Supporting Information

Silver-promoted cinnamamidyl radicals-mediated oxidative cascade cyclization: Highly regioselective synthesis of phosphorylated azaspiro[4.5]decenones

Zhao-Zhao Zhou,[a] Lan Zheng,[a] Xiao-Biao Yan,[a] Dong-Po Jin,[a] Yu-Tao He[a] and Yong-Min Liang*[ab]

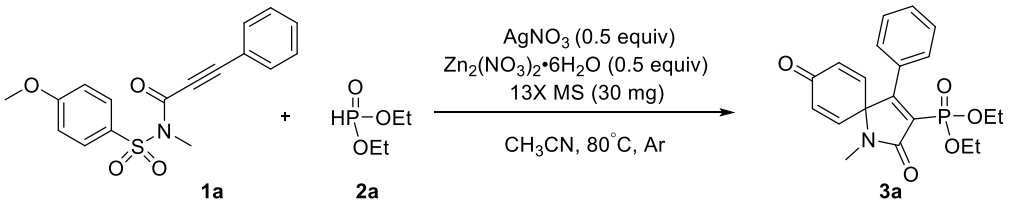
[a] *State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, P.R. China*
[b] *State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Science, Lanzhou, 730000, P.R. China*
Corresponding author: Tel.: +86 931 8912593; Fax: +86 931 8912582;
E-mail: liangym@lzu.edu.cn

Table of Contents

1. General Remarks:

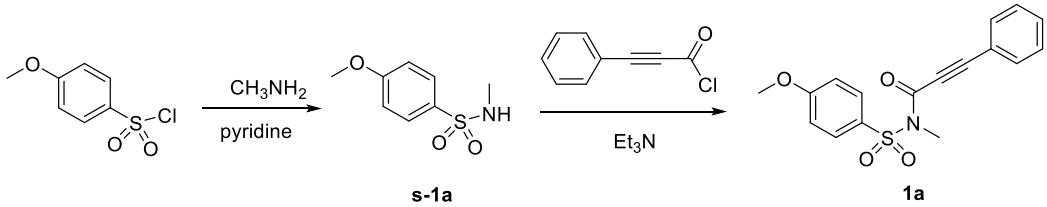
For product purification by flash column chromatography, silica gel (200~300 mesh) and *n*-hexane were used. ^{1}H NMR spectra were recorded at 400 MHz in $CDCl_3$, ^{13}C NMR spectra were recorded at 100 MHz in $CDCl_3$ and ^{31}P NMR spectra were recorded at 162 MHz in $CDCl_3$ using TMS as an internal standard. IR spectra were recorded on an FT-IR spectrometer and only major peaks were reported in cm^{-1}. Melting points were determined on a microscopic apparatus and were uncorrected. All products were further characterized by HRMS (high resolution mass spectra). Copies of the ^{1}H NMR and ^{13}C NMR spectra are provided. The starting materials, purchased from Aldrich, Alfa Aesar, Acros Organics, J&K Chemicals or TCI, were used without further purification. 4A Molecular Sieves (Acros Organics powder <50 micron). 5A Molecular Sieves (Alfa Aesar powder, 87955). 13X Molecular Sieves (Alfa Aesar powder, A10378).

2. General Procedure for the oxidative cascade cyclization:



In a tinfoil-covered Schlenk tube, *N*-((4-methoxyphenyl)sulfonyl)-*N*-methyl-3-phenylpropiolamide **1a** (0.2 mmol), diethyl phosphite **2a** (0.4 mmol), $AgNO_3$ (0.1 mmol), and $Zn(NO_3)_2 \cdot 6H_2O$ (0.1 mmol) were added and charged with Ar more than three times. Anhydrous CH_3CN (2 mL) was added and the mixture was allowed to stir at 80 °C for 24 h. When the reaction was considered complete, as determined by TLC analysis, the mixture was diluted with CH_2Cl_2 (15 mL) and transferred to a 25 mL round bottomed flask. The solvent was removed under vacuo, and the residue was purified with chromatography column on silica gel (*n*-hexane/ EtOAc = 2:1) to give the corresponding products **3a**.

3. Preparation of Starting Materials:



(a) For the synthesis of *4*-methoxy-*N*-methylbenzenesulfonamide **s-1a**: To a stirred solution of *4*-methoxybenzenesulfonyl chloride (1.03 g, 5 mmol) and pyridine (0.59 g, 7.5 mmol) in CH_2Cl_2 (20 mL) was added methanamine (0.17 g, 5.5 mmol) at 0 ºC. After 0.5 h, the reaction was reacted at r.t. for more than 16 h. CH_2Cl_2 was removed, and the reaction was quenched with saturated $CuSO_4$ solvent (30 mL*3) and extracted with EtOAc (30 mL). The organic layer was washed with water, brine, dried Na_2SO_4, and concentrated to furnish the corresponding sulfamide *4*-methoxy-*N*-

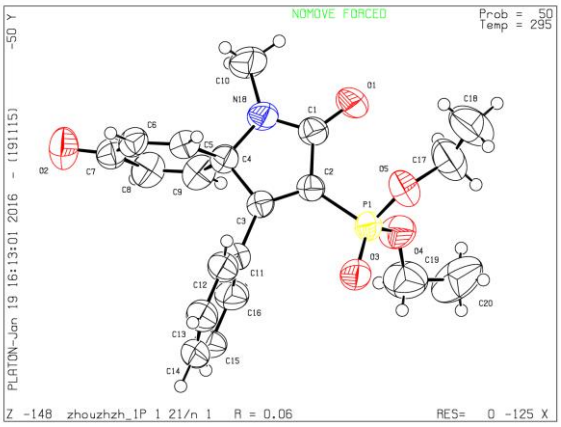
methylbenzenesulfonamide (0.95 g, 4.55 mmol) in 91% yield.

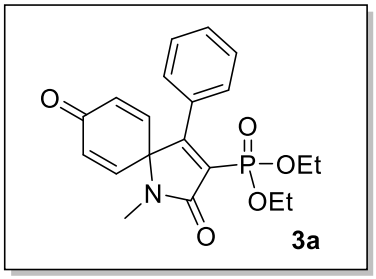
(a) For the synthesis of **1a:** To a stirred solution of *4*-methoxy-*N*-methylbenzenesulfonamide (1.01 g, 5 mmol) and Et_3N (1.26 g, 12.5 mmol) in CH_2Cl_2 (20 mL) was added *3*-phenylpropioloyl chloride (1.24 g, 7.5 mmol) at 0 ºC. After 0.5 h, the reaction was reacted at r.t. overnight. CH_2Cl_2 was removed and the reaction was quenched with H_2O (30 mL) and extracted with EtOAc (30 mL). The organic layer was washed with brine, dried Na_2SO_4, and purified by a silica gel column chromatography (*n*-hexane/EtOAc = 8:1) to give **1** (1.38 g, 4.2 mmol) in 84% yield.

4. References:

For substituted 3-phenylpropioloyl chloride, please see: K. Park, J.-M. You, S. Jeon, and S. Lee. *Eur. J. Org. Chem.* 2013, 1973–1978.

5. The Crystal Structure of Product 3a (Figure 1):





Datablock: CCDC 1448314

Bond precision: C-C = 0.0051 A Wavelength=0.71000

Cell: a=8.3931(6) b=12.0705(7) c=19.3724(10)
alpha=90 beta=95.807(5) gamma=90

Temperature: 295 K

	Calculated	Reported
Volume	1952.5(2)	1952.5(2)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C20 H22 N O5 P	C20 H22 N O5 P
Sum formula	C20 H22 N O5 P	C20 H22 N O5 P
Mr	387.36	387.36
Dx,g cm-3	1.318	1.318
Z	4	4
Mu (mm-1)	0.169	0.171
F000	816.0	816.0
F000'	816.80	
h,k,lmax	10,14,23	10,14,23
Nref	3841	3834
Tmin,Tmax	0.966,0.975	0.754,1.000
Tmin'	0.965	

Correction method= # Reported T Limits: Tmin=0.754
Tmax=1.000 AbsCorr = MULTI-SCAN

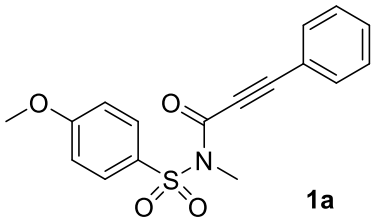
Data completeness= 0.998 Theta(max)= 25.990

R(reflections)= 0.0592(2275) wR2(reflections)= 0.1785(3834)

S = 1.034 Npar= 247

---

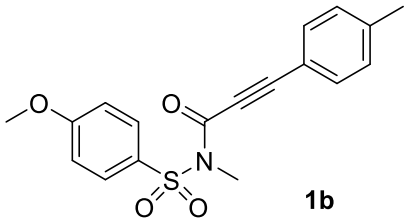
6. Characterization Data of Starting Materials 1a-1t:



1a

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 3.52 (s, 3H), 3.86 (s, 3H), 6.97-6.99 (d, 2H, *J* = 9.2 Hz), 7.37-7.41 (dd, 2H, J_1 = 7.2 Hz, J_2 = 14.8 Hz), 7.46-7.49 (dd, 1H, J_1 = 7.6 Hz, J_2 = 14.8 Hz),7.56-7.58 (d, 2H, *J* = 7.2 Hz), 7.95-7.97 (d, 2H, *J* = 9.6 Hz);

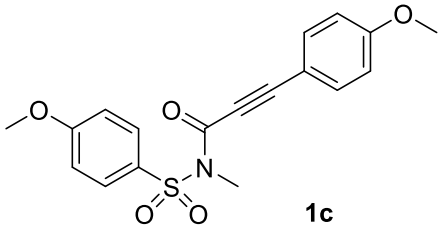
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 33.3, 55.7, 81.5, 93.4, 114.1, 119.4, 128.6, 129.8, 130.4, 130.9, 132.7, 152.7, 163.9.



1b

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 2.39 (s, 3H), 3.50 (s, 3H), 3.86 (s, 3H), 6.96-6.98 (d, 2H, *J* = 9.2 Hz), 7.19-7.21 (d, 2H, *J* = 8.0 Hz), 7.46-7.48 (d, 2H, *J* = 8.0 Hz), 7.94-7.96 (d, 2H, *J* = 8.8 Hz);

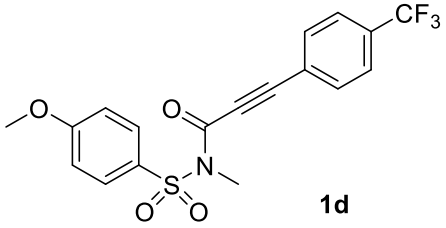
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 21.7, 33.4, 55.7, 81.3, 94.1, 114.2, 116.4, 129.5, 130.0, 130.5, 132.8, 141.7, 152.9, 163.9.



1c

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 3.49 (s, 3H), 3.84 (s, 3H), 3.86 (s, 3H), 6.89-6.91 (d, 2H, *J* = 8.0 Hz), 6.96-6.98 (d, 2H, *J* = 8.0 Hz), 7.52-7.54 (d, 2H, *J* = 8.0 Hz), 7.94-7.96 (d, 2H, *J* = 8.4 Hz);

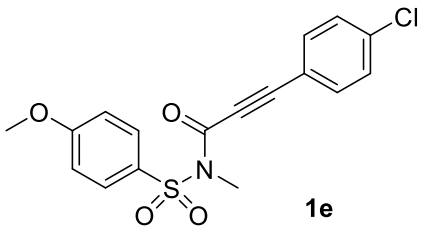
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 33.3, 55.4, 55.7, 81.3, 94.5, 111.2, 114.2, 114.4, 130.1, 130.4, 134.8, 152.9, 161.8, 163.9.



1d

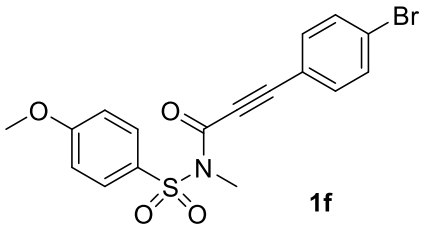
^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 3.50 (s, 3H), 3.88 (s, 3H), 6.98-7.02 (m, 2H), 7.67-7.70 (m, 4H), 7.93-7.97 (m, 2H);

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 33.3, 55.7, 82.9, 91.1, 114.3, 114.5, 121.9, 122.1, 123.3, 125.6, 125.6, 125.7, 127.3, 129.6, 130.4, 132.9, 152.2, 164.1.



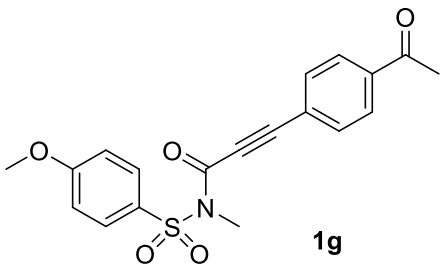
1e

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 3.48 (s, 3H), 3.87 (s, 3H), 6.97-6.99 (d, 2H, *J* = 9.2 Hz), 7.37-7.39 (d, 2H, *J* = 8.8 Hz), 7.50-7.52 (d, 2H, *J* = 8.4 Hz), 7.92-7.94 (d, 2H, *J* = 8.8 Hz);
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 33.2, 55.7, 82.3, 92.1, 114.2, 118.0, 129.1, 129.9, 130.4, 133.9, 137.4, 152.4, 164.0.



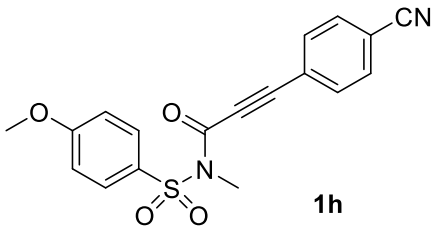
1f

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 3.49 (s, 3H), 3.87 (s, 3H), 6.97-6.99 (d, 2H, *J* = 8.8 Hz), 7.43-7.45 (d, 2H, *J* = 8.4 Hz), 7.54-7.56 (d, 2H, *J* = 8.4 Hz), 7.93-7.95 (d, 2H, *J* = 8.8 Hz),
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 33.3, 55.7, 82.4, 92.2, 114.2, 118.4, 125.8, 129.7, 130.4, 132.1, 134.0, 152.5, 164.0.



1g

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 2.63 (s, 3H), 3.51 (s, 3H), 3.88 (s, 3H), 6.98-7.01 (d, 2H, *J* = 9.2 Hz), 7.65-7.68 (d, 2H, *J* = 8.4 Hz), 7.93-7.99 (m, 3H);
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 26.6, 33.2, 55.7, 83.4, 91.7, 114.2, 123.9, 128.3, 129.5, 130.3, 132.7, 138.1, 152.2, 164.0, 196.9.

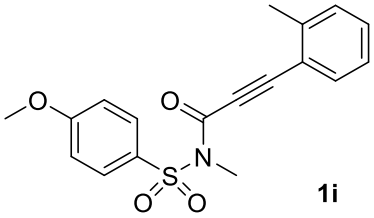


1h

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 3.46 (s, 3H), 3.88 (s, 3H), 6.98-7.00 (d, 2H, *J* = 9.2 Hz), 7.66-7.71 (dd, 2H,

J_1 = 8.4 Hz, J_2 = 12.8 Hz), 7.91-7.94 (d, 2H, J = 8.8 Hz);

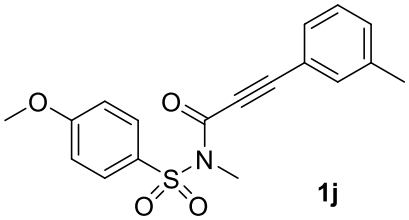
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 33.1, 55.7, 84.3, 90.4, 114.2, 114.3, 117.7, 124.3, 129.6, 130.3, 132.3, 133.0, 151.9, 164.1.



1i

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 2.47 (s, 3H), 3.54 (s, 3H), 3.87 (s, 3H), 6.97-6.99 (d, 2H, J = 9.2 Hz), 7.18-7.27 (m, 2H), 7.34-7.38 (m, 1H), 7.52-7.54 (d, 1H, J = 7.6 Hz), 7.95-7.97 (d, 2H, J = 8.8 Hz);

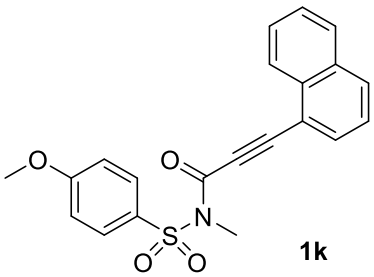
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 20.6, 33.5, 55.7, 85.0, 92.8, 114.1, 119.3, 125.9, 129.8, 129.8, 130.6, 130.9, 133.3, 142.2, 152.9, 163.9.



1j

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 2.36 (s, 3H), 3.51 (s, 3H), 3.87 (s, 3H), 6.97-6.99 (d, 2H, J = 9.2 Hz), 7.28-7.29 (m, 2H), 7.37-7.39 (d, 2H, J = 5.6 Hz), 7.94-7.98 (dd, 2H, J_1 = 2.8 Hz, J_2 = 11.6 Hz);

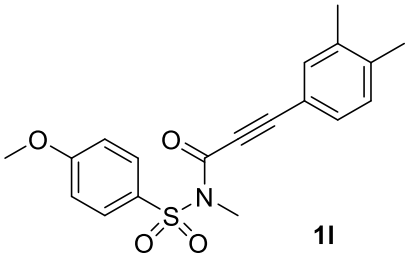
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 21.2, 33.4, 55.7, 81.2, 93.9, 114.2, 119.2, 128.6, 129.9, 129.9, 130.5, 131.9, 133.2, 138.5, 152.8, 163.9.



1k

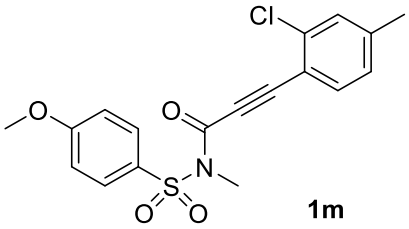
^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 3.56 (s, 3H), 3.81 (s, 3H), 6.92-6.94 (d, 2H, J = 9.2 Hz), 7.44-7.48 (t, 1H, J = 8.0 Hz), 7.53-7.62 (m, 2H), 7.82-7.88 (m, 2H), 7.94-7.97 (m, 3H), 8.31-8.33 (d, 1H, J = 8.4 Hz);

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 33.3, 55.6, 86.0, 92.3, 114.2, 117.1, 125.1, 125.7, 126.9, 127.8, 128.4, 129.9, 130.4, 131.6, 132.9, 133.0, 133.5, 152.7, 163.9.



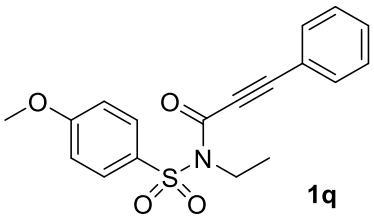
1l

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 2.25 (s, 3H), 2.29 (s, 3H), 3.51 (s, 3H), 3.86 (s, 3H), 6.95-6.99 (m, 2H), 7.14-7.16 (d, 1H, *J* = 7.6 Hz), 7.31-7.34 (m, 2H), 7.94-7.98 (m, 2H);
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 19.5, 20.0, 33.4, 55.7, 81.1, 94.4, 114.1, 116.5, 129.9, 129.9, 130.4, 130.5, 133.6, 137.2, 140.6, 152.9, 163.9.



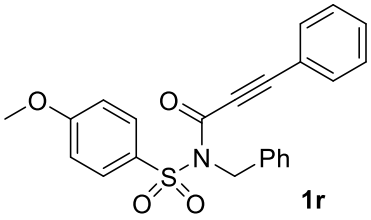
1m

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 2.40 (s, 3H), 3.50 (s, 3H), 3.50 87(s, 3H), 6.89-7.00 (d, 2H, *J* = 8.8 Hz), 7.24-7.26 (d, 1H, *J* = 7.6 Hz), 7.36-7.38 (d, 1H, *J* = 7.6 Hz), 7.52 (s, 1H), 7.93-7.95 (d, 2H, *J* = 8.8 Hz);
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 20.3, 33.3, 55.7, 81.7, 92.0, 114.2, 118.2, 129.6, 130.3, 130.8, 131.1, 132.7, 134.5, 139.8, 152.4, 163.9.



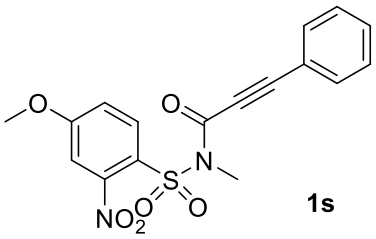
1q

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.43-1.46 (t, 3H, *J* = 6.8 Hz), 3.86 (s, 3H), 4.09-4.14 (dd, 2H, J_1 = 7.2 Hz, J_2 = 14.0 Hz), 6.95-6.98 (d, 2H, *J* = 8.8 Hz), 7.37-7.40 (t, 2H, *J* = 7.2 Hz), 7.45-7.49 (d, 1H, *J* = 7.6 Hz), 7.53-7.55 (d, 2H, *J* = 7.2 Hz), 7.96-7.98 (d, 2H, *J* = 8.8 Hz);
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 15.7, 43.0, 55.7, 81.5, 92.4, 114.0, 119.5, 128.7, 130.5, 130.8, 130.9, 132.7, 152.6, 163.8.



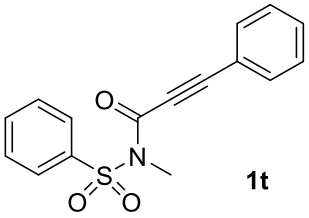
1r

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 3.82 (s, 3H), 5.29 (s, 2H), 6.82-6.84 (d, 2H, *J* = 9.2 Hz), 7.33-7.36 (m, 5H), 7.42-7.45 (m, 5H), 7.67-7.69 (d, 2H, *J* = 9.2 Hz);
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 50.4, 55.6, 81.7, 93.5, 113.7, 119.3, 128.0, 128.6, 130.0, 130.9, 131.0, 132.7, 136.3, 152.9, 163.8.



1s

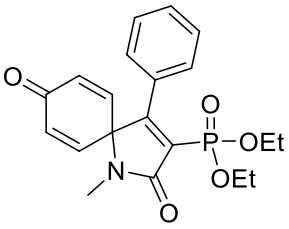
^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 3.65 (s, 3H), 3.93 (s, 2H), 7.14-7.17 (dd, 1H, J_1 = 2.4 Hz, J_2 = 9.2 Hz), 7.24-7.25 (m, 1H), 7.37-7.41 (t, 2H, J = 7.2 Hz), 7.46-7.50 (t, 1H, J = 7.6 Hz), 7.54-7.56 (d, 2H, J = 7.2 Hz);
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 34.4, 56.5, 80.9, 94.0, 110.7, 116.0, 119.0, 123.3, 126.9, 128.7, 131.2, 132.8, 137.1, 149.4, 153.1, 164.2.



1t

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 3.53 (s, 3H), 7.38-7.42 (m, 2H), 7.46- 7.50 (m, 1H), 7.52-7.58 (m, 4H), 7.63-7.67 (m, 1H), 8.01-8.03 (d, 2H, J = 7.2 Hz)
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 33.4, 81.4, 93.8, 119.3, 128.0, 128.7, 129.1, 131.0, 132.7, 134.0, 138.5, 152.7.

7. Characterization Data of Products 3a-3t:



3a

diethyl (1-methyl-2,8-dioxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)phosphonate (3a): White Solid; Melting Point: 130-132 °C; Eluent (n-hexane/EtOAc = 4:1);

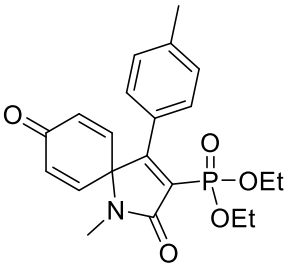
^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.09-1.12 (t, 6H, *J* = 7.2 Hz), 2.88 (s, 3H), 3.99-4.13 (m, 4H), 6.43-6.53 (dd, 4H, J_1 = 10.0 Hz, J_2 = 30.0 Hz), 7.21-7.23 (d, 2H, *J* = 7.2 Hz), 7.29-7.40 (m, 3H);

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 16.0, 16.0, 26.0, 62.8, 62.9, 69.2, 69.4, 76.7, 77.0, 77.3, 127.9, 129.8, 129.9, 130.9, 130.9, 133.6, 143.5, 165.3, 165.4, 167.6, 167.8, 183.5;

^{31}P NMR (162 MHz, $CDCl_3$, δ ppm): 7.46;

IR (KBr): υmax 3382, 3054, 2371, 1701, 1671, 1630, 1367, 1255, 1167, 1060, 970, 817, 732, 573 cm^{-1};

HRMS (ESI) calcd for $C_{20}H_{22}N_1O_5P_1$ $[M+Na]^+$ m/z 410.1122, found 410.1127.



3b

3b: Pale Yellow Liquid; Eluent (n-hexane/EtOAc = 4:1);

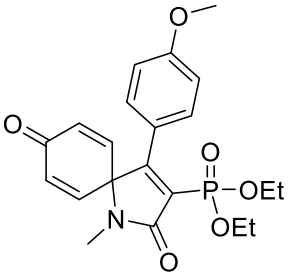
^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.11-1.14 (t, 6H, *J* = 7.2 Hz), 2.34 (s, 3H), 2.88 (s, 3H), 4.00-4.14 (m, 4H), 6.44-6.53 (dd, 4H, J_1 = 10.4 Hz, J_2 = 26.4 Hz), 7.13 (s, 4H);

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 15.9, 16.0, 21.2, 26.0, 62.9, 62.9, 69.1, 69.3, 126.9, 127.8, 128.6, 128.9, 133.5, 140.2, 143.7, 165.8, 165.9, 167.7, 167.9, 183.6;

^{31}P NMR (162 MHz, $CDCl_3$, δ ppm): 7.77;

IR (KBr): υmax 2982, 2928, 2239, 1700, 1630, 1509, 1368, 1252, 1169, 1027, 976, 877, 834, 733, 572 cm^{-1};

HRMS (ESI) calcd for $C_{21}H_{24}N_1O_5P_1$ $[M+Na]^+$ m/z 424.1274, found 424.1278.



3c

3c: Pale Yellow Liquid; Eluent (n-hexane/EtOAc = 4:1);

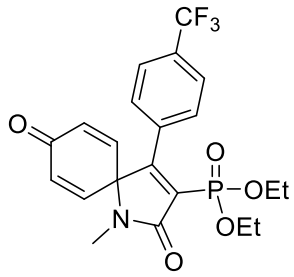
^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.14-1.18 (t, 6H, *J* = 7.2 Hz), 2.87 (s, 3H), 3.80 (s, 3H), 4.01-4.17 (m, 4H), 6.46-6.54 (dd, 4H, J_1 = 10.4 Hz, J_2 = 20.8 Hz), 6.83-6.86 (d, 2H, *J* = 8.8 Hz), 7.26-7.28 (d, 2H, *J* = 9.2 Hz);

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm):15.9, 16.0, 25.8, 55.1, 62.8, 62.8, 68.9, 69.0, 113.3, 122.9, 123.0, 126.1, 128.1, 129.6, 129.6, 133.4, 143.9, 161.0, 165.4, 165.5, 167.7, 167.9, 183.5;

^{31}P NMR (162 MHz, $CDCl_3$, δ ppm): 8.03;

IR (KBr): υmax 3049, 2982, 2932, 2841, 2241, 1698, 1630, 1510, 1384, 1253, 1181, 1057, 974, 877, 841, 734, 571 cm^{-1};

HRMS (ESI) calcd for $C_{21}H_{24}N_1O_6P_1$ $[M+Na]^+$ m/z 440.1250, found 440.1243.



3d

3d: Red Liquid; Eluent (n-hexane/EtOAc = 4:1);

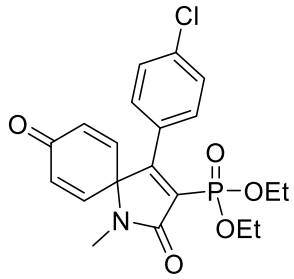
^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.10-1.13 (t, 6H, *J* = 6.8 Hz), 2.91 (s, 3H), 4.04-4.16 (m, 4H), 6.46-6.55 (dd, 4H, J_1 = 10.4 Hz, J_2 = 26.4 Hz), 7.34-7.36 (d, 2H, *J* = 8.0 Hz), 7.60-7.62 (d, 2H, *J* = 8.0 Hz);

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm):15.9, 15.9, 26.1, 63.0, 63.0, 69.1, 69.2, 122.1, 124.8, 124.8, 128.5, 128.5, 129.1, 131.6, 131.9, 134.0, 134.5, 142.9, 163.4, 163.5, 167.1, 167.3, 183.1;

^{31}P NMR (162 MHz, $CDCl_3$, δ ppm): 6.67;

IR (KBr): υmax 2982, 2930, 2245, 1701, 1632, 1370, 1326, 1252, 1129, 1027, 977, 846, 571 cm^{-1};

HRMS (ESI) calcd for $C_{21}H_{21}F_3N_1O_5P_1$ $[M+Na]^+$ m/z 478.1049, found 478.1044.



3e

3e: Pale Yellow Solid; Melting point: 100-102 °C; Eluent (n-hexane/EtOAc = 4:1);

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.14-1.17 (t, 6H, *J* = 7.2 Hz), 2.88 (s, 3H), 4.04-4.16 (m, 4H), 6.45-6.52 (dd, 4H, J_1 = 10.4 Hz, J_2 = 18.4 Hz), 7.18-7.20 (d, 2H, *J* = 8.4 Hz), 7.31-7.33 (d, 2H, *J* = 8.8 Hz);

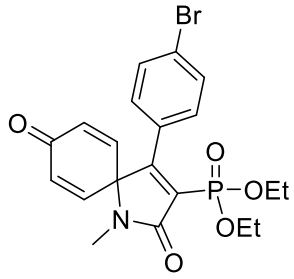
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm):16.0, 16.0, 26.0, 62.9, 63.0, 69.0, 69.2, 128.2, 129.2, 129.2, 129.3, 129.3, 130.3, 133.8, 136.2, 143.3, 164.0, 164.0, 167.3, 167.5, 183.2;

^{31}P NMR (162 MHz, $CDCl_3$, δ ppm): 7.09;

IR (KBr): υmax 2983, 2930, 2241, 1702, 1671, 1631, 1489, 1368, 1251, 1169, 1092, 1054, 1026, 977, 876,

841, 732, 572 cm^{-1};

HRMS (ESI) calcd for $C_{20}H_{21}Cl_1N_1O_5P_1$ $[M+Na]^+$ m/z 444.0731, found 444.0733.



3f

3f: Brown Liquid; Eluent (n-hexane/EtOAc = 4:1);

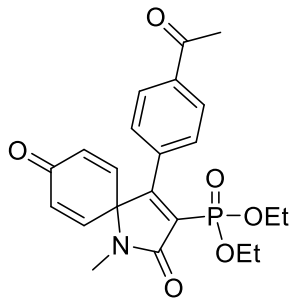
^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.14-1.17 (t, 6H, *J* = 7.2 Hz), 2.88 (s, 3H), 4.04-4.16 (m, 4H), 6.46-6.52 (dd, 4H, J_1 = 10.4 Hz, J_2 = 15.6 Hz), 7.11-7.13 (d, 2H, *J* = 8.4 Hz), 7.47-7.49 (d, 2H, *J* = 8.4 Hz);

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm):16.0, 16.0, 26.0, 62.9, 63.0, 68.9, 69.1, 124.5, 128.2, 129.5, 129.6, 129.6, 130.2, 131.1, 133.8, 143.2, 164.0, 164.1, 167.3, 167.4, 183.2;

^{31}P NMR (162 MHz, $CDCl_3$, δ ppm): 7.06;

IR (KBr): υmax 2981, 2929, 2242, 1701, 1632, 1485, 1368, 1251, 1168, 1027, 977, 876, 839, 734, 572 cm^{-1};

HRMS (ESI) calcd for $C_{20}H_{21}Br_1N_1O_5P_1$ $[M+Na]^+$ m/z 488.0239, found 488.0244.



3g

3g: Pale Yellow Liquid; Eluent (n-hexane/EtOAc = 4:1);

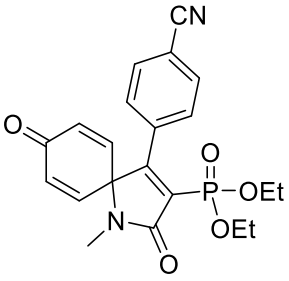
^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.11-1.15 (t, 6H, *J* = 7.2 Hz), 2.60 (s, 3H), 2.90 (s, 3H), 4.03-4.16 (m, 4H), 6.45-6.56 (dd, 4H, J_1 = 10.0 Hz, J_2 = 33.6 Hz), 7.31-7.33 (d, 2H, *J* = 8.4 Hz), 7.91-7.93 (d, 2H, *J* = 8.4 Hz);

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 16.0, 16.0, 26.1, 26.6, 63.0, 63.0, 69.1, 69.2, 127.6, 128.3, 128.3, 128.6, 130.6, 133.9, 135.3, 135.4, 137.7, 143.0, 164.1, 164.2, 167.2, 167.3, 183.1, 197.0;

^{31}P NMR (162 MHz, $CDCl_3$, δ ppm): 6.77;

IR (KBr): υmax 2982, 2929, 2243, 1702, 1631, 1366, 1266, 1168, 1026, 976, 878, 844, 731, 571 cm^{-1};

HRMS (ESI) calcd for $C_{22}H_{24}N_1O_6P_1$ $[M+Na]^+$ m/z 452.1224, found 452.1229.



3h

3h: Pale Yellow Liquid; Eluent (n-hexane/EtOAc = 4:1);

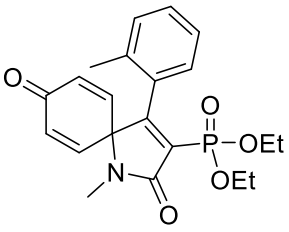
^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.13-1.17 (t, 6H, *J* = 7.2 Hz), 2.91 (s, 3H), 4.06-4.17 (m, 4H), 6.46-6.54 (dd, 4H, J_1 = 10.0 Hz, J_2 = 20.4 Hz), 7.33-7.35 (d, 2H, *J* = 8.4 Hz), 7.64-7.66 (d, 2H, *J* = 8.4 Hz);

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 16.0, 16.1, 26.1, 63.1, 63.1, 69.0, 69.1, 113.7, 117.7, 128.8, 128.8, 129.4, 131.4, 131.6, 134.1, 135.4, 135.4, 142.7, 162.8, 162.9, 166.9, 167.0, 182.9;

^{31}P NMR (162 MHz, $CDCl_3$, δ ppm): 6.33;

IR (KBr): υmax 2983, 2929, 2230, 1703, 1671, 1632, 1369, 1252, 1168, 1025, 977, 845, 734, 572 cm^{-1};

HRMS (ESI) calcd for $C_{21}H_{21}N_2O_5P_1$ $[M+Na]^+$ m/z 435.1131, found 435.1133.



3i

3i: Pale Yellow Liquid; Eluent (n-hexane/EtOAc = 4:1);

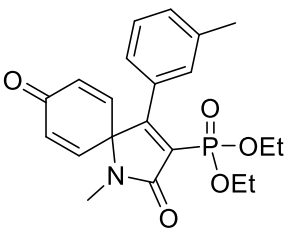
^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.04-1.08 (t, 3H, *J* = 6.8 Hz), 1.09-1.12 (t, 3H, *J* = 6.8 Hz), 2.24 (s, 3H), 2.92 (s, 3H), 3.84-3.89 (m, 1H), 4.02-4.13 (m, 3H), 6.30-6.33 (m, 1H), 6.48-6.51 (dd, 4H, J_1 = 2.0 Hz, J_2 = 10.0 Hz), 6.56-6.62 (m, 2H), 6.84-6.85 (d, 1H, *J* = 7.6 Hz); 7.07-7.11 (t, 1H, *J* = 7.2 Hz), 7.16-7.18 (d, 1H, *J* = 7.2 Hz), 7.21-7.23 (m, 1H);

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 16.0, 16.0, 26.1, 26.6, 63.0, 63.0, 69.1, 69.2, 127.6, 128.3, 128.3, 128.6, 130.6, 133.9, 135.3, 135.4, 137.7, 143.0, 164.1, 164.2, 167.2, 167.3, 183.1, 197.0;

^{31}P NMR (162 MHz, $CDCl_3$, δ ppm): 7.25;

IR (KBr): υmax 2983, 2929, 2240, 1702, 1671, 1630, 1369, 1263, 1247, 1167, 1056, 1027, 976, 877, 821, 736, 573 cm^{-1};

HRMS (ESI) calcd for $C_{21}H_{24}N_1O_5P_1$ $[M+Na]^+$ m/z 424.1274, found 452.1280.



3j

3j: Pale Yellow Solid; Melting point: 92-94 °C; Eluent (n-hexane/EtOAc = 4:1);

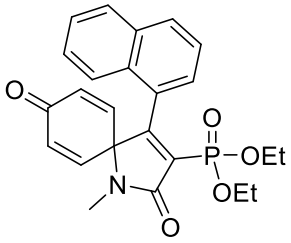
^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.11-1.13 (t, 6H, *J* = 7.2 Hz), 2.32 (s, 3H), 2.88 (s, 3H), 3.97-4.15 (m, 4H), 6.44-6.53 (dd, 4H, J_1 = 10.4 Hz, J_2 = 36.0 Hz), 6.99-7.02 (m, 2H), 7.19-7.21 (d, 2H, *J* = 6.4 Hz);

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm):16.0, 16.0, 21.3, 26.0, 62.8, 62.9, 69.2, 69.3, 124.8, 124.8, 127.4, 127.8, 128.5, 129.4, 130.7, 130.7, 130.8, 133.6, 137.6, 143.6, 165.6, 165.7, 167.7, 167.9, 183.6;

^{31}P NMR (162 MHz, $CDCl_3$, δ ppm): 7.67;

IR (KBr): υmax 2983, 2925, 2242, 1703, 1628, 1511, 1369, 1254, 1169, 1027, 976, 877, 836, 734, 573 cm^{-1};

HRMS (ESI) calcd for $C_{21}H_{24}N_1O_5P_1$ $[M+Na]^+$ m/z 424.1274, found 452.1277.



3k

3k: Pale Yellow Solid; Melting point: 94-96 °C; Eluent (n-hexane/EtOAc = 4:1);

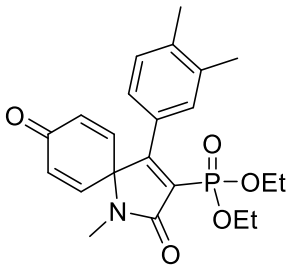
^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 0.81-0.84 (t, 3H, *J* = 6.4 Hz), 0.85-0.89 (t, 3H, *J* = 7.2 Hz), 2.97 (s, 3H), 3.73-3.85 (m, 2H), 3.89-3.99 (m, 2H), 6.04-6.07 (dd, 1H, J_1 = 1.6 Hz, J_2 = 6.0 Hz), 6.51-6.54 (m, 1H), 6.57-6.60 (m, 1H), 6.66-6.69 (m, 1H), 7.10-7.12 (m, 1H), 7.37-7.41 (t, 1H, *J* = 8.4 Hz), 7.49-7.52 (m, 1H), 7.68-7.70 (m, 1H), 7.83-7.85 (m, 1H);

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm):15.7, 15.7, 15.8, 26.4, 62.6, 62.6, 62.7, 62.8, 70.7, 70.8, 123.9, 125.0, 125.8, 125.8, 126.2, 126.8, 128.0, 128.5, 129.8, 131.0, 131.0, 133.0, 133.1, 134.1, 143.5, 143.5, 162.9, 163.0, 167.6, 167.8, 183.2;

^{31}P NMR (162 MHz, $CDCl_3$, δ ppm): 6.83;

IR (KBr): υmax 2959, 2928, 2857, 2372, 1701, 1671, 1631, 1459, 1369, 1257, 1164, 1026, 976, 858, 784, 573 cm^{-1};

HRMS (ESI) calcd for $C_{24}H_{24}N_1O_5P_1$ $[M+Na]^+$ m/z 460.1273, found 460.1270.



3l

3l: Pale Yellow Solid; Melting point: 104-106 °C; Eluent (n-hexane/EtOAc = 4:1);

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.11-1.14 (t, 6H, *J* = 7.2 Hz), 2.22 (s, 3H), 2.24 (s, 3H), 2.87 (s, 3H), 4.00-4.14 (m, 4H), 6.44-6.52 (dd, 4H, J_1 = 10.4 Hz, J_2 = 22.8 Hz), 6.96-6.98 (d, 2H, *J* = 7.6 Hz), 7.01 (s, 1H), 7.06-

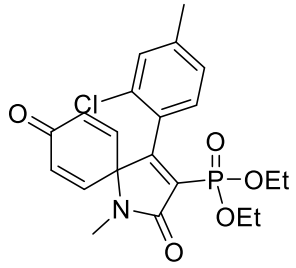
7.08 (d, 2H, *J* = 8.0 Hz);

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 15.9, 16.0, 19.6, 19.6, 25.9, 62.7, 62.8, 69.0, 69.2, 125.1, 125.1, 126.7, 128.2, 128.2, 128.7, 129.0, 129.0, 129.0, 133.4, 136.1, 138.9, 143.8, 165.9, 166.0, 167.7, 167.9, 183.7;

^{31}P NMR (162 MHz, $CDCl_3$, δ ppm): 7.88;

IR (KBr): υmax 2979, 2927, 2869, 2239, 1700, 1670, 1630, 1449, 1386, 1368, 1253, 1164, 1056, 1026, 864, 734, 573 cm^{-1};

HRMS (ESI) calcd for $C_{22}H_{26}N_1O_5P_1$ $[M+Na]^+$ m/z 438.1281, found 438.1280.



3m

3m: Pale Yellow Solid; Melting point: 102-104 °C; Eluent (n-hexane/EtOAc = 4:1);

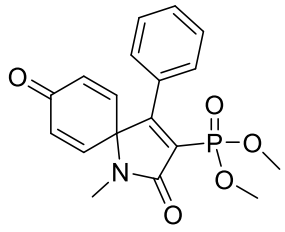
^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.14-1.18 (t, 6H, *J* = 6.8 Hz), 2.36 (s, 3H), 2.88 (s, 3H), 4.05-4.17 (m, 4H), 6.46-6.53 (dd, 4H, J_1 = 10.4 Hz, J_2 = 14.0 Hz), 7.01-7.03 (d, 1H, *J* = 8.0 Hz), 7.18-7.21 (m, 2H);

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm):15.9, 16.0, 19.9, 26.0, 62.9, 63.0, 69.0, 69.2, 126.0, 128.0, 128.4, 129.6, 129.7, 130.0, 130.3, 133.8, 133.9, 138.1, 143.3, 163.7, 163.8, 167.3, 167.5, 183.3;

^{31}P NMR (162 MHz, $CDCl_3$, δ ppm): 7.14;

IR (KBr): υmax 2981, 2928, 2866, 2242, 1702, 1671, 1631, 1368, 1250, 1169, 1054, 1026, 977, 861, 733,573 cm^{-1};

HRMS (ESI) calcd for $C_{21}H_{23}ClN_1O_5P_1$ $[M+Na]^+$ m/z 458.0897, found 458.0899.



3n

3n: Pale Yellow Liquid; Eluent (n-hexane/EtOAc = 4:1);

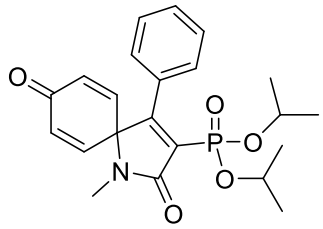
^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 2.89 (s, 3H), 3.63 (s, 3H), 3.66 (s, 3H), 6.45-6.53 (dd, 4H, J_1 = 10.0 Hz, J_2 = 25.2 Hz), 7.22-7.23 (d, 2H, *J* = 7.2 Hz), 7.33-7.40 (m, 3H),

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 26.1, 53.3, 53.3, 69.3, 69.4, 127.2, 127.8, 127.8, 128.0, 129.2, 130.1, 130.5, 130.6, 133.7, 143.3, 166.0, 166.0, 167.5, 167.7, 183.4;

^{31}P NMR (162 MHz, $CDCl_3$, δ ppm): 10.24;

IR (KBr): υmax 2982, 2932, 2241, 1698, 1630, 1510, 1387, 1295, 1169, 1027, 976, 875, 834, 733, 574 cm^{-1};

HRMS (ESI) calcd for $C_{18}H_{18}N_1O_5P_1$ $[M+Na]^+$ m/z 382.0810, found 382.0815.



3o

3o: Pale Yellow Liquid; Eluent (n-hexane/EtOAc = 4:1);

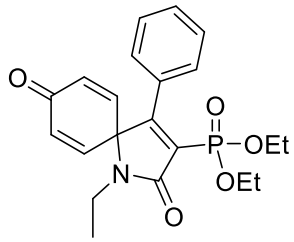
^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.08-1.10 (d, 3H, *J* = 6.4 Hz), 1.21-1.23 (d, 3H, *J* = 6.4 Hz), 1,34-1.35 (d, 3H, *J* = 6.0 Hz), 1.37-1.38 (d, 3H, *J* = 6.0 Hz), 2.88 (s, 3H), 4.73-4.84 (m, 2H), 6.42-6.45 (dd, 1H, J_1 = 10.0 Hz, J_2 = 34.4 Hz), 7.19-7.20 (d, 2H, *J* = 7.2 Hz), 7.29-7.37 (m, 4H);

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 23.3, 23.4, 24.0, 24.1, 26.0, 69.0, 69.2, 71.9, 71.9, 72.9, 73.0, 127.7, 128.0, 128.0, 128.3, 129.6, 130.3, 131.1, 131.2, 133.5, 143.8, 164.7, 164.8, 167.6, 167.8, 183.6;

^{31}P NMR (162 MHz, $CDCl_3$, δ ppm): 5.35;

IR (KBr): υmax 2980, 2932, 2240, 1698, 1632, 1515, 1387, 1295, 1165, 1027, 981, 834, 733, 574 cm^{-1};

HRMS (ESI) calcd for $C_{22}H_{25}N_1O_5P_1$ $[M+Na]^+$ m/z 438.1429, found 438.1434.



3q

3q: Pale Yellow Liquid; Eluent (n-hexane/EtOAc = 4:1);

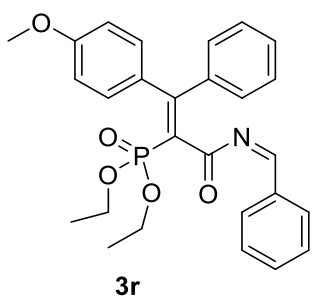
^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.08-1.11 (t, 6H, *J* = 6.8 Hz), 1.19-1.22 (t, 3H, *J* = 6.8 Hz), 3.33-3.38 (m, 2H), 3.96-4.13 (m, 4H), 6.39-6.57 (dd, 4H, J_1 = 10.4 Hz, J_2 = 60.4 Hz), 7.19-7.21 (d, 2H, *J* = 7.2 Hz), 7.30-7.39 (m, 3H);

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 15.0, 15.9, 15.9, 36.0, 62.8, 62.89, 69.5, 69.7, 127.8, 127.9, 129.7, 130.8, 130.8, 133.0, 143.9, 165.0, 165.0, 167.5, 167.7, 183.6;

^{31}P NMR (162 MHz, $CDCl_3$, δ ppm): 7.68;

IR (KBr): υmax 3385, 3052, 2369, 1701, 1697, 1629, 1392, 1255, 1170, 1053, 930, 842, 767, 573 cm^{-1};

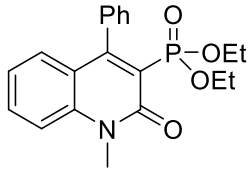
HRMS (ESI) calcd for $C_{21}H_{24}N_1O_5P_1$ $[M+Na]^+$ m/z 424.1277, found 424.1281.



3r

3r: Yellow Liquid; Eluent (n-hexane/EtOAc = 4:1);

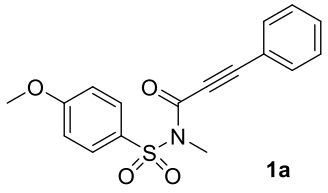
^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 0.98-1.01 (t, 3H, *J* = 6.8 Hz), 1.07-1.10 (t, 3H, *J* = 7.2 Hz), 3.86 (s, 3H), 3.90-4.00 (m, 2H), 4.05-4.10 (m, 2H), 5.45 (s, 1H), 6.83-6.85 (d, 2H, *J* = 9.2 Hz), 6.99-7.01 (m, 2H), 7.18-7.32 (m, 8H), 7.63-7.65 (d, 2H, *J* = 9.2 Hz);
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 15.8, 15.9, 16.0, 16.1, 55.7, 63.0, 63.0, 63.3, 63.3, 95.3, 95.5, 113.8, 126.2, 127.5, 128.6, 129.2, 129.8, 129.8, 130.9, 135.8, 164.0, 165.1, 171.5;
^{31}P NMR (162 MHz, $CDCl_3$, δ ppm): 6.60;
IR (KBr): υmax 3384, 3056, 2389, 1701, 1674, 1631, 1354, 1249, 1167, 1057, 974, 732, 573 cm^{-1};
HRMS (ESI) calcd for $C_{27}H_{28}N_1O_5P_1$ $[M+Na]^+$ m/z 500.1609, found 500.1614.



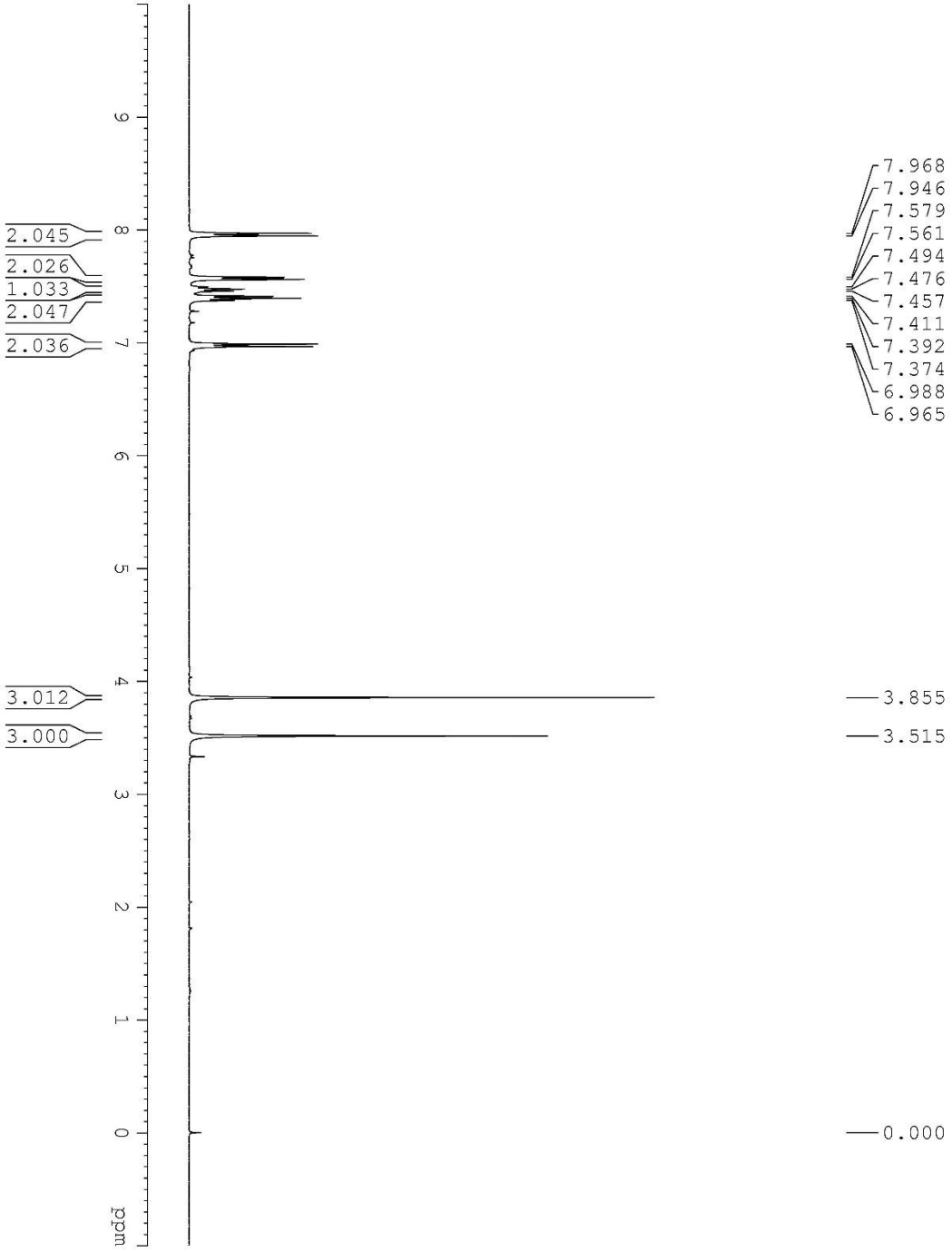
3t

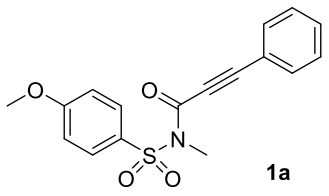
3t: Colorless Liquid; Eluent (n-hexane/EtOAc = 4:1);
^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.09-1.13 (t, 6H, *J* = 7.2 Hz), 2.88 (s, 3H), 3.99-4.13 (m, 4H), 6.43-6.52 (dd, 4H, J_1 = 10.0 Hz, J_2 = 26.8 Hz), 7.21-7.22 (d, 2H, *J* = 6.8 Hz), 7.30-7.38 (m, 3H);
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 16.0, 16.0, 26.0, 62.8, 62.9, 69.2, 69.4, 127.9, 127.9, 129.9, 130.9, 130.9, 133.7, 143.6, 165.3, 165.3, 167.6, 167.8, 183.5;
IR (KBr): υmax 3377, 3053, 2374, 1701, 1671, 1629, 1357, 1245, 1167, 970, 818, 733, 574 cm^{-1};
HRMS (ESI) calcd for $C_{20}H_{22}N_1O_4P_1$ $[M+Na]^+$ m/z 394.1225, found 394.1226.

8. ^{1}H NMR, ^{13}C NMR Spectra of the Products 1a-1t:

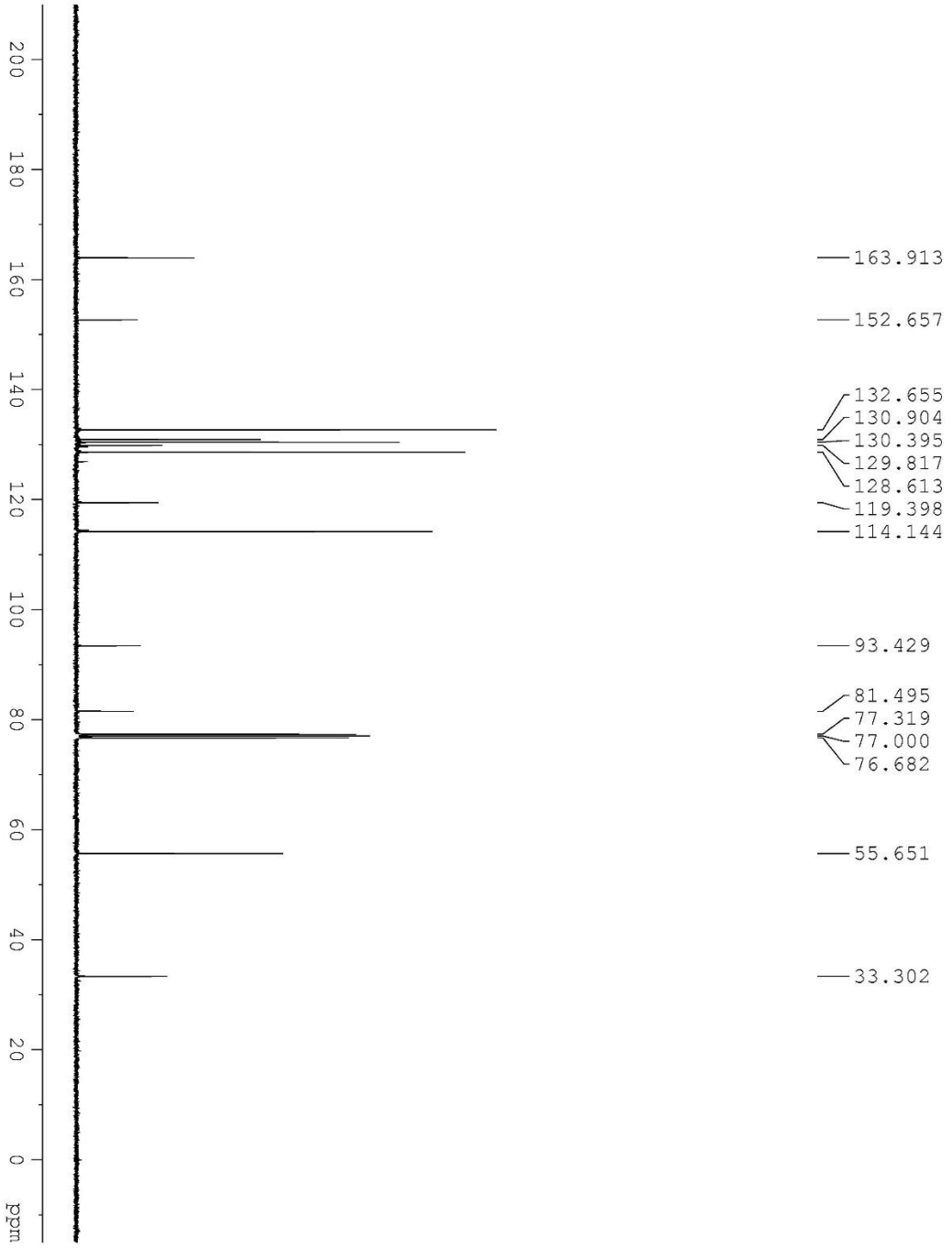


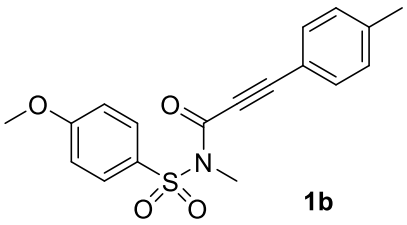
1a



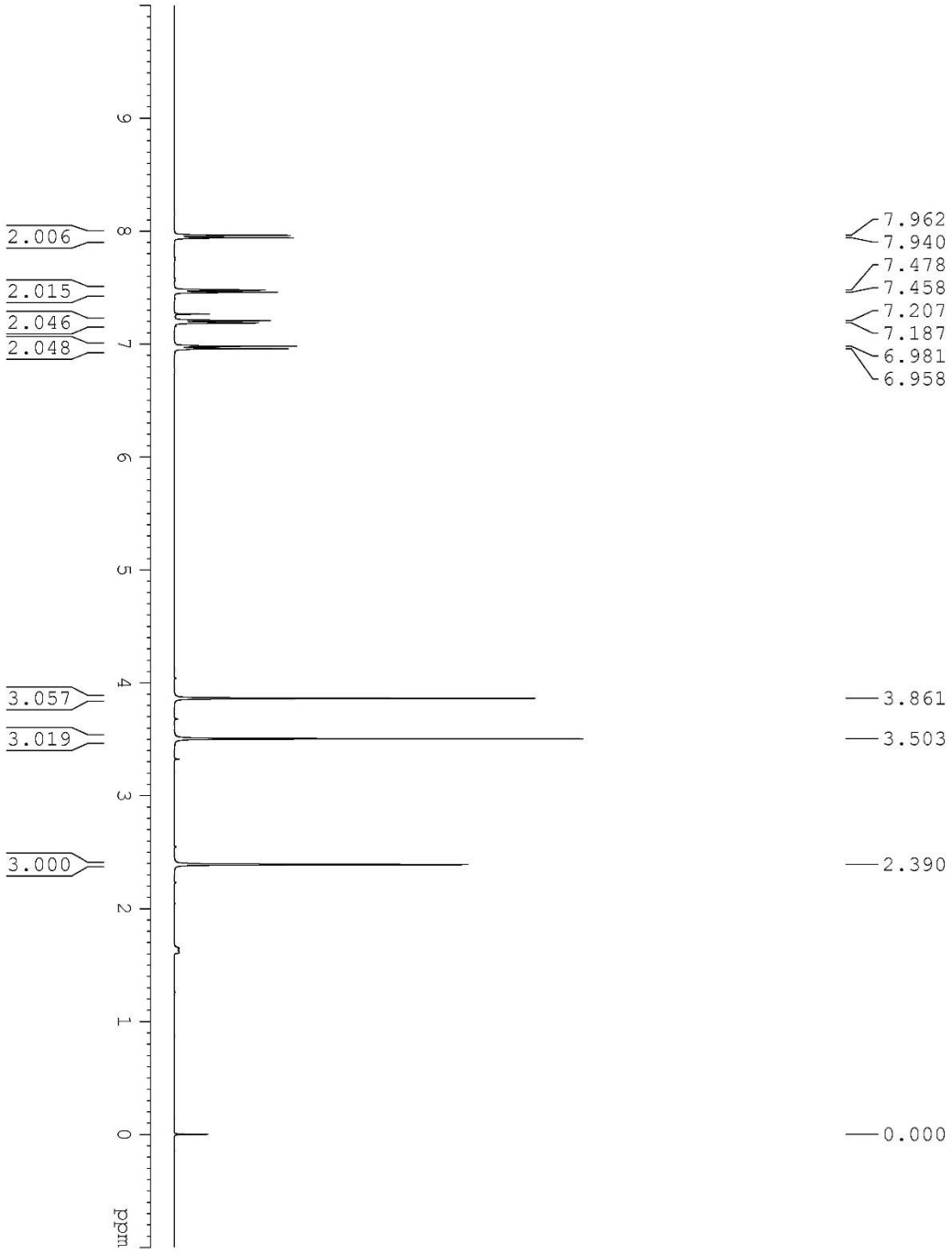


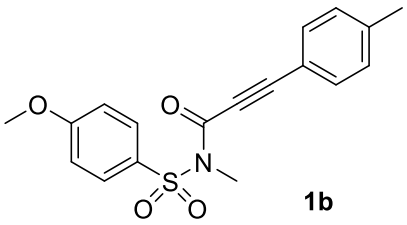
1a


163.913
152.657
132.655
130.904
130.395
129.817
128.613
119.398
114.144
93.429
81.495
77.319
77.000
76.682
55.651
33.302
200
180
160
140
120
100
80
60
40
20
0
ppm

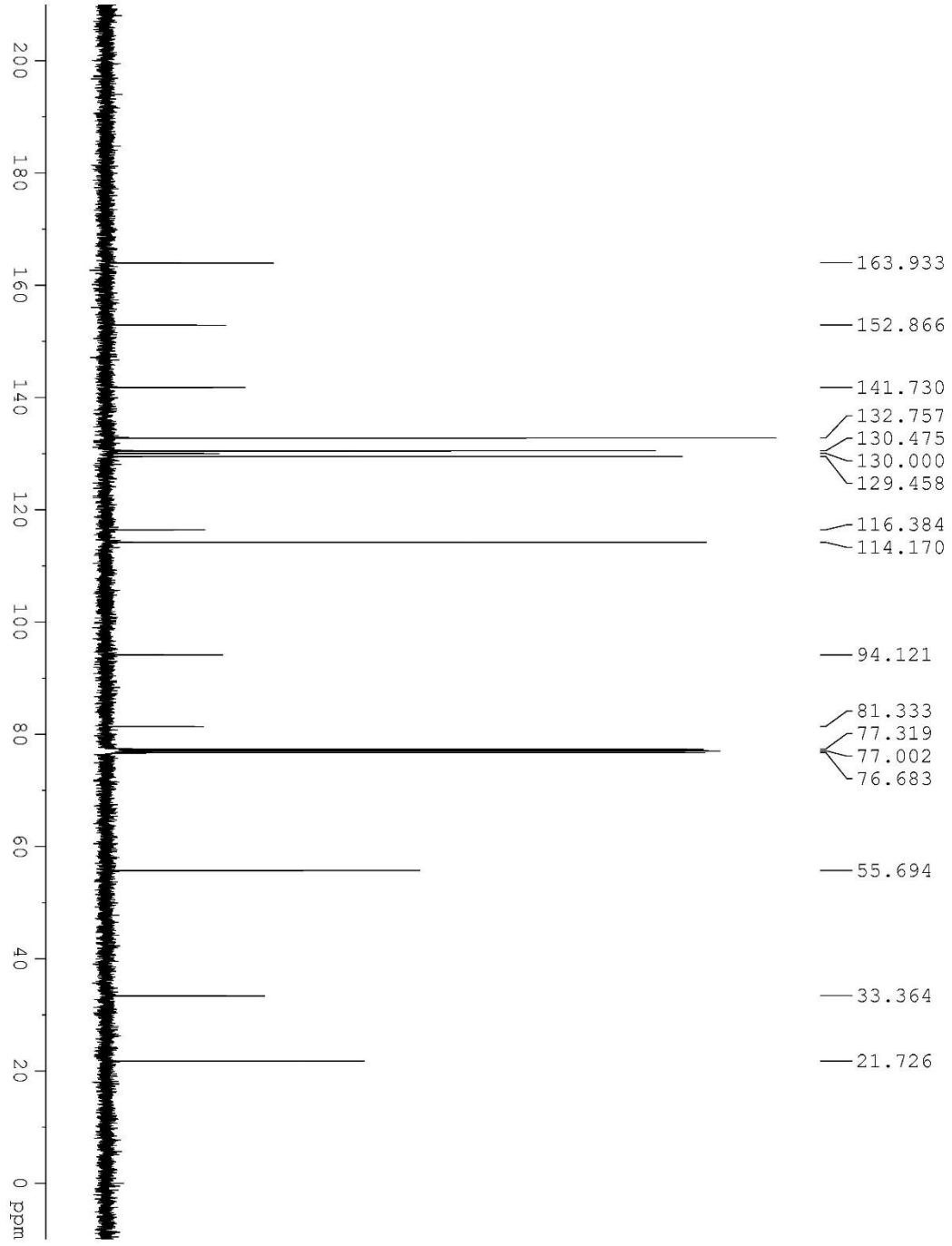


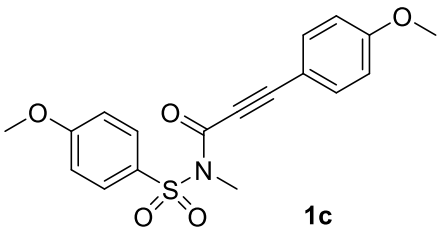
1b


2.006
2.015
2.046
2.048
3.057
3.019
3.000
7.962
7.940
7.478
7.458
7.207
7.187
6.981
6.958
3.861
3.503
2.390
0.000
ppm

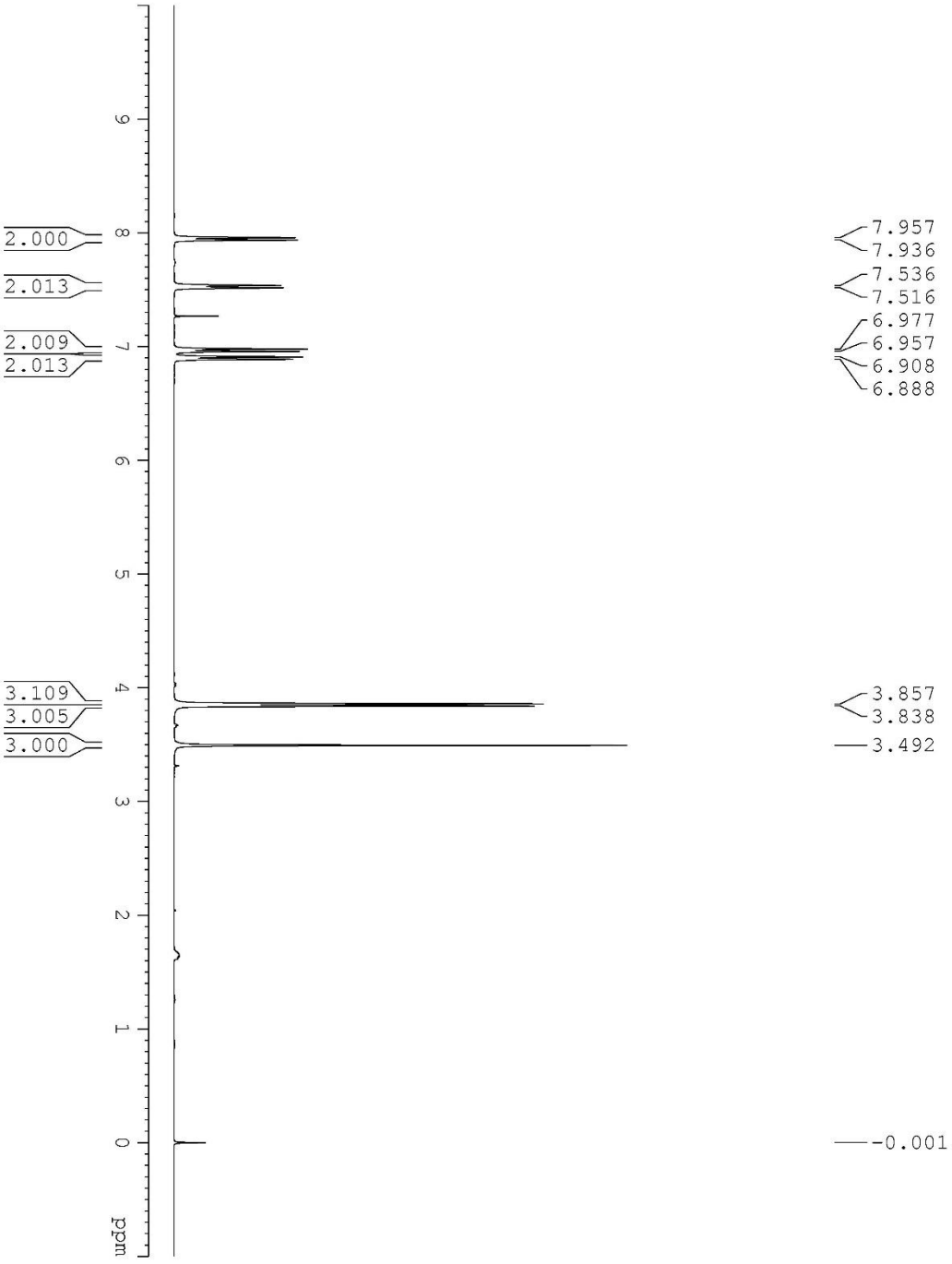

O
O
N
S
O
O

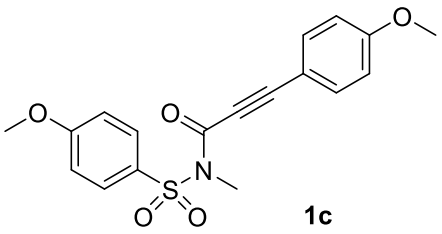
1b


200
180
160
140
120
100
80
60
40
20
0 ppm
163.933
152.866
141.730
132.757
130.475
130.000
129.458
116.384
114.170
94.121
81.333
77.319
77.002
76.683
55.694
33.364
21.726

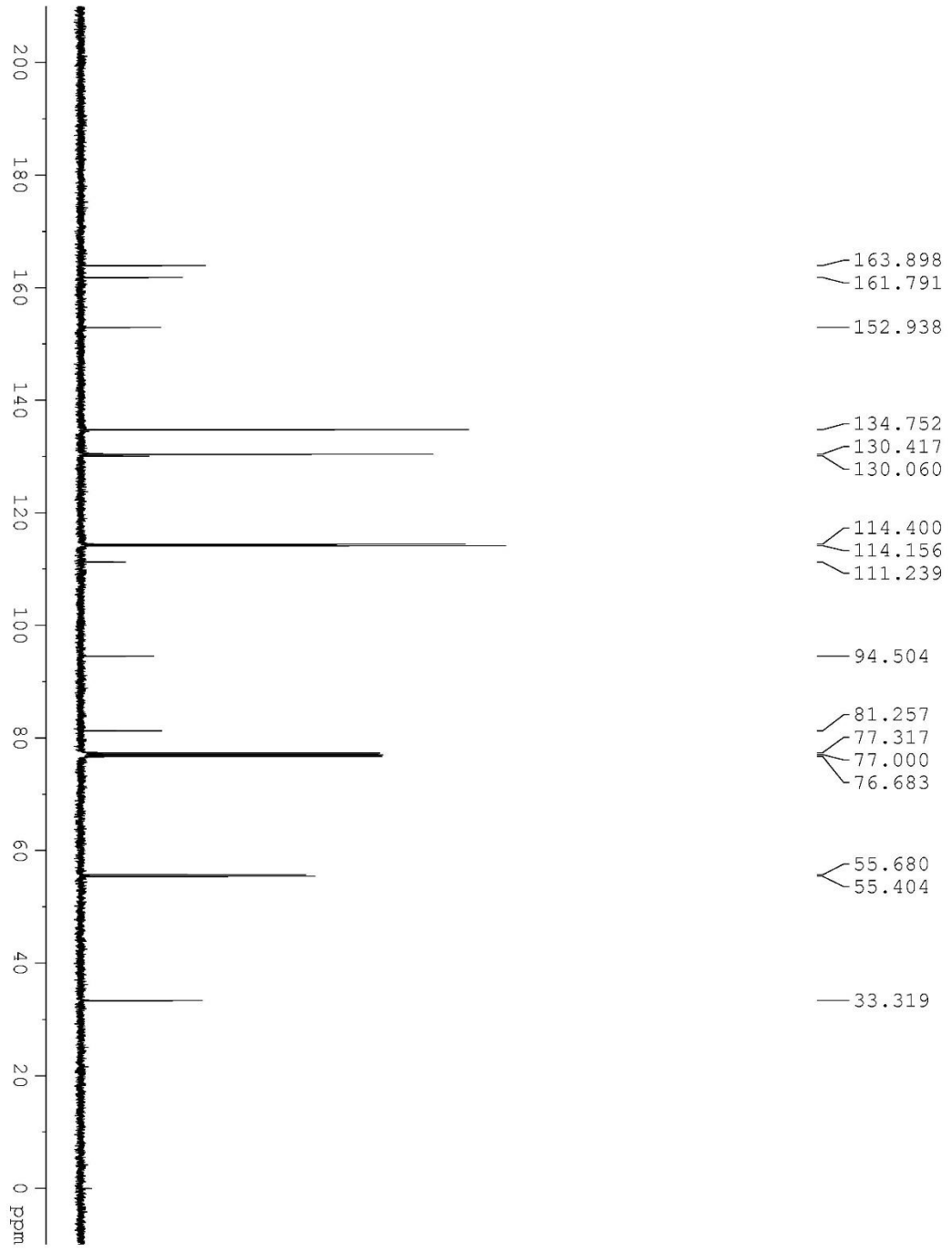


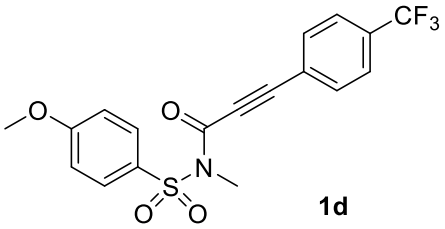
1c


2.000
2.013
2.009
2.013
3.109
3.005
3.000
7.957
7.936
7.536
7.516
6.977
6.957
6.908
6.888
3.857
3.838
3.492
-0.001
ppm

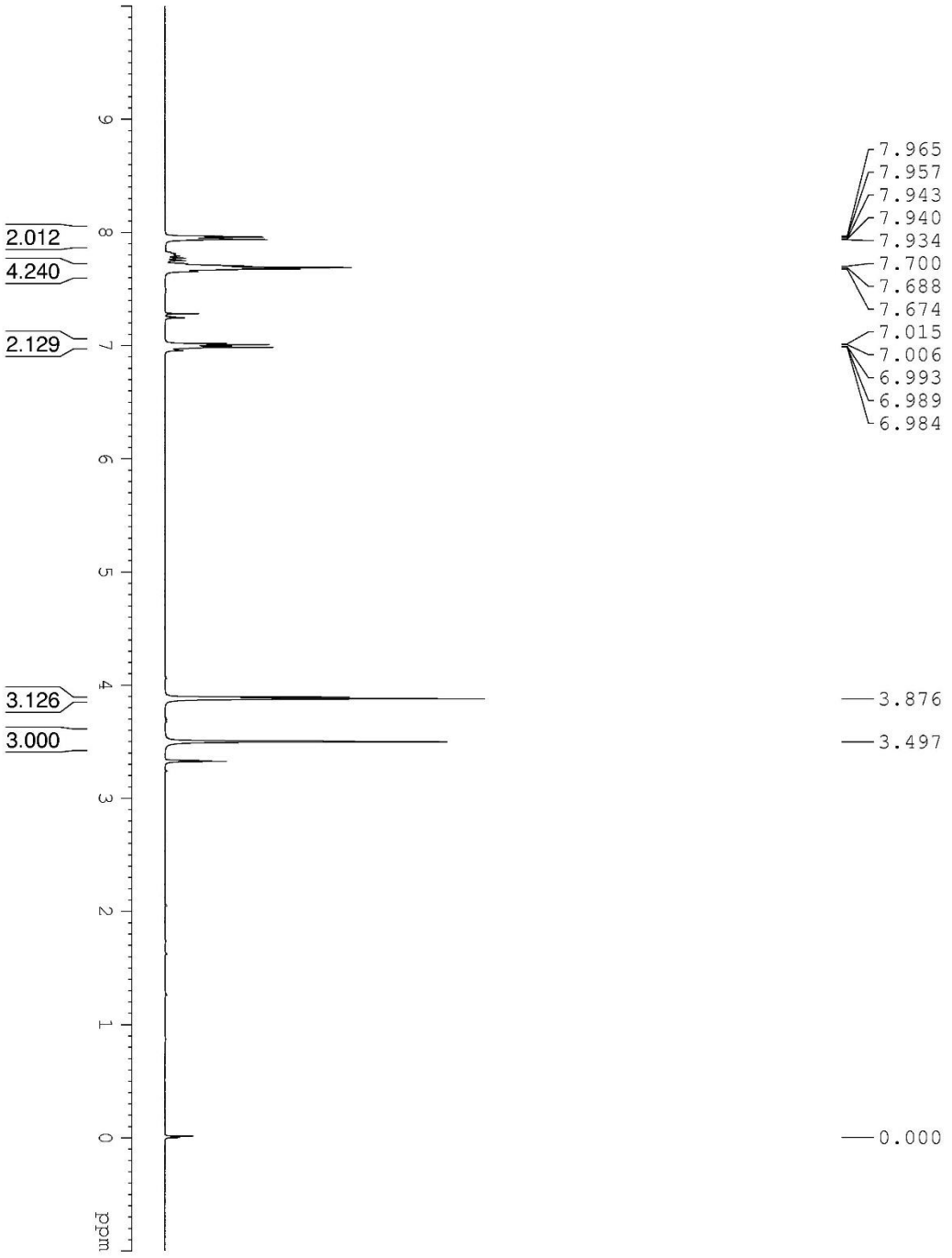


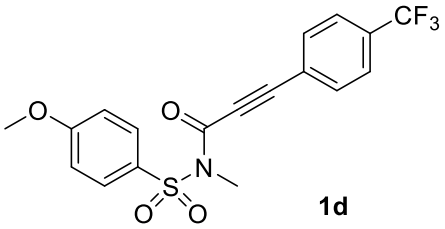
1c


200
180
160
140
120
100
80
60
40
20
0 ppm
163.898
161.791
152.938
134.752
130.417
130.060
114.400
114.156
111.239
94.504
81.257
77.317
77.000
76.683
55.680
55.404
33.319

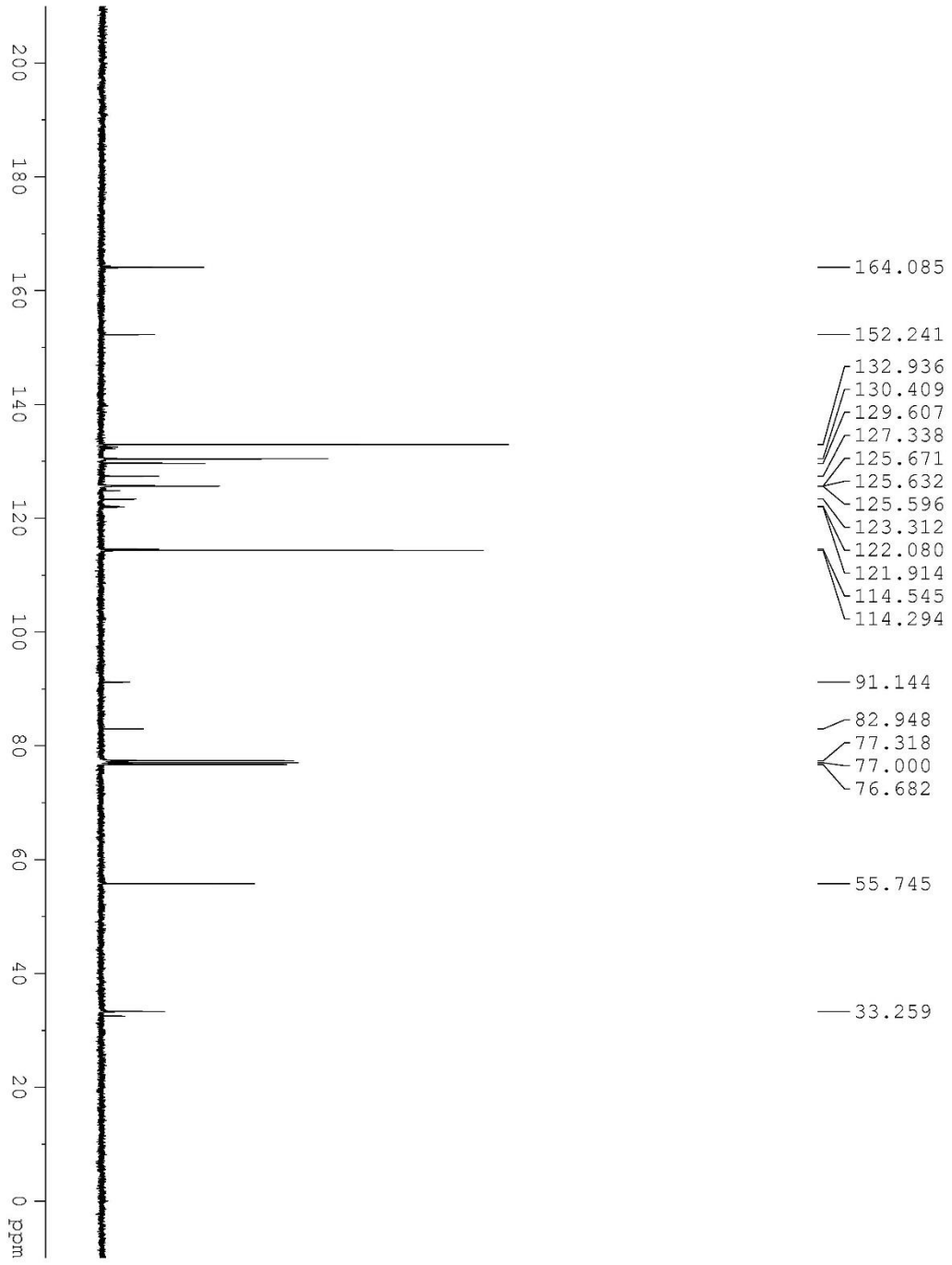

CF3
O
O
N
S
O
O

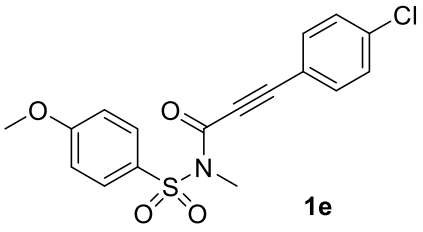
1d


2.012
4.240
2.129
3.126
3.000
7.965
7.957
7.943
7.940
7.934
7.700
7.688
7.674
7.015
7.006
6.993
6.989
6.984
3.876
3.497
0.000
ppm

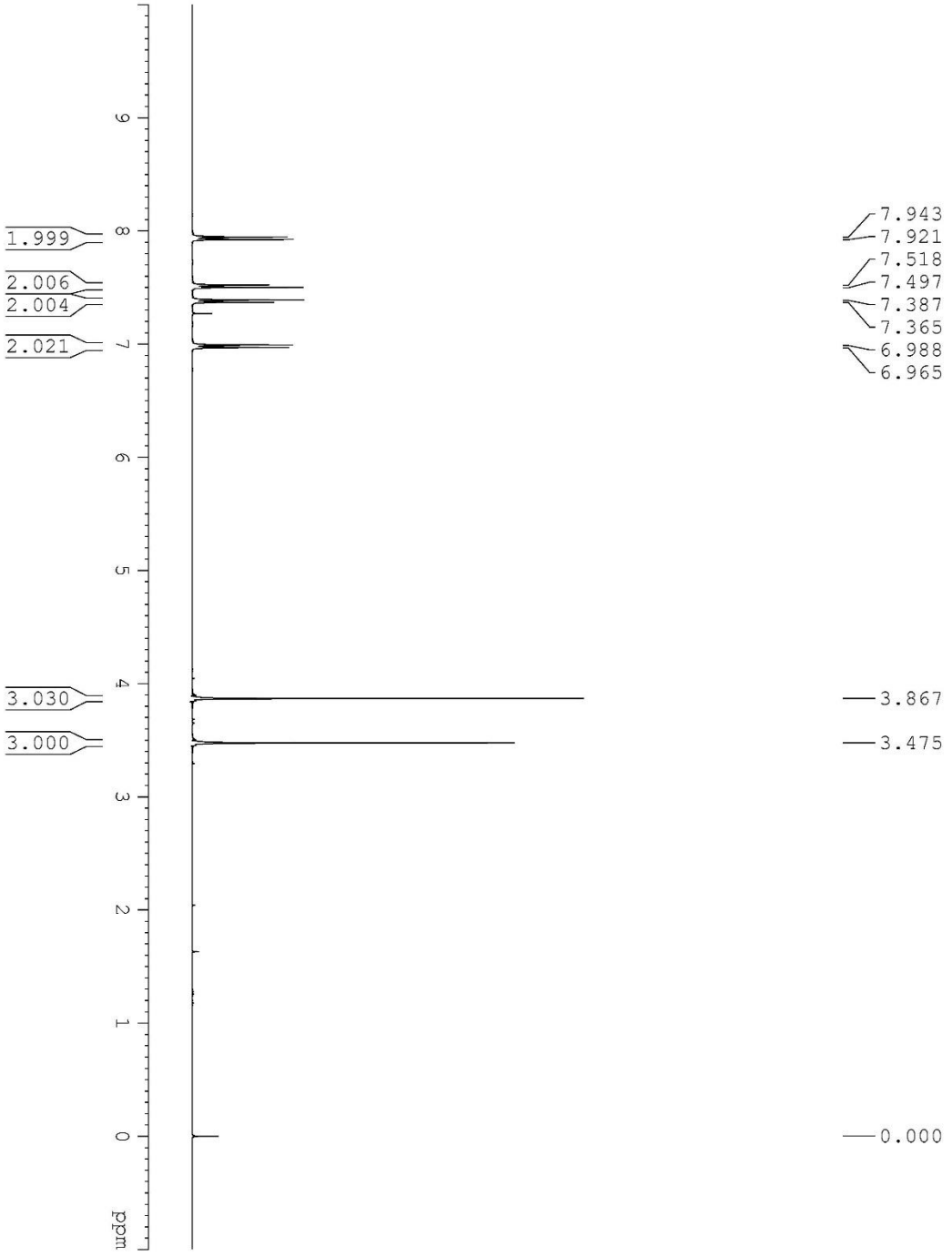

CF3
O
O
N
S
O
O

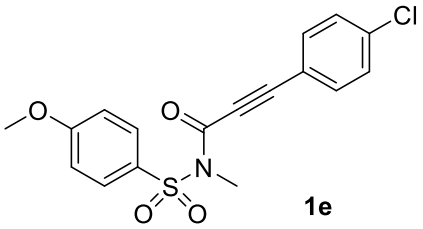
1d


200
180
160
140
120
100
80
60
40
20
0 ppm
164.085
152.241
132.936
130.409
129.607
127.338
125.671
125.632
125.596
123.312
122.080
121.914
114.545
114.294
91.144
82.948
77.318
77.000
76.682
55.745
33.259

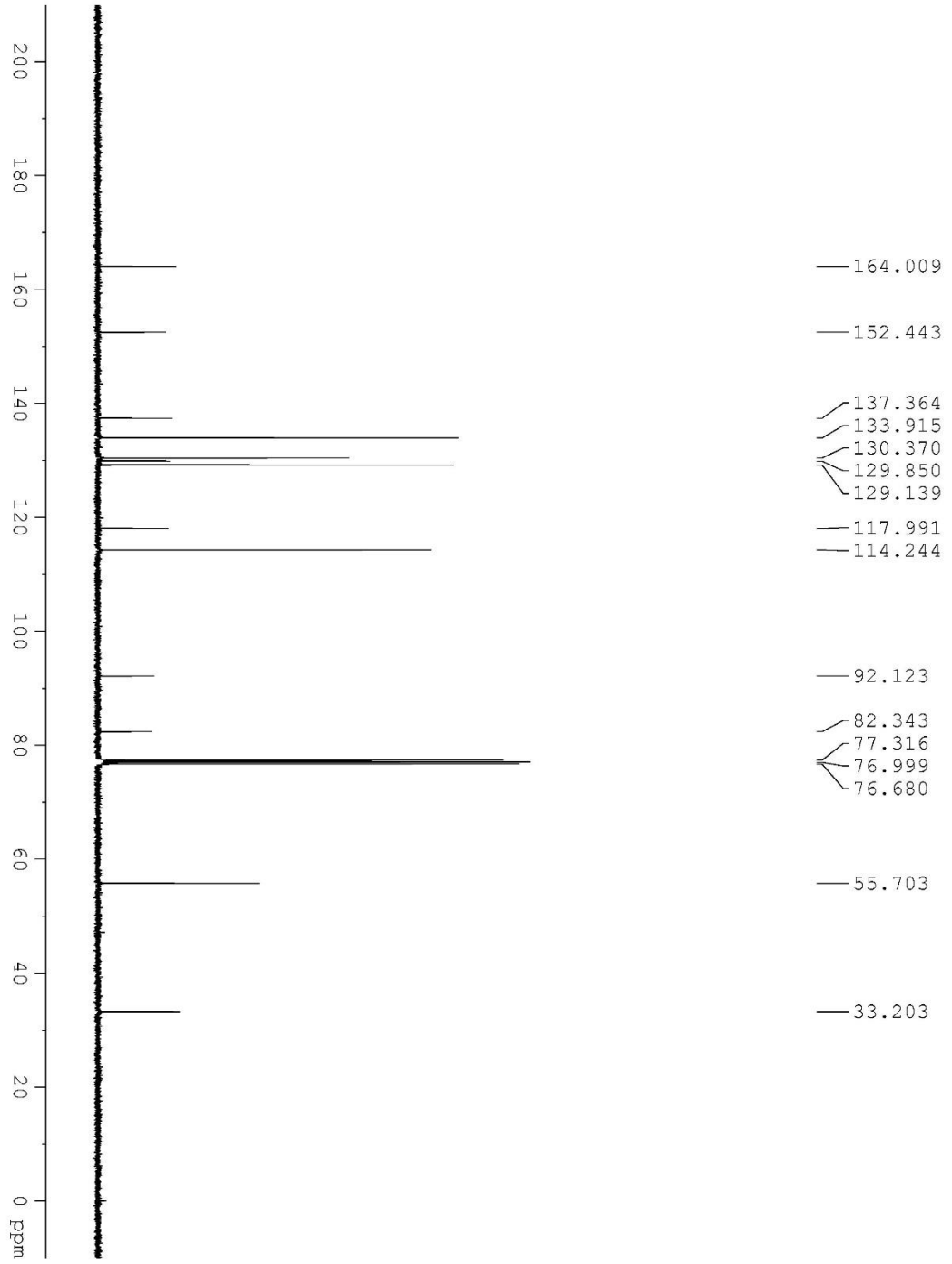

Cl
O
O
N
S
O
O

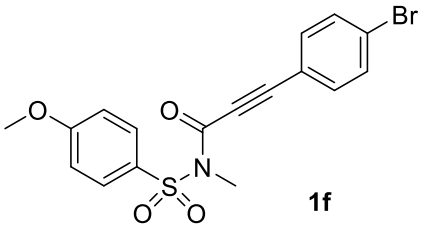
1e


1.999
2.006
2.004
2.021
3.030
3.000
7.943
7.921
7.518
7.497
7.387
7.365
6.988
6.965
3.867
3.475
0.000
ppm

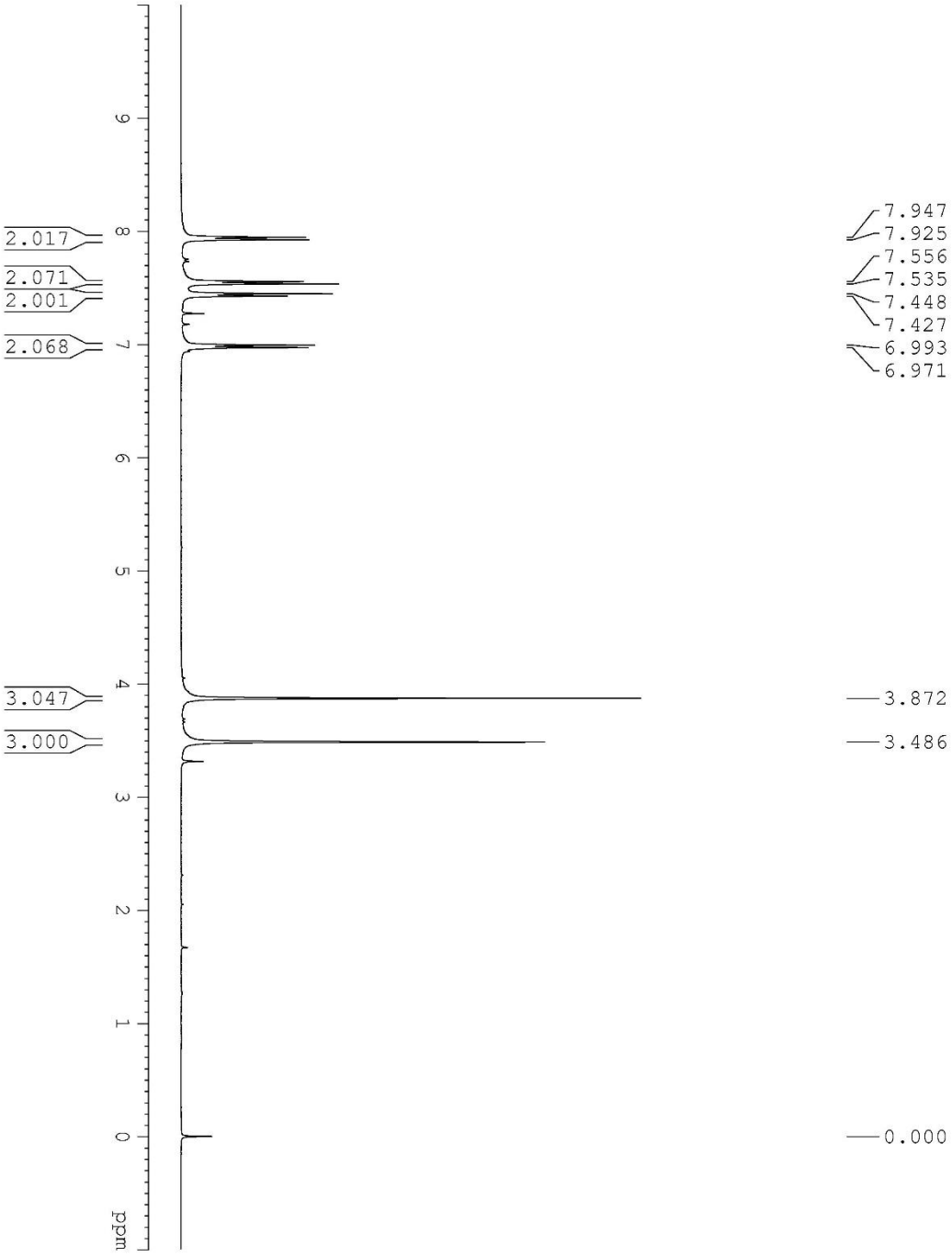

Cl
O
O
N
S
O
O

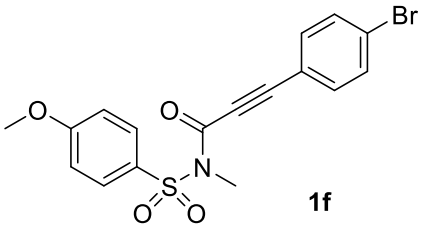
1e


200
180
160
140
120
100
80
60
40
20
0 ppm
164.009
152.443
137.364
133.915
130.370
129.850
129.139
117.991
114.244
92.123
82.343
77.316
76.999
76.680
55.703
33.203

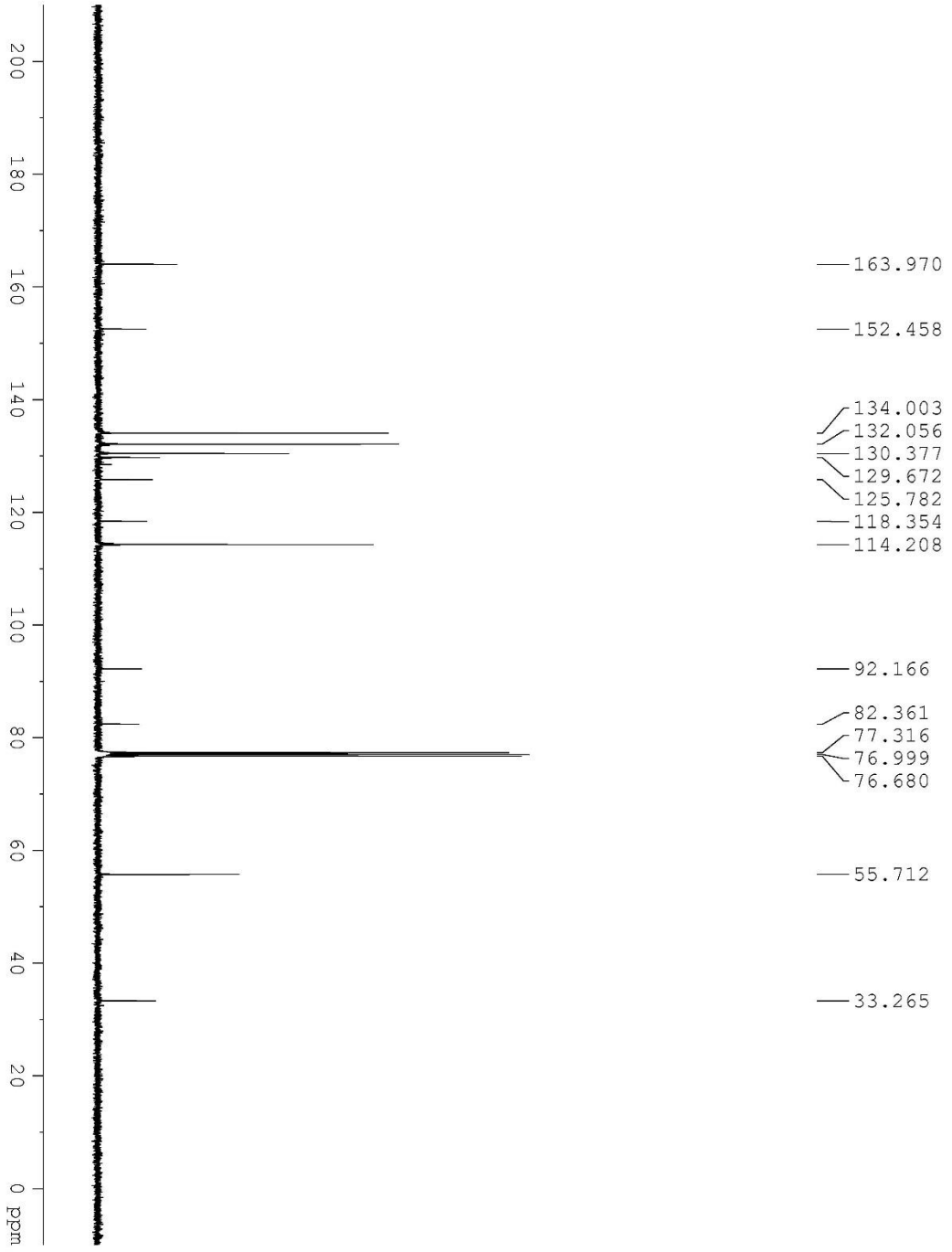

Br
O
O
N
S
O
O

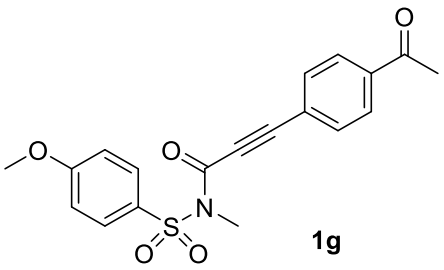
1f


2.017
2.071
2.001
2.068
3.047
3.000
7.947
7.925
7.556
7.535
7.448
7.427
6.993
6.971
3.872
3.486
0.000
ppm

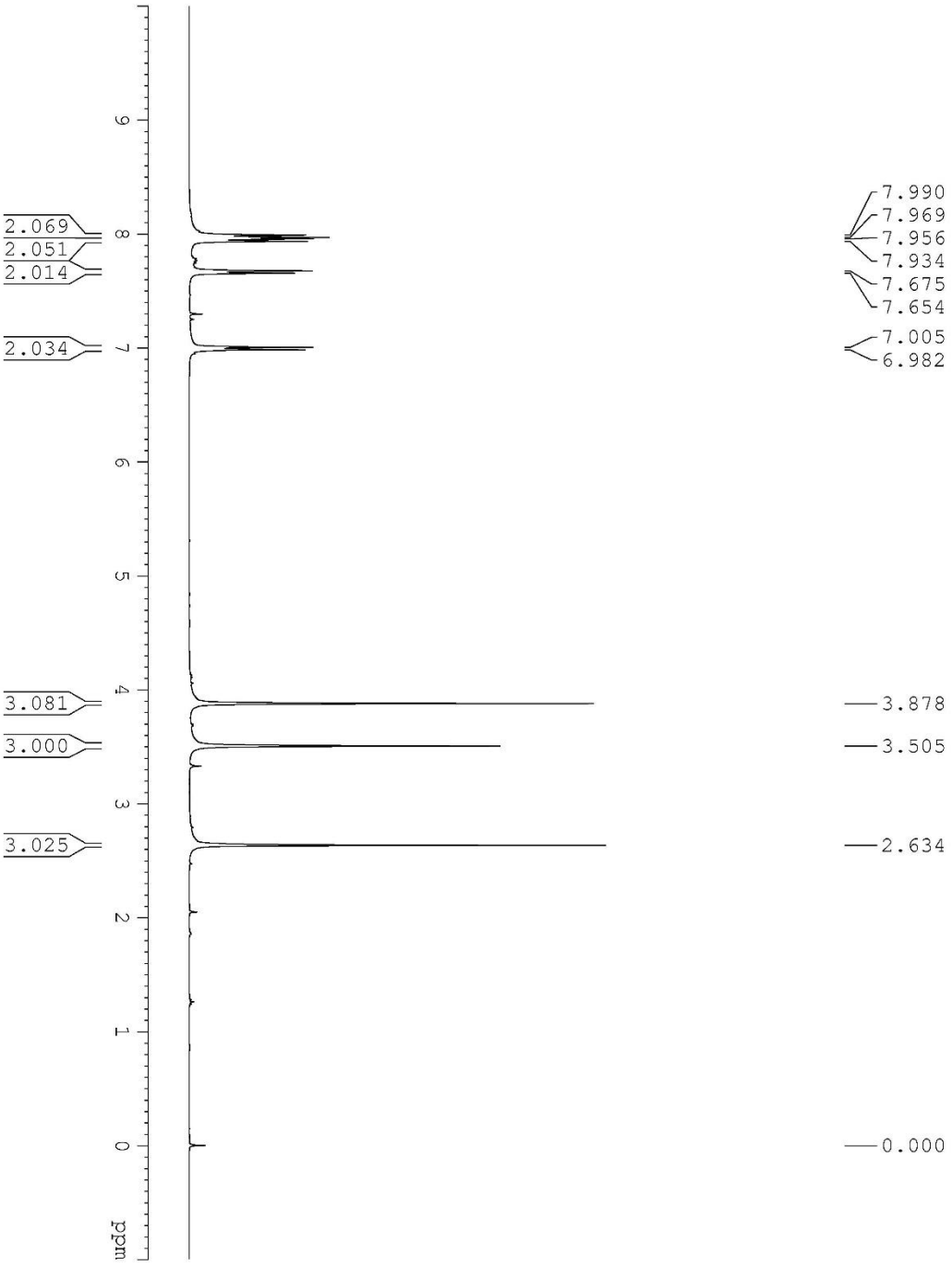

Br
O
O
N
S
O
O

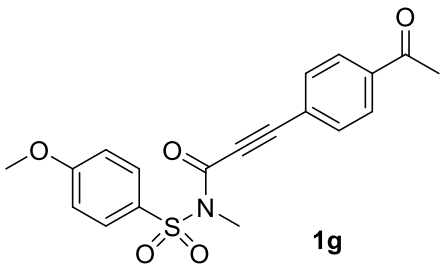
1f


200
180
160
140
120
100
80
60
40
20
0 ppm
163.970
152.458
134.003
132.056
130.377
129.672
125.782
118.354
114.208
92.166
82.361
77.316
76.999
76.680
55.712
33.265

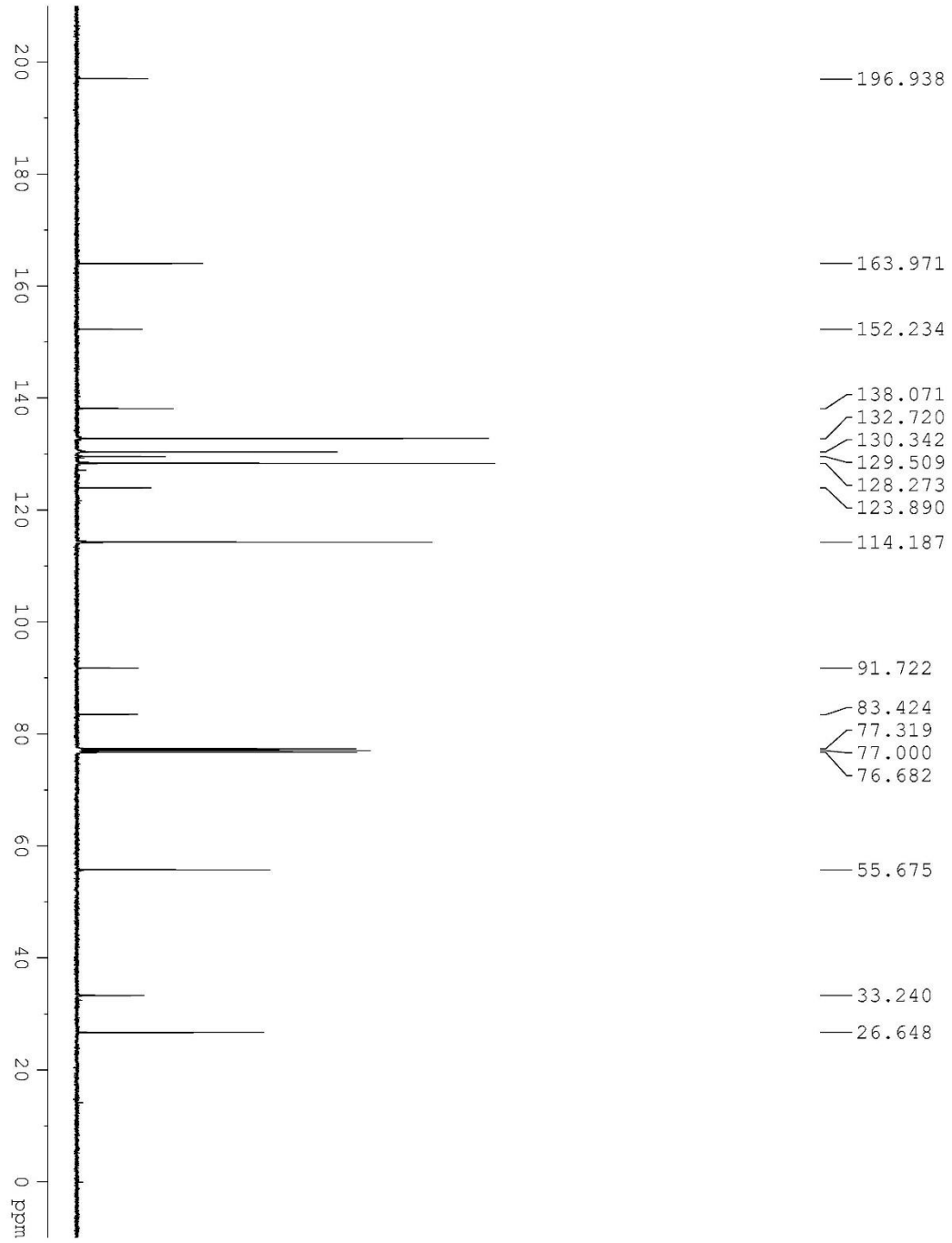


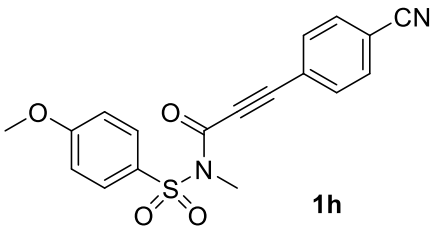
1g


2.069
2.051
2.014
2.034
3.081
3.000
3.025
7.990
7.969
7.956
7.934
7.675
7.654
7.005
6.982
3.878
3.505
2.634
0.000
ppm

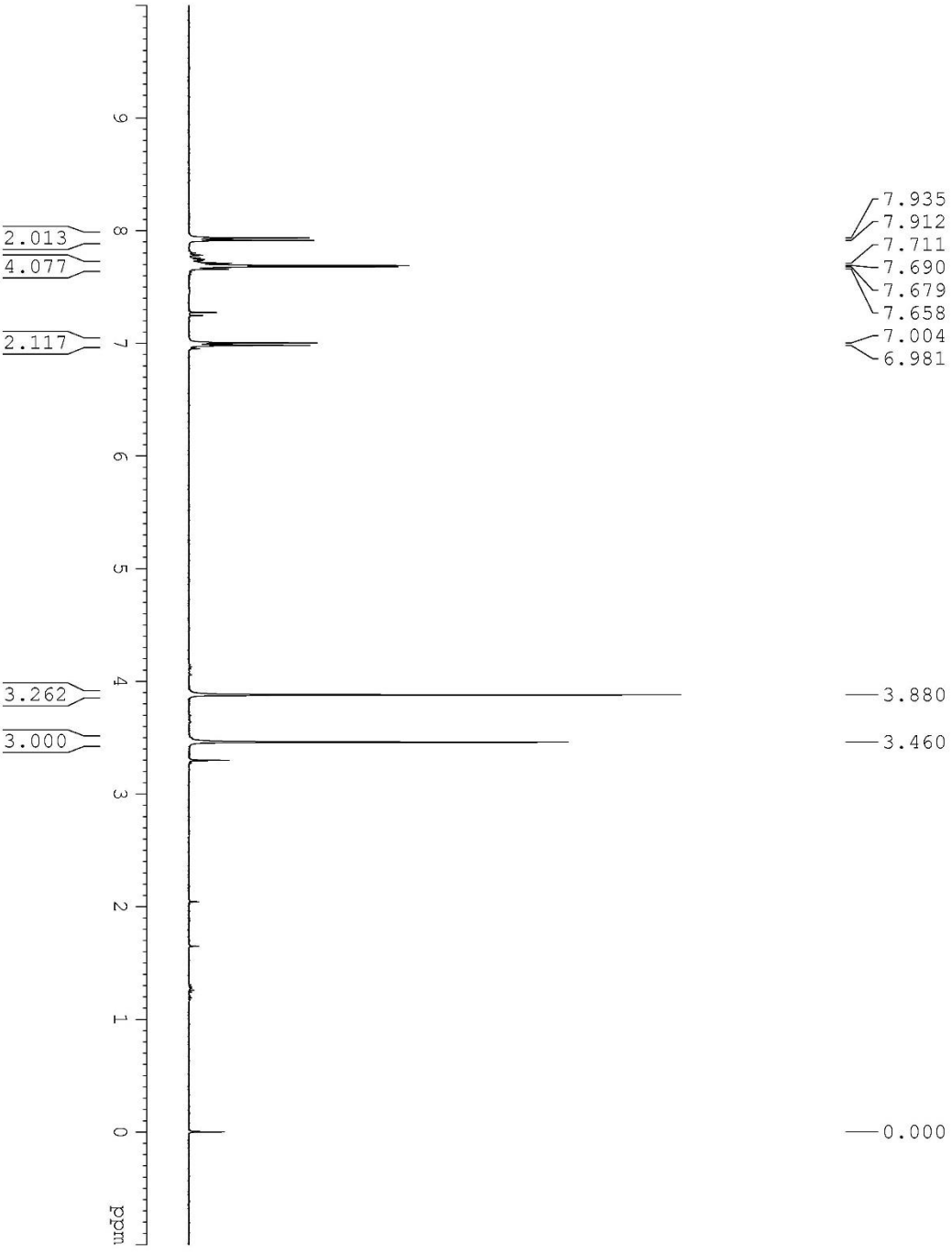

O
O
O
N
S
O
O

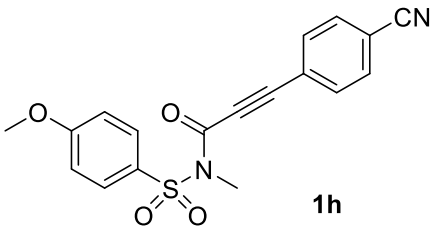
1g


200
180
160
140
120
100
80
60
40
20
0 ppm
196.938
163.971
152.234
138.071
132.720
130.342
129.509
128.273
123.890
114.187
91.722
83.424
77.319
77.000
76.682
55.675
33.240
26.648

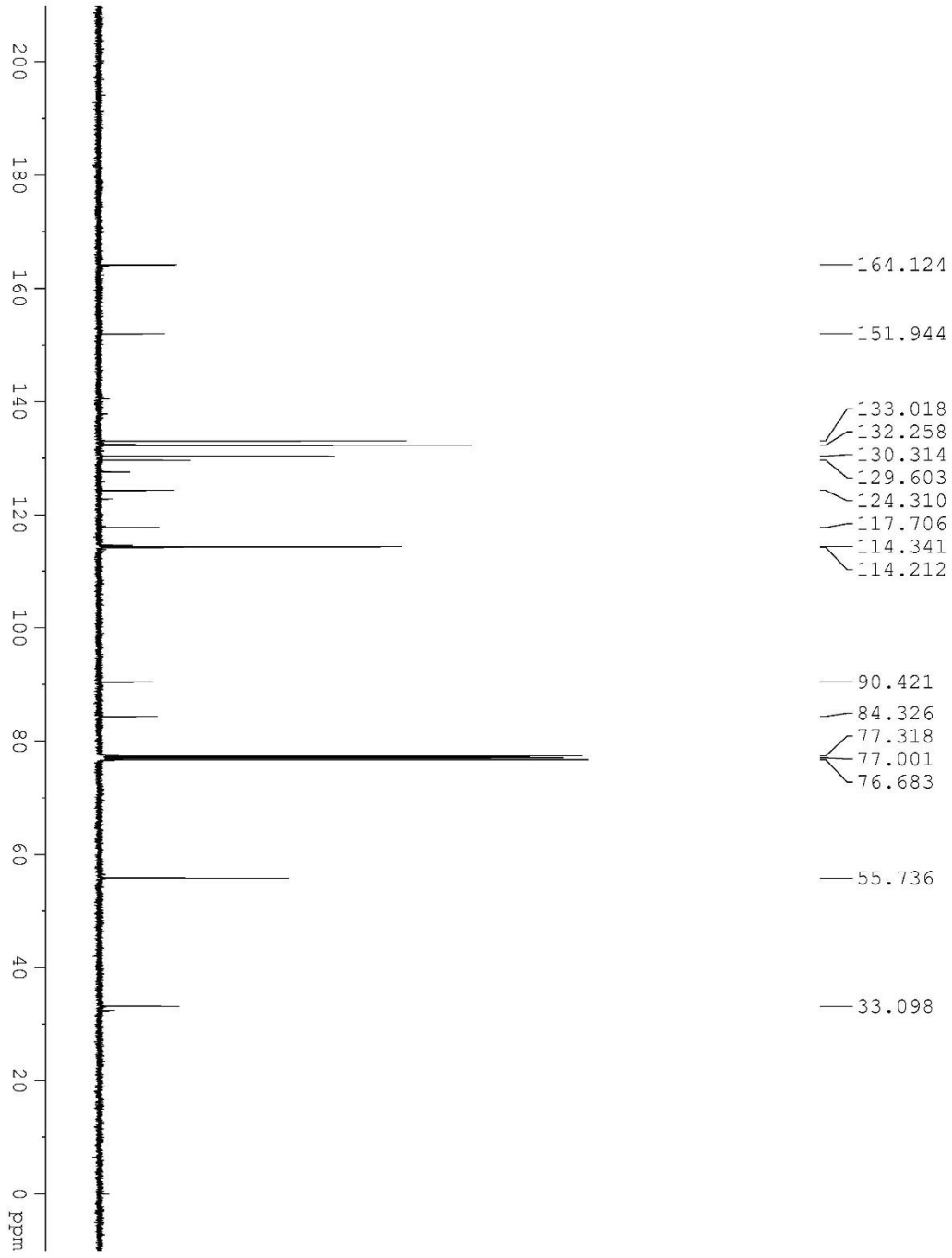

CN
O
O
N
S
O
O

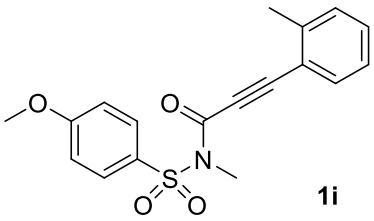
1h


7.935
7.912
7.711
7.690
7.679
7.658
7.004
6.981
3.880
3.460
0.000
2.013
4.077
2.117
3.262
3.000
ppm

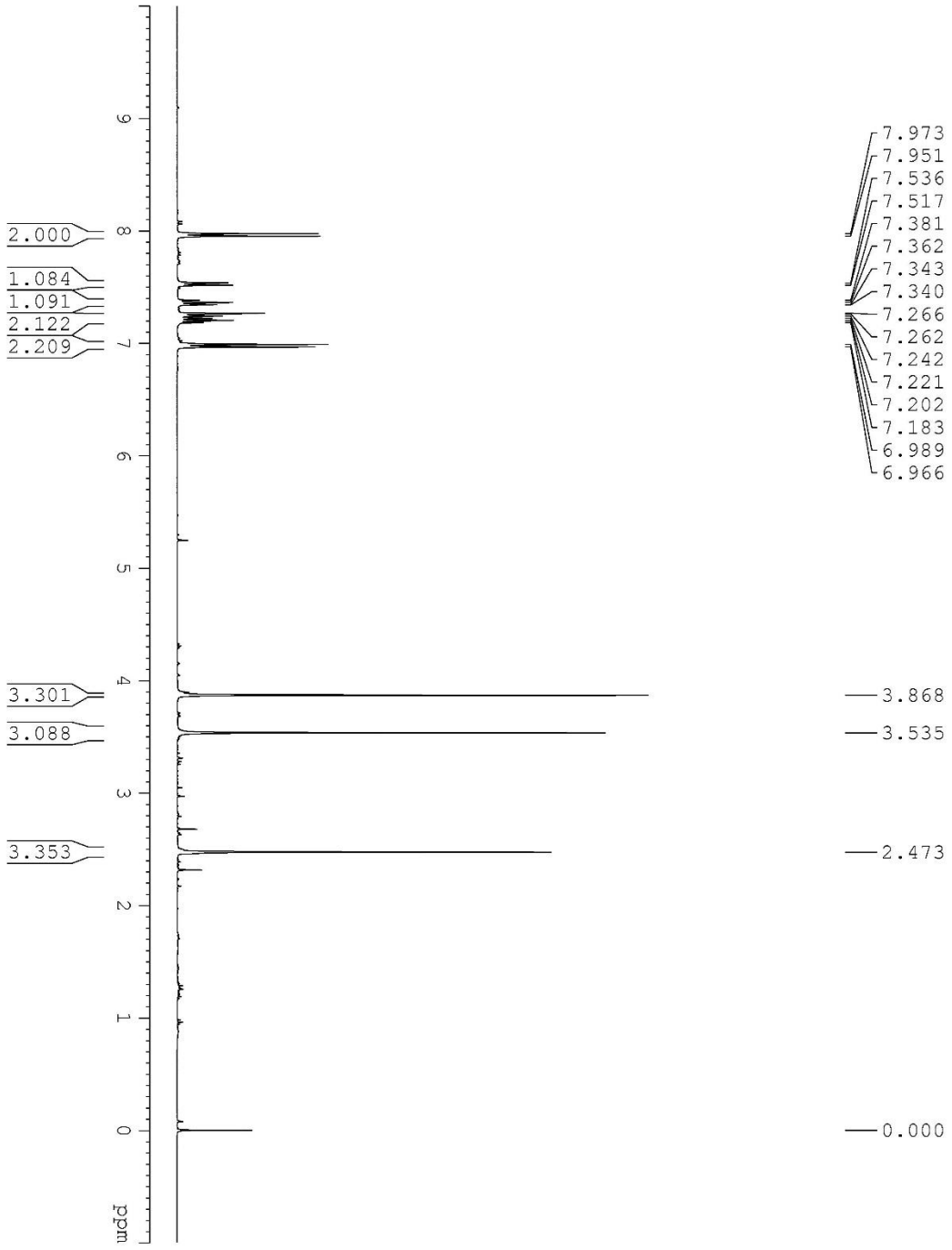

CN
O
O
N
S
O
O

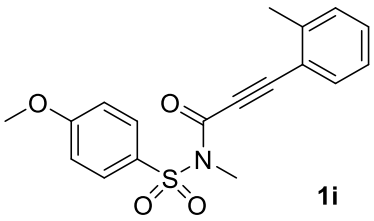
1h


200
180
160
140
120
100
80
60
40
20
0 ppm
164.124
151.944
133.018
132.258
130.314
129.603
124.310
117.706
114.341
114.212
90.421
84.326
77.318
77.001
76.683
55.736
33.098

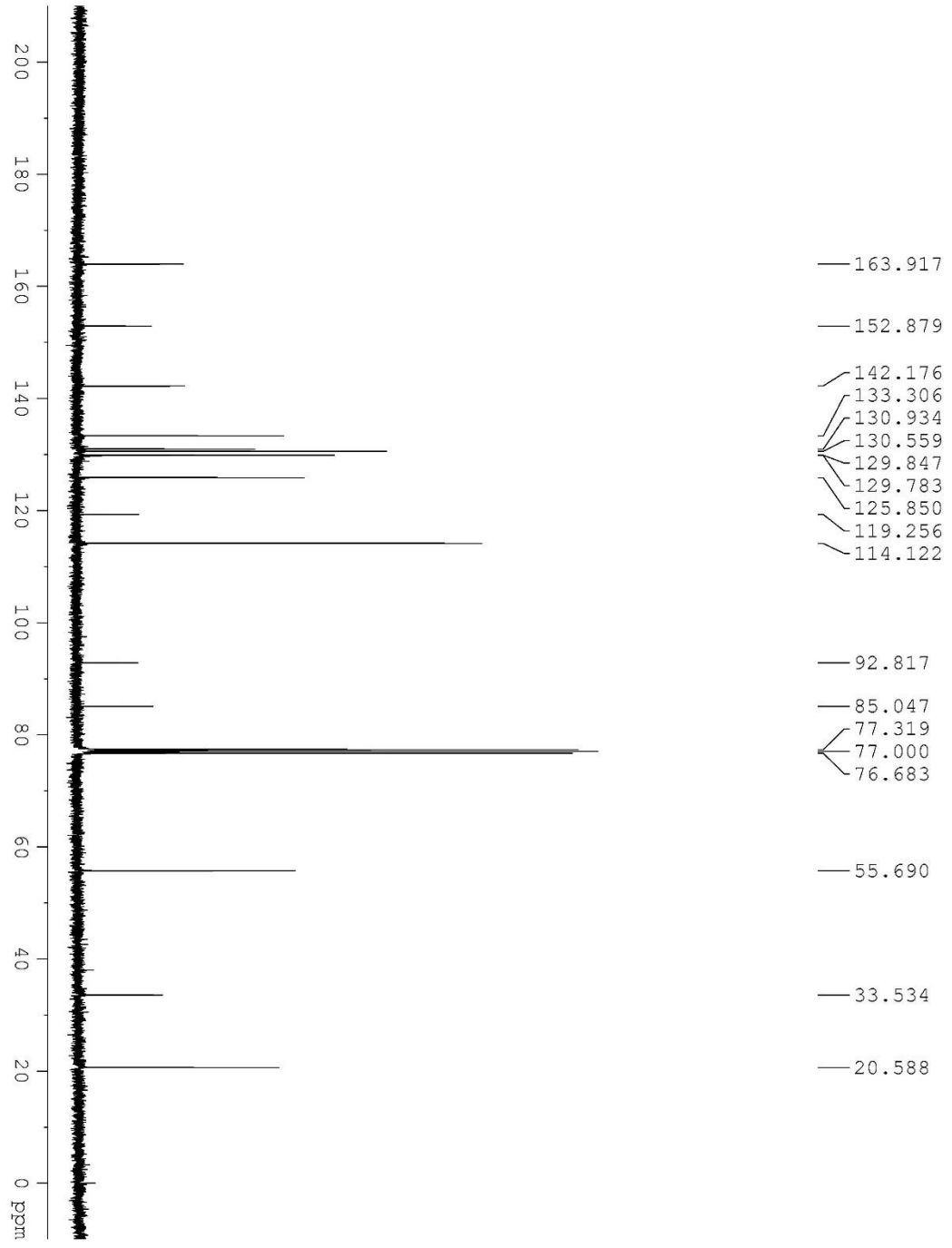

O
O
N
S
O
O

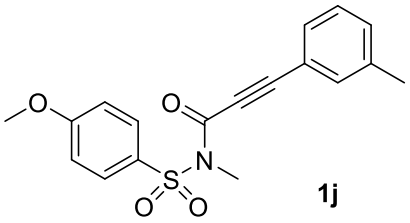
1i


2.000
1.084
1.091
2.122
2.209
3.301
3.088
3.353
7.973
7.951
7.536
7.517
7.381
7.362
7.343
7.340
7.266
7.262
7.242
7.221
7.202
7.183
6.989
6.966
3.868
3.535
2.473
0.000
ppm

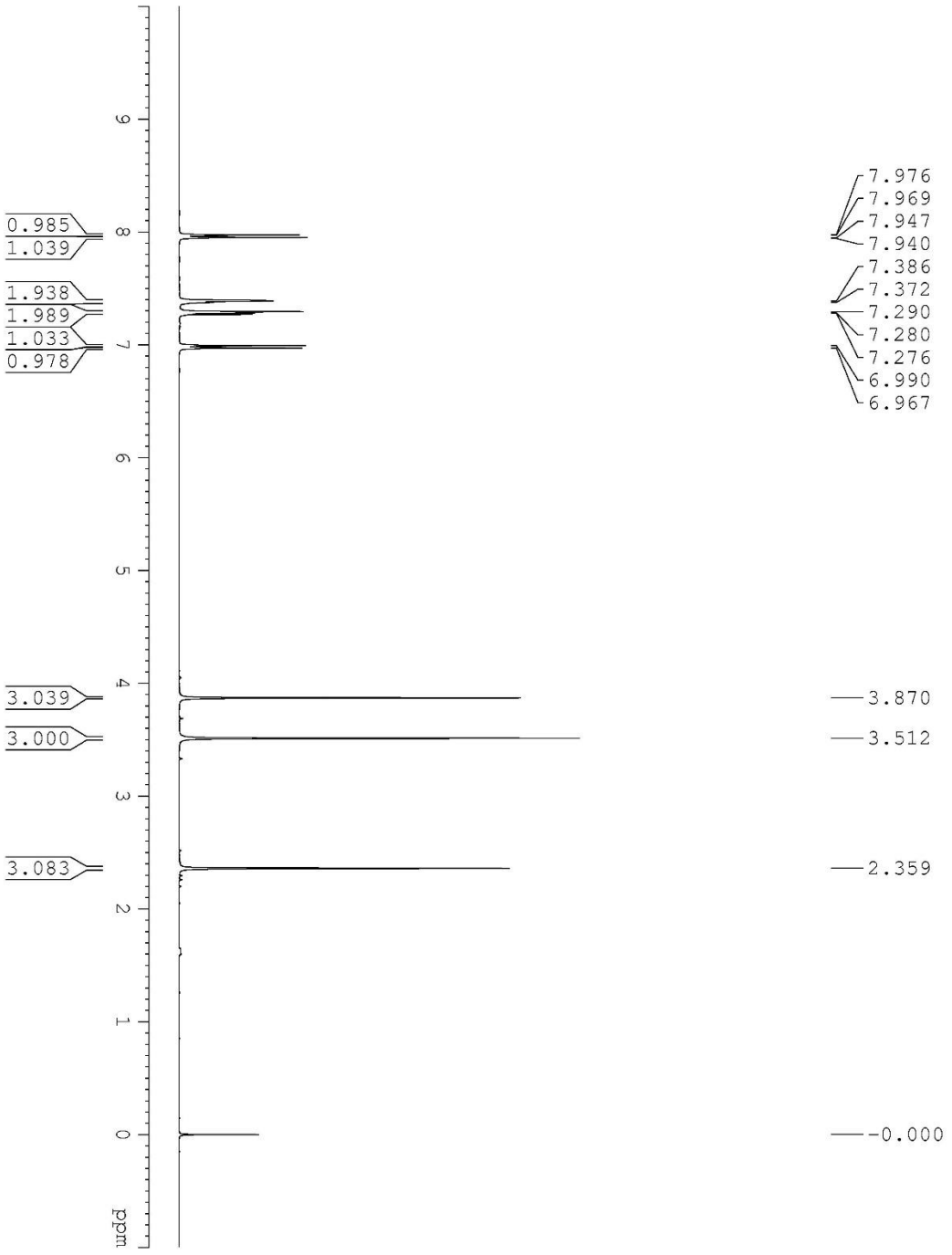


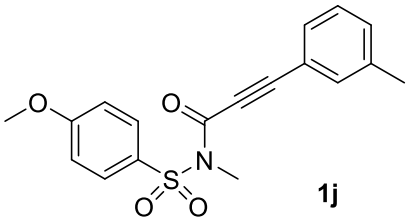
1i


200
180
160
140
120
100
80
60
40
20
0 ppm
163.917
152.879
142.176
133.306
130.934
130.559
129.847
129.783
125.850
119.256
114.122
92.817
85.047
77.319
77.000
76.683
55.690
33.534
20.588

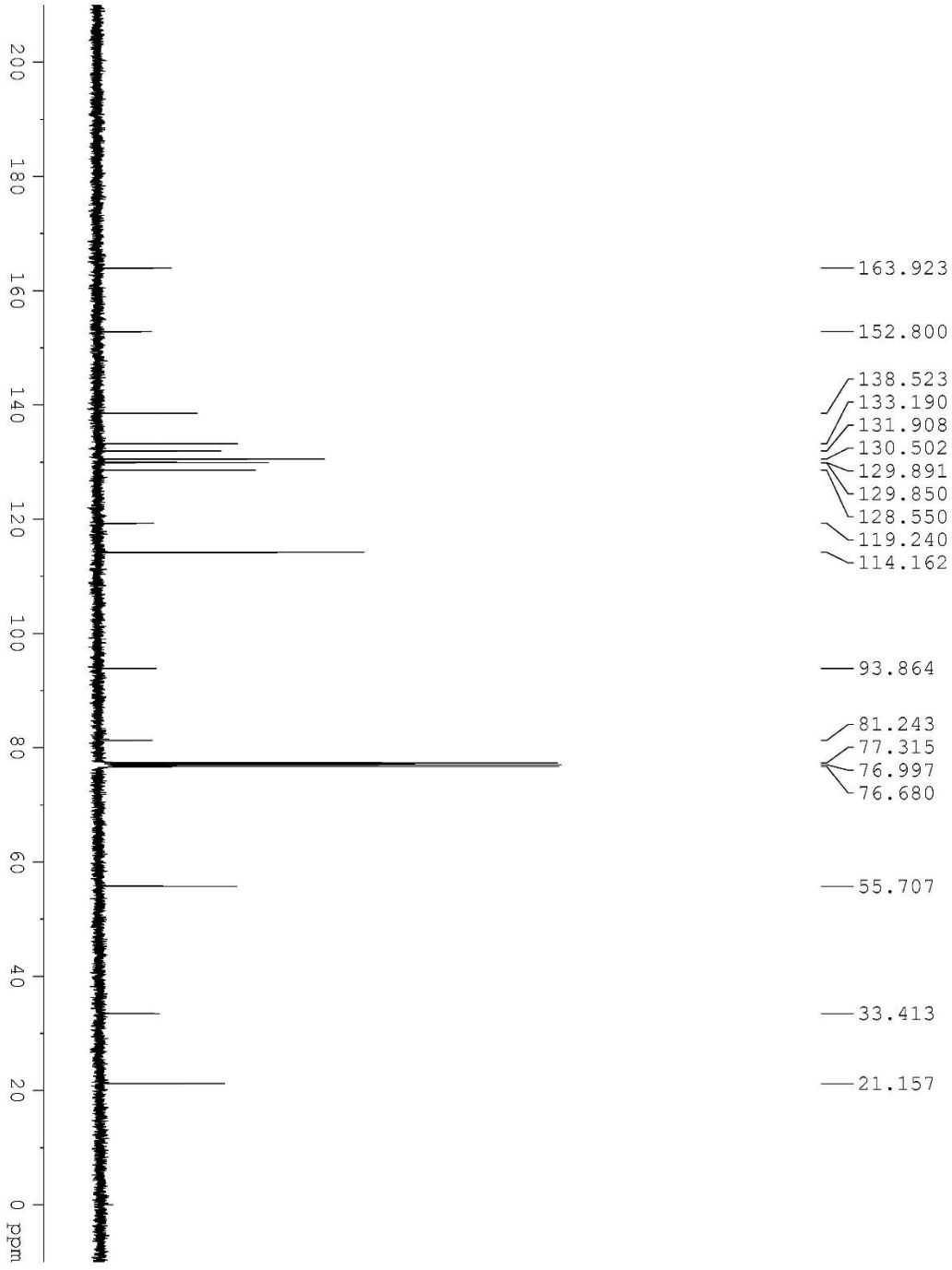


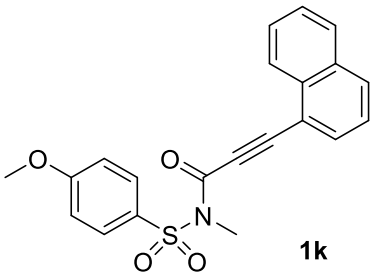
1j


0.985
1.039
1.938
1.989
1.033
0.978
3.039
3.000
3.083
7.976
7.969
7.947
7.940
7.386
7.372
7.290
7.280
7.276
6.990
6.967
3.870
3.512
2.359
-0.000
ppm

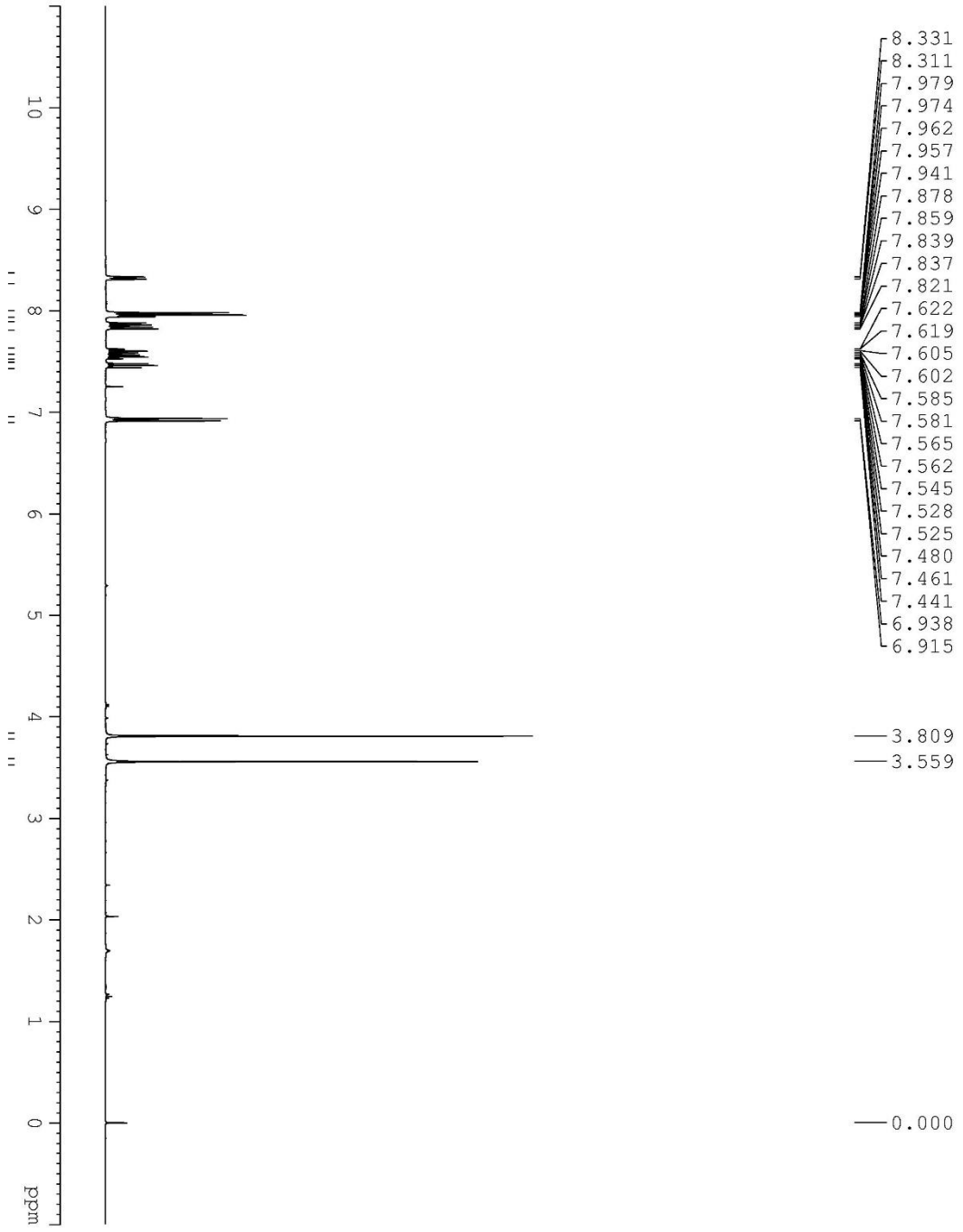


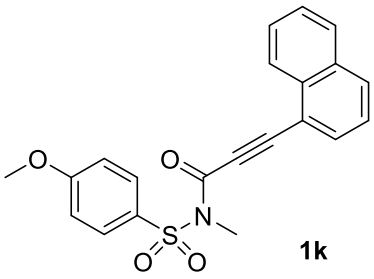
1j


200
180
160
140
120
100
80
60
40
20
0 ppm
163.923
152.800
138.523
133.190
131.908
130.502
129.891
129.850
128.550
119.240
114.162
93.864
81.243
77.315
76.997
76.680
55.707
33.413
21.157

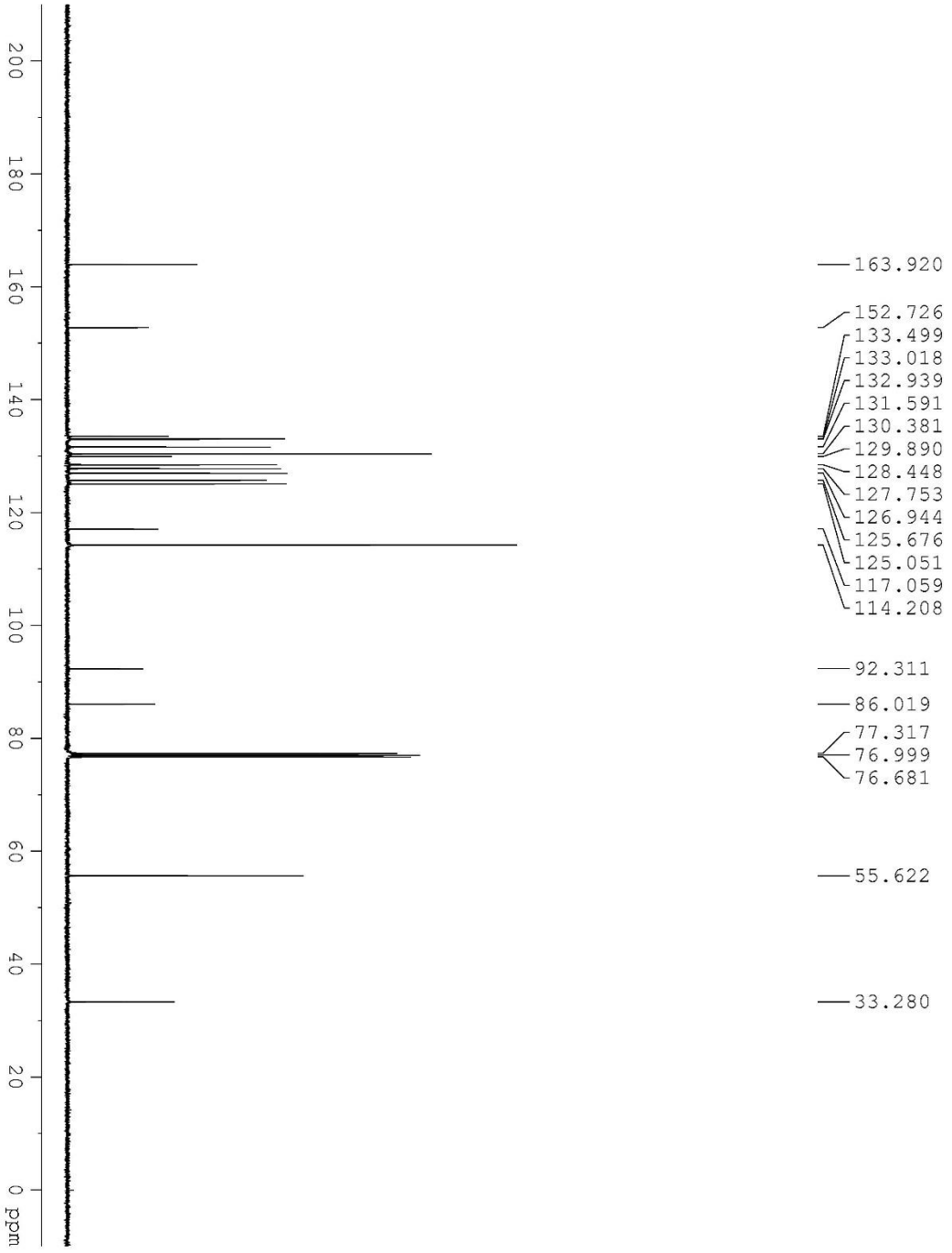


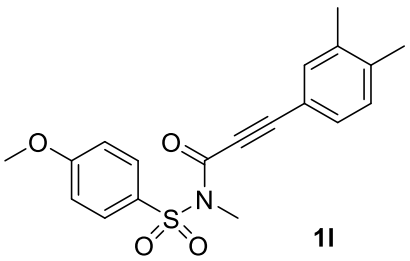
1k


8.331
8.311
7.979
7.974
7.962
7.957
7.941
7.878
7.859
7.839
7.837
7.821
7.622
7.619
7.605
7.602
7.585
7.581
7.565
7.562
7.545
7.528
7.525
7.480
7.461
7.441
6.938
6.915
3.809
3.559
0.000
ppm

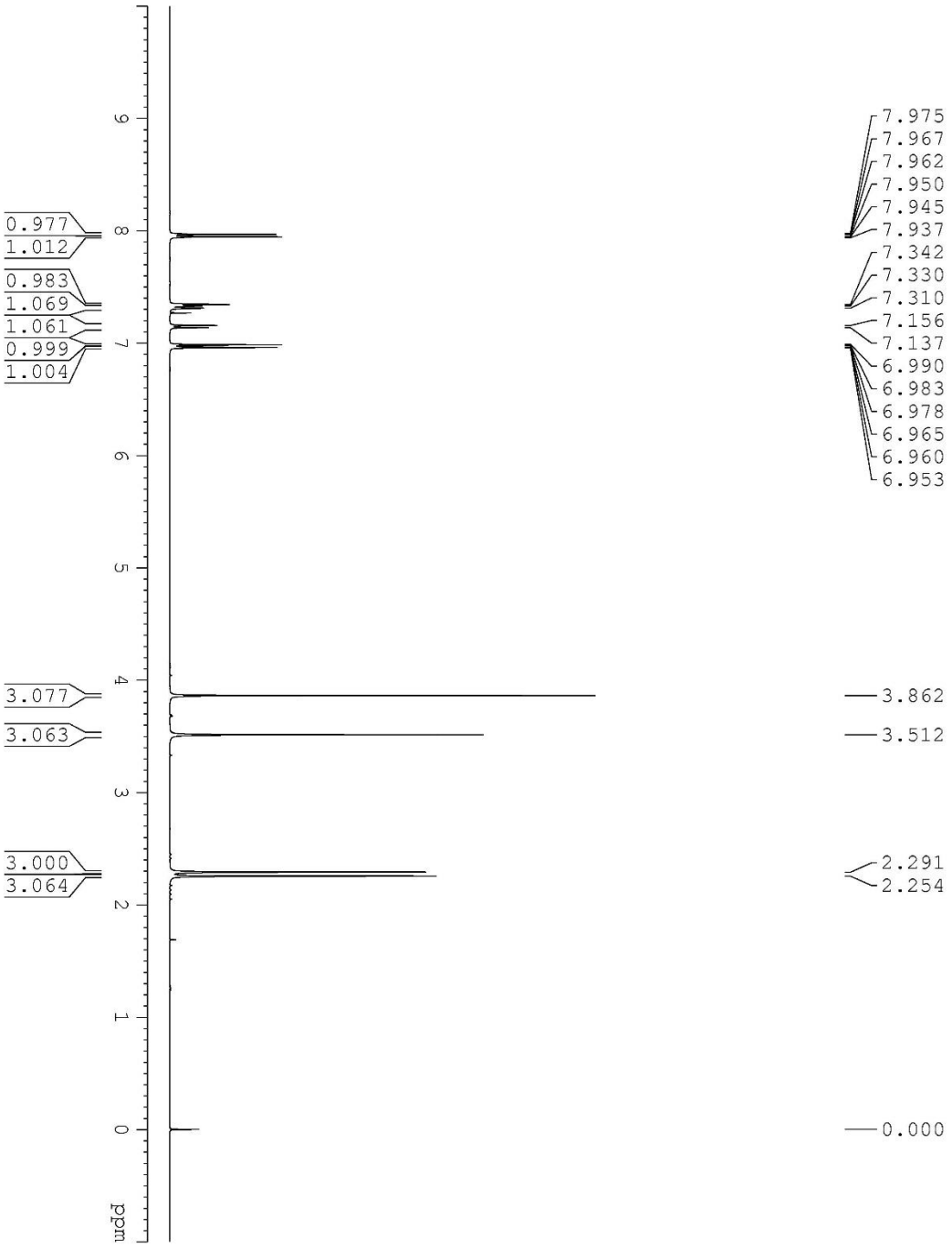

O
O
N
S
O
O

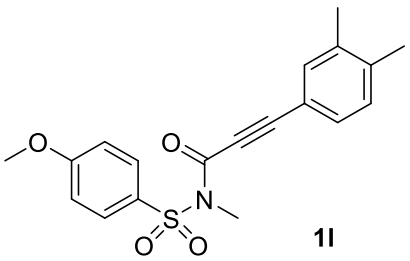
1k


200
180
160
140
120
100
80
60
40
20
0 ppm
163.920
152.726
133.499
133.018
132.939
131.591
130.381
129.890
128.448
127.753
126.944
125.676
125.051
117.059
114.208
92.311
86.019
77.317
76.999
76.681
55.622
33.280

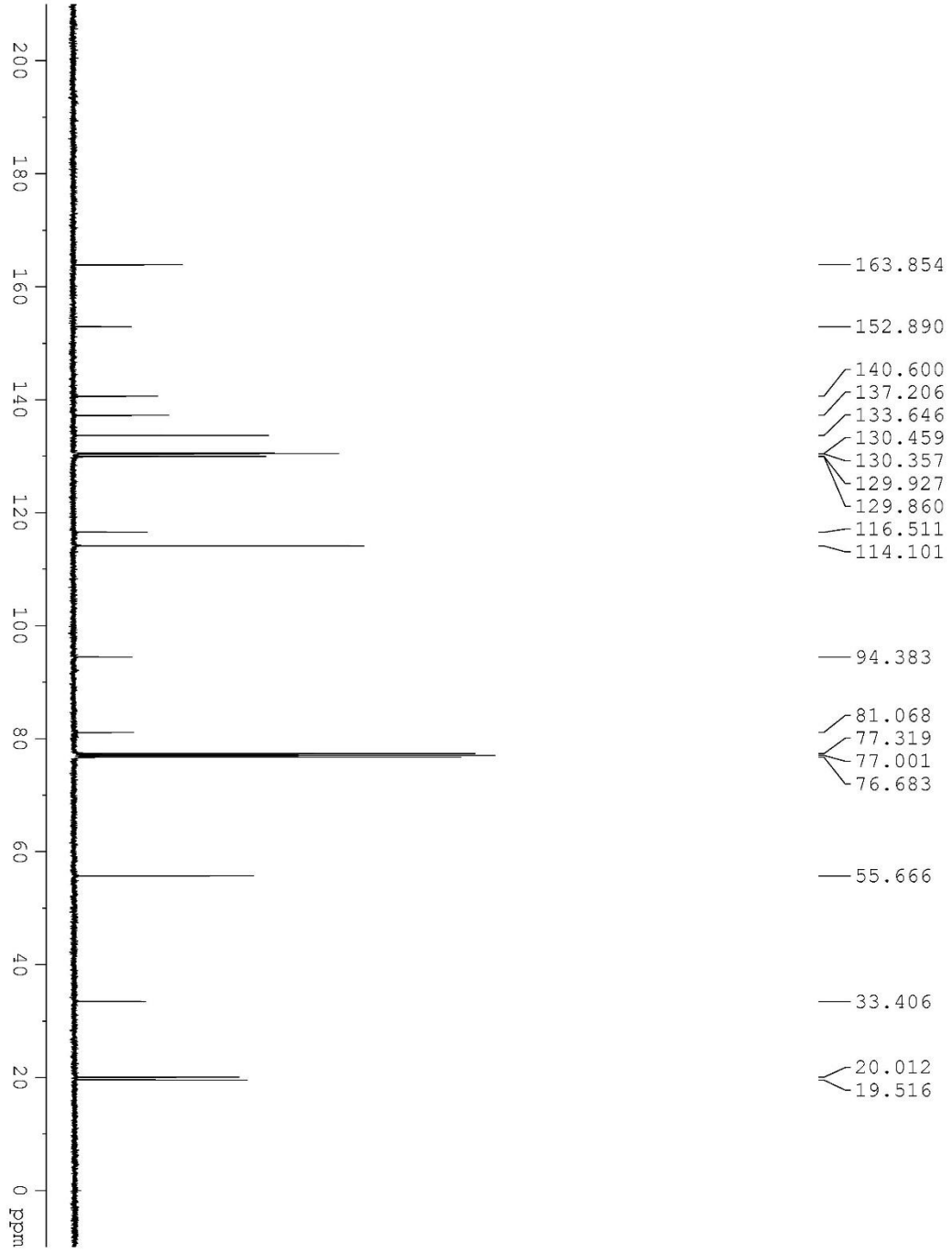


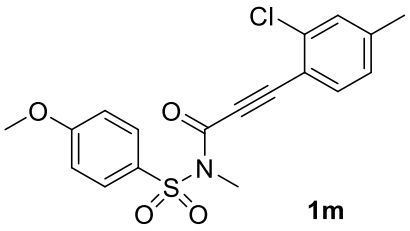
1l


0.977
1.012
0.983
1.069
1.061
0.999
1.004
3.077
3.063
3.000
3.064
7.975
7.967
7.962
7.950
7.945
7.937
7.342
7.330
7.310
7.156
7.137
6.990
6.983
6.978
6.965
6.960
6.953
3.862
3.512
2.291
2.254
0.000
ppm

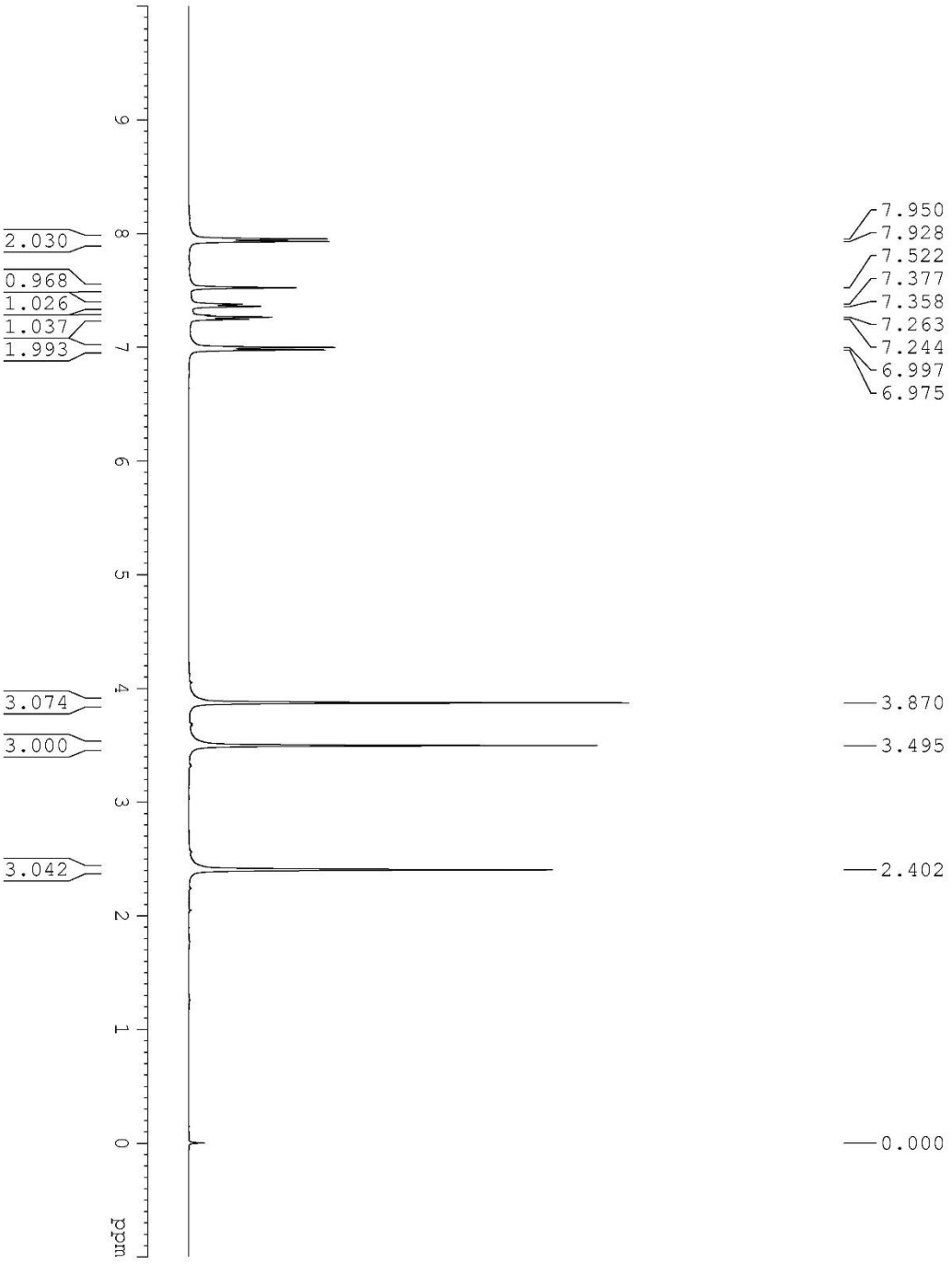


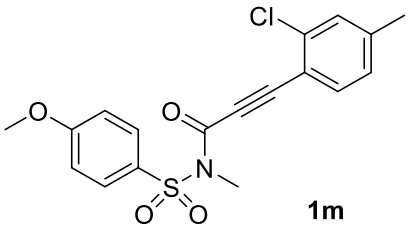
1l


200
180
160
140
120
100
80
60
40
20
0 ppm
163.854
152.890
140.600
137.206
133.646
130.459
130.357
129.927
129.860
116.511
114.101
94.383
81.068
77.319
77.001
76.683
55.666
33.406
20.012
19.516

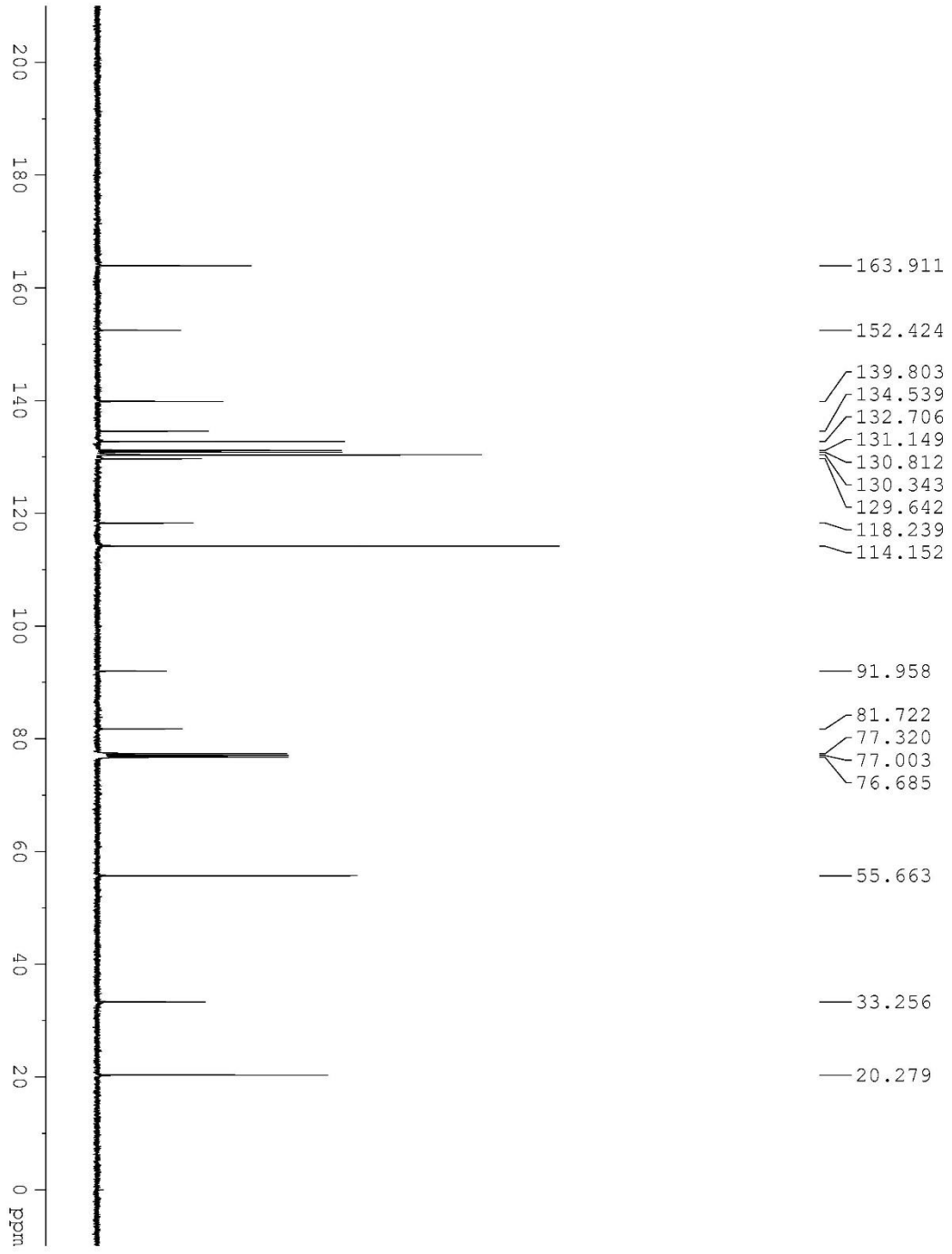

Cl
O
O
N
S
O
O
O

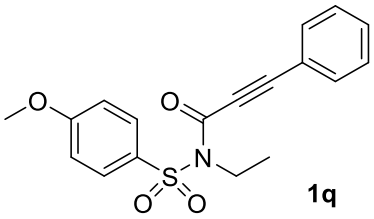
1m


7.950
7.928
7.522
7.377
7.358
7.263
7.244
6.997
6.975
3.870
3.495
2.402
0.000
2.030
0.968
1.026
1.037
1.993
3.074
3.000
3.042
ppm

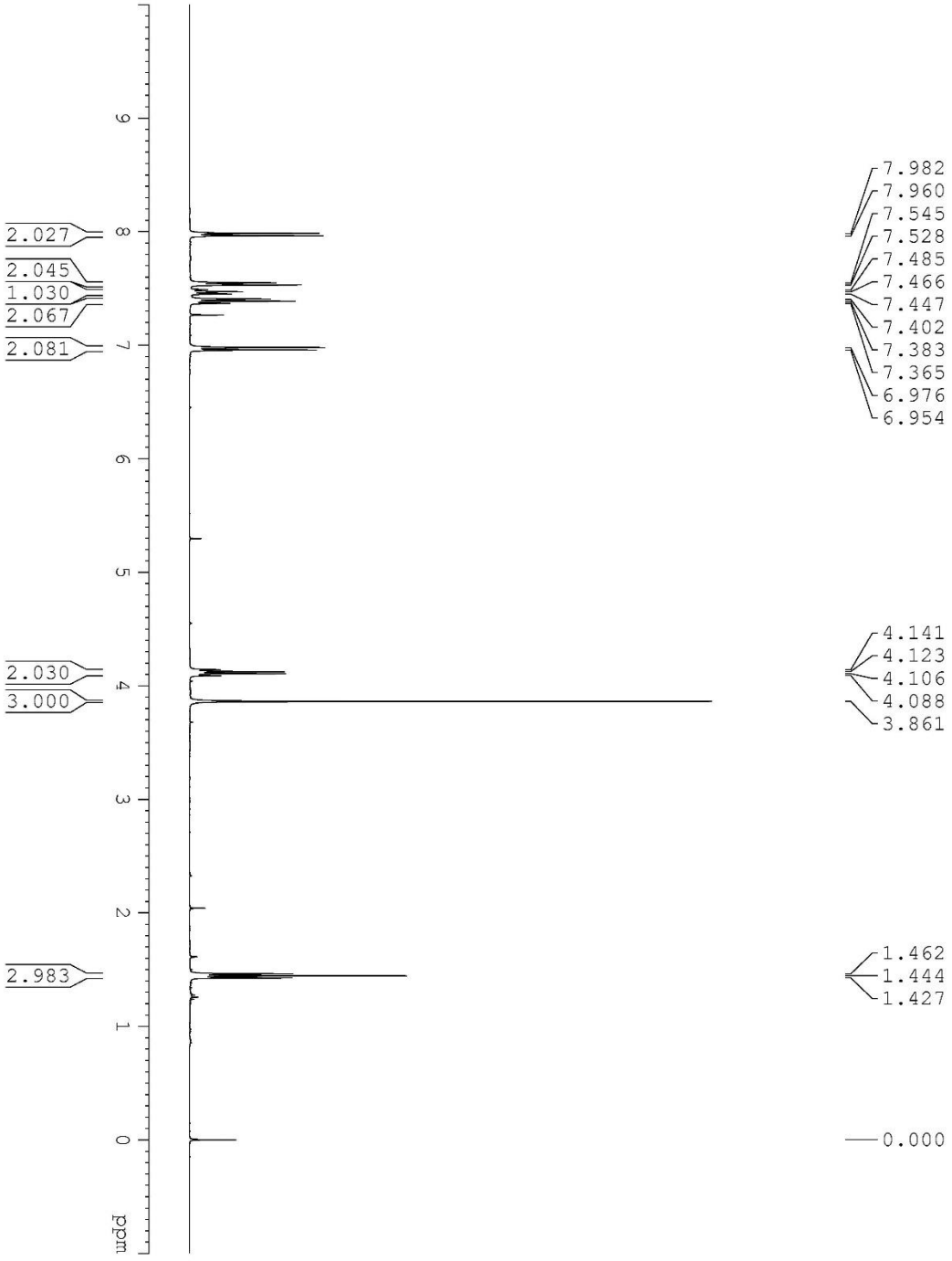

Cl
O
O
N
S
O
O

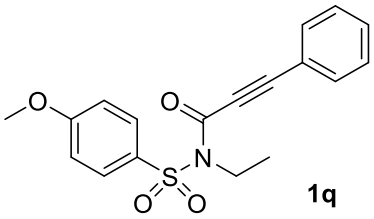
1m


200
180
160
140
120
100
80
60
40
20
0 ppm
163.911
152.424
139.803
134.539
132.706
131.149
130.812
130.343
129.642
118.239
114.152
91.958
81.722
77.320
77.003
76.685
55.663
33.256
20.279

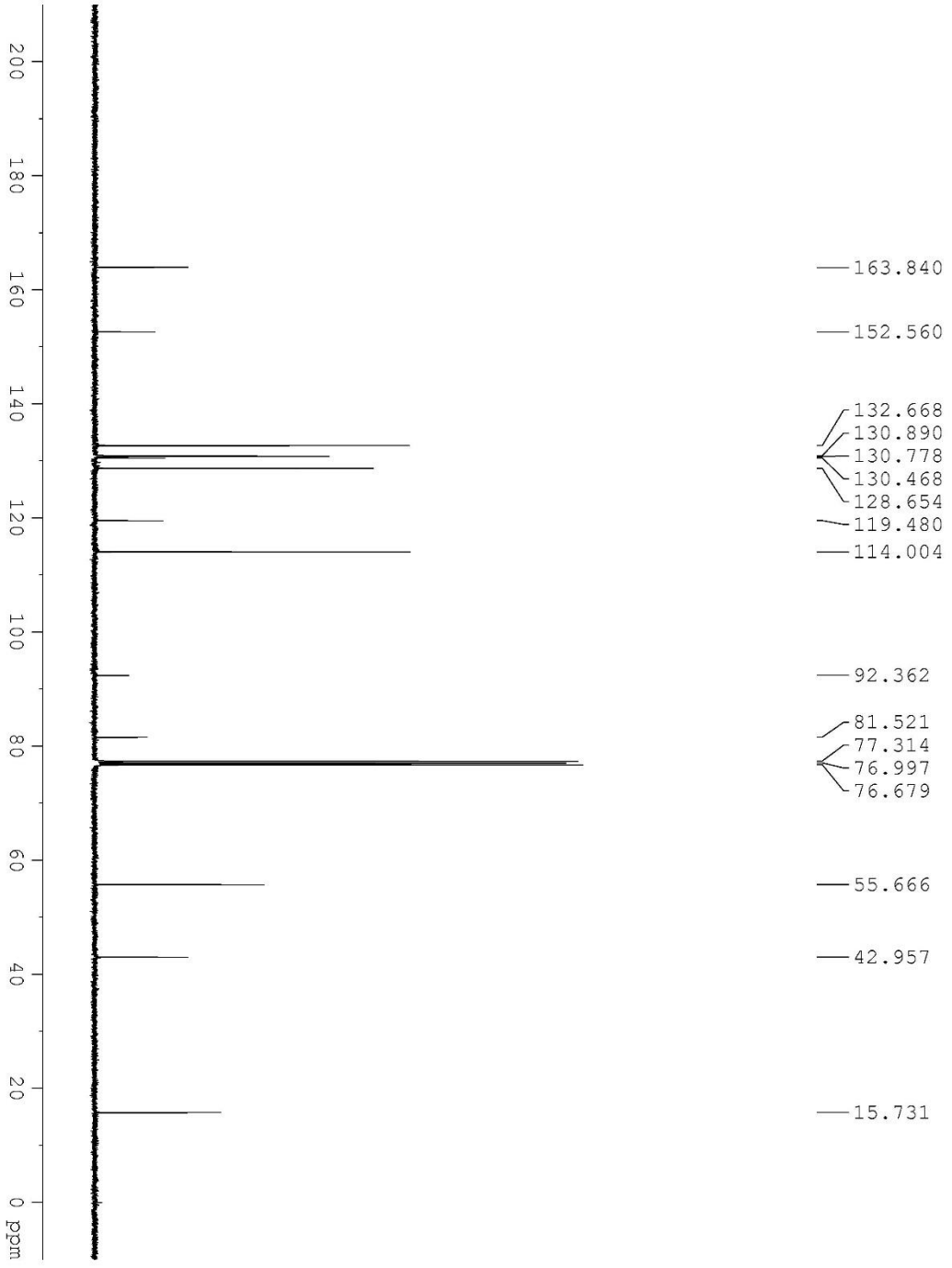


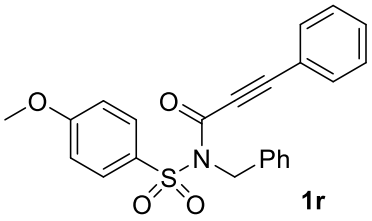
1q


2.027
2.045
1.030
2.067
2.081
2.030
3.000
2.983
7.982
7.960
7.545
7.528
7.485
7.466
7.447
7.402
7.383
7.365
6.976
6.954
4.141
4.123
4.106
4.088
3.861
1.462
1.444
1.427
0.000
ppm

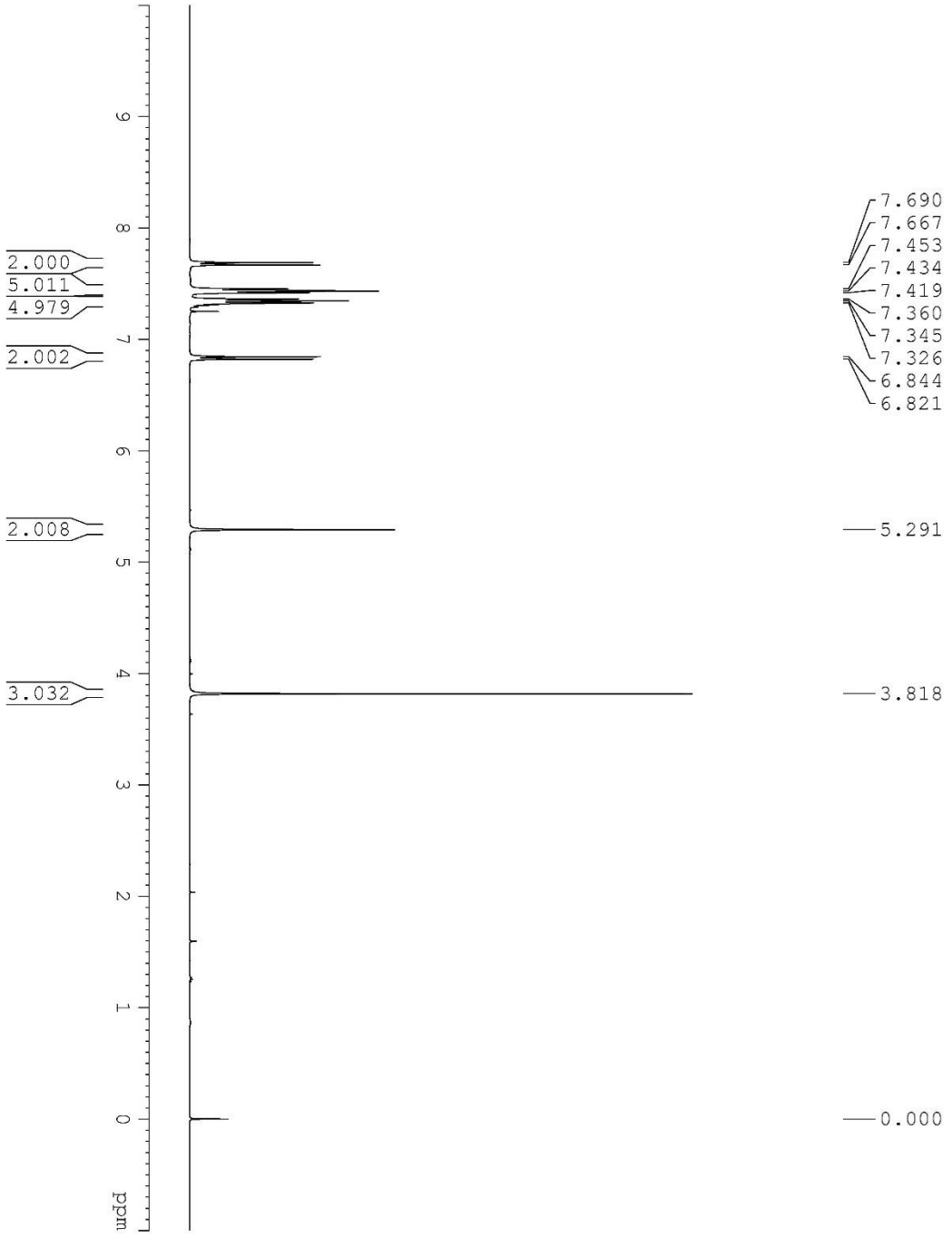

O
O
N
S
O
O

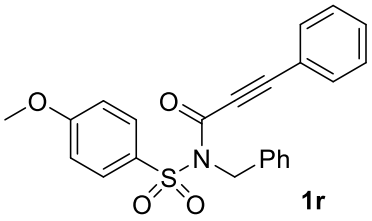
1q


200
180
160
140
120
100
80
60
40
20
0 ppm
163.840
152.560
132.668
130.890
130.778
130.468
128.654
119.480
114.004
92.362
81.521
77.314
76.997
76.679
55.666
42.957
15.731

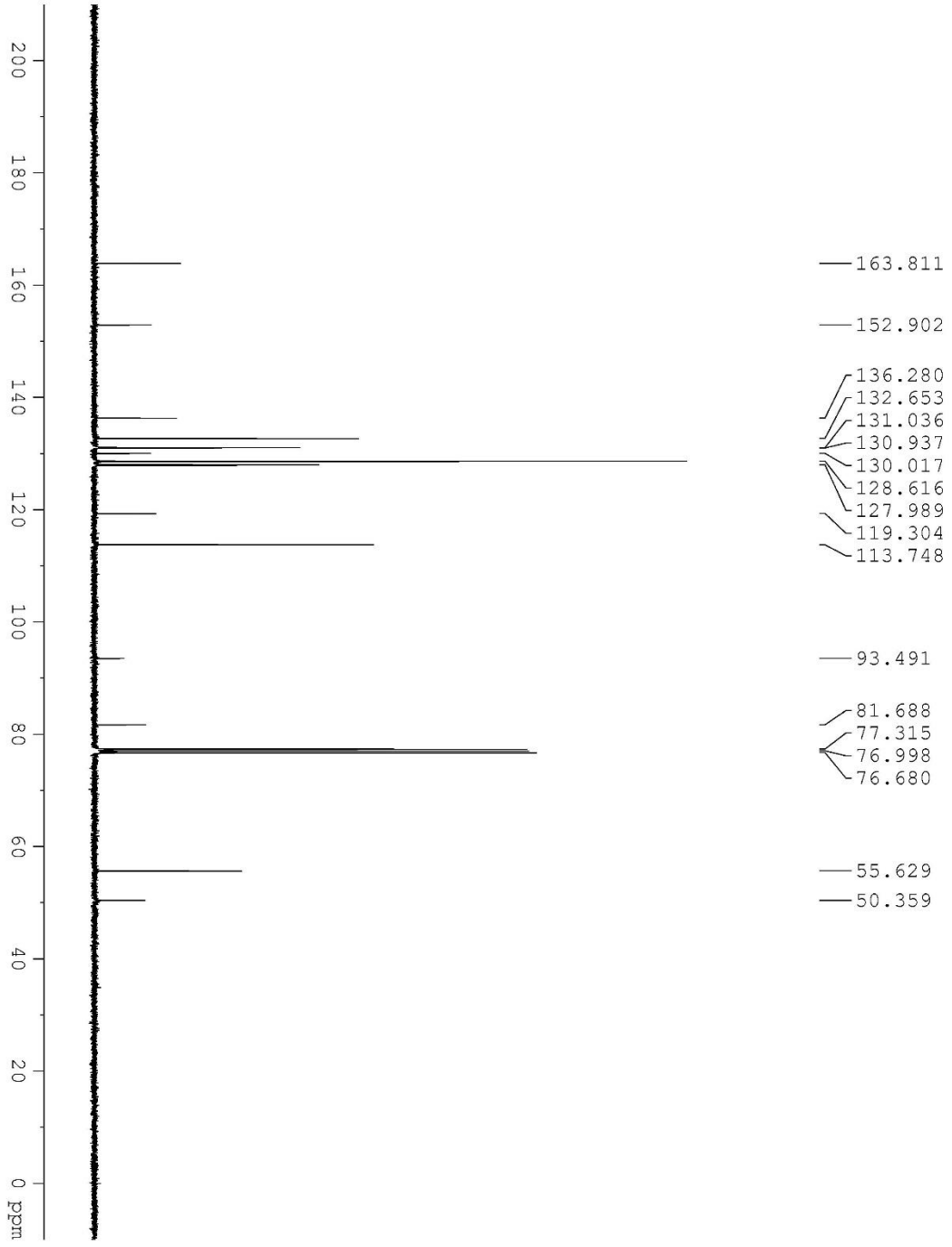

O
O
N
Ph
S
O
O

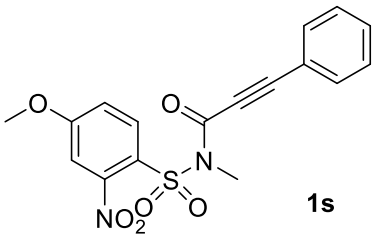
1r


2.000
5.011
4.979
2.002
2.008
3.032
7.690
7.667
7.453
7.434
7.419
7.360
7.345
7.326
6.844
6.821
5.291
3.818
0.000
ppm

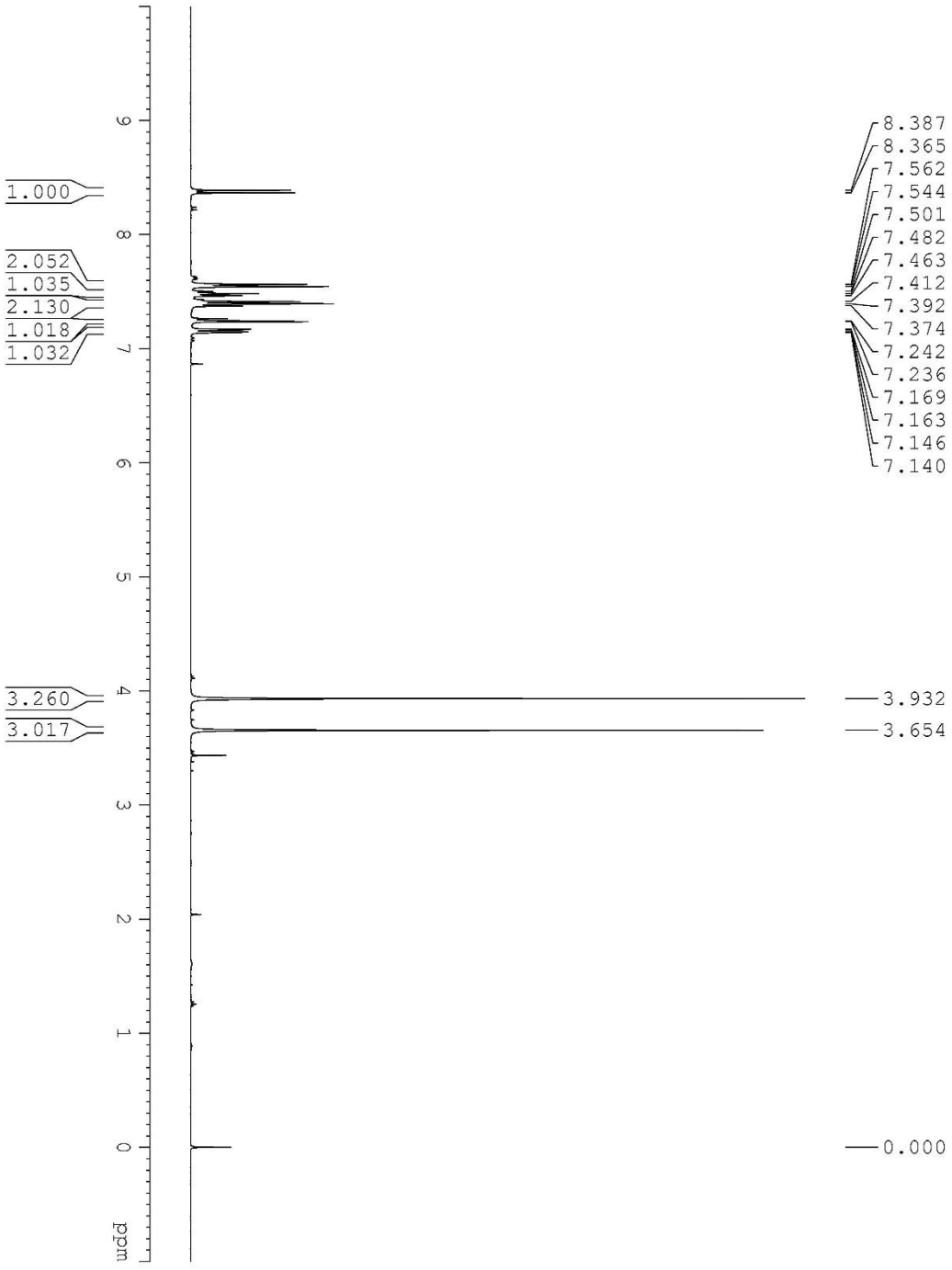

O
O
N
Ph
S
O
O

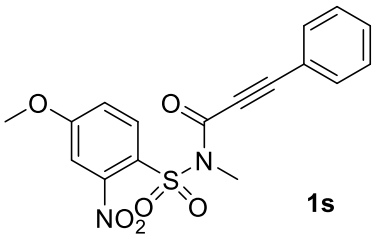
1r


200
180
160
140
120
100
80
60
40
20
0 ppm
163.811
152.902
136.280
132.653
131.036
130.937
130.017
128.616
127.989
119.304
113.748
93.491
81.688
77.315
76.998
76.680
55.629
50.359

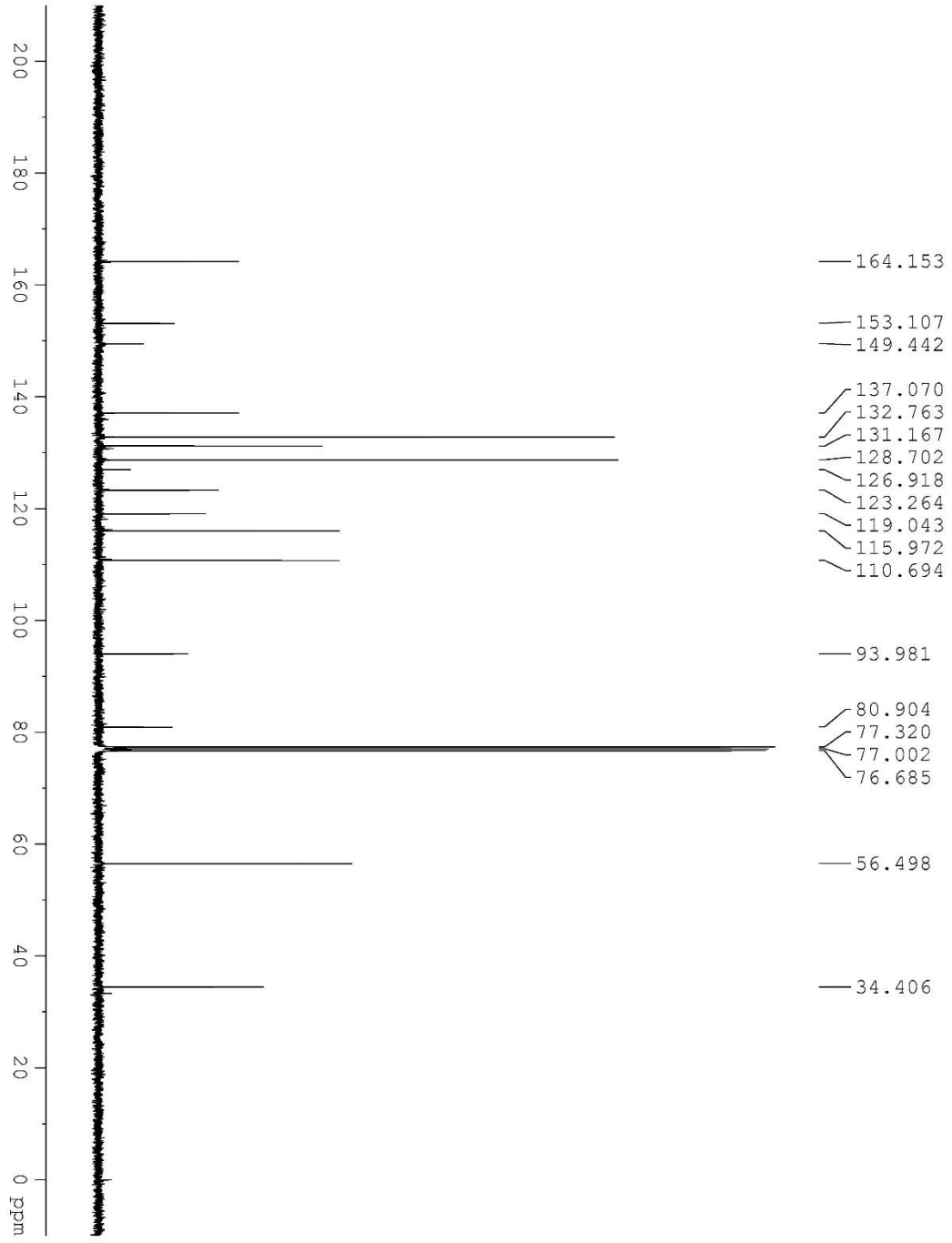

O
O
N
S
O
O
NO2

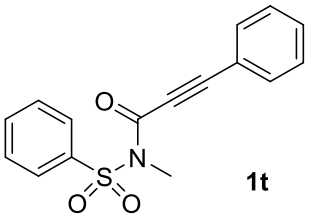
1s


1.000
2.052
1.035
2.130
1.018
1.032
3.260
3.017
8.387
8.365
7.562
7.544
7.501
7.482
7.463
7.412
7.392
7.374
7.242
7.236
7.169
7.163
7.146
7.140
3.932
3.654
0.000
ppm

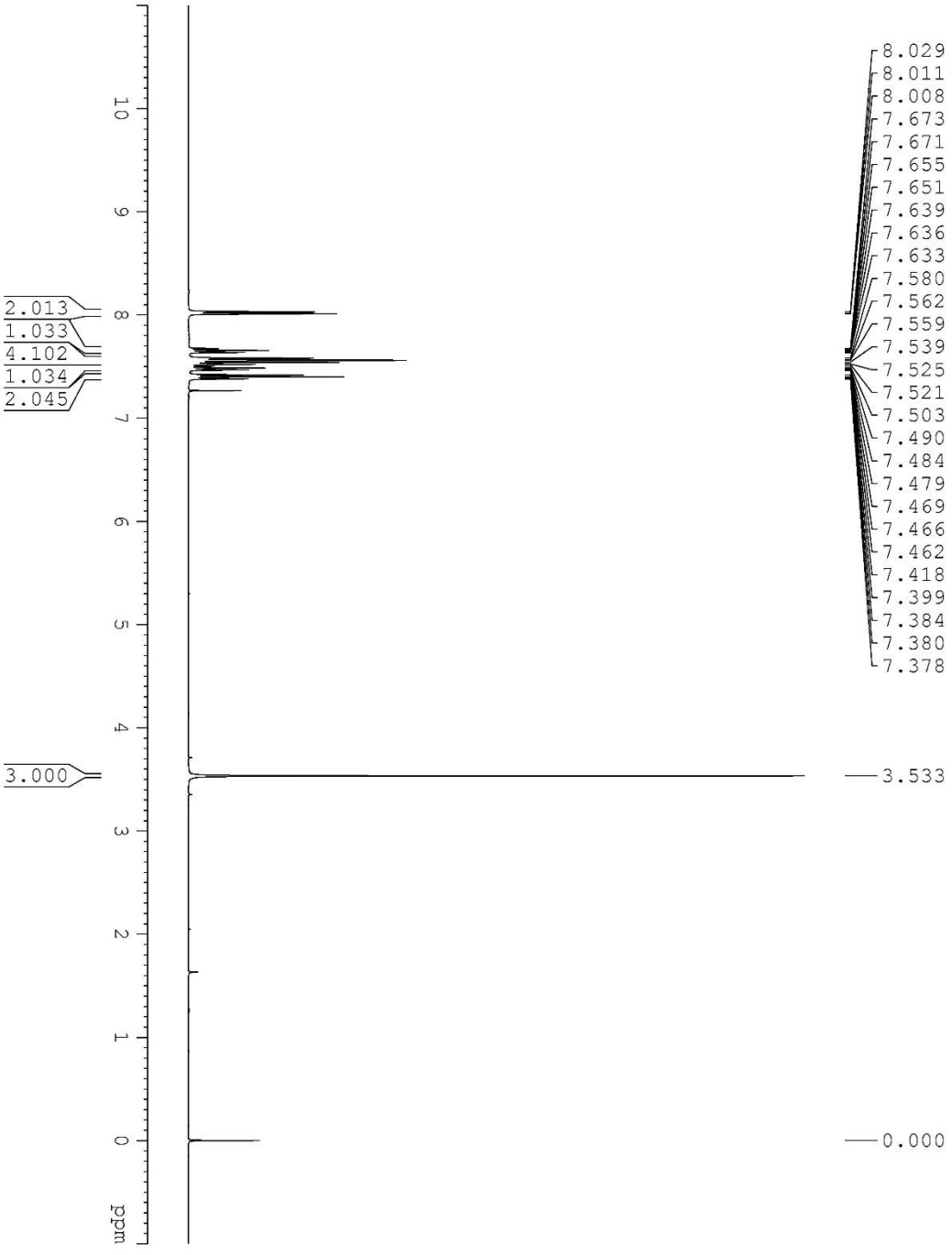

O
O
N
S
O
O
NO2

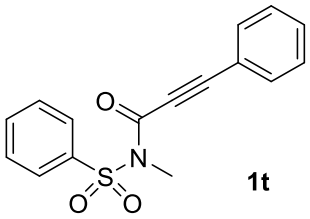
1s


200
180
160
140
120
100
80
60
40
20
0 ppm
164.153
153.107
149.442
137.070
132.763
131.167
128.702
126.918
123.264
119.043
115.972
110.694
93.981
80.904
77.320
77.002
76.685
56.498
34.406

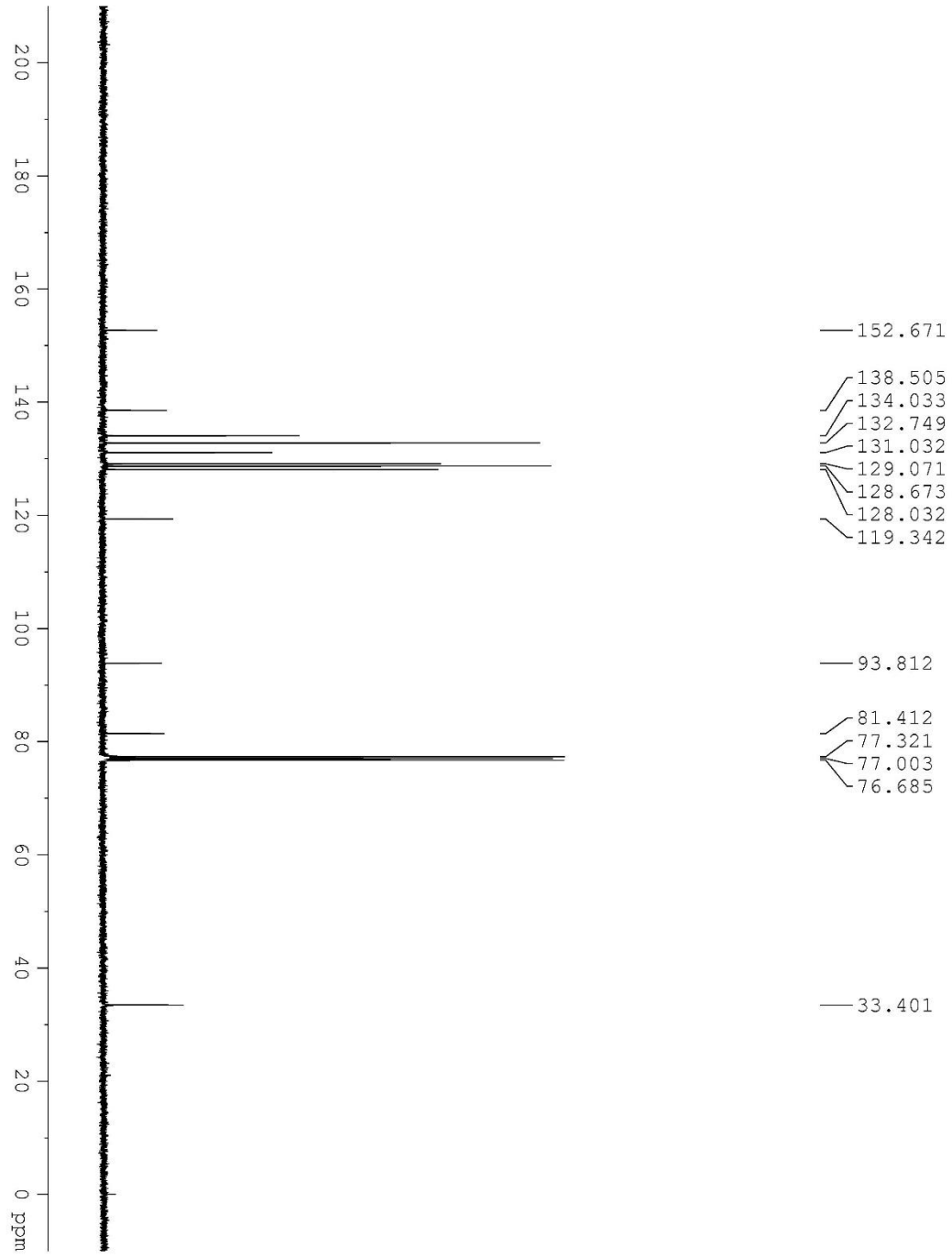


1t

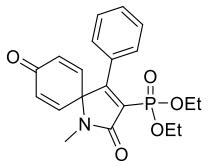

8.029
8.011
8.008
7.673
7.671
7.655
7.651
7.639
7.636
7.633
7.580
7.562
7.559
7.539
7.525
7.521
7.503
7.490
7.484
7.479
7.469
7.466
7.462
7.418
7.399
7.384
7.380
7.378
2.013
1.033
4.102
1.034
2.045
3.000
3.533
0.000
ppm


O
N
S
O
O

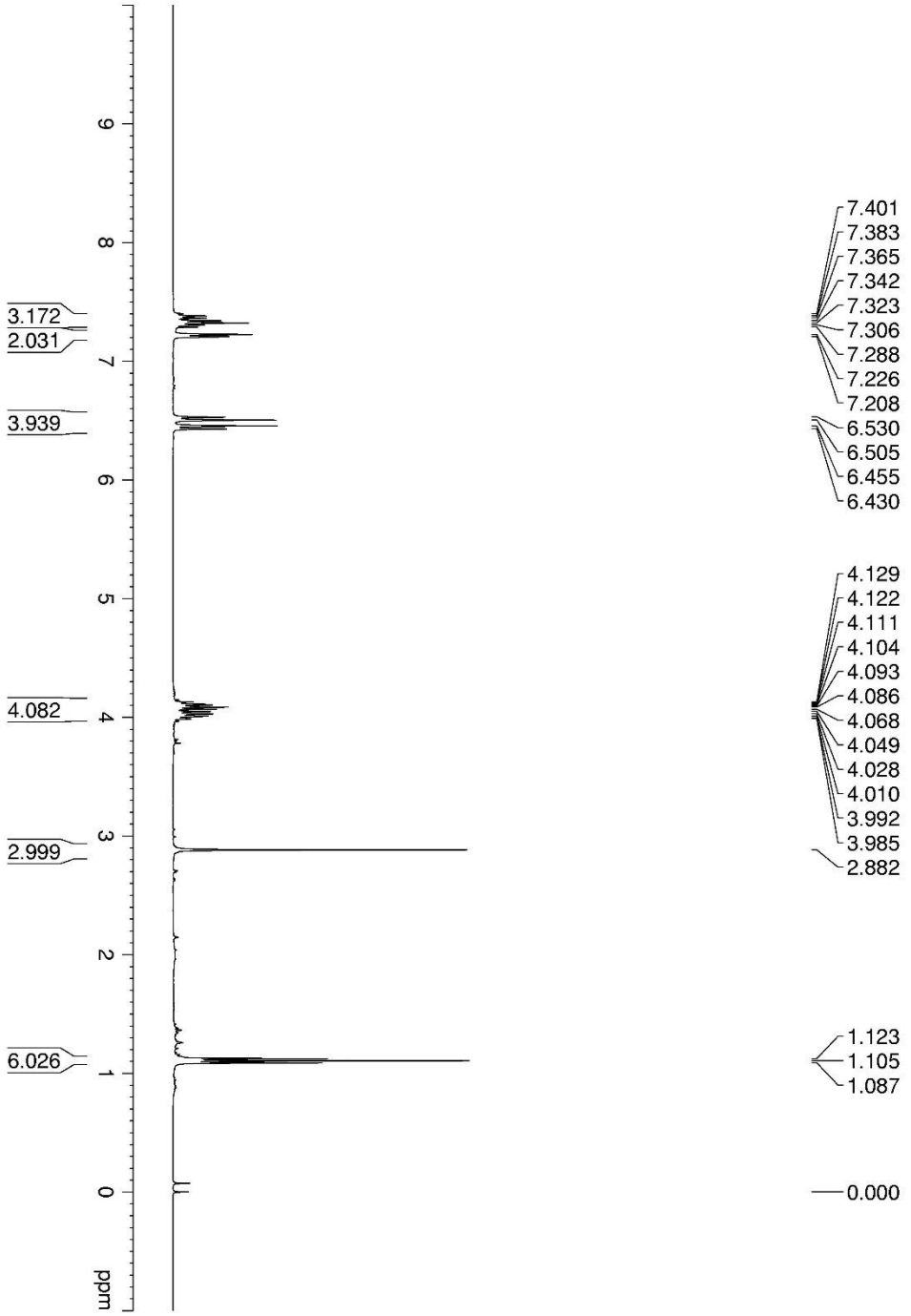
1t

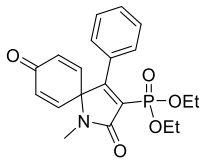

200
180
160
140
120
100
80
60
40
20
0 ppm
152.671
138.505
134.033
132.749
131.032
129.071
128.673
128.032
119.342
93.812
81.412
77.321
77.003
76.685
33.401

9. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR Spectra of the Products 3a-3t:

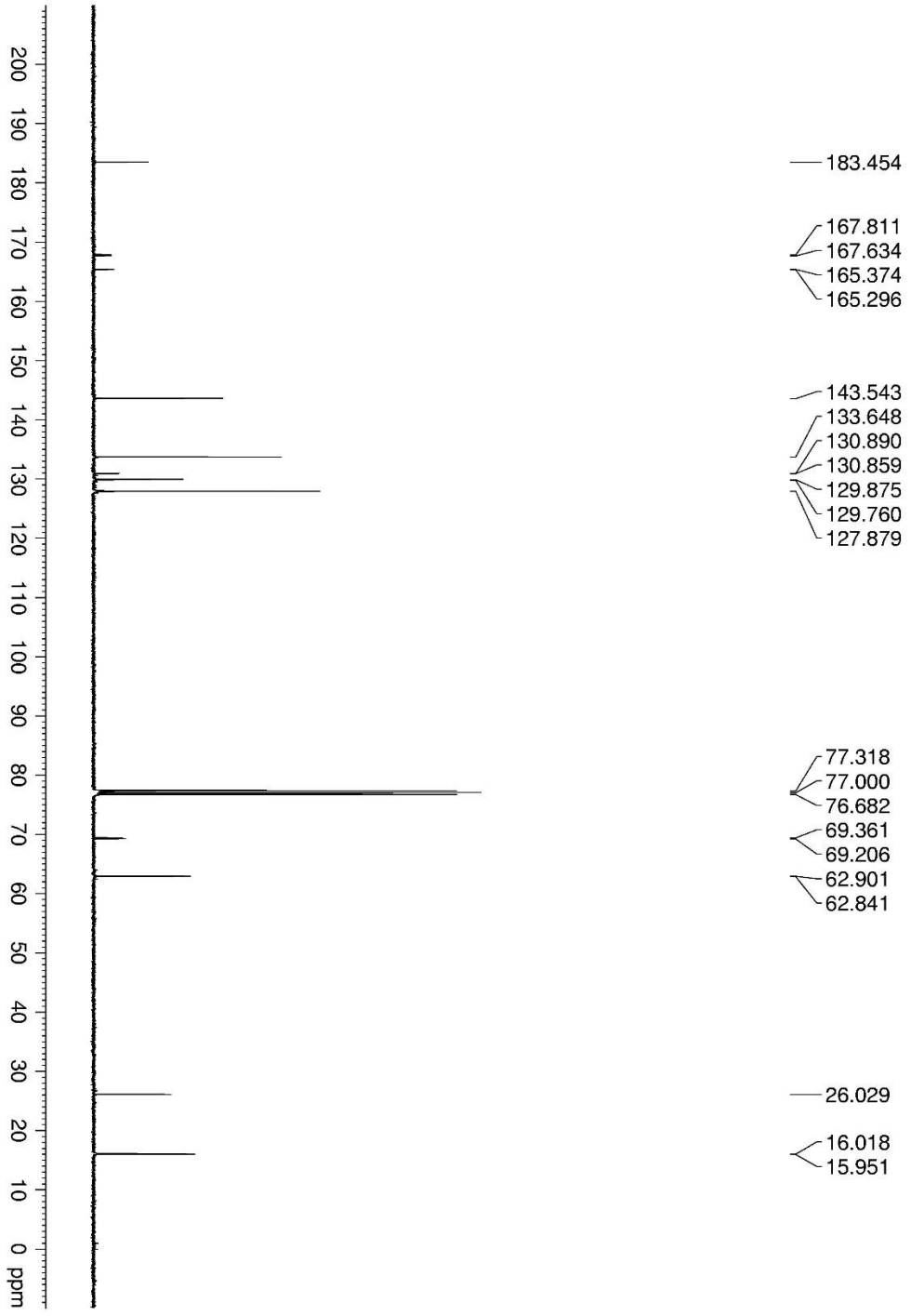


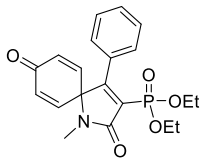
3a



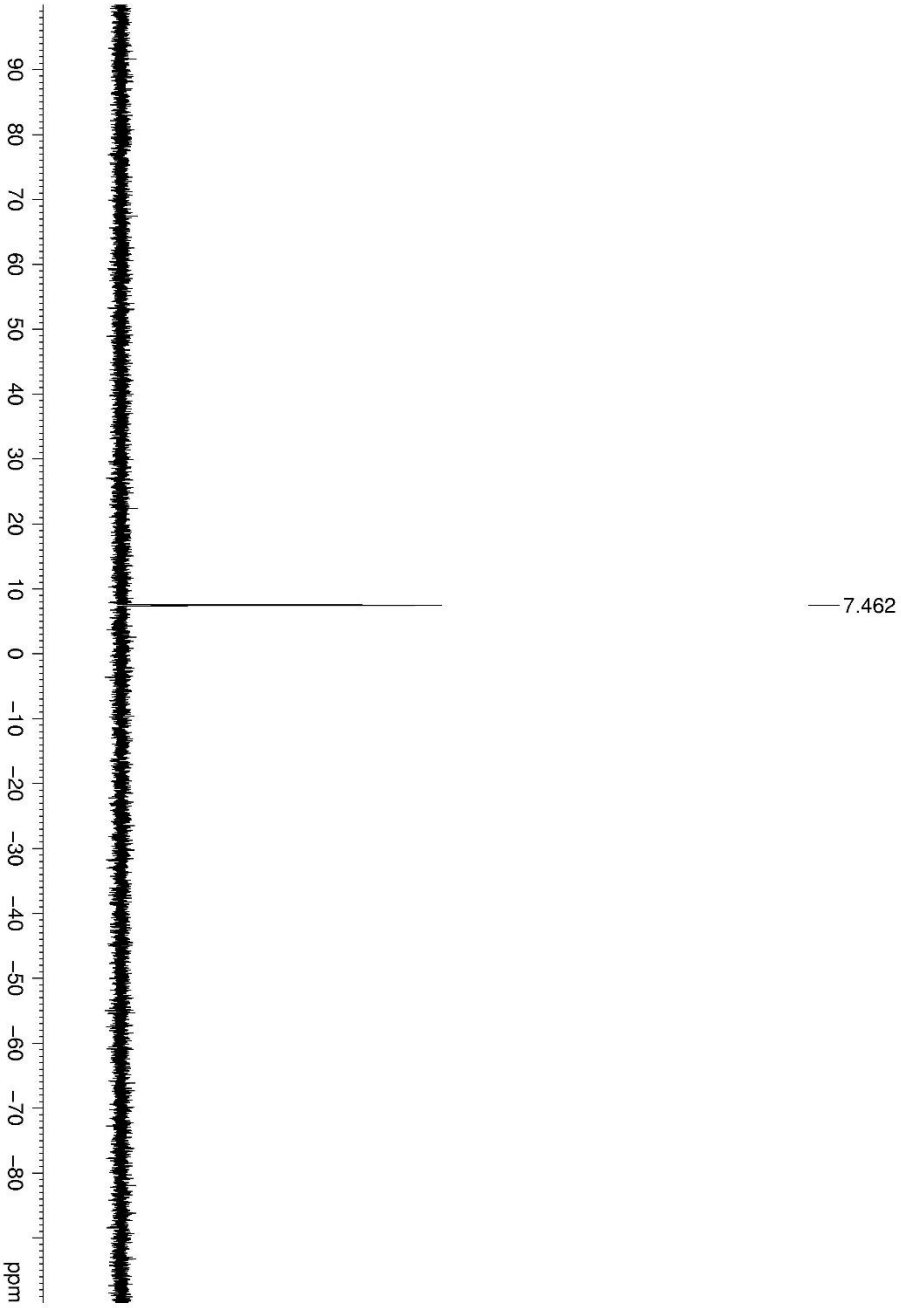

O
O
P
OEt
OEt
N
O

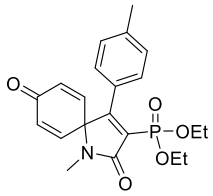
3a


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm
183.454
167.811
167.634
165.374
165.296
143.543
133.648
130.890
130.859
129.875
129.760
127.879
77.318
77.000
76.682
69.361
69.206
62.901
62.841
26.029
16.018
15.951

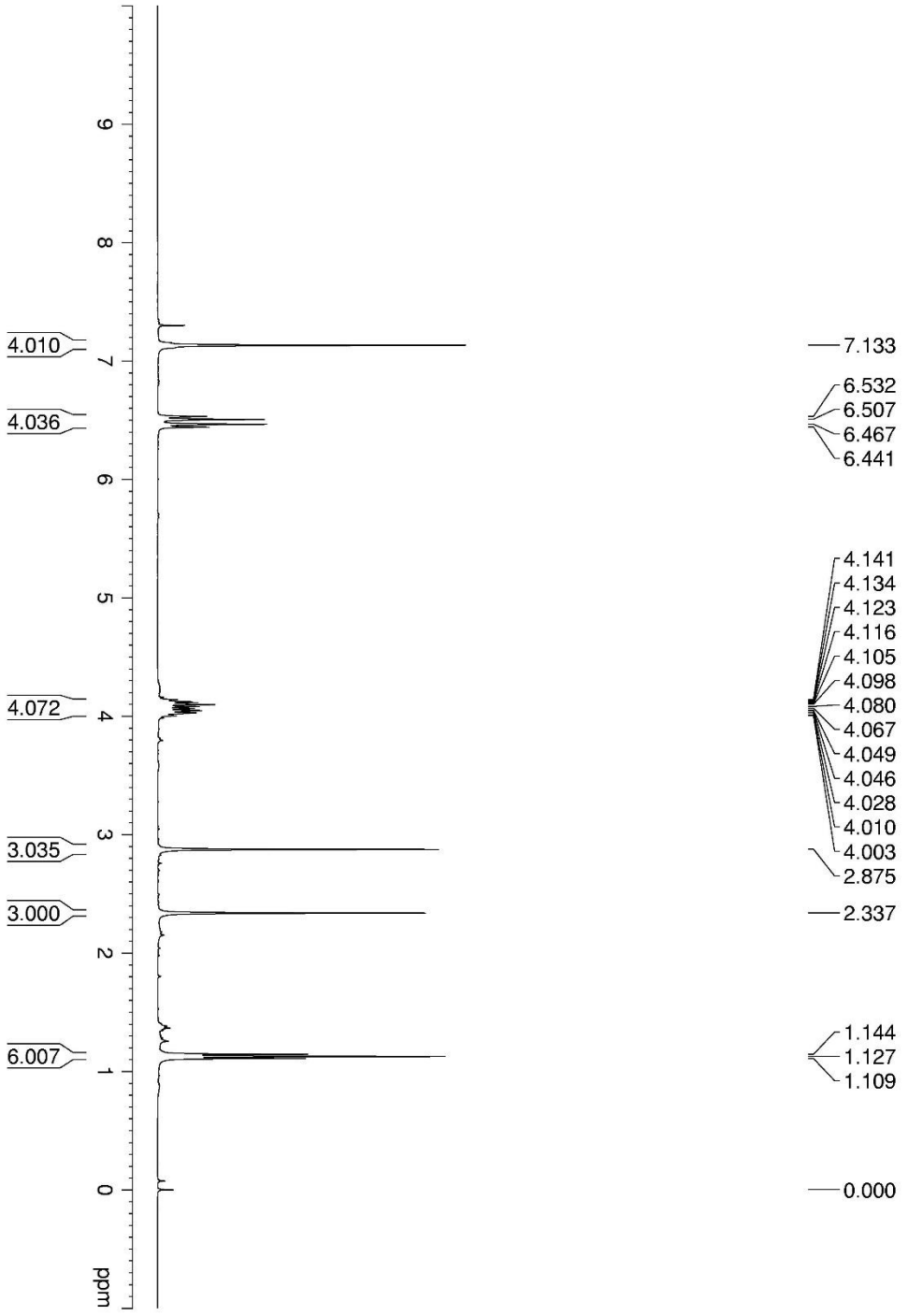

O
O
P
OEt
OEt
N
O

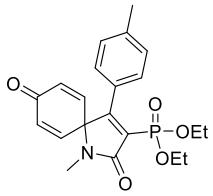
3a


90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
ppm
7.462

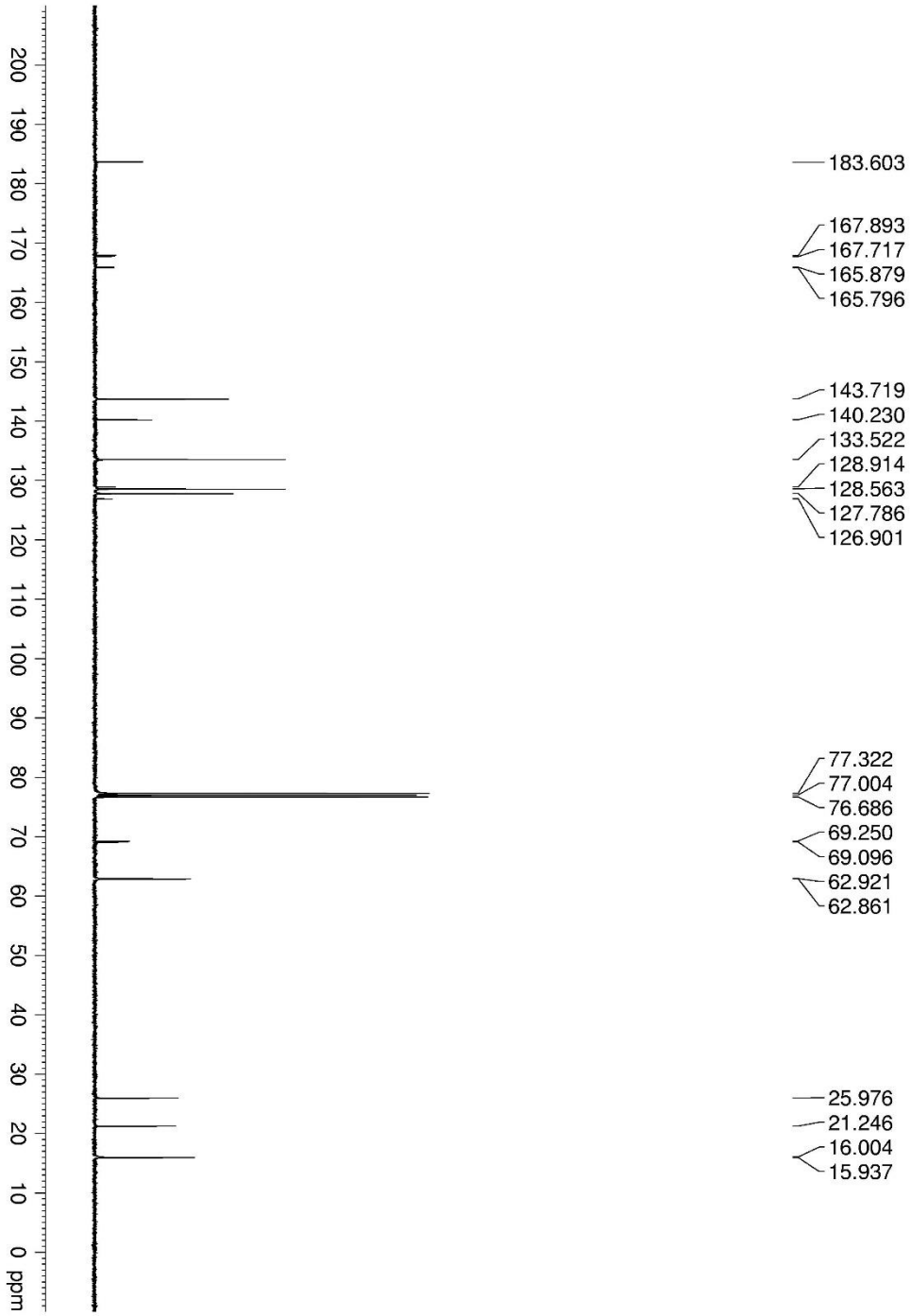

O
O
P
OEt
OEt
N
O

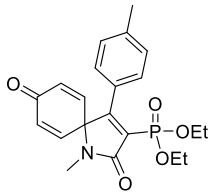
3b


4.010
4.036
4.072
3.035
3.000
6.007
ppm
7.133
6.532
6.507
6.467
6.441
4.141
4.134
4.123
4.116
4.105
4.098
4.080
4.067
4.049
4.046
4.028
4.010
4.003
2.875
2.337
1.144
1.127
1.109
0.000

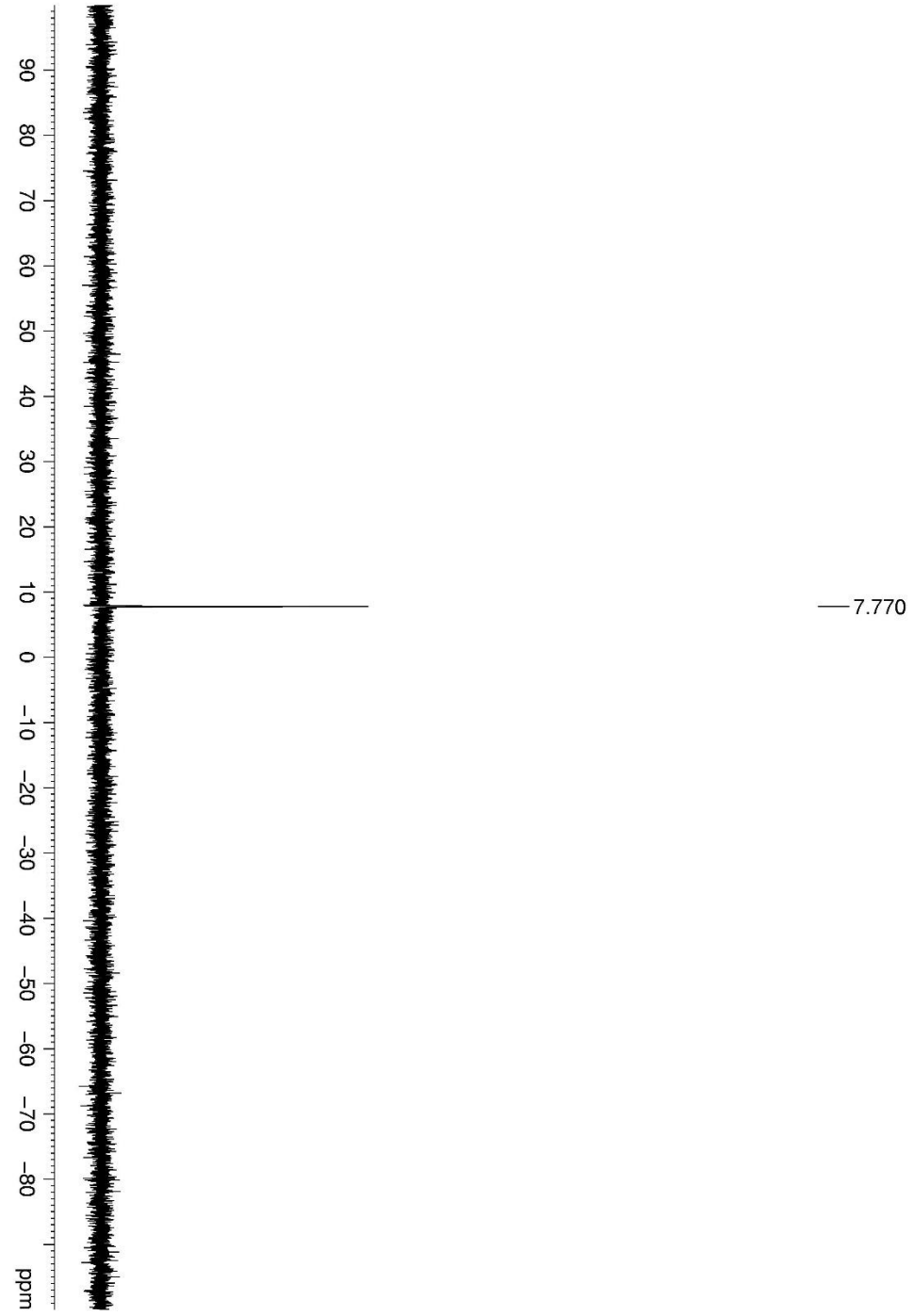

O
O
P
OEt
OEt
N
O

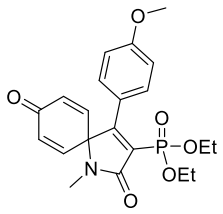
3b


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm
183.603
167.893
167.717
165.879
165.796
143.719
140.230
133.522
128.914
128.563
127.786
126.901
77.322
77.004
76.686
69.250
69.096
62.921
62.861
25.976
21.246
16.004
15.937

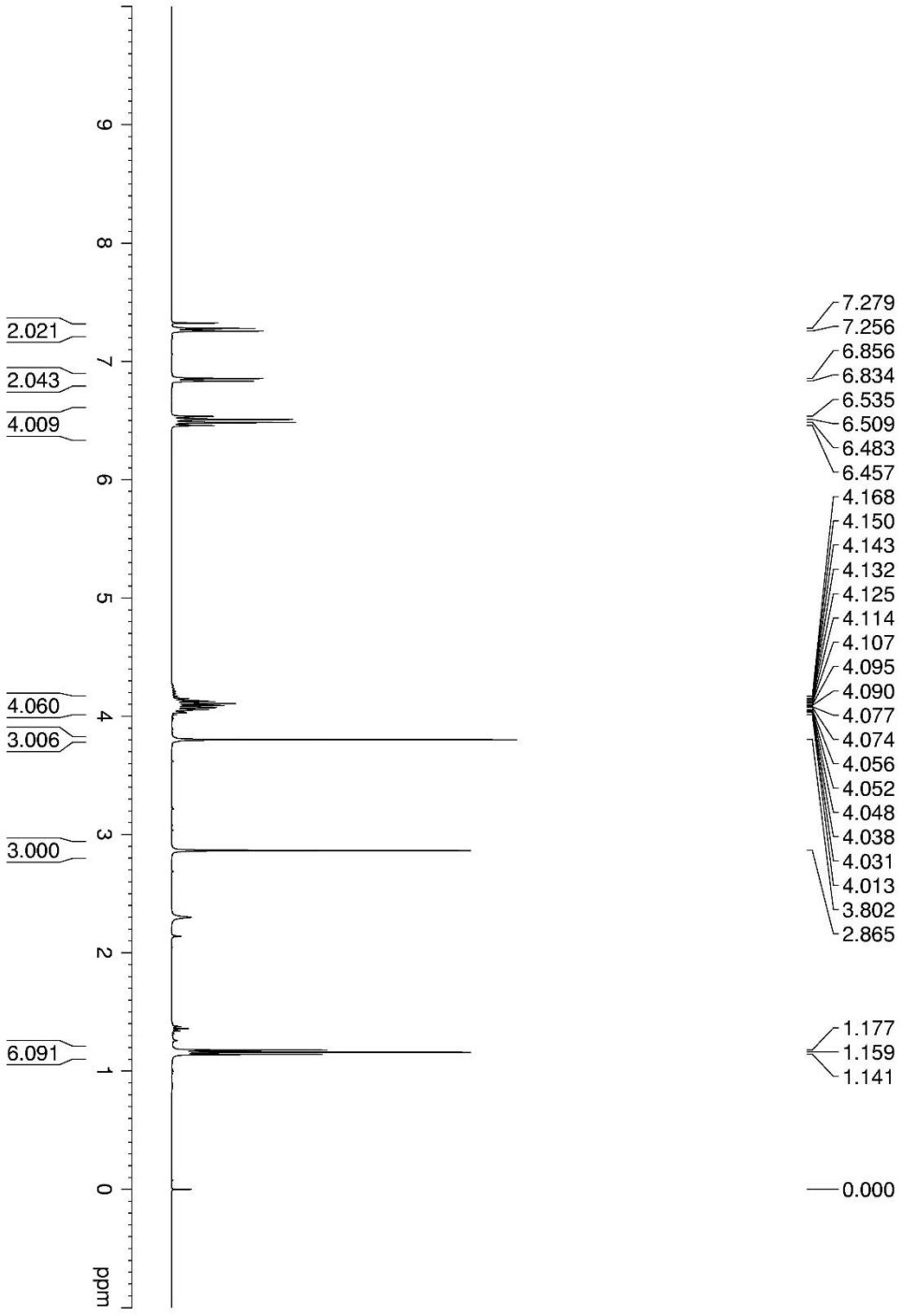

O
O
P
OEt
OEt
N
O

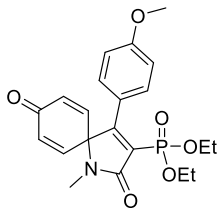
3b


90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
ppm
7.770

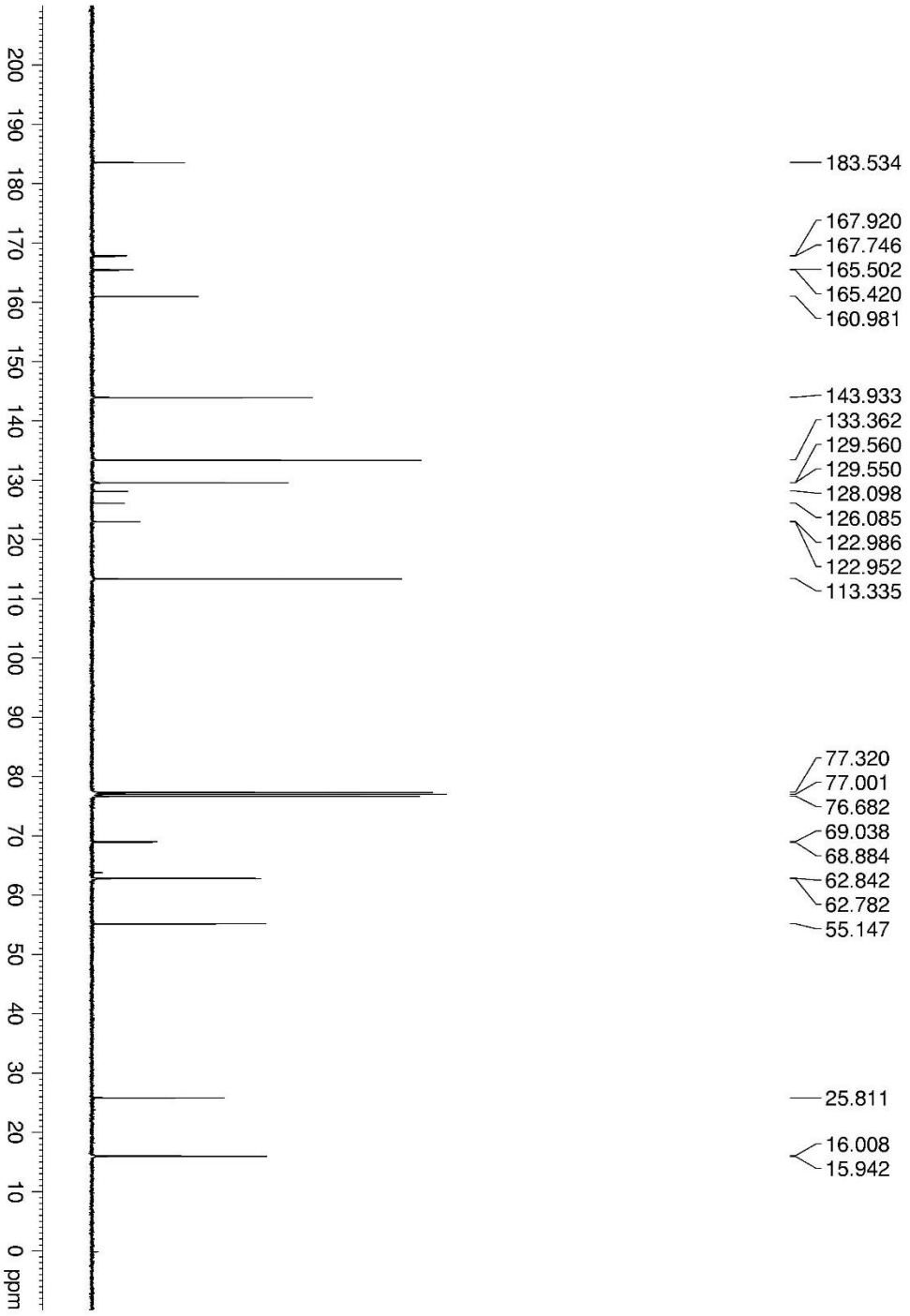


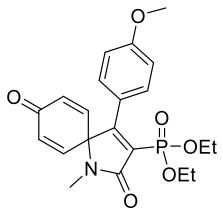
3c


2.021
2.043
4.009
4.060
3.006
3.000
6.091
ppm
7.279
7.256
6.856
6.834
6.535
6.509
6.483
6.457
4.168
4.150
4.143
4.132
4.125
4.114
4.107
4.095
4.090
4.077
4.074
4.056
4.052
4.048
4.038
4.031
4.013
3.802
2.865
1.177
1.159
1.141
0.000

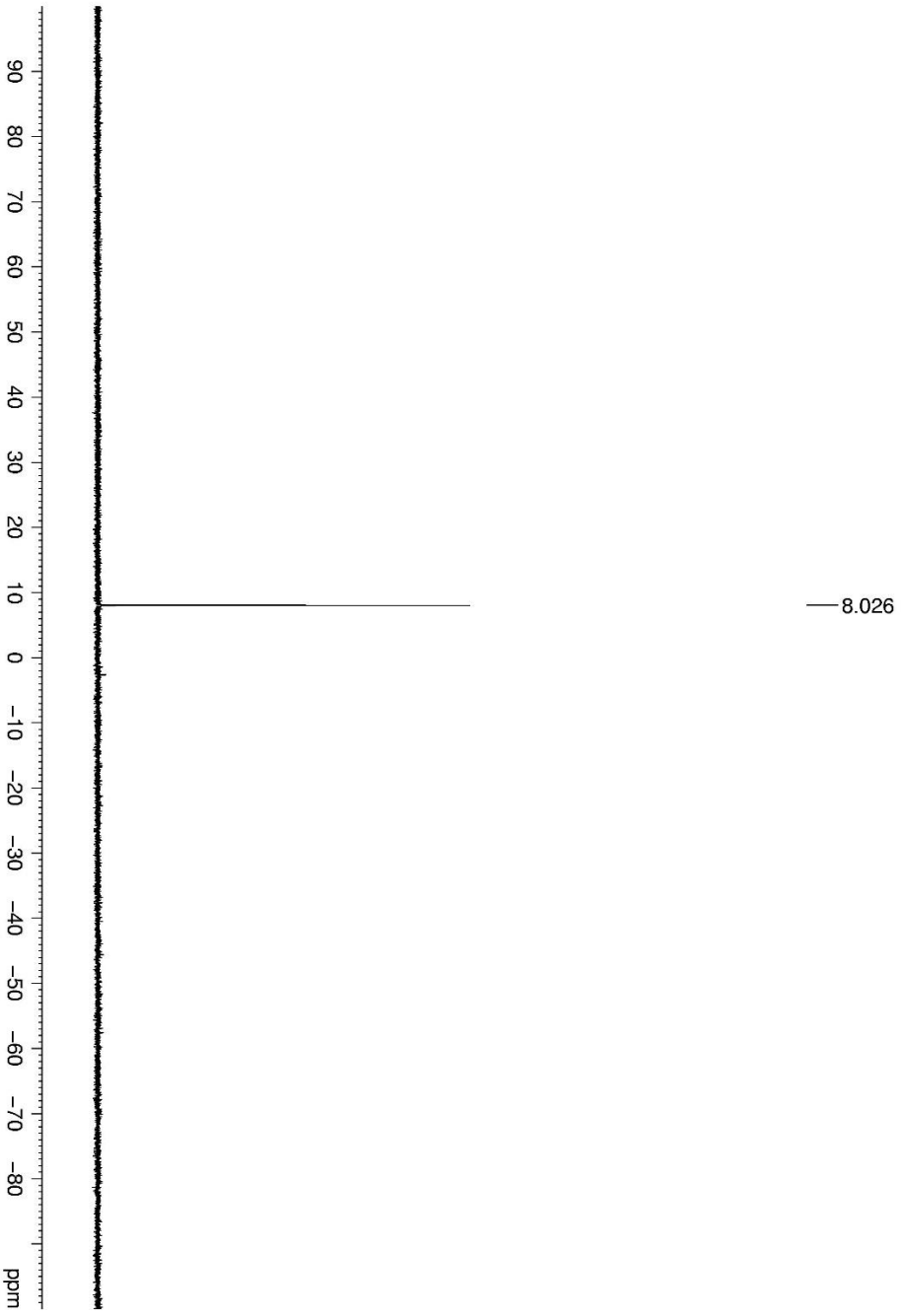

O
O
O
P
OEt
OEt
N
O

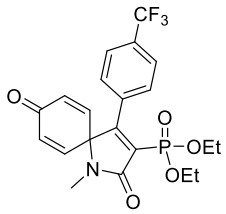
3c


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm
183.534
167.920
167.746
165.502
165.420
160.981
143.933
133.362
129.560
129.550
128.098
126.085
122.986
122.952
113.335
77.320
77.001
76.682
69.038
68.884
62.842
62.782
55.147
25.811
16.008
15.942

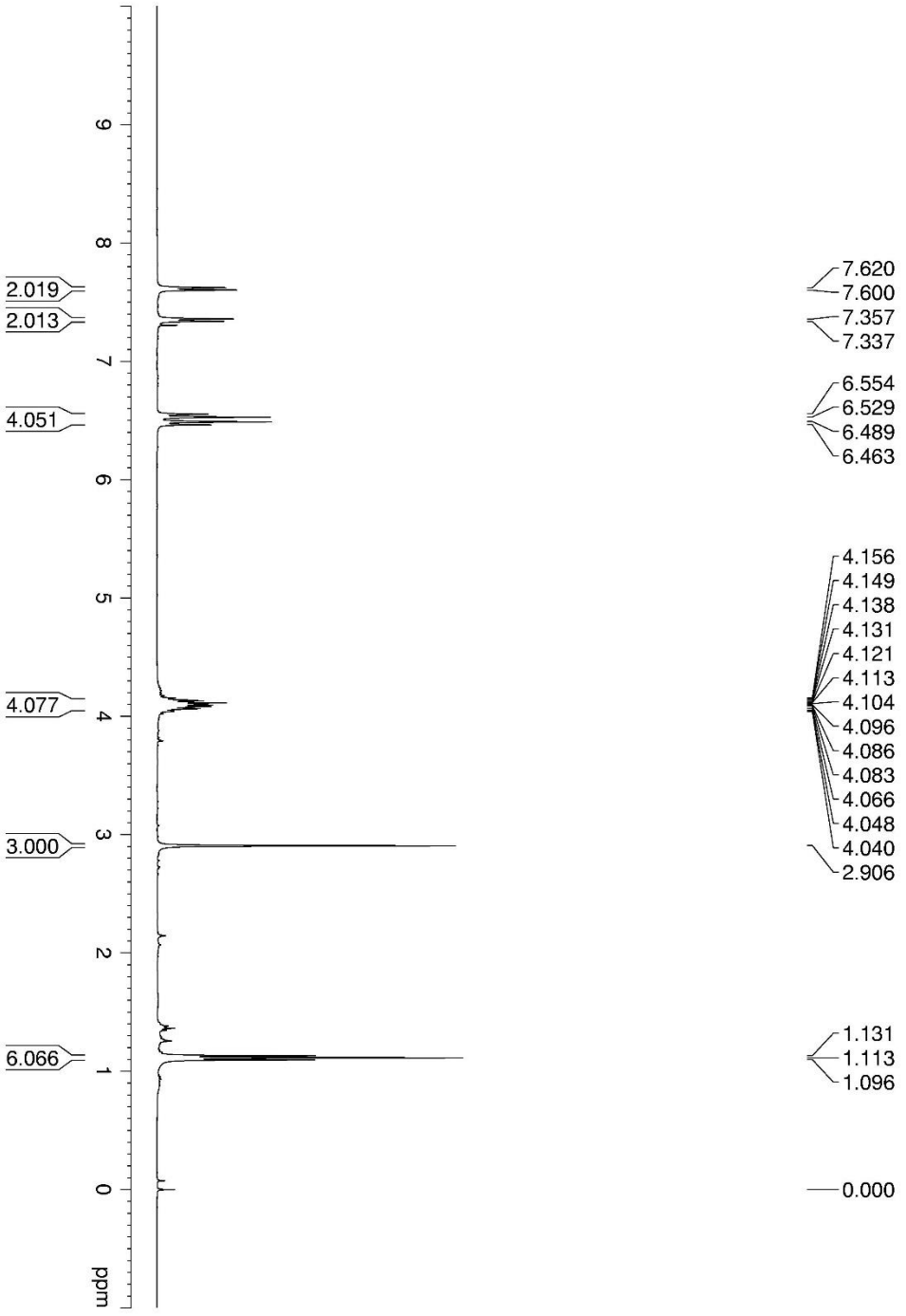

O
O
O
P
OEt
OEt
N
O

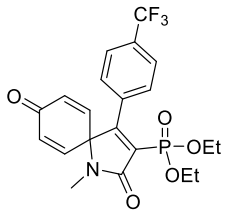
3c


90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
ppm
8.026

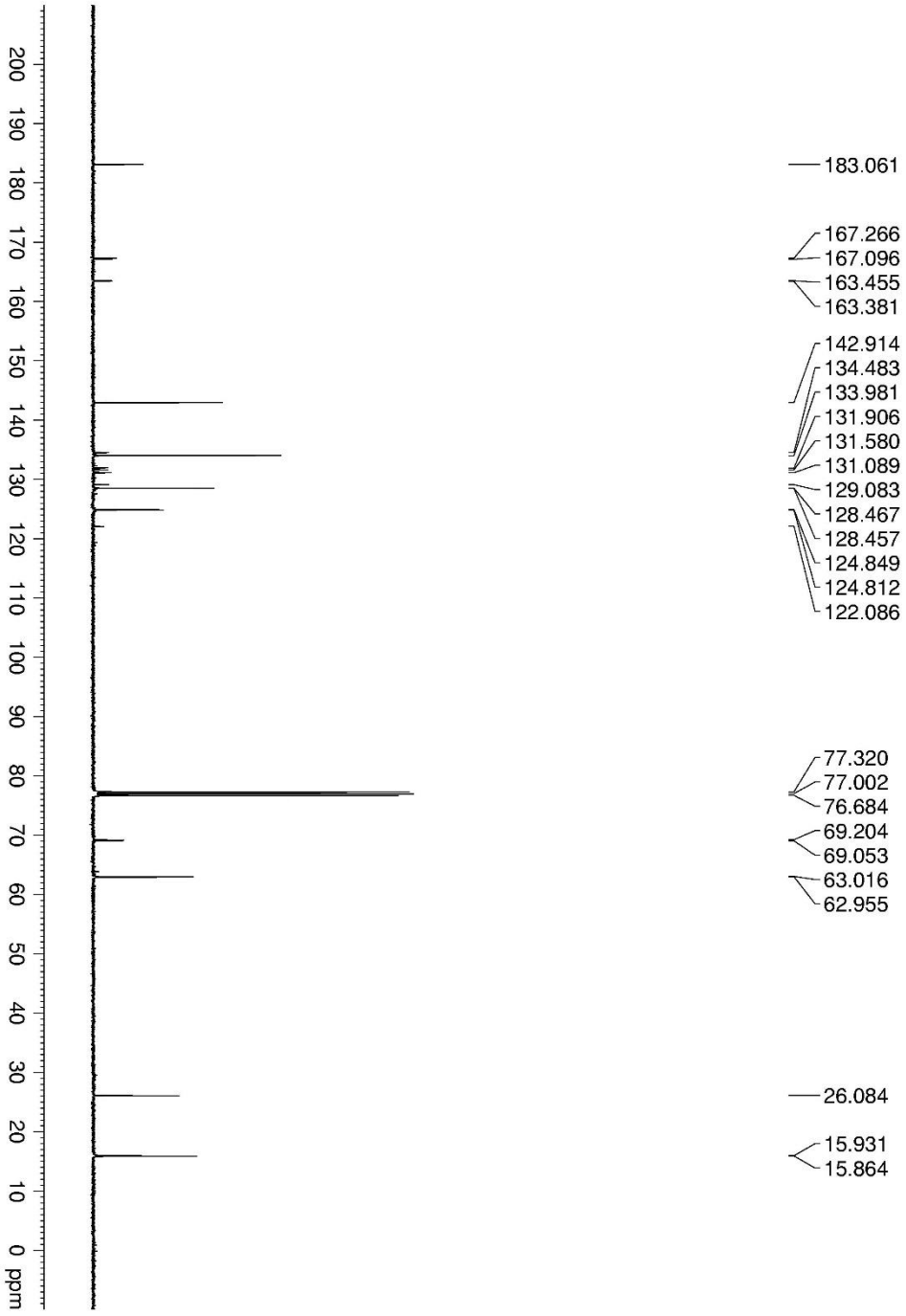

CF3
O
O
P
OEt
OEt
N
O

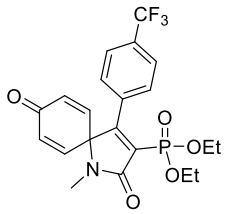
3d


2.019
2.013
4.051
4.077
3.000
6.066
ppm
7.620
7.600
7.357
7.337
6.554
6.529
6.489
6.463
4.156
4.149
4.138
4.131
4.121
4.113
4.104
4.096
4.086
4.083
4.066
4.048
4.040
2.906
1.131
1.113
1.096
0.000

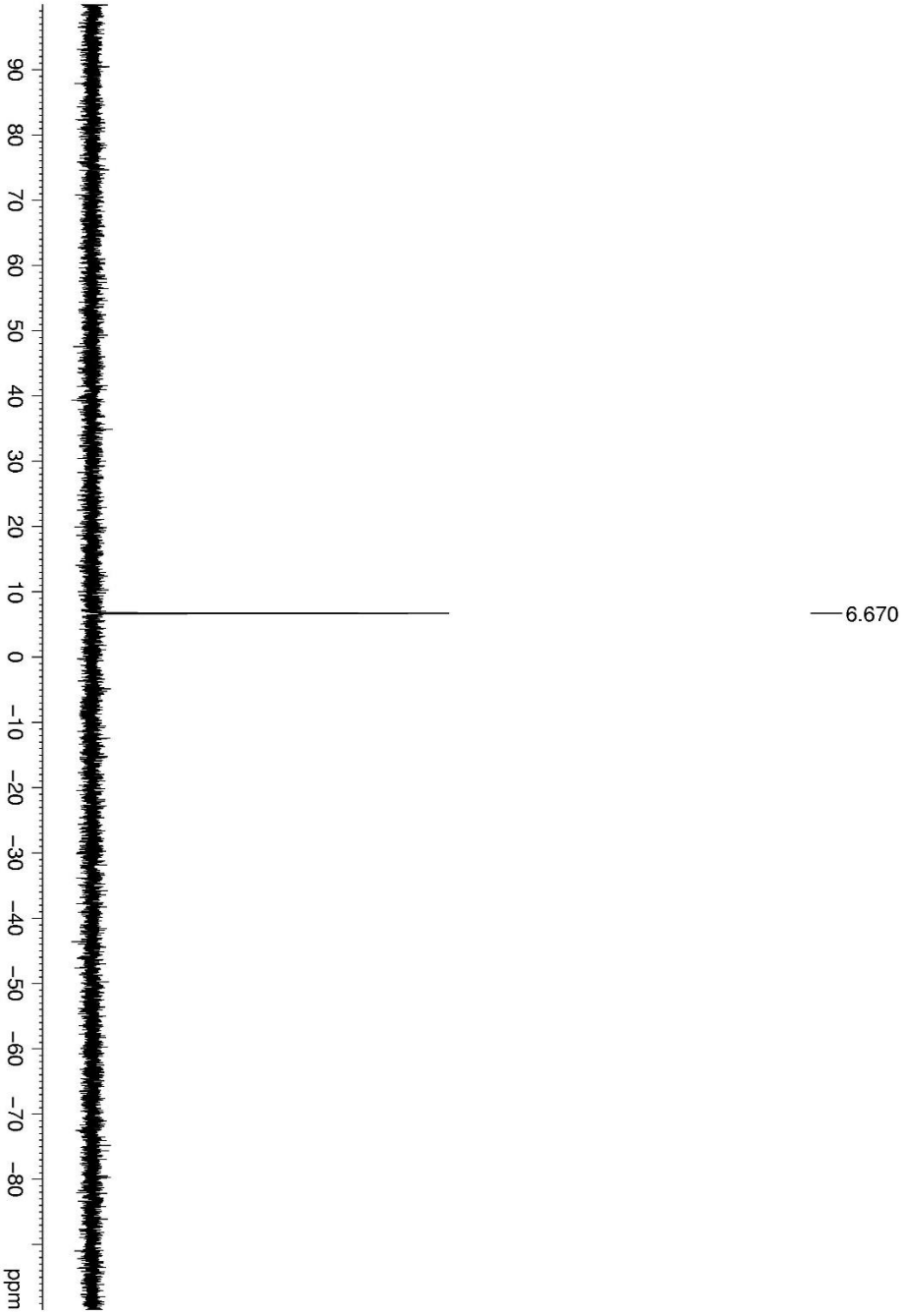

CF3
O
O
P
OEt
OEt
N
O

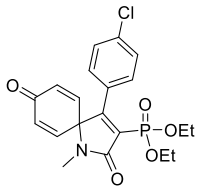
3d


183.061
167.266
167.096
163.455
163.381
142.914
134.483
133.981
131.906
131.580
131.089
129.083
128.467
128.457
124.849
124.812
122.086
77.320
77.002
76.684
69.204
69.053
63.016
62.955
26.084
15.931
15.864
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

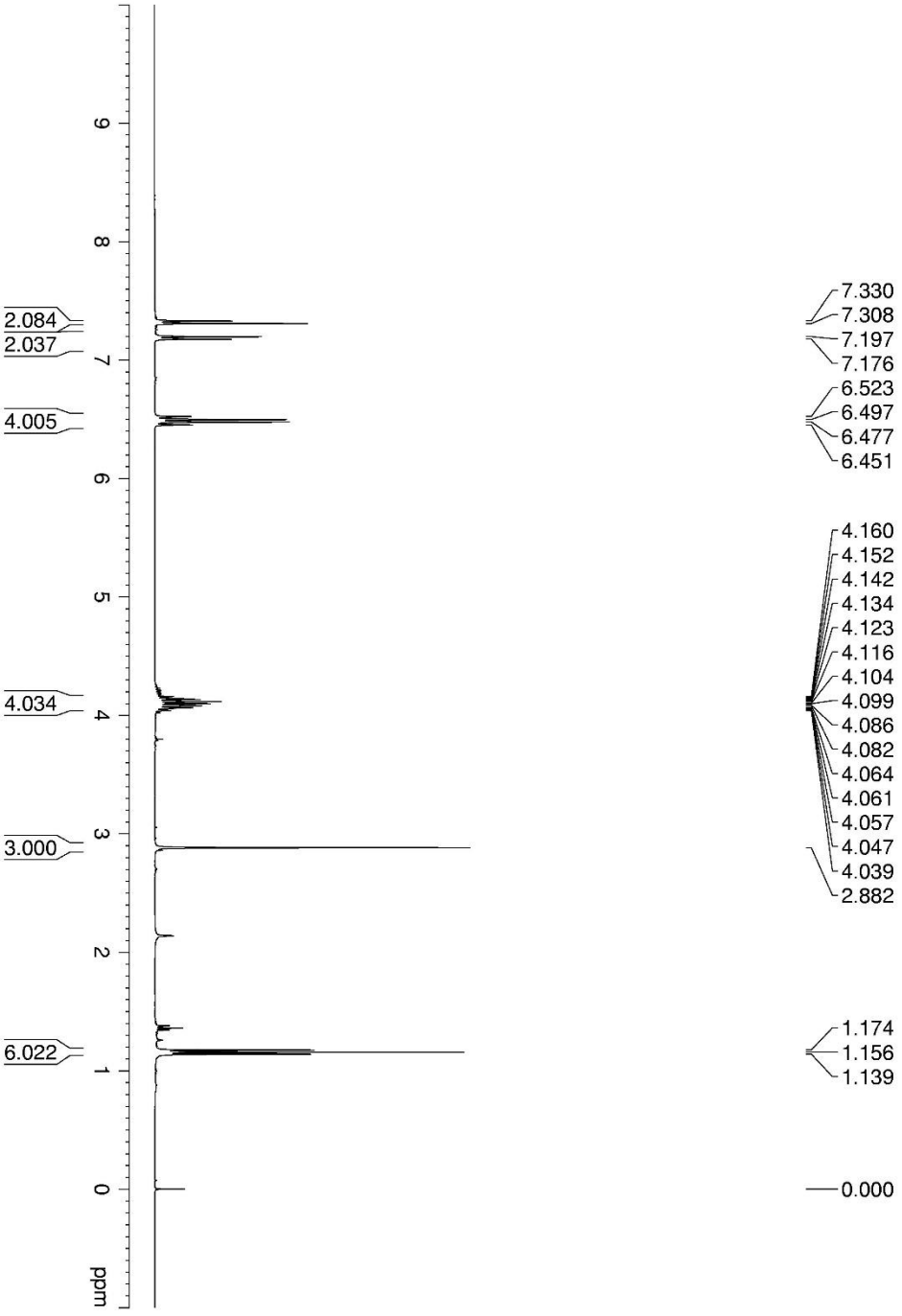

CF3
O
O
P
OEt
OEt
N
O

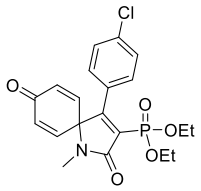
3d


90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
ppm
6.670

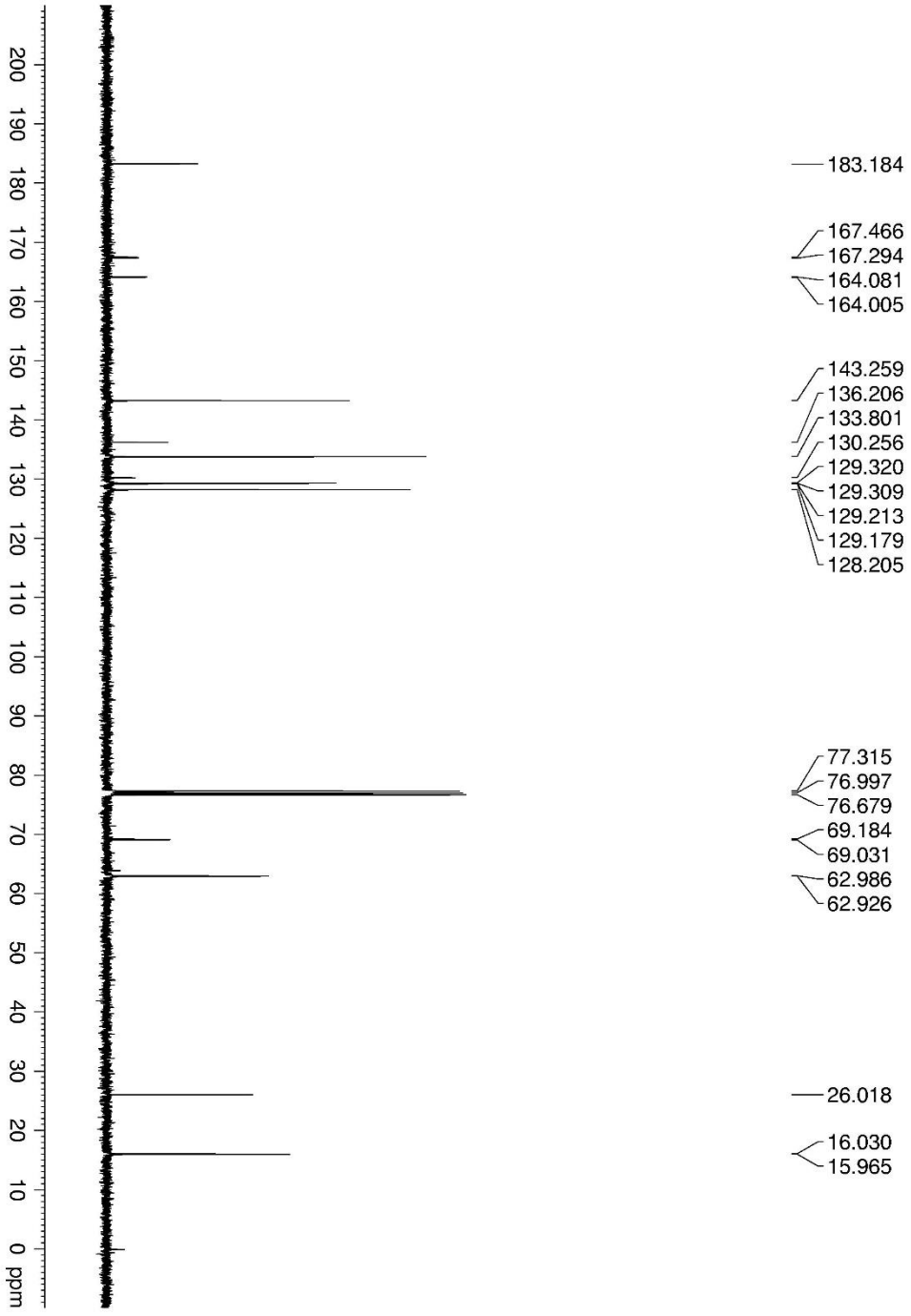

Cl
O
O
P
OEt
OEt
N
O

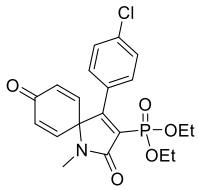
3e


2.084
2.037
4.005
4.034
3.000
6.022
ppm
9
8
7
6
5
4
3
2
1
0
7.330
7.308
7.197
7.176
6.523
6.497
6.477
6.451
4.160
4.152
4.142
4.134
4.123
4.116
4.104
4.099
4.086
4.082
4.064
4.061
4.057
4.047
4.039
2.882
1.174
1.156
1.139
0.000

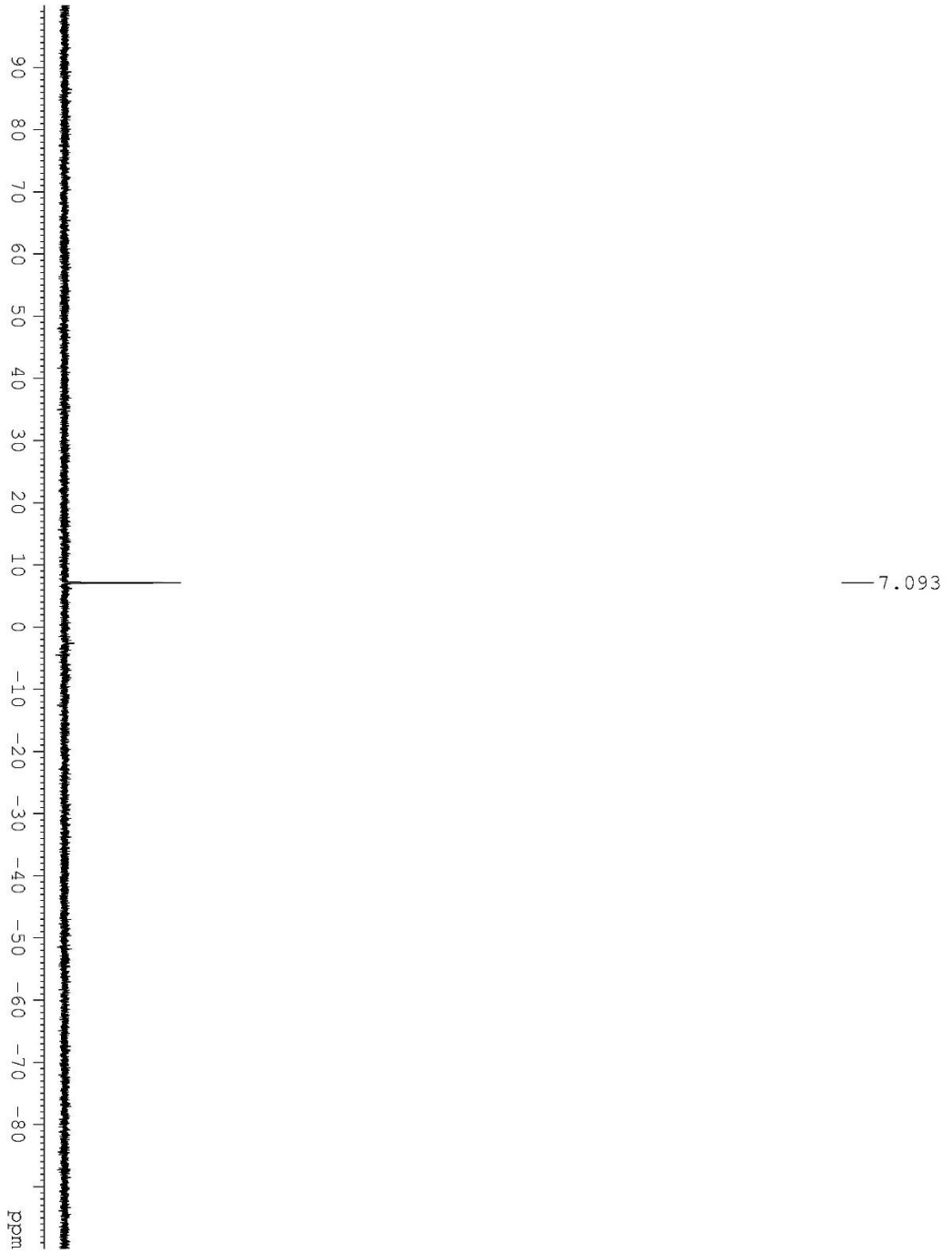

Cl
O
O
P
OEt
OEt
N
O

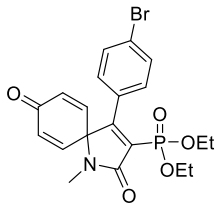
3e


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
183.184
167.466
167.294
164.081
164.005
143.259
136.206
133.801
130.256
129.320
129.309
129.213
129.179
128.205
77.315
76.997
76.679
69.184
69.031
62.986
62.926
26.018
16.030
15.965

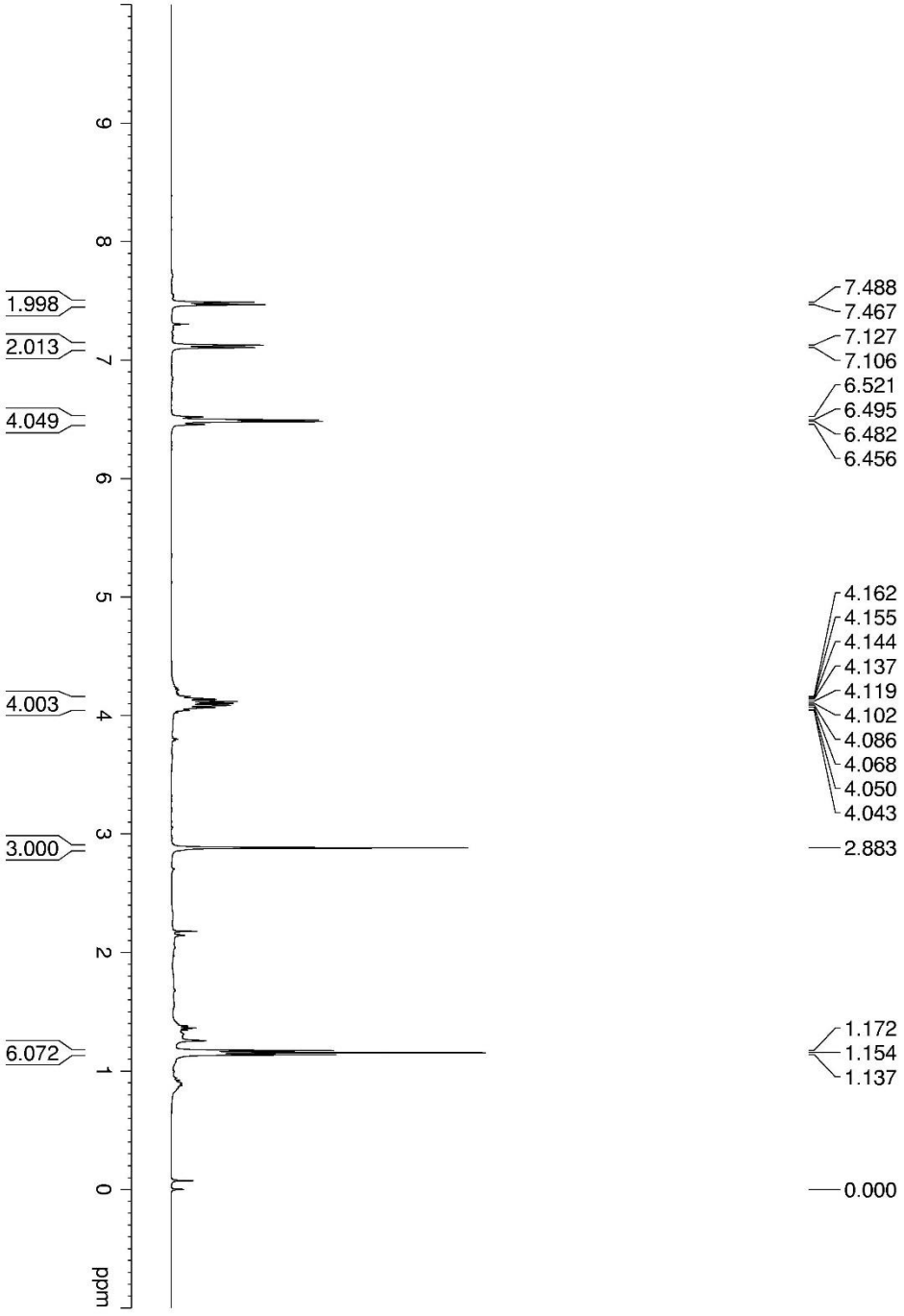

Cl
O
O
P
OEt
OEt
N
O

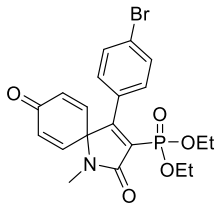
3e


90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
ppm
7.093

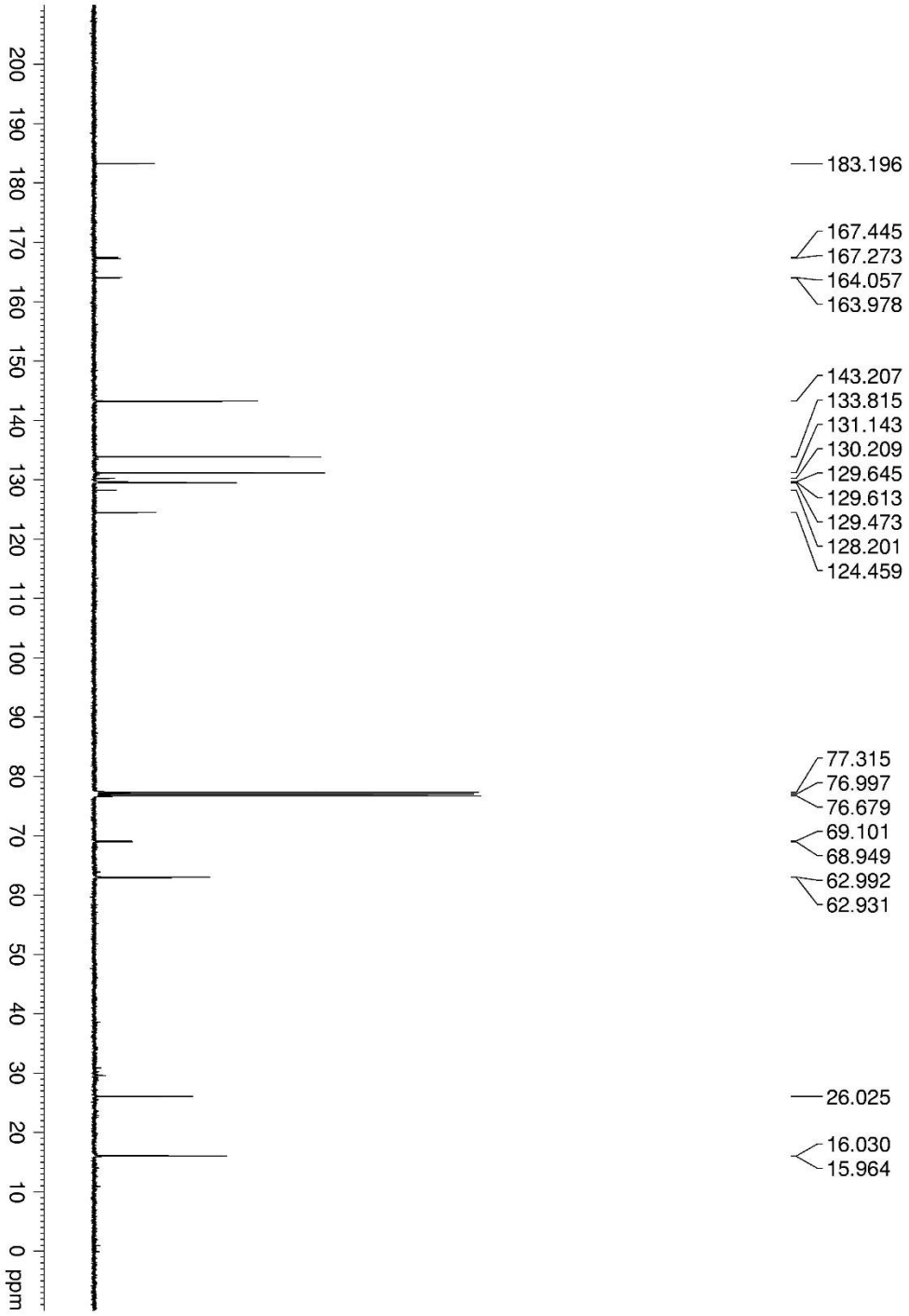

Br
O
O
P
OEt
OEt
N
O

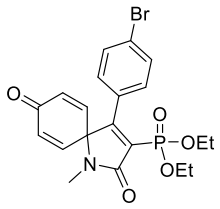
3f


1.998
2.013
4.049
4.003
3.000
6.072
9
8
7
6
5
4
3
2
1
0
ppm
7.488
7.467
7.127
7.106
6.521
6.495
6.482
6.456
4.162
4.155
4.144
4.137
4.119
4.102
4.086
4.068
4.050
4.043
2.883
1.172
1.154
1.137
0.000

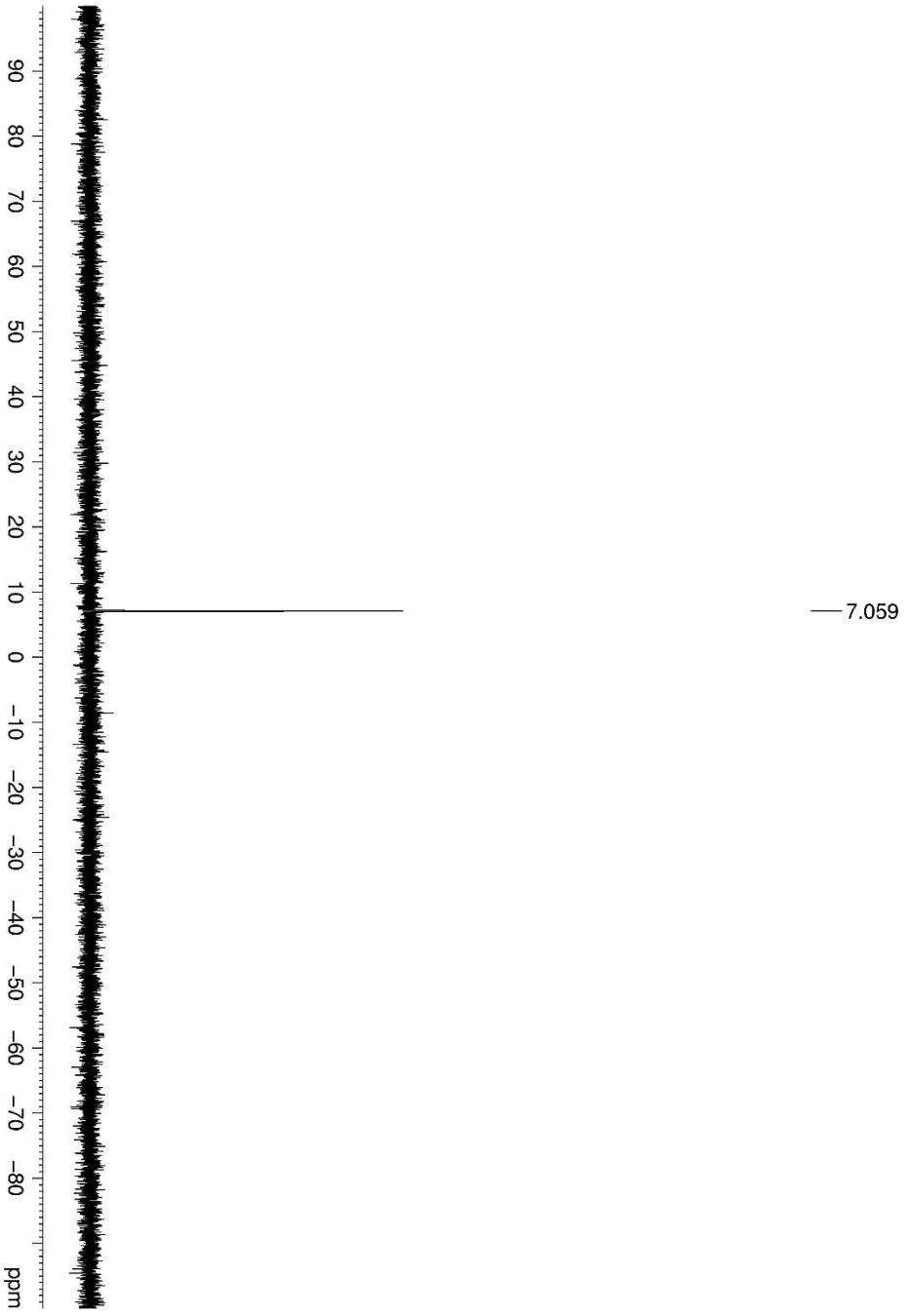

Br
O
O
P
OEt
OEt
N
O

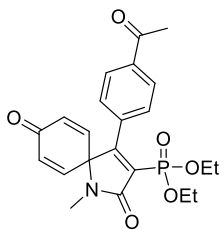
3f


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm
183.196
167.445
167.273
164.057
163.978
143.207
133.815
131.143
130.209
129.645
129.613
129.473
128.201
124.459
77.315
76.997
76.679
69.101
68.949
62.992
62.931
26.025
16.030
15.964

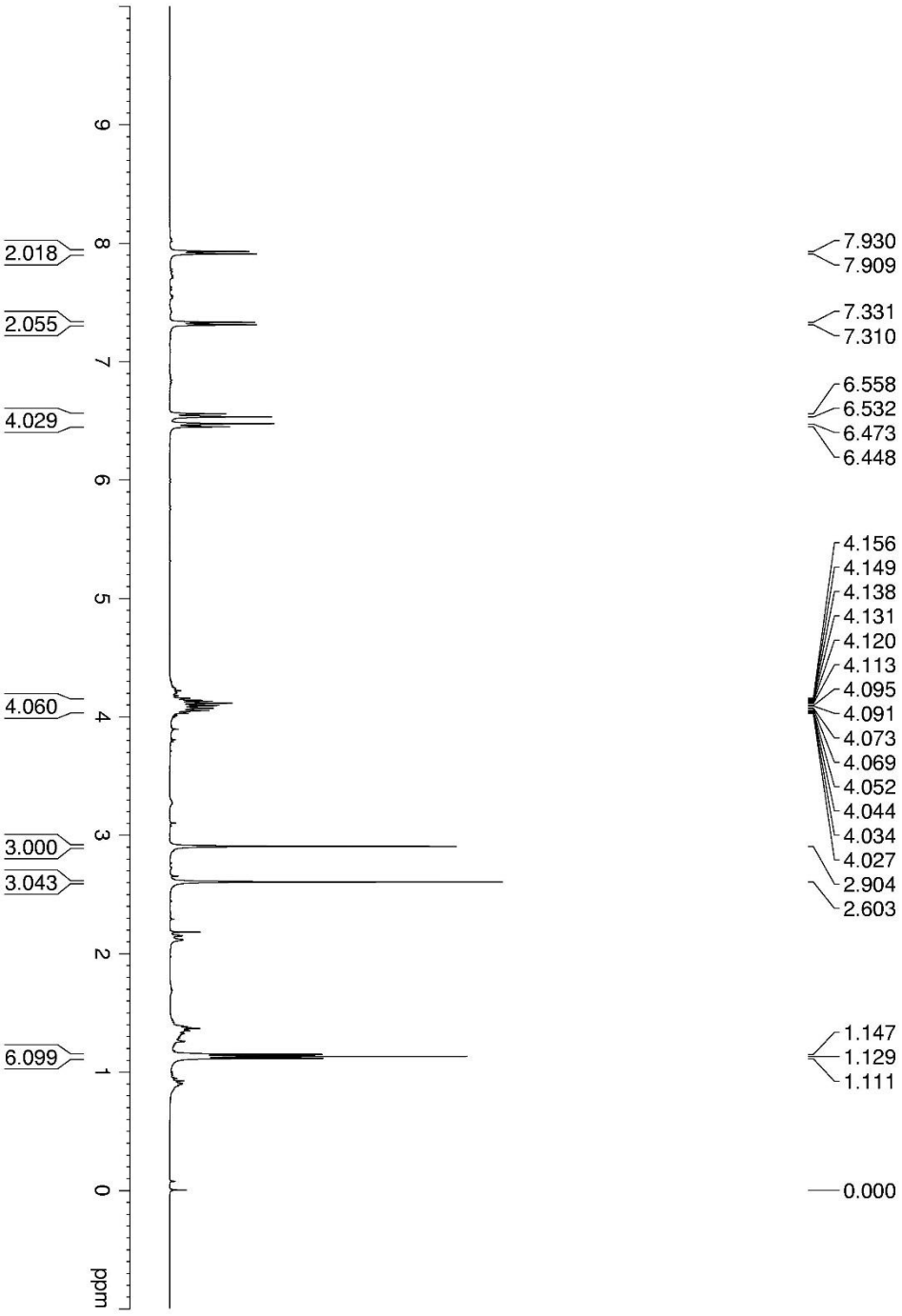

Br
O
O
P
OEt
OEt
N
O

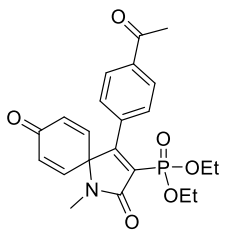
3f


90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
ppm
7.059

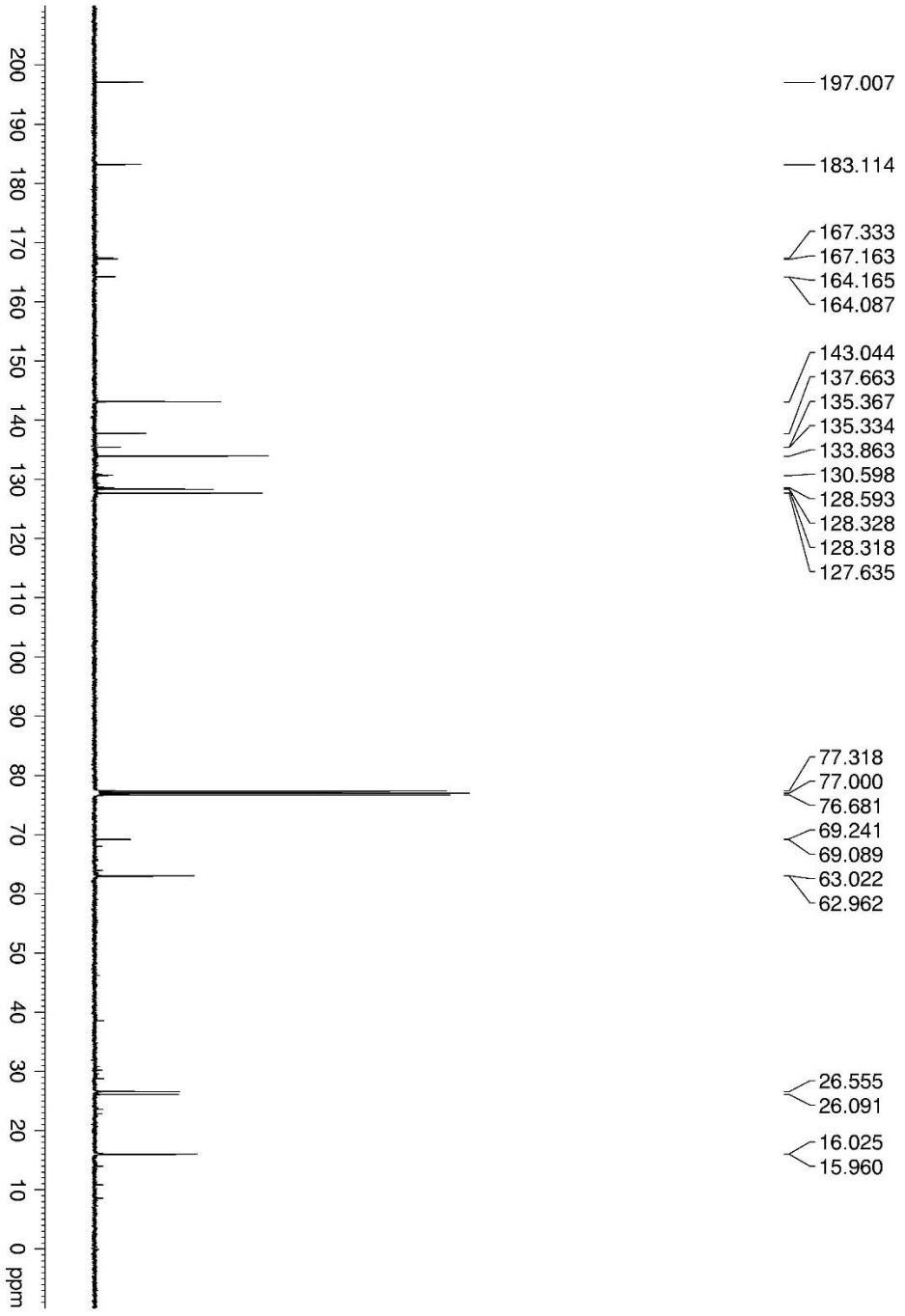


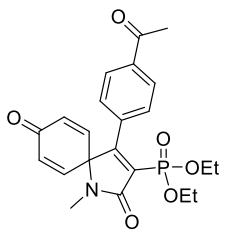
3g


2.018
2.055
4.029
4.060
3.000
3.043
6.099
ppm
7.930
7.909
7.331
7.310
6.558
6.532
6.473
6.448
4.156
4.149
4.138
4.131
4.120
4.113
4.095
4.091
4.073
4.069
4.052
4.044
4.034
4.027
2.904
2.603
1.147
1.129
1.111
0.000

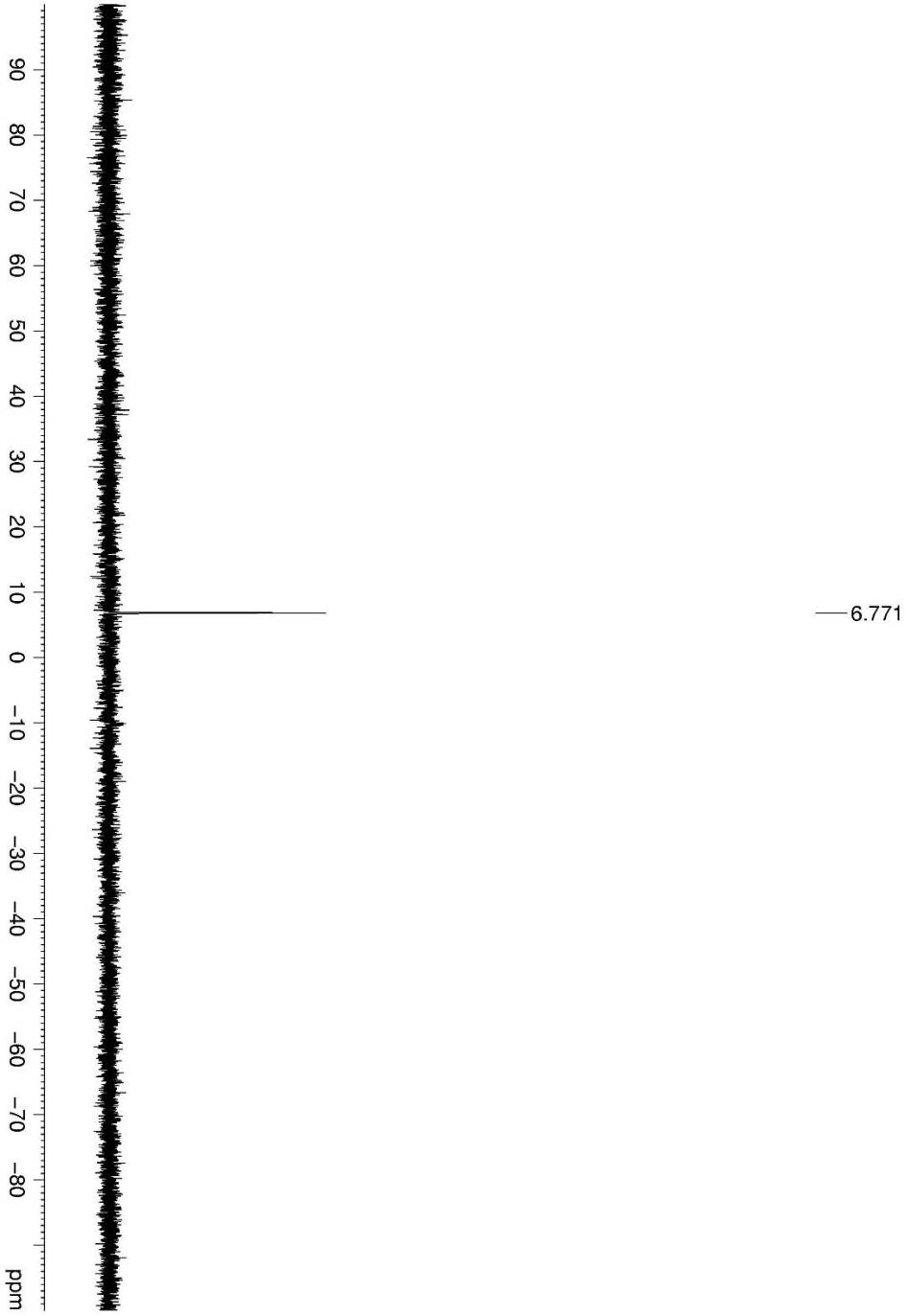

O
O
O
P
OEt
OEt
N
O

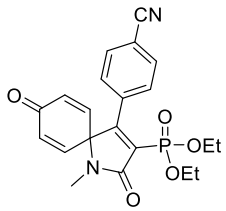
3g


197.007
183.114
167.333
167.163
164.165
164.087
143.044
137.663
135.367
135.334
133.863
130.598
128.593
128.328
128.318
127.635
77.318
77.000
76.681
69.241
69.089
63.022
62.962
26.555
26.091
16.025
15.960
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

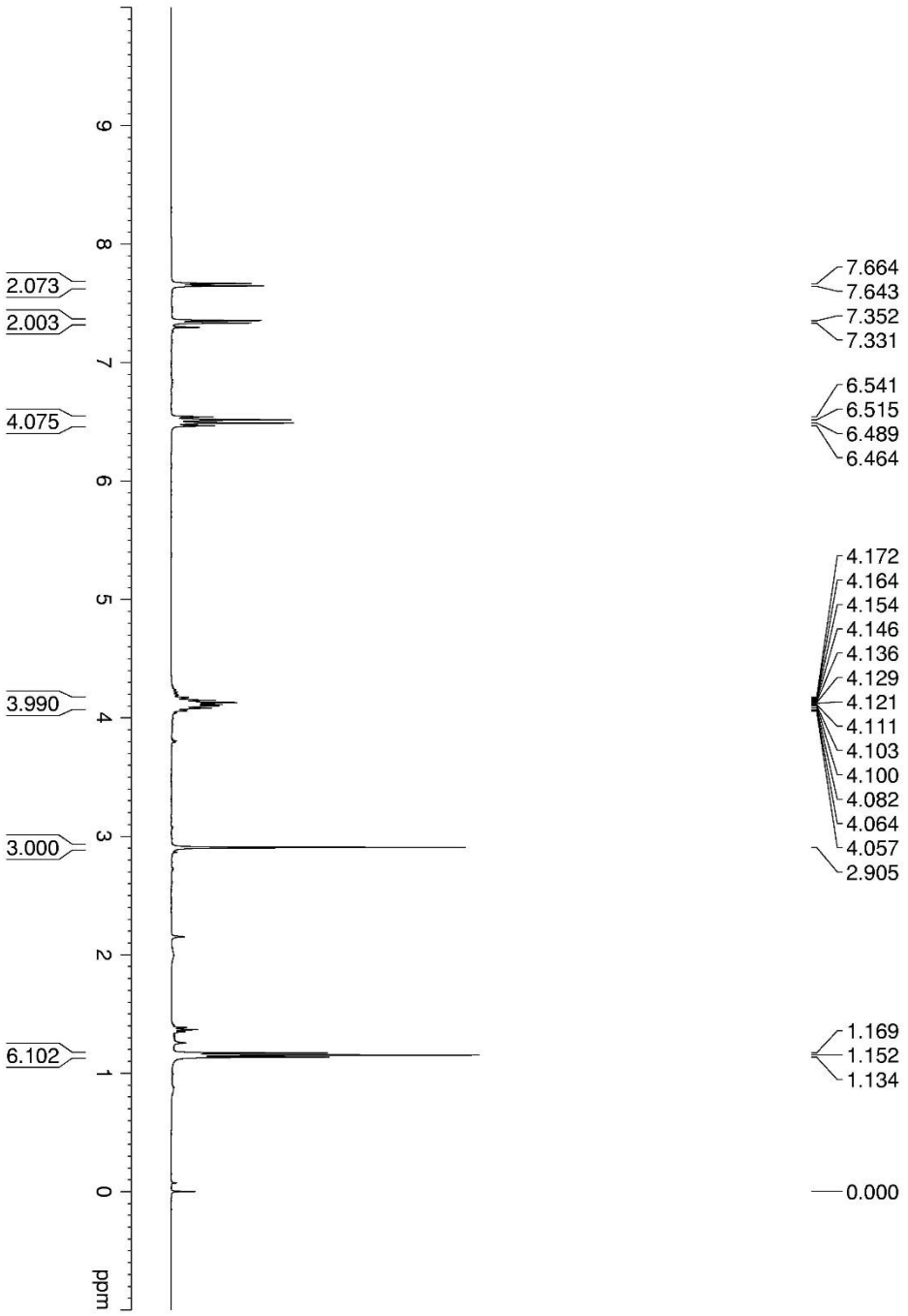

O
O
O
P
OEt
OEt
N
O

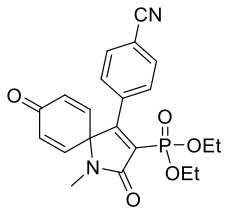
3g


90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
ppm
6.771

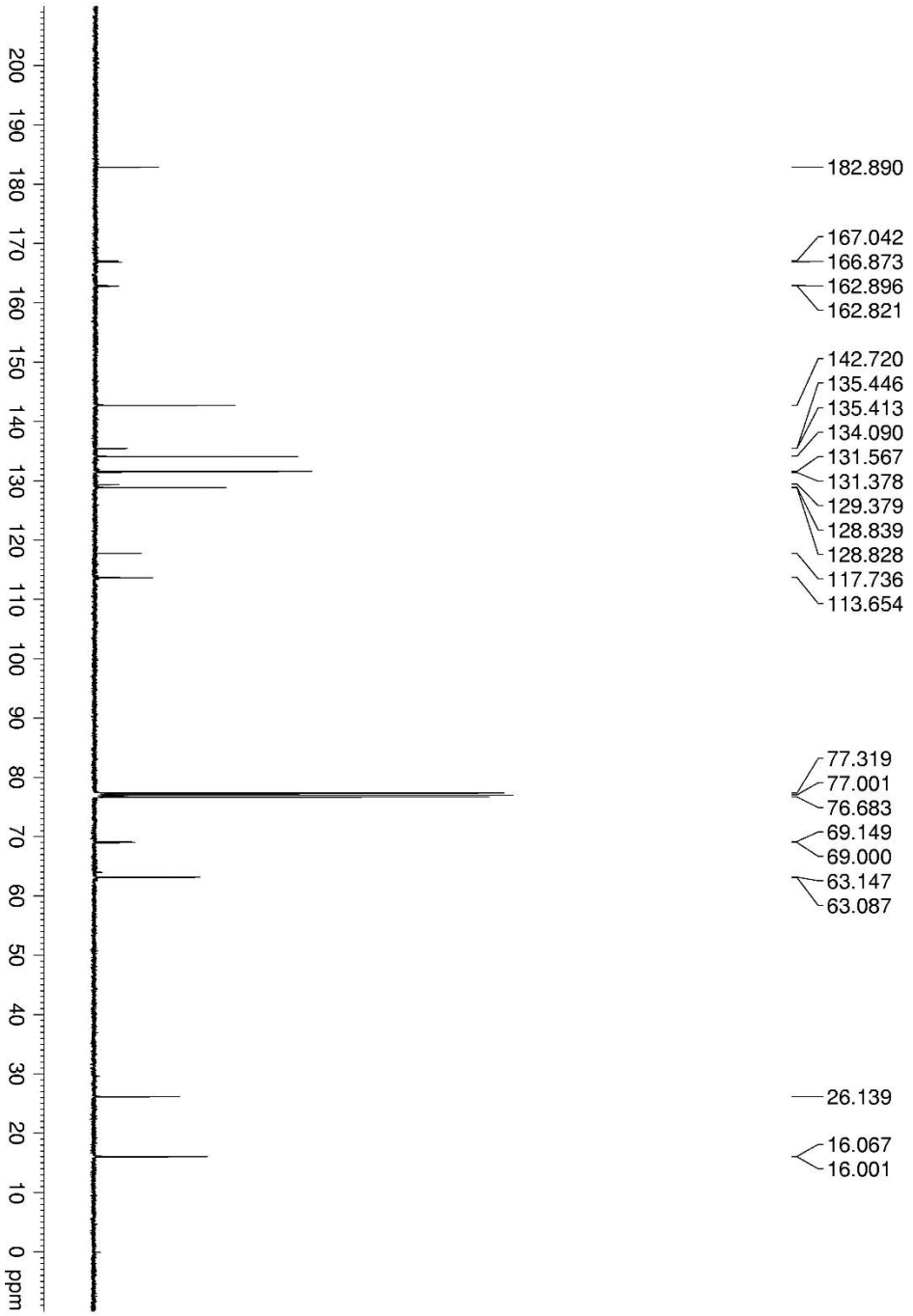

CN
O
O
P
OEt
OEt
N
O

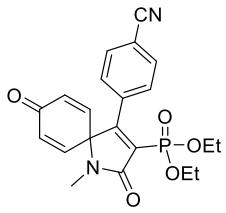
3h


2.073
2.003
4.075
3.990
3.000
6.102
ppm
7.664
7.643
7.352
7.331
6.541
6.515
6.489
6.464
4.172
4.164
4.154
4.146
4.136
4.129
4.121
4.111
4.103
4.100
4.082
4.064
4.057
2.905
1.169
1.152
1.134
0.000

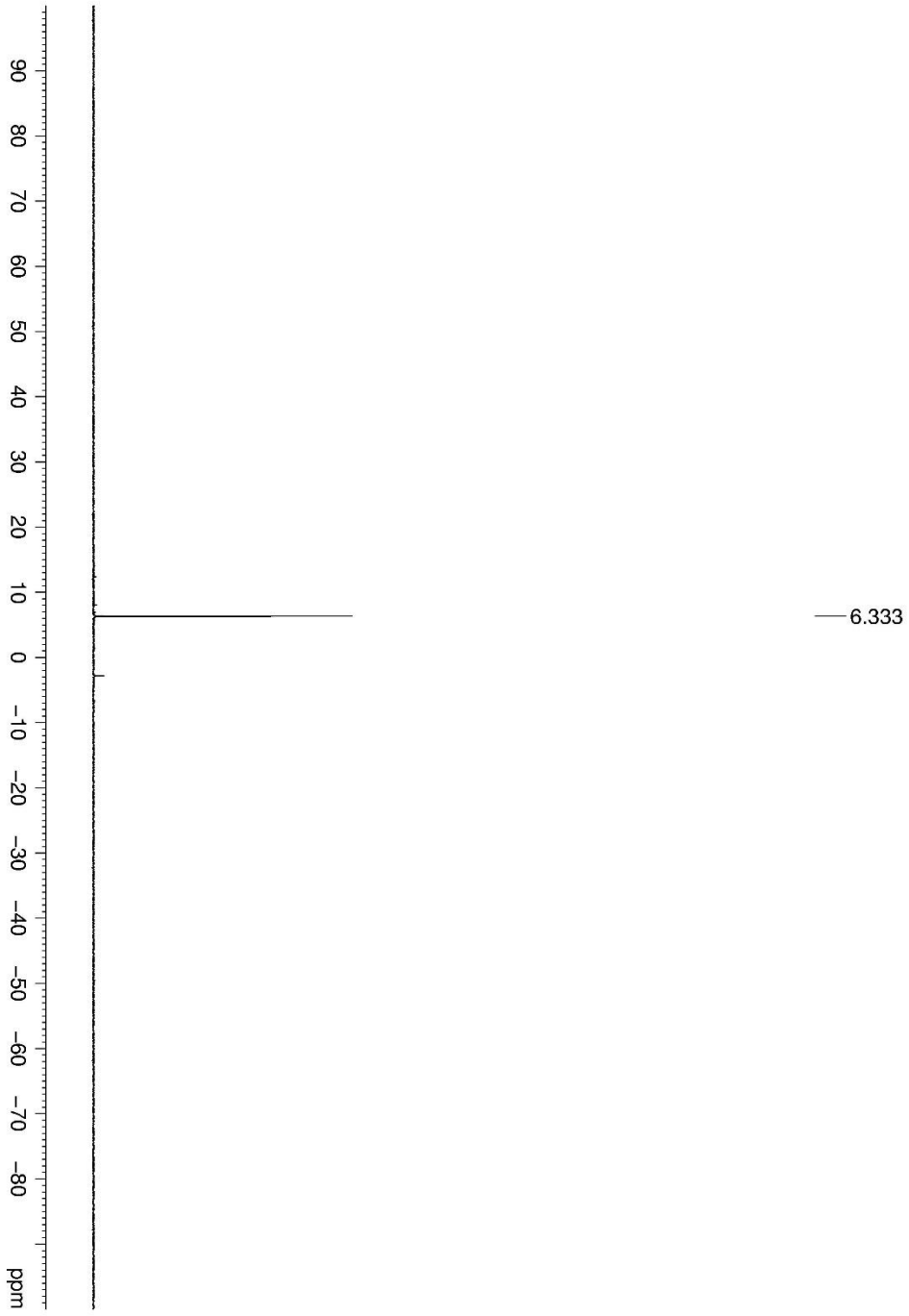

CN
O
O
P
OEt
OEt
N
O

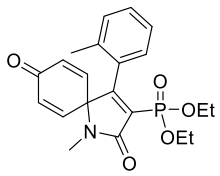
3h


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm
182.890
167.042
166.873
162.896
162.821
142.720
135.446
135.413
134.090
131.567
131.378
129.379
128.839
128.828
117.736
113.654
77.319
77.001
76.683
69.149
69.000
63.147
63.087
26.139
16.067
16.001

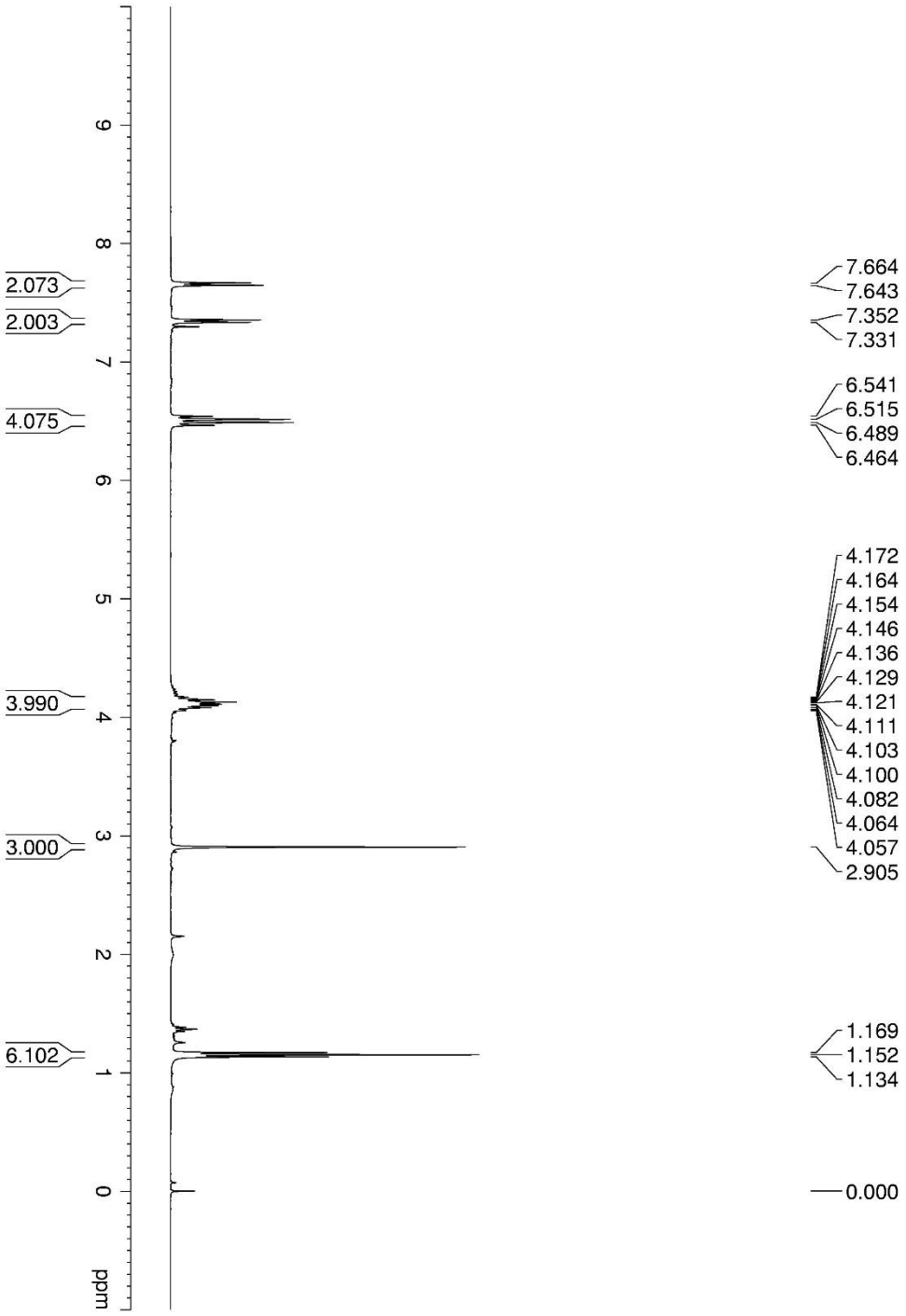

CN
O
O
P
OEt
OEt
N
O

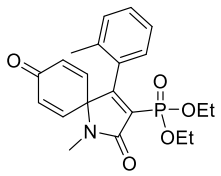
3h


90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
ppm
6.333

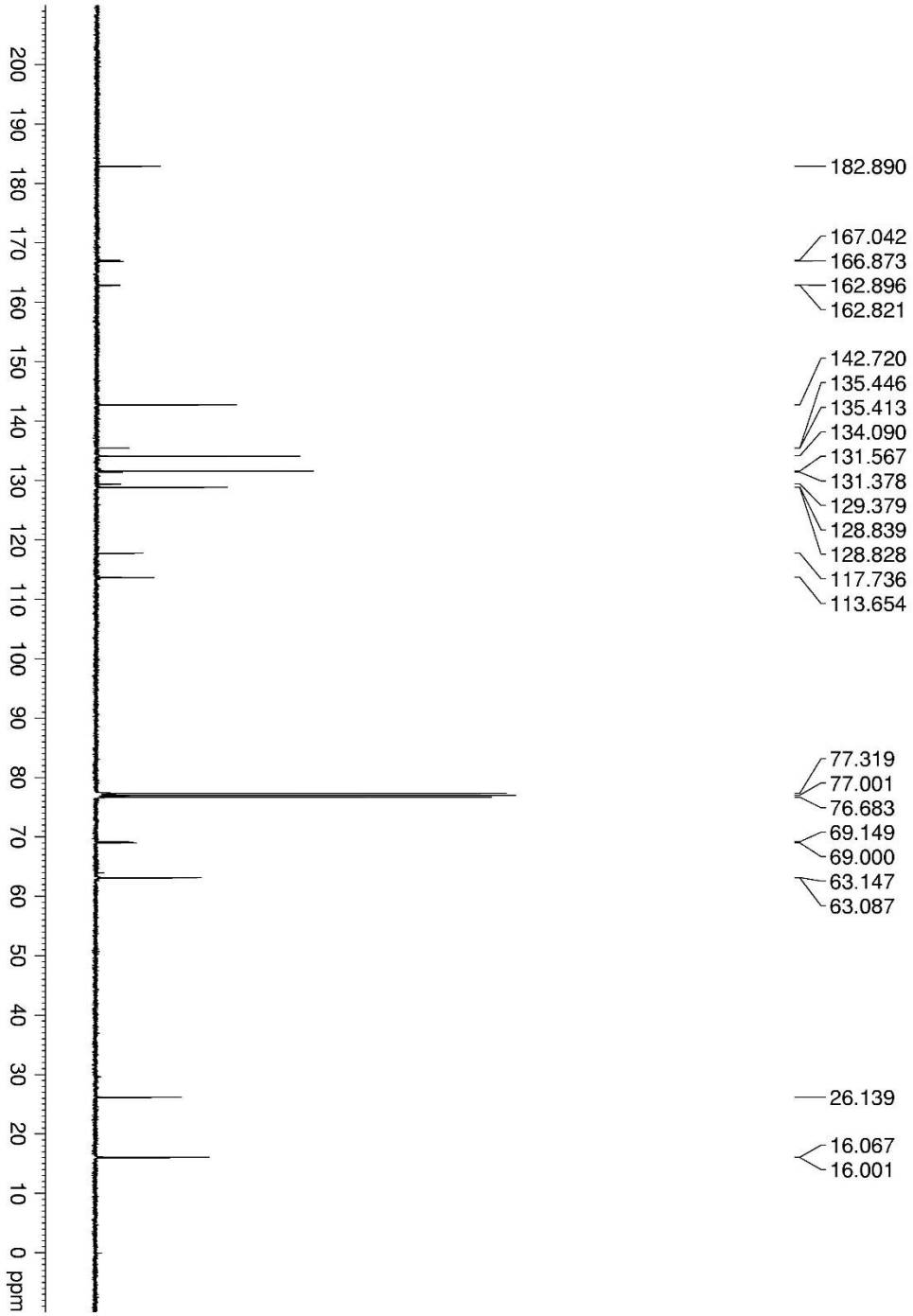

O
O
P
OEt
OEt
N
O

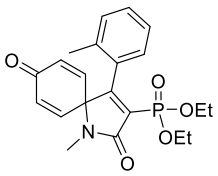
3i


2.073
2.003
4.075
3.990
3.000
6.102
ppm
7.664
7.643
7.352
7.331
6.541
6.515
6.489
6.464
4.172
4.164
4.154
4.146
4.136
4.129
4.121
4.111
4.103
4.100
4.082
4.064
4.057
2.905
1.169
1.152
1.134
0.000

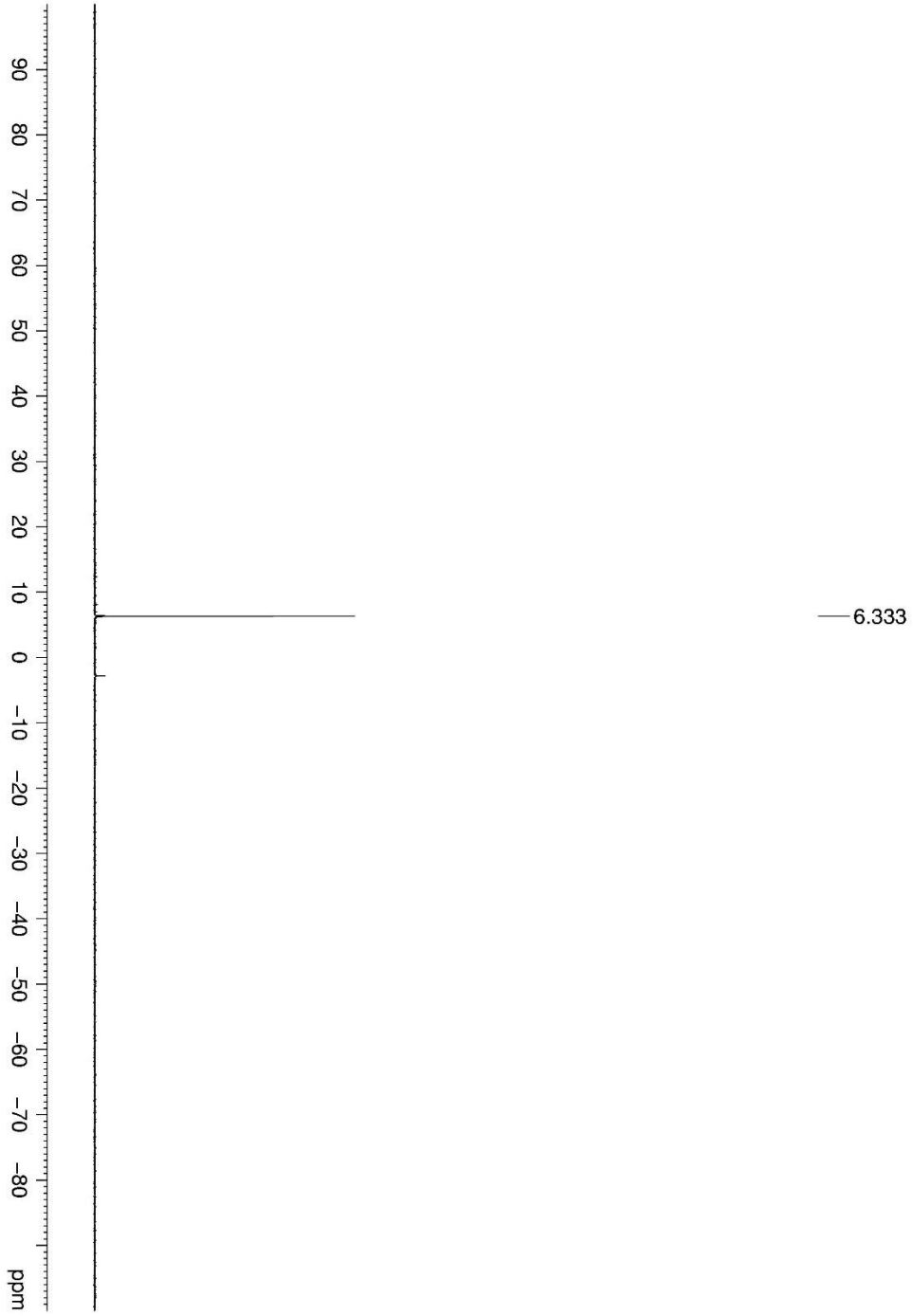

O
O
P
OEt
OEt
N
O

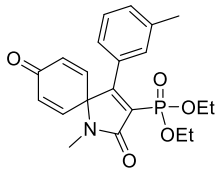
3i


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm
182.890
167.042
166.873
162.896
162.821
142.720
135.446
135.413
134.090
131.567
131.378
129.379
128.839
128.828
117.736
113.654
77.319
77.001
76.683
69.149
69.000
63.147
63.087
26.139
16.067
16.001

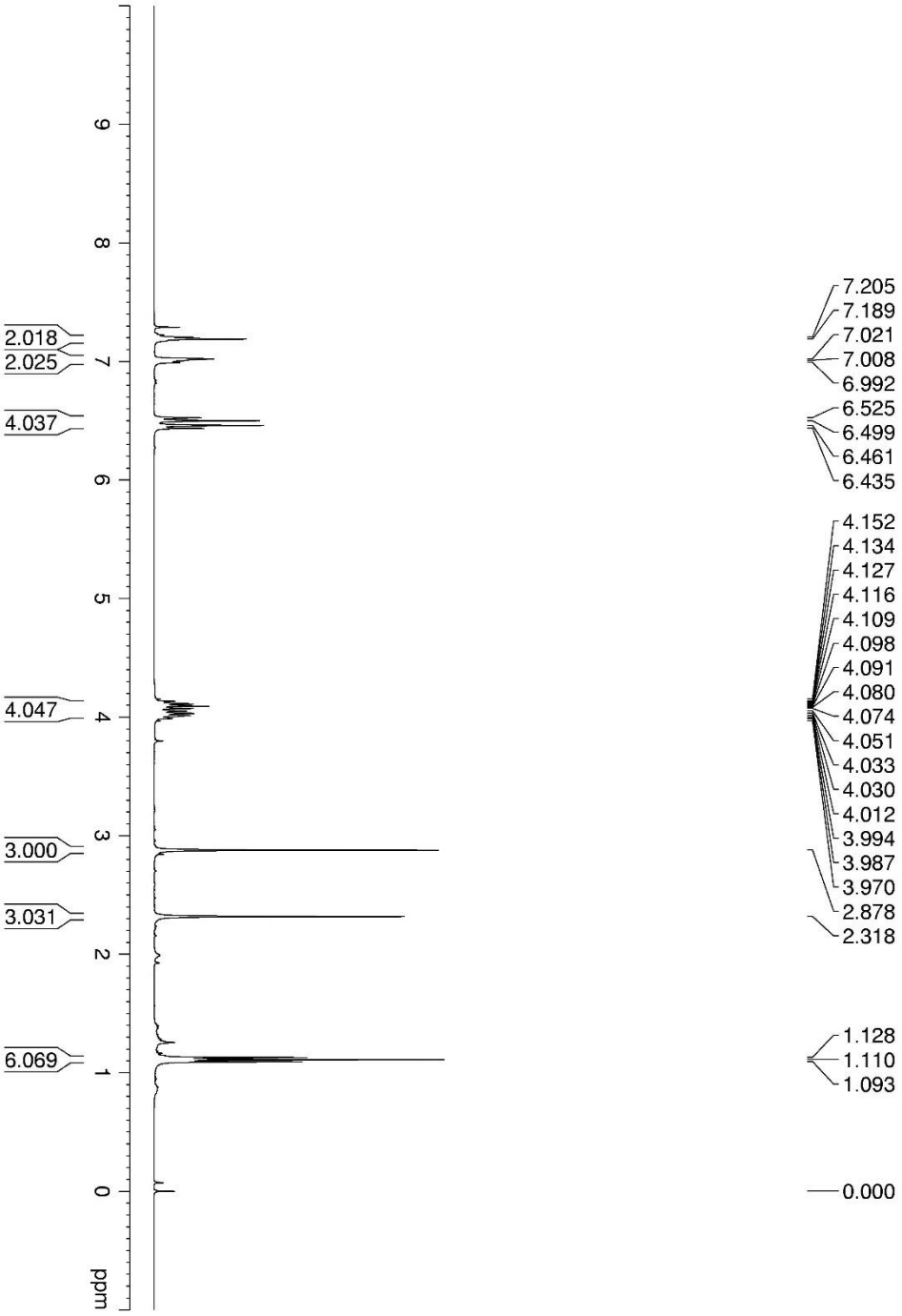

O
O
P
OEt
OEt
N
O

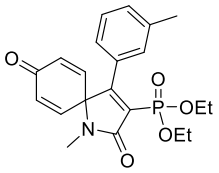
3i


90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
ppm
6.333

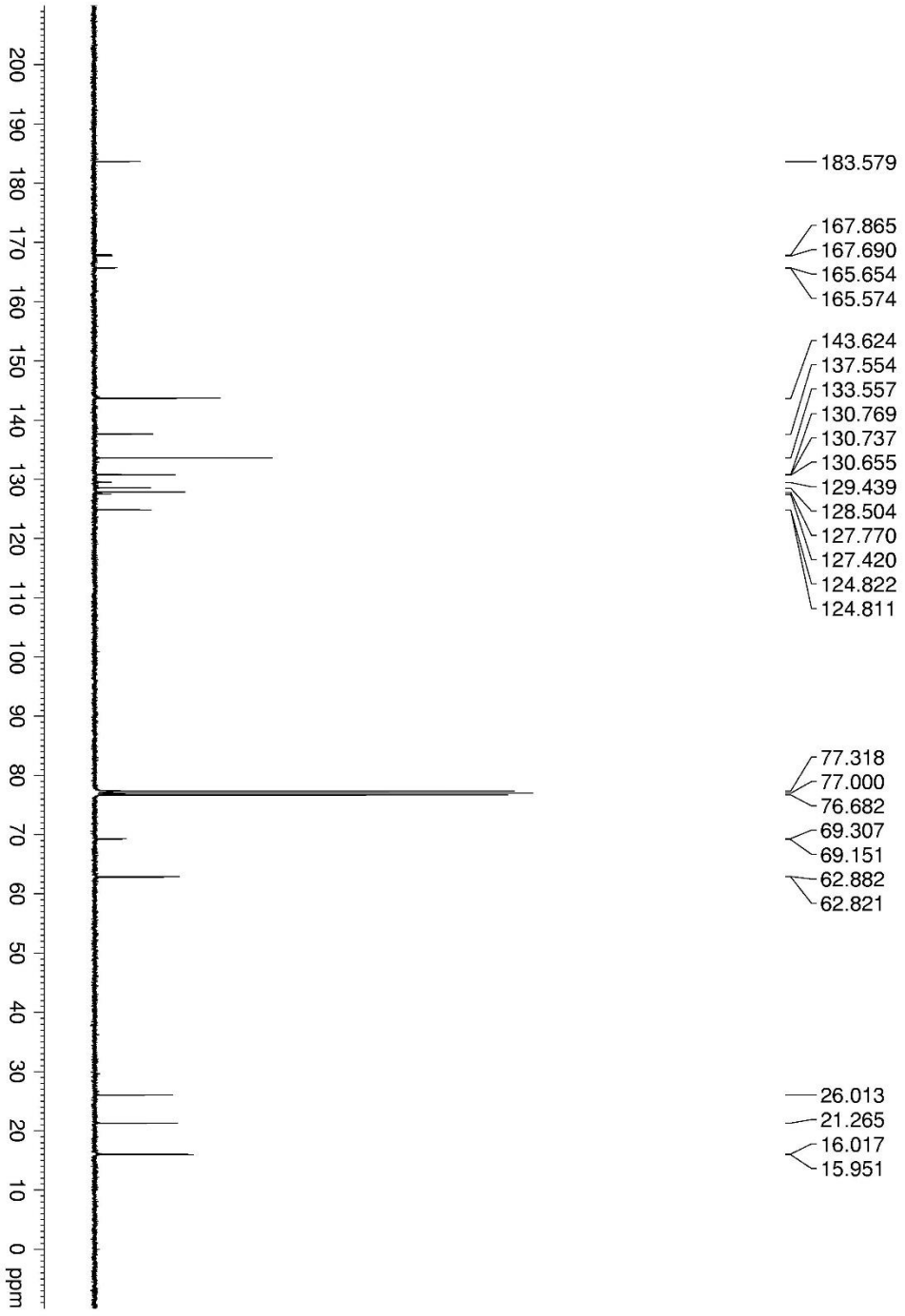

O
O
P
OEt
OEt
N
O

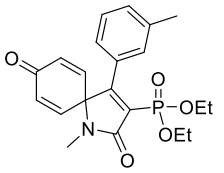
3j


2.018
2.025
4.037
4.047
3.000
3.031
6.069
9
8
7
6
5
4
3
2
1
0
ppm
7.205
7.189
7.021
7.008
6.992
6.525
6.499
6.461
6.435
4.152
4.134
4.127
4.116
4.109
4.098
4.091
4.080
4.074
4.051
4.033
4.030
4.012
3.994
3.987
3.970
2.878
2.318
1.128
1.110
1.093
0.000

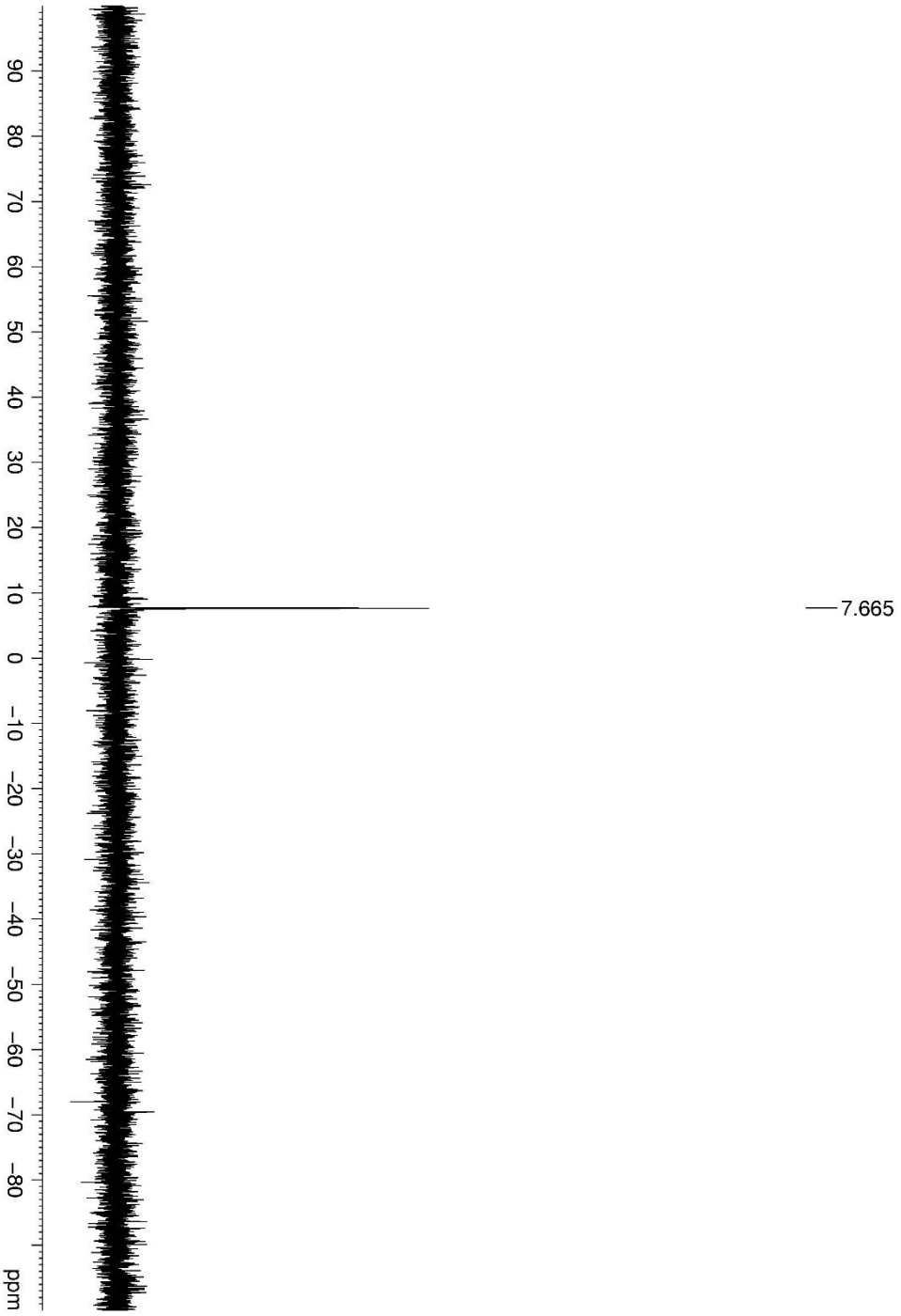

O
O
P
OEt
OEt
N
O

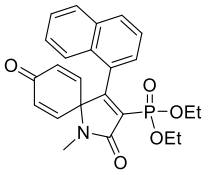
3j


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm
183.579
167.865
167.690
165.654
165.574
143.624
137.554
133.557
130.769
130.737
130.655
129.439
128.504
127.770
127.420
124.822
124.811
77.318
77.000
76.682
69.307
69.151
62.882
62.821
26.013
21.265
16.017
15.951

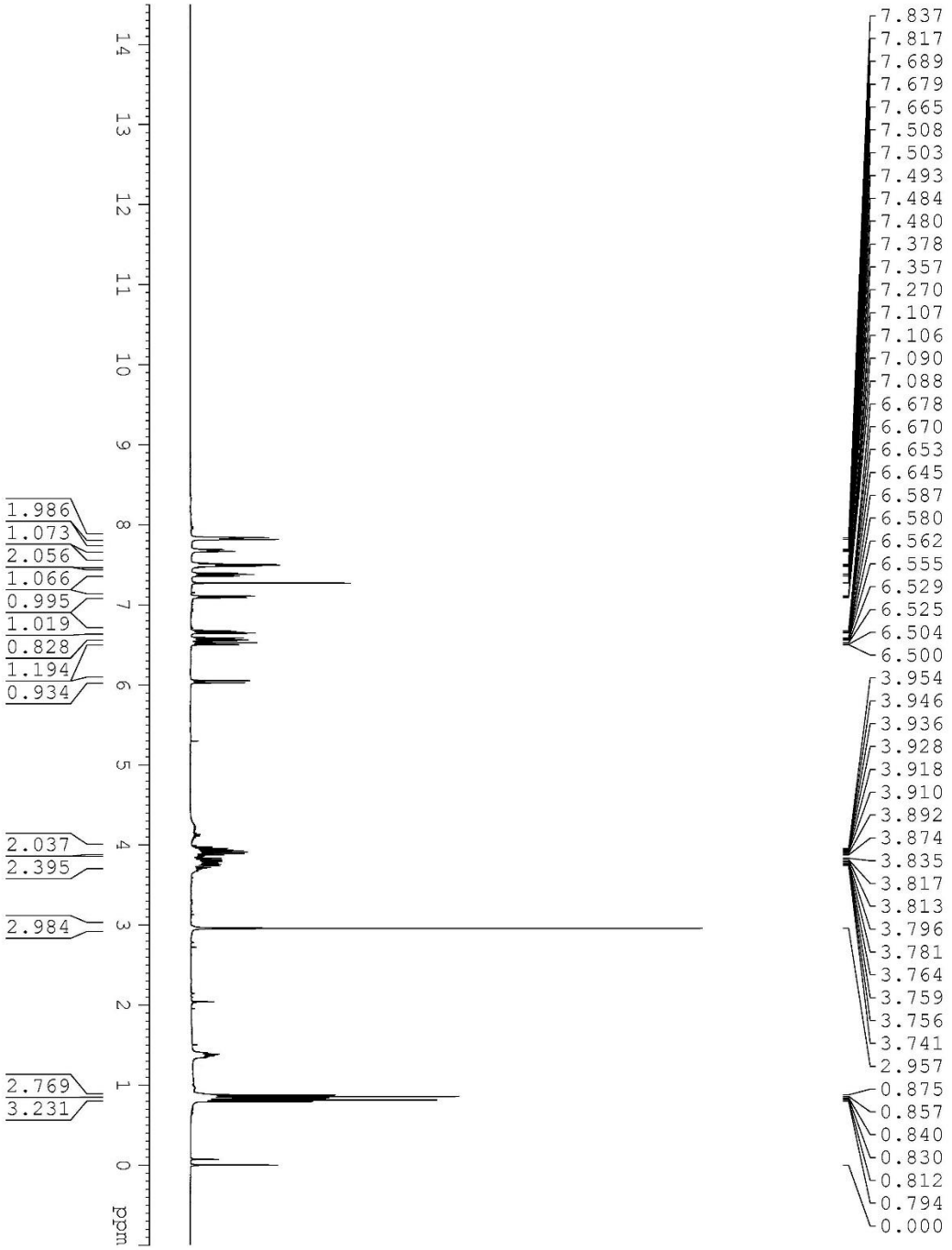

O
O
P
OEt
OEt
N
O

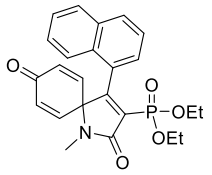
3j


90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
ppm
7.665

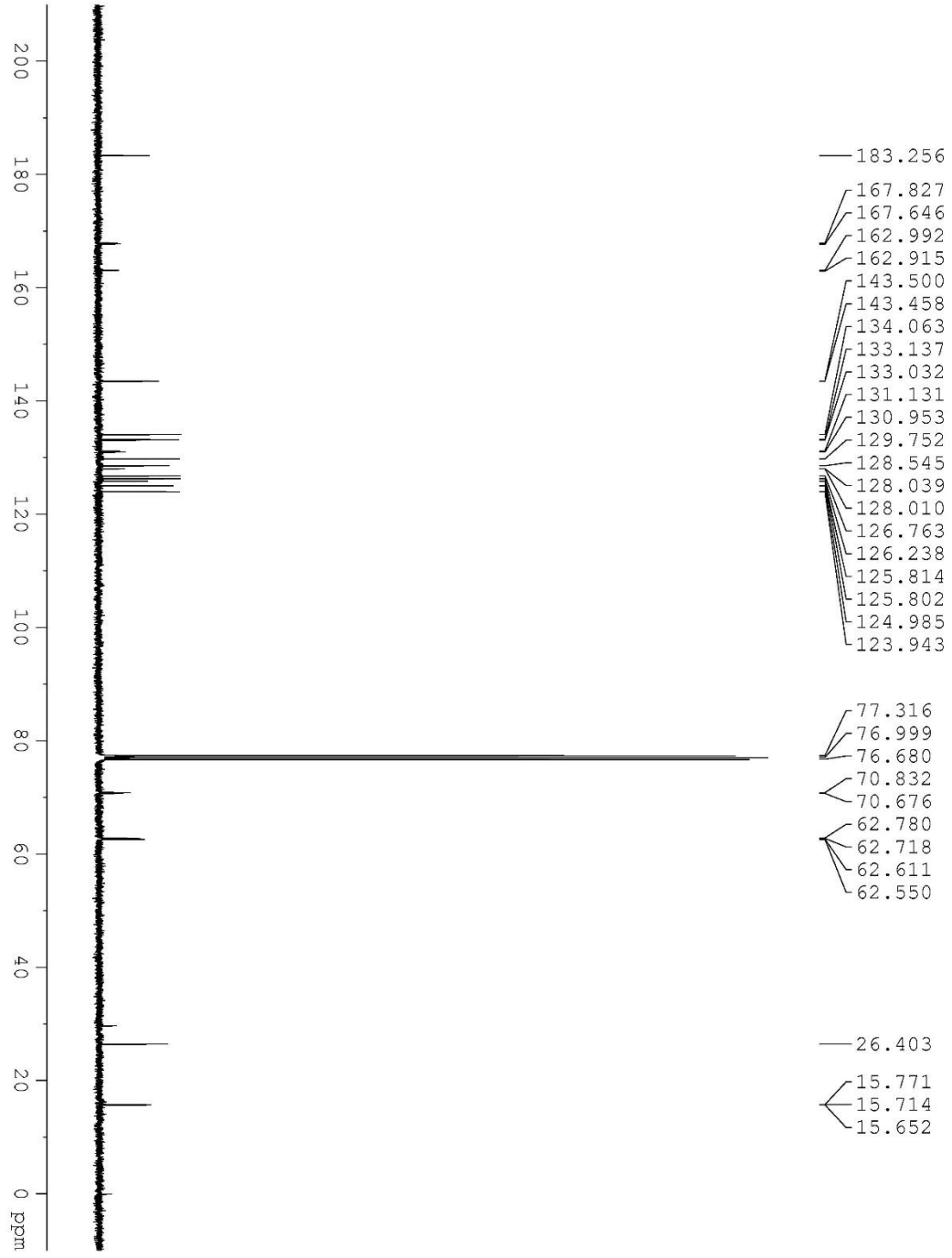

O
O
P
OEt
OEt
N
O

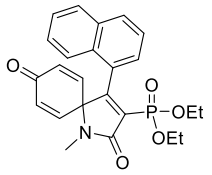
3k


1.986
1.073
2.056
1.066
0.995
1.019
0.828
1.194
0.934
2.037
2.395
2.984
2.769
3.231
ppm
7.837
7.817
7.689
7.679
7.665
7.508
7.503
7.493
7.484
7.480
7.378
7.357
7.270
7.107
7.106
7.090
7.088
6.678
6.670
6.653
6.645
6.587
6.580
6.562
6.555
6.529
6.525
6.504
6.500
3.954
3.946
3.936
3.928
3.918
3.910
3.892
3.874
3.835
3.817
3.813
3.796
3.781
3.764
3.759
3.756
3.741
2.957
0.875
0.857
0.840
0.830
0.812
0.794
0.000

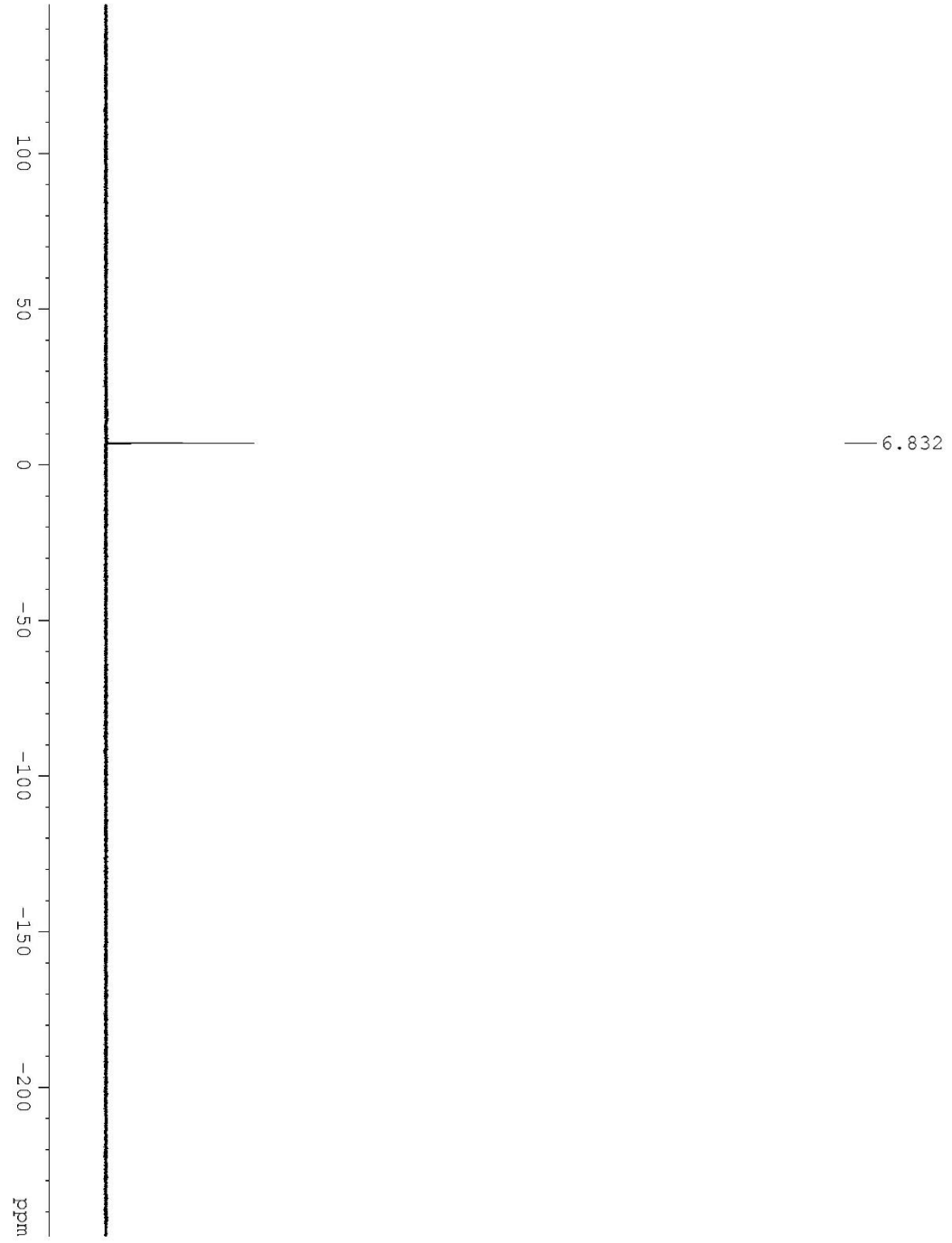

O
O
P
OEt
OEt
N
O

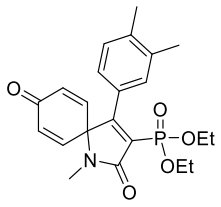
3k


200
180
160
140
120
100
80
60
40
20
0 ppm
183.256
167.827
167.646
162.992
162.915
143.500
143.458
134.063
133.137
133.032
131.131
130.953
129.752
128.545
128.039
128.010
126.763
126.238
125.814
125.802
124.985
123.943
77.316
76.999
76.680
70.832
70.676
62.780
62.718
62.611
62.550
26.403
15.771
15.714
15.652

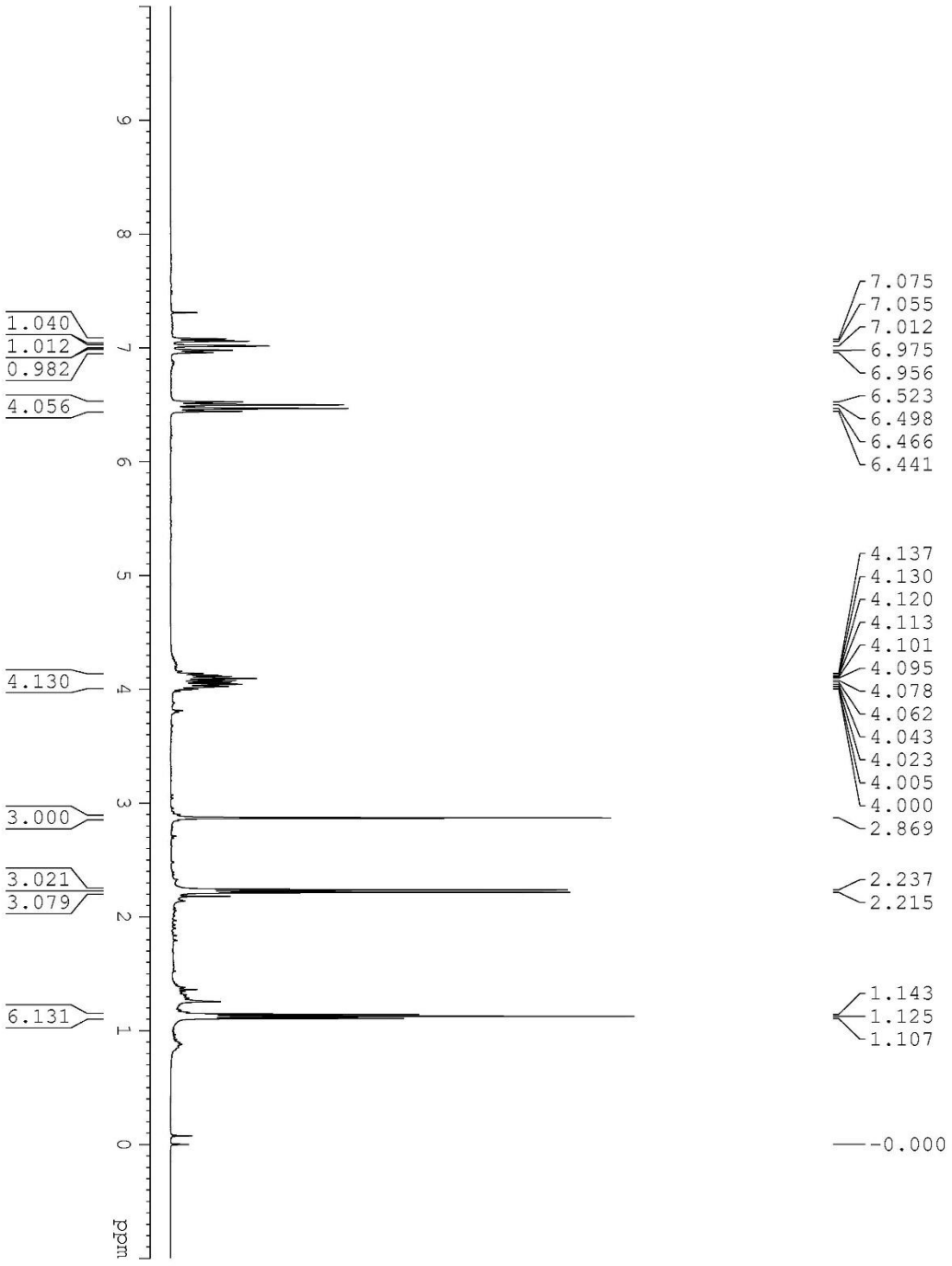


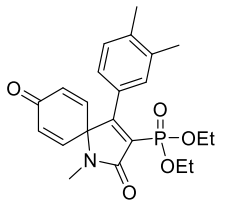
3k



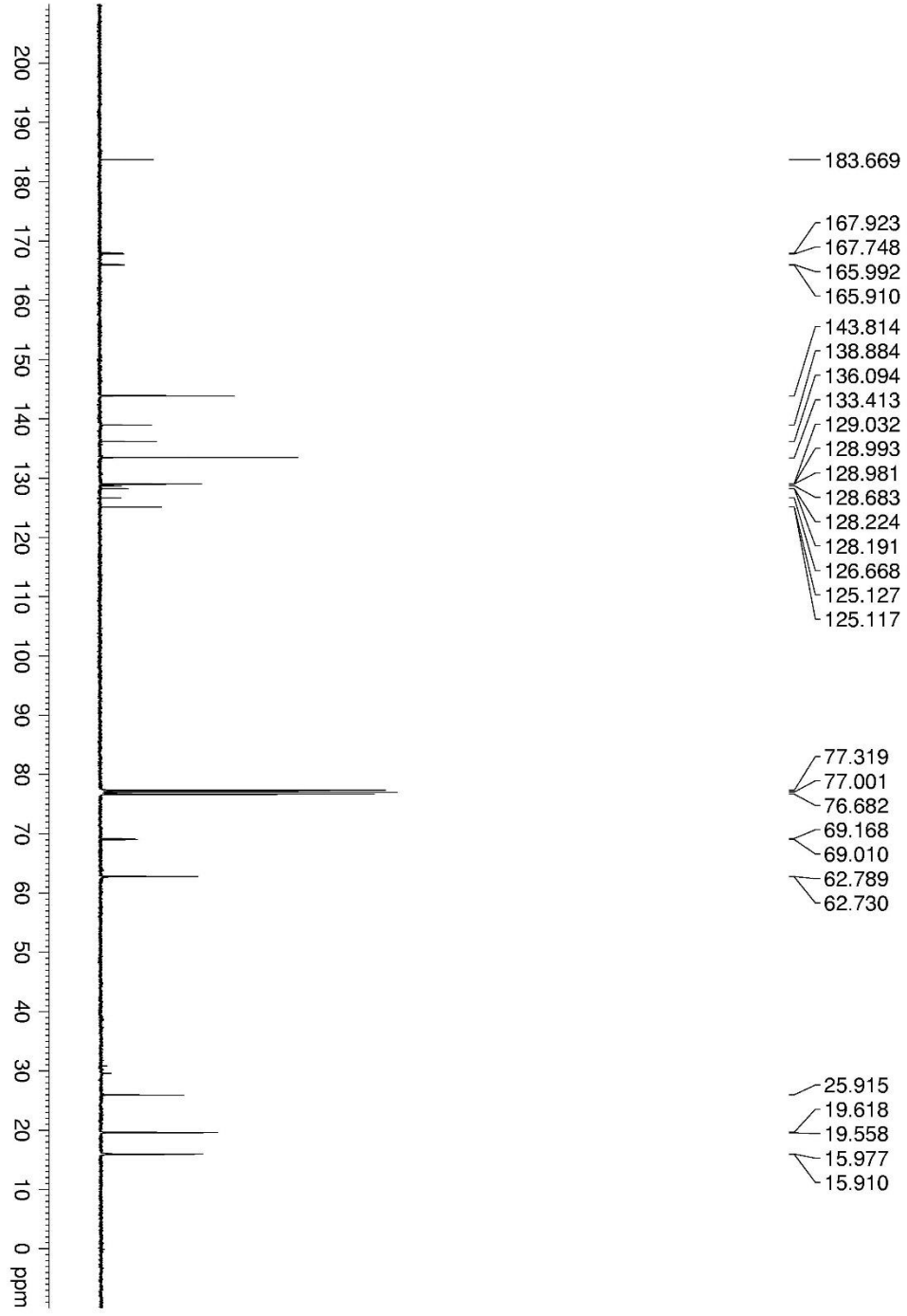

O
O
P
OEt
OEt
N
O

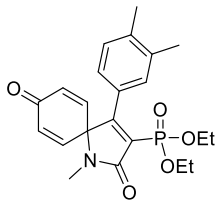
3l


1.040
1.012
0.982
4.056
4.130
3.000
3.021
3.079
6.131
ppm
7.075
7.055
7.012
6.975
6.956
6.523
6.498
6.466
6.441
4.137
4.130
4.120
4.113
4.101
4.095
4.078
4.062
4.043
4.023
4.005
4.000
2.869
2.237
2.215
1.143
1.125
1.107
-0.000

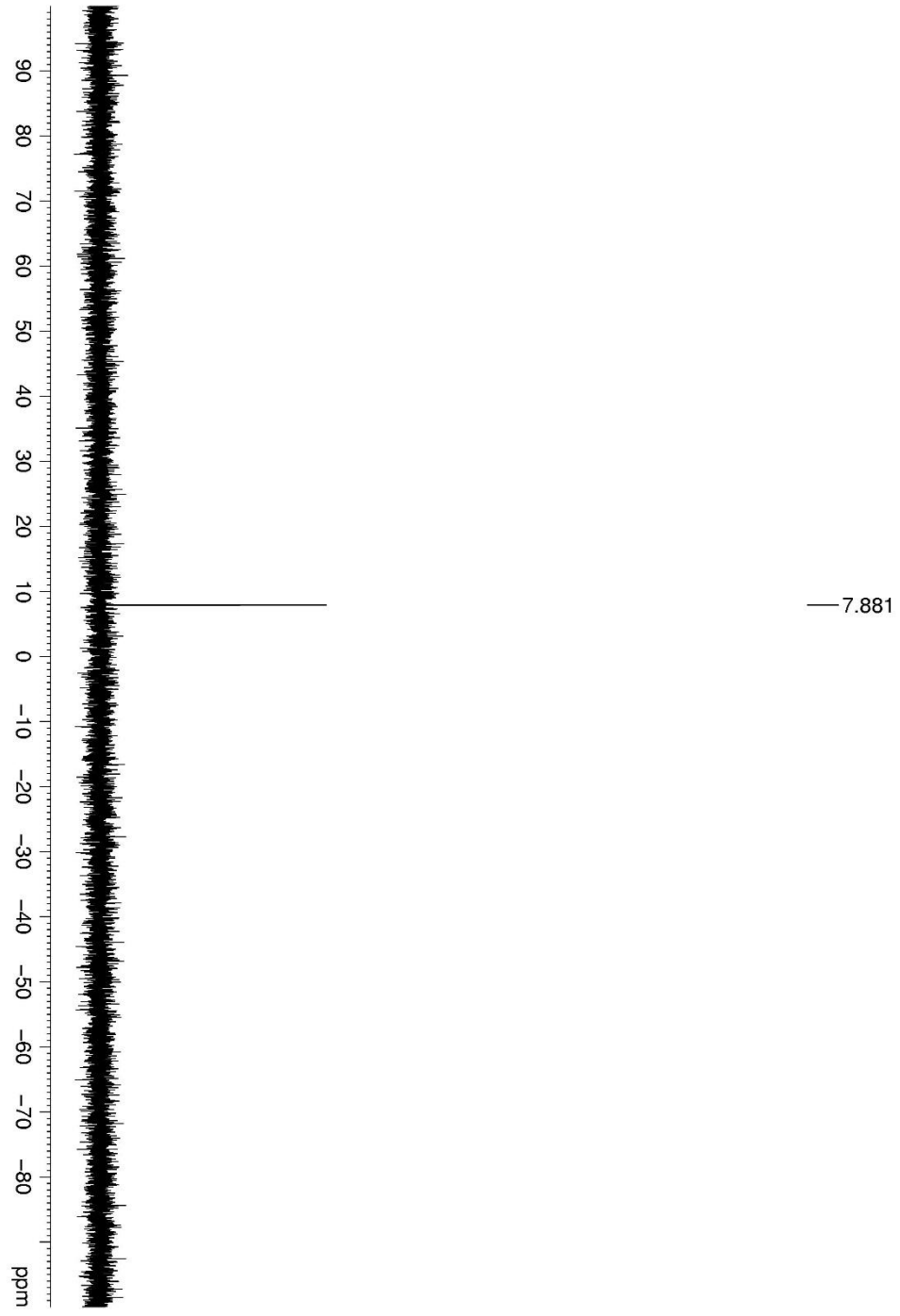

O
O
P
OEt
OEt
N
O

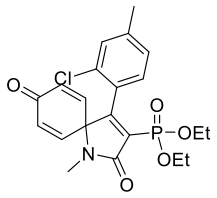
3l


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm
183.669
167.923
167.748
165.992
165.910
143.814
138.884
136.094
133.413
129.032
128.993
128.981
128.683
128.224
128.191
126.668
125.127
125.117
77.319
77.001
76.682
69.168
69.010
62.789
62.730
25.915
19.618
19.558
15.977
15.910

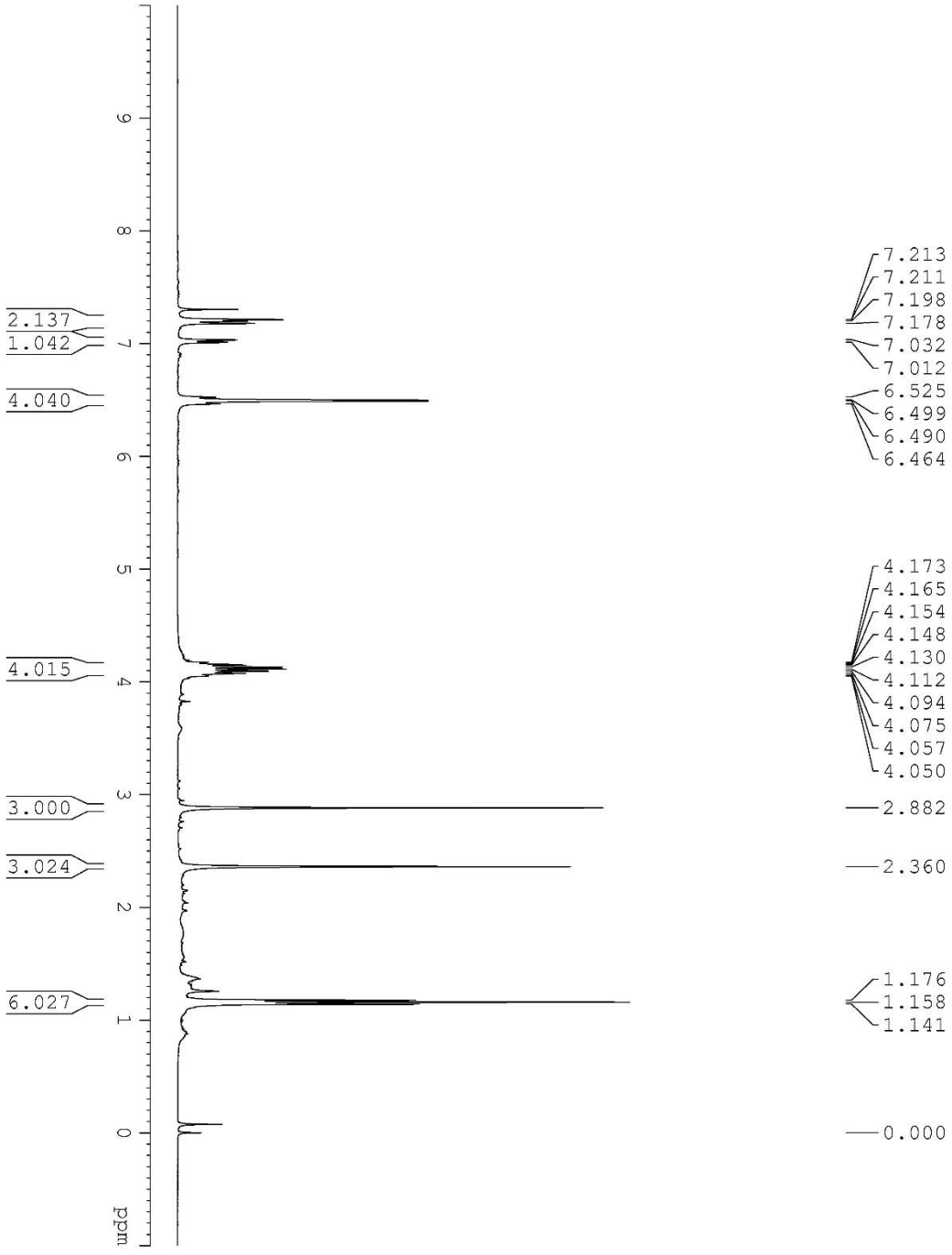

O
O
P
OEt
OEt
N
O

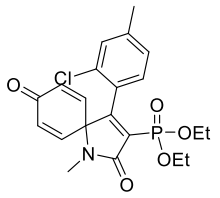
3l


90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
ppm
7.881

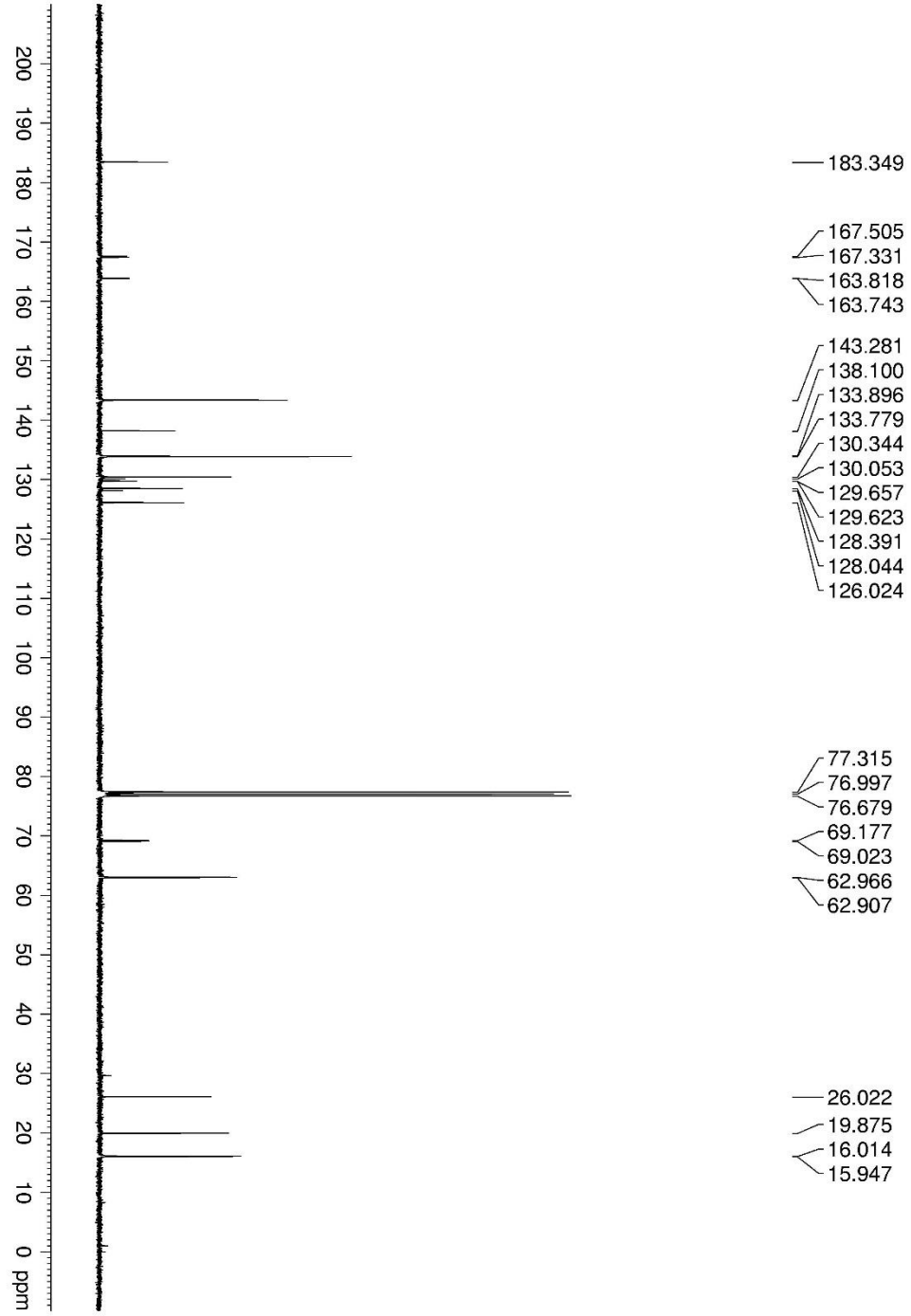

Cl
O
O
P
OEt
OEt
N
O

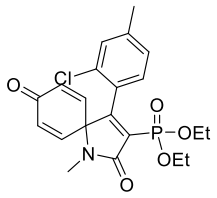
3m


2.137
1.042
4.040
4.015
3.000
3.024
6.027
ppm
7.213
7.211
7.198
7.178
7.032
7.012
6.525
6.499
6.490
6.464
4.173
4.165
4.154
4.148
4.130
4.112
4.094
4.075
4.057
4.050
2.882
2.360
1.176
1.158
1.141
0.000

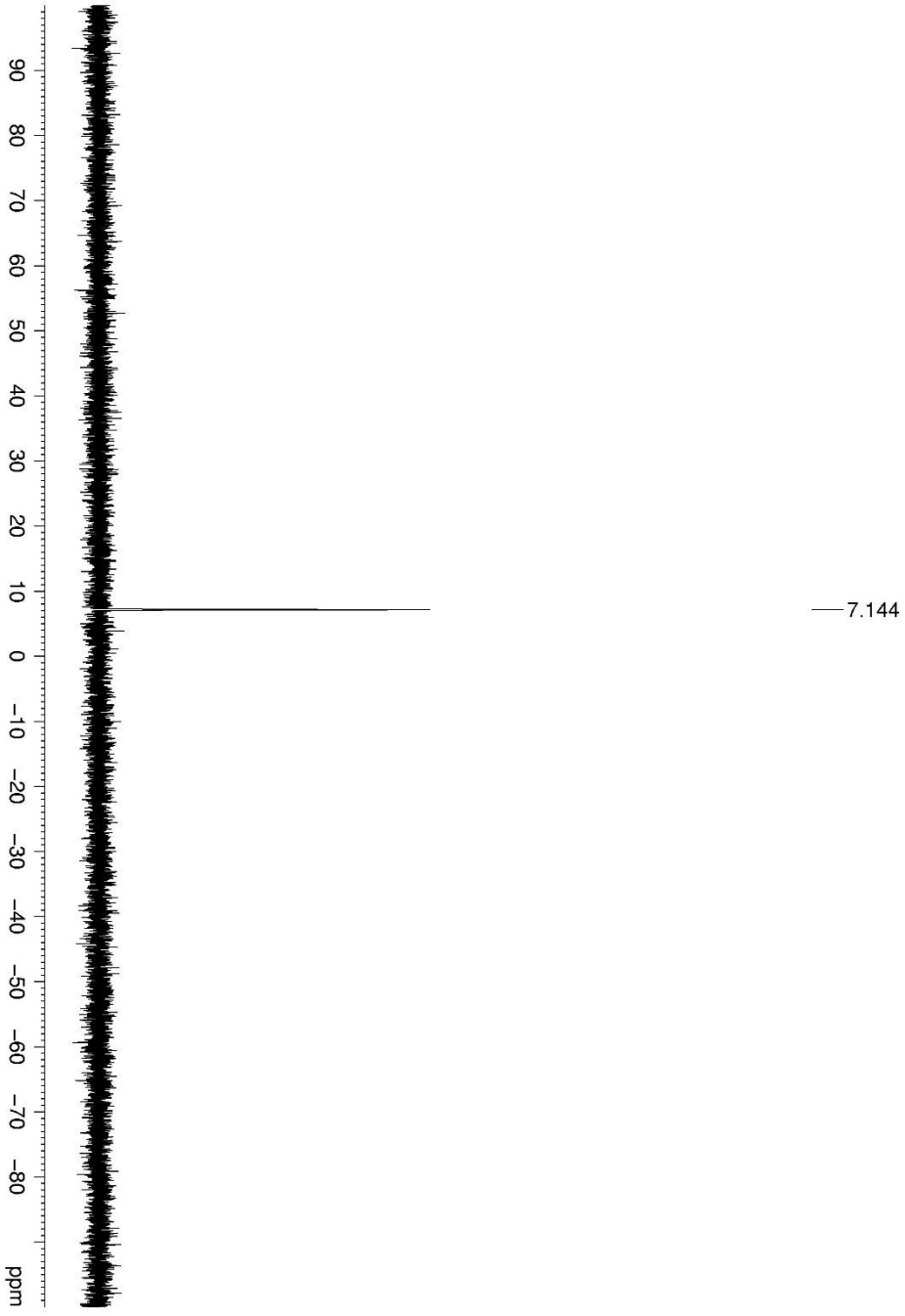

Cl
O
O
P
OEt
OEt
N
O

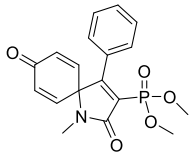
3m


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
183.349
167.505
167.331
163.818
163.743
143.281
138.100
133.896
133.779
130.344
130.053
129.657
129.623
128.391
128.044
126.024
77.315
76.997
76.679
69.177
69.023
62.966
62.907
26.022
19.875
16.014
15.947

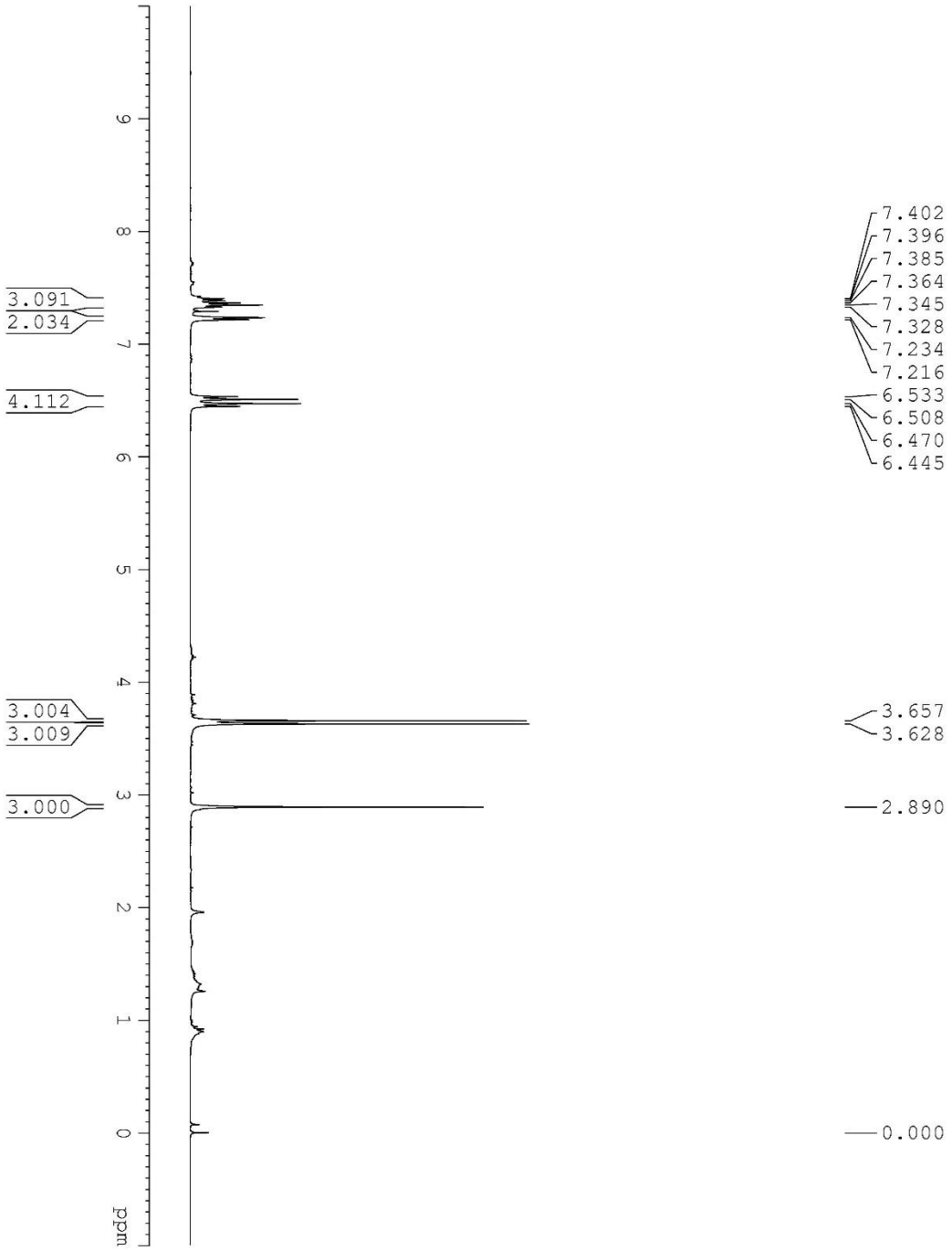

Cl
O
O
P
OEt
OEt
N
O

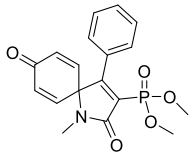
3m


90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
ppm
7.144

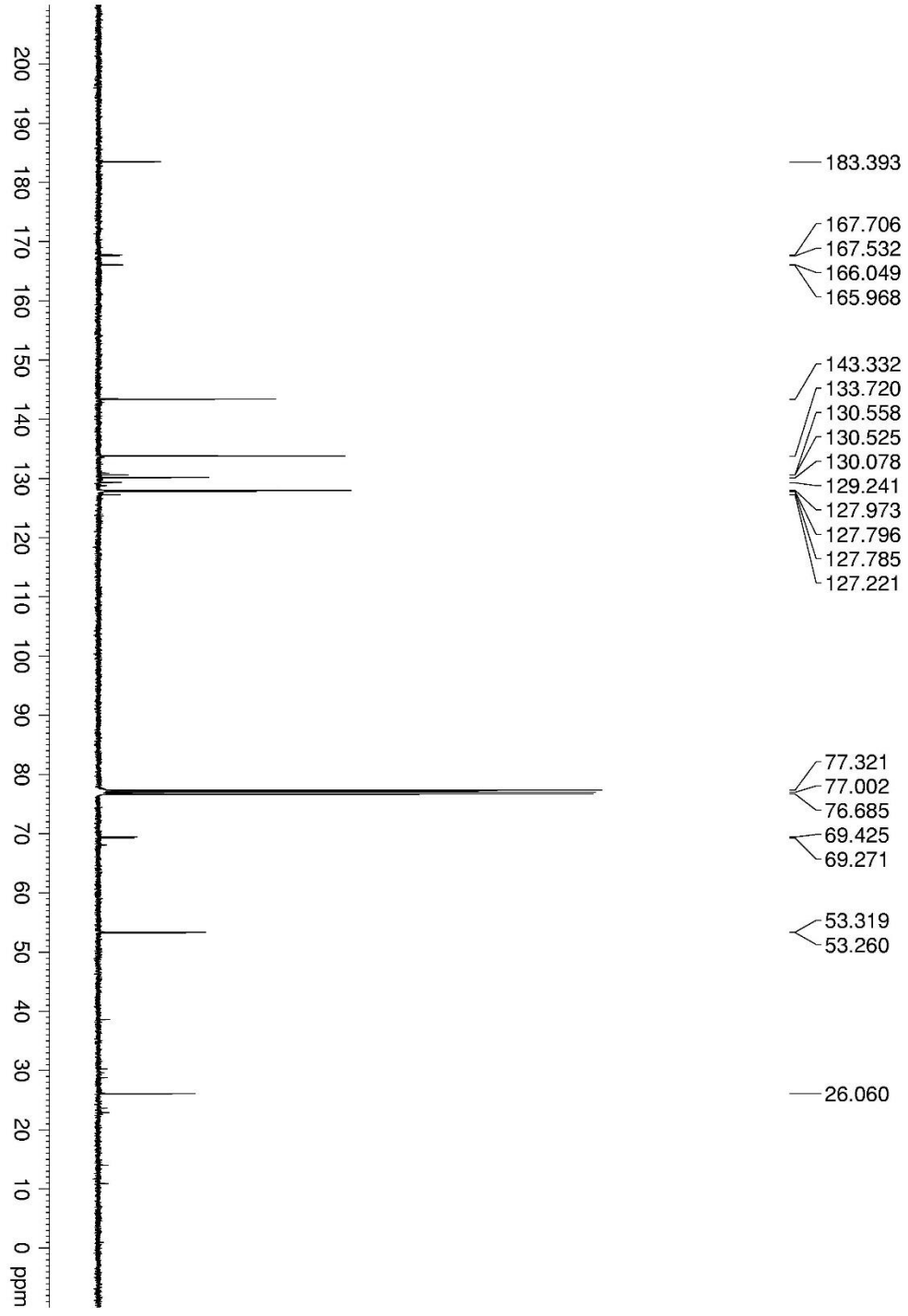


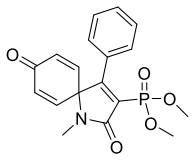
3n


7.402
7.396
7.385
7.364
7.345
7.328
7.234
7.216
6.533
6.508
6.470
6.445
3.657
3.628
2.890
0.000
3.091
2.034
4.112
3.004
3.009
3.000
ppm

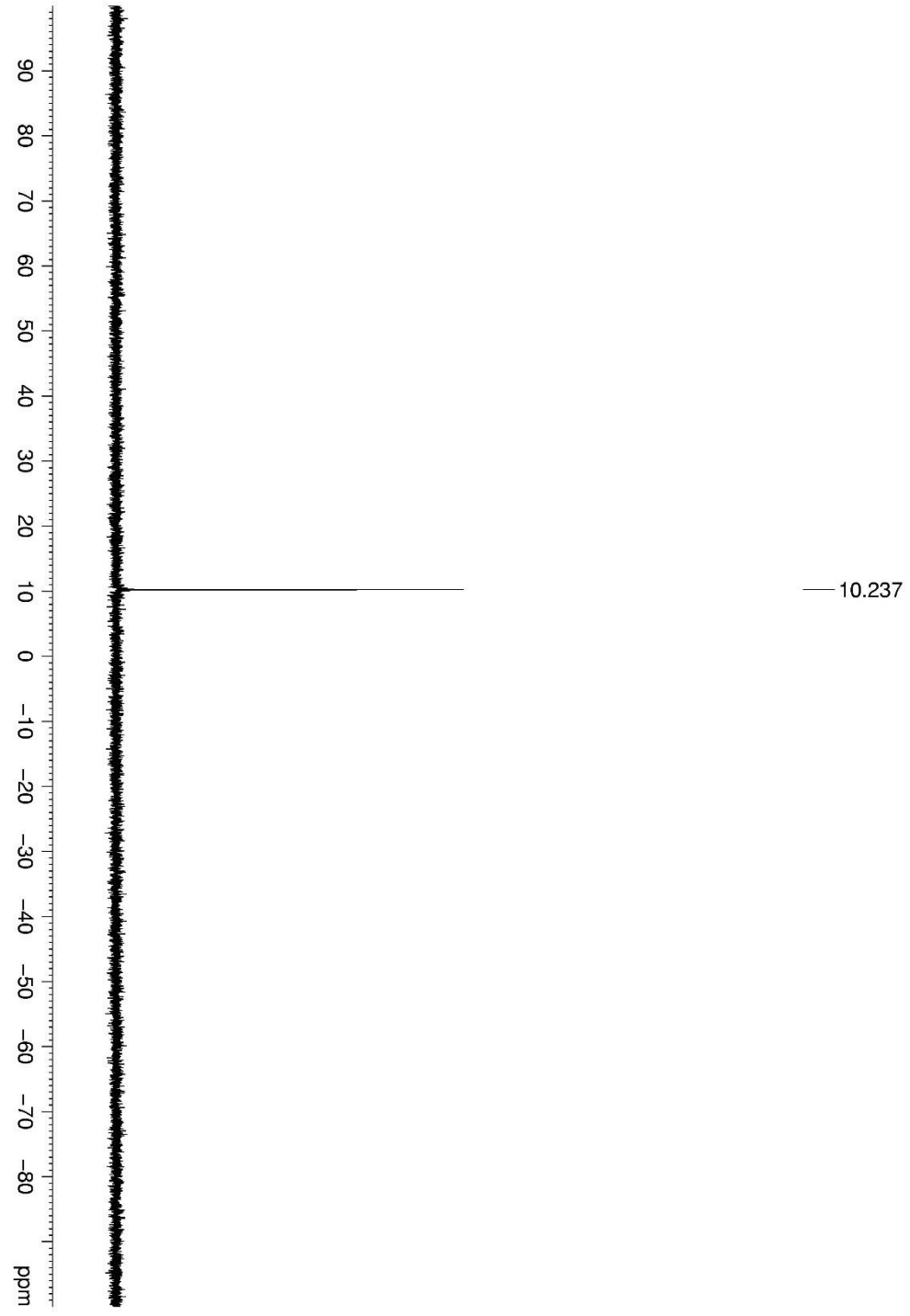


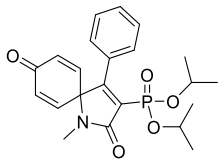
3n


183.393
167.706
167.532
166.049
165.968
143.332
133.720
130.558
130.525
130.078
129.241
127.973
127.796
127.785
127.221
77.321
77.002
76.685
69.425
69.271
53.319
53.260
26.060
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

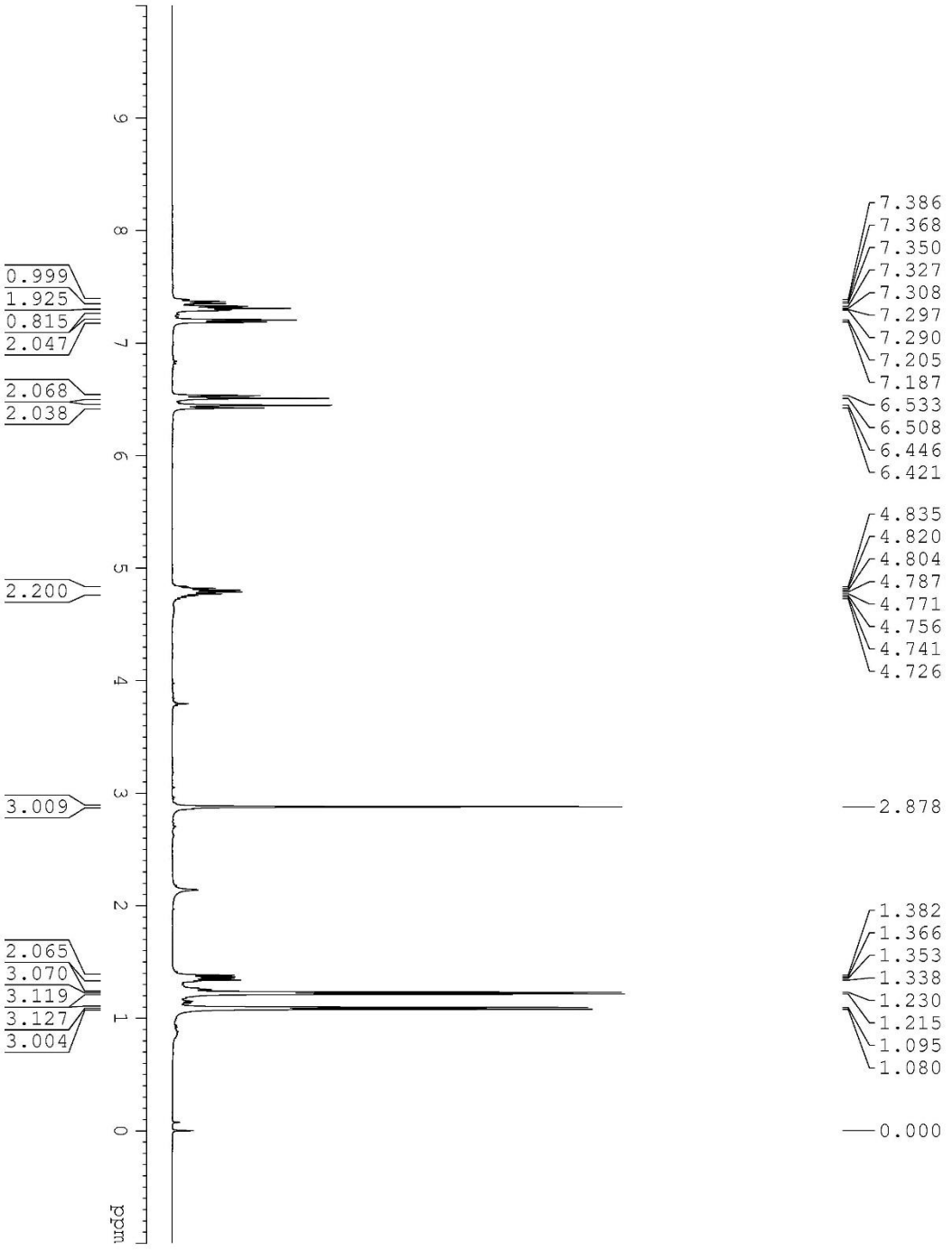

O
O
P
O
O
N
O

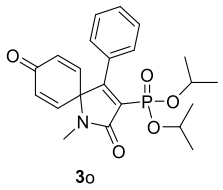
3n


90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
ppm
10.237

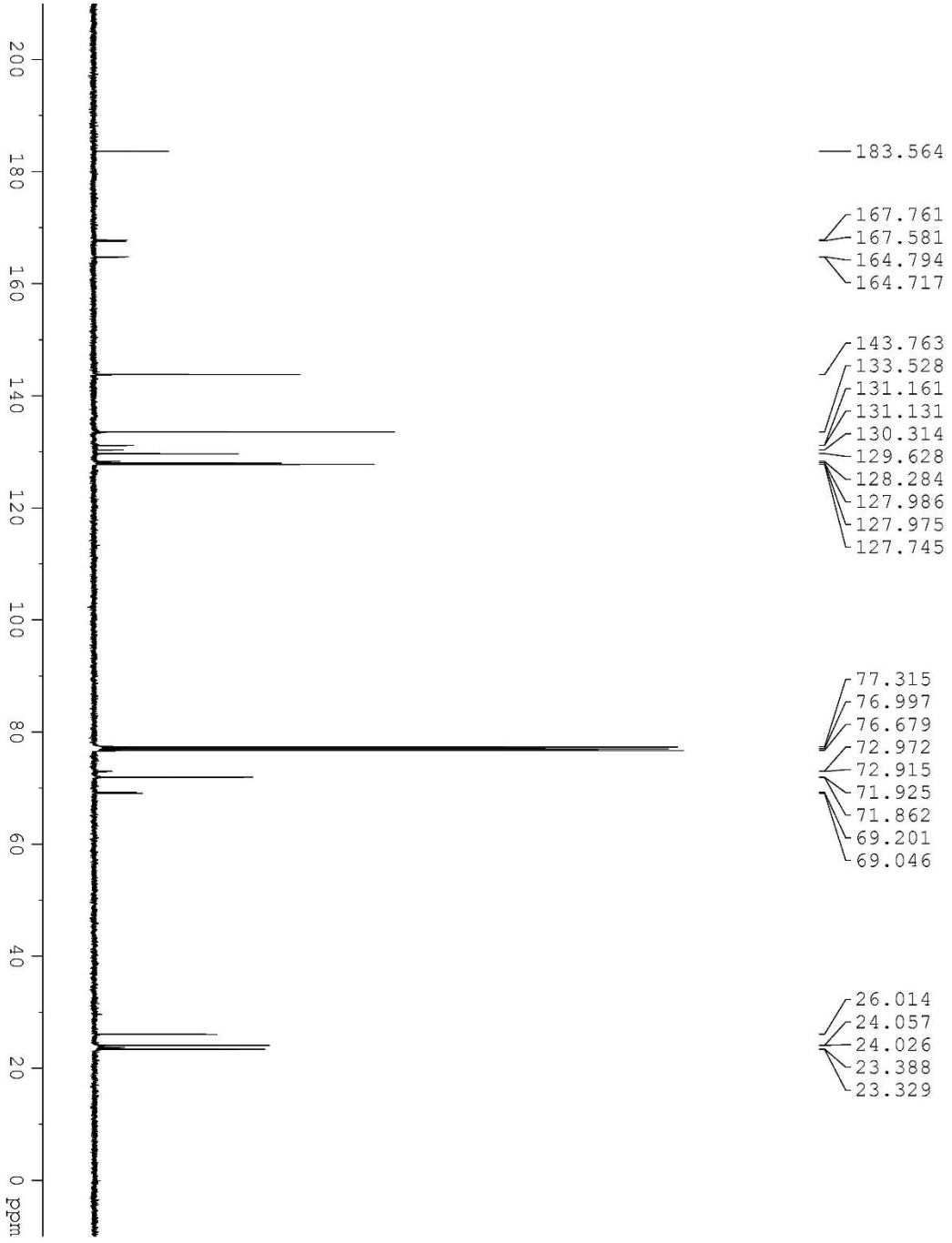


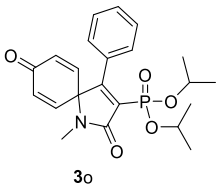
3o


0.999
1.925
0.815
2.047
2.068
2.038
2.200
3.009
2.065
3.070
3.119
3.127
3.004
7.386
7.368
7.350
7.327
7.308
7.297
7.290
7.205
7.187
6.533
6.508
6.446
6.421
4.835
4.820
4.804
4.787
4.771
4.756
4.741
4.726
2.878
1.382
1.366
1.353
1.338
1.230
1.215
1.095
1.080
0.000
wpd

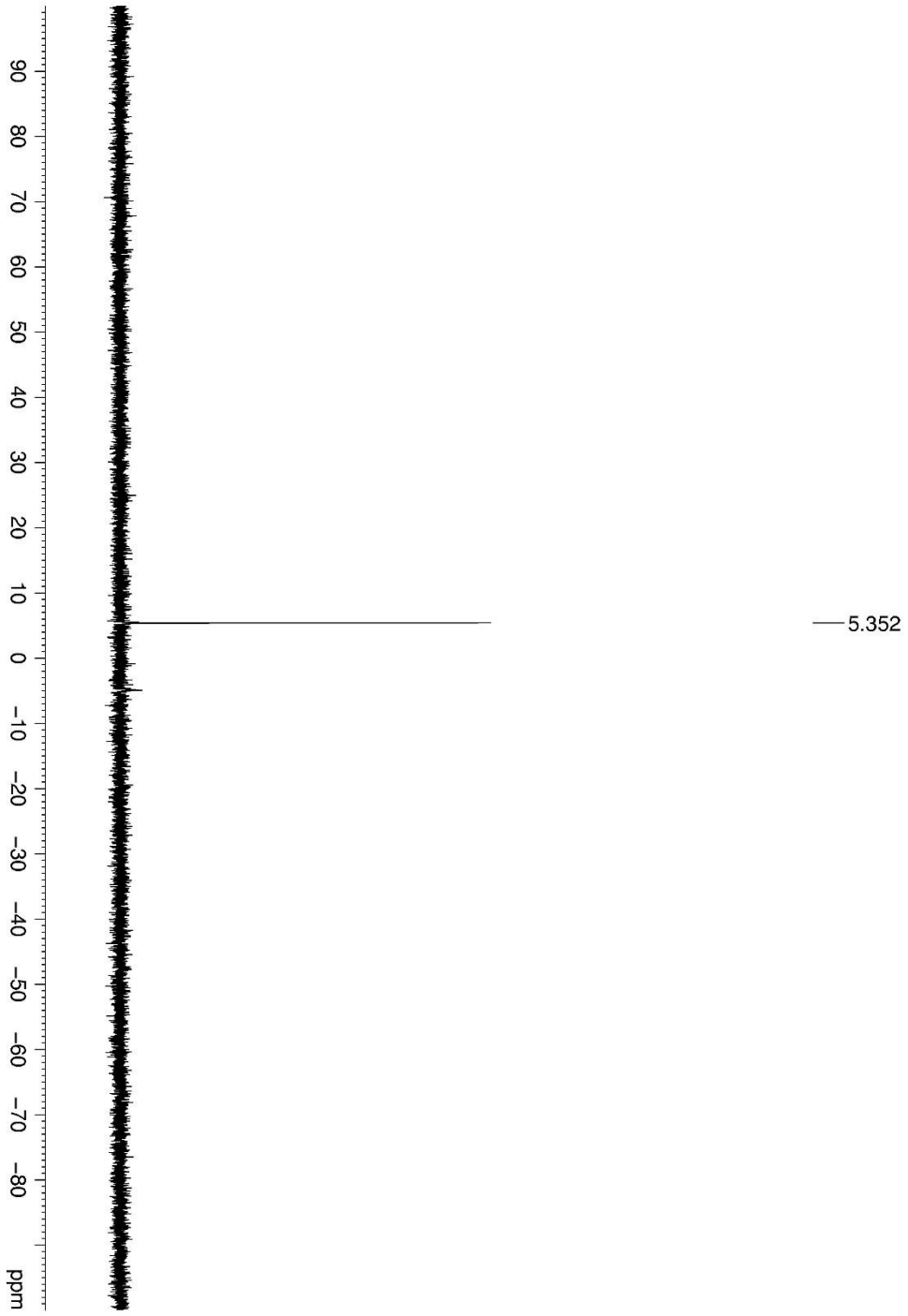


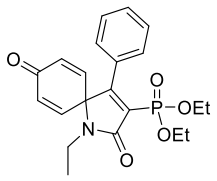
3o


200
180
160
140
120
100
80
60
40
20
0 ppm
183.564
167.761
167.581
164.794
164.717
143.763
133.528
131.161
131.131
130.314
129.628
128.284
127.986
127.975
127.745
77.315
76.997
76.679
72.972
72.915
71.925
71.862
69.201
69.046
26.014
24.057
24.026
23.388
23.329

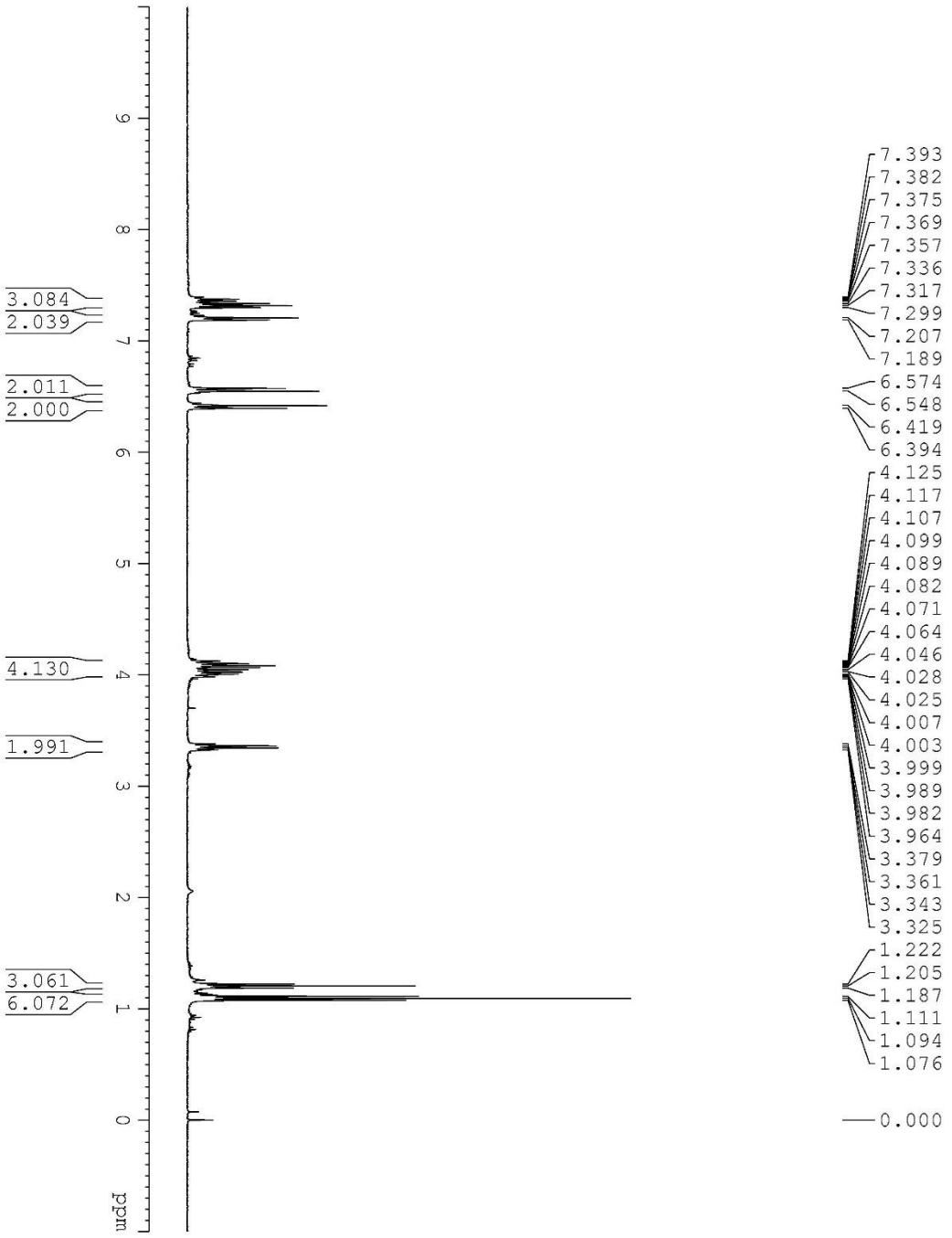


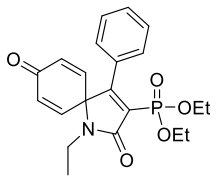
3o



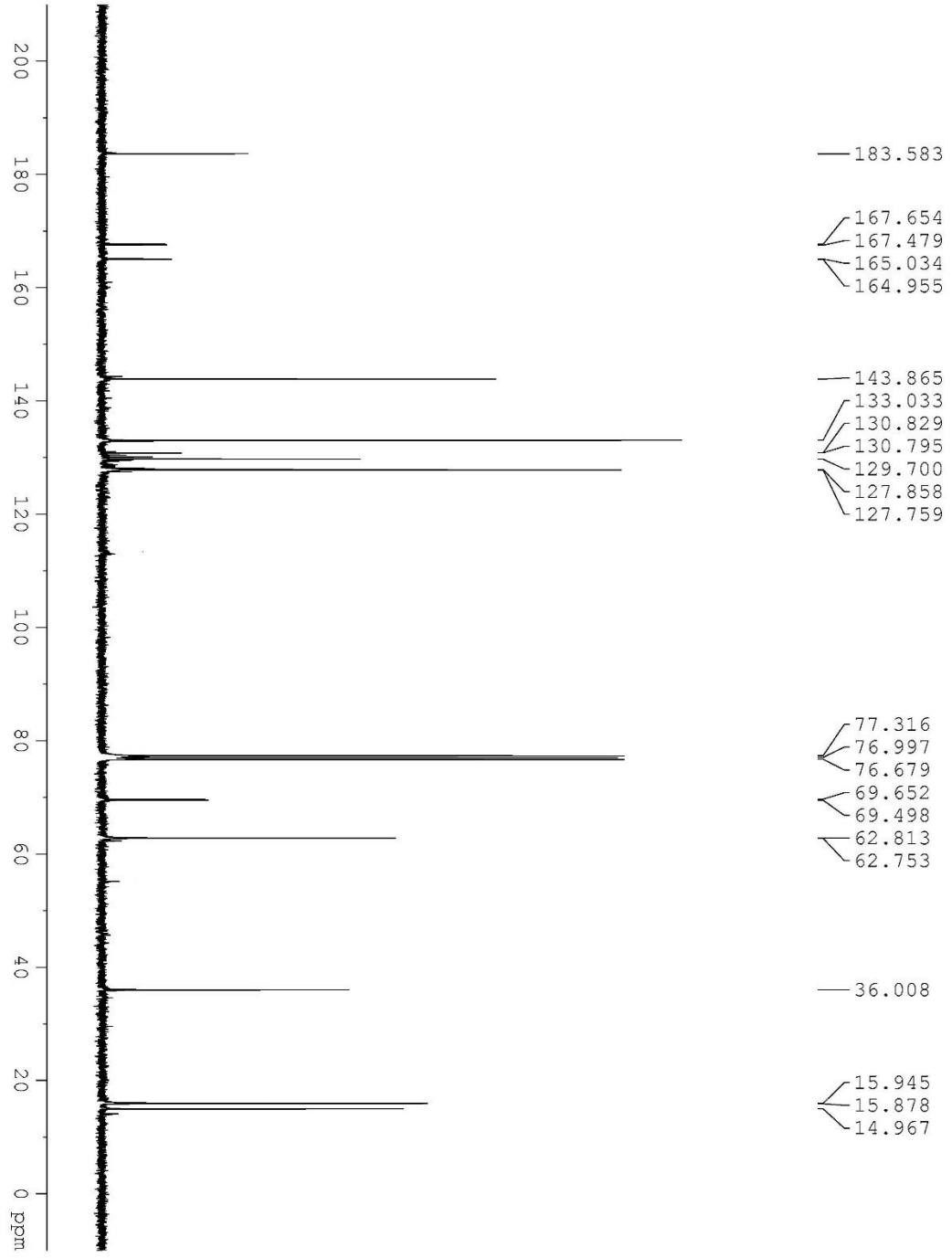

O
O
P–OEt
OEt
N
O

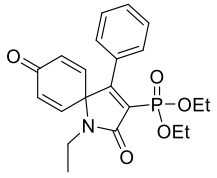
3q


3.084
2.039
2.011
2.000
4.130
1.991
3.061
6.072
ppm
0
1
2
3
4
5
6
7
8
9
7.393
7.382
7.375
7.369
7.357
7.336
7.317
7.299
7.207
7.189
6.574
6.548
6.419
6.394
4.125
4.117
4.107
4.099
4.089
4.082
4.071
4.064
4.046
4.028
4.025
4.007
4.003
3.999
3.989
3.982
3.964
3.379
3.361
3.343
3.325
1.222
1.205
1.187
1.111
1.094
1.076
0.000

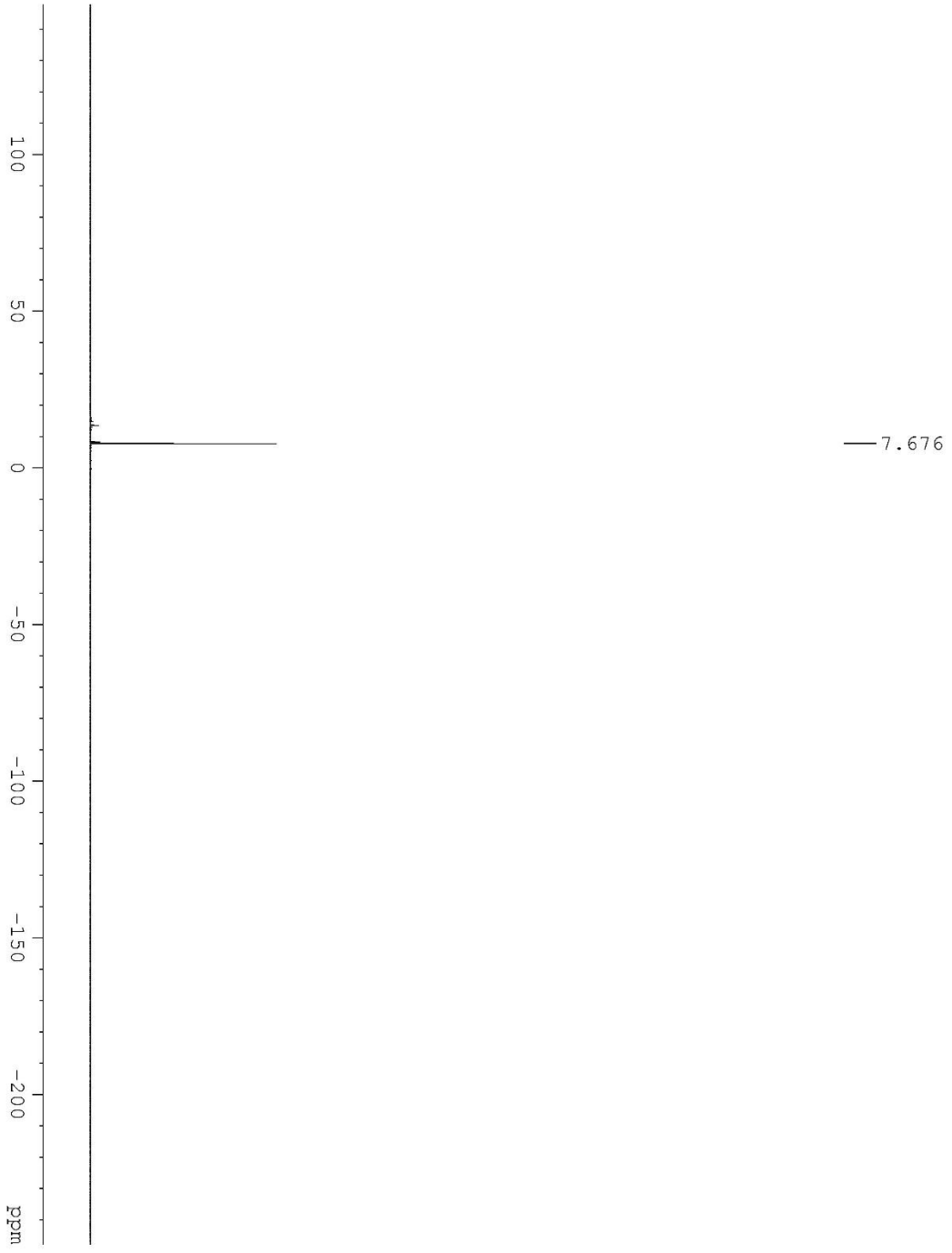

O
O
P
OEt
OEt
N
O

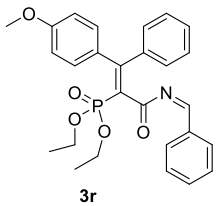
3q


200
180
160
140
120
100
80
60
40
20
0 ppm
183.583
167.654
167.479
165.034
164.955
143.865
133.033
130.829
130.795
129.700
127.858
127.759
77.316
76.997
76.679
69.652
69.498
62.813
62.753
36.008
15.945
15.878
14.967

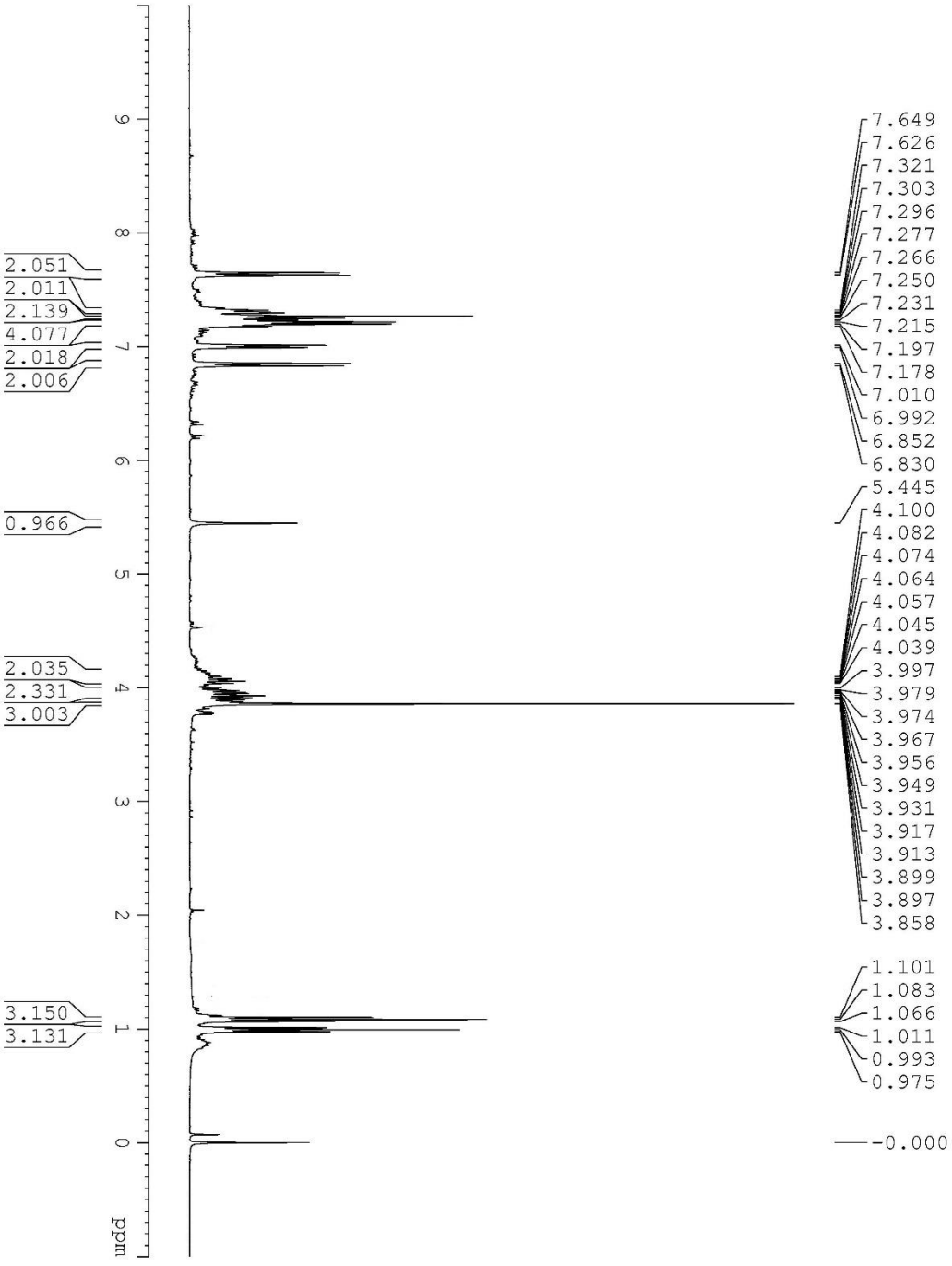


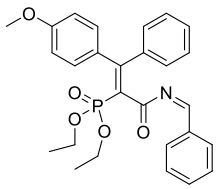
3q



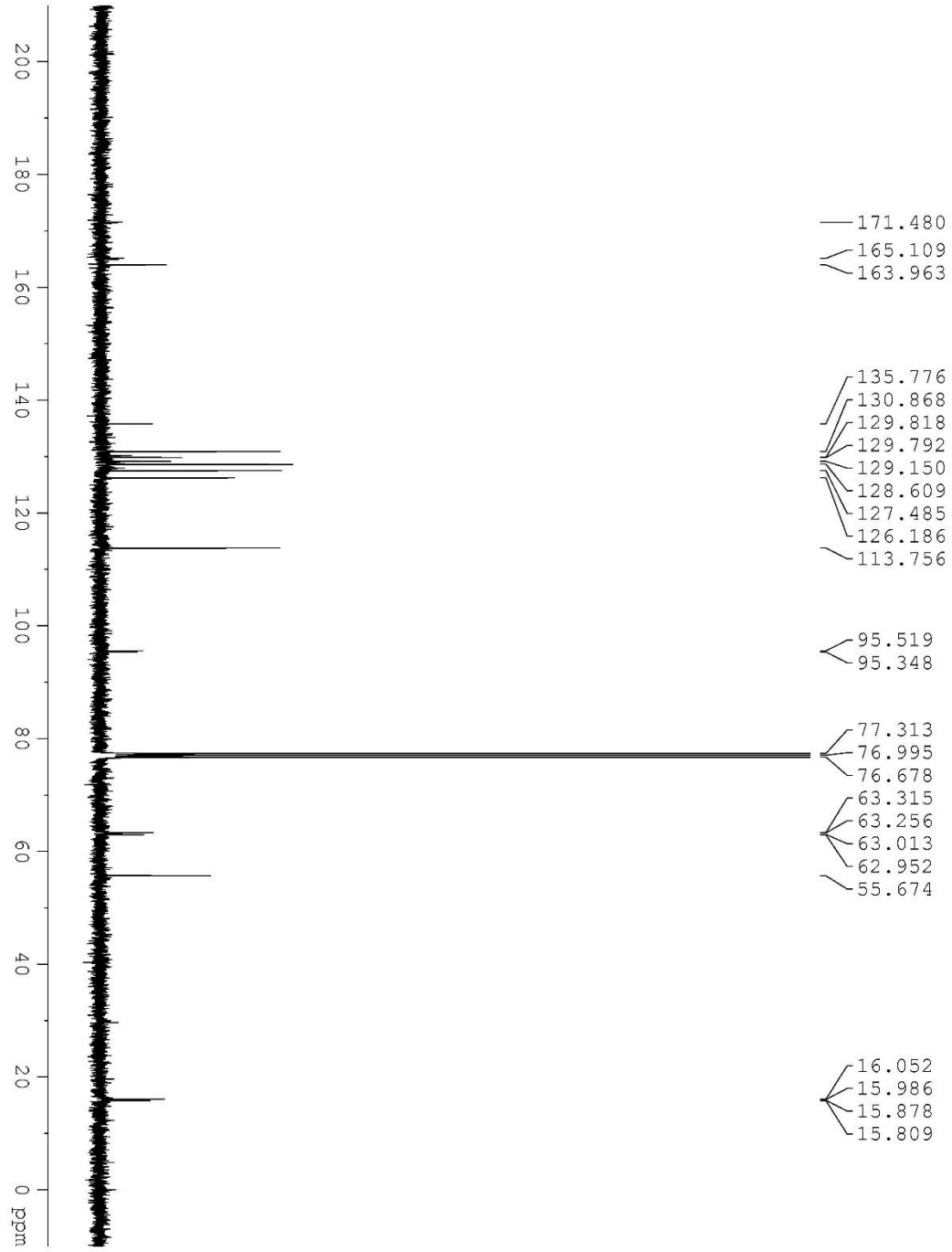


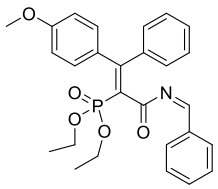
3r


2.051
2.011
2.139
4.077
2.018
2.006
0.966
2.035
2.331
3.003
3.150
3.131
ppm
7.649
7.626
7.321
7.303
7.296
7.277
7.266
7.250
7.231
7.215
7.197
7.178
7.010
6.992
6.852
6.830
5.445
4.100
4.082
4.074
4.064
4.057
4.045
4.039
3.997
3.979
3.974
3.967
3.956
3.949
3.931
3.917
3.913
3.899
3.897
3.858
1.101
1.083
1.066
1.011
0.993
0.975
-0.000

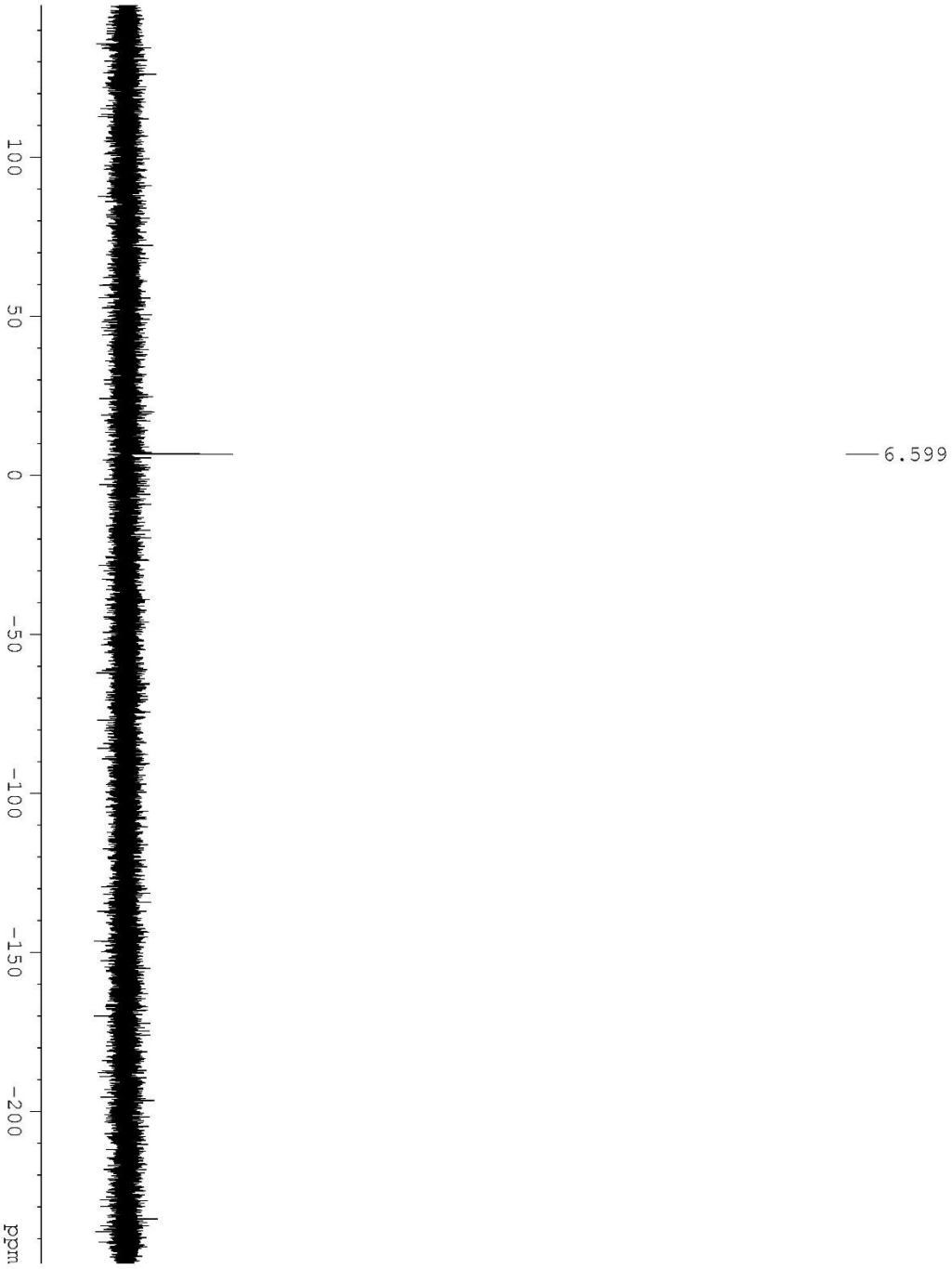


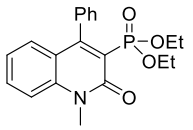
3r


171.480
165.109
163.963
135.776
130.868
129.818
129.792
129.150
128.609
127.485
126.186
113.756
95.519
95.348
77.313
76.995
76.678
63.315
63.256
63.013
62.952
55.674
16.052
15.986
15.878
15.809
200
180
160
140
120
100
80
60
40
20
0
ppm

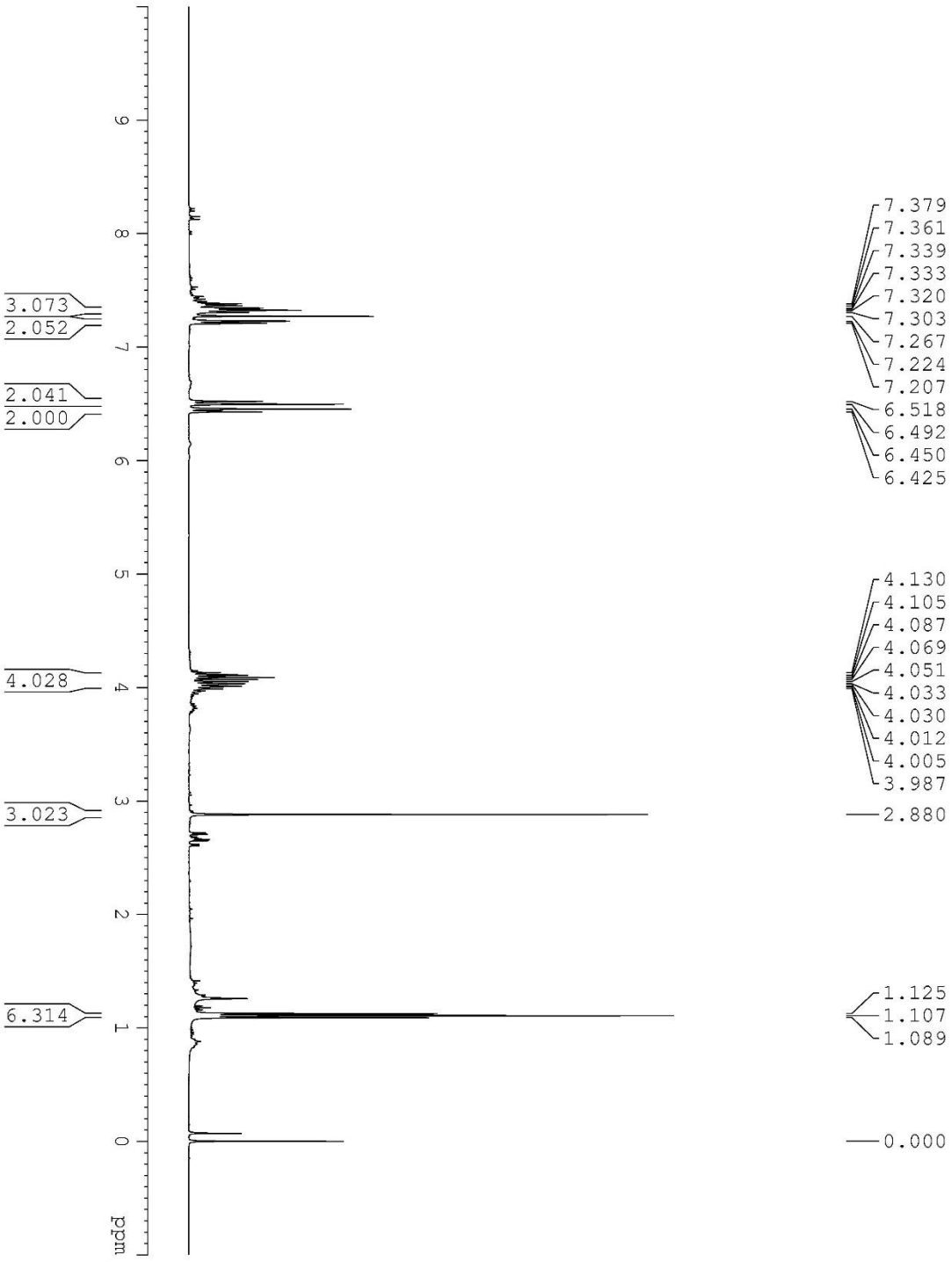


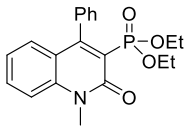
3r



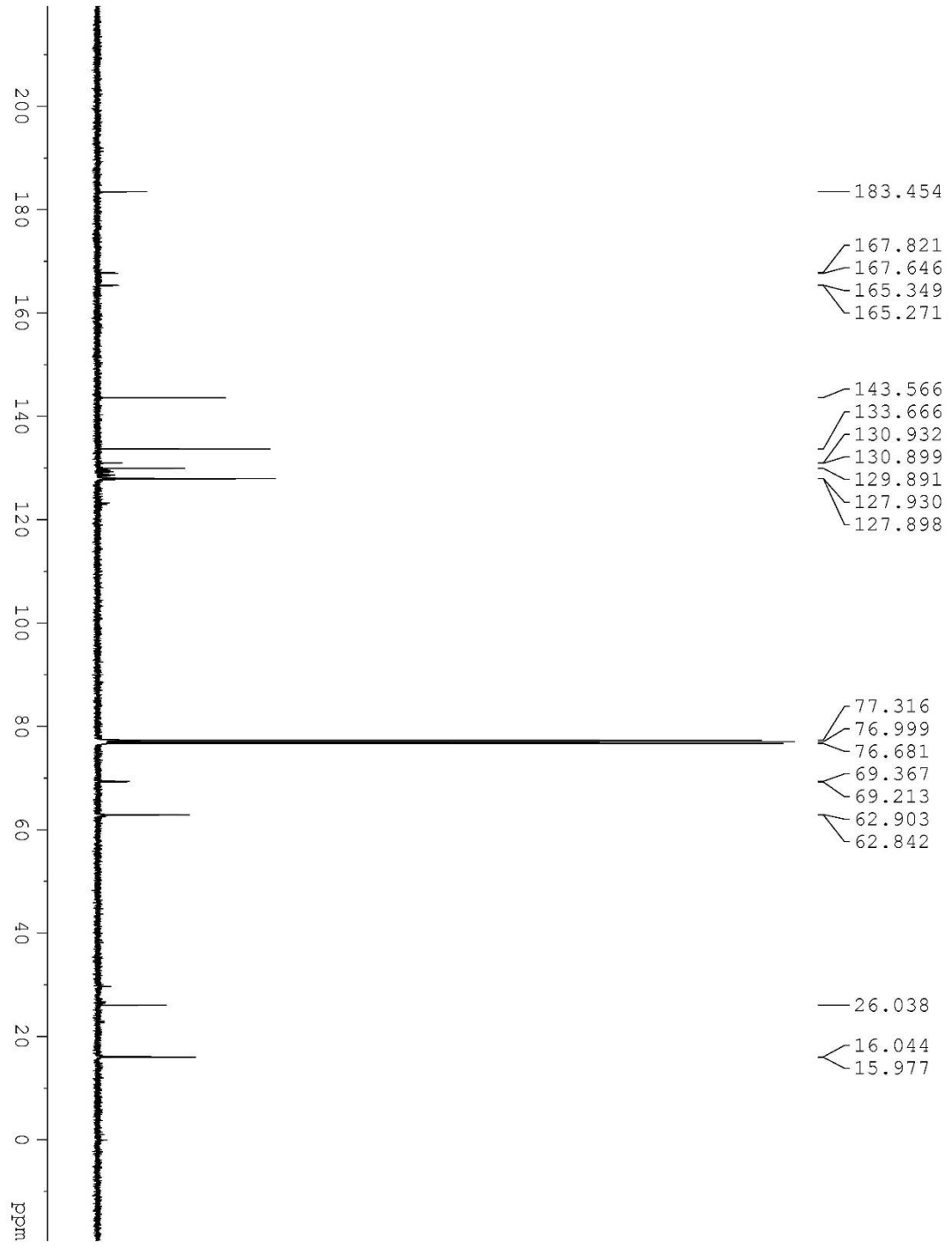

Ph
O
P
OEt
OEt
N
O

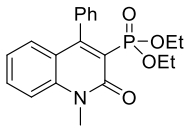
3t


3.073
2.052
2.041
2.000
4.028
3.023
6.314
ppm
7.379
7.361
7.339
7.333
7.320
7.303
7.267
7.224
7.207
6.518
6.492
6.450
6.425
4.130
4.105
4.087
4.069
4.051
4.033
4.030
4.012
4.005
3.987
2.880
1.125
1.107
1.089
0.000


Ph
O
P
OEt
OEt
N
O

3t


200
180
160
140
120
100
80
60
40
20
0
ppm
183.454
167.821
167.646
165.349
165.271
143.566
133.666
130.932
130.899
129.891
127.930
127.898
77.316
76.999
76.681
69.367
69.213
62.903
62.842
26.038
16.044
15.977



3t