Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Pd-nanoparticles catalyzed one-pot sequential Heck and Suzuki couplings of bromo-chloroarenes in ionic liquids and water

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Electronic Supplementary Information

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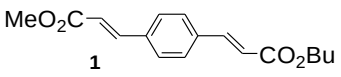
General Remarks: All chemicals used for synthetic procedures such as aryl halides, reductants and tetraalkylammonium salts, were commercially available and were used without further purification. Reactions were monitored by GLC and GC-MS techniques by using an Agilent 5890 A gaschromatograph and an Agilent 6850/MSD 5975C instrument, respectively. Both the instruments were equipped with a capillary column HP-5MS (Agilent, l. 30 m, i.d. 0.25 mm, s.p.t. 0.25 μ). NMR spectra were recorded on a Varian Inova 400 MHz spectrometer.
Identification of compounds of tables 1-4 was made by comparison of their spectral data with those reported in the literature (most of them are identified with the help of the NIST library). For unknown compounds the complete characterization was provided.

Representative procedure for sequential one-pot double Heck couplings. In a 10 ml vial, equipped with a screw cap and a magnetic bar, tetrabutylammonium bromide (TBAB, 1 g), tetrabutylammonium acetate (TBAA, 0.45 g, 1.5 mmol), $Pd(OAc)_2$, (1.7 mg, 0.0075 mmol, 1.5 mol%), olefin 1 (0.5 mmol), and bromoclorobenzene (0.5 mmol) were placed. The solution was heated to 100 °C under air until the disappearance of the first olefin monitored by GC-MS. Olefin 2 (0.5 mmol) was then added and the reaction mixture was heated to 120 °C for the proper reaction time (see tables 1). Monitoring of the reaction mixture by glc and GC-MS provided reagents conversion. After completion of the reaction, mixture was added to 20 mL of water and extracted with dichloromethane (3 × 20 mL). The combined organic layers were washed with water (2 × 20 mL), dried with anhydrous $MgSO_4$ and concentrated in vacuo. The residue was purified by chromatography on silica gel to give the desired product. Unknown compounds were identified by NMR analysis (see below).

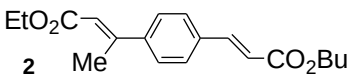
Representative procedure for sequential one-pot Heck/Suzuki couplings. In a 10 ml vial, equipped with a screw cap and a magnetic bar, TBAB (1 g), 4-bromoclorobenzene (0.5 mmol), olefin (0.5 mmol), TBAA (0.75 mmol), and $Pd(OAc)_2$, (1.7 mg, 0.0075 mmol, 1.5 mol%) were placed. The mixture was heated to 100°C and stirred under air. The reaction was monitored by GC-Ms until the completion of the Heck coupling. Then, boronic acid (0.75 mmol) and Cs_2CO_3 (1 mmol) and 150 μl of H_2O were added and the temperature was raised to 120°C. Monitoring of the reaction mixture by glc and GC-MS provided reagents conversion (see table 3). After completion of the reaction, both yields and products identification were carried out after extraction of the mixture followed by column chromatography as reported in the previous procedure.

Representative procedure for sequential one-pot double Suzuki couplings. In a 10 ml vial, equipped with a screw cap and a magnetic bar, a solution of TBAOH 1.5 M (1 ml, 1.5 mmol), bromochloroarene (0.5 mmol), Pd acetate (1 mol%), boronic acid (R^1, 0.6 mmol) were placed. The reaction mixture was heated to 60°C and stirred under air until the completion of the first step. Then, a boronic acid (R^2, 0.6 mmol) was added and the reaction temperature was raised to 100 °C for the proper time (see table 4). Monitoring of the reaction mixture by glc and GC-MS provided reagents conversion. After completion of the reaction, both yields and products identification were carried out after extraction of the mixture followed by column chromatography as reported in the previous procedure.

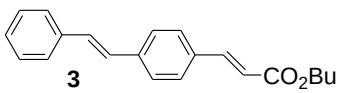
Spectral data and characterisation of the coupling products.

(E)-butyl 3-(4-((E)-3-methoxy-3-oxoprop-1-en-1-yl)phenyl)acrylate (**1**). Lit.[1] 

1
^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm: 0.94 (t, *J*= 7.3 Hz, 3H), 1.35-1.47 (m, 2H), 1.60-1.72 (m, 2H), 3.79 (s, 3H), 4.19 (t, *J*= 6.8 Hz, 2H), 6.44 (two doublets almost overlapped, *J*= 15.9 Hz, 2H), 7.51 (b s, 4H), 7.63 and 7.65 (two doublets overlapped, *J*= 15.9 and 16.1 Hz, 2H). ^{13}C NMR δ ppm: 13.90, 19.38, 30.96, 51.97, 64.76, 119.07, 119.66, 128.69, 136.26, 136.47, 143.53, 143.89, 166.99, 167.35. EI m/z: 288 (M^+, 28), 257 (16), 232 (100), 215 (52), 201 (39), 183 (34), 155 (22), 127 (44), 102 (10), 92 (7), 78 (9).

(E)-ethyl 3-(4-((E)-3-butoxy-3-oxoprop-1-en-1-yl)phenyl)but-2-enoate (**2**). 

2
^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm: 0.94 (t, *J*= 7.3 3H), 1.29 (t, *J*= 7.1 3H), 1.35-1.49 (m, 2H), 1.61-1.72 (m, 2H), 2.54 (d, *J*= 1.3 Hz, 3H), 4.19 (m, 4H), 6.14 (q, *J*= 1.3 Hz, 1H), 6.45 (d, *J*= 15.9, 1H), 7.42-7.54 (m, 4H), 7.64 (d, *J*= 15.9, 1H). ^{13}C NMR δ ppm: 13.83, 13.99, 15.06, 19.38, 30.95, 60.37, 64.75, 118.29, 119.30, 128.18, 128.25, 135.60, 138.71, 142.58, 143.71, 155.55, 166.12, 167.09. EI m/z: 316 (M^+, 25), 271 (31), 243 (36), 214 (100), 197 (41), 186 (25), 141 (50), 115 (62), 102 (7). $C_{19}H_{24}O_4$ (316,17): calcd. C, 72.13; H, 7.65; O, 20.23, found C, 72.31; H, 7.68; O, 20.01.

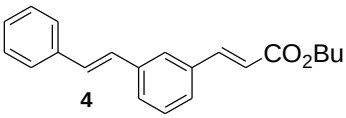
(E)-butyl 3-(4-((E)-styryl)phenyl)acrylate (**3**). Lit.[2] 

3
^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm: 0.95 (t, *J*= 7.3 Hz, 3H), 1.40-1.49 (m, 2H), 1.62-1.70 (m, 2H), 4.19 (t, *J*= 6.6 Hz, 2H), 6.42 (d, *J*= 15.9 Hz, 1H), 7.07 (d, *J*= 16.3 Hz, 1H), 7.15 (d,

[1] C. Burmester, S. Mataka, T. Thiemann *Synth. Commun.* 2010, **40**, 3196.
[2] X. Zhang, A. Liu, W. Chen, *Org. Lett.*, 2008**, 10**, 3849.

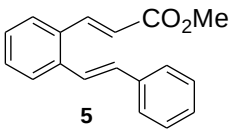
J= 16.3 Hz, 1H), 7.22-7.39 (m, 3H), 7.50 (b s, 6H), 7.65 (d, *J*= 15.9 Hz, 1H). ^{13}C NMR δ ppm: 13.93, 19.40, 31.00, 64.60, 118.08, 133.90, 126.86, 127.10, 127.99, 128.21, 128.68, 128.94, 130.28, 137.18, 139.52, 144.20, 167.35. EI m/z: 306 (M^+, 100), 250 (48), 203 (45), 178 (39), 101 (19), 77 (15).

(E)-butyl 3-(3-((E)-styryl)phenyl)acrylate (**4**). Lit.[2] ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm: 0.96 (t, *J*= 7.3 Hz, 3H), 1.37-1.48 (m, 2H), 1.63-1.72 (m, 2H), 4.21 (t, *J*= 6.8 Hz, 2H), 6.47 (d, *J*= 15.9 Hz, 1H), 7.10 (d, *J*= 6.2 Hz, 2H), 7.30-7.42 (m, 4H), 7.45-7.53 (m, 4H), 7.63 (b s, 1H), 7.67 (d, *J*= 16.1 Hz, 1H). ^{13}C NMR δ ppm: 13.93, 19.41, 30.99, 64.66, 118.86, 126.31, 126.79, 127.25, 128.02, 128.09, 128.36, 128.92, 129.34, 129.88, 135.12, 137.19, 138.22, 144.56, 167.21. EI m/z: 306 (M^+, 100), 250 (23), 233 (24), 203 (51), 189 (19), 178 (32), 101 (11), 77 (6).



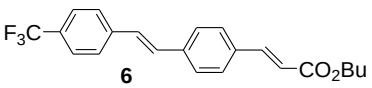
4

(E)-methyl 3-(2-((E)-styryl)phenyl)acrylate (**5**). Lit.[3] ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm: 3.79 (s, 3H), 6.35 (d, *J*= 15.7 Hz, 1H), 6.96 (d, *J*= 16.1 Hz, 1H), 7.21-7.43 (m, 6H), 7.48-7.63 (m, 4H), 8.09 (d, *J*= 15.7 Hz, 1H). ^{13}C NMR δ ppm: 51.91, 120.21, 125.73, 126.99, 127.17, 127.49, 127.95, 128.26, 128.92, 130.25, 132.91, 133.015, 137.28, 137.78, 142.81, 167.45. EI m/z: 306 (M^+, 100), 264 (17), 323 (14), 205 (100), 204 (50), 190 (16), 178 (14), 127 (18), 101 (22), 91 (58), 77 (13).



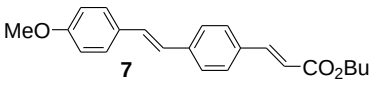
5

(E)-butyl 3-(4-((E)-4-(trifluoromethyl)styryl)phenyl)acrylate (**6**). Lit.[4] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.66 (d, *J* = 16.1 Hz, 1H), 7.62-7.57 (m, 4H), 7.55-7.50 (m, 4H), 7.16 (s, 2H), 6.44 (d, *J* = 16.1 Hz, 1H), 4.20 (t, *J* = 6.8 Hz, 2H), 1.70-1.63 (m, 2H), 1.46-1.36 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR: δ 167.05, 143.77, 138.49, 134.33, 130.26, 128.53, 128.37, 127.18, 126.71, 125.66, 118.33, 64.47, 30.78, 19.20, 13.73. EI m/z: 375 (M^++1, 25), 374 (M^+, 100), 318 (98), 301 (43), 274 (21), 261 (11), 246 (13), 203 (35), 150 (12), 127 (12), 101 (10).



6

(E)-butyl 3-(4-((E)-4-methoxystyryl)phenyl)acrylate (**7**)**.** 1H-NMR ($CDCl_3$, 400 MHz) δ ppm: 0.95 (t, *J*= 7.4 Hz, 3H), 1.41 (sestet, *J*= 7.4 2H), 1.63-1.72 (m, 2H), 3.79 (s, 3H), 4.19 (t, *J*= 6.7 2H), 6.40 (d, *J*= 16.1 1H), 6.87 (d, *J*= 8.7 2H), 6.92 (d, *J*= 16.3 1H), 7.08 (d, *J*= 16.3, 1H), 7.42 (d, *J*= 8.7, 2H), 7.44-7.48 (m, 4H), 7.62 (d, *J*=

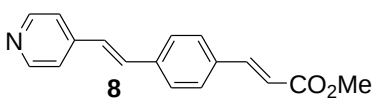


7

[3] C. Wang, L.-S. Tan, J.-P., He, H.-W, Hu, J.-H. Xu, *Synth. Commun.* 2003, **33**, 773.
[4] V. Calò, A. Nacci, A. Monopoli, P. Cotugno, *Angew. Chem. Int. Ed.* 2009, **48**, 6101.

16.1, 1H). ^{13}C-NMR δ: 13.77, 19.19, 30.75, 55.28, 64.38, 114.14, 117.45, 125.56, 126.56, 127.91, 128.46, 129.55, 129.67, 133.15, 139.64, 144.09, 159.54, 167.21. EI m/z: 336 (M^+, 100), 280 (16), 261 (8), 236 (8), 220 (8), 201 (8), 189 (9), 135 (11), 117 (6). $C_{22}H_{24}O_3$ (336.17): calcd. C, 78.54; H, 7.19; O, 14.27; found C, 78.72; H, 7.32; O, 14.05.

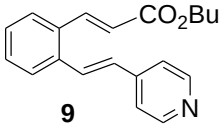
(E)-methyl 3-(4-((E)-2-(pyridin-4-yl)vinyl)phenyl)acrylate (**8**). Lit.[5]



8

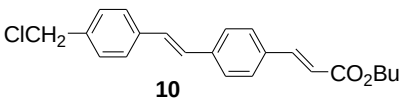
^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm: 3.82 (s, 3H), 6.49 (d, *J*= 15.9, 1H), 7.14 (d, *J*=16.3, 1H), 7.40-7.81 (m, 8H), 8.69 (b s, 2H). ^{13}C NMR δ ppm: 51.99, 119.18, 125.44, 128.26, 128.90, 136.15, 136.82, 137.05, 143.74, 144.99, 149.72, 167.29. EI m/z: 265 (M^+, 100), 234 (48), 206 (57), 178 (16), 152 (17), 102 (16), 89 (11).

(E)-butyl 3-(2-((E)-2-(pyridin-4-yl)vinyl)phenyl)acrylate (**9**). ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm: 0.95 (t, *J*= 7.4 3H), 1.37-1.48 (m, 2H), 1.63-1.72 (m, 2H), 4.19 (t, *J*= 6.7 2H), 6.40 (d, *J*= 15.9, 1H), 6.92 (d, *J*=16.1, 1H), 7.34-7.61 (m, 6H), 7.65 (d, *J*= 16.1, 1H), 8.08 (d, *J*= 15.9, 1H), 8.60 (b s, 2H). ^{13}C NMR δ ppm: 13.94, 19.42, 30.94, 64.83, 121.53, 127.41, 127.74, 129.21, 129.55, 130.30, 131.35, 133.74, 136.11, 141.85, 145.74, 149.10, 166.94. EI m/z: 307 (M^+, 3), 251 (7), 234 (7), 206 (100), 178 (8), 165 (2), 152 (6), 128 (10), 115 (5), 102 (7), 79 (5), 57 (9). $C_{20}H_{21}NO_2$ (307,16): calcd. C, 78.15; H, 6.89; N, 4.56; O, 10.41; found C, 78.40; H, 6.92; N, 4.50; O, 10.22.



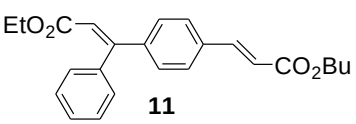
9

(E)-butyl 3-(4-((E)-4-(chloromethyl)styryl)phenyl)acrylate (**10**). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm: 0.96 (t, *J*= 7.4 3H), 1.36-1.48 (m, 2H), 1.61-1.73 (m, 2H), 4.20 (t, *J*= 6.6 2H), 5.11 (s, 2H), 6.45 (d, *J*=15.7, 1H), 7.13 (two doublets, *J*=16.3, 2H), 7.36 (d, *J*= 8.1, 2H), 7.52 (d, *J*= 8.1, 2H), 7.53 (br s, 4H), 7.67 (d, *J*= 16.3, 1H). ^{13}C-NMR δ ppm: 14.00, 19.42, 30.98, 64.66, 66.23, 118.10, 127.01, 127.14, 128.43, 128.72, 128.97, 129.59, 133.97, 135.79, 137.20, 139.29, 144.19, 167.38. $C_{22}H_{23}ClO_2$ (354,14): calcd. C, 74.46; H, 6.53; Cl, 9.99; O, 9.02; found C, 74.63; H, 6.45; Cl, 9.90; O, 8.96.



10

(E)-ethyl 3-(4-((E)-3-butoxy-3-oxoprop-1-en-1-yl)phenyl)-3-phenylacrylate (**11**). ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm: 0.93 (t, *J*= 7.3, 3H), 1.09 (t, *J*= 7.1, 3H), 1.34-1.46 (m, 2H), 1.61-1.71 (m, 2H), 4.02 (q, *J*= 7.1 Hz, 2H), 4.18 (t, *J*= 6.8, 2H), 6.37 (s, 1H), 6.42 (d, *J*= 15.9, 1H), 7.15-7.18 (m, 2H), 7.29 (d, *J*= 8.4, 2H), 7.34-7.39 (m, 3H), 7.45 (d, *J*= 8.4, 2H), 7.62 (d, *J*= 15.9, 1H). ^{13}C-NMR δ



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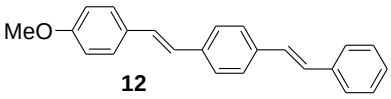
[5] C. M. Chung, M. Hasegawa, *J. Am Chem. Soc.* 1991, **113**, 7311

ppm: 13.80,13.89, 19.18, 30.74, 60.16, 64.54, 118.20, 119.09, 127.94, 127.97, 128.03, 128.21, 128.27, 128.95, 128.66, 129.12, 135.39, 138.49, 142.37, 143.44, 143.49, 155.34, 165.90, 166.88. EI m/z: 378 (M^+, 93), 333 (50), 305 (20), 277 (44), 259 (54), 250 (62), 231 (35), 202 (100), 178 (18), 138 (10), 105 (20), 77 (12). $C_{24}H_{26}O_4$ (378,18) calcd. C, 76.17; H, 6.92; O, 16.91; found C, 76.32; H, 6.96; O, 16.72.

1-methoxy-4-((E)-4-((E)-styryl)styryl)benzene (**12**). Lit.[6] ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm: 3.84 (s, 3H), 6.91 (d, J = 8.8 Hz, 2H), 7.08-7.17 (m, 3H), 7.26 (s, 5H), 7.37 (t, J= 7.3 Hz, 1H), 7.45-.754 (m, 6H). ^{13}C NMR δ ppm: 55.34, 114.22, 125.68, 126.50, 126.58, 126.84, 127.58, 127.75, 128.01, 128.22, 128.41, 128.69, 129.81, 135.31, 136.44, 137.33, 159.42. EI m/z: 312 (M^+, 3), 251 (7), 234 (7), 206 (100), 178 (8), 165 (2), 152 (6), 128 (10), 115 (5), 102 (7), 79 (5), 57 (9).



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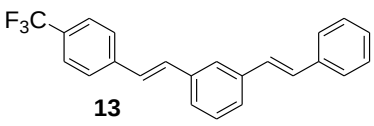
1-((E)-styryl)-3-((E)-4-(trifluoromethyl)styryl)benzene (**13**). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm: 7.10-7.15 (m, 3H), 7.17 (d, *J*= 8.6 Hz, 1H), 7.31-7.38 (m, 4H), 7.39-7.47 (m, 2H), 7.51 (m, 3H), 7.58-7.62 (m, 3H), 7.64 (bs, 1H). ^{13}C-NMR δ ppm: 125.16, 125.19, 125.83, 125.90, 126.78, 128.49, 128.71, 128.95, 129.23,129.25, 129.31, 137.23, 137.36, 137.47, 137.93, 138.07, 140.95. EI m/z: 350 (M^+, 100), 265 (9), 203 (21), 178 (25), 165 (14). $C_{23}H_{17}F_3$ (350,13): calcd. C, 78.84; H, 4.89; F, 16.27; found C, 78.96; H, 4.95; F, 16.09.



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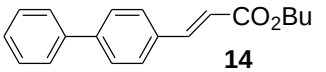
(E)-butyl 3-(biphenyl-4-yl)acrylate (**14**). Lit.[2] ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm: 0.98 (t, *J* = 7.5 Hz, 3H), 1.41-1.51 (m, 2H), 1.64-1.75 (m, 2H), 4.23 (t, *J* = 6.8 Hz, 2H), 6.48 (d, *J* = 15.9 Hz, 1H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.2 Hz, 2H), 7.57-7.66 (m, 6H), 7.72 (d, *J* = 15.9 Hz, 1H). ^{13}C NMR: δ 13.71, 19.21, 30.81, 64.43, 118.19, 127.01, 127.50, 127.80, 128.51, 128.87, 133.47, 140, 18, 142.97, 144.03, 167.08. EI m/z: 280 (M^+, 53), 224 (100), 207 (55), 178 (65), 165 (22), 152 (19), 103 (5), 89 (12).



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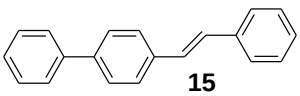
(E)-4-styryl-biphenyl (**15**). Lit.[7] ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm: 7.16 (m, 2H), 7.27 (t, *J*= 7.3 Hz, 1H), 7.33-7.40 (m, 3H), 7.45 (t, *J*= 7.3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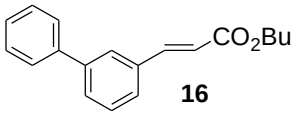
[6] D. P. Flaherty, Y. Dong, J. L. Vennerstrom *Tetrahedron Lett.*, 2009, **50**, 6228.
[7] M. Gruber, S. Chouzier, K. Koehler, L. Djakovitch *Appl. Catal., A: General* 2004, **265**, 161.

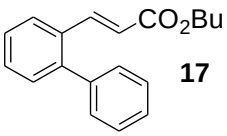
Hz, 2H), 7.50–7.56 (m, 3H), 7.59-7.65 (m, 5H). ^{13}C NMR: δ 126.53, 126.92, 127.35, 127.65, 128.23, 128.31, 128.70, 128.79, 136.42, 137.37, 140.37, 140.69. EI m/z: 256 (M^+, 100), 178 (21), 165 (12), 152 (8), 101 (3).

(E)-butyl 3-(biphenyl-3-yl)acrylate (**16**). Lit.[2] ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.96 (t, *J* = 7.3 Hz, 3H), 1.38-1.47 (m, 2H), 1.62-1.73 (m, 2H), 4.20 (t, *J* = 6.6 Hz, 2H), 6.48 (d, *J* = 16.1, 1H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.43 (t, *J*= 7.3, 3H), 7.49 (d, *J* = 7.5 Hz, 1H), 7.55-7.62 (m, 3H), 7.72 (d, *J* = 16.1 Hz, 1H), 7.71 (s, 1H). ^{13}C-NMR δ ppm: 13.72, 19.21, 30.79, 64.47, 118.69, 126.79, 126.85, 127.14, 127.66, 128.86, 128.98, 129.30, 135.99, 140.45, 141.97, 144.44, 167.02. EI m/z: 280 (M^+, 38), 224 (100), 207 (53), 178 (68), 165 (26), 152 (24), 103 (6), 89 (14).



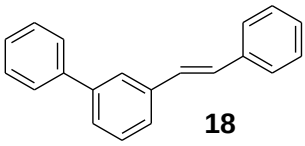
16

(E)-butyl 3-(biphenyl-2-yl)acrylate (**17**). Lit.[8] ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm: 0.93 (t, *J* = 7.3 Hz, 3H), 1.35-1.45 (m, 2H), 1.58-1.67 (m, 2H), 4.14 (t, *J* = 6.6 Hz, 2H), 6.39 (d, *J* = 15.9 Hz, 1H), 7.29-7.33 (m, 2H), 7.35-7.46 (m,, 7H), 7.72 (d, *J* = 15.9 Hz, 1H). ^{13}C NMR: δ 13.70, 19.18, 30.74, 64.26, 119.23, 126.73, 127.53, 127.62, 128.26, 129.77, 129.81, 130.50, 132.69, 142.98, 139.95, 143.63, 166.90. EI m/z: 280 (M^+, 5), 179 (10), 165 (13), 152 (8), 103 (2), 89 (6).

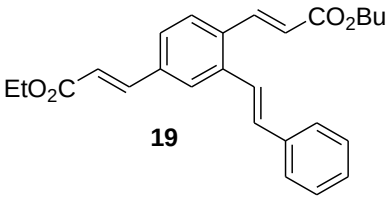


17

(E)-3-styryl-biphenyl (**18**). Lit.[9] ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm: 7.19 (s, 2H), 7.28 (t, *J*= 7.3 Hz, 1H), 7.35-7.55 (m, 10H), 7.64 (dm, *J*= 7.1 Hz, 2H), 7.73 (t, *J*= 1..8 Hz, 1H). ^{13}C NMR: δ 125.38, 125.44, 126.52, 126.56, 127.20, 127.39, 127.69, 128.65, 128.70, 128.77, 129.08, 129.12, 137.33, 137.85, 141.16, 141.77. EI m/z: 256 (M^+, 100), 178 (26), 165 (14), 152 (10), 128 (5), 101 (4).


18

(E)-butyl 3-(4-((E)-3-ethoxy-3-oxoprop-1-en-1-yl)-2-((E)-styryl)phenyl)acrylate (**19**). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm: 0.96 (t, *J*= 7.4 3H), 1.32 (t, J=7.3 3H), 1.36-1.48 (m, 2H), 1.61-1.73 (m, 2H), 4.20 (t, *J*= 6.6 2H), 4.25 (q, *J*= 7.3 2H), 6.39 (d, *J*=15.7, 1H), 6.50 (d, *J*=16.1, 1H), 7.00 (d, *J*=16.1, 1H), 7.26-764 (m, 10H), 8.05 (d, *J*=16.1, 1H). ^{13}C-NMR δ ppm: 13.94, 14.52, 19.43, 30.94, 60.86, 64.80, 119.66, 121.38, 125.00, 126.95, 127.03, 127.06, 127.95, 128.53, 128.99, 133.61, 134.57, 136.16, 136.95, 138.30,

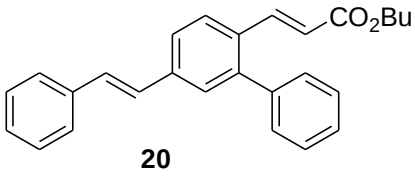


19

[8] M. Feuerstein, H. Doucet, M. Santelli, *Synlett* 2001, **12**, 1980.
[9] S. Mochida, K. Hirano, T. Satoh, M. Miura, *J. Org. Chem.* 2011, **76**, 3024.

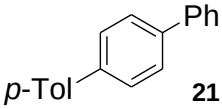
141.45, 143.71, 166.92, 166.94. EI m/z: 404 (M^+, 18), 359 (5), 331 (7), 303 (21), 284 (4), 257 (39), 229 (96), 202 (39), 181 (9), 152 (25), 115 (9), 91 (100), 58 (32). $C_{26}H_{28}O_4$ (404,2): calcd. C, 77.20; H, 6.98; O, 15.82; found C, 77.42; H, 6.85; O, 15.77.

(E)-butyl 3-((2-phenyl-4-(E)-styryl)phenyl)acrylate (**20**). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm: 0.91 (t, *J*= 7.3 Hz, 3H), 1.29-1.41 (m, 2H), 1.53-1.63 (m, 2H), 4.12 (t, *J*= 6.6, 2H), 6.38 (d, *J*= 15.9, 1H), 7.14 (d, *J*= 14.4, 2H), 7.29-7.57 (m, 12H), 7.66-7.71 (m, 2H). ^{13}C-NMR δ ppm: 13.96, 19.37, 30.91, 64.46, 118.97, 128.50, 128.53, 128.57, 128.82, 128.91, 126.91, 127.25, 127.92, 128.99, 129.94, 130.01, 131.94, 137.14, 139.04, 140.02, 143.23, 143.68, 167.21. EI m/z: 382 (M^+, 38), 280 (56), 265 (21), 203 (100), 132 (17), 103 (14). $C_{27}H_{26}O_2$ (382,19): calcd. C, 84.78; H, 6.85; O, 8.37; found C, 84.91; H, 6.81; O, 8.28.



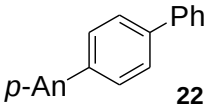
20

4(4-Tolyl)biphenyl (**21**). Lit.[10] ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm: 2.42 (s, 3H), 7.27 (d, *J*= 7.7 Hz, 2H), 7.36 (t, *J*=7.3 Hz, 1H), 7.46 (t, *J*= 7.3 Hz, 2H), 7.55 (2H, d, *J*= 7.5 Hz, 2H), 7.64 (d, *J*= 7.3 Hz, 2H), 7.66 (4H, m). ^{13}C-NMR δ ppm: 21.09, 126.87, 127.02, 127.28, 127.45, 128.78, 129.52, 137.12, 137.86, 139.87, 140.10, 140.82. EI m/z: 244 (M^+, 100), 228 (10), 165 (21), 152 (12), 122 (8), 91 (10).



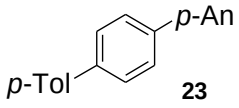
21

4(4-Anisyl)biphenyl (**22**). Lit.[11] ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm: 3.86 (s, 3H), 7.00 (d, *J*=8.8 Hz, 2H), 7.35 (tt, *J*= 7.3 and 1.3 Hz, 1H), 7.46 (t, *J*= 7.3 Hz, 2H) 7.55-7.68 (s, 8H). ^{13}C-NMR δ ppm: 55.36, 114.29, 126.97, 127.01, 127.20, 127.42, 128.02, 128.76, 133.27, 139.51, 139.75, 140.79, 159.25. EI m/z: 260 (M^+, 100), 245 (47), 217 (26), 202 (11), 189 (8), 94 (5).



22

4(4-Anisyl)-1(4-tolyl)benzene (**23**). Lit.[12] ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm: 2.41 (s, 3H), 3.87 (s, 3H), 6.99 (d, *J*= 8.8 Hz, 2H), 7.27 (d, *J*= 7.9 Hz, 2H), 7.54 (d, *J*= 8.2 Hz, 2H), 7.58 (t, *J*= 8.8 Hz, 2H), 7.63 (m, 4H). ^{13}C-NMR δ ppm: 21.06, 55.37, 114.30, 126.83, 127.01, 127.26, 128.03, 129.52, 133.38, 137.04, 137.96, 139.49, 160.08. EI m/z: 274 (M^+, 100), 259 (47), 231 (23), 215 (23), 165 (9), 137 (11), 115 (15).



23

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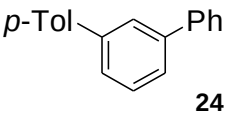
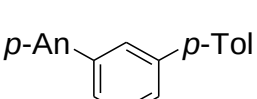
[11] C.-H. Cho, I.-S. Kim, K. Park, *Tetrahedron* 2004, **60**, 4589.
[12] B.-T. Guan, Y. Wang, B.-Y. Li, D.-G. Yu, Z.-J. Shi, *J. Am. Chem. Soc.* 2008, **130**, 14468

3(4-Tolyl)biphenyl (**24**). Lit.[10] ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm: 2.43 (s, 3H), 7.29 (d, *J*= 7.9 Hz, 2H), 7.38 (tt, *J*= 7.4 and 1.3 Hz, 1H), 7.46 (t, *J*= 7.9 Hz, 2H), 7.52 (d, *J*=7.7 Hz, 1H), 7.55–7.60 (m, 4H), 7.66 (m, 2H), 7.81 (t, *J*= 1.8 Hz, 1H). ^{13}C-NMR δ ppm: 21.09, 125.85, 125.93, 125.96, 127.08, 127.26, 127.34, 128.76, 129.11, 129.51, 137.18, 138.34, 141.31, 141.73, 141.77. EI m/z: 244 (M^+, 100), 228 (12), 165 (12), 152 (6), 122 (6), 91 (5).



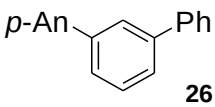
24

3(4-Anisyl)-1(4-tolyl)benzene (**25**). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm: 2.38 (s, 3H), 3.83 (s, 3H), 6.96 (d, *J*=8.79, 2H), 7.24 (d, *J*=8.79, 2H), 7.40-7.65 (m, 7H), 7.72 (td like, *J*= 1.6 0.5, 1H); ^{13}C-NMR δ ppm: 21.24, 55.53, 114.44, 125.53, 125.61, 125.72, 127.25, 128.41, 129.23, 129.64, 134.03, 137.28, 138.61, 141.52, 141.87, 159.47. EI m/z: 274 (M^+, 100), 259 (27), 231 (16), 215 (26), 202 (5), 189 (6), 165 (5), 152 (3), 137 (9), 115 (11), 101 (6), 89 (3). $C_{20}H_{18}O$ (274,14) calcd. C, 87.56; H, 6.61; O, 5.83; found. C, 87.44; H, 6.65; O, 5.94.



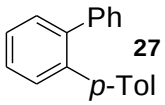
25

3(4-Anisyl)biphenyl (**26**). Lit.[13] ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm: 3.88 (s, 3H), 7.05 (d, *J*=8.8 Hz, 2H), 7.39 (tt, *J*= 7.3 and 1.3 Hz, 1H), 7.46-7.69 (m, 9H), 7.8 (t, *J*= 1.28 Hz, 1H); ^{13}C-NMR δ ppm: 55.34, 114.27, 125.53, 125.69, 125.72, 127.24, 127.33, 128.23, 128.75, 129.11, 133.72, 141.31, 141.37, 141.76, 159.30. EI m/z: 260 (M^+, 100), 245 (29), 217 (22), 202 (16), 189 (8), 130 (11), 94 (7).



26

2(4-Anisyl)biphenyl (**27**). Lit.[10] ^{1}H-NMR ($CDCl_3$, 400 MHz) δ ppm: 2.31 (s, 3H), 7.00–7.06 (m, 4H), 7.12–7.25 (m, 5H), 7.38–7.45 (4H, m). ^{13}C-NMR δ ppm: 21.06, 126.35, 127.21, 127.42, 127.83, 128.58, 129.73, 129.87, 130.59, 136.02, 138.58, 140.54, 141.73. EI m/z: 244 (M^+, 89), 229 (100), 228 (58), 215 (12), 202 (14), 165 (7), 152 (4), 113 (12).



27

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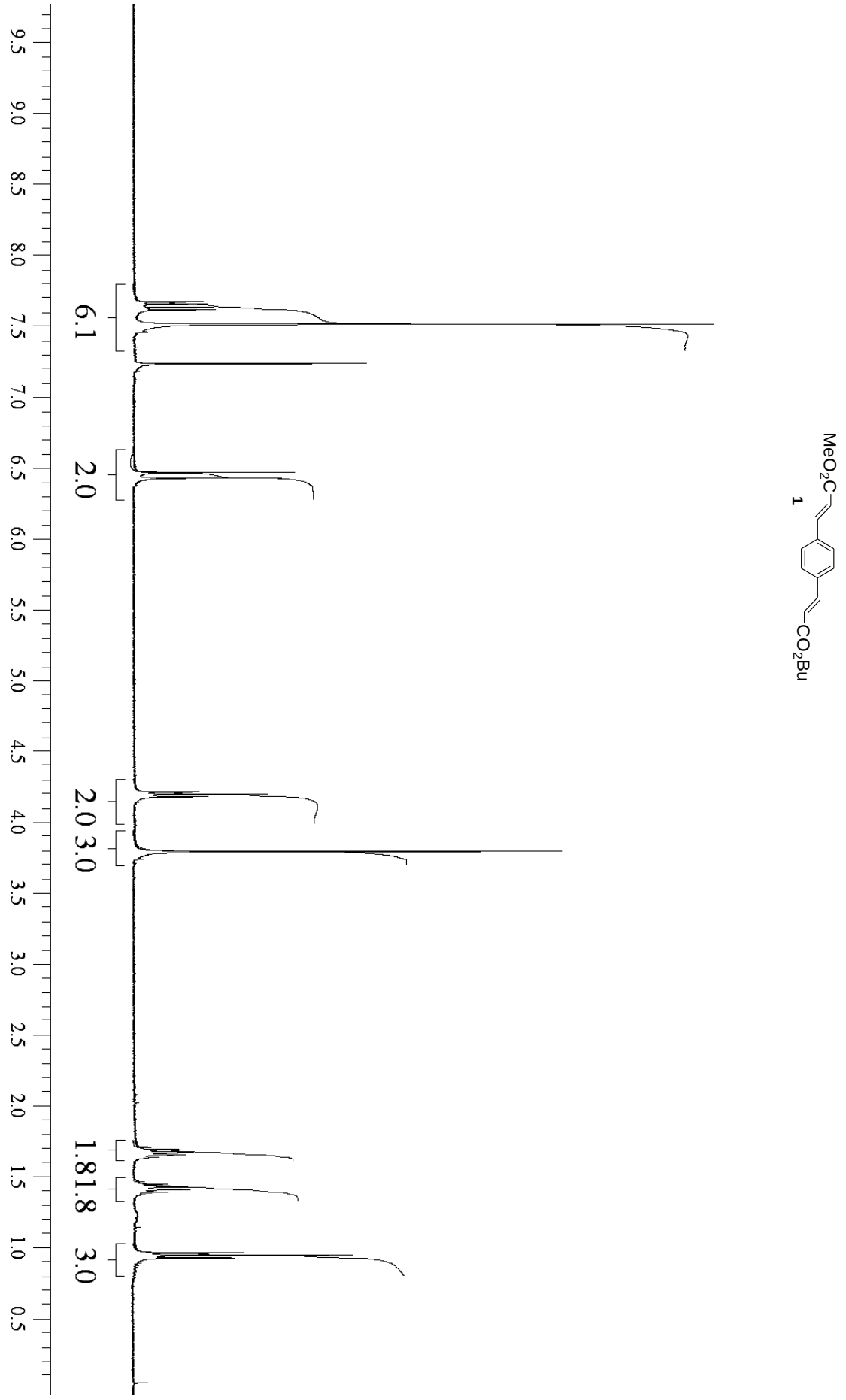

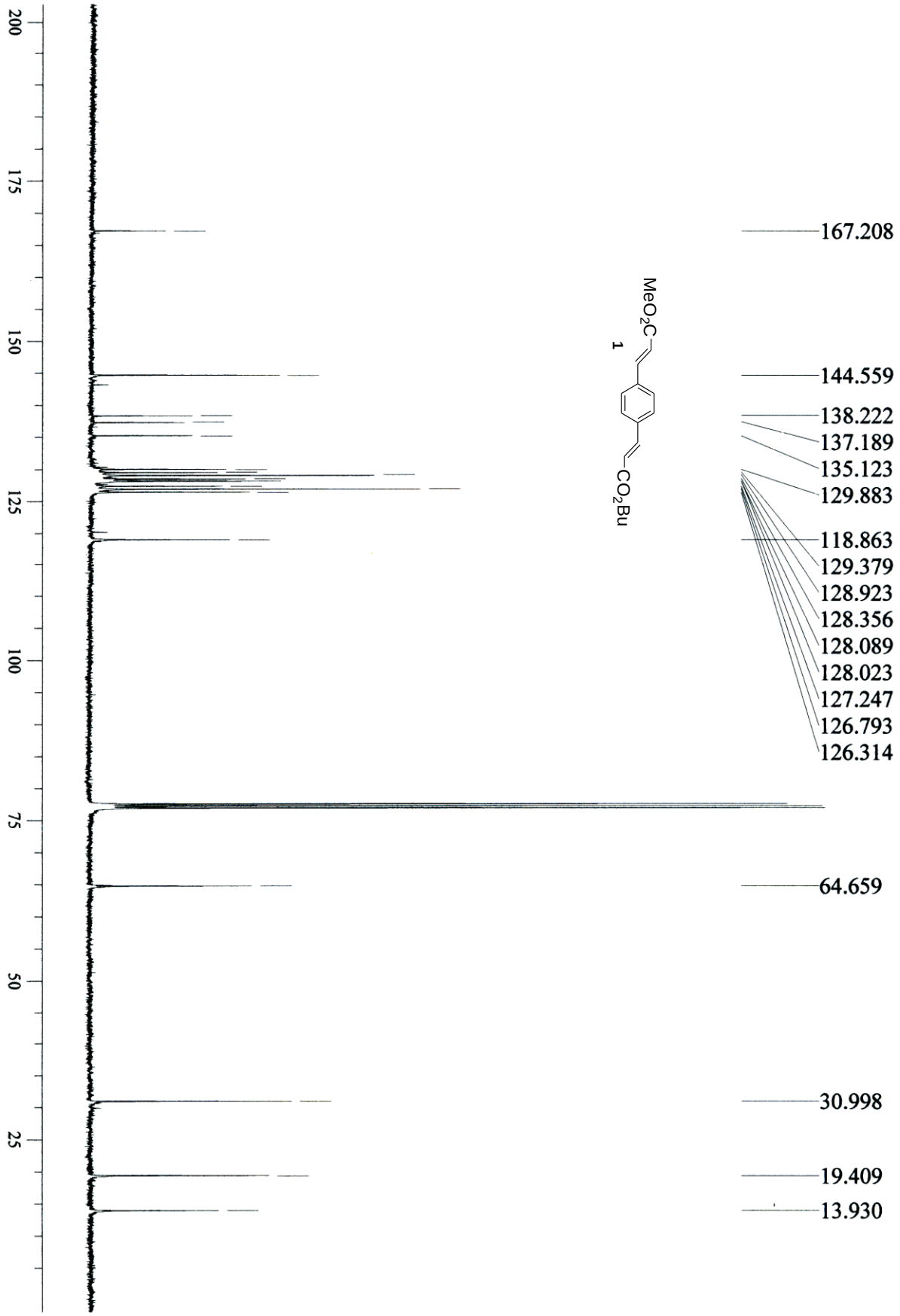

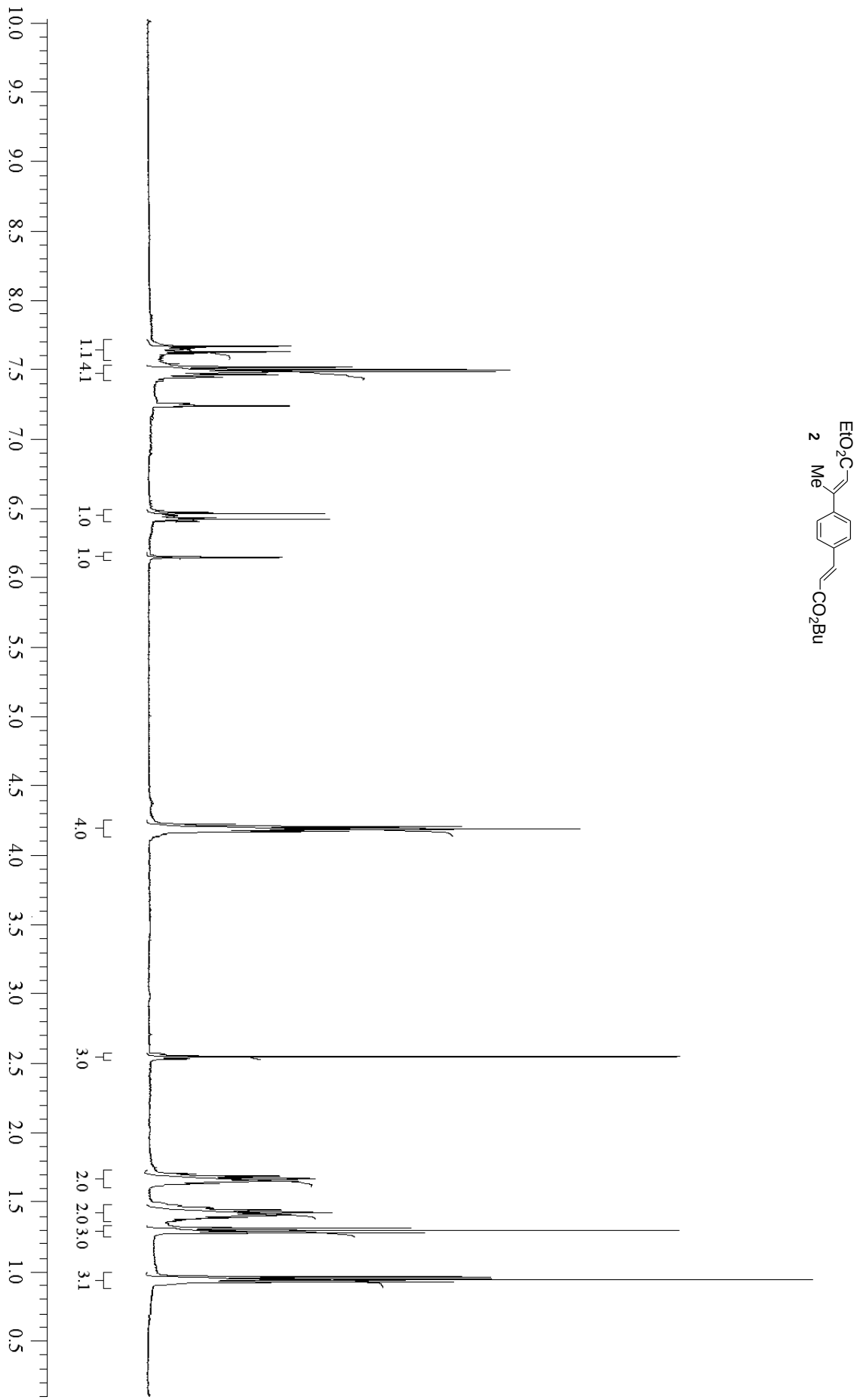

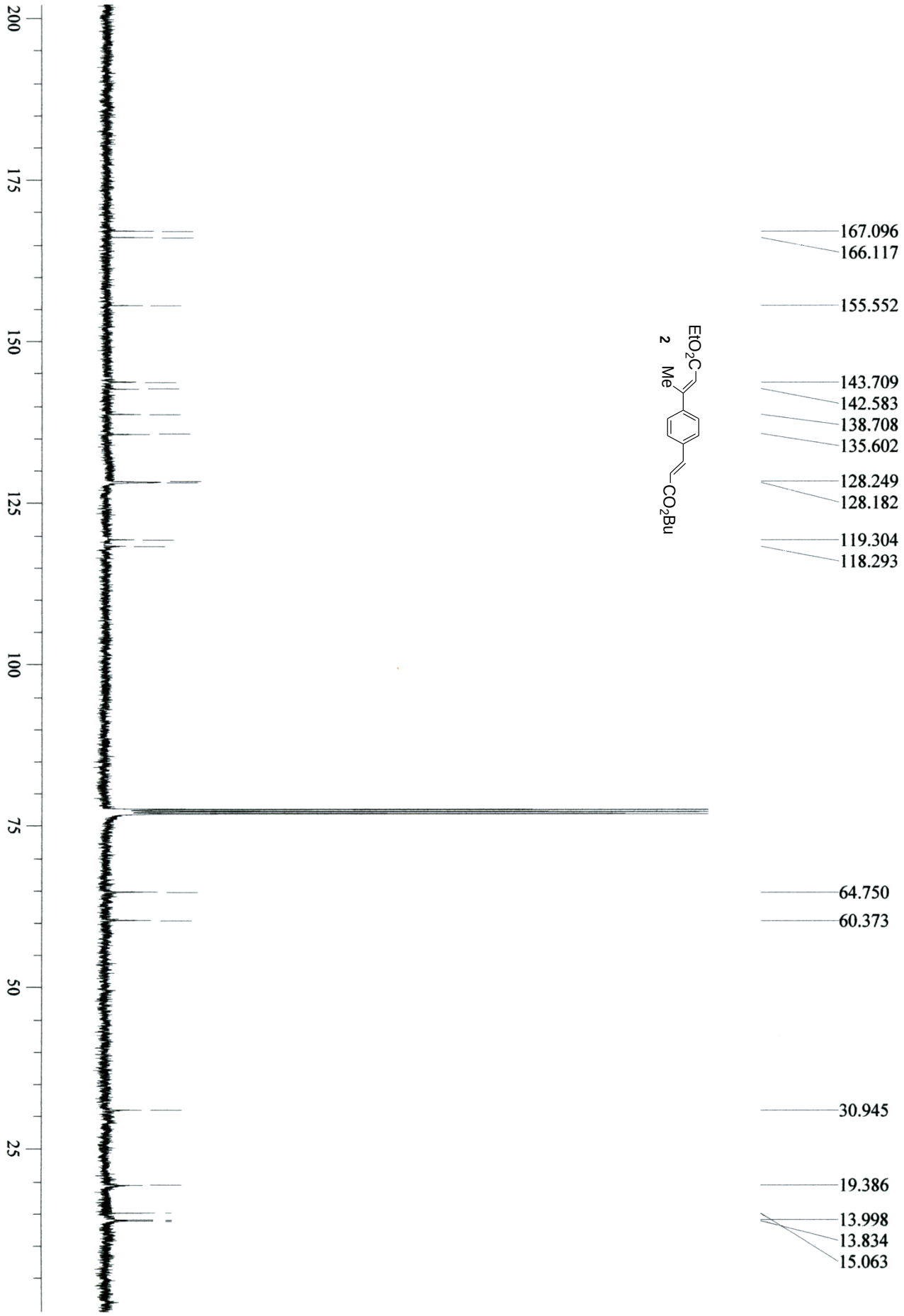

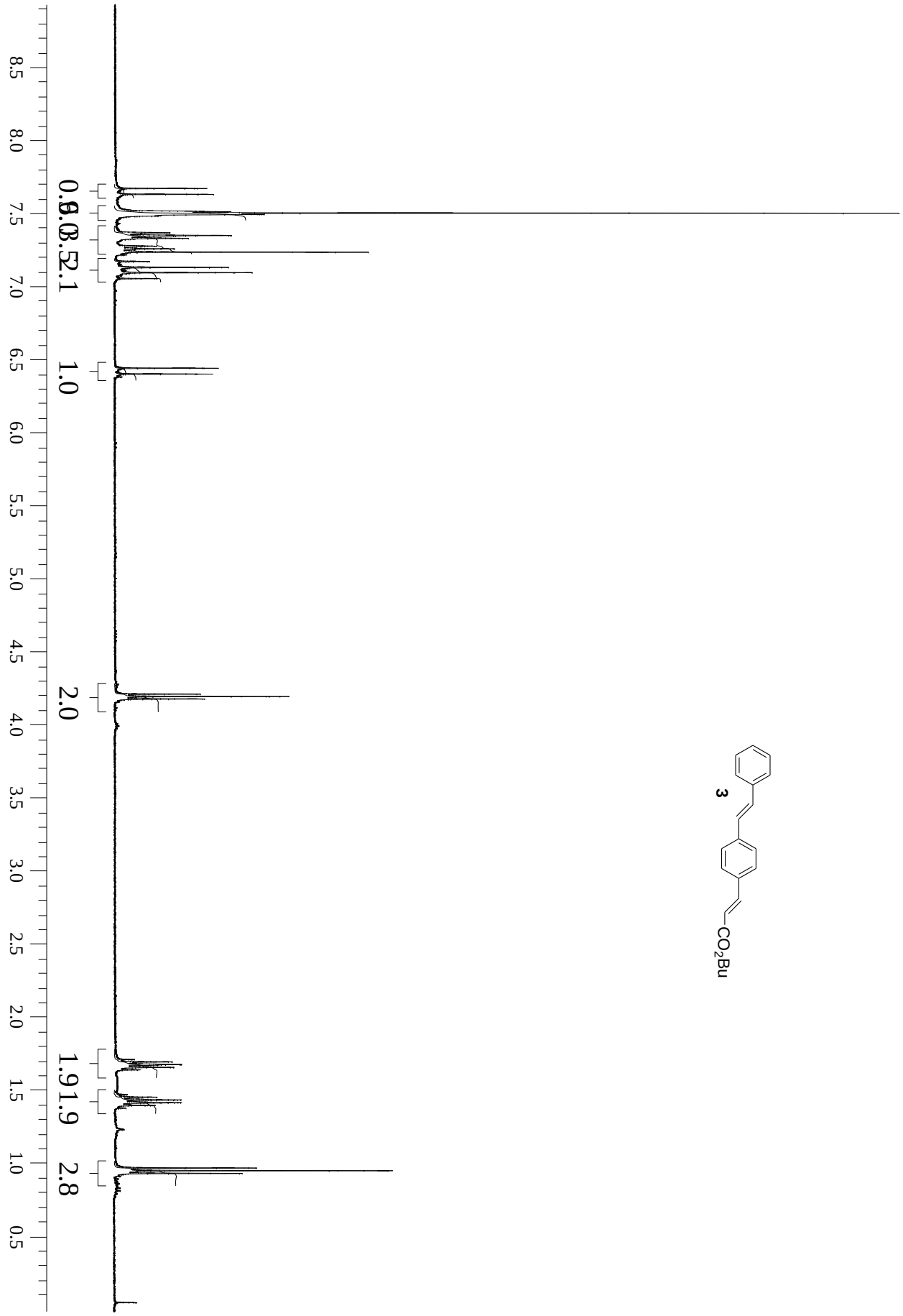

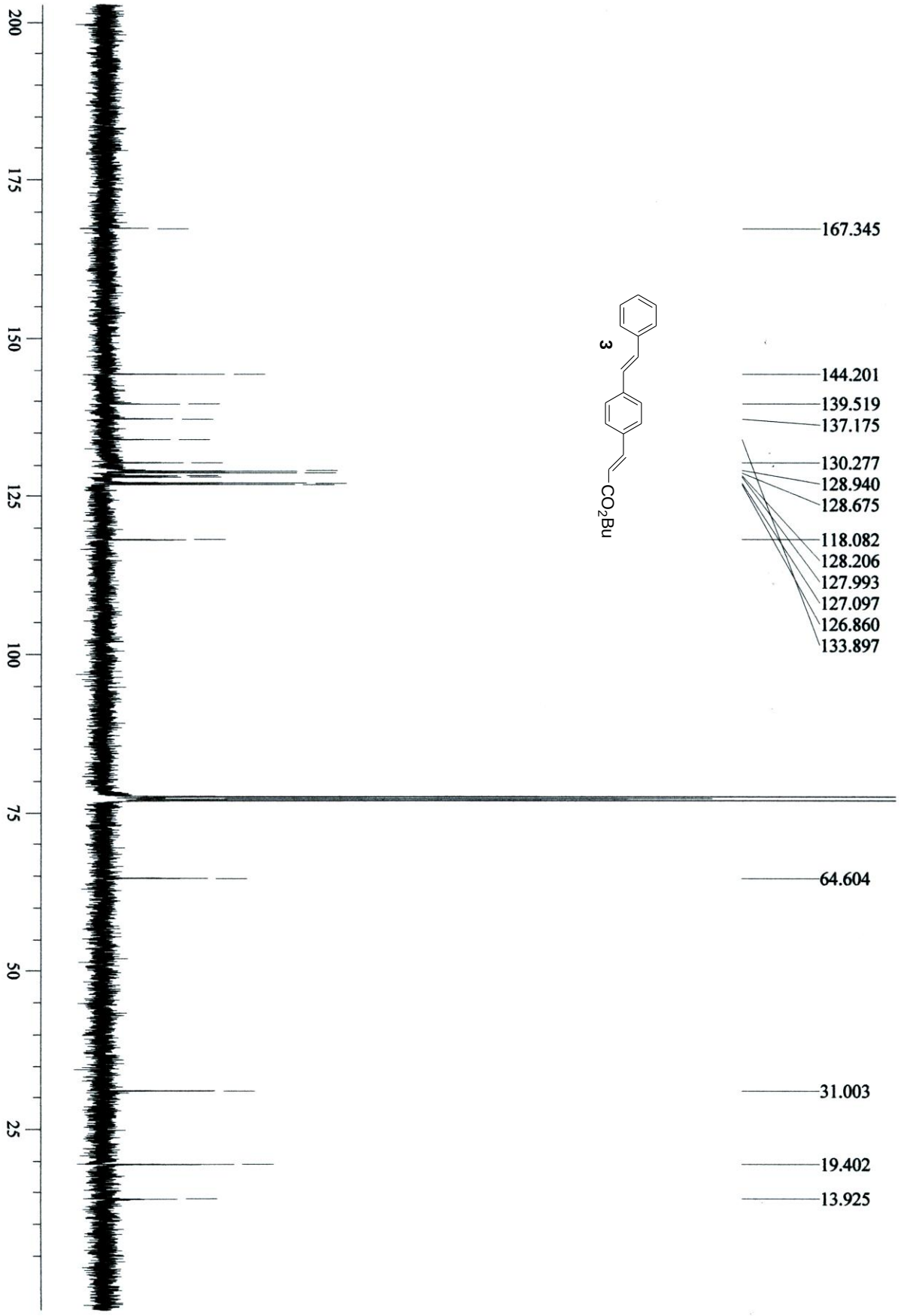

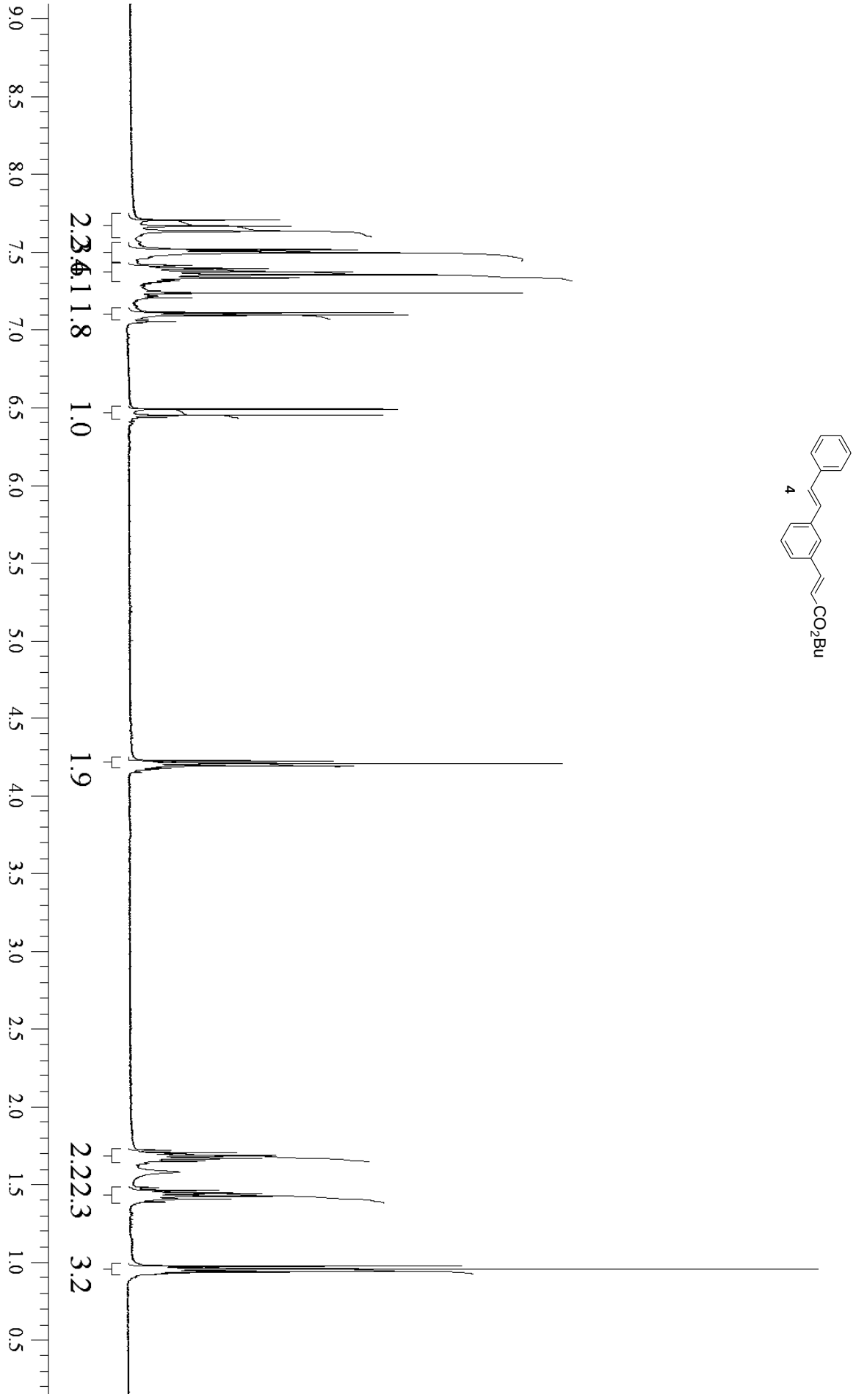
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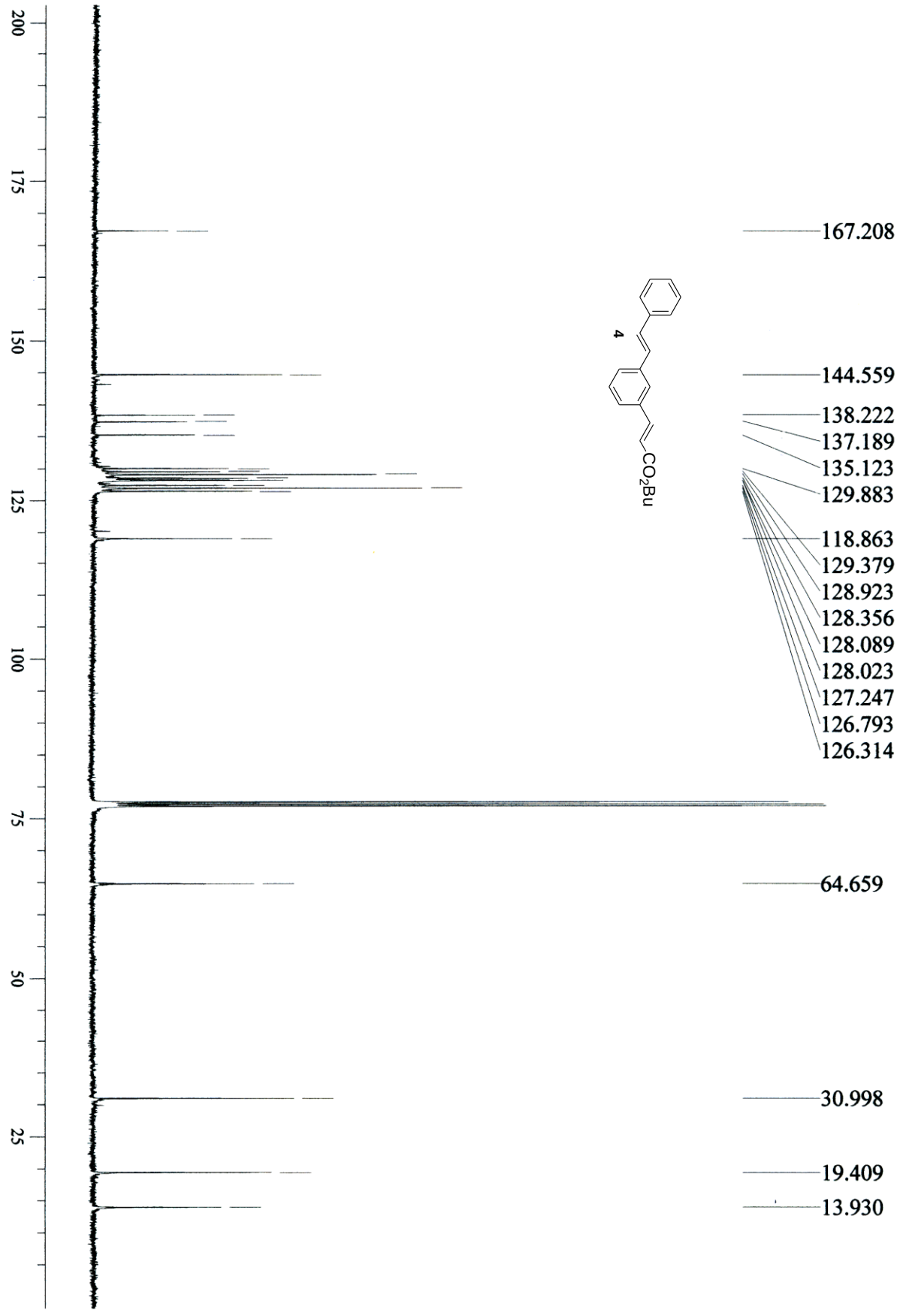

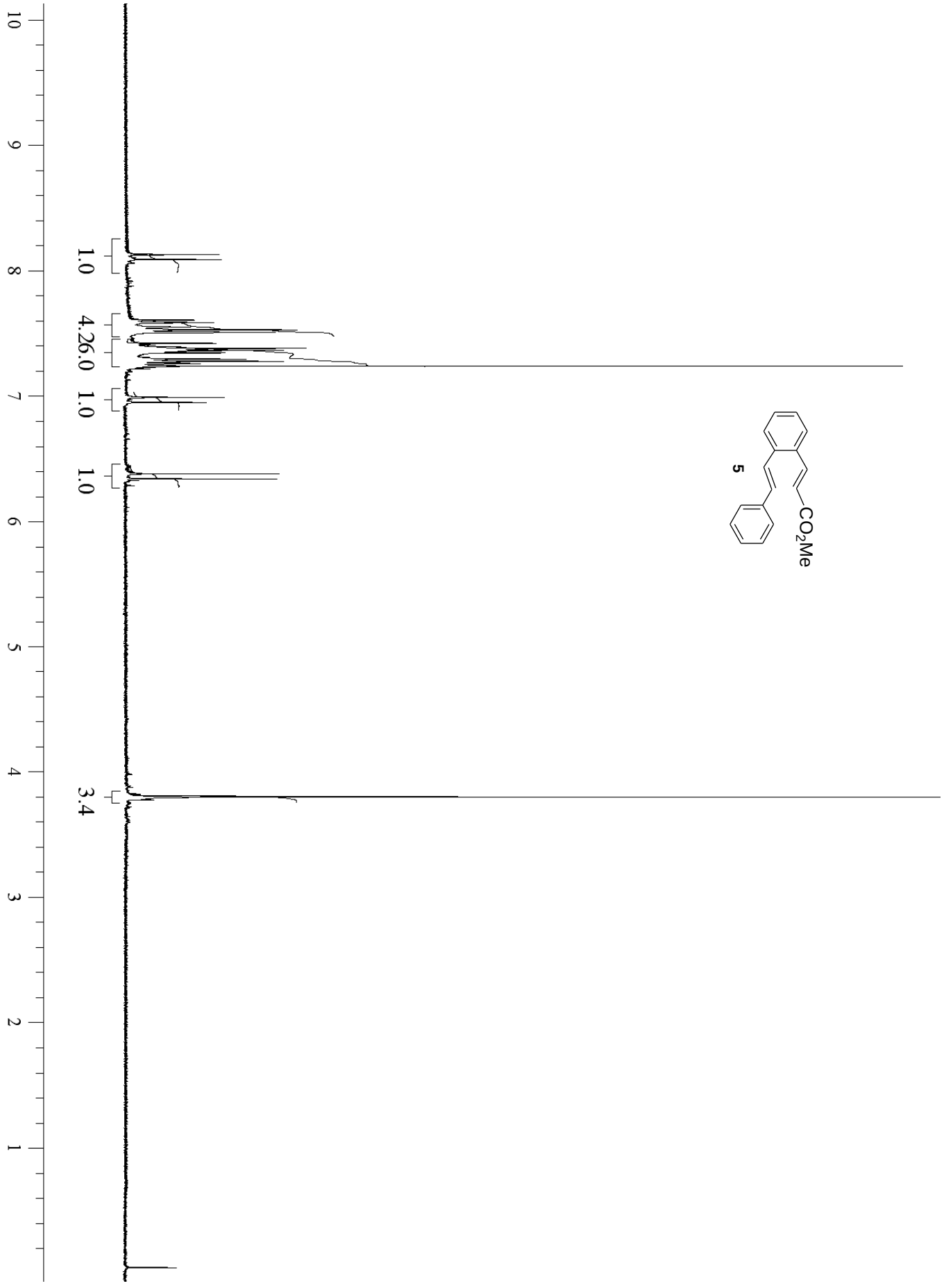

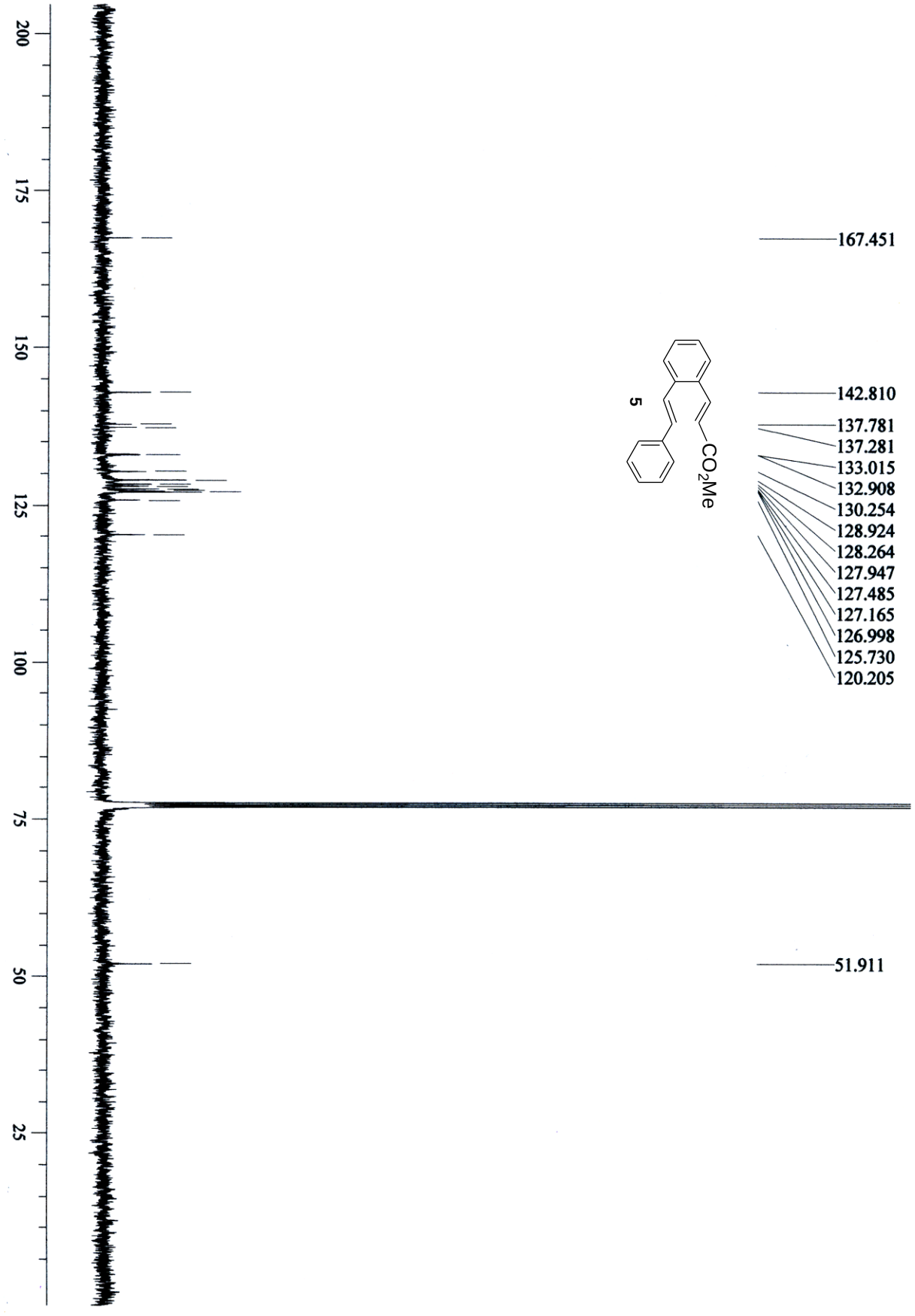

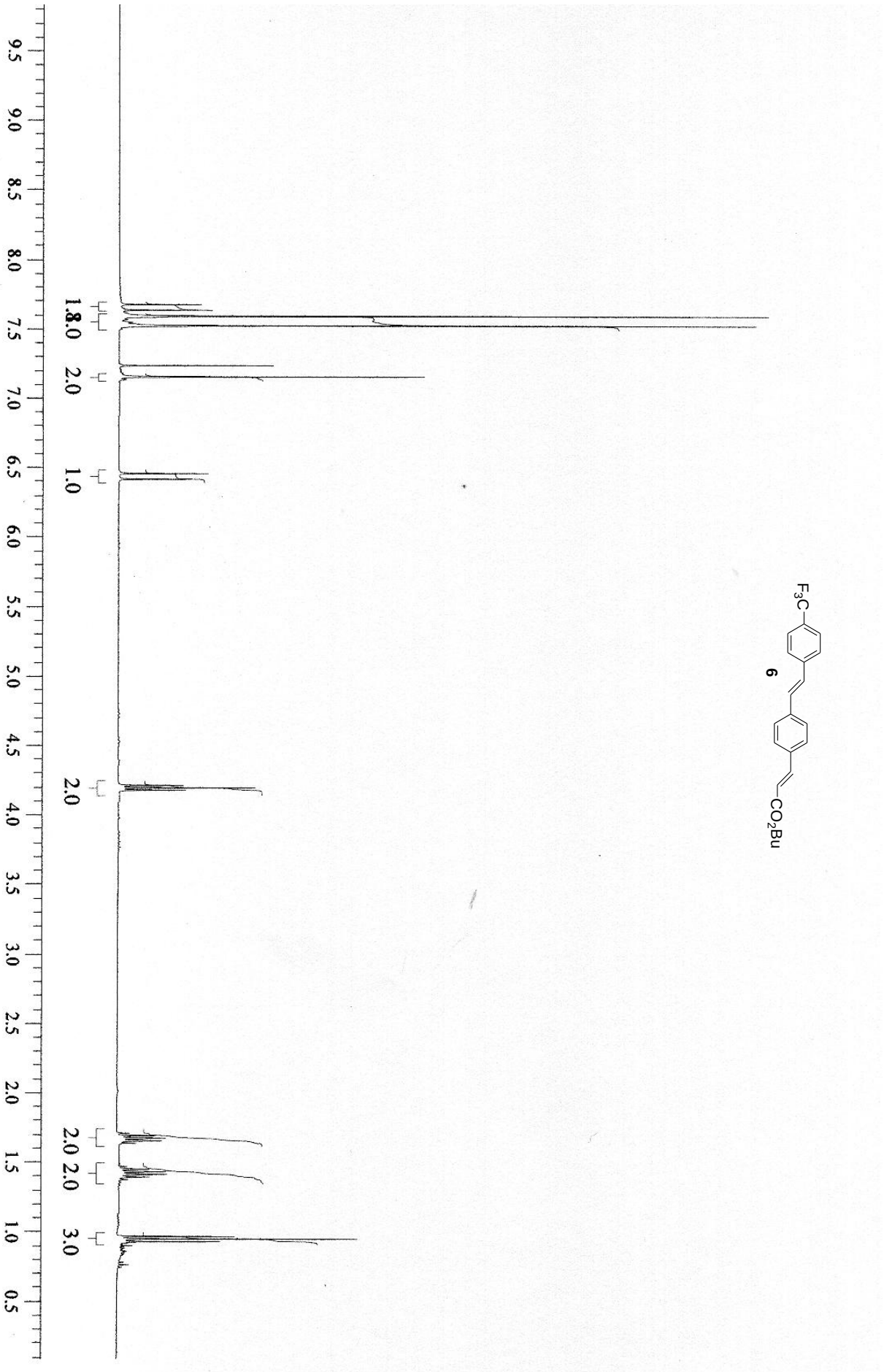

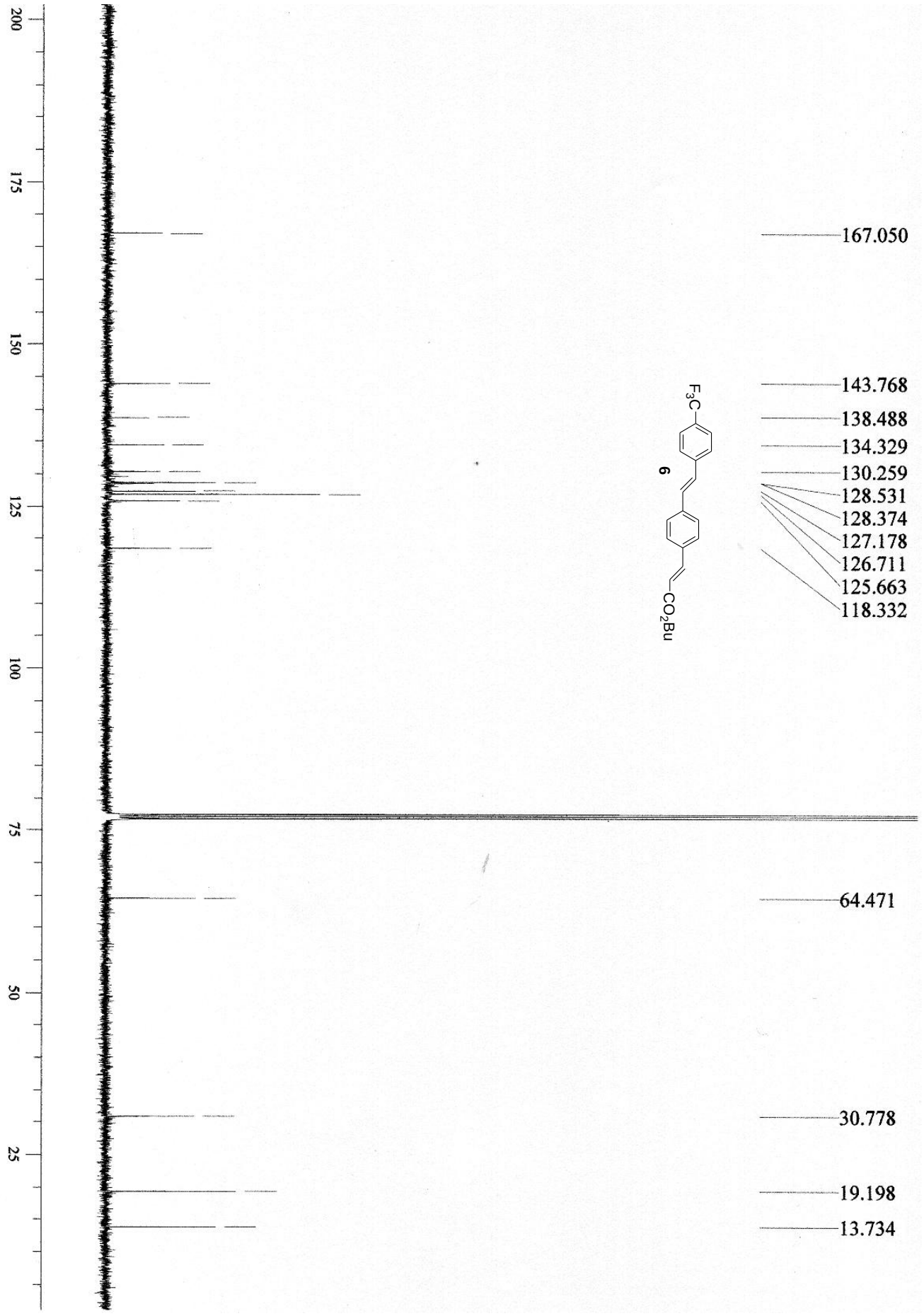
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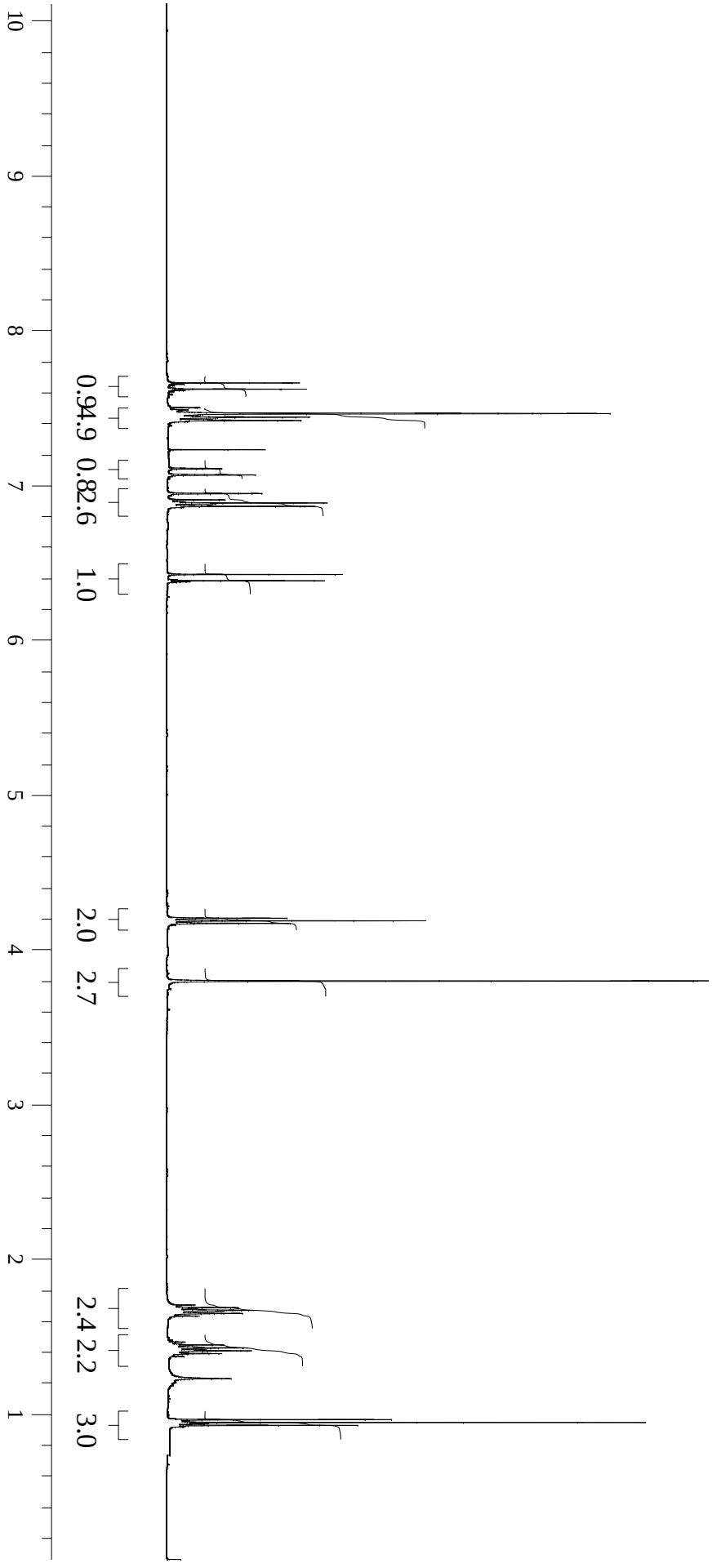

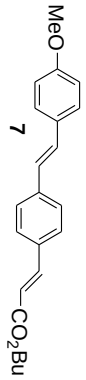

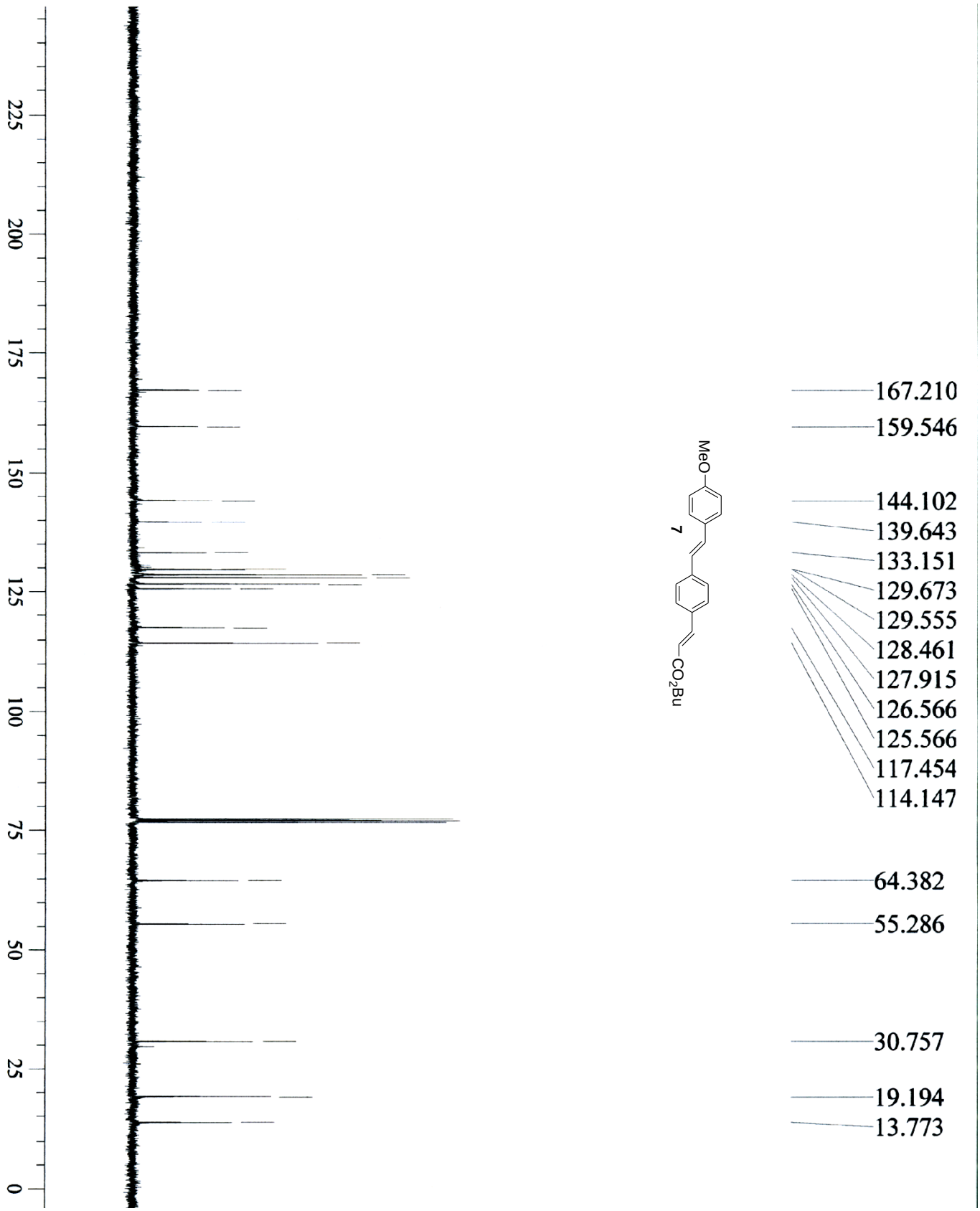

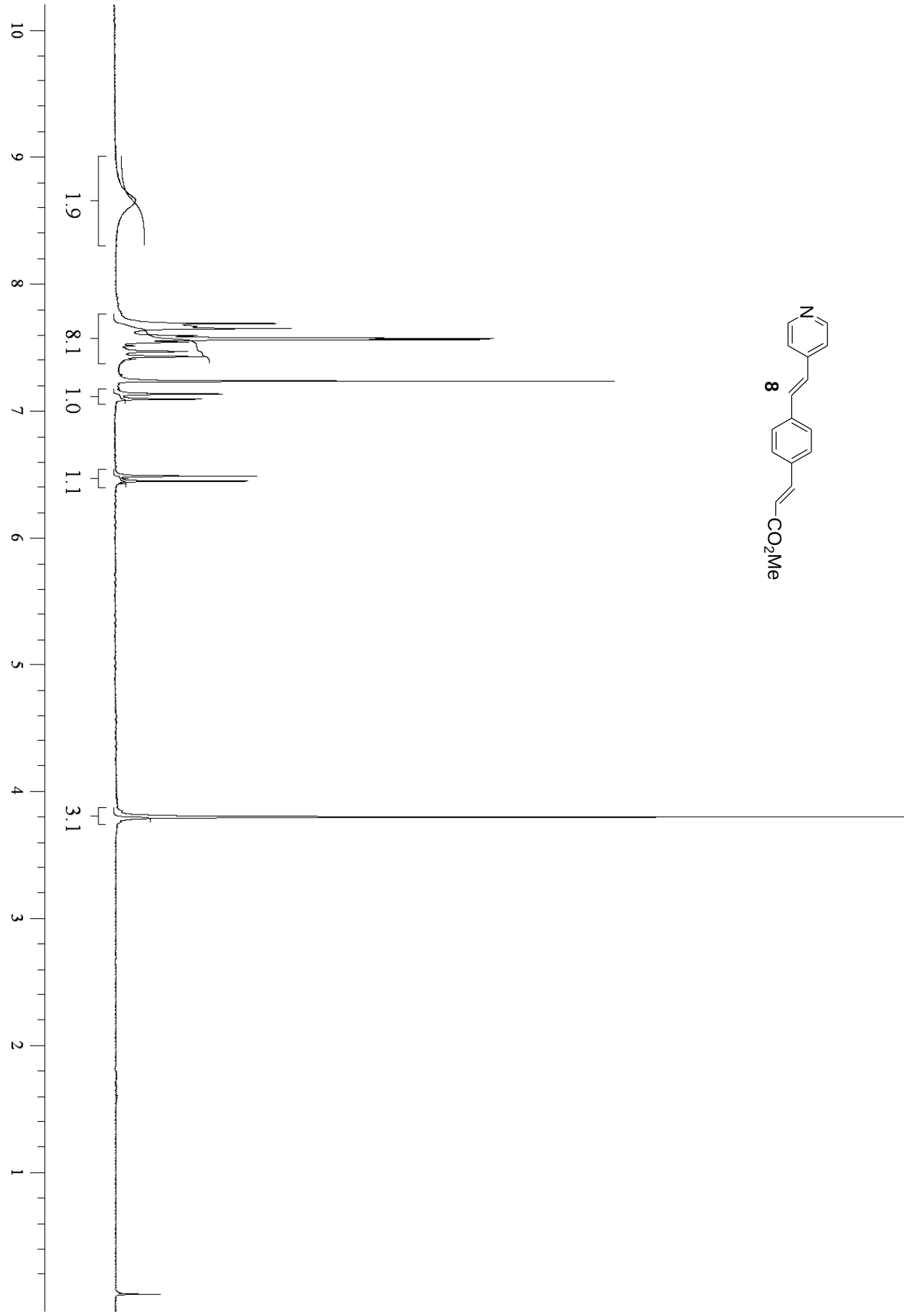

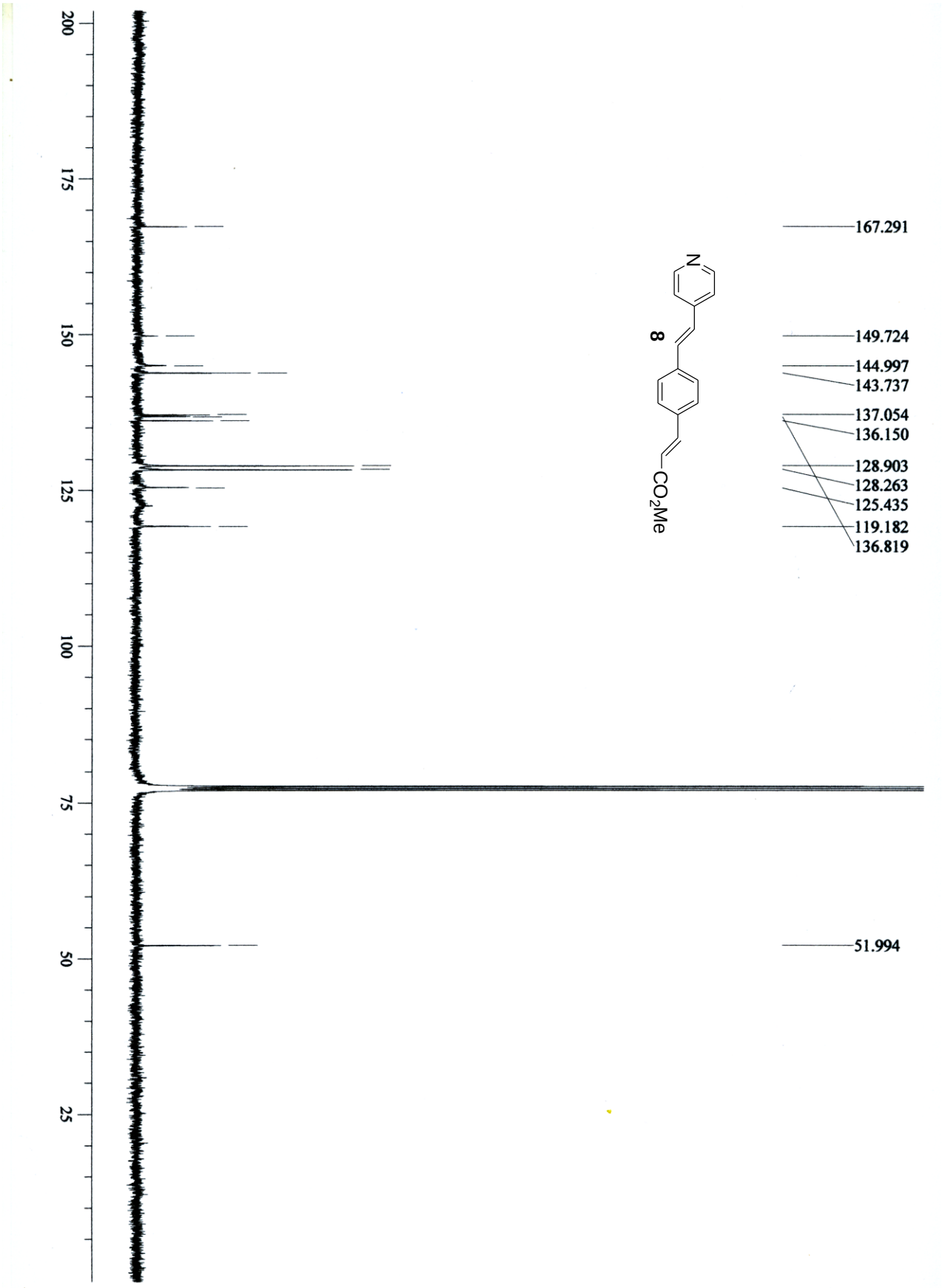

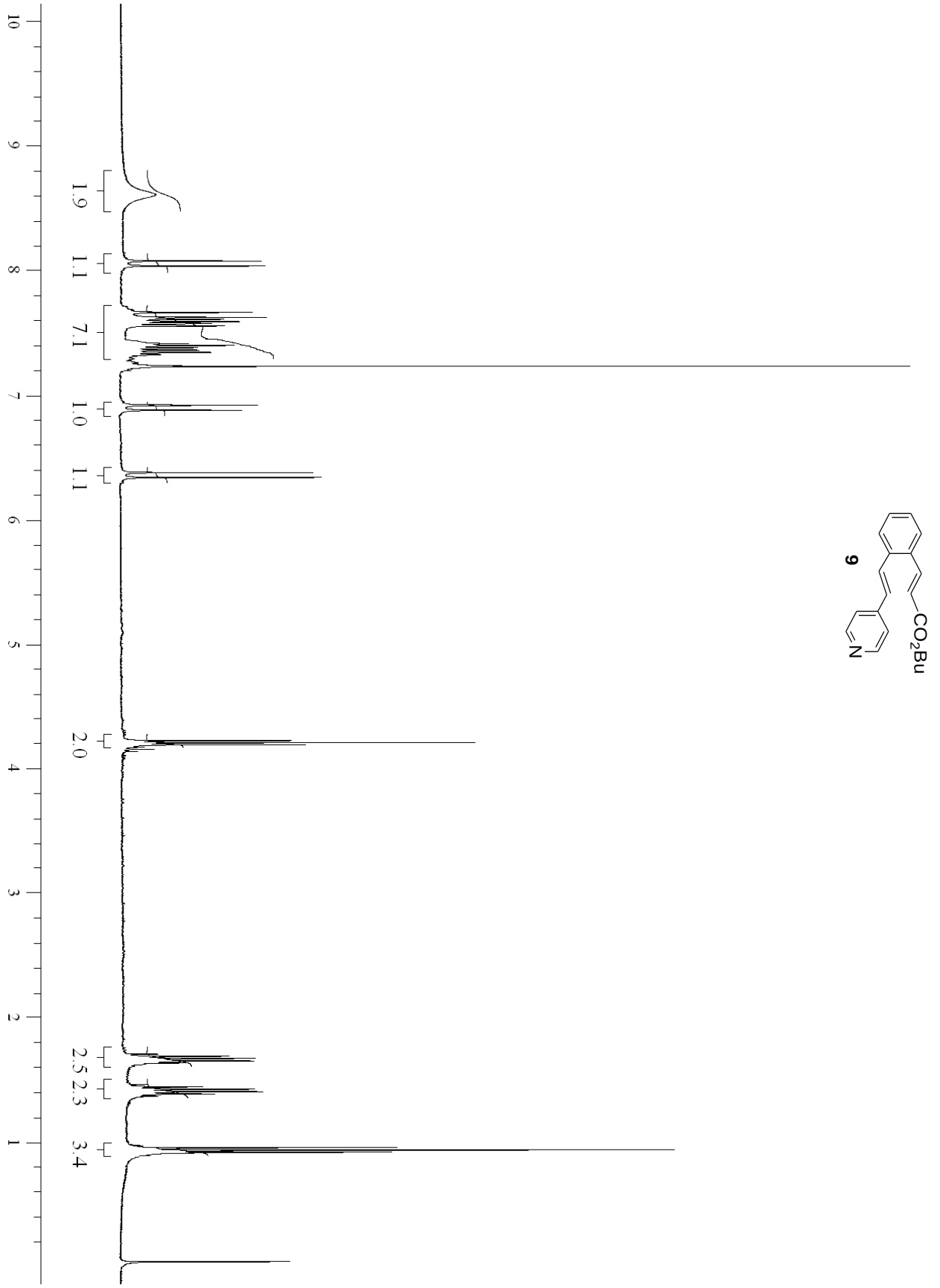

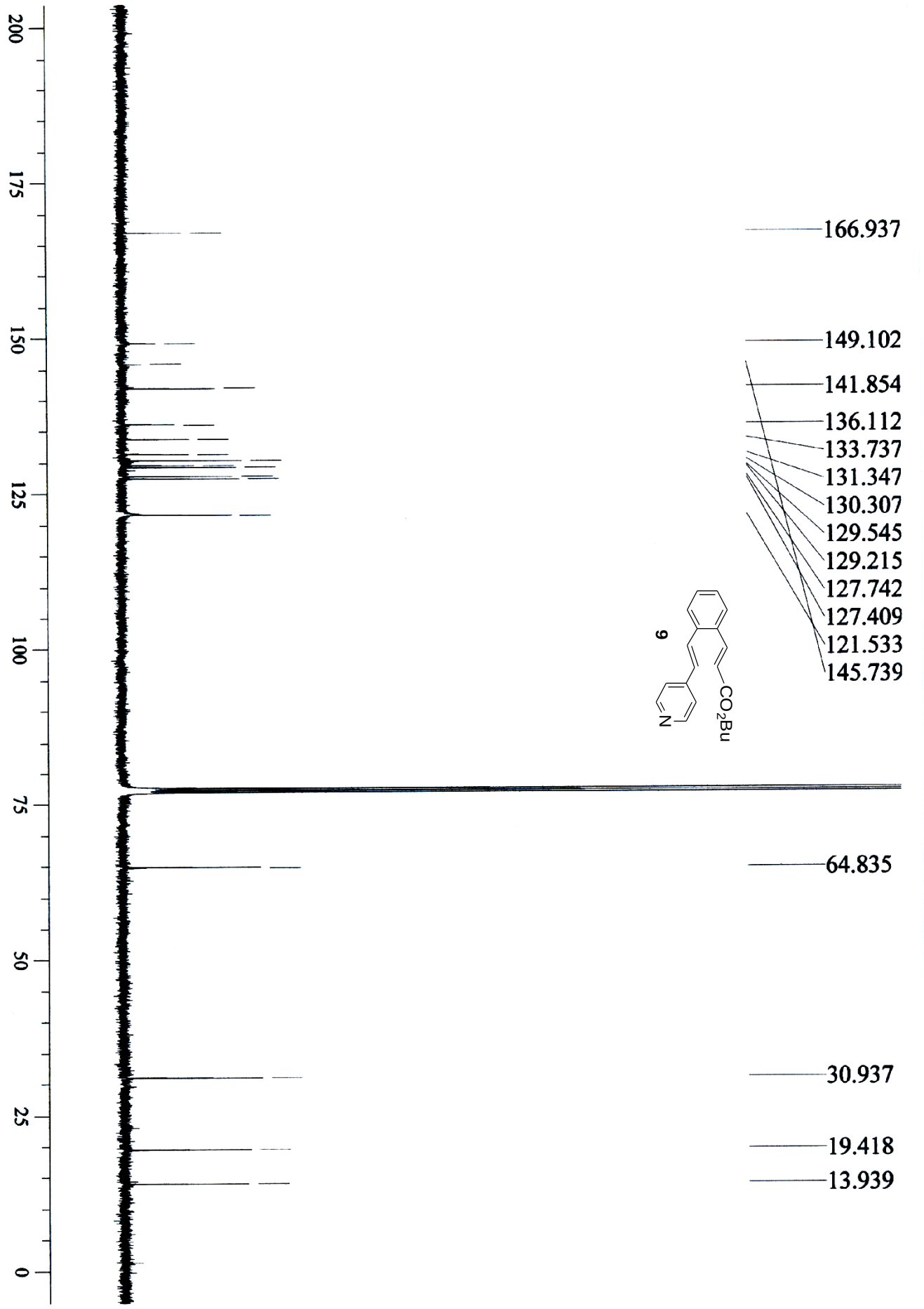

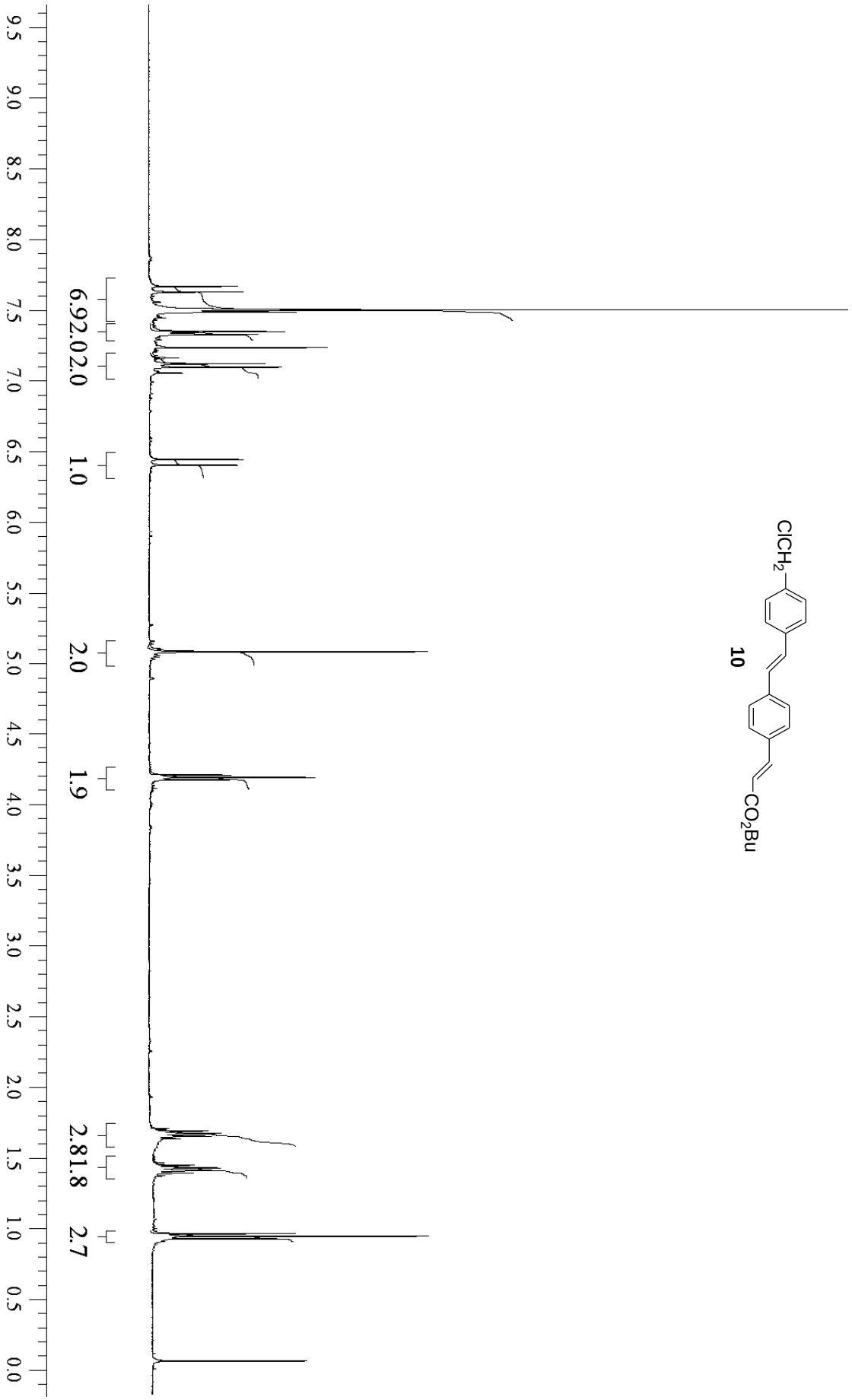

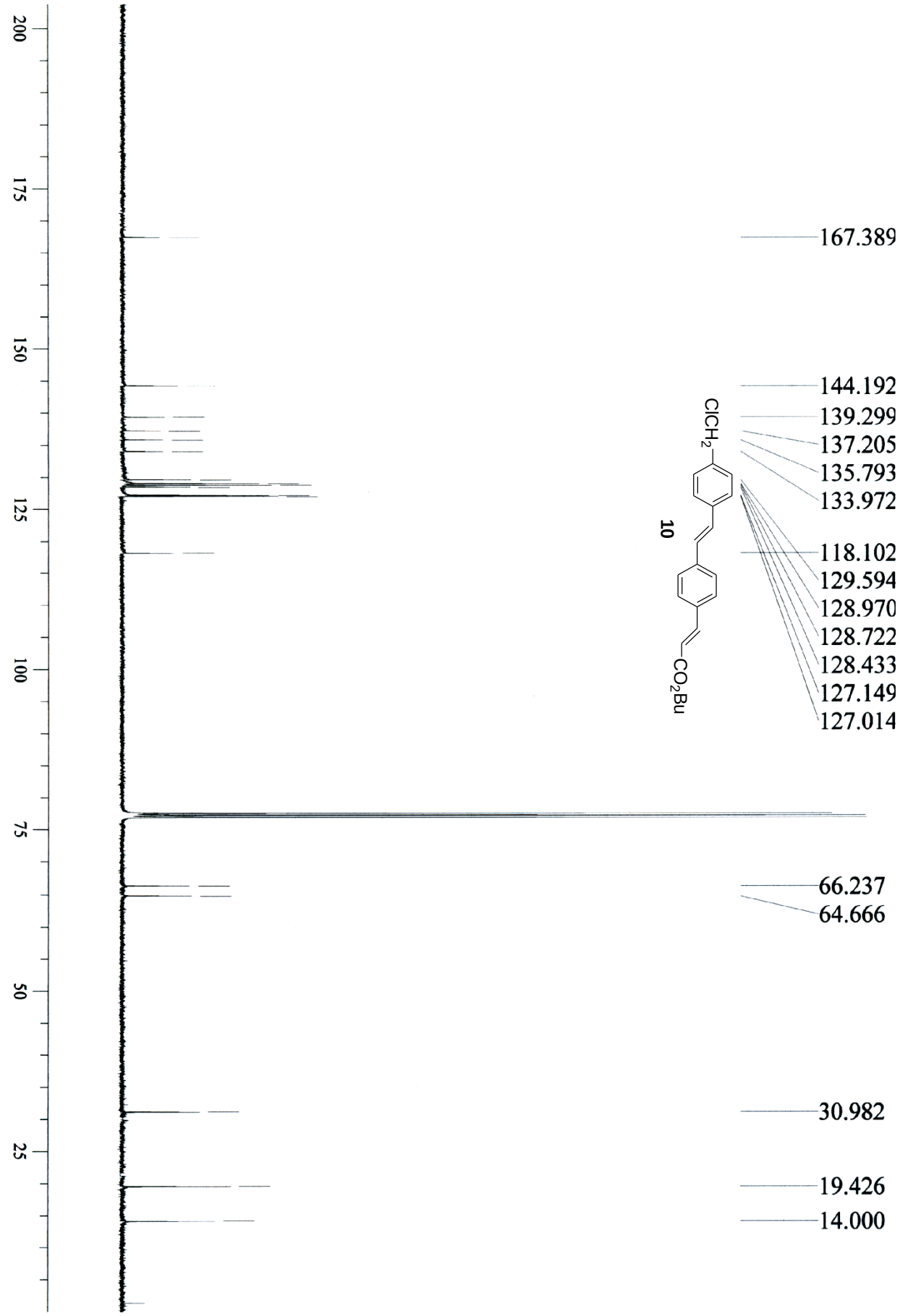

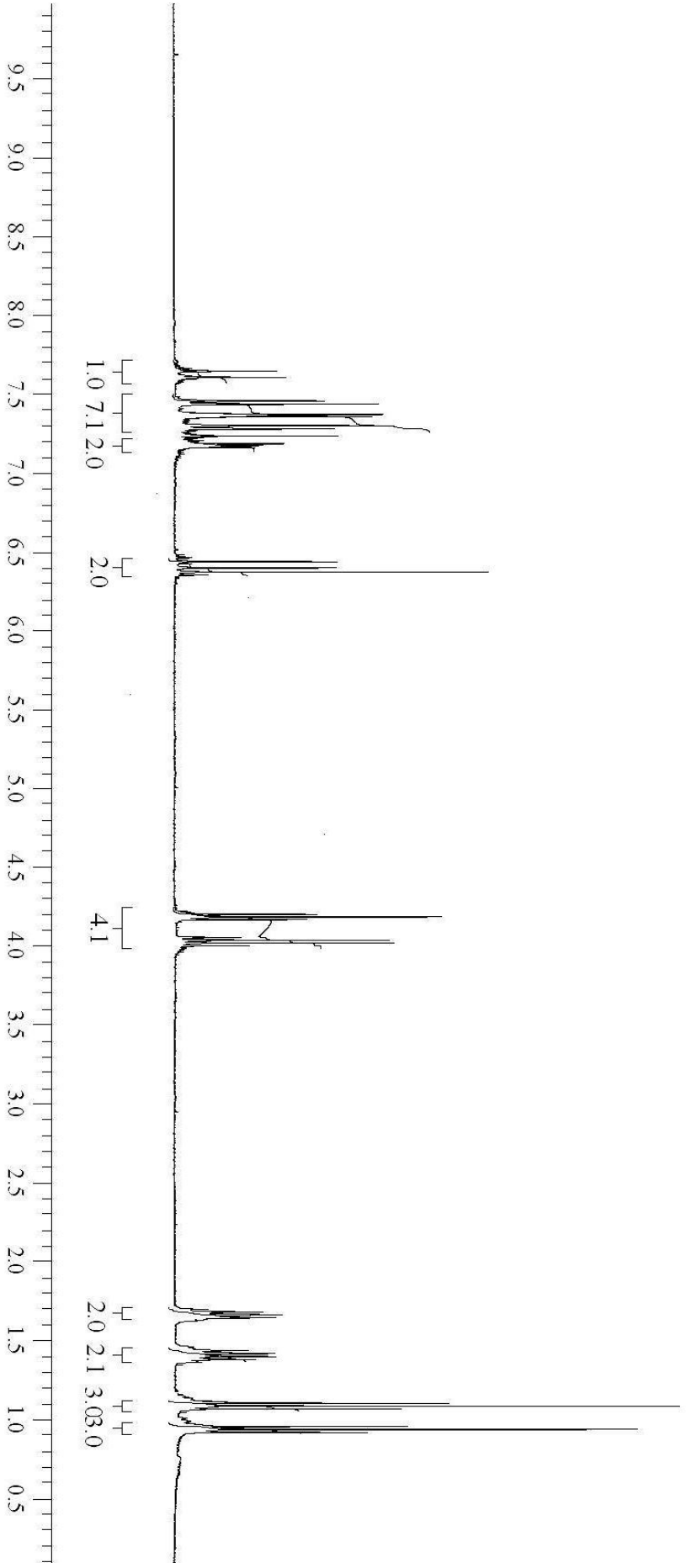
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3.0
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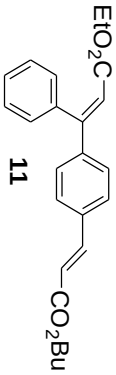
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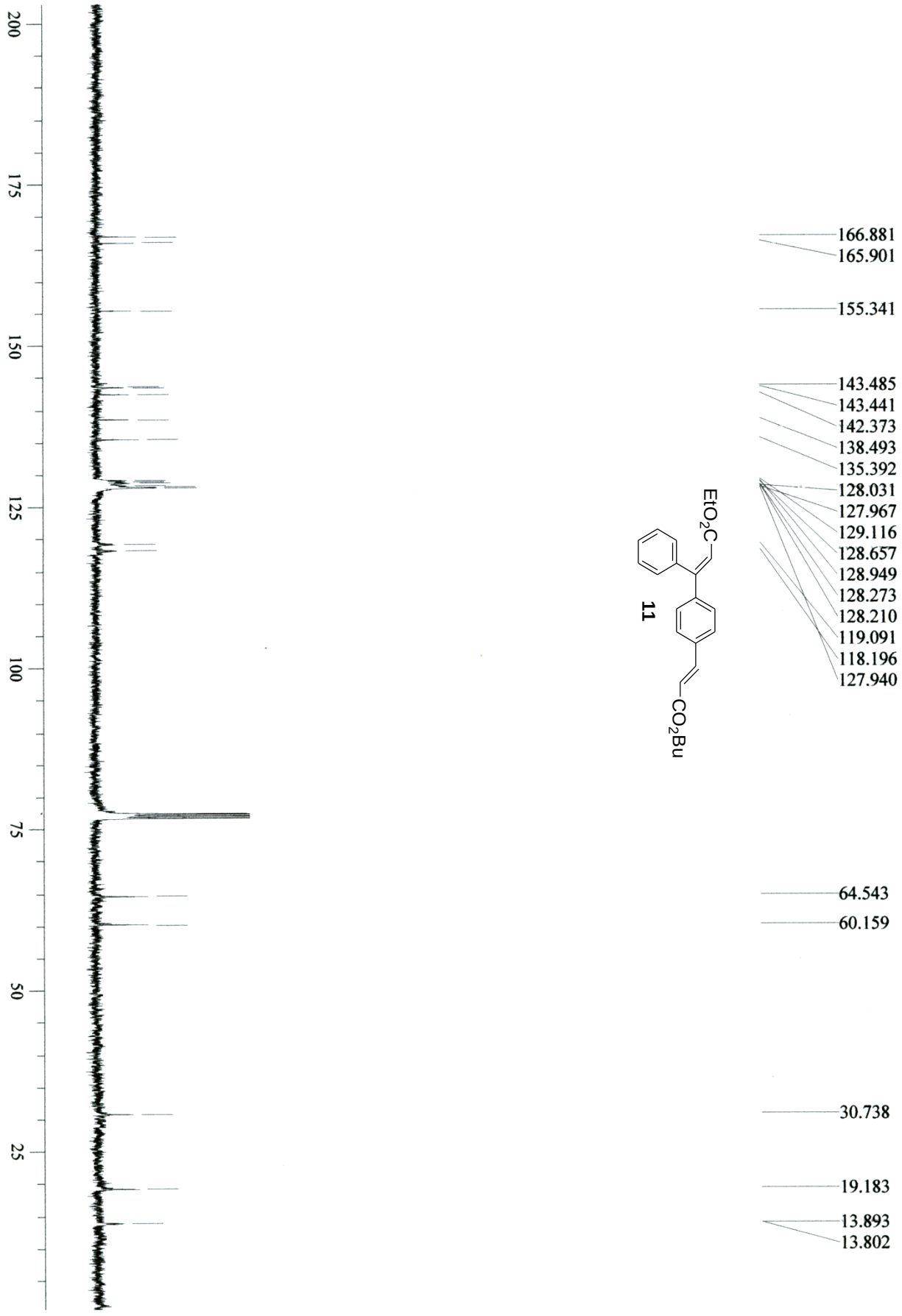
11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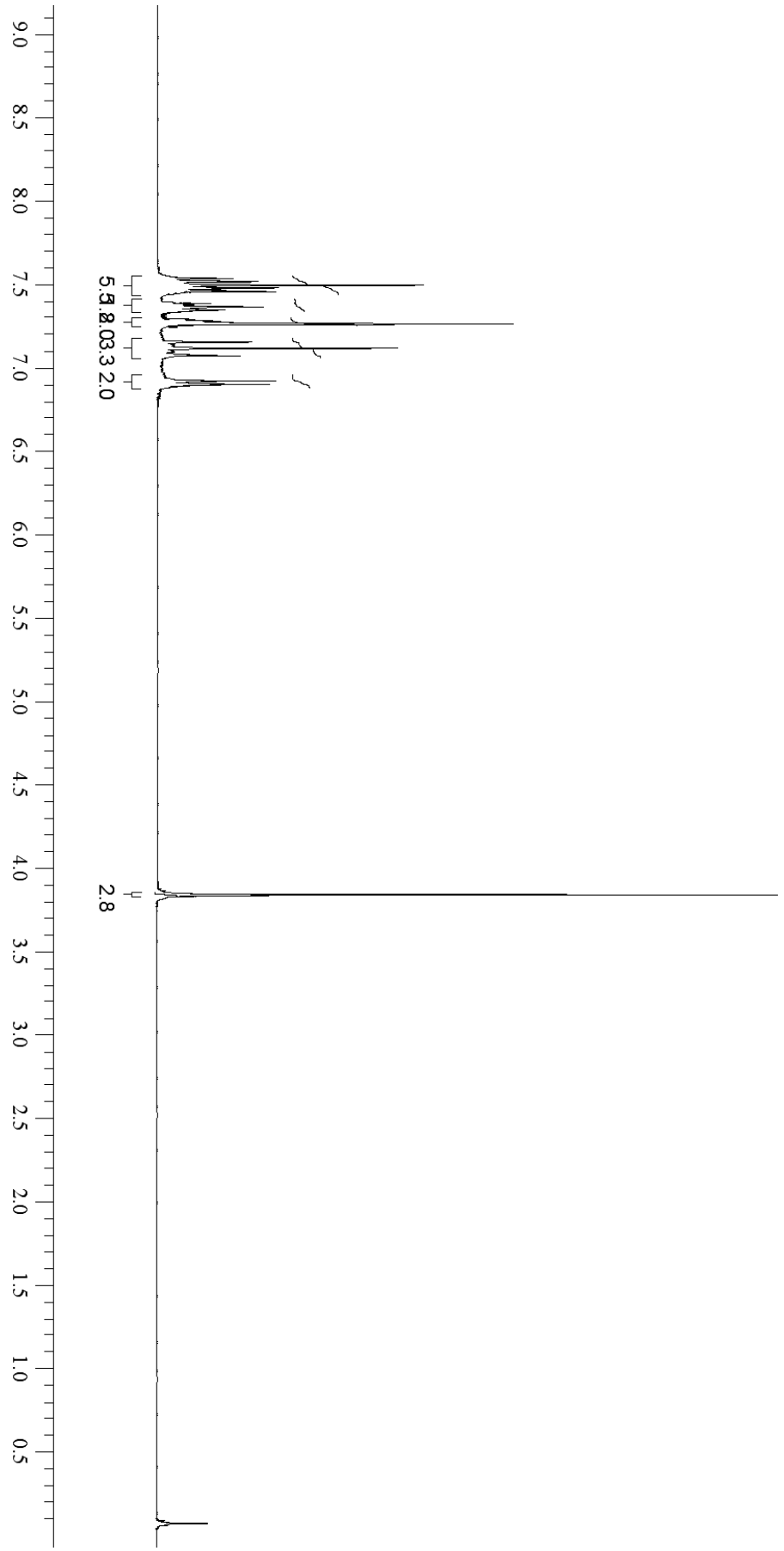
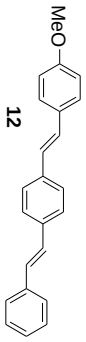
EtO2C
CO2Bu
11





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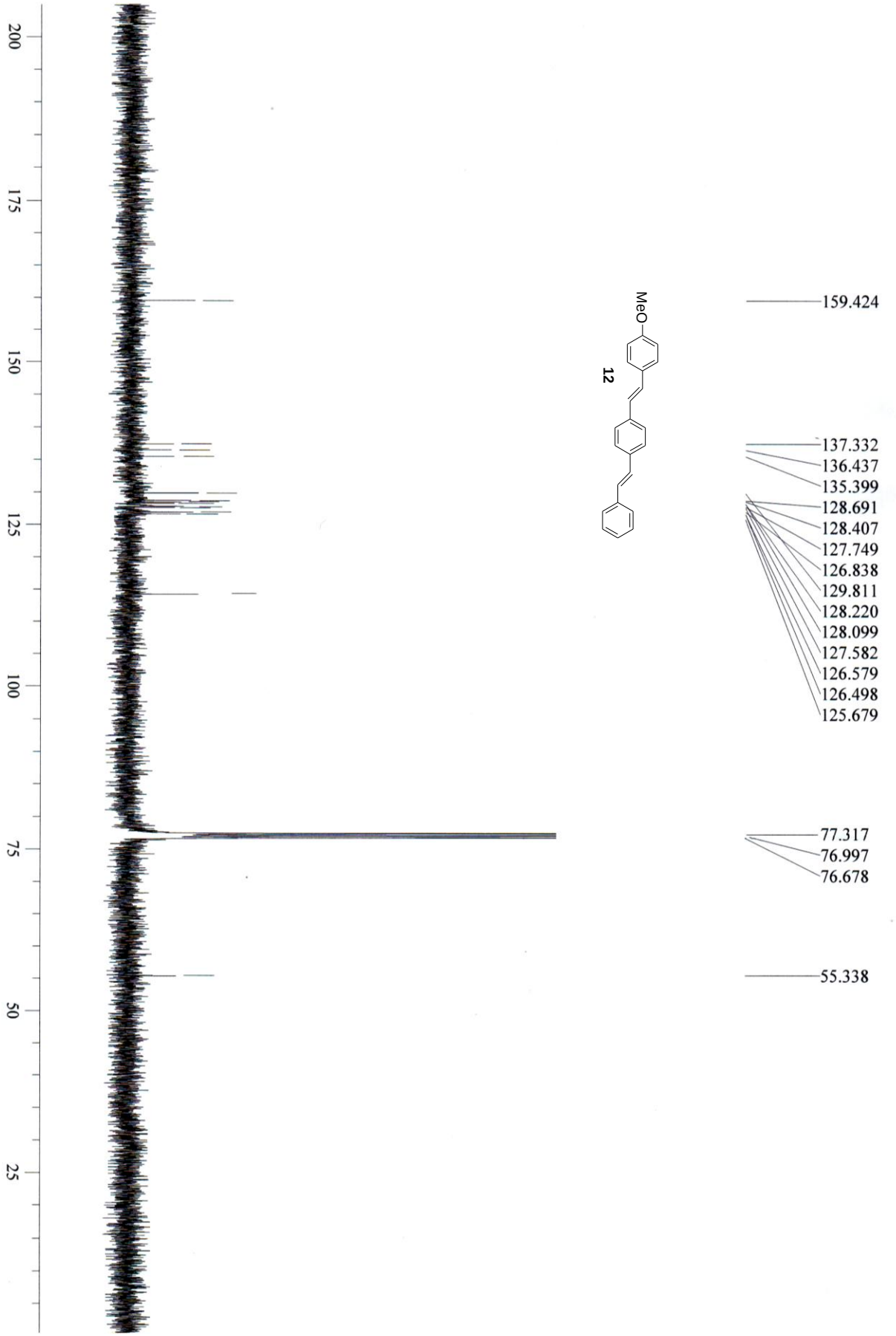
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MeO
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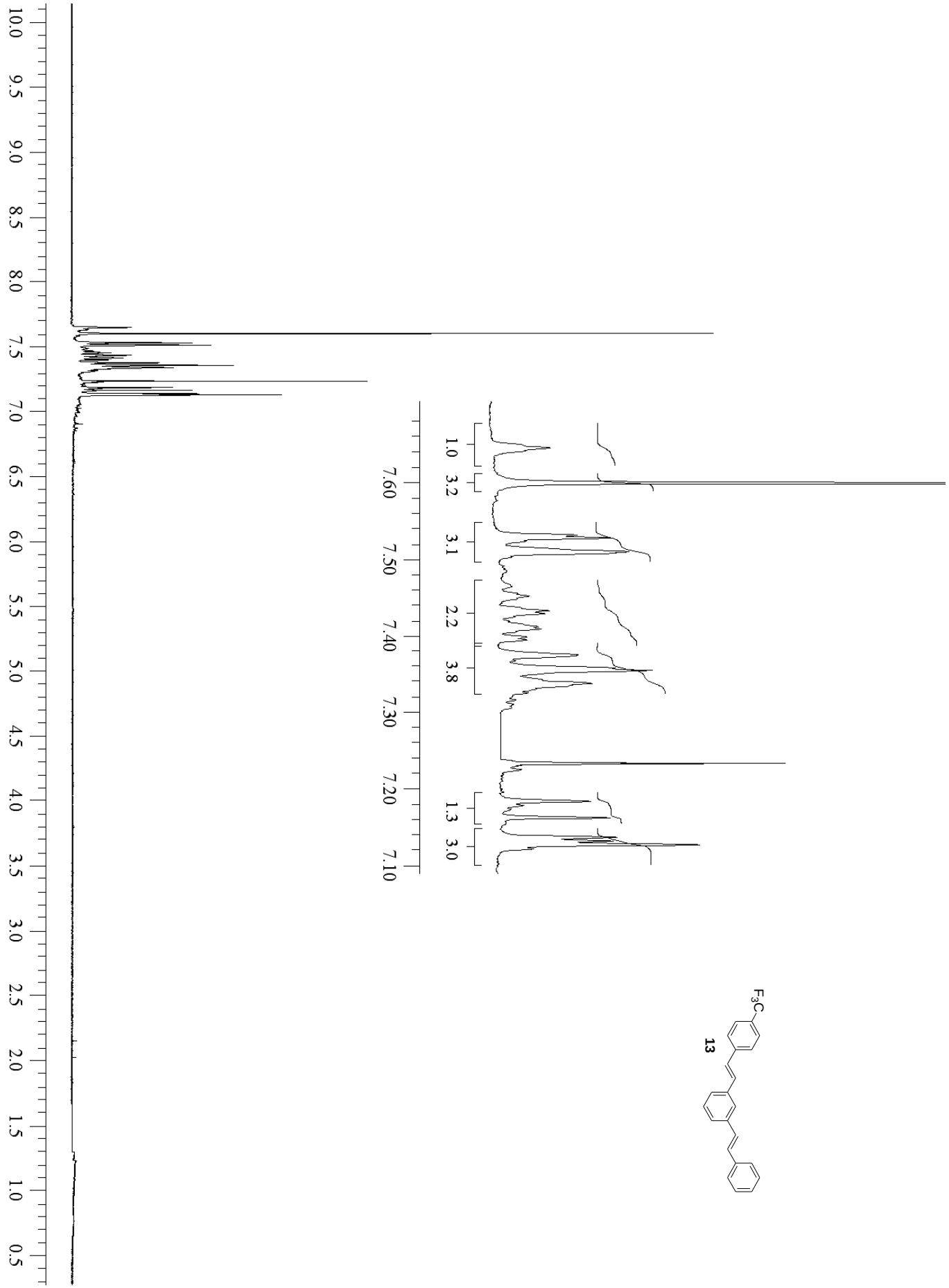

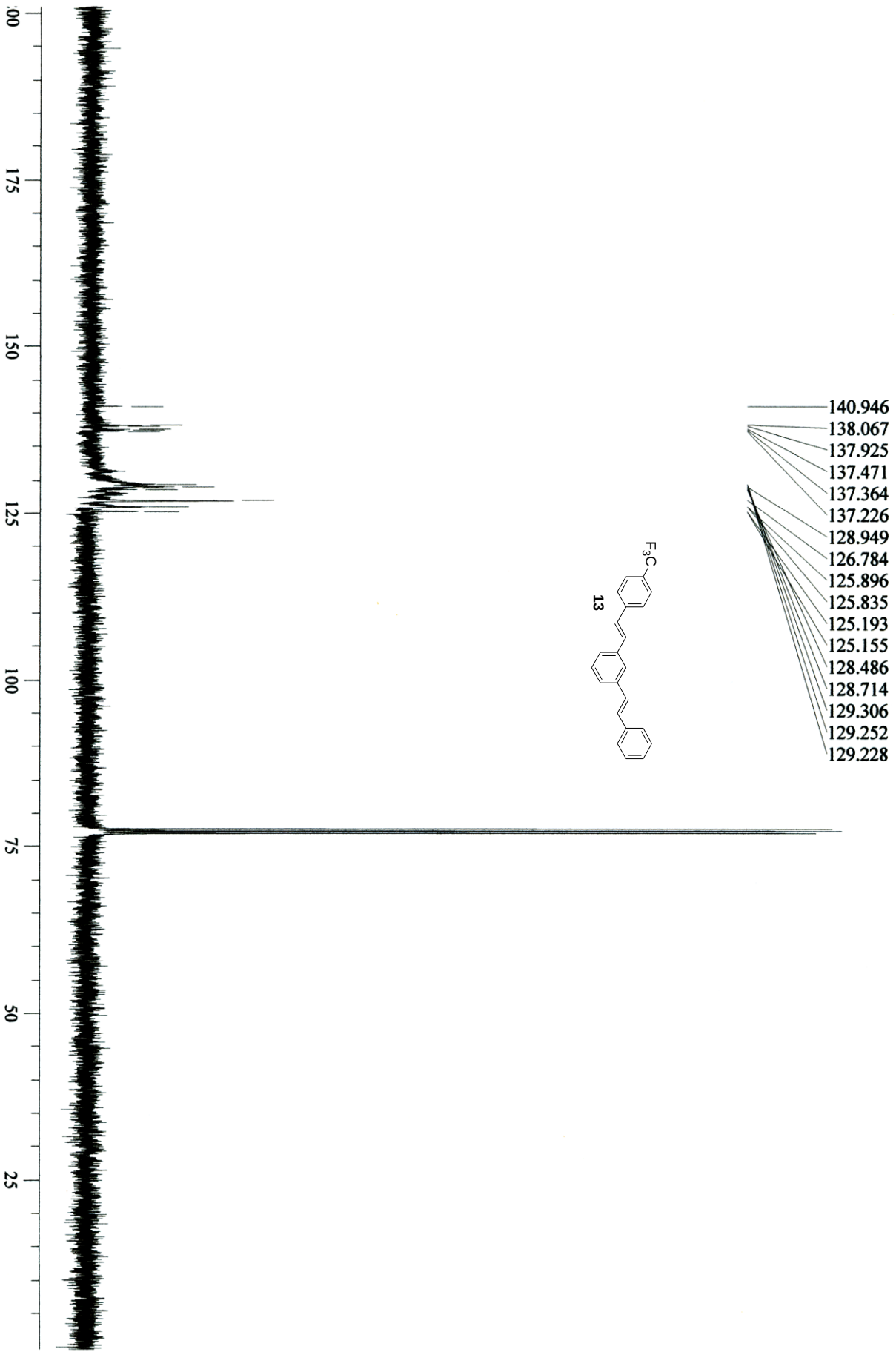

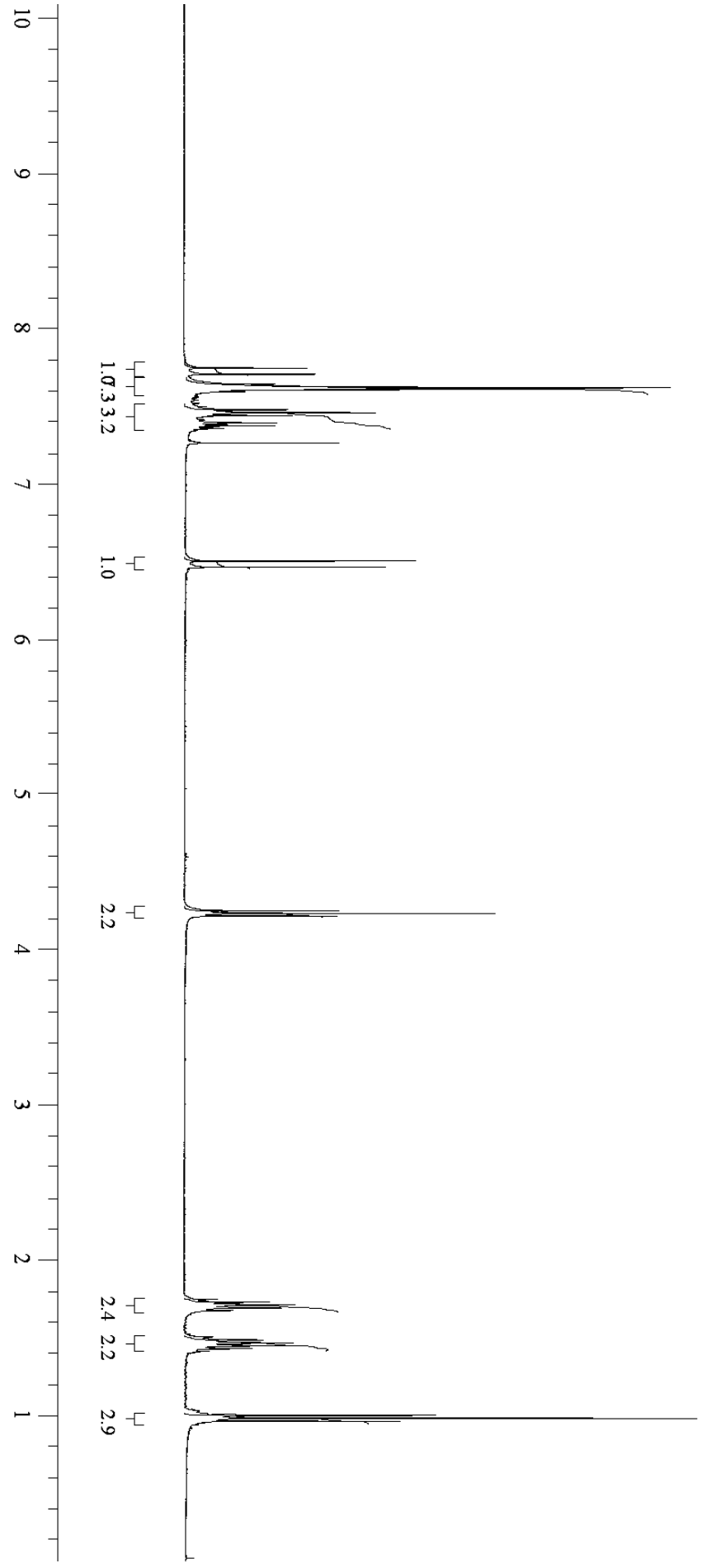

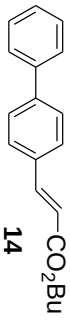

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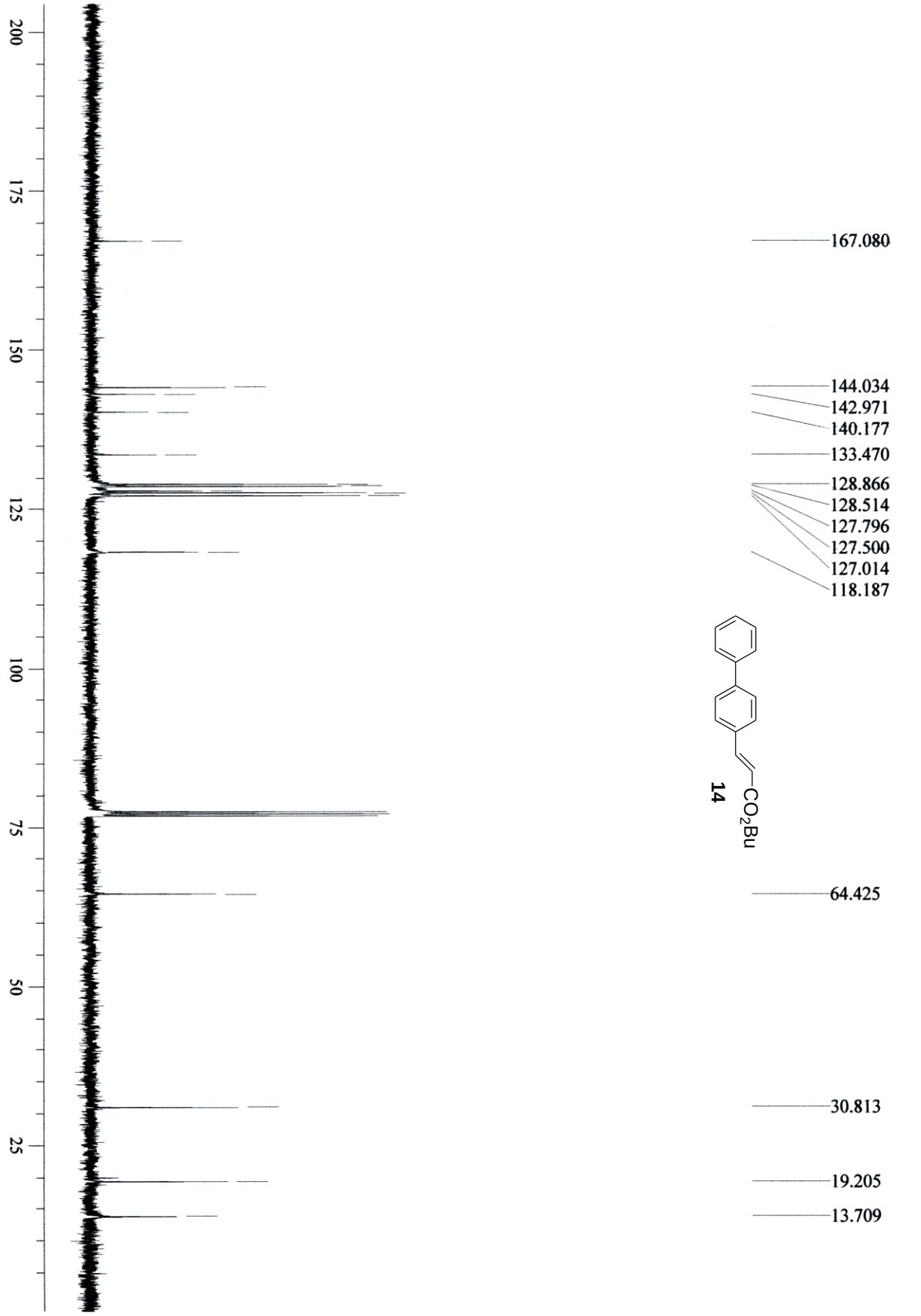

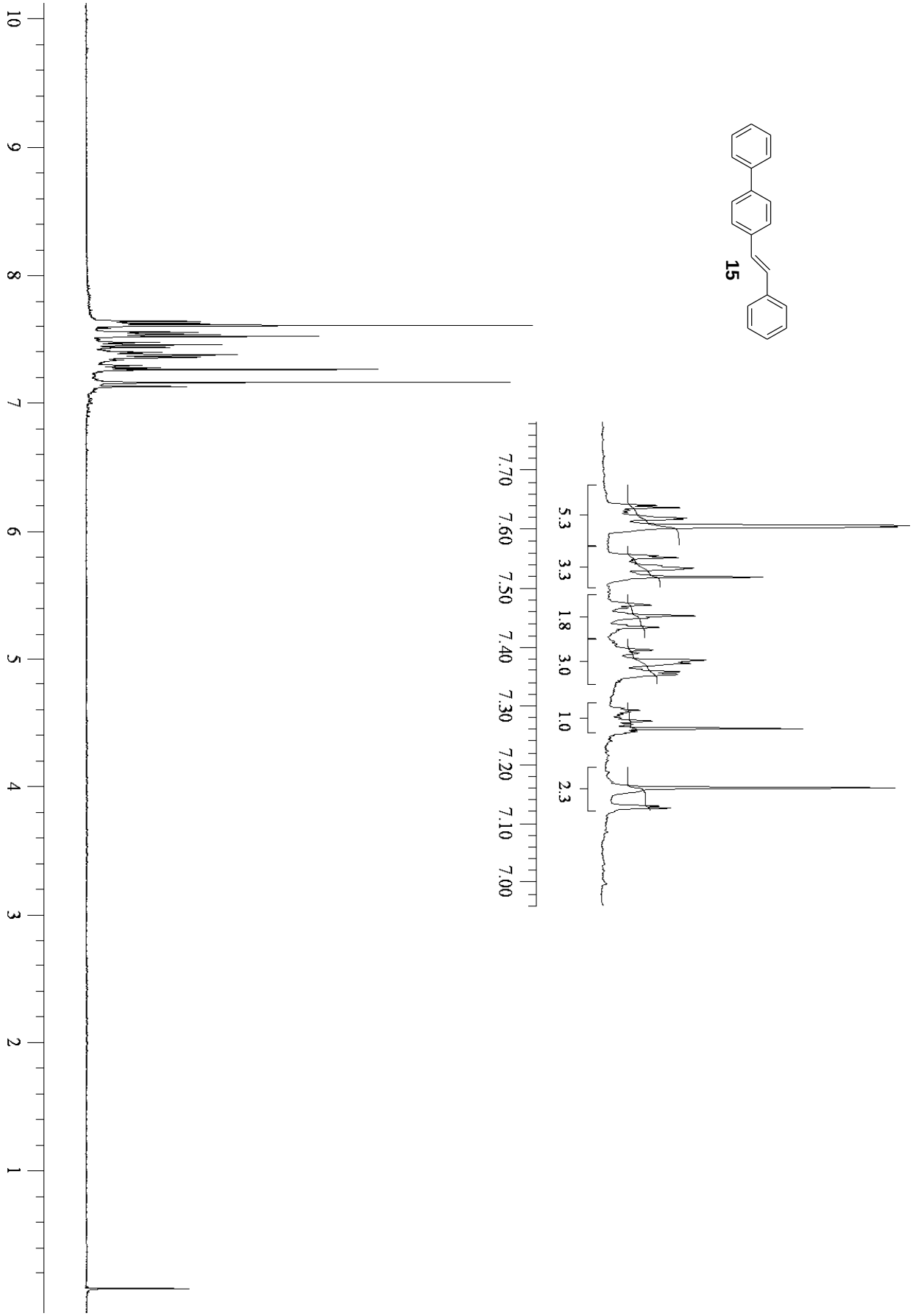
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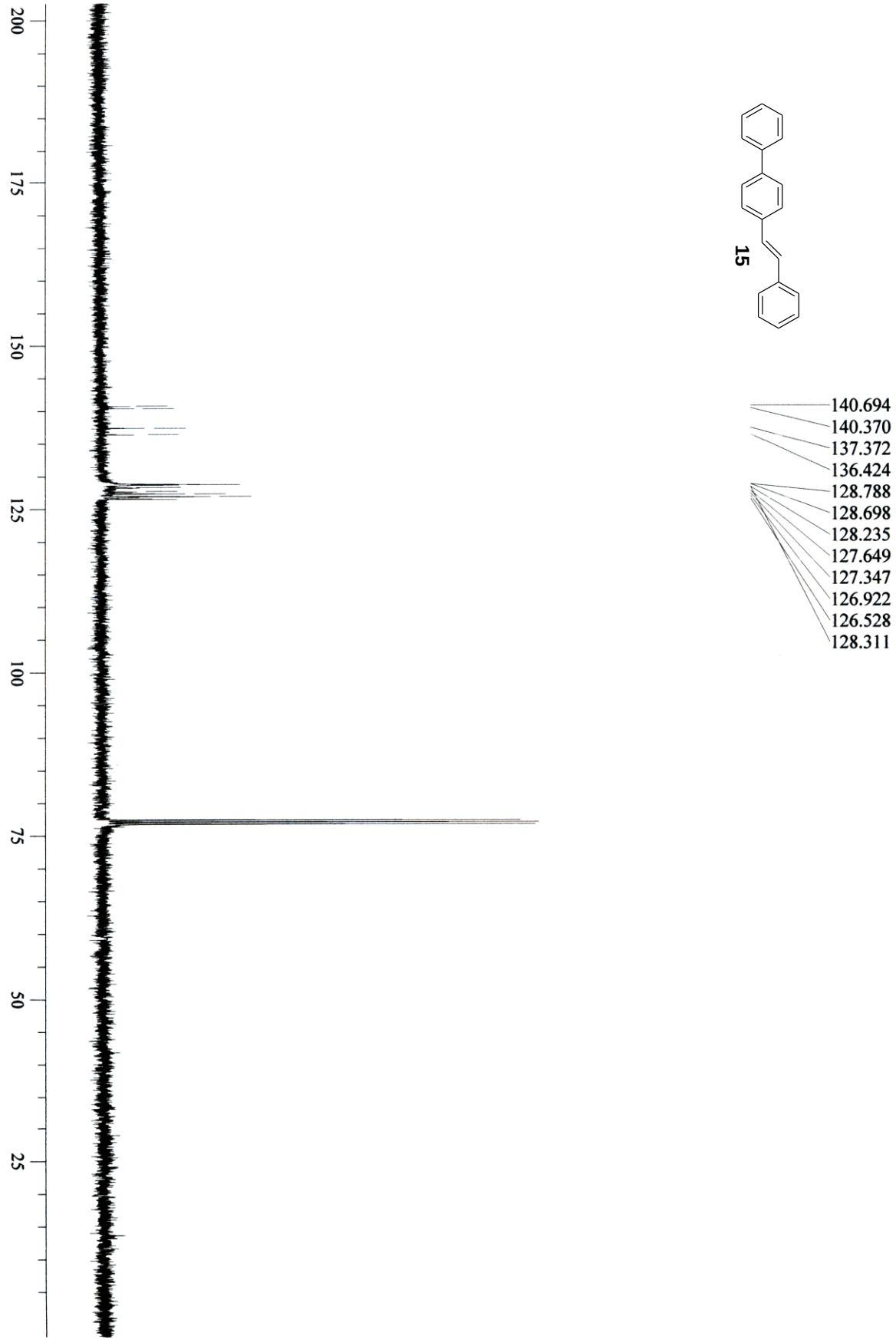
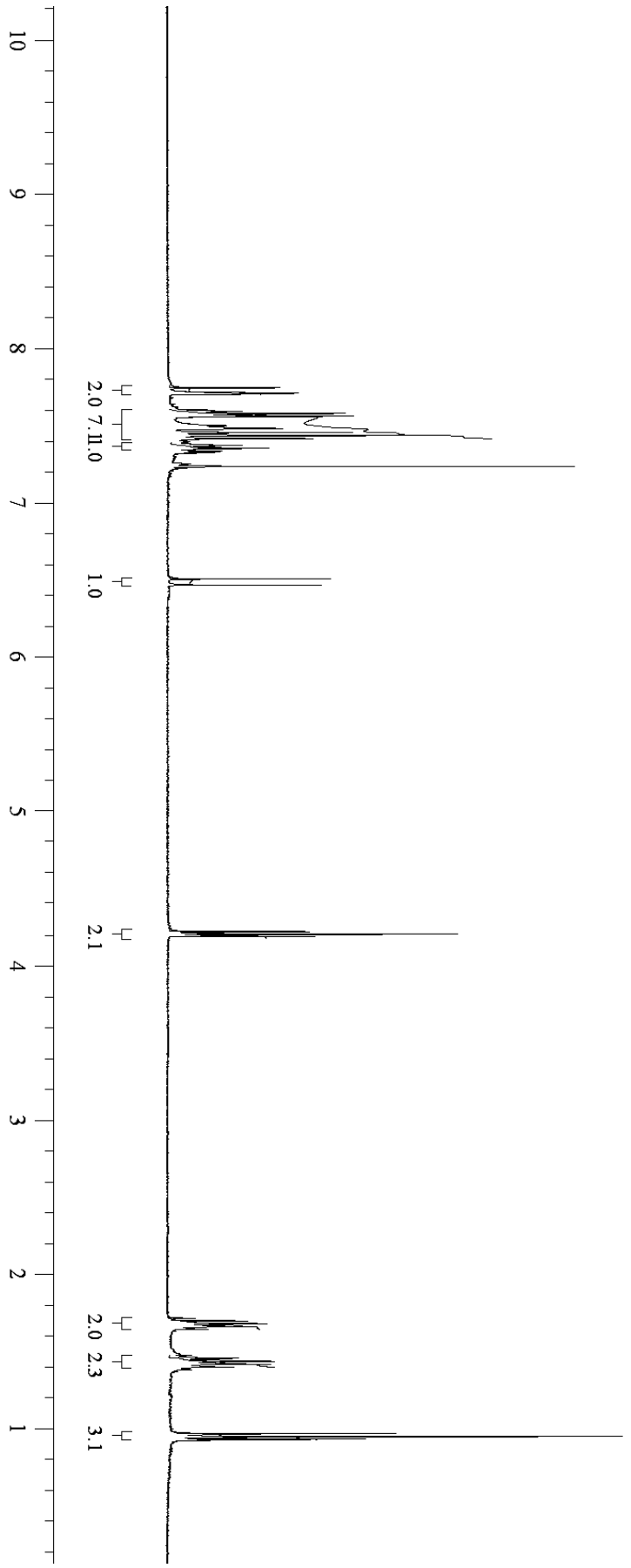
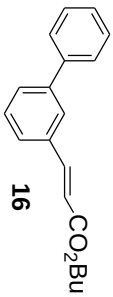
3.0
1.0
2.3







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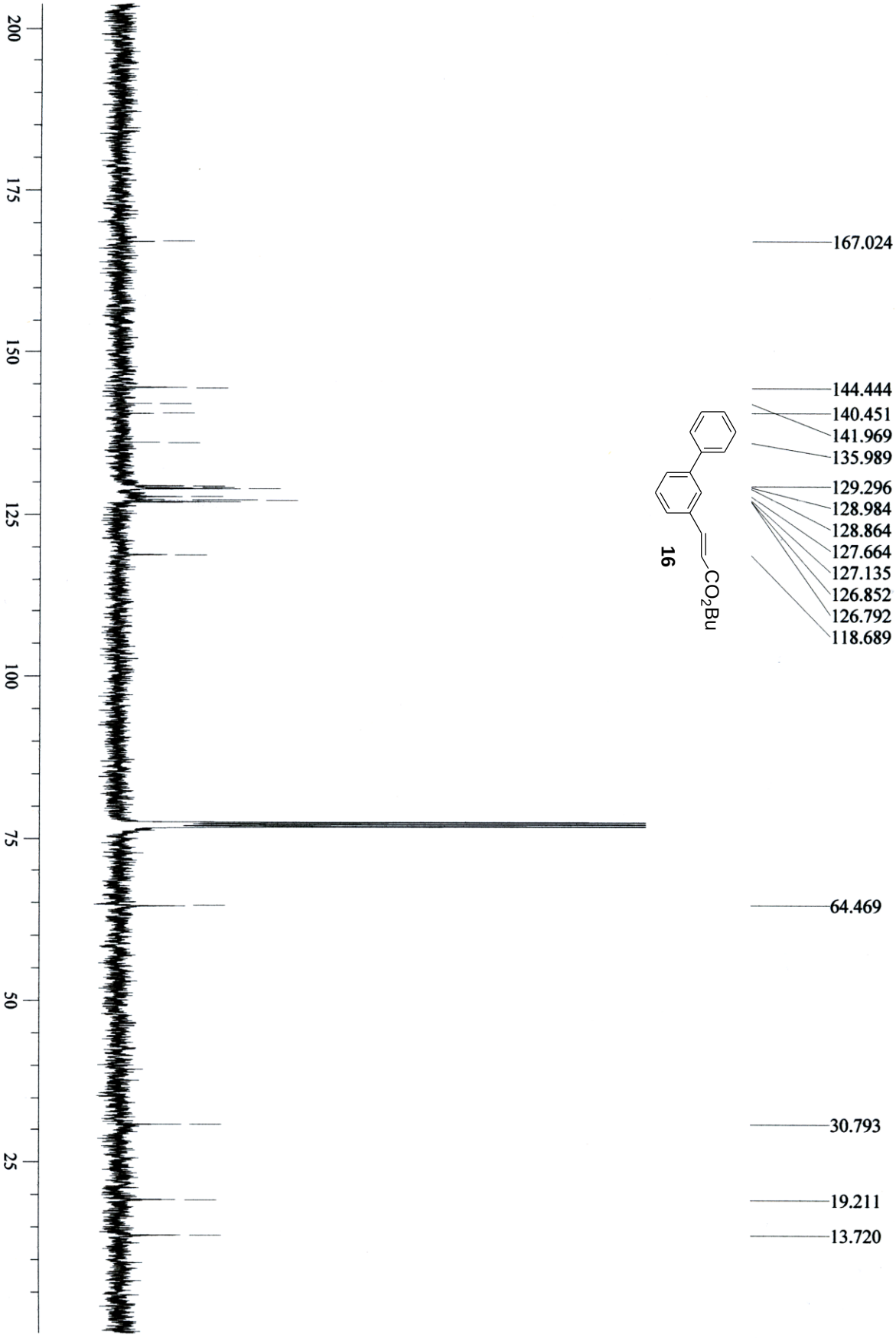

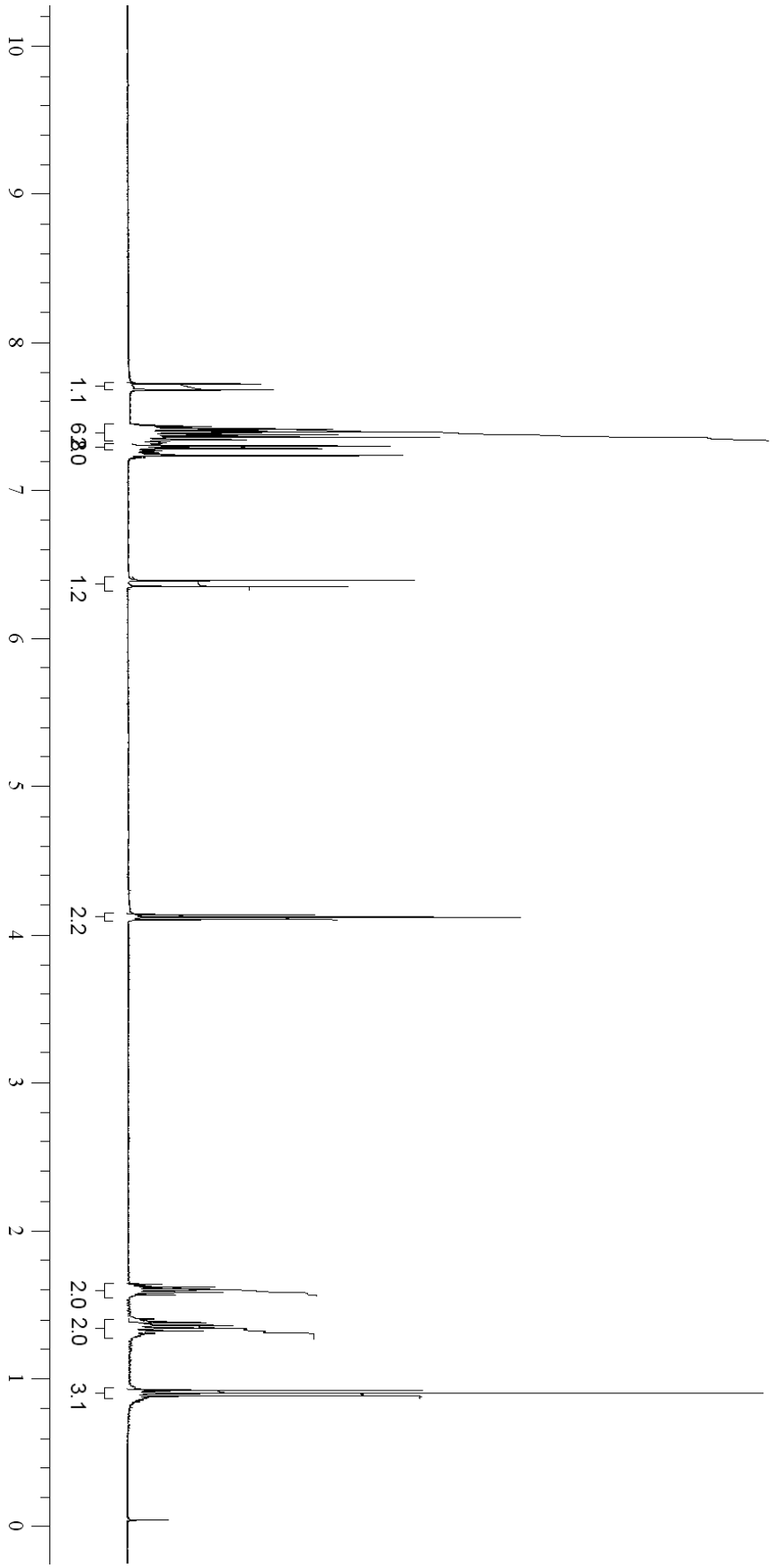

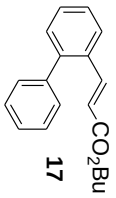

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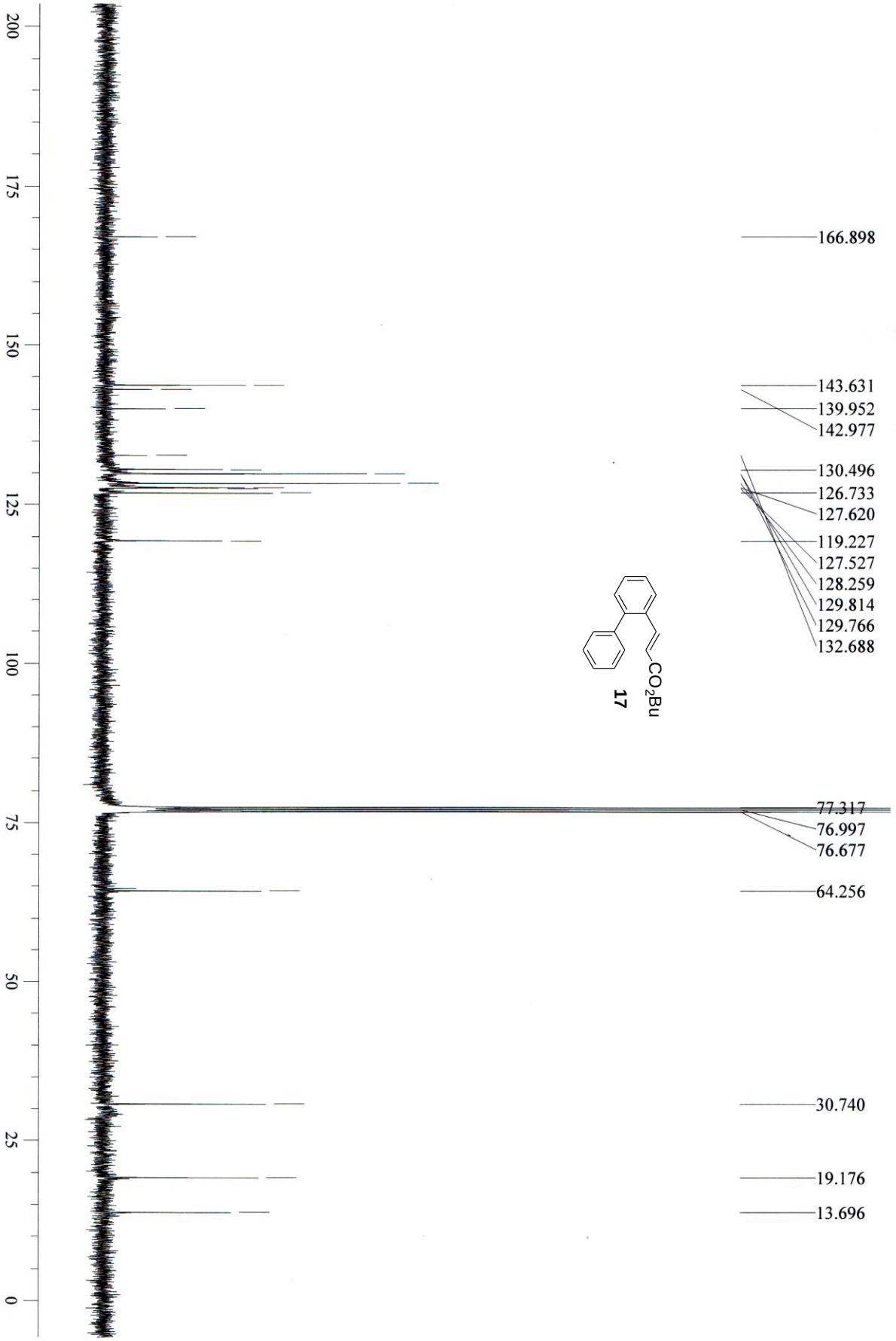

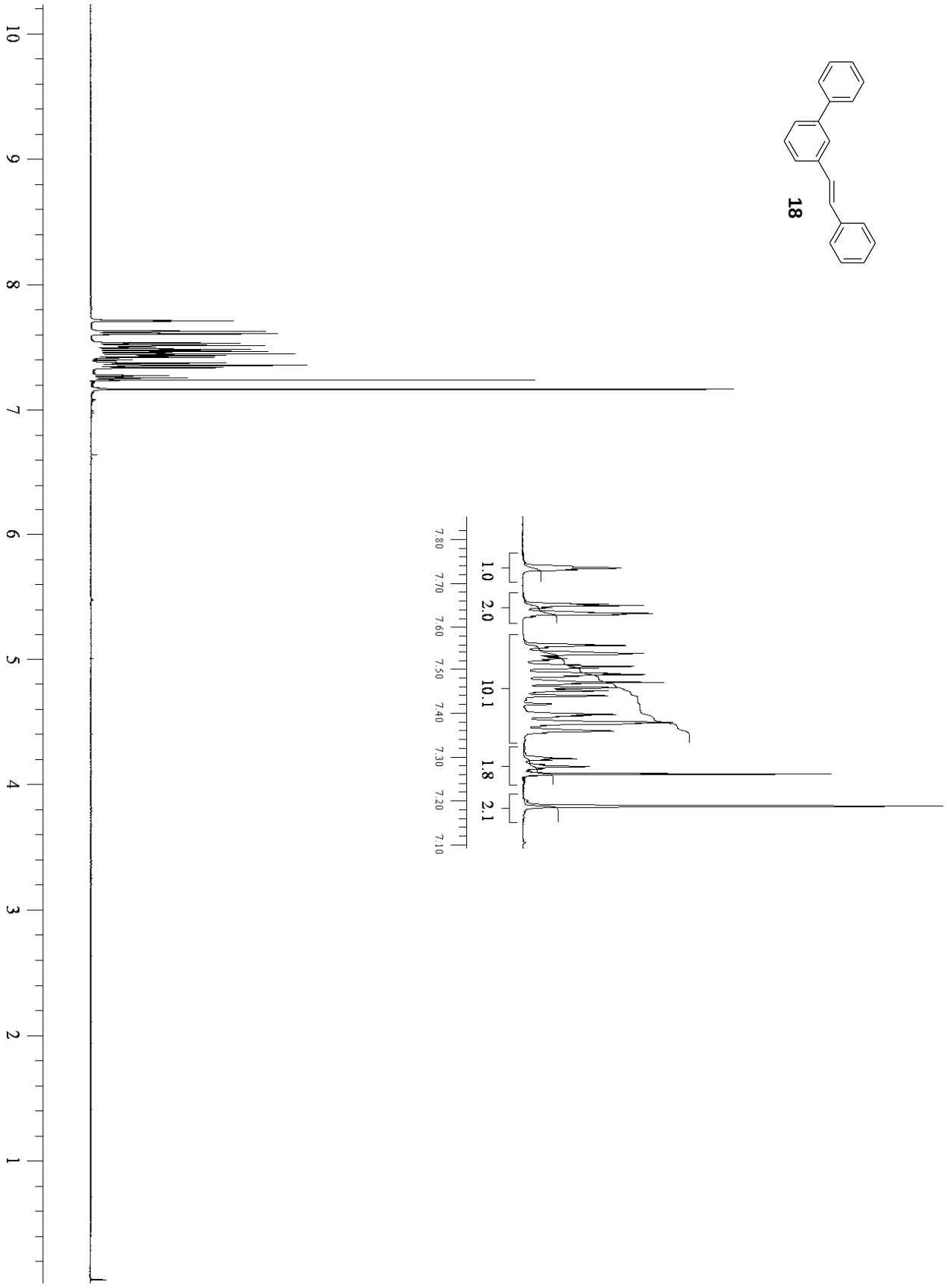

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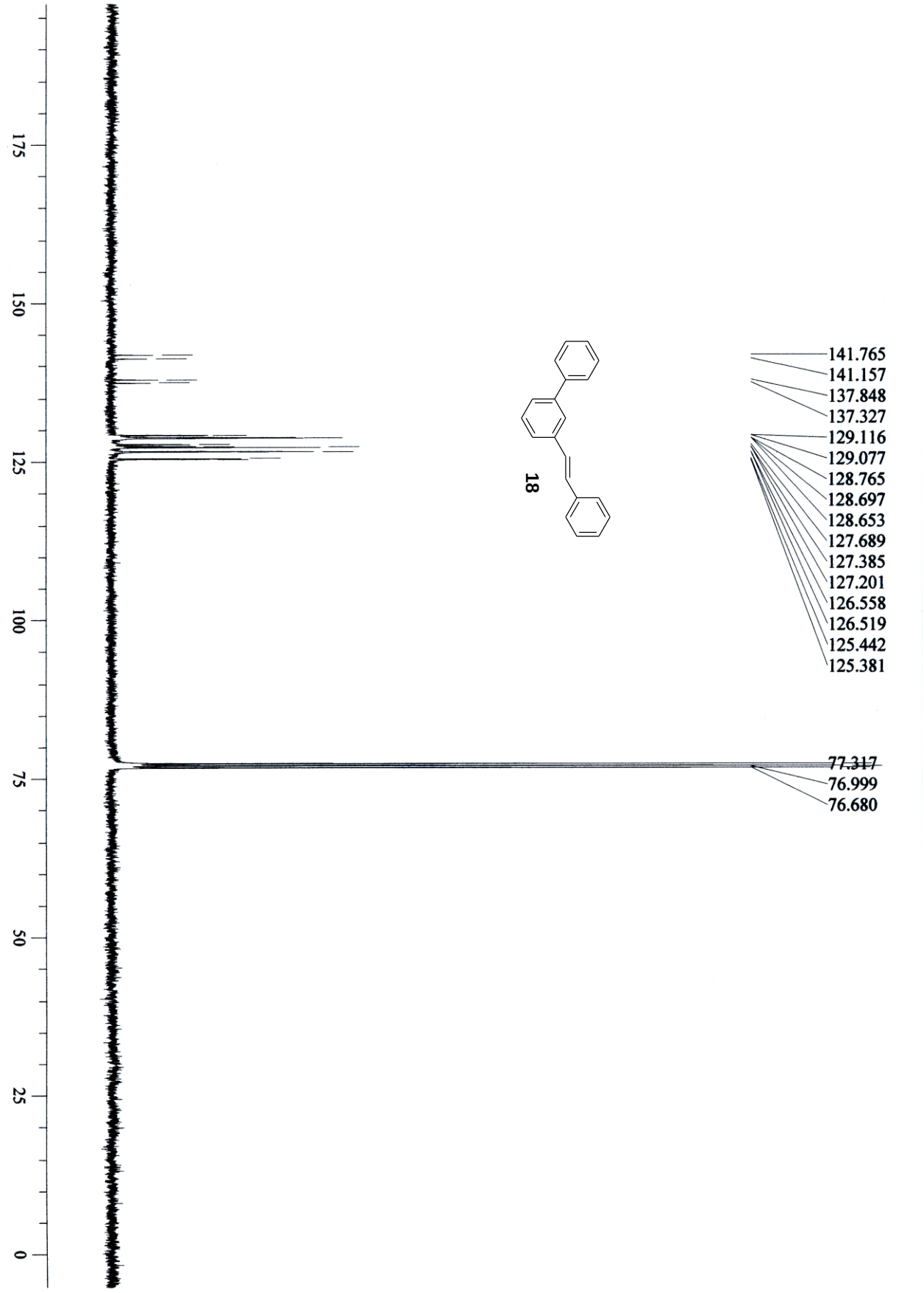

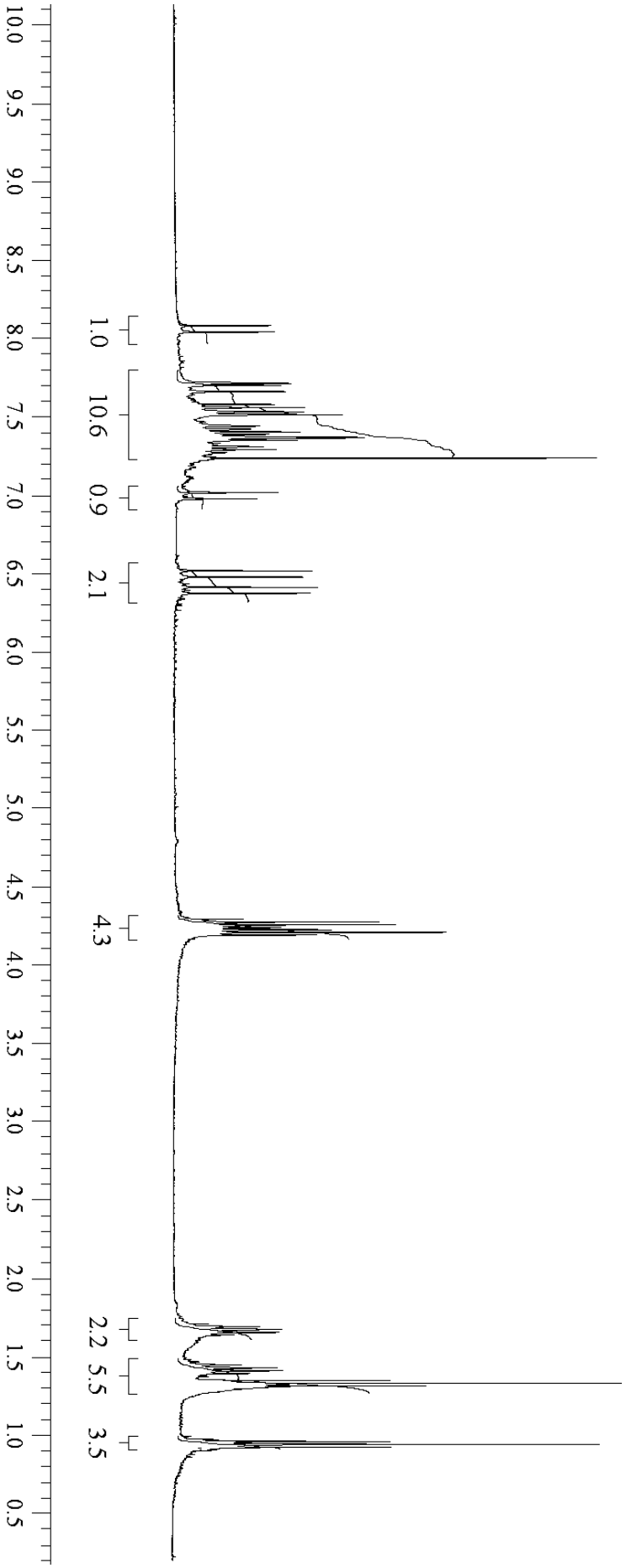
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3.0
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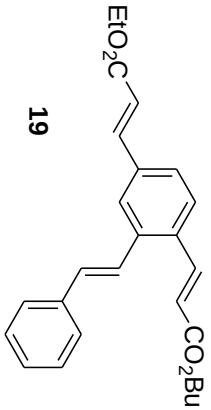
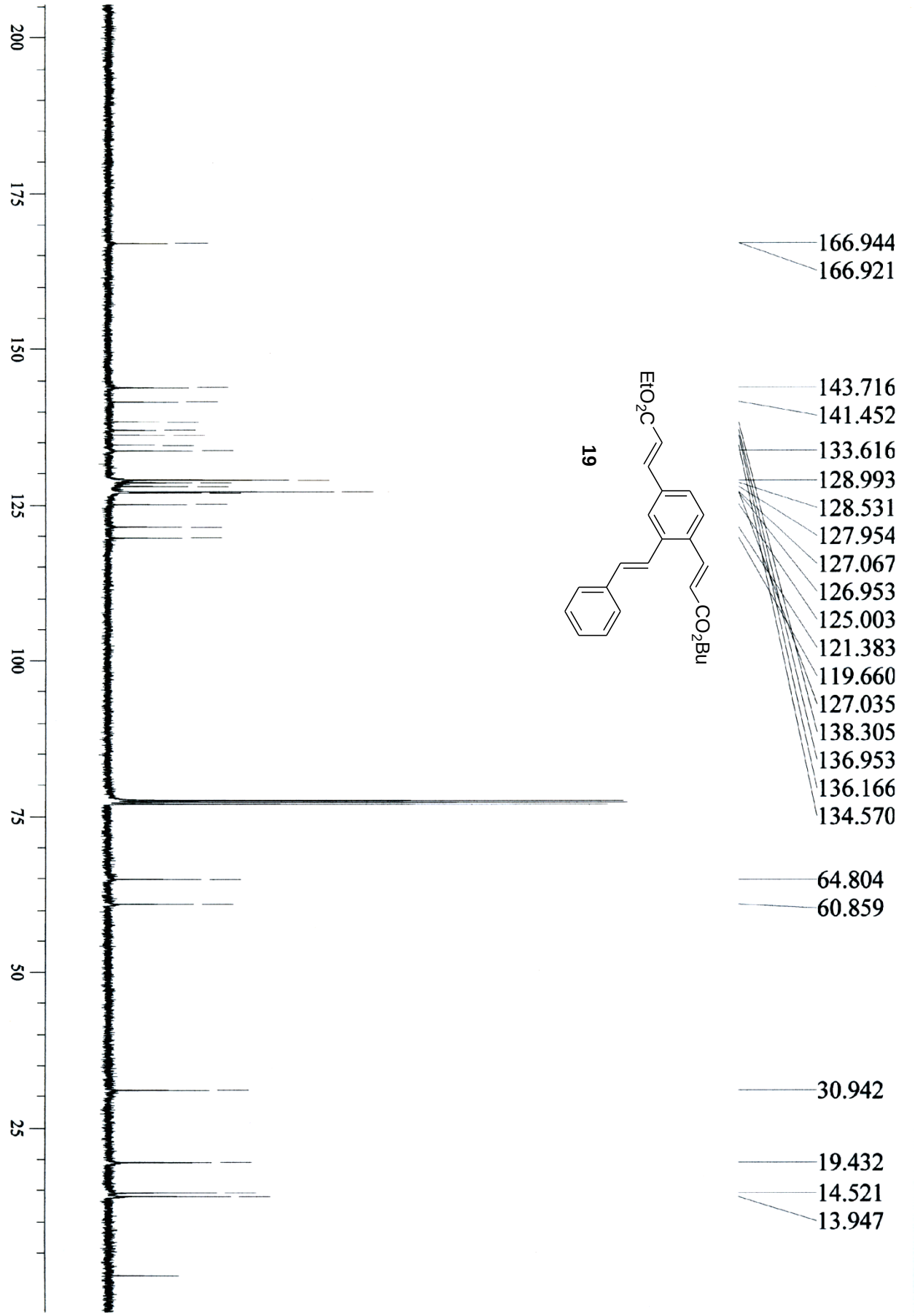
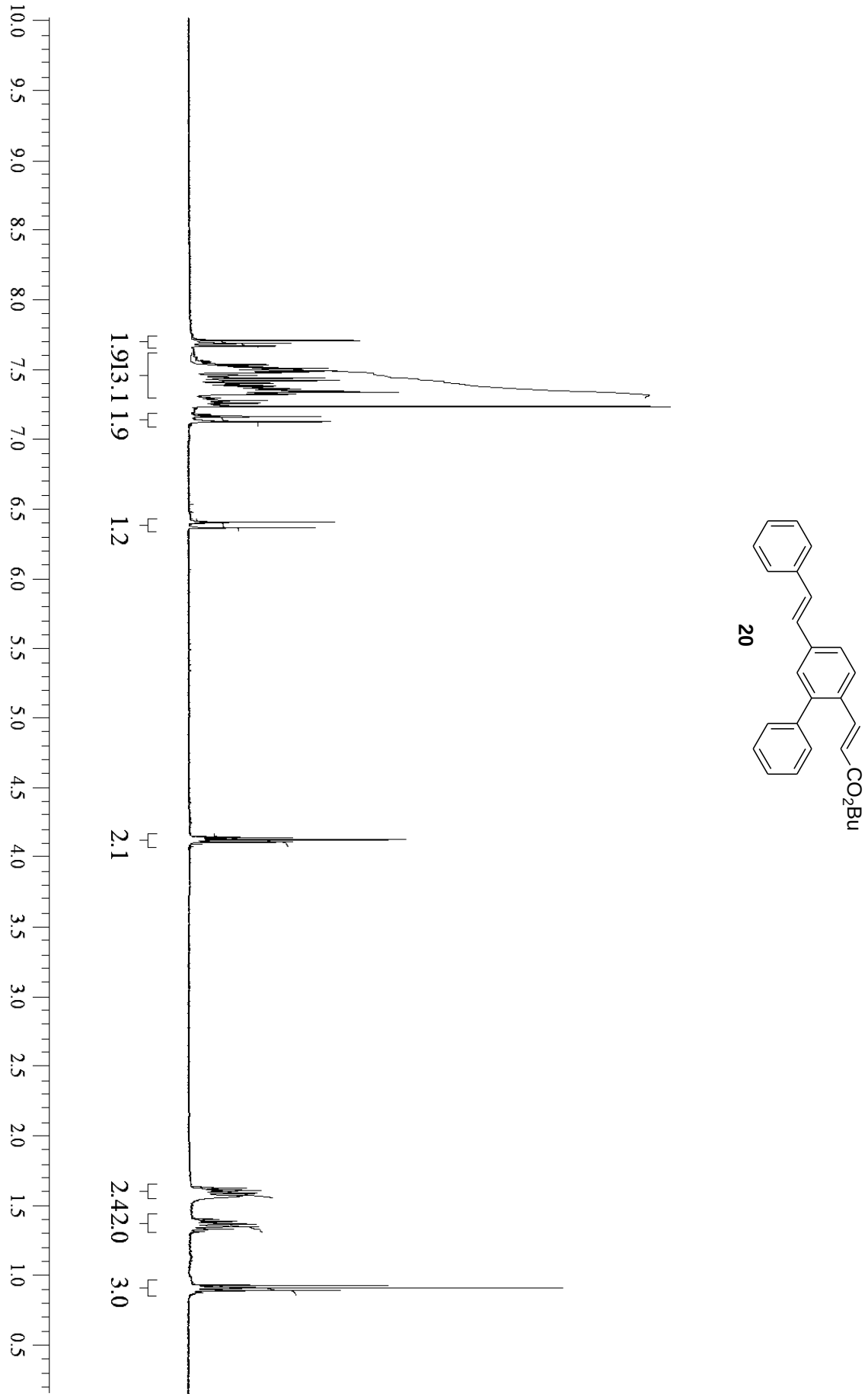
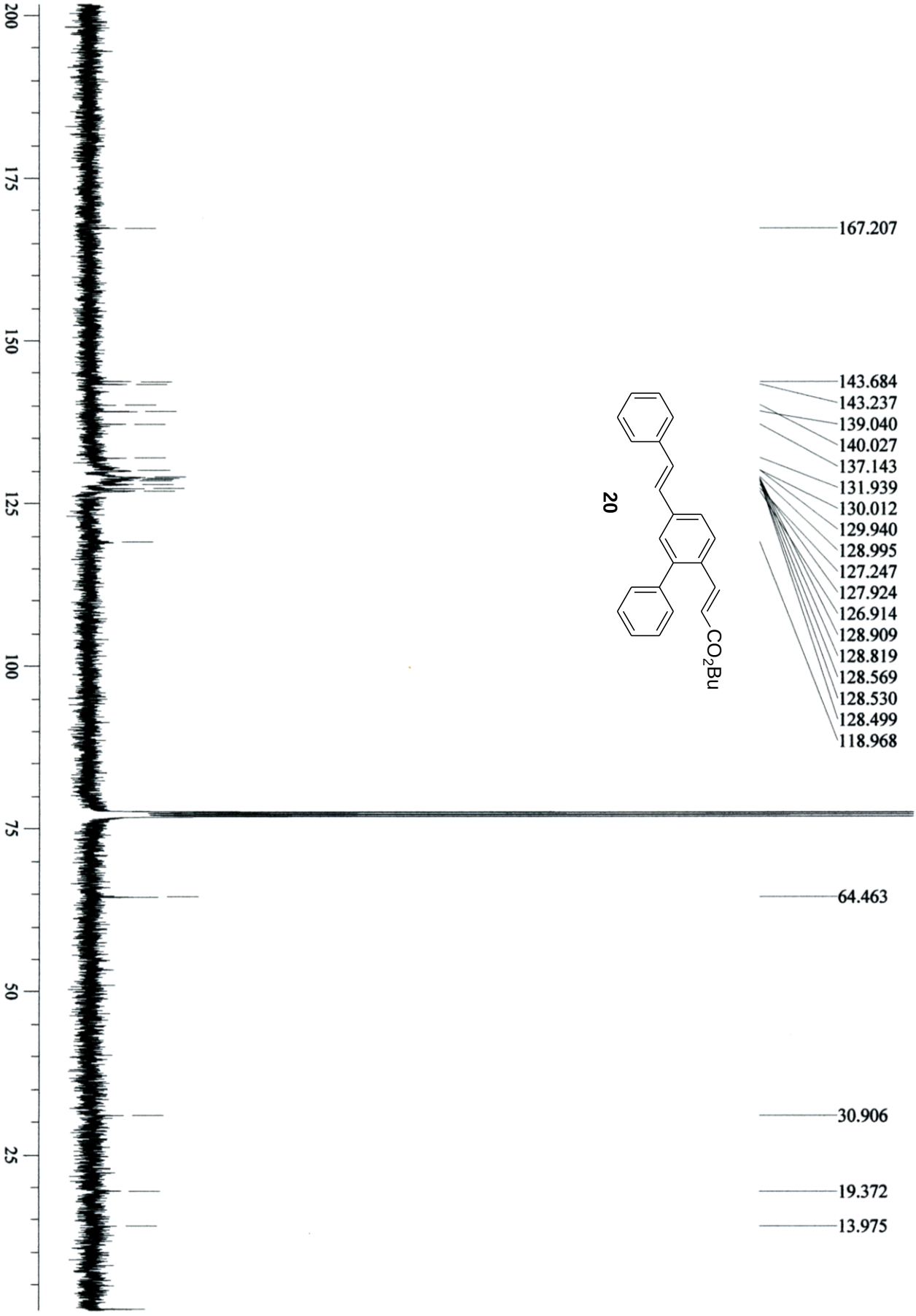
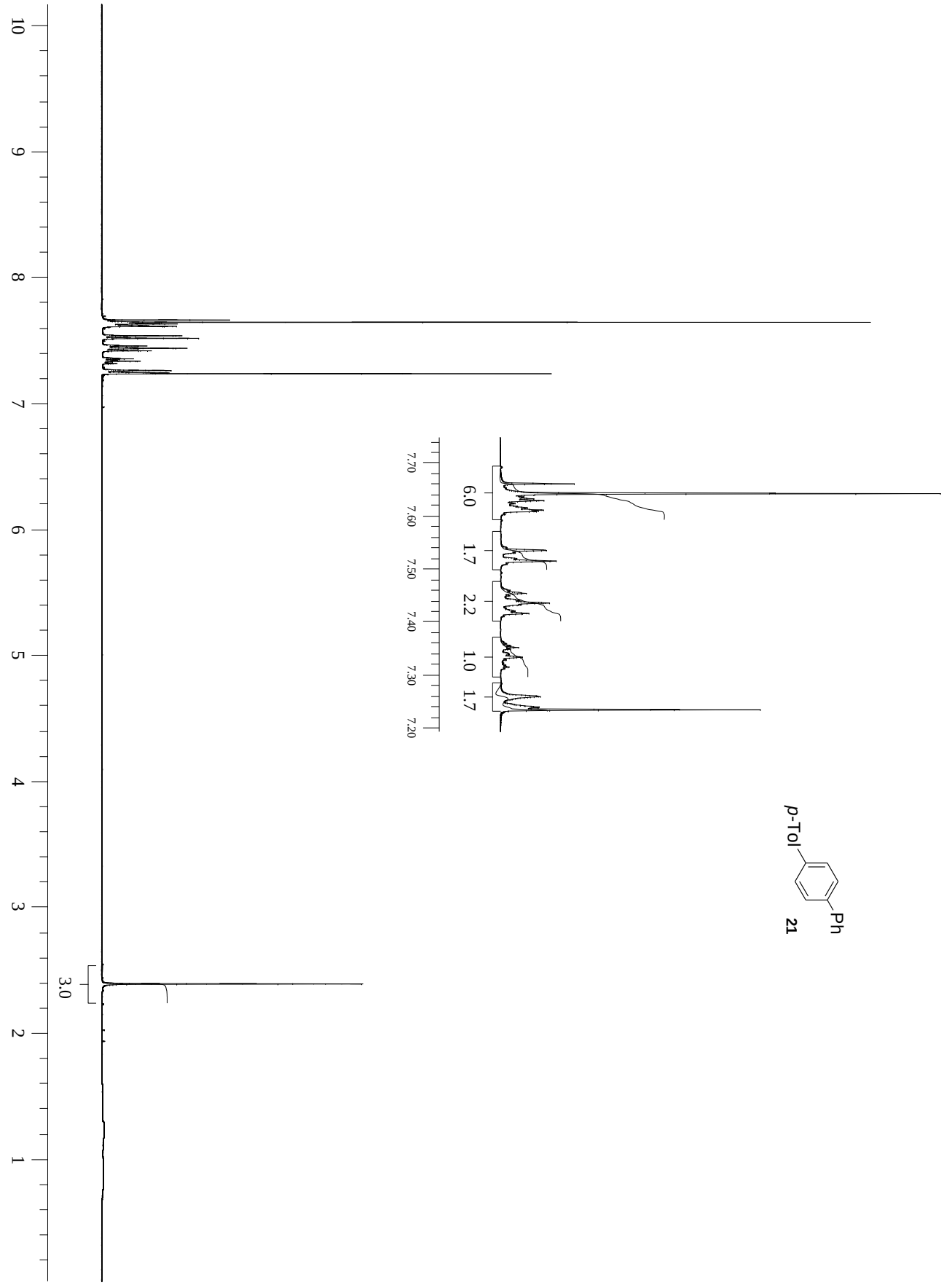

EtO2C
CO2Bu

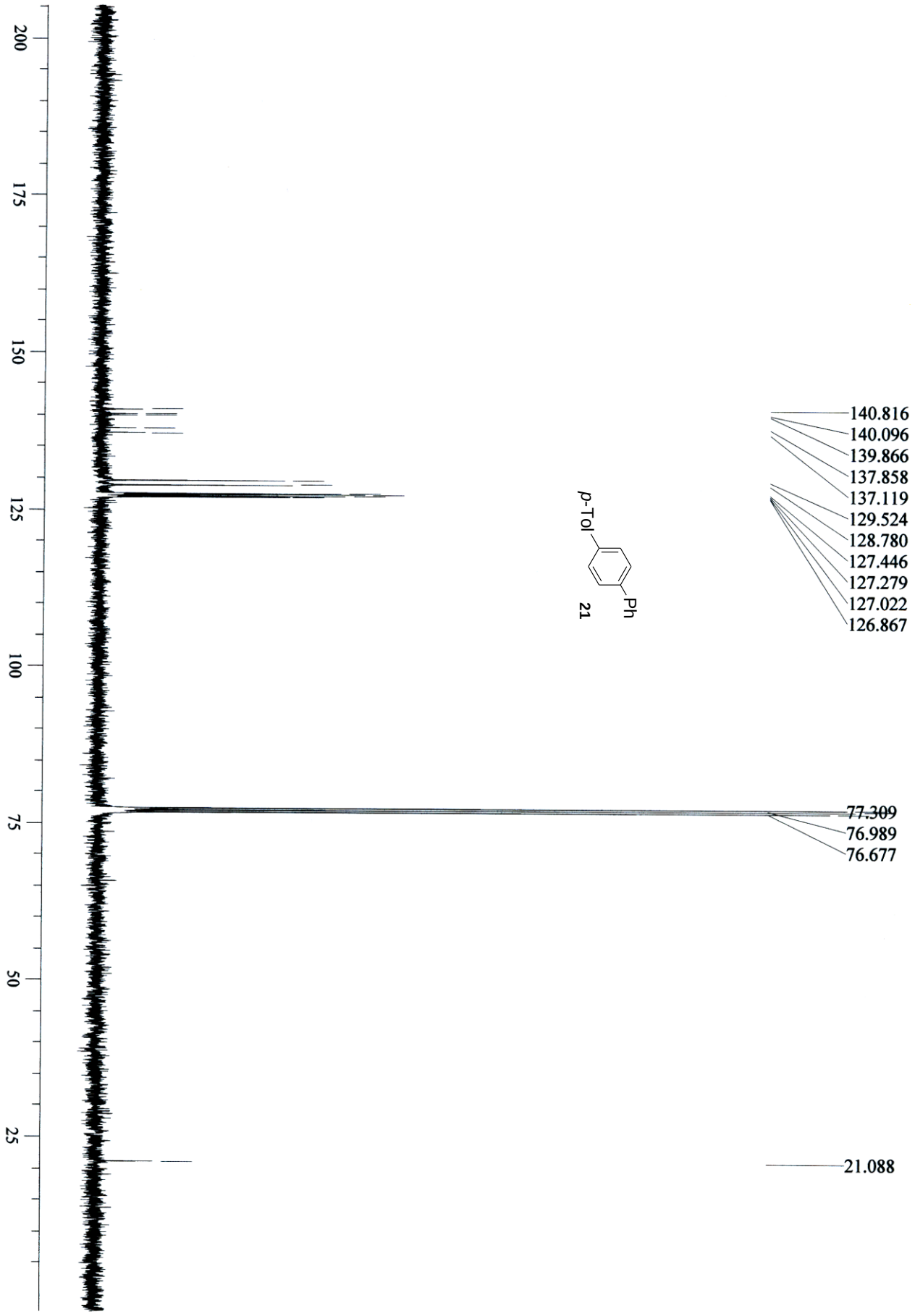
19







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175
150
125
100
75
50
25
p-Tol
Ph
21
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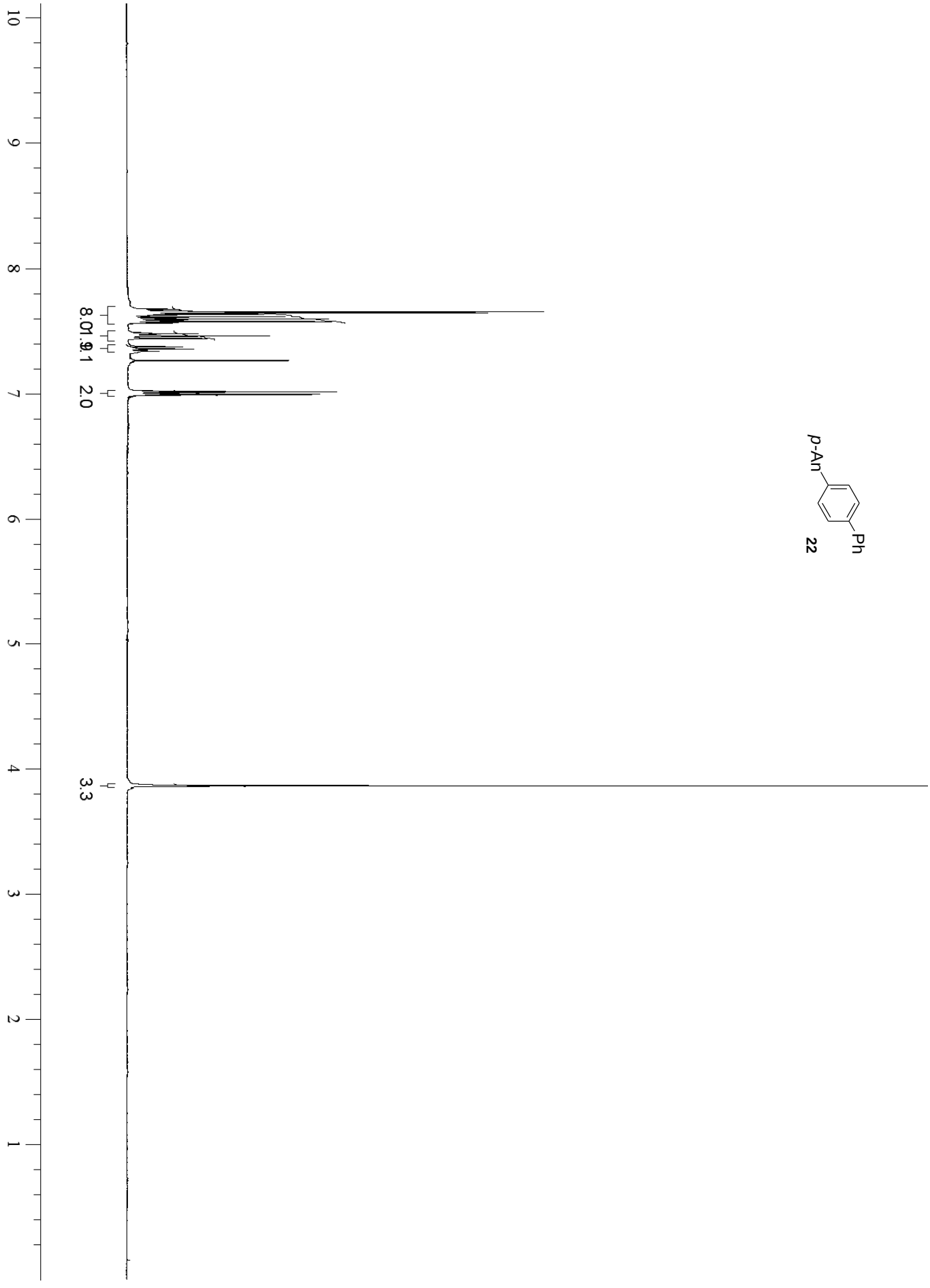
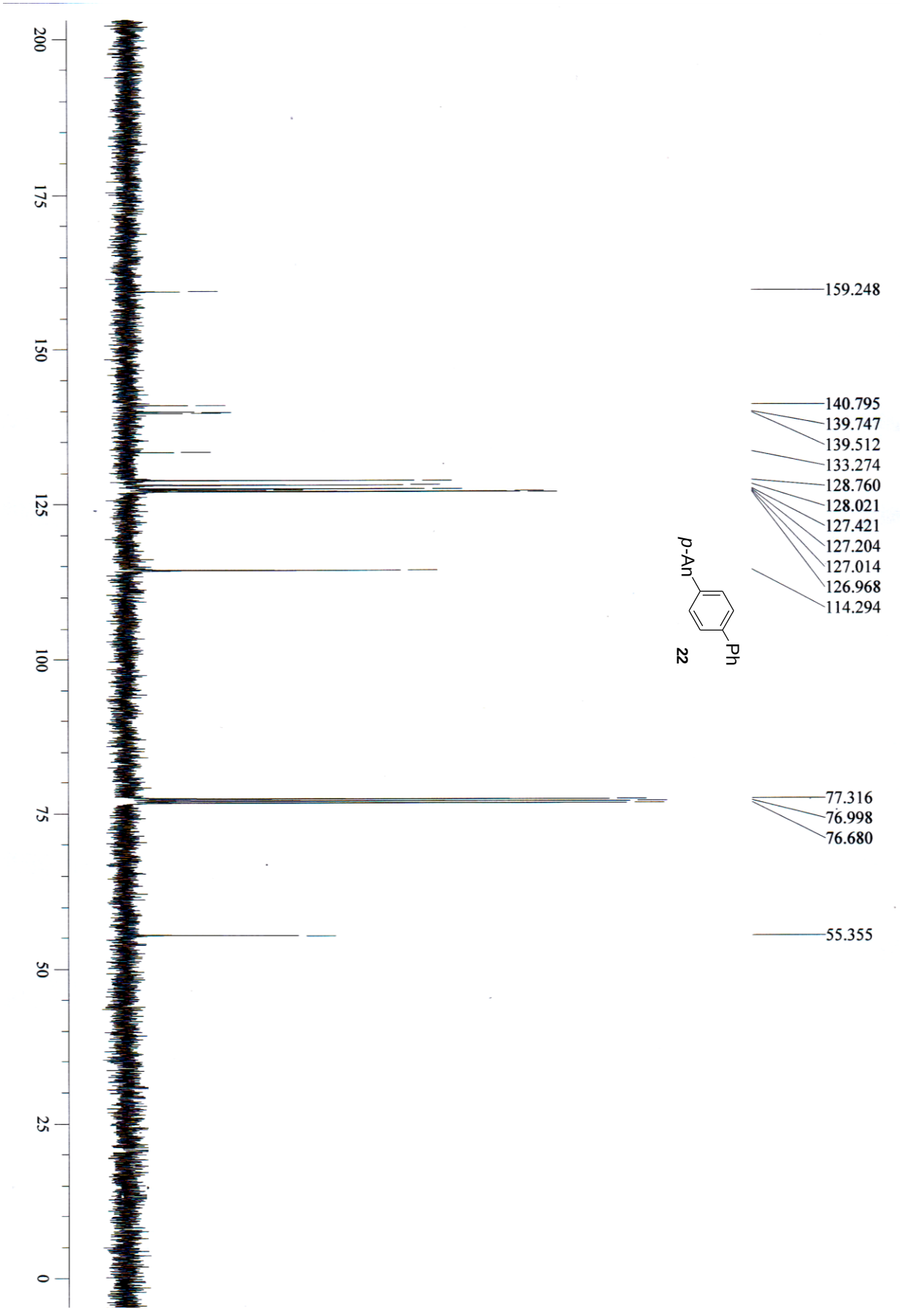
76.677
21.088

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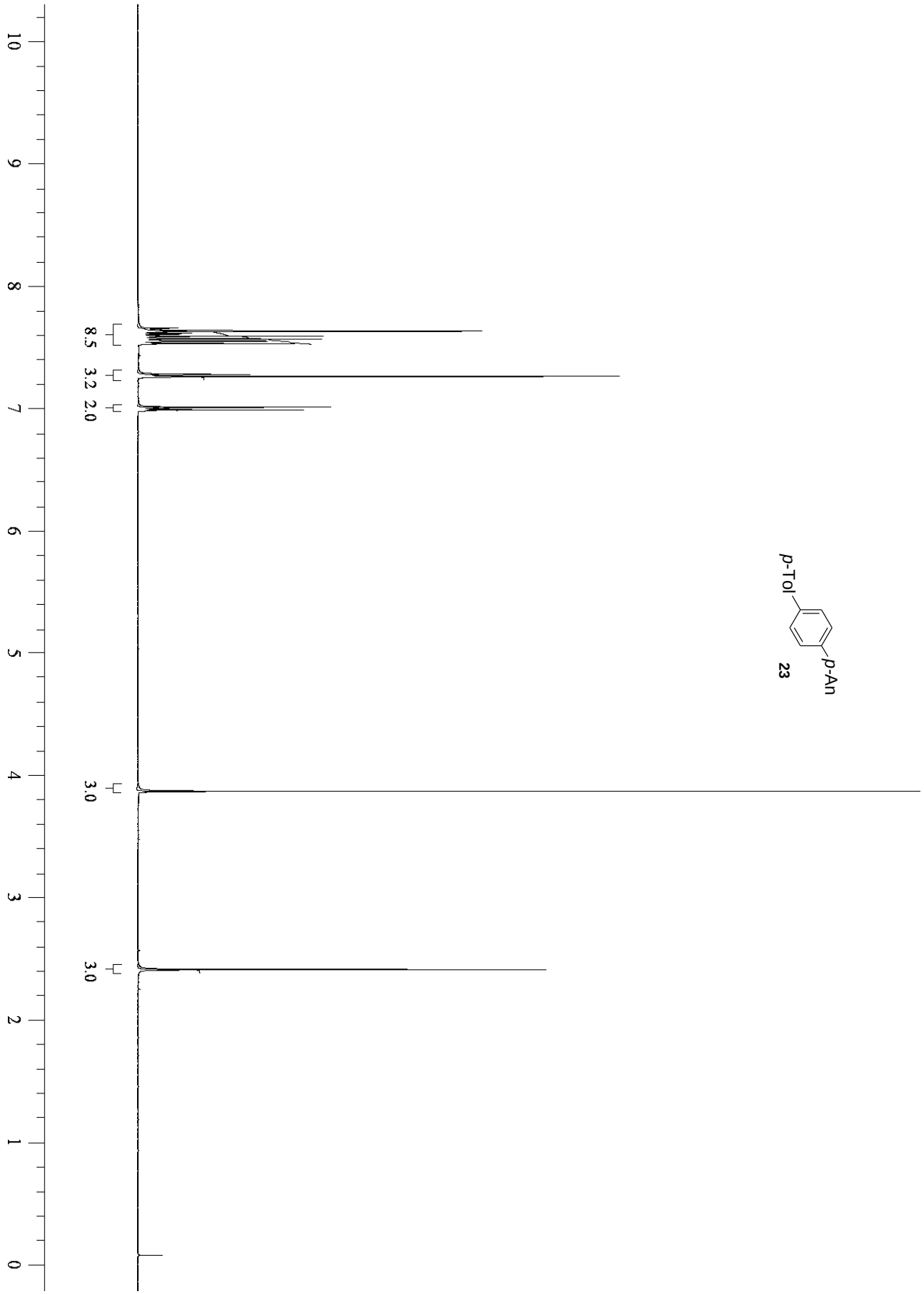
76.998
76.680
55.355
p-An
Ph
22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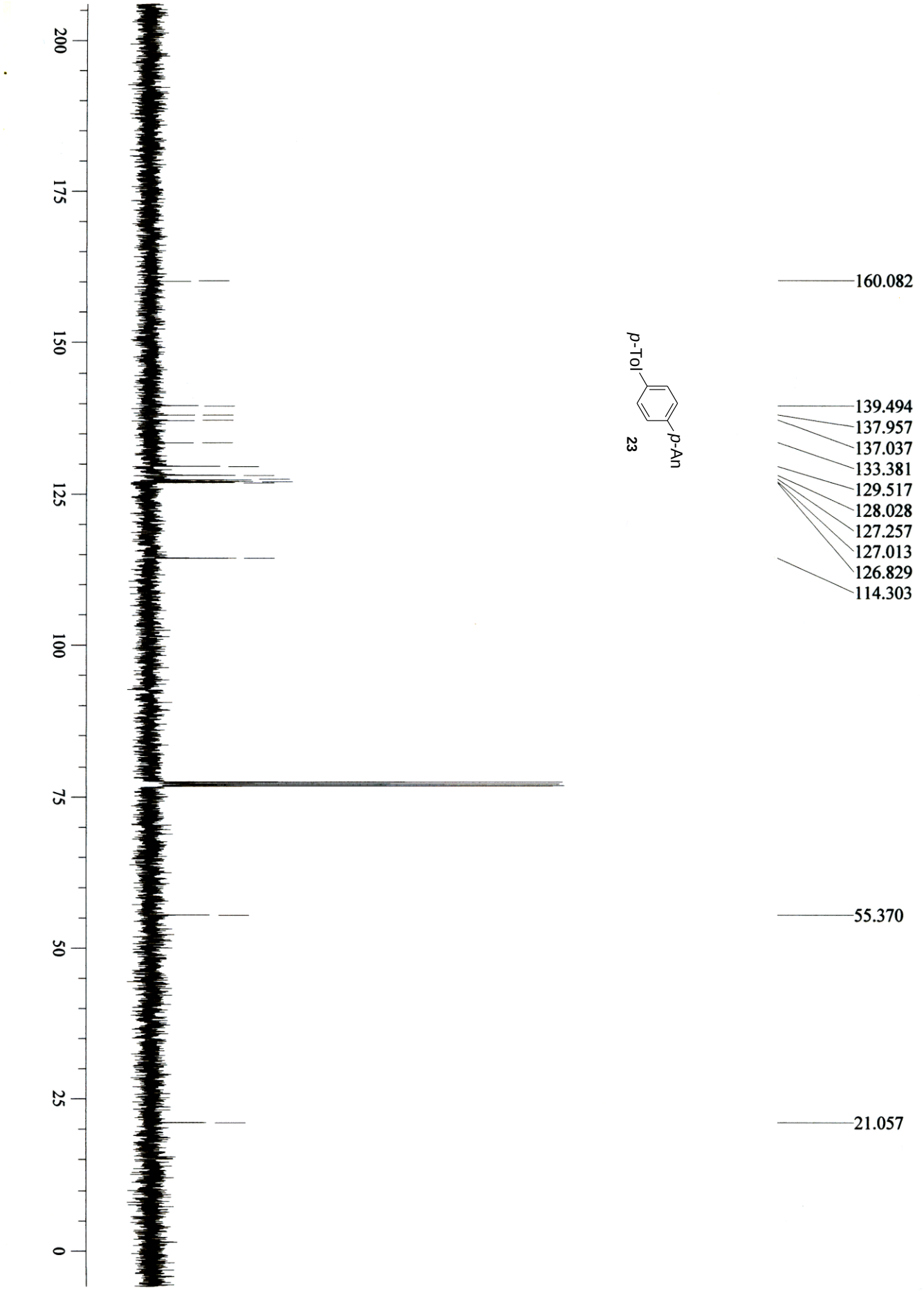
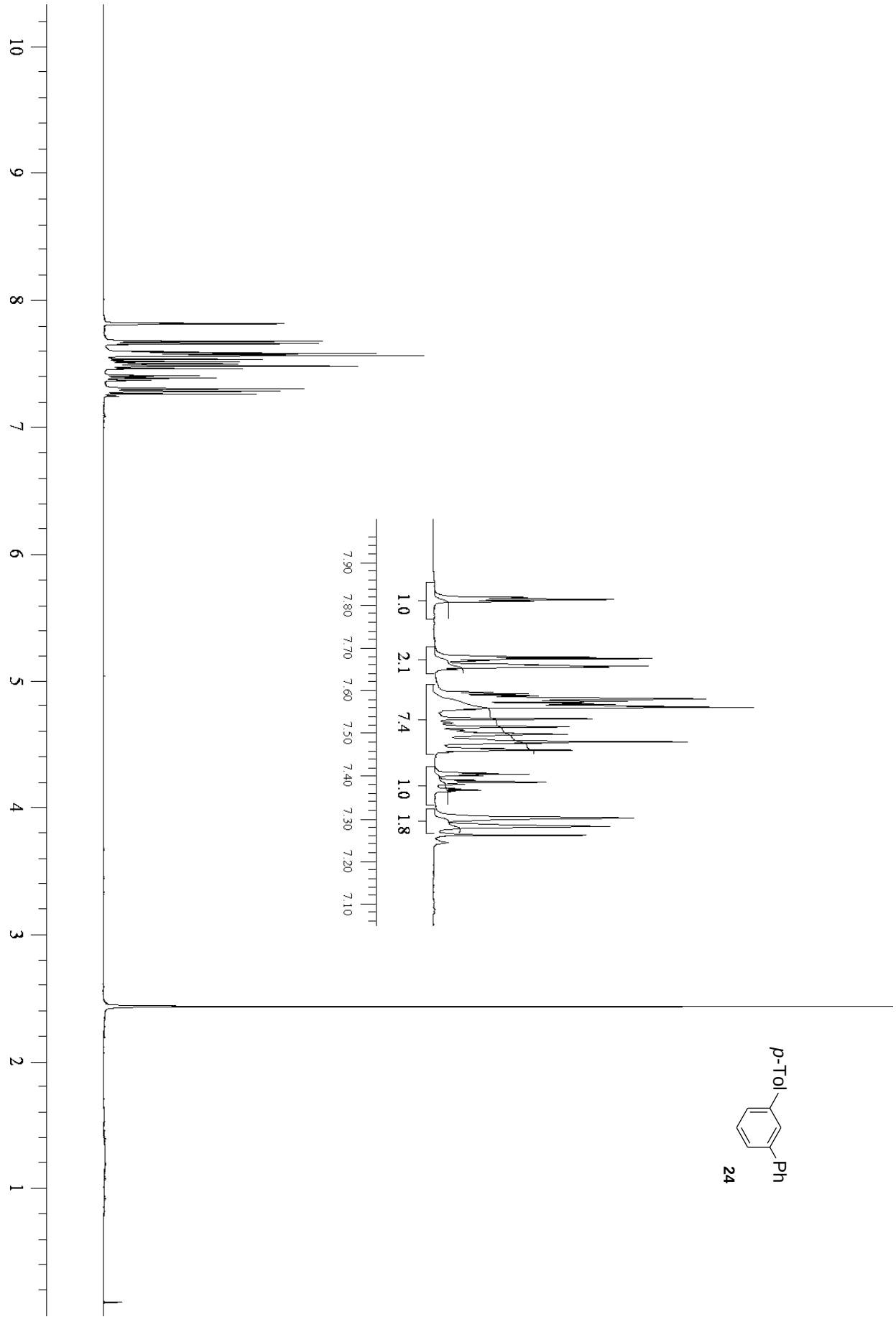
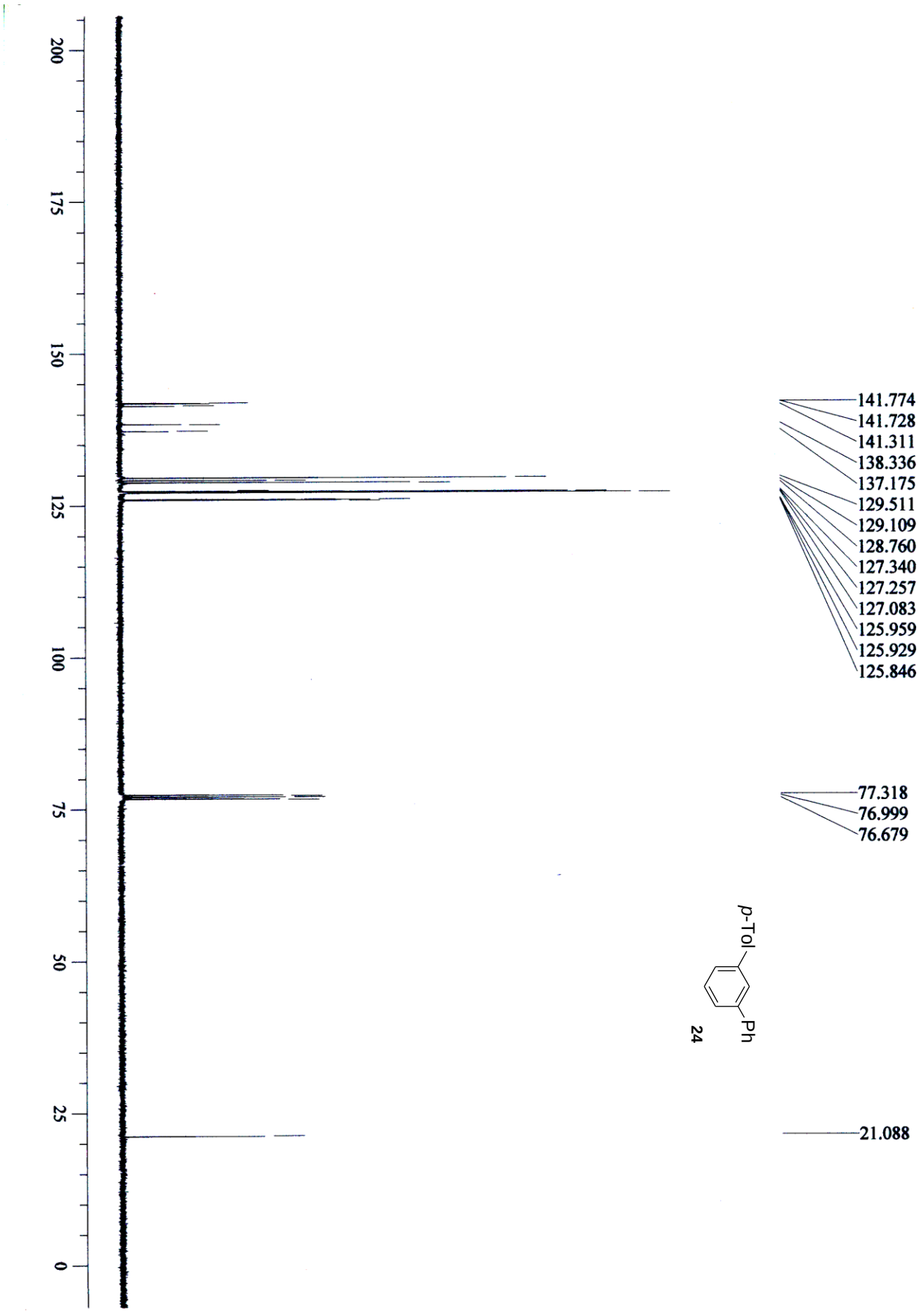
3.2
2.0
3.0
3.0
p-Tol
p-An
23



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128.760
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76.679
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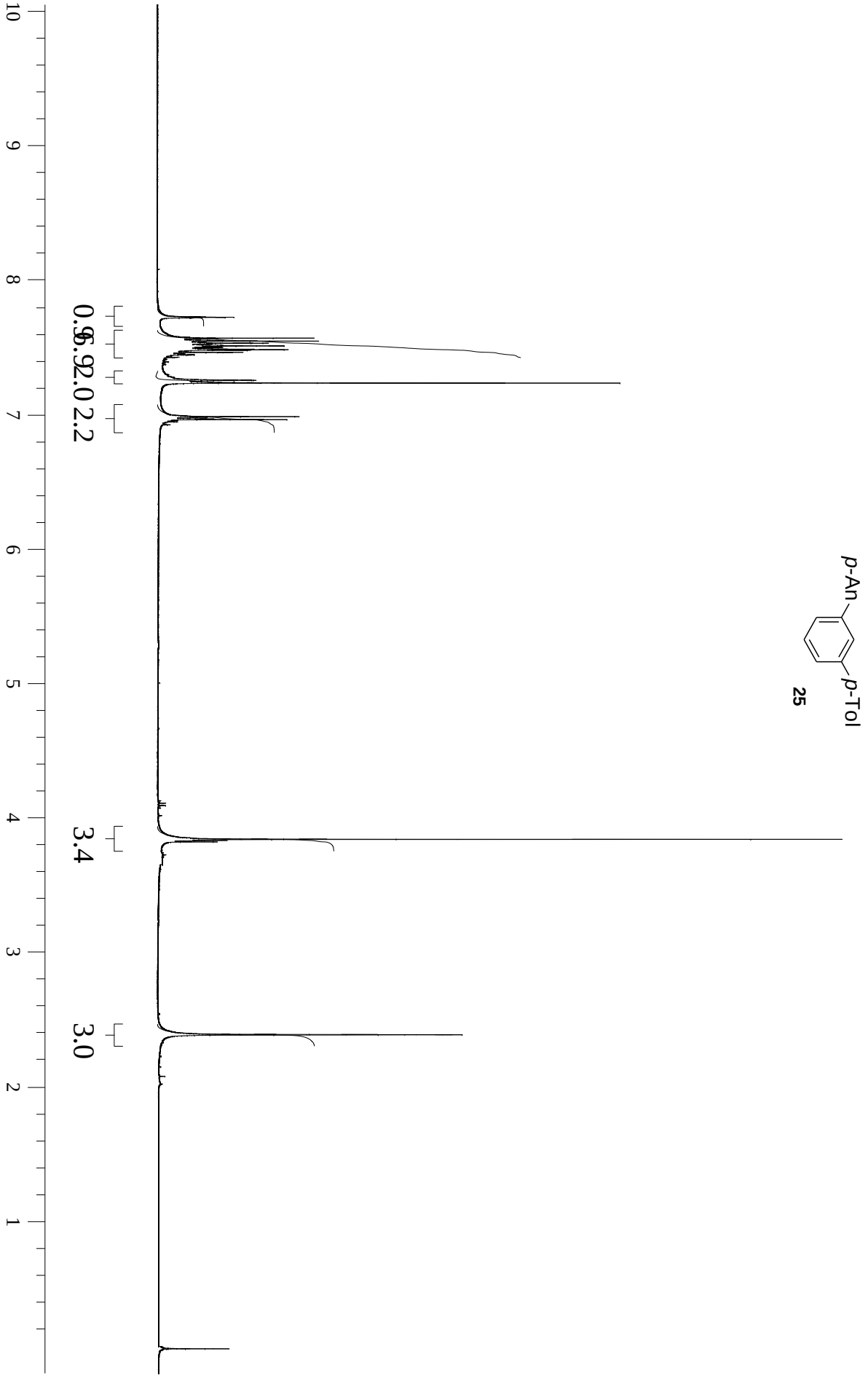
p-Tol
Ph
24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6.9
2.0
2.2
3.4
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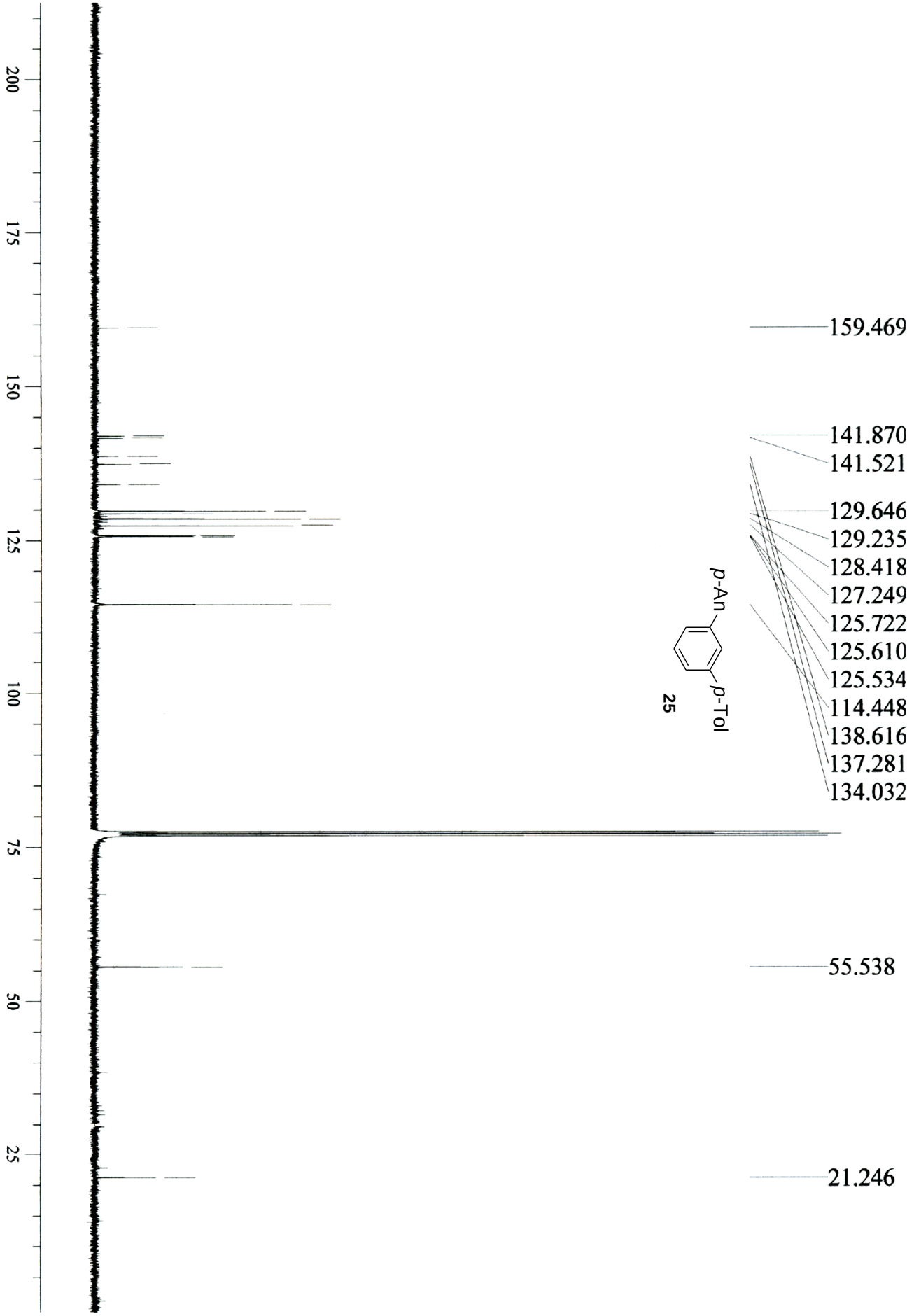
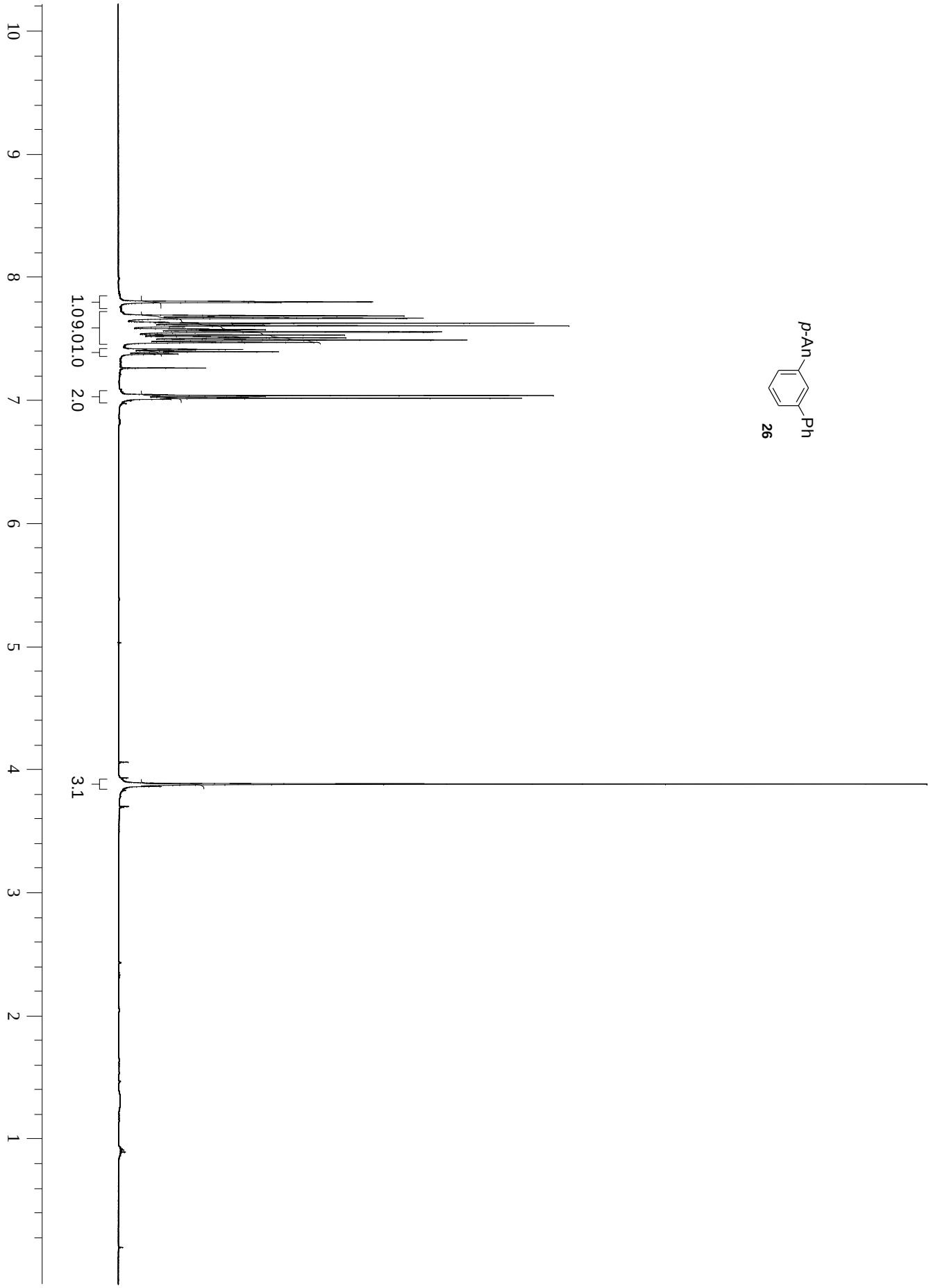
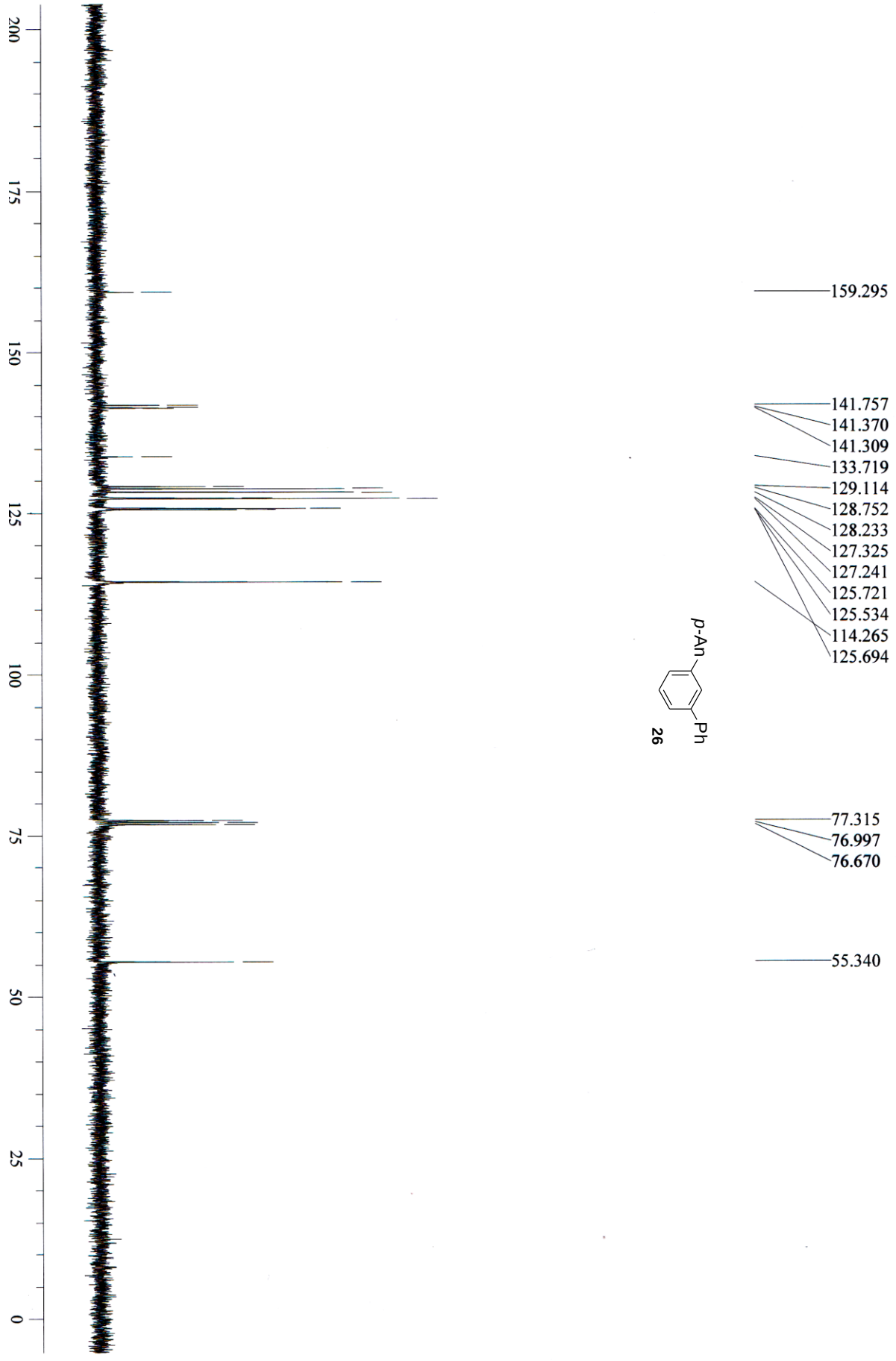
p-An
p-Tol
25



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128.233
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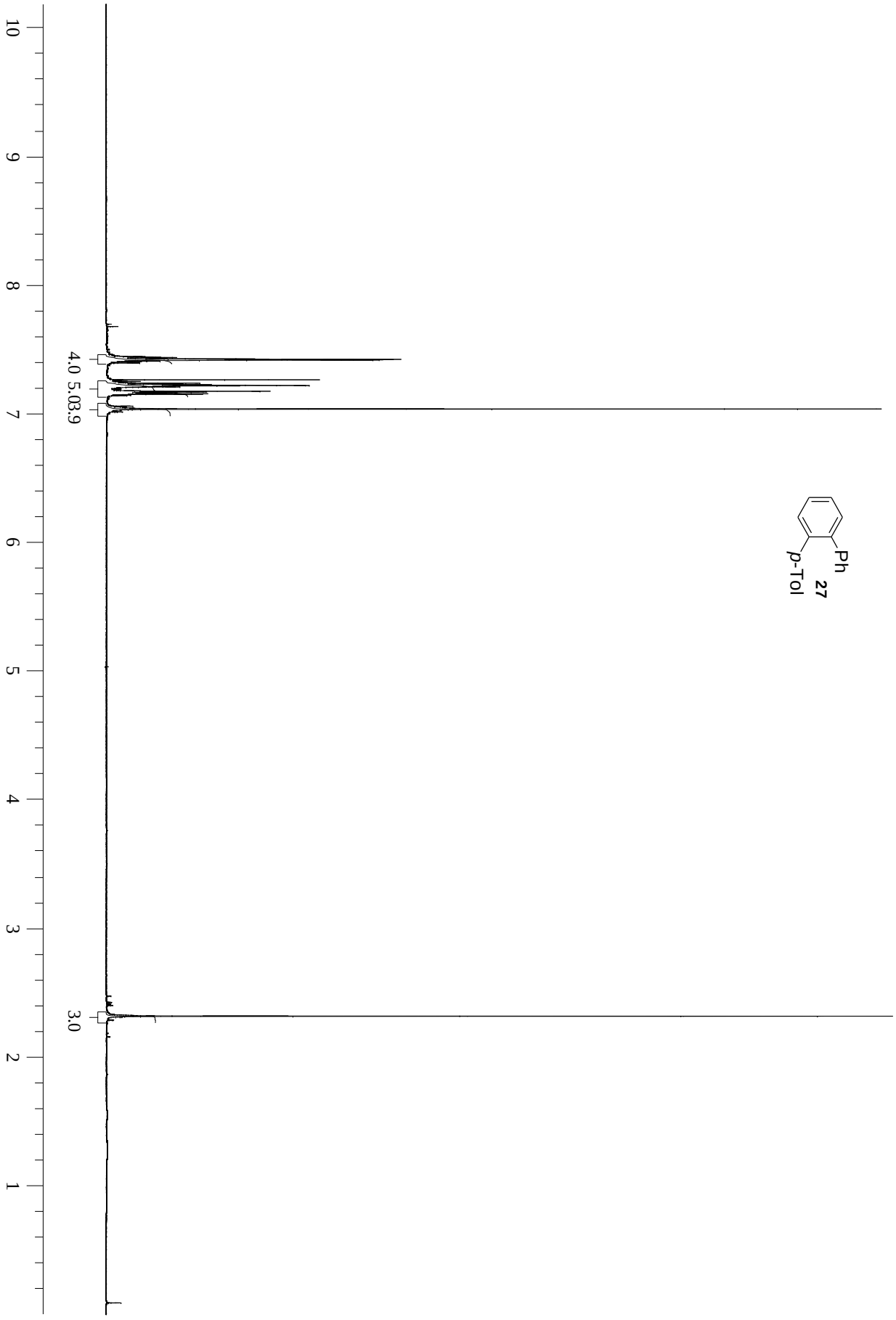
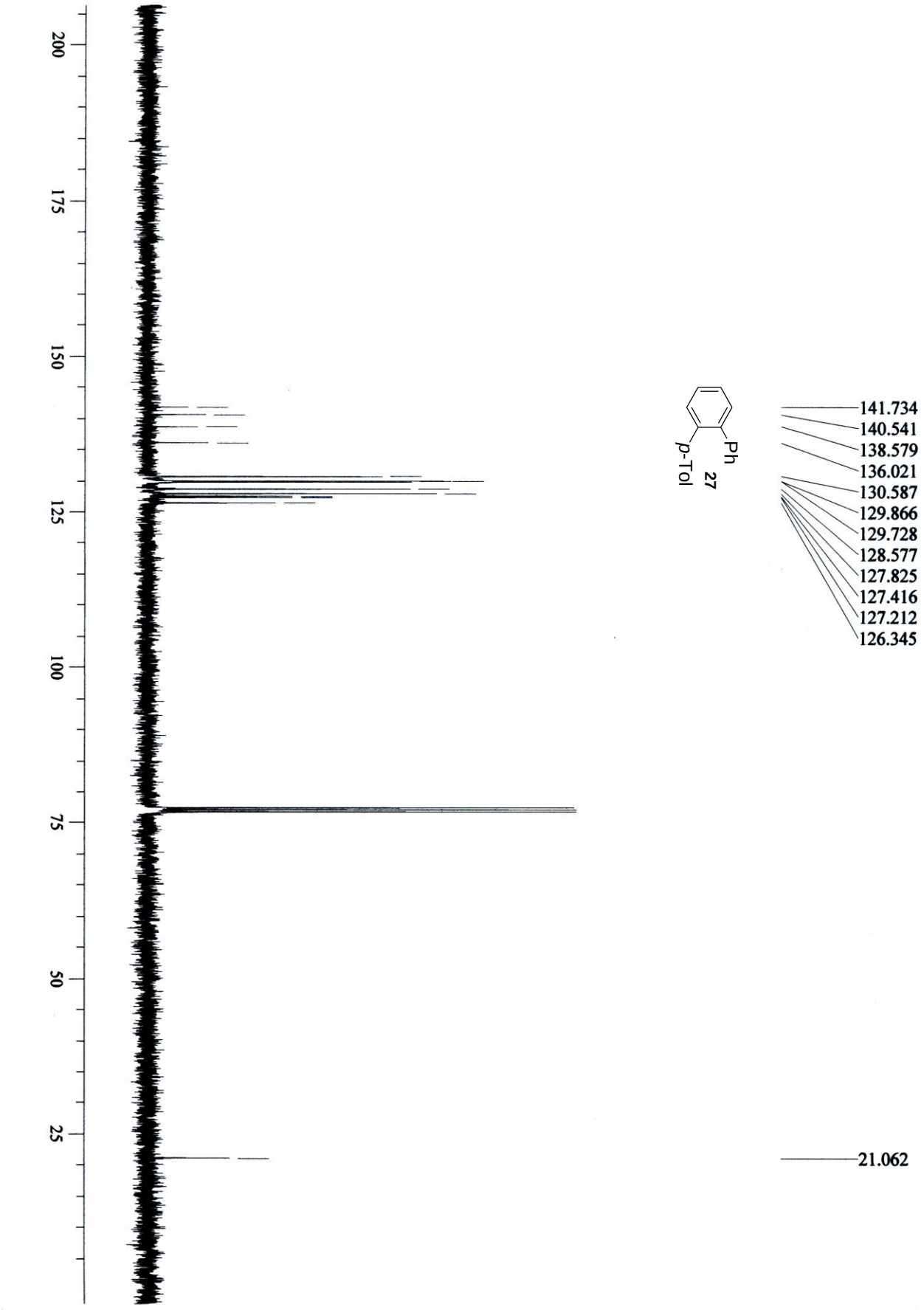
p-An
Ph
26




200
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100
75
50
25
Ph
p-Tol
27
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138.579
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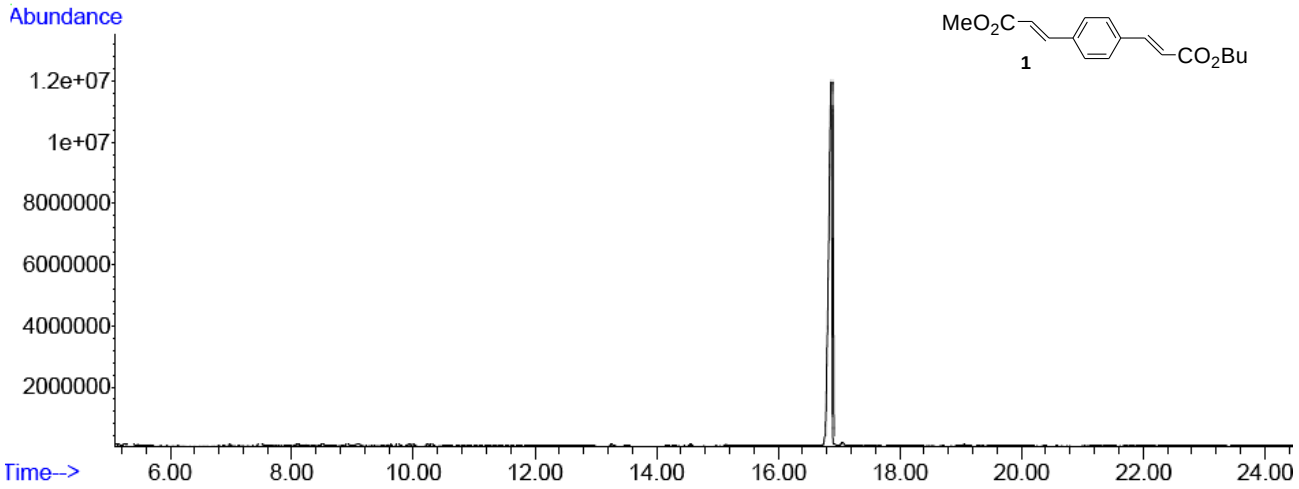
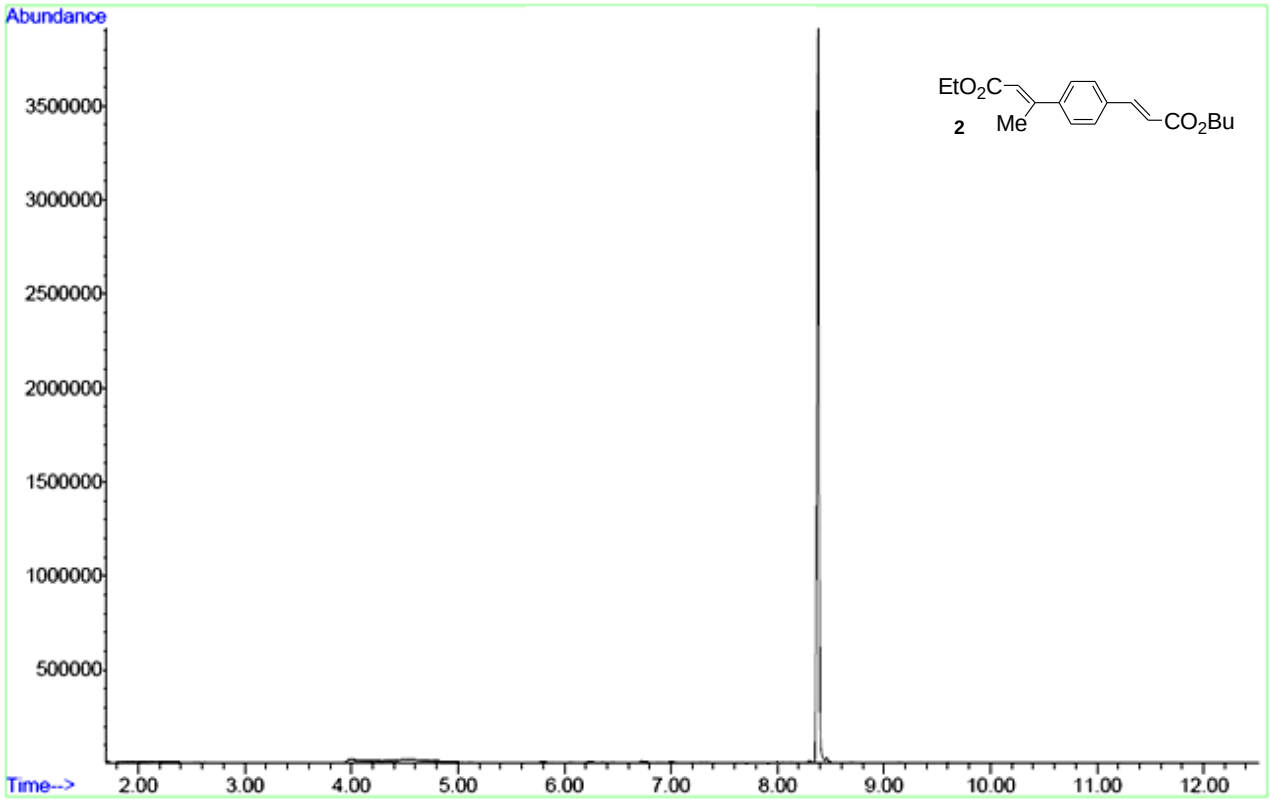
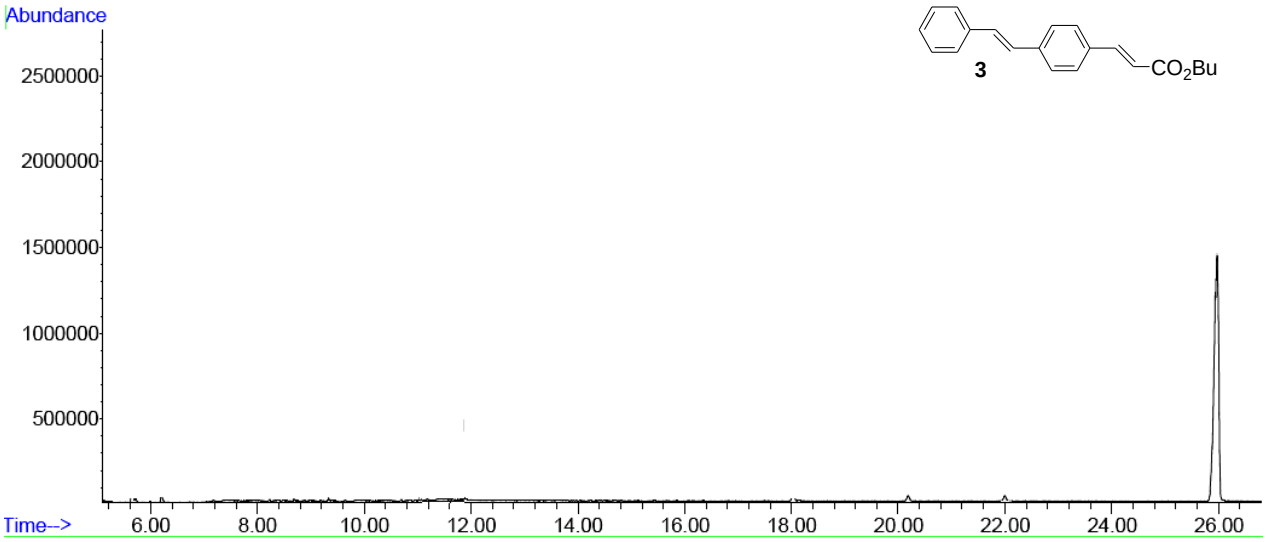
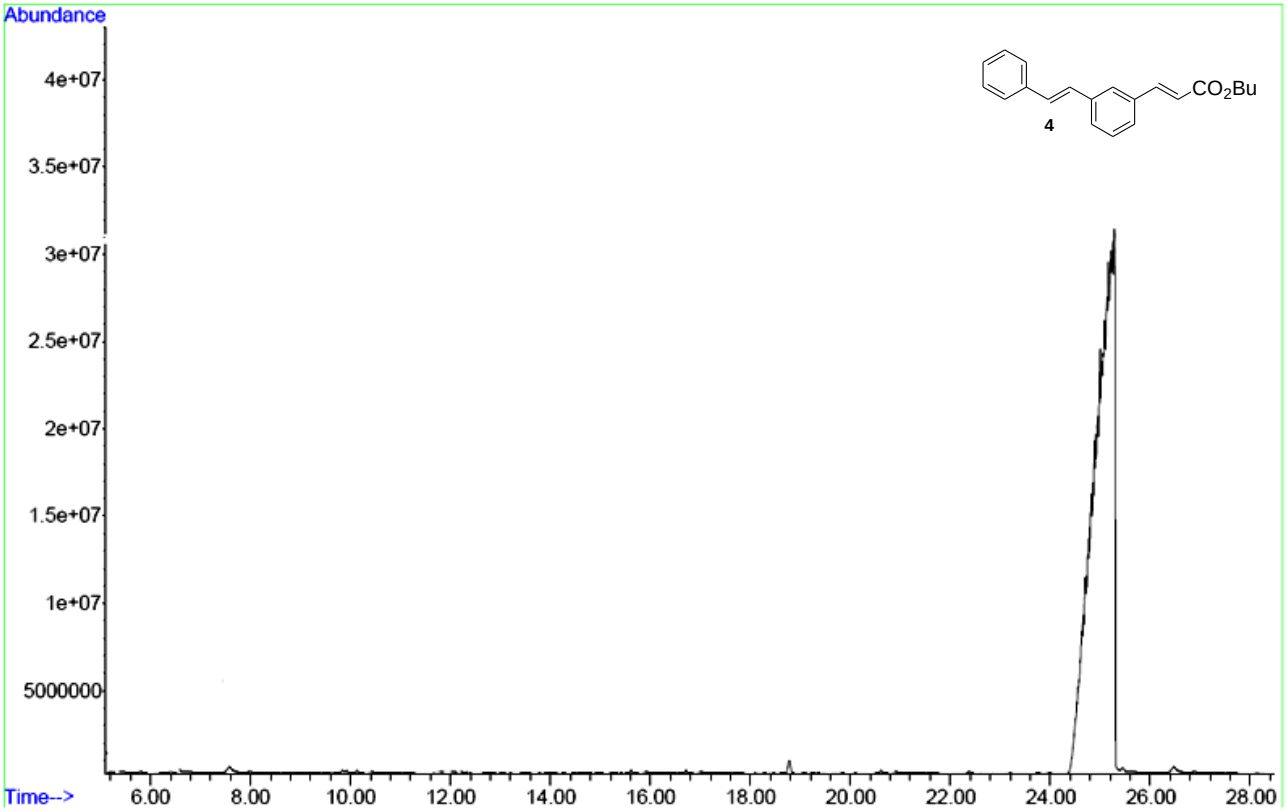
127.416
127.212
126.345
21.062

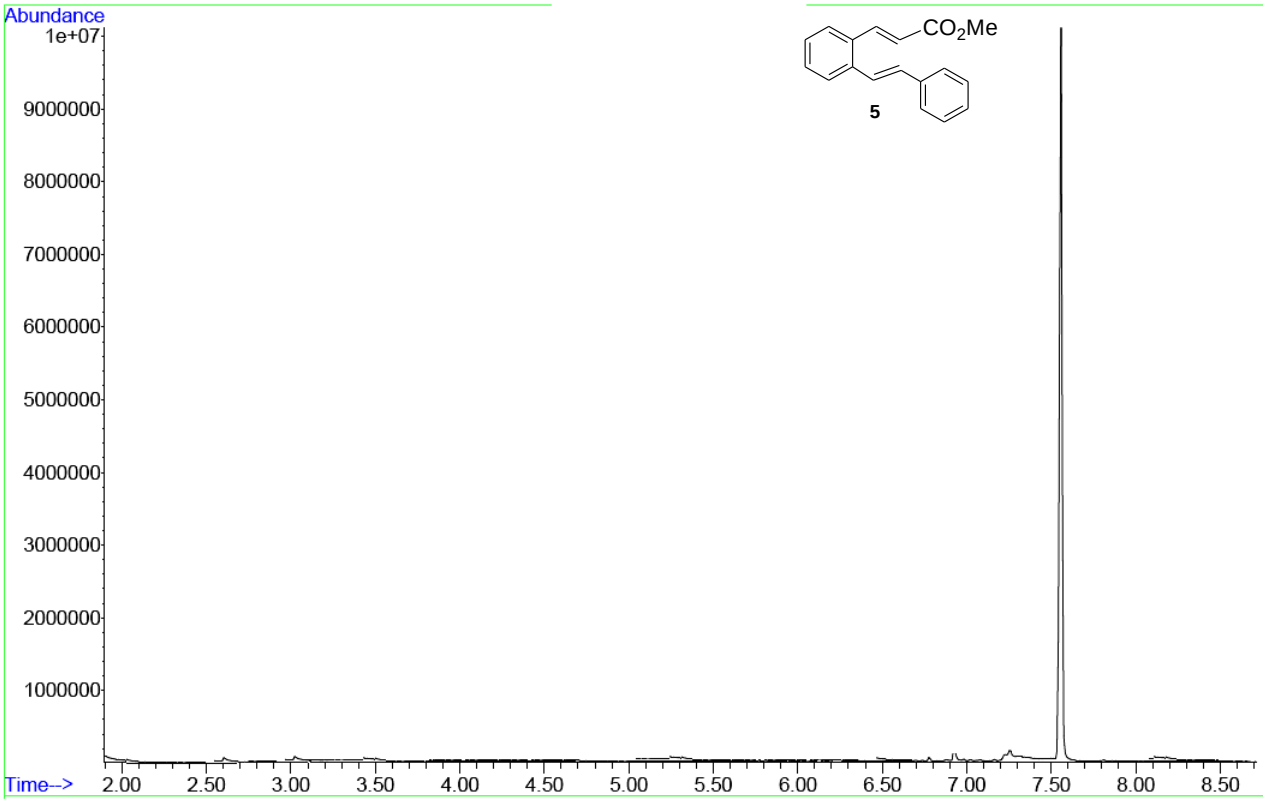
GLC chromatograms of the reaction products:







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8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
Time-->
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3.00
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4.00
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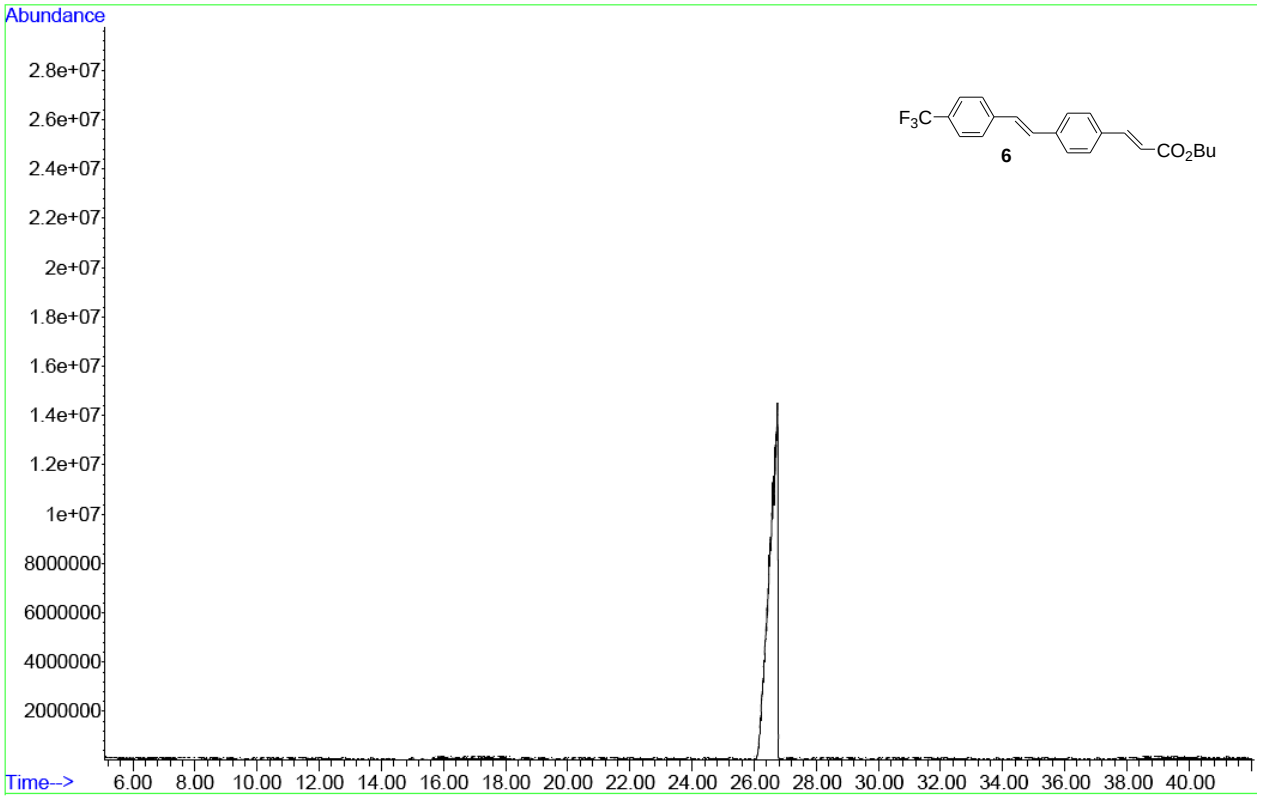
7.50
8.00
8.50
CO2Me
5


Abundance
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2.6e+07
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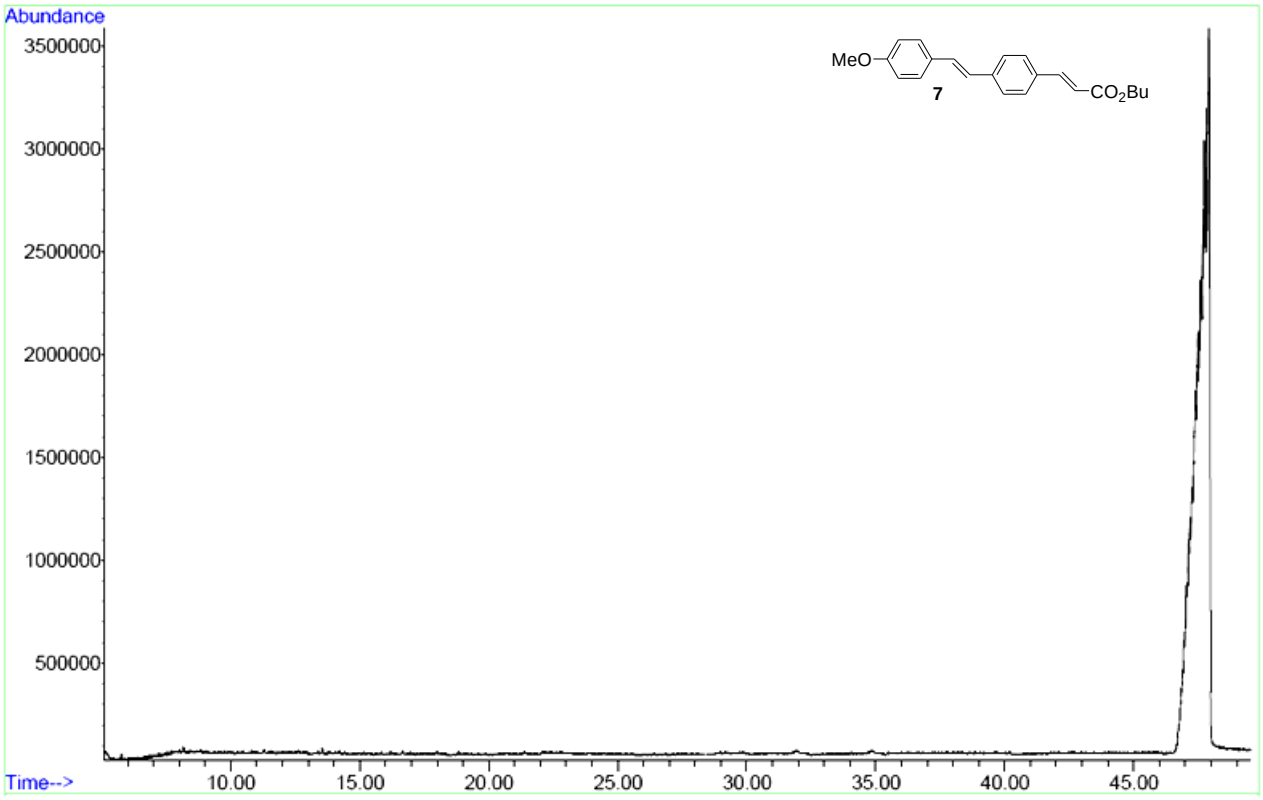
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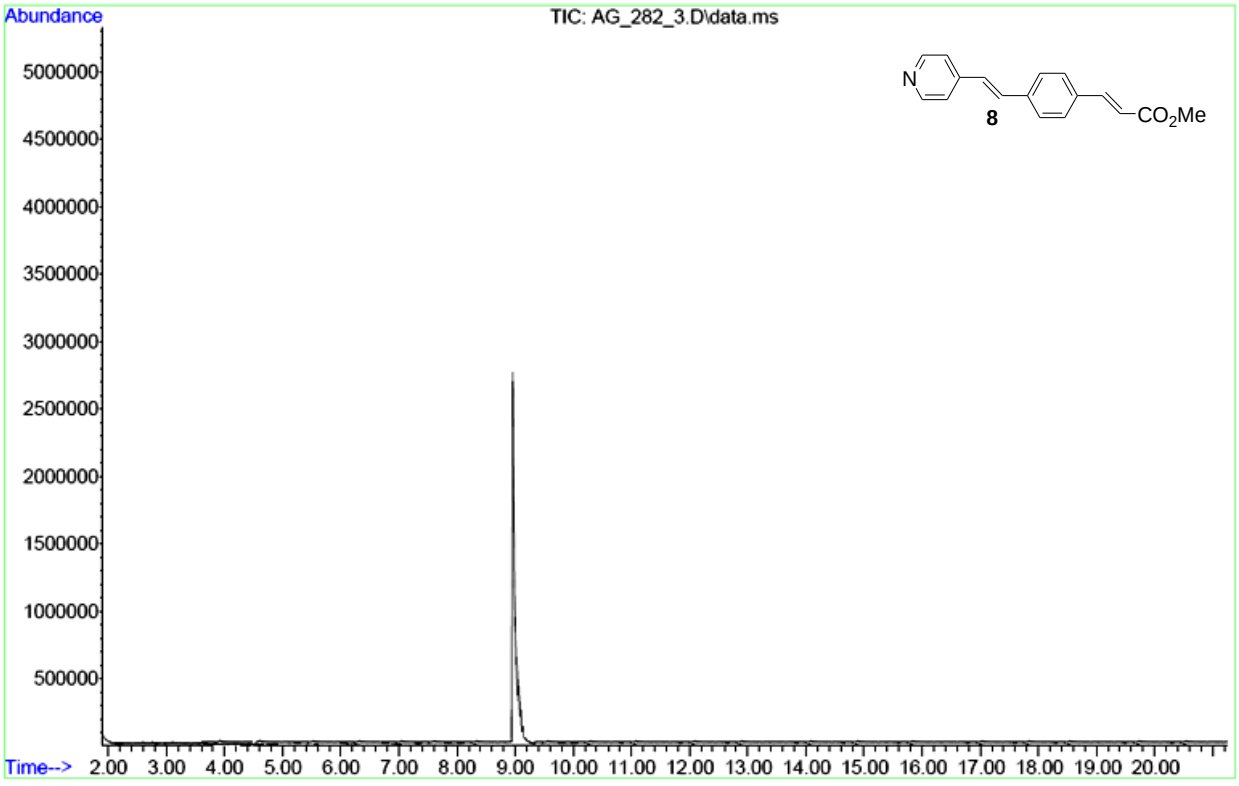
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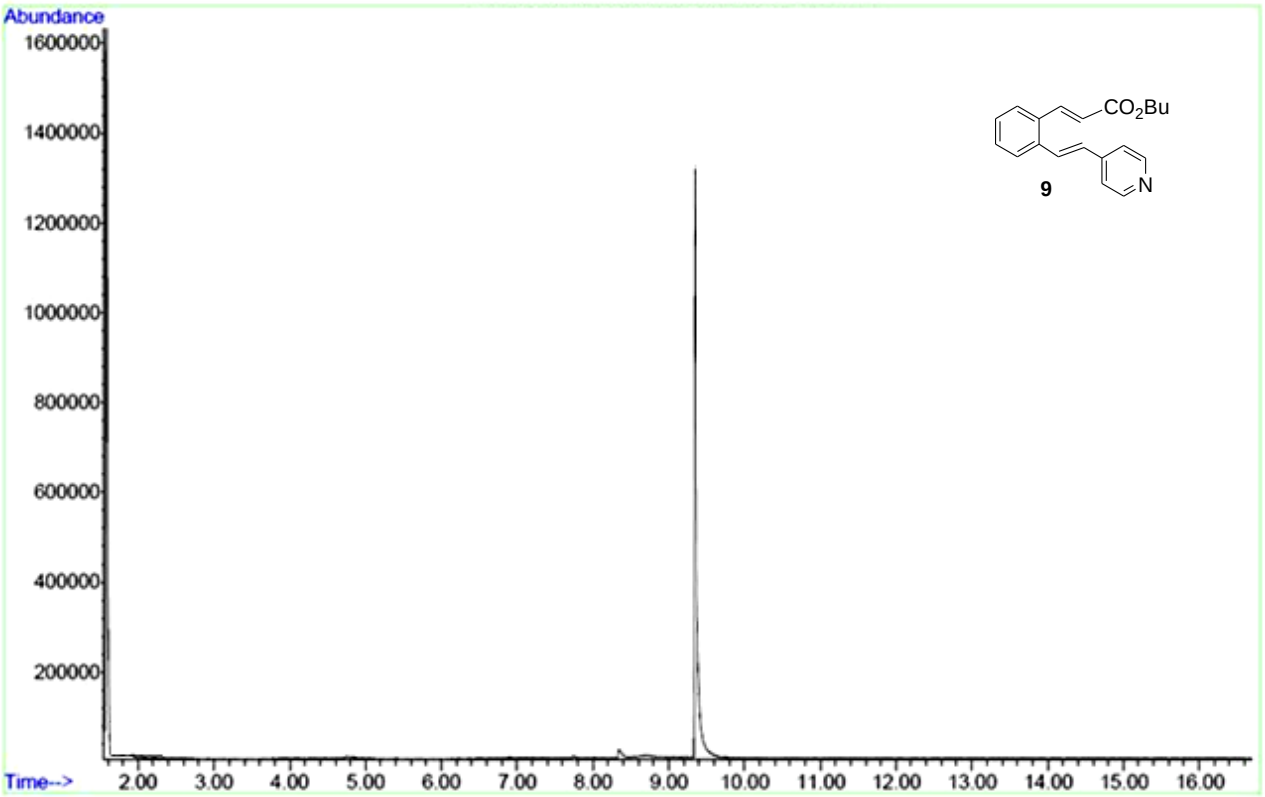
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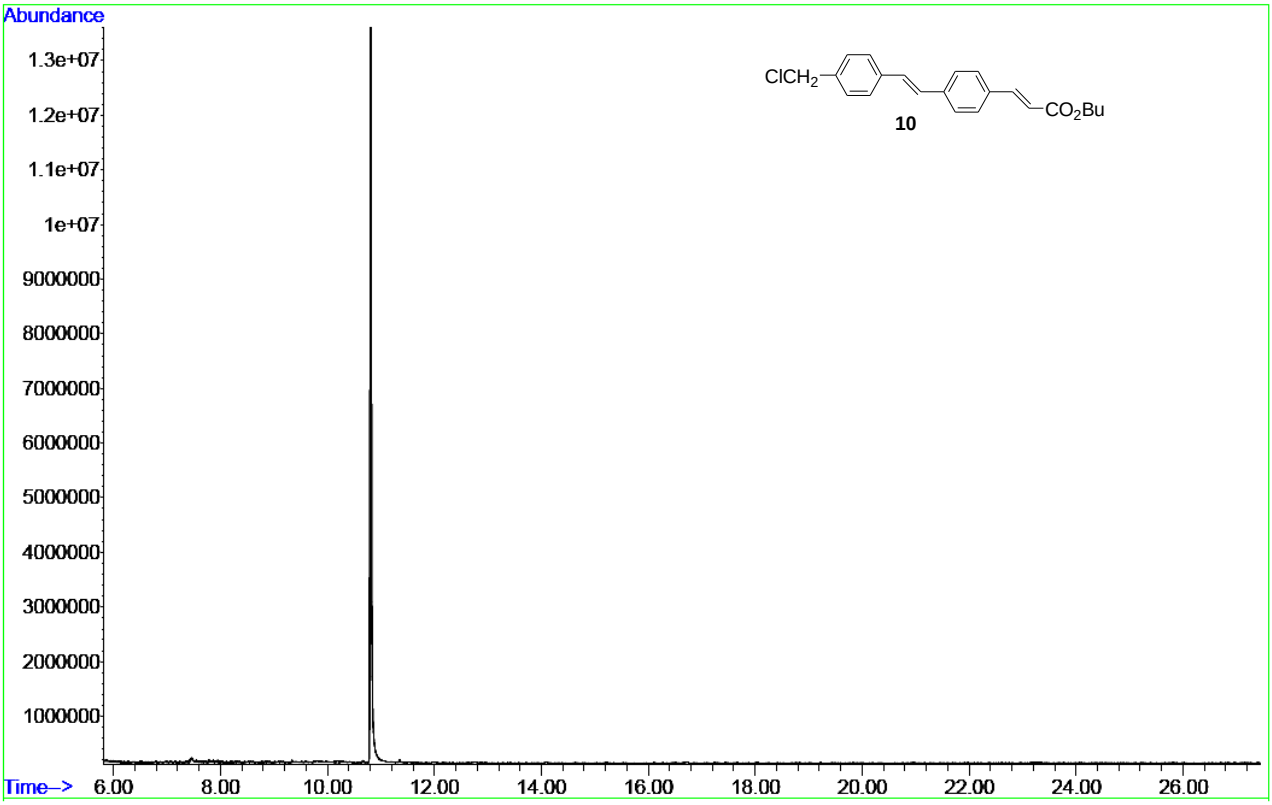
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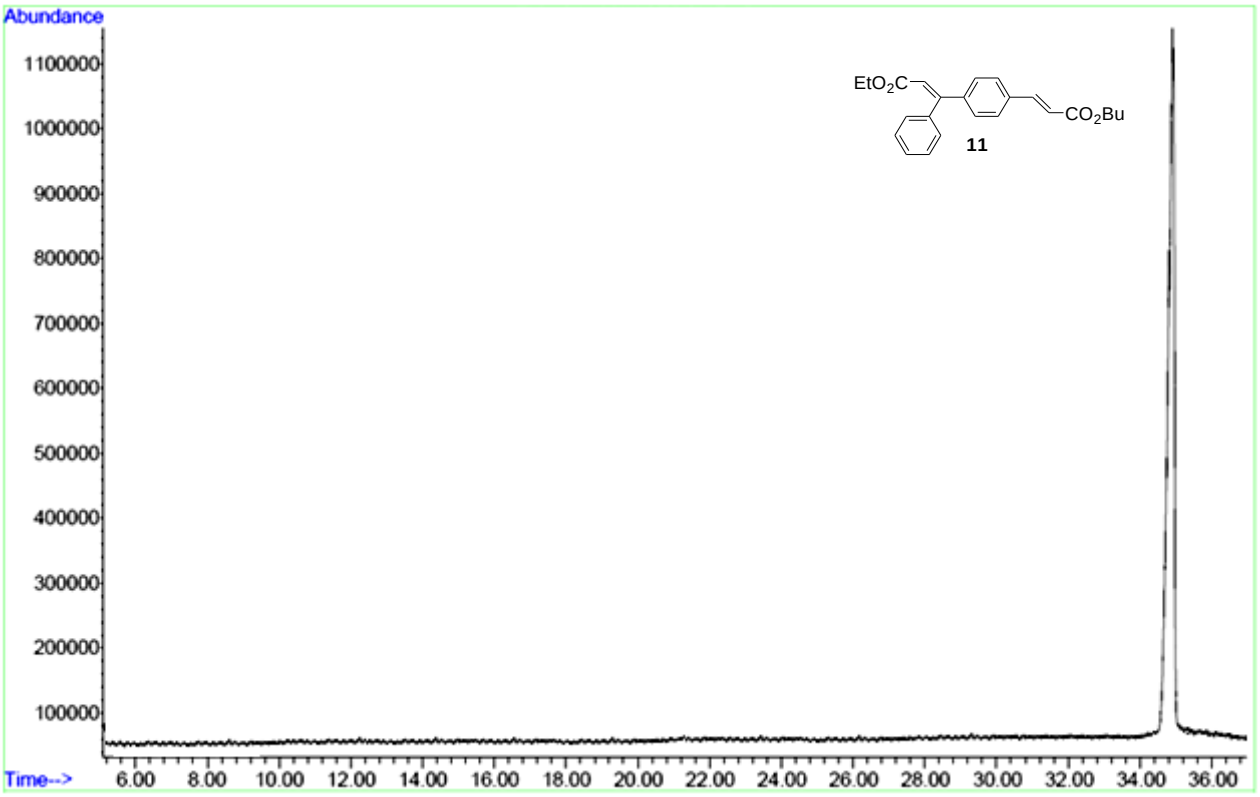
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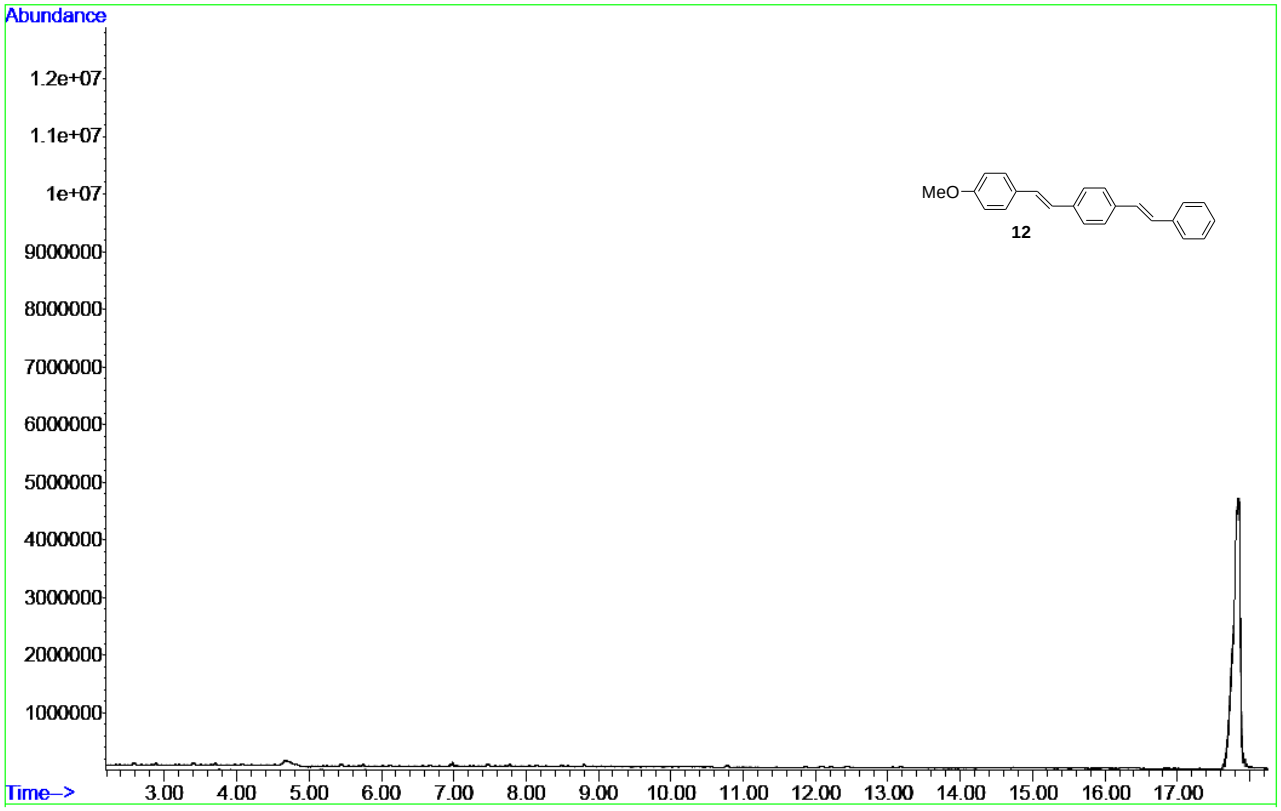
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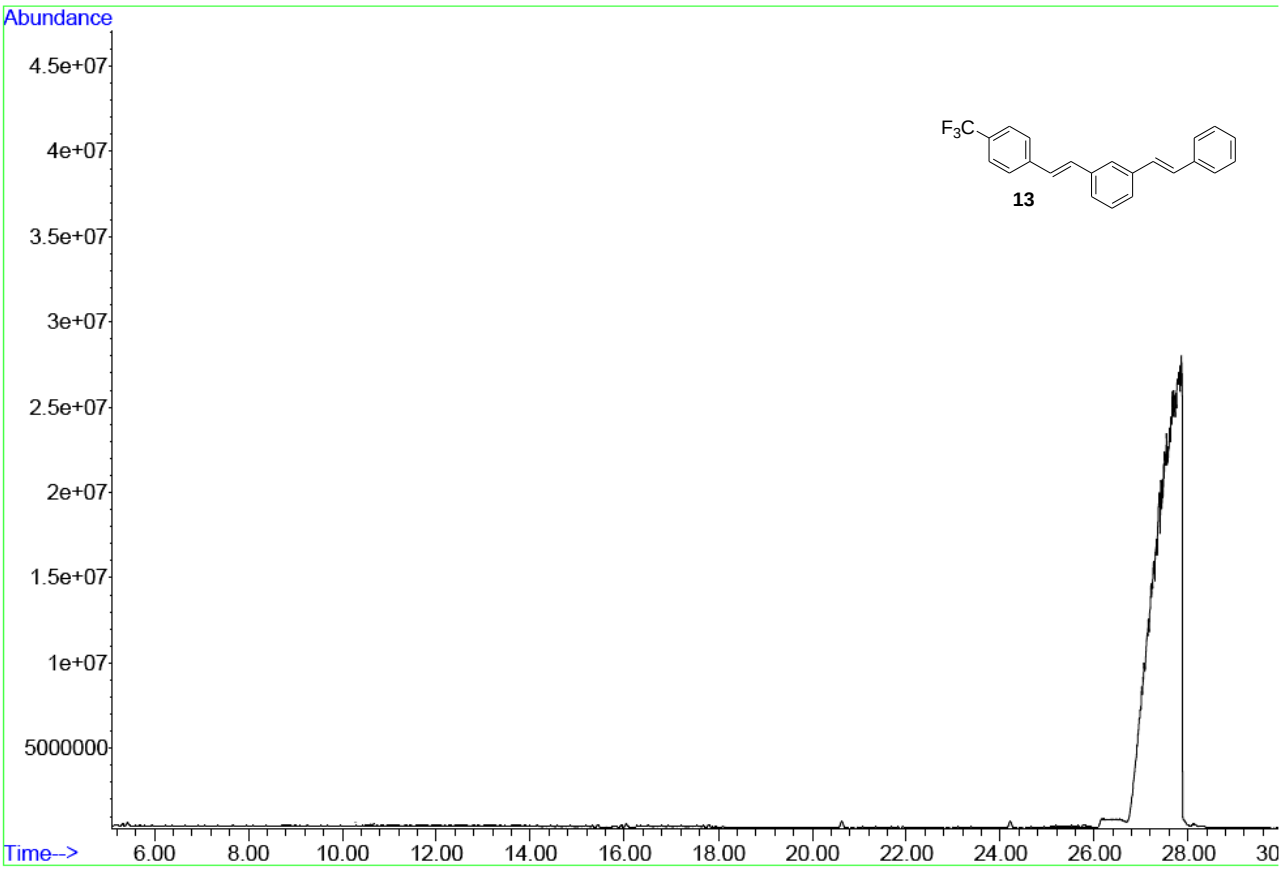
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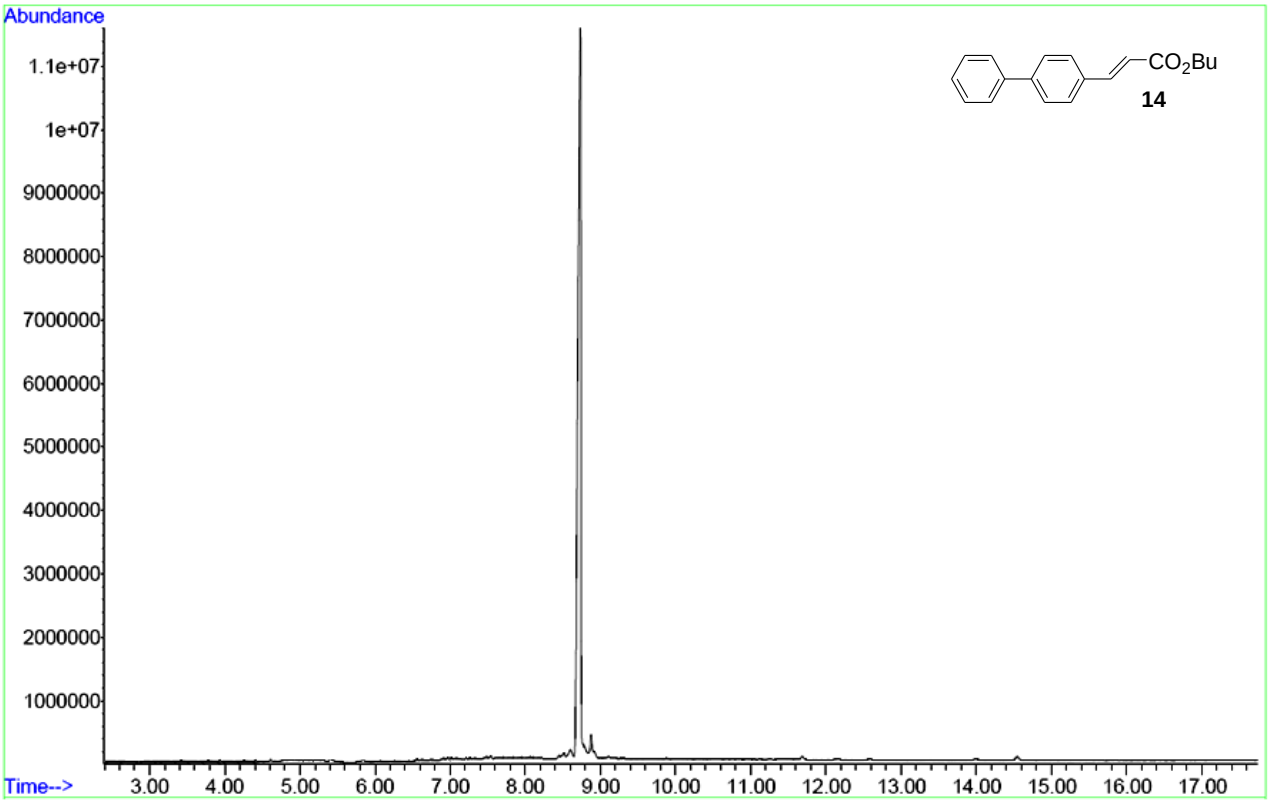
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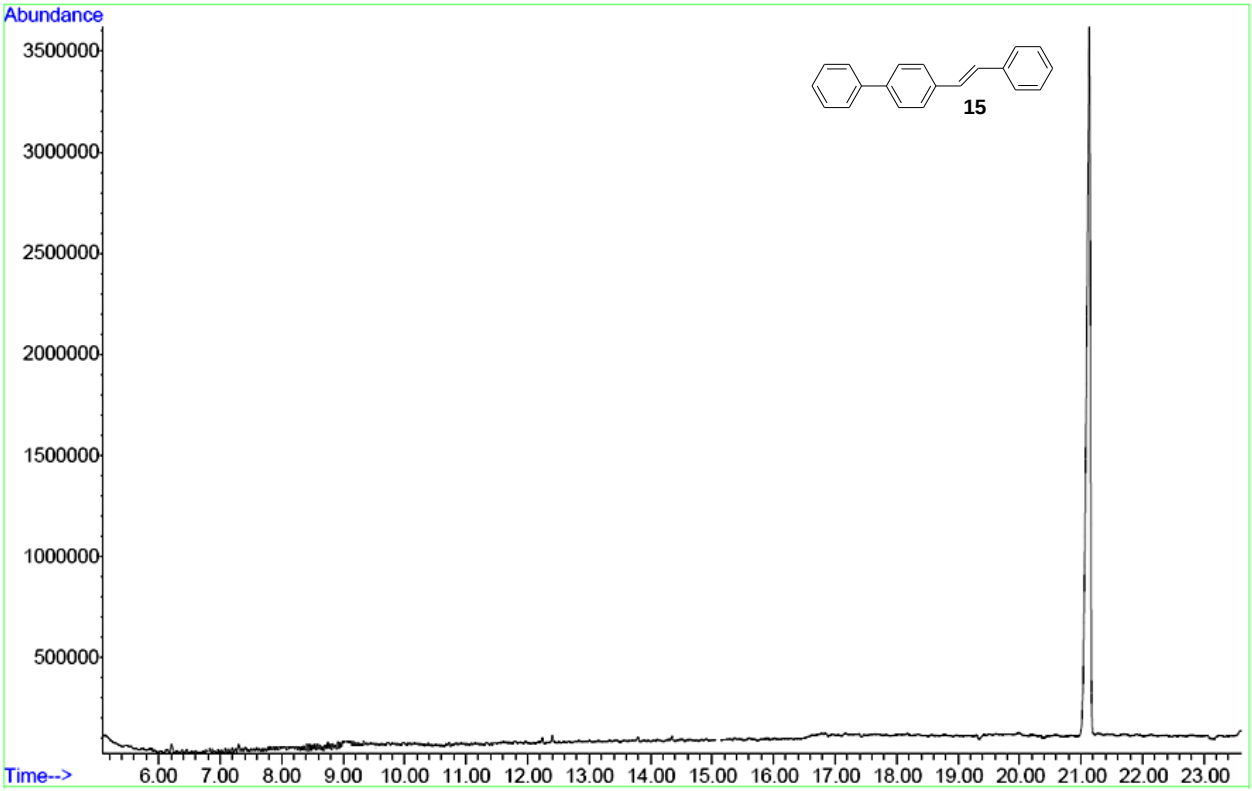
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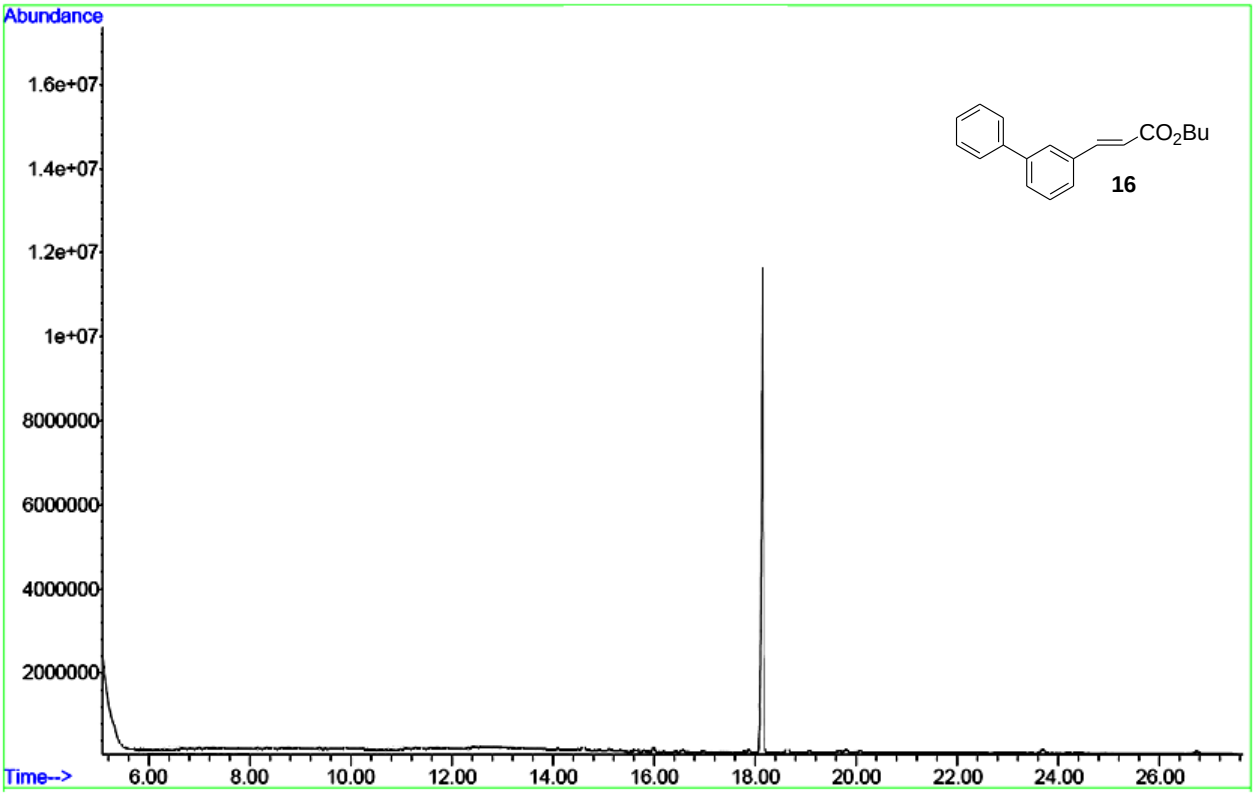
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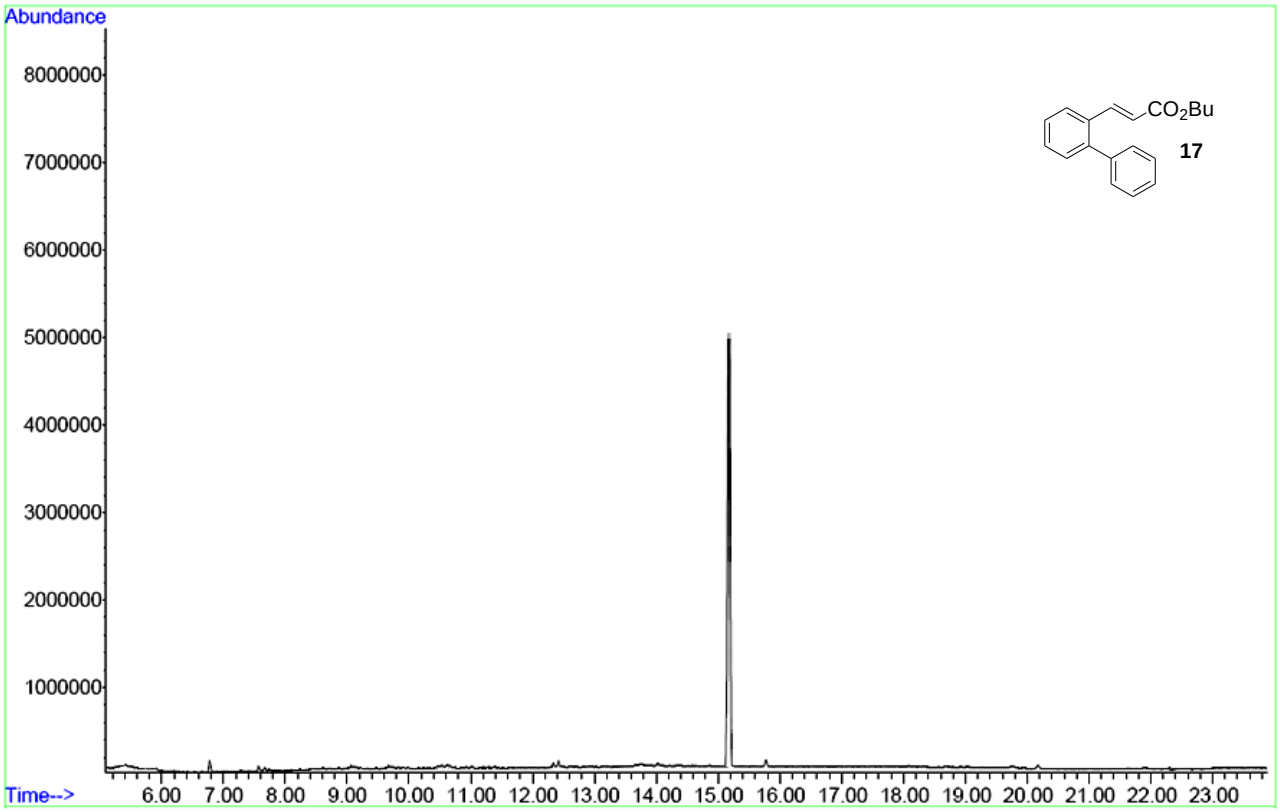

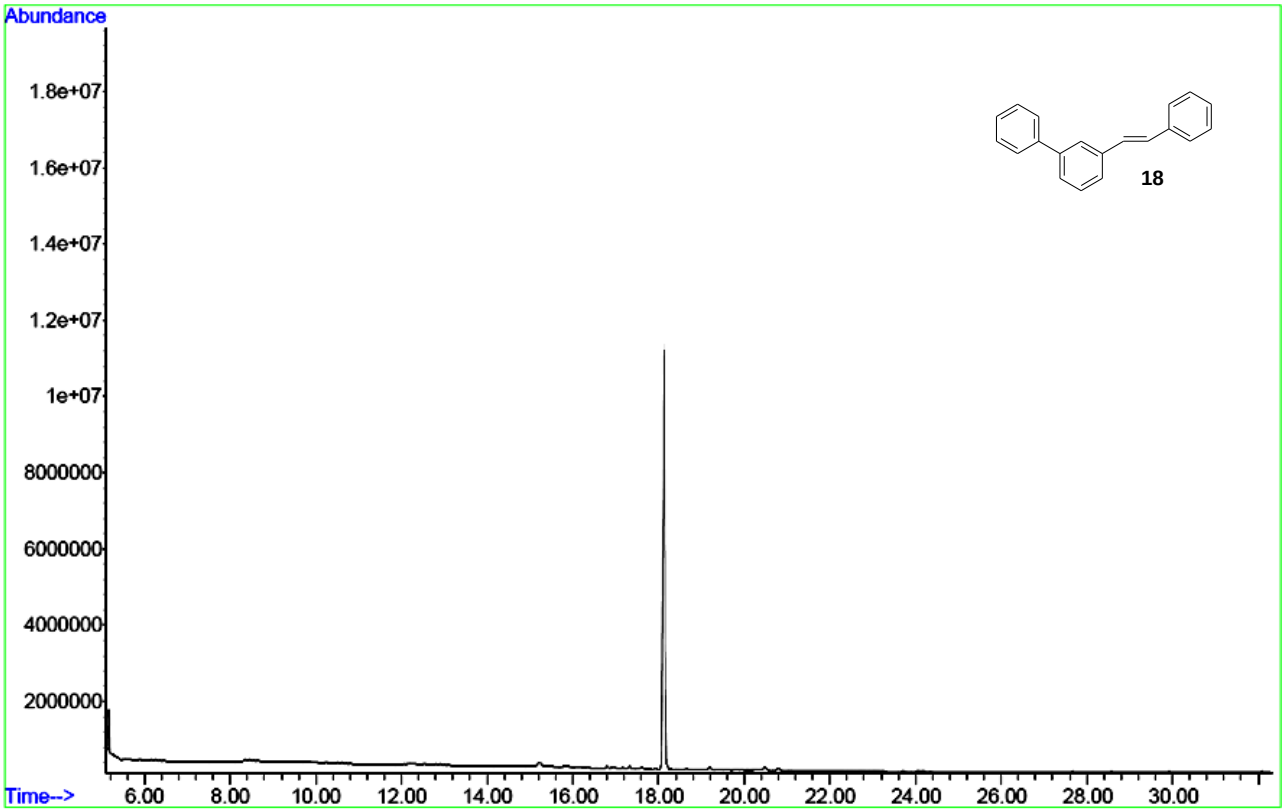

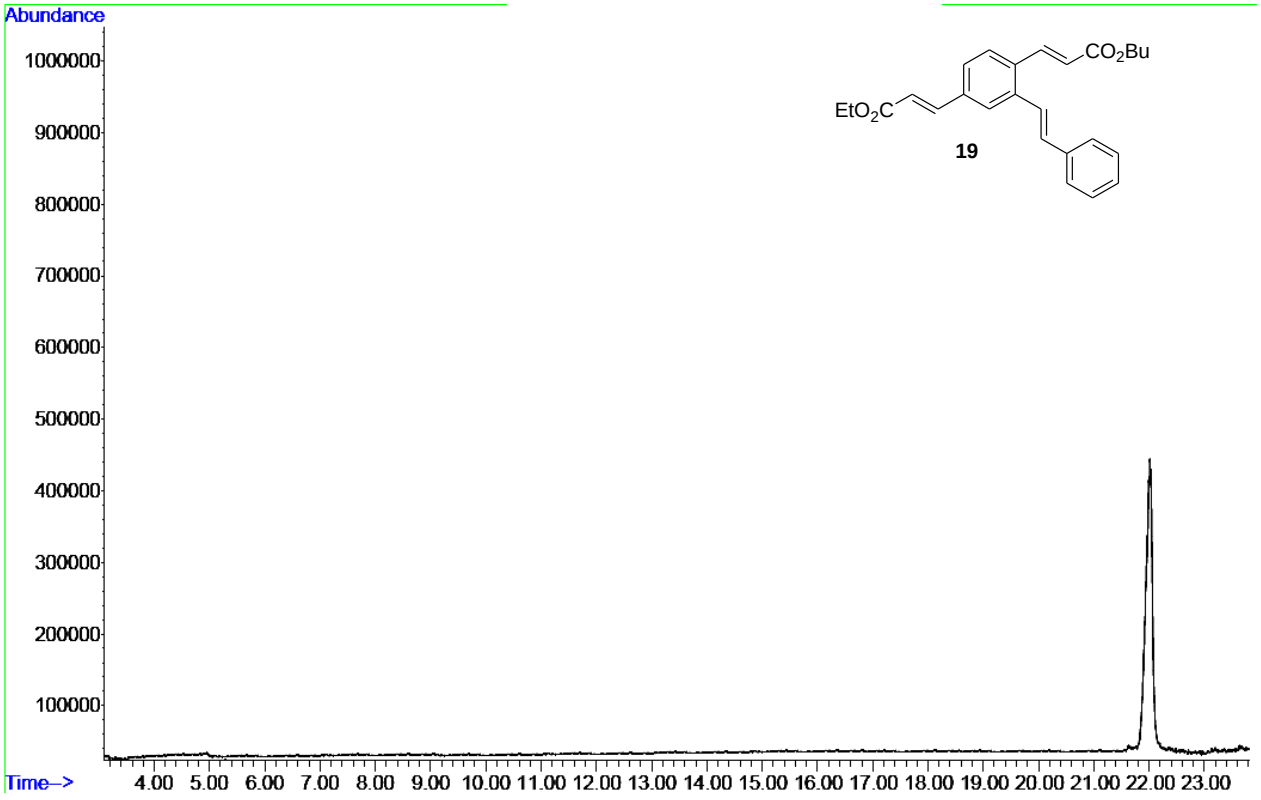
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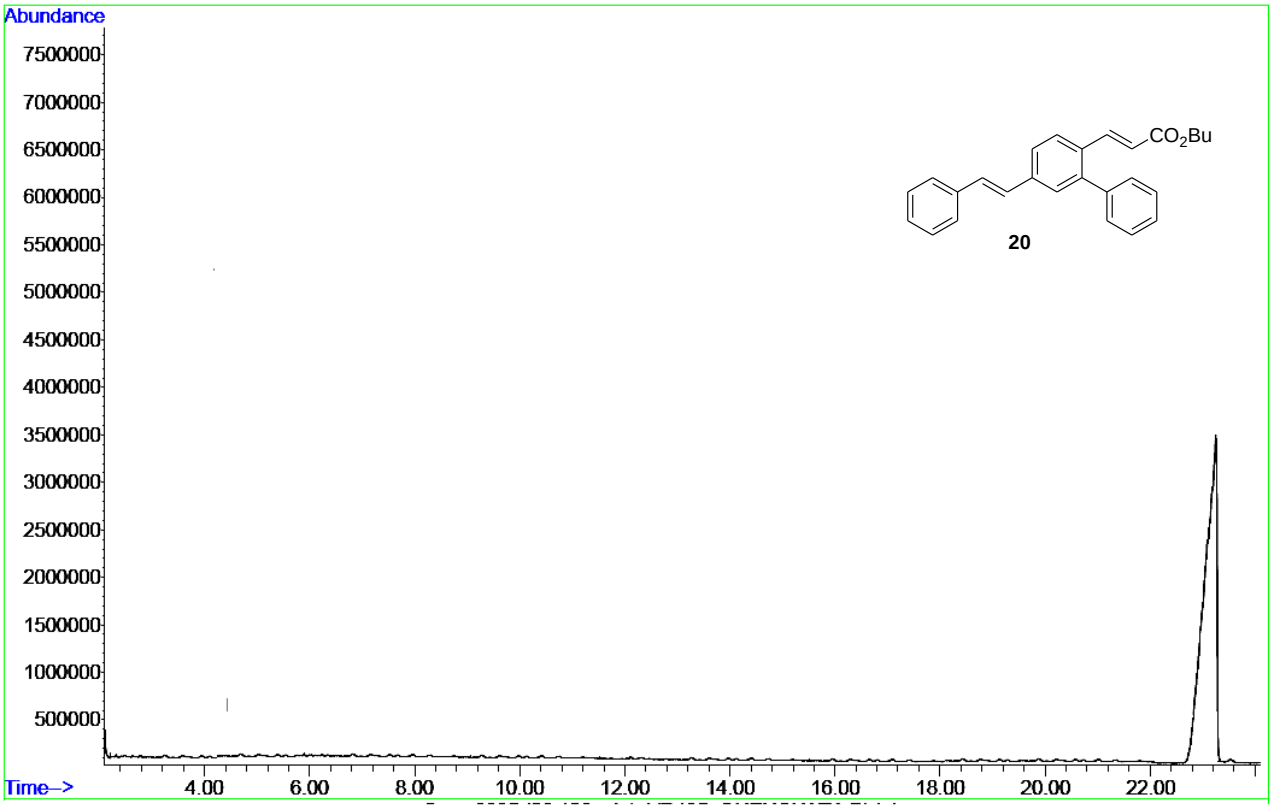
EtO2C
19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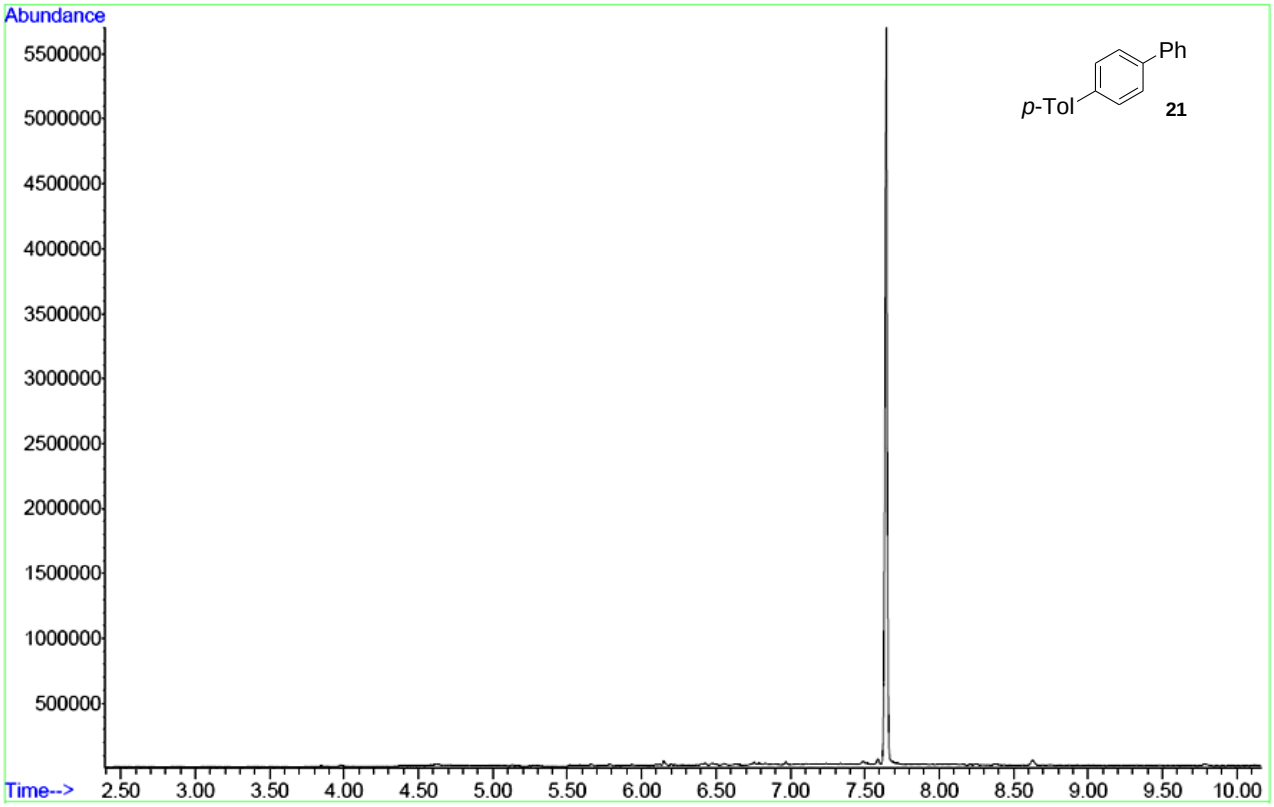

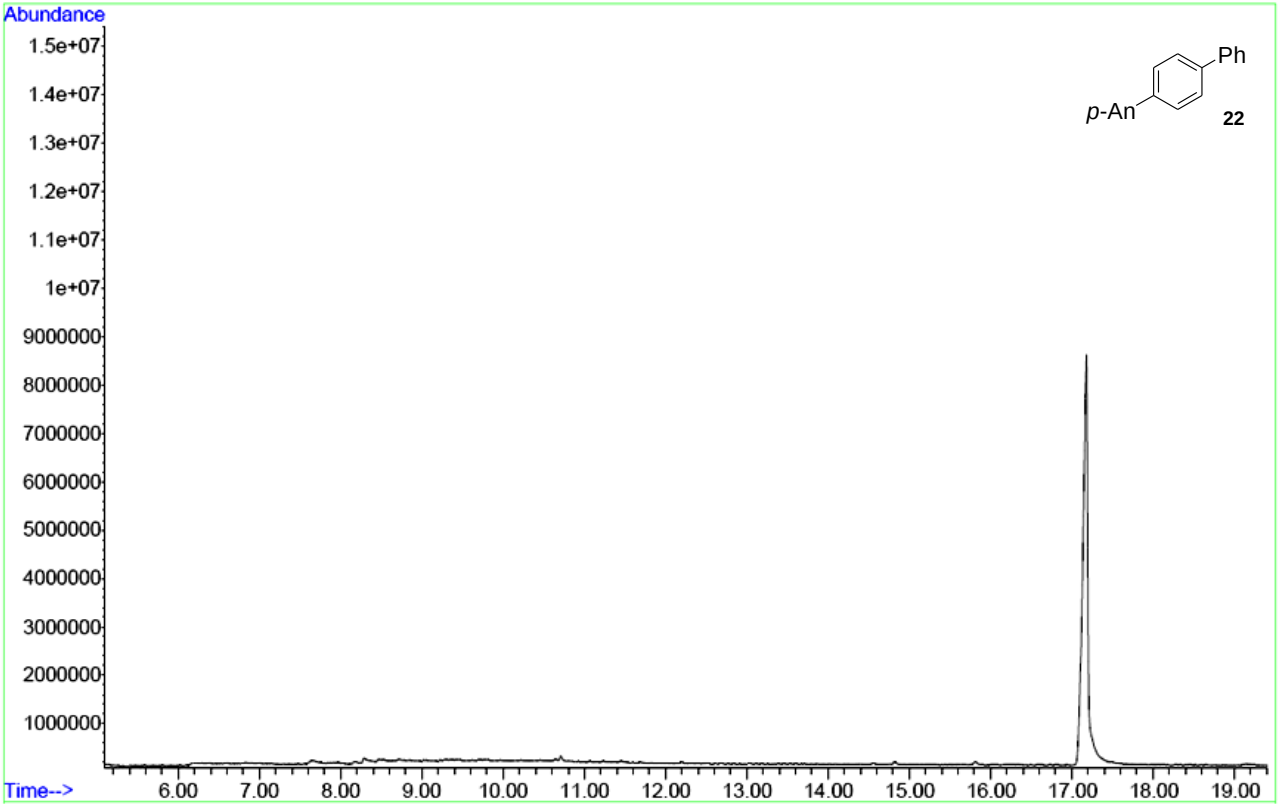

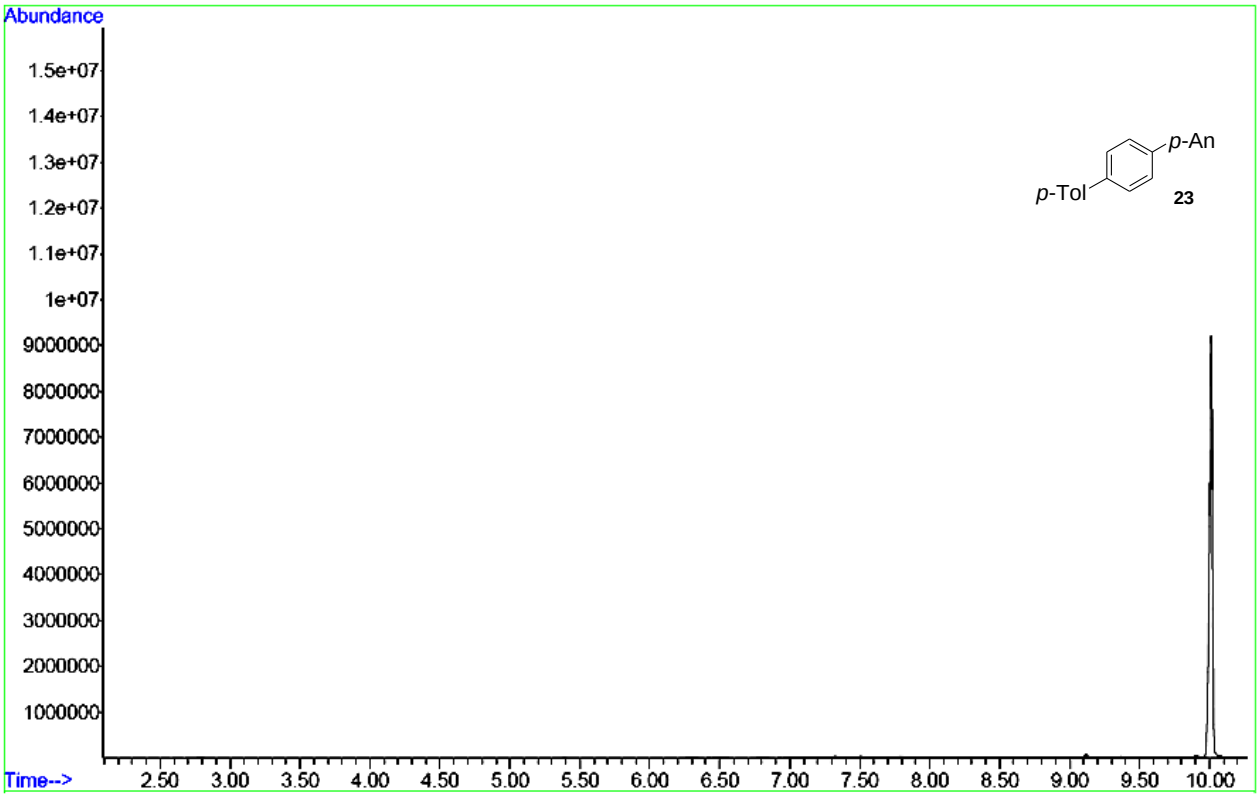

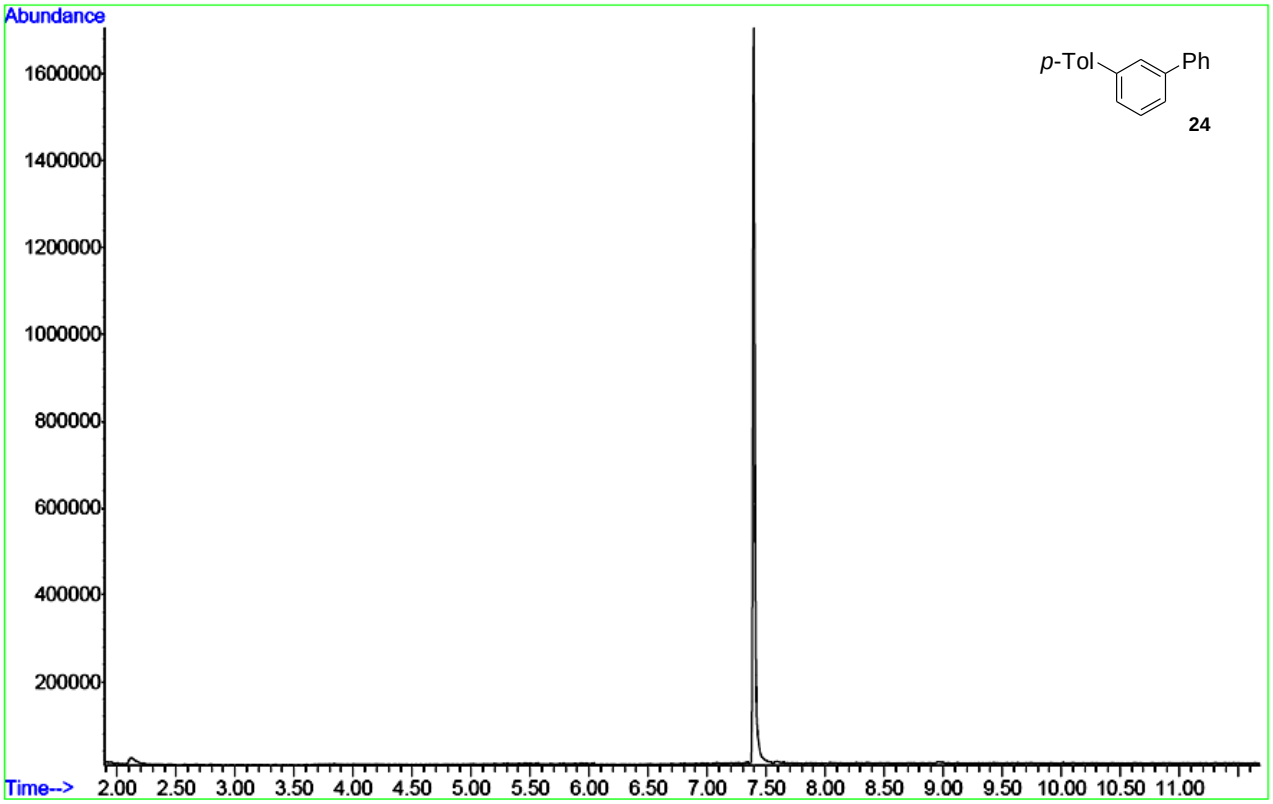

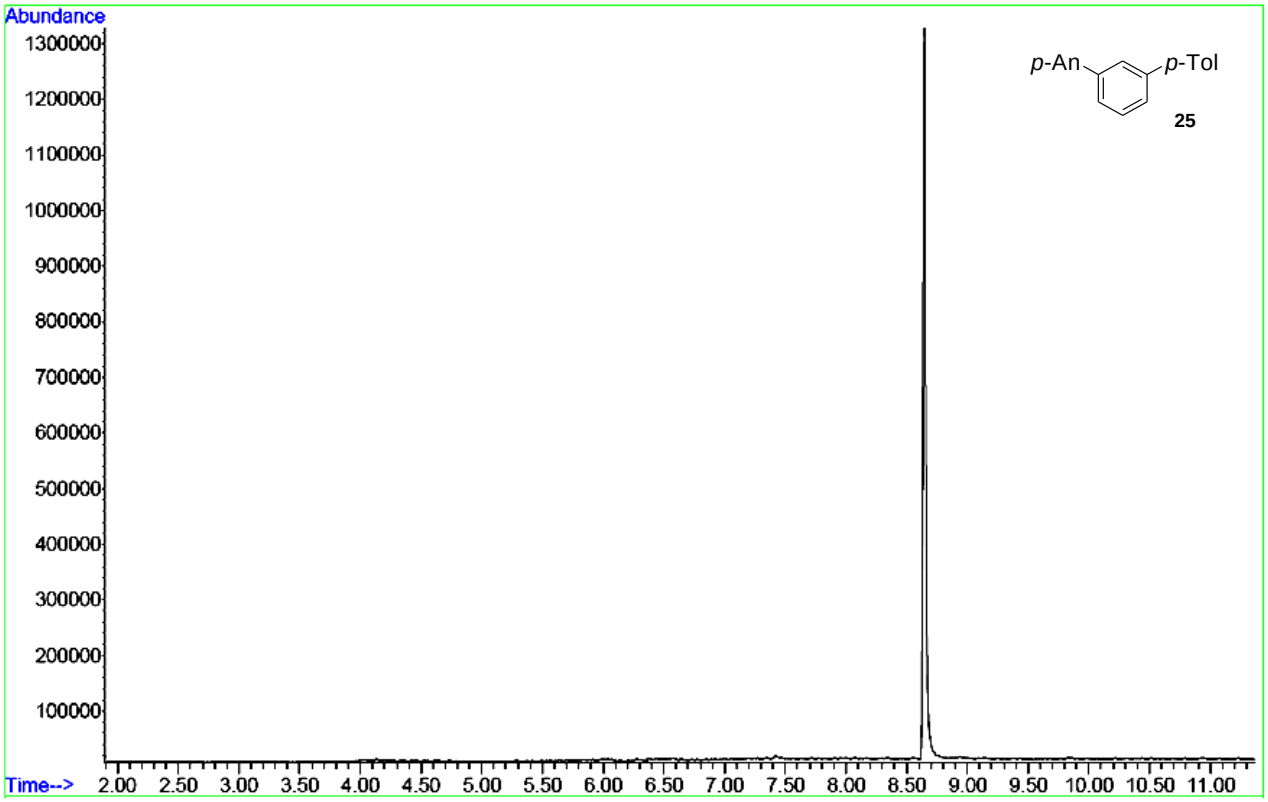
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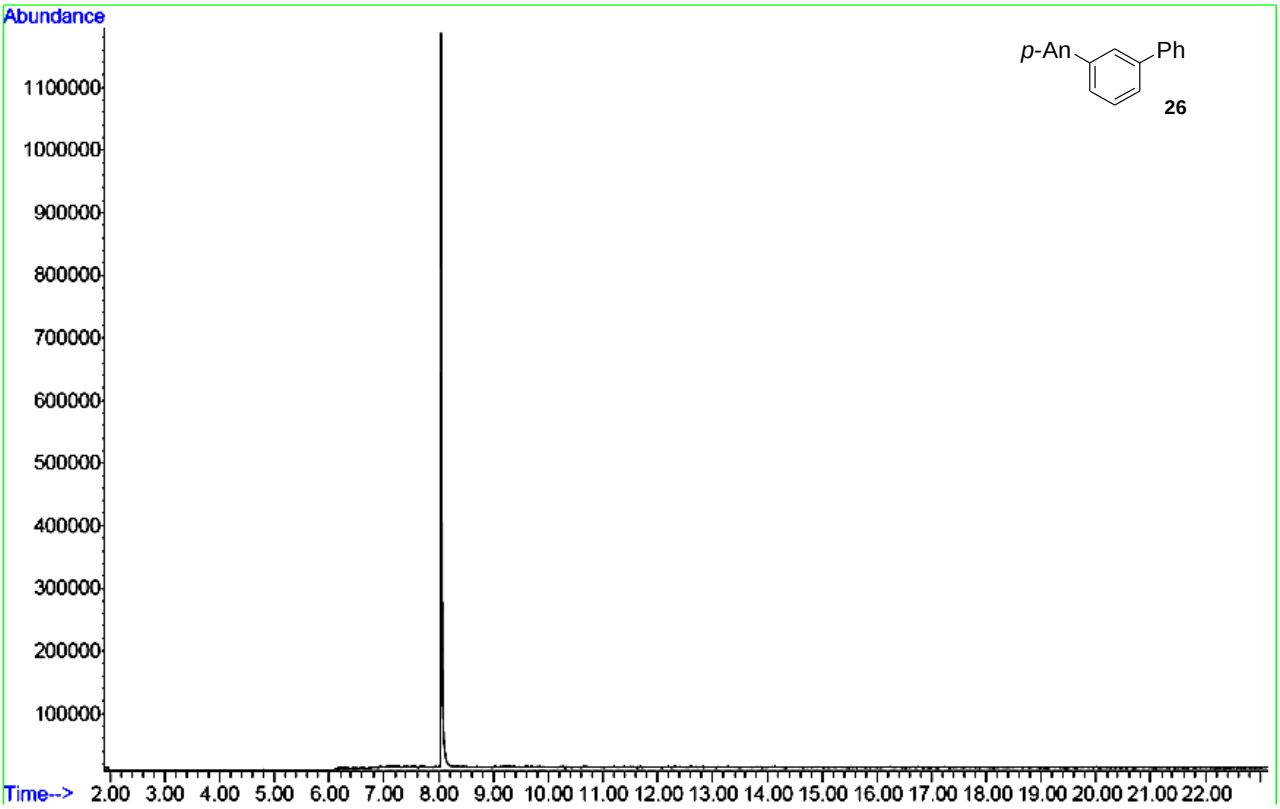
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Ph
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