Nickel-Catalyzed Heck-Type Coupling of Benzyl Chlorides and Simple Olefins

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Materials and Methods

All reactions were performed under an argon atmosphere with rigorous exclusion of moisture from reagents and glassware, unless otherwise noted. Toluene, dichloromethane, tetrahydrofuran, triethylamine and diethyl ether were obtained from an SG Water solvent purification system. Nickel catalyst $Ni(cod)_2$ and phosphine ligand P(*o*-Anisyl)$_3$ were purchased from Strem Chemicals (Newburyport, MA) and stored in a glove box under nitrogen atmosphere. Ethylene and propylene were purchased from BOC Gases (Murray Hill, NJ) and Sigma-Aldrich Chemical Company (Milwaukee, WI), respectively, and used as received. Vinylcyclohexane and 1-octene were distilled from CaH_2 prior to use. All other reagents were used as received. Commercially available chemicals were purchased from either Sigma-Aldrich Chemical Company (Milwaukee, WI), Alfa Aesar (Ward Hill, MA), Acros Organics (Pittsburgh, PA), TCI America (Portland, OR), or GFS Chemicals (Columbus, OH). Analytical and preparative thin-layer chromatography (TLC) were performed on 0.2 mm coated Science silica gel (EM 60-F254) plates. Visualization was accomplished with UV light (254 nm) and exposure to either ethanolic phosphomolybdic acid (PMA), anisaldehyde or $KMnO_4$ solution followed by heating. Melting points are uncorrected. ^{1}H NMR spectra were acquired on either a Varian Mercury 300 (at 300 MHz), a Bruker AVANCE (at 400 MHz), or a Varian Inova 500 (at 500 MHz) and chemical shifts are reported relative to the residual solvent peak. ^{13}C NMR spectra were acquired on a either a Bruker AVANCE (at 100 MHz) or a Varian Inova 500 (at 125 MHz) and chemical shifts are reported in ppm relative to the residual solvent peak. All IR spectra were obtained on sodium chloride plates with a Perkin-Elmer Model 2000 FT-IR. High-resolution mass spectrometry data were acquired by the Department of Chemistry Instrumentation Facility, Massachusetts Institute of Technology (http://web.mit.edu/speclab/www/Facility/MS/ms.html) on a Bruker Daltonics APEXIV 4.7 Tesla FT-ICR Mass Spectrometer.

General Procedure for the Nickel-Catalyzed Benzylation of Ethylene: In a glove box, an oven-dried test tube was charged with Ni(cod)$_2$ (5 mol %) and PCyPh$_2$ (10 mol %). The test tube was then sealed, removed from the glove box, and connected to an argon line. Toluene (0.2 M) was then added to the metal–ligand mixture, and the solution was and stirred for 15–30 min at room temperature. Ethylene (1 atm) was introduced to the reaction by bubbling for 1 min, and the atmosphere was maintained with an ethylene balloon for the remainder of the reaction. To the reaction were then added triethylamine (6.0 equiv), benzyl chloride (1.0 equiv) and Et$_3$SiOTf (1.75 equiv),[1] and the reaction mixture was stirred at room temperature for 2 h. The reaction was then exposed to air, diluted with a small amount of pentane (~500 μL), and stirred for an additional 5 min. The mixture was then passed through a small plug of silica gel (1:1 EtOAc/hexanes eluent). The filtrate was concentrated in vacuo to provide the benzylated adducts, which were further purified by flash chromatography. Where indicated, yields were determined by ^{1}H NMR spectroscopy of the crude mixture using 1,4-dioxane as an internal standard.

Compounds **2a** and **2l** are commercially available. Compounds **2d**,[2] **2u**,[3] **2s**,[7b] **2e**,[7b] **2h**,[4] **2g**,[5] **2t**,[6] **2i**,[8] **2c**,[8,7] **2f**,[8] **2b**,[8] **2n**[9] and **2q**[10] are known compounds. The spectroscopic data of the obtained compounds matched the literature values. For the reactions with ethylene, the formation of polyethylene as a side product was typically observed. Product volatility and extremely low polarity render the separation of the ethylene-coupled allylbenzene products from polyethylene and toluene (the solvent) difficult. In the cases where product volatility was prohibitive (**2a**, **2c**, **2g**, **2h, 2t**), the yields given were determined by GC or ^{1}H NMR spectroscopy with an internal standard.[11]

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[1] For solid benzyl chlorides, a solution of the catalyst and Et$_3$N in toluene was cannulated into a flask containing the benzyl chloride under an ethylene flow. Et$_3$SiOTf was added to this mixture, and the solution kept under ethylene for the remainder of the reaction.

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[3] (a) Gerbino, D. C.; Mandolesí, S. D.; Schmalz, H.-G.; Podestá, J. C. *Eur. J. Org. Chem.* **2009**, 3964. (b) Denmark, S. E.; Werner, N. S. *J. Am. Chem. Soc.* **2008**, *130*, 16382.

[4] Gomes, P.; Gosmini, C.; Périchon, J. *Org. Lett.* **2003**, *5*, 1043.

[5] Mariampillai, B.; Herse, C.; Lautens, M. *Org. Lett.* **2005**, *7*, 4745.

[6] Padwa, A.; Lipka, H.; Watterson, S. H.; Murphree, S. S. *J. Org. Chem.* **2003**, *68*, 6238.

[7] For the characterization of 4-cyano-b-methylstyrene, see: Peyroux, E.; Berthiol, F.; Doucet, H.; Santelli, M. *Eur. J. Org. Chem.* **2004**, 1075.

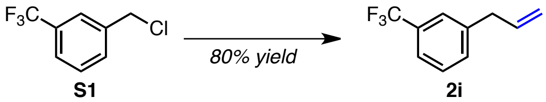
[8] Saá, J. M.; Martorell, G. *J. Org. Chem.* **1993**, *58*, 1963.

[9] Fuwa, H.; Sasaki, M. *Org. Biomol. Chem.* **2007**, *5*, 2214.

[10] Ishikura, M.; Uemura, R.; Yamada, K.; Yanada, R. *Heterocycles* **2006**, *68*, 2349.

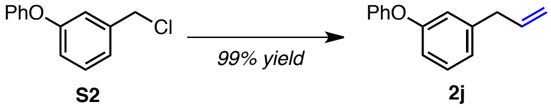
[11] For GC analysis, dodecane was used as an internal standard; for ^{1}H NMR analysis, 1,4-dioxane was employed.

Preparatory Scale Example



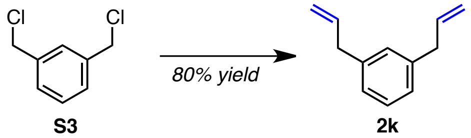
According to the general procedure, 71.0 mg Ni(cod)$_2$ (0.258 mmol) and 139 mg PCyPh$_2$ (0.516 mmol), were dissolved in 25.8 mL toluene and stirred at room temperature for 5 min. The reaction was then purged with ethylene for 1 min, and the atmosphere was maintained with a balloon for the remainder of the reaction. To the stirring solution were then added 4.32 mL triethylamine (31.0 mmol), 800 µL benzyl chloride **S1** (5.16 mmol) and 2.04 mL Et$_3$SiOTf (9.03 mmol), and stirring was continued for 2 h. Purification of the residue by flash chromatography (0→5% Et$_2$O/hexanes eluent) afforded alkene **2i** (481 mg, 80% yield, R_f = 0.90 in 5% Et$_2$O/hexanes) as a colorless oil.

Allylbenzene 2i: ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.50-7.37 (comp m, 4H), 6.00-5.92 (m, 1H), 5.15-5.09 (comp m, 2H), 3.45 (d, J = 6.6 Hz, 2H).



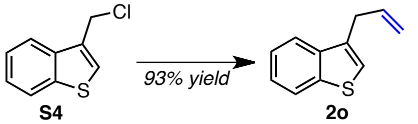
According to the general procedure, 6.9 mg Ni(cod)$_2$ (0.0250 mmol) and 13.4 mg PCyPh$_2$ (0.0500 mmol), were dissolved in 2.50 mL toluene and stirred at room temperature for 5 min. The reaction was then purged with ethylene for 1 min, and the atmosphere was maintained with a balloon for the remainder of the reaction. To the stirring solution were then added 418 µL triethylamine (3.00 mmol), 93.8 µL benzyl chloride **S2** (0.500 mmol) and 198 µL Et$_3$SiOTf (0.875 mmol), and stirring was continued for 2 h. Purification of the residue by flash chromatography (20:1 hexanes/Et$_2$O eluent) afforded alkene **2j** (105 mg, 99% yield, R_f = 0.25 in hexanes) as a colorless oil.

1-Allyl-3-phenoxybenzene (2j): ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.27-7.33 (comp m, 2H), 7.23 (t, J = 7.8 Hz, 1H), 7.05-7.09 (m, 1H), 6.97-7.01 (comp m, 2H), 6.92 (app d, J = 7.6 Hz, 1H), 6.87 (s, 1H), 6.83 (app d, J = 8.1 Hz, 1H), 5.94 (ddt, J = 16.8, 10.2, 6.7 Hz, 1H), 5.04-5.10 (comp m, 2H), 3.35 (d, J = 6.7 Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 157.3, 157.2, 142.1, 136.9, 129.7, 129.6, 123.5, 123.0, 119.2, 118.7, 116.5, 116.1, 40.0; IR (NaCl plate, thin film): 3075, 3039, 2978, 2905, 1935, 1844, 1639, 1583, 1488, 1443, 1249, 1213, 1162, 1139, 1072, 1023, 994, 962, 915, 817, 753, 692 cm^{-1}; HRMS-DART (m/z): [M+H]$^+$ calc'd for $C_{15}H_{15}O$, 211.1117; found 211.1119.



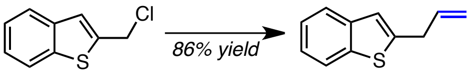
According to the general procedure, 6.9 mg Ni(cod)$_2$ (0.0250 mmol) and 13.4 mg PCyPh$_2$ (0.0500 mmol), were dissolved in 2.50 mL toluene and stirred at room temperature for 5 min. The reaction was then purged with ethylene for 1 min, and the atmosphere was maintained with a balloon for the remainder of the reaction. To the stirring solution were then added 418 µL triethylamine (3.00 mmol), 87.5 mg benzyl chloride **S3** (0.500 mmol) and 198 µL Et$_3$SiOTf (0.875 mmol), and stirring was continued for 2 h. Purification of the residue by flash chromatography (100% hexanes eluent) afforded alkene **2k** (63.0 mg, 80% yield, R$_f$ = 0.50 in 100% hexanes) as a colorless oil.

1,3-Diallylbenzene (2k): ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.21 (app d, *J* = 7.9 Hz, 1H), 7.02 (app d, *J* = 7.7 Hz, 3H), 5.96 (ddt, *J* = 10.1, 16.9, 6.8 Hz, 1H), 5.03-5.10 (comp m, 2H), 3.36 (d, *J* = 6.7 Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 140.1, 137.5, 128.8, 128.4, 126.3, 115.7, 40.2; IR (NaCl plate, thin film): 3078, 3058, 3005, 2978, 2902, 2833, 1830, 1639, 1606, 1588, 1487, 1431, 1279, 993, 913, 786, 752, 701 cm^{-1}; HRMS-DART (m/z): [M+H]$^+$ calc'd for $C_{12}H_{15}$, 159.1168; found 159.1161.



According to the general procedure, 6.9 mg Ni(cod)$_2$ (0.0250 mmol) and 13.4 mg PCyPh$_2$ (0.0500 mmol), were dissolved in 2.50 mL toluene and stirred at room temperature for 5 min. The reaction was then purged with ethylene for 1 min, and the atmosphere was maintained with a balloon for the remainder of the reaction. To the stirring solution were then added 418 µL triethylamine (3.00 mmol), 91.3 mg benzyl chloride **S4** (0.500 mmol) and 198 µL Et$_3$SiOTf (0.875 mmol), and stirring was continued for 2 h. Purification of the residue by flash chromatography (100% hexanes eluent) afforded alkene **2o** (81.3 mg, 93% yield, R$_f$ = 0.70 in 5% Et$_2$O/hexanes) as a colorless oil.

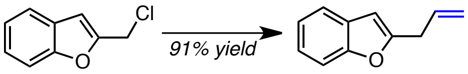
3-Allylbenzo[β]thiophene (2o): ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.81-7.85 (m, 1H), 7.71-7.74 (m, 1H), 7.30-7.38 (comp m, 2H), 7.09 (s, 1H), 6.04 (ddt, *J* = 10.1, 17.0, 6.5 Hz, 1H), 5.11-5.18 (comp m, 2H), 3.57 (dd, *J* = 1.3, 6.5 Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 140.5, 138.7, 135.5, 134.5, 124.2, 123.8, 122.8, 122.1, 121.8, 116.6, 33.0; IR (film): 3077, 3029, 3005, 2977, 2899, 1638, 1459, 1427, 1362, 1249, 1156, 1077, 1020, 993, 916, 852, 833, 755, 728 cm^{-1}; HRMS-DART (m/z): [M+H]$^+$ calc'd for $C_{11}H_{11}S$, 175.0576; found 175.0578.



S5 **2p**

According to the general procedure, 7.0 mg Ni(cod)$_2$ (0.0255 mmol) and 13.6 mg PCyPh$_2$ (0.0507 mmol), were dissolved in 2.50 mL toluene and stirred at room temperature for 5 min. The reaction was then purged with ethylene for 1 min, and the atmosphere was maintained with a balloon for the remainder of the reaction. To the stirring solution were then added 418 µL triethylamine (3.00 mmol), 92.6 mg benzyl chloride **S5** (0.507 mmol) and 198 µL Et$_3$SiOTf (0.875 mmol), and stirring was continued for 2 h. Purification of the residue by flash chromatography (100% hexanes eluent) afforded alkene **2p** (75.9 mg, 86% yield, $R_f = 0.66$ in 100% hexanes) as a colorless oil.

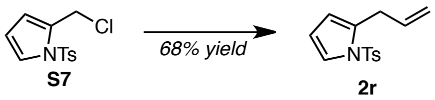
2-Allylbenzo[b]thiophene (2p): ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.74 (app d, J = 6.4 Hz, 1H), 7.65 (app d, J = 7.1 Hz, 1H), 7.28 (app dt, J = 1.2, 7.5 Hz, 1H), 7.23 (app dt, J = 1.4, 7.6 Hz, 1H), 7.00 (d, J = 0.9 Hz, 1H), 6.02 (ddt, J = 10.0, 17.0, 6.7 Hz, 1H), 5.21 (qd, J = 1.6, 17.0 Hz, 1H), 5.15 (qd, J = 1.3, 10.0 Hz, 1H), 3.62 (dd, J = 1.3, 6.7 Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 143.9, 140.1, 140.0, 135.6, 124.1, 123.5, 122.8, 122.1, 121.1, 116.9, 35.0; IR (film): 3059, 3006, 2979, 2900, 1936, 1901, 1824, 1788, 1679, 1640, 1567, 1537, 1456, 1435, 1307, 1251, 1228, 1180, 1155, 1132, 1064, 1015, 990, 918, 855, 821, 744, 725, 667 cm^{-1}; HRMS-DART (m/z): [M+H]$^+$ calc'd for $C_{11}H_{11}S$, 175.0576, found 175.0579.



S6 **2m**

According to the general procedure, 6.9 mg Ni(cod)$_2$ (0.0250 mmol) and 13.4 mg PCyPh$_2$ (0.0500 mmol), were dissolved in 2.50 mL toluene and stirred at room temperature for 5 min. The reaction was then purged with ethylene for 1 min, and the atmosphere was maintained with a balloon for the remainder of the reaction. To the stirring solution were then added 418 µL triethylamine (3.00 mmol), 83.3 mg benzyl chloride **S6** (0.500 mmol) and 198 µL Et$_3$SiOTf (0.875 mmol), and stirring was continued for 2 h. Purification of the residue by flash chromatography (100% hexanes eluent) afforded alkene **2m** (71.8 mg, 91% yield, $R_f = 0.33$ in 100% hexanes) as a colorless oil.

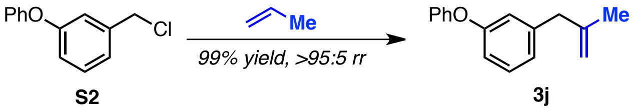
2-Allylbenzofuran (2m): ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.46-7.49 (m, 1H), 7.40-7.43 (m, 1H), 7.15-7.22 (comp m, 2H), 6.40 (q, J = 1.0 Hz, 1H), 6.00 (ddt, J = 10.1, 17.1, 6.6 Hz, 1H), 5.22 (dq, J = 17.1, 1.6 Hz, 1H), 5.18 (dq, J = 10.1, 1.4 Hz, 1H), 3.52 (ddt, J = 1.2, 6.6, 1.3 Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 157.0, 154.8, 133.1, 128.8, 123.3, 122.5, 120.3, 117.6, 110.8, 102.6, 33.0; IR (film): 3082, 2981, 2903, 1930, 1890, 1849, 1774, 1642, 1600, 1586, 1454, 1424, 1317, 1295, 1254, 1205, 1168, 1104, 1009, 992, 955, 920, 798, 750, 741 cm^{-1}; HRMS-DART (m/z): [M+H]$^+$ calc'd for $C_{11}H_{11}O$, 159.0805; found 159.0805.



According to the general procedure, 6.9 mg Ni(cod)$_2$ (0.0250 mmol) and 13.4 mg PCyPh$_2$ (0.0500 mmol), were dissolved in 2.50 mL toluene and stirred at room temperature for 5 min. The reaction was then purged with ethylene for 1 min, and the atmosphere was maintained with a balloon for the remainder of the reaction. To the stirring solution were then added 418 µL triethylamine (3.00 mmol), 135 mg benzyl chloride **S7** (0.500 mmol) and 198 µL Et$_3$SiOTf (0.875 mmol), and stirring was continued for 2 h. Purification of the residue by flash chromatography (10:1 hexanes/Et$_2$O eluent) afforded alkene **2r** (89.5 mg, 68% yield, R_f = 0.50 in 5:1 hexanes/Et$_2$O) as tan solid.

2-Allyl-1-tosyl-1H-pyrrole (2r): Mp. 64-65 ^{o}C; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.63-7.65 (comp m, 2H), 7.25-7.32 (comp m, 3H), 6.20 (t, *J* = 3.4 Hz, 1H), 5.97-6.00 (m, 1H), 5.08 (ddt, *J* = 10.5, 16.6, 6.7 Hz, 1H), 5.04-5.06 (m, 1H), 5.01-5.04 (m, 1H), 3.45 (dd, *J* = 1.1, 6.8 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 144.8, 136.2, 134.2, 133.4, 129.9, 126.8, 122.4, 117.0, 112.6, 111.3, 31.6, 21.6; IR (film): 3150, 3080, 2981, 2923, 1923, 1642, 1597, 1566, 1483, 1430, 1366, 1189, 1176, 1152, 1122, 1090, 1052, 1005, 994, 921, 812, 755, 715, 704, 673, 593, 576, 542 cm^{-1}; HRMS-DART (m/z): [M+H]$^{+}$ calc'd for $C_{14}H_{16}NO_2S$, 262.0896; found 262.0898.

Experimental Procedure for Benzylation of Propylene (3j)

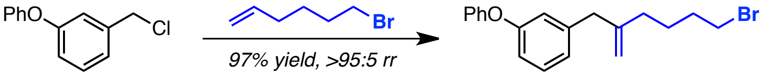


In a glove box, an oven-dried test tube was charged with Ni(cod)$_2$ (13.8 mg, 0.0500 mmol) and PCy$_2$Ph (27.4 mg, 0.100 mmol). The test tube was then sealed with a septum, taken out of the glove box, and connected to an argon line. The catalyst mixture was dissolved in toluene (2.50 mL) and stirred for 15 min at room temperature. The reaction mixture was purged with propylene for 1 min to remove argon, and the propylene atmosphere was maintained with a propylene balloon for the remainder of the reaction. Triethylamine (418 µL, 3.00 mmol), benzyl chloride **S2** (93.8 µL, 0.500 mmol) and Et$_3$SiOTf (198 µL, 0.875 mmol) were added in that order. The mixture was stirred at room temperature for 3.5 h, then passed through a small plug of silica gel (1:1 EtOAc/hexanes eluent). The filtrate was concentrated in vacuo to provide the benzylated adduct, which was further purified by silica gel chromatography (20:1 hexanes/Et$_2$O) to afford **3j** (114 mg, 100% yield, R_f = 0.20 in 100% hexanes as a colorless oil.).

1-(2-Methylallyl)-3-phenoxybenzene (3j): ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.29-7.34 (comp m, 2H), 7.23 (t, *J* = 7.9 Hz, 1H), 7.07 (app tt, *J* = 1.1, 7.4 Hz, 1H), 6.97-7.01 (comp m, 2H), 6.92-6.95 (m, 1H), 6.87-6.89 (m, 1H), 6.82-6.86 (m, 1H), 4.79-4.82 (m, 1H), 4.71-4.74 (m, 1H), 3.29 (s, 2H), 1.67 (s, 3H); ^{13}C NMR

(125 MHz, $CDCl_3$): δ 157.3, 157.0, 144.6, 141.8, 129.6, 129.4, 123.9, 122.9, 119.6, 118.6, 116.6, 112.2, 44.4, 22.0; IR (film): 3073, 3039, 2970, 2935, 2912, 1934, 1652, 1583, 1489, 1456, 1443, 1374, 1331, 1249, 1213, 1162, 1139, 1072, 1022, 952, 892, 817, 773, 749, 691 cm^{-1}; HRMS-ESI (m/z): $[M+H]^+$ calc'd for $C_{16}H_{17}O$, 225.1274; found 225.1282.

General Procedure for Nickel-Catalyzed Benzylation of 1-Substituted Olefins: In a glove box, an oven-dried vial was charged with Ni(cod)$_2$ (10–20 mol %, in general 10 mol %) and PCy$_2$Ph (20–40 mol %, in general 20 mol %). The vial was then sealed, removed from the glove box, and connected to an argon line. The catalyst mixture was dissolved in the indicated olefin[12] (1.5–5.0 equiv, in general 5.0 equiv) and triethylamine (6.0 equiv) and the mixture was stirred for 5 min at room temperature. To the mixture were added benzyl chloride[13] (1 equiv) and Et$_3$SiOTf (1.75 equiv). The mixture was stirred at room temperature for 16 h, then passed through a small plug of silica gel (1:1 EtOAc/hexanes eluent). The filtrate was concentrated in vacuo to provide the benzylated adducts, which were further purified by flash chromatography. Where indicated, yields were determined by ^{1}H NMR spectroscopy of the crude mixture using 1,4-dioxane as an internal standard.



S2 **3i**

According to the general procedure, 338 μL 6-bromohexene (2.53 mmol) and 423 μL Et$_3$N (3.04 mmol) were added to 13.9 mg Ni(cod)$_2$ (0.0506 mmol) and 27.8 mg PCy$_2$Ph (0.101 mmol) and stirred at room temperature for 5 min. To the solution was then added 95.0 μL benzyl chloride **S2** (0.506 mmol) and 200 μL Et$_3$SiOTf (0.886 mmol), and stirring was continued for 16 h. Purification of the residue by flash chromatography (1→10% Et$_2$O/hexanes) afforded alkene **3i** (170 mg, 97% yield, R_f = 0.60 in 5% Et$_2$O/hexanes) as a colorless oil.

Allylbenzene 3i: ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.36-7.33 (comp m, 2H), 7.28-7.25 (m, 1H), 7.13-7.09 (m, 1H), 7.03-7.00 (comp m, 2H), 6.96-6.94 (m, 1H), 6.89-6.86 (comp m, 2H), 4.85 (dd, *J* = 1.1, 0.6 Hz, 1H), 4.80 (d, *J* = 0.6 Hz, 1H), 3.40 (t, *J* = 6.8 Hz, 2H), 3.33 (s, 2H), 2.01 (t, *J* = 7.6 Hz, 2H), 1.84 (dt, *J* = 14.7, 7.2 Hz, 2H), 1.62-1.55 (comp m, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 157.4, 157.2, 147.8, 141.8, 129.8, 129.6, 124.1, 123.1, 119.7, 118.7, 116.8, 112.0, 42.8, 34.4, 33.8, 32.3, 26.0; IR (film) 2929, 1582, 1488, 1248, 696 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $[C_{19}H_{21}BrO]^+$: 345.0849, found 345.0847.

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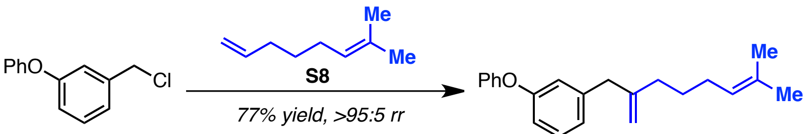
[12] For solid olefins, toluene was used as the solvent for the reaction. The ligand–catalyst mixture was dissolved in a minimal amount of toluene and cannulated into a flask containing the solid olefin under an argon atmosphere.

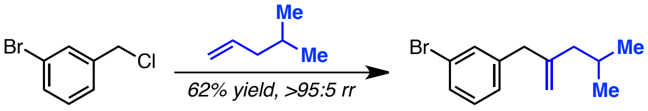
[13] For solid benzyl chlorides, two alternatives were used: (a) A solution of the catalyst, olefin and Et$_3$N was cannulated into a flask containing the benzyl chloride under an argon flow. Et$_3$SiOTf was added to this mixture, and the solution kept under argon for the remainder of the reaction. (b) Inside of a glovebox, the solid the benzyl chloride was added to a vial containing a solution of the catalyst, olefin and Et$_3$N. The vial was then sealed, removed from the glovebox, connected to an argon line, and the Et$_3$SiOTf then added.



S2 3b

According to the general procedure, 417 μL **S8** (2.53 mmol) and 423 μL Et_3N (3.04 mmol) were added to 13.9 mg $Ni(cod)_2$ (0.0506 mmol) and 27.8 mg PCy_2Ph (0.101 mmol) and stirred at room temperature for 5 min. To the solution was then added 95.0 μL benzyl chloride **S2** (0.506 mmol) and 200 μL Et_3SiOTf (0.886 mmol), and stirring was continued for 16 h. Purification of the residue by flash chromatography (2→16% Et_2O/hexanes eluent) afforded alkene **3b** (119 mg, 77% yield, $R_f = 0.70$ in 9% Et_2O/hexanes) as a colorless oil.

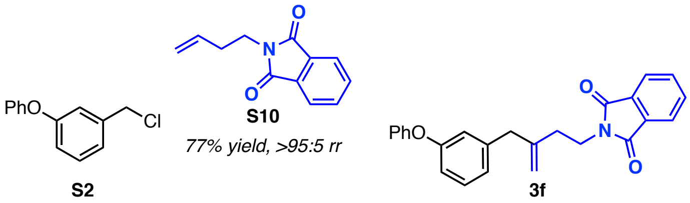
Allylbenzene 3b: ^1H NMR (500 MHz, $CDCl_3$): δ 7.35-7.32 (comp m, 2H), 7.26-2.43 (m, 1H), 7.11-7.08 (m, 1H), 7.02-6.99 (comp m, 2H), 6.95 (d, J = 7.6 Hz, 1H), 6.88-6.84 (comp m, 2H), 5.10 (ddt, J = 7.8, 6.5, 1.3 Hz, 1H), 4.83 (s, 1H), 4.74 (s, 1H), 3.35-3.28 (comp m, 2H), 1.96 (dt, J = 14.9, 7.5 Hz, 4H), 1.69 (s, 3H), 1.59 (d, J = 6.2 Hz, 3H), 1.50-1.43 (comp m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.5, 157.1, 148.7, 142.1, 131.7, 129.8, 129.5, 124.5, 124.2, 123.1, 119.9, 118.7, 116.7, 111.4, 43.0, 35.1, 27.9, 27.8, 25.8, 17.8; IR (film) 2922, 1584, 1485, 1245, 686 cm^{-1}; HRMS (ESI^+) *m/z* calc'd for $[C_{22}H_{26}O]^+$: 306.1984, found xxx.xxxx.



S9 3c

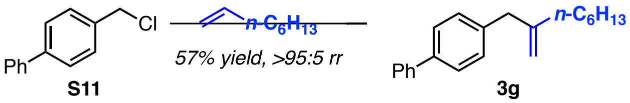
According to the general procedure, 320 μL 4-methylpentene (2.53 mmol) and 423 μL Et_3N (3.04 mmol) were added to 13.9 mg $Ni(cod)_2$ (0.0506 mmol) and 27.8 mg PCy_2Ph (0.101 mmol) and stirred at room temperature for 5 min. To the solution was then added 64.7 μL benzyl chloride **S9** (0.506 mmol) and 200 μL Et_3SiOTf (0.886 mmol), and stirring was continued for 16 h. Purification of the residue by flash chromatography (1→3% Et_2O/hexanes eluent) afforded alkene **3c** (79.3 mg, 62% yield, $R_f = 0.90$ in 5% Et_2O/hexanes) as a colorless oil.

Allylbenzene 3c: ^1H NMR (500 MHz, $CDCl_3$): δ 7.35-7.34 (comp m, 2H), 7.17-7.10 (comp m, 2H), 4.83 (s, 1H), 4.75 (s, 1H), 3.27 (s, 2H), 1.84 (d, J = 7.0 Hz, 2H), 1.82-1.74 (m, 1H), 0.88 (d, J = 6.4 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 147.2, 142.3, 132.1, 129.9, 129.2, 127.8, 122.4, 113.2. 45.2, 42.3, 26.0, 22.5 ; IR (film) 2942, 1567, 1472, 1073, 777 cm^{-1}; HRMS (ESI^+) *m/z* calc'd for $[C_{13}H_{17}Br]^+$: 252.0514, found xxx.xxxx.



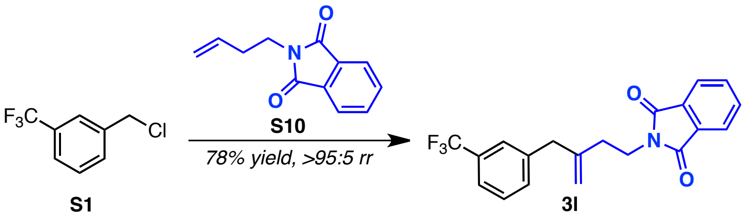
According to the general procedure,[11] 153 mg **S10** (0.759 mmol), 370 µL toluene, and 423 µL Et_3N (3.04 mmol) were added to 13.9 mg $Ni(cod)_2$ (0.0506 mmol) and 27.8 mg PCy_2Ph (0.101 mmol) and stirred at room temperature for 5 min. To the solution was then added 95.0 µL benzyl chloride **S2** (0.506 mmol) and 200 µL Et_3SiOTf (0.886 mmol), and stirring was continued for 16 h. Purification of the residue by flash chromatography (5→50% Et_2O/hexanes eluent) afforded alkene **3f** (150 mg, 77% yield, $R_f = 0.40$ in 30% Et_2O/hexanes) as a colorless oil.

Allylbenzene 3f: ^1H NMR (500 MHz, $CDCl_3$): δ 7.84-7.80 (comp m, 2H), 7.72-7.68 (comp m, 2H), 7.34-7.31 (comp m, 2H), 7.24 (t, *J* = 7.8 Hz, 1H), 7.10-7.07 (m, 1H), 7.01-6.96 (comp m, 3H), 6.91-6.90 (m, 1H), 6.85-6.83 (m, 1H), 4.84 (s, 1H), 4.77 (s, 1H), 3.83 (t, *J* = 7.1 Hz, 2H), 3.42 (s, 2H), 2.38 (t, *J* = 7.1 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.9, 158.1, 157.9, 145.6, 142.0, 134.6, 132.8, 130.4, 130.3, 124.9, 123.9, 123.7, 120.5, 119.4, 117.5, 114.9, 42.9, 37.0, 34.7; IR (film) 2936, 2366, 1776, 1712, 1580 cm^{-1}; HRMS (ESI^+) *m/z* calc'd for $[C_{25}H_{21}NO_3 + H]^+$: 384.1600, found 384.1594.



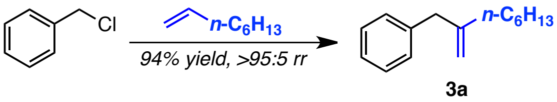
According to the general procedure, 397 µL octene (2.53 mmol) and 423 µL Et_3N (3.04 mmol) were added to a vial containing 13.9 mg $Ni(cod)_2$ (0.0506 mmol) and 27.8 mg PCy_2Ph (0.101 mmol), and the mixture was stirred in the glovebox for 5 min. To the stirring solution was then added 103 mg benzyl chloride **S11** (0.506 mmol), and the vial was removed from the glovebox.[12b] Triethylsilyl trifluoromethanesulfonate (200 µL, 0.886 mmol) was then added, and stirring was continued for 16 h. Purification of the residue by flash chromatography (1→3% Et_2O/hexanes eluent) afforded alkene **3g** (79.7 mg, 57% yield, $R_f = 0.95$ in 5% Et_2O/hexanes) as a colorless oil.

Allylbenzene 3g: ^1H NMR (500 MHz, $CDCl_3$): δ 7.62-7.59 (comp m, 2H), 7.55-7.53 (comp m, 2H), 7.46-7.42 (comp m, 2H), 7.36-7.32 (m, 1H), 7.29-7.26 (comp m, 2H), 4.86 (s, 1H), 4.79 (s, 1H), 3.39 (s, 2H), 2.01 (t, *J* = 7.7 Hz, 2H), 1.50-1.44 (comp m, 2H), 1.33-1.26 (comp m, 6H), 0.91-0.88 (comp m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.3, 141.2, 139.2, 139.0, 129.5, 128.8, 127.10, 127.08, 127.07, 111.1, 42.7, 35.6, 31.9, 29.1, 27.7, 22.7, 14.2; IR (film) 2915, 2364, 1649, 1486, 886, 761 cm^{-1}; HRMS (ESI^+) *m/z* calc'd for $[C_{21}H_{26}]^+$: 278.2035, **found xxx.xxxx.**



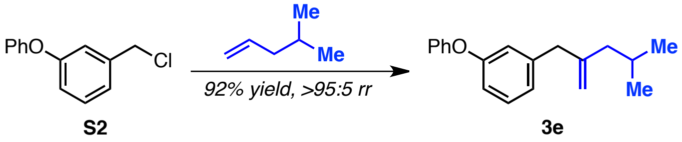
According to the general procedure,[11] 474 mg olefin **S10** (2.53 mmol) and 423 µL Et_3N (3.04 mmol) were added to a solution of 13.9 mg $Ni(cod)_2$ (0.0506 mmol) and 27.8 mg PCy_2Ph (0.101 mmol) in toluene (420 µL) and stirred at room temperature for 5 min. To the solution was then added 78.5 µL benzyl chloride **S1** (0.506 mmol) and 200 µL Et_3SiOTf (0.886 mmol), and stirring was continued for 16 h. Purification of the residue by flash chromatography (6→60% Et_2O/hexanes eluent) afforded alkene **3l** (142 mg, 78% yield, R_f = 0.40 in 30% Et_2O/hexanes) as a colorless oil.

Alkene 3l: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85-7.80 (comp m, 2H), 7.72-7.69 (comp m, 2H), 7.46-7.43 (comp m, 2H), 7.41-7.37 (comp m, 2H), 4.86 (s, 1H), 4.71 (s, 1H), 3.84 (t, *J* = 7.1 Hz, 2H), 3.49 (s, 2H), 2.37 (t, *J* = 7.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.31, 144.6, 140.1, 132.6, 132.1, 128.8, 125.9, 125.8, 123.17, 114.9, 42.0, 36.3, 34.2; IR (film) 2949, 2364, 1774, 1712, 1331 cm^{-1}; HRMS (ESI$^+$) *m/z* calc'd for $[C_{20}H_{16}F_3NO_2 + Na]^+$: 382.1031, found 382.1025.



According to the general procedure, 392 µL octene (2.50 mmol) and 418 µL Et_3N (3.00 mmol) were added to 13.8 mg $Ni(cod)_2$ (0.0500 mmol) and 27.4 mg PCy_2Ph (0.100 mmol) and stirred at room temperature for 5 min. To the solution was then added 57.5 µL benzyl chloride (0.500 mmol) and 197 µL Et_3SiOTf (0.875 mmol), and stirring was continued for 16 h. Purification of the residue by flash chromatography (100% hexanes eluent) afforded alkene **3a** (95.2 mg, 94% yield) as a colorless oil.

(2-Methyleneoctyl)benzene (3a): ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25-7.30 (comp m, 2H), 7.15-7.21 (comp m, 3H), 4.80-4.82 (m, 1H), 4.70-4.73 (m, 1H), 3.32 (s, 2H), 1.95 (t, *J* = 7.7 Hz, 2H), 1.35-1.45 (comp m, 2H), 1.21-1.32 (comp m, 6H), 0.87 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.3, 139.9, 129.0, 128.2, 126.0, 110.9, 43.0, 35.4, 31.7, 29.0, 27.6, 22.6, 14.1; IR (thin film): 3085, 3064, 3027, 2956, 2927, 2856, 1644, 1602, 1494, 1453, 893, 736, 698 cm^{-1}; HRMS-DART (m/z): $[M+H]^+$ calc'd for $C_{15}H_{23}$, 203.1794; found 203.1800.



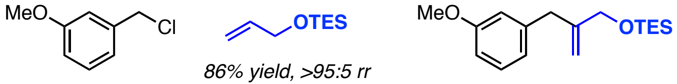
According to the general procedure, 316 µL olefin (2.50 mmol) and 418 µL Et_3N (3.00 mmol) were added to 13.8 mg $Ni(cod)_2$ (0.0500 mmol) and 27.4 mg PCy_2Ph (0.100 mmol) and stirred at room temperature for 5 min. To the solution was then added 93.8 µL benzyl chloride **S2** (0.500 mmol) and 197 µL Et_3SiOTf (0.875 mmol), and stirring was continued for 16 h. Purification of the residue by flash chromatography (100% hexanes eluent) afforded alkene **3e** (123 mg, 92% yield, R_f = 0.66 in 5% Et_2O/hexanes) as a colorless oil.

1-(4-Methyl-2-methylenepentyl)-3-phenoxybenzene (3e): ^1H NMR (500 MHz, $CDCl_3$): δ 7.28-7.34 (comp m, 2H), 7.16-7.26 (m, 1H), 7.07 (app t, *J* = 7.4 Hz, 1H), 6.96-7.02 (comp m, 2H), 6.93 (app d, *J* = 7.6 Hz, 1H), 6.80-6.88 (comp m, 2H), 4.79 (s, 1H), 4.74 (d, *J* = 1.3 Hz, 1H), 3.27 (s, 2H), 1.84 (d, *J* = 7.3 Hz, 2H), 1.71-1.83 (m, 1H), 0.85 (d, *J* = 6.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.4, 157.0, 147.5, 142.0, 129.6, 129.4, 124.1, 122.9, 119.8, 118.6, 116.6, 112.7, 45.2, 42.5, 25.9, 22.4; IR (film): 3071, 3039, 2954, 2924, 2868, 1933, 1645, 1583, 1489, 1445, 1383, 1366, 1249, 1214, 1162, 1141, 1072, 1023, 964, 896, 819, 749, 691 cm^{-1}; HRMS-ESI (m/z): $[M+Na]^+$ calc'd for $C_{19}H_{22}ONa$, 289.1563; found 289.1564.

S13 **3h**

According to the general procedure, 573 µL olefin (2.50 mmol) and 418 µL Et_3N (3.00 mmol) were added to 13.8 mg $Ni(cod)_2$ (0.0500 mmol) and 27.4 mg PCy_2Ph (0.100 mmol) and stirred at room temperature for 5 min. To the solution was then added 74.8 µL benzyl chloride **S13** (0.500 mmol) and 197 µL Et_3SiOTf (0.875 mmol), and stirring was continued for 16 h. Purification of the residue by flash chromatography (20:1 hexanes/Et_2O eluent) afforded alkene **3h** (166 mg, 99% yield, R_f = 0.50 in 20:1 hexanes/Et_2O) as a colorless oil.

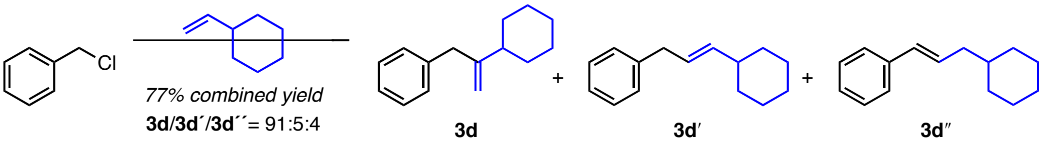
***tert*-Butyl((3-(3-methoxybenzyl)but-3-en-1-yl)oxy)dimethylsilane (3h)**: ^1H NMR (500 MHz, $CDCl_3$): δ 7.20-7.24 (m, 1H), 6.74-6.84 (comp m, 3H), 4.88 (dd, *J* = 0.7, 1.2 Hz, 1H), 4.84 (dd, *J* = 1.3, 1.8 Hz, 1H), 3.81 (s, 3H), 3.71 (t, *J* = 7.0 Hz, 2H), 3.36 (s, 2H), 2.23 (dt, *J* = 0.9, 7.0 Hz, 2H), 0.91 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.6, 145.9, 141.2, 129.2, 121.5, 114.7, 112.9, 111.4, 62.3, 55.1, 43.5, 38.6, 25.9, 18.3, -5.3; IR (film): 2929, 2857, 1646, 1601, 1585, 1489, 1471, 1436, 1387, 1361, 1257, 1149, 1098, 1053, 1006, 938, 894, 834, 775, 694 cm^{-1}; HRMS-ESI (m/z): $[M+Na]^+$ calc'd for $C_{18}H_{30}O_2SiNa$, 329.1907; found 329.1906.



S13 **3k**

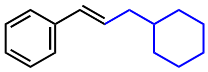
According to the general procedure, 514 µL olefin (2.50 mmol) and 418 µL Et_3N (3.00 mmol) were added to 13.8 mg $Ni(cod)_2$ (0.0500 mmol) and 27.4 mg PCy_2Ph (0.100 mmol) and stirred at room temperature for 5 min. To the solution was then added 74.8 µL benzyl chloride **S13** (0.500 mmol) and 197 µL Et_3SiOTf (0.875 mmol), and stirring was continued for 16 h. Purification of the residue by preparative thin layer chromatography (20:1 hexanes/Et_2O eluent) afforded alkene **3k** (127 mg, 86% yield) as a colorless oil.

Triethyl((2-(3-methoxybenzyl)allyl)oxy)silane (3k): ^1H NMR (500 MHz, $CDCl_3$): δ 7.16-7.21 (m, 1H), 6.77-6.80 (m, 1H), 6.72-6.76 (comp m, 2H), 5.14 (d, *J* = 1.8 Hz, 1H), 4.83-4.86 (m, 1H), 4.03 (s, 2H), 3.78 (s, 3H), 3.34 (s, 2H), 0.95 (t, *J* = 7.9 Hz, 6H), 0.59 (q, *J* = 7.9 Hz, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.6, 147.6, 140.9, 129.2, 121.3, 114.5, 111.5, 110.9, 64.9, 55.1, 39.6, 6.8, 4.4; IR (film): 2954, 2911, 2876, 1653, 1601, 1585, 1488, 1464, 1455, 1436, 1414, 1313, 1260, 1149, 1108, 1081, 1053, 1014, 901, 819, 783, 744, 694 cm^{-1}; HRMS-ESI (m/z): $[M+Na]^+$ calc'd for $C_{17}H_{28}O_2SiNa$, 315.1751; found 315.1755.



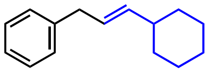
According to the general procedure, 342 µL olefin (2.50 mmol) and 418 µL Et_3N (3.00 mmol) were added to 13.8 mg $Ni(cod)_2$ (0.0500 mmol) and 27.4 mg PCy_2Ph (0.100 mmol) and stirred at room temperature for 5 min. To the solution was then added 57.5 µL benzyl chloride (0.500 mmol) and 197 µL Et_3SiOTf (0.875 mmol), and stirring was continued for 16 h. Purification of the residue by flash chromatography (100% hexanes eluent) afforded alkene **3d** as a mixture of isomers (77.5 mg total, 77% combined yield) as a colorless oil.

(2-Cyclohexylallyl)benzene (3d): Obtained as a mixture with linear isomers **3d′** and **3d″**; ^1H NMR (500 MHz, $CDCl_3$): δ 7.24-7.29 (comp m, 2H), 7.15-7.21 (comp m, 3H), 4.84 (app s, 1H), 4.63 (q, *J* = 1.4 Hz, 1H), 3.36 (s, 2H), 1.60-1.85 (comp m, 6H), 1.05-1.30 (comp m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.5, 140.2, 129.1, 128.1, 125.8, 109.5, 43.4, 41.8, 32.5, 26.7, 26.3; IR (film): 3083, 3062, 3026, 2925, 2851, 1941, 1802, 1640, 1602, 1494, 1449, 1074, 1029, 965, 888, 743, 697 cm^{-1}; HRMS-DART (m/z): $[M+H]^+$ calc'd for $C_{15}H_{21}$, 201.1643; found 201.1648.



3d″

(*E*)-(3-Cyclohexylprop-1-enyl)benzene (3d″): Distinguishable peaks are shown. ^1H NMR (500 MHz, $CDCl_3$): δ 6.34 (d, *J* = 15.7 Hz, 1H), 6.22 (dt, *J* = 15.7, 7.3 Hz, 1H).

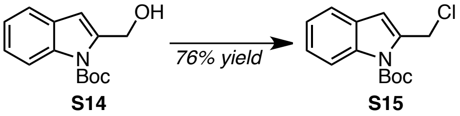


3d′

(*E*)-(3-Cyclohexylallyl)benzene (3d′): Distinguishable peaks are shown. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.51 (dt, *J* = 15.4, 5.9 Hz, 1H), 5.47 (dd, *J* = 15.4, 5.6 Hz, 1H), 3.31 (d, *J* = 5.9 Hz, 2H).

Substrate Syntheses

Arylmethyl chlorides **1a-o** are commercially available. **1p**,[14] **1q**,[15] **1r**,[16] **1t**,[2] and **1u**[17] were synthesized according to the reported procedures.



To a mixture of LiCl (424 mg, 10 equiv, 10.0 mmol), Et_3N (349 ml, 2.5 equiv, 2.50 mmol) and tert-butyl 2-(hydroxymethyl)-1*H*-indole-1-carboxylate (**S14**)[18] (247 mg, 1 equiv, 1.00 mmol) in THF (2.50 mL) was added MsCl (163 ml, 2.1 equiv, 2.10 mmol) at 0 °C. The mixture was stirred for 30 min, then poured into a mixture of Et_2O and water. The mixture was extracted with Et_2O, dried over Na_2SO_4, and concentrated in vacuo. The crude material was purified by silica gel column chromatography to afford chloride **S15** (203 mg, 76% yield).

tert-Butyl 2-(chloromethyl)-1*H*-indole-1-carboxylate (S15): Mp. 33-34 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.15 (dd, *J* = 0.7, 8.4 Hz, 1H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.31 (ddd, *J* = 1.3, 7.3, 8.4 Hz, 1H), 7.21 (app dt, *J* = 0.9, 7.5 Hz, 1H), 6.66 (d, *J* = 0.6 Hz, 1H), 4.95 (s, 2H), 1.69 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.8, 137.2, 135.8, 128.2, 125.0, 123.0, 120.8, 115.8, 111.3, 84.6, 40.6, 28.0; IR (film): 3053, 2979, 2933, 1736, 1591, 1565, 1476, 1453, 1431, 1370, 1343, 1328, 1261, 1220, 1159, 1119, 1094, 849, 768, 746, 703 cm^{-1}.

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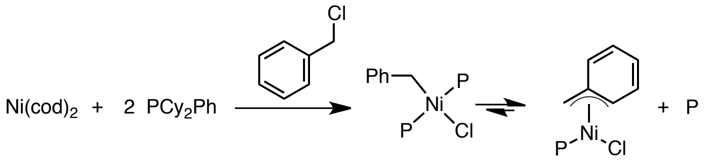
NMR Spectroscopic Analyses for Oxidative Addition Step of Nickel(0) into Benzyl Chloride

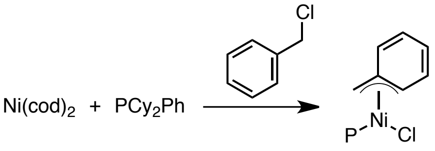
The oxidative addition of a nickel(0) species into a benzyl halide has been previously investigated, however the reported studies were conducted with PMe_3[19] and PPh_3,[20] and the results showed a dependency on the specific phosphine ligand used. Therefore, we examined the oxidative addition of a nickel(0)–PCy_2Ph complex (ratio of Ni/PR_3 = 1:2) into benzyl chloride (eq 1).



15 **14**

(1)

To a solution of $Ni(cod)_2$ (13.8 mg, 0.0500 mmol, 1 equiv) and PCy_2Ph (27.4 mg, 0.100 mmol, 2 equiv) in C_6D_6 (1.00 mL) was added benzyl chloride (6.90 mL, 0.0600 mmol, 1.2 equiv) at room temperature. The mixture was stirred for 30 min, affording a violet-colored homogeneous solution. At room temperature, the ^{31}P NMR spectrum of the solution showed two broad peaks at 2.6 and 38.6 ppm. The observed two peaks had similar heights, indicating the equimolar amounts of the two species corresponding to those two peaks existed in the solution. The compound corresponding to the peak at 2.6 ppm is free PCy_2Ph, and the compound corresponding to the peak at 38.6 ppm is allyl complex **14**. Complex **14** was independently synthesized according to the procedure described in the following section, and characterized crystallographically. These experimental results and the preceding reports[15,16] support a mechanism whereby upon combining 1 equivalent of $Ni(cod)_2$, 2 equivalents of phosphine ligand and excess benzyl chloride in solution, an equilibrium is formed between η^3-complex **14** and η^1-complex **15** that favors complex **14**.



14

To a solution of $Ni(cod)_2$ (110 mg, 0.400 mmol, 1 equiv) and PCy_2Ph (110 mg, 0.400 mmol, 1 equiv) in toluene (4.00 mL) was added benzyl chloride (55.2 mL, 0.480 mmol, 1.2 equiv) at room temperature in a glove box. The mixture was stirred at room temperature for 1.5 h. The solution was subjected to gradual diffusion of pentane and left for 2 days. The supernatant was decanted off and the obtained solid was washed with pentane three times, then dried under vacuum, affording **14** as a purple solid. The single crystal suitable for X-ray diffraction analysis was obtained by recrystallization from C_6D_6/pentane.

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[19] (a) Carmona, E.; Marín, J. M.; Paneque, M.; Poveda, M. L. *Organometallics* **1987**, *6*, 1757. (b) Carmona, E.; Paneque, M.; Poveda, M. *Polyhedron* **1989**, *8*, 285.

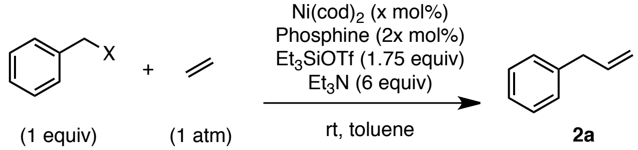
[20] (a) Stille, J. K.; Cowell, A. B. *J. Organomet. Chem.* **1977**, *124*, 253. (b) Bartsch, E.; Dinjus, E.; Fischer, R.; Uhilig, E. *Z. Anorg. Allg. Chem.* **1977**, *433*, 5.

Nickel complex [Ni(η^3-$CH_2C_6H_5$)Cl(PCy_2Ph)] (14): ^{1}H NMR (500 MHz, C_6D_6): δ 7.47 (dt, *J* = 1.7, 8.2 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.25 (t, *J* = 7.7 Hz, 2H), 7.04-7.14 (comp m, 3H), 6.82 (d, *J* = 7.8 Hz, 2H), 2.20-2.34 (comp m, 4H), 1.55-1.68 (comp m, 6H), 1.51 (t, *J* = 15.7 Hz, 4H), 1.14-1.30 (comp m, 4H), 1.09 (tq, *J* = 3.1, 12.7 Hz, 2H), 1.05 ($CH_2C_6H_5$, d, *J* = 3.8 Hz, 2H), 0.95 (tq, *J* = 3.5, 12.8 Hz, 2H); ^{13}C NMR (125 MHz, C_6D_6): δ 134.3 (d, *J* = 2.1 Hz), 133.8 (d, *J* = 9.0 Hz), 130.0 (d, *J* = 2.3 Hz), 129.7 (d, *J* = 36.0 Hz), 128.7 (d, *J* = 2.6 Hz), 128.3, 127.9 (d, *J* = 9.0 Hz), 118.0 (d, *J* = 5.3 Hz), 115.0, 32.4 (d, *J* = 23.5 Hz), 29.0 (d, *J* = 3.6 Hz), 28.5 (d, *J* = 1.9 Hz), 27.2 (d, *J* = 13.2 Hz), 27.0 (d, *J* = 9.9 Hz), 26.5 (d, *J* = 1.3 Hz), 24.2 ($CH_2C_6H_5$, d, *J* = 9.9 Hz); ^{31}P NMR (202.4 MHz, C_6D_6): δ 38.6 (sharp singlet).

Additional Optimization Data

In addition to the data described in Table 1 of the communication, the following reactions were conducted as part of optimization process.

Table S1. Optimization Conditions for the Benzylation of Ethylene



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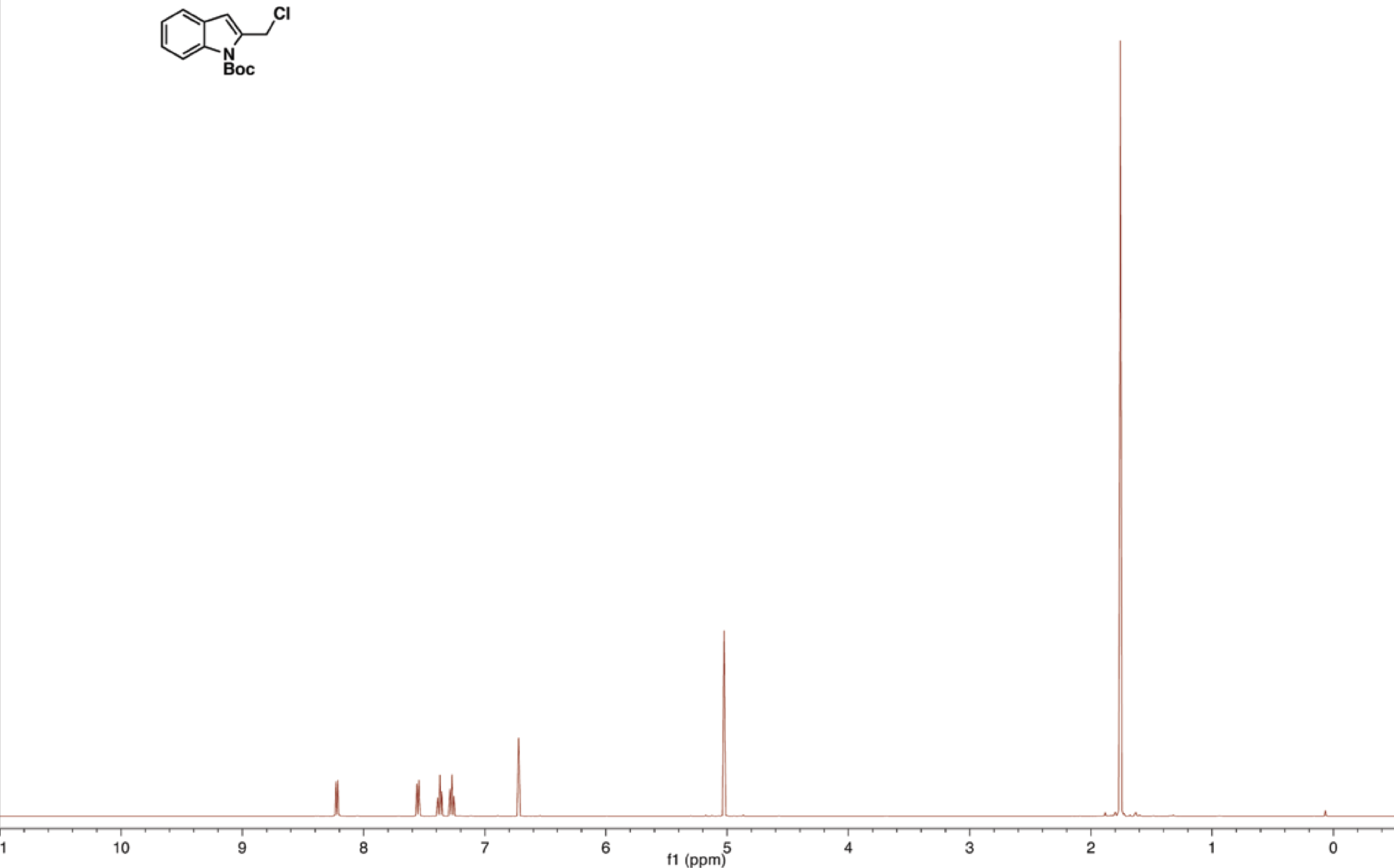
2	P(*o*-anisyl)$_3$	OCO_2Me	10	18	0	0
3	P(*o*-anisyl)$_3$	Cl (**1**)	20	23	76	73
4	P(*o*-anisyl)$_3$	Br	20	2	100	21
8[b]	$PCyPh_2$	Cl	0	15	0	0

[a] Determined by GC. [b] 10 mol % $PCyPh_2$ used.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Boc
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8
7
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5
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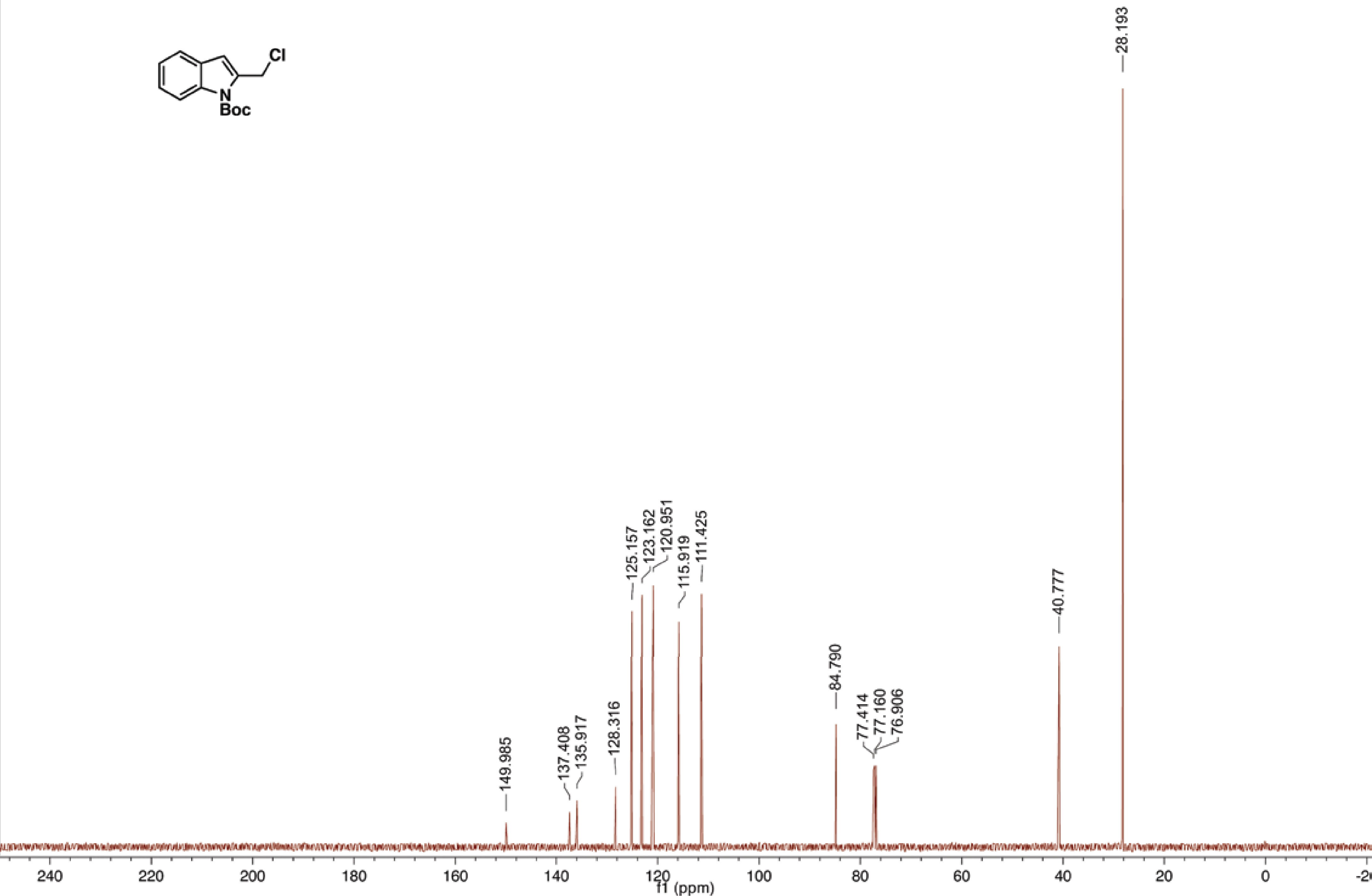
f1 (ppm)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125.157
123.162
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77.414
77.160
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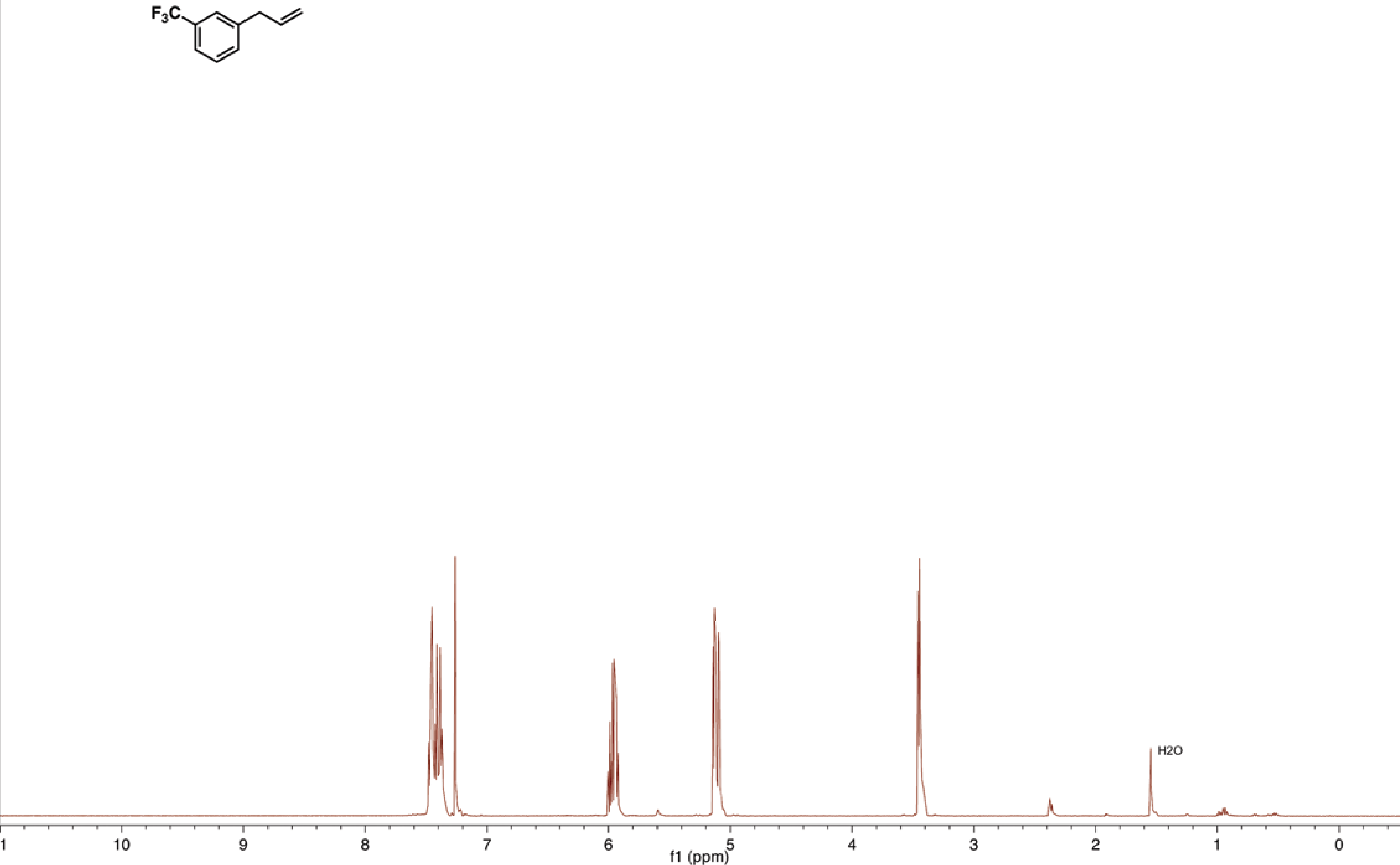
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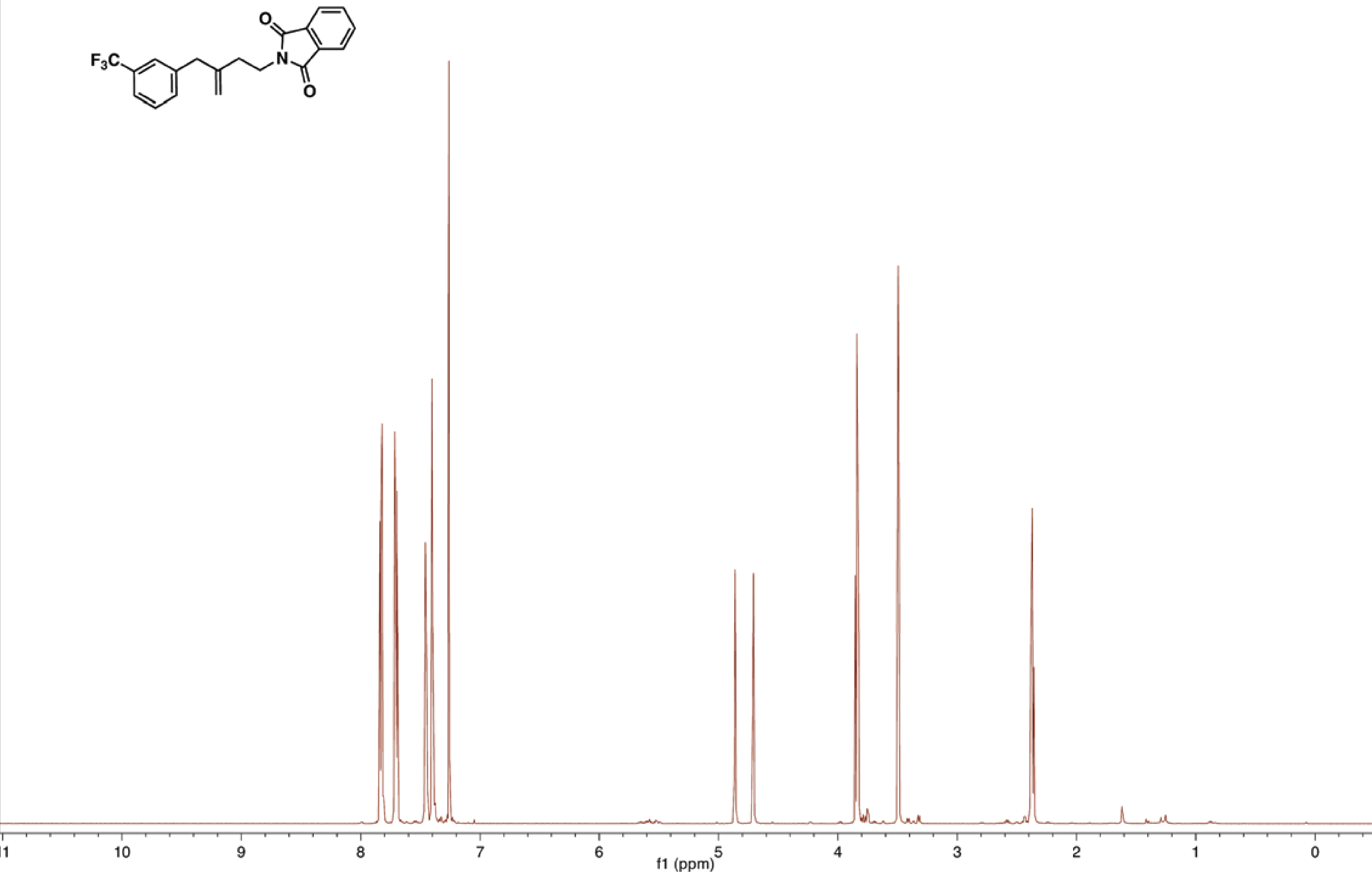
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O
O
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3
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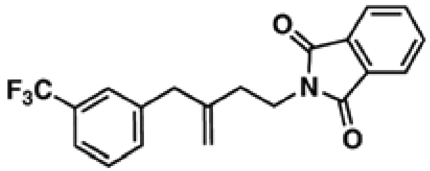
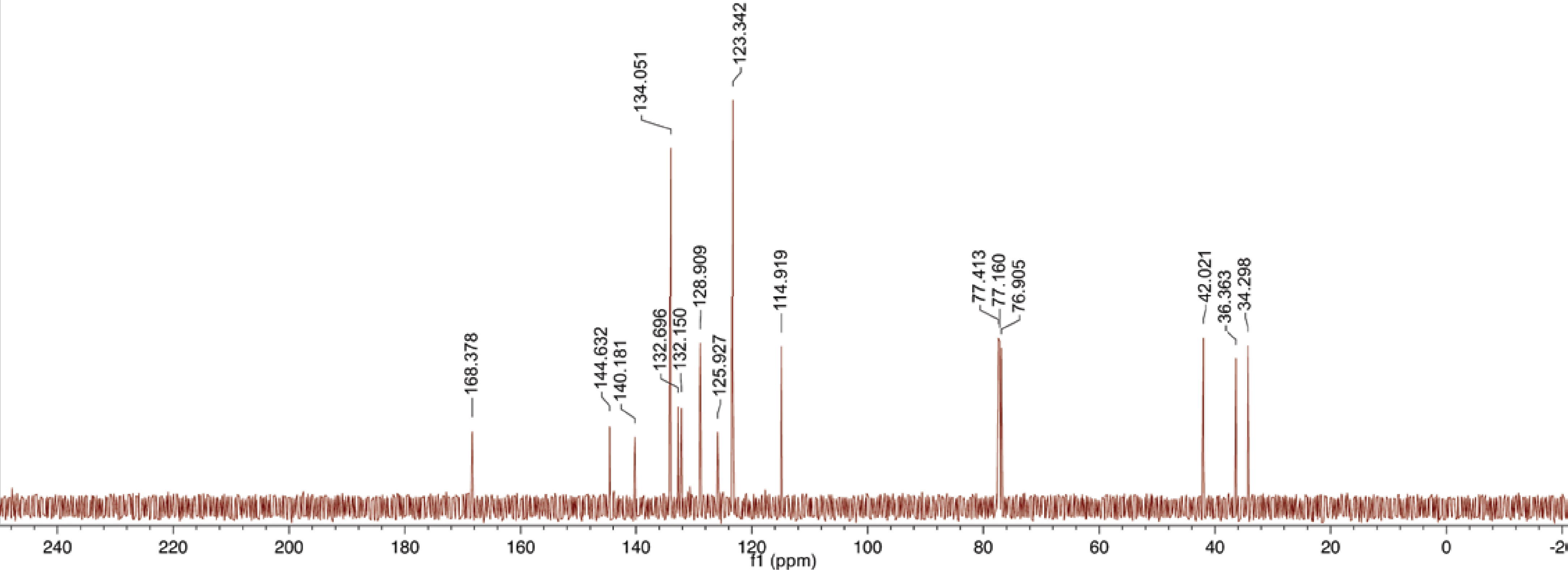
f1 (ppm)



F3C
N
O
O



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132.150
128.909
125.927
123.342
114.919
77.413
77.160
76.905
42.021
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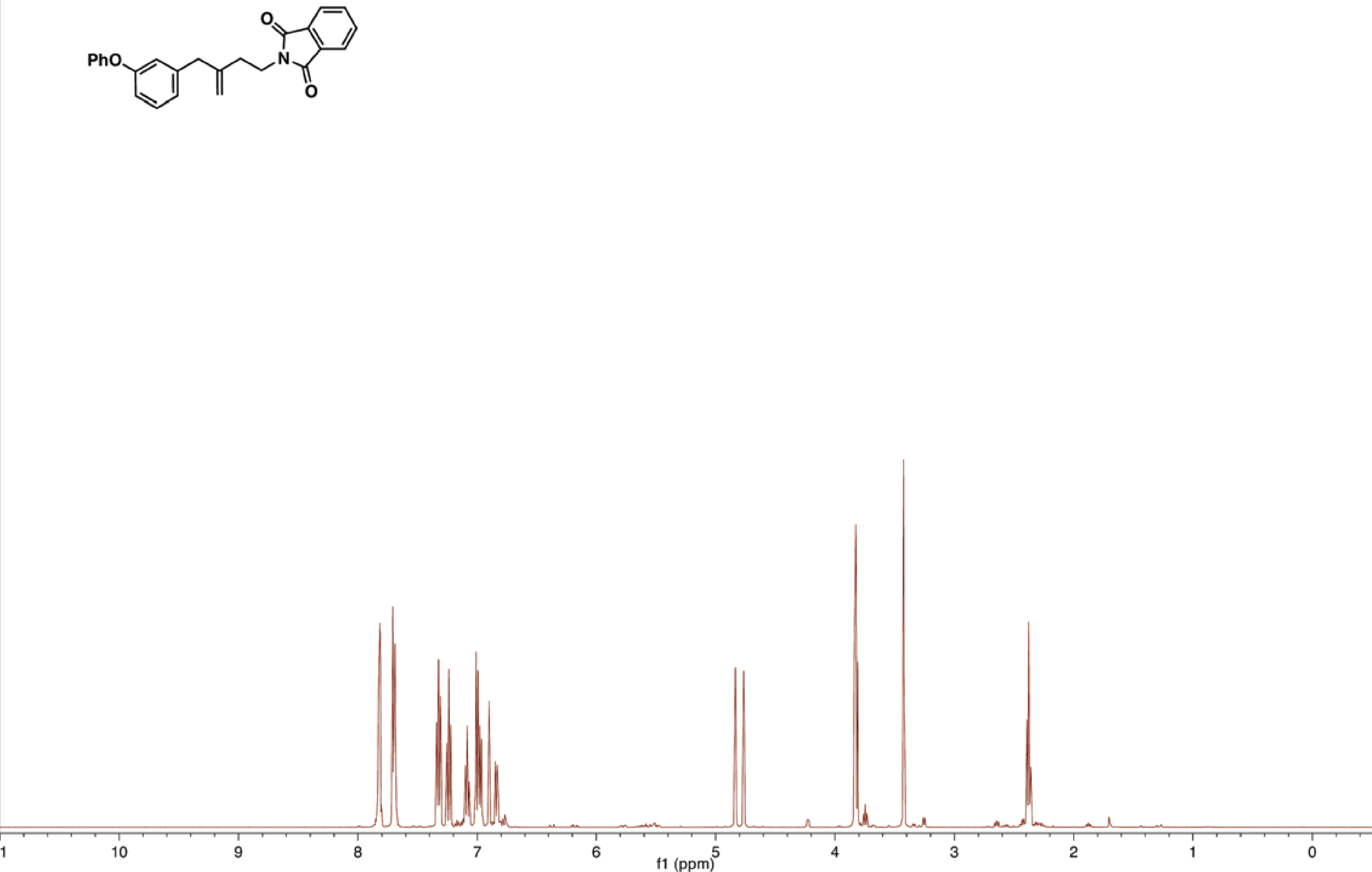
f1 (ppm)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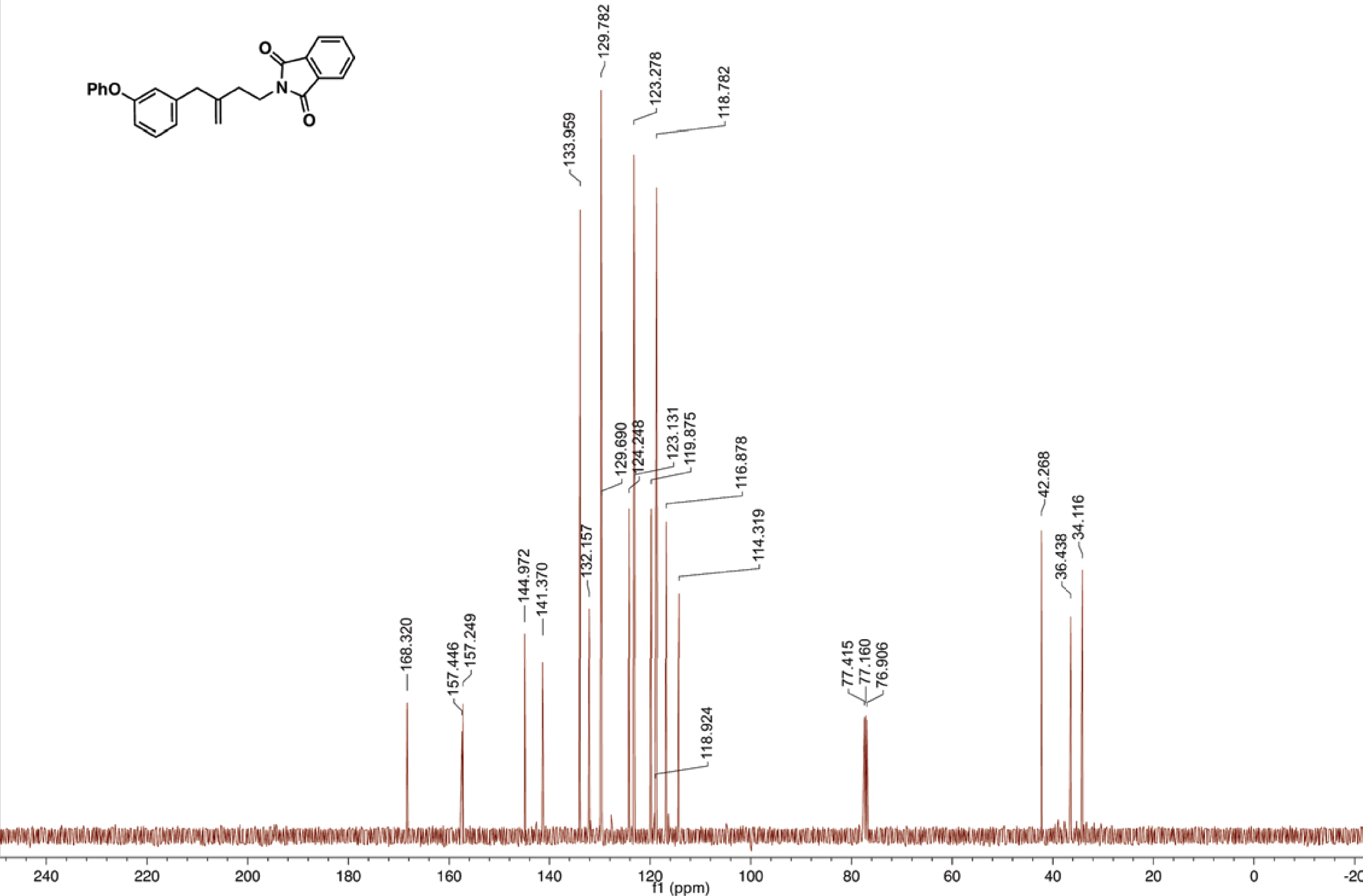
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O
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132.157
129.782
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124.248
123.278
123.131
119.875
118.924
118.782
116.878
114.319
77.415
77.160
76.906
42.268
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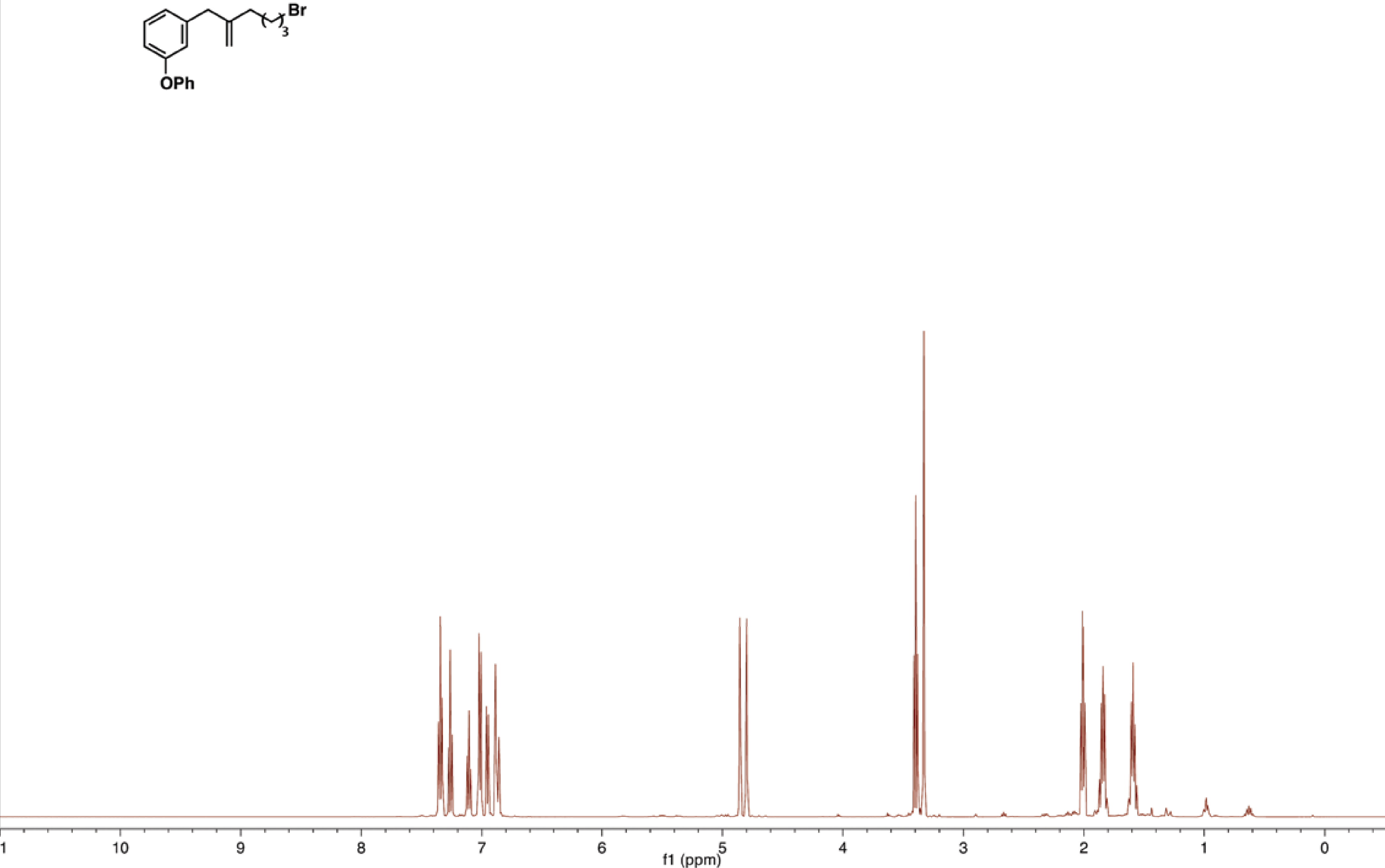
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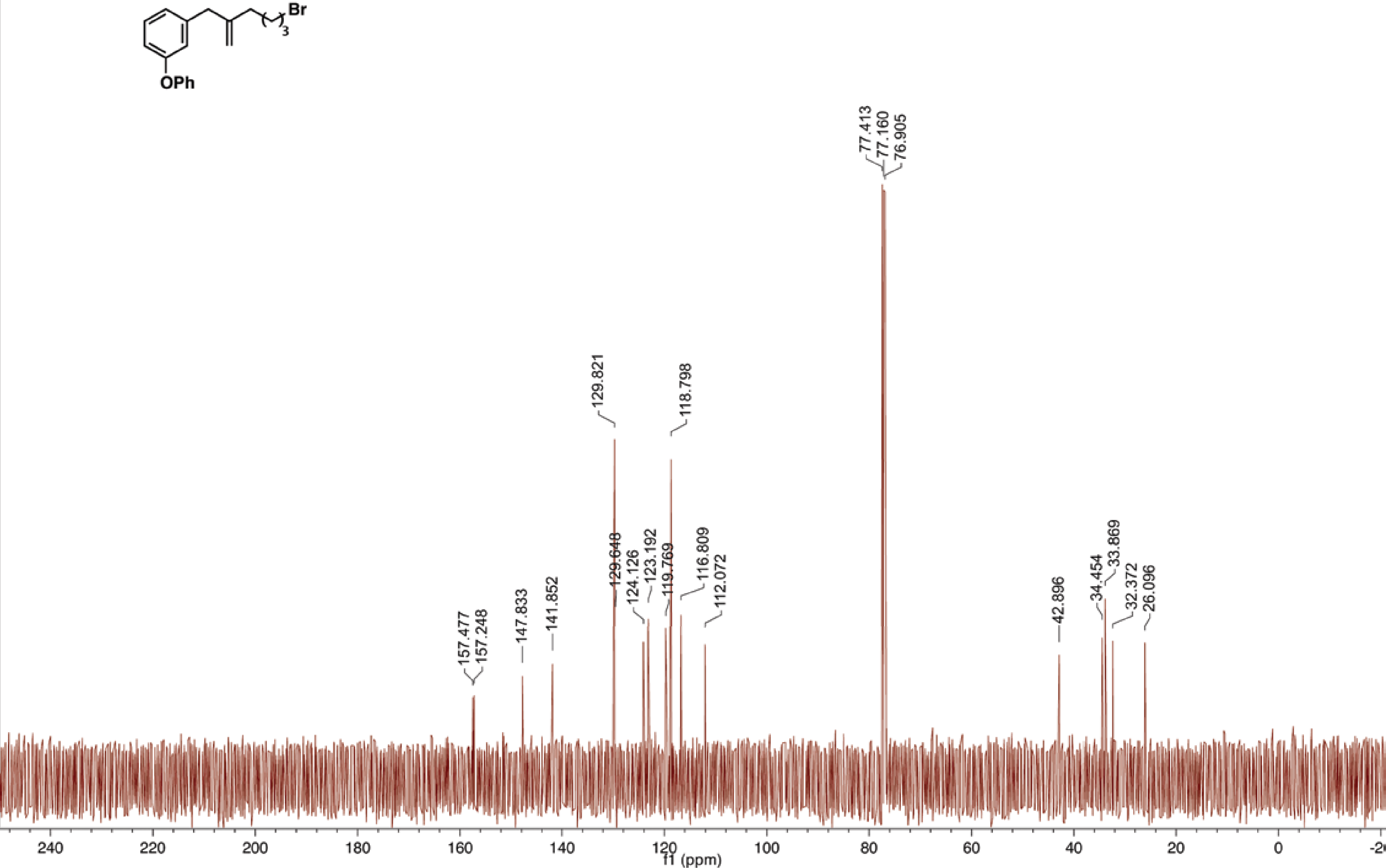
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147.833
141.852
129.648
124.126
123.192
119.769
116.809
112.072
42.896
34.454
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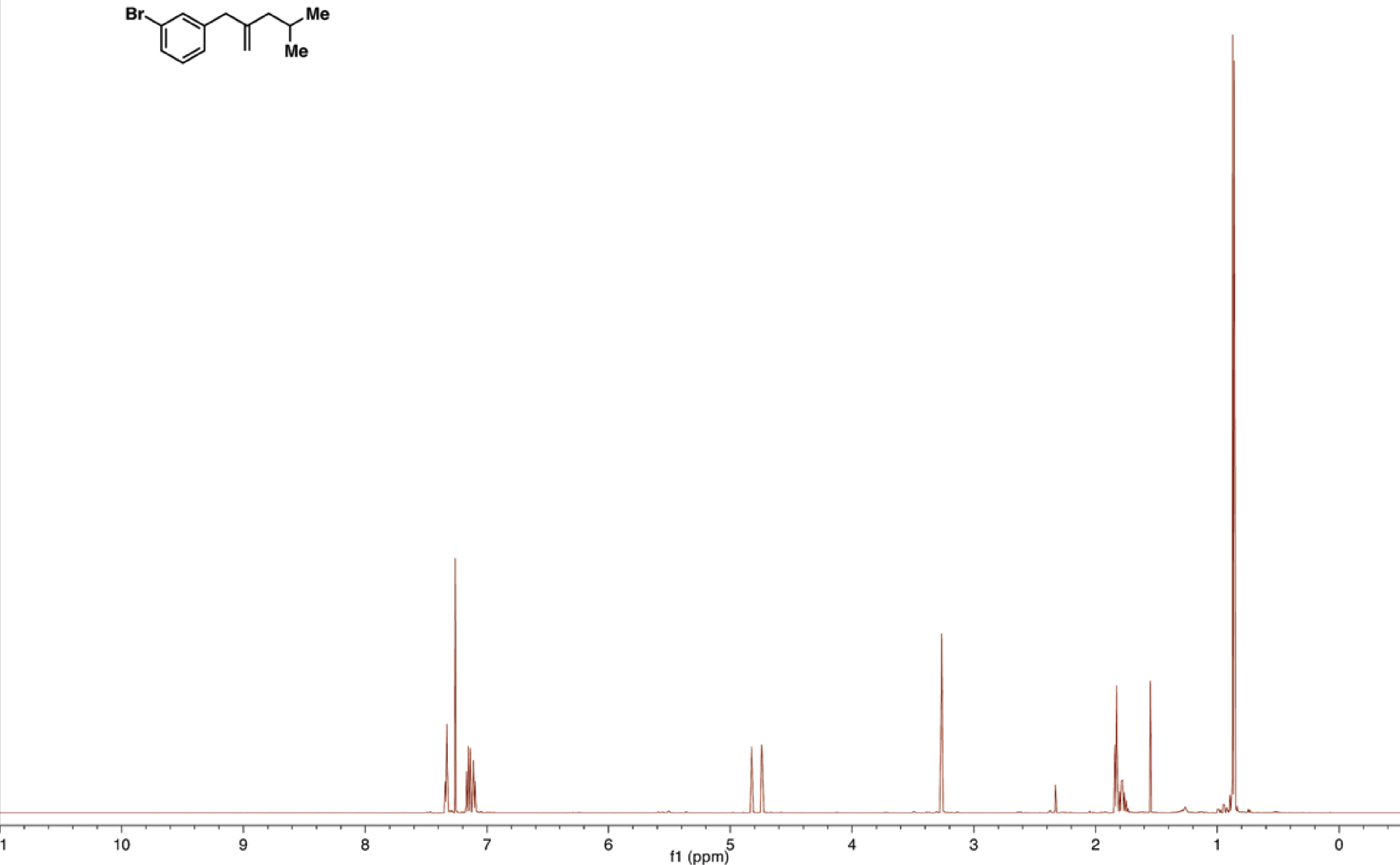
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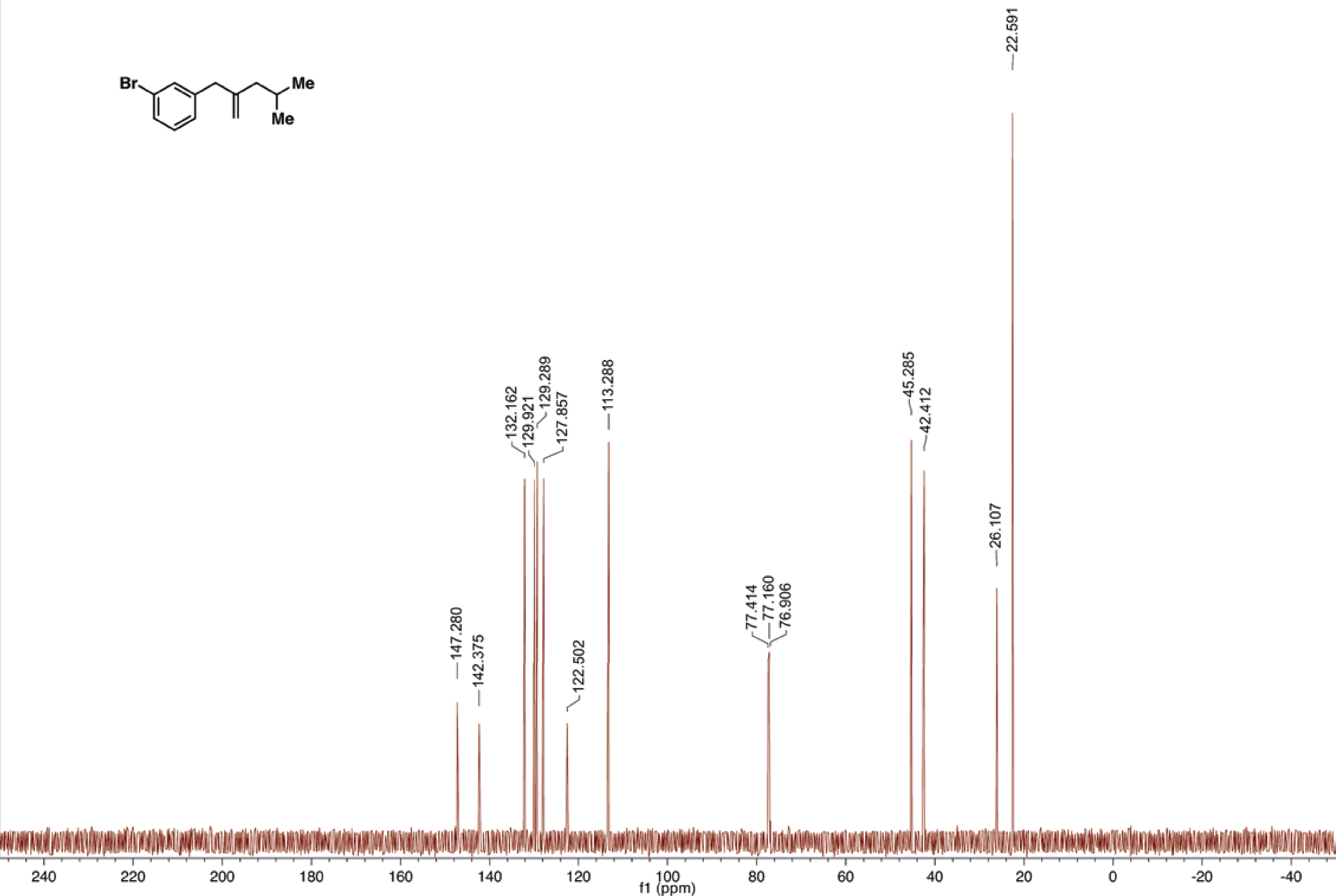
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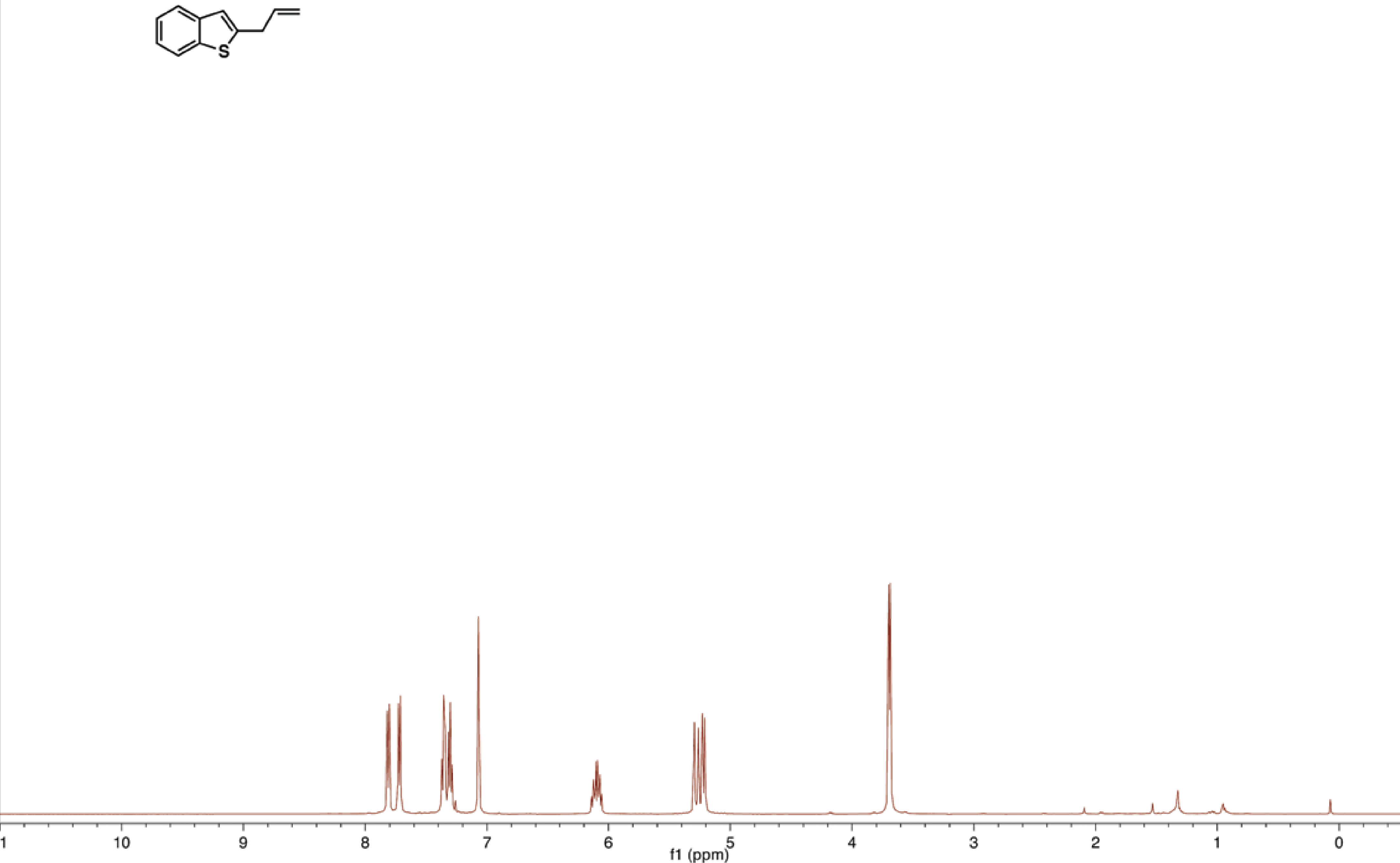
f1 (ppm)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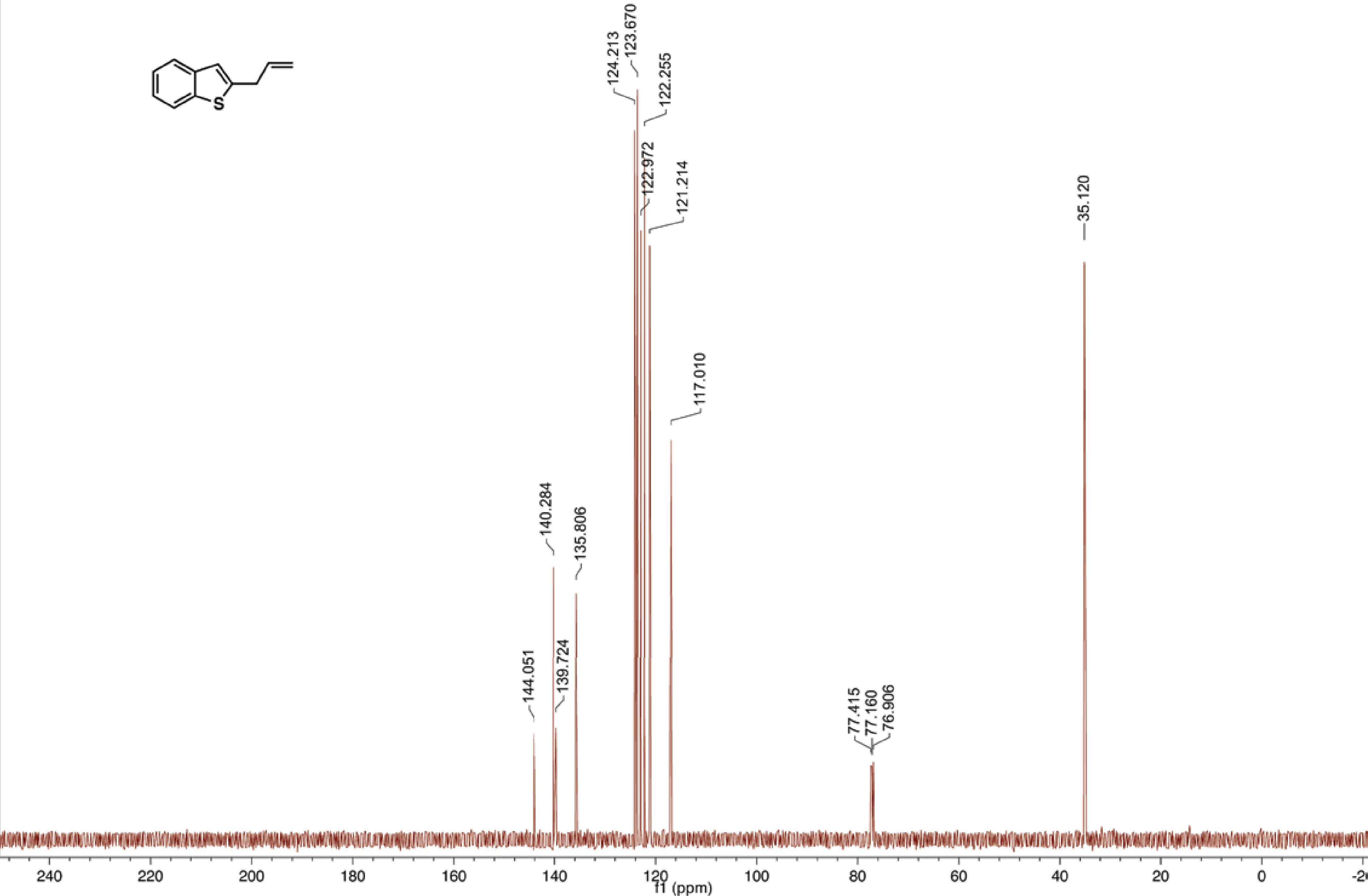
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180
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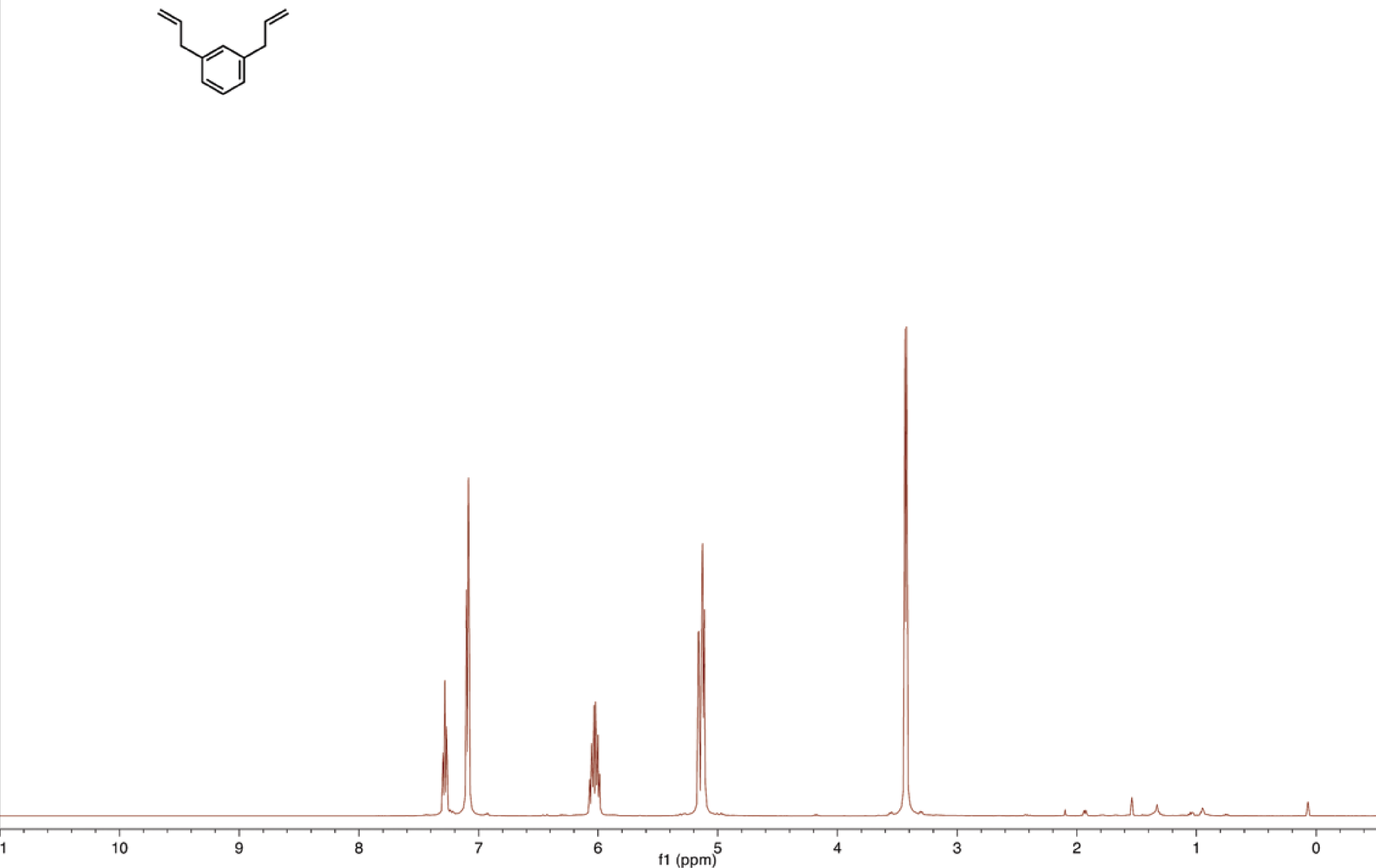
f1 (ppm)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4
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2
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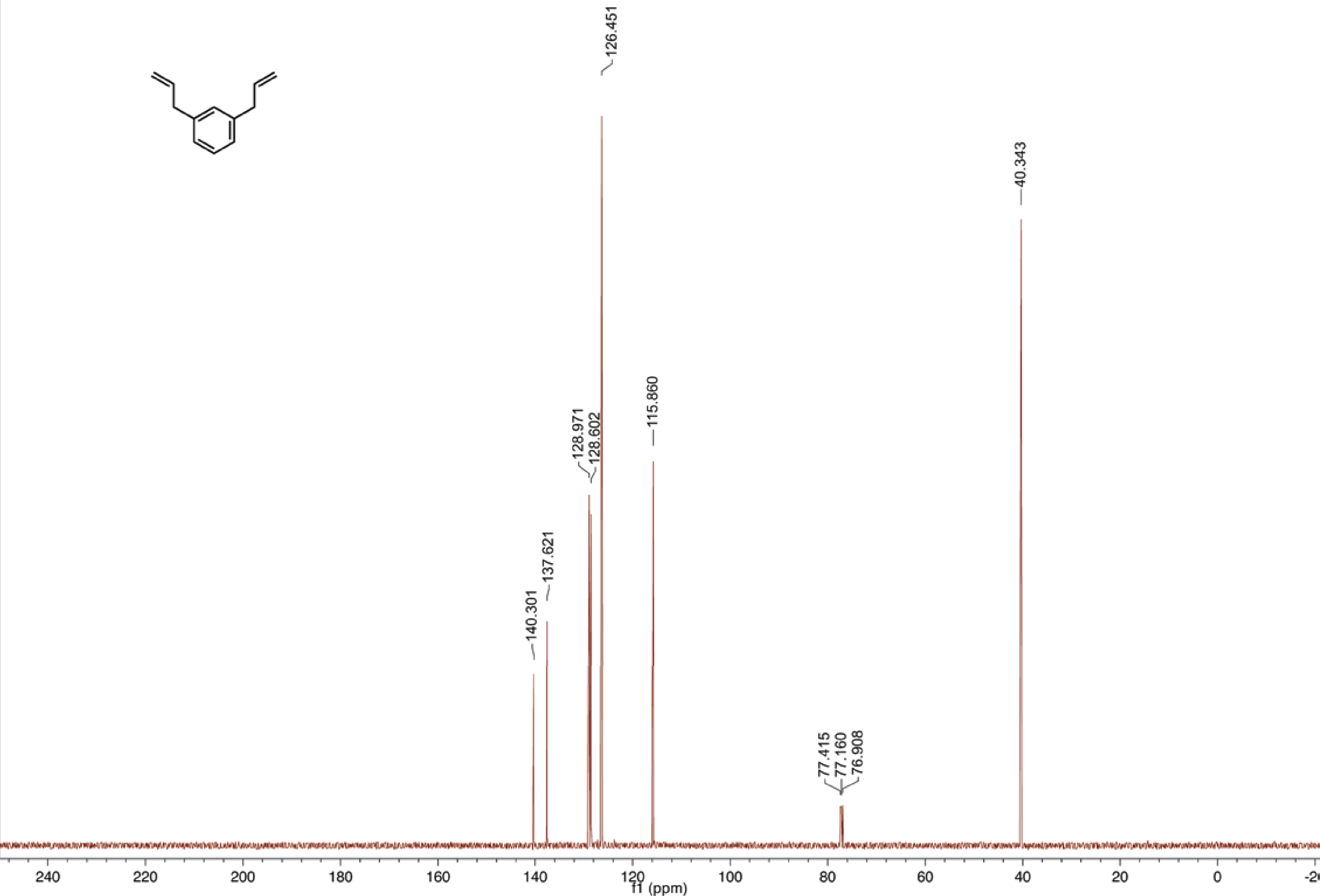
f1 (ppm)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137.621
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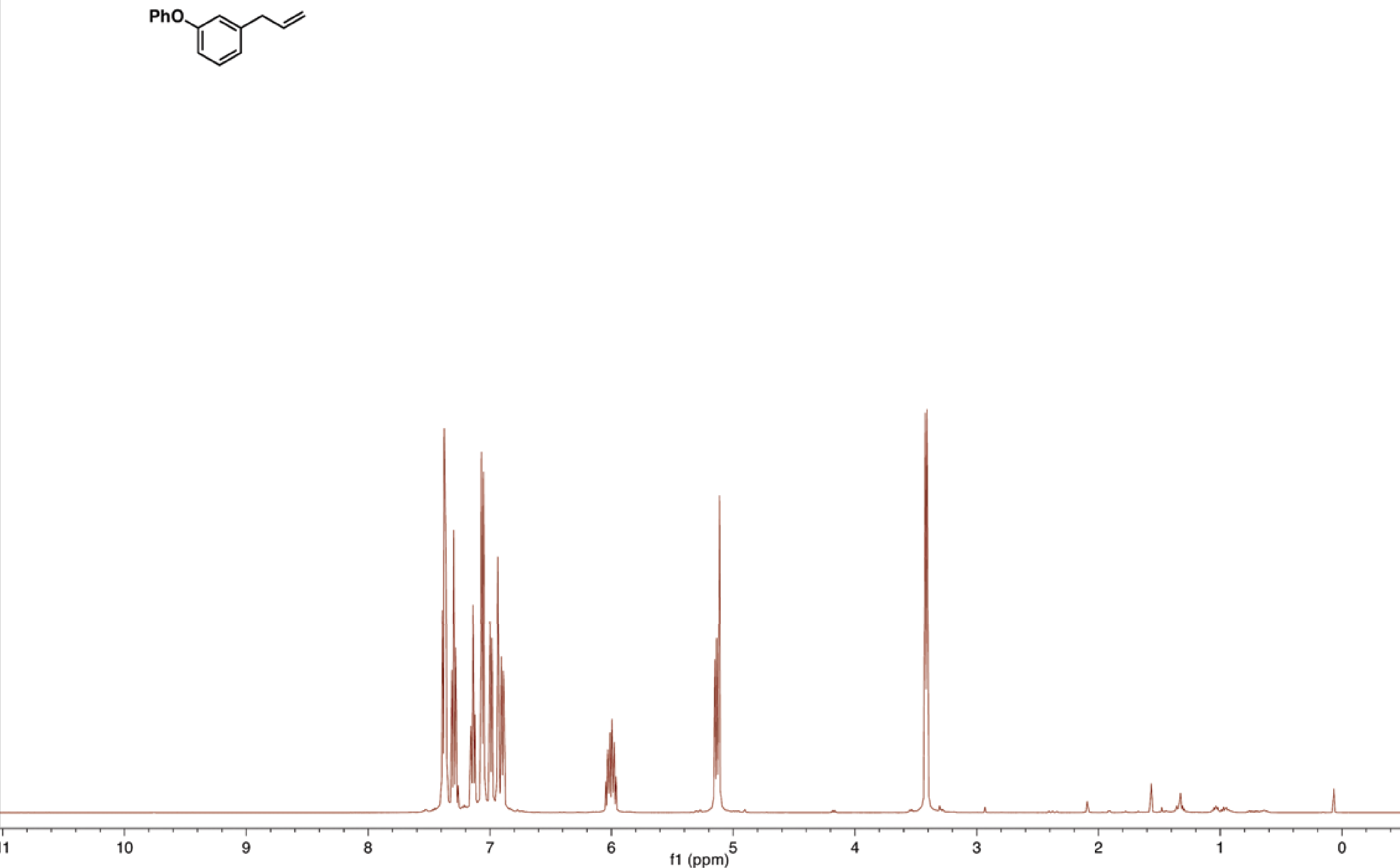
f1 (ppm)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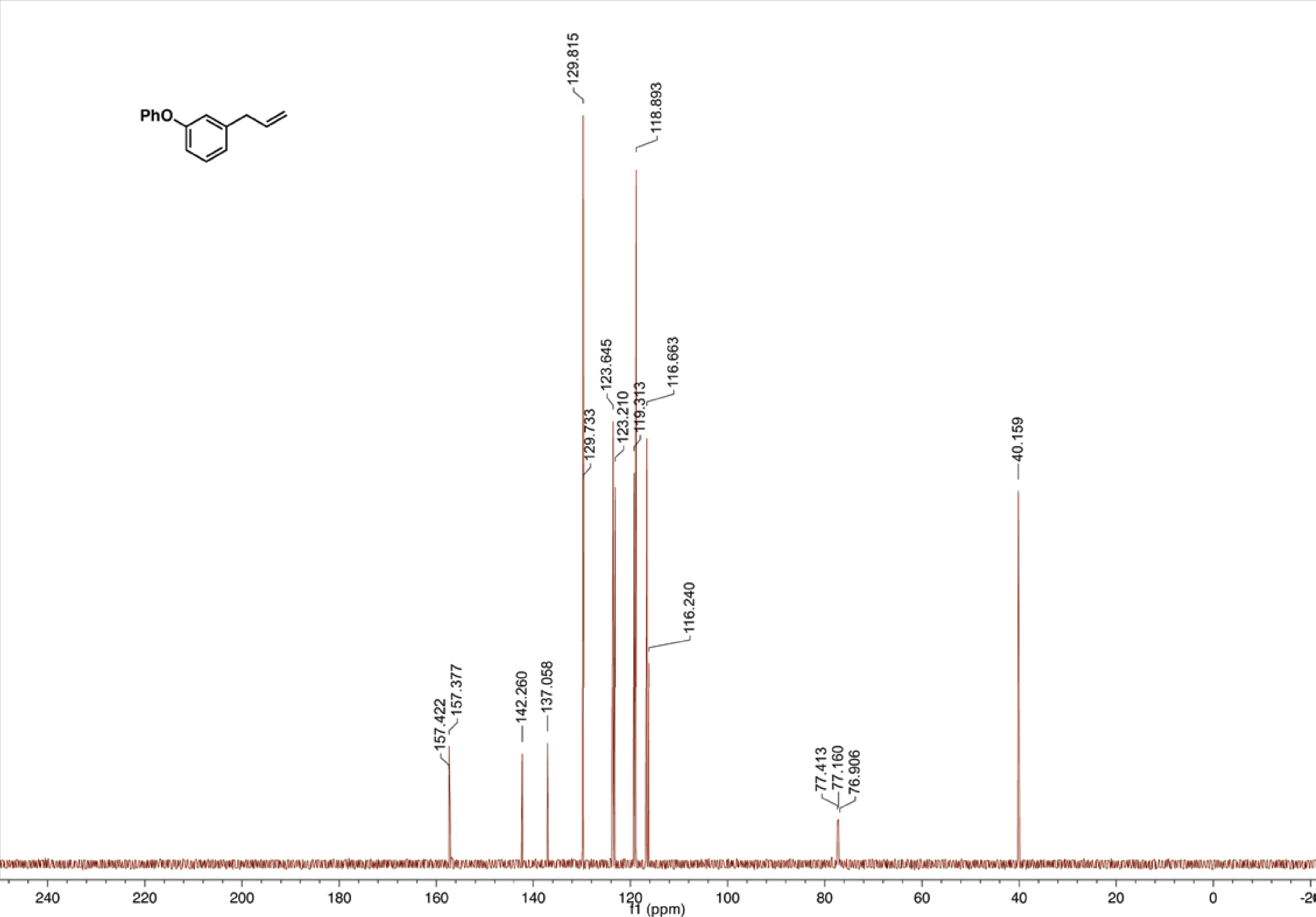
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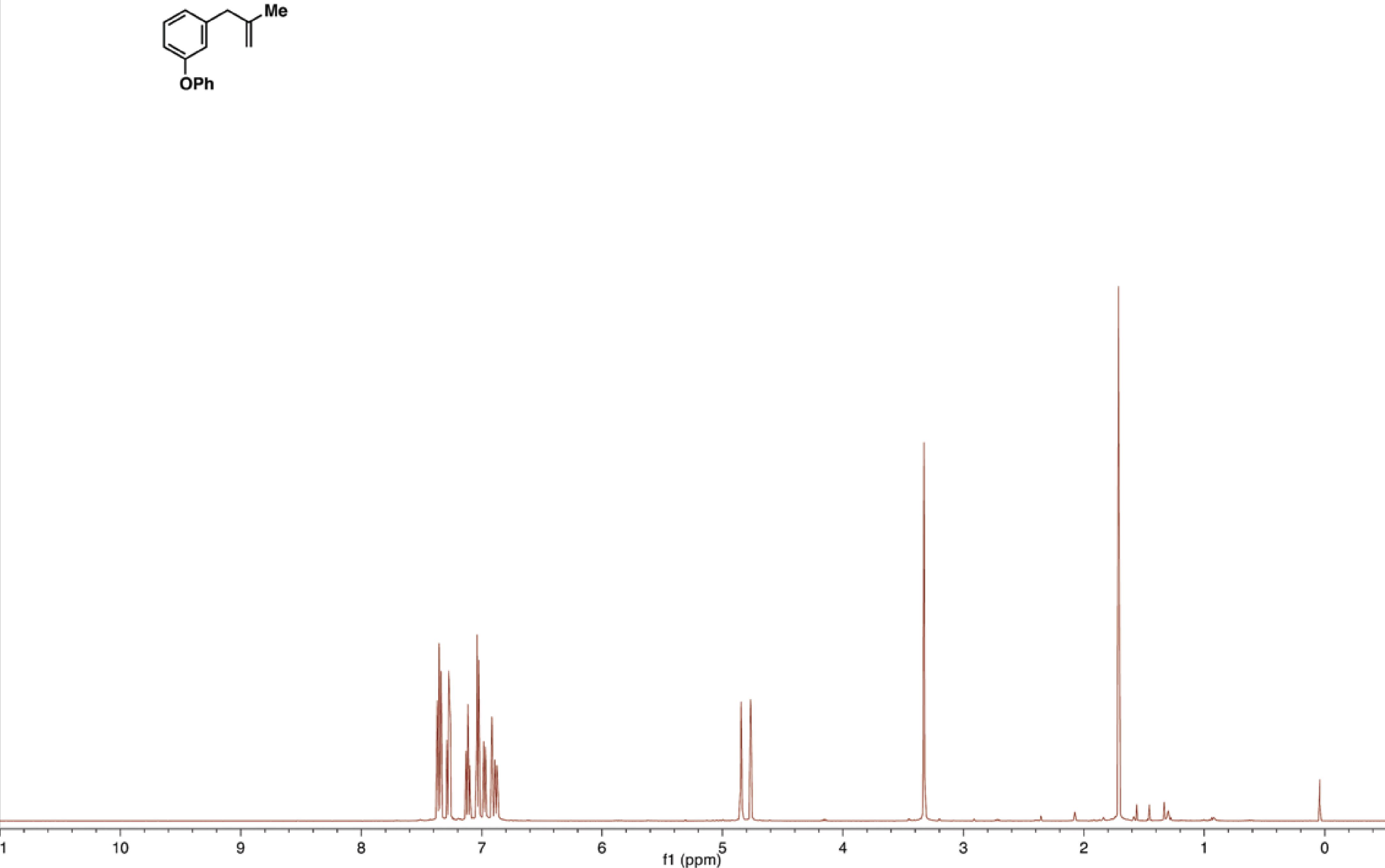
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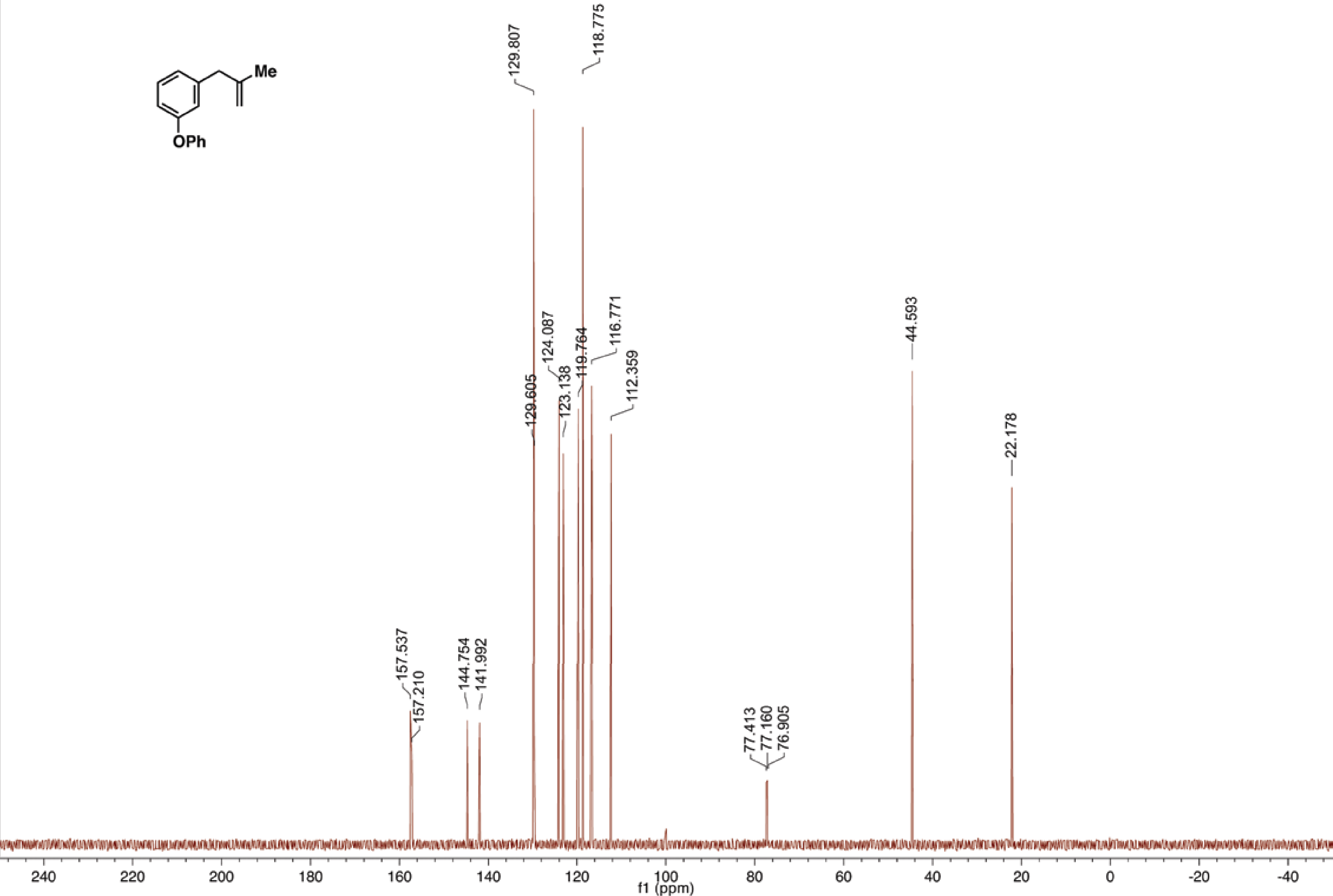
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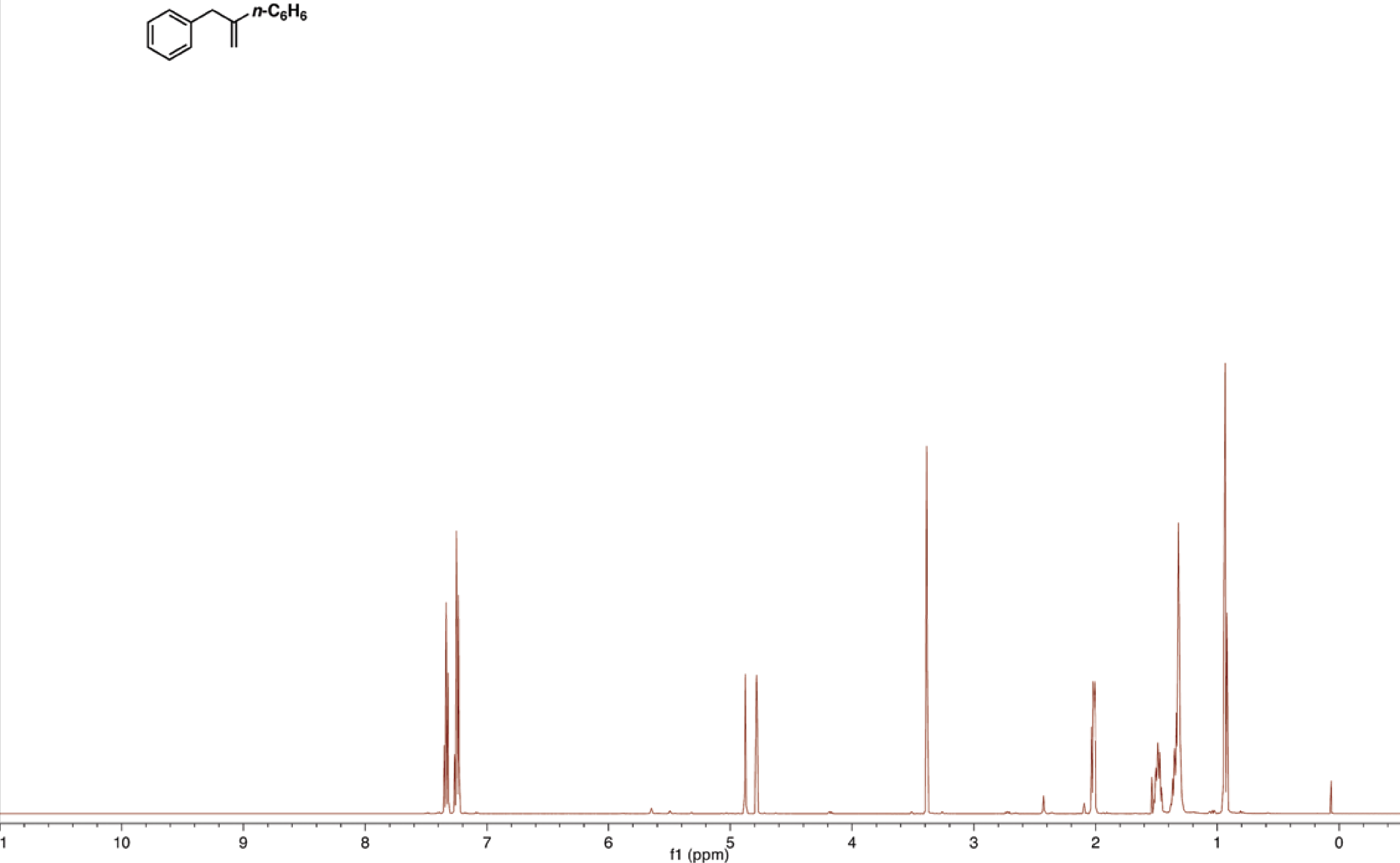
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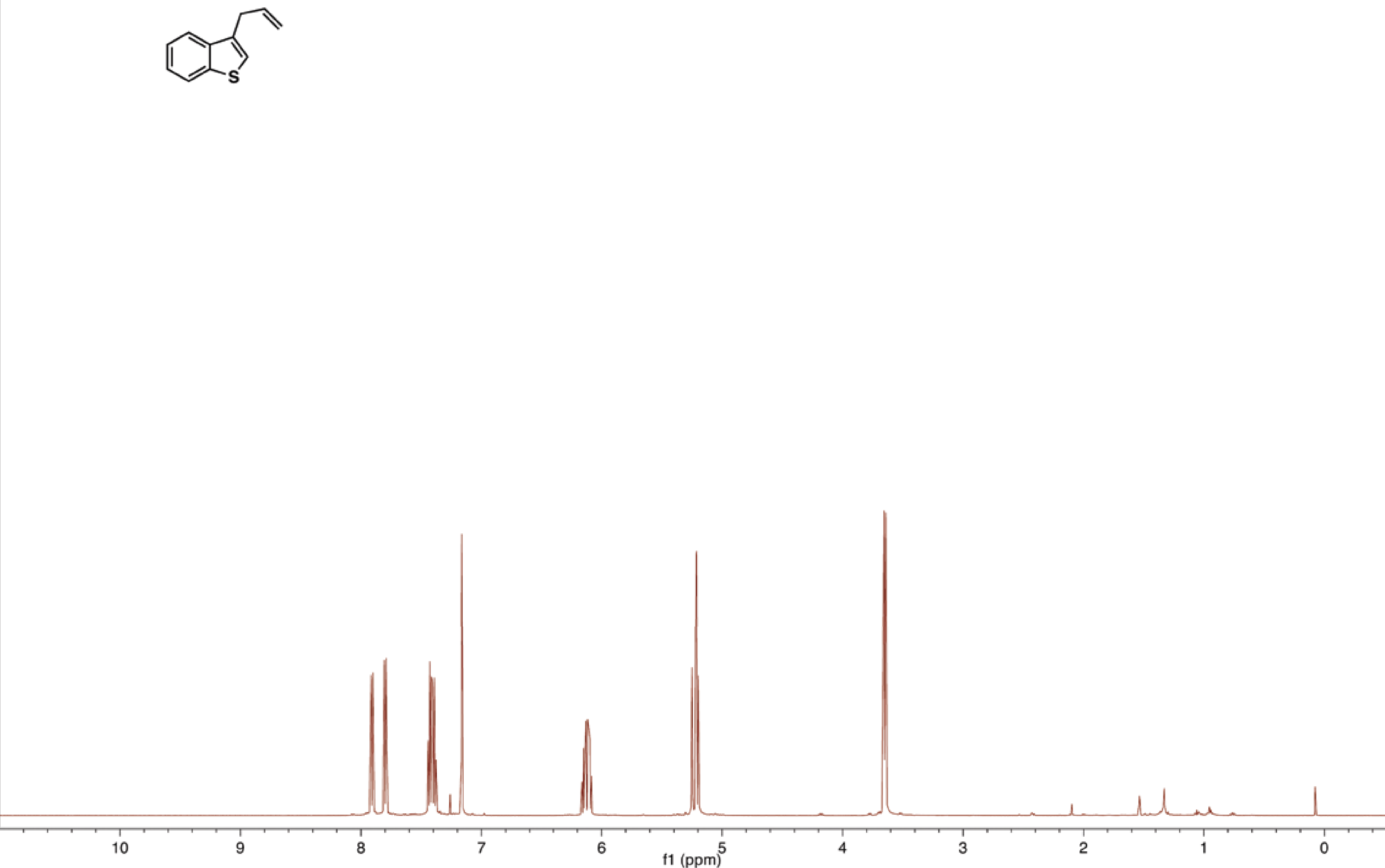
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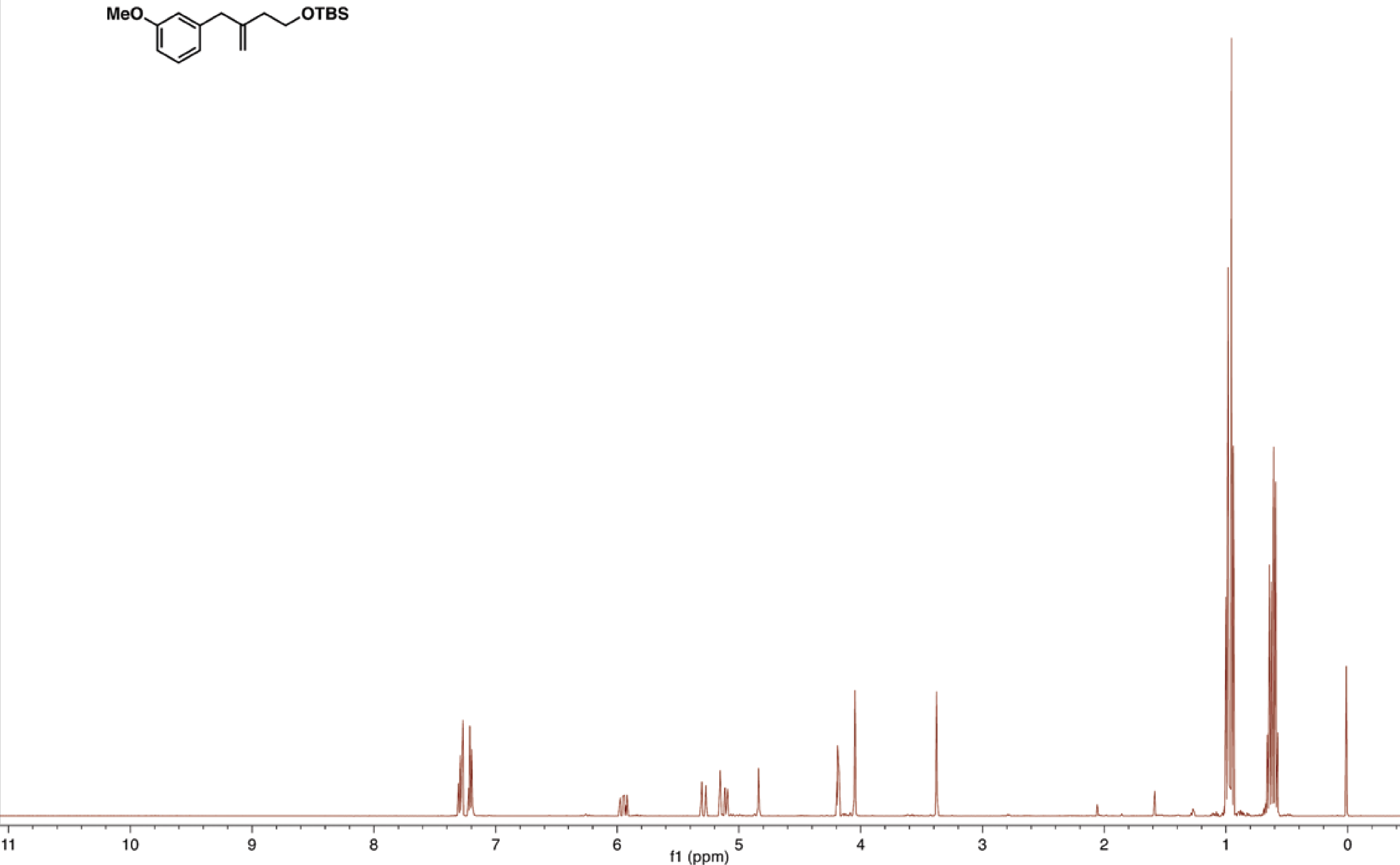

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5
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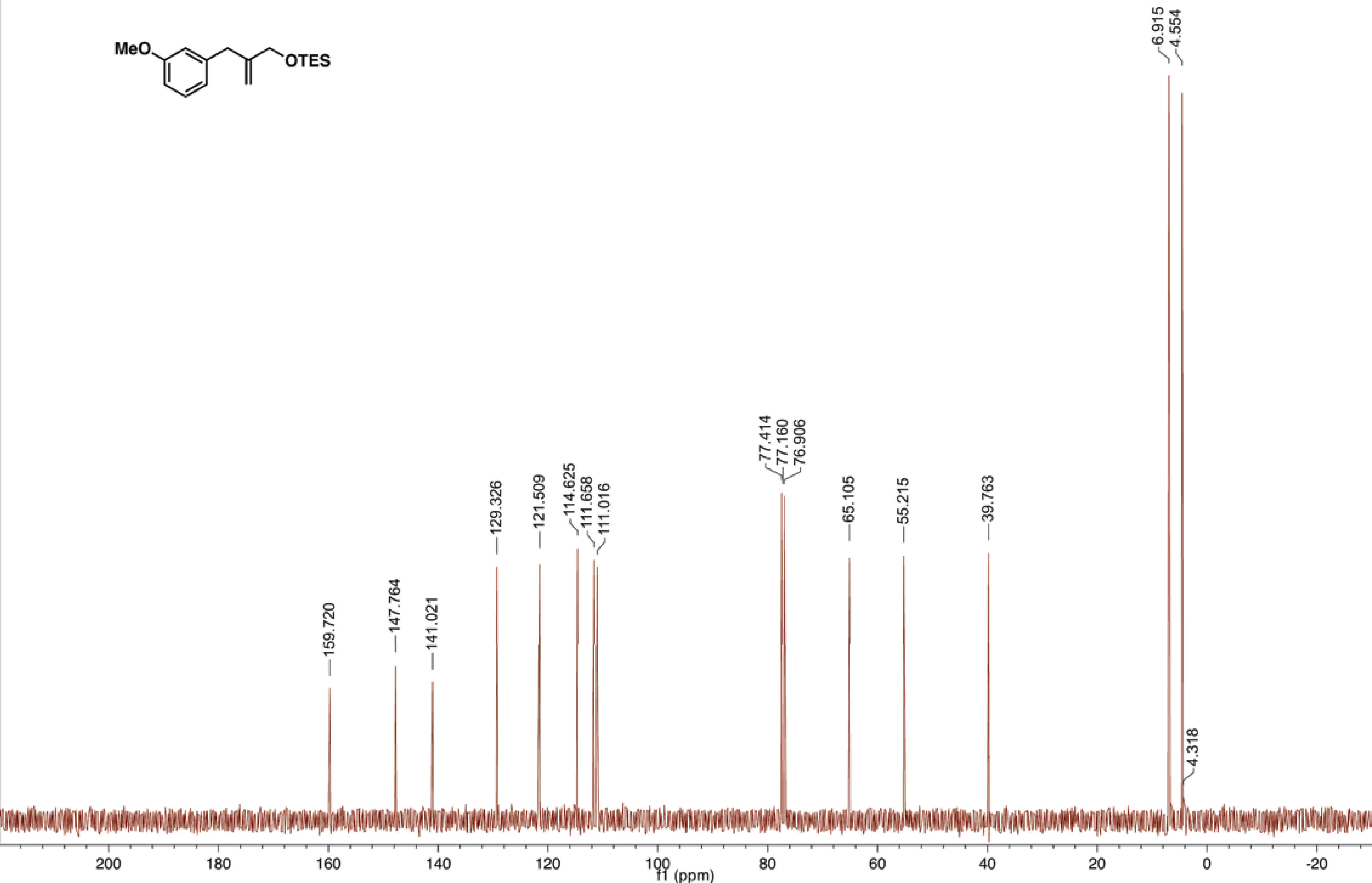
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55.215
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60
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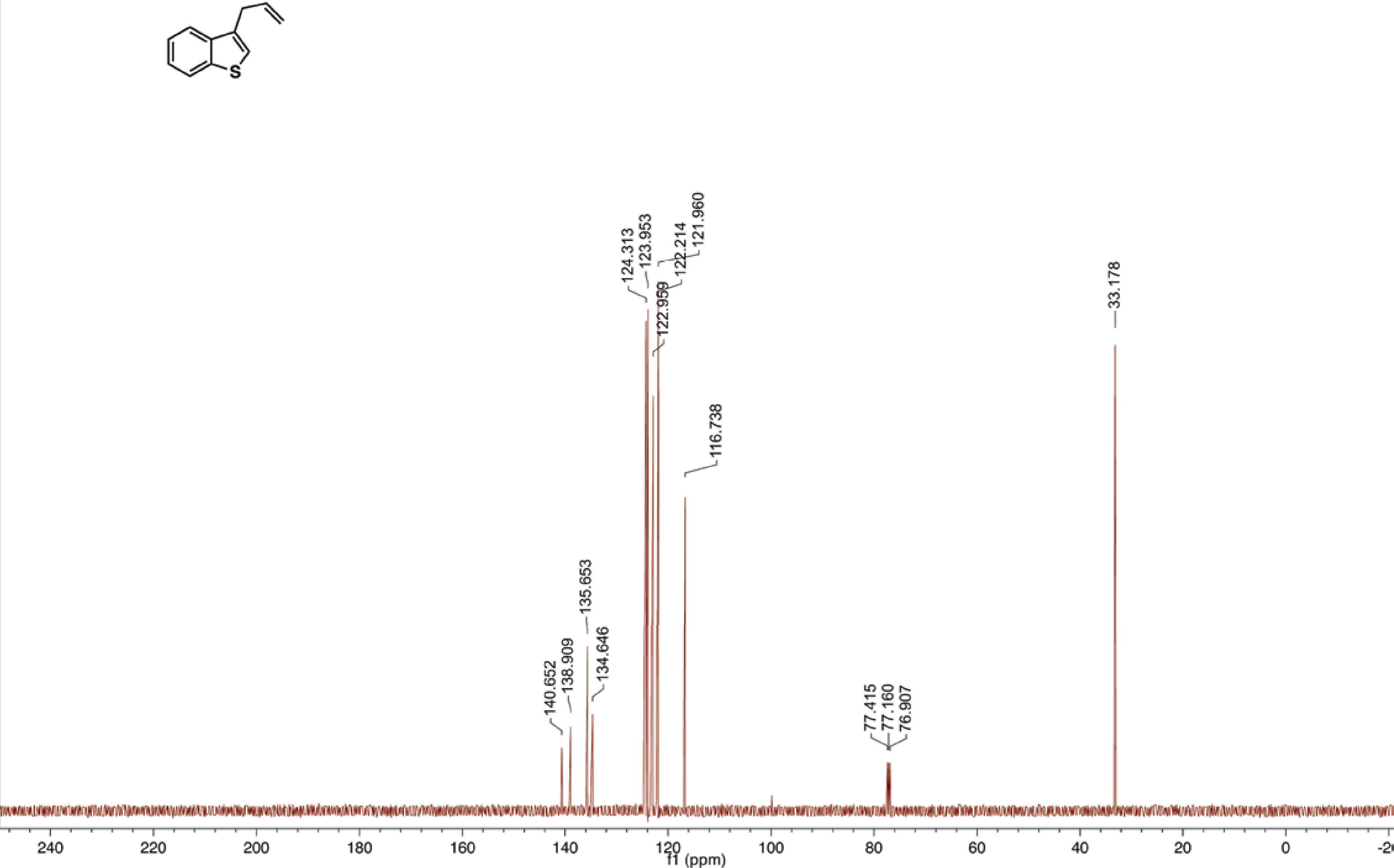
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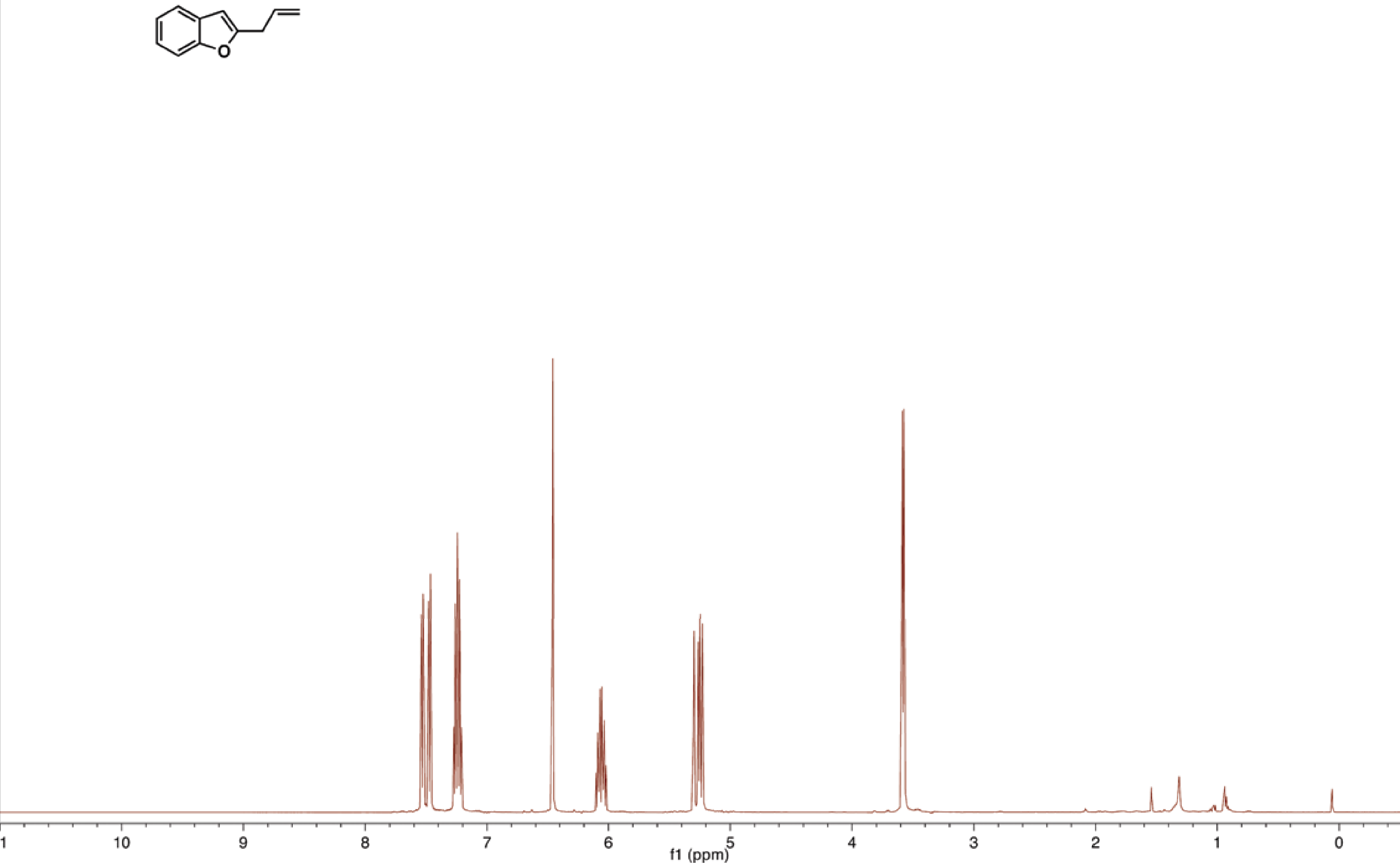
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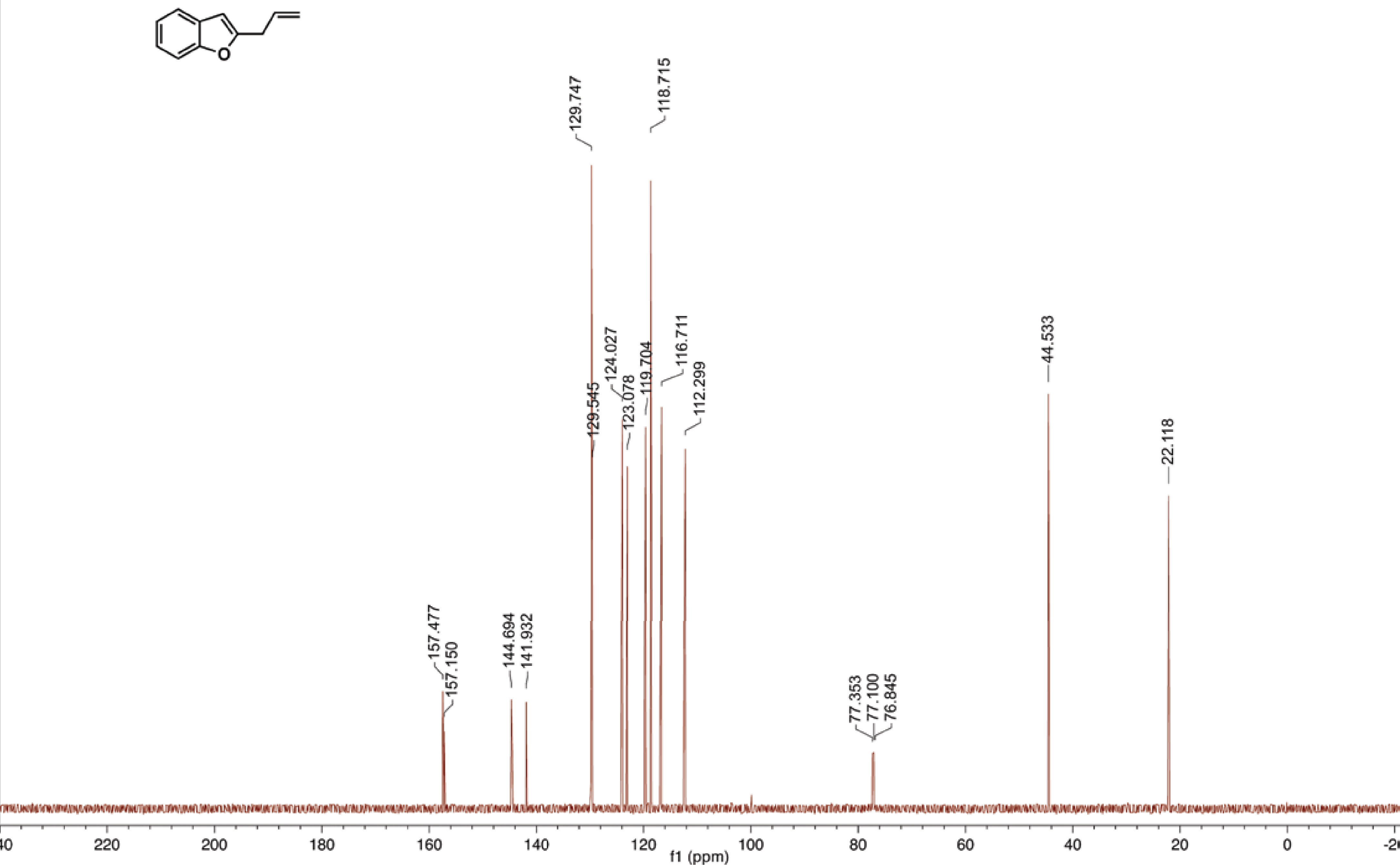
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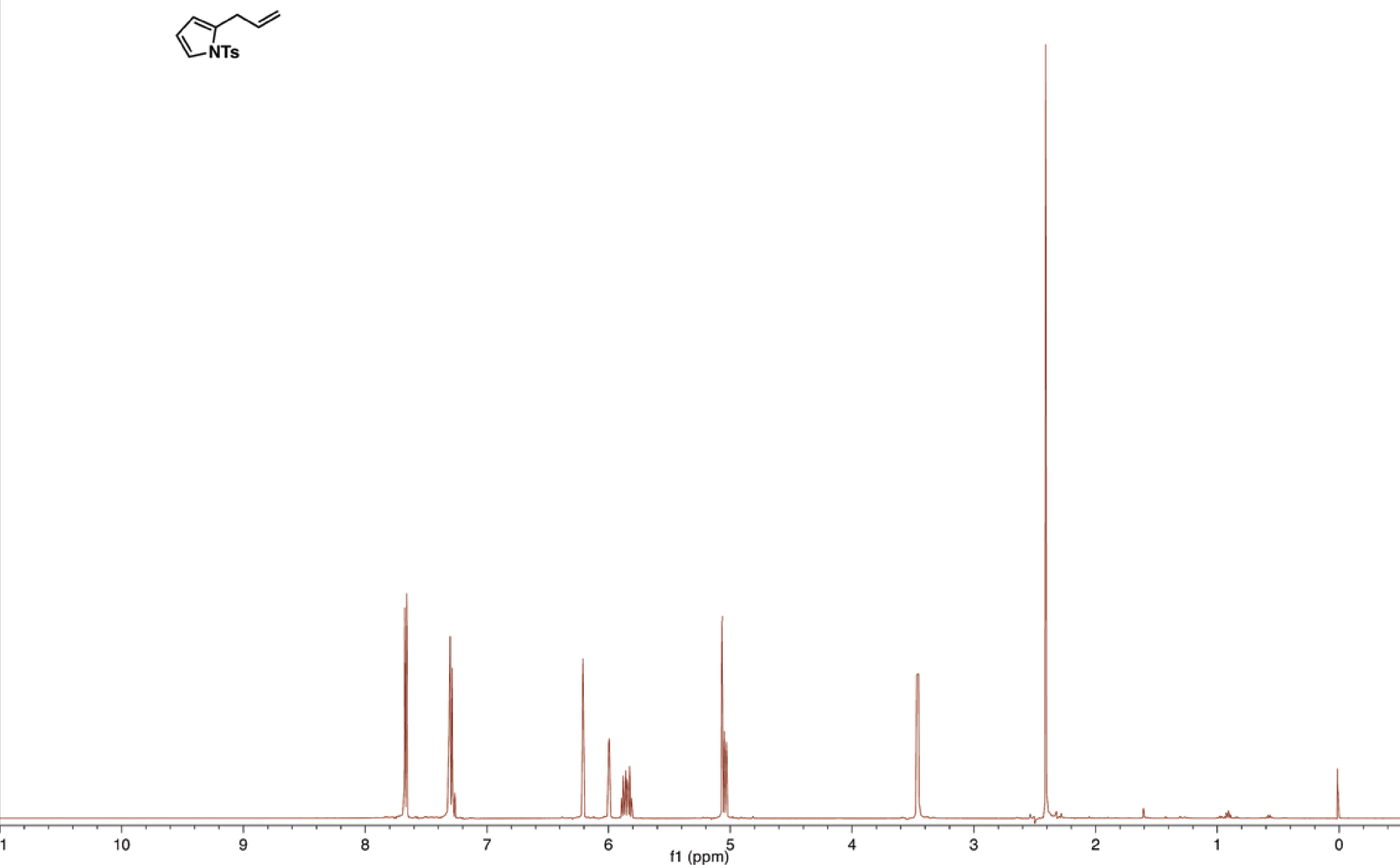
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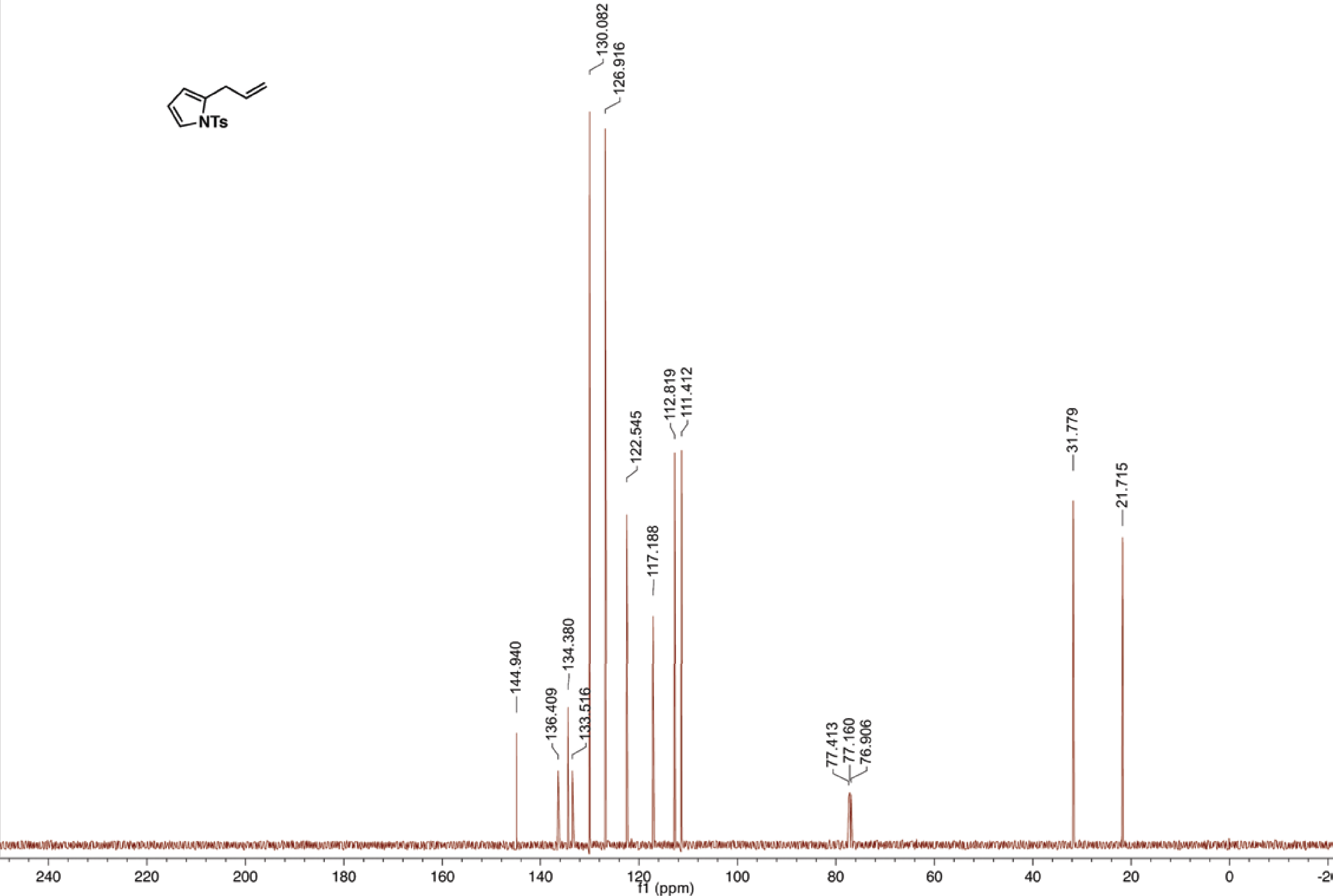
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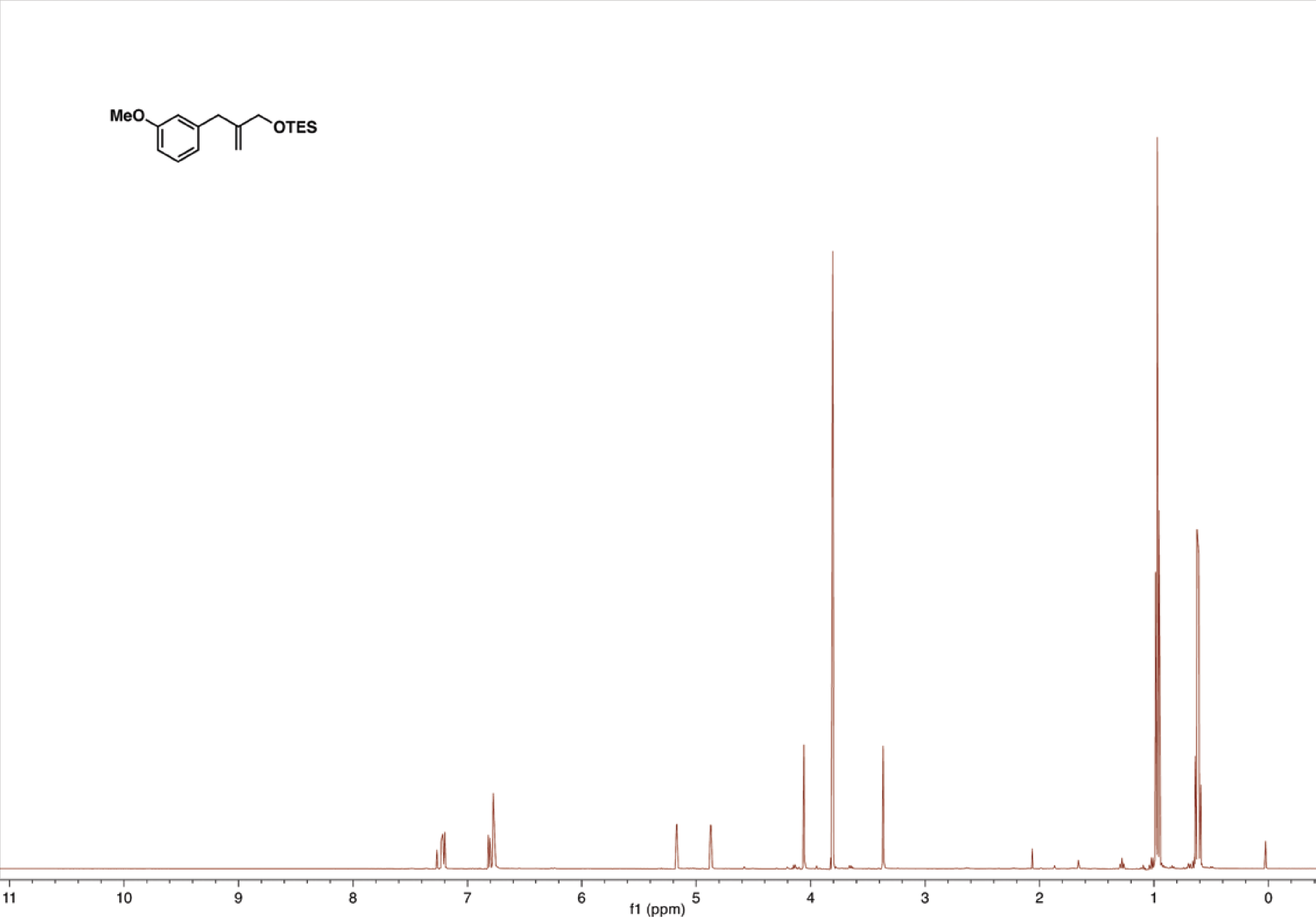
f1 (ppm)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7
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5
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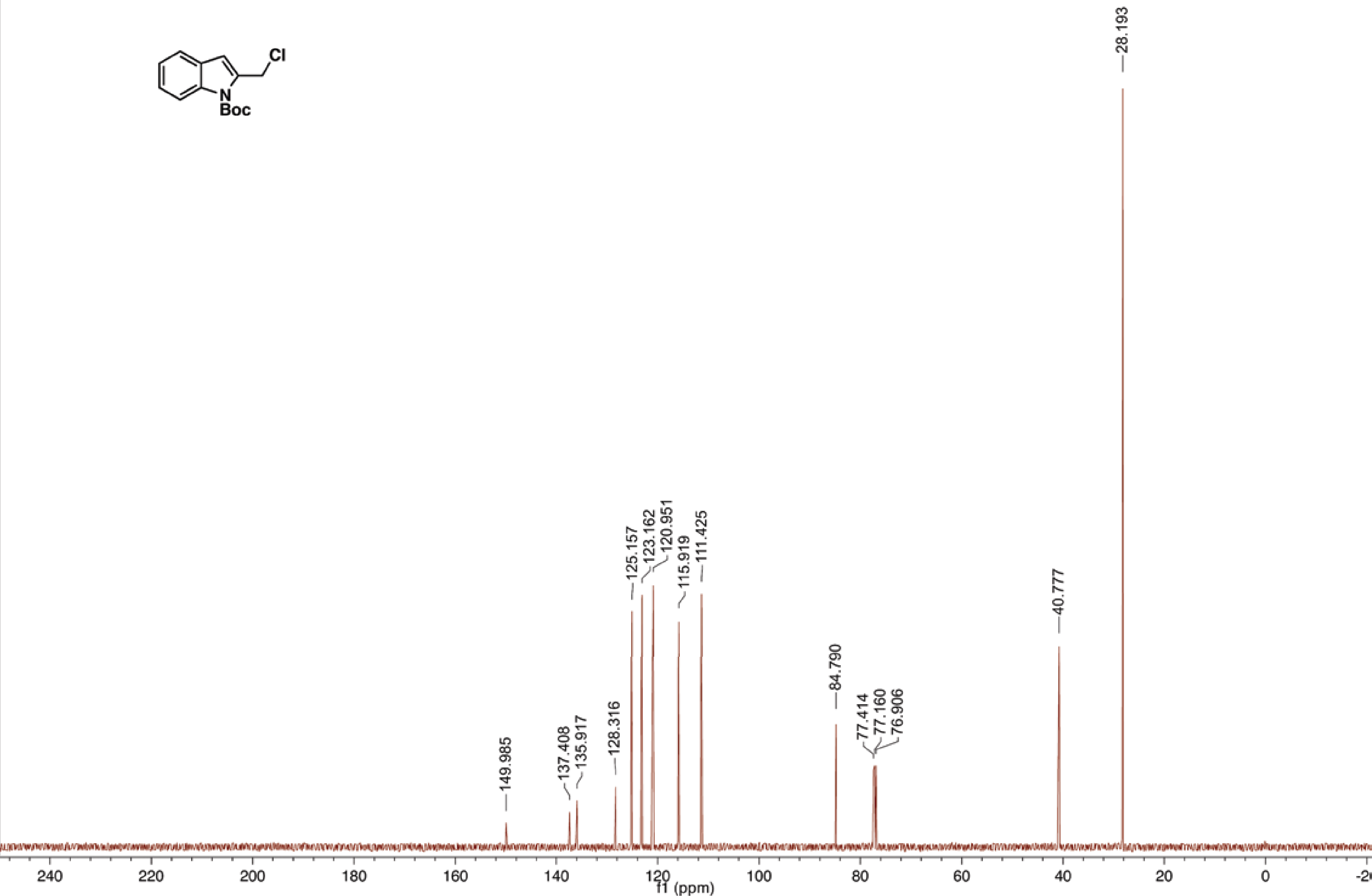
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77.414
77.160
76.906
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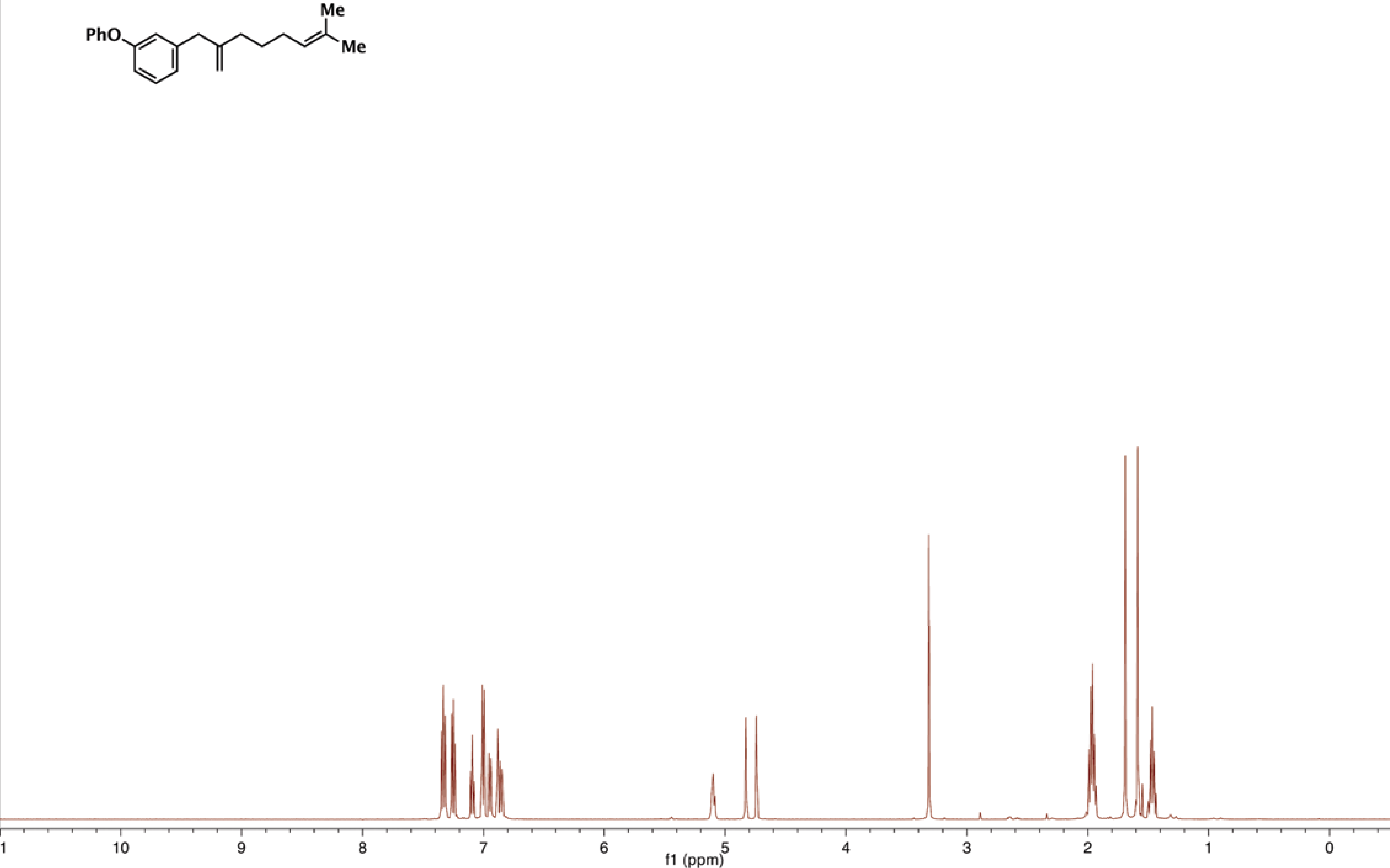
f1 (ppm)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Me
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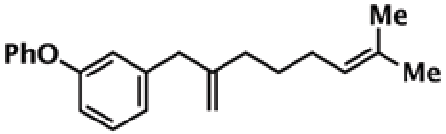
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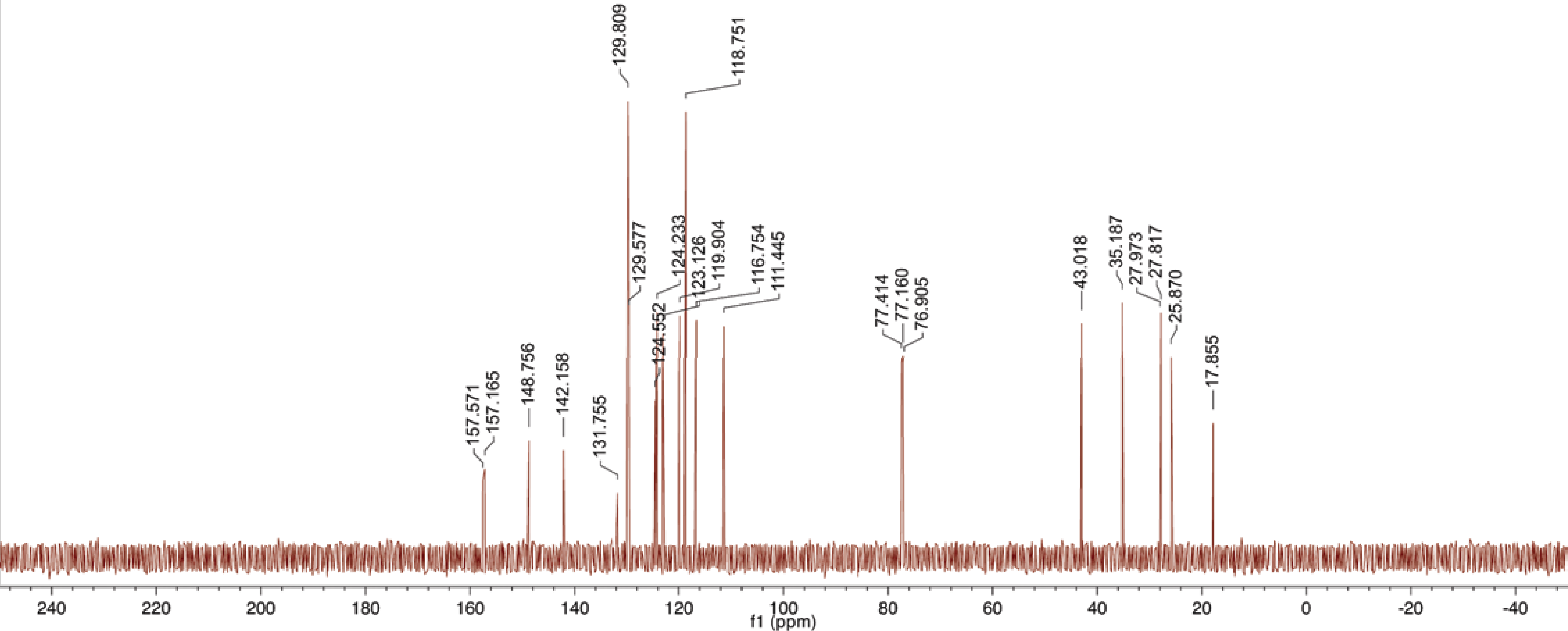
Me
Me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123.126
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116.754
111.445
77.414
77.160
76.905
43.018
35.187
27.973
27.817
25.870
17.855
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220
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180
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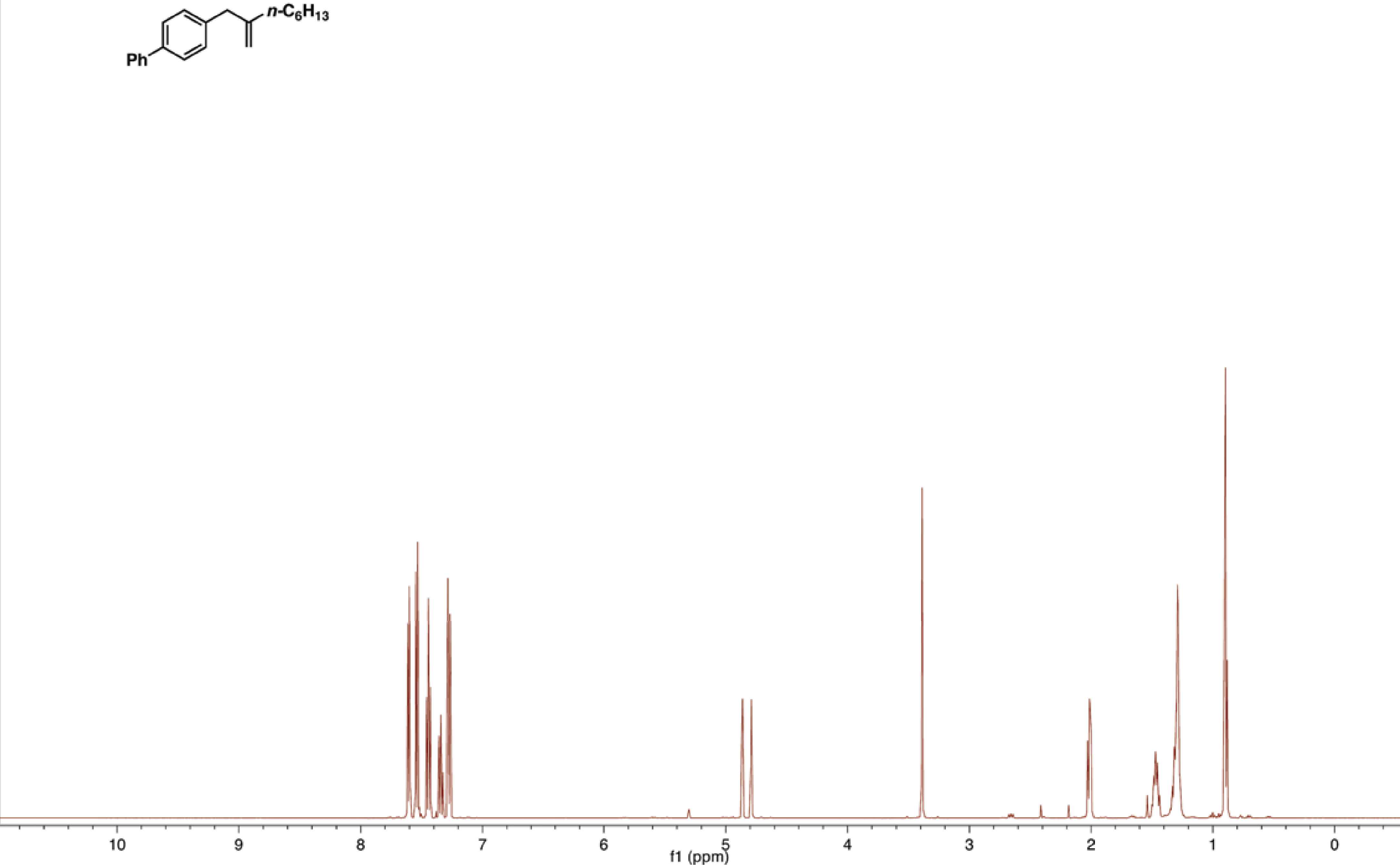
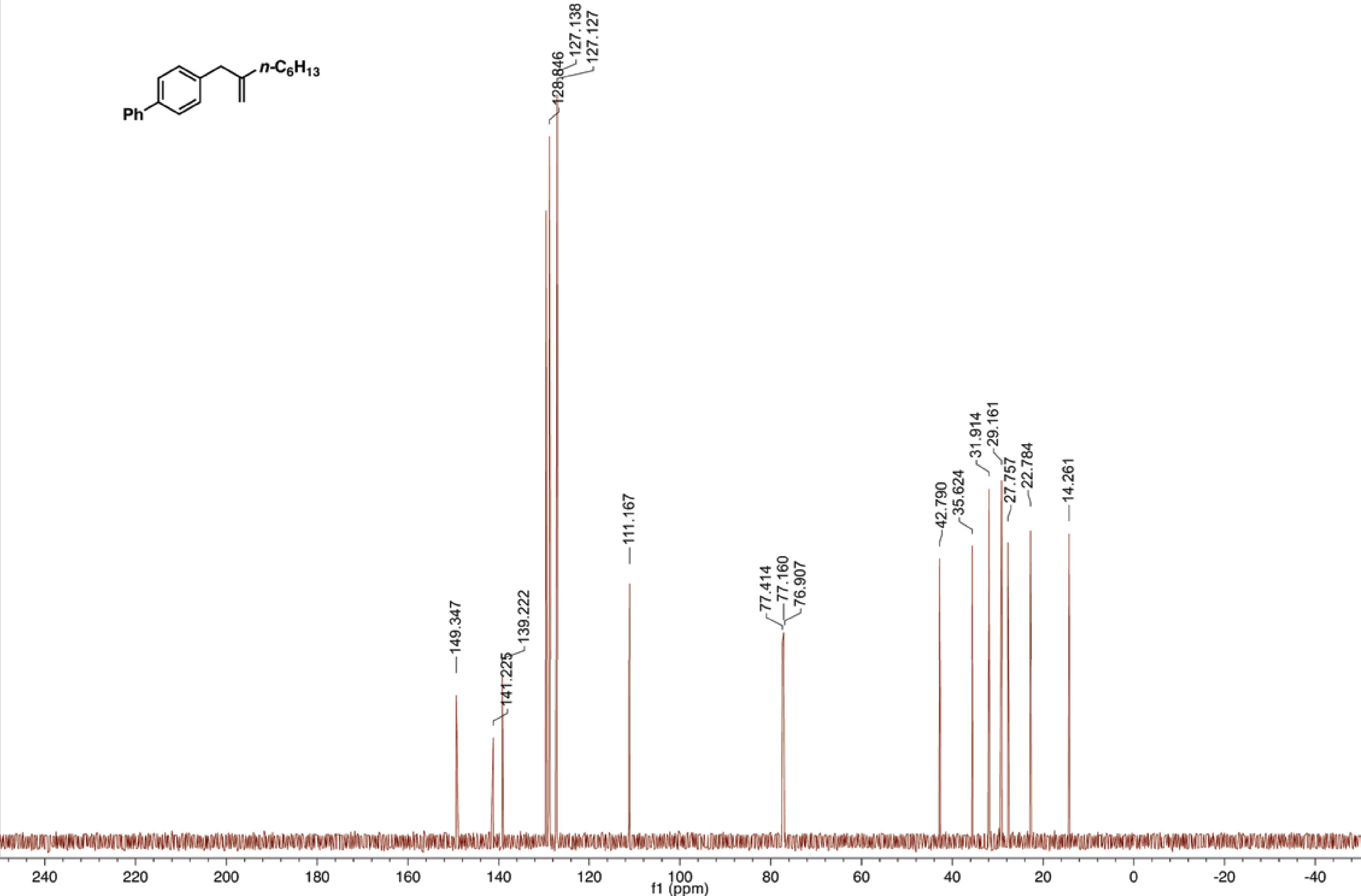
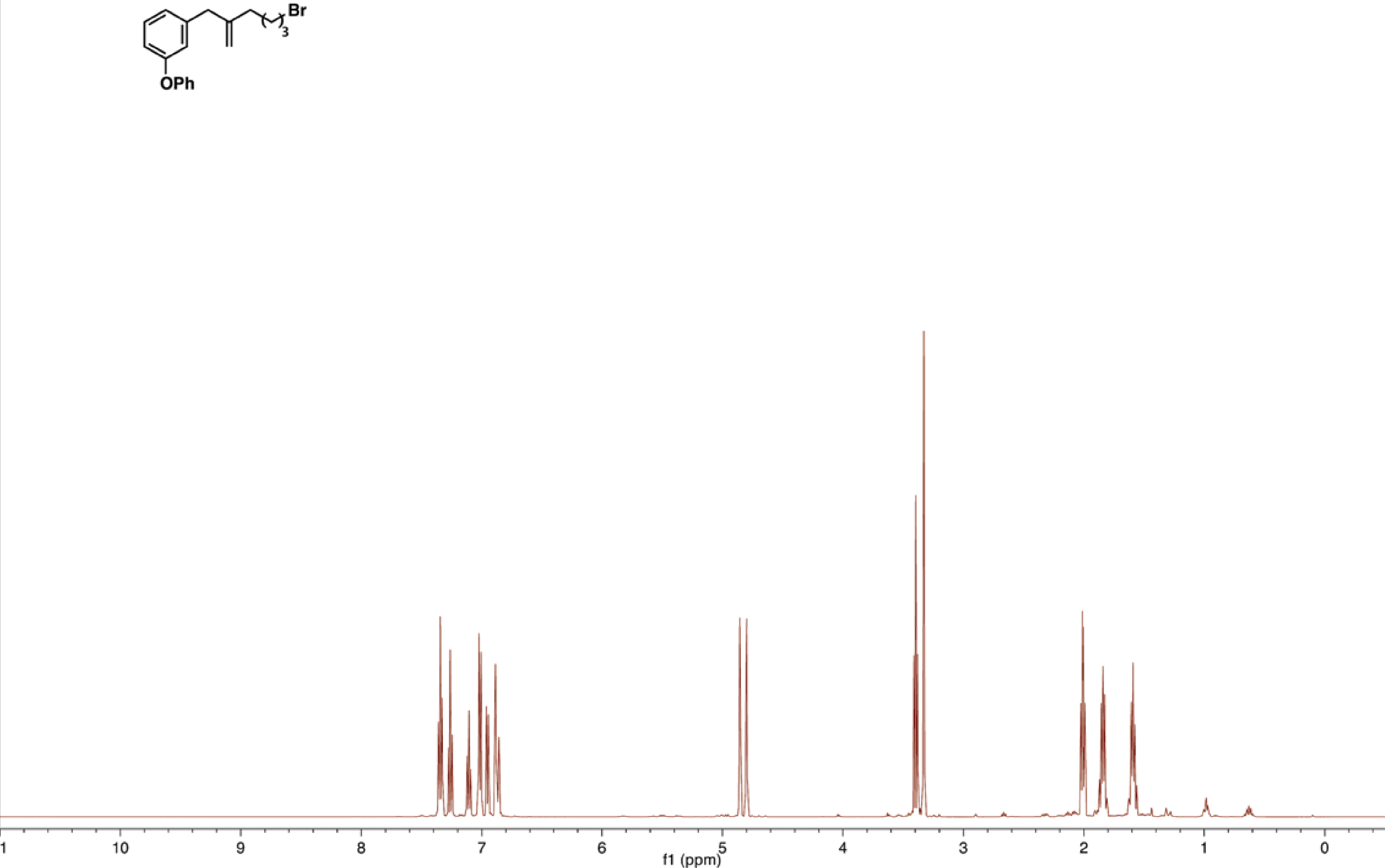
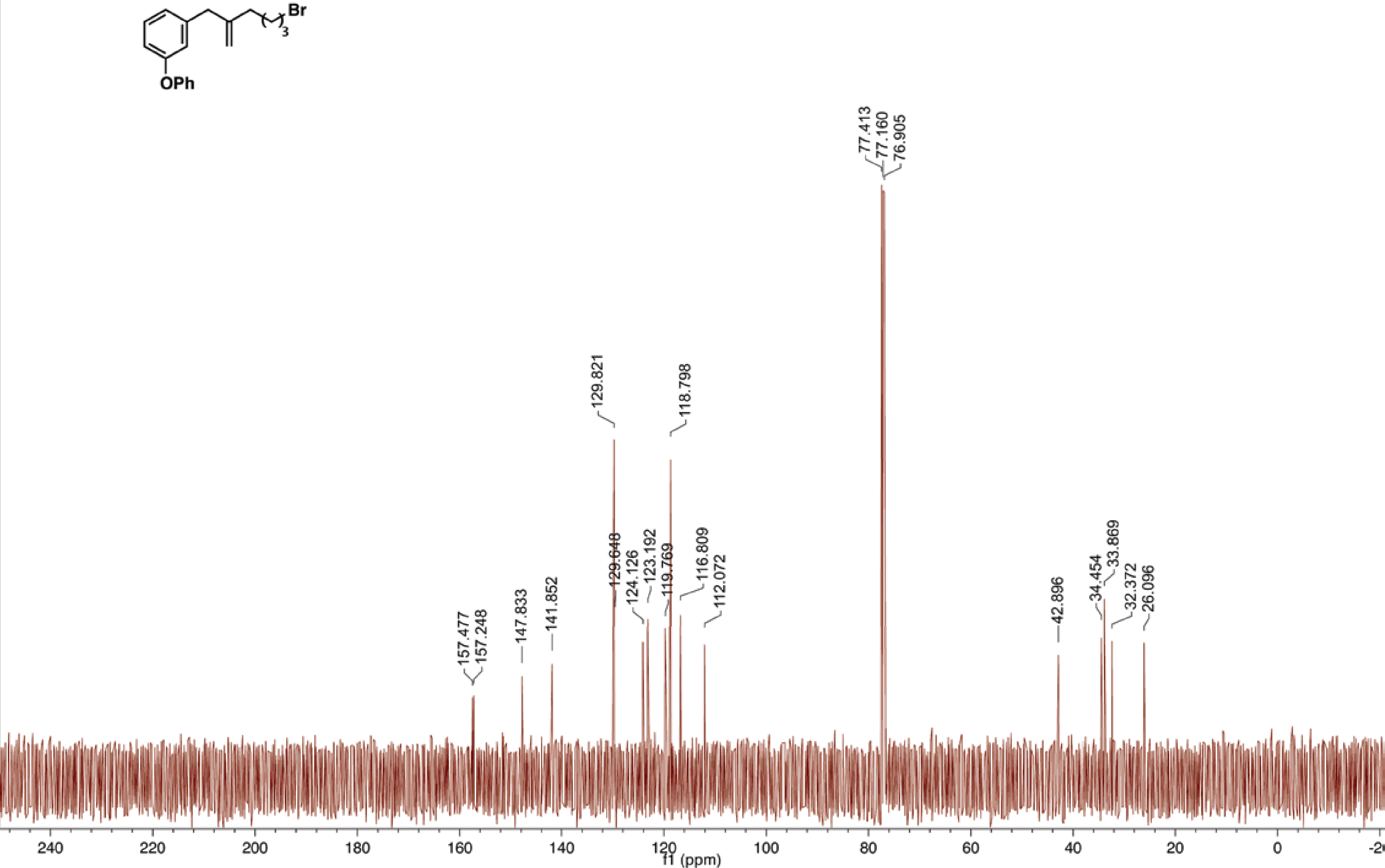
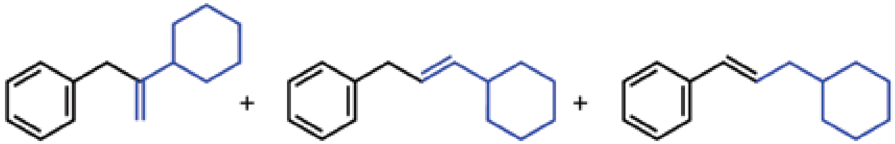
140
120
100
80
60
40
20
0
-20
-40
f1 (ppm)

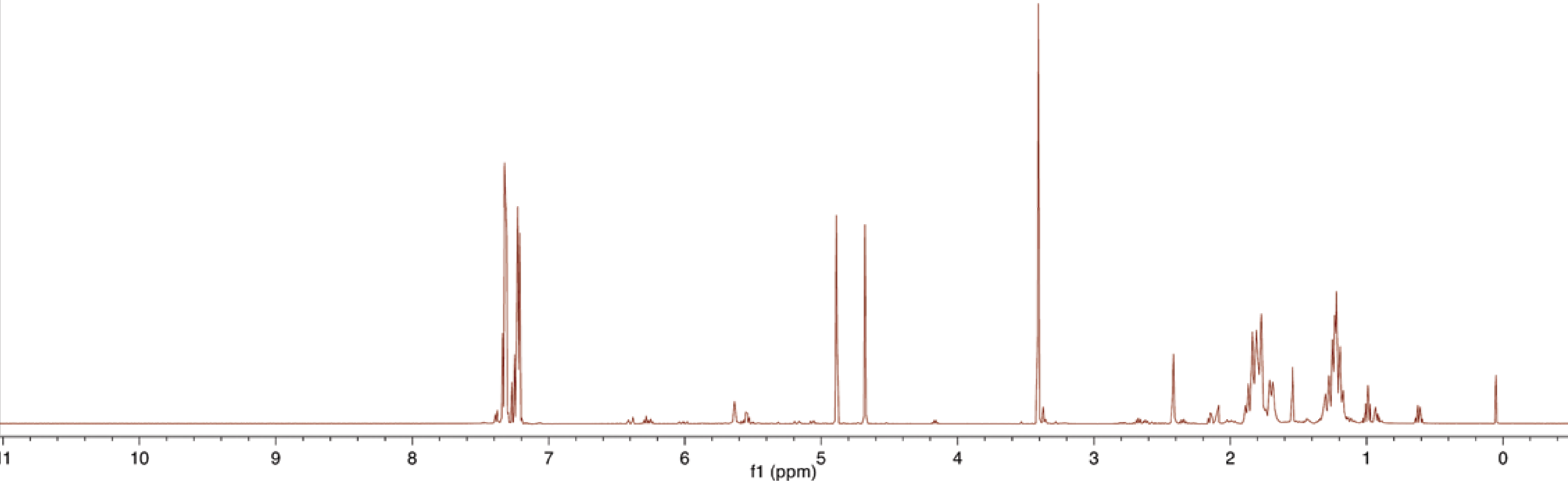

Ph
n-C6H13
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

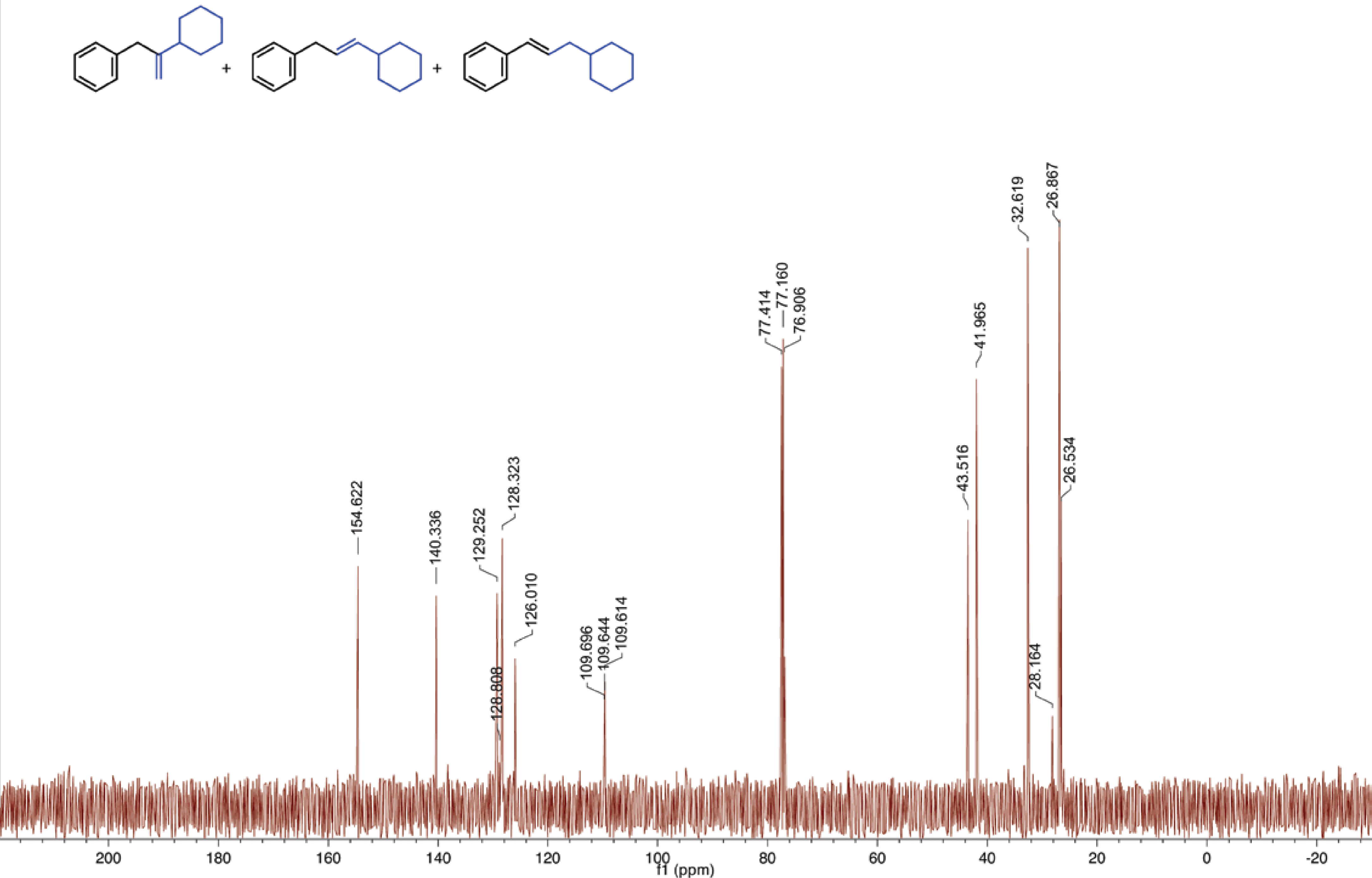

Ph
n-C6H13
149.347
141.225
139.222
128.846
127.138
127.127
111.167
77.414
77.160
76.907
42.790
35.624
31.914
29.161
27.757
22.784
14.261
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
f1 (ppm)


Br
3
OPh
1
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


Br
3
OPh
77.413
77.160
76.905
129.821
118.798
157.477
157.248
147.833
141.852
129.648
124.126
123.192
119.769
116.809
112.072
42.896
34.454
33.869
32.372
26.096
240
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


+
+


11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


+
+
154.622
140.336
129.252
128.808
128.323
126.010
109.696
109.644
109.614
77.414
77.160
76.906
43.516
41.965
32.619
28.164
26.867
26.534
200
180
160
140
120
100
80
60
40
20
0
-20
f1 (ppm)