Ruthenium-Catalyzed Intramolecular Carbocyclization of Alkynes with an sp^3 Carbon by an Oxidative Deprotonation Process

Bo-Xiao Tang,[b,c] Ren-Jie Song,[a,c] Cui-Yan Wu,[a,b] Zhi-Qiang Wang,[a,b] Yu Liu,[a] Xiao-Cheng Huang,[a,b] Ye-Xiang Xie,[a] and Jin-Heng Li*[a]

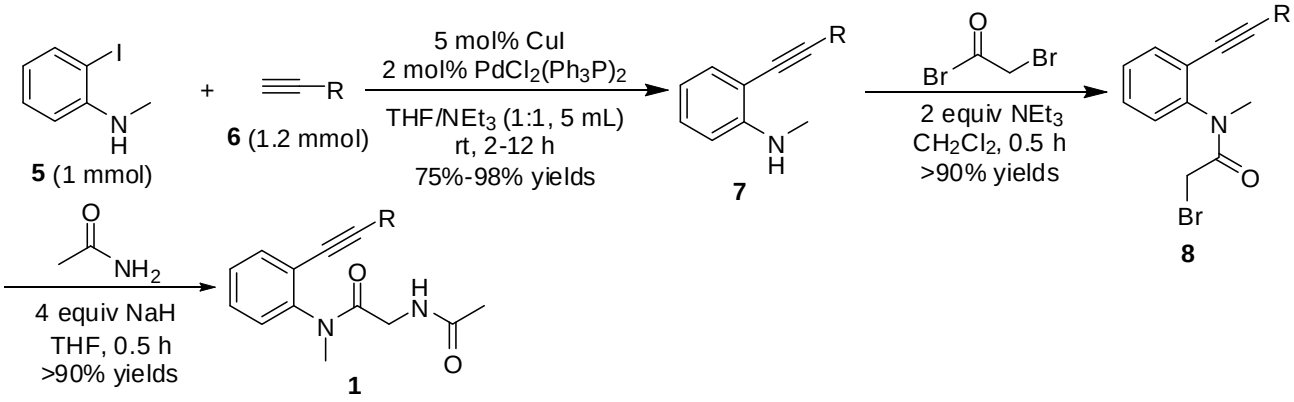
[a] *State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, China. Fax: 0086731 8887 2531; Tel: 0086731 8887 2576; E-mail: jhli@hnu.edu.cn*
[b] *Key Laboratory of Chemical Biology & Traditional Chinese Medicine Research (Ministry of Education), Hunan Normal University, Changsha 410081, China*
[c] *These authors contributed equally.*

Supporting Information

List of Contents

(A) Typical Experimental Procedure

(a) Synthesis of substrates 1 by the known procedure[1]



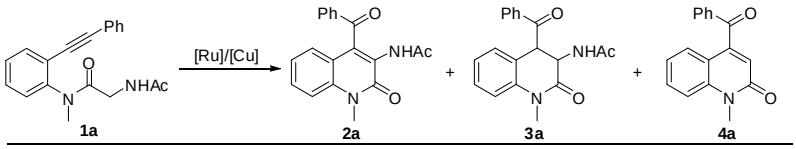
(b) Typical Experimental Procedure for the $RuCl_3$-Catalyzed Intramolecular Carbocyclization in the Presence of $CuCl_2$ and O_2:

To a Schlenk tube were added 2-acetamido-*N*-(2-ethynyl)aryl)acetamides **1** (0.3 mmol), $RuCl_3$ (10 mol %), $CuCl_2$ (20 mol %), H_2O (6 equiv) and anhydrous THF (3 mL). Then the tube was charged with O_2 (1 atm), and was stirred at 120 ^oC (oil bath temperature) for the indicated time until complete consumption of starting material as monitored by TLC and GC-MS analysis. After the reaction was finished, the reaction mixture was cooled to room temperature, diluted in diethyl ether, and washed with brine. The aqueous phase was re-extracted with diethyl ether. The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated in vacuo, and the resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate) to afford the desired products **2**, **3** and **4**.

(c) Table *S1*

It is noted that the reaction can not take place without Ru catalysis (entry 11), and three other Ru ctalysts ($RuCl_2(Ph_3P)$, dichloro(*p*-cymene)ruthenium(II) dimer and Rhodium(III) 2,4-pentanedionate) display less efficiency for the reaction. It was found that water affected the reaction (entries 4, 14 and 15), and the yields were decreased to 36% and 44%, respectively, using 4 equiv or 8 equiv water.

Table S1. Cyclization of N-Methyl-2-oxo-N-phenylacetamide (**1a**)[a]



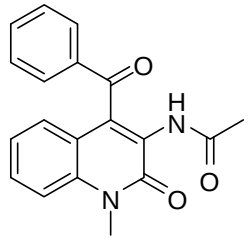
1a **2a** **3a** **4a**

Entry	[Ru] (mol %)	[Cu] (mol %)	Solvent	T (°C)	Isolated yield (%)		
					2a	**3a**	**4a**
1	$RuCl_3$ (10)	—	THF	120	9	trace	trace
2[b]	$RuCl_3$ (10)	$CuCl_2$ (100)	THF	120	14	trace	trace
3	$RuCl_3$ (10)	$CuCl_2$ (40)	THF	120	55	5	6
4	$RuCl_3$ (10)	$CuCl_2$ (20)	THF	120	59	6	6
5	$RuCl_3$ (10)	$CuCl_2$ (10)	THF	120	49	trace	trace
6[c]	$RuCl_3$ (10)	$CuCl_2$ (20)	THF	120	16	trace	trace
7	$RuCl_3$ (10)	$CuCl_2$ (20)	THF	100	40	6	4
8	$RuCl_3$ (10)	$CuCl_2$ (20)	THF	130	55	6	9
9	—	$CuCl_2$ (20)	THF	120	0	0	0
10	$RuCl_3$ (5)	$CuCl_2$ (20)	THF	120	45	trace	trace
11	$RuCl_3$ (20)	$CuCl_2$ (20)	THF	120	43	trace	trace
12[d]	$RuCl_3$ (10)	$CuCl_2$ (20)	THF	120	65	3	5
13	$RuCl_2(Ph_3P)$ (10)	$CuCl_2$ (20)	THF	120	7	trace	trace
14[e]	$Ru_2Cl_4(C_{10}H_{14})_2$ (10)	$CuCl_2$ (20)	THF	120	8	trace	trace
15[f]	$Ru(C_5H_7O_2)_3$ (10)	$CuCl_2$ (20)	THF	120	<5	0	0
16[g]	$RuCl_3$ (10)	$CuCl_2$ (20)	THF	120	41	trace	trace
17[h]	$RuCl_3$ (10)	$CuCl_2$ (20)	THF	120	49	trace	trace
18	$RuCl_3$ (10)	$CuBr_2$ (20)	THF	100	10	trace	trace
19	$RuCl_3$ (10)	CuI (20)	THF	100	8	trace	trace
20	$RuCl_3$ (10)	CuCl (20)	THF	100	30	8	7
21	$RuCl_3$ (10)	oxone (100)	THF	100	trace	trace	trace
22	$RuCl_3$ (10)	$CuCl_2$ (20)	dioxane	100	20	trace	trace
23	$RuCl_3$ (10)	$CuCl_2$ (20)	DMF	100	trace	trace	trace
24	$RuCl_3$ (10)	$CuCl_2$ (20)	toluene	100	10	trace	trace

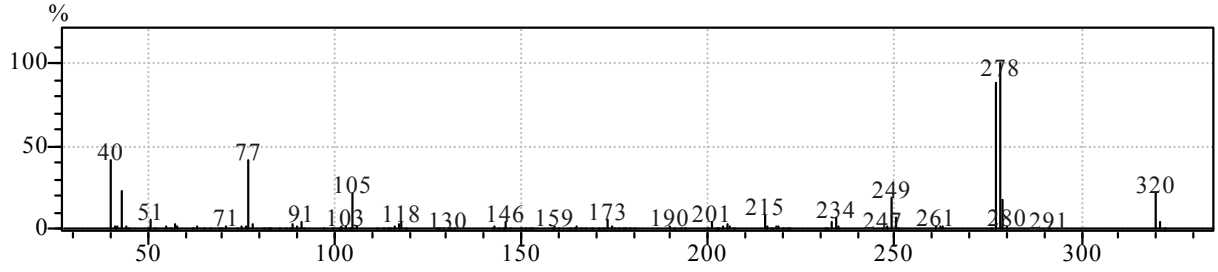
[a] Reaction conditions: **1a** (0.3 mmol), H_2O (6 equiv), [Ru], additive, O_2 (1 atm) and THF (3 mL) for 10 h. [b] In argon. [c] Air (1 atm) instead of O_2. [d] diglyme (3 mL) instead of THF. [e] $Ru_2Cl_4(C_{10}H_{14})_2$ = dichloro(*p*-cymene)ruthenium(II) dimer. [f] $Ru(C_5H_7O_2)_3$ = Rhodium(III) 2,4-pentanedionate. [g] H_2O (4 equiv) was added. [h] H_2O (8 equiv) as added.

(d) The ^{18}O-labeled Experiments Determined by GC-MS Analysis (Figure S1).

Figure S1 **The ^{18}O-labeled Experiments Determined by GC-MS Analysis.**

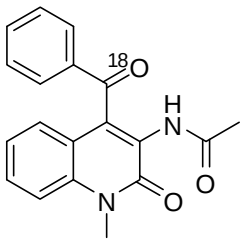


Chemical Formula: $C_{19}H_{16}N_2O_3$
Molecular Weight: 320.34194

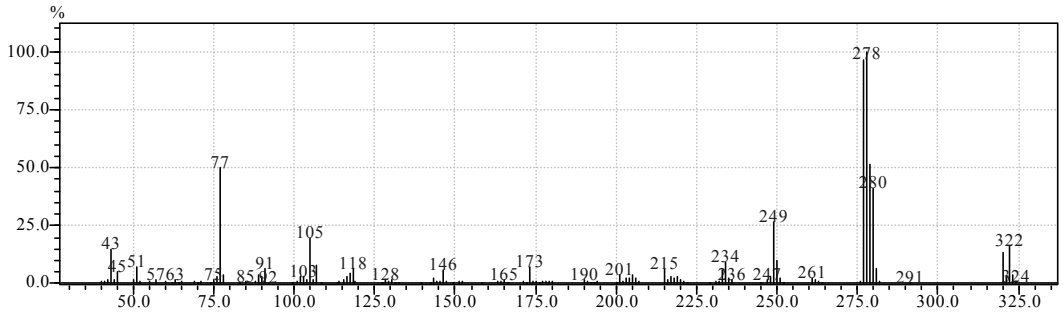


[MS Spectrum]
# of Peaks127
Raw Spectrum 4.125 (scan : 436)
Background No Background Spectrum
Base Peakm/z 278.10 (Inten : 241,828)

m/z	Absolute Intensity	Relative Intensity
40.00	95108	39.33
41.05	3918	1.62
42.05	4295	1.78
43.05	50568	20.91
44.05	4478	1.85
50.05	2789	1.15
51.05	13375	5.53
55.10	2696	1.11
57.10	6801	2.81
58.05	6257	2.59
63.05	3466	1.43
65.10	2520	1.04
69.05	2831	1.17
71.10	4779	1.98
75.05	3373	1.39
76.05	6574	2.72
77.05	90628	37.48
78.10	77483	3.20
85.10	3166	1.31
88.10	2494	1.03
89.10	8353	3.45
90.10	5771	2.39
91.10	12225	5.06
102.10	4888	2.02
103.10	5102	2.11
104.10	3009	1.24
105.10	51870	21.45
106.05	4060	1.68
116.10	5012	2.07
117.15	9383	3.88
118.15	10699	4.42
128.10	3096	1.28
130.15	3050	1.26
143.10	3806	1.57
146.05	8585	3.55
159.05	5213	2.16
165.10	4244	1.75
173.10	15054	6.23
174.10	2510	1.04
175.10	2577	1.07
190.05	3012	1.25
201.05	12030	4.97
204.00	4670	1.93
205.00	6532	2.70
206.05	4784	1.98
215.05	16833	6.96
216.10	2891	1.20
218.10	4728	1.96
219.05	6025	2.49
220.05	2987	1.24
233.10	9704	4.01
234.05	17944	7.42
235.00	4446	1.84
248.10	5403	2.23
249.10	42526	17.59
250.10	15483	6.40
251.10	2654	1.10
261.05	4494	1.86
262.05	3456	1.43
263.05	3326	1.38
277.05	207248	85.70
278.10	241828	100.00
279.10	40158	16.61
280.05	4399	1.82
291.10	1483	0.61
320.10	***47028***	***19.45***
321.10	9800	4.05
322.10	***1688***	***0.70***



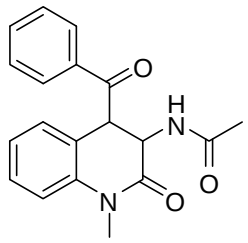
Chemical Formula: $C_{19}H_{16}N_2O_2{}^{18}O$
Molecular Weight: 322



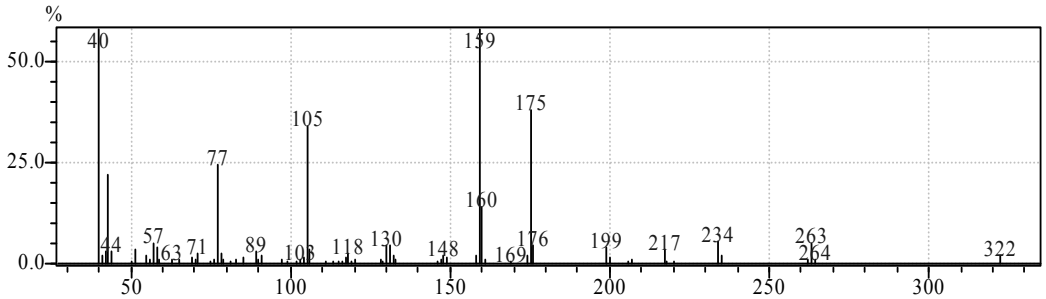
[MS Spectrum]
# of Peaks130
Raw Spectrum 3.267 (scan : 333)
Background No Background Spectrum
Base Peakm/z 278.05 (Inten : 223,263)

m/z	Absolute Intensity	Relative Intensity
40.05	2881	1.29
41.10	3009	1.35
42.05	3366	1.51
43.05	33776	15.13
44.05	4220	1.89
45.05	11736	5.26
50.10	3412	1.53
51.10	16292	7.30
52.10	2497	1.12
55.10	2404	1.08
57.10	4376	1.96
60.05	1562	0.70
62.10	1348	0.60
63.05	3401	1.52
64.05	1095	0.49
65.05	2514	1.13
69.10	1700	0.76
70.10	1515	0.68
71.10	3073	1.38
74.05	1263	0.57
75.05	4506	2.02
76.05	7547	3.38
77.05	111057	49.74
78.10	9185	4.11
83.15	1228	0.55
85.15	1745	0.78
88.05	2677	1.20
89.05	9225	4.13
90.10	6971	3.12
91.10	14420	6.46
92.10	1512	0.68
99.20	1259	0.56
101.10	2120	0.95

102.10	61872.77		165.05	45892.06		229.00	13160.59	
103.10	65162.92		166.05	13190.59		231.05	25441.14	
104.10	32751.47		171.05	22981.03		232.00	18600.83	
105.10	43608	19.53	172.10	12680.57		233.05	13288	5.95
106.15	36621.64		173.05	15896	7.12	234.05	20631	9.24
107.10	17419	7.80	174.10	26441.18		235.00	48332.16	
108.15	13890.62		175.10	25521.14		236.05	31331.40	
113.15	10260.46		176.00	14120.63		245.00	10960.49	
114.10	28461.27		177.10	19500.87		247.00	30861.38	
115.15	31211.40		178.05	21180.95		248.05	70373.15	
116.15	69953.13		179.10	16840.75		249.05	59561	26.68
117.15	10785	4.83	180.00	16240.73		250.10	22212	9.95
118.15	13878	6.22	190.05	32881.47		251.10	49742.23	
119.10	16520.74		191.00	16200.73		252.10	12970.58	
127.20	12140.54		192.05	10100.45		261.05	53982.42	
128.10	34701.55		193.05	14280.64		262.05	36641.64	
129.10	26031.17		194.10	21100.95		263.05	29521.32	
130.10	32721.47		200.00	11370.51		264.10	13740.62	
131.10	13290.60		201.00	89454.01		276.05	22951.03	
132.10	11180.50		202.00	22160.99		277.05	214608	96.12
139.05	11720.52		203.05	51632.31		278.05	223263	100.00
142.05	14060.63		204.10	54922.46		279.05	114488	51.28
143.10	48562.18		205.05	83463.74		280.05	91516	40.99
144.10	20110.90		206.05	48002.15		281.05	15329	6.87
145.10	19050.85		207.05	23701.06		282.05	23441.05	
146.10	12539	5.62	215.05	14146	6.34	291.10	14380.64	
147.10	19120.86		216.05	31461.41		***320.05***	***30237***	***13.54***
149.05	14390.64		217.05	65672.94		321.05	63222.83	
151.05	22241.00		218.00	56332.52		***322.05***	***35724***	***16.00***
152.05	18840.84		219.05	74793.35		323.10	83313.73	
158.05	13850.62		220.05	35511.59		324.05	2670	1.20
163.05	17150.77		221.05	22891.03				
164.10	17800.80		222.05	14300.64				

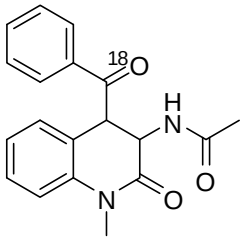


Chemical Formula: $C_{19}H_{18}N_2O_3$
Molecular Weight: 322

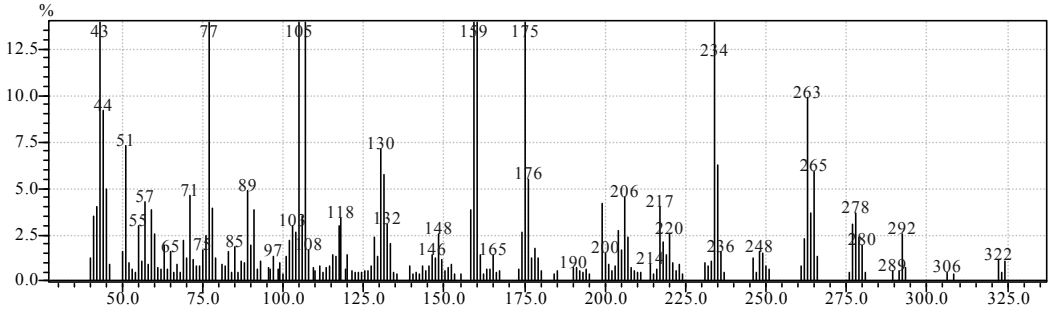


[MS Spectrum]			40.00	87729	58.47	58.10	63634.24	
# of Peaks357			41.05	36342.42		59.10	17611.17	
Raw Spectrum 21.750 (scan : 2131)			42.05	45843.06		70.10	18641.24	
Background	No	Background	43.05	33495	22.32	71.10	43822.92	
Spectrum			44.00	48493.23		76.10	19761.32	
Base Peakm/z	234.10	(Inten :	51.10	58413.89		77.05	36750	24.49
31,051)			55.10	30542.04		78.10	37772.52	
m/z Absolute Intensity		Relative	56.10	17901.19		89.10	45613.04	
Intensity			57.10	75055.00		90.05	17501.17	

91.10	36752.45		149.05	23291.55		234.10	88435.89	
105.10	51163	34.10	158.10	30252.02		235.05	33692.25	
106.10	52913.53		159.10	150040	100.00	263.05	79615.31	
117.10	26761.78		160.05	21594	14.39	264.10	16081.07	
118.10	37902.53		161.10	19311.29		***322.10***	***3163***	***2.11***
120.10	17231.15		174.10	31342.09		323.30	480	0.39
130.10	72654.84		175.10	57192	38.12	***324.30***	***4***	***0.00***
131.10	68464.56		176.10	67314.49				
132.10	36172.41		199.10	63954.26				
148.05	30902.06		217.10	57073.80				

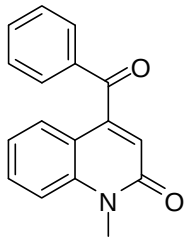


Chemical Formula: $C_{19}H_{18}N_2O_2{}^{18}O$
Molecular Weight: 324

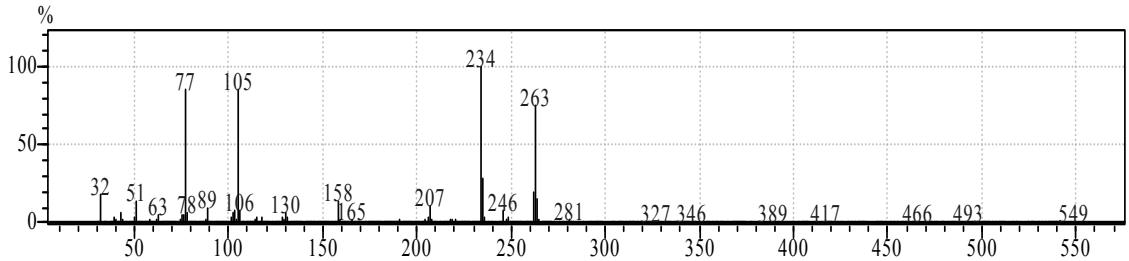


[MS Spectrum]			66.05	13780.50		100.15	10630.39	
# of Peaks191			67.10	25450.93		101.15	35951.31	
Raw Spectrum 6.208 (scan : 686)			68.10	13100.48		102.15	60312.20	
Background	No Background		69.10	59852.18		103.10	82513.01	
Spectrum			70.10	34601.26		104.10	72562.65	
Base Peakm/z 159.10 (Inten :			71.10	12564	4.58	105.10	89403	32.59
274,312)			72.10	31471.15		106.15	96973.54	
m/z	Absolute Intensity	Relative	73.05	23270.85		107.10	50782	18.51
Intensity			74.10	22220.81		108.10	45771.67	
40.05	35131.28		75.05	46481.69		109.20	19150.70	
41.10	95313.47		76.10	67792.47		110.10	14280.52	
42.10	10980	4.00	77.10	112203	40.90	111.20	22480.82	
43.10	56296	20.52	78.10	10753	3.92	112.25	12440.45	
44.05	25104	9.15	79.10	35081.28		113.20	20110.73	
45.05	13705	5.00	81.10	24680.90		114.15	22830.83	
46.10	25550.93		82.10	23280.85		115.15	40001.46	
50.05	44461.62		83.15	42831.56		116.15	37601.37	
51.10	19972	7.28	84.15	13160.48		117.15	80862.95	
52.10	27401.00		85.15	51391.87		118.10	92403.37	
53.10	16780.61		86.15	12800.47		119.15	18770.68	
54.10	12110.44		87.05	29861.09		120.10	39791.45	
55.10	81712.98		88.10	27080.99		121.15	15840.58	
56.10	29001.06		89.10	13339	4.86	122.15	12310.45	
57.10	11691	4.26	90.10	52301.91		123.20	13260.48	
58.10	23850.87		91.10	10532	3.84	124.15	12550.46	
59.10	10619	3.87	92.05	17450.64		125.20	16110.59	
60.05	70362.56		93.10	30351.11		126.10	14380.52	
61.05	20030.73		95.25	21110.77		127.20	21610.79	
62.00	17550.64		96.15	17530.64		128.15	64612.36	
63.05	53131.94		97.15	36451.33		129.10	37481.37	
64.05	18200.66		98.20	16940.62		130.15	19426	7.08
65.10	42921.56		99.15	28311.03		131.15	15800	5.76

132.15	84003.06		178.10	48621.77		231.05	26390.96	
133.15	56522.06		179.10	35021.28		232.05	21640.79	
134.15	13830.50		180.05	15090.55		233.10	29841.09	
135.10	10670.39		184.05	10220.37		234.05	56470	20.59
139.10	21870.80		185.10	15440.56		235.05	17177	6.26
140.10	11660.43		190.00	19400.71		236.05	44641.63	
141.20	13100.48		191.05	19250.70		237.10	13840.50	
142.10	10320.38		192.10	15660.57		246.10	34761.27	
143.10	21480.78		193.05	12950.47		247.00	13580.50	
144.10	14440.53		194.05	17660.64		248.05	44381.62	
145.10	22250.81		195.05	10710.39		249.10	41131.50	
146.10	39631.44		199.10	11518	4.20	250.10	21420.78	
147.10	33231.21		200.10	42061.53		251.10	16880.62	
148.10	70282.56		201.05	25370.92		261.10	23440.85	
149.05	30851.12		202.05	16340.60		262.05	63362.31	
150.10	16110.59		203.10	22090.81		263.05	27076	9.87
151.10	20400.74		204.05	74722.72		264.05	10025	3.65
152.10	25610.93		205.10	45421.66		265.10	16209	5.91
153.10	11340.41		206.05	12494	4.55	266.10	35821.31	
155.20	11440.42		207.05	65192.38		276.10	13100.48	
158.10	10504	3.83	208.05	20220.74		277.05	84653.09	
159.10	274312	100.00	209.10	14410.53		278.05	10034	3.66
160.10	42129	15.36	210.05	13850.50		279.05	66192.41	
161.05	40201.47		211.05	13290.48		280.05	53081.94	
162.10	11500.42		214.05	25110.92		281.05	13840.50	
163.10	17230.63		215.10	10920.40		289.10	16270.59	
164.10	18190.66		216.05	17080.62		291.10	14440.53	
165.10	38351.40		217.10	11025	4.02	292.10	69742.54	
166.10	14190.52		218.05	57582.10		293.10	20140.73	
167.10	14960.55		219.05	39631.44		306.10	12430.45	
173.10	16880.62		220.05	69072.52		308.10	10160.37	
174.10	72592.65		221.05	26790.98		***322.10***	***31531.15***	
175.10	111784	40.75	222.05	15220.55		323.10	12560.46	
176.05	15069	5.49	223.10	25360.92		***324.05***	***28731.05***	
177.10	33681.23		224.10	10030.37				



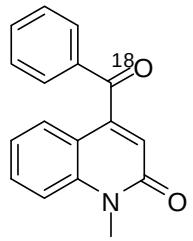
Chemical Formula: $C_{17}H_{13}NO_2$
Molecular Weight: 263



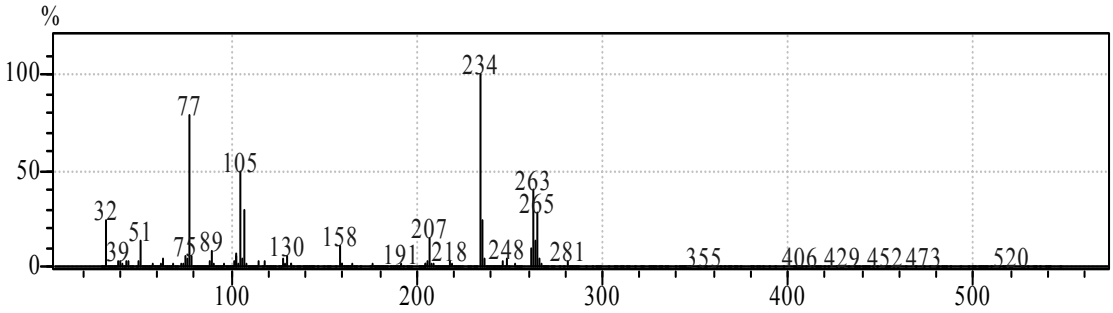
[MS Spectrum]
# of Peaks377
Raw Spectrum 21.592 (scan : 2172)
Background No Background Spectrum
Base Peakm/z 234.15 (Inten : 77,370)

m/z	Absolute Intensity	Relative Intensity
32.05	13796	17.83
50.05	22852.95	
51.05	10950	14.15
52.10	10961.42	
62.00	14971.93	
63.05	36074.66	
74.05	14421.86	
75.10	44755.78	
76.10	34724.49	
77.10	66496	85.95
78.10	48356.25	
88.10	19182.48	
89.10	75609.77	
90.05	876	1.13
96.10	944	1.22
101.10	30113.89	
102.15	46466.00	
103.15	59297.66	
104.05	17912.31	
105.10	66537	86.00
106.15	57237.40	

115.15	27553.56	
117.70	32194.16	
128.10	30433.93	
129.20	18512.39	
130.15	45305.85	
131.65	26183.38	
158.10	10761	13.91
159.15	13451.74	
163.15	867	1.12
165.15	18392.38	
178.15	109311.41	
206.15	27943.61	
207.10	857211.08	
208.10	16062.08	
209.05	792	1.02
218.15	21532.78	
219.15	20292.62	
220.10	13471.74	
234.15	77370	100.00
235.15	22014	28.45
236.20	243833.15	
246.10	62528.08	
247.15	13011.68	
248.10	26603.44	
262.10	15321	19.80
263.15	***58669***	***75.83***
264.15	11736	15.17
265.10	***1176***	***1.52***



Chemical Formula: $C_{17}H_{13}NO^{18}O$
Molecular Weight: 265

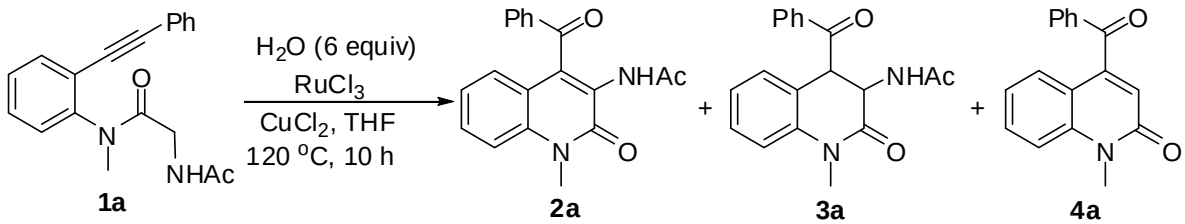


[MS Spectrum]
# of Peaks357
Raw Spectrum 21.750 (scan : 2131)
Background No Background Spectrum
Base Peakm/z 234.10 (Inten : 31,051)
m/z Absolute Intensity Relative Intensity

30.00	68	0.22
31.10	72	0.23
32.05	93303	0.05
34.10	40	0.13
37.10	9	0.03
38.10	163	0.52
39.10	11643	.75
40.00	11453	.69
41.00	323	1.04
42.00	323	1.04
43.10	14404	.64
44.05	946	3.05
45.10	236	0.76
46.10	36	0.12
47.10	12	0.04
49.10	16	0.05
50.00	11163	.59
51.10	49561	5.96
52.05	659	2.12
53.00	148	0.48
54.00	56	0.18
55.00	334	1.08
56.00	164	0.53
57.00	214	0.69
58.00	304	0.98
61.00	155	0.50
62.10	744	2.40
63.05	16275	.24
64.00	264	0.85
65.00	310	1.00
66.00	219	0.71
68.00	91	0.29
69.00	420	1.35
70.00	100	0.32
71.00	200	0.64
72.00	59	0.19
73.10	814	2.62
74.00	704	2.27
75.05	20546	.61
76.10	14464	.66
77.10	28809	92.78
78.10	22967	.39
79.10	436	1.40
80.10	65	0.21
81.10	315	1.01
82.10	280	0.90
83.10	110	0.35
84.10	30	0.10
85.10	272	0.88
86.10	171	0.55
87.00	580	1.87
88.10	844	2.72
89.10	34381	1.07
90.10	387	1.25
91.10	401	1.29
92.10	35	0.11
94.10	65	0.21
95.10	185	0.60
96.20	686	2.21
97.20	320	1.03
98.20	121	0.39
99.20	70	0.23
101.10	15044	.84
102.15	15114	.87
103.15	24968	.04
104.05	672	2.16
105.10	17806	57.34
106.10	15935	.13
107.10	10656	34.32
108.10	10003	.22
109.10	243	0.78
110.10	262	0.84
111.10	222	0.71
112.10	81	0.26
113.10	81	0.26
114.15	568	1.83
115.10	13374	.31
115.70	78	0.25

116.65	541	1.74	175.20	65	0.21	223.10	83	0.27
117.65	1357	4.37	176.20	228	0.73	225.10	89	0.29
118.70	123	0.40	177.20	380	1.22	226.10	38	0.12
119.70	22	0.07	178.10	512	1.65	227.10	64	0.21
120.70	6	0.02	179.10	312	1.00	228.10	33	0.11
121.70	46	0.15	180.10	121	0.39	230.10	62	0.20
123.70	20	0.06	181.10	27	0.09	231.10	76	0.24
124.70	19	0.06	182.10	20	0.06	232.10	232	0.75
125.70	46	0.15	183.10	59	0.19	234.10	31051	100.00
126.70	67	0.22	184.10	60	0.19	235.15	9679	31.17
128.10	1683	5.42	186.10	137	0.44	236.15	1991	6.41
129.20	801	2.58	187.10	28	0.09	237.20	179	0.58
130.20	1902	6.13	188.10	137	0.44	239.20	41	0.13
131.50	576	1.86	189.10	192	0.62	240.20	24	0.08
132.80	552	1.78	190.10	452	1.46	242.20	9	0.03
133.80	3	0.01	191.05	750	2.42	243.20	3	0.01
134.80	99	0.32	192.10	304	0.98	245.20	57	0.18
135.80	8	0.03	193.10	283	0.91	246.10	1686	5.43
137.80	11	0.04	194.10	121	0.39	247.10	393	1.27
138.80	99	0.32	195.10	4	0.01	248.15	1862	6.00
140.80	35	0.11	196.10	28	0.09	249.10	403	1.30
142.80	56	0.18	197.10	91	0.29	250.10	540	1.74
143.80	49	0.16	201.10	100	0.32	251.10	147	0.47
144.80	94	0.30	202.10	203	0.65	252.10	3	0.01
146.80	192	0.62	203.10	289	0.93	253.10	531	1.71
147.80	43	0.14	204.10	859	2.77	254.10	115	0.37
149.80	118	0.38	205.00	582	1.87	255.10	160	0.52
150.80	91	0.29	206.15	1146	3.69	257.10	16	0.05
151.80	89	0.29	207.10	4742	15.27	258.10	96	0.31
153.80	11	0.04	208.05	986	3.18	261.10	20	0.06
158.10	4129	13.30	209.05	522	1.68	262.15	4016	12.93
159.10	443	1.43	210.00	84	0.27	***263.15***	***15621***	***50.31***
160.10	755	2.43	213.00	6	0.02	264.15	4965	15.99
161.10	128	0.41	215.00	35	0.11	***265.15***	***9841***	***31.69***
162.10	83	0.27	216.00	268	0.86	266.15	1556	5.01
163.10	409	1.32	217.00	120	0.39	267.10	473	1.52
164.10	440	1.42	218.10	792	2.55	268.10	75	0.24
165.15	871	2.81	219.10	945	3.04	269.10	48	0.15
166.20	168	0.54	220.10	587	1.89	270.10	14	0.05
167.20	116	0.37	221.10	467	1.50			
169.20	224	0.72	222.10	198	0.64			

(e) Data of *in situ* FTIR Analysis (Figure S2)

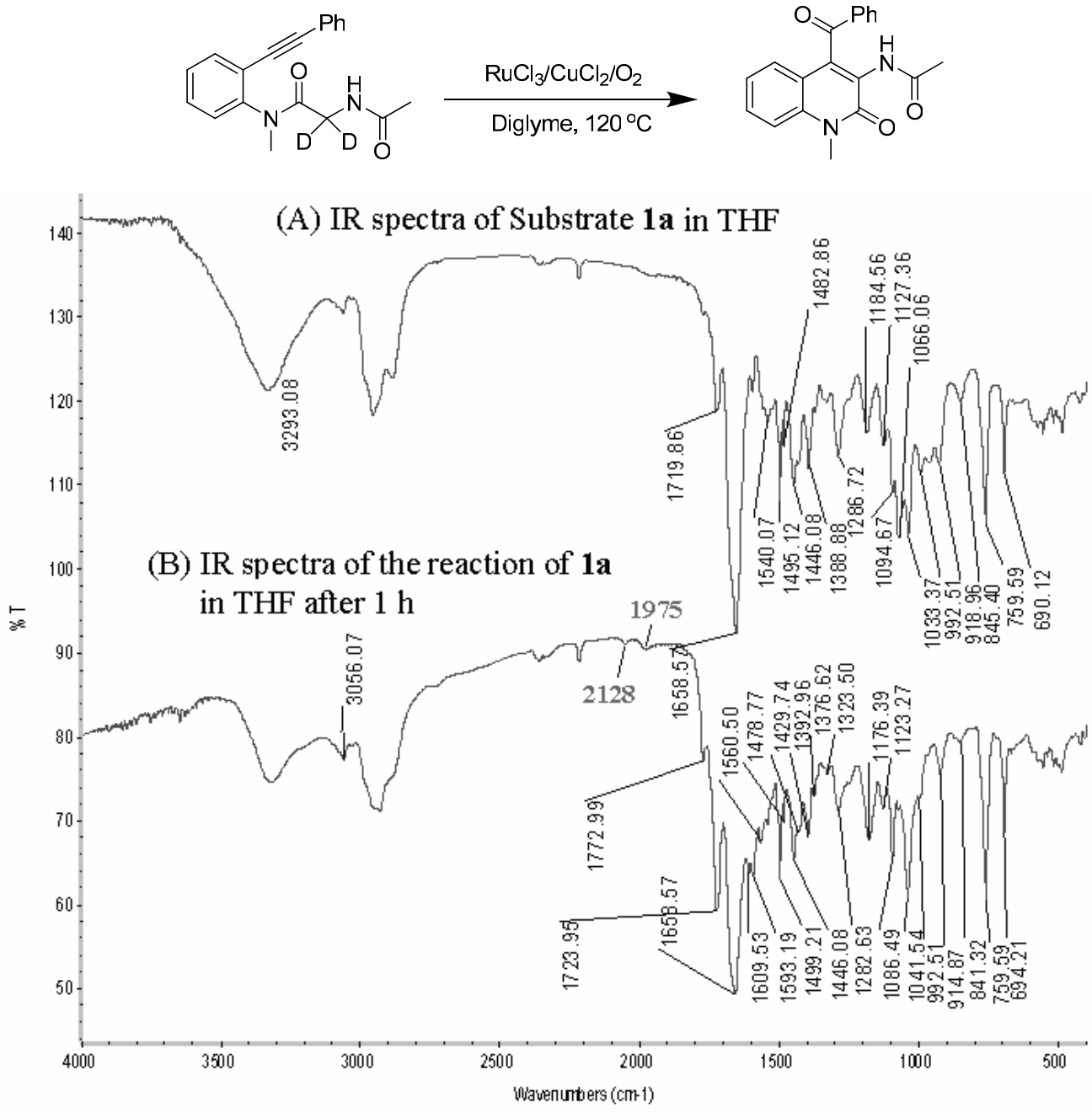


Substrate **1a**, IR : 1671, 1654, 1562 cm^{-1}.

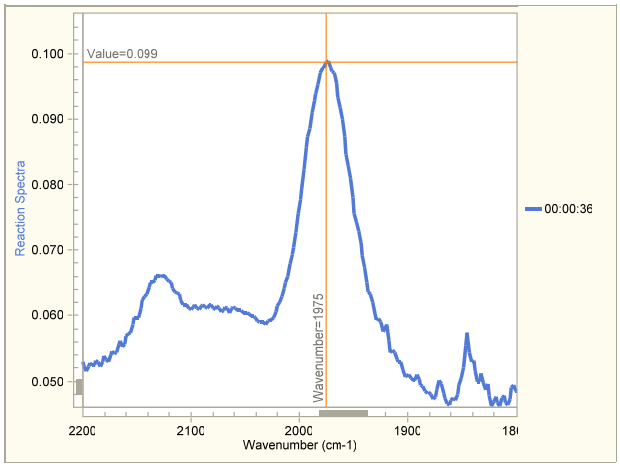
Product **2a**, IR: 1688, 1659, 1634, 1593 cm^{-1}.

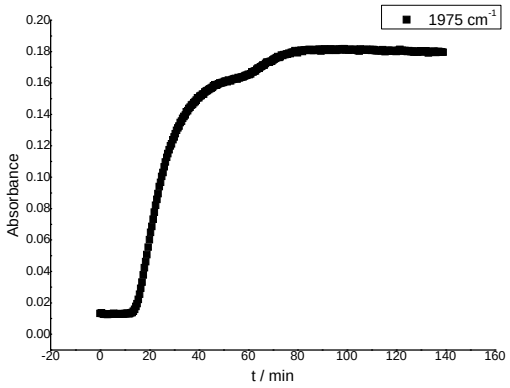
Product **3a**, IR: 1679, 1653, 1593 cm^{-1}.

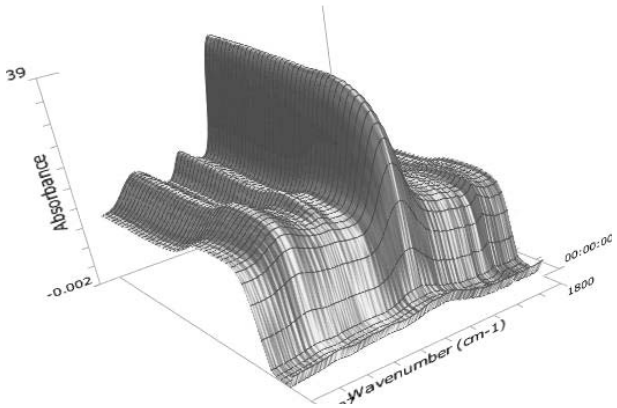
Figure S2 Data of *in situ* FTIR Analysis.

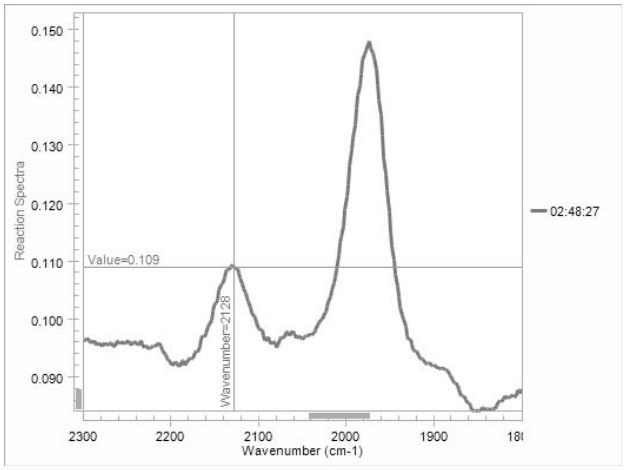


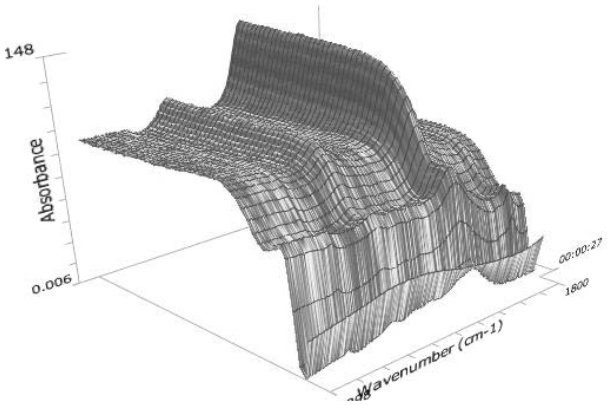
(C) Data of *in situ* FTIR analysis of the reaction of **1a** in diglyme





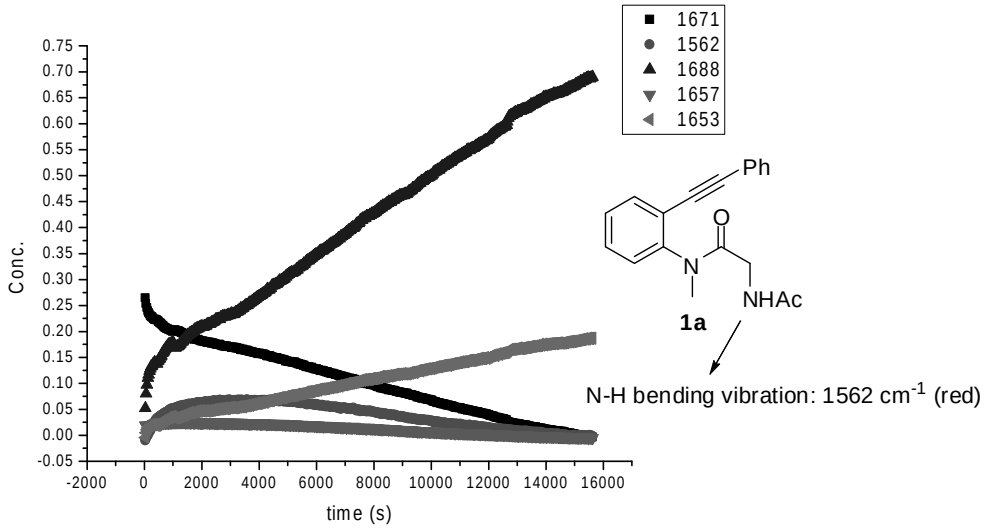






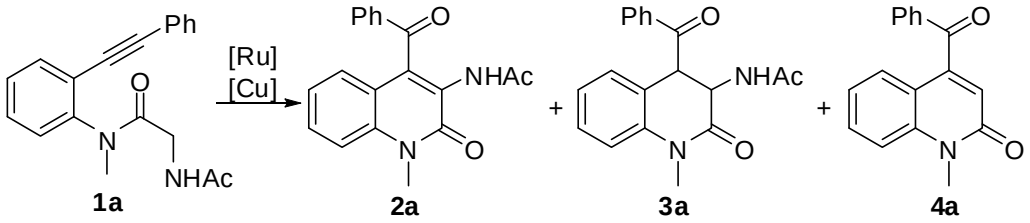
The concentration of two peaks, 1975 cm^{-1} and 2128 cm^{-1}, were increased among 0 – 1.5 h during the reaction of **1a** process using diglyme as the solvent (the results are consistent with the following Reaction Profiles in diglyme. See: Figure S3), but they were disappeared after quenching the reaction.

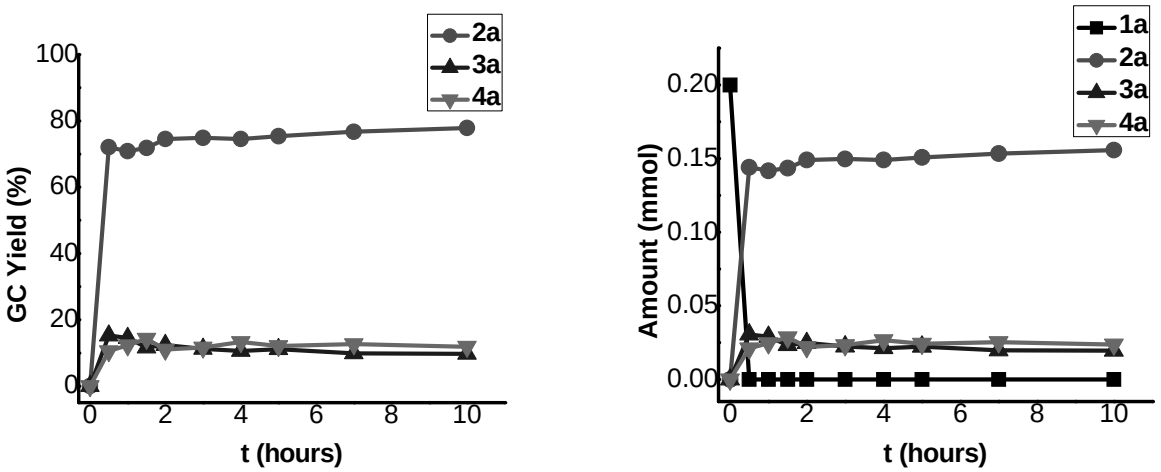
It is noteworthy that the two peaks, 1975 cm^{-1} and 2128 cm^{-1}, are also found in THF after 1 h.



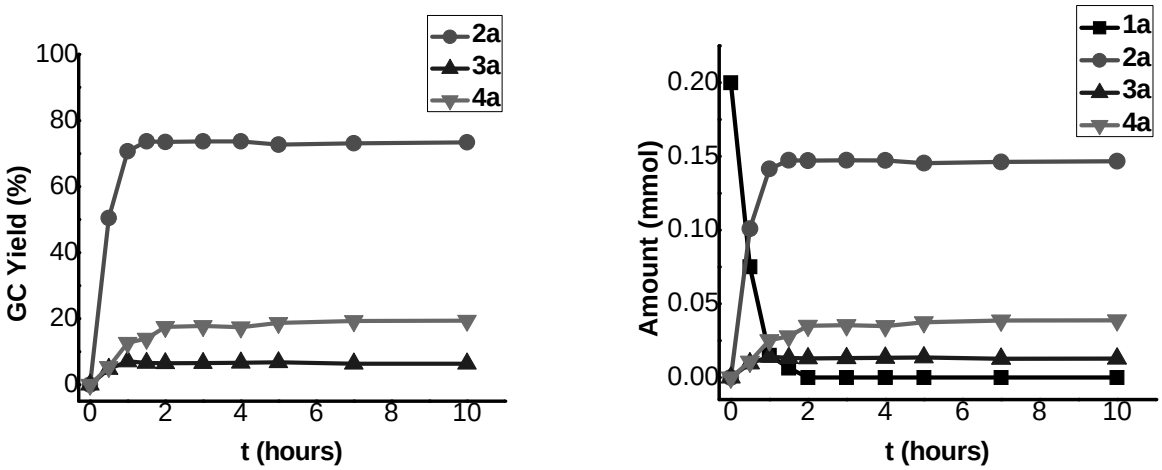
Generally, 1671 cm^{-1} and 1654 cm^{-1} are the C=O stretching vibration, and 1562 cm^{-1} is the N-H bending vibration (diglyme as the solvent). According to the N-H bending vibration data of *in situ* FTIR analysis, the 1562 cm^{-1} peak is increased among 0 - 4 h (The reason may be that the complexation of Ru with nitrogen atom takes place, see: intermediate **A** in Scheme 3), and decreased slowly after 4 h (The reason is that the N-H group links an aromatic group, also supporting by the following Reaction Profiles in diglyme. See: Figure S3 and *Structure Determination of Organic Compounds, Tables of Spectral Data*, 4 ed.; Pretsch, E. Bühlmannn, P.; Affolter, C. Eds.; Springer-Verlag: Berlin Heidelberg, 2009).

Figure S3 **Reaction Profiles.**





(A) Reaction profile of the reaction of **1a** with $RuCl_3$, $CuCl_2$ and O_2 in THF.



(B) Reaction profile of the reaction of **1a** with $RuCl_3$, $CuCl_2$ and O_2 in diglyme.

The reaction profiles as outlined in Figure S3 show that substrate **1a** can be consumed completely at about 0.5 h in THF and 2 h in diglyme. However, the yields of products **2a**, **3a** and **4a** were changed slightly with time after 0.5 in THF: from decrease to increase for **2a**, decrease in the whole reaction for **3a**, and from increase to decrease for **4a**. In diglyme, the yields both products **2a** and **3a** did not changed after 2 h, but the yield of **4a** was enhanced to some extwnt throughout the reaction. It is noteworthy that the yield of product **3a** has a maximal peak at about 0.5 h in THF and 1 h in diglyme. The reason may be that some product **3a** is converted to product **2a** (Figure S3A and Scheme 2).

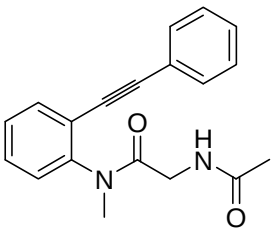
The above results of the reaction profiles also indicate that product **2a** is mainly generated form intermediate **C**, and product **4a** is not from product **3a** (Schemes 2 and 3). In THF, we find that in

THF the yield of **2a** is contrary to the yield of **4a** and has a maximal peak at about 1.5 h, suggesting that product **4a** may be from the same intermediate (intermediate **E**) with product **2a**, and the intermediate is stable to some extent among 0.5 h-1.5 h.

Notably, the rate of the reaction in diglyme is slower than that of in THF.

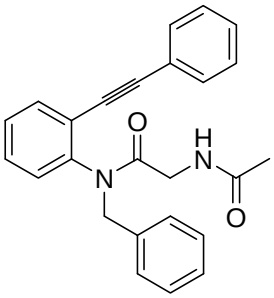
(B) Analytical data

2-Aetamido-*N*-methyl-*N*-(2-(phenylethynyl)phenyl)acetamide (1a)



Pale yellow oil, ^{1}H NMR (500 MHz) δ: 7.63 (d, *J* = 9.0 Hz, 1H), 7.48-7.35 (m, 7H), 7.27 (d, *J* = 6.5 Hz, 1H), 6.55 (s, 1H), 3.86 (d, *J* = 18.0 Hz, 1H), 3.69 (d, *J* = 17.5 Hz, 1H), 3.34 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (125 MHz) δ: 169.8, 168.6, 142.7, 133.4, 131.7, 130.1, 129.0, 128.9, 128.4, 128.1, 122.6, 122.2, 95.0, 84.4, 42.2, 36.5, 22.9; IR (KBr, cm^{-1}): 1671, 1654, 1562; LRMS (EI 70 ev) *m*/z (%): 306 (M^+, 8), 263 (100); HRMS (EI) for $C_{19}H_{18}N_2O_2$ (M^+): calcd 306.1143, found 306.1140.

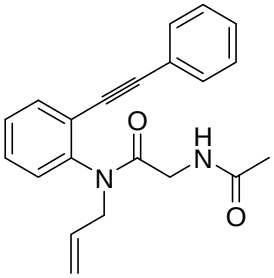
2-Acetamido-*N*-benzyl-*N*-(2-(phenylethynyl)phenyl)acetamide (1b)



Pale yellow solid, mp 148.2-150.4 ^{o}C (uncorrected); ^{1}H NMR (500 MHz) δ: 7.60 (d, *J* = 7.0 Hz, 1H), 7.47-7.45 (m, 2H), 7.36-7.33 (m, 4H), 7.25-7.20 (m, 6H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.54 (s, 1H), 5.53 (d, *J* =9.5 Hz, 1H), 4.40 (d, *J* = 9.0 Hz, 1H), 3.85 (d, *J* = 18.0 Hz, 1H), 3.72 (d, *J* = 18.0 Hz, 1H), 1.97 (s, 3H); ^{13}C NMR (125 MHz) δ: 169.8, 168.6, 141.0, 136.4, 133.4, 131.7, 129.6, 129.4, 129.2, 129.0, 128.9, 128.4, 128.3, 127.6, 123.0, 122.3, 95.2, 84.7, 52.6, 42.4, 23.0; IR (KBr, cm^{-1}):

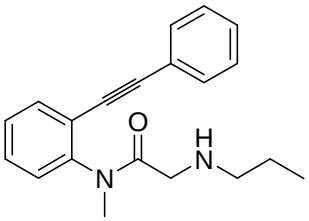
1654, 1499; LRMS (EI 70 ev) *m*/z (%): 382 (M^+, 1), 283 (100); HRMS (EI) for $C_{25}H_{22}N_2O_2$ (M^+): calcd 382.1401, found 382.1403.

2-Acetamido-*N*-allyl-*N*-(2-(phenylethynyl)phenyl)acetamide (1c)



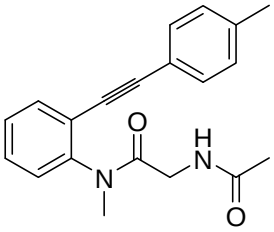
Pale yellow solid, mp 115.8-118.7 °C (uncorrected); ^{1}H NMR (500 MHz) δ: 7.63-7.61 (m, 1H), 7.48-7.46 (m, 2H), 7.41-7.38 (m, 2H), 7.36-7.34 (m, 3H), 7.22-7.20 (m, 1H), 6.52 (s, 1H), 5.93-5.87 (m, 1H), 5.14-5.10 (m, 2H), 4.75-4.70 (m, 1H), 4.09-4.05 (m, 1H), 3.84 (d, *J* = 18.0 Hz, 1H), 3.71 (d, *J* = 18.0 Hz, 1H), 1.96 (s, 3H); ^{13}C NMR (125 MHz) δ: 169.8, 168.3, 141.1, 133.3, 132.3, 131.6, 129.7, 129.2, 128.9, 128.8, 128.4, 123.1, 122.3, 118.7, 95.2, 84.9, 52.0, 42.4, 22.9; IR (KBr, cm^{-1}): 1650, 1499; LRMS (EI 70 ev) *m*/z (%): 332 (M^+, 2), 232 (100); HRMS (EI) for $C_{21}H_{20}N_2O_2$ (M^+): calcd 332.1278, found 332.1274.

***N*-methyl-*N*-(2-(phenylethynyl)phenyl)-2-(propylamino)acetamide (1d)**



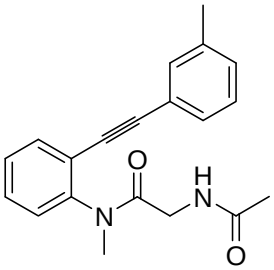
Pale yellow oil; ^{1}H NMR (500 MHz) δ: 7.63 (d, *J* = 7.0 Hz, 1H), 7.50-7.48 (m, 2H), 7.41-7.38 (m, 2H), 7.37-7.33 (m, 3H), 7.27-7.24 (m, 1H), 3.34 (s, 3H), 3.13 (d, *J* = 8.0 Hz, 2H), 2.91-2.39 (m, 2H), 1.44-1.40 (m, 2H), 0.79 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz) δ: 171.4, 143.9, 133.1, 131.7, 129.8, 128.8, 128.4, 128.4, 128.2, 122.7, 122.3, 94.9, 84.7, 51.5, 50.5, 36.3, 22.9, 11.5; IR (KBr, cm^{-1}): 1653; LRMS (EI 70 ev) *m*/z (%): 306 (M^+, 5), 72 (100); HRMS (EI) for $C_{20}H_{22}N_2O$ (M^+): calcd 306.1485, found 306.1483.

2-Acetamido-*N*-methyl-*N*-(2-(p-tolylethynyl)phenyl)acetamide (1e)



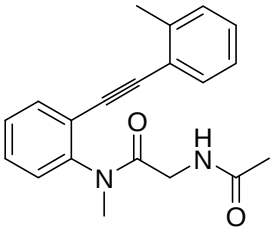
Pale yellow solid, mp 130.2-132.7 °C (uncorrected); ^{1}H NMR (500 MHz) δ: 7.61-7.59 (m, 1H), 7.41-7.38 (m, 2H), 7.36 (d, *J* = 7.5 Hz, 2H), 7.28-7.25 (m, 1H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.55 (s, 1H), 3.86 (d, *J* = 18.0 Hz, 1H), 3.72 (d, *J* = 18.0 Hz, 25.5H), 3.33 (s, 3H), 2.36 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (125 MHz) δ: 169.8, 168.6, 142.7, 139.1, 133.2, 131.5, 130.6, 129.2, 128.9, 128.0, 122.8, 119.1, 95.2, 83.8, 42.1, 36.5, 22.9, 21.5; IR (KBr, cm^{-1}): 1654, 1511; LRMS (EI 70 ev) *m*/z (%): 320 (M^+, 19), 220 (100); HRMS (EI) for $C_{20}H_{20}N_2O_2$ (M^+): calcd 320.1283, found 320.1286.

2-Acetamido-*N*-methyl-*N*-(2-(m-tolylethynyl)phenyl)acetamide (1f)



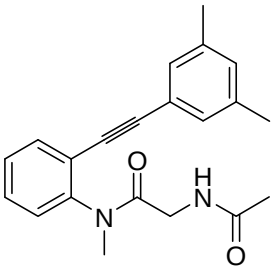
Pale yellow oil; ^{1}H NMR (500 MHz) δ: 7.62-7.60 (m, 1H), 7.43-7.38 (m, 2H), 7.28-7.22 (m, 4H), 7.17 (d, *J* = 7.5 Hz, 1H), 6.60 (s, 1H), 3.86 (d, *J* = 17.5 Hz, 1H), 3.68 (d, *J* = 18.0 Hz, 1H), 3.34 (s, 3H), 2.35 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (125 MHz) δ: 169.8, 168.5, 142.6, 138.0, 133.2, 131.9, 129.9, 129.7, 128.8, 128.7, 128.2, 127.9, 122.5, 121.9, 95.0, 83.9, 42.0, 36.3, 22.7, 21.0; IR (KBr, cm^{-1}): 1653, 1510; LRMS (EI 70 ev) *m*/z (%): 320 (M^+, 19), 221 (100); HRMS (EI) for $C_{20}H_{20}N_2O_2$ (M^+): calcd 320.1283, found 320.1280.

2-Acetamido-*N*-methyl-*N*-(2-(o-tolylethynyl)phenyl)acetamide (1g)



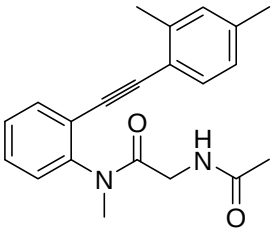
Pale yellow solid, mp 128.2-129.6 °C (uncorrected); ^{1}H NMR (500 MHz) δ: 7.65-7.63 (m, 1H), 7.46-7.39 (m, 3H), 7.27-7.24 (m, 3H), 7.22-7.15 (m, 1H), 6.55 (s, 1H), 3.85 (d, *J* = 17.5 Hz, 1H), 3.71 (d, *J* = 18.0 Hz, 1H), 3.34 (s, 3H), 2.43 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (125 MHz) δ: 169.8, 168.3, 142.4, 140.1, 133.6, 132.2, 130.0, 129.5, 129.0, 128.9, 128.1, 125.6, 122.8, 122.1, 93.7, 88.2, 42.2, 36.4, 23.0, 20.7; IR (KBr, cm^{-1}): 1654, 1514; LRMS (EI 70 ev) *m*/z (%): 320 (M^+, 13), 220 (100); HRMS (EI) for $C_{20}H_{20}N_2O_2$ (M^+): calcd 320.1283, found 320.1282.

2-Acetamido-*N*-(2-((3,5-dimethylphenyl)ethynyl)phenyl)-*N*-methylacetamide (1h)



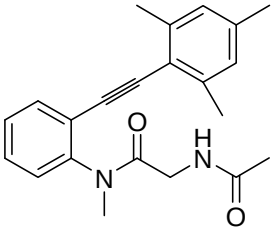
Pale yellow oil; ^{1}H NMR (500 MHz) δ: 7.61-7.59 (m, 1H), 7.42-7.37 (m, 2H), 7.28-7.24 (m, 1H), 7.10 (s, 2H), 7.00 (s, 1H), 6.64 (s, 1H), 3.87 (d, *J* = 18.0 Hz, 1H), 3.67 (d, *J* = 18.0 Hz, 1H), 3.34 (s, 3H), 2.30 (s, 6H), 1.97 (s, 3H); ^{13}C NMR (125 MHz) δ: 169.8, 168.5, 142.6, 137.9, 133.3, 130.8, 129.8, 129.2, 128.8, 128.0, 122.7, 121.8, 95.3, 83.6, 42.1, 36.4, 22.8, 21.0; IR (KBr, cm^{-1}): 1654, 1513; LRMS (EI 70 ev) *m*/z (%): 334 (M^+, 19), 235 (100); HRMS (EI) for $C_{21}H_{22}N_2O_2$ (M^+): calcd 334.1423, found 334.1420.

2-Acetamido-*N*-(2-((2,4-dimethylphenyl)ethynyl)phenyl)-*N*-methylacetamide (1i)



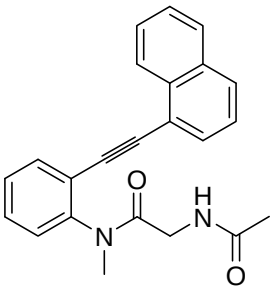
Pale yellow solid, mp 143.2-145.8 °C (uncorrected); ^{1}H NMR (500 MHz) δ: 7.63 (d, *J* = 8.5 Hz, 1H), 7.41-7.37 (m, 2H), 7.34 (d, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.03 (s, 1H), 6.97 (d, *J* = 7.5 Hz, 1H), 6.71 (s, 1H), 3.82 (d, *J* = 18.0 Hz, 1H), 3.70 (d, *J* = 17.5 Hz, 1H), 3.33 (s, 3H), 2.39 (s, 3H), 2.32 (s, 3H), 1.96 (s, 3H); ^{13}C NMR (125 MHz) δ: 169.8, 168.3, 142.1, 139.8, 139.1, 133.3, 132.0, 130.2, 129.7, 128.8, 127.9, 126.3, 122.9, 118.9, 93.9, 87.5, 42.0, 36.3, 22.7, 21.3, 20.5; IR (KBr, cm^{-1}): 1653, 1516; LRMS (EI 70 ev) *m*/z (%): 334 (M^+, 10), 43 (100); HRMS (EI) for $C_{21}H_{22}N_2O_2$ (M^+): calcd 334.1423, found 334.1421.

2-Acetamido-*N*-(2-(mesitylethynyl)phenyl)-*N*-methylacetamide (1j)



Pale yellow solid, mp 166.2-168.8 °C (uncorrected); ^{1}H NMR (500 MHz) δ: 7.65-7.63 (m, 1H), 7.41-7.38 (m, 2H), 7.25-7.23 (m, 1H), 6.89 (s, 2H), 6.57 (s, 1H), 3.85 (d, *J* = 18.0 Hz, 1H), 3.72-3.69 (d, *J* = 18.0 Hz, 1H), 3.34 (s, 3H), 2.40 (s, 6H), 2.29 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (125 MHz) δ: 169.7, 168.1, 141.8, 140.3, 138.6, 133.6, 129.7, 128.9, 128.1, 127.7, 123.2, 119.0, 92.7, 92.1, 42.1, 36.4, 22.9, 21.3, 20.9; IR (KBr, cm^{-1}): 1655, 1518; LRMS (EI 70 ev) *m*/z (%): 348 (M^+, 12), 249 (100); HRMS (EI) for $C_{22}H_{24}N_2O_2$ (M^+): calcd 348.1563, found 348.1565.

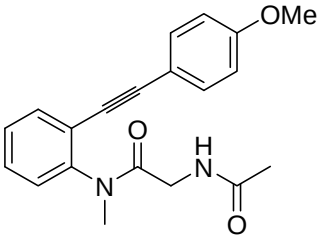
2-Acetamido-*N*-methyl-*N*-(2-(naphthalen-1-ylethynyl)phenyl)acetamide (1k)



Pale yellow oil; ^{1}H NMR (500 MHz) δ: 8.26 (d, *J* = 8.5 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.72 (t, *J* = 7.0 Hz, 2H), 7.61 (t, *J* = 8.0 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.44-7.41 (m, 3H), 7.29 (d, *J* =

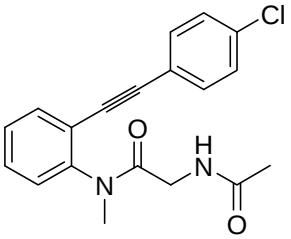
8.0 Hz, 1H), 6.73 (s, 1H), 3.91 (d, *J* = 18.0 Hz, 1H), 3.76 (d, *J* = 18.0 Hz, 1H), 3.40 (s, 3H), 1.92 (s, 3H); ^{13}C NMR (125 MHz) δ: 169.9, 168.4, 142.5, 133.5, 132.9, 132.8, 130.9, 130.1, 129.3, 128.9, 128.2, 128.1, 127.0, 126.4, 125.7, 125.1, 122.5, 119.7, 92.9, 89.1, 42.1, 36.5, 22.7; IR (KBr, cm^{-1}): 1654, 1544; LRMS (EI 70 ev) *m*/z (%): 356 (M^+, 43), 256 (100); HRMS (EI) for $C_{23}H_{20}N_2O_2$ (M^+): calcd 356.1267, found 356.1263.

2-Acetamido-*N*-(2-((4-methoxyphenyl)ethynyl)phenyl)-*N*-methylacetamide (1l)



Pale yellow oil; ^{1}H NMR (500 MHz) δ: 7.60-7.57 (m, 1H), 7.42-7.37 (m, 4H), 7.27-7.24 (m, 1H), 6.89-6.86 (m, 2H), 6.56 (s, 1H), 3.86 (d, *J* = 18.0 Hz, 1H), 3.82 (s, 3H), 3.68 (d, *J* = 18.0 Hz, 1H), 3.33 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (125 MHz) δ: 169.8, 168.6, 160.1, 142.5, 133.2, 133.1, 129.6, 128.9, 128.0, 122.9, 114.3, 114.1, 95.2, 83.2, 55.3, 42.1, 36.5, 22.9; IR (KBr, cm^{-1}): 1658, 1539; LRMS (EI 70 ev) *m*/z (%): 336 (M^+, 8), 236 (100); HRMS (EI) for $C_{20}H_{20}N_2O_3$ (M^+): calcd 336.1227, found 336.1225.

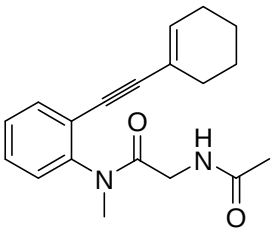
2-Acetamido-*N*-(2-((4-chlorophenyl)ethynyl)phenyl)-*N*-methylacetamide (1m)



Pale yellow solid, mp 103.9-105.8 °C (uncorrected); ^{1}H NMR (500 MHz) δ: 7.61-7.60 (m, 1H), 7.44-7.38 (m, 4H), 7.31-7.27 (m, 3H), 6.72 (s, 1H), 3.84 (d, *J* = 18.0 Hz, 1H), 3.73 (d, *J* = 18.0 Hz, 1H), 3.32 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (125 MHz) δ: 169.8, 168.5, 142.7, 134.8, 133.2, 130.2, 129.4, 128.8, 128.6, 128.0, 122.1, 120.5, 93.6, 85.2, 42.0, 36.4, 22.7; IR (KBr, cm^{-1}): 1654, 1520;

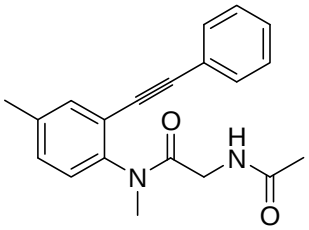
LRMS (EI 70 ev) *m*/z (%): 342 (M^++2, 7), 340 (M^+, 18), 241 (100); HRMS (EI) for $C_{19}H_{17}ClN_2O_2$ (M^+): calcd 340.0979, found 340.0974.

2-Acetamido-*N*-(2-(cyclohexenylethynyl)phenyl)-*N*-methylacetamide (1n)



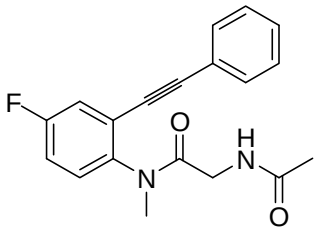
Pale yellow oil; ^{1}H NMR (500 MHz) δ: 7.50 (d, *J* = 7.0 Hz, 1H), 7.37-7.33 (m, 2H), 7.23 (d, *J* =7.0 Hz, 1H), 6.77 (s, 1H), 6.19 (s, 1H), 3.82 (d, *J* = 18.0 Hz, 1H), 3.61 (d, *J* = 18.0 Hz, 1H), 3.27 (s, 3H), 2.14 (s, 4H), 1.97 (s, 3H), 1.66-1.60 (m, 4H); ^{13}C NMR (125 MHz) δ: 170.0, 168.6, 142.6, 136.6, 133.1, 129.5, 128.8, 127.9, 123.0, 120.2, 97.0, 81.9, 42.0, 36.3, 28.9, 25.7, 22.8, 22.1, 21.3; IR (KBr, cm^{-1}): 1657, 1548; LRMS (EI 70 ev) *m*/z (%): 310 (M^+, 1), 238 (100), 210 (40); HRMS (EI) for $C_{19}H_{22}N_2O_2$ (M^+): calcd 310.1434, found 310.1432.

2-Acetamido-*N*-methyl-*N*-(4-methyl-2-(phenylethynyl)phenyl)acetamide (1p)



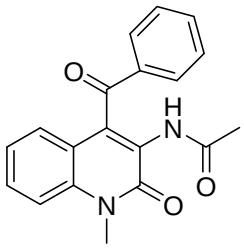
Pale yellow oil; ^{1}H NMR (500 MHz) δ: 7.46-7.43 (m, 3H), 7.35 (s, 3H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 1H), 6.56 (s, 1H), 3.84 (d, *J* = 18.0 Hz, 1H), 3.68 (d, *J* = 17.5 Hz, 1H), 3.32 (s, 3H), 2.39 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (125 MHz) δ: 169.8, 168.7, 140.2, 139.1, 133.8, 131.6, 130.9, 128.8, 128.4, 127.7, 122.3, 122.1, 94.5, 84.6, 42.1, 36.5, 22.9, 20.9; IR (KBr, cm^{-1}): 1654, 1495; LRMS (EI 70 ev) *m*/z (%): 320 (M^+, 14), 220 (100); HRMS (EI) for $C_{20}H_{20}N_2O_2$ (M^+): calcd 320.1283, found 320.1287.

2-Acetamido-*N*-(4-fluoro-2-(phenylethynyl)phenyl)-*N*-methylacetamide (1q)



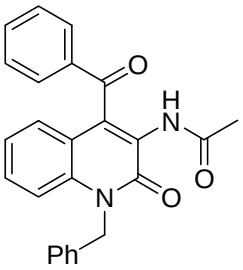
Pale yellow solid, mp 124.3-126.8 °C (uncorrected); ^{1}H NMR (500 MHz) δ: 7.48-7.46 (m, 2H), 7.40-7.37 (m, 3H), 7.35-7.30 (m, 1H), 7.27-7.24 (m, 1H), 7.14-7.10 (m, 1H), 6.52 (s, 2H), 3.85 (d, *J* = 18.0 Hz, 1H), 3.69 (d, *J* = 17.5 Hz, 1H), 3.32 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (125 MHz) δ: 169.3 (d, *J* = 144.4 Hz, 1C), 161.9 (d, *J* = 248.9 Hz, 1C), 139.0, 131.8, 129.9, 129.8, 129.2, 128.5, 124.6 (d, *J* = 10.6 Hz, 1C), 121.7, 119.9 (d, *J* = 24.3 Hz, 1C), 117.4 (d, *J* = 22.8 Hz, 1C), 96.0, 83.4 (d, *J* = 2.8 Hz, 1C), 42.1, 36.6, 22.9; IR (KBr, cm^{-1}): 1654, 1516; LRMS (EI 70 ev) *m*/z (%): 324 (M^+, 11), 225 (100); HRMS (EI) for $C_{19}H_{17}FN_2O_2$ (M^+): calcd 324.1049, found 324.1047.

_N_-(4-Benzoyl-1-methyl-2-oxo-1,2-dihydroquinolin-3-yl)acetamide (2a)



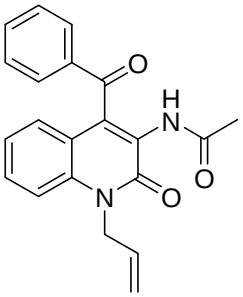
Hoar solid, mp 114.2-116.4 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.50 (s, 1H), 7.91 (d, *J* = 8.5 Hz, 2H), 7.57-7.49 (m, 2H), 7.44 (t, *J* = 8.0 Hz, 3H), 7.39 (d, *J* = 9.0 Hz, 1H), 7.13-7.10 (m, 1H), 3.87 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 192.0, 168.1, 158.2, 138.0, 136.1, 133.0, 129.4, 129.3, 128.5, 127.2, 123.8, 123.1, 118.7, 114.4, 30.9, 23.8; IR (KBr, cm^{-1}): 1686, 1659, 1634, 1593; LRMS (EI 70 ev) *m*/z (%): 320 (M^+, 19), 278 (100); HRMS (EI) for $C_{19}H_{16}N_2O_3$ (M^+): calcd 320.1161, found 320.1163.

_N_-(4-Benzoyl-1-benzyl-2-oxo-1,2-dihydroquinolin-3-yl)acetamide (2b)



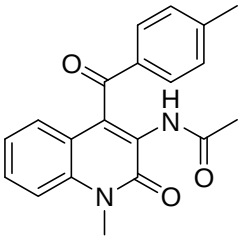
Hoar solid, mp 254.2-256.3 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.55 (s, 1H), 7.95 (d, *J* = 8.5 Hz, 2H), 7.58-7.55 (m, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.38-7.33 (m, 5H), 7.29-7.24 (m, 3H), 7.07-7.04 (m, 1H), 5.67 (s, 2H), 2.06 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 192.0, 168.1, 158.5, 137.9, 135.5, 135.3, 133.1, 129.4, 129.3, 129.0, 128.5, 127.7, 127.3, 126.5, 123.7, 123.2, 119.0, 115.2, 47.5, 23.8; IR (KBr, cm^{-1}): 1667, 1634, 1601; LRMS (EI 70 ev) *m*/z (%): 396 (M^+, 45), 354 (100); HRMS (EI) for $C_{25}H_{20}N_2O_3$ (M^+): calcd 396.1474, found 396.1473.

_N_-(1-Allyl-4-benzoyl-2-oxo-1,2-dihydroquinolin-3-yl)acetamide (2c)



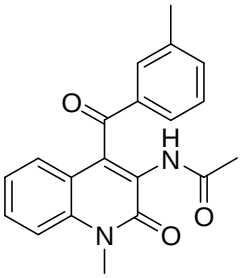
Hoar solid, mp 126.3-128.1 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.53 (s, 1H), 7.93 (d, *J* = 8.5 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.48-7.43 (m, 3H), 7.40-7.37 (m, 2H), 7.10 (t, *J* = 8.5 Hz, 1H), 6.04-5.96 (m, 1H), 5.31 (d, *J* = 10.5 Hz, 1H), 5.20 (d, *J* = 17.5 Hz, 1H), 5.07 (s, 2H), 2.05 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 192.0, 168.1, 157.9, 137.9, 135.3, 133.0, 130.8, 129.3, 129.2, 128.4, 127.2, 123.7, 123.1, 118.8, 117.8, 114.9, 46.0, 23.7; IR (KBr, cm^{-1}): 1671, 1634, 1601; LRMS (EI 70 ev) *m*/z (%): 346 (M^+, 24), 304 (100); HRMS (EI) for $C_{21}H_{18}N_2O_3$ (M^+): calcd 346.1317, found 346.1315.

_N_-(1-Methyl-4-(4-methylbenzoyl)-2-oxo-1,2-dihydroquinolin-3-yl)acetamide (2e)



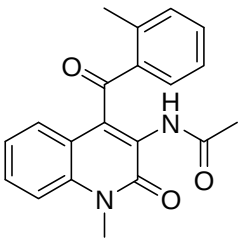
Hoar solid, mp 138.3-140.2 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.47 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.43-7.38 (m, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.11 (t, *J* = 7.5 Hz, 1H), 3.86 (s, 3H), 2.40 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 191.9, 168.2, 158.3, 143.9, 136.1, 135.4, 129.4, 129.2, 127.2, 123.7, 123.0, 118.7, 114.3, 30.8, 23.7, 21.7; IR (KBr, cm^{-1}): 1667, 1634, 1601; LRMS (EI 70 ev) *m*/z (%): 334 (M^+, 28), 292 (100); HRMS (EI) for $C_{20}H_{18}N_2O_3$ (M^+): calcd 334.1317, found 334.1313.

_N_-(1-Methyl-4-(3-methylbenzoyl)-2-oxo-1,2-dihydroquinolin-3-yl)acetamide (2f)



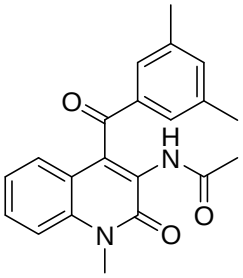
Hoar solid, mp 120.3-122.8 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.50 (s, 1H), 7.78 (s, 1H), 7.65 (d, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.5 Hz, 1H), 7.38-7.35 (m, 2H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 3.87 (s, 3H), 2.38 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 192.2, 168.1, 158.2, 138.2, 137.9, 136.0, 133.9, 129.4, 128.3, 127.2, 126.9, 123.6, 123.1, 118.7, 114.3, 30.8, 23.7, 21.3; IR (KBr, cm^{-1}): 1670, 1638, 1601; LRMS (EI 70 ev) *m*/z (%): 334 (M^+, 26), 292 (100); HRMS (EI) for $C_{20}H_{18}N_2O_3$ (M^+): calcd 334.1317, found 334.1315.

_N_-(1-Methyl-4-(2-methylbenzoyl)-2-oxo-1,2-dihydroquinolin-3-yl)acetamide (2g)



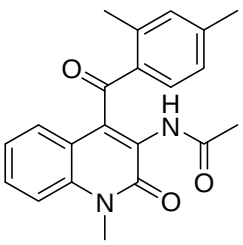
Hoar solid, mp 190.6-192.3 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.36 (s, 1H), 7.55-7.46 (m, 3H), 7.42-7.37 (m, 2H), 7.31 (d, *J* = 7.5 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 2H), 3.84 (s, 3H), 2.73 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 193.5, 168.3, 158.4, 140.4, 136.3, 136.0, 132.2, 132.1, 129.4, 126.8, 125.4, 123.6, 123.1, 118.7, 114.3, 30.7, 23.6, 21.8; IR (KBr, cm^{-1}): 1667, 1637, 1601; LRMS (EI 70 ev) *m*/z (%): 334 (M^+, 23), 292 (100); HRMS (EI) for $C_{20}H_{18}N_2O_3$ (M^+): calcd 334.1317, found 334.1319.

_N_-(4-(3,5-Dimethylbenzoyl)-1-methyl-2-oxo-1,2-dihydroquinolin-3-yl)acetamide (2h)



Hoar solid, mp 191.6-193.8 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.54 (s, 1H), 7.52 (s, 2H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.5 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.18 (s, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 3.87 (s, 3H), 2.31 (s, 6H), 2.07 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 192.4, 168.0, 158.2, 138.0, 137.9, 136.0, 135.0, 129.3, 127.2, 127.0, 123.5, 123.0, 118.7, 114.3, 30.8, 23.7, 21.2 (2C); IR (KBr, cm^{-1}): 1671, 1634, 1601; LRMS (EI 70 ev) *m*/z (%): 348 (M^+, 38), 306 (100); HRMS (EI) for $C_{21}H_{20}N_2O_3$ (M^+): calcd 348.1474, found 348.1471.

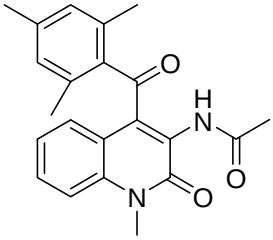
_N_-(4-(2,4-Dimethylbenzoyl)-1-methyl-2-oxo-1,2-dihydroquinolin-3-yl)acetamide (2i)



Hoar solid, mp 172.1-174.6 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.33 (s, 1H), 7.51-7.48 (m, 1H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 1H), 7.14 (s, 1H), 7.12 (d, *J* = 6.0 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 3.84 (s, 3H), 2.71 (s, 3H), 2.34 (s, 3H), 2.03 (s, 3H); ^{13}C NMR

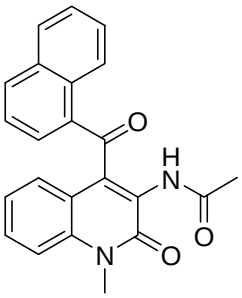
(125 MHz, $CDCl_3$) δ: 193.0, 168.0, 158.2, 142.6, 140.3, 136.0, 133.2, 132.8, 132.4, 129.1, 126.7, 125.9, 123.2, 122.8, 118.5, 114.0, 30.5, 23.4, 21.7, 21.2; IR (KBr, cm^{-1}): 1658, 1634, 1593; LRMS (EI 70 ev) *m*/z (%): 348 (M^+, 36), 306 (100); HRMS (EI) for $C_{21}H_{20}N_2O_3$ (M^+): calcd 348.1474, found 348.1473.

_N_-(1-Methyl-2-oxo-4-(2,4,6-trimethylbenzoyl)-1,2-dihydroquinolin-3-yl)acetamide (2j)



Hoar solid, mp 227.3-229.4 °C (uncorrected); ^1H NMR (500 MHz, $CDCl_3$) δ: 7.79 (d, *J* = 9.5 Hz, 1H), 7.73 (s, 1H), 7.57-7.54 (m, 1H), 7.43 (d, *J* = 8.5 Hz, 1H), 7.23-7.20 (m, 1H), 6.87 (s, 2H), 3.81 (s, 3H), 2.29 (s, 3H), 2.25 (s, 6H), 1.93 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 195.0, 169.0, 159.0, 141.2, 138.7, 137.6, 137.4, 134.8, 130.5, 130.0, 126.4, 124.4, 123.3, 117.8, 114.6, 30.7, 23.5, 22.0 (2C), 21.2; IR (KBr, cm^{-1}): 1659, 1634, 1595; LRMS (EI 70 ev) *m*/z (%): 362 (M^+, 13), 303 (100); HRMS (EI) for $C_{22}H_{22}N_2O_3$ (M^+): calcd 362.1630, found 362.1631.

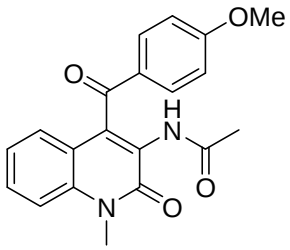
_N_-(4-(1-Naphthoyl)-1-methyl-2-oxo-1,2-dihydroquinolin-3-yl)acetamide (2k)



Hoar solid, mp 203.4-205.7 °C (uncorrected); ^1H NMR (500 MHz, $CDCl_3$) δ: 9.27 (d, *J* = 8.5 Hz, 1H), 8.30 (s, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.71-7.68 (m, 1H), 7.59-7.55 (m, 2H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 8.5 Hz, 1H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 7.5 Hz, 1H), 3.86 (s, 3H), 1.89 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 193.8, 168.6, 158.5, 136.5, 134.1, 134.0, 133.4, 132.4, 130.7, 129.6, 128.5, 128.4, 127.1, 126.5,

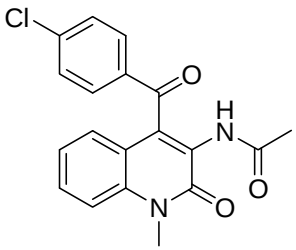
126.4, 124.2, 123.8, 123.2, 118.9, 114.4, 30.8, 23.5; IR (KBr, cm^{-1}): 1656, 1634, 1597; LRMS (EI 70 ev) *m*/z (%): 370 (M^+, 30), 327 (100); HRMS (EI) for $C_{23}H_{18}N_2O_3$ (M^+): calcd 370.1317, found 370.1316.

_N_-(4-(4-Methoxybenzoyl)-1-methyl-2-oxo-1,2-dihydroquinolin-3-yl)acetamide (2l)



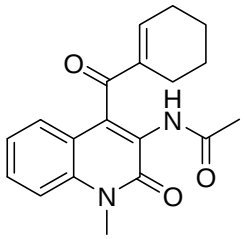
Hoar solid, mp 161.3-162.8 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.38 (s, 1H), 7.89 (d, *J* = 8.5 Hz, 2H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 7.0 Hz, 2H), 7.13 (t, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 8.5 Hz, 2H), 3.86 (s, 3H), 3.85 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 191.0, 163.5, 158.4, 136.3, 131.7, 130.8, 129.5, 127.3 (2C), 123.7, 123.1 (2C), 118.7, 114.3, 113.8, 55.4, 30.8, 23.7; IR (KBr, cm^{-1}): 1638, 1593, 1507; LRMS (EI 70 ev) *m*/z (%): 350 (M^+, 13), 271 (63), 40 (100); HRMS (EI) for $C_{20}H_{18}N_2O_4$ (M^+): calcd 350.1266, found 350.1263.

_N_-(4-(4-Chlorobenzoyl)-1-methyl-2-oxo-1,2-dihydroquinolin-3-yl)acetamide (2m)



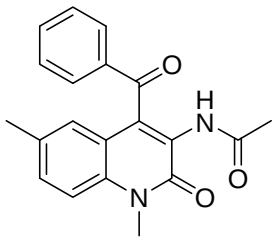
Hoar solid, mp 116.7-118.9 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.60 (s, 1H), 7.86 (d, *J* = 8.5 Hz, 2H), 7.54-7.50 (m, 1H), 7.46-7.40 (m, 3H), 7.17 (d, *J* = 9.5 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 3.87 (s, 3H), 2.09 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 190.7, 168.2, 158.1, 139.4, 136.5, 136.0, 130.6, 129.5, 129.1, 128.8, 127.0, 123.8, 123.2, 118.5, 114.5, 30.9, 23.8; IR (KBr, cm^{-1}): 1667, 1638, 1597; LRMS (EI 70 ev) *m*/z (%): 356 (M^++2, 8), 354 (M^+, 21), 312 (100); HRMS (EI) for $C_{19}H_{15}ClN_2O_3$ (M^+): calcd 354.0771, found 354.0768.

_N_-(4-(Cyclohex-1-enecarbonyl)-1-methyl-2-oxo-1,2-dihydroquinolin-3-yl)acetamide (2n)



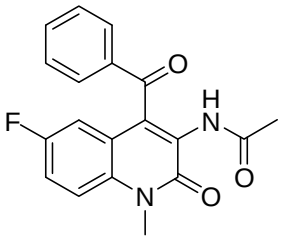
Hoar solid, mp 184.6-186.8 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.30 (s, 1H), 7.54-7.52 (m, 2H), 7.40 (d, J = 8.5 Hz, 1H), 7.24 (t, J = 7.5 Hz, 1H), 6.60 (s, 1H), 3.82 (s, 3H), 2.47 (br, 2H), 2.19 (br, 2H), 2.15 (s, 3H), 1.71 (br, 2H), 1.65 (br, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 193.4, 168.6, 158.4, 144.1, 139.7, 136.4, 133.2, 129.7, 127.0, 123.4, 123.2, 118.9, 114.3, 30.7, 26.2, 25.7, 22.6, 21.9, 21.6; IR (KBr, cm^{-1}): 1642, 1597, 1503; LRMS (EI 70 ev) m/z (%): 324 (M^+, 100), 239 (91); HRMS (EI) for $C_{19}H_{20}N_2O_3$ (M^+): calcd 324.1474, found 324.1476.

_N_-(4-Benzoyl-1,6-dimethyl-2-oxo-1,2-dihydroquinolin-3-yl)acetamide (2o)



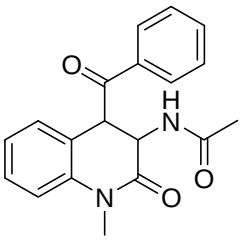
Hoar solid, mp 197.1-199.8 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.50 (s, 1H), 7.90 (d, J = 7.5 Hz, 2H), 7.55 (t, J = 7.5 Hz, 1H), 7.44 (t, J = 7.5 Hz, 2H), 7.32 (s, 2H), 7.19 (s, 1H), 3.84 (s, 3H), 2.23 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 192.1, 168.2, 158.0, 137.7, 134.2, 133.0, 132.7, 130.8, 129.2, 128.4, 126.8, 123.7, 118.5, 114.2, 30.8, 23.6, 20.8; IR (KBr, cm^{-1}): 1656, 1634, 1597; LRMS (EI 70 ev) m/z (%): 334 (M^+, 21), 292 (100); HRMS (EI) for $C_{20}H_{18}N_2O_3$ (M^+): calcd 334.1317, found 334.1312.

_N_-(4-Benzoyl-6-fluoro-1-methyl-2-oxo-1,2-dihydroquinolin-3-yl)acetamide (2o)



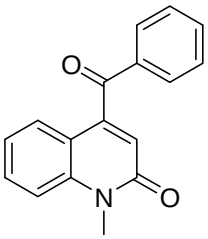
Hoar solid, mp 206.4-208.8 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.55 (s, 1H), 7.89 (d, *J* = 7.5 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.41-7.38 (m, 1H), 7.26-7.22 (m, 1H), 7.14-7.11 (m, 1H), 3.87 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 191.3, 168.1, 157.8, 137.6, 133.2, 129.2, 128.6, 124.8, 117.2 (d, *J* = 24.1 Hz, 1C), 115.9 (d, *J* = 8.6 Hz, 1C), 112.7 (d, *J* = 24.6 Hz, 1C), 31.2, 23.8; IR (KBr, cm^{-1}): 1667, 1638, 1503; LRMS (EI 70 ev) *m*/z (%): 338 (M^+, 21), 296 (100); HRMS (EI) for $C_{19}H_{15}FN_2O_3$ (M^+): calcd 338.1067, found 338.1065.

_N_-(4-Benzoyl-1-methyl-2-oxo-1,2,3,4-tetrahydroquinolin-3-yl)acetamide (3a)



Hoar solid, mp 128.3-130.4 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.00 (d, *J* = 8.5 Hz, 2H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.29-7.23 (m, 2H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.97 (t, *J* = 8.0 Hz, 1H), 6.85 (d, *J* = 5.0 Hz, 1H), 5.55 (d, *J* = 5.5 Hz, 1H), 4.85 (t, *J* = 5.5 Hz, 1H), 3.44 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 197.5, 170.7, 167.5, 140.0, 136.0, 133.8, 129.8, 129.1, 128.9, 128.8, 123.5, 121.6, 116.0, 50.9, 47.5, 30.4, 23.1; IR (KBr, cm^{-1}): 1679, 1654, 1593; LRMS (EI 70 ev) *m*/z (%): 322 (M^+, 2), 159 (100); HRMS (EI) for $C_{19}H_{18}N_2O_3$ (M^+): calcd 322.1317, found 322.1313.

4-Benzoyl-_N_-methylquinolin-2(1H)-one (4a)



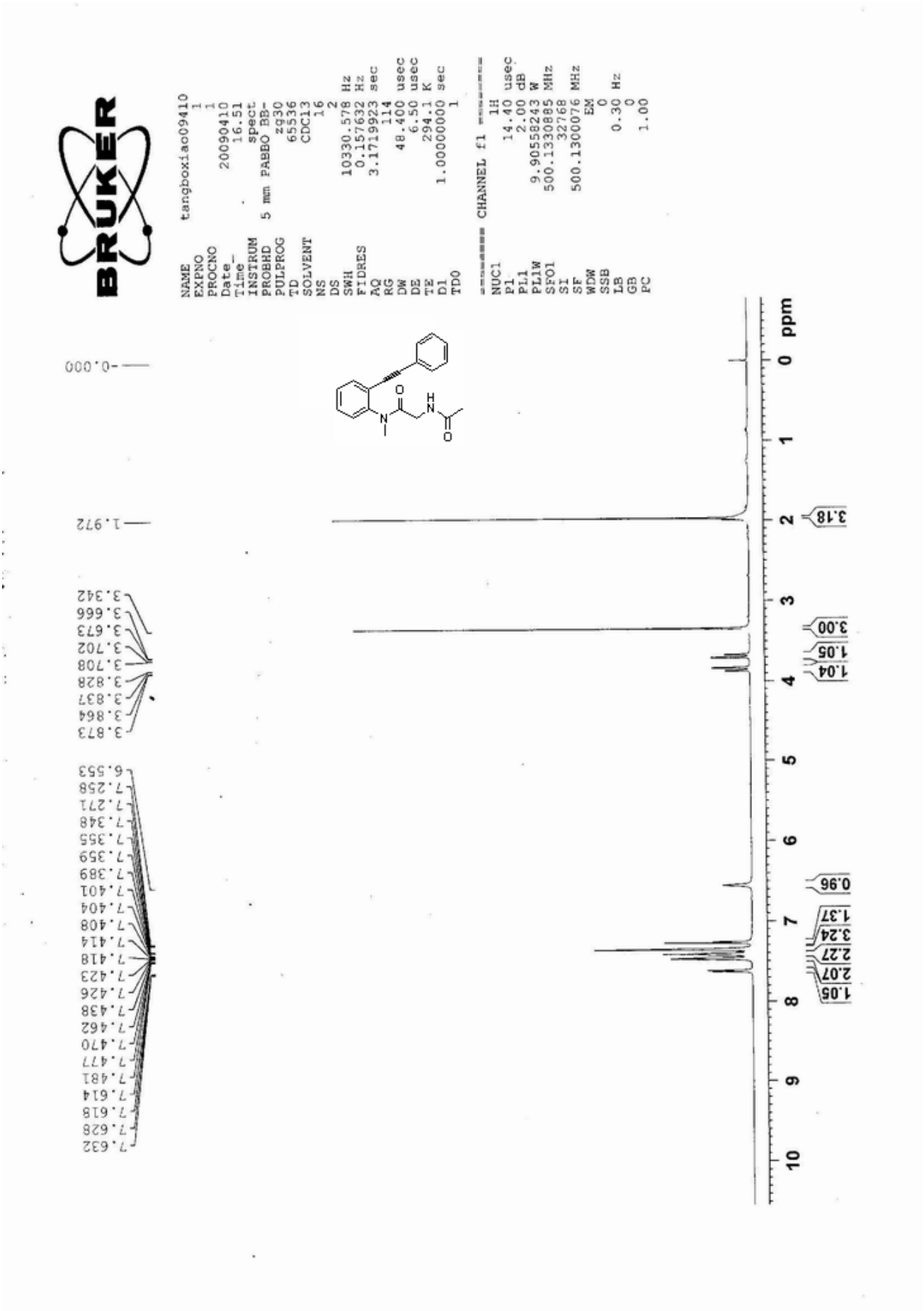
Plae yellow solid, mp 118.1-120.5 ^{o}C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.96 (d, *J* = 9.5 Hz, 2H), 7.67-7.61 (m, 2H), 7.56 (d, *J* = 9.0 Hz, 1H), 7.51-7.46 (m, 3H), 7.20 (t, *J* = 8.0 Hz, 1H), 6.73 (s, 1H), 3.80 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 194.7, 161.2, 147.3, 140.4, 135.8, 134.5, 131.4, 130.2, 128.9, 127.0, 122.6, 120.5, 118.1, 114.7, 29.7; IR (KBr, cm^{-1}): 1659, 1585; LRMS (EI 70 ev) *m*/z (%): 263 (M^+, 76), 234 (100); HRMS (EI) for $C_{17}H_{13}NO_2$ (M^+): calcd 263.0946, found 263.0943.

(C) References

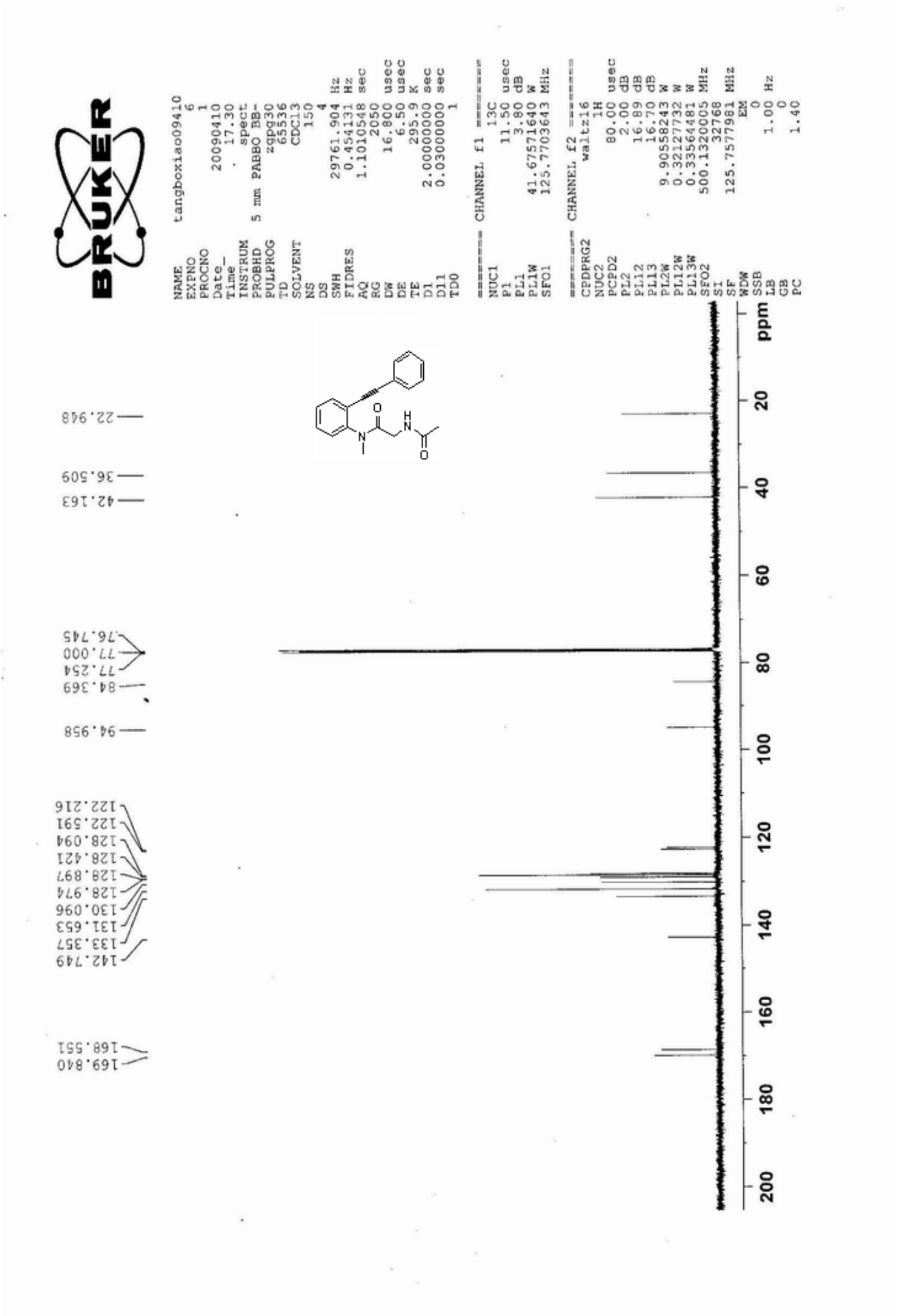
(1) Thorand, S.; Krause, N. *J. Org. Chem.* **1998**, *63*, 8551.

(D) Spectra

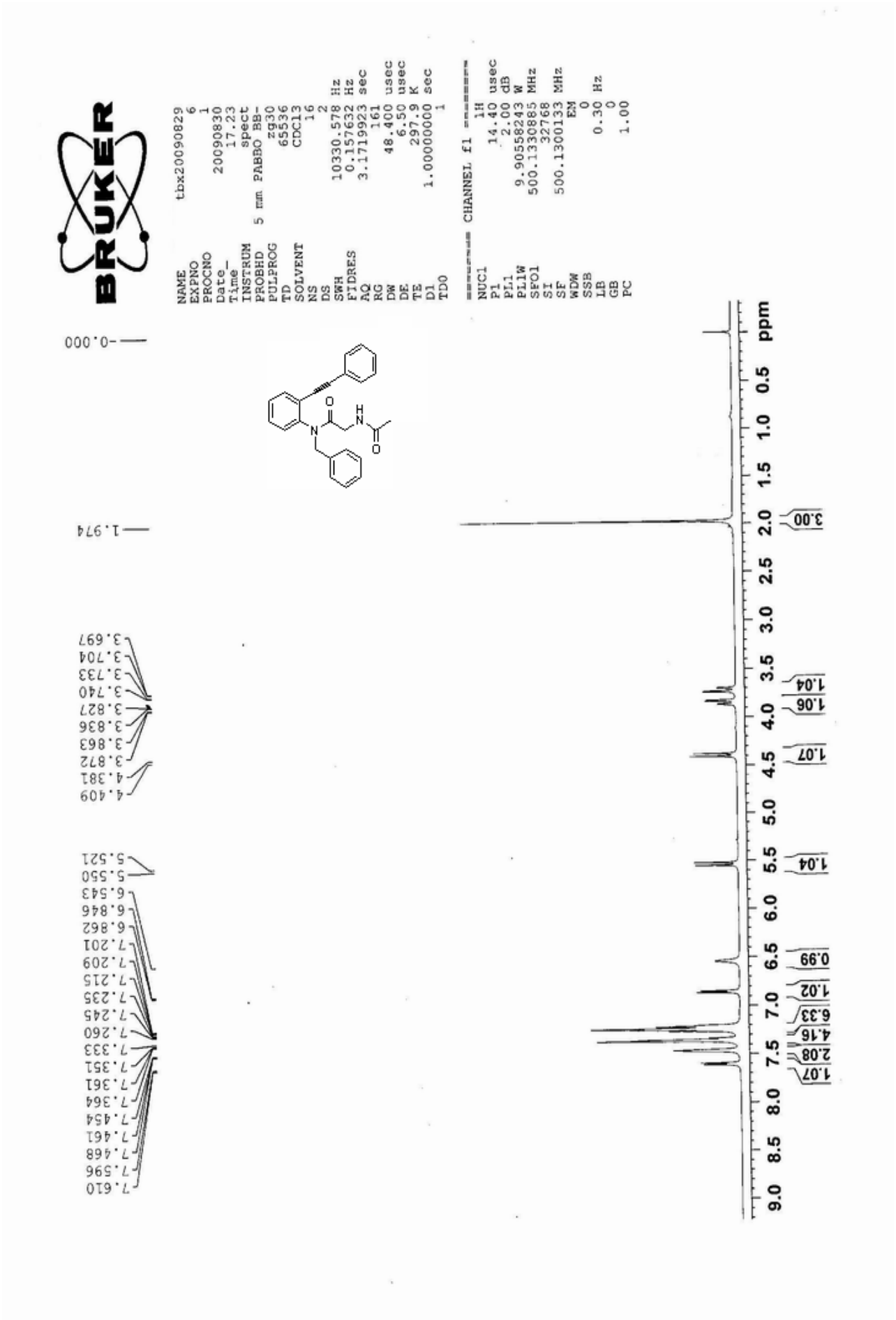
2-Aetamido-*N*-methyl-*N*-(2-(phenylethynyl)phenyl)acetamide (1a)



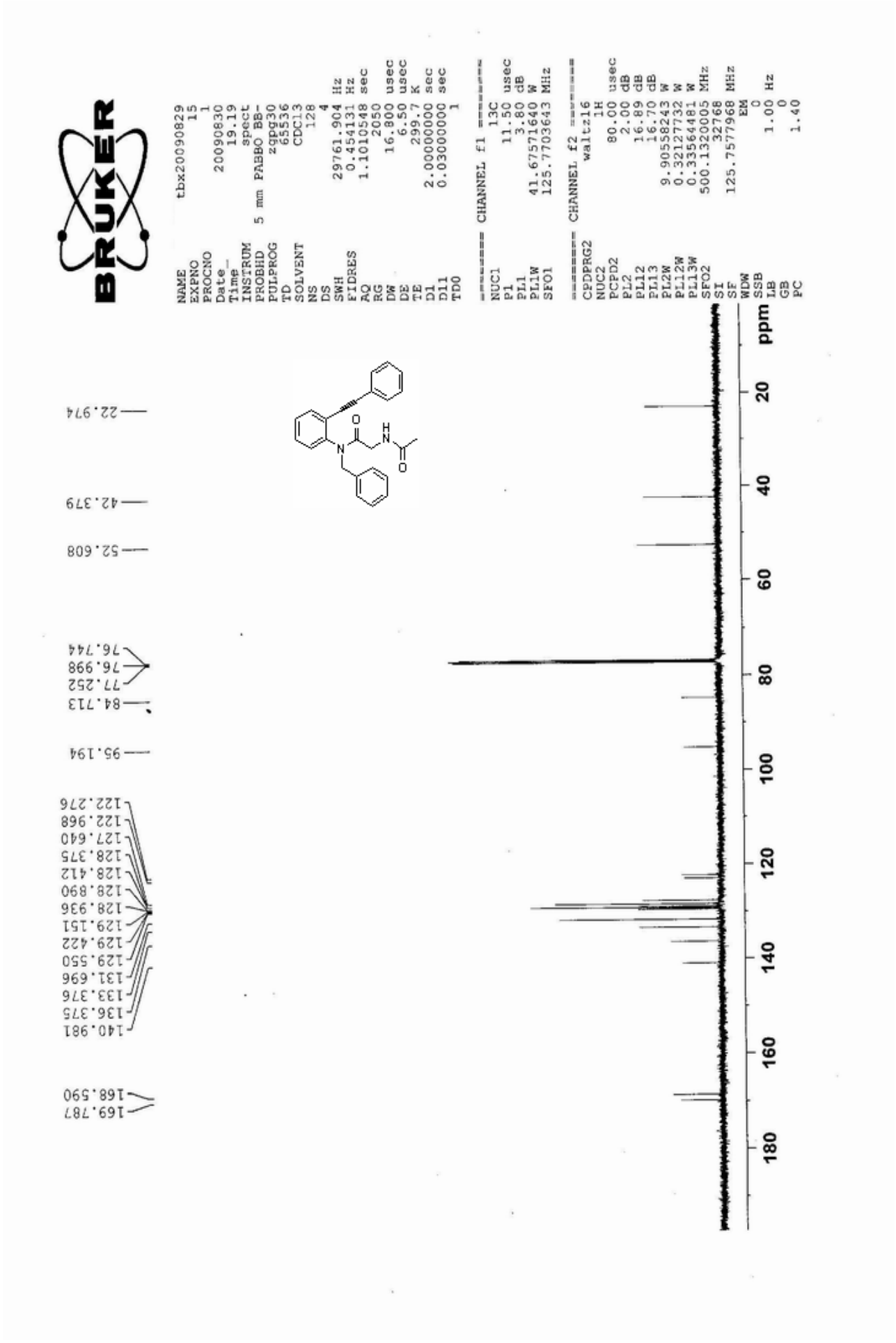
2-Aetamido-*N*-methyl-*N*-(2-(phenylethynyl)phenyl)acetamide (1a)



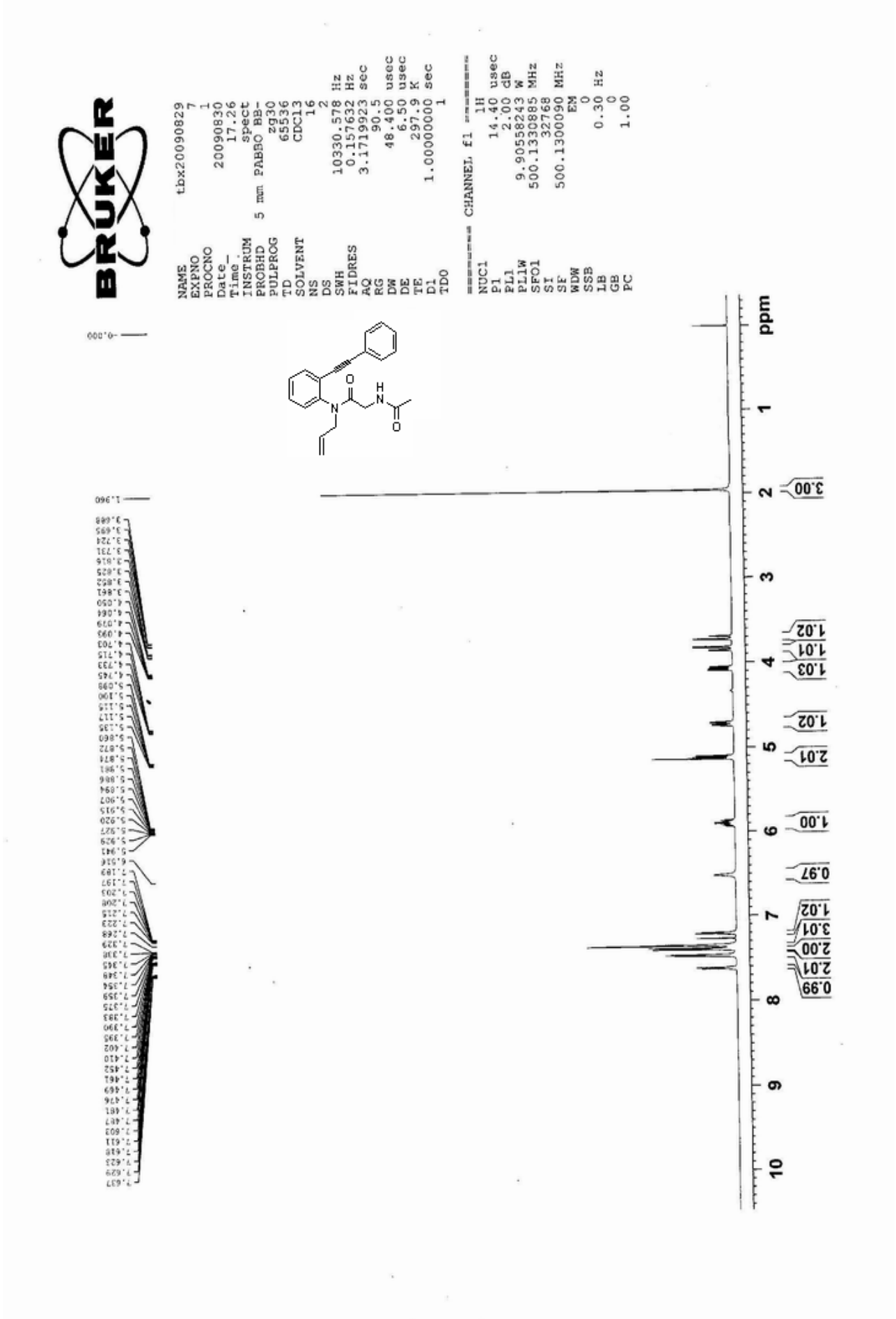
2-Acetamido-*N*-benzyl-*N*-(2-(phenylethynyl)phenyl)acetamide (1b)



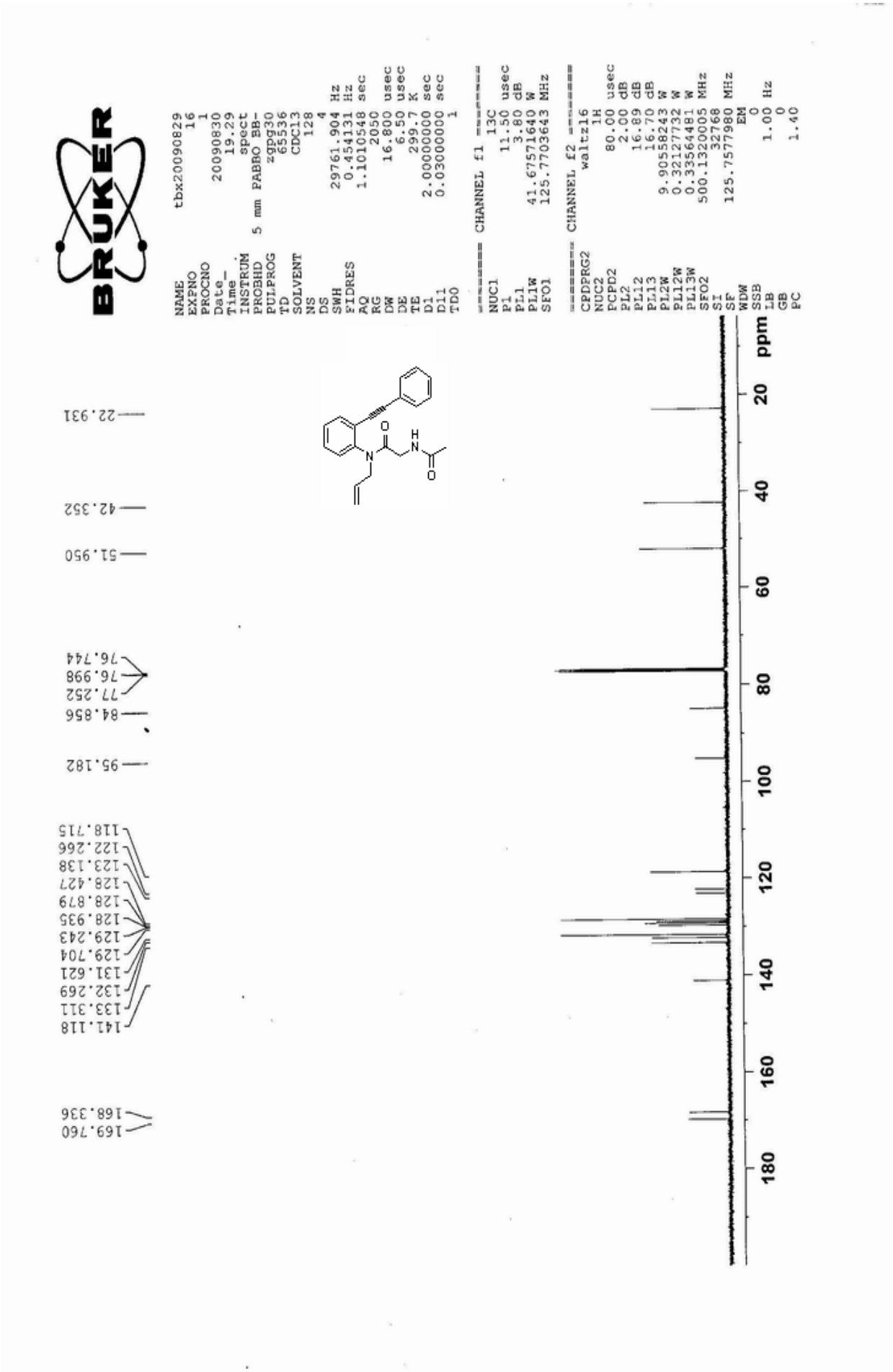
2-Acetamido-*N*-benzyl-*N*-(2-(phenylethynyl)phenyl)acetamide (1b)



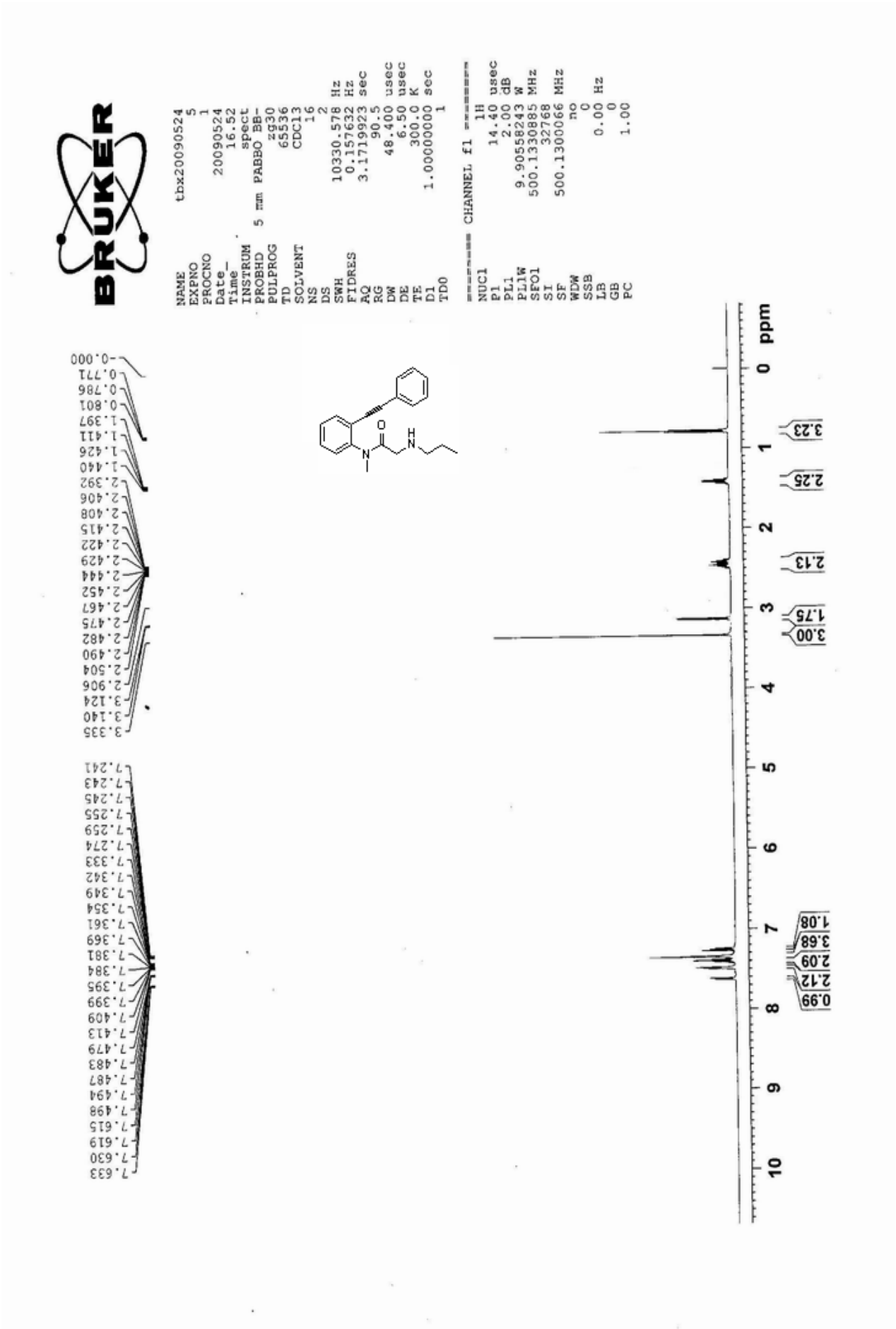
2-Acetamido-*N*-allyl-*N*-(2-(phenylethynyl)phenyl)acetamide (1c)



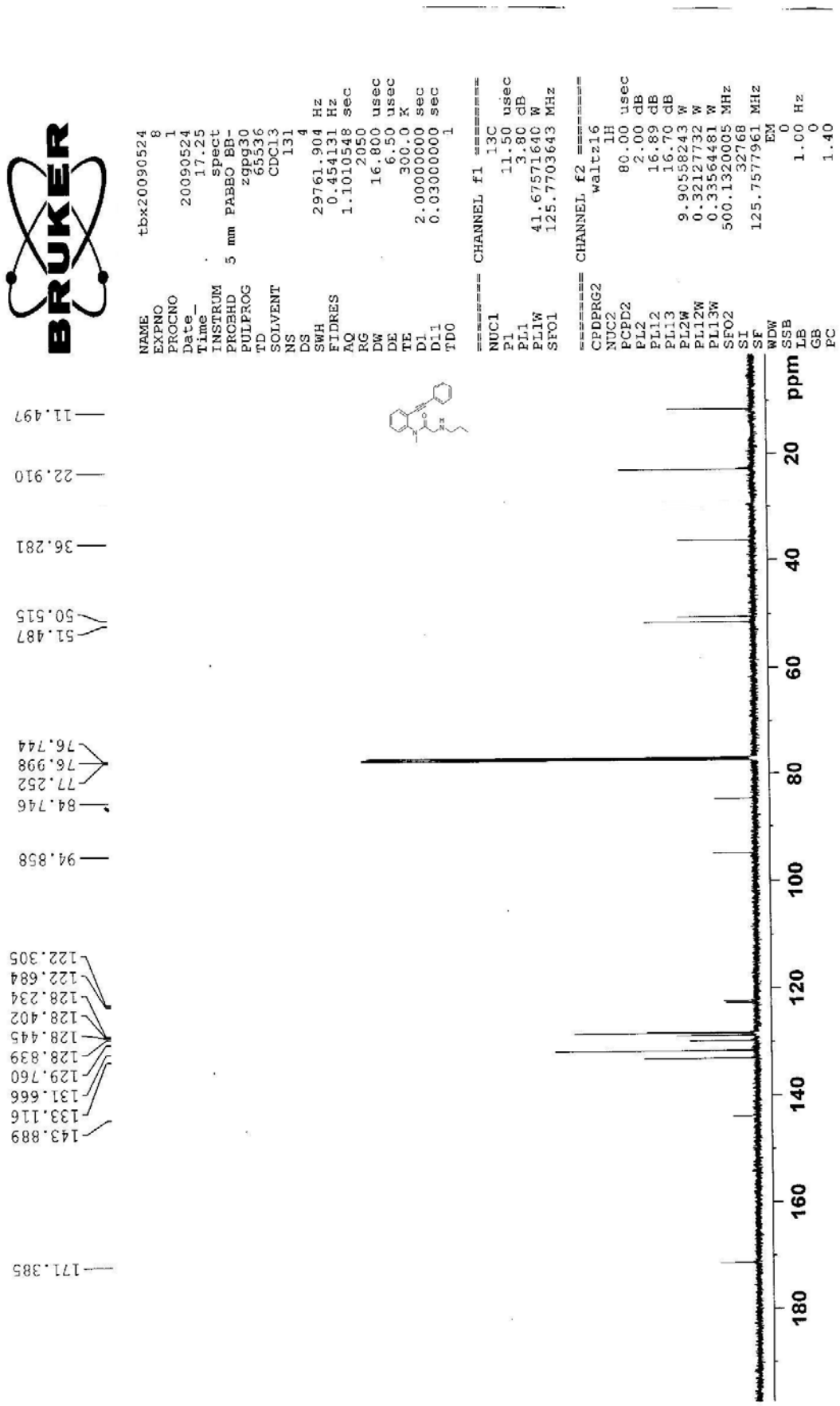
2-Acetamido-*N*-allyl-*N*-(2-(phenylethynyl)phenyl)acetamide (1c)



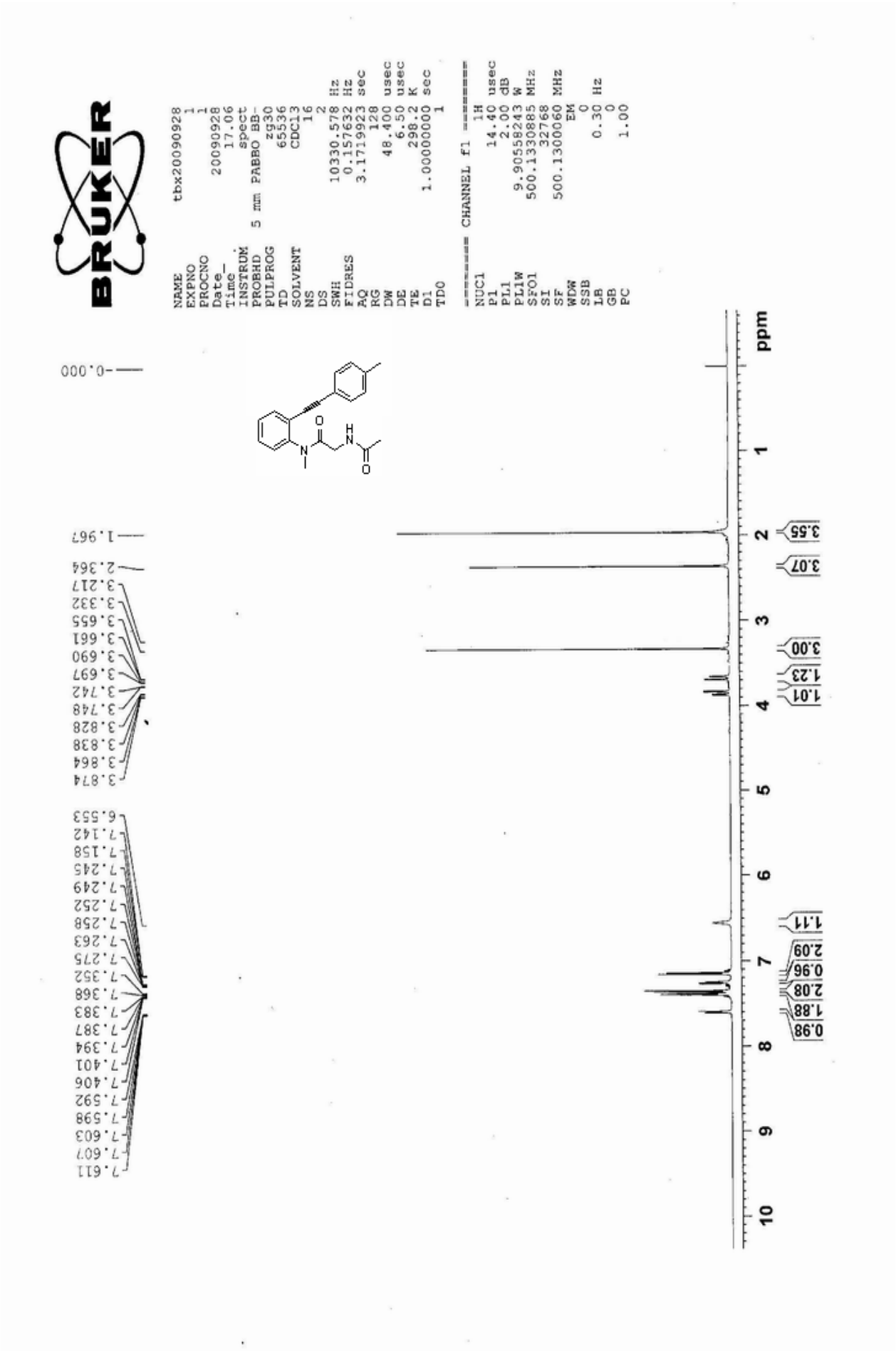
_N_-methyl-_N_-(2-(phenylethynyl)phenyl)-2-(propylamino)acetamide (1d)



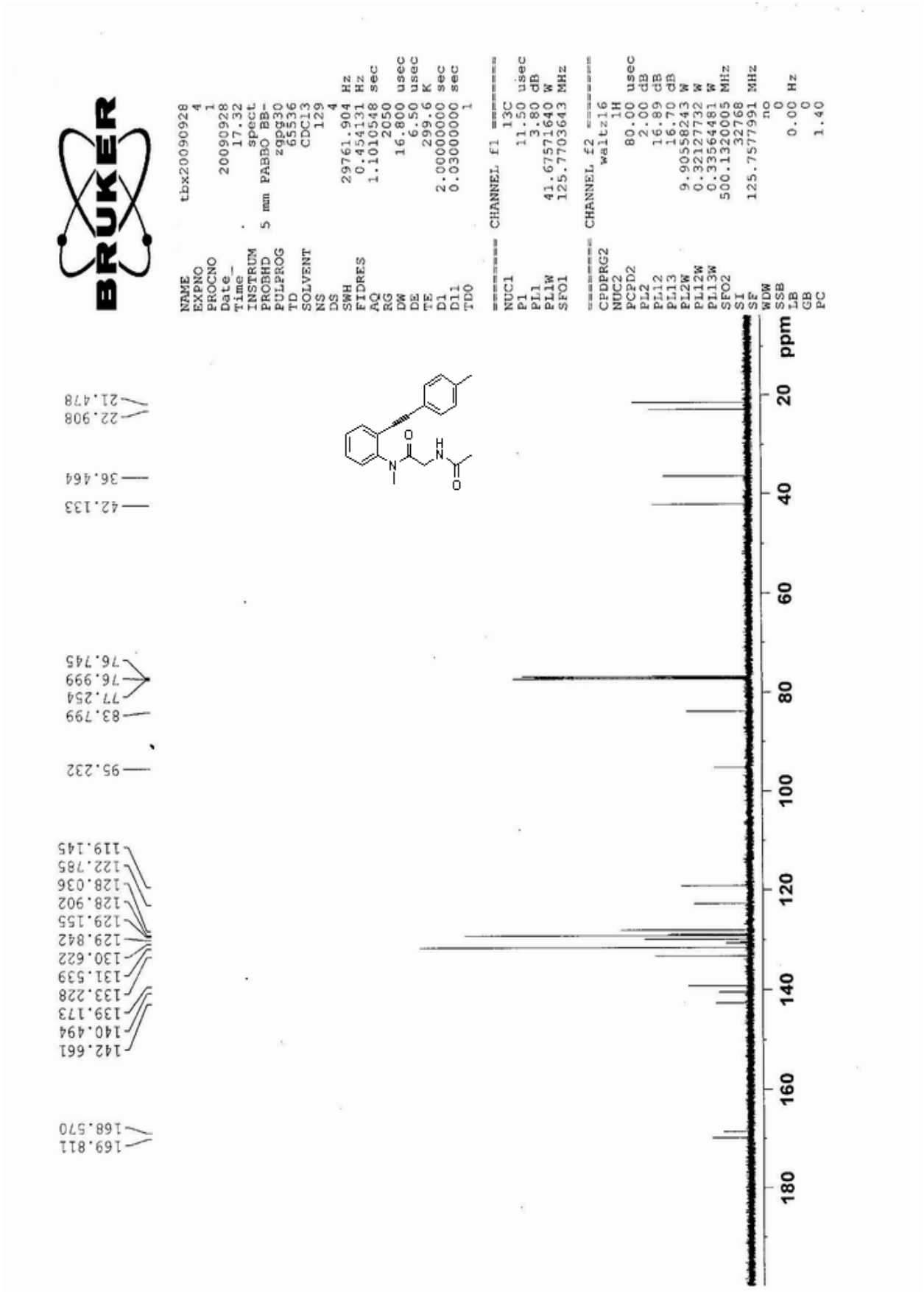
_N_-methyl-_N_-(2-(phenylethynyl)phenyl)-2-(propylamino)acetamide (1d)



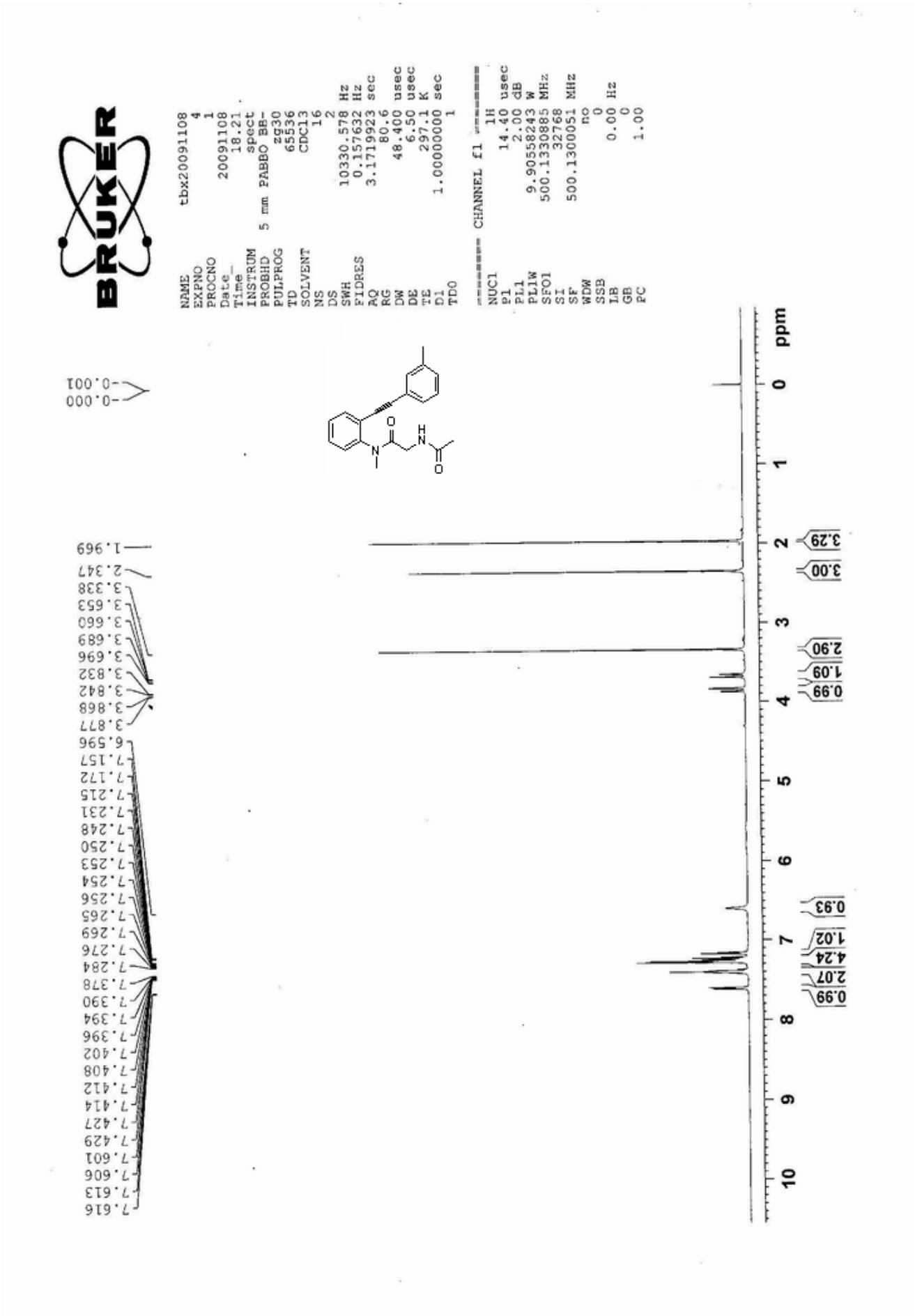
2-Acetamido-*N*-methyl-*N*-(2-(p-tolylethynyl)phenyl)acetamide (1e)



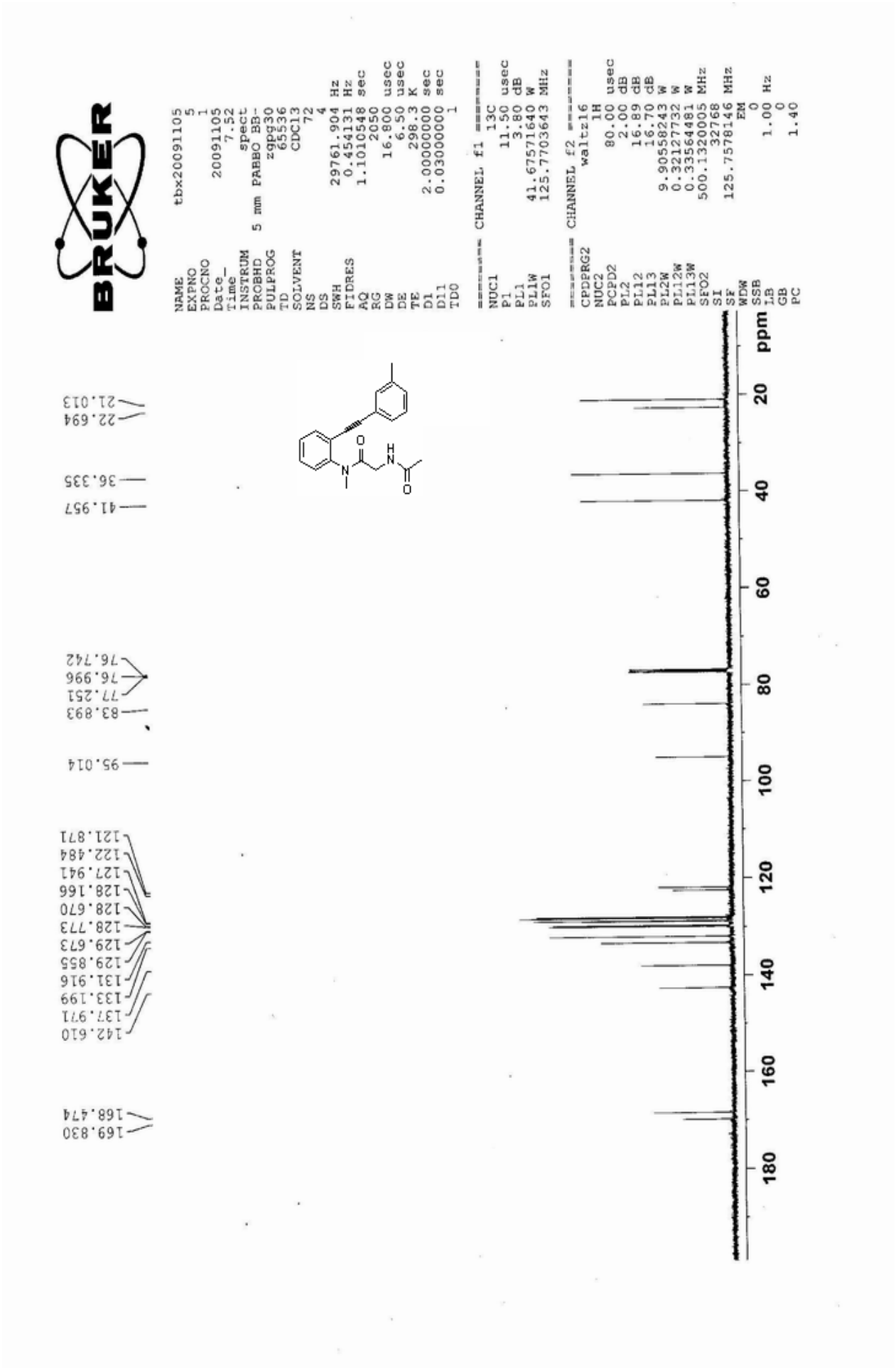
2-Acetamido-*N*-methyl-*N*-(2-(p-tolylethynyl)phenyl)acetamide (1e)



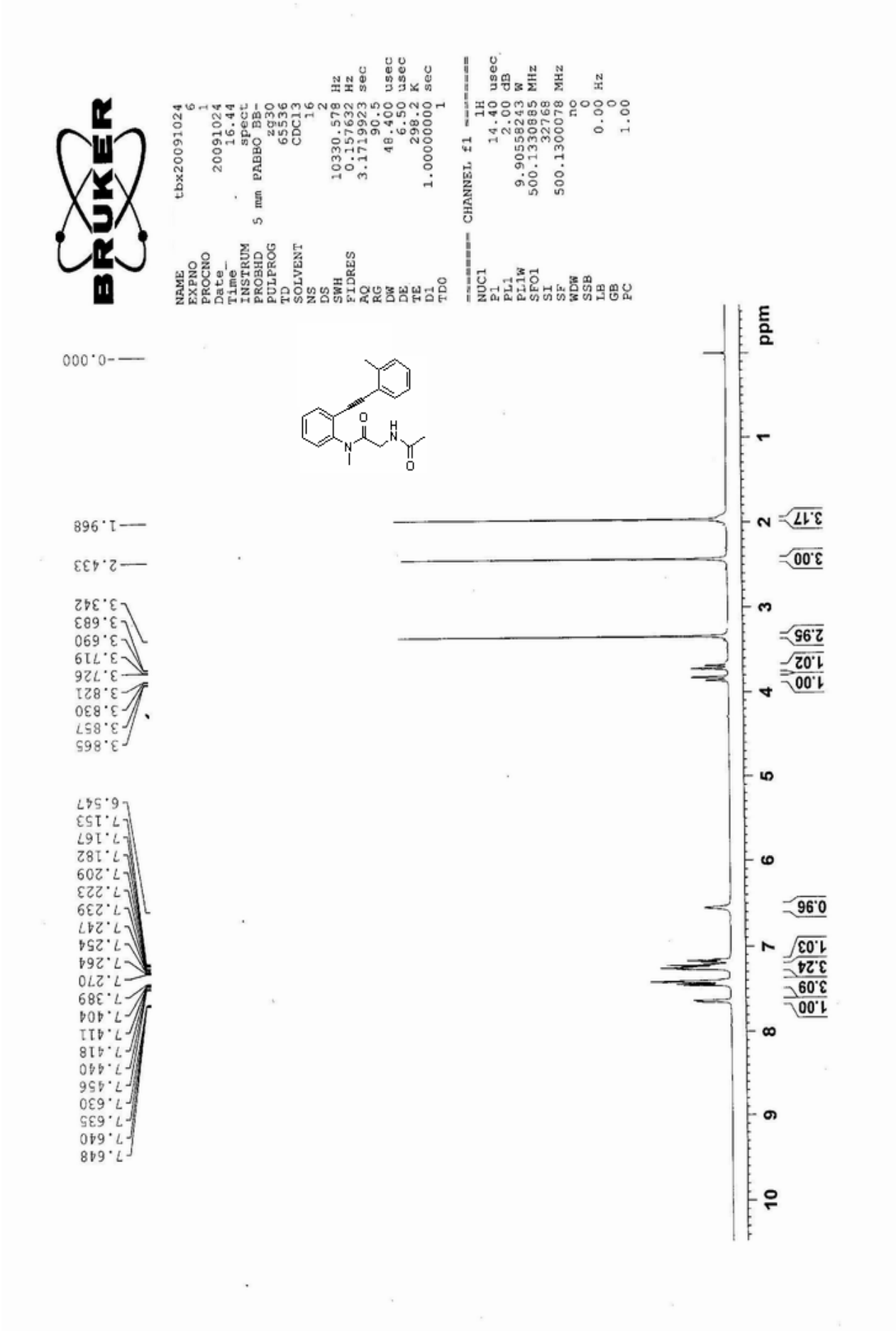
2-Acetamido-*N*-methyl-*N*-(2-(m-tolylethynyl)phenyl)acetamide (1f)



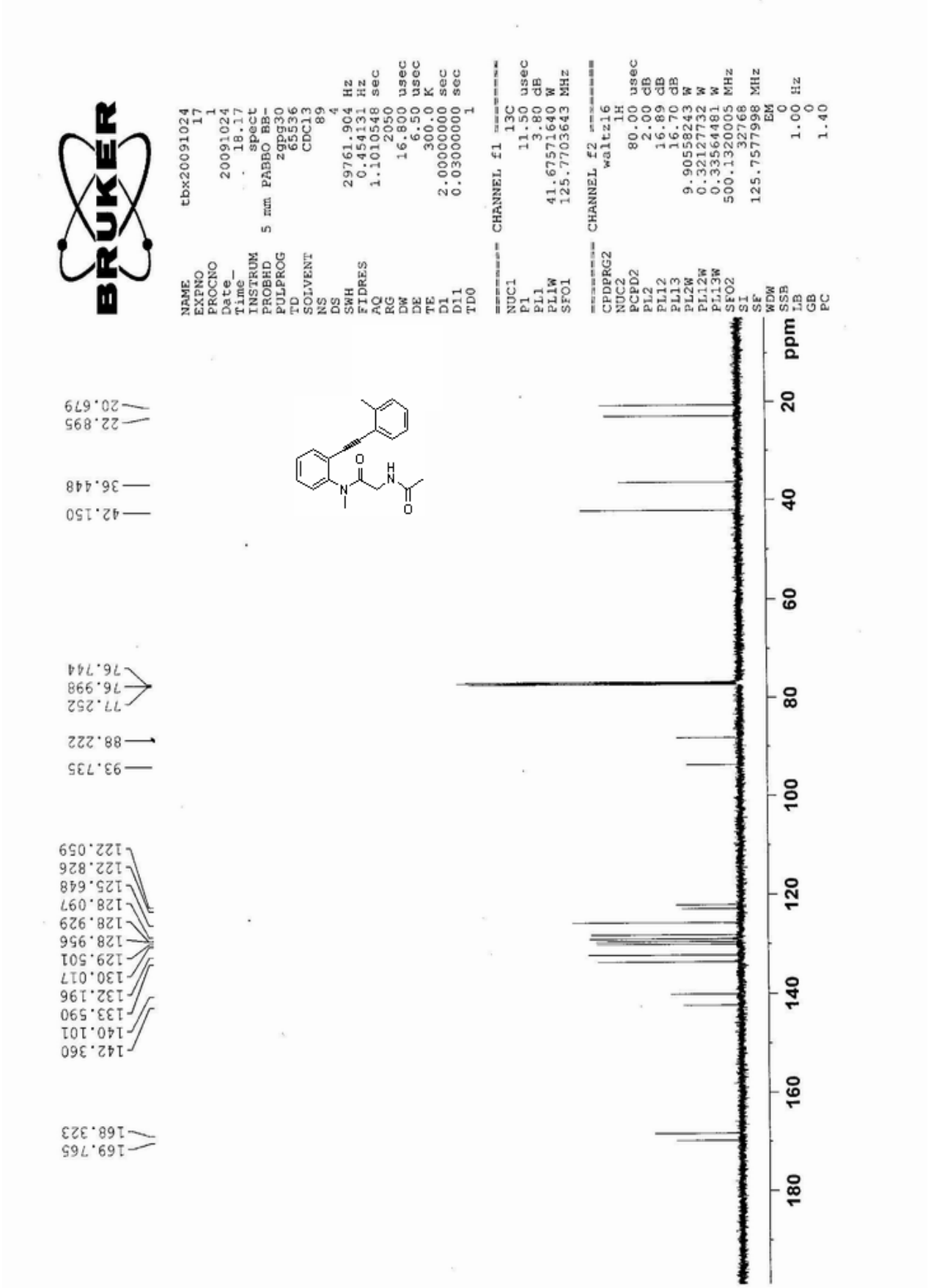
2-Acetamido-*N*-methyl-*N*-(2-(m-tolylethynyl)phenyl)acetamide (1f)



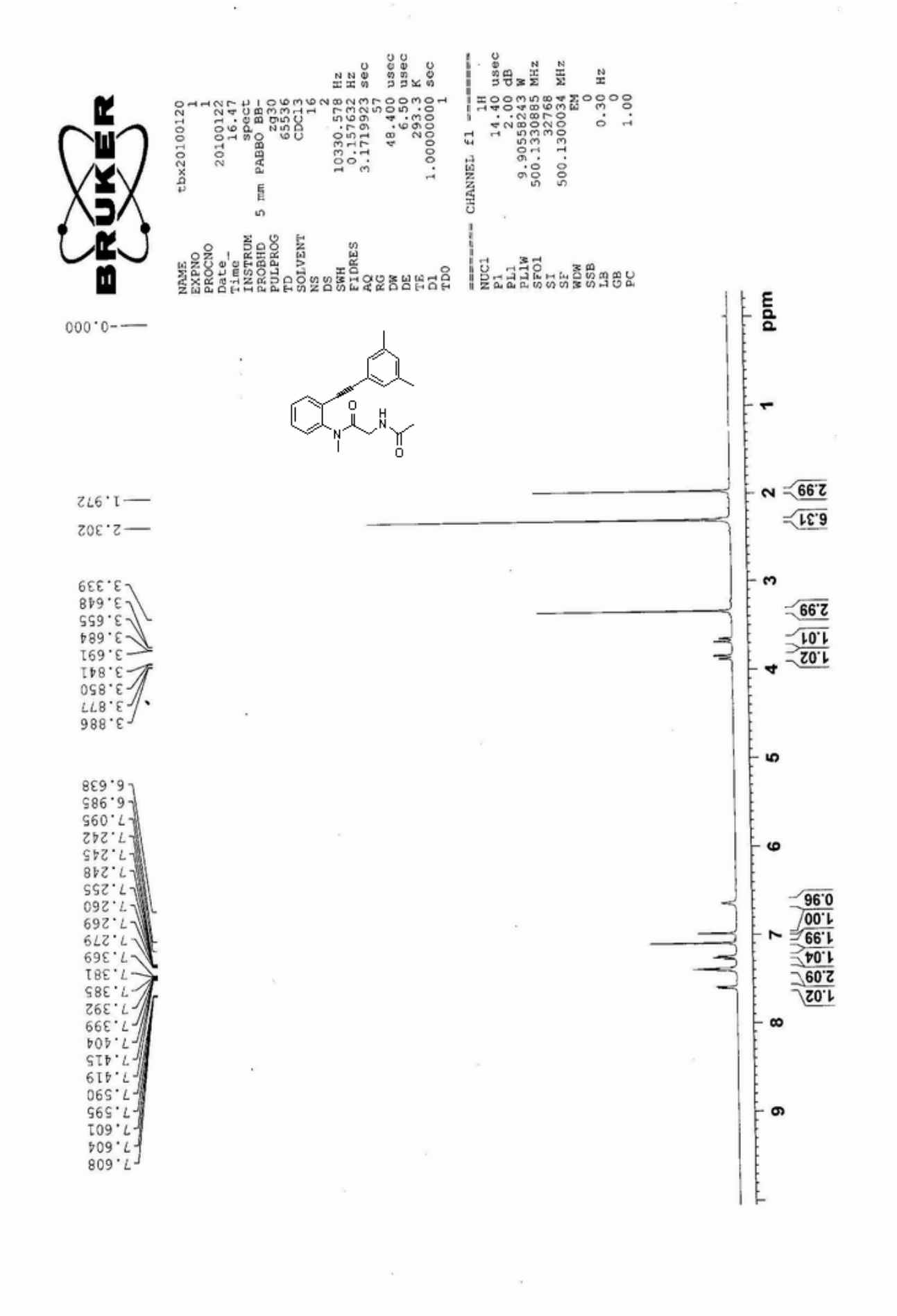
2-Acetamido-*N*-methyl-*N*-(2-(o-tolylethynyl)phenyl)acetamide (1g)



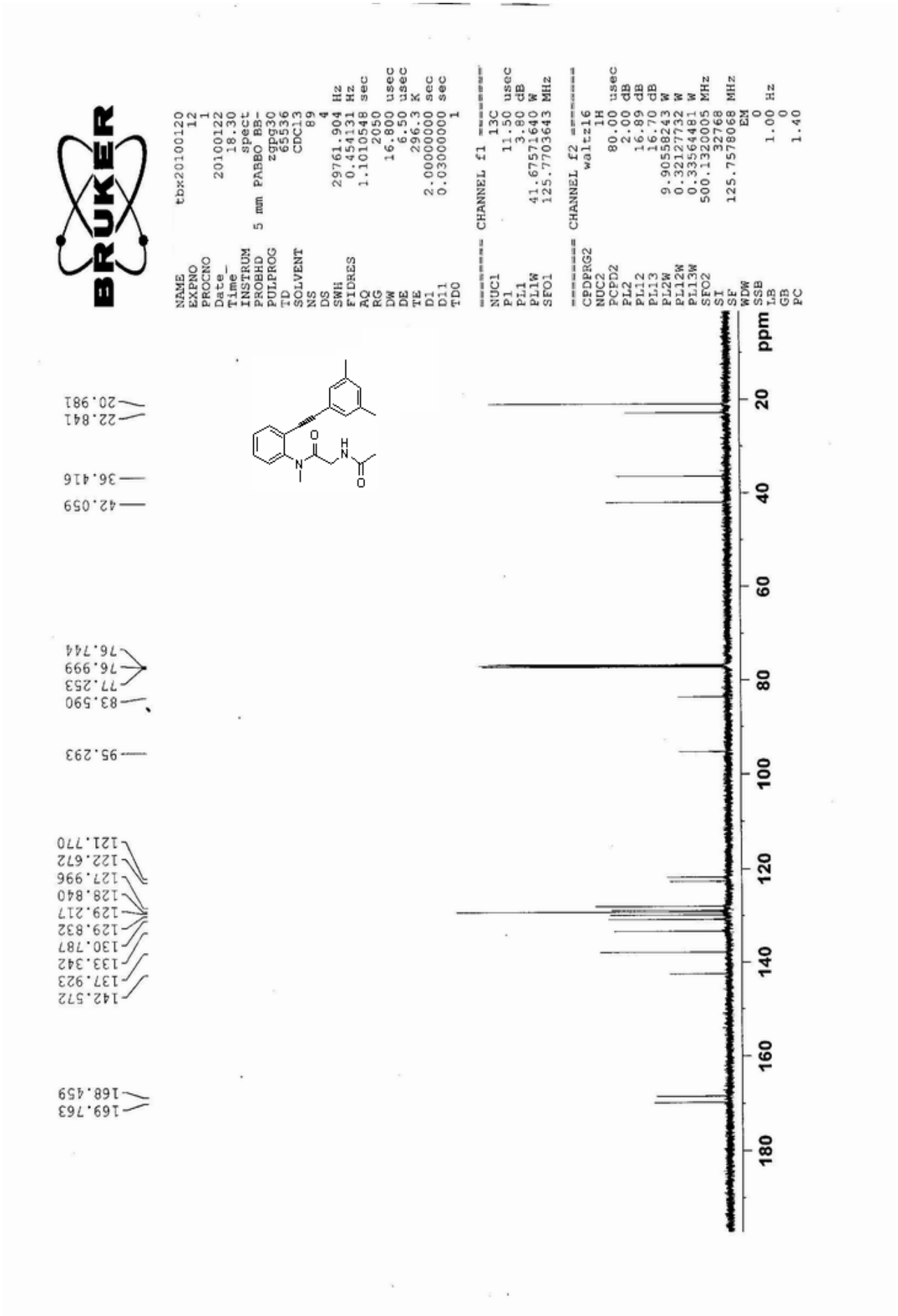
2-Acetamido-*N*-methyl-*N*-(2-(o-tolylethynyl)phenyl)acetamide (1g)



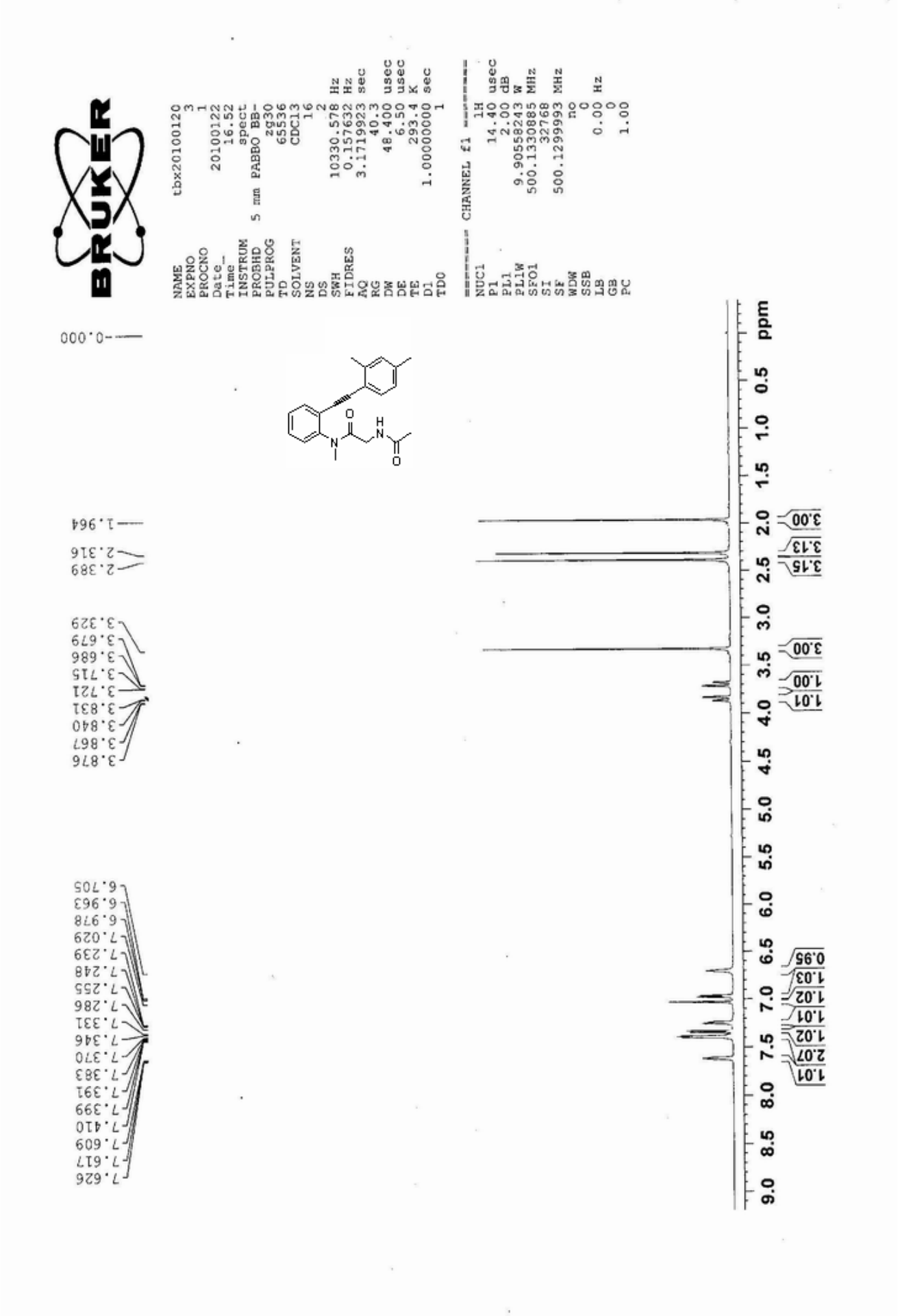
2-Acetamido-*N*-(2-((3,5-dimethylphenyl)ethynyl)phenyl)-*N*-methylacetamide (1h)



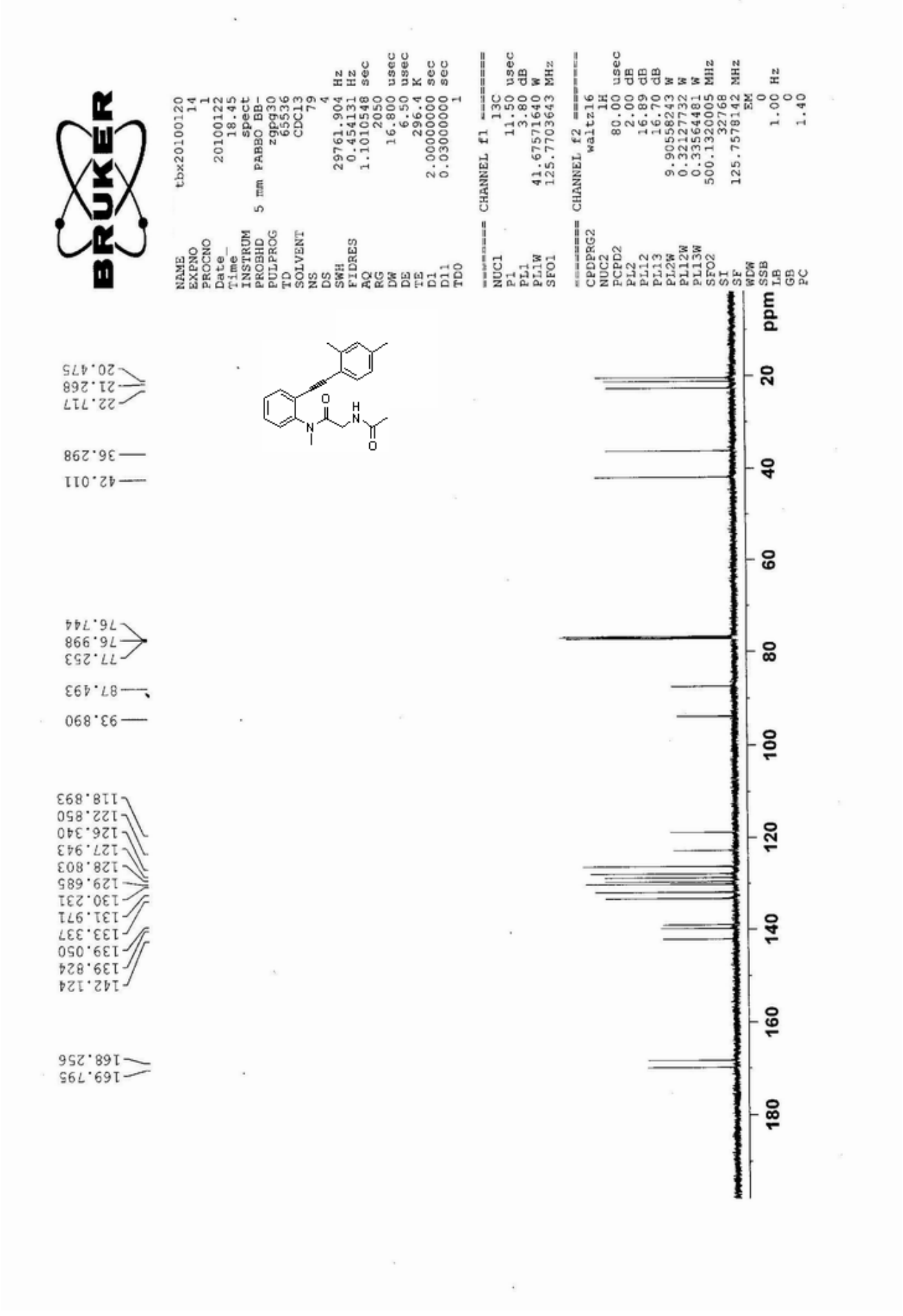
2-Acetamido-*N*-(2-((3,5-dimethylphenyl)ethynyl)phenyl)-*N*-methylacetamide (1h)



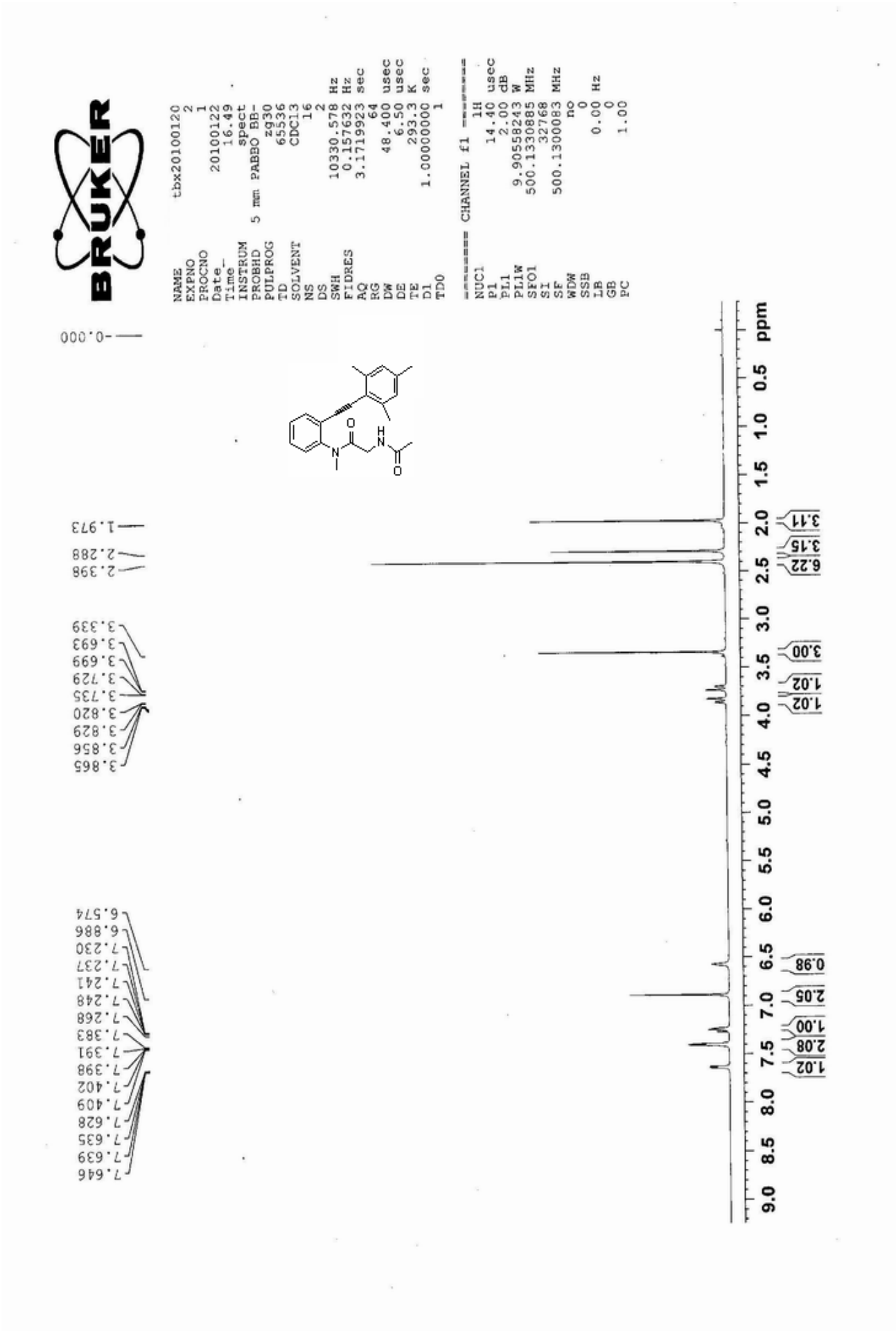
2-Acetamido-*N*-(2-((2,4-dimethylphenyl)ethynyl)phenyl)-*N*-methylacetamide (1i)



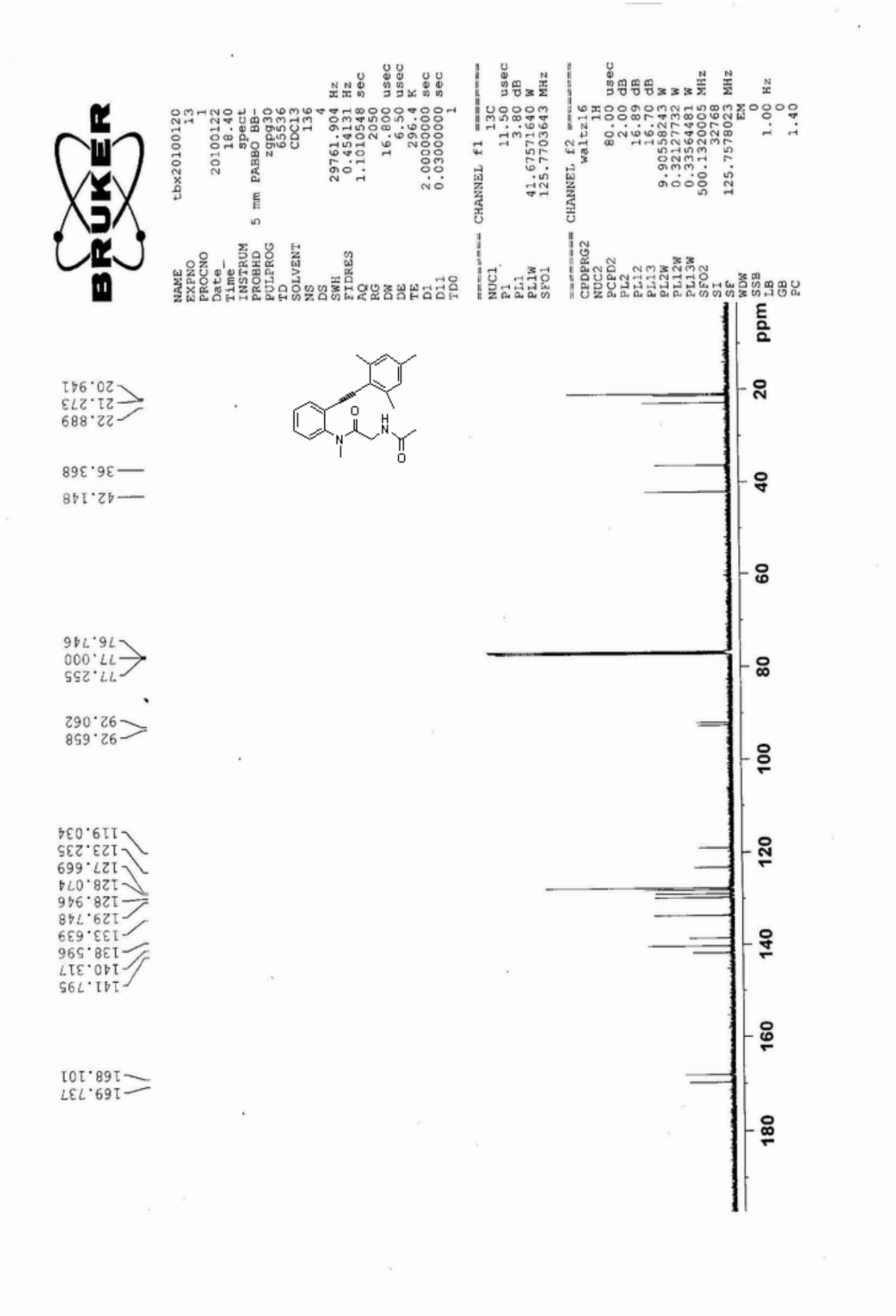
2-Acetamido-*N*-(2-((2,4-dimethylphenyl)ethynyl)phenyl)-*N*-methylacetamide (1i)



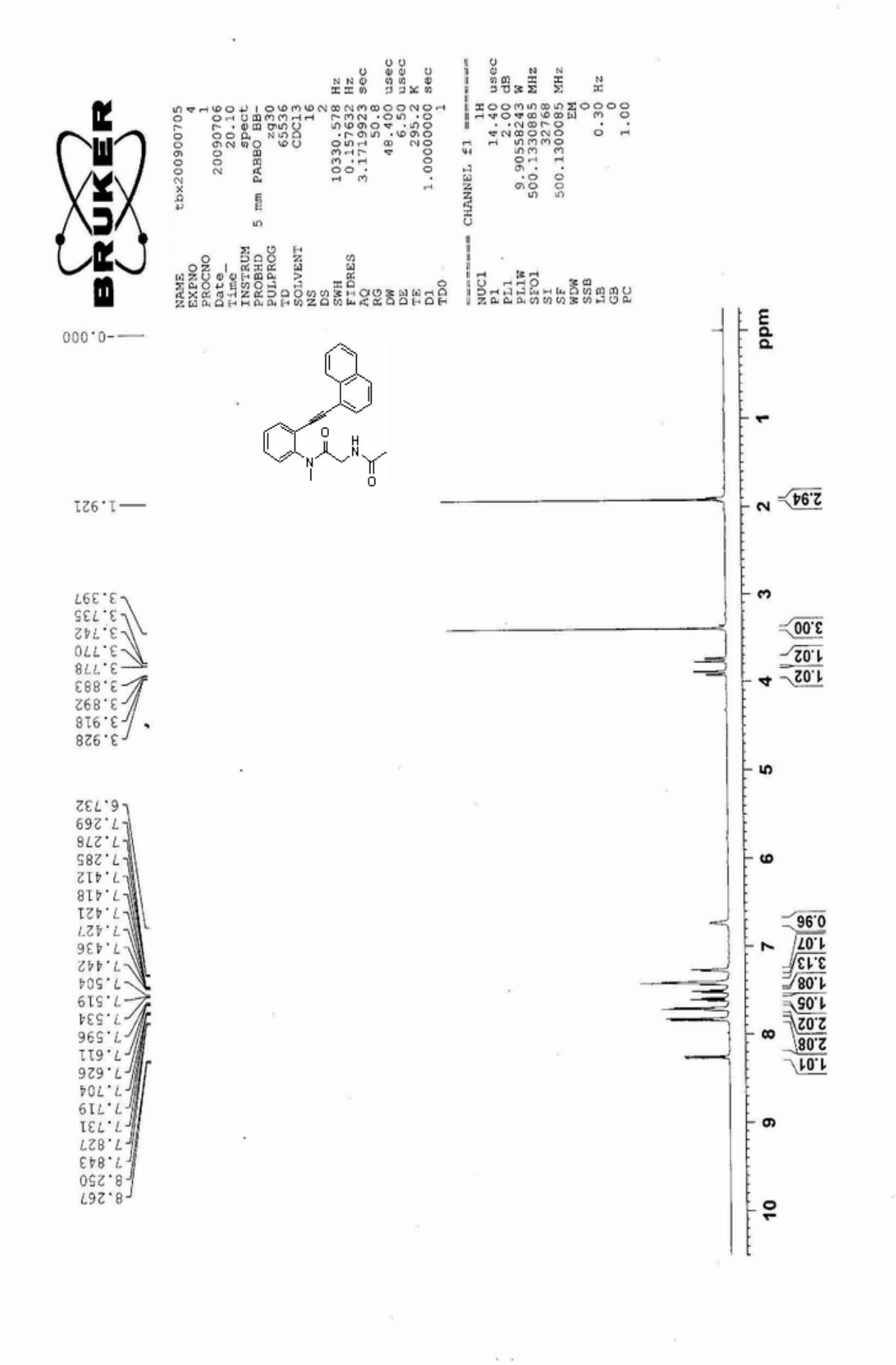
2-Acetamido-*N*-(2-(mesitylethynyl)phenyl)-*N*-methylacetamide (1j)



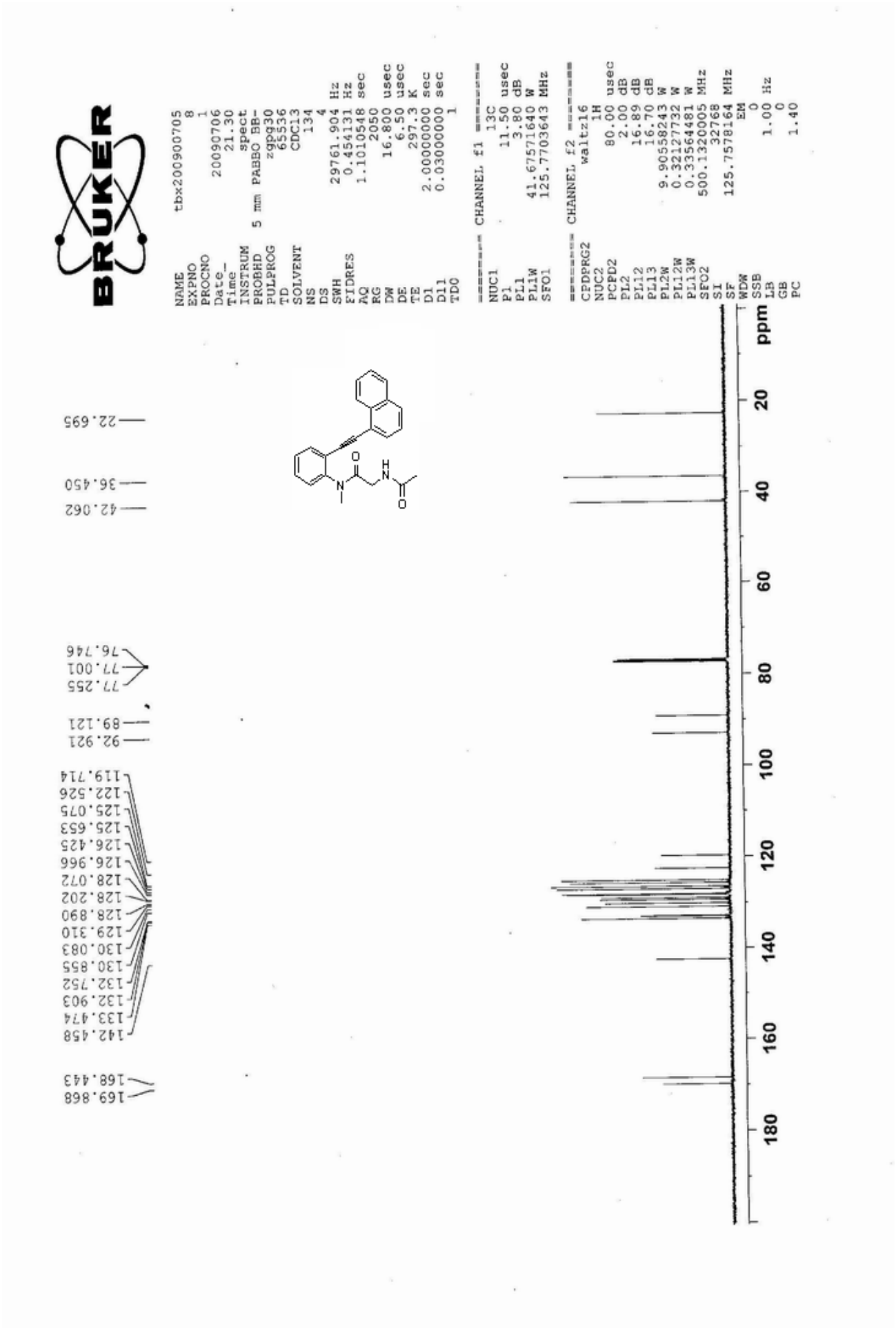
2-Acetamido-*N*-(2-(mesitylethynyl)phenyl)-*N*-methylacetamide (1j)



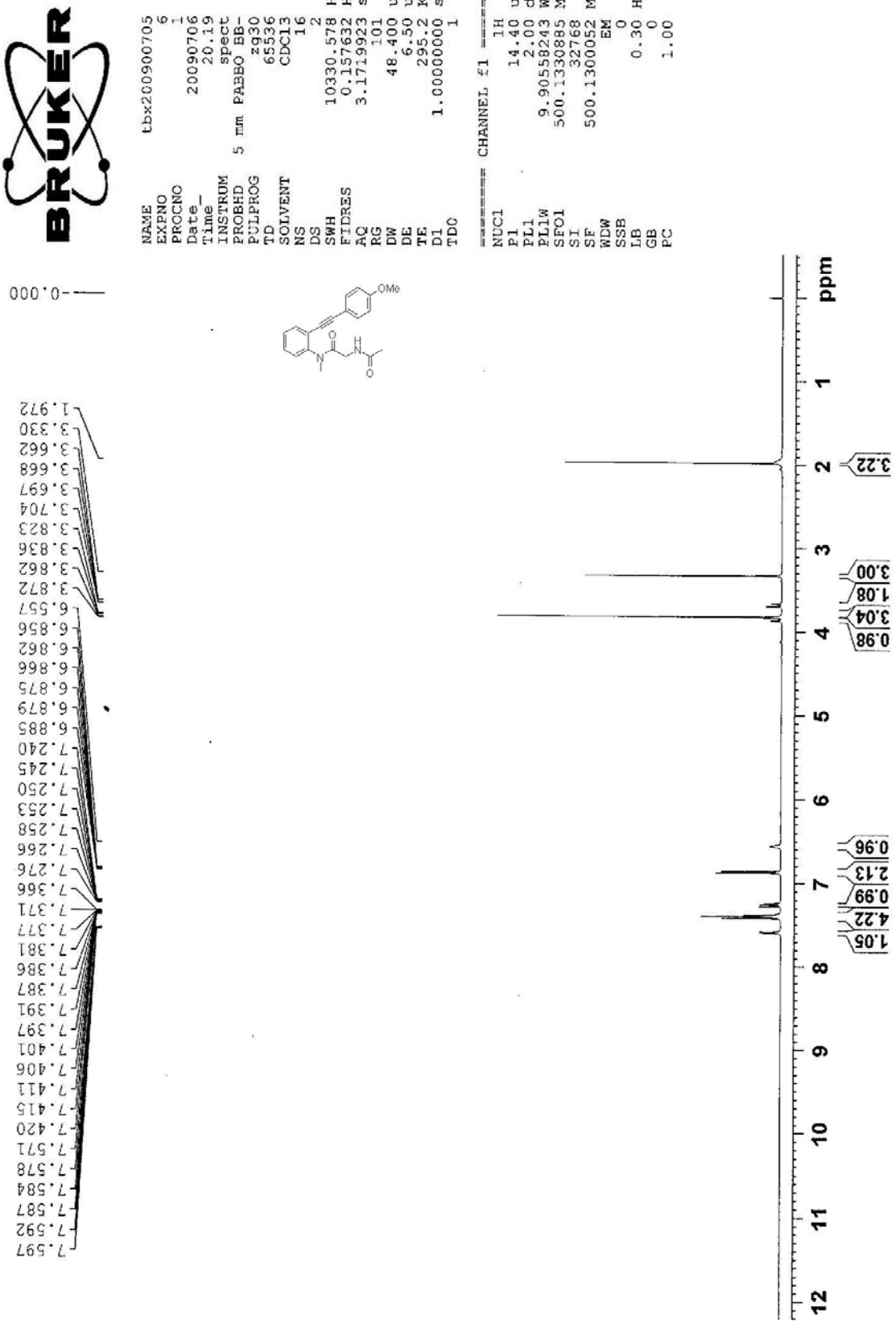
2-Acetamido-*N*-methyl-*N*-(2-(naphthalen-1-ylethynyl)phenyl)acetamide (1k)



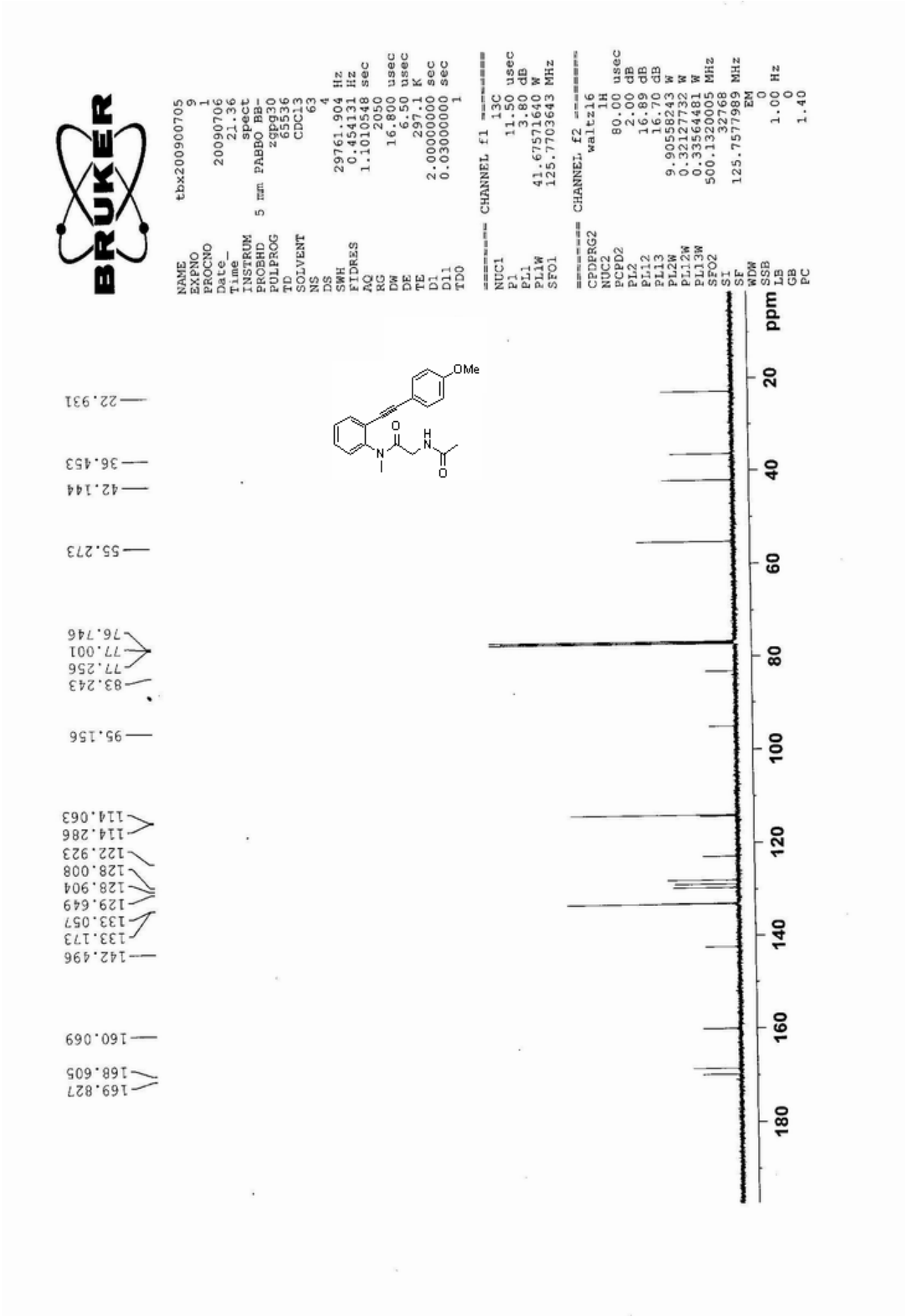
2-Acetamido-*N*-methyl-*N*-(2-(naphthalen-1-ylethynyl)phenyl)acetamide (1k)



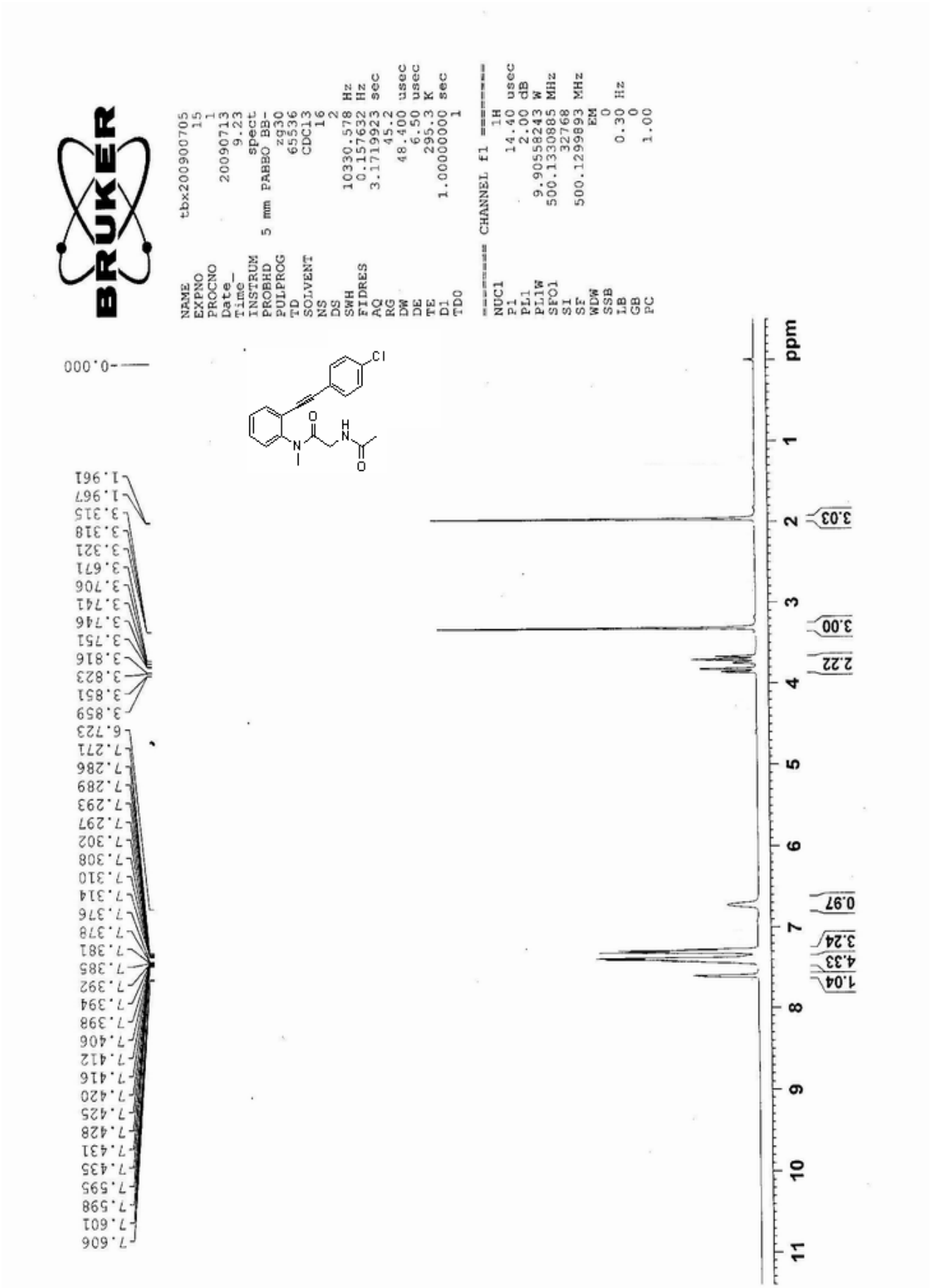
2-Acetamido-*N*-(2-((4-methoxyphenyl)ethynyl)phenyl)-*N*-methylacetamide (1l)



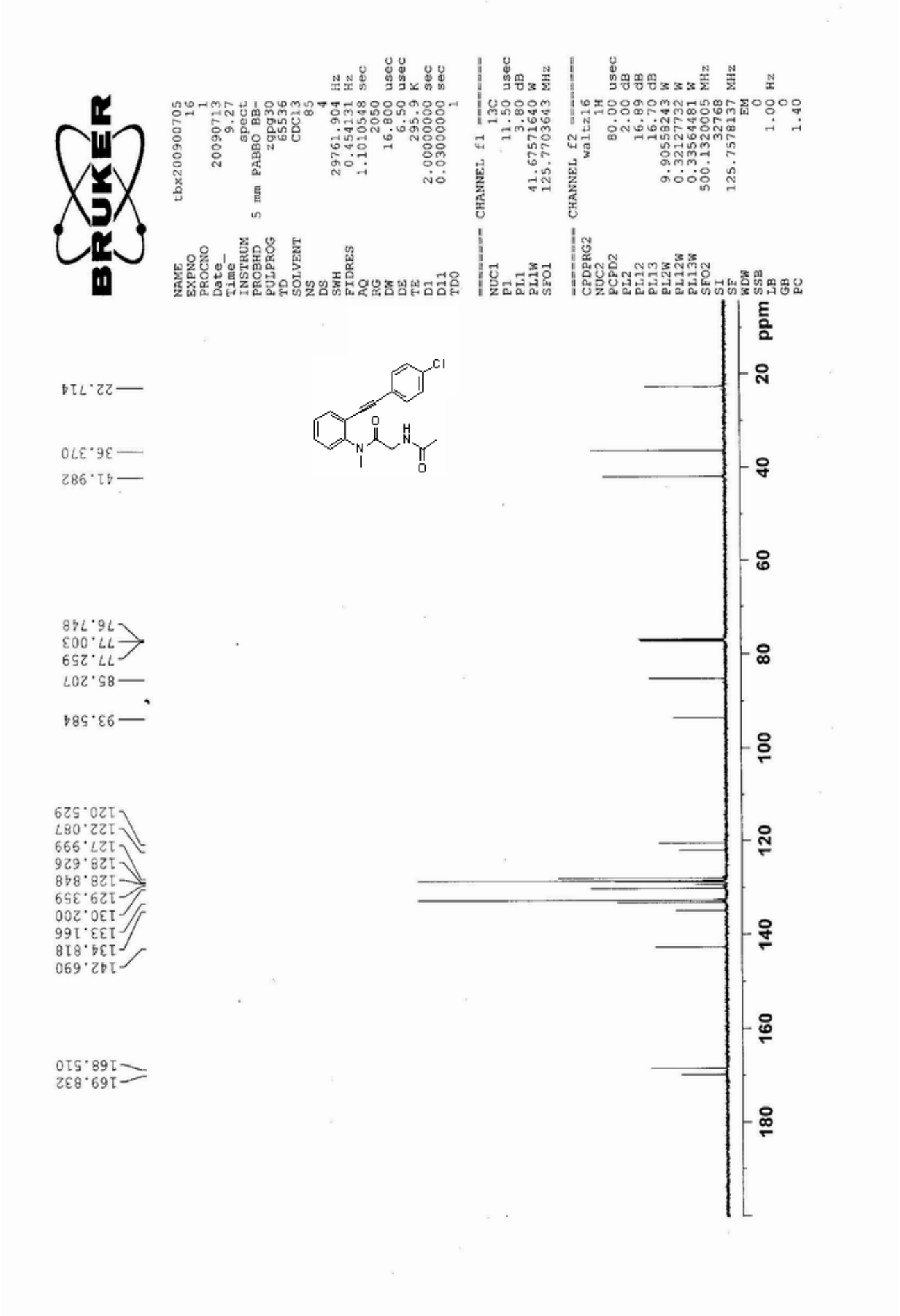
2-Acetamido-*N*-(2-((4-methoxyphenyl)ethynyl)phenyl)-*N*-methylacetamide (1l)



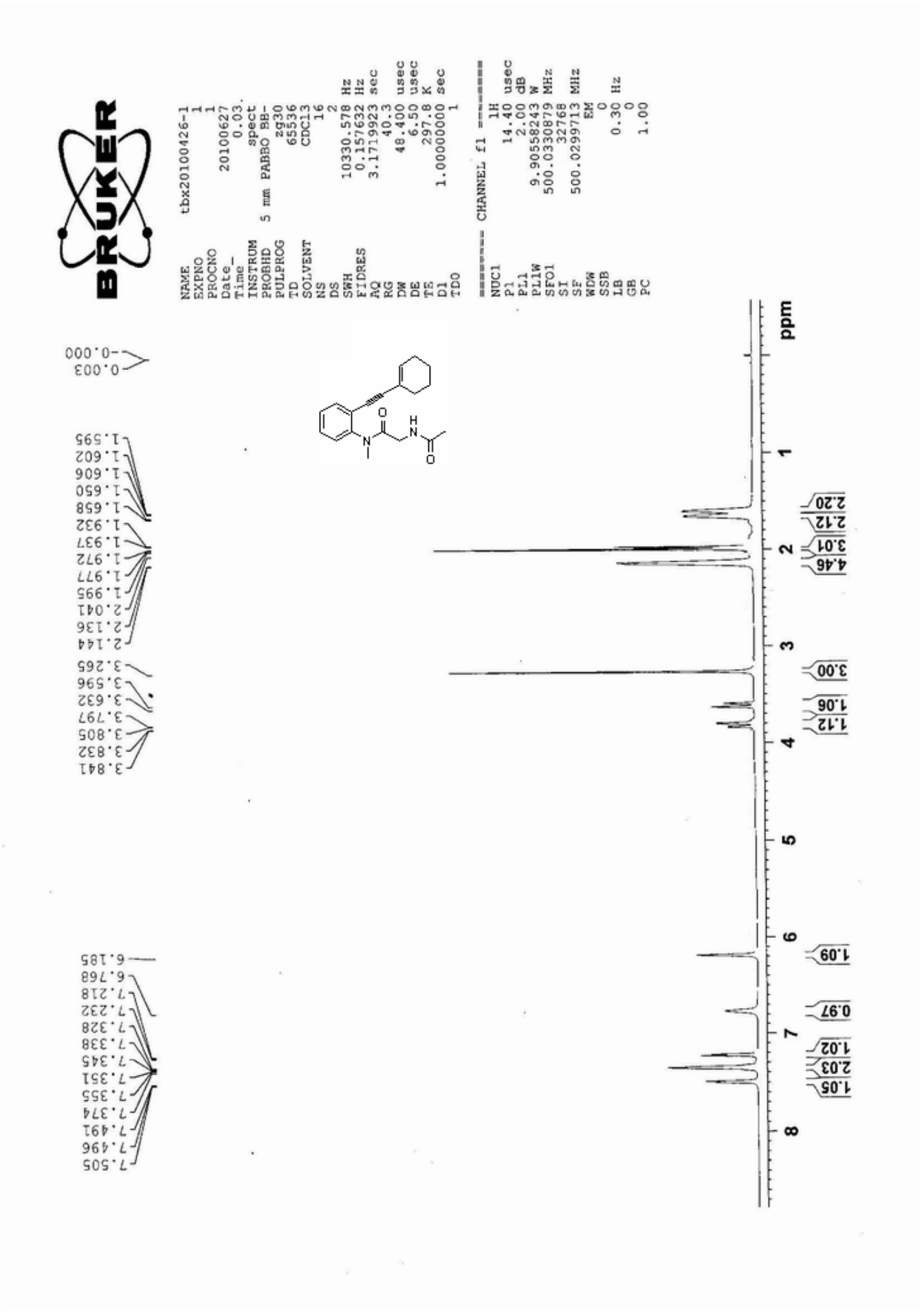
2-Acetamido-*N*-(2-((4-chlorophenyl)ethynyl)phenyl)-*N*-methylacetamide (1m)



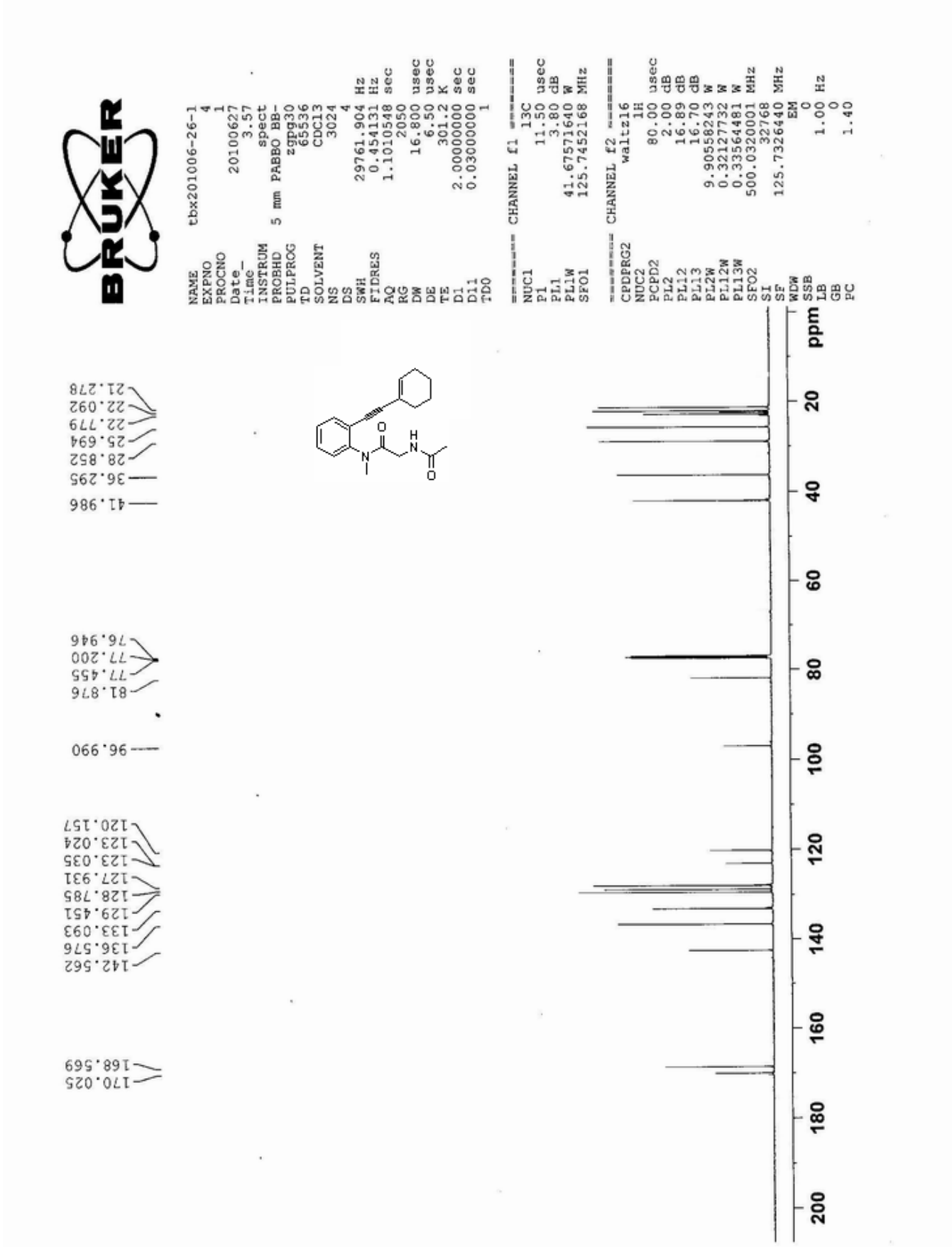
2-Acetamido-*N*-(2-((4-chlorophenyl)ethynyl)phenyl)-*N*-methylacetamide (1m)



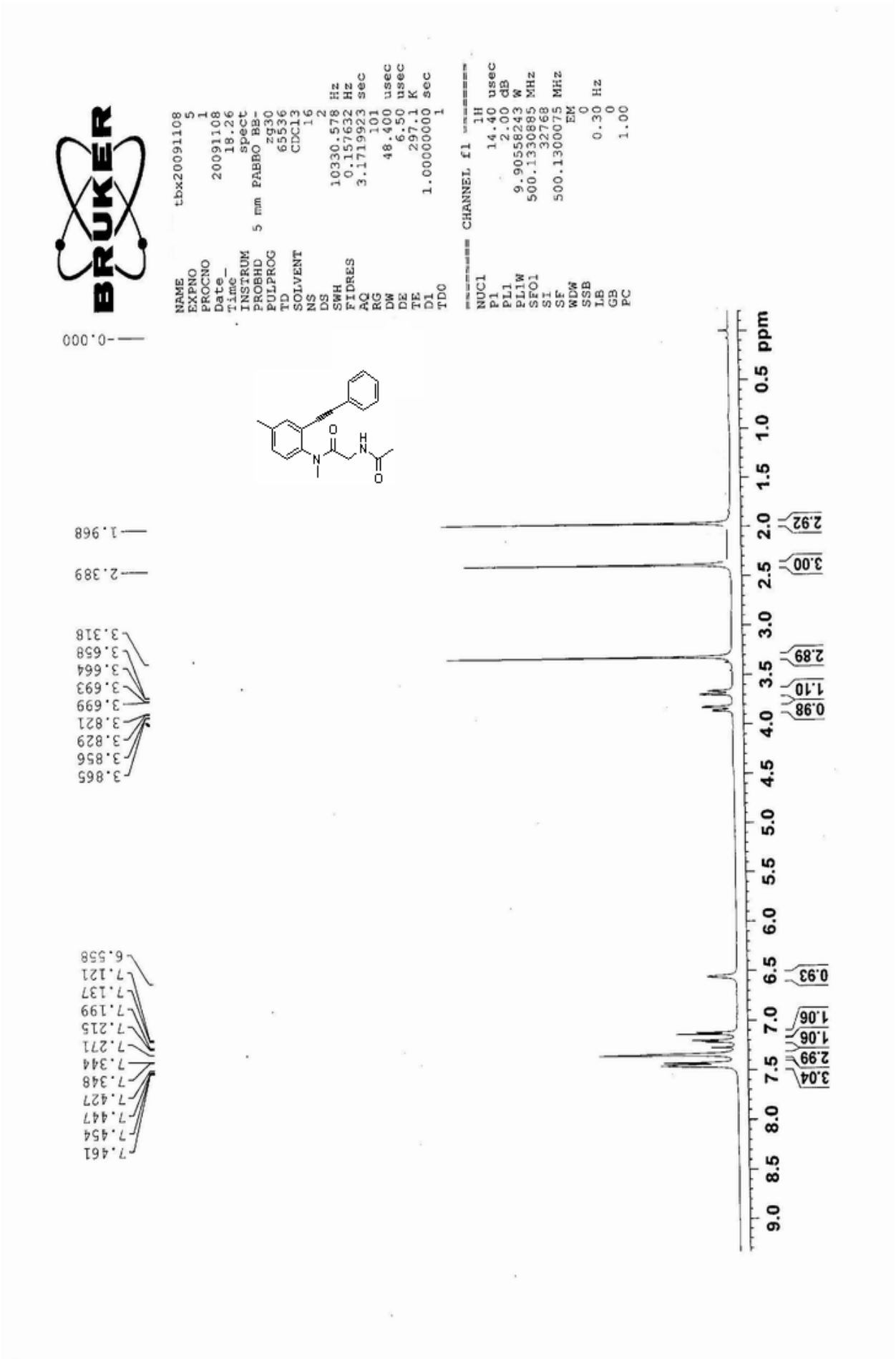
2-Acetamido-*N*-(2-(cyclohexenylethynyl)phenyl)-*N*-methylacetamide (1n)



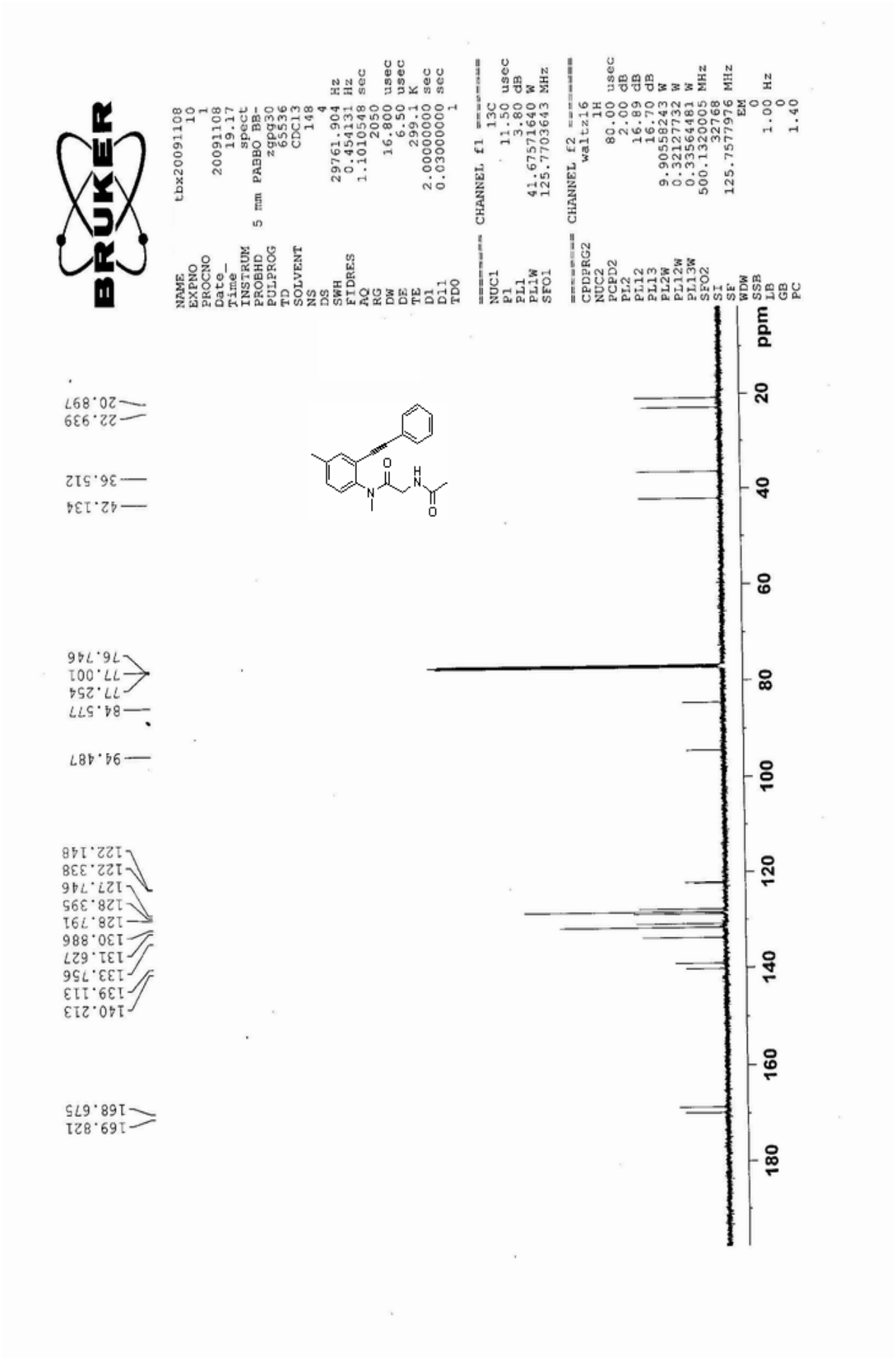
2-Acetamido-*N*-(2-(cyclohexenylethynyl)phenyl)-*N*-methylacetamide (1n)



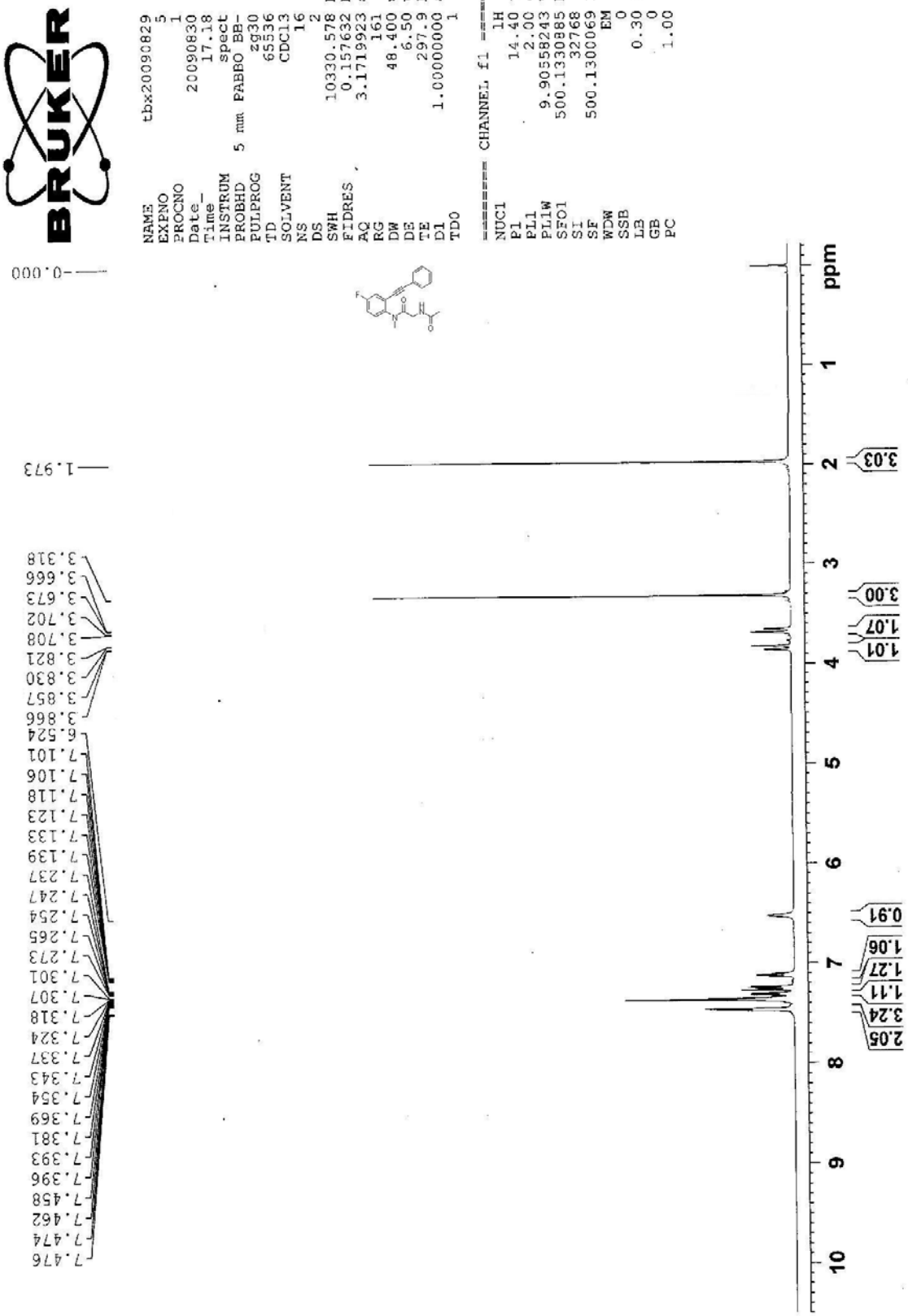
2-Acetamido-*N*-methyl-*N*-(4-methyl-2-(phenylethynyl)phenyl)acetamide (1p)



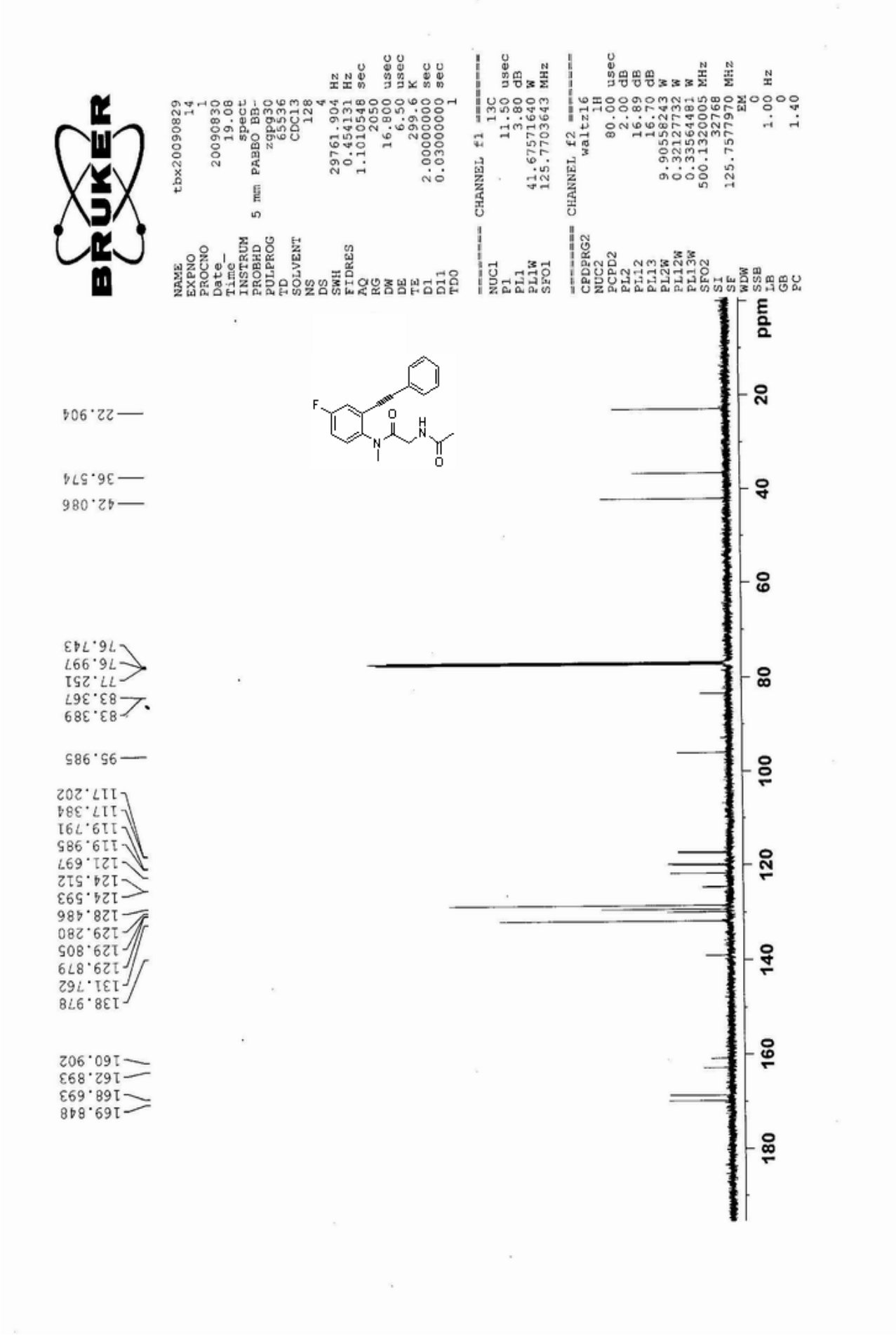
2-Acetamido-*N*-methyl-*N*-(4-methyl-2-(phenylethynyl)phenyl)acetamide (1p)



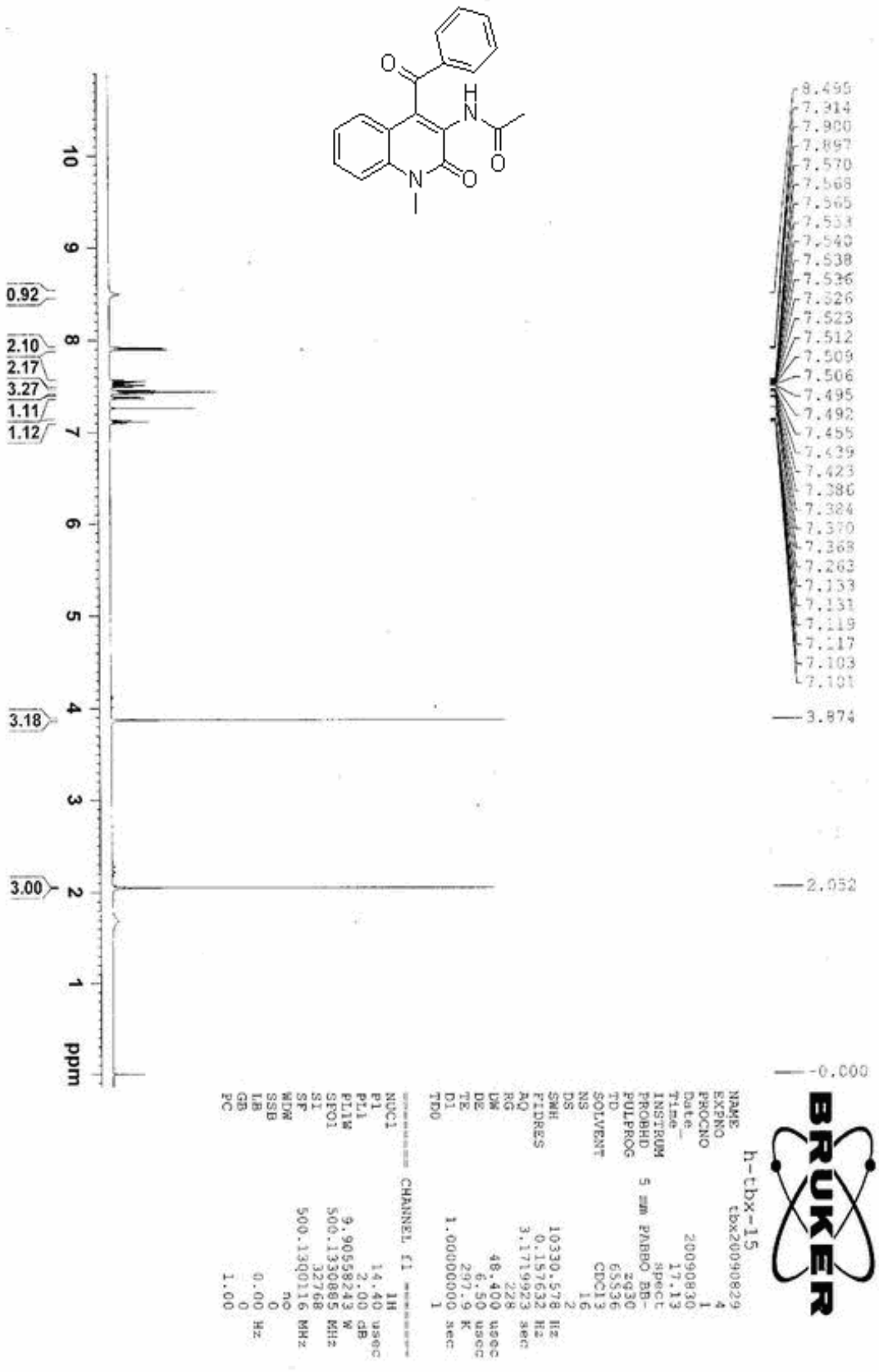
2-Acetamido-*N*-(4-fluoro-2-(phenylethynyl)phenyl)-*N*-methylacetamide (1q)



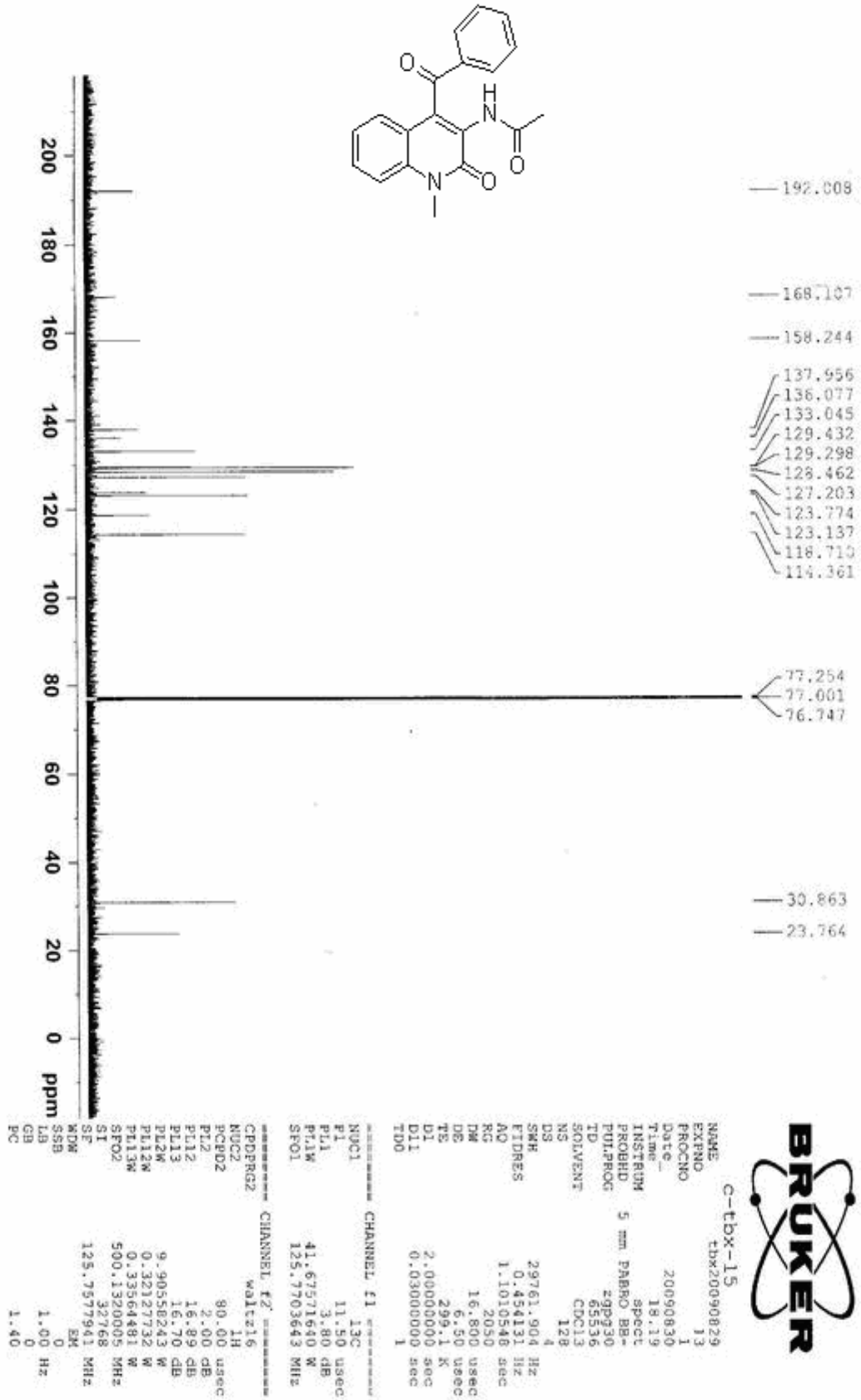
2-Acetamido-*N*-(4-fluoro-2-(phenylethynyl)phenyl)-*N*-methylacetamide (1q)



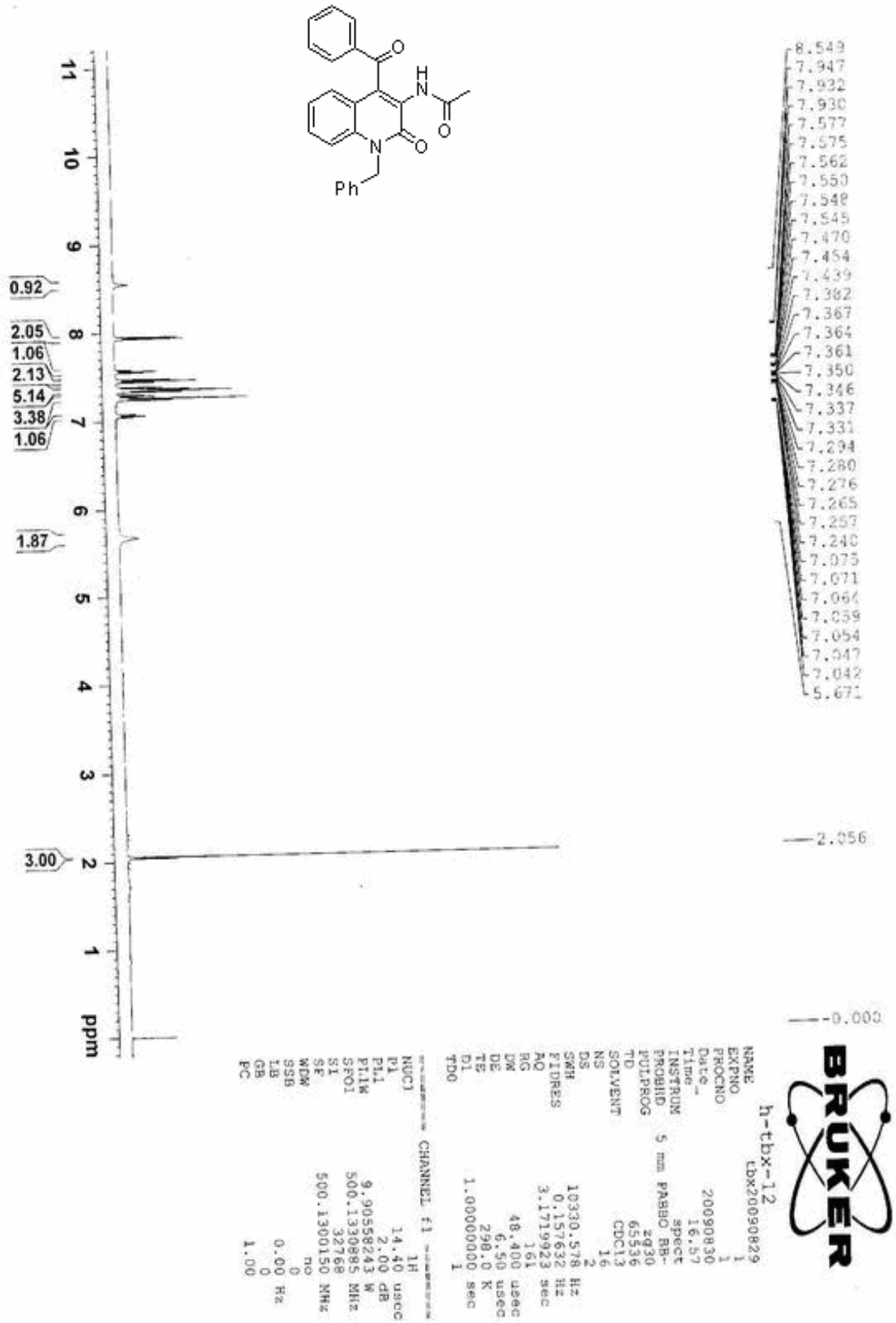
_N_-(4-benzoyl-1-methyl-2-oxo-1,2-dihydroquinolin-3-yl)acetamide (2a)



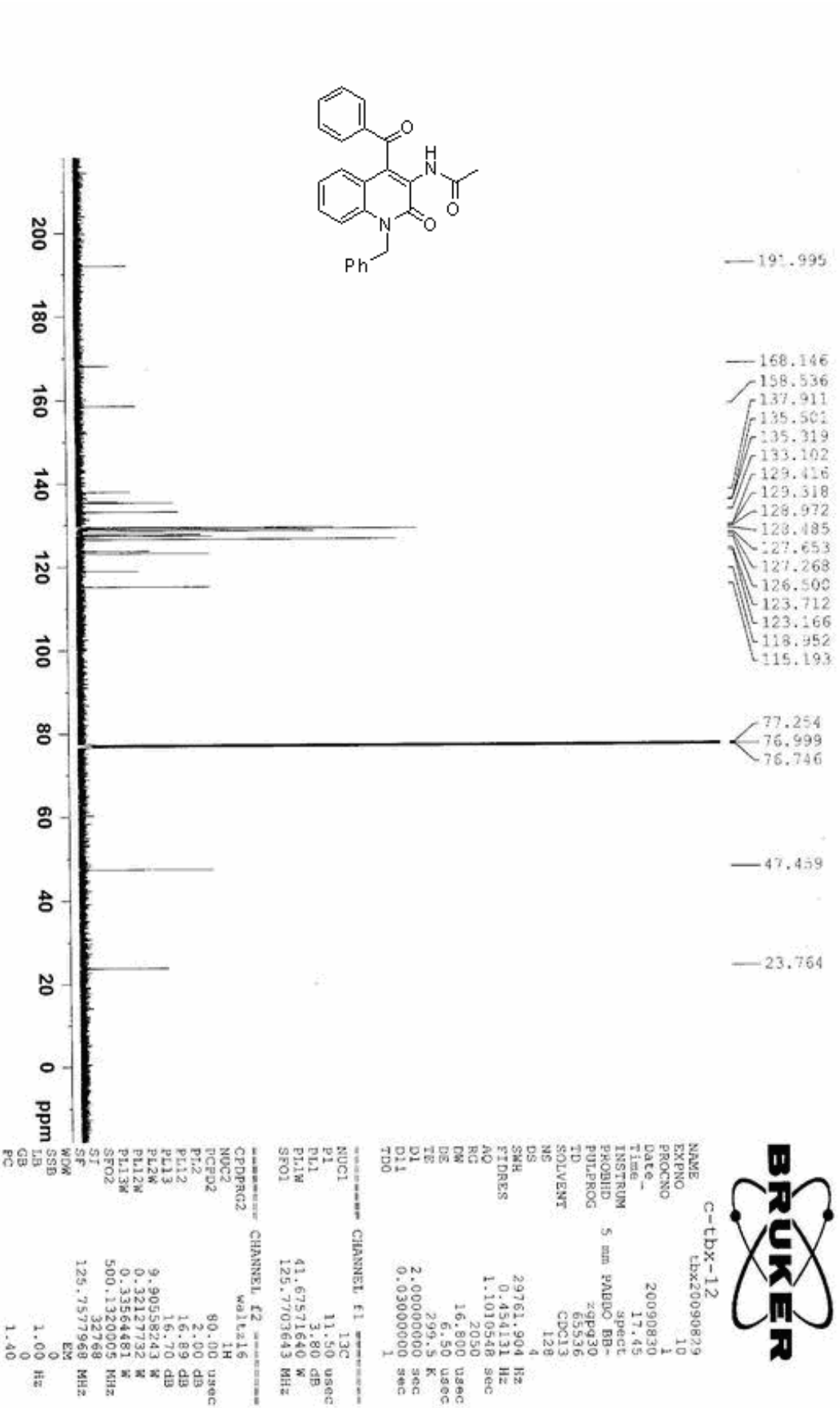
_N_-(4-benzoyl-1-methyl-2-oxo-1,2-dihydroquinolin-3-yl)acetamide (2a)



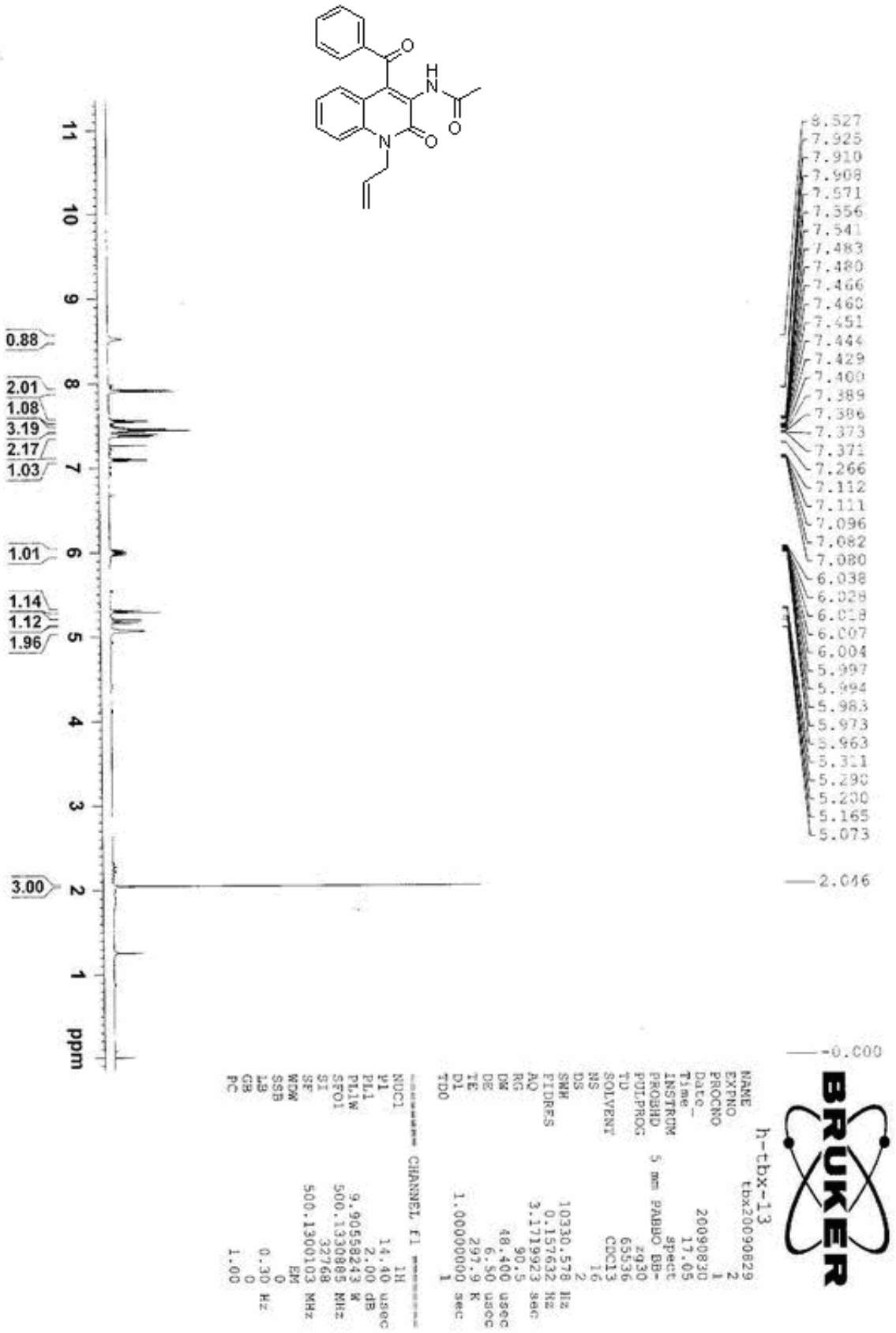
_N_-(4-benzoyl-1-benzyl-2-oxo-1,2-dihydroquinolin-3-yl)acetamide (2b)



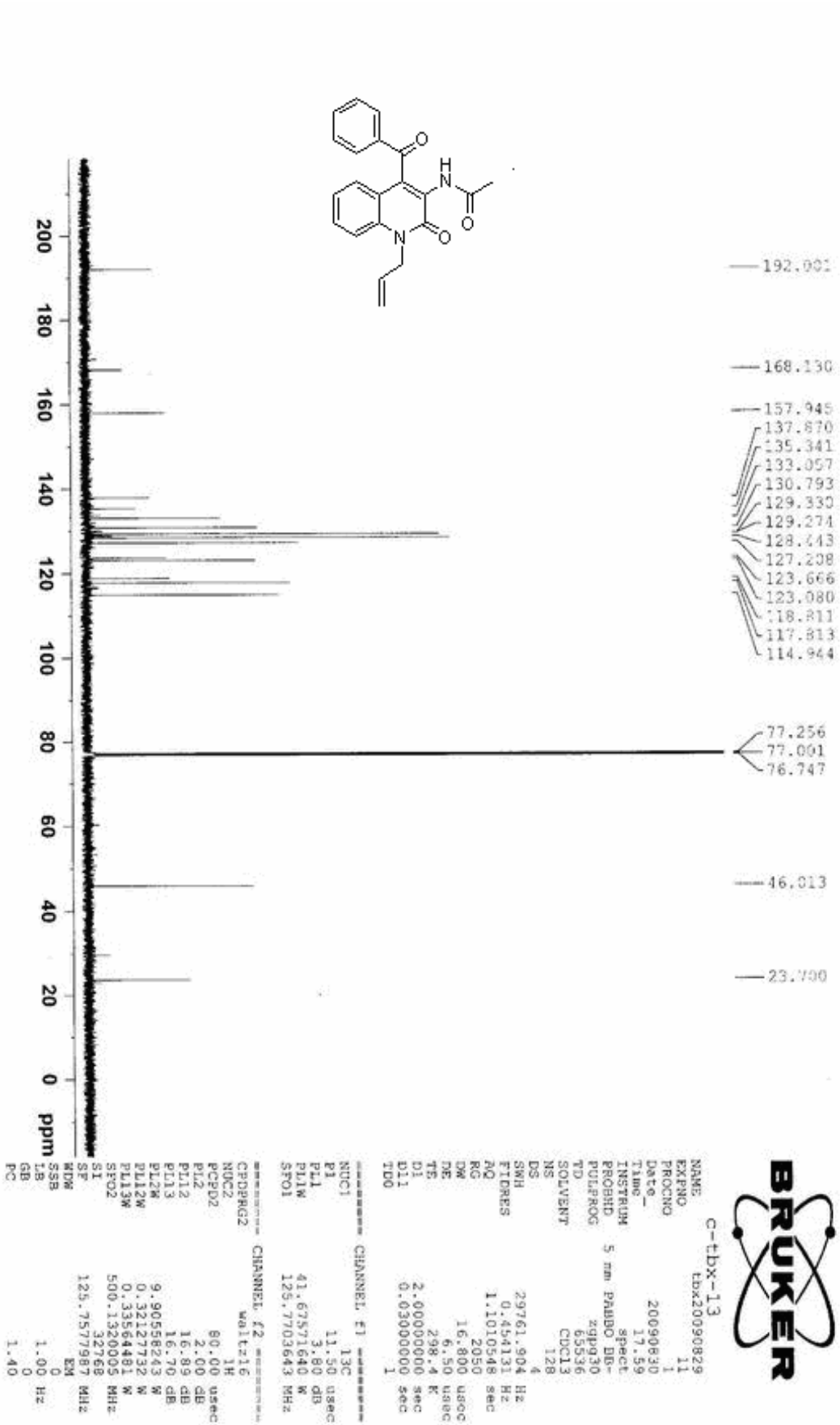
_N_-(4-benzoyl-1-benzyl-2-oxo-1,2-dihydroquinolin-3-yl)acetamide (2b)



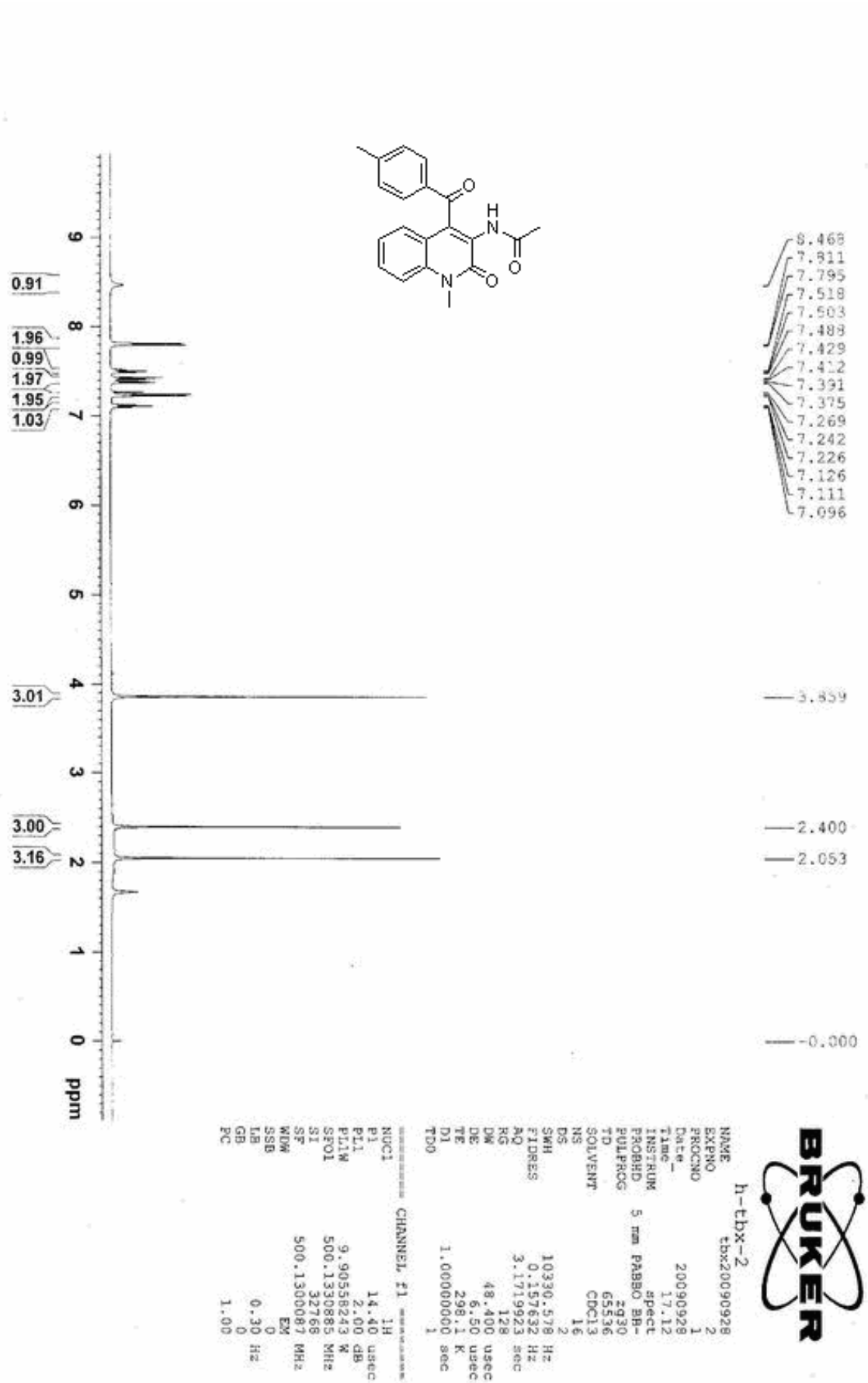
_N_-(1-allyl-4-benzoyl-2-oxo-1,2-dihydroquinolin-3-yl)acetamide (2c)



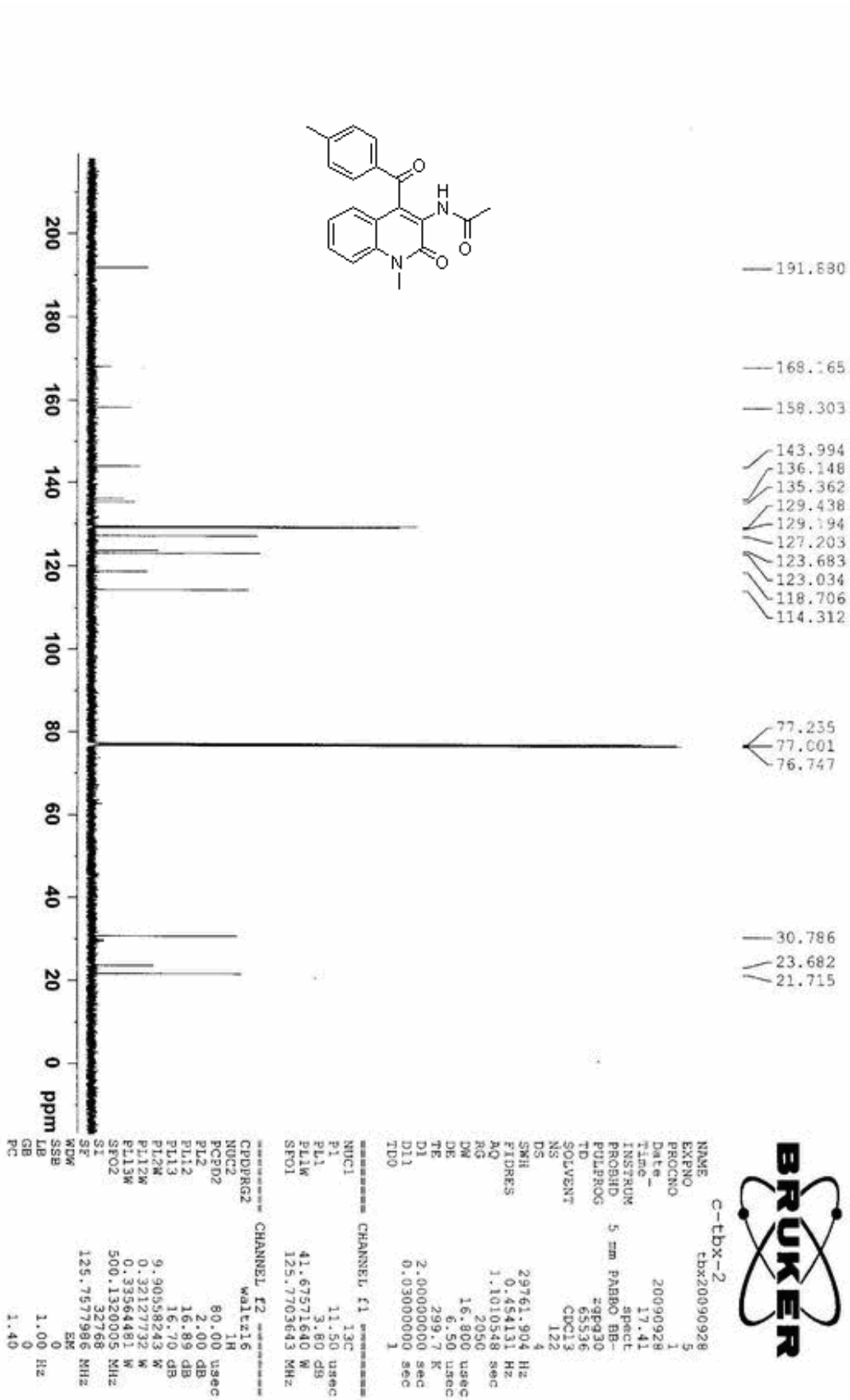
_N_-(1-allyl-4-benzoyl-2-oxo-1,2-dihydroquinolin-3-yl)acetamide (2c)



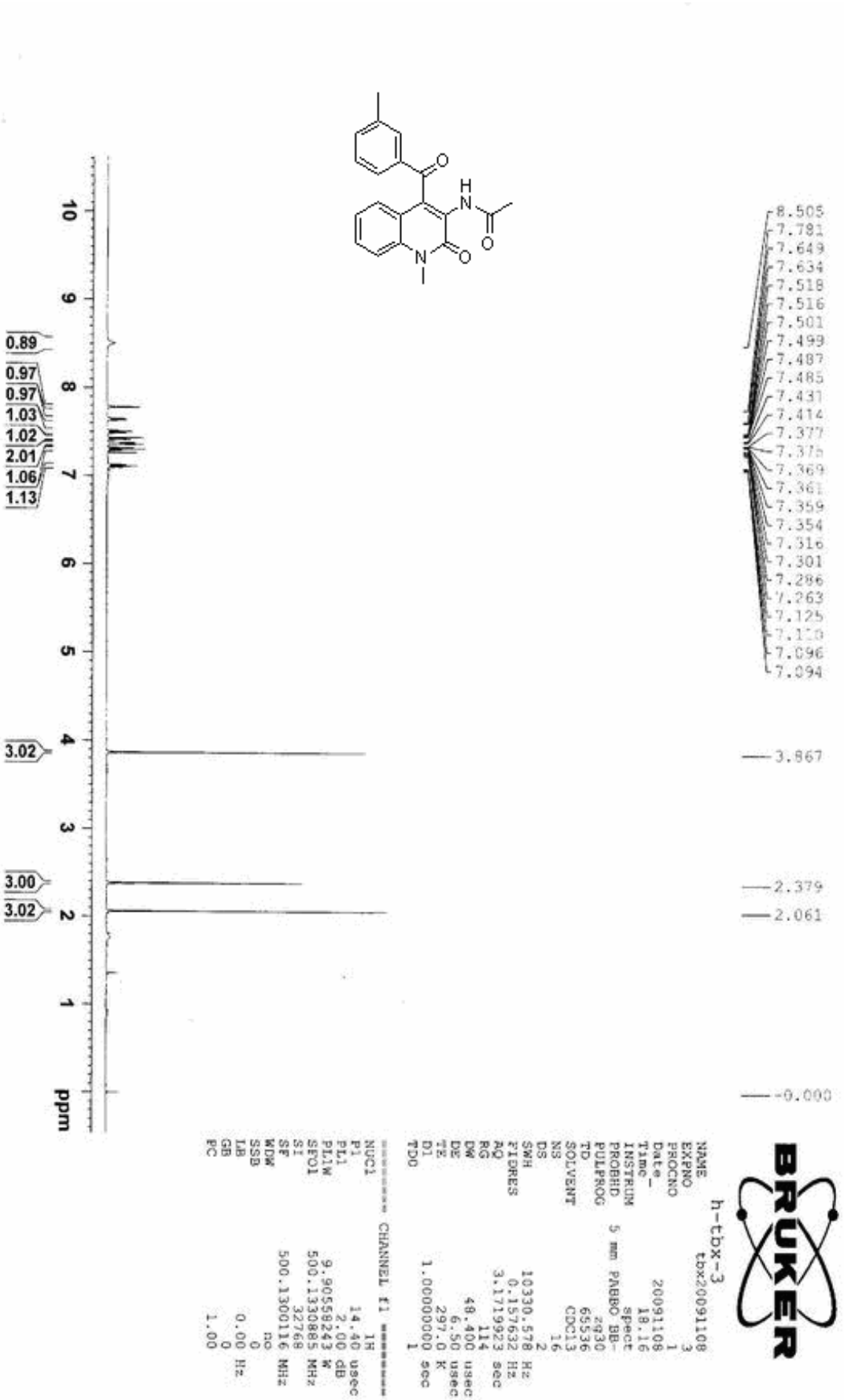
_N_-(1-methyl-4-(4-methylbenzoyl)-2-oxo-1,2-dihydroquinolin-3-yl)acetamide (2e)



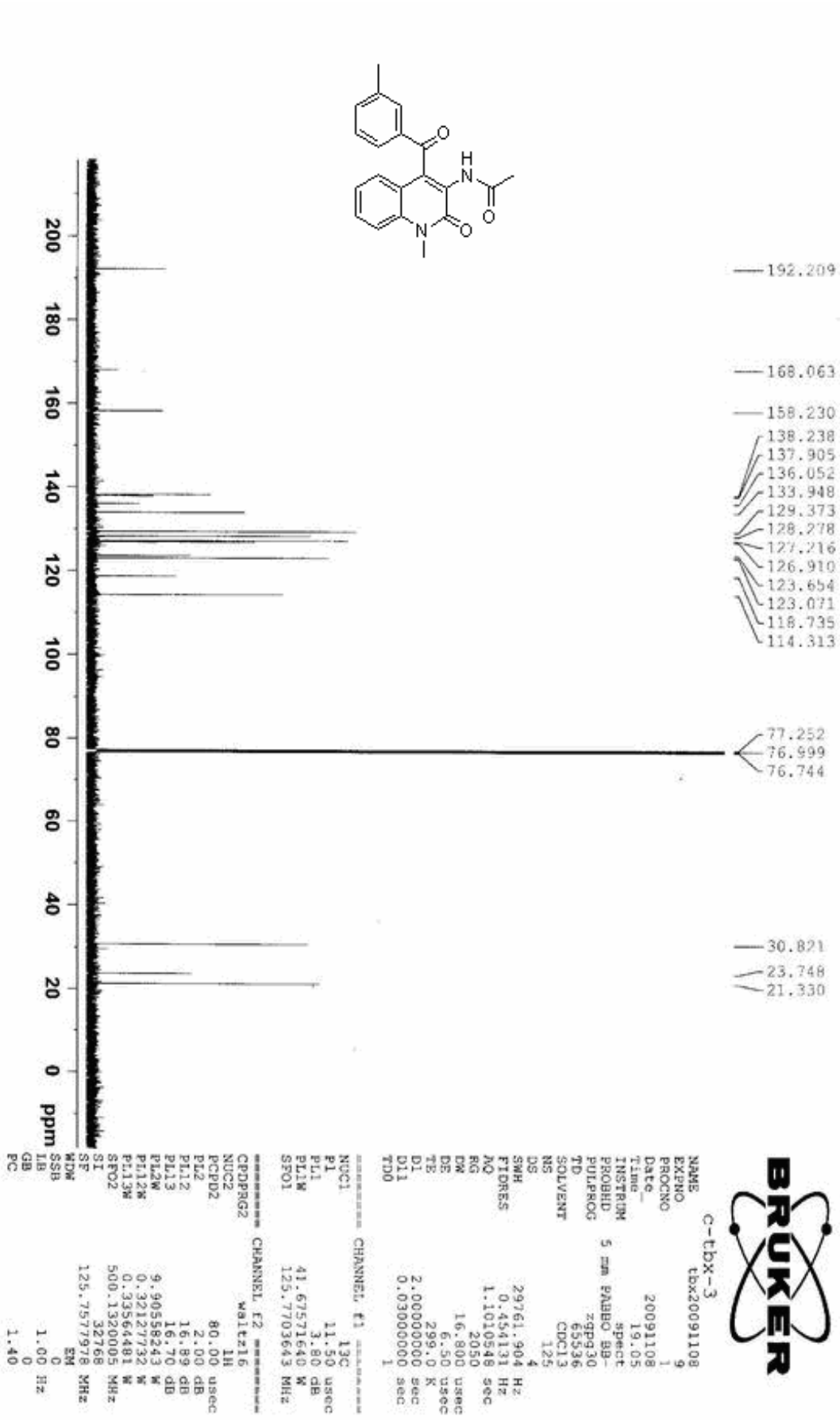
_N_-(1-methyl-4-(4-methylbenzoyl)-2-oxo-1,2-dihydroquinolin-3-yl)acetamide (2e)



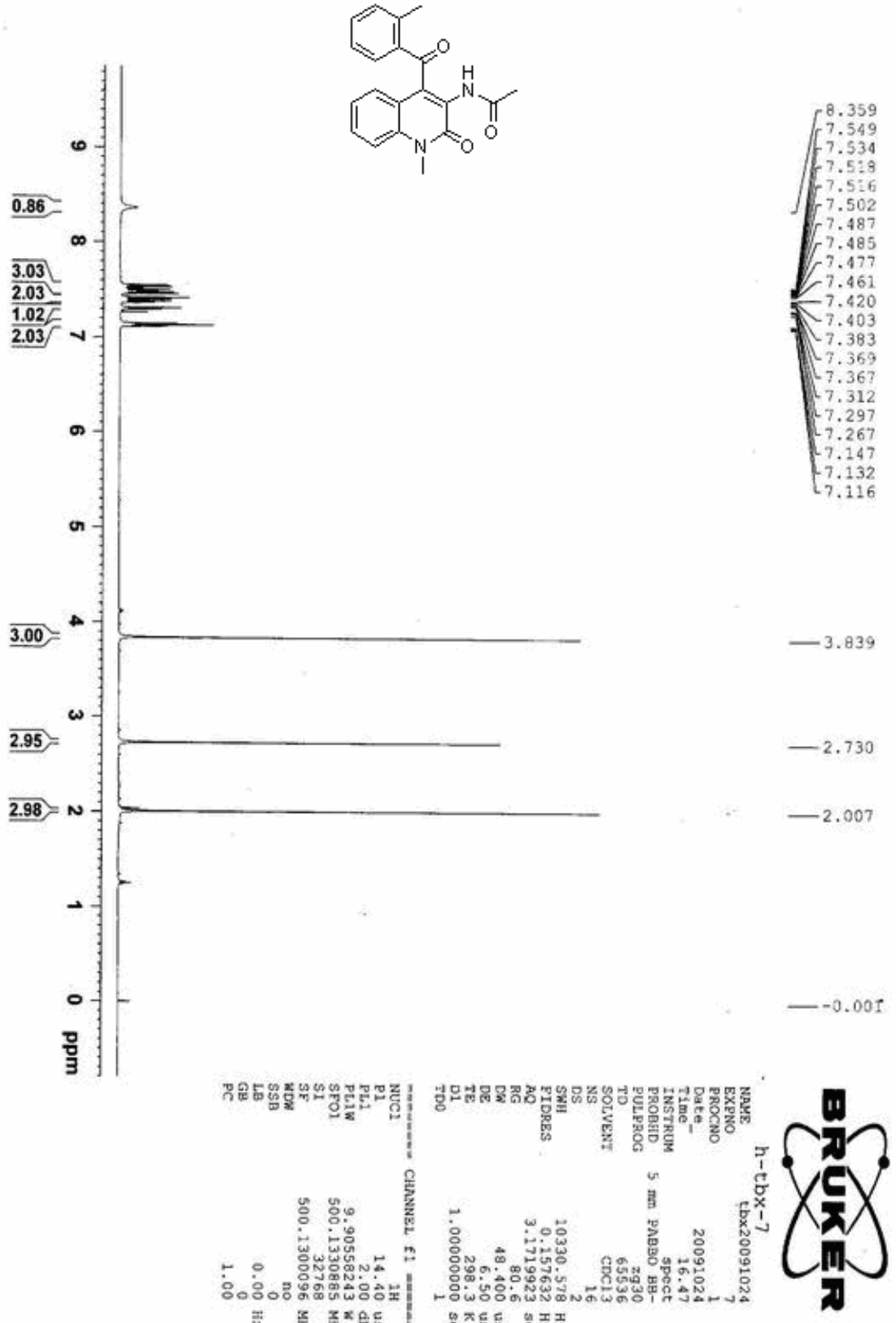
_N_-(1-methyl-4-(3-methylbenzoyl)-2-oxo-1,2-dihydroquinolin-3-yl)acetamide (2f)



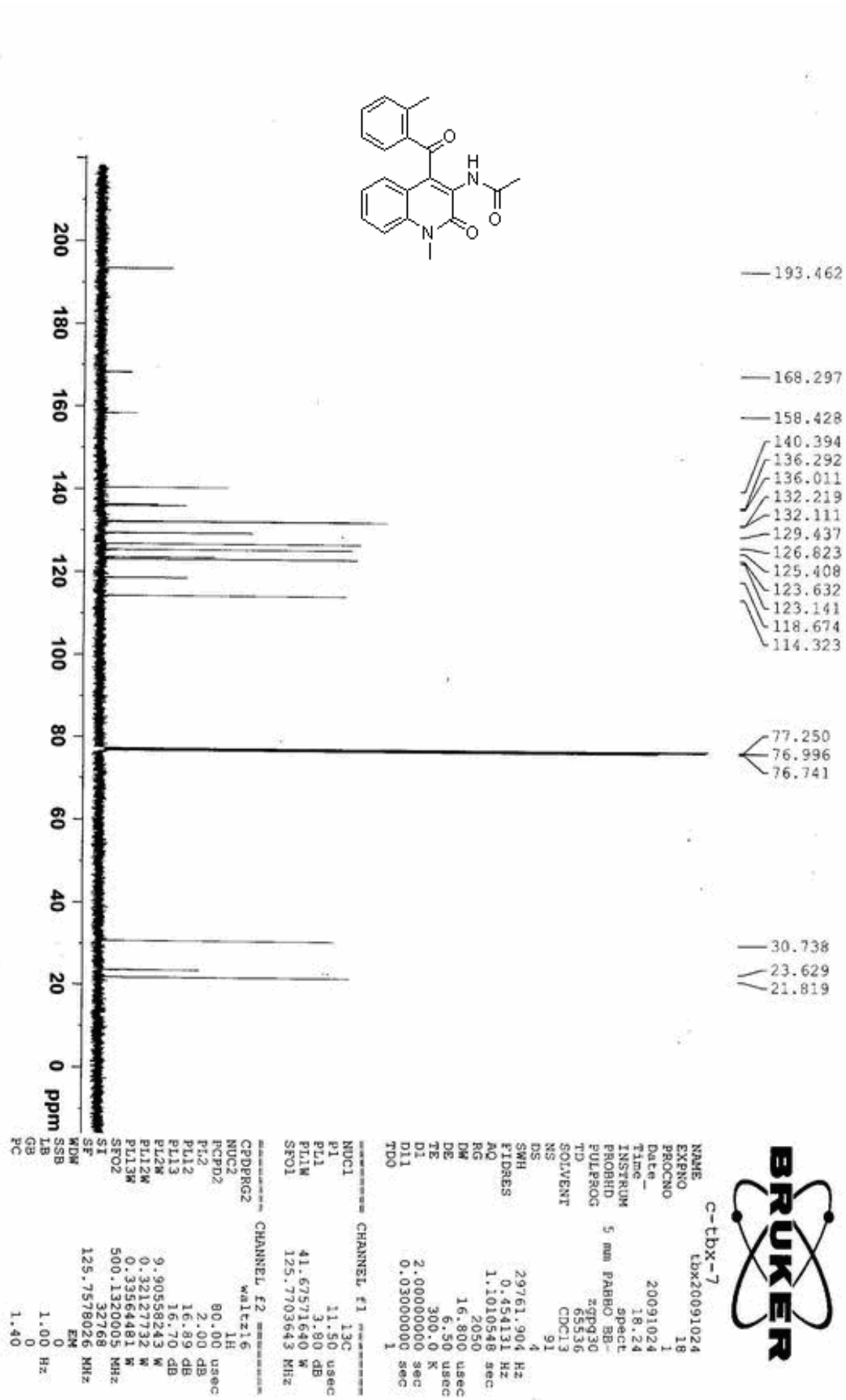
_N_-(1-methyl-4-(3-methylbenzoyl)-2-oxo-1,2-dihydroquinolin-3-yl)acetamide (2f)



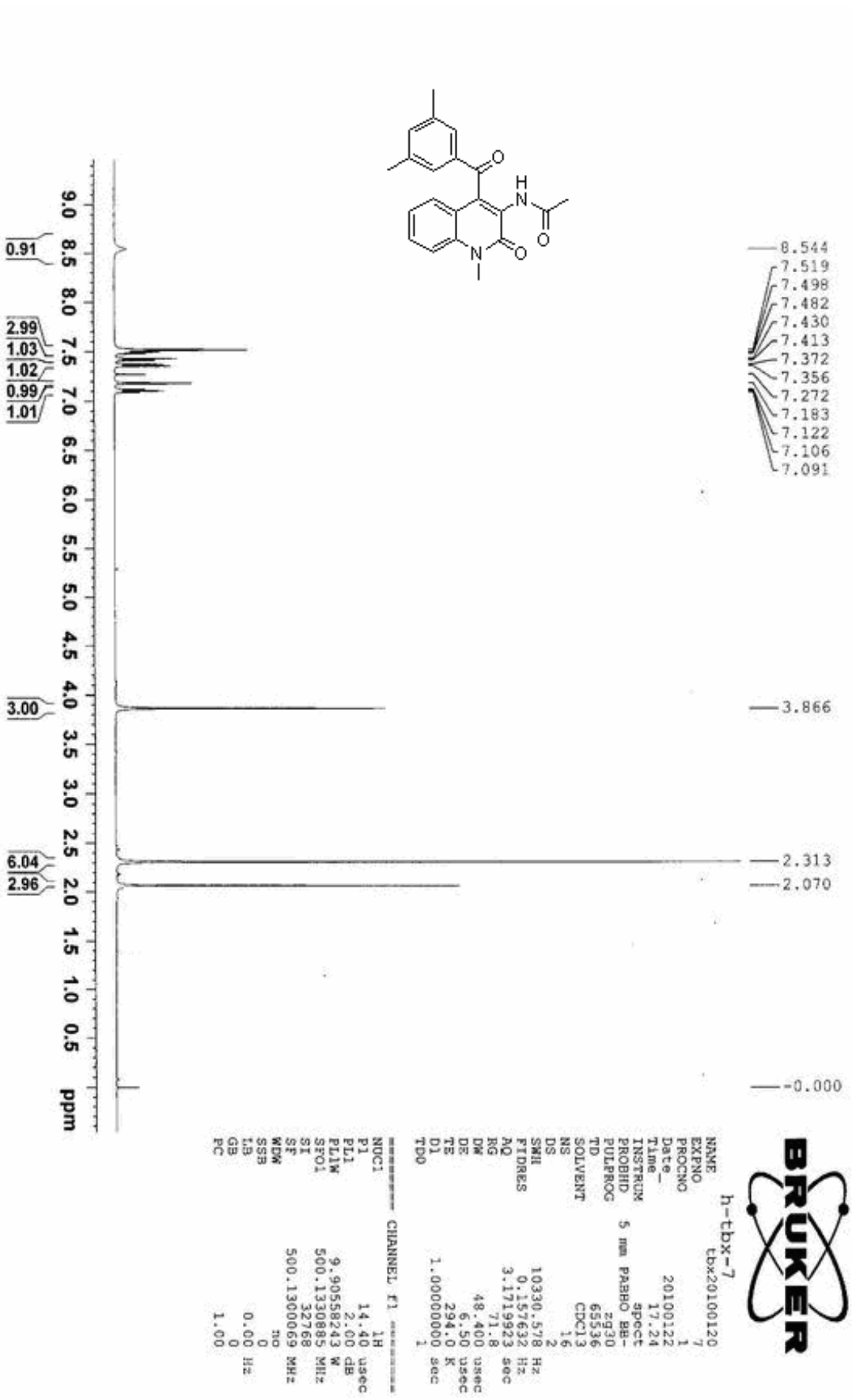
_N_-(1-methyl-4-(2-methylbenzoyl)-2-oxo-1,2-dihydroquinolin-3-yl)acetamide (2g)



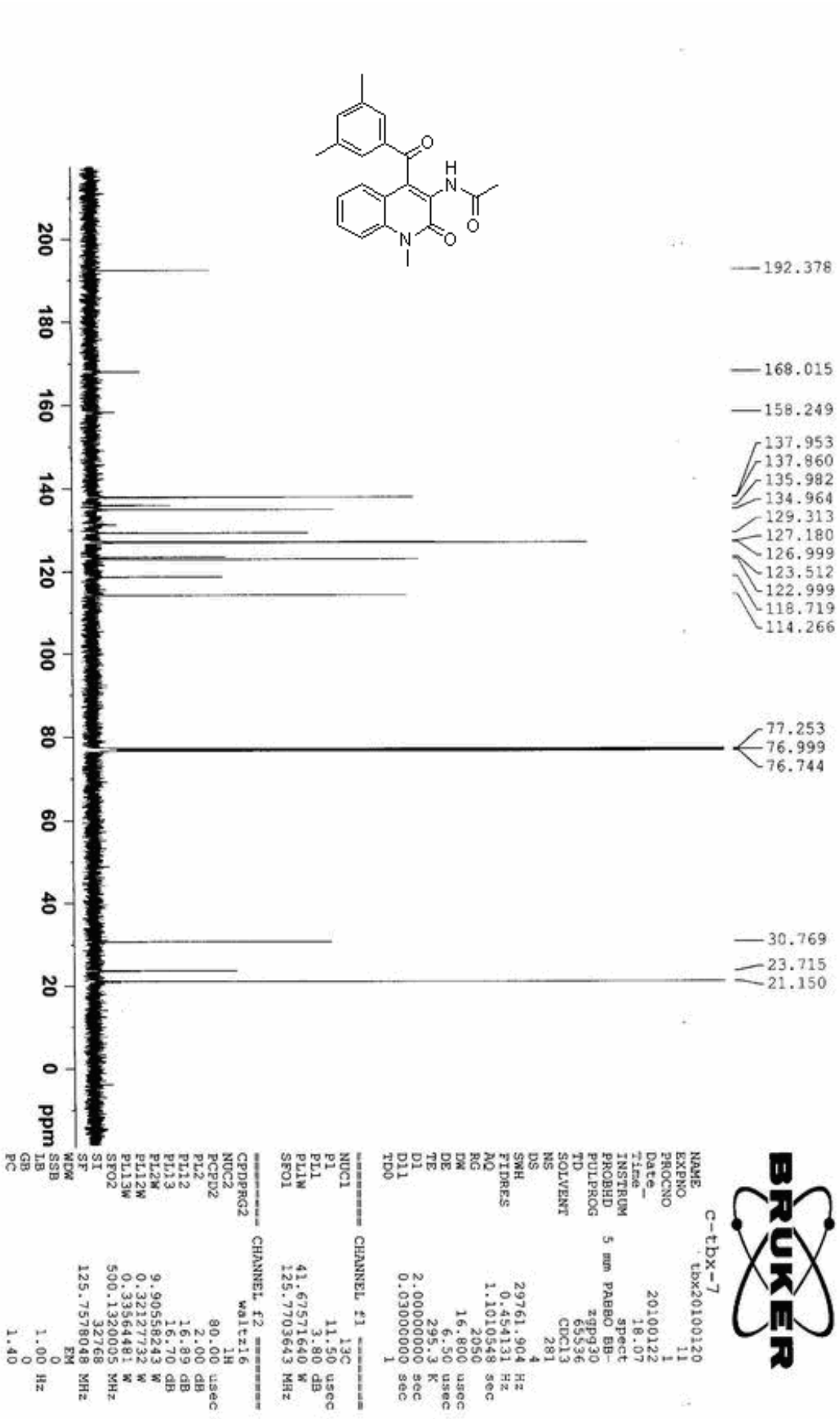
_N_-(1-methyl-4-(2-methylbenzoyl)-2-oxo-1,2-dihydroquinolin-3-yl)acetamide (2g)



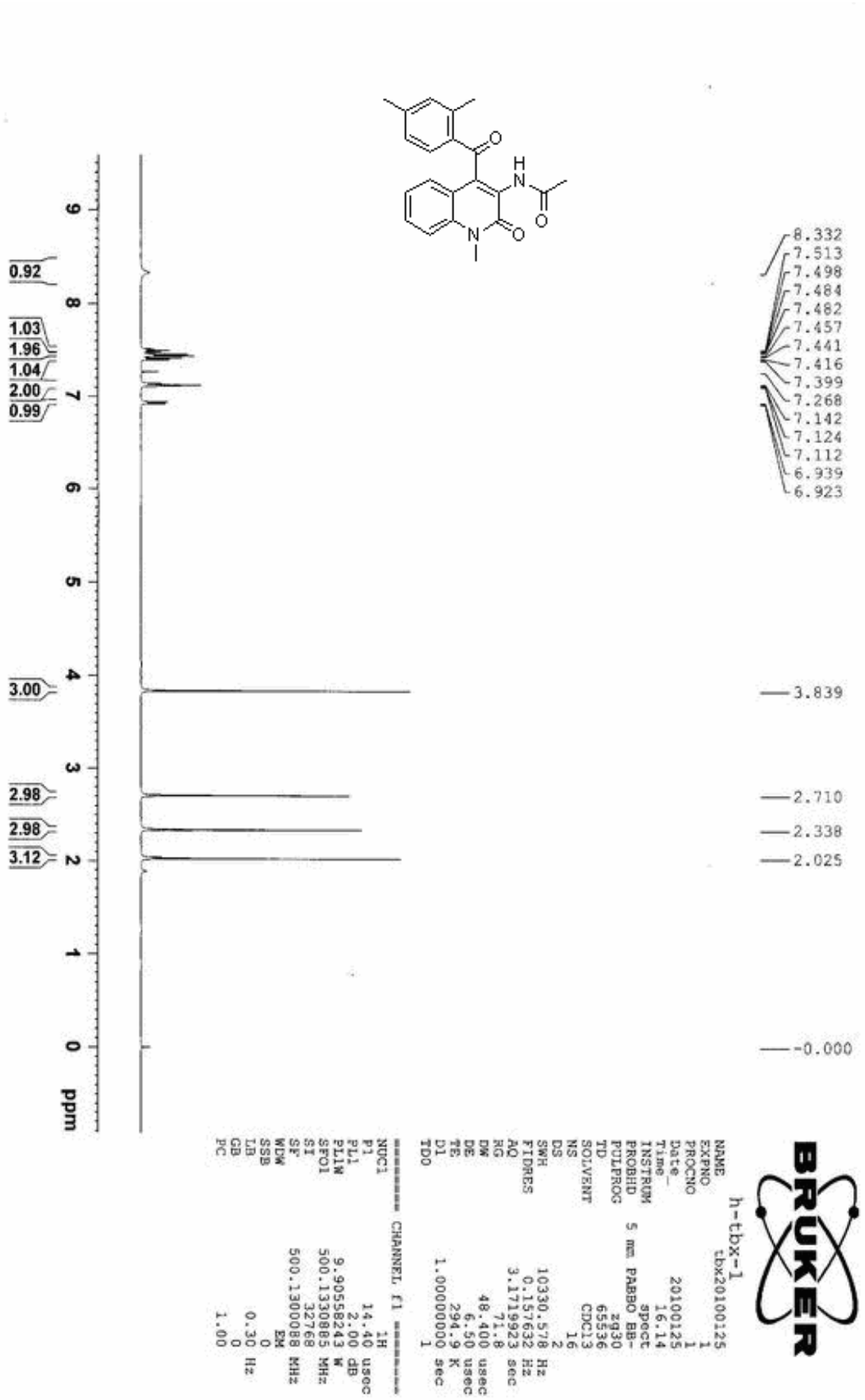
_N_-(4-(3,5-dimethylbenzoyl)-1-methyl-2-oxo-1,2-dihydroquinolin-3-yl)acetamide (2h)



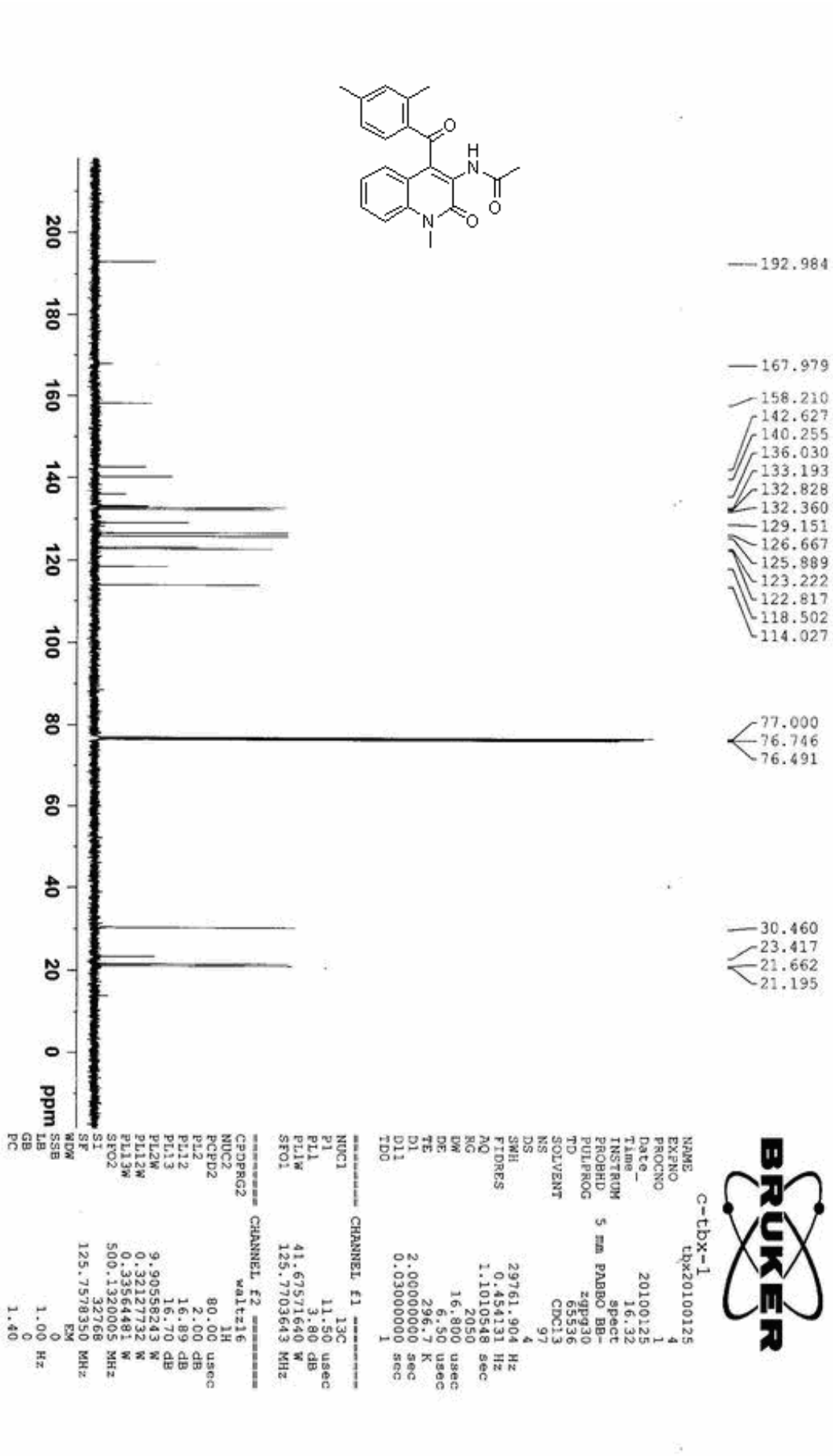
_N_-(4-(3,5-dimethylbenzoyl)-1-methyl-2-oxo-1,2-dihydroquinolin-3-yl)acetamide (2h)



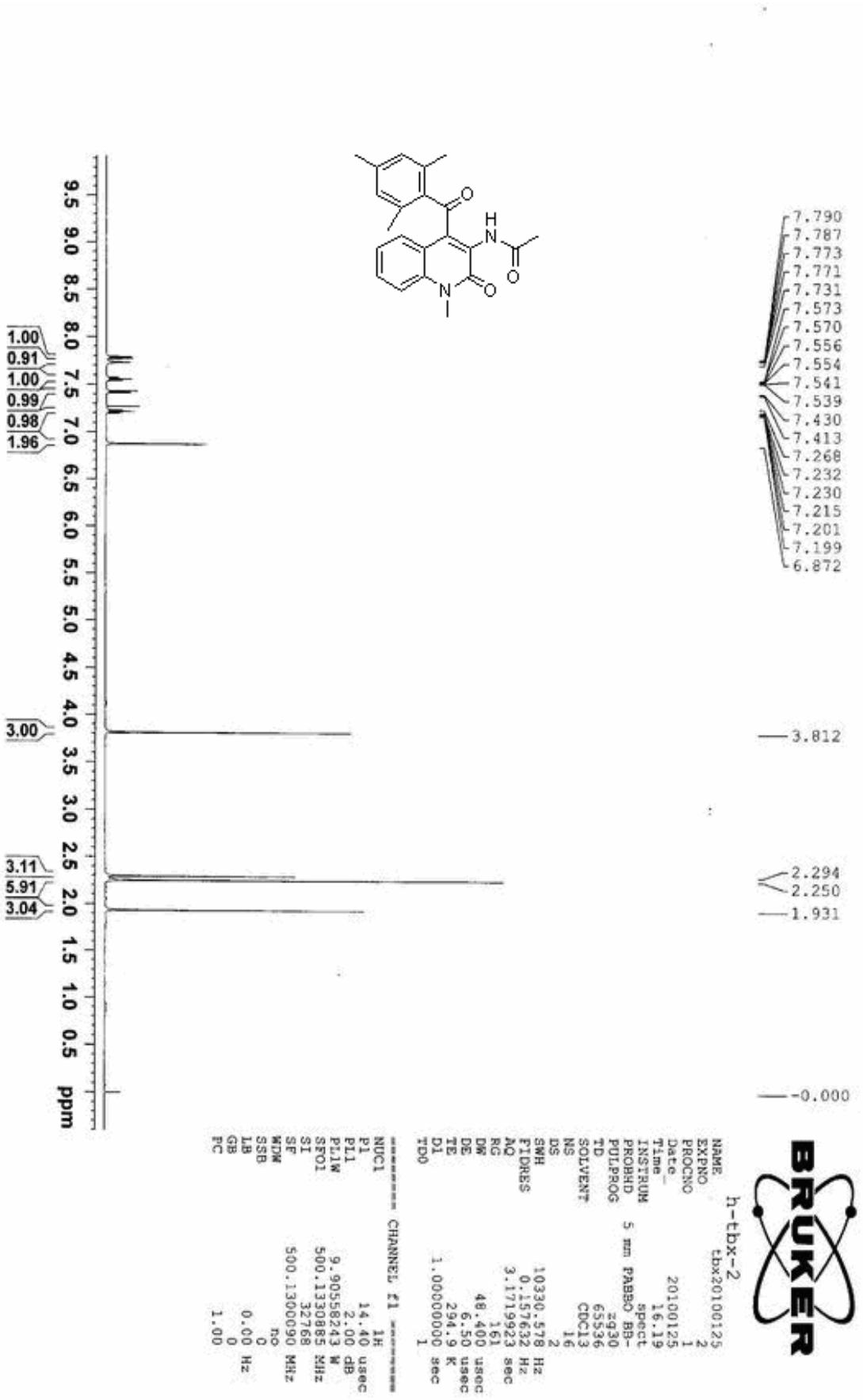
_N_-(4-(2,4-dimethylbenzoyl)-1-methyl-2-oxo-1,2-dihydroquinolin-3-yl)acetamide (2i)



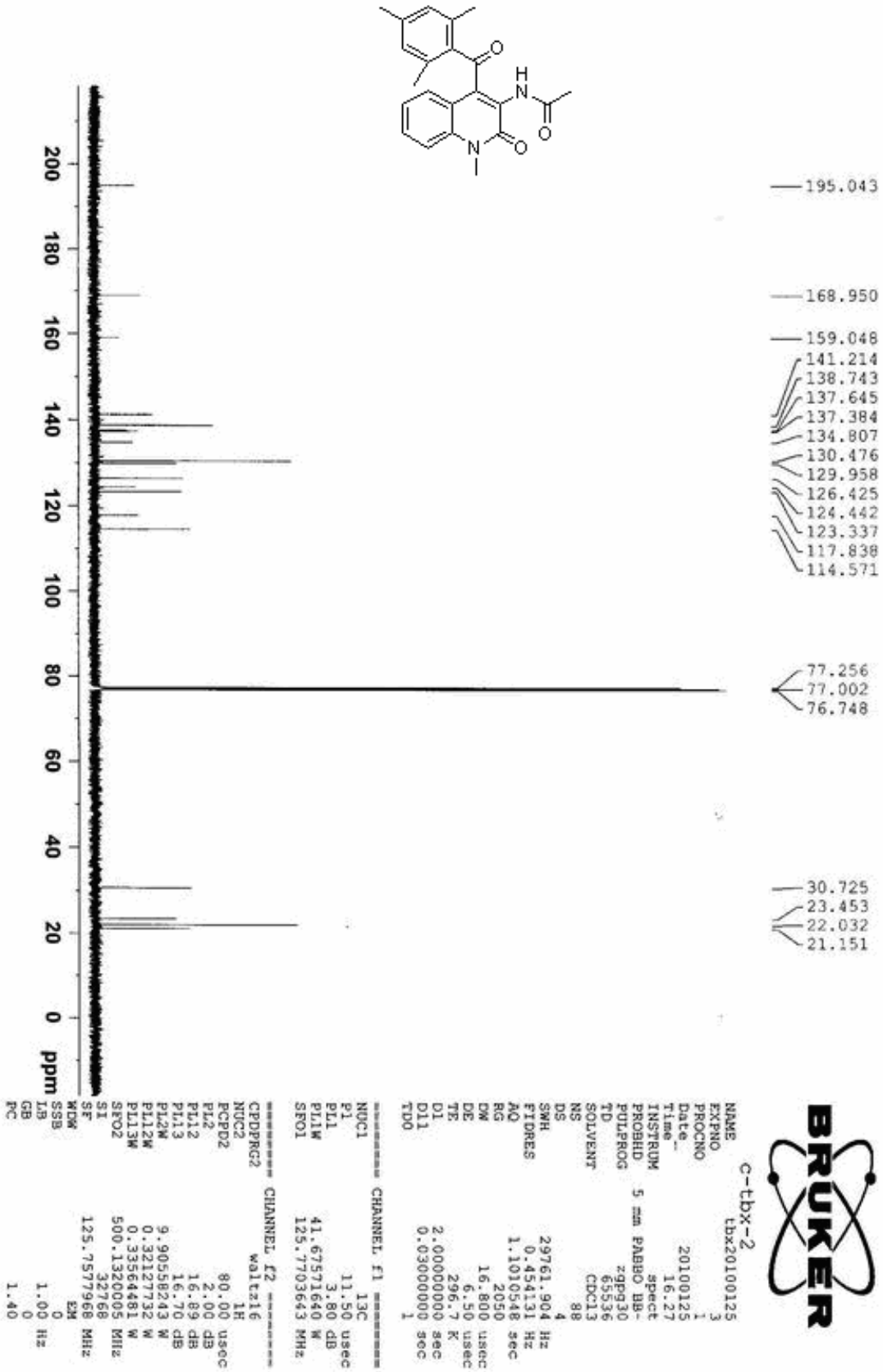
_N_-(4-(2,4-dimethylbenzoyl)-1-methyl-2-oxo-1,2-dihydroquinolin-3-yl)acetamide (2i)



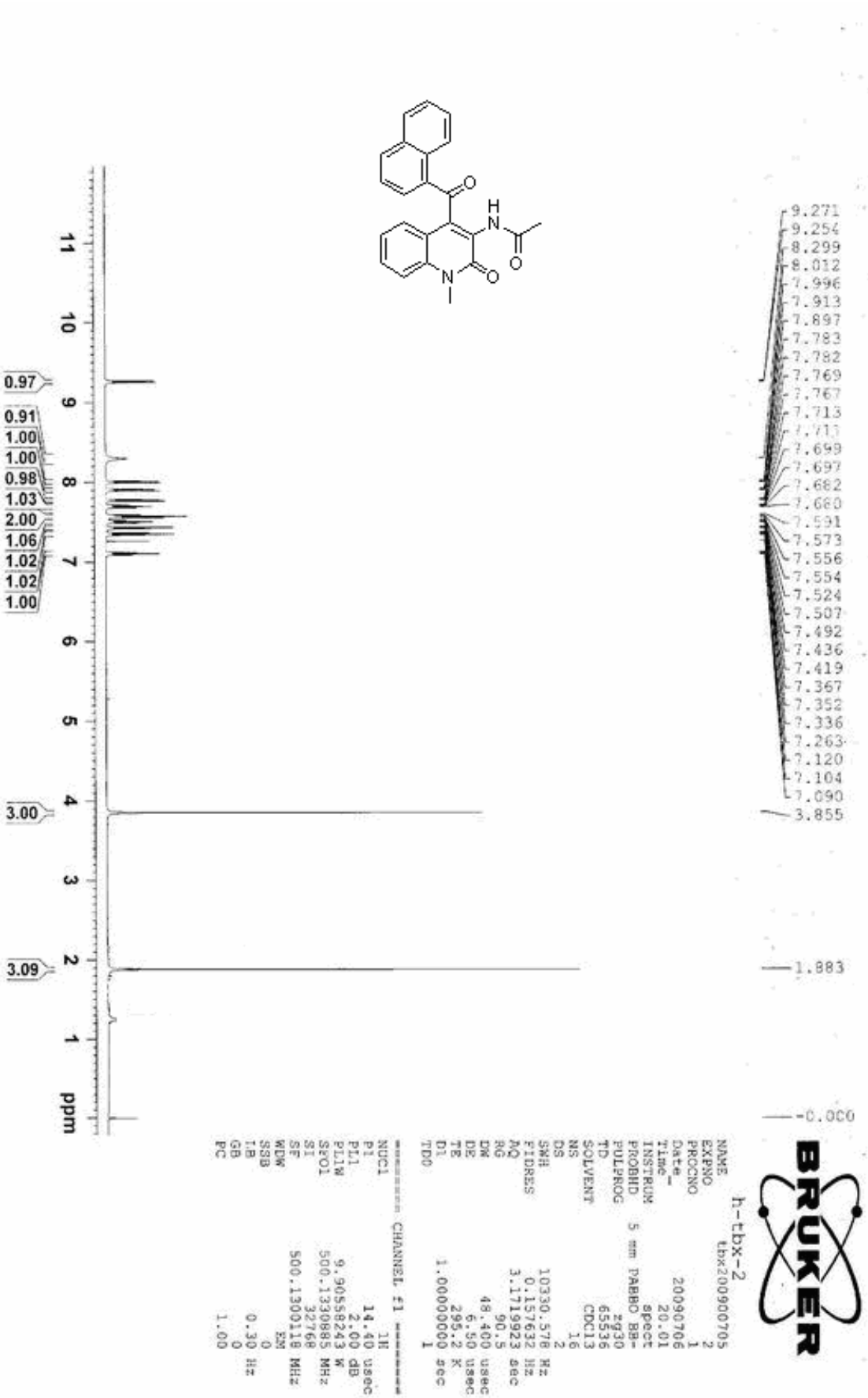
_N_-(1-methyl-2-oxo-4-(2,4,6-trimethylbenzoyl)-1,2-dihydroquinolin-3-yl)acetamide (2j)



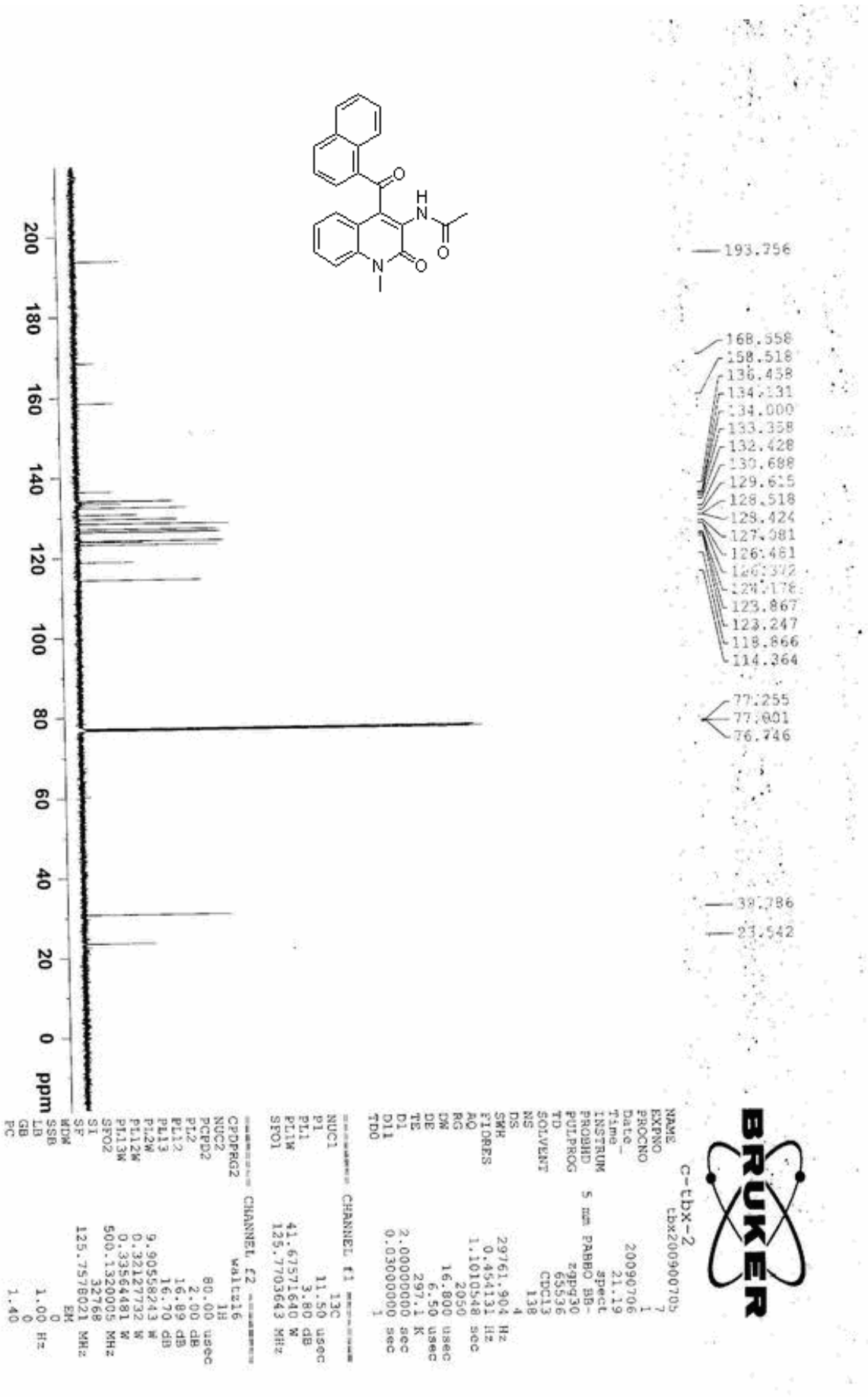
_N_-(1-methyl-2-oxo-4-(2,4,6-trimethylbenzoyl)-1,2-dihydroquinolin-3-yl)acetamide (2j)



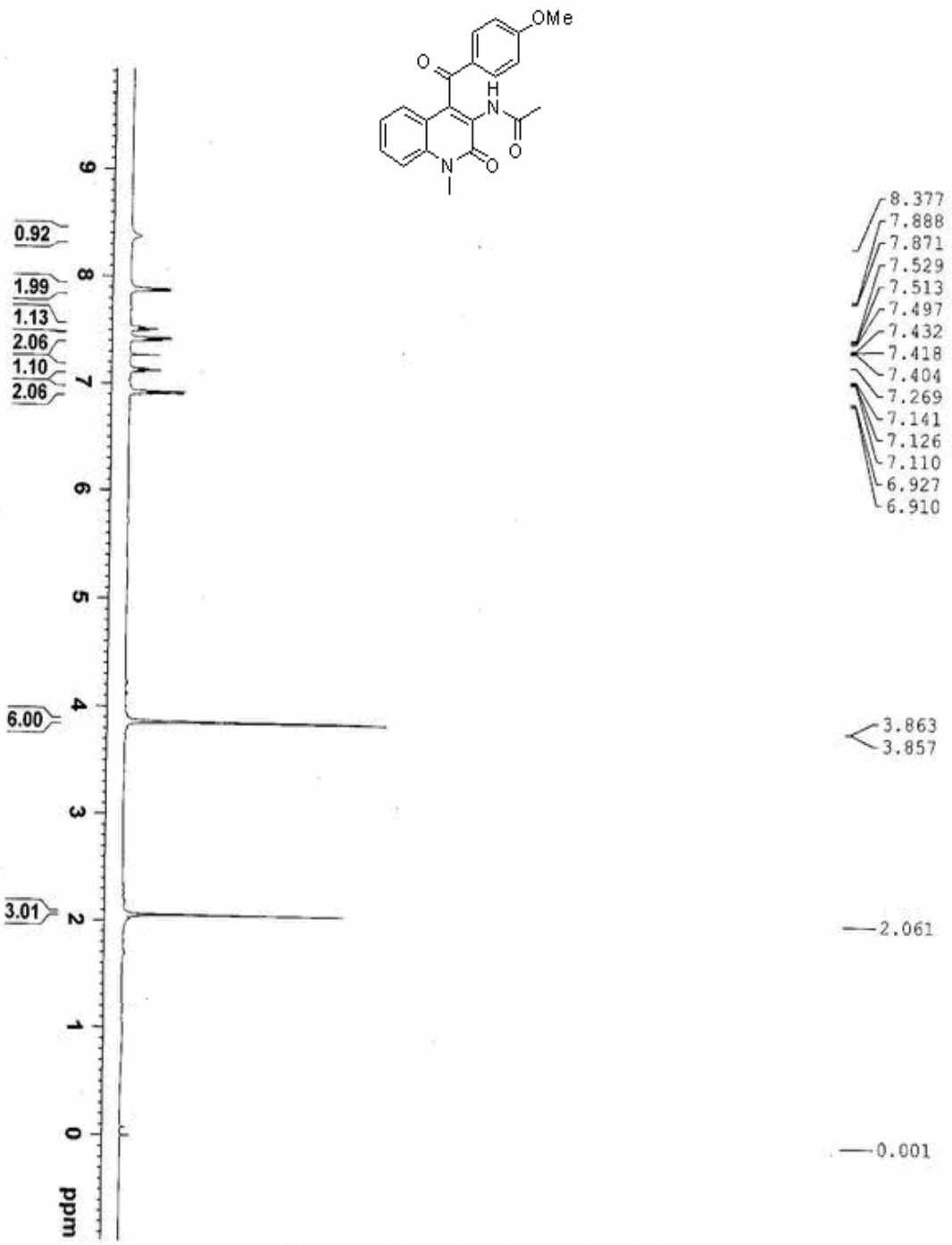
_N_-(4-(1-naphthoyl)-1-methyl-2-oxo-1,2-dihydroquinolin-3-yl)acetamide (2k)



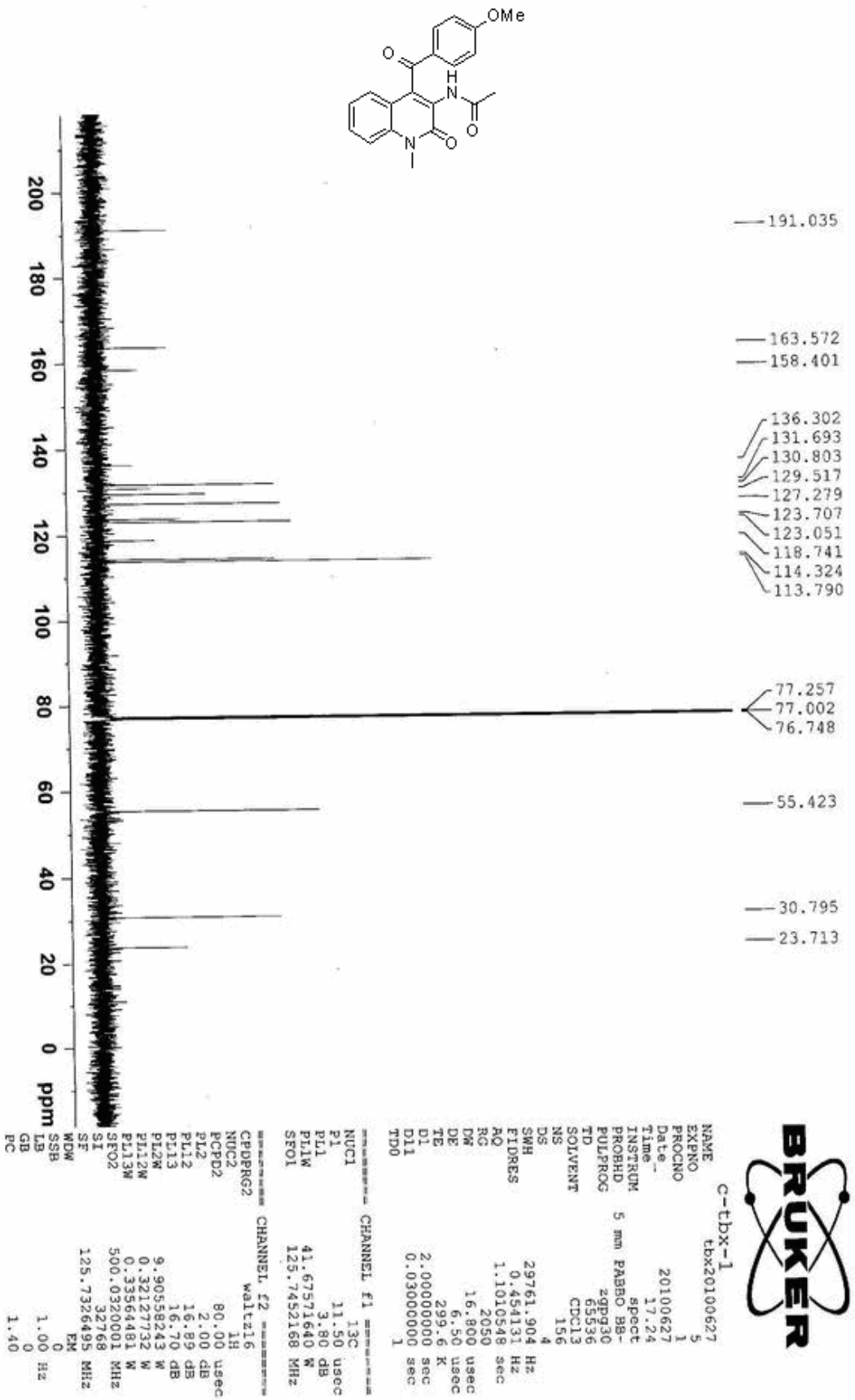
_N_-(4-(1-naphthoyl)-1-methyl-2-oxo-1,2-dihydroquinolin-3-yl)acetamide (2k)



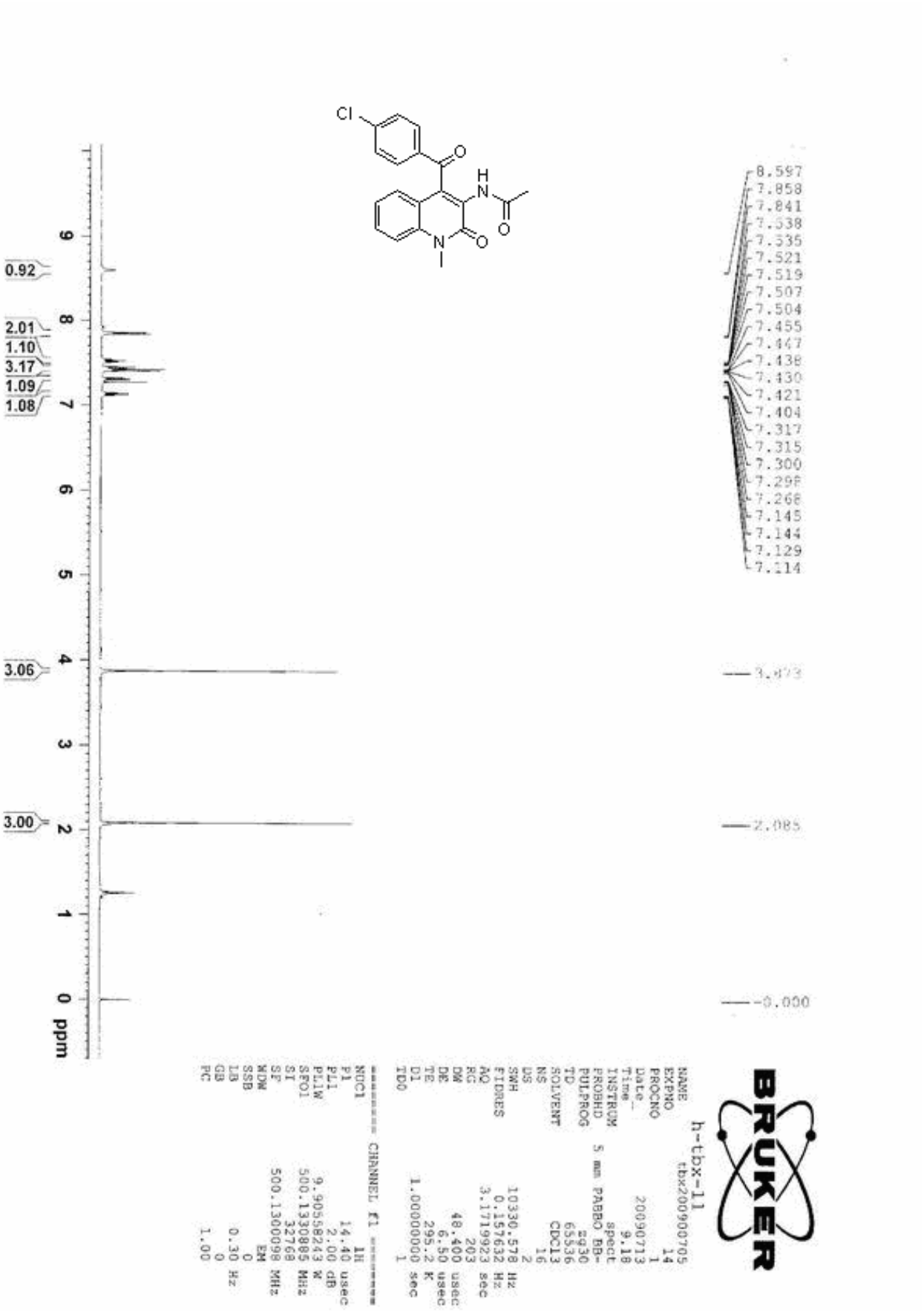
_N_-(4-(4-methoxybenzoyl)-1-methyl-2-oxo-1,2-dihydroquinolin-3-yl)acetamide (2l)



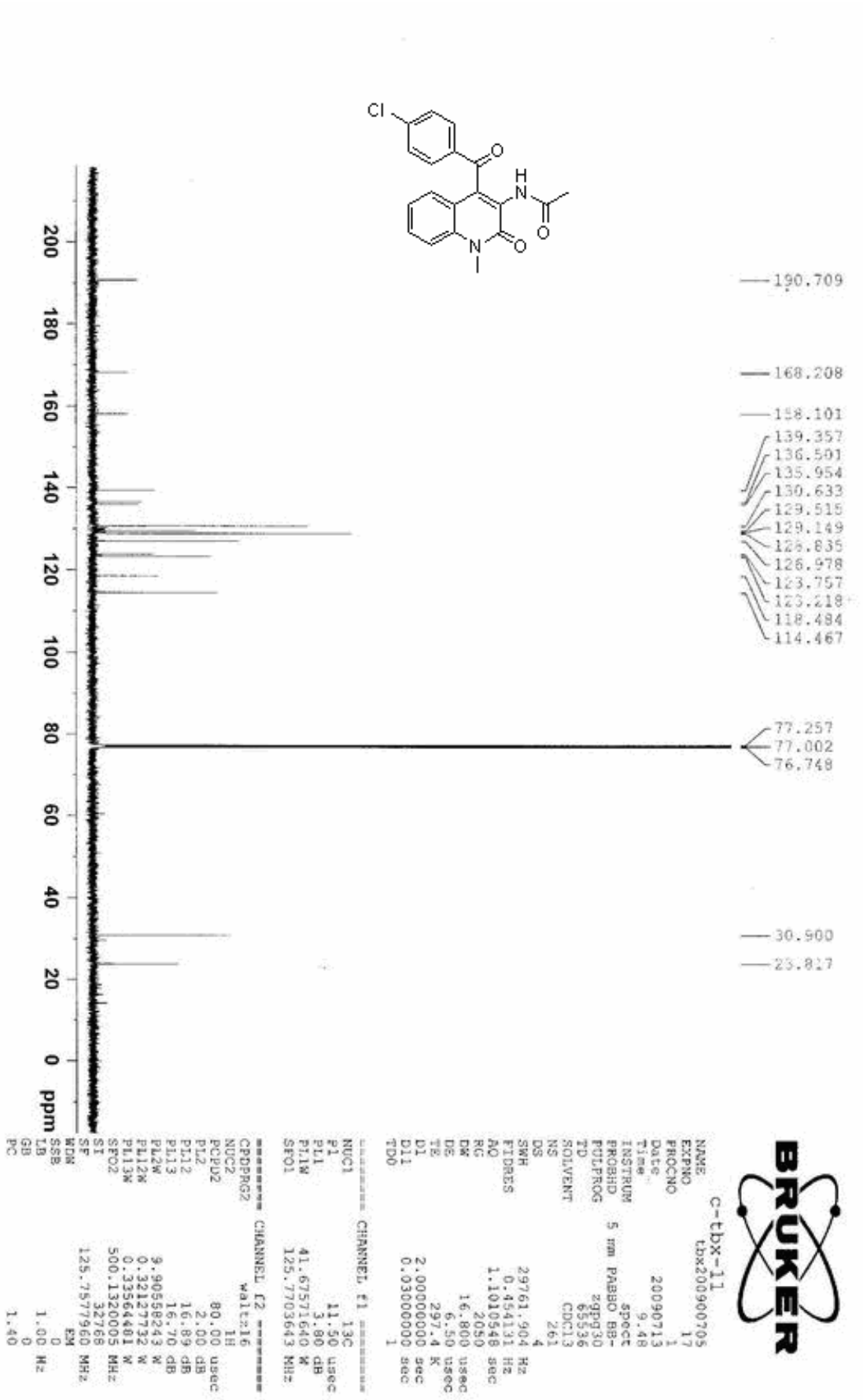
_N_-(4-(4-methoxybenzoyl)-1-methyl-2-oxo-1,2-dihydroquinolin-3-yl)acetamide (2l)



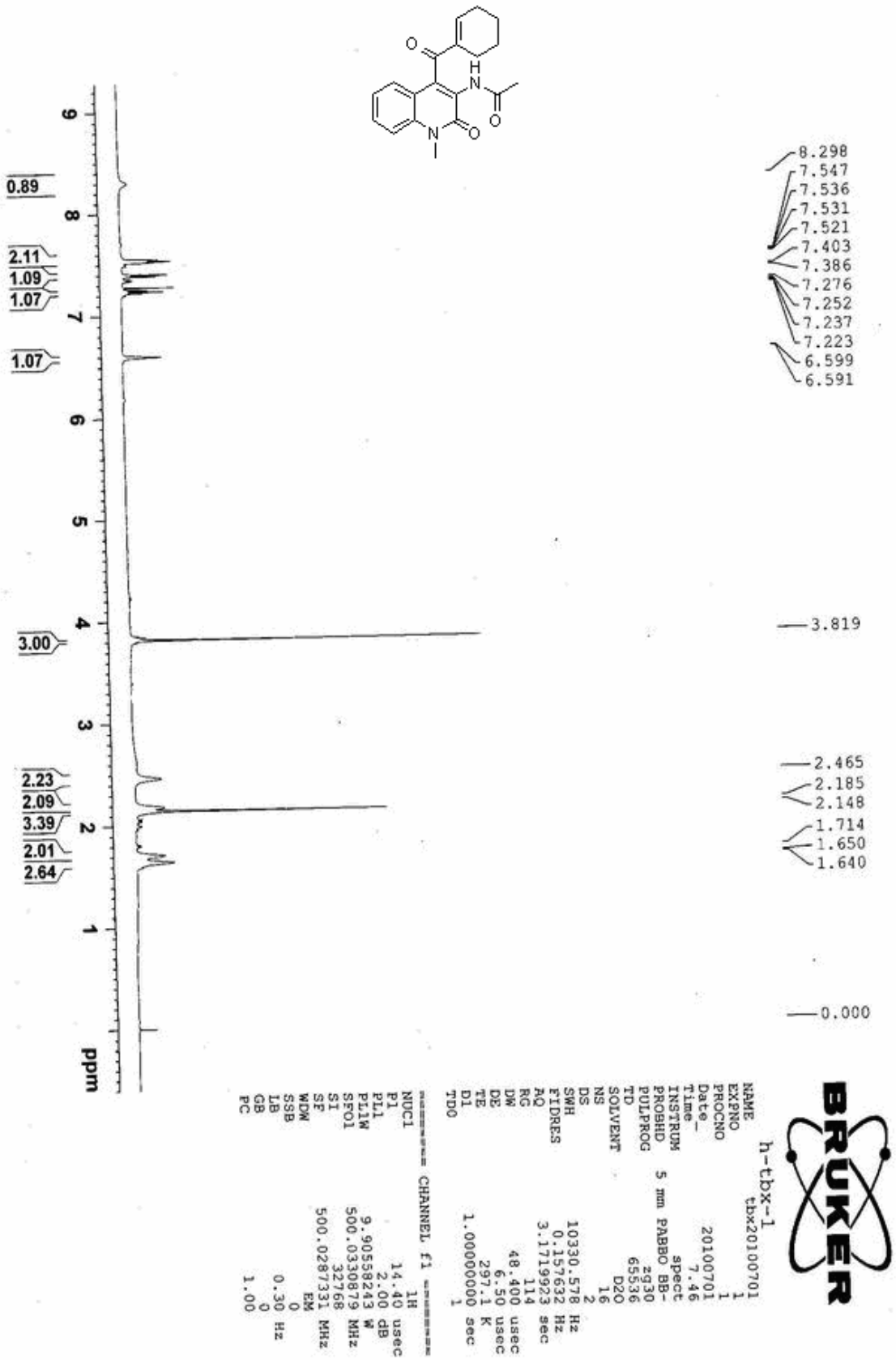
_N_-(4-(4-chlorobenzoyl)-1-methyl-2-oxo-1,2-dihydroquinolin-3-yl)acetamide (2m)



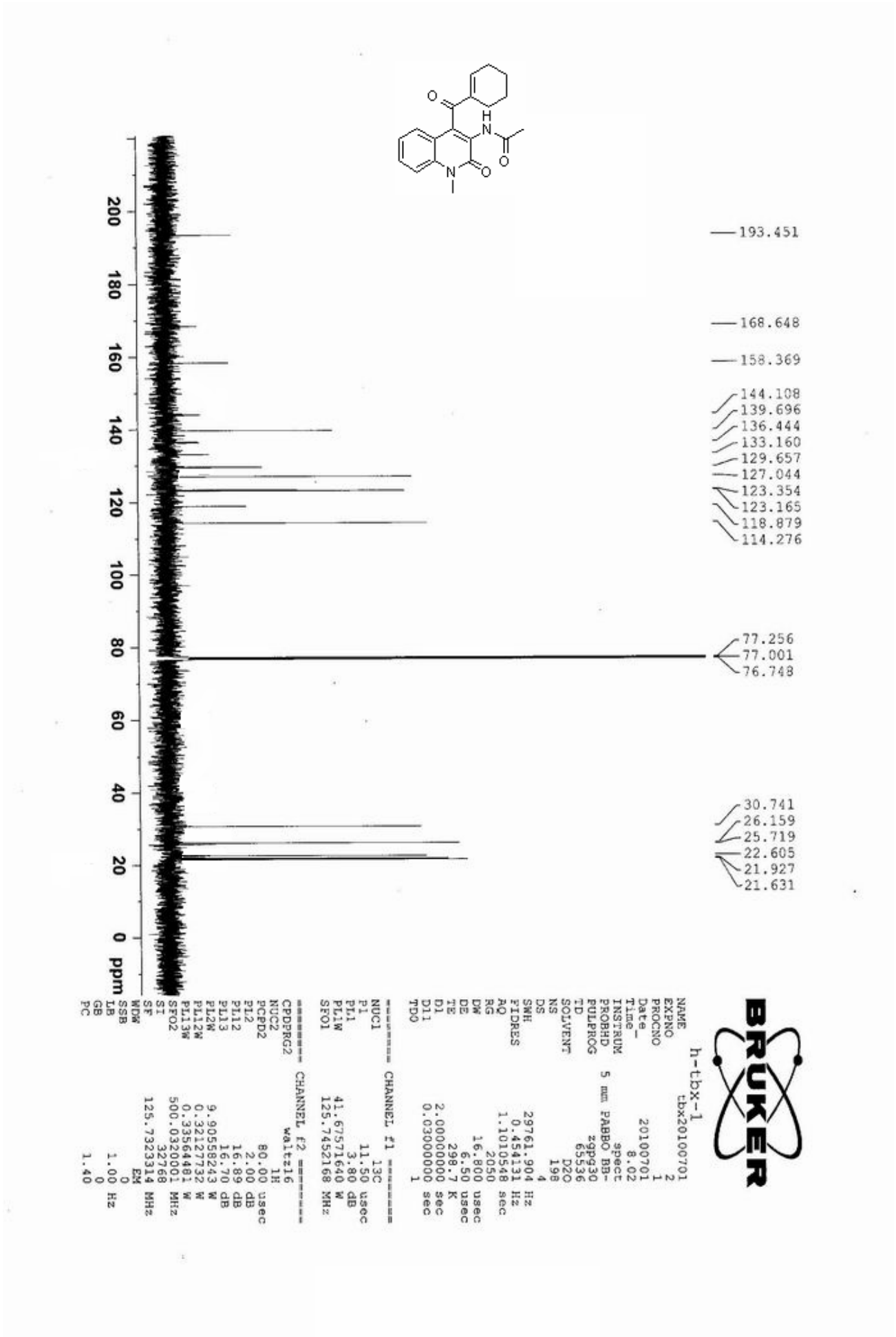
_N_-(4-(4-chlorobenzoyl)-1-methyl-2-oxo-1,2-dihydroquinolin-3-yl)acetamide (2m)



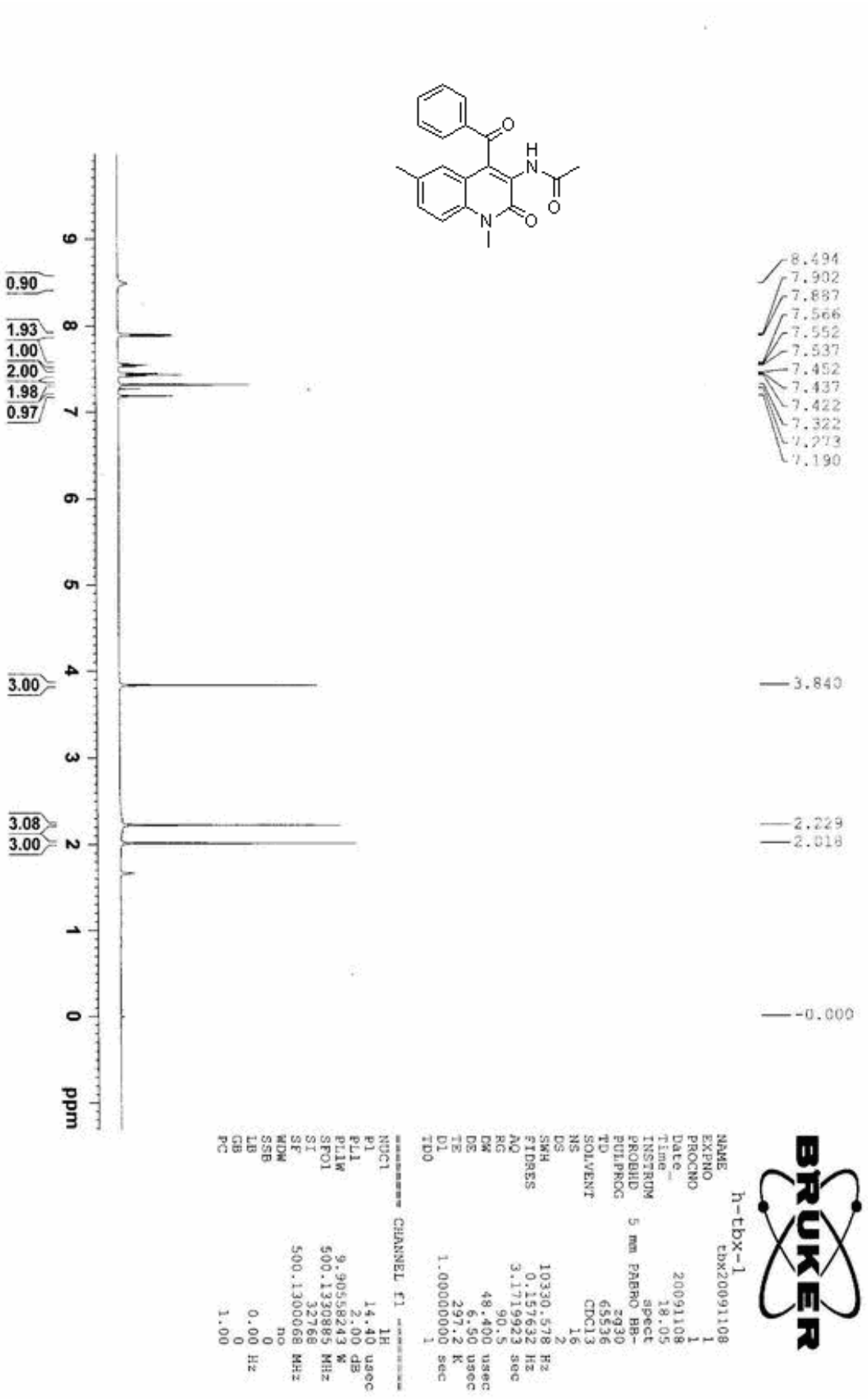
_N_-(4-(cyclohex-1-enecarbonyl)-1-methyl-2-oxo-1,2-dihydroquinolin-3-yl)acetamide (2n)



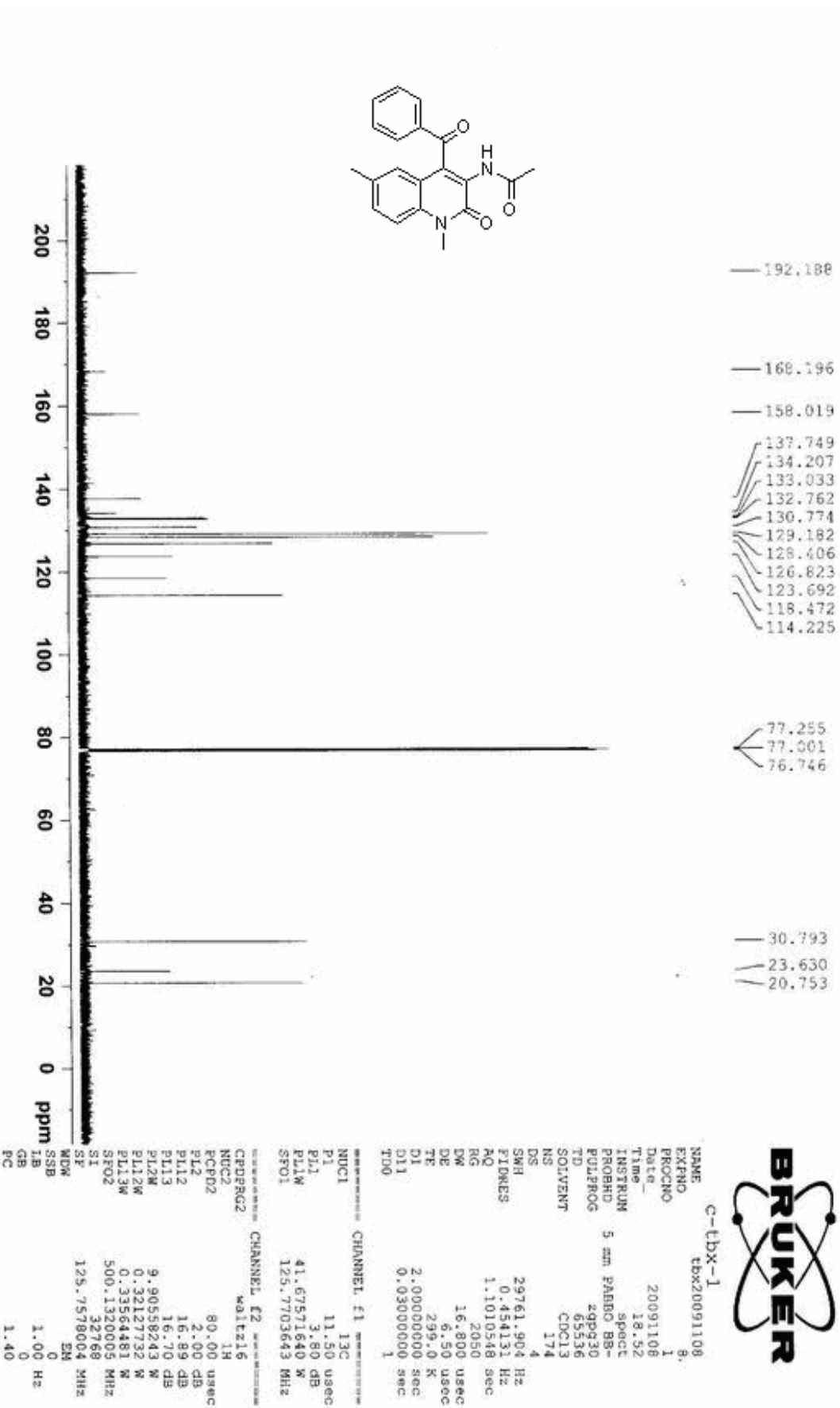
_N_-(4-(cyclohex-1-enecarbonyl)-1-methyl-2-oxo-1,2-dihydroquinolin-3-yl)acetamide (2n)



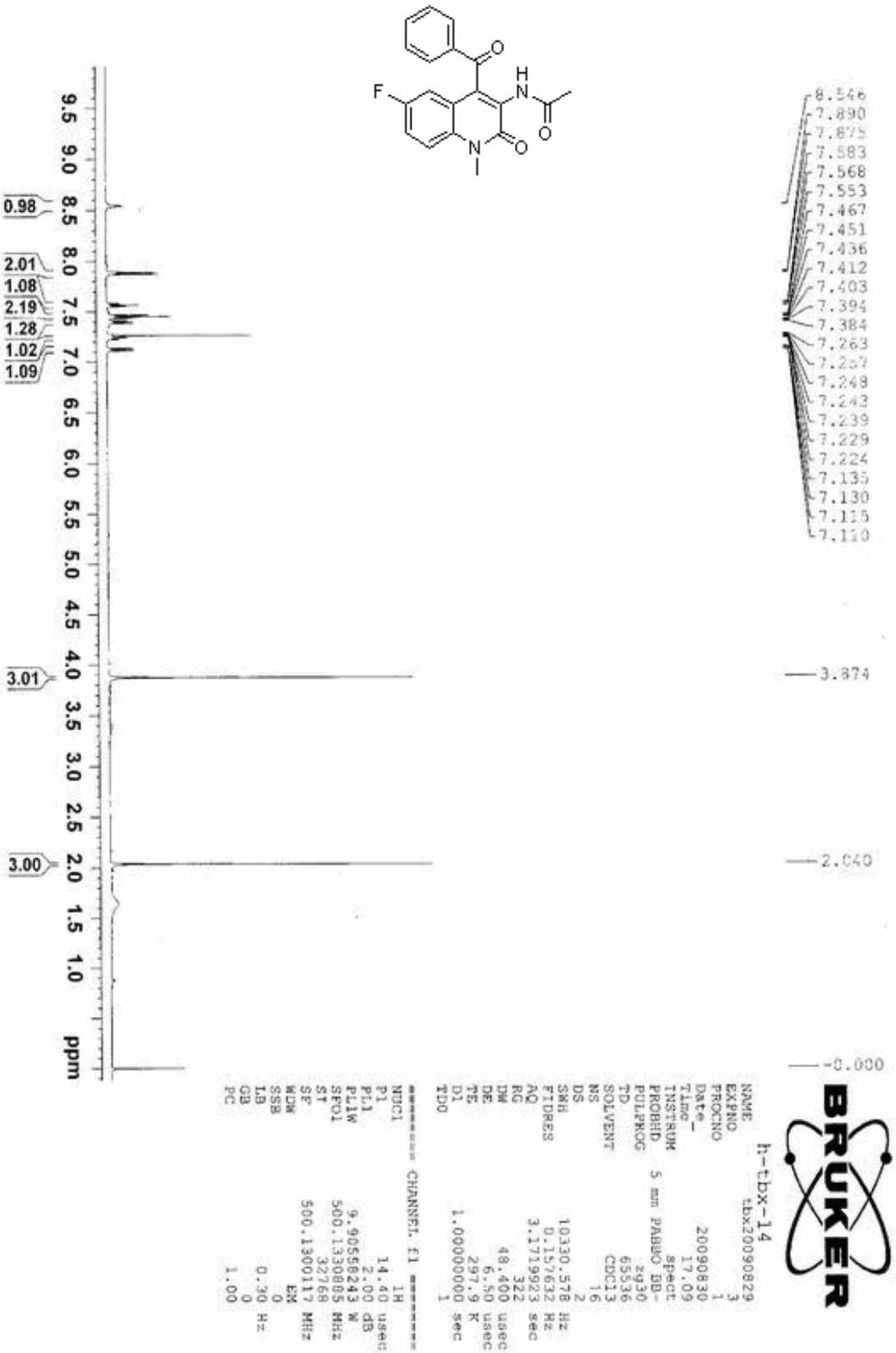
_N_-(4-benzoyl-1,6-dimethyl-2-oxo-1,2-dihydroquinolin-3-yl)acetamide (2o)



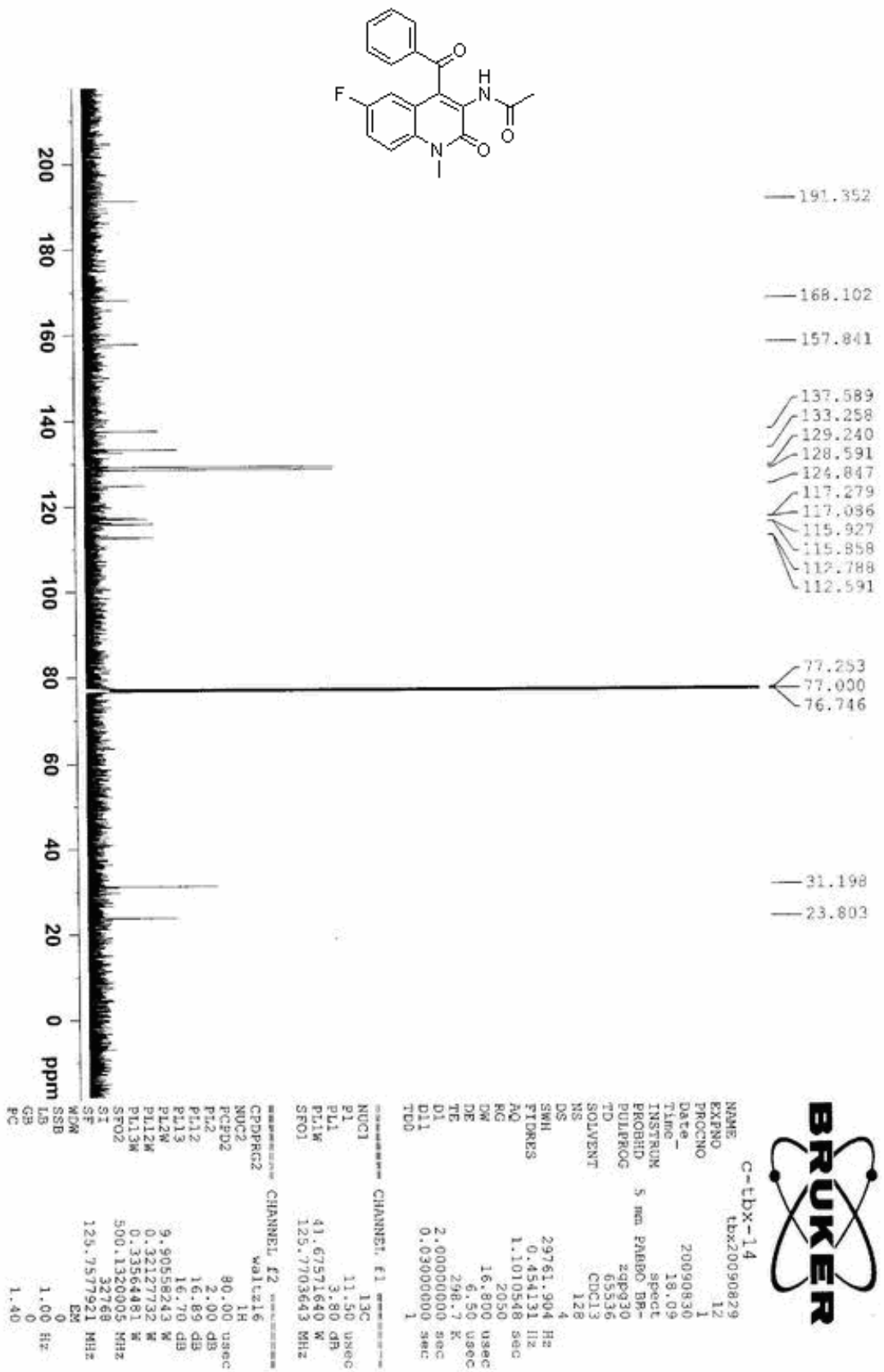
_N_-(4-benzoyl-1,6-dimethyl-2-oxo-1,2-dihydroquinolin-3-yl)acetamide (2o)



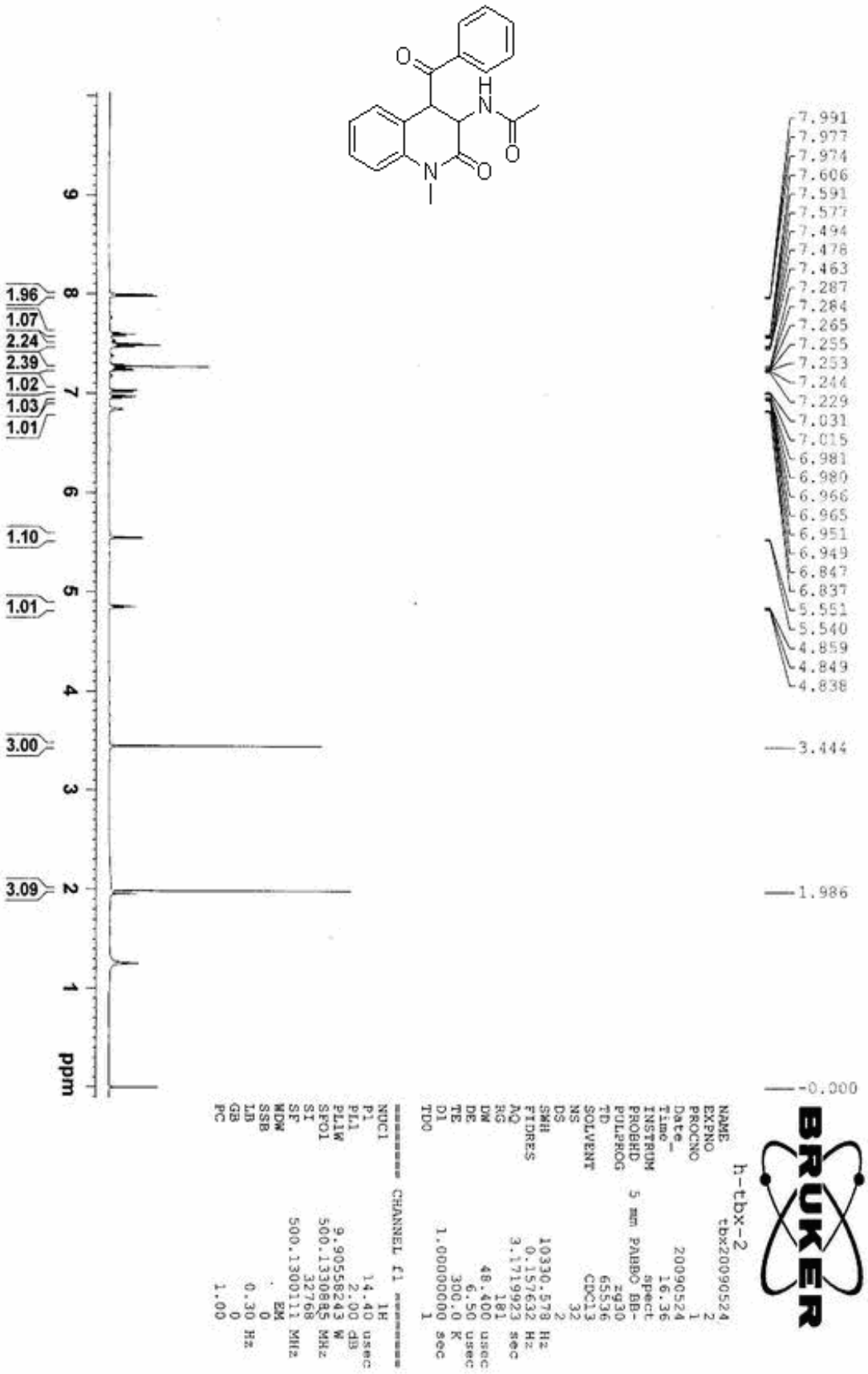
_N_-(4-benzoyl-6-fluoro-1-methyl-2-oxo-1,2-dihydroquinolin-3-yl)acetamide (2p)



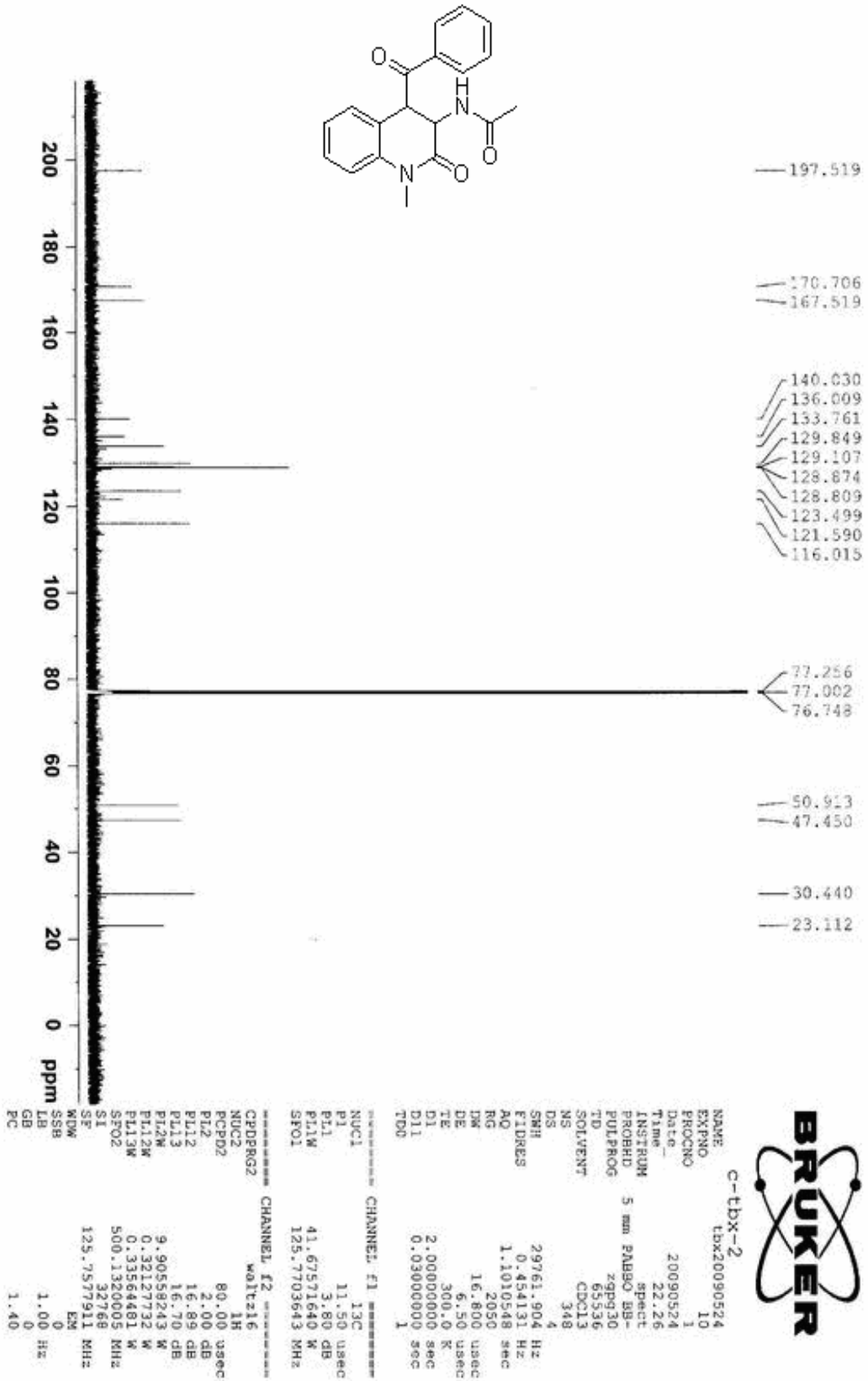
N-(4-benzoyl-6-fluoro-1-methyl-2-oxo-1,2-dihydroquinolin-3-yl)acetamide (2p)



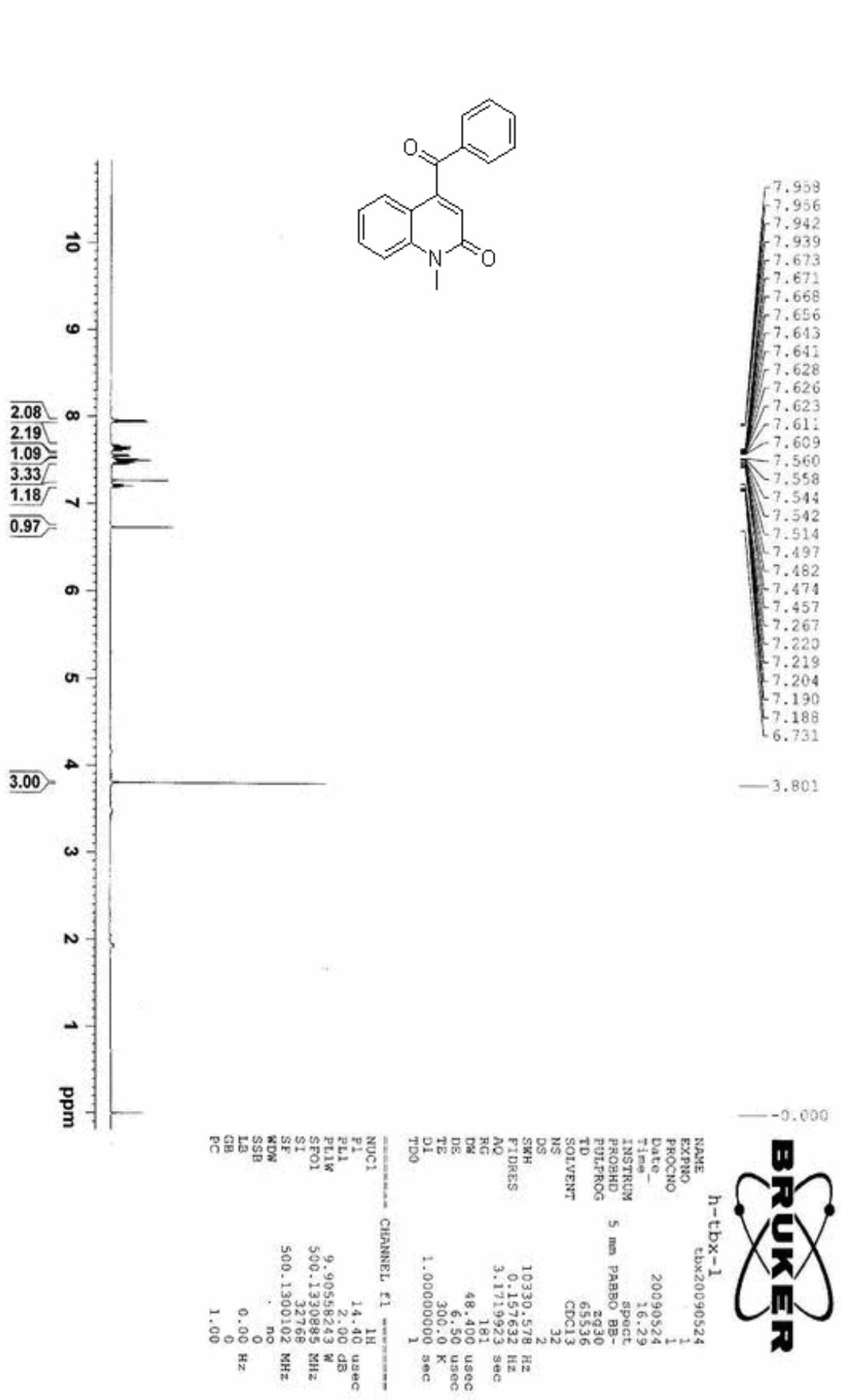
_N_-(4-benzoyl-1-methyl-2-oxo-1,2,3,4-tetrahydroquinolin-3-yl)acetamide (3a)



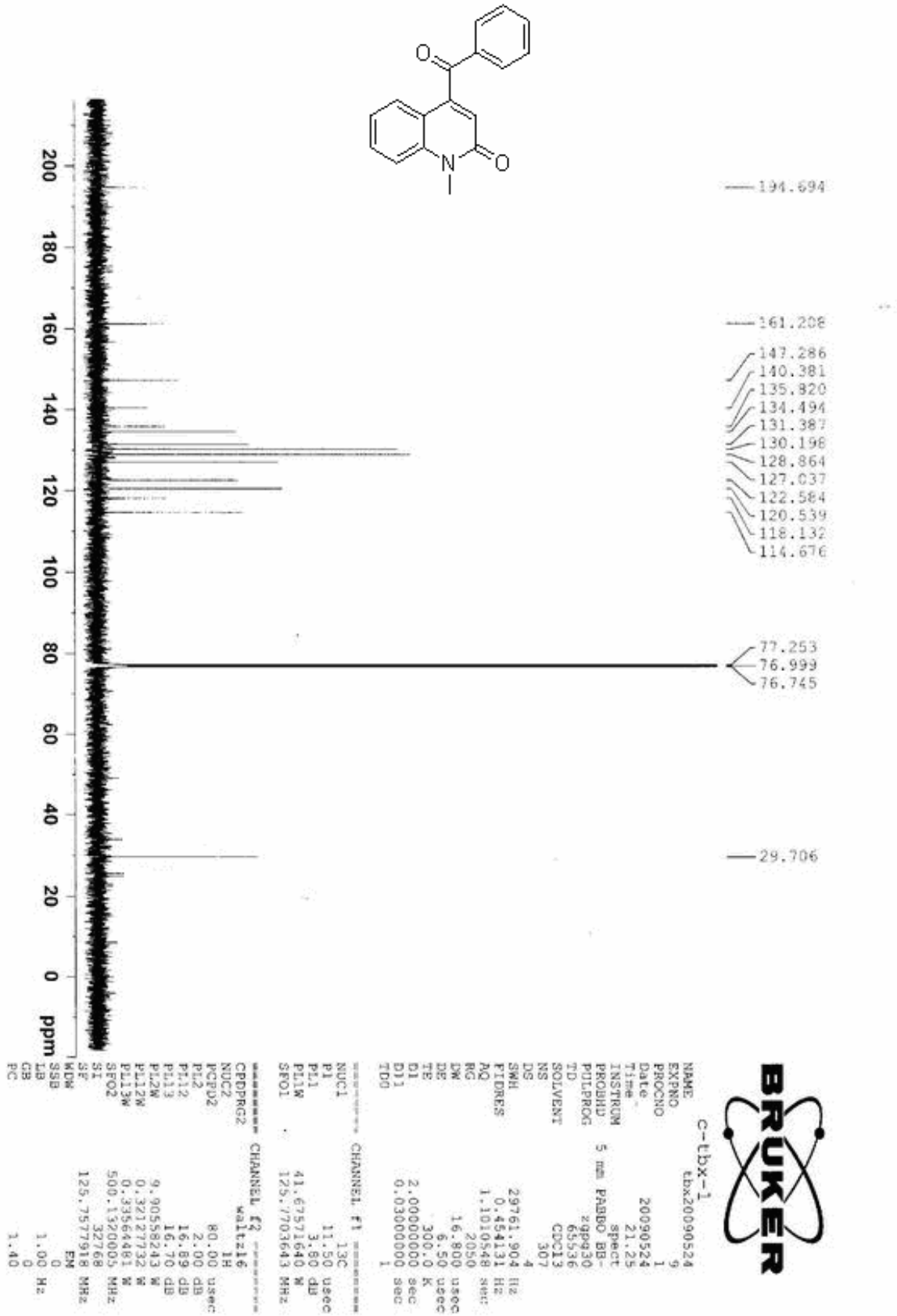
_N_-(4-benzoyl-1-methyl-2-oxo-1,2,3,4-tetrahydroquinolin-3-yl)acetamide (3a)



4-benzoyl-*N*-methylquinolin-2(1H)-one (4a)

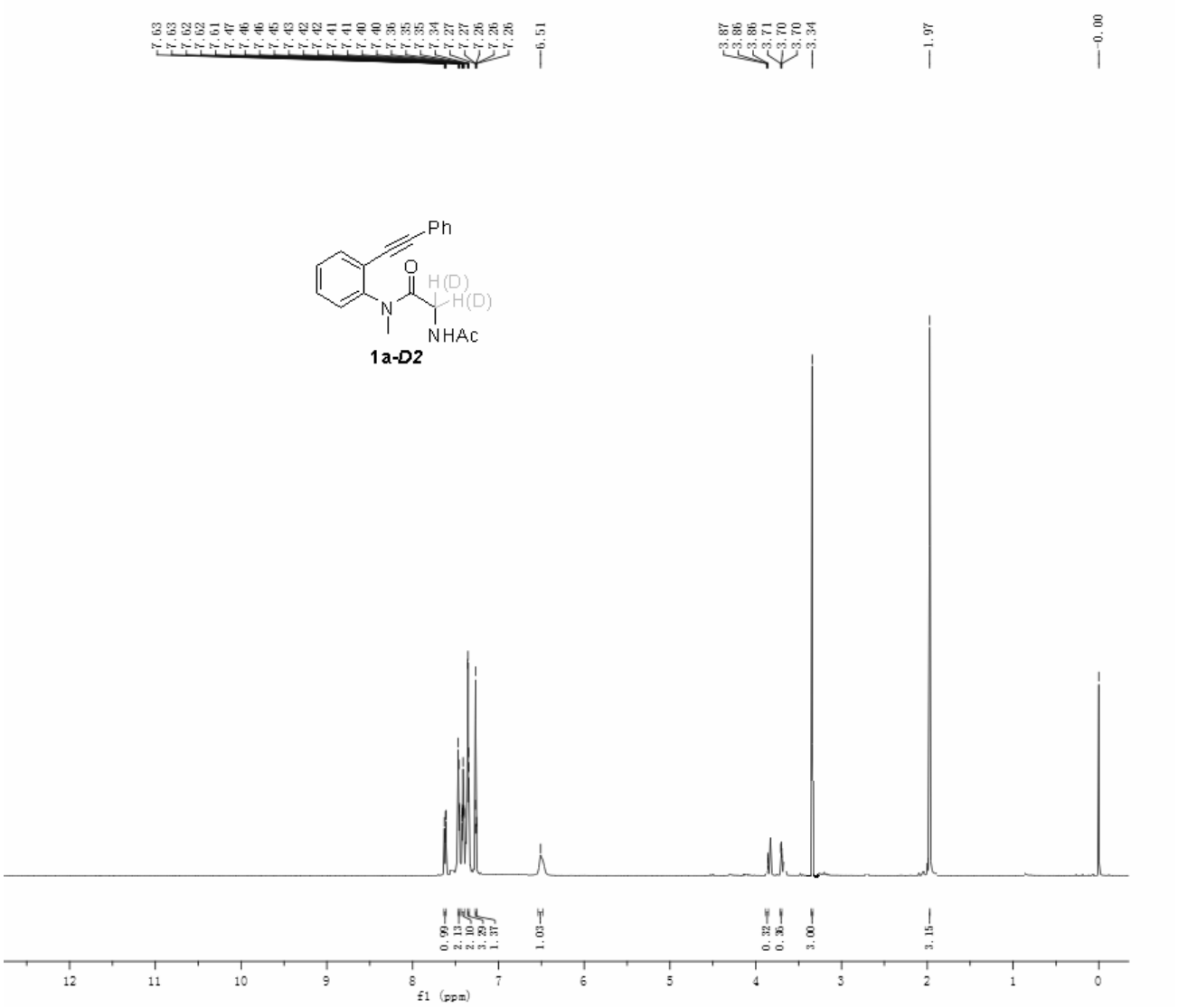


4-benzoyl-*N*-methylquinolin-2(1H)-one (4a)



(E) The intermolecular kinetic isotope effect experiment

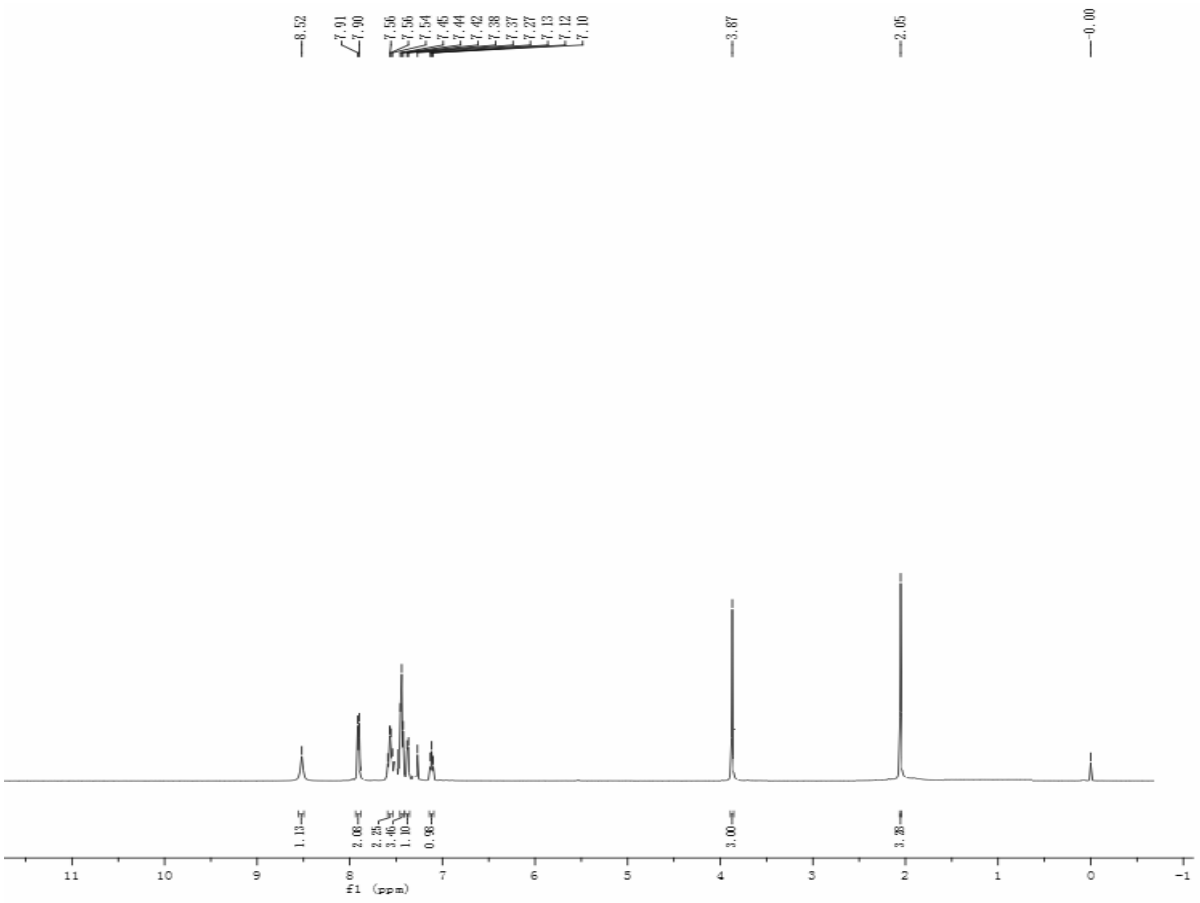
Substrate 1a-*D2*



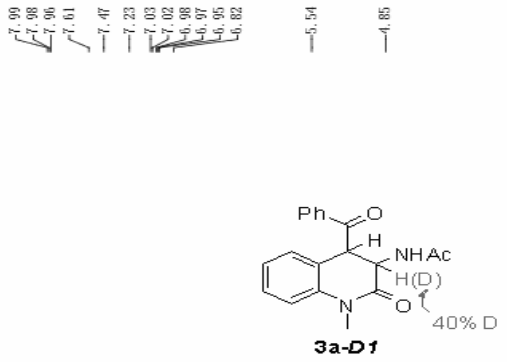
Typical Experimental Procedure for the intermolecular kinetic isotope effect experiments:

To a Schlenk tube were added **1a** (0.15 mmol), **1a-*D2*** (0.15 mmol), $RuCl_3$ (10 mol %), $CuCl_2$ (20 mol %), H_2O (6 equiv) and anhydrous THF (3 mL). Then the tube was charged with O_2 (1 atm), and was stirred at 120 ^oC (oil bath temperature) for 15 min. After the reaction was finished, the reaction mixture was cooled to room temperature, diluted in diethyl ether, and washed with brine. The aqueous phase was re-extracted with diethyl ether. The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated in vacuo, and the resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate) to afford the desired products **1a-*D2***, **2a** and **3a-*D1***.

Product 2a

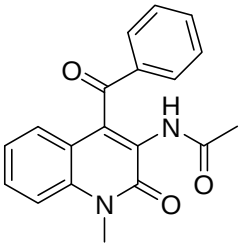


Product 3a-*D1*



3a-*D1*

(F) The X-ray single-crystal diffraction analysis of product 2a



2a

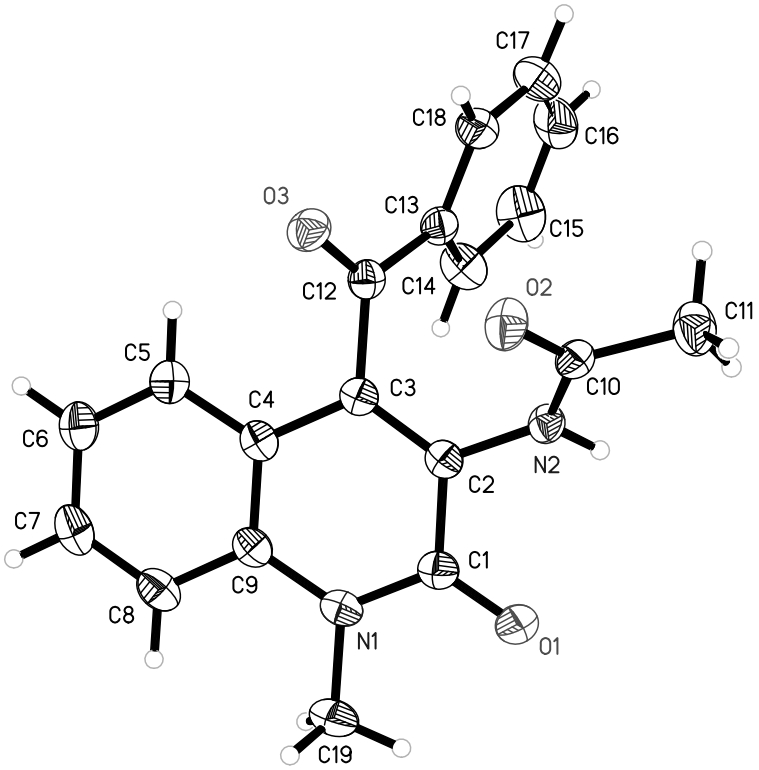


Table 1. Crystal data and structure refinement for cd29238.

Identification code	**cd29238**
Empirical formula	**C19 H16 N2 O3**
Formula weight	**320.34**
Temperature	**293(2) K**
Wavelength	**0.71073 A**
Crystal system, space group	**Monoclinic, P2(1)/c**
Unit cell dimensions	**a = 10.4908(14) A alpha = 90 deg.** **b = 17.614(2) A beta = 106.541(2) deg.** **c = 9.1784(12) A gamma = 90 deg.**
Volume	**1625.8(4) A^3**
Z, Calculated density	**4, 1.309 Mg/m^3**
Absorption coefficient	**0.090 mm^-1**
F(000)	**672**
Crystal size	**0.397 x 0.361 x 0.201 mm**
Theta range for data collection	**2.03 to 25.99 deg.**
Limiting indices	**-12<=h<=12, -21<=k<=14, -11<=l<=11**
Reflections collected / unique	**8791 / 3203 [R(int) = 0.0779]**
Completeness to theta = 25.99	**100.0 %**
Absorption correction	**Empirical**
Max. and min. transmission	**1.00000 and 0.77427**
Refinement method	**Full-matrix least-squares on F^2**
Data / restraints / parameters	**3203 / 1 / 224**
Goodness-of-fit on F^2	**0.984**
Final R indices [I>2sigma(I)]	**R1 = 0.0524, wR2 = 0.1339**
R indices (all data)	**R1 = 0.0706, wR2 = 0.1441**
Extinction coefficient	**0.069(5)**
Largest diff. peak and hole	**0.215 and -0.215 e.A^-3**

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for cd29238. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
N(1)	9789(1)	273(1)	7411(2)	44(1)
N(2)	7720(1)	1931(1)	7452(2)	39(1)
O(1)	9757(1)	1466(1)	6449(2)	61(1)
O(2)	7546(1)	2150(1)	9806(1)	53(1)
O(3)	6248(1)	689(1)	10053(1)	50(1)
C(1)	9288(2)	996(1)	7139(2)	43(1)
C(2)	8144(2)	1172(1)	7681(2)	37(1)
C(3)	7542(2)	641(1)	8317(2)	37(1)
C(4)	8092(2)	-113(1)	8575(2)	39(1)
C(5)	7525(2)	-693(1)	9223(2)	48(1)
C(6)	8070(2)	-1403(1)	9447(2)	57(1)
C(7)	9205(2)	-1554(1)	9029(2)	59(1)
C(8)	9784(2)	-1007(1)	8383(2)	53(1)
C(9)	9230(2)	-284(1)	8123(2)	41(1)
C(10)	7455(2)	2380(1)	8532(2)	40(1)
C(11)	7018(2)	3168(1)	8048(2)	64(1)
C(12)	6306(2)	816(1)	8775(2)	40(1)
C(13)	5140(2)	1108(1)	7579(2)	43(1)
C(14)	4949(2)	951(1)	6067(2)	60(1)
C(15)	3798(2)	1198(1)	4998(3)	76(1)
C(16)	2864(2)	1600(1)	5462(3)	75(1)
C(17)	3067(2)	1768(1)	6951(3)	74(1)
C(18)	4184(2)	1520(1)	8015(3)	57(1)
C(19)	10975(2)	91(1)	6930(2)	60(1)

Table 3. Bond lengths [A] and angles [deg] for cd29238.

N(1)-C(1)	1.373(2)
N(1)-C(9)	1.397(2)
N(1)-C(19)	1.469(2)
N(2)-C(10)	1.357(2)
N(2)-C(2)	1.405(2)
N(2)-H(2)	0.886(14)
O(1)-C(1)	1.228(2)
O(2)-C(10)	1.2152(19)
O(3)-C(12)	1.212(2)
C(1)-C(2)	1.457(2)
C(2)-C(3)	1.350(2)
C(3)-C(4)	1.440(2)
C(3)-C(12)	1.505(2)
C(4)-C(5)	1.397(2)
C(4)-C(9)	1.404(2)
C(5)-C(6)	1.366(3)
C(5)-H(5)	0.9300
C(6)-C(7)	1.377(3)
C(6)-H(6)	0.9300
C(7)-C(8)	1.362(3)
C(7)-H(7)	0.9300
C(8)-C(9)	1.391(3)
C(8)-H(8)	0.9300
C(10)-C(11)	1.489(3)
C(11)-H(11A)	0.9600
C(11)-H(11B)	0.9600
C(11)-H(11C)	0.9600
C(12)-C(13)	1.483(2)
C(13)-C(14)	1.373(3)
C(13)-C(18)	1.386(3)
C(14)-C(15)	1.391(3)
C(14)-H(14)	0.9300
C(15)-C(16)	1.370(4)
C(15)-H(15)	0.9300
C(16)-C(17)	1.355(4)
C(16)-H(16)	0.9300
C(17)-C(18)	1.366(3)
C(17)-H(17)	0.9300
C(18)-H(18)	0.9300
C(19)-H(19A)	0.9600
C(19)-H(19B)	0.9600
C(19)-H(19C)	0.9600

C(1)-N(1)-C(9)	123.11(15)
C(1)-N(1)-C(19)	117.43(16)
C(9)-N(1)-C(19)	119.46(15)
C(10)-N(2)-C(2)	124.59(15)
C(10)-N(2)-H(2)	115.4(12)
C(2)-N(2)-H(2)	119.2(12)
O(1)-C(1)-N(1)	122.01(16)

O(1)-C(1)-C(2)	121.49(17)
N(1)-C(1)-C(2)	116.48(16)
C(3)-C(2)-N(2)	123.79(15)
C(3)-C(2)-C(1)	122.07(16)
N(2)-C(2)-C(1)	114.13(15)
C(2)-C(3)-C(4)	119.73(16)
C(2)-C(3)-C(12)	121.70(15)
C(4)-C(3)-C(12)	118.57(15)
C(5)-C(4)-C(9)	117.99(16)
C(5)-C(4)-C(3)	123.07(16)
C(9)-C(4)-C(3)	118.92(16)
C(6)-C(5)-C(4)	121.50(18)
C(6)-C(5)-H(5)	119.2
C(4)-C(5)-H(5)	119.2
C(5)-C(6)-C(7)	119.59(19)
C(5)-C(6)-H(6)	120.2
C(7)-C(6)-H(6)	120.2
C(8)-C(7)-C(6)	120.78(19)
C(8)-C(7)-H(7)	119.6
C(6)-C(7)-H(7)	119.6
C(7)-C(8)-C(9)	120.43(19)
C(7)-C(8)-H(8)	119.8
C(9)-C(8)-H(8)	119.8
C(8)-C(9)-N(1)	120.81(17)
C(8)-C(9)-C(4)	119.66(17)
N(1)-C(9)-C(4)	119.53(15)
O(2)-C(10)-N(2)	122.07(16)
O(2)-C(10)-C(11)	122.11(16)
N(2)-C(10)-C(11)	115.80(16)
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
O(3)-C(12)-C(13)	121.47(16)
O(3)-C(12)-C(3)	121.16(16)
C(13)-C(12)-C(3)	117.28(15)
C(14)-C(13)-C(18)	119.17(19)
C(14)-C(13)-C(12)	122.05(17)
C(18)-C(13)-C(12)	118.70(17)
C(13)-C(14)-C(15)	119.8(2)
C(13)-C(14)-H(14)	120.1
C(15)-C(14)-H(14)	120.1
C(16)-C(15)-C(14)	119.8(2)
C(16)-C(15)-H(15)	120.1
C(14)-C(15)-H(15)	120.1
C(17)-C(16)-C(15)	120.4(2)
C(17)-C(16)-H(16)	119.8
C(15)-C(16)-H(16)	119.8
C(16)-C(17)-C(18)	120.4(2)
C(16)-C(17)-H(17)	119.8
C(18)-C(17)-H(17)	119.8
C(17)-C(18)-C(13)	120.4(2)

C(17)-C(18)-H(18)	**119.8**
C(13)-C(18)-H(18)	**119.8**
N(1)-C(19)-H(19A)	**109.5**
N(1)-C(19)-H(19B)	**109.5**
H(19A)-C(19)-H(19B)	**109.5**
N(1)-C(19)-H(19C)	**109.5**
H(19A)-C(19)-H(19C)	**109.5**
H(19B)-C(19)-H(19C)	**109.5**

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for cd29238.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
N(1)	37(1)	52(1)	43(1)	-4(1)	9(1)	5(1)
N(2)	46(1)	41(1)	32(1)	3(1)	13(1)	1(1)
O(1)	55(1)	65(1)	71(1)	17(1)	31(1)	7(1)
O(2)	81(1)	46(1)	36(1)	-2(1)	23(1)	0(1)
O(3)	54(1)	57(1)	41(1)	3(1)	18(1)	0(1)
C(1)	40(1)	51(1)	36(1)	-2(1)	8(1)	1(1)
C(2)	38(1)	42(1)	29(1)	-1(1)	5(1)	2(1)
C(3)	36(1)	42(1)	29(1)	-4(1)	3(1)	-1(1)
C(4)	40(1)	41(1)	31(1)	-5(1)	1(1)	0(1)
C(5)	53(1)	45(1)	45(1)	-1(1)	11(1)	-1(1)
C(6)	67(1)	43(1)	59(1)	2(1)	13(1)	-1(1)
C(7)	64(1)	43(1)	62(1)	1(1)	2(1)	8(1)
C(8)	45(1)	52(1)	55(1)	-6(1)	3(1)	8(1)
C(9)	37(1)	47(1)	34(1)	-4(1)	-1(1)	1(1)
C(10)	43(1)	41(1)	37(1)	-1(1)	14(1)	-4(1)
C(11)	93(2)	47(1)	58(1)	2(1)	33(1)	9(1)
C(12)	41(1)	36(1)	40(1)	-3(1)	9(1)	-4(1)
C(13)	37(1)	41(1)	47(1)	1(1)	8(1)	-5(1)
C(14)	54(1)	64(1)	53(1)	-10(1)	-1(1)	3(1)
C(15)	72(2)	79(2)	55(1)	-8(1)	-15(1)	-5(1)
C(16)	46(1)	72(2)	88(2)	15(1)	-11(1)	4(1)
C(17)	50(1)	80(2)	90(2)	18(1)	16(1)	18(1)
C(18)	49(1)	62(1)	62(1)	10(1)	18(1)	8(1)
C(19)	45(1)	72(1)	64(1)	-3(1)	20(1)	12(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for cd29238.

	x	y	z	U(eq)
H(5)	6759	-593	9508	58
H(6)	7678	-1781	9880	69
H(7)	9581	-2036	9189	71
H(8)	10554	-1116	8114	64
H(11A)	6121	3240	8085	95
H(11B)	7061	3249	7029	95
H(11C)	7592	3524	8718	95
H(14)	5588	681	5757	72
H(15)	3662	1091	3973	91
H(16)	2087	1757	4751	90
H(17)	2441	2055	7251	89
H(18)	4304	1628	9037	68
H(19A)	11213	522	6422	90
H(19B)	10789	-334	6248	90
H(19C)	11698	-33	7805	90
H(2)	7745(19)	2166(10)	6608(18)	51(6)

Table 6. Torsion angles [deg] for cd29238.

C(9)-N(1)-C(1)-O(1)	-176.53(17)
C(19)-N(1)-C(1)-O(1)	3.9(3)
C(9)-N(1)-C(1)-C(2)	2.0(2)
C(19)-N(1)-C(1)-C(2)	-177.59(15)
C(10)-N(2)-C(2)-C(3)	49.4(2)
C(10)-N(2)-C(2)-C(1)	-131.84(17)
O(1)-C(1)-C(2)-C(3)	173.81(17)
N(1)-C(1)-C(2)-C(3)	-4.7(2)
O(1)-C(1)-C(2)-N(2)	-5.0(2)
N(1)-C(1)-C(2)-N(2)	176.45(15)
N(2)-C(2)-C(3)-C(4)	-176.80(15)
C(1)-C(2)-C(3)-C(4)	4.5(2)
N(2)-C(2)-C(3)-C(12)	2.9(2)
C(1)-C(2)-C(3)-C(12)	-175.74(15)
C(2)-C(3)-C(4)-C(5)	-179.80(16)
C(12)-C(3)-C(4)-C(5)	0.5(2)
C(2)-C(3)-C(4)-C(9)	-1.5(2)
C(12)-C(3)-C(4)-C(9)	178.72(14)
C(9)-C(4)-C(5)-C(6)	1.5(3)
C(3)-C(4)-C(5)-C(6)	179.78(17)
C(4)-C(5)-C(6)-C(7)	0.0(3)
C(5)-C(6)-C(7)-C(8)	-0.5(3)
C(6)-C(7)-C(8)-C(9)	-0.5(3)
C(7)-C(8)-C(9)-N(1)	-177.68(17)
C(7)-C(8)-C(9)-C(4)	2.1(3)
C(1)-N(1)-C(9)-C(8)	-179.46(17)
C(19)-N(1)-C(9)-C(8)	0.1(3)
C(1)-N(1)-C(9)-C(4)	0.8(2)
C(19)-N(1)-C(9)-C(4)	-179.64(15)
C(5)-C(4)-C(9)-C(8)	-2.5(2)
C(3)-C(4)-C(9)-C(8)	179.11(16)
C(5)-C(4)-C(9)-N(1)	177.25(15)
C(3)-C(4)-C(9)-N(1)	-1.1(2)
C(2)-N(2)-C(10)-O(2)	-1.3(3)
C(2)-N(2)-C(10)-C(11)	179.95(17)
C(2)-C(3)-C(12)-O(3)	-126.47(18)
C(4)-C(3)-C(12)-O(3)	53.3(2)
C(2)-C(3)-C(12)-C(13)	56.9(2)
C(4)-C(3)-C(12)-C(13)	-123.38(17)
O(3)-C(12)-C(13)-C(14)	-150.77(19)
C(3)-C(12)-C(13)-C(14)	25.9(2)
O(3)-C(12)-C(13)-C(18)	26.0(3)
C(3)-C(12)-C(13)-C(18)	-157.36(16)
C(18)-C(13)-C(14)-C(15)	-0.9(3)
C(12)-C(13)-C(14)-C(15)	175.90(19)
C(13)-C(14)-C(15)-C(16)	0.4(4)
C(14)-C(15)-C(16)-C(17)	1.1(4)
C(15)-C(16)-C(17)-C(18)	-2.0(4)
C(16)-C(17)-C(18)-C(13)	1.5(4)
C(14)-C(13)-C(18)-C(17)	-0.1(3)

C(12)-C(13)-C(18)-C(17)	**-176.94(19)**

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for cd29238 [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(11)-H(11B)...O(3)#1	0.96	2.58	3.317(3)	134.1
C(11)-H(11B)...O(2)#1	0.96	2.35	3.227(2)	152.2
N(2)-H(2)...O(2)#1	0.886(14)	2.009(15)	2.8820(19)	168.3(17)

Symmetry transformations used to generate equivalent atoms:
#1 x,-y+1/2,z-1/2