Electronic Supplementary Material (ESI) for Photochemical & Photobiological Science

Supporting Information for

Solvent-Directed Excited State Intramolecular Proton Transfer (ESIPT) Pathways from Phenol to Carbon in 2,5-dihydroxyphenyl Arenes

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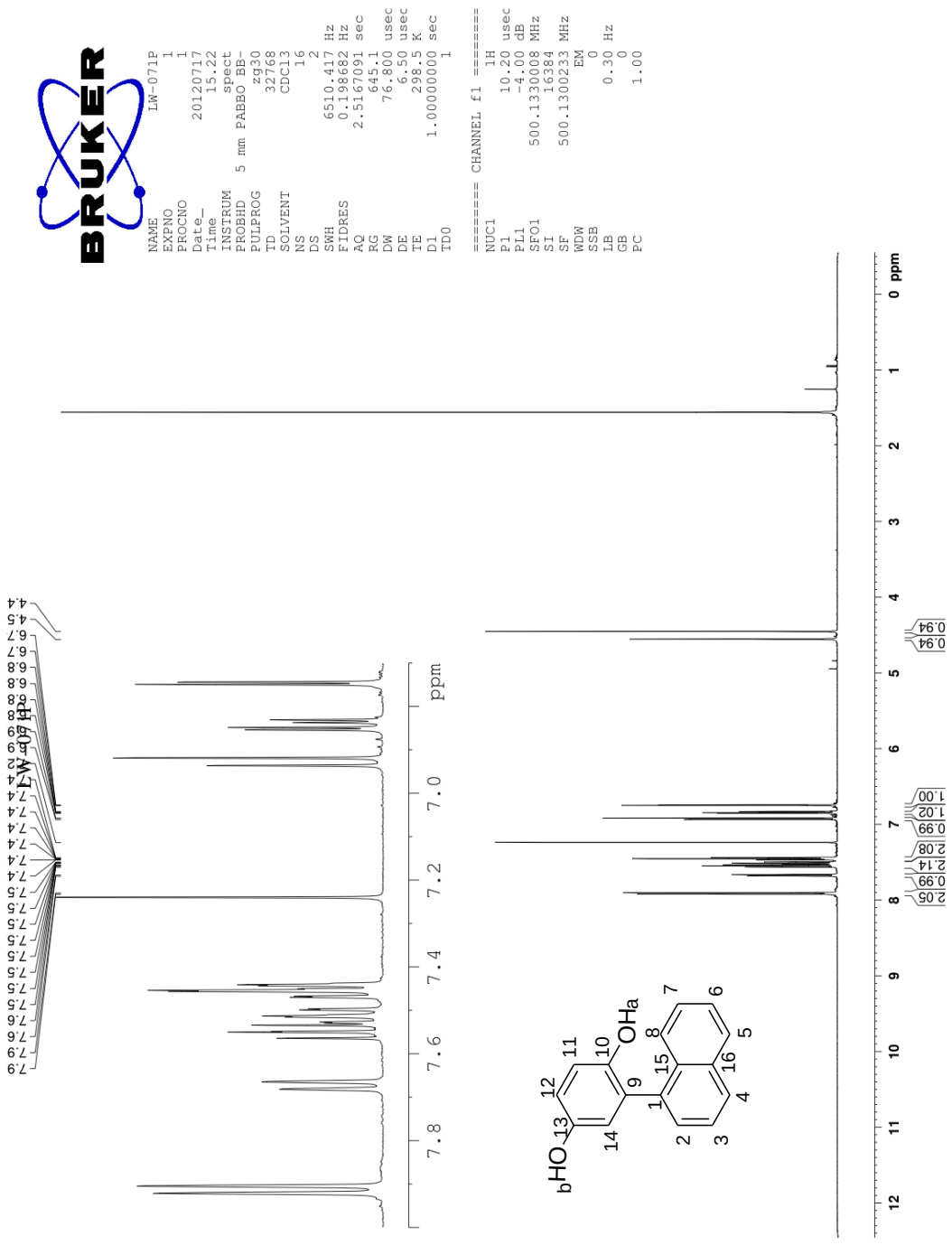
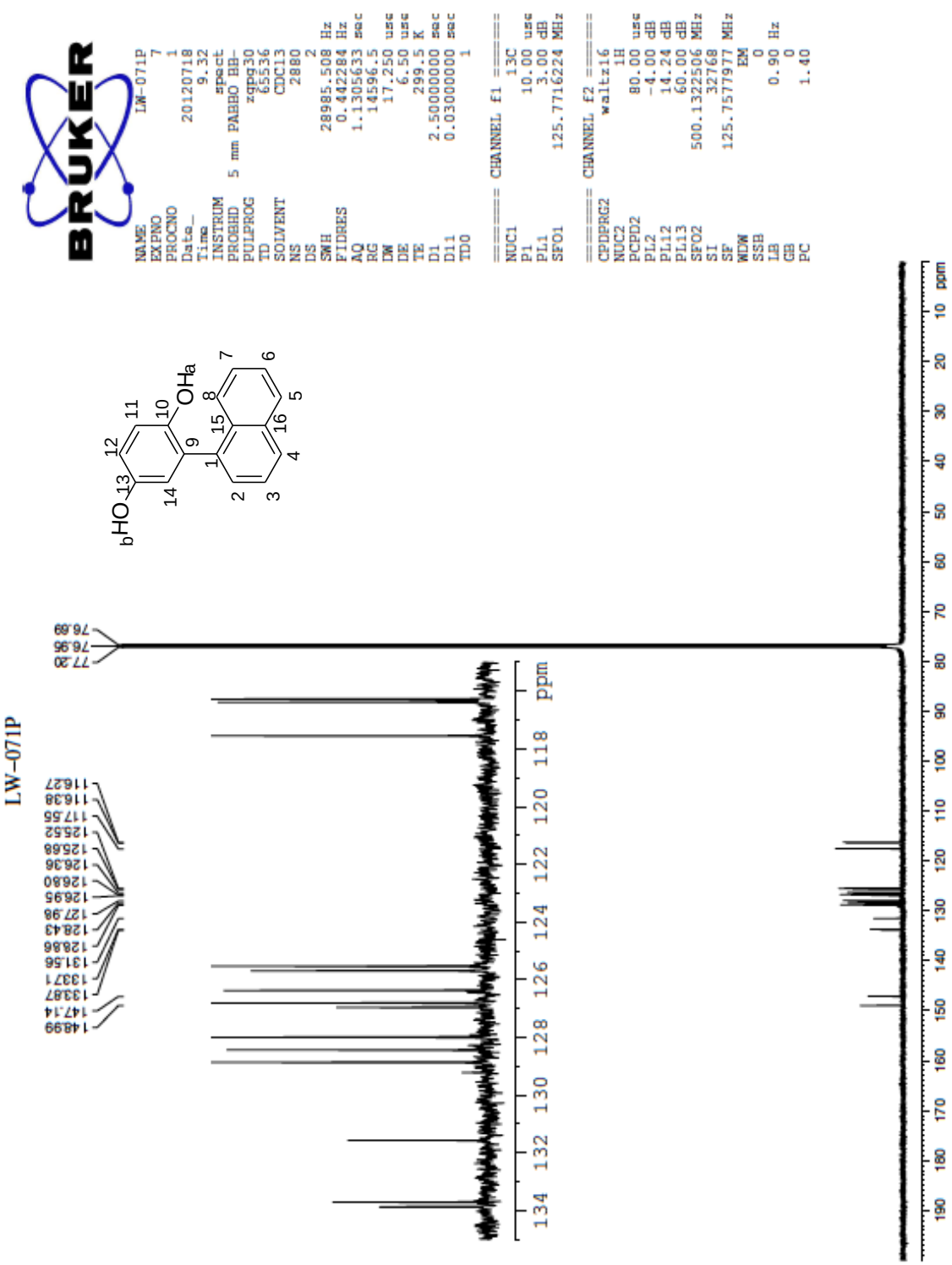
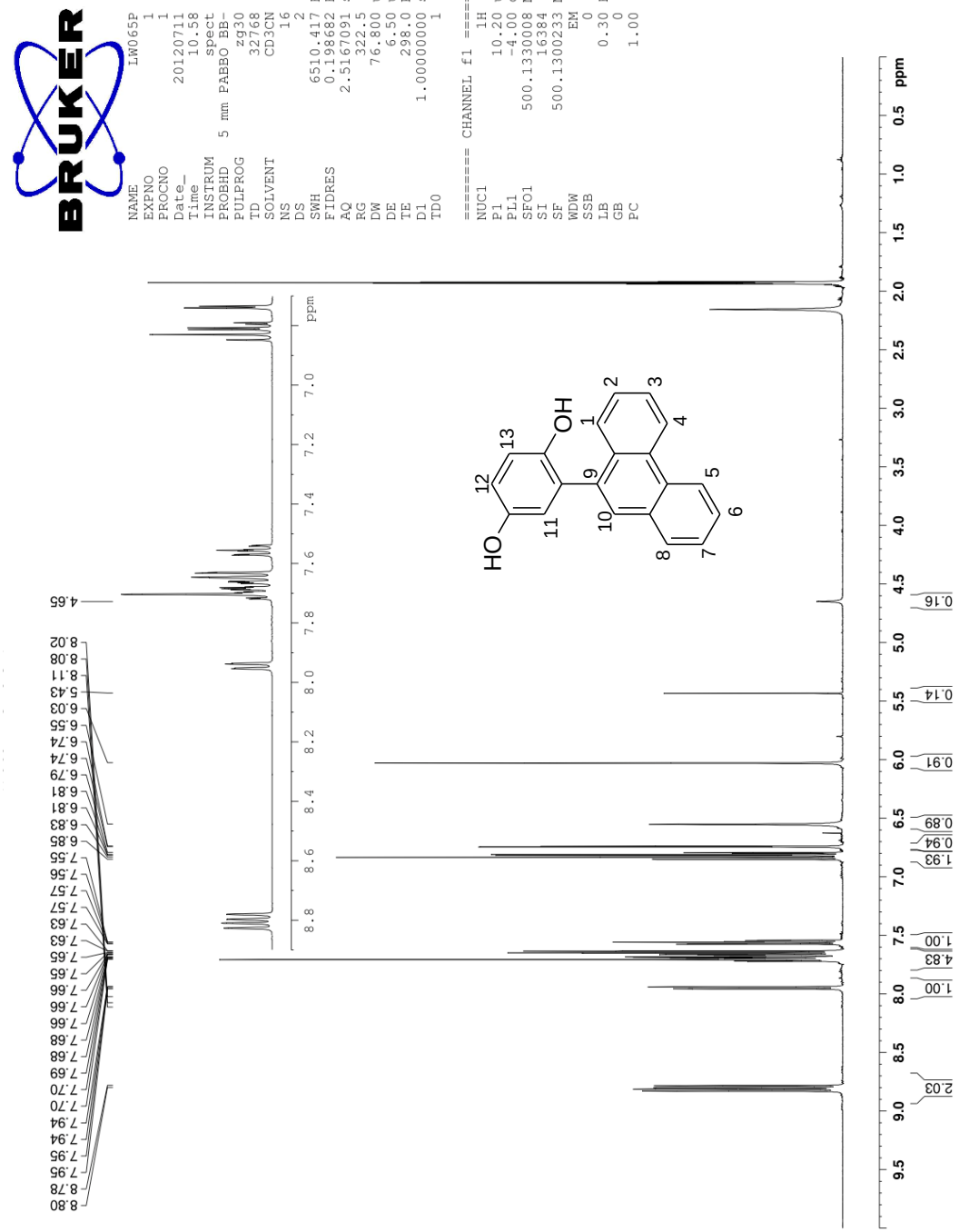
^{1}H NMR (500 MHz, $CDCN_3$) spectrum of **9**



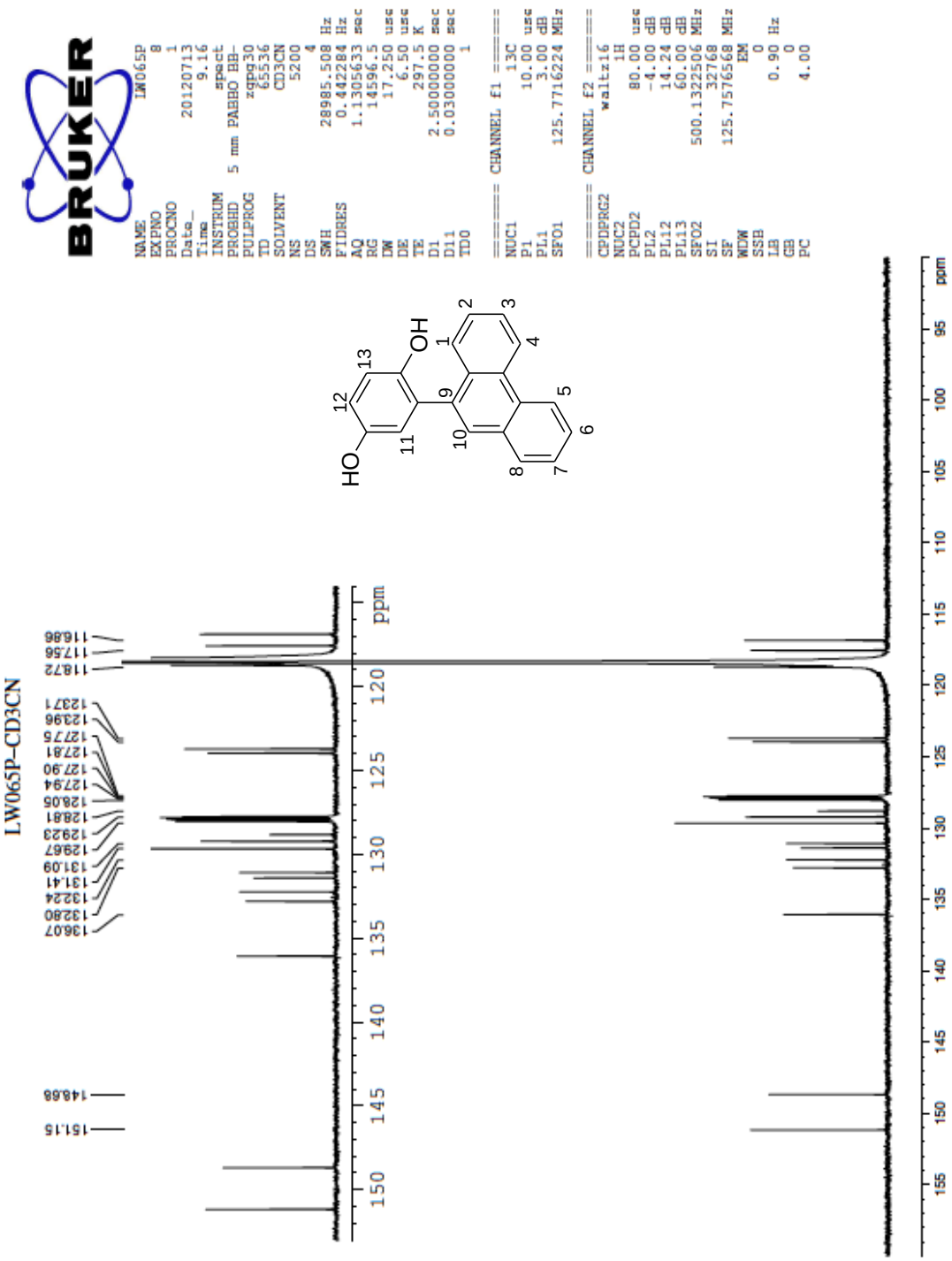
^{13}C NMR (125 MHz, $CDCN_3$) spectrum of **9**



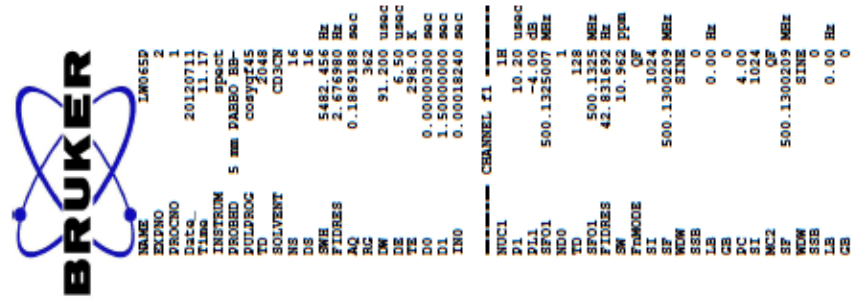
^{1}H NMR (500 MHz, $CDCN_3$) spectrum of **10**

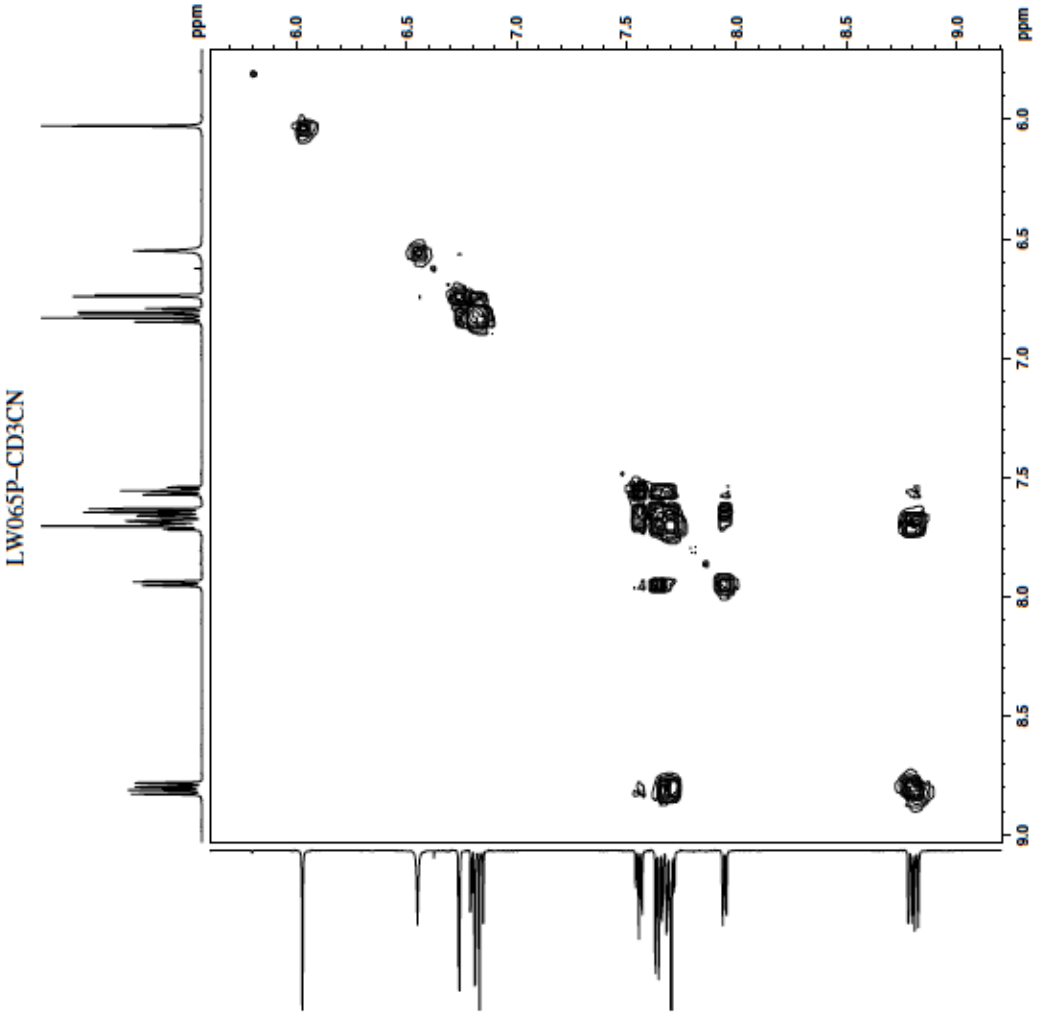


^{13}C NMR (500 MHz, $CDCN_3$) spectrum of **10**

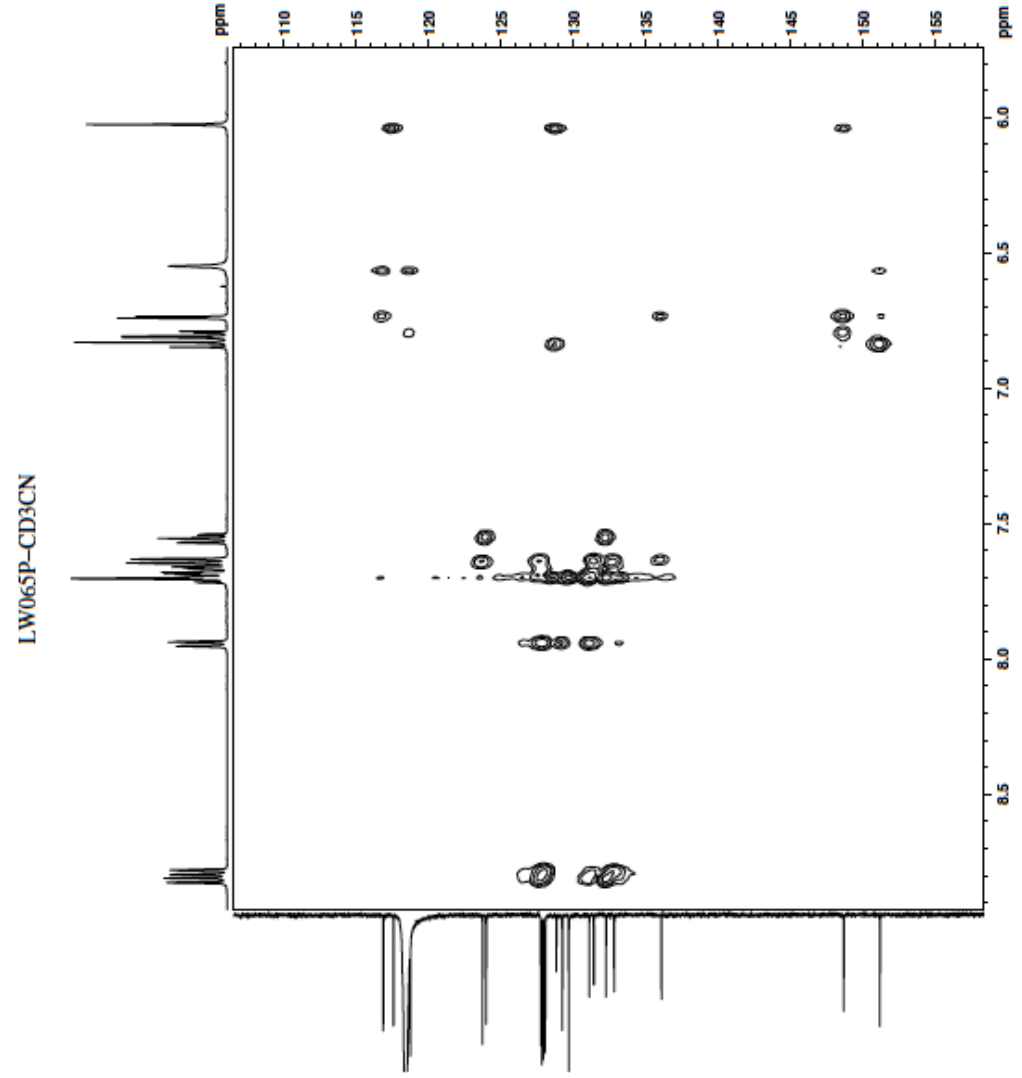


gCOSY spectrum of **10** in $CDCN_3$

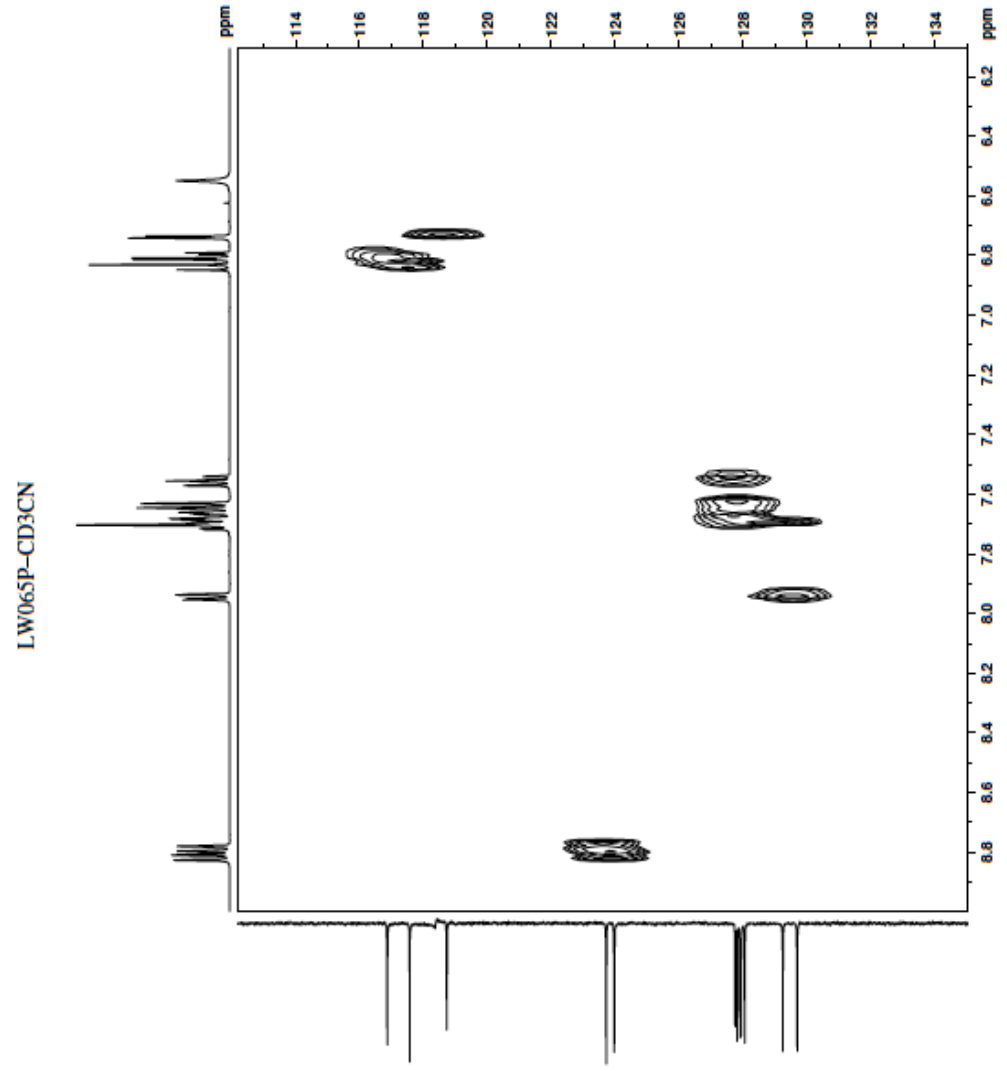




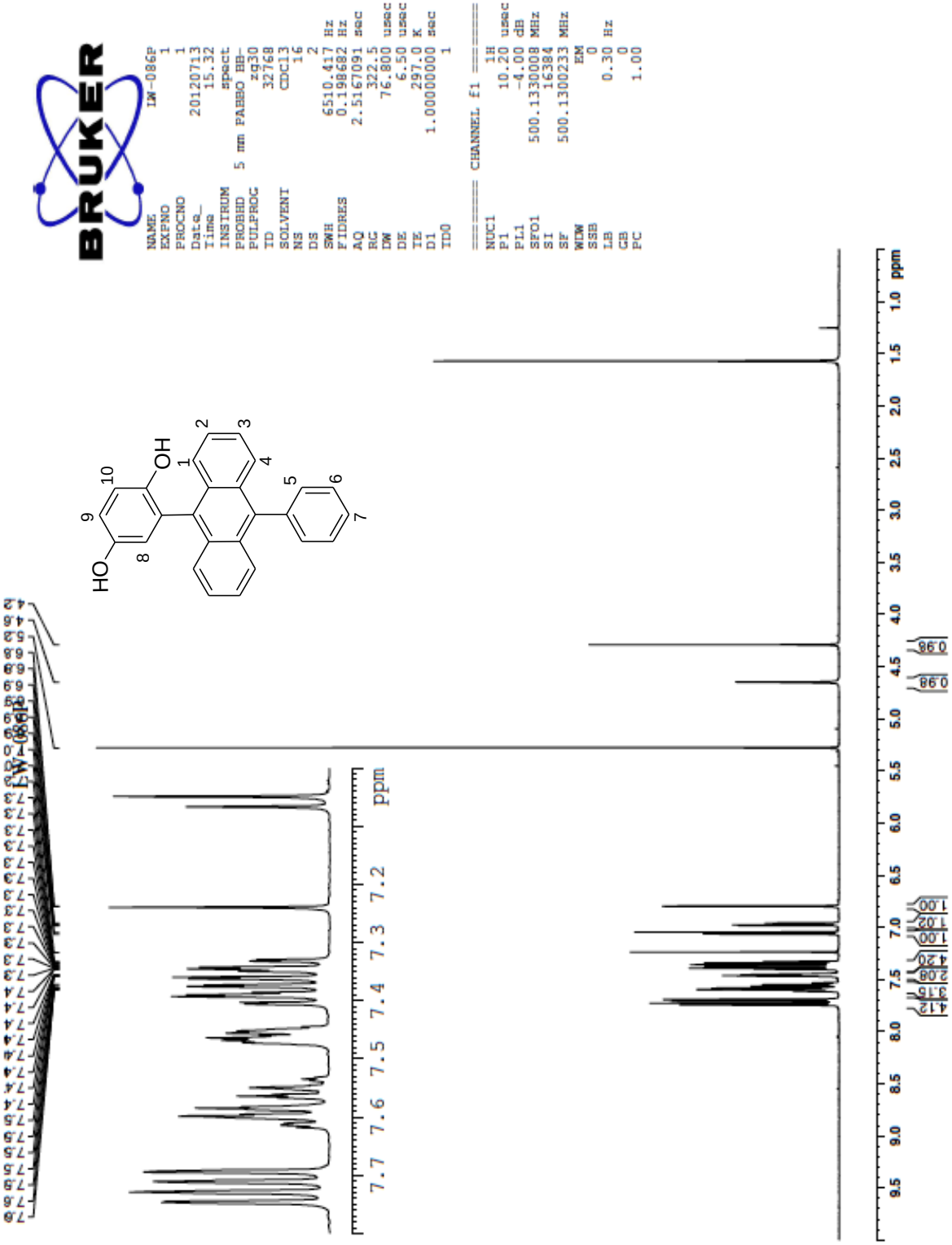
gHMBC spectrum of **10** in $CDCN_3$



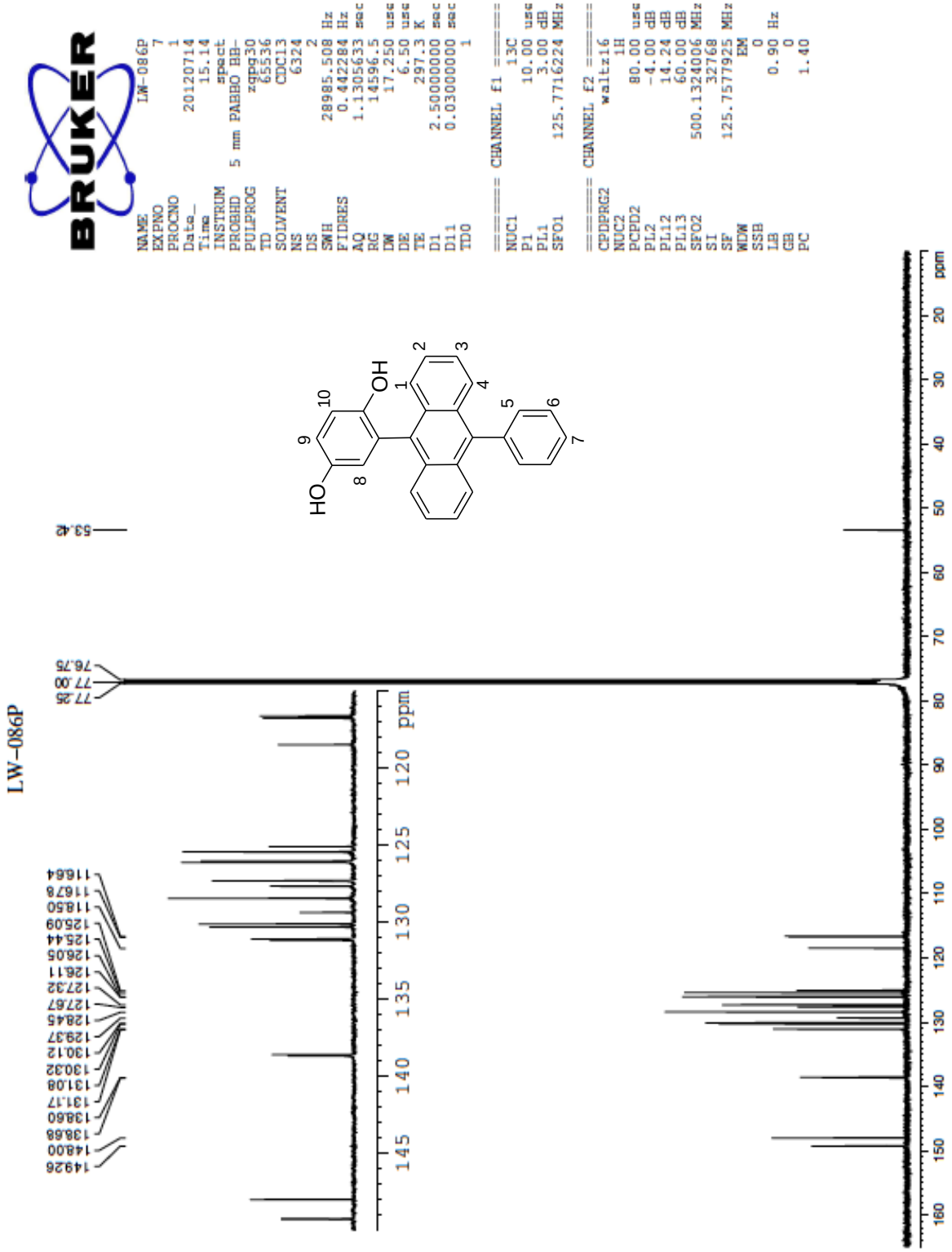
gHSQC spectrum of **10** in $CDCN_3$



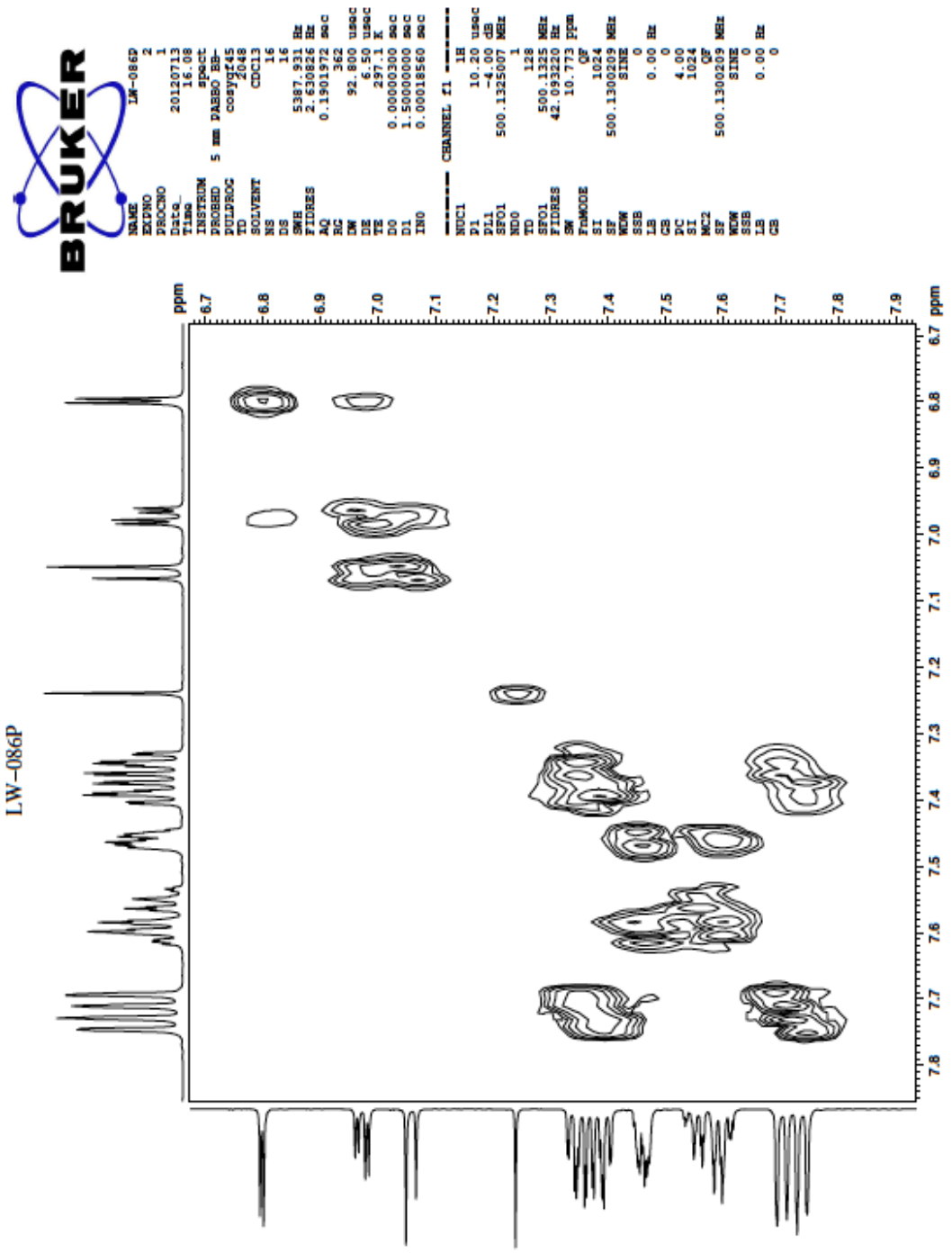
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **11**



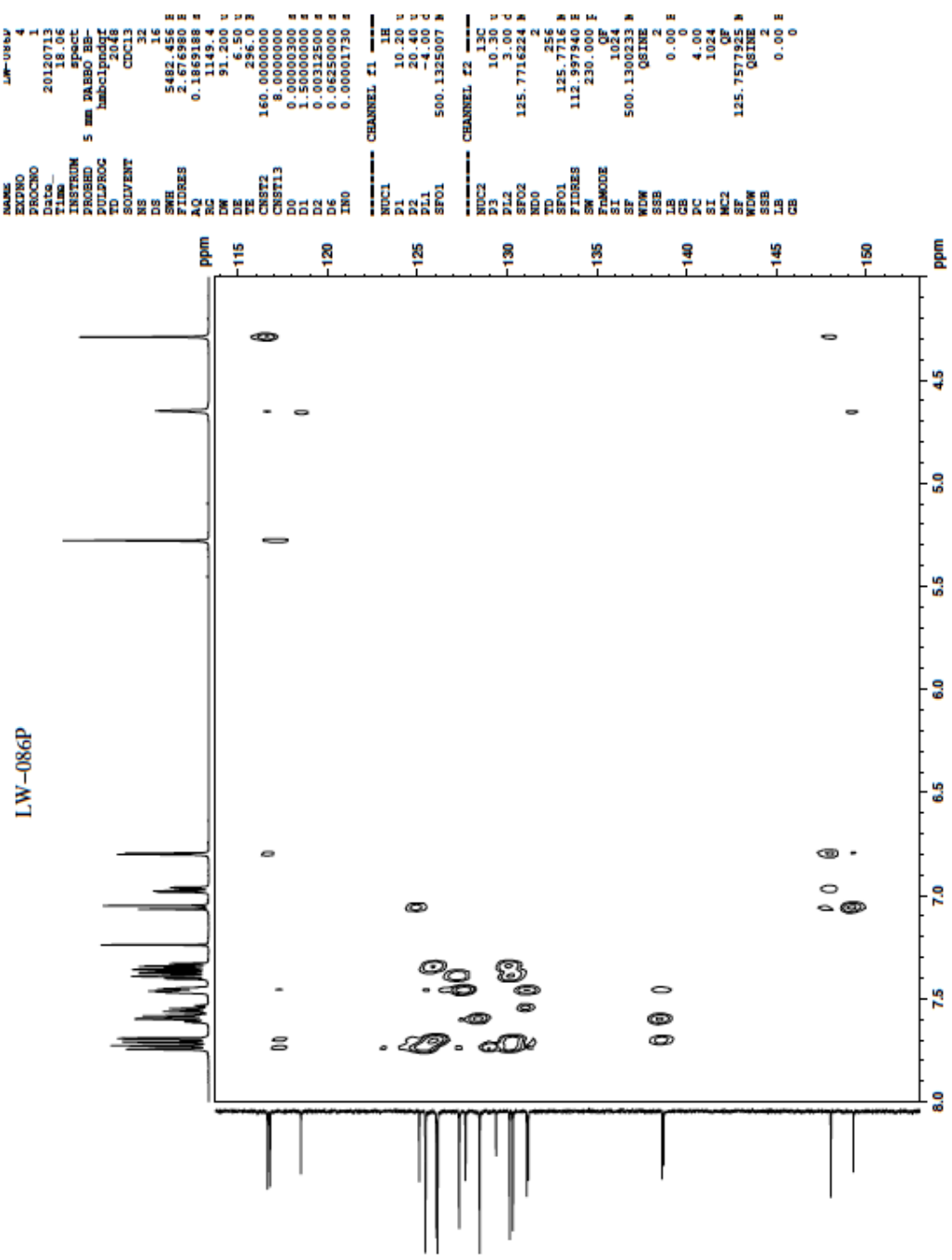
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **11**



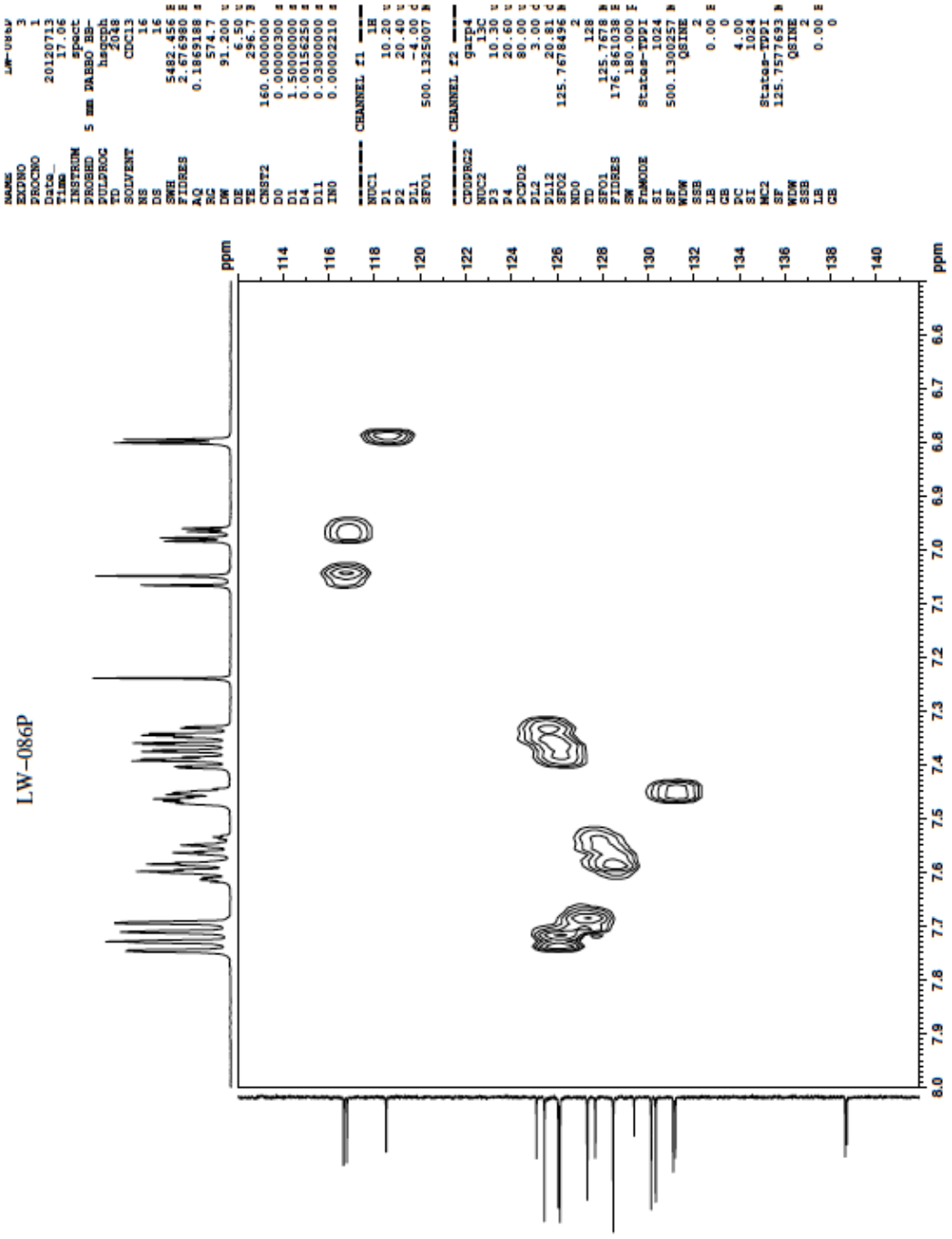
gCOSY spectrum of **11** in $CDCl_3$



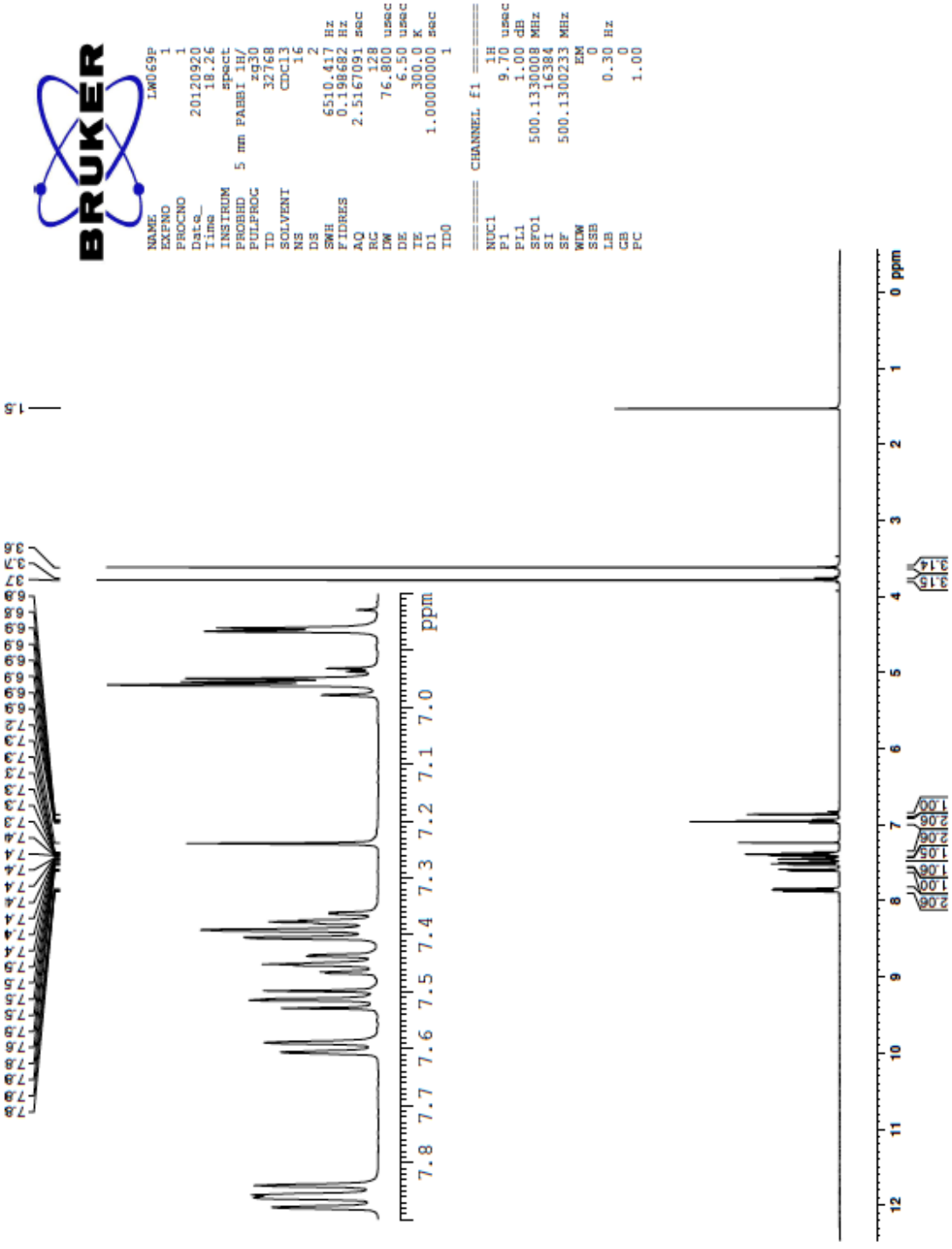
gHMBC spectrum of **11** in $CDCl_3$



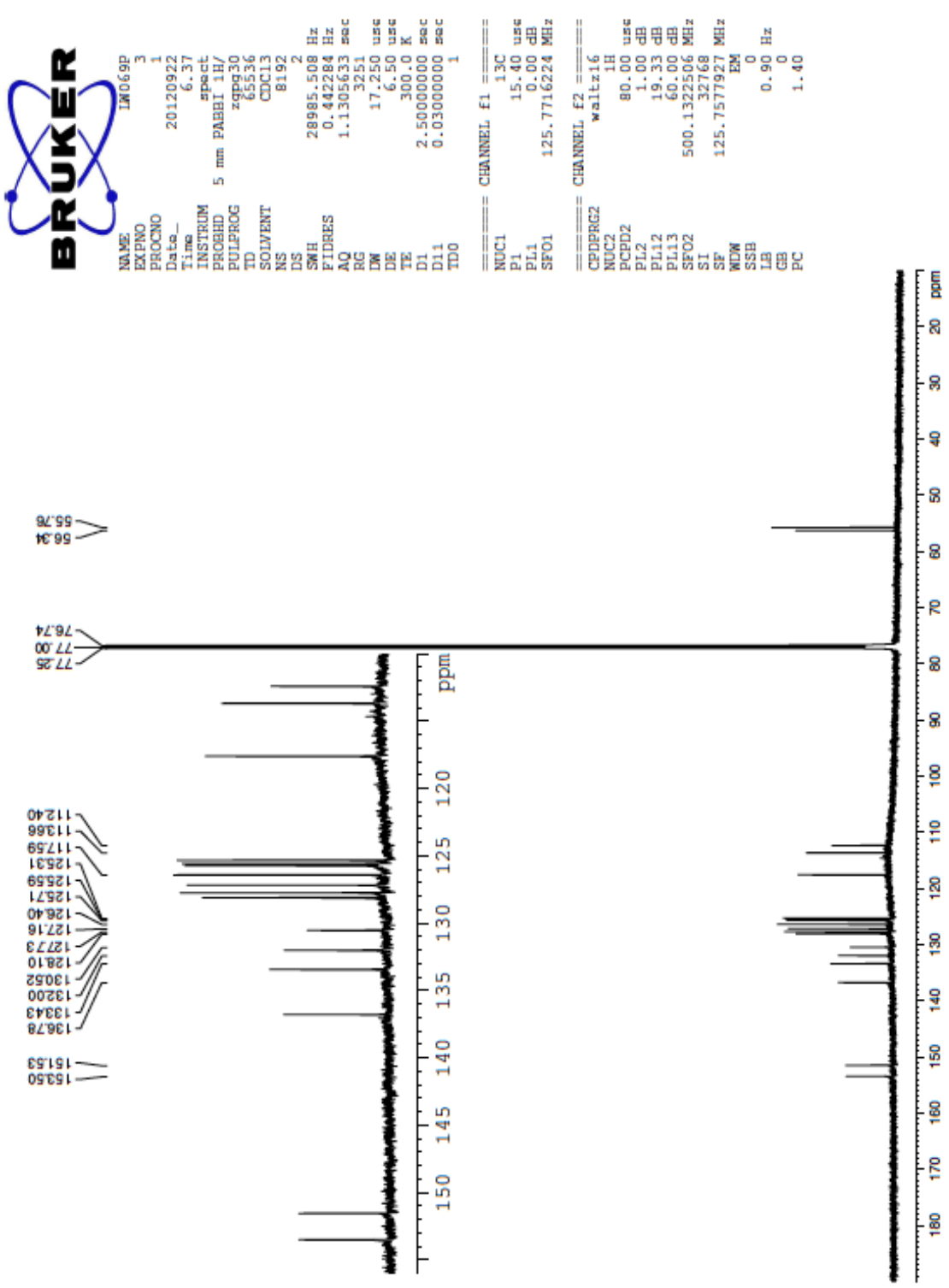
gHSQC spectrum of **11** in $CDCl_3$



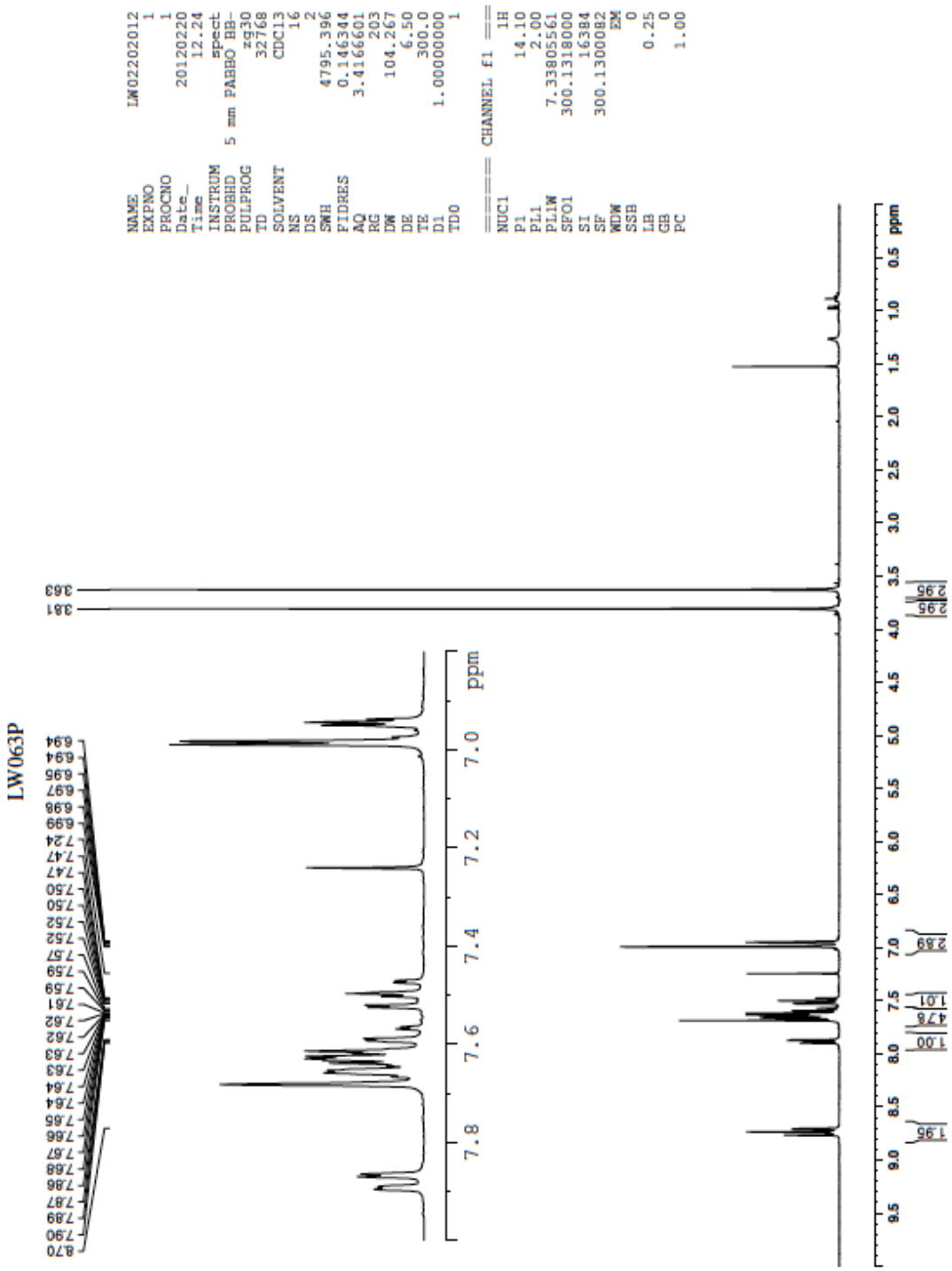
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **12**



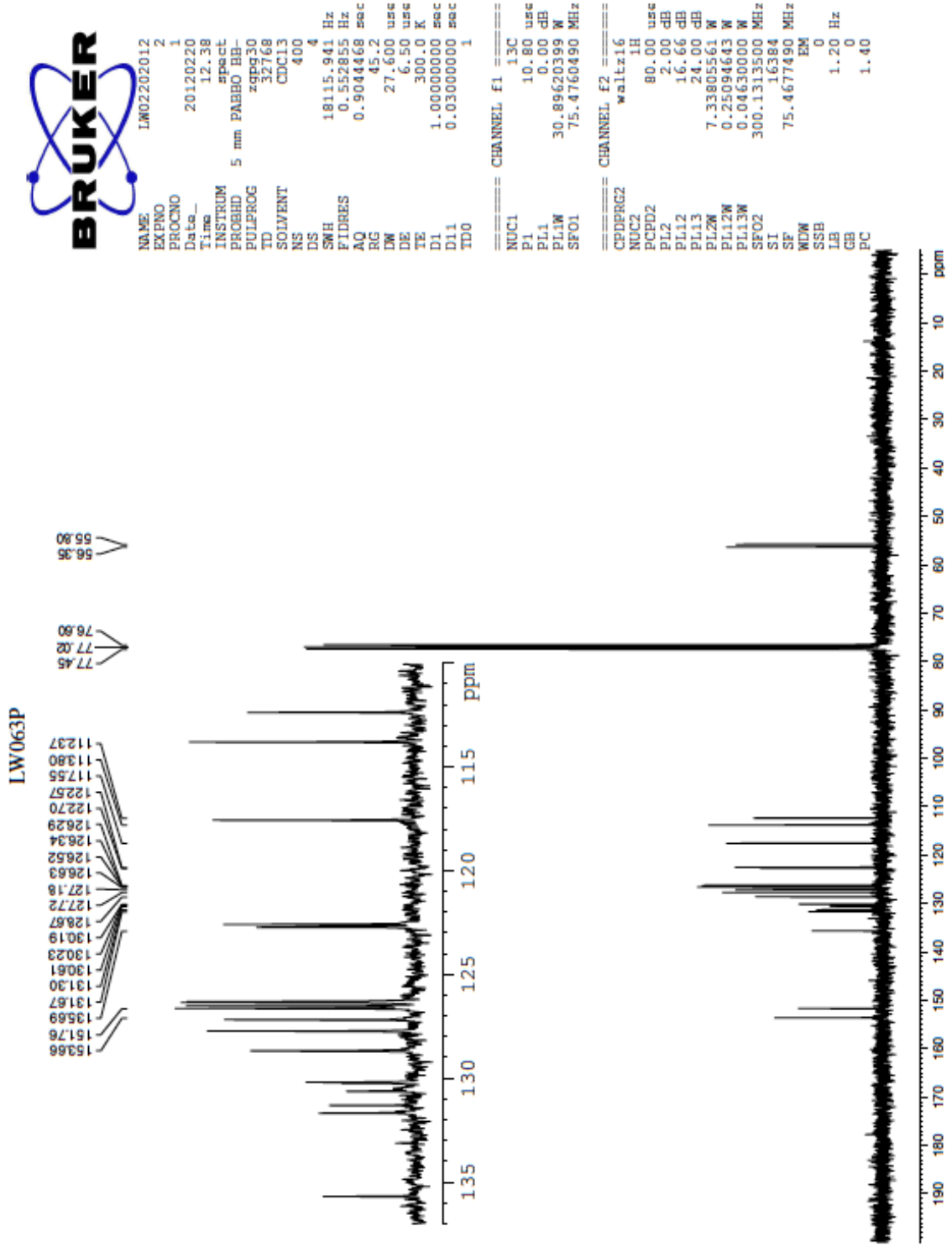
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **12**



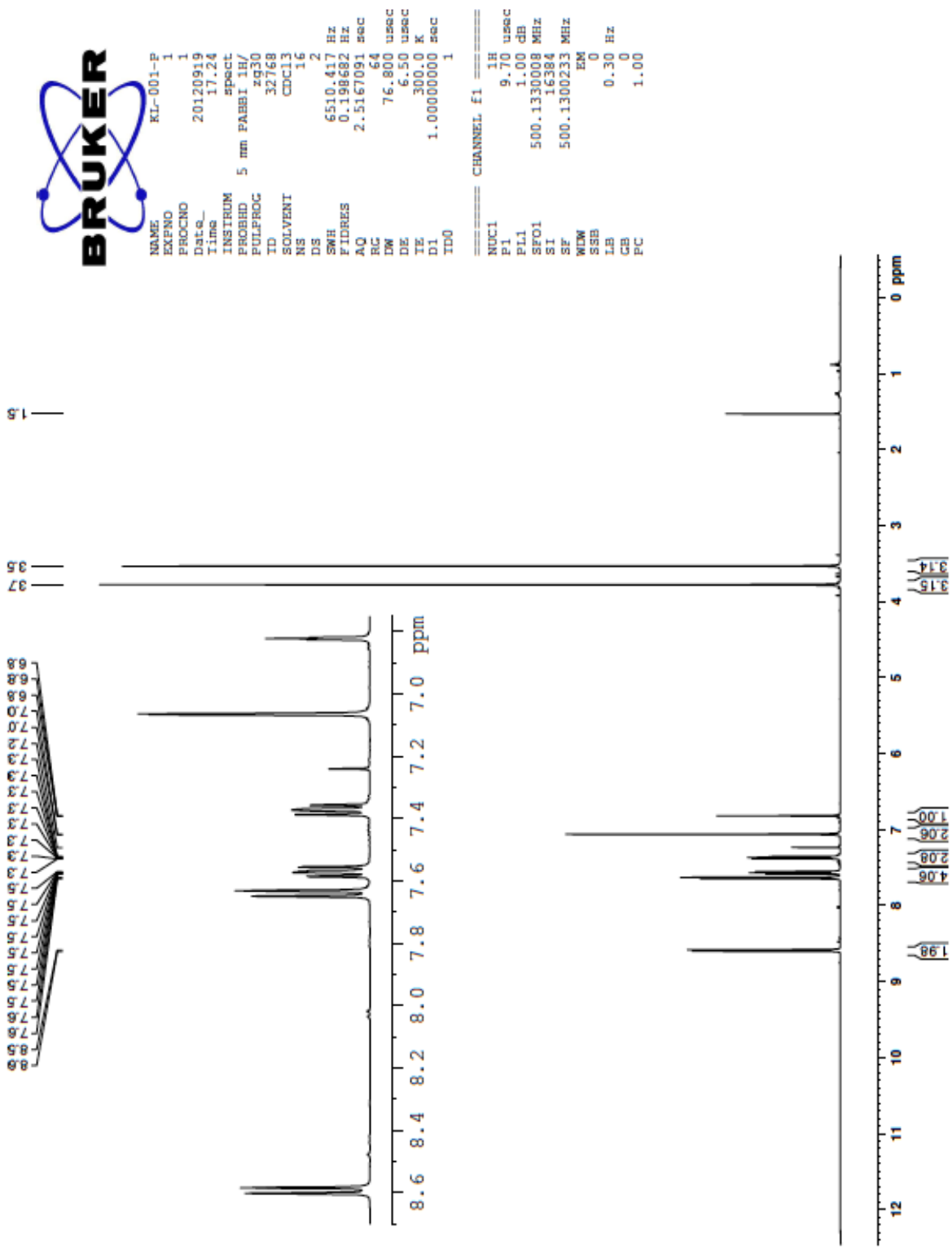
^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **13**



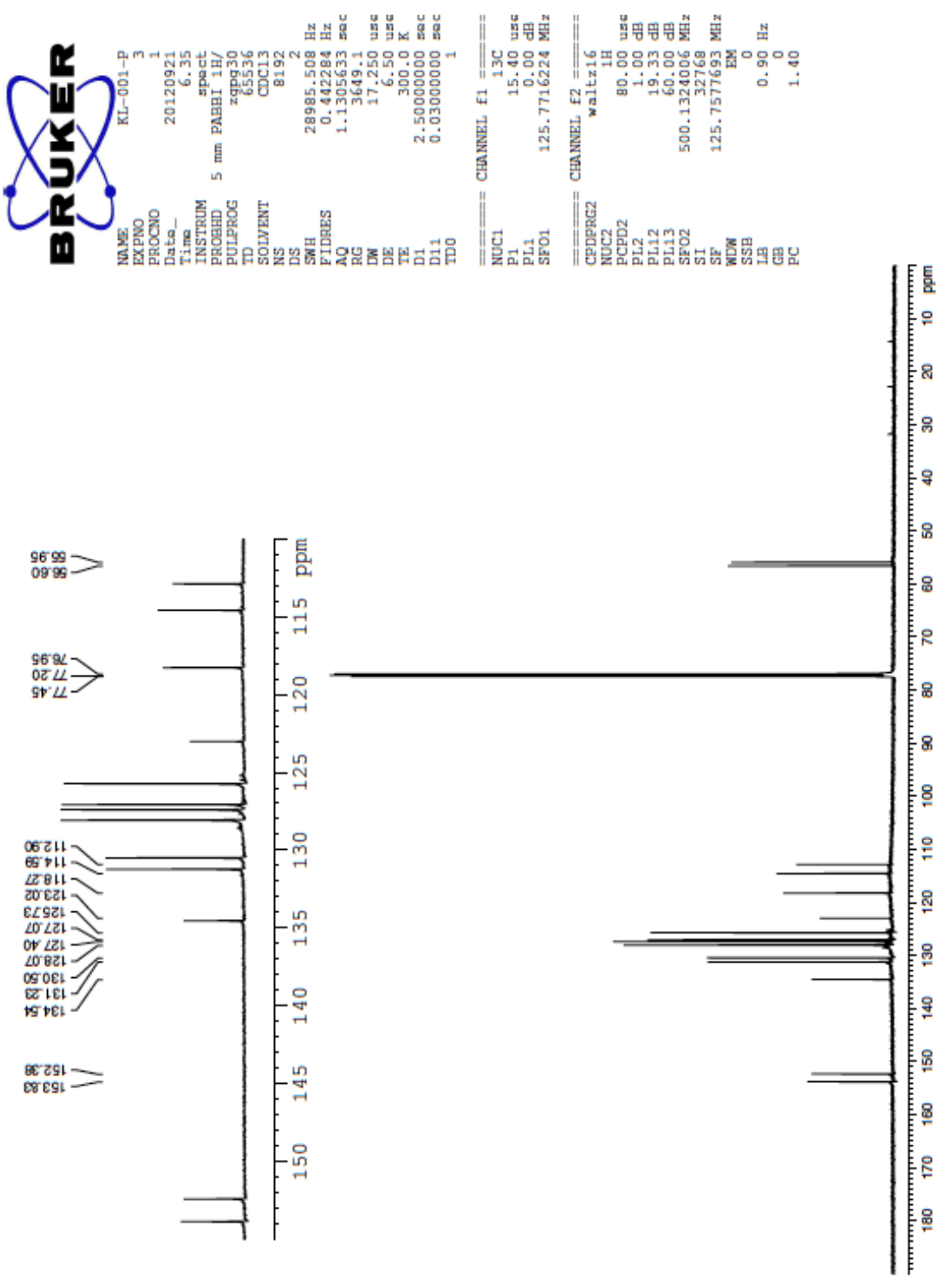
^{13}C NMR (75 MHz, $CDCl_3$) spectrum of **13**



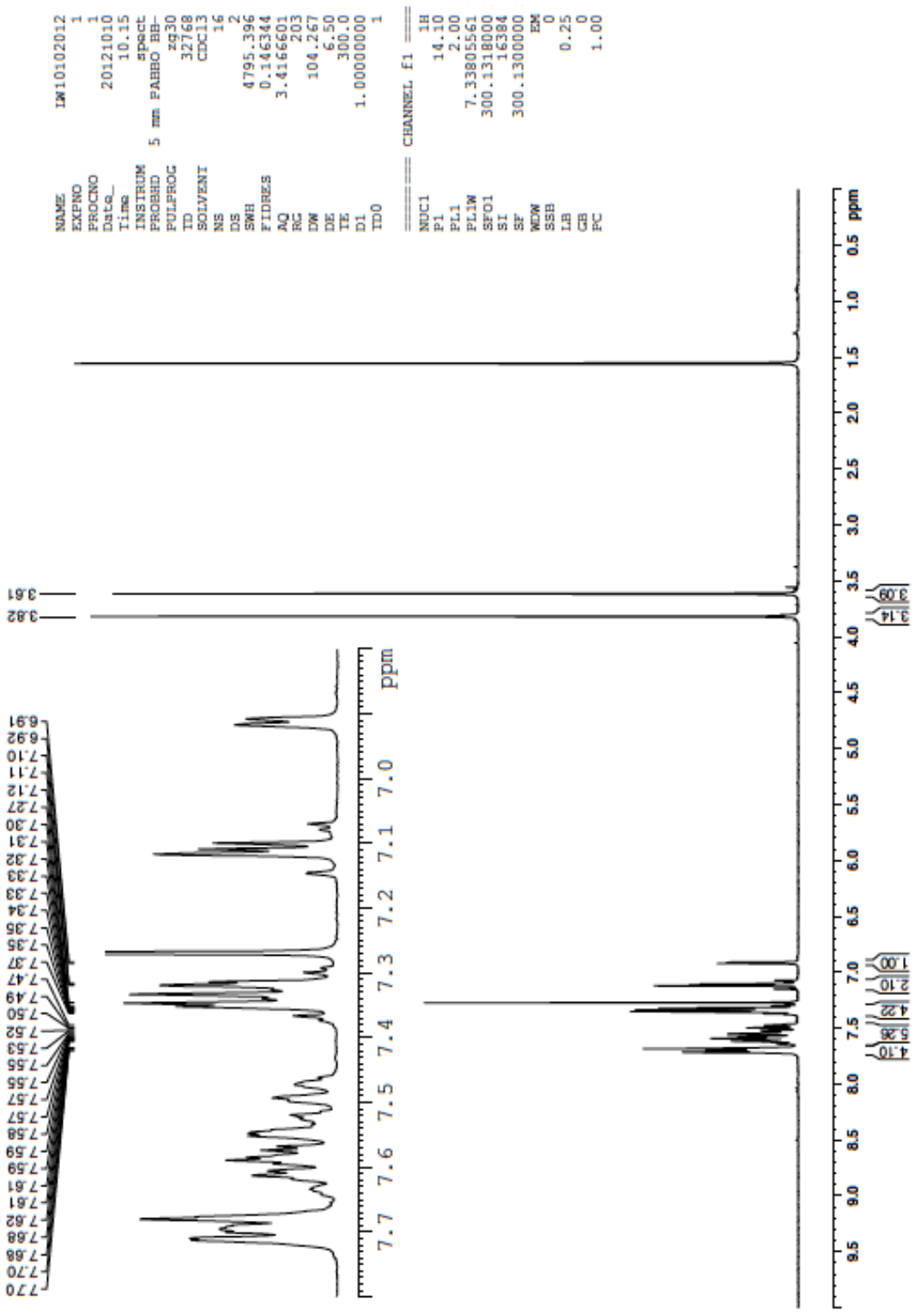
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **14**



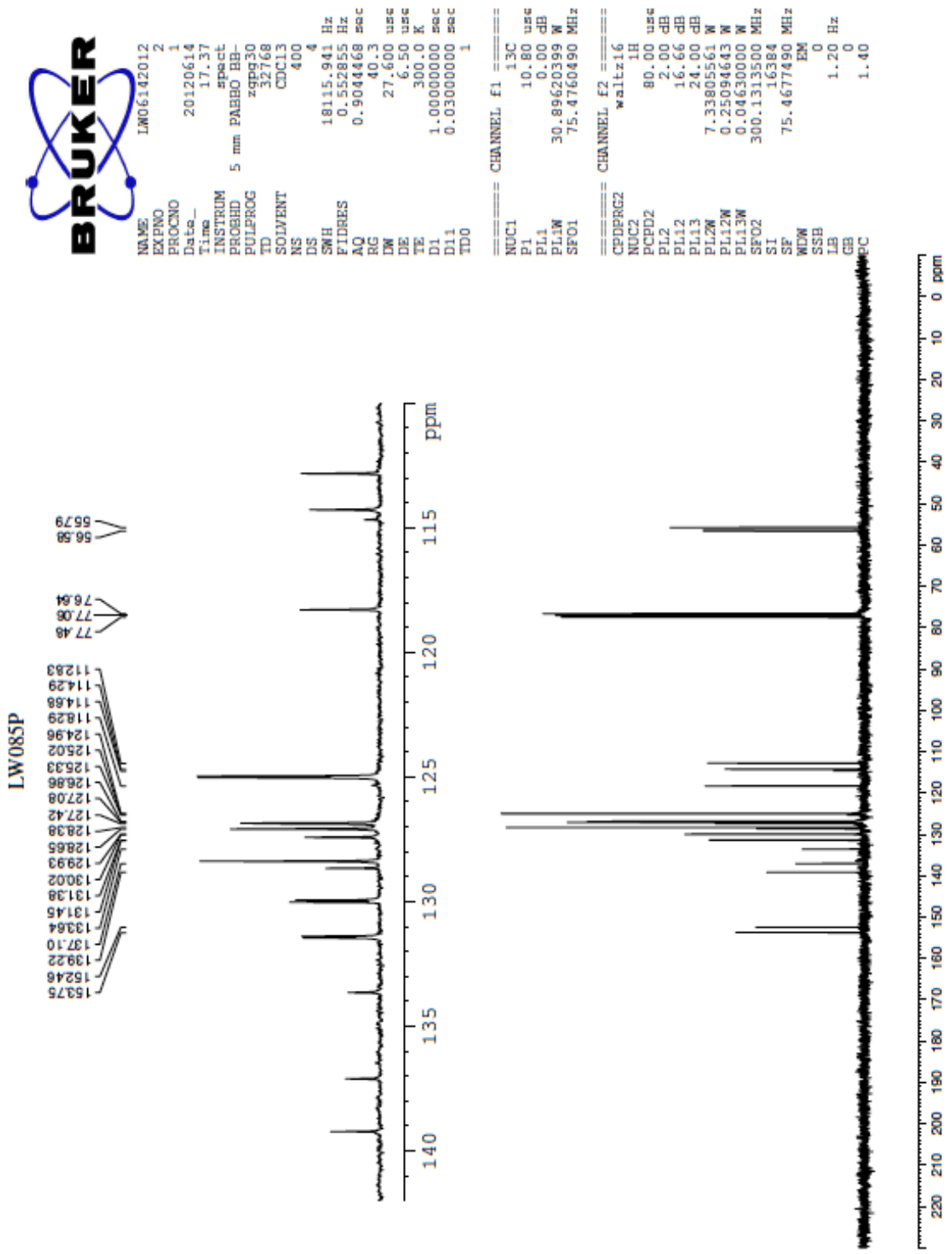
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **14**



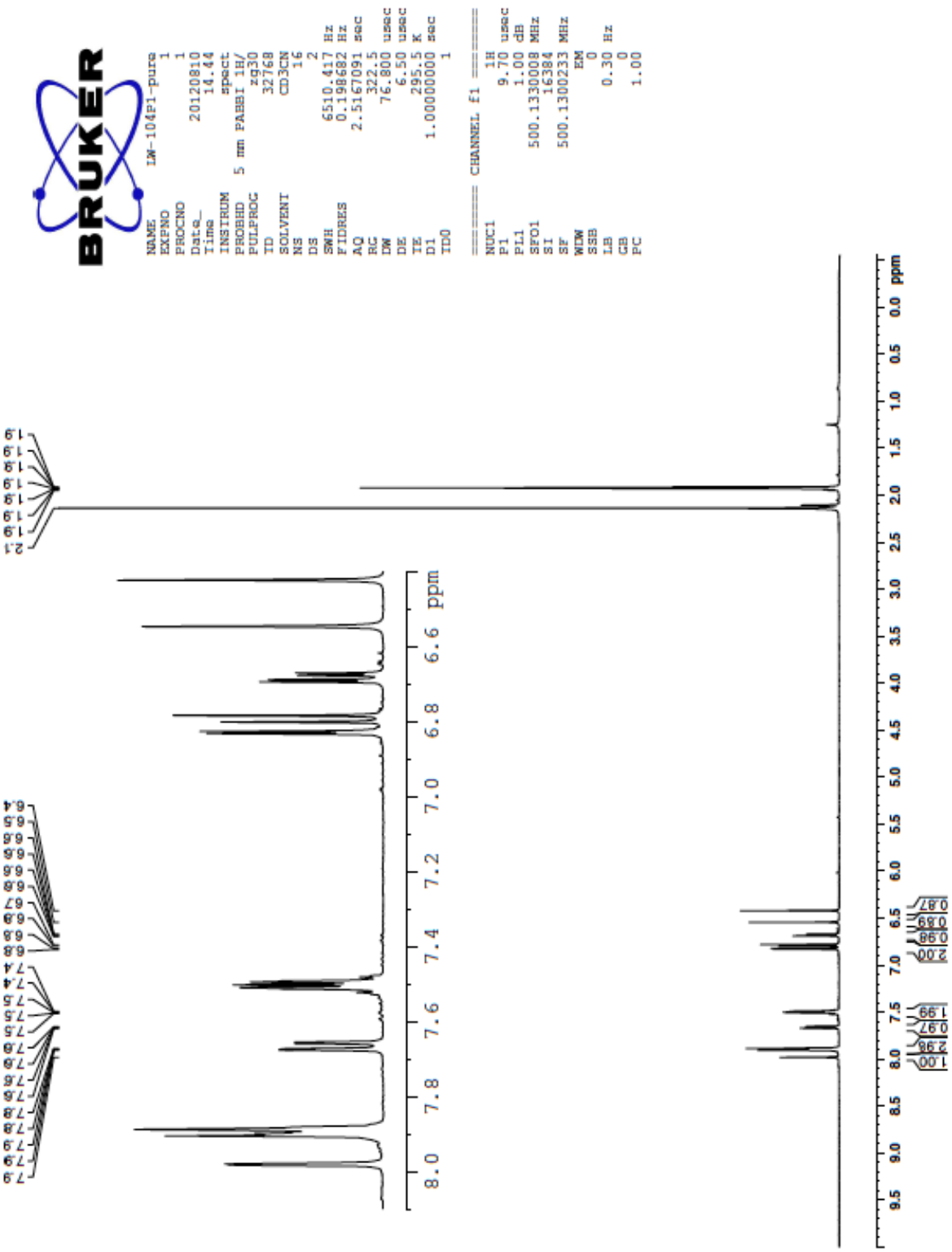
^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **15**



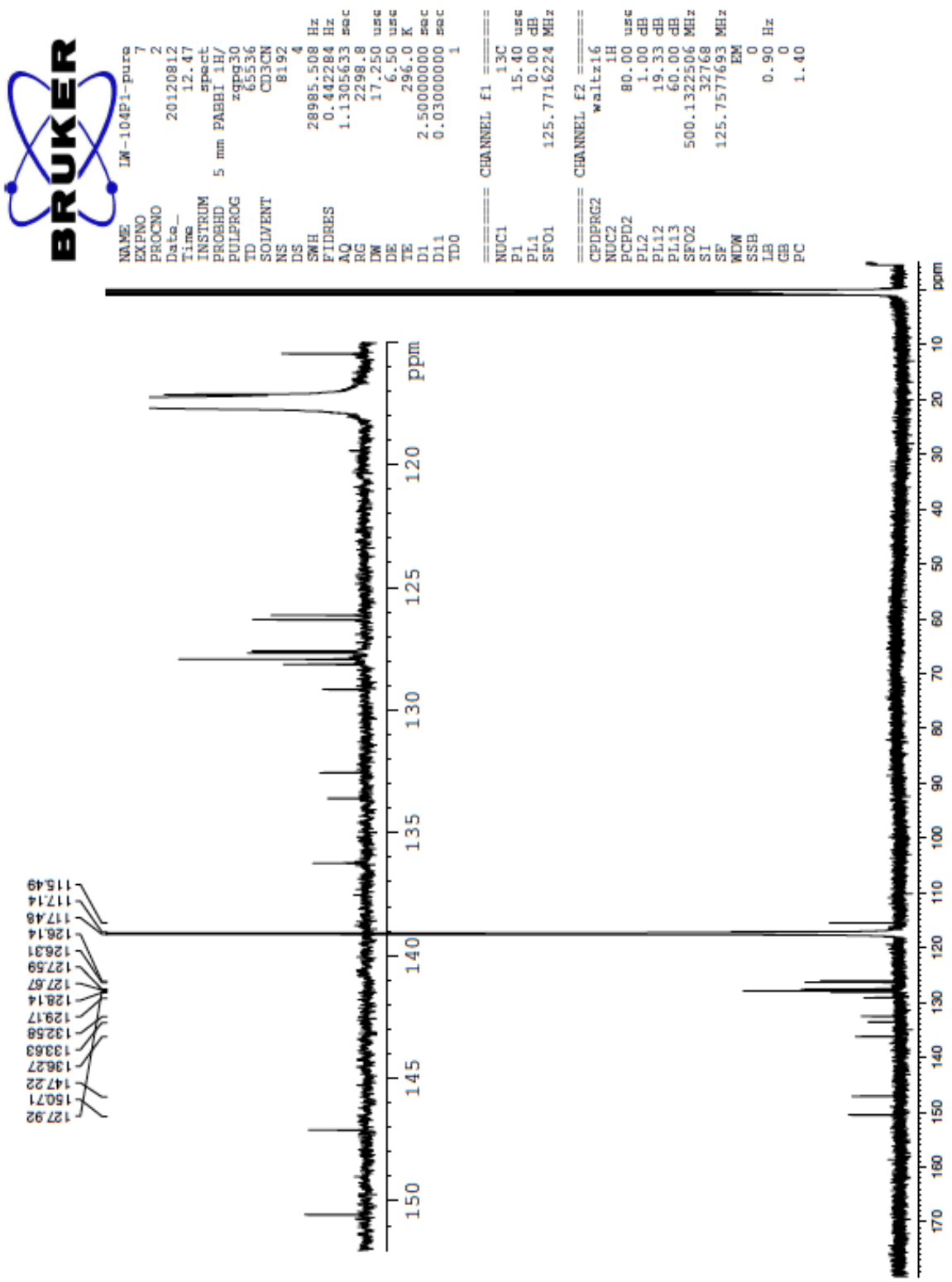
^{13}C NMR (75 MHz, $CDCl_3$) spectrum of **15**



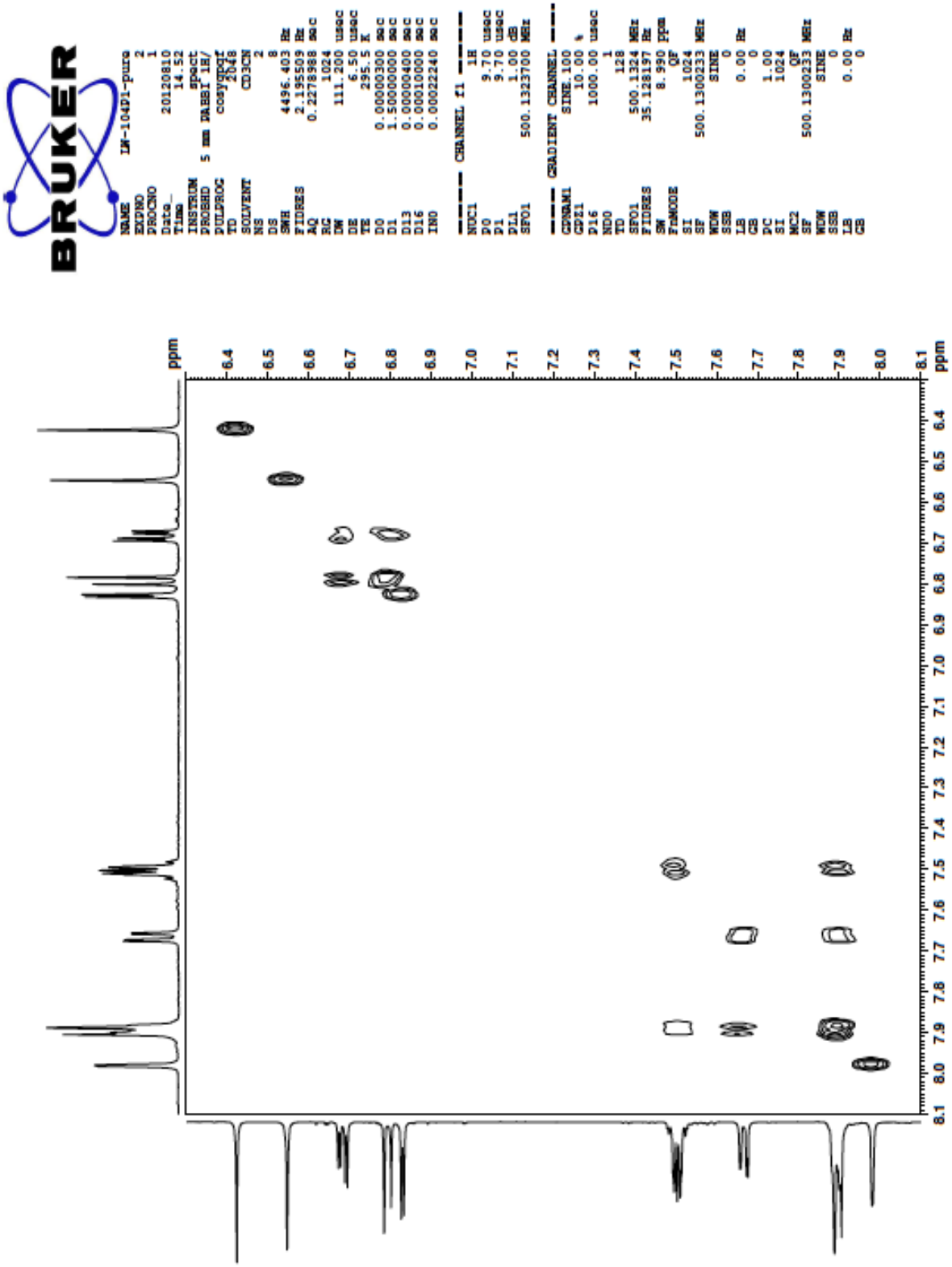
^{1}H NMR (500 MHz, $CDCN_3$) spectrum of **16**



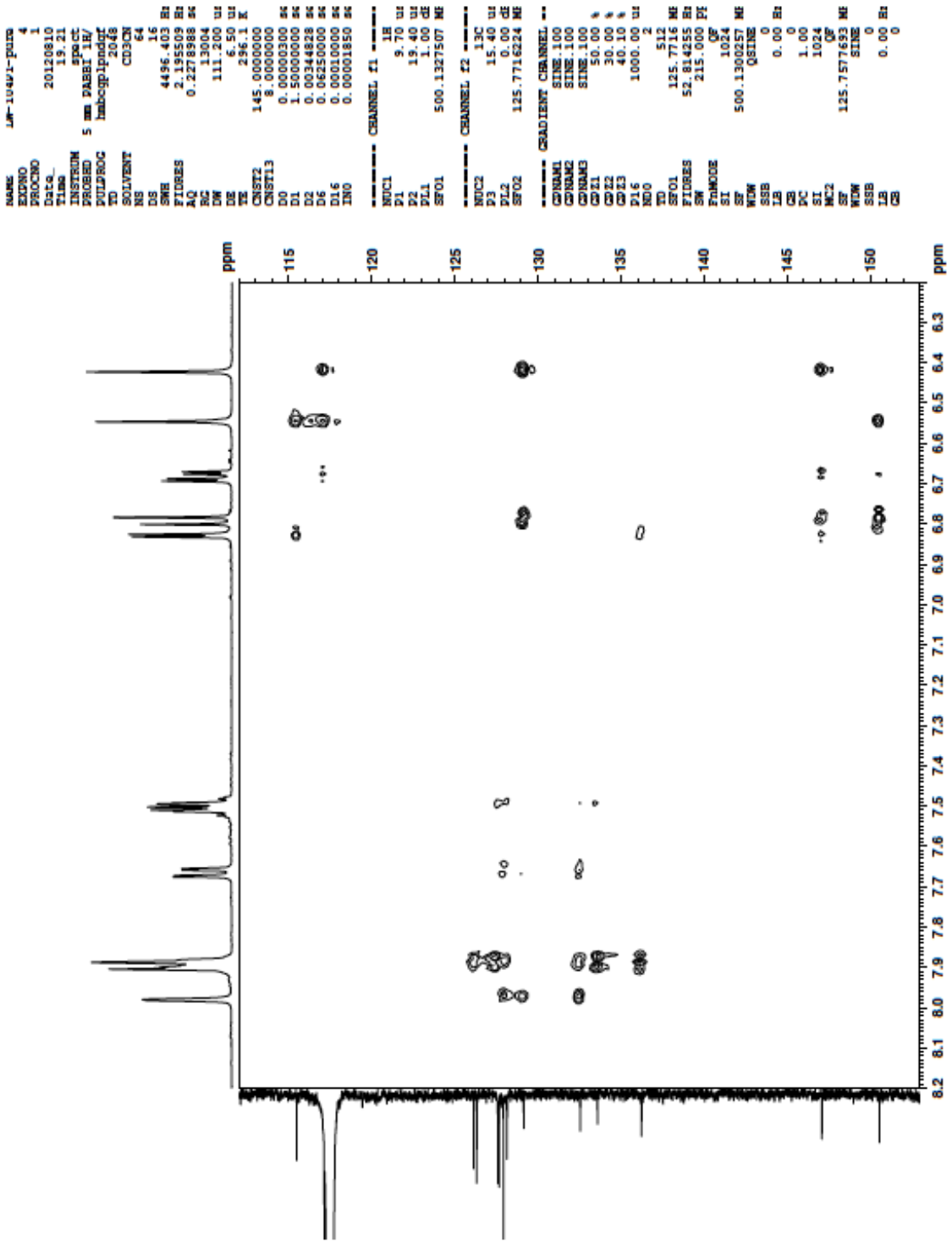
^{13}C NMR (125 MHz, $CDCN_3$) spectrum of **16**



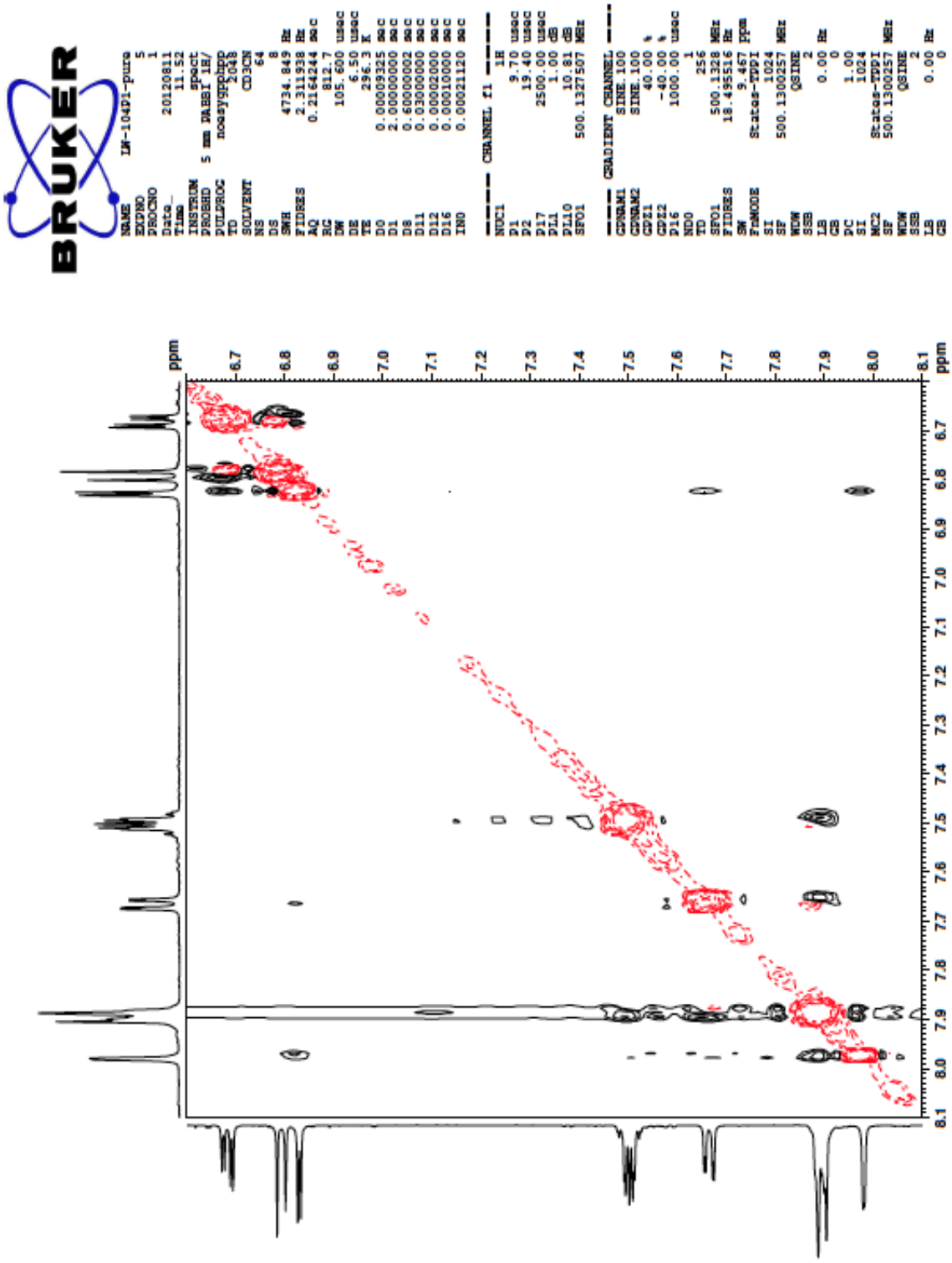
gCOSY spectrum of **16** in $CDCN_3$



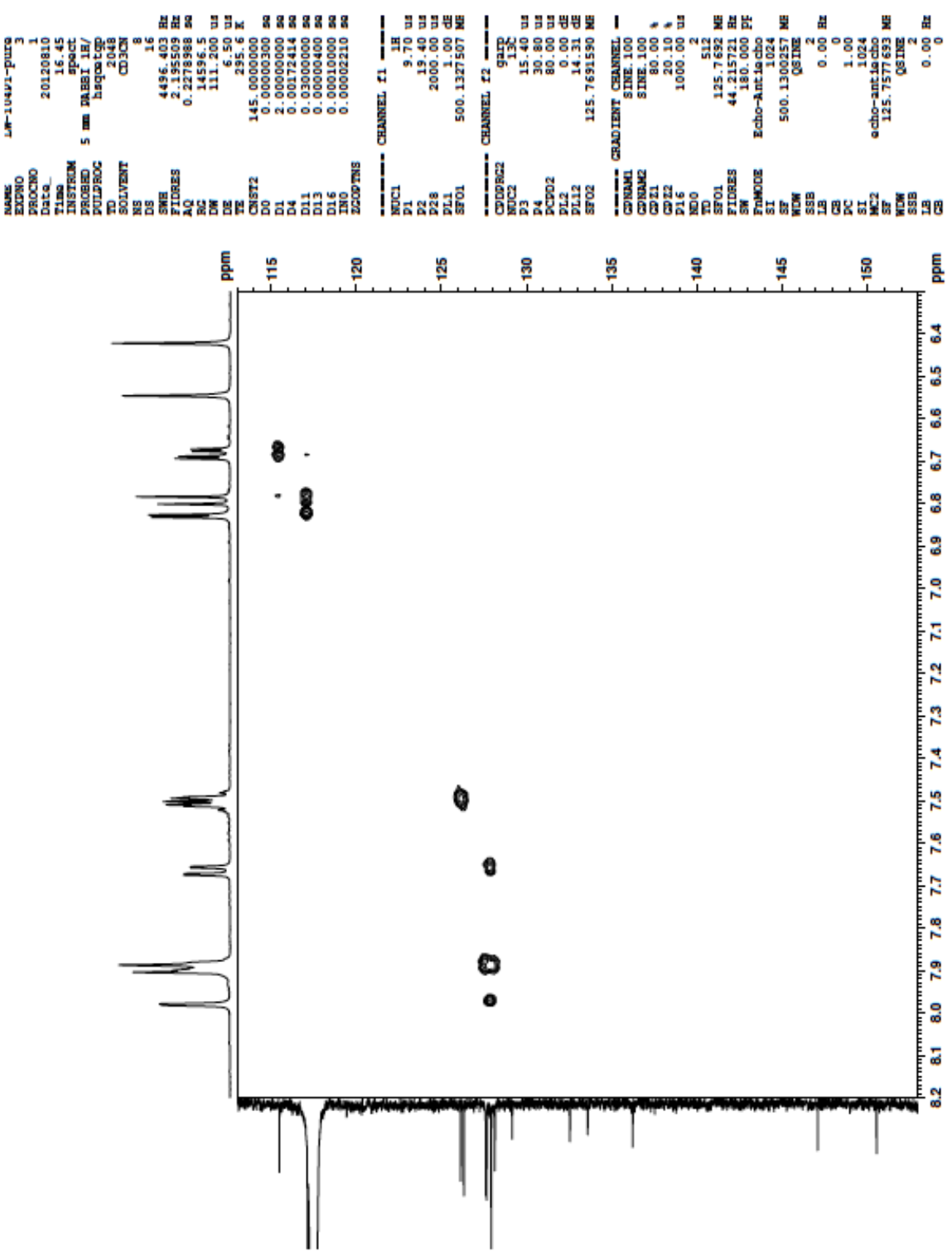
gHMBC spectrum of **16** in $CDCN_3$



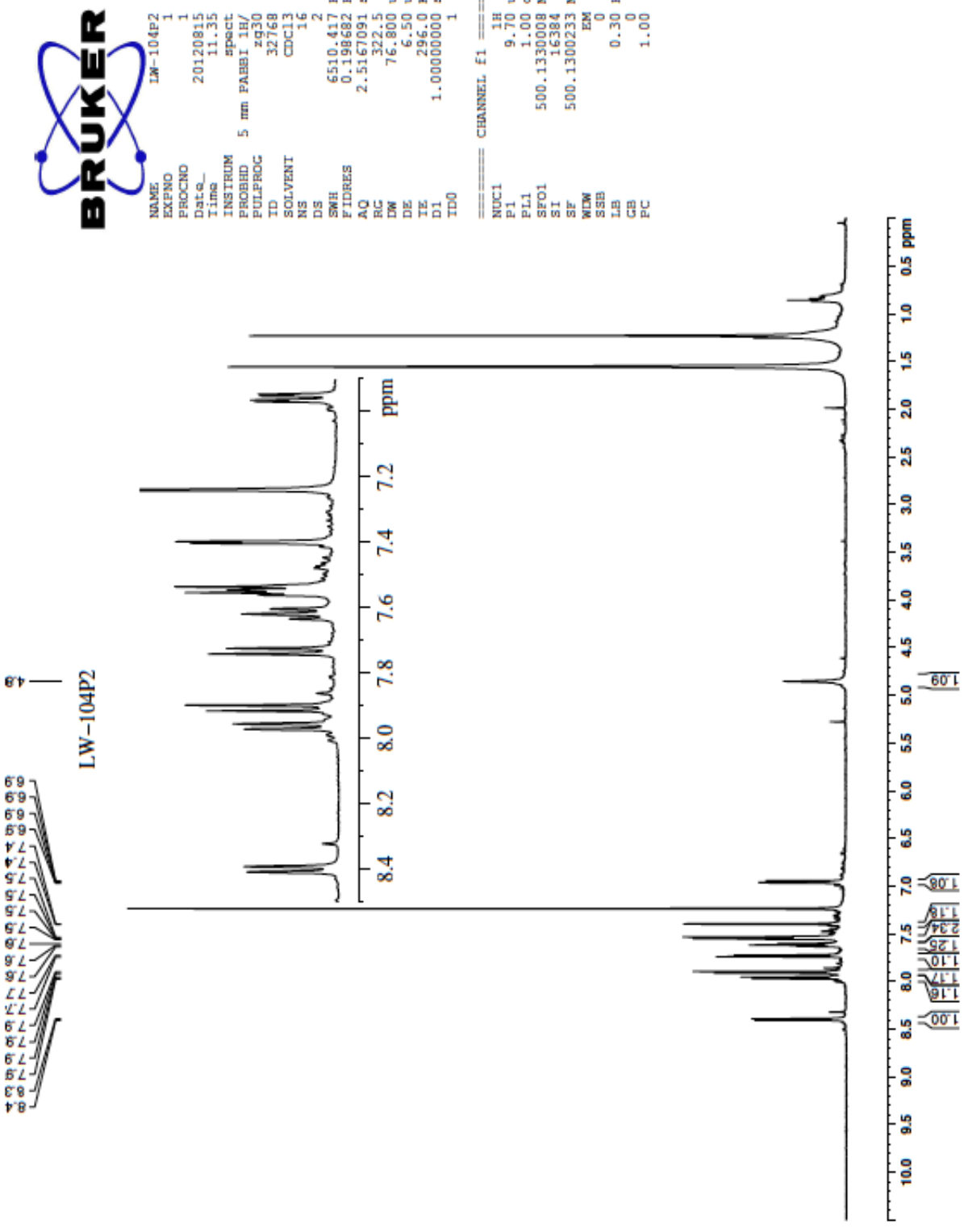
gNOESY spectrum of **16** in $CDCN_3$



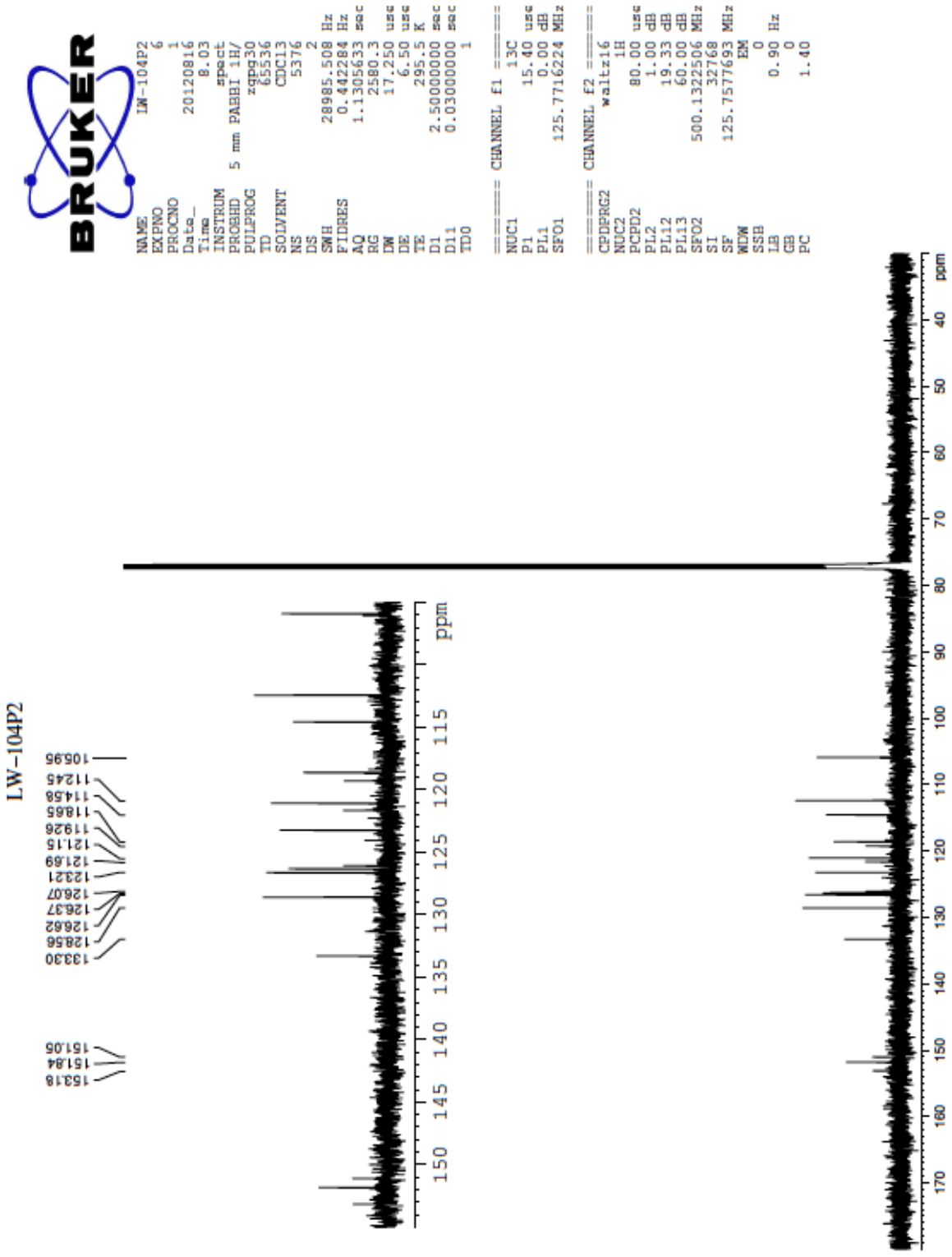
gHSQC spectrum of **16** in $CDCN_3$



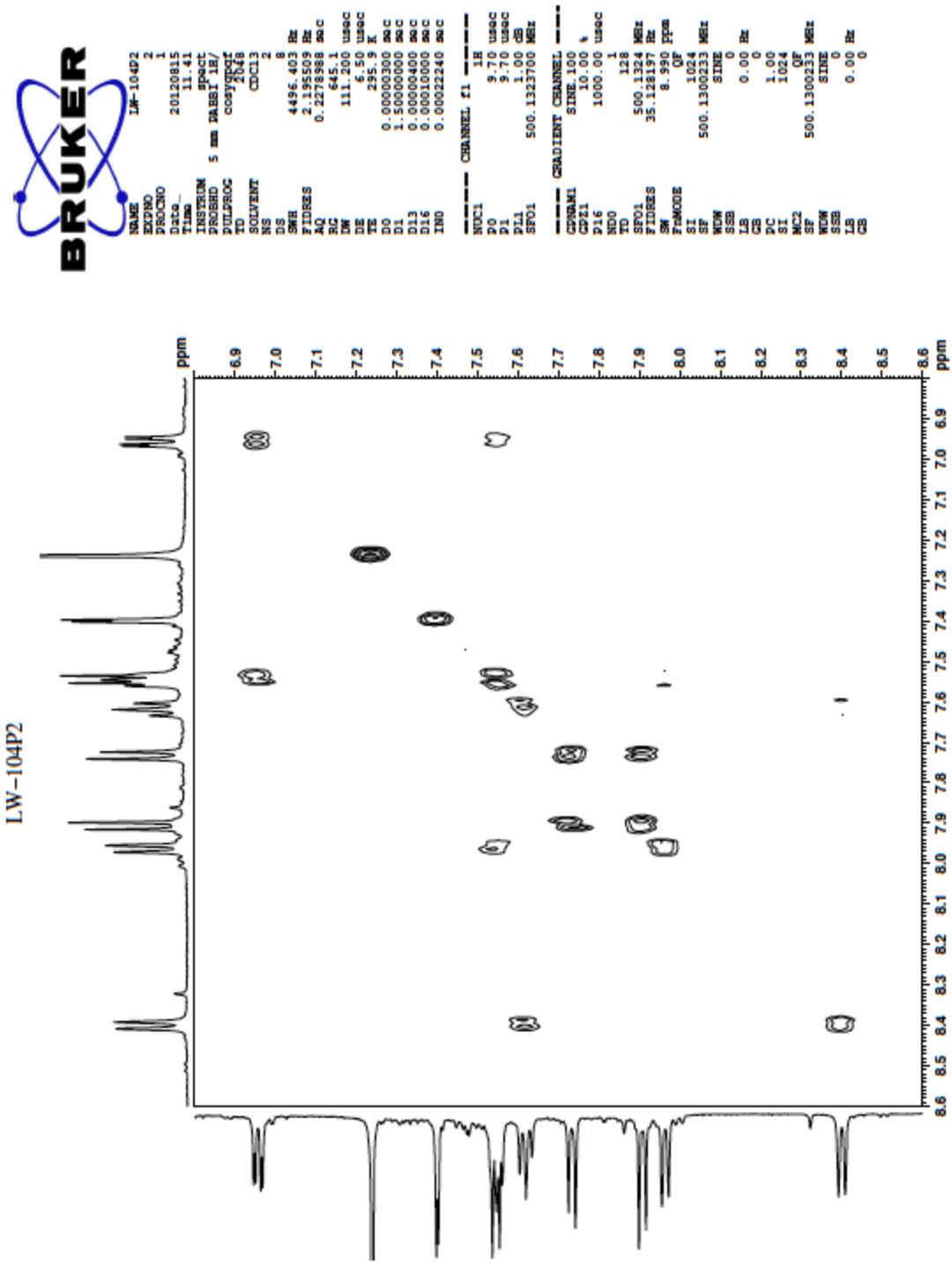
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **17**



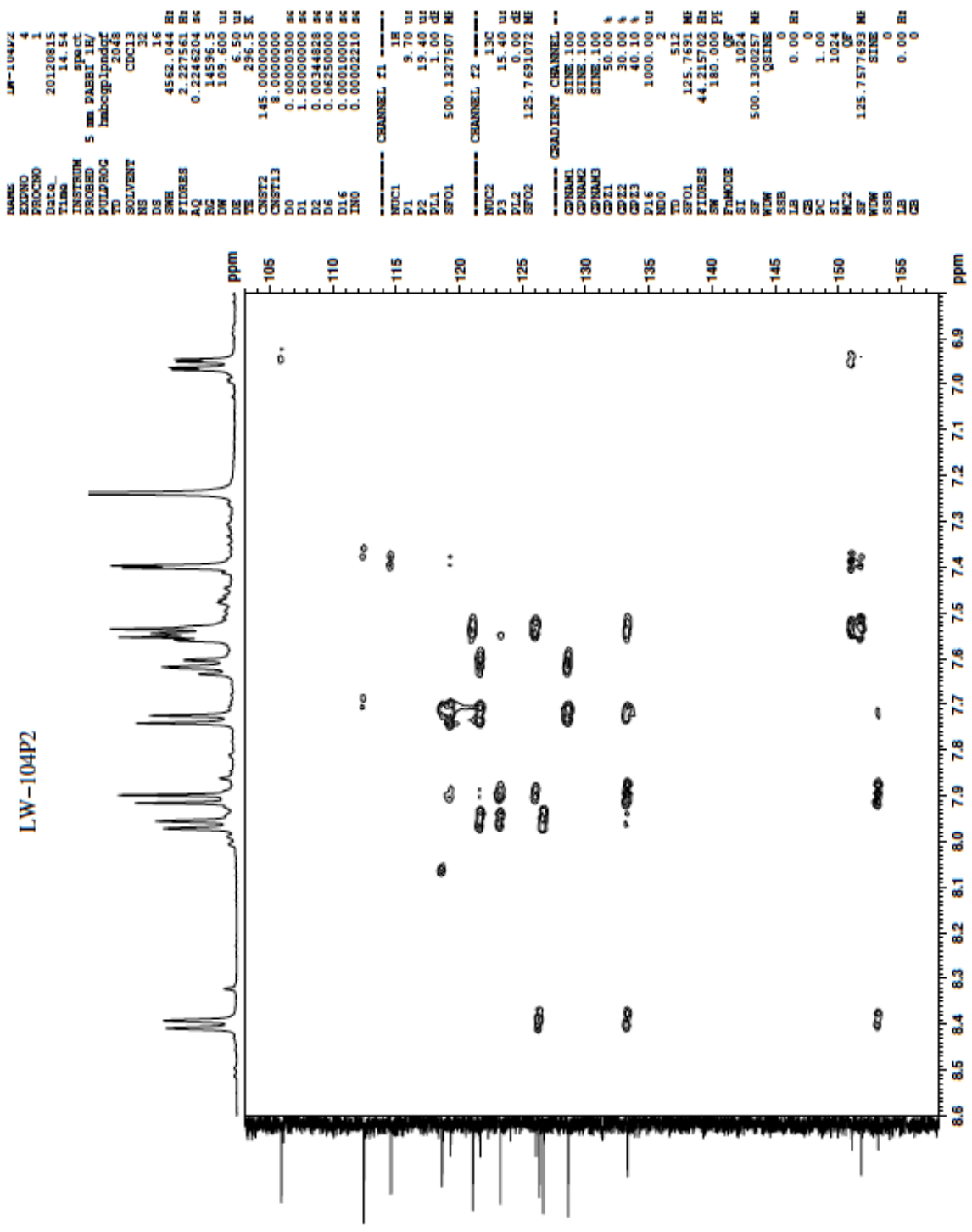
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **17**



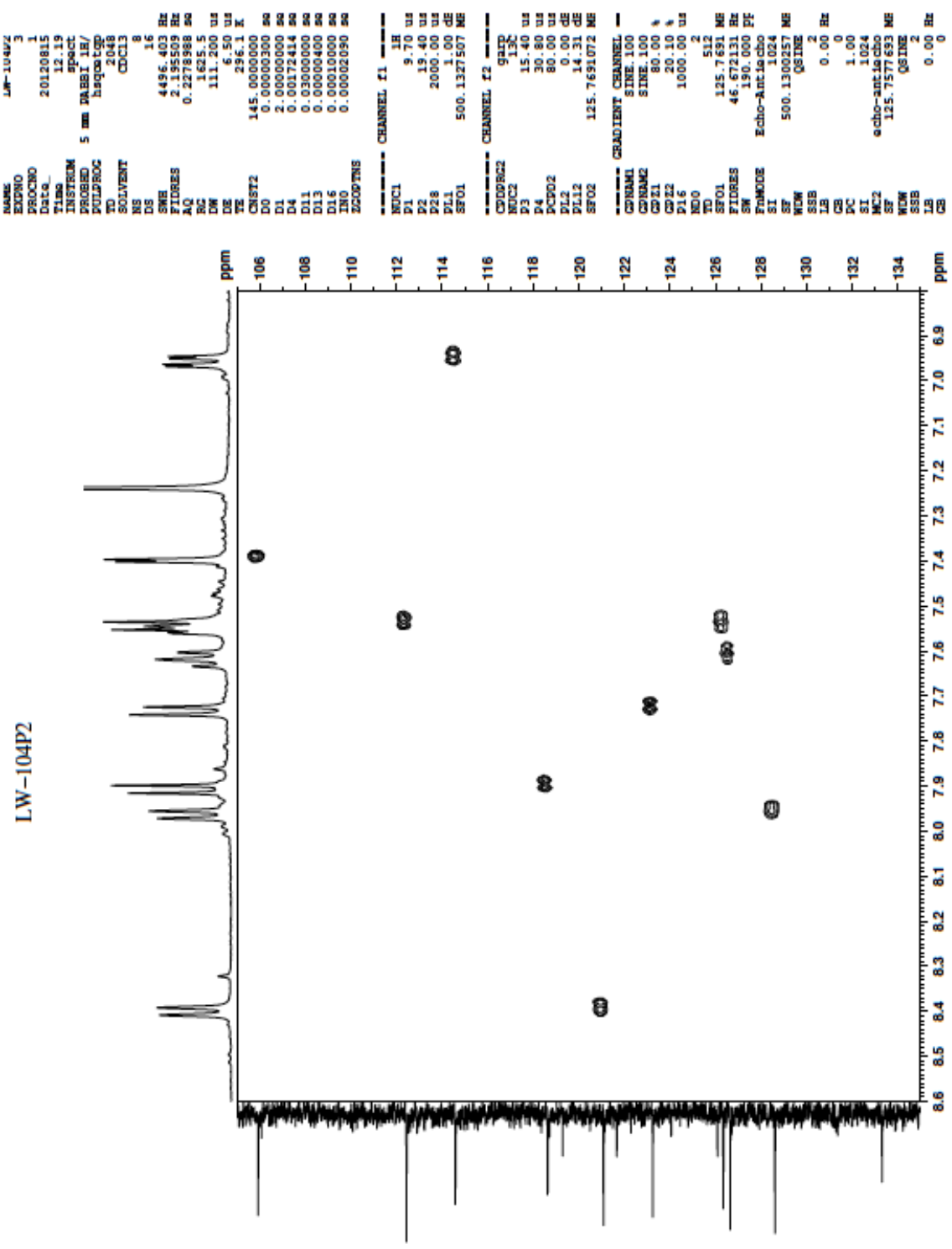
gCOSY spectrum of **17** in $CDCl_3$



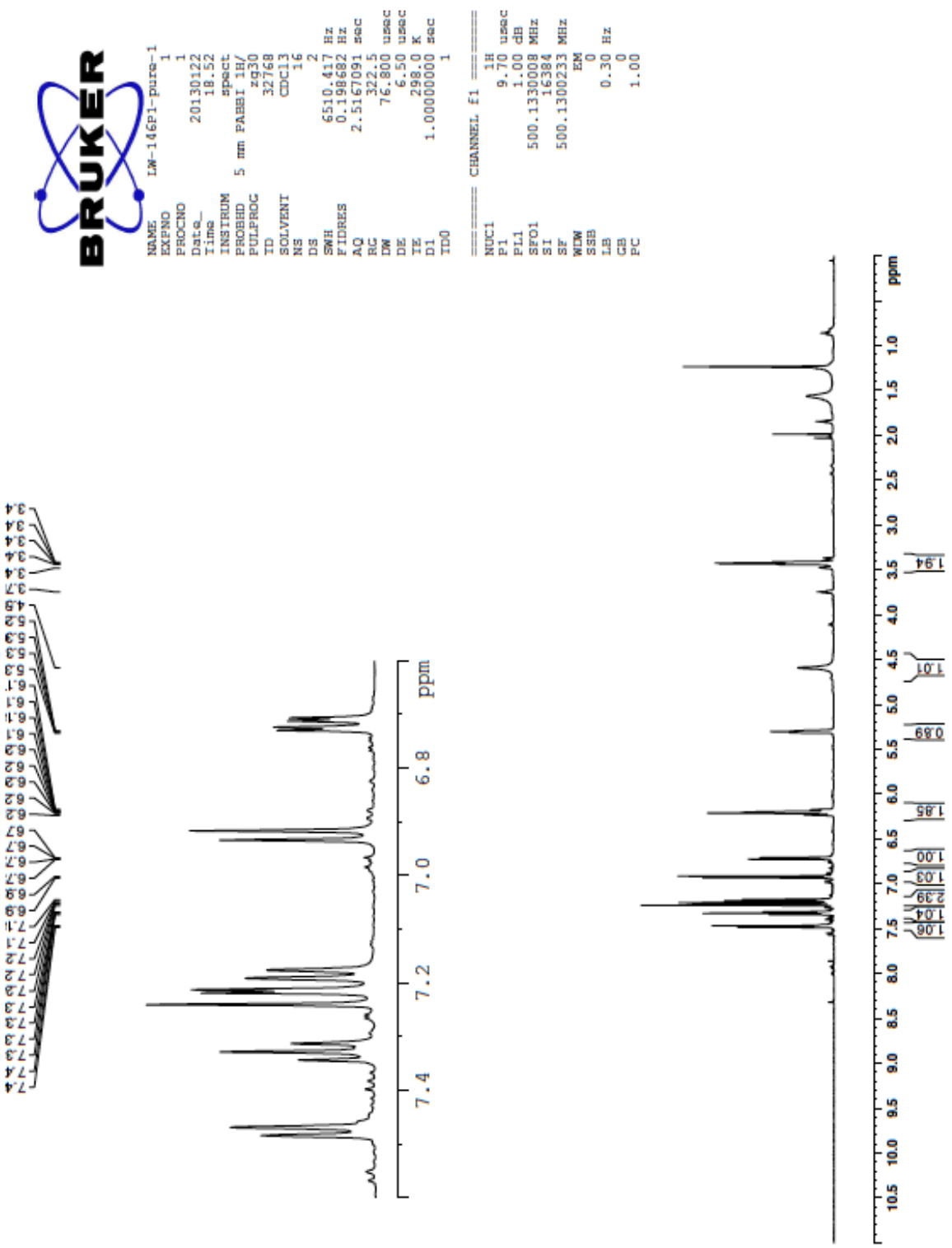
gHMBC spectrum of **17** in $CDCl_3$



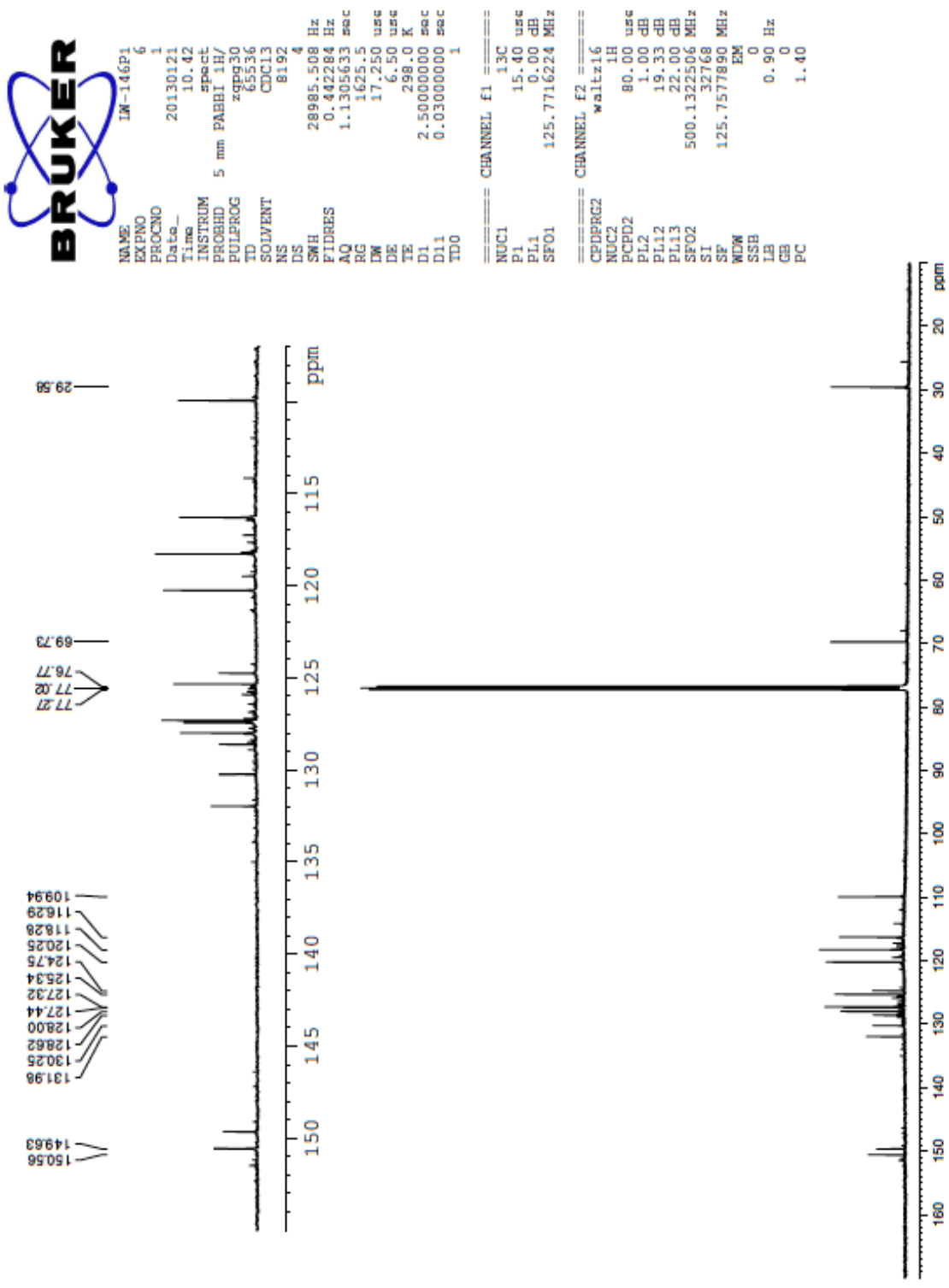
gHSQC spectrum of **17** in $CDCl_3$



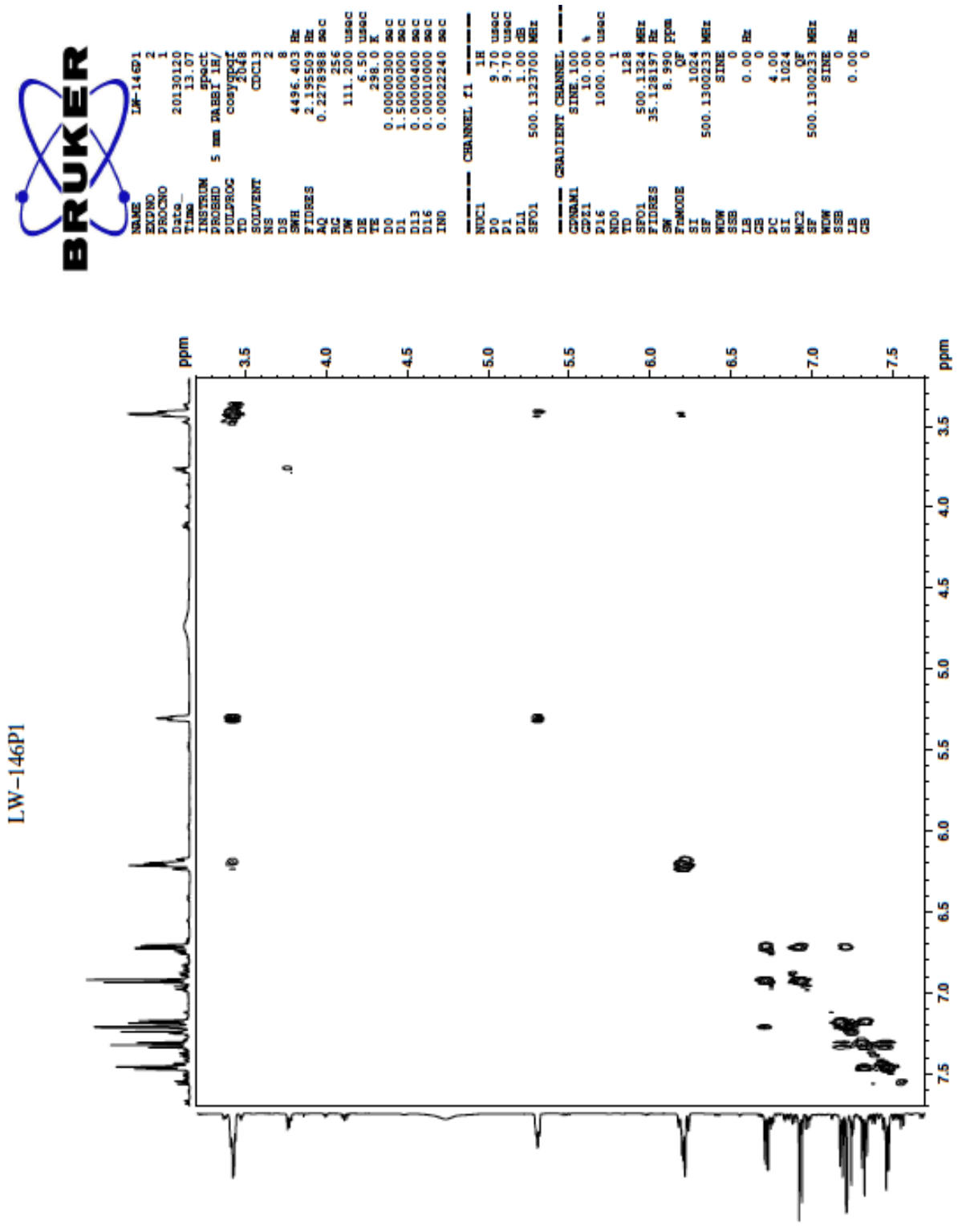
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **19**



^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **19**



gCOSY spectrum of **19** in $CDCl_3$



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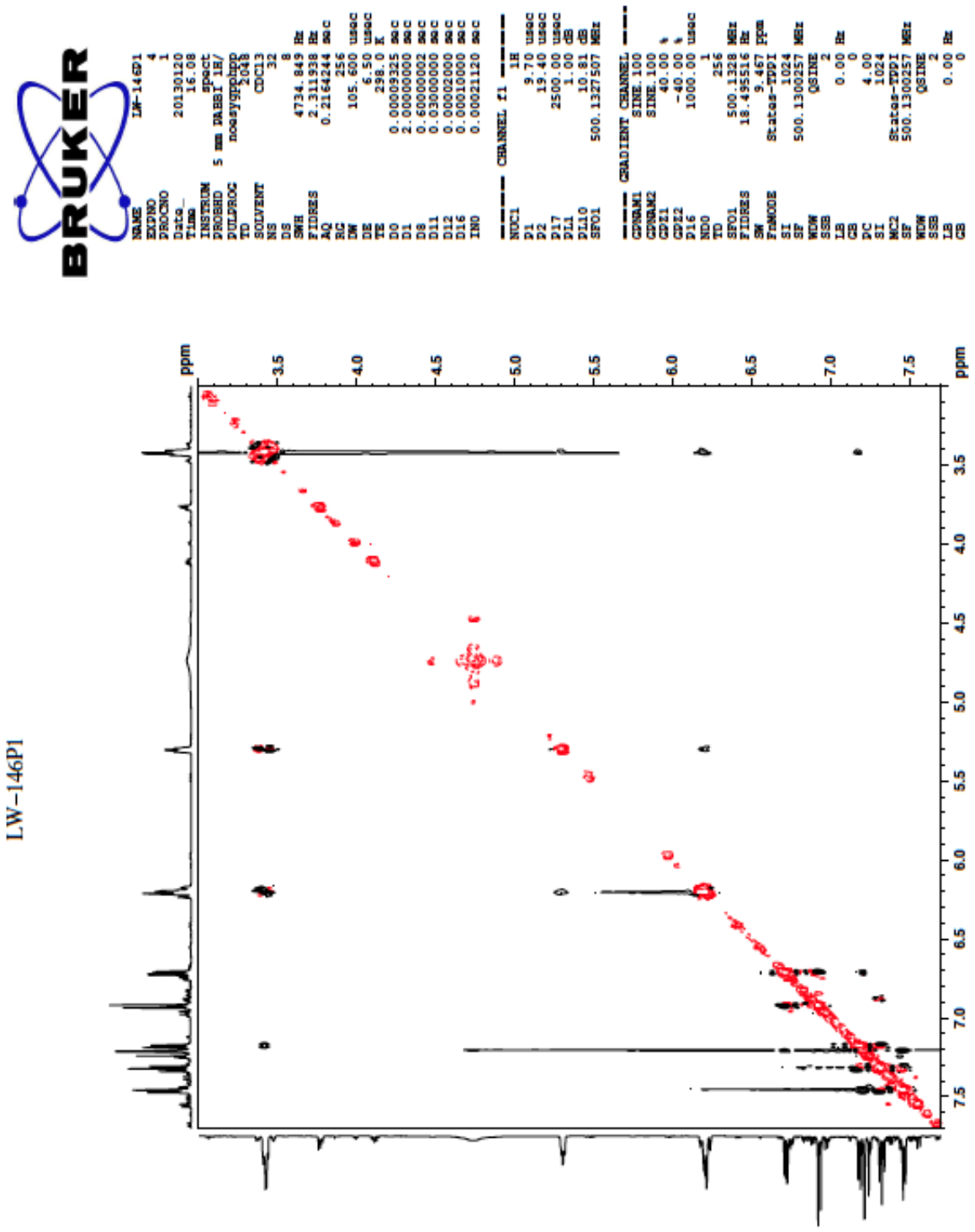
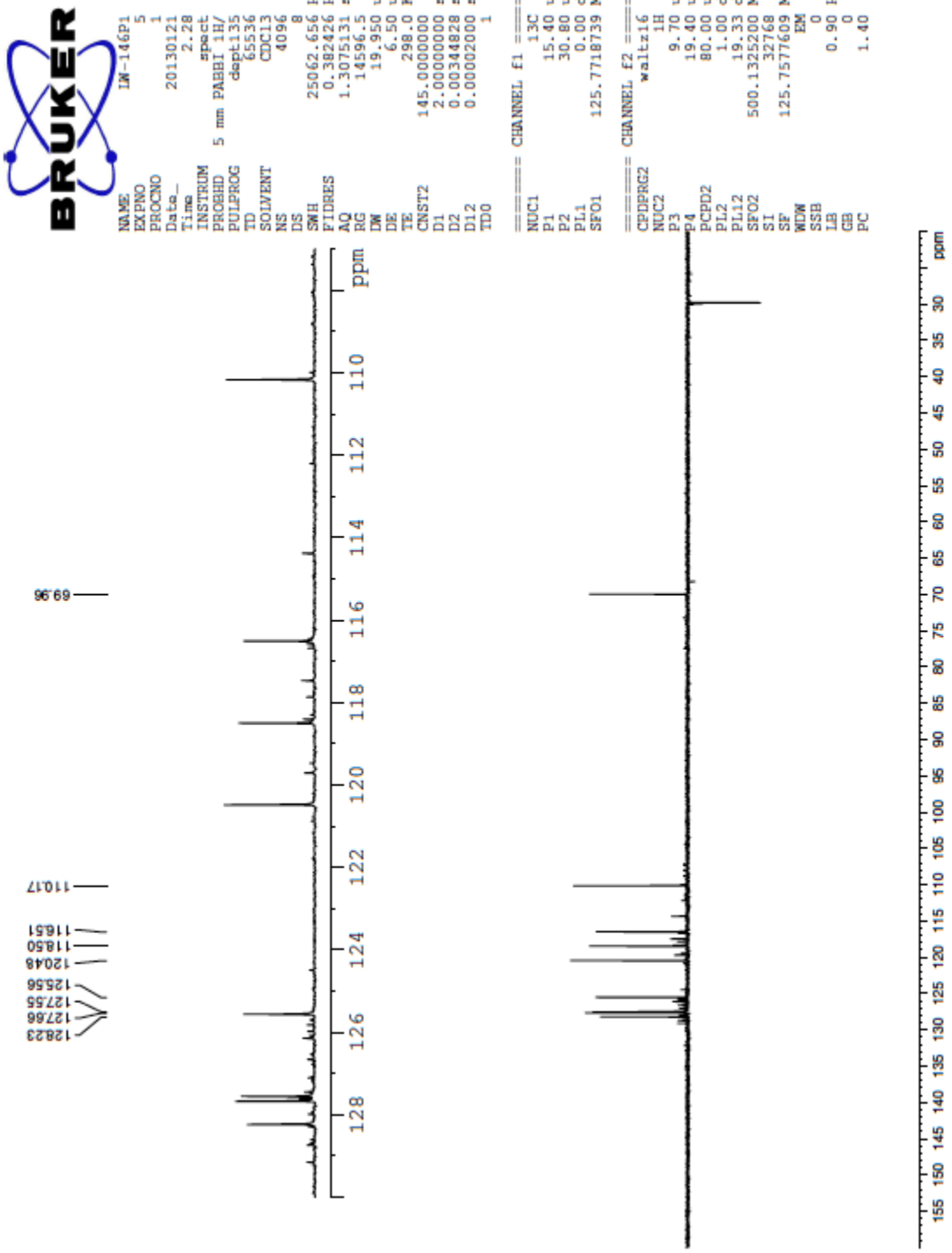
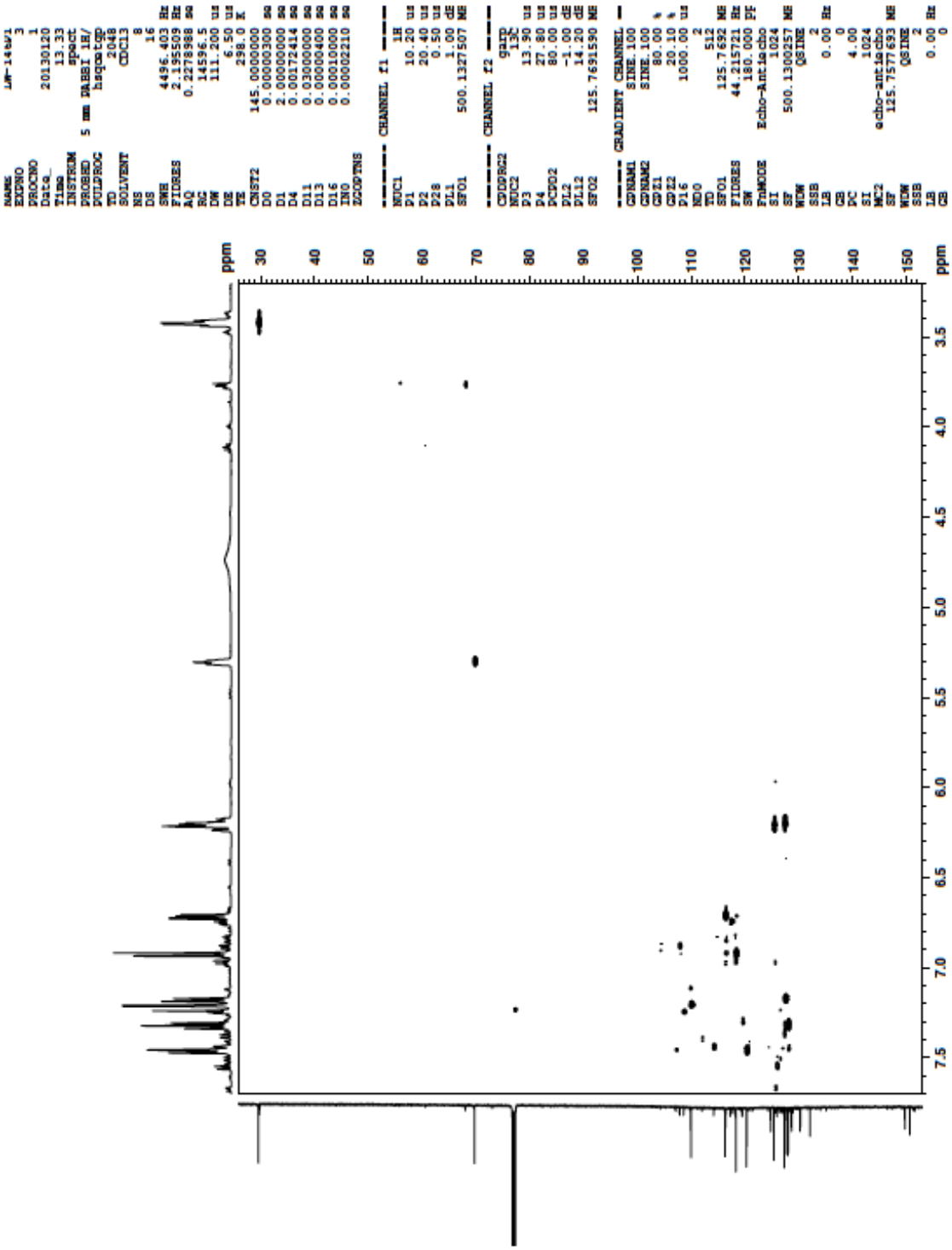


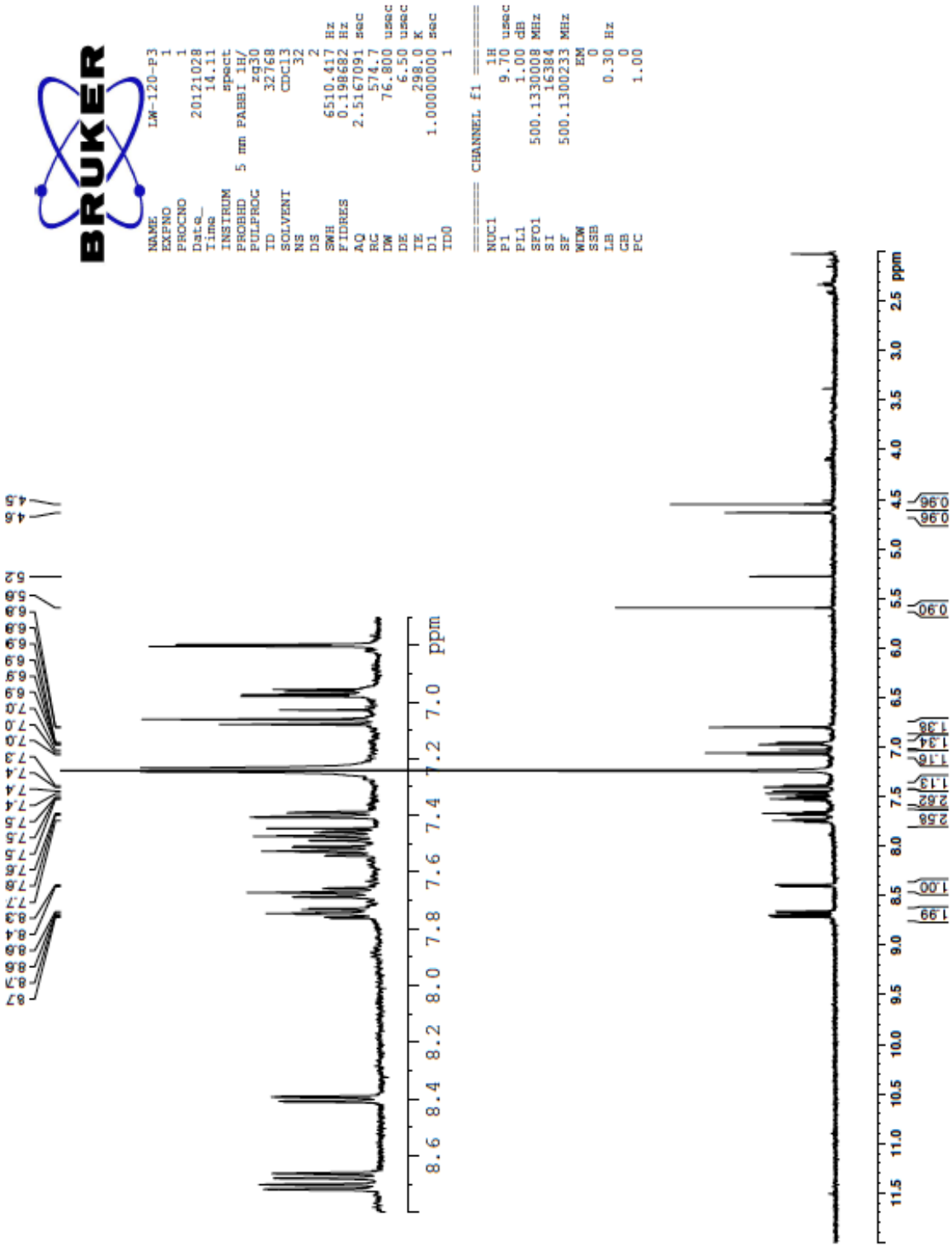
DEPT135 (125 MHz, $CDCl_3$) spectrum of **19**



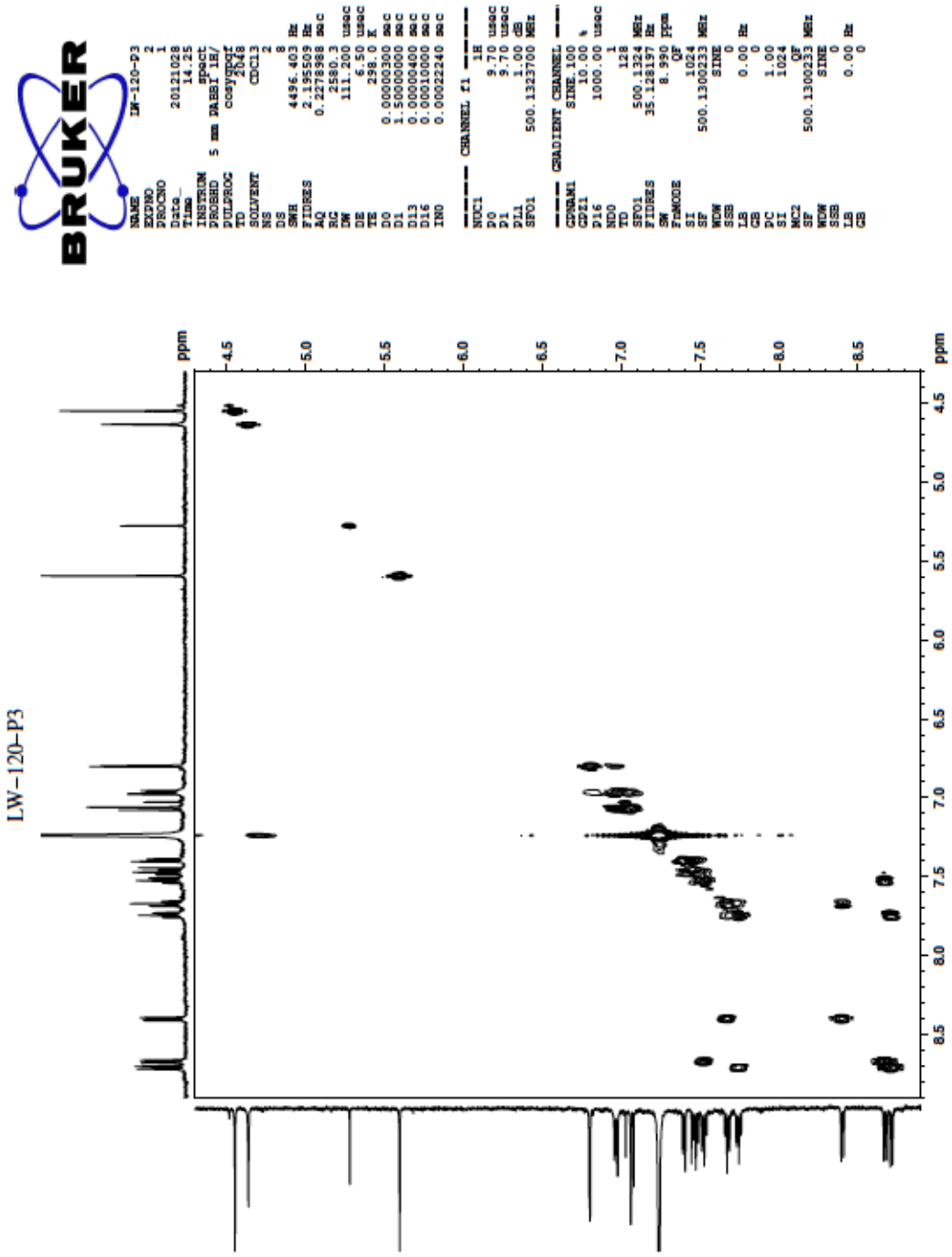
gHSQC spectrum of **19** in $CDCl_3$



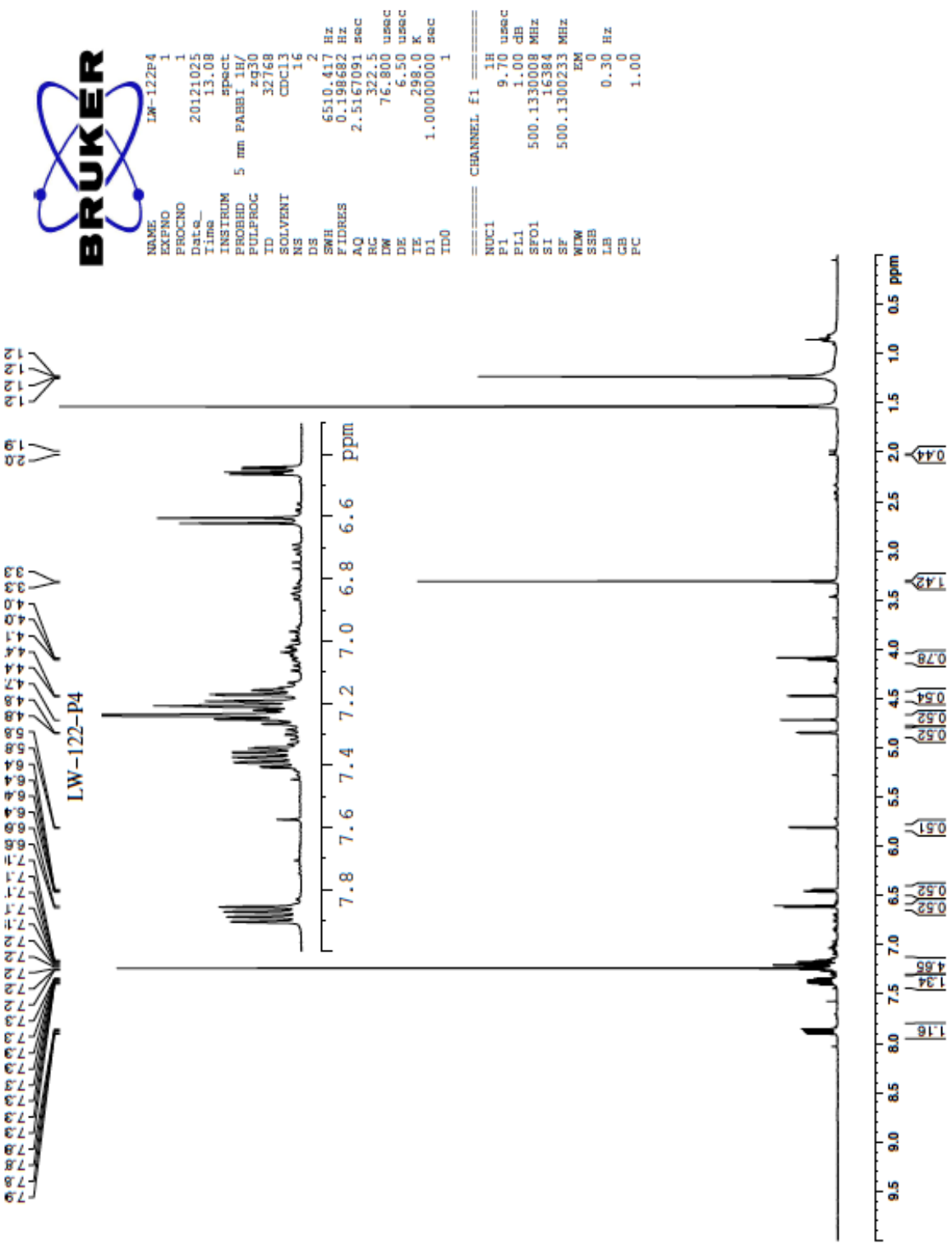
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **23**



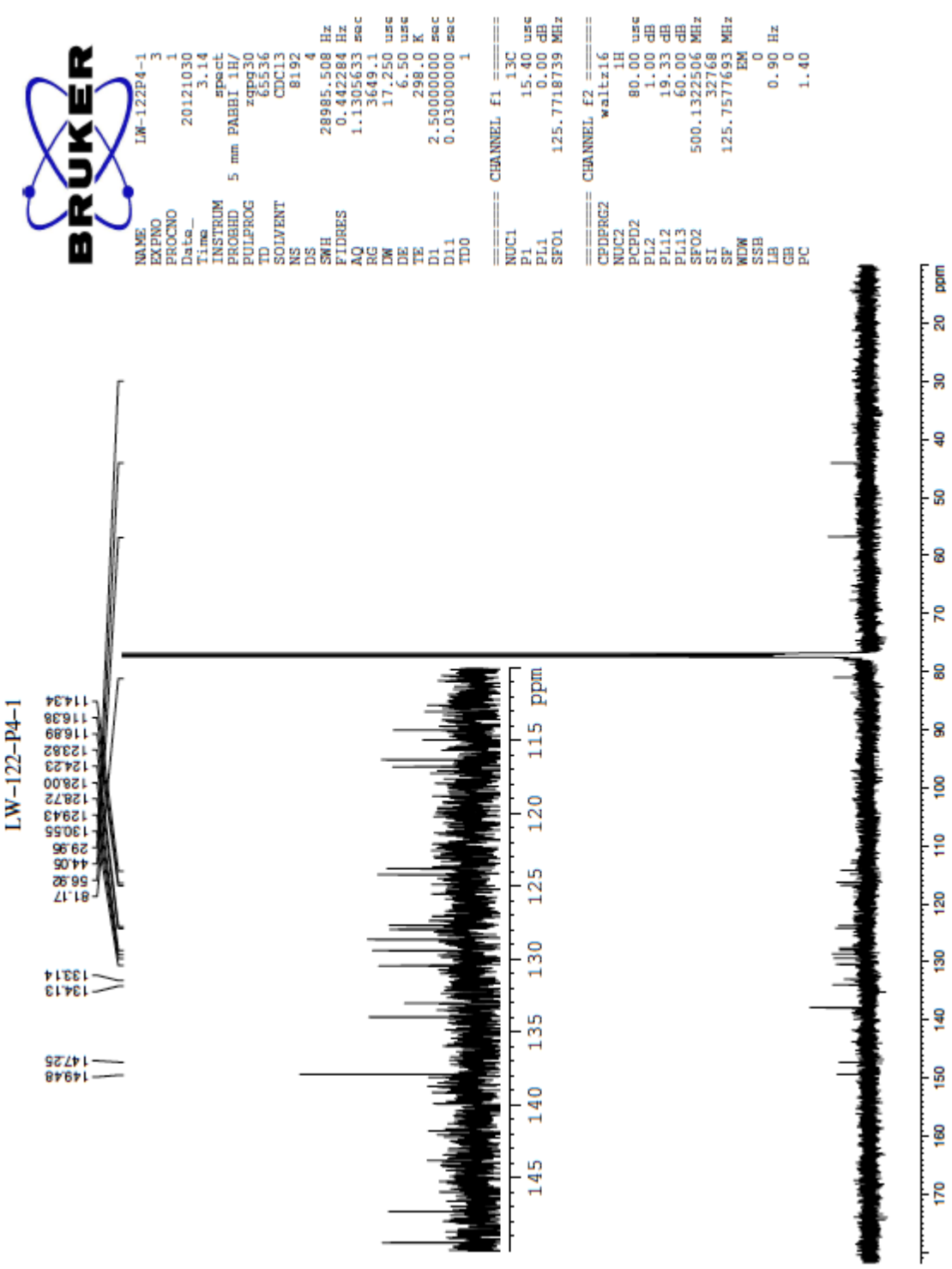
gCOSY spectrum of **23** in $CDCl_3$



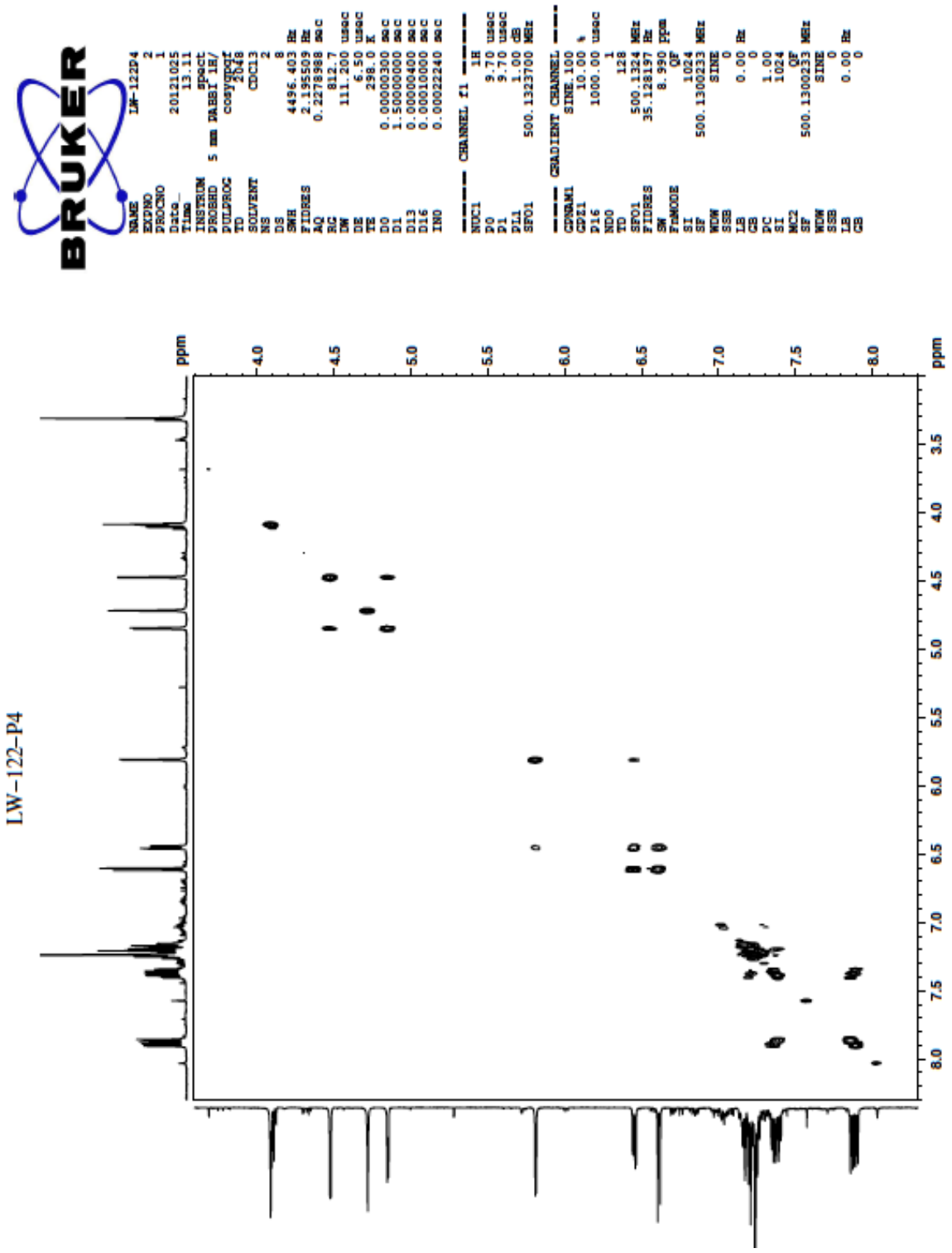
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **24**



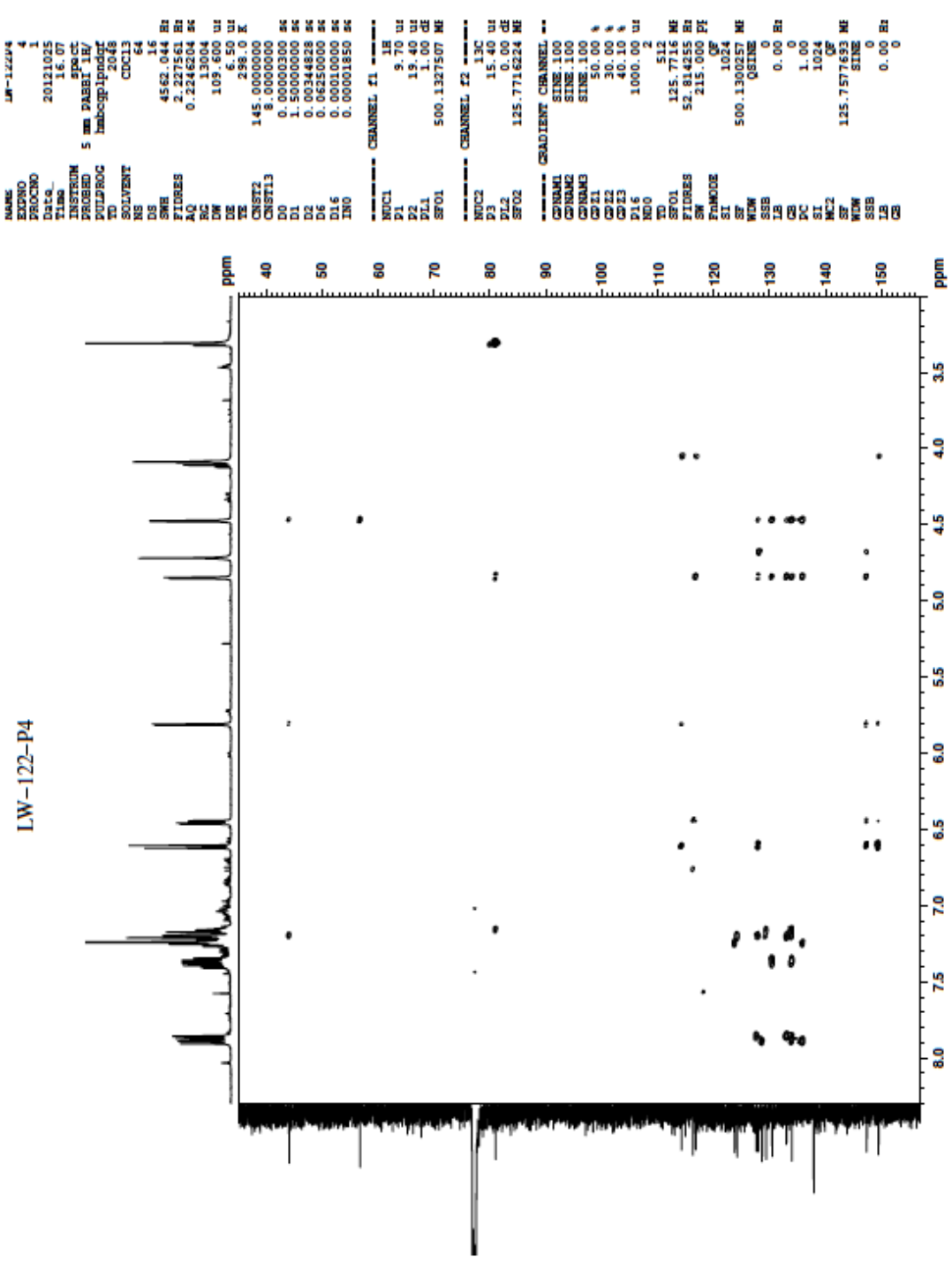
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **24**



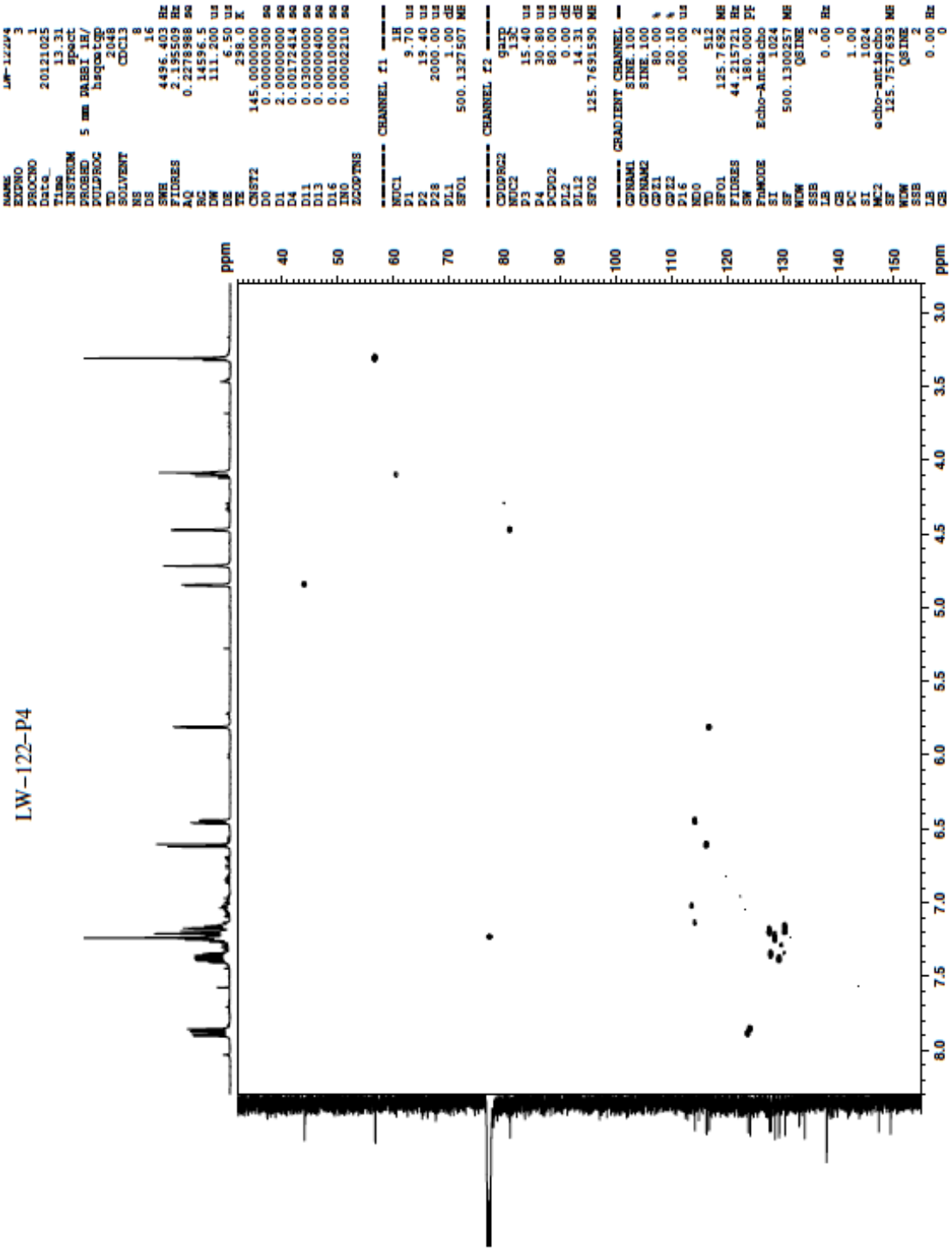
gCOSY spectrum of **24** in $CDCl_3$



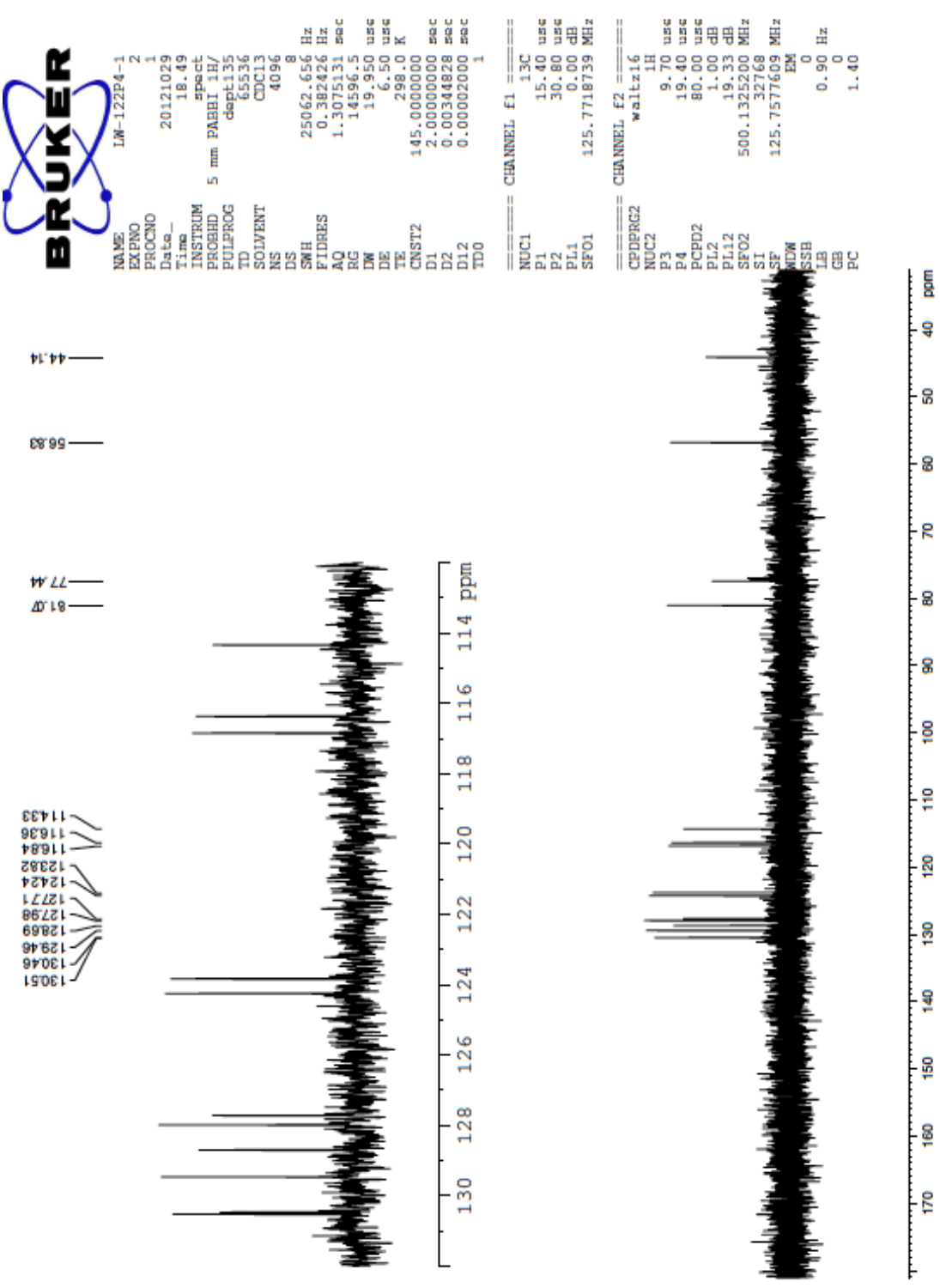
gHMBC spectrum of **24** in $CDCl_3$



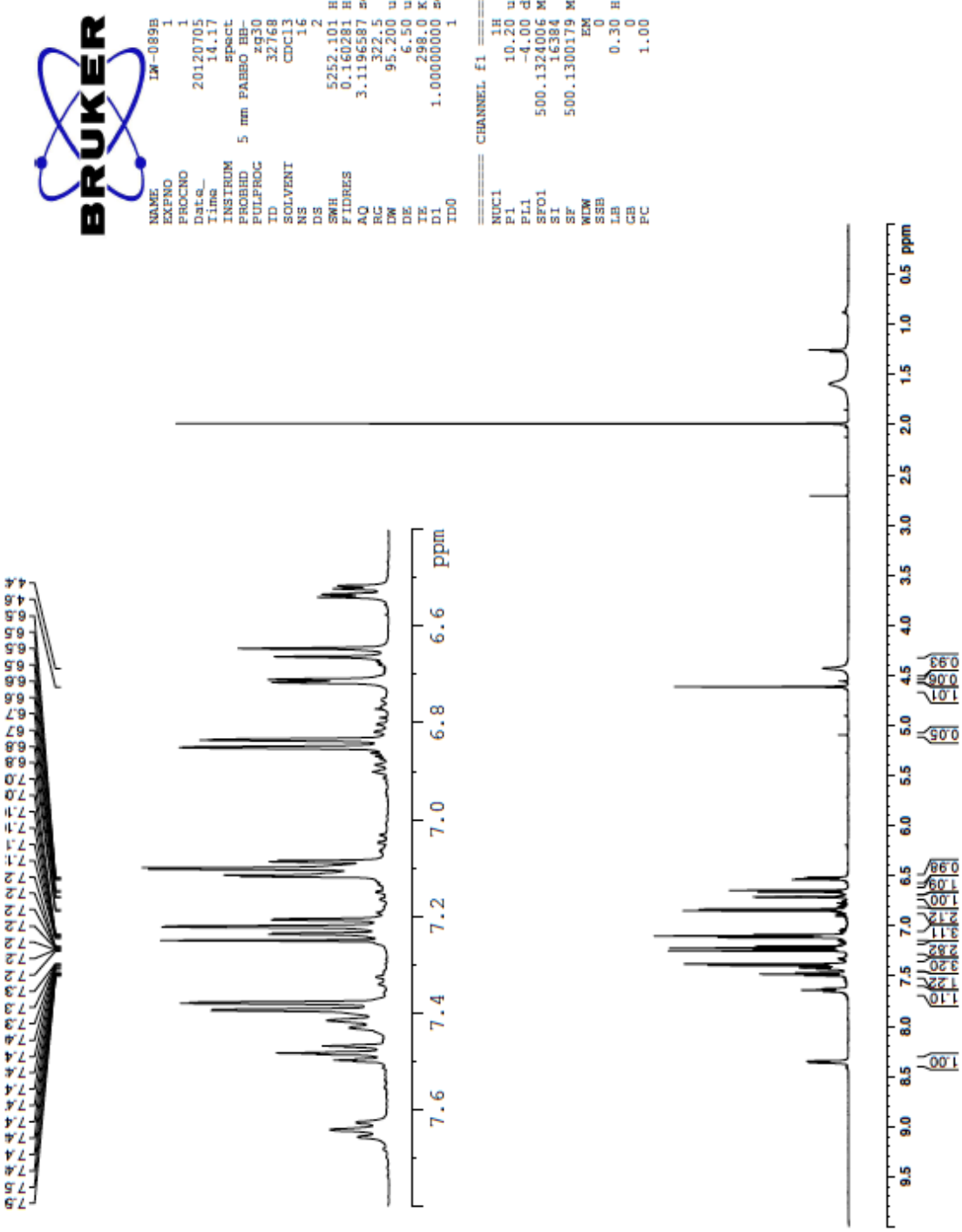
gHSQC spectrum of **24** in $CDCl_3$



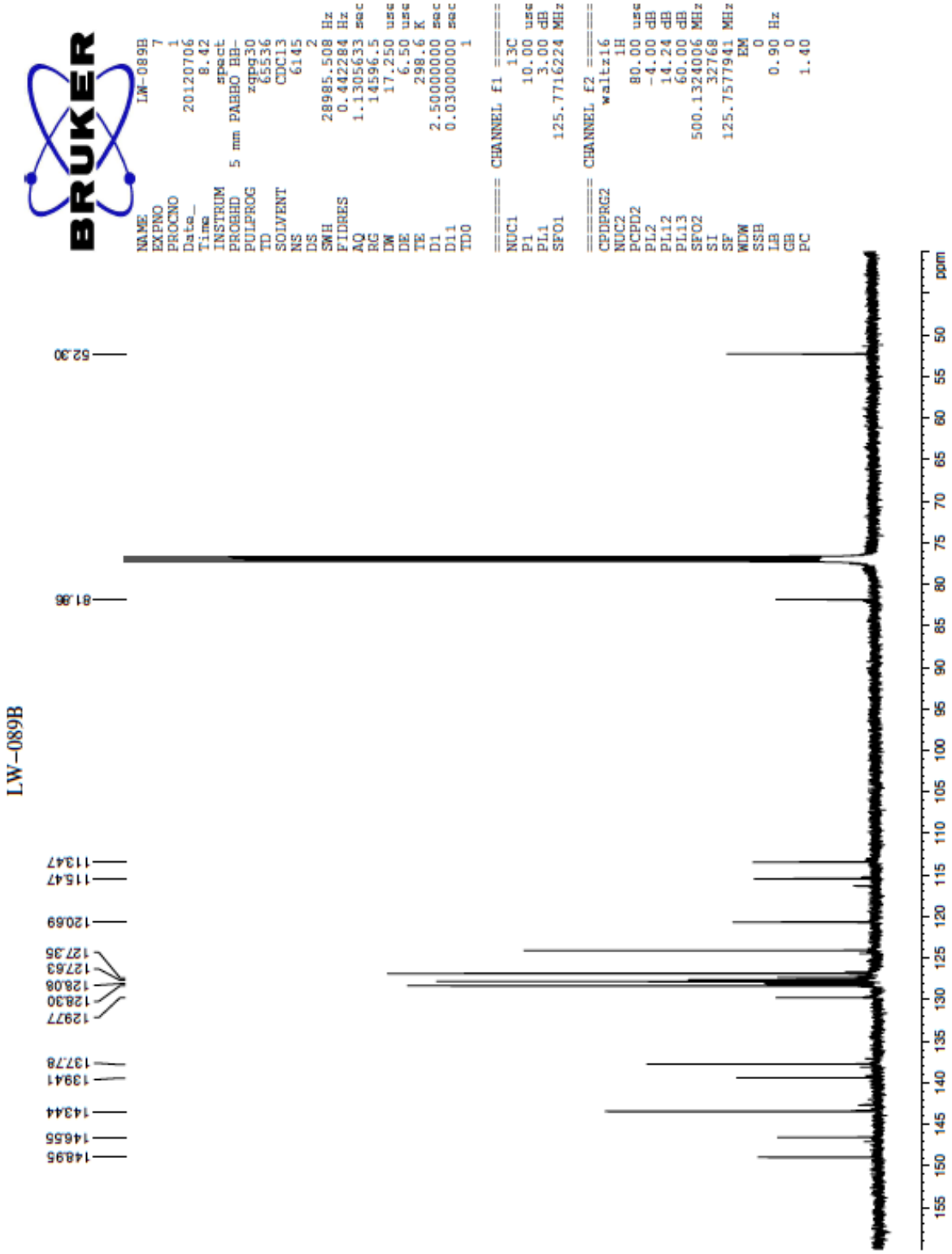
DEPT135 NMR (125 MHz, $CDCN_3$) spectrum of **24**



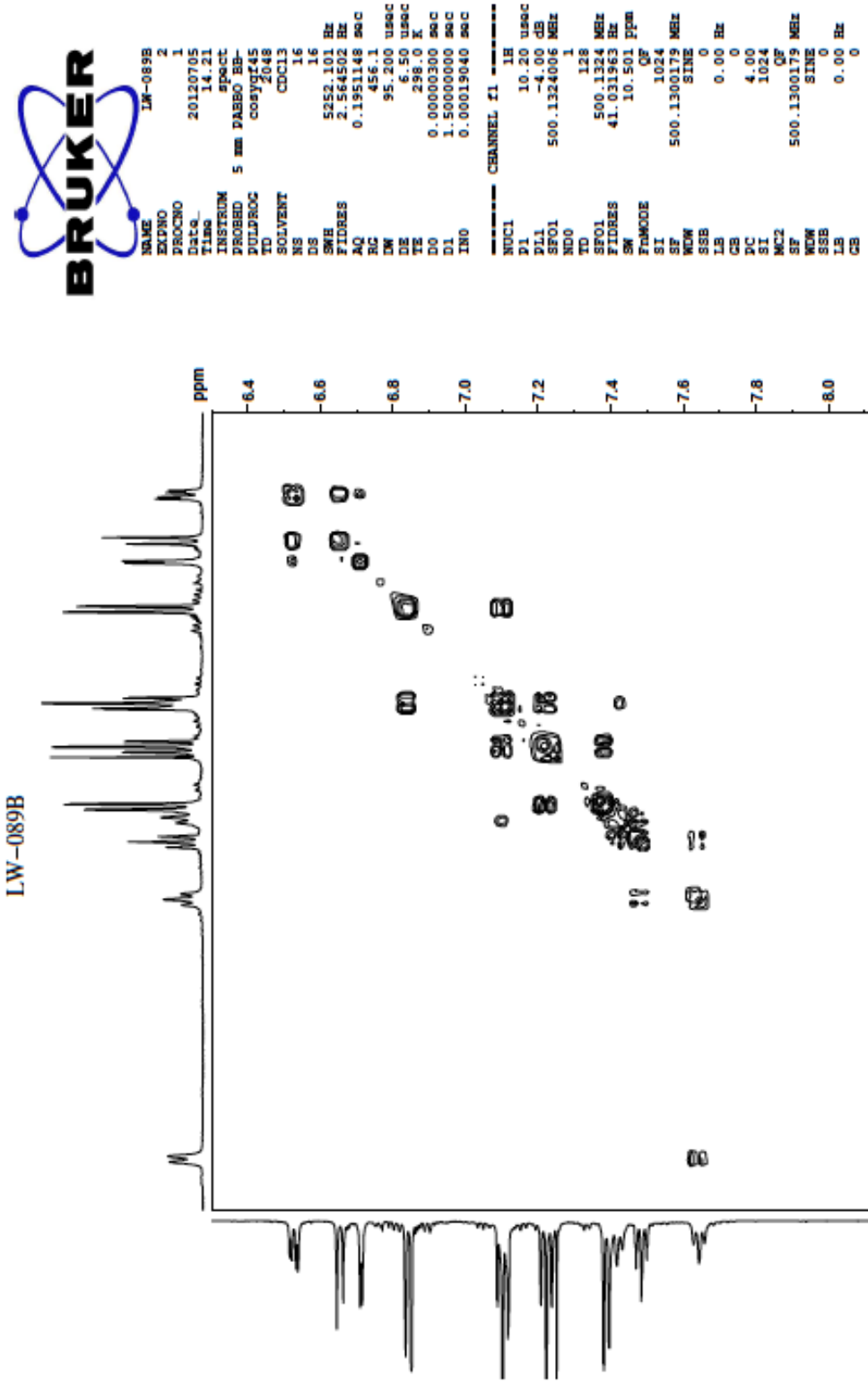
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **28**



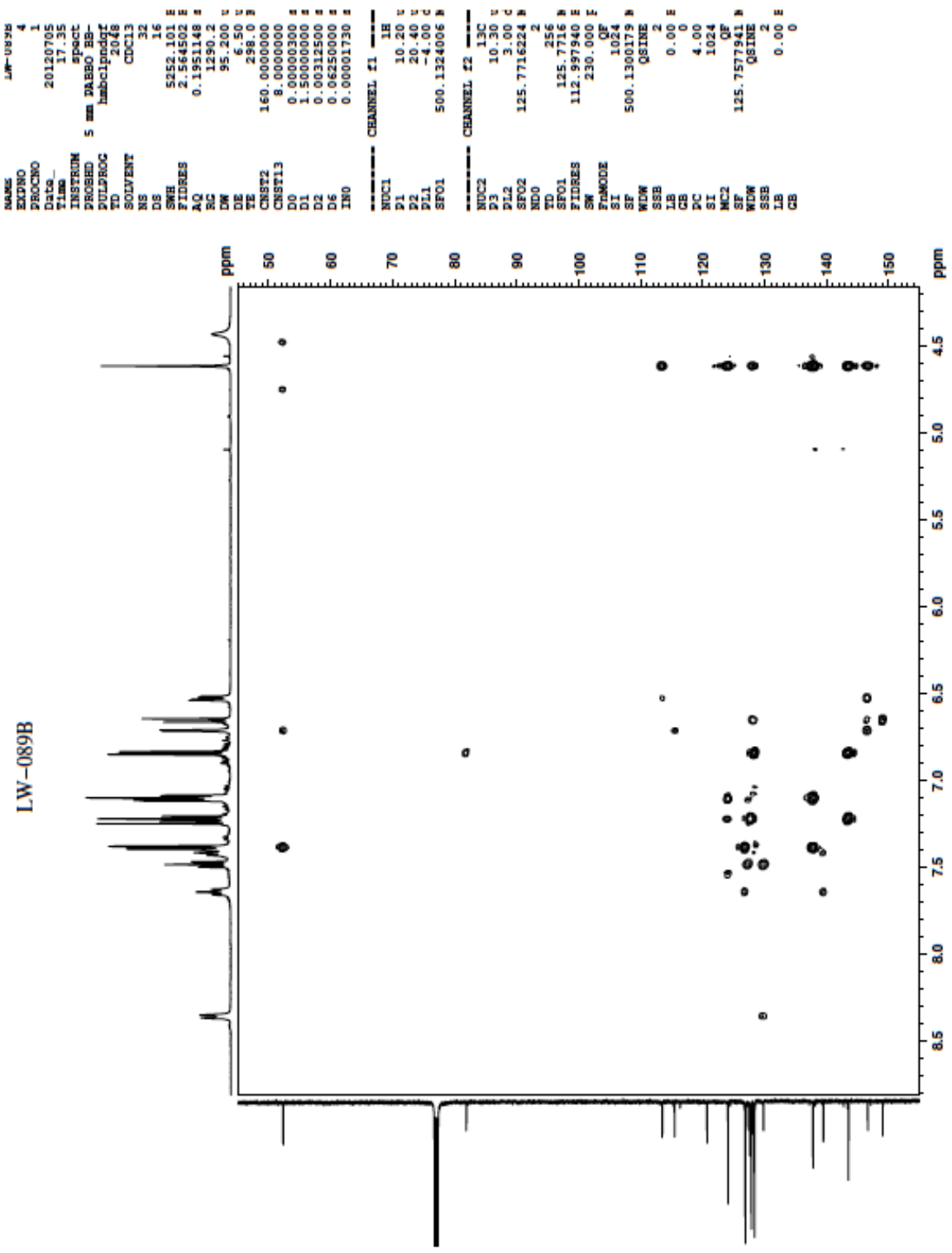
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **28**



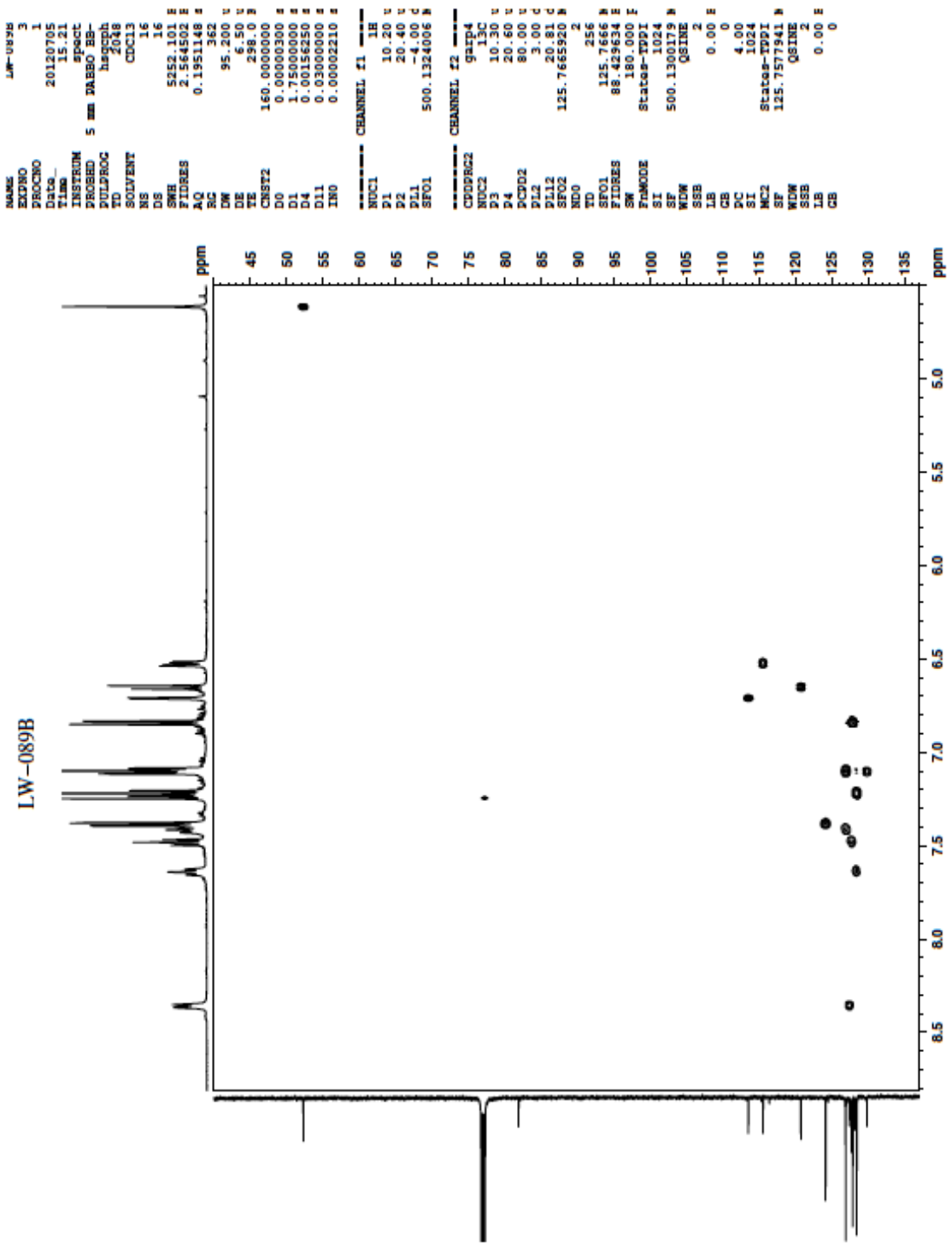
gCOSY spectrum of **28** in $CDCl_3$



gHMBC spectrum of **28** in $CDCl_3$



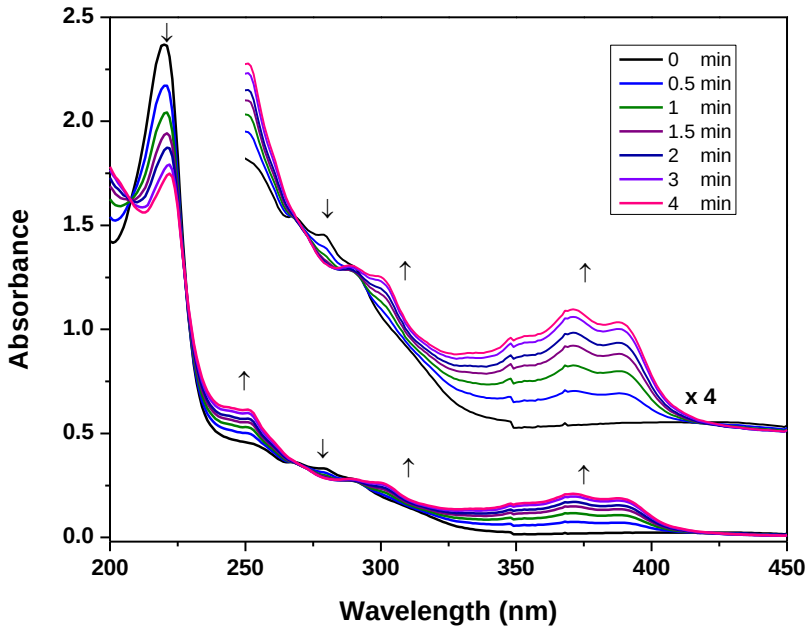
gHSQC spectrum of **28** in $CDCl_3$



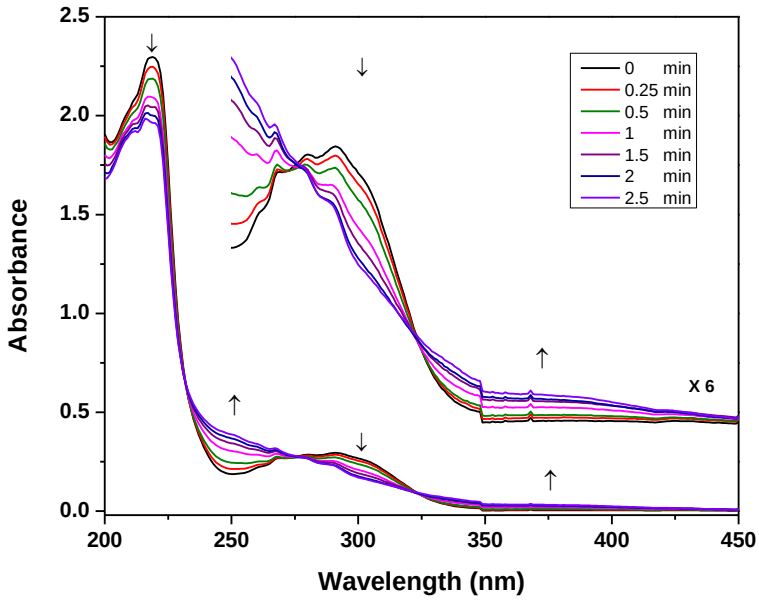
2. Irradiations of 9 – 11 in UV-Vis cuvettes

Absorption spectra of **9** in (a) CH_3CN and (b) 1:1 = H_2O :CH_3CN after irradiation at 300 nm (photolysis in the UV-vis cuvette, 16 lamps, Rayonet reactor)

(a) in CH_3CN

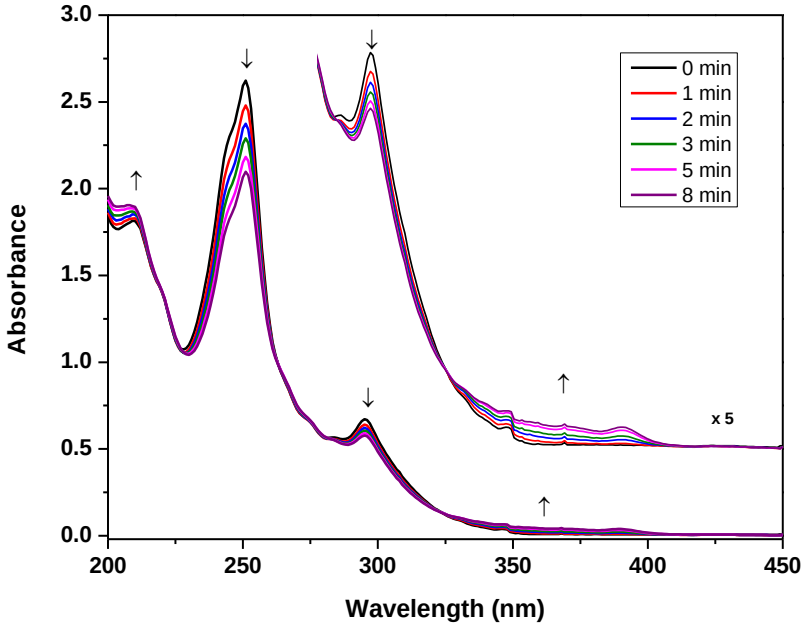


(b) in 1:1 = H_2O :CH_3CN

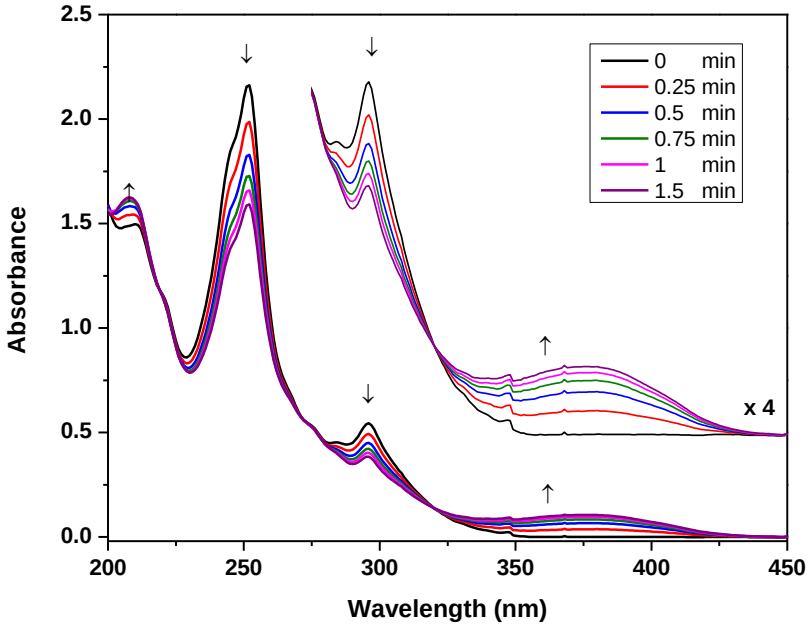


Absorption spectra of **10** in (a) CH_3CN and (b) 1:1 = H_2O : CH_3CN after irradiation at 300 nm (photolysis in the UV-vis cuvette, 16 lamps, Rayonet reactor)

(a) in CH_3CN

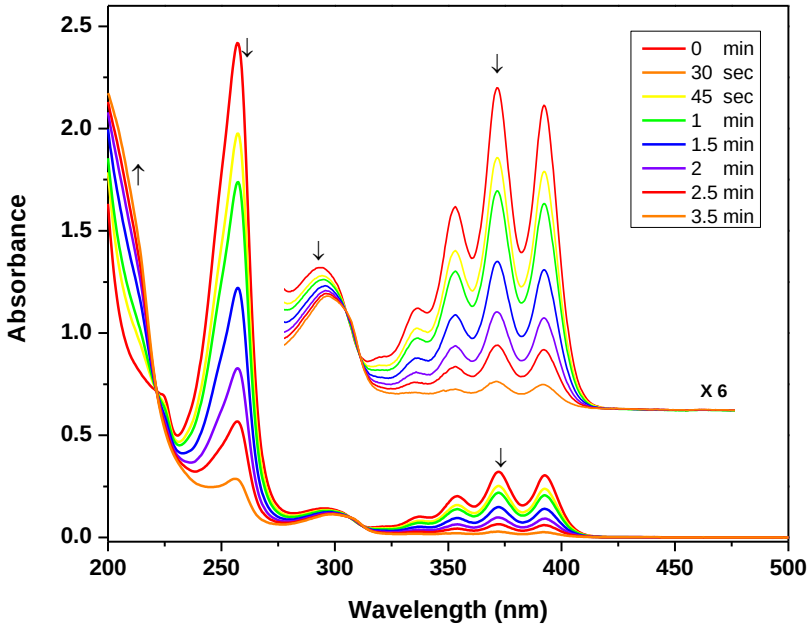


(b) in 1:1 = H_2O :CH_3CN

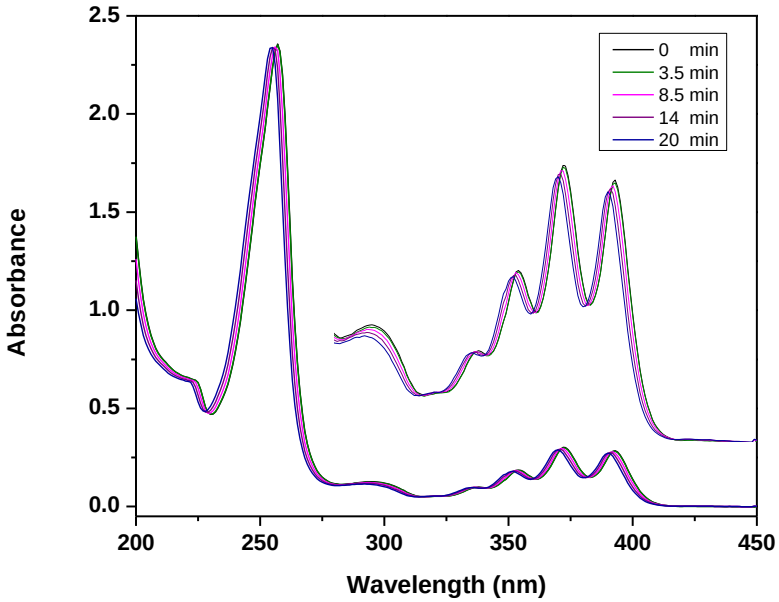


Absorption spectra of **11** in (a) CH_3CN and (b) 1:1 = H_2O :CH_3CN (c) cyclohexane (d) diethyl ether (e) THF (f) methanol after irradiation at 350 nm (photolysis in the UV-vis cuvette, 16 lamps, Rayonet reactor)

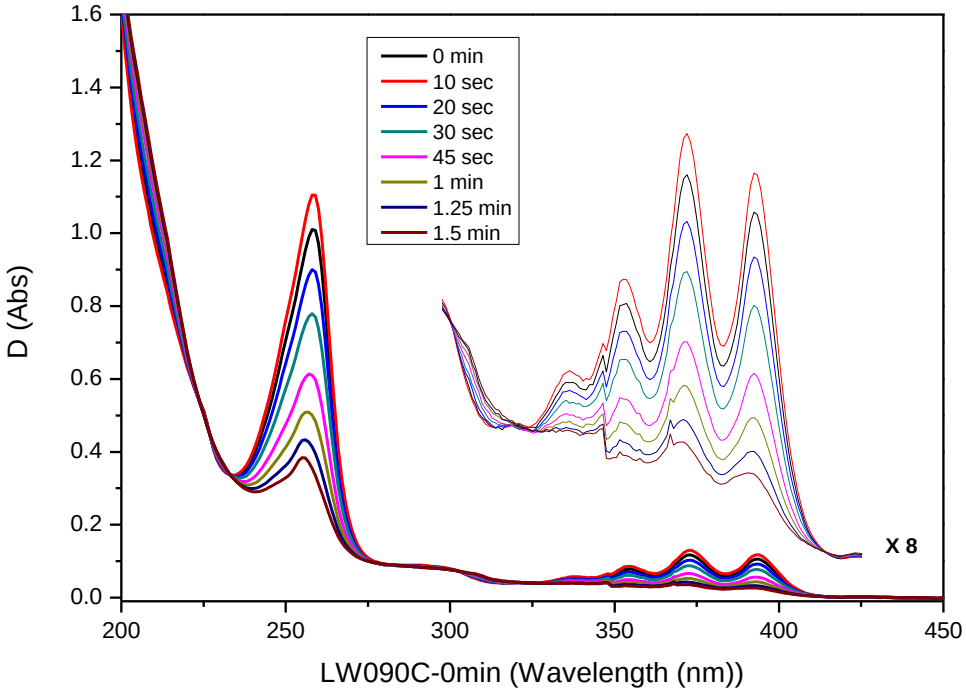
(a) in CH_3CN



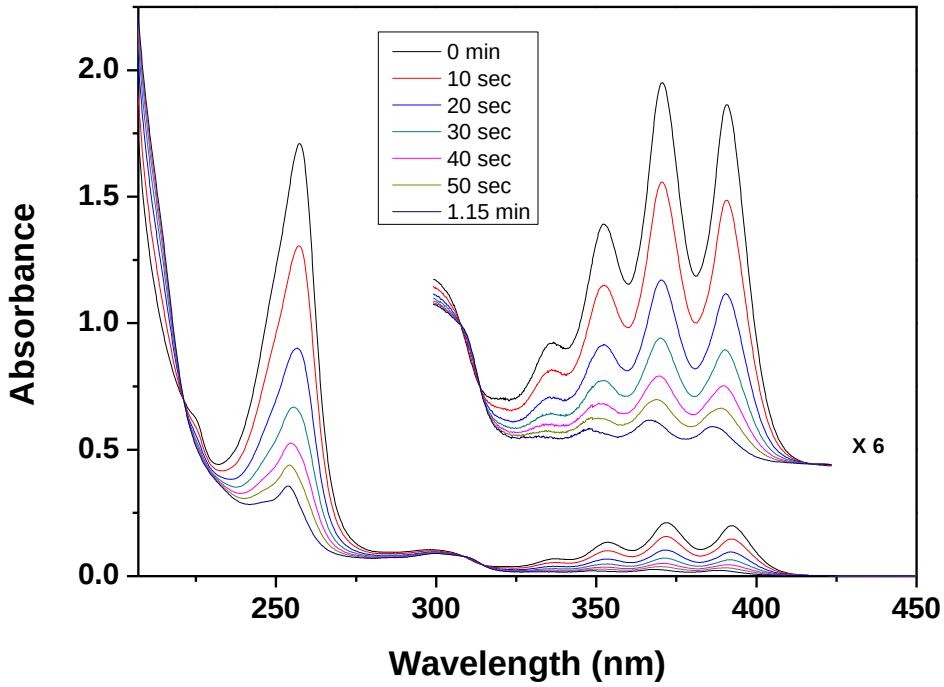
(b) in 1:1 = H_2O :CH_3CN



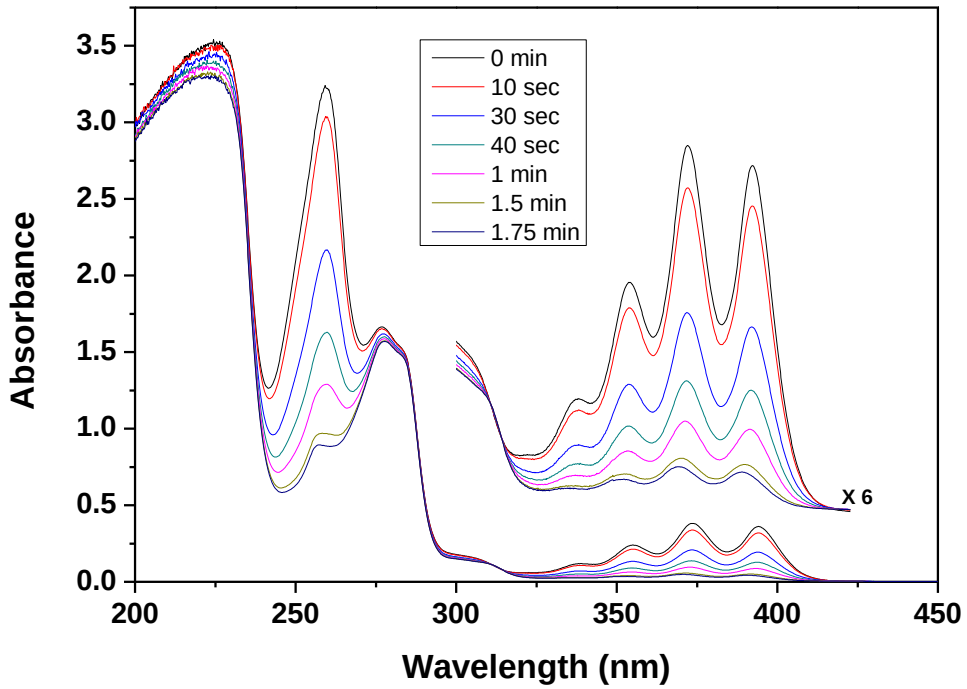
(c) in cyclohexane



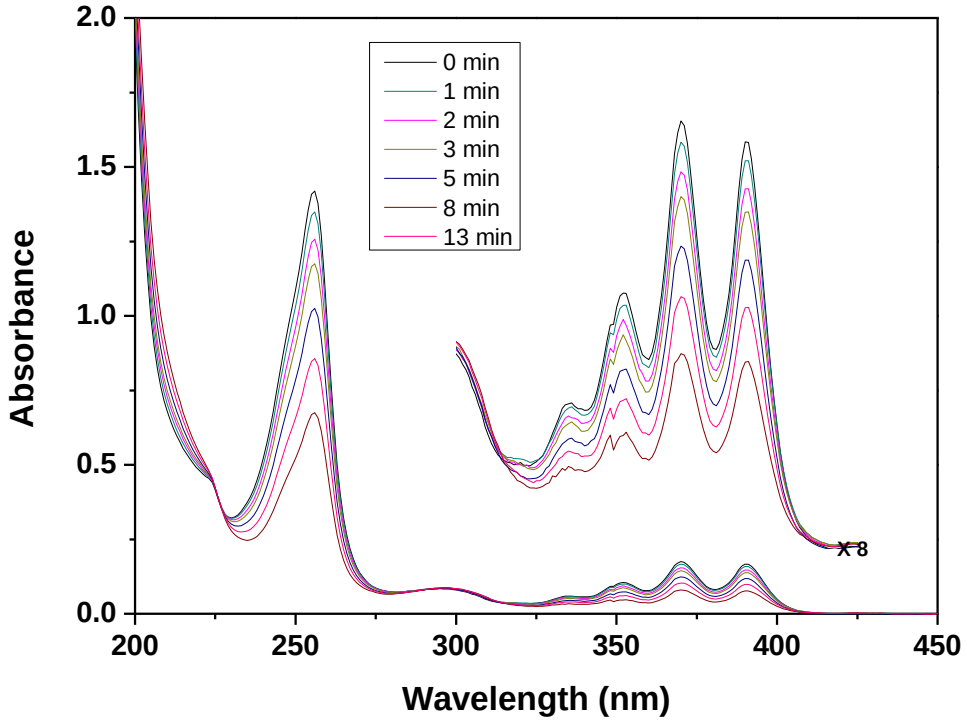
(d) in diethyl ether



(e) in THF

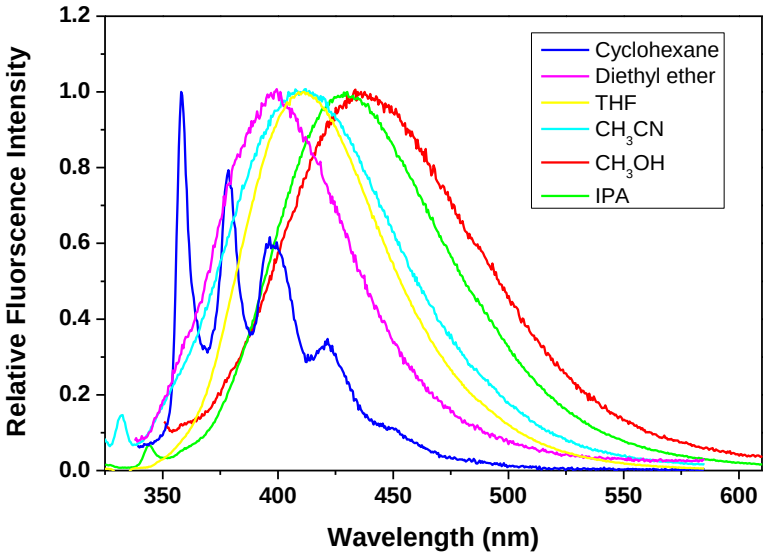


(f) in CH_3OH

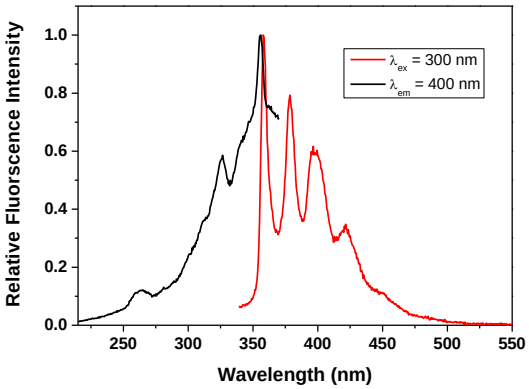


3. Fluorescence spectra of 9 –11 and 15 in various solvents

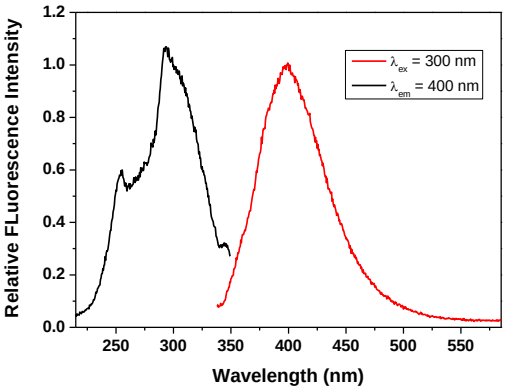
Excitation and emission spectra of 9 in (a) cyclohexane (b) diethyl ether (c) THF (d) CH_3CN (e) CH_3OH & isopropyl alcohol (IPA)



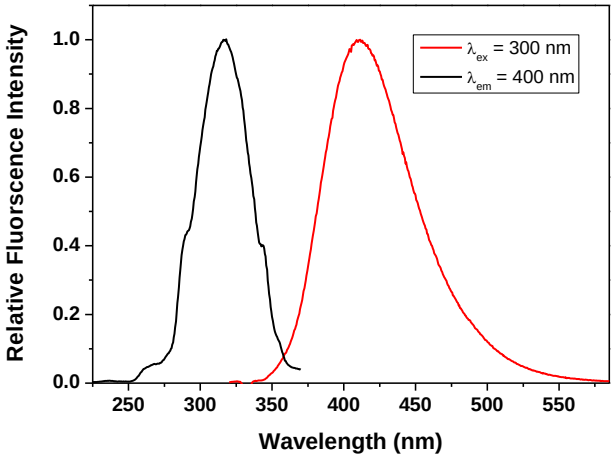
(a) in cyclohexane



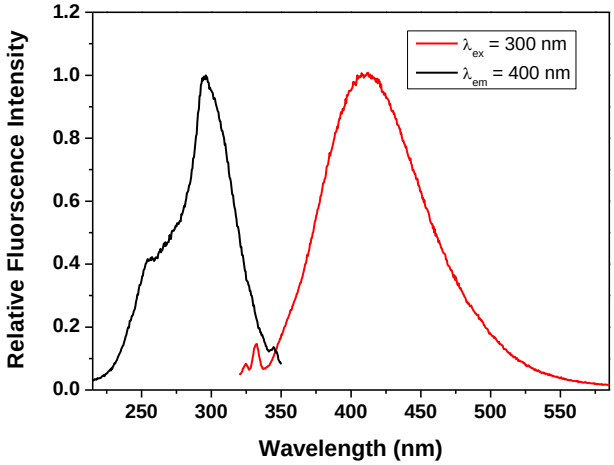
(b) in diethyl ether



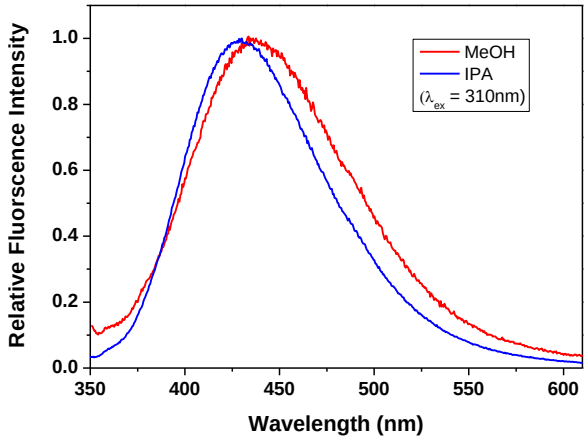
(c) in THF



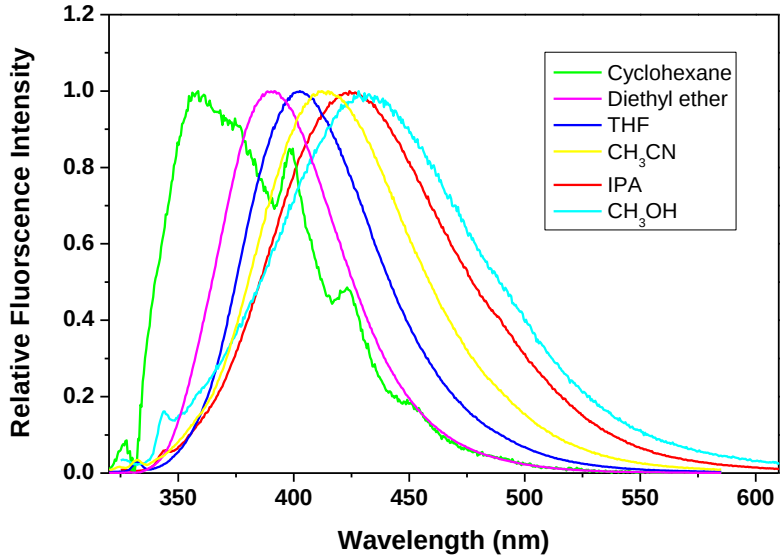
(d) in CH_3CN



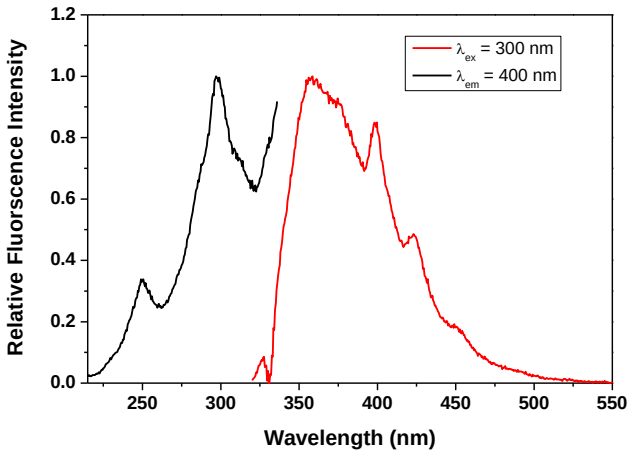
(e) in CH_3OH & IPA



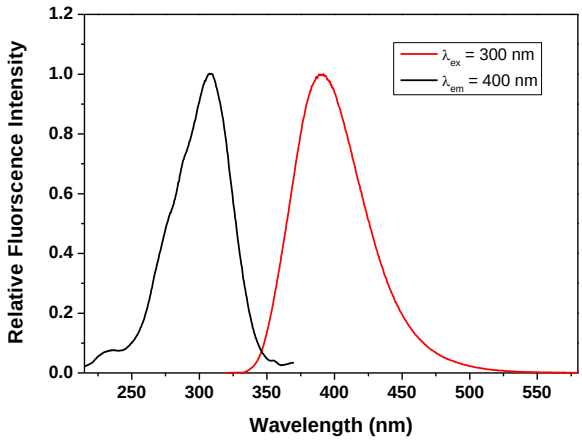
Excitation and emission spectra of 10 in (a) cyclohexane (b) diethyl ether (c) THF (d) CH_3CN (e) CH_3OH (f) IPA



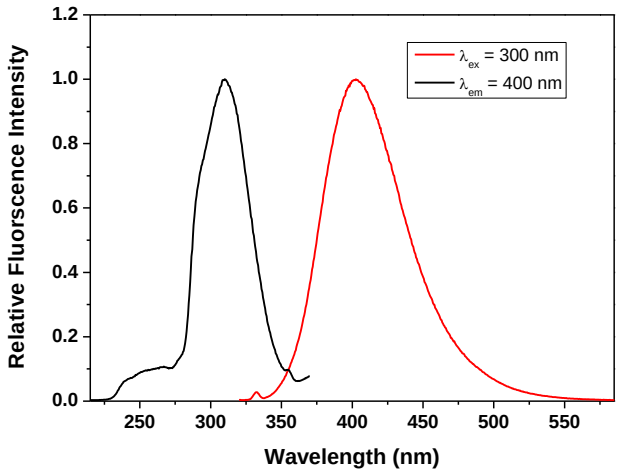
(a) in cyclohexane



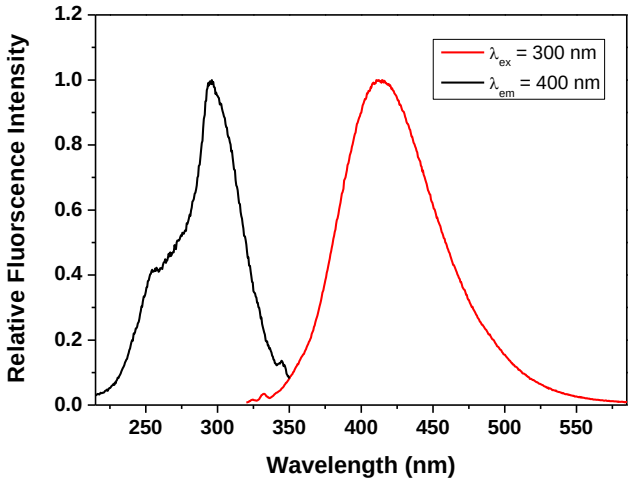
(b) in diethyl ether



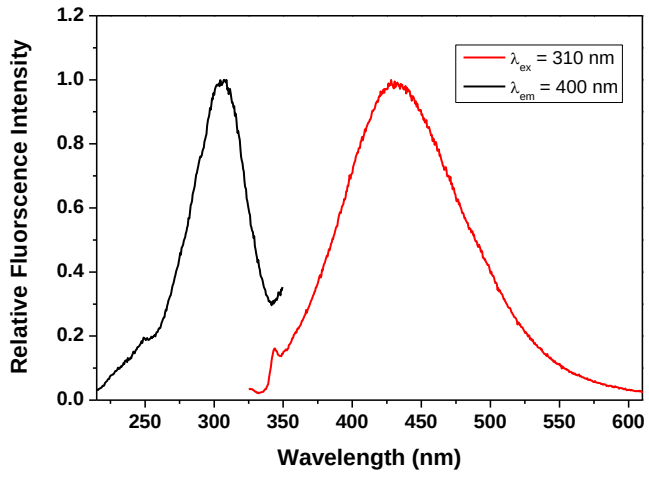
(c) in THF



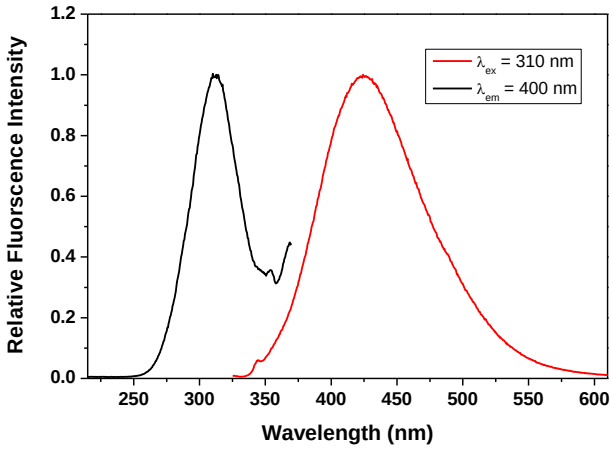
(d) in CH_3CN



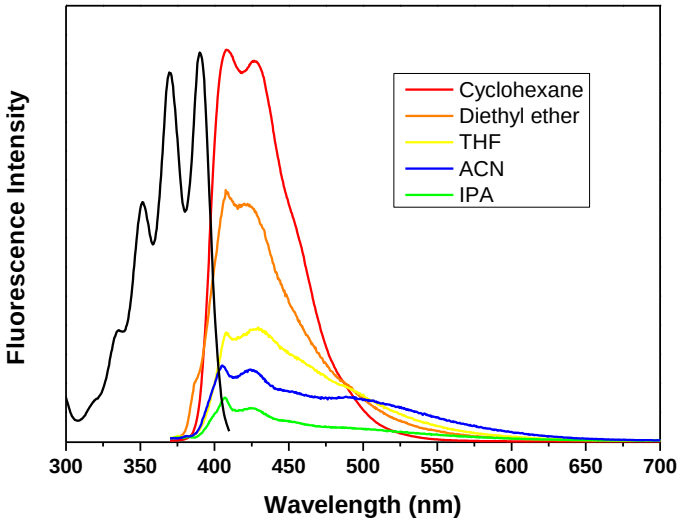
(e) in CH_3OH



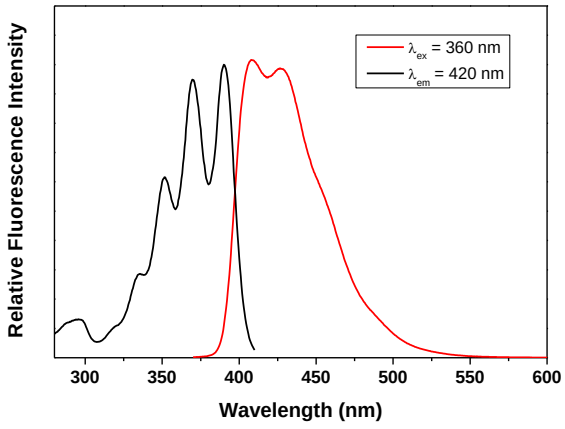
(f) in IPA



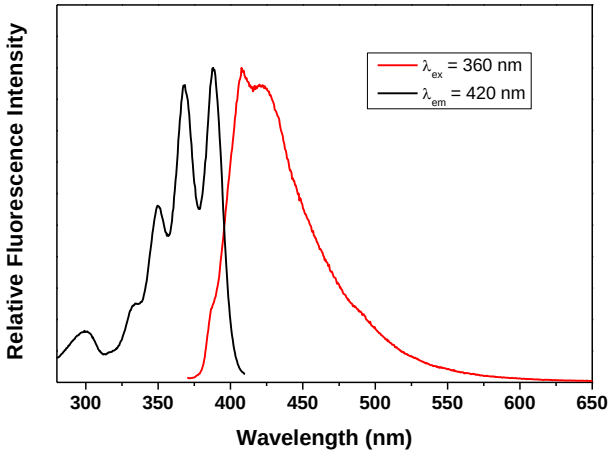
Excitation and emission spectra of 11 in (a) cyclohexane (b) diethyl ether (c) THF (d) CH_3CN (e) IPA (f) CH_3OH



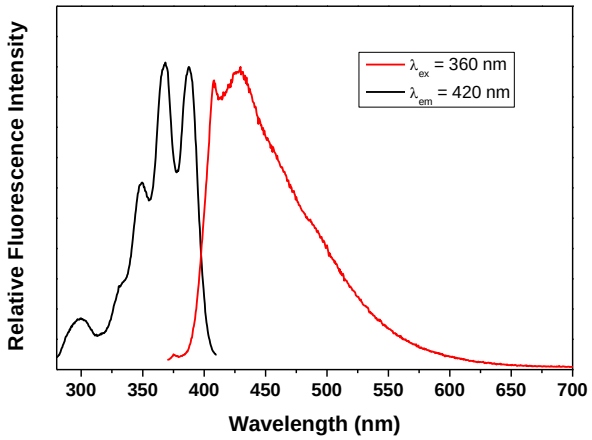
(a) in cyclohexane



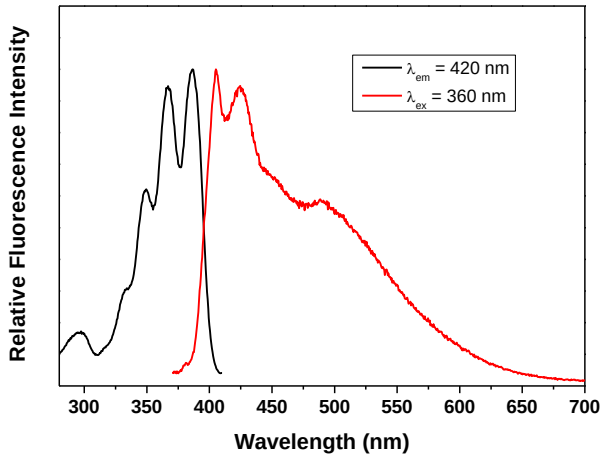
(b) in diethyl ether



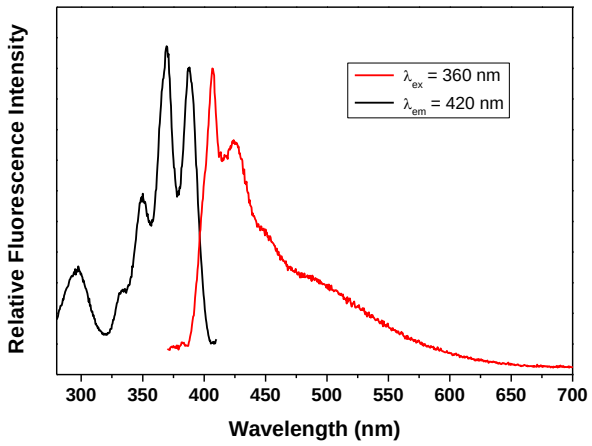
(c) in THF



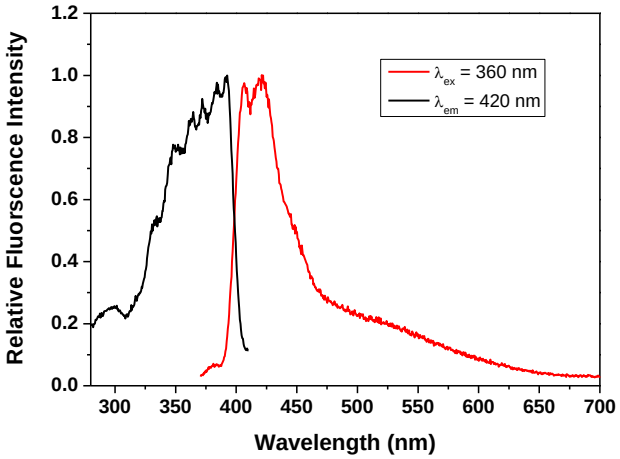
(d) in CH_3CN



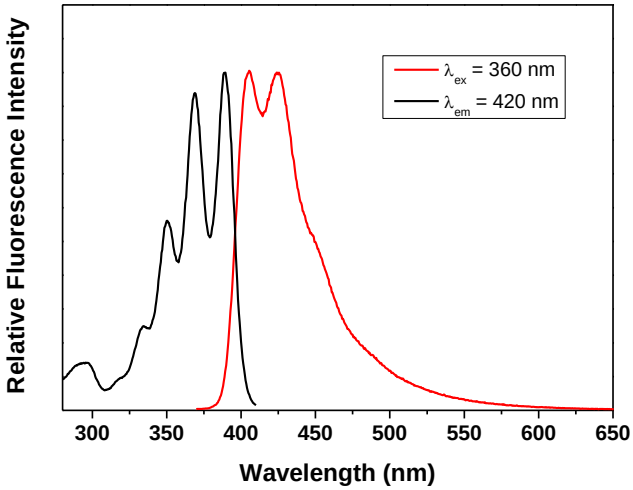
(e) in IPA



(f) in CH_3OH



Excitation and emission spectra of 15 in neat CH_3CN



4. Photophysical and Photochemical Parameters for 9 – 11 in various solvents

(a) Table 1. Compound **9** in various solvents

Solvent	λ_{abs}/nm[a]	λ_{em}/nm[b]	τ_f (ns)[c]	τ_f (ns)[d]
Cyclohexane	327 (sh), 356	359, 380, 399, 424, 450 (sh)	0.88 (33%), 3.3 (13%), 13.8 (54%)	0.05 (10%) 2.1 (6%) 14.8 (84%)
Diethyl ether	254 (sh), 295	399	0.15 (80%), 0.95 (16%), 4.7 (4%)	0.19 (90%) 1.5 (10%)
THF	318	413	0.24 (26%), 0.87 (71%), 4.4 (3%)	0.23 (21%) 0.94 (79%)
CH_3OH	320	427	0.29 (18%), 0.89 (37%), 5.4 (45%)	0.6 (88%) 3.8 (12%)
IPA	321	439	0.06 (17%), 1.1 (70%), 5.3 (13%)	0.9 (91%) 2.5 (9%)

[a] Maxima in the absorption spectra. [b] Maxima in the emission spectra. [c] Fluorescence lifetimes measured at λ_{em} = 400 nm by time correlated single photon counting (SPC). Estimated error is ±0.1 ns. [d] Fluorescence lifetimes measured at λ_{em} = 450 nm except for cyclohexane at λ_{em} = 360 nm.

(b) Table 2. Compound **10** in various solvents

Solvent	λ_{abs}/nm[a]	λ_{em}/nm[b]	τ_f (ns)[c]
Cyclohexane	248 (sh), 298	357, 401, 426, 453 (sh)	-[d]
Diethyl ether	311	392	2.5 (100%)
THF	311	405	1.6 (85%), 3.5 (15%)
CH_3OH	308	432	-[d]
IPA	313	426	1.2 (100%)

[a] Maxima in the absorption spectra. [b] Maxima in the emission spectra. [c] Fluorescence lifetimes measured at λ_{em} = 400 nm by time correlated single photon counting (SPC). Estimated error is ±0.1 ns. [d] Fluorescence is too weak for decay lifetimes to be detected.

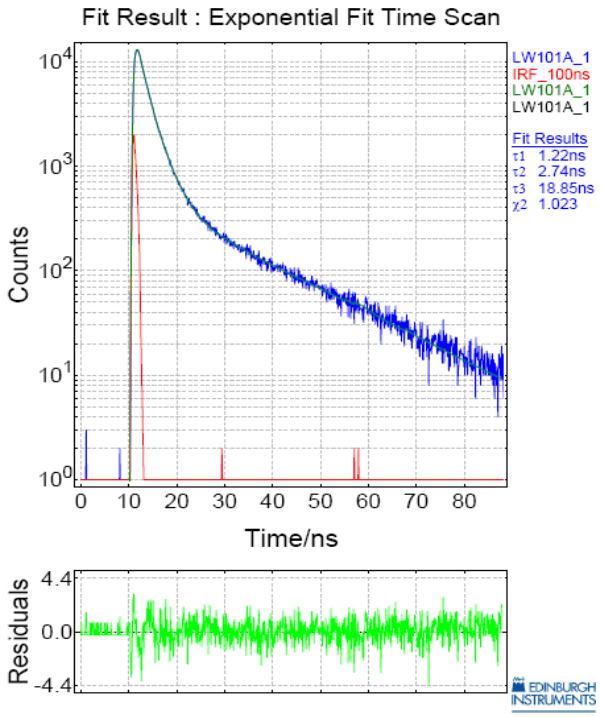
(c) Table 3. Compound **11** in various solvents

Solvent	λ_{abs}/nm[a]	λ_{em}/nm[b]	Φ_f[c]	τ_f (ns)[d]	τ_f (ns)[e]
cyclohexane	335 (sh), 352, 370, 390	409, 429, 454 (sh)	0.245±0.02	0.17 (4%), 2.2 (96%)	2.2 (100%)
Diethyl ether	335 (sh), 351, 368, 389	409, 425, 490 (sh)	0.037±0.002	0.30 (48%), 5.0 (52%)	0.46 (90%) 4.0 (10%)
THF	333 (sh), 351, 367, 389	409, 431,500 (sh)	0.009±0.003	0.56 (19%), 1.9 (19%), 13 (62%)	0.95 (95%) 8.8 (5%)

[a] Maxima in the absorption spectra. [b] Maxima in the emission spectra. [c] Fluorescence quantum yield measured by using quinine bisulfate (Φ = 0.55) in 0.1 N H_2SO_4.[23] [d] Fluorescence lifetimes measured at λ_{em} = 400 nm by time correlated single photon counting (SPC). Estimated error is ±0.1 ns. [e] Fluorescence lifetimes measured at λ_{em} = 500 nm.

5. Fluorescence decay profiles of 9 (a), 10 (b), and 11 (c) and 15 (d) in CH_3CN

(a) Compound 9 at λ_{em} = 400 nm



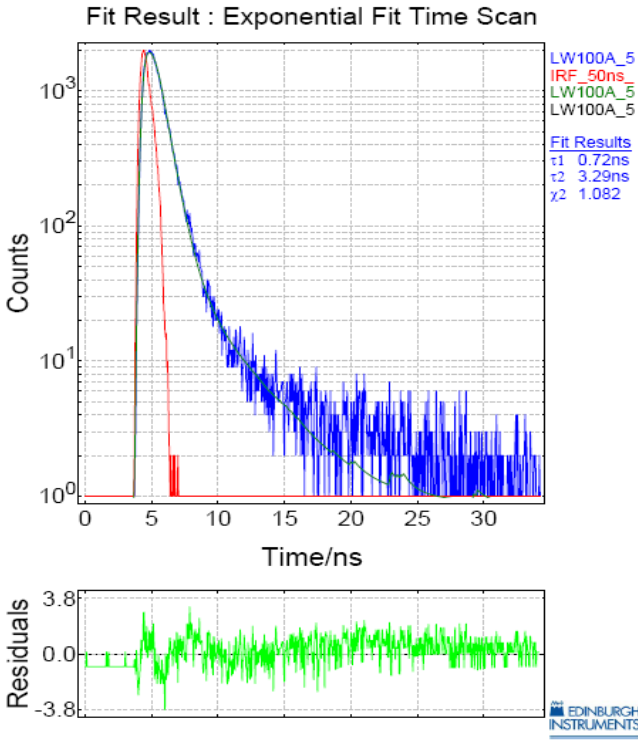
Fit Results

Fit : $A+B1\exp(-t/\tau_1)+B2\exp(-t/\tau_2)+B3\exp(-t/\tau_3)$

Instrument Response	**IRF_100ns_2000count**
Range (ch)	:0 to 1023
Peak Count	:927 in channel 120
Total Count	:515928
Background	:0.000
Decay Scan	**LW101A_100ns_400nm**
File location	:File has not been saved.
Range (ch)	:0 to 1023
Peak Count	:12883 in channel 120
Total Count	:515928
Time Calibration	:0.098 ns/ch
Total Experiment Time	:214.39 s
Fit Range (ch)	:1 to 900

Parameter	Value	Std. Dev.	Rel %
τ_1	1.220E-009 s	5.5223E-011 s	
τ_2	2.736E-009 s	4.9705E-011 s	
τ_3	1.885E-008 s	1.4876E-010 s	
Shift	1.933E-011 s	1.535E-012 s	
B1	0.519	0.0295	22.41
B2	0.601	0.0326	58.18
B3	0.029	0.0004	19.41
A	0.267		
χ^2	1.023		

(b) Compound 10 at λ_{em} = 400 nm



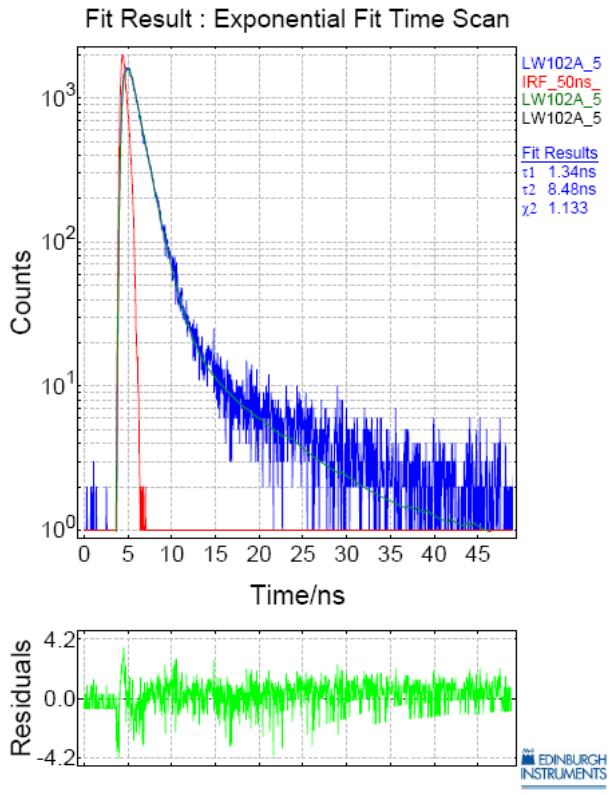
Fit Results

Fit : $A+B1\exp(-t/\tau_1)+B2\exp(-t/\tau_2)$

Instrument Response	**IRF_50ns_2000count**
Range (ch)	:0 to 1023
Peak Count	:1099 in channel 100
Total Count	:70763
Background	:0.000
Decay Scan	**LW100A_50ns_400nm_1**
File location	:File has not been saved.
Range (ch)	:0 to 1023
Peak Count	:1956 in channel 100
Total Count	:70763
Time Calibration	:0.049 ns/ch
Total Experiment Time	:147.06 s
Fit Range (ch)	:1 to 700

Parameter	Value	Std. Dev.	Rel %
τ_1	7.219E-010 s	6.9355E-012 s	
τ_2	3.292E-009 s	1.4980E-010 s	
Shift	1.798E-011 s	2.553E-012 s	
B1	0.122	0.0009	91.87
B2	0.002	0.0002	8.13
A	0.874		
χ^2	1.082		

(c) Compound 11 at λ_{em} = 400 nm



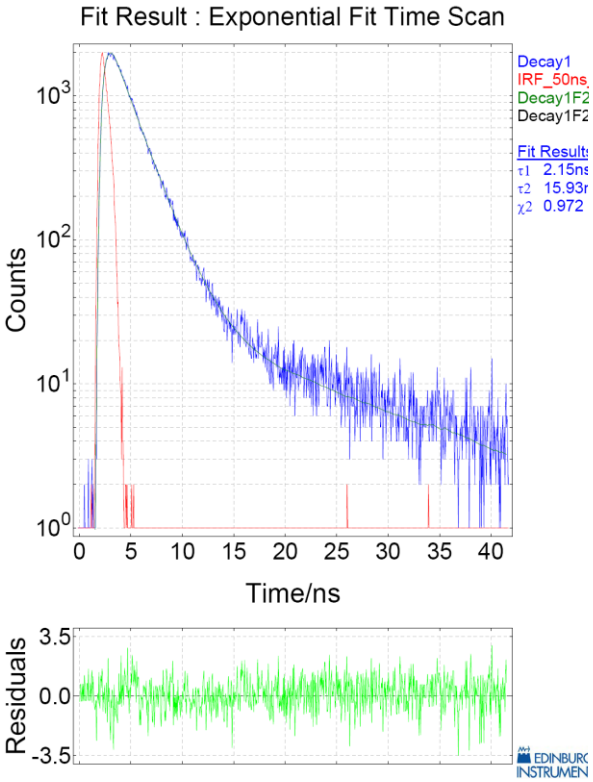
Fit Results

Fit : $A+B1\exp(-t/\tau_1)+B2\exp(-t/\tau_2)$

Instrument Response	:**IRF_50ns_2000count**
Range (ch)	:0 to 1023
Peak Count	:1449 in channel 98
Total Count	:83286
Background	:0.000
Decay Scan	:**LW102A_50ns_400nm**
File location	:File has not been saved.
Range (ch)	:0 to 1023
Peak Count	:1550 in channel 98
Total Count	:83286
Time Calibration	:0.049 ns/ch
Total Experiment Time	:1338.52 s
Fit Range (ch)	:1 to 1000

Parameter	Value	Std. Dev.	Rel %
τ_1	1.343E-009 s	8.5333E-012 s	
τ_2	8.481E-009 s	4.2216E-010 s	
Shift	1.052E-010 s	2.513E-012 s	
B1	0.078	0.0005	93.21
B2	0.001	0.0001	6.79
A	0.710		
χ^2	1.133		

(d) Compound 15 at λ_{em} = 400 nm



Fit : $A+B1\exp(-t/\tau_1)+B2\exp(-t/\tau_2)$

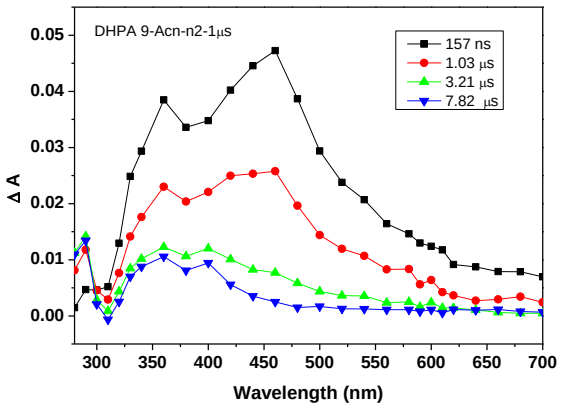
Instrument Response	:**IRF_50ns_2000count**
Range (ch)	:0 to 1023
Peak Count	:929 in channel 107
Total Count	:140756
Background	:0.090
Decay Scan	:**Decay1**
File location	:File has not been saved.
Range (ch)	:0 to 1023
Peak Count	:1803 in channel 107
Total Count	:140756
Time Calibration	:0.049 ns/ch
Total Experiment Time	:283.19 s
Fit Range (ch)	:50 to 900

Parameter	Value	Std. Dev.	Rel %
τ_1	2.151E-009 s	9.9864E-012 s	
τ_2	1.593E-008 s	7.2253E-010 s	
Shift	3.776E-012 s	2.453E-012 s	
B1	0.083	0.0004	92.13
B2	0.001	0.0001	7.87
A	0.105		
χ^2	0.972		

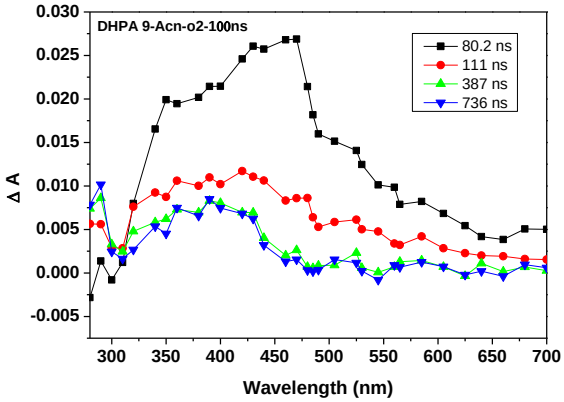
6. Laser Flash Photolysis of 9-11, 13 and 15

(a) Transient absorption spectra observed for 9 in CH_3CN solution

(i) N_2 purged

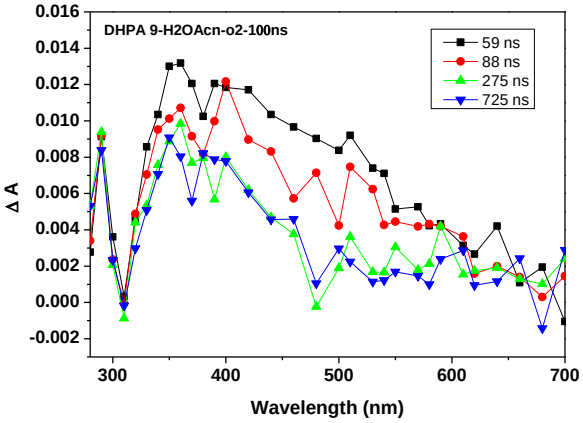


(ii) O_2 purged

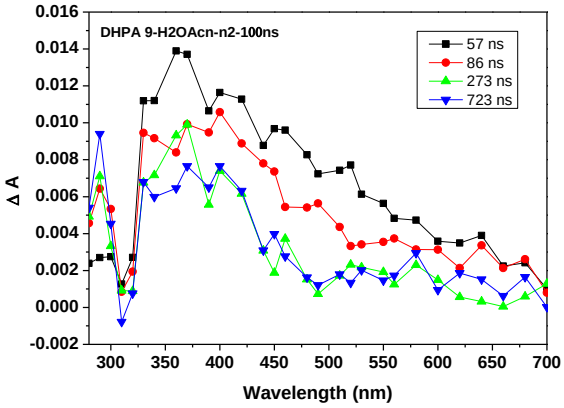


(b) Transient absorption spectra observed for 9 in 10% H_2O/CH_3CN

(i) N_2 purged

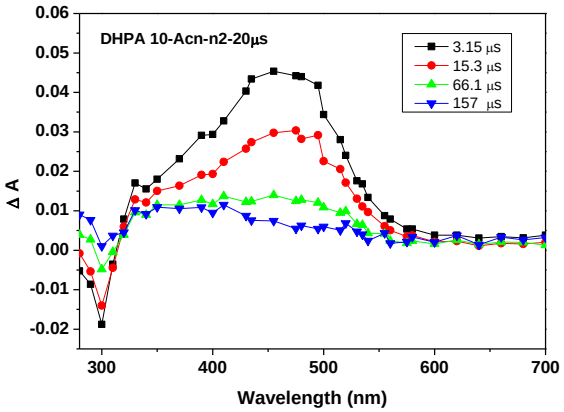


(ii) O_2 purged

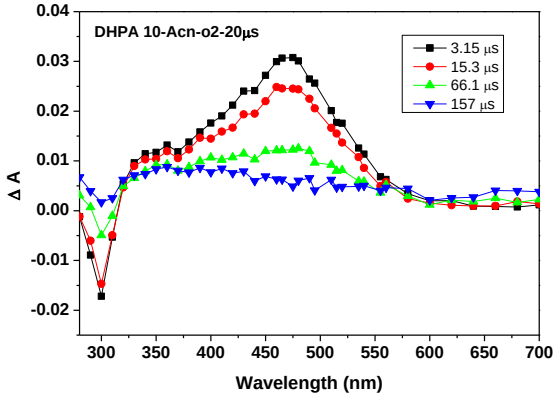


(c) Transient absorption spectra observed for 10 in CH_3CN solution

(i) N_2 purged

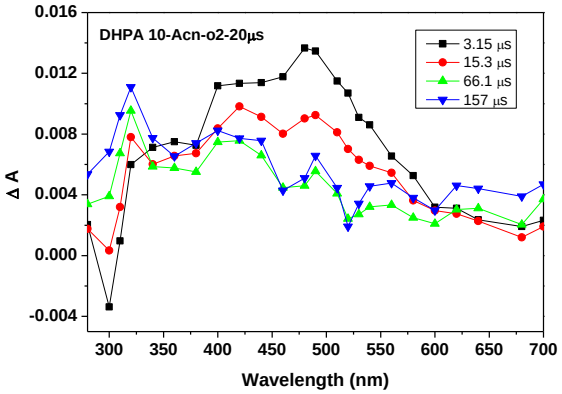


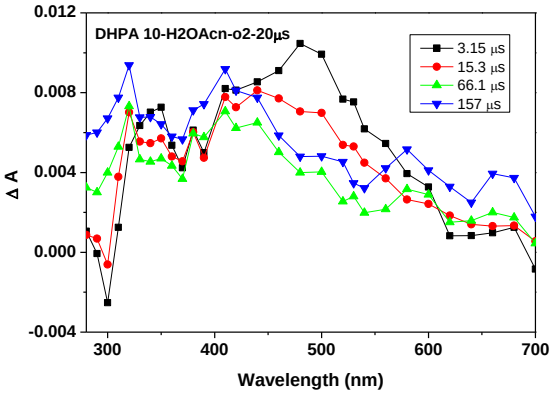
(ii) O_2 purged



(d) Transient absorption spectra observed for 10 in 50% H_2O/CH_3CN

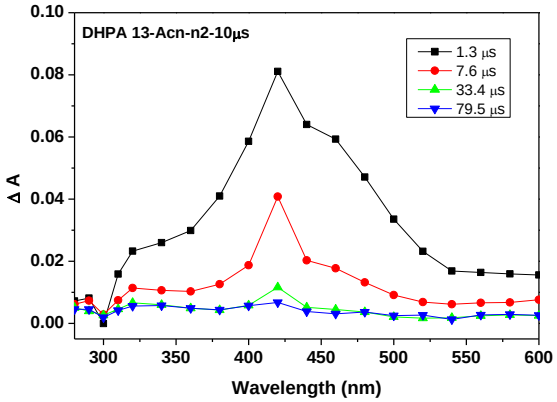
(i) N_2 purged **(ii) O_2 purged**

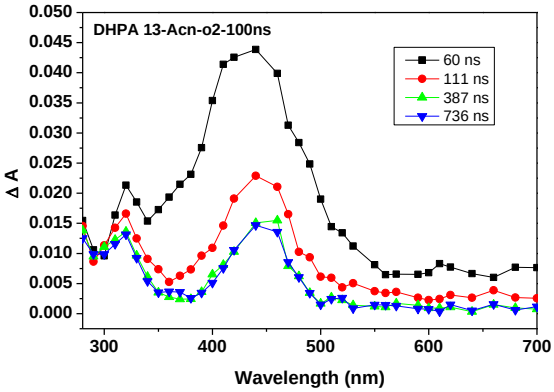




(e) Transient absorption spectra observed for 13 in CH_3CN

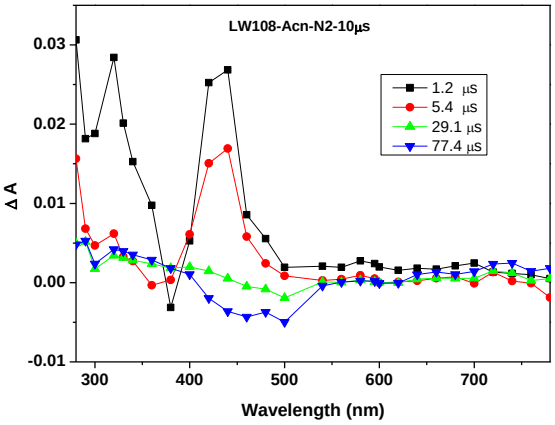
(i) N_2 purged **(ii) O_2 purged**

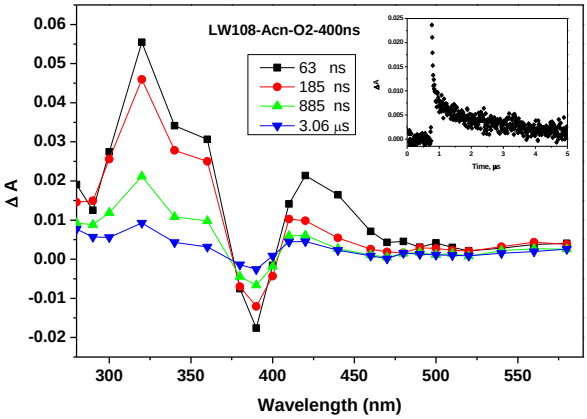




(f) Transient absorption spectra observed for 11 in CH_3CN

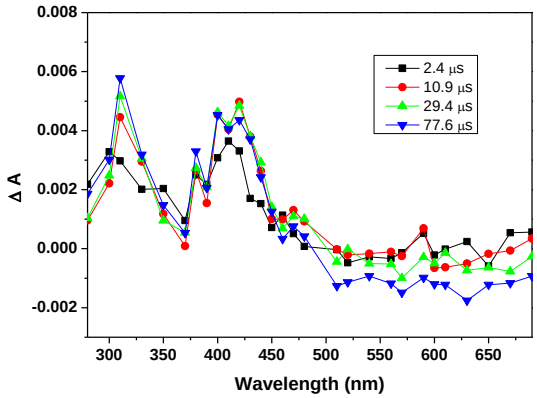
(i) N_2 purged **(ii) O_2 purged**



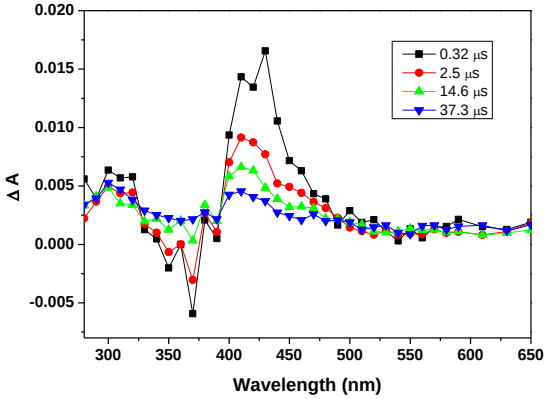


(g) Transient absorption spectra observed for 11 in O_2 purged

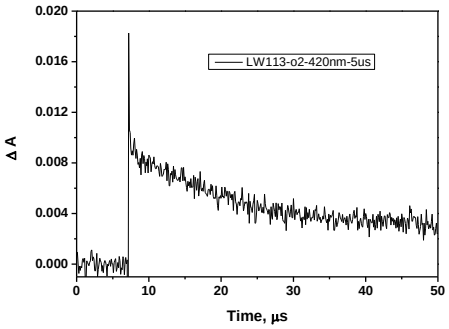
(i) 50% H_2O/CH_3CN

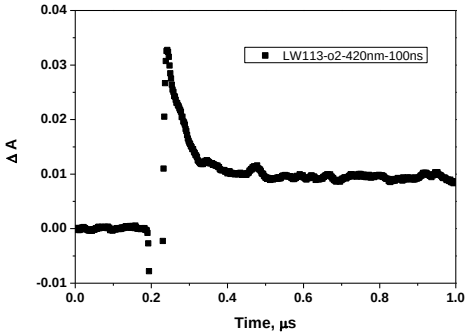


(ii) TFE



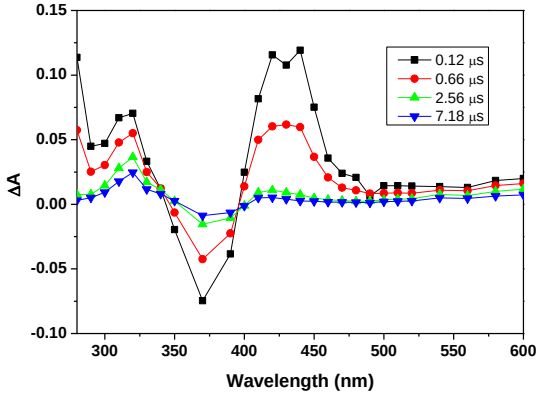
Decay lifetime observed at 420 nm in TFE: 15 μs (left) and 57 ns (right)



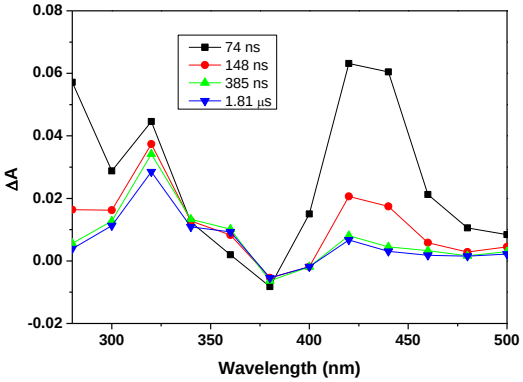


(h) Transient absorption spectra observed for 15 in CH_3CN solution

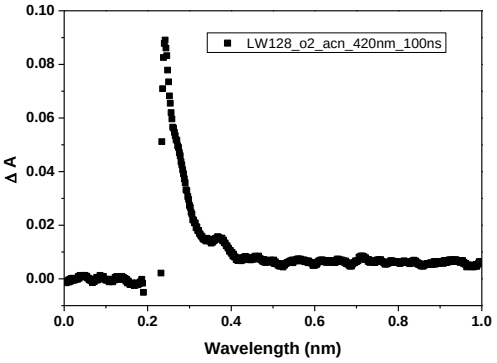
(i) N_2 purged



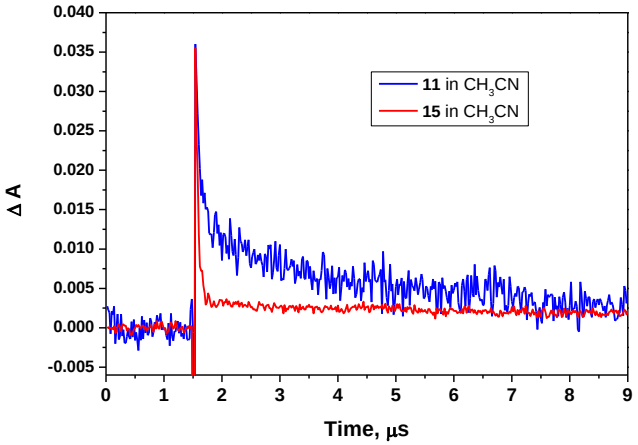
(ii) O_2 purged



Decay lifetime observed at 420 nm: 50 ns



(i) Decay transient of 11 *vs* 15 in CH_3CN



7. Computational data of 10

Structure optimization at B3LYP/6-311 level of theory for S10-1

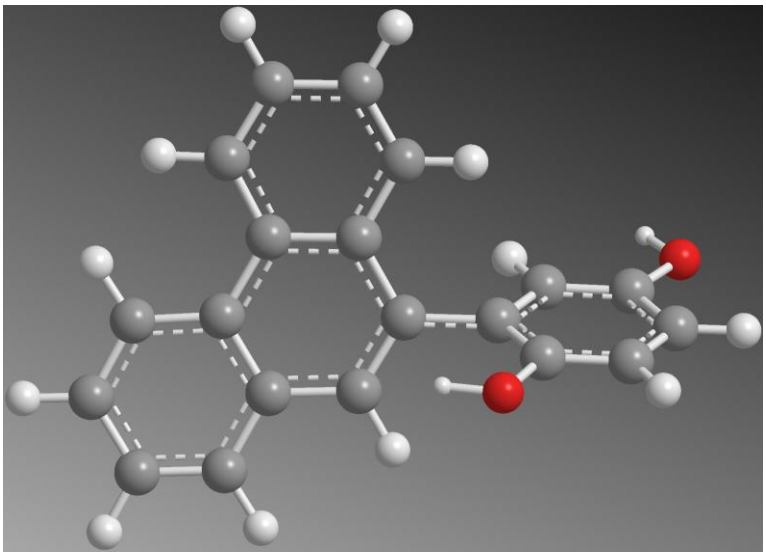


Table 1. Atomic Coordinates for S10-1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.770988	-1.172071	-0.433577
2	6	0	-4.037972	-0.011794	-0.253552
3	6	0	-2.625110	-0.040037	-0.152415
4	6	0	-1.974754	-1.306044	-0.243826
5	6	0	-2.745439	-2.480632	-0.428070
6	6	0	-4.122335	-2.419816	-0.521412
7	6	0	-1.812731	1.155386	0.046545
8	6	0	-0.388170	1.040422	0.132670
9	6	0	0.239578	-0.263905	0.000362
10	6	0	-0.544813	-1.374697	-0.164929
11	6	0	-2.387049	2.444414	0.173227
12	6	0	-1.608977	3.567854	0.386976
13	6	0	-0.210938	3.448461	0.490680
14	6	0	0.383665	2.206940	0.366085
15	6	0	1.727822	-0.413113	0.040922
16	6	0	2.351941	-1.052320	1.123878
17	6	0	3.740968	-1.207558	1.155463
18	6	0	4.524456	-0.734681	0.109884
19	6	0	3.915433	-0.100444	-0.976855
20	6	0	2.533042	0.061608	-1.010747
21	8	0	1.640755	-1.559173	2.214068
22	8	0	4.758913	0.347010	-2.000749
23	1	0	-5.849016	-1.119664	-0.507232
24	1	0	-4.565486	0.928383	-0.190464
25	1	0	-2.233581	-3.432353	-0.497075

26	1	0	-4.701117	-3.322626	-0.661978
27	1	0	-0.075277	-2.345058	-0.273219
28	1	0	-3.458563	2.561894	0.108936
29	1	0	-2.078208	4.538019	0.481558
30	1	0	0.396635	4.324764	0.672283
31	1	0	1.455608	2.111553	0.454228
32	1	0	4.182980	-1.701898	2.007972
33	1	0	5.598410	-0.847693	0.114631
34	1	0	2.059277	0.548481	-1.854779
35	1	0	0.685775	-1.393868	2.115510
36	1	0	4.259430	0.759534	-2.724784

Structure optimization at B3LYP/6-311 level of theory for S10-2

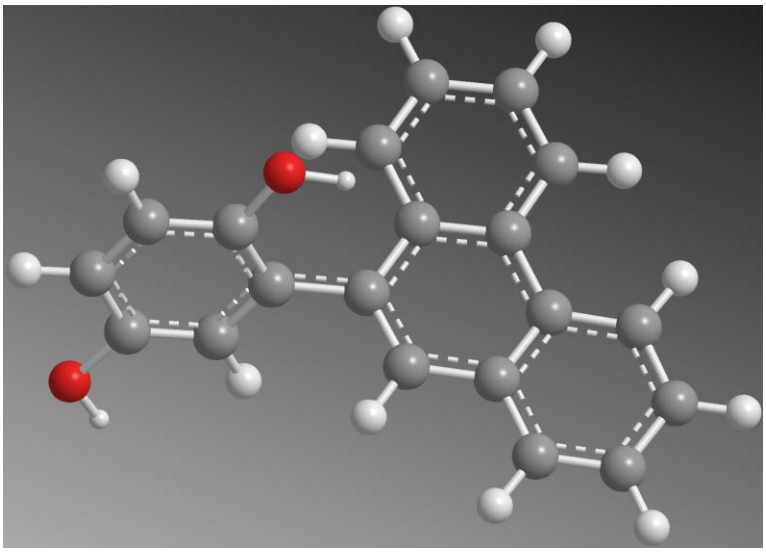


Table 2. Atomic Coordinates for S10-2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.695051	-1.501712	0.047603
2	6	0	4.034272	-0.295550	-0.107775
3	6	0	2.619906	-0.219379	-0.070497
4	6	0	1.890790	-1.427955	0.135235
5	6	0	2.589047	-2.650990	0.292740
6	6	0	3.969009	-2.692494	0.249510
7	6	0	1.881344	1.027514	-0.234803
8	6	0	0.450031	1.017067	-0.182004
9	6	0	-0.255788	-0.233447	0.051652
10	6	0	0.459382	-1.391290	0.192937
11	6	0	2.531619	2.265786	-0.461372
12	6	0	1.819451	3.438691	-0.635325
13	6	0	0.412965	3.422690	-0.596974

14	6	0	-0.254877	2.233339	-0.375335
15	6	0	-1.749545	-0.276019	0.125914
16	6	0	-2.444754	0.290722	1.206708
17	6	0	-3.837698	0.209296	1.279562
18	6	0	-4.558095	-0.437301	0.281768
19	6	0	-3.879672	-1.009150	-0.797338
20	6	0	-2.491004	-0.931278	-0.874059
21	8	0	-1.804992	0.953188	2.257317
22	8	0	-4.659920	-1.645394	-1.769964
23	1	0	5.776000	-1.529653	0.014597
24	1	0	4.619463	0.599189	-0.259937
25	1	0	2.018750	-3.557927	0.450116
26	1	0	4.491897	-3.631486	0.371120
27	1	0	-0.067423	-2.320509	0.370983
28	1	0	3.609921	2.303559	-0.504271
29	1	0	2.345769	4.368170	-0.806512
30	1	0	-0.144667	4.337778	-0.743282
31	1	0	-1.334707	2.217510	-0.359081
32	1	0	-4.333367	0.653276	2.130358
33	1	0	-5.634831	-0.509723	0.321072
34	1	0	-1.962523	-1.365928	-1.713987
35	1	0	-0.838119	0.950014	2.149429
36	1	0	-4.115459	-2.007857	-2.488305