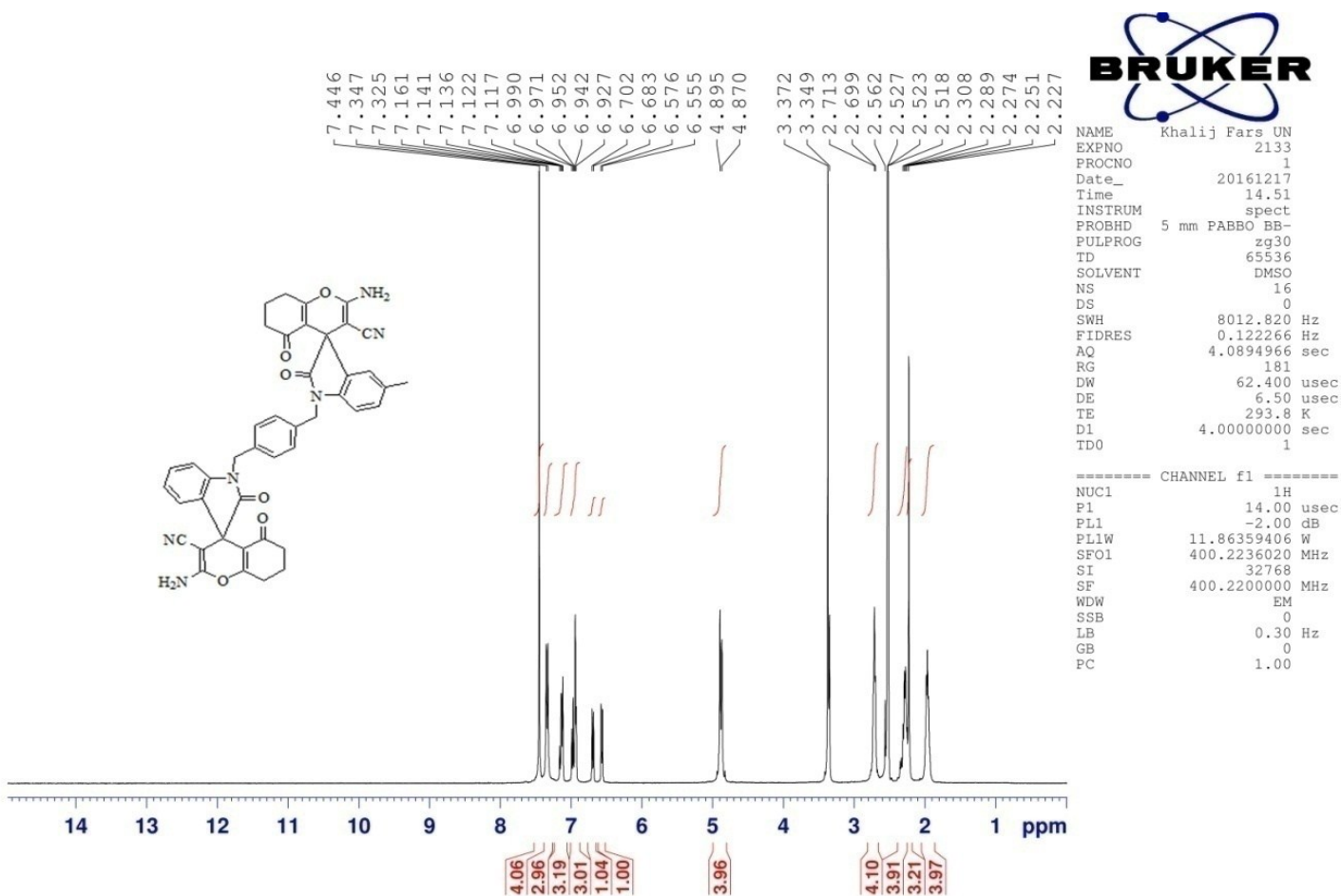


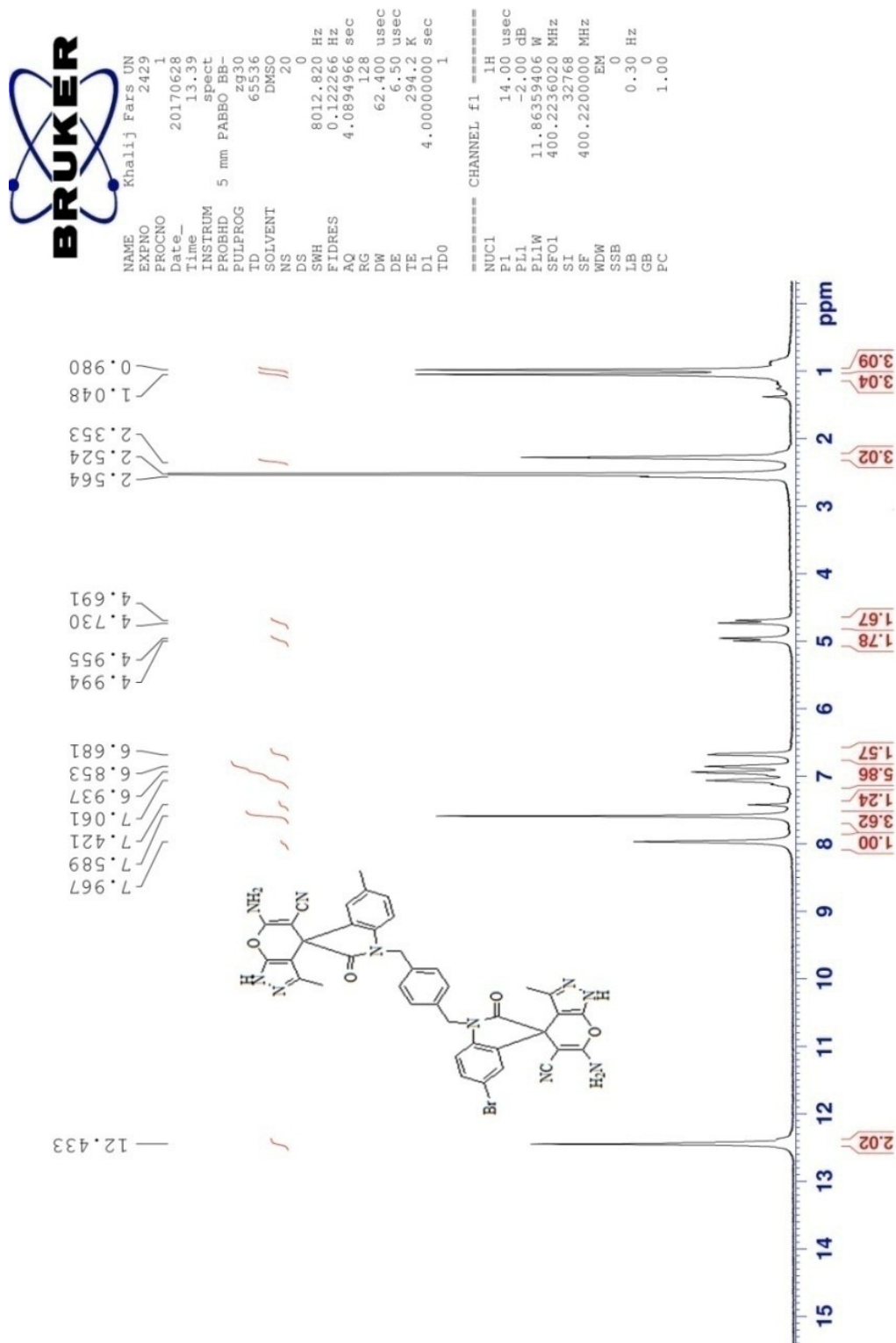
Eco-friendly polyethylene glycol (PEG-400): a green reaction medium for one-pot, four-component synthesis of novel asymmetrical bis-spirooxindole derivatives at room temperature

Alireza Hasaninejad,^{*†}Maryam Beyrati[†]

2-amino-1'-(4-((2-amino-3-cyano-5'-methyl-2',5-dioxo-5,6,7,8-tetrahydrospiro[chromene-4,3'-indolin]-1'-yl)methyl)benzyl)-2',5-dioxo-5,6,7,8-tetrahydrospiro[chromene-4,3'-indoline]-3-carbonitrile **6a**



6'-amino-1-(4-(((6'-amino-5'-cyano-3',5-dimethyl-2-oxo-1'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazol]-1-yl)methyl)benzyl)-5-bromo-3'-methyl-2-oxo-1'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-5'-carbonitrile **6b**

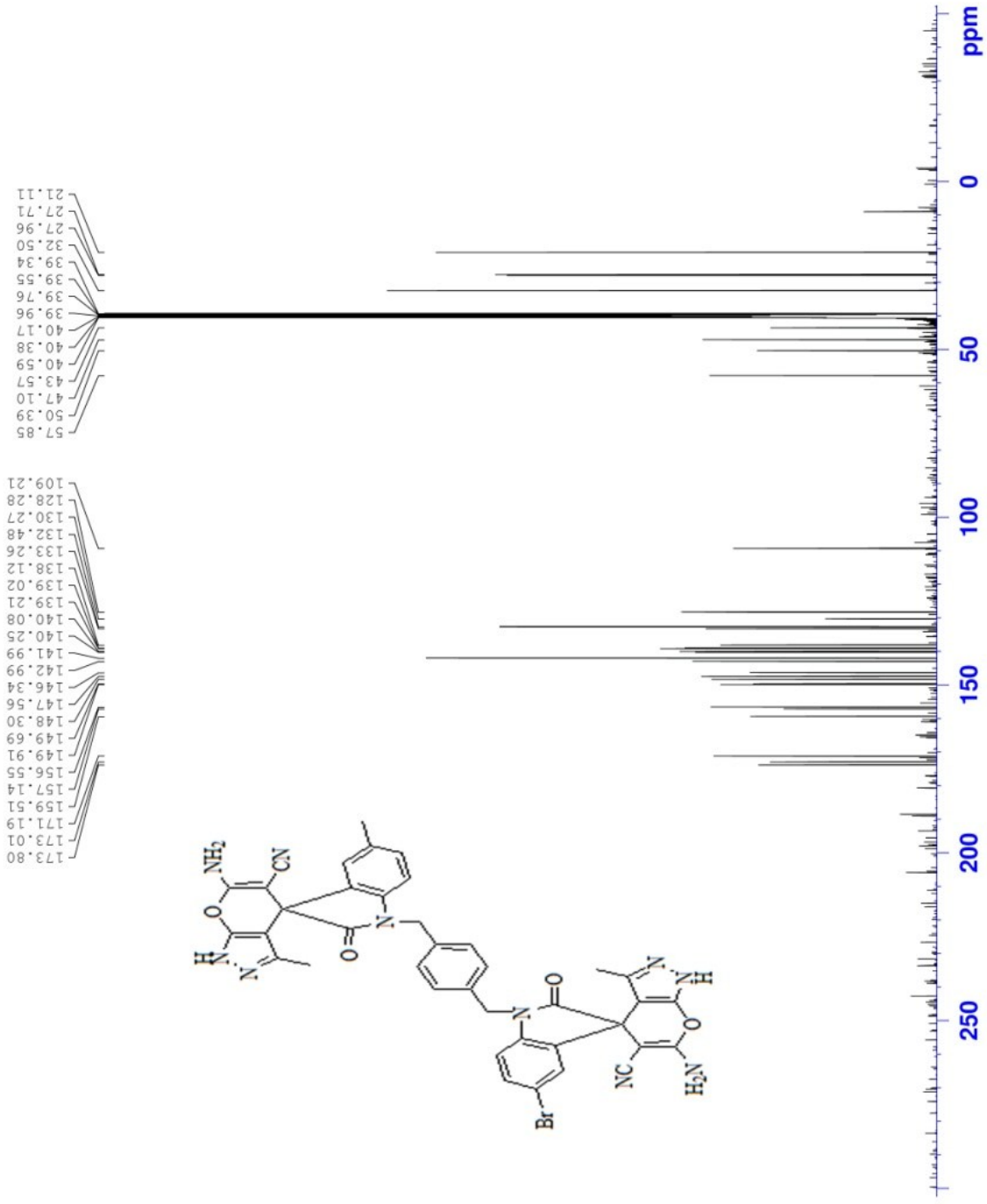




NAME Khaliq Fars UN
EXPNO 1
PROCNO 2450
Date_ 20170719
Time_ 8.11
INSTRUM spect
PROBHD 5 mm FAPBO BB-
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 600
DS 0
SWH 35714.285 Hz
FIDRES 0.544957 Hz
AQ 0.9175540 sec
RG 2050
DW 14.000 usec
DE 6.50 usec
TE 292.8 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 9.00 usec
PL1 -0.90 dB
PL1W 42.02801895 W
SFO1 100.6479784 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -2.00 dB
PL12 14.48 dB
PL13 17.90 dB
PL2W 11.86359406 W
PL12W 0.26681873 W
PL13W 0.12139934 W
SFO2 400.2216009 MHz
SI 32768
SF 100.6353990 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

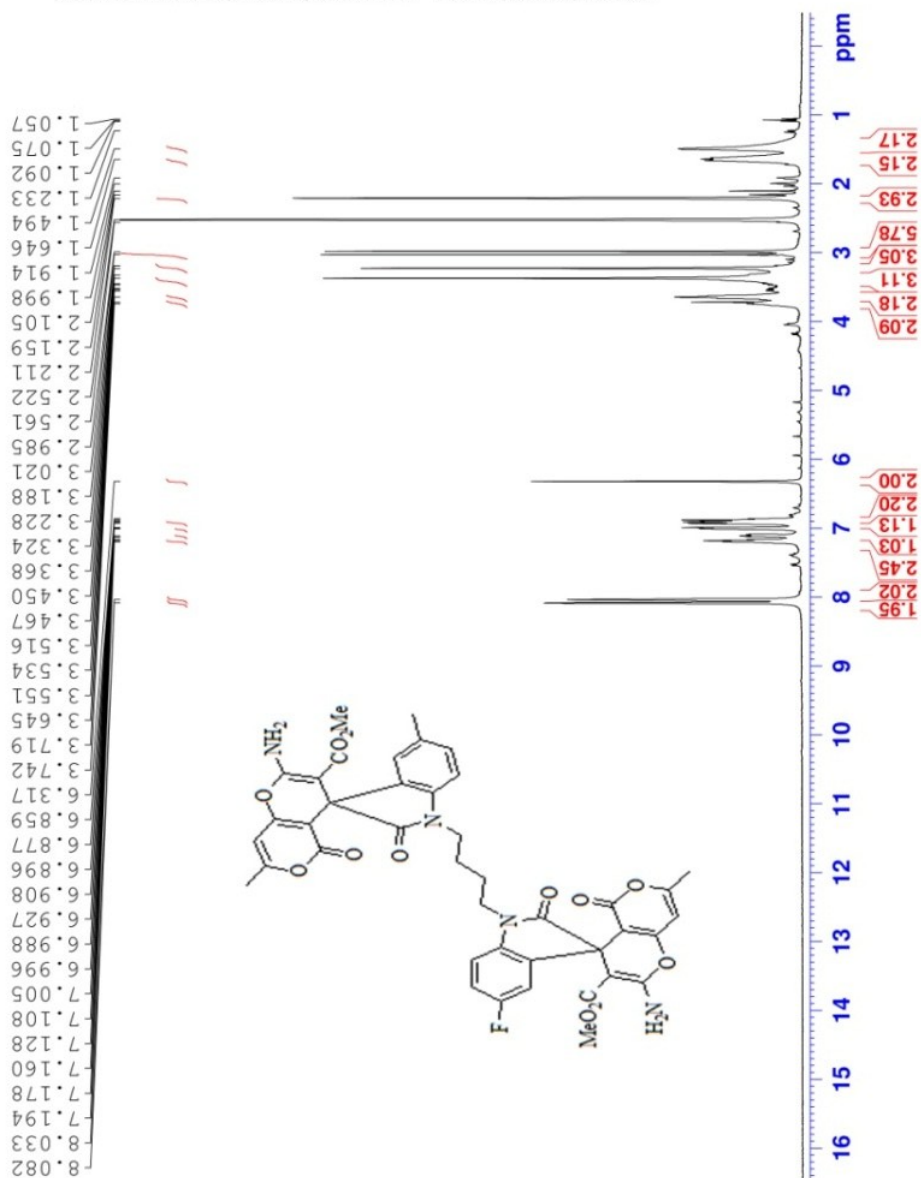


methyl 2'-amino-1-(4-(2'-amino-3'-(methoxycarbonyl)-5,7'-dimethyl-2,5'-dioxo-5'H-spiro[indoline-3,4'-pyrano[4,3-b]pyran]-1-yl)butyl)-5-fluoro-7'-methyl-2,5'-dioxo-5'H-spiro[indoline-3,4'-pyrano[4,3-b]pyran]-3'-carboxylate **6c**



NAME Khalij Fars UN
 EXPNO 2428
 PROCNO 1
 Date_ 20170628
 Time 13.30
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zg30
 ID 65536
 SOLVENT DMSO
 NS 40
 DS 0
 SWH 8012.820 Hz
 FIDRES 0.122266 Hz
 AQ 4.0894966 sec
 RG 128
 DW 62.400 usec
 DE 6.50 usec
 TE 294.2 K
 D1 4.0000000 sec
 TDO 1

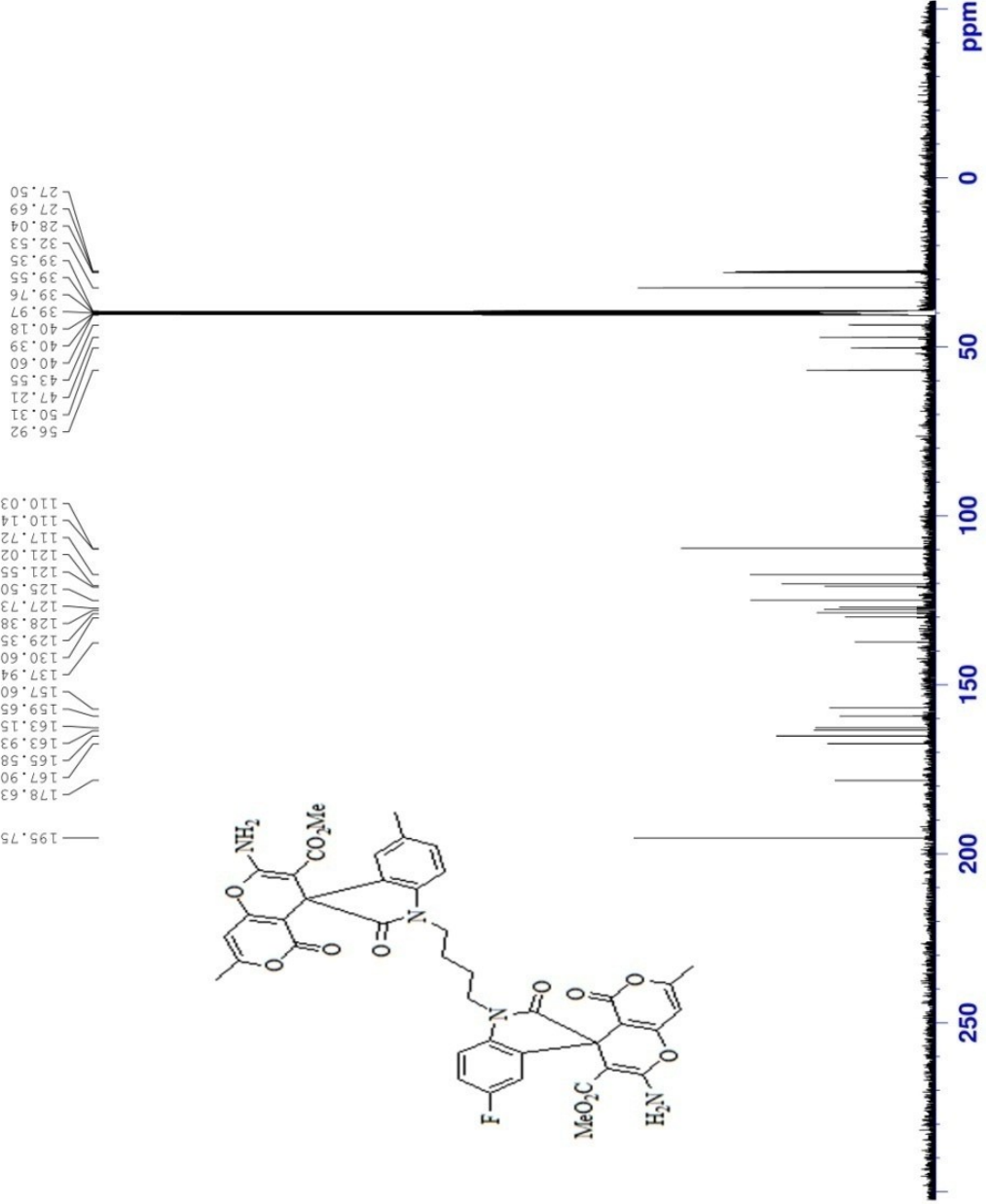
===== CHANNEL f1 =====
 NUC1 1H
 P1 14.00 usec
 PL1 -2.00 dB
 PL1W 11.86359406 W
 SFOL 400.2236020 MHz
 SI 32768
 SF 400.2200000 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00





NAME: Khalij Fars UN
 EXPNO: 2445
 PROCNO: 1
 Date_: 20170718
 Time: 16.56
 INSTRUM: spect
 PROBHD: 5 mm PABBO BB-
 PULPROG: zgpg30
 ID: 65536
 SOLVENT: DMSO
 NS: 904
 DS: 0
 SWH: 35714.285 Hz
 FIDRES: 0.544957 Hz
 AQ: 0.9175540 sec
 RG: 2050
 DW: 14.000 usec
 DE: 6.50 usec
 TE: 294.1 K
 D1: 1.00000000 sec
 D11: 0.03000000 sec
 TD0: 1

===== CHANNEL f1 =====
 NUC1: 13C
 P1: 9.00 usec
 PL1: -0.90 dB
 PL1W: 42.02801895 W
 SF01: 100.6479784 MHz
 ===== CHANNEL f2 =====
 CPDPRG2: waltz16
 NUC2: 1H
 PCPD2: 90.00 usec
 PL2: -2.00 dB
 PL12: 14.48 dB
 PL13: 17.90 dB
 PL12W: 11.86359406 W
 PL13W: 0.26681873 W
 SF02: 0.12139934 W
 SI: 400.2216009 MHz
 SF: 100.6353990 MHz
 WDW: EM
 SSB: 0
 LB: 1.00 Hz
 GB: 0
 PC: 1.40

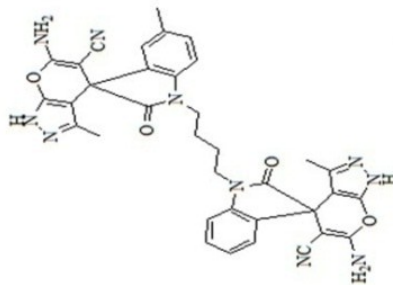
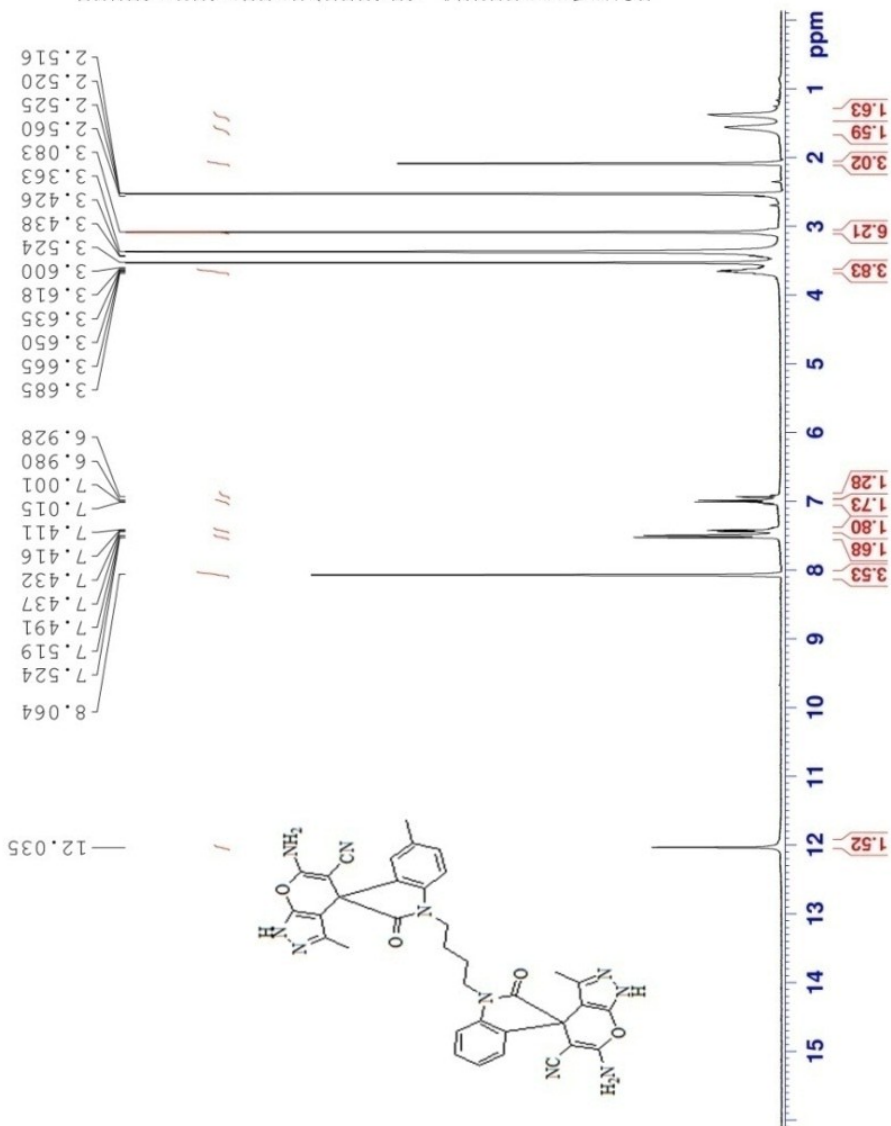


6'-amino-1-(4-(6'-amino-5'-cyano-3',5-dimethyl-2-oxo-1'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazol]-1-yl)butyl)-3'-methyl-2-oxo-1'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-5'-carbonitrile **6d**



NAME Khalilij Farsi UN
 EXPNO 2426
 F2ACQNO 1
 Date_ 20170628
 Time 13.15
 INSTRUM Spect
 PROBHD 5 mm PABBO BB-
 PULPROG zg30
 ID 65536
 SOLVENT DMSO
 NS 20
 DS 0
 SWH 8012.820 Hz
 FIDRES 0.122266 Hz
 AQ 4.0894966 sec
 RG 228
 DW 62.400 usec
 DE 6.50 usec
 TE 294.2 K
 D1 4.0000000 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 1H
 PL 14.00 usec
 PL1 -2.00 dB
 PL1W 11.86359406 W
 SF01 400.2236020 MHz
 ST 32768
 SF 400.2200000 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

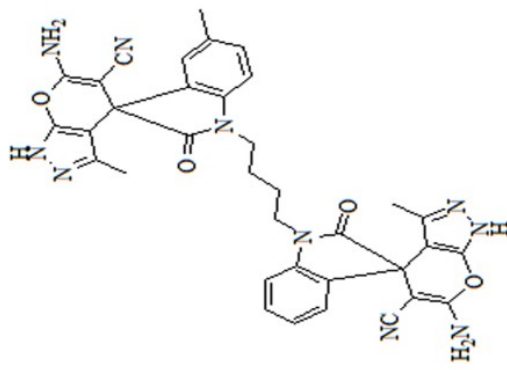
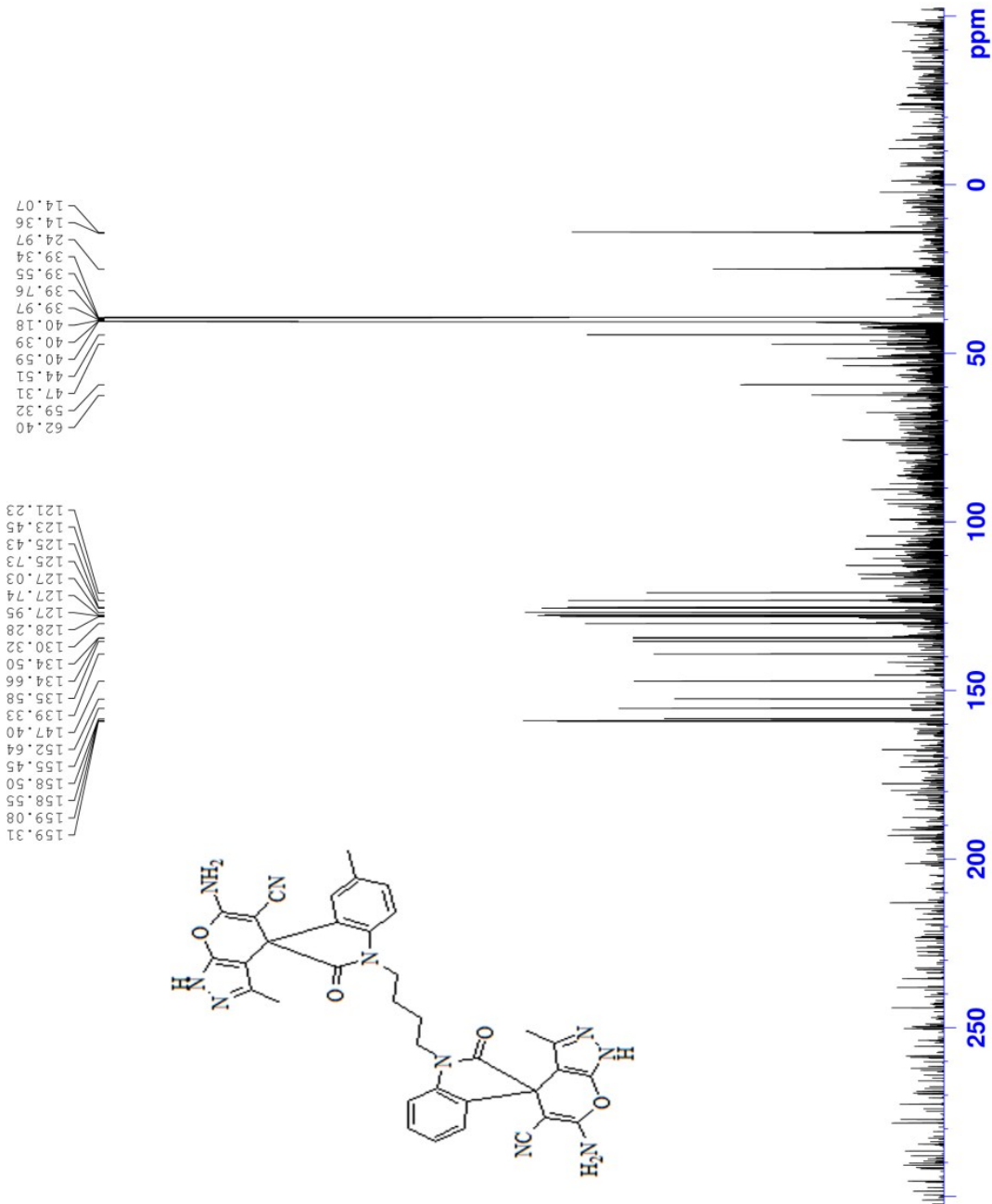




NAME: Khalij Fars UN
 EXPNO: 2456
 PROCNO: 1
 Date_: 20170719
 Time: 17.56
 INSTRUM: spect
 PROBHD: 5 mm PABBO BB-
 PULPROG: zgpg30
 TD: 65536
 SOLVENT: DMSO
 NS: 6330
 DS: 0
 SWH: 35714.285 Hz
 FIDRES: 0.544957 Hz
 AQ: 0.9175540 sec
 RG: 2050
 DW: 14.000 usec
 DE: 6.50 usec
 TE: 293.4 K
 D1: 1.00000000 sec
 D11: 0.03000000 sec
 TD0: 1

===== CHANNEL f1 =====
 NUC1: 13C
 P1: 9.00 usec
 PL1: -0.90 dB
 PL1W: 42.02801895 W
 SF01: 100.6479784 MHz

===== CHANNEL f2 =====
 CPDPRG2: waltz16
 NUC2: 1H
 PCPD2: 90.00 usec
 PL2: -2.00 dB
 PLI2: 14.48 dB
 PLI3: 17.90 dB
 PL2W: 11.86359406 W
 PLI2W: 0.26681873 W
 PLI3W: 0.12139934 W
 SFO2: 400.2216009 MHz
 SI: 32768
 SF: 100.6353990 MHz
 WDW: EM
 SSB: 0
 LB: 1.00 Hz
 GB: 0
 PC: 1.40

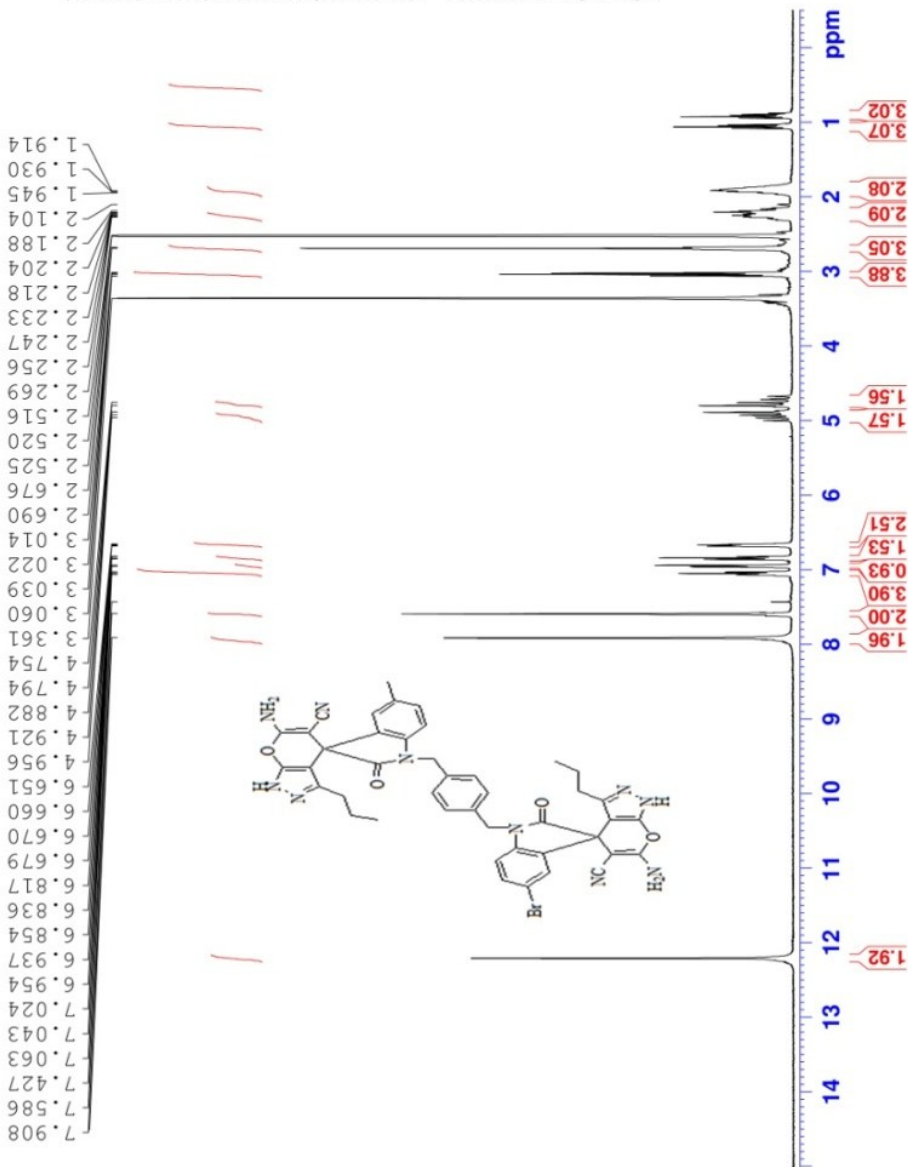


6'-amino-1-(4-(((6'-amino-5'-cyano-5-methyl-2-oxo-3'-propyl-1'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazol]-1-yl)methyl)benzyl)-5-bromo-2-oxo-3'-propyl-1'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-5'-carbonitrile) **6e**



NAME Khaliq Fares UN
 EXPNO 2425
 PROCNO 1
 Date_ 20170628
 Time 13.05
 INSTRUM spect
 PROBD 5 mm PABBO BB-
 PULPROG zg30
 TD 65536
 SOLVENT DMSO
 NS 20
 DS 0
 SWH 8012.820 Hz
 FIDRES 0.122266 Hz
 AQ 4.0894966 sec
 RG 228
 DW 62.400 usec
 DE 6.50 usec
 TE 294.1 K
 D1 4.00000000 sec
 TD0 1

CHANNEL f1
 NUC1 1H
 P1 14.00 usec
 PL1 -2.00 dB
 PL1W 11.86359406 W
 SFO1 400.2236020 MHz
 SI 32768
 SF 400.2200000 MHz
 MDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



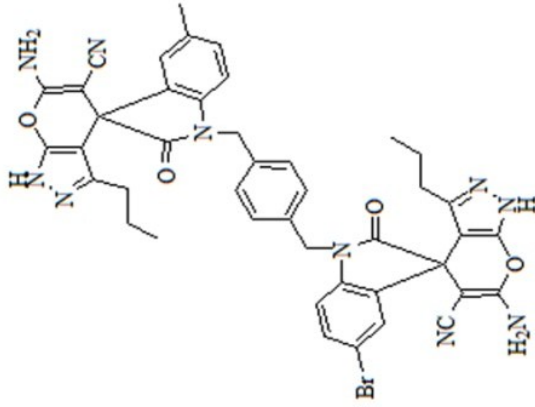


NAME Khallij Fars UN
EXPNO 2458
PROCNO 1
Date_ 20170722
Time 15.18
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 4400
DS 0
SWH 35714.285 Hz
FIDRES 0.544957 Hz
AQ 0.9175540 sec
RG 2050
DW 14.000 usec
DE 6.50 usec
TE 295.1 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1

=====
CHANNEL f1
NUC1 13C
P1 9.00 usec
PL1 -0.90 dB
PL1W 42.02801895 W
SFO1 100.6479784 MHz

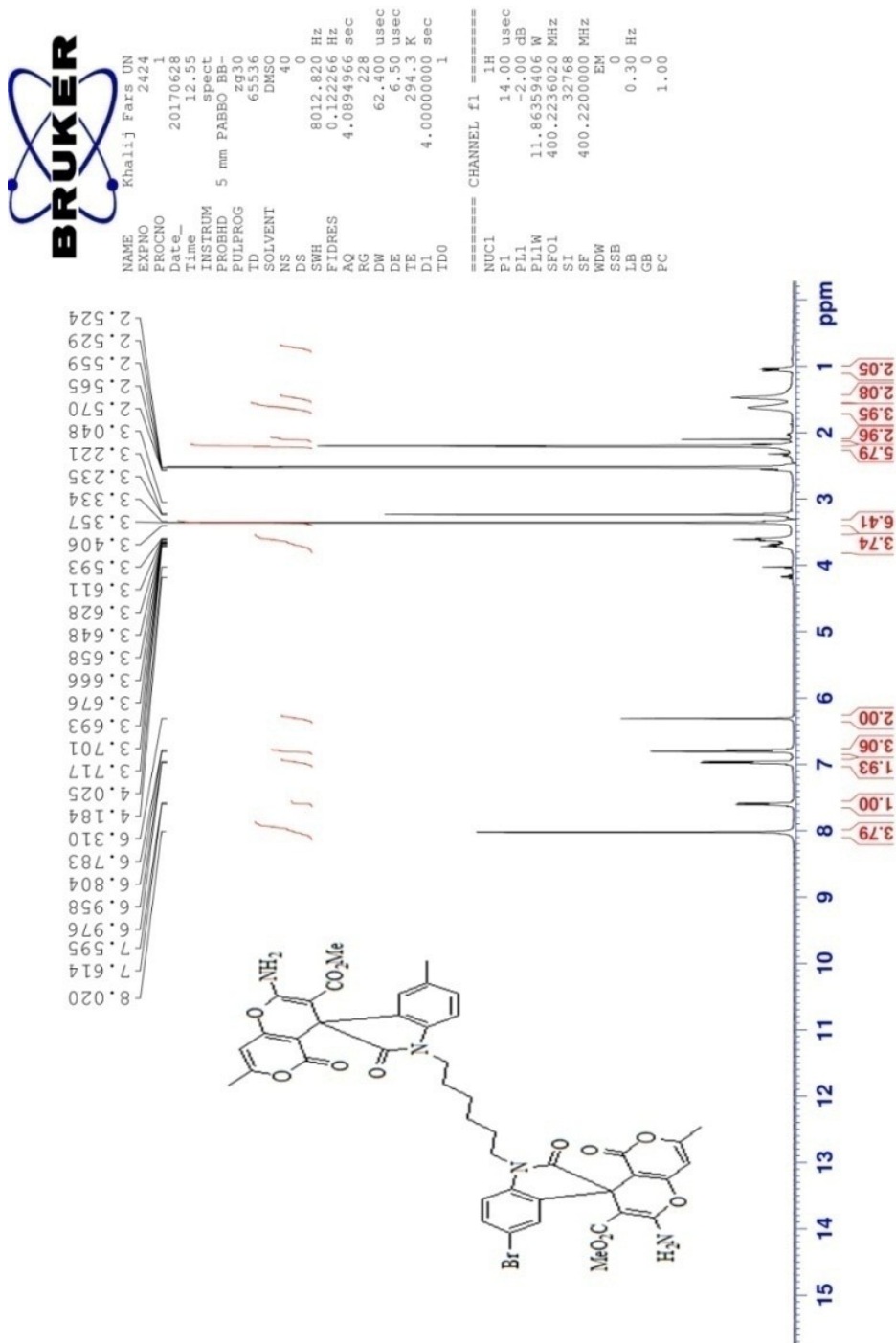
=====
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -2.00 dB
PL12 14.48 dB
PL13 17.90 dB
PL2W 11.86359406 W
PL12W 0.26681873 W
PL13W 0.12139934 W
SFO2 400.2216009 MHz
SI 32768
SF 100.6353990 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

179.29
179.18
168.89
168.82
161.23
161.19
161.15
144.95
142.59
137.63
137.46
136.21
136.19
133.91
130.92
130.74
129.57
126.12
125.57
124.94
119.68
119.57
114.01
113.95
76.58
62.40
59.04
51.06
46.60
44.98
40.60
40.39
39.98
39.77
39.56
39.35
32.06
28.31
27.11
24.97
14.36
14.12



ppm 0 50 100 150 200 250

methyl 2'-amino-1-(6-(2'-amino-3'-(methoxycarbonyl)-5,7'-dimethyl-2,5'-dioxo-5'H-spiro[indoline-3,4'-pyrano[4,3-b]pyran]-1-yl)hexyl)-5-bromo-7'-methyl-2,5'-dioxo-5'H-spiro[indoline-3,4'-pyrano[4,3-b]pyran]-3'-carboxylate **6f**



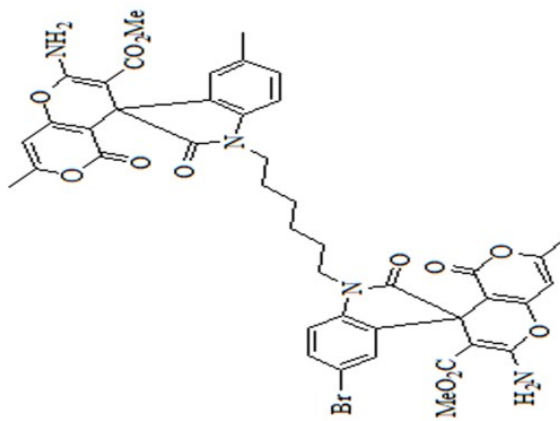


NAME: Khaliq Fars UN
EXPNO: 2453
PROCNO: 1
Date_ Time: 20170719 11.09
INSTRUM: spect
PROBHD: 5 mm PABBO BB-
PULPROG: zgpg30
TD: 65536
SOLVENT: DMSO
NS: 991
DS: 0
SWH: 35714.285 Hz
FIDRES: 0.544957 Hz
AQ: 0.9175540 sec
RG: 2050
DW: 14.000 usec
DE: 6.50 usec
TE: 293.4 K
D1: 1.00000000 sec
D11: 0.03000000 sec
TDO: 1

=====
CHANNEL f1
NUC1: 13C
P1: 9.00 usec
PL1: -0.90 dB
PL1W: 42.02801895 W
SF01: 100.6479784 MHz

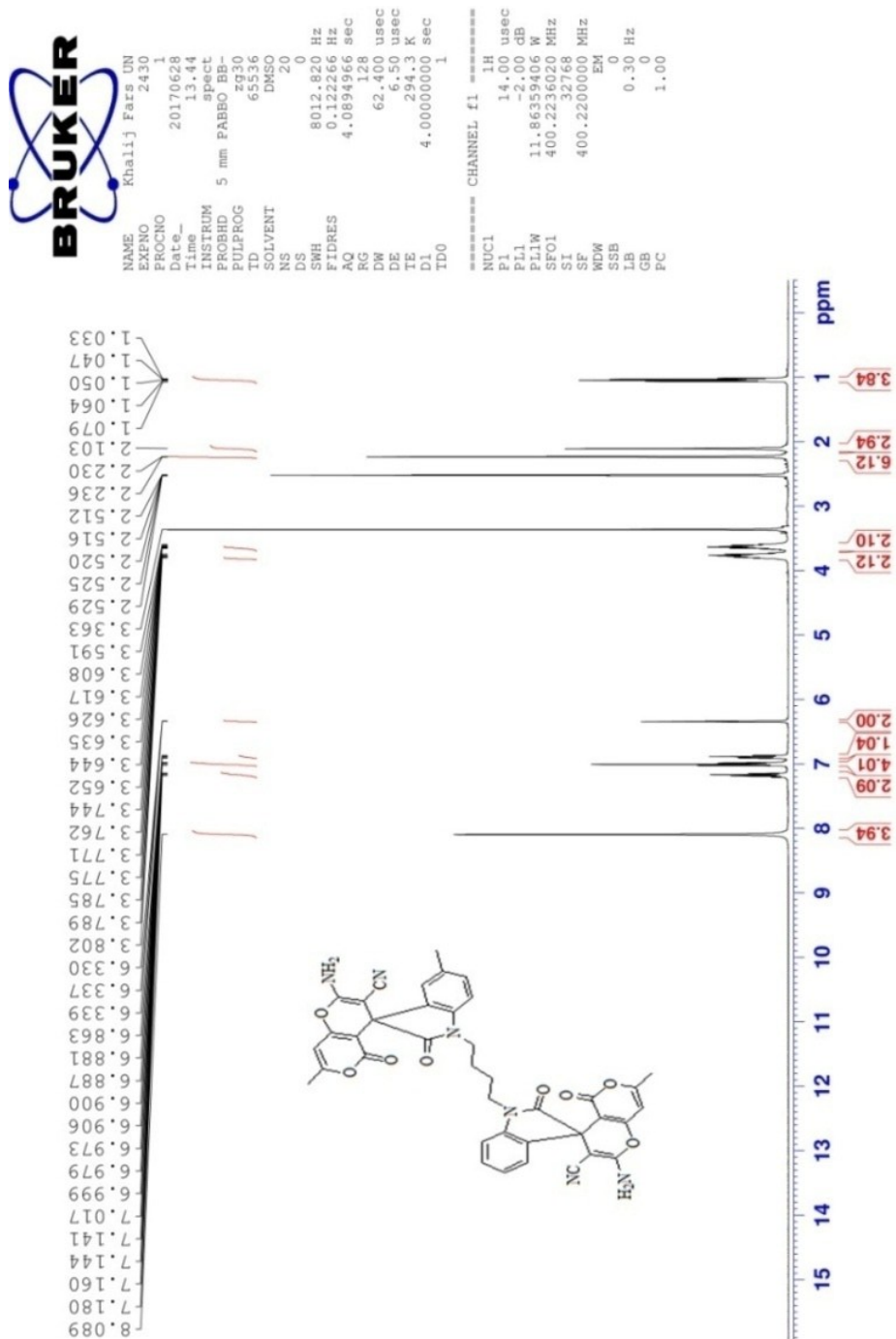
=====
CHANNEL f2
CFDPRG2: waltz16
NUC2: 1H
PCPD2: 90.00 usec
PL2: -2.00 dB
PL12: 14.48 dB
PL13: 17.90 dB
PL2W: 11.86359406 W
PL12W: 0.26681873 W
PL13W: 0.12139934 W
SF02: 400.2216009 MHz
SI: 32768
SF: 100.6353990 MHz
WDW: EM
SSB: 0
LB: 1.00 Hz
GB: 0
PC: 1.40

174.59
171.15
171.10
170.28
167.42
164.71
159.49
149.40
149.13
147.44
146.74
146.41
142.55
140.18
139.91
138.93
137.77
137.73
135.44
133.26
130.42
129.56
129.26
128.12
125.02
114.18
76.00
59.30
50.89
46.55
40.59
40.38
40.17
39.96
39.76
39.55
39.34
27.37
26.70
21.03
19.61
14.04

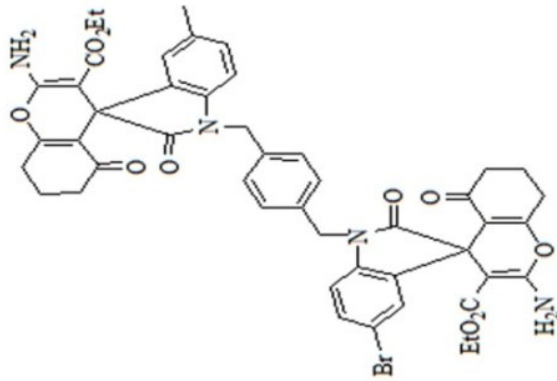


250 200 150 100 50 0 ppm

2'-amino-1-(4-(2'-amino-3'-cyano-5,7'-dimethyl-2,5'-dioxo-5'H-spiro[indoline-3,4'-pyrano[4,3-b]pyran]-1-yl)butyl)-7'-methyl-2,5'-dioxo-5'H-spiro[indoline-3,4'-pyrano[4,3-b]pyran]-3'-carbonitrile **6g**



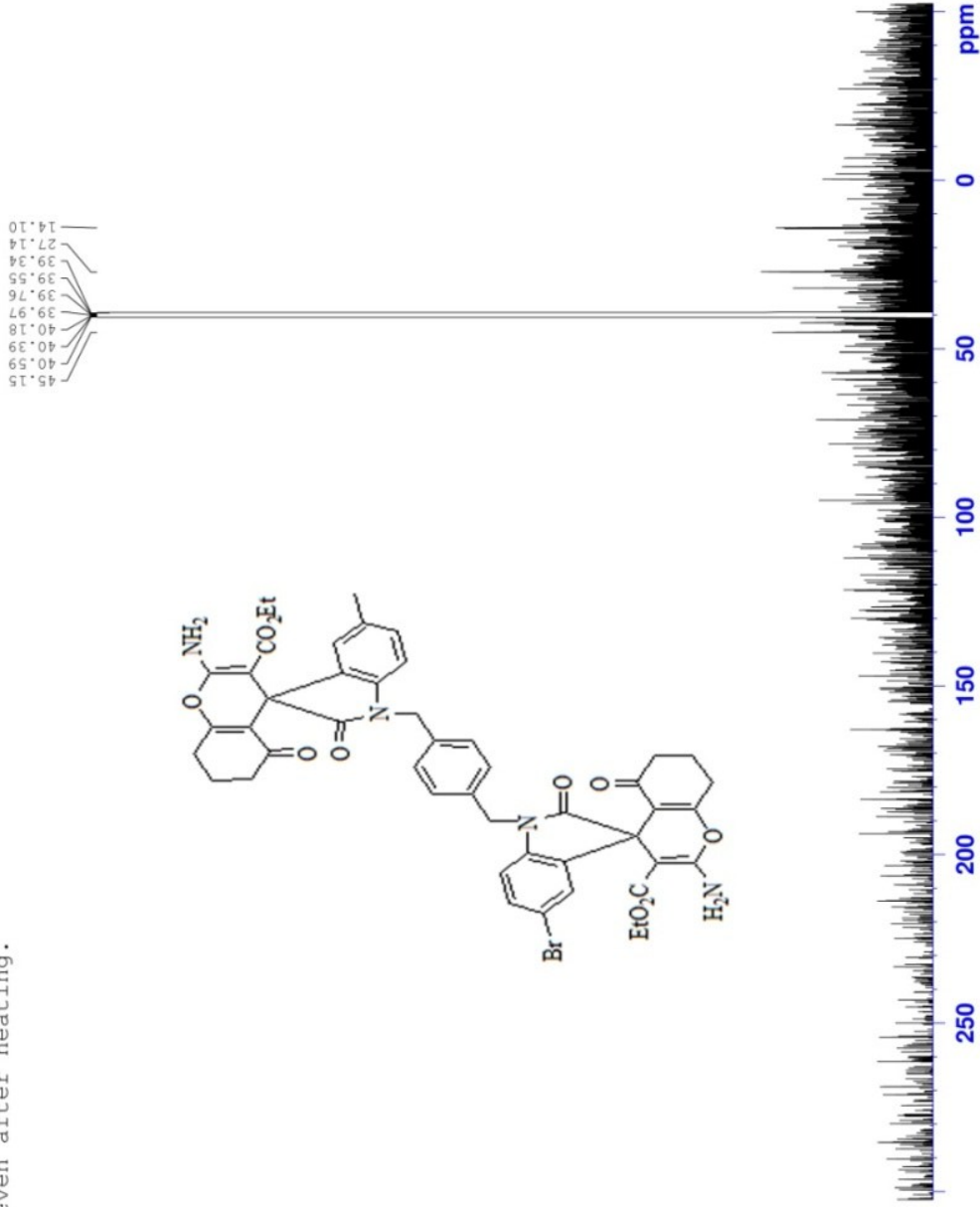
Sample solubility was too low for ¹³C-NMR even after heating.



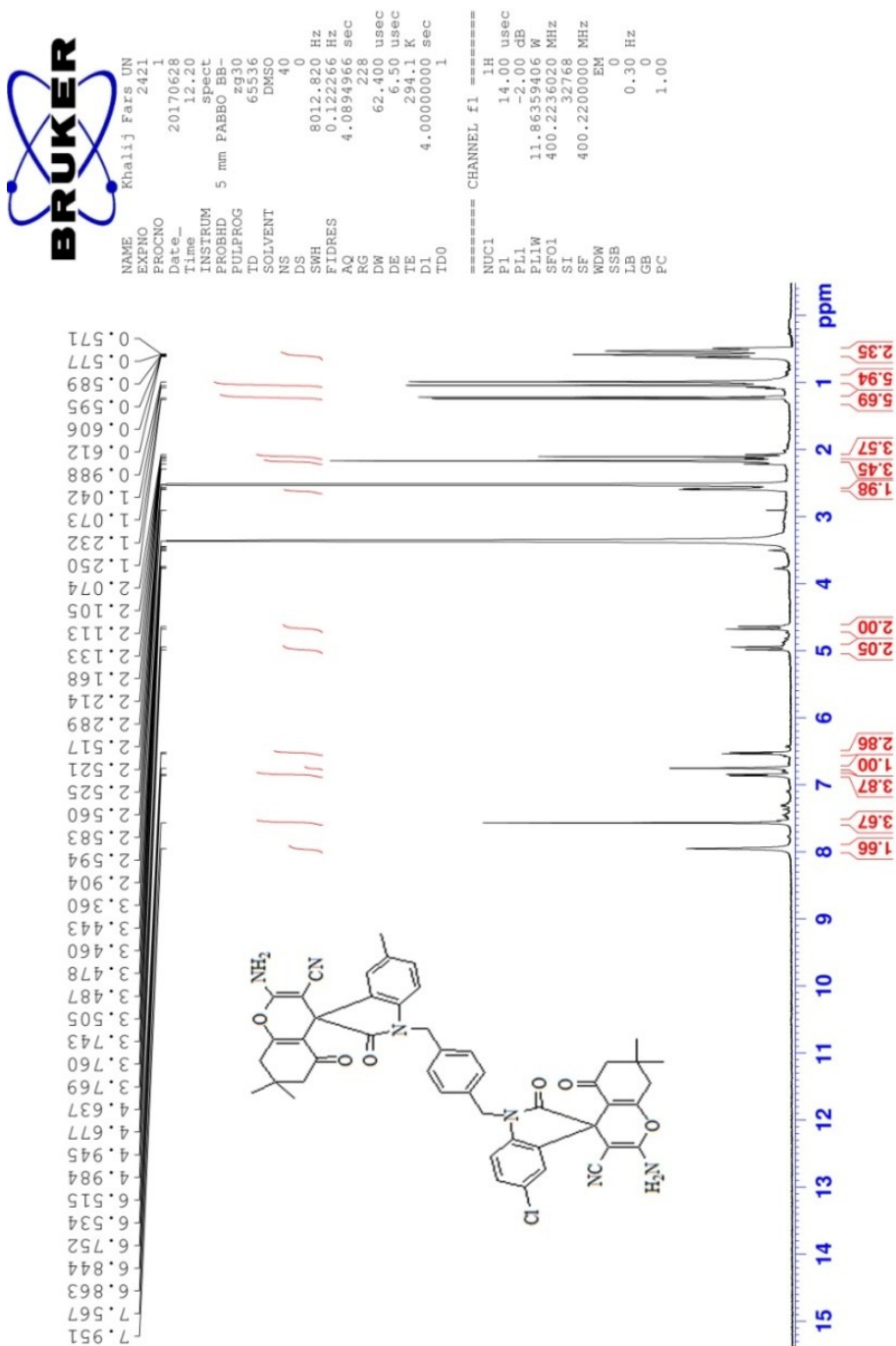
NAME Khalij Fars UN
 EXPNO 1
 PROCNO 2455
 Date_ 20170719
 Time 13.51
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zgpg30
 ID 65536
 SOLVENT DMSO
 NS 1598
 DS 0
 SWH 35714.285 Hz
 FIDRES 0.544957 Hz
 AQ 0.9175540 sec
 RG 2050
 DW 14.000 usec
 DE 6.50 usec
 TE 293.8 K
 D1 1.00000000 sec
 D11 0.03000000 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 ¹³C
 P1 9.00 usec
 PL1 -0.90 dB
 PL1W 42.02801895 W
 SF01 100.6479784 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 ¹H
 FCPD2 90.00 usec
 PL2 -2.00 dB
 PL12 14.48 dB
 PL13 17.90 dB
 PL2W 11.86359406 W
 PL12W 0.26681873 W
 PL13W 0.12139934 W
 SF02 400.2216009 MHz
 SI 32766
 SF 100.6353990 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40



2-amino-1'-(4-((2-amino-3-cyano-5',7,7-trimethyl-2',5-dioxo-5,6,7,8-tetrahydrospiro[chromene-4,3'-indolin]-1'-yl)methyl)benzyl)-5'-chloro-7,7-dimethyl-2',5-dioxo-5,6,7,8-tetrahydrospiro[chromene-4,3'-indoline]-3-carbonitrile **6i**





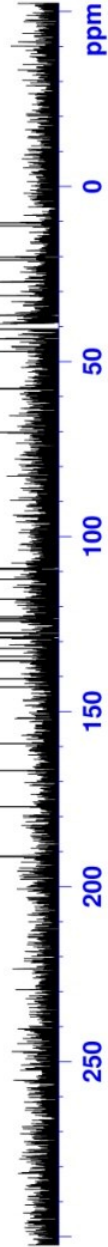
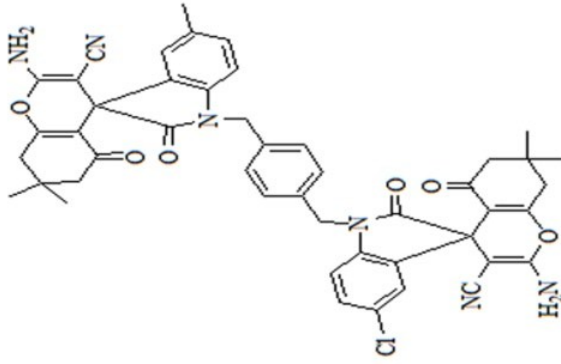
```

NAME      Khaliij Fars UN
EXPNO     1
PROCNO    1
Date_     20170718
Time      17.34
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zgpg30
TD         65536
SOLVENT   DMSO
NS         708
DS         0
SWH        35714.285 Hz
FIDRES     0.544957 Hz
AQ         0.9175540 sec
RG         2050
DE         14.000 usec
TE         294.1 K
D1         1.00000000 sec
D11        0.03000000 sec
TD0        1

===== CHANNEL f1 =====
NUC1       13C
P1         9.00 usec
PL1        -0.90 dB
PL1W       42.02801895 W
SFO1       100.6479784 MHz

===== CHANNEL f2 =====
CPDPRG2   waltz16
NUC2       1H
P2         90.00 usec
PL2        -2.00 dB
PL12       14.48 dB
PL13       17.90 dB
PL2W       11.86359406 W
PL12W      0.26681873 W
PL13W      0.12139934 W
SFO2       400.2216009 MHz
SI         32768
SF         100.6353990 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
  
```

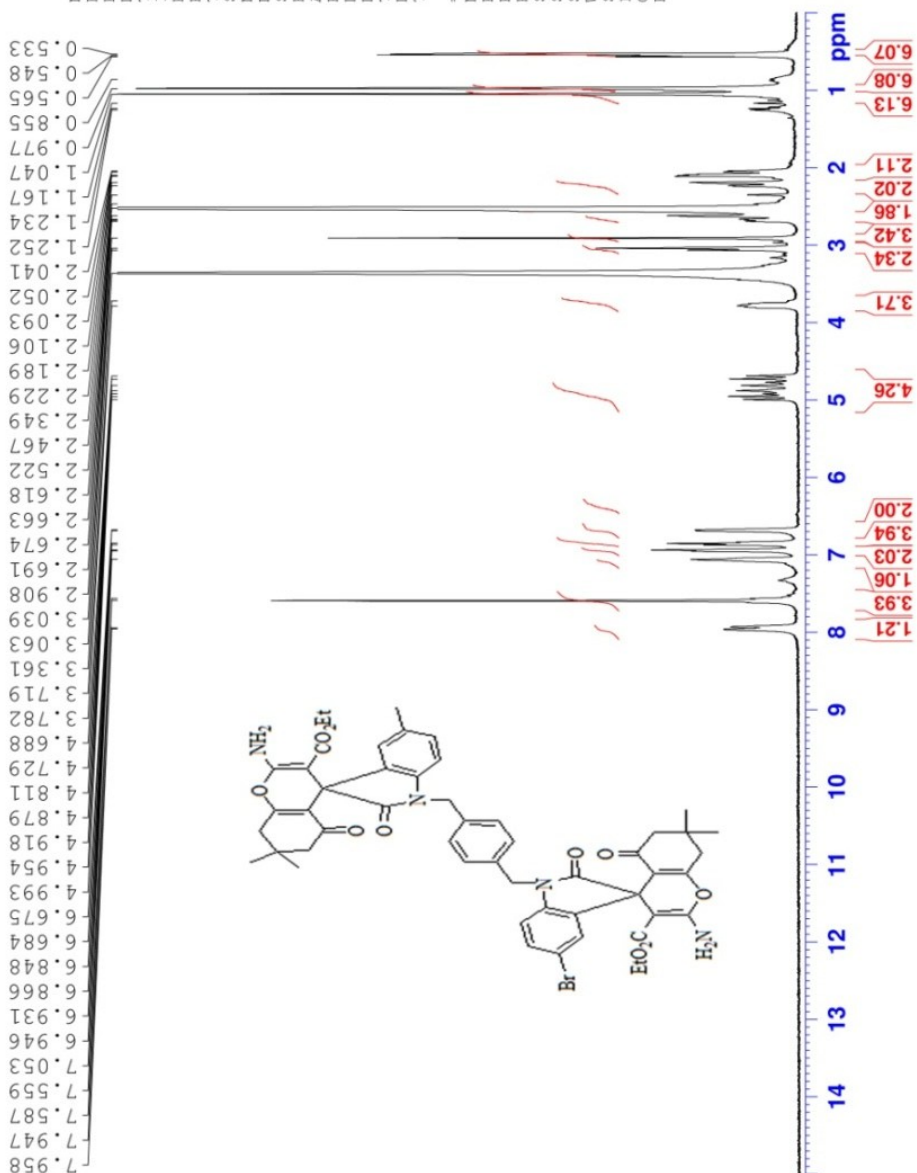
192.54
192.54
177.27
177.16
166.88
166.83
159.23
159.22
159.19
143.01
140.64
135.63
135.43
134.21
134.18
131.99
128.92
128.78
127.55
124.21
123.57
122.99
117.93
117.88
112.28
112.20
109.33
109.33
109.09
70.33
57.95
57.73
47.17
47.11
43.54
40.60
40.39
40.18
39.97
39.77
39.56
39.39
36.67
31.23
27.32
21.22
20.20
11.33
10.43



ethyl 2-amino-1'-(4-((2-amino-3-(ethoxycarbonyl)-5',7,7-trimethyl-2',5-dioxo-5,6,7,8-tetrahydrospiro[chromene-4,3'-indolin]-1'-yl)methyl)benzyl)-5'-bromo-7,7-dimethyl-2',5-dioxo-5,6,7,8-tetrahydrospiro[chromene-4,3'-indoline]-3-carboxylate **6j**



NAME Khallij Fars UN
 EXPNO 1
 PROCNO 2420
 Date_ 20170628
 Time 12.13
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zg30
 TD 65536
 SOLVENT DMSO
 NS 20
 DS 0
 SWH 8012.820 Hz
 FIDRES 0.122266 Hz
 AQ 4.0894966 sec
 RG 228
 DW 62.400 usec
 DE 6.50 usec
 TE 294.3 K
 D1 4.0000000 sec
 TD0 1
 ===== CHANNEL f1 =====
 NUC1 1H
 P1 14.00 usec
 PL1 -2.00 dB
 PLLW 11.86359406 W
 SF01 400.2236020 MHz
 SI 32768
 SF 400.2200000 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

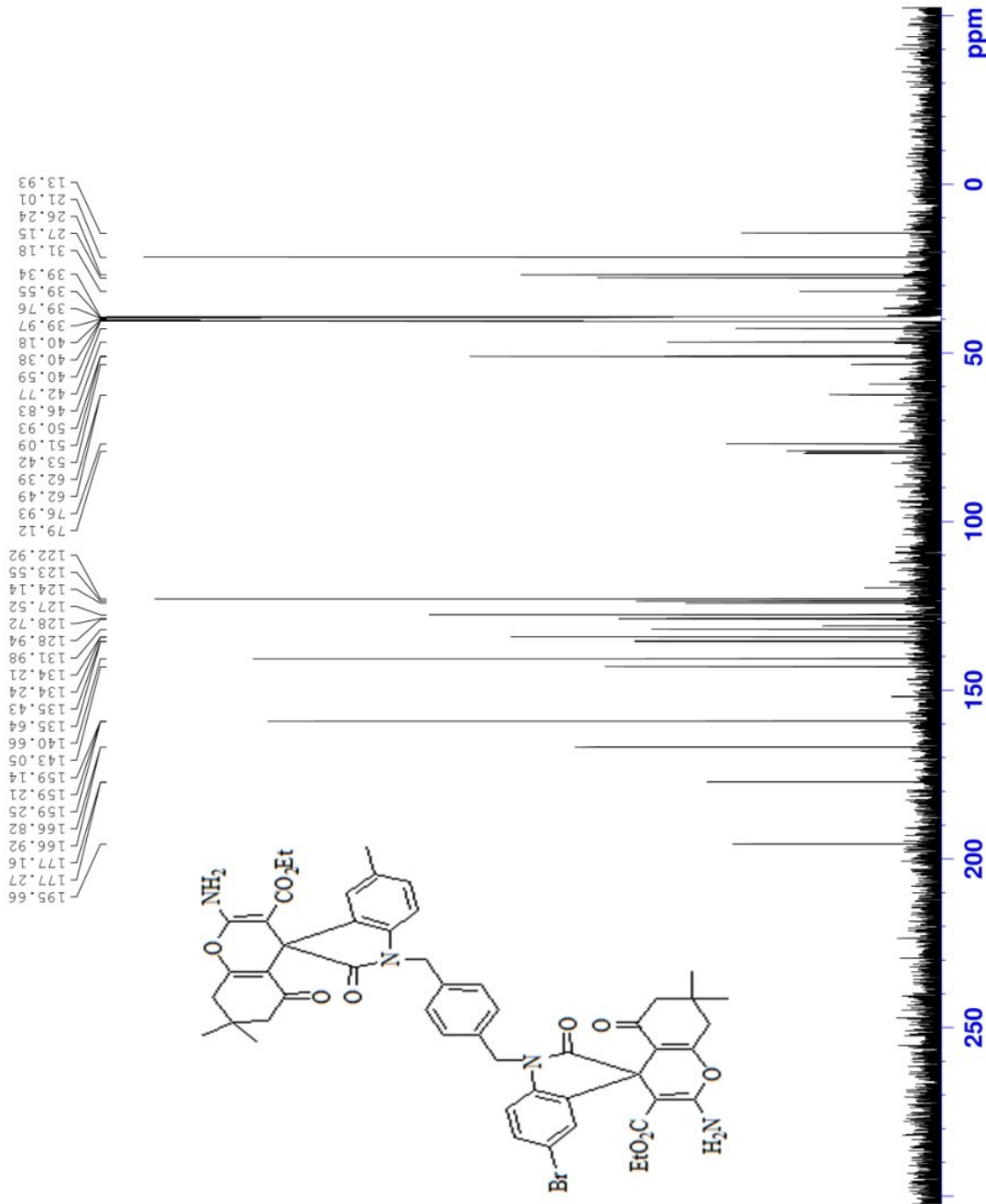




NAME Khaliq Fars UN
 EXPNO 1
 PROCNO 2451
 Date_ 20170719
 Time 8.33
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zgpg30
 TD 65536
 SOLVENT DMSO
 NS 1302
 DS 0
 SWH 35714.285 Hz
 FIDRES 0.544957 Hz
 AQ 0.9175540 sec
 RG 2050
 DW 14.000 usec
 DE 6.50 usec
 TE 293.1 K
 D1 1.00000000 sec
 D11 0.03000000 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 13C
 P1 9.00 usec
 PL1 -0.90 dB
 PL1W 42.02801895 W
 SF01 100.6479784 MHz

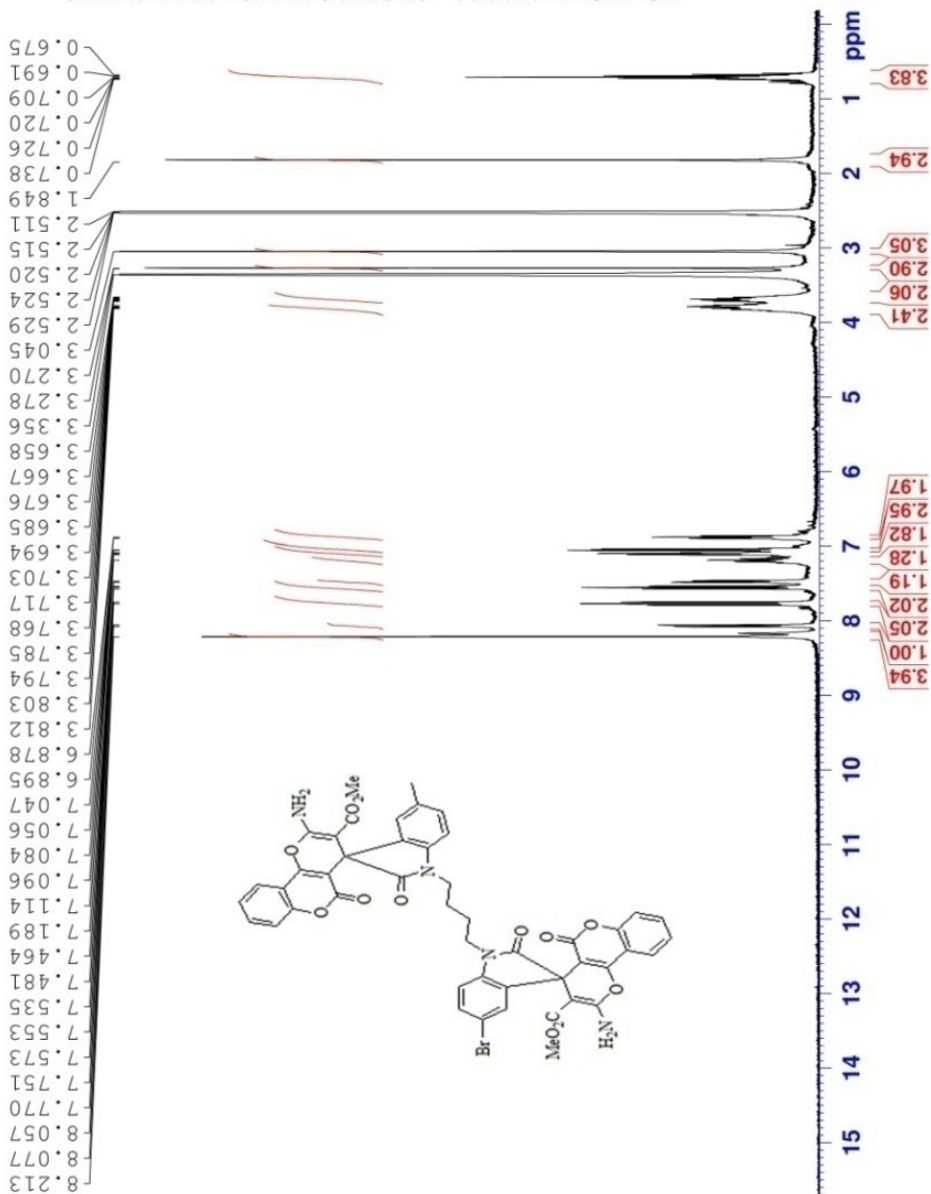
===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 90.00 usec
 PL2 -2.00 dB
 PLI2 14.48 dB
 PLI3 17.90 dB
 PL2W 11.86359406 W
 PL12W 0.26681873 W
 PL13W 0.12139934 W
 SFO2 400.2216009 MHz
 SI 32768
 SF 100.6353990 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40



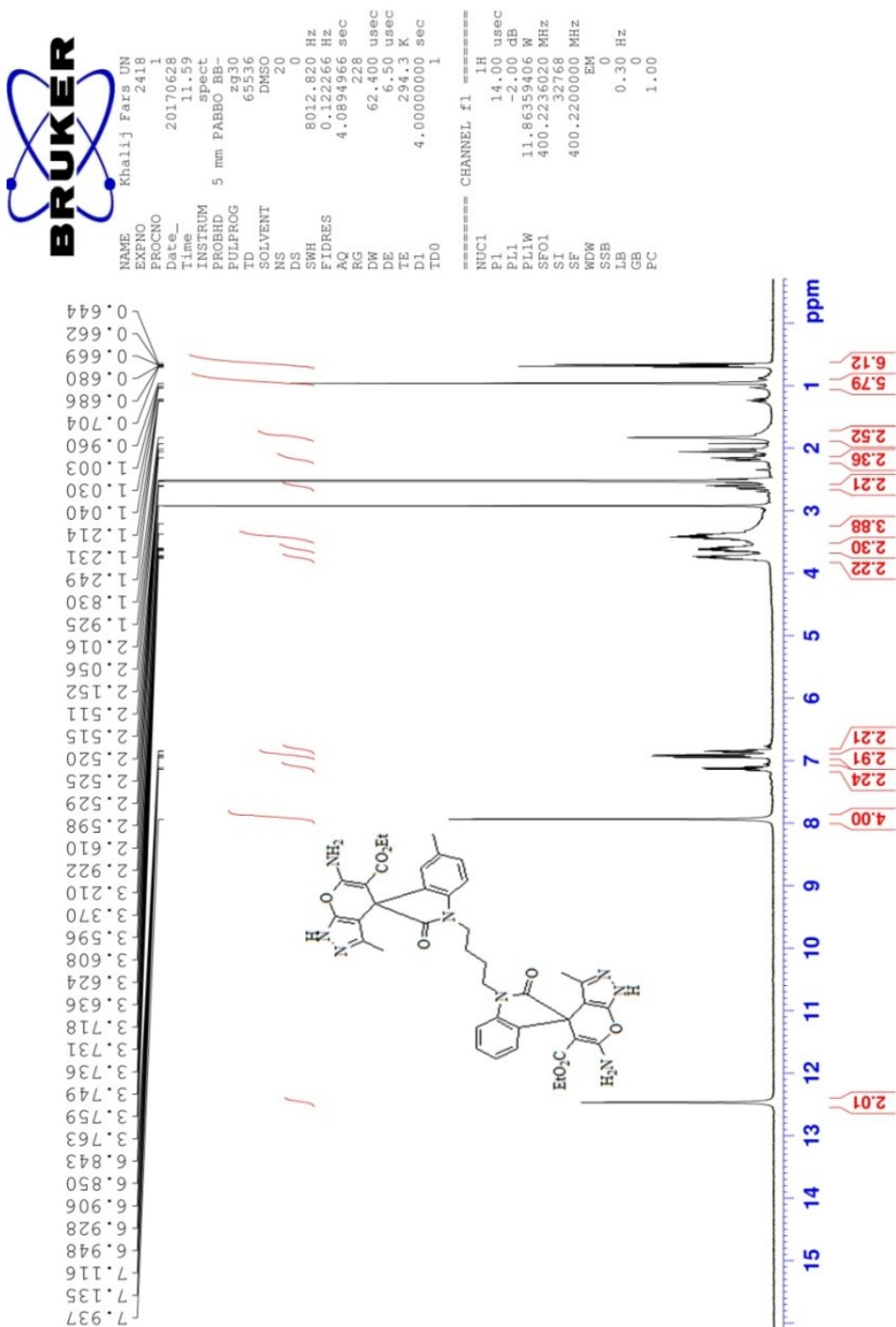
methyl 2'-amino-1-(4-(2'-amino-3'-(methoxycarbonyl)-5-methyl-2,5'-dioxo-5'H-spiro[indoline-3,4'-pyrano[3,2-c]chromen]-1-yl)butyl)-5-bromo-2,5'-dioxo-5'H-spiro[indoline-3,4'-pyrano[3,2-c]chromene]-3'-carboxylate **6k**



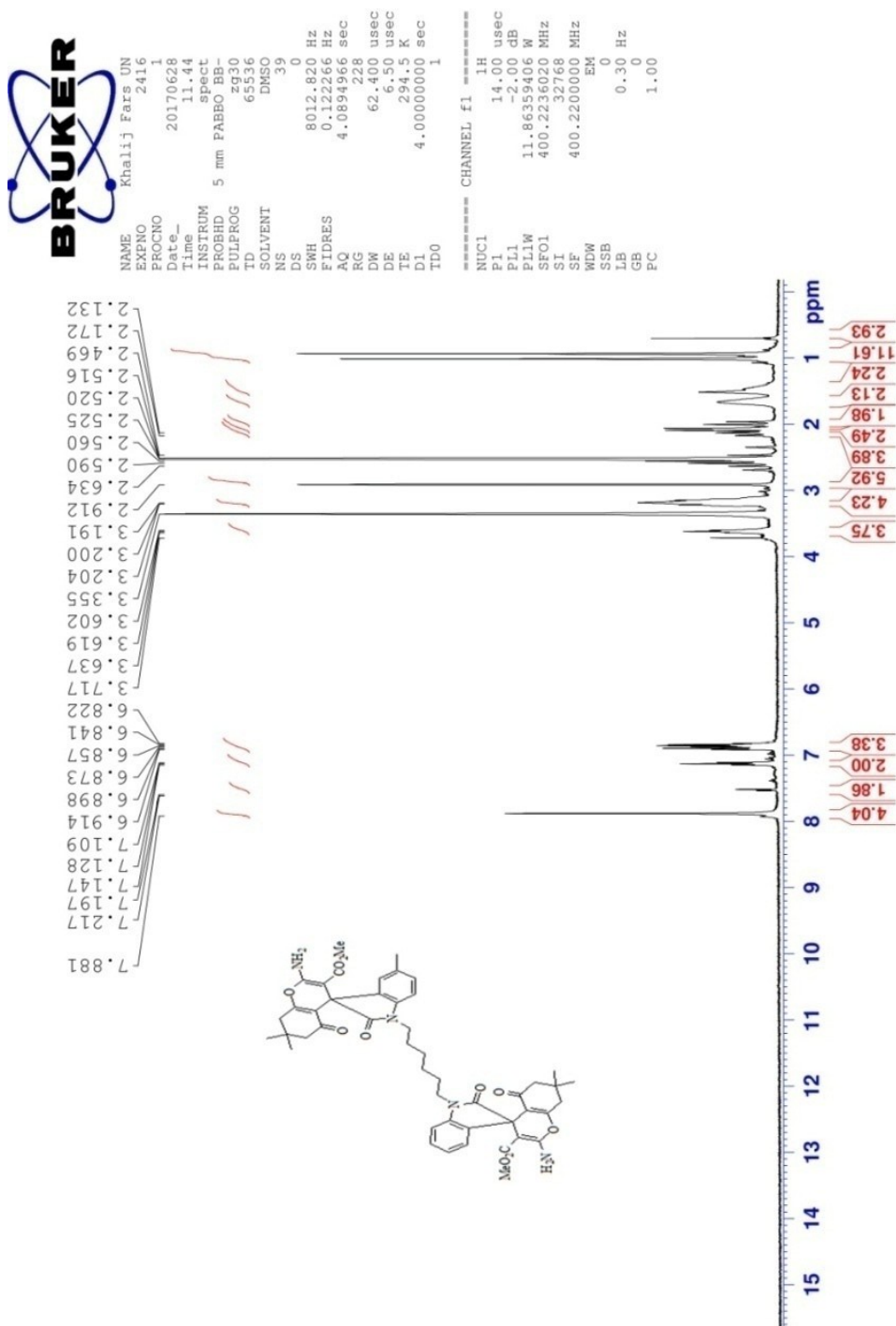
NAME Khalij Fars UN
 EXPNO 2419
 PROCNO 1
 Date_ 20170628
 Time_ 12.06
 INSTRUM spect
 PROBHID 5 mm PABBO BB-
 PULPROG zg30
 ID 65536
 SOLVENT DMSO
 NS 20
 DS 0
 SWH 8012.820 Hz
 FIDRES 0.122266 Hz
 AQ 4.0894966 sec
 RG 228
 DW 62.400 usec
 DE 6.50 usec
 TE 294.3 K
 D1 4.0000000 sec
 TD0 1
 ===== CHANNEL f1 =====
 NUC1 1H
 P1 14.00 usec
 PL1 -2.00 dB
 PL1W 11.86359406 W
 SF01 400.2236020 MHz
 SI 32768
 SF 400.2200000 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



ethyl 6'-amino-1-(4-(6'-amino-5'-(ethoxycarbonyl)-3',5-dimethyl-2-oxo-1'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazol]-1-yl)butyl)-3'-methyl-2-oxo-1'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-5'-carboxylate **6l**



methyl 2-amino-1'-(6-(2-amino-3-(methoxycarbonyl)-5',7,7-trimethyl-2',5-dioxo-5,6,7,8-tetrahydrospiro[chromene-4,3'-indolin]-1'-yl)hexyl)-7,7-dimethyl-2',5-dioxo-5,6,7,8-tetrahydrospiro[chromene-4,3'-indoline]-3-carboxylate **6m**





NAME: Khalij Fars UN
EXPNO: 2454
PROCNO: 1
Date_ Time: 20170719 11:46
INSTRUM: spect
PROBHD: 5 mm PABBO BB-
PULPROG: zgpg30
TD: 65536
SOLVENT: DMSO
NS: 3624
DS: 0
SWH: 35714.285 Hz
FIDRES: 0.544957 Hz
AQ: 0.9175540 sec
RG: 2050
DW: 14.000 usec
DE: 6.50 usec
TE: 293.5 K
D1: 1.00000000 sec
D11: 0.03000000 sec
TD0: 1

===== CHANNEL f1 =====
NUC1: 13C
P1: 9.00 usec
PL1: -0.90 dB
PL1W: 42.02801895 W
SFO1: 100.6479784 MHz

===== CHANNEL f2 =====
CPDPRG2: waltz16
NUC2: 1H
PCPD2: 90.00 usec
PL2: -2.00 dB
PL12: 14.48 dB
PL13: 17.90 dB
PL2W: 11.86359406 W
PL12W: 0.26681873 W
PL13W: 0.12139934 W
SFO2: 400.2216009 MHz
SI: 32768
SF: 100.6353990 MHz
WDW: EM
SSB: 0
LB: 1.00 Hz
GB: 0
PC: 1.40

