Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting information

Copper-catalyzed carbon-carbon bond cleavage of primary propargyl alcohols: β-carbon elimination of hemiaminal intermediates

Ye-Won Kang,[a] Yu Jin Cho,[a] Kwang-Youn Ko,[c] Hye-Young Jang[a,b]*

[a]*Department of Energy Systems Research, Ajou University, Suwon 443-749, Korea,* [b]*Korea Carbon Capture & Sequestration R&D Center, Deajeon 305-343, Korea,* [c]*Department of Chemistry, Ajou University, Suwon 443-749*

Table of Contents

Experimental Section

General. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded with a Varian Mercury plus (400 MHz) spectrometer at 25 °C. Chemical shifts are reported in delta (δ) units, part per million (ppm) downfield from trimethylsilane. Coupling constants are reported in Hertz (Hz). Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded with a Varian Mercury plus (100 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, part per million (ppm) relative to the center of the triplet at 77.16 ppm for deuteriochloroform. High resolution mass spectra were obtained with a magnetic sector-electric sector double focusing mass analyzer equipment. IR spectra were recorded with a FT-IR spectrometer. Products **1d'**[1] and **1e**[2], exhibited spectral properties consistent with previous literature reports.

Representative procedure for the reaction: Copper(II) acetate (4.5 mg, 0.025 mmol), 2,2,6,6-tetramethylpiperidine *N*-oxy (TEMPO, 3.9 mg, 0.025 mmol), and morpholine (65.3 mg, 0.75 mmol) were added to a solution of 3-phenylprop-2-yn-1-ol **1a** (66.1 mg, 0.5 mmol) in toluene (0.5 M, 1 ml). A slow stream of O_2 was passed through this solution for 1 min. It stirred for 18 h at 100 °C under O_2 atmosphere. The reaction mixture was evaporated and purified by flash silica gel column chromatography using 1% ethyl acetate/hexane to afford 1,4-diphenylbuta-1,3-diyne **1b** (42.1 mg, 83 %).

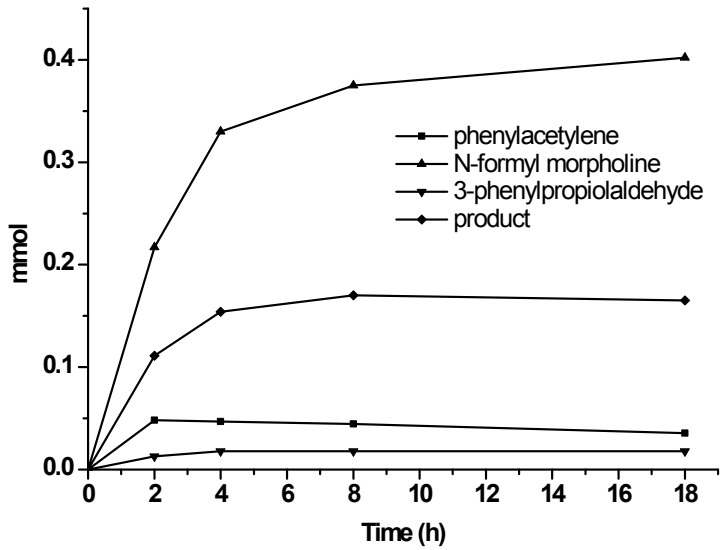
Representative procedure for the triazole formation: Copper(II) acetylacetonate (6.5 mg, 0.025 mmol), 2,2,6,6-tetramethylpiperidine *N*-oxy (TEMPO, 3.9 mg, 0.025 mmol), and *N*-benzylmethylamine (90.9 mg, 0.75 mmol) were added to a solution of 3-phenylprop-2-yn-1-ol **1a** (66.1 mg, 0.5 mmol) and azidomethylbenzene **1c** (99.9 mg, 0.75 mmol) in toluene (0.5 M, 1 ml). A slow stream of O_2 was passed through this solution for 1 min. It stirred for 18h at 100 °C under O_2 atmosphere. The reaction mixture was evaporated and purified by flash silica gel column chromatography using 8% ethyl acetate/hexane to afford 1-benzyl-4-phenyl-1H-1,2,3-triazole **1d** (100.4 mg, 85 %).

[1] G. Cheng, X. Zeng, J. Shen, X. Wang, X. Cui, *Angew. Chem. Int. Ed.* **2013**, *52*, 13265.
[2] A. V. Khramchikhin, M. D. Stadnichuk, *J. Gen. Chem. USSR*, **1991**, *61*, 1864.

The reaction of 1a was monitored by gas chromatography (GC).

General GC conditions

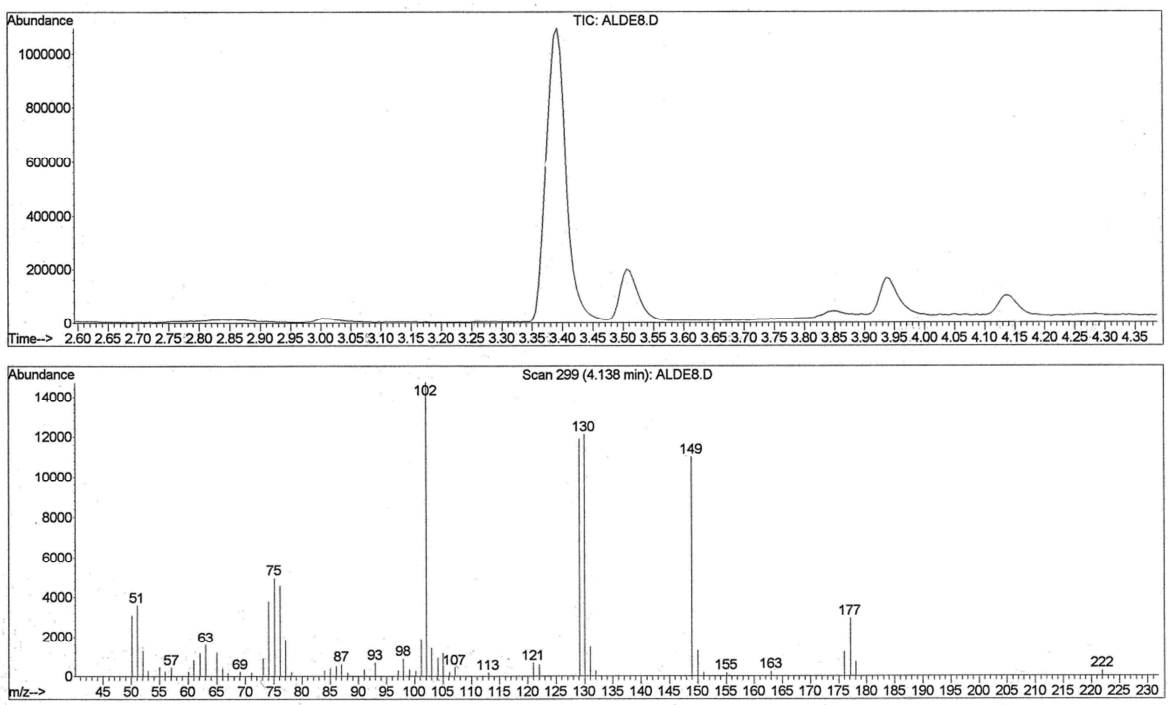
Gas chromatography analysis was performed on an Agilent 6890N instrument with a FID detector and HP-5 capillary column (polydimethylsiloxane with 5% phenyl groups, 30m, 0.32 mmi.d., 0.25 mm film thickness) using nitrogen as a carrier gas.



The copper-catalyzed conversion of 1a to 1b was analyzed by GC-MS to detect phenylpropiolaldehydes. (The below spectrum was obtained after 2 h)

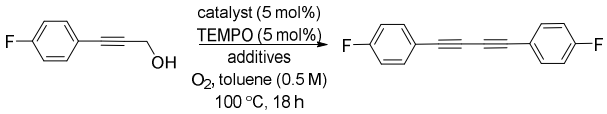
GC-MS conditions

The GC-MS analysis of a reaction mixture was performed using a temperature program of 110 ºC for 0 minutes, 10 ºC/min up to 200 ºC and hold for 10 minutes, on Agilent GC-MS system (6890 GC and 5973 mass spectrum analyzer with EI ionization) with a HP-5MS (30 m x 250 μm x 0.25 μm) capillary column. The flow rate of helium as carrier gas was 0.6 mL min^{-1} under a condition of constant flow. Qualitative analysis was based on the comparison of retention times and the computer mass spectra libraries using Wiley 275 GC/MS Library (Wiley, New York).



Optimization of each compound: Initially, aliphatic compound **5b** was optimized after the best conditions for **1b** were observed. Both aromatic and aliphatic propargyl alcohols favor either $Cu(OAc)_2$ or $Cu(acac)_2$. Depending on substrates, different additives and the concentration were selected to obtain the good yield.

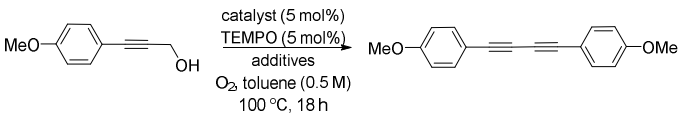
Optimization results of 2b



entry	catalyst	additives (equiv)	Yield
1	$Cu(OAc)_2$	morpholine (1.5)	42%
2	$Cu(OAc)_2$	piperidine (1.5)	52%
3	$Cu(OAc)_2$	pyrrolidine (1.5)	59%(66%)[a]
4	$Cu(OAc)_2$	MeNHBn (1.5)	43%
5	$Cu(acac)_2$	morpholine (1.5)	51%(26%)[a]
6	$Cu(acac)_2$	piperidine (1.5)	39%
7	$Cu(acac)_2$	pyrrolidine (1.5)	41%
8	$Cu(acac)_2$	MeNHBn (1.5)	40%

[a]0.25 M concentration

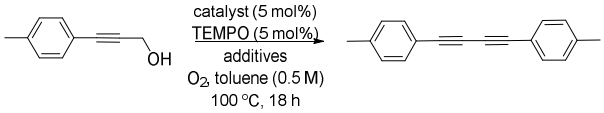
Optimization results of 3b



entry	catalyst	additives (equiv)	Yield
1	$Cu(OAc)_2$	morpholine (1.5)	63%
2	$Cu(OAc)_2$	piperidine (1.5)	67%(62%)[a]
3	$Cu(OAc)_2$	pyrrolidine (1.5)	61%
4	$Cu(OAc)_2$	MeNHBn (1.5)	35%
5	$Cu(acac)_2$	morpholine (1.5)	47%
6	$Cu(acac)_2$	piperidine (1.5)	46%
7	$Cu(acac)_2$	pyrrolidine (1.5)	55%(68%)[a]
8	$Cu(acac)_2$	MeNHBn (1.5)	36%

[a]0.25 M concentration

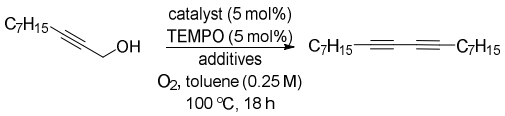
Optimization results of 4b



entry	catalyst	additives (equiv)	Yield
1	$Cu(OAc)_2$	morpholine (1.5)	37%
2	$Cu(OAc)_2$	piperidine (1.5)	50%
3	$Cu(OAc)_2$	pyrrolidine (1.5)	56%(75%)[a]
4	$Cu(OAc)_2$	MeNHBn (1.5)	45%
5	$Cu(acac)_2$	morpholine (1.5)	63%(57%)[a]
6	$Cu(acac)_2$	piperidine (1.5)	59%
7	$Cu(acac)_2$	pyrrolidine (1.5)	55%
8	$Cu(acac)_2$	MeNHBn (1.5)	47%

[a]0.25 M concentration

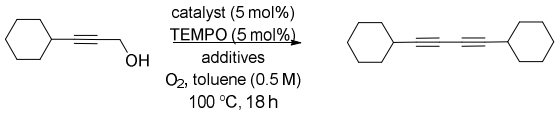
Optimization results of 5b



entry	catalyst	additives (equiv)	Yield
1	$Cu(OAc)_2$	morpholine (1.5)	40% (22%)[a]
2	CuOAc	morpholine (1.5)	37%
3	$CuCl_2$	morpholine (1.5)	-
4	$Cu(acac)_2$	morpholine (1.5)	50%
5	CuCl	morpholine (1.5)	15%
6	CuI	morpholine (1.5)	-
7	$Cu(acac)_2$	piperidine (1.5)	57%
8	$Cu(acac)_2$	pyrrolidine (1.5)	74%
9	$Cu(acac)_2$	MeNHBn (1.5)	75%
10	$Cu(acac)_2$	MeNHBu (1.5)	38%

[a]0.5 M concentration

Optimization results of 6b

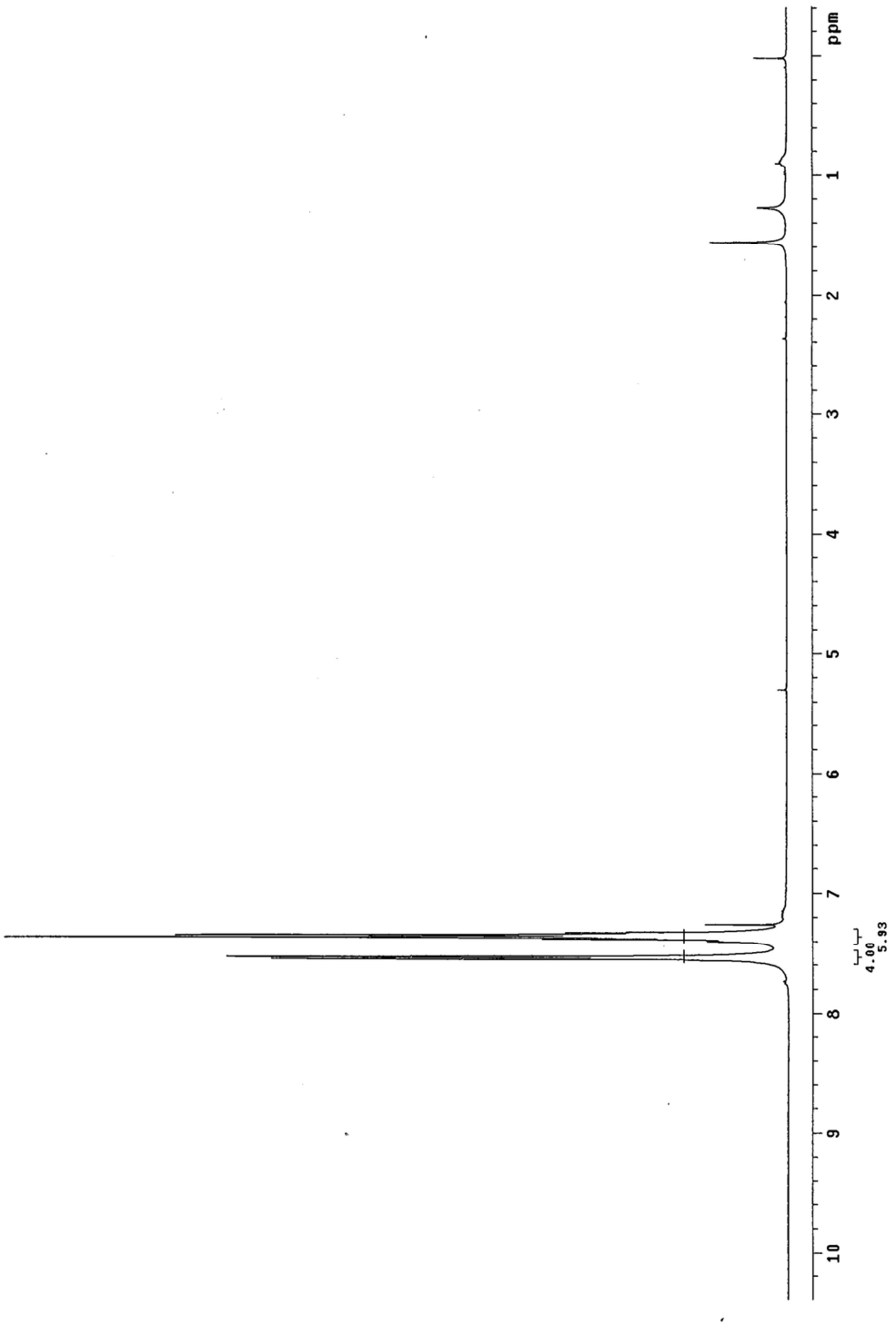


entry	catalyst	additives (equiv)	Yield
1	$Cu(OAc)_2$	morpholine (1.5)	44%
2	$Cu(OAc)_2$	piperidine (1.5)	39%
3	$Cu(OAc)_2$	pyrrolidine (1.5)	46%
4	$Cu(OAc)_2$	MeNHBn (1.5)	49%(31%)[a]
5	$Cu(acac)_2$	morpholine (1.5)	55%(42%)[a]
6	$Cu(acac)_2$	piperidine (1.5)	48%
7	$Cu(acac)_2$	pyrrolidine (1.5)	46%
8	$Cu(acac)_2$	MeNHBn (1.5)	47%

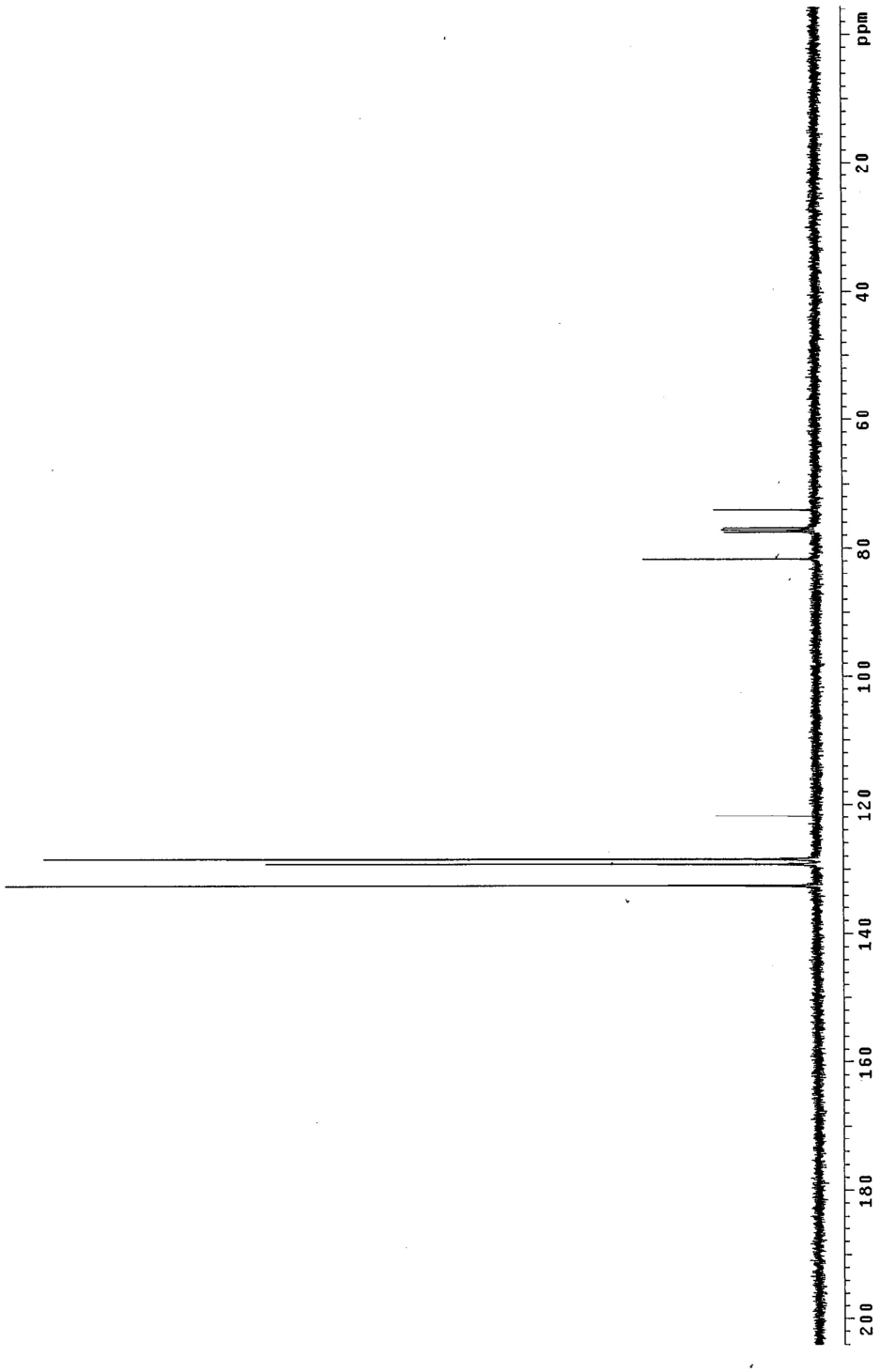
[a]0.25 M concentration

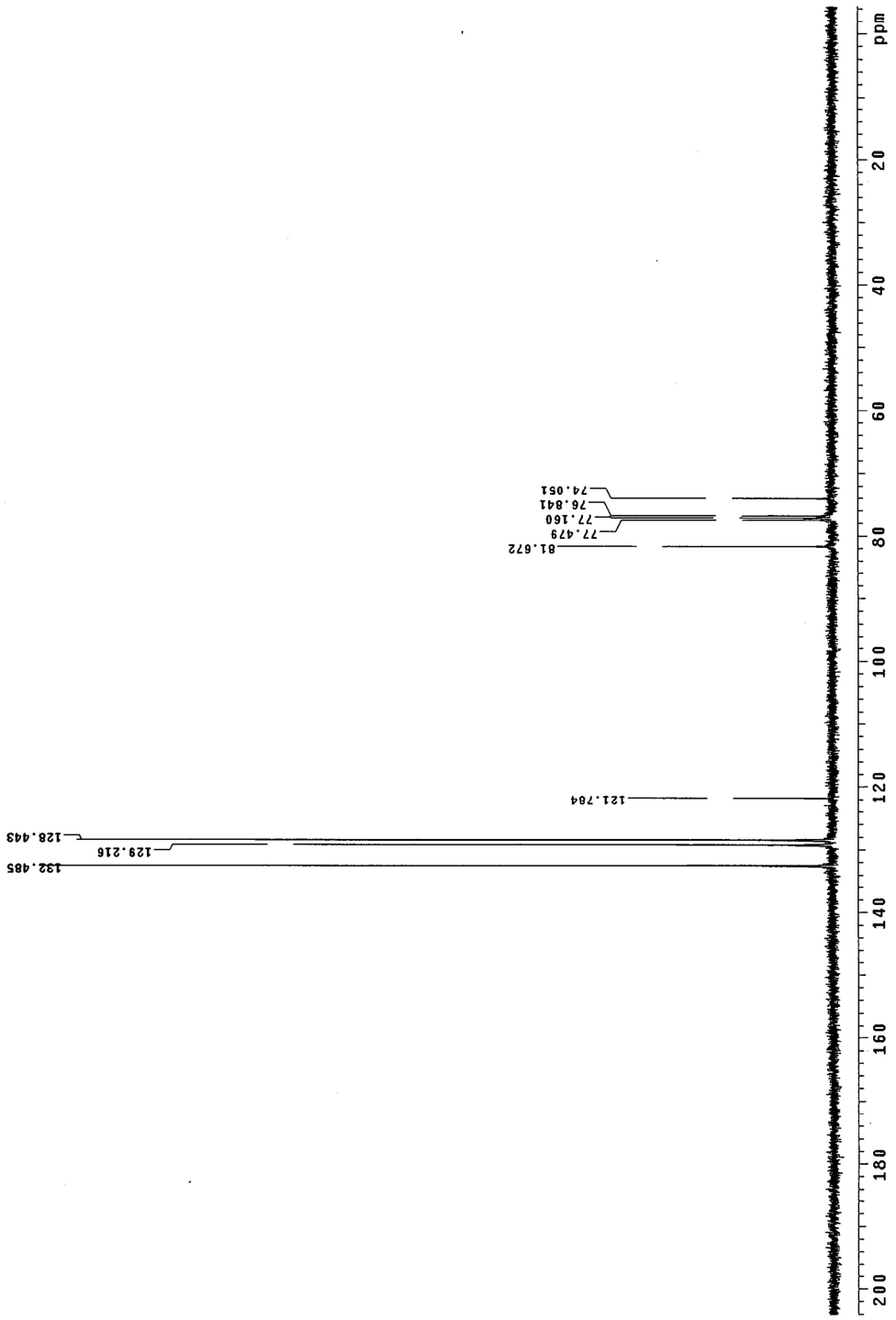
1,4-diphenylbutadiyne (Table 1, 1b). The representative procedure was followed to yield **1b** (42.1mg, 83%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (m, 4H), 7.36 (m, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.5, 129.2, 128.4, 121.8, 81.7, 74.1 ppm; IR (neat) 3049, 2148, 1592, 1485 cm^{-1}; HRMS (EI+) cacld for $C_{16}H_{10}(M^{+})$ 202.0783, found 202.0780.

^{1}H NMR (400 MHz) at 25 °C



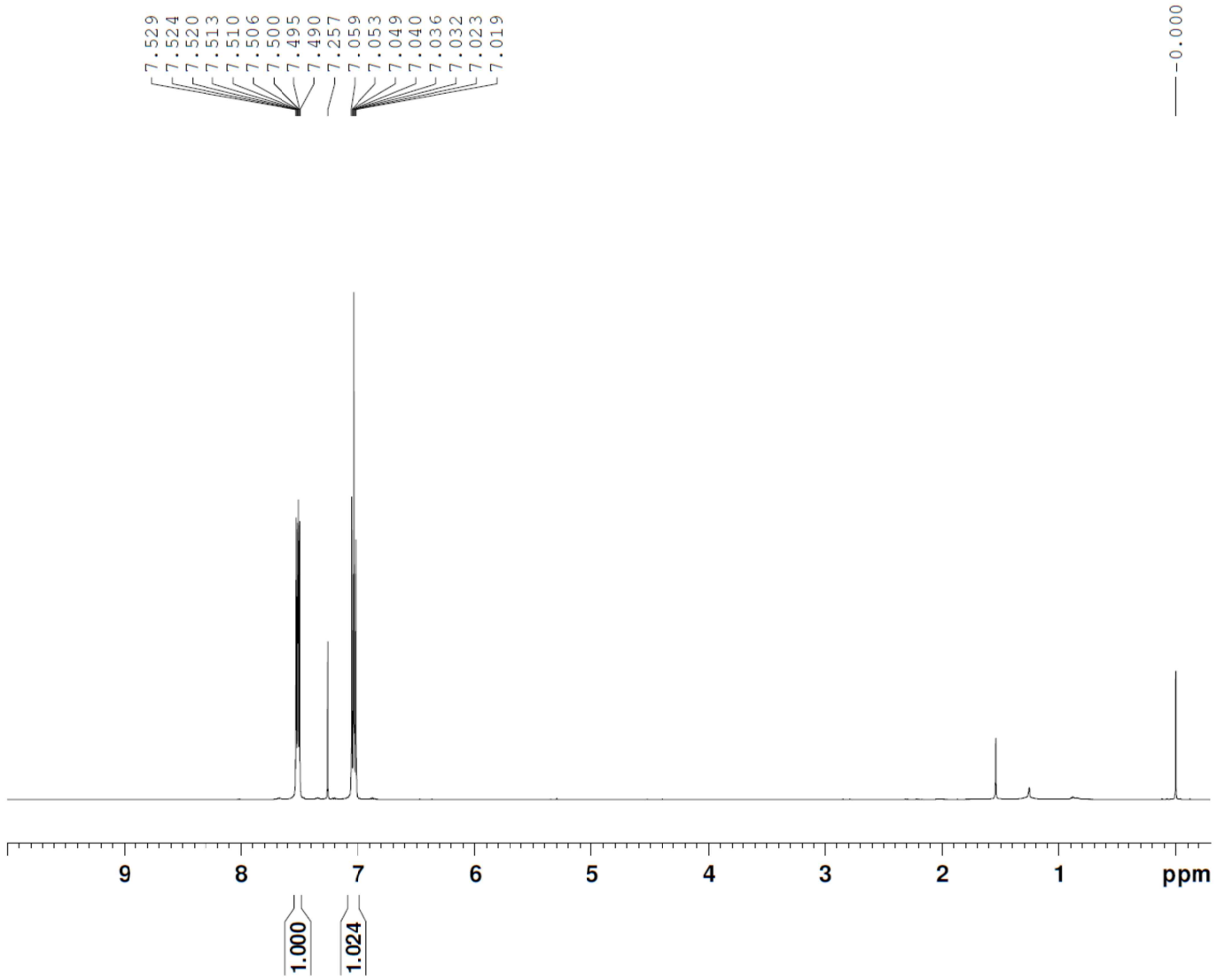
^{13}C NMR (100 MHz) at 25 °C




132.485
129.216
128.443
121.764
81.672
77.479
77.160
76.841
74.051
ppm
200
180
160
140
120
100
80
60
40
20

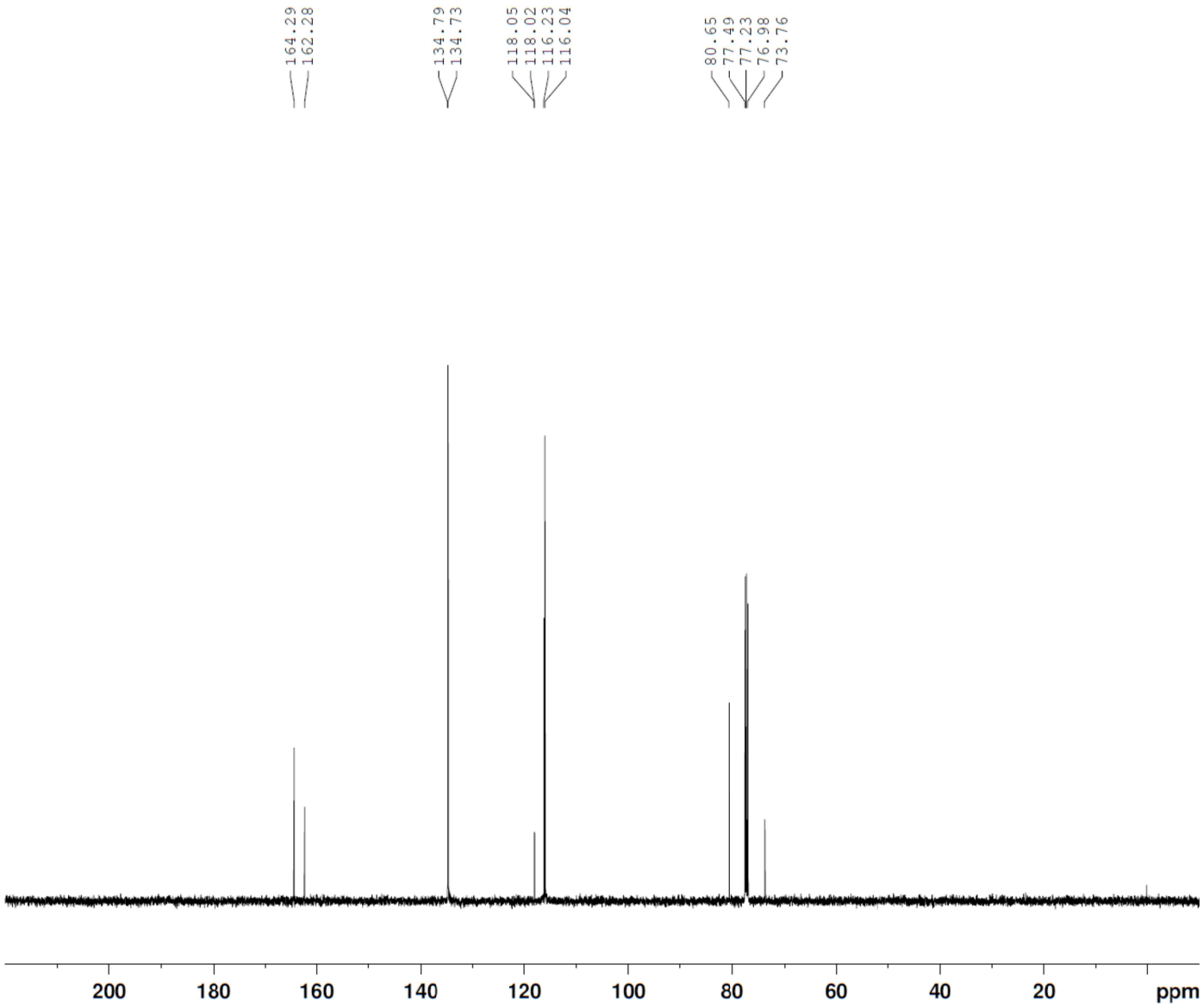
*1,4-bis(4-fluorophenyl)buta-1,3-diyne (**2b**)*. The general procedure was followed to yield **2b** (39.3 mg, 66 %); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (m, 4H), 7.04 (m, 4H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.3 (d, J = 251.3 Hz), 134.8 (d, J =7.5 Hz), 118.0 (d, J = 3.8 Hz), 116.1 (d, J = 23.8 Hz), 80.7, 73.8 ppm; IR (neat) 3357, 1643, 1502, 1225, 828 cm^{-1}; HRMS (EI+) calcd for $C_{16}H_8F_2(M^+)$ 208.0594, found 238.0592.

2b / 1H



서 울 대 학 교
SEOUL NATIONAL UNIVERSITY
기초과학공동기기원
핵자기공명연구실

```
Current Data Parameters
NAME       may22-aju-jhy
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameter
Date_           20150522
Time               16.40
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    32
DS                     4
SWH             6555.944 Hz
FIDRES          0.200072 Hz
AQ              2.4991062 se
RG                   161
DW                76.267 us
DE                 6.50 us
TE                298.0 K
D1           1.00000000 se
TD0                    1

======== CHANNEL f1 =======
SFO1         500.1325435 MH
NUC1                1H
P1                10.20 us
PLW1        19.00000000 W

F2 - Processing parameters
SI                 16384
SF           500.1300144 MH
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

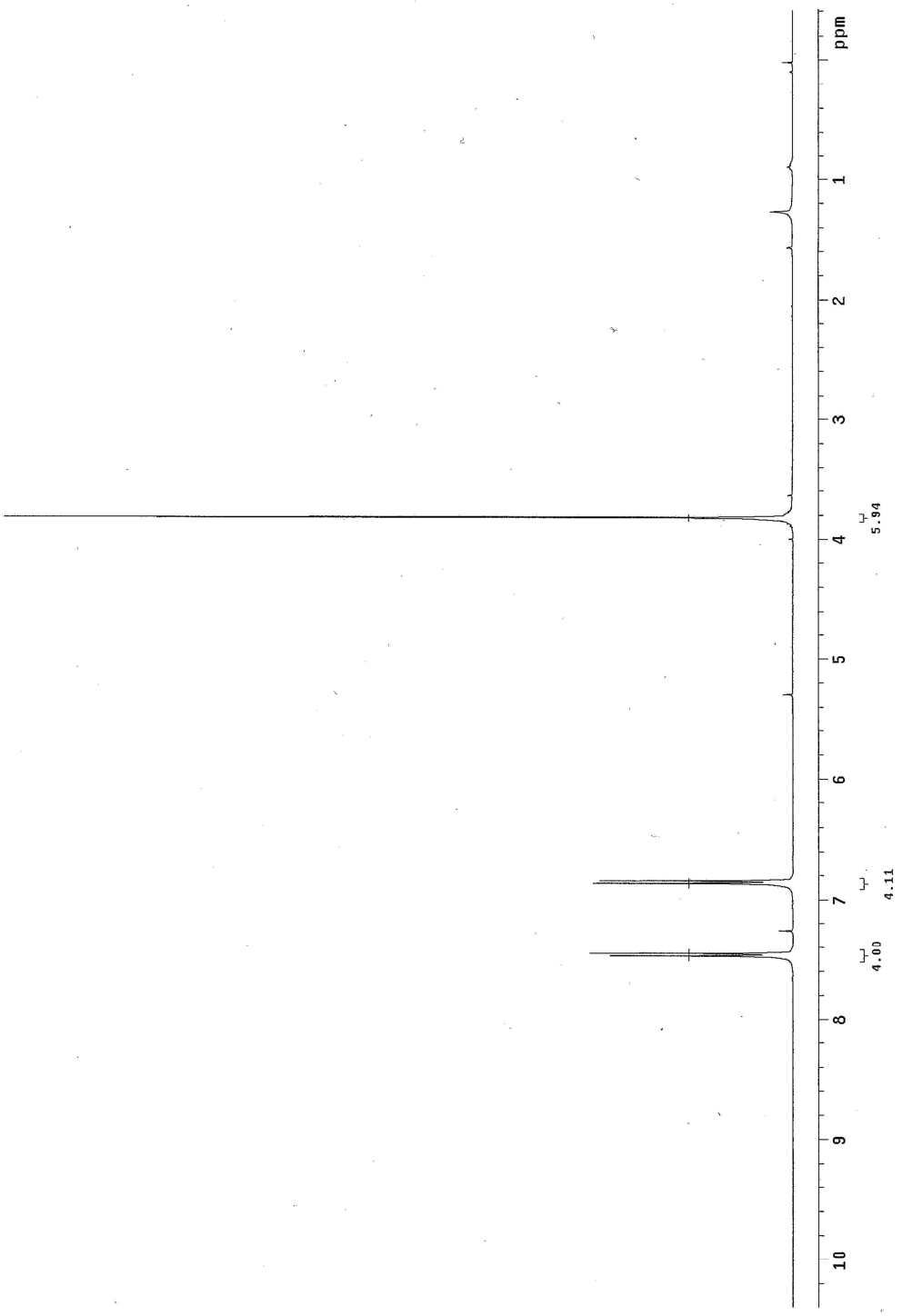


서울대학교 SEOUL NATIONAL UNIVERSITY
기초과학공동기기원
핵자기공명연구실

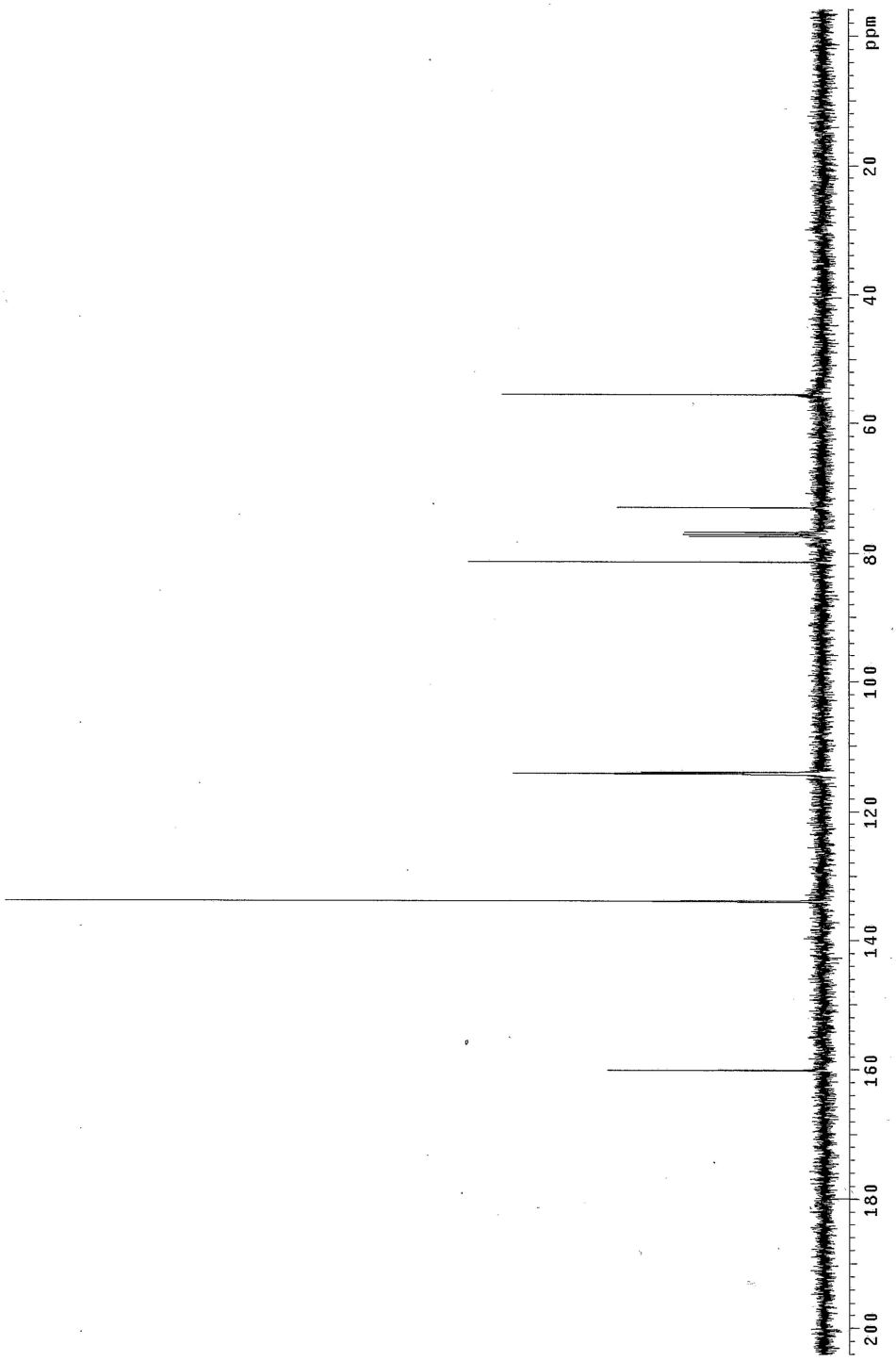
```
Current Data Parameters
NAME       may22-aju-jhy
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150522
Time               17.04
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zgdc
TD                 32768
SOLVENT            CDCl3
NS                   640
DS                     4
SWH            29761.904 Hz
FIDRES         0.908261 Hz
AQ             0.5505024 sec
RG                  2050
DW                16.800 usec
DE                 6.50 usec
TE                298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         125.7709936 MHz
NUC1                  13C
P1                 10.00 usec
PLW1         90.00000000 W

======== CHANNEL f2 ========
SFO2         500.1320005 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2              80.00 usec
PLW2         19.00000000 W
PLW12         0.30886999 W

F2 - Processing parameters
SI                 16384
SF           125.7577618 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

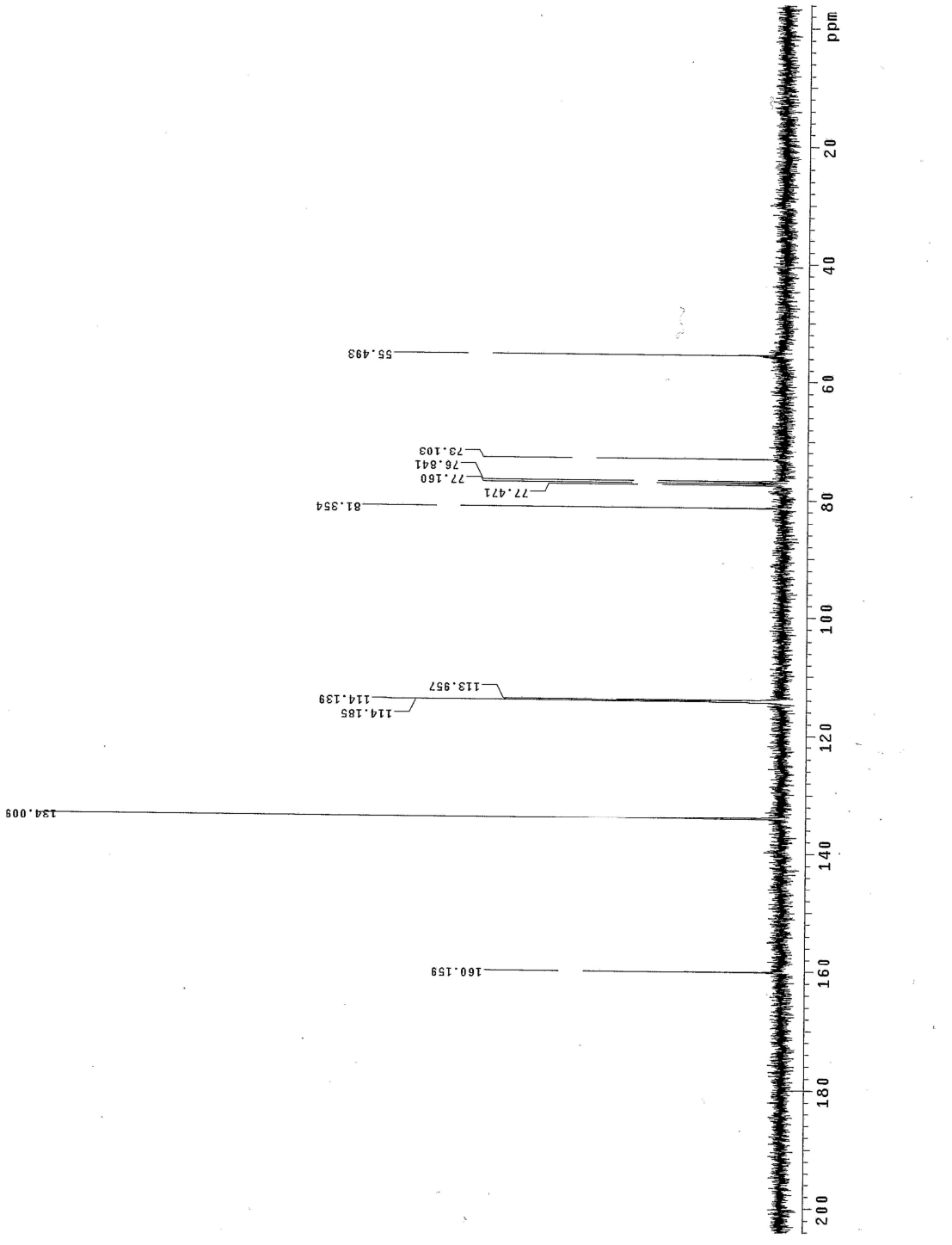
*1,4-bis(4-methoxyphenyl)buta-1,3-diyne (**3b**)*. The general procedure was followed to yield **3b** (44.7 mg, 68 %); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, 4H, J = 8.8 Hz), 6.86 (d, 4H, J = 8.8 Hz), 3.82 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 134.0, 114.2, 114.1, 114.0, 81.4, 73.1, 55.5 ppm; IR (neat) 3484, 1599, 1264, 742 cm^{-1}; HRMS (EI+) calcd for $C_{18}H_{14}O_2(M^+)$ 262.0994, found 262.0992.

^{1}H NMR (400 MHz) at 25 °C



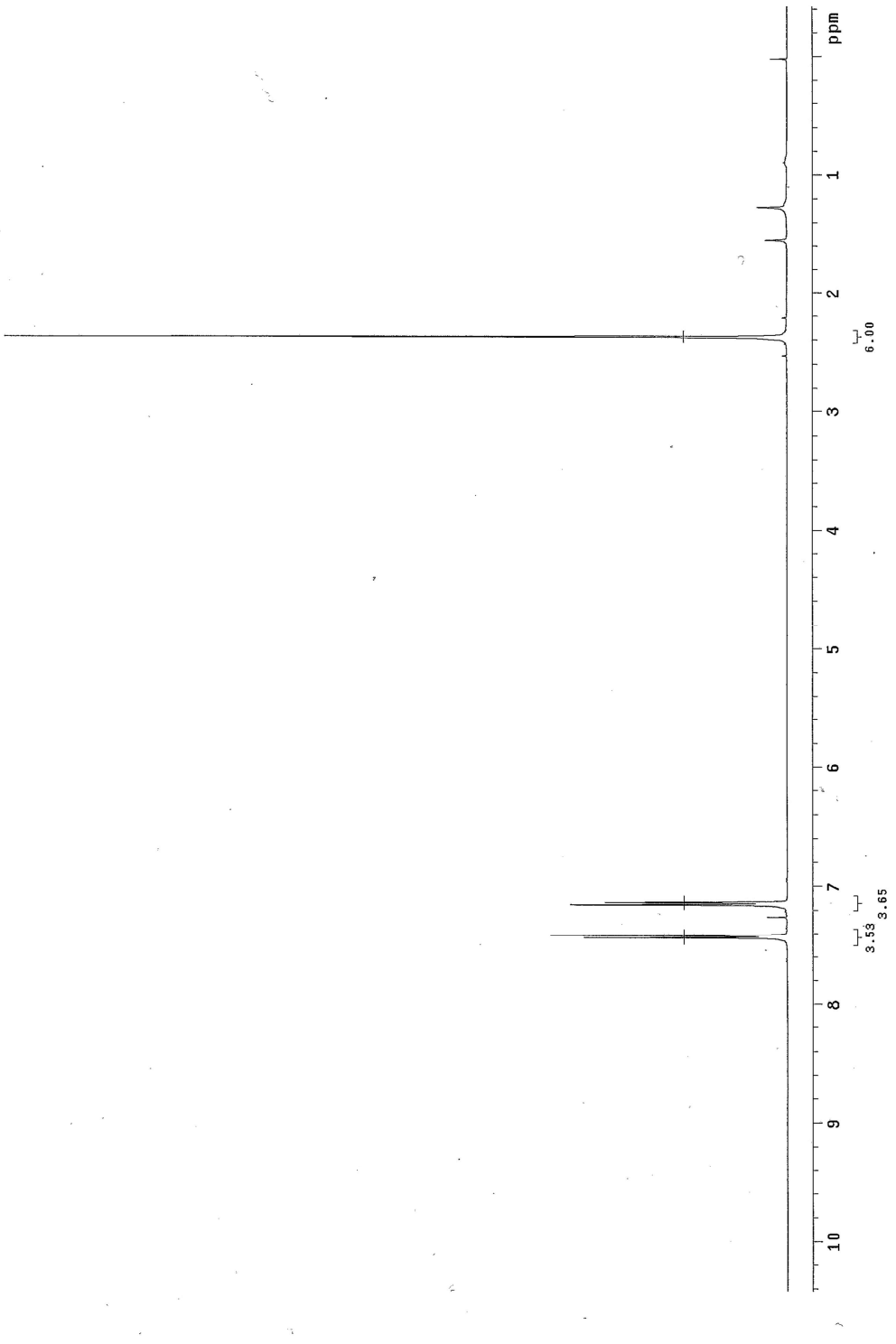
^{13}C NMR (100 MHz) at 25 °C



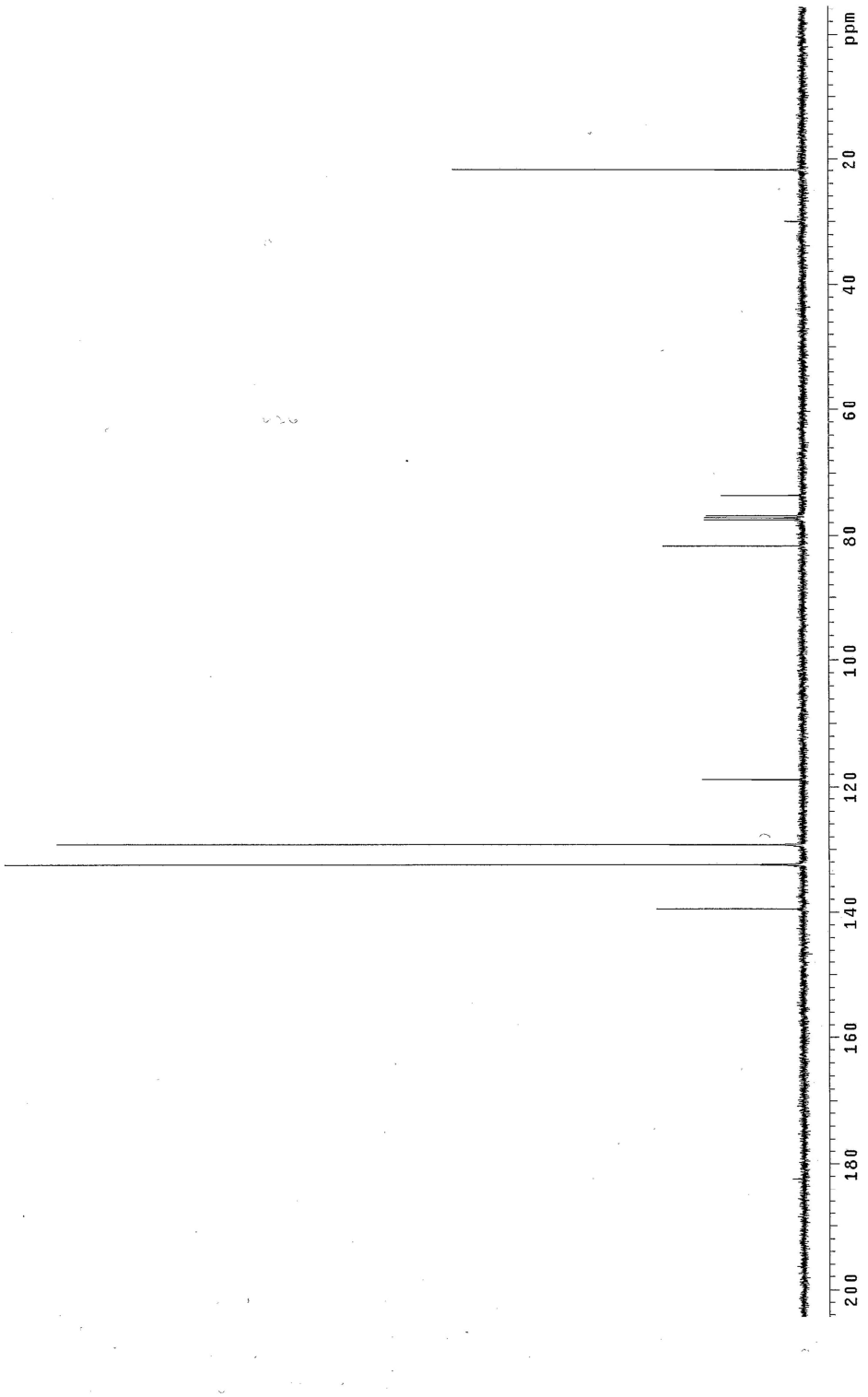

160.159
134.009
114.185
114.139
113.957
81.354
77.471
77.160
76.841
73.103
55.493
ppm
200
180
160
140
120
100
80
60
40
20

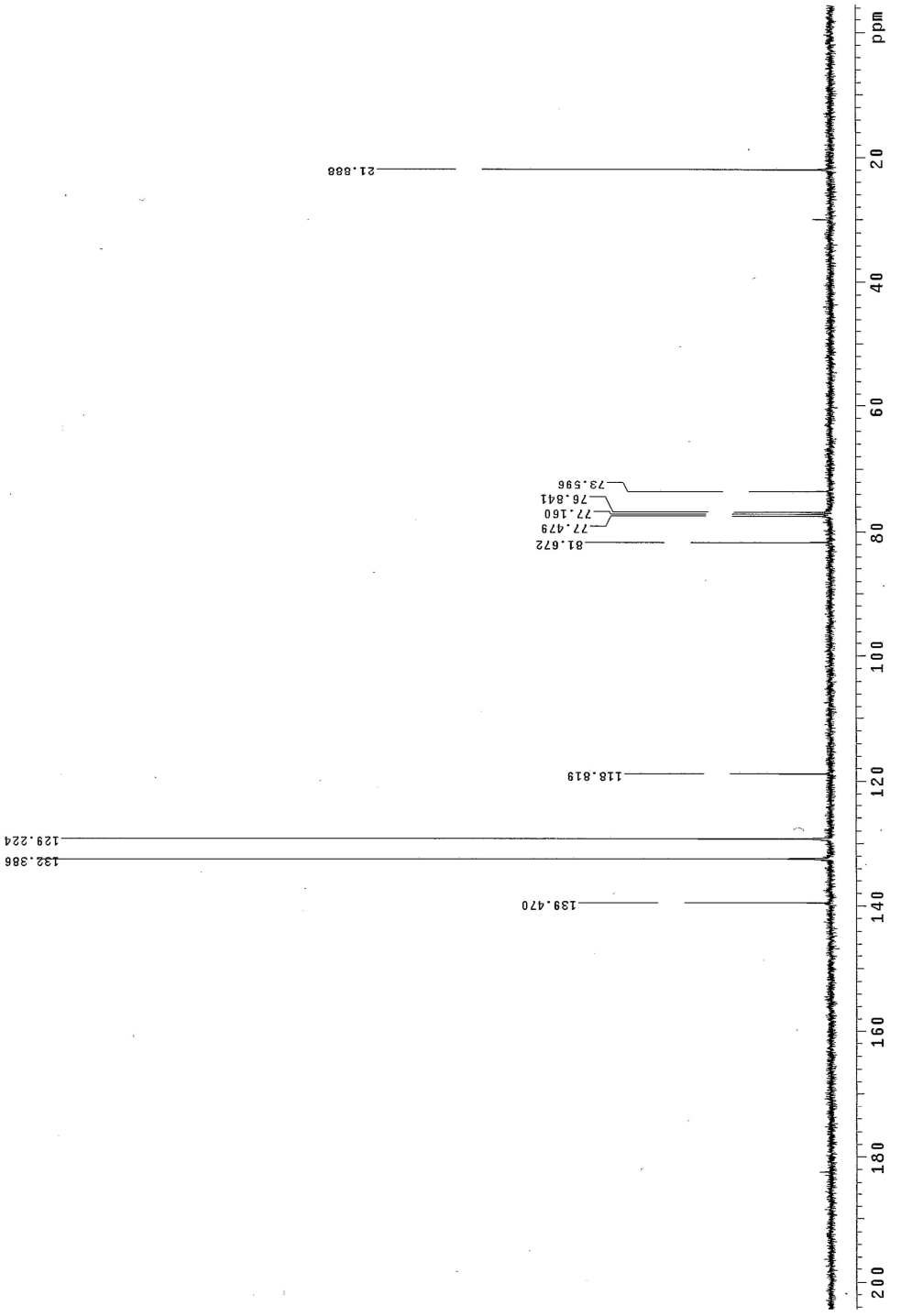
*1,4-dip-tolybuta-1,3-diyne (**4b**)*. The general procedure was followed to yield **4b** (43.1 mg, 75 %); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, 4H, J = 8.0 Hz), 7.15 (d, 4H, J = 8.0 Hz), 2.37 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.5, 132.4, 129.2, 118.8, 81.7, 73.6, 21.9 ppm; IR (neat) 3382, 1636, 1504, 810 cm^{-1}; HRMS (EI+) calcd for $C_{18}H_{10}(M^{+})$ 230.1096, found 230.1095

^{1}H NMR (400 MHz) at 25 °C



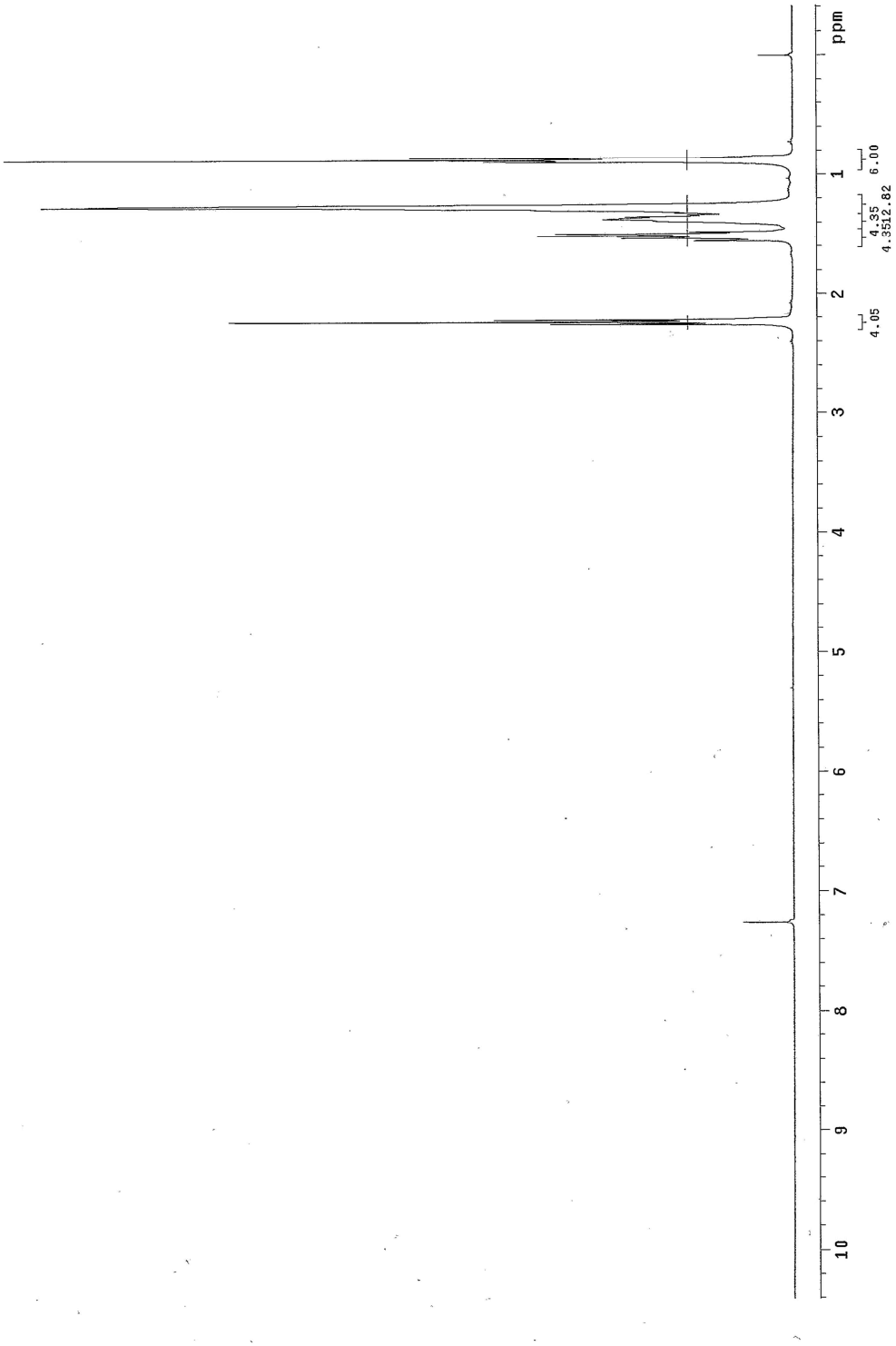
^{13}C NMR (100 MHz) at 25 °C



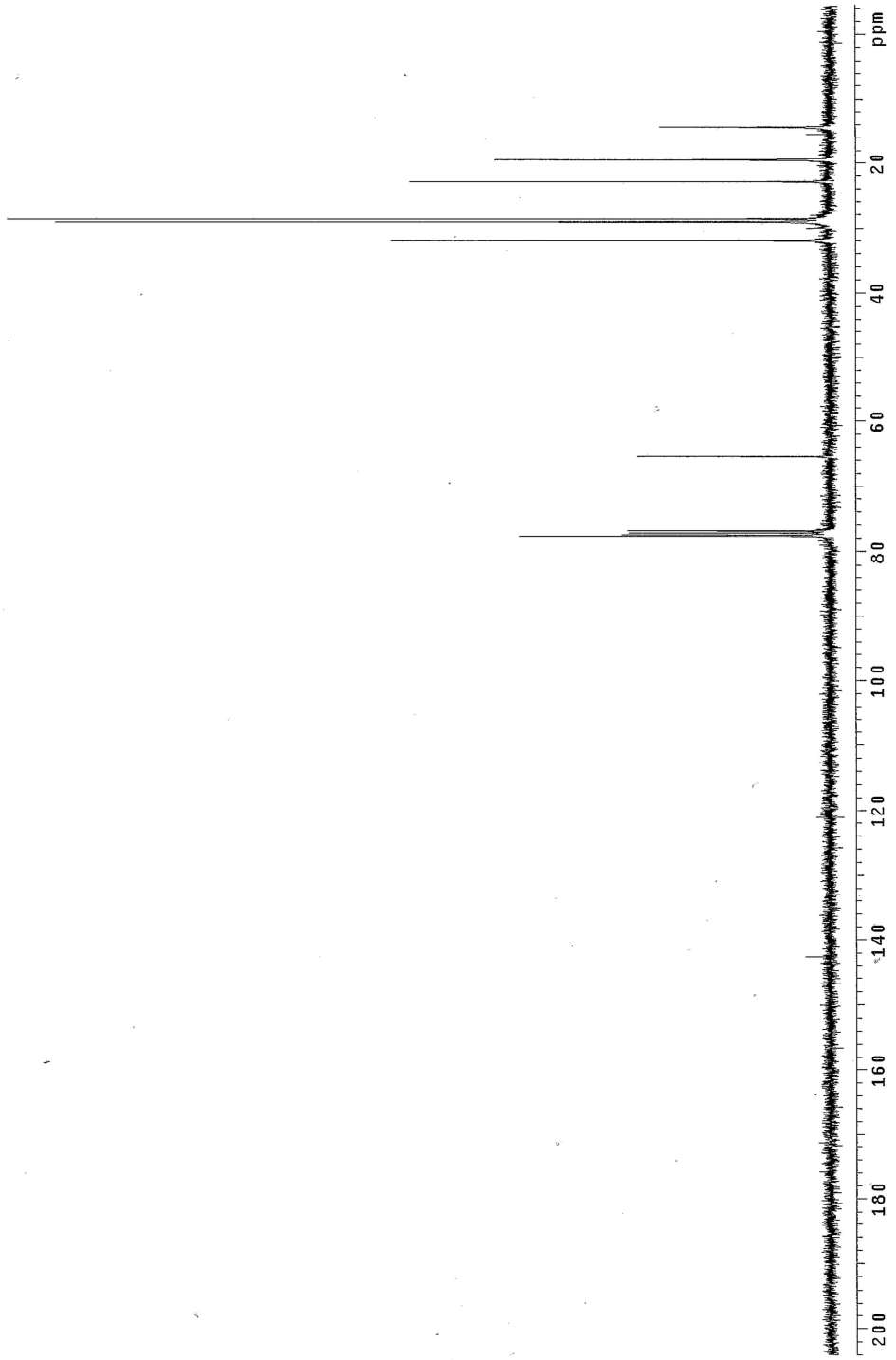

21.888
73.596
76.841
77.160
77.479
81.672
118.819
129.224
132.386
139.470
ppm
20
40
60
80
100
120
140
160
180
200

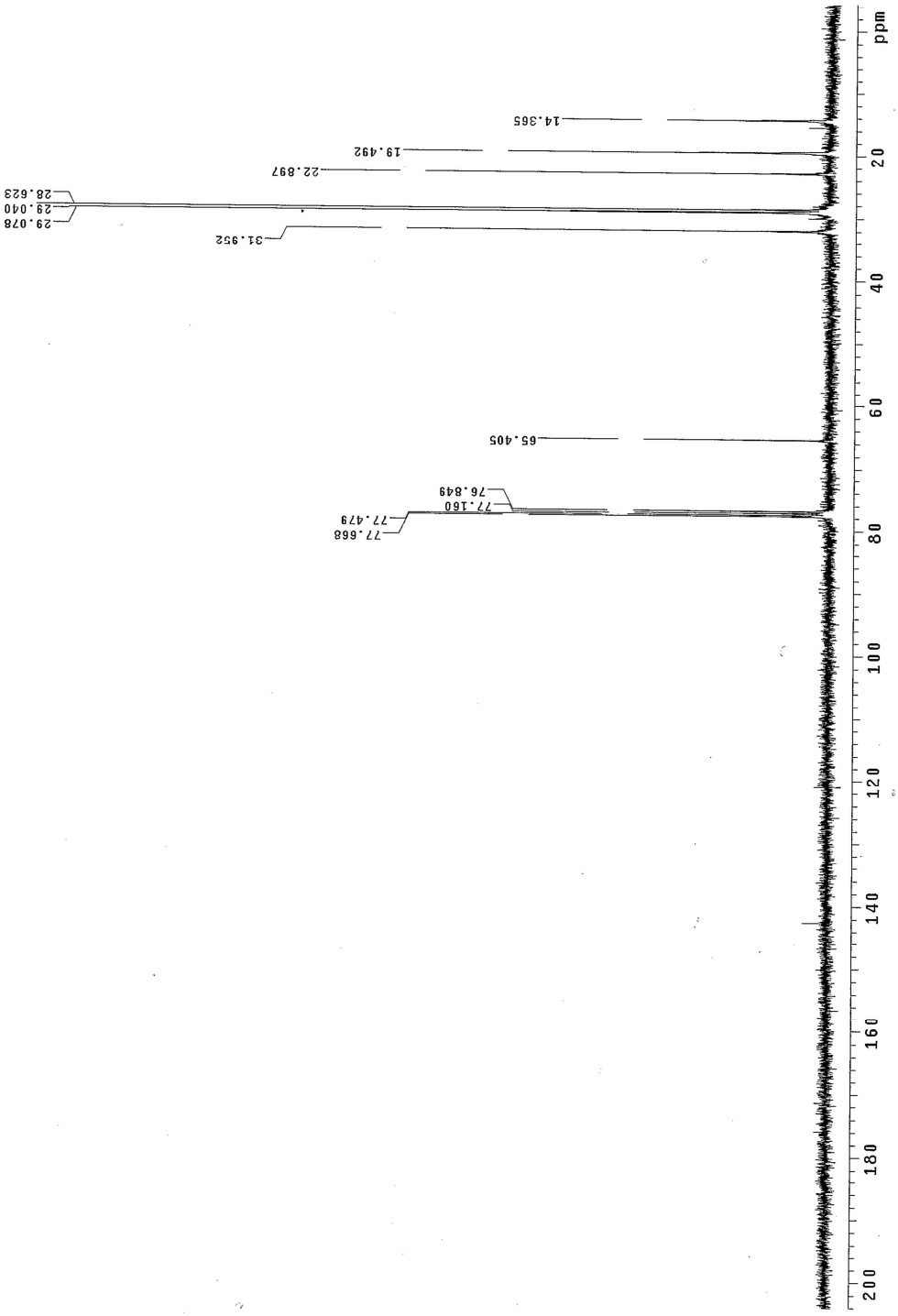
*1,4-bis(4-heptylphenyl)buta-1,3-diyne (**5b**)*. The general procedure was followed to yield **5b** (46.1 mg, 75 %); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.24 (t, 4H, J = 6.8 Hz), 1.52 (m, 4H), 1.36 (m, 4H), 1.29 (m, 12H), 0.88 (t, 6H, J = 6.4 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 76.8, 65.4, 32.0, 29.1, 29.0, 28.6, 22.9, 19.5, 14.4 ppm; IR (neat) 3447, 2955, 2929, 1652, 1465 cm^{-1}; HRMS (EI+) calcd for $C_{18}H_{30}(M^{+})$ 246.2348, found 246.2346.

^{1}H NMR (400 MHz) at 25 °C



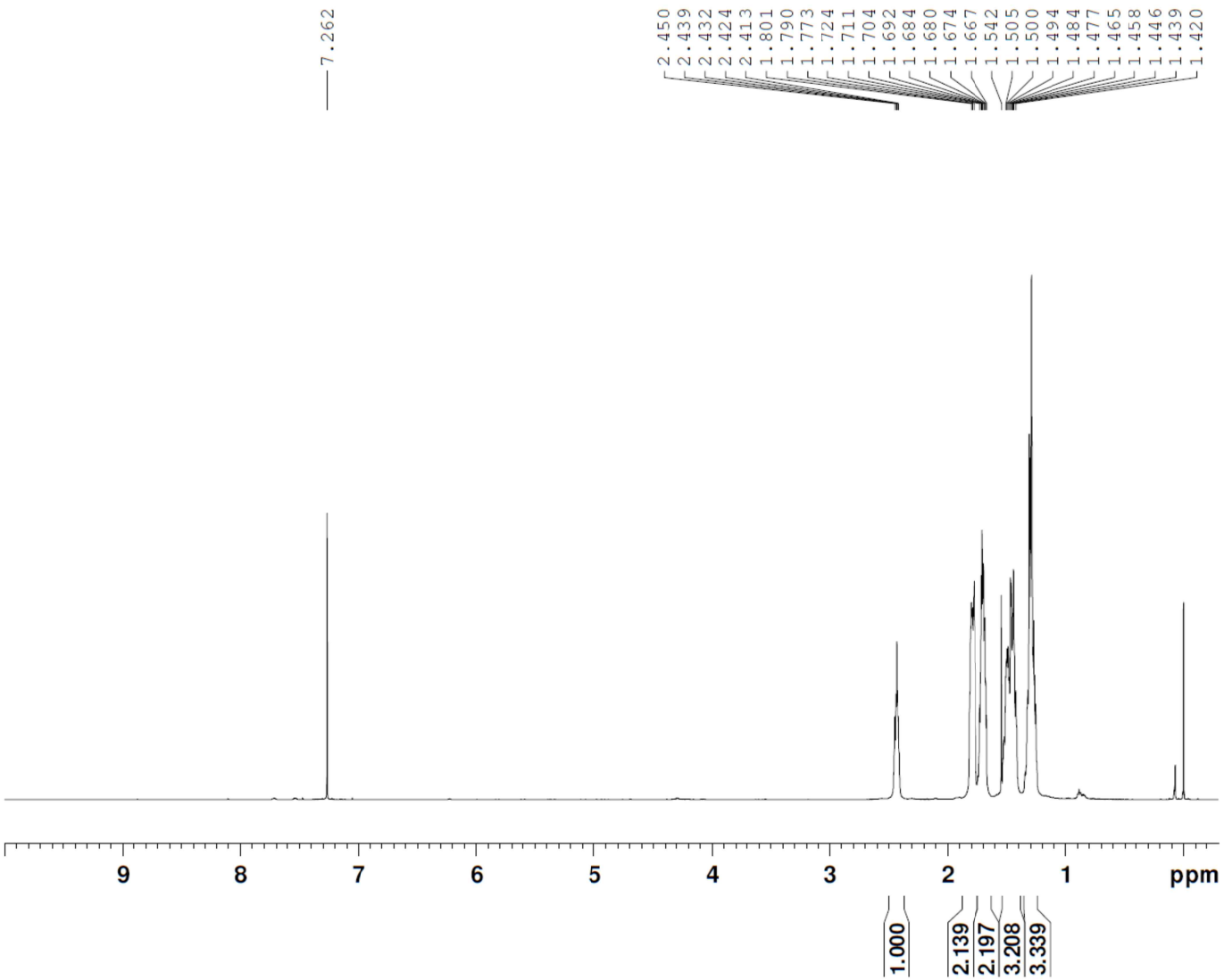
^{13}C NMR (100 MHz) at 25 °C




14.365
19.492
22.897
28.623
29.040
29.078
31.952
65.405
76.849
77.160
77.479
77.668
ppm
20
40
60
80
100
120
140
160
180
200

*1,4-dicyclohexylbuta-1,3-diyne (**6b**)*. The general procedure was followed to yield **6b** (29.6 mg, 55 %); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.43 (m, 2H), 1.79 (m, 4H), 1.70 (m, 4H), 1.48 (m, 6H), 1.29 (m, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 82.1, 65.3, 32.5, 29.7, 26.0, 25.0 ppm; IR (neat) 2929, 2344, 1448, 750 cm^{-1}; HRMS (EI+) calcd for $C_{16}H_{10}(M^{+})$ 214.1722, found 214.1721.

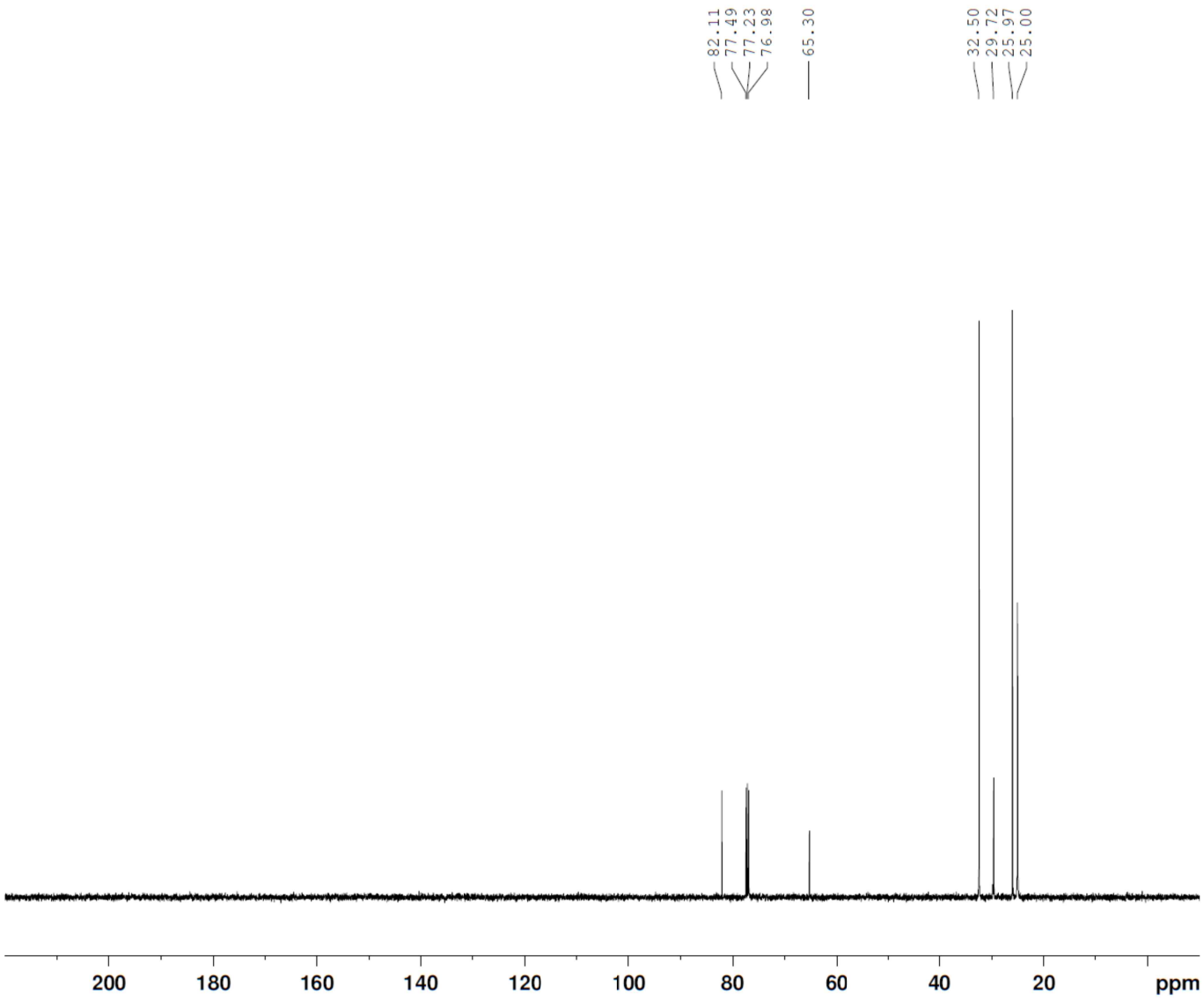
6b / 1H



서 울 대 학 교
SEOUL NATIONAL UNIVERSITY
기초과학공동기기원
핵자기공명연구실

```
Current Data Parameters
NAME       may22-aju-jhy
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameter
Date_           20150522
Time               16.27
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    32
DS                     4
SWH             6487.889 Hz
FIDRES          0.197995 Hz
AQ              2.5253205 se
RG                  80.6
DW                77.067 us
DE                 6.50 us
TE                298.0 K
D1           1.00000000 se
TD0                    1

======== CHANNEL f1 =======
SFO1         500.1325092 MH
NUC1                1H
P1                10.20 us
PLW1        19.00000000 W

F2 - Processing parameters
SI                 16384
SF           500.1300119 MH
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

6b / 13C

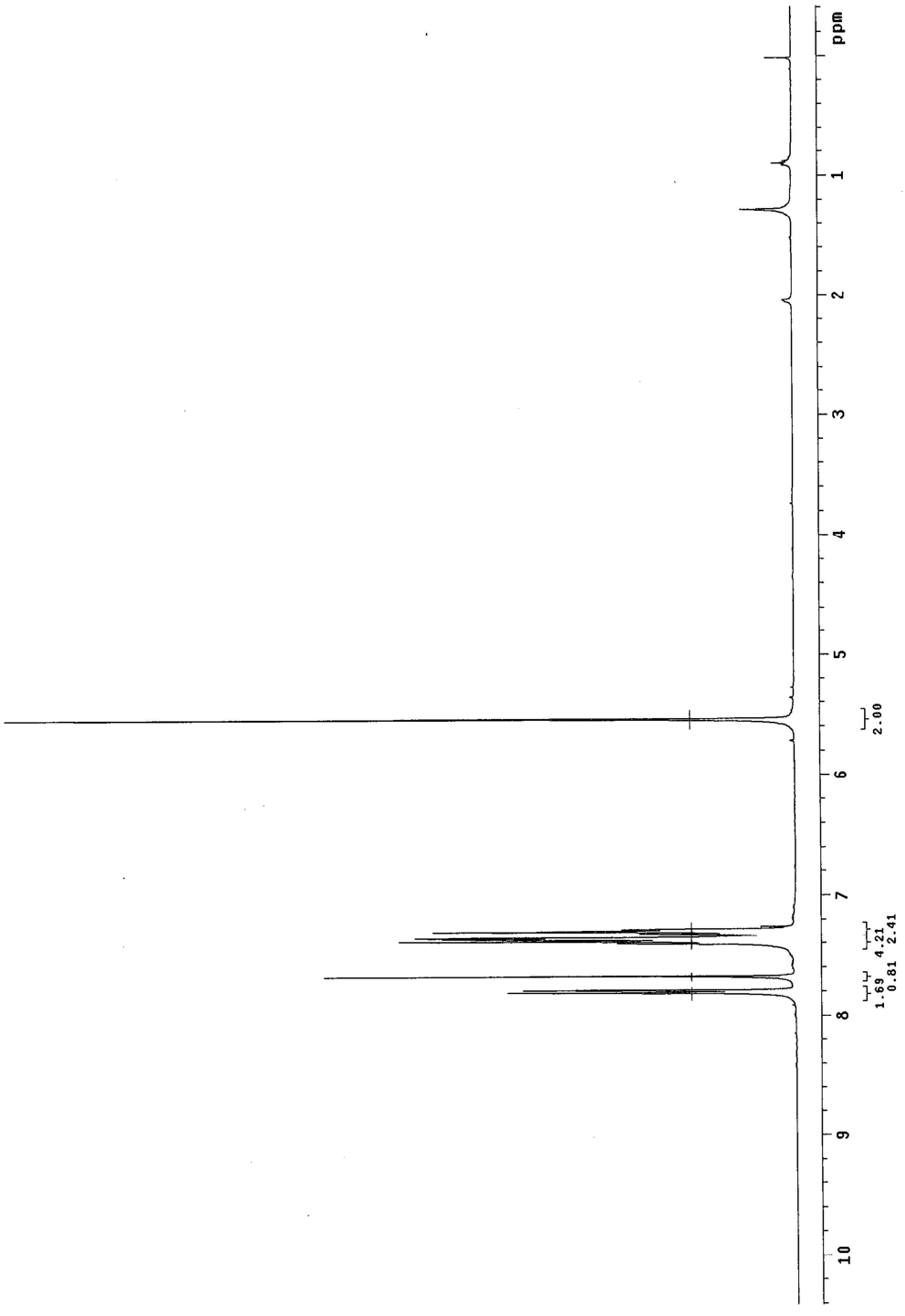


서 울 대 학 교
SEOUL NATIONAL UNIVERSITY
기초과학공동기기원
핵자기공명연구실

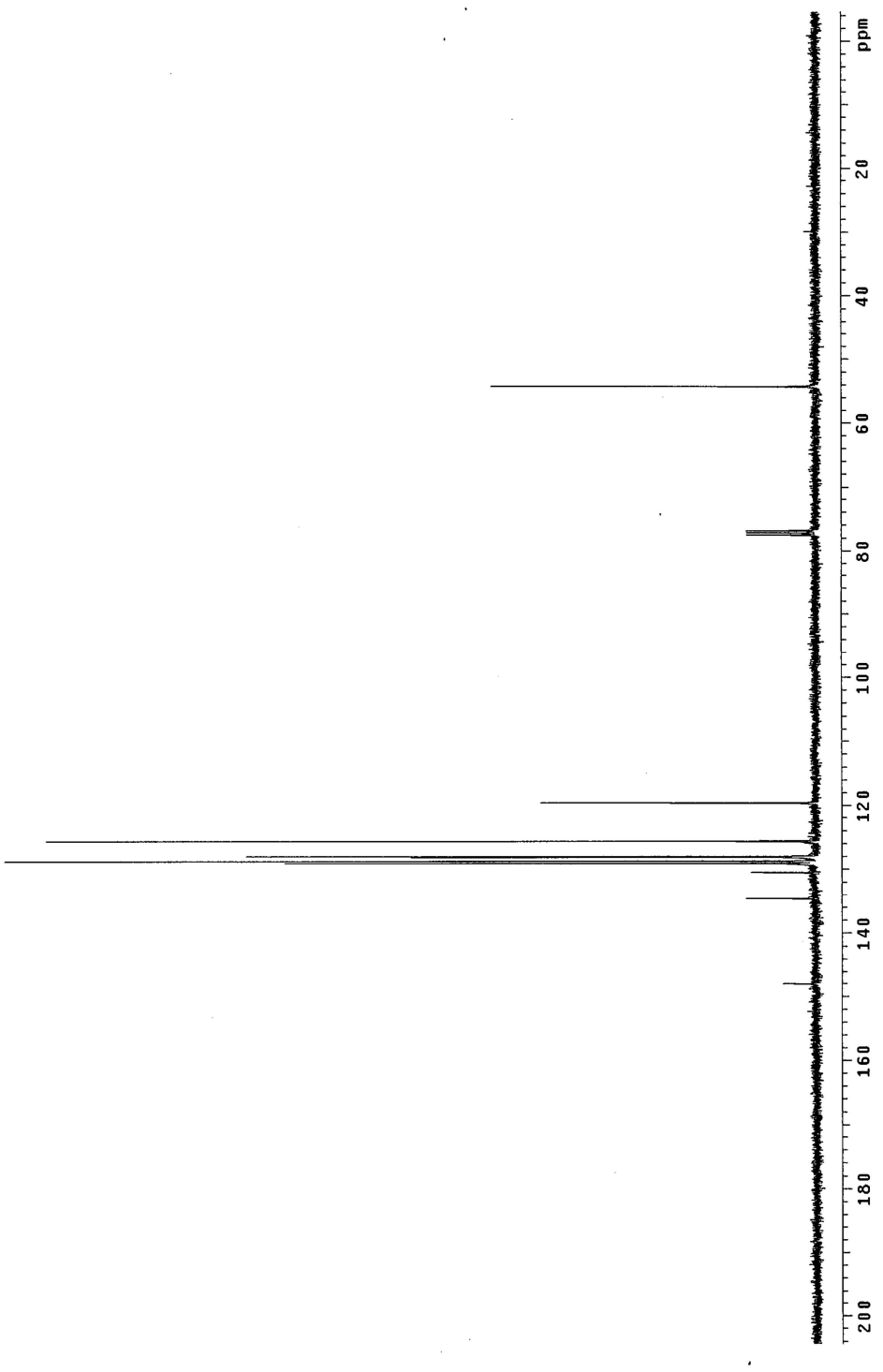
```
Current Data Parameters
NAME       may22-aju-jhy
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150522
Time               16.29
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zgdc
TD                 32768
SOLVENT            CDCl3
NS                   128
DS                     4
SWH            29761.904 Hz
FIDRES          0.908261 Hz
AQ              0.5505024 sec
RG                  2050
DW                16.800 usec
DE                 6.50 usec
TE                298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         125.7709936 MHz
NUC1                 13C
P1                 10.00 usec
PLW1         90.00000000 W

======== CHANNEL f2 ========
SFO2         500.1320005 MHz
NUC2                 1H
CPDPRG[2          waltz16
PCPD2              80.00 usec
PLW2         19.00000000 W
PLW12         0.30886999 W

F2 - Processing parameters
SI                 16384
SF           125.7577617 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

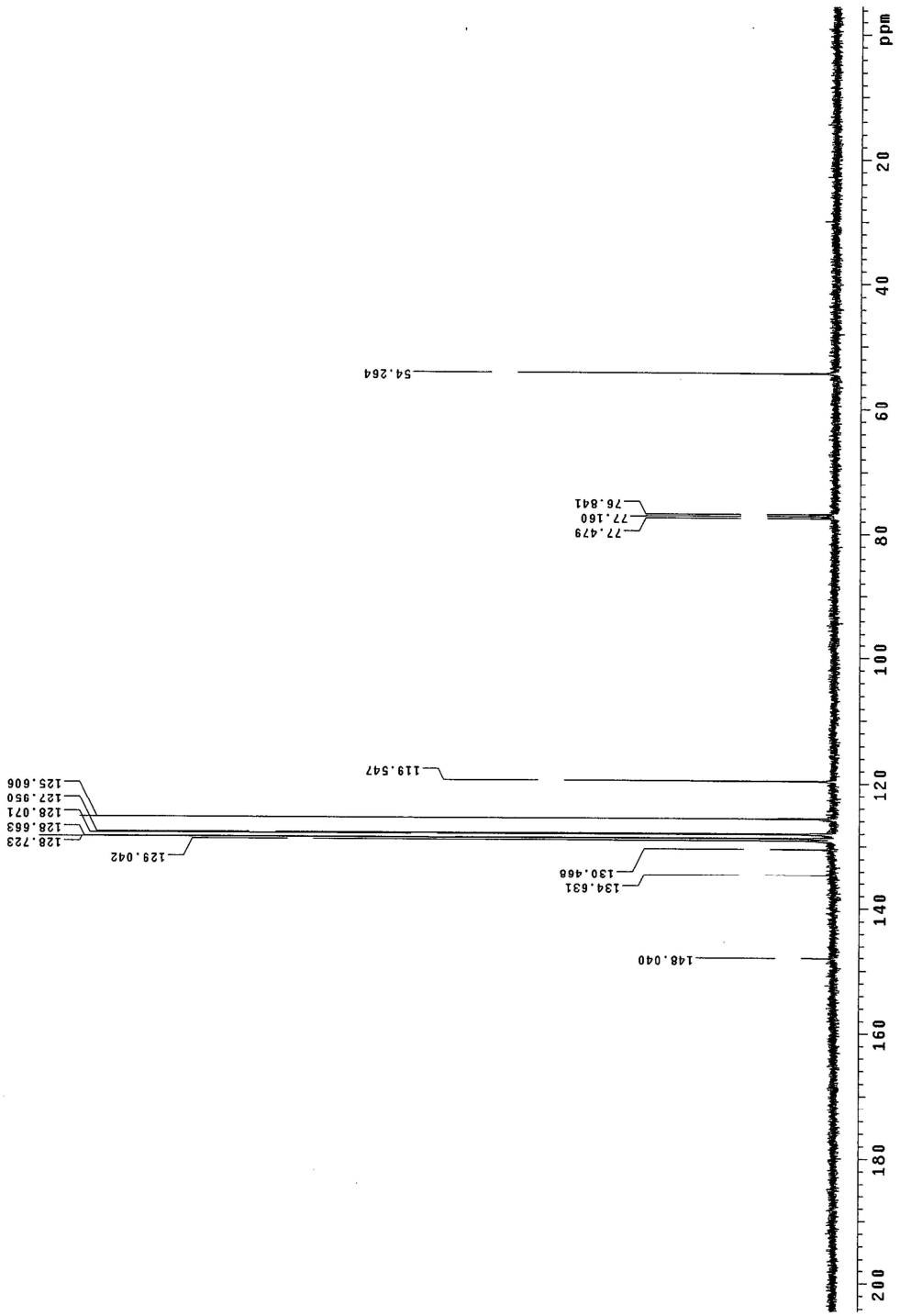
1-benzyl-4-m-tolyl-1H-1,2,3-triazole (Table 2, 1d). The representative procedure was followed to yield **1d** (100.4mg, 85%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (m, 2H), 7.68 (s, 1H), 7.38 (m, 5H), 7.31 (m, 3H), 5.54 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 134.6, 130.5, 129.0, 128.7 (2C), 128.1, 128.0, 125.6, 119.5, 54.3 ppm; IR (neat) 3091, 2360, 1600, 1496, 1223 cm^{-1}; HRMS (EI+) cacld for $C_{15}H_{13}N_3$ (M^+) 235.1109, found 235.1108.

^{1}H NMR (400 MHz) at 25 °C



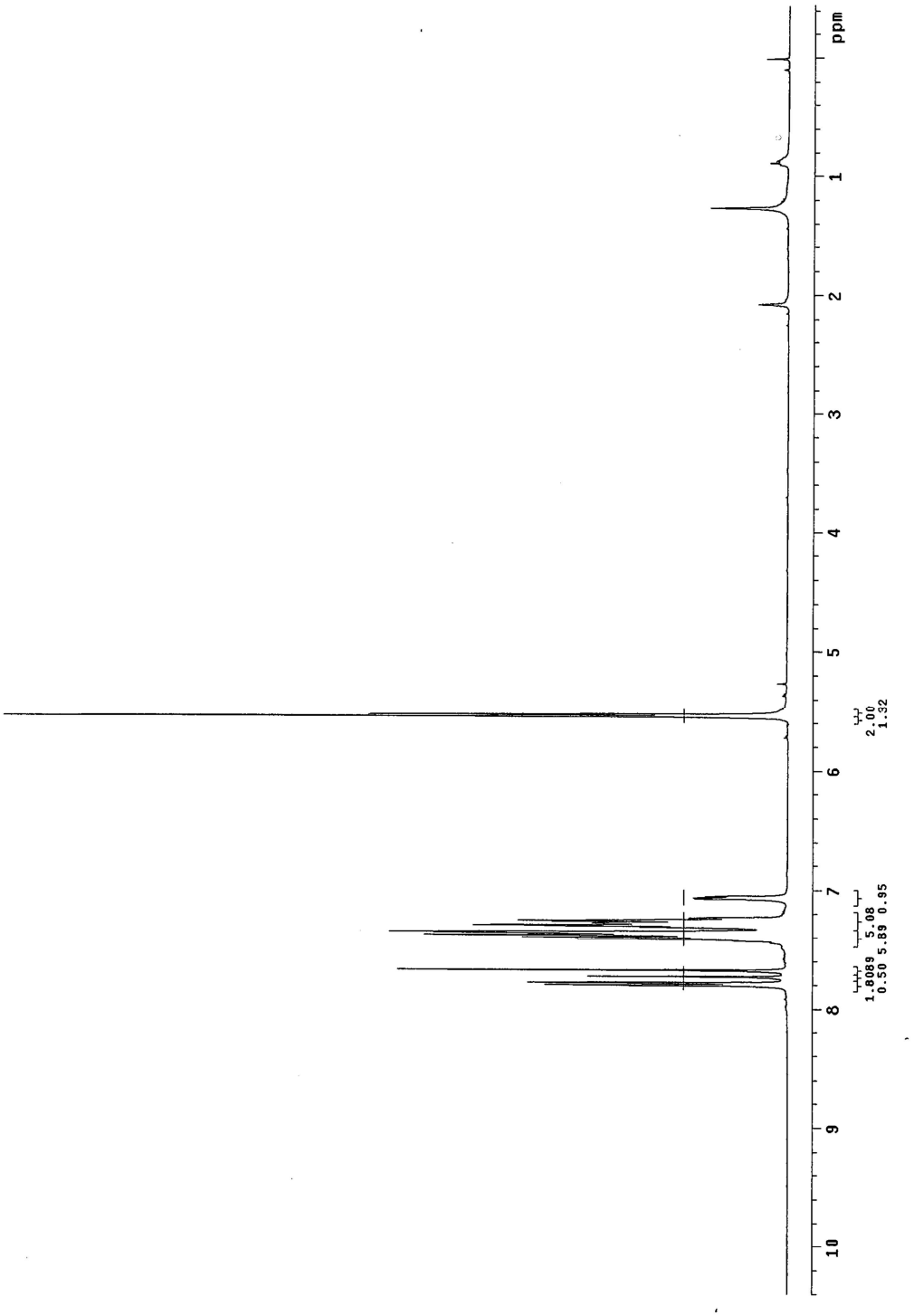
^{13}C NMR (100 MHz) at 25 °C



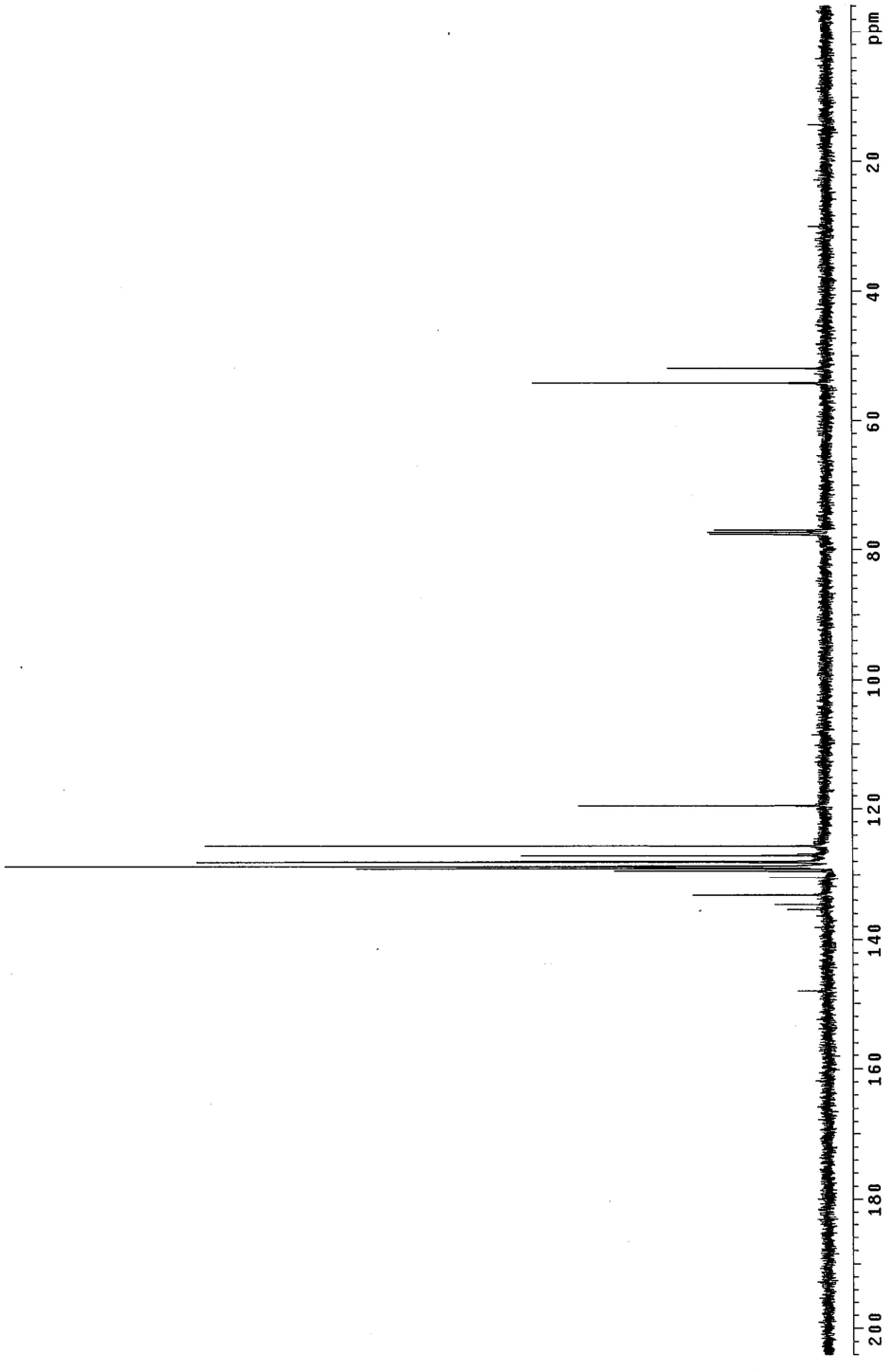

54.264
76.841
77.160
77.479
119.547
125.606
127.950
128.071
128.663
128.723
129.042
130.466
134.631
148.040
ppm
20
40
60
80
100
120
140
160
180
200

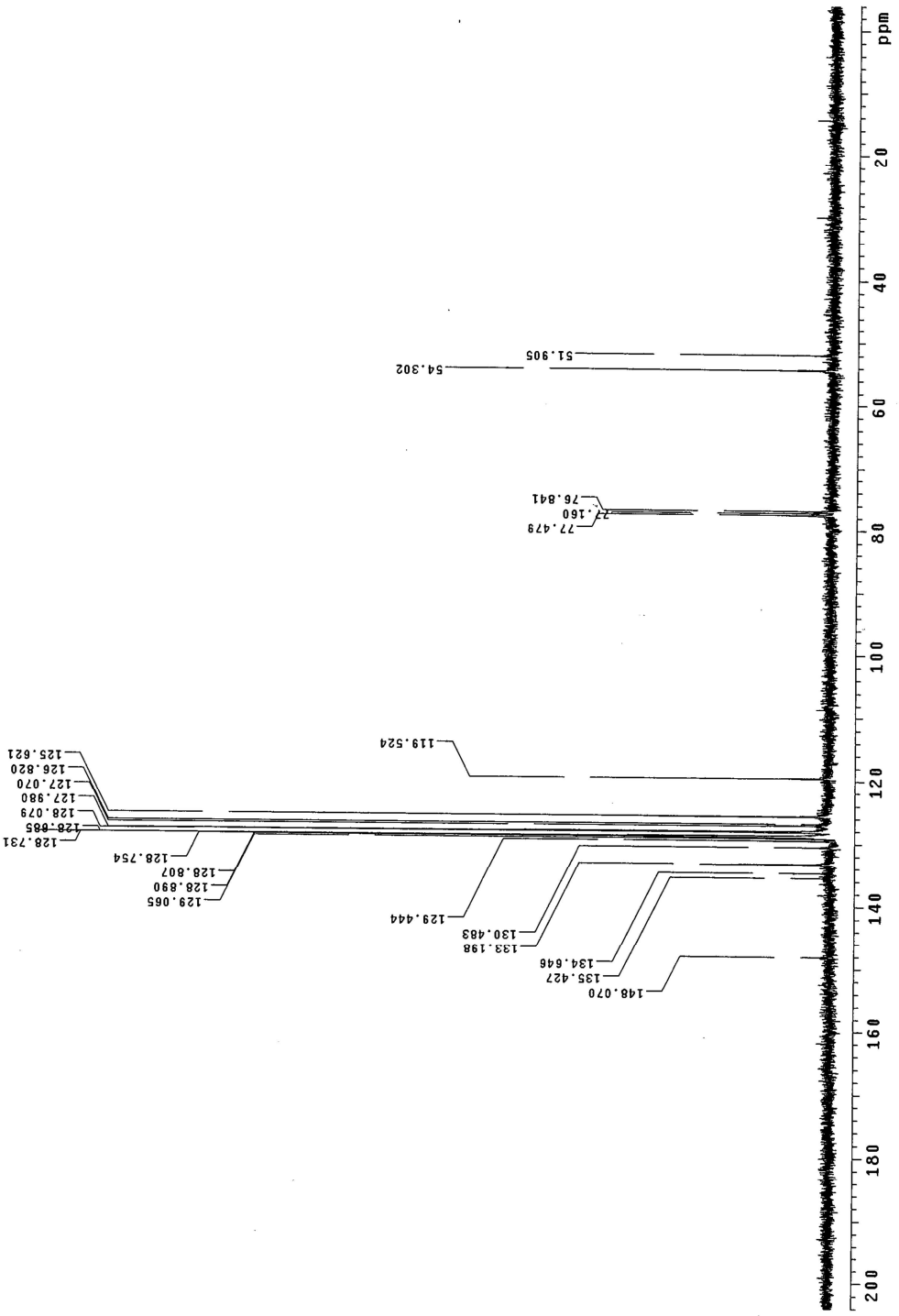
1-benzyl-5-phenyl-1H-1,2,3-triazole (Scheme 3, 1d'). ^{1}H NMR (400 MHz, $CDCl_3$) 1d+1d' (major : minor = 2:1) δ 7.80 (m, 2H, major), 7.73 (s, 1H, minor), 7.68 (s, 1H, major), 7.43 - 7.23 (m, 16H, major : minor = 2:1), 7.06 (m, 2H, minor), 5.55 (s, 2H, major), 5.53 (s, 2H, minor) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 135.4, 134.6, 133.2, 130.5, 129.4, 129.1, 128.9, 128.8 (2C), 128.7 (2C), 128.1, 128.0, 127.1, 126.8, 125.6, 119.5, 54.3, 51.9 ppm; IR (neat) 3122, 2360, 1606, 1497, 1207 cm^{-1}; HRMS (EI+) cacld for $C_{15}H_{13}N_3$ (M^+) 235.1109, found 235.1108.

^{1}H NMR (400 MHz) at 25 °C



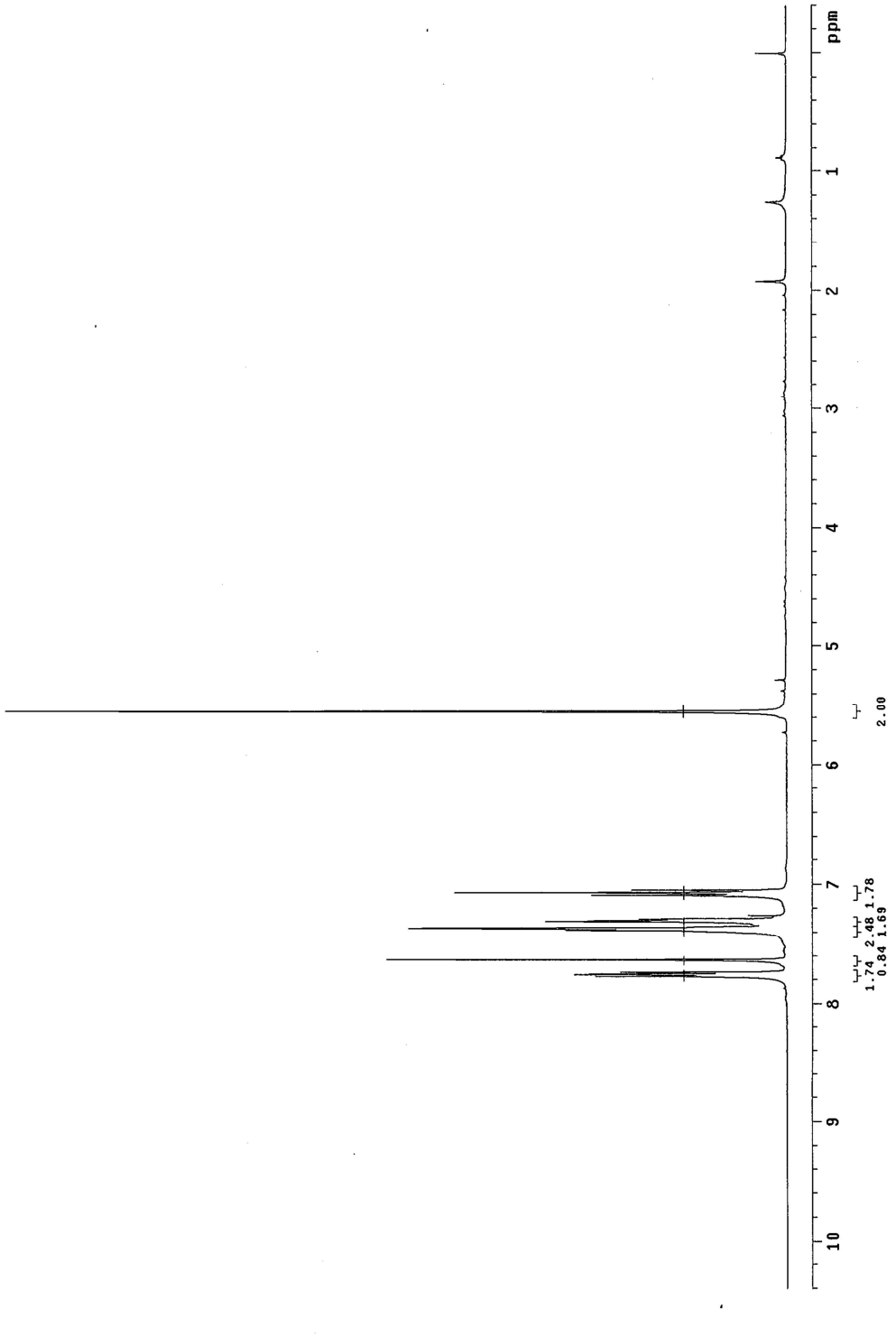
^{13}C NMR (100 MHz) at 25 °C



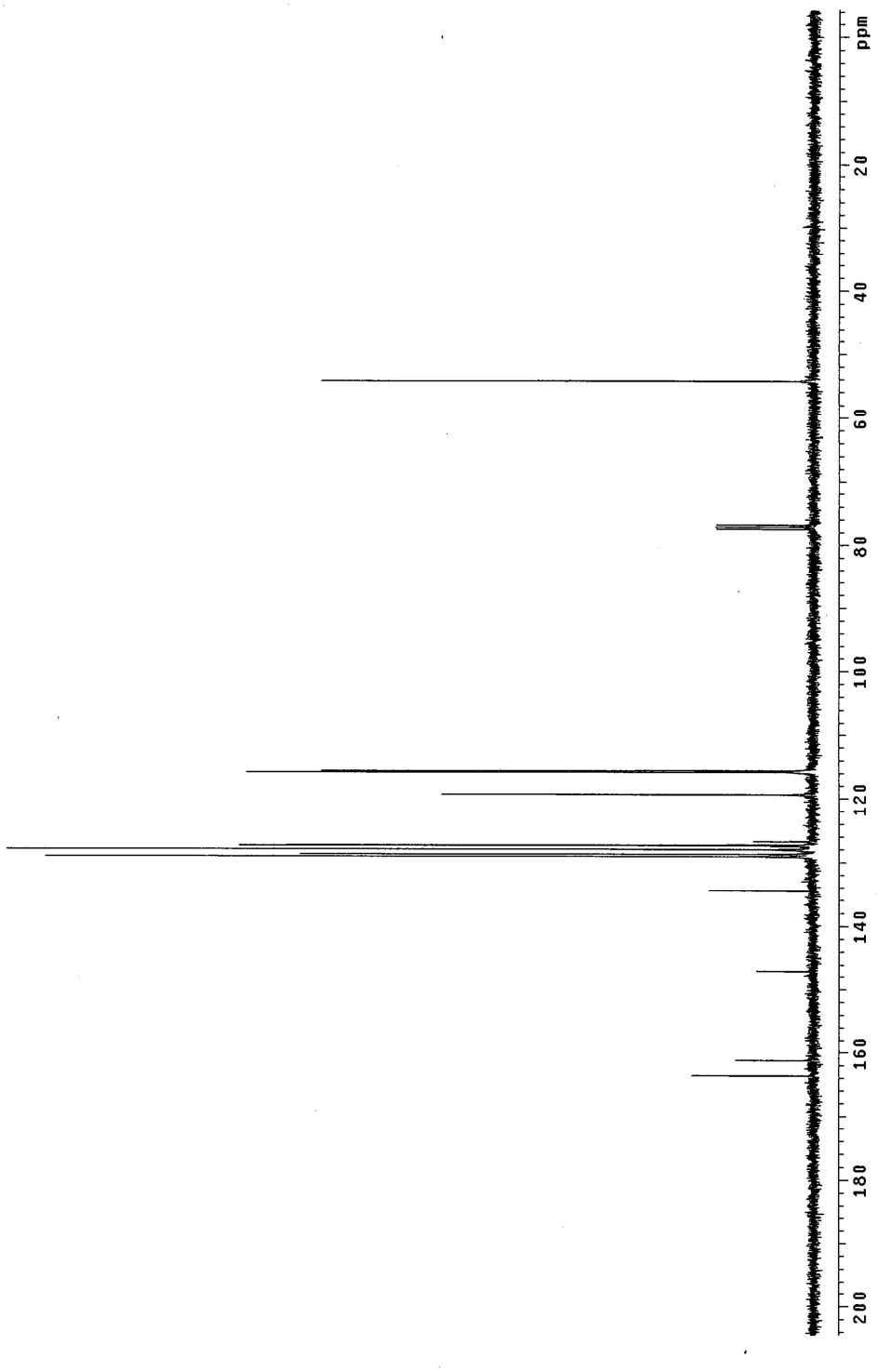

148.070
135.427
134.646
133.198
130.483
129.444
129.065
128.890
128.807
128.754
128.731
128.685
128.079
127.980
127.070
126.820
125.621
119.524
77.479
77.160
76.841
54.302
51.905
ppm
200
180
160
140
120
100
80
60
40
20

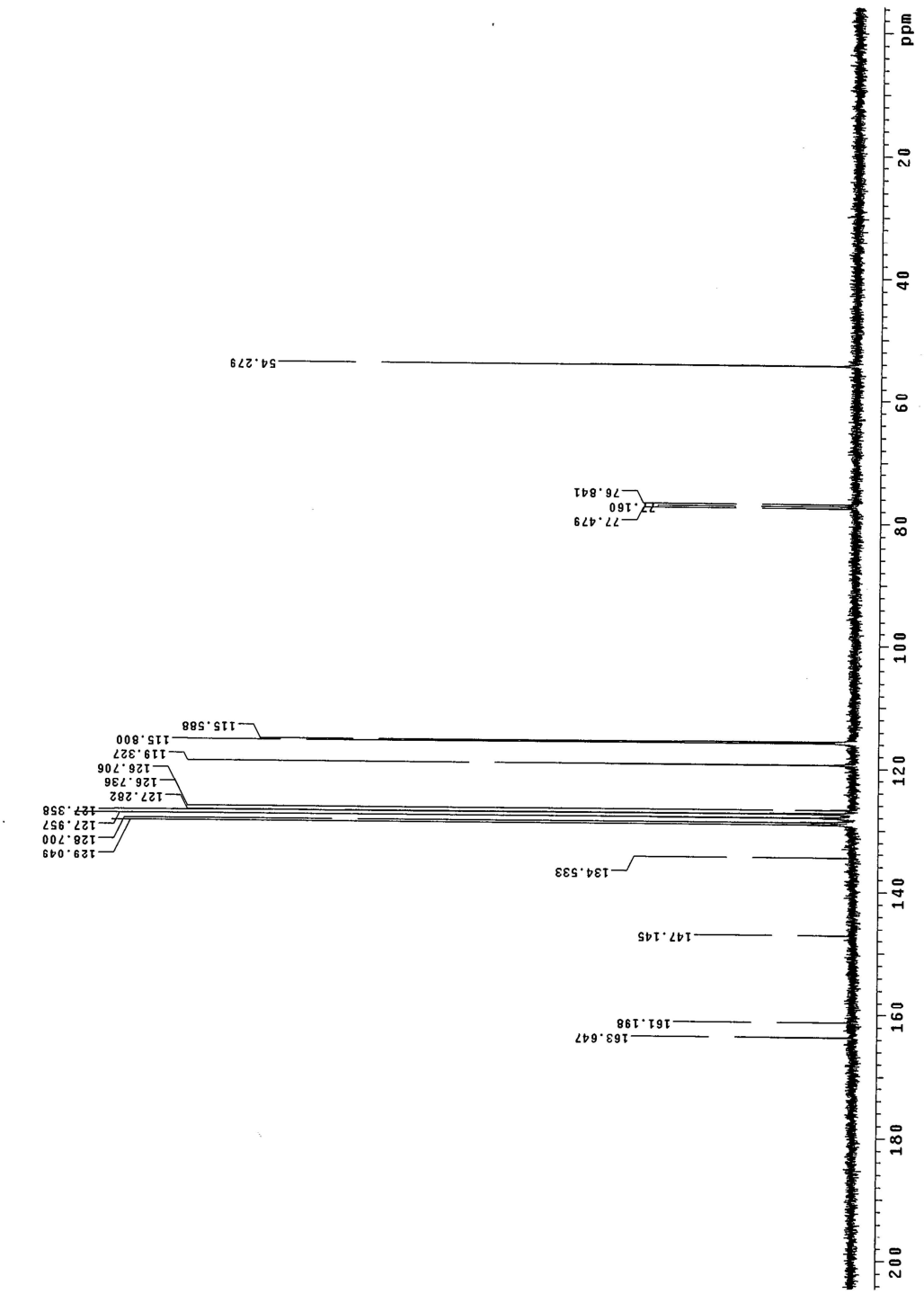
1-benzyl-4-(4-flourophenyl)-1H-1,2,3-triazole (Figure 1, 2d). The representative procedure was followed to yield **2d** (97.1 mg, 77%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (m, 2H), 7.63 (s, 1H), 7.39 (m, 2H), 7.30 (m, 2H), 7.07 (m, 2H), 5.55 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4 (d, J_{CF} = 244.9 Hz), 147.1, 134.5, 129.0, 128.7, 128.0, 127.3 (d, J_{CF} = 7.6 Hz), 126.7 (d, J_{CF} = 3.0 Hz), 119.3, 115.7 (d, J_{CF} = 21.2 Hz), 54.3 ppm; IR (neat) 3102, 1611, 1495, 1226 cm^{-1}; HRMS (EI+) cacld for $C_{15}H_{12}FN_3$ (M^+) 253.1015, found 253.1014.

^{1}H NMR (400 MHz) at 25 °C



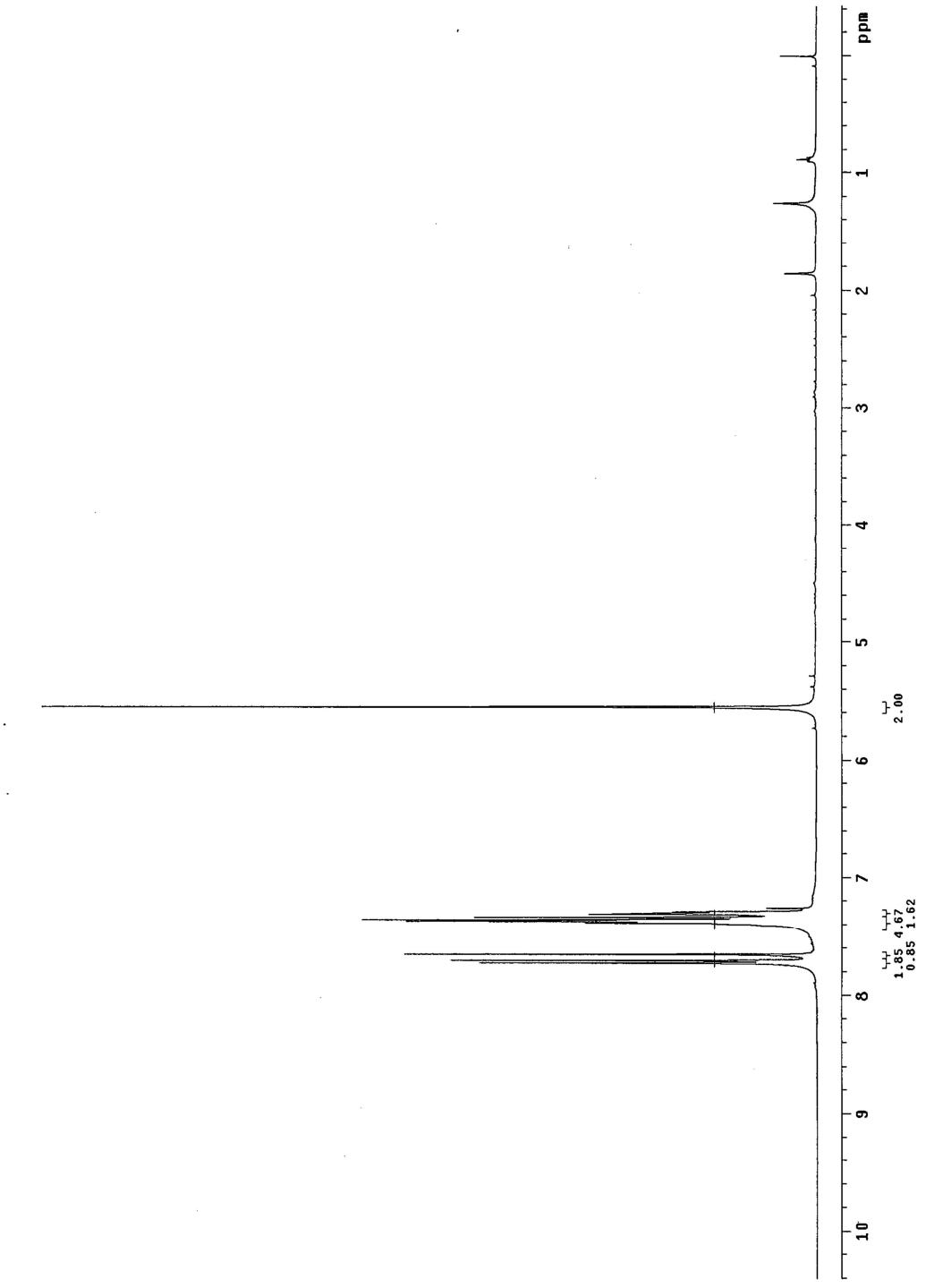
^{13}C NMR (100 MHz) at 25 °C



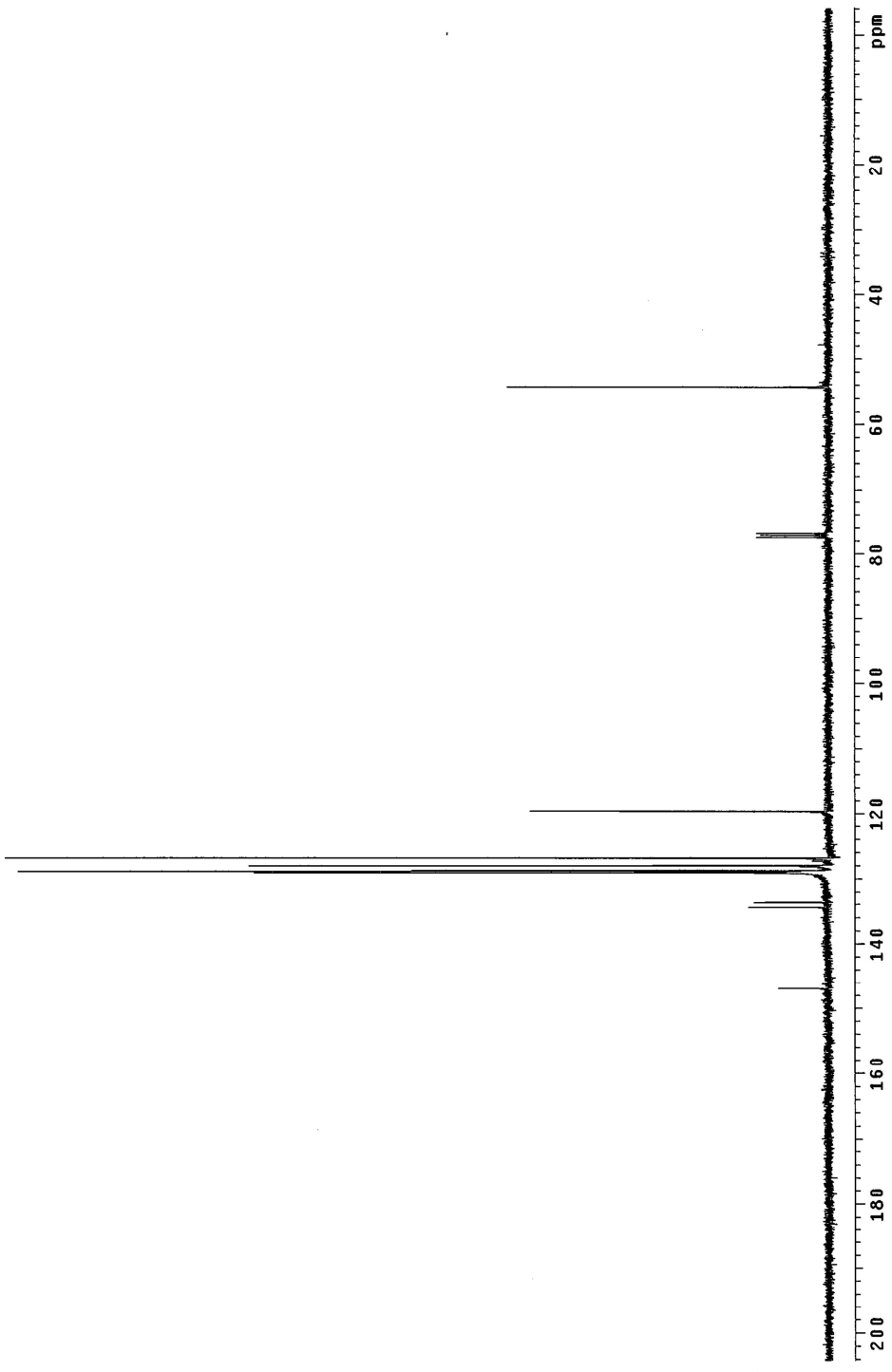

ppm
20
40
60
80
100
120
140
160
180
200
54.279
76.841
77.160
77.479
115.588
115.800
119.327
126.706
126.736
127.282
127.358
127.957
128.700
129.049
134.533
147.145
161.198
163.647

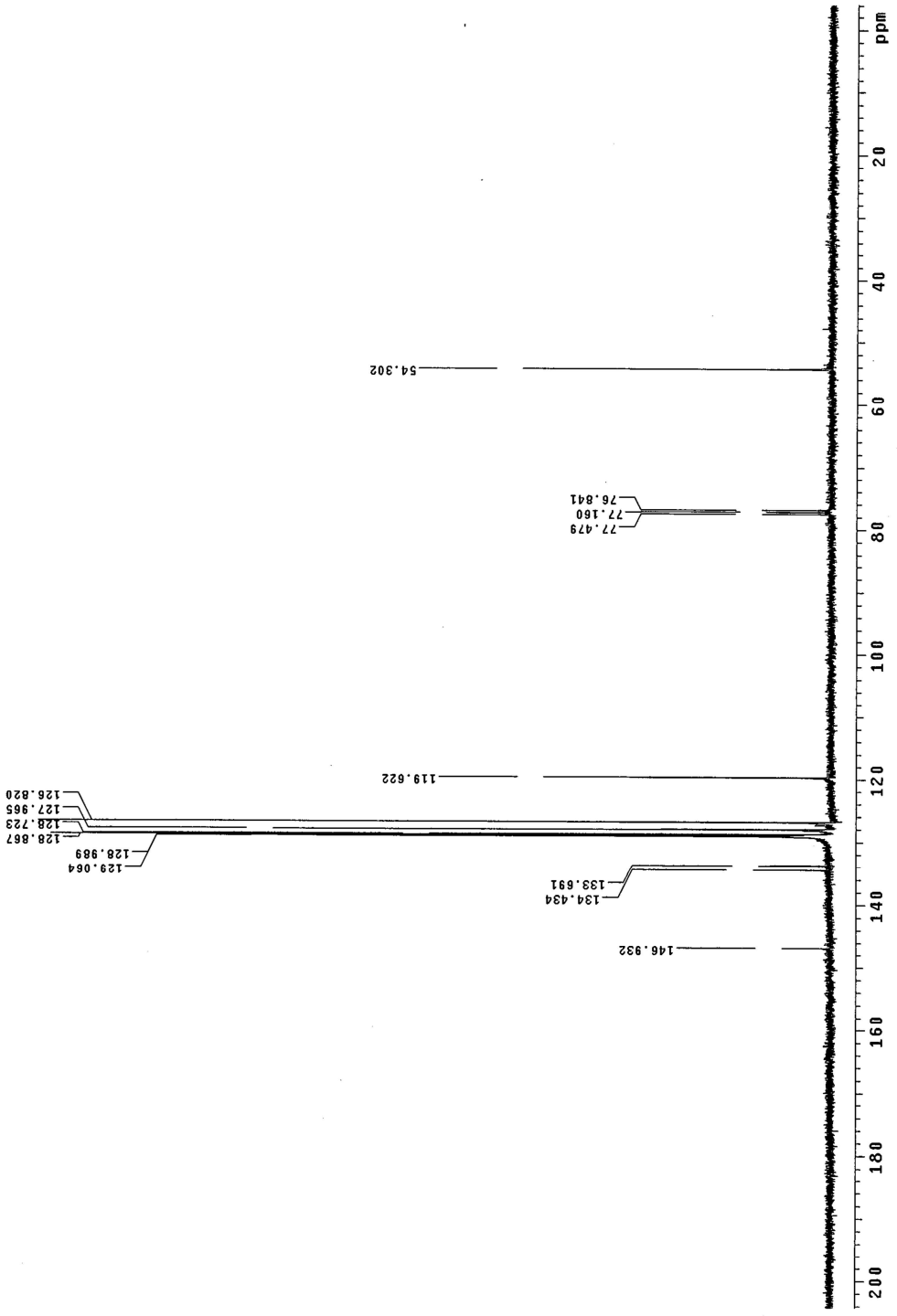
1-benzyl-4-(4-chlorophenyl)-1H-1,2,3-triazole (Figure 1, 3d). The representative procedure was followed to yield **3d** (115.3 mg, 85%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (m, 2H), 7.66 (s, 1H), 7.37 (m, 5H), 7.30 (m, 2H), 5.56 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9, 134.4, 133.7, 129.1, 129.0, 128.9, 128.7, 128.0, 126.8, 119.6, 54.3 ppm; IR (neat) 3117, 1631, 1480, 1225 cm^{-1}; HRMS (EI+) cacld for $C_{15}H_{12}ClN_3$ (M^+) 269.0720, found 269.0717.

^{1}H NMR (400 MHz) at 25 °C



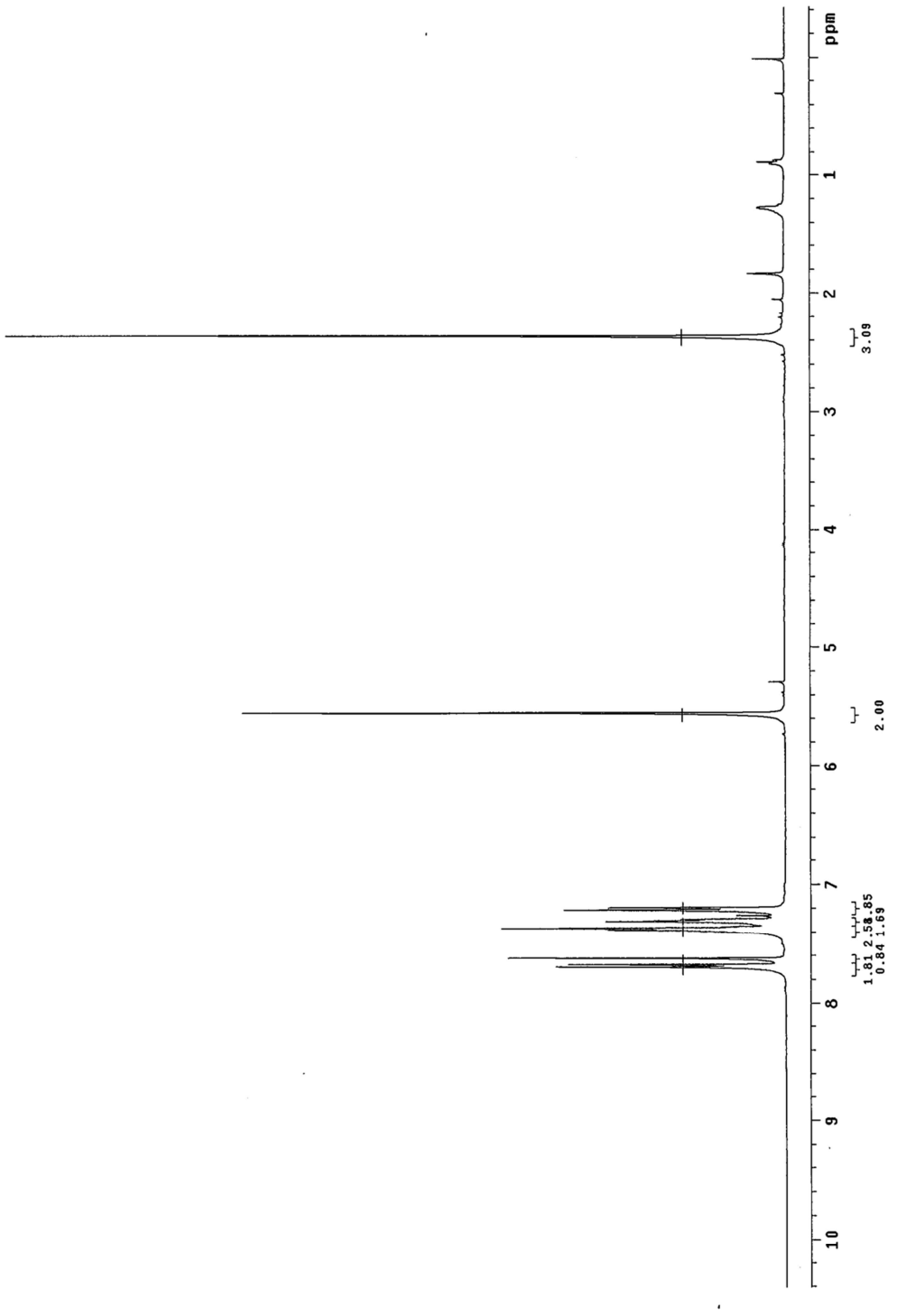
^{13}C NMR (100 MHz) at 25 °C



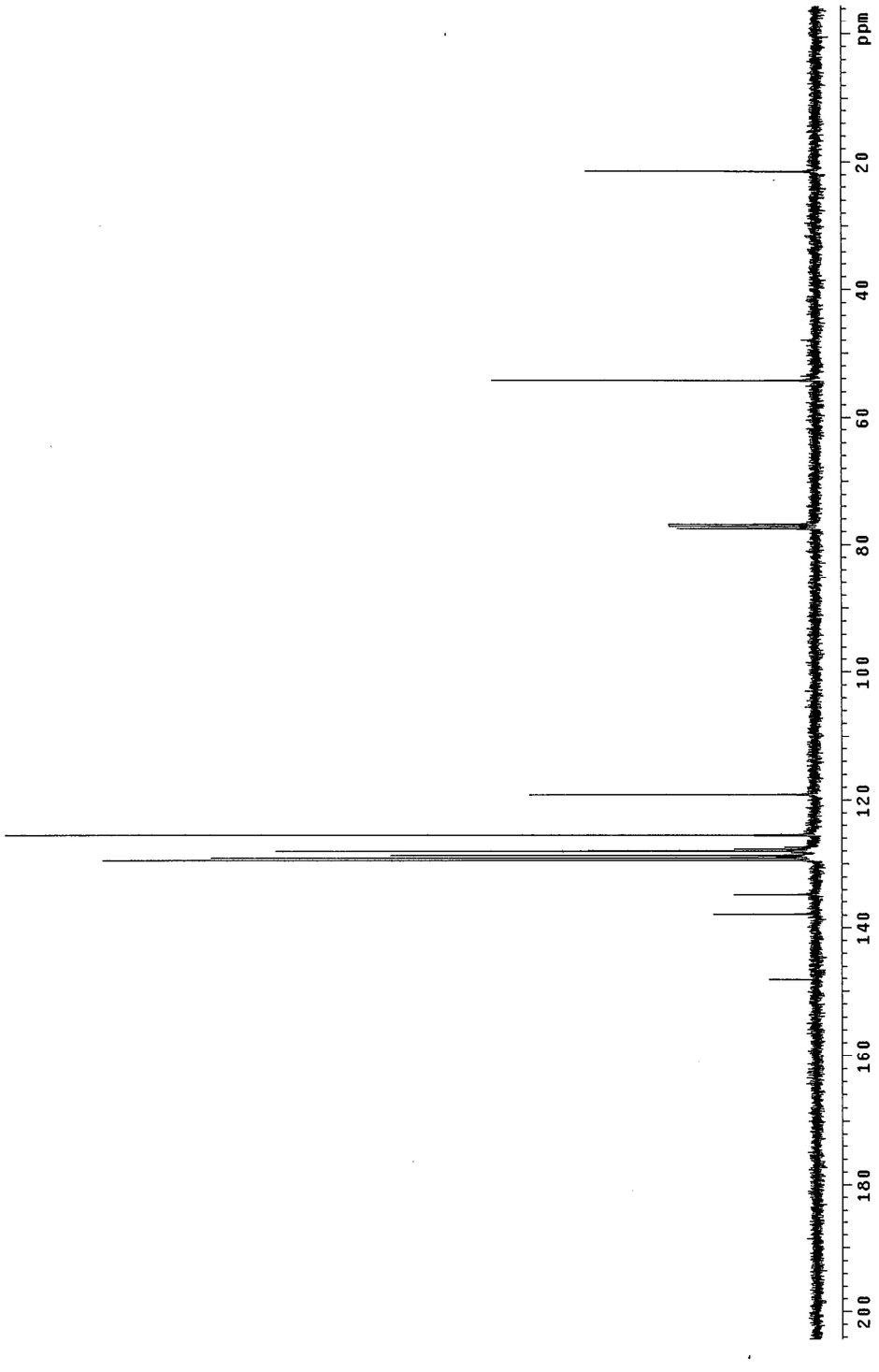

ppm
20
40
60
80
100
120
140
160
180
200
54.302
77.479
77.160
76.841
119.622
126.820
127.965
128.723
128.867
128.989
129.064
133.691
134.434
146.932

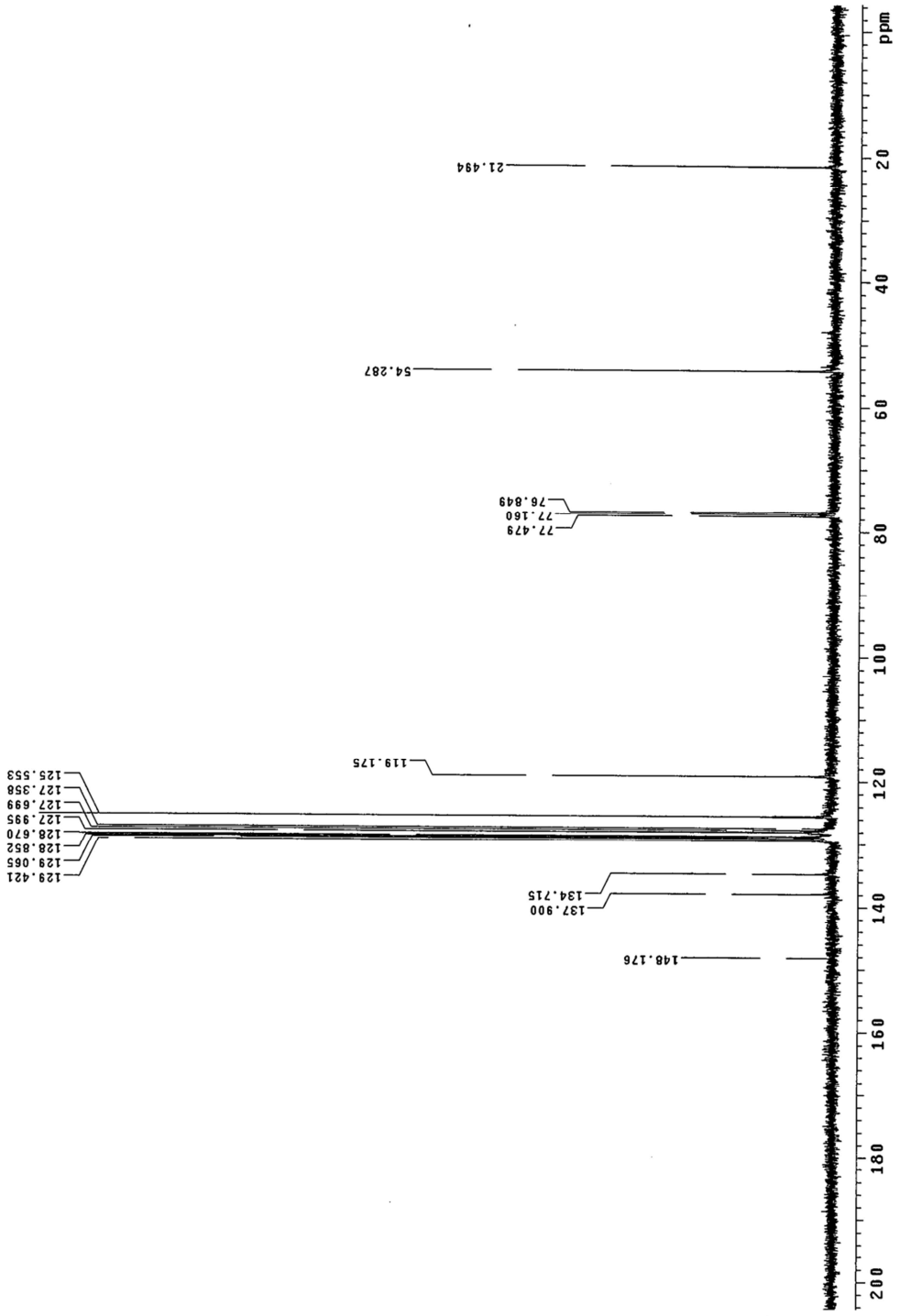
1-benzyl-4-p-tolyl-1H-1,2,3-triazole (Figure 1, 4d). The representative procedure was followed to yield **4d** (97.3 mg, 78%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.0*Hz,* 2H), 7.63 (s, 1H), 7.38 (m, 3H), 7.32 (m, 2H), 7.21 (d, J = 7.6*Hz*, 2H), 5.56 (s, 2H), 2.36 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 137.9, 134.7, 129.4, 129.1, 128.9, 128.7, 128.0, 127.7, 127.4, 125.6 , 119.2, 54.3, 21.5 ppm; IR (neat) 3145, 2360, 1553, 1222 cm^{-1}; HRMS (EI+) cacld for $C_{16}H_{15}N_3$ (M^+) 249.1266, found 249.1264.

^{1}H NMR (400 MHz) at 25 °C



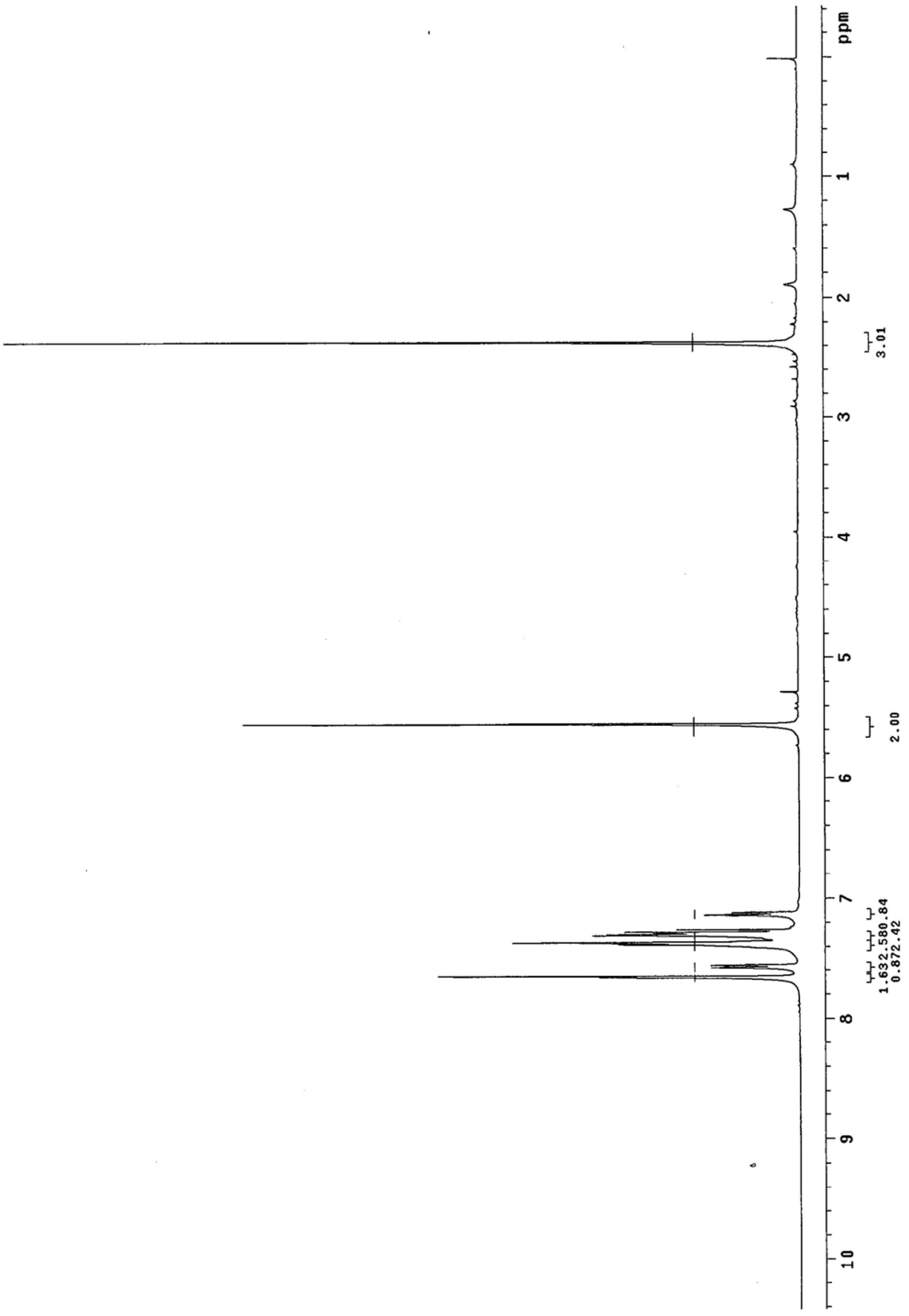
^{13}C NMR (100 MHz) at 25 °C



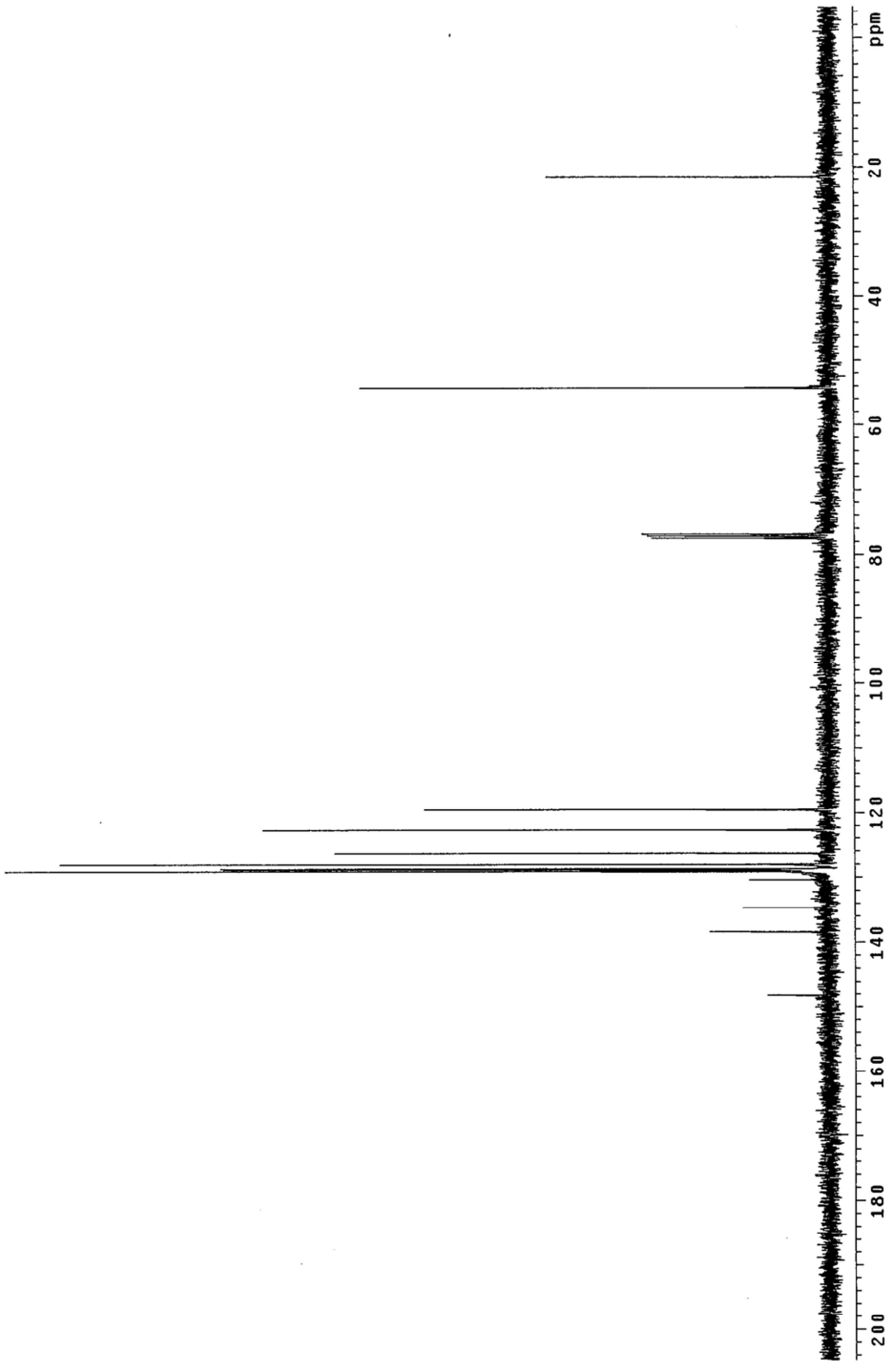

21.494
54.287
76.849
77.160
77.479
119.175
125.553
127.358
127.699
127.995
128.670
128.852
129.065
129.421
137.900
134.715
148.176
ppm

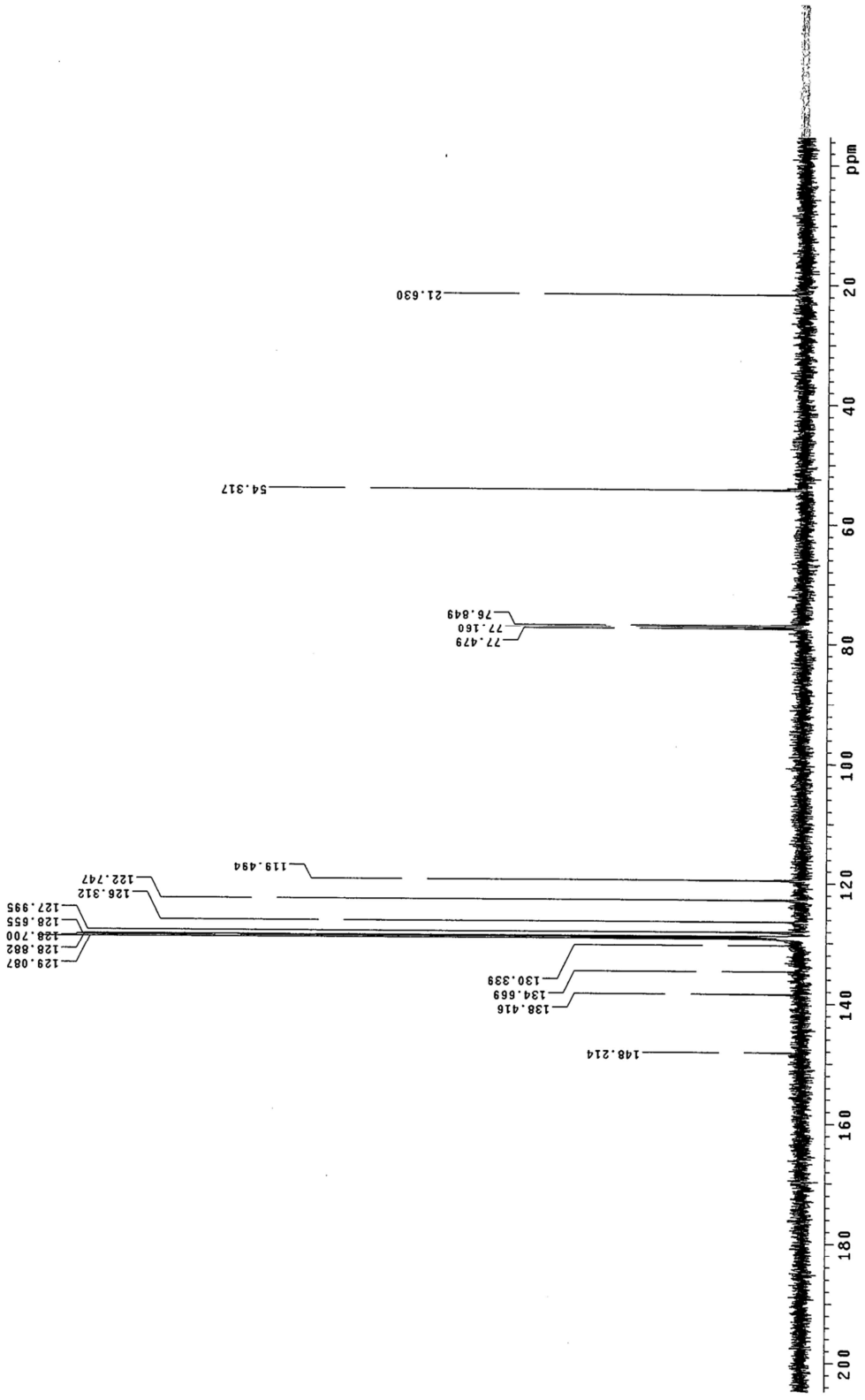
1-benzyl-4-m-tolyl-1H-1,2,3-triazole (Figure 1, 5d). The representative procedure was followed to yield **5d** (105.7 mg, 85%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.65 (s, 1H), 7.57 (d, J = 8.0*Hz,* 1H), 7.41 - 7.28 (m, 6H), 7.13 (d, J = 3.6*Hz*, 1H), 5.56 (s, 2H), 2.38 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 138.4, 134.7, 130.3, 129.1, 128.9, 128.7 (2C), 128.0, 126.3, 122.7, 119.5, 54.3, 21.6 ppm; IR (neat) 3137, 2354, 1644, 1591, 1219 cm^{-1}; HRMS (EI+) cacld for $C_{16}H_{15}N_3$ (M^+) 249.1266, found 249.1267.

^{1}H NMR (400 MHz) at 25 °C



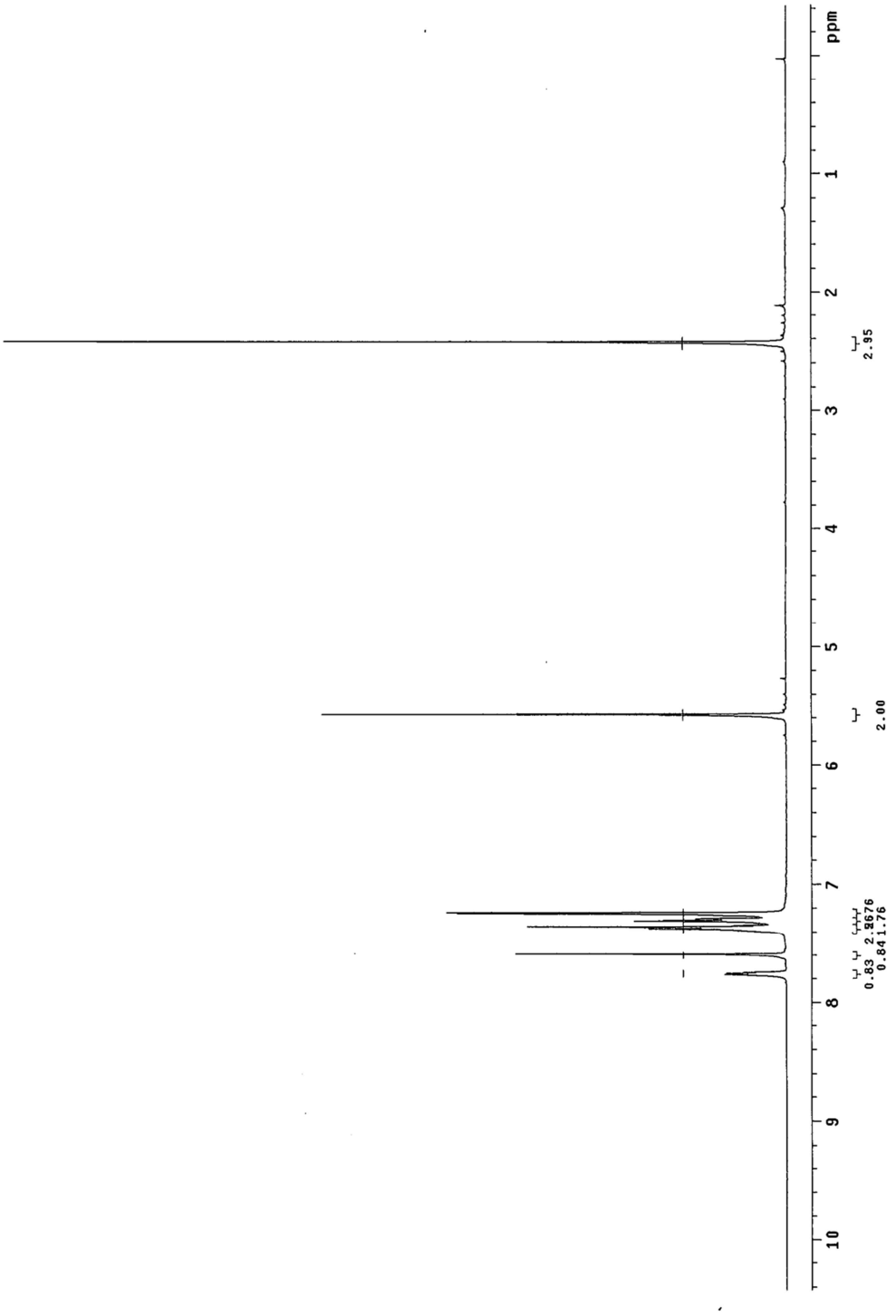
^{13}C NMR (100 MHz) at 25 °C



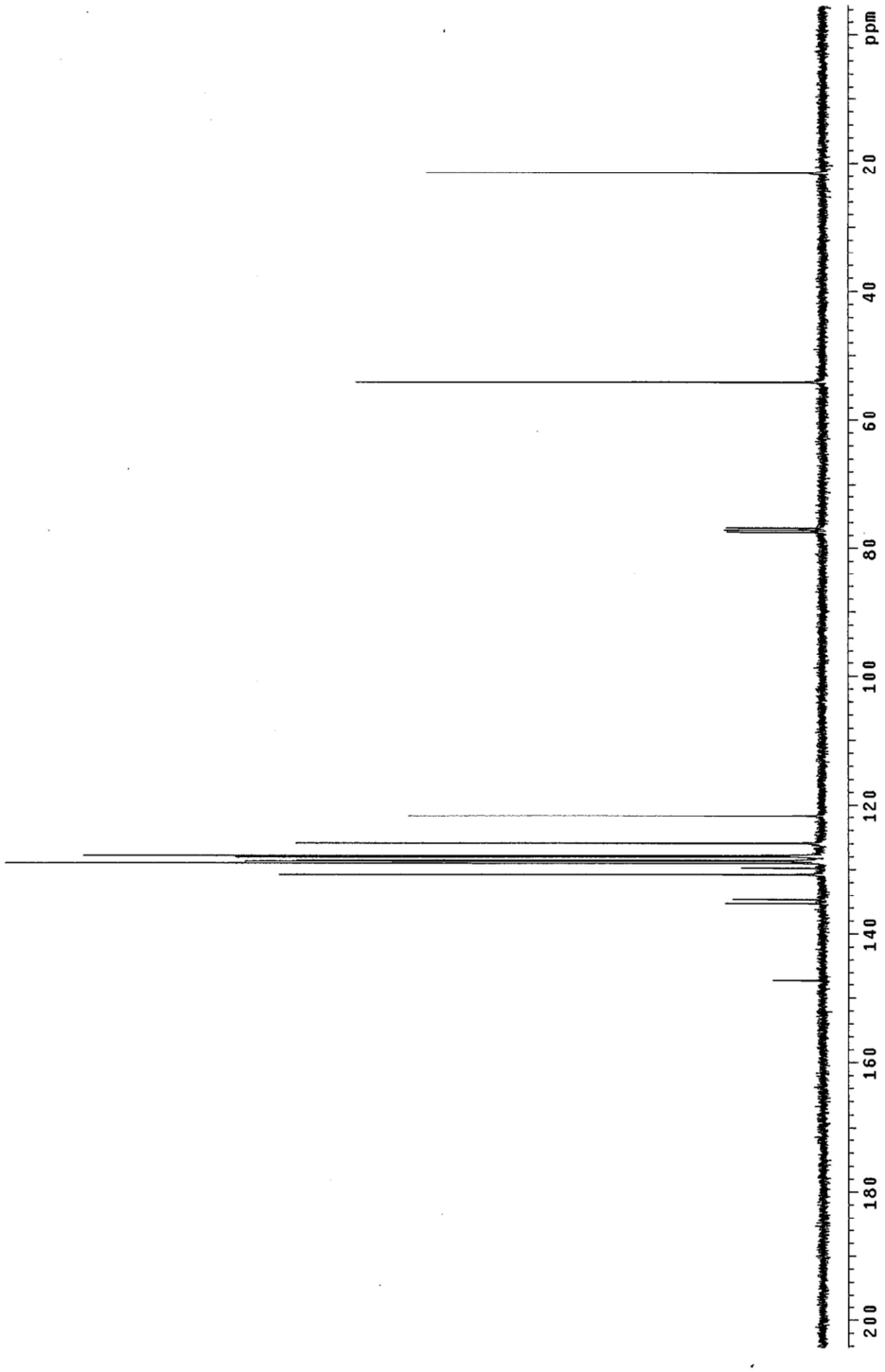

21.630
54.317
76.849
77.160
77.479
119.494
122.747
126.312
127.995
128.655
128.700
128.862
129.087
130.339
134.669
138.416
148.214
ppm
20
40
60
80
100
120
140
160
180
200

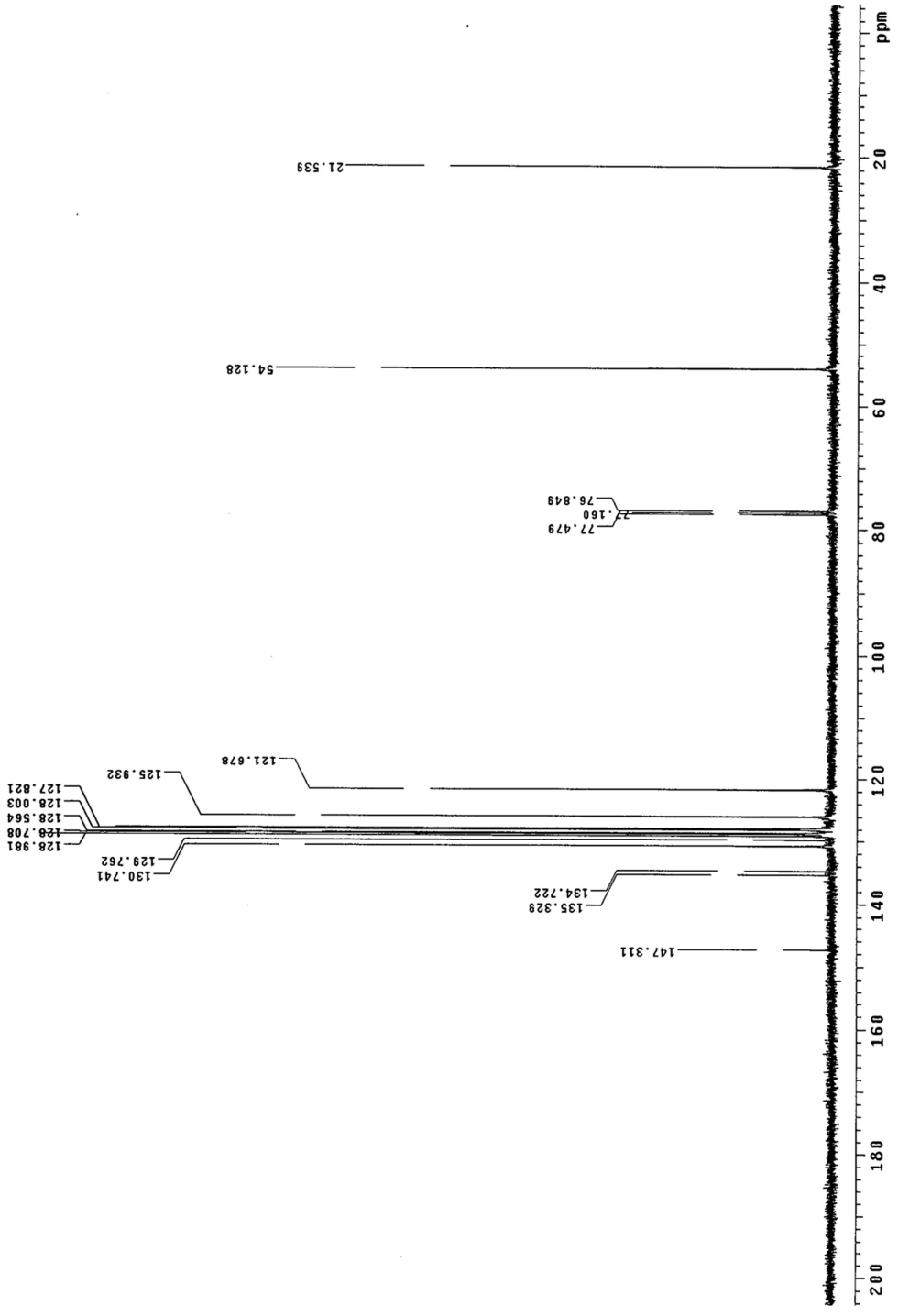
1-benzyl-4-o-tolyl-1H-1,2,3-triazole (Figure 1, 6d). The representative procedure was followed to yield **6d** (97.6mg, 78%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (m, 1H), 7.60 (s, 1H), 7.37 (m, 3H), 7.29 (m, 2H), 7.26 (m, 3H), 5.57 (s, 2H), 2.43 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.3, 135.3, 134.7, 130.7, 129.8, 129.0, 128.7, 128.6, 128.0, 127.8, 125.9, 121.7, 54.1, 21.5 ppm; IR (neat) 3154, 2360, 1606, 1487, 1229 cm^{-1}; HRMS (EI+) cacld for $C_{16}H_{15}N_3$ (M^+) 249.1266, found 249.1268.

^{1}H NMR (400 MHz) at 25 °C



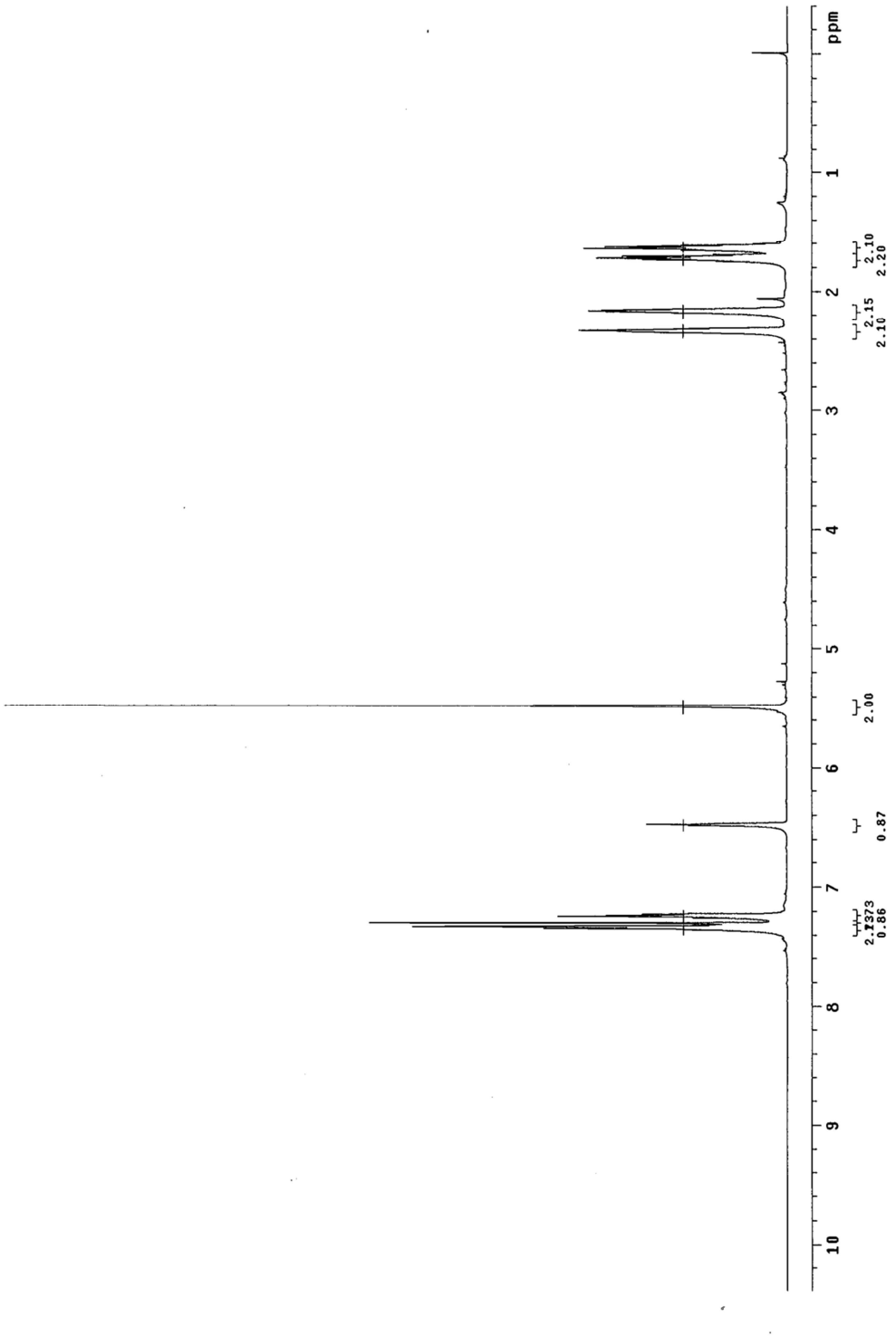
^{13}C NMR (100 MHz) at 25 °C



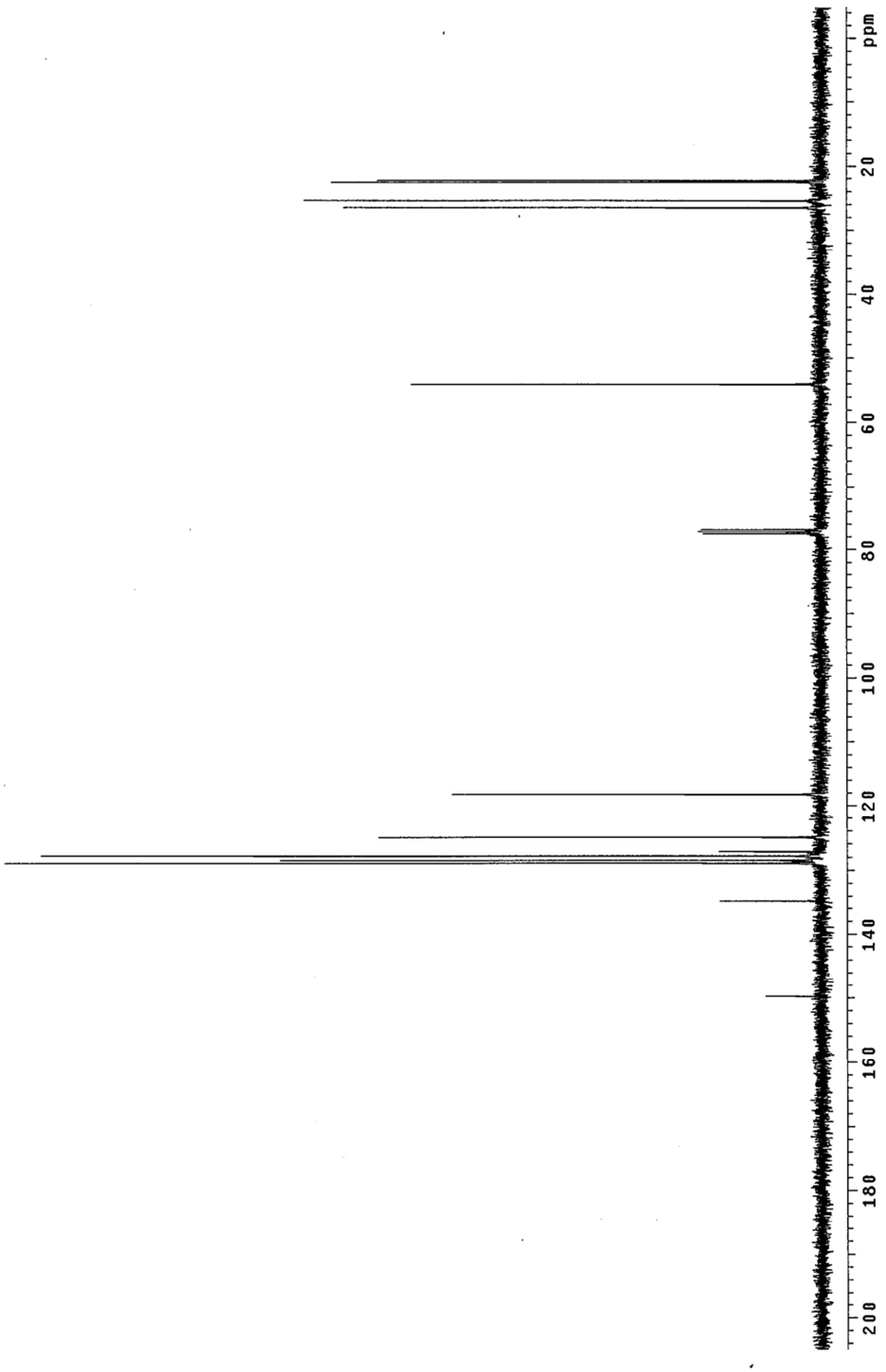

147.311
135.329
134.722
130.741
129.762
128.981
128.708
128.564
128.003
127.821
125.932
121.678
77.479
77.160
76.849
54.128
21.539
ppm

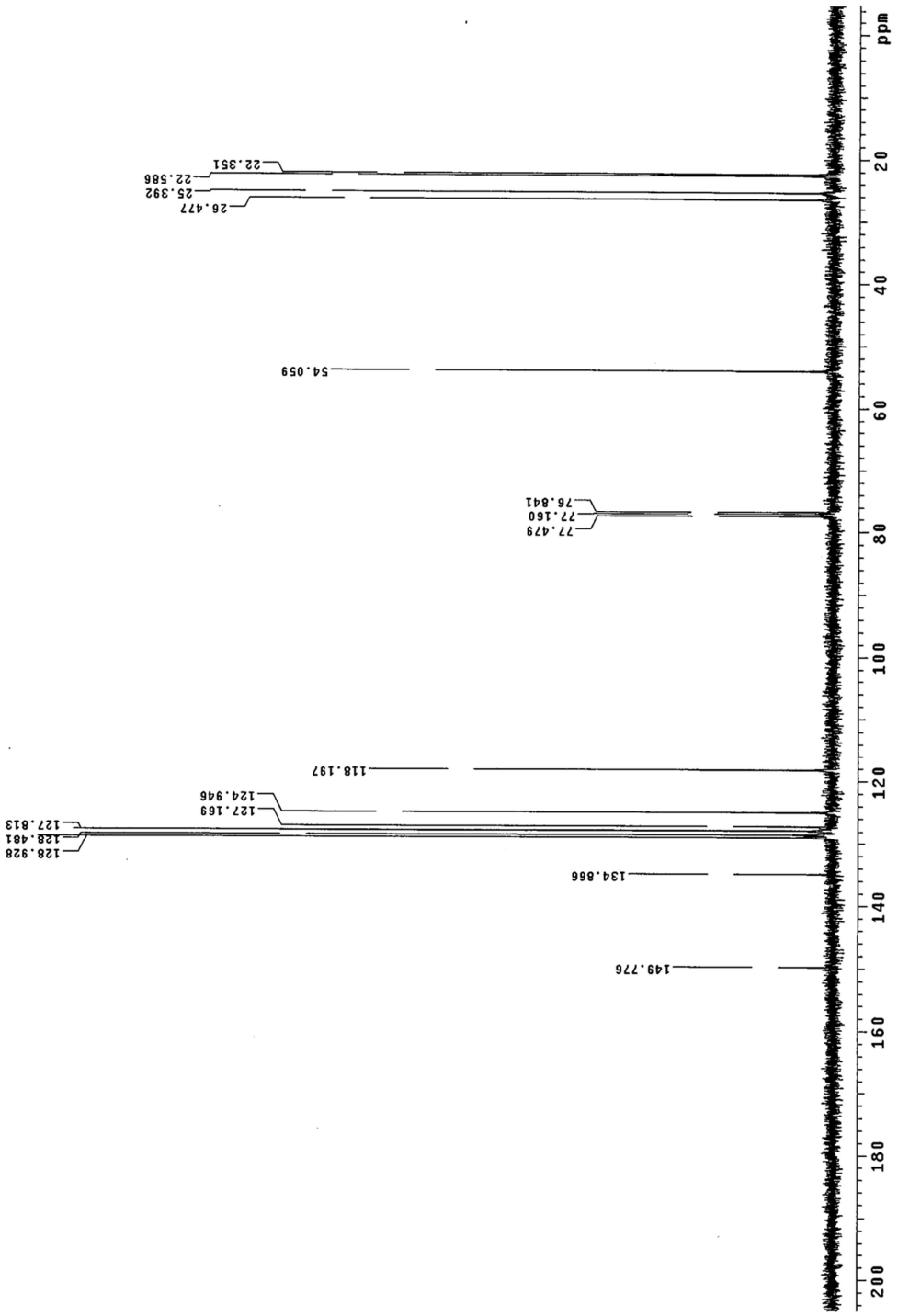
1-benzyl-4-cyclohexenyl-1H-1,2,3-triazole (Figure 1, 7d). The representative procedure was followed to yield **7d** (68.1 mg, 57%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (m, 3H), 7.30 (s, 1H), 7.24 (m, 2H), 6.48 (m, 1H), 5.48 (s, 2H), 2.33 (m, 2H), 2.16 (m, 2H), 1.72 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 134.9, 128.9, 128.5, 127.8, 127.2, 124.9, 118.2, 54.1, 26.5, 25.4, 22.6, 22.4 ppm; IR (neat) 3120, 2360, 1625, 1540, 1258 cm^{-1}; HRMS (EI+) cacld for $C_{15}H_{17}N_3$ (M^+) 239.1422, found 239.1423.

^{1}H NMR (400 MHz) at 25 °C



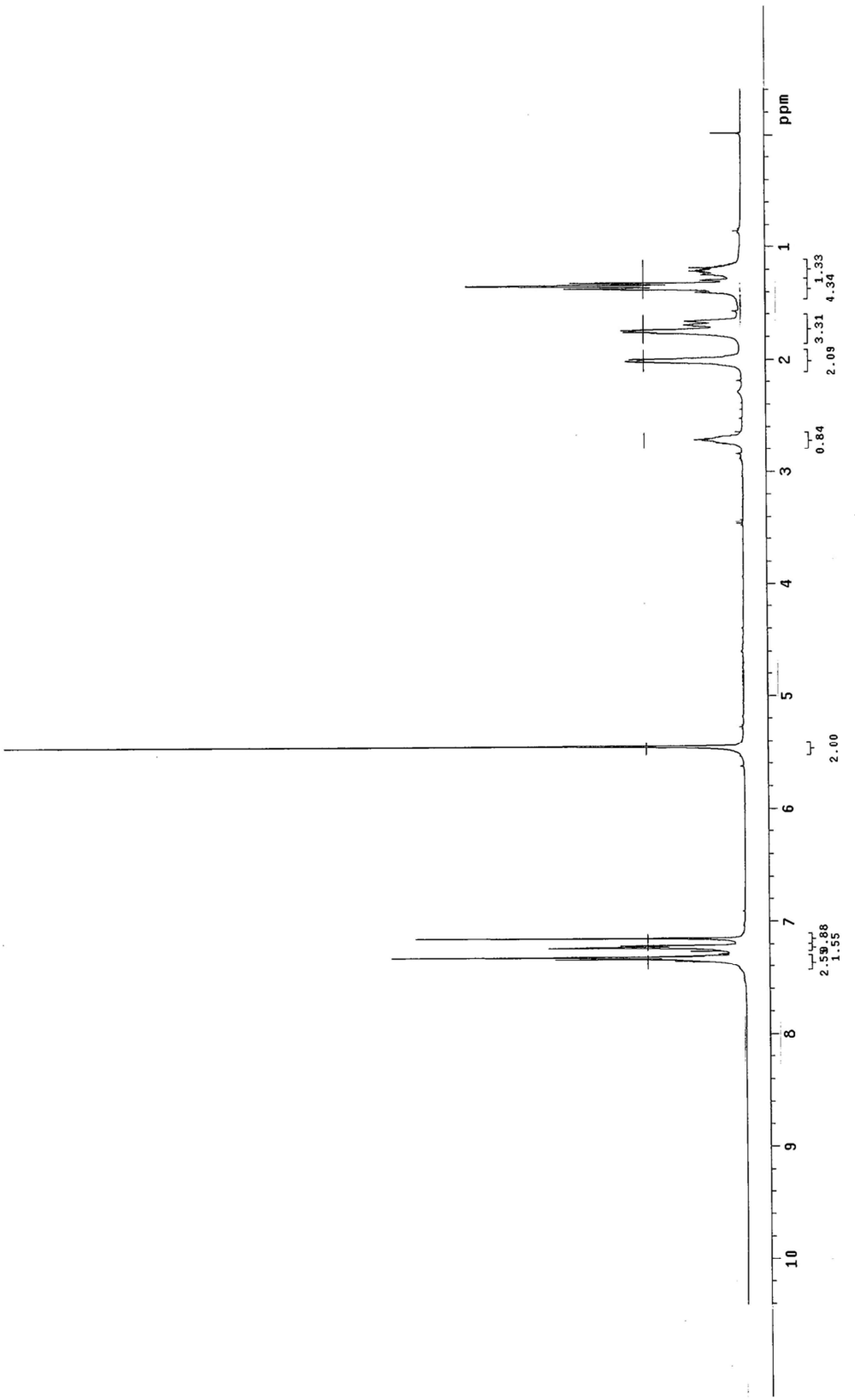
^{13}C NMR (100 MHz) at 25 °C



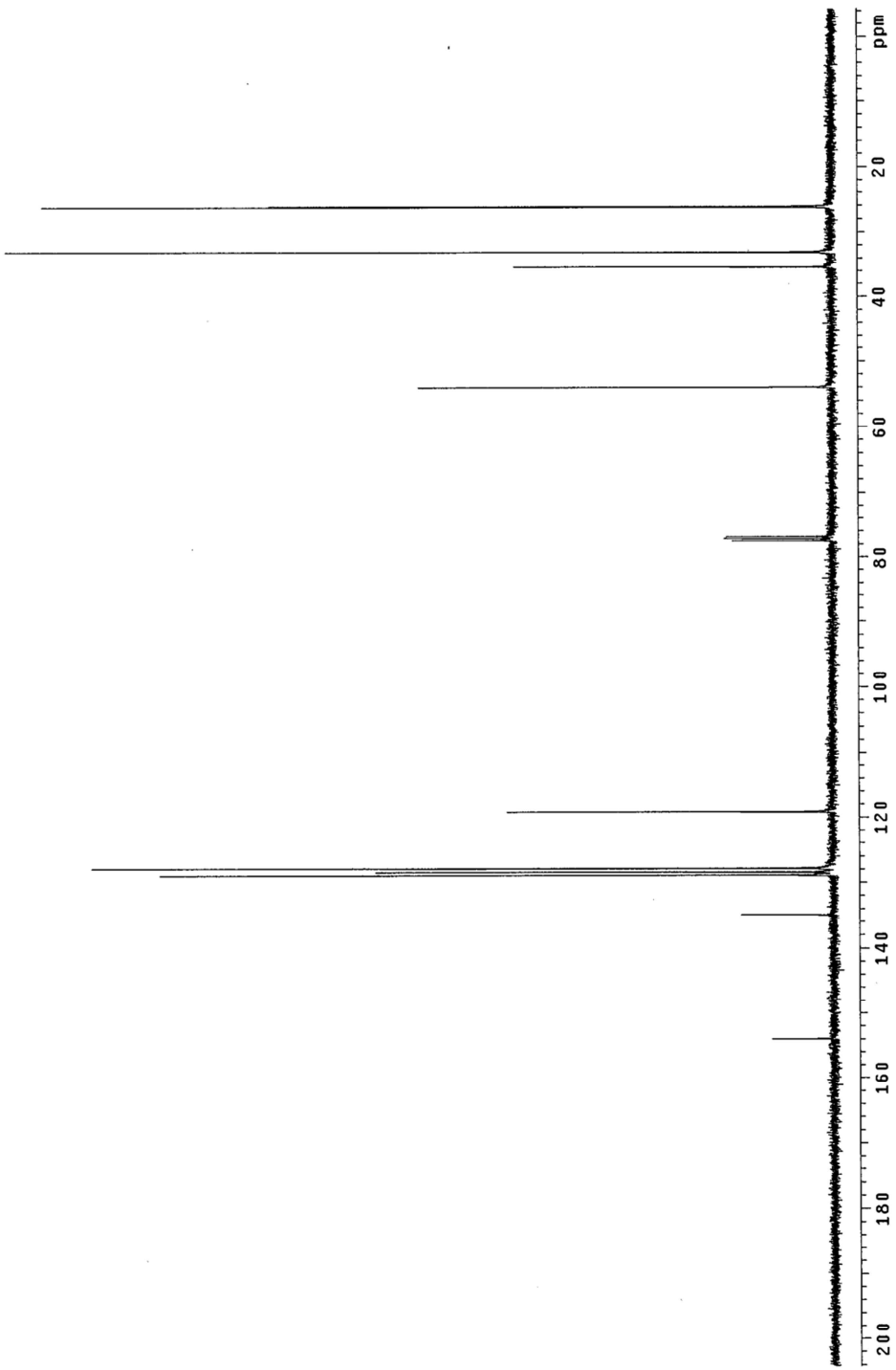

22.351
22.586
25.392
26.477
54.059
76.841
77.160
77.479
118.197
124.946
127.169
127.813
128.481
128.928
134.866
149.776
ppm
20
40
60
80
100
120
140
160
180
200

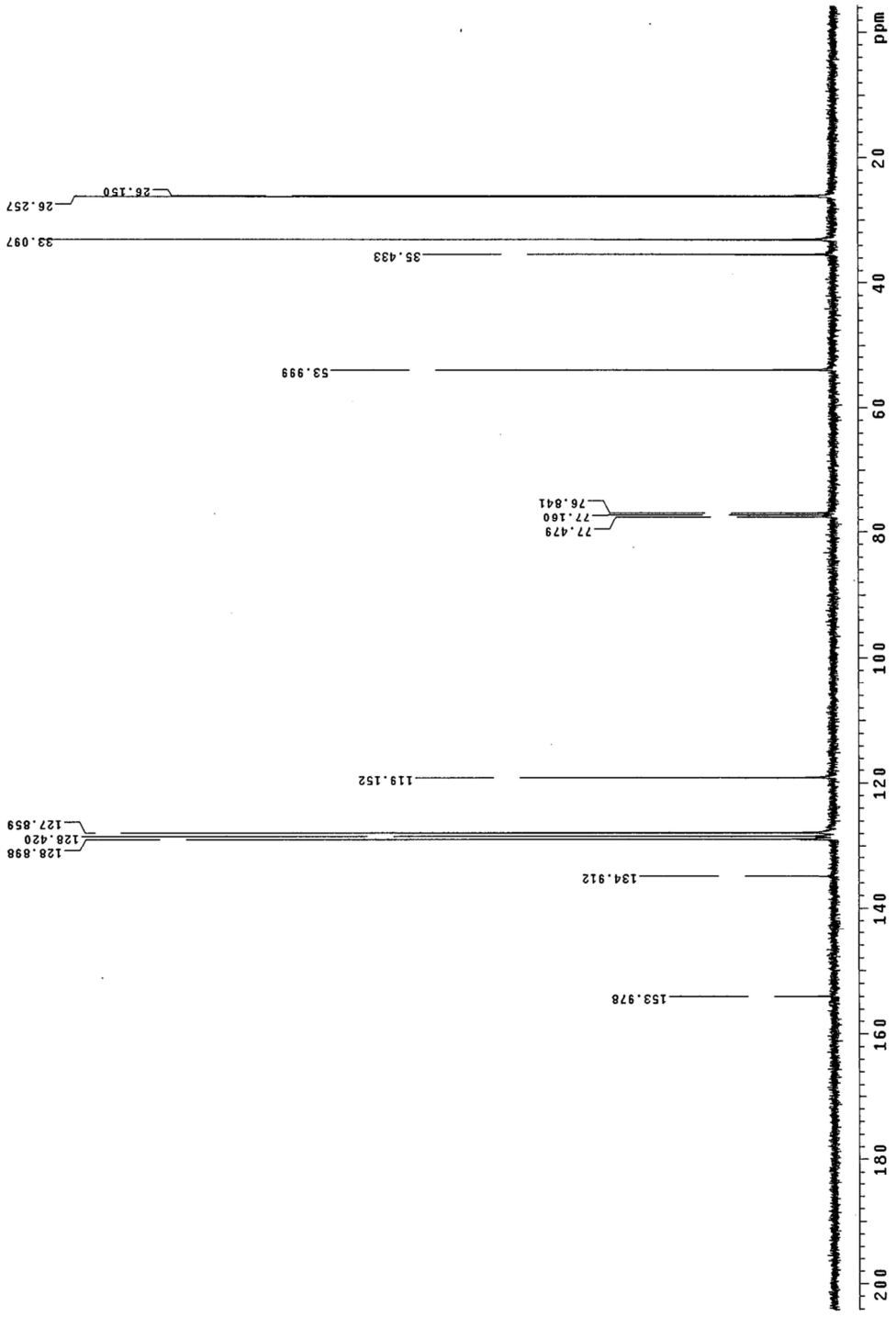
1-benzyl-4-cyclohexyl-1H-1,2,3-triazole (Figure 1, 8d). The representative procedure was followed to yield **8d** (99.3 mg, 82%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (m, 3H), 7.23 (m, 2H), 7.15 (s, 1H), 5.45 (s, 2H), 2.72 (m, 1H), 2.01 (m, 2H), 1.71 (m, 3H), 1.35 (m, 4H), 1.21 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0, 134.9, 128.9, 128.4, 127.9, 119.2, 54.0, 35.4, 33.1, 26.3, 26.2 ppm; IR (neat) 3107, 2354, 1632, 1453, 1211 cm^{-1}; HRMS (EI+) cacld for $C_{15}H_{19}N_3$ (M^+) 241.1579, found 241.1579.

^{1}H NMR (400 MHz) at 25 °C



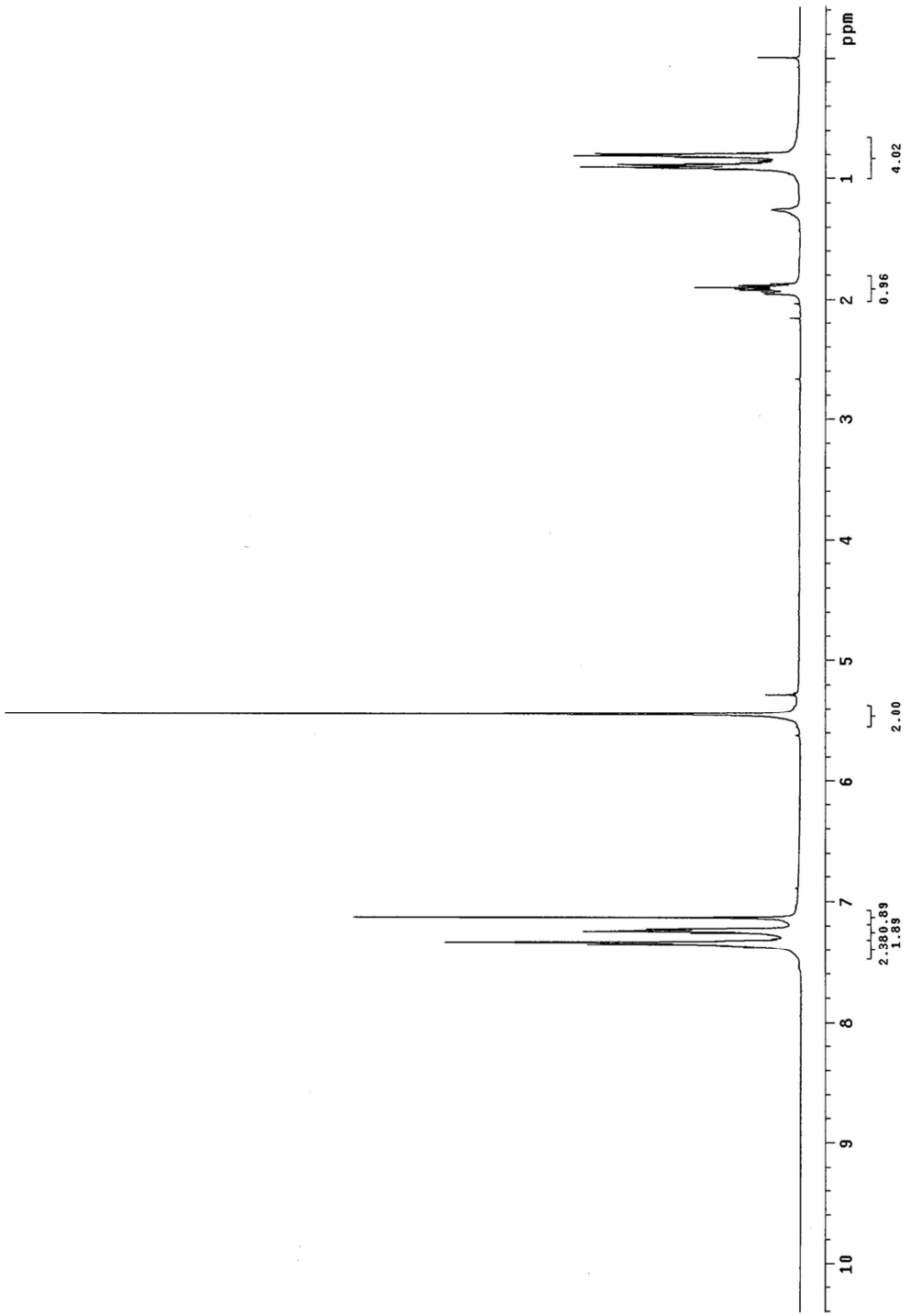
^{13}C NMR (100 MHz) at 25 °C



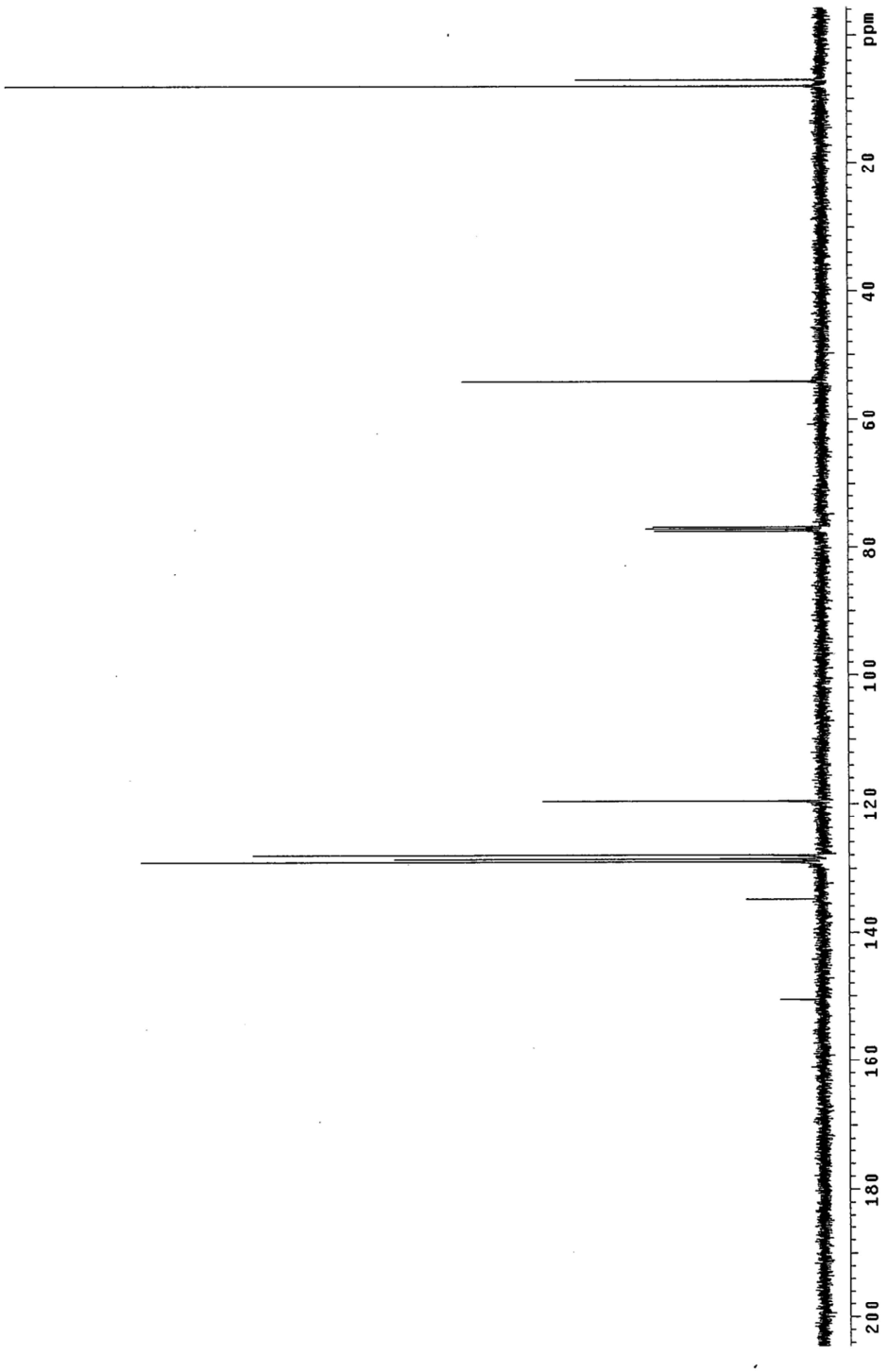

153.978
134.912
128.898
128.420
127.859
119.152
76.841
77.160
77.479
53.999
35.433
33.097
26.257
26.150
ppm
200
180
160
140
120
100
80
60
40
20

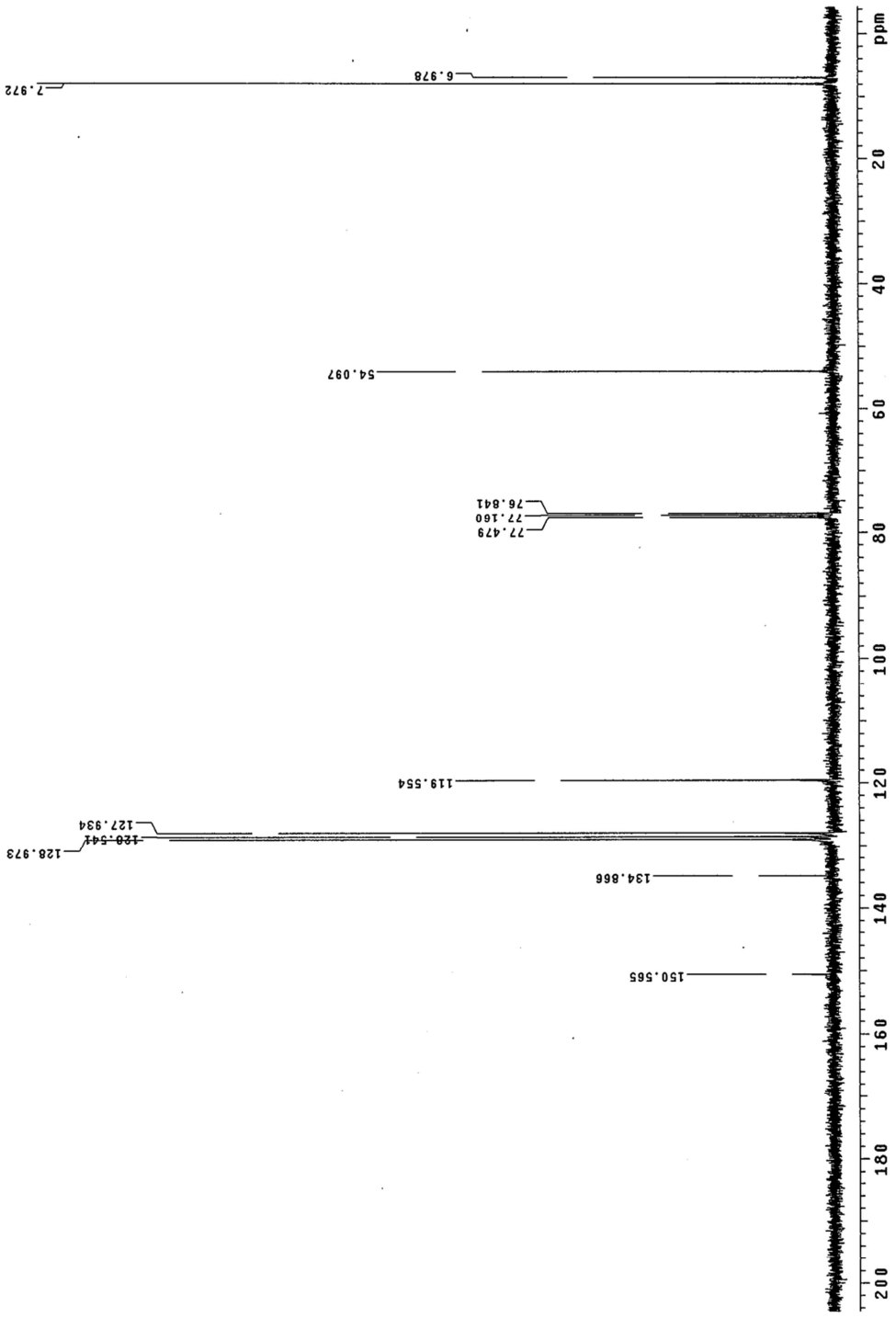
1-benzyl-4-cyclopropyl-1H-1,2,3-triazole (Figure 1, 9d). The representative procedure was followed to yield **9d** (51.5 mg, 52%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (m, 3H), 7.27 (m, 2H), 7.13 (s, 1H), 5.45 (s, 2H), 1.91 (m, 1H), 0.87 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 134.9, 129.0, 128.5, 128.0, 119.6, 54.1, 8.0, 7.0 ppm; IR (neat) 3072, 2250, 1562, 1497, 1218 cm^{-1}; HRMS (FAB+) cacld for $C_{12}H_{13}N_3$ $(M+H)^+$ 200.1188, found 200.1190.

^{1}H NMR (400 MHz) at 25 °C



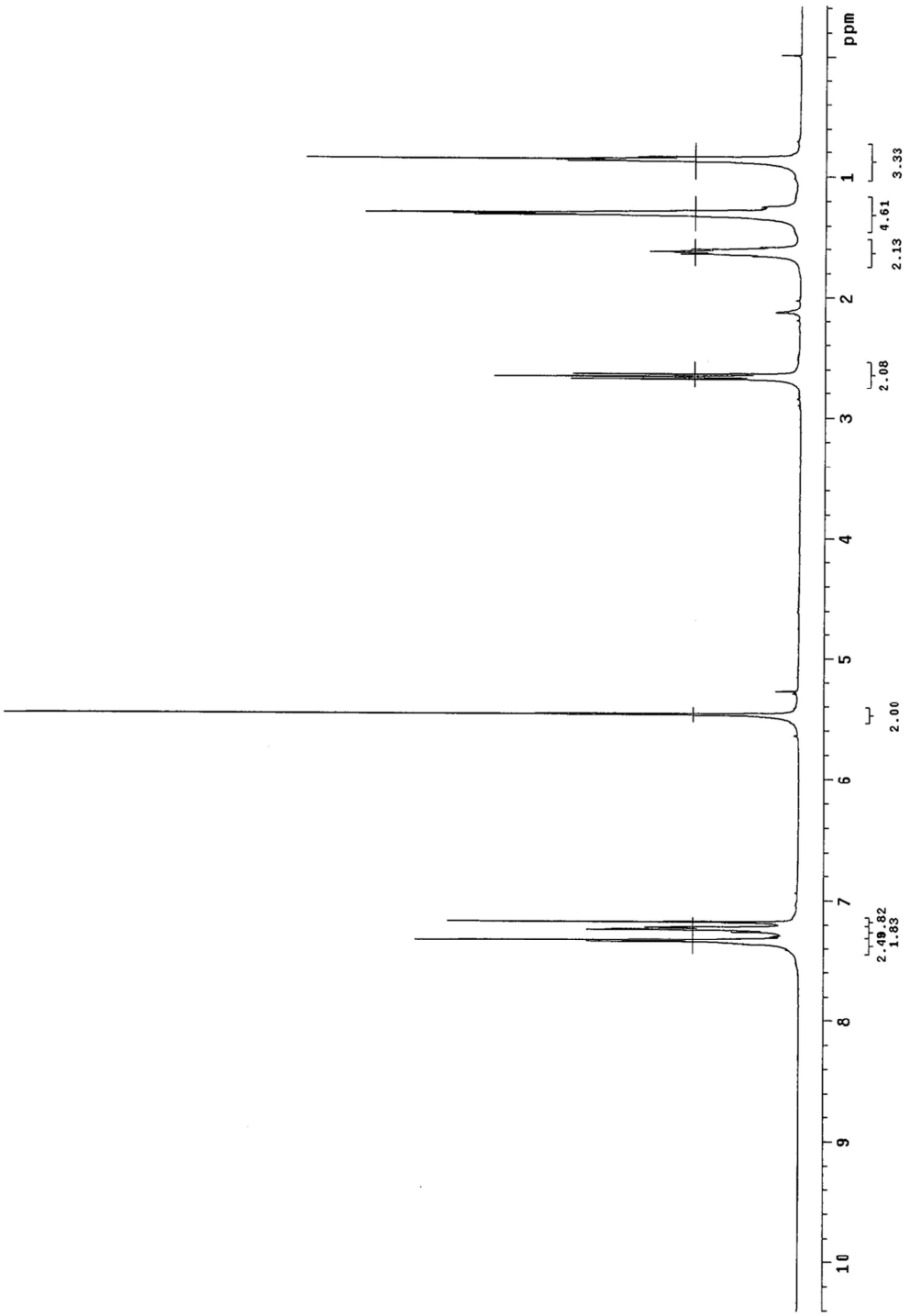
^{13}C NMR (100 MHz) at 25 °C



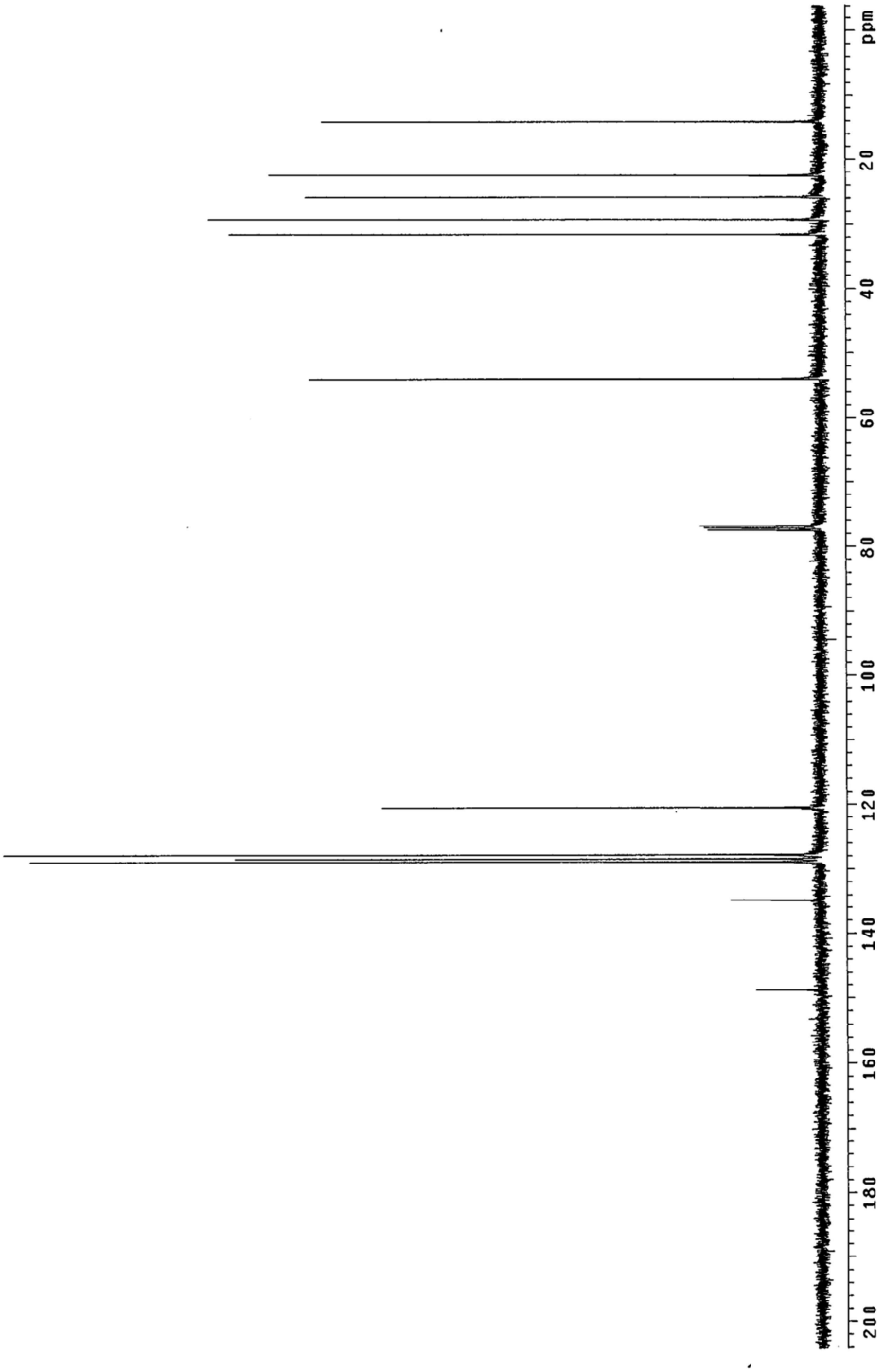

7.972
6.978
54.097
77.479
77.160
76.841
119.554
128.973
127.934
134.866
150.565
200
180
160
140
120
100
80
60
40
20
ppm

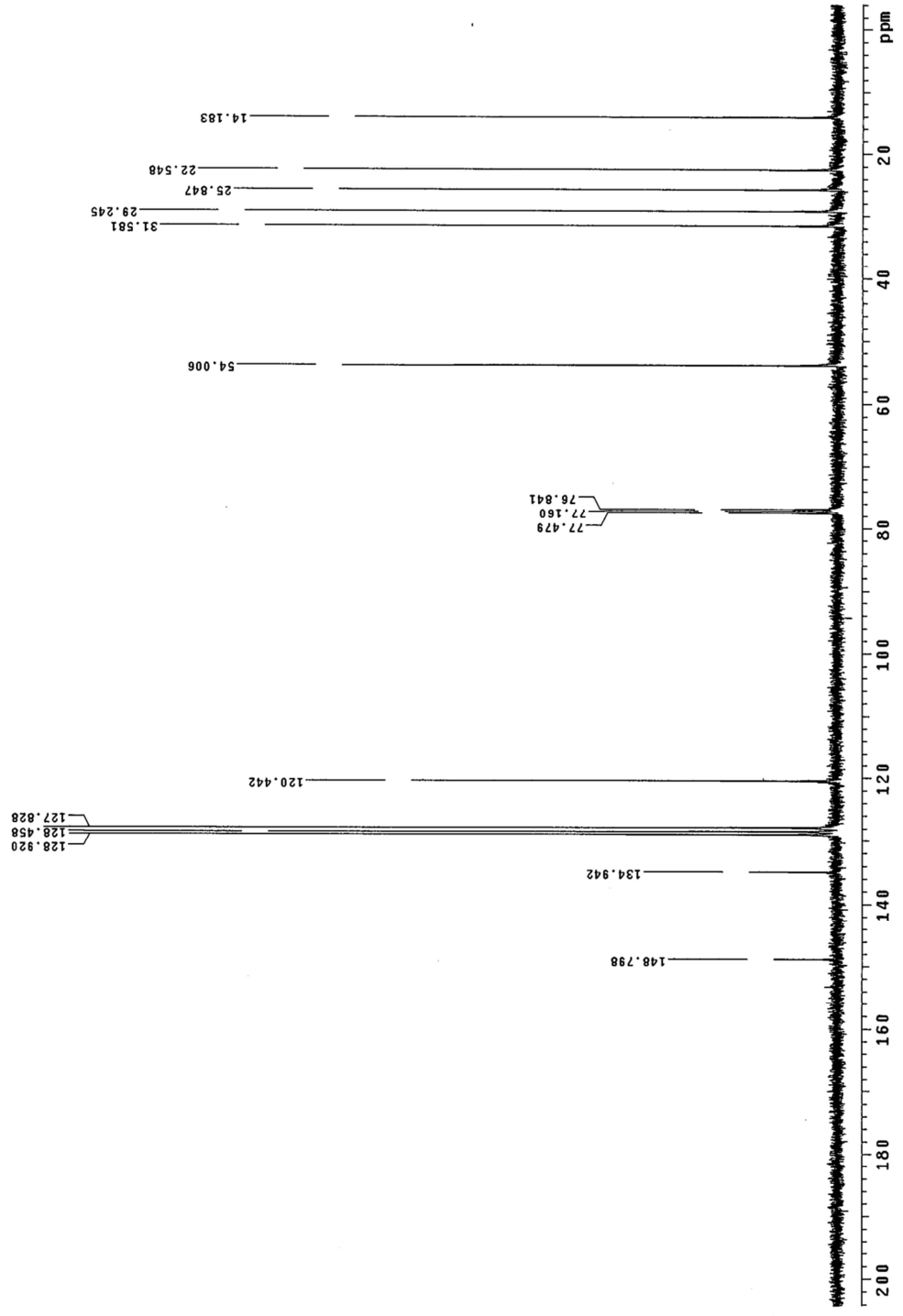
1-benzyl-4-pentyl-1H-1,2,3-triazole (Figure 1, 10d). The representative procedure was followed to yield **10d** (81.5 mg, 71%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (m, 3H), 7.25 (m, 2H), 7.17 (s, 1H), 5.47 (s, 2H), 2.66 (t, J = 7.6 *Hz,* 2H), 1.63 (m, 2H), 1.28 (m, 4H), 0.86 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 134.9, 128.9, 128.5, 127.8, 120.4, 54.0, 31.6, 29.2, 25.8, 22.5, 14.2 ppm; IR (neat) 3065, 2350, 1643, 1456, 1213 cm^{-1}; HRMS (FAB+) cacld for $C_{14}H_{19}N_3$ $(M+H)^+$ 230.1657, found 230.1658.

^{1}H NMR (400 MHz) at 25 °C



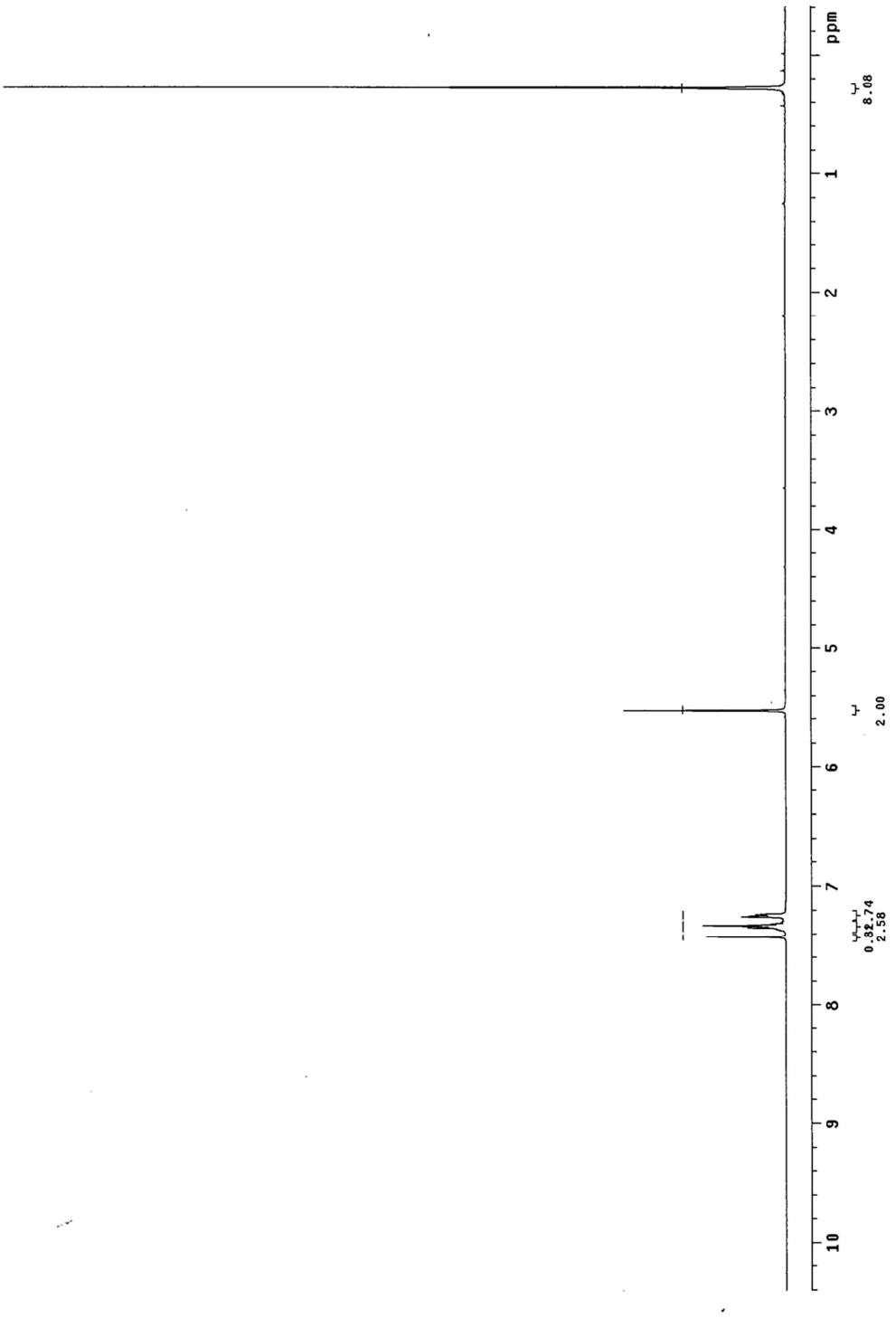
^{13}C NMR (100 MHz) at 25 °C



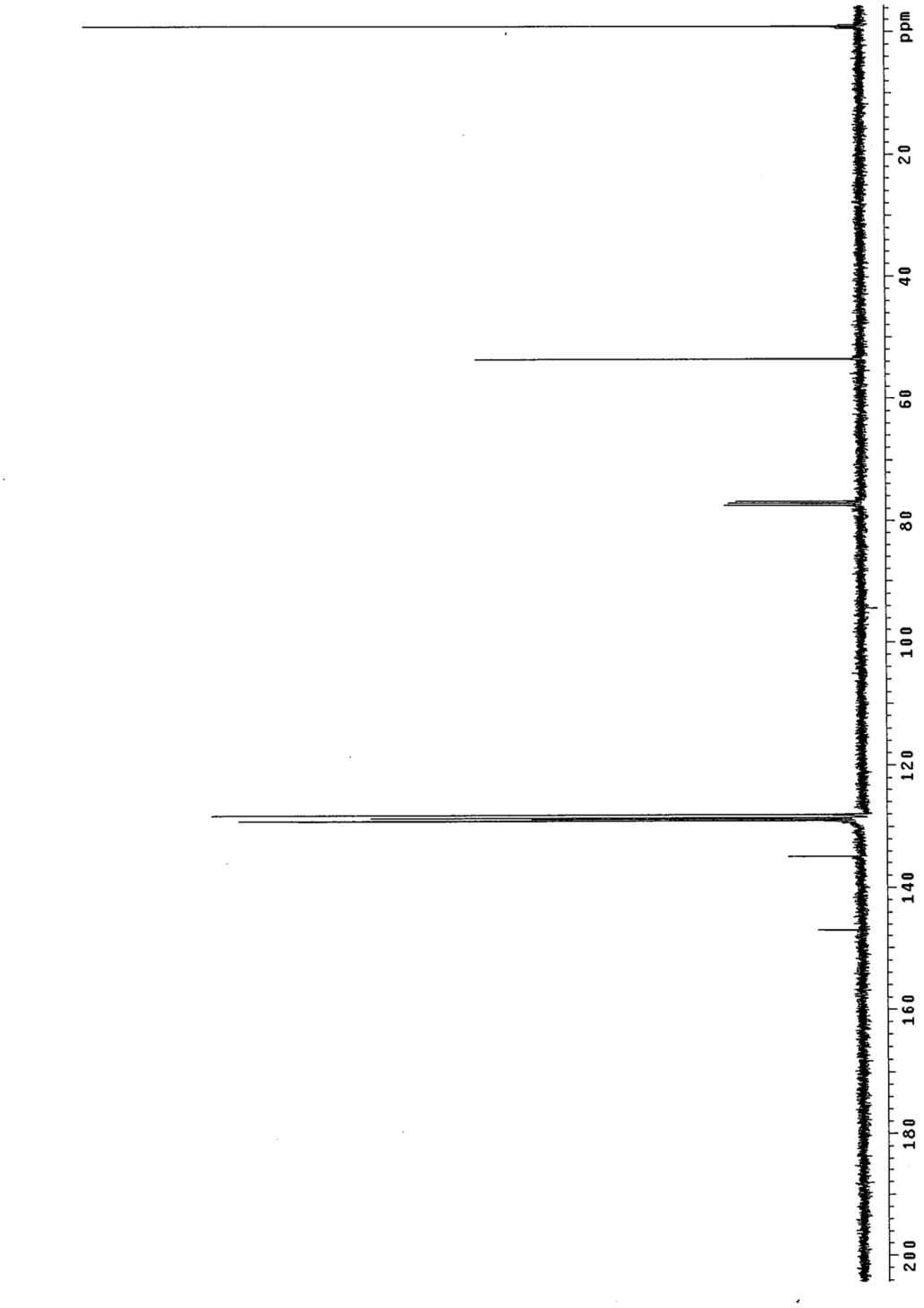

14.183
22.548
25.847
29.245
31.581
54.006
76.841
77.160
77.479
120.442
127.828
128.458
128.820
134.942
148.798
ppm
20
40
60
80
100
120
140
160
180
200

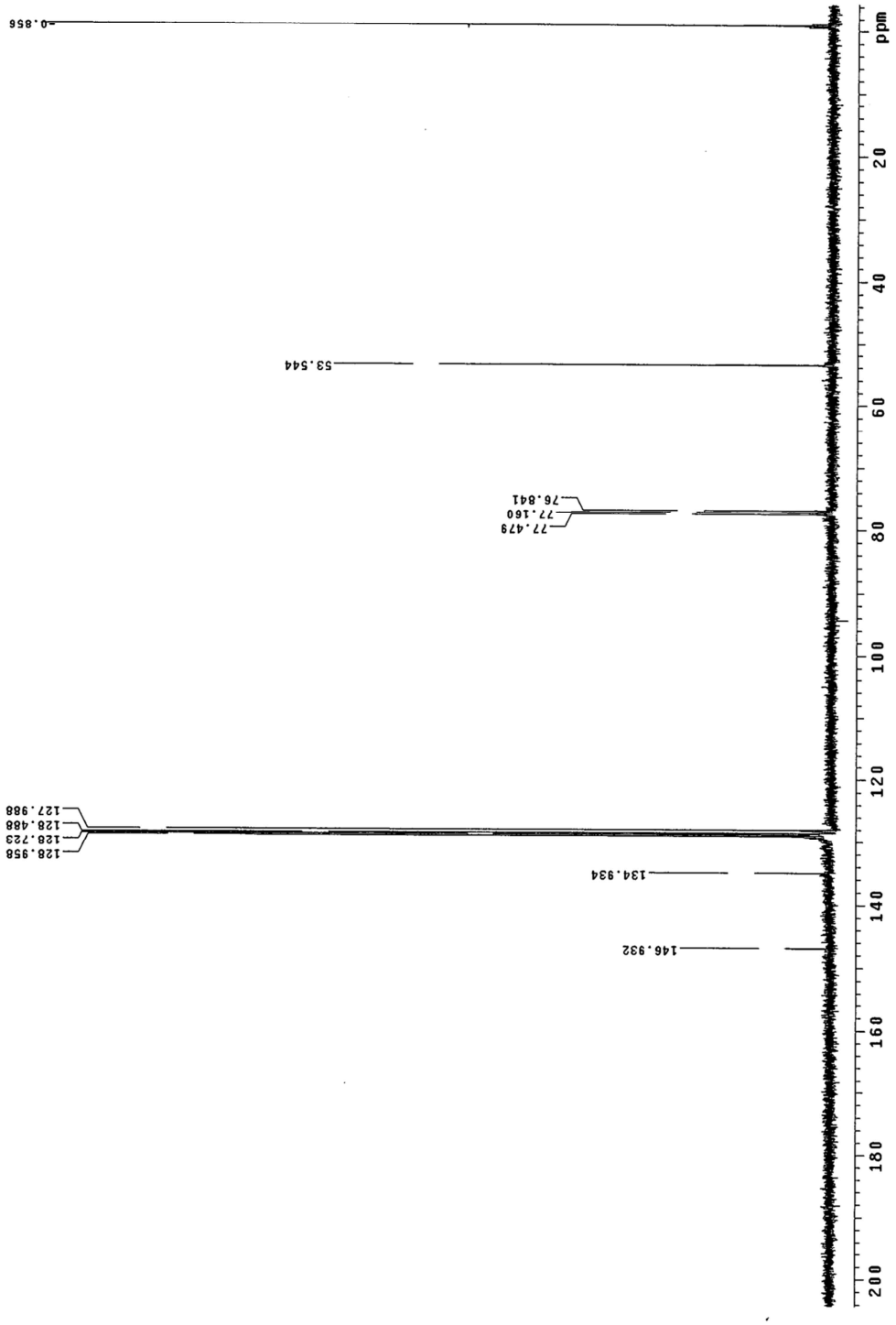
1-benzyl-4-(trimethylsilyl)-1H-1,2,3-triazole (Figure 1, 11d). The representative procedure was followed to yield **11d** (93.4 mg, 81%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.34 (m, 3H), 7.25 (m, 2H), 5.53 (s, 2H), 0.28 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9, 134.9, 129.0, 128.7, 128.5, 128.0, 53.5, -0.9 ppm; IR (neat) 3106, 2360, 1679, 1449, 1248 cm^{-1}; HRMS (EI+) cacld for $C_{12}H_{17}N_3S_1$ (M^+) 231.1192, found 231.1193.

^{1}H NMR (400 MHz) at 25 °C



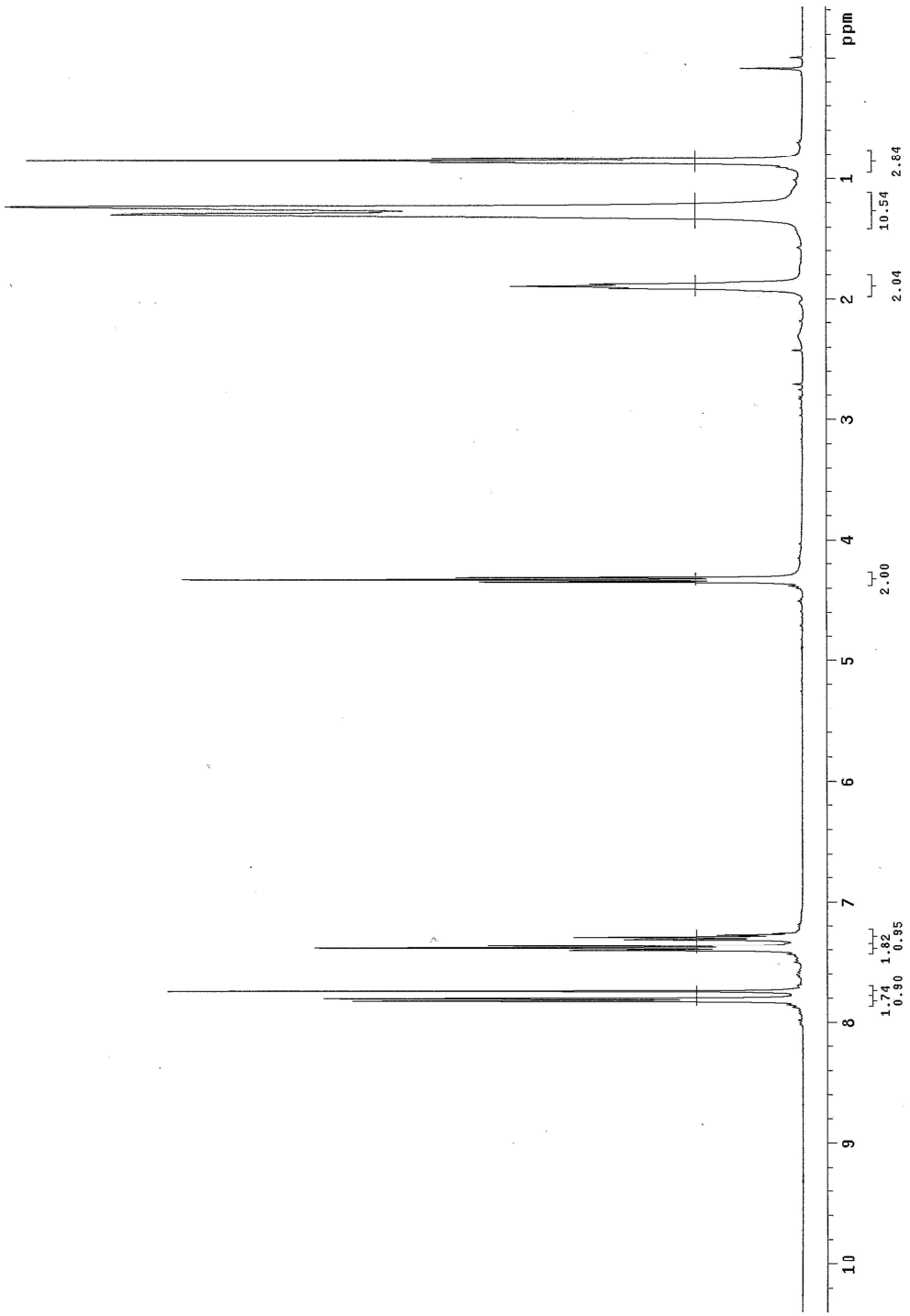
^{13}C NMR (100 MHz) at 25 °C



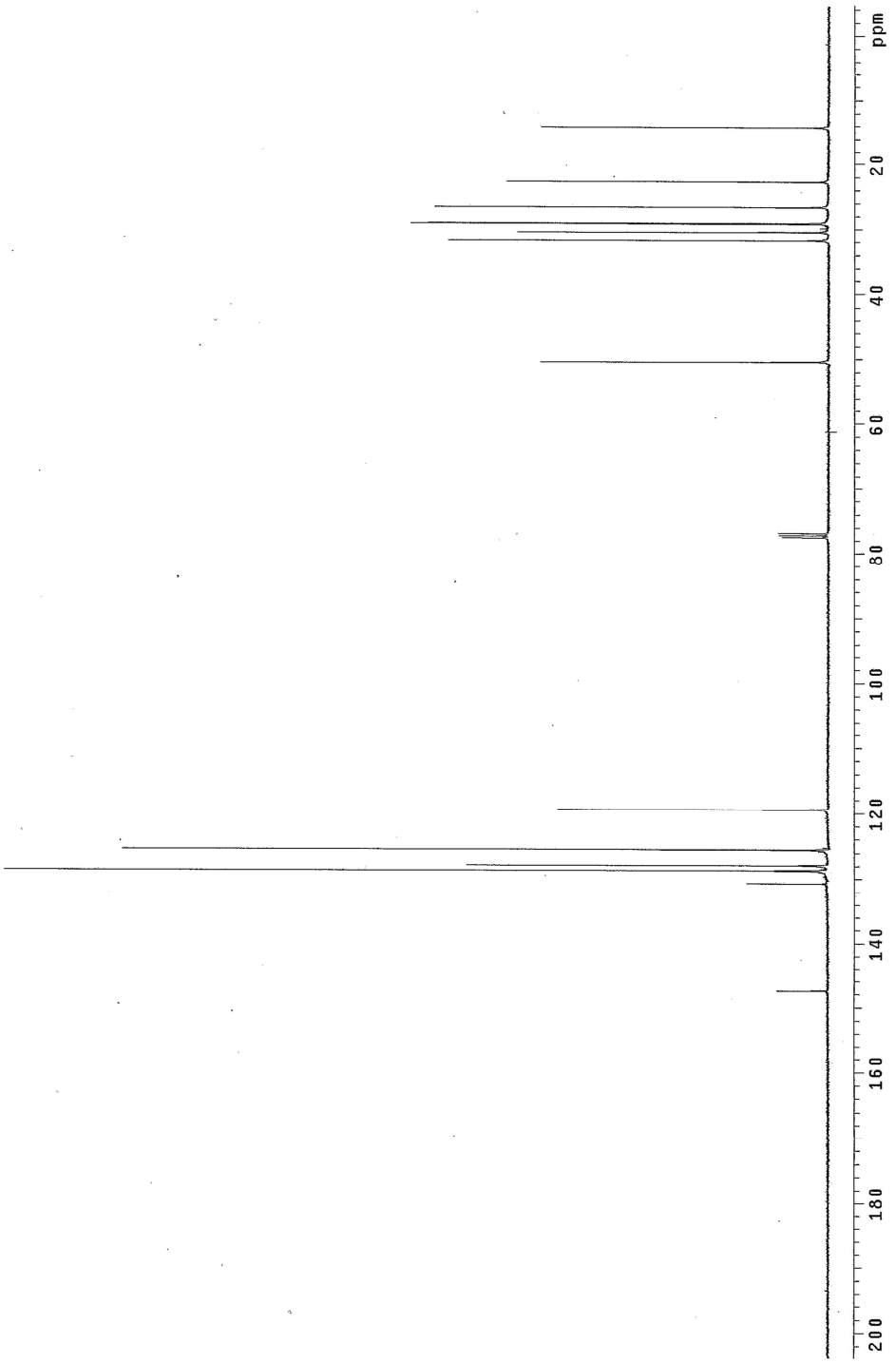

0.856
53.544
77.479
77.160
76.841
128.958
128.723
128.486
127.988
134.934
146.932
ppm
200
180
160
140
120
100
80
60
40
20

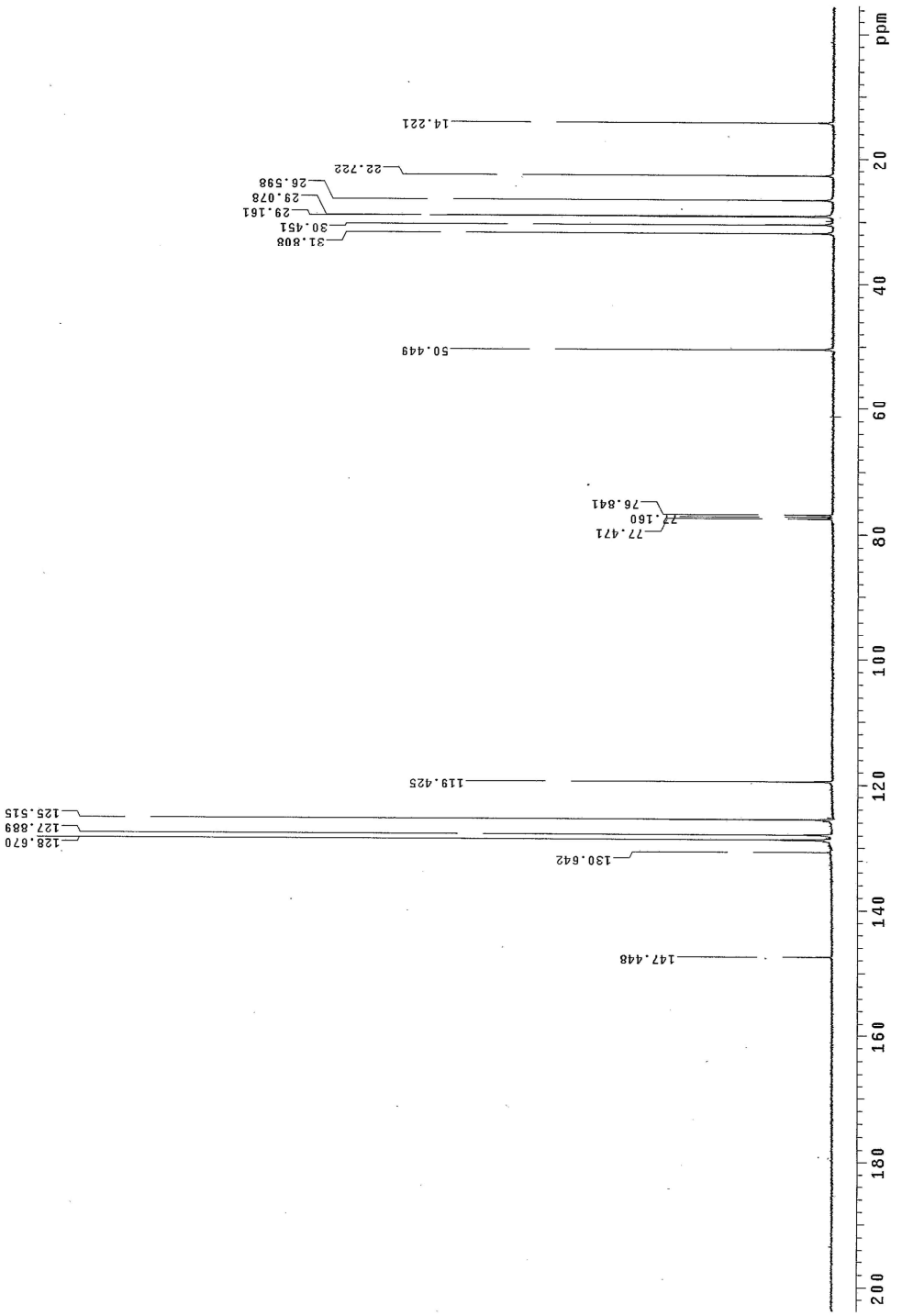
*1-octyl-4-phenyl-1H-1,2,3-triazole (**12d**)*. The general procedure was followed to yield **12d** (120.3 mg, 93 %); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, 2H, J = 8.4 Hz), 7.74 (s, 1H), 7.39 (t, 2H, J = 7.6 Hz), 7.29 (t, 1H, J = 7.6 Hz), 4.33 (t, 2H, J = 7.2 Hz), 1.89 (m, 2H), 1.27 (m, 10H), 0.86 (t, 3H, J = 5.6 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.4, 130.6, 128.7, 127.9, 125.5, 119.4, 50.4, 31.8, 30.5, 29.2, 29.1, 26.6, 22.7, 14.2 ppm; IR (neat) 3392, 2955, 1635, 1217 cm^{-1}; HRMS (EI+) calcd for $C_{16}H_{23}N_3$(M^+) 257.1892, found 257.1889.

^{1}H NMR (400 MHz) at 25 °C



^{13}C NMR (100 MHz) at 25 °C




147.448
130.642
128.670
127.889
125.515
119.425
77.471
77.160
76.841
50.449
31.808
30.451
29.161
29.078
26.598
22.722
14.221
ppm