SUPPLEMENTARY MATERIAL

A Practical Method for Oxazole Synthesis by Cycloisomerization of Propargyl Amides

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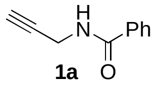
Experimental procedures and spectral data for **2a-e**, **3a**,**b**,**d**,**e**, **4a-d**, **5a**,**b**, **6a**,**b**, **7a**,**b**, **10**, **11**, **13**, **14**, **15**, **16**, **19**, **20**, **21**, **22**, **23**, including copies of ^{1}H and ^{13}C NMR spectra.

General: All reactions were performed in flamed-dried or oven-dried glassware under a dry nitrogen atmosphere. THF was distilled over Na/benzophenone ketyl; CH_2Cl_2 and Et_3N were distilled from CaH_2. Reactions were monitored by TLC analysis (EM Science pre-coated silica gel 60 F_{254} plates, 250 μM layer thickness) and visualization was accomplished with a 254 nm UV light and basic $KMnO_4$ solution (1.5 g of $KMnO_4$, 10 g of K_2CO_3 and 2.5 mL of 5% aqueous NaOH in 150 mL of water). Flash chromatography on SiO_2 (Merck, EM-9385-9, 230-400 mesh) or preparative thin-layer chromatography (Analtech, Uniplate, silica gel GF, 20 x 20 cm, 1000 μm) was used to purify the crude reaction mixtures. Silica gel mediated reactions were performed on SiO_2 from E. Merck (EM-9385-9, 230-400 mesh). Melting points were determined using a Laboratory Devices Mel-Tem II. Infrared spectra were determined on a Nicolet Avatar 360 FT-IR spectrometer. NMR spectra were recorded in $CDCl_3$ (unless otherwise noted) at either 300 MHz (^{1}H NMR) or 75 MHz (^{13}C NMR) using Bruker Avance 300 instruments with XWIN-NMR software. Mass spectra were obtained on a Micromass Autospec double focusing instrument.



1a

***N*-Prop-2-ynylbenzamide** (**1a**).[1] To a solution of 1.00 g (18.2 mmol) of propargylamine in 40 mL of CH_2Cl_2 was added 2.57 g (18.3 mmol) of benzoyl chloride and 3.00 mL (22.0 mmol) of Et_3N at 0 °C. The reaction mixture was stirred at rt for 1 h, poured into 1.0 M HCl (100 mL) and extracted with $CHCl_3$ (2 x 50 mL). The combined organic layers were washed with brine (100 mL), dried ($MgSO_4$), and concentrated under reduced pressure to afford 2.85 g (98%) of **1a** as a white solid: ^{1}H NMR δ 7.79 (d, 2 H, *J* = 7.3 Hz), 7.56-7.40 (m, 3 H), 6.35 (br, 1 H), 4.26 (dd, 2 H, *J* = 5.1, 2.5 Hz), 2.29 (t, 1 H, *J* = 2.4 Hz).

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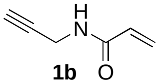
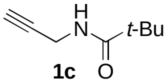
[1] Arcadi, A.; Cacchi, S.; Cascia, L.; Fabrizi, G.; Marinelli, F. *Org. Lett.* **2001**, *3*, 2501-2504.



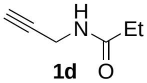
1b

***N*-Prop-2-ynylacrylamide (1b)**. According to the procedure used for the preparation of **1a**, 0.995 g (18.0 mmol) of propargylamine, 35.0 mL (25.1 mmol) of Et_3N, and 1.45 mL (17.8 mmol) of acryloyl chloride gave 0.921 g (47%) of **1b** as a white solid: R_f 0.26 (65% hexanes:EtOAc); ^1H NMR δ 6.32 (d, 1 H, *J* = 16.9 Hz), 6.11 (dd, 1 H, *J* = 17.0, 10.2 Hz), 5.82 (br, 1 H), 5.70 (d, 1 H, *J* = 10.2 Hz), 4.14 (dd, 2 H, *J* = 5.1, 2.5 Hz), 2.25 (t, 1 H, *J* = 2.3 Hz); ^{13}C NMR δ 165.4, 130.2, 127.3, 79.3, 71.7, 29.3; HRMS (EI) *m/z* calculated for C_6H_7NO (M-H) 109.0528, found 109.0524.



1c

2,2-Dimethyl-*N*-prop-2-ynylpropionamide (1c).[2] According to the procedure used for the preparation of **1a**, 0.997 g (18.1 mmol) of propargylamine, 3.50 mL (25.1 mmol) of Et_3N, and 2.16 g (17.9 mmol) of trimethylacetyl chloride gave 2.16 g (87%) of **1c** as a white solid: ^1H NMR δ 5.89 (br, 1 H), 4.06 (dd, 2 H, *J* = 5.2, 2.5 Hz), 2.25 (q, 2 H, *J* = 7.6 Hz), 2.24 (t, 1 H, *J* = 2.5 Hz), 1.17 (t, 3 H, *J* = 7.5 Hz).



1d

***N*-Prop-2-ynylpropionamide (1d)**.[3] According to the procedure used for the preparation of **1a**, 1.02 g (18.2 mmol) of propargylamine, 3.50 mL (25.1 mmol) of Et_3N, and 1.50 mL (17.3 mmol) of propionyl chloride gave 1.73 g (90%) of **1d** as a pale yellow oil: R_f 0.20 (50% hexanes:EtOAc); ^1H NMR δ 6.19 (br, 1 H), 4.04 (dd, 2 H, *J* = 5.2, 2.6 Hz), 2.25 (t, 1 H, *J* = 2.6 Hz), 1.22 (s, 9 H).

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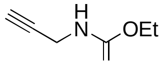
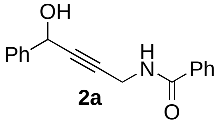
[2] Gao, G.; Sanda, F.; Masuda, T. *Macromolecules* **2003**, *36*, 3938-3943.
[3] Nomura, R.; Tabei, J.; Masuda, T. *Macromolecules* **2002**, *35*, 2955-2961.



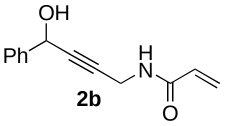
1e

Prop-2-ynylcarbamic acid ethyl ester (**1e**): According to the procedure used for the preparation of **1a**, 1.01 g (18.3 mmol) of propargylamine, 2.00 g (18.5 mmol) of ethyl chloroformate, and 3.00 mL (21.5 mmol) of Et_3N gave 2.12 g (91%) of **1e** as a yellow oil: ^{1}H NMR δ 4.80 (br, 1 H), 4.15 (q, 2 H, *J* = 7.1 Hz), 3.98 (dd, 2 H, *J* = 5.3, 2.0 Hz), 2.24 (t, 1 H, *J* = 2.5 Hz), 1.25 (t, 3 H, *J* = 7.1 Hz).



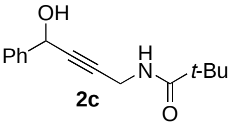
2a

***N*-(4-Hydroxy-4-phenylbut-2-ynyl)-benzamide** (**2a**). A solution of 2.85 g (17.9 mmol) of **1a** in 60 mL of THF was treated at –78 °C with 23.0 mL (36.8 mmol) of a 1.0 M solution of *n*-BuLi in THF, stirred for 30 min at –78 °C, treated with a solution of 1.59 g (15.0 mmol) of benzaldehyde in 10 mL of THF, warmed to 0 °C over 1 h, and stirred for 3.5 h. The reaction mixture was quenched with 1.0 M HCl (100 mL) and extracted with EtOAc (2 x 100 mL). The combined organic layers were washed with brine (100 mL), dried ($MgSO_4$), concentrated under reduced pressure, and chromatographed on SiO_2 (60% hexanes:EtOAc) to give 2.15 g (52%) of **2a** as a white solid: R_f 0.33 (50% hexanes:EtOAc); mp 91.5-92.0 °C (hexanes/EtOAc); IR (neat) 3370, 3217, 2244, 1634, 1538, 1435, 1304, 1125, 1015 cm^{-1}; ^{1}H NMR δ 7.74 (d, 2 H, *J* = 7.1 Hz), 7.58-7.28 (m, 8 H), 6.58 (br, 1 H), 5.47 (s, 1 H), 4.30-4.25 (m, 2 H, *J* = 5.1, 1.6 Hz), 3.21 (br 1 H); ^{13}C NMR δ 167.3, 140.4, 133.6, 131.8, 128.6, 128.6, 128.4, 127.1, 126.6, 83.6, 82.1, 64.5, 30.1; MS (EI) *m/z* (rel intensity) 265 (M$^+$, 0.8), 264 (4), 248 (4), 247 (5), 231 (3), 219 (2), 191 (4), 162 (2), 122 (18), 105 (100); HRMS (EI) *m/z* calculated for $C_{17}H_{14}NO_2$ (M-H) 264.1025, found 264.1028.



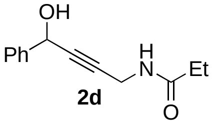
2b

***N*-(4-Hydroxy-4-phenylbut-2-ynyl)-acrylamide** (**2b**). A solution of 0.511 g (4.68 mmol) of **1b** in 30 mL of THF was treated at –78 °C with 5.80 mL (9.30 mmol) of a 1.6 M solution of *n*-BuLi in hexane, stirred for 15 min at –78 °C, treated with a solution of 0.481 g (4.53 mmol) of benzaldehyde in 1 mL of THF, warmed to 0 °C over 1 h, and stirred for 1 h. The reaction mixture was quenched with 1.0 M HCl (40 mL) and extracted with EtOAc (2 x 25 mL). The combined organic layers were washed with brine (40 mL), dried ($MgSO_4$), concentrated under reduced pressure, and chromatographed on SiO_2 (65%-40% hexanes:EtOAc) to afford 0.697 g (71%) of **2b** as a colorless oil: R_f 0.15 (50% hexanes:EtOAc); IR (neat) 3313, 3066, 2924, 2243, 1655, 1542, 1451, 1248, 1133, 1004 cm^{-1}; ^{1}H NMR δ 7.52 (dd, 2 H, *J* = 7.8, 1.6 Hz), 7.43-7.32 (m, 3 H), 6.32 (dd, 1 H, *J* = 17.0, 1.3 Hz), 6.08 (dd, 1 H, *J* = 17.0, 10.3 Hz), 5.70 (br, 1 H), 5.69 (dd, 1 H, *J* = 10.3, 1.2 Hz), 5.49 (br, 1 H), 4.25-4.23 (m, 2 H), 2.17 (br, 1 H); ^{13}C NMR δ 165.6, 140.4, 130.0, 128.6, 128.4, 127.4, 126.6, 83.5, 81.8, 64.3, 29.6; MS (EI) *m/z* (rel intensity) 215 (M$^+$, 3), 214 (18), 198 (7), 197 (15), 169 (12), 168 (10), 144 (47), 143 (30), 131 (26), 116 (25), 115 (49), 105 (23); HRMS (EI) *m/z* calculated for $C_{13}H_{12}NO_2$ (M-H) 214.0868, found 214.0867.



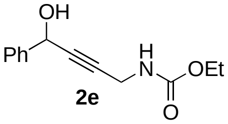
2c

***N*-(4-Hydroxy-4-phenylbut-2-ynyl)-2,2-dimethylpropionamide** (**2c**). A solution of 1.05 g (7.57 mmol) of **1c** in 30 mL of THF was treated at –78 °C with 10.0 mL (16.0 mmol) of a 1.6 M solution of *n*-BuLi in THF, stirred for 30 min at –78 °C, treated with a solution of 0.852 g (8.03 mmol) of benzaldehyde, warmed to rt over 1 h, and stirred for 2.5 h. The reaction mixture was quenched with 1.0 M HCl (100 mL) and extracted with EtOAc (2 x 75 mL). The combined organic layers were washed with brine (50 mL), dried ($MgSO_4$), concentrated under reduced pressure, and chromatographed on SiO_2 (80%-35% hexanes:EtOAc) to give 0.932 g (50%) of **2c** as a yellow oil: R_f 0.32 (50% hexanes:EtOAc); IR (neat) 3357, 3063, 2967, 2249, 1655, 1528, 1452, 1208, 1130, 1002 cm^{-1}; ^{1}H NMR δ 7.51 (d, 2 H, *J* = 6.9 Hz), 7.40-7.27 (m, 3 H), 6.01 (br, 1 H), 5.46 (s, 1 H), 4.08-4.06 (m, 2 H), 3.59 (br, 1 H), 1.17 (s, 9 H); ^{13}C NMR δ 178.5, 140.6, 128.5, 128.3, 126.6, 83.5, 82.2, 64.3, 38.6, 29.9, 27.4; MS (EI) *m/z* (rel intensity) 245 (M$^+$, 0.7), 244 (5), 228 (3), 227 (4), 212 (5), 199 (2), 184 (3), 144 (18), 105 (43), 102 (32); HRMS (EI) *m/z* calculated for $C_{15}H_{18}NO_2$ (M-H) 244.1338, found 244.1336.



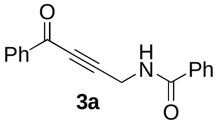
2d

***N*-(4-Hydroxy-4-phenylbut-2-ynyl)-propionamide** (**2d**). A solution of 0.0970 g (0.873 mmol) of **1d** in 5 mL of THF was treated at –78 °C with 1.80 mL (1.80 mmol) of a 1.0 M solution of LiHMDS in THF, stirred for 15 min at –78 °C, treated with a solution of 0.0967 mg (0.911 mmol) of benzaldehyde in 1 mL of THF, warmed to 0 °C over 1 h, and stirred for 1 h. The reaction mixture was quenched with 1.0 M HCl (10 mL) and extracted with EtOAc (2 x 10 mL). The combined organic layers were washed with brine (10 mL), dried ($MgSO_4$), concentrated under reduced pressure, and purified by chromatography on SiO_2 (85%-40% hexanes:EtOAc) to yield 0.0994 g (52%) of **2d** as a yellow oil: R_f 0.13 (50% hexanes:EtOAc); IR (neat) 3293, 3064, 2979, 2244, 1654, 1542, 1458, 1233, 1133, 1000 cm^{-1}; ^{1}H NMR δ 7.50 (dd, 2 H, *J* = 8.1, 1.7 Hz), 7.40-7.27 (m, 3 H), 6.12 (br, 1 H), 5.45 (s, 1 H), 4.07-4.05 (m, 1 H), 3.75 (br, 1 H), 2.15 (q, 2 H, *J* = 7.6 Hz), 1.10 (t, 3 H , *J* = 7.6 Hz); ^{13}C NMR δ 173.9, 140.6, 128.6, 128.3, 126.6, 83.3, 82.1, 64.3, 29.5, 29.3, 9.6; MS (EI) *m/z* (rel intensity) 217 (M$^+$, 6), 216 (47), 200 (17), 161 (15), 160 (10), 144 (88), 143 (100), 116 (47), 115 (77), 105 (43); HRMS (EI) *m/z* calculated for $C_{13}H_{14}NO_2$ (M-H) 216.1025, found 216.1023.



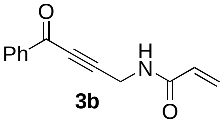
2e

(4-Hydroxy-4-phenylbut-2-ynyl)-carbamic acid ethyl ester (**2e**). A solution of 2.12 g (16.7 mmol) of **1e** in 60 mL of THF was treated at –78 °C with 21.0 mL (33.6 mmol) of a 1.6 M solution of *n*-BuLi in hexane, stirred for 15 min at –78 °C, treated with a solution of 1.49 g (14.1 mmol) of benzaldehyde in 1 mL of THF, warmed to 0 °C over 1 h, and stirred for 1 h. The reaction mixture was quenched with 1.0 M HCl (100 mL) and extracted with EtOAc (2 x 100 mL). The combined organic layers were washed with brine (100 mL), dried ($MgSO_4$), concentrated under reduced pressure, and purified by column chromatography on SiO_2 (65%-50% hexanes:EtOAc) to yield 2.73 g (83%) of **2e** as a pale yellow oil: R_f 0.39 (50% hexanes:EtOAc); IR (neat) 3337, 3063, 2982, 2238, 1686, 1560, 1451, 1254, 1117, 1041 cm^{-1}; ^1H NMR δ 7.52 (dd, 2 H, *J* = 7.8, 1.3 Hz), 7.42-7.30 (m, 3 H), 5.47 (s, 1 H), 4.86 (br, 1 H), 4.11 (q, 2 H, *J* = 7.1 Hz), 4.06 (d, 2 H, *J* = 5.0 Hz), 2.42 (br, 1 H), 1.25 (t, 3 H, *J* = 7.1 Hz); ^{13}C NMR δ 156.4, 140.5, 128.6, 128.3, 126.6, 83.2, 82.4, 64.3, 61.4, 31.0, 14.6; MS (EI) *m/z* (rel intensity) 233 (M^+, 10), 232 (52), 216 (18), 215 (21), 204 (34), 144 (99), 143 (44), 131 (49), 116 (53), 115 (100), 105 (78); HRMS (EI) *m/z* calculated for $C_{13}H_{14}NO_3$ (M-H) 232.0974, found 232.0975.



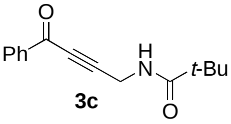
3a

***N*-(4-Oxo-4-phenylbut-2-ynyl)-benzamide** (**3a**). A mixture of 0.569 g (2.15 mmol) of **2a** and 1.00 g (2.36 mmol) of Dess-Martin reagent in 10 mL of CH_2Cl_2 was stirred at rt for 15 h, concentrated under reduced pressure, and purified by chromatography on SiO_2 (90%-65% hexanes:EtOAc) to yield 0.404 g (71%) of **3a** as a white solid and 0.085 g (*ca*. 15%) of crude oxazole **4a** as a yellow oil. **3a**: R_f 0.32 (65% hexanes:EtOAc); mp 111.0-111.5 °C (hexanes/EtOAc); IR (neat) 3270, 2238, 2203, 1635, 1526, 1406, 1266, 966 cm^{-1}; ^1H NMR δ 8.13 (dd, 2 H, *J* = 7.8, 1.3 Hz), 7.83 (dd, 2 H, *J* = 7.7, 1.4 Hz), 7.66-7.40 (m, 6 H), 6.61 (br, 1 H), 4.57 (d, 2 H, *J* = 5.3 Hz); ^{13}C NMR δ 177.7, 167.2, 136.3, 134.4, 133.4, 132.1, 129.7, 128.7, 128.7, 127.1, 89.8, 81.3, 30.0; MS (EI) *m/z* (rel intensity) 263 (M^+, 6), 235 (6), 206 (6), 160 (27), 158 (35), 130 (7), 106 (14), 105 (100), 104 (9); HRMS (EI) *m/z* calculated for $C_{17}H_{13}NO_2$ 263.0946, found 263.0945.



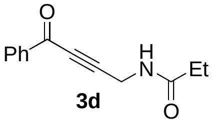
3b

***N*-(4-Oxo-4-phenylbut-2-ynyl)-acrylamide** (**3b**). A mixture of 0.249 g (1.16 mmol) of **2b** and 0.541 g (1.28 mmol) of Dess-Martin reagent in 5 mL of CH_2Cl_2 was stirred at rt for 15 h, concentrated under reduced pressure, and purified by chromatography on SiO_2 (80%-50% hexanes:EtOAc) to yield 0.210 g (84%) of **3b** as a white amorphous solid: R_f 0.43 (50% hexanes:EtOAc); IR (neat) 3257, 3052, 2244, 2198, 1634, 1621, 1538, 1504, 1405, 1312, 1270, 1239, 971 cm^{-1}; ^1H NMR δ 8.12 (dd, 2 H, *J* = 7.8, 1.4 Hz), 7.63 (tt, 1 H, *J* = 7.4, 1.3 Hz), 7.49 (t, 2 H, *J* = 7.8 Hz), 6.38 (dd, 1 H, *J* = 17.0, 1.4 Hz), 6.16 (dd, 1 H, *J* = 17.0, 10.2 Hz), 6.10 (br, 1 H), 5.75 (dd, 1 H, *J* = 10.2, 1.4 Hz), 4.46 (d, 2 H, *J* = 5.5 Hz); ^{13}C NMR δ 177.7, 165.3, 136.2, 134.5, 129.8, 129.7, 128.7, 127.9, 89.8, 81.1, 29.5; MS (EI) *m/z* (rel intensity) 263 (M^+, 6), 235 (6), 206 (6), 160 (27), 158 (35), 130 (7), 106 (14), 105 (100), 104 (9); HRMS (EI) *m/z* calculated for $C_{17}H_{13}NO_2$ 263.0946, found 263.0945.



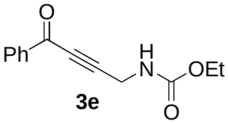
3c

2,2-Dimethyl-*N*-(4-oxo-4-phenyl-but-2-ynyl)-propionamide (**3c**). A mixture of 0.527 g (2.15 mmol) of **2c** and 1.21 g (2.76 mmol) of Dess-Martin reagent in 10 mL of CH_2Cl_2 was stirred at rt for 24 h, concentrated under reduced pressure, and purified by chromatography on SiO_2 to yield 0.435 g (83%) of crude **3c** as a yellow oil that was used without further purification: R_f 0.55 (50% hexanes:EtOAc); ^1H NMR δ 8.12 (d, 2 H, *J* = 7.8 Hz), 7.62 (t, 1 H, *J* = 7.0 Hz), 7.48 (t, 2 H, *J* = 7.3 Hz), 6.07 (br, 1 H), 4.36 (d, 2 H, *J* = 5.3 Hz), 1.25 (s, 9 H).



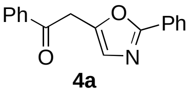
3d

***N*-(4-Oxo-4-phenylbut-2-ynyl)-propionamide** (**3d**). A mixture of 0.247 g (1.14 mmol) of **2d** and 0.556 g (1.31 mmol) of Dess-Martin reagent in 5 mL of CH_2Cl_2 was stirred at rt for 15 h, concentrated under reduced pressure, and purified by chromatography on SiO_2 to yield 0.172 g (70%) of **3d** as a yellow amorphous solid: R_f 0.19 (50% hexanes:EtOAc); IR (neat) 3292, 3068, 2976, 2238, 2218, 1643, 1539, 1455, 1260, 1096, 1025 cm^{-1}; ^1H NMR δ 8.12 (dd, 2 H, *J* = 7.8, 1.4 Hz), 7.63 (t, 1 H, *J* = 7.4 Hz), 7.49 (t, 2 H, *J* = 7.7 Hz), 5.83 (br, 1 H), 4.38 (d, 2 H, *J* = 5.4 Hz), 2.29 (q, 2 H, *J* = 7.6 Hz), 1.20 (t, 3 H, *J* = 7.6 Hz); ^{13}C NMR δ 177.9, 174.0, 136.2, 134.4, 129.7, 128.6, 90.8, 80.7, 29.3, 29.3, 9.7; MS (EI) *m/z* (rel intensity) 215 (M^+, 5), 187 (6), 160 (52), 159 (83), 158 (53), 130 (57), 115 (47), 105 (100); HRMS (EI) *m/z* calculated for $C_{13}H_{13}NO_2$ 215.0946, found 215.0938.



3e

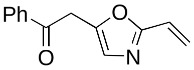
(4-Oxo-4-phenylbut-2-ynyl)-carbamic acid ethyl ester (**3e**). A mixture of 0.531 g (2.28 mmol) of **2e** and 1.06 g (2.50 mmol) of Dess-Martin reagent in 10 mL of CH_2Cl_2 was stirred at rt for 15 h, concentrated under reduced pressure, and purified by chromatography on SiO_2 (90%-80% hexanes:EtOAc) to yield 0.490 g (93%) of **3e** as a pale yellow oil: R_f 0.41 (65% hexanes:EtOAc); IR (neat) 3334, 2983, 2228, 1694, 1651, 1505, 1264, 1022 cm^{-1}; ^1H NMR δ 8.12 (dd, 2 H, *J* = 8.0, 1.5 Hz), 7.62 (tt, 1 H, *J* = 7.4, 1.1 Hz), 7.48 (t, 2 H, *J* = 7.3 Hz), 5.23 (br, 1 H), 4.29 (d, 2 H, *J* = 5.7 Hz), 4.18 (d, 2 H, *J* = 6.9 Hz), 1.27 (t, 3 H, *J* = 7.1 Hz); ^{13}C NMR δ 177.7, 156.2, 136.3, 134.4, 129.7, 128.6, 90.3, 81.0, 61.6, 31.2, 14.6; MS (EI) *m/z* (rel intensity) 231 (M^+, 7), 203 (19), 186 (12), 175 (20), 159 (28), 158 (66), 131 (25), 130 (60), 115 (54), 105 (100); HRMS (EI) *m/z* calculated for $C_{13}H_{13}NO_3$ 231.0895, found 231.0886.



4a

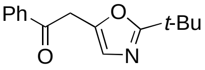
1-Phenyl-2-(2-phenyl-oxazol-5-yl)-ethanone (**4a**). A mixture of 0.0711 g (0.260 mmol) of **3a** and 0.214 g of SiO_2 in 5 mL of CH_2Cl_2 was stirred at rt for 24 h, filtered, concentrated under reduced pressure, and purified by chromatography on SiO_2 to yield 0.0711 g (>99%) of **4a** as a white amorphous solid.

Alternatively, a mixture of 0.103 g (0.386 mmol) of **2a** and 0.180 g (0.424 mmol) of Dess-Martin reagent in 5 mL of CH_2Cl_2 was stirred at rt for 15 h. The remaining Dess-Martin reagent and its by-products were removed by filtration through a short pad of SiO_2. The filtrate was stirred with 0.309 g of SiO_2 in 5 mL of CH_2Cl_2 at rt for 24 h, filtered, concentrated under reduced pressure, and purified by chromatography on SiO_2 (60% hexanes:EtOAc) to give 0.0866 g (85%) of **4a** as a white amorphous solid: R_f 0.35 (65% hexanes:EtOAc); IR (neat) 3061, 2917, 1690, 1603, 1552, 1489, 1454, 1339, 1212, 1126, 1062 cm^{-1}; ^1H NMR δ 8.03 (d, 2 H, *J* = 8.4 Hz), 8.02-7.96 (m, 2 H), 7.63-7.40 (m, 6 H), 7.13 (s, 1 H), 4.43 (s, 2 H); ^{13}C NMR δ 193.7, 161.6, 145.5, 135.9, 133.8, 130.2, 128.8, 128.7, 128.5, 127.5, 126.8, 126.2, 36.0; MS (EI) *m/z* (rel intensity) 263 (M^+, 15), 158 (18), 105 (100); HRMS (EI) *m/z* calculated for $C_{17}H_{13}NO_2$ 263.0946, found 263.0948.



4b

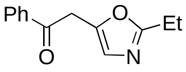
1-Phenyl-2-(2-vinyloxazol-5-yl)-ethanone (**4b**). A mixture of 0.0815 g (0.382 mmol) of **3b** and 0.245 g of SiO_2 in 5 mL of CH_2Cl_2 was stirred at rt for 24 h, filtered, concentrated under reduced pressure, and purified by chromatography on SiO_2 to yield 0.0710 g (87%) of **4b** as a yellow oil: R_f 0.33 (65% hexanes:EtOAc); IR (neat) 3073, 2917, 1694, 1597, 1449, 1207, 1112, 998 cm^{-1}; ^1H NMR δ 8.01 (dd, 2 H, *J* = 7.9, 1.5 Hz), 7.62 (tt, 1 H, *J* = 7.4, 1.3 Hz), 7.50 (t, 2 H, *J* = 7.9 Hz), 7.05 (s, 1 H), 6.56 (dd, 1 H, *J* = 17.7, 11.2 Hz), 6.11 (dd, 1 H, *J* = 17.7, 1.0 Hz), 5.58 (dd, 1 H, *J* = 11.2, 1.0 Hz), 4.38 (d, 2 H, *J* = 0.8 Hz); ^{13}C NMR δ 193.7, 161.0, 145.2, 135.9, 133.8, 128.9, 128.5, 126.7, 123.4, 121.4, 35.9; MS (EI) *m/z* (rel intensity) 213 (M^+, 15), 105 (100); HRMS (EI) *m/z* calculated for $C_{13}H_{11}NO_2$ 213.0790, found 213.0799.



4c

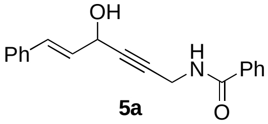
2-(2-*tert*-Butyloxazol-5-yl)-1-phenylethanone (**4c**). A mixture of 0.0915 g (0.373 mmol) of **2c** and 0.174 g (0.410 mmol) of Dess-Martin reagent in 5 mL of CH_2Cl_2 was stirred at rt for 15 h.

The remaining Dess-Martin reagent and its by-products were removed by filtration through a short pad of SiO_2. The filtrate was treated with 0.275 g of SiO_2 in 5 mL of CH_2Cl_2 at rt for 24 h, filtered, concentrated under reduced pressure, and purified by chromatography on SiO_2 to give 0.0780 g (86%) of **4c** as a colorless amorphous solid: R_f 0.40 (65% hexanes:EtOAc); IR (neat) 2972, 2934, 1686, 1560, 1449 cm^{-1}; ^1H NMR δ 8.03-7.99 (m, 2 H), 7.61 (tt, 1 H, *J* = 7.4, 2.0 Hz), 7.52-7.47 (m, 2 H), 6.88 (t, 1 H, *J* = 0.9 Hz), 4.34 (d, 2 H, *J* = 1.0 Hz), 1.36 (s, 9 H); ^{13}C NMR δ 194.0, 171.0, 144.6, 136.0, 133.6, 128.8, 128.4, 124.8, 36.0, 33.7, 28.5; MS (EI) *m/z* (rel intensity) 243 (M^+, 10), 106 (15), 105 (100); HRMS (EI) *m/z* calculated for $C_{15}H_{17}NO_2$ 243.1259, found 243.1269.



4d

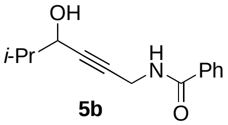
2-(2-Ethyloxazol-5-yl)-1-phenylethanone (**4d**). A mixture of 0.0810 g (0.382 mmol) of **3d** and 0.243 g of SiO_2 in 5 mL of CH_2Cl_2 was stirred at rt for 24 h, filtered, concentrated under reduced pressure, and purified by chromatography on SiO_2 (80%-65% hexanes:EtOAc) to yield 0.0259 g (32%) of **4d** as a pale yellow oil: R_f 0.38 (50% hexanes:EtOAc); IR (neat) 2980, 1688, 1558, 1450 cm^{-1}; ^1H NMR δ 8.00 (dd, 2 H, *J* = 7.8, 1.3 Hz), 7.60 (tt, 1 H, *J* = 7.2, 1.0 Hz), 7.49 (t, 2 H, *J* = 7.7 Hz), 6.89 (s, 1 H), 4.32 (s, 2 H), 2.77 (q, 2 H, *J* = 7.6 Hz), 1.32 (t, 3 H, *J* = 7.6 Hz); ^{13}C NMR δ 194.0, 165.8, 144.8, 135.9, 133.7, 128.8, 128.4, 125.1, 35.8, 21.7, 11.1; MS (EI) *m/z* (rel intensity) 215 (M^+, 21), 105 (100); HRMS (EI) *m/z* calculated for $C_{13}H_{13}NO_2$ 215.0946, found 215.0953.



5a

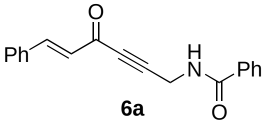
(5*E*)-*N*-(4-Hydroxy-6-phenylhex-5-en-2-ynyl)-benzamide (**5a**). A solution of 0.711g (4.47 mmol) of **1a** in 30 mL of THF was treated at –78 °C with 9.83 mL (9.83 mmol) of a 1.0 M solution of LiHMDS in THF, stirred for 15 min at –78 °C, treated with a solution of 0.650 g (4.92 mmol) of *trans*-cinnamaldehyde in 1 mL of THF, warmed to 0 °C over 1 h, and stirred for 1

h. The reaction mixture was quenched with 1.0 M HCl (50 mL) and extracted with EtOAc (2 x 30 mL). The combined organic layers were washed with brine (50 mL), dried ($MgSO_4$), concentrated under reduced pressure, and purified by chromatography on SiO_2 to yield 0.937 g (72%) of **5a** as a pale yellow foam: R_f 0.27 (50% hexanes:EtOAc); IR (neat) 3308, 3028, 2924, 2222, 1645, 1538, 1448, 1293, 1157, 1070 cm^{-1}; ^1H NMR δ 7.78 (dd, 2 H, *J* = 7.8, 1.4 Hz), 7.57-7.22 (m, 8 H), 6.72 (d, 1 H, *J* = 15.8 Hz), 6.58 (br, 1 H), 6.27 (dd, 1 H, *J* = 15.8, 6.1 Hz), 5.07 (dd, 1 H, *J* = 6.0, 1.3 Hz), 4.31 (dd, 2 H , *J* = 5.2, 1.7 Hz), 2.91 (br, 1 H); ^{13}C NMR δ 167.7, 136.0, 133.4, 131.8, 131.6, 128.5, 128.5, 128.5, 128.0, 127.2, 126.7, 82.7, 81.8, 62.6, 30.1; MS (EI) *m/z* (rel intensity) 291 (M^+, 0.8), 290 (1), 273 (28), 169 (18), 142 (33), 105 (100); HRMS (EI) *m/z* calculated for $C_{19}H_{16}NO_2$ (M-H) 290.1181, found 290.1170.



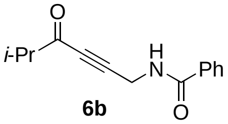
5b

***N*-(4-Hydroxy-5-methylhex-2-ynyl)-benzamide** (**5b**). A solution of 0.894 g (5.62 mmol) of **1a** in 30 mL of THF was treated at –78 °C with 12.0 mL (12.0 mmol) of a 1.0 M solution of LiHMDS in THF, stirred for 15 min at –78 °C, treated with a solution of 0.437 g (6.06 mmol) of isopropyl aldehyde in 1 mL of THF, warmed to 0 °C over 1 h, and stirred for 1 h. The reaction mixture was quenched with 1.0 M HCl (50 mL) and extracted with EtOAc (2 x 30 mL). The combined organic layers were washed with brine (50 mL), dried ($MgSO_4$), concentrated under reduced pressure, and purified by chromatography on SiO_2 to yield 1.22 g (94%) of **5b** as a colorless oil: R_f 0.39 (50% hexanes:EtOAc); IR (neat) 3307, 3068, 2963, 2246, 1651, 1538, 1487, 1307, 1158, 1027 cm^{-1}; ^1H NMR δ 7.79 (dd, 2 H, *J* = 8.1, 1.4 Hz), 7.53 (t, 1 H, *J* = 4.9 Hz), 7.55-7.51 (m, 1 H), 7.33 (t, 2 H, *J* = 7.9 Hz), 4.20 (dd, 2 H, *J* = 5.0, 1.0 Hz), 4.15-4.11 (m, 1 H), 3.98 (br, 1 H), 1.84-1.76 (m, 1 H), 0.95 (d, 3 H, *J* = 7.0 Hz), 0.92 (d, 3 H, *J* = 7.4 Hz); ^{13}C NMR δ 167.6, 133.4, 131.5, 128.2, 127.1, 83.2, 80.7, 67.4, 34.2, 29.8, 18.0, 17.4; MS (EI) *m/z* (rel intensity) 231 (M^+, 0.02), 230 (0.1), 214 (2). 189 (20), 188 (16), 173 (16), 105 (100); HRMS (EI) *m/z* calculated for $C_{14}H_{16}NO_2$ (M-H) 230.1181, found 230.1175.



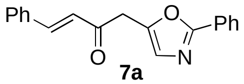
6a

(5*E*) *N*-(4-Oxo-6-phenylhex-5-en-2-ynyl)-benzamide (**6a**). A mixture of 0.536 g (2.19 mmol) of **5a** and 1.02 g (2.40 mmol) of Dess-Martin reagent in 10 mL of CH_2Cl_2 was stirred at rt for 15 h, filtered, concentrated under reduced pressure, and purified by chromatography on SiO_2 to yield 0.213 g (40%) of **6a** as a white solid: mp 129.0-130.0 °C (hexanes/EtOAc); IR (neat) 3280, 3053, 2223, 1633, 1531, 1312, 1253, 1209, 984 cm^{-1}; ^1H NMR δ 7.85 (d, 1 H, *J* = 16.0 Hz), 7.83 (d, 2 H, *J* = 7.1 Hz), 7.60-7.38 (m, 8 H), 6.77 (d, 1 H, *J* = 16.1 Hz), 6.69 (br, 1 H), 4.52 (d. 2 H, *J* = 5.4 Hz); ^{13}C NMR δ 177.9, 167.2, 149.5, 133.9, 133.4, 132.1, 131.4, 129.1, 128.8, 128.8, 127.9, 127.1, 88.3, 80.9, 30.0; MS (EI) *m/z* (rel intensity) 289 (M^+, 6), 288 (3), 184 (46), 131 (95), 105 (100), 103 (44); HRMS (EI) *m/z* calculated for $C_{19}H_{15}NO_2$ 289.1103, found 289.1100.



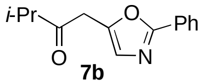
6b

***N*-(5-Methyl-4-oxohex-2-ynyl)-benzamide** (**6b**). A mixture of 0.128 g (0.553 mmol) of **5b** and 0.258 g (0.608 mmol) of Dess-Martin reagent in 10 mL of CH_2Cl_2 was stirred at rt for 15 h, filtered, concentrated under reduced pressure, and purified by chromatography on SiO_2 to yield 0.122 g (96%) of **6b** as a white solid: R_f 0.69 (65% hexanes:EtOAc); mp 69.5-70.5 °C (hexanes/EtOAc); IR (neat) 3271, 3068, 2976, 2218, 1688, 1634, 1538, 1488, 1408, 1298, 981 cm^{-1}; ^1H NMR δ 7.81 (dd, 2 H, *J* = 7.9, 1.6 Hz), 7.50 (tt, 1 H, *J* = 7.4, 1.2 Hz), 7.40 (t, 2 H, *J* = 7.8 Hz), 7.26 (br, 1 H), 4.41 (d. 2 H, *J* = 5.5 Hz), 2.62 (septet, 1 H, *J* = 7.0 Hz), 1.16 (d, 6 H, *J* = 6.9 Hz); ^{13}C NMR δ 191.8, 167.4, 133.5, 131.9, 128.6, 127.2, 89.0, 81.2, 42.9, 29.8, 17.8; MS (EI) *m/z* (rel intensity) 229 (M^+, 4), 201 (4), 186 (57), 172 (50), 159 (40), 105 (100); HRMS (EI) *m/z* calculated for $C_{14}H_{15}NO_2$ 229.1103, found 229.1076.



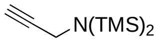
7a

(3*E*) 4-Phenyl-1-(2-phenyloxazol-5-yl)-but-3-en-2-one (7a). A mixture of 0.0520 g (0.180 mmol) of **6a** and 0.156 g of SiO_2 in 5 mL of CH_2Cl_2 was stirred at rt for 24 h, filtered, concentrated under reduced pressure, and purified by chromatography on SiO_2 to yield 0.0516 g (>99%) of **7a** as a pale yellow amorphous solid: R_f 0.38 (65% hexanes:EtOAc); IR (neat) 3063, 2925, 1693, 1613, 1446, 1340, 1086 cm^{-1}; ^{1}H NMR δ 8.05-7.98 (m, 2 H), 7.70 (d, 1 H, *J* = 16.1 Hz), 7.59-7.53 (m, 2 H), 7.47-7.38 (m, 6 H), 7.13 (brs, 1 H), 6.84 (d, 1 H, *J* = 16.1 Hz), 4.10 (d, 2 H, *J* = 0.8 Hz); ^{13}C NMR δ 193.3, 161.6, 145.5, 144.4, 134.0, 130.9, 130.2, 129.0, 128.7, 128.5, 127.4, 126.7, 126.2, 124.3, 38.3; MS (EI) *m/z* (rel intensity) 289 (M$^+$, 4), 131 (100), 103 (27); HRMS (EI) *m/z* calculated for $C_{19}H_{15}NO_2$ 289.1103, found 289.1109.



7b

3-Methyl-1-(2-phenyloxazol-5-yl)-butan-2-one (**7b**). A mixture of 0.0732 g (0.319 mmol) of **6b** and 0.220 g of SiO_2 in 5 mL of CH_2Cl_2 was stirred at rt for 24 h, filtered, concentrated under reduced pressure, and purified by chromatography on SiO_2 to yield 0.0732 g (>99%) of **7b** as a pale yellow oil: R_f 0.56 (50% hexanes:EtOAc); IR (neat) 2971, 2933, 1721, 1603, 1552, 1445, 1358, 1122, 1040 cm^{-1}; ^{1}H NMR δ 8.03-7.97 (m, 2 H), 7.47-7.41 (m, 3 H), 7.08 (s, 1 H), 3.90 (s, 2 H), 2.77 (septet, 1 H, *J* = 6.9 Hz), 1.18 (d, 6 H, *J* = 6.8 Hz); ^{13}C NMR δ 208.2, 161.5, 145.6, 130.2, 128.7, 127.4, 126.6, 126.2, 40.5, 37.6, 18.1; MS (EI) *m/z* (rel intensity) 229 (M$^+$, 4), 229 (26), 160 (23), 159 (100), 158 (83), 130 (32), 104 (40); HRMS (EI) *m/z* calculated for $C_{14}H_{15}NO_2$ 229.1103, found 229.1102.



8

1,1,1,3,3,3-Hexamethyl-2-prop-2-ynyldisilazane (**8**).[4] A mixture of 1.01 g (18.3 mmol) of propargylamine, 4.80 mL (37.8 mmol) of chlorotrimethylsilane, and 7.70 mL (55.2 mmol) of

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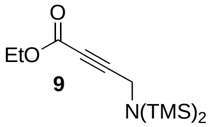
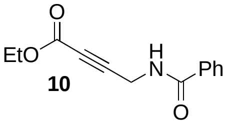
[4] Corriu, R. J. P.; Huynh, V.; Iqbal, J.; Moreau, J. J. E.; Vernhet, C. *Tetrahedron* **1992**, *48*, 6231-6244.

Et_3N in 30 mL of CH_2Cl_2 was stirred at rt for 12 h, quenched with brine (50 mL), and extracted with $CHCl_3$ (2 x 30 mL). The combined organic layers were washed with brine (50 mL), dried ($MgSO_4$), and concentrated under reduced pressure to give 2.11 g (58%) of **8** as a pale yellow oil: ^{1}H NMR δ 3.53 (d, 2 H, *J* = 2.4 Hz), 2.13 (t, 1 H, *J* = 2.4 Hz), 0.15 (s, 18 H).



9

4-(1,1,1,3,3,3-Hexamethyldisilazan-2-yl)-but-2-ynoic acid ethyl ester (**9**).[5] A solution of 1.63 g (8.16 mmol) of **8** in 10 mL of THF was treated at –78 °C with 5.50 mL (8.80 mmol) of a 1.6 M solution of *n*-BuLi in hexane, stirred for 15 min at –78 °C, treated with a solution of 0.956 g (8.81 mmol) of ethyl chloroformate in 2 mL of THF, warmed to rt over 1 h, and stirred for 1 h. The reaction mixture was quenched with brine (30 mL) and extracted with EtOAc (2 x 30 mL). The combined organic layers were washed with brine (50 mL), dried ($MgSO_4$), and concentrated under reduced pressure to give 2.21 g of crude ester **9** as an orange oil: ^{1}H NMR δ 4.21 (q, 2 H, *J* = 7.0 Hz), 3.67 (s, 2 H), 1.30 (t, 3 H, *J* = 7.1 Hz), 0.16 (s, 18 H).



10

4-Benzoylaminobut-2-ynoic acid ethyl ester (**10**). To a solution of 2.21 g of crude ester **9** and 1.26 g (8.96 mmol) of benzoyl chloride in 15 mL of THF was added 0.40 mL (0.40 mmol) of a 1.0 M solution of TBAF in THF. The reaction mixture was stirred at rt for 12 h, quenched with 1.0 M HCl (40 mL), and extracted with EtOAc (2 x 30 mL). The combined organic layers were washed with brine (40 mL), dried ($MgSO_4$), concentrated under reduced pressure, and purified by chromatography on SiO_2 to afford 1.26 g (67%, 2 steps from **8**) of **10** as a white solid: R_f 0.47 (50% hexanes:EtOAc); mp 103.8.-105.8 °C (hexanes/EtOAc); IR (neat) 3298, 2983, 2243, 1713, 1640, 1530, 1487, 1409, 1274, 1076, 984 cm^{-1}; ^{1}H NMR δ 7.78 (dd, 2 H, *J* = 7.8, 1.6 Hz), 7.54

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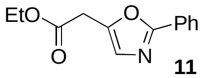
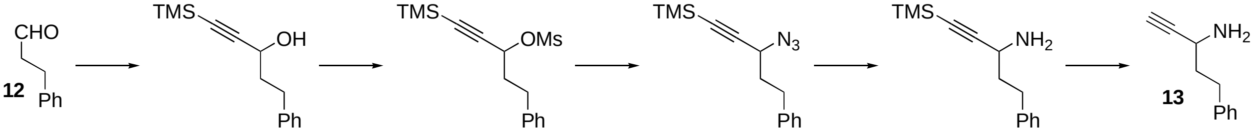
[5] Corriu, R. J. P.; Bolin, G.; Iqbal, J.; Moreau, J. E.; Vernhet, C. *Tetrahedron* **1993**, *49*, 4603-4618.

(tt, 1 H, *J* = 7.3, 1.3 Hz), 7.45 (t, 2 H, *J* = 7.0 Hz), 6.35 (br, 1 H), 4.42 (d, 2 H, *J* = 5.4 Hz), 4.24 (q, 2 H, *J* = 7.1 Hz), 1.31 (t, 3 H, *J* = 7.1 Hz); ^{13}C NMR δ 167.4, 153.3, 133.3, 132.0, 128.6, 127.2, 83.4, 75.1, 62.2, 29.5, 14.0; MS (EI) *m/z* (rel intensity) 231 (M$^+$, 2), 187 (11), 186 (28), 160 (11), 159 (65), 158 (15), 130 (21), 105 (100); HRMS (EI) *m/z* calculated for $C_{13}H_{13}NO_3$ 231.0895, found 231.0890.



11

(2-Phenyloxazol-5-yl)-acetic acid ethyl ester (**11**). A mixture of 0.0444 g (0.192 mmol) of **10** and 0.145 g of SiO_2 in 4 mL of CH_2Cl_2 was stirred at rt for 72 h, filtered, concentrated under reduced pressure, and purified by chromatography on SiO_2 to yield 0.0401 g (90%) of **11** as a white amorphous solid: IR (neat) 2975, 1726, 1609, 1486, 1450, 1399, 1337, 1235, 1122, 1034, 994 cm^{-1}; ^{1}H NMR δ 8.04-7.99 (m, 2 H), 7.46-7.42 (m, 3 H), 7.09 (s, 1 H), 4.22 (q, 2 H, *J* = 7.1 Hz), 3.79 (s, 2 H), 1.29 (t, 3 H, *J* = 7.1 Hz); ^{13}C NMR δ 168.4, 161.5, 145.0, 130.3, 128.7, 127.4, 126.4, 126.2, 61.5, 31.9, 14.1; MS (EI) *m/z* (rel intensity) 231 (M$^+$, 46), 159 (22), 158 (100), 130 (21), 104 (23); HRMS (EI) *m/z* calculated for $C_{13}H_{13}NO_3$ 231.0895, found 231.0898.



5-Phenyl-1-trimethylsilanylpent-1-yn-3-ol.[6] A solution of 1.05 g (10.7 mmol) of (trimethylsilyl)acetylene in 30 mL of THF was treated at –78 °C with 6.40 mL (10.2 mmol) of a 1.6 M solution of *n*-BuLi in hexane, stirred for 15 min at –78 °C, treated with a solution of 1.43 g (9.59 mmol) of hydrocinnamaldehyde (**12**) in 2 mL of THF, warmed to rt over 1 h, and stirred for 1 h. The reaction mixture was quenched with 1N HCl (50 mL) and extracted with EtOAc (2 x 50 mL). The combined organic layers were washed with brine (50 mL), dried ($MgSO_4$), concentrated under reduced pressure, and purified by chromatography on SiO_2 to yield 1.93 g (81%) of the propargylic alcohol as a colorless oil: R_f 0.69 (50% hexanes:EtOAc); ^{1}H NMR δ

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[6] López, F.; Castedo, L.; Mascareñas, J. L. *J. Am. Chem. Soc.* **2002**, *124*, 4218-4219.

7.32-7.13 (m, 5 H), 4.36 (t, 1 H, *J* = 6.5 Hz), 2.79 (t, 2 H, *J* = 8.0 Hz), 2.06-1.96 (m, 2 H), 1.75 (br, 1 H), 0.18 (s, 9 H).

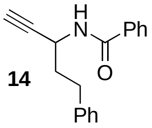
Methanesulfonic acid 1-phenethyl-3-trimethylsilanylprop-2-ynyl ester. A mixture of 1.79 g (7.69 mmol) of propargylic alcohol, 0.888 g (7.75 mmol) of methanesulfonyl chloride and 1.30 mL (9.33 mmol) of Et_3N in 20 mL of CH_2Cl_2 was stirred at rt for 12 h, quenched with 1N HCl (30 mL), and extracted with $CHCl_3$ (2 x 30 mL). The combined organic layers were washed with brine (40 mL), dried ($MgSO_4$), and concentrated under reduced pressure to give 2.39 g (>99%) of the mesylate as a colorless oil: IR (neat) 3029, 2960, 2177, 1604, 1497, 1455, 1361, 1252, 1176, 1093, 1032, 974 cm^{-1}; ^1H NMR δ 7.35-7.15 (m, 5 H), 5.13 (t, 1 H, *J* = 6.5 Hz), 3.13 (s, 3 H), 2.90-2.70 (m, 2 H), 2.33-2.08 (m, 2 H), 0.20 (s, 9 H); ^{13}C NMR δ 140.0, 128.6, 128.5, 126.4, 100.2, 94.7, 71.6, 39.2, 37.2, 37.2, 31.0, -0.4; MS (EI) *m/z* (rel intensity) 310 (M^+, 0.1), 215 (16), 214 (73), 199 (100), 183 (17), 153 (26), 141 (25), 91 (59); HRMS (EI) *m/z* calculated for $C_{14}H_{18}Si$ ($M-CH_3SO_3H$) 214.1178, found 214.1176.

(3-Azido-5-phenylpent-1-ynyl)-trimethylsilane. A mixture of 2.24 g (7.21 mmol) of the mesylate and 0.901 g (13.9 mmol) of NaN_3 in 15 mL of DMF was stirred at rt for 3 h, quenched with brine (50 mL), and extracted with EtOAc (2 x 70 mL). The combined organic layers were washed with brine (4 x 30 mL), dried ($MgSO_4$), and concentrated under reduced pressure to afford 1.67 g (90%) of the azide as a colorless oil: ^1H NMR δ 7.35-7.15 (m, 5 H), 4.05 (t, 1 H, *J* = 6.9 Hz), 2.80-2.70 (m, 2 H), 2.03-1.94 (m, 2 H), 0.21 (s, 9 H).

1-Phenethyl-3-trimethylsilanylprop-2-ynylamine. A mixture of 1.37 g (5.31 mmol) of the azide and 1.51 g (7.95 mmol) of $SnCl_2$ in 10 mL of MeOH was stirred at rt for 15 h, quenched with saturated aqueous $NaHCO_3$ (40 mL), filtered through a pad of Celite, and extracted with $CHCl_3$ (2 x 40 mL). The combined organic layers were washed with brine (40 mL), dried ($MgSO_4$), and concentrated under reduced pressure to give 1.04 g (85%) of the amine as an orange oil: IR (neat) 3380, 3298, 3027, 2957, 2163, 1603, 1496, 1455, 1250, 1045 cm^{-1}; ^1H NMR δ 7.31-7.15 (m, 5 H), 3.52 (t, 1 H, *J* = 7.0 Hz), 2.88-2.70 (m, 2 H), 1.98-1.80 (m, 2 H), 1.57 (br, 2 H), 0.18 (s, 9 H); ^{13}C NMR δ 141.6, 128.5, 128.4, 126.0, 109.8, 86.9, 43.7, 39.7, 32.4, 0.1; MS

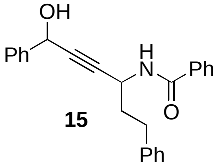
(EI) *m/z* (rel intensity) 231 (M^+, 4), 230 (4), 158 (30), 153 (39), 126 (100), 98 (41), 91 (70); HRMS (EI) *m/z* calculated for $C_{14}H_{20}NSi$ (M-H) 230.1365, found 230.1356.

1-Phenethylprop-2-ynylamine (**13**). A mixture of 0.622 g (2.69 mmol) of the amine and 0.187 g (3.22 mmol) of KF in 5 mL of MeOH was stirred at rt for 15 h, quenched with saturated aqueous $NaHCO_3$ (30 mL), and extracted with EtOAc (2 x 30 mL). The combined organic layers were washed with brine (40 mL), dried ($MgSO_4$), concentrated under reduced pressure, and purified by chromatography on SiO_2 (95% $CHCl_3$:MeOH) to give 0.428 g (>99%) of **13** as an orange oil: R_f 0.18 (35% hexanes:EtOAc); IR (neat) 3291, 3067, 3026, 2923, 2110, 1602, 1496, 1454, 1317, 1035 cm^{-1}; ^1H NMR δ 7.33-7.15 (m, 5 H), 3.54 (td, 1 H, *J* = 6.9, 2.0 Hz), 2.89-2.70 (m, 2 H), 2.34 (d, 1 H, *J* = 2.2 Hz), 1.98-1.85 (m, 2 H), 1.47 (br, 2 H); ^{13}C NMR δ 141.2, 128.3, 128.3, 125.8, 87.4, 70.7, 42.6, 39.4, 32.0; MS (EI) *m/z* (rel intensity) 159 (M^+, 9), 158 (25), 143 (14), 142 (47), 141 (29), 105 (14), 91 (27); HRMS (EI) *m/z* calculated for $C_{11}H_{12}N$ (M-H) 158.0970, found 158.0970.



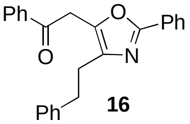
14

***N*-(1-Phenethylprop-2-ynyl)-benzamide** (**14**). To a solution of 0.200 g (1.26 mmol) of **13** in 10 mL of CH_2Cl_2 were added 0.216 g (1.53 mmol) of benzoyl chloride and 0.30 mL (2.15 mmol) of Et_3N at 0 °C. The reaction mixture was stirred at rt for 2 h, poured into 1.0 M HCl (20 mL), and extracted with $CHCl_3$ (2 x 20 mL). The combined organic layers were washed with brine (30 mL), dried ($MgSO_4$), concentrated under reduced pressure, and purified by chromatography on SiO_2 to give 0.205 g (62%) of **14** as a white solid: R_f 0.51 (65% hexanes:EtOAc); mp 115.5-116.0 °C (hexanes/EtOAc); IR (neat) 3267, 2980, 2120, 1629, 1531, 1454, 1286 cm^{-1}; ^1H NMR δ 7.66 (d, 2 H, *J* = 7.3 Hz), 7.53-7.38 (m, 3 H), 7.33-7.18 (m, 5 H), 6.19 (bd 1 H, *J* = 6.8 Hz), 5.07-4.99 (m, 1 H), 2.97-2.77 (m, 2 H), 2.39 (d, 1 H, *J* = 1.7 Hz), 2.24-2.02 (m, 2 H); ^{13}C NMR δ 166.5, 140.9, 133.7, 131.6, 128.5, 128.4, 128.4, 127.1, 126.1, 82.8, 71.9, 41.6, 36.9, 31.9; MS (EI) *m/z* (rel intensity) 263 (M^+, 6), 262 (10), 235 (16), 172 (13), 160 (16), 159 (83), 158 (24), 142 (18), 141 (23), 130 (36), 105 (100); HRMS (EI) *m/z* calculated for $C_{18}H_{16}NO$ (M-H) 262.1232, found 262.1230.



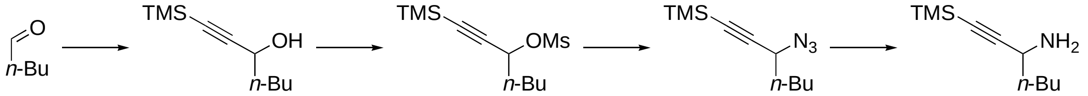
15

***N*-(4-Hydroxy-1-phenethyl-4-phenylbut-2-ynyl)-benzamide** (**15**). A solution of 0.0976 g (0.371 mmol) of **14** in 5 mL of THF was treated at –78 °C with 0.85 mL (0.85 mmol) of a 1.0 M solution of LiHMDS in THF, stirred for 15 min at –78 °C, treated with a solution of 0.0605 g (0.570 mmol) of benzaldehyde in 1 mL of THF, warmed to 0 °C over 1 h, and stirred for 1 h. The reaction mixture was quenched with 1.0 M HCl (10 mL) and extracted with EtOAc (2 x 10 mL). The combined organic layers were washed with brine (10 mL), dried ($MgSO_4$), concentrated under reduced pressure, and purified by chromatography on SiO_2 to give 0.0778 g (51%) of **15** as a pale yellow oil: R_f 0.30 (65% hexanes:EtOAc); IR (neat) 3368, 2980, 2243, 1634, 1533, 1440 cm^{-1}; ^{1}H NMR δ 7.63 (dd, 2 H, *J* = 7.7, 1.4 Hz), 7.53 (dd, 2 H, *J* = 7.8, 1.6 Hz), 7.47 (tt, 1 H, *J* = 7.4, 1.3 Hz), 7.40-7.14 (m, 10 H), 6.43 (d, 1 H, *J* = 8.1 Hz), 5.49 (s, 1 H), 5.11-5.02 (m, 1 H), 3.09 (br, 1 H), 2.89-2.72 (m, 2 H), 2.21-2.00 (m, 2 H); ^{13}C NMR δ 166.5, 141.0, 140.5, 133.7, 131.7, 128.7, 128.6, 128.5, 128.5, 128.4, 127.0, 126.6, 126.1, 85.3, 83.9, 64.5, 42.0, 37.1, 32.1; MS (EI) *m/z* (rel intensity) 369 (M$^+$, 3), 368 (10), 352 (22), 341 (25), 265 (45), 248 (62), 105 (100); HRMS (EI) *m/z* calculated for $C_{25}H_{22}NO_2$ (M-H) 368.1651, found 368.1639.



16

2-(4-Phenethyl-2-phenyloxazol-5-yl)-1-phenylethanone (**16**). A mixture of 0.0721 g (0.195 mmol) of **15** and 0.0915 g (0.216 mmol) of Dess-Martin reagent in 5 mL of CH_2Cl_2 was stirred at rt for 15 h. The remaining Dess-Martin reagent and its by-products were removed by filtration through a short pad of SiO_2. The filtrate was treated with 0.216 g of SiO_2 in 5 mL of CH_2Cl_2 at rt for 24 h, filtered, concentrated under reduced pressure, and purified by chromatography on SiO_2 to give 0.0444 g (62%) of **16** as a pale yellow amorphous solid: R_f 0.69 (65% hexanes:EtOAc); IR (neat) 3027, 2926, 1694, 1598, 1556, 1486, 1454, 1330, 1213, 1070 cm^{-1}; ^1H NMR δ 8.02-7.96 (m, 2 H), 7.94 (dd, 2 H, *J* = 7.8, 1.5 Hz), 7.59 (tt, 1 H, *J* = 7.4, 1.3 Hz), 7.48 (t, 2 H, *J* = 7.8 Hz), 7.46-7.40 (m, 3 H), 7.30-7.15 (m, 5 H), 4.03 (s, 2 H), 2.99 (t, 2 H, *J* = 6.9 Hz), 2.83 (t, 2 H, *J* = 7.9 Hz); ^{13}C NMR δ 194.0, 160.6, 141.5, 140.6, 138.2, 136.0, 133.6, 130.0, 128.7, 128.7, 128.7, 128.5, 128.4, 127.6, 126.2, 126.0, 35.1, 35.0, 28.3; MS (EI) *m/z* (rel intensity) 367 (M^+, 21), 271 (33), 262 (35), 170 (100), 141 (90), 105 (55), 91 (46); HRMS (EI) *m/z* calculated for $C_{25}H_{21}NO_2$ 367.1572, found 367.1584.



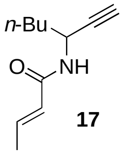
1-(Trimethylsilanyl)-hept-1-yn-3-ol.[7] A solution of 1.51 mL (10.7 mmol) of (trimethylsilyl)acetylene in 30 mL of THF was treated at –78 °C with 6.3 mL (10.1 mmol) of a 1.6 M solution of *n*-BuLi in hexane, stirred for 15 min at –78 °C, treated with a solution of 1.01 mL (9.54 mmol) of valeraldehyde in 2 mL of THF, warmed to rt over 1 h, and stirred for 1 h. The clear, yellow reaction mixture was quenched with 10% HCl (50 mL) and extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine (50 mL), dried ($MgSO_4$), concentrated under reduced pressure, and purified by chromatography on SiO_2 (90% hexanes:EtOAc) to give 1.42 g (81%) of the propargylic alcohol as a colorless oil: R_f 0.35 (90% hexanes:EtOAc); ^1H NMR δ 4.37-4.31 (m, 1 H), 1.90 (d, 1 H, *J* = 5.5 Hz), 1.71-1.65 (m, 2 H), 1.43-1.34 (m, 4 H), 0.91 (t, 3 H, *J* = 7.0 Hz), 0.16 (s, 9 H).

Methanesulfonic acid 1-butyl-3-(trimethylsilanyl)-prop-2-ynyl ester. A mixture of 6.22 g (33.7 mmol) of the propargylic alcohol, 2.87 mL (37.1 mmol) of methanesulfonyl chloride, and 5.69 mL (40.5 mmol) of Et_3N in 85 mL of CH_2Cl_2 was stirred at 0 ºC for 15 min and allowed to warm to rt. After 20 h, the reaction mixture was quenched with 10% HCl (50 mL) and extracted with CH_2Cl_2 (2 x 100 mL). The organic layers were combined, washed with brine (50 mL), dried

($MgSO_4$), and concentrated under reduced pressure to give the crude mesylate as a colorless oil: R_f 0.39 (80% hexanes:Et_2O).

(3-Azidohept-1-ynyl)-trimethylsilane. A mixture of the crude mesylate and 4.17 g (64.1 mmol) of NaN_3 in 67.5 mL of DMF was stirred at rt for 15 h, diluted with EtOAc (150 mL), washed with H_2O (7 x 75 mL) and brine (1 x 75 mL), dried ($MgSO_4$), and concentrated under reduced pressure to give 6.34 g (90%, 2 steps from the propargylic alcohol) of the azide as a yellow oil: R_f 0.90 (80% hexanes:Et_2O); ^1H NMR δ 4.05 (t, 1 H, J = 6.8 Hz), 1.72-1.65 (m, 2 H), 1.45-1.26 (m, 4 H), 0.92 (t, 3 H, J = 7.1 Hz), 0.21 (s, 9 H).

1-Butyl-3-(trimethylsilanyl)-prop-2-ynylamine. A mixture of 6.34 g (30.3 mmol) of the azide and 8.61 g (45.4 mmol) of $SnCl_2$ was stirred in 60 mL of MeOH at rt for 14 h, quenched with saturated aqueous $NaHCO_3$ (250 mL) at 0 °C, and filtered through a pad of Celite. The solid was washed with MeOH (200 mL). The filtrate was concentrated under reduced pressure, diluted with H_2O (100 mL), and extracted with CH_2Cl_2 (3 x 250 mL). The combined organic layers were washed with brine (100 mL), dried ($MgSO_4$), and concentrated under reduced pressure to give 4.33 g (78%) of **18** as a tan oil: R_f 0.12 (50% hexanes:EtOAc); ^1H NMR δ 3.51 (t, 1 H, J = 6.6 Hz), 1.55-1.50 (m, 3 H), 1.46-1.24 (m, 5 H), 0.90 (t, 3 H, J = 7.0 Hz), 0.16 (s, 9 H).



17

But-2-enoic acid (1-butylprop-2-ynyl)-amide (17). To a solution of 0.250 g (1.34 mmol) of the amine and 0.280 mL (2.00 mmol) of Et_3N in 5 mL of CH_2Cl_2 was added at 0 °C 0.140 mL (1.40 mmol) of *trans*-crotonyl chloride. The reaction mixture was allowed to warm to rt, stirred for 2 h, poured into 10% HCl (15 mL) and extracted with $CHCl_3$ (3 x 10 mL). The combined organic layers were washed with H_2O (5 mL), dried (Na_2SO_4), concentrated under reduced pressure, and purified by chromatography on SiO_2 (80% hexanes:EtOAc) to give the crude intermediate amide as a yellow oil which was used without further purification: R_f 0.70 (60%

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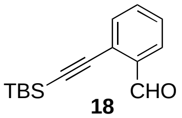
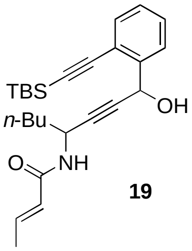
[7] Ivanov, I. V.; Romanov, S. G.: Groza, N. V.; Nigam, S.; Kuhn, H.; Myagkova, G. I. *Bioorg. Med. Chem.* **2002**,

hexanes:EtOAc). A mixture of 0.920 g of crude propargylic amide and NaOMe (prepared from 10.0 mg of sodium metal) was stirred in 1 mL of MeOH for 2 h. Then, activated Amberlite IR-120 Na ion-exchange resin was added until pH 7. The reaction mixture was filtered and concentrated under reduced pressure to give 0.630 g (96%, 2 steps from the propargyl amide) of crude **17** as an oil: R_f 0.53 (60% hexanes:EtOAc); ^{1}H NMR δ 6.87-6.77 (m, 1 H), 6.13 (d, 1 H, *J* = 8.1 Hz), 5.81 (dd, 1 H, *J* = 15.1, 1.6), 4.80-4.73 (m, 1 H), 2.22 (d, 1 H, *J* = 2.3 Hz), 1.82 (d, 3 H, *J* = 6.8 Hz), 1.67-1.63 (m, 2 H), 1.38-1.19 (m, 4 H), 0.86 (t, 3 H, *J* = 7.0 Hz).



18

2-[(*tert*-Butyldimethylsilanyl)-ethynyl]-benzaldehyde (18). A mixture of 1.11 mL (9.50 mmol) of 2-bromobenzaldehyde, 2.00 g (14.3 mmol) of (*tert*-butyldimethylsilyl)acetylene, 0.333 g (0.480 mmol) of $PdCl_2(PPh_3)_2$, and 0.180 g (0.950 mmol) of CuI was stirred in 20 mL of Et_3N at rt for 24 h, concentrated under reduced pressure to remove excess Et_3N, poured into 1.0 M HCl (150 mL), and extracted with CH_2Cl_2 (150 mL x 2). The combined organic layers were washed with brine (100 mL), dried (Na_2SO_4), concentrated under reduced pressure, and purified by chromatography on SiO_2 (95% hexanes:Et_2O) to give 2.24 g (96%) of **18** as a yellow oil: R_f 0.80 (80% hexanes:Et_2O); ^{1}H NMR δ 10.57 (s, 1 H), 7.90 (d, 1 H, *J* = 7.7 Hz), 7.57-7.43 (m, 3 H), 1.00 (s, 9 H), 0.22 (s, 6 H).



19

But-2-enoic acid (1-butyl-4-{2-[(*tert*-butyldimethylsilanyl)-ethynyl]-phenyl}-4-hydroxy-but-2-ynyl)-amide (19). A solution of 0.0780 g (0.435 mmol) of **17** in 3 mL of THF was treated

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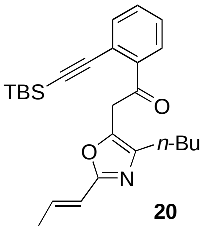
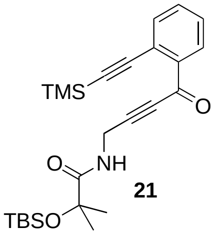
10, 2335-2343.

at –78 °C with 0.80 mL (1.31 mmol) of a 1.6 M solution of *n*-BuLi in hexane, stirred for 15 min at –78 °C, treated with a solution of 0.117 g (0.479 mmol) of **18** in 1.5 mL of THF, warmed to 0 °C over 1 h, and stirred for 2 h. The reaction mixture was quenched with 10% HCl (5 mL) and extracted with EtOAc (2 x 10 mL). The combined organic layers were washed with brine (5 mL), dried (Na_2SO_4), concentrated under reduced pressure, and purified by chromatography on SiO_2 (75% hexanes:EtOAc) to give 0.0830 g (46%) of **19** as a red oil: R_f 0.10 (80% hexanes:EtOAc); ^{1}H NMR δ 7.66 (d, 1 H, *J* = 7.5 Hz), 7.48 (d, 1 H, *J* = 7.5), 7.38-7.24 (m, 2 H), 6.89-6.78 (m, 1 H), 5.89 (s, 1 H), 5.76-5.69 (m, 2 H), 4.88 (q, 1 H, *J* = 6.9 Hz), 1.84 (d, 3 H, *J* = 6.8 Hz), 1.71-1.66 (m, 2 H), 1.41-1.22 (m, 4 H), 1.01 (s, 9 H), 0.90-0.87 (m, 3 H), 0.21 (s, 6 H).



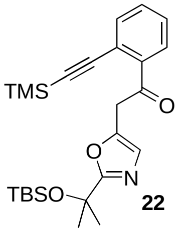
20

1-{2-[(*tert*-Butyldimethylsilanyl)-ethynyl]-phenyl}-2-(4-butyl-2-propenyloxazol-5-yl)-ethanone (20). A solution of 0.0510 g (0.120 mmol) of **19** and 0.0580 g (0.138 mmol) of Dess-Martin periodinane in 2 mL of CH_2Cl_2 was stirred at rt for 4 h. The light orange, cloudy reaction mixture was filtered through a plug of SiO_2 (80% hexanes:EtOAc). The filtrate was concentrated under reduced pressure to give the crude ketone as an orange oil: R_f 0.48 (60% hexanes:EtOAc); IR (NaCl, film) 3275, 3060, 2955, 2929, 2858, 2213, 2156, 1655, 1534, 1471, 1442, 1362, 1342, 1293, 1248, 1007, 966, 837, 807, 776, 758, 682 cm^{-1}; ^{1}H NMR δ 7.60 (dd, 1H, *J* = 7.5, 1.1 Hz), 7.62-7.58 (m, 1 H), 7.52-7.41 (m, 2 H), 6.89 (sextet, 1 H, *J* = 6.9 Hz), 5.84-5.83 (m, 1H), 5.80-5.78 (m, 1 H), 5.13-5.06 (m, 1 H), 1.85 (dd, 3 H, *J* = 6.8, 1.6 Hz), 1.85-1.79 (m, 2 H), 1.50-1.26 (m, 4 H), 1.03 (s, 9 H), 0.92 (t, 3 H, *J* = 7.1 Hz), 0.21 (s, 3 H), 0.20 (s, 3 H); ^{13}C NMR δ 176.5, 164.9, 141.2, 137.9, 135.4, 132.4, 132.2, 128.0, 124.4, 122.7, 103.6, 99.7, 93.1, 81.5, 41.4, 35.1, 27.8, 26.2, 26.1, 25.5, 22.4, 22.2, 17.7, 13.8, -4.7, -4.8; HRMS (ES) *m/z* calculated for $C_{26}H_{35}NO_2Si$ 421.2437, found: 421.2433. The crude orange oil was stirred with 0.500 g (1,000%, w/w) of SiO_2 in 4 mL of CH_2Cl_2 at rt for 48 h, filtered, and concentrated under reduced pressure to give 0.0290 g (58%, 2 steps from **19**) of **20** as a red oil: R$_f$ 0.40 (80% hexanes:EtOAc); IR (NaCl, film) 2955, 2930, 2857, 2360, 2342, 2156, 1694, 1665, 1640, 1591, 1535, 1471, 1441, 1362, 1327, 1250, 1200, 1096, 1051, 964, 838, 808, 776, 761, 680 cm^{-1}; ^{1}H NMR δ 7.60-7.57 (m, 2 H), 7.47-7.35 (m, 2 H), 6.61 (dq, 1 H, *J* = 15.9, 6.9 Hz), 6.21 (dq, 1 H, *J* = 15.9, 1.5 Hz), 4.49 (s, 2 H), 2.38 (t, 2 H, *J* = 7.5 Hz), 1.89 (dd, 3 H, *J* = 6.9, 1.5 Hz), 1.52 (quinted, 2 H, *J* = 7.5 Hz), 1.29 (sextet, 2 H, *J* = 7.5 Hz), 1.00 (s, 9 H), 0.88 (t, 3 H, *J* = 7.2 Hz), 0.21 (s, 6 H); ^{13}C NMR δ 197.8, 160.2, 140.7, 138.9, 134.5, 134.3, 131.3, 128.8, 128.6, 121.2, 118.1, 104.2, 100.2, 38.6, 31.1, 26.2, 25.7, 22.5, 18.5, 16.9, 14.0, -4.7; MS (EI) *m/z* (rel intensity) 421 (M+, 18), 365 (11), 243 (100), 194 (20), 187 (48), 178 (28), 143 (30), 136 (18); HRMS (EI) *m/z* calculated for $C_{26}H_{35}NO_2Si$ 421.2437, found 421.2433.



21

2-(*tert*-Butyldimethylsilanyloxy)-2-methyl-*N*-[4-oxo-4-(2-trimethylsilanylethynylphenyl)-but-2-ynyl]-propionamide (**21**). A mixture of 1.11 g (2.43 mmol) of the propargylic alcohol and 1.15 g (2.71 mmol) of Dess-Martin reagent in 40 mL of CH_2Cl_2 was stirred at rt for 15 h, filtered, concentrated under reduced pressure, and purified by chromatography on SiO_2 to yield 1.05 g (95%) of **21** as an orange oil: R$_f$ 0.47 (75% hexanes:EtOAc); IR (neat) 3434, 3073, 2955, 2858, 2232, 2157, 1655, 1592, 1561, 1501, 1250, 1167, 1033 cm^{-1}; ^{1}H NMR δ 8.05 (dd, 1 H, *J* = 7.7, 1.0 Hz), 7.60 (dd, 1 H, *J* = 7.7, 1.2 Hz), 7.50 (td, 1 H, *J* = 7.5, 1.4 Hz), 7.41 (td, 1 H, *J* = 7.7, 1.4 Hz), 7.13 (br, 1 H), 4.31 (d, 2 H, *J* = 5.4 Hz), 1.47 (s, 6 H), 0.92 (s, 9 H), 0.28 (s, 9 H), 0.18 (s, 6 H); ^{13}C NMR δ 176.4, 176.3, 138.0, 135.0, 132.4, 131.7, 128.1, 122.5, 102.9, 101.1, 89.6, 81.8, 76.8, 29.4, 27.8, 25.8, 17.9, -0.2, -2.4; MS (EI) *m/z* (rel intensity) 455 (M$^+$, 2), 440 (6), 399 (42), 398 (99), 340 (27), 173 (100); HRMS (EI) *m/z* calculated for $C_{24}H_{34}NO_3Si_2$ (M-CH_3) 440.2077, found 440.2070.



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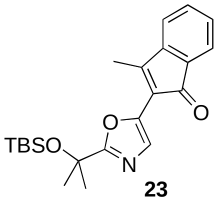
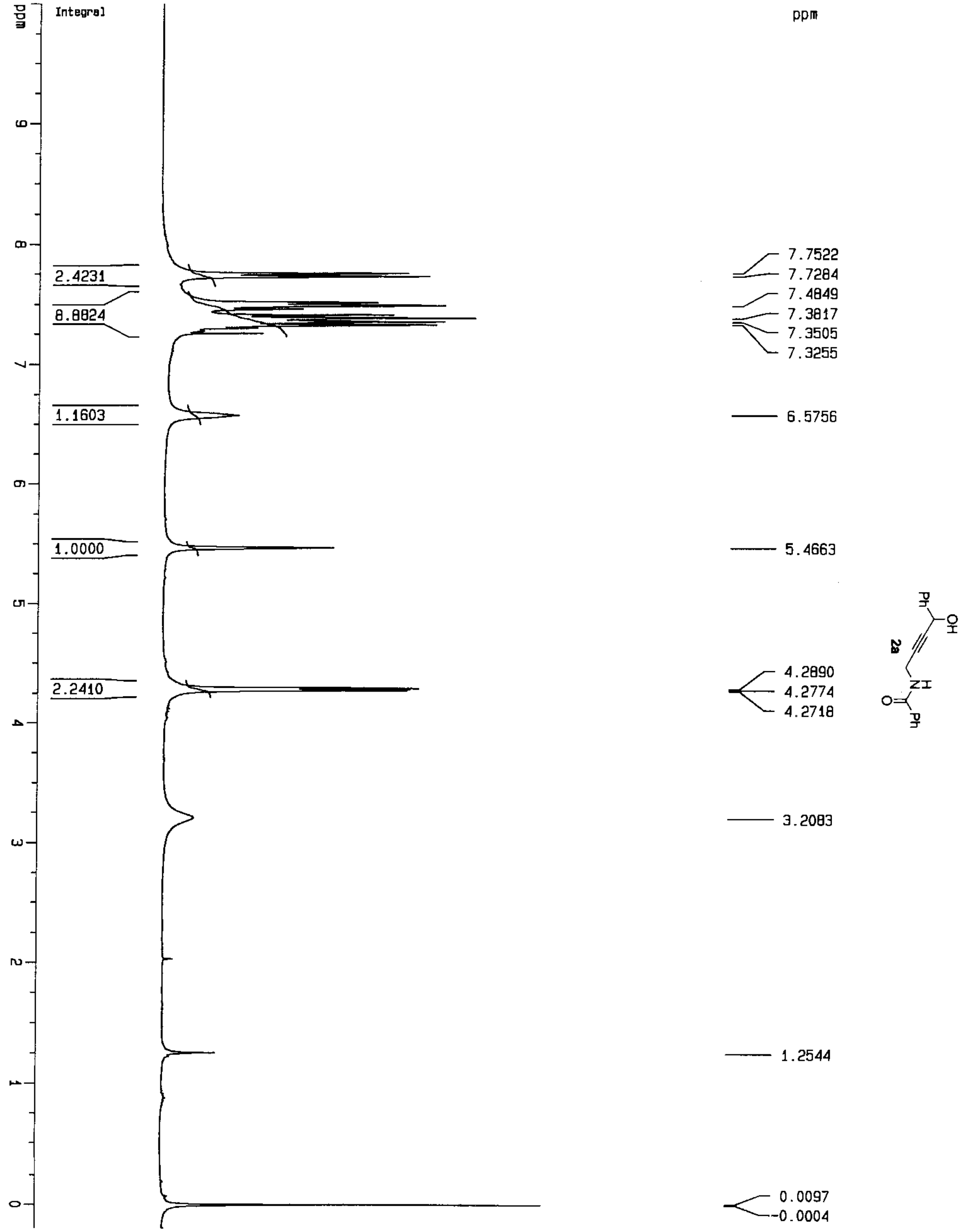


23

2-{2-[1-(*tert*-Butyldimethylsilanyloxy)-1-methylethyl]-oxazol-5-yl}-1-(2-trimethylsilanylethynylphenyl)-ethanone (22). A mixture of 0.740 g (1.62 mmol) of **21** and 3.70 g of SiO_2 in 25 mL of CH_2Cl_2 was stirred at rt for 48 h, filtered, concentrated under reduced pressure, and purified by chromatography on SiO_2 to yield 0.112 g (18%) of **21** as a red amorphous solid, 0.255 g (34%) of **22** as an orange oil, and 0.234 g (32%) of **23**. **22**: R_f 0.54 (75% hexanes:EtOAc); IR (neat) 2957, 2857, 2157, 1694, 1592, 1556, 1473, 1251, 1172, 1134, 1044, 1004 cm^{-1}; ^1H NMR δ 7.66 (d, 1 H, *J* = 7.5 Hz), 7.57 (d, 1 H, *J* = 7.3 Hz), 7.48-7.35 (m, 2 H), 6.95 (s, 1 H), 4.61 (s, 2 H), 1.61 (s, 6 H), 0.84 (s, 9 H), 0.27 (s, 9 H), -0.12 (s, 6 H); ^{13}C NMR δ 196.7, 167.3, 145.2, 140.3, 134.2, 131.4, 128.8, 128.7, 124.9, 121.1, 103.6, 101.7, 70.6, 39.2, 29.4, 25.7, 17.9, -0.4, -3.6; MS (EI) *m/z* (rel intensity) 455 (M^+, 0.1), 442 (1), 441 (2), 440 (6), 400 (15), 399 (40), 398 (100), 341 (9), 340 (30), 201 (35); HRMS (EI) *m/z* calculated for $C_{24}H_{34}NO_3Si_2$ (M-CH_3) 440.2077, found 440.2081.

2-{2-[1-(*tert*-Butyldimethylsilanyloxy)-1-methylethyl]-oxazol-5-yl}-3-methylinden-1-one (23). R_f 0.67 (75% hexanes:EtOAc); IR (neat) 2960, 2928, 2858, 1714, 1603, 1562, 1455, 1383, 1367, 1260, 1173, 1037 cm^{-1}; ^1H NMR δ 7.63 (s, 1 H), 7.46 (t, 1 H, *J* = 7.2 Hz), 7.40 (d, 1 H, *J* = 7.8 Hz), 7.24 (t, 1 H, *J* = 7.3 Hz), 7.18 (d, 1 H, *J* = 7.2 Hz), 2.52 (s, 3 H), 1.71 (s, 6 H), 0.87 (s, 9 H), -0.07 (s, 6 H); ^{13}C NMR δ 194.3, 167.4, 152.6, 146.6, 145.2, 134.3, 131.1, 129.5, 126.8, 122.7, 121.3, 120.3, 71.2, 29.7, 26.0, 18.3, 13.1, -3.0; MS (EI) *m/z* (rel intensity) 368 (15), 328 (11), 327 (35), 326 ($[M\text{-}t\text{-}Bu]^+$, 100), 270 (5), 269 (20), 268 (76); HRMS (EI) *m/z* calculated for $C_{18}H_{20}NO_3Si$ (M-$C(CH_3)_3$) 326.1212, found 326.1211.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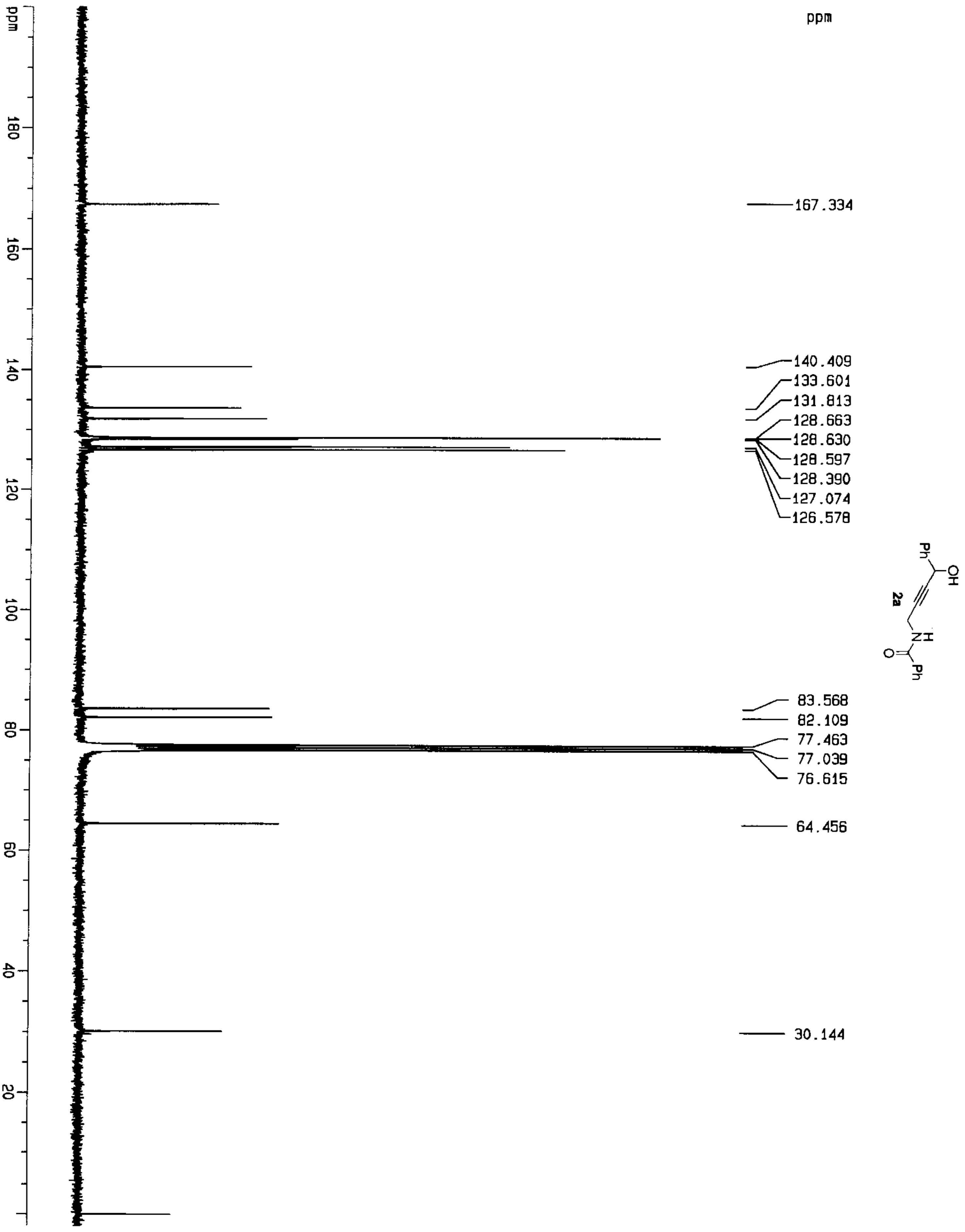
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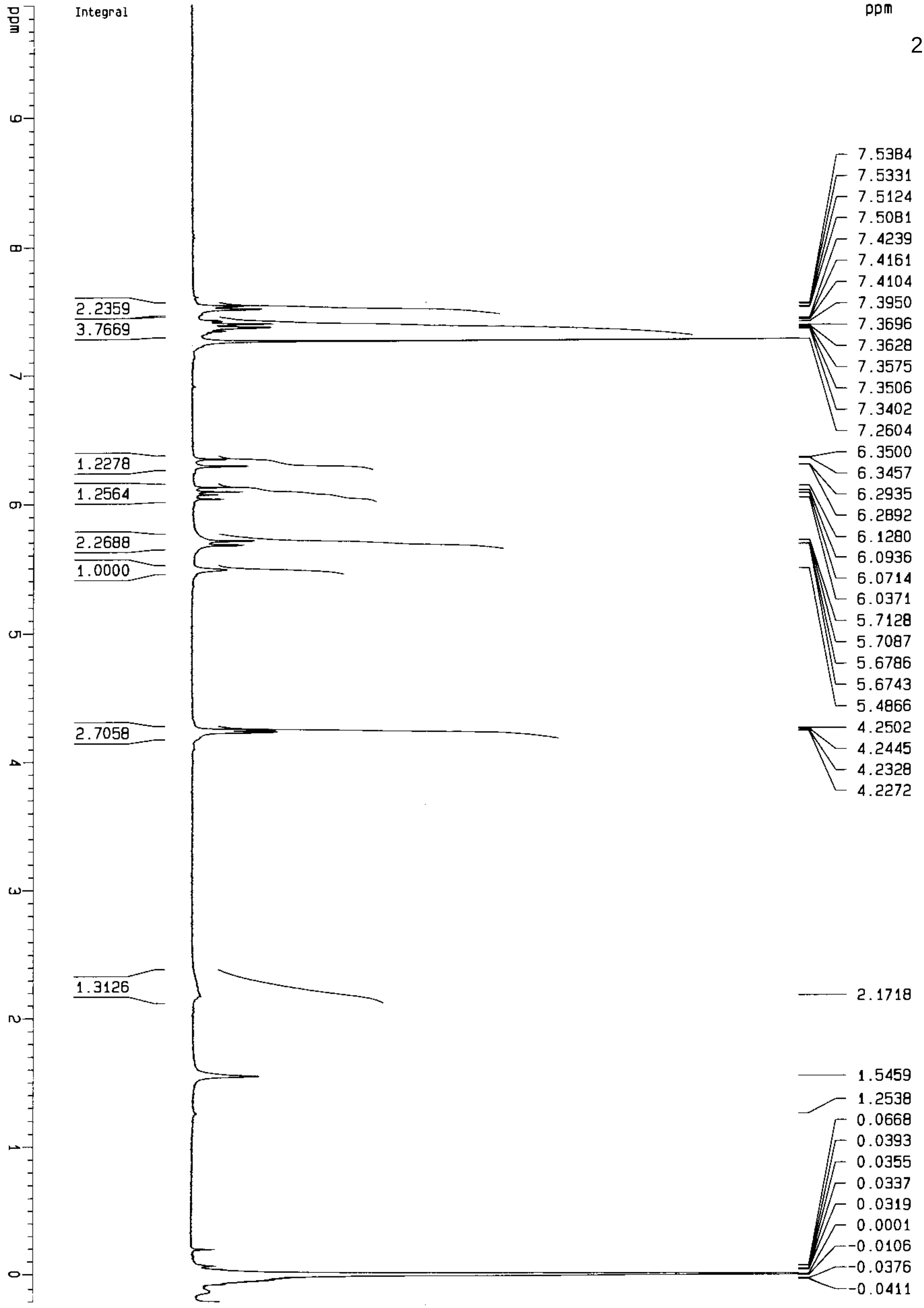
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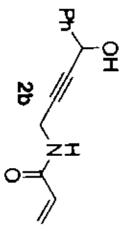
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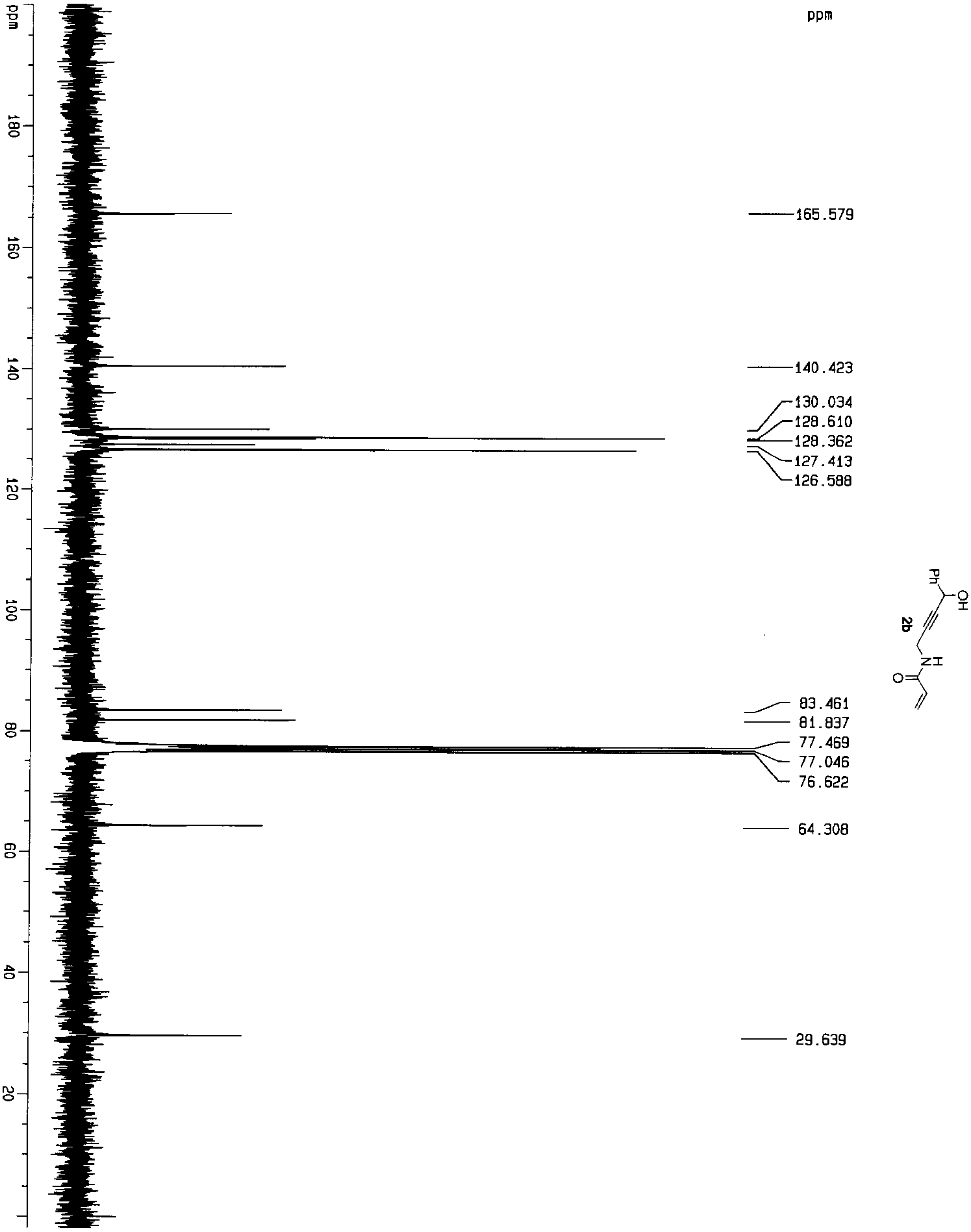
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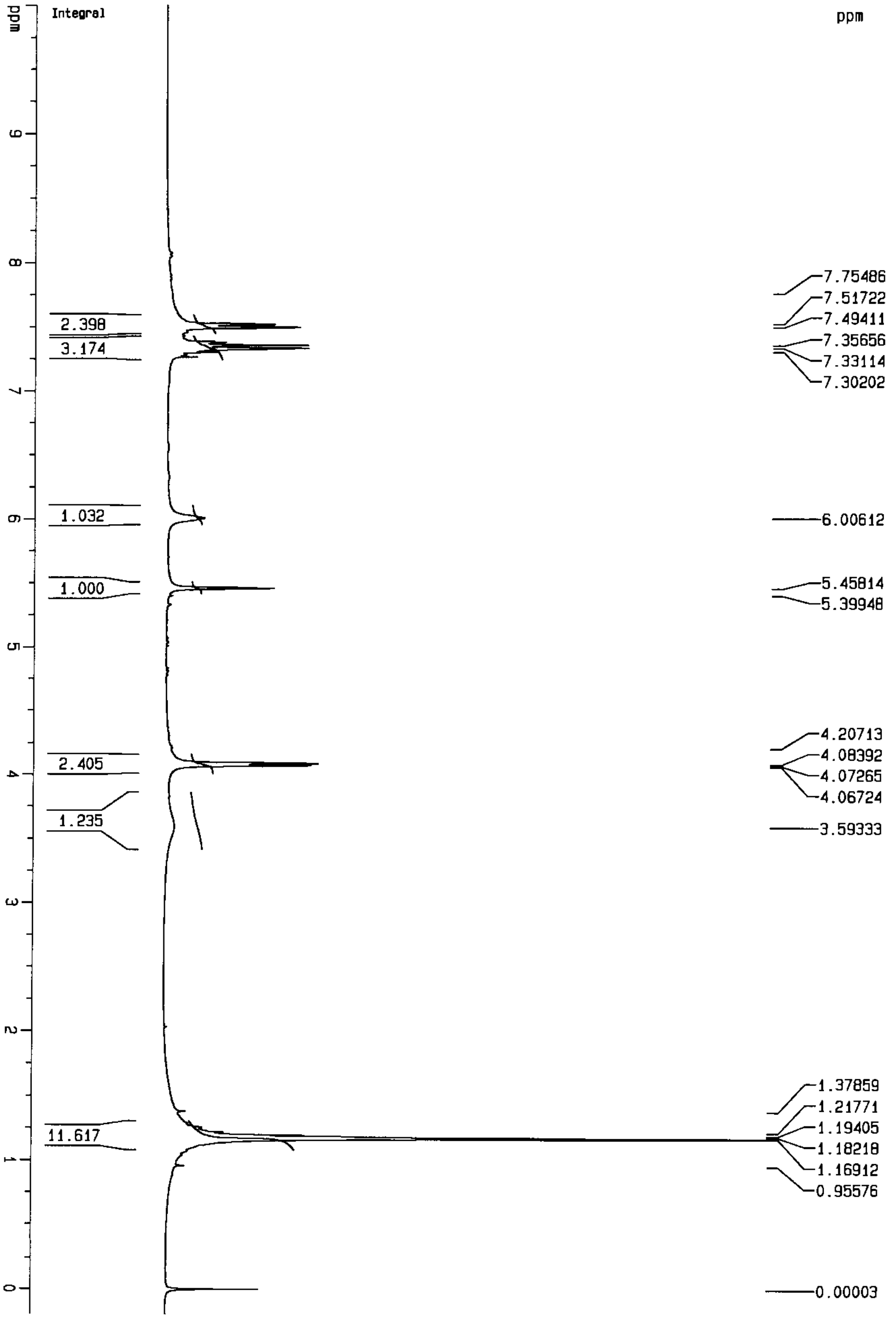
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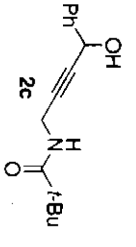
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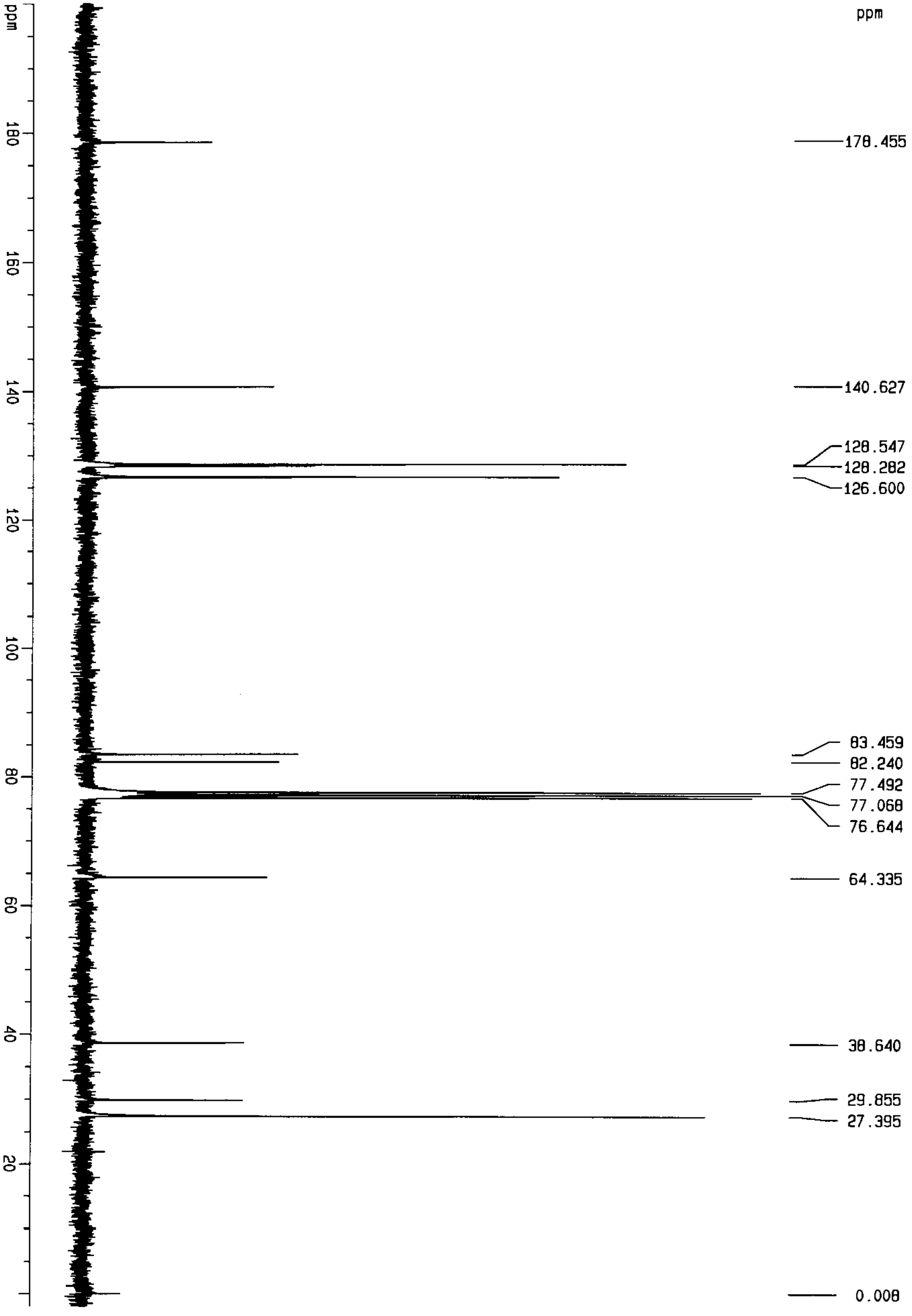
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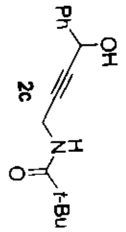
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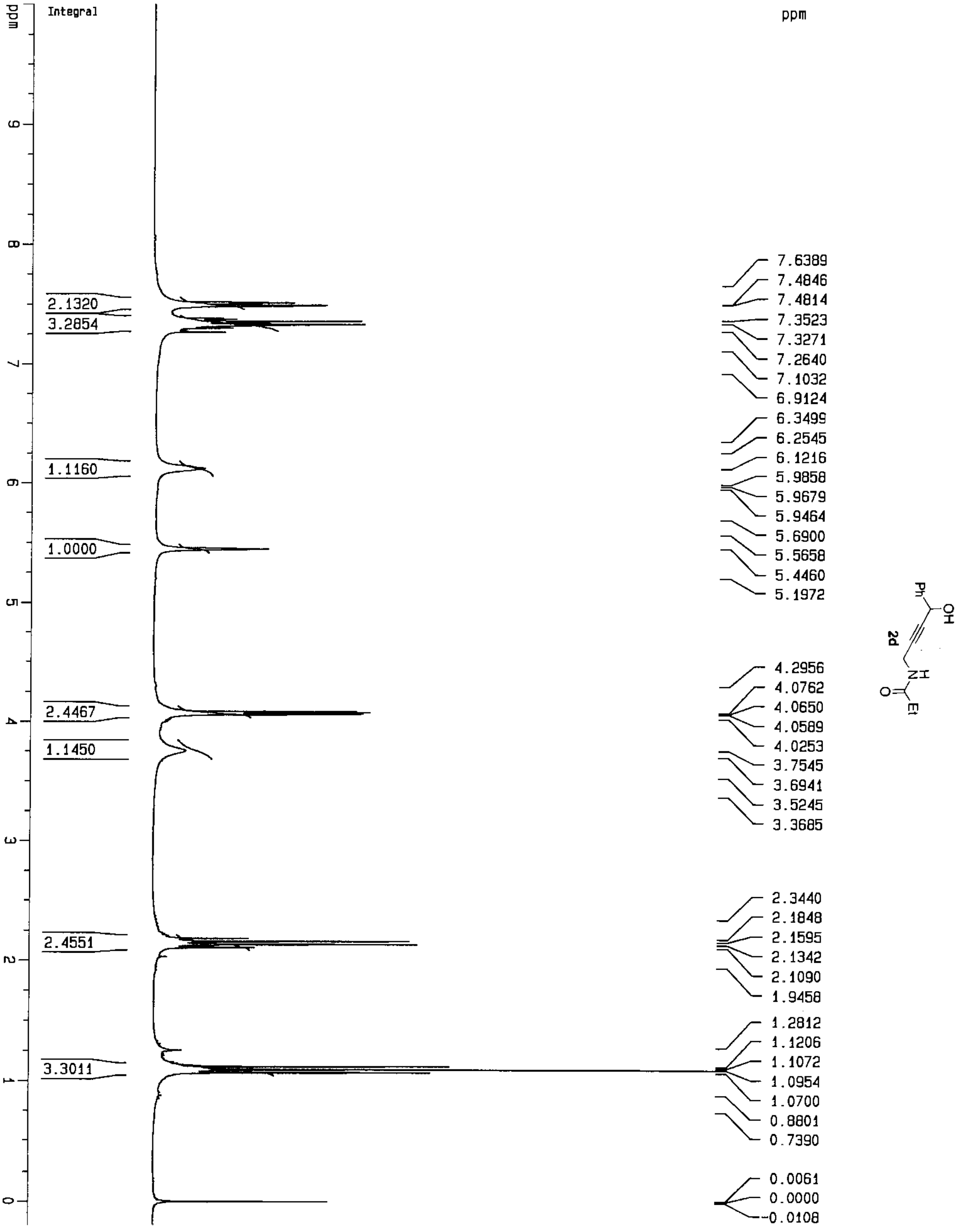
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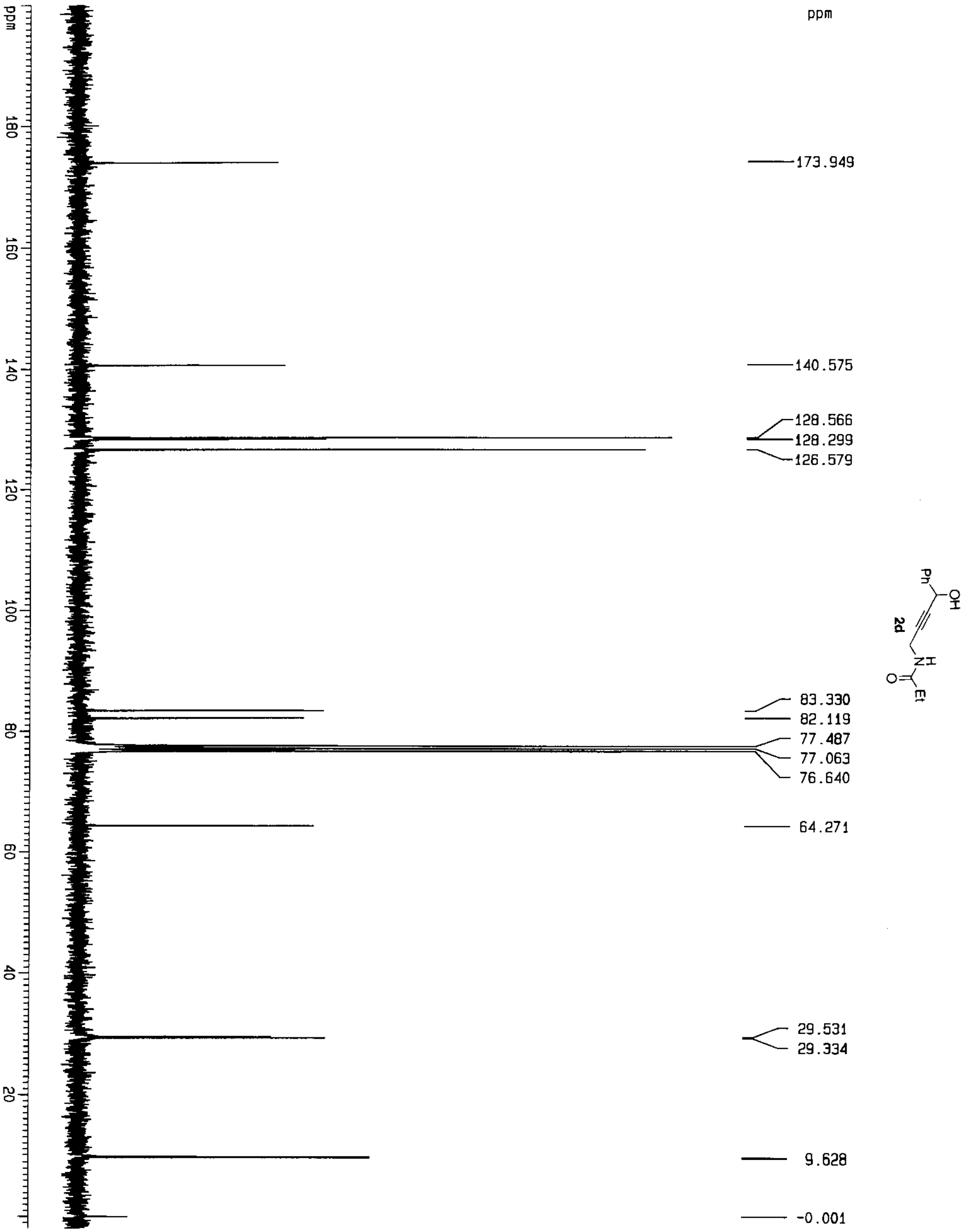
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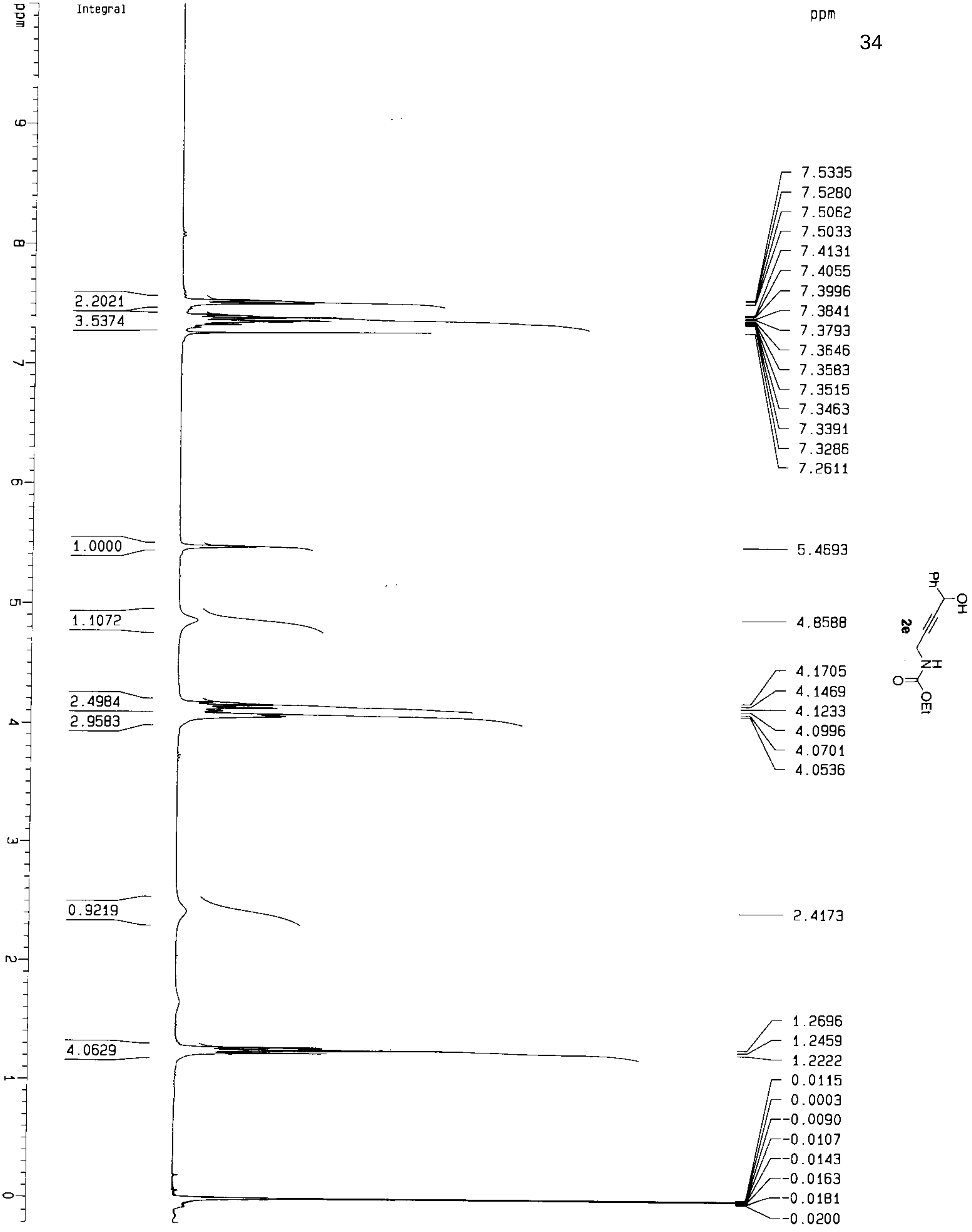
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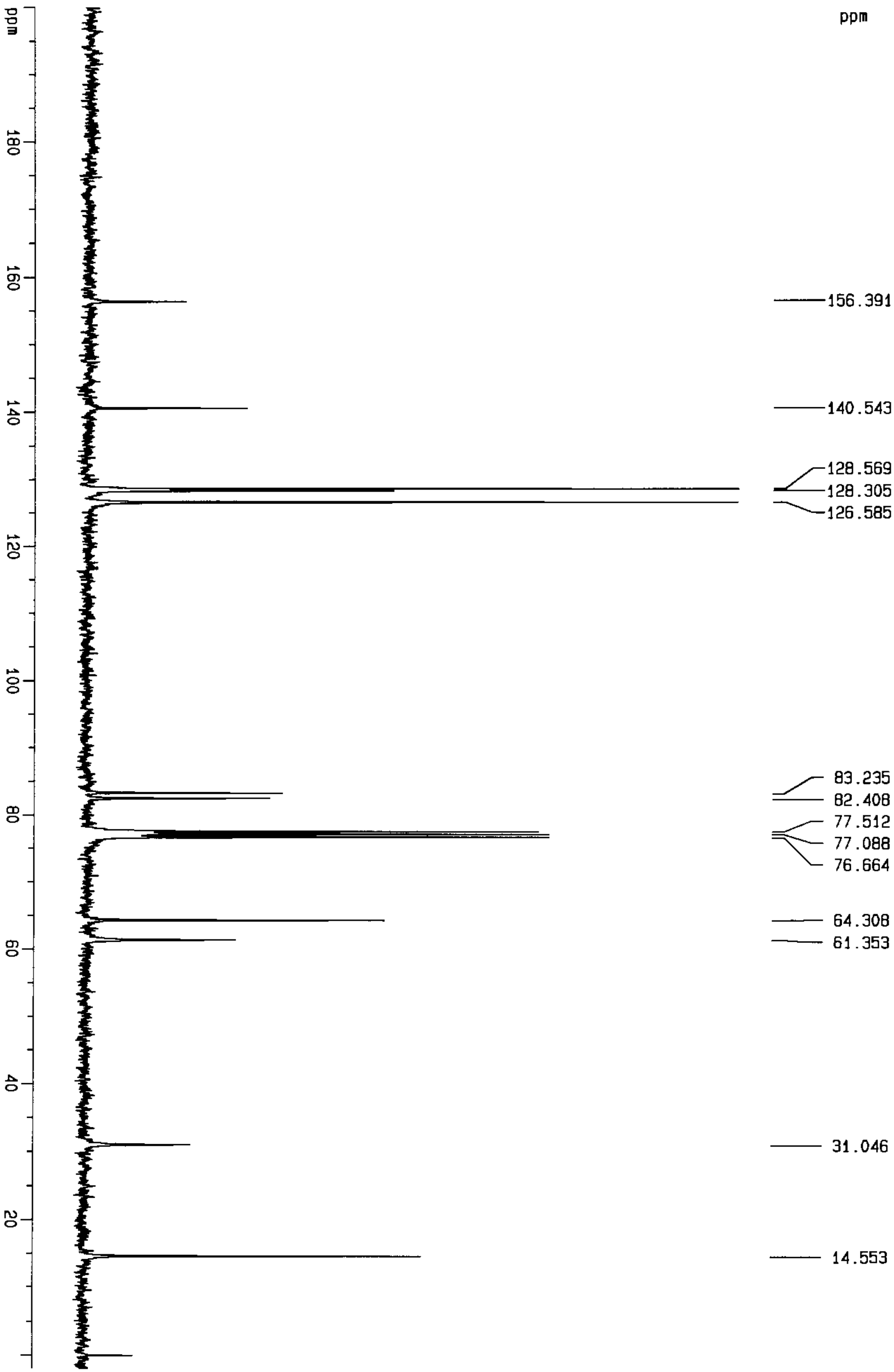

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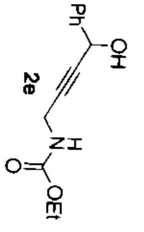

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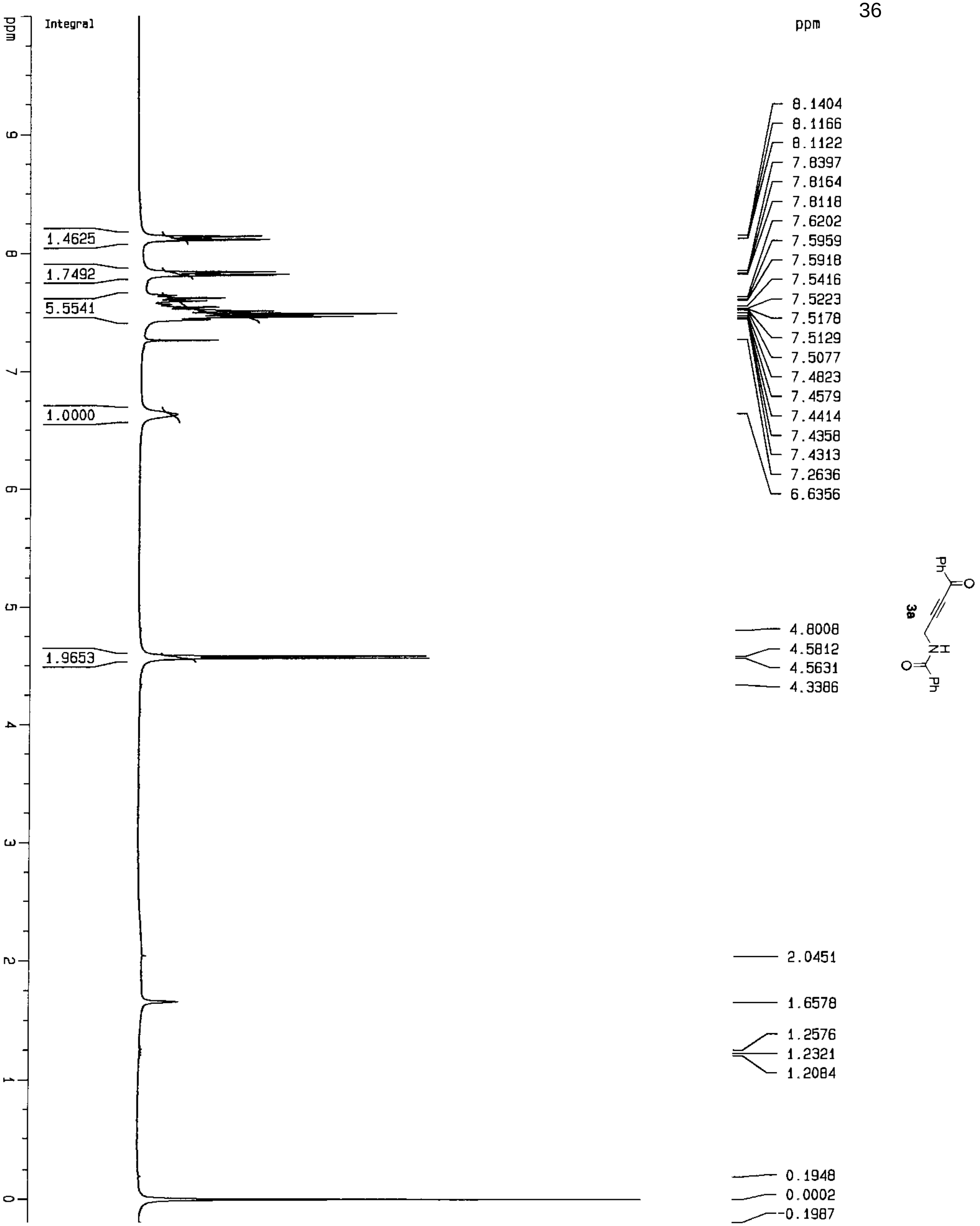
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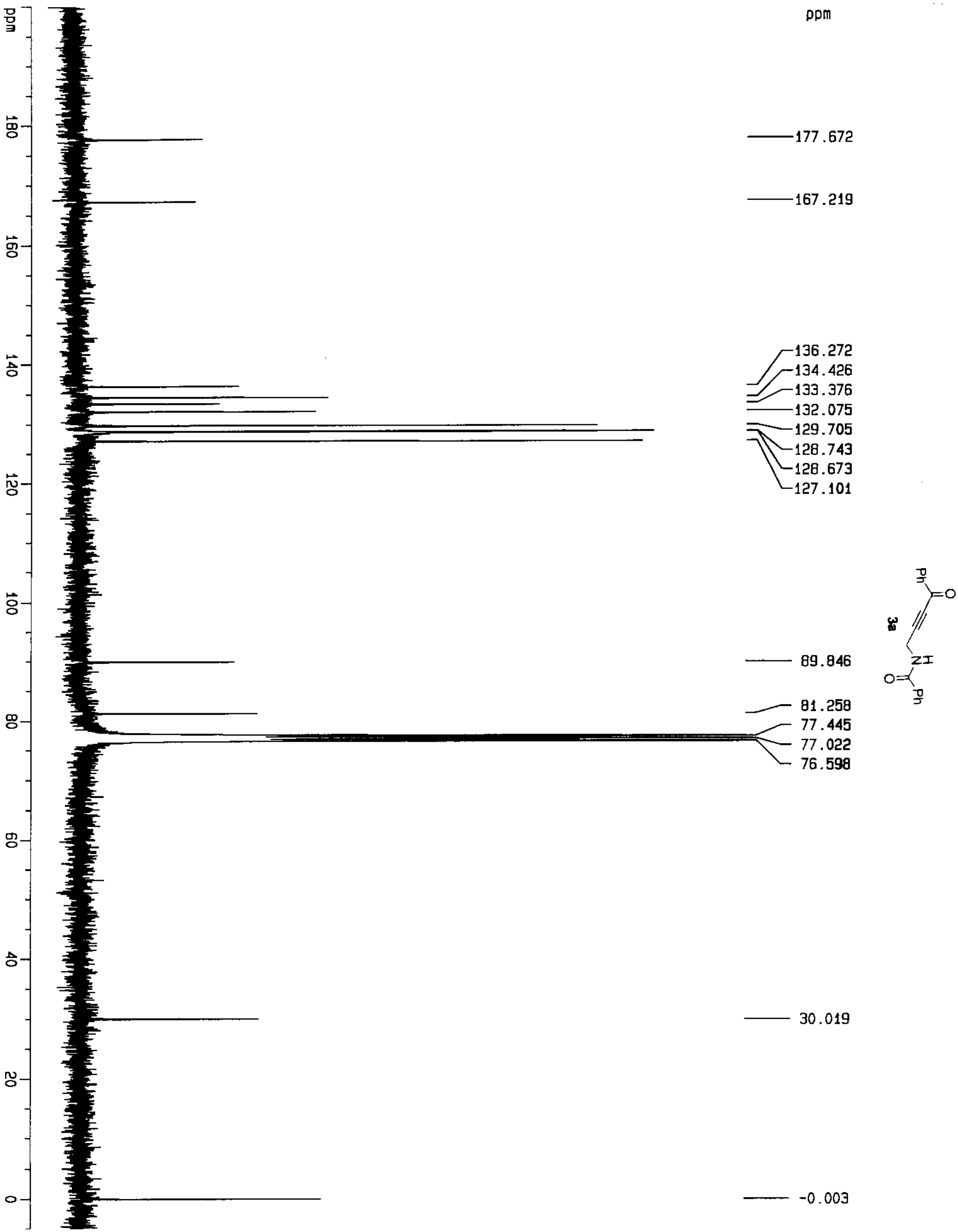

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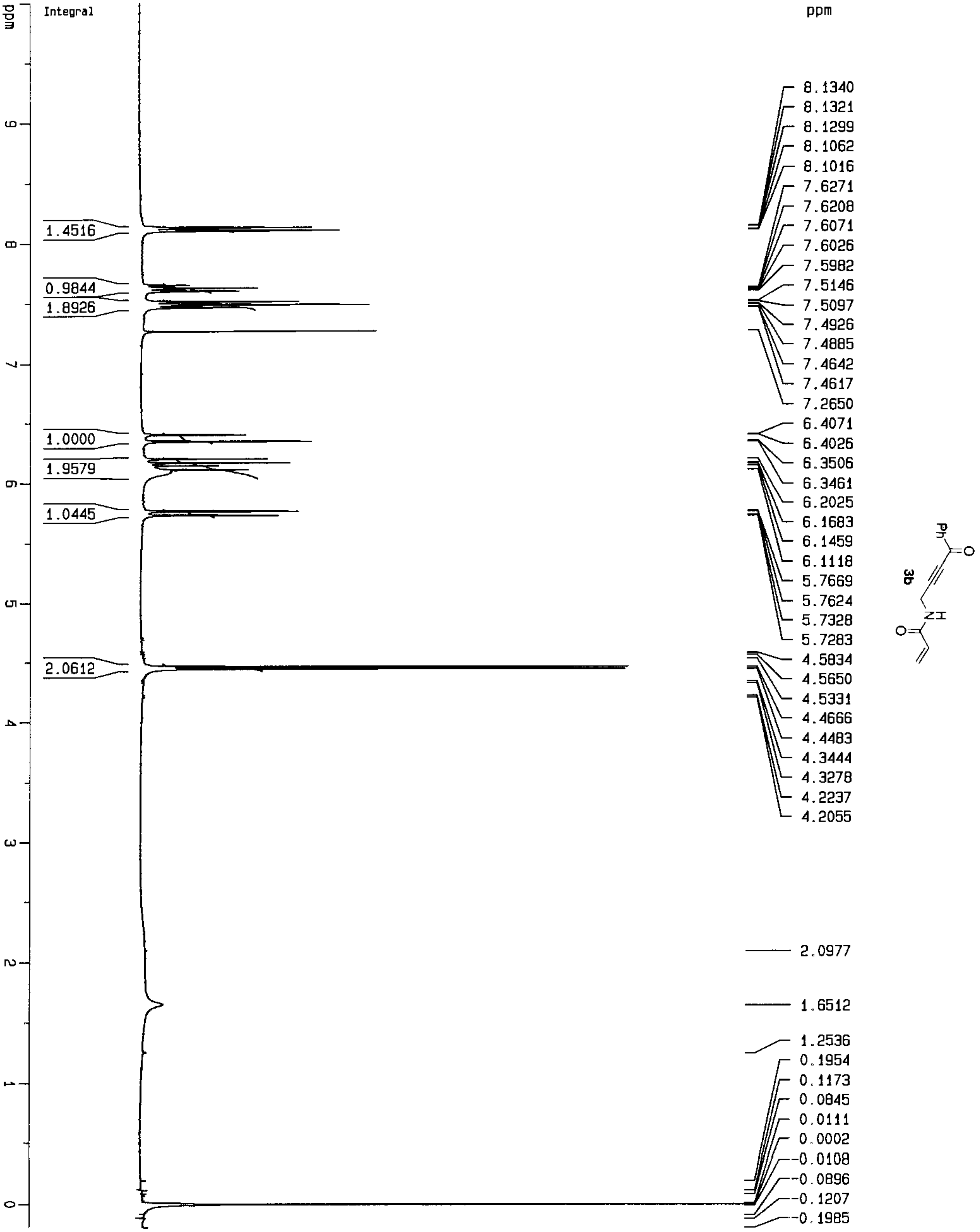
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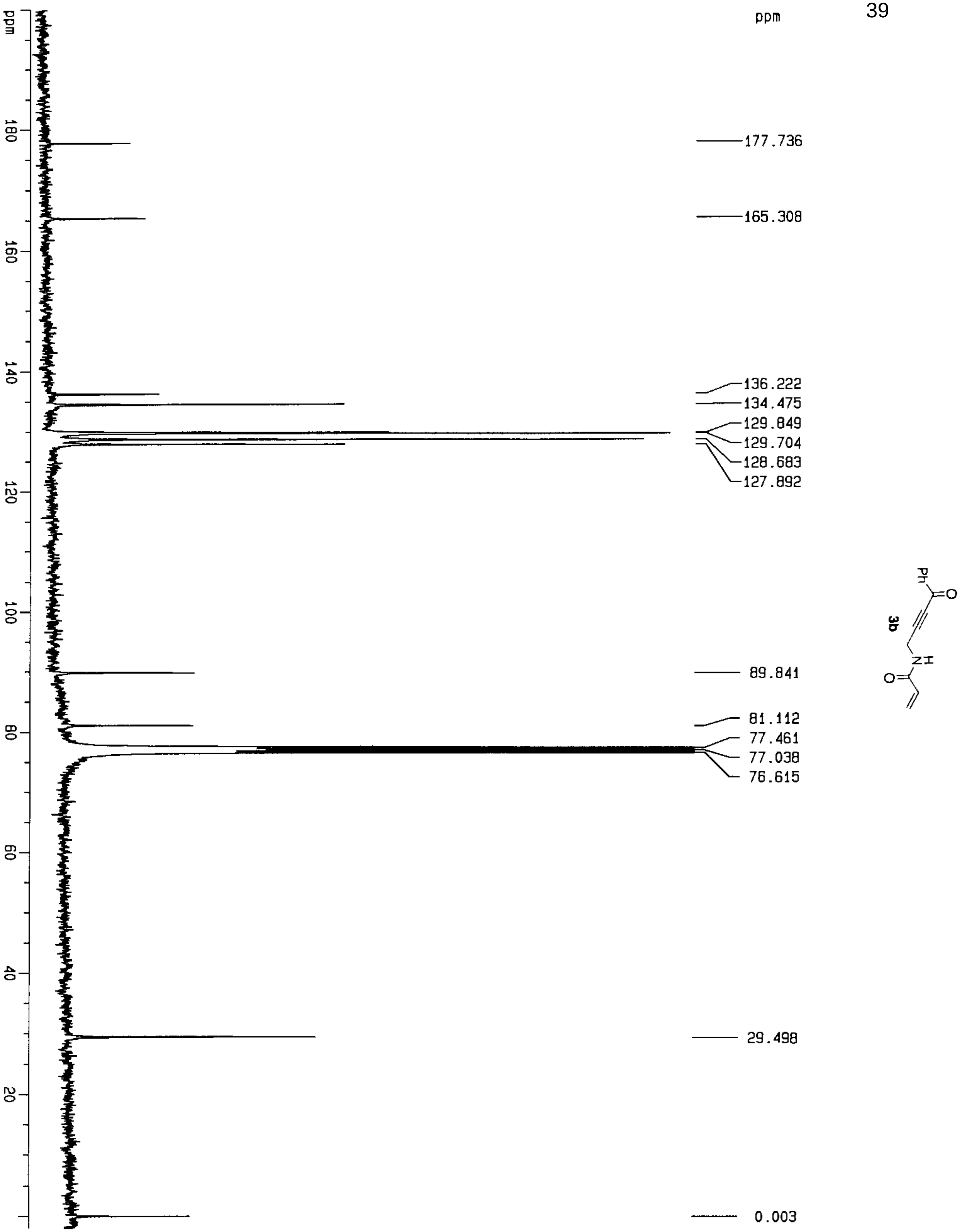
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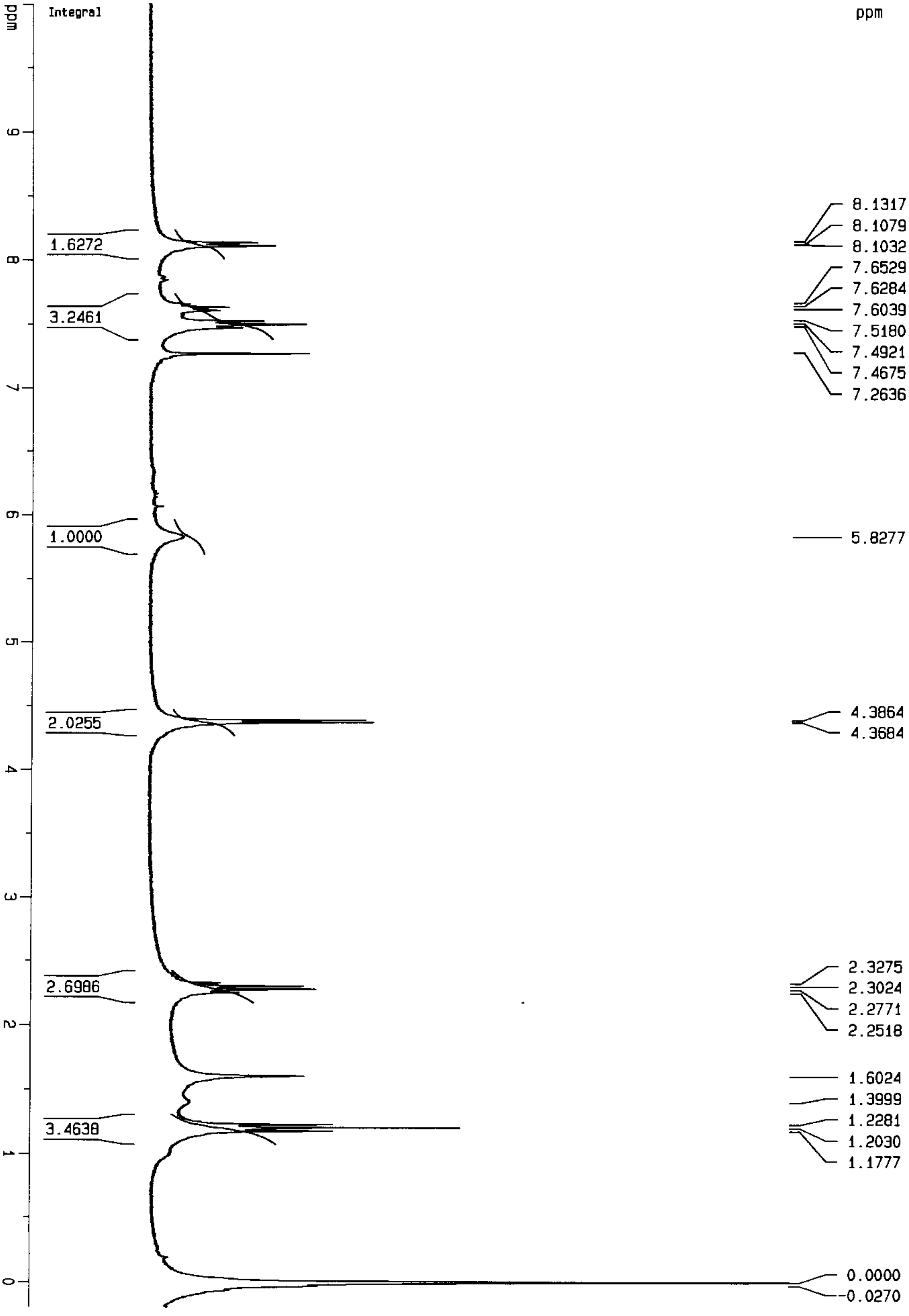
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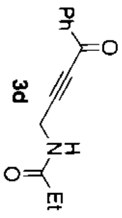
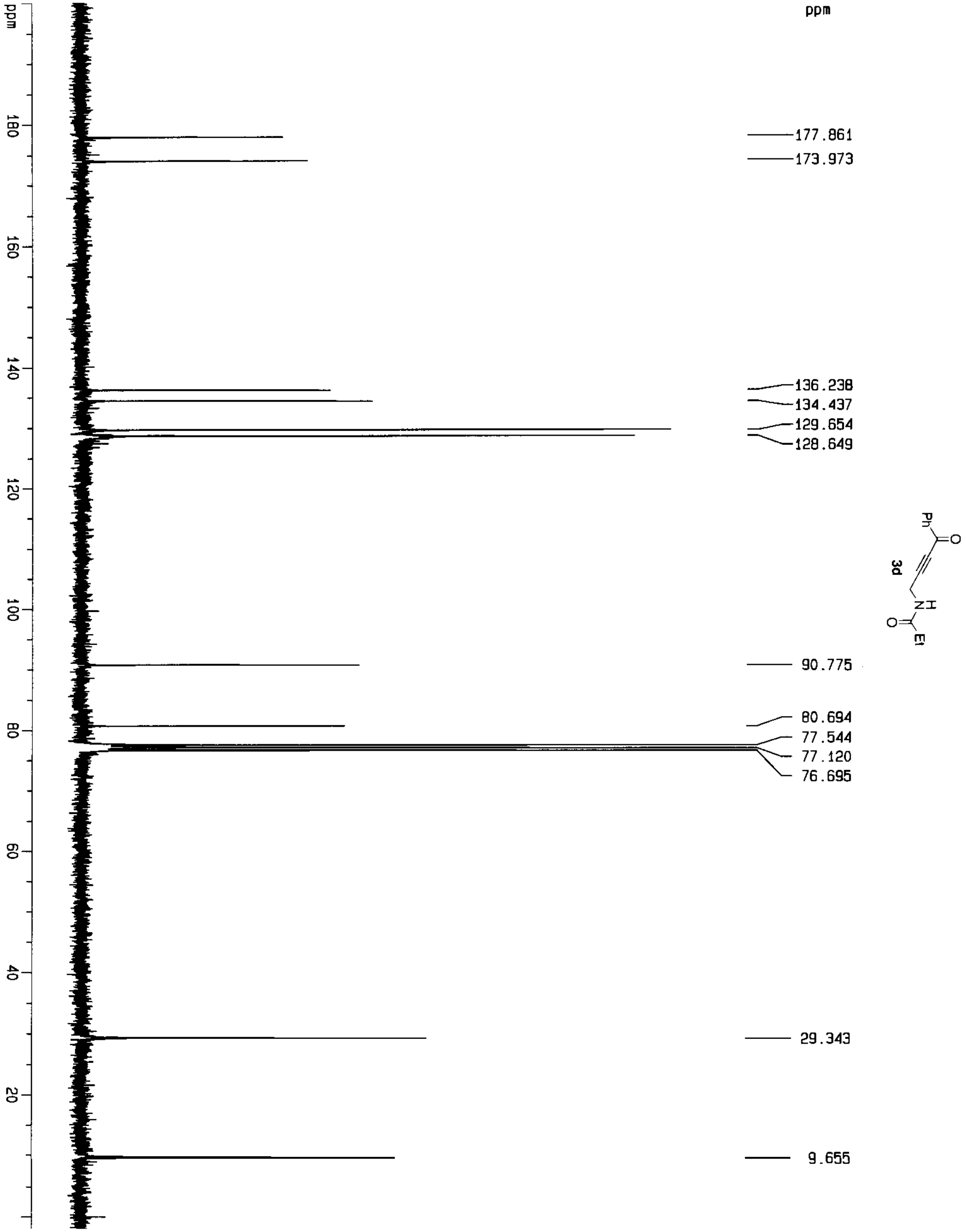
0
1.6272
3.2461
1.0000
2.0255
2.6986
3.4638
ppm
8.1317
8.1079
8.1032
7.6529
7.6284
7.6039
7.5180
7.4921
7.4675
7.2636
5.8277
4.3864
4.3684
2.3275
2.3024
2.2771
2.2518
1.6024
1.3999
1.2281
1.2030
1.1777
0.0000
-0.0270


Ph
O
H
N
O
Et

3d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160
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80
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40
20
ppm
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136.238
134.437
129.654
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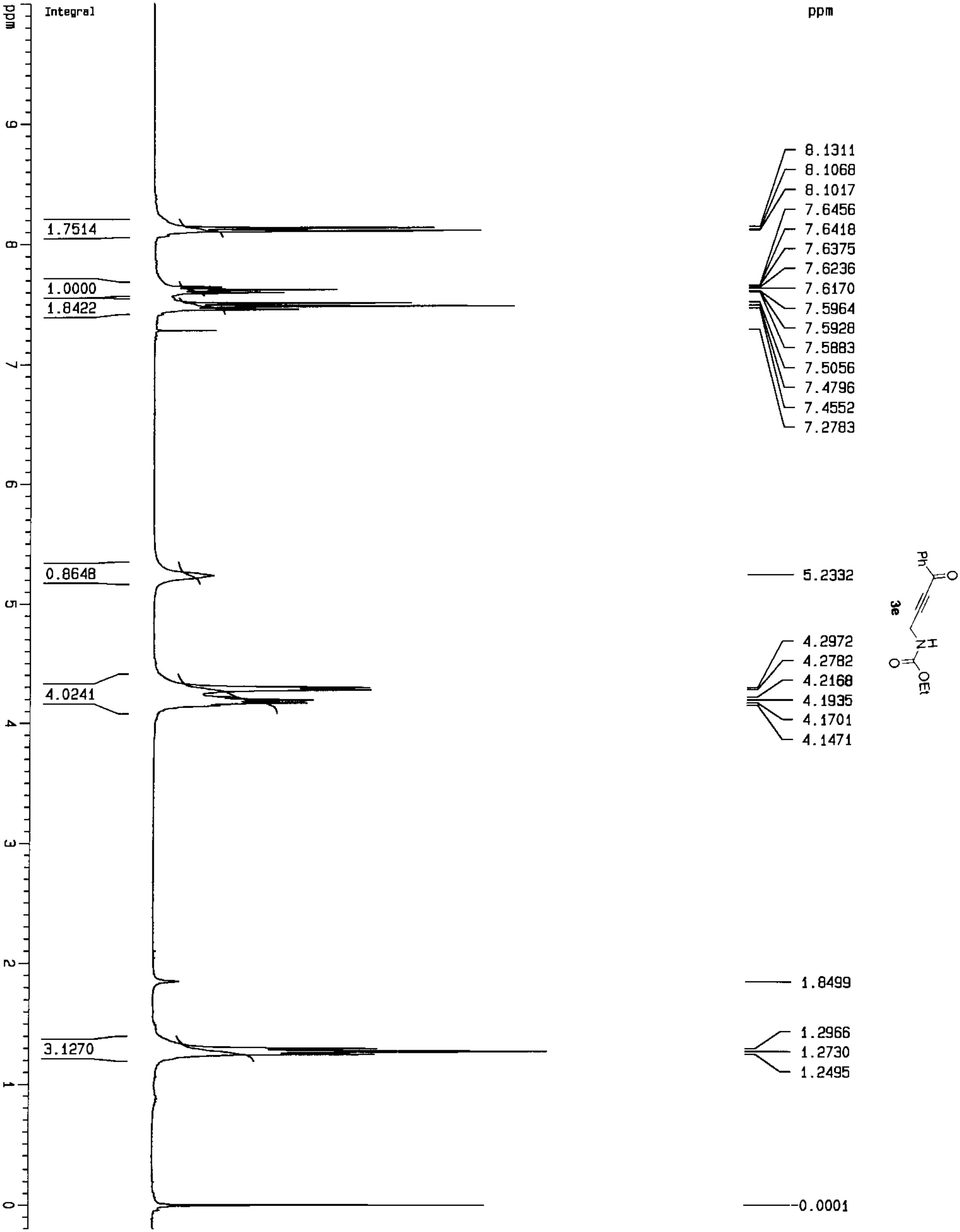
90.775
80.694
77.544
77.120
76.695
29.343
9.655
Ph
O
H
N
O
Et

3d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1.0000
1.8422
0.8648
4.0241
3.1270
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8
7
6
5
4
3
2
1
0
ppm
8.1311
8.1068
8.1017
7.6456
7.6418
7.6375
7.6236
7.6170
7.5964
7.5928
7.5883
7.5056
7.4796
7.4552
7.2783
5.2332
4.2972
4.2782
4.2168
4.1935
4.1701
4.1471
1.8499
1.2966
1.2730
1.2495
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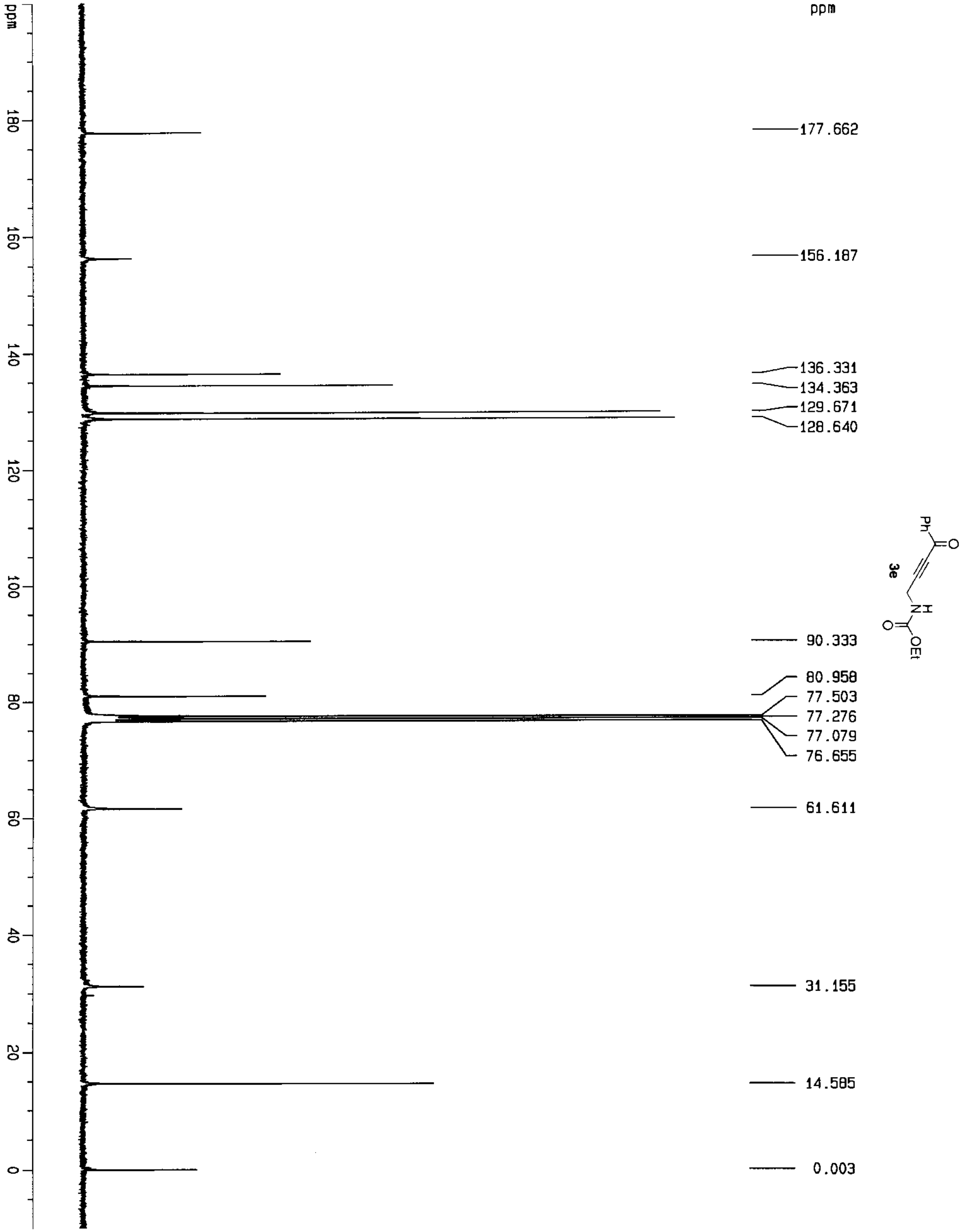
Ph
O
H
N
O
OEt

3e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120
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80
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40
20
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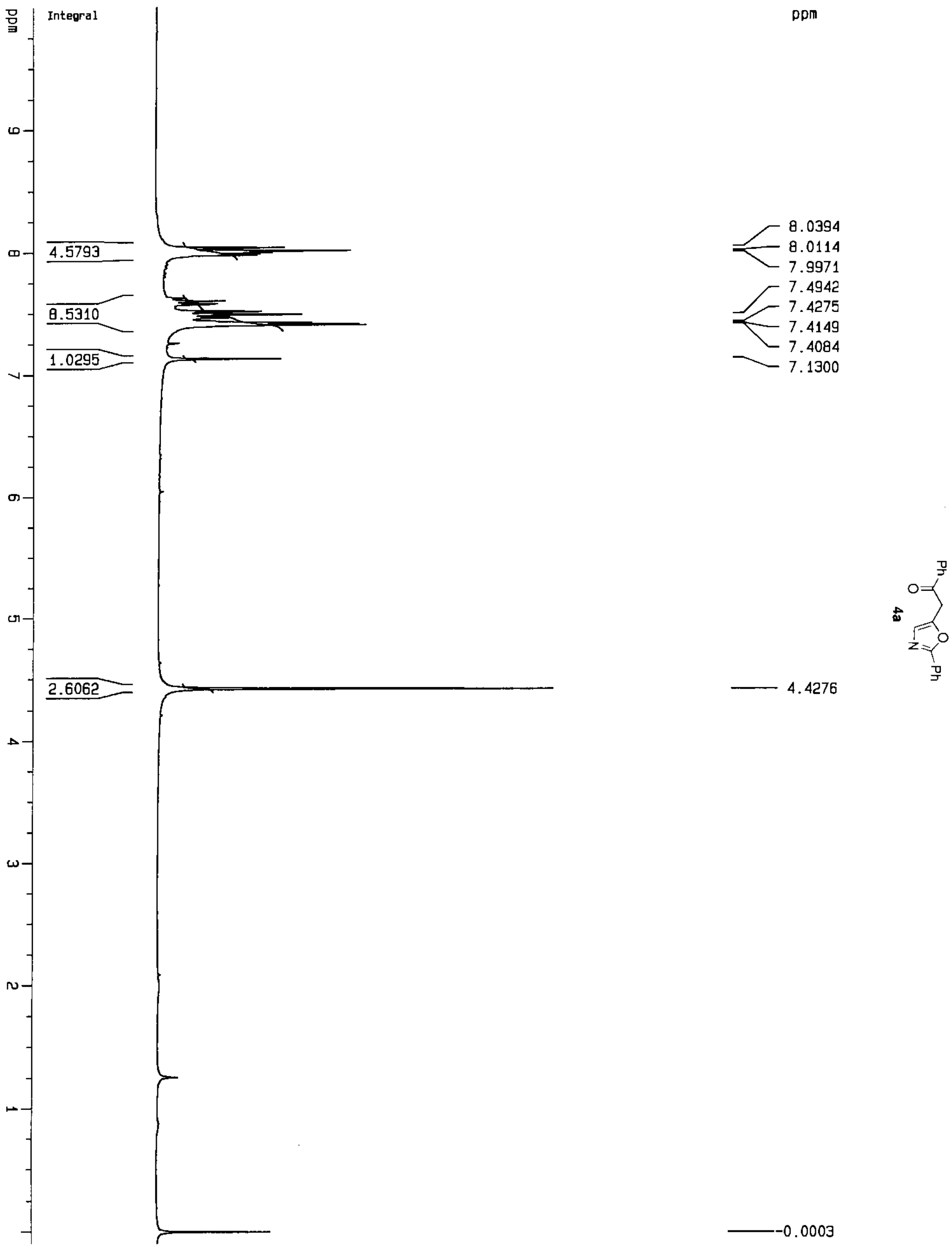
136.331
134.363
129.671
128.640
90.333
80.958
77.503
77.276
77.079
76.655
61.611
31.155
14.585
0.003
Ph
O
3e
H
N
O
OEt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Integral
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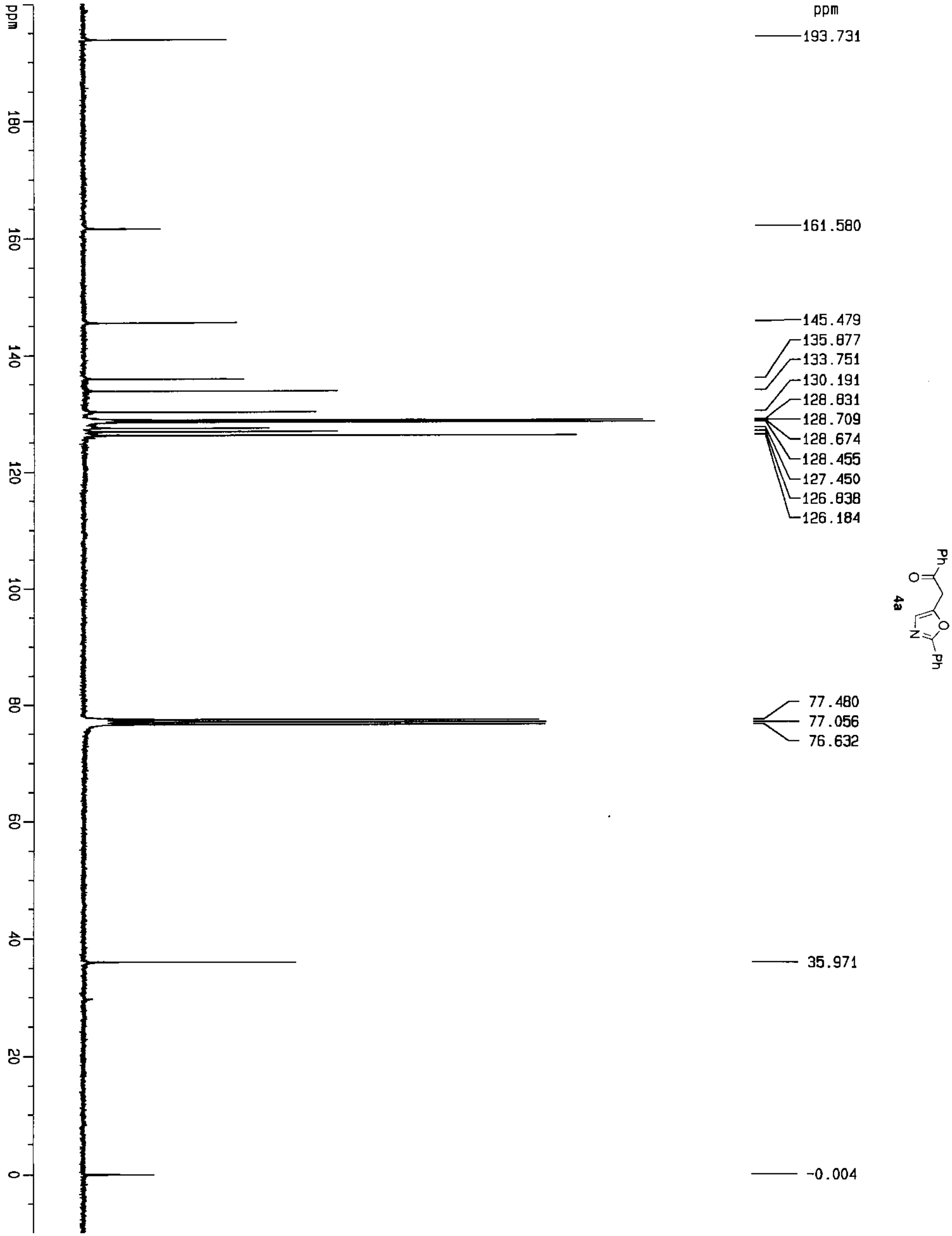
8
7
6
5
4
3
2
1
4.5793
8.5310
1.0295
2.6062
ppm
8.0394
8.0114
7.9971
7.4942
7.4275
7.4149
7.4084
7.1300
4.4276
-0.0003
Ph
O
O
N
Ph
4a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133.751
130.191
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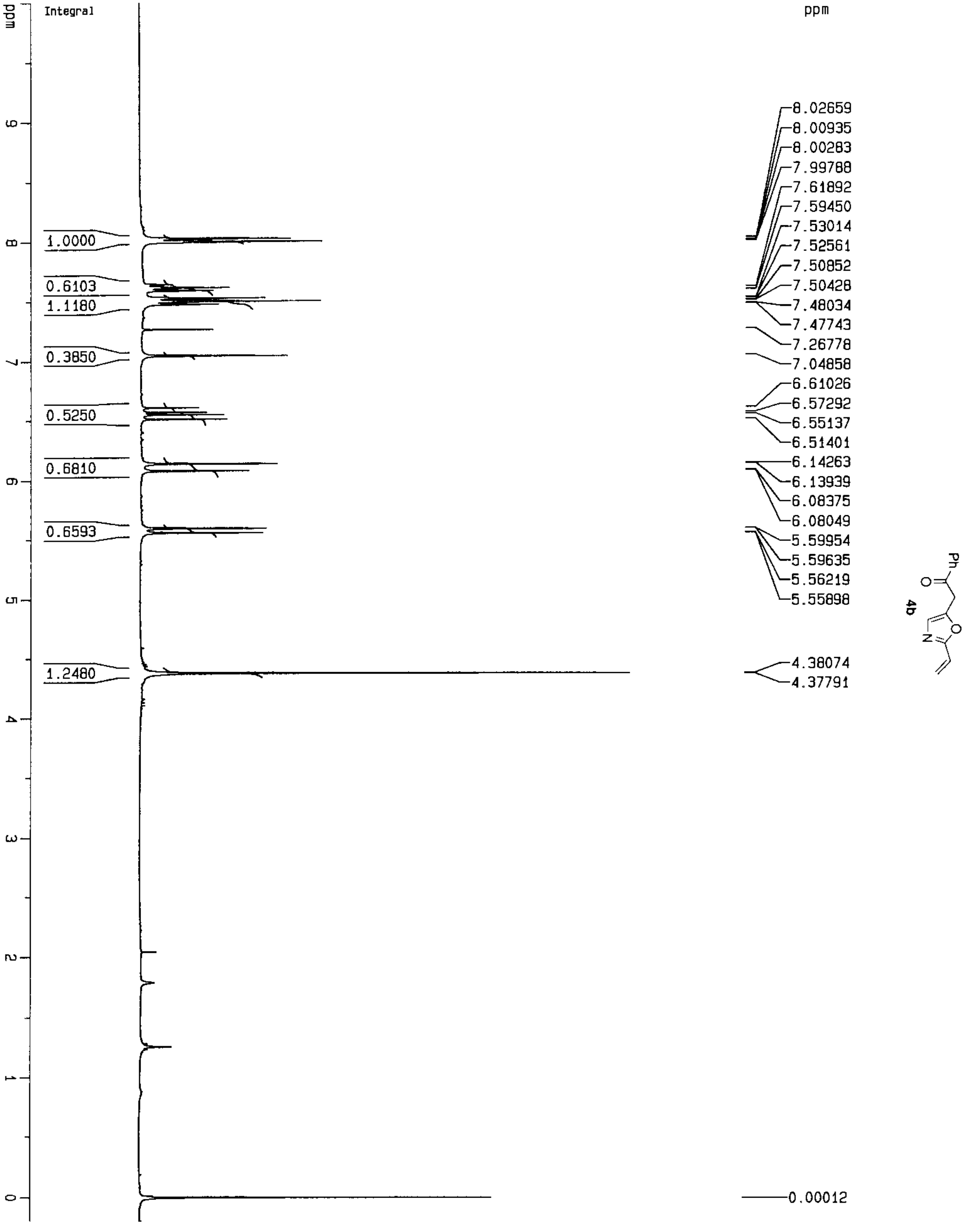
128.674
128.455
127.450
126.838
126.184
77.480
77.056
76.632
35.971
-0.004
ppm
180
160
140
120
100
80
60
40
20
0
Ph
O
O
N
Ph
4a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8
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6
5
4
3
2
1
0
1.0000
0.6103
1.1180
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0.5250
0.6810
0.6593
1.2480
ppm
8.02659
8.00935
8.00283
7.99788
7.61892
7.59450
7.53014
7.52561
7.50852
7.50428
7.48034
7.47743
7.26778
7.04858
6.61026
6.57292
6.55137
6.51401
6.14263
6.13939
6.08375
6.08049
5.59954
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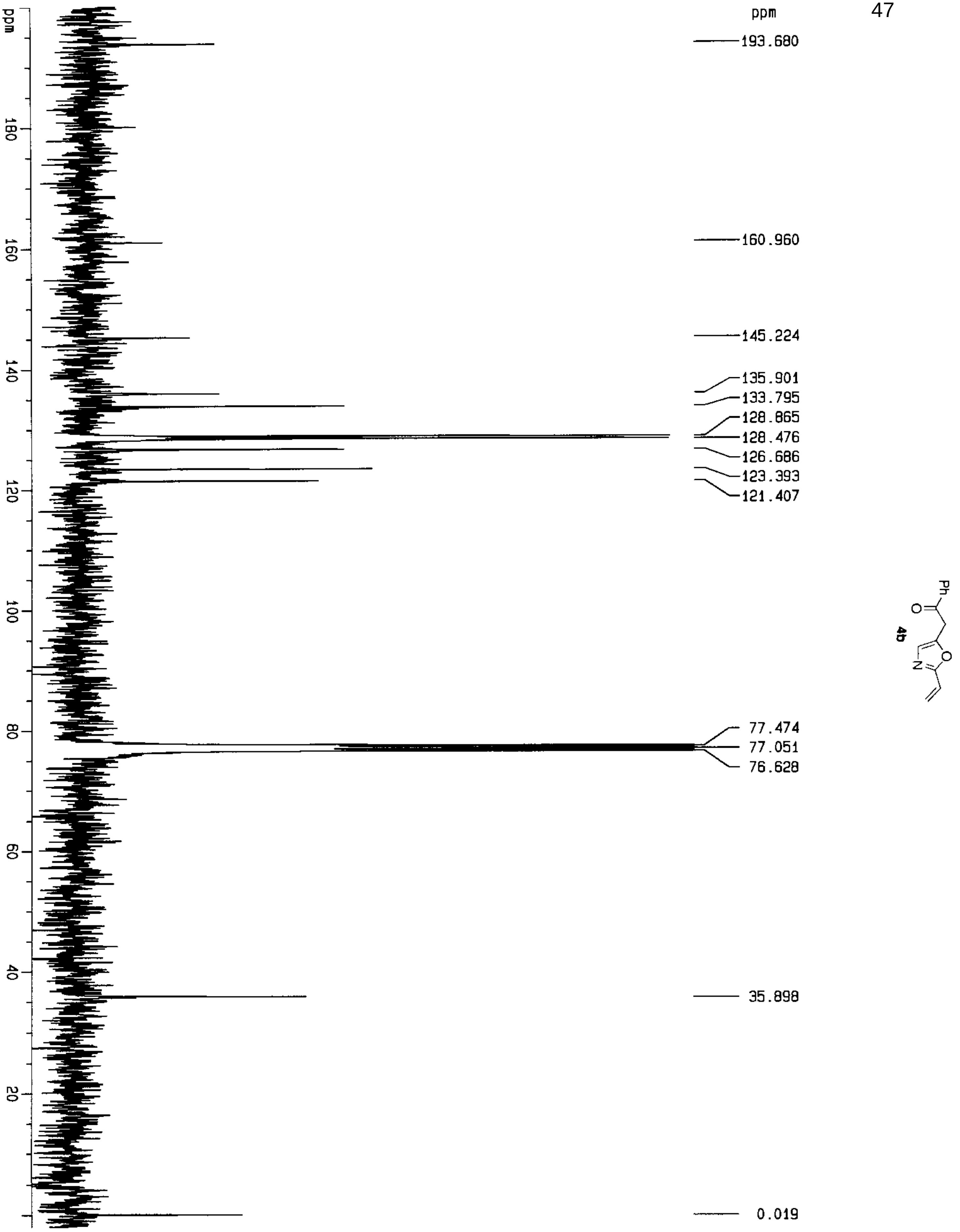
5.56219
5.55898
4.38074
4.37791
0.00012
Ph
O
O
N
4b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160
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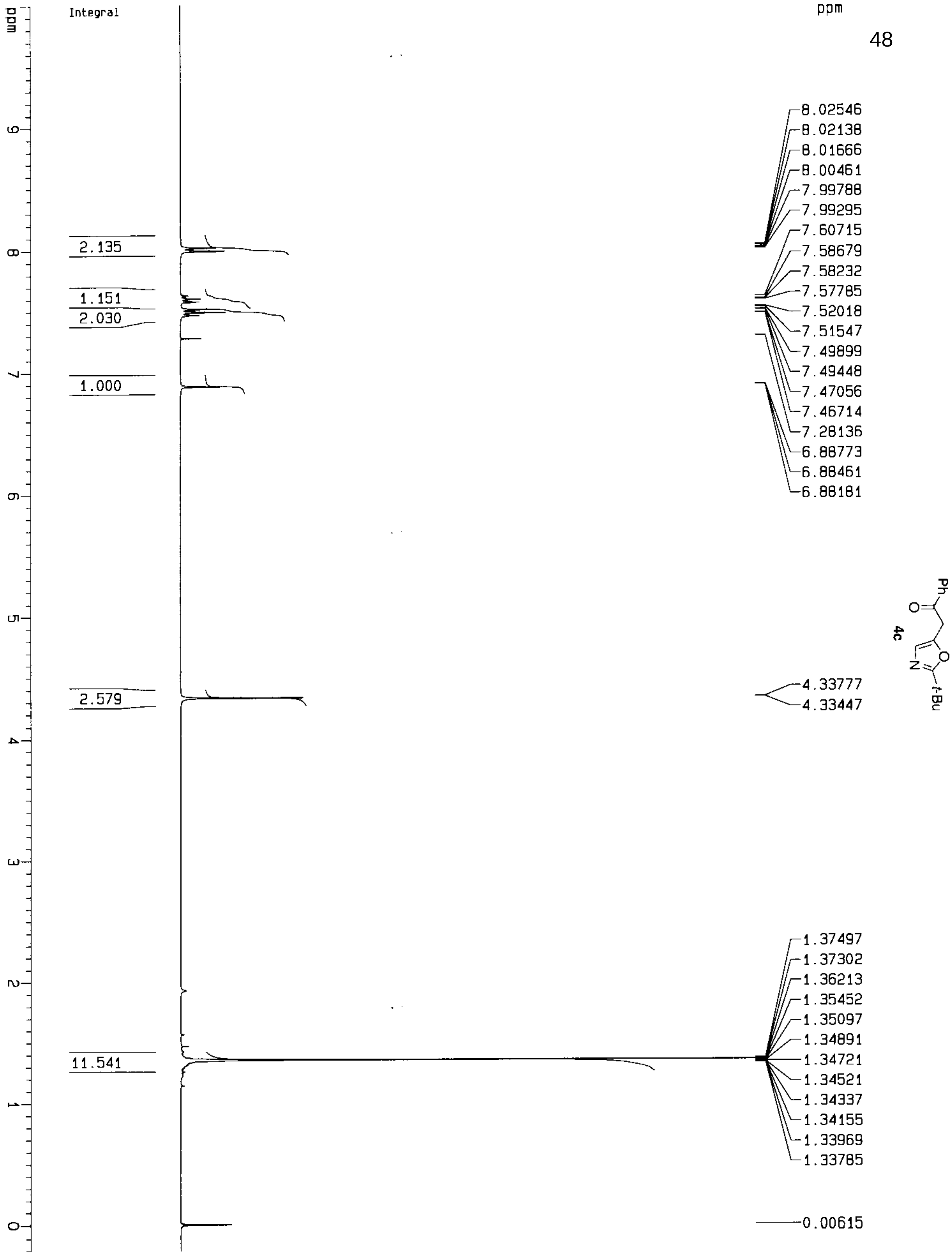
120
100
80
60
40
20
ppm
193.680
160.960
145.224
135.901
133.795
128.865
128.476
126.686
123.393
121.407
77.474
77.051
76.628
35.898
0.019
Ph
O
O
N

4b


4c
Integral
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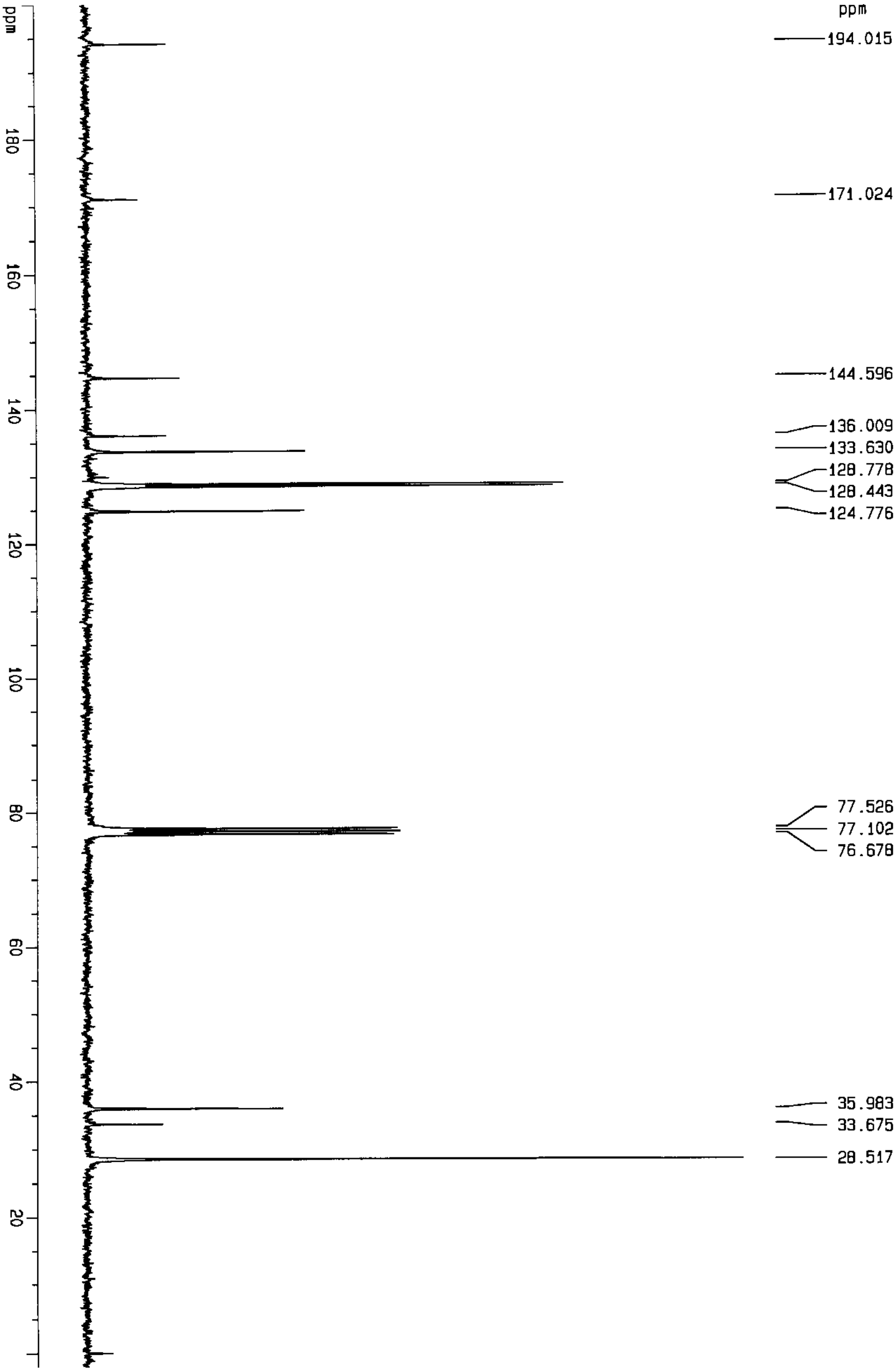
1.151
2.030
1.000
2.579
11.541
9
8
7
6
5
4
3
2
1
0
8.02546
8.02138
8.01666
8.00461
7.99788
7.99295
7.60715
7.58679
7.58232
7.57785
7.52018
7.51547
7.49899
7.49448
7.47056
7.46714
7.28136
6.88773
6.88461
6.88181
4.33777
4.33447
1.37497
1.37302
1.36213
1.35452
1.35097
1.34891
1.34721
1.34521
1.34337
1.34155
1.33969
1.33785
0.00615
Ph
O
O
N
t-Bu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120
100
80
60
40
20
ppm
194.015
171.024
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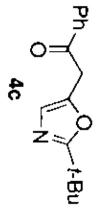
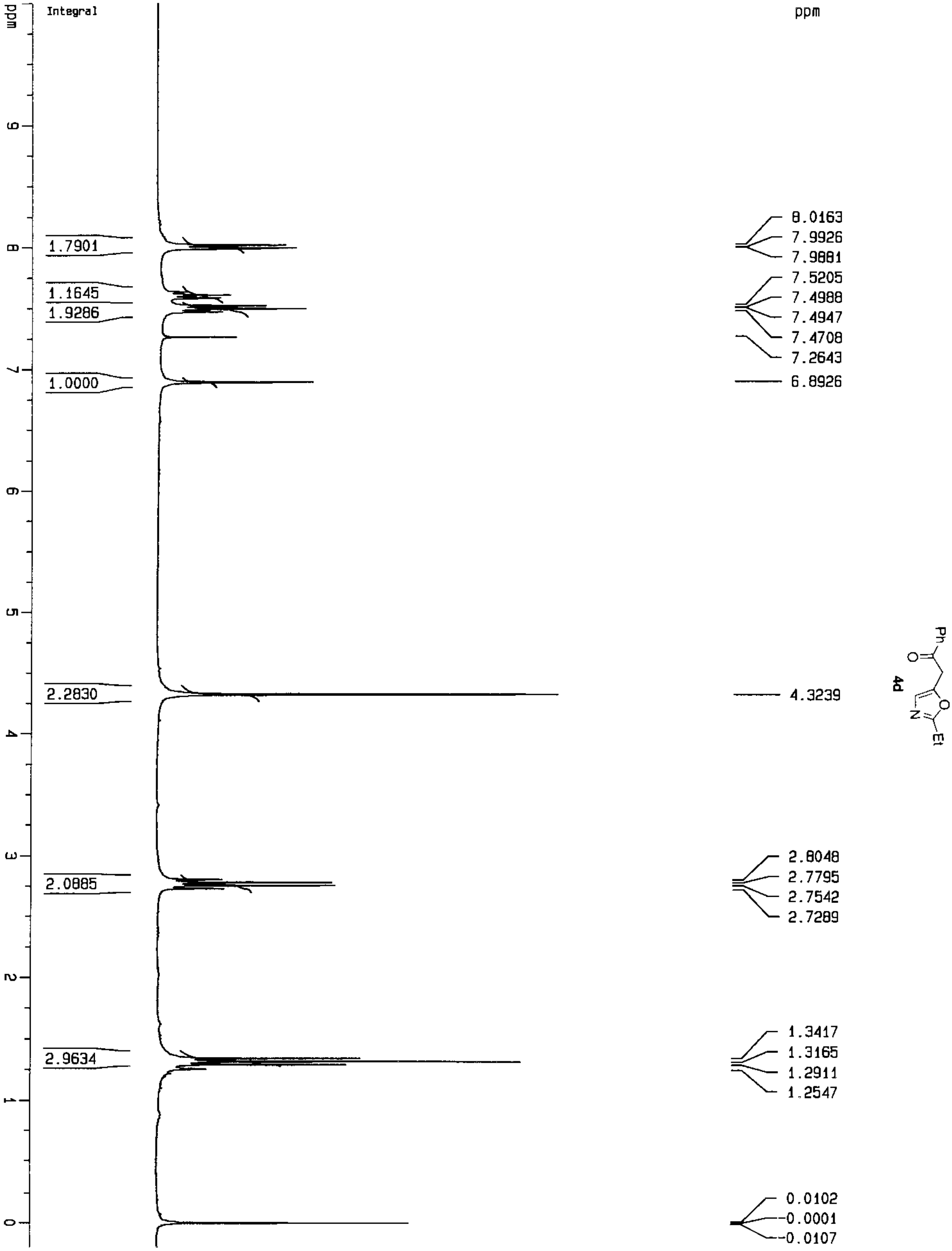
136.009
133.630
128.778
128.443
124.776
77.526
77.102
76.678
35.983
33.675
28.517


Ph
O
O
N
t-Bu

4c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Integral
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8
7
6
5
4
3
2
1
0
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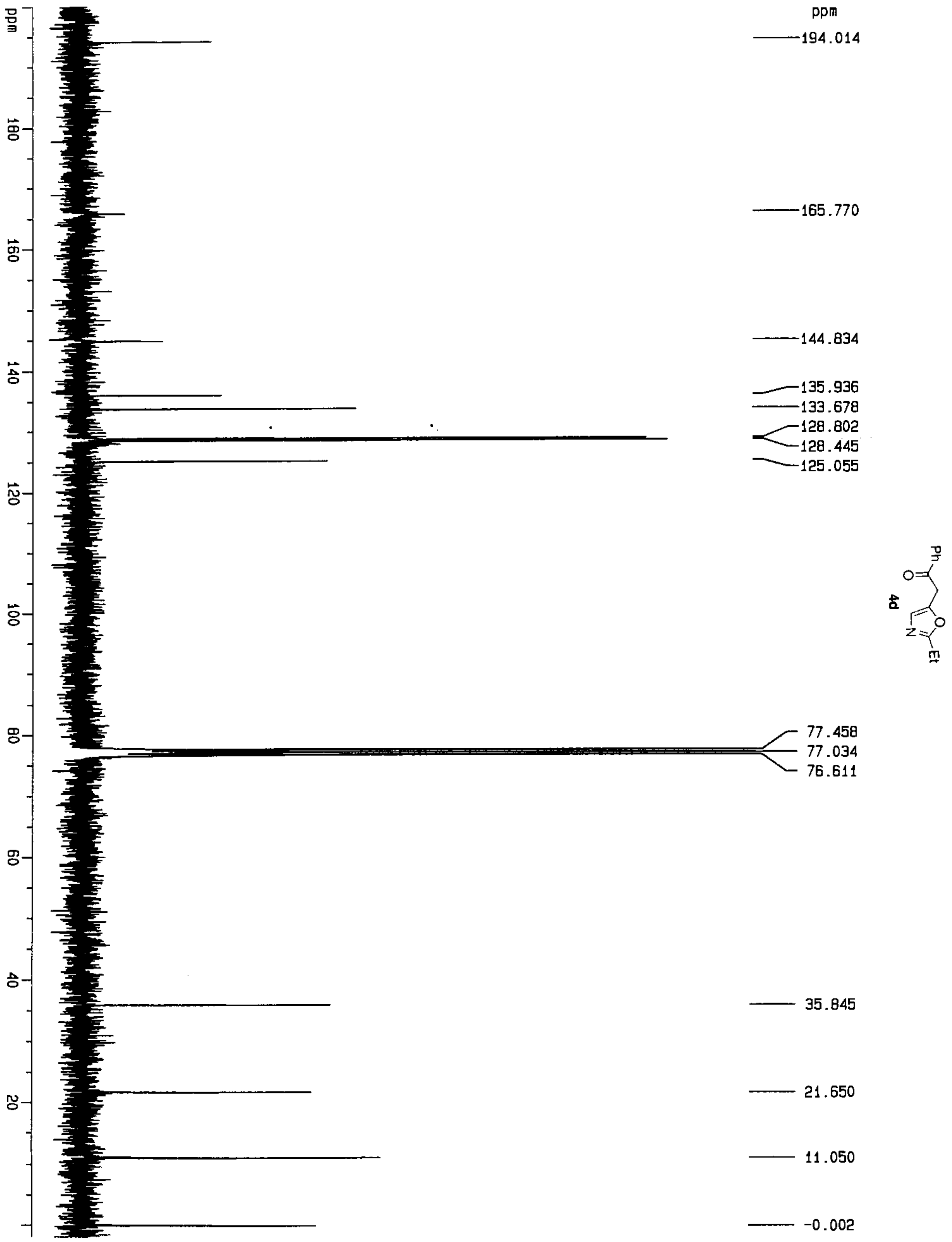
1.1645
1.9286
1.0000
2.2830
2.0885
2.9634
ppm
8.0163
7.9926
7.9881
7.5205
7.4988
7.4947
7.4708
7.2643
6.8926
4.3239
2.8048
2.7795
2.7542
2.7289
1.3417
1.3165
1.2911
1.2547
0.0102
-0.0001
-0.0107
Ph
O
O
N
Et
4d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133.678
128.802
128.445
125.055
77.458
77.034
76.611
35.845
21.650
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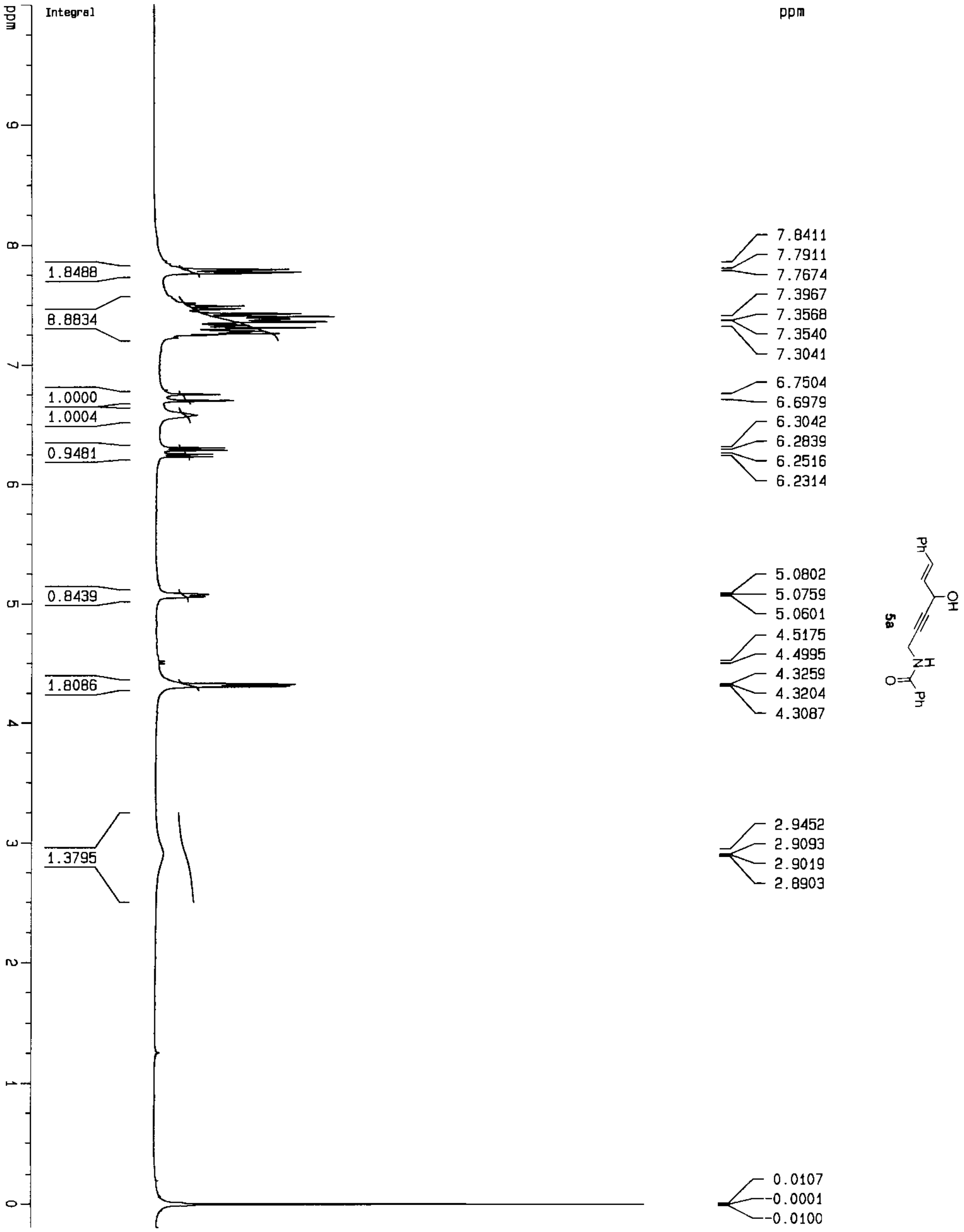
-0.002
ppm
180
160
140
120
100
80
60
40
20
Ph
O
O
N
Et
4d


5a

ppm
Integral
9
8
7
6
5
4
3
2
1
0
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8.8834
1.0000
1.0004
0.9481
0.8439
1.8086
1.3795
ppm
7.8411
7.7911
7.7674
7.3967
7.3568
7.3540
7.3041
6.7504
6.6979
6.3042
6.2839
6.2516
6.2314
5.0802
5.0759
5.0601
4.5175
4.4995
4.3259
4.3204
4.3087
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2.9019
2.8903
0.0107
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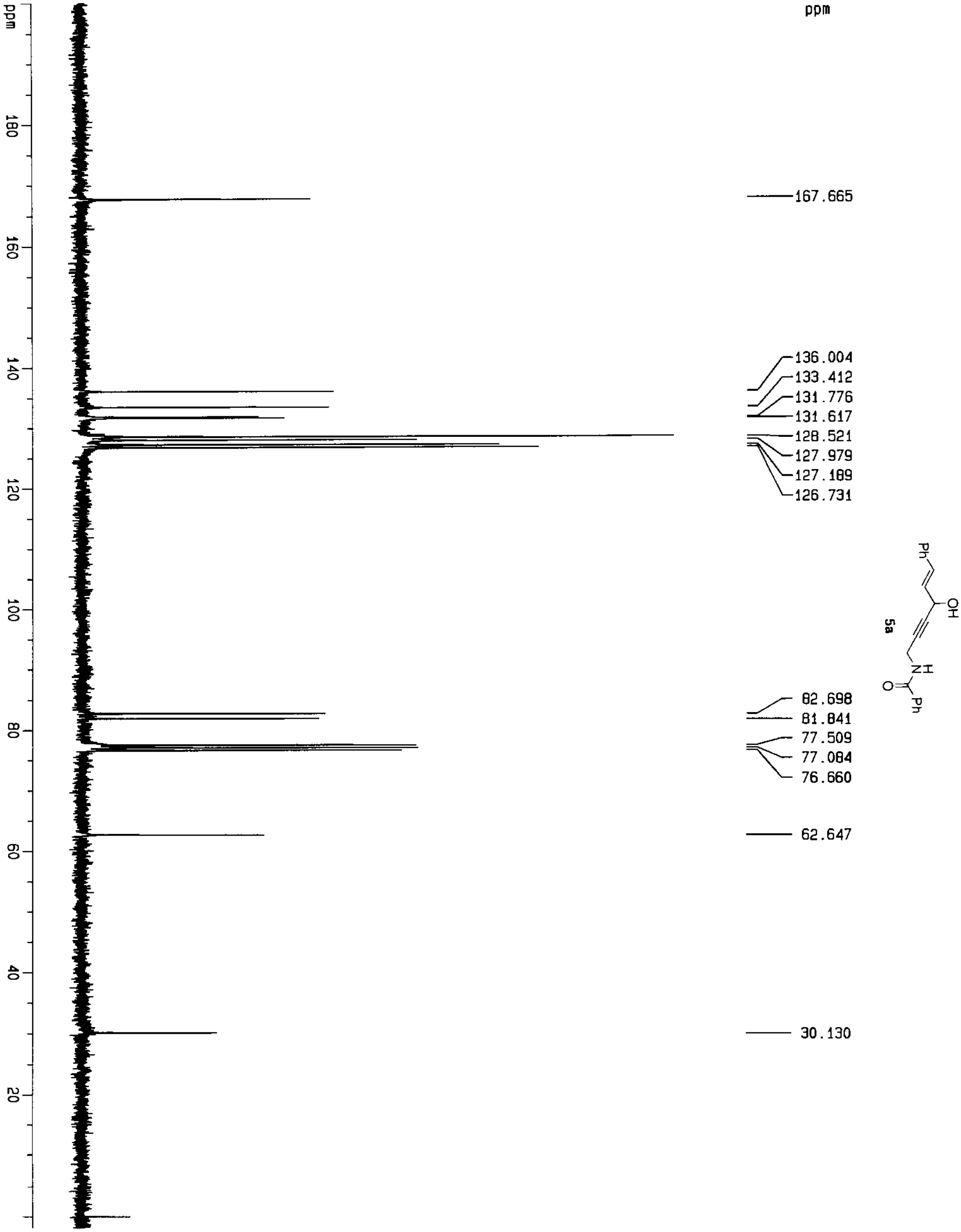
-0.0100
Ph
OH
N
H
O
Ph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160
140
120
100
80
60
40
20
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133.412
131.776
131.617
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127.979
127.189
126.731
82.698
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77.509
77.084
76.660
62.647
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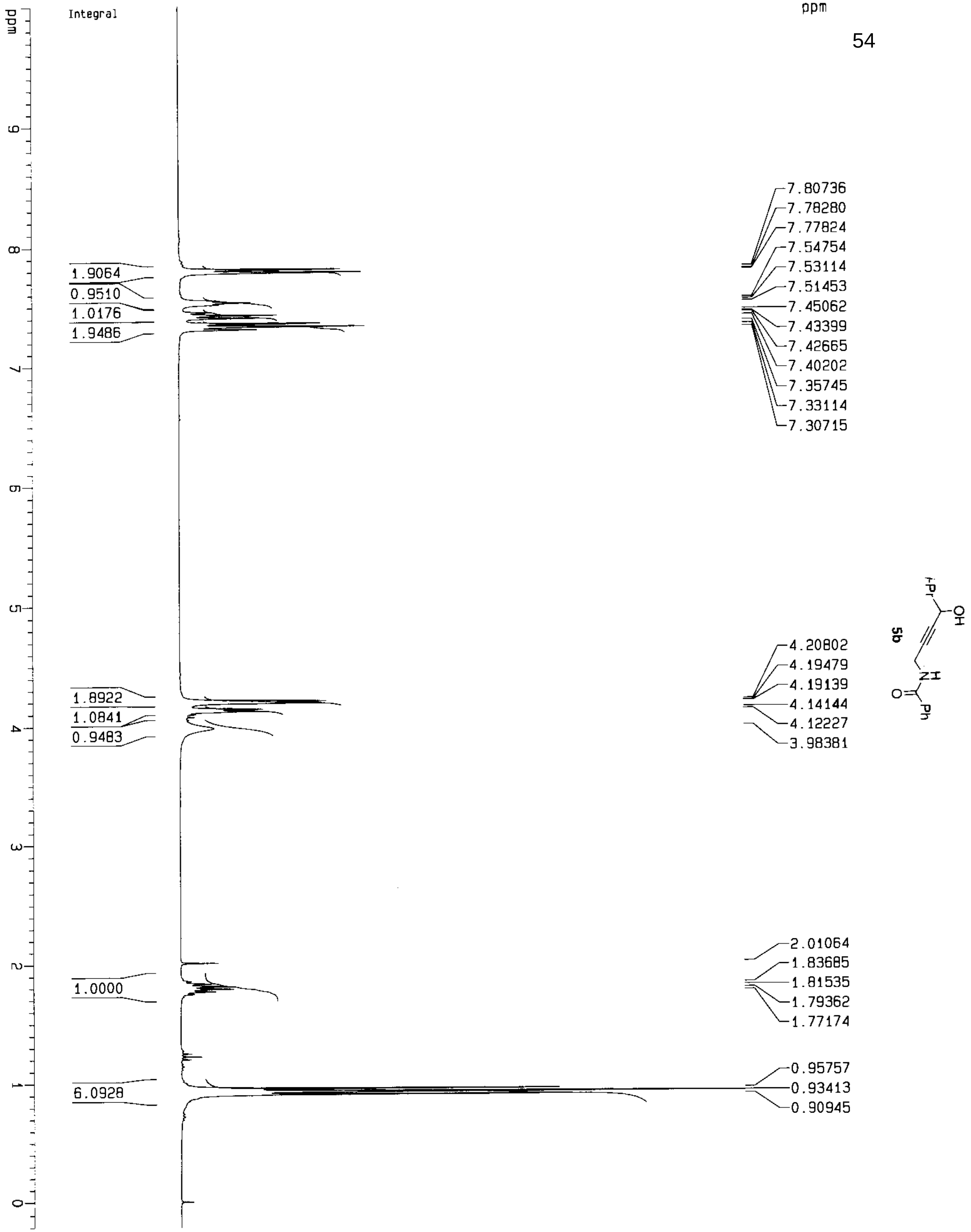
Ph
OH
H
N
O
Ph
5a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Integral
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8
7
6
5
4
3
2
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0
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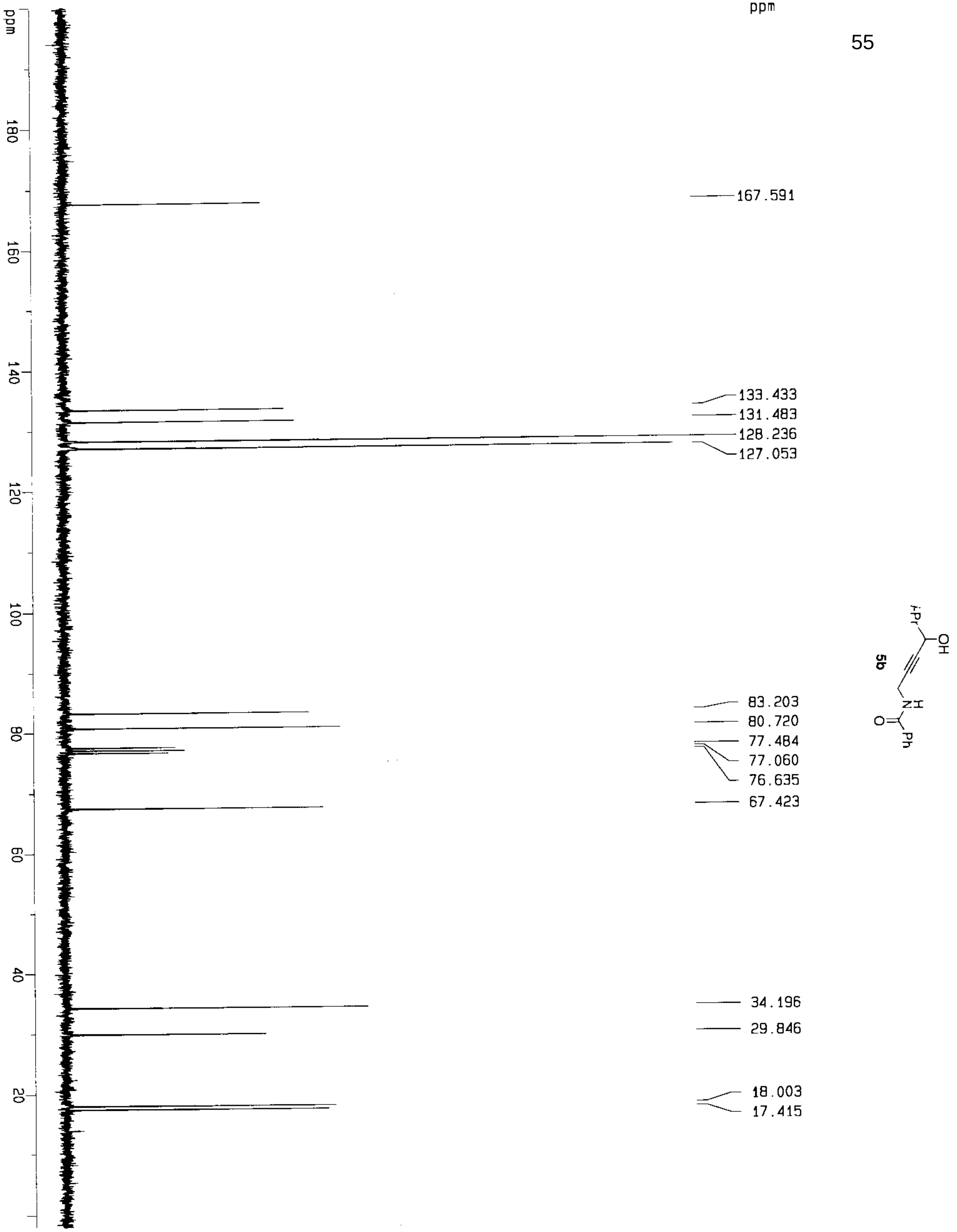
0.9510
1.0176
1.9486
1.8922
1.0841
0.9483
1.0000
6.0928
ppm
7.80736
7.78280
7.77824
7.54754
7.53114
7.51453
7.45062
7.43399
7.42665
7.40202
7.35745
7.33114
7.30715
4.20802
4.19479
4.19139
4.14144
4.12227
3.98381
2.01064
1.83685
1.81535
1.79362
1.77174
0.95757
0.93413
0.90945
i-Pr
OH
N
H
O
Ph

5b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120
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80
60
40
20
ppm
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127.053
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80.720
77.484
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67.423
34.196
29.846
18.003
17.415
i-Pr
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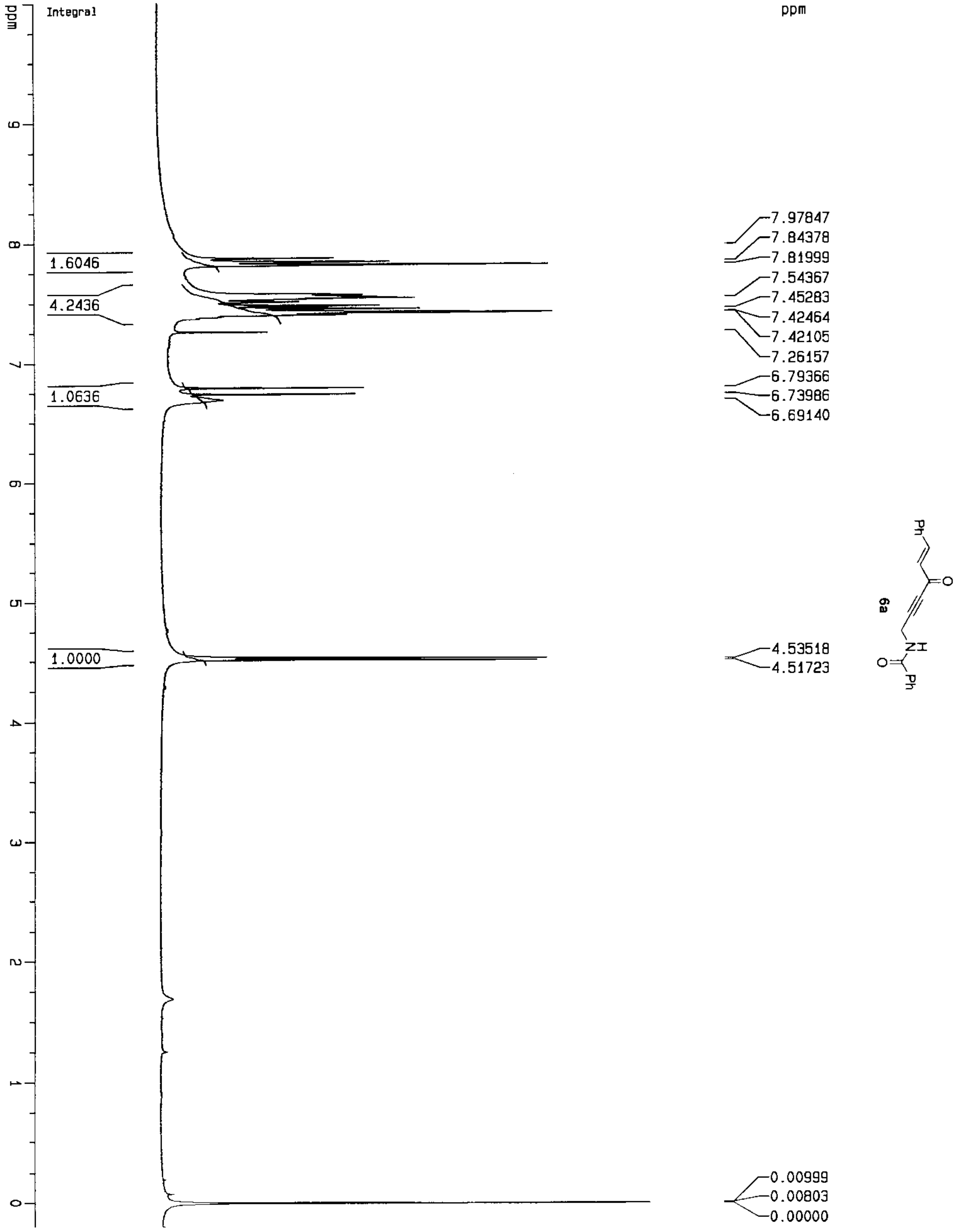
H
N
O
Ph

5b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4
3
2
1
0
ppm
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7.84378
7.81999
7.54367
7.45283
7.42464
7.42105
7.26157
6.79366
6.73986
6.69140
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4.51723
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0.00803
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Ph
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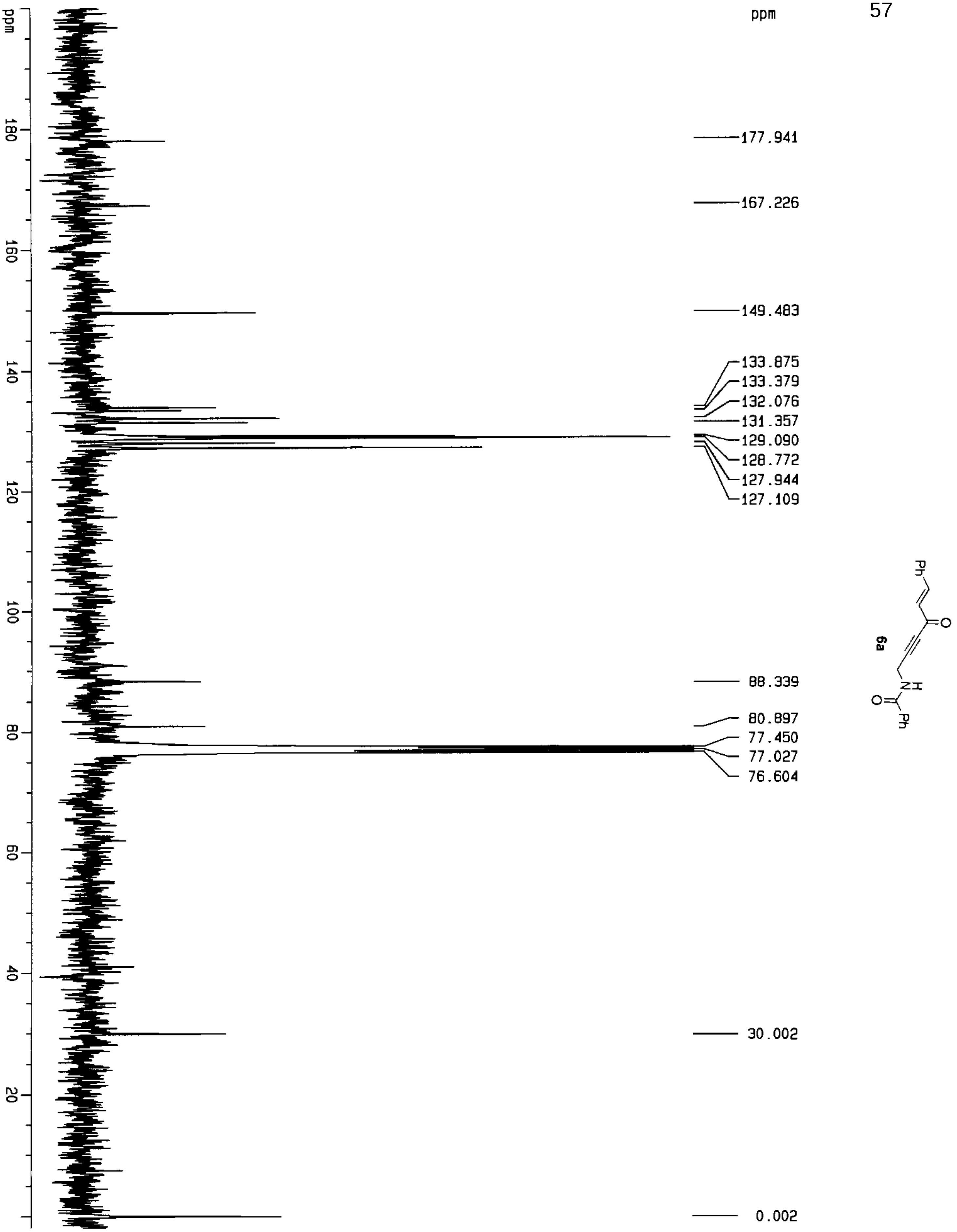
N
O
Ph
6a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80
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40
20
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149.483
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128.772
127.944
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77.450
77.027
76.604
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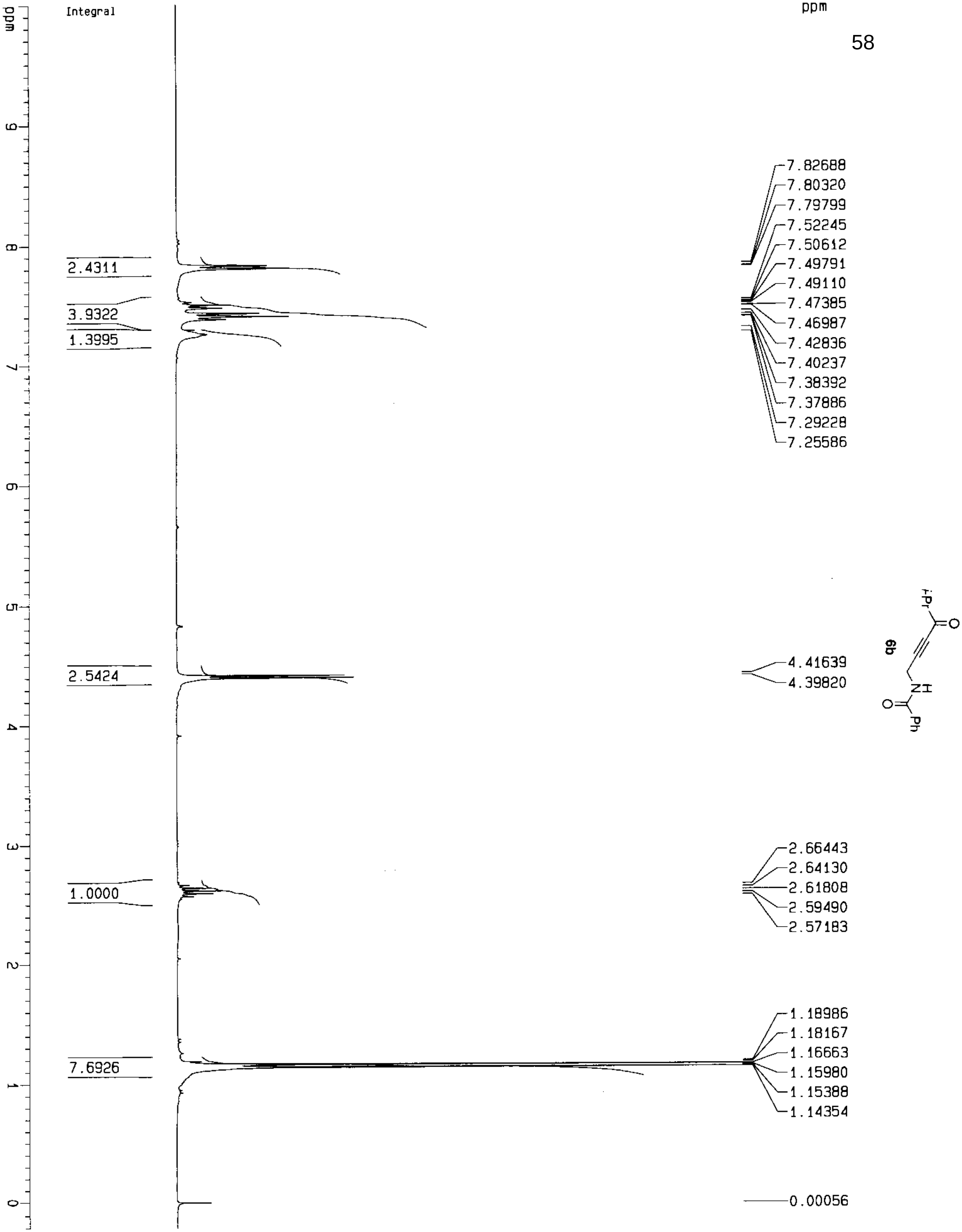
N
O
Ph
6a


6b
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6
5
4
3
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2.5424
1.0000
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7.80320
7.79799
7.52245
7.50612
7.49791
7.49110
7.47385
7.46987
7.42836
7.40237
7.38392
7.37886
7.29228
7.25586
4.41639
4.39820
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2.64130
2.61808
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2.57183
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1.16663
1.15980
1.15388
1.14354
0.00056
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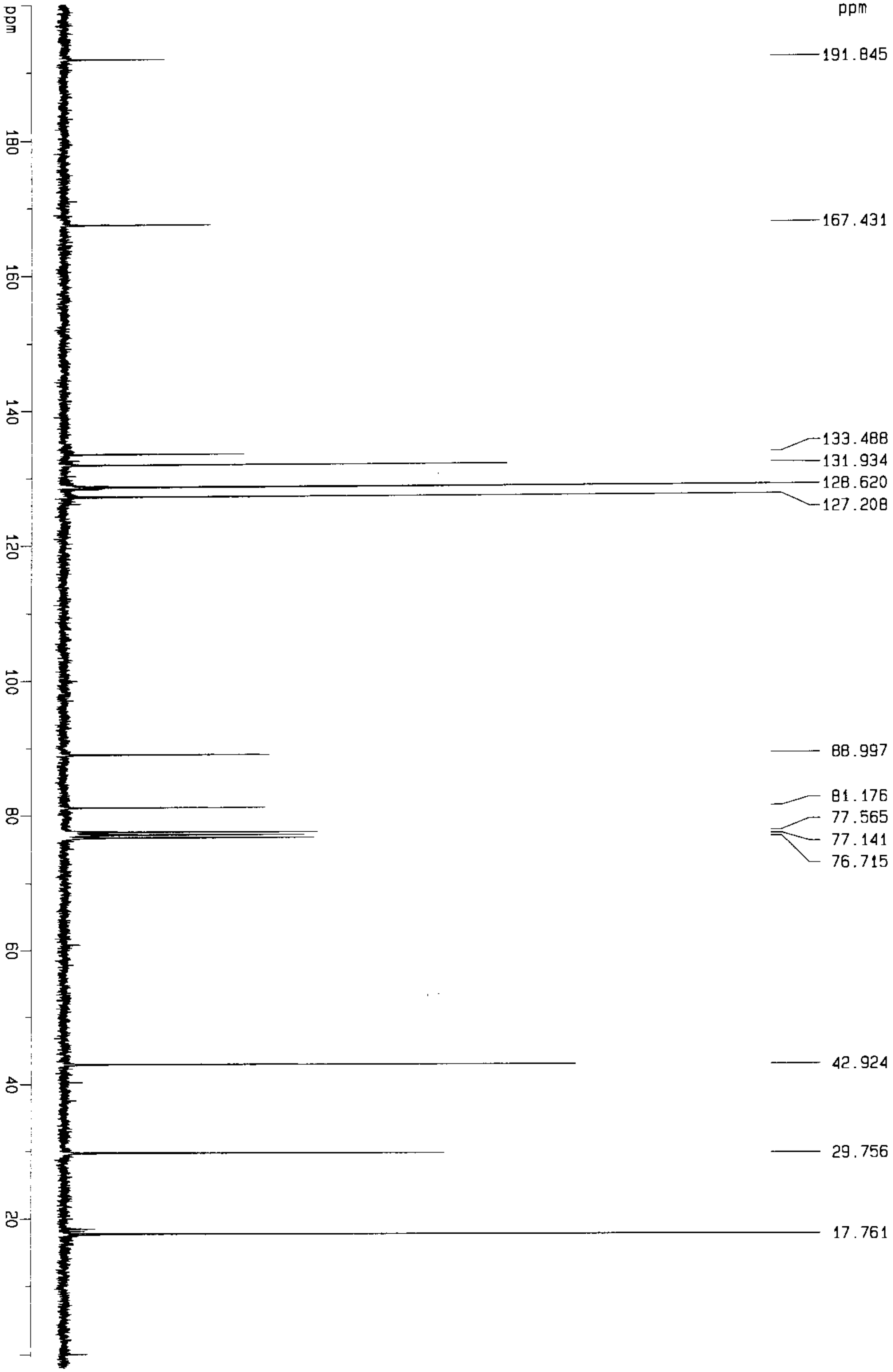
H
N
O
Ph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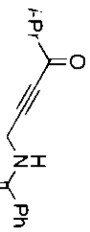
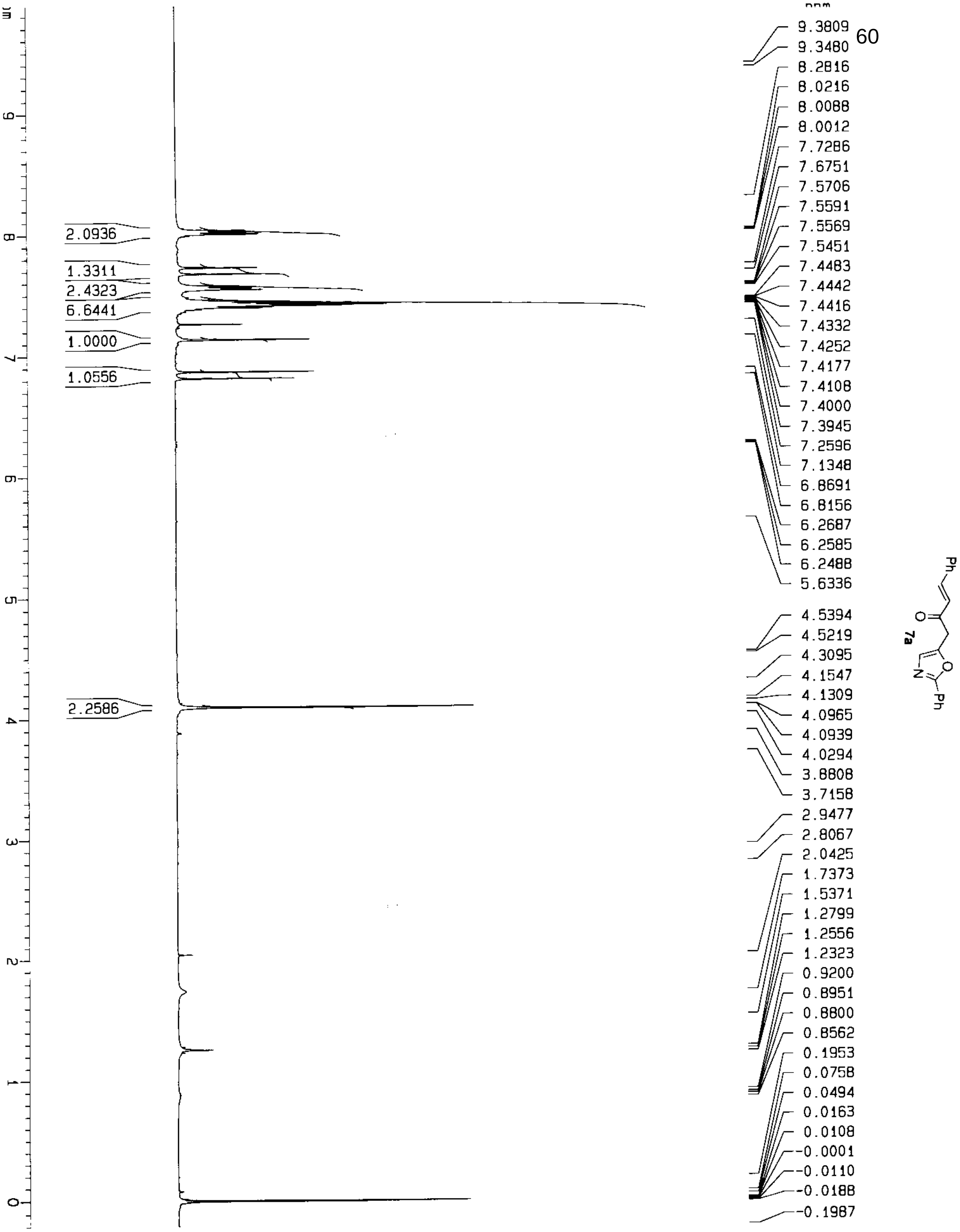
17.761


i-Pr
O
H
N
O
Ph

6b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7.5569
7.5451
7.4483
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7.4416
7.4332
7.4252
7.4177
7.4108
7.4000
7.3945
7.2596
7.1348
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6.8156
6.2687
6.2585
6.2488
5.6336
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4.5219
4.3095
4.1547
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4.0939
4.0294
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2.9477
2.8067
2.0425
1.7373
1.5371
1.2799
1.2556
1.2323
0.9200
0.8951
0.8800
0.8562
0.1953
0.0758
0.0494
0.0163
0.0108
-0.0001
-0.0110
-0.0188
-0.1987
2.0936
1.3311
2.4323
6.6441
1.0000
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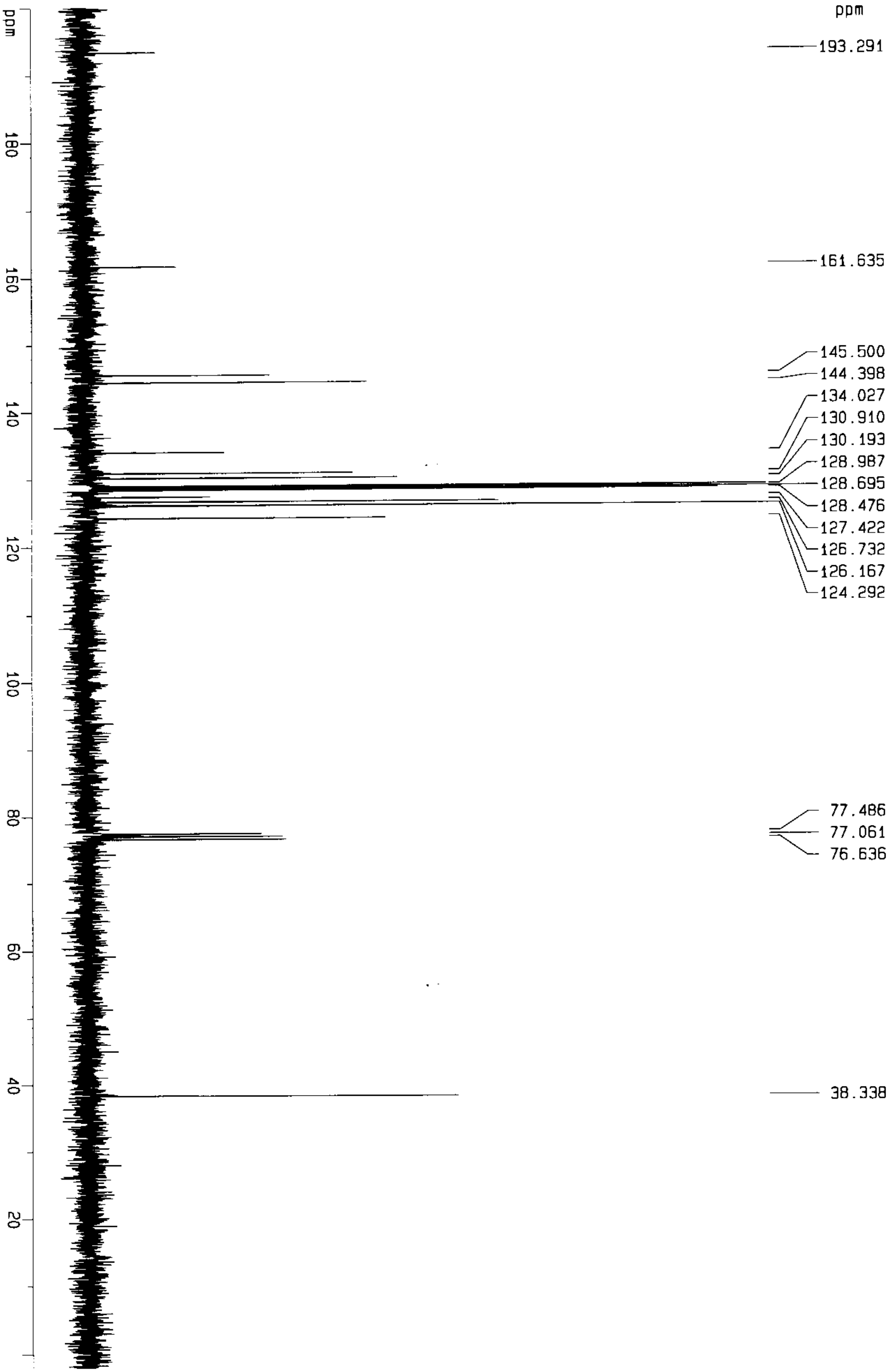
O
N
Ph
7a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128.695
128.476
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126.732
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124.292
77.486
77.061
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140
120
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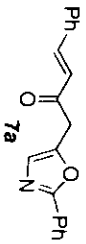
80
60
40
20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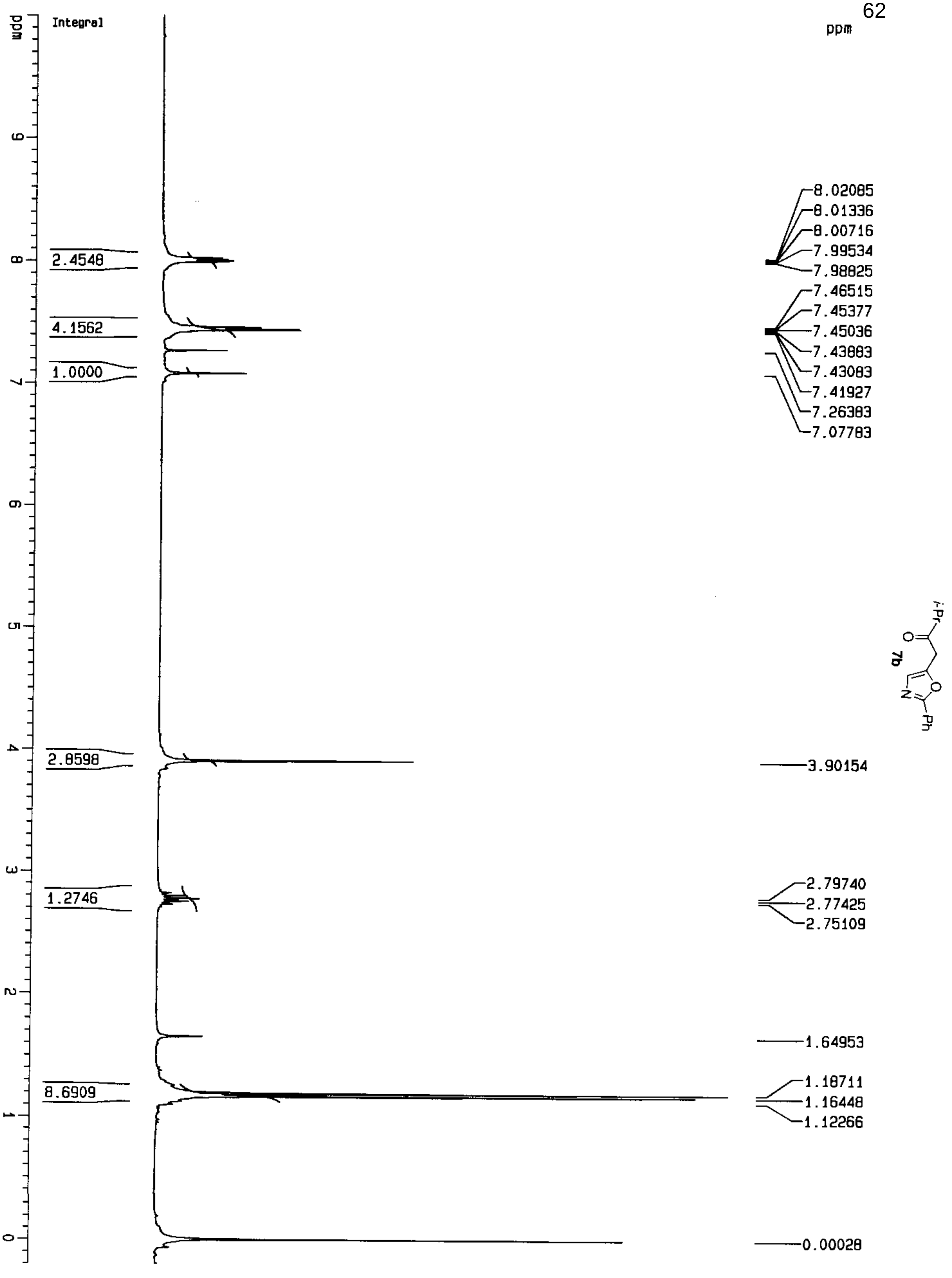
N
Ph

7a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Integral
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5
4
3
2
1
0
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8.6909
ppm
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7.46515
7.45377
7.45036
7.43883
7.43083
7.41927
7.26383
7.07783
3.90154
2.79740
2.77425
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1.18711
1.16448
1.12266
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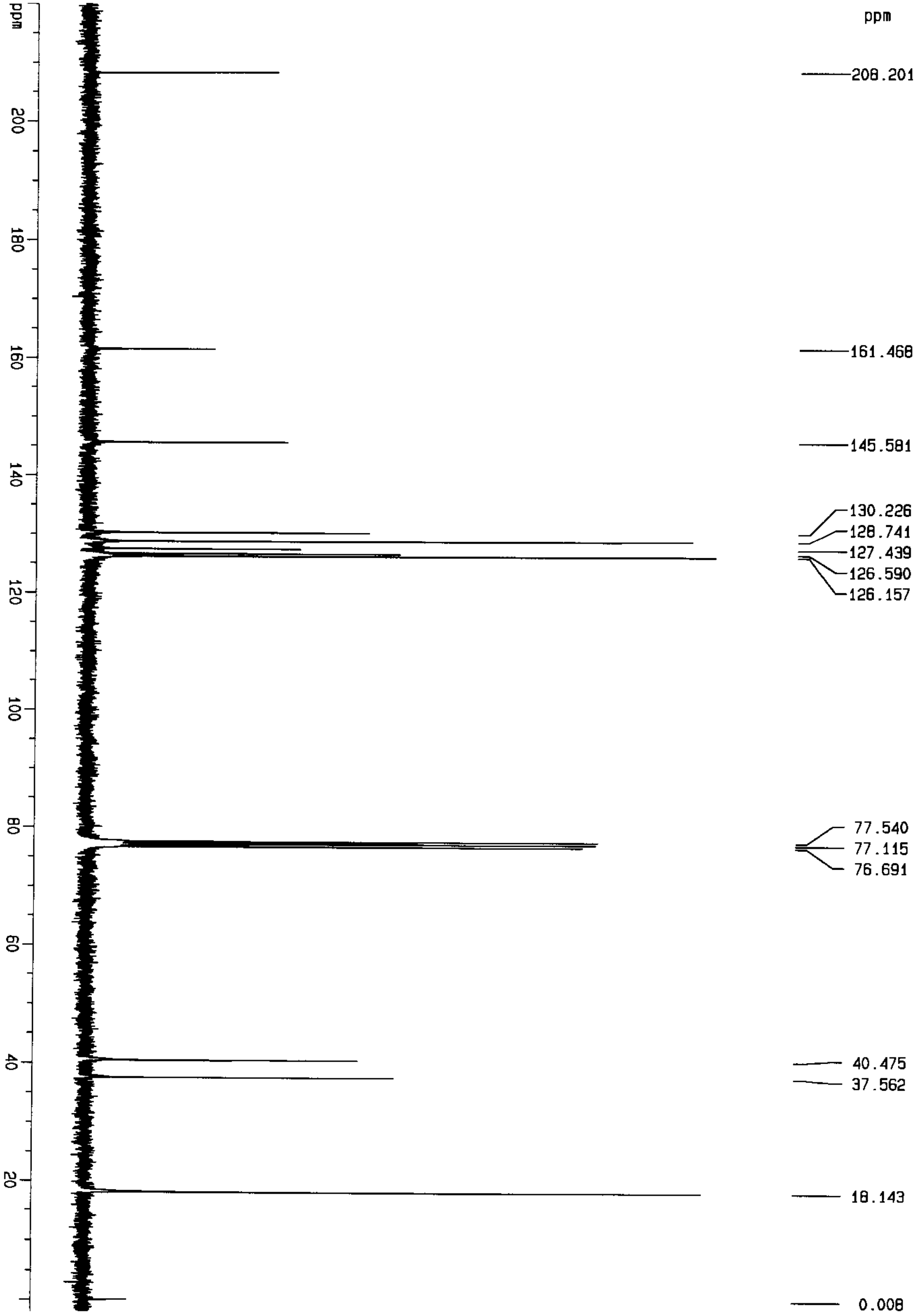
O
N
Ph
7b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140
120
100
80
60
40
20
ppm
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145.581
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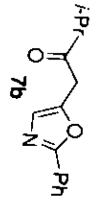
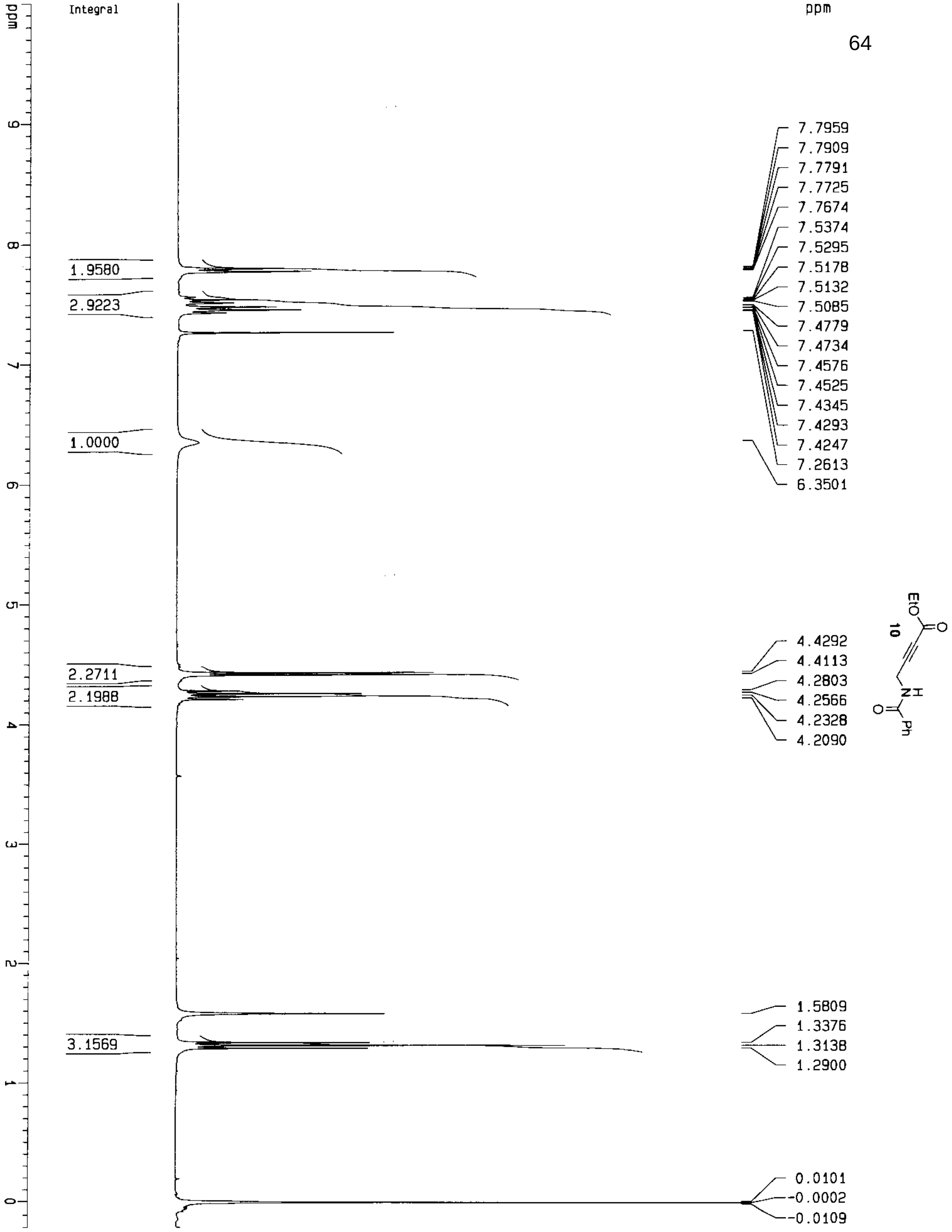
18.143
0.008


i-Pr
O
O
N
Ph

7b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Integral
ppm
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6
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2.1988
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7.7725
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7.5374
7.5295
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7.5132
7.5085
7.4779
7.4734
7.4576
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7.4293
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7.2613
6.3501
4.4292
4.4113
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4.2566
4.2328
4.2090
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1.3376
1.3138
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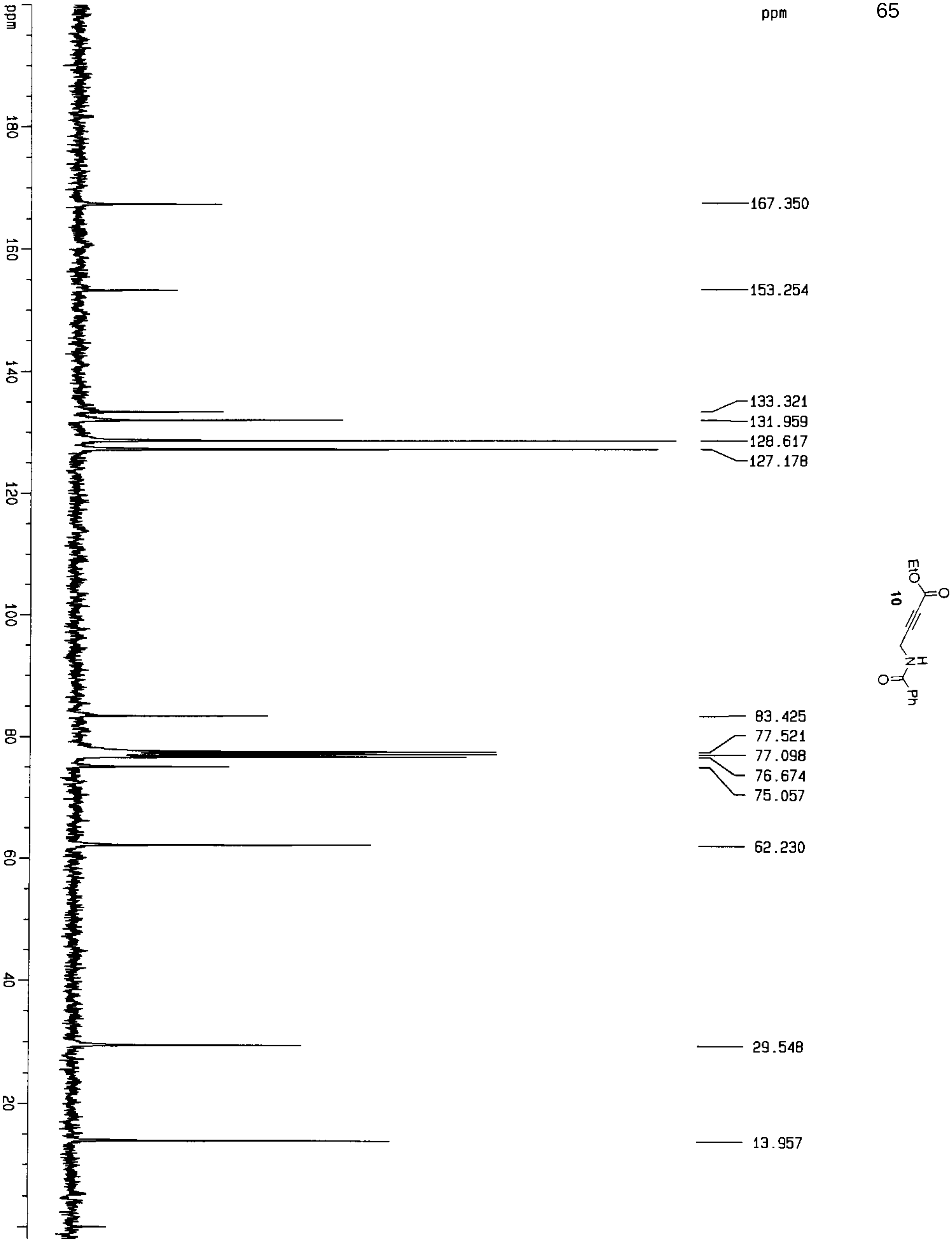
EtO
O
H
N
O
Ph

10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160
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120
100
80
60
40
20
ppm
167.350
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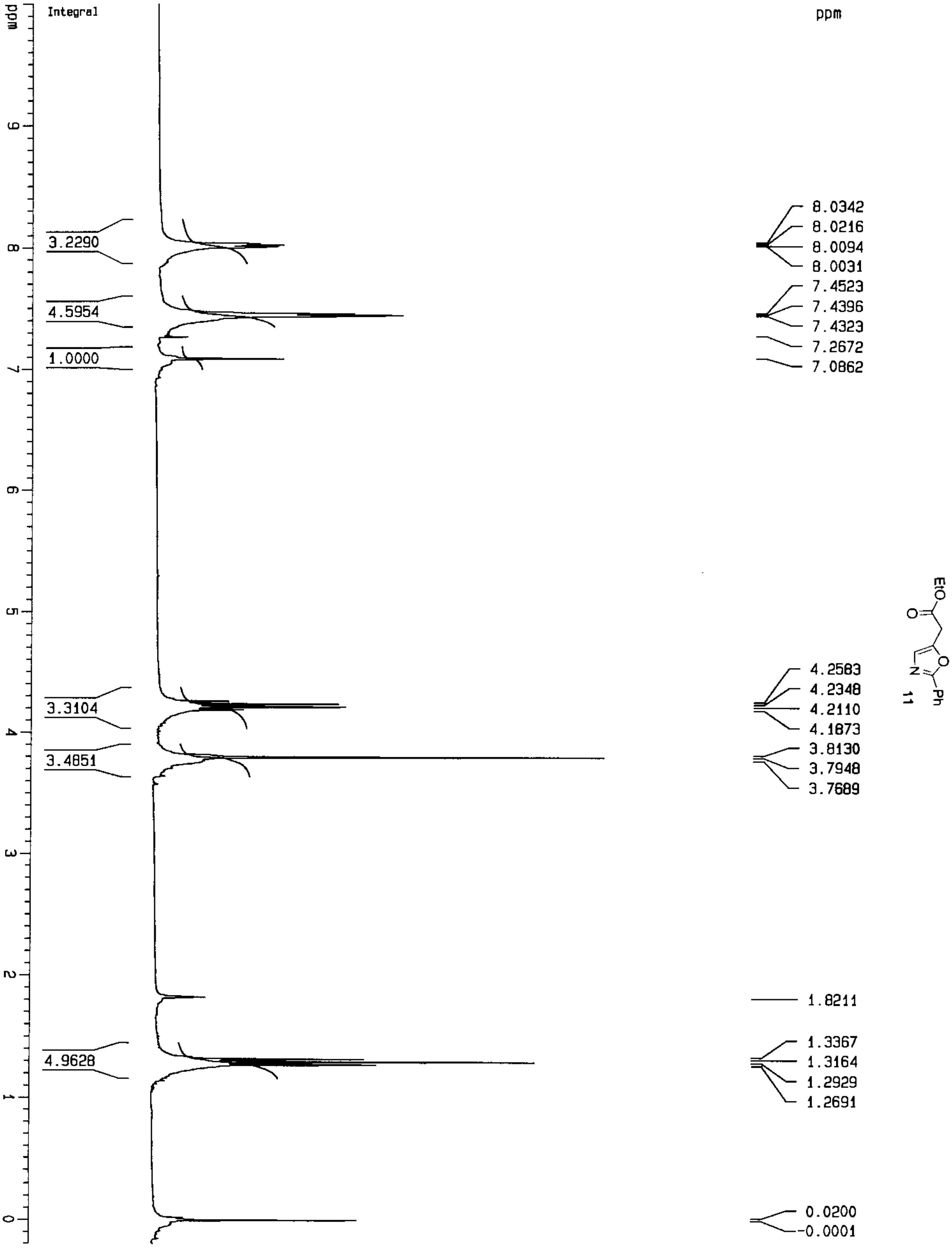
133.321
131.959
128.617
127.178
83.425
77.521
77.098
76.674
75.057
62.230
29.548
13.957
EtO
O
10
H
N
O
Ph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3.3104
3.4851
4.9628
9
8
7
6
5
4
3
2
1
0
ppm
8.0342
8.0216
8.0094
8.0031
7.4523
7.4396
7.4323
7.2672
7.0862
4.2583
4.2348
4.2110
4.1873
3.8130
3.7948
3.7689
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1.3164
1.2929
1.2691
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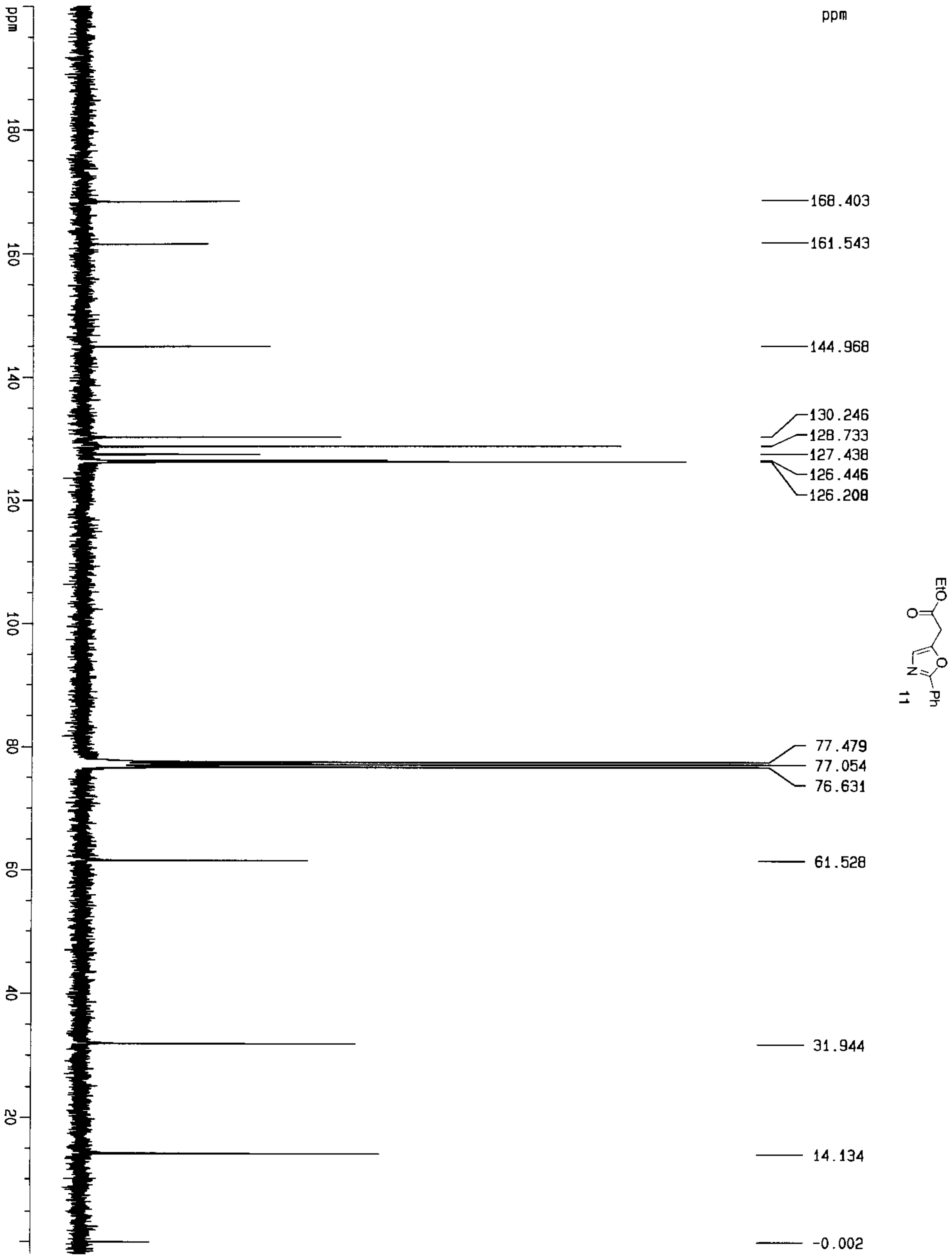
O
O
N
Ph
11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20
ppm
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127.438
126.446
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76.631
61.528
31.944
14.134
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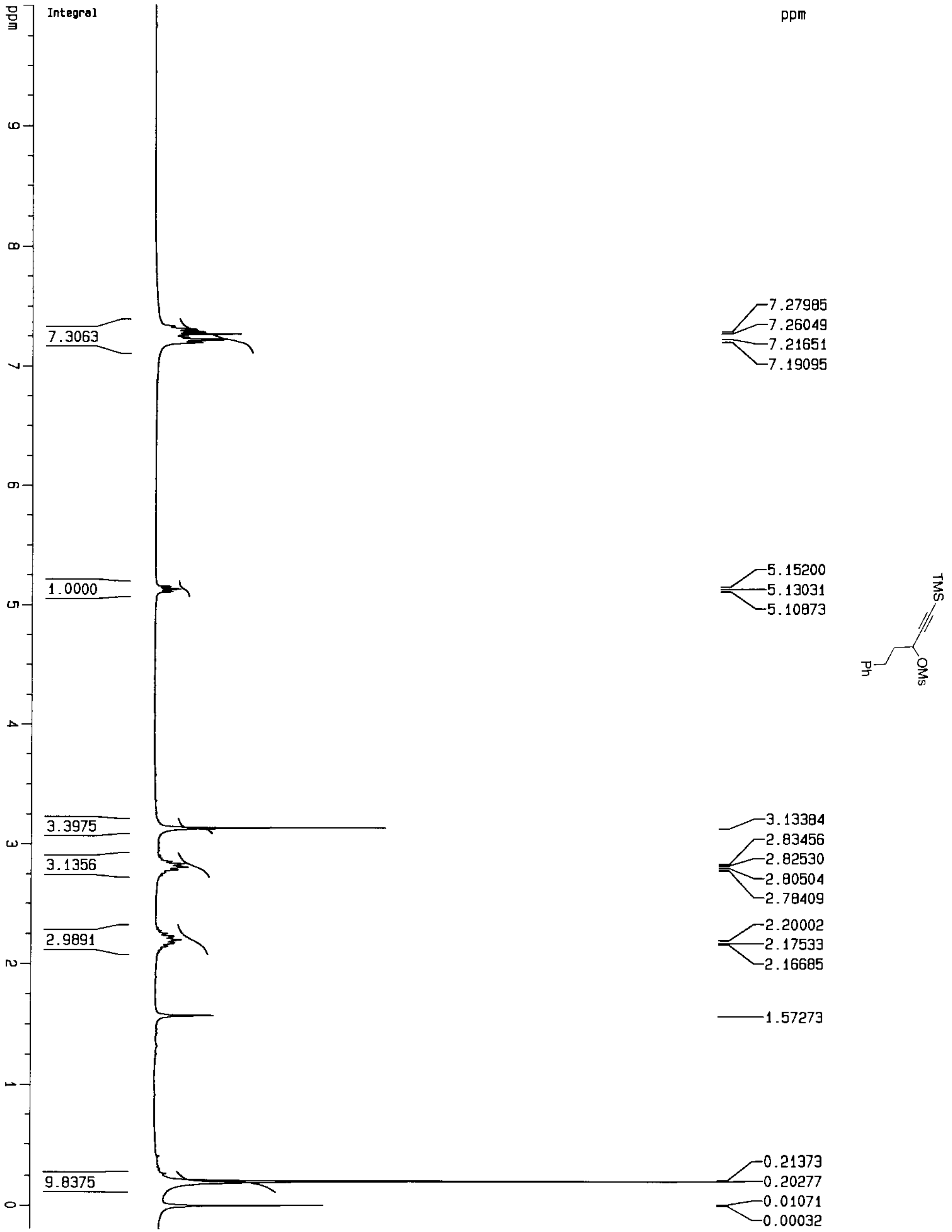
EtO
O
O
N
Ph

11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3.1356
2.9891
9.8375
9
8
7
6
5
4
3
2
1
0
ppm
7.27985
7.26049
7.21651
7.19095
5.15200
5.13031
5.10873
3.13384
2.83456
2.82530
2.80504
2.78409
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2.16685
1.57273
0.21373
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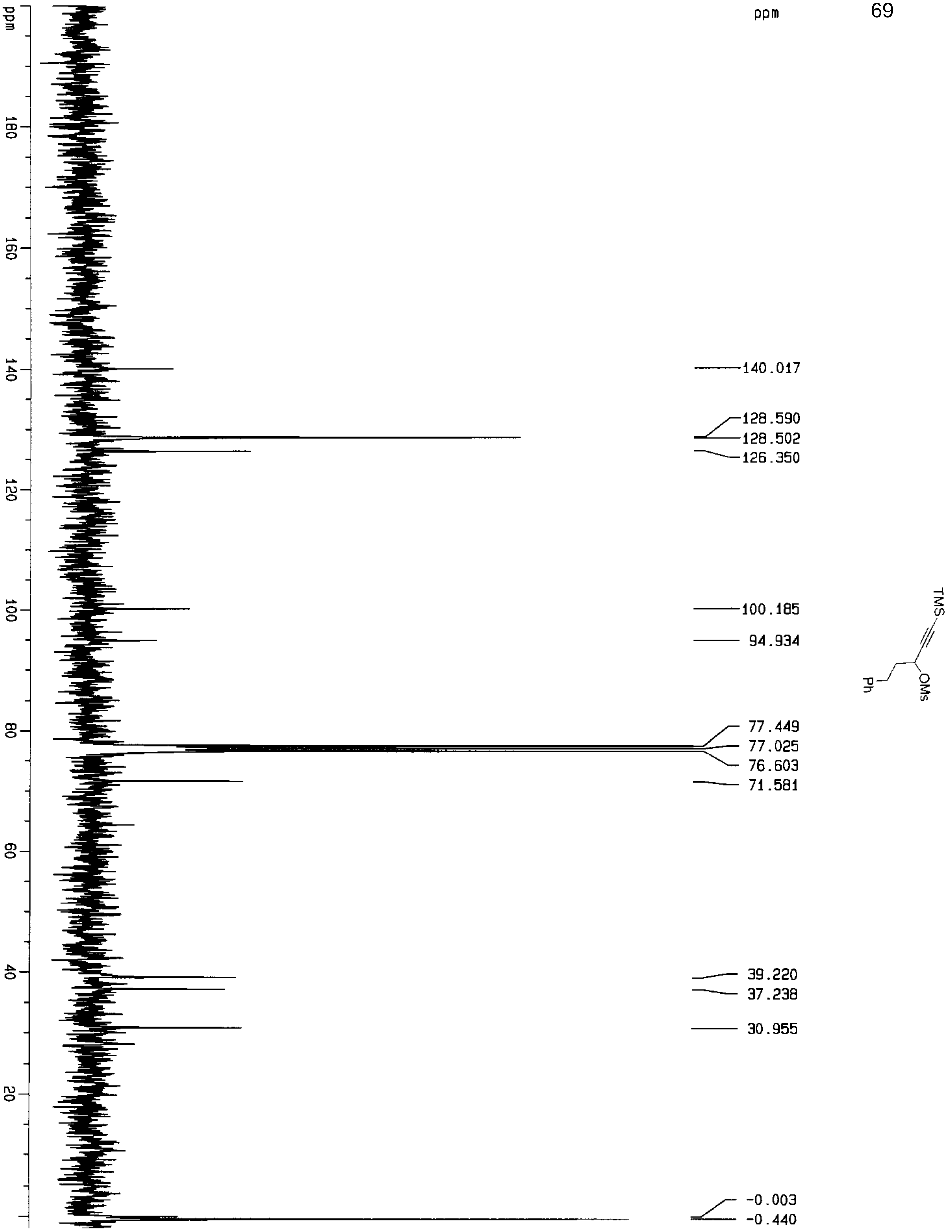
0.01071
0.00032
TMS
OMs
Ph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160
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120
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80
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40
20
ppm
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128.502
126.350
100.185
94.934
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77.025
76.603
71.581
39.220
37.238
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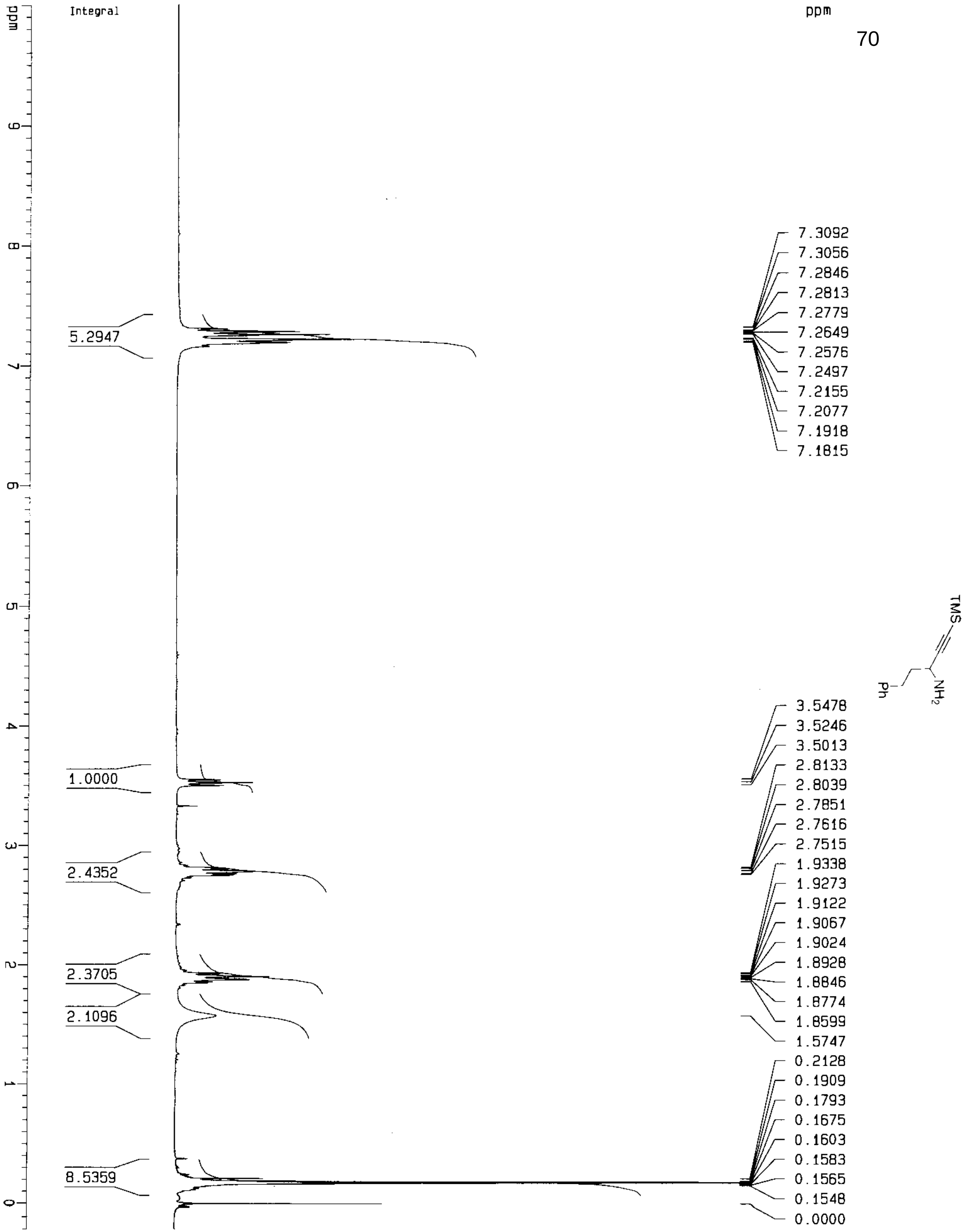
-0.003
-0.440
TMS
OMs
Ph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Integral
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8
7
6
5
4
3
2
1
0
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1.0000
2.4352
2.3705
2.1096
8.5359
7.3092
7.3056
7.2846
7.2813
7.2779
7.2649
7.2576
7.2497
7.2155
7.2077
7.1918
7.1815
3.5478
3.5246
3.5013
2.8133
2.8039
2.7851
2.7616
2.7515
1.9338
1.9273
1.9122
1.9067
1.9024
1.8928
1.8846
1.8774
1.8599
1.5747
0.2128
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0.1675
0.1603
0.1583
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0.1548
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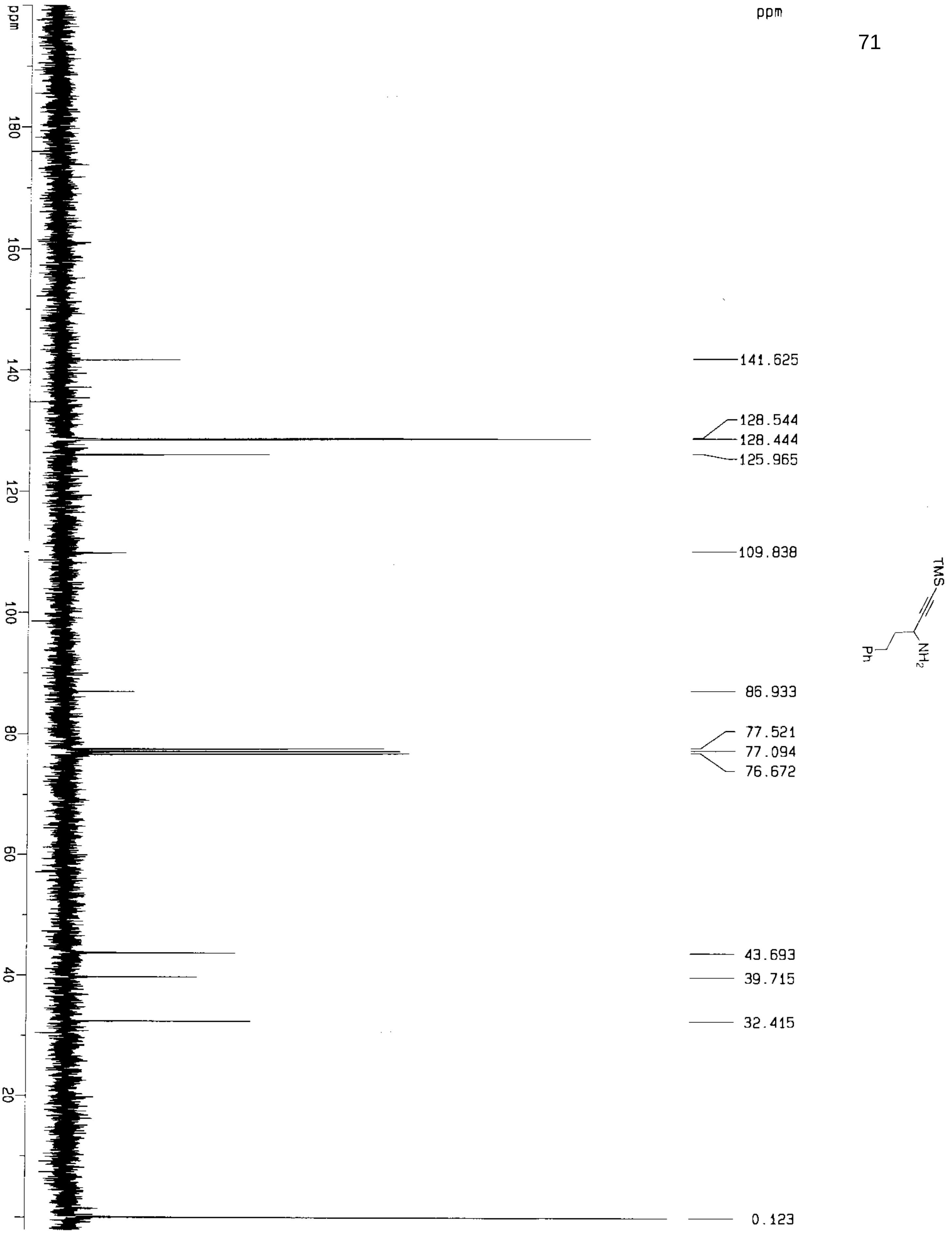
TMS
NH2
Ph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120
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80
60
40
20
ppm
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128.444
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43.693
39.715
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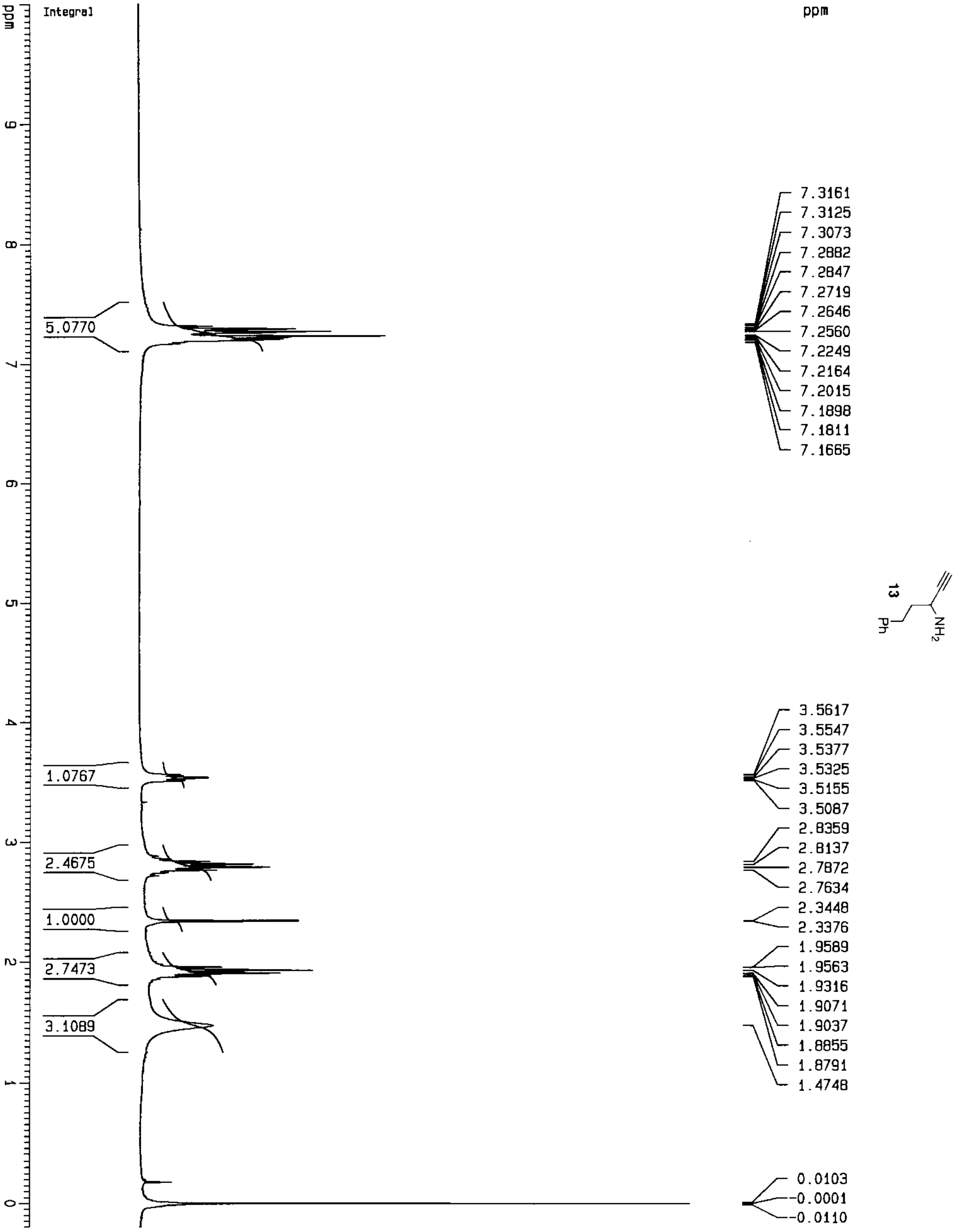
NH2
Ph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7.3073
7.2882
7.2847
7.2719
7.2646
7.2560
7.2249
7.2164
7.2015
7.1898
7.1811
7.1665
3.5617
3.5547
3.5377
3.5325
3.5155
3.5087
2.8359
2.8137
2.7872
2.7634
2.3448
2.3376
1.9589
1.9563
1.9316
1.9071
1.9037
1.8855
1.8791
1.4748
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8
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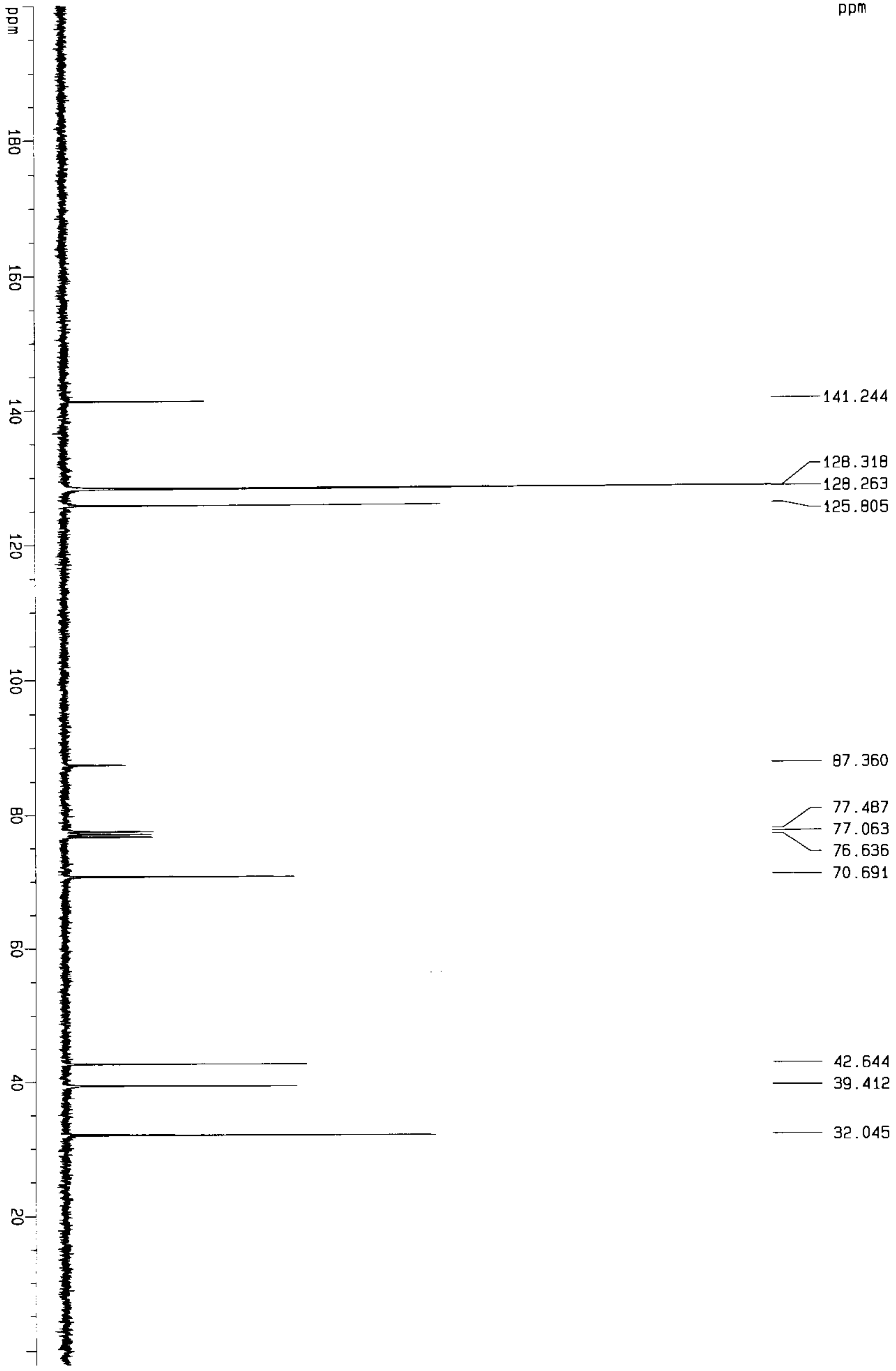
4
3
2
1
0
13
NH2
Ph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ppm
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140
120
100
80
60
40
20
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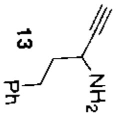
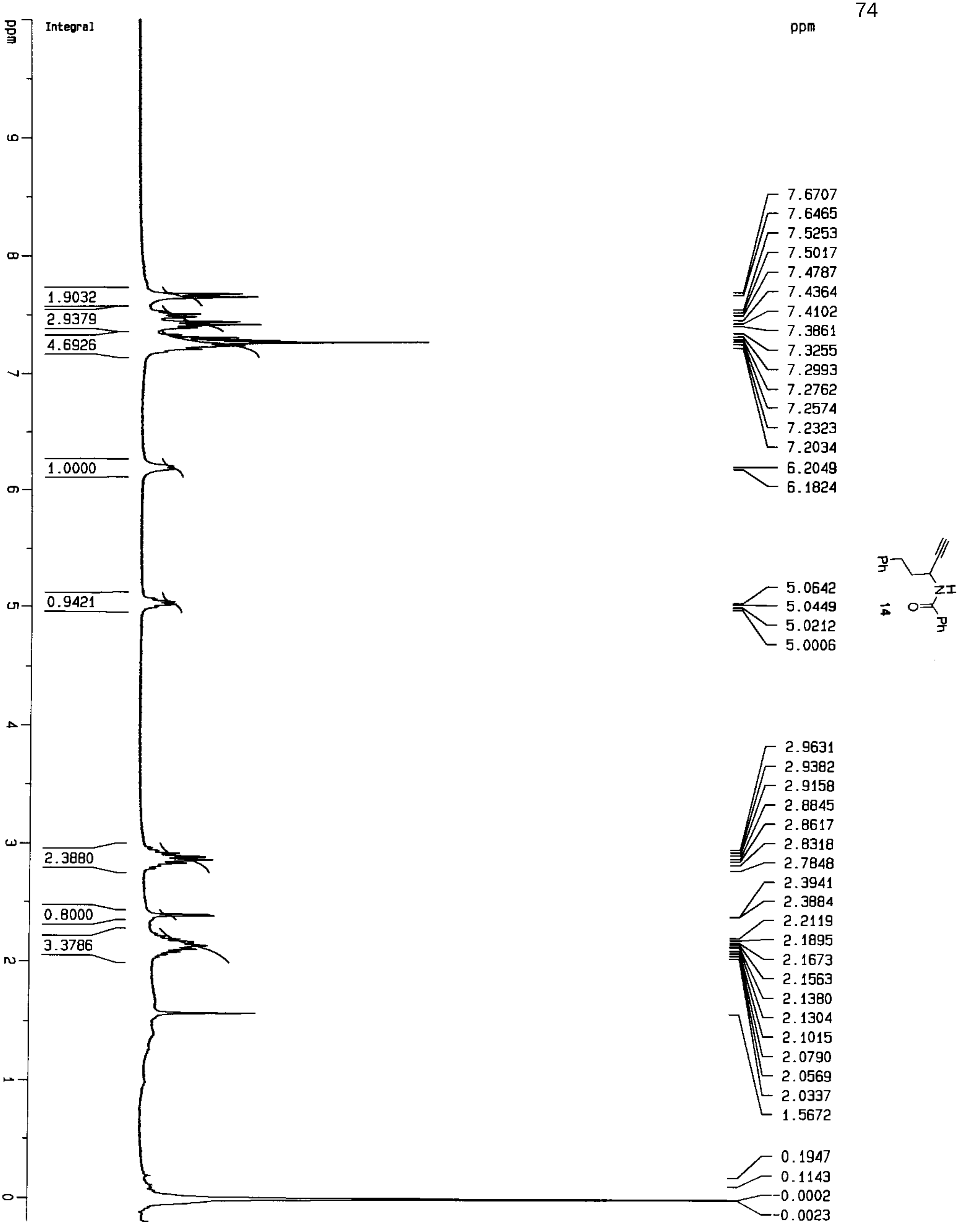
128.263
125.805
87.360
77.487
77.063
76.636
70.691
42.644
39.412
32.045


NH2
Ph

13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6
5
4
3
2
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4.6926
1.0000
0.9421
2.3880
0.8000
3.3786
ppm
7.6707
7.6465
7.5253
7.5017
7.4787
7.4364
7.4102
7.3861
7.3255
7.2993
7.2762
7.2574
7.2323
7.2034
6.2049
6.1824
5.0642
5.0449
5.0212
5.0006
2.9631
2.9382
2.9158
2.8845
2.8617
2.8318
2.7848
2.3941
2.3884
2.2119
2.1895
2.1673
2.1563
2.1380
2.1304
2.1015
2.0790
2.0569
2.0337
1.5672
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0.1143
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-0.0023
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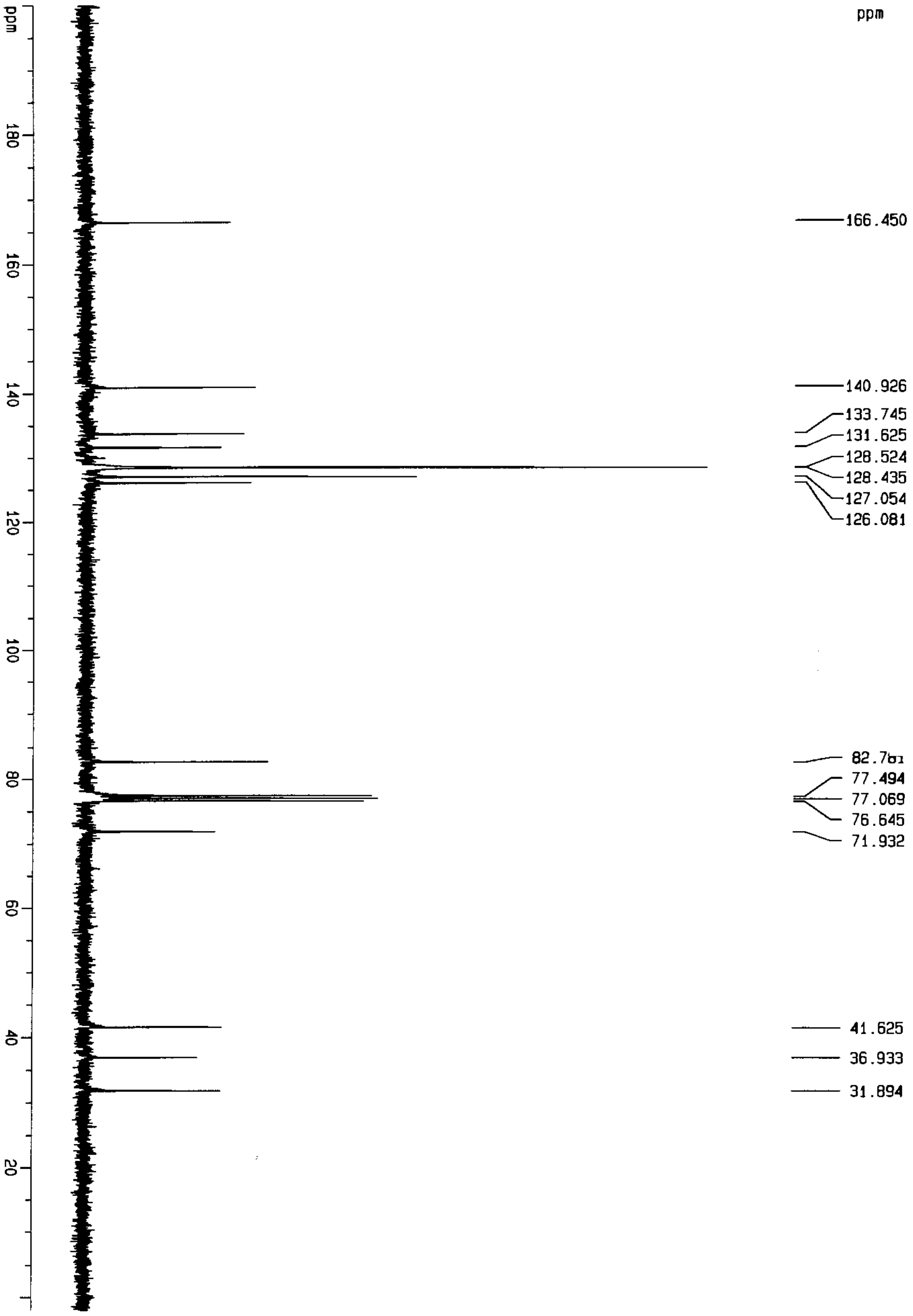
H
N
O
Ph
14


ppm
ppm
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160
140
120
100
80
60
40
20
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133.745
131.625
128.524
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126.081
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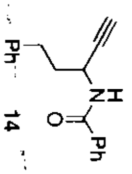
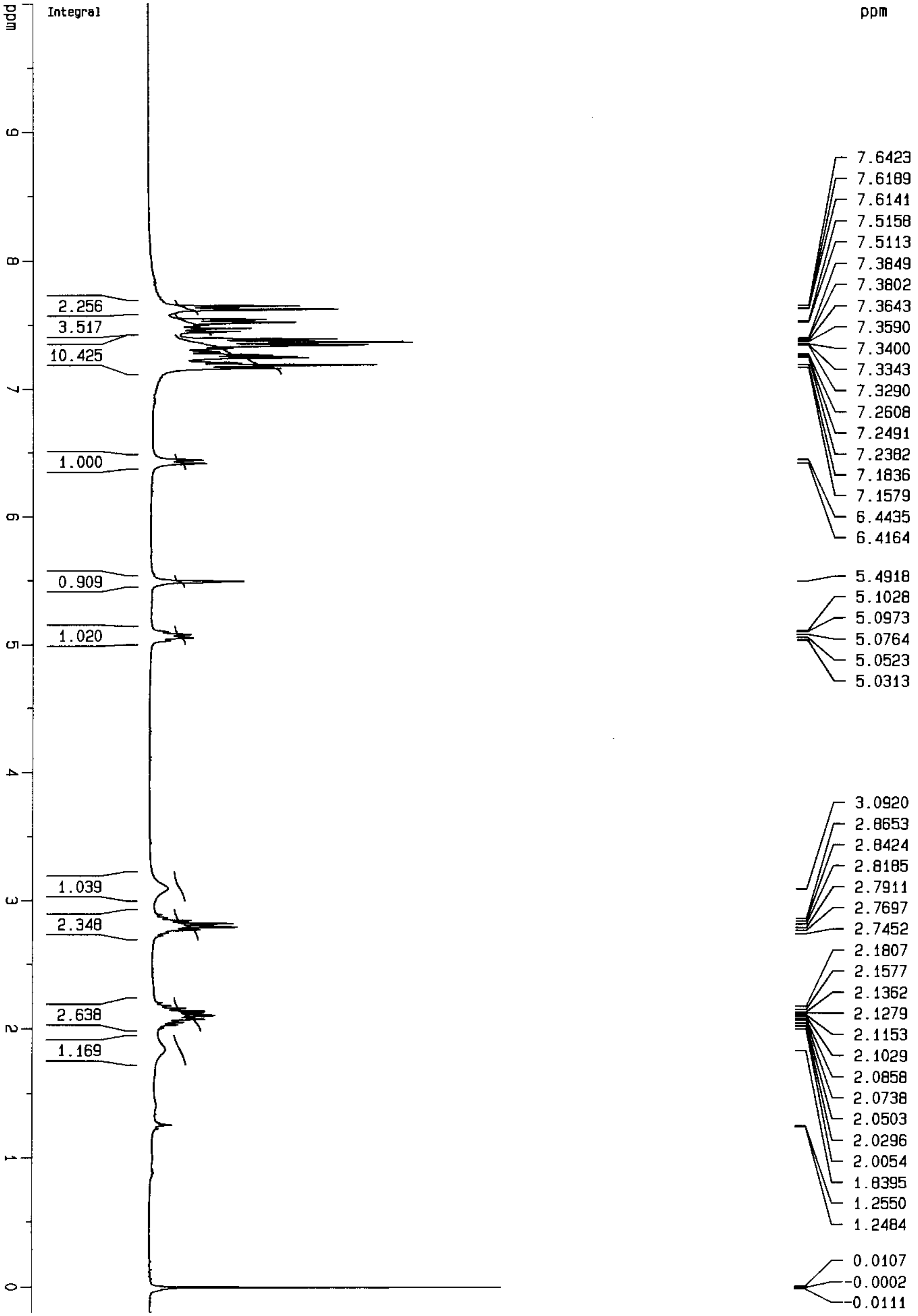
77.494
77.069
76.645
71.932
41.625
36.933
31.894


Ph
H
N
O
Ph

14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Integral
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8
7
6
5
4
3
2
1
0
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3.517
10.425
1.000
0.909
1.020
1.039
2.348
2.638
1.169
ppm
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7.6189
7.6141
7.5158
7.5113
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7.3802
7.3643
7.3590
7.3400
7.3343
7.3290
7.2608
7.2491
7.2382
7.1836
7.1579
6.4435
6.4164
5.4918
5.1028
5.0973
5.0764
5.0523
5.0313
3.0920
2.8653
2.8424
2.8185
2.7911
2.7697
2.7452
2.1807
2.1577
2.1362
2.1279
2.1153
2.1029
2.0858
2.0738
2.0503
2.0296
2.0054
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1.2550
1.2484
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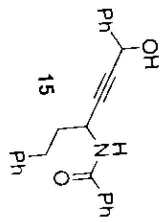
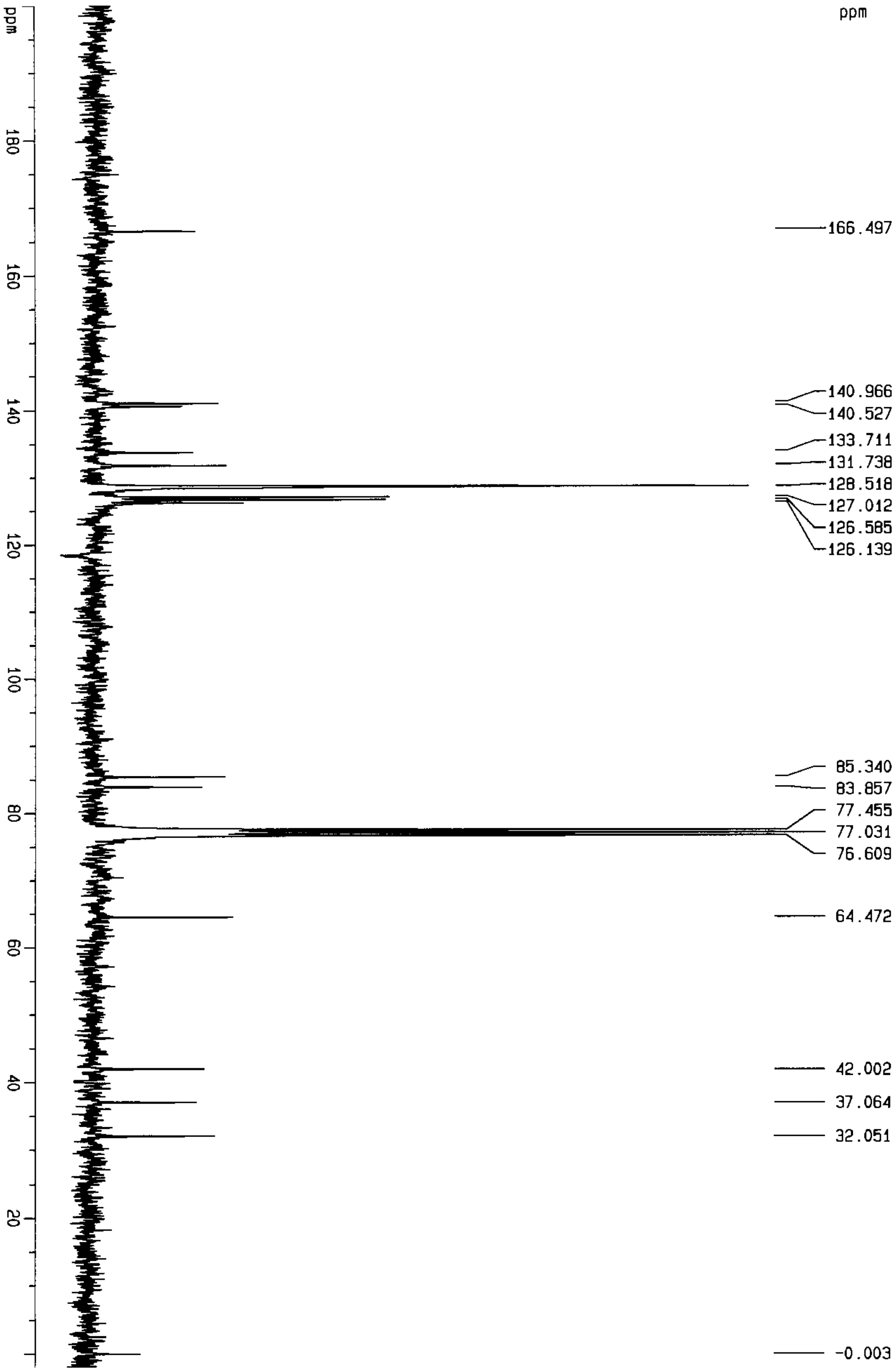

Ph
OH
15
H
N
Ph
O
Ph


ppm
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120
100
80
60
40
20
ppm
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140.527
133.711
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128.518
127.012
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83.857
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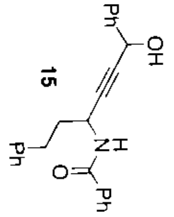
Ph
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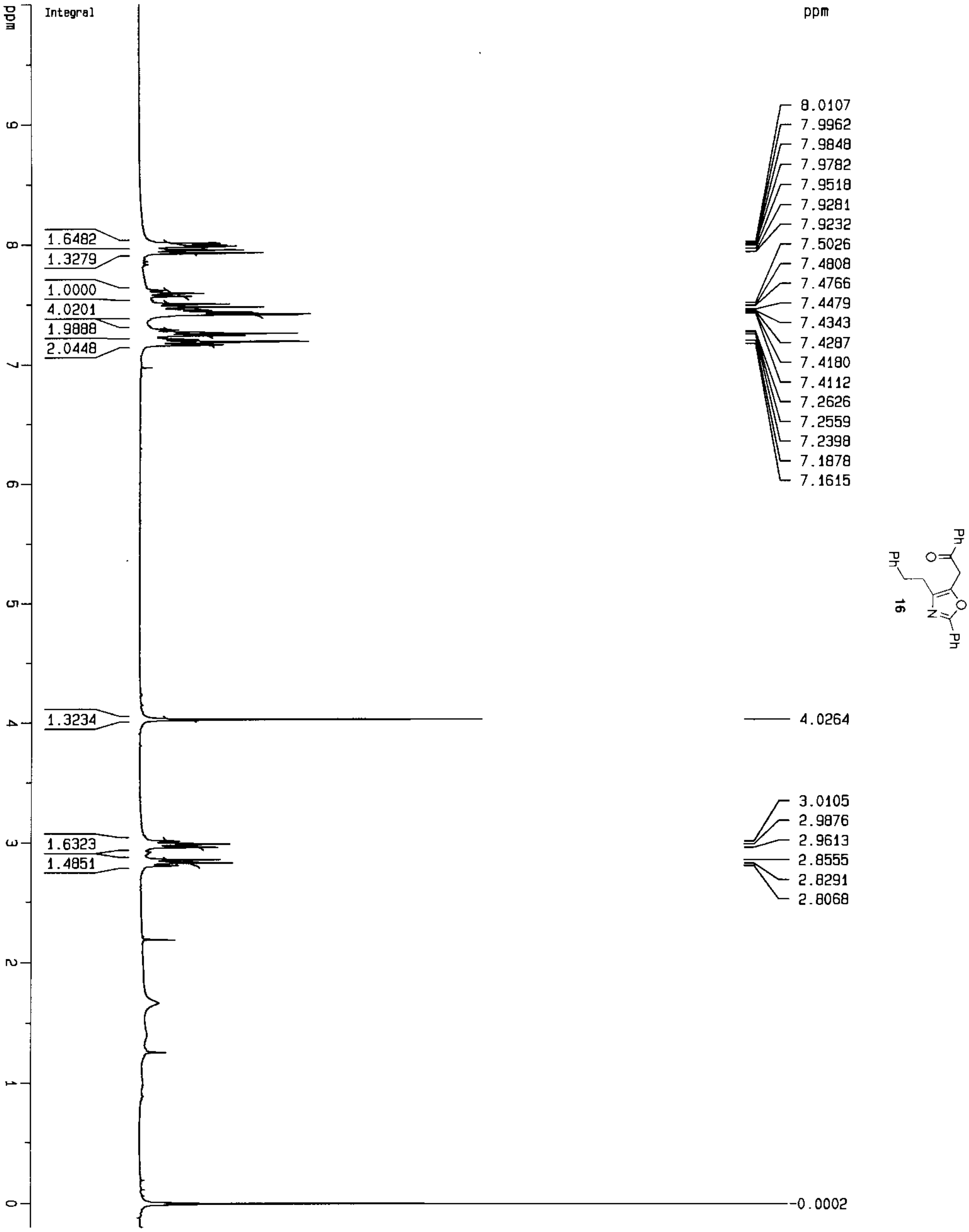
N
Ph
O
Ph

15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1.9888
2.0448
1.3234
1.6323
1.4851
9
8
7
6
5
4
3
2
1
0
ppm
8.0107
7.9962
7.9848
7.9782
7.9518
7.9281
7.9232
7.5026
7.4808
7.4766
7.4479
7.4343
7.4287
7.4180
7.4112
7.2626
7.2559
7.2398
7.1878
7.1615
4.0264
3.0105
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2.8555
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2.8068
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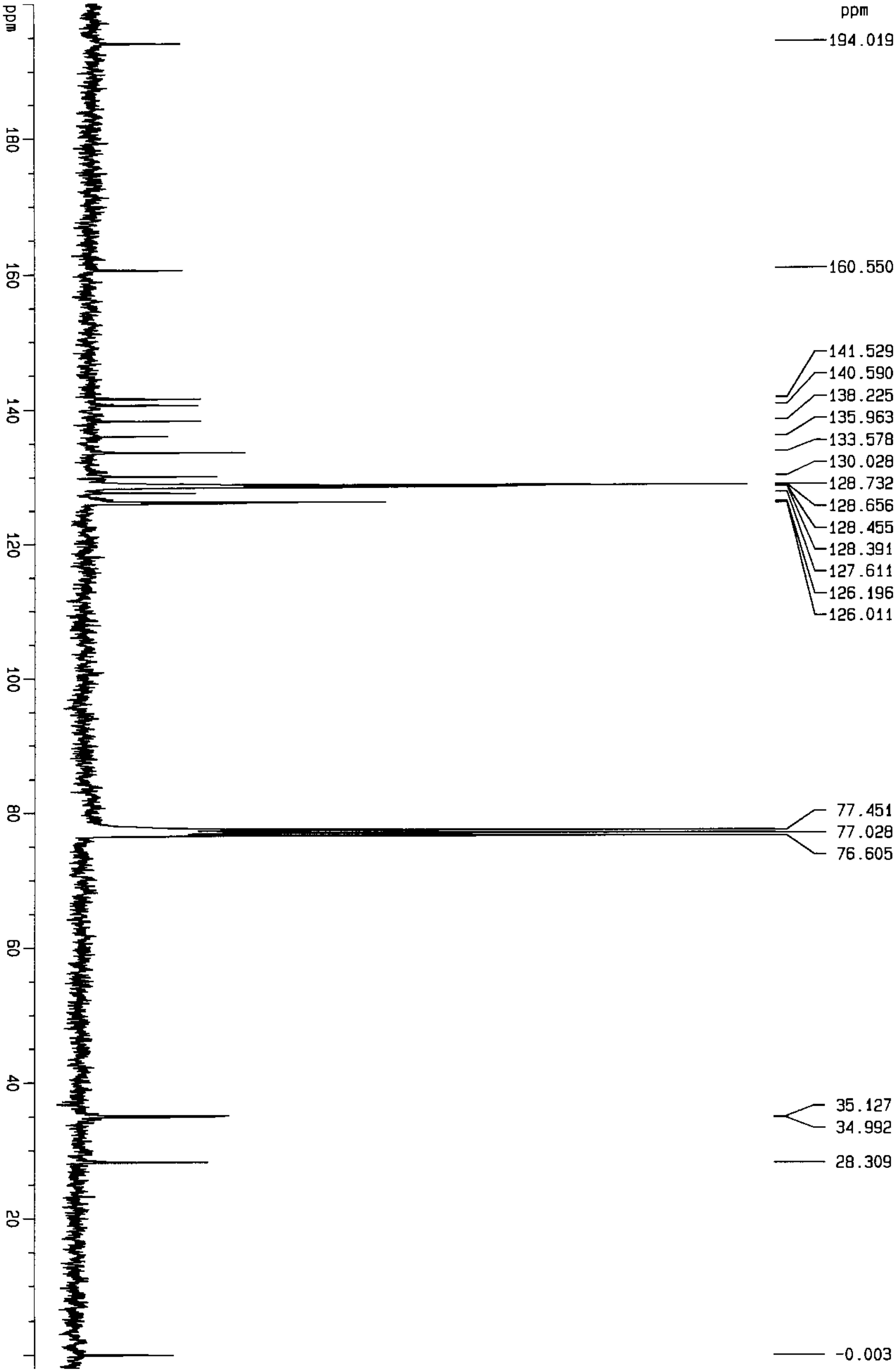
Ph
O
N
Ph
16


ppm
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120
100
80
60
40
20
ppm
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141.529
140.590
138.225
135.963
133.578
130.028
128.732
128.656
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126.196
126.011
77.451
77.028
76.605
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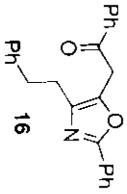
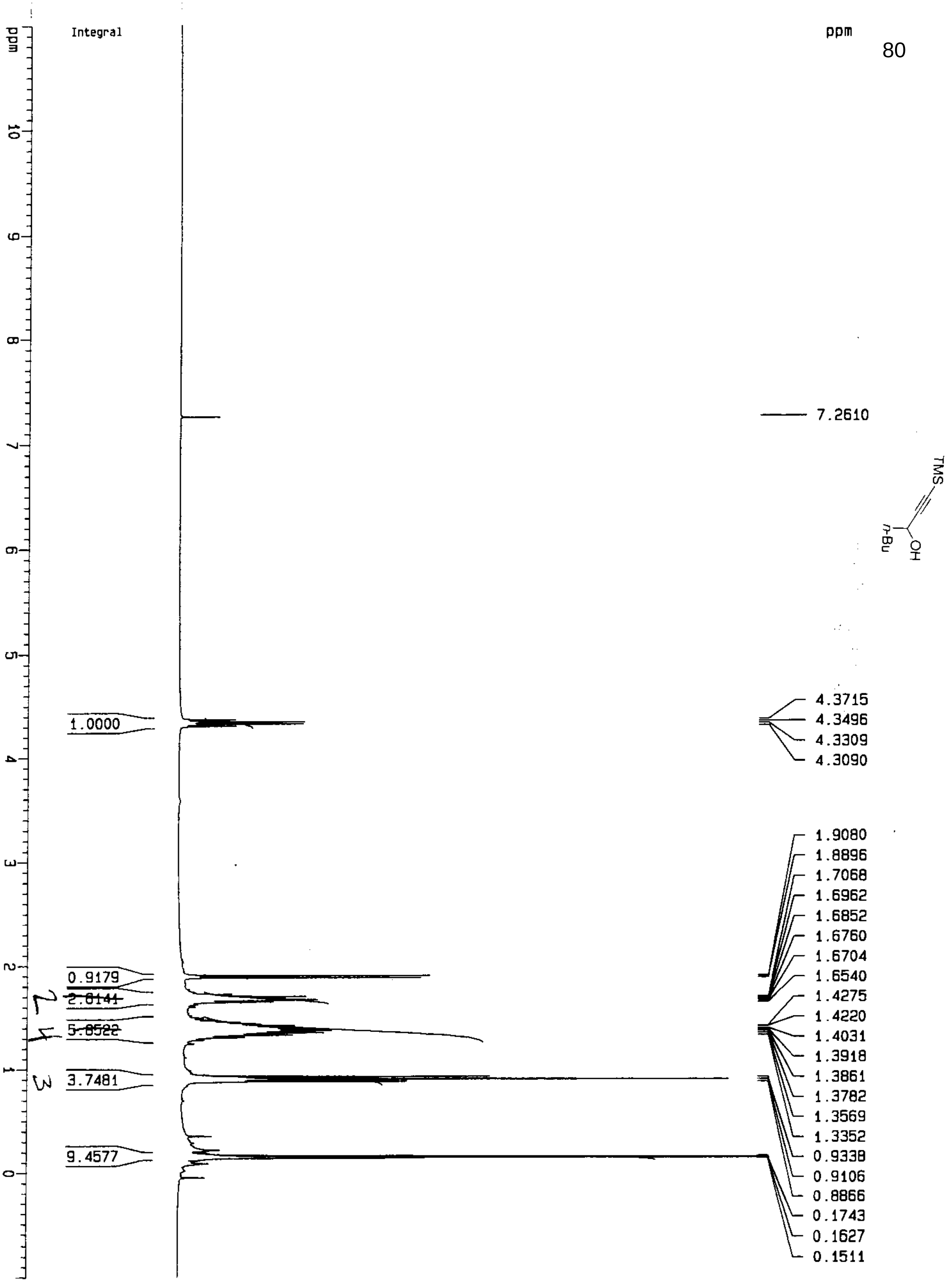

Ph
O
Ph
O
N
Ph

16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Integral
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9
8
7
6
5
4
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2
1
0
7.2610
TMS
OH
n-Bu
1.0000
4.3715
4.3496
4.3309
4.3090
0.9179
~~2.8141~~
2
~~5.8522~~
4
3.7481
3
9.4577
1.9080
1.8896
1.7068
1.6962
1.6852
1.6760
1.6704
1.6540
1.4275
1.4220
1.4031
1.3918
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1.3569
1.3352
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0.8866
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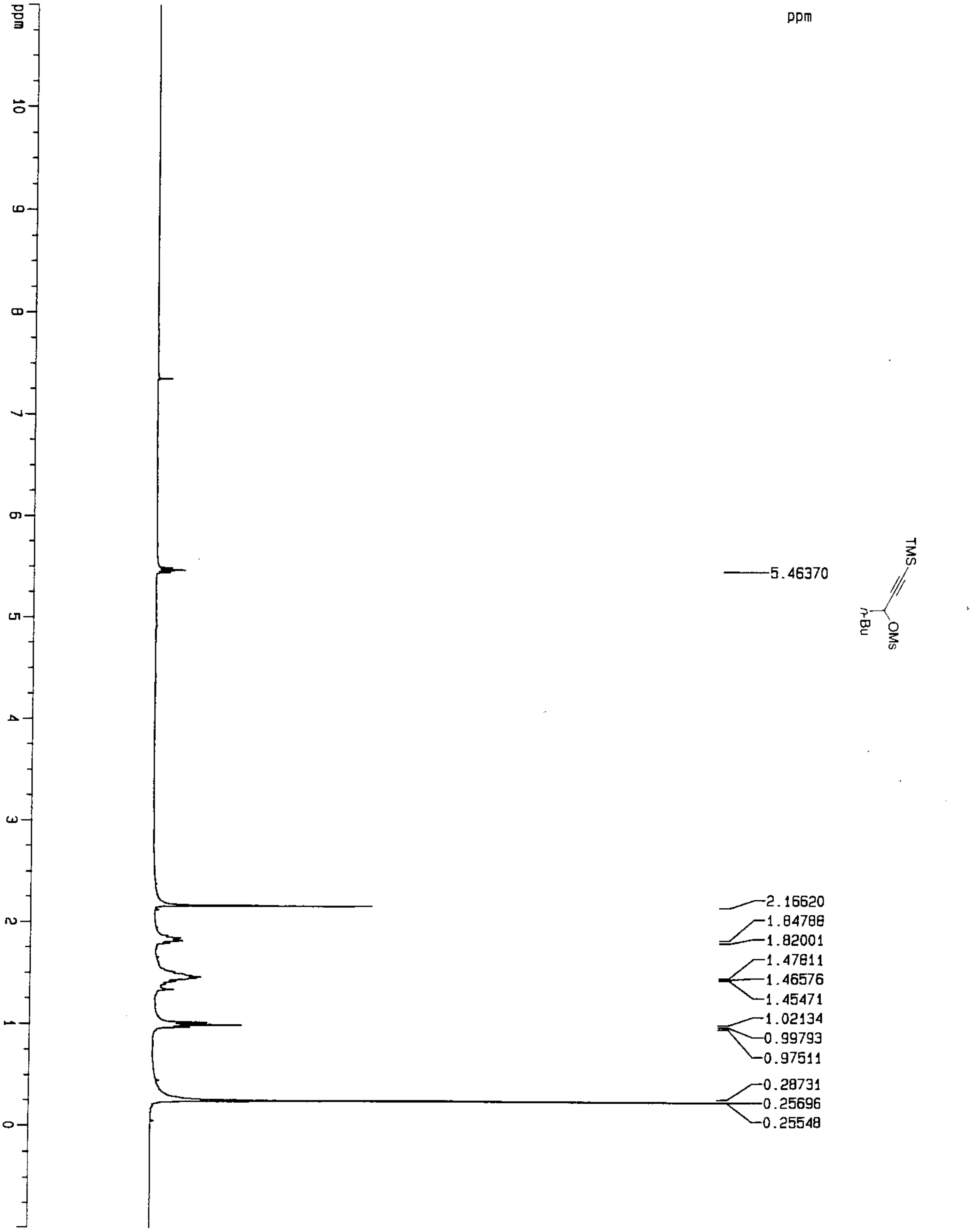
0.1627
0.1511


ppm
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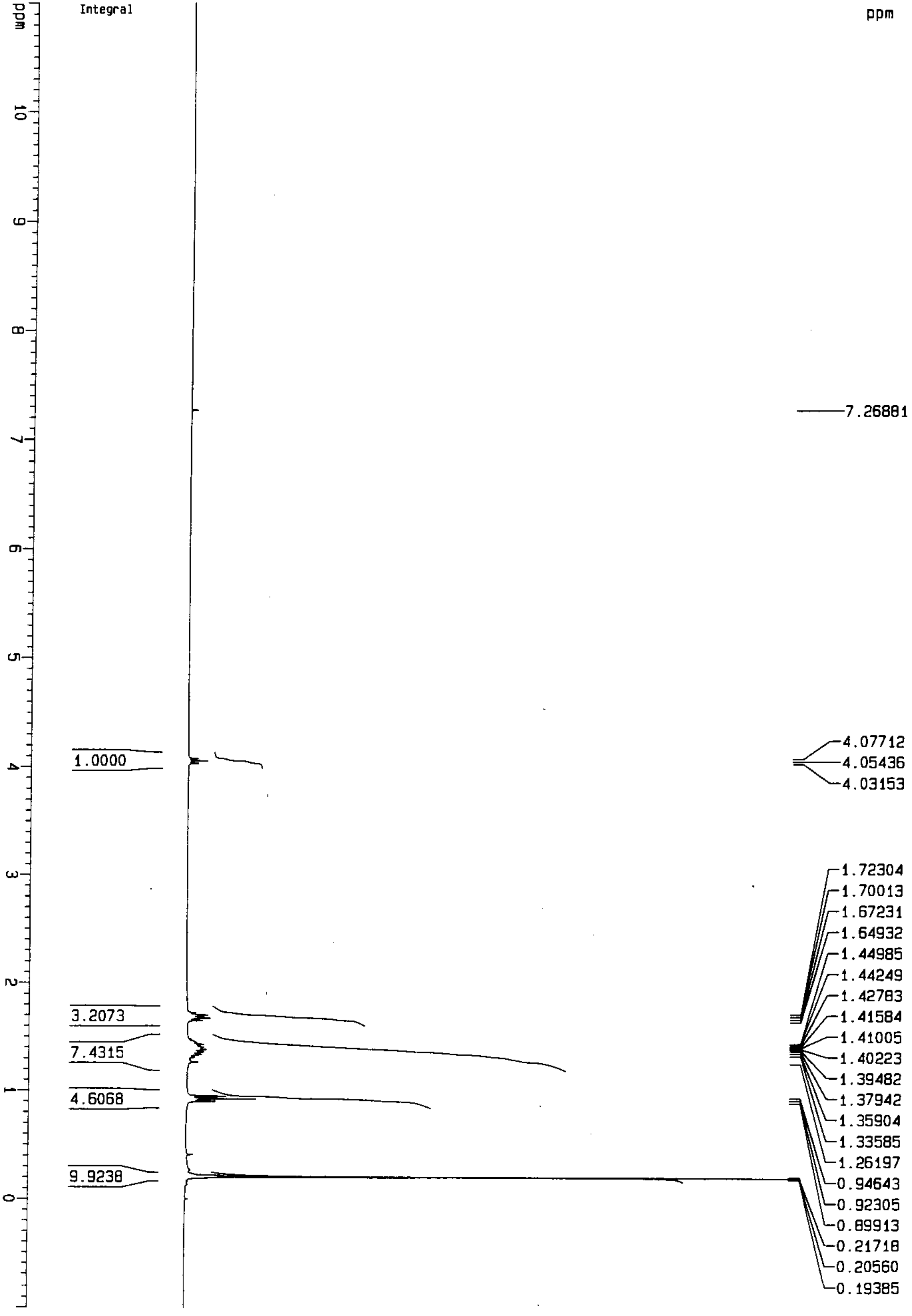
TMS
OMs
n-Bu


ppm
Integral
ppm
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9
8
7
6
5
4
3
2
1
0
1.0000
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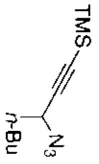
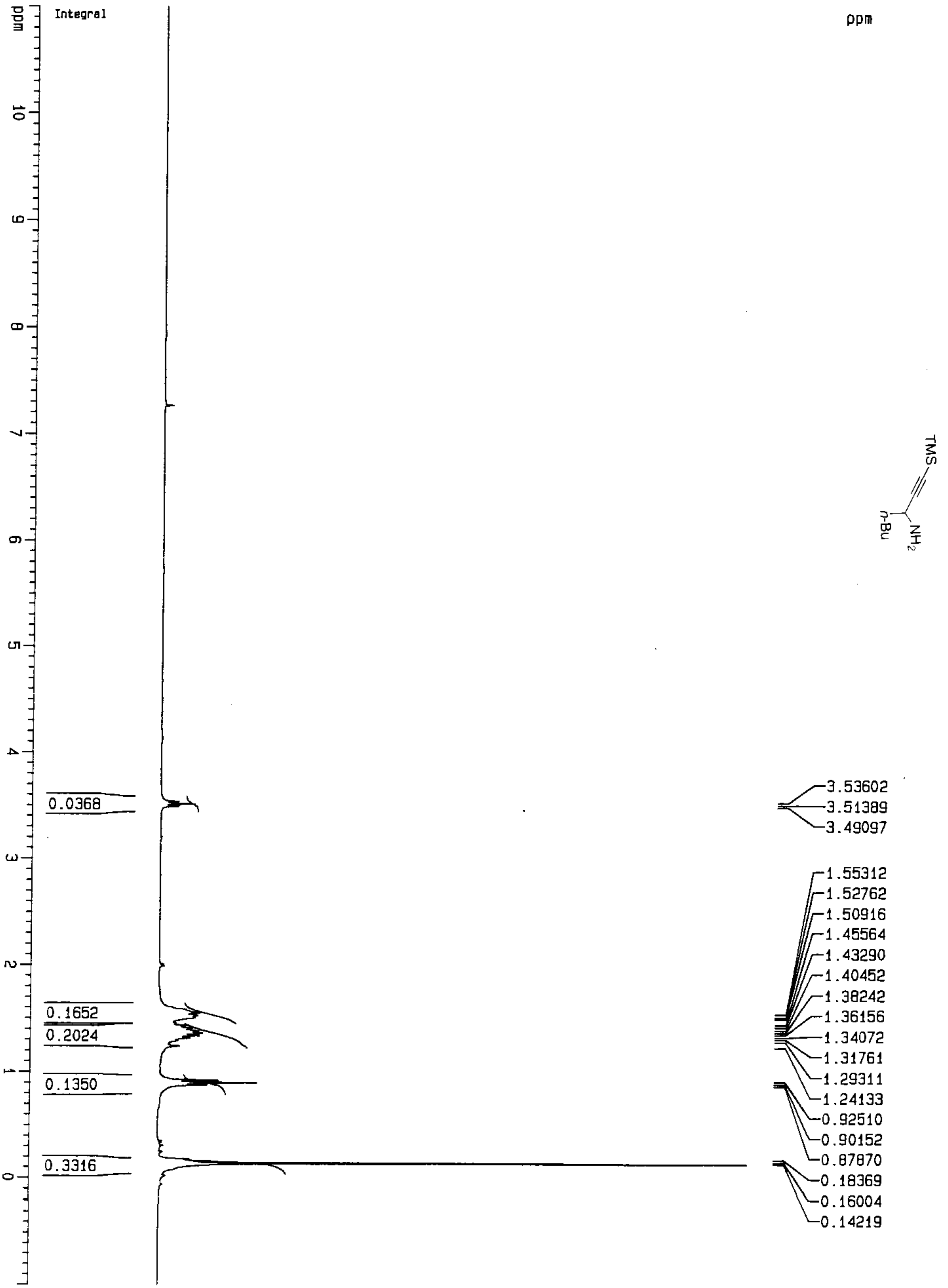
4.6068
9.9238
7.26881
4.07712
4.05436
4.03153
1.72304
1.70013
1.67231
1.64932
1.44985
1.44249
1.42783
1.41584
1.41005
1.40223
1.39482
1.37942
1.35904
1.33585
1.26197
0.94643
0.92305
0.89913
0.21718
0.20560
0.19385


TMS
N3
n-Bu


ppm
Integral
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9
8
7
6
5
4
3
2
1
0
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0.1652
0.2024
0.1350
0.3316
ppm
TMS
NH$_2$
n-Bu
3.53602
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3.49097
1.55312
1.52762
1.50916
1.45564
1.43290
1.40452
1.38242
1.36156
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1.29311
1.24133
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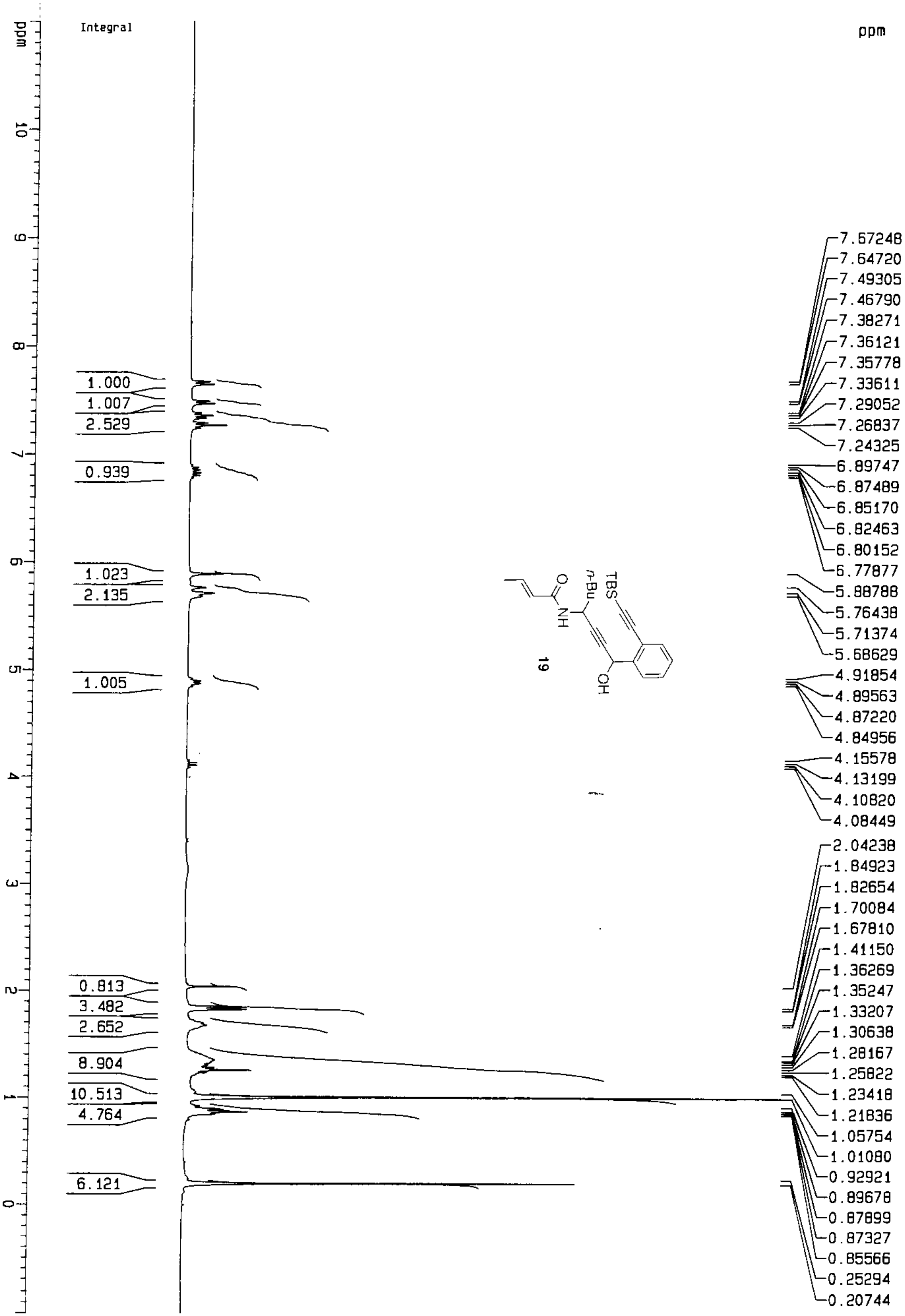
0.87870
0.18369
0.16004
0.14219


Integral
ppm
ppm
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9
8
7
6
5
4
3
2
1
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1.007
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0.939
1.023
2.135
1.005
0.813
3.482
2.652
8.904
10.513
4.764
6.121
7.67248
7.64720
7.49305
7.46790
7.38271
7.36121
7.35778
7.33611
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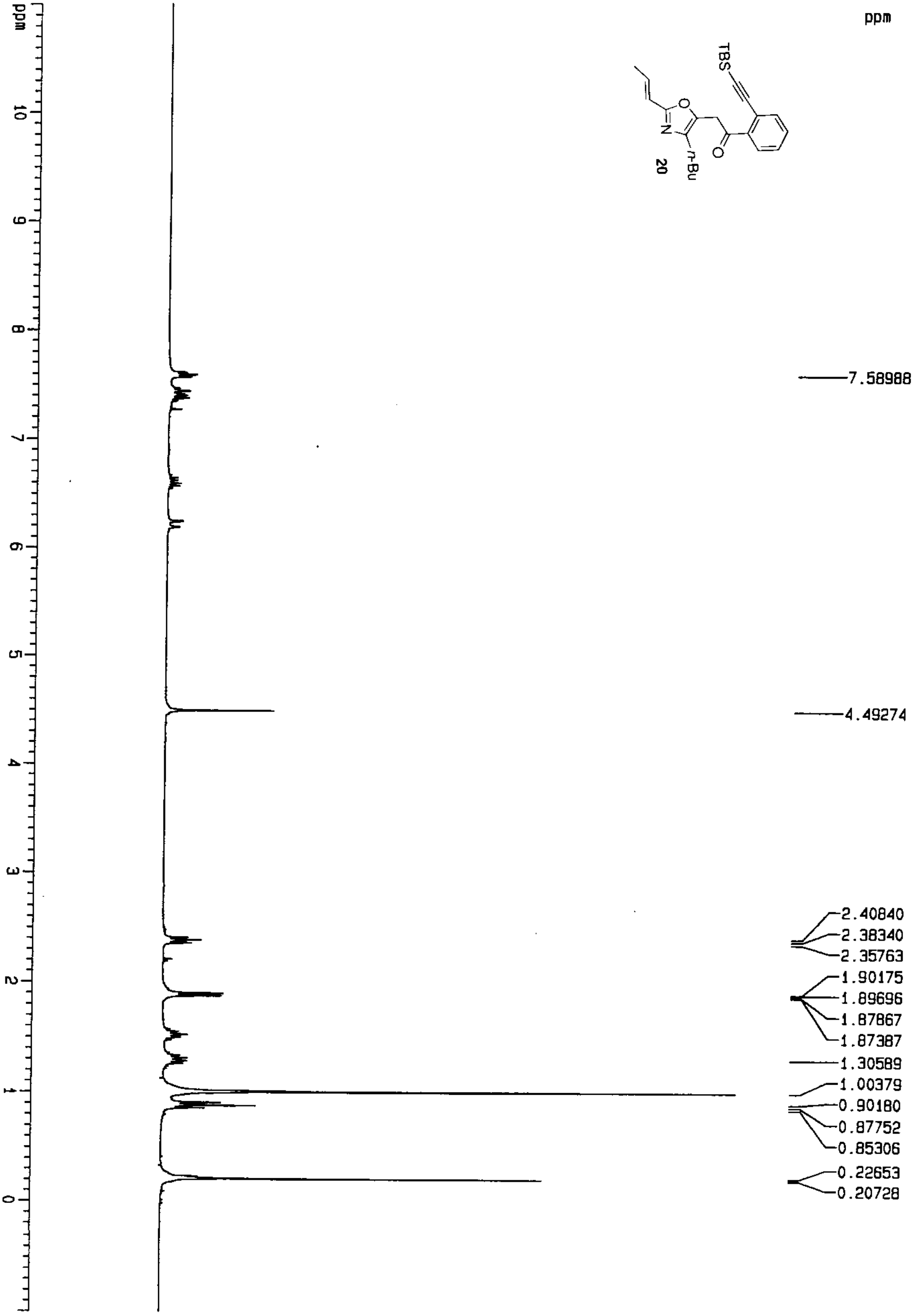
TBS
n-Bu
O
NH
OH
19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N
O
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1.00379
0.90180
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0.20728
ppm
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7
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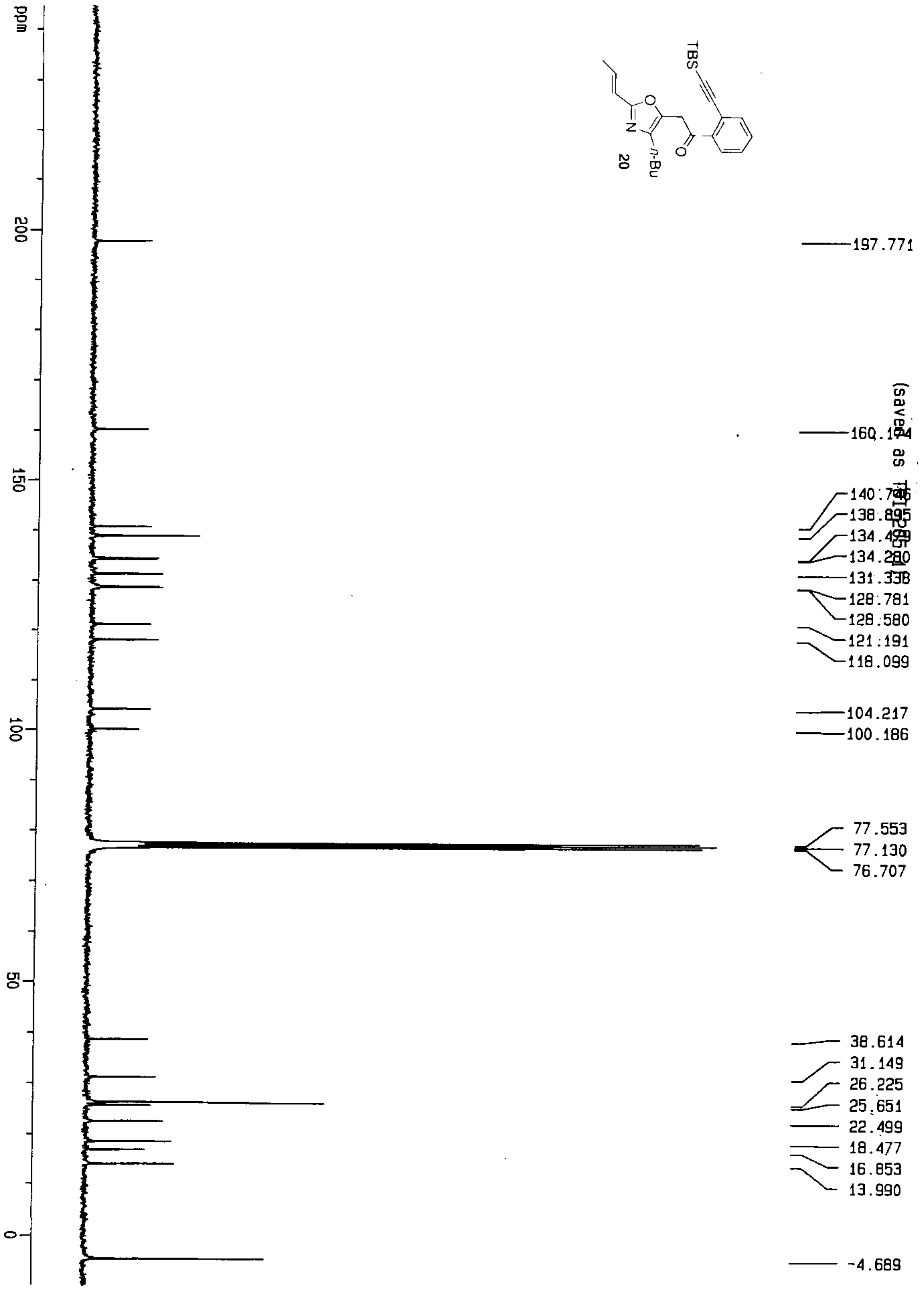
4
3
2
1
0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100
50
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TBS
O
N
n-Bu
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140.796
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134.409
134.280
131.338
128.781
128.580
121.191
118.099
104.217
100.186
77.553
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76.707
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31.149
26.225
25.651
22.499
18.477
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-4.689
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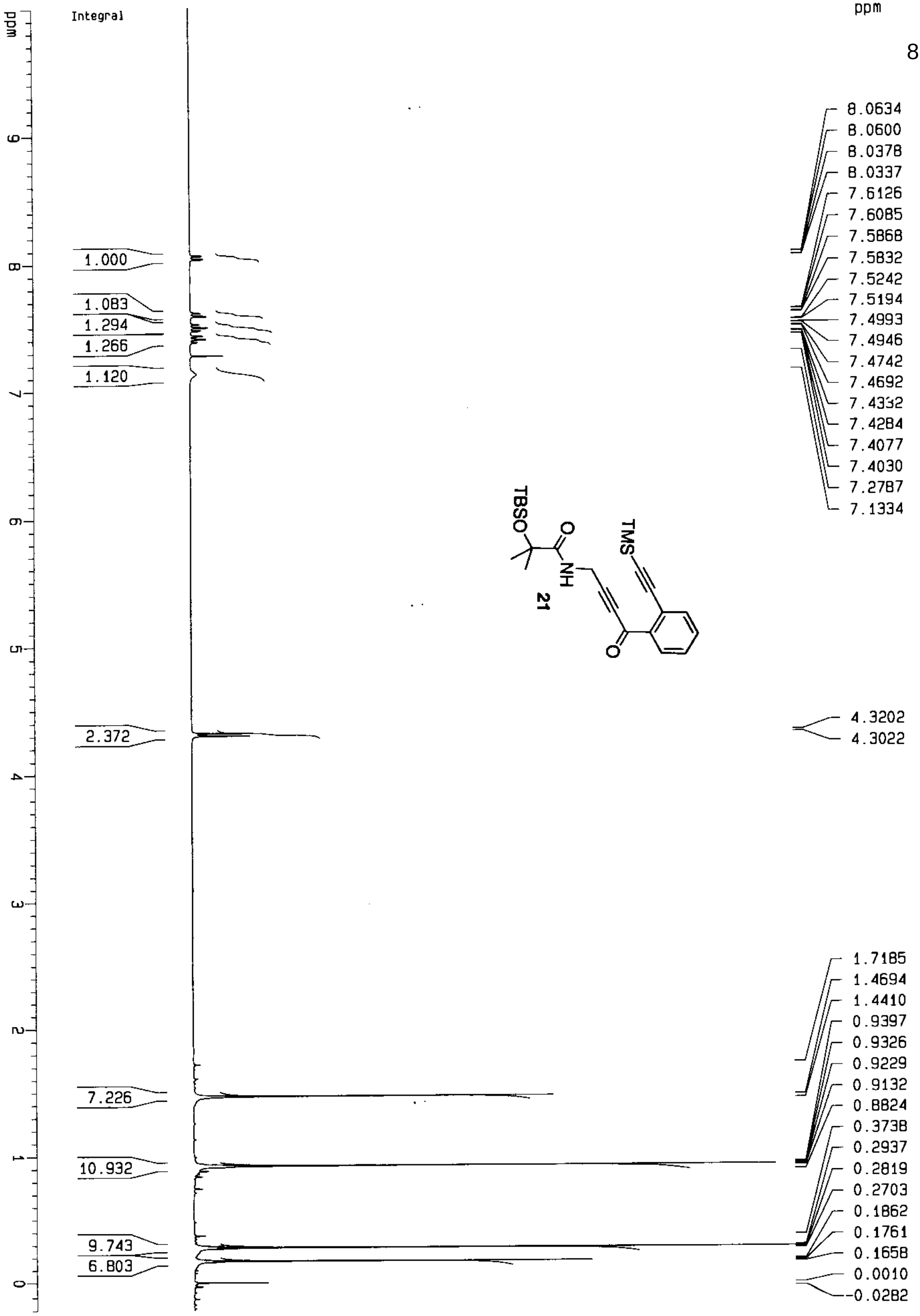
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Integral
ppm
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8
7
6
5
4
3
2
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0
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1.294
1.266
1.120
2.372
7.226
10.932
9.743
6.803
8.0634
8.0600
8.0378
8.0337
7.6126
7.6085
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7.5832
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7.5194
7.4993
7.4946
7.4742
7.4692
7.4332
7.4284
7.4077
7.4030
7.2787
7.1334
4.3202
4.3022
1.7185
1.4694
1.4410
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0.9326
0.9229
0.9132
0.8824
0.3738
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0.2819
0.2703
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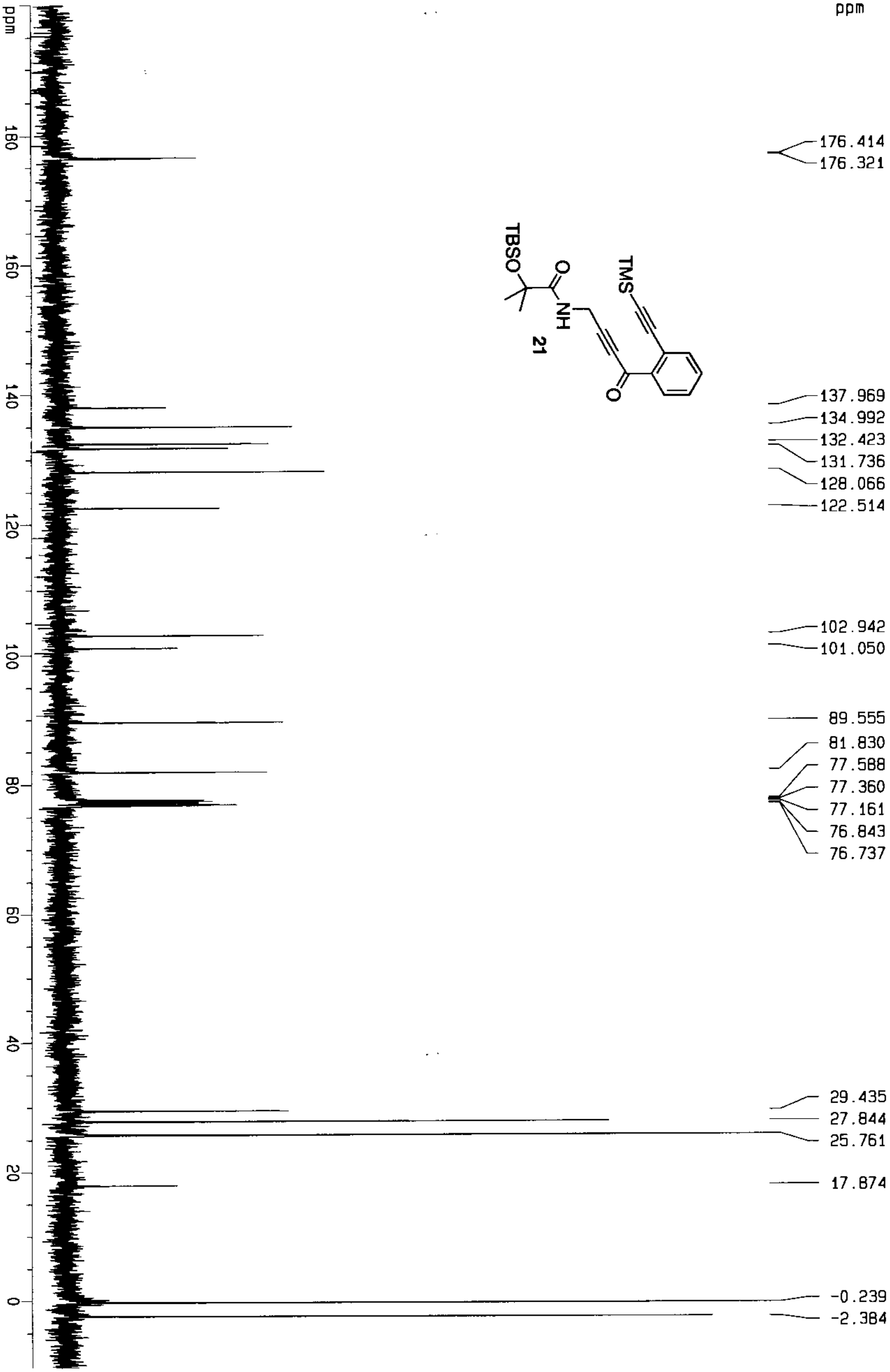
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128.066
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101.050
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81.830
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77.161
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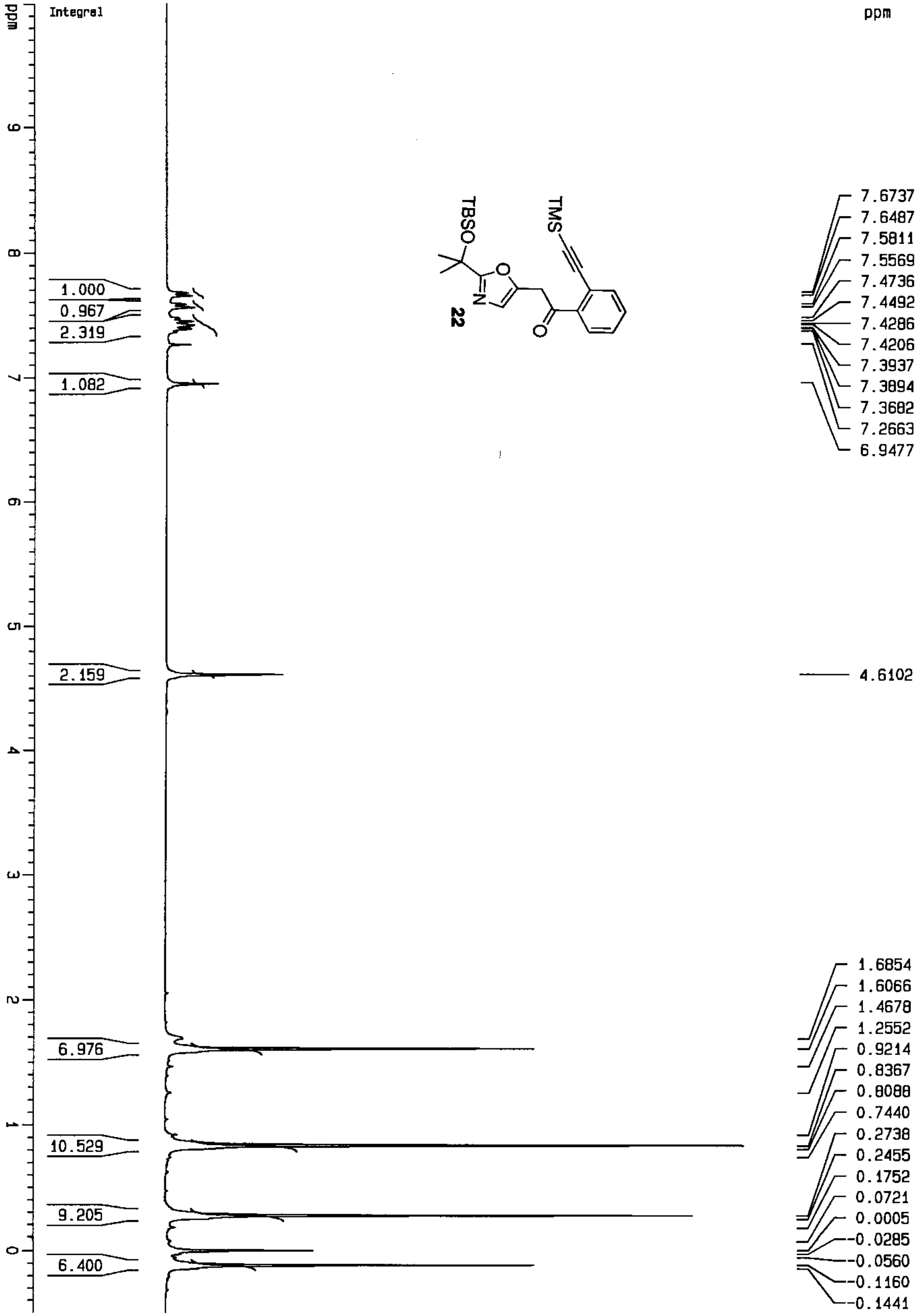
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6.976
10.529
9.205
6.400
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TBSO
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N
O
22
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6.9477
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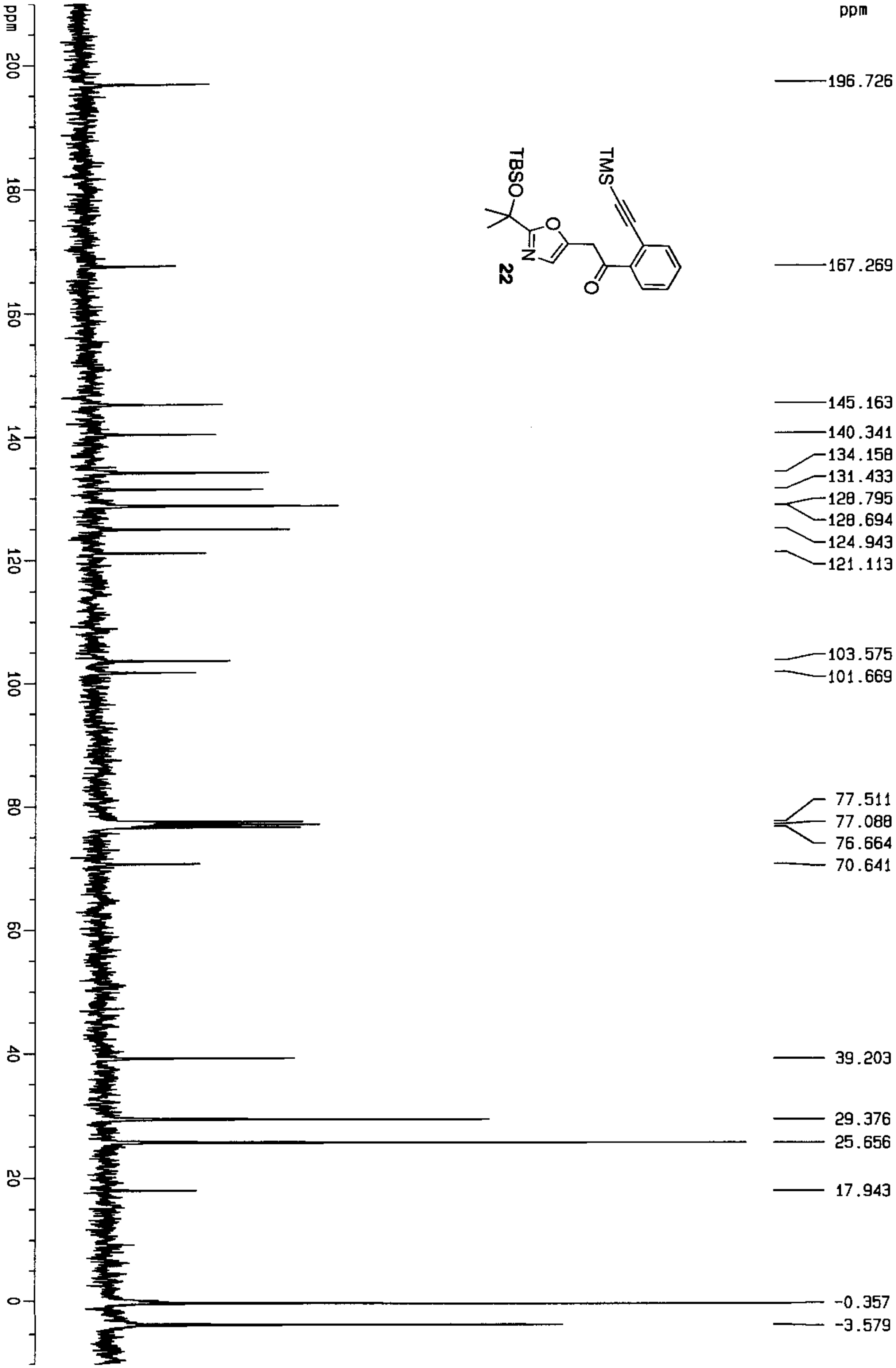
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128.694
124.943
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101.669
77.511
77.088
76.664
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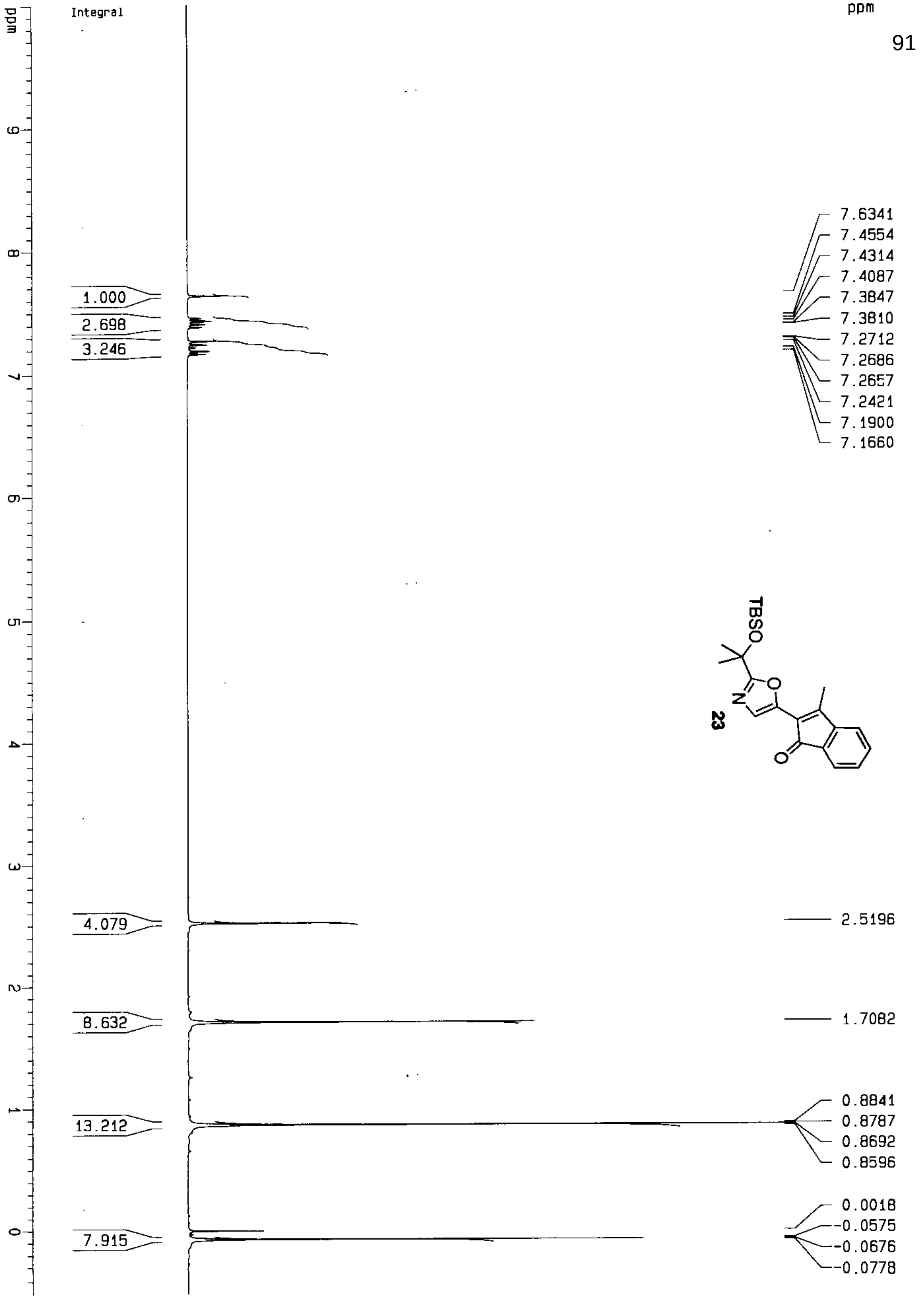
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7.6341
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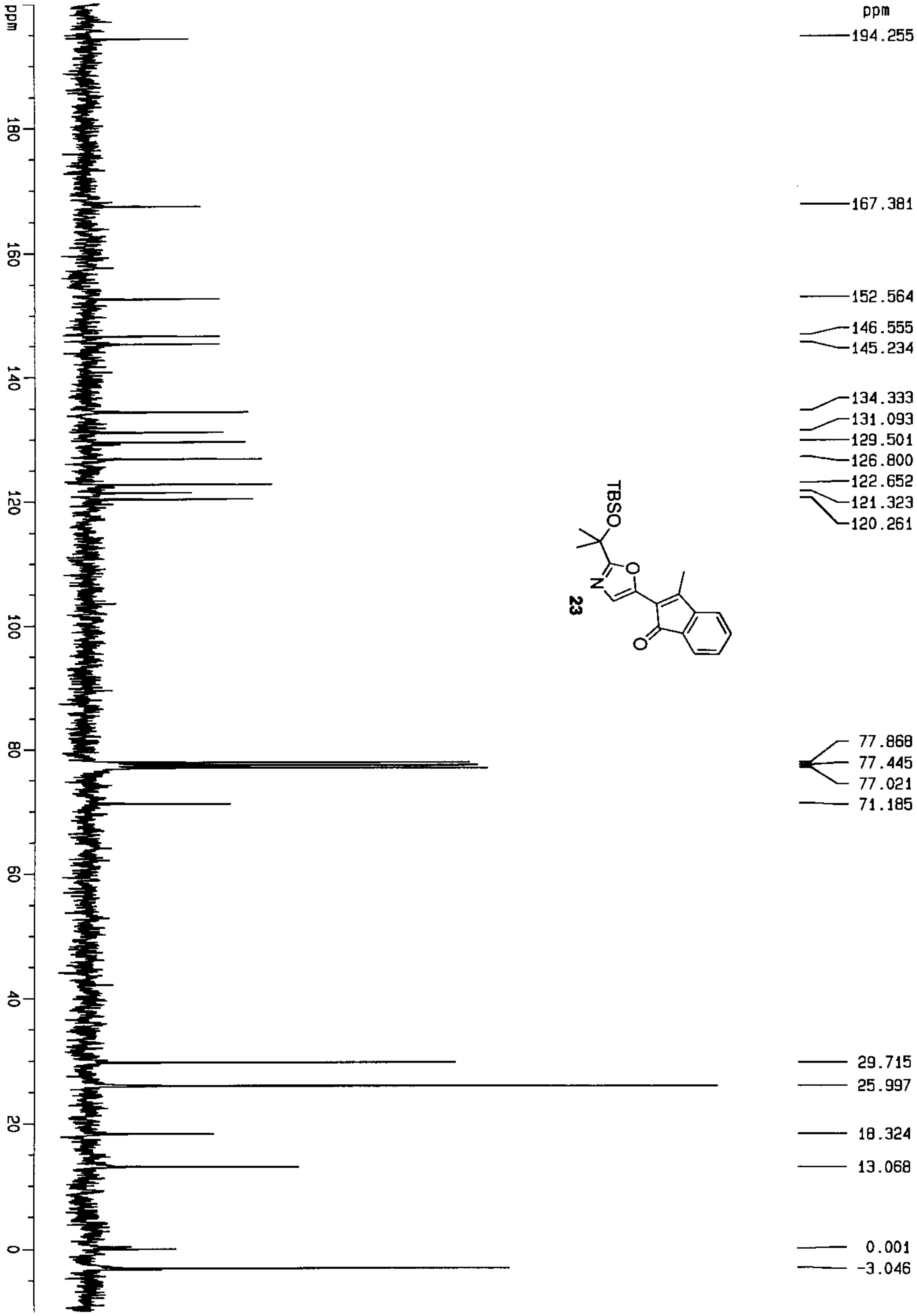
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129.501
126.800
122.652
121.323
120.261
77.868
77.445
77.021
71.185
29.715
25.997
18.324
13.068
0.001
-3.046
TBSO
O
N
O
23