Supporting Information for

Gold-catalyzed Michael Addition/Intramolecular Annulation Cascade: an Effective Pathway for the Chemoselective- and Regioselective Synthesis of Tetracyclic Indole Derivatives in Water

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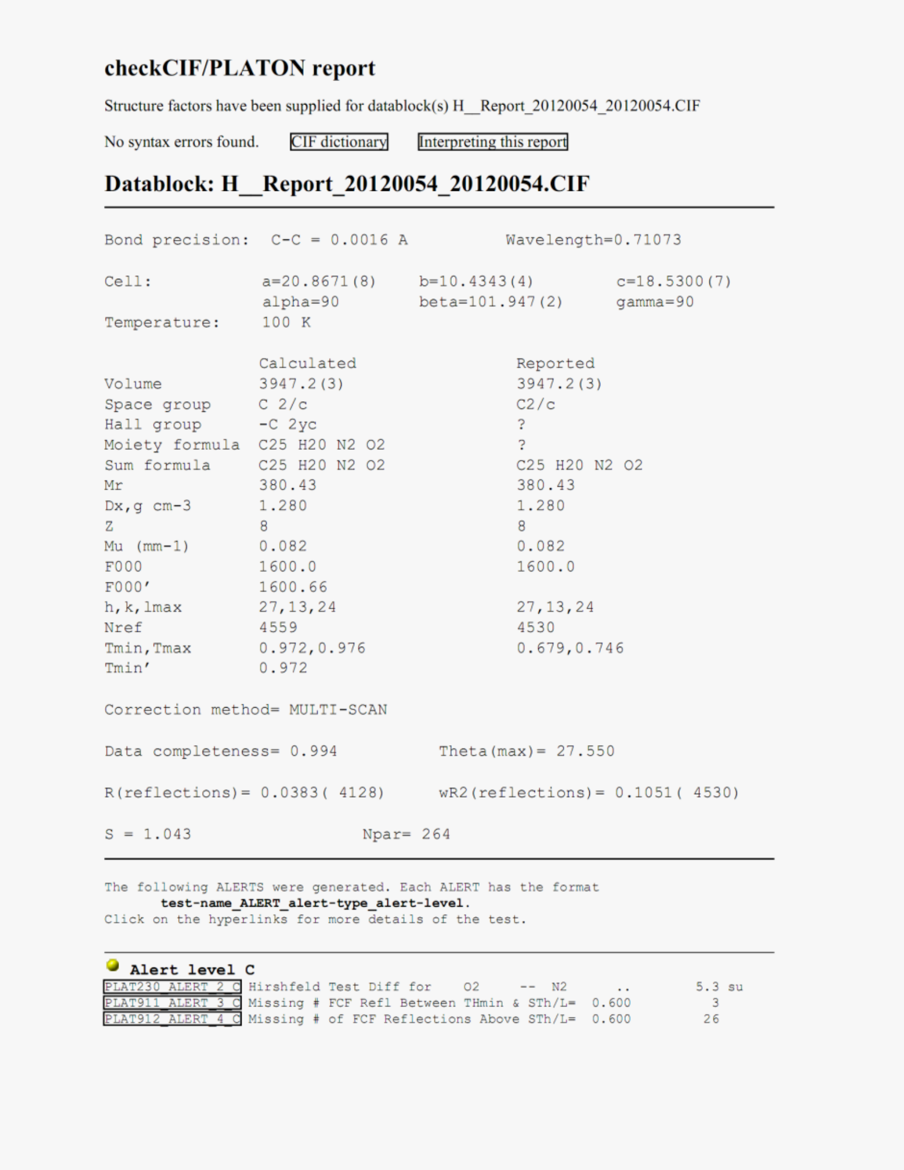
X-ray crystallographic structure of compound 3Ba



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Temperature:     100 K

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Hall group      -C 2yc                    ?
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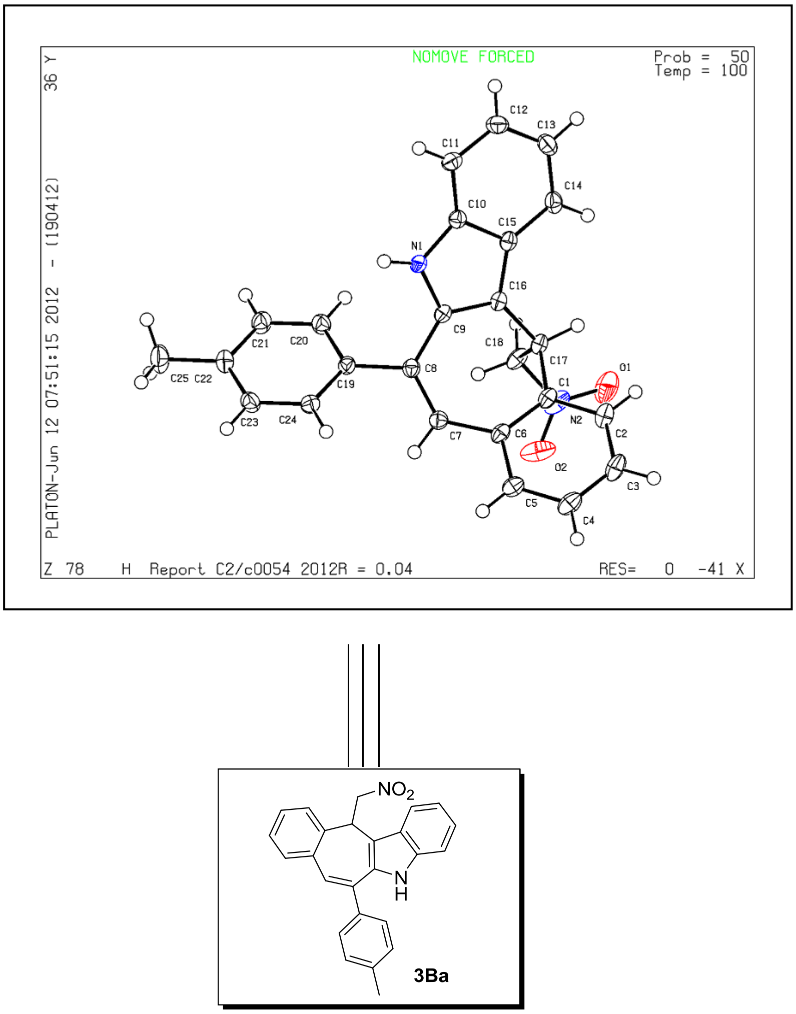


X-ray crystallographic structure of compound 3Ba

CCDC 894928 contains the supplementary crystallographic data for this paper. These data can be also obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

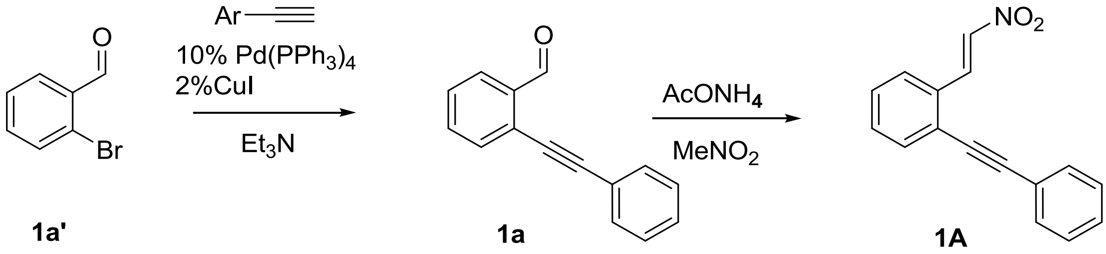
General Information

Commercially available reagents and solvents were used without further purification. Column chromatography was carried out on silica gel. ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra were obtained on Varian Mercury-400 and/or Varian Mercury-500 spectrometers (TMS as IS). Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), quartet (q), double doublet (dd), multipet (m) and broad (br). Low- and high-resolution mass spectra (LRMS and HRMS) were measured on

Finnigan MAT 95 spectrometer.

General Procedures for the Synthesis of Starting Materials

General Procedure for Synthesis of (*E*)-1-(2-nitrovinyl)-2-(phenylethynyl) Benzene (1A)



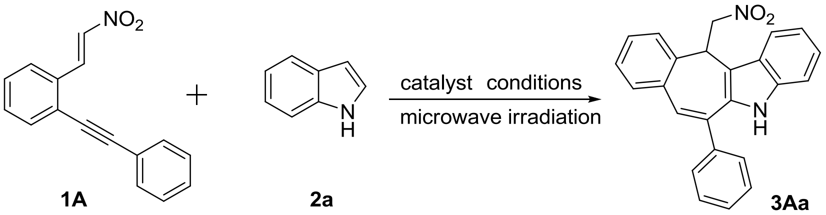
A dry round bottom flask was charged with 2-bromobenzaldehyde (5.0g, 27.0mmol, 1equiv.), CuI (0.103g, 0.54mmol, 0.02equiv.) and $Pd(PPh_3)_4$ (3.13g, 2.7mmol, 0.1equiv.). This mixture was then subjected to three purge cycles of vacuum and argon gas. 30 mL of Et_3N and phenylacetylene (5.52g, 54.0mmol, 2equiv.) were added to the reaction mixture and allowed to stir at 60°C for 2h. The reaction mixture was then diluted with ether and water. The aqueous phase was extracted three times with ether. The concentrated organic phases were dried over Na_2SO_4 and concentrated in vacuo. **1a** was obtained by flash column chromatography of the crude product (pure pentane) to yield a yellow liquid (5.09g, 24.68 mmol, 91%).

The titled compound **1A** was prepared according to the literature procedure[1]. A solution of **1a** (1g, 4.85mmol, 1equiv.) and ammonium acetate (448mg, 5.82 mmol, 1.2equiv.) in dry nitromethane (5.0 mL) was stirred at 100°C for 1h. After concentration, the residue was partitioned between EtOAc and water. The aqueous layer was extracted with EtOAc, and the combined organic layers were washed with water and brine, dried over Na_2SO_4 and concentrated. Column chromatography (EtOAc:*n*-hexane = 1/100, v/v) to give the titled product **1A** (1.08g, 89%) as a light yellow solid.

Reference:

[1] A. Poschalko, S. Welzig, M. Treu, S. Nerdinger, K. Mereiter and U. Jordis, *Tetrahedron*, 2002, **58**, 1513-1518.

Table 1S. Optimization of the reaction conditions[a]

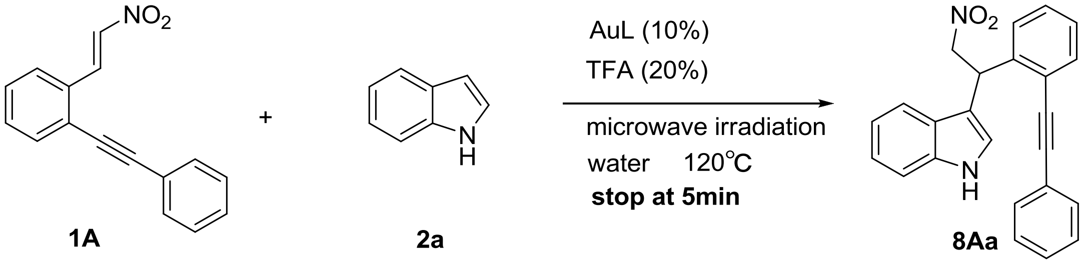


Entry	Catalyst system	Additive	Solvent	Yield (%)
1	Au catalyst I	DBSA[b]	H_2O	0
2	AuCl	TFA	H_2O	43
3	$AuBr_3$	TFA	H_2O	57
4	Au catalyst I	TFA	H_2O	59[c]

[a] *Reaction conditions*: 1A (0.2 mmol), 2a (0.3 mmol), catalyst (0.02 mmol), additive (0.04 mmol), water (3 mL) under 120°C for 20 min. [b] DBAS= Dodecyl benzenesulfonic acid. [c] Reaction was performed at 120°C in water using oil bath for 14h.

Characterization of the Michael Addition Intermediate 8Aa

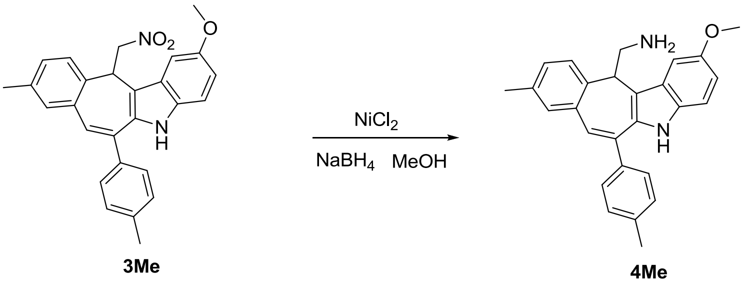
3-(2-nitro-1-(2-(phenylethynyl) phenyl) ethyl)-1H-indole (8Aa)



To a mixture of (*E*)-1-(2-nitrovinyl)-2-(phenylethynyl)benzene (**1A**, 0.2 mmol) and indole (**2a**, 0.3 mmol) in 3 mL of H_2O was added Au catalyst I (0.02 mmol) and trifluoroethanoic acid (0.04 mmol). The reaction vial was sealed and the mixture was then irradiated at 120°C for 5 min. After the reaction was cooled to ambient temperature, the mixture was concentrated in vacuum, and the resulting residue was purified by flash chromatography (petroleum ether/ethyl acetate = 10/1, v/v) to afford the expected product **8Aa** (46mg, 62%) as light yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.62-7.60 (m, 3H), 7.48-7.46 (d, *J* = 8.0 Hz, 1H), 7.36-7.35 (m, 4H), 7.26-7.18 (m, 5H), 7.05 (t, *J* = 7.6 Hz, 1H), 5.95 (dd, *J* = 9.6, 6.4 Hz, 1H), 5.13-5.03 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.6, 136.5, 132.7, 131.7, 128.8, 128.6, 128.5, 127.6, 127.4, 126.5, 122.8, 122.8, 122.7, 121.7, 119.9, 119.2, 113.7, 111.3, 95.3, 86.8, 78.4, 39.5; LRMS (ESI) *m/z* 367 $(M+H)^+$.

Derivatization of Product 3Me

2-Methoxy-9-methyl-6-(*p*-tolyl)-5,12-dihydrobenzo[4,5]cyclohepta[1,2-*b*]indol-12-yl) methanamine (4Me)



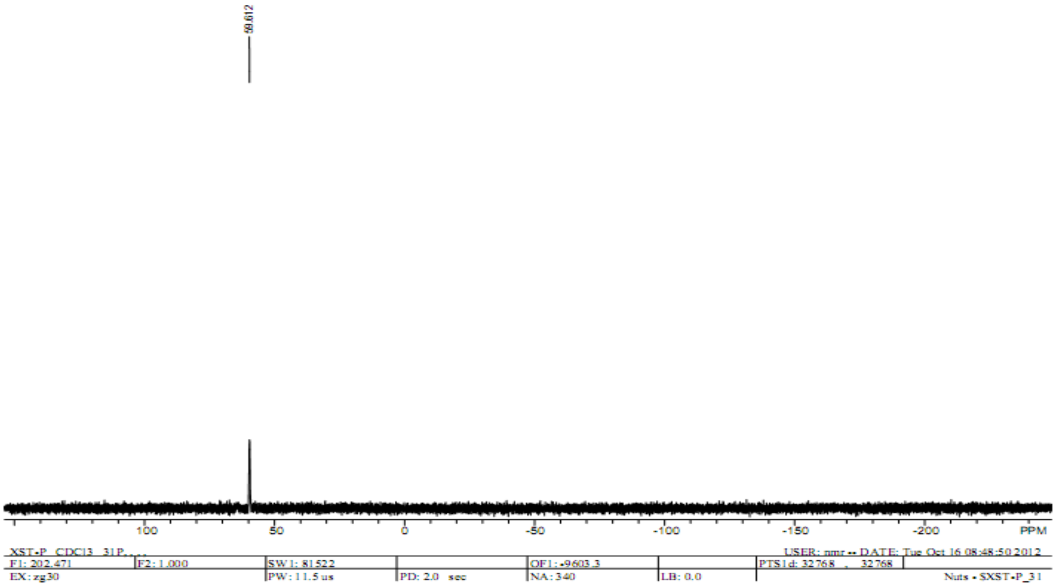
To a suspension of **3Me** (51.0 mg, 0.12 mmol, 1equiv.), $NiCl_2$ (15.6 mg, 0.12 mmol, 1 equiv.) in 5 mL MeOH was added $NaBH_4$ (22.7 mg, 0.60 mmol, 5 equiv.) at 0 °C for 1h. The reaction mixture was then quenched with saturated NH_4Cl solution and extracted with CH_2Cl_2. The combined organic phases was washed with brine and dried over $MgSO_4$. The concentrated organic fractions was then purified by flash column chromatography (DCM/MeOH = 15/1, v/v) to yield a yellow solid (32.0 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.48-7.46 (m, 2H), 7.29-7.26 (m, 5H), 7.18-7.07 (m, 2H), 6.92 (s, 1H), 6.81-6.79 (m, 1H), 4.47 (t, J = 8.0 Hz, 1H), 3.89 (s, 3H), 2.98 (d, J = 7.6 Hz, 2H), 2.44 (s, 3H), 2.35 (s, 3H), 2.25-2.15 (br, 2H); LRMS (ESI) m/z 395 [M + H]+.

Stability test of Au catalyst I

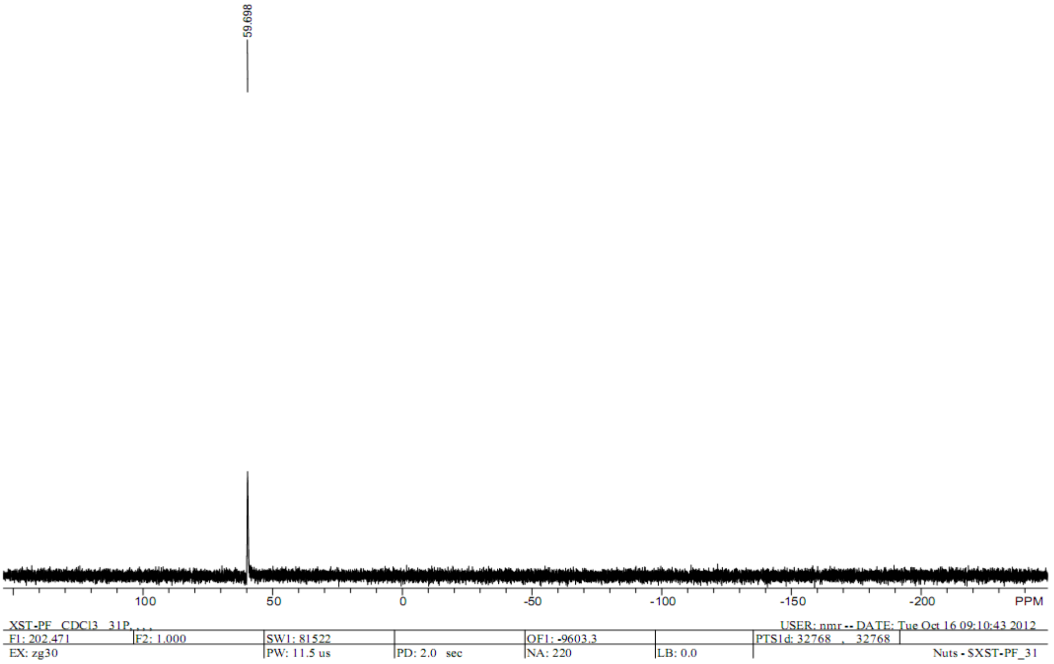
Experiments were conducted to detect the stability of the Au catalyst I at high temperature: Au catalyst I+TFA were heated at 140°C for 30min, and followed by ^{31}P NMR. As references, the ^{31}P of the pure Au catalyst I and Au catalyst I+TFA at room temperature are measured.

Comparing ^{31}P NMR of three spectrums shows Au catalyst I did not decompose and generate any leaching of the ligand in the presence of TFA at high temperature.

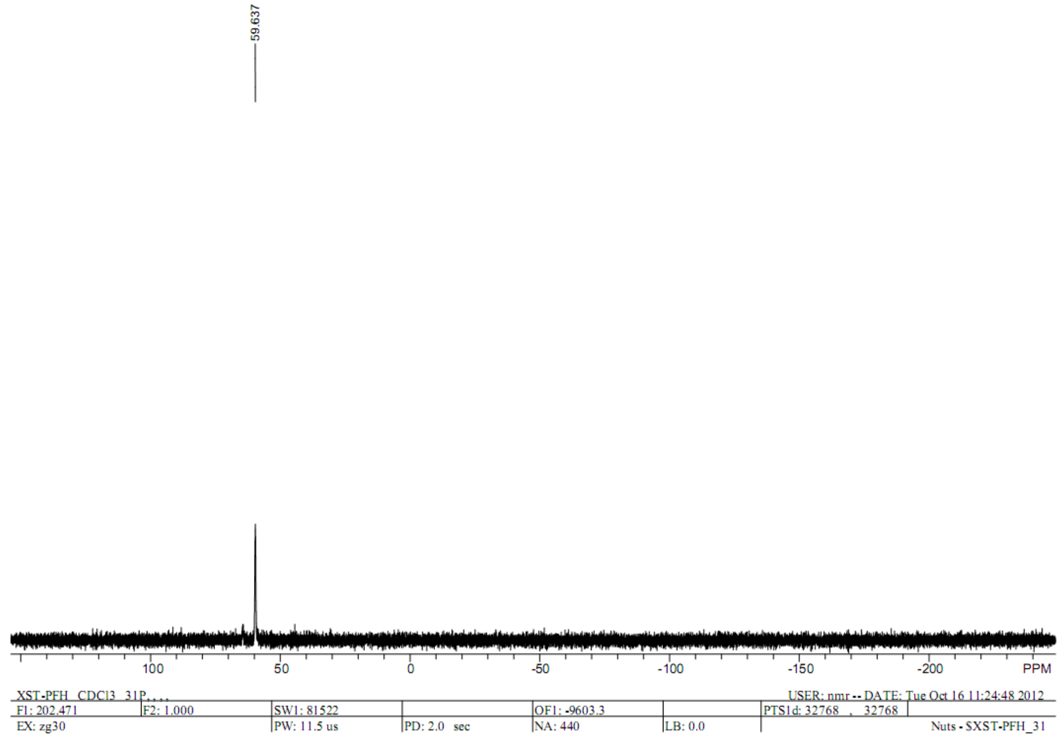
a) ^{31}P NMR of pure Au catalyst I at room temperature



b) ^{31}P NMR of Au catalyst I and TFA at room temperature

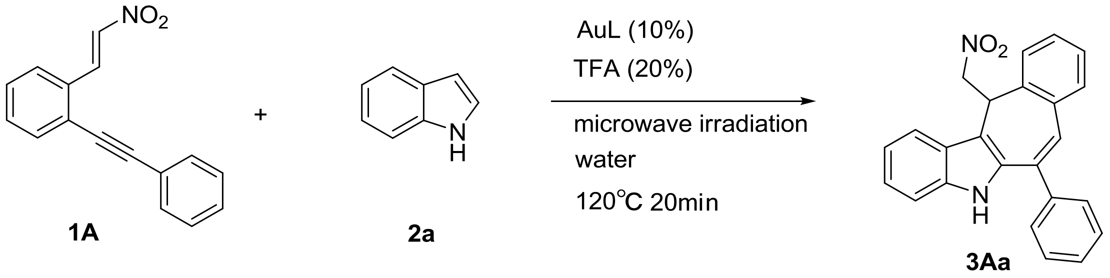


c) ^{31}P NMR of Au catalyst I and TFA at 140 °C for 30min



General Procedure for Synthesis of 3Aa-3Mk

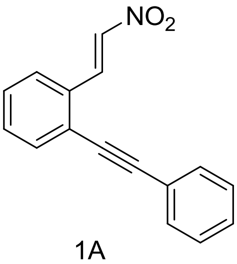
Typical procedure for synthesis of the 12-(Nitromethyl)-6-phenyl-5, 12-dihydrobenzo [4,5]cyclohepta[1,2-*b*]indoles (3Aa as an Example) in water.



To a mixture of (*E*)-1-(2-nitrovinyl)-2-(phenylethynyl)benzene (**1A**, 0.2 mmol) and indole (**2a**, 0.3 mmol) in 3 mL of H_2O was added Au catalyst I (0.02 mmol) and trifluoroethanoic acid (0.04 mmol). The reaction vial was sealed and the mixture was then irradiated at 120°C for 20 min. After cooling to ambient temperature, the mixture was concentrated in vacuum, and the resulting residue was purified by flash chromatography (petroleum ether/ethyl acetate = 10/1, v/v) to afford the expected product **3Aa** (64 mg, 87%) as white solid.

Characterization Data for Starting Materials

(*E*)-1-(2-nitrovinyl)-2-(phenylethynyl) benzene (1A)

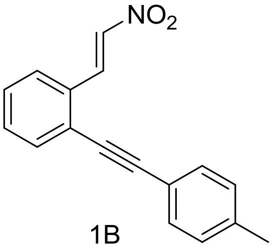


1A

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.55 (d, *J* = 13.6 Hz, 1H), 7.80 (d, *J* = 13.6 Hz, 1H), 7.65-7.58 (m, 4H), 7.49-7.42 (m, 1H), 7.40-7.38 (m, 4H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 137.8, 136.7, 132.8, 131.2, 131.1, 131.0, 130.7, 128.7, 128.3, 128.1, 127.3, 124.8, 121.8, 96.5, 85.9, 76.5; LRMS (ESI) *m/z* 250 (M+H)$^+$.

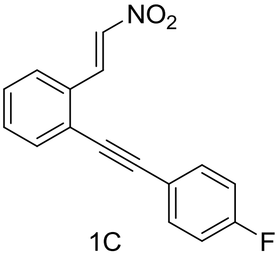
(*E*)-1-(2-nitrovinyl)-2-(*p*-tolylethynyl) benzene (1B)

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.56 (d, *J* = 13.6 Hz, 1H), 7.81 (d, *J* = 13.6 Hz, 1H), 7.64-7.58 (m, 2H), 7.53-7.42 (m, 3H), 7.40-7.34 (m, 1H), 7.23-7.19 (m, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 139.4, 138.1, 137.2, 133.2, 131.5, 131.4, 131.1, 129.3, 128.5, 127.8, 125.5, 119.1, 97.3, 85.9, 21.6; LRMS (ESI) *m/z* 264 (M+H)$^+$.



1B

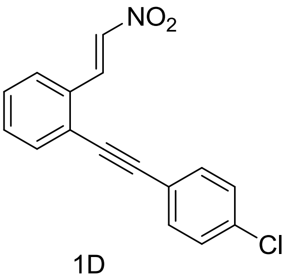
(*E*)-1-((4-fluorophenyl) ethynyl)-2-(2-nitrovinyl) benzene (1C)



1C

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.53 (d, *J* = 13.5 Hz, 1H), 7.79 (d, *J* = 13.5 Hz, 1H), 7.67-7.55 (m, 4H), 7.52-7.44 (m, 2H), 7.14-7.08 (m, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 164.0 (d, *J* = 278 Hz), 138.3, 137.1, 133.7(d, *J* = 8 Hz), 133.3 (d, *J* = 8 Hz), 131.6, 131.2, 128.3, 127.8, 125.1, 116.0 (d, *J* = 22 Hz), 115.6 (d, *J* = 22 Hz), 95.9, 86.2; LRMS (ESI) *m/z* 268 (M+H)$^+$.

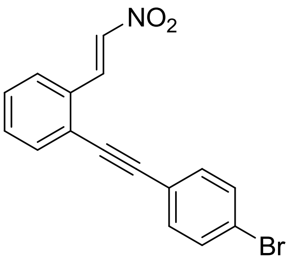
(*E*)-1-((4-chlorophenyl) ethynyl)-2-(2-nitrovinyl) benzene (1D)



1D

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 (d, J = 13.5 Hz, 1H), 7.78 (d, J = 13.5 Hz, 1H), 7.64-7.58 (m, 2H), 7.56-7.50 (m, 2H), 7.50-7.44 (m, 1H), 7.44-7.36 (m, 3H)； ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.3, 137.0, 135.3, 133.3, 132.9, 131.6, 131.3, 129.0, 129.0, 127.7, 125.0, 120.7, 95.8, 87.3; LRMS (ESI) *m/z* 284 $(M+H)^+$.

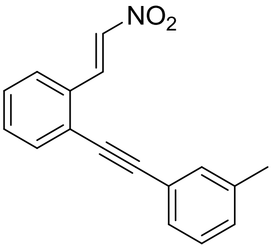
(*E*)-1-((4-bromophenyl) ethynyl)-2-(2-nitrovinyl) benzene (1E)



1E

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (d, J = 13.5 Hz, 1H), 7.77 (d, J = 13.5 Hz, 1H), 7.64-7.59 (m, 2H), 7.55-7.51 (m, 2H), 7.48-7.41 (m, 3H), 7.33-7.25 (m, 1H)； ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.3, 137.0, 133.3, 133.0, 132.8, 131.9, 131.6, 131.5, 131.3, 129.1, 127.7, 124.9, 123.5, 121.2, 95.8, 87.5; LRMS (ESI) *m/z* 329 $(M+H)^+$.

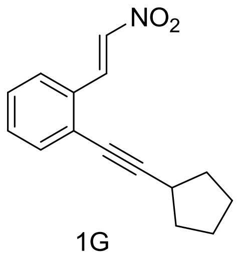
(*E*)-1-(2-nitrovinyl)-2-(*m*-tolylethynyl) benzene (1F)



1F

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.52 (d, J = 13.5 Hz, 1H), 7.81 (d, J = 13.5 Hz, 1H), 7.69-7.54 (m, 2H), 7.5-7.36 (m, 4H), 7.33-7.08 (m, 2H), 2.39 (s, 3H)；^{13}C NMR (125 MHz, $CDCl_3$) δ 138.3, 138.2, 137.2, 133.3, 132.2, 131.5, 131.2, 130.1, 128.8, 128.7, 128.5, 127.8, 125.4, 122.1, 97.3, 86.1, 21.3; LRMS (ESI) *m/z* 264$(M+H)^+$.

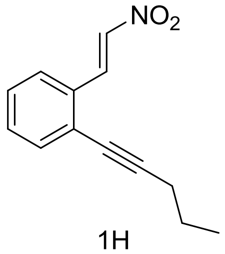
(*E*)-1-(cyclopentylethynyl)-2-(2-nitrovinyl) benzene (1G)



1G

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.43 (d, J = 13.5 Hz, 1H), 7.76 (d, J = 13.5 Hz, 1H), 7.57-7.45 (m, 2H), 7.42-7.27 (m, 2H), 3.13- 2.77 (m, 1H), 2.14-1.93 (m, 2H), 1.90-1.71 (m, 4H), 1.70 -1.57 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.9, 137.5, 133.2, 131.3, 131.1, 128.0, 127.7, 126.2, 103.1, 77.6, 33.8, 31.0, 25.0; LRMS (ESI) *m/z* 242 $(M+H)^+$.

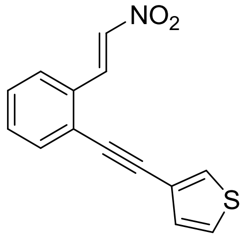
(*E*)-1-(2-nitrovinyl)-2-(pent-1-ynyl) benzene (1H)



1H

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.46 (d, J = 13.5 Hz, 1H), 7.74 (d, J = 13.5 Hz, 1H), 7.57-7.48 (m, 2H), 7.43-7.28 (m, 2H), 2.49 (t, J = 7.0 Hz, 2H), 1.79-1.63 (m, 2H), 1.09 (t, J = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.9, 137.5, 133.4, 131.4, 131.2, 128.1, 127.5, 126.2, 98.7, 78.1, 22.0, 21.7, 13.6; LRMS (ESI) *m/z* 216 $(M+H)^+$.

(*E*)-3-((2-(2-nitrovinyl) phenyl) ethynyl) thiophene (1I)

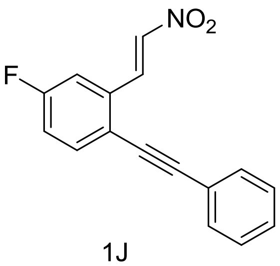


1I

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (d, J = 13.5 Hz, 1H), 7.81 (d, J = 13.5 Hz, 1H), 7.66-7.57 (m, 3H), 7.49-7.44 (m, 1H), 7.41-7.35 (m, 2H), 7.30-7.26 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.3, 137.2, 133.2, 131.5, 131.1, 129.8, 129.7, 128.7, 127.9, 125.9, 125.2, 121.3, 92.3, 86.1; LRMS (ESI) *m/z* 256 $(M+H)^+$.

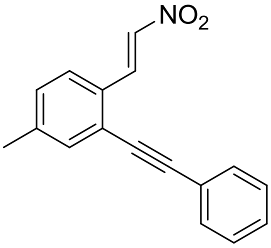
(*E*)-4-fluoro-2-(2-nitrovinyl)-1-(phenylethynyl) benzene (1J)

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.51 (d, J = 13.5 Hz, 1H), 7.74 (d, J = 13.5 Hz, 1H), 7.66-7.56 (m, 3H), 7.44-7.37 (m, 3H),


1J

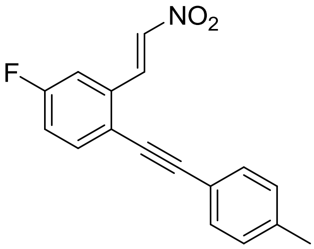
7.34-7.16 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.1 (d, J = 243 Hz), 139.1, 136.1 (d, J = 2 Hz), 135.2 (d, J = 8 Hz), 133.3 (d, J = 8 Hz), 131.6, 129.2, 128.6, 122.1, 121.6, 121.5, 119.1 (d, J = 22 Hz), 114.4 (d, J = 22 Hz), 96.7, 85.4; LRMS (ESI) m/z 268 $(M+H)^+$.

(*E*)-4-methyl-1-(2-nitrovinyl)-2-(phenylethynyl) benzene (1K)


1K

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.52 (d, J = 13.5 Hz, 1H), 7.79 (d, J = 13.5 Hz, 1H), 7.64-7.57 (m, 2H), 7.51-7.45 (m, 2H), 7.44-7.37 (m, 3H), 7.23-7.16 (m, 1H), 2.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.4, 137.5, 137.2, 133.8, 131.7, 129.9, 129.1, 128.6, 128.5, 127.9, 125.2, 122.4, 96.6, 86.6, 21.4; LRMS (ESI) m/z 264 $(M+H)^+$.

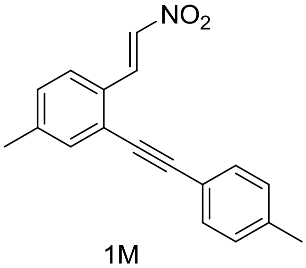
(*E*)-4-fluoro-2-(2-nitrovinyl)-1-(*p*-tolylethynyl) benzene (1L)


1L

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.53 (d, J = 13.5 Hz, 1H), 7.80 (d, J = 13.5 Hz, 1H), 7.53-7.38 (m, 4H), 7.23-7.20 (m, 1H), 7.17-7.07 (m, 2H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.0 (d, J = 237 Hz), 139.5 (d, J = 10 Hz), 139.0, 136.1 (d, J = 2 Hz), 135.1 (d, J = 9 Hz), 133.1, 132.4, 131.5, 129.4, 129.2, 121.7, 119.1 (d, J = 22 Hz), 118.9, 114.3 (d, J = 23 Hz), 97.0, 84.9, 21.6; LRMS (ESI) m/z 282 $(M+H)^+$.

(*E*)-4methyl-1-(2-nitrovinyl)-2-(*p*-tolylethynyl) benzene (1M)

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.50 (d, J = 13.5 Hz, 1H), 7.79 (d, J = 13.5 Hz, 1H), 7.54-7.42 (m, 4H), 7.24-7.14 (m, 3H), 2.40 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$)

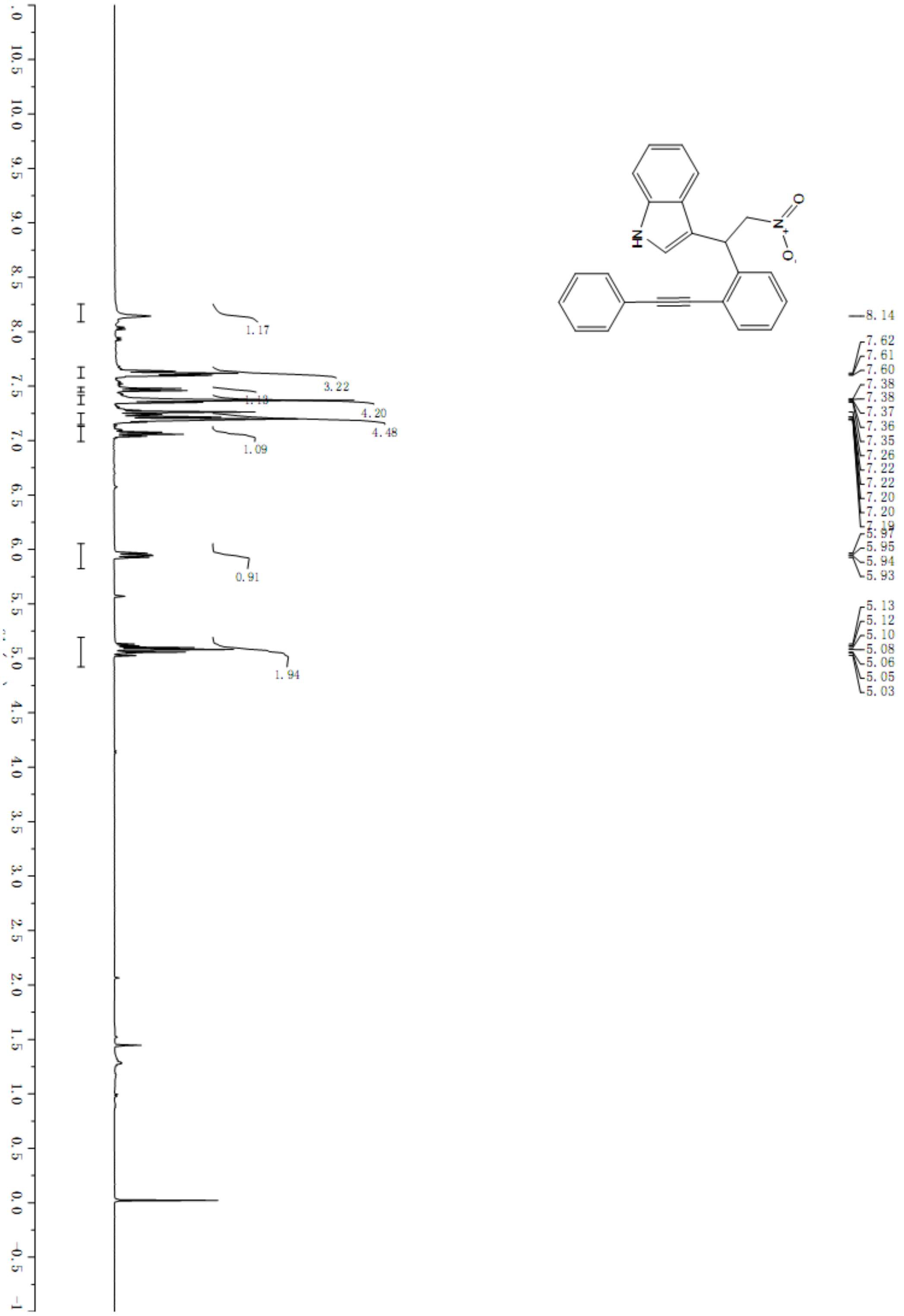


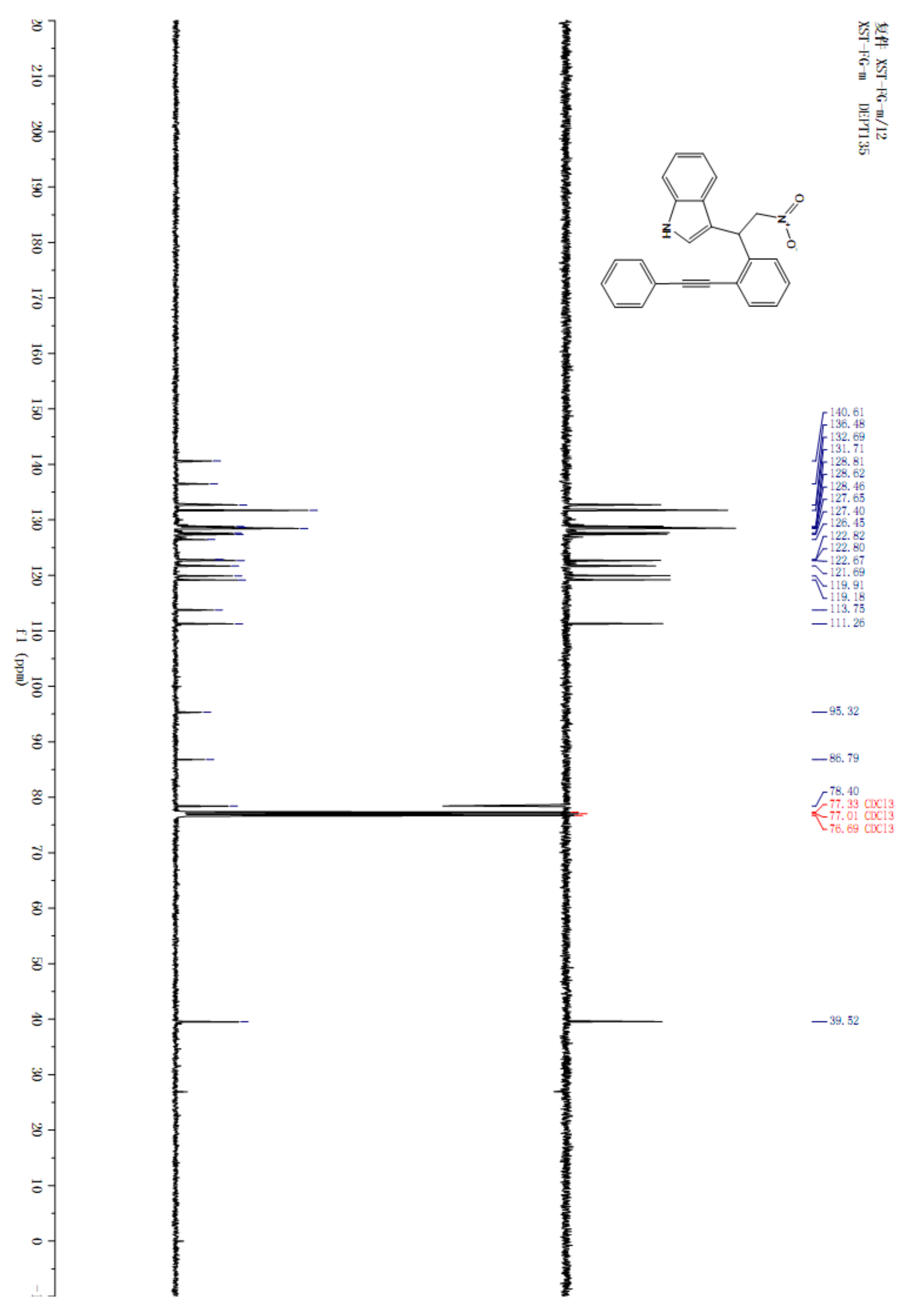
1M

δ 142.4, 139.4, 137.4, 137.3, 133.8, 131.6, 129.7, 129.4, 128.3, 127.9, 125.4, 119.3, 96.9, 86.1, 21.6, 21.4; LRMS (ESI) *m/z* 278 $(M+H)^+$.

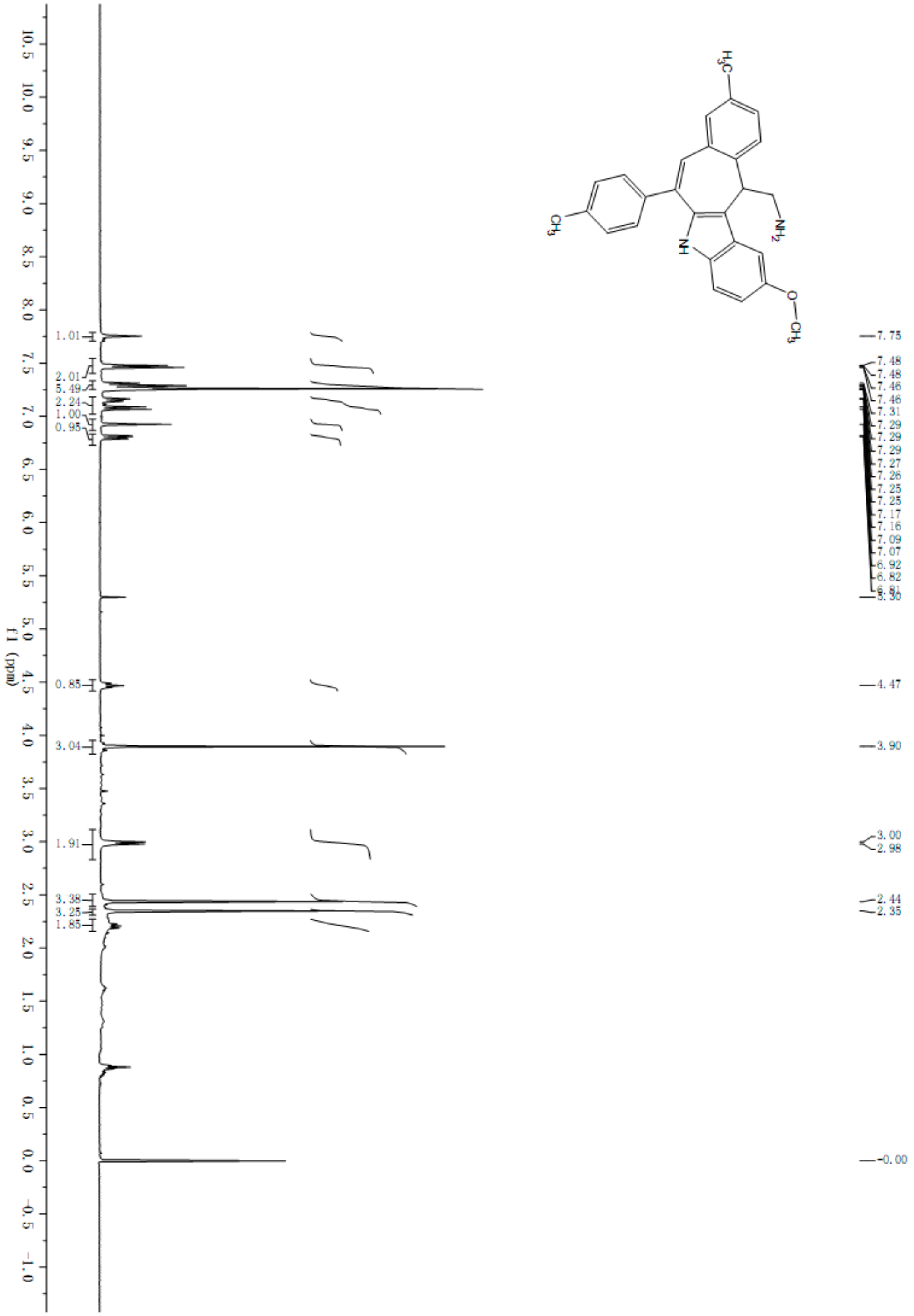
NMR Date

3-(2-Nitro-1-(2-(phenylethynyl)phenyl)ethyl)-1H-indole (8Aa)

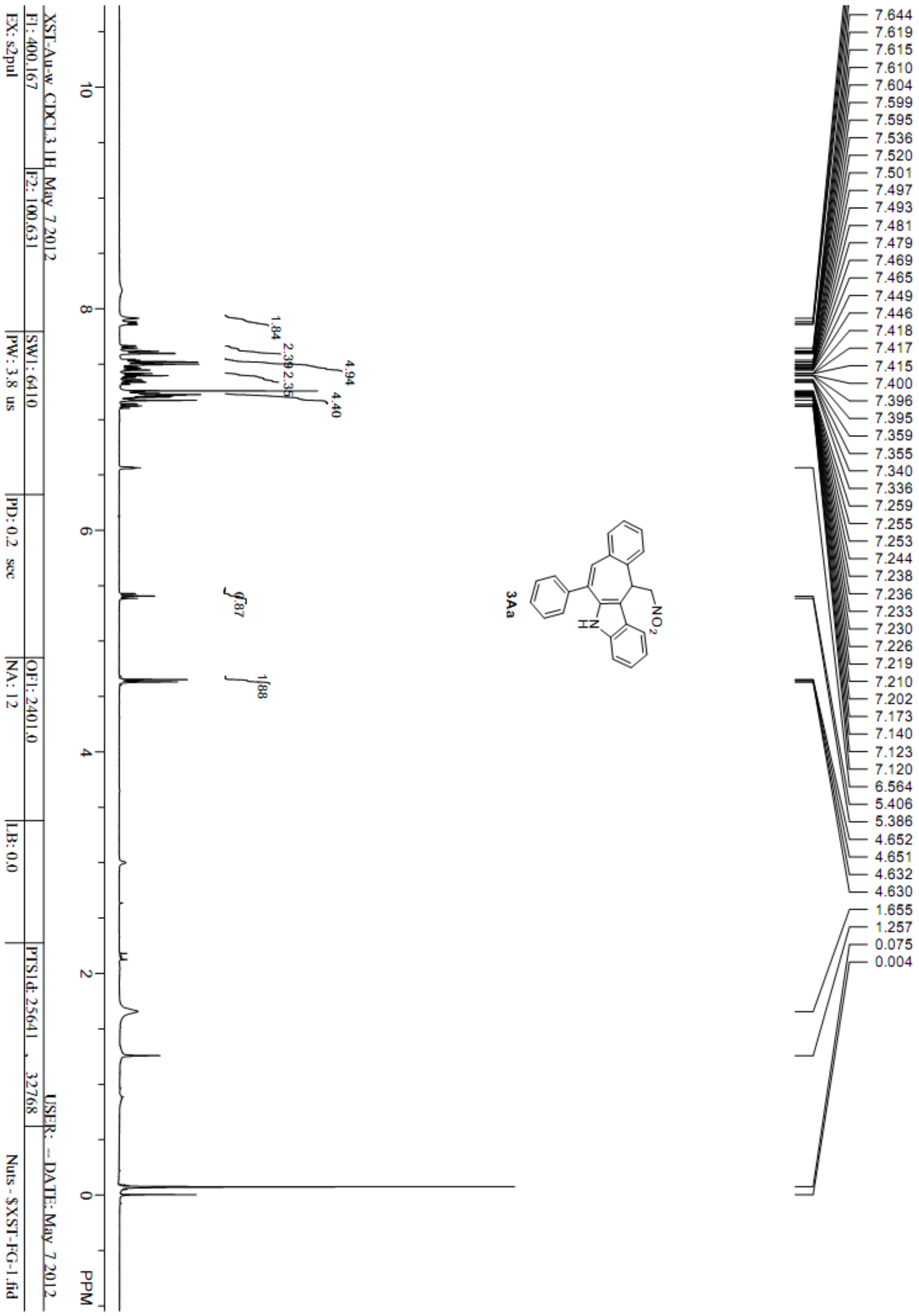


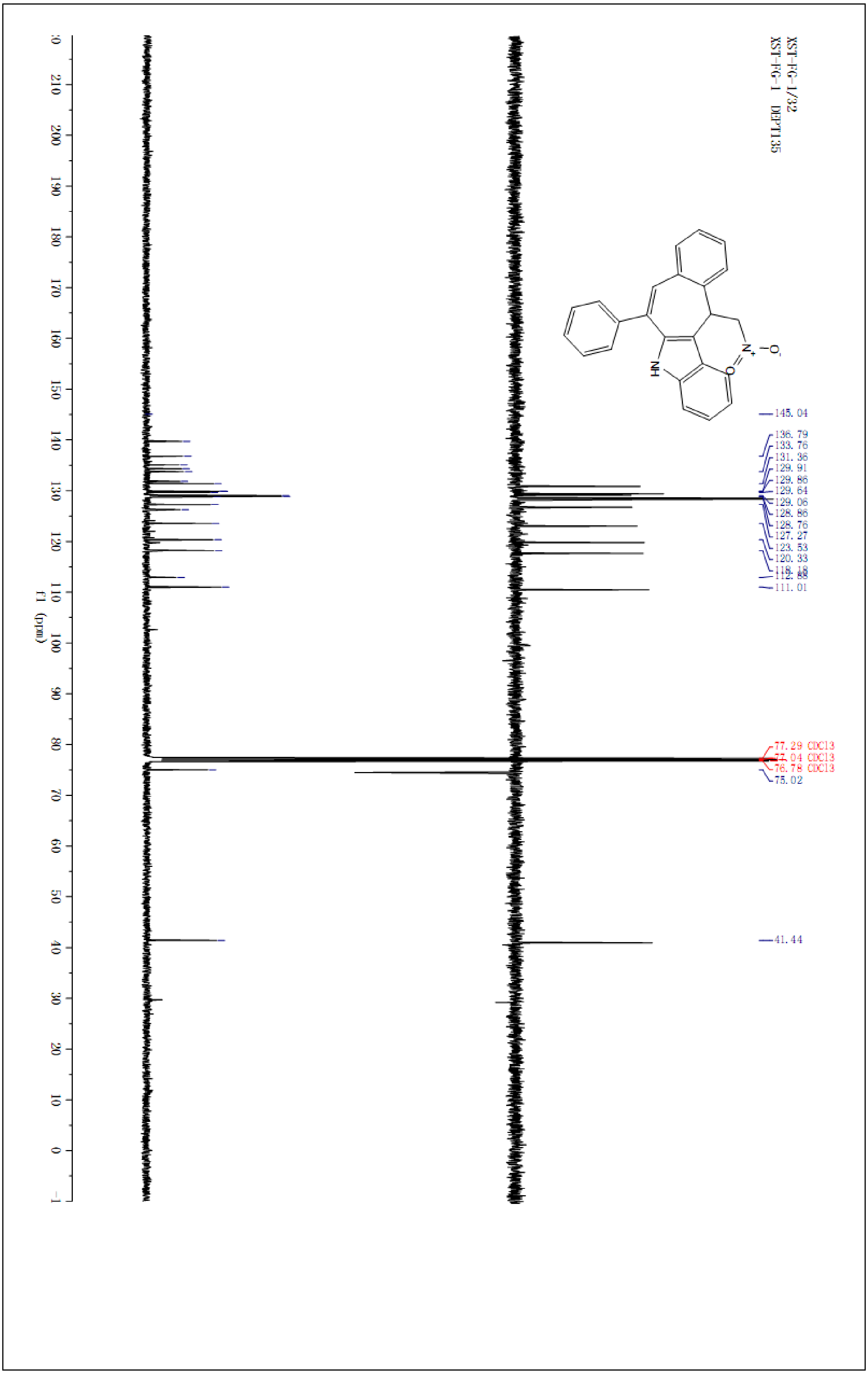

复件 XST-FG-m/12
XST-FG-m DEPT135
NH
N
O
O
140.61
136.48
132.69
131.71
128.81
128.62
128.46
127.65
127.40
126.45
122.82
122.80
122.67
121.69
119.91
119.18
113.75
111.26
95.32
86.79
78.40
77.33 CDCl3
77.01 CDCl3
76.69 CDCl3
39.52
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

2-Methoxy-9-methyl-6-(*p*-tolyl)-5,12-dihydrobenzo[4,5]cyclohepta[1,2-*b*]indol-12-yl) methanamine (4Me)

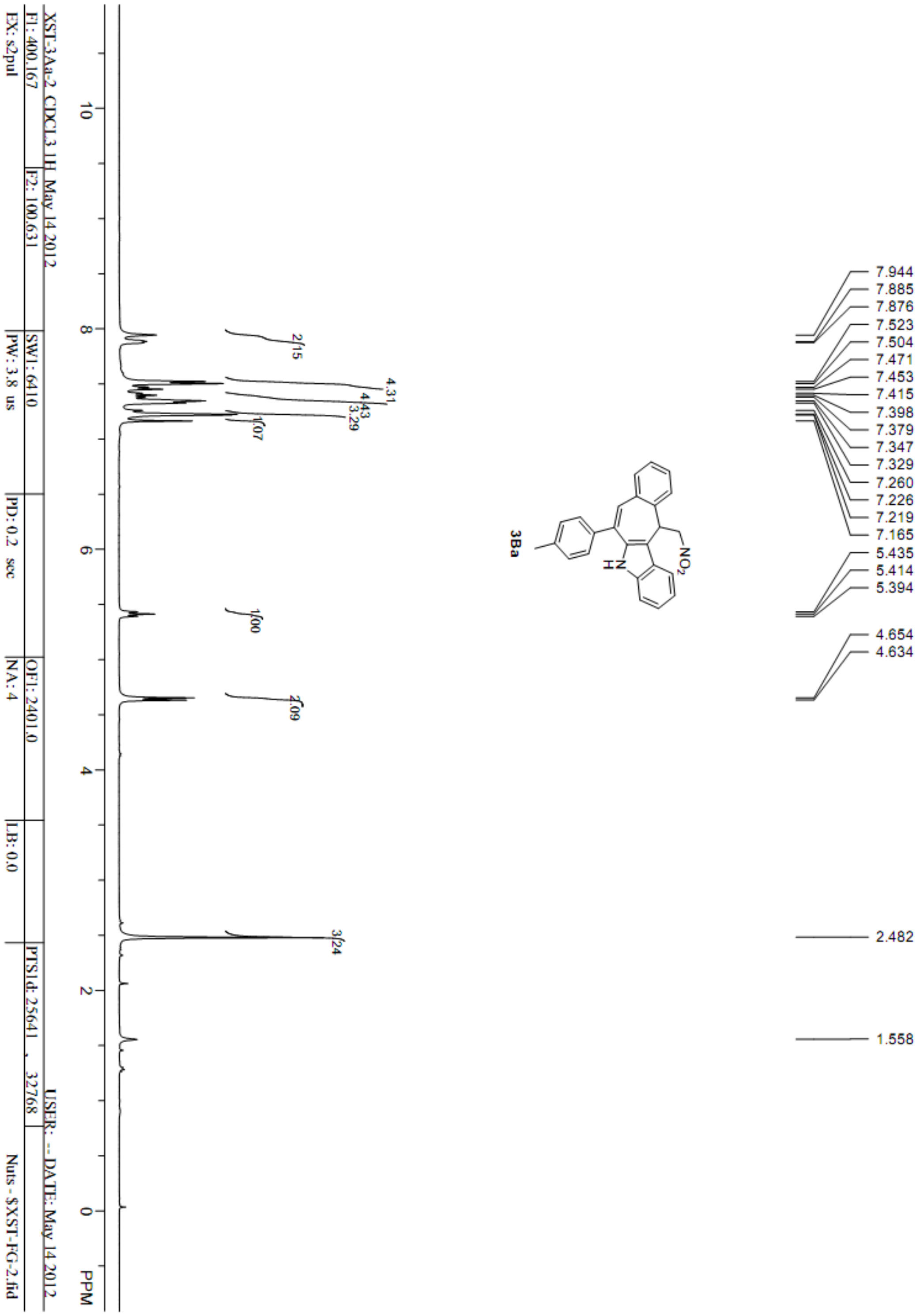


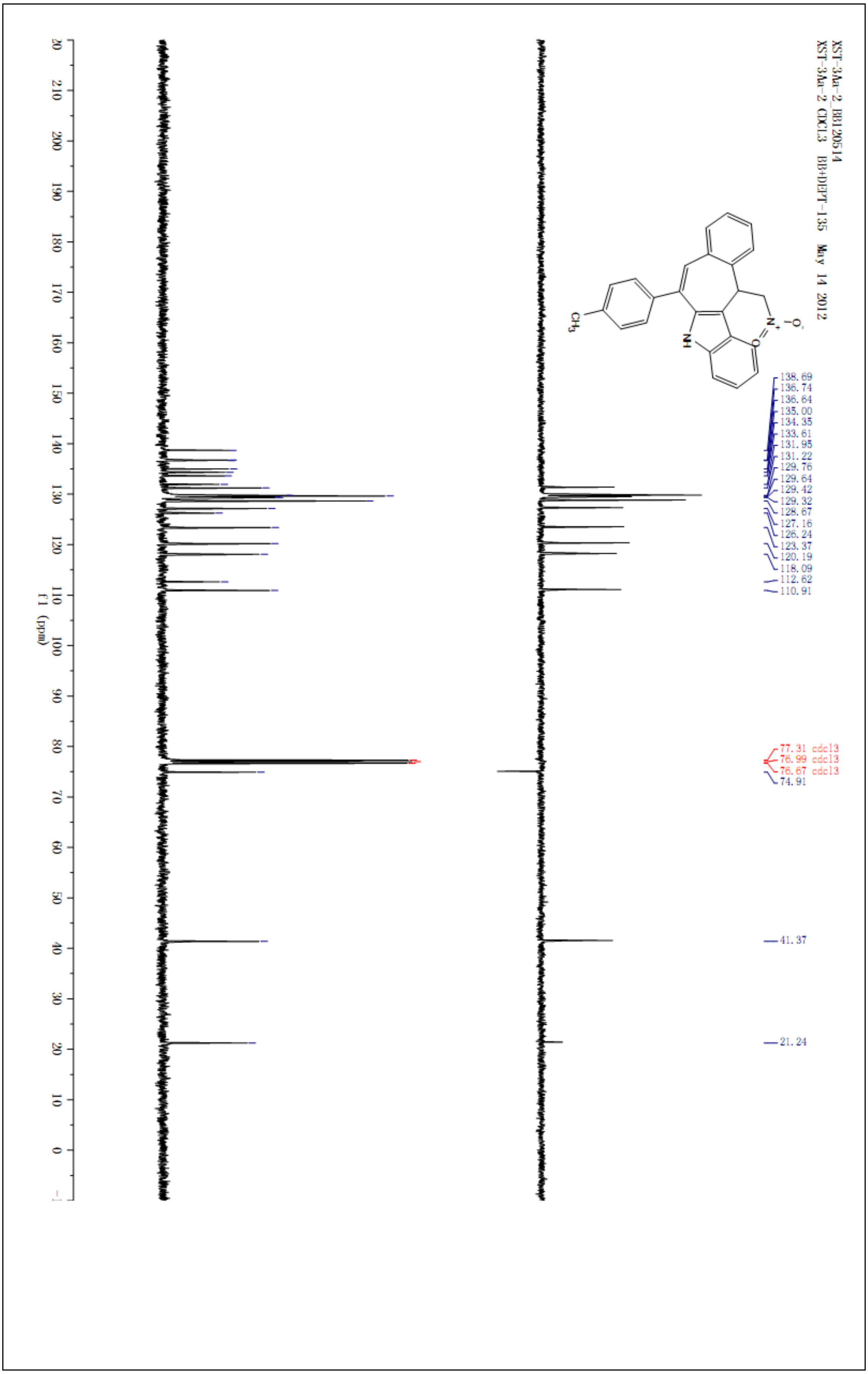
12-(Nitromethyl)-6-phenyl-5,12-dihydrobenzo[4,5]cyclohepta[1,2-*b*]indole (3Aa)



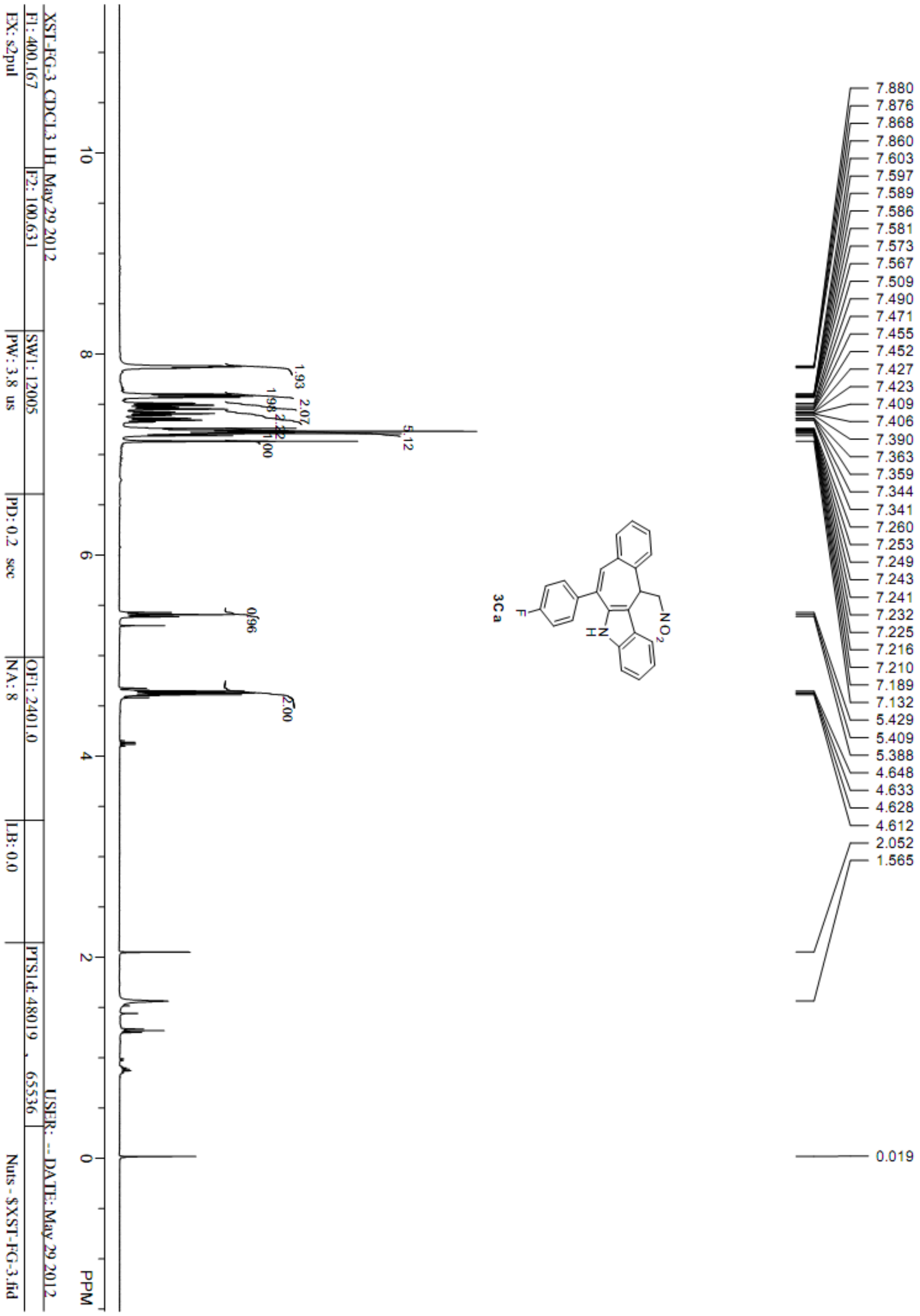

XST-FG-1/32
XST-FG-1 DEPT135
NH
N+
O-
O
145.04
136.79
133.76
131.36
129.91
129.86
129.64
129.06
128.86
128.76
127.27
123.53
120.33
118.18
112.88
111.01
77.29 CDCl3
77.04 CDCl3
76.78 CDCl3
75.02
41.44
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

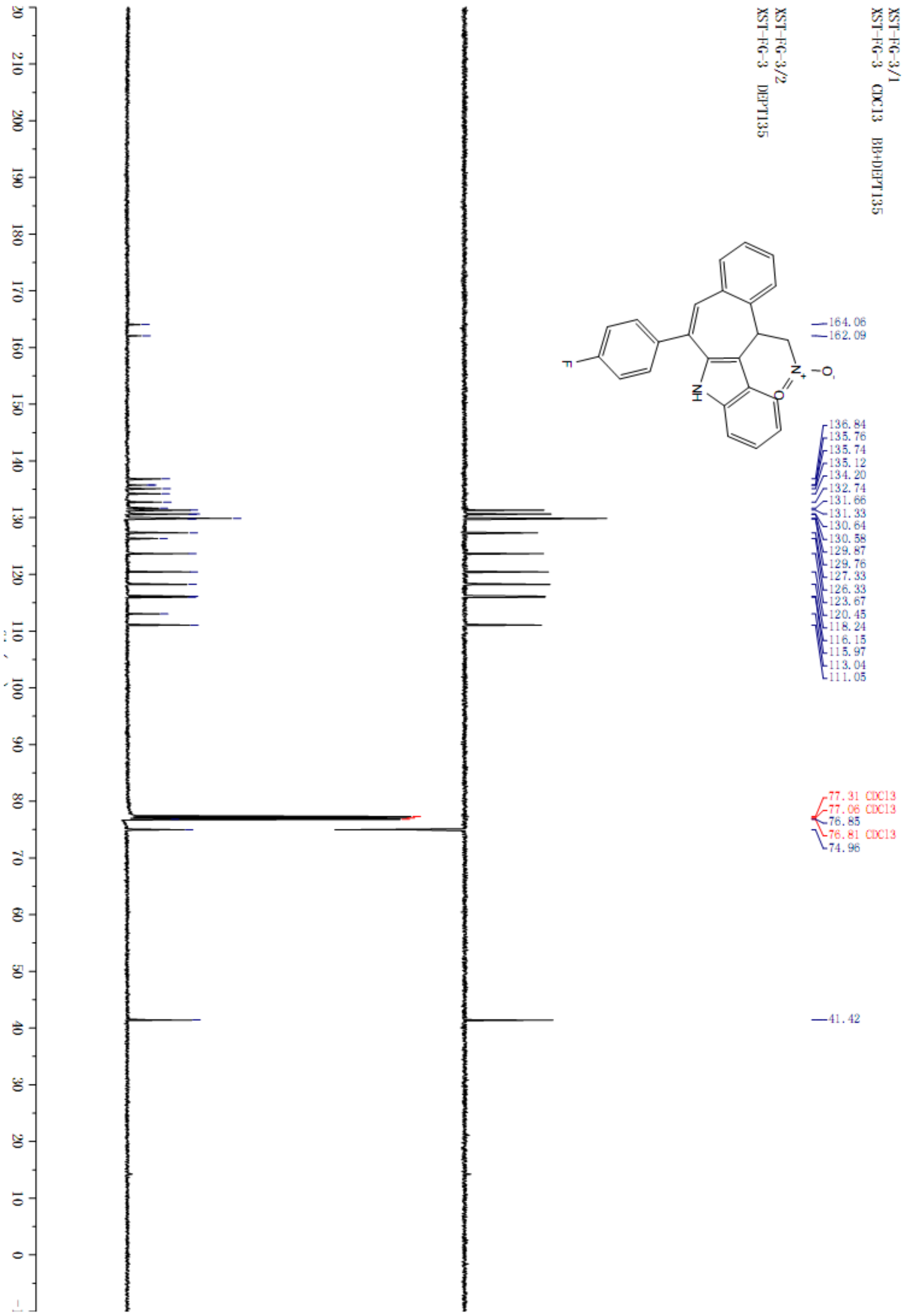
12-(Nitromethyl)-6-(*p*-tolyl)-5,12-dihydrobenzo[4,5]cyclohepta[1,2-*b*]indole (3Ba)

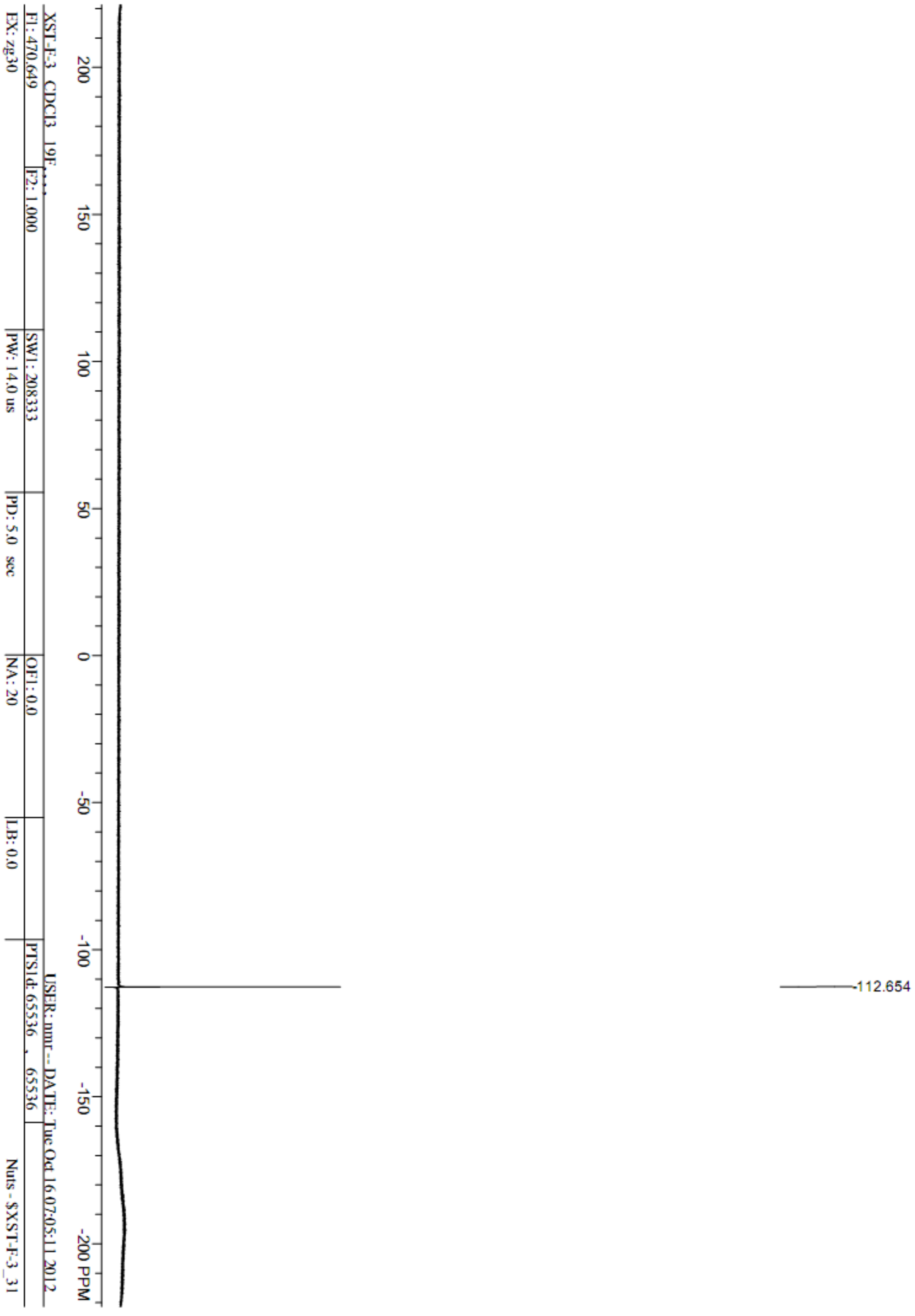



XST-3Aa-2_BB120514
XST-3Aa-2 CDCL3 BB+DEPT-135 May 14 2012
O⁻
N⁺
O
NH
CH3
138.69
136.74
136.64
135.00
134.35
133.61
131.95
131.22
129.76
129.64
129.42
129.32
128.67
127.16
126.24
123.37
120.19
118.09
112.62
110.91
77.31 cdcl3
76.99 cdcl3
76.67 cdcl3
74.91
41.37
21.24
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

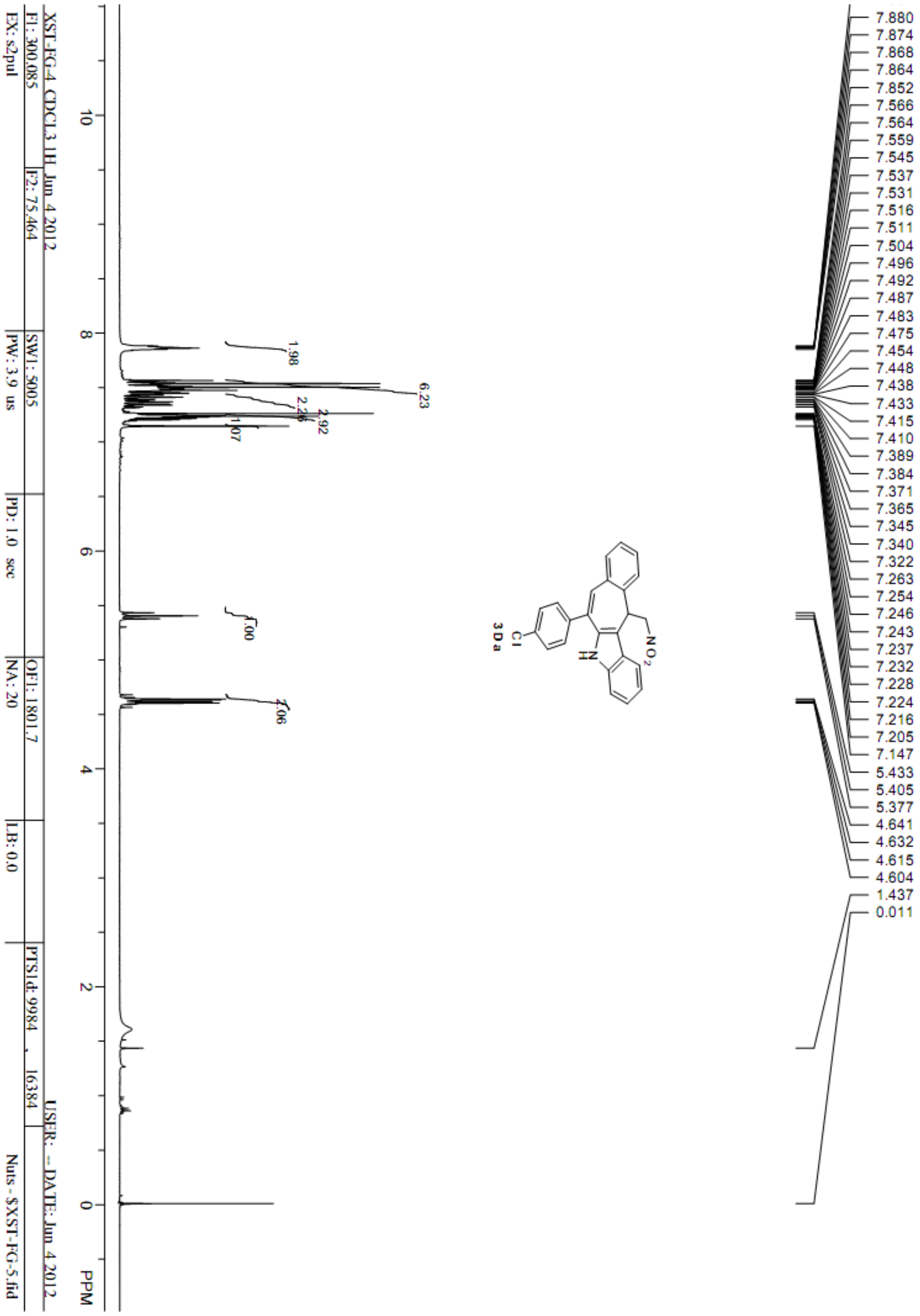
12-(Nitromethyl)-6-(4-fluorophenyl)-5,12-dihydrobenzo[4,5]cyclohepta[1,2-*b*] indole (3Ca)

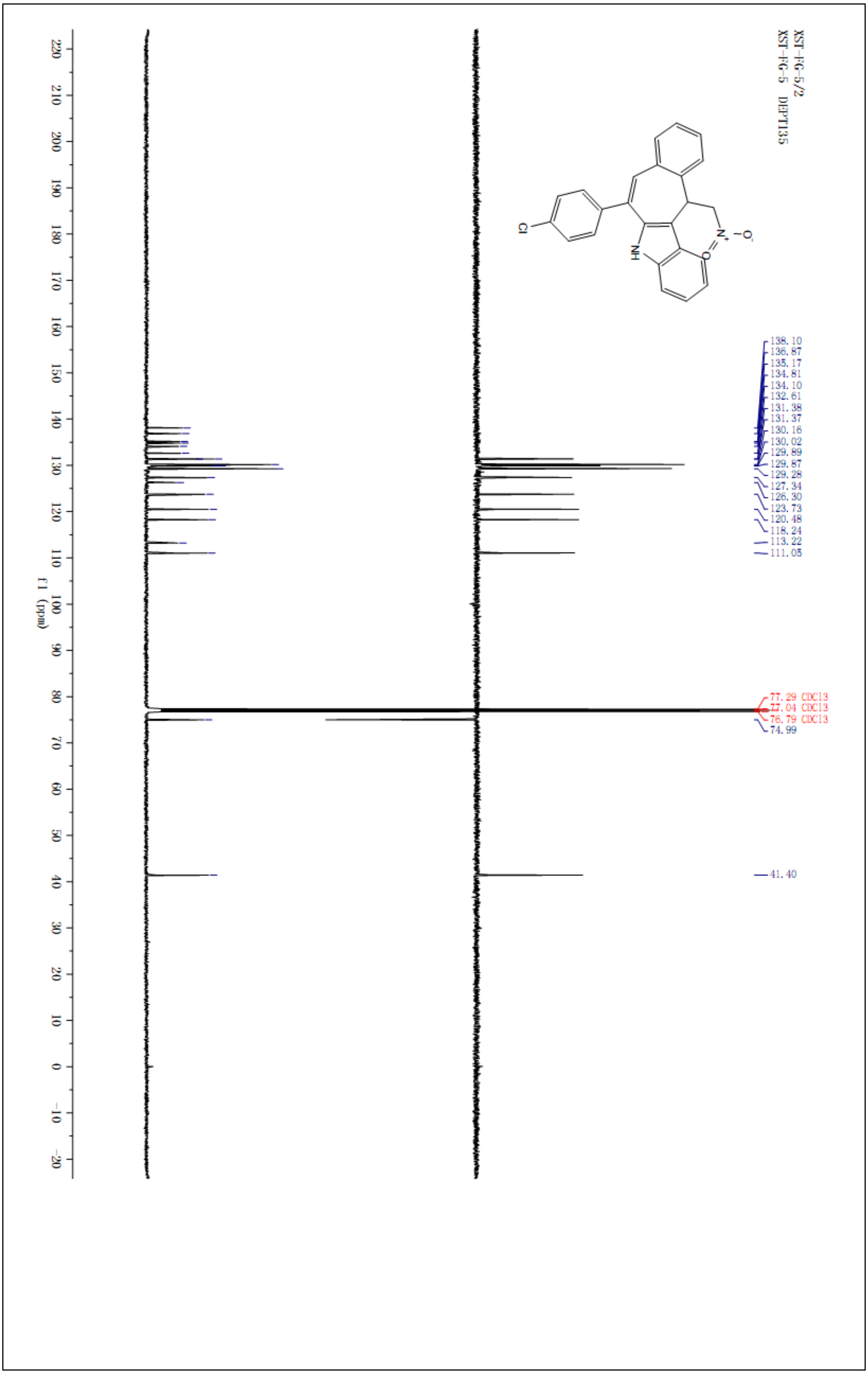



XST-FG-3/1
XST-FG-3 CDCl3 BB+DEPT135
XST-FG-3/2
XST-FG-3 DEPT135
F
NH
N+
O-
O
164.06
162.09
136.84
135.76
135.74
135.12
134.20
132.74
131.66
131.33
130.64
130.58
129.87
129.76
127.33
126.33
123.67
120.45
118.24
116.15
115.97
113.04
111.05
77.31 CDCl3
77.06 CDCl3
76.85
76.81 CDCl3
74.96
41.42
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

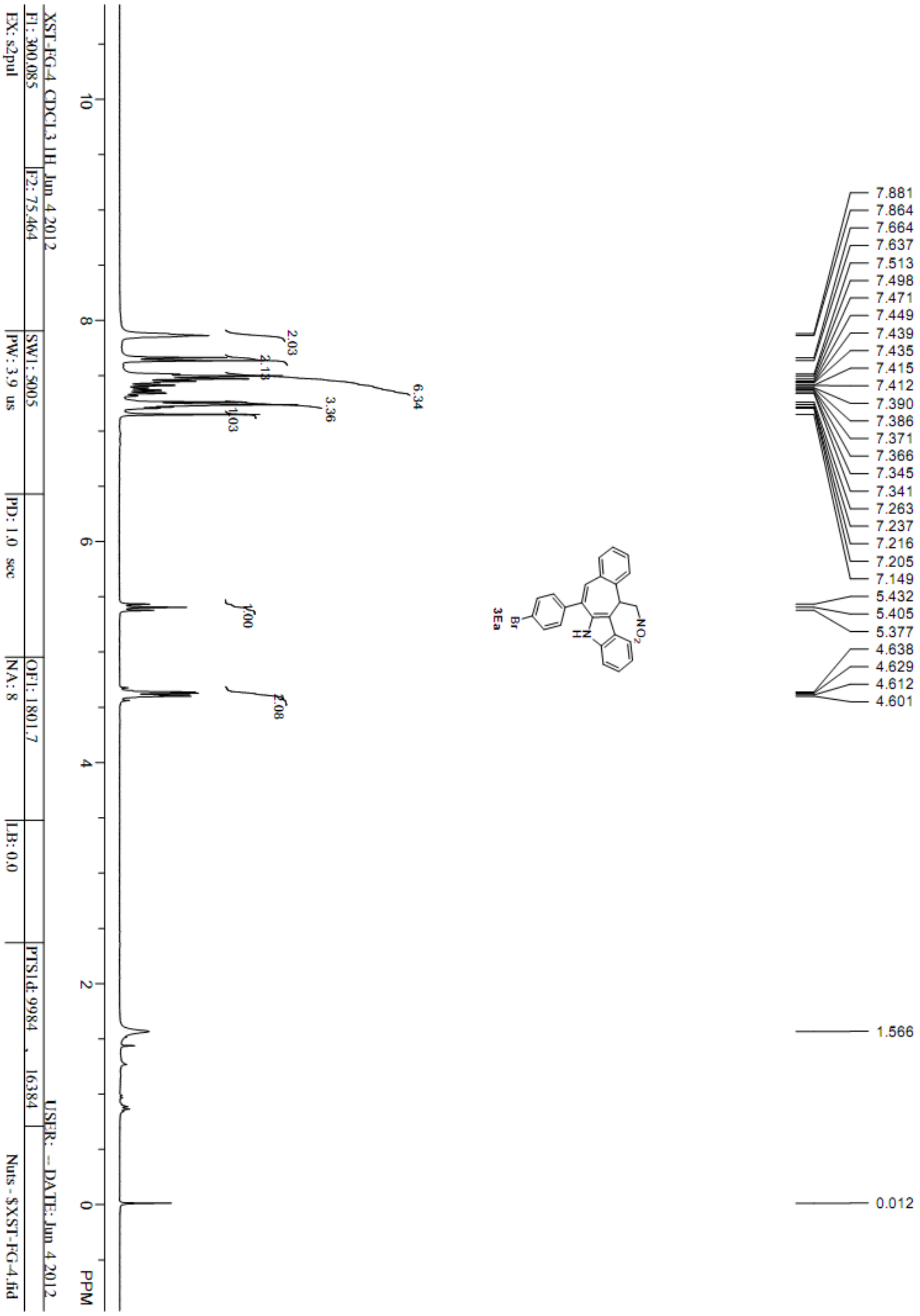

XST-F-3_CDCl3_19F
F1: 470.649
F2: 1.000
SW1: 208333
OF1: 0.0
PTS1d: 65536 , 65536
USER: nmr -- DATE: Tue Oct 16 07:05:11 2012
EX: zg30
PW: 14.0 us
PD: 5.0 sec
NA: 20
LB: 0.0
Nuts - $XST-F-3_31
200
150
100
50
0
-50
-100
-150
-200 PPM
-112.654

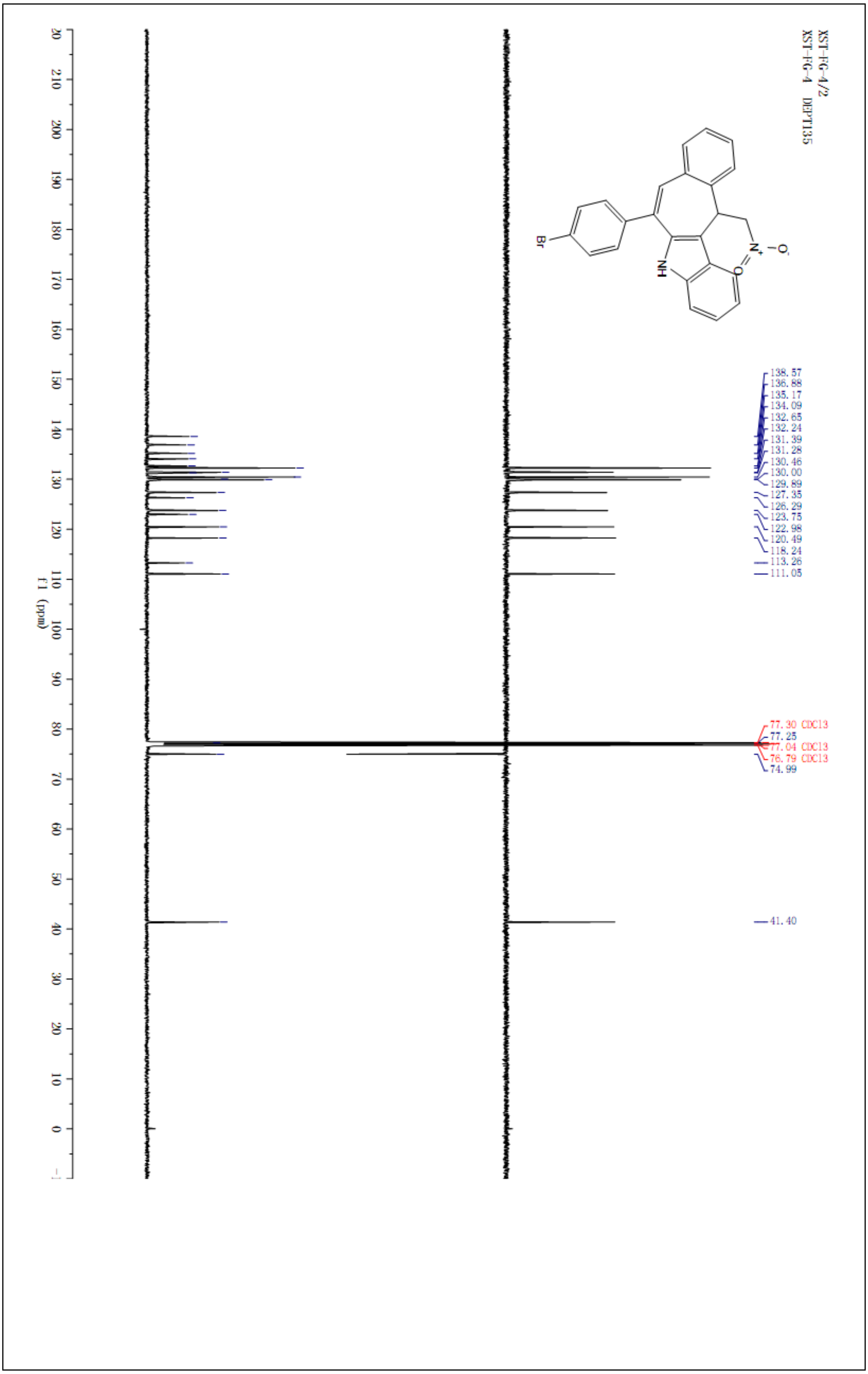
12-(Nitromethyl)-6-(4-chlorophenyl)-5,12-dihydrobenzo[4,5]cyclohepta[1,2-*b*] indole (3Da)



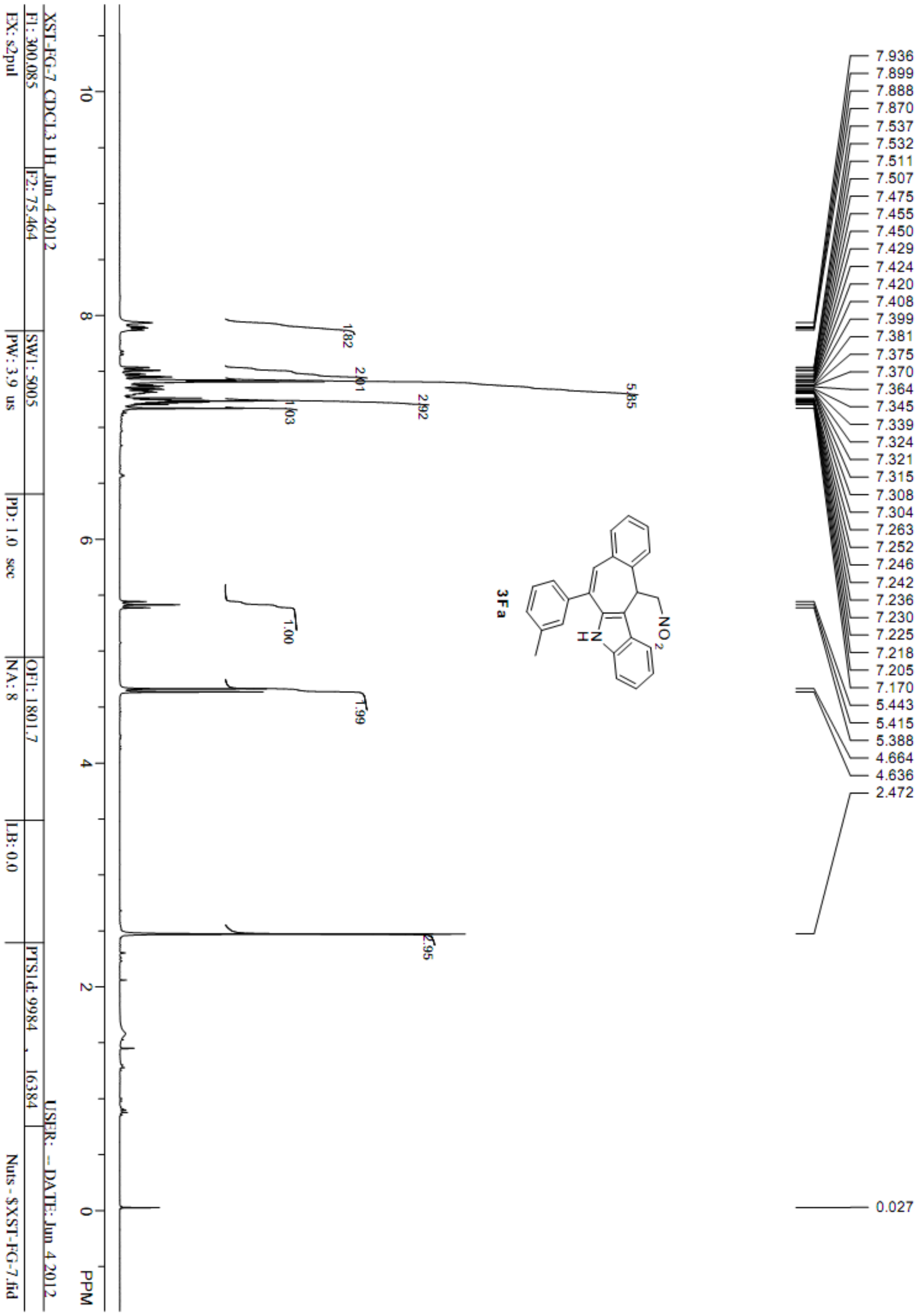

XST-FG-5/2
XST-FG-5 DEPT135
Cl
NH
N+
O-
O
138.10
136.87
135.17
134.81
134.10
132.61
131.38
131.37
130.16
130.02
129.89
129.87
129.28
127.34
126.30
123.73
120.48
118.24
113.22
111.05
77.29 CDCl3
77.04 CDCl3
76.79 CDCl3
74.99
41.40
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

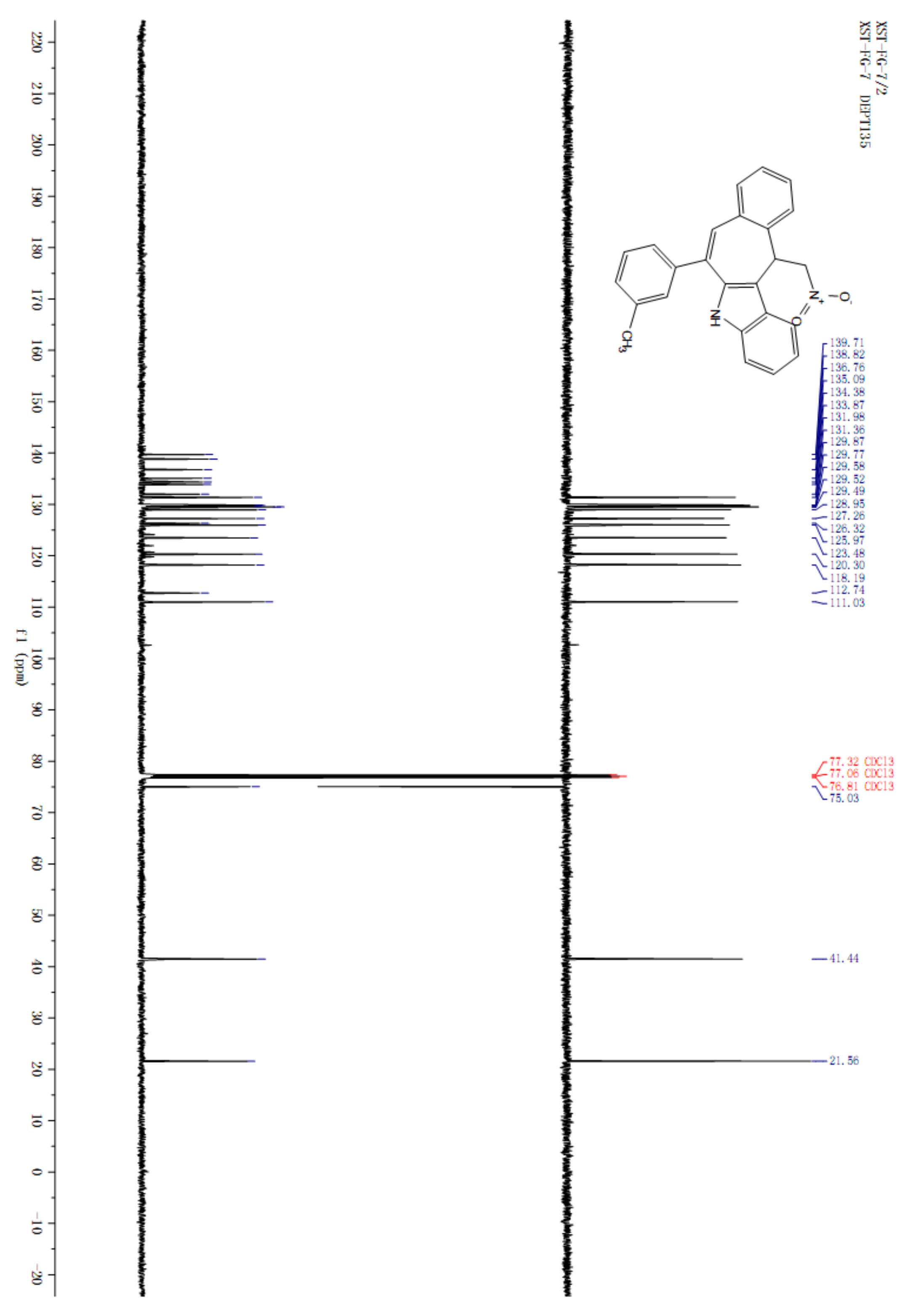
12-(Nitromethyl)-6-(4-bromophenyl)-5,12-dihydrobenzo[4,5]cyclohepta[1,2-*b*] indole (3Ea)



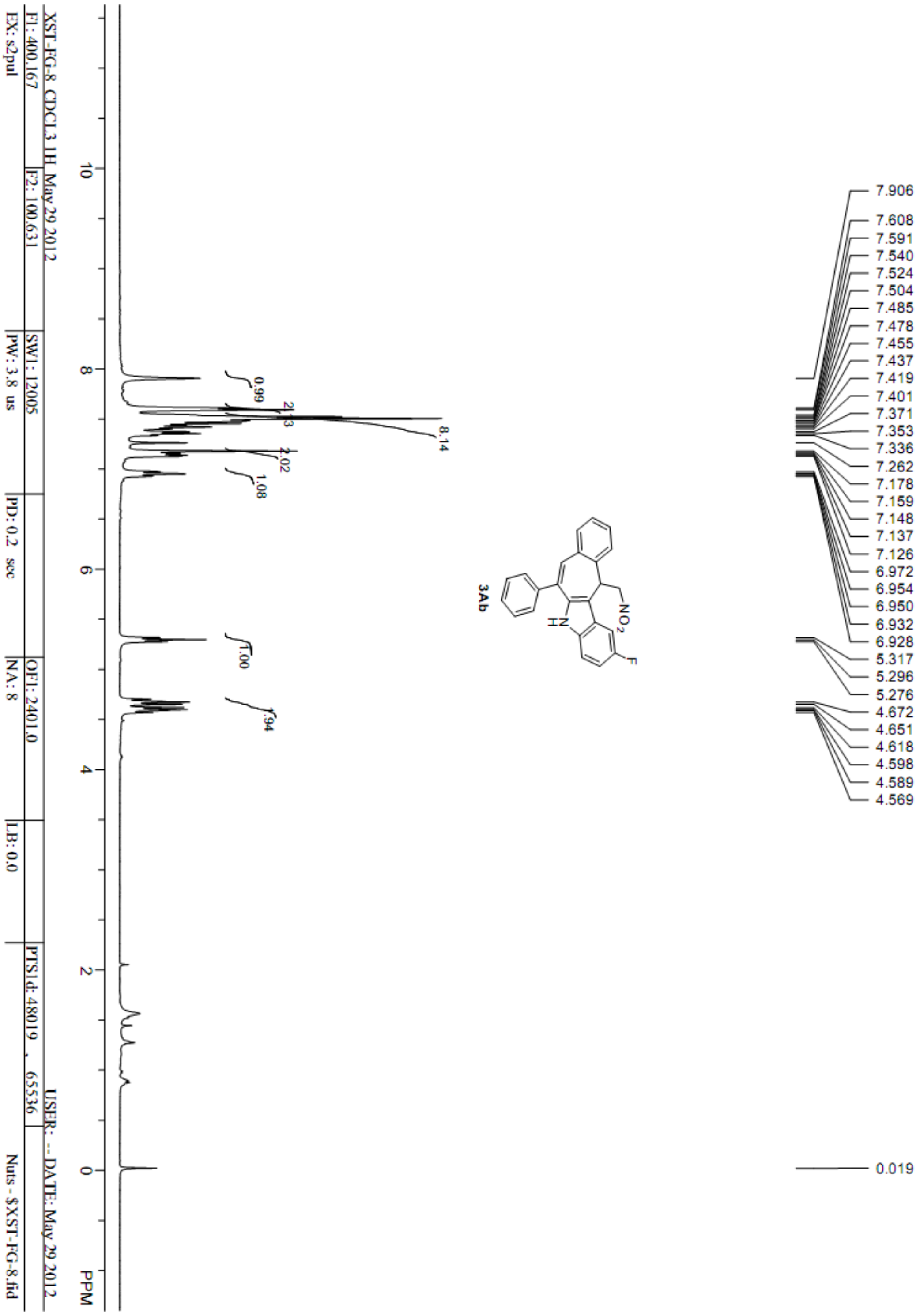

XST-FG-4/2
XST-FG-4 DEPT135
Br
NH
N+
O-
O
138.57
136.88
135.17
134.09
132.65
132.24
131.39
131.28
130.46
130.00
129.89
127.35
126.29
123.75
122.98
120.49
118.24
113.26
111.05
77.30 CDCl3
77.25
77.04 CDCl3
76.79 CDCl3
74.99
41.40
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1

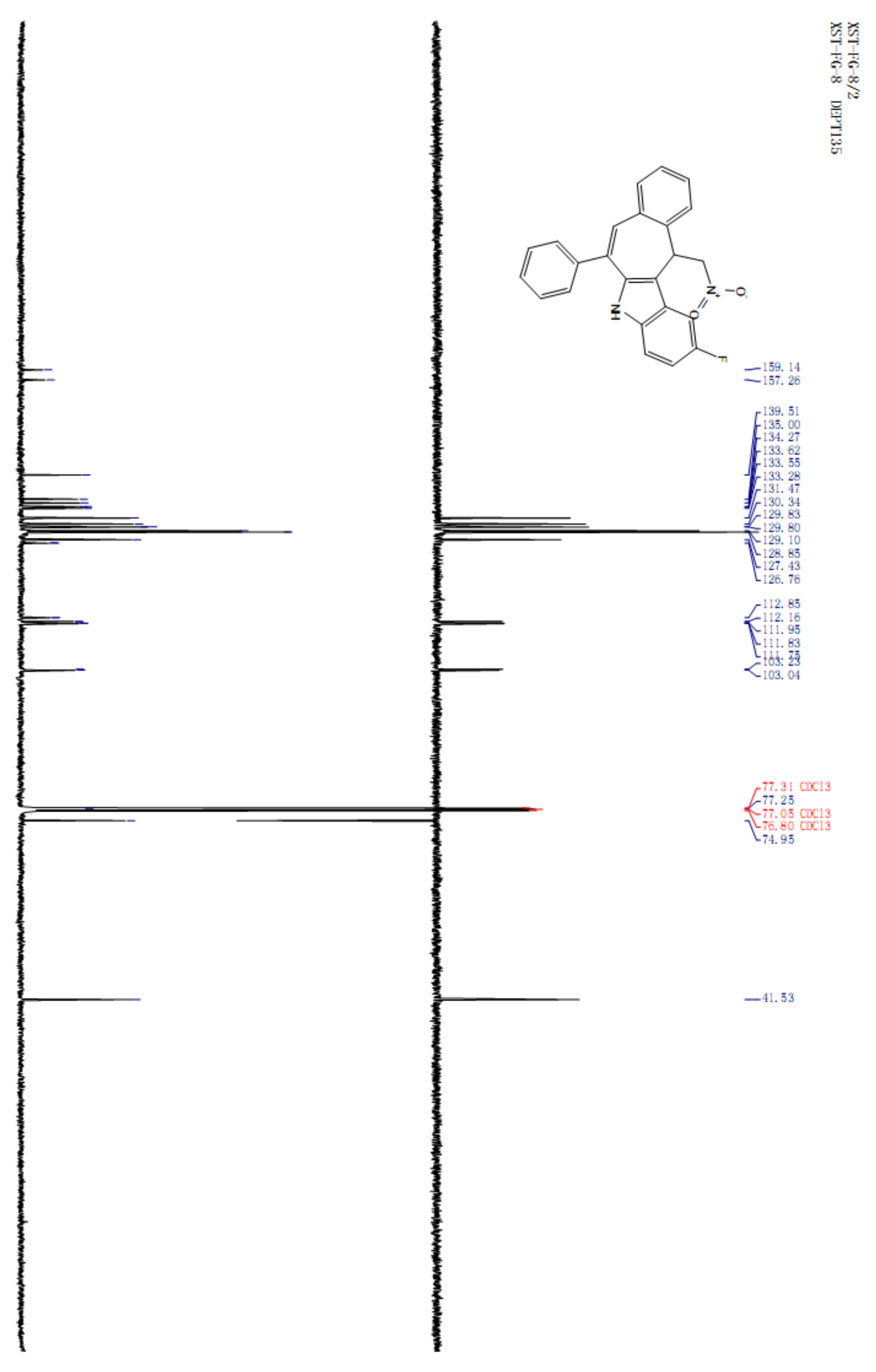
12-(Nitromethyl)-6-(*m*-tolyl)-5,12-dihydrobenzo[4,5]cyclohepta[1,2-*b*]indole (3Fa)

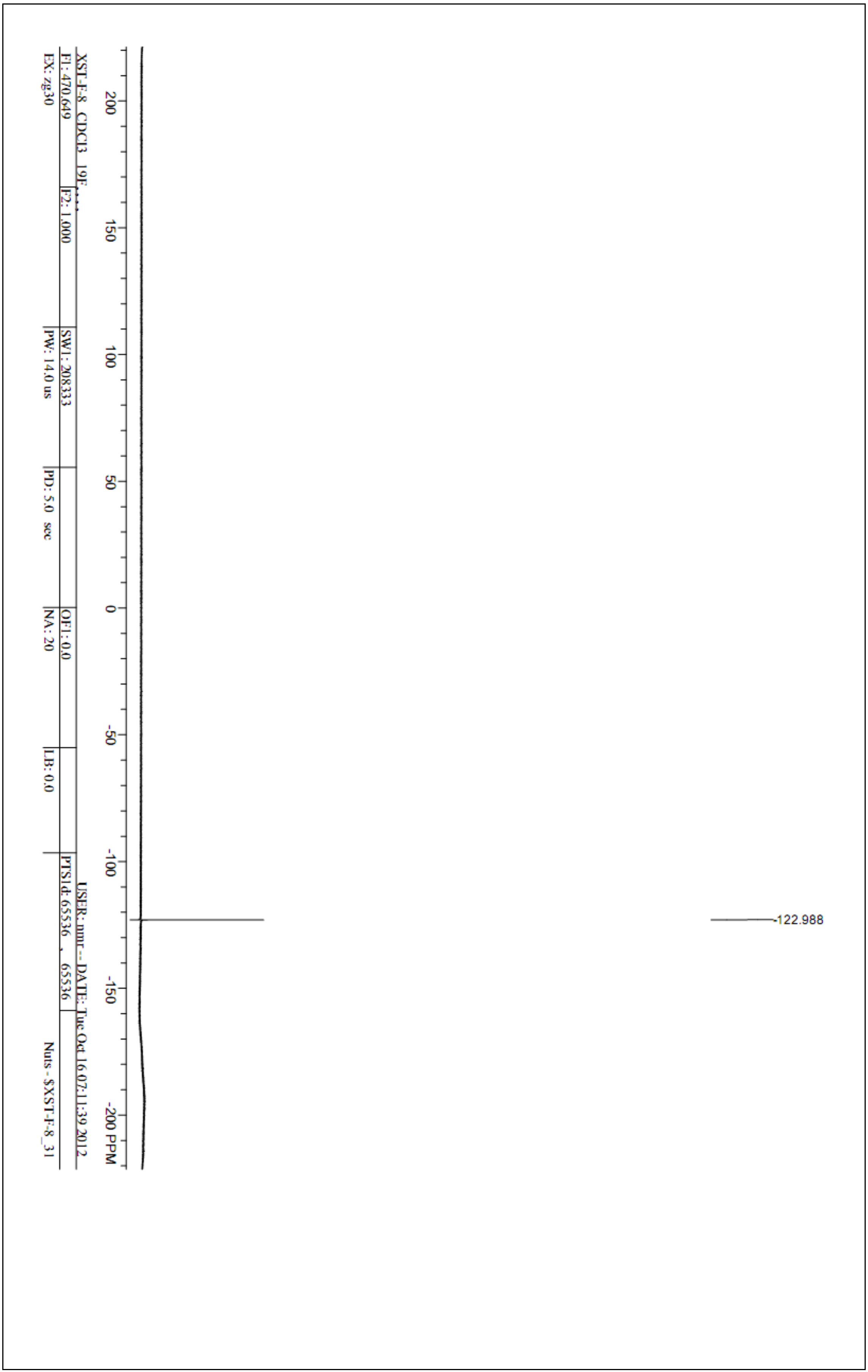



XST-FG-7/2
XST-FG-7 DEPT135
NH
N+
O-
O
CH3
139.71
138.82
136.76
135.09
134.38
133.87
131.98
131.36
129.87
129.77
129.58
129.52
129.49
128.95
127.26
126.32
125.97
123.48
120.30
118.19
112.74
111.03
77.32 CDCl3
77.06 CDCl3
76.81 CDCl3
75.03
41.44
21.56
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

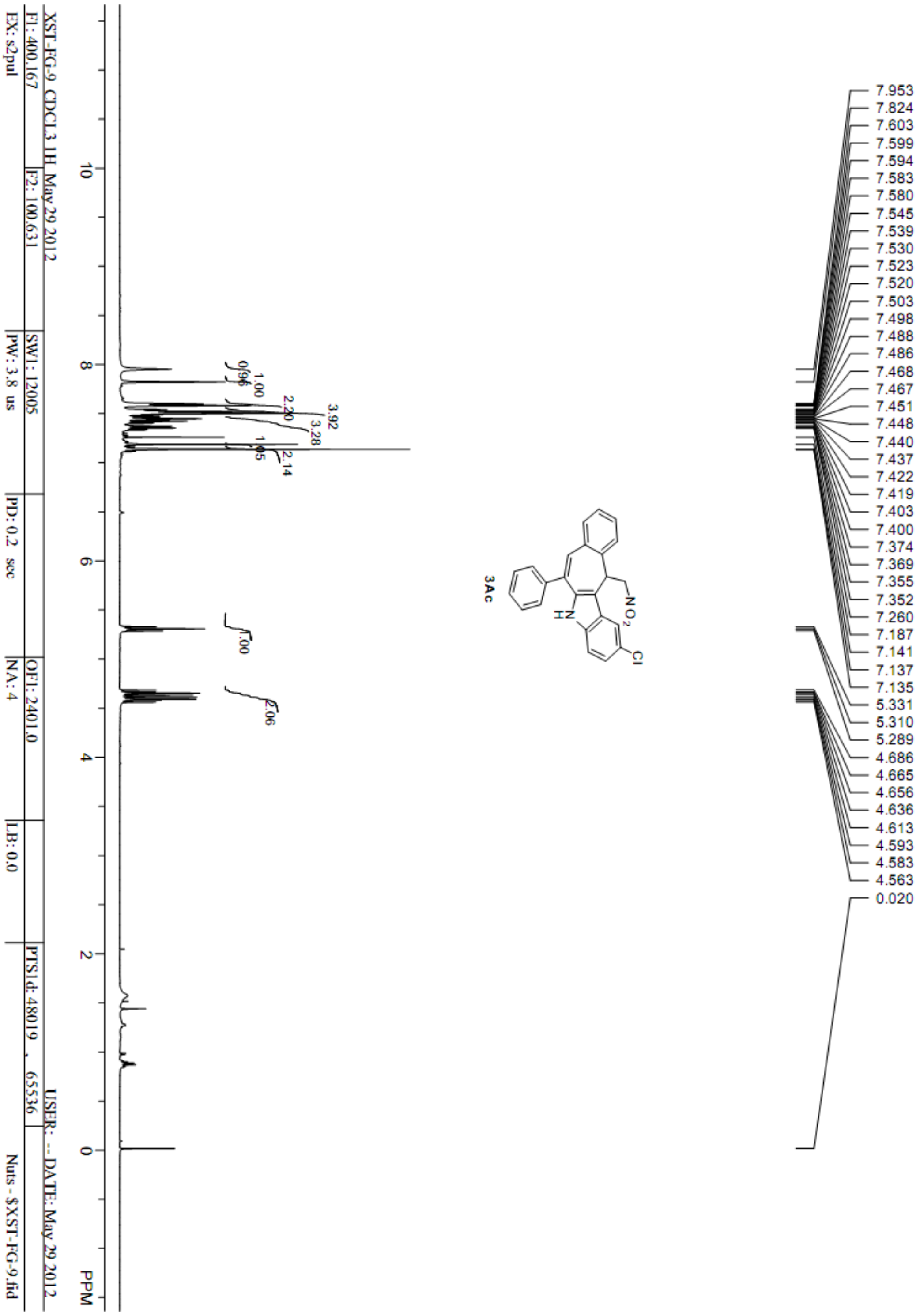
2-Fluoro-12-(nitromethyl)-6-phenyl-5,12-dihydrobenzo[4,5]cyclohepta [1,2-*b*] indole(3Ab)

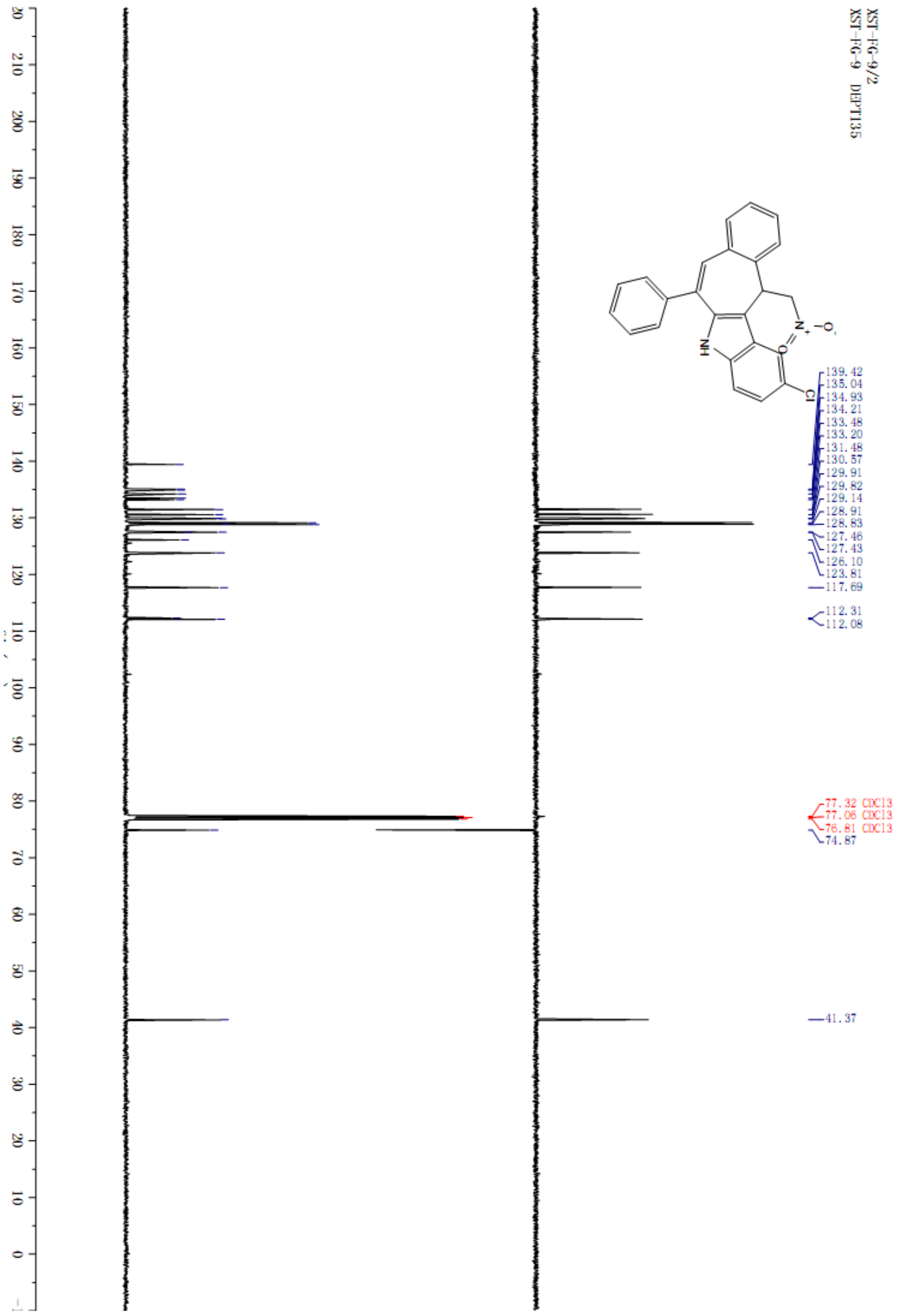



XST-FG-8/2
XST-FG-8 DEPT135
NH
N+
O-
O
F
159. 14
157. 26
139. 51
135. 00
134. 27
133. 62
133. 55
133. 28
131. 47
130. 34
129. 83
129. 80
129. 10
128. 85
127. 43
126. 76
112. 85
112. 16
111. 95
111. 83
111. 75
103. 23
103. 04
77. 31 CDCl3
77. 25
77. 05 CDCl3
76. 80 CDCl3
74. 95
41. 53

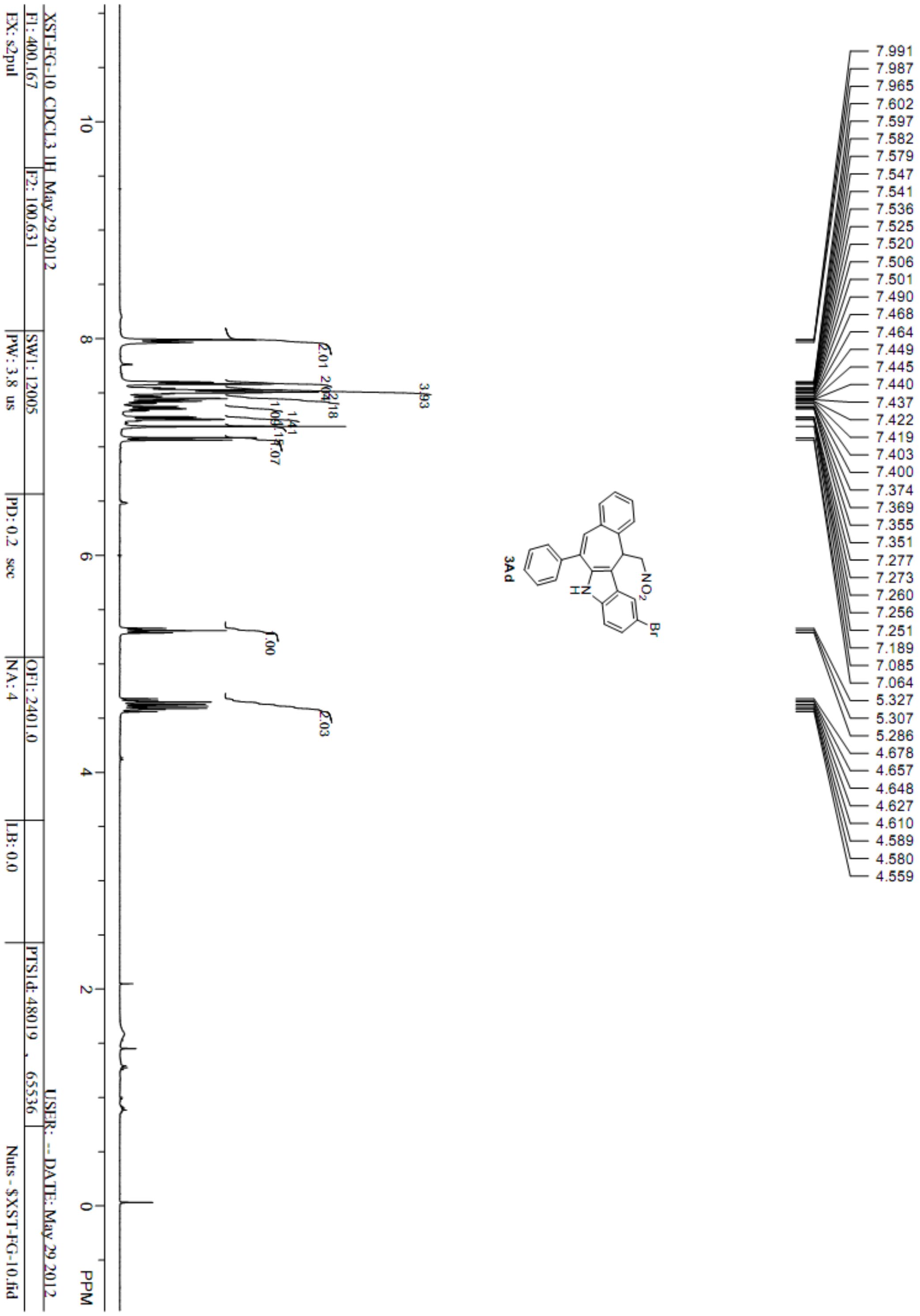

XST-F-8_CDCl3_19F
F1: 470.649
F2: 1.000
SW1: 208333
OF1: 0.0
PTS1d: 65536 , 65536
EX: zg30
PW: 14.0 us
PD: 5.0 sec
NA: 20
LB: 0.0
USER: nmr -- DATE: Tue Oct 16 07:11:39 2012
Nuts - $XST-F-8_31
200
150
100
50
0
-50
-100
-150
-200 PPM
-122.988

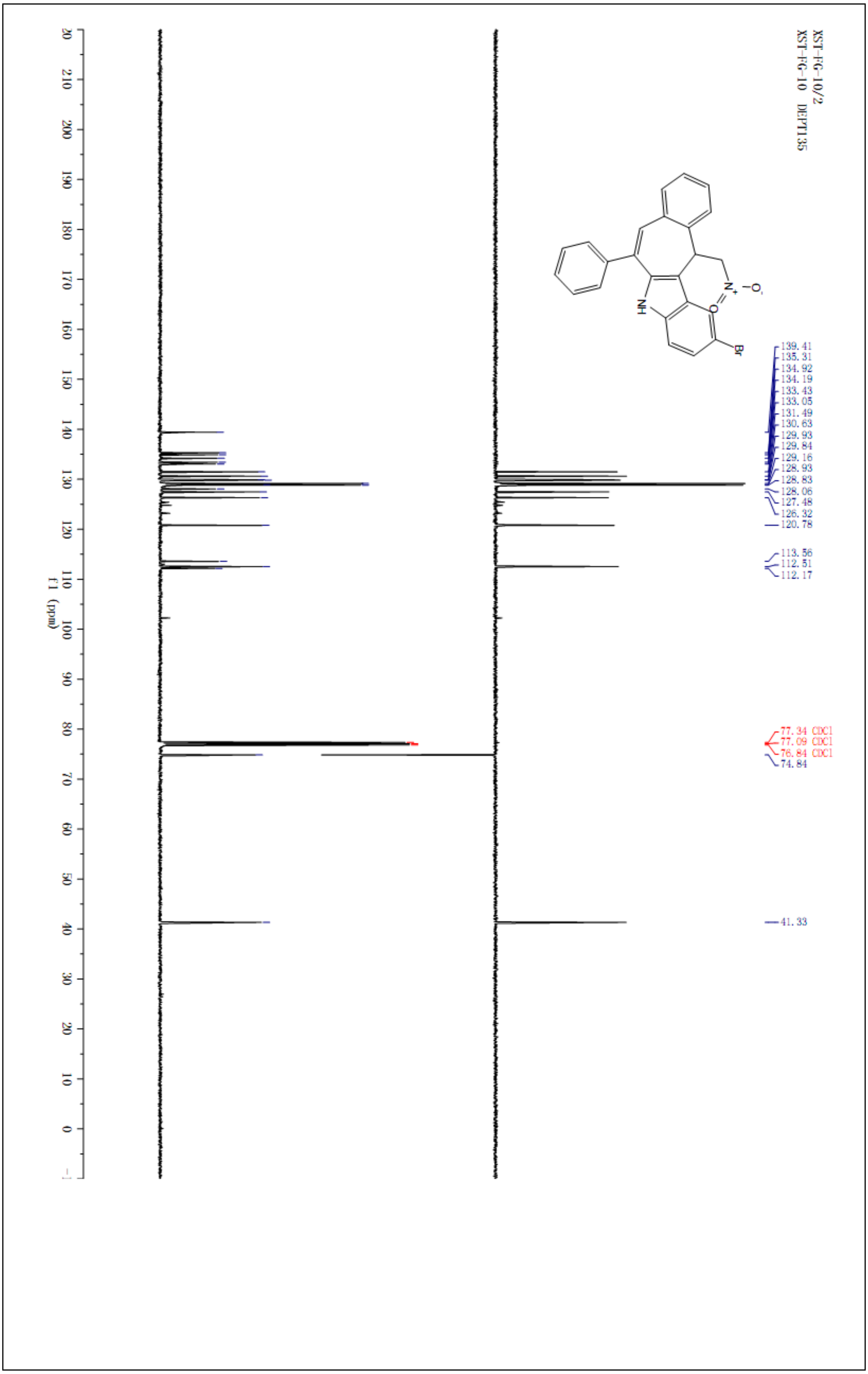
2-Chloro-12-(nitromethyl)-6-phenyl-5,12-dihydrobenzo[4,5]cyclohepta [1,2-*b*] indole(3Ac)



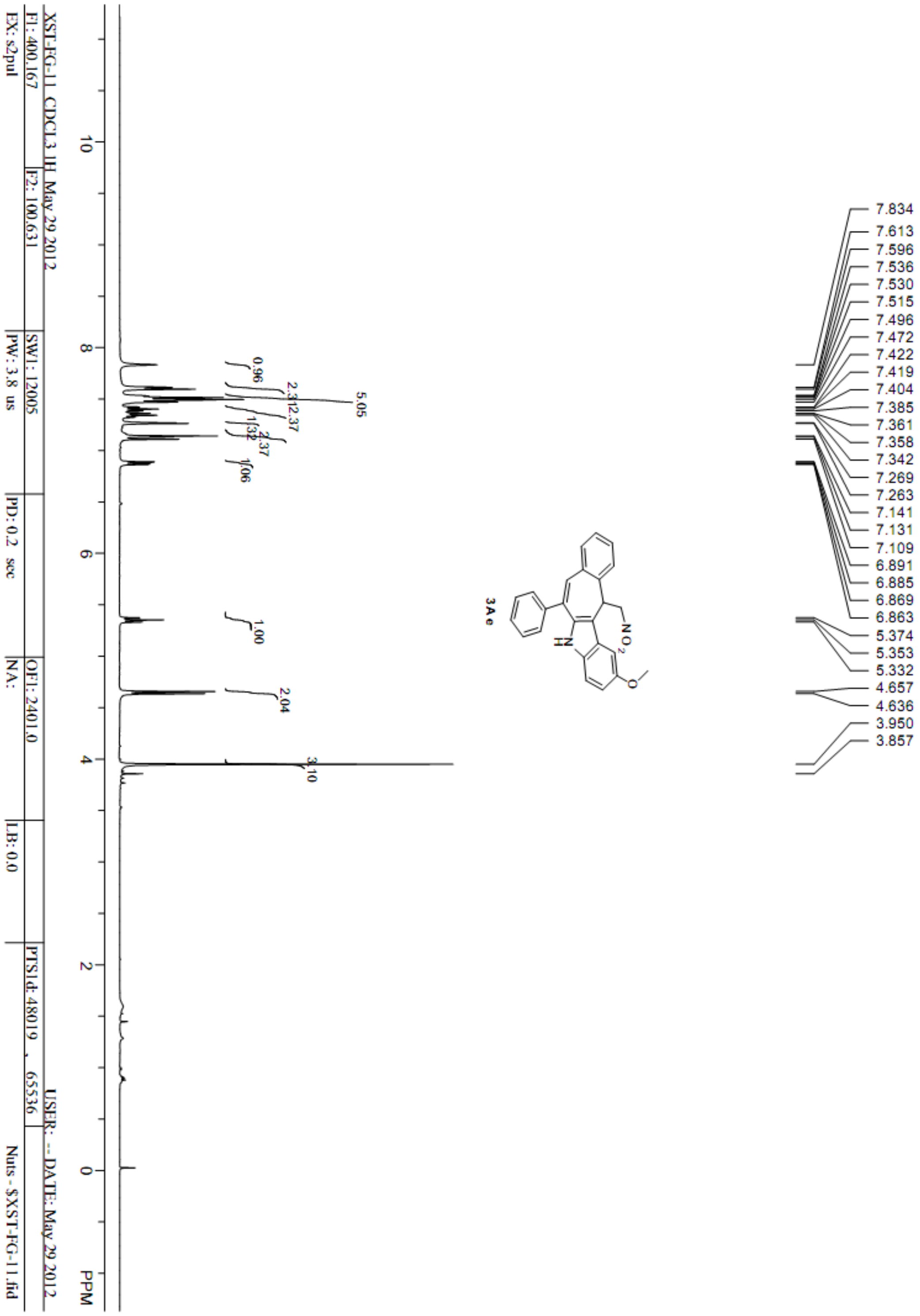

XST-FG-9/2
XST-FG-9 DEPT135
NH
N
O
O
Cl
139.42
135.04
134.93
134.21
133.48
133.20
131.48
130.57
129.91
129.82
129.14
128.91
128.83
127.46
127.43
126.10
123.81
117.69
112.31
112.08
77.32 CDCl3
77.06 CDCl3
76.81 CDCl3
74.87
41.37
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

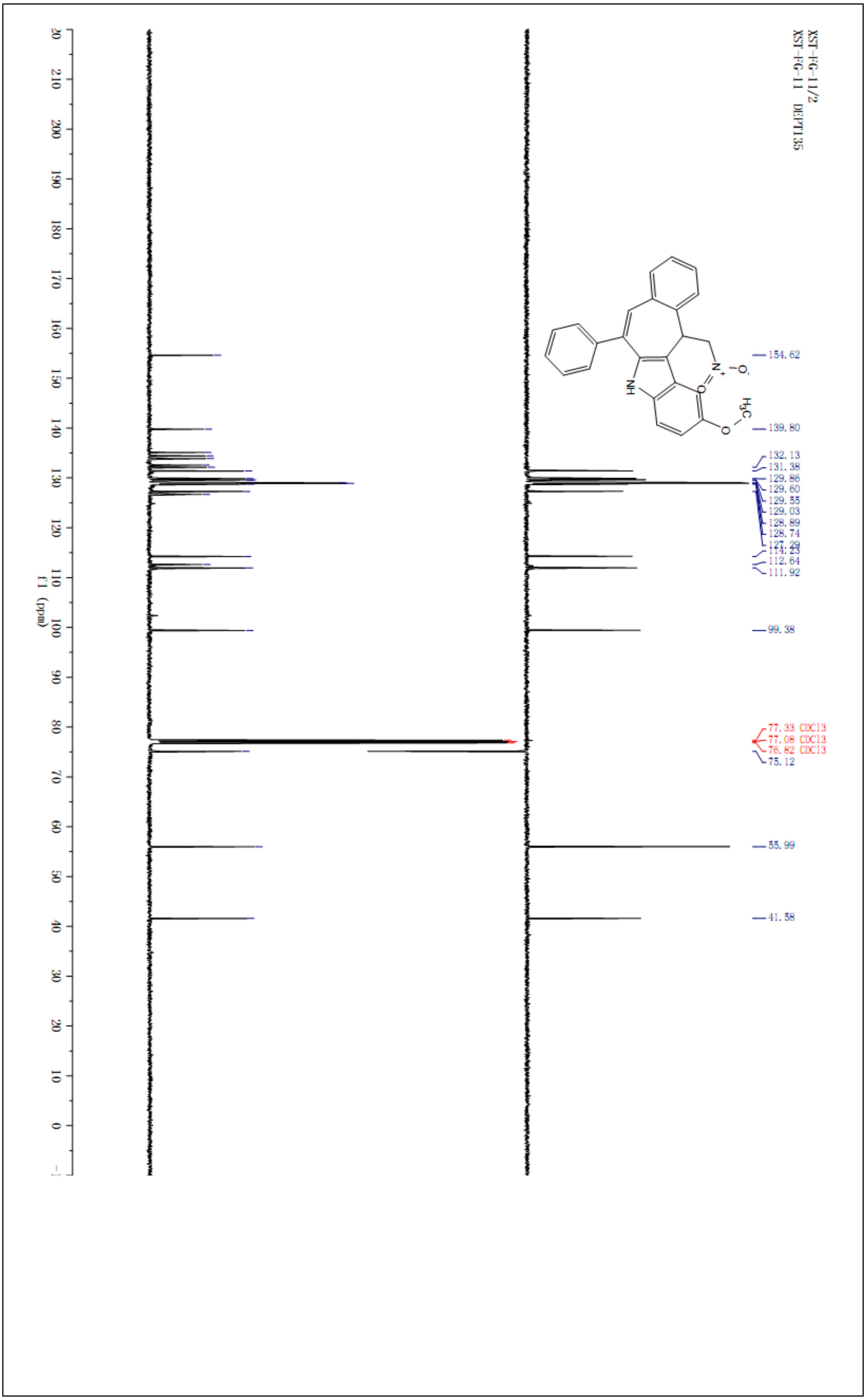
2-Bromo-12-(nitromethyl)-6-phenyl-5,12-dihydrobenzo[4,5]cyclohepta [1,2-*b*] indole(3Ad)



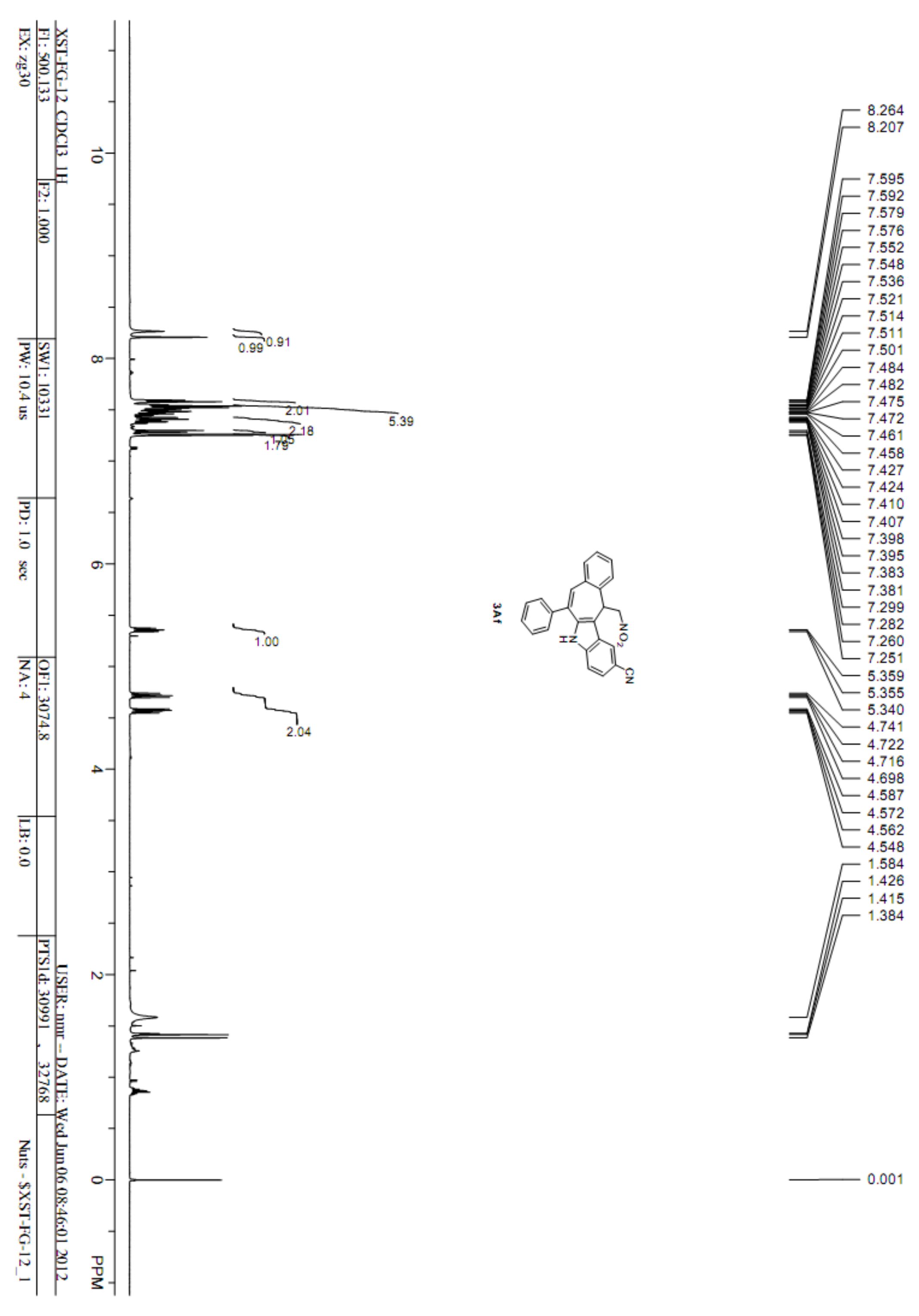

XST-FG-10/2
XST-FG-10 DEPT135
139.41
135.31
134.92
134.19
133.43
133.05
131.49
130.63
129.93
129.84
129.16
128.93
128.83
128.06
127.48
126.32
120.78
113.56
112.51
112.17
77.34 CDCl
77.09 CDCl
76.84 CDCl
74.84
41.33
NH
Br
N+
O
O-
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1

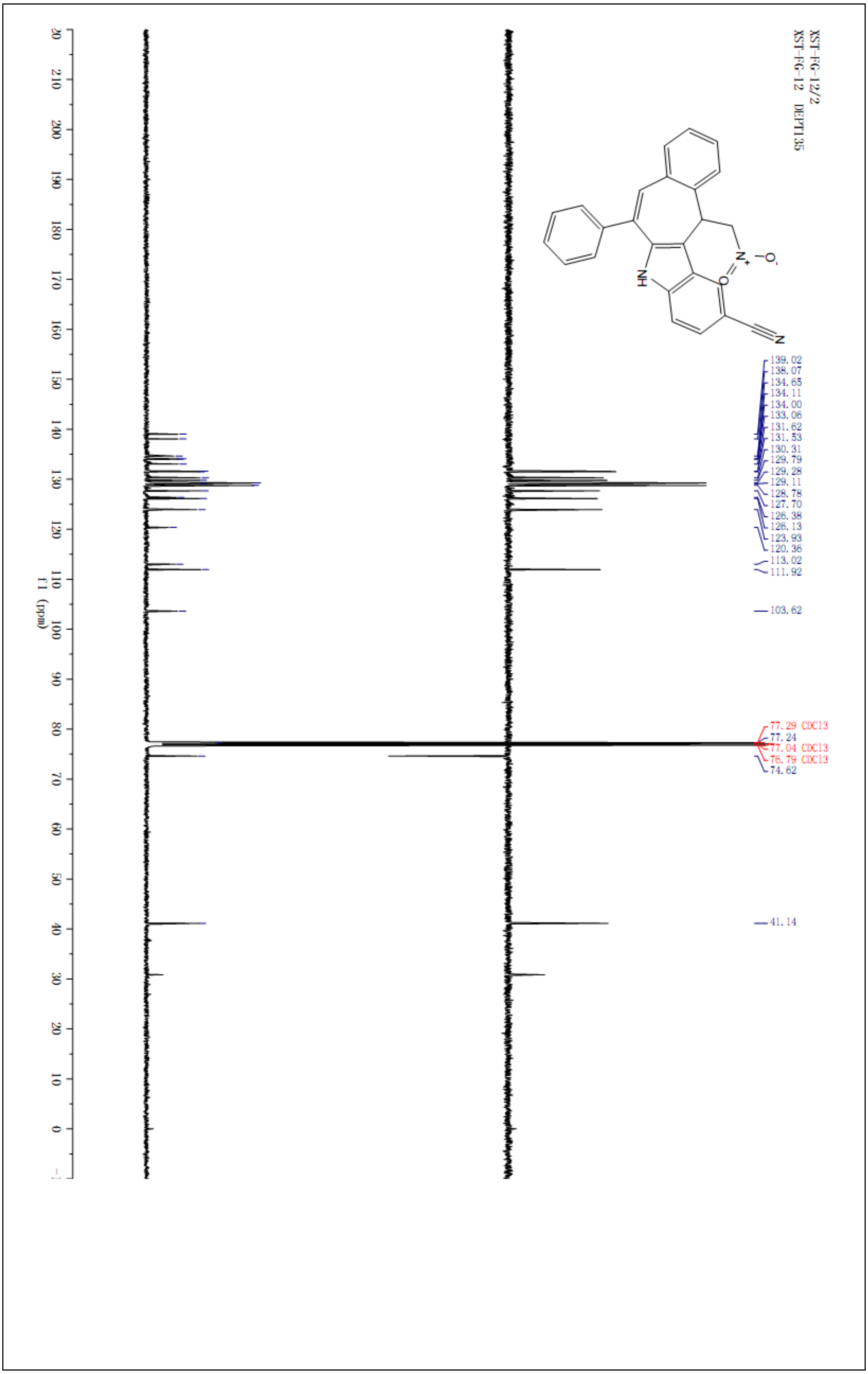
2-Methoxy-12-(nitromethyl)-6-phenyl-5,12-dihydrobenzo[4,5]cyclohepta [1,2-*b*] indole(3Ae)



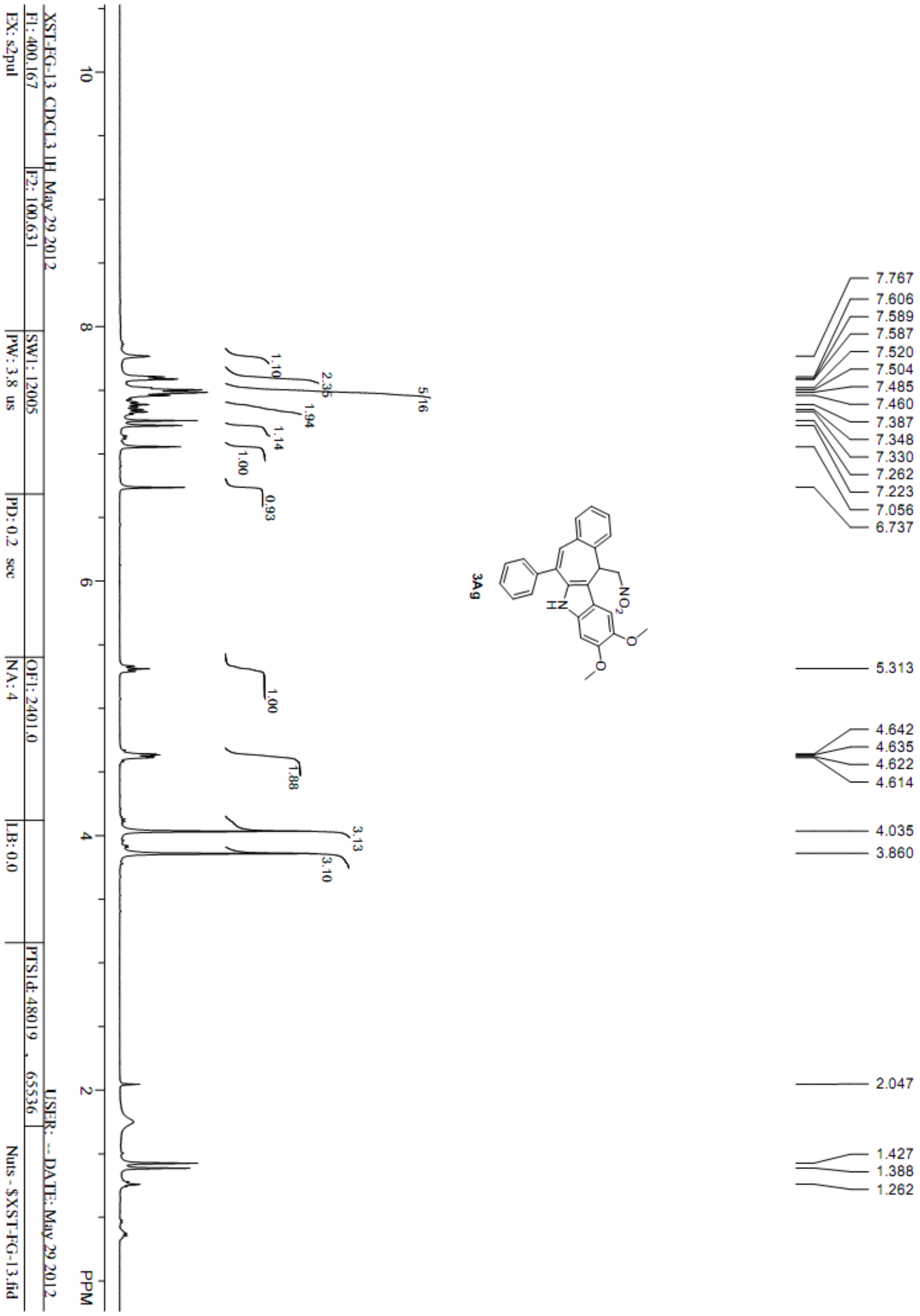

XST-FG-11/2
XST-FG-11 DEPT135
154.62
139.80
132.13
131.38
129.86
129.60
129.55
129.03
128.89
128.74
127.29
114.23
112.64
111.92
99.38
77.33 CDCl3
77.08 CDCl3
76.82 CDCl3
75.12
55.99
41.58
O
N+
O-
H3C
O
HN
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

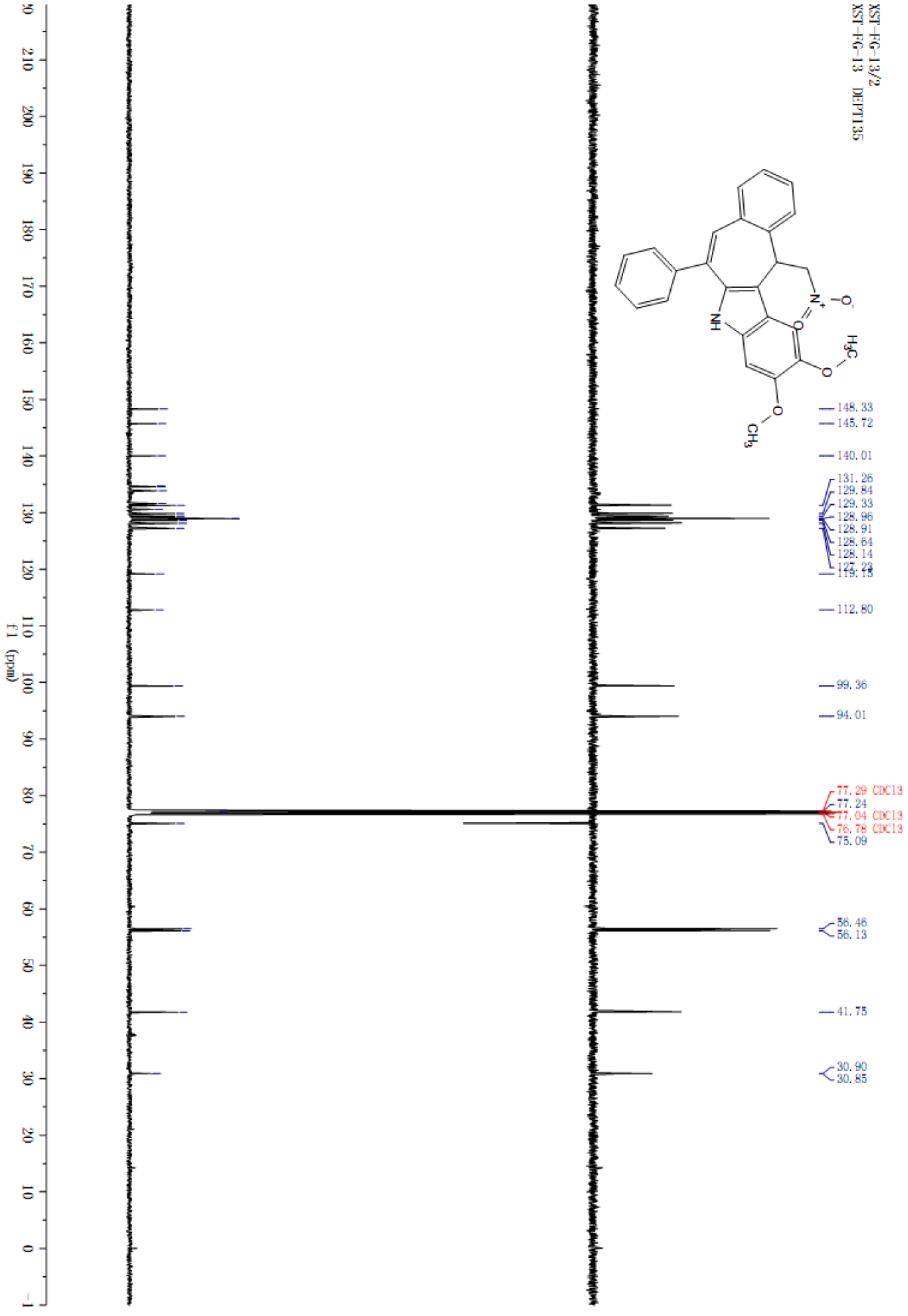
2-Carbonitrile-12-(nitromethyl)-6-phenyl-5,12-dihydrobenzo[4,5]cyclohepta [1,2-*b*] indole(3Af)



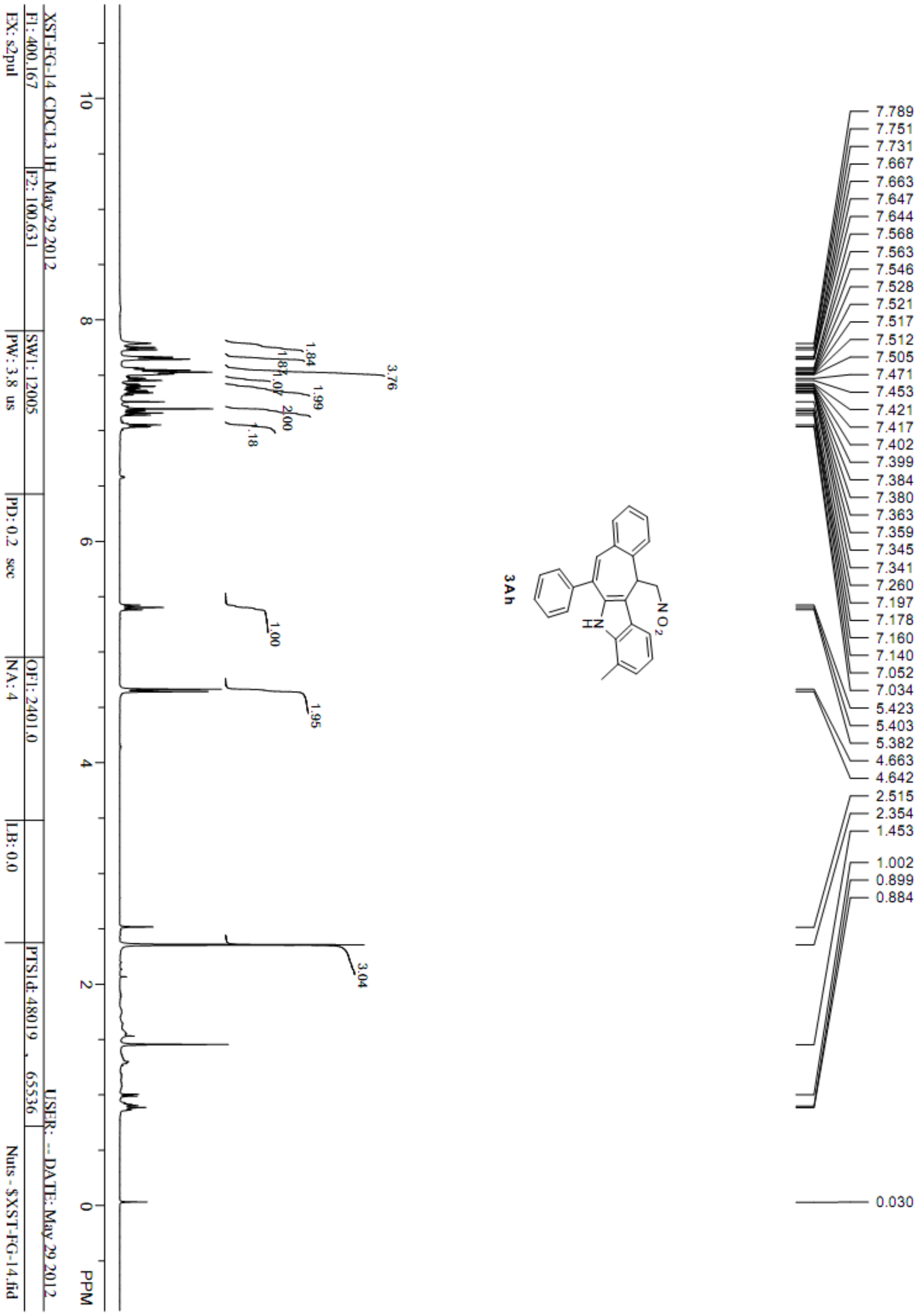

XST-FG-12/2
XST-FG-12 DEPT135
NH
N+
O-
O
N
139.02
138.07
134.65
134.11
134.00
133.06
131.62
131.53
130.31
129.79
129.28
129.11
128.78
127.70
126.38
126.13
123.93
120.36
113.02
111.92
103.62
77.29 CDCl3
77.24
77.04 CDCl3
76.79 CDCl3
74.62
41.14
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1

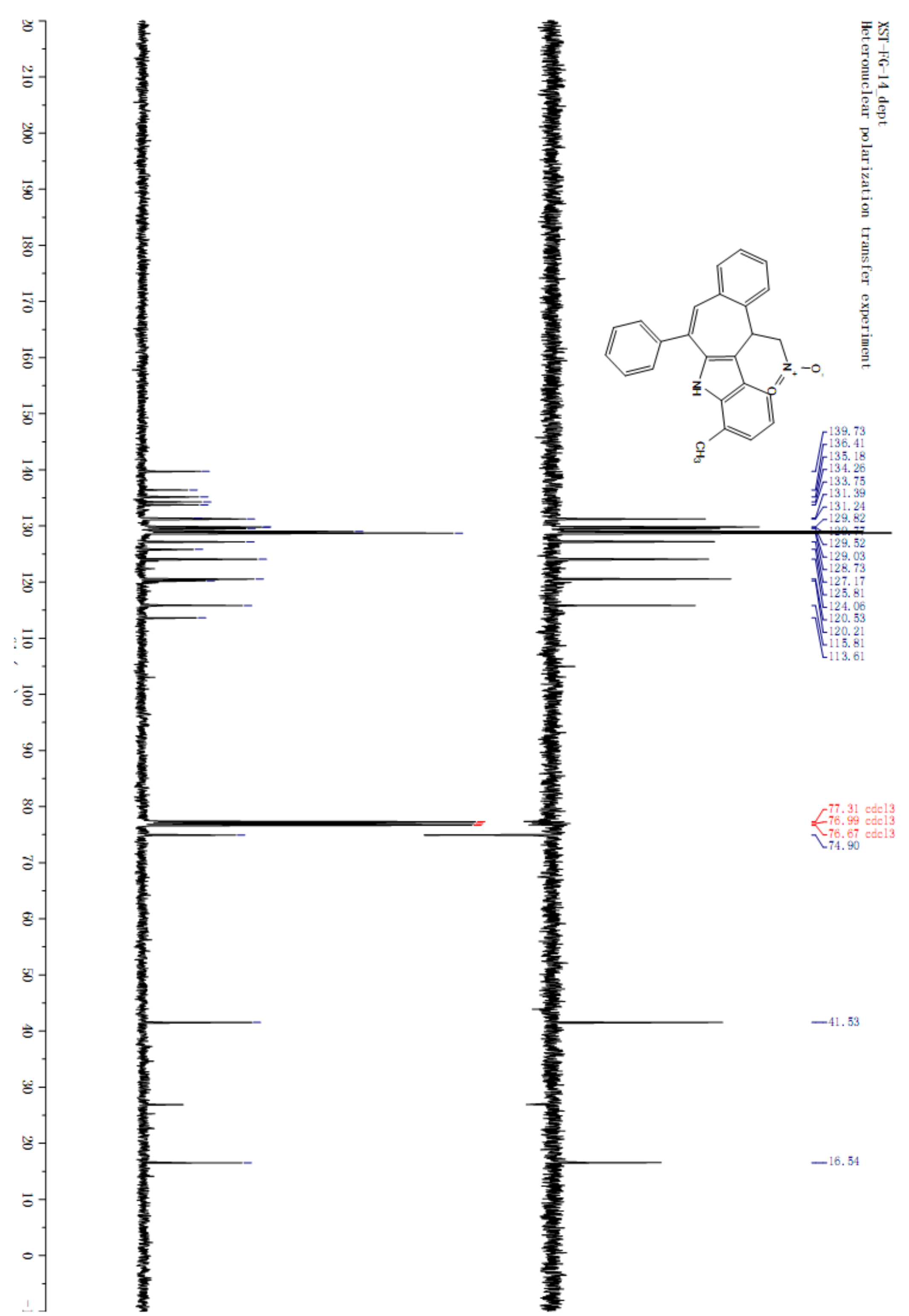
2, 3-Dimethoxy-12-(nitromethyl)-6-phenyl-5,12-dihydrobenzo[4,5]cyclohepta [1,2-*b*] indole(3Ag)



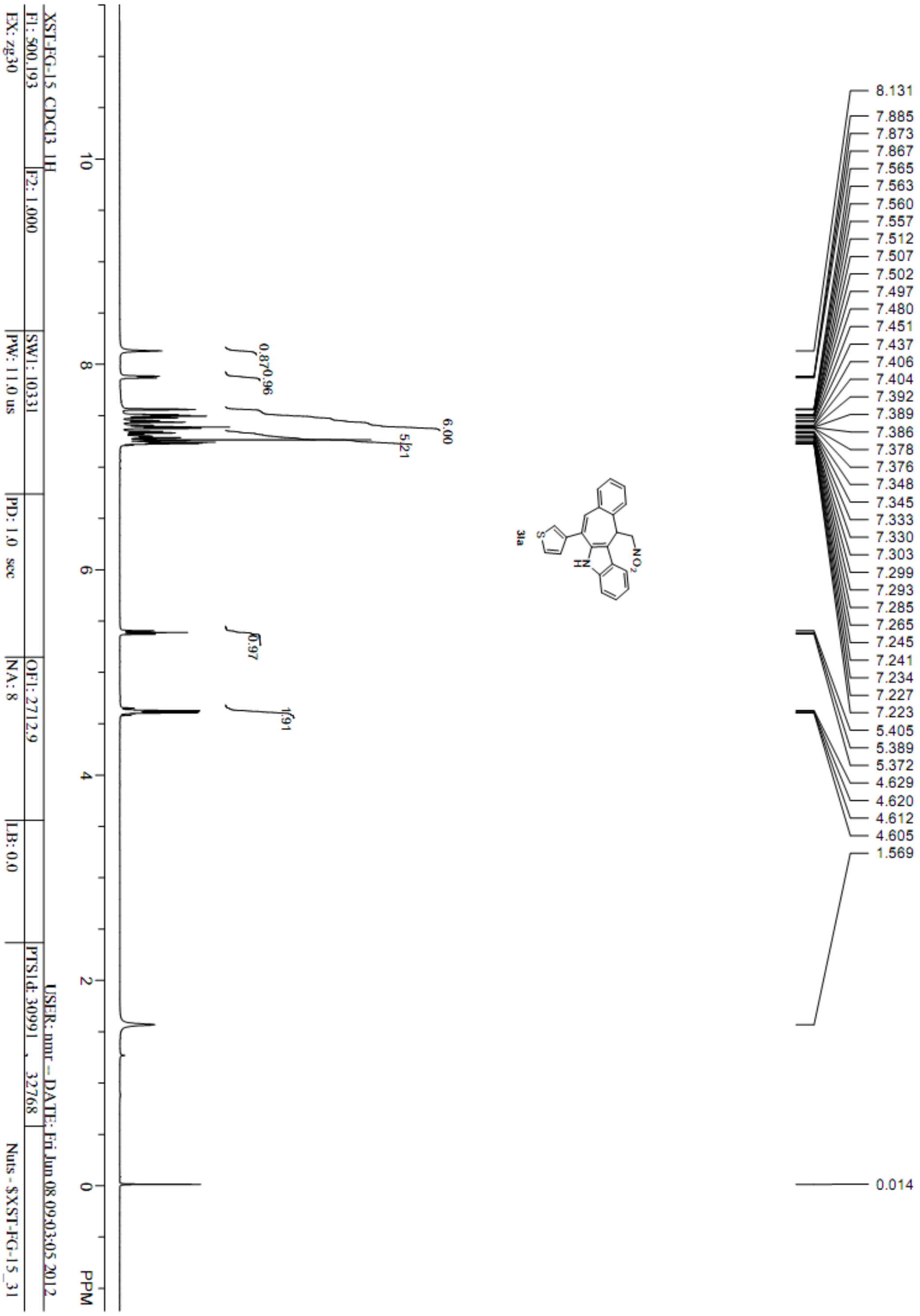

XST-FG-13/2
XST-FG-13 DEPT135
NH
N+
O-
O
H3C
O
O
CH3
148.33
145.72
140.01
131.26
129.84
129.33
128.96
128.91
128.64
128.14
127.22
119.15
112.80
99.36
94.01
77.29 CDCl3
77.24
77.04 CDCl3
76.78 CDCl3
75.09
56.46
56.13
41.75
30.90
30.85
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1

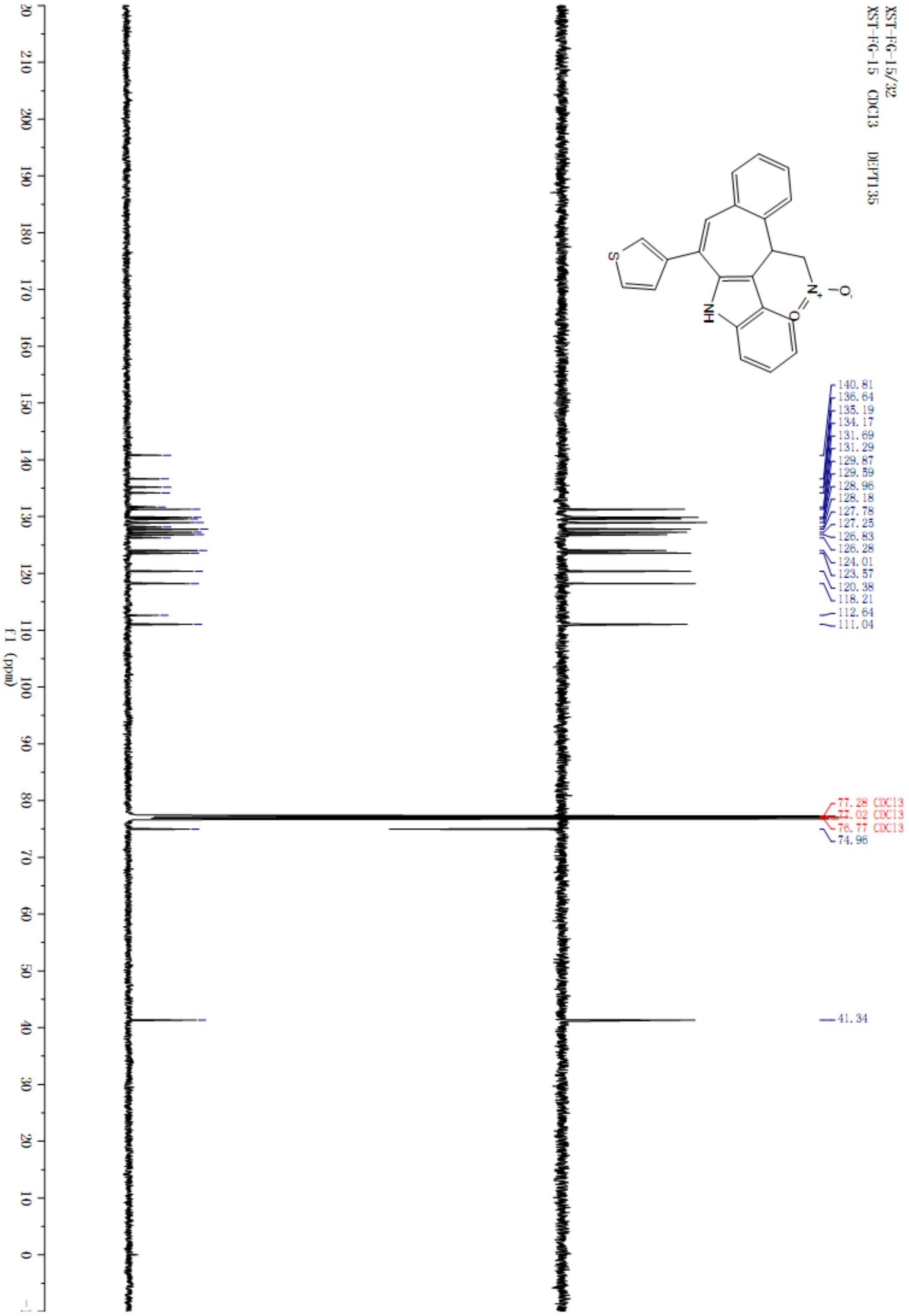
4-Methyl-12-(nitromethyl)-6-phenyl-5,12-dihydrobenzo[4,5]cyclohepta [1,2-*b*] indole(3Ah)



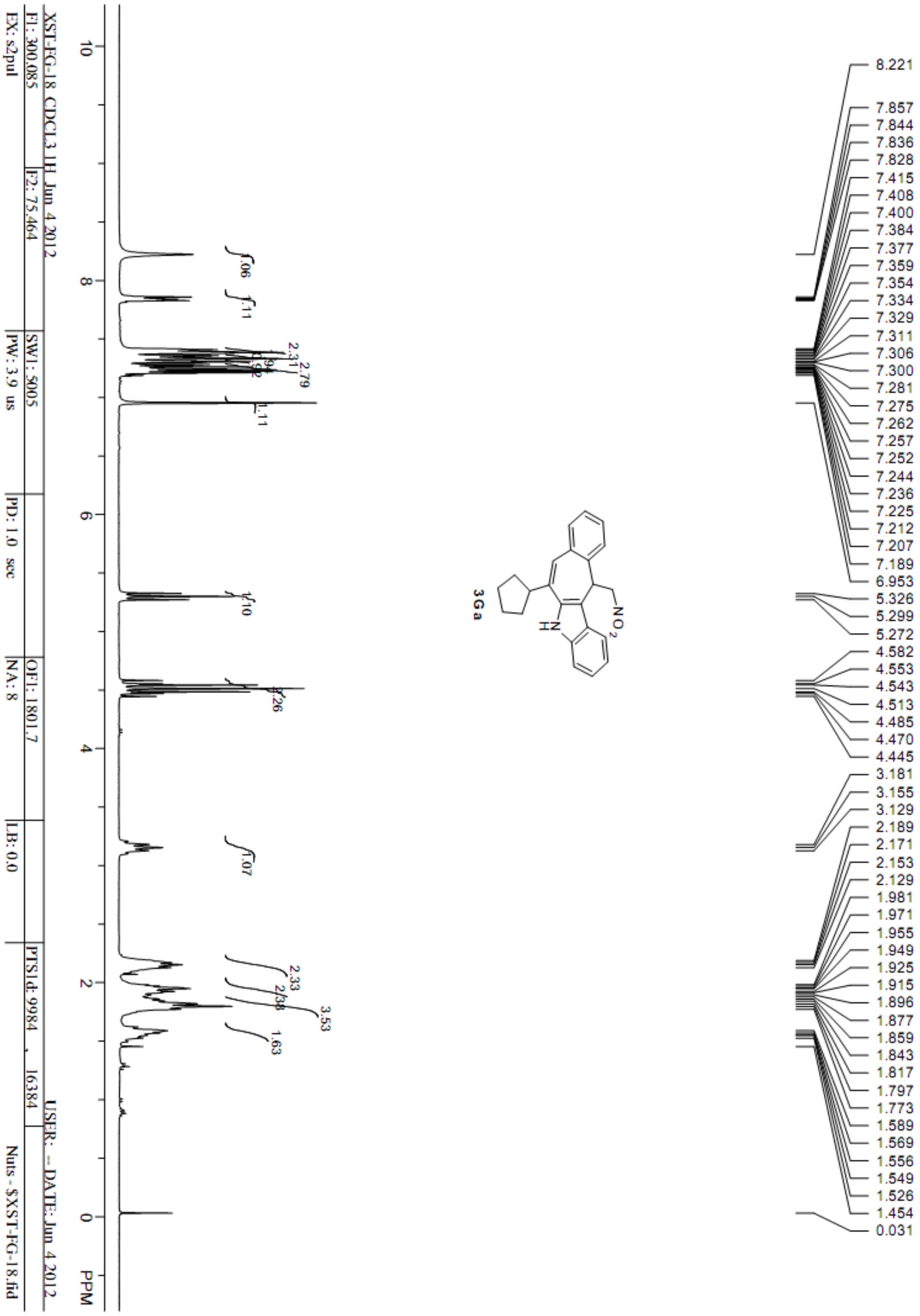

XST-FG-14_dept
Heteronuclear polarization transfer experiment
NH
CH3
N+
O-
O
139.73
136.41
135.18
134.26
133.75
131.39
131.24
129.82
129.77
129.52
129.03
128.73
127.17
125.81
124.06
120.53
120.21
115.81
113.61
77.31 cdcl3
76.99 cdcl3
76.67 cdcl3
74.90
41.53
16.54
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1

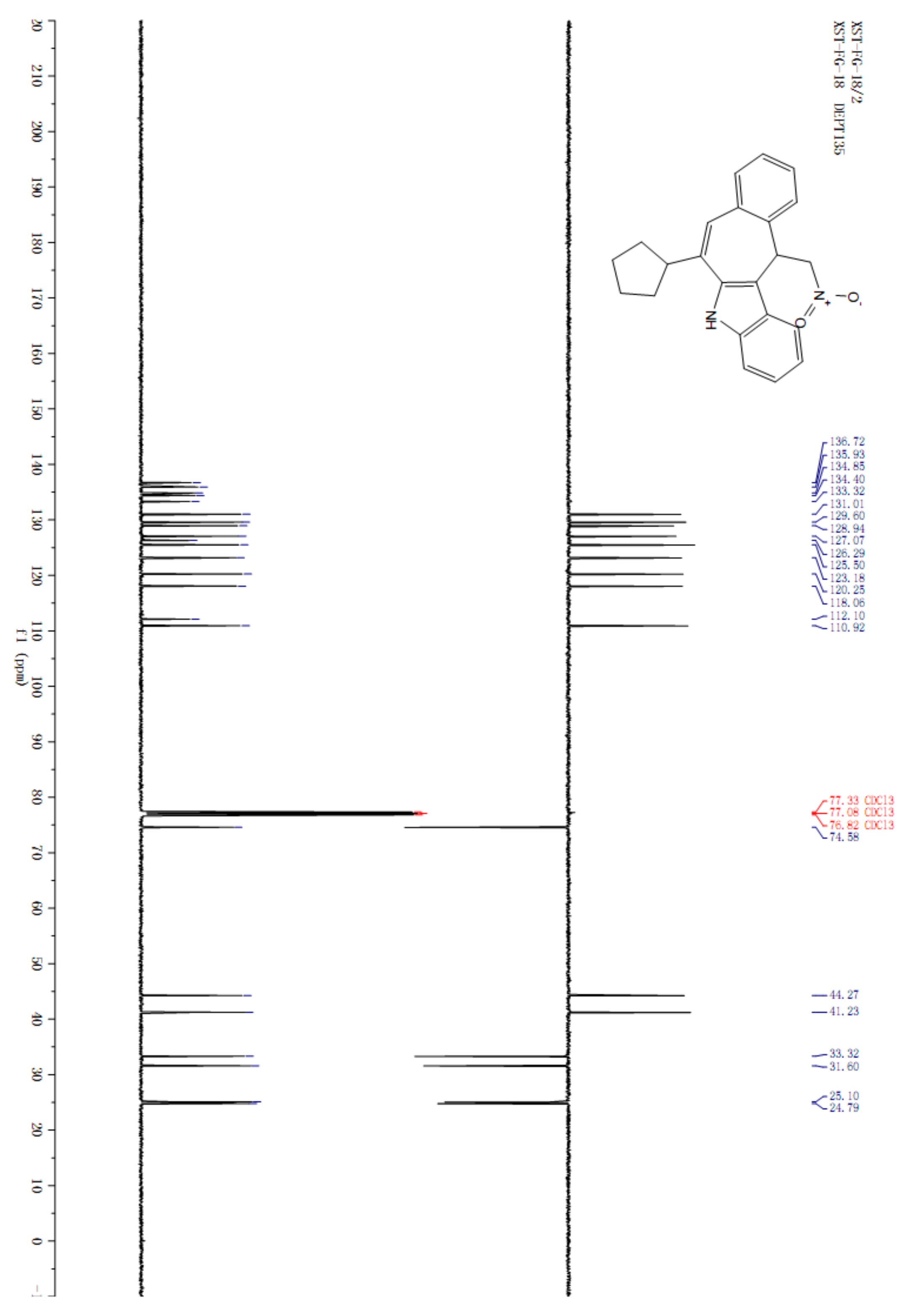
12-(Nitromethyl)-6-(thiophen-3-yl)-5,12-dihydrobenzo[4,5]cyclohepta[1,2-*b*] indole(3Ia)



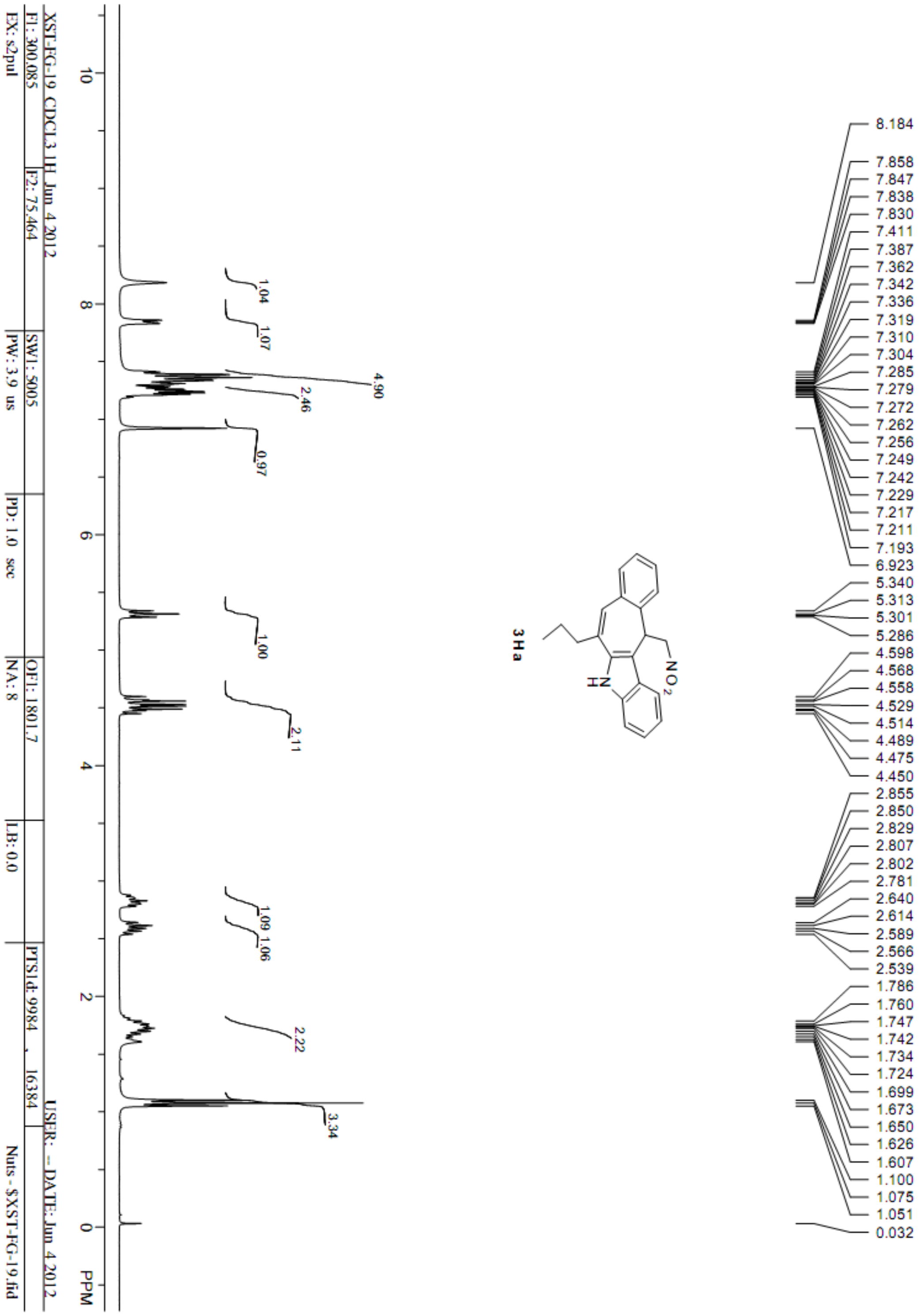

XST-FG-15/32
XST-FG-15 CDCl3 DEPT135
S
NH
N+
O
O-
140.81
136.64
135.19
134.17
131.69
131.29
129.87
129.59
128.96
128.18
127.78
127.25
126.83
126.28
124.01
123.57
120.38
118.21
112.64
111.04
77.28 CDCl3
77.02 CDCl3
76.77 CDCl3
74.96
41.34
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

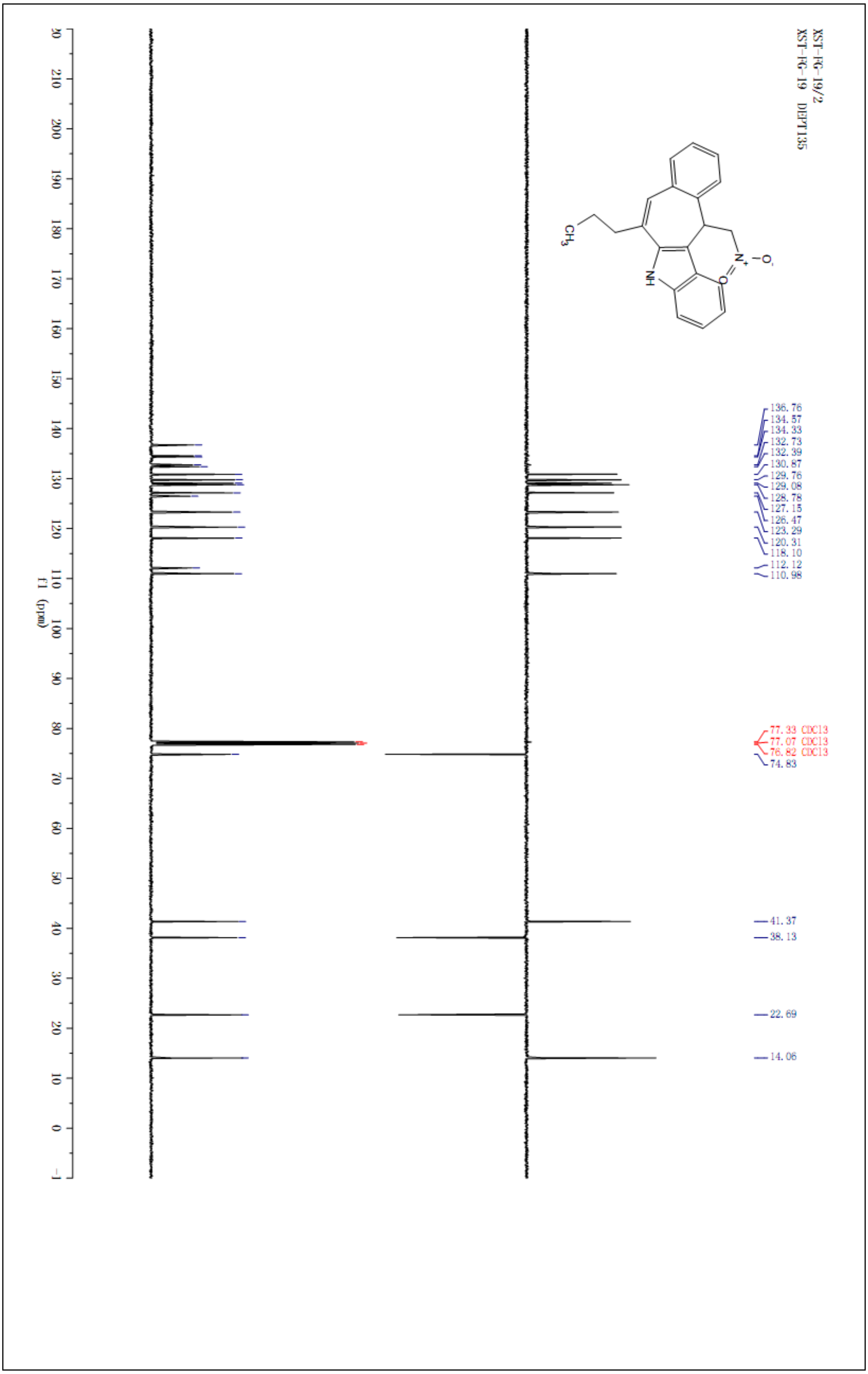
12-(Nitromethyl)-6-cyclopentyl-5,12-dihydrobenzo[4,5]cyclohepta[1,2-*b*]indole(3Ga)



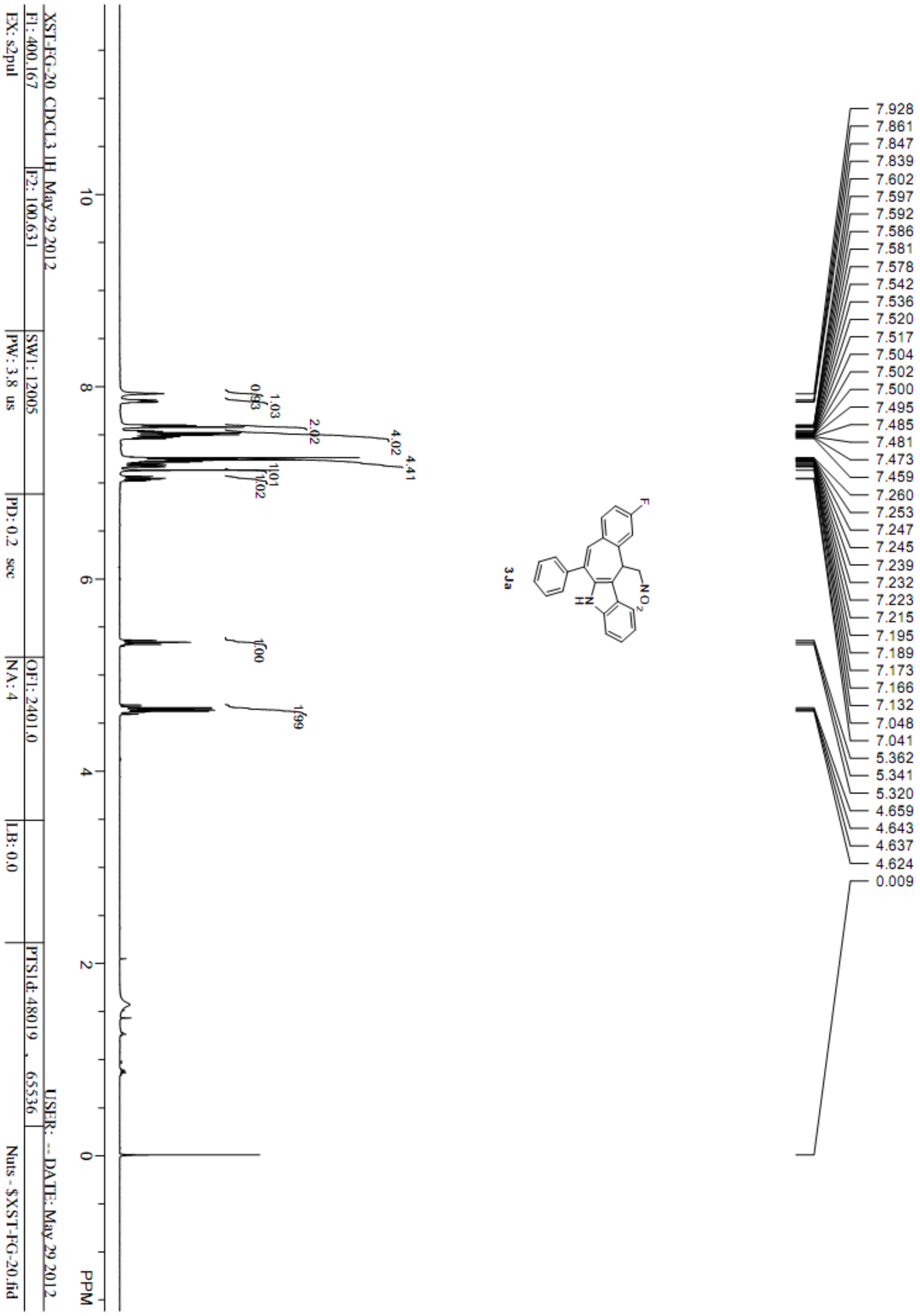

XST-FG-18/2
XST-FG-18 DEPT135
NH
N+
O-
O
136.72
135.93
134.85
134.40
133.32
131.01
129.60
128.94
127.07
126.29
125.50
123.18
120.25
118.06
112.10
110.92
77.33 CDCl3
77.08 CDCl3
76.82 CDCl3
74.58
44.27
41.23
33.32
31.60
25.10
24.79
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

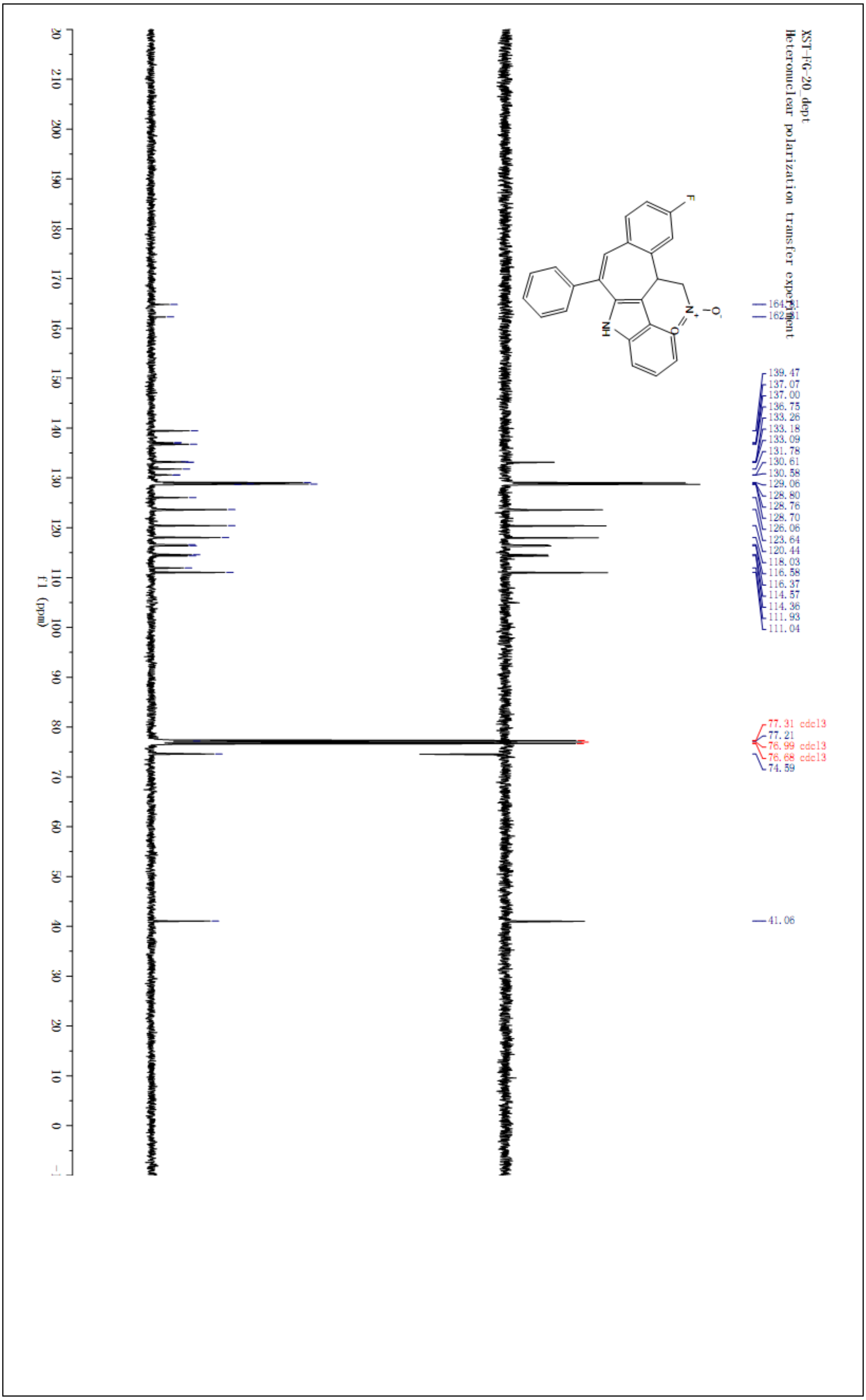
12-(Nitromethyl)-6-propyl-5,12-dihydrobenzo[4,5] cyclohepta [1,2-*b*] indole(3Ha)

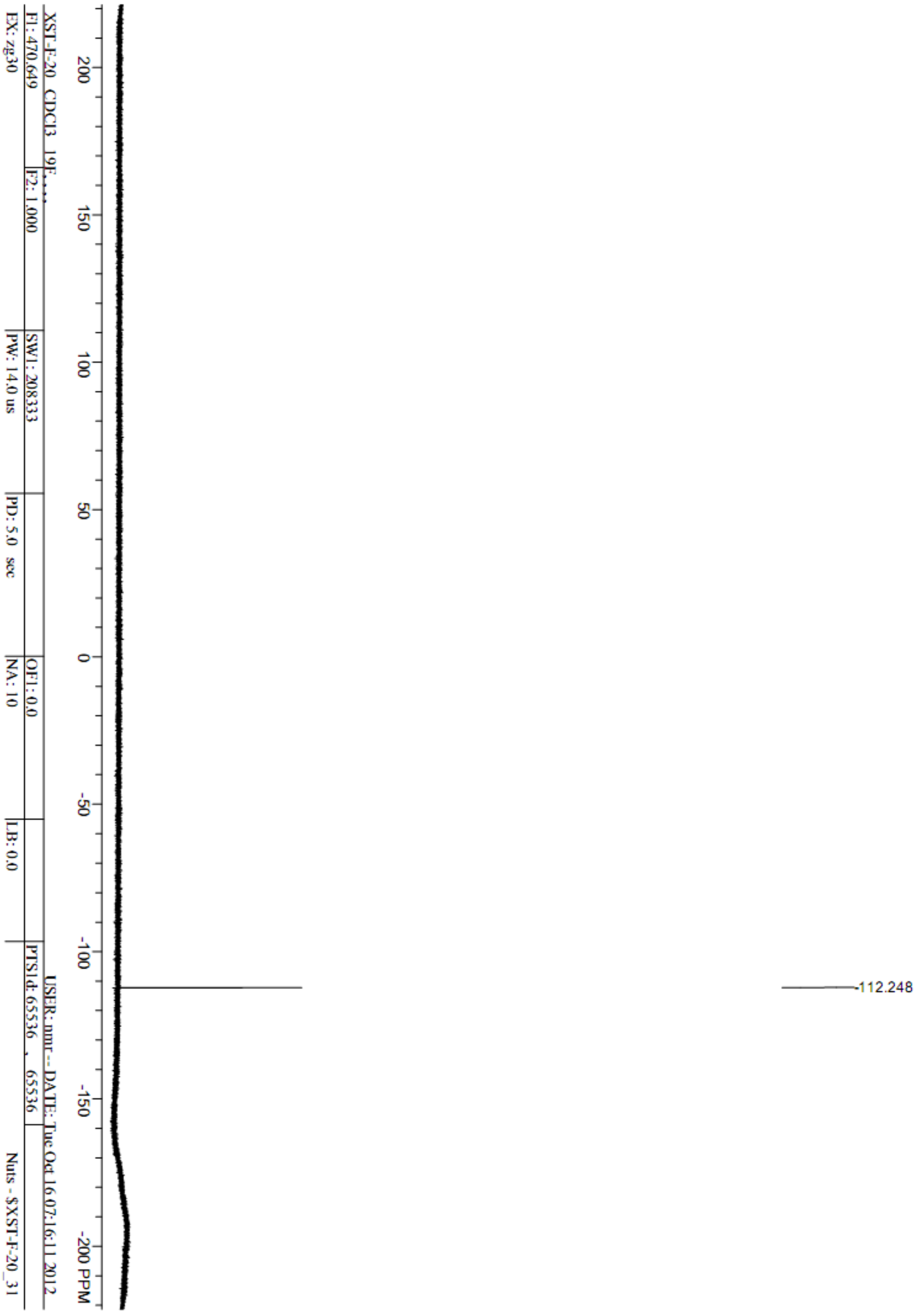



XST-FG-19/2
XST-FG-19 DEPT135
CH3
NH
N+
O-
O
136.76
134.57
134.33
132.73
132.39
130.87
129.76
129.08
128.78
127.15
126.47
123.29
120.31
118.10
112.12
110.98
77.33 CDCl3
77.07 CDCl3
76.82 CDCl3
74.83
41.37
38.13
22.69
14.06
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

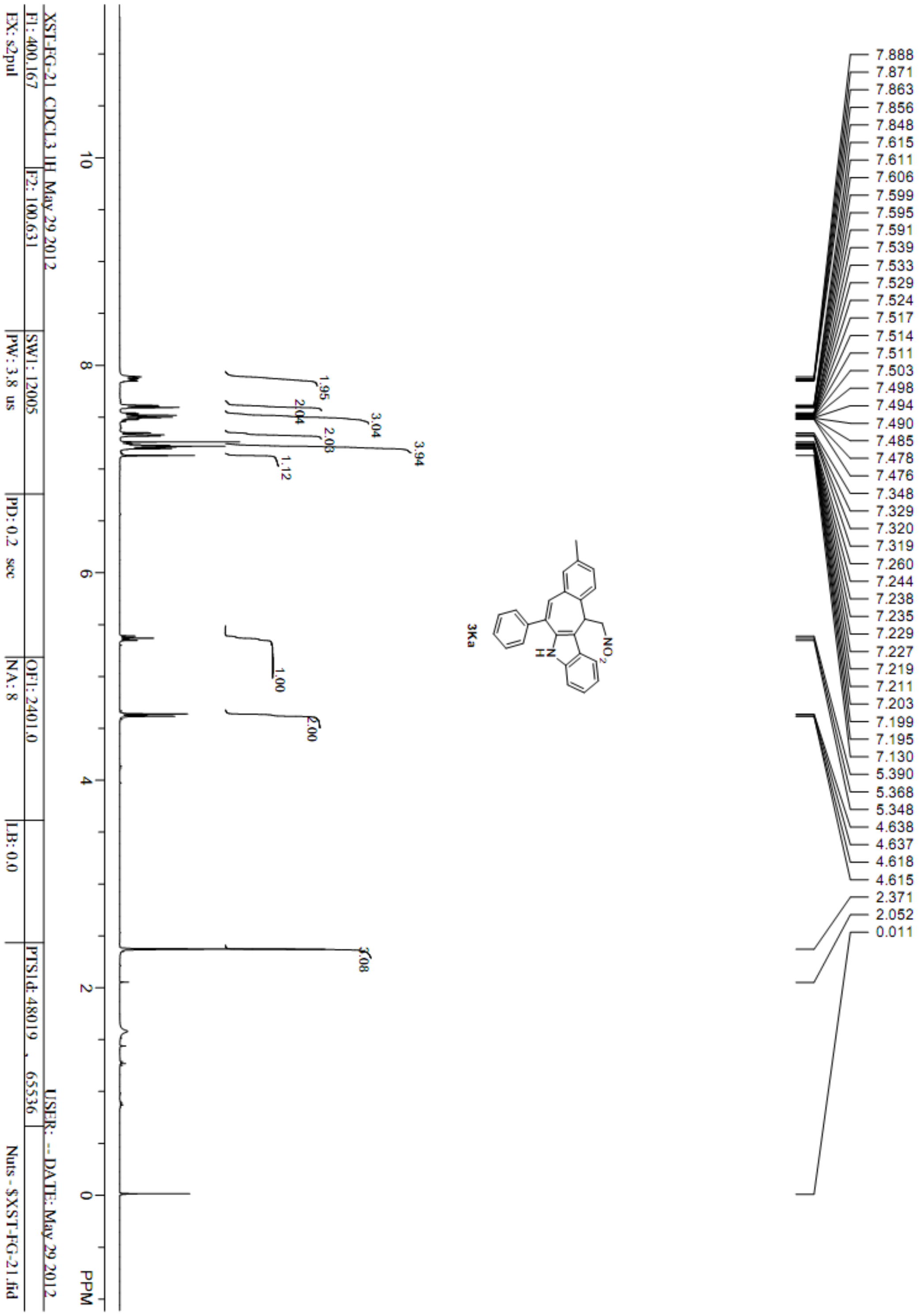
10-Fluoro-12-(nitromethyl)-6-phenyl-5,12-dihydrobenzo[4,5]cyclohepta[1,2-*b*] indole (3Ja)

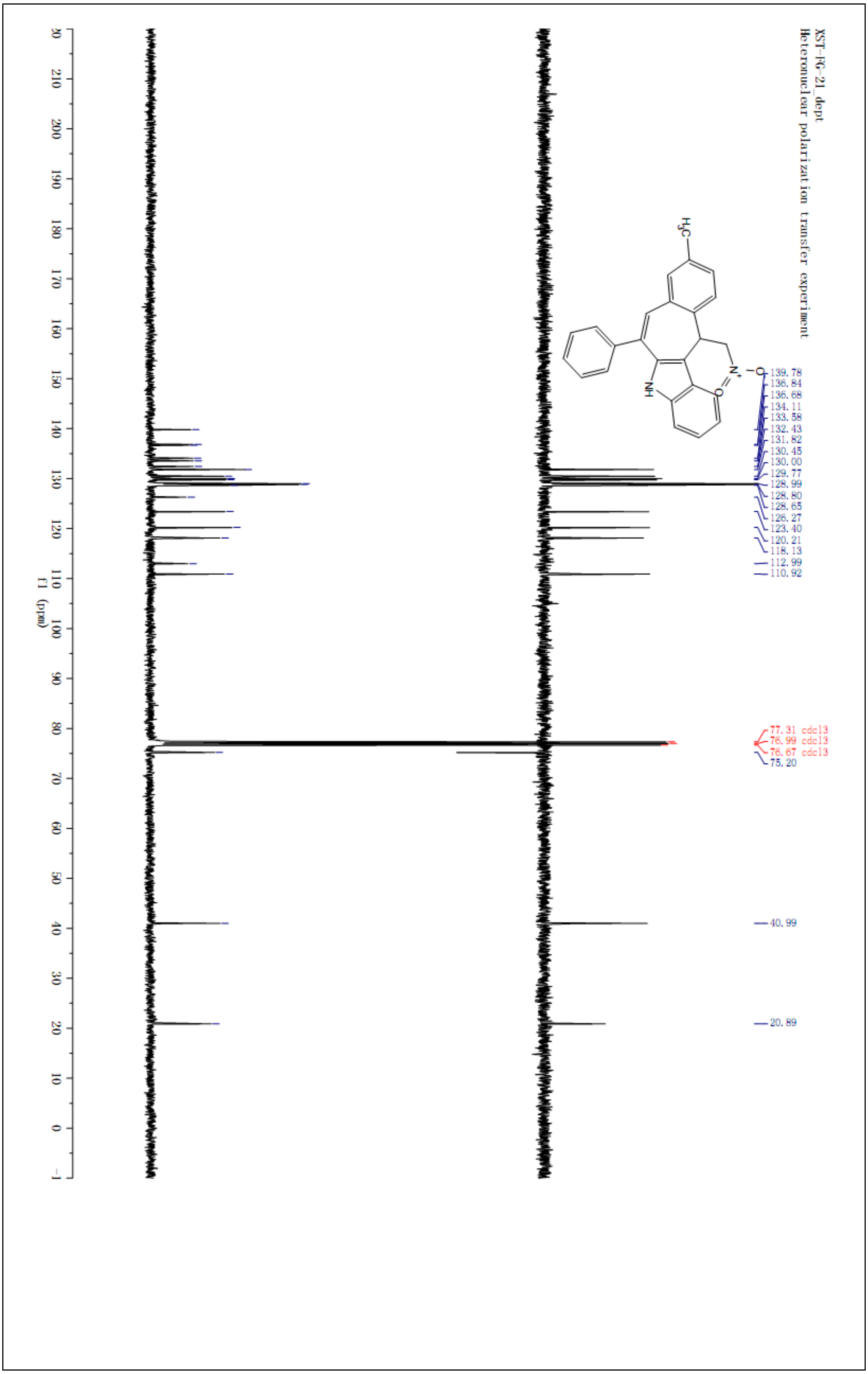



XST-FG-20_dept
Heteronuclear polarization transfer experiment
F
N
O
NH
164.81
162.81
139.47
137.07
137.00
136.75
133.26
133.18
133.09
131.78
130.61
130.58
129.06
128.80
128.76
128.70
126.06
123.64
120.44
118.03
116.58
116.37
114.57
114.36
111.93
111.04
77.31 cdcl3
77.21
76.99 cdcl3
76.68 cdcl3
74.59
41.06
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

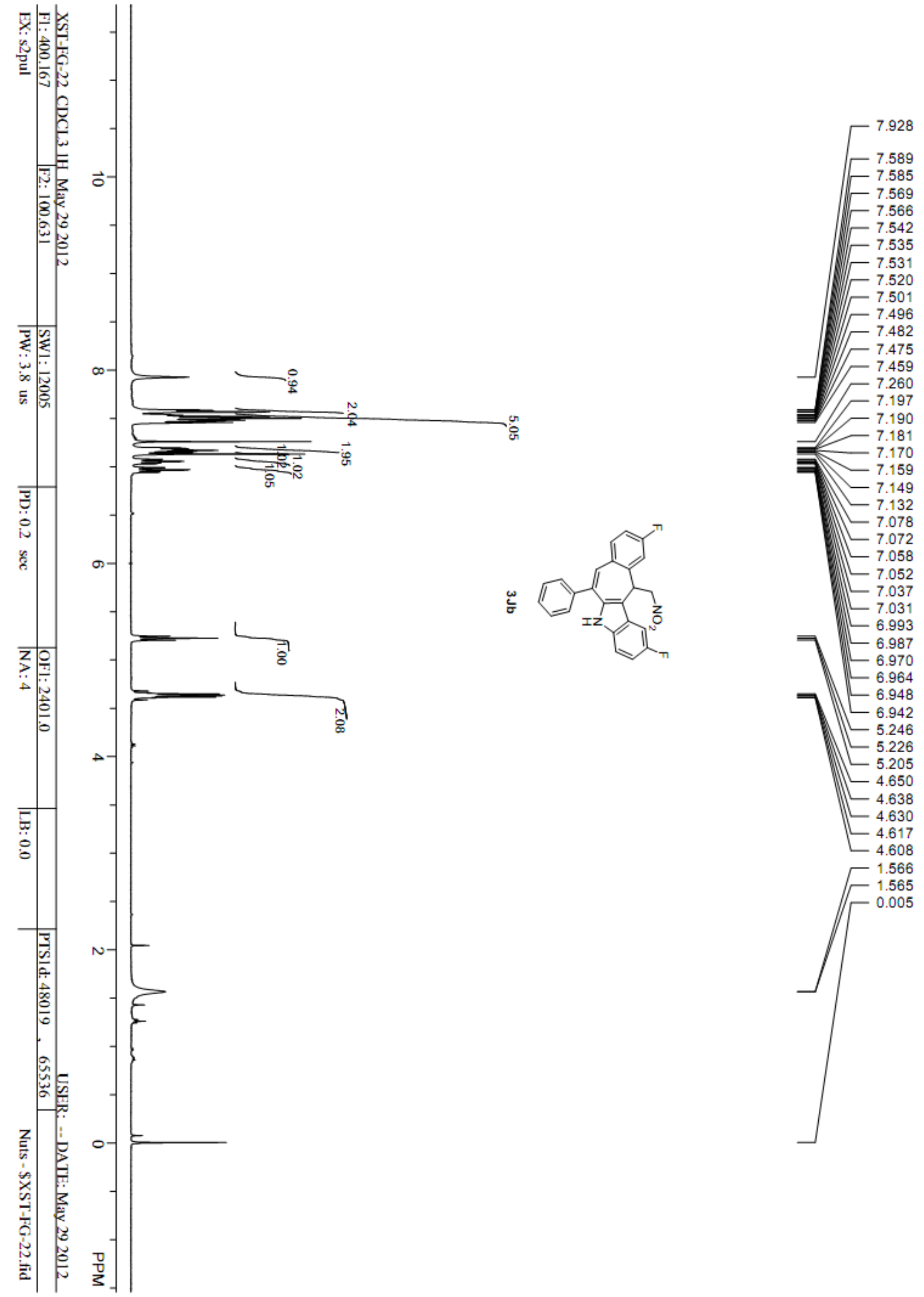

XST-F-20 CDCl3 19F
F1: 470.649
F2: 1.000
SW1: 208333
OF1: 0.0
PTS1d: 65536 , 65536
USER: nmr -- DATE: Tue Oct 16 07:16:11 2012
EX: zg30
PW: 14.0 us
PD: 5.0 sec
NA: 10
LB: 0.0
Nuts - $XST-F-20_31
200
150
100
50
0
-50
-100
-150
-200 PPM
-112.248

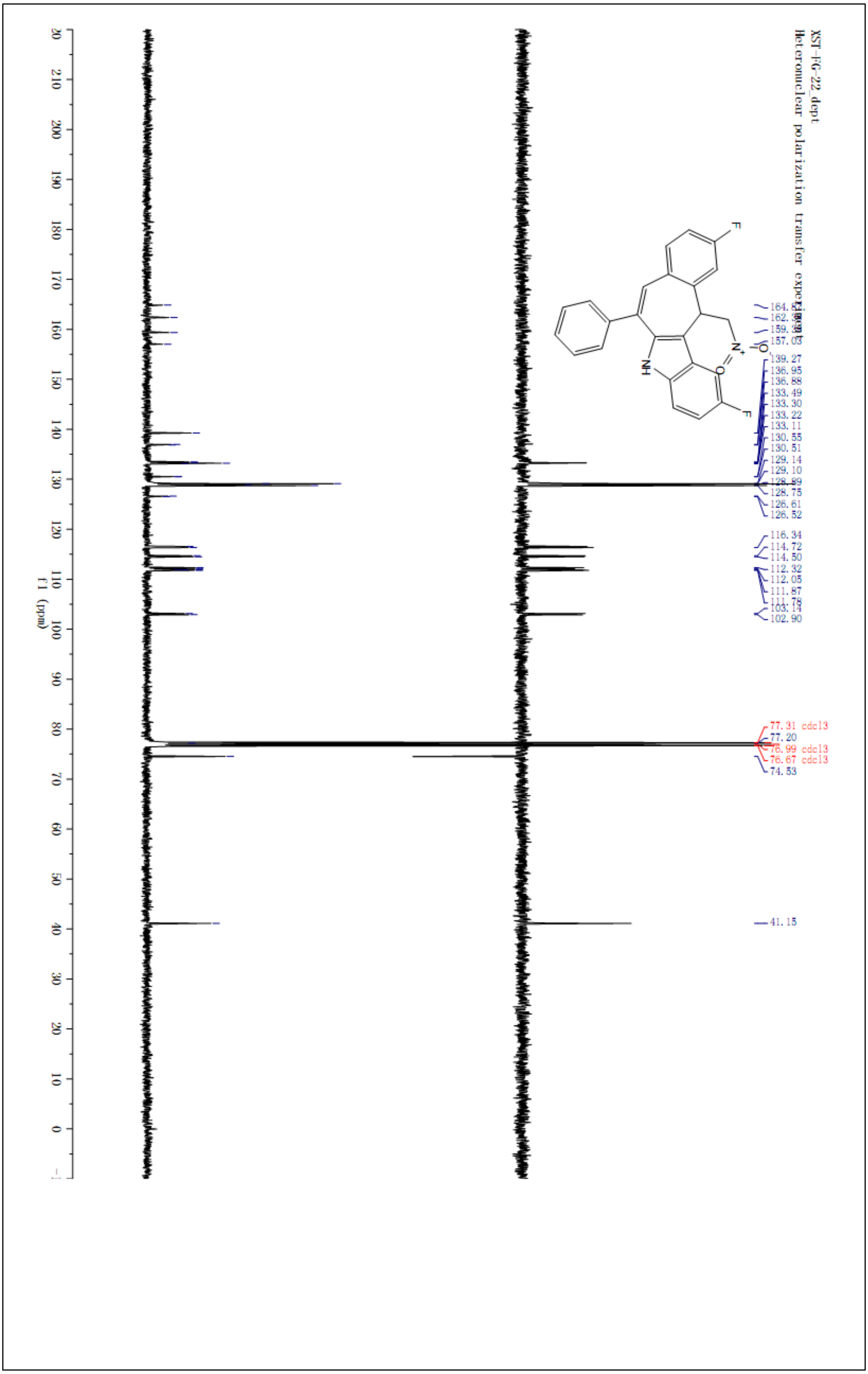
9-Methyl-12-(nitromethyl)-6-phenyl-5,12-dihydrobenzo[4,5]cyclohepta[1,2-*b*] indole (3Ka)

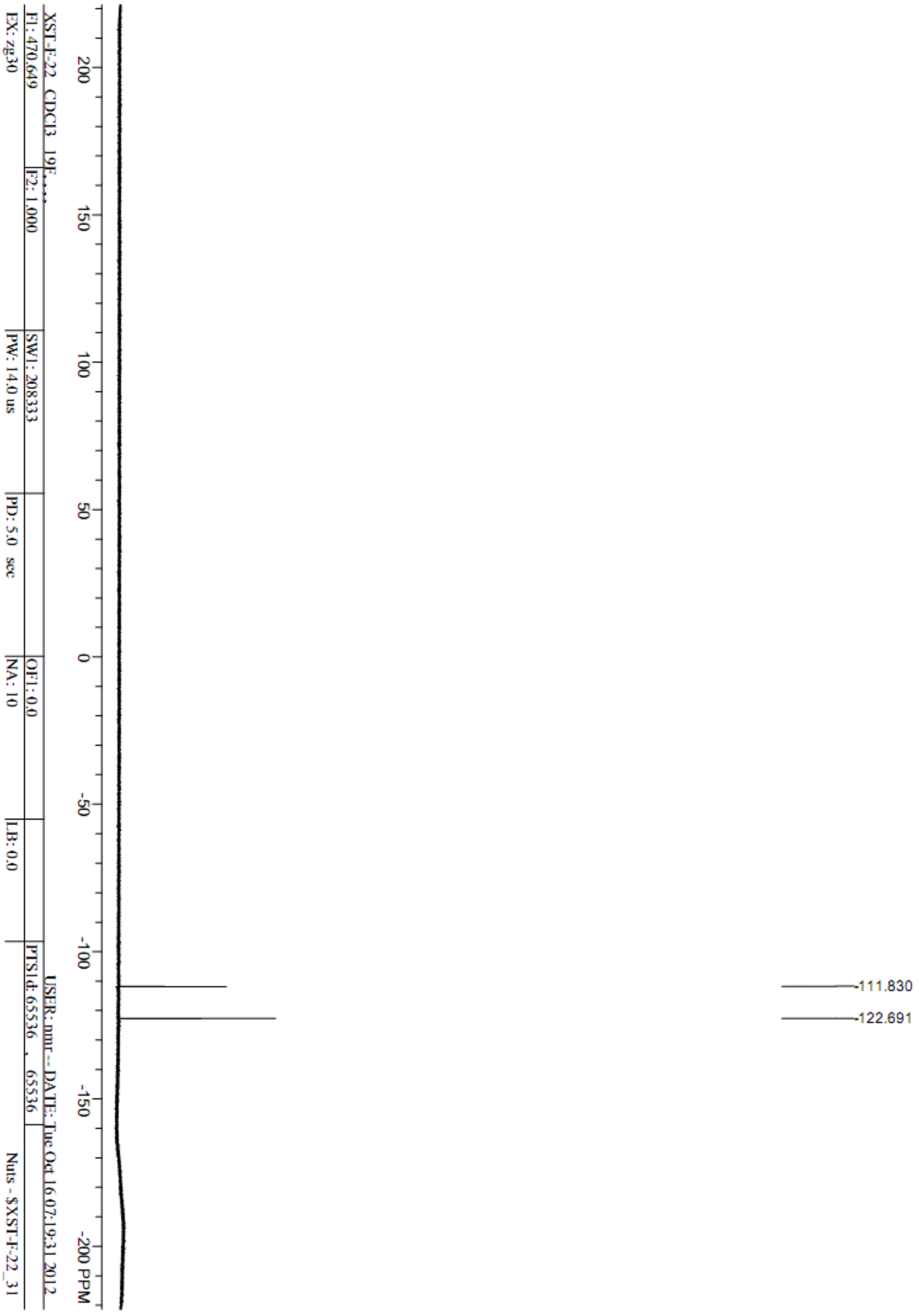



XST-FG-21_dept
Heteronuclear polarization transfer experiment
H_3C
NH
N^+
O^-
O
139.78
136.84
136.68
134.11
133.58
132.43
131.82
130.45
130.00
129.77
128.99
128.80
128.65
126.27
123.40
120.21
118.13
112.99
110.92
77.31 cdcl3
76.99 cdcl3
76.67 cdcl3
75.20
40.99
20.89
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

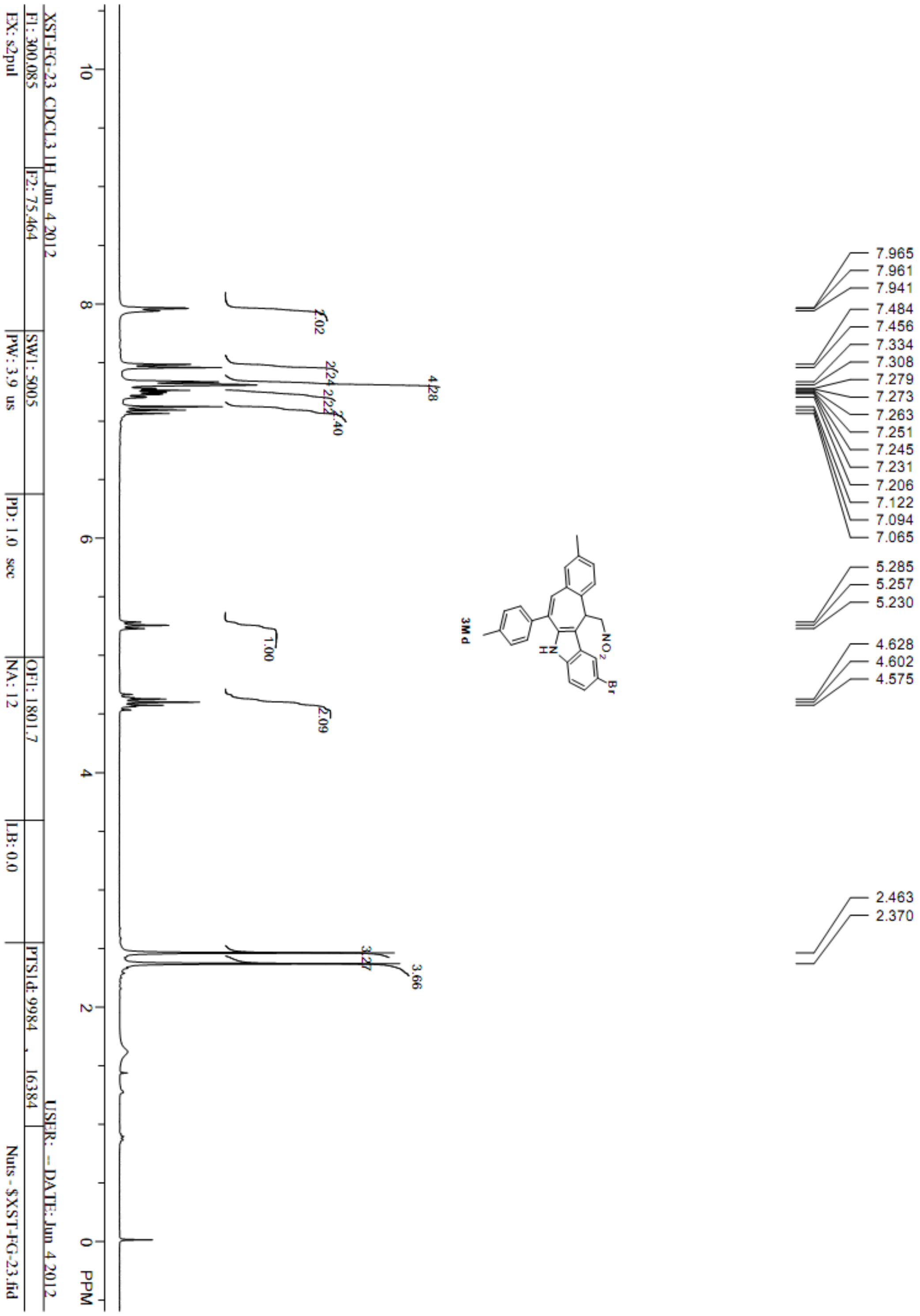
2,10-Difluoro-12-(nitromethyl)-6-phenyl-5,12-dihydrobenzo[4,5]cyclohepta[1,2-*b*] indole (3Jb)

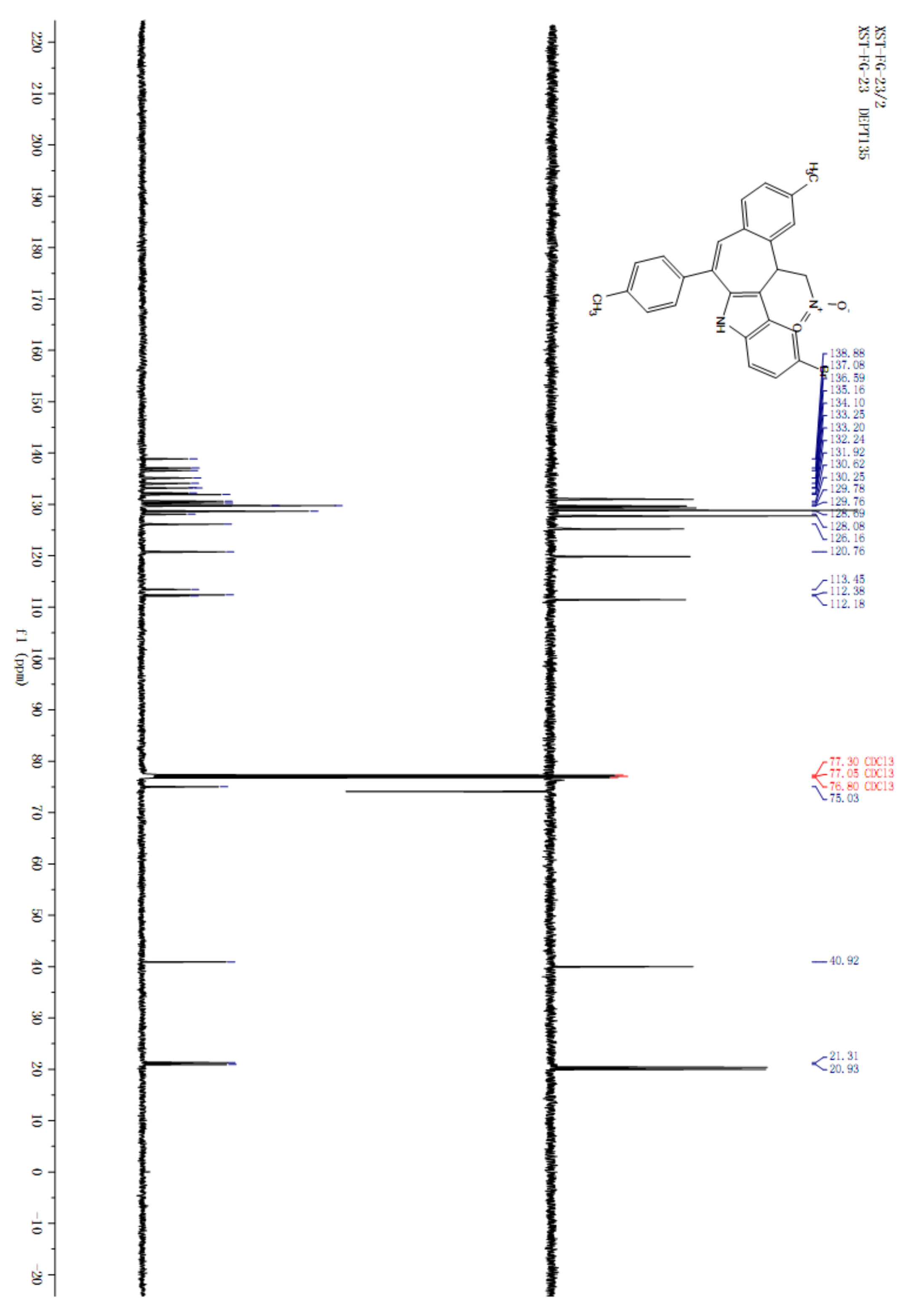



XST-FG-22_dept
Heteronuclear polarization transfer experiment
164.8
162.3
159.3
157.03
139.27
136.95
136.88
133.49
133.30
133.22
133.11
130.55
130.51
129.14
129.10
128.89
128.75
126.61
126.52
116.34
114.72
114.50
112.32
112.05
111.87
111.78
103.14
102.90
77.31 cdcl3
77.20
76.99 cdcl3
76.67 cdcl3
74.53
41.15
F
F
NH
N+
O
O-
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1

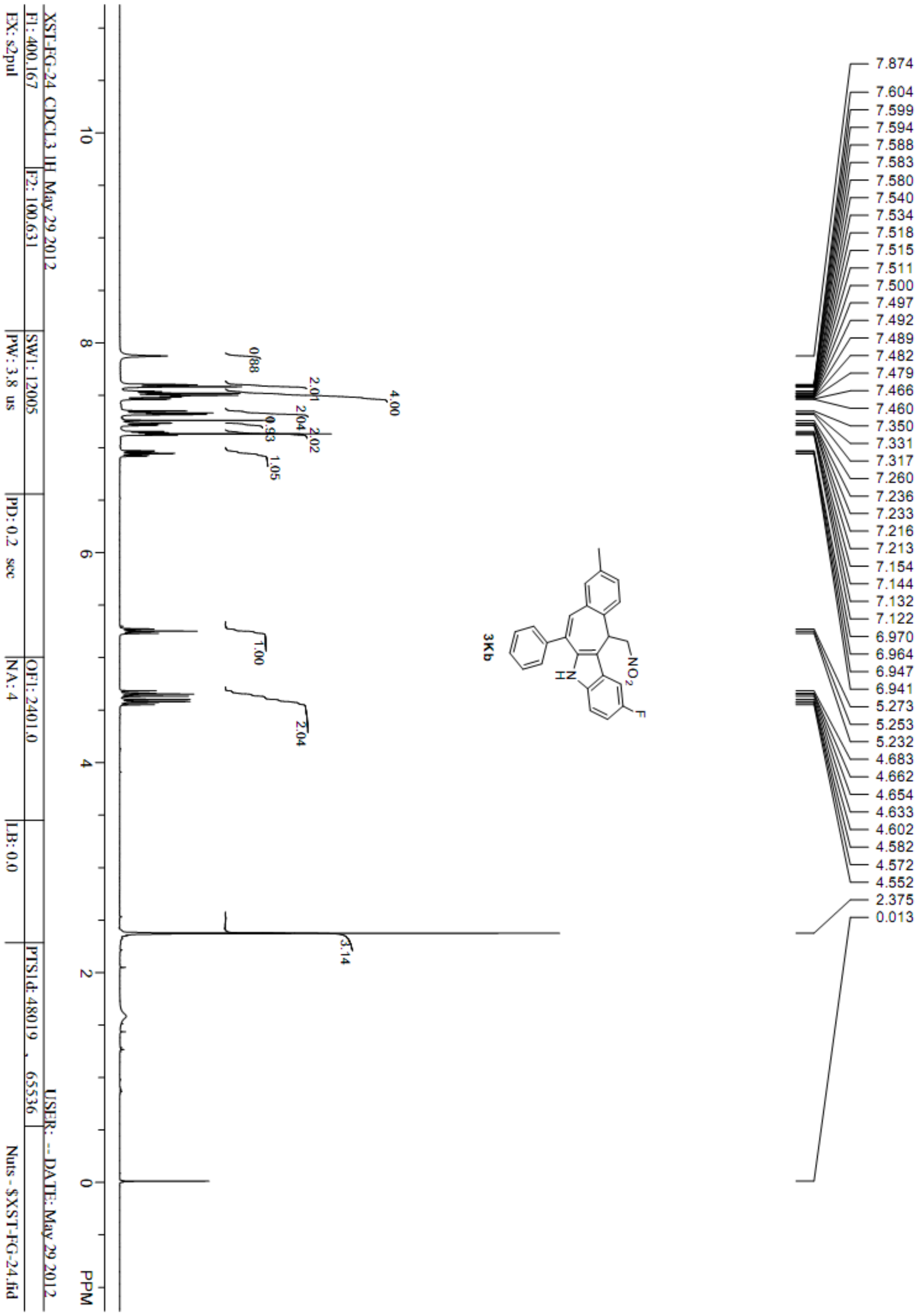

XST-F-22_CDCl3_19F
F1: 470.649
F2: 1.000
SW1: 208333
OF1: 0.0
PTS1d: 65536 , 65536
USER: nmr -- DATE: Tue Oct 16 07:19:31 2012
EX: zg30
PW: 14.0 us
PD: 5.0 sec
NA: 10
LB: 0.0
Nuts - $XST-F-22_31
200
150
100
50
0
-50
-100
-150
-200 PPM
-111.830
-122.691

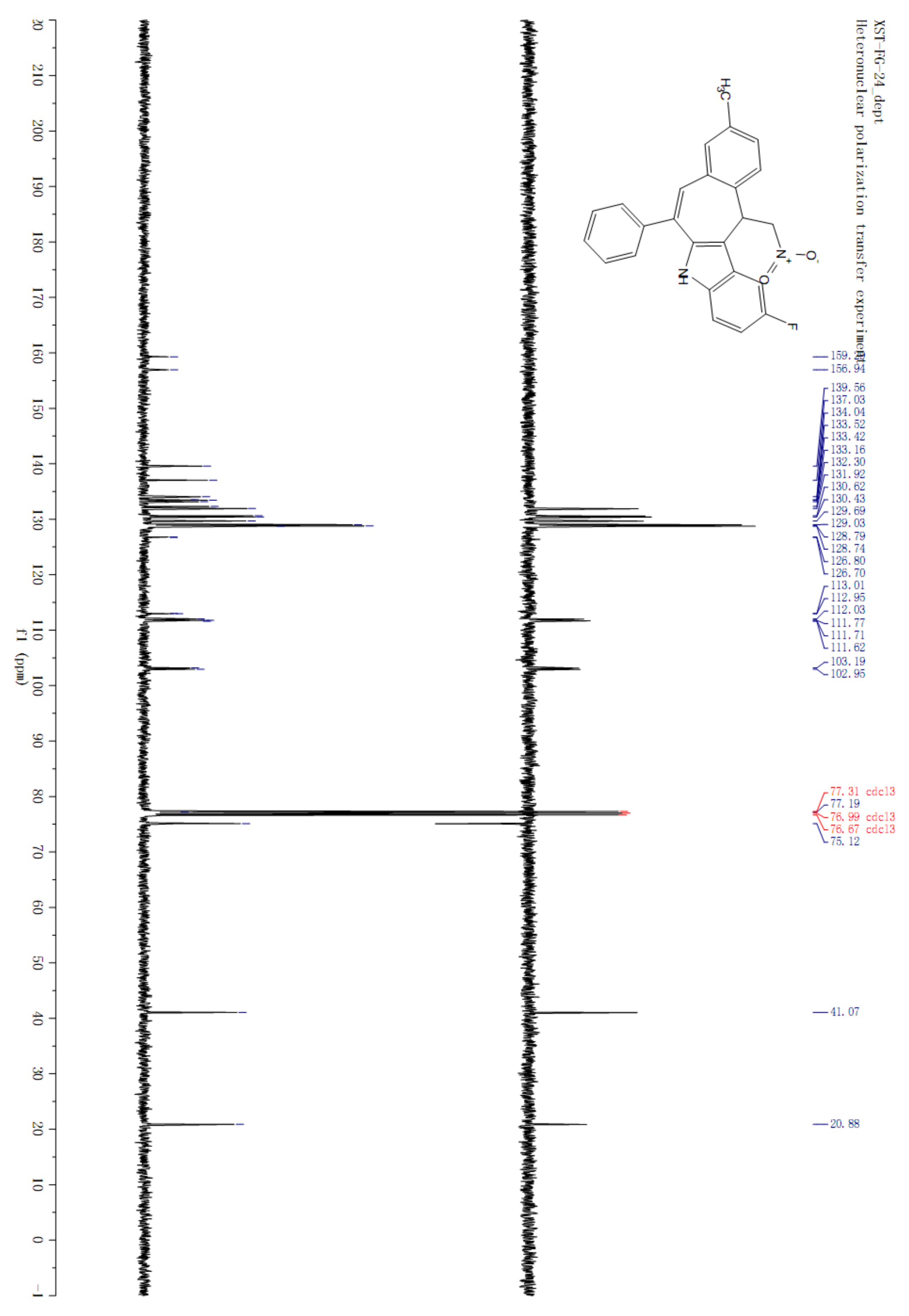
2-Bromo-10-methyl-12-(nitromethyl)-6-(*p*-tolyl)-5,12-dihydrobenzo[4,5]cyclohepta[1,2-*b*] indole (3Md)

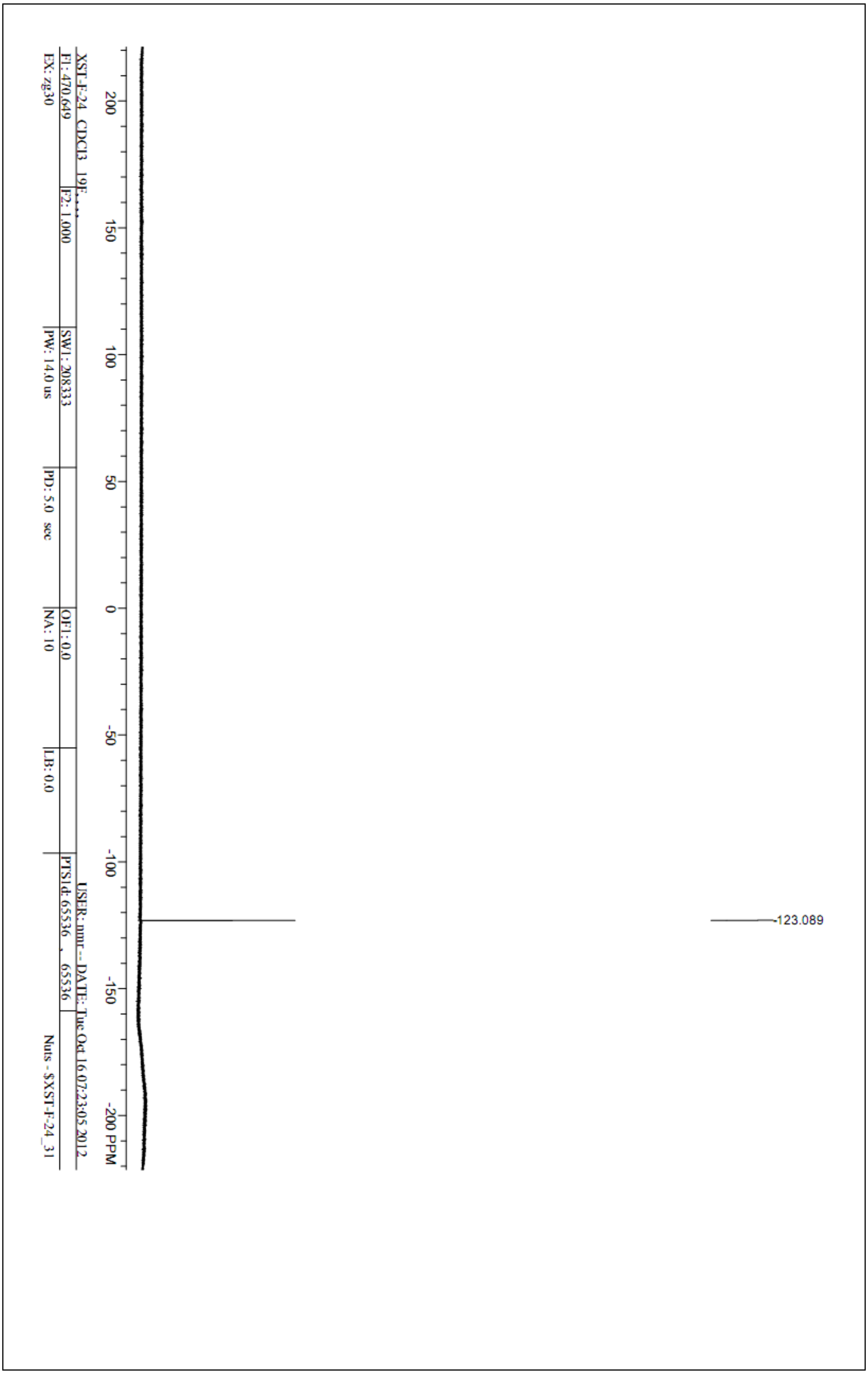



XST-FG-23/2
XST-FG-23 DEPT135
H3C
CH3
NH
N+
O-
O
Br
138.88
137.08
136.59
135.16
134.10
133.25
133.20
132.24
131.92
130.62
130.25
129.78
129.76
128.69
128.08
126.16
120.76
113.45
112.38
112.18
77.30 CDCl3
77.05 CDCl3
76.80 CDCl3
75.03
40.92
21.31
20.93
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

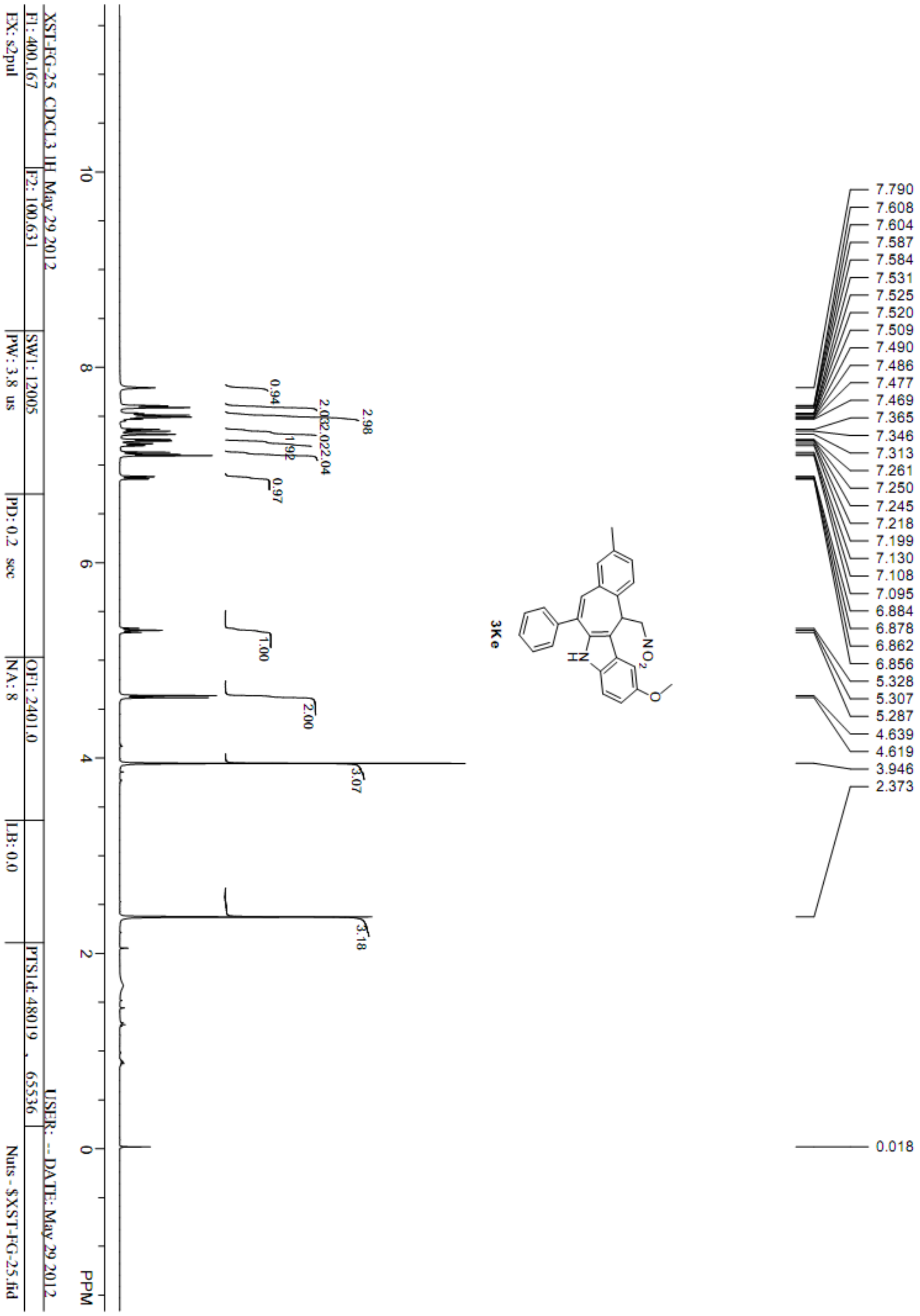
2-Fluoro-9-methyl-12-(nitromethyl)-6-phenyl-5,12-dihydrobenzo[4,5] cyclohepta[1,2-*b*] indole (3Kb)

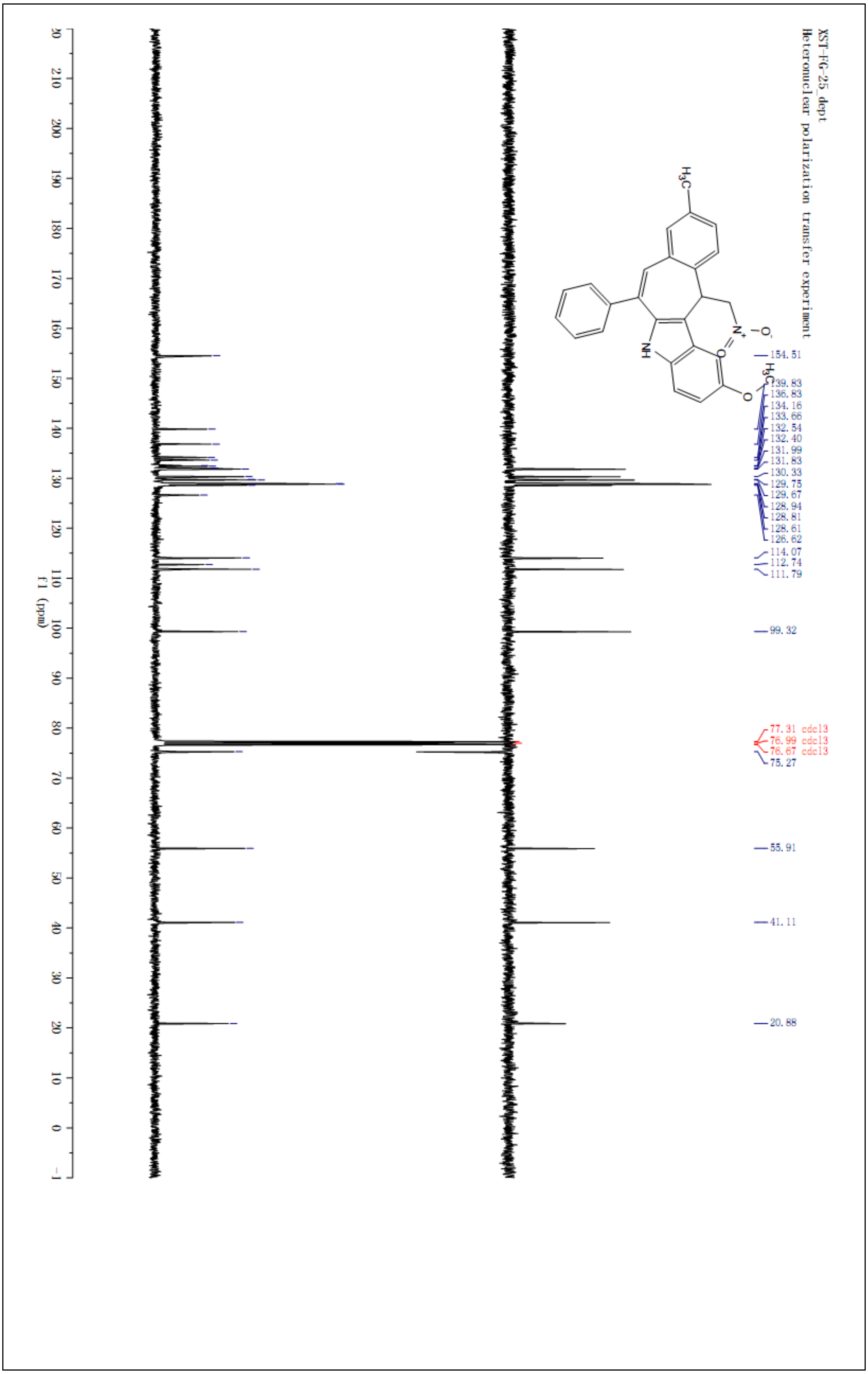



XST-FG-24_dept
Heteronuclear polarization transfer experiment
H3C
NH
N+
O-
O
F
159.2
156.94
139.56
137.03
134.04
133.52
133.42
133.16
132.30
131.92
130.62
130.43
129.69
129.03
128.79
128.74
126.80
126.70
113.01
112.95
112.03
111.77
111.71
111.62
103.19
102.95
77.31 cdcl3
77.19
76.99 cdcl3
76.67 cdcl3
75.12
41.07
20.88
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

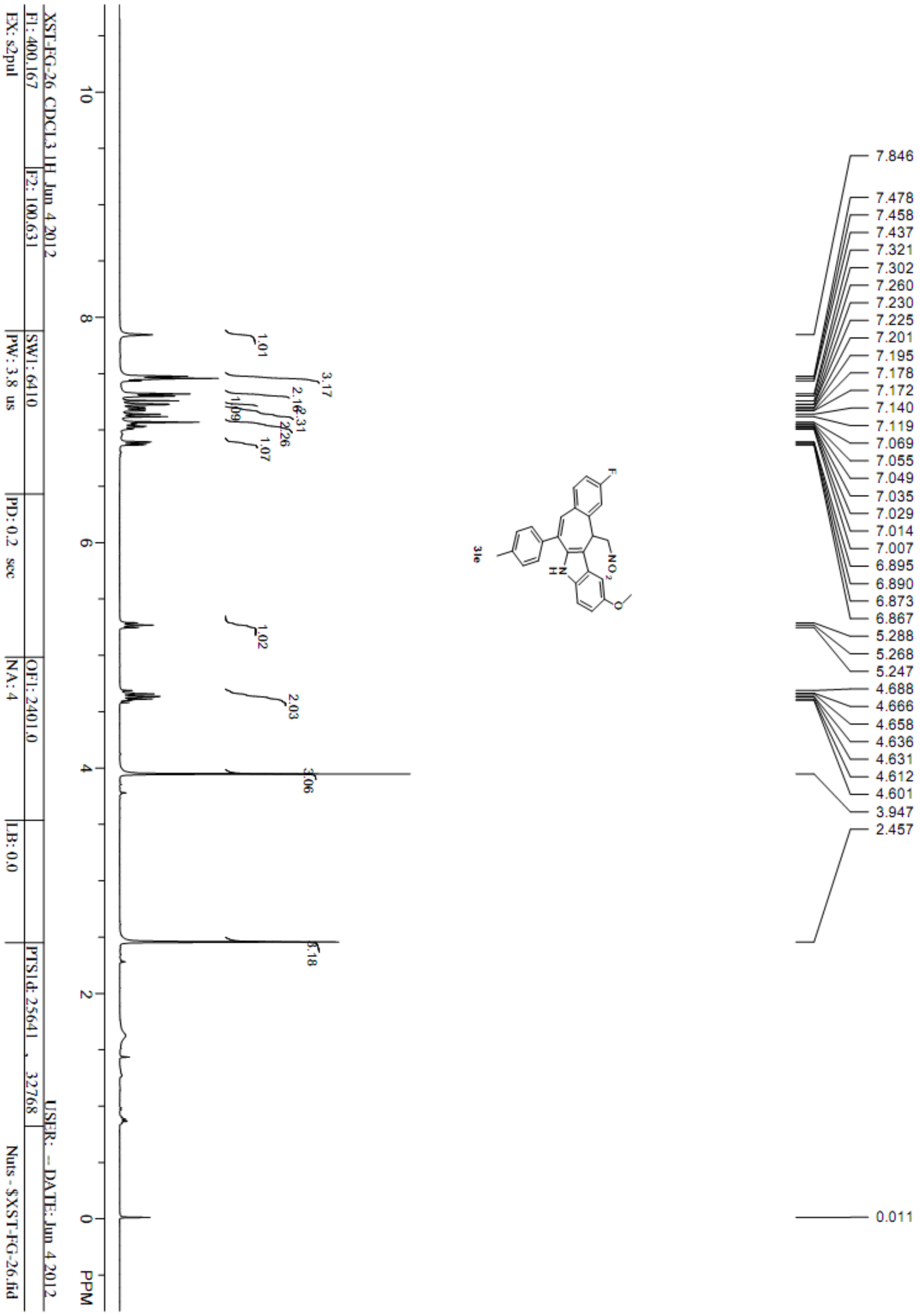

XST-F-24 CDCl3 19F
F1: 470.649
F2: 1.000
SW1: 208333
OF1: 0.0
PTS1d: 65536 , 65536
USER: nmr -- DATE: Tue Oct 16 07:23:05 2012
EX: zg30
PW: 14.0 us
PD: 5.0 sec
NA: 10
LB: 0.0
Nuts - $XST-F-24_31
200
150
100
50
0
-50
-100
-150
-200 PPM
-123.089

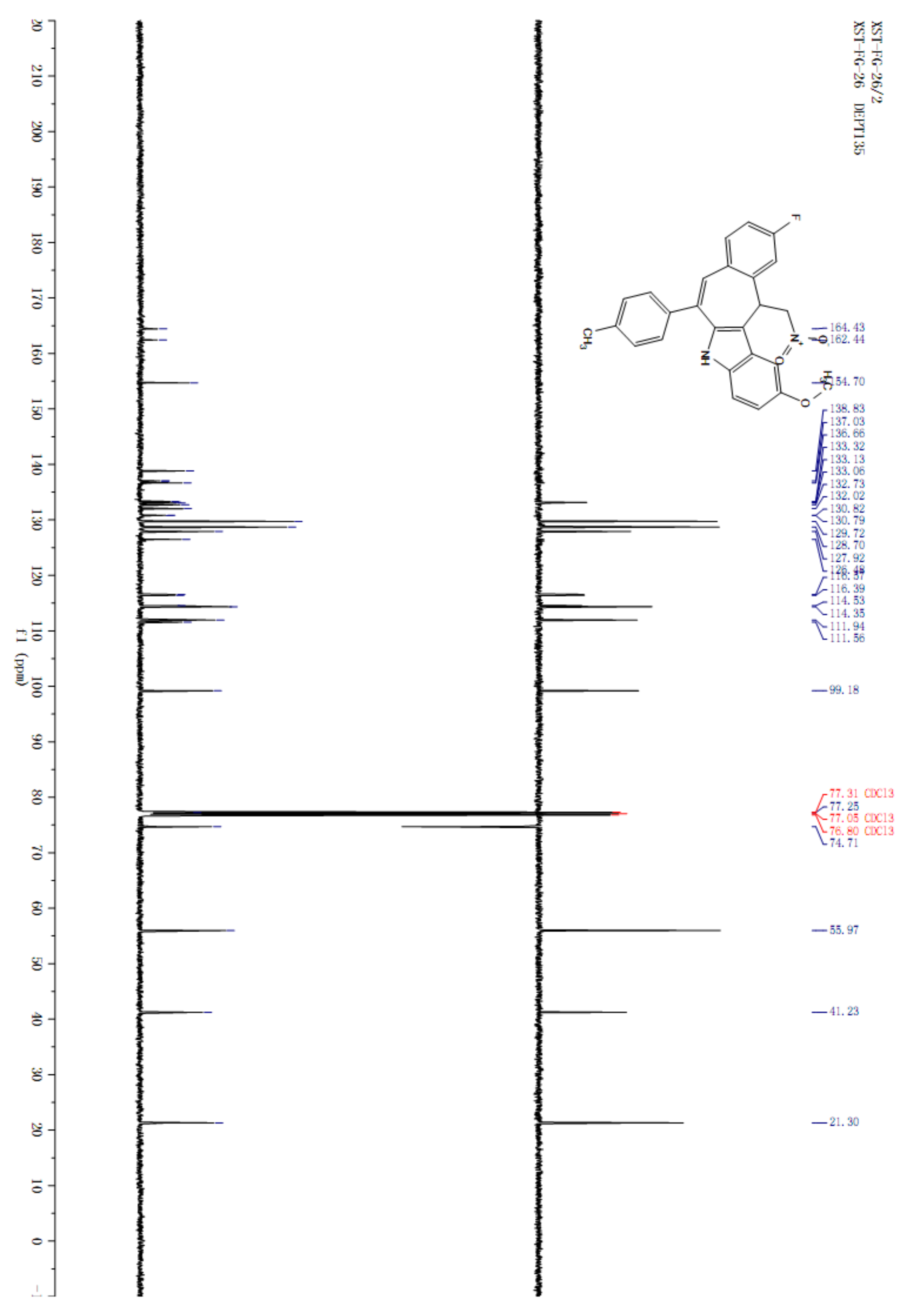
2-Methoxy-9-methyl-12-(nitromethyl)-6-phenyl-5,12-dihydrobenzo[4,5] cyclohepta[1,2-*b*] indole (3Ke)

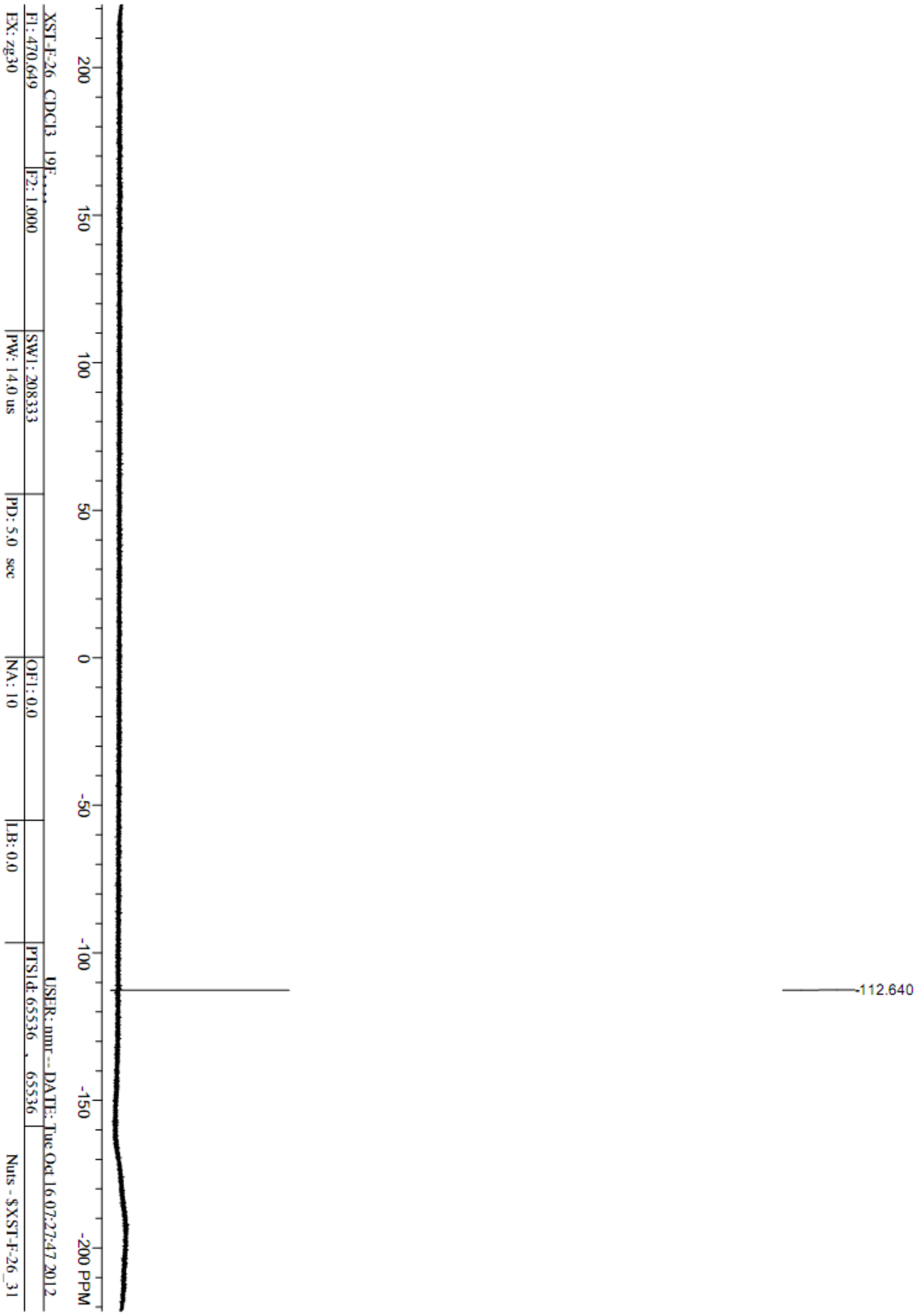



XST-FG-25_dept
Heteronuclear polarization transfer experiment
H$_3$C
NH
N$^+$
O$^-$
O
H$_3$C
O
154.51
139.83
136.83
134.16
133.66
132.54
132.40
131.99
131.83
130.33
129.75
129.67
128.94
128.81
128.61
126.62
114.07
112.74
111.79
99.32
77.31 cdcl3
76.99 cdcl3
76.67 cdcl3
75.27
55.91
41.11
20.88
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

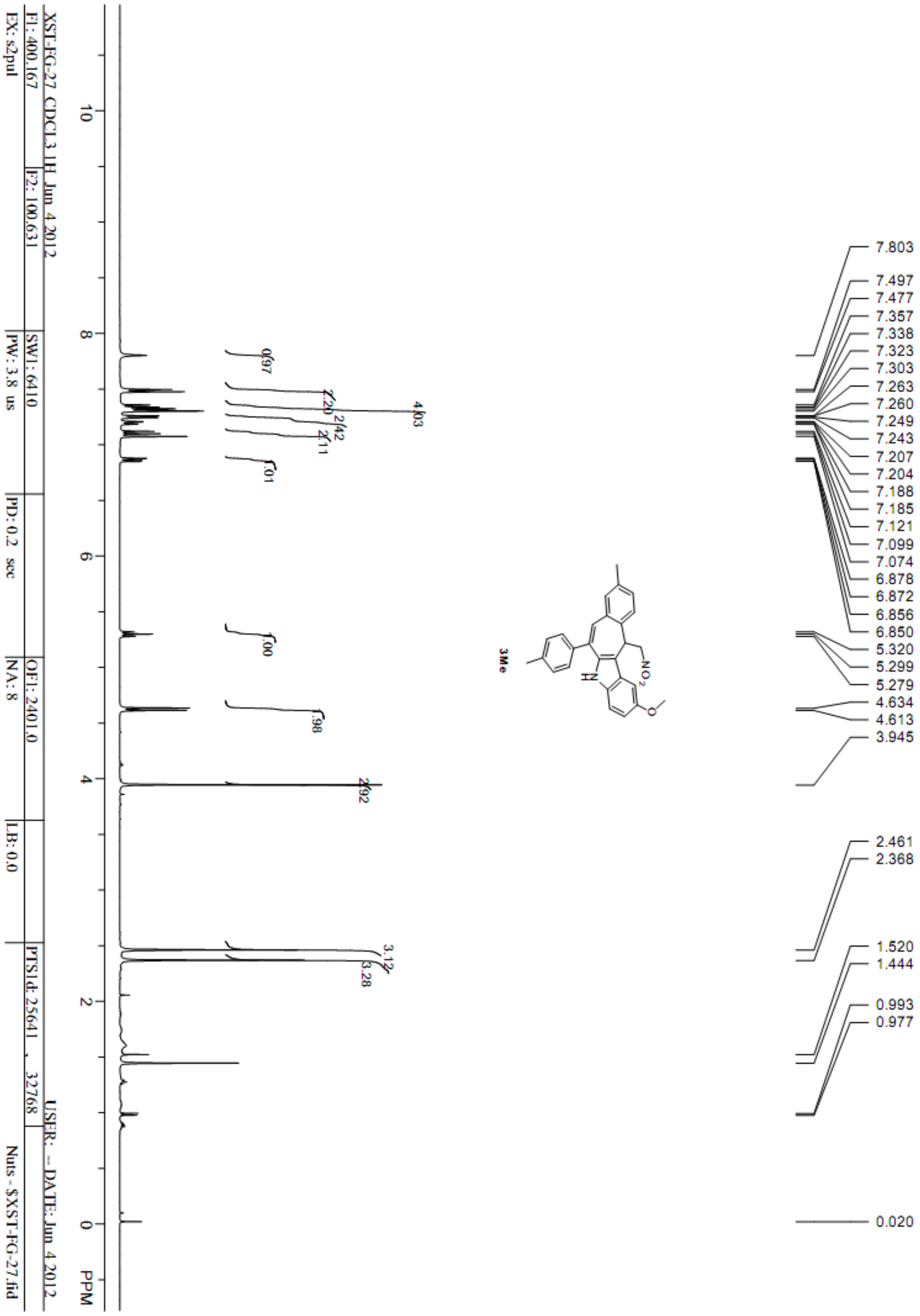
2-Methoxy-10-fluoro-12-(nitromethyl)-6-(*p*-tolyl)-5,12-dihydrobenzo[4,5] cyclohepta[1,2-*b*] indole (3Le)

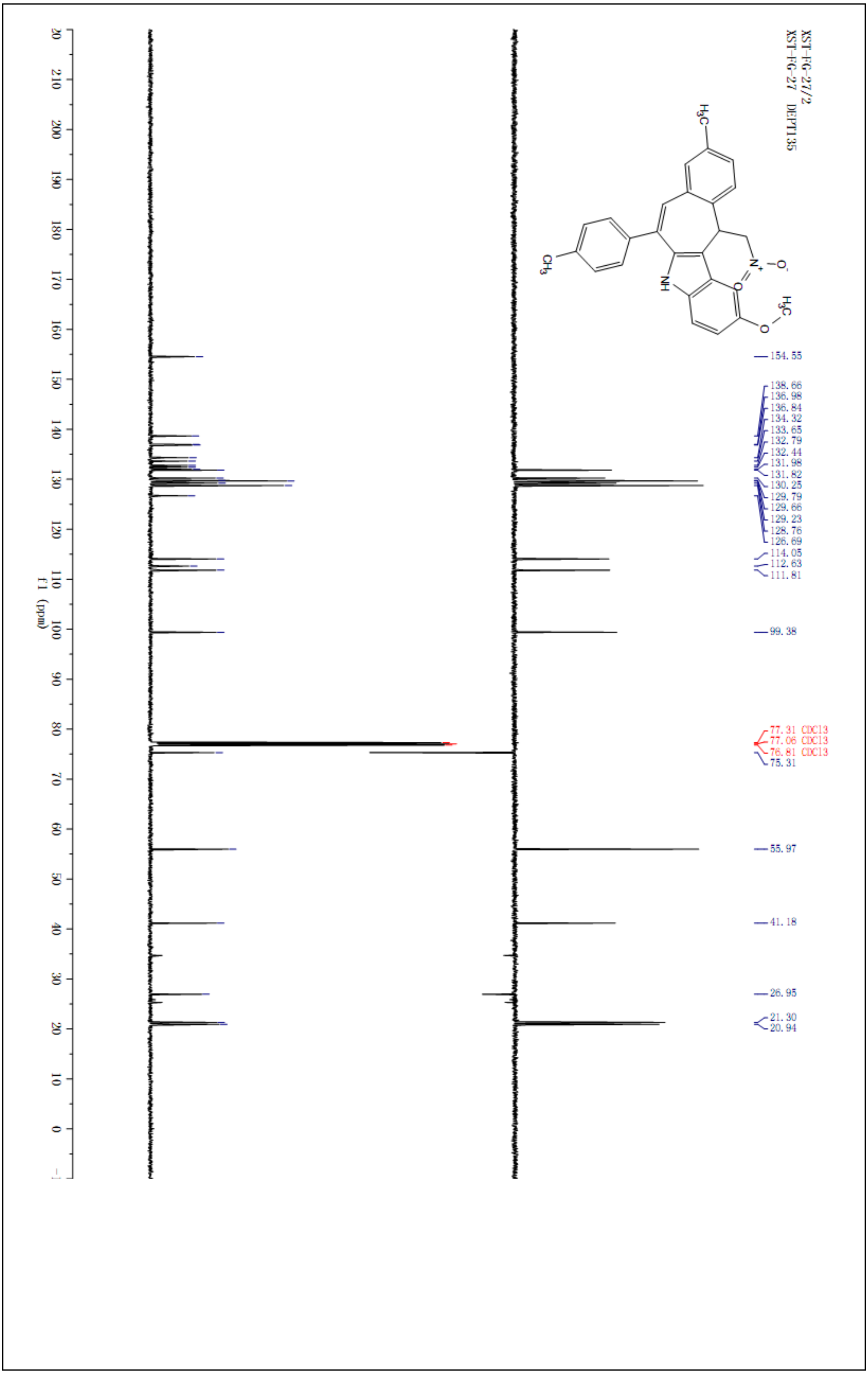



XST-FG-26/2
XST-FG-26 DEPT135
164.43
162.44
154.70
138.83
137.03
136.66
133.32
133.13
133.06
132.73
132.02
130.82
130.79
129.72
128.70
127.92
126.48
116.57
116.39
114.53
114.35
111.94
111.56
99.18
77.31 CDCl3
77.25
77.05 CDCl3
76.80 CDCl3
74.71
55.97
41.23
21.30
F
N
O
NH
CH3
H3C
O
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1

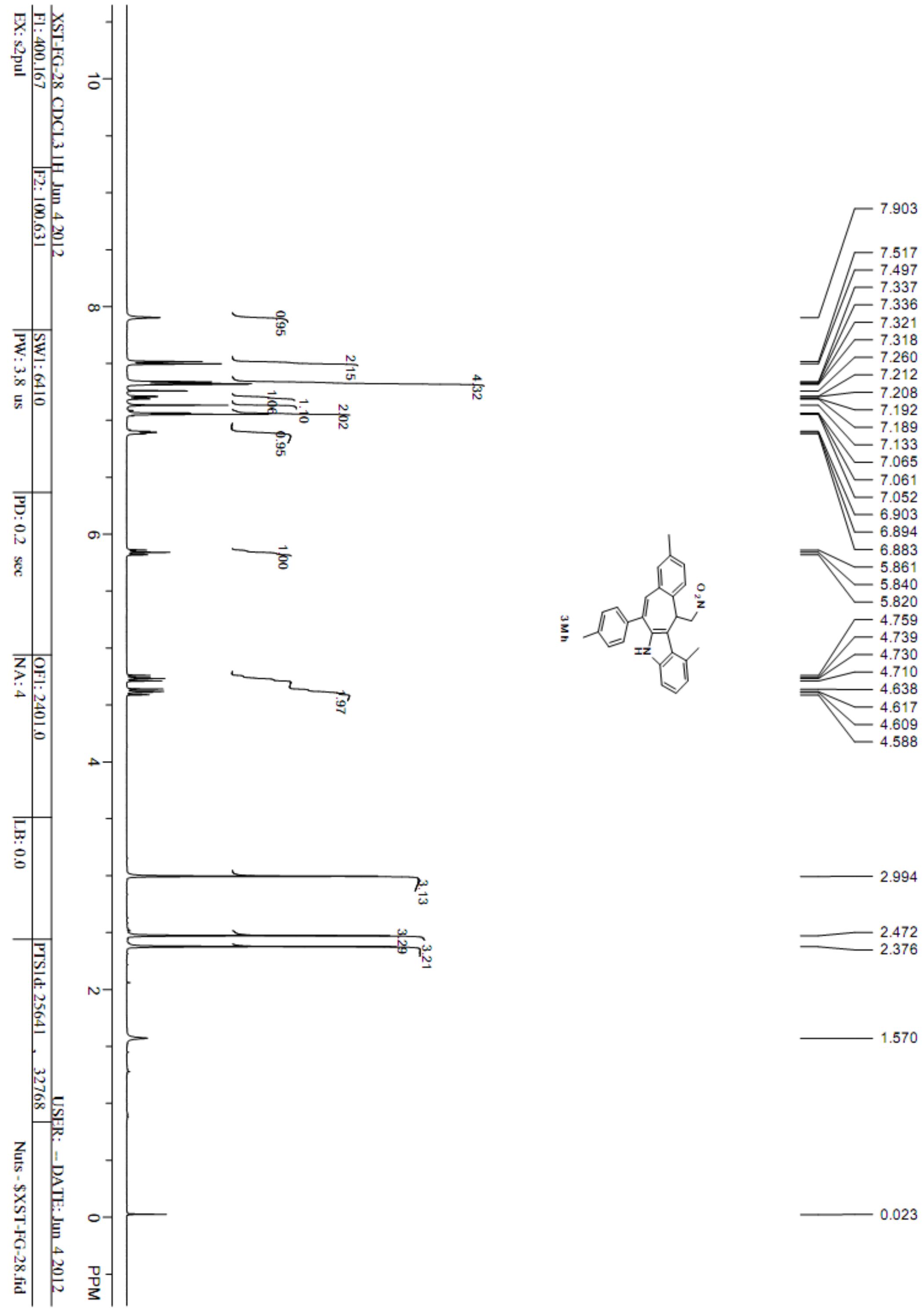

XST-F-26 CDCl3 19F
F1: 470.649
F2: 1.000
SW1: 208333
OF1: 0.0
PTS1d: 65536 , 65536
EX: zg30
PW: 14.0 us
PD: 5.0 sec
NA: 10
LB: 0.0
USER: nmr -- DATE: Tue Oct 16 07:27:47 2012
Nuts - $XST-F-26_31
200
150
100
50
0
-50
-100
-150
-200 PPM
-112.640

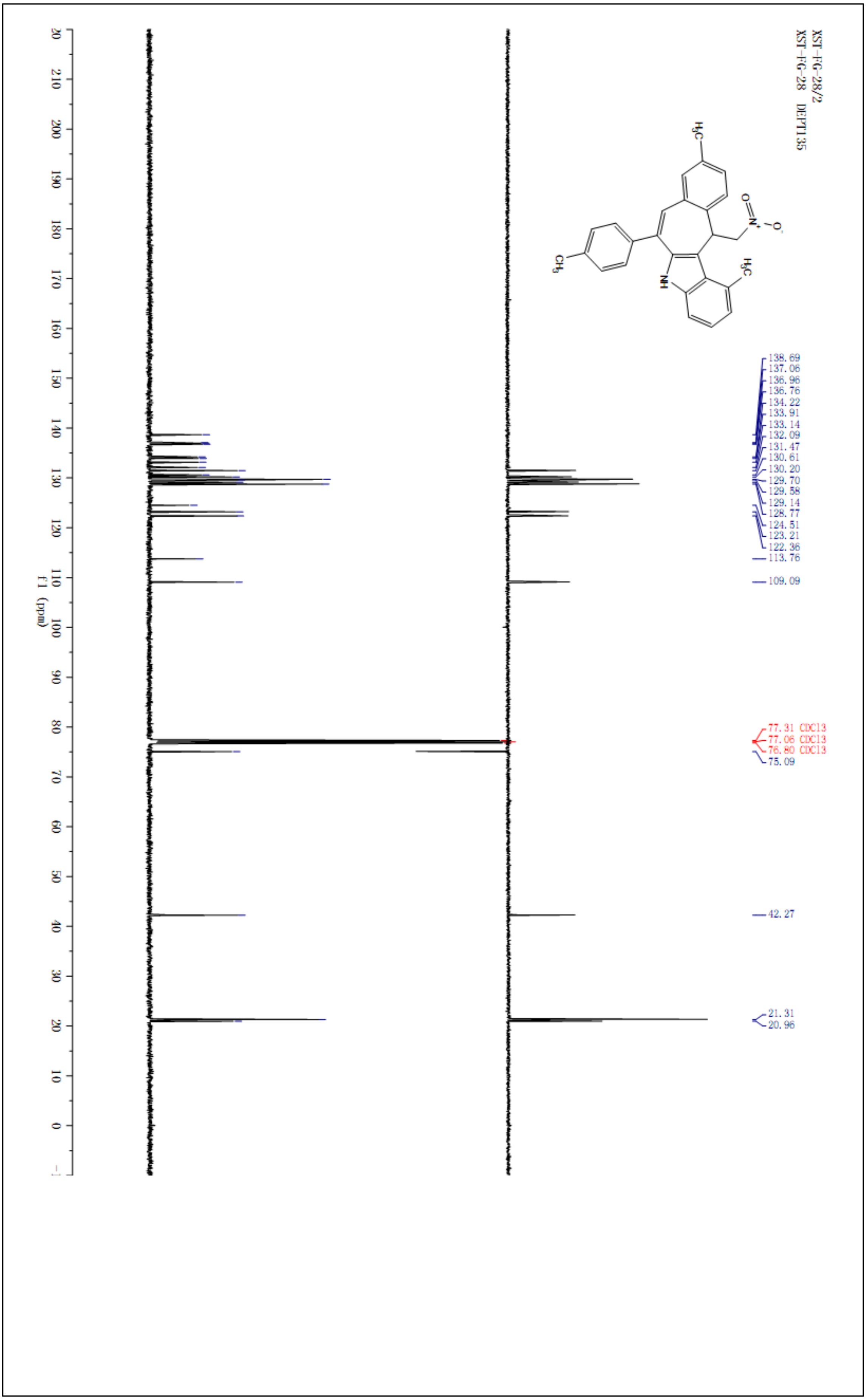
2-Methoxy-9-methyl-12-(nitromethyl)-6-(*p*-tolyl)-5,12-dihydrobenzo[4,5]cyclohepta[1,2-*b*] indole (3Me)



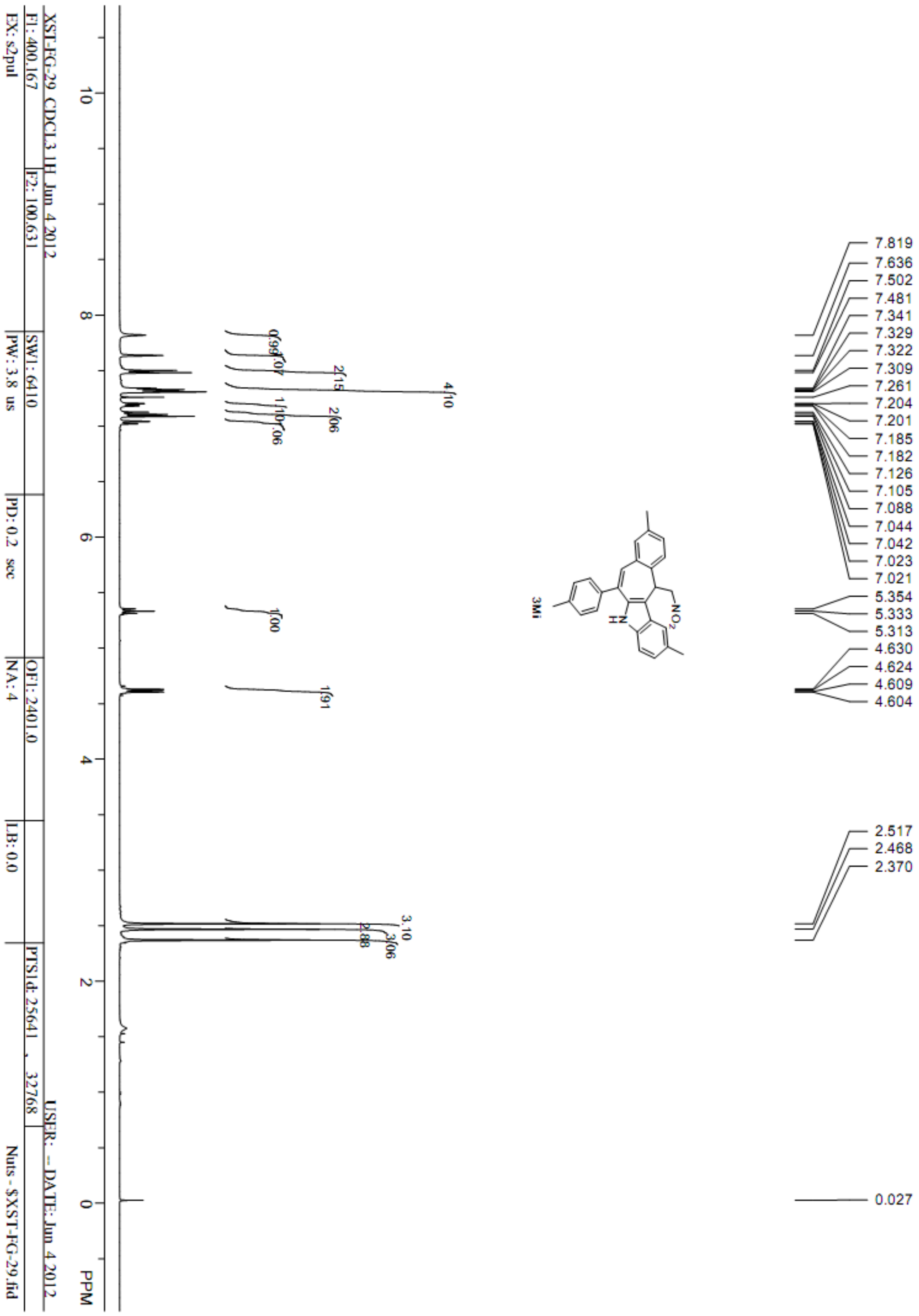

XST-FG-27/2
XST-FG-27 DEPT135
H3C
CH3
NH
N+
O-
O
H3C
O
154.55
138.66
136.98
136.84
134.32
133.65
132.79
132.44
131.98
131.82
130.25
129.79
129.66
129.23
128.76
126.69
114.05
112.63
111.81
99.38
77.31 CDCl3
77.06 CDCl3
76.81 CDCl3
75.31
55.97
41.18
26.95
21.30
20.94
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1

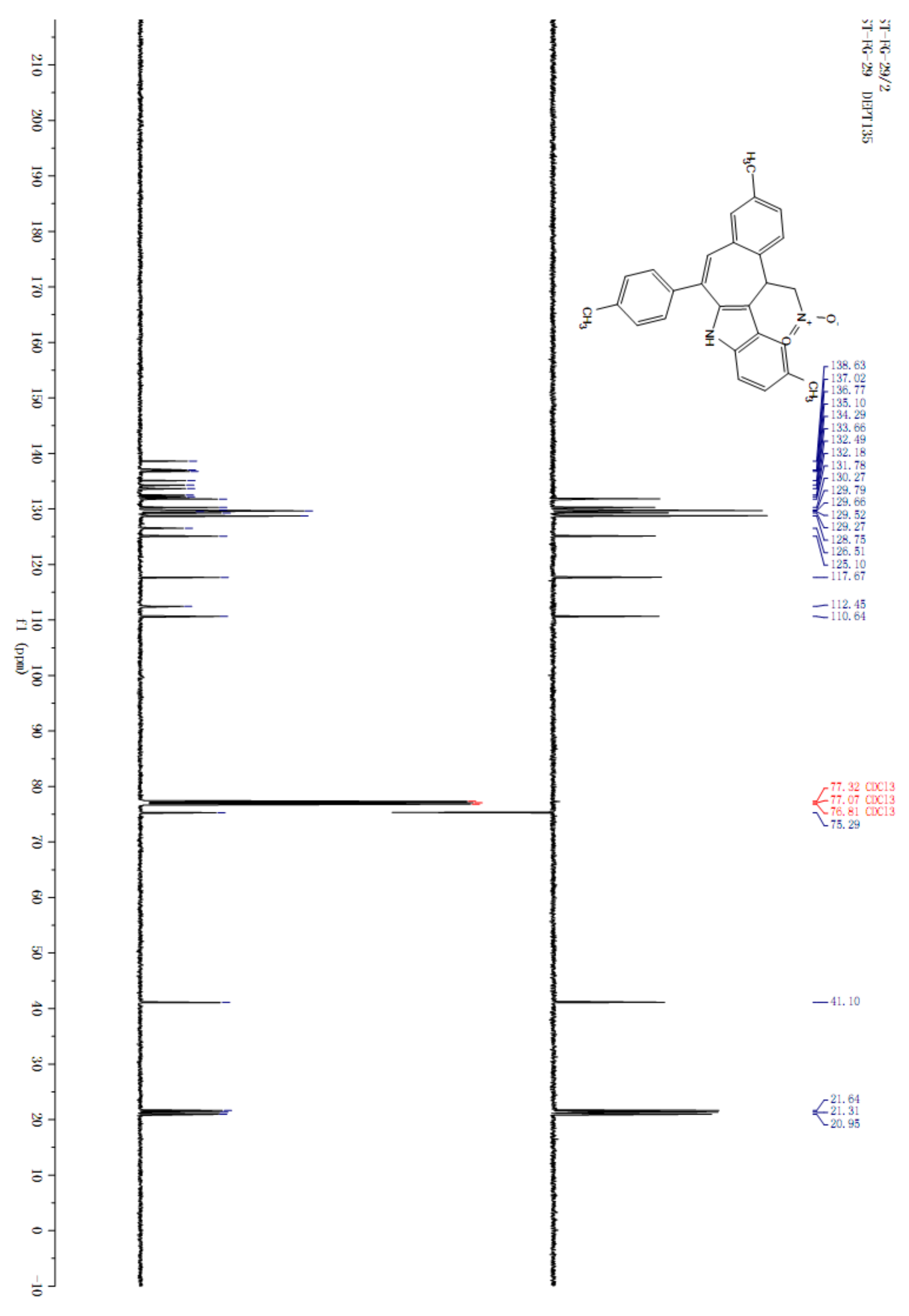
1-Methyl-9-methyl-12-(nitromethyl)-6-(*p*-tolyl)-5,12-dihydrobenzo[4,5] cyclohepta[1,2-*b*] indole (3Mh)



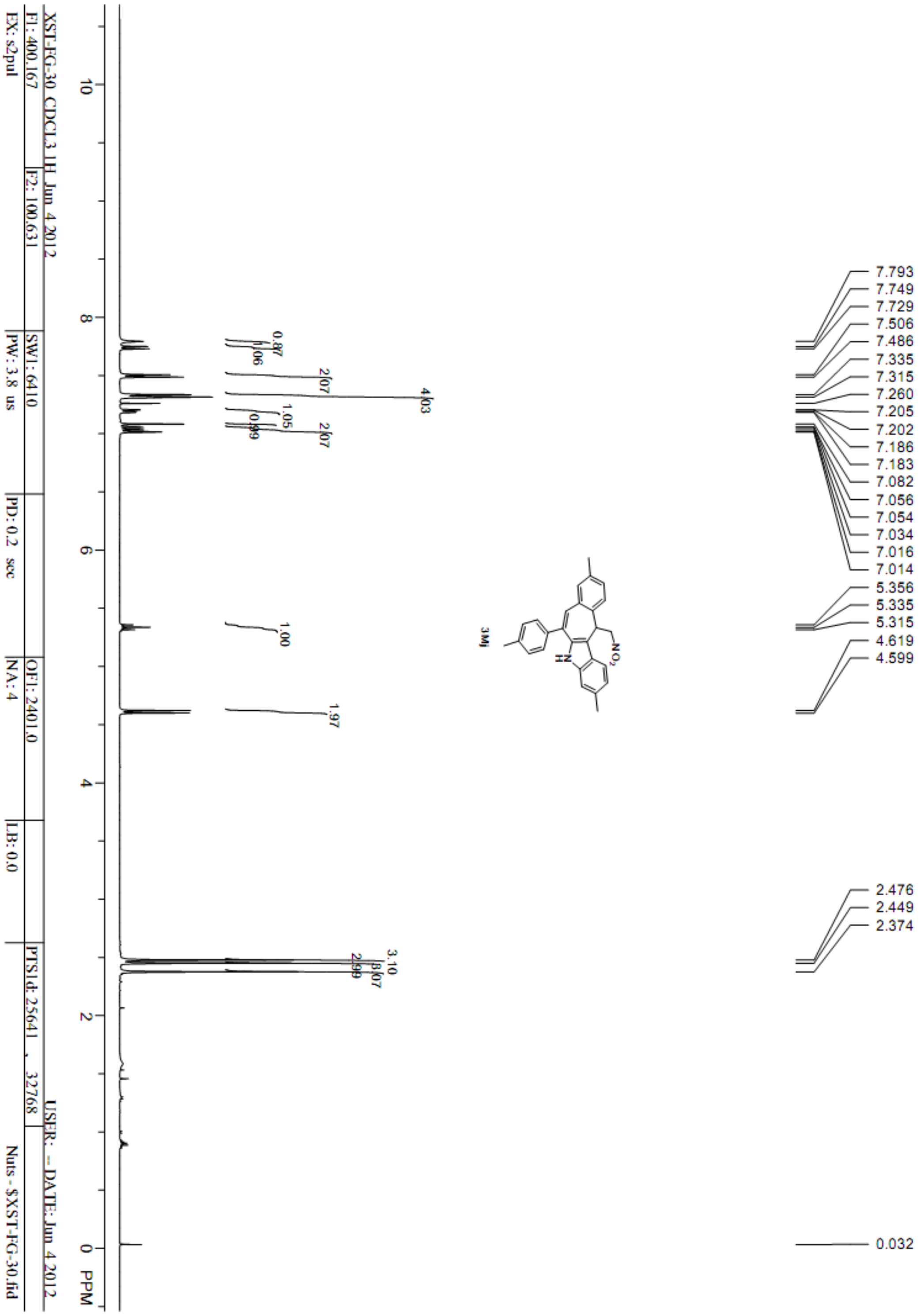

XST-FG-28/2
XST-FG-28 DEPT135
H3C
CH3
H3C
NH
O=N+
O-
138.69
137.06
136.96
136.76
134.22
133.91
133.14
132.09
131.47
130.61
130.20
129.70
129.58
129.14
128.77
124.51
123.21
122.36
113.76
109.09
77.31 CDCl3
77.06 CDCl3
76.80 CDCl3
75.09
42.27
21.31
20.96
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1

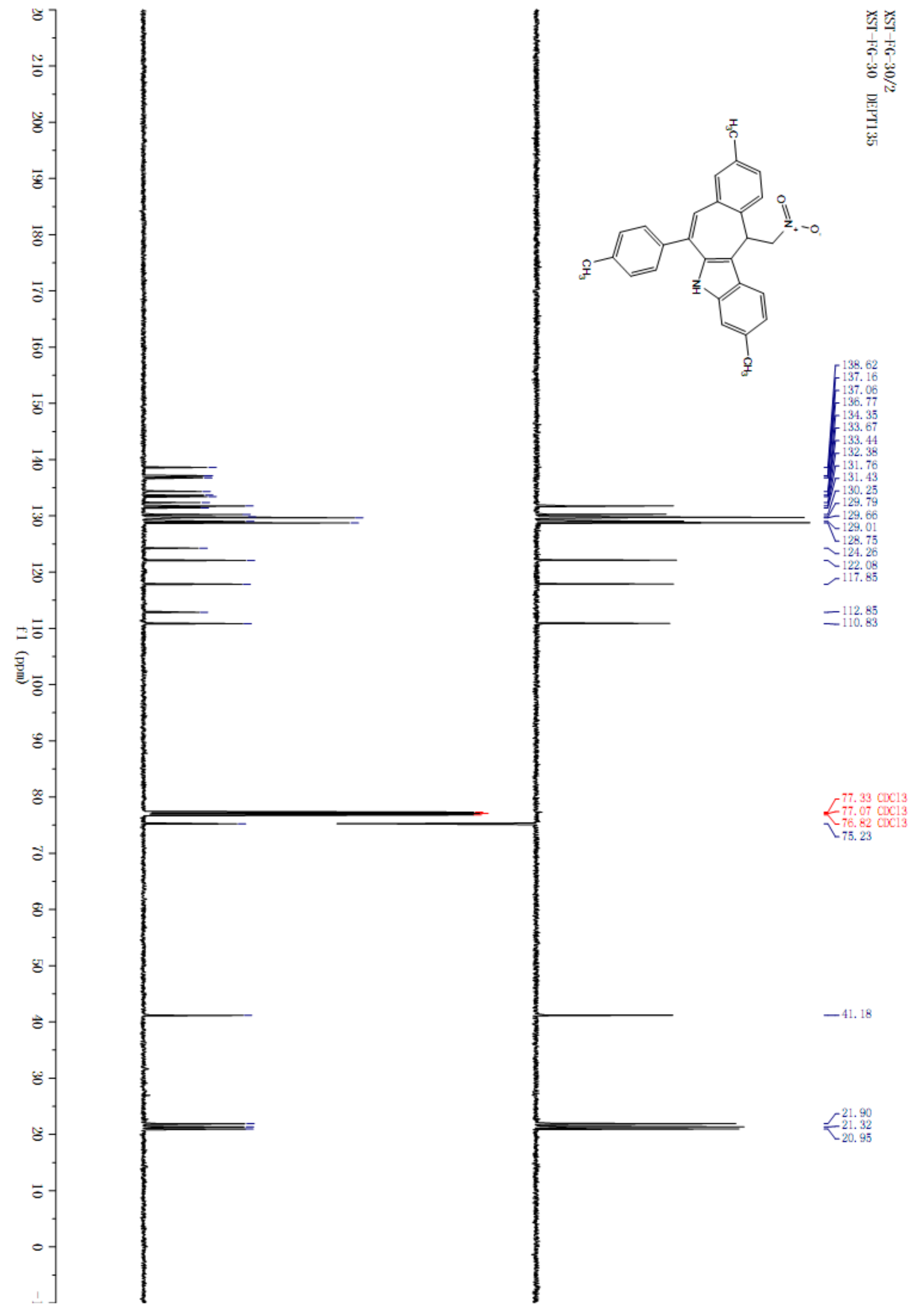
2-Methyl-9-methyl-12-(nitromethyl)-6-(*p*-tolyl)-5,12-dihydrobenzo[4,5]cyclohepta[1,2-*b*] indole (3Mi)



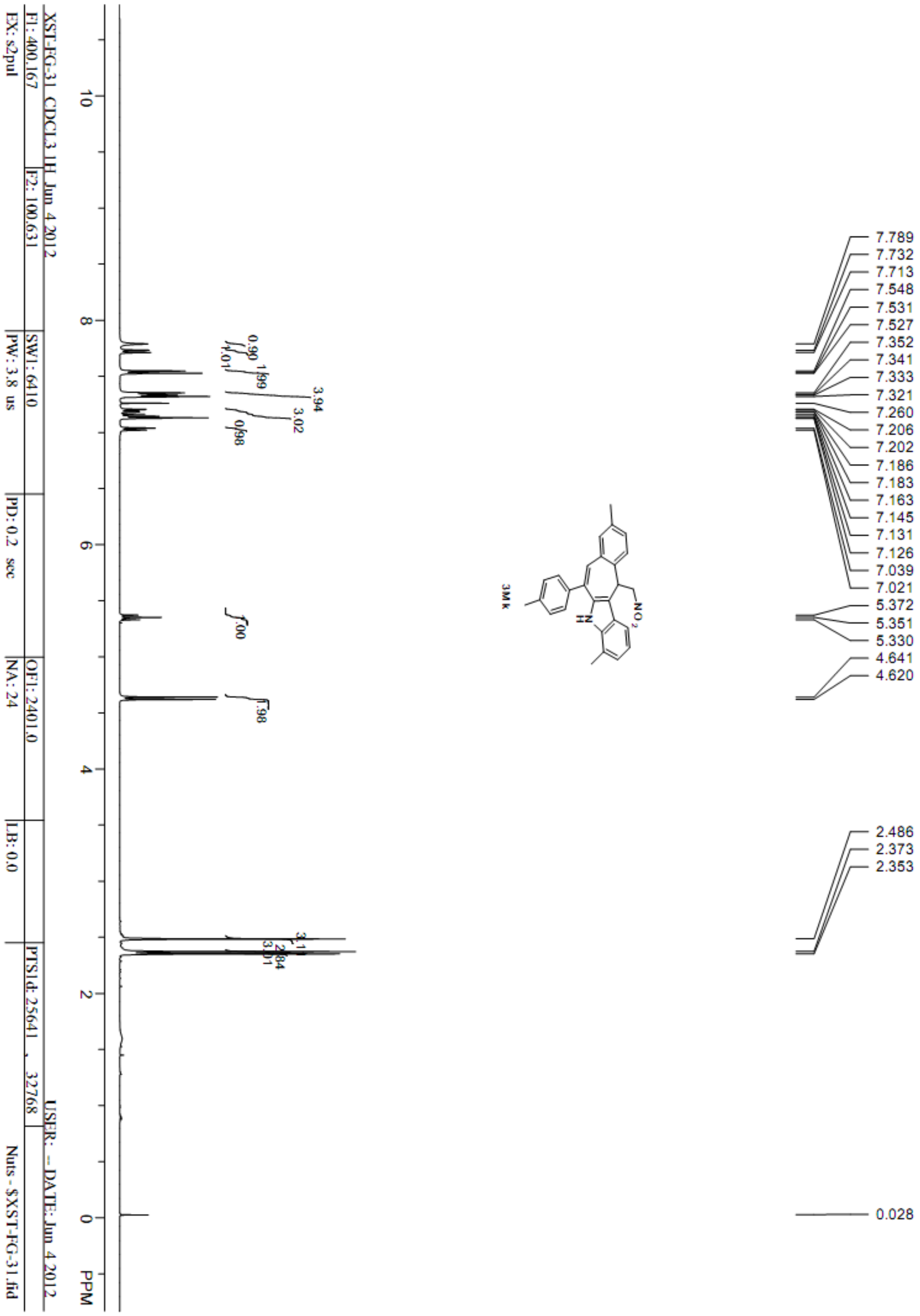

ST-FG-29/2
ST-FG-29 DEPT135
H3C
CH3
NH
N+
O-
O
CH3
138.63
137.02
136.77
135.10
134.29
133.66
132.49
132.18
131.78
130.27
129.79
129.66
129.52
129.27
128.75
126.51
125.10
117.67
112.45
110.64
77.32 CDCl3
77.07 CDCl3
76.81 CDCl3
75.29
41.10
21.64
21.31
20.95
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

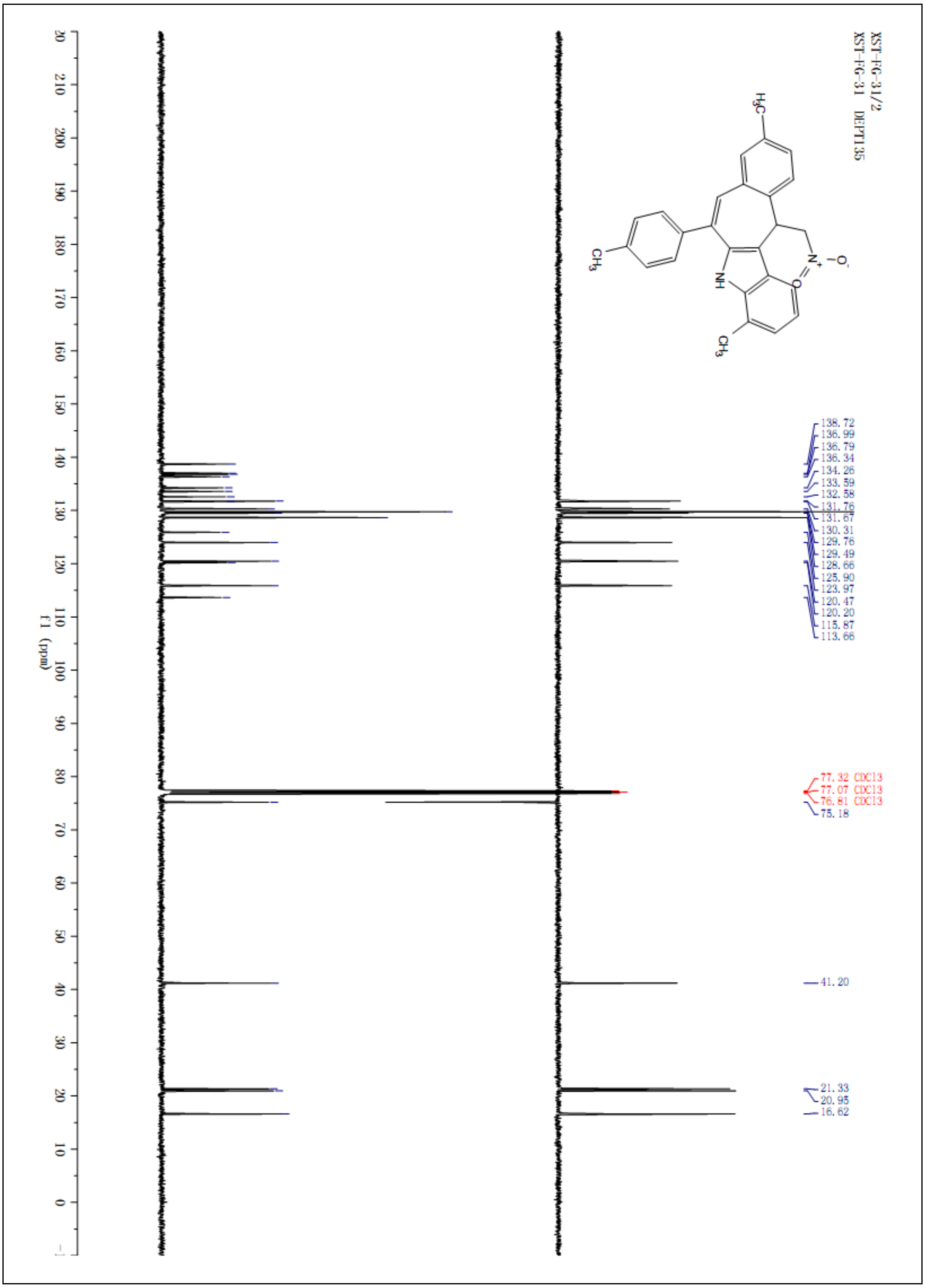
3-Methyl-9-methyl-12-(nitromethyl)-6-(*p*-tolyl)-5,12-dihydrobenzo[4,5] cyclohepta[1,2-*b*] indole (3Mj)




XST-FG-30/2
XST-FG-30 DEPT135
H3C
O
N+
O-
CH3
NH
CH3
138.62
137.16
137.06
136.77
134.35
133.67
133.44
132.38
131.76
131.43
130.25
129.79
129.66
129.01
128.75
124.26
122.08
117.85
112.85
110.83
77.33 CDCl3
77.07 CDCl3
76.82 CDCl3
75.23
41.18
21.90
21.32
20.95
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1

4-Methyl-9-methyl-12-(nitromethyl)-6-(*p*-tolyl)-5,12-dihydrobenzo[4,5] cyclohepta[1,2-*b*] indole (3Mk)




XST-FG-31/2
XST-FG-31 DEPT135
H3C
CH3
NH
CH3
N+
O-
O
138.72
136.99
136.79
136.34
134.26
133.59
132.58
131.76
131.67
130.31
129.76
129.49
128.66
125.90
123.97
120.47
120.20
115.87
113.66
77.32 CDCl3
77.07 CDCl3
76.81 CDCl3
75.18
41.20
21.33
20.95
16.62
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)