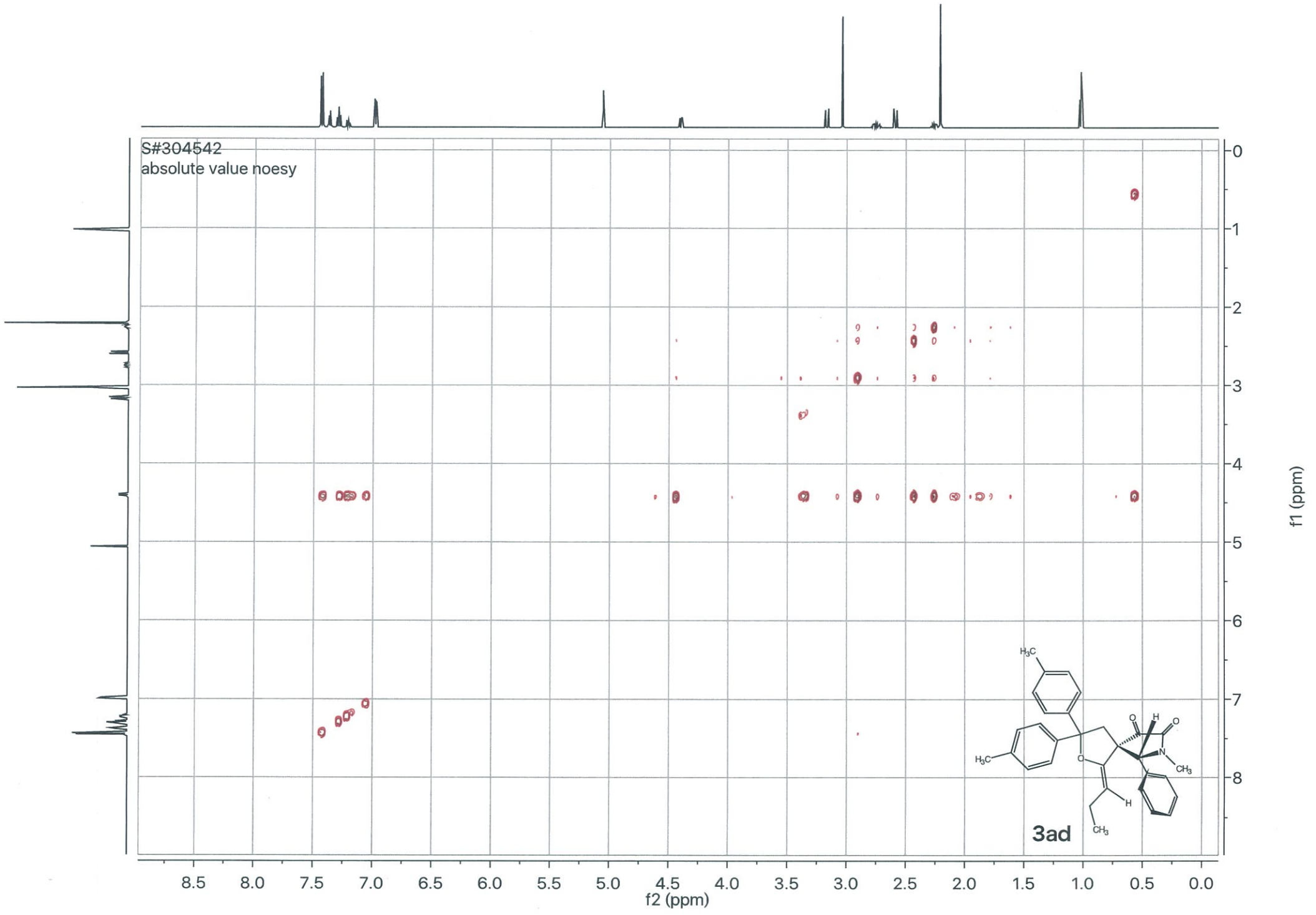


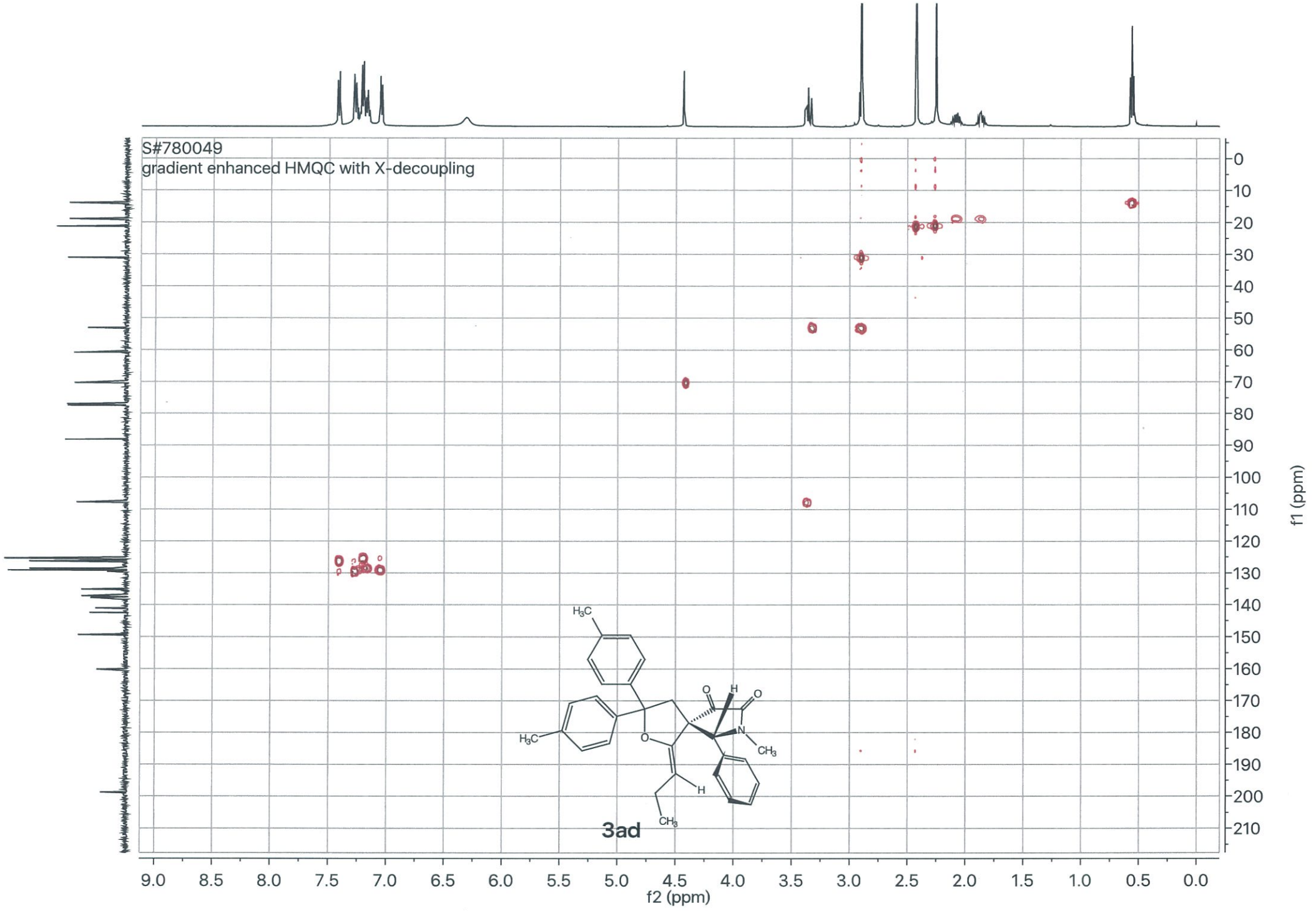
3ad

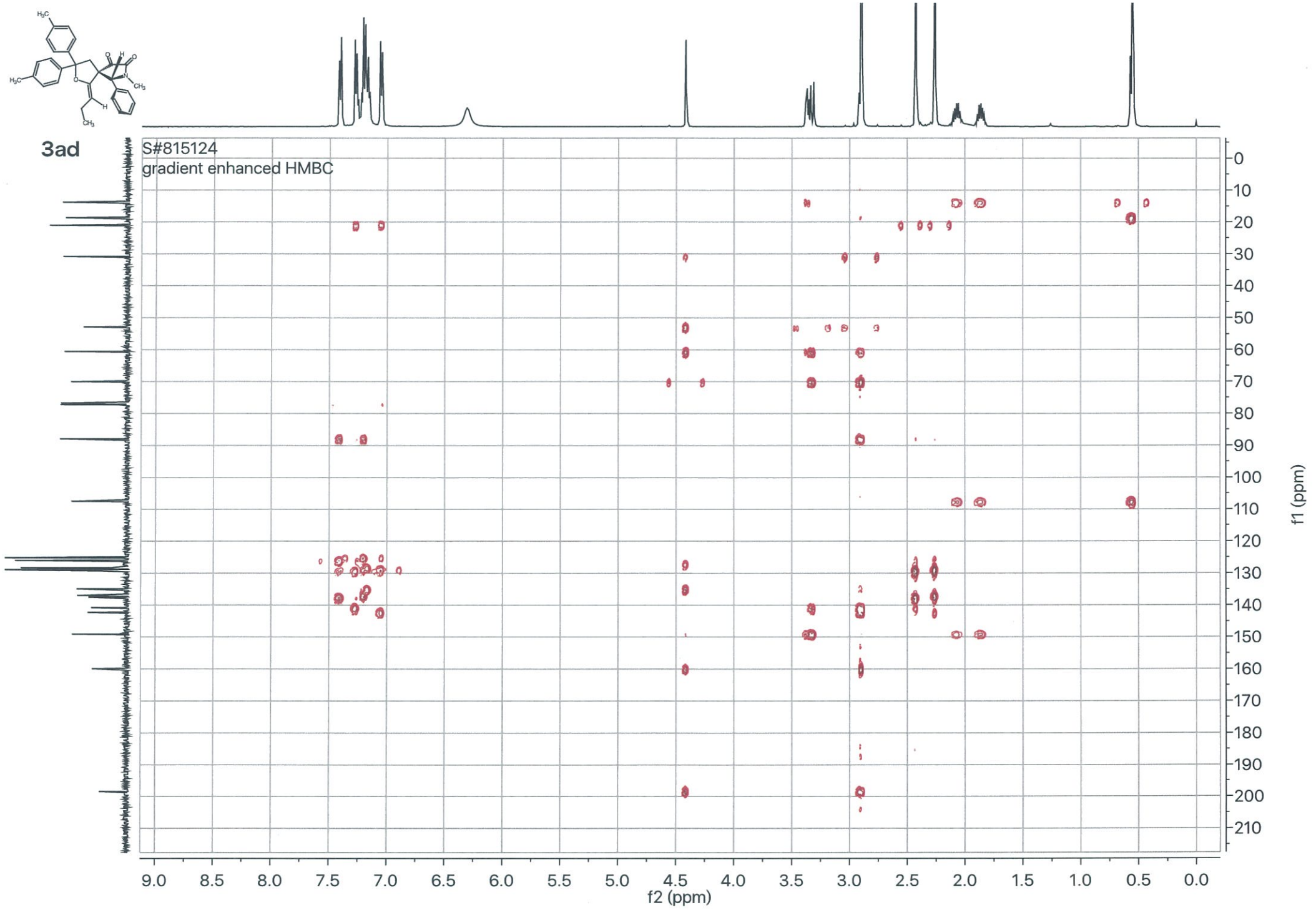
129.27
128.85
128.54
128.29
126.02
125.14
107.52
70.08
52.82
30.82
20.98
20.81
18.65
13.70

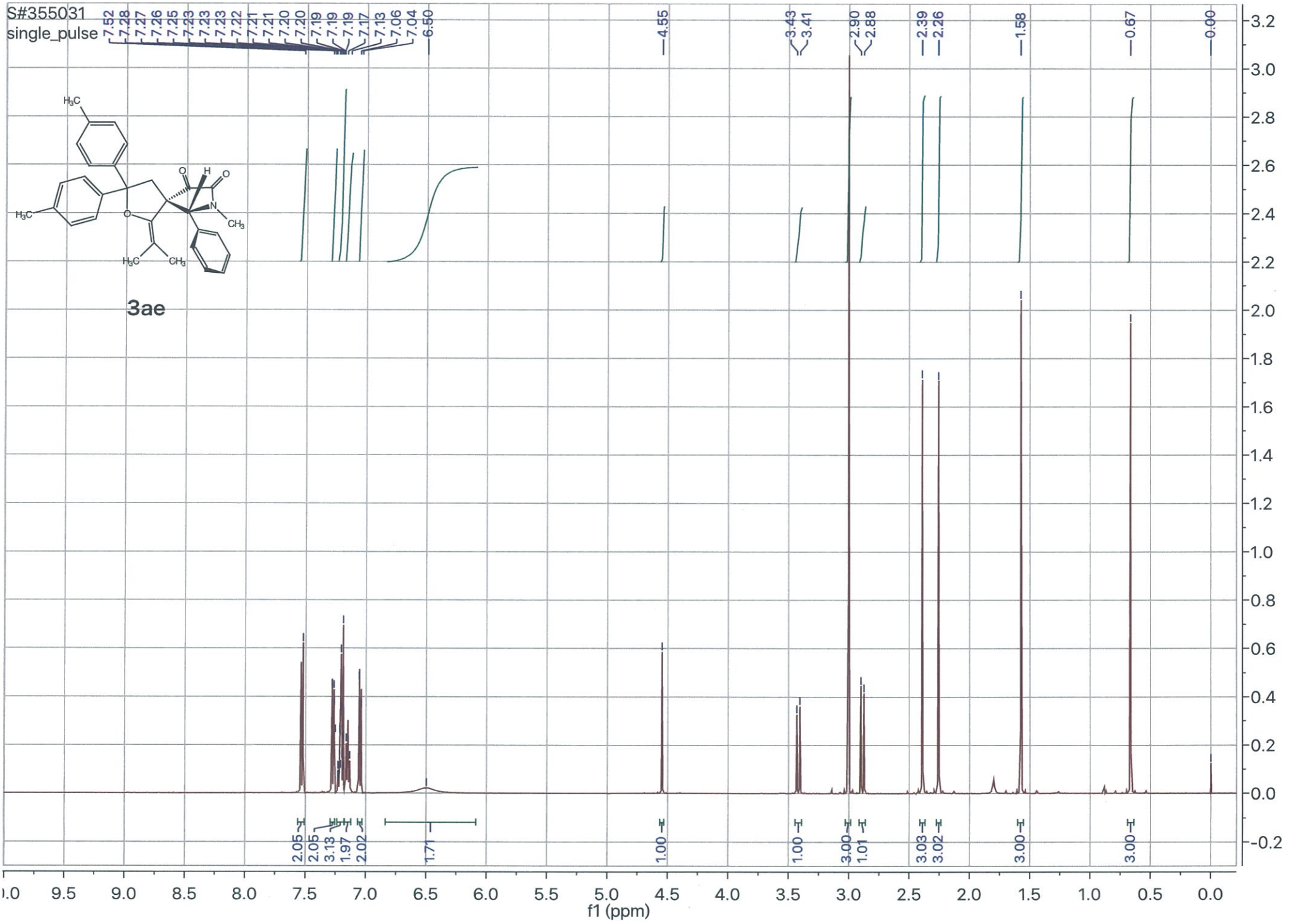
f1 (ppm)

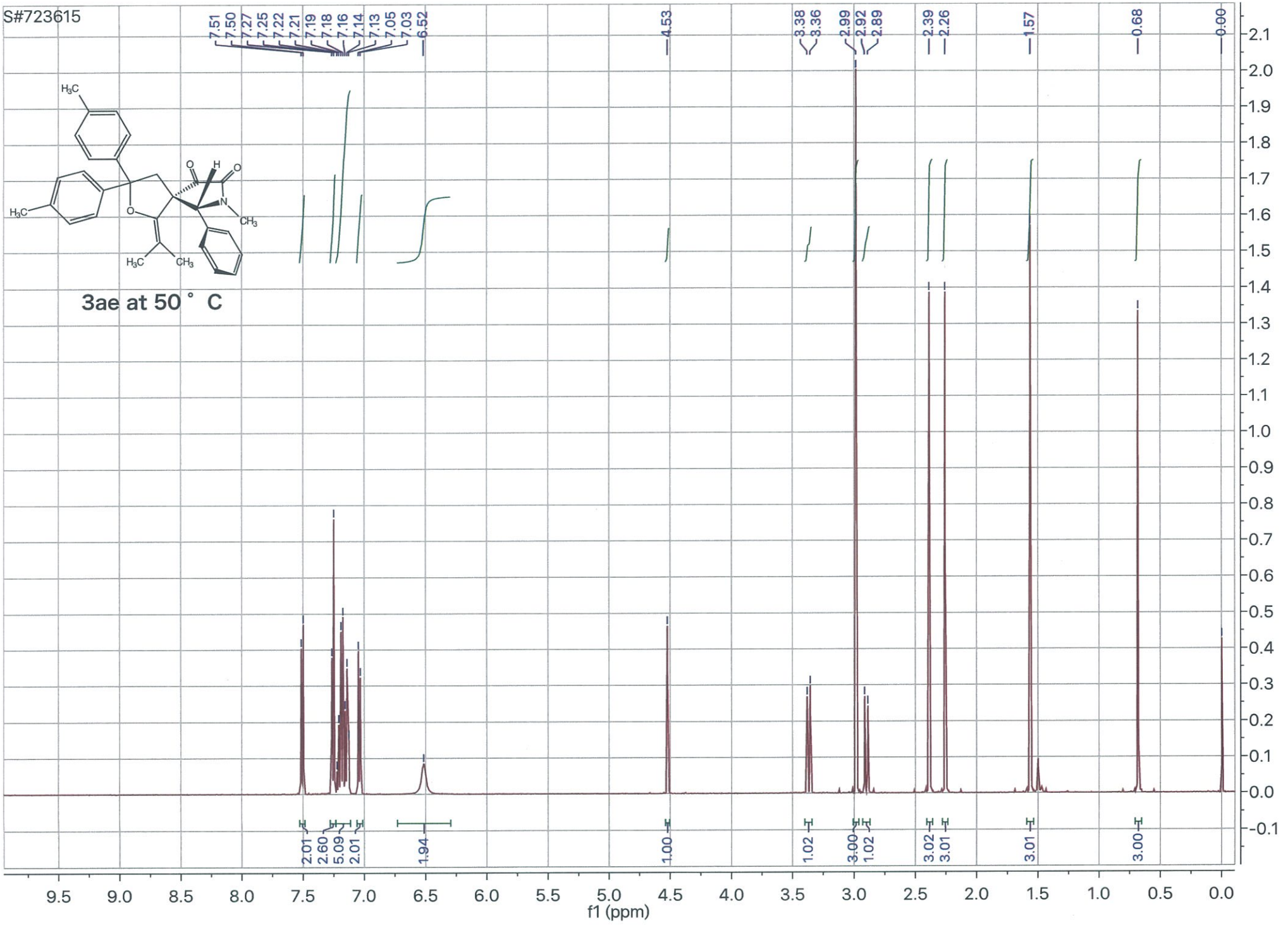

S#751658
gradient absolute value cosy
f2 (ppm)
f1 (ppm)
3ad

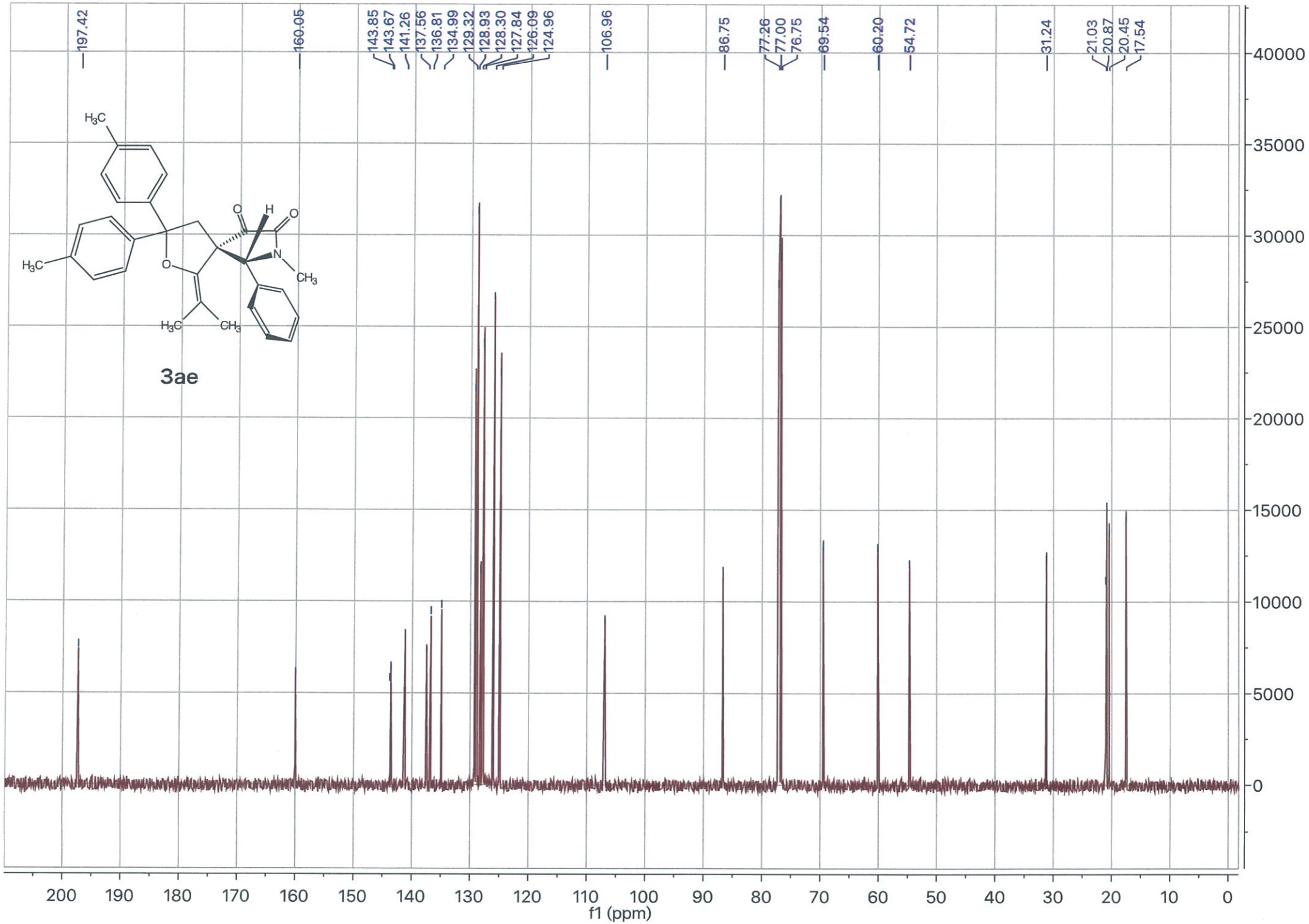

S#304542
absolute value noesy
f2 (ppm)
f1 (ppm)
3ad

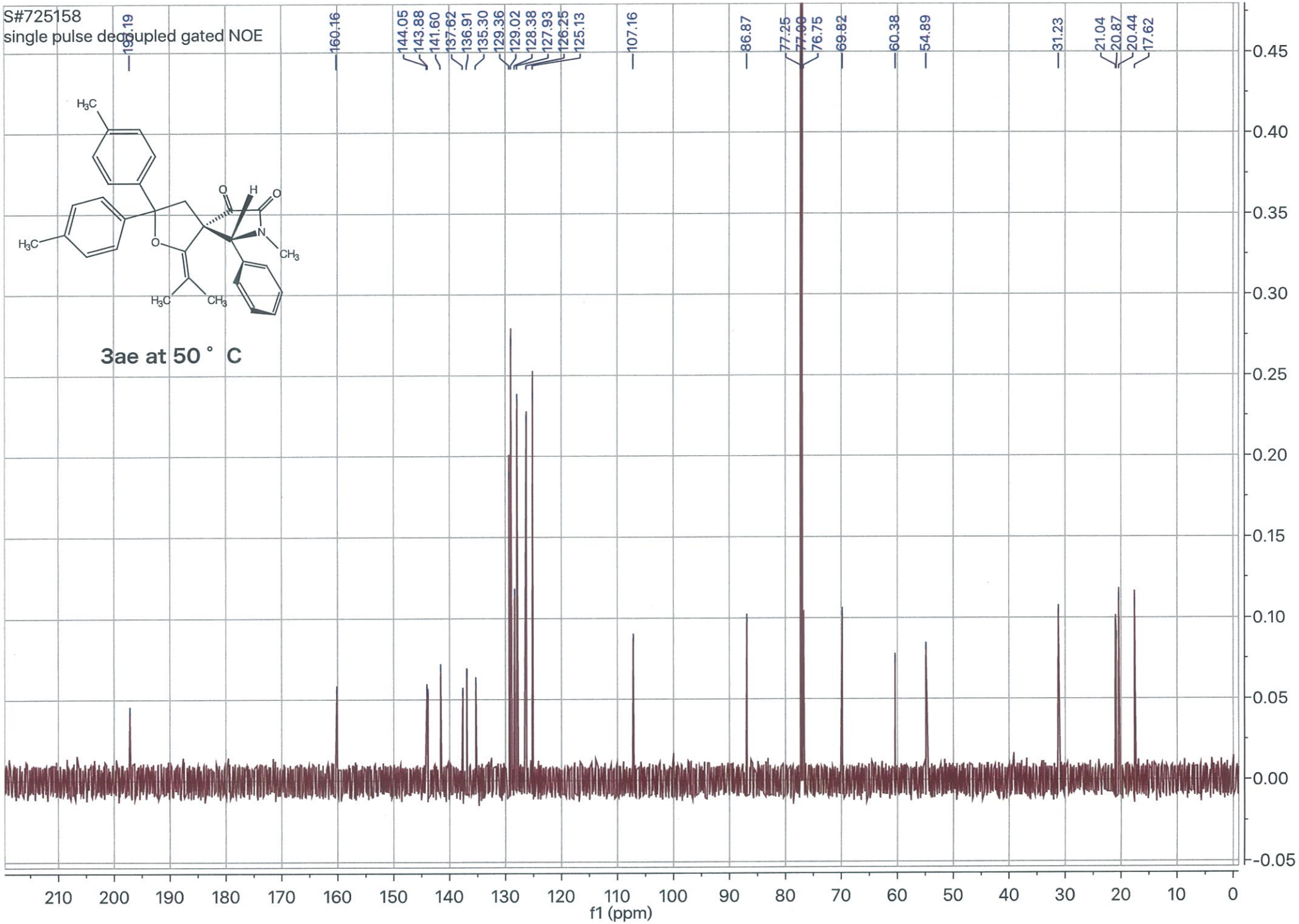

S#780049
gradient enhanced HMQC with X-decoupling
f2 (ppm)
f1 (ppm)
3ad

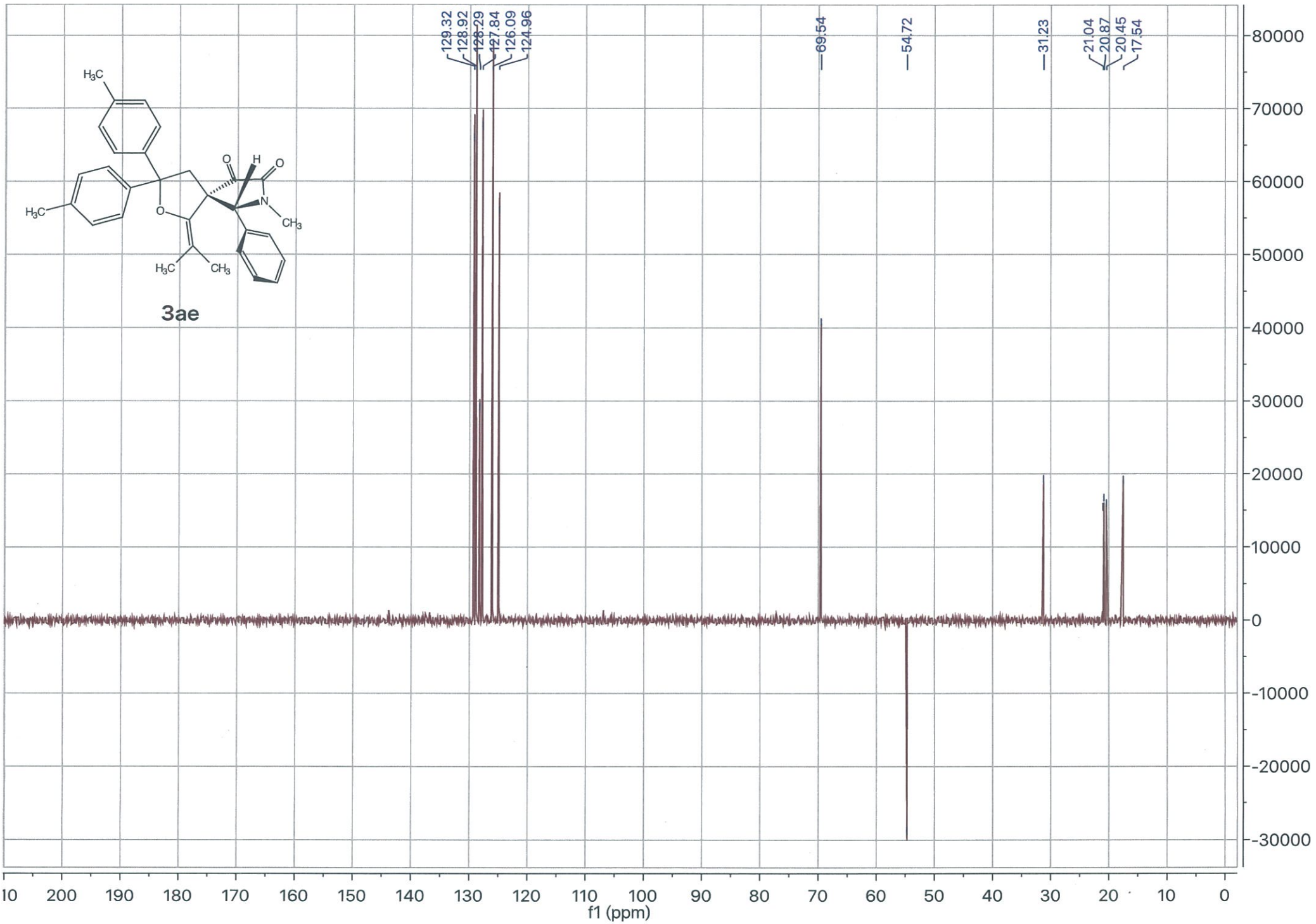

3ad
S#815124
gradient enhanced HMBC
f2 (ppm)
f1 (ppm)


S#355031
single_pulse
7.52
7.28
7.27
7.26
7.25
7.23
7.23
7.23
7.22
7.21
7.21
7.20
7.20
7.19
7.19
7.19
7.17
7.13
7.06
7.04
6.50
4.55
3.43
3.41
2.90
2.88
2.39
2.26
1.58
0.67
0.00
3ae
f1 (ppm)


S#723615
7.51
7.50
7.27
7.25
7.22
7.21
7.19
7.18
7.16
7.14
7.13
7.05
7.03
6.52
4.53
3.38
3.36
2.99
2.92
2.89
2.39
2.26
1.57
0.68
0.00
3ae at 50 ° C
2.01
2.60
5.09
2.01
1.94
1.00
1.02
3.00
1.02
3.02
3.01
3.01
3.00
f1 (ppm)

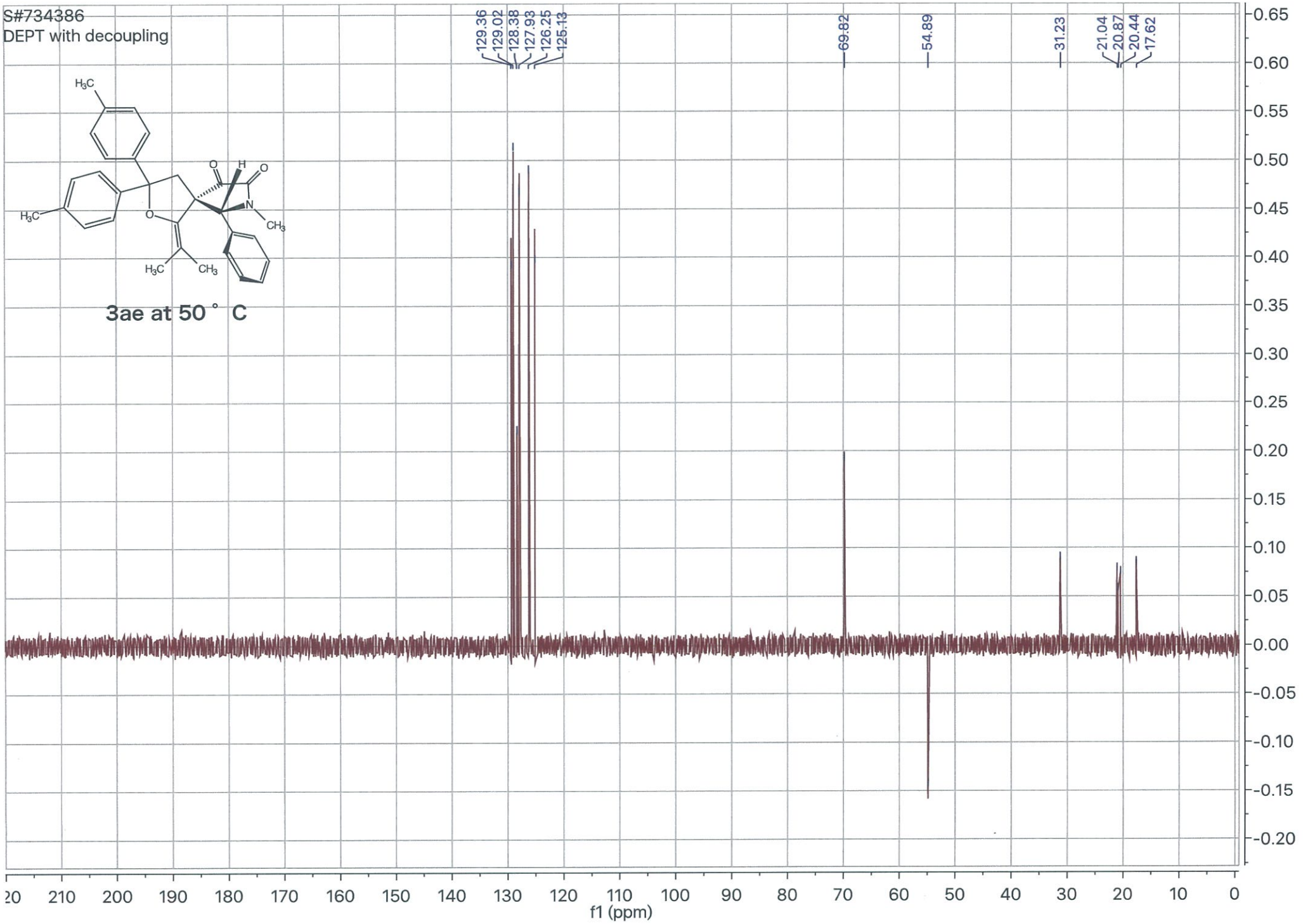

197.42
160.05
143.85
143.67
141.26
137.56
136.81
134.99
129.32
128.93
128.30
127.84
126.09
124.96
106.96
86.75
77.26
77.00
76.75
69.54
60.20
54.72
31.24
21.03
20.87
20.45
17.54
H3C
O
H
O
N
CH3
H3C
O
H3C
CH3
3ae
40000
35000
30000
25000
20000
15000
10000
5000
0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

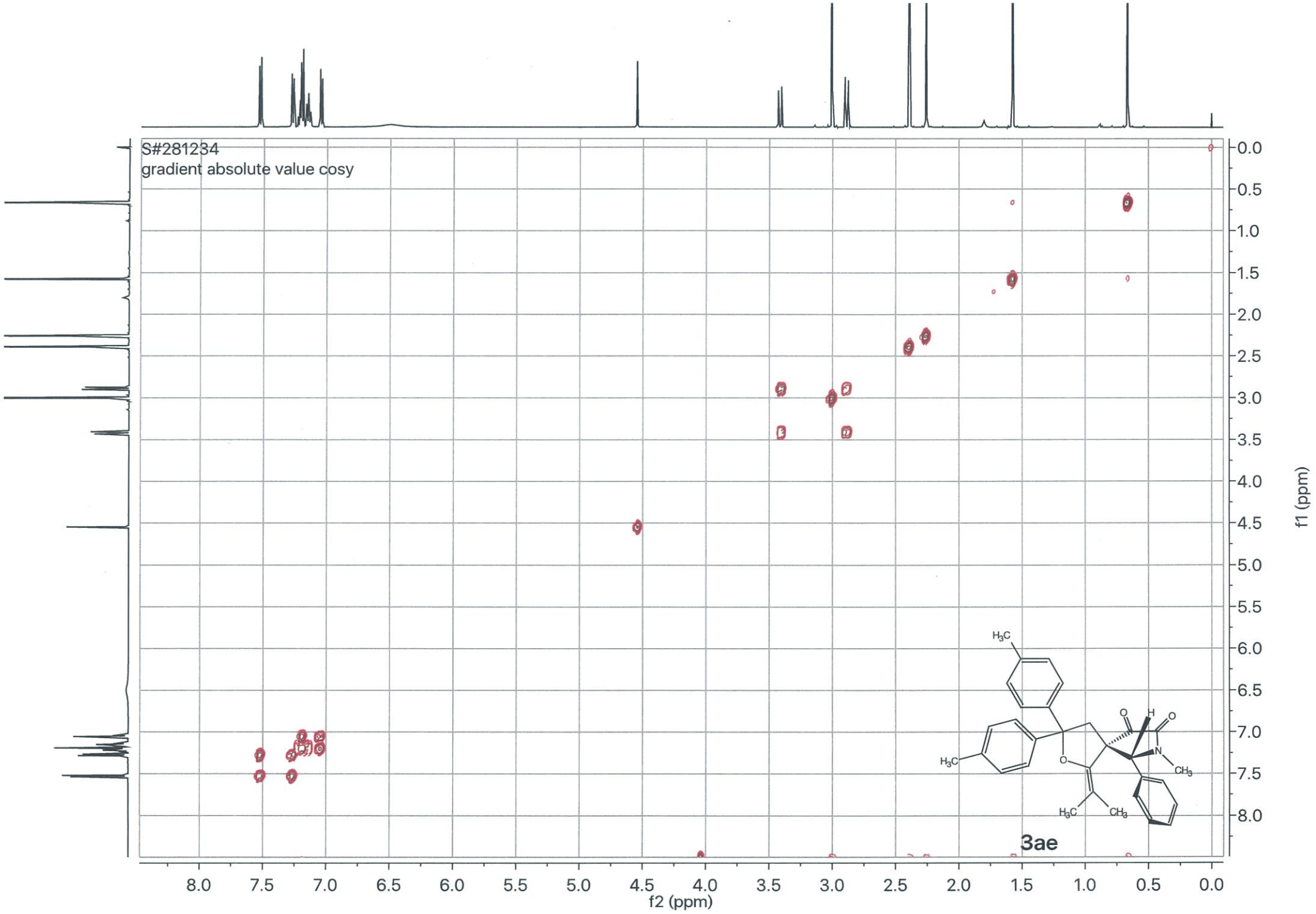

S#725158
single pulse decoupled gated NOE
199.19
160.16
144.05
143.88
141.60
137.62
136.91
135.30
129.36
129.02
128.38
127.93
126.25
125.13
107.16
86.87
77.25
77.00
76.75
69.82
60.38
54.89
31.23
21.04
20.87
20.44
17.62
3ae at 50 ° C
f1 (ppm)

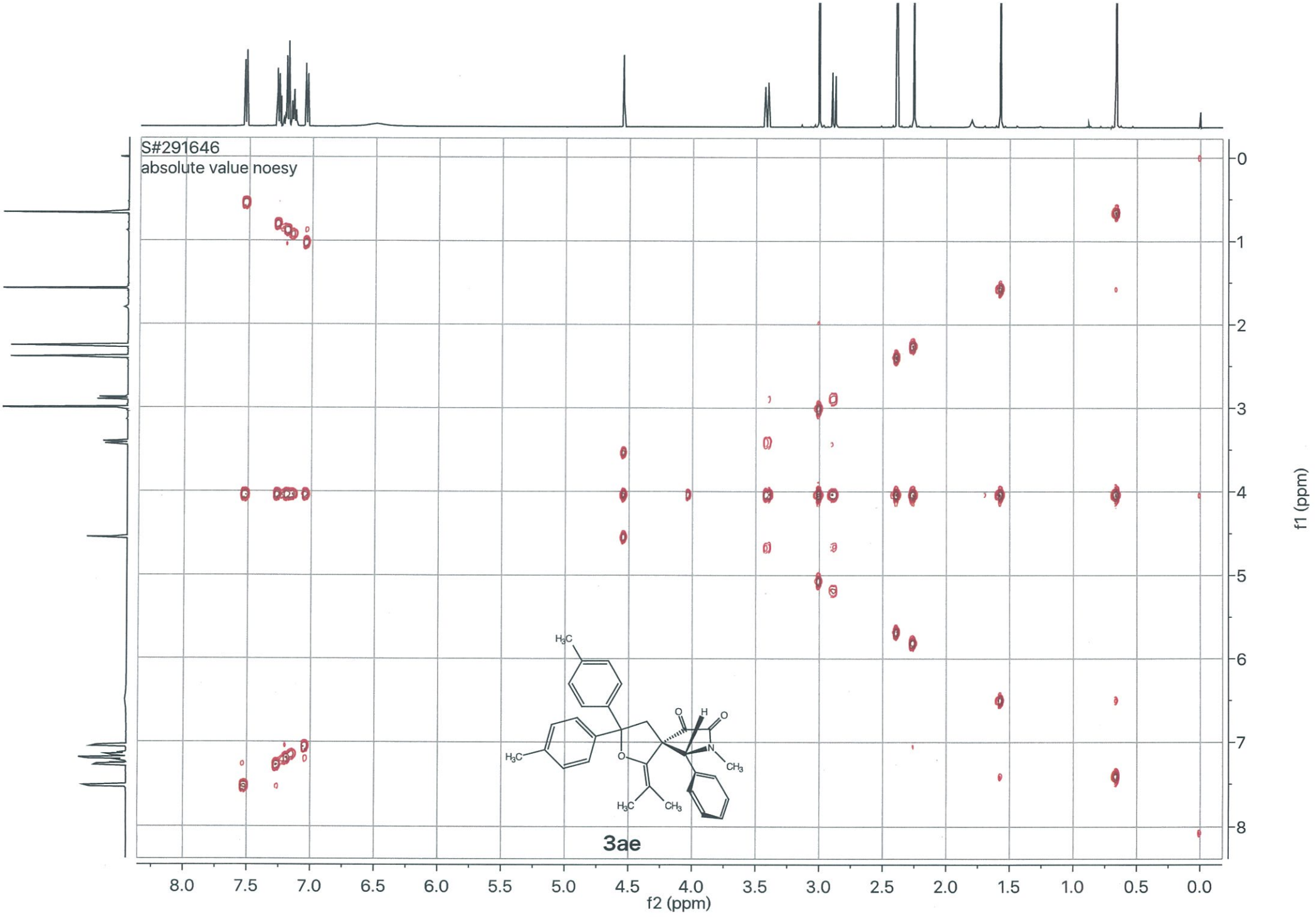

129.32
128.92
128.29
127.84
126.09
124.96
69.54
54.72
31.23
21.04
20.87
20.45
17.54
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
-20000
-30000
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
H3C
O
H
O
N
CH3
H3C
CH3
H3C
O
3ae

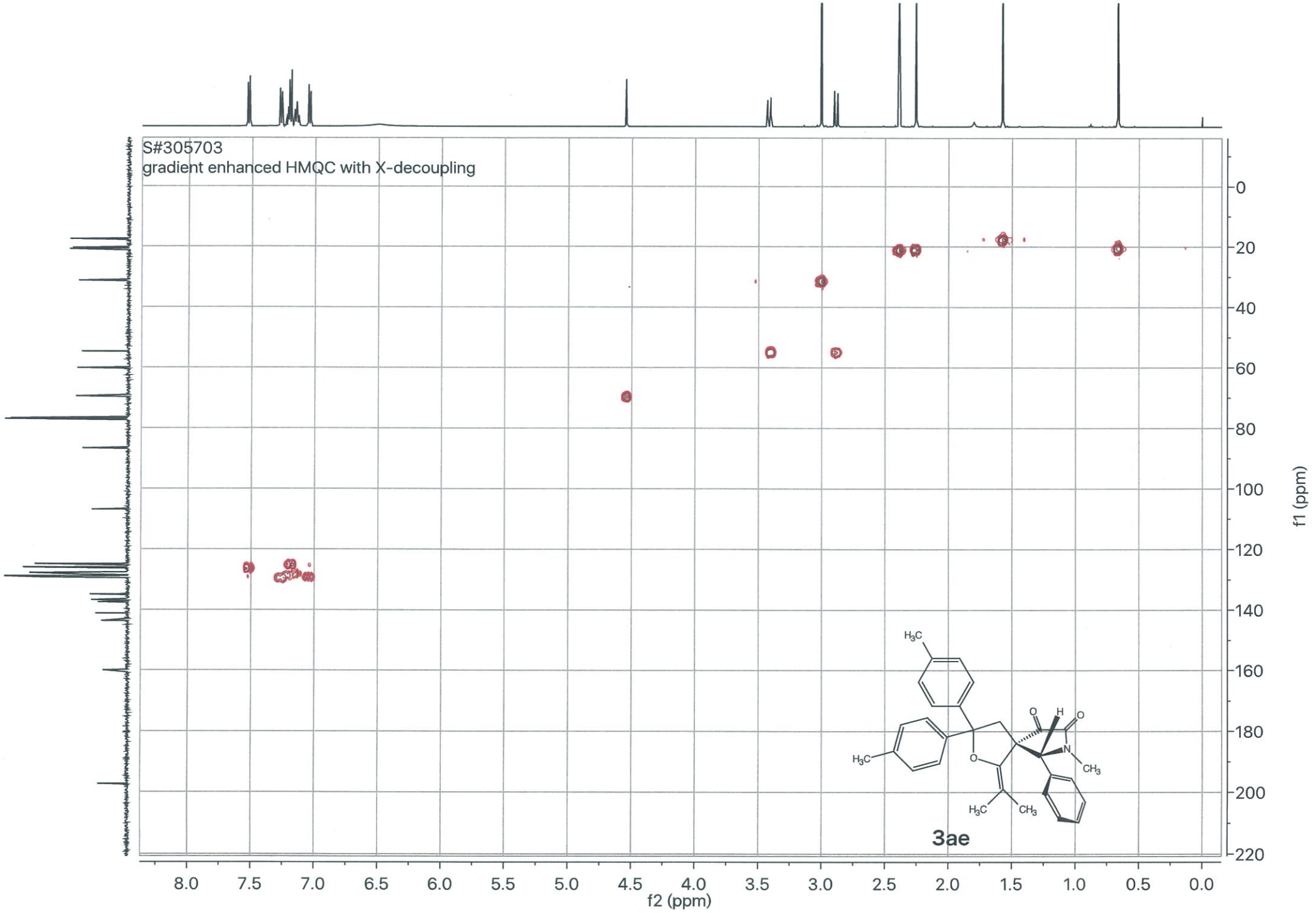
S#734386
DEPT with decoupling

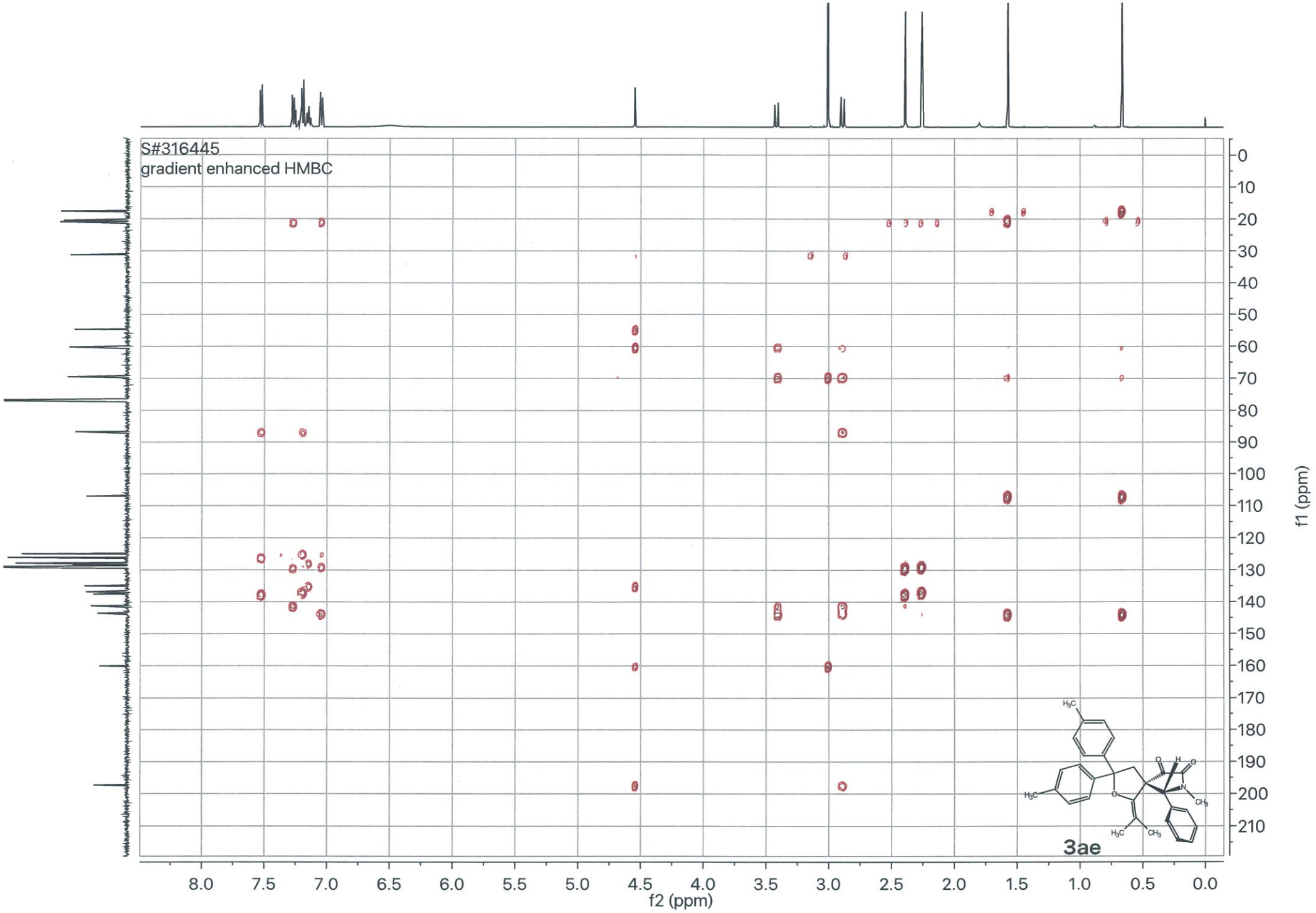
3ae at 50 ° C

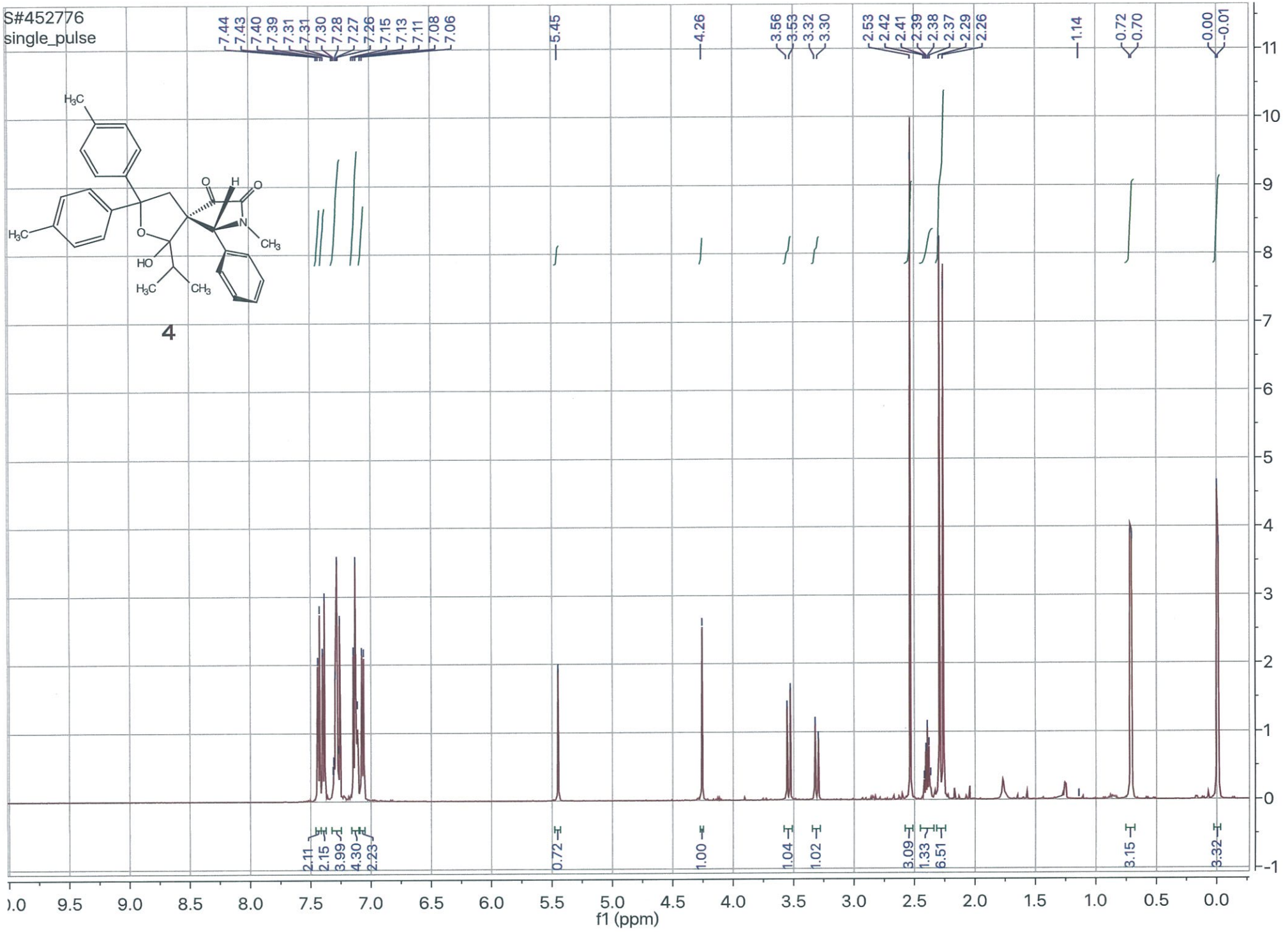



S#281234
gradient absolute value cosy
f2 (ppm)
f1 (ppm)
3ae


S#291646
absolute value noesy
f2 (ppm)
f1 (ppm)
3ae

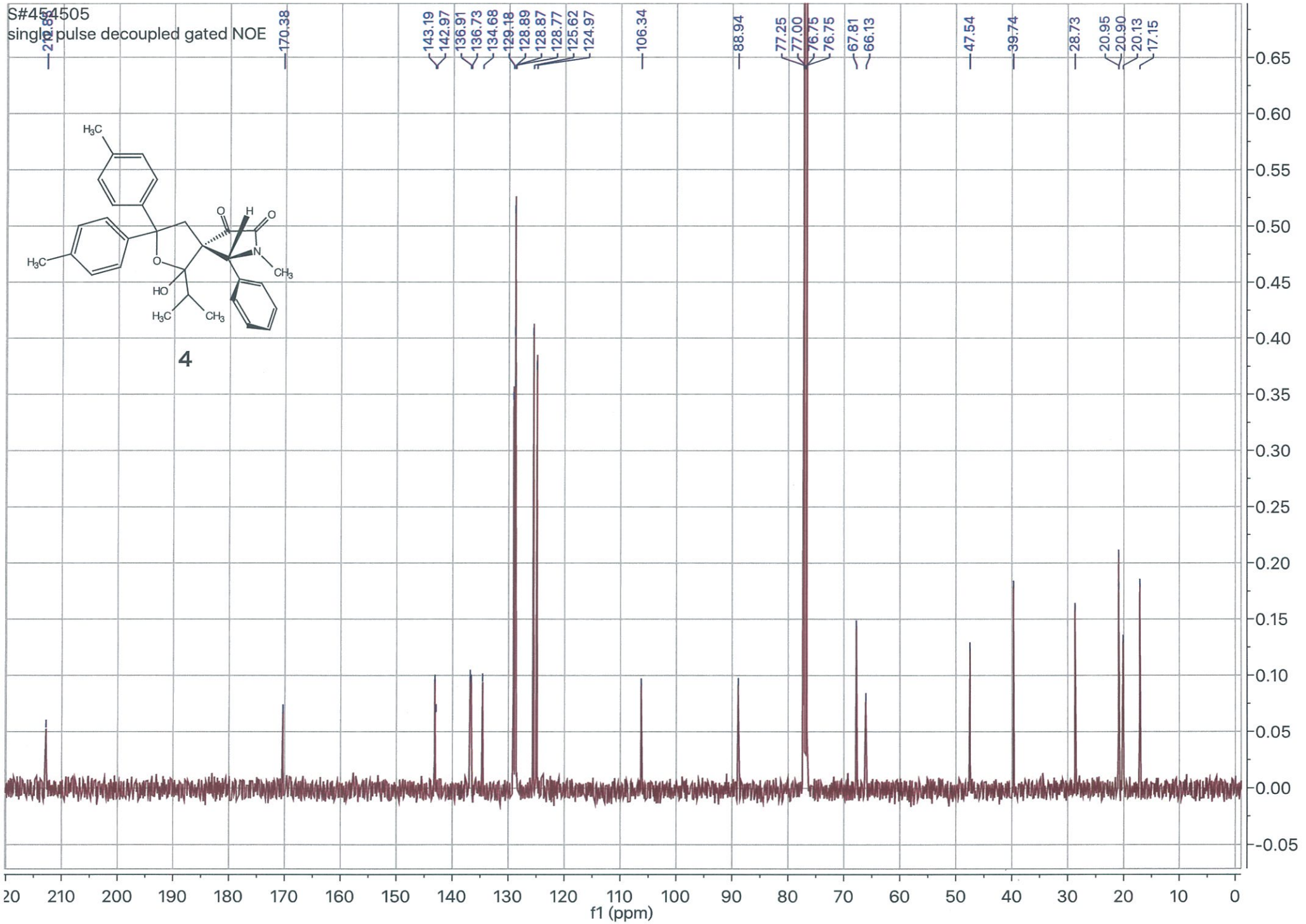

S#305703
gradient enhanced HMQC with X-decoupling
f2 (ppm)
f1 (ppm)
3ae


S#316445
gradient enhanced HMBC
f2 (ppm)
f1 (ppm)
3ae

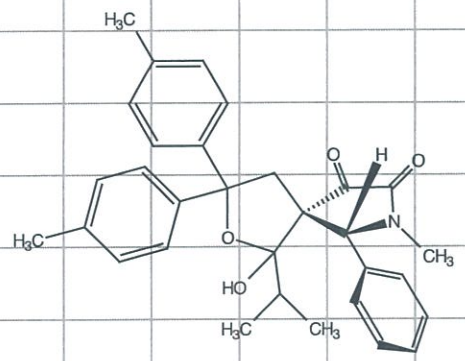

S#452776
single_pulse
7.44
7.43
7.40
7.39
7.31
7.31
7.30
7.28
7.27
7.26
7.15
7.13
7.11
7.08
7.06
5.45
4.26
3.56
3.53
3.32
3.30
2.53
2.42
2.41
2.39
2.38
2.37
2.29
2.26
1.14
0.72
0.70
0.00
-0.01
H3C
O
H
O
N
CH3
H3C
O
HO
H3C
CH3
4
2.11
2.15
3.99
4.30
2.23
0.72
1.00
1.04
1.02
3.09
1.33
6.51
3.15
3.32
f1 (ppm)

S#454505
single pulse decoupled gated NOE

4



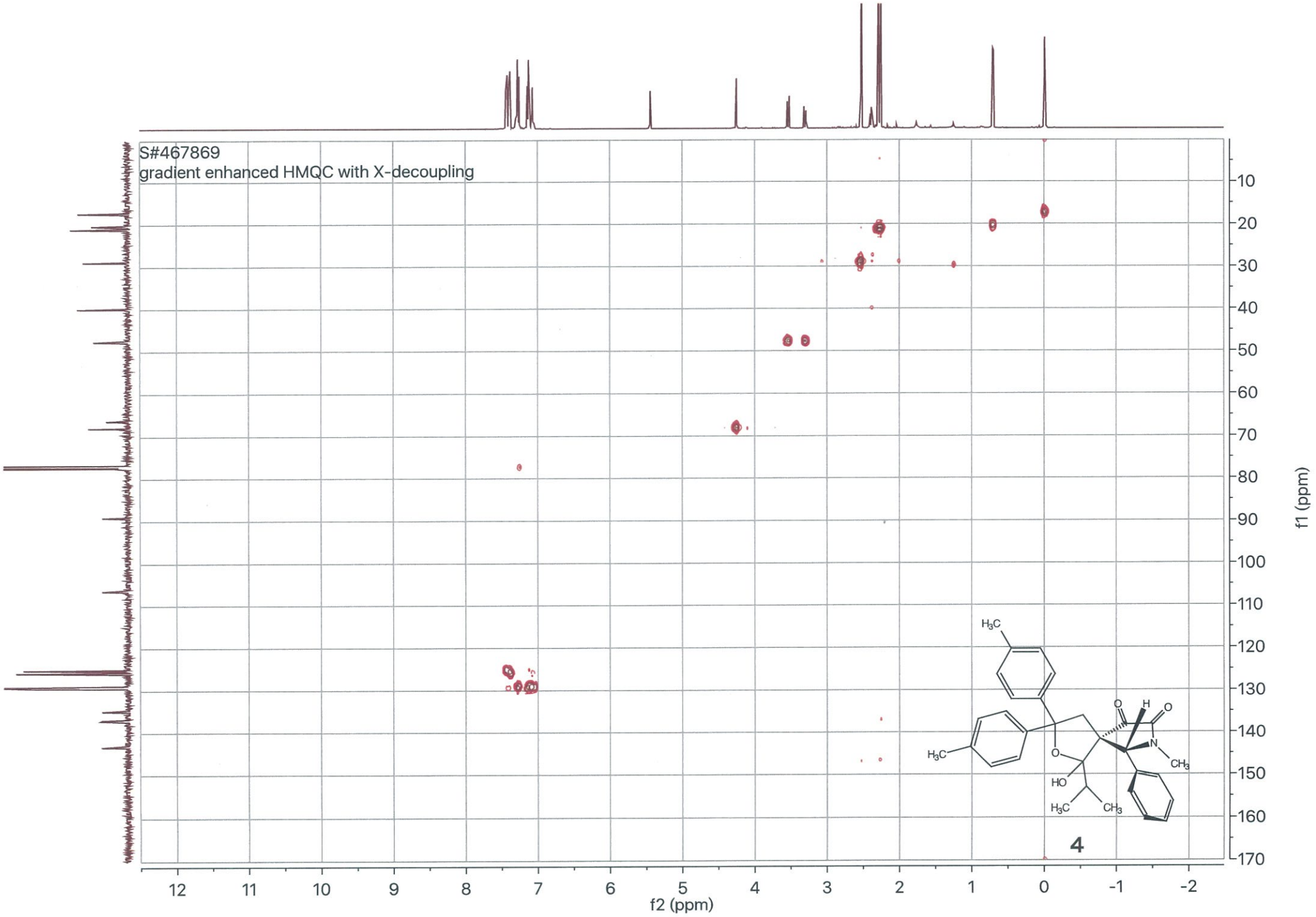
S#485235
DEPT with decoupling



4

144.57
129.18
128.92
128.92
128.90
128.87
128.78
125.63
124.98
67.85
67.81
47.54
39.75
28.73
20.96
20.90
20.13
17.15

f1 (ppm)

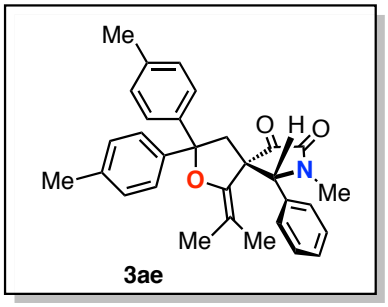

S#467869
gradient enhanced HMQC with X-decoupling
f2 (ppm)
f1 (ppm)
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
H3C
H3C
O
H
O
N
CH3
O
HO
H3C
CH3
4

X-ray Structure Report

for

3,3-Bis(4-methylphenyl)-7-methyl-6-phenyl-1-(propan-2-ylidene)-
2-oxa-7-azaspiro[4.4]nonane-8,9-dione (**3ae**)

June 9, 2017



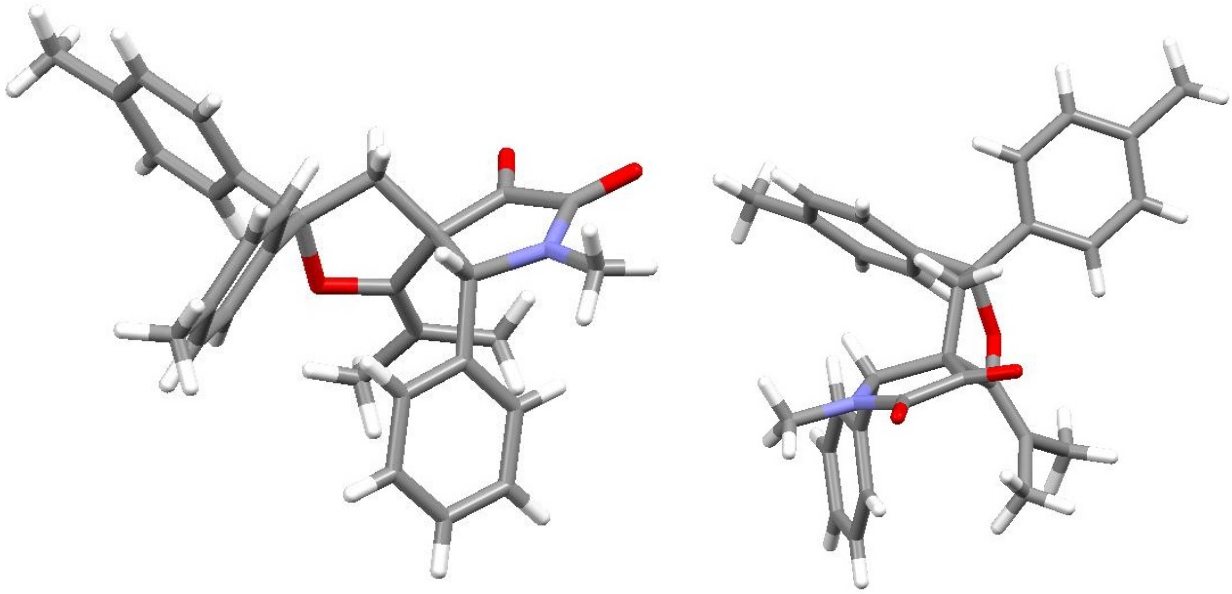


Fig. 3. X-ray crystal structure of the product **3ae**

Experimental

Data Collection

A colorless block crystal of $C_{31}H_{31}NO_3$ having approximate dimensions of 0.370 x 0.327 x 0.187 mm was mounted on a glass fiber. All measurements were made on a Rigaku R-AXIS RAPID diffractometer using graphite monochromated Mo-Kα radiation.

The crystal-to-detector distance was 127.40 mm.

Cell constants and an orientation matrix for data collection corresponded to a primitive triclinic cell with dimensions:

a	= 9.6559(4) Å	α	= 75.345(2)°
b	= 9.9138(5) Å	β	= 69.807(2)°
c	= 14.9614(8) Å	γ	= 78.722(1)°
V	= 1291.2(1) Å^3		

For Z = 2 and F.W. = 465.59, the calculated density is 1.197 g/cm^3. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be:

P-1 (#2)

The data were collected at a temperature of 23 $\pm$ 1°C to a maximum 2θ value of 54.9°. A total of 44 oscillation images were collected. A sweep of data was done using ω scans from 130.0 to 190.0° in 5.0° step, at χ=45.0° and ϕ = 0.0°. The exposure rate was 120.0 [sec./°]. A second sweep was performed using ω scans from 0.0 to 160.0° in 5.0° step, at χ=45.0° and ϕ = 180.0°. The exposure rate was 120.0 [sec./°]. The crystal-to-detector distance was 127.40 mm. Readout was performed in the 0.100 mm pixel mode.

Data Reduction

Of the 12647 reflections that were collected, 5759 were unique (R_{int} = 0.0259).

The linear absorption coefficient, μ, for Mo-Kα radiation is 0.763 cm^{-1}. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods[1] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement[2] on F^2 was based on 5759 observed reflections and 316 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R_1 = \Sigma \; ||Fo| - |Fc|| \; / \; \Sigma \; |Fo| = 0.0688$$

$$wR_2 = [\; \Sigma \; (\; w \; (Fo^2 - Fc^2)^2 \;) / \; \Sigma \; w(Fo^2)^2]^{1/2} = 0.2614$$

The standard deviation of an observation of unit weight[3] was 1.13. Unit weights were used. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.33 and -0.36 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[4]. Anomalous dispersion effects were included in Fcalc[5]; the values for Δf' and Δf" were those of Creagh and McAuley[6]. The values for the mass attenuation coefficients are those of Creagh and Hubbell[7]. All calculations were performed using the CrystalStructure[8] crystallographic software package except for refinement, which was performed using SHELXL-97[9].

References

(1) SIR2008: M.C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G.L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, D. Siliqi, R. Spagna (2007)

(2) Least Squares function minimized: (SHELXL97)

$\Sigma w(F_o^2-F_c^2)^2$ where w = Least Squares weights.

(3) Standard deviation of an observation of unit weight:

$[\Sigma w(F_o^2-F_c^2)^2/(N_o-N_v)]^{1/2}$

where: N_o = number of observations
N_v = number of variables

(4) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

(5) Ibers, J. A. & Hamilton, W. C.; Acta Crystallogr., 17, 781 (1964).

(6) Creagh, D. C. & McAuley, W.J .; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

(7) Creagh, D. C. & Hubbell, J.H..; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

(8) CrystalStructure 4.0: Crystal Structure Analysis Package, Rigaku Corporation (2000-2010). Tokyo 196-8666, Japan.

(9) SHELX97: Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{31}H_{31}NO_3$
Formula Weight	465.59
Crystal Color, Habit	colorless, block
Crystal Dimensions	0.370 X 0.327 X 0.187 mm
Crystal System	triclinic
Lattice Type	Primitive
Lattice Parameters	a = 9.6559(4) Å b = 9.9138(5) Å c = 14.9614(8) Å α = 75.345(2)° β = 69.807(2)° γ = 78.722(1)° V = 1291.2(1) Å^3
Space Group	P-1 (#2)
Z value	2
D_{calc}	1.197 g/cm^3
F_{000}	496.00
μ(MoKα)	0.763 cm^{-1}

B. Intensity Measurements

Diffractometer	R-AXIS RAPID
Radiation	MoKα (λ = 0.71075 Å) graphite monochromated
Voltage, Current	50kV, 40mA
Temperature	23.0 $^{\circ}$C
Detector Aperture	280 x 256 mm
Data Images	44 exposures
ω oscillation Range (χ=45.0, ϕ=0.0)	130.0 - 190.0°
Exposure Rate	120.0 sec./$^{\circ}$
ω oscillation Range (χ=45.0, ϕ=180.0)	0.0 - 160.0°
Exposure Rate	120.0 sec./$^{\circ}$
Detector Position	127.40 mm
Pixel Size	0.100 mm
$2\theta_{max}$	54.9°
No. of Reflections Measured	Total: 12647 Unique: 5759 (R_{int} = 0.0259)
Corrections	Lorentz-polarization

C. Structure Solution and Refinement

Structure Solution	Direct Methods
Refinement	Full-matrix least-squares on F^2
Function Minimized	Σ w $(Fo^2 - Fc^2)^2$
Least Squares Weights	$w = 1/ [\sigma^2(Fo^2) + (0.1177 \cdot P)^2 + 0.5065 \cdot P]$ where $P = (Max(Fo^2,0) + 2Fc^2)/3$
$2\theta_{max}$ cutoff	54.9^o
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	5759
No. Variables	316
Reflection/Parameter Ratio	18.22
Residuals: R1 (I>2.00σ(I))	0.0688
Residuals: R (All reflections)	0.1444
Residuals: wR2 (All reflections)	0.2614
Goodness of Fit Indicator	1.131
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	0.33 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.36 $e^-/Å^3$