

Supporting Information

Silver-Catalyzed Carbon-Phosphorus Functionalization of *N*-(*p*-Methoxyaryl)propiolamides Coupled with Dearomatization: Access to Phosphorylated Aza-decenones

Li-Jing Wang, An-Qi Wang, Yu Xia, Xin-Xing Wu, Xue-Yuan Liu and Yong-Min Liang*

State Key Laboratory of Applied Organic Chemistry, Lanzhou University 730000,
P.R. China.

e-mail: liangym@lzu.edu.cn

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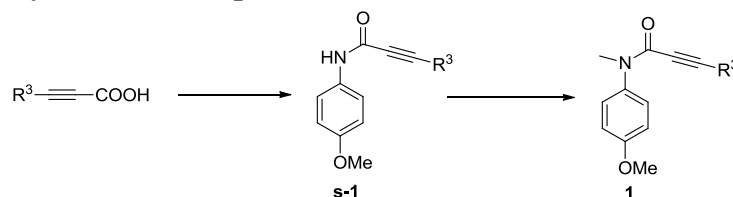
General experimental procedures

Column chromatography was carried out on silica gel. ^1H NMR spectra were recorded on 400 MHz in CDCl_3 , ^{13}C NMR spectra were recorded on 100 MHz in CDCl_3 and ^{31}P NMR spectra were recorded on 160 MHz in CDCl_3 . Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard. Multiplicities are given as: s (singlet), d (doublet), t (triplet), dd (doublet of doublets), or m (multiplet). IR spectra were recorded on a FT-IR spectrometer and only major peaks are reported in cm^{-1} . Melting points were determined on a microscopic apparatus and were uncorrected. All products were further characterized by high resolution MS; copies of their ^1H NMR, ^{13}C NMR and ^{31}P NMR spectra are provided in the Supporting Information. Commercially available reagents and solvents were used without further purification. CH_3CN was dried over calcium hydride.

Starting materials

For this study, all substrates **1** were synthesized according to the literature by a modification of the procedure^[1].

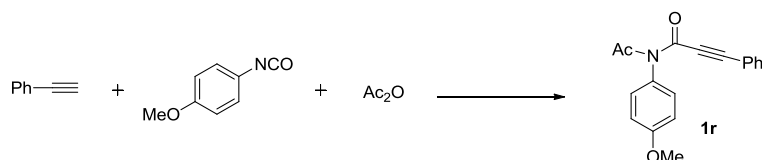
Method A^[1a]: Synthesis of **1a-q** and **1s-u**



(a) For the synthesis of **s-1a**: To a stirred solution of 3-phenylpropionic acid (438 mg, 3.00 mmol) and 4-methylmorpholine (455.2 mg, 4.50 mmol) in THF (20 mL) was added isobutyl chloroformate (491.7 mg, 3.60 mmol) in THF (3 mL) at 0 °C, and the mixture was stirred at 0 °C for 0.5 h. 4-methoxyaniline (381.3 mg, 3.10 mmol) in THF (2 mL) was added to the solution at 0 °C, and the mixture was stirred at 0 °C for 1 h and at room temperature for 16 h. The reaction was quenched with water and extracted with CH_2Cl_2 . The organic layer was washed with brine, dried over Na_2SO_4 , and concentrated to furnish the corresponding crude amide **s-1a**.

(b) For the synthesis of **1a**: To a suspension of 55% sodium hydride (180.0 mg, 4.50 mmol) in THF (12 mL) was added the crude amide **s-1a** (753 mg, 3.0 mmol) in THF (12 mL) at 0 °C, and the mixture was stirred at 0 °C for 0.5 h. CH_3I (639 mg, 4.50 mmol) in THF (1.5 mL) was added to the solution at 0 °C, and the mixture was stirred at 0 °C for 0.5 h and at room temperature for 2 h. The residue was purified by a silica gel column chromatography to give **1a** (715.5 mg, 2.70 mmol) in 90% yield from 3-phenylpropionic acid. The above reactions were carried out under an atmosphere of argon.

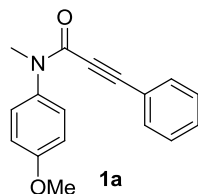
Method B^[1b]: Synthesis of **1r**



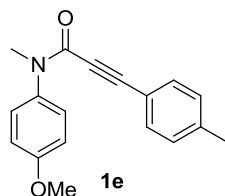
In a heat gun dried and nitrogen filled Schlenk flask 1.1 equiv. of ethynylbenzene were dissolved in THF and cooled to -78°C . At this temperature 1.0 equiv. of *n*-BuLi (2.5 M in hexane) were slowly added by syringe, then, the solution was stirred for 30 min and subsequently treated with 1.0 equiv. of 1-isocyanato-4-methoxybenzene, dissolved in a small amount of THF and allowed to warm up to -40°C within 2 h. At this temperature 1.1 equiv. of Ac_2O dissolved in a small amount of THF were added and the solution was allowed to warm to rt over night. For work up a saturated aqueous solution of NH_4Cl was added, the organic layer was separated and the aqueous phases were extracted three times with diethyl ether. The combined organic phases were dried with MgSO_4 , filtered and, finally, the solvents were removed in vacuum. Column chromatography on silica (petroleum/ethyl acetate) afforded the products **1r**.

Note: All substrates **1** exist as a 6:1-10:1 mixture of rotamers and the spectroscopic datas of their major rotamers are reported.

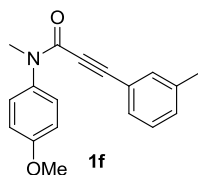
Characterization Data of **1a** and **1e-1u**



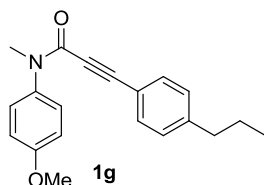
***N*-(4-methoxyphenyl)-*N*-methyl-3-phenylpropionamide **1a**.** Eluent: petroleum ether/ethyl acetate (20:1). Yield 2.70mmol (90%), light yellow solid. ^1H NMR (CDCl_3 , 400 MHz) δ 7.34-7.29 (m, 1H), 7.27-7.22 (m, 4H), 7.17 (dd, $J = 8.4\text{Hz}$, $J = 1.2\text{Hz}$, 2H), 6.97-6.92 (m, 2H), 3.84 (s, 3H), 3.34 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 159.0, 154.5, 136.0, 132.3, 129.7, 128.4, 128.2, 120.4, 114.2, 90.7, 82.6, 55.5, 36.4. IR (neat, cm^{-1}): 3342, 3065, 2968, 2838, 2540, 2364, 2218, 2050, 1950, 1874, 1743, 1634, 1511, 1374, 1251, 1122, 1028, 921, 810, 756, 650, 595, 535, 415.



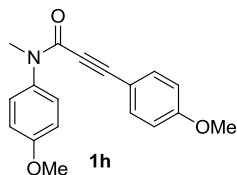
***N*-(4-methoxyphenyl)-*N*-methyl-3-(*p*-tolyl)propionamide **1e**.** Eluent: petroleum ether/ethyl acetate (20:1). Yield 2.76mmol (92%), light yellow solid. ^1H NMR (CDCl_3 , 400 MHz) δ 7.26 (d, $J = 9.2\text{Hz}$, 2H), 7.08-7.03 (m, 4H), 6.94 (d, $J = 8.8\text{Hz}$, 2H), 3.84 (s, 3H), 3.34 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 158.9, 154.6, 140.3, 136.1, 132.3, 129.0, 128.5, 117.4, 114.2, 91.2, 82.2, 55.5, 36.4, 21.5. IR (neat, cm^{-1}): 3449, 2956, 2838, 2546, 2362, 2213, 1910, 1635, 1511, 1442, 1374, 1249, 1180, 1122, 1031, 914, 818, 730, 628, 554, 426.



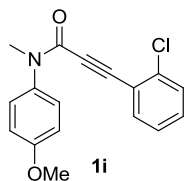
***N*-(4-methoxyphenyl)-*N*-methyl-3-(*m*-tolyl)propiolamide 1f.** Eluent: petroleum ether/ethyl acetate (20:1). Yield 2.68mmol (89%), light yellow liquid. ^1H NMR (CDCl_3 , 400 MHz) δ 7.27-7.25 (m, 2H), 7.13-7.12 (m, 2H), 7.00-6.94 (m, 4H), 3.85 (s, 3H), 3.35 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 159.0, 154.6, 138.4, 136.2, 132.9, 130.7, 129.4, 128.5, 128.1, 120.3, 114.3, 91.2, 82.4, 55.5, 36.5, 21.0. IR (neat, cm^{-1}): 3487, 3043, 2955, 2839, 2546, 2367, 2209, 1947, 1793, 1638, 1511, 1442, 1372, 1293, 1179, 1057, 950, 882, 787, 690, 567, 522, 444.



***N*-(4-methoxyphenyl)-*N*-methyl-3-(4-propylphenyl)propiolamide 1g.** Eluent: petroleum ether/ethyl acetate (20:1). Yield 2.39 mmol (80%), light yellow liquid. ^1H NMR (CDCl_3 , 400 MHz) δ 7.25 (d, $J = 8.8\text{Hz}$, 2H), 7.07 (dd, $J = 17.6\text{Hz}$, $J = 8.4\text{Hz}$, 4H), 6.94 (d, $J = 8.8\text{Hz}$, 2H), 3.84 (s, 3H), 3.34 (s, 3H), 2.53 (t, $J = 7.6\text{Hz}$, 2H), 1.62-1.53 (m, 2H), 0.89 (t, $J = 7.2\text{Hz}$, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 158.9, 154.6, 145.0, 136.1, 132.3, 128.5, 128.4, 117.6, 114.2, 91.3, 82.2, 55.4, 37.9, 36.4, 24.0, 13.6. IR (neat, cm^{-1}): 3408, 3000, 2932, 2839, 2367, 2213, 1914, 1799, 1709, 1637, 1511, 1463, 1374, 1292, 1205, 1121, 1031, 913, 837, 801, 731, 630, 544.

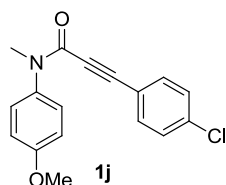


***N*,3-bis(4-methoxyphenyl)-*N*-methylpropiolamide 1h.** Eluent: petroleum ether/ethyl acetate (20:1). Yield 2.22 mmol (74%), light yellow solid. ^1H NMR (CDCl_3 , 400 MHz) δ 7.28-7.25 (m, 2H), 7.11 (d, $J = 9.2\text{Hz}$, 2H), 6.95 (d, $J = 8.8\text{Hz}$, 2H), 6.75 (d, $J = 8.8\text{Hz}$, 2H), 3.85 (s, 3H), 3.80 (s, 3H), 3.34 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 160.8, 158.9, 154.8, 136.2, 134.1, 128.5, 114.2, 113.9, 112.3, 91.4, 82.0, 55.5, 55.2, 36.4. IR (neat, cm^{-1}): 3455, 3046, 2935, 2839, 2429, 2210, 1888, 1633, 1512, 1442, 1375, 1293, 1173, 1108, 1030, 912, 814, 731, 646, 563, 502.

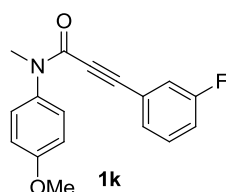


3-(2-chlorophenyl)-*N*-(4-methoxyphenyl)-*N*-methylpropiolamide 1i. Eluent: petroleum ether/ethyl acetate (20:1). Yield 2.55 mmol (85%), light yellow solid. ^1H NMR (CDCl_3 , 400 MHz) δ 7.32 (dd, $J = 7.6\text{Hz}$, $J = 1.2\text{Hz}$, 1H), 7.28-7.24 (m, 4H), 7.16-7.12 (m, 1H), 6.95-6.91 (m, 2H), 3.82 (s, 3H), 3.35 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 159.1, 154.1, 136.4, 135.7, 134.2, 130.7, 129.2, 128.5, 126.3, 120.8, 114.5, 86.9, 86.9, 55.5, 36.7. IR (neat, cm^{-1}): 3443, 3065, 2933, 2838,

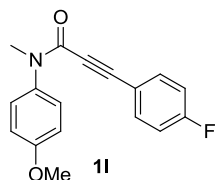
2367, 2217, 1931, 1883, 1638, 1562, 1511, 1431, 1295, 1249, 1124, 1031, 912, 836, 731, 671, 592, 529, 457.



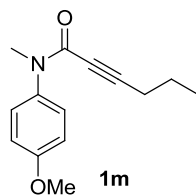
3-(4-chlorophenyl)-N-(4-methoxyphenyl)-N-methylpropiolamide 1j. Eluent: petroleum ether/ethyl acetate (20:1). Yield 2.08 mmol (70%), light yellow solid. ^1H NMR (CDCl_3 , 400 MHz) δ 7.28-7.21 (m, 4H), 7.09 (d, $J = 8.8\text{Hz}$, 2H), 6.95 (d, $J = 8.8\text{Hz}$, 2H), 3.85 (s, 3H), 3.34 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 159.1, 154.2, 136.1, 135.9, 133.5, 128.7, 128.5, 119.0, 114.2, 89.5, 83.4, 55.5, 36.5. IR (neat, cm^{-1}): 3449, 3056, 2932, 2543, 2217, 1904, 1742, 1638, 1442, 1376, 1249, 1123, 1031, 912, 833, 784, 642, 592, 466.



3-(3-fluorophenyl)-N-(4-methoxyphenyl)-N-methylpropiolamide 1k. Eluent: petroleum ether/ethyl acetate (20:1). Yield 2.59 mmol (87%), light yellow solid. ^1H NMR (CDCl_3 , 400 MHz) δ 7.28-7.27 (m, 2H), 7.25-7.19 (m, 1H), 7.06-7.03 (m, 1H), 7.01-6.93 (m, 3H), 6.86-6.82 (m, 1H), 3.85 (s, 3H), 3.35 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 163.2, 160.8, 159.2, 154.2, 135.9, 130.0, 129.9, 128.5, 128.2, 128.2, 126.7, 122.4, 122.3, 119.1, 118.9, 117.3, 117.1, 114.3, 89.2, 89.2, 83.2, 55.5, 36.5. IR (neat, cm^{-1}): 3438, 3069, 2839, 2432, 2214, 1883, 1636, 1581, 1511, 1431, 1373, 1269, 1173, 1119, 1031, 911, 837, 730, 651, 544, 462.

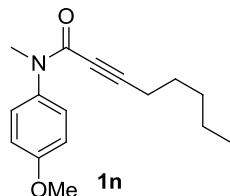


3-(4-fluorophenyl)-N-(4-methoxyphenyl)-N-methylpropiolamide 1l. Eluent: petroleum ether/ethyl acetate (20:1). Yield 2.76 mmol (92%), light yellow solid. ^1H NMR (CDCl_3 , 400 MHz) δ 7.29-7.23 (m, 2H), 7.18-7.11 (m, 2H), 6.97-6.91 (m, 4H), 3.85 (s, 3H), 3.34 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 164.5, 162.0, 159.0, 154.3, 136.0, 134.5, 134.4, 128.5, 126.6, 116.6, 116.5, 115.8, 115.6, 114.4, 114.2, 89.7, 82.4, 55.5, 36.4. IR (neat, cm^{-1}): 3470, 3068, 2839, 2438, 2217, 1894, 1635, 1511, 1416, 1375, 1294, 1173, 1054, 912, 801, 645, 533, 451.

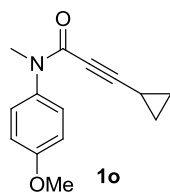


N-(4-methoxyphenyl)-N-methylhex-2-ynamide 1m. Eluent: petroleum ether/ethyl acetate (20:1). Yield 1.82 mmol (61%), light yellow liquid. ^1H NMR (CDCl_3 , 400 MHz) δ 7.19-7.16 (m, 2H), 6.90 (d, $J = 8.8\text{Hz}$, 2H), 3.83 (s, 3H), 3.28 (s, 3H), 2.08 (t, $J = 7.2\text{Hz}$, 2H), 1.35-1.26 (m, 2H), 0.73

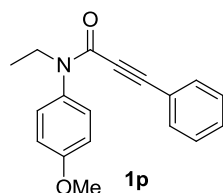
(t, $J = 7.6\text{Hz}$, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 158.9, 154.7, 136.4, 128.4, 114.2, 93.8, 55.5, 36.4, 21.0, 20.7, 13.0. IR (neat, cm^{-1}): 3432, 3043, 2874, 2544, 2226, 1882, 1636, 1512, 1427, 1292, 1168, 1106, 916, 837, 733, 647, 566, 494.



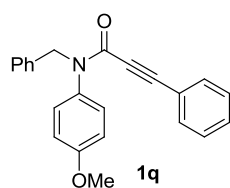
***N*-(4-methoxyphenyl)-*N*-methyloct-2-ynamide 1n.** Eluent: petroleum ether/ethyl acetate (20:1). Yield 2.10 mmol (70%), light yellow liquid. ^1H NMR (CDCl_3 , 400 MHz) δ 7.18 (dd, $J = 6.8\text{Hz}$, $J = 2.0\text{Hz}$, 2H), 6.90 (d, $J = 8.8\text{Hz}$, 2H), 3.82 (s, 3H), 3.27 (s, 3H), 2.10 (t, $J = 6.8\text{Hz}$, 2H), 1.30-1.23 (m, 2H), 1.20-1.12 (m, 2H), 1.09-1.03 (m, 2H), 0.82 (t, $J = 7.2\text{Hz}$, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 158.8, 154.7, 136.3, 128.4, 114.1, 94.0, 75.0, 55.4, 36.5, 30.5, 27.1, 22.0, 18.7, 13.7. IR (neat, cm^{-1}): 3410, 2957, 2860, 2226, 1881, 1638, 1512, 1427, 1291, 1248, 1107, 1034, 915, 796, 647, 570, 540.



3-cyclopropyl-*N*-(4-methoxyphenyl)-*N*-methylpropiolamide 1o. Eluent: petroleum ether/ethyl acetate (20:1). Yield 2.19 mmol (73%), light yellow liquid. ^1H NMR (CDCl_3 , 400 MHz) δ 7.16 (d, $J = 8.8\text{Hz}$, 2H), 6.90 (d, $J = 8.8\text{Hz}$, 2H), 3.84 (s, 3H), 3.26 (s, 3H), 1.15-1.08 (m, 1H), 0.75-0.70 (m, 2H), 0.50-0.46 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 158.8, 154.6, 136.3, 128.4, 114.1, 97.5, 70.1, 55.5, 36.3, 8.8, -0.6. IR (neat, cm^{-1}): 3410, 2956, 2853, 2483, 2222, 1882, 1743, 1635, 1511, 1427, 1290, 1166, 1112, 1031, 890, 815, 731, 644, 539.

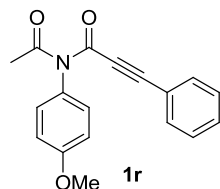


***N*-ethyl-*N*-(4-methoxyphenyl)-3-phenylpropiolamide 1p.** Eluent: petroleum ether/ethyl acetate (20:1). Yield 2.04 mmol (68%), light yellow solid. ^1H NMR (CDCl_3 , 400 MHz) δ 7.32-7.29 (m, 1H), 7.27-7.21 (m, 4H), 7.15-7.13 (m, 2H), 6.96-6.94 (m, 2H), 3.85-3.80 (m, 5H), 1.17 (t, $J = 7.2\text{Hz}$, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 159.2, 154.2, 134.4, 132.4, 129.7, 128.5, 128.2, 120.6, 114.2, 90.7, 82.9, 55.5, 43.5, 12.8. IR (neat, cm^{-1}): 3442, 3058, 2934, 2838, 2486, 2215, 1957, 1813, 1742, 1633, 1462, 1397, 1313, 1172, 1107, 1031, 913, 806, 732, 671, 582, 536.

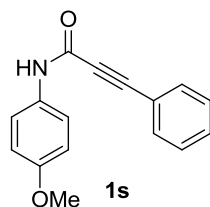


***N*-benzyl-*N*-(4-methoxyphenyl)-3-phenylpropiolamide 1q.** Eluent: petroleum ether/ethyl acetate (20:1). Yield 2.49 mmol (83%), light yellow solid. ^1H NMR (CDCl_3 , 400 MHz) δ

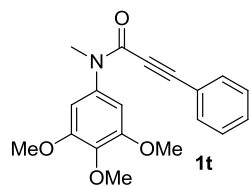
7.30-7.19 (m, 8H), 7.13 (dd, $J = 8.0\text{Hz}$, $J = 1.2\text{Hz}$, 2H), 7.04 (dd, $J = 6.8\text{Hz}$, $J = 2.0\text{Hz}$, 2H), 4.95 (s, 2H), 3.78 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 159.1, 154.6, 136.7, 134.3, 132.3, 129.8, 129.7, 128.7, 128.4, 128.2, 127.5, 120.4, 114.0, 91.4, 82.6, 55.4, 52.3. IR (neat, cm^{-1}): 3257, 3004, 2931, 2592, 2218, 1957, 1742, 1635, 1492, 1391, 1297, 1203, 1108, 1030, 913, 836, 730, 631, 535, 467.



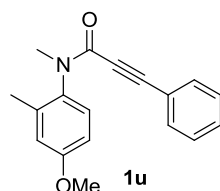
***N*-acetyl-*N*-(4-methoxyphenyl)-3-phenylpropiolamide 1r.** Eluent: petroleum ether/ethyl acetate (20:1). Yield 2.28 mmol (76%), light yellow solid. ^1H NMR (CDCl_3 , 400 MHz) δ 7.38 (t, $J = 7.6\text{Hz}$, 1H), 7.28 (t, $J = 7.6\text{Hz}$, 2H), 7.20-7.15 (m, 4H), 7.00 (dd, $J = 6.8\text{Hz}$, $J = 2.0\text{Hz}$, 2H), 3.86 (s, 3H), 2.63 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 172.6, 160.0, 155.0, 133.0, 131.0, 130.8, 130.6, 128.5, 119.6, 114.6, 96.2, 82.9, 55.6, 27.3. IR (neat, cm^{-1}): 3322, 3057, 2925, 2545, 2404, 2205, 1898, 1711, 1606, 1549, 1489, 1416, 1261, 1170, 1040, 912, 761, 690, 581, 537.



***N*-(4-methoxyphenyl)-3-phenylpropiolamide 1s.** Eluent: petroleum ether/ethyl acetate (20:1). Yield 2.88 mmol (96%), light yellow solid. ^1H NMR (CDCl_3 , 400 MHz) δ 7.92 (s, 1H), 7.53-7.47 (m, 4H), 7.42-7.40 (m, 1H), 7.39-7.31 (m, 2H), 6.85 (d, $J = 8.8\text{Hz}$, 2H), 3.77 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 156.8, 151.0, 132.5, 130.5, 130.1, 128.5, 121.8, 120.1, 114.2, 85.6, 83.5, 55.4. IR (neat, cm^{-1}): 3280, 3130, 2997, 2838, 2591, 2371, 2209, 1969, 1880, 1774, 1605, 1509, 1411, 1306, 1180, 1116, 961, 830, 724, 605, 520.



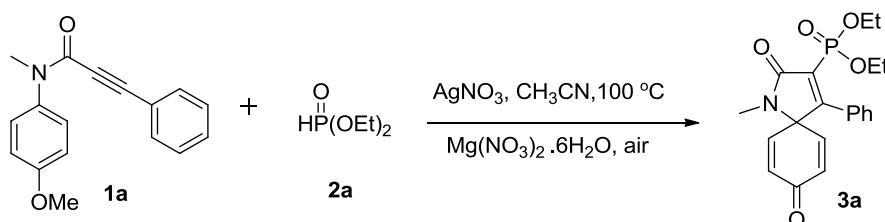
***N*-methyl-3-phenyl-*N*-(3,4,5-trimethoxyphenyl)propiolamide 1t.** Eluent: petroleum ether/ethyl acetate (20:1). Yield 2.14 mmol (71%), light yellow solid. ^1H NMR (CDCl_3 , 400 MHz) δ 7.34 (t, $J = 7.6\text{Hz}$, 1H), 7.30-7.24 (m, 2H), 7.19 (d, $J = 7.2\text{Hz}$, 2H), 6.60 (s, 2H), 3.89 (s, 3H), 3.86 (s, 6H), 3.38 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 154.2, 153.3, 138.8, 137.7, 132.3, 129.9, 128.3, 120.3, 104.9, 90.7, 82.5, 60.8, 56.2, 36.3. IR (neat, cm^{-1}): 3272, 2939, 2842, 2218, 1956, 1640, 1504, 1418, 1345, 1234, 1128, 1006, 917, 835, 731, 691, 612, 532, 476.



***N*-(4-methoxy-2-methylphenyl)-*N*-methyl-3-phenylpropiolamide 1u.** Eluent: petroleum

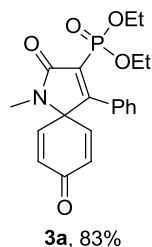
ether/ethyl acetate (20:1). Yield 2.54 mmol (85%), light yellow liquid. ^1H NMR (CDCl_3 , 400 MHz) δ 7.33-7.27 (m, 1H), 7.22 (t, $J = 7.6\text{Hz}$, 2H), 7.16 (d, $J = 8.4\text{Hz}$, 1H), 7.12-7.10 (m, 2H), 6.84-6.78 (m, 2H), 3.83 (s, 3H), 3.27 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 159.3, 155.0, 137.5, 134.9, 132.4, 129.7, 129.5, 128.2, 120.4, 115.9, 112.0, 89.9, 82.4, 55.4, 35.5, 17.7. IR (neat, cm^{-1}): 3265, 3001, 2928, 2839, 2568, 2218, 1889, 1741, 1640, 1465, 1375, 1295, 1162, 1106, 1037, 942, 850, 732, 650, 589, 533, 466.

Typical procedure for the preparation of product 3a

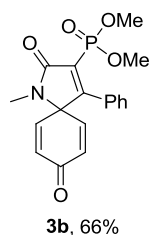


0.4 mmol diethyl phosphate **2a** in 1 mL CH_3CN was added into the Schlenk-tube charged with 0.2 mmol **1a**, 10 mol% AgNO_3 , 0.1 mmol $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The mixture was stirred at 100 °C for 5 h, then cooled down to room temperature. The resulting solution was directly filtered through a pad of silica gel using a sintered glass funnel, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (elute: EtOAc/Petroleum ether 1/1 - 5/1, v/v) to give the desired product **3a** (83%).

Characterization Data of 3a-3r and 3t-3u

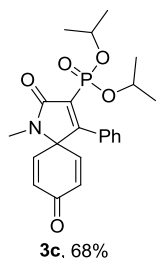


diethyl (1-methyl-2,8-dioxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)phosphonate 3a. Eluent: ethyl acetate/ petroleum ether (3:1). white solid, mp 129-131 °C. ^1H NMR (CDCl_3 , 400 MHz) δ 7.40-7.37 (m, 1H), 7.34-7.30 (m, 2H), 7.22 (d, $J = 7.2\text{Hz}$, 2H), 6.53 (d, $J = 10.4\text{Hz}$, 2H), 6.45 (d, $J = 10.4\text{Hz}$, 2H), 4.13-3.98 (m, 4H), 2.88 (s, 3H), 1.11 (t, $J = 7.2\text{Hz}$, 6H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 183.4, 167.8, 167.6, 165.4, 165.4, 143.5, 133.6, 130.8, 130.8, 129.8, 127.9, 127.8, 26.0, 16.0, 15.9. ^{31}P NMR (162 MHz, CDCl_3): δ 7.5. IR (neat, cm^{-1}): 3453, 3053, 2931, 2366, 2243, 1964, 1699, 1631, 1475, 1420, 1248, 1168, 1042, 921, 820, 731, 647, 572, 428. HRMS (ESI) Calcd for $\text{C}_{20}\text{H}_{22}\text{N}_1\text{O}_5\text{P}_1$: $[\text{M}+\text{Na}]^+ = 410.1122$ Found:410.1128.



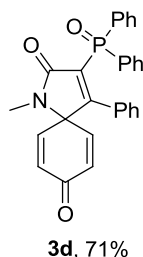
dimethyl (1-methyl-2,8-dioxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)phosphonate 3b.

Eluent: ethyl acetate/ petroleum ether (3:1). Light yellow solid, mp 142-144°C. ¹H NMR (CDCl₃, 400 MHz) δ 7.42-7.31 (m, 3H), 7.23-7.21 (m, 2H), 6.53 (d, *J* = 10.0Hz, 2H), 6.45 (d, *J* = 10.0Hz, 2H), 3.65 (s, 3H), 3.62 (s, 3H), 2.89 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ 183.3, 167.7, 167.5, 166.1, 166.0, 143.3, 133.7, 130.5, 130.5, 130.0, 129.2, 127.9, 127.8, 127.8, 127.1, 69.4, 69.3, 53.2, 53.2, 26.0. ³¹P NMR (162 MHz, CDCl₃): δ 10.2. IR (neat, cm⁻¹): 3456, 3052, 2853, 2548, 2245, 1890, 1669, 1595, 1444, 1369, 1251, 1180, 1043, 917, 824, 731, 647, 569, 423. HRMS (ESI) Calcd for C₁₈H₁₈N₁O₅P₁: [M+Na]⁺ = 382.0810 Found: 382.0815.



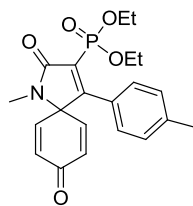
diisopropyl (1-methyl-2,8-dioxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)phosphonate

3c. Eluent: ethyl acetate/ petroleum ether (3:1). Light yellow solid, mp 106-108°C. ¹H NMR (CDCl₃, 400 MHz) δ 7.38-7.34 (m, 1H), 7.32-7.28 (m, 2H), 7.20-7.18 (m, 2H), 6.52-6.49 (m, 2H), 6.44-6.41 (m, 2H), 4.83-4.75 (m, 2H), 2.88 (s, 3H), 1.22 (d, *J* = 6.4Hz, 6H), 1.09 (d, *J* = 6.4Hz, 6H). ¹³C NMR (CDCl₃, 100 MHz) δ 183.5, 167.8, 167.6, 164.8, 164.8, 143.8, 133.5, 131.2, 131.2, 130.4, 129.6, 128.3, 128.0, 128.0, 127.7, 71.9, 71.9, 69.2, 69.1, 26.0, 24.0, 24.0, 23.4, 23.3. ³¹P NMR (162 MHz, CDCl₃): δ 5.2. IR (neat, cm⁻¹): 3383, 2979, 2372, 2240, 1960, 1702, 1607, 1511, 1420, 1373, 1247, 1142, 1023, 874, 788, 732, 647, 575, 492. HRMS (ESI) Calcd for C₂₂H₂₅N₁O₅P₁: [M+Na]⁺ = 438.1429 Found: 438.1441.



3-(diphenylphosphoryl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione **3d.**

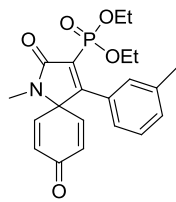
Eluent: ethyl acetate/ petroleum ether (3:1). Light yellow solid, mp 83-85°C. ¹H NMR (CDCl₃, 400 MHz) δ 7.80-7.75 (m, 4H), 7.50-7.46 (m, 2H), 7.42-7.37 (m, 4H), 7.24 (dd, *J* = 14.4Hz, *J* = 7.6Hz, 1H), 7.14 (t, *J* = 8.4Hz, 2H), 7.08 (d, *J* = 7.6Hz, 2H), 6.52 (d, *J* = 10.0Hz, 2H), 6.43 (d, *J* = 10.0Hz, 2H), 2.83 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ 183.4, 168.8, 168.7, 168.2, 168.1, 143.7, 133.7, 132.0, 132.0, 132.0, 131.6, 131.5, 131.0, 129.8, 128.4, 128.2, 128.1, 127.6, 69.6, 69.5, 26.1. ³¹P NMR (162 MHz, CDCl₃): δ 18.3. IR (neat, cm⁻¹): 3656, 3390, 3058, 2928, 2591, 2248, 1971, 1811, 1669, 1590, 1487, 1370, 1270, 1195, 1119, 1042, 999, 913, 843, 784, 729, 646, 547, 489, 433. HRMS (ESI) Calcd for C₂₈H₂₂N₁O₃P₁: [M+Na]⁺ = 474.1223 Found: 474.1230.



3e, 69%

diethyl (1-methyl-2,8-dioxo-4-(p-tolyl)-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)phosphonate 3e.

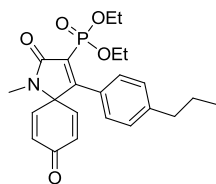
Eluent: ethyl acetate/ petroleum ether (3:1). Light yellow liquide. ^1H NMR (CDCl_3 , 400 MHz) δ 7.13 (s, 4H), 6.51 (d, $J = 10.0\text{Hz}$, 2H), 6.45 (dd, $J = 10.8\text{Hz}$, $J = 2.0\text{Hz}$, 2H), 4.14-4.02 (m, 4H), 2.87 (s, 3H), 2.33 (s, 3H), 1.13 (t, $J = 7.2\text{Hz}$, 6H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 183.6, 167.9, 167.7, 166.0, 165.9, 143.7, 140.2, 133.5, 129.0, 128.6, 127.9, 127.9, 127.0, 69.3, 69.2, 26.0, 21.2, 16.0, 15.9. ^{31}P NMR (162 MHz, CDCl_3): δ 7.7. IR (neat, cm^{-1}): 3387, 3043, 2929, 2243, 1698, 1630, 1510, 1419, 1368, 1249, 1169, 1030, 920, 834, 733, 646, 572, 506, 425. HRMS (ESI) Calcd for $\text{C}_{21}\text{H}_{24}\text{N}_1\text{O}_5\text{P}_1$: $[\text{M}+\text{Na}]^+ = 424.1274$ Found: 424.1284.



3f, 72%

diethyl (1-methyl-2,8-dioxo-4-(m-tolyl)-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)phosphonate 3f.

Eluent: ethyl acetate/ petroleum ether (3:1). Light yellow solid, mp 92-94°C. ^1H NMR (CDCl_3 , 400 MHz) δ 7.22-7.17 (m, 2H), 7.02-6.99 (m, 2H), 6.51 (d, $J = 10.4\text{Hz}$, 2H), 6.44 (d, $J = 10.4\text{Hz}$, 2H), 4.13-4.01 (m, 4H), 2.88 (s, 3H), 2.32 (s, 3H), 1.11 (t, $J = 6.8\text{Hz}$, 6H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 183.5, 167.9, 167.7, 165.7, 165.7, 143.6, 137.5, 133.5, 130.8, 130.8, 130.6, 129.4, 128.5, 127.8, 127.4, 124.8, 69.3, 69.2, 62.9, 62.8, 26.0, 21.2, 16.0, 15.9. ^{31}P NMR (162 MHz, CDCl_3): δ 7.6. IR (neat, cm^{-1}): 3402, 2982, 2367, 1964, 1699, 1631, 1512, 1420, 1369, 1205, 1098, 1044, 918, 824, 733, 623, 573, 470. HRMS (ESI) Calcd for $\text{C}_{21}\text{H}_{24}\text{N}_1\text{O}_5\text{P}_1$: $[\text{M}+\text{Na}]^+ = 424.1274$ Found: 424.1284.



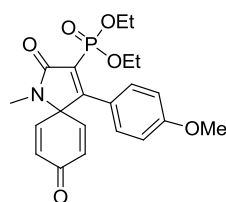
3g, 72%

Diethyl

(1-methyl-2,8-dioxo-4-(4-propylphenyl)-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)phosphonate 3g.

Eluent: ethyl acetate/ petroleum ether (3:1). Light yellow liquide. ^1H NMR (CDCl_3 , 400 MHz) δ 7.14 (dd, $J = 15.6\text{Hz}$, $J = 8.0\text{Hz}$, 4H), 6.52 (d, $J = 10.0\text{Hz}$, 2H), 6.45 (d, $J = 10.0\text{Hz}$, 2H), 4.13-3.99 (m, 4H), 2.87 (s, 3H), 2.57 (t, $J = 7.6\text{Hz}$, 2H), 1.65-1.56 (m, 2H), 1.11 (t, $J = 7.2\text{Hz}$, 6H), 0.91 (t, $J = 7.2\text{Hz}$, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 183.6, 168.0, 167.8, 165.9, 165.8, 145.0, 143.8, 133.6, 129.1, 128.3, 128.2, 128.0, 127.9, 127.9, 127.1, 69.4, 69.2, 63.0, 62.9, 37.7, 26.0, 24.2, 16.1, 16.0, 13.7. ^{31}P NMR (162 MHz, CDCl_3): δ 7.8. IR (neat, cm^{-1}): 3387, 2964, 2870, 2242, 1700, 1630, 1510, 1419, 1368, 1248, 1099, 1030, 877, 805, 646, 526, 470. HRMS (ESI)

Calcd for C₂₃H₂₈N₁O₅P₁: [M+Na]⁺ = 452.1584 Found: 452.1597.

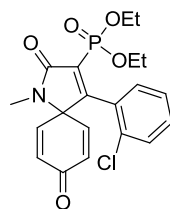


3h, 72%

diethyl

(4-(4-methoxyphenyl)-1-methyl-2,8-dioxo-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)phosphonate

3h. Eluent: ethyl acetate/ petroleum ether (3:1). Light yellow liquide. ¹H NMR (CDCl₃, 400 MHz) δ 7.26 (d, *J* = 8.8Hz, 2H), 6.85-6.83 (m, 2H), 6.49 (dd, *J* = 19.6Hz, *J* = 10.4Hz, 4H), 4.13-4.06 (m, 4H), 3.80 (s, 3H), 2.86 (s, 3H), 1.16 (t, *J* = 7.2Hz, 6H). ¹³C NMR (CDCl₃, 100 MHz) δ 183.6, 168.0, 167.8, 165.6, 165.5, 161.1, 144.0, 133.4, 129.6, 129.6, 128.2, 126.2, 123.1, 123.0, 113.4, 69.1, 69.0, 62.9, 62.9, 55.2, 25.9, 16.1, 16.0. ³¹P NMR (162 MHz, CDCl₃): δ 8.0. IR (neat, cm⁻¹): 3389, 2980, 2846, 2371, 2030, 1696, 1630, 1510, 1444, 1385, 1250, 1042, 919, 841, 763, 733, 572, 468. HRMS (ESI) Calcd for C₂₁H₂₄N₁O₆P₁: [M+Na]⁺ = 440.125 Found:440.1233.

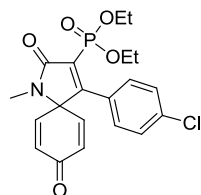


3i, 77%

diethyl

(4-(2-chlorophenyl)-1-methyl-2,8-dioxo-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)phosphonate 3i.

Eluent: ethyl acetate/ petroleum ether (3:1). Light yellow liquid. ¹H NMR (CDCl₃, 400 MHz) δ 7.39 (dd, *J* = 8.0Hz, *J* = 1.2Hz, 1H), 7.33-7.28 (m, 1H), 7.24-7.19 (m, 1H), 6.98 (dd, *J* = 7.6Hz, *J* = 1.6Hz, 1H), 6.77 (dd, *J* = 10.0Hz, *J* = 2.8Hz, 1H), 6.55 (dd, *J* = 10.0Hz, *J* = 2.8Hz, 1H), 6.48 (dd, *J* = 10.0Hz, *J* = 1.6Hz, 1H), 6.34 (dd, *J* = 10.0Hz, *J* = 1.6Hz, 1H), 4.20-4.07 (m, 4H), 2.92 (s, 3H), 1.21 (t, *J* = 7.2Hz, 3H), 1.08 (t, *J* = 7.2Hz, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ 183.3, 167.4, 167.2, 161.9, 161.8, 143.5, 143.1, 134.1, 133.0, 132.7, 132.7, 132.7, 130.7, 130.6, 129.6, 129.5, 129.5, 129.5, 129.5, 125.8, 70.6, 70.4, 63.0, 63.0, 62.7, 62.6, 26.3, 16.1, 16.1, 16.0, 15.9. ³¹P NMR (162 MHz, CDCl₃): δ 6.1. IR (neat, cm⁻¹): 3396, 3058, 2928, 2370, 2243, 1705, 1632, 1589, 1512, 1472, 1369, 1246, 1169, 1043, 918, 818, 733, 645, 572, 454. HRMS (ESI) Calcd for C₂₀H₂₁Cl₁N₁O₅P₁: [M+Na]⁺ = 444.0731 Found: 444.0738.



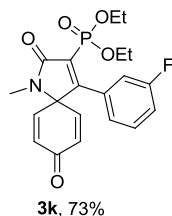
3j, 75%

diethyl

(4-(4-chlorophenyl)-1-methyl-2,8-dioxo-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)phosphonate 3j.

Eluent: ethyl acetate/ petroleum ether (3:1). Light yellow solid, mp 97-99°C. ¹H NMR (CDCl₃, 400 MHz) δ 7.33-7.30 (m, 2H), 7.18 (d, *J* = 8.4Hz, 2H), 6.48 (dd, *J* = 17.6Hz, *J* = 10.4Hz, 4H),

4.13-4.06 (m, 4H), 2.88 (s, 3H), 1.16 (t, $J = 7.2\text{Hz}$, 6H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 183.2, 167.5, 167.4, 164.2, 164.1, 143.3, 136.3, 133.8, 130.3, 129.4, 129.4, 129.3, 129.2, 128.2, 69.2, 69.1, 63.0, 63.0, 26.0, 16.1, 16.0. ^{31}P NMR (162 MHz, CDCl_3): δ 7.1. IR (neat, cm^{-1}): 3428, 2982, 2345, 2245, 1853, 1670, 1607, 1511, 1420, 1368, 1248, 1093, 916, 804, 647, 572, 507. HRMS (ESI) Calcd for $\text{C}_{20}\text{H}_{21}\text{Cl}_1\text{N}_1\text{O}_5\text{P}_1$: $[\text{M}+\text{Na}]^+ = 444.0731$ Found: 444.0738.

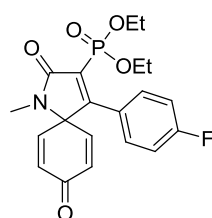


3k, 73%

diethyl

(4-(3-fluorophenyl)-1-methyl-2,8-dioxo-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)phosphonate **3k**.

Eluent: ethyl acetate/ petroleum ether (3:1). Light yellow liquide. ^1H NMR (CDCl_3 , 400 MHz) δ 7.34-7.29 (m, 1H), 7.10 (dd, $J = 8.4\text{Hz}$, $J = 2.4\text{Hz}$, 1H), 7.08-6.99 (m, 1H), 6.94 (dd, $J = 9.2\text{Hz}$, $J = 2.0\text{Hz}$, 1H), 6.49 (dd, $J = 21.6\text{Hz}$, $J = 10.4\text{Hz}$, 4H), 4.16-4.04 (m, 4H), 2.89 (s, 3H), 1.15 (t, $J = 7.2\text{Hz}$, 6H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 183.2, 167.4, 167.3, 163.7, 163.6, 163.0, 160.5, 143.1, 133.8, 132.8, 132.7, 132.7, 130.5, 129.7, 129.6, 128.5, 123.9, 123.9, 116.9, 116.7, 115.4, 115.2, 69.3, 69.1, 63.0, 62.9, 29.6, 26.0, 16.0, 15.9. ^{31}P NMR (162 MHz, CDCl_3): δ 6.9. IR (neat, cm^{-1}): 3374, 2980, 2859, 2367, 1968, 1853, 1697, 1628, 1584, 1482, 1385, 1262, 1165, 1026, 914, 786, 693, 547. HRMS (ESI) Calcd for $\text{C}_{20}\text{H}_{21}\text{F}_1\text{N}_1\text{O}_5\text{P}_1$: $[\text{M}+\text{Na}]^+ = 428.1023$ Found: 428.1034.

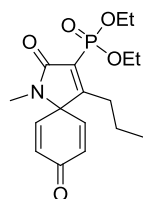


3l, 75%

diethyl

(4-(4-fluorophenyl)-1-methyl-2,8-dioxo-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)phosphonate **3l**.

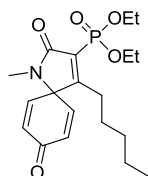
Eluent: ethyl acetate/ petroleum ether (3:1). Light yellow liquide. ^1H NMR (CDCl_3 , 400 MHz) δ 7.27-7.23 (m, 2H), 7.04 (t, $J = 8.4\text{Hz}$, 2H), 6.49 (dd, $J = 20.8\text{Hz}$, $J = 10.4\text{Hz}$, 4H), 4.16-4.04 (m, 4H), 2.88 (s, 3H), 1.16 (t, $J = 6.8\text{Hz}$, 6H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 183.3, 167.6, 167.4, 164.8, 164.4, 164.3, 162.3, 143.4, 133.8, 130.8, 130.1, 130.1, 130.1, 128.7, 128.0, 126.9, 126.8, 126.8, 115.3, 115.1, 69.3, 69.1, 63.0, 62.9, 29.6, 26.0, 16.1, 16.0. ^{31}P NMR (162 MHz, CDCl_3): δ 7.3. IR (neat, cm^{-1}): 3466, 3050, 2931, 2321, 2024, 1700, 1631, 1506, 1387, 1234, 1099, 1209, 878, 796, 646, 573, 469. HRMS (ESI) Calcd for $\text{C}_{20}\text{H}_{21}\text{F}_1\text{N}_1\text{O}_5\text{P}_1$: $[\text{M}+\text{Na}]^+ = 428.1023$ Found: 428.1034.



3m, 38%

diethyl (1-methyl-2,8-dioxo-4-propyl-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)phosphonate 3m.

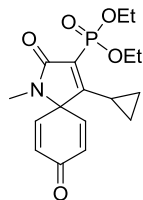
Eluent: ethyl acetate/ petroleum ether (3:1). Light yellow liquide. ^1H NMR (CDCl_3 , 400 MHz) δ 6.58 (d, $J = 10.4\text{Hz}$, 2H), 6.37 (d, $J = 10.0\text{Hz}$, 2H), 4.31-4.21 (m, 4H), 2.82 (s, 3H), 2.44-2.39 (m, 2H), 1.59-1.49 (m, 2H), 1.38 (t, $J = 6.8\text{Hz}$, 6H), 0.94 (t, $J = 7.2\text{Hz}$, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 183.8, 171.0, 170.9, 168.3, 168.1, 144.4, 133.6, 127.6, 125.6, 69.6, 69.5, 62.9, 62.8, 29.5, 29.5, 26.0, 24.8, 16.4, 16.3, 14.5. ^{31}P NMR (162 MHz, CDCl_3): δ 8.2. IR (neat, cm^{-1}): 3389, 3047, 2930, 2374, 2242, 1961, 1694, 1616, 1461, 1385, 1247, 1167, 1028, 890, 809, 733, 647, 569, 419. HRMS (ESI) Calcd for $\text{C}_{17}\text{H}_{24}\text{N}_1\text{O}_5\text{P}_1$: $[\text{M}+\text{Na}]^+ = 376.1279$ Found: 376.1284.



3m, 41%

diethyl (1-methyl-2,8-dioxo-4-pentyl-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)phosphonate 3n.

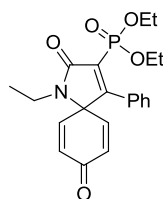
Eluent: ethyl acetate/ petroleum ether (3:1). Light yellow liquide. ^1H NMR (CDCl_3 , 400 MHz) δ 6.58 (dd, $J = 8.0\text{Hz}$, $J = 2.0\text{Hz}$, 2H), 6.38-6.36 (m, 2H), 4.31-4.21 (m, 4H), 2.82 (s, 3H), 2.45-2.41 (m, 2H), 1.54-1.51 (m, 2H), 1.50-1.46 (m, 6H), 1.40-1.26 (m, 4H), 0.85 (t, $J = 7.2\text{Hz}$, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 183.8, 171.4, 171.2, 168.3, 168.1, 144.5, 133.6, 127.4, 125.4, 69.7, 69.5, 62.9, 62.8, 32.1, 31.0, 27.6, 27.6, 26.1, 22.1, 16.4, 16.3, 13.8. ^{31}P NMR (162 MHz, CDCl_3): δ 8.2. IR (neat, cm^{-1}): 3392, 2959, 2866, 2371, 2242, 1848, 1670, 1612, 1546, 1459, 1368, 1259, 1166, 1029, 862, 805, 732, 624, 569, 468. HRMS (ESI) Calcd for $\text{C}_{19}\text{H}_{28}\text{N}_1\text{O}_5\text{P}_1$: $[\text{M}+\text{Na}]^+ = 404.1584$ Found: 404.1597.



3n, 67%

diethyl (4-cyclopropyl-1-methyl-2,8-dioxo-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)phosphonate 3o.

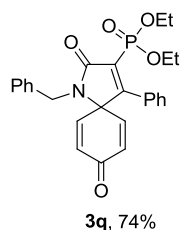
Eluent: ethyl acetate/ petroleum ether (3:1). Light yellow liquide. ^1H NMR (CDCl_3 , 400 MHz) δ 6.54 (d, $J = 10.0\text{Hz}$, 2H), 6.42 (d, $J = 10.0\text{Hz}$, 2H), 4.29-4.22 (m, 4H), 2.72 (s, 3H), 2.48-2.41 (m, 1H), 1.39 (t, $J = 7.2\text{Hz}$, 6H), 1.20-1.15 (m, 2H), 1.07-1.02 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 183.7, 172.8, 172.7, 167.9, 167.8, 144.6, 132.7, 125.9, 123.9, 67.4, 67.2, 62.9, 62.8, 25.0, 16.3, 16.3, 12.6, 12.6, 10.7. ^{31}P NMR (162 MHz, CDCl_3): δ 8.9. IR (neat, cm^{-1}): 3431, 2982, 2377, 2242, 1963, 1697, 1629, 1511, 1419, 1365, 1247, 1166, 1056, 973, 865, 811, 769, 646, 573, 426. HRMS (ESI) Calcd for $\text{C}_{17}\text{H}_{22}\text{N}_1\text{O}_5\text{P}_1$: $[\text{M}+\text{Na}]^+ = 374.1120$ Found: 374.1128.



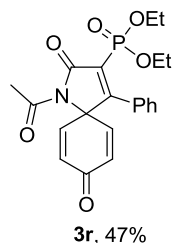
3o, 80%

diethyl (1-ethyl-2,8-dioxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)phosphonate 3p.

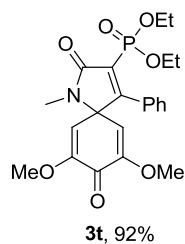
Eluent: ethyl acetate/ petroleum ether (3:1). Light yellow liquide. ^1H NMR (CDCl_3 , 400 MHz) δ 7.39-7.30 (m, 3H), 7.20 (d, $J = 7.2\text{Hz}$, 2H), 6.57 (d, $J = 10.0\text{Hz}$, 2H), 6.41 (d, $J = 10.0\text{Hz}$, 2H), 4.12-4.02 (m, 4H), 3.38-3.33 (m, 2H), 1.21 (t, $J = 7.2\text{Hz}$, 3H), 1.10 (t, $J = 6.8\text{Hz}$, 6H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 183.6, 167.6, 167.6, 165.2, 165.1, 143.9, 133.1, 130.9, 130.8, 130.0, 129.7, 128.0, 127.9, 127.8, 69.7, 69.6, 62.9, 62.9, 36.1, 16.0, 15.9, 15.0. ^{31}P NMR (162 MHz, CDCl_3): δ 7.6. IR (neat, cm^{-1}): 3384, 3053, 2932, 2373, 2244, 1962, 1697, 1630, 1511, 1443, 1391, 1320, 1248, 1166, 1052, 921, 848, 767, 699, 618, 573, 509, 456. HRMS (ESI) Calcd for $\text{C}_{21}\text{H}_{24}\text{N}_1\text{O}_5\text{P}_1$: $[\text{M}+\text{Na}]^+ = 424.1277$ Found: 424.1284.



diethyl (1-benzyl-2,8-dioxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)phosphonate 3q.
 Eluent: ethyl acetate/ petroleum ether (3:1). Light yellow liquide. ^1H NMR (CDCl_3 , 400 MHz) δ 7.34 (t, $J = 7.2\text{Hz}$, 1H), 7.29-7.25 (m, 7H), 7.13 (d, $J = 8.0\text{Hz}$, 2H), 6.32 (d, $J = 9.6\text{Hz}$, 2H), 6.21-6.19 (m, 2H), 4.54 (s, 2H), 4.16-3.98 (m, 4H), 1.11 (t, $J = 7.2\text{Hz}$, 6H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 183.6, 167.9, 167.7, 165.6, 165.5, 143.7, 137.0, 132.7, 130.6, 130.6, 129.7, 129.6, 128.9, 128.4, 127.9, 127.9, 127.8, 127.7, 127.6, 69.6, 69.5, 44.7, 16.0, 15.9. ^{31}P NMR (162 MHz, CDCl_3): δ 7.5. IR (neat, cm^{-1}): 3369, 3048, 2927, 2775, 2248, 1966, 1816, 1695, 1633, 1512, 1473, 1389, 1327, 1246, 1182, 1096, 1025, 914, 847, 760, 702, 625, 579, 514, 428. HRMS (ESI) Calcd for $\text{C}_{26}\text{H}_{26}\text{N}_1\text{O}_5\text{P}_1$: $[\text{M}+\text{Na}]^+ = 486.1440$ Found: 486.1441.

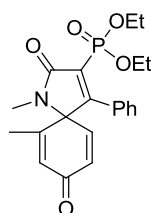


diethyl (1-acetyl-2,8-dioxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)phosphonate 3r.
 Eluent: ethyl acetate/ petroleum ether (3:1). Light yellow solid, mp 123-125°C. ^1H NMR (CDCl_3 , 400 MHz) δ 7.41-7.37 (m, 1H), 7.31 (dd, $J = 14.8\text{Hz}$, $J = 7.6\text{Hz}$, 2H), 7.12-7.09 (m, 2H), 6.55 (d, $J = 10.0\text{Hz}$, 2H), 6.35 (d, $J = 10.0\text{Hz}$, 2H), 4.13-4.03 (m, 4H), 2.61 (s, 3H), 1.10 (t, $J = 7.2\text{Hz}$, 6H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 183.5, 168.9, 168.4, 168.3, 166.7, 166.5, 142.6, 132.6, 130.1, 129.4, 129.3, 128.2, 128.2, 127.6, 25.6, 16.0, 16.0. ^{31}P NMR (162 MHz, CDCl_3): δ 5.8. IR (neat, cm^{-1}): 3406, 3058, 2928, 2368, 2248, 1971, 1854, 1738, 1668, 1547, 1443, 1371, 1203, 1227, 1160, 1044, 869, 794, 699, 626, 533, 468. HRMS (ESI) Calcd for $\text{C}_{21}\text{H}_{22}\text{N}_1\text{O}_6\text{P}_1$: $[\text{M}+\text{Na}]^+ = 438.1068$ Found: 438.1077.



diethyl

(7,9-dimethoxy-1-methyl-2,8-dioxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)phosphonate 3t. Eluent: ethyl acetate/ petroleum ether (3:1). Light yellow solid, mp 226-228°C. ¹H NMR (CDCl₃, 400 MHz) δ 7.38-7.34 (m, 1H), 7.32-7.28 (m, 2H), 7.18-7.16 (m, 2H), 5.40 (s, 2H), 4.13-3.98 (m, 4H), 3.67 (s, 6H), 2.86 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ 174.8, 167.8, 167.7, 167.1, 167.0, 153.6, 131.1, 131.0, 130.8, 129.6, 128.7, 128.4, 127.8, 127.7, 126.3, 110.4, 69.3, 69.2, 62.7, 62.7, 55.8, 25.5, 15.9, 15.9. ³¹P NMR (162 MHz, CDCl₃): δ 8.0. IR (neat, cm⁻¹): 3344, 3063, 2927, 2854, 2377, 2253, 1953, 1726, 1651, 1594, 1460, 1383, 1260, 1110, 1043, 911, 802, 735, 648, 574, 508. HRMS (ESI) Calcd for C₂₂H₂₆N₁O₇P₁: [M+Na]⁺ = 470.1332 Found: 470.1339.



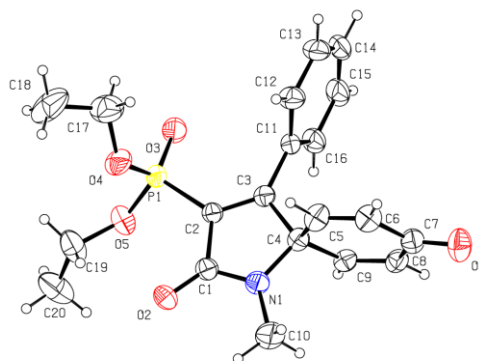
3u, 16%

diethyl (1,6-dimethyl-2,8-dioxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-trien-3-yl)phosphonate 3u. Eluent: ethyl acetate/ petroleum ether (3:1). Light yellow liquide. ¹H NMR (CDCl₃, 400 MHz) δ 7.41-7.37 (m, 1H), 7.43-7.30 (m, 2H), 7.25-7.22 (m, 2H), 6.51-6.44 (m, 2H), 6.31 (t, *J* = 1.6Hz, 1H), 4.15-4.01 (m, 4H), 2.80 (s, 3H), 1.80 (d, *J* = 1.2Hz, 3H), 1.12 (t, *J* = 6.8Hz, 6H). ¹³C NMR (CDCl₃, 100 MHz) δ 184.2, 168.3, 168.1, 165.9, 165.9, 152.0, 143.7, 133.3, 132.4, 130.7, 130.7, 130.2, 128.2, 128.1, 127.8, 127.8, 71.7, 63.0, 63.0, 62.9, 62.9, 29.7, 25.7, 17.7, 16.1, 16.0. ³¹P NMR (162 MHz, CDCl₃): δ 7.4, 7.3. IR (neat, cm⁻¹): 3449, 3055, 2928, 2373, 2244, 1967, 1699, 1638, 1574, 1442, 1384, 1333, 1246, 1165, 1098, 1045, 917, 816, 732, 646, 574, 483. HRMS (ESI) Calcd for C₂₁H₂₄N₁O₅P₁: [M+Na]⁺ = 424.1274 Found: 424.1284.

References

- [1] (a) L-J. Wang, H-T. Zhu, Y-F. Qiu, X-Y. Liu and Y-M. Liang, *Org. Biomol. Chem.*, 2014, 12, 643. (b) Daniel. M.D'Souza, A. Kiel, D.-Peter. Herten, F. Rominger, T. J. J. Müller, *Chem. Eur. J.* **2008**, 14,529.

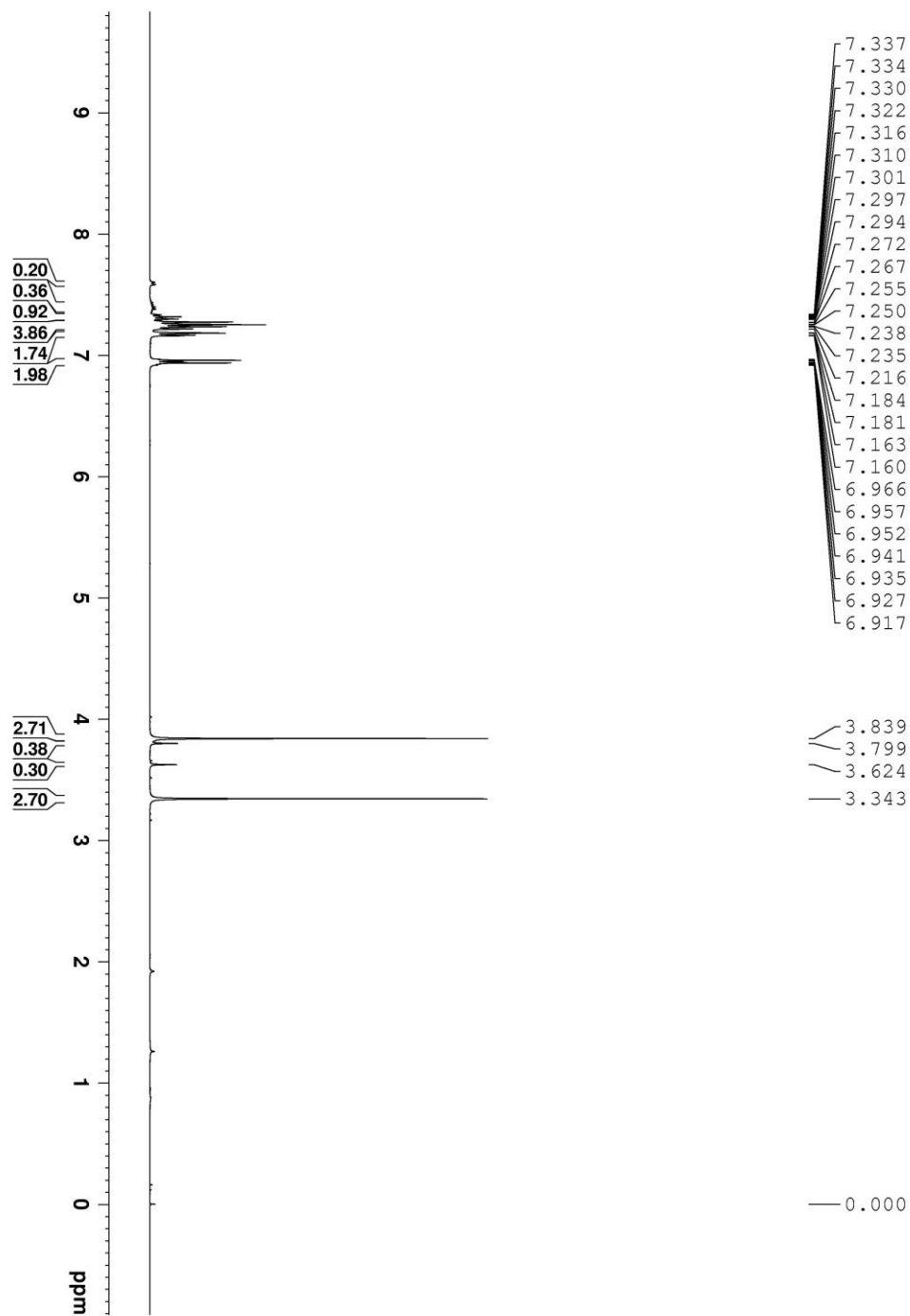
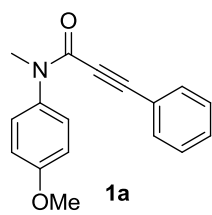
X-ray diffraction analysis of compound 3a

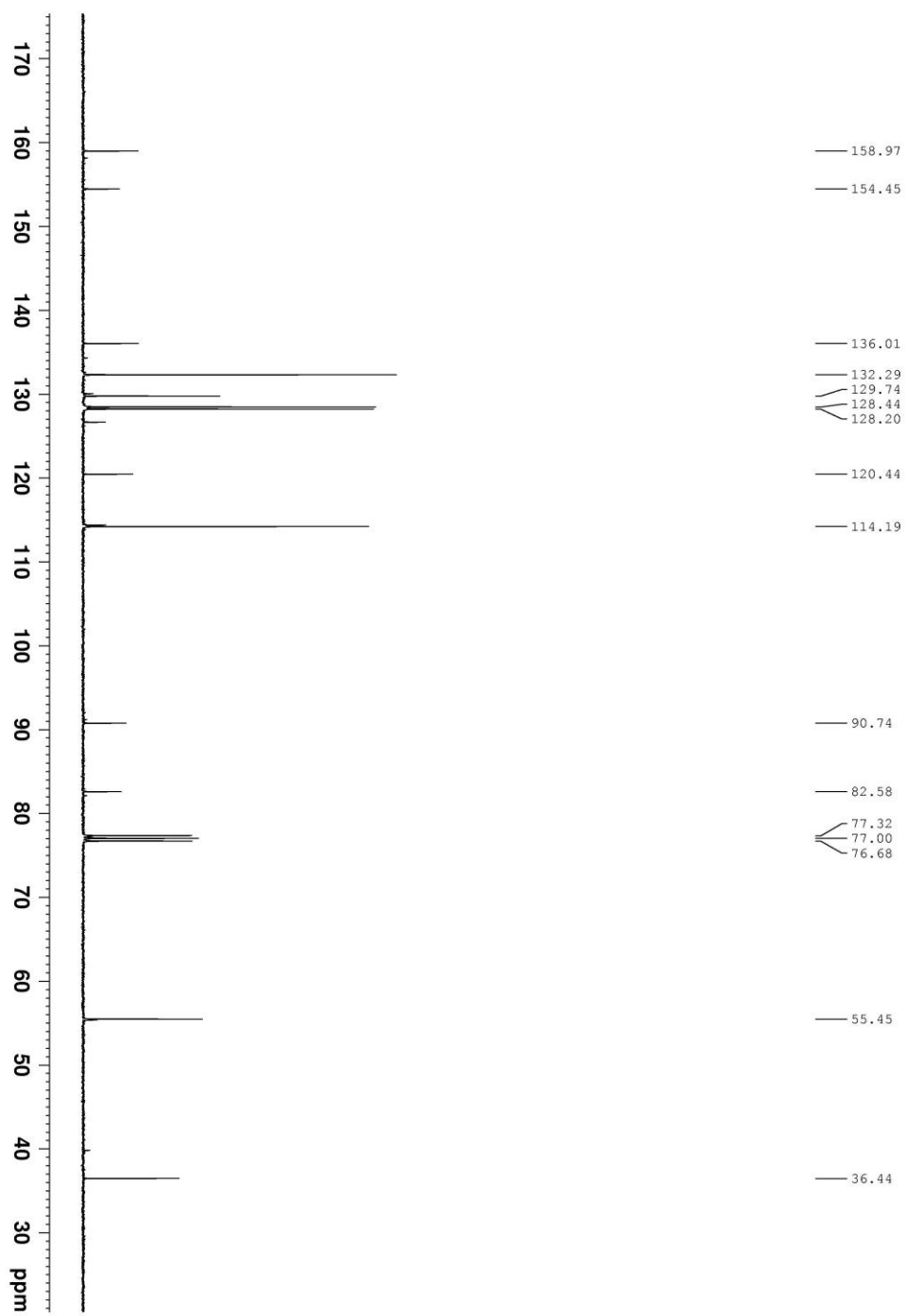
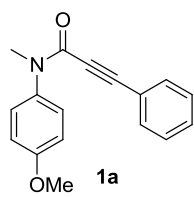


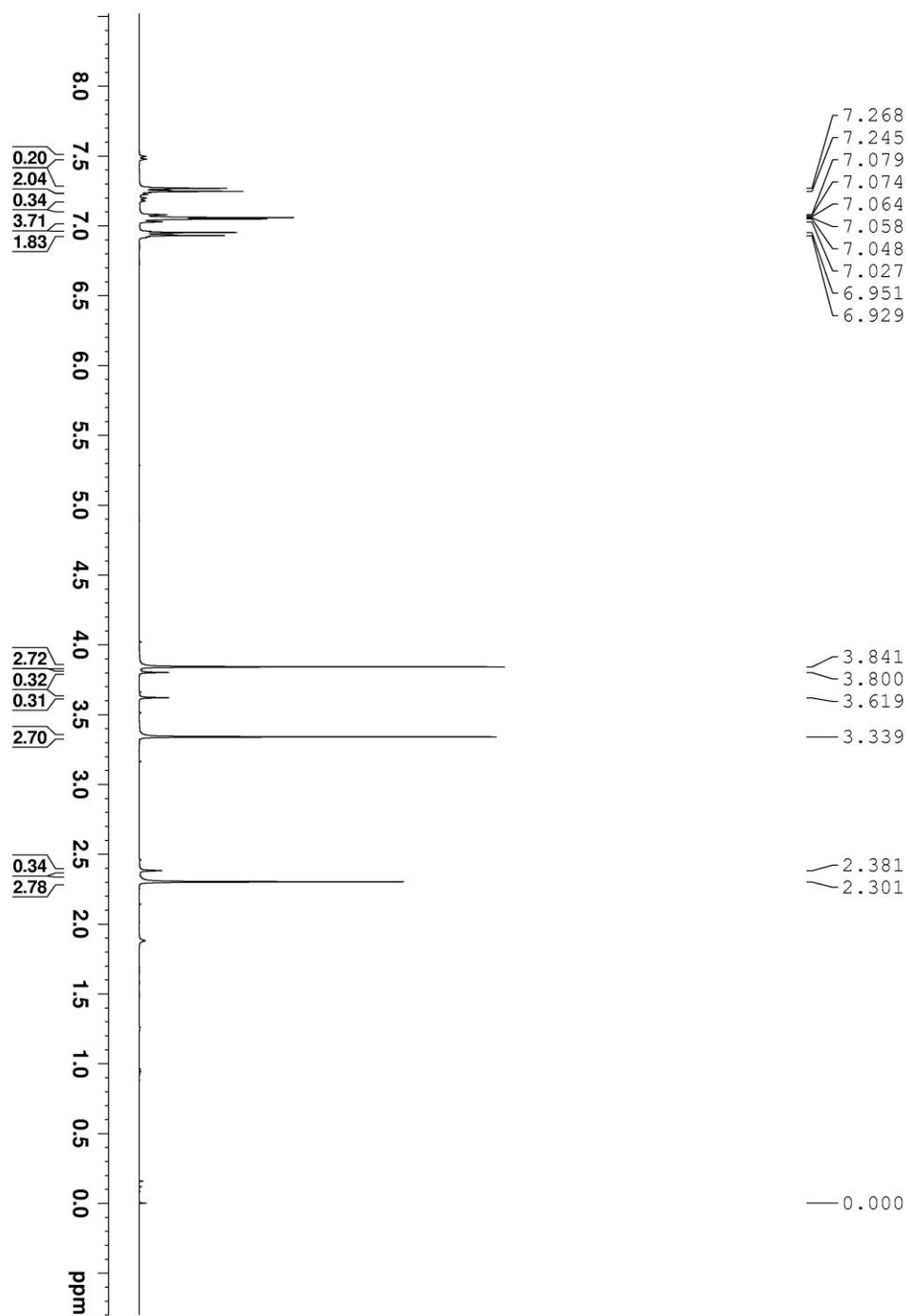
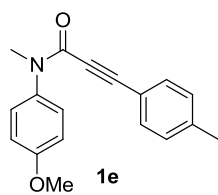
X-ray structure of 3a (CCDC 1022183)

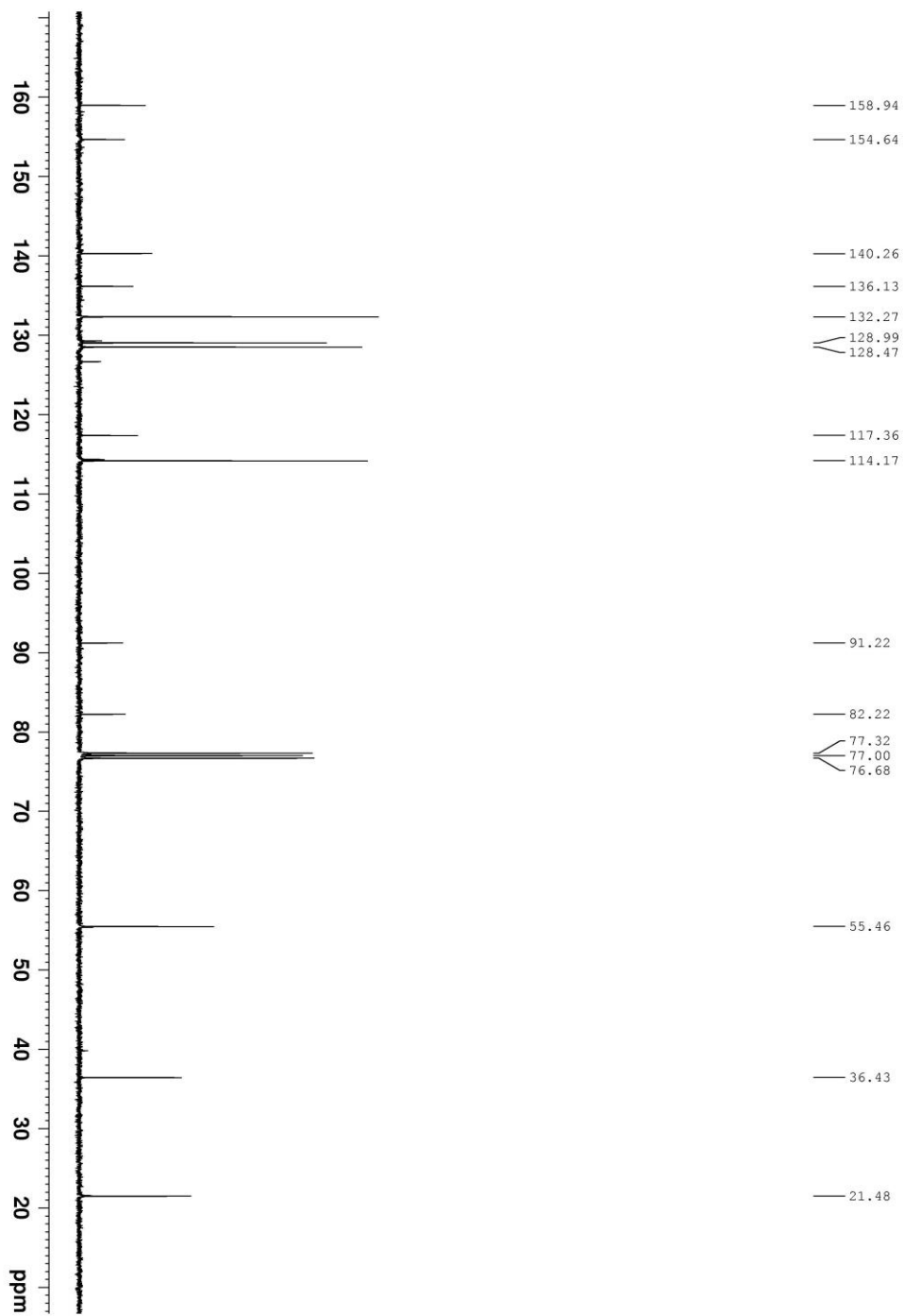
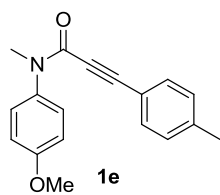
Bond precision: C-C = 0.0037 Å Wavelength=1.54184
Cell: a=8.3849 (3) b=12.0609 (4) c=19.3266 (6)
alpha=90 beta=95.801 (3) gamma=90
Temperature: 293 K

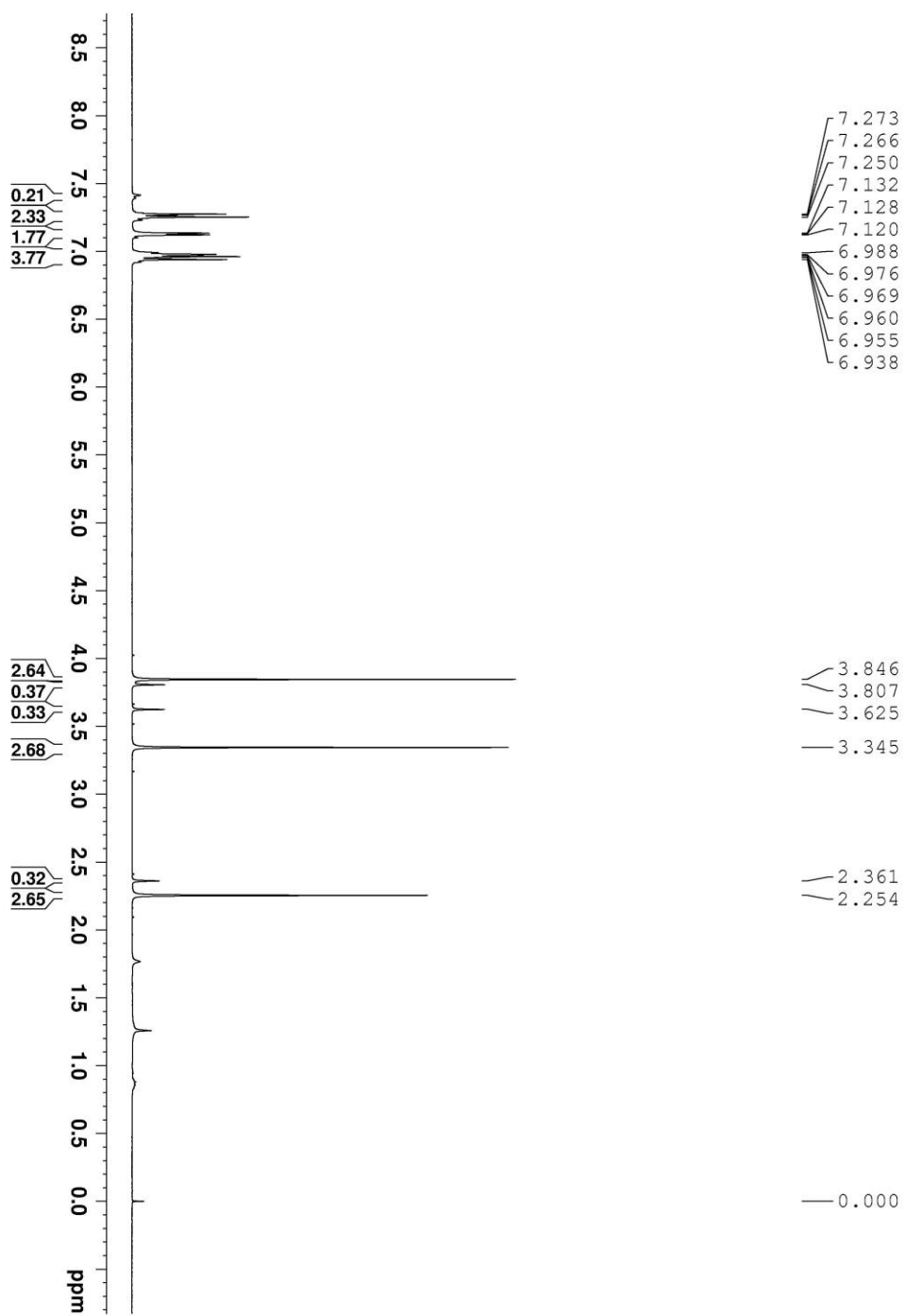
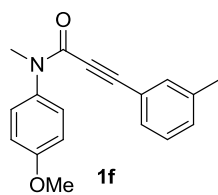
	Calculated	Reported
Volume	1944.48 (11)	1944.50 (12)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C20 H22 N O5 P	C20 H22 N O5 P
Sum formula	C20 H22 N O5 P	C20 H22 N O5 P
Mr	387.36	387.36
Dx, g cm ⁻³	1.323	1.323
Z	4	4
Mu (mm ⁻¹)	1.519	1.519
F000	816.0	816.0
F000'	819.64	
h, k, lmax	10, 14, 23	10, 14, 23
Nref	3678	3611
Tmin, Tmax	0.697, 0.749	0.772, 1.000
Tmin'	0.632	
Correction method=	MULTI-SCAN	
Data completeness=	0.982	Theta (max)= 69.880
R(reflections)=	0.0497 (2887)	wR2(reflections)= 0.1501 (3611)
S =	1.037	Npar= 247

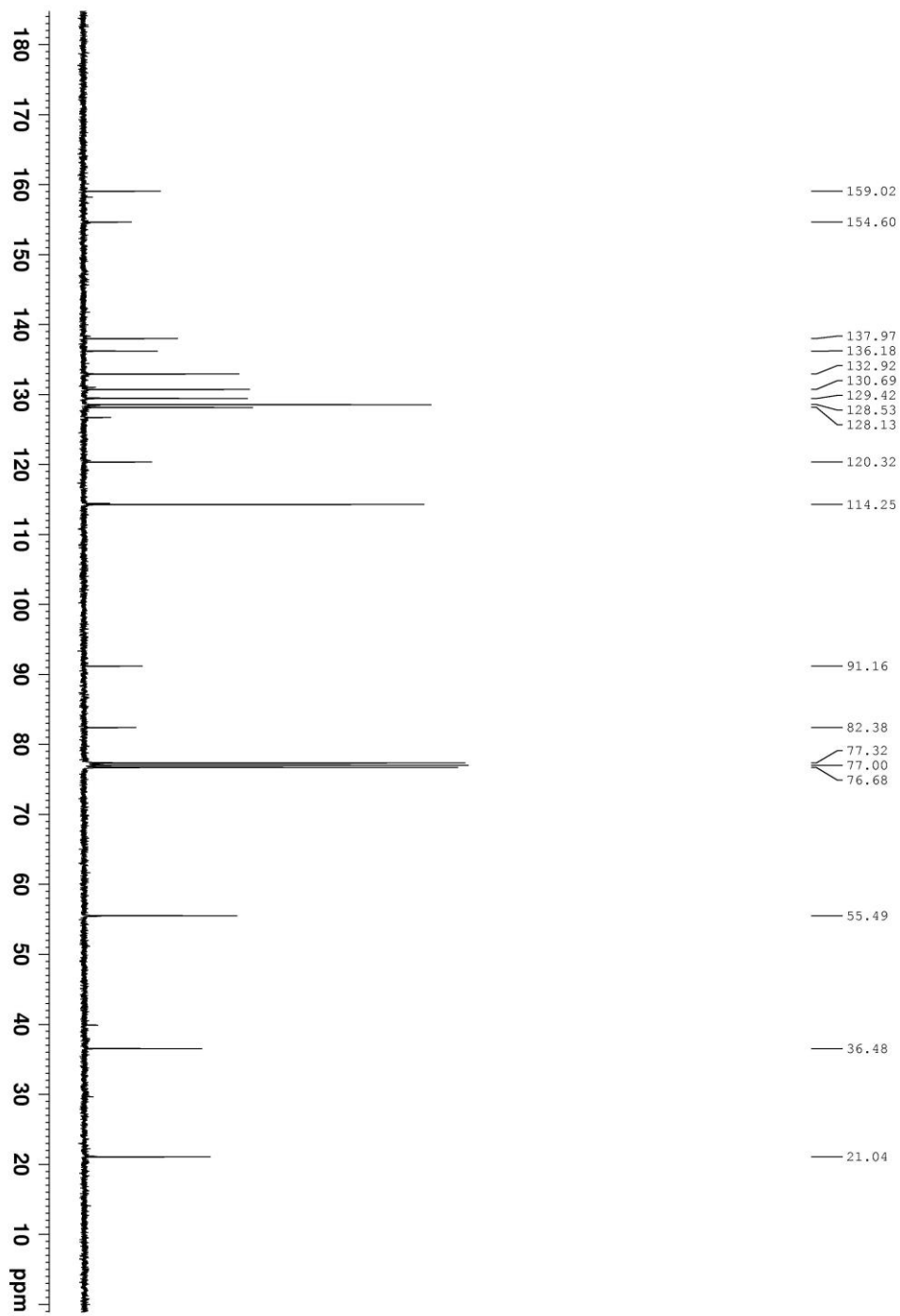
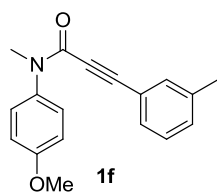


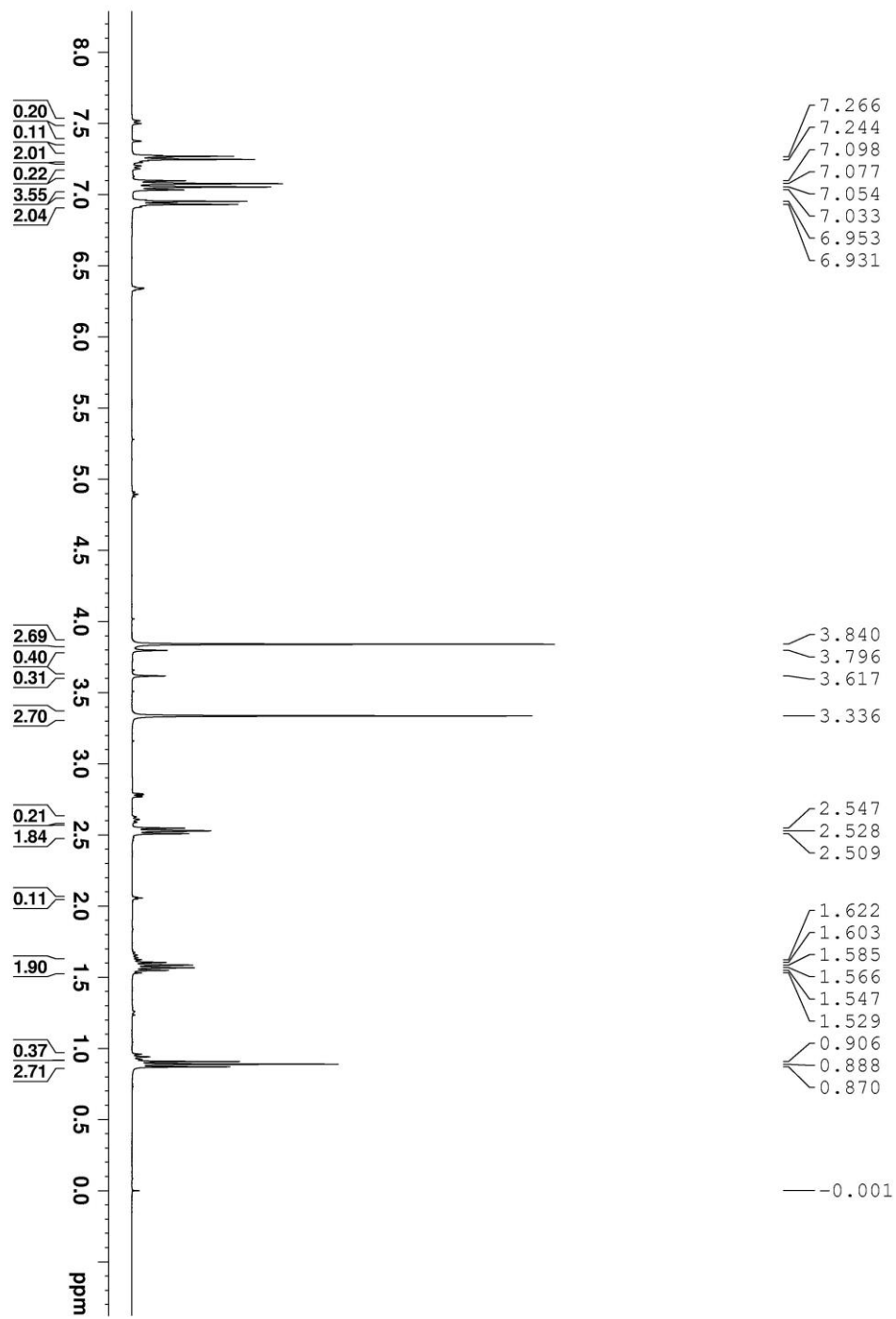
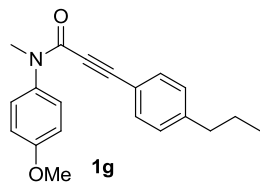


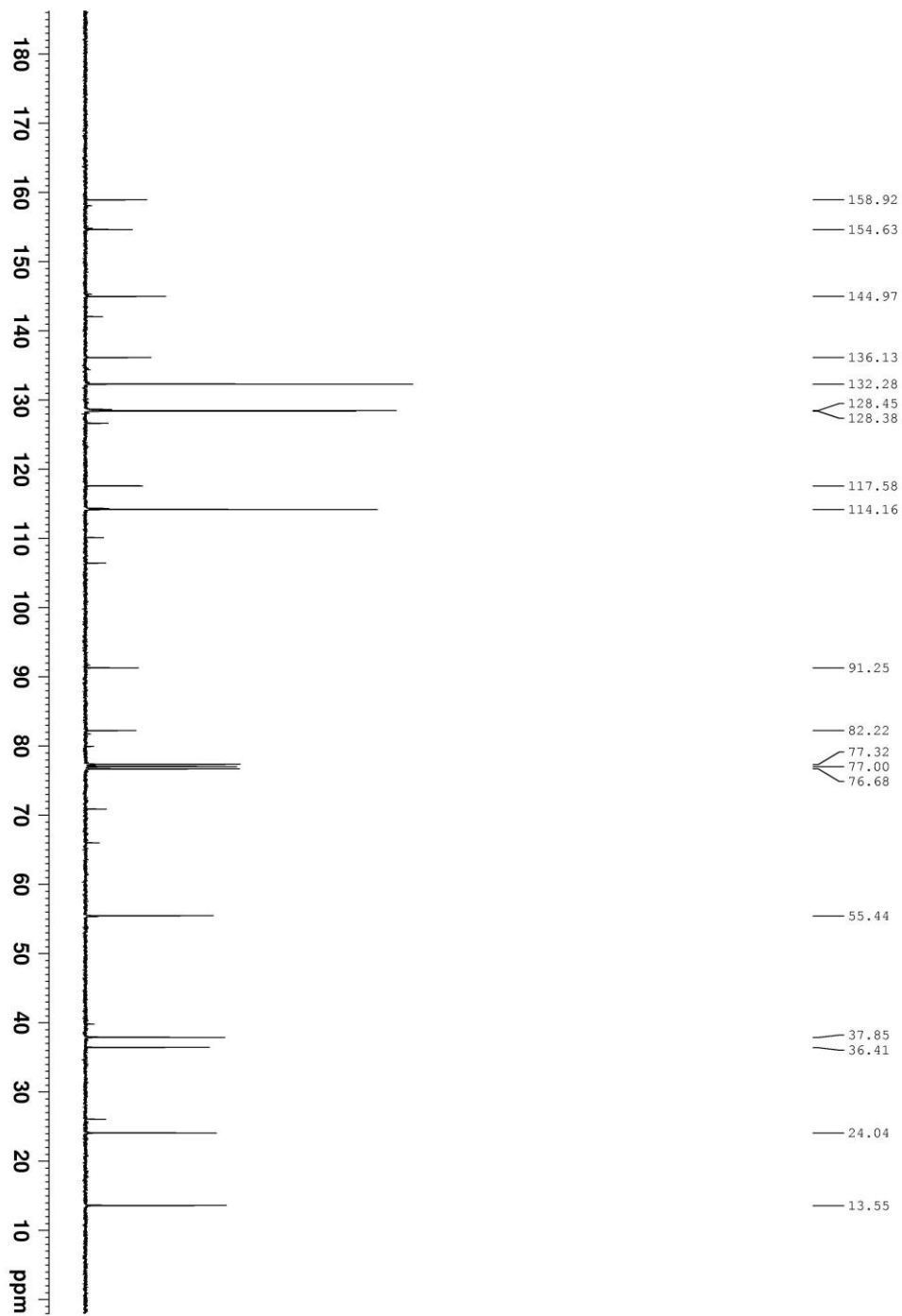
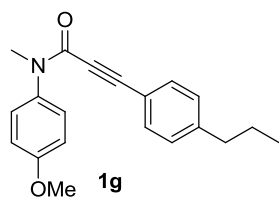


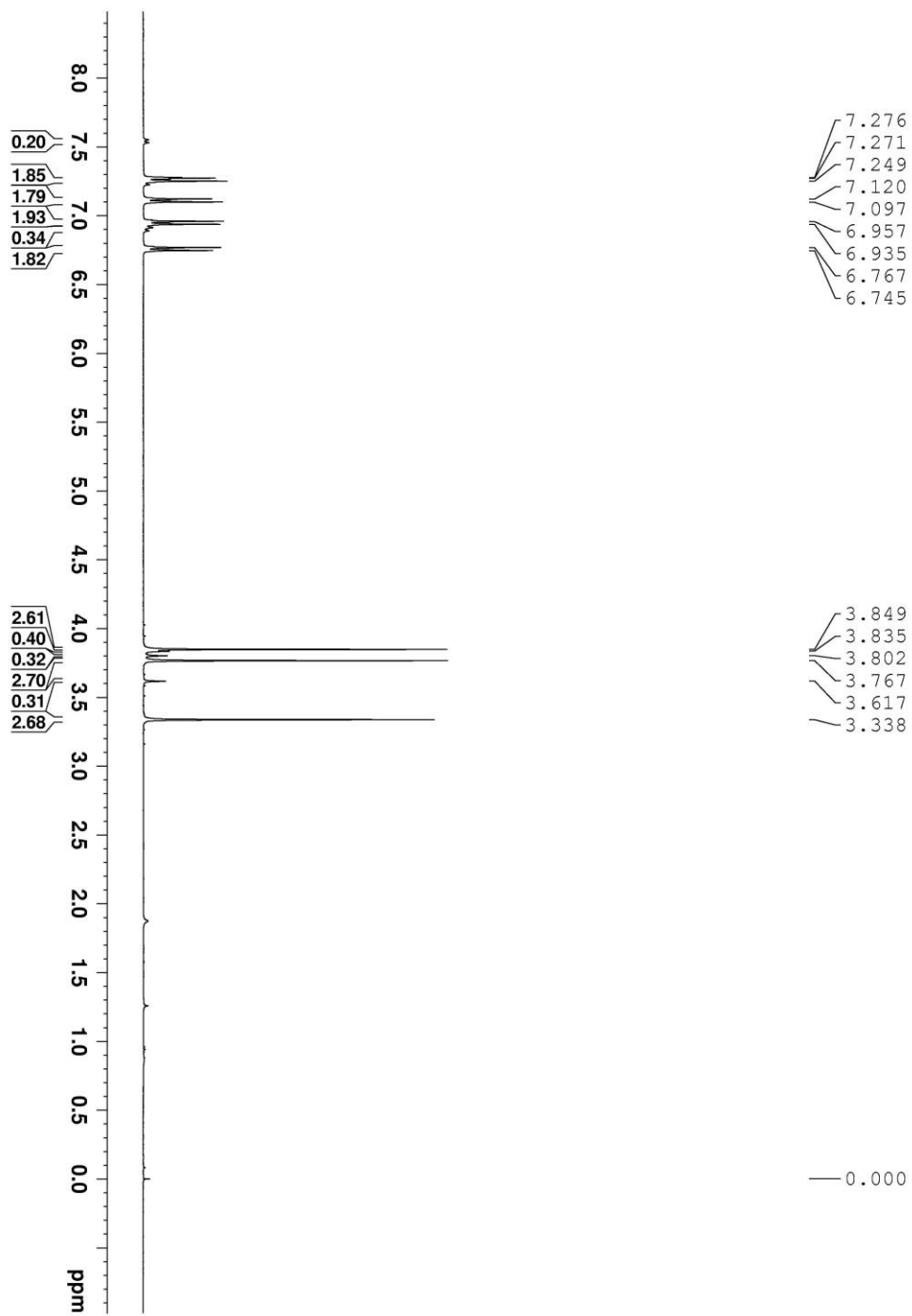
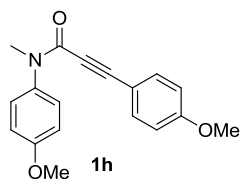


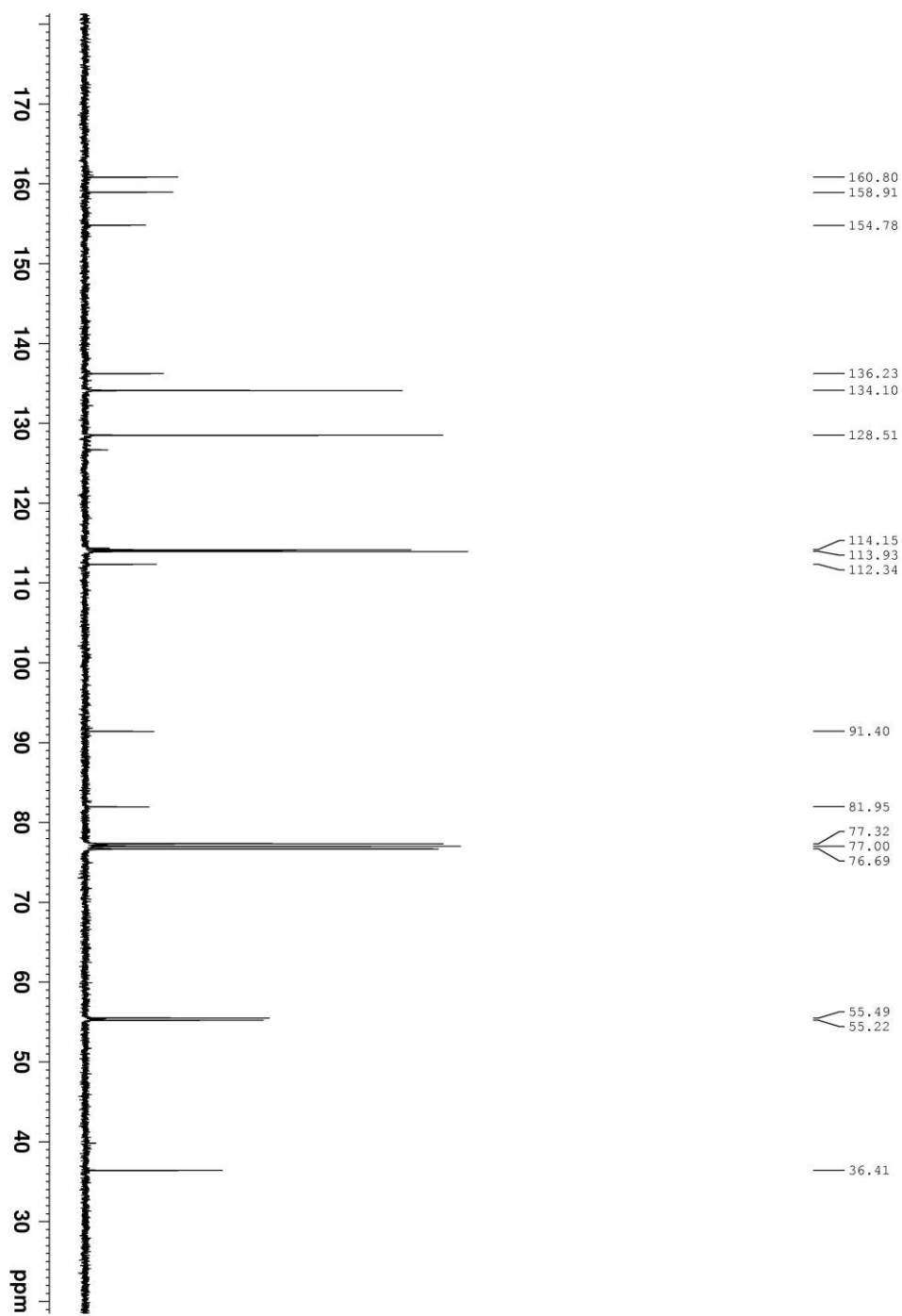
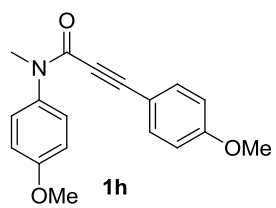


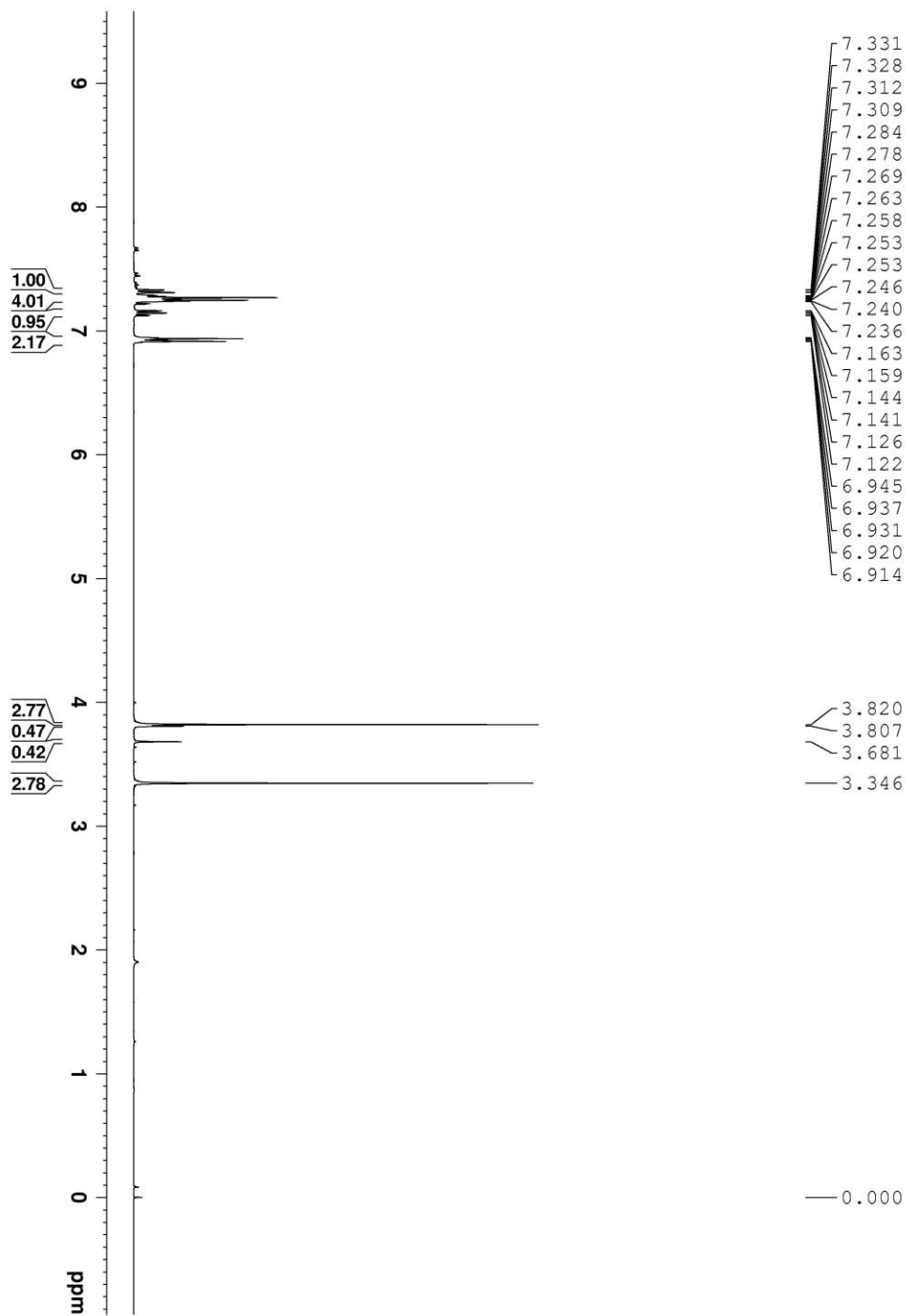
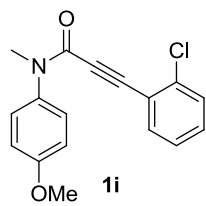


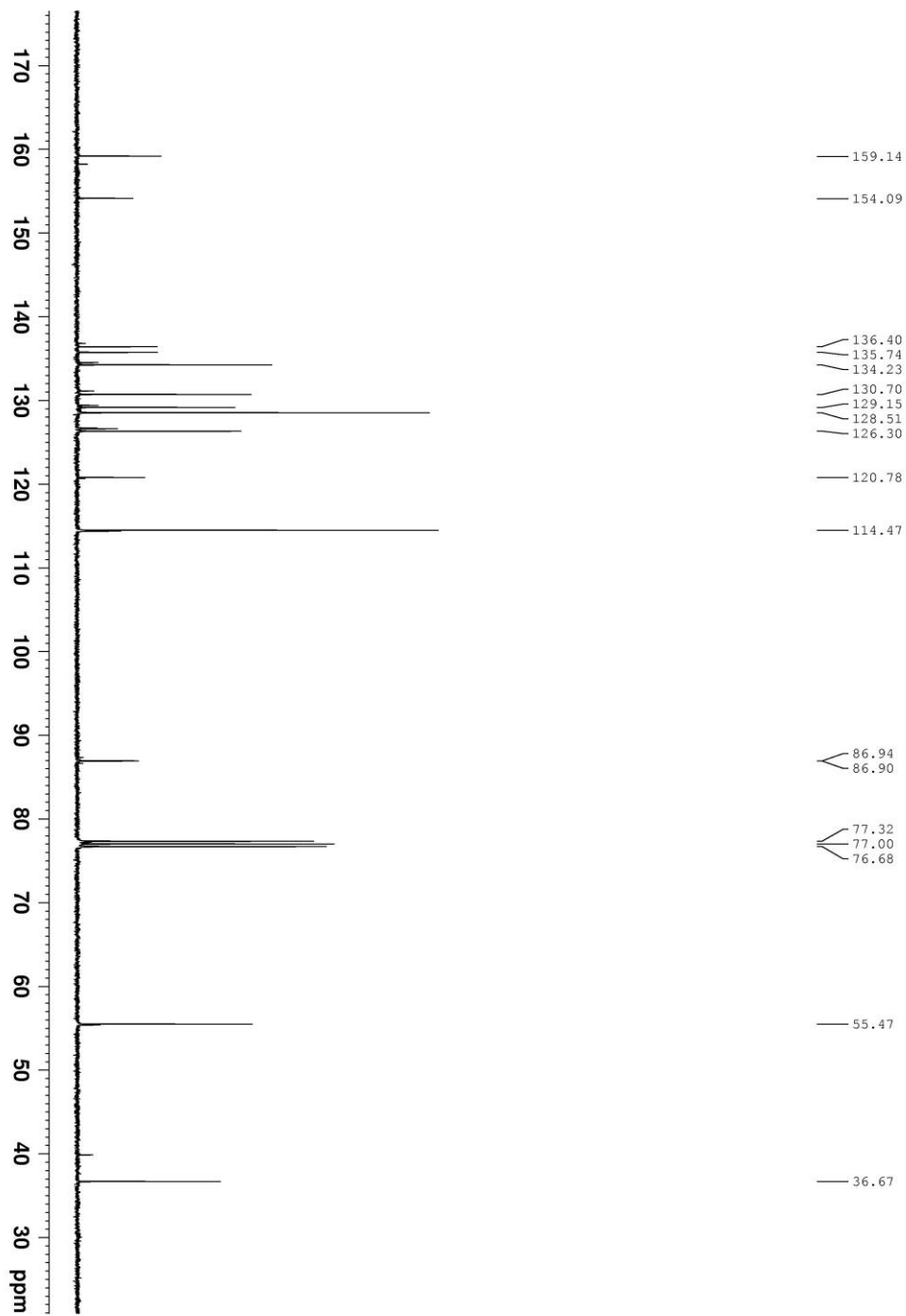
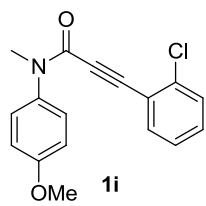


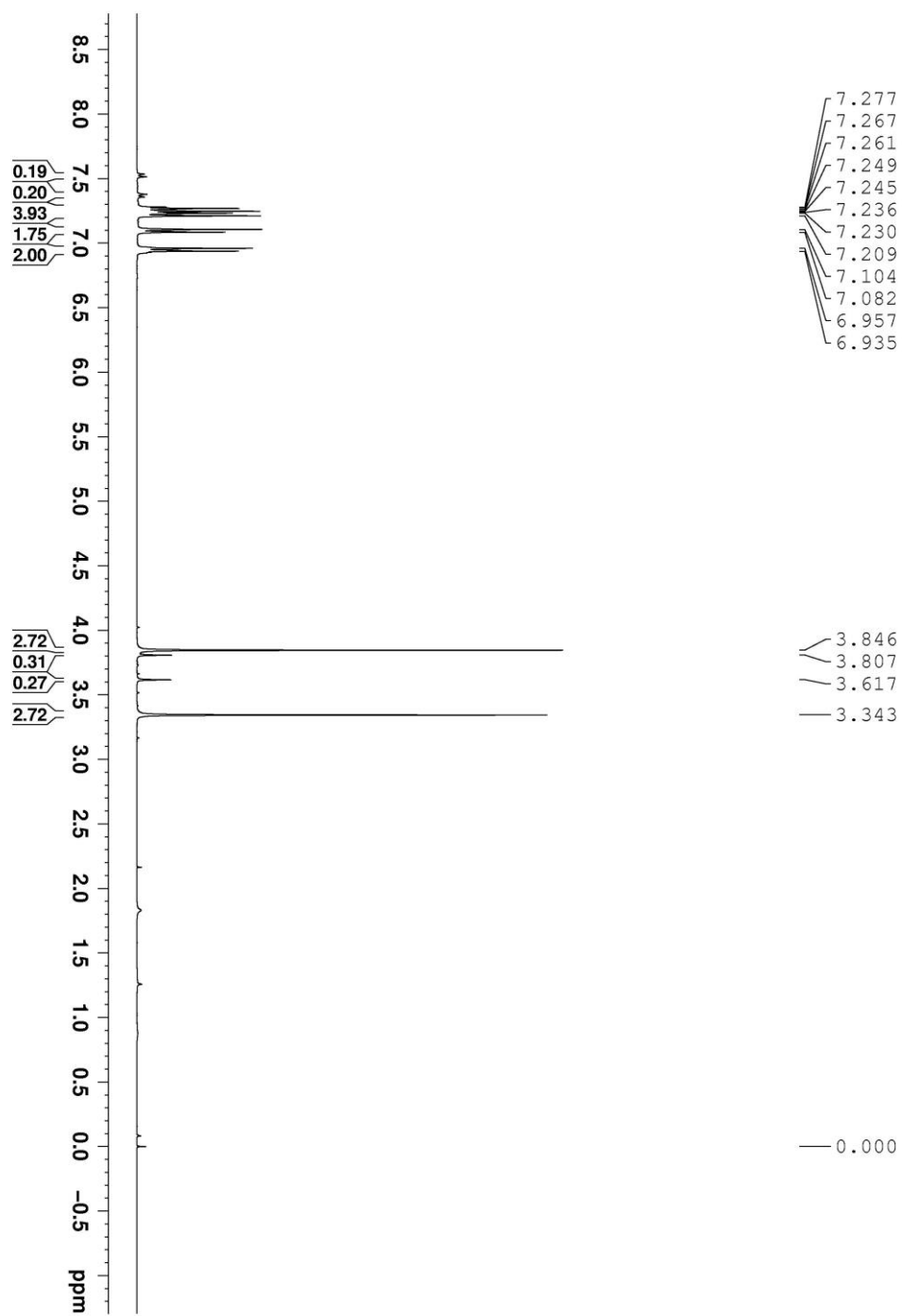
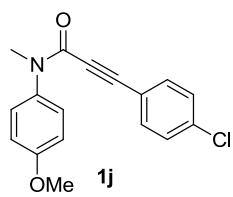


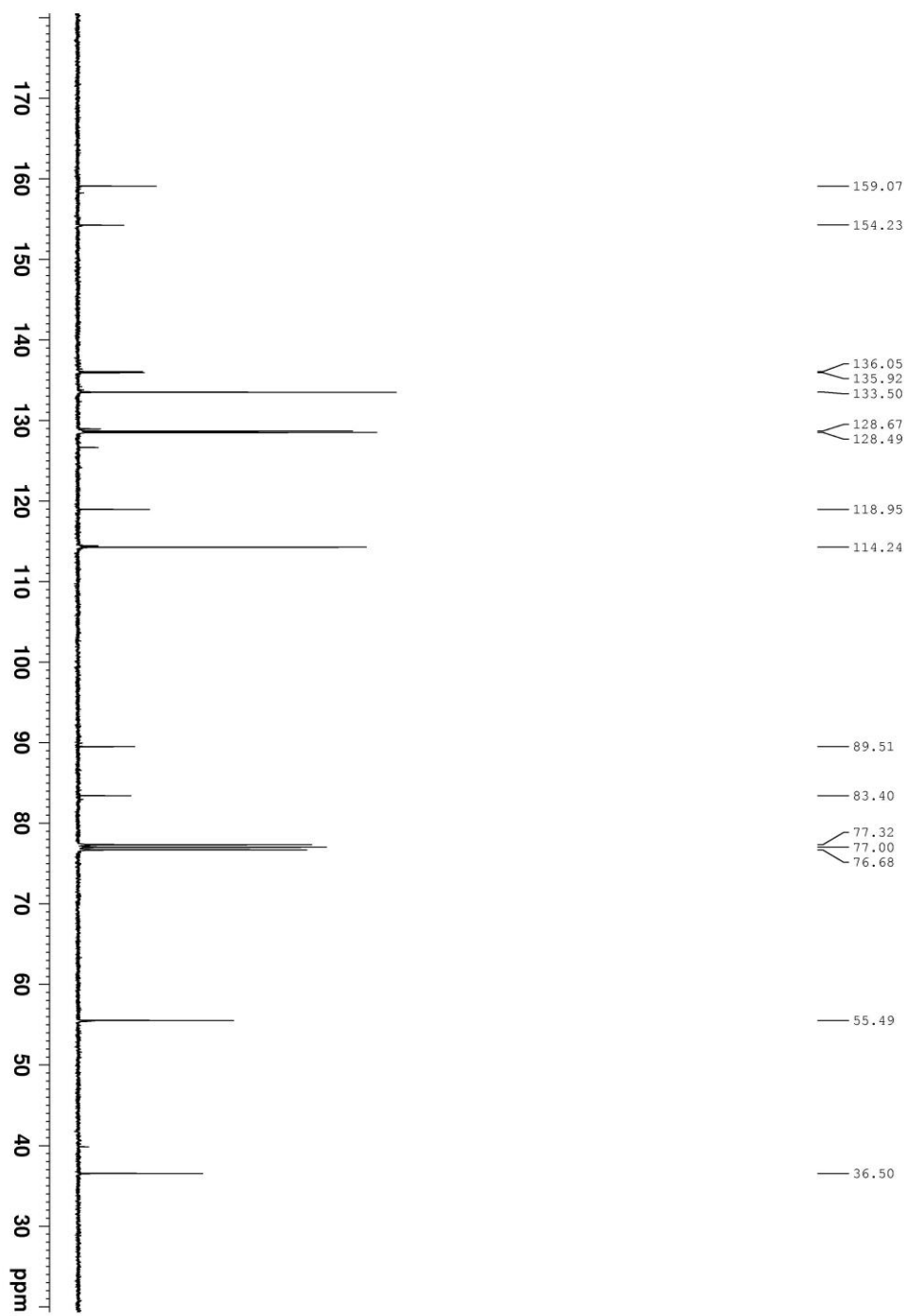
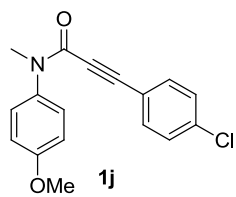


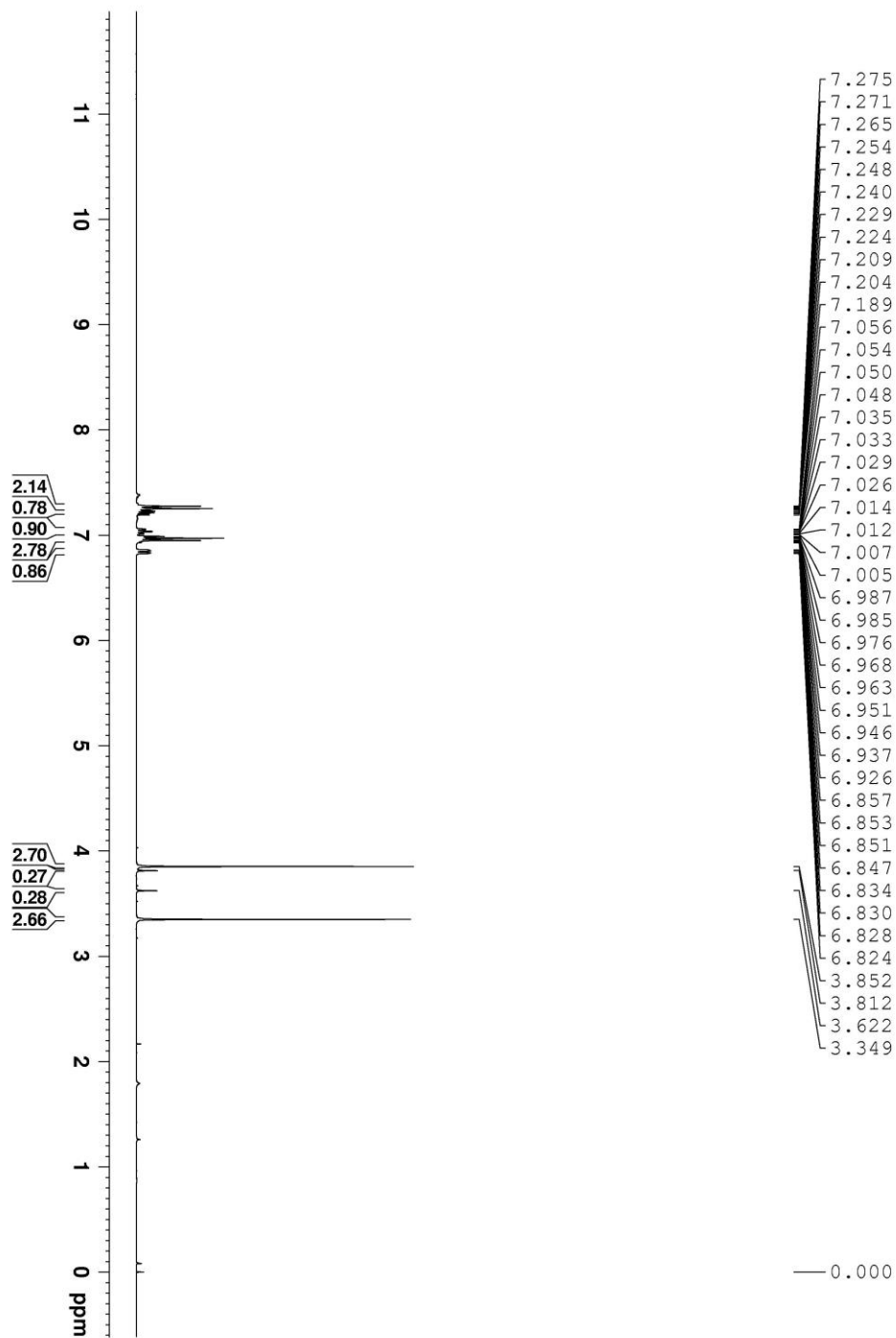
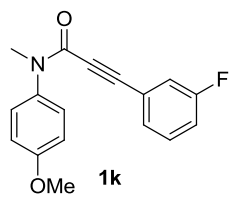


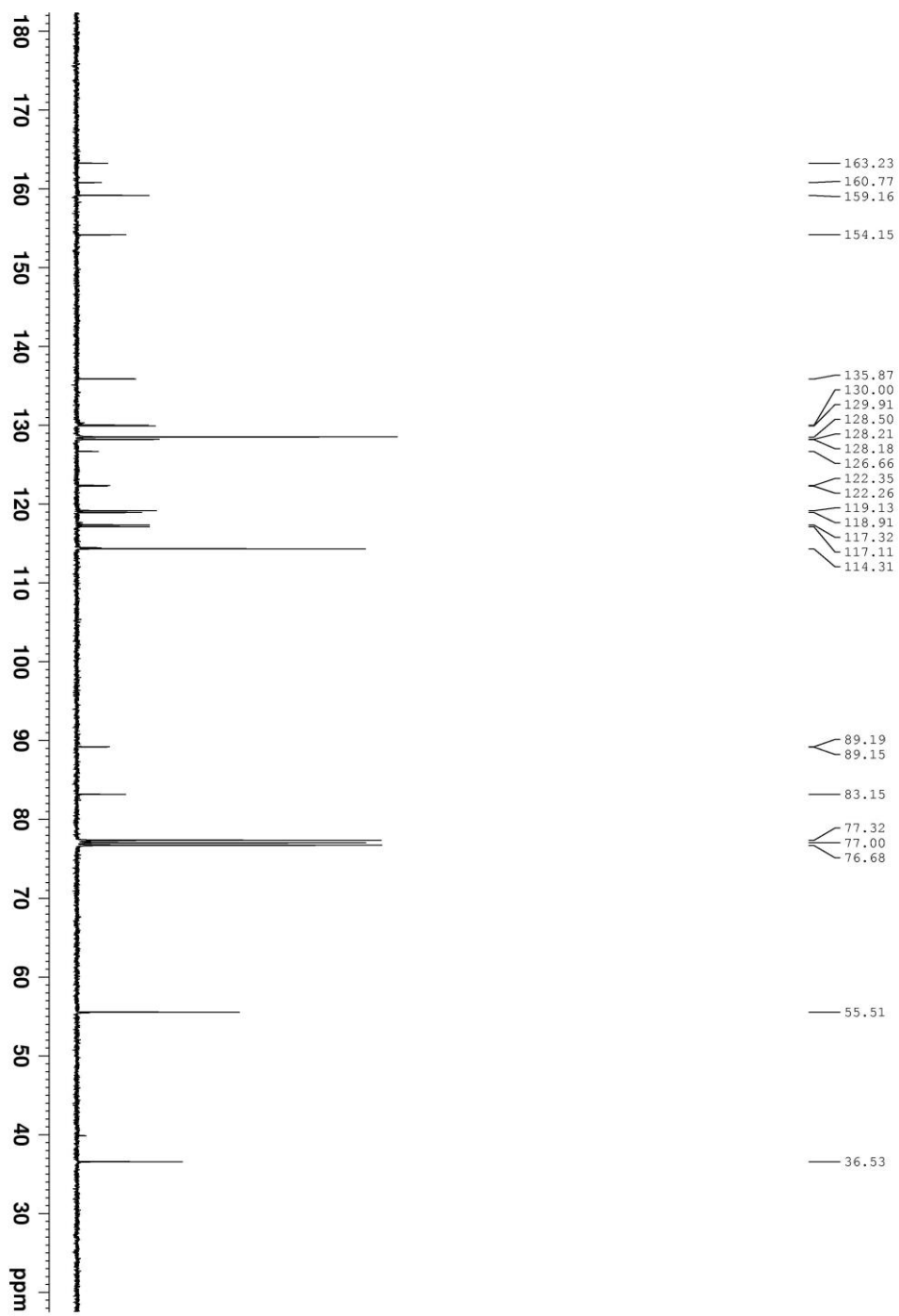
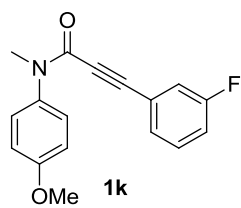


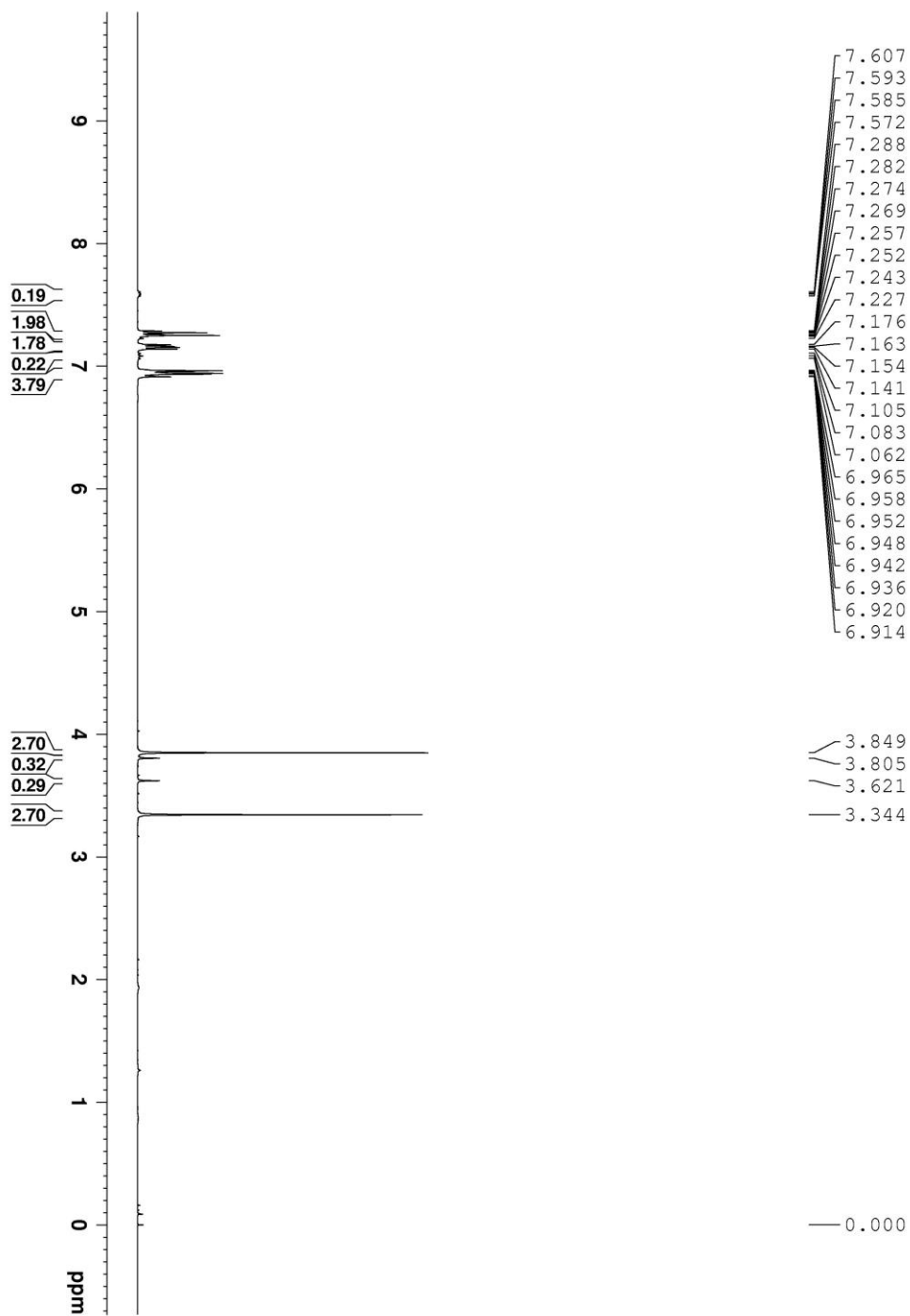
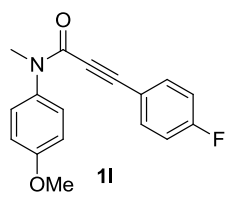


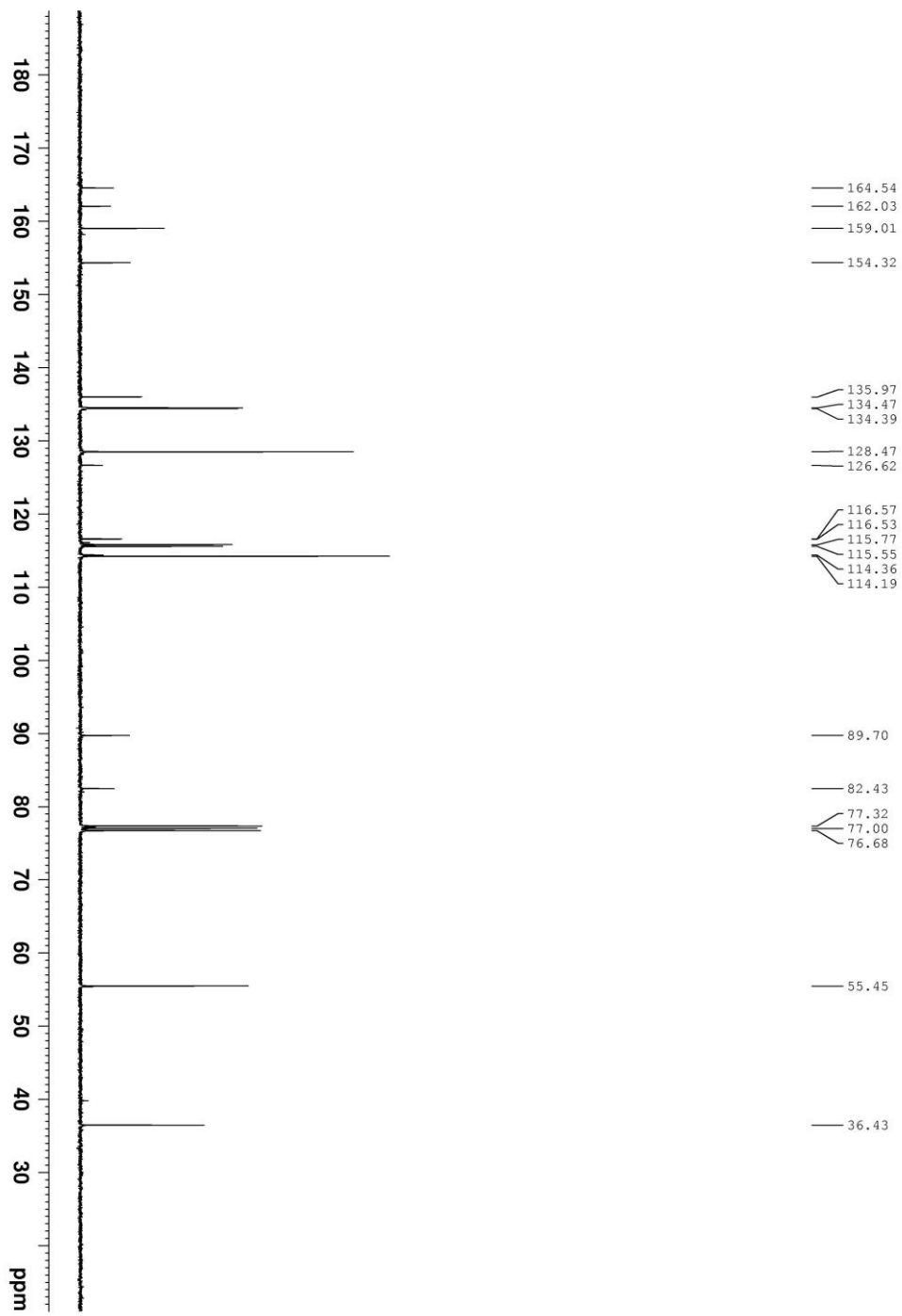
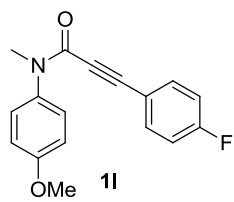


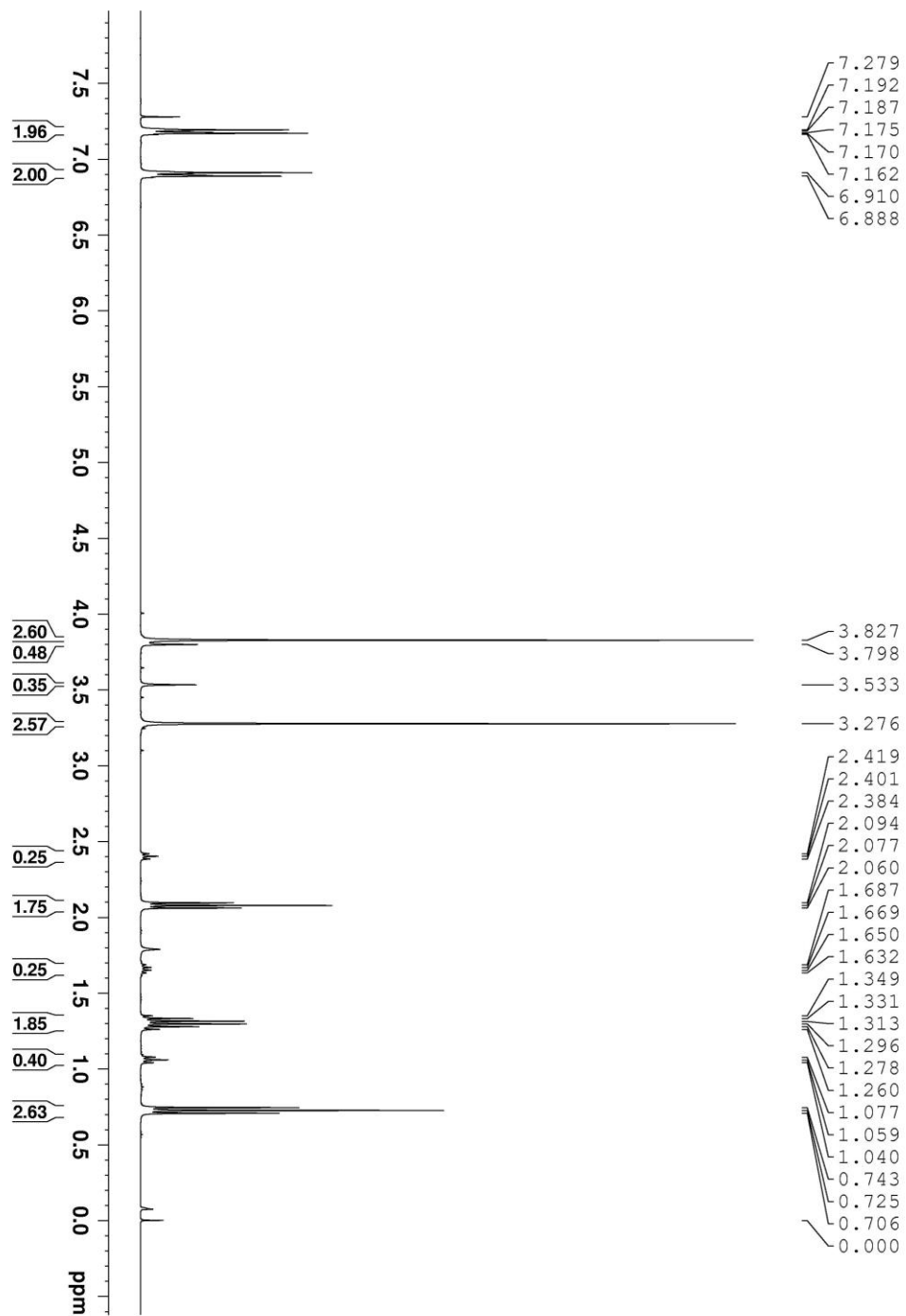
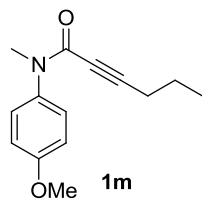


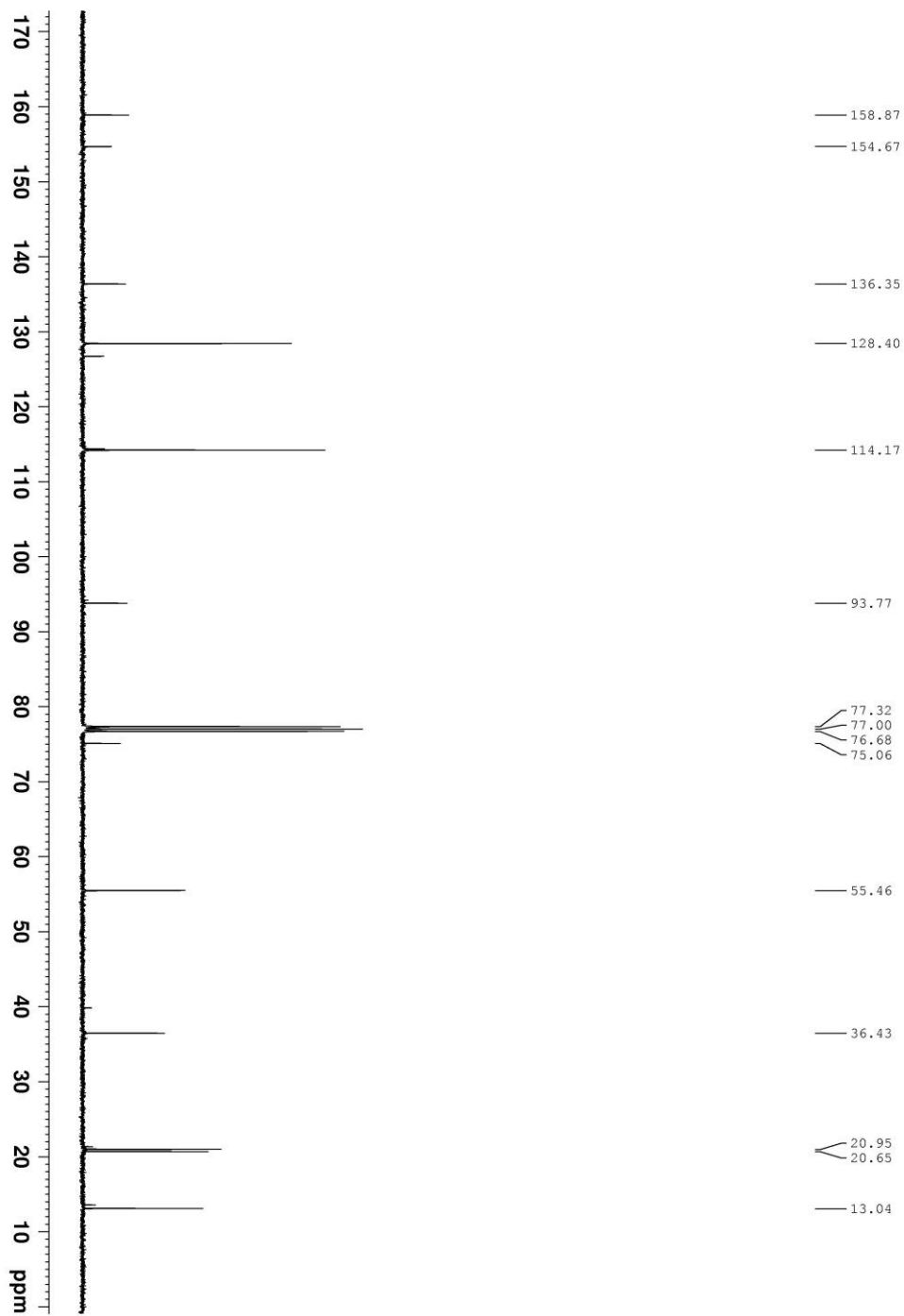
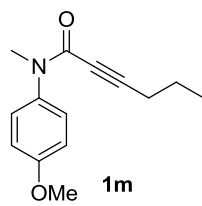


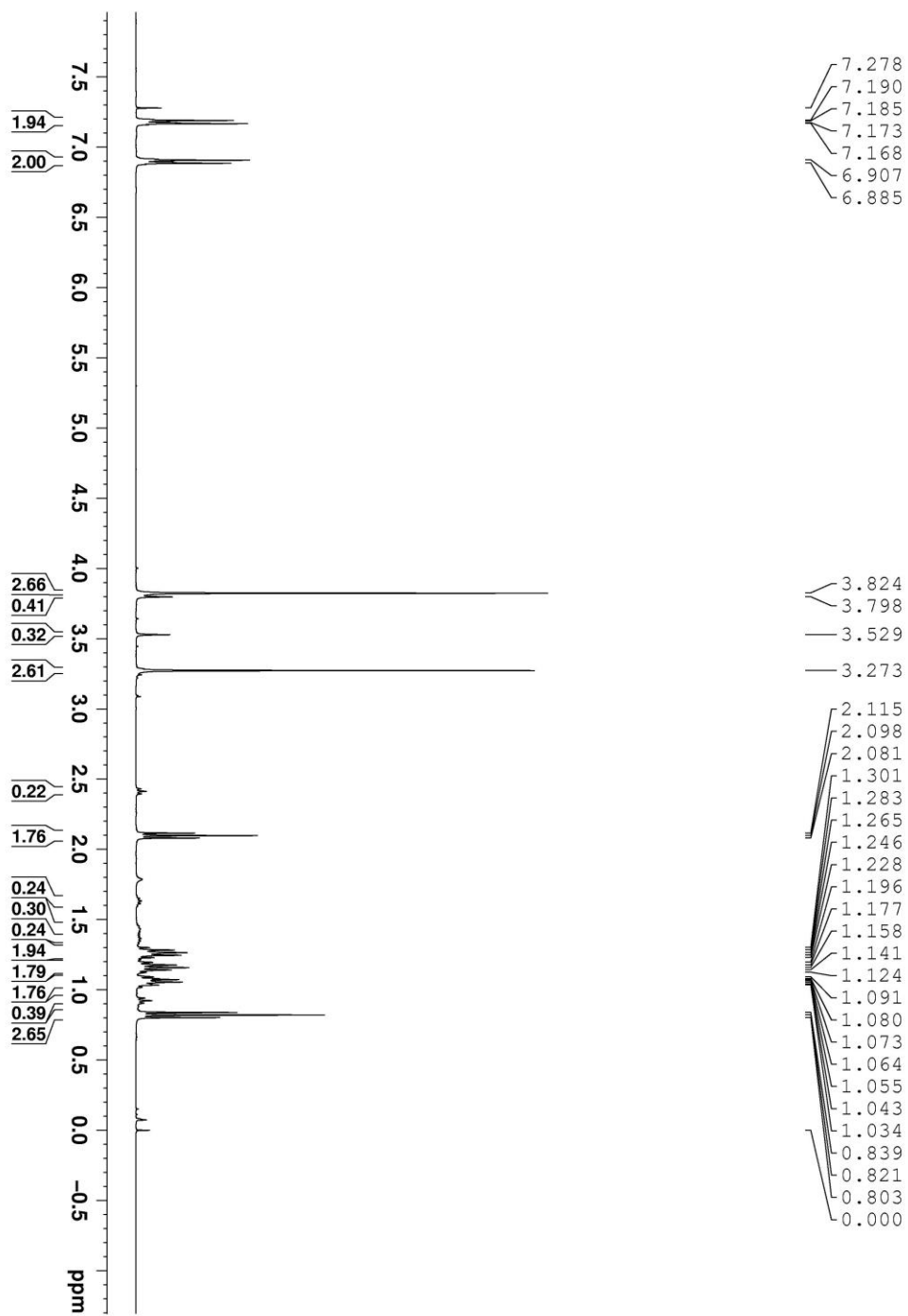
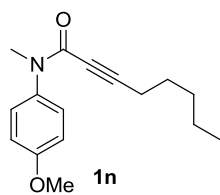


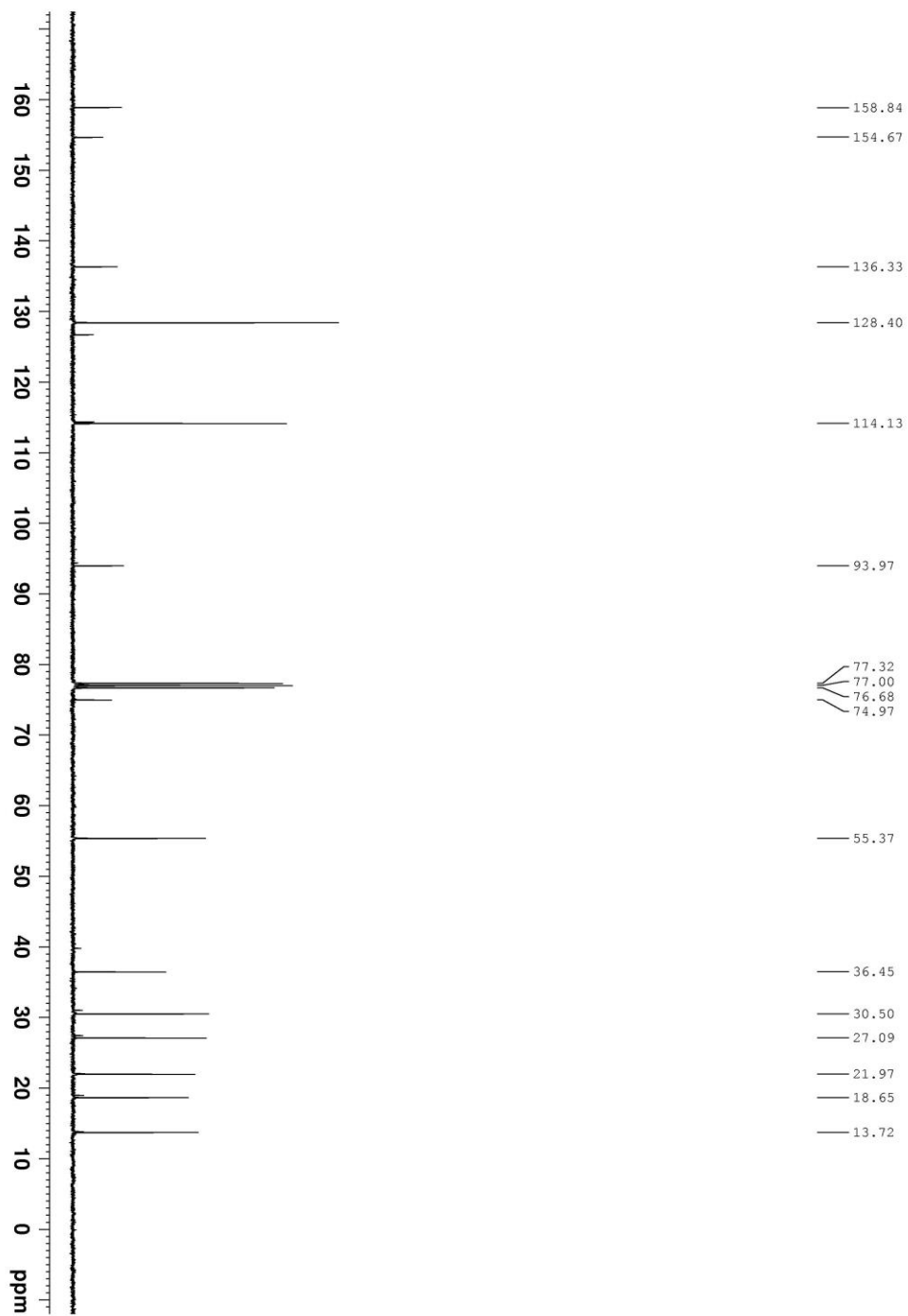
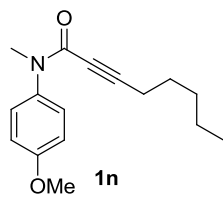


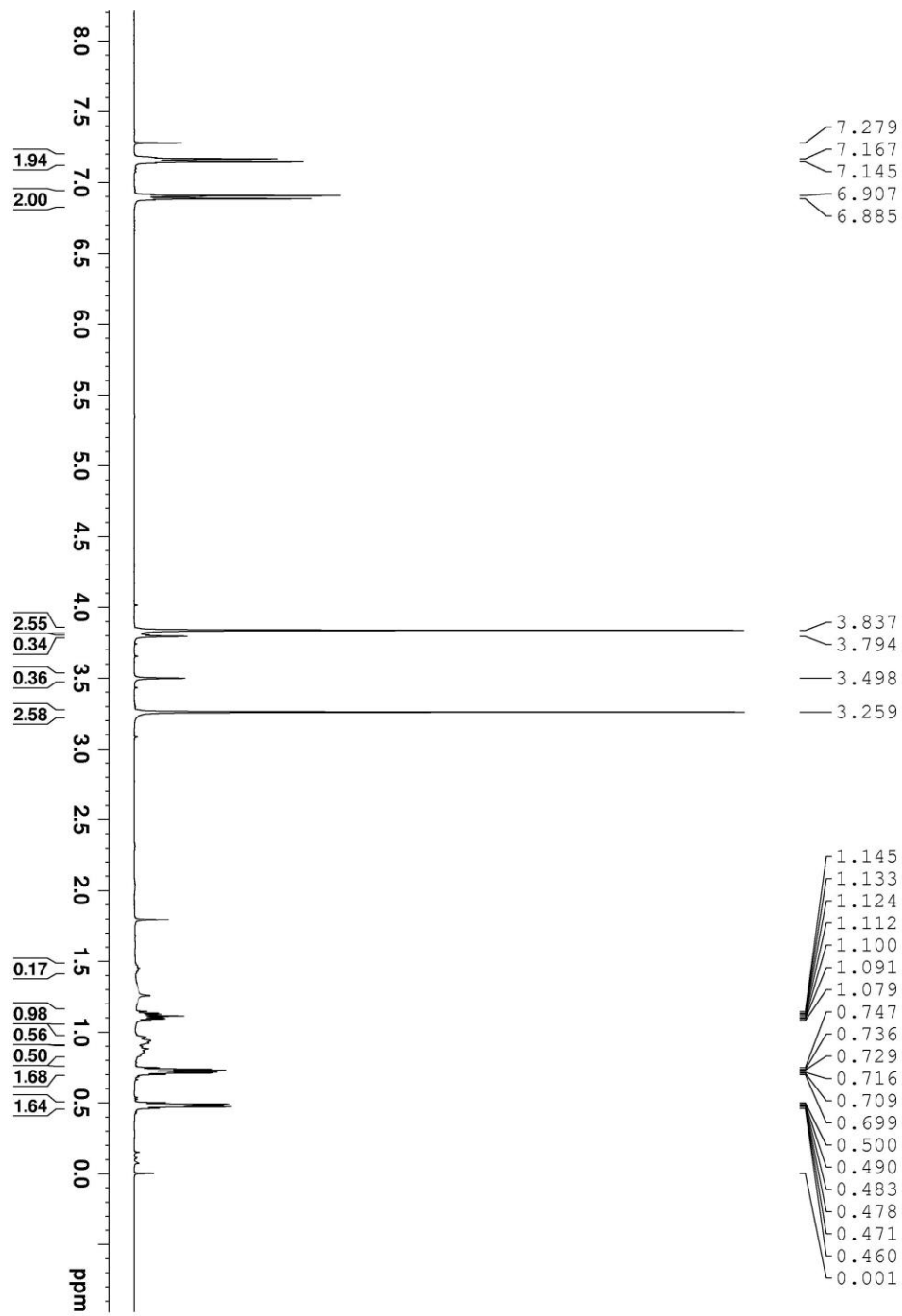
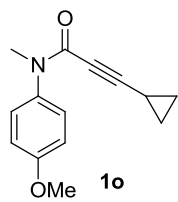


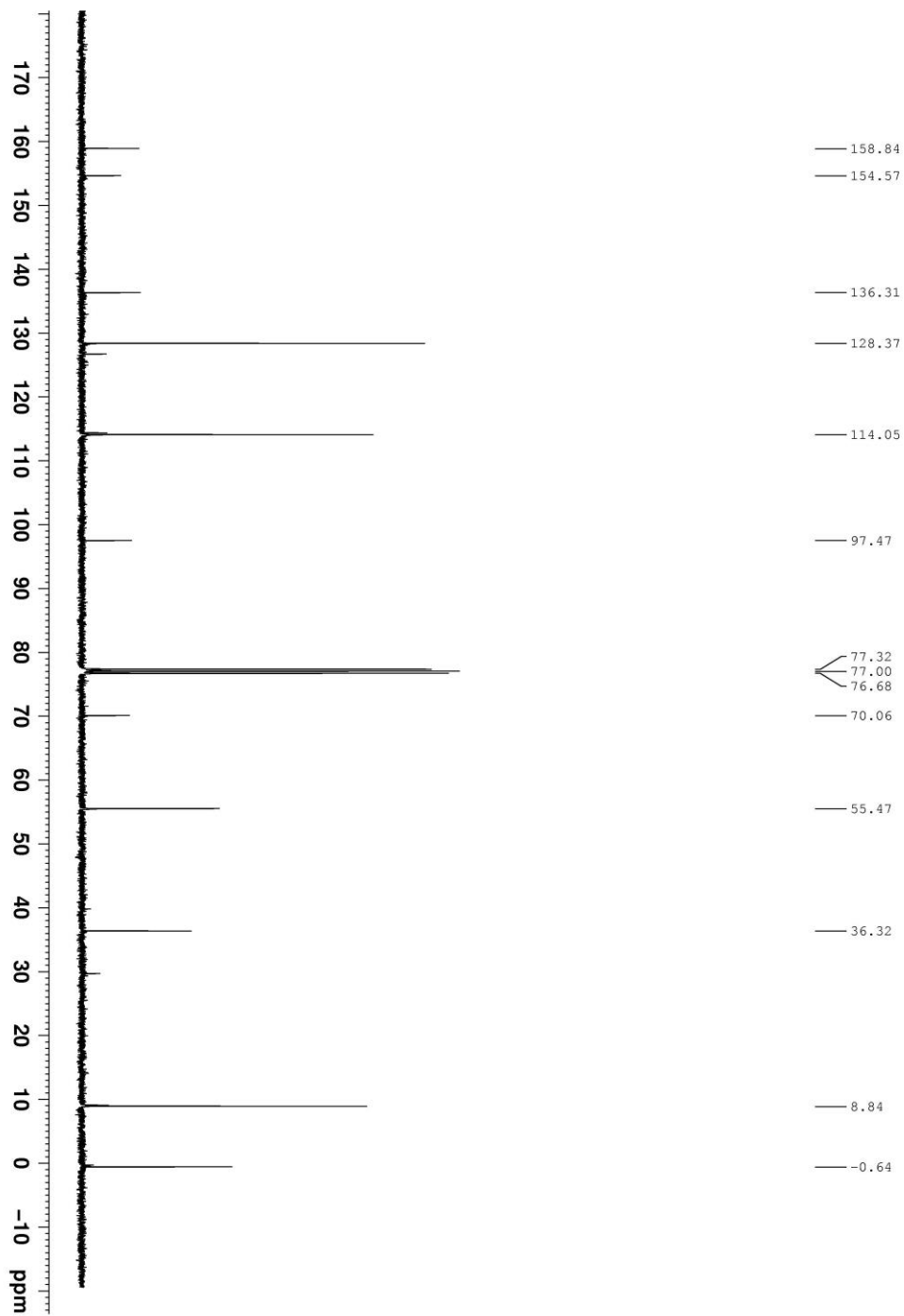
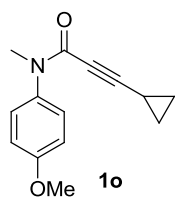


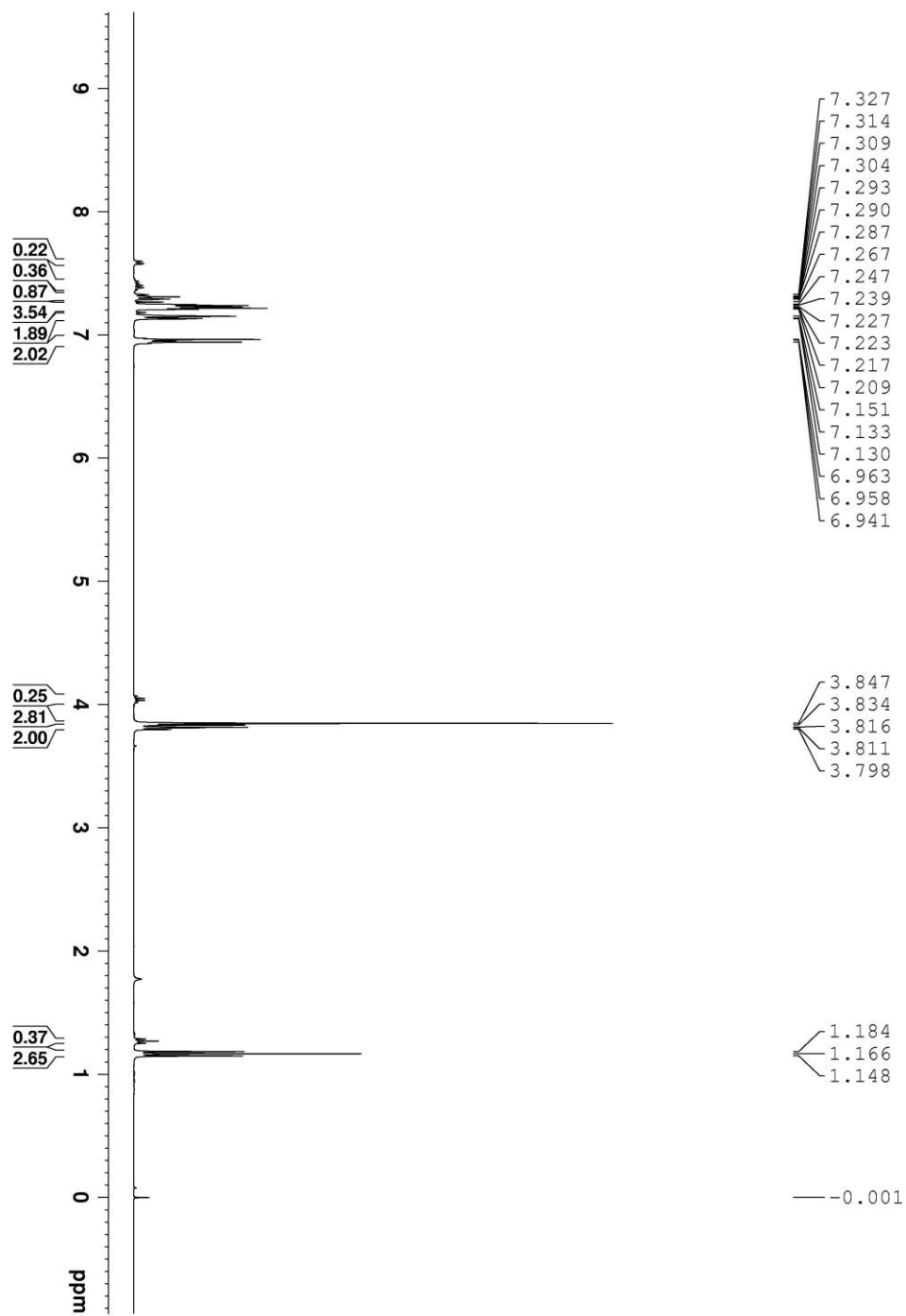
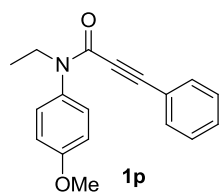


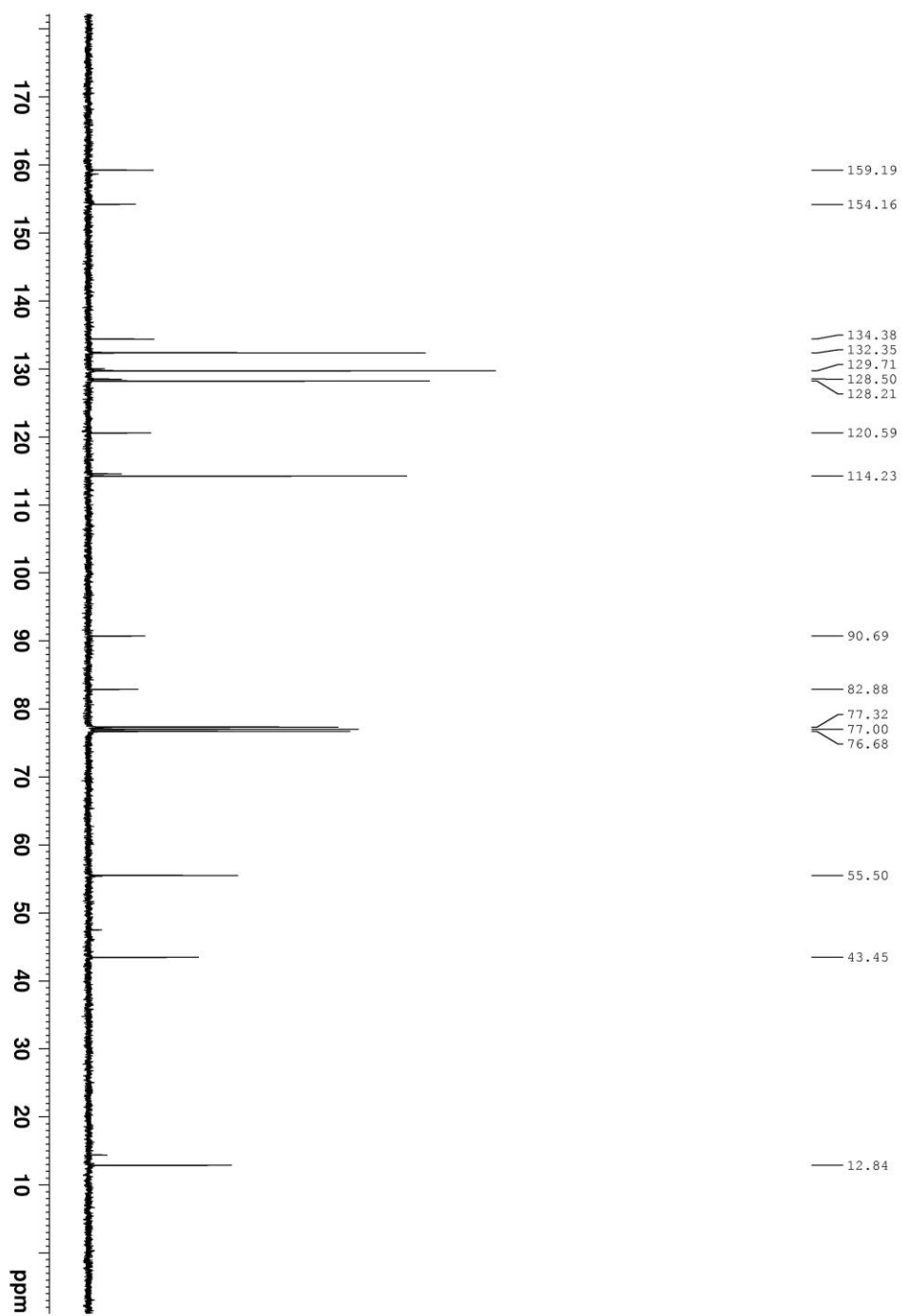
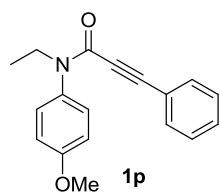


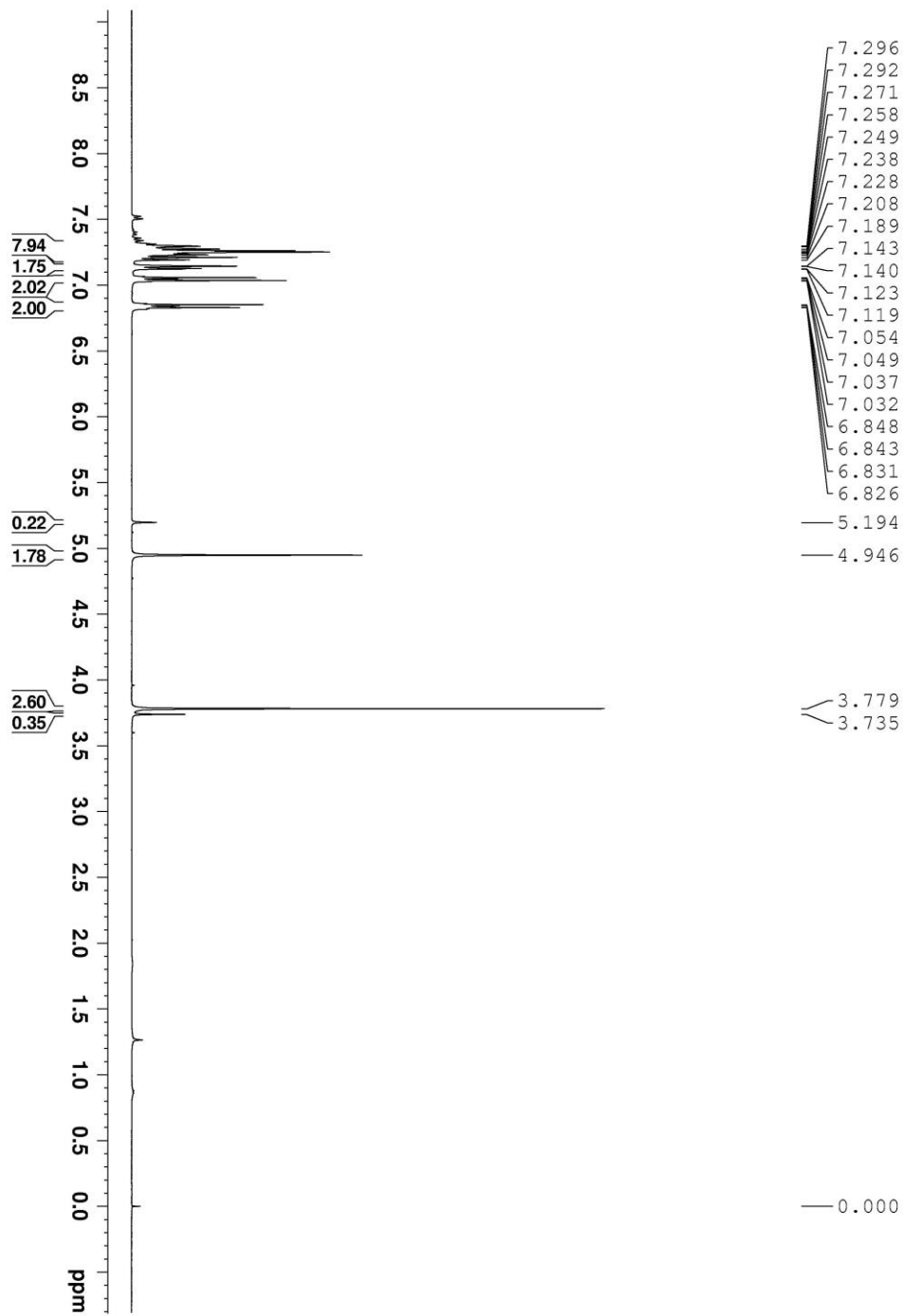
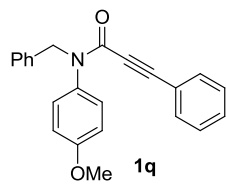


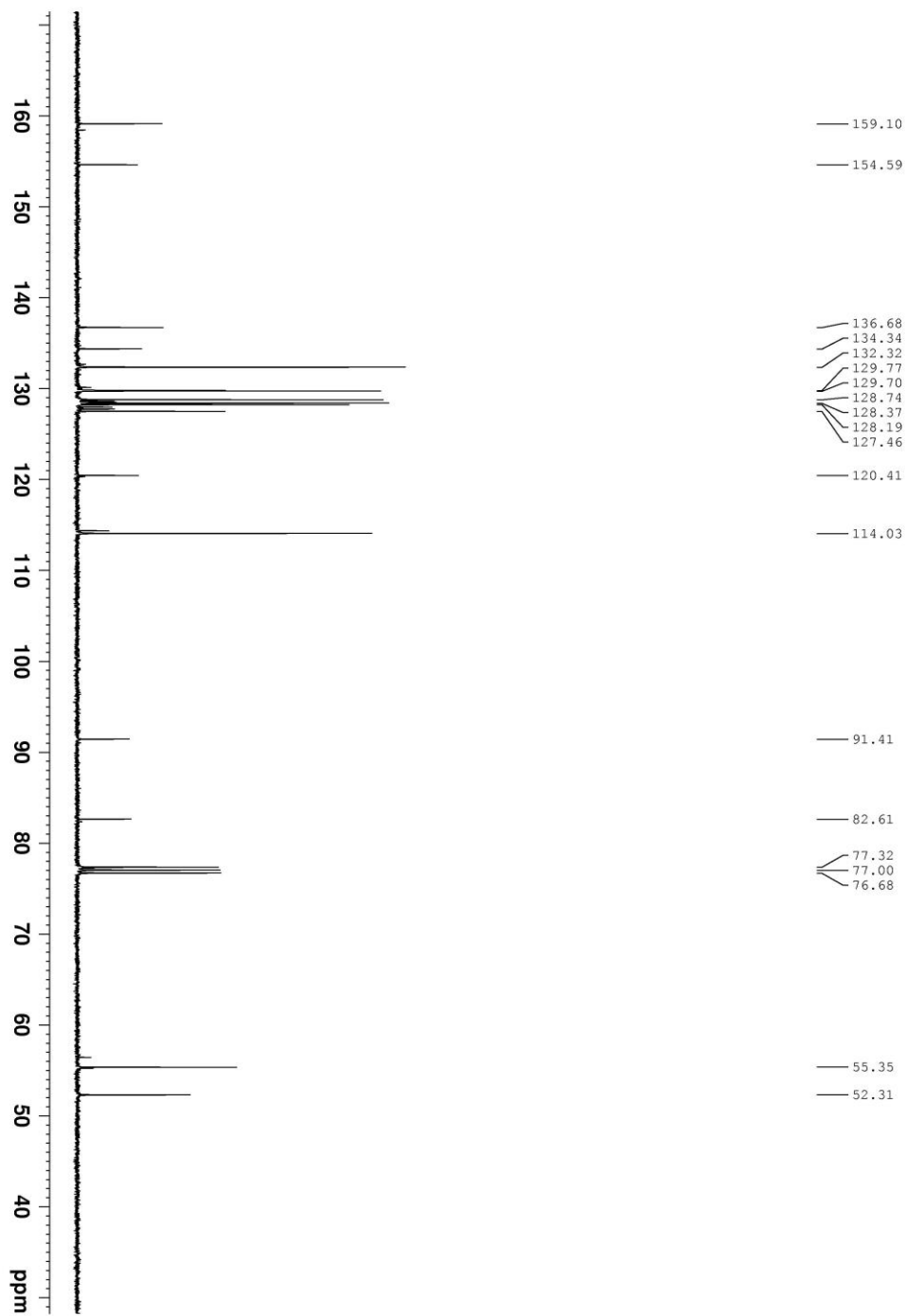
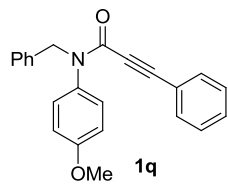


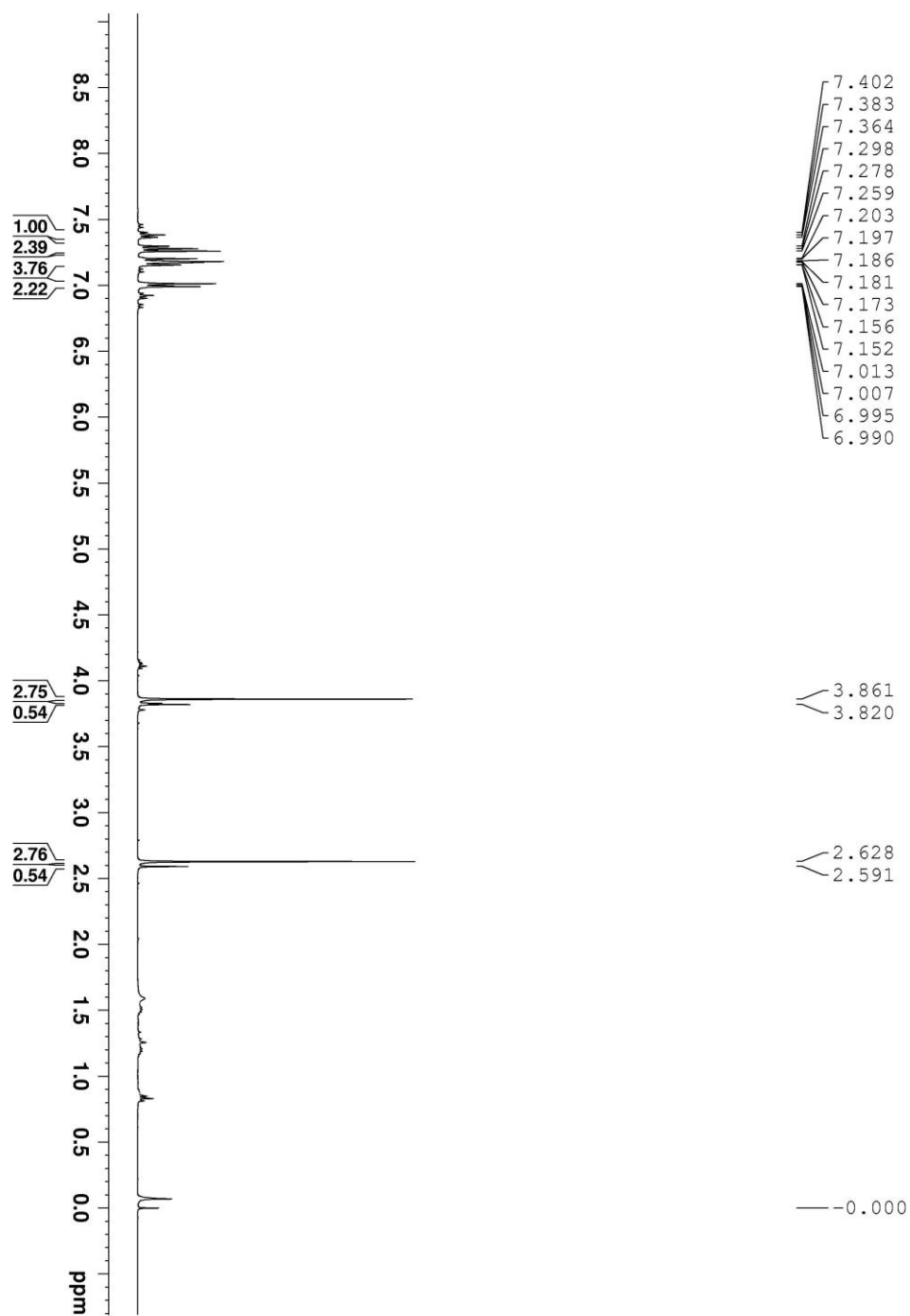
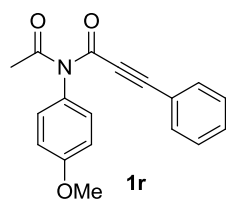


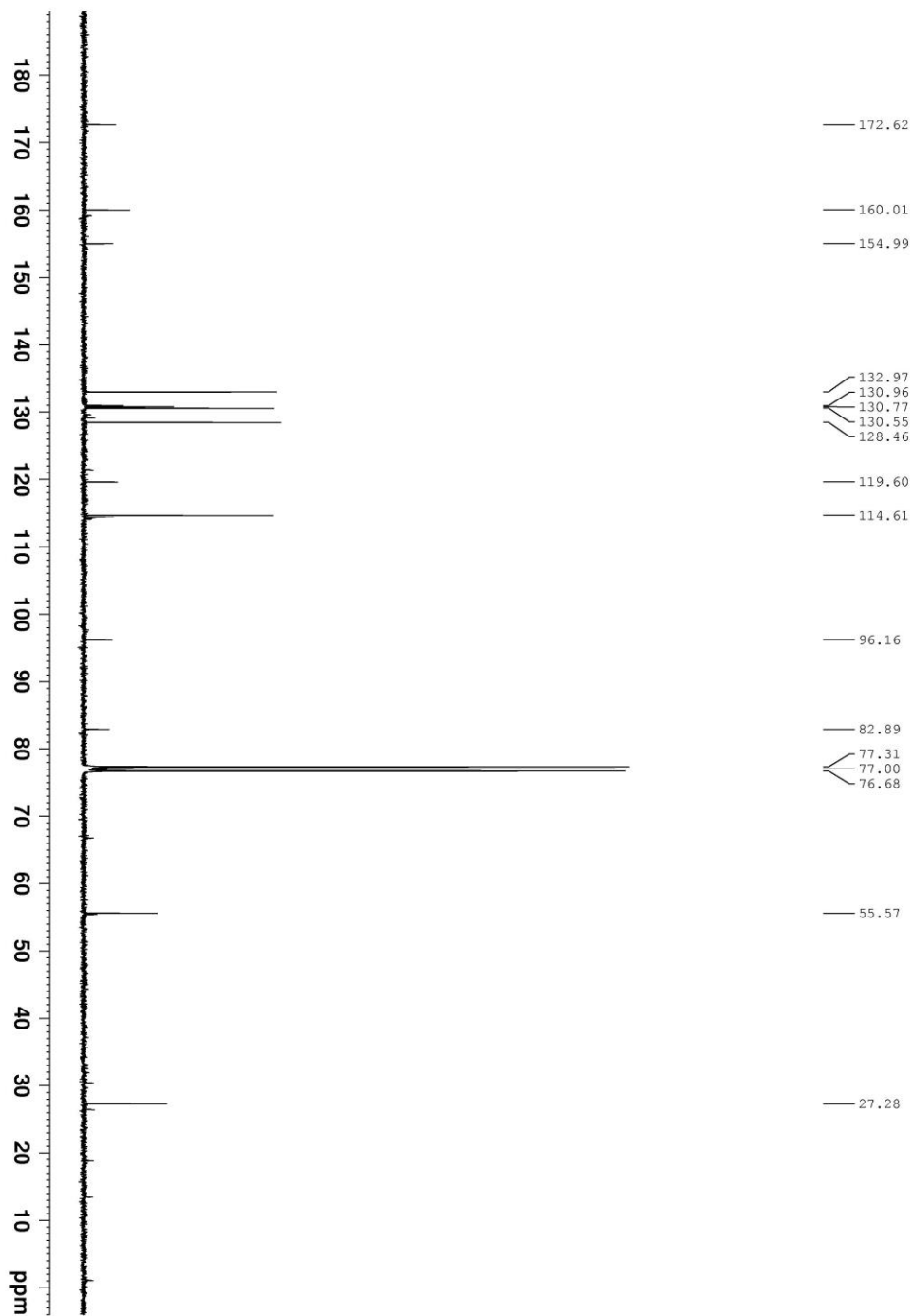
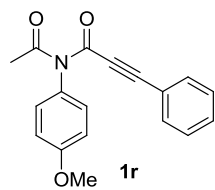


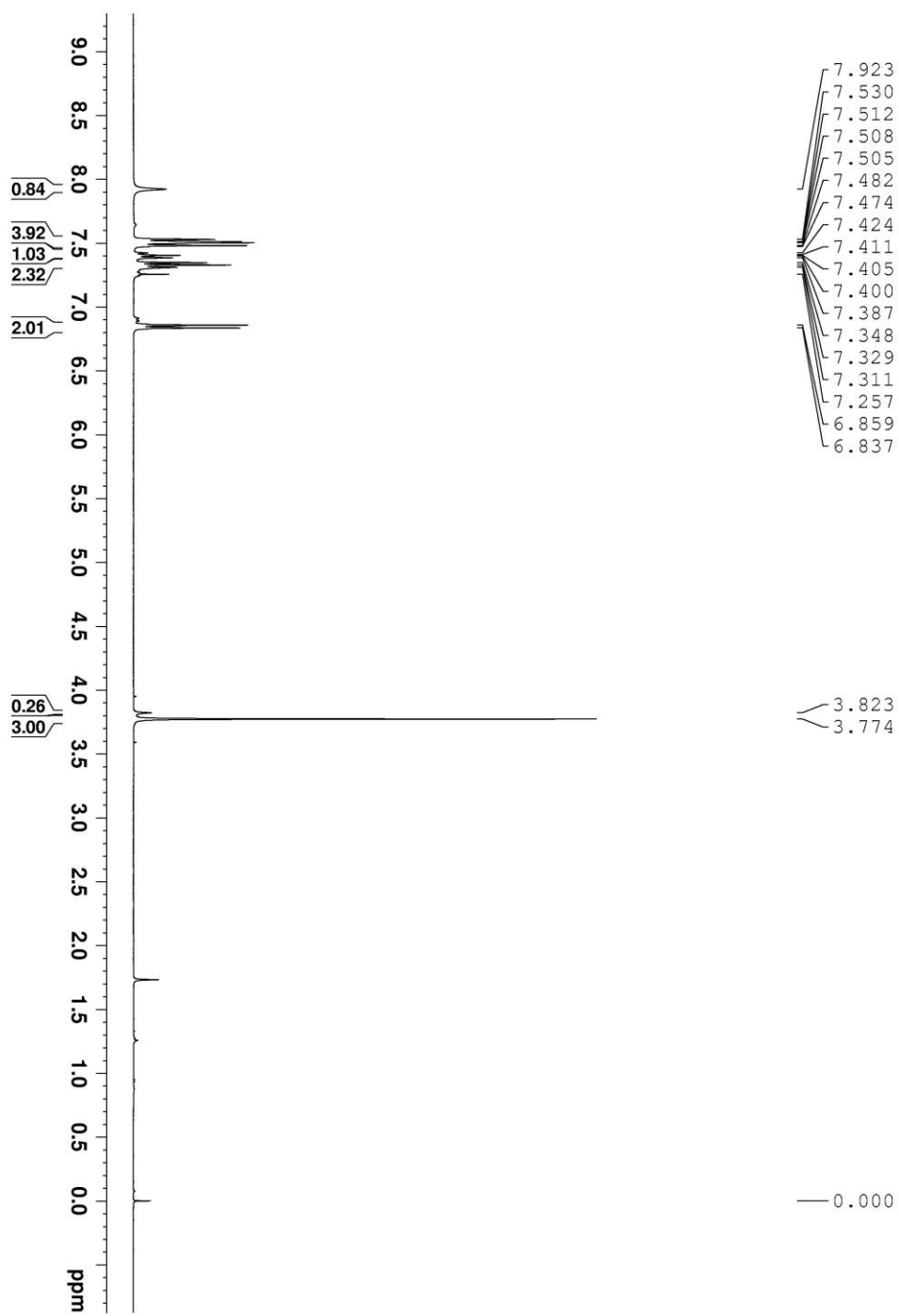
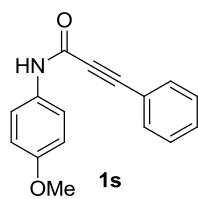


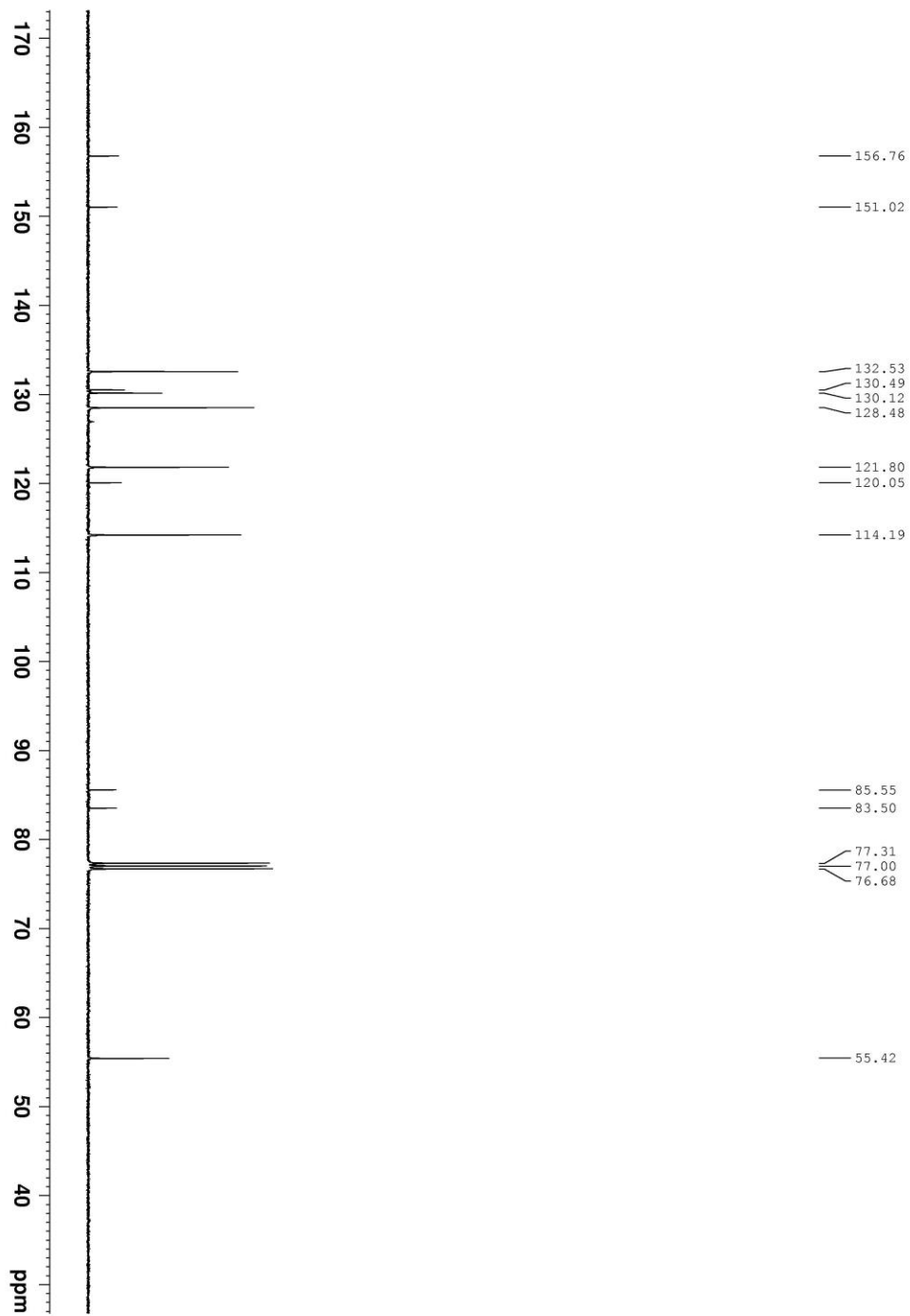
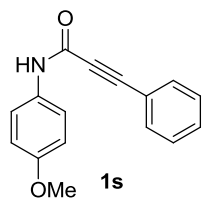


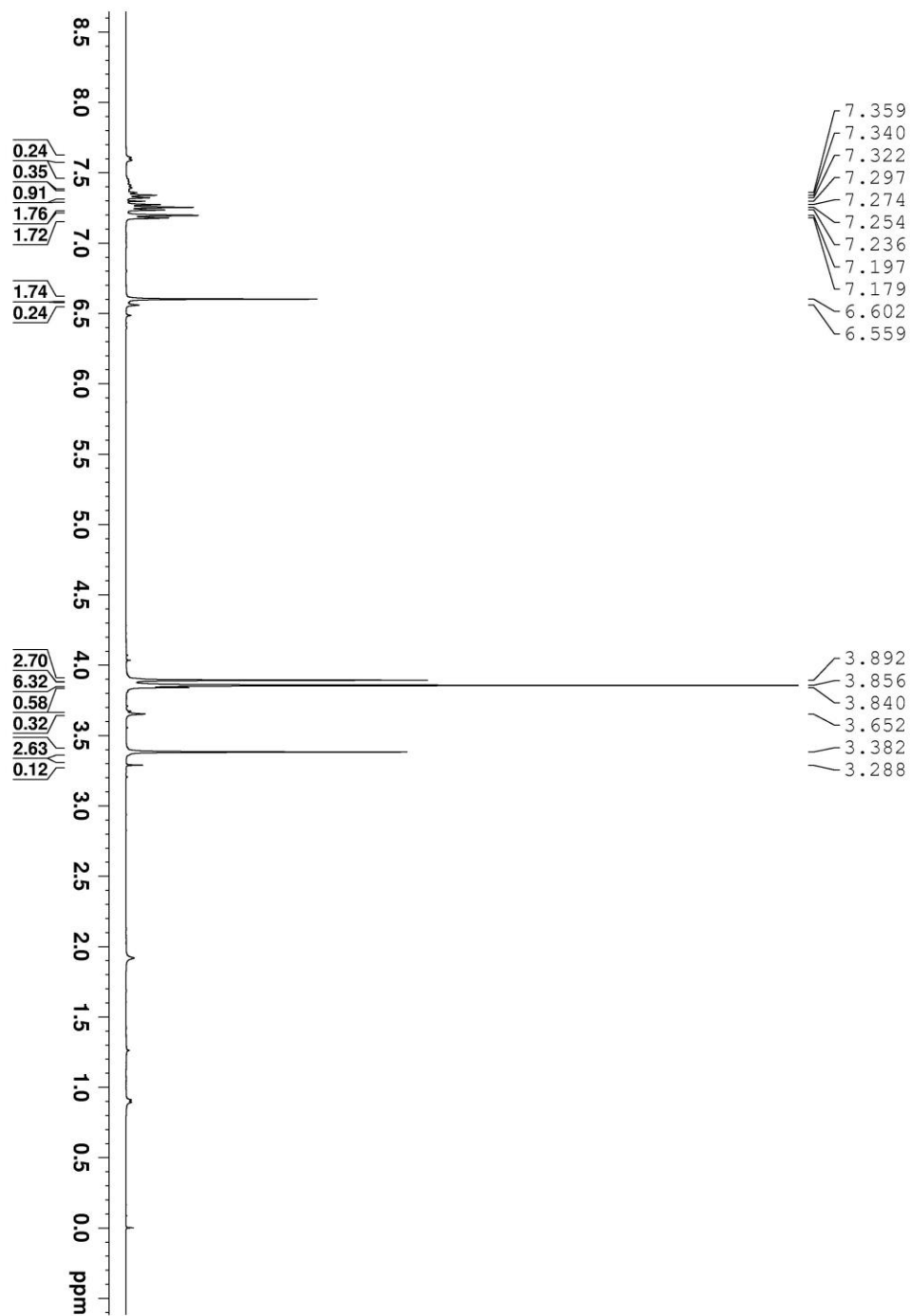
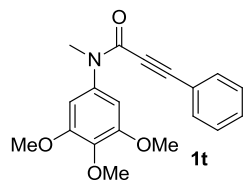


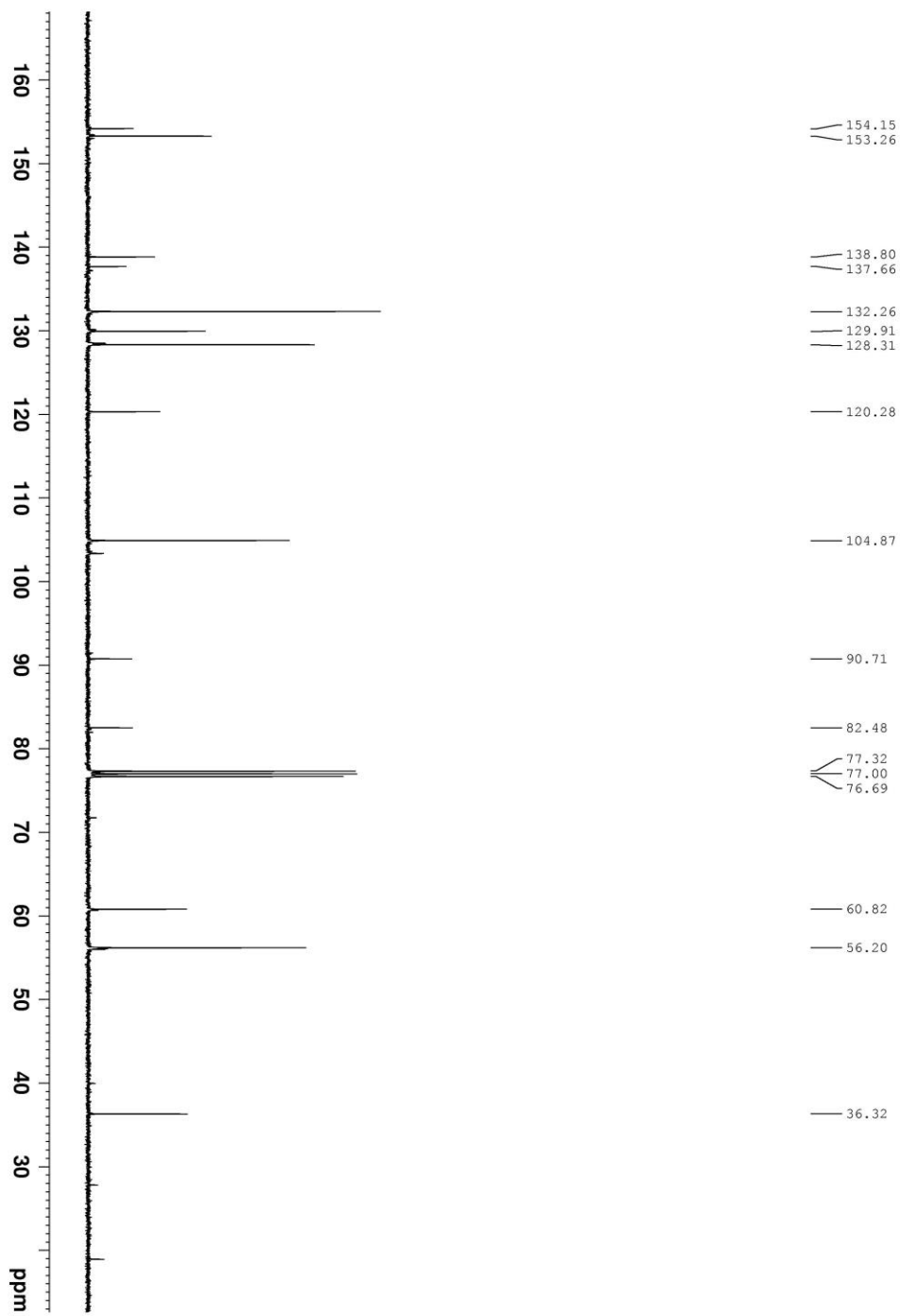
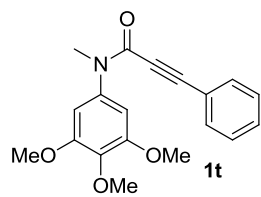


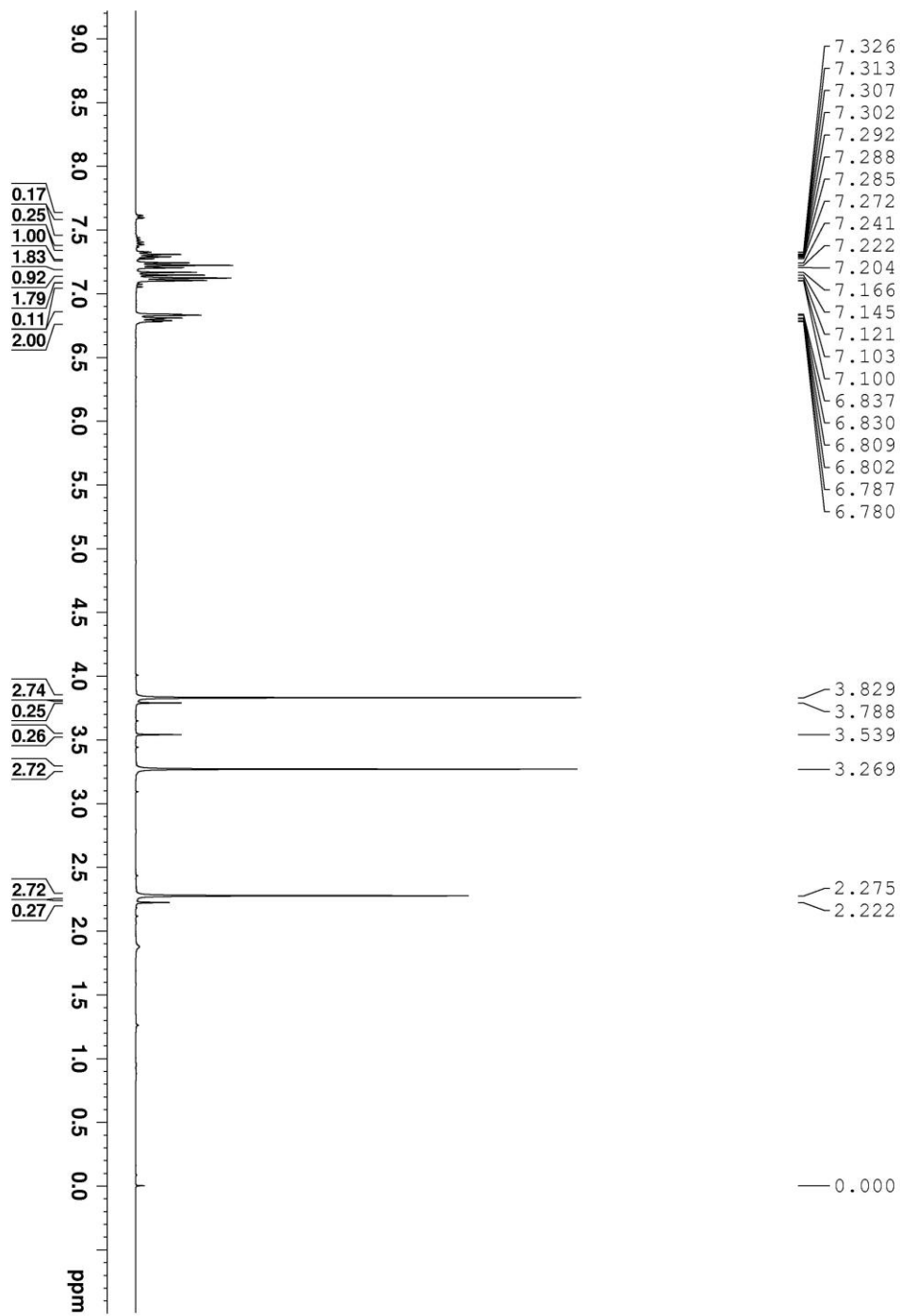
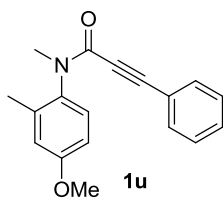


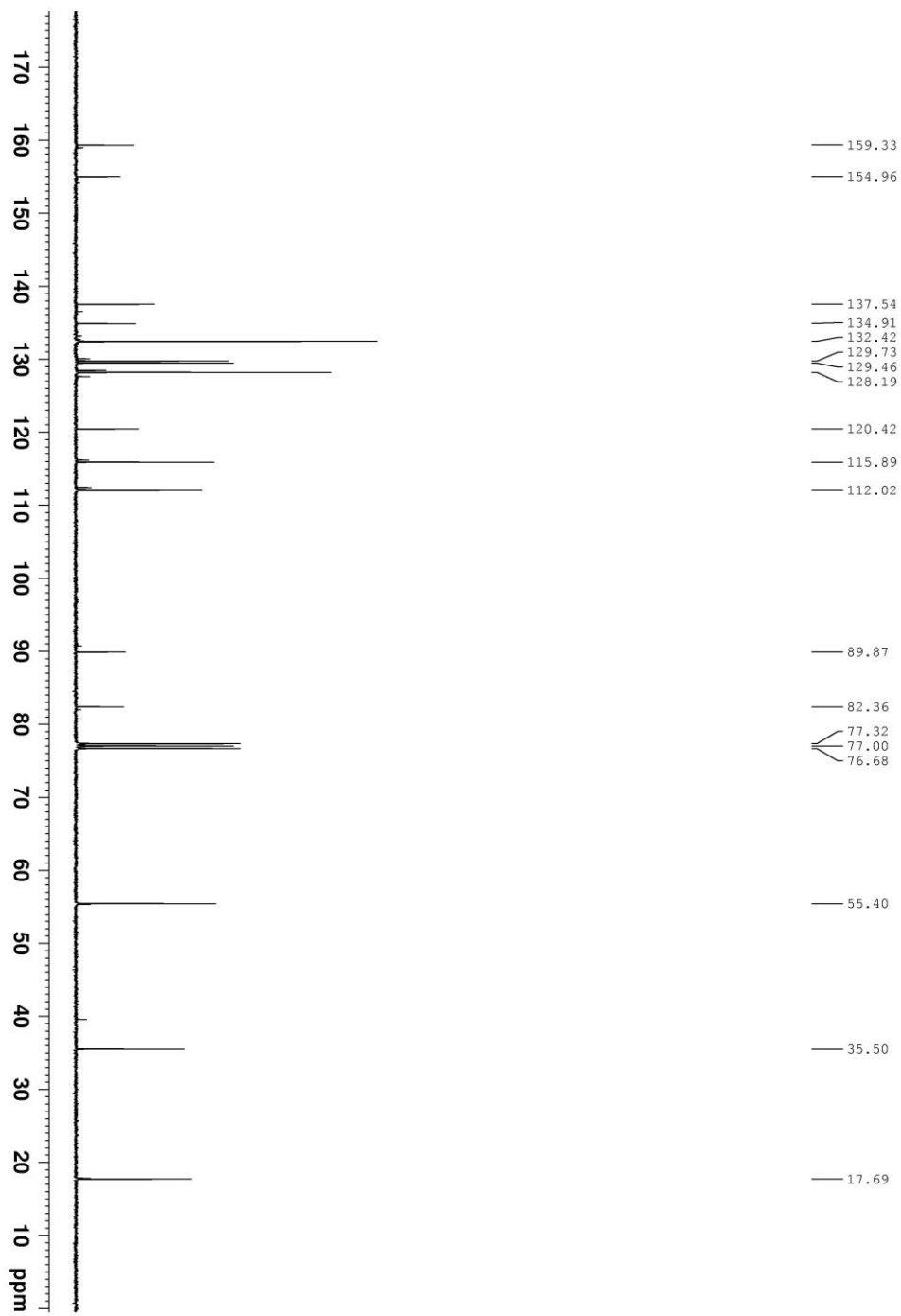
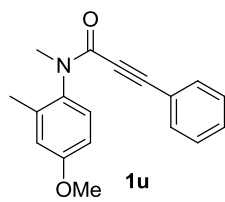


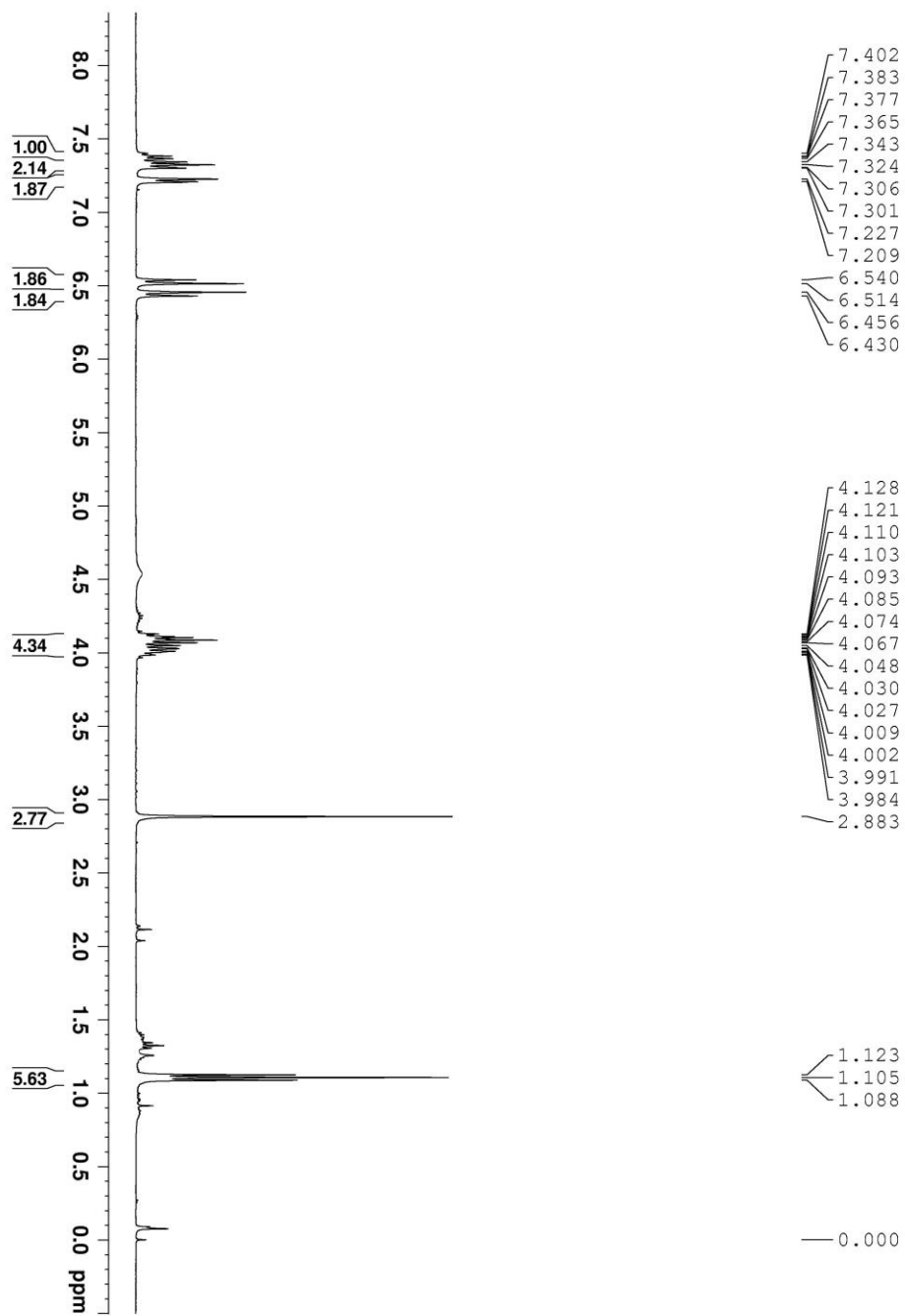
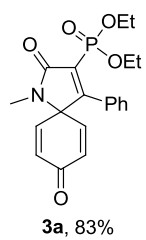


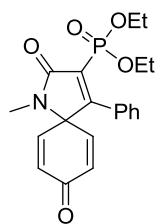




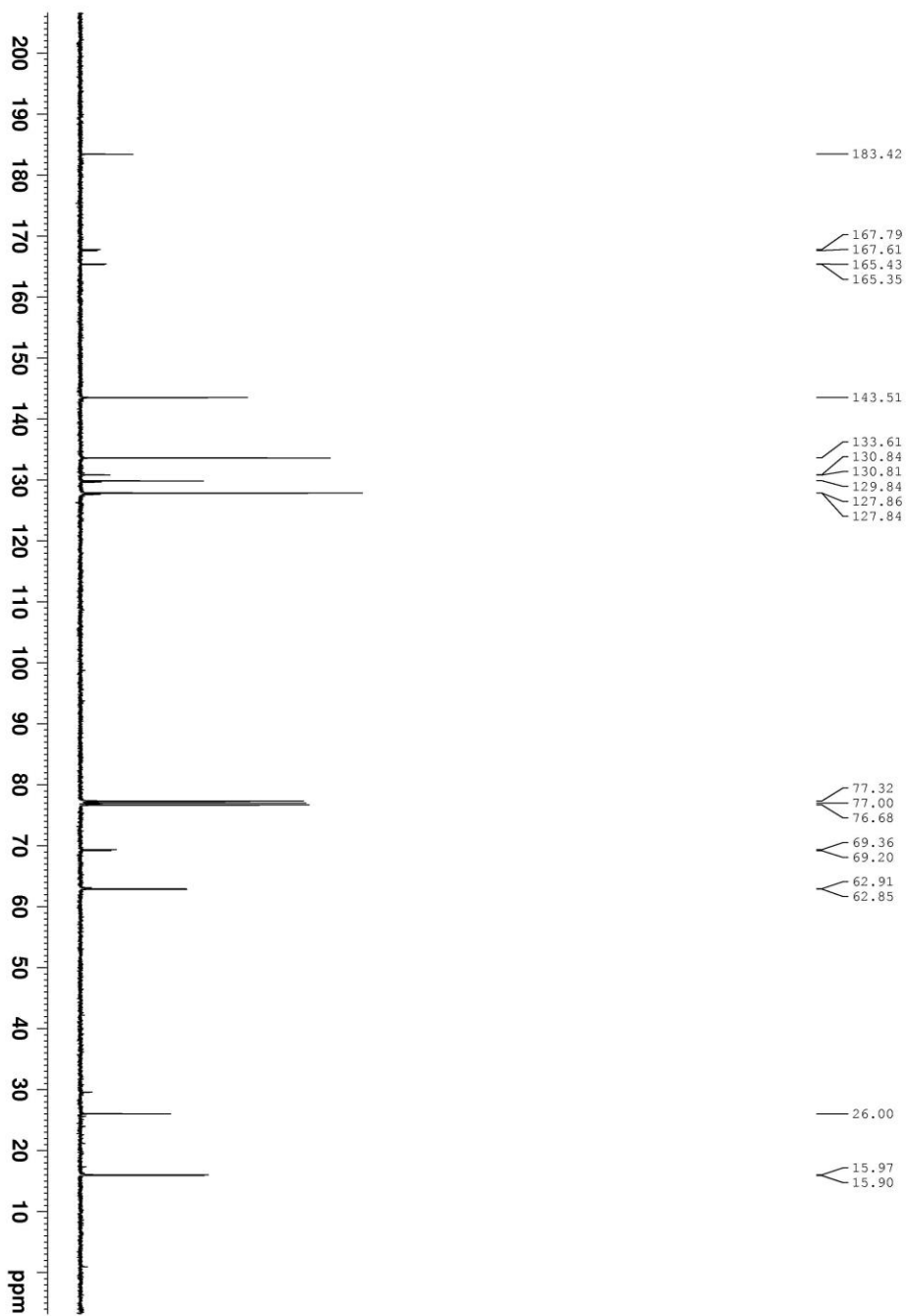


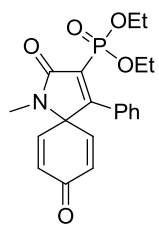




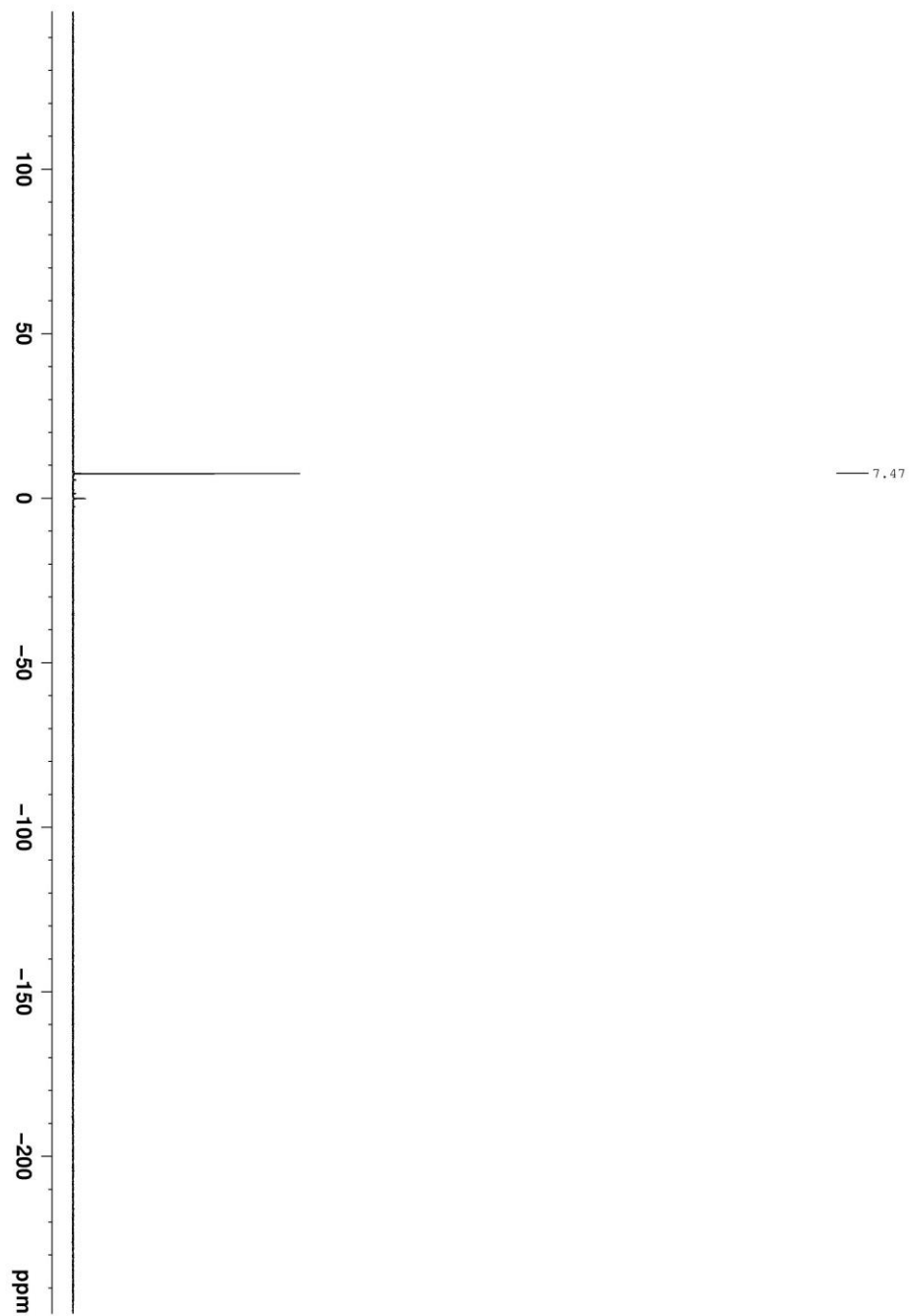


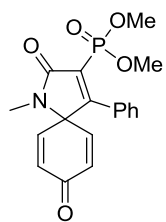
3a, 83%



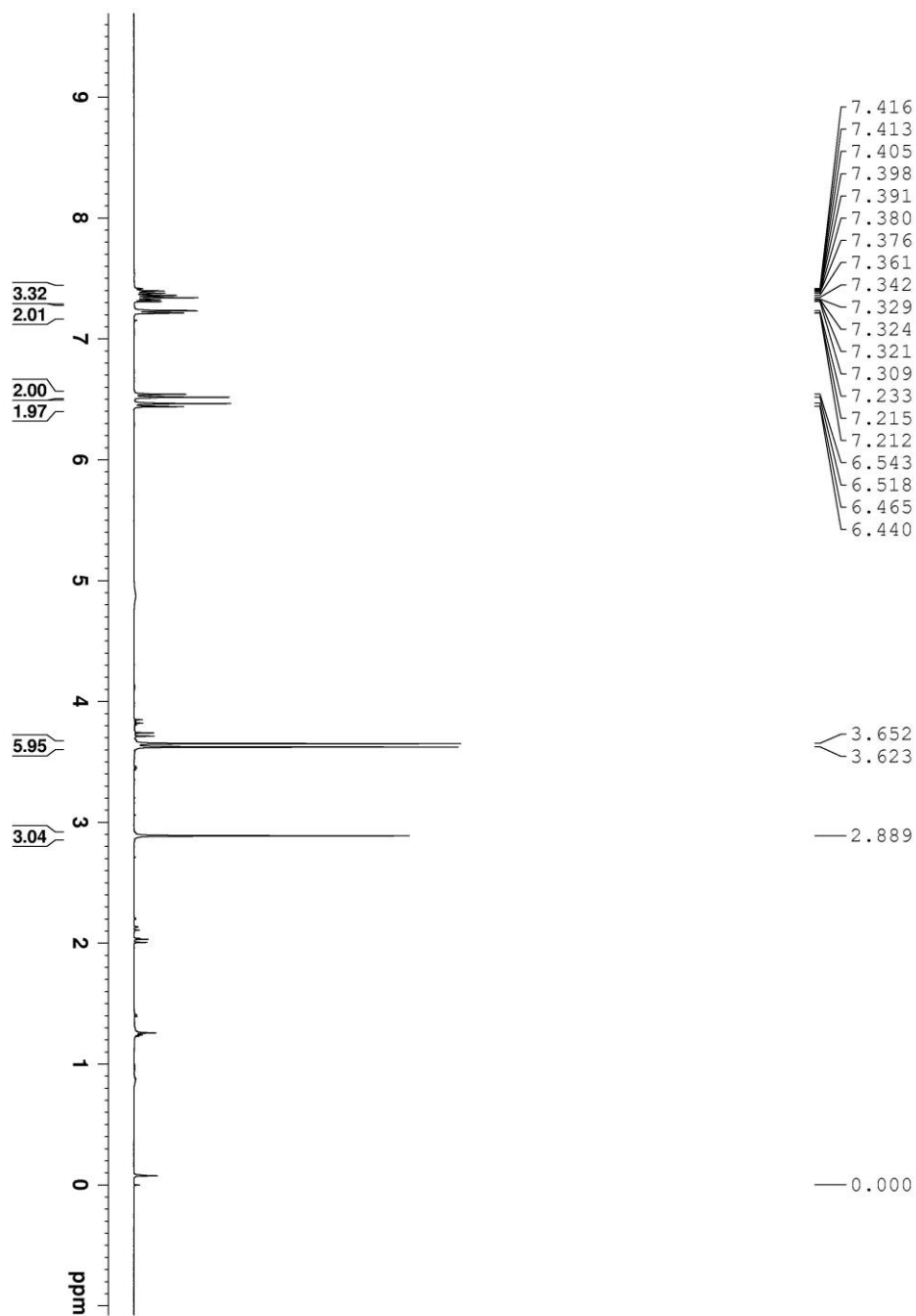


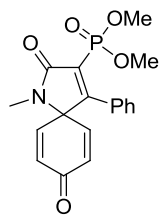
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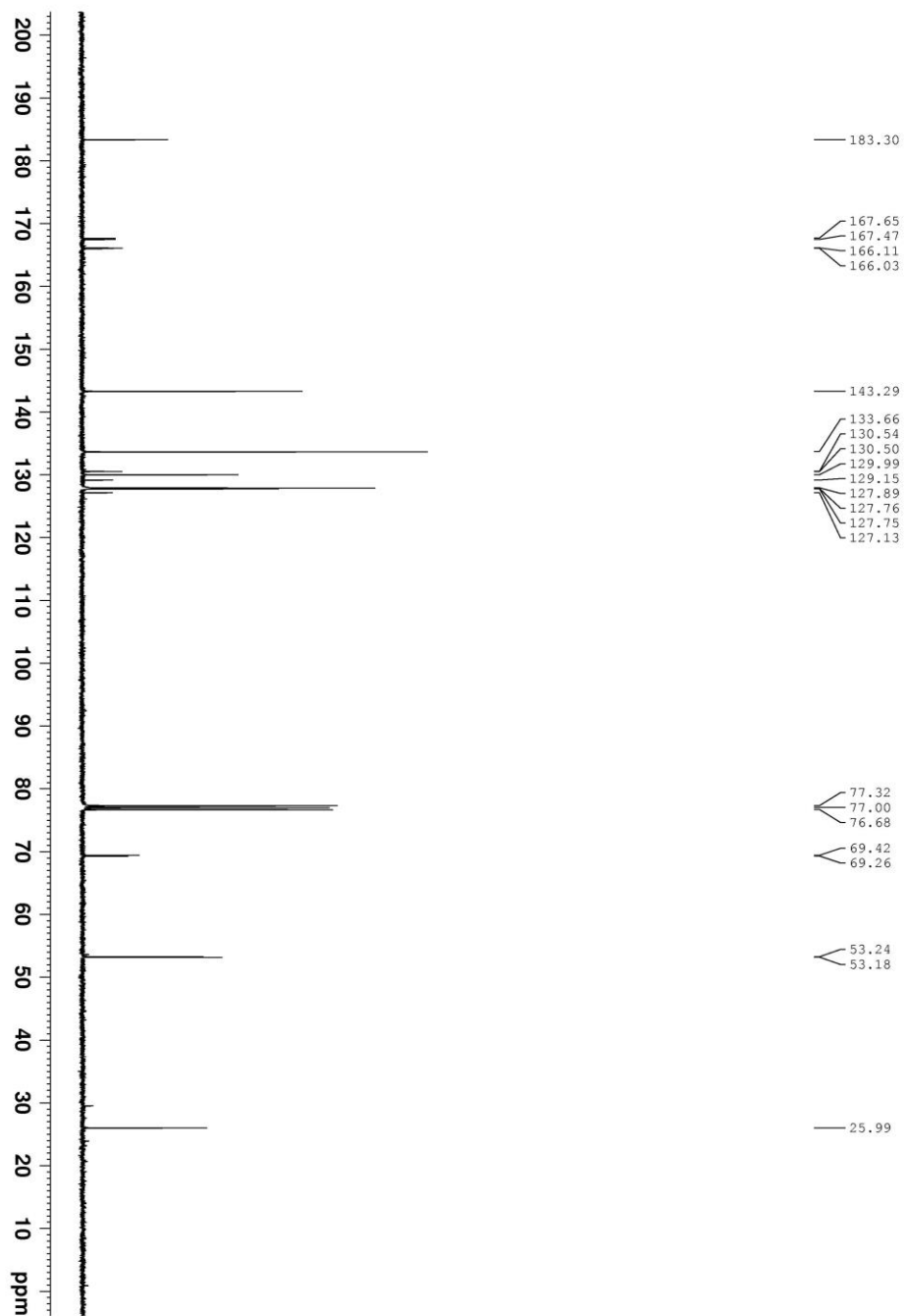


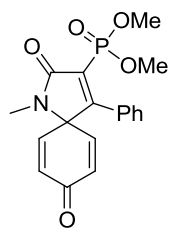
3b, 66%



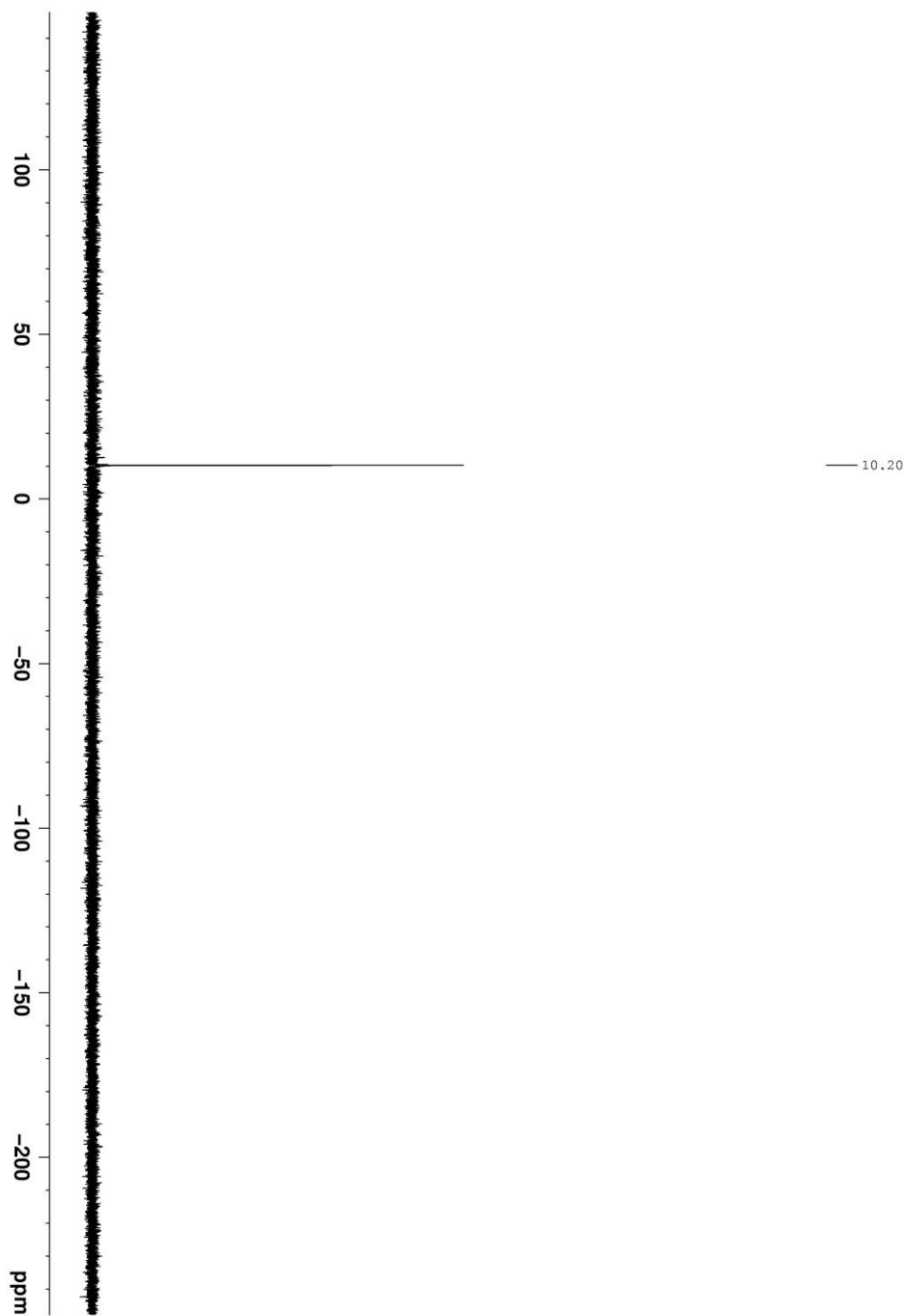


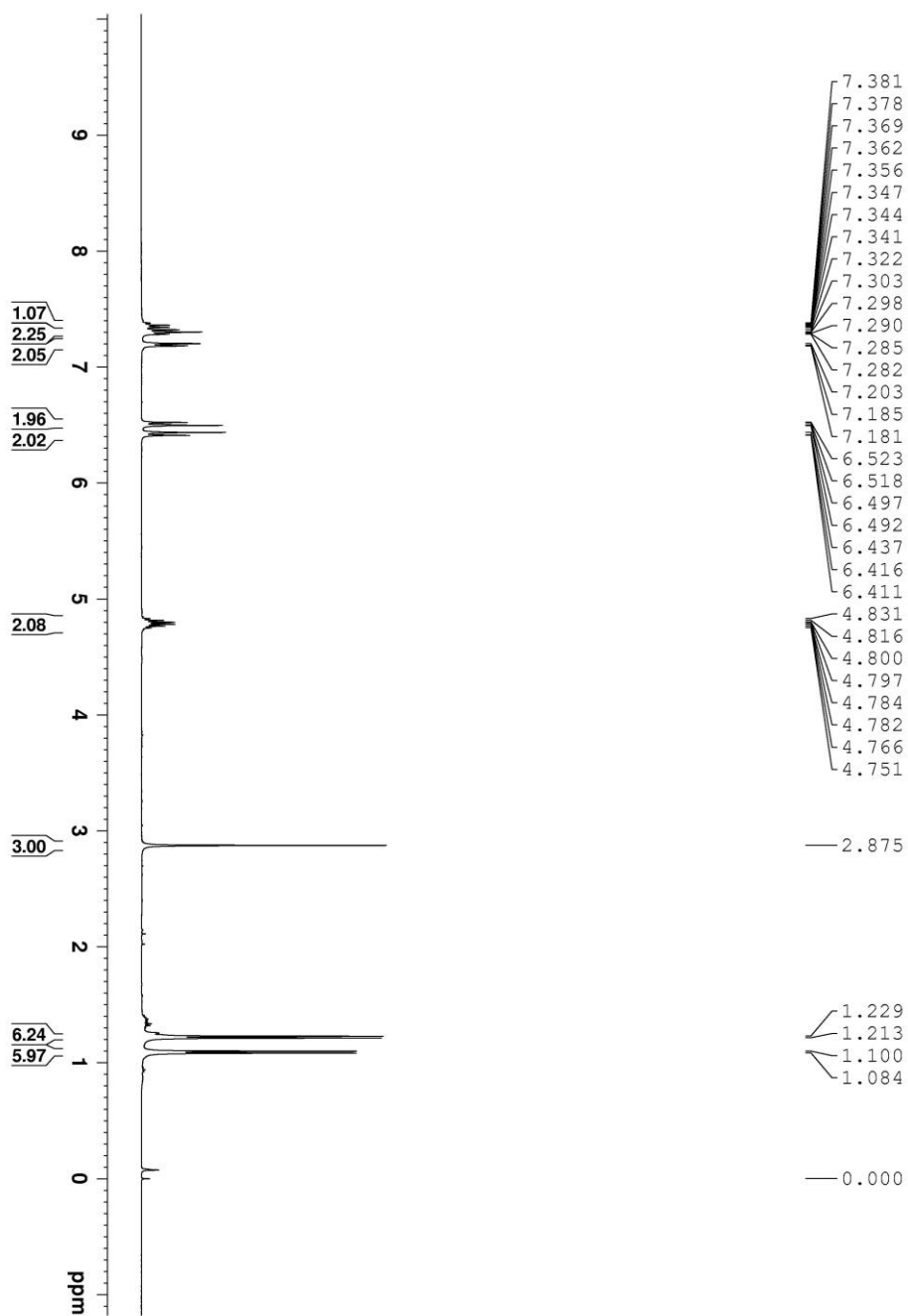
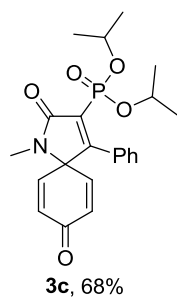
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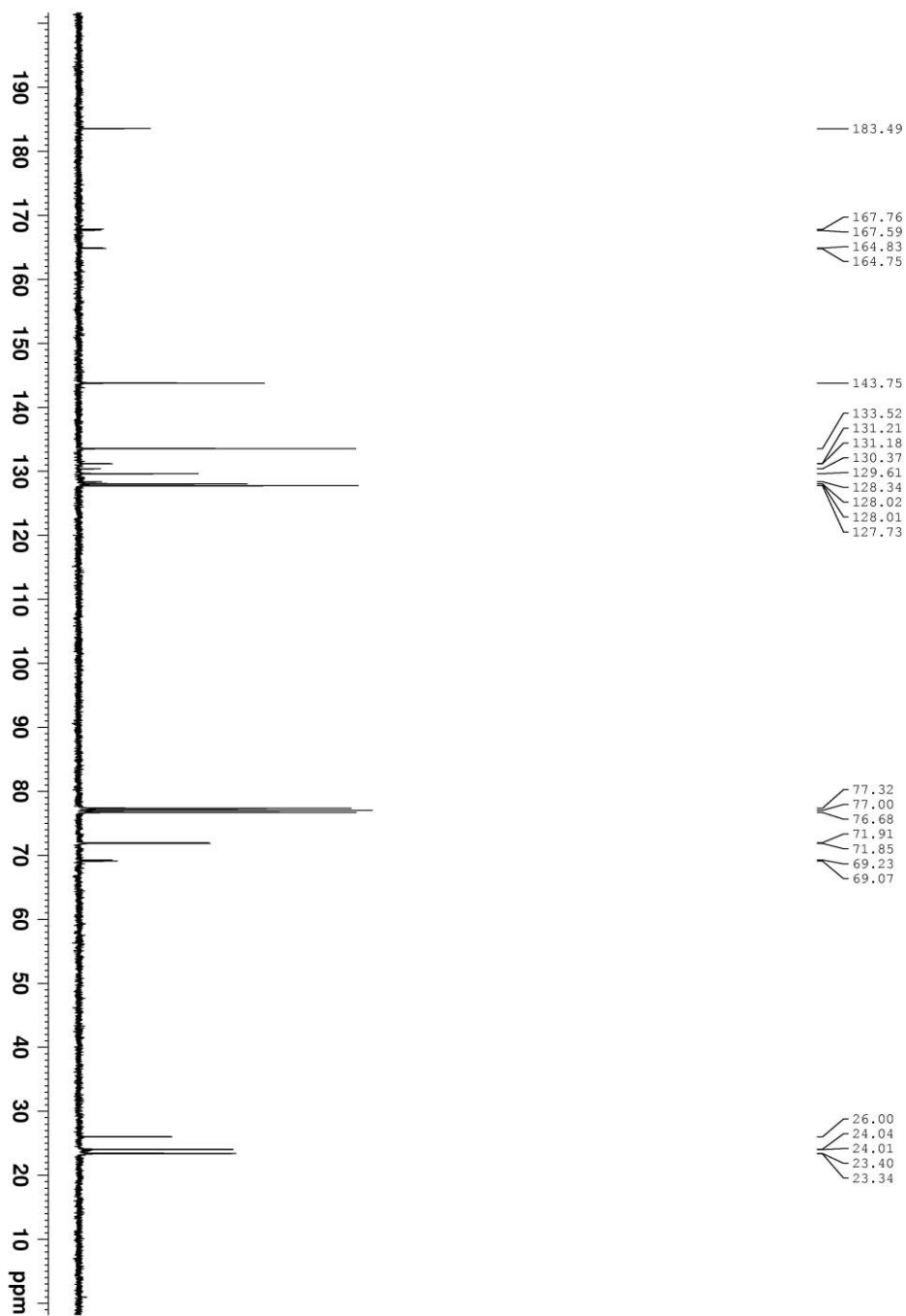
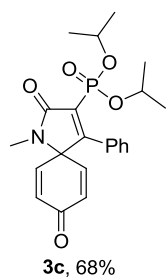


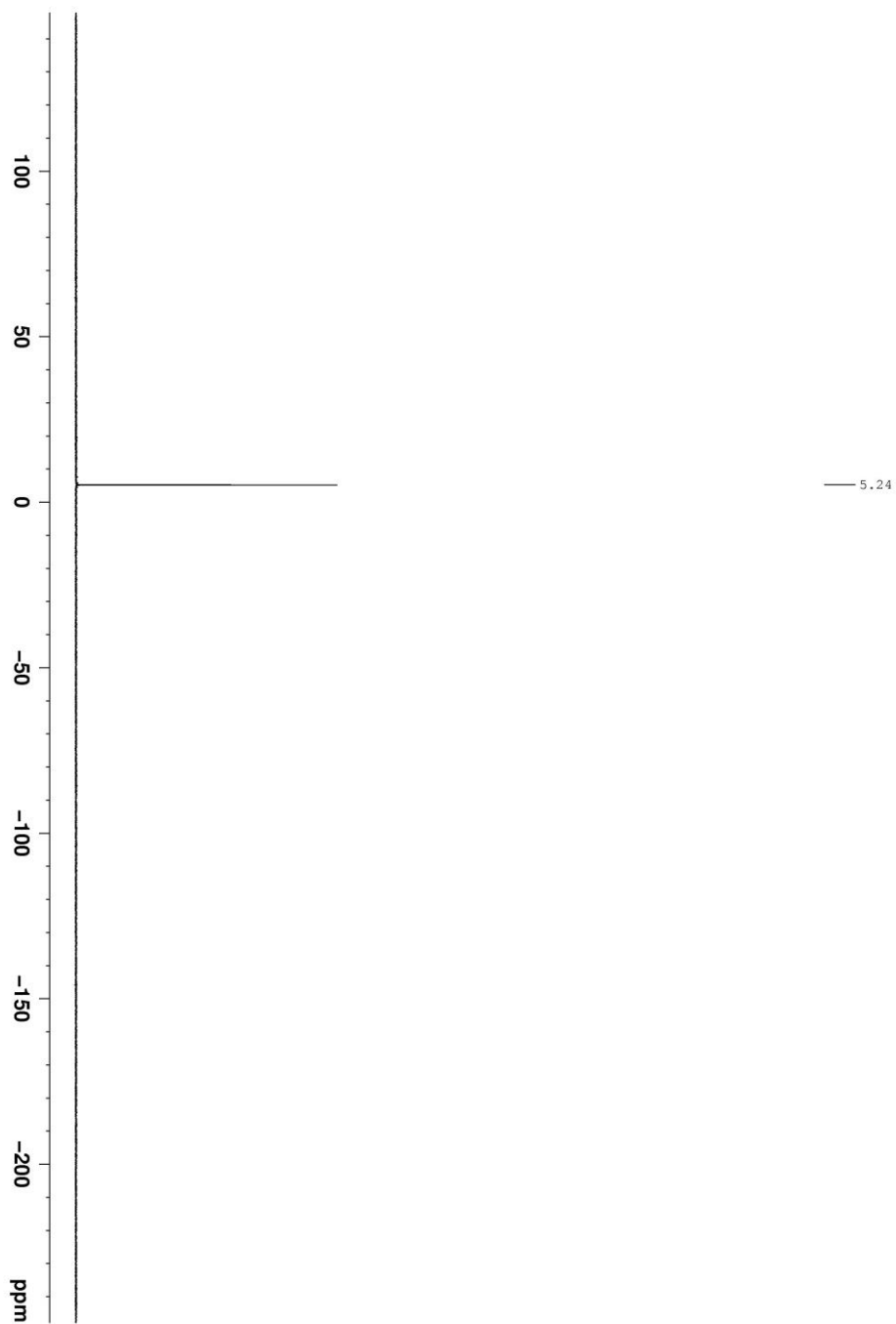
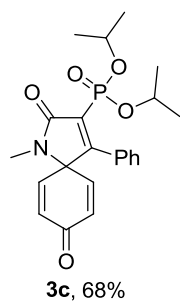


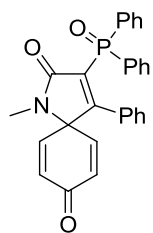
3b, 66%



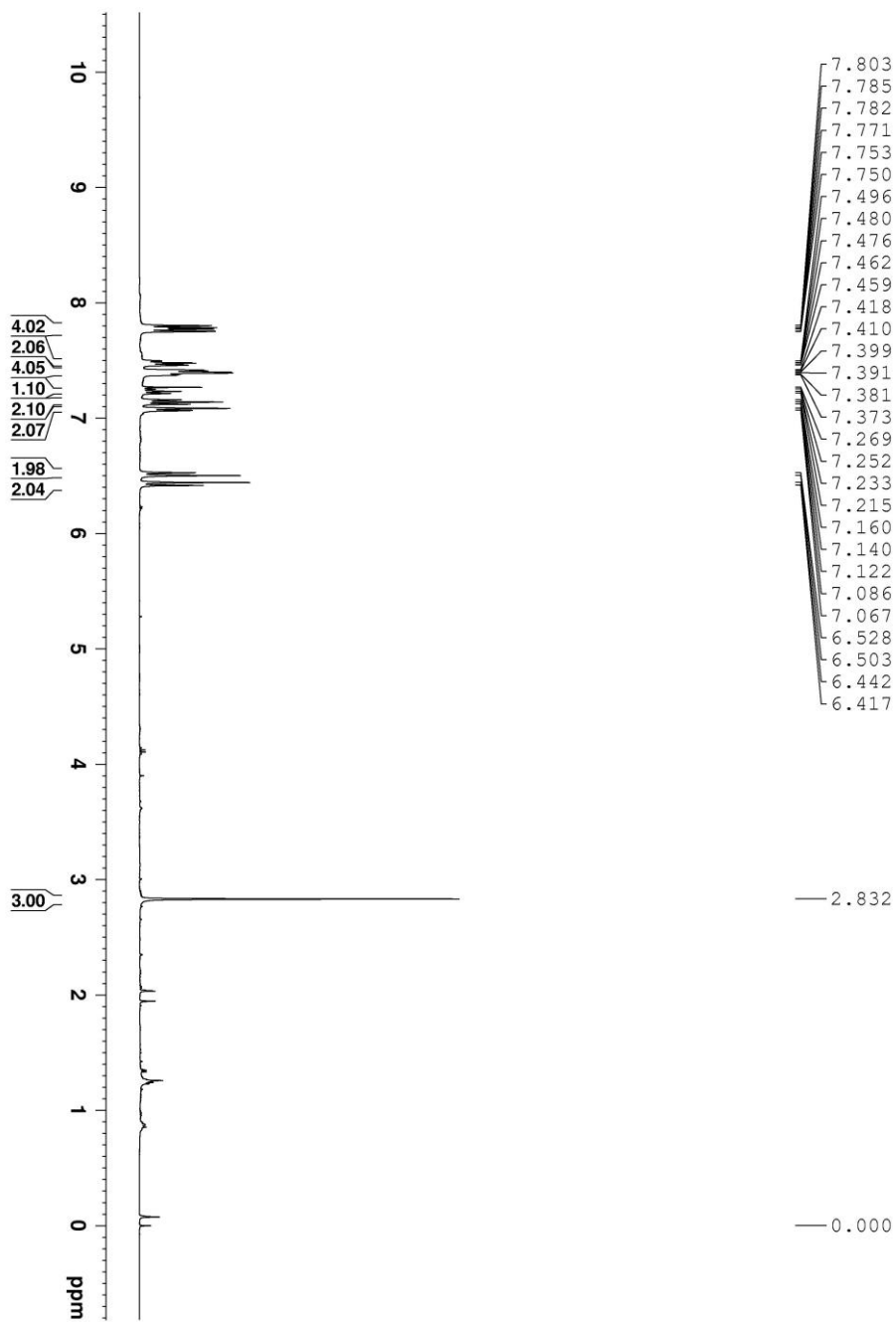


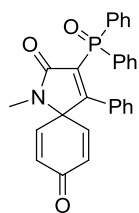




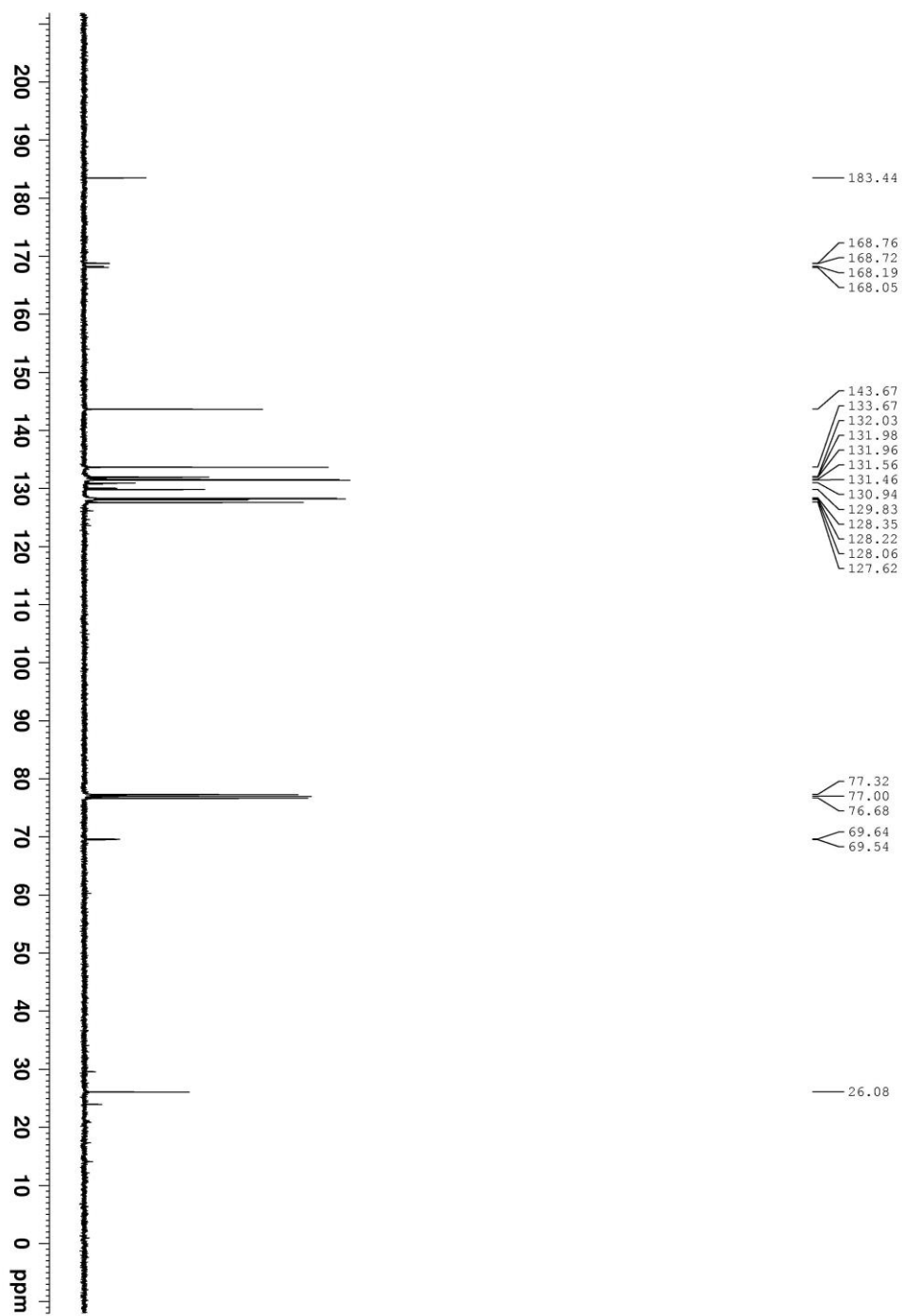


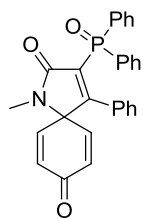
3d, 71%



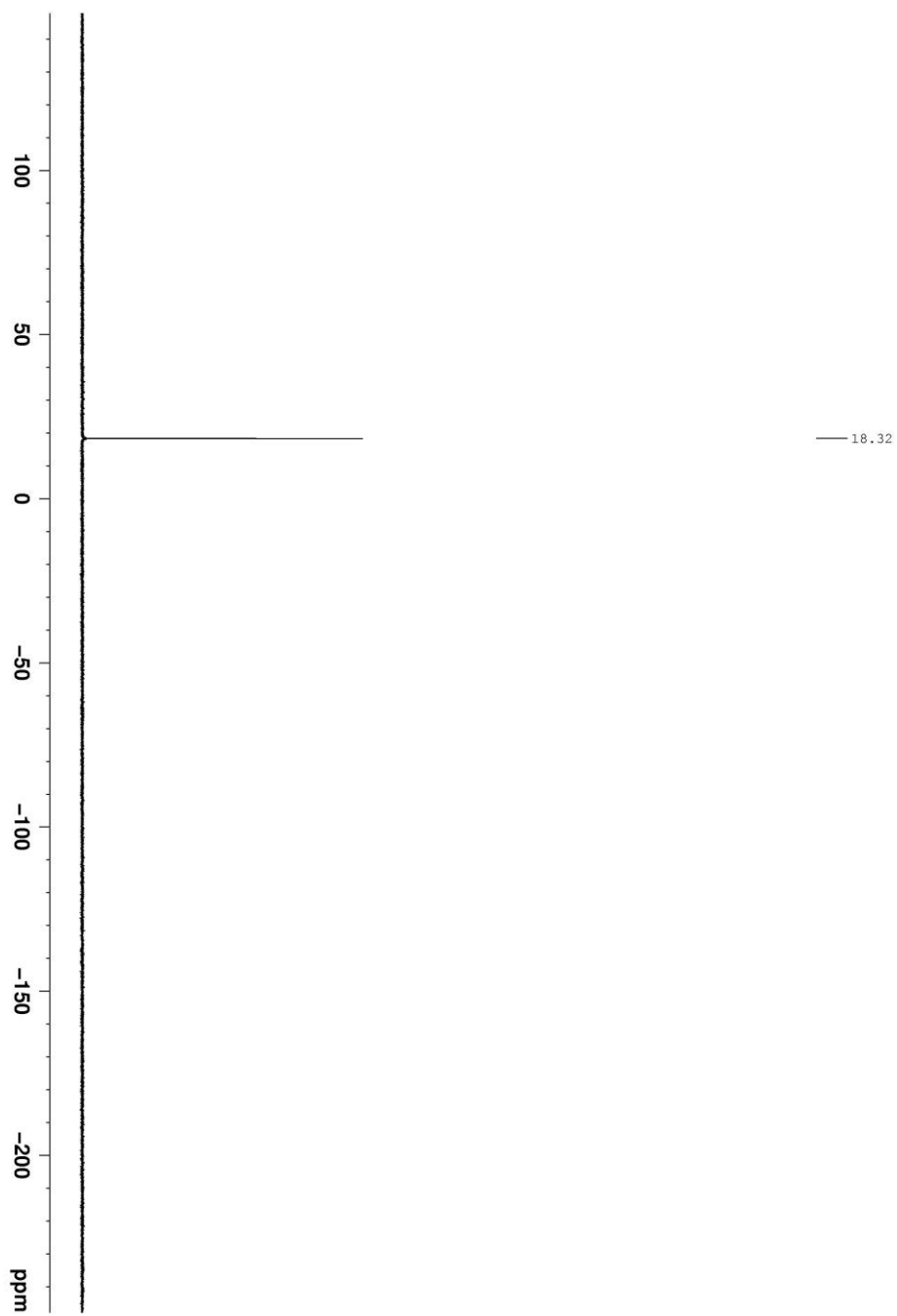


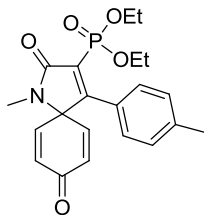
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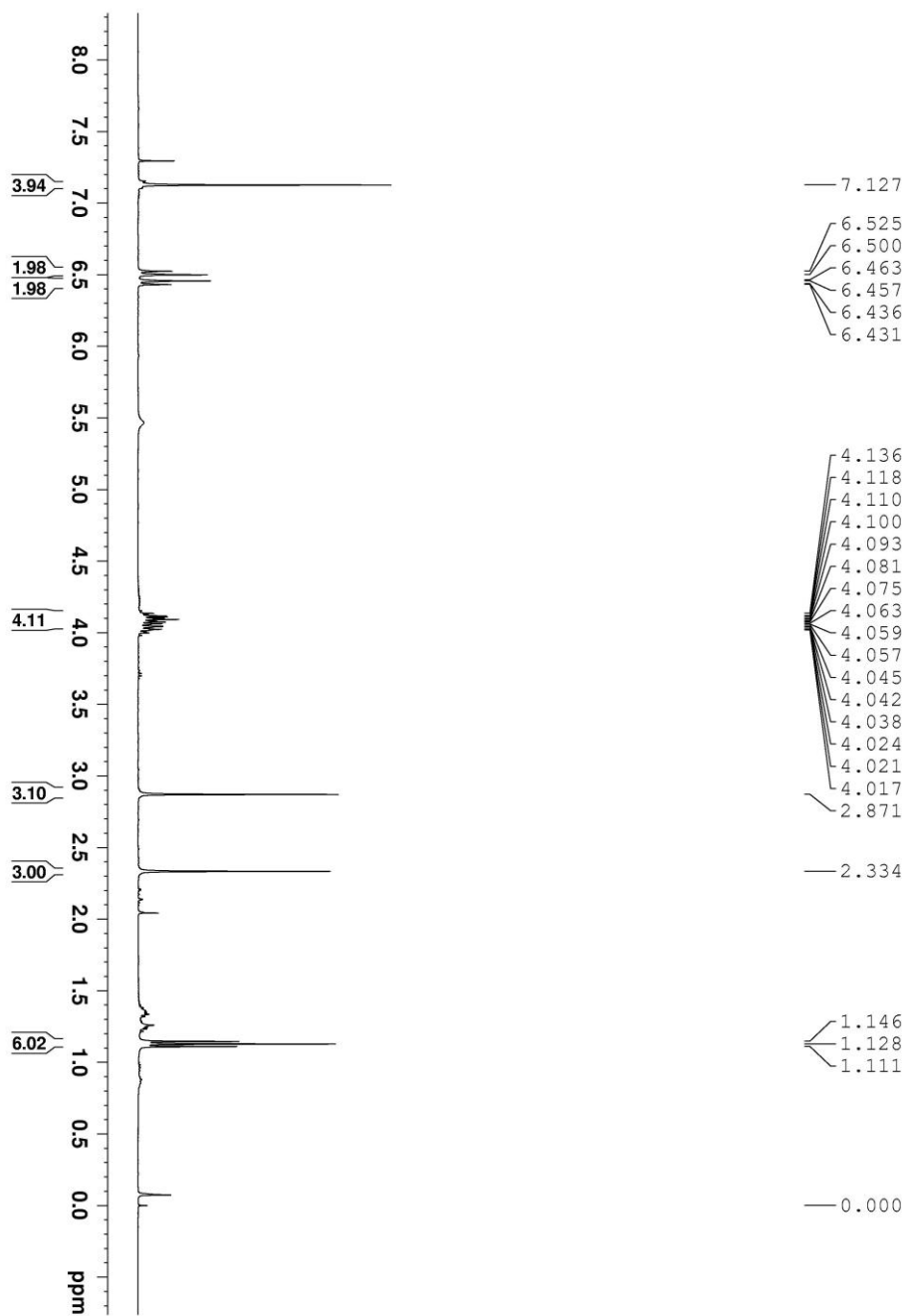


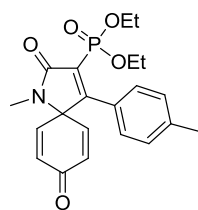
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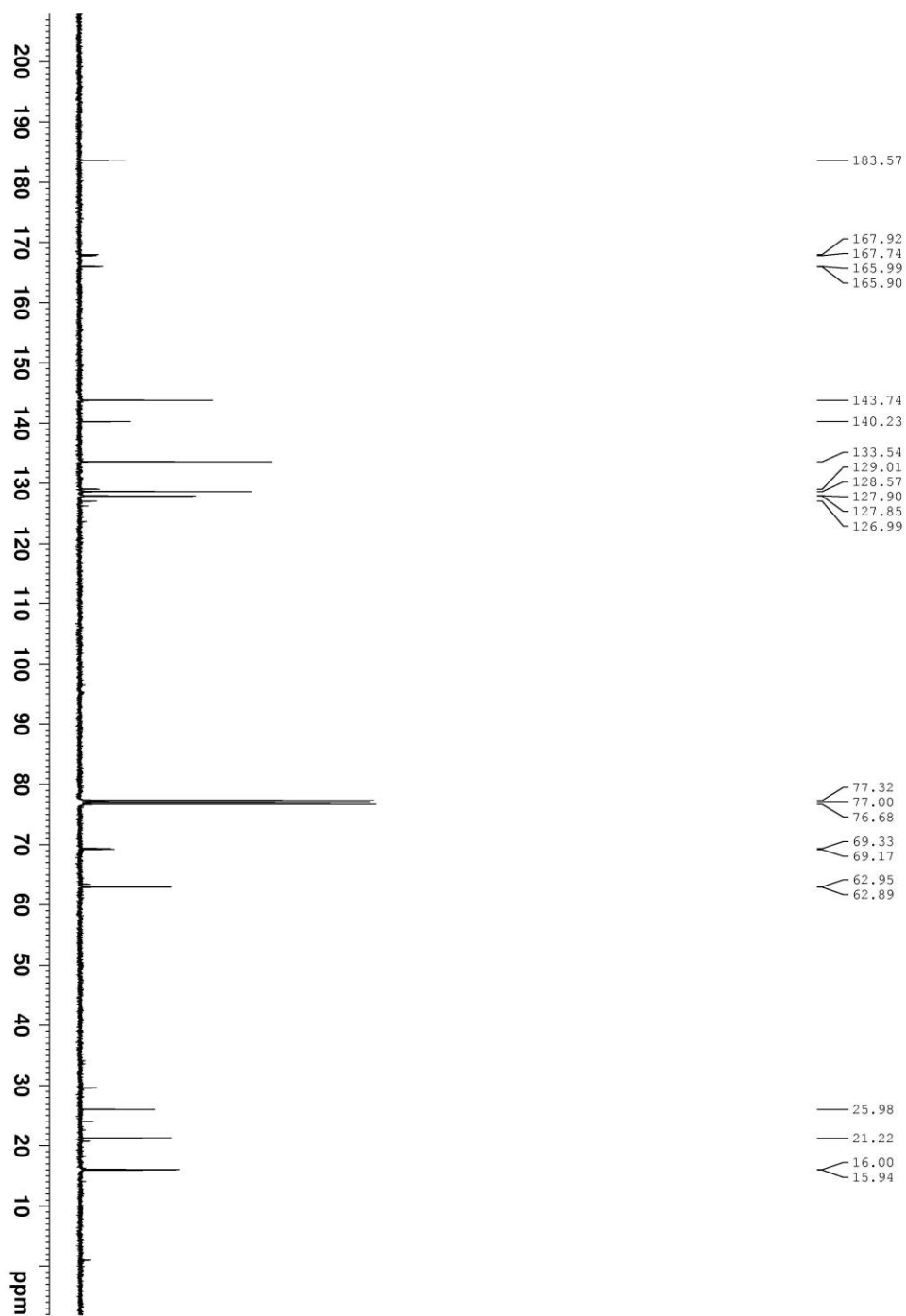


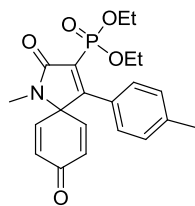
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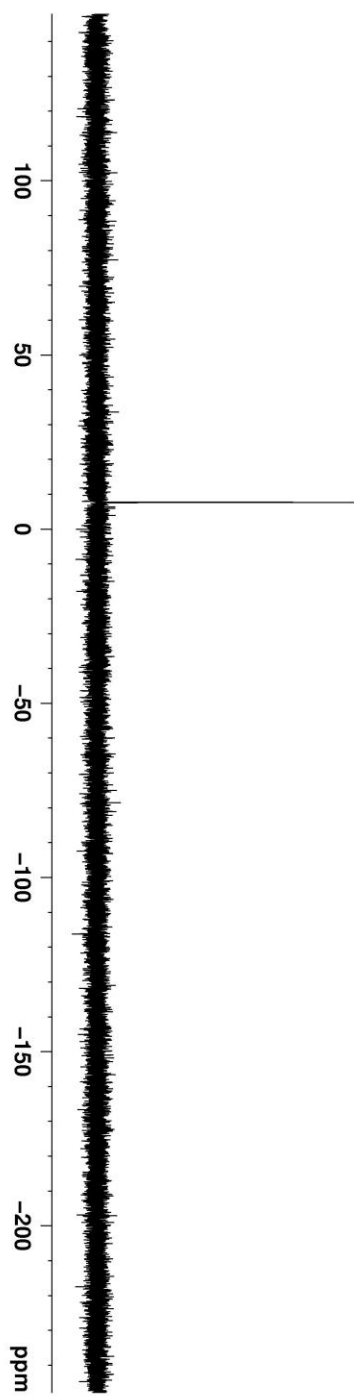


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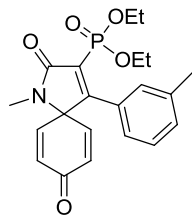




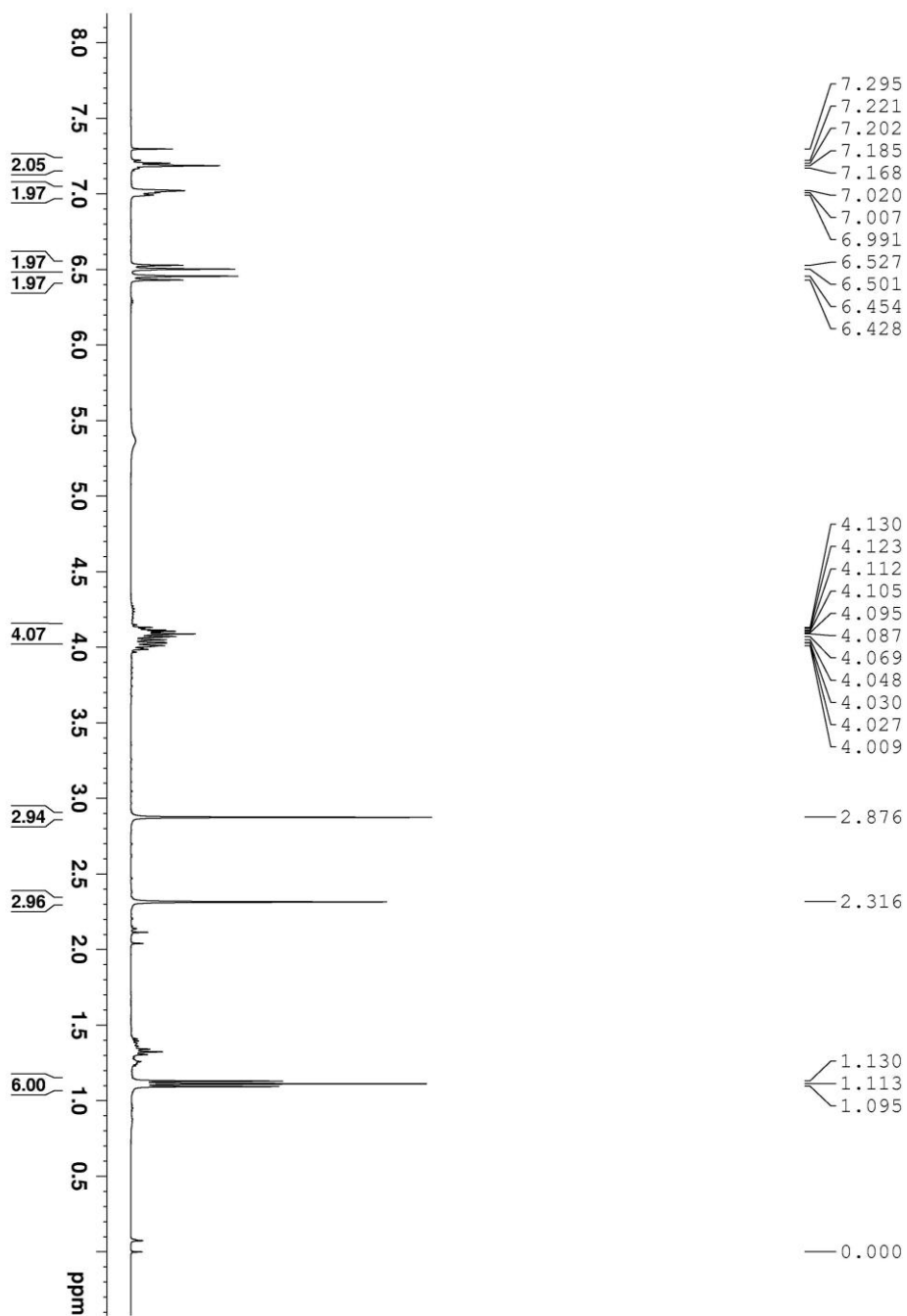
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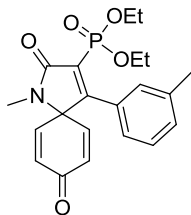


— 7.71

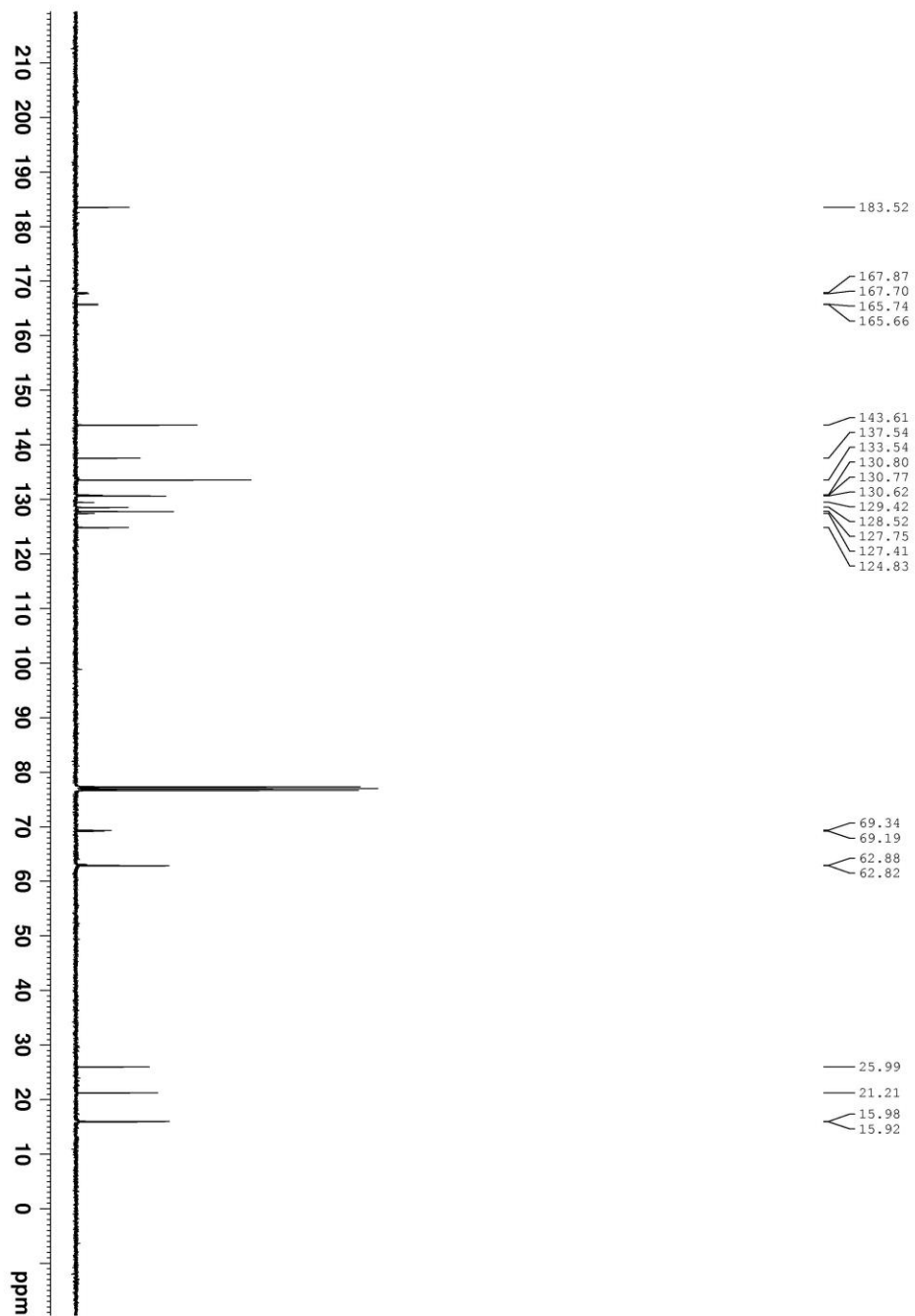


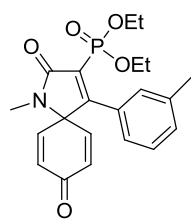
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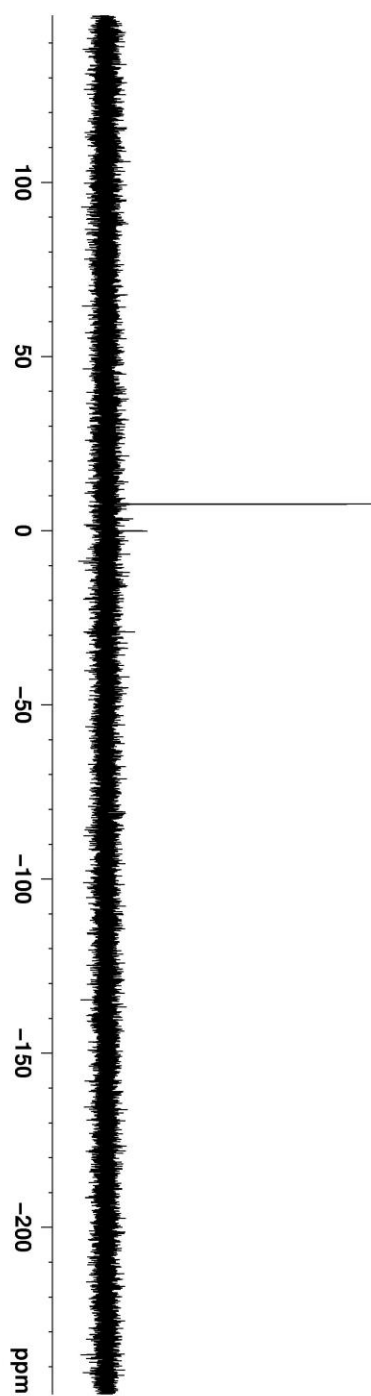


3f, 72%

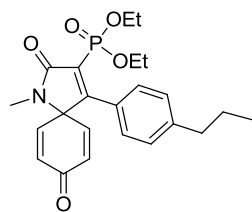




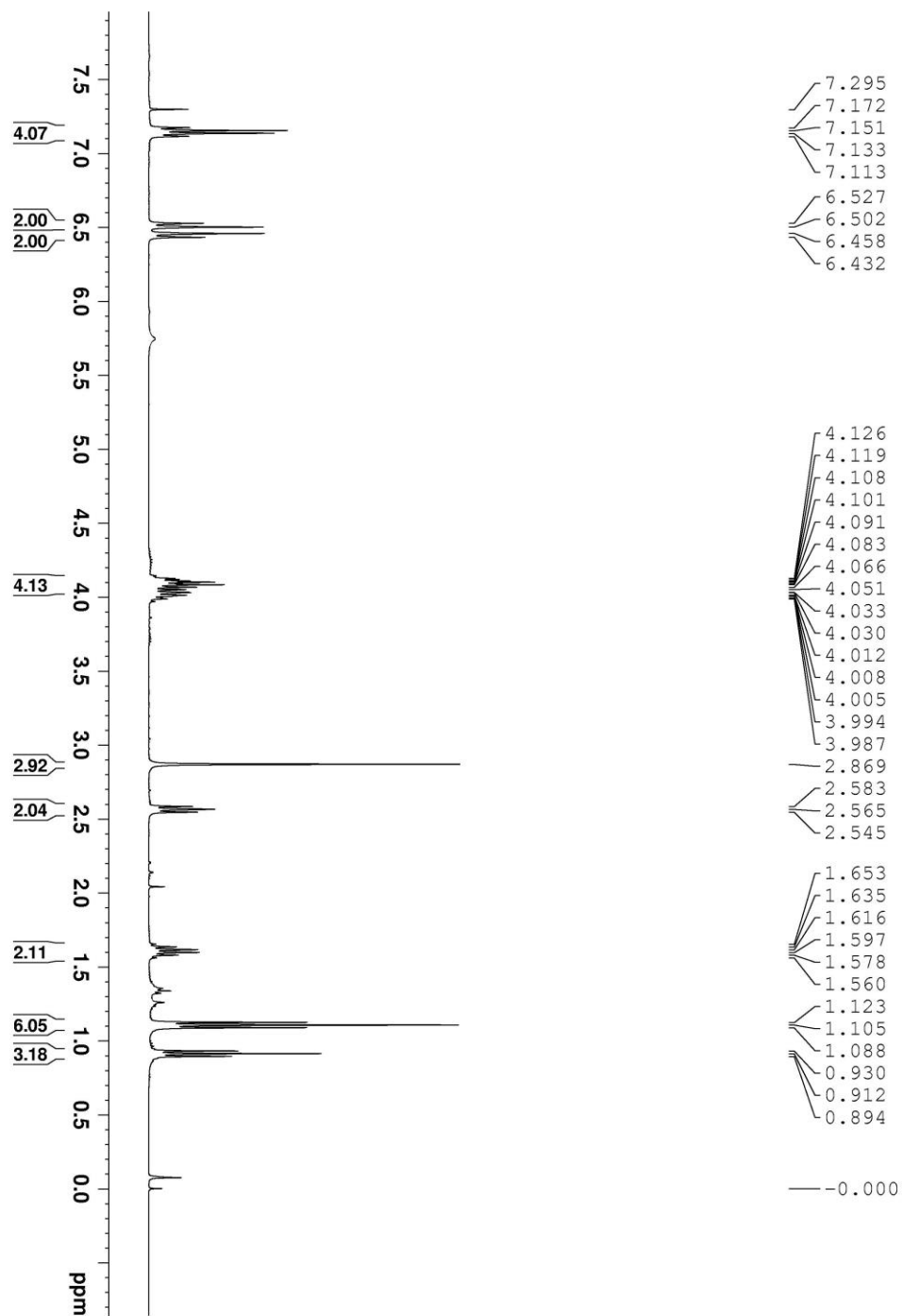
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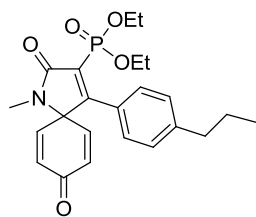


7.63

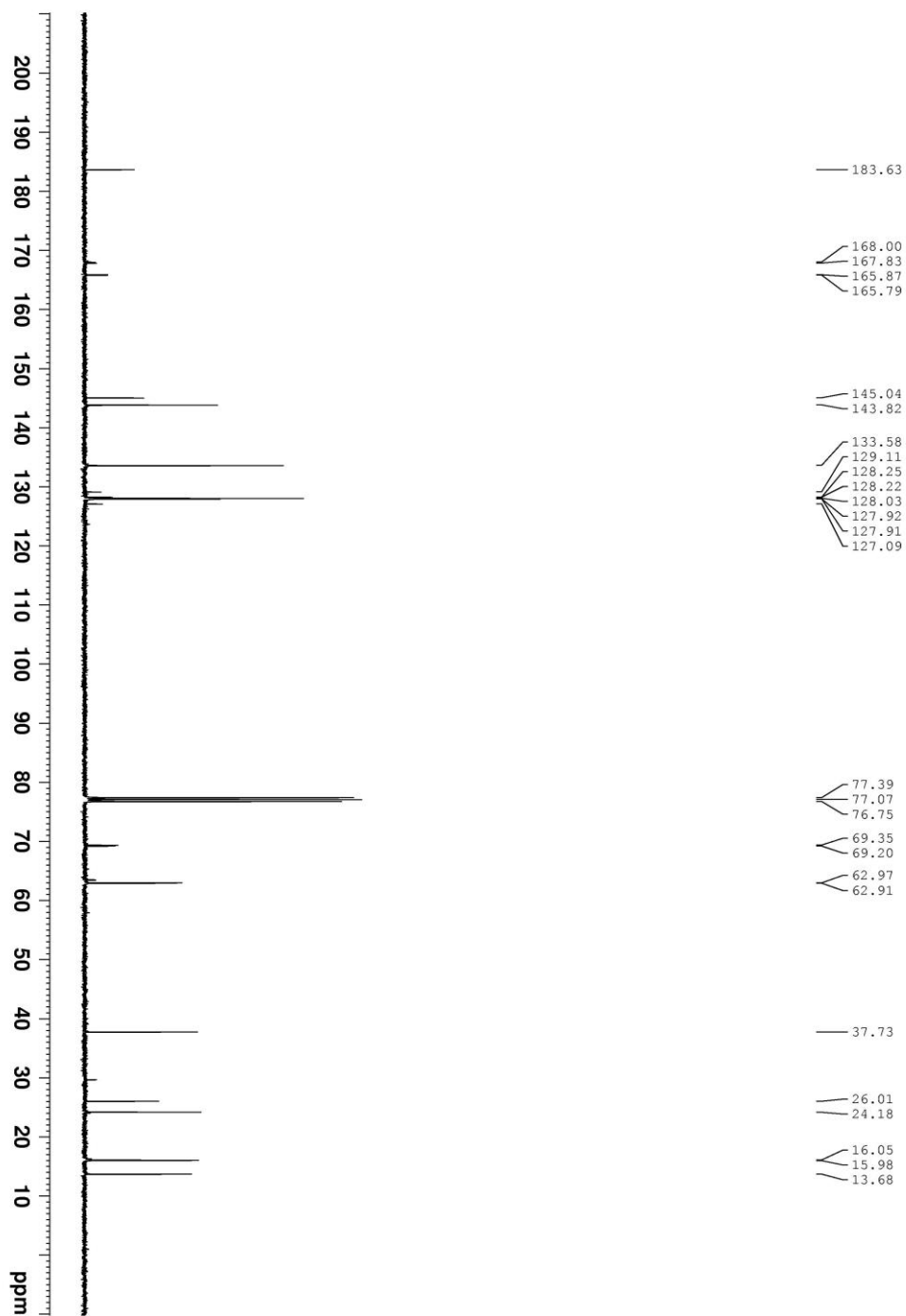


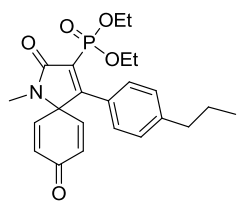
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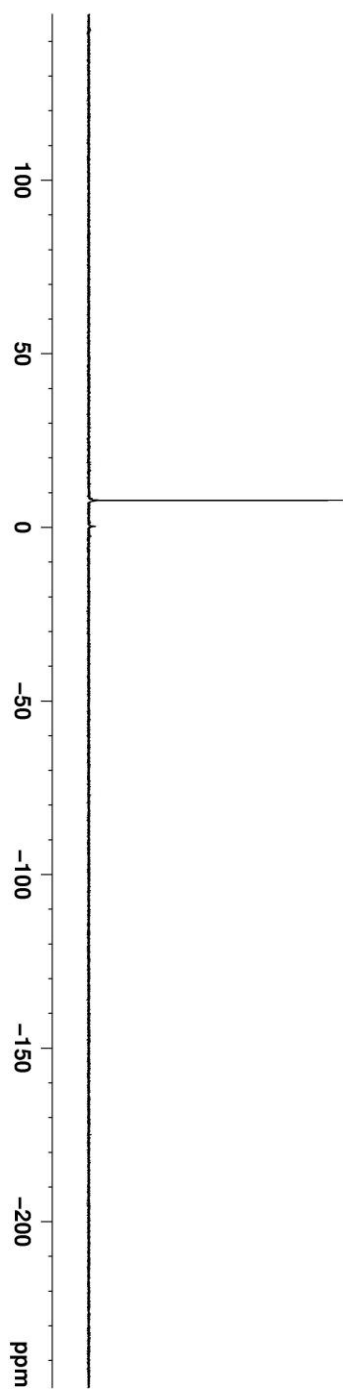


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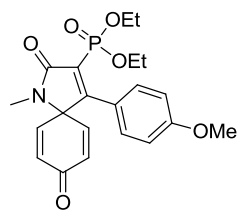




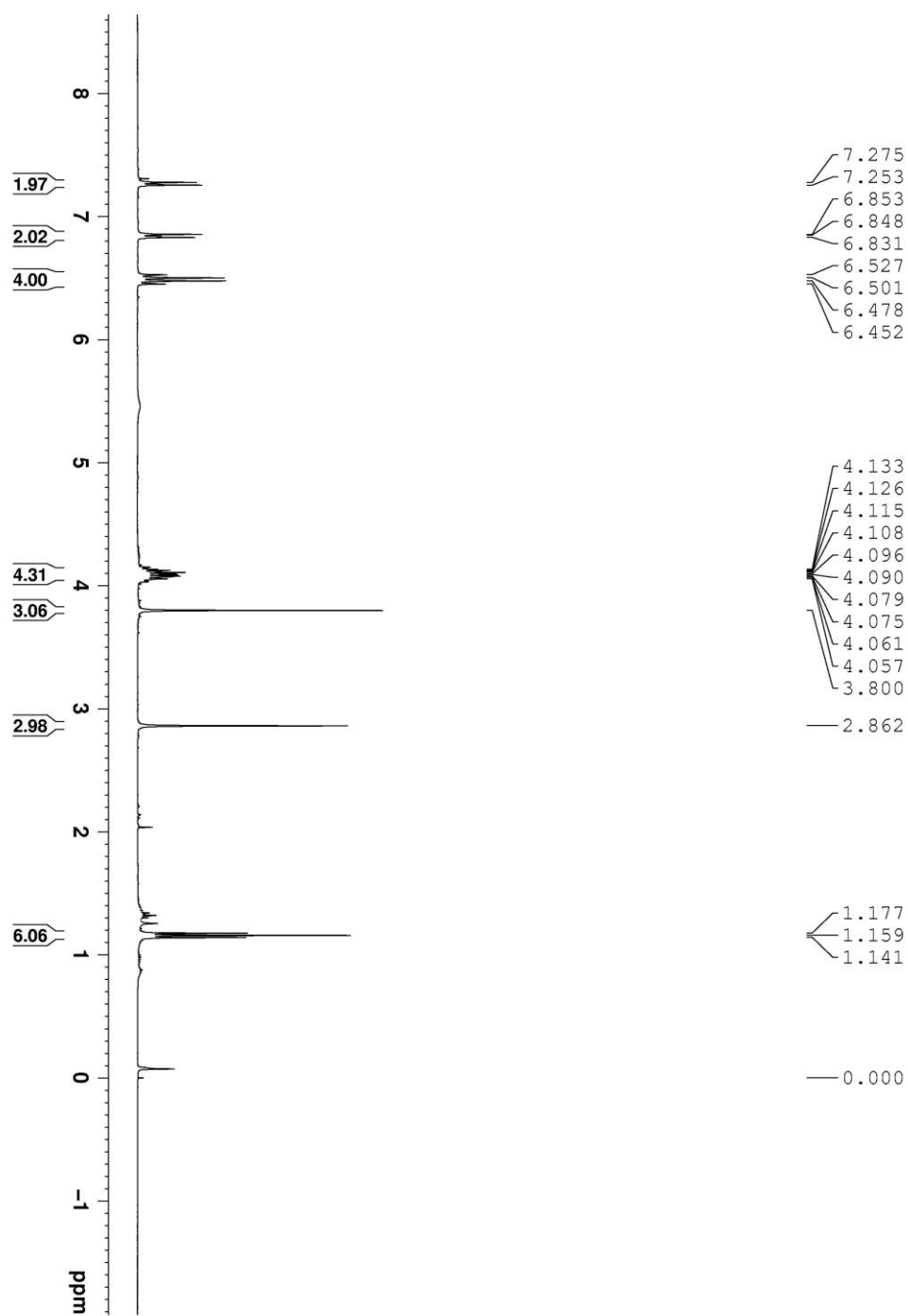
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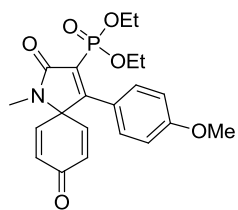


7.78

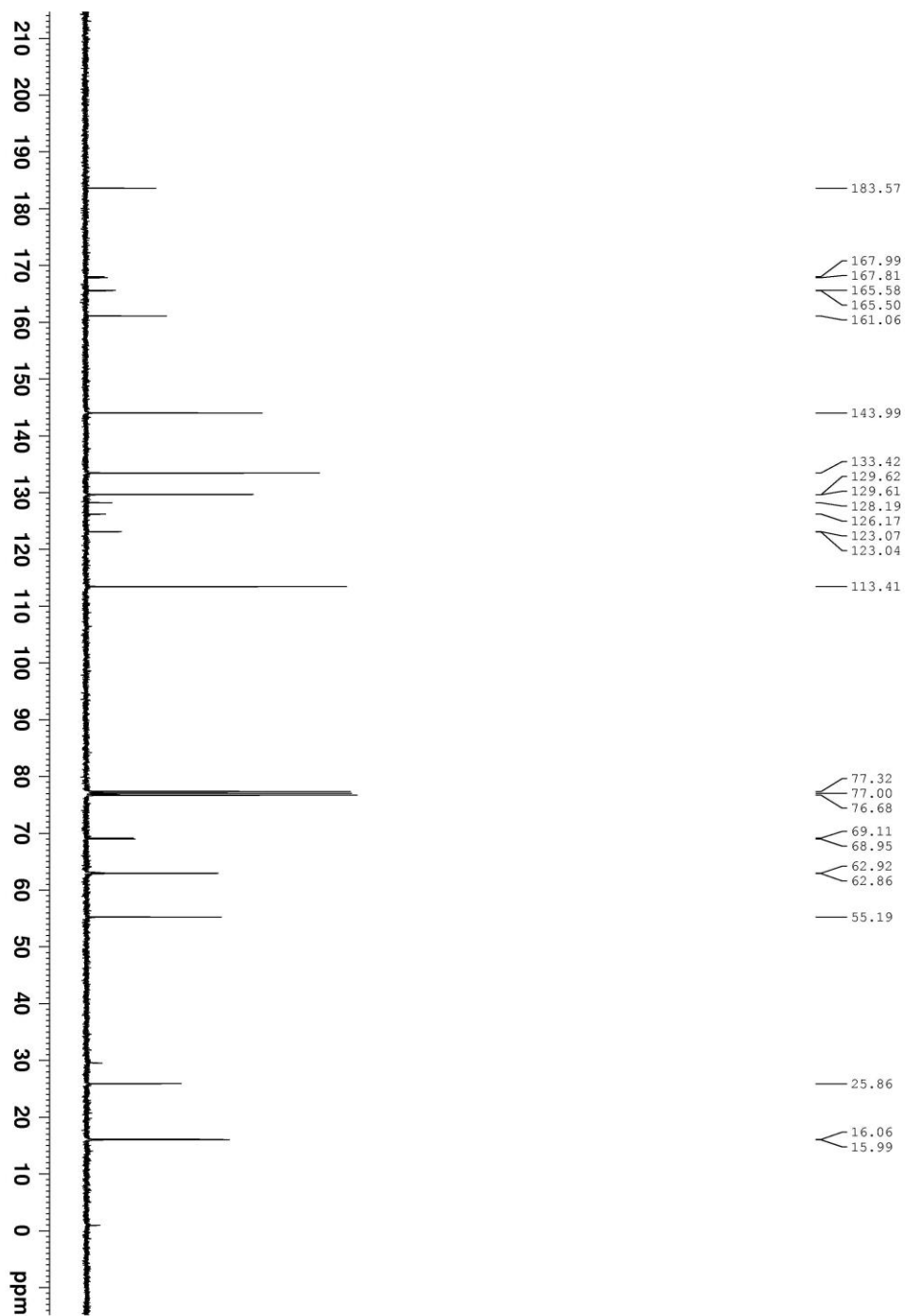


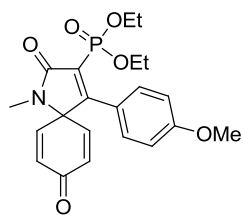
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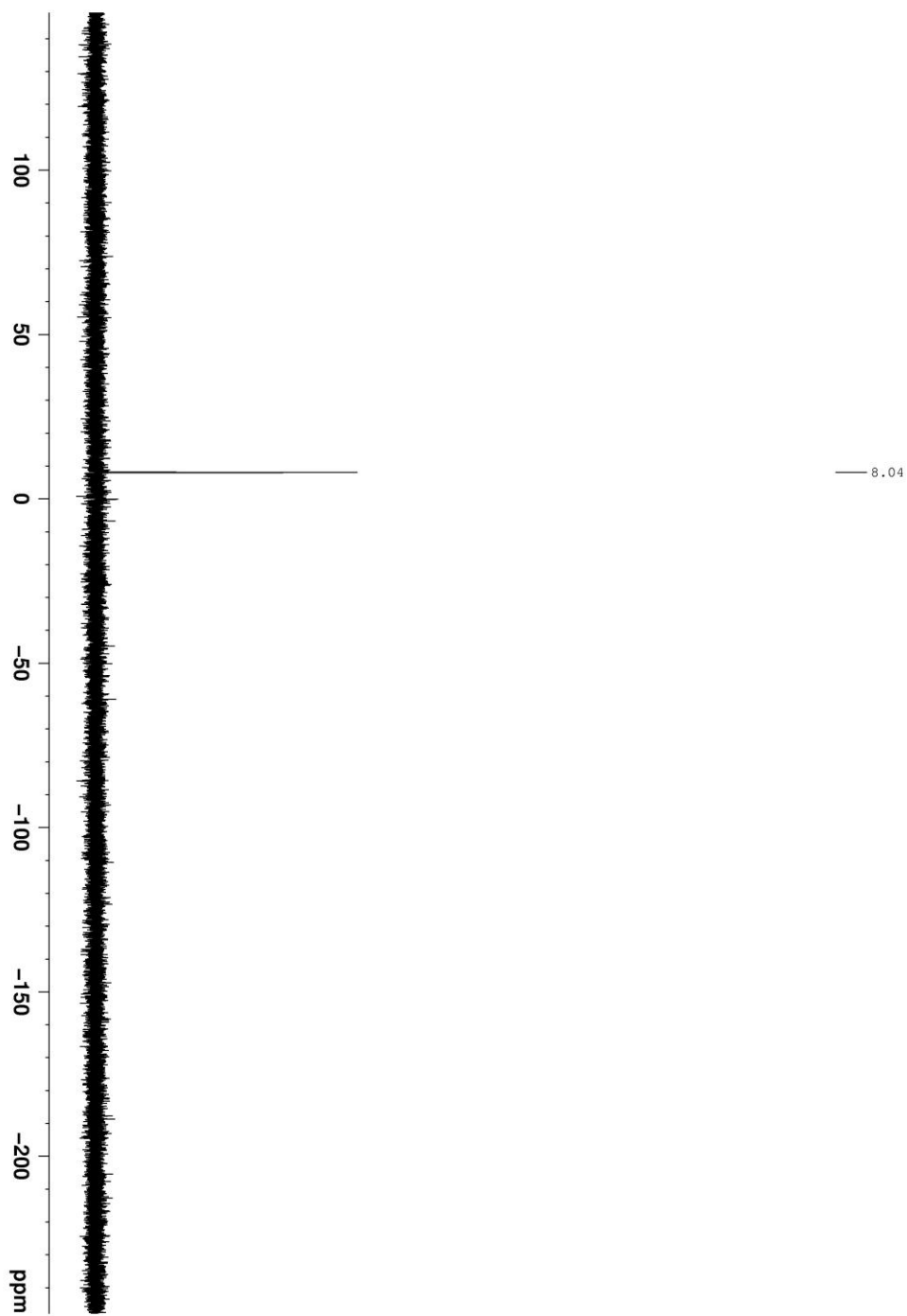


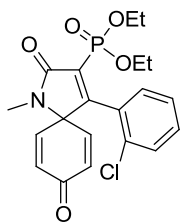
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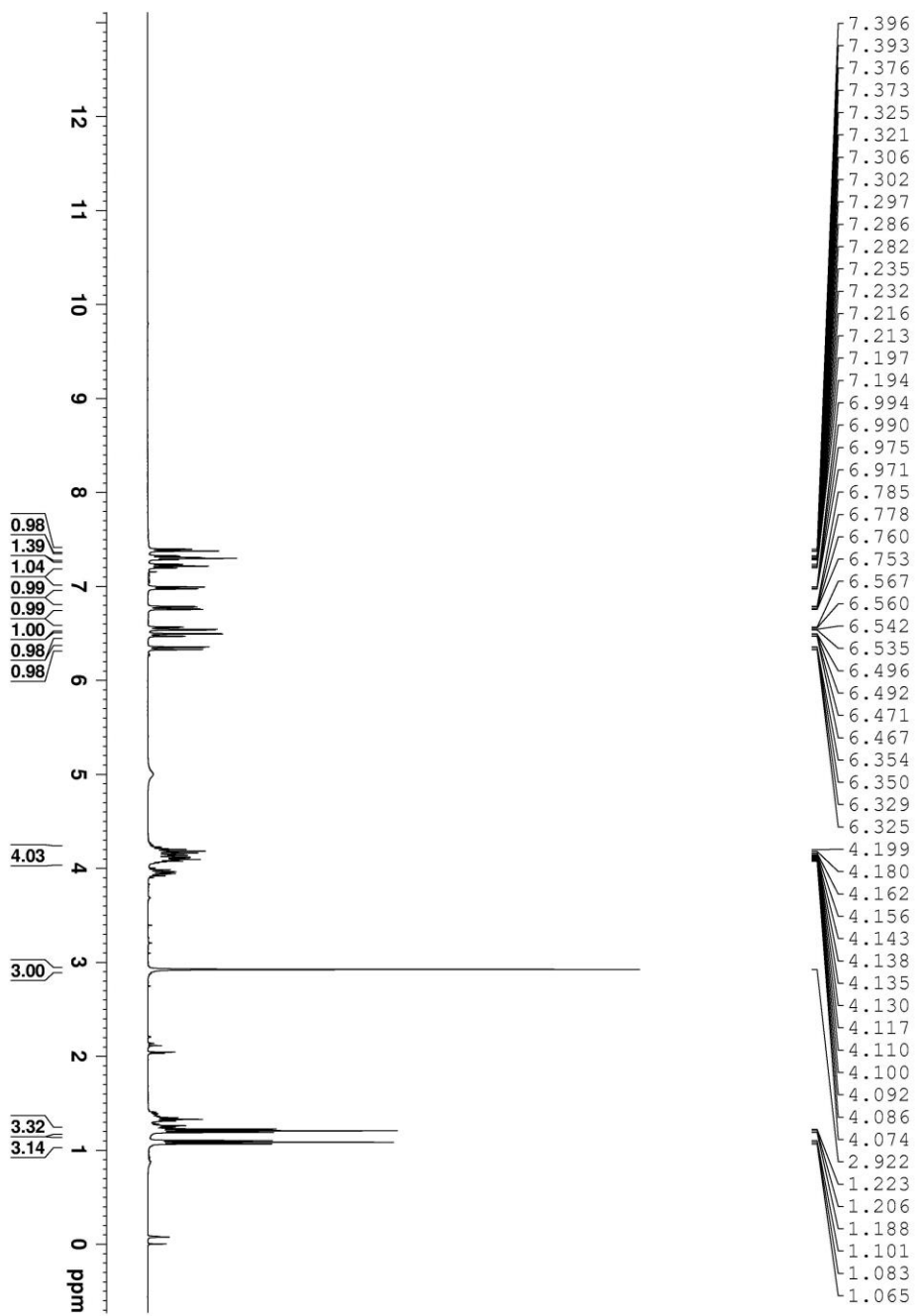


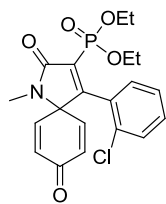
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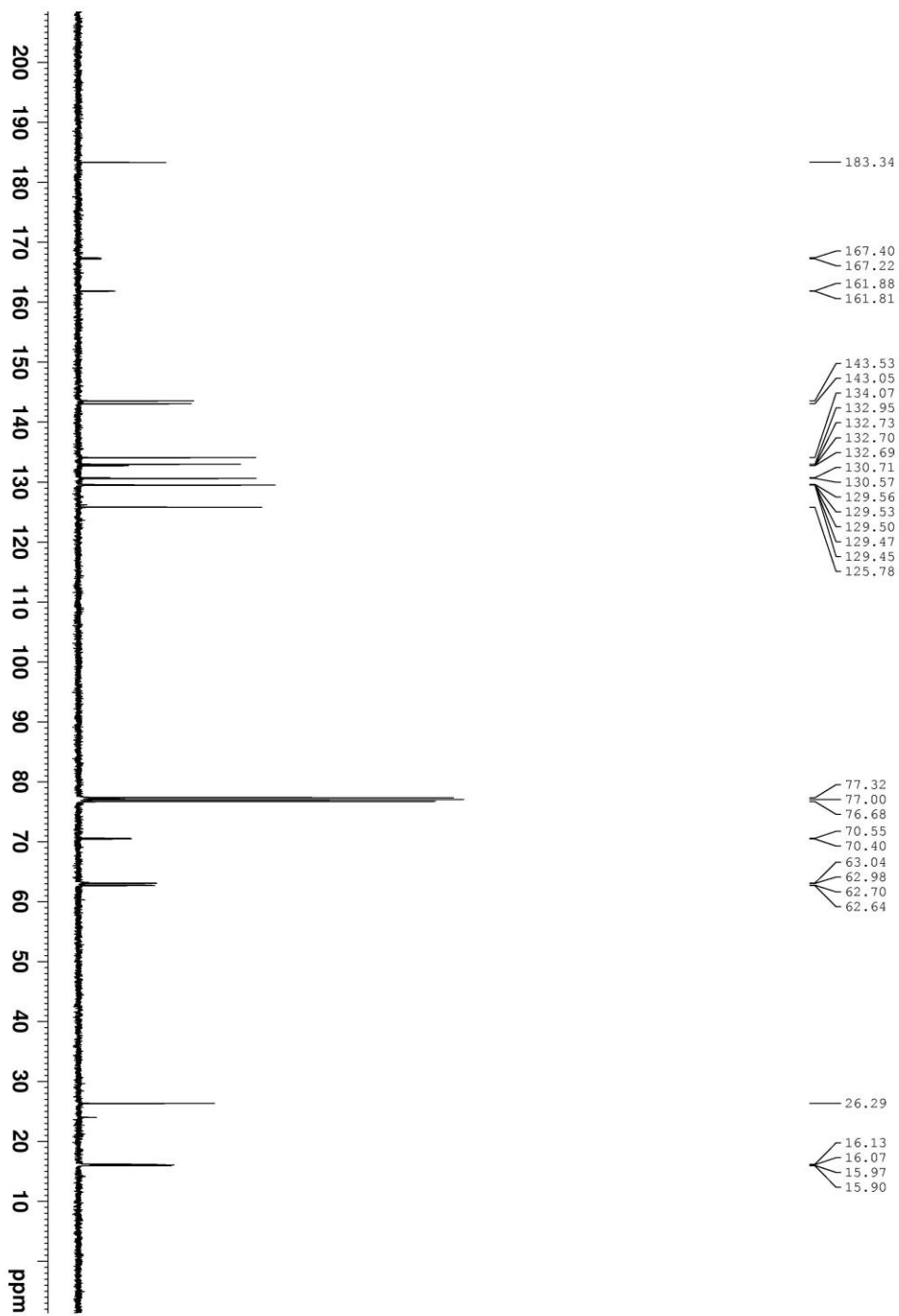


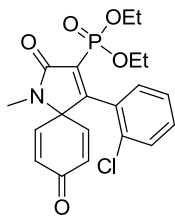
3i, 77%



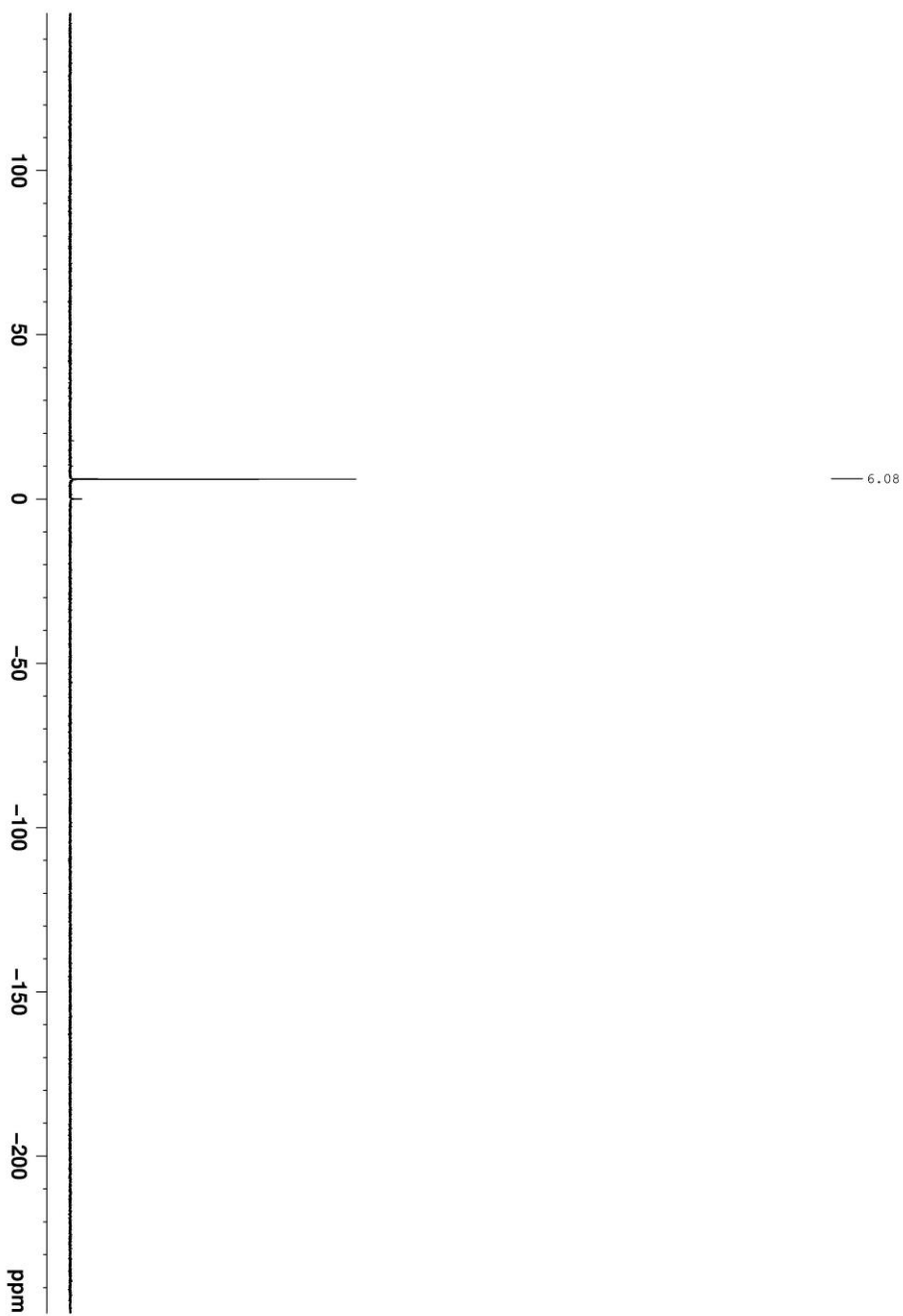


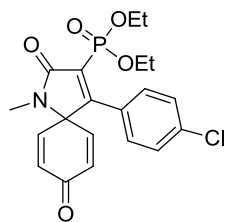
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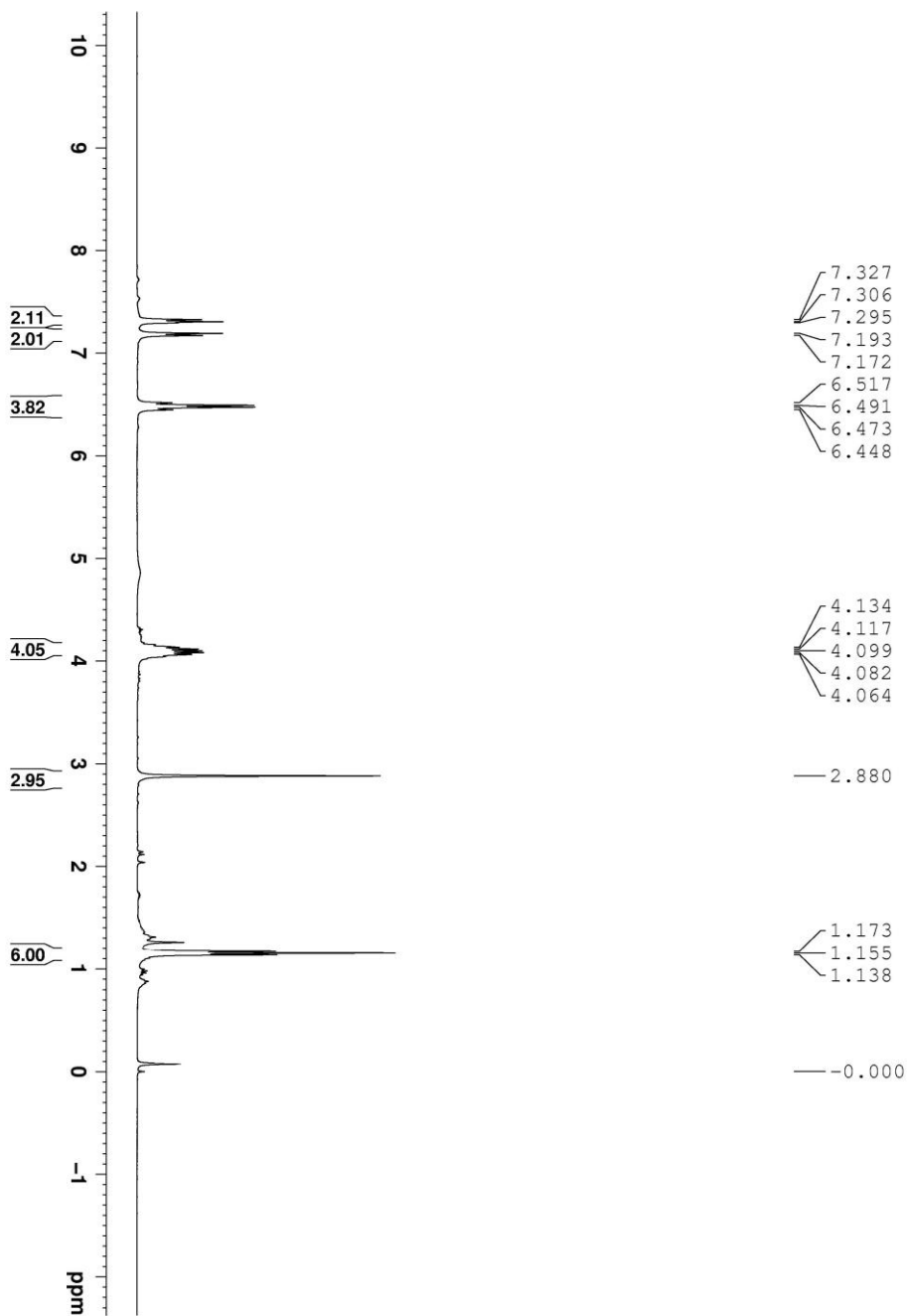


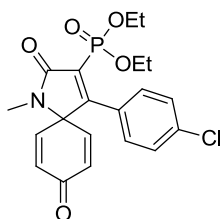
3i, 77%



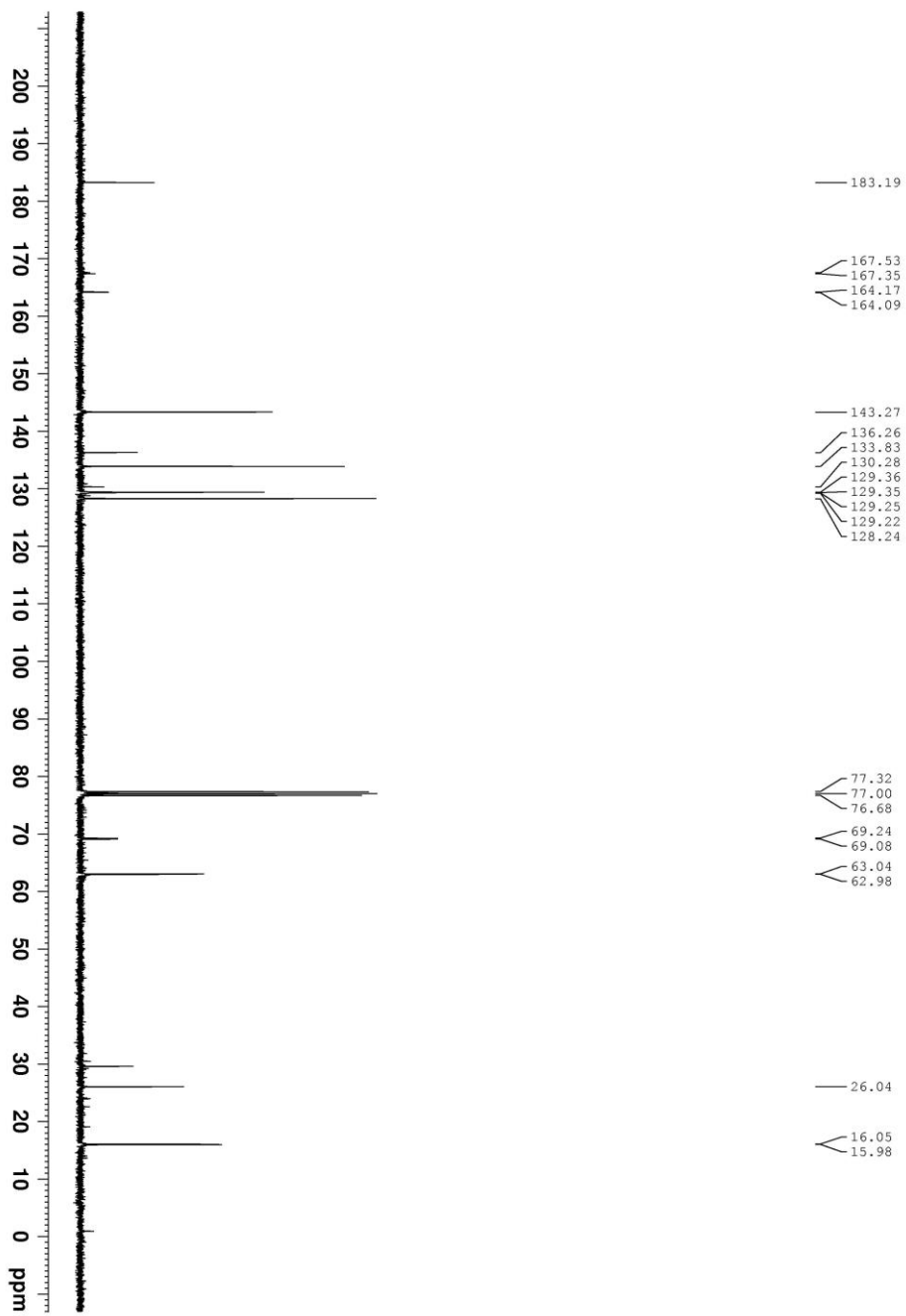


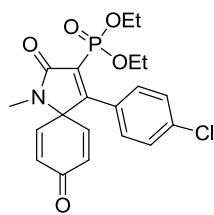
3j, 75%



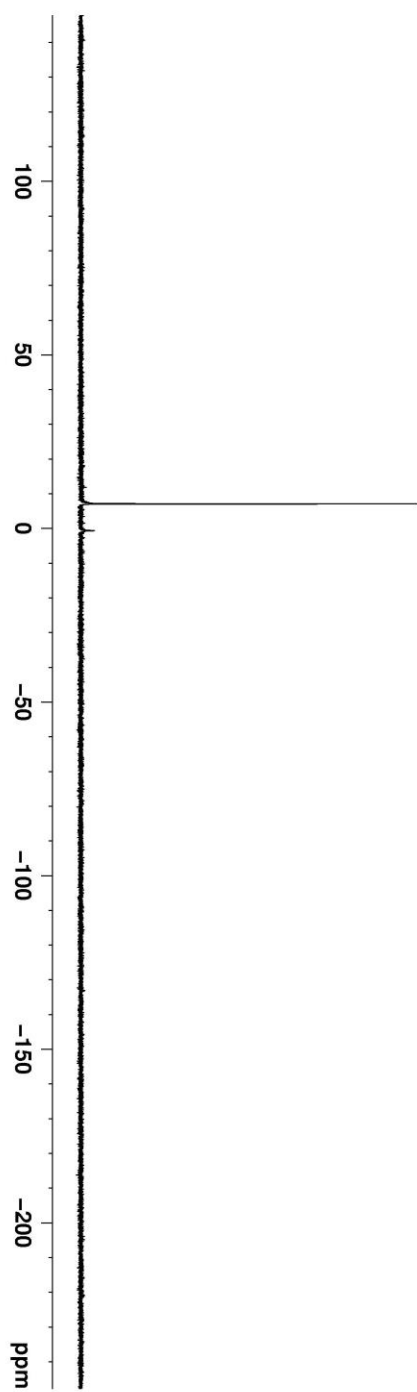


3j, 75%

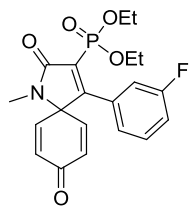




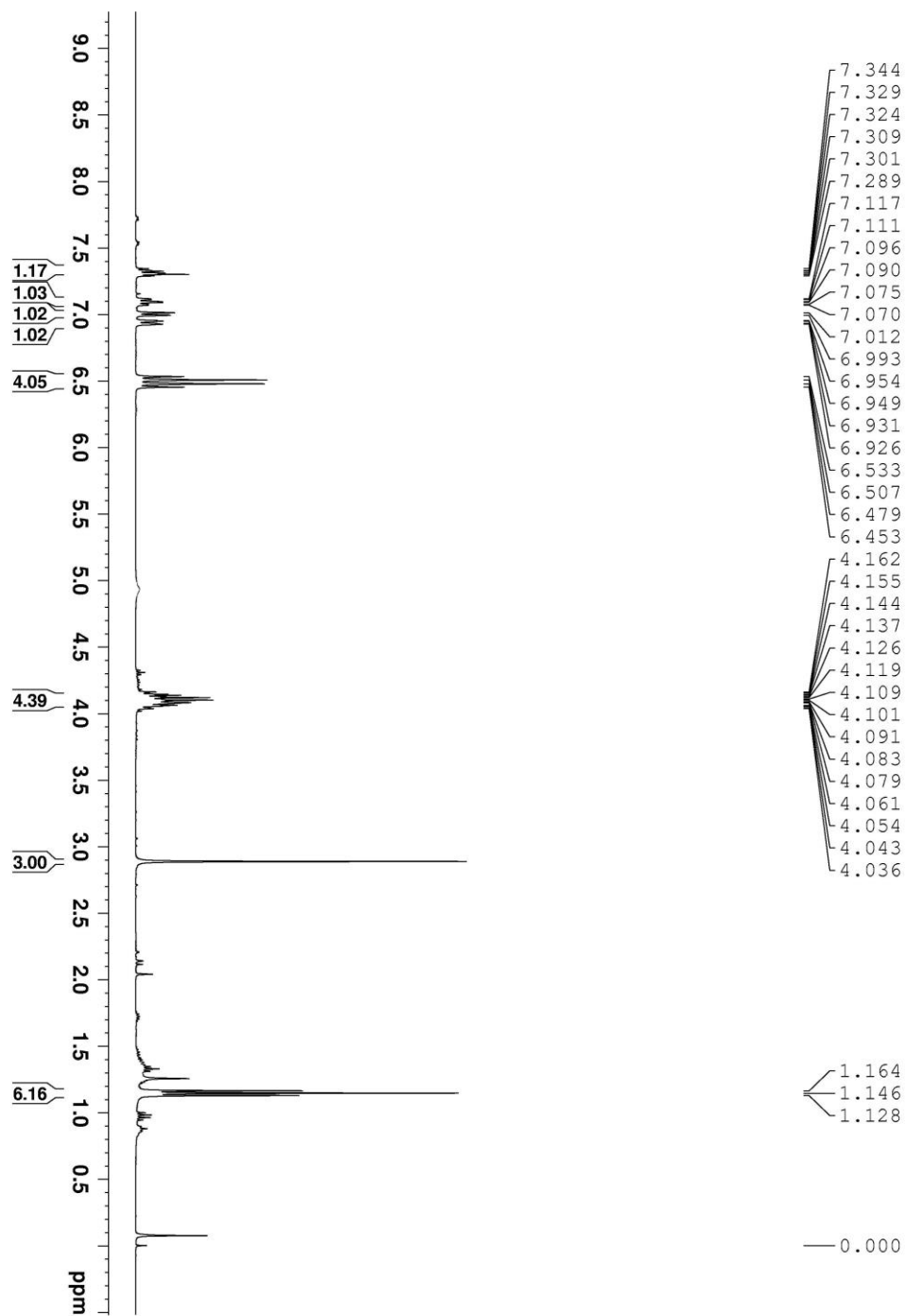
3j, 75%

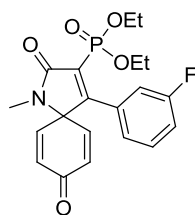


7.06

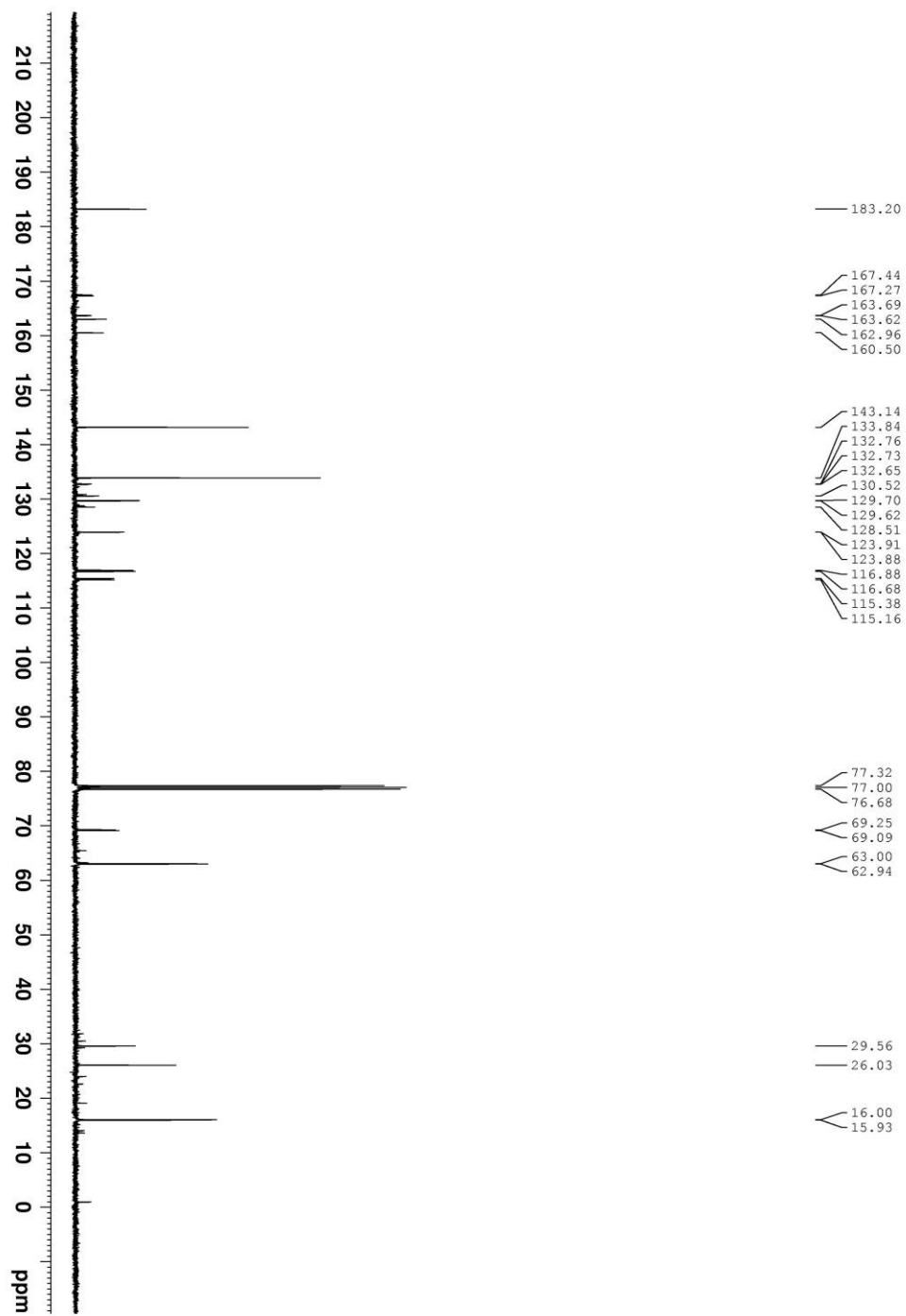


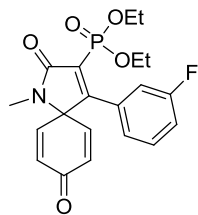
3k, 73%



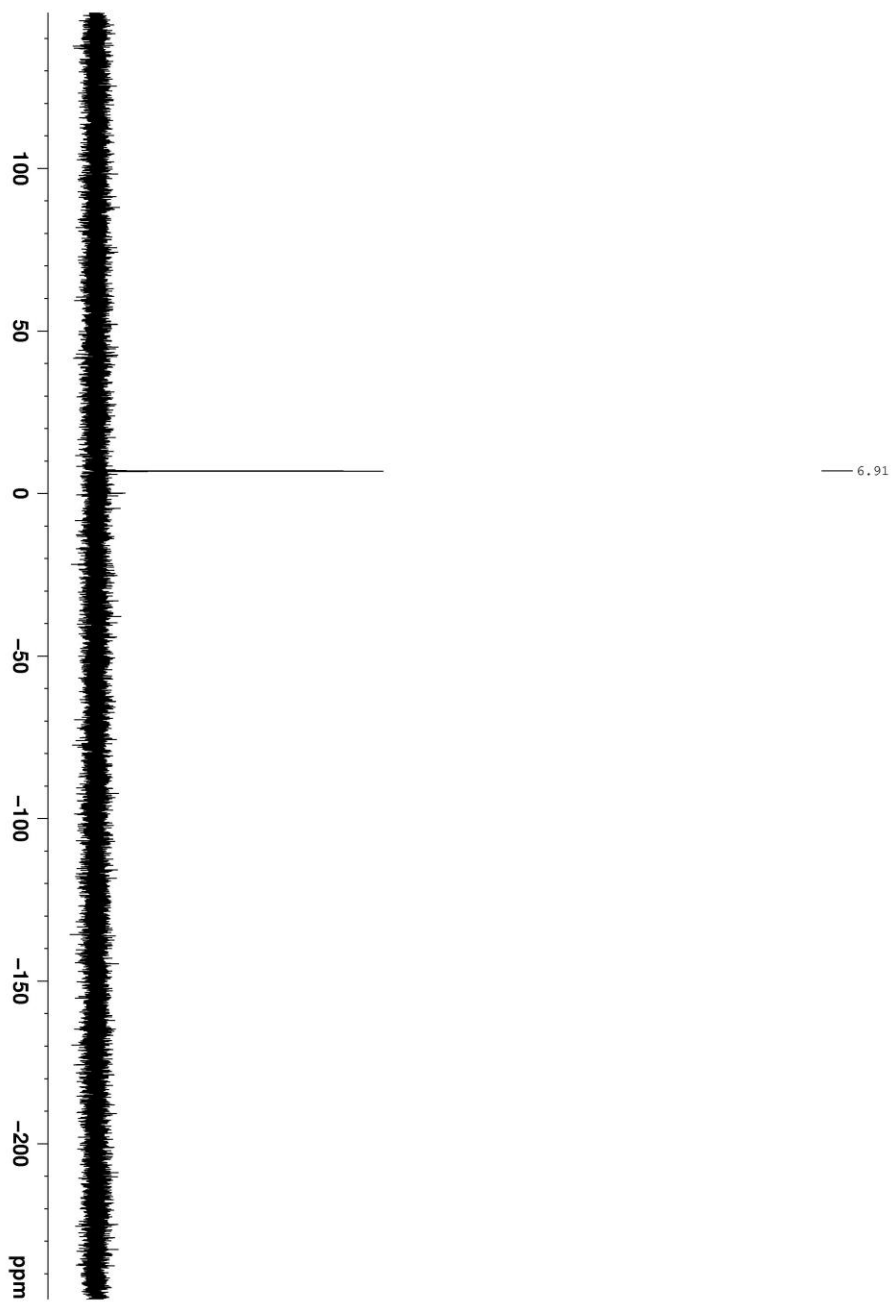


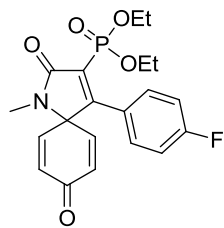
3k, 73%



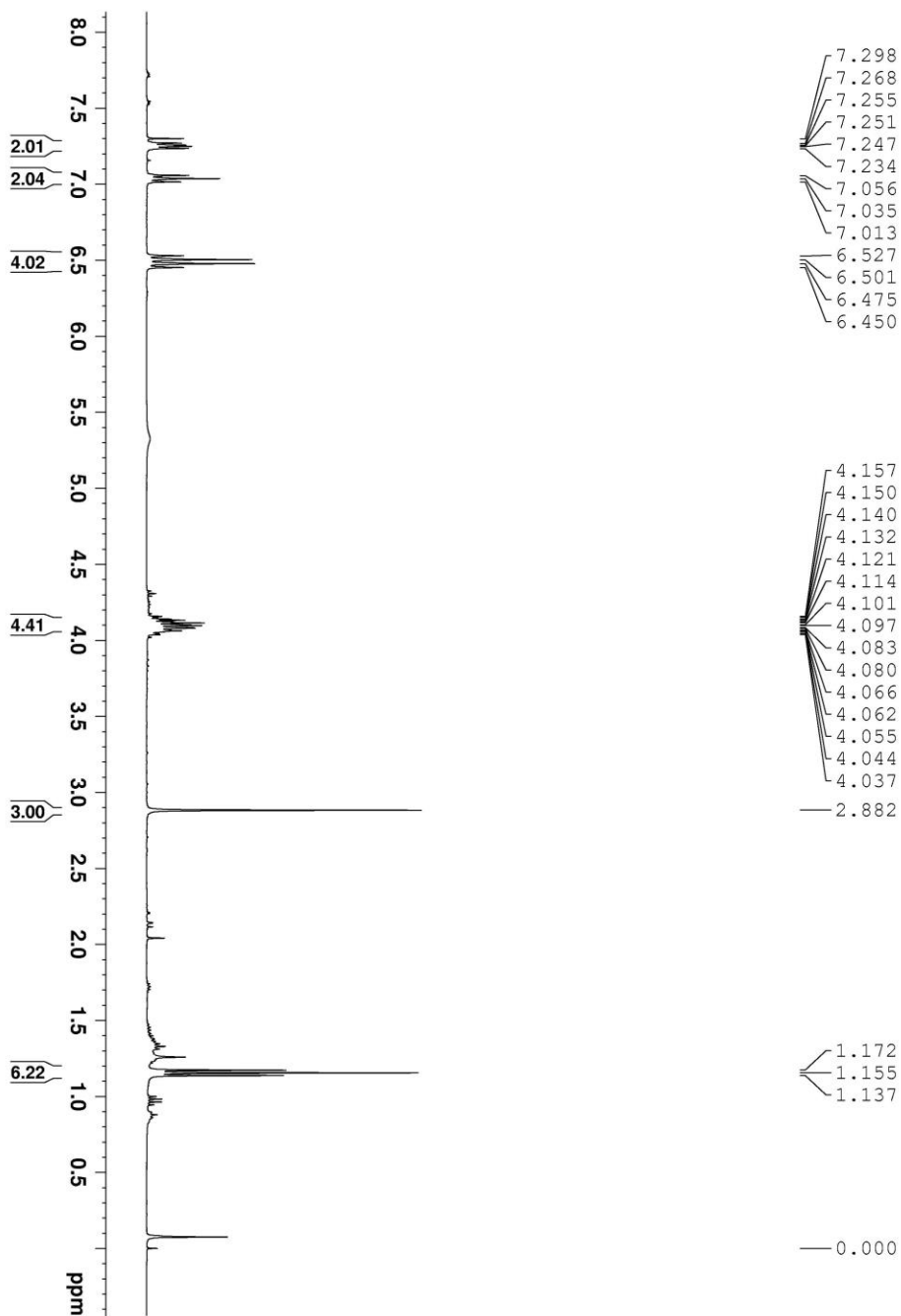


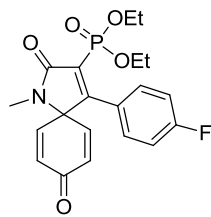
3k, 73%



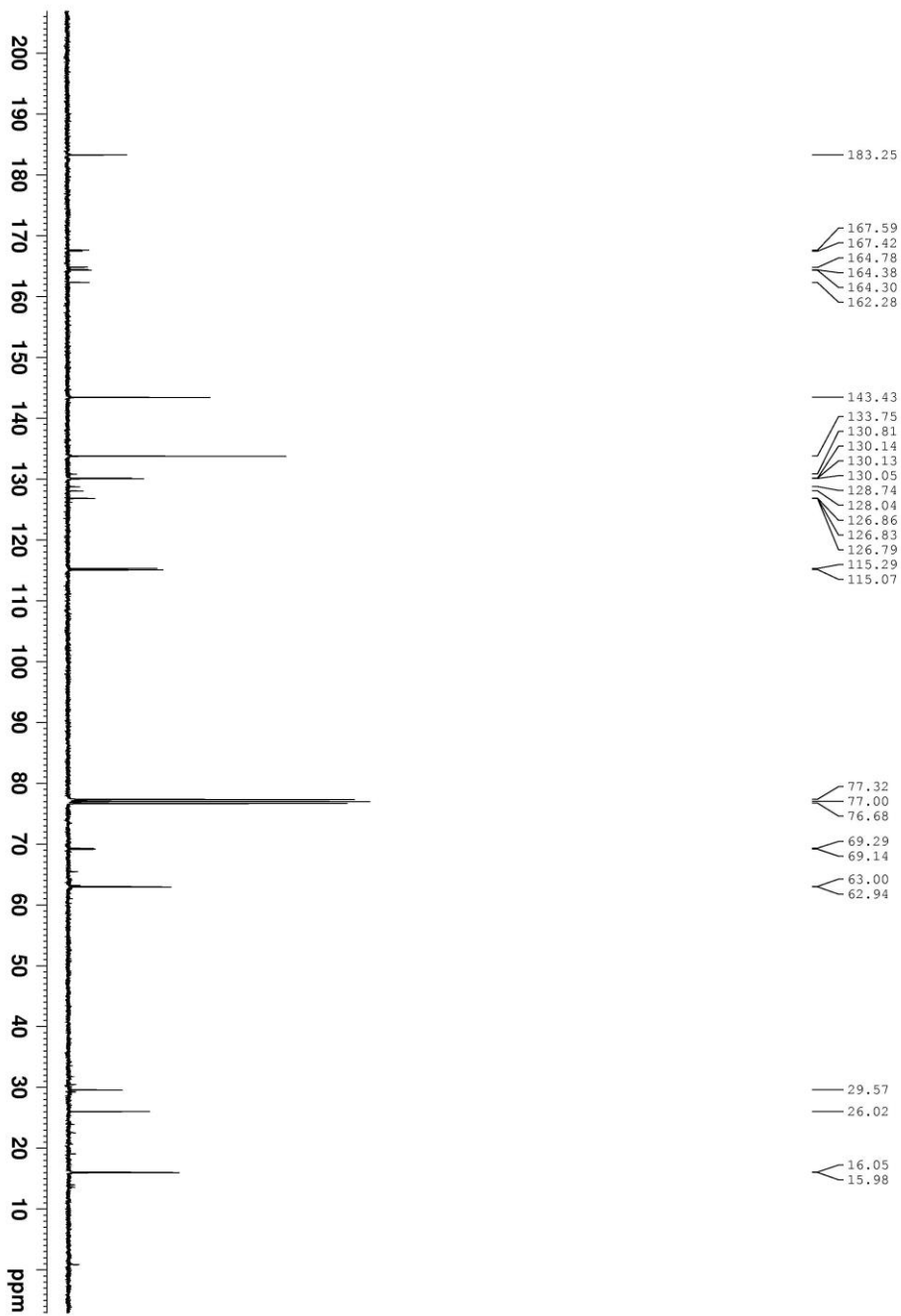


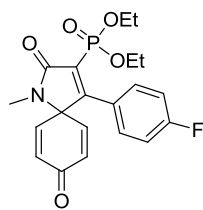
3I, 75%



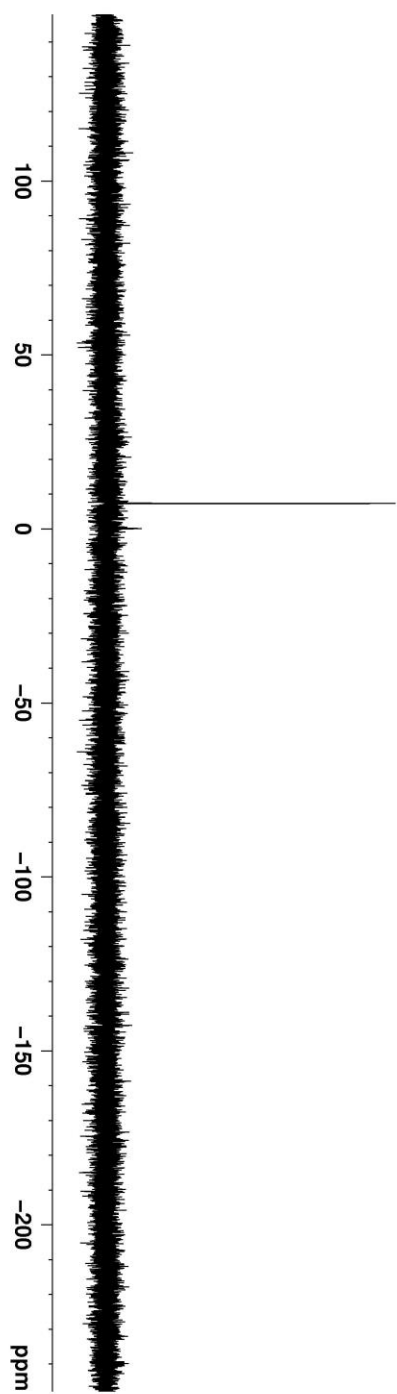


3I, 75%

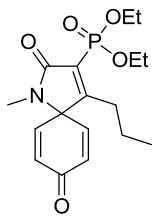




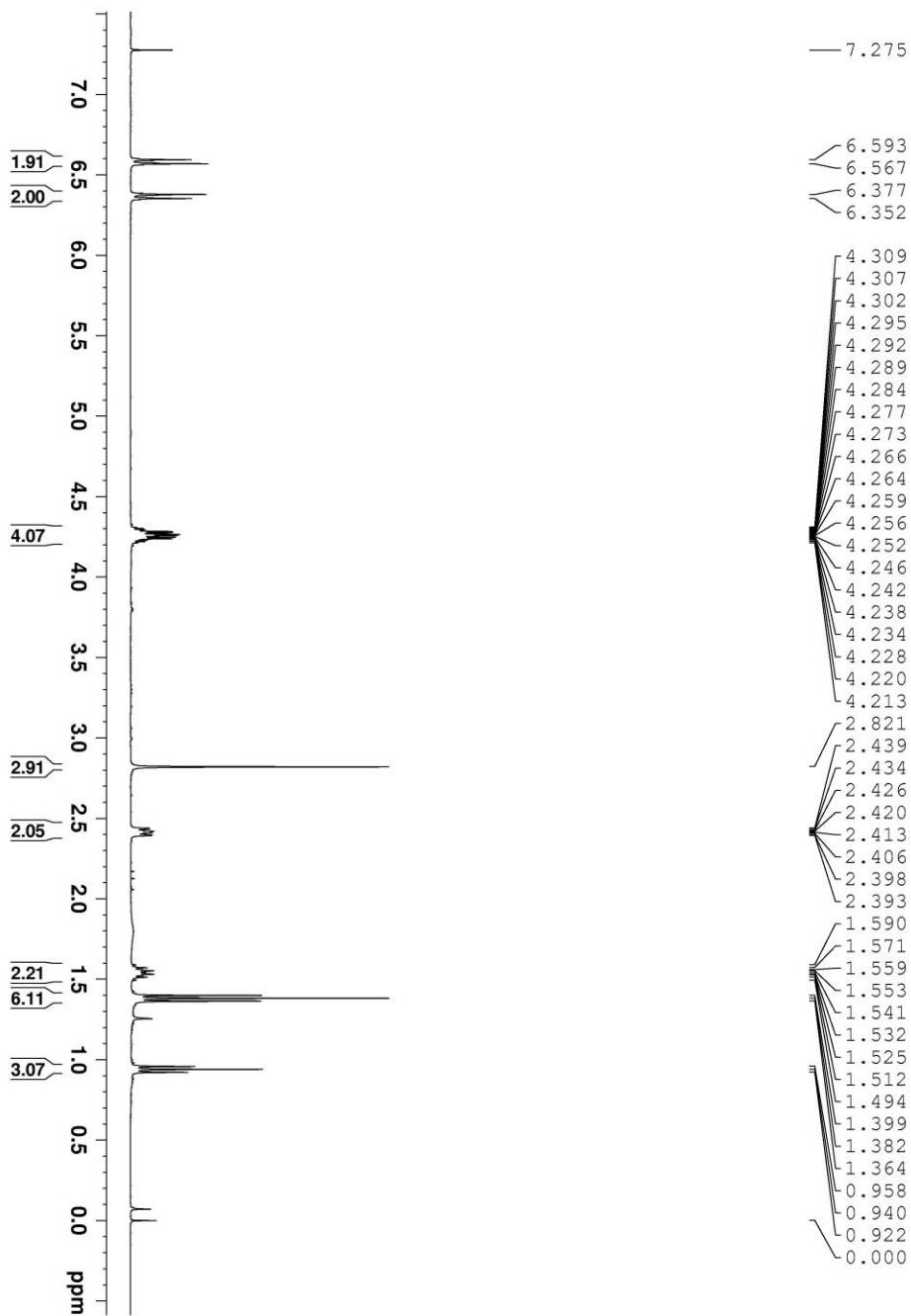
3l, 75%

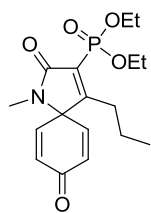


7.27

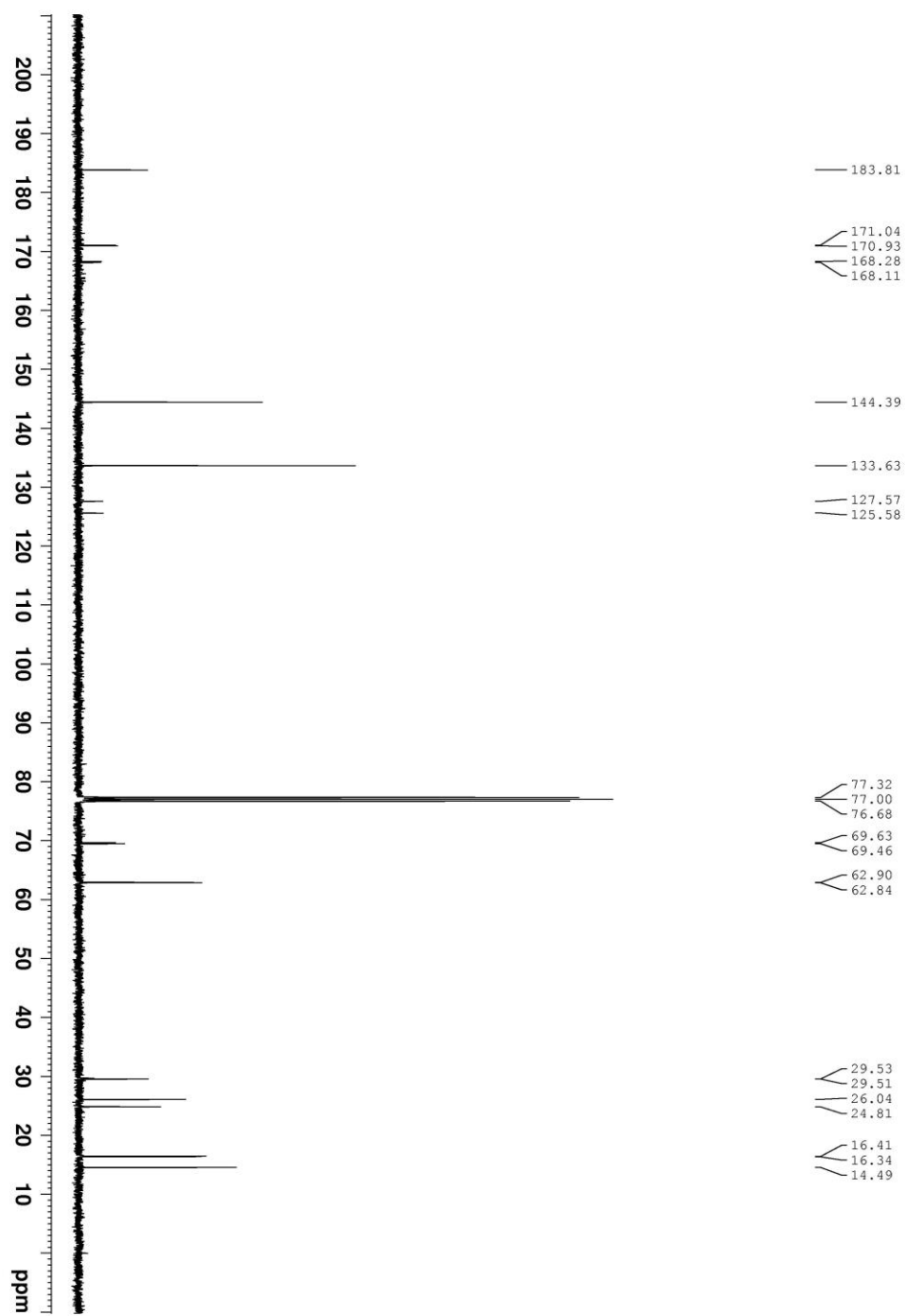


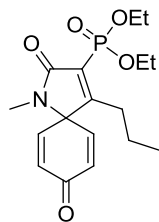
3m, 38%



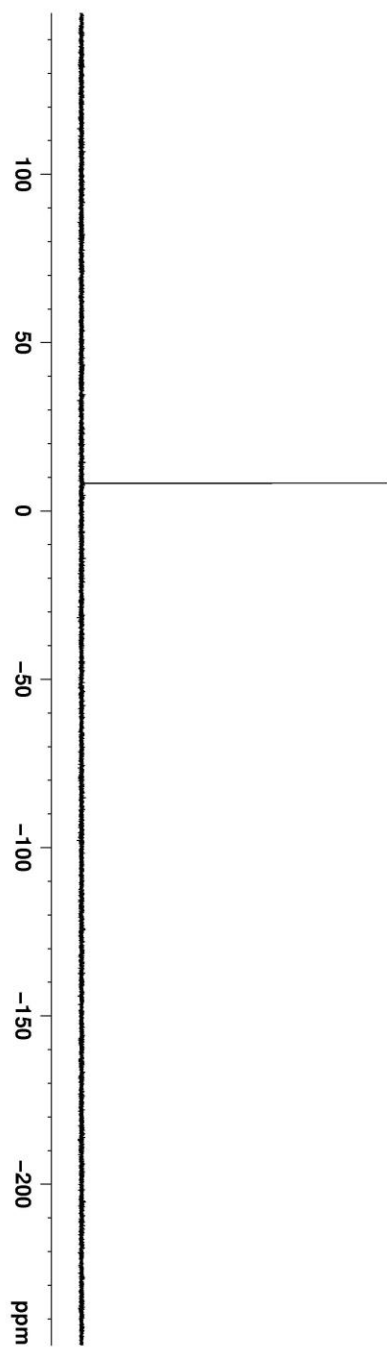


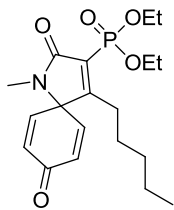
3m, 38%



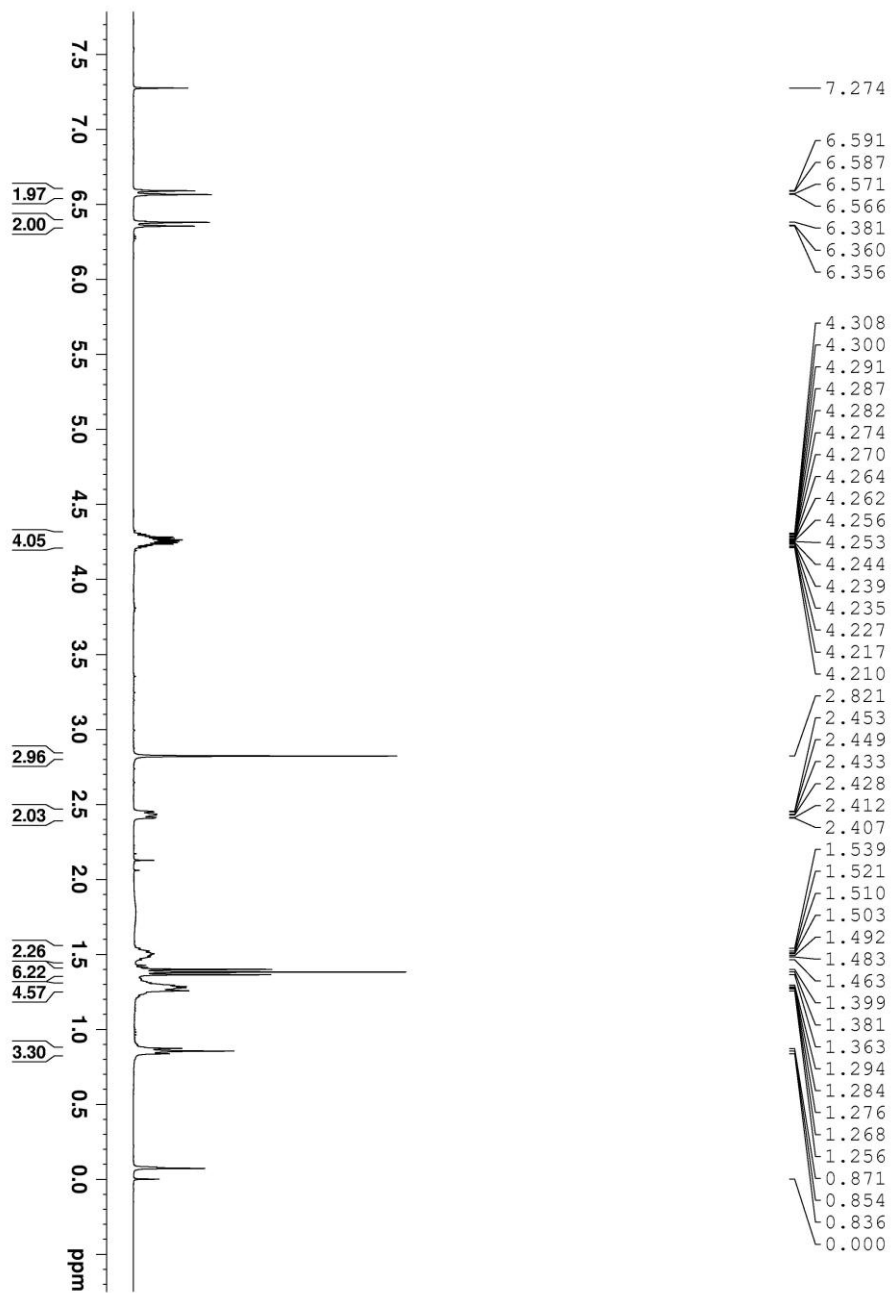


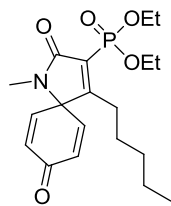
3m, 38%



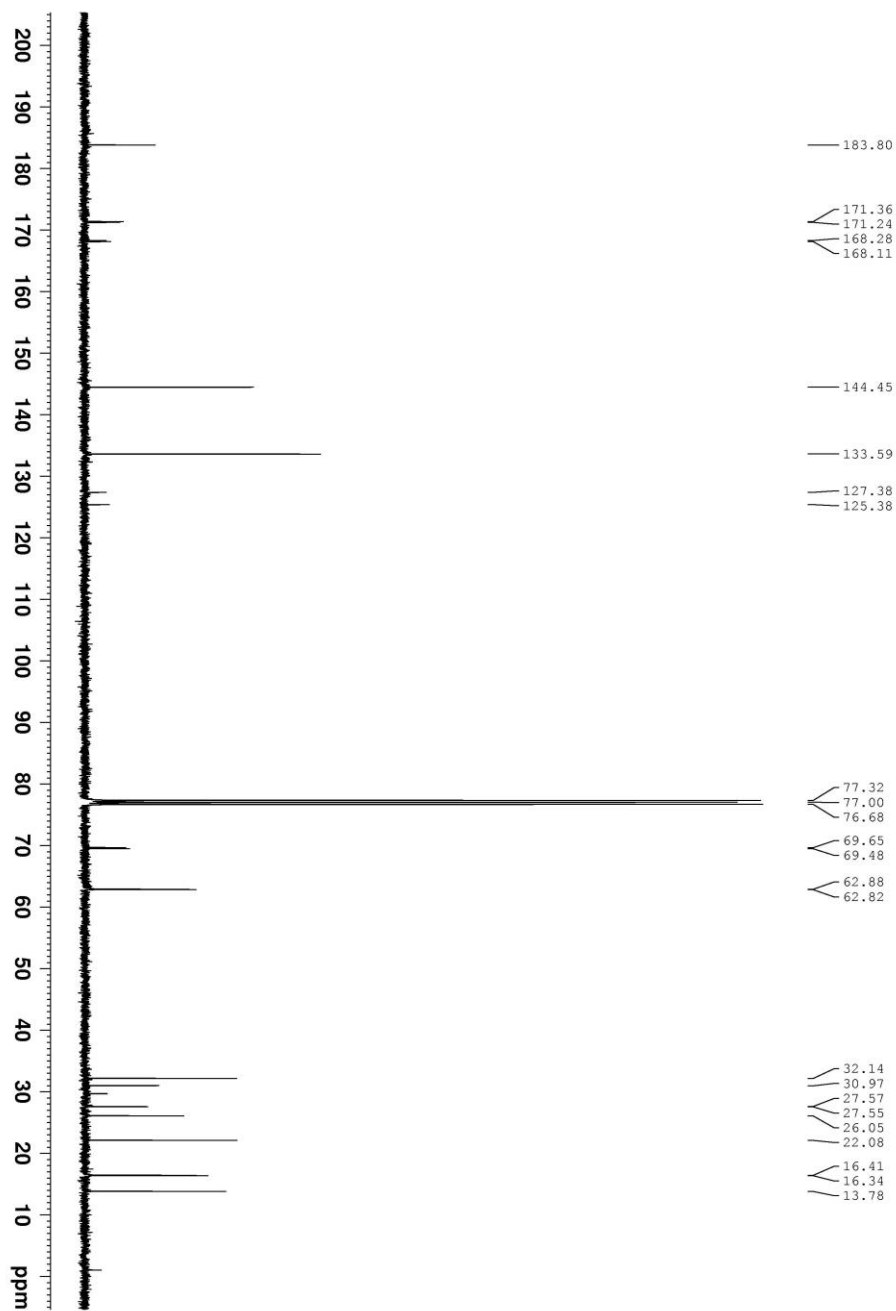


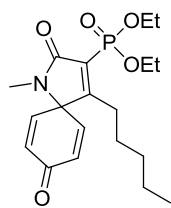
3n, 41%



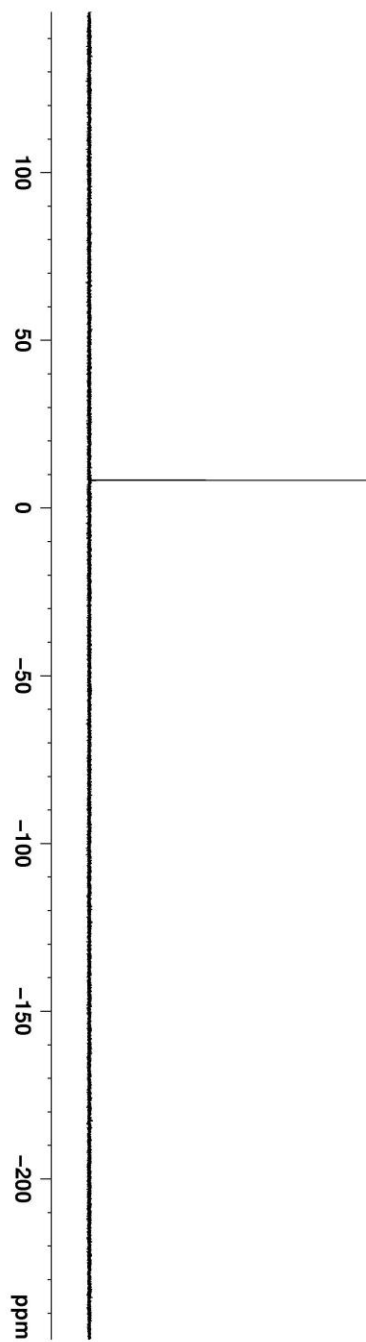


3n, 41%

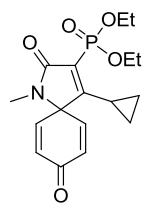




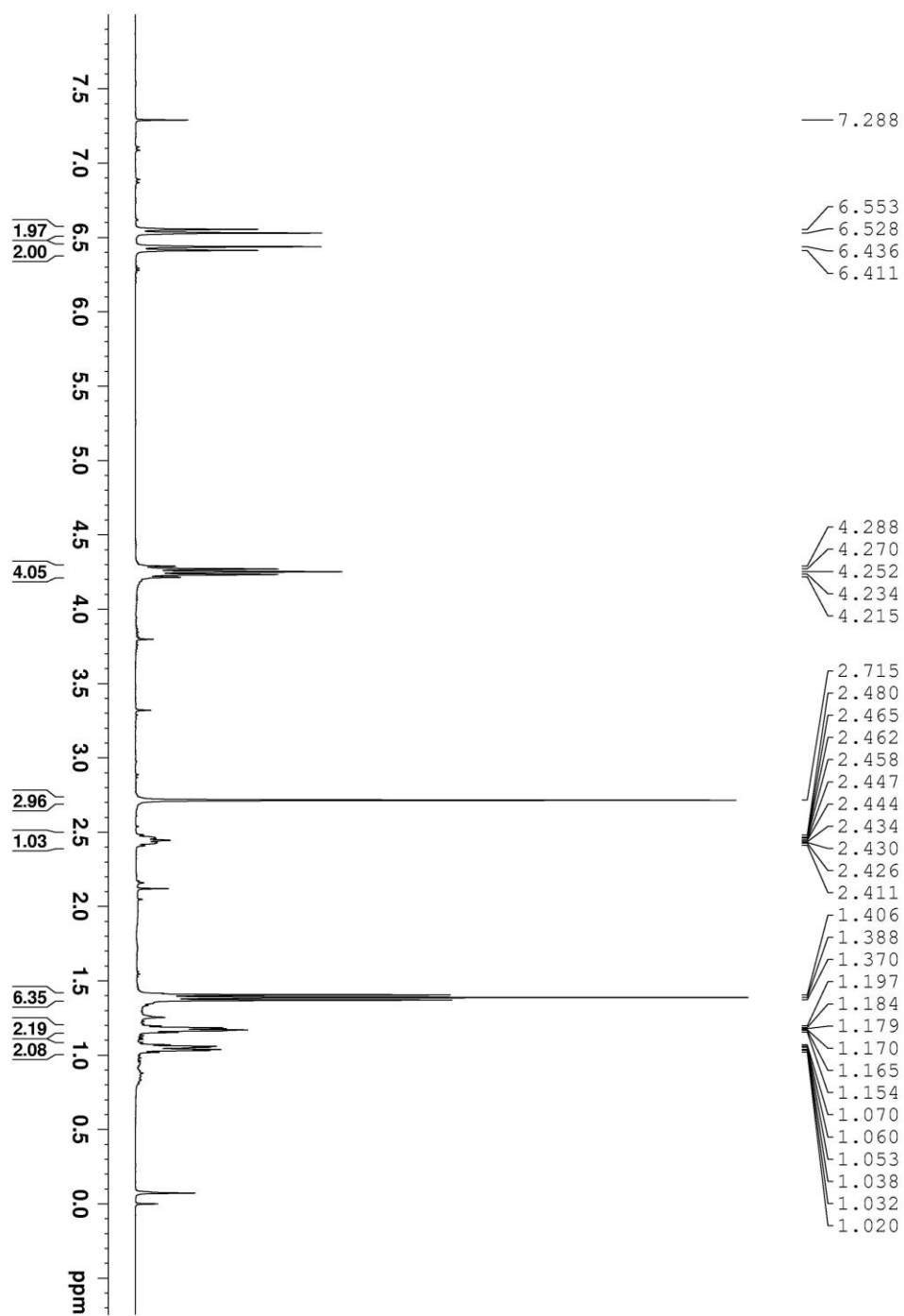
3n, 41%

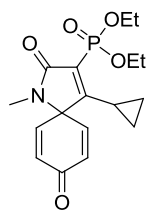


8.22

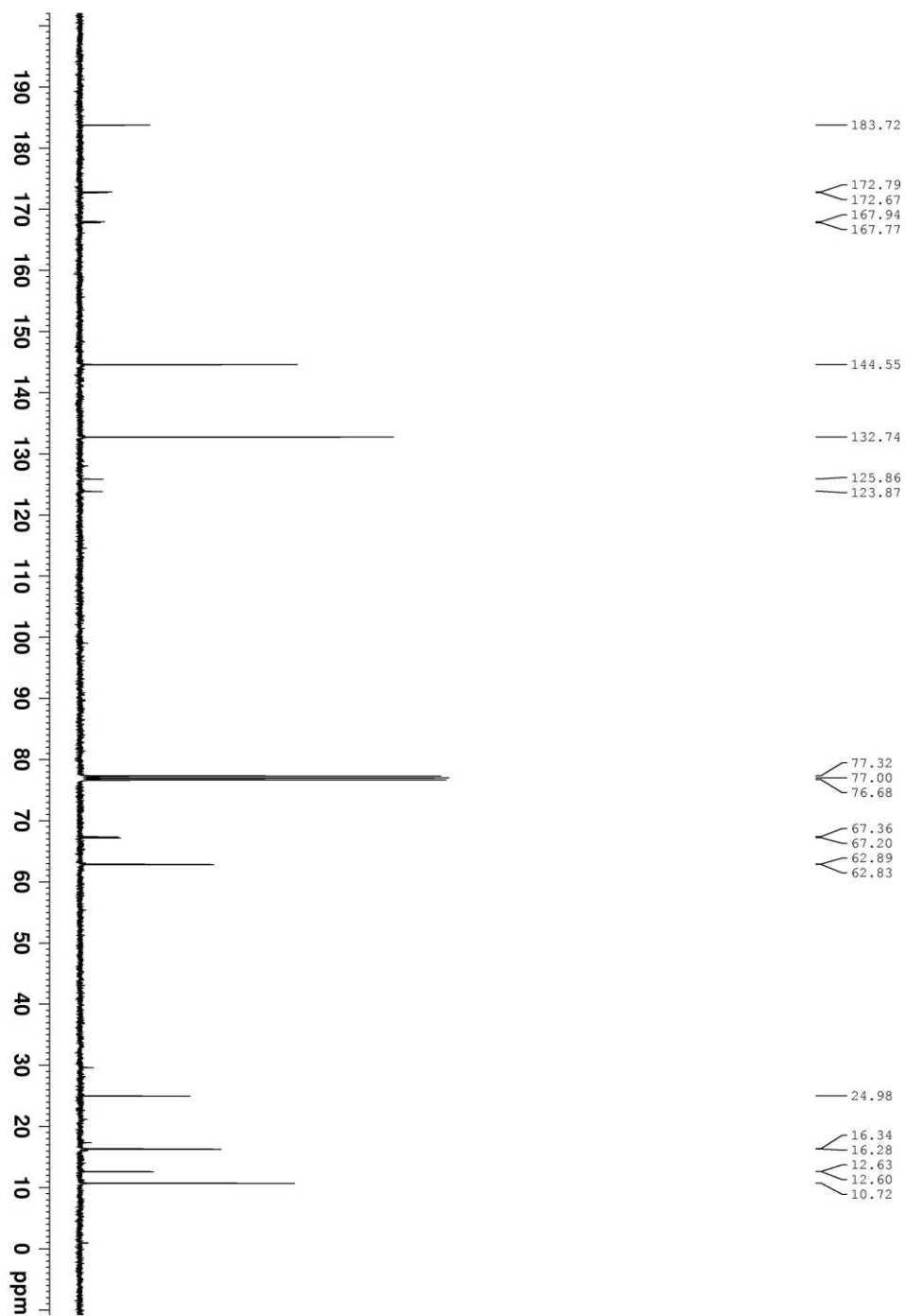


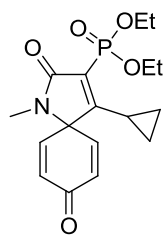
3a, 67%



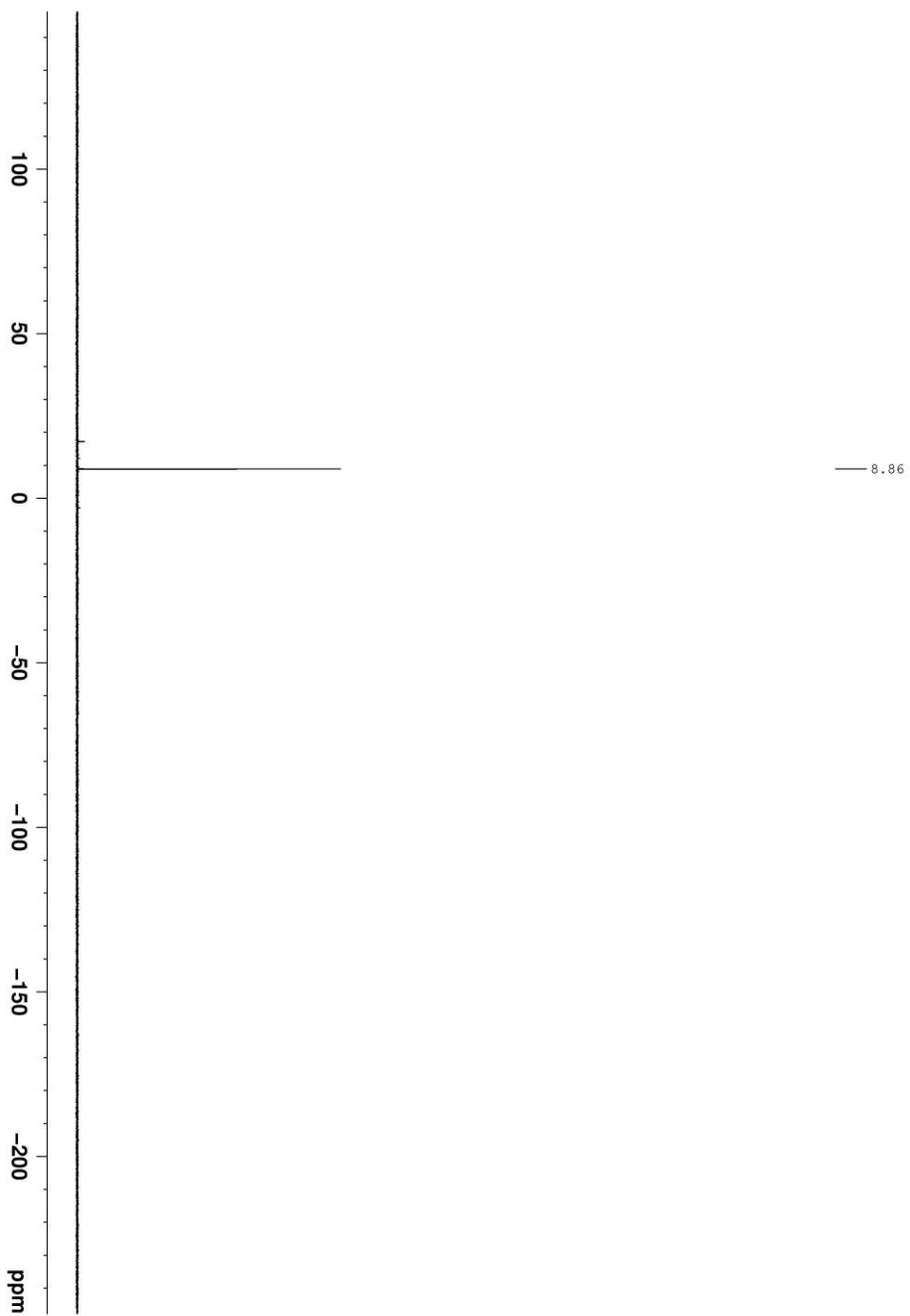


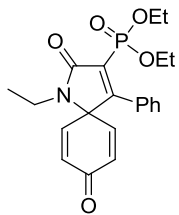
3o, 67%



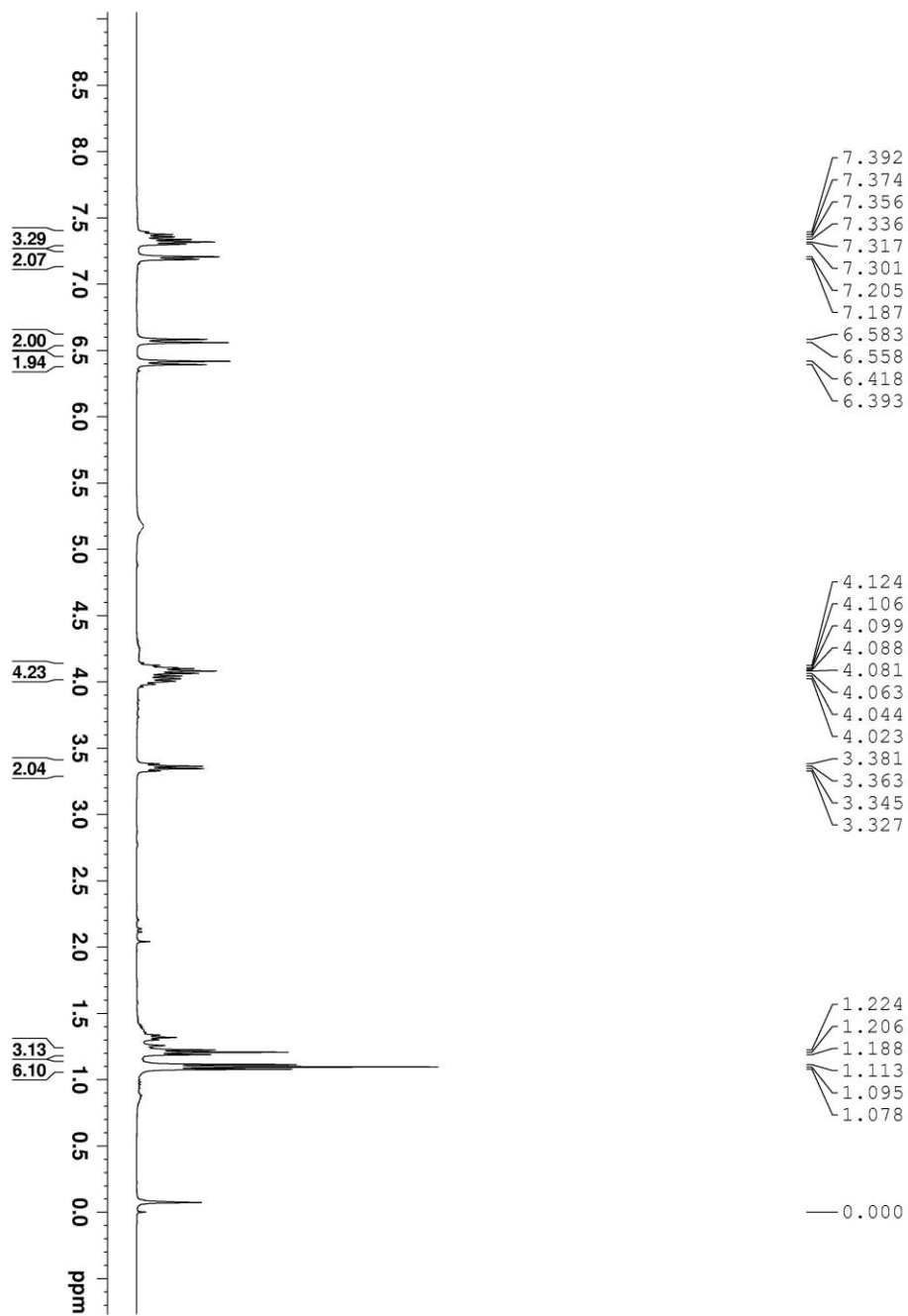


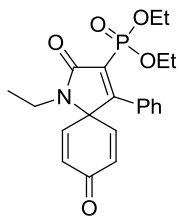
3o, 67%



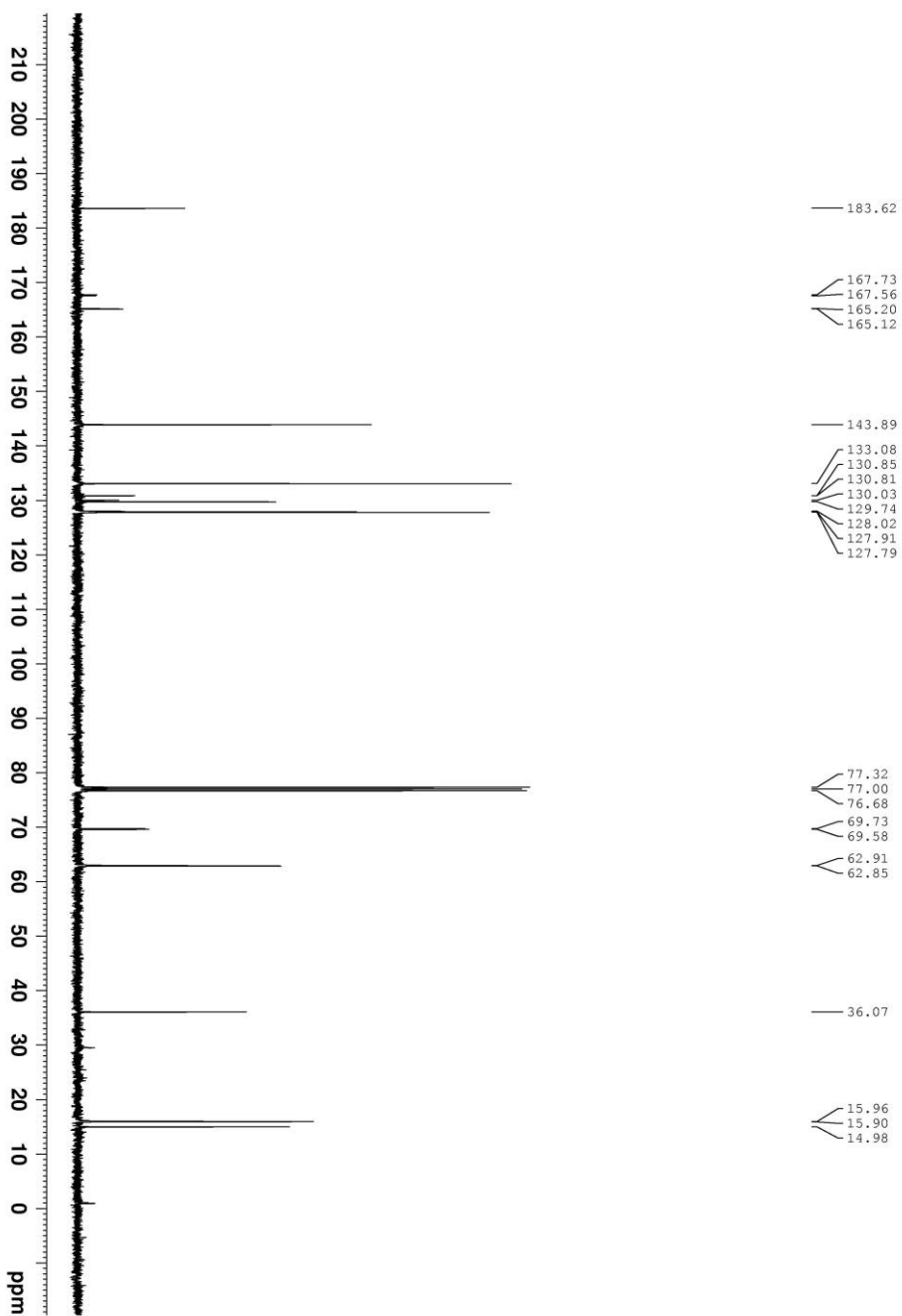


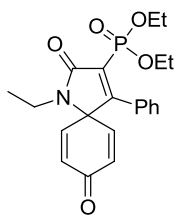
3p, 80%



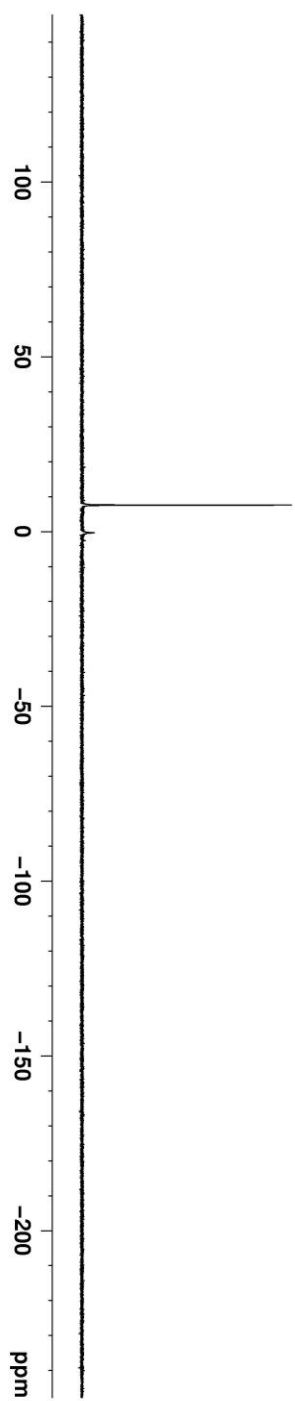


3p, 80%

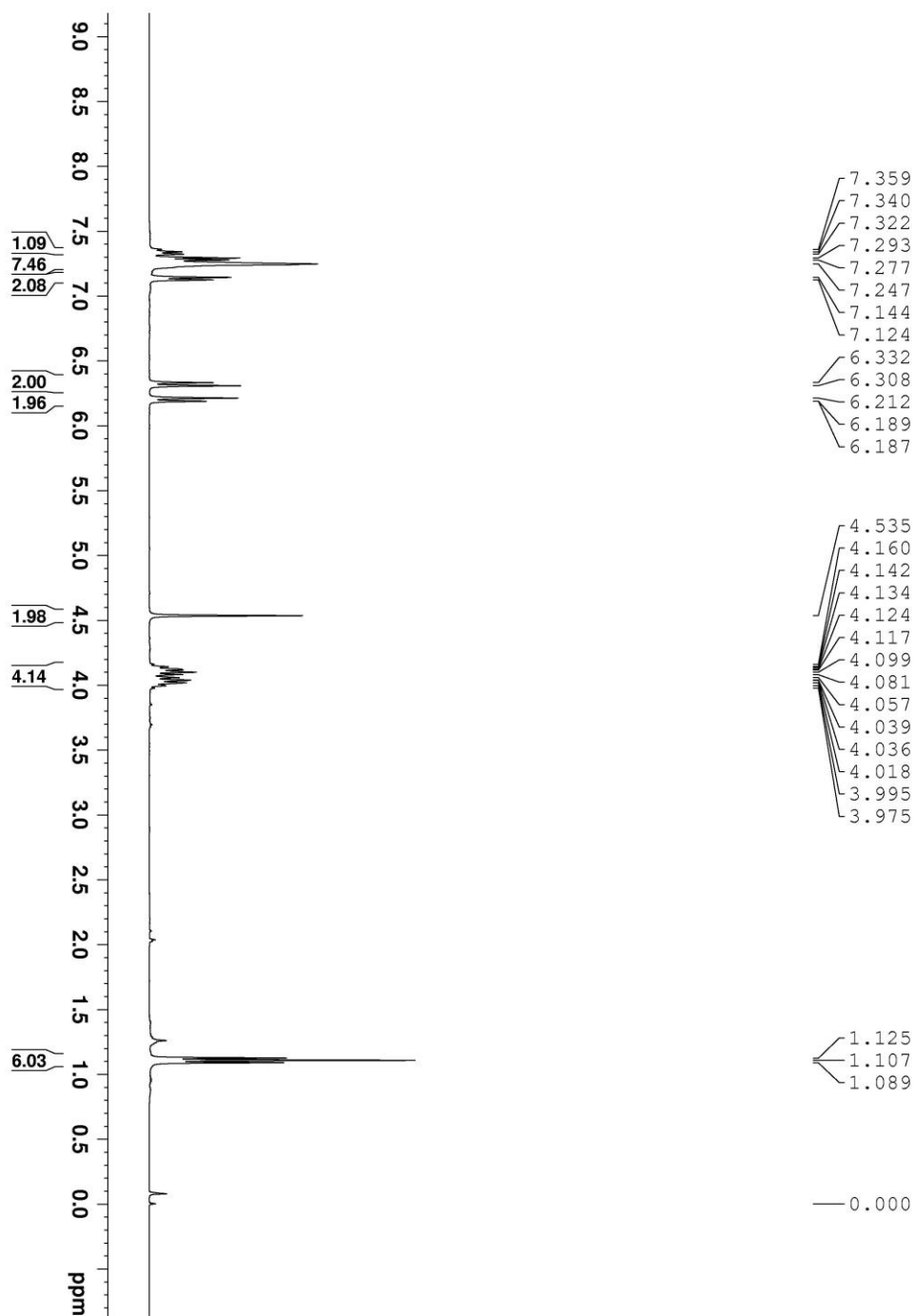
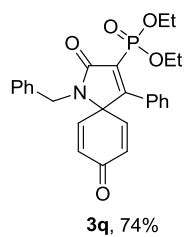


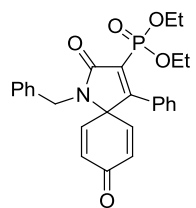


3p, 80%

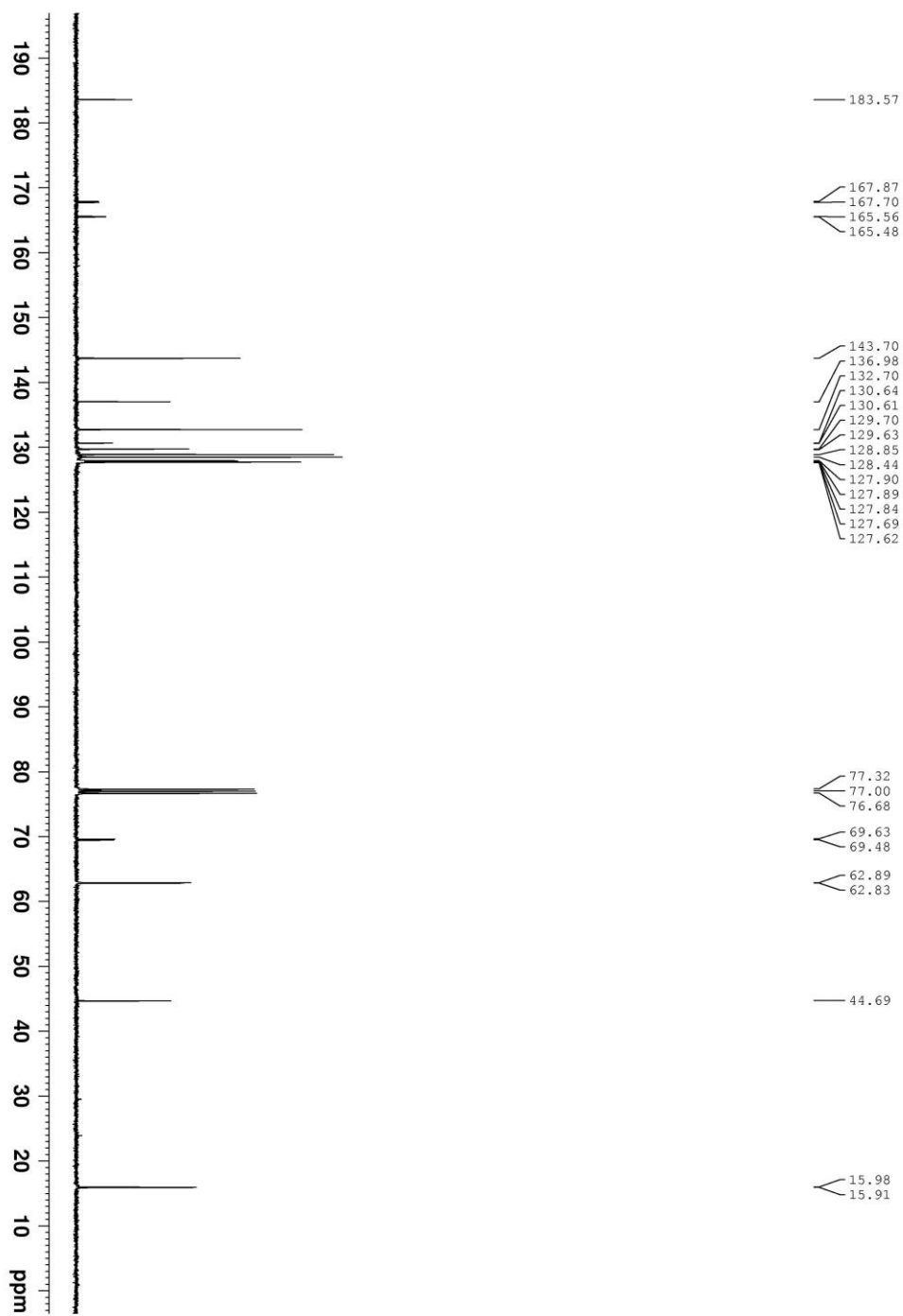


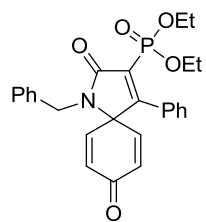
7.60



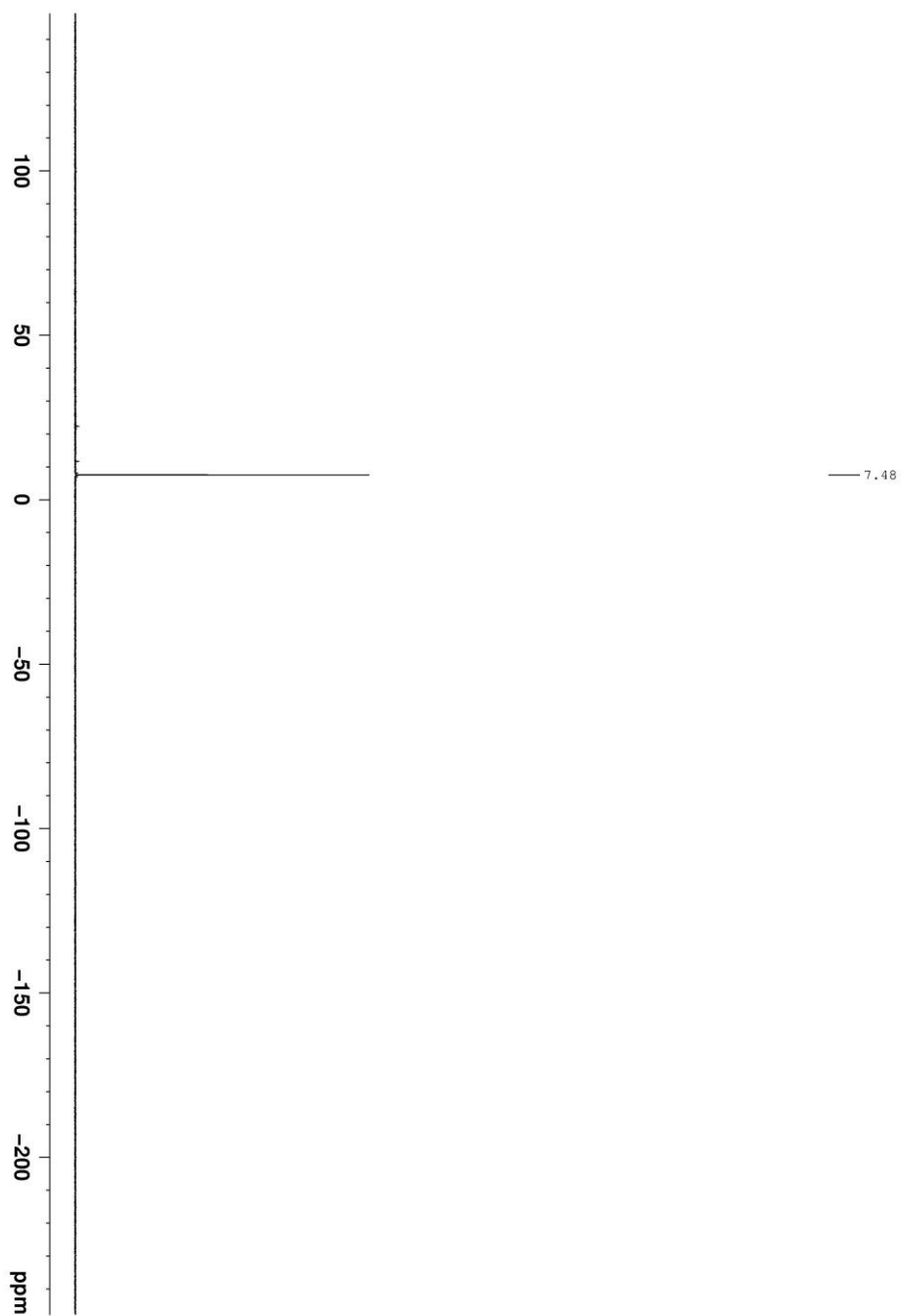


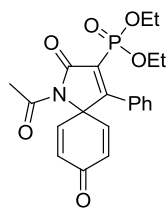
3q, 74%



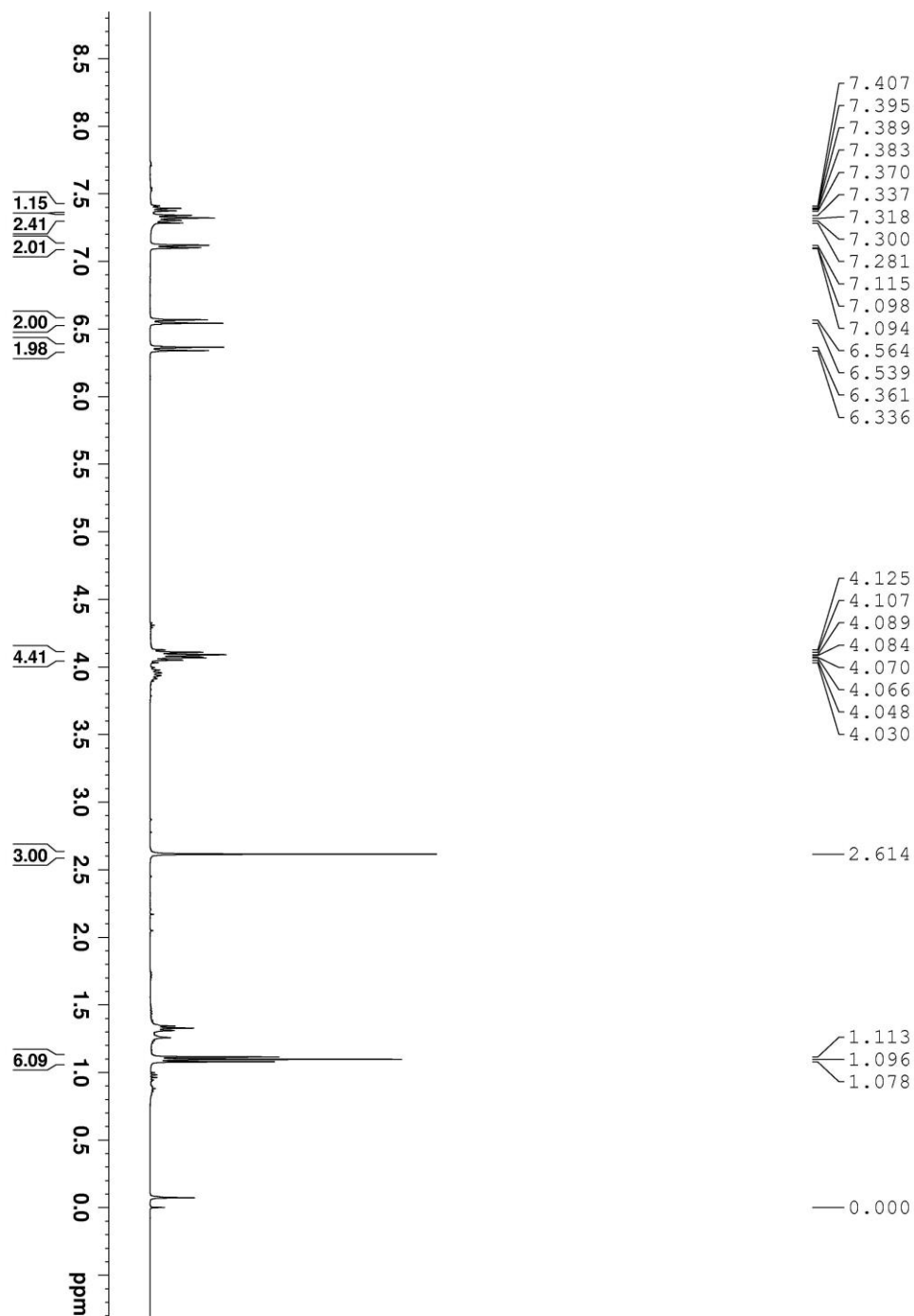


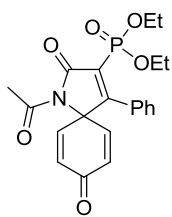
3q, 74%



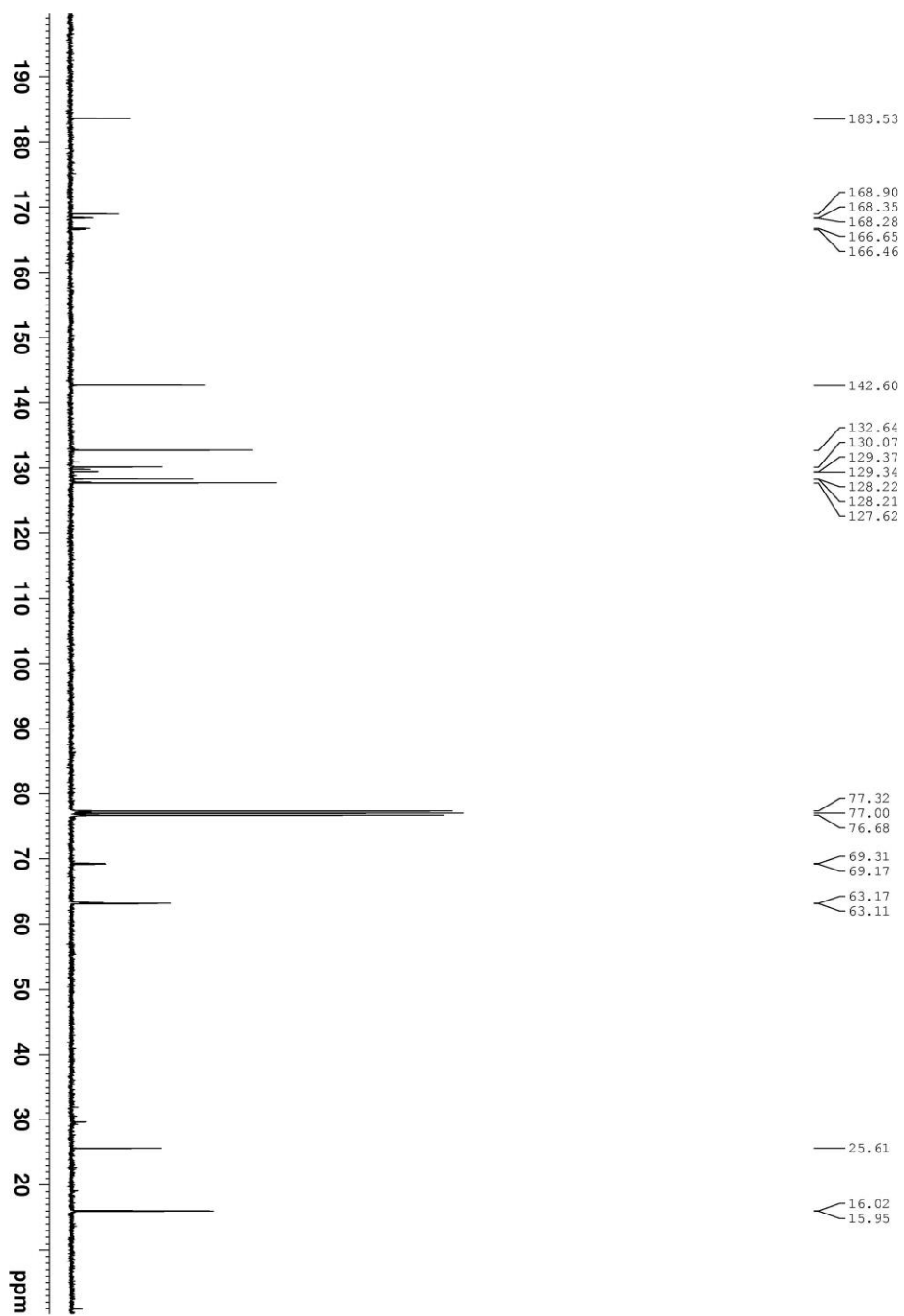


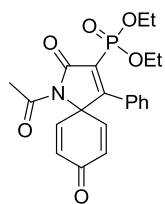
3r, 47%



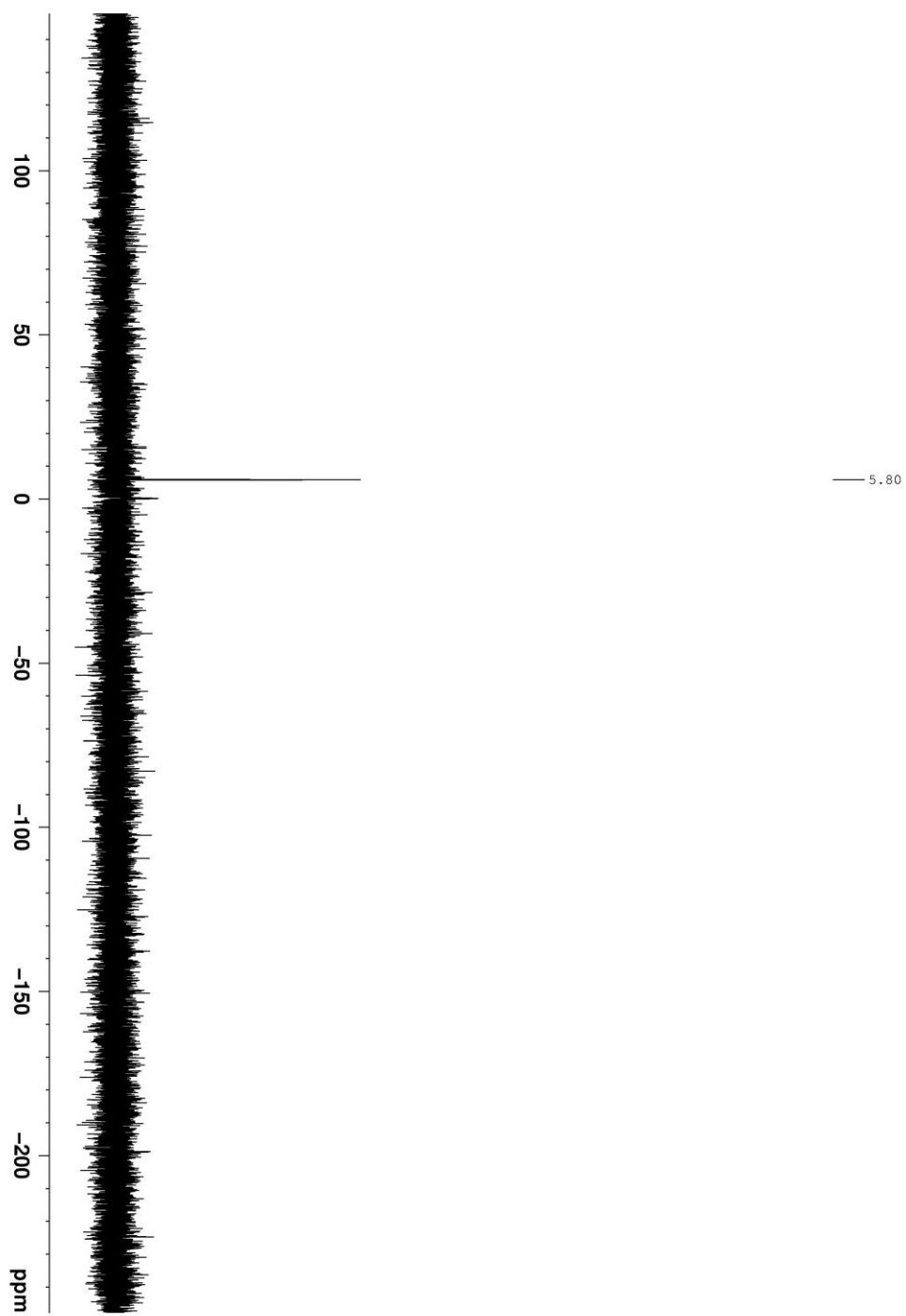


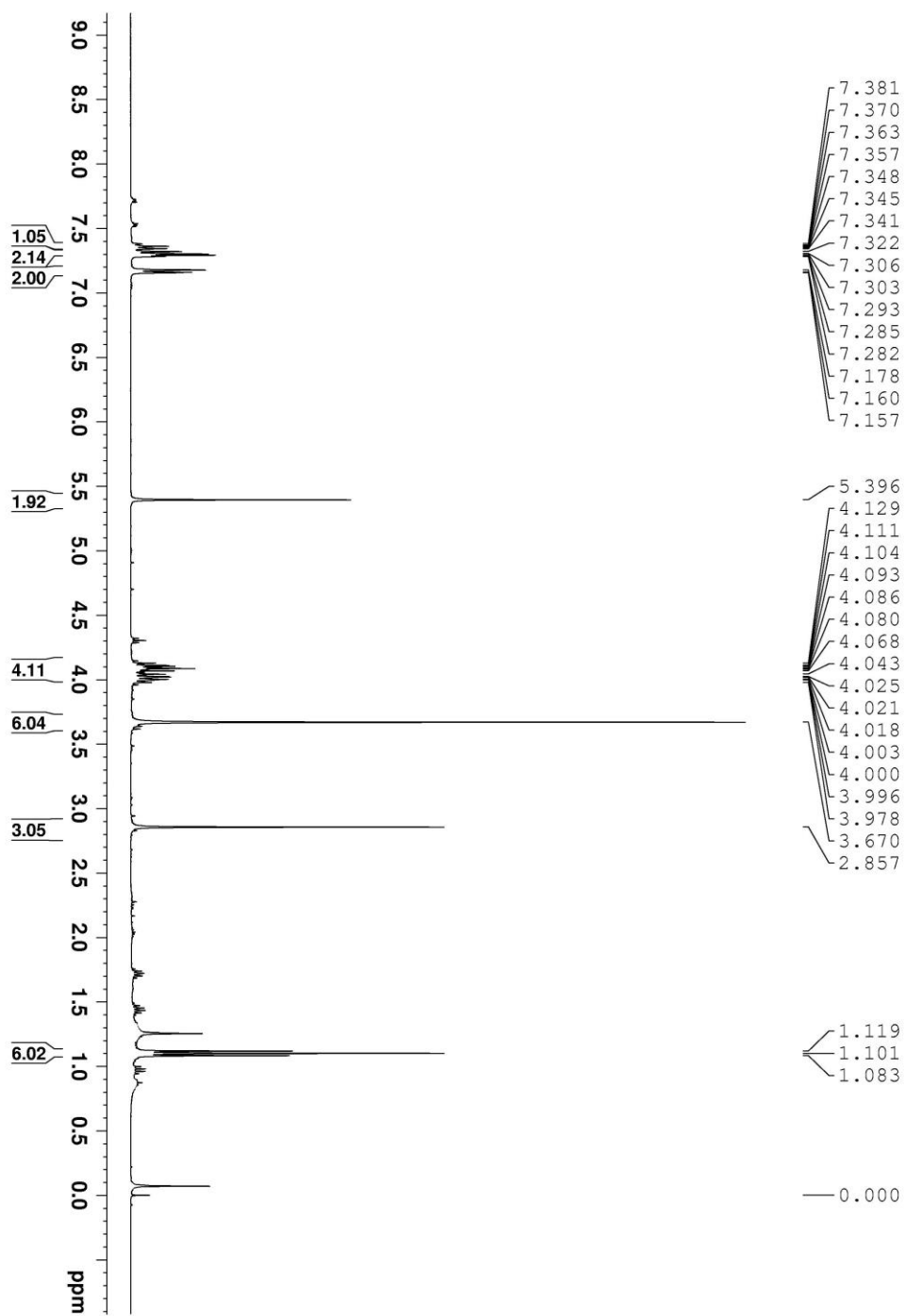
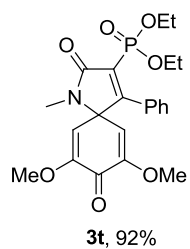
3r, 47%

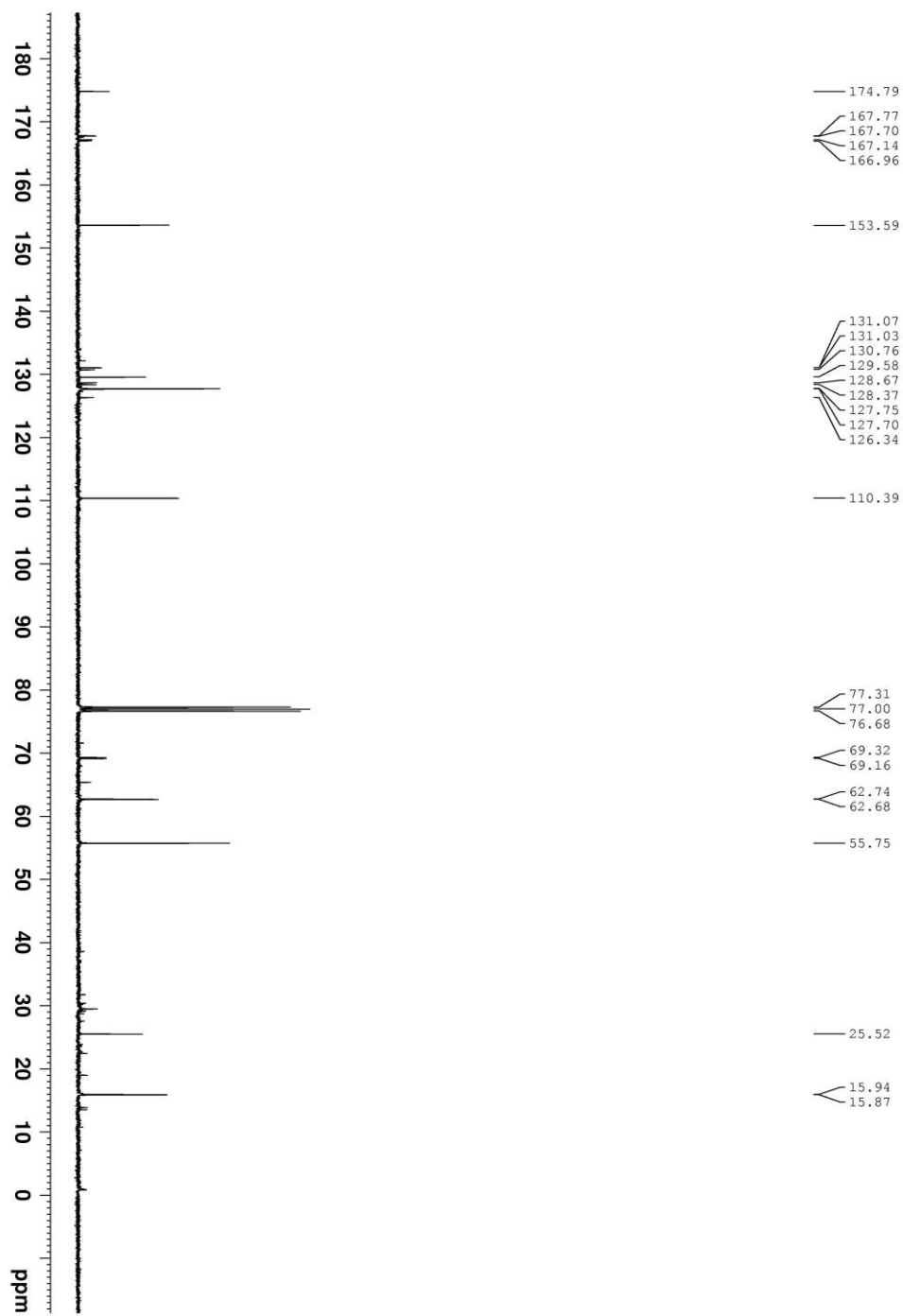
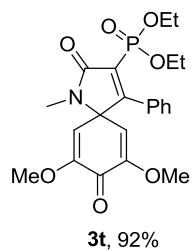


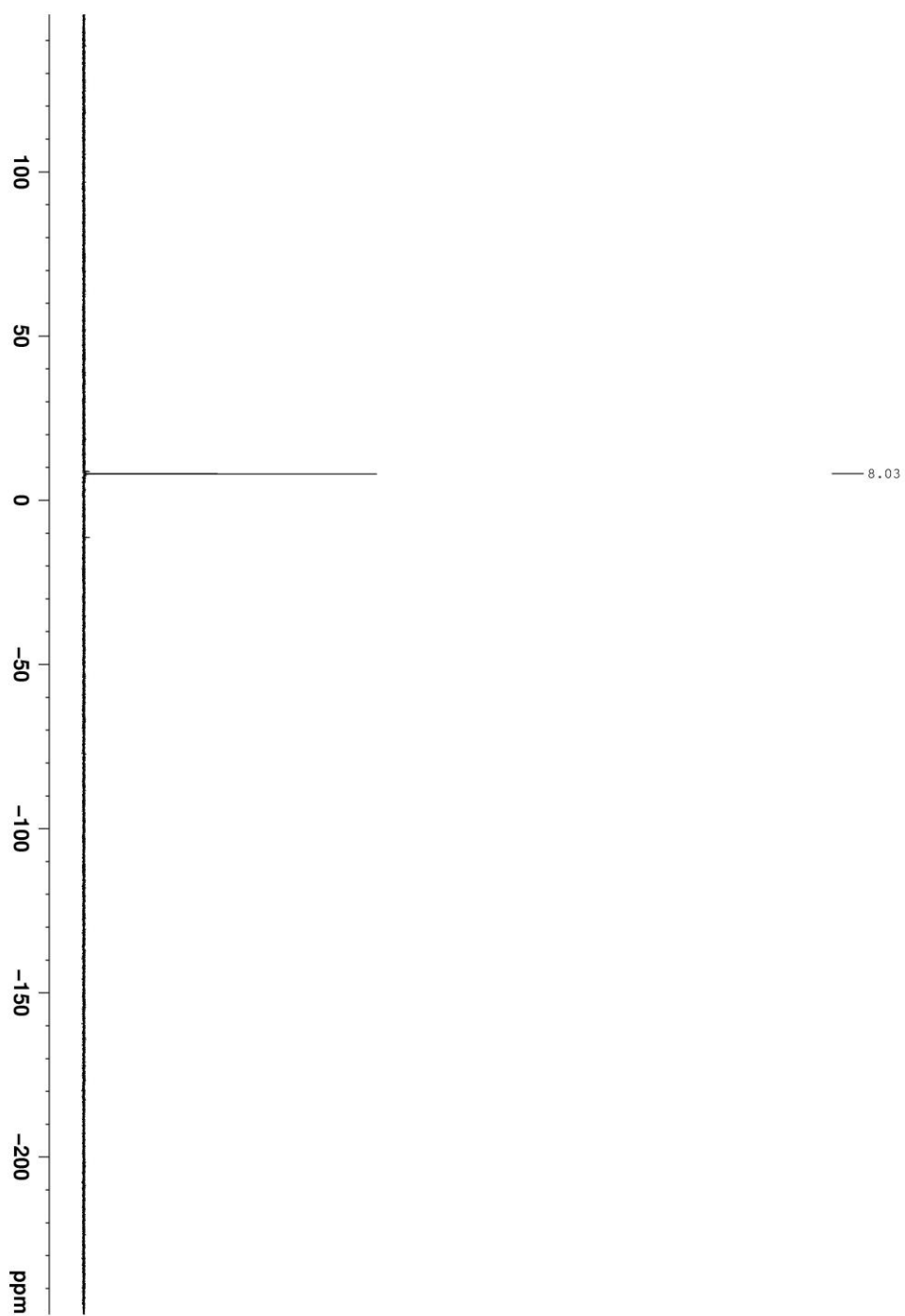
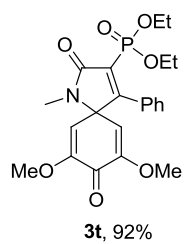


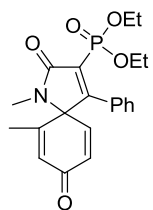
3r, 47%



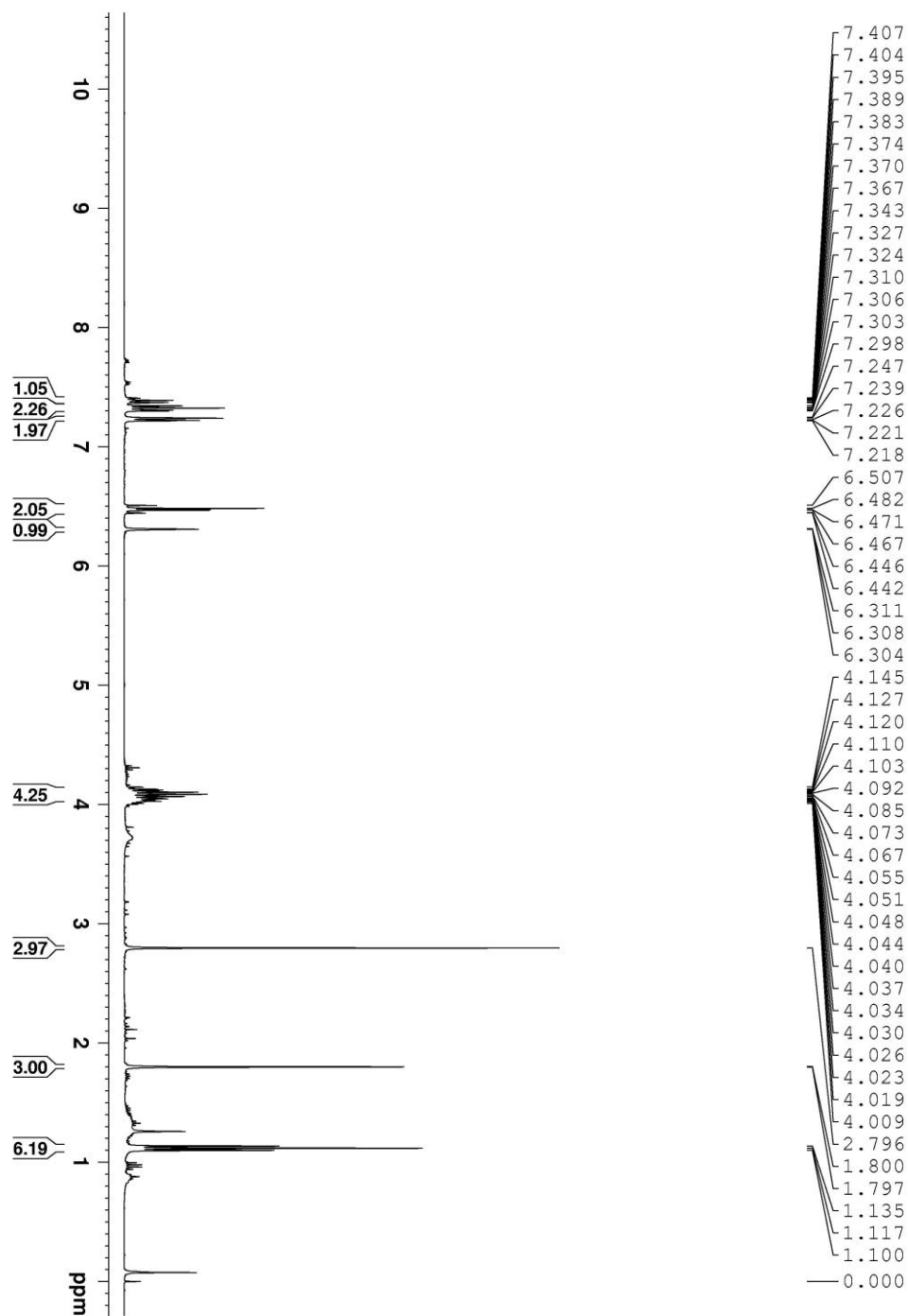


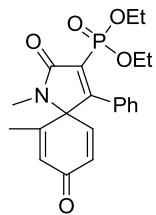




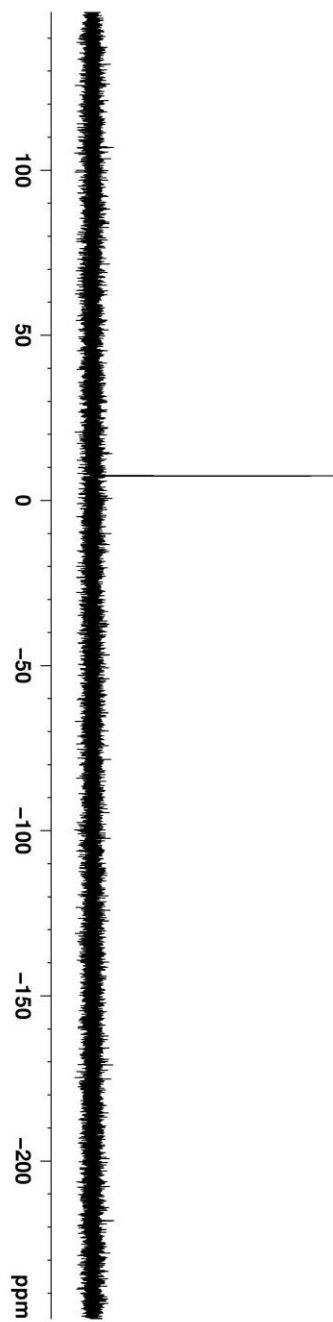


3u, 16%





3u, 16%



7.38
7.34