Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Ligand-free hydroboration of alkynes catalyzed by heterogeneous copper powder with high efficiency

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General methods

All reactions were performed in reaction tubes under argon atmosphere. Micro copper powder was supplied by Ningbo Guangbo New Nanomaterials Stock Co. Ltd.. MeONa, bis(pinacolato)diboron and other alkynes were purchased from Alfa Aesar or J&K company and used without further purification. Column chromatography was performed on silica gel (200~300 mesh). Proton and carbon magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were obtained on JEON 400 systems, using tetramethylsilane (TMS) in the solvent of $CDCl_3$ or DMSO-d_6 as the internal standard (^{1}H NMR: TMS at 0.00 ppm, $CDCl_3$ at 7.26 ppm, DMSO-d_6 at 2.50 ppm; ^{13}C NMR: $CDCl_3$ at 77.16 ppm, DMSO-d_6 at 39.52 ppm). GC-MS analysis was performed on Thermo Fisher Trace 1300-ISO instrument.

General procedure for synthesis of compounds 2a–x: B_2Pin_2 (0.75 mmol, 190.5 mg), micro copper powder (0.05 mmol, 3.2 mg) and MeONa (0.1 mmol, 5.4 mg) were added to a Schlenk tube equipped with a magnetic stirrer. The tube was purged under vacuum and then refilled with argon for three times. Alkyne (0.5 mmol) and EtOH (2 mL) were added under argon atmosphere, and the tube was sealed and stirred under room temperature for 11 h (for aliphatic alkynes) or 24 h (for aromatic alkynes). After the reaction finished, the resulting solution was dropped into water (20 mL). The aqueous solution was extracted with CH_2Cl_2 (10 mL x 2). The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated, and the residue was purified by column chromatography on silica gel to provide the desired product (**2**).

Detail information of catalyst

Micro copper powder we use were from Ningbo Guangbo New Nanomaterials Stock Co.,Ltd., and its identifer is Cu-GB0501. The photo and XRD image are as below.

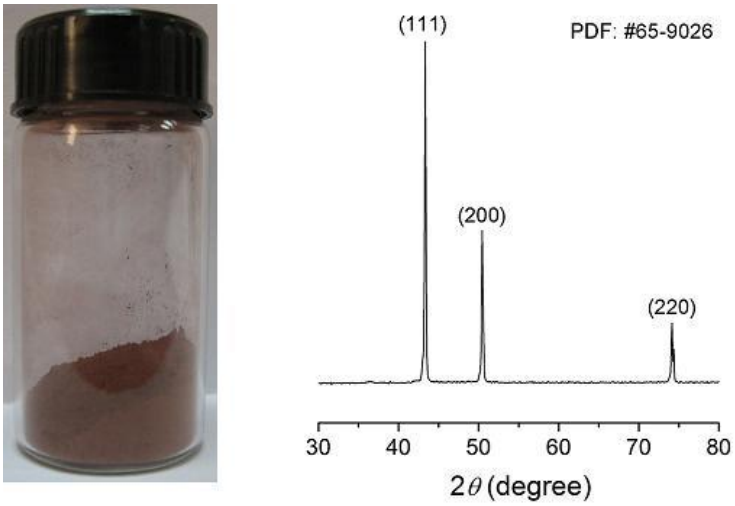


Figure S1. Photo and XRD image of Micro copper powder

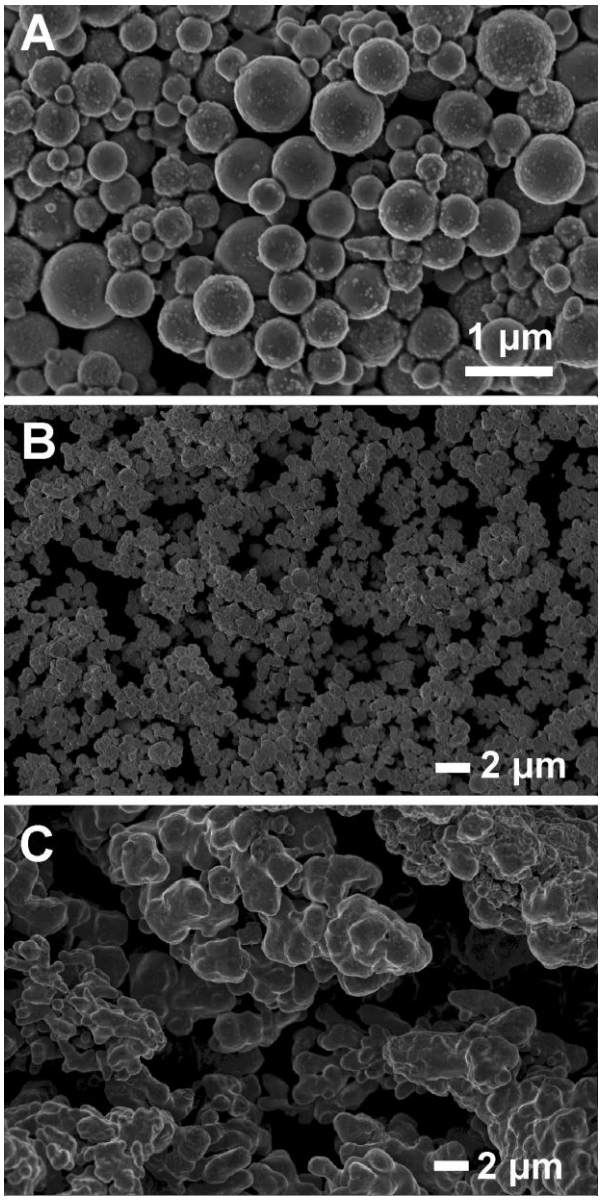


Figure S2. SEM images of the three kinds of micro copper. [A] Micro copper powder from Chinese company and exhibited the most well-distributed shape and size comparing to the other two kinds. [B] Cu (β), Micro copper powder, -625 mesh, 0.5-1.5 μm, metal basis (provided by Alfa Aesar company). [C] Cu (γ), Copper powder, spherical, -170+270 mesh, metals basis (provided by Alfa Aesar company).

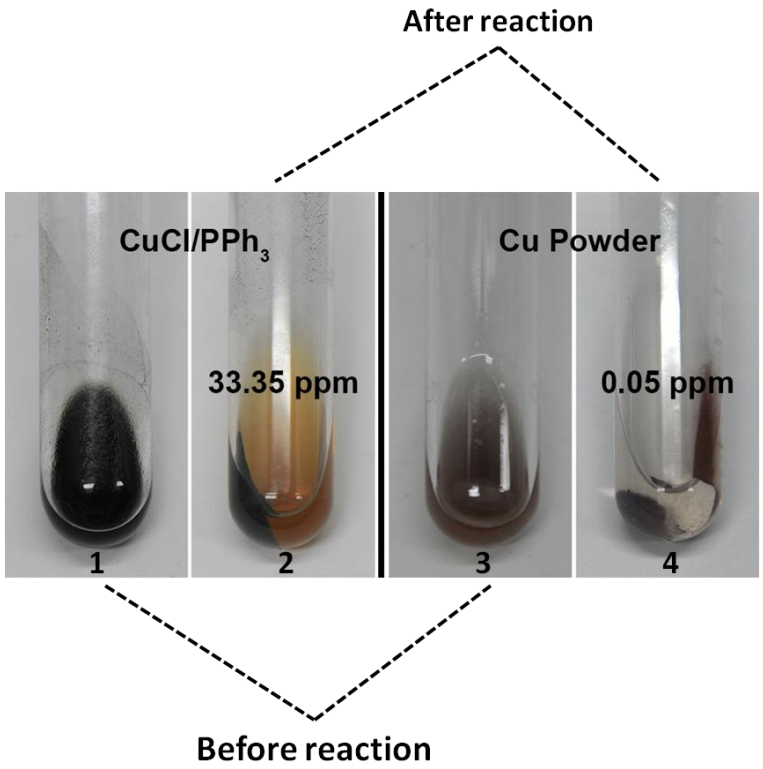
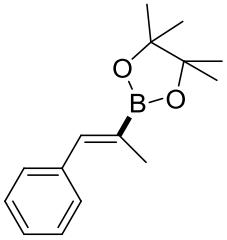


Figure S3. Photographs of reaction solutions: before reaction and after reaction of B_2Pin_2 and but-1-ynylbenzene. Left two are $CuCl/PPh_3$ system, and the right two are Cu powder catalytic system. Image 1 and 3 were taken at the start of the reactions, while image 2 and 4 were taken after the reaction (centrifugated at 10000 rpm for 5 min).

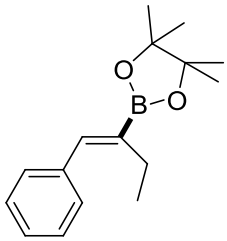
Characterization data of compounds 2a–x



2a

(*Z*)-4,4,5,5-Tetramethyl-2-(1-phenylprop-1-en-2-yl)-1,3,2-dioxaborolane (2a).[1]

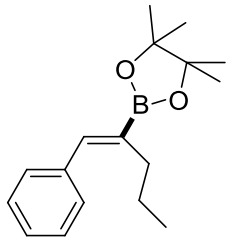
Eluent: petroleum ester/ ethyl acetate = 100: 1. Yield 90% (110 mg). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.36 (m, 4H), 7.23 (m, 2H), 1.98 (s, 3H), 1.31 (S, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 142.4, 138.0, 129.4, 128.1, 127.1, 83.5, 24.9, 15.9. GC-MS [M] m/z 244.3.



2b

(*Z*)-4,4,5,5-Tetramethyl-2-(1-phenylbut-1-en-2-yl)-1,3,2-dioxaborolane (2b).[2]

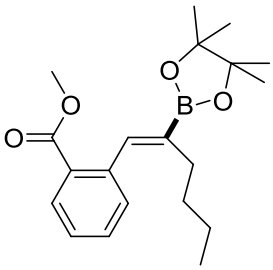
Eluent: petroleum ester/ ethyl acetate = 100: 1. Yield 72% (93 mg). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.32 (m, 4H), 7.20 (m, 2H), 2.38 (q, J = 7.79, 2H), 1.31 (S, 12H), 1.09 (t, J = 7.79, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 141.4, 137.9, 129.0, 128.1, 127.0, 83.4, 24.8, 22.7, 14.7. GC-MS M^+ m/z 258.2.



2c

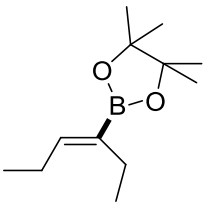
(*Z*)-4,4,5,5-Tetramethyl-2-(1-phenylpent-1-en-2-yl)-1,3,2-dioxaborolane (2c).[3]

Eluent: petroleum ester/ ethyl acetate = 100:1. Yield 82% (111 mg). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.32 (m, 4H), 7.21 (m, 2H), 2.34 (t, J = 8.01, 3H), 1.50 (m, 2H), 1.30 (S, 12H), 0.91 (t, J = 7.33, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 141.9, 138.0, 129.0, 128.1, 127.0, 83.4, 31.6, 24.8, 23.3, 14.3. GC-MS M^+ m/z 272.3.



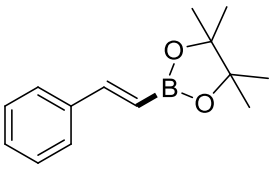
2d

(*Z*)-Methyl 2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-1-enyl)benzoate (2d): Eluent: petroleum ester/ ethyl acetate = 50: 1. Yield 89% (153 mg). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.94 (dd, J = 1.37 and 7.94, 1H), 7.56 (s, 1H), 7.45 (td, J = 1.37 and 7.33, 1H), 7.30 (t, J = 7.33, 1H), 7.23 (d, J = 7.79, 1H), 3.85 (s, 3H), 7.12 (t, J = 7.79, 2H), 1.35 (m, 2H), 1.31 (S, 12H), 1.21 (m, 2H), 0.7 (t, J = 7.33, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 167.7, 142.4, 139.9, 131.5, 130.4, 130.3, 129.3, 126.8, 83.3, 51.8, 32.2, 29.1, 24.8, 22.6, 14.0. ESI-MS $[M+Na]^+$ m/z 345.2.



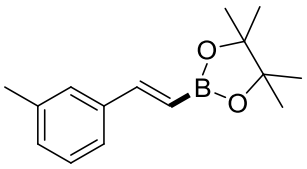
2e

(*Z*)-2-(Hex-3-en-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2e).[4] Eluent: petroleum ester/ ethyl acetate = 100: 1. Yield 91% (100 mg). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 6.25 (t, J = 7.33, 1H), 2.14 (m, 4H), 1.26 (S, 12H), 0.99 (t, J = 7.79, 3H), 0.94 (t, J = 7.79, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 147.0, 83.0, 77.4, 77.0, 76.7, 24.8, 21.7, 21.5, 14.9, 13.8. GC-MS M^+ m/z 210.



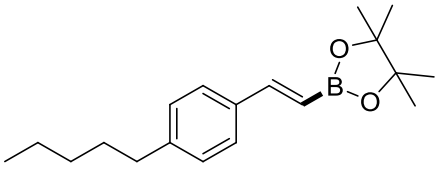
2f

(*E*)-4,4,5,5-Tetramethyl-2-styryl-1,3,2-dioxaborolane (2f).[5] Eluent: petroleum ester/ ethyl acetate = 100: 1. Yield 93% (107 mg). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.48 (m, 2H), 7.40 (d, J = 18.3, 1H), 7.30 (m, 3H), 6.16 (d, J = 18.3, 1H),1.31 (S, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 149.5, 137.5, 128.9, 128.6, 127.1, 83.4, 24.8. GC-MS M^+ m/z 230.2.



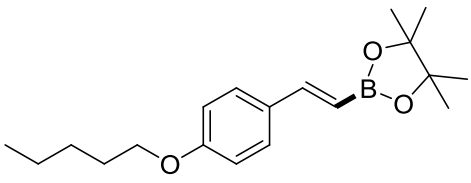
2g

(*E*)-4,4,5,5-Tetramethyl-2-(3-methylstyryl)-1,3,2-dioxaborolane (2g).[6] Eluent: petroleum ester/ ethyl acetate = 100:1. Yield 96% (117 mg). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.36 (d, J = 18.7, 1H), 7.29 (m, 2H), 7.22 (t, J = 7.79, 1H), 7.10 (d, J = 7.33, 1H), 6.14 (d, J = 18.3, 1H), 2.34 (s, 3H), 1.32 (S, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 149.7, 138.1, 137.5, 129.7, 128.5, 127.8, 124.3, 83.3, 24.8, 21.4. GC-MS M^+ m/z 244.3.



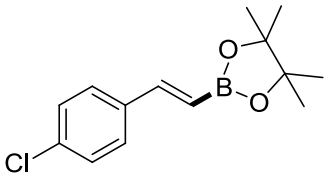
2h

(*E*)-4,4,5,5-Tetramethyl-2-(4-pentylstyryl)-1,3,2-dioxaborolane (2h).[7] Eluent: petroleum ester/ ethyl acetate = 100: 1. Yield 96% (130 mg). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.38 (d, J = 8.24, 2H), 7.36 (d, J = 18.3, 1H), 7.13 (d, J = 8.24, 2H), 6.09 (d, J = 18.3, 1H), 2.57 (t, J = 7.79, 2H), 1.59 (m, 2H), 1.30 (m, 4H) , 1.29 (S, 12H), 0.87 (t, J = 6.87, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 149.6, 144.1, 135.0, 128.7, 127.1, 83.3, 35.8, 31.5, 31.0, 24.8, 22.6, 14.0. GC-MS M^+ m/z 300.3.



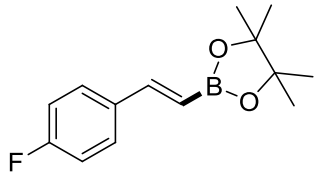
2i

(*E*)-4,4,5,5-Tetramethyl-2-(4-(pentyloxy)styryl)-1,3,2-dioxaborolane (2i). Eluent: petroleum ester/ ethyl acetate = 100: 1. Yield 76% (120 mg). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.41 (d, J = 9.16, 2H), 7.34 (d, J = 18.3, 1H), 6.84 (d, J = 8.70, 2H), 6.00 (d, J = 18.3, 1H), 3.95 (t, J = 6.41, 2H), 1.78 (m, 2H), 1.40 (m, 4H) , 1.30 (S, 12H), 0.92 (t, J = 6.87, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 159.9, 149.6, 130.2, 128.5, 114.5, 83.2, 68.1, 28.9, 28.2, 24.8, 22.5, 14.0. GC-MS M^+ m/z 316.3.



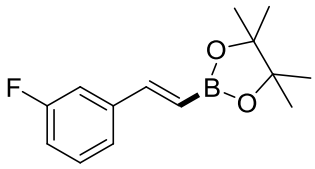
2j

(*E*)-2-(4-Chlorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2j).[8] Eluent: petroleum ester/ ethyl acetate = 100:1. Yield 85% (112 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.40 (d, J = 7.79, 2H), 7.33 (d, J = 18.3, 1H), 7.30 (d, J = 7.79, 2H), 6.13 (d, J = 18.3, 1H), 1.31 (S, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 148.0, 136.0, 134.6, 128.8, 128.2, 83.5, 24.8. GC-MS M^+ m/z 264.0.



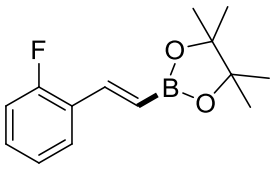
2k

(*E*)-2-(4-Fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2k).[9] Eluent: petroleum ester/ ethyl acetate = 100:1. Yield 77% (96 mg). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.45 (m, 2H), 7.35 (d, J = 18.7, 1H), 7.02 (m, 2H), 6.07 (d, J = 18.3, 1H), 1.31 (S, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 163.2(d, J = 248), 148.2, 133.7(d, J = 2.88), 128.7(d, J = 8.63), 115.6(d, J = 21.0), 83.4, 24.8. GC-MS M^+ m/z 248.3.



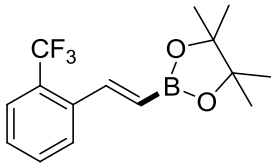
2l

(*E*)-2-(4-Fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2l).[10] Eluent: petroleum ester/ ethyl acetate = 100:1. Yield 97% (120 mg). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.34 (d, J = 18.3, 1H), 7.28 (m, 1H), , 7.24 (m, 1H), 7.17 (m, 1H), 6.98 (m, 1H), 6.16 (d, J = 18.7, 1H), 1.31 (S, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 163.1(d, J = 245), 148.1(d, J = 1.92), 130(d, J = 7.67), 123.0(d, J = 1.92), 115.7 (d, J = 22.0),113.3(d, J = 22.0), 83.5, 24.8. GC-MS M^+ m/z 248.3.



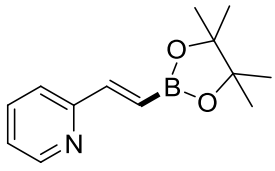
2m

(*E*)-2-(2-Fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2m).[11] Eluent: petroleum ester/ ethyl acetate = 100:1. Yield 85% (106 mg). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.57 (d, J = 18.3, 1H), 7.54 (m, 1H), , 7.24 (m, 1H), 7.09 (m, 1H), 7.01 (m, 1H), 6.22 (d, J = 18.7, 1H), 1.30 (S, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ160.7 (d, J = 252), 141.3(d, J = 3..8), 130.2 (d, J = 7.67), 127.4, 125.4 (d, J = 11.5),124.1, 115.8 (d, J = 22.0), 83.5, 24.7. GC-MS M^+ m/z 248.2.



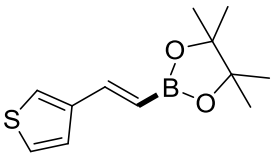
2n

(*E*)-4,4,5,5-Tetramethyl-2-(2-(trifluoromethyl)styryl)-1,3,2-dioxaborolane (2n).[12] Eluent: petroleum ester/ ethyl acetate = 100:1. Yield 84% (125 mg). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.70 (m, 2H), 7.63 (d, J = 7.79, 1H), 7.51 (d, J = 8.24, 1H), 7.37 (d, J = 7.79, 1H), 6.15 (d, J = 17.8, 1H), 1.31 (S, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 144.8, 137.0, 131.9, 128.2, 127.8 (d, J = 29.7), 125.7 (d, J = 5.75), 124.2 (d, J = 275), 83.6, 24.8. GC-MS M^+ m/z 298.3.



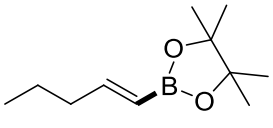
2o

(*E*)-2-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)pyridine (2o).[13] Eluent: petroleum ester/ ethyl acetate = 50:1. Yield 95% (110 mg). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.58 (d, J = 4.58, 1H), 7.63 (t, J = 7.79, 1H), 7.43 (d, J = 18.32, 1H), 7.38 (d, J = 7.79, 1H), 6.61 (d, J = 18.32, 1H), 1.29 (S, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 155.5, 149.7, 148.8, 136.5, 123.1, 122.2, 83.5, 24.8. GC-MS M^+ m/z 231.3.



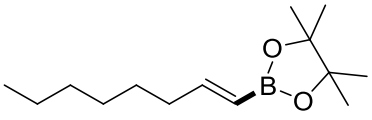
2p

(*E*)-4,4,5,5-Tetramethyl-2-(2-(thiophen-3-yl)vinyl)-1,3,2-dioxaborolane (2p).[6] Eluent: petroleum ester/ ethyl acetate = 50: 1. Yield 80% (94 mg). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.37 (d, J = 18.7, 1H), 7.29 (m, *3*H), 5.94 (d, J = 18.3, 1H), 1.30 (S, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 143.2, 141.3, 126.1, 125.1, 124.9, 83.3, 24.8. GC-MS M^+ m/z 236.3.



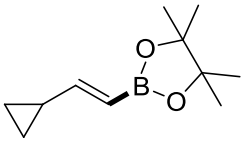
2q

(*E*)-4,4,5,5-Tetramethyl-2-(pent-1-enyl)-1,3,2-dioxaborolane (2q).[14] Eluent: petroleum ester/ ethyl acetate = 100:1. Yield 82% (80 mg). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 6.63 (m, 1H), 5.42 (d, J = 17.4, 1H), 2.12 (q, 2H), 1.44 (m, 2H), 1.26 (S, 12H), 0.90 (t, J = 7.33, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 154.6, 83.0, 37.9, 24.8, 21.4, 13.8. GC-MS M^+ m/z 196.2.



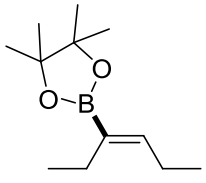
2r

(*E*)-4,4,5,5-Tetramethyl-2-(oct-1-enyl)-1,3,2-dioxaborolane (2r).[15] Eluent: petroleum ester/ ethyl acetate = 100:1. Yield 67% (80 mg). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 6.63 (m, 1H), 5.42 (d, J = 17.8, 1H), 2.14 (q, 2H), 1.40 (m, 2H), 1.26 (m, 18H), 0.87 (t, J = 6.87, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 154.9, 83.0, 35.9, 31.7, 28.9, 28.2, 24.8, 22.6, 14.1. GC-MS M^+ m/z 238.3.



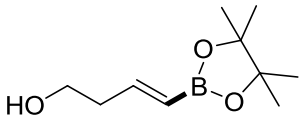
2s

(*E*)-2-(2-Cyclopropylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2s).[9] Eluent: petroleum ester/ ethyl acetate = 100: 1. Yield 89% (86 mg). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 6.07 (m, 1H), 5.49 (d, J = 17.8, 1H), 1.51 (m, 1H), 1.25 (s, 12H), 0.79 (m, 2H), 0.53 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 158.6, 82.9, 24.8, 17.0, 7.9. GC-MS M^+ m/z 194.3.



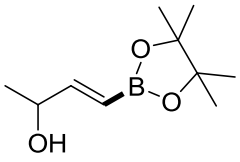
2t

(Z)-2-(hex-3-en-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2t).[16] Eluent: petroleum ester/ ethyl acetate = 100:1. Yield 91% (100 mg). Colorless oil. ^{1}H NMR (400 MHz, d6-DMSO, ppm) δ 6.24 (t, J = 7.3, 1H), 2.12 (m, 4H), 1.24 (s, 12H), 0.98 (t, J = 7.7, 3H), 0.92 (t, J = 7.3, 3H),. ^{13}C NMR (100 MHz, d6-DMSO, ppm) δ 147, 83.0, 24.8, 21.7, 21.5, 14.9, 13.8. GC-MS M^+ m/z 209.2.



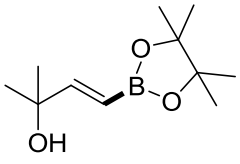
2u

(*E*)-4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-ol (2u).[17] Eluent: petroleum ester/ ethyl acetate = 20:1. Yield 80% (79 mg). Colorless oil. ^{1}H NMR (400 MHz, d6-DMSO, ppm) δ 6.47 (m, 1H), 5.31 (d, J = 17.8, 1H), 4.48 (t, J = 5.4, 1H), 3.42 (q, 2H), 2.22 (m, 2H), 1.14 (s, 12H). ^{13}C NMR (100 MHz, d6-DMSO, ppm) δ 152.3, 83.2, 60.3,39.8, 25.4, 25.1, 25.0. ESI-MS $[M+K]^+$ 237.4.



2v

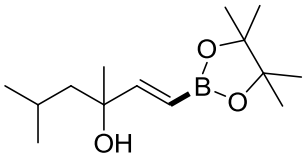
(*E*)-4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-2-ol (2v).[18] Eluent: petroleum ester/ ethyl acetate = 20:1. Yield 96% (95 mg). Colorless oil. ^{1}H NMR (400 MHz, d6-DMSO, ppm) δ 6.50 (dd, J = 17.8 and 4.58, 1H), 5.44 (d, J = 18.0, 1H), 4.59 (s, 1H), 4.12 (m, 1H), 1.19 (s, 12H), 1.15(s, 6H) ^{13}C NMR (100 MHz, d6-DMSO, ppm) δ 158.7, 83.3, 68.0, 25.1, 23.0. ESI-MS $[M+Na]^+$ 277.3.



2w

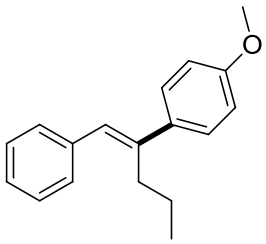
(*E*)-2-Methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-2-ol (2w).[19] Eluent: petroleum ester/ ethyl acetate = 20:1. Yield 94% (100 mg). Colorless oil. ^{1}H NMR (400 MHz, d6-DMSO, ppm) δ 6.58 (d, J = 17.8, 1H), 5.42 (d, J = 17.8, 1H),

4.78 (d, *J* = 4.58, 1H), 4.12 (m, 1H), 1.19 (s, 12H), 1.10(d, *J* = 6.41, 3H) ^{13}C NMR (100 MHz, d6-DMSO, ppm) δ 162.1, 113.1, 70.5, 29.6, 25.1. GC-MS M^+ m/z 235.2.



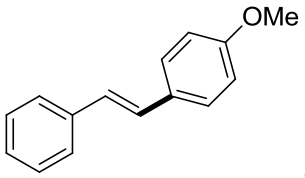
2x

(*E*)-3,5-Dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-1-en-3-ol (2x). Eluent: petroleum ester/ ethyl acetate = 20:1. Yield 80% (102 mg). Colorless oil. ^{1}H NMR (400 MHz, d6-DMSO, ppm) *δ* 6.53 (d, *J* = 17.8, 1H), 5.45 (d, *J* = 17.8, 1H), 4.40 (s, 1H), 1.65 (m, 1H),1.33 (d, *J* = 5.95, 2H), 1.19 (s, 12H), 1.12(s, 3H), 0.86 (d, *J* = 6.87, 3H), 0.83 (d, *J* = 6.87, 3H). ^{13}C NMR (100 MHz, d6-DMSO, ppm) δ 161.8, 83.2, 73.2, 50.8, 25.1, 25.0(9), 25.0(0), 24.3. ESI-MS $[M+Na]^+$ 277.3.



4a

(E)-1-methoxy-4-(1-phenylpent-1-en-2-yl)benzene (4a). Eluent: petroleum ester. Yield 90% (127 mg). Colorless oil. ^{1}H NMR (400 MHz, d6-DMSO, ppm) *δ* 7.34 (m, 6H), 7.23 (m, 1H), 6.90 (d, *J* = 9.16, 2H), 6.65 (s, 1H), 3.83 (s, 3H), 2.65 (m, 2H), 1.45 (m, 2H), 0.89 (t, *J* = 7.33, 3H). ^{13}C NMR (100 MHz, d6-DMSO, ppm) δ 158.9, 142.6, 138.6, 135.5, 128.8, 128.2, 127.7, 127.0, 126.3, 113.7, 55.3, 32.2, 22.1, 14.1.



4b

(E)-1-methoxy-4-styrylbenzene (4b).[20] Eluent: petroleum ester. Yield 92% (97 mg). Colorless oil. ^{1}H NMR (400 MHz, d6-DMSO, ppm) *δ* 7.45 (m, 4H), 7.34 (t, *J* = 7.79, 2H), 7.22 (t, *J* = 7.79, 1H), 7.01 (m, 2H), 6.89 (t, *J* = 8.70, 1H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, d6-DMSO, ppm) δ 159.3, 137.7, 130.2, 128.7, 127.8, 127.2, 126.7, 126.3, 114.2, 55.4.

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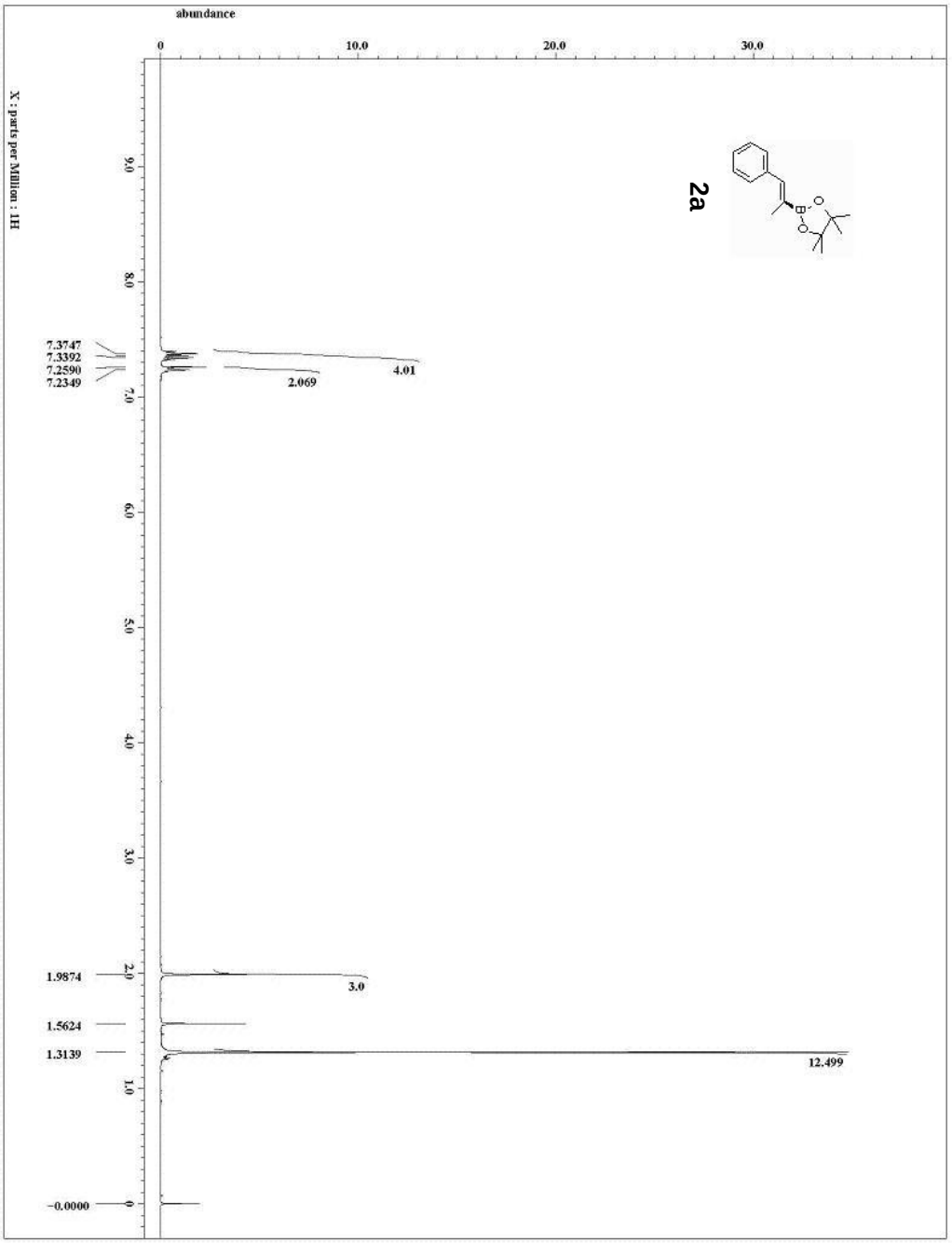
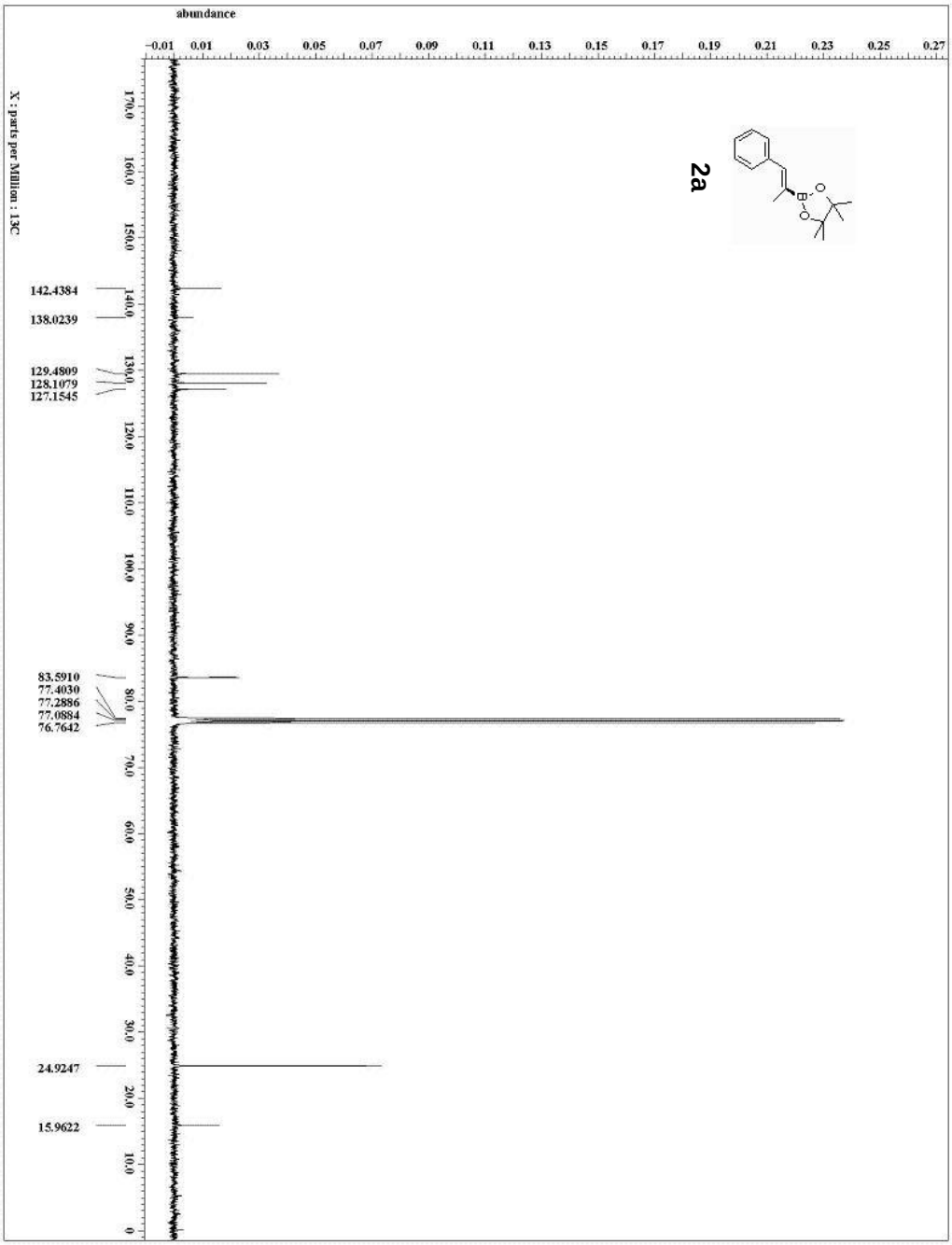
^{1}H and ^{13}C NMR spectra of compounds **2a-w**, **4a** and **4b**

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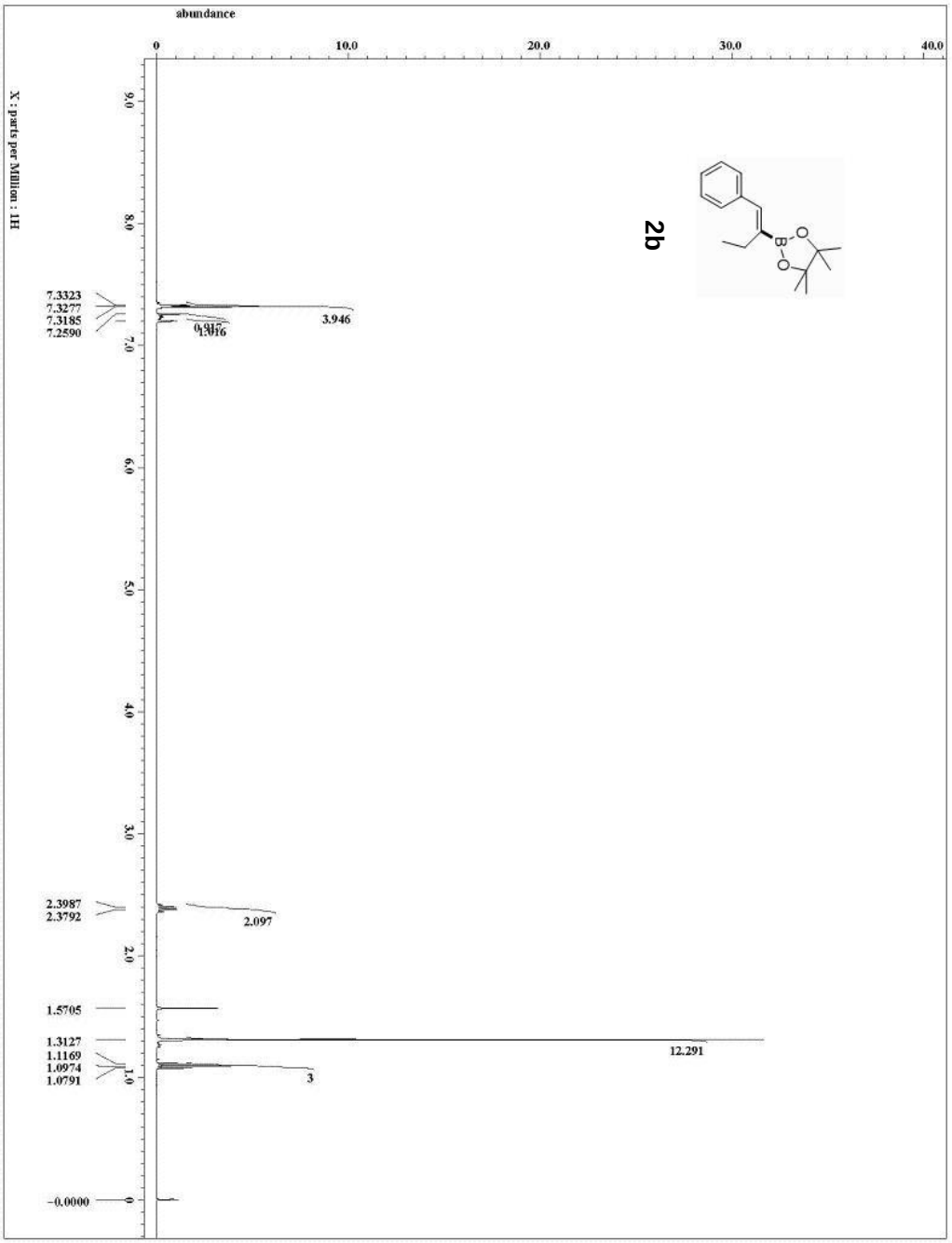
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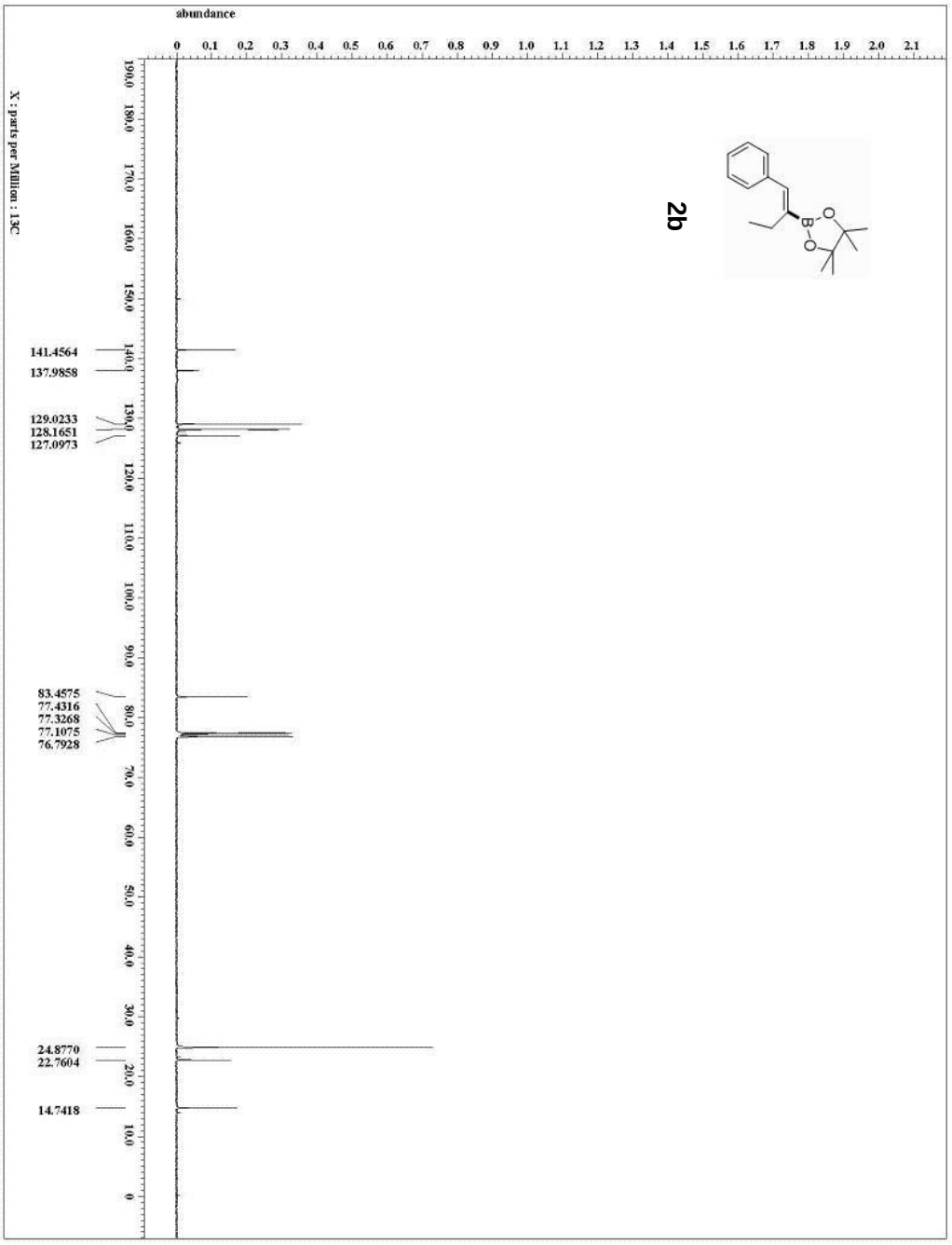
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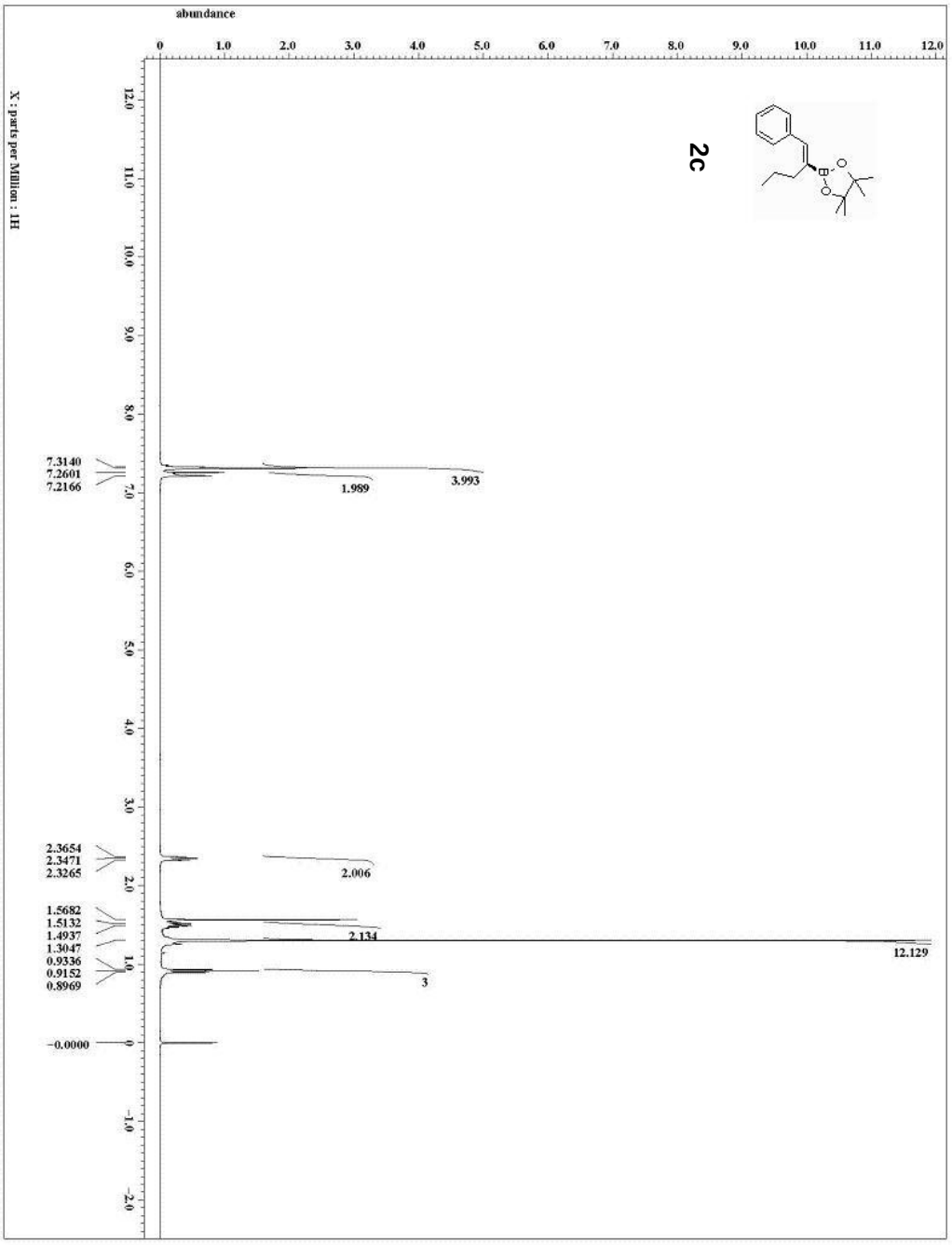
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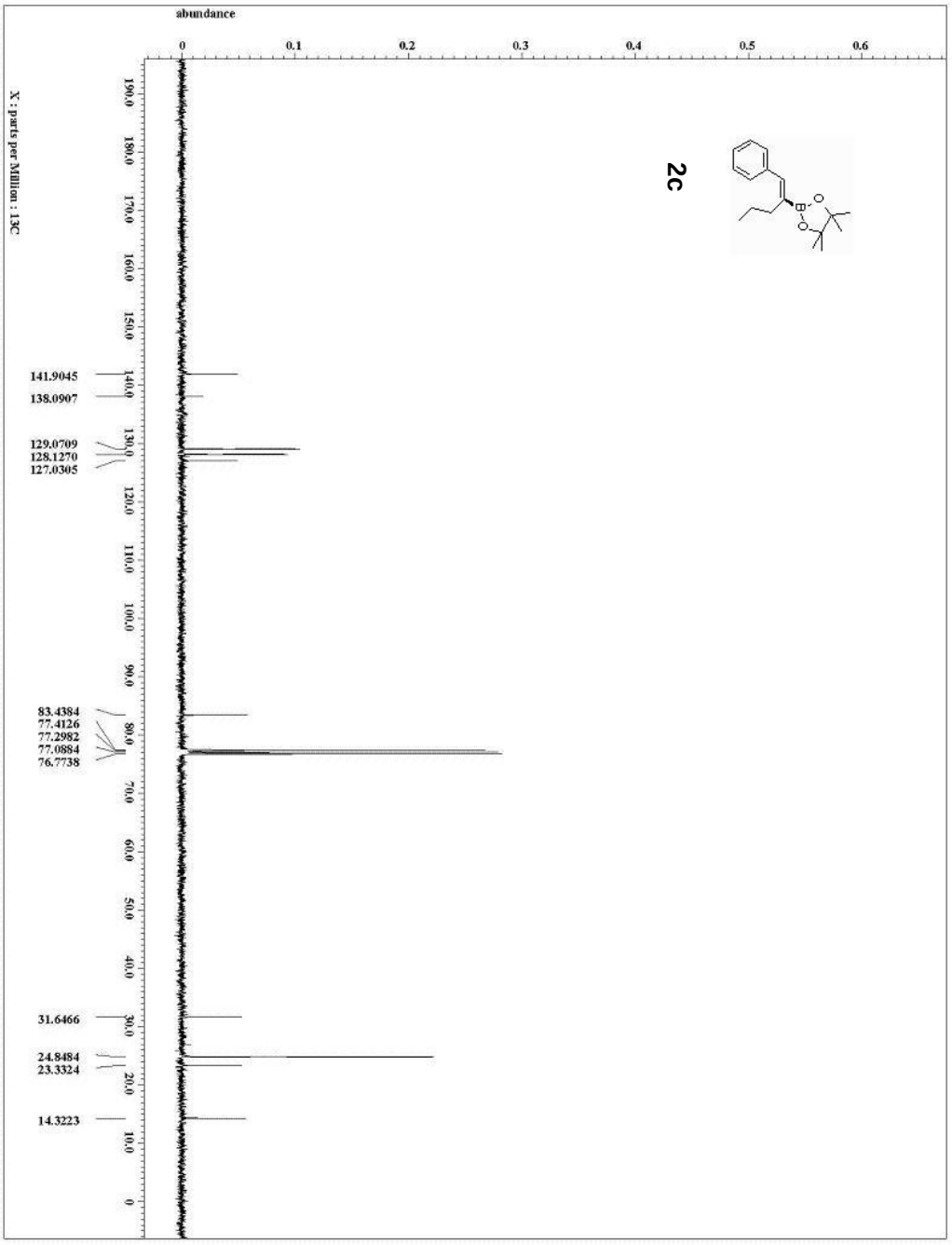
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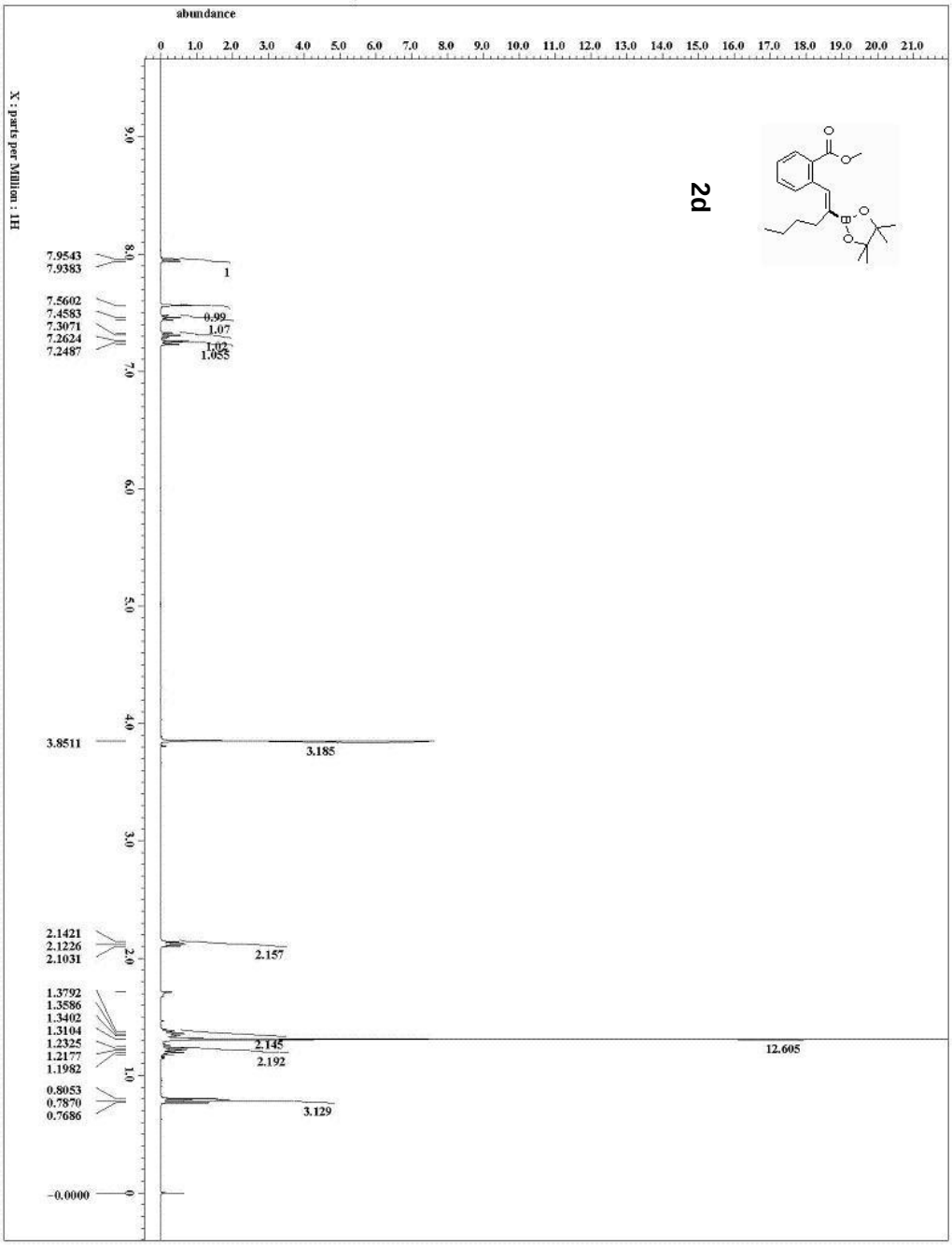
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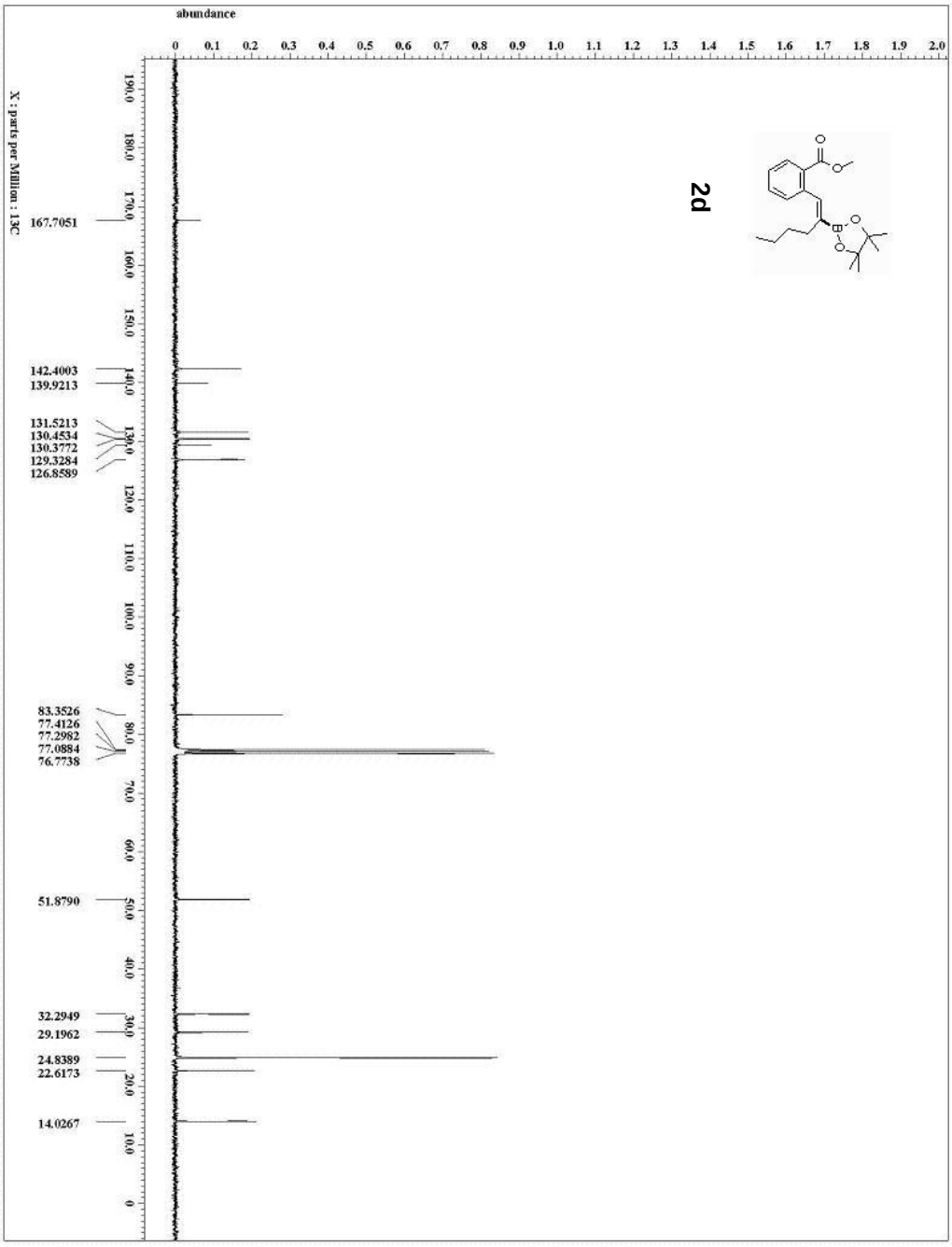
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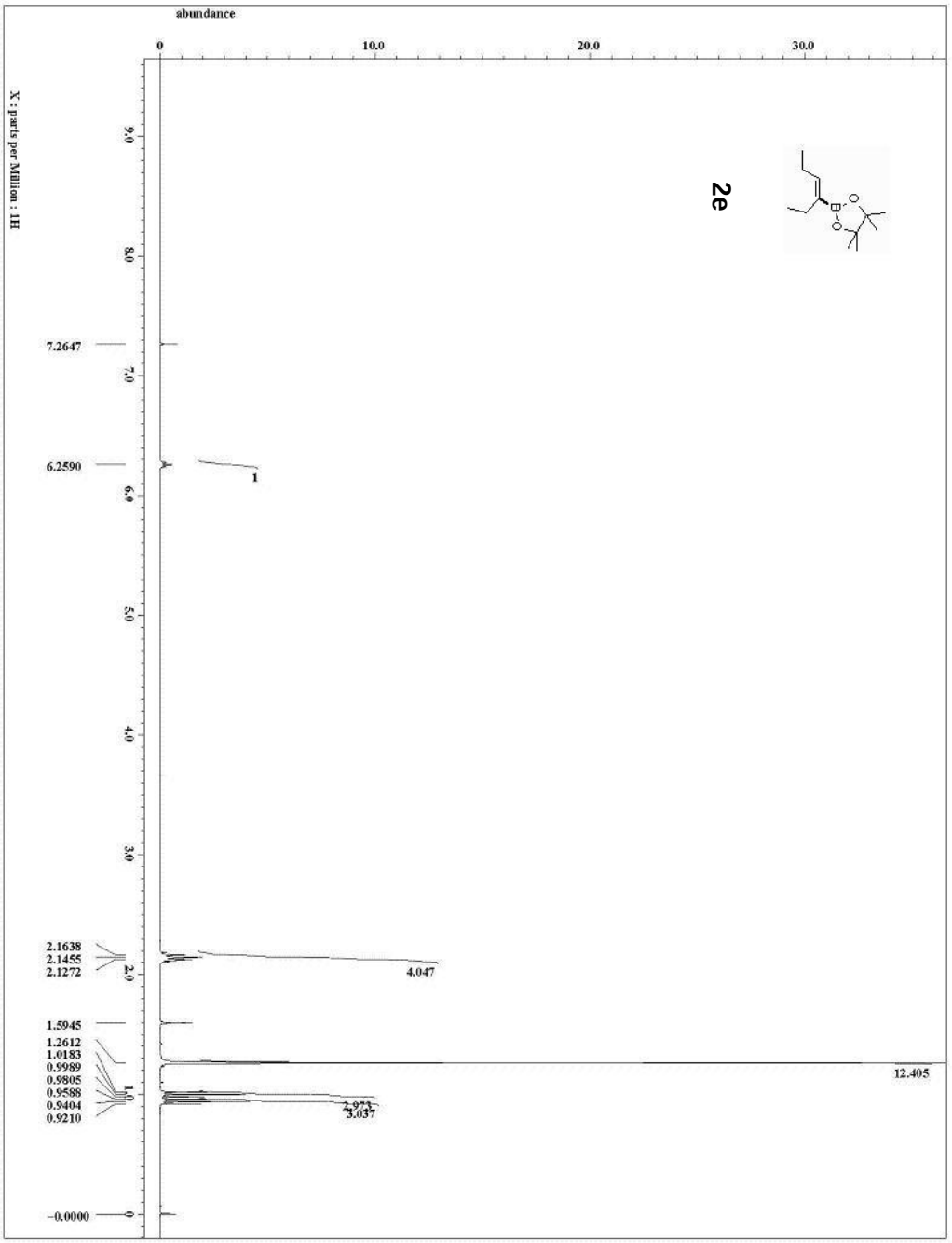
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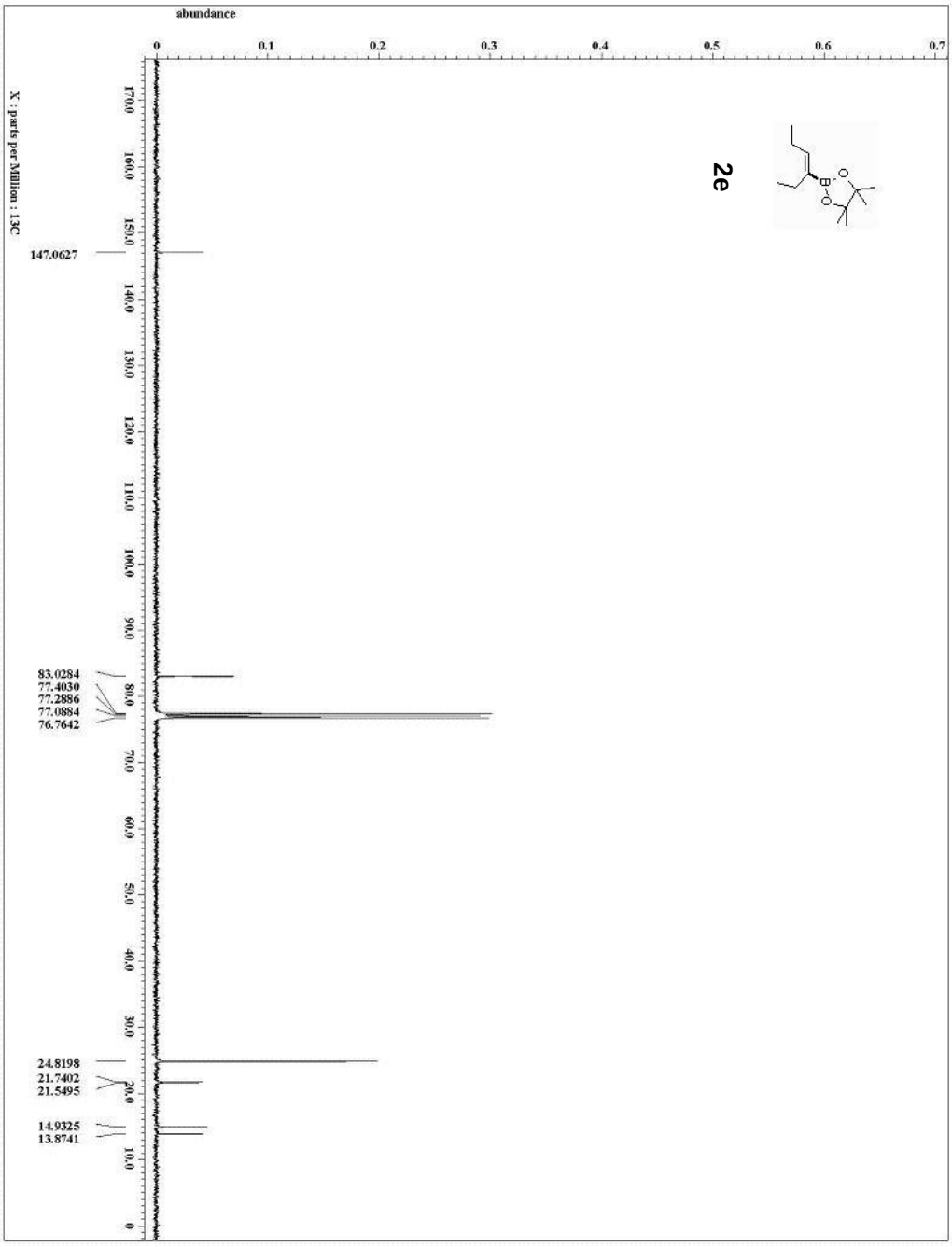
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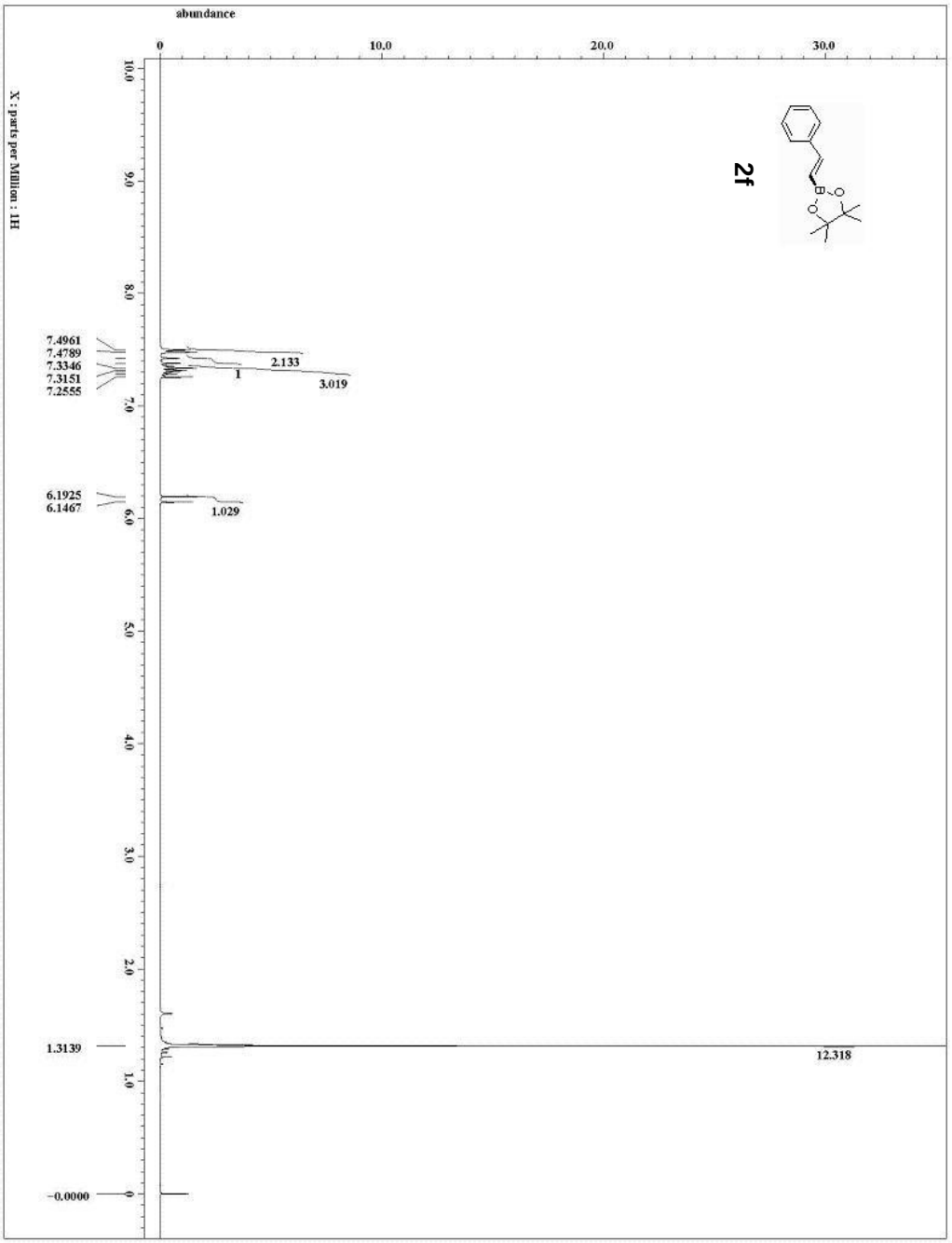
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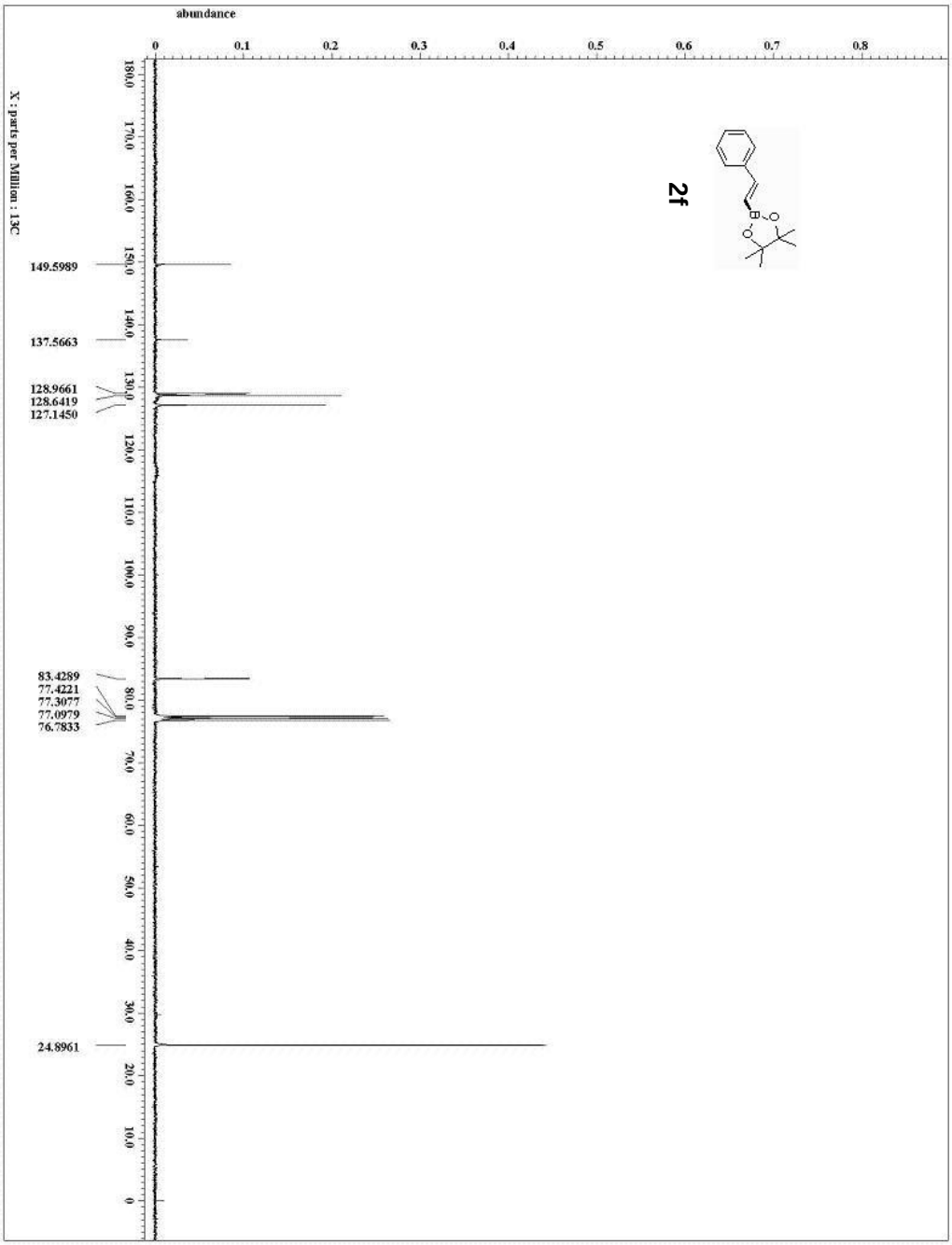
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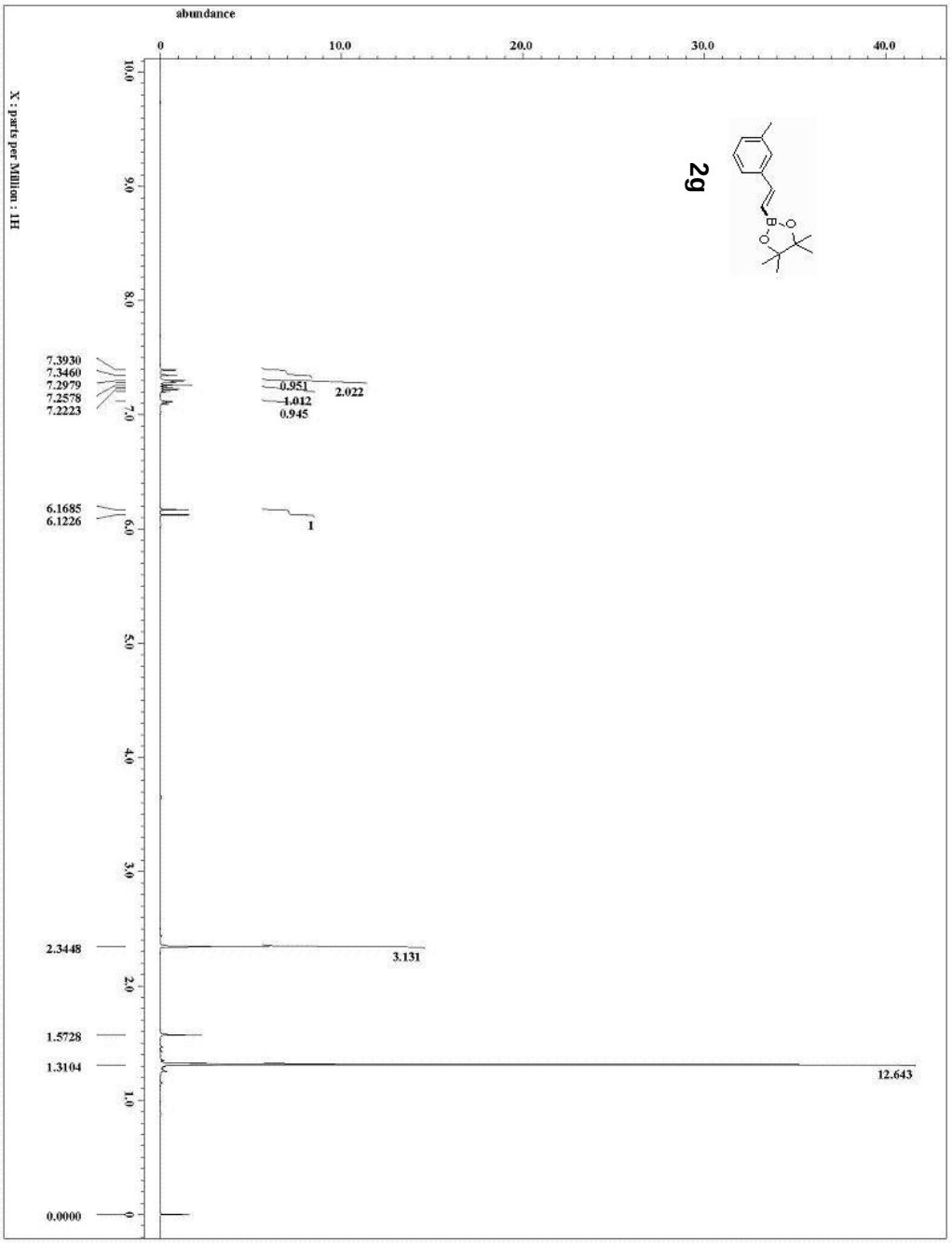
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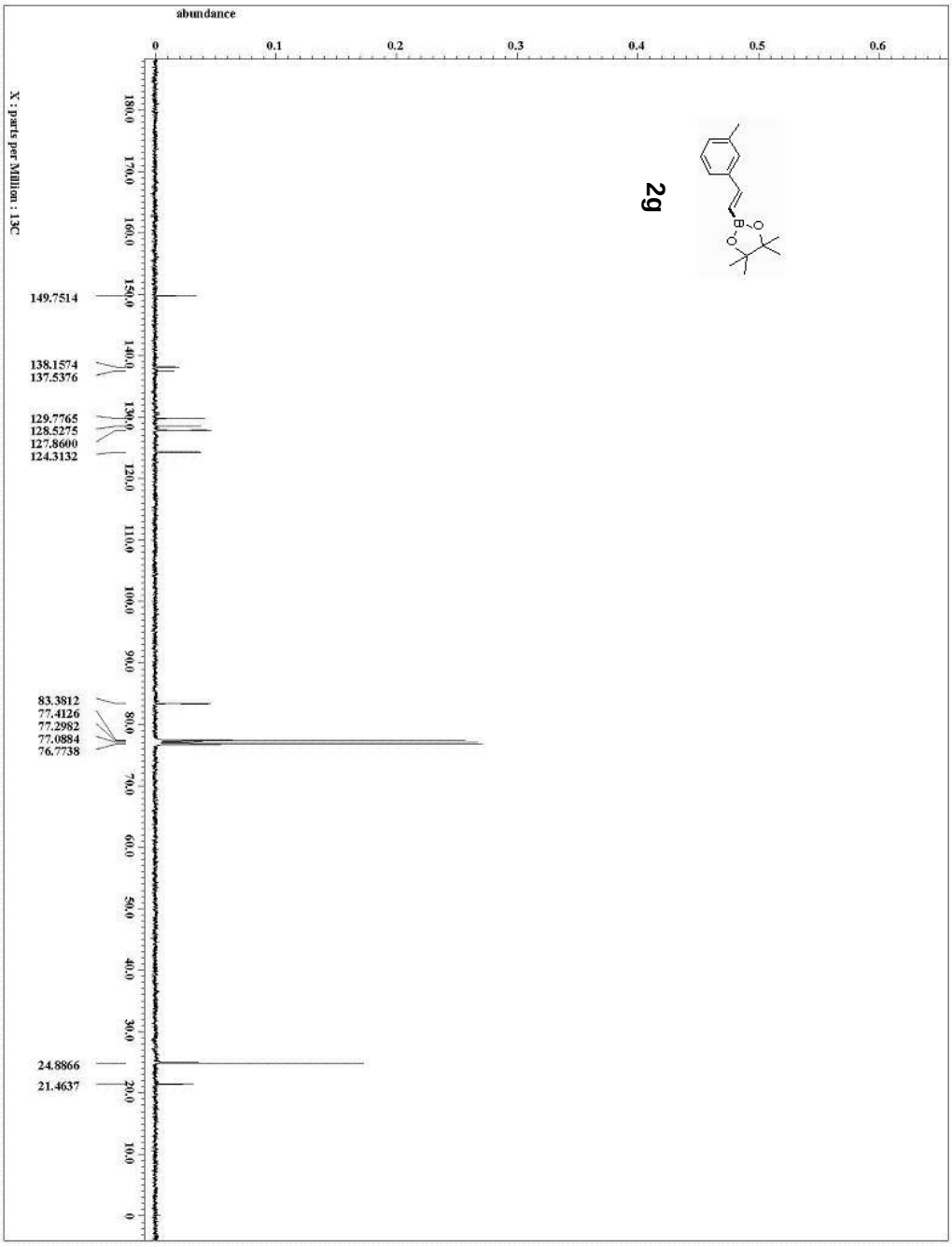
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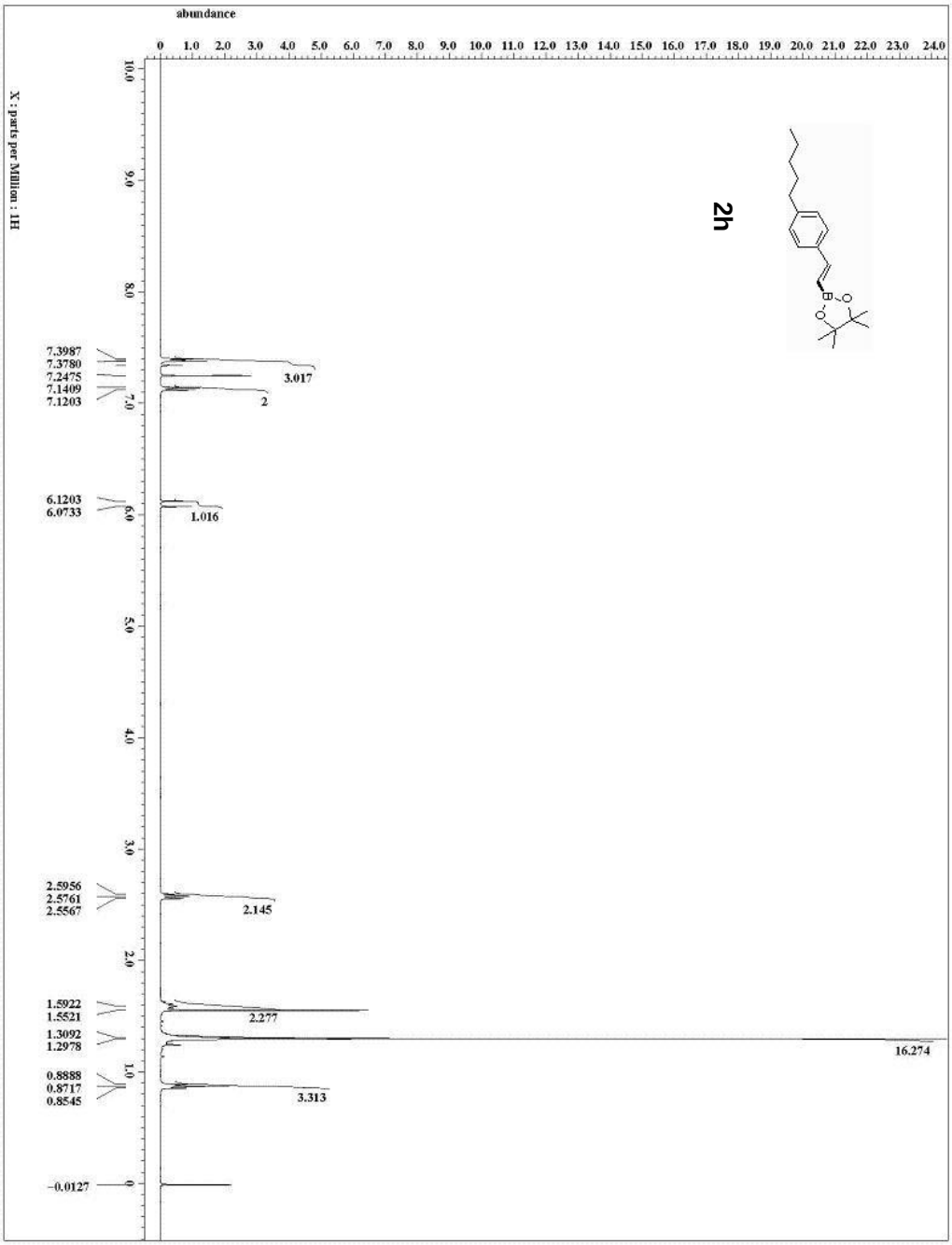
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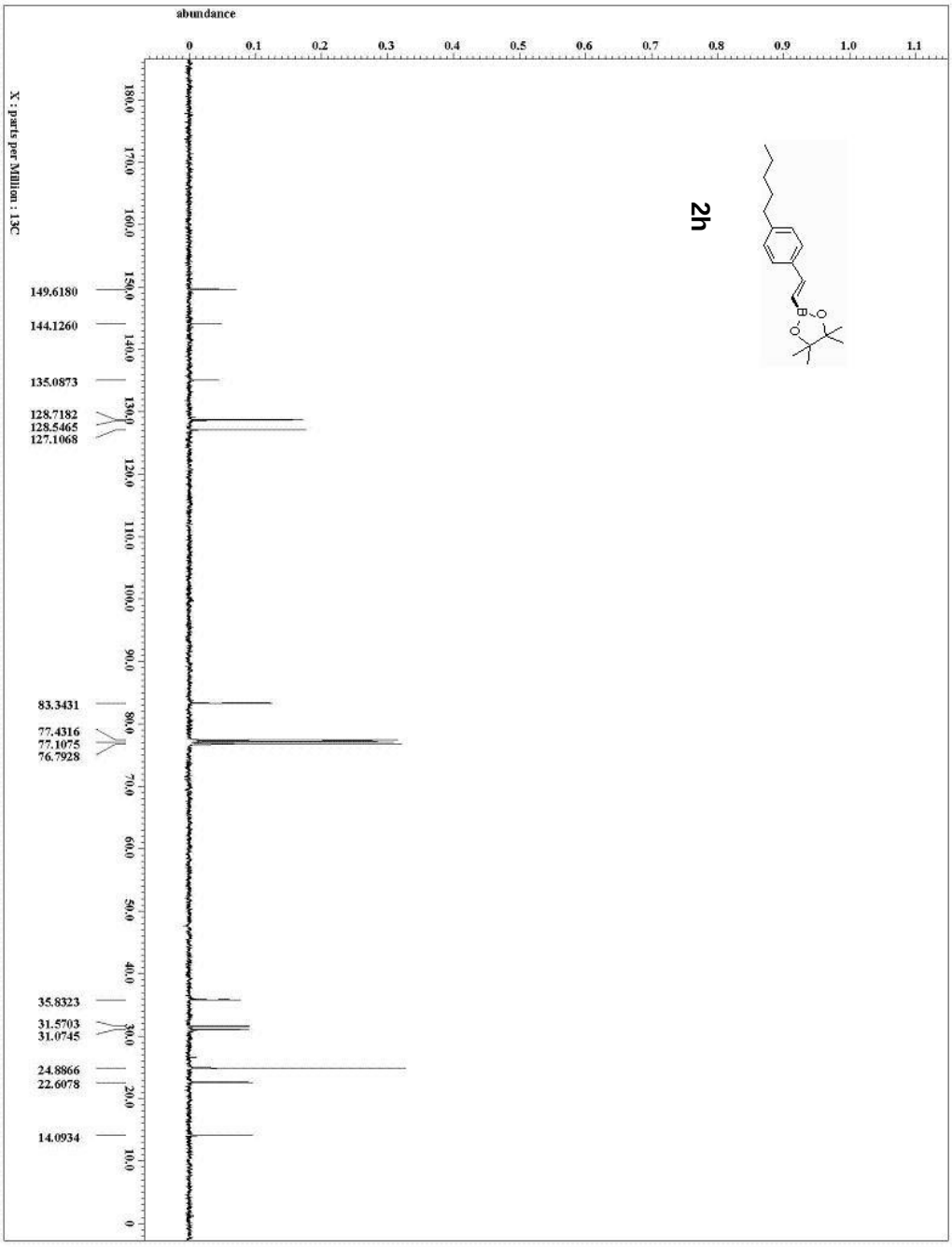
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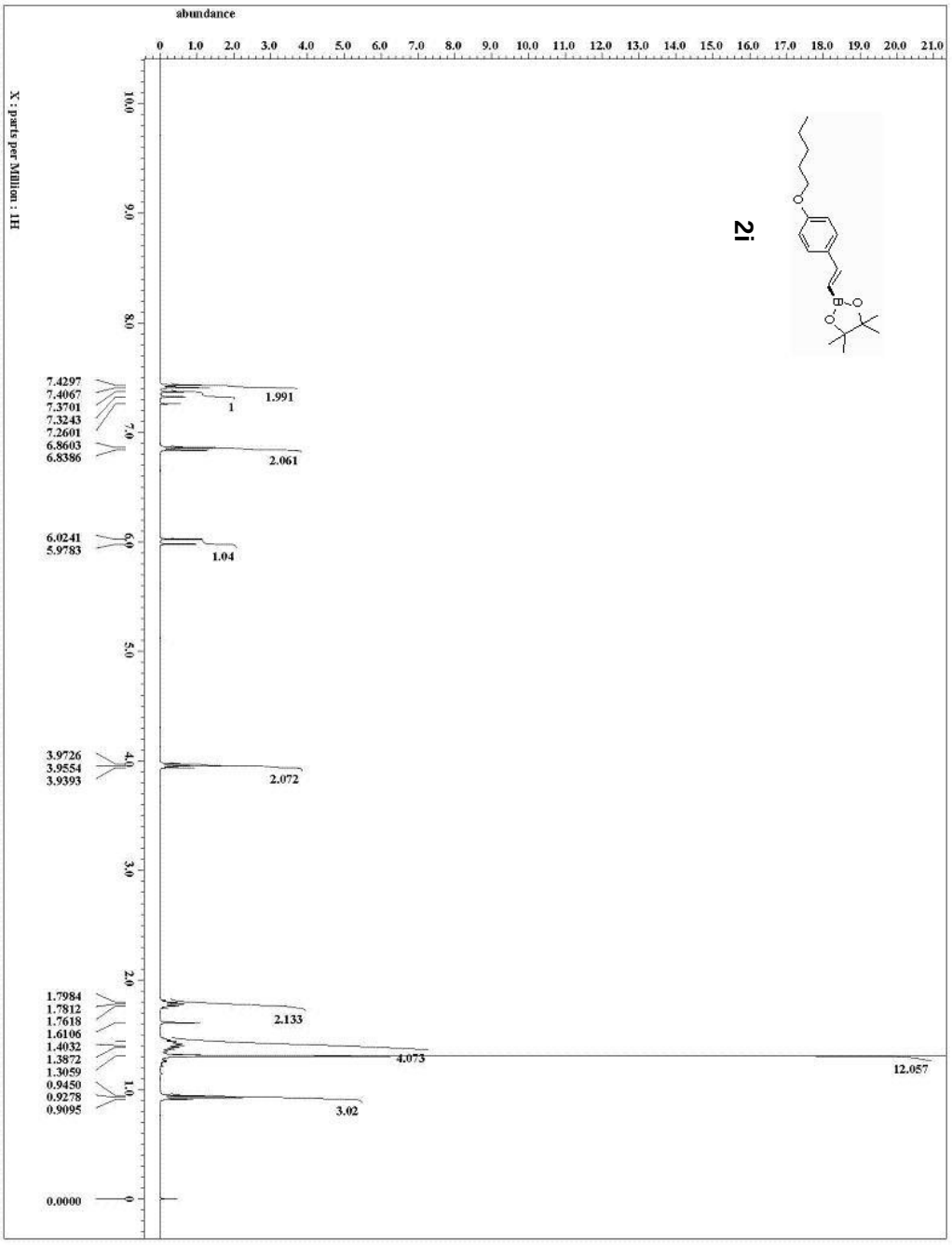
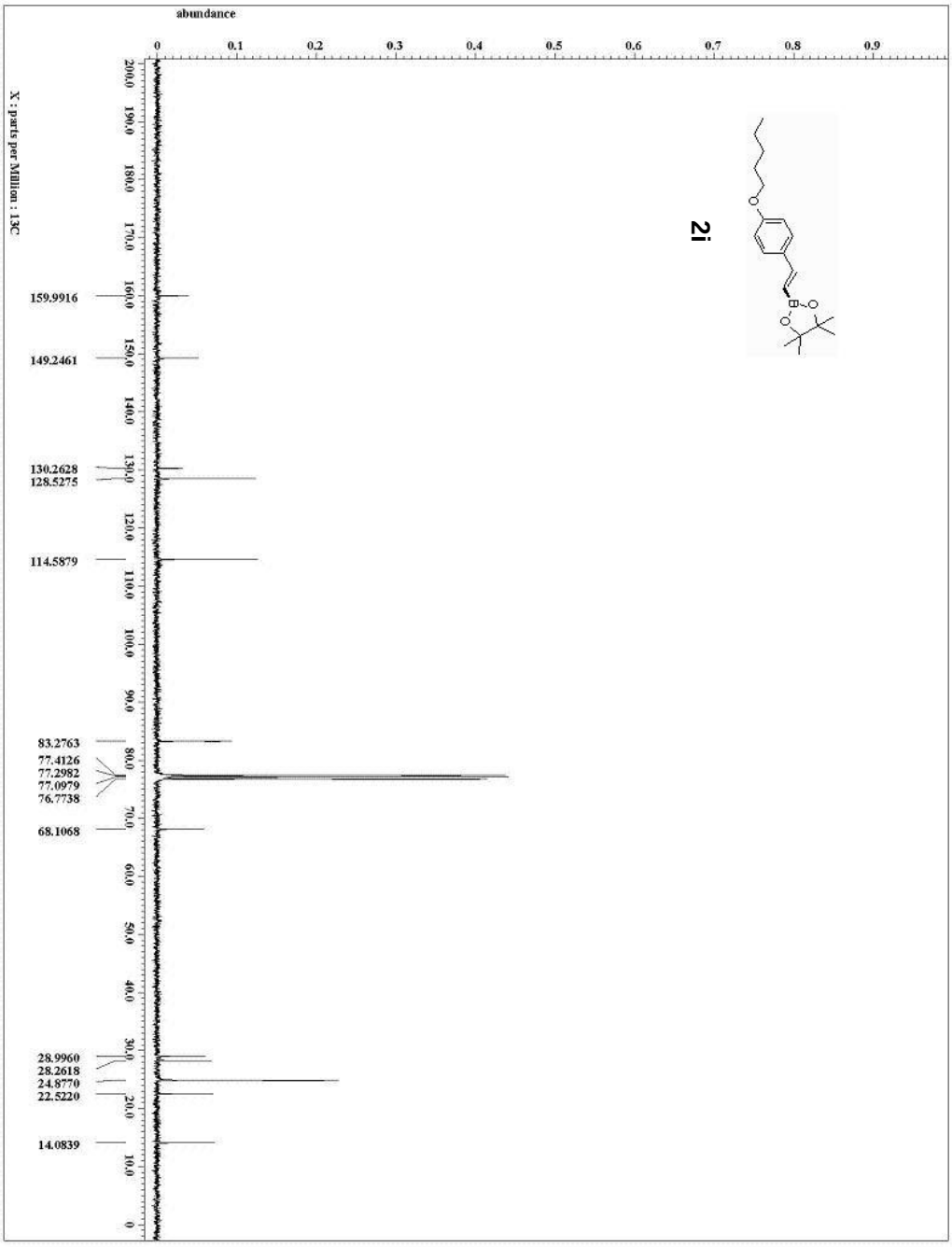
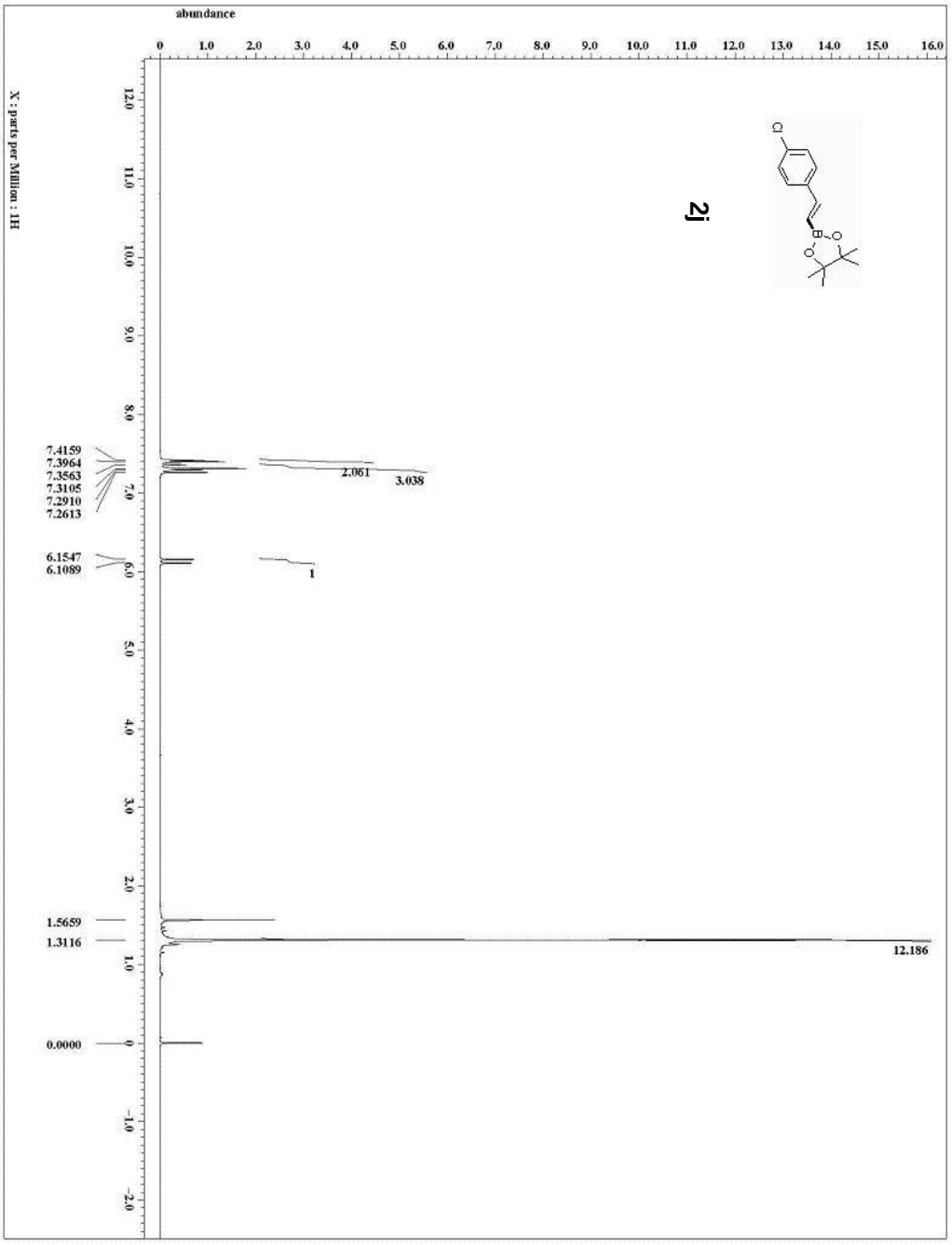
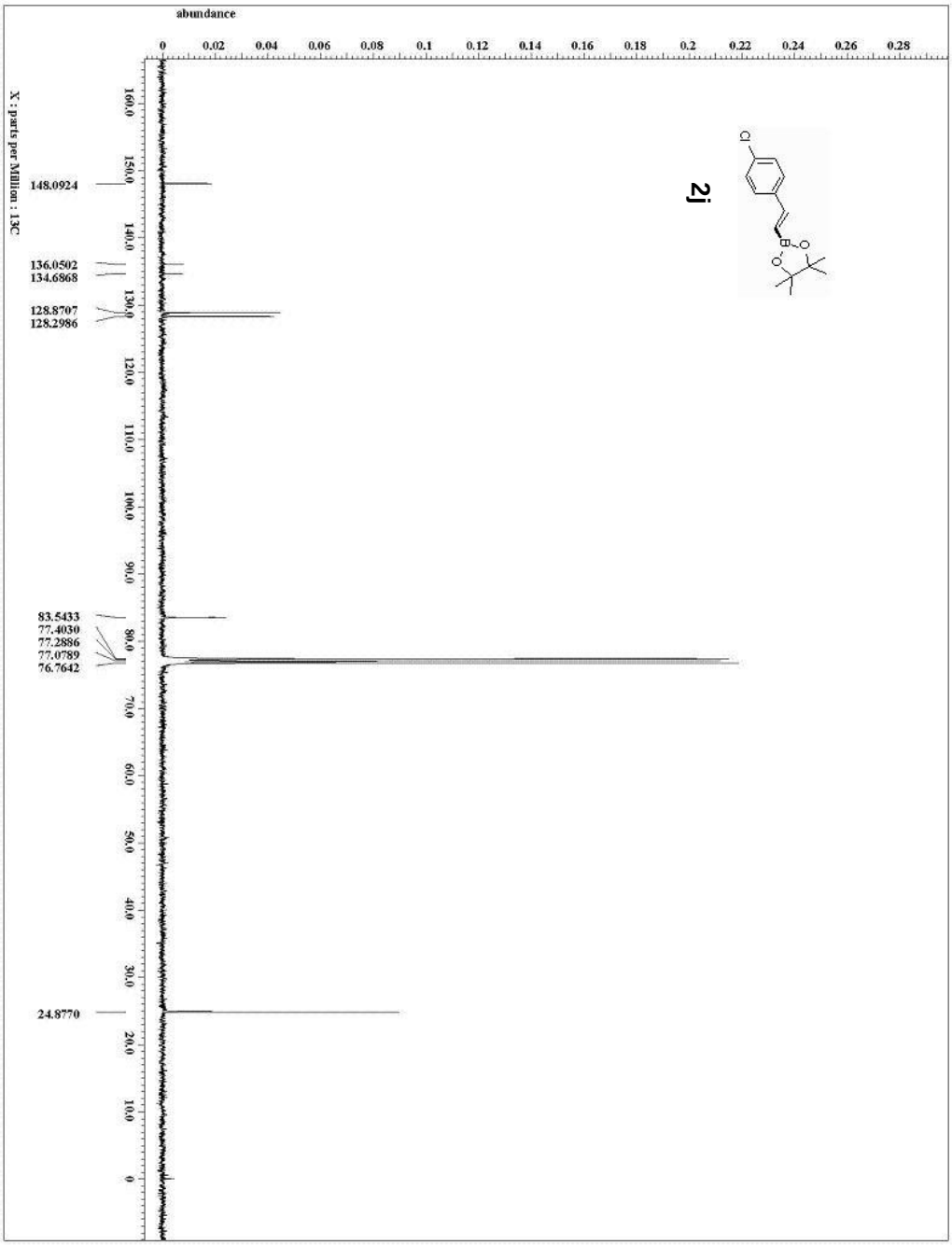
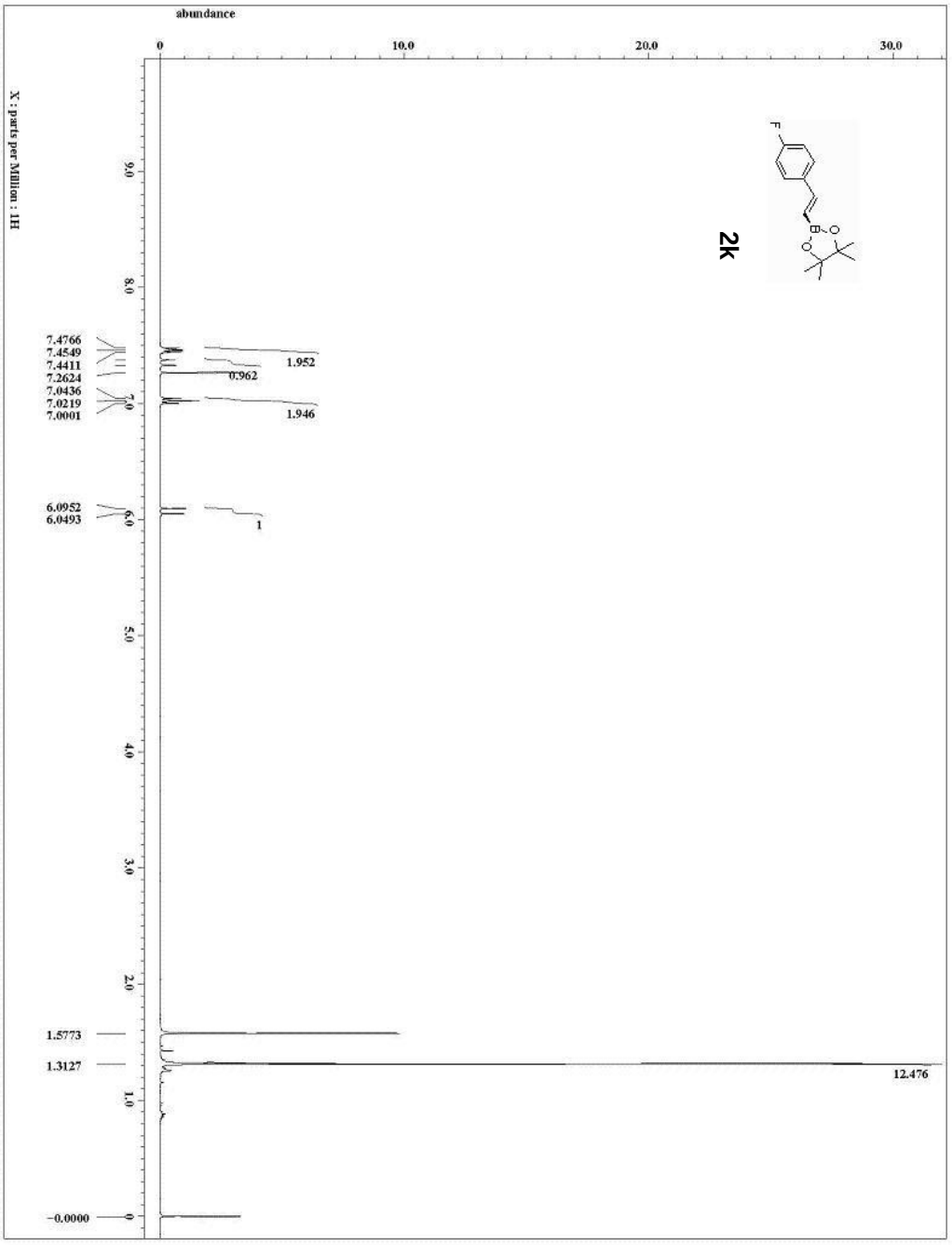
14.0934
2h

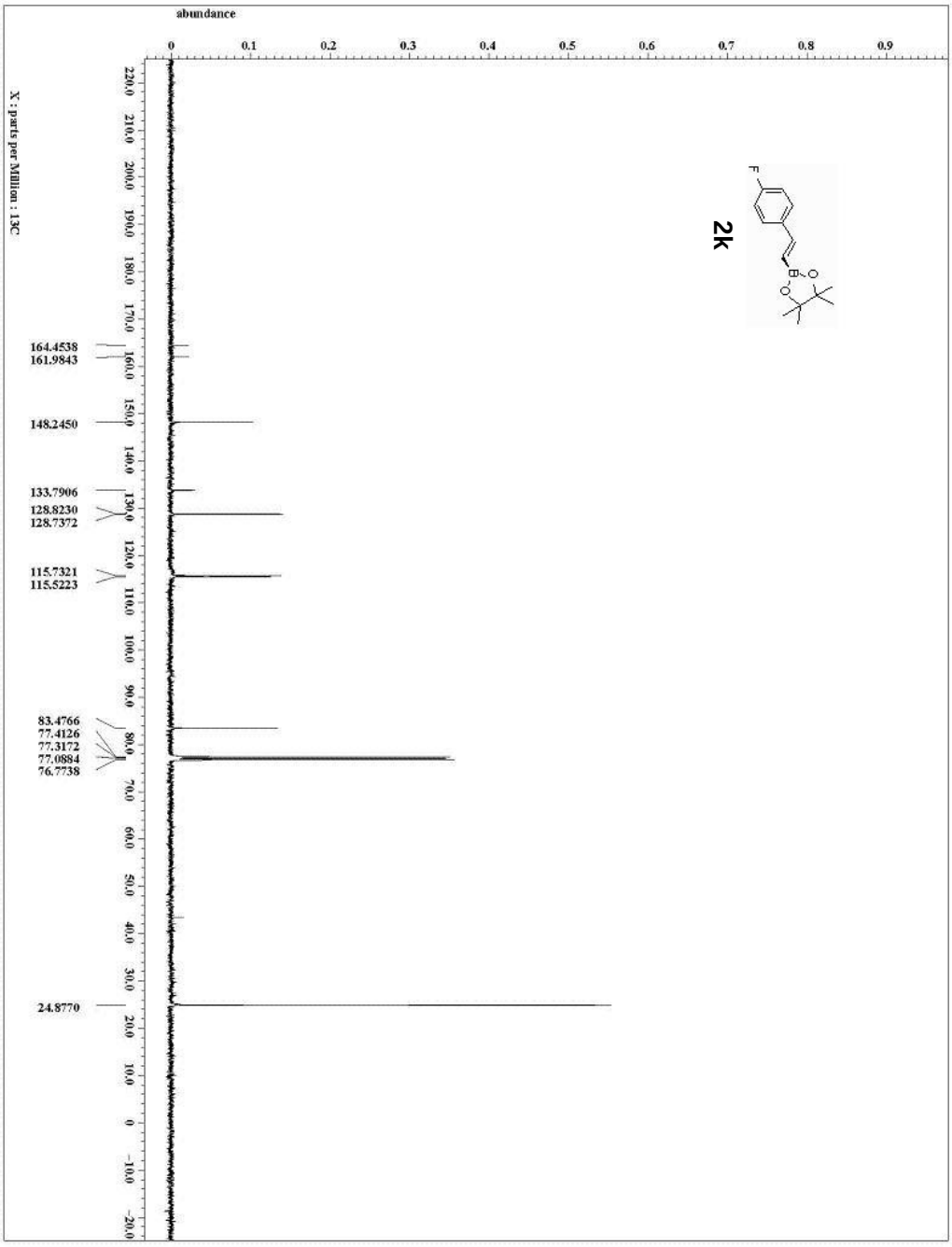

abundance
X : parts per Million : 1H
2i
7.4297
7.4067
7.3701
7.3243
7.2601
6.8603
6.8386
6.0241
5.9783
3.9726
3.9554
3.9393
1.7984
1.7812
1.7618
1.6106
1.4032
1.3872
1.3059
0.9450
0.9278
0.9095
0.0000
1.991
2.061
1.04
2.072
2.133
4.073
12.057
3.02

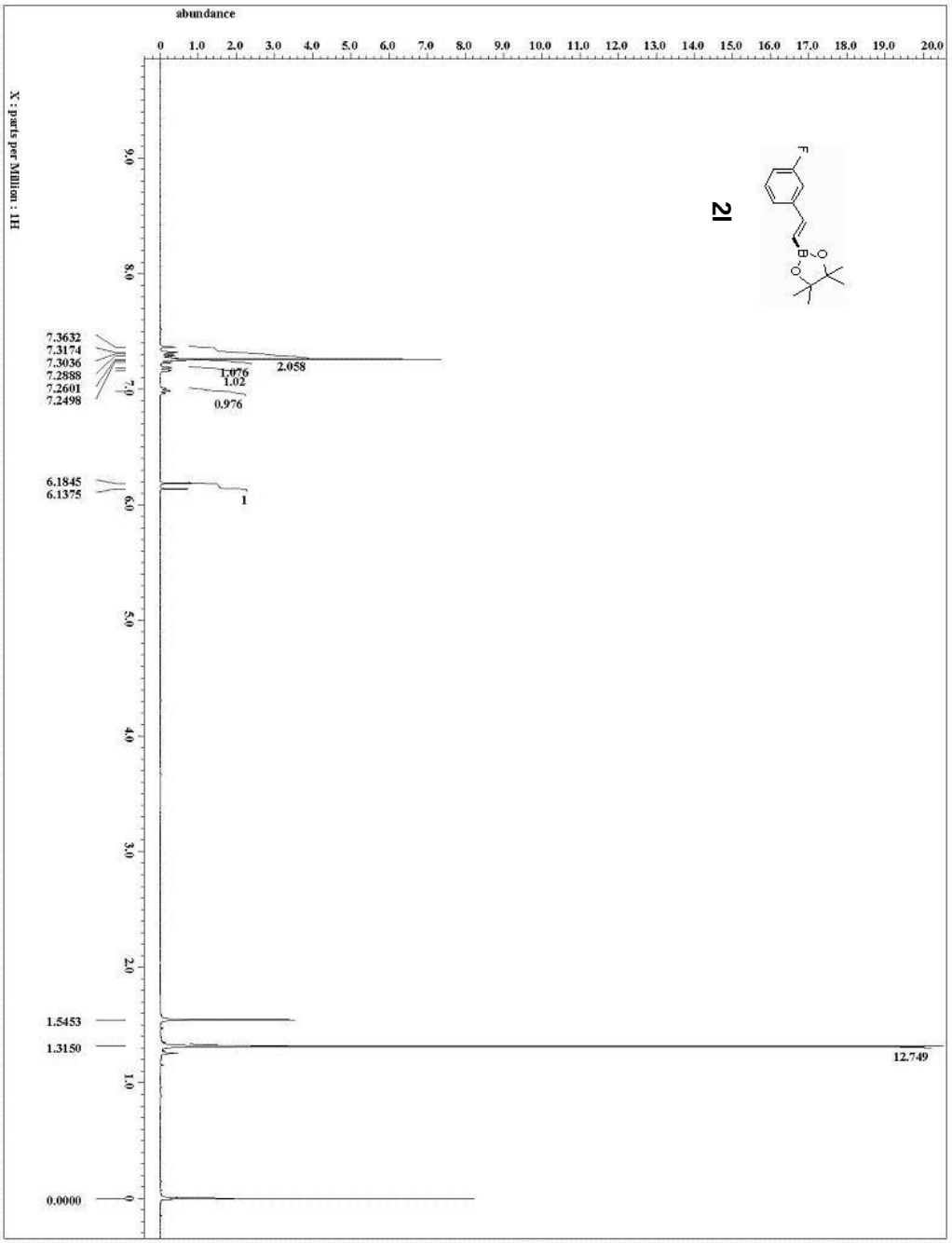

abundance
X : parts per Million : 13C
159.9916
149.2461
130.2628
128.5275
114.5879
83.2763
77.4126
77.2982
77.0979
76.7738
68.1068
28.9960
28.2618
24.8770
22.5220
14.0839
2i

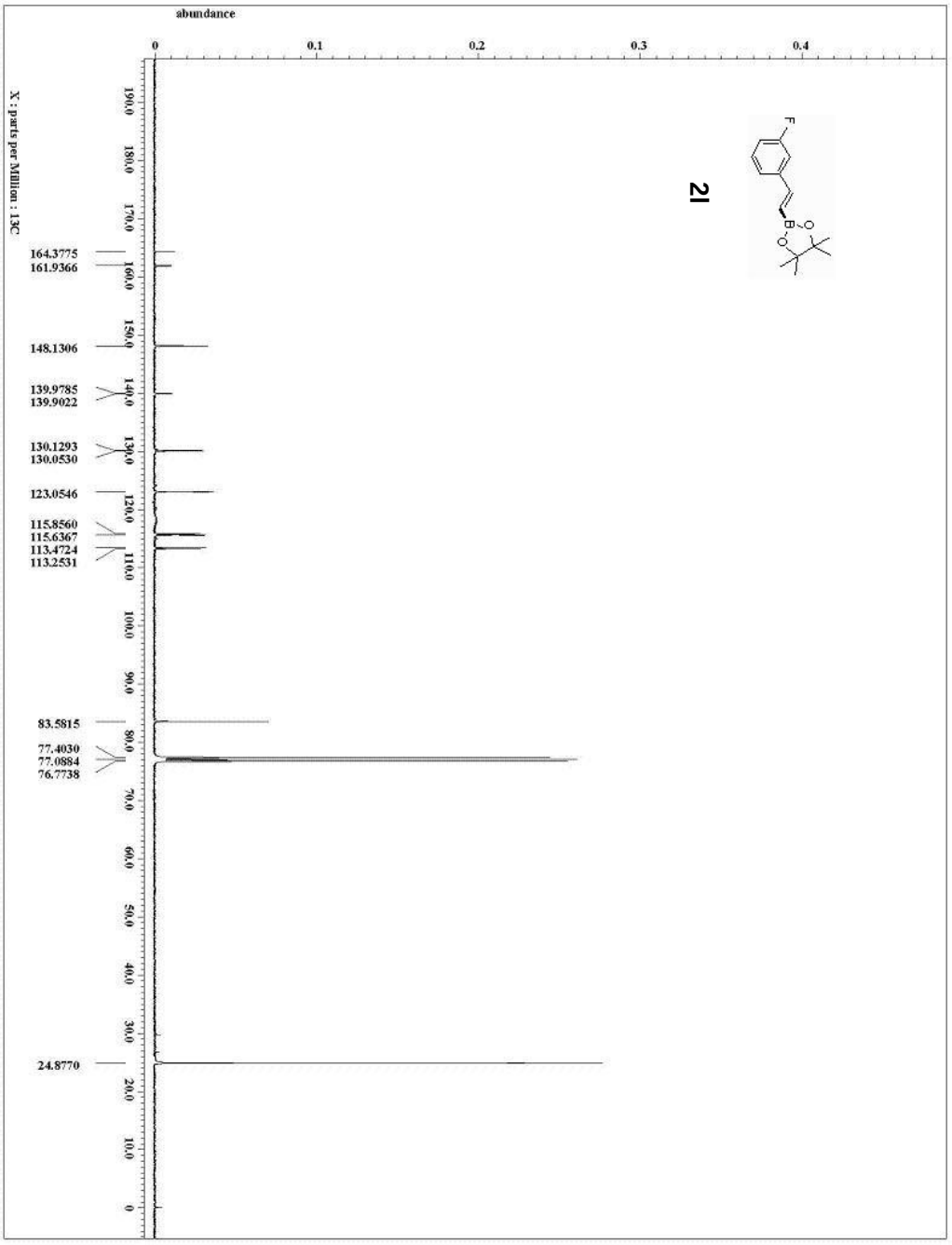

abundance
X : parts per Million : 1H
2j
Cl
7.4159
7.3964
7.3563
7.3105
7.2910
7.2613
6.1547
6.1089
1.5659
1.3116
0.0000
2.061
3.038
1
12.186

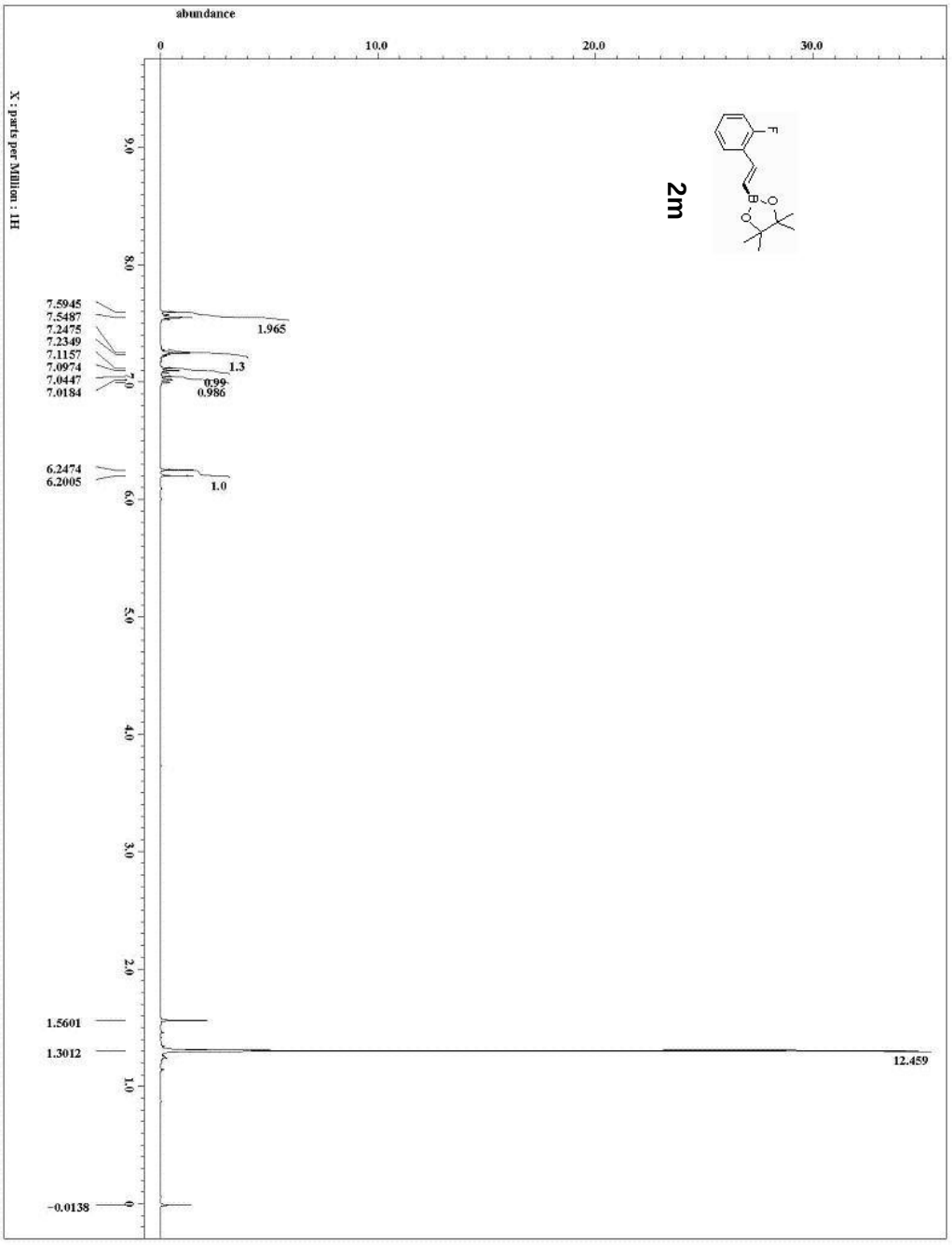

abundance
X : parts per Million : 13C
148.0924
136.0502
134.6868
128.8707
128.2986
83.5433
77.4030
77.2886
77.0789
76.7642
24.8770
2j

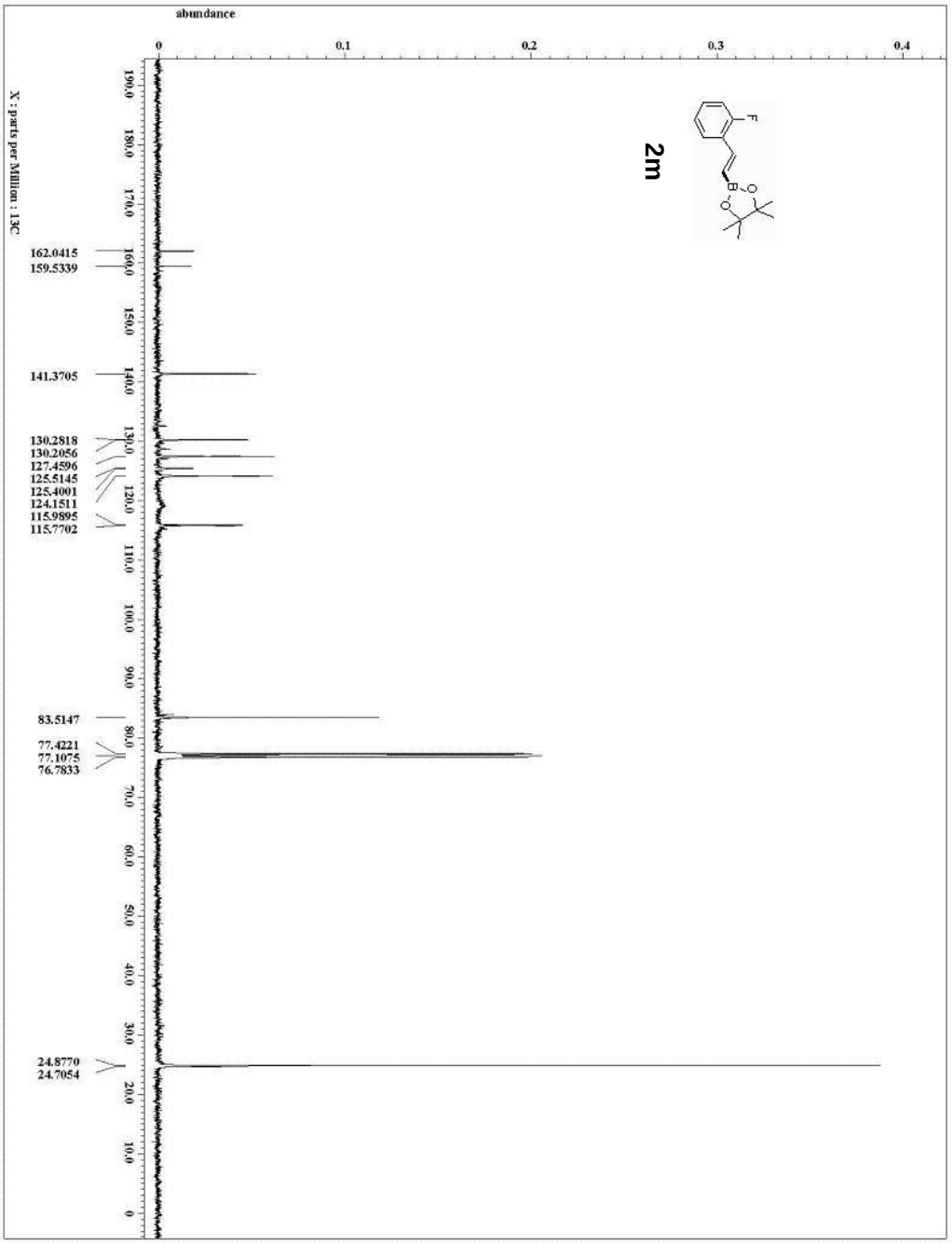


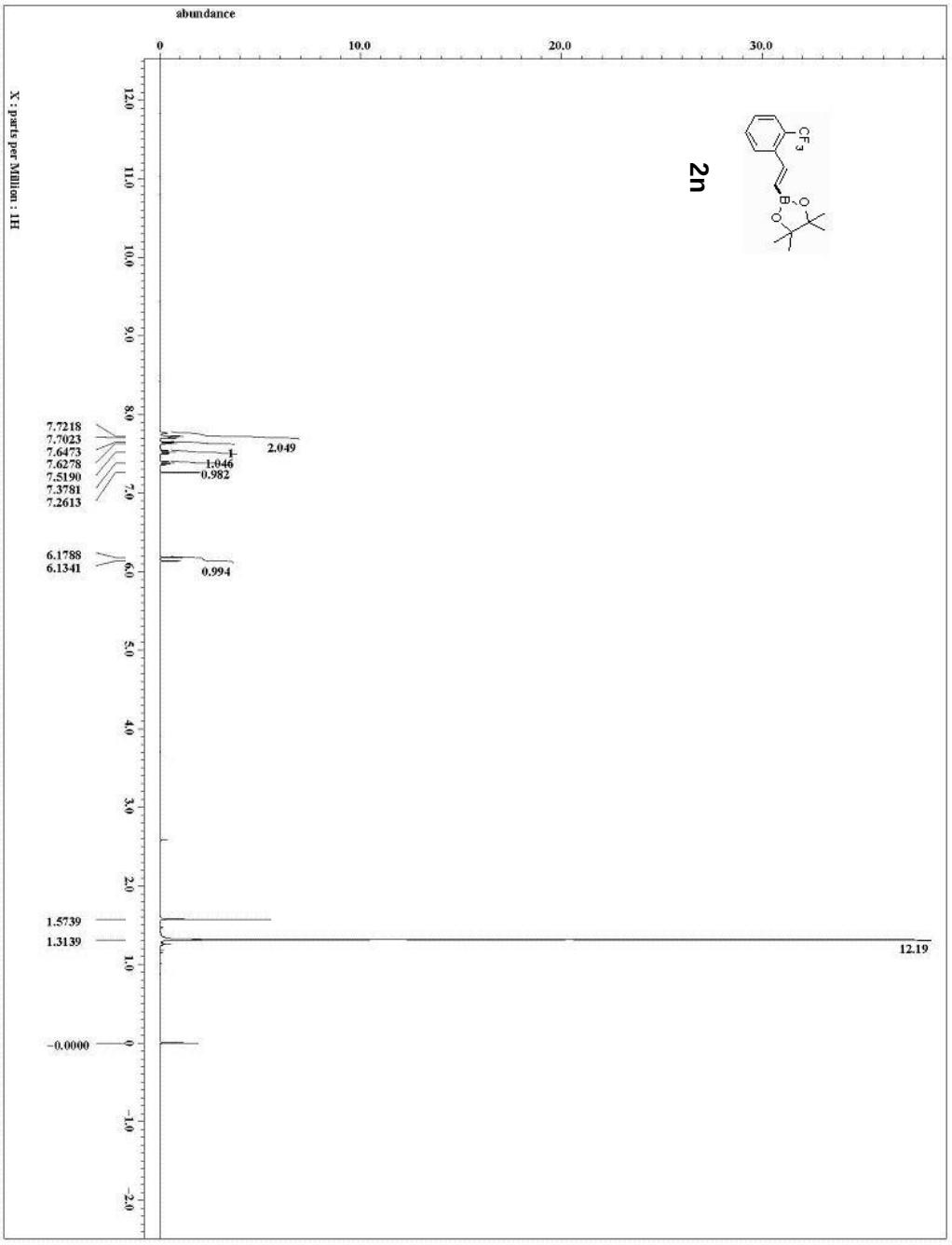

abundance
X : parts per Million : 13C
2k
164.4538
161.9843
148.2450
133.7906
128.8230
128.7372
115.7321
115.5223
83.4766
77.4126
77.3172
77.0884
76.7738
24.8770

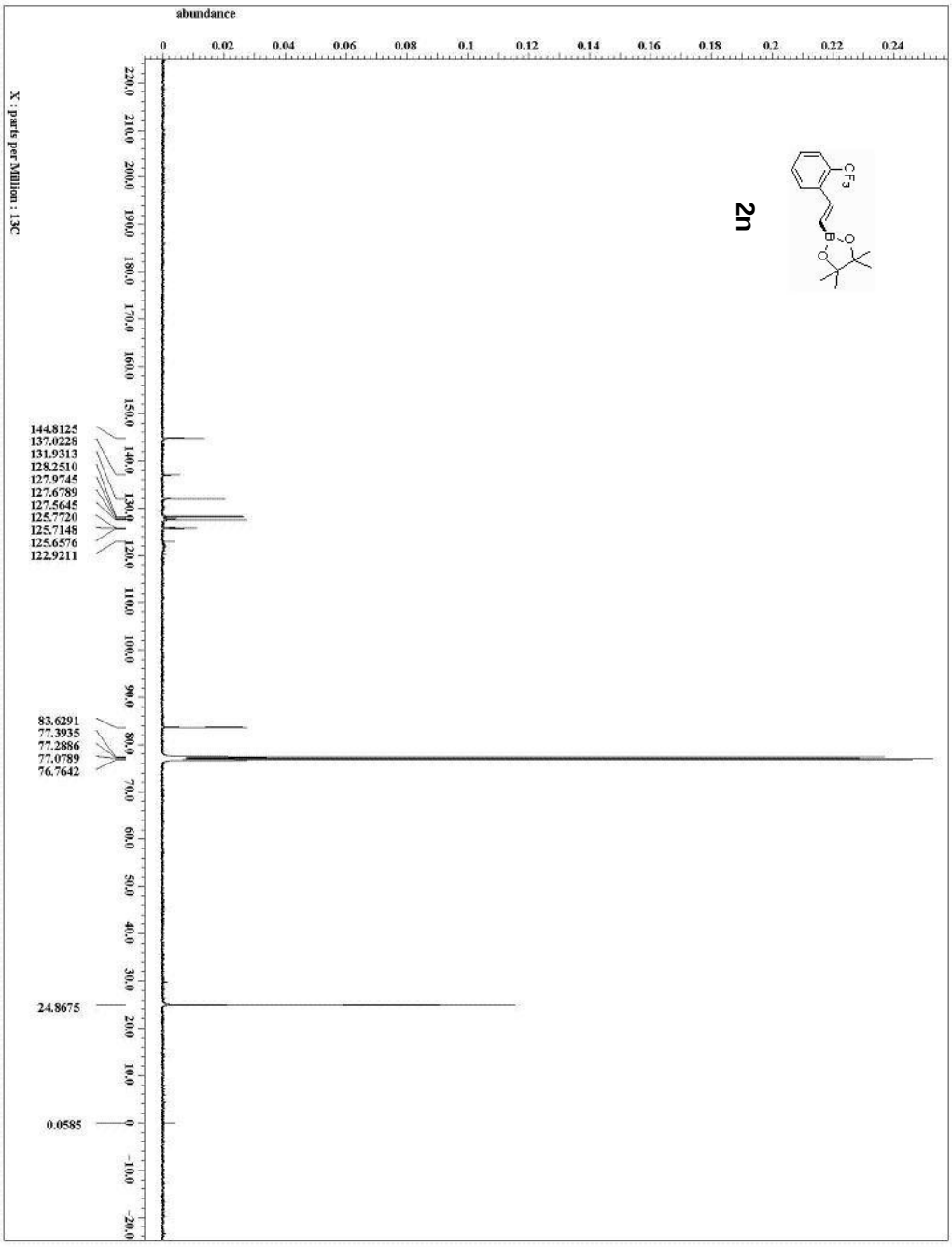

abundance
X : parts per Million : 1H
2l
7.3632
7.3174
7.3036
7.2888
7.2601
7.2498
2.058
1.076
1.02
0.976
6.1845
6.1375
1
1.5453
1.3150
12.749
0.0000

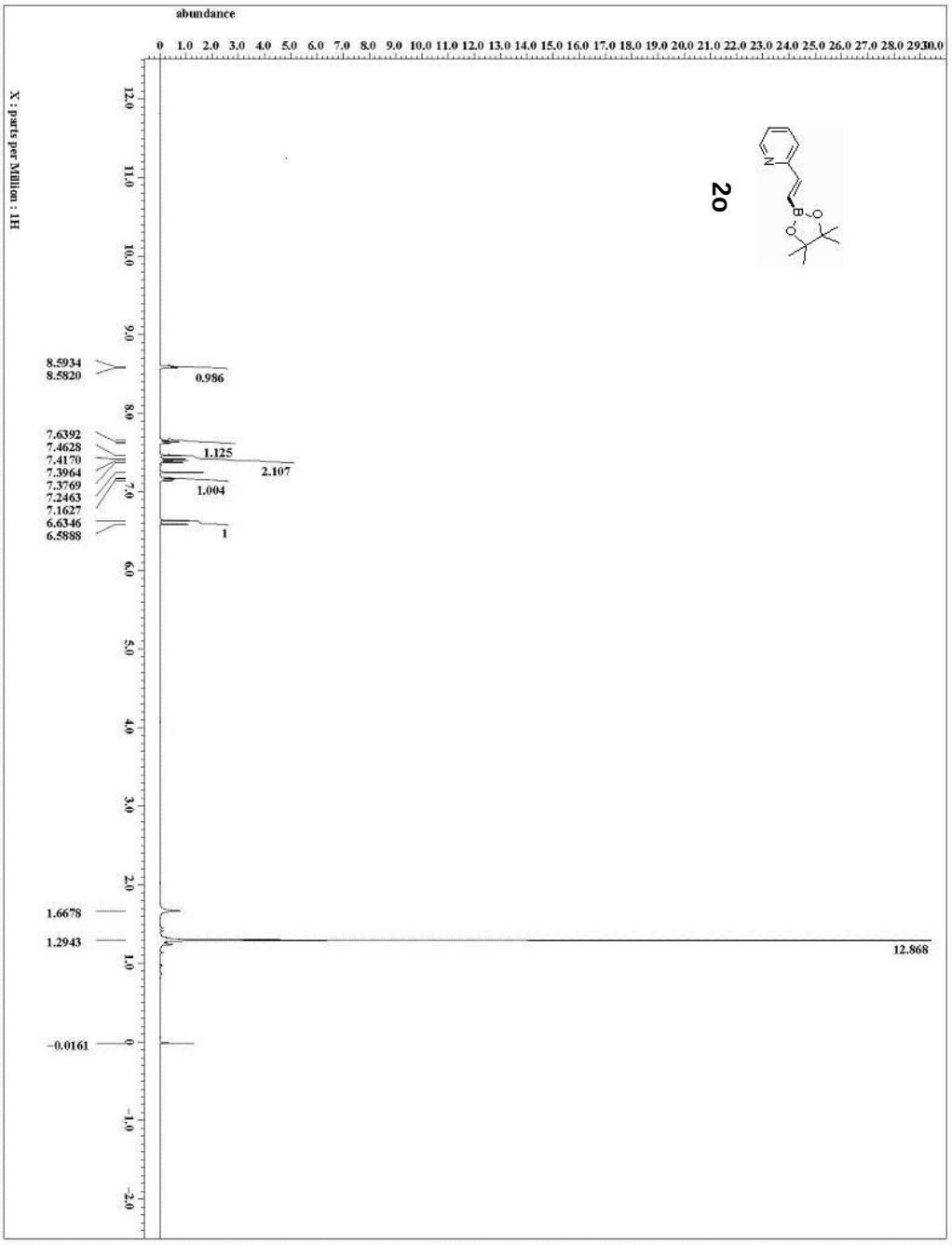

abundance
0
0.1
0.2
0.3
0.4
X : parts per Million : 13C
190.0
180.0
170.0
164.3775
161.9366
160.0
150.0
148.1306
140.0
139.9785
139.9022
130.1293
130.0530
130.0
123.0546
120.0
115.8560
115.6367
113.4724
113.2531
110.0
100.0
90.0
83.5815
80.0
77.4030
77.0884
76.7738
70.0
60.0
50.0
40.0
30.0
24.8770
20.0
10.0
0
21
F
B
O
O

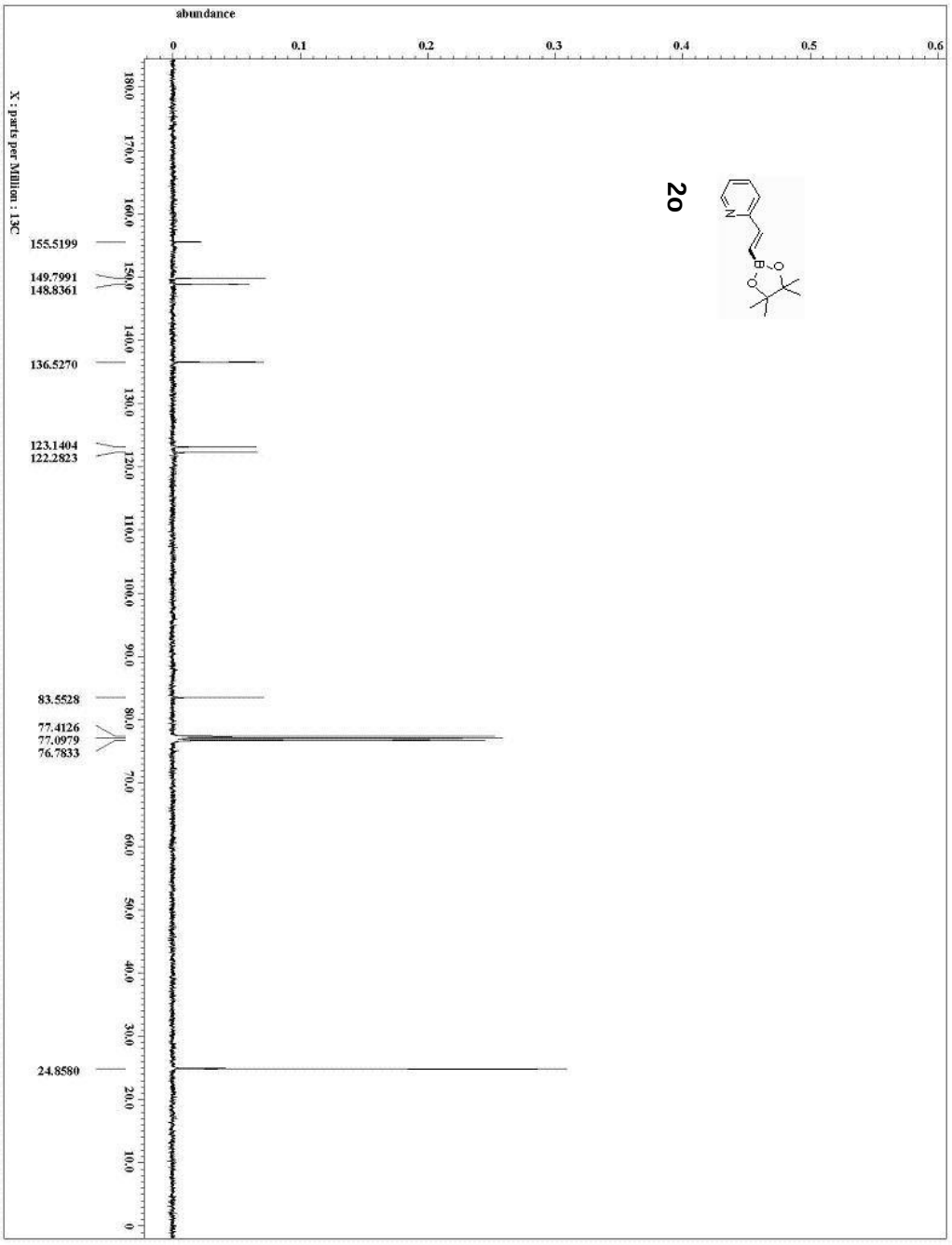

abundance
0
10.0
20.0
30.0
X : parts per Million : 1H
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
2m
F
B
O
O
7.5945
7.5487
7.2475
7.2349
7.1157
7.0974
7.0447
7.0184
1.965
1.3
0.99
0.986
6.2474
6.2005
1.0
1.5601
1.3012
12.459
-0.0138

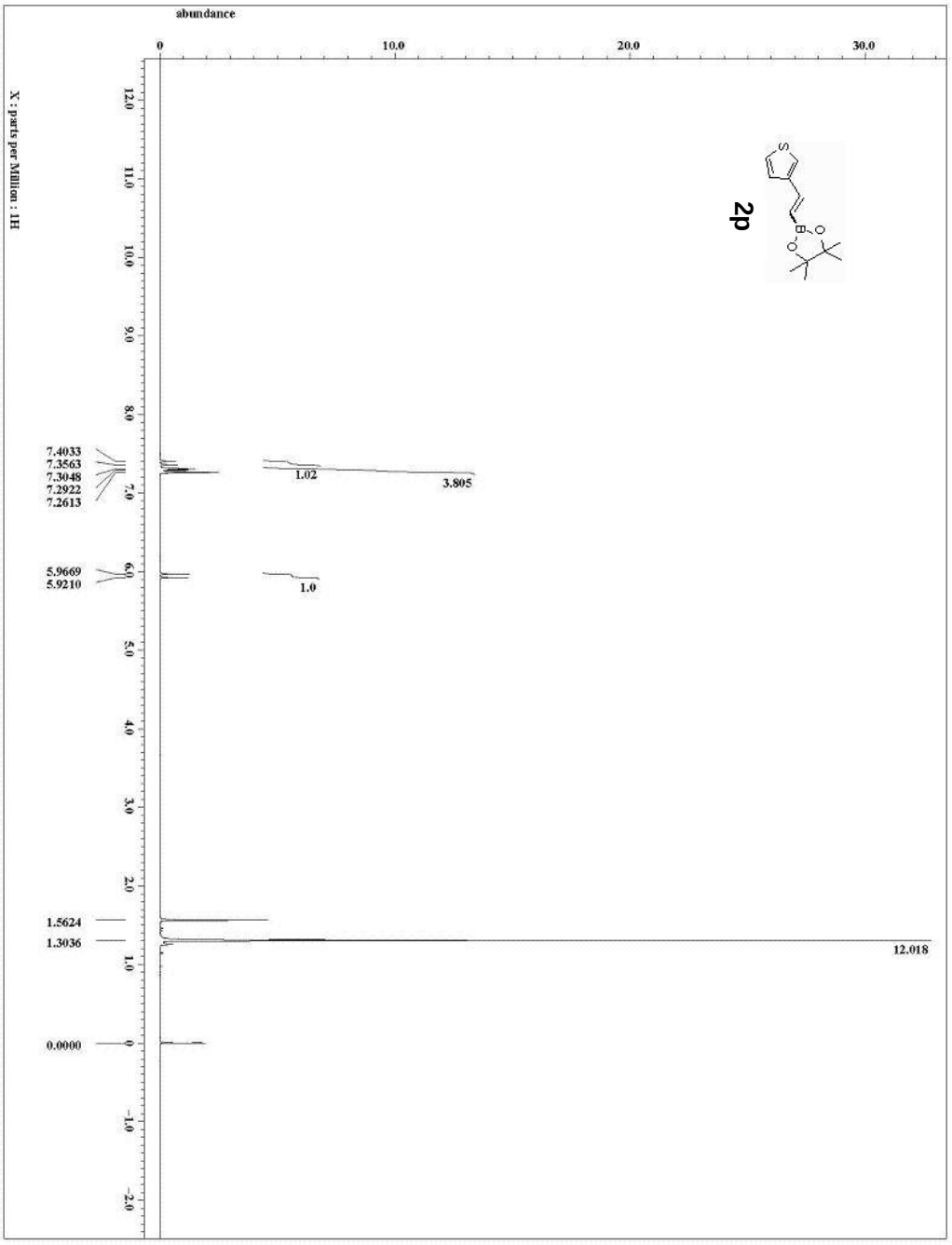

abundance
0
0.1
0.2
0.3
0.4
X : parts per Million : 13C
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
162.0415
159.5339
141.3705
130.2818
130.2056
127.4596
125.5145
125.4001
124.1511
115.9895
115.7702
83.5147
77.4221
77.1075
76.7833
24.8770
24.7054
2m

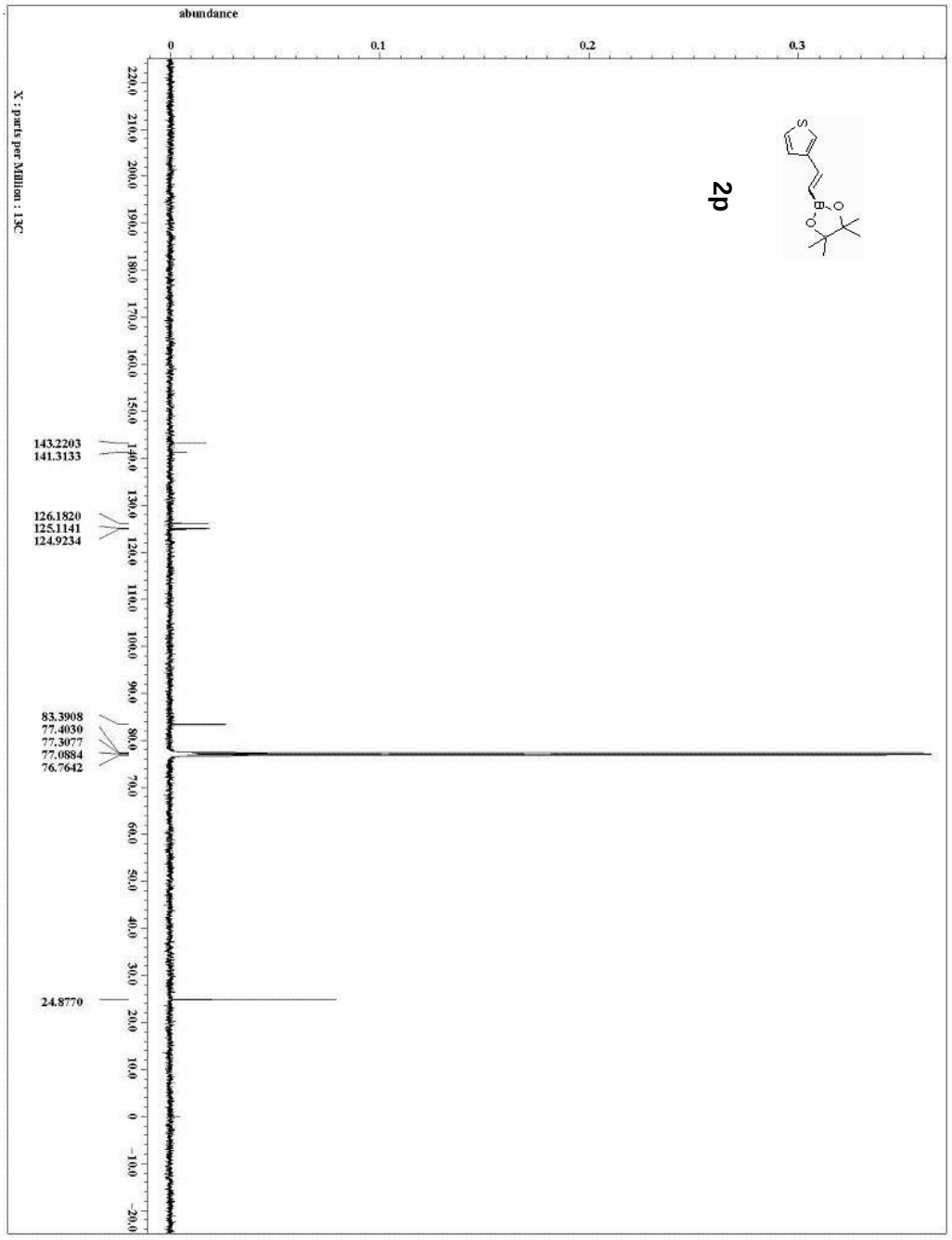


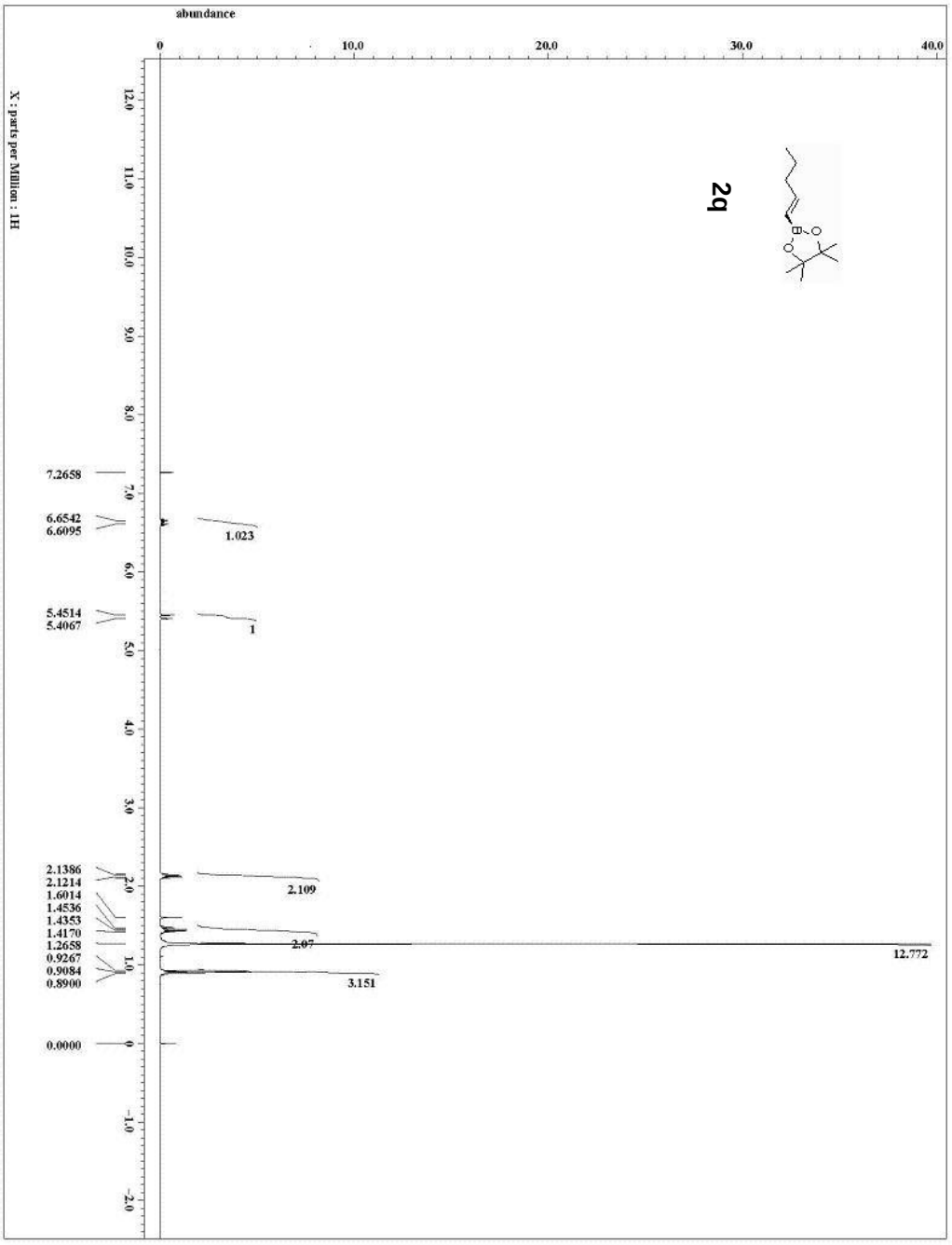

abundance
X : parts per Million : 13C
2n
144.8125
137.0228
131.9313
128.2510
127.9745
127.6789
127.5645
125.7720
125.7148
125.6576
122.9211
83.6291
77.3935
77.2886
77.0789
76.7642
24.8675
0.0585

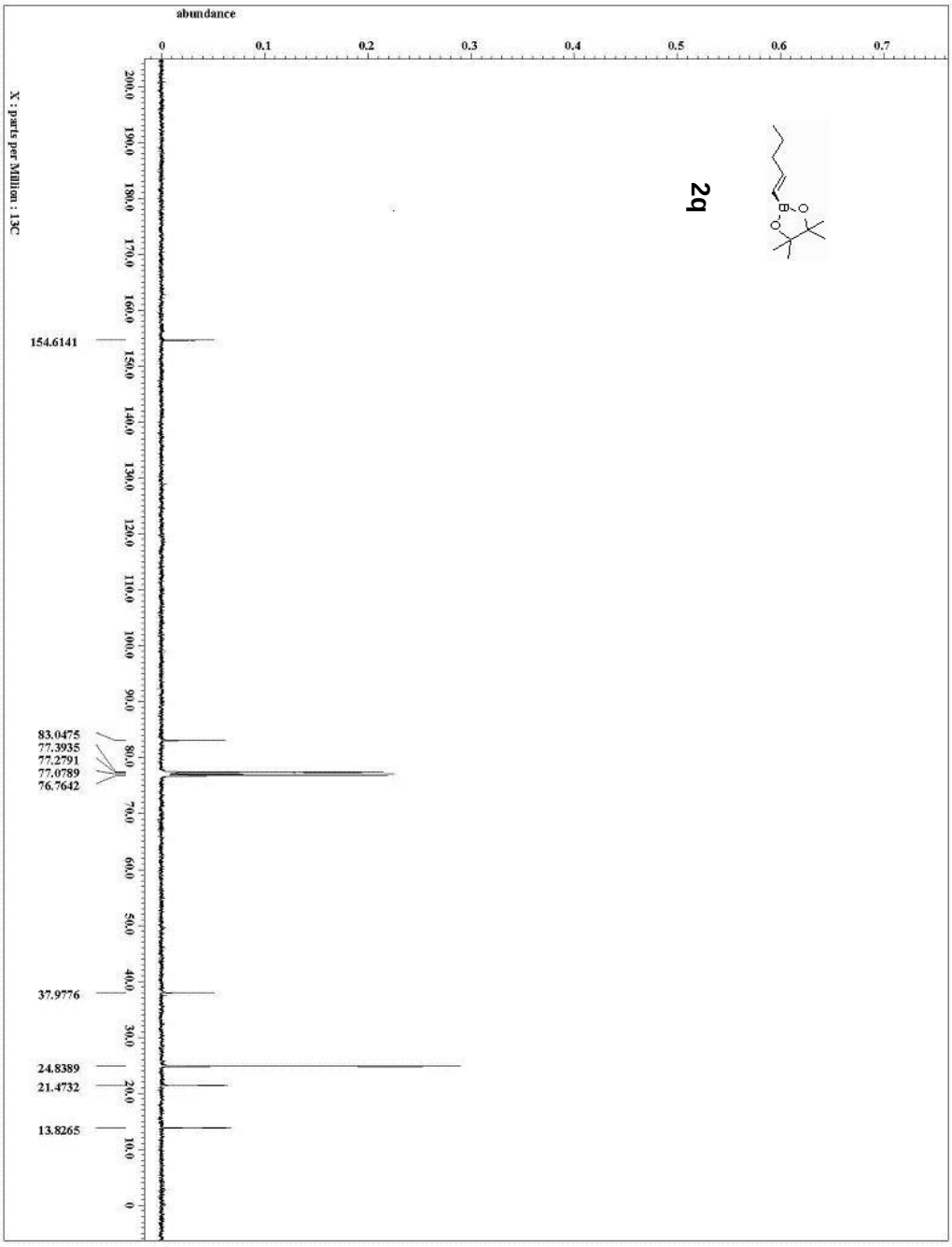

abundance
X : parts per Million : 1H
20
8.5934
8.5820
0.986
7.6392
7.4628
7.4170
7.3964
7.3769
7.2463
7.1627
6.6346
6.5888
1.125
2.107
1.004
1
1.6678
1.2943
12.868
-0.0161

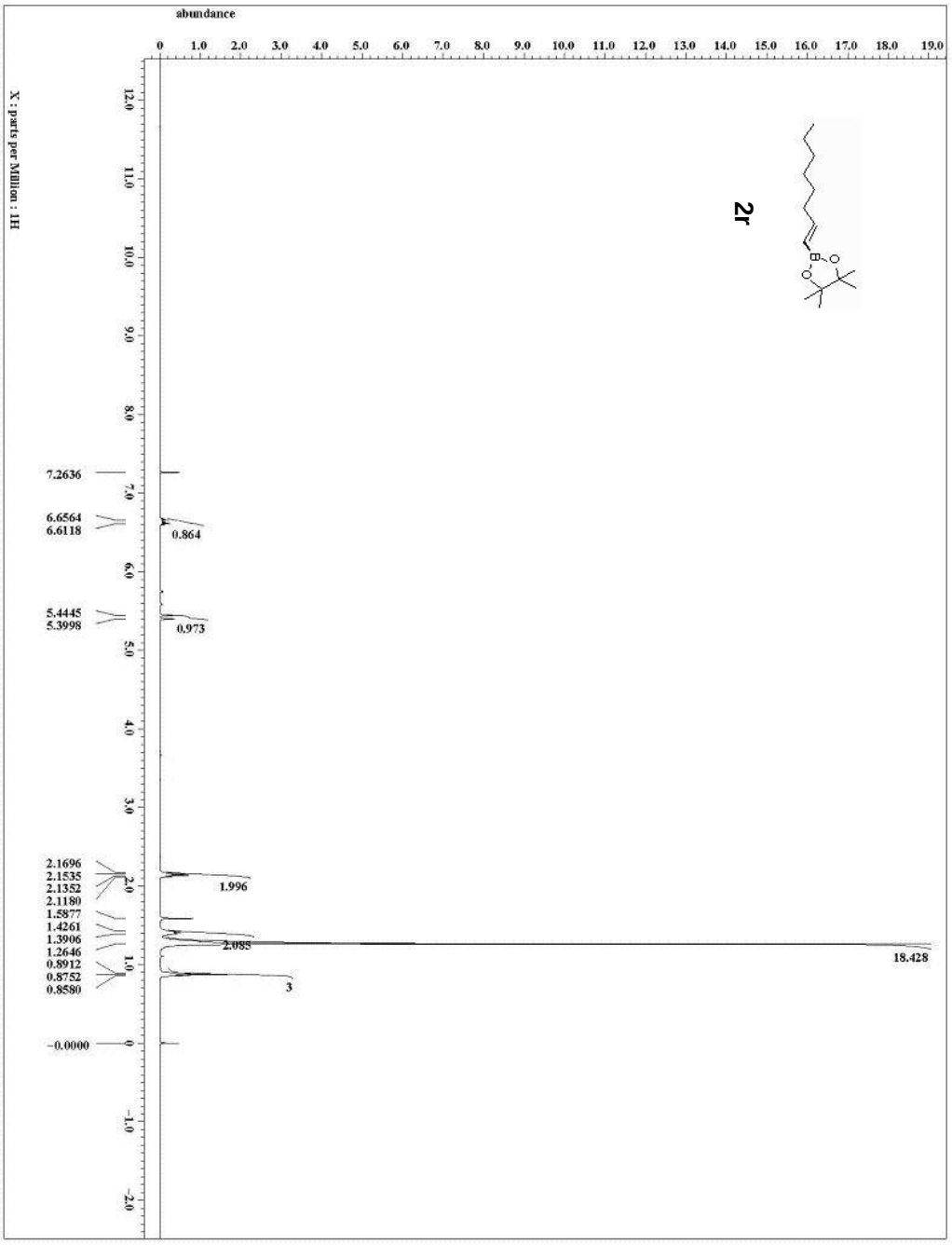

abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
X : parts per Million : 13C
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
155.5199
149.7991
148.8361
136.5270
123.1404
122.2823
83.5528
77.4126
77.0979
76.7833
24.8580
2o
N
B
O
O

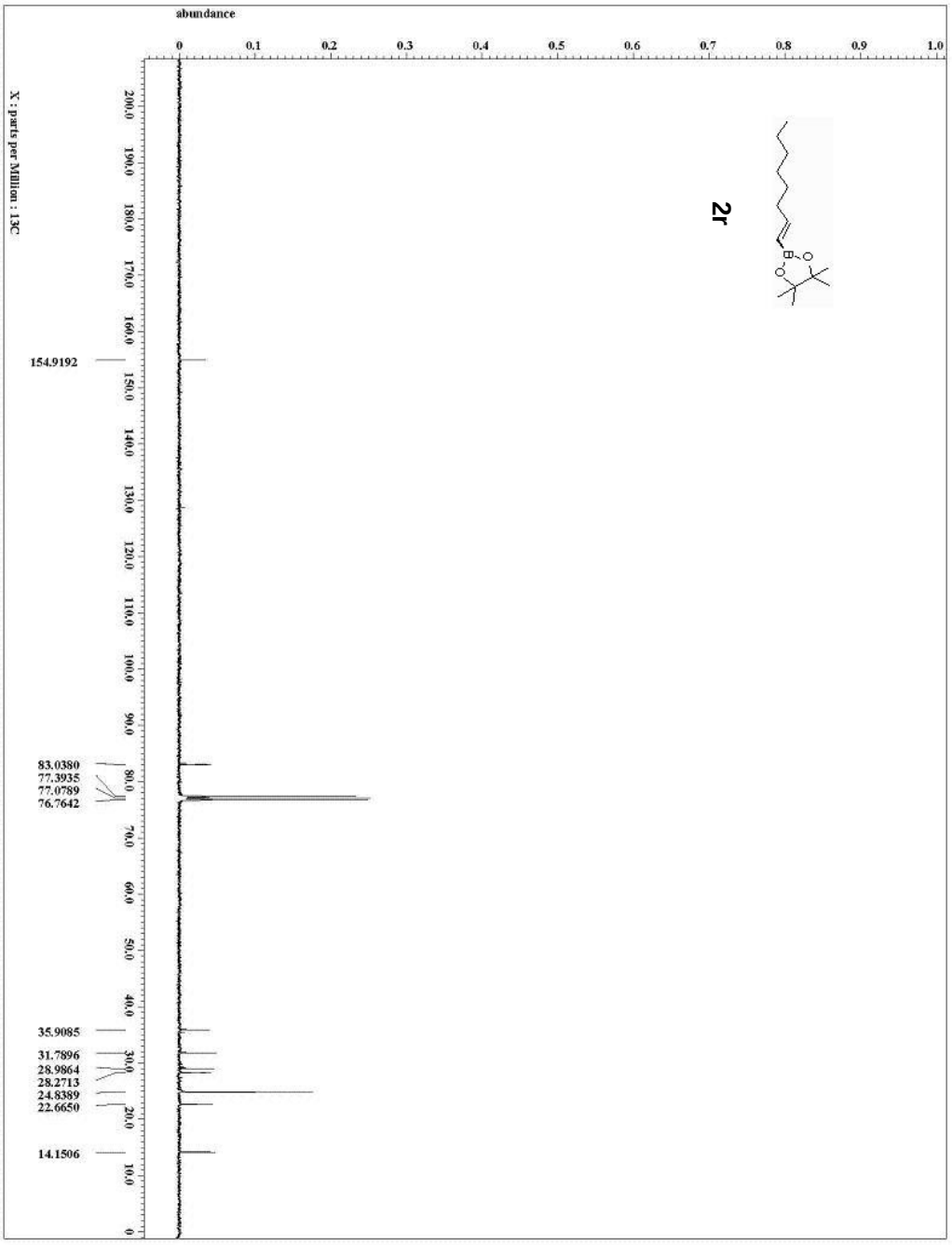

abundance
0
10.0
20.0
30.0
X : parts per Million : 1H
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.4033
7.3563
7.3048
7.2922
7.2613
1.02
3.805
5.9669
5.9210
1.0
1.5624
1.3036
12.018
0.0000
2p

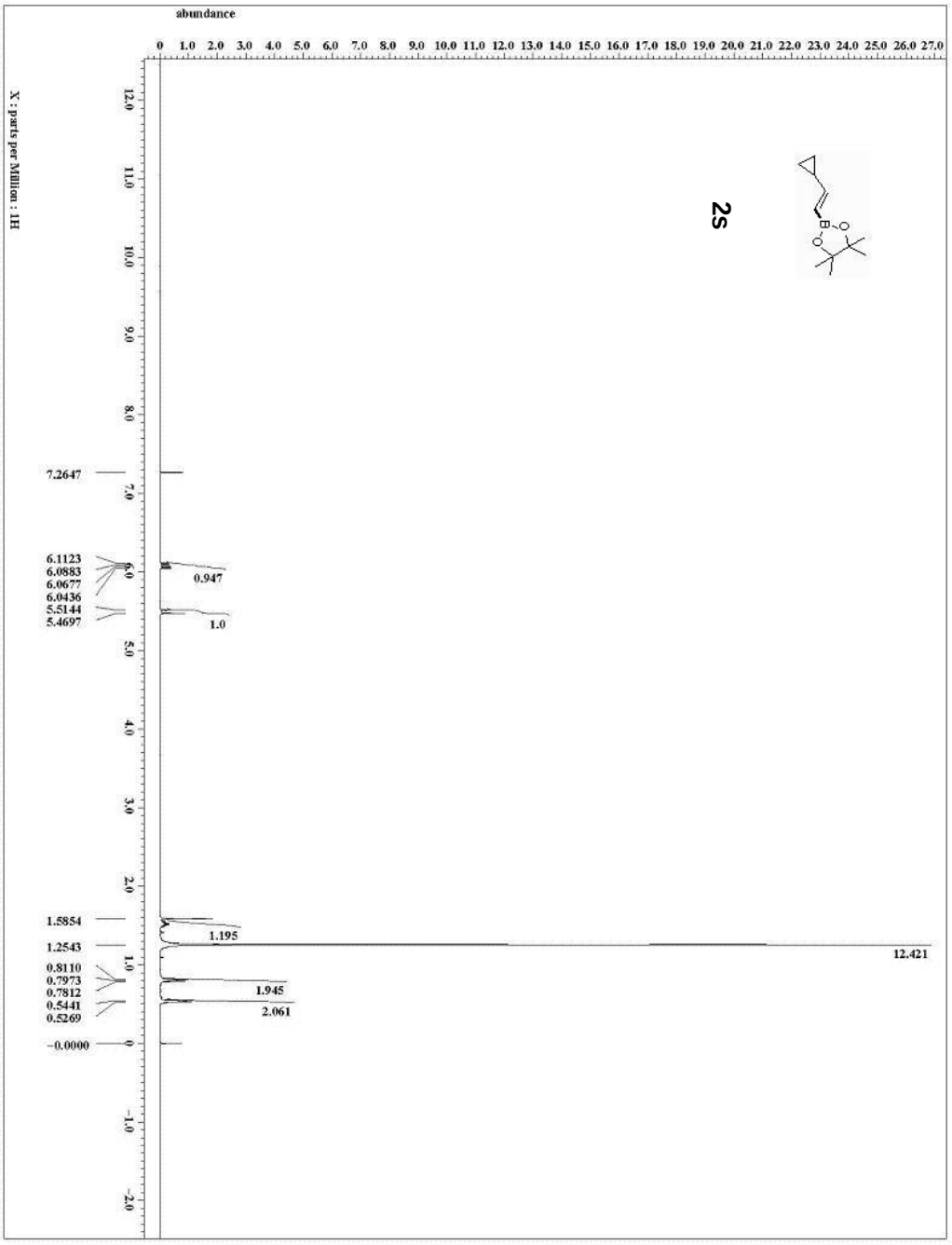

abundance
0
0.1
0.2
0.3
X : parts per Million : 13C
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
143.2203
141.3133
126.1820
125.1141
124.9234
83.3908
77.4030
77.3077
77.0884
76.7642
24.8770
2p

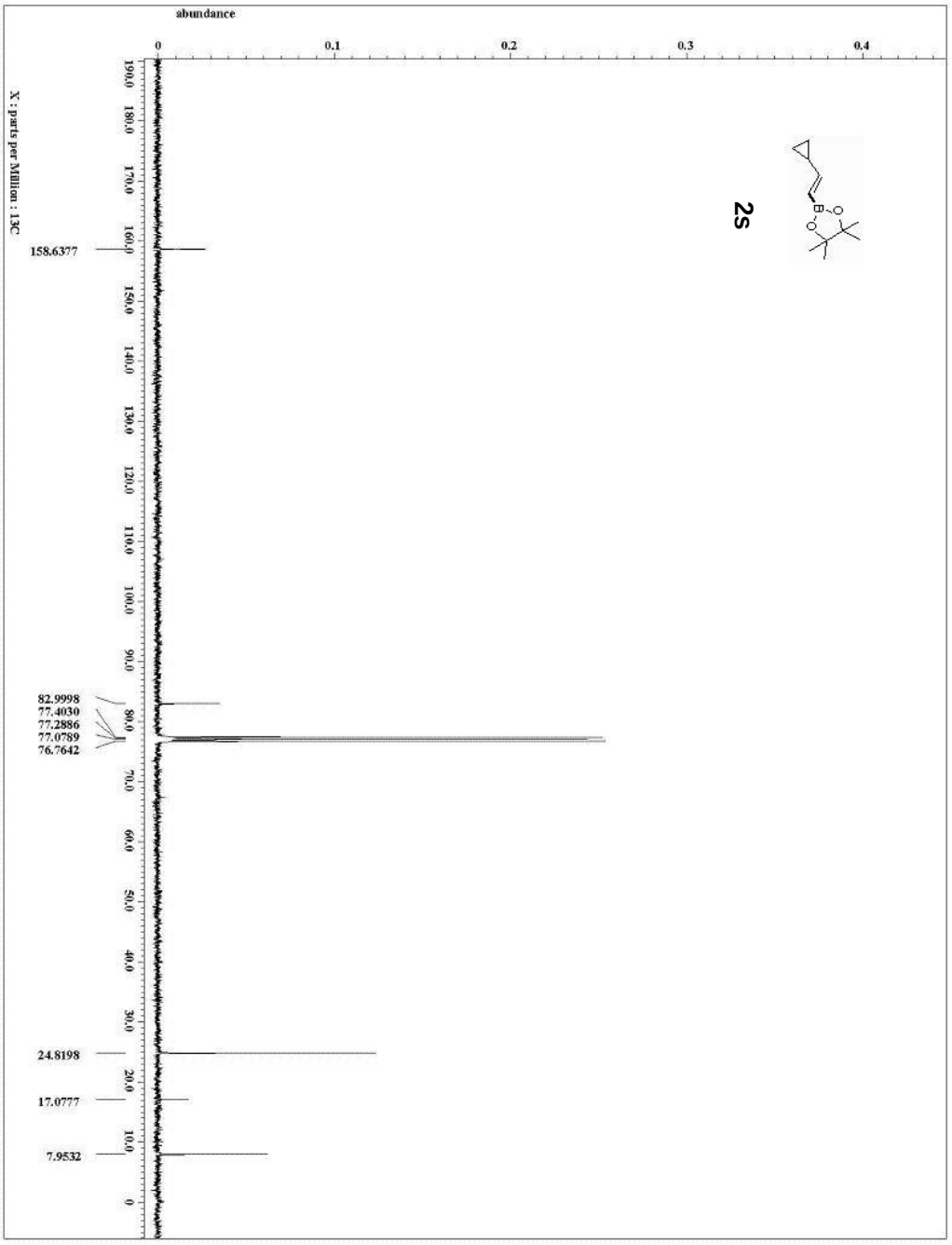

abundance
0
10.0
20.0
30.0
40.0
X : parts per Million : 1H
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.2658
6.6542
6.6095
1.023
5.4514
5.4067
1
2.1386
2.1214
1.6014
1.4536
1.4353
1.4170
1.2658
0.9267
0.9084
0.8900
2.109
2.07
12.772
3.151
0.0000
2q

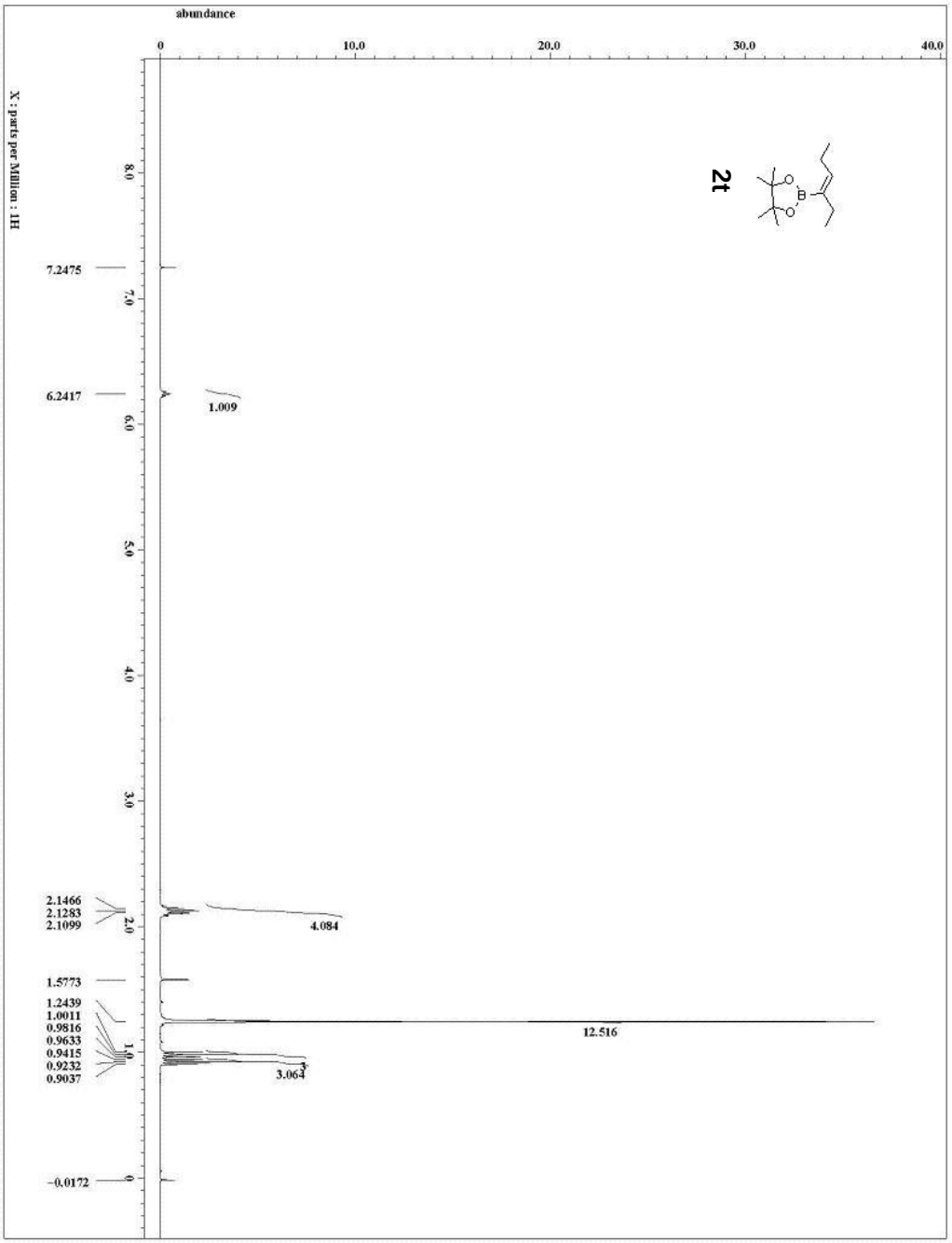


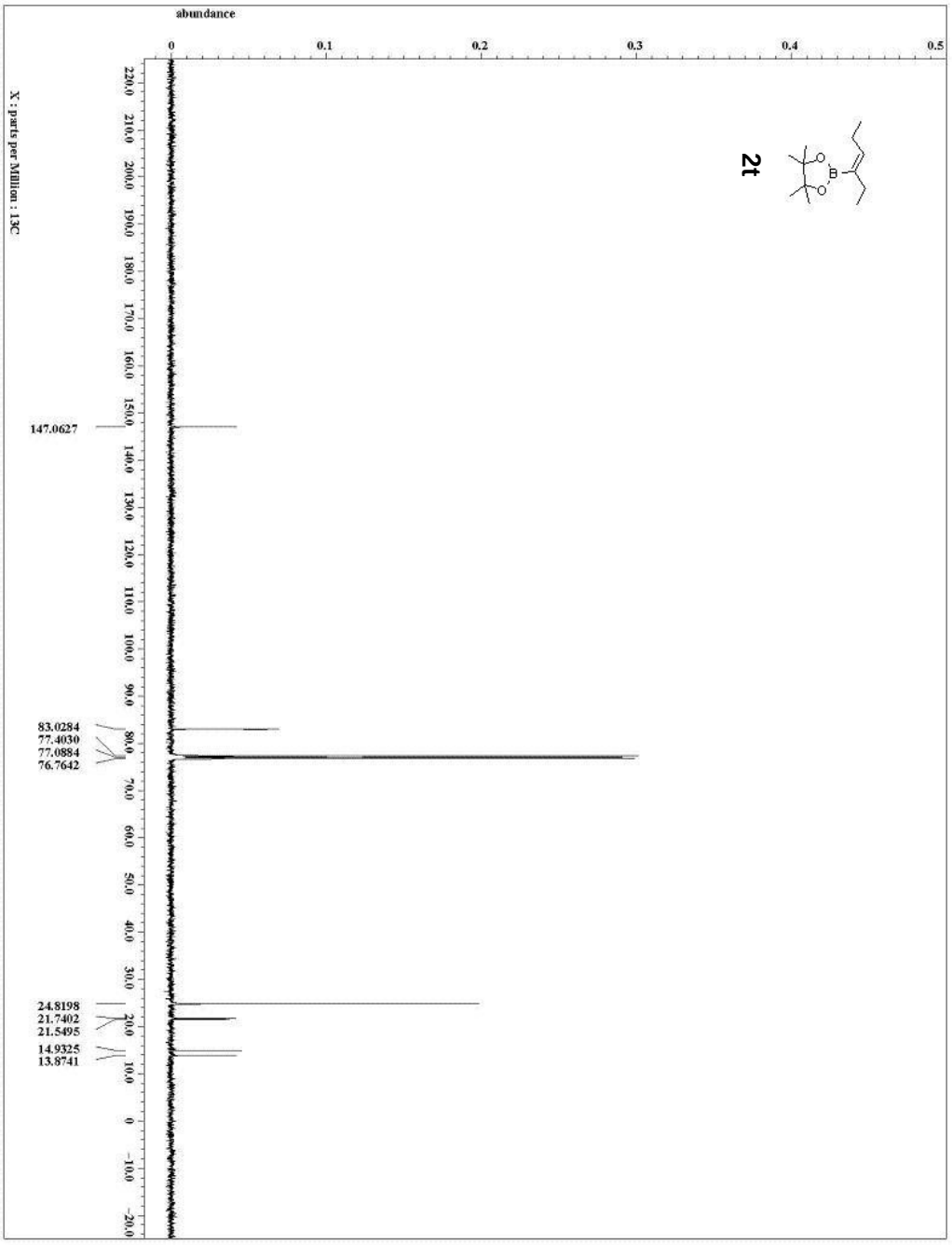

abundance
X : parts per Million : 1H
2r
7.2636
6.6564
6.6118
5.4445
5.3998
2.1696
2.1535
2.1352
2.1180
1.5877
1.4261
1.3906
1.2646
0.8912
0.8752
0.8580
−0.0000
0.864
0.973
1.996
2.085
3
18.428

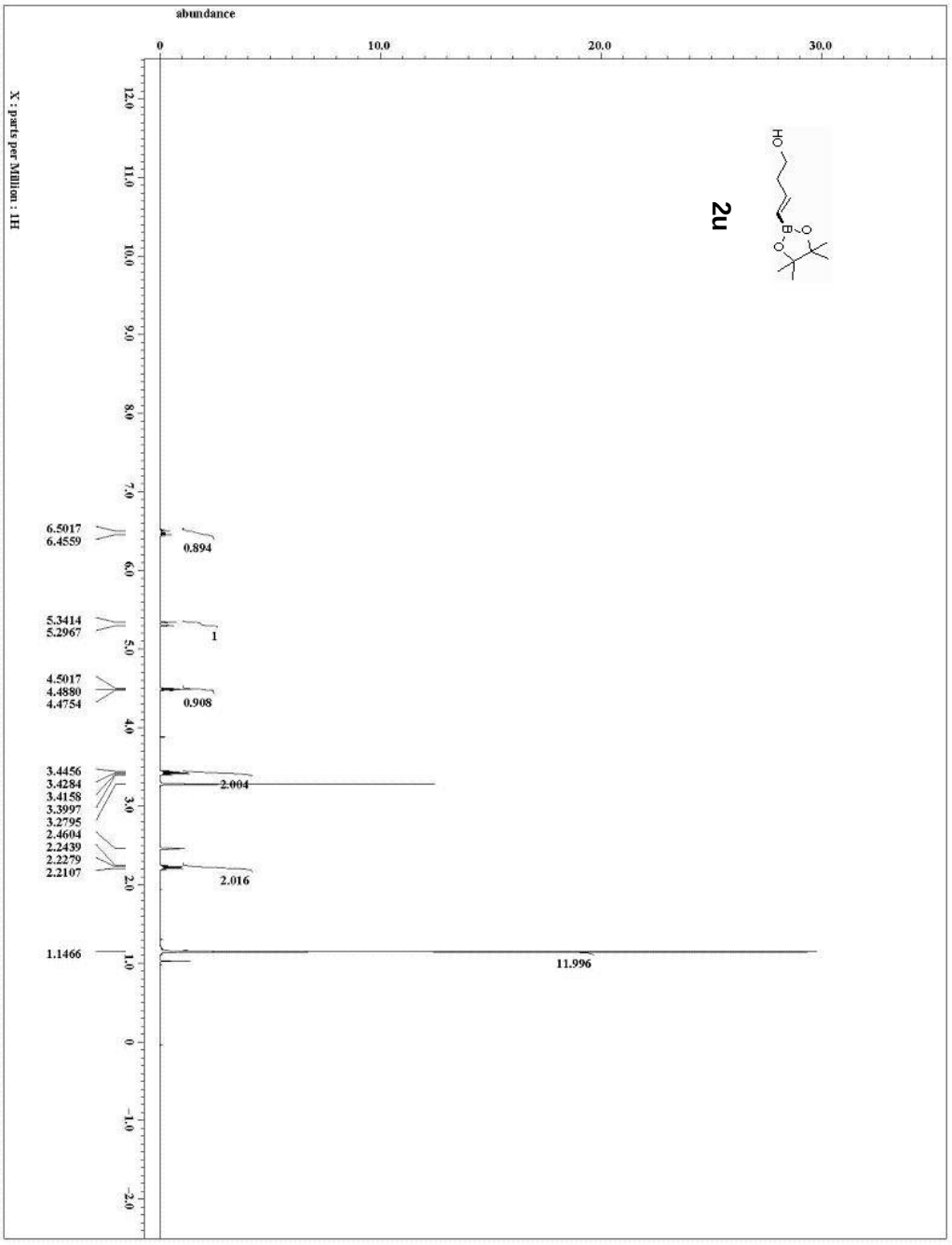

abundance
X : parts per Million : 13C
2r
154.9192
83.0380
77.3935
77.0789
76.7642
35.9085
31.7896
28.9864
28.2713
24.8389
22.6650
14.1506

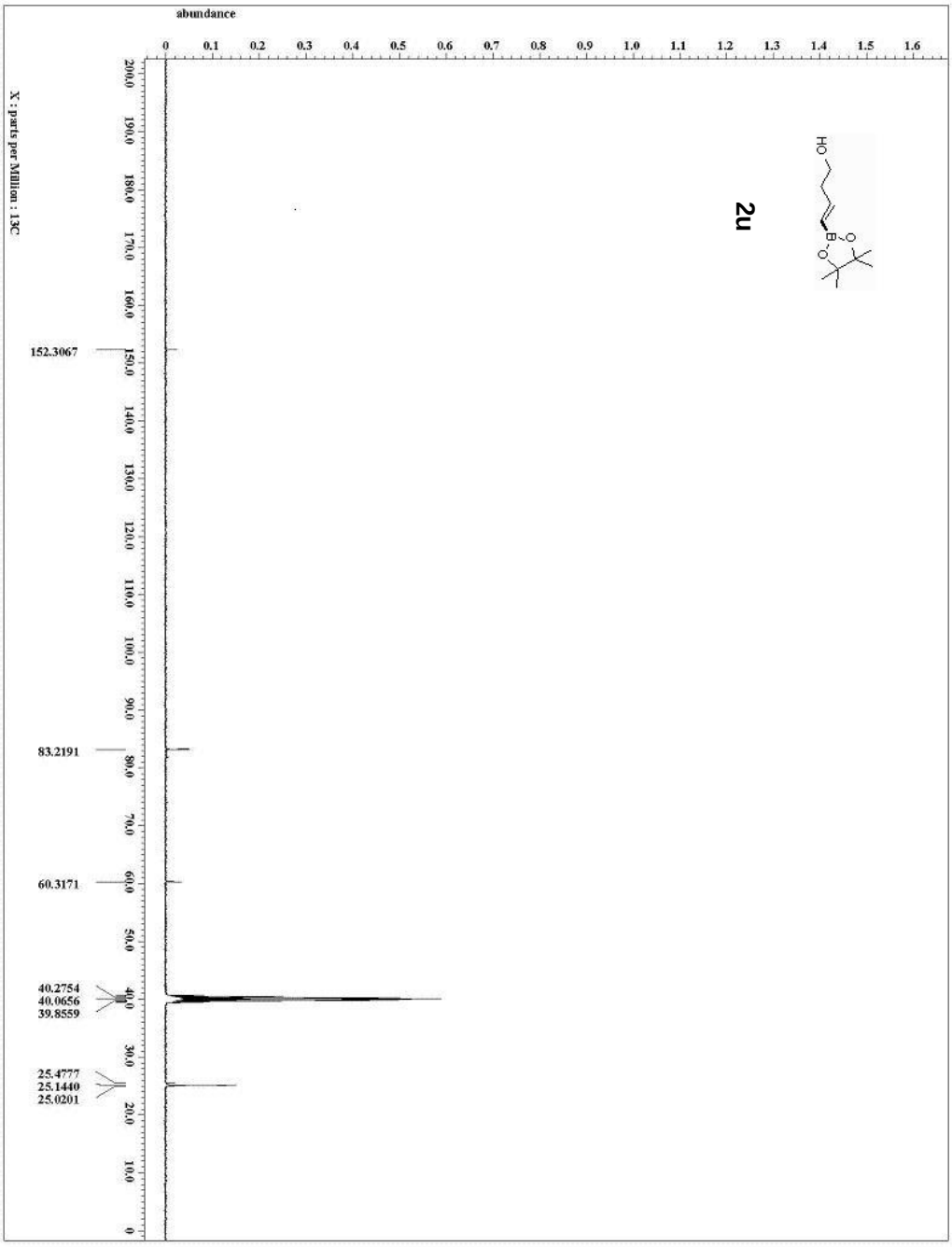

abundance
X : parts per Million : 1H
2S
7.2647
6.1123
6.0883
6.0677
6.0436
5.5144
5.4697
0.947
1.0
1.5854
1.2543
0.8110
0.7973
0.7812
0.5441
0.5269
−0.0000
1.195
12.421
1.945
2.061

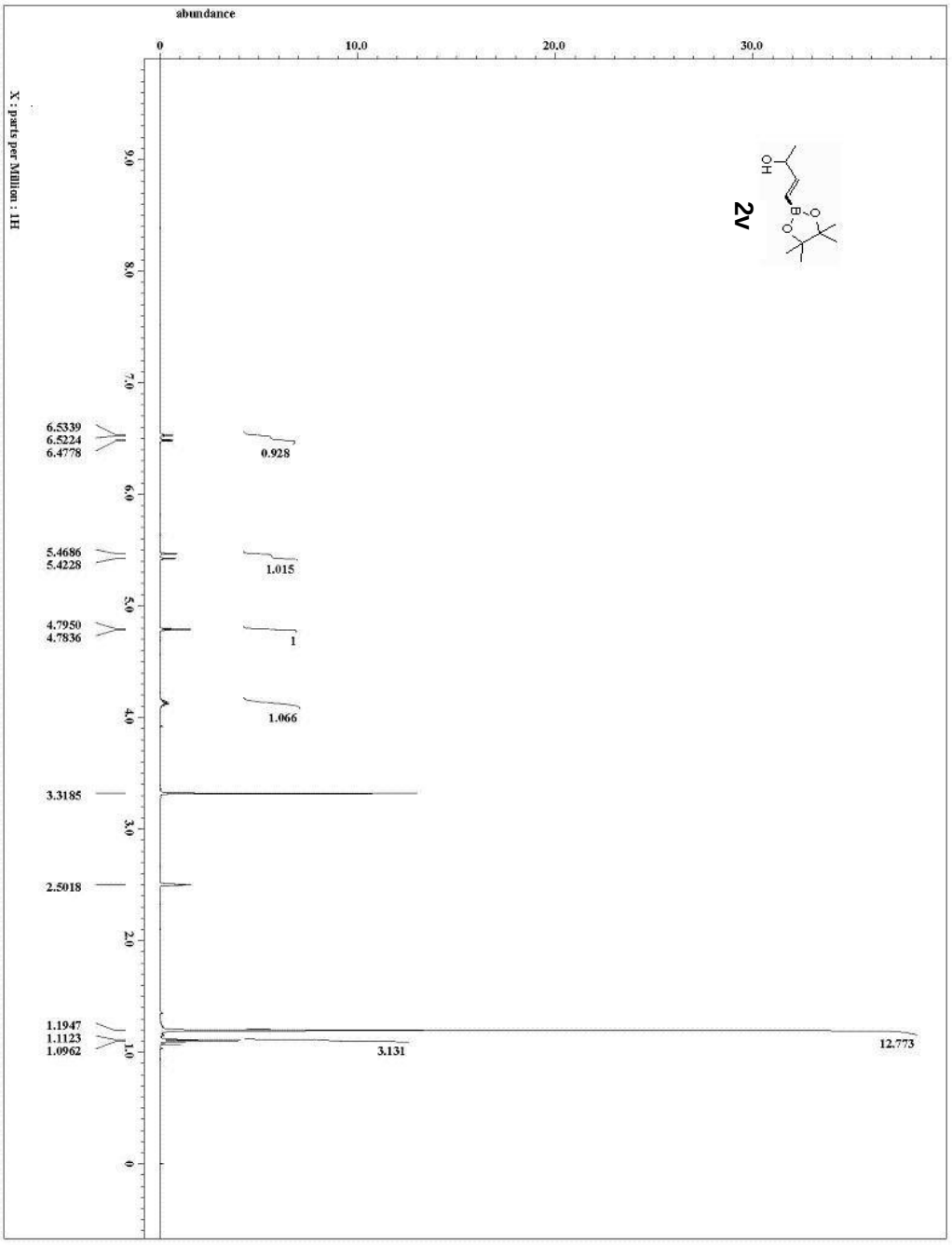

abundance
0
0.1
0.2
0.3
0.4
X : parts per Million : 13C
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
158.6377
82.9998
77.4030
77.2886
77.0789
76.7642
24.8198
17.0777
7.9532
2s

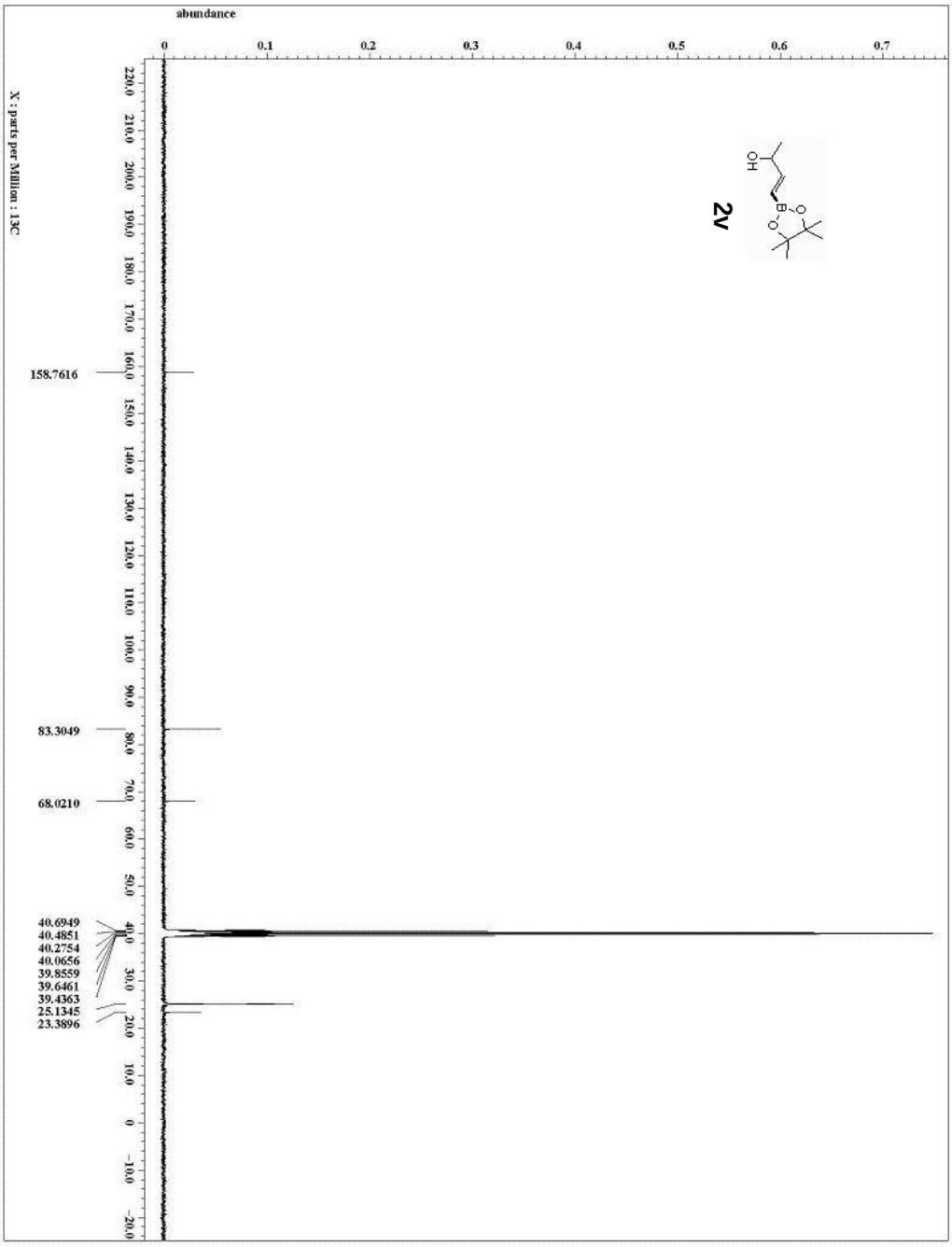

abundance
0
10.0
20.0
30.0
40.0
X : parts per Million : 1H
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.2475
6.2417
1.009
2.1466
2.1283
2.1099
4.084
1.5773
1.2439
1.0011
0.9816
0.9633
0.9415
0.9232
0.9037
12.516
3.064
-0.0172
2t
B
O
O

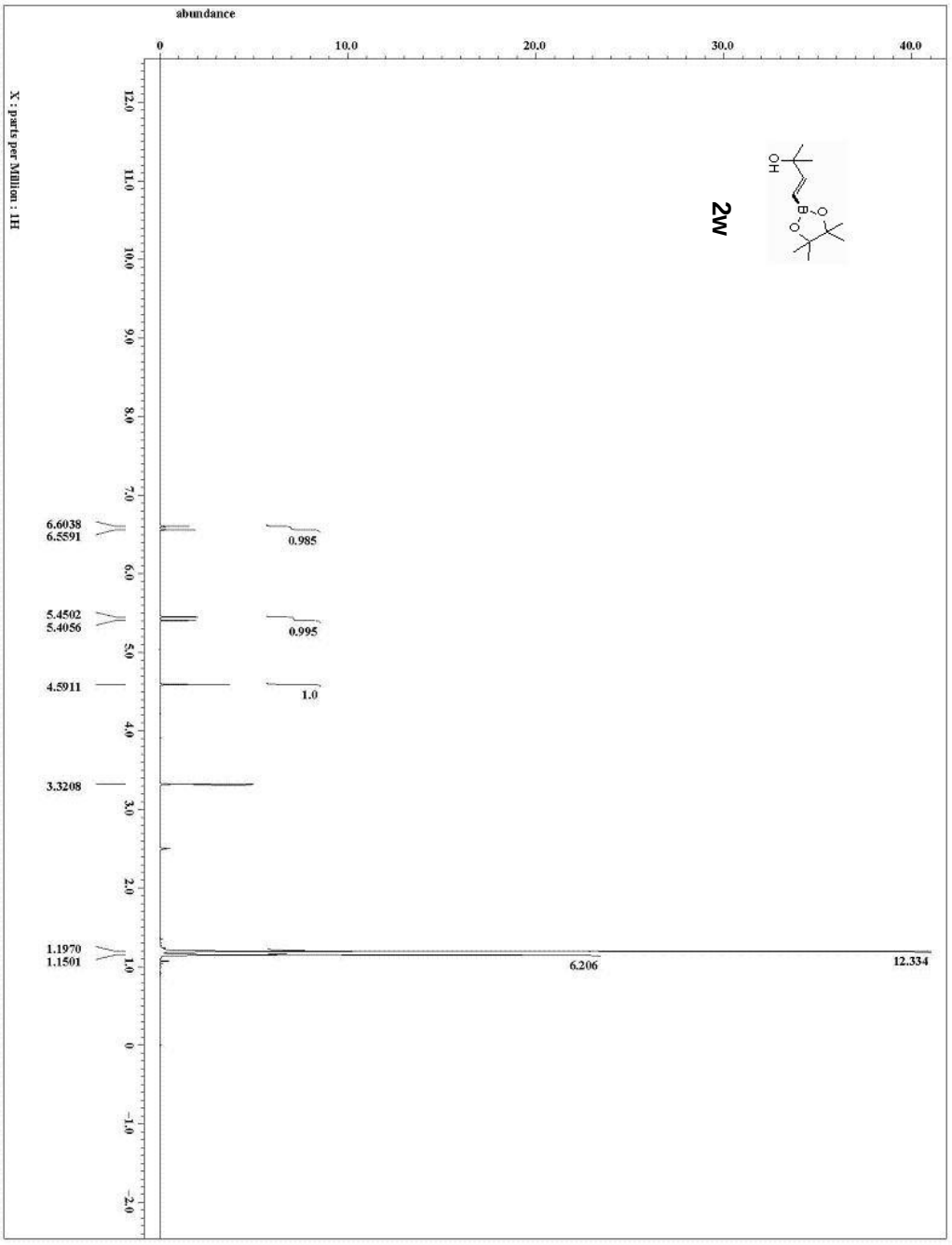

abundance
0
0.1
0.2
0.3
0.4
0.5
X : parts per Million : 13C
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
147.0627
83.0284
77.4030
77.0884
76.7642
24.8198
21.7402
21.5495
14.9325
13.8741
2t
B
O
O

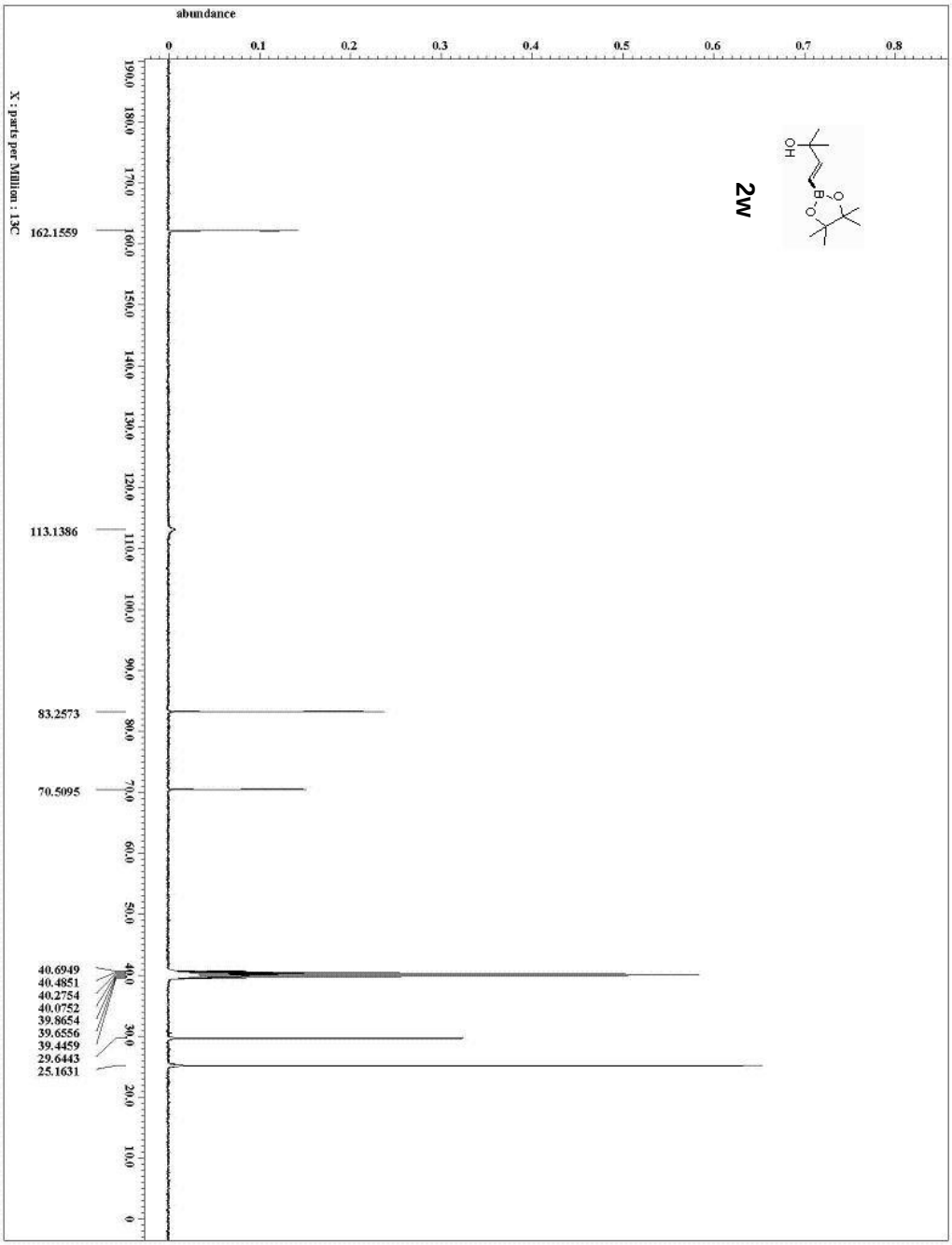

abundance
X : parts per Million : 1H
2u
6.5017
6.4559
0.894
5.3414
5.2967
1
4.5017
4.4880
4.4754
0.908
3.4456
3.4284
3.4158
3.3997
3.2795
2.4604
2.2439
2.2279
2.2107
2.004
2.016
1.1466
11.996

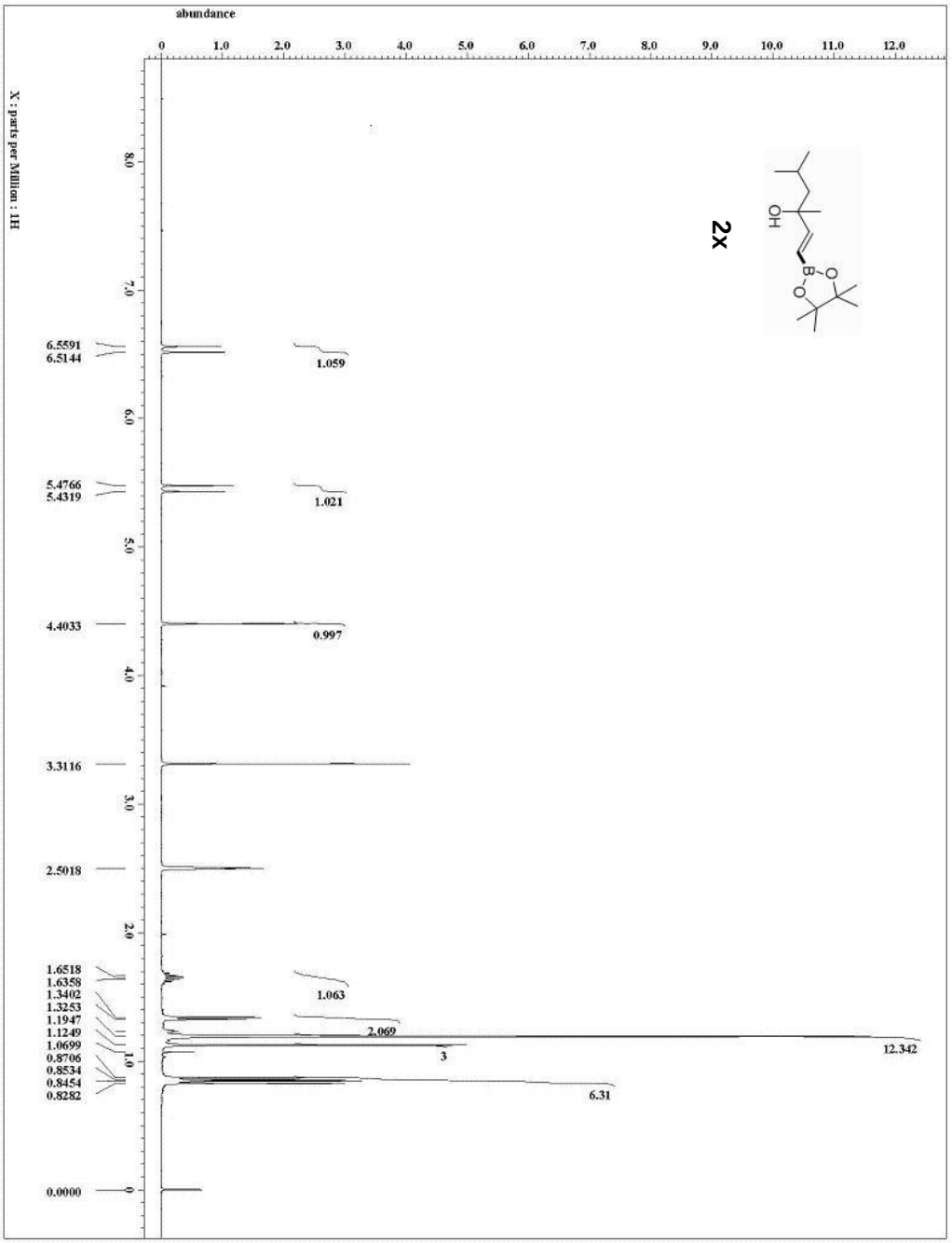

abundance
X : parts per Million : 13C
152.3067
83.2191
60.3171
40.2754
40.0656
39.8559
25.4777
25.1440
25.0201
2u
OH
B
O
O

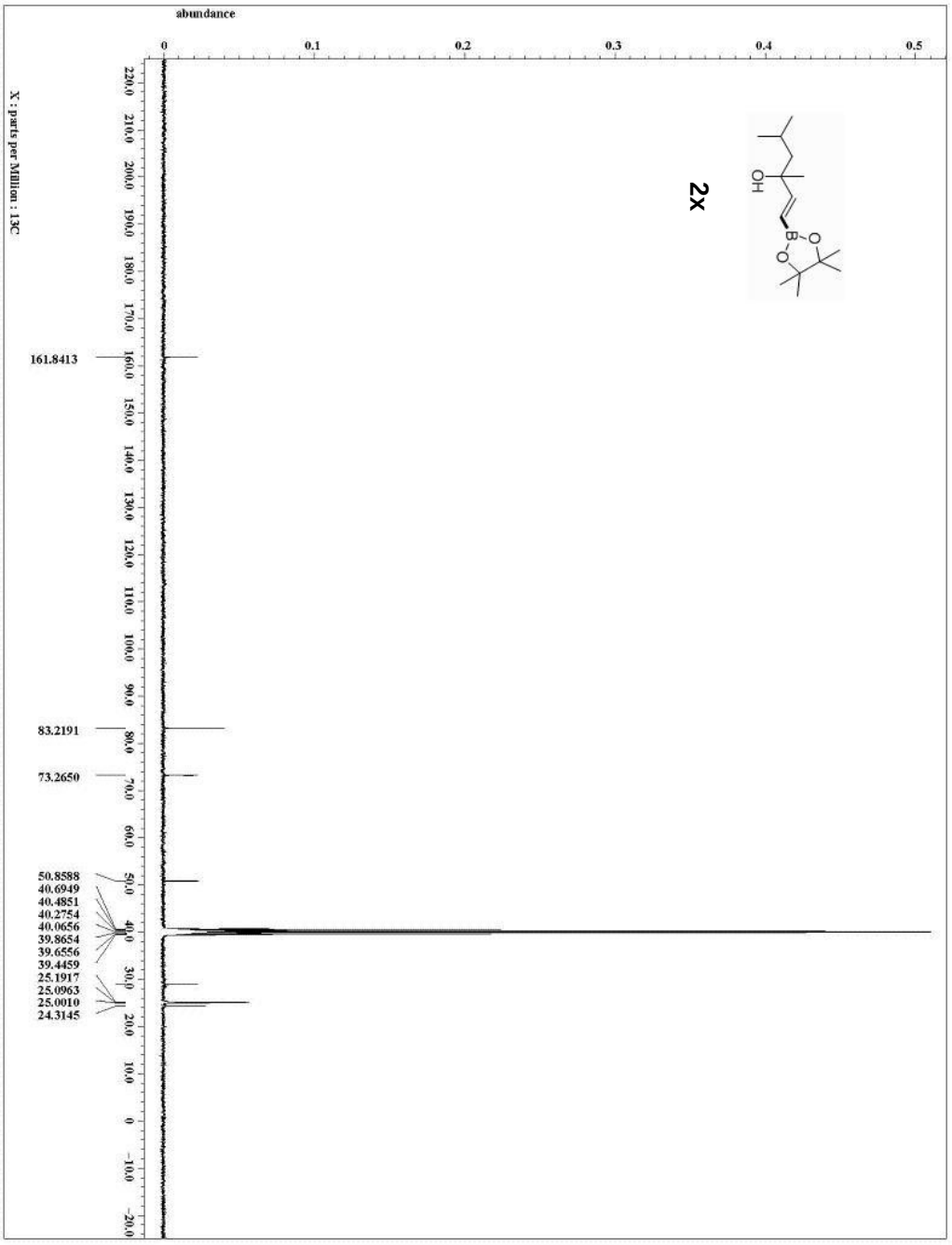

abundance
X : parts per Million : 1H
2v
6.5339
6.5224
6.4778
0.928
5.4686
5.4228
1.015
4.7950
4.7836
1
1.066
3.3185
2.5018
1.1947
1.1123
1.0962
3.131
12.773

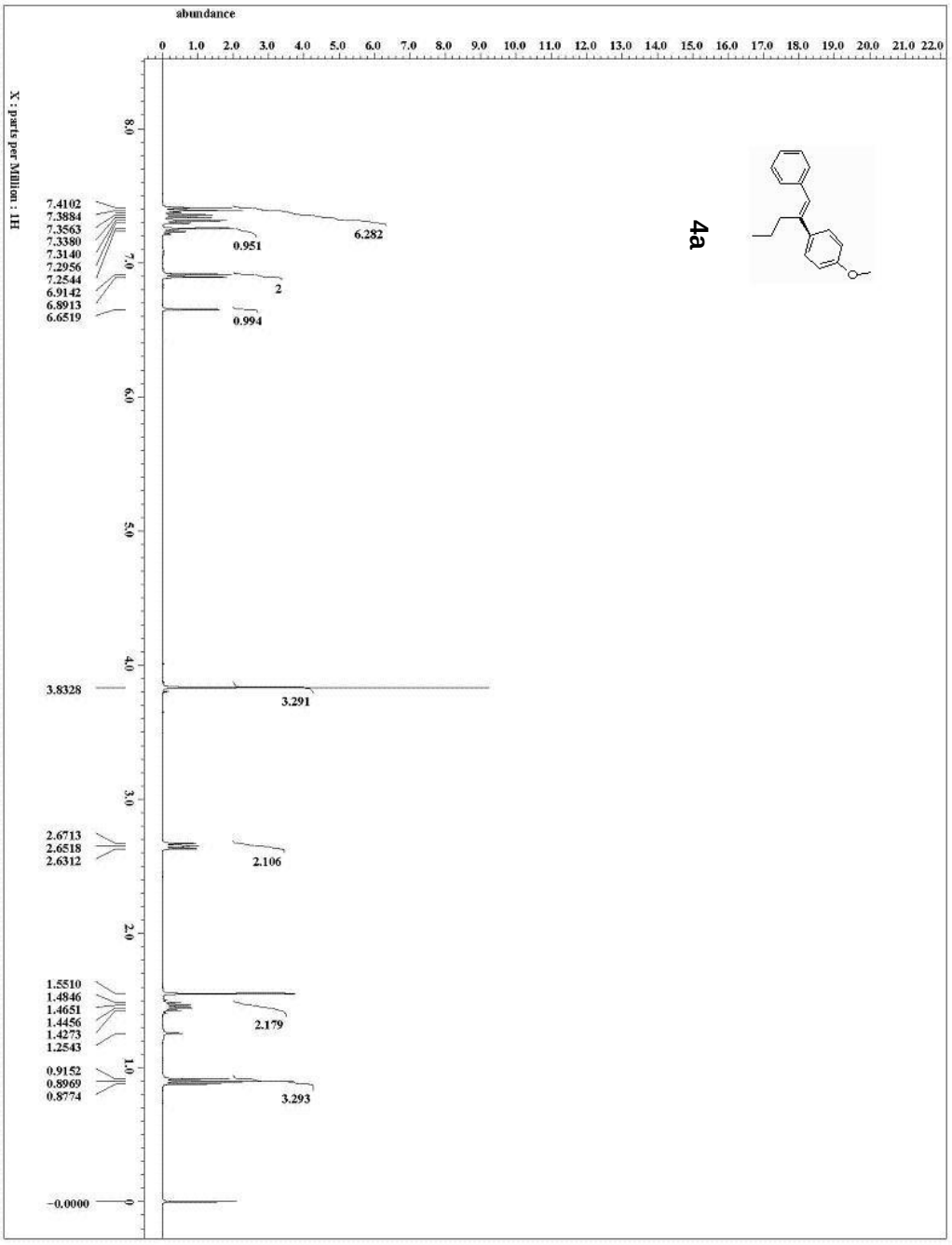

abundance
X : parts per Million : 13C
158.7616
83.3049
68.0210
40.6949
40.4851
40.2754
40.0656
39.8559
39.6461
39.4363
25.1345
23.3896
2v

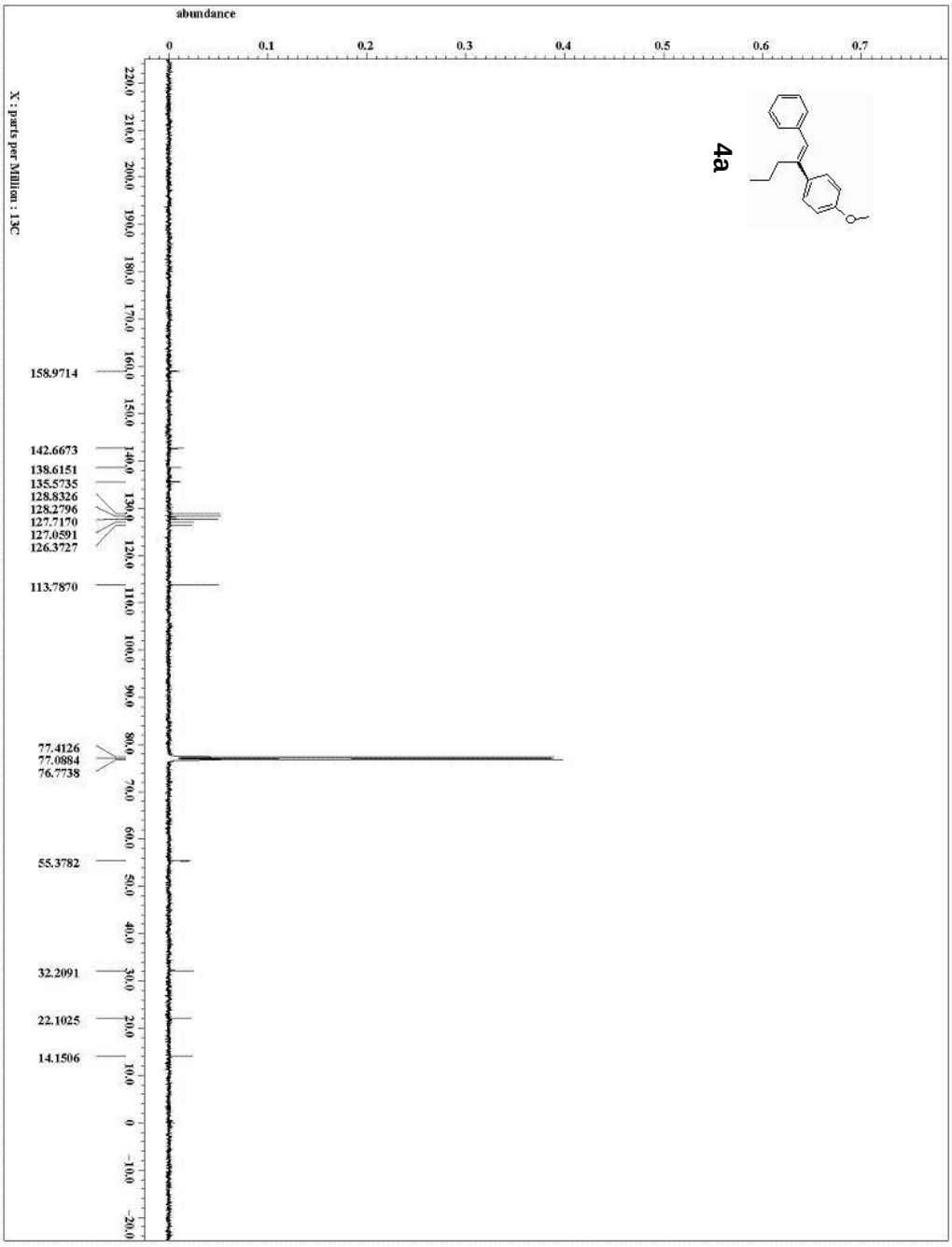

abundance
0
10.0
20.0
30.0
40.0
X : parts per Million : 1H
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
6.6038
6.5591
0.985
5.4502
5.4056
0.995
4.5911
1.0
3.3208
1.1970
1.1501
6.206
12.334
2w
OH
B
O
O

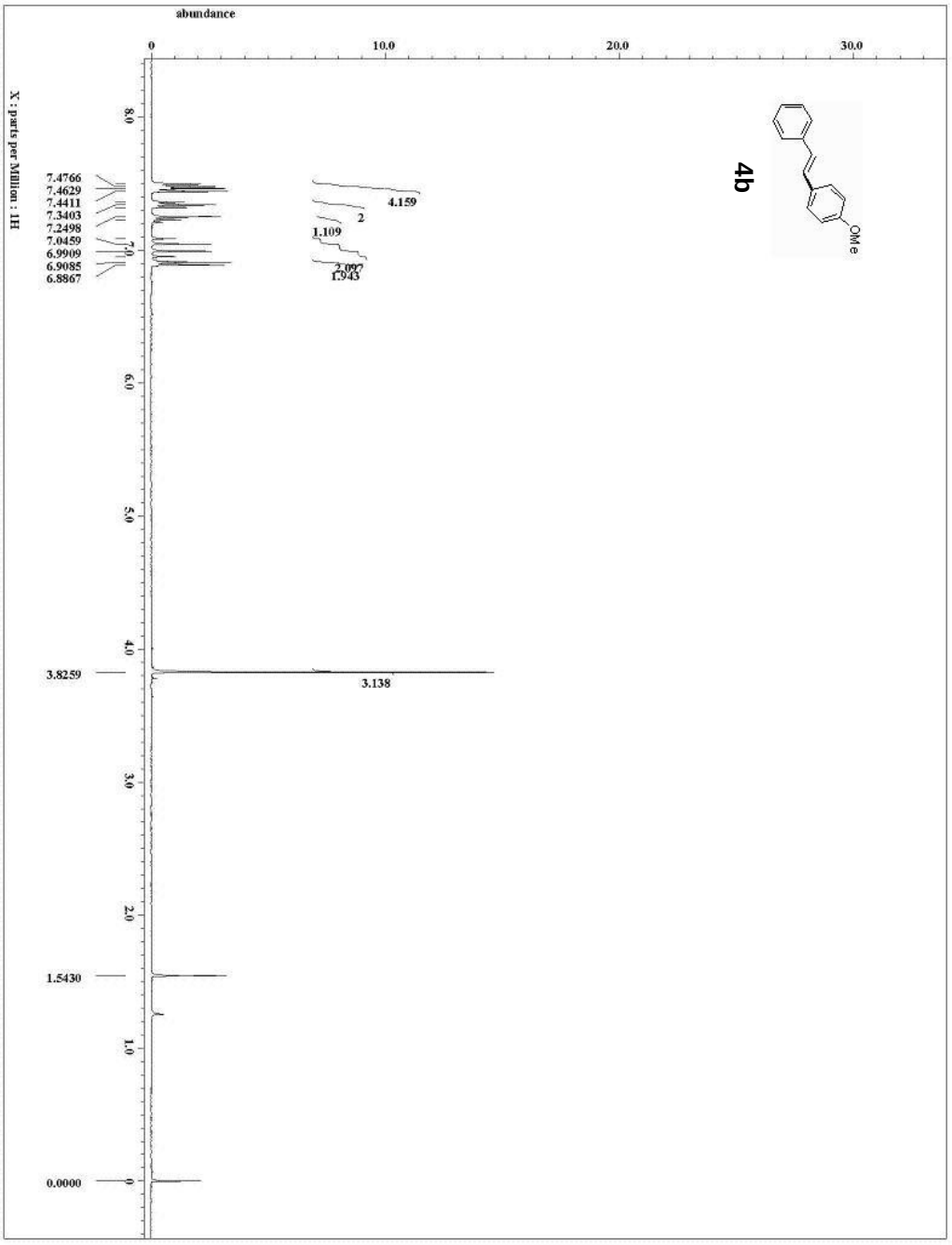

abundance
X : parts per Million : 13C
2w
162.1559
113.1386
83.2573
70.5095
40.6949
40.4851
40.2754
40.0752
39.8654
39.6556
39.4459
29.6443
25.1631

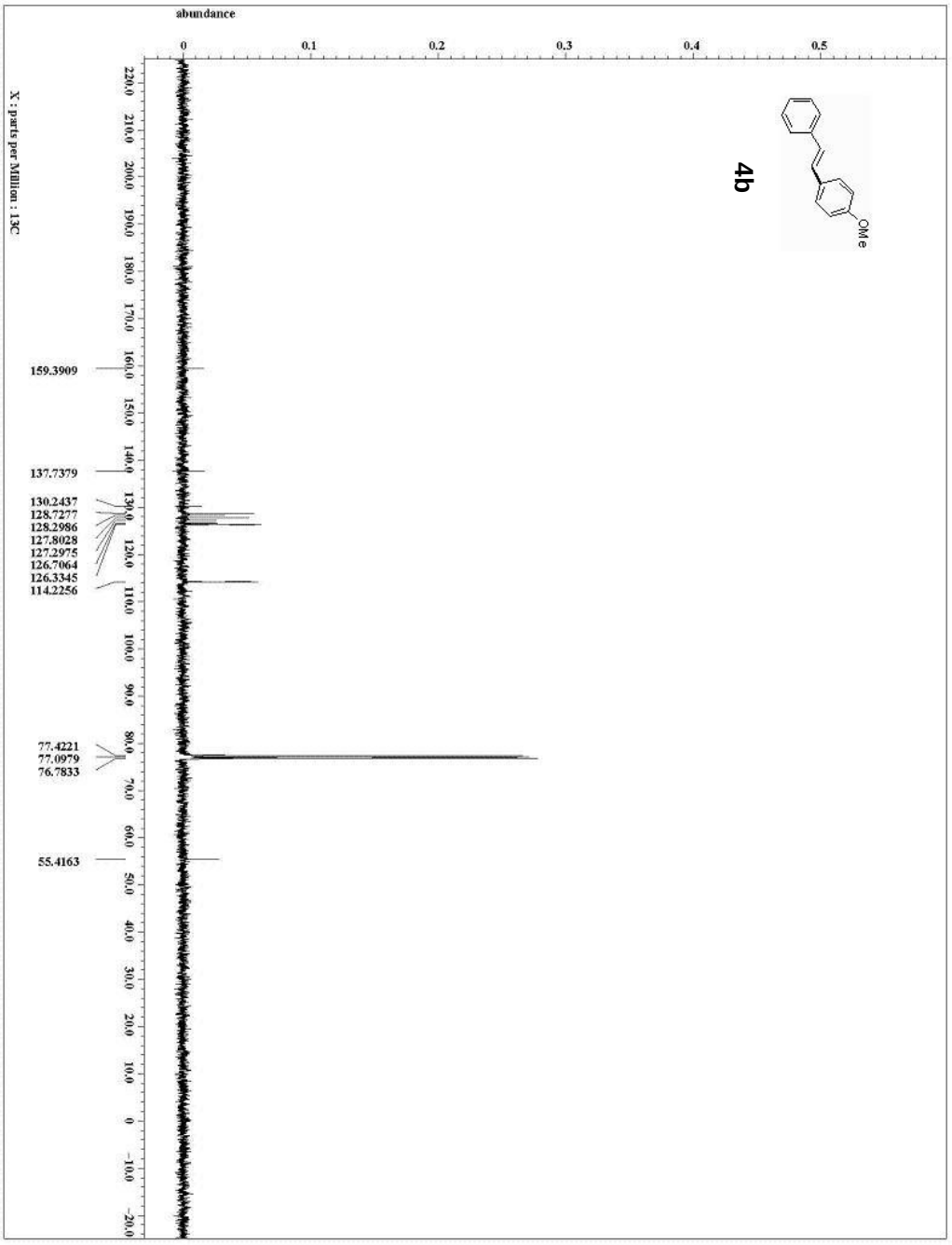

abundance
X : parts per Million : 1H
2x
6.5591
6.5144
1.059
5.4766
5.4319
1.021
4.4033
0.997
3.3116
2.5018
1.6518
1.6358
1.3402
1.3253
1.1947
1.1249
1.0699
0.8706
0.8534
0.8454
0.8282
1.063
2.069
3
12.342
6.31
0.0000


abundance
0
0.1
0.2
0.3
0.4
0.5
X : parts per Million : 13C
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
161.8413
83.2191
73.2650
50.8588
40.6949
40.4851
40.2754
40.0656
39.8654
39.6556
39.4459
25.1917
25.0963
25.0010
24.3145
2x
OH
B
O
O


abundance
X : parts per Million : 1H
4a
7.4102
7.3884
7.3563
7.3380
7.3140
7.2956
7.2544
6.9142
6.8913
6.6519
3.8328
2.6713
2.6518
2.6312
1.5510
1.4846
1.4651
1.4456
1.4273
1.2543
0.9152
0.8969
0.8774
−0.0000
6.282
0.951
2
0.994
3.291
2.106
2.179
3.293


abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
X : parts per Million : 13C
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
158.9714
142.6673
138.6151
135.5735
128.8326
128.2796
127.7170
127.0591
126.3727
113.7870
77.4126
77.0884
76.7738
55.3782
32.2091
22.1025
14.1506
4a


abundance
X : parts per Million : 1H
7.4766
7.4629
7.4411
7.3403
7.2498
7.0459
6.9909
6.9085
6.8867
3.8259
1.5430
0.0000
4.159
2
1.109
2.097
1.943
3.138
4b
OMe


abundance
0
0.1
0.2
0.3
0.4
0.5
X : parts per Million : 13C
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
159.3909
137.7379
130.2437
128.7277
128.2986
127.8028
127.2975
126.7064
126.3345
114.2256
77.4221
77.0979
76.7833
55.4163
4b
OMe