Stille Reactions Catalytic in Tin: A Sn-F Route for Intermolecular and Intramolecular Couplings

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Supporting Information

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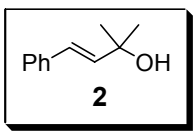
Materials and Methods

All air or moisture sensitive reactions were carried out in oven- or flame-dried glassware under a nitrogen atmosphere unless otherwise noted. All commercial reagents were used without purification. All solvents were reagent grade. Diethyl ether and THF were freshly distilled from sodium/benzophenone under nitrogen. Except as otherwise noted, all reactions were magnetically stirred and monitored by thin-layer chromatography with 0.25-mm precoated silica gel plates or capillary GC with a fused silica column. Flash chromatography was performed with silica gel 60 Å (particle size 230-400 mesh ASTM). Yields refer to chromatographically and spectroscopically pure compounds unless otherwise stated. The reported melting points are uncorrected. Chemical shifts for ^1H NMR and ^{13}C NMR are reported in parts per million (ppm) relative to $CDCl_3$ (δ = 7.24 ppm for ^1H NMR or δ = 77.0 ppm for ^{13}C NMR). GC/MS were performed with a fused silica column (30 m by 0.25 mm i.d.).



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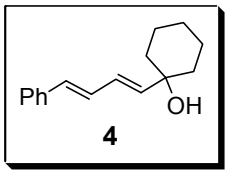
Initial Tin Catalyzed Stille Reaction with Bu_3SnH: The "Sn-F" Approach. Procedure for the preparation of (*E*)-2-methyl-4-phenylbut-3-en-2-ol (2) (Scheme 2). Tri-2-furylphosphine (2.3 mg, 0.01 mmol) was added to a solution of Pd_2dba_3 (3.7 mg, 0.004 mmol) in THF (5 mL). After stirring at room temperature for 15 min, 2-methyl-3-

butyn-2-ol (0.1 mL, 1 mmol), iodobenzene (0.17 mL, 1.5 mmol), Bu_3SnCl (16 μL, 0.06 mmol), PMHS (0.09 mL, 1.5 mmol) and aq. KF (0.1743 g, 3 mmol; 1 mL H_2O) were added to the solution. The solution was allowed to reflux for 48 h. The organics were separated, washed with brine, dried ($MgSO_4$) and concentrated. The resulting residue was purified by flash chromatography [silica gel; 90/10 pentane/ EtOAc] to afford (*E*)-2-methyl-4-phenylbut-3-en-2-ol (**2**) (34 mg, 21%)[1] as a clear oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.42 (s, 6 H), 1.69 (br s, 1 H), 6.35 (d, *J* = 15.9 Hz, 1 H), 6.58 (d, *J* = 15.9 Hz, 1 H), 7.18-7.43 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.0, 66.2, 121.5, 121.6, 122.6, 123.7, 132.1, 132.7.



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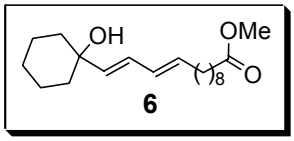
Representative procedure for the tin loading experiments. Preparation of 1-((1*E*,3*E*)-4-phenylbuta-1,3-dienyl)cyclohexanol (4), use of 4 mol % Me_3SnCl (Scheme 3). Following the general procedure below using Me_3SnCl (0.04 mL of a 1 M solution in THF, 0.04 mmol), 1-ethynyl-cyclohexanol (**3**) (124 mg, 1 mmol) and *E*-β-bromostyrene (275 mg, 1.5 mmol) after column chromatography [silica gel; 90:10 hexane/EtOAc] 1-(4-phenyl-buta-1,3-dienyl)-cyclohexanol (**4**) (144 mg, 63%) as an oil. IR ($CHCl_3$) 3594, 2938, 2859, 2402, 1703, 1597, 1491, 1451, 1350, 1125, 992, 909 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.21-1.77 (m, 10 H), 5.92 (d, *J* = 15.4 Hz, 1 H), 6.42 (dd, *J* = 15.4, 10.4 Hz, 1 H), 6.53 (d, *J* = 15.4 Hz, 1 H), 6.75 (dd, *J* = 15.4, 10.4 Hz, 1 H), 7.19-7.38 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.0, 25.4, 37.8, 71.6, 126.2, 127.4, 127.6, 128.5, 128.8, 132.0, 137.3, 141.7; HRMS (EI) *m/z* 228.1519 [$(M)^+$ calcd. for $C_{16}H_{20}O$ 228.1514].

Preparation of 1-((1*E*,3*E*)-4-phenylbuta-1,3-dienyl)cyclohexanol (4), use of 2 mol % Me_3SnCl (Scheme 3). Following the general procedure below using Me_3SnCl (0.02 mL of a 1 M solution in THF, 0.02 mmol), 1-ethynyl-cyclohexanol (**3**) (124 mg, 1 mmol) and *E*-β-bromostyrene (275 mg, 1.5 mmol) after column chromatography [silica gel; 90:10

hexane/EtOAc] 1-(4-phenyl-buta-1,3-dienyl)-cyclohexanol (**4**) (89 mg, 39%) as an oil. For spectroscopic data see above.

Preparation of 1-((1*E*,3*E*)-4-phenylbuta-1,3-dienyl)cyclohexanol (4), use of 1 mol % Me_3SnCl (Scheme 3). Following the general procedure below using Me_3SnCl (0.01 mL of a 1 M solution in THF, 0.01 mmol), 1-ethynyl-cyclohexanol (**3**) (124 mg, 1 mmol) and *E*-β-bromostyrene (275 mg, 1.5 mmol) after column chromatography [silica gel; 90:10 hexane/EtOAc] 1-(4-phenyl-buta-1,3-dienyl)-cyclohexanol (**4**) (43 mg, 19%) as an oil. For spectroscopic data see above.



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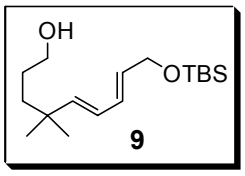
Representative procedure for the tandem one pot hydrostannation/Stille coupling with 6 mol% Me_3SnCl using the "Sn-F" route. Preparation of 13-(1-hydroxy-cyclohexyl)-trideca-10,12-dienoic acid methyl ester (6) (Table 1, entry 1). Tri-2-furylphosphine (9.3 mg, 0.04 mmol) was added to a solution of Pd_2bda_3 (9.2 mg, 0.01 mmol) in Et_2O (5 mL). After stirring at room temperature for 15 min, (*E*)-11-iodo-undec-10-enoic acid methyl ester (**5**, see below for preparation) (486.3 mg, 1.5 mmol), Me_3SnCl (0.06 mL, 0.06 mmol; 1M solution in THF), aq. KF (0.1743 g, 3 mmol; 1 mL H_2O), TBAF (0.8 μL of a 1M solution in THF, 0.008 mmol) and $PdCl_2(PPh_3)_2$ (7.0 mg, 0.01 mmol) were all added to the solution. The solution was heated to reflux and then a solution of 1-ethynyl-cyclohexanol (**3**) (124.2 mg, 1.0 mmol) and PMHS (0.09 mL, 1.5 mmol) in Et_2O (4mL) was added via a syringe pump over 11 hrs. The phases were separated and the organics washed with brine, dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash chromatography [silica gel; 90:10 hexane/EtOAc] 13-(1-hydroxy-cyclohexyl)-trideca-10,12-dienoic acid methyl ester (**6**) (235 mg, 73%) as an oil. IR(neat) 3356, 1774 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.21-1.38 (m, 11 H), 1.42-1.68 (m, 12 H), 2.03 (q, J = 7.51 Hz, 2 H), 2.26 (t, J =

7.29 Hz, 2 H), 3.70 (s, 3 H), 5.65 (m, 2 H), 5.99 (dd, J = 10.38, 15.02 Hz, 1 H); 6.19 (dd, J = 10.38, 15.46 Hz, 1 H); ^{13}C (75 MHz, $CDCl_3$) δ 22.1, 24.9, 25.5, 29.1, 29.1, 29.2, 29.2, 29.2, 32.5, 34.0, 37.9, 51.4, 71.3, 127.6, 129.8, 134.8, 138.6, 174.3; HRMS (EI) *m/z* 322.2511[(M^+) calcd. for $C_{20}H_{34}O_3$ 322.2508].



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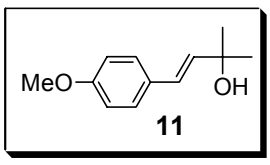
Preparation of 9-(*tert*-butyl-dimethyl-silanyloxy)-4,4-dimethyl-nona-5,7-dien-1-ol (9) (Table 1, entry 2). Applying the above conditions to 4,4-dimethyl-hex-5-yn-1-ol (**32**) (0.1262 g, 1 mmol) and (*E*)-(3-iodo-allyloxy)-*tert*-butyl-dimethyl-silane (**8**) (0.4470 g, 1.5 mmol) afforded after column chromatography [silica gel; 80:20 hexane/EtOAc] 9-(*tert*-butyl-dimethyl-silanyloxy)-4,4-dimethyl-nona-5,7-dien-1-ol (**9**) (63 mg, 43%) as an oil. IR (neat) 3348 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.06 (s, 6 H), 0.90 (s, 9 H), 1.00 (s, 6 H), 1.30-1.35 (m, 2 H), 1.43-1.52 (m, 2 H), 1.55 (br s, 1 H), 3.57 (t, J = 6.52 Hz, 2 H), 4.18 (dd, J = 1.44, 5.30 Hz, 2 H), 5.59 (d, J = 15.02 Hz, 1 H), 5.65 (dt, J = 5.30, 15.24 Hz, 1 H), 5.94 (dd, J = 10.38, 15.57 Hz, 1 H), 6.17 (dd, J = 10.38, 15.24, 1 H); ^{13}C (125 MHz, $CDCl_3$) δ -5.2, 18.4, 25.9, 27.2, 28.1, 35.7, 38.9, 63.5, 63.6, 125.9, 130.3, 130.5, 143.8; HRMS (EI) m/z 298.2331 [(M^+) calcd. for $C_{17}H_{34}O_2Si$ 298.2328].

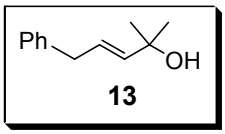
Preparation of 9-(*tert*-butyl-dimethyl-silanyloxy)-4,4-dimethyl-nona-5,7-dien-1-ol (9) (Table 1, entry 3). Applying the above conditions to 4,4-dimethyl-hex-5-yn-1-ol (**32**) (0.1262 g, 1 mmol) and (*E*)-(3-bromo-allyloxy)-*tert*-butyl-dimethyl-silane (**10**) (0.3754 g, 1.5 mmol) afforded after column chromatography [silica gel; 80:20 hexane/EtOAc] afforded 9-(*tert*-butyl-dimethyl-silanyloxy)-4,4-dimethyl-nona-5,7-dien-1-ol (**9**) (105 mg, 72%) as an oil.



11

Preparation of 4-(4-methoxy-phenyl)-2-methyl-but-3-en-2-ol (11) (Table 1, entry 4). Applying the above conditions to 2-methyl-but-3-yn-2-ol (**1**) (0.10 mL, 1.0 mmol) and *p*-iodoanisole (351.1 mg, 1.5 mmol),

afforded after column chromatography [silica gel; 90:10 hexane/EtOAc] 4-(4-methoxy-phenyl)-2-methyl-but-3-en-2-ol (**11**) (198mg, 78%) as an oil.[2]



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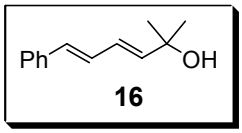
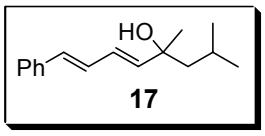
Preparation of 2-methyl-5-phenyl-pent-3-en-2-ol (13) (Table 1, entry 6). Applying the above conditions to 2-methyl-but-3-yn-2-ol (**1**) (0.10 mL, 1.0 mmol) and benzyl bromide (0.18 mL, 1.5 mmol) afforded after column chromatography [silica gel; 90:10 hexane/EtOAc] 2-methyl-5-phenyl-pent-3-en-2-ol (**13**) (149 mg, 85%) as an oil.[3]



16

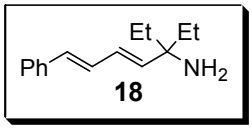
Preparation of 2-methyl-6-phenyl-hexa-3,5-dien-2-ol (16) (Table 1, entry 9). Applying the above conditions to 2-methyl-but-3-yn-2-ol (**1**) (0.10 mL, 1 mmol) and (*E*)-β-bromostyrene (274.5 mg, 1.5 mmol), afforded after column chromatography [silica gel, 90:10 hexane/EtOAc] 2-methyl-6-phenyl-hexa-3,5-dien-2-ol (**16**) (165 mg, 88%) as an oil. IR ($CHCl_3$) 3598, 3451 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.31 (s, 6 H), 5.86 (d, J = 15.4 Hz, 1 H), 6.38 (ddd, J = 15.4, 10.4, 0.6 Hz, 1 H), 6.53 (d, J = 15.7 Hz, 1 H), 6.76 (ddd, J = 15.7, 10.4, 0.6 Hz, 1 H), 7.16-7.39 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 29.8, 77.0, 126.2, 127.3, 127.8, 128.5, 128.6, 131.9, 137.2, 140.8; HRMS (EI) *m*/*z* 188.1204 [$(M)^+$ calcd for $C_{13}H_{16}O$ 188.1201].



17

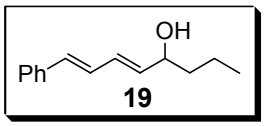
Preparation of 2,4-dimethyl-8-phenyl-octa-5,7-dien-4-ol (17) (Table 1, entry 10). Applying the above conditions to 3,5-dimethyl-hex-1-yn-3-ol (0.15 mL, 1.0 mmol) and (*E*)-β-bromostyrene (274.5 mg, 1.5 mmol), afforded after column chromatography [silica gel; 90:10 hexane/EtOAc] 2,4-dimethyl-8-phenyl-octa-5,7-dien-4-ol (**17**) (205 mg, 89%) as an oil. IR ($CHCl_3$) 3594, 2955 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.92 (d, J = 4.7 Hz, 3 H), 0.94 (d, J = 4.4 Hz, 3 H), 1.33 (s, 3 H), 1.50 (d, J = 6.0 Hz, 2 H), 1.76 (m, 1 H), 5.88 (d, J = 15.4 Hz, 1 H), 6.39 (dd, J = 15.4, 10.4 Hz, 1 H), 6.53 (d, J = 15.7 Hz, 1 H), 6.76 (dd, J = 15.7, 10.4 Hz, 1 H), 7.22-7.39 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.4, 24.6, 29.1, 51.4,

73.6, 126.2, 127.2, 127.3, 128.5, 128.6, 131.8, 137.3, 141.6; HRMS (EI) *m/z* 212.1570 [(M - $H_2O)^+$ calcd. for $C_{16}H_{20}$ 212.1565.



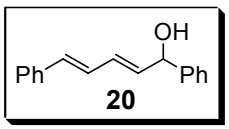
18

Preparation of 1,1-diethyl-5-phenyl-penta-2,4-dienylamine (18) (Table 1, entry 11). Applying the above conditions to 1,1-diethyl-prop-2-ynylamine (0.10 mL, 1.0 mmol) and (*E*)-β-bromostyrene (274.5 mg, 1.5 mmol), afforded after column chromatography [silica gel; 60:40 hexane/EtOAc] 1,1-diethyl-5-phenyl-penta-2,4-dienylamine (**18**) (163 mg, 82%) as an oil. IR ($CHCl_3$) 3180, 2934 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.84 (t, *J* = 7.4 Hz, 6 H), 1.33 (br, 2 H), 1.48 (q, *J* = 7.4 Hz, 4 H), 5.74 (d, *J* = 15.4 Hz, 1 H), 6.28 (dd, *J* = 15.4, 10.4 Hz, 1 H), 6.49 (d, *J* = 15.7 Hz, 1 H), 6.78 (dd, *J* = 15.6, 10.3 Hz, 1 H), 7.15-7.38 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 8.1, 34.0, 56.3, 126.1, 127.1, 128.1, 128.6, 129.1, 130.9, 137.5, 142.4; HRMS (EI) *m/z* 198.1411 (M - $NH_3)^+$ calcd. for $C_{15}H_{18}$ 198.1409.



19

Preparation of 8-phenyl-octa-5,7-dien-4-ol (19) (Table 1, entry 12). Applying the above conditions to hex-1-yn-3-ol (0.12 mL, 1.0 mmol) and (*E*)-β-bromostyrene (274.5 mg, 1.5 mmol) afforded after column chromatography [silica gel; 90:10 hexane/EtOAc] 8-phenyl-octa-5,7-dien-4-ol (**19**) (117 mg, 60%) as an oil. IR (neat) 3352 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.98 (t, *J* = 7.2 Hz, 3 H), 1.34-1.72 (m, 4 H), 1.81 (br s, 1 H), 4.24 (q, *J* = 6.5 Hz, 1 H), 5.85 (dd, *J* = 6.9, 15.6 Hz, 1 H), 6.41 (dd, *J* = 10.4, 15.3 Hz, 1 H), 6.57 (d, *J* = 15.7 Hz, 1 H), 6.80 (dd, *J* = 10.4, 15.6 Hz, 1 H), 7.21-7.49 (m, 5 H) ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9, 18.5, 39.5, 72.5, 126.3, 127.5, 128.3, 128.6, 130.5, 132.5, 136.8, 137.1; HRMS (EI) m/z 202.1349 [(M^+) calcd. for $C_{14}H_{18}O$ 202.1358].



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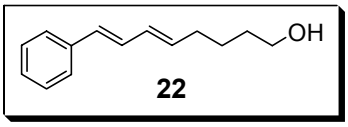
Preparation of 1,5-diphenyl-penta-2,4-dien-1-ol (20) (Table 1, entry 13). Applying the above conditions to 1-phenyl-prop-2-yn-1-ol (0.13 mL, 1.0 mmol) and (*E*)-β-bromostyrene (274.5 mg, 1.5 mmol) afforded after column chromatography

[silica gel; 90:10 hexane/EtOAc] 1,5-diphenyl-penta-2,4-dien-1-ol (**20**) (137 mg, 68%) as an oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.34 (d, *J* = 7.1 Hz, 1 H), 6.03 (dd, *J* = 7.1, 15.1Hz, 1 H), 6.50 (dd, *J* = 10.4, 15.1 Hz, 1 H), 6.60 (d, *J* = 15.9 Hz, 1 H), 6.81 (dd, *J* = 10.4, 15.5 Hz, 1 H), 7.11-7.47 (m, 10 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 74.9, 126.3, 126.4, 127.6, 127.7, 128.2, 128.6, 130.9, 133.2, 135.5, 137.0; whose spectroscopic data was consistent with those reported earlier.[4]

Preparation of 6-phenyl-hexa-3,5-dien-1-ol (21) (Table 1, entry 14): Applying the above conditions to 3-butyn-1-ol (0.08 ml, 1.0 mmol), and (*E*)-β-bromostyrene (1.5 mmol, 274.5 mg) in diethyl ether (4 mL) afford after column chromatography [silica gel; 80:20 pentane/EtOAc, 1% Et_3N] 6-phenyl-hexa-3,5-dien-1-ol (**30**) (60 mg, 34%) as a white solid (mp = 63-64 °C). IR ($CHCl_3$) 3435 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.45 (q, *J* = 7.2 Hz, 2 H) 3.75 (t, *J* = 6.6 Hz, 2 H), 5.82 (dt, *J* = 7.2, 15.4 Hz, 1 H), 6.35 (dd, *J* = 10.4, 15.4 Hz, 1 H), 6.51 (d, *J* = 15.9 Hz, 1 H), 6.79 (dd, *J* = 10.4, 15.9 Hz, 1 H), 7.17-7.53 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 36.2, 65.8, 126.2, 127.3, 128.5, 128.7, 130.7, 131.2, 133.4, 137.3; HRMS (EI) *m/z* 174.1039 [(M^+) calcd. for $C_{12}H_{14}O$ 174.1045].



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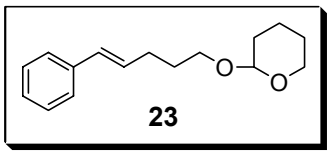
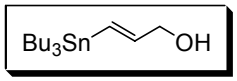
Preparation of 8-phenyl-octa-5,7-dien-1-ol (22) (Table 1, entry 15). Applying the above conditions to 6-bromo-hex-5-yn-1-ol[5] (0.13 mL, 1.0 mmol) and (*E*)-β-bromostyrene (274.5 mg, 1.5 mmol) afforded after column chromatography [silica gel; 80:20 hexane/EtOAc] 8-phenyl-octa-5,7-dien-1-ol (**22**) (123 mg, 61%) as a white solid. (mp = 38.6 °C): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.51 (m, 2 H), 1.61 (m, 2 H), 1.73 (br s, 1 H), 2.19 (q, *J* = 7.9 Hz, 2 H), 3.65 (t, *J* = 6.6 Hz, 2 H), 5.83 (dt, *J* = 7.5, 15.5 Hz, 1 H), 6.23 (dd, *J* = 10.4, 15.9 Hz 1 H), 6.46 (d, *J* = 15.9 Hz, 1 H), 6.76 (dd, *J* = 10.2, 15.7 Hz 1 H), 7.14-7.46 (m, 5 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.5, 135.2, 130.9, 130.2, 129.3, 128.5,

127.1, 126.1, 62.7, 32.5, 32.2, 25.3. Spectroscopic data was consistent with those reported earlier.[6]

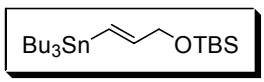


23

Preparation of 2-((*E*)-5-phenylpent-4-enyloxy)-tetrahydro-2H-pyran (23) (Table 1, entry 16). Applying the above conditions to 2-(5-bromopent-4-ynyloxy)-tetrahydro-2H-pyran[5] (246 mg, 1.0 mmol) and iodobenzene (0.15 mL, 1.5 mmol) afforded after column chromatography [silica gel; 80:20 hexane/EtOAc] 2-((*E*)-5-phenylpent-4-enyloxy)-tetrahydro-2H-pyran (**23**) (128 mg, 52%) as an oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.49-1.89 (m, 8 H), 2.31 (dt, *J* = 7.1, 7.1 Hz, 2 H), 3.41 (dt, *J* = 9.6, 6.5 Hz, 1 H), 3.5 (m, 1 H), 3.74 (dt, *J* = 6.8, 9.6 Hz, 1 H), 3.85 (m, 1 H), 4.60 (t, *J* = 3.5 Hz, 1 H), 6.24 (dt, *J* = 6.6 15.8 Hz, 1 H), 6.41 (d, *J* = 15.8 Hz, 1 H), 7.15-7.40 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.6, 25.4, 29.3, 29.4, 30.7, 62.3, 66.9, 98.8, 125.9, 126.8, 128.4, 130.1, 130.3, 137.7. Spectroscopic data was consistent with those reported earlier.[7]

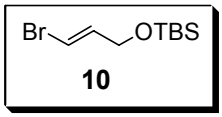


Preparation of vinyl halides 8 and 10. Procedure for the preparation of 3-tributylstannanyl-prop-2-en-1-ol (Table 1). To 50 mL of THF was added $PdCl_2(PPh_3)_2$ (0.0702 g, 10 mmol), propargyl alcohol (0.582 mL, 10 mmol), Bu_3SnCl (3.25 mL, 12 mmol), KF (1.743 g, 30 mmol; 33 mL H_2O), PMHS (0.9 mL, 15 mmol), and TBAF (2 drops of a 1M solution in THF, ca. 0.8 mol%). This mixture was then stirred for 1 hour. The reaction was then separated and the aqueous phase extracted with Et_2O (2x). The combined organics were then washed with Brine, dried over $MgSO_4$, filtered, and concentrated. The resulting residue was purified by column chromatography [silica gel; 90:10 hexane/EtOAc, 1% NEt_3] to afford (*E*)-3-tributylstannanyl-prop-2-en-1-ol[8] (2.25 g, 65%) as a clear oil.



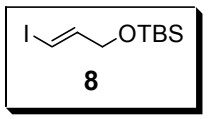
Procedure for the preparation of (*E*)-*tert*-butyl-dimethyl-(3-tributyl stannanyl-allyloxy)-silane (Table 1). TBSCl (1.86 g, 12.32 mmol) was added to a cooled (0

°C) solution of afford (*E*)-3-tributylstannanyl-prop-2-en-1-ol (4.50 g, 13 mmol), imidazole (1.10 g, 15.6 mmol), DMAP (0.16 g, 1.3 mmol) in CH_2Cl_2 (25 mL). The mixture was stirred until complete by TLC (~40 min). When complete the reaction was washed with brine, dried over $MgSO_4$, filtered and concentrated. The resulting residue was purified by column chromatography [silica gel; hexane, 1% NEt_3] to afford (*E*)-*tert*-butyl-dimethyl-(3-tributylstannanyl-allyloxy)-silane (5.70 g, 95%) as clear liquid.[9]



10

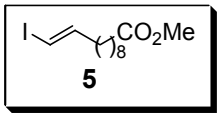
Procedure for the preparation of (3-bromo-allyloxy)-*tert*-butyl-dimethyl-silane (10) (Table 1). *N*-Bromosuccinimide (1.83 g, 10.24 mmol) was added to a cold solution of (*E*)-*tert*-butyl-dimethyl-(3-tributylstannanyl-allyloxy)-silane (4.50 g, 9.75 mmol) in dry CH_2Cl_2 (50 mL). When the reaction was complete (TLC, 1 hr), the reaction was quenched by the addition of sat. aq. $Na_2S_2O_3$ (25 mL). CH_2Cl_2 was added and the aqueous phase extracted with CH_2Cl_2 (3X). The combined organics were washed with brine, dried over Na_2SO_4, filtered, and concentrated. The resulting residue was purified by column chromatography [silica gel; hexanes] to afford (*E*)-(3-bromo-allyloxy)-*tert*-butyl-dimethyl-silane[10] (**10**) (2.43 g, 99%) as a clear liquid. IR (neat) 2957, 2858 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.09 (s, 6 H), 0.92 (s, 9 H), 4.14 (m, 2 H), 6.30 (m, 2 H); ^{13}C (75 MHz, $CDCl_3$) δ -5.4, 18.3, 25.8, 63.3, 106.1, 136.7; HRMS (EI) m/z 250.0387 [(M^+) calcd. for $C_9H_{19}BrOSi$ 250.0389].



8

Procedure for the preparation of (3-iodo-allyloxy)-*tert*-butyl-dimethyl-silane (8) (Table 1). I_2 (3.45 g, 13.6 mmol) was added to a cold solution of (*E*)-*tert*-butyl-dimethyl-(3-tributylstannanyl-allyloxy)-silane (5.7 g, 12.4 mmol) in dry CH_2Cl_2 (20 mL). When the reaction was complete (TLC, 1 hr), the reaction was quenched by the addition of sat. aq. $Na_2S_2O_3$ (25 mL). CH_2Cl_2 was added and the aqueous phase extracted with

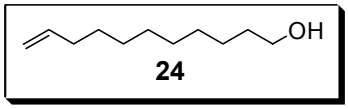
CH_2Cl_2 (3X). The combined organics were washed with Brine, dried over Na_2SO_4, filtered and concentrated. The resulting residue was purified by column chromatography [silica gel; hexanes] to afford (*E*)-(3-iodo-allyloxy)-*tert*-butyl-dimethyl-silane (**8**) (0.32 g, 90%) as a clear liquid.[11]



5

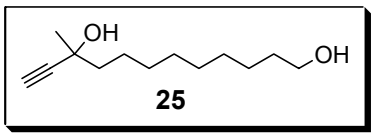
Preparation[12] of (*E*)-11-iodo-undec-10-enoic acid methyl ester (5). Methyl 10-undecenoate (10.0 g, 50.42 mmol) was dissolved in a 2:1 CH_2Cl_2/MeOH solution (200 mL) with 1 mL of NEt_3 added. The solution was purged with N_2 for 15 min. and then cooled to –78 °C. O_3 was then bubbled through the solution until a blue color persisted (~1.5 h). At this time, N_2 was bubbled through the solution until the blue color disappeared. Dimethyl sulfide (15 mL, 202 mmol) was added dropwise and the solution was allowed to warm to room temperature overnight (~8 h). The solvent was then concentrated and the resulting residue was purified by column chromatography [silica gel; 80:20 hexanes/EtOAc] to afford 10-oxo-decanoic acid methyl ester (8.96 g, 90%) as a clear liquid. Under an Ar atmosphere, TMSCl (15.3 mL, 120 mmol) was added to a suspension of $CrCl_3$ (0.6334 g, 4 mmol), Zn (7.84 g, 120 mmol), and NaI (3.0 g, 20 mmol) in dioxane (100 mL) at 25 °C. After the reaction was stirred for 40 min, a solution of 10-oxo-decanoic acid methyl ester (4.01 g, 20 mmol) and CHI_3 (15.75 g, 40 mmol) in dioxane (50 mL) was added at 25 °C via a syringe pump over 24 hours. After the addition the mixture became very thick. The reaction was quenched by the addition of water. The reaction was then extracted with hexanes (5X). The combined organics were washed with brine, dried over $MgSO_4$, filtered, and concentrated. The resulting residue was purified by column chromatography [silica gel; 100:0 to 95:5 hexanes/EtOAc] to afford (*E*)-11-iodo-undec-10-enoic acid methyl ester (**5**)[13] (12.14 g, 63%) as a peach colored liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.14-1.40 (m, 10 H), 1.45-1.62 (m, 2 H), 1.98 (q, *J* = 6.94 Hz, 2 H), 2.24 (t, J = 7.42

Hz, 2 H), 3.60 (s, 3 H), 5.92 (dt, J = 1.40, 14.34 Hz, 1 H), 6.44 (dt, J = 7.14, 14.34 Hz, 1 H); ^{13}C (75 MHz, $CDCl_3$) δ 24.8, 28.3, 28.8, 29.0, 29.1, 29.1, 34.2, 35.9, 51.3, 74.4, 146.6, 174.4.



24

Procedure for the reduction of Ethyl undecylenate. Preparation of undec-10-en-1-ol (24) (Scheme 4). Ethyl undecylenate (25 mmol, 5.31 g) was dissolved in CH_2Cl_2 (150 ml) and cooled to –78 °C and flushed with N_2. DIBAL (62.5 mmol, 62.5 mL of a 1M in THF) was added dropwise via an addition funnel and the mixture was then stirred for 3 hrs at –78 °C. The reaction was quenched by the addition of Rochelle's Salt (300 mL, sat aq.) and then allowed to warm to room temperature for ~3 hrs. The phases are then separated and the aqueous phase was then extracted with CH_2Cl_2 (3X). Organics were then combined, dried over $MgSO_4$, filtered, and concentrated. The resulting residue was the purified by column chromatography [silica gel; 80:20 hexane/EtOAc] to afford 4.30 g (96%) of undec-10-en-1-ol (**24**) (compared with commercial material).



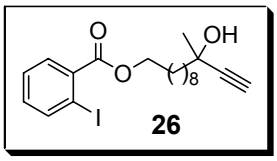
25

Preparation of 10-methyl-dodec-11-yne-1,10-diol (25) (Scheme 4). Using Uemura's[14] method, pyridine (3.53 mmol, 0.29 mL) was added to a mixture of $Pd(OAc)_2$ (0.89 mmol, 0.1978 g) and toluene (88 mL) in a 3 neck flask equipped with an O_2 balloon. O_2 was introduced into the flask and 2-propanol (17.62 mL) was added and the mixture heated to 60 °C with an oil bath. After the reaction had been left for 5 min at 60 °C, undec-10-en-1-ol (**24**) (17.62 mmol, 3.00 g) in 2-propanol (71 mL, 4 mL/1mmol) and the reaction was stirred for 25 hours at 60 °C under O_2. When complete, the reaction was concentrated and the resulting residue was purified by column chromatography [silica gel; 75:25 hexane/EtOAc] to afford 11-hydroxyundecan-2-one (3.05 g, 85%) as a white solid (mp 39 °C).[14]

To a 0 °C solution of ethynylmagnesium bromide (37.66 mmol, 76 mL of a 1M THF solution) was added 11-hydroxyundecan-2-one (16.37 mmol, 3.05 g) in 150 mL of THF. This

mixture was stirred for 1 hour after the addition and then was quenched by the addition of 100 ml of sat. aq. NH_4Cl. The phases were separated and the aqueous phase was extracted with Et_2O. The organics were combined, dried over $MgSO_4$, filtered, and concentrated. The resulting residue was purified by column chromatography [silica gel; 50:50 hexane/EtOAc] to afford 10-methyl-dodec-11-yne-1,10-diol (**25**) (2.94 g, 85%) as a thick yellow oil. IR (neat) 3304 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.20-1.68 (m, 19 H), 2.41 (s, 1 H), 2.54 (br s, 2 H), 3.60 (t, J = 6.7 Hz, 2 H), ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.4, 25.6, 29.2, 29.3, 29.4, 29.6, 32.6, 43.4, 62.7, 67.9, 71.0, 87.8; HRMS (EI) *m/z* 212.1771 [(M^+) calcd. for $C_{13}H_{24}O_2$ 212.1776].

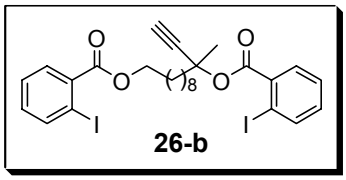
Procedure for the DCC coupling. Preparation of 2-iodo-benzoic acid 10-hydroxy-10-methyl-dodec-11-ynyl ester (26) (Scheme 4). To 285 mL of CH_2Cl_2 was added 2-iodobenzoic acid (7.44 g, 30 mmol), 10-methyl-dodec-11-yne-1,10-diol (**25**) (5.31 g, 25 mmol), DCC (30 mL of 1M solution in CH_2Cl_2, 30 mmol) and then DMAP (0.61 g, 5 mmol). This mixture was stirred for 8 h at room temperature. The reaction was then filtered through a bed a celite and then the celite cake was washed with CH_2Cl_2 (3X). The filtrate was concentrated and purified by column chromatography [silica gel; 85:15 hexane/EtOAc] to afford 2-iodo-benzoic acid 10-hydroxy-10-methyl-dodec-11-ynyl ester (**26**) (9.64 g, 88%) as an oil and diester adduct (**26-b**) (170 mg, 1.5 %) as an oil.



26

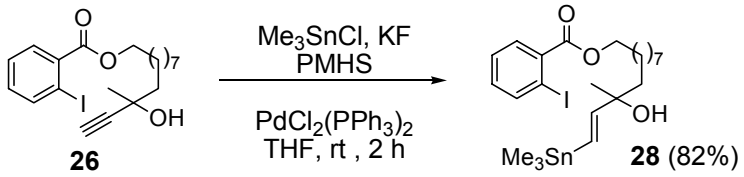
Data for the mono ester (**26**): IR (neat) 3443, 3302, 1726 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.15-1.56 (m, 15 H), 1.60-1.72 (m, 2 H), 1.73-1.86 (m, 2 H), 2.08 (br s, 1 H), 2.44 (s, 1 H), 4.34 (t, J = 6.5 Hz, 2 H), 7.15 (td, J = 1.7, 8.0 Hz, 1 H), 7.41 (td, J = 1.3, 8.5 Hz, 1 H), 7.79 (dd, J = 1.2, 7.4 Hz, 1 H), 7.99 (d, J = 8.0 Hz, 1 H); ^{13}C (75 MHz, $CDCl_3$) δ 24.5, 25.9, 28.5, 29.1, 29.3, 29.4, 29.6, 29.7, 43.4, 65.8,

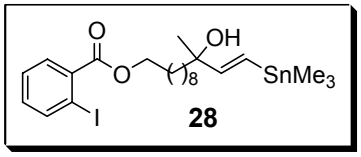
67.9, 71.2, 87.7, 93.9, 127.8, 130.8, 132.4, 135.4, 141.1, 166.6; HRMS (EI) *m/z* 442.1010 [(M^+) calcd. for $C_{20}H_{27}IO_3$ 442.1005].



26-b

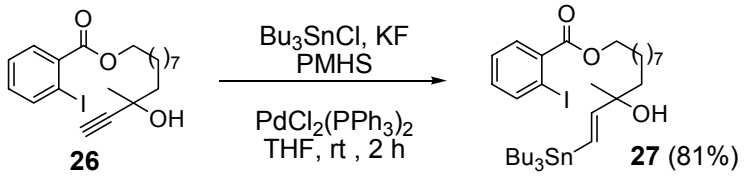
Data for diester (**26-b**): IR (neat) 3300, 1734 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.18-1.66 (m, 12 H), 1.70-1.89 (m, 5 H), 1.90-2.20 (m, 2 H), 2.65 (s, 1 H), 4.34 (t, *J* = 6.5 Hz, 2 H), 7.08-7.20 (m, 2 H), 7.35–7.45 (m, 2 H), 7.72-7.83 (m, 2 H), 7.94-8.03 (m, 2 H); ^{13}C (75 MHz, $CDCl_3$) δ 24.1, 26.0, 26.4, 28.5, 29.1, 29.3, 29.4, 41.3, 65.8, 73.9, 76.7, 83.5, 93.7, 93.9, 127.8, 127.8, 130.7, 130.8, 132.3, 132.4, 135.4, 135.8, 141.1, 141.2, 164.8, 166.6; HRMS (EI) *m/z* 672.0224 [(M^+) calcd. for $C_{27}H_{30}I_2O_4$ 672.0234].

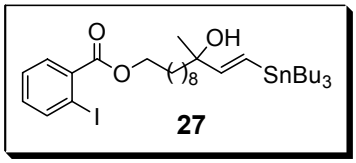




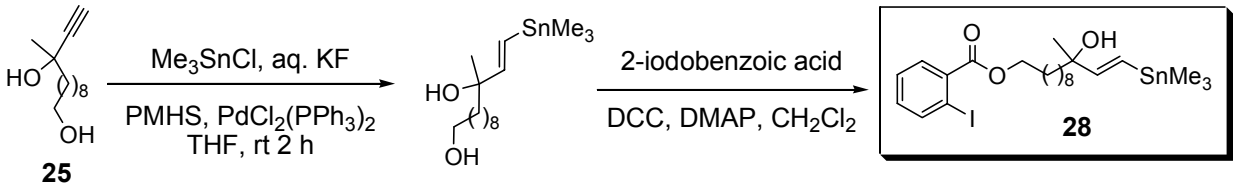
Procedure for the KF/PMHS hydrostannation of an alkyne in the presence of an aryl iodide. Preparation of 2-iodo-benzoic acid 10-hydroxy-10-methyl-12-trimethyl stannanyl-dodec-11-enyl ester (28) (Scheme 5). To 10 mL of THF were added Me_3SnCl (1.2 mL of a 1M THF solution, 1.2 mmol), KF (175 mg, 3.0 mmol), 1 mL of water, PMHS (0.08 mL, 1.2 mmol), $PdCl_2(PPh_3)_2$ (7.0 mg, 0.01 mmol) and 2-iodo-benzoic acid 10-hydroxy-10-methyl-dodec-11-ynyl ester (**26**) (442 mg, 1.0 mmol). This mixture was stirred at room temperature for 2 h. The mixture was then washed with water and separated. The combined organics were dried ($MgSO_4$), filtered, and concentrated. The resulting residue was purified by column chromatography [silica gel; 90:10 hexane/EtOAc, 1% TEA] to afford 2-iodo-benzoic acid 10-hydroxy-10-methyl-12-trimethylstannanyl-dodec-11-enyl ester (**28**) (500 mg, 82%) as an oil. IR

(neat) 3387 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.14 (m, 9 H), 1.20-1.60 (m, 18 H), 1.79 (m, 2 H), 4.34 (t, *J* = 6.7 Hz, 2 H), 6.03 (d, *J* = 19.3 Hz, 1 H), 6.17 (d, *J* = 19.0 Hz, 1 H), 7.15 (tt, *J* = 1.7, 7.9, 1 H), 7.41 (tt, *J* = 1.2, 7.6, 1 H), 7.79 (dt, *J* = 1.4, 7.8, 1 H), 7.99 (dt, *J* = 1.2, 7.9, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -9.6, 23.8, 25.9, 27.6, 28.5, 29.2, 29.4, 29.4, 29.9, 42.2, 65.8, 74.4, 93.9, 124.1, 127.8, 130.8, 132.4, 135.5, 141.2, 154.2, 166.6; HRMS (EI) *m/z* 593.0563[(M^+-CH_3) calcd. for $C_{22}H_{34}IO_3Sn$] 593.0579.

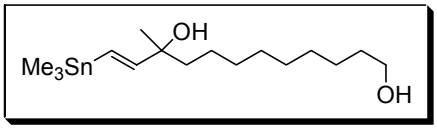




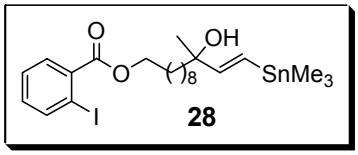
Procedure for the KF/PMHS hydrostannation of an alkyne in the presence of an aryl iodide. Preparation of 2-iodo-benzoic acid 10-hydroxy-10-methyl-12-tributyl stannanyl-dodec-11-enyl ester (27) (Scheme 5). Applying the same conditions as for the trimethylvinylstannane (**28**), except that Bu_3SnCl was used, produced, after column chromatography [silica gel; column chromatography [silica gel; 95:5 hexane/EtOAc, 1% TEA] 2-iodo-benzoic acid 10-hydroxy-10-methyl-12-tributylstannanyl-dodec-11-enyl ester (1.32 g, 65%) as an oil. IR (neat) 3447 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.2 Hz, 9 H), 1.20–1.62 (m, 36 H), 1.77 (m, 2 H), 4.33 (t, *J* = 6.7 Hz, 2 H), 6.05 (m, 2 H), 7.13 (td, *J* = 1.8, 7.8 Hz, 1 H), 7.39 (td, *J* = 1.1, 7.6 Hz, 1 H), 7.78 (dd, *J* = 1.6, 7.7 Hz, 1 H), 7.98 (dd, *J* = 1.1, 8.0 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 9.4, 13.7, 23.9, 25.9, 27.2, 27.8, 28.5, 29.0, 29.2, 29.4, 29.5, 29.9, 42.2, 65.7, 74.6, 93.9, 122.9, 127.8, 130.7, 132.4, 135.4, 141.1, 154.7, 166.5; HRMS (EI) *m/z* 677.1502 [(M^+) calcd. for $C_{32}H_{55}IO_3Sn$ 677.1519].



Procedure for the KF/PMHS hydrostannation of an alkyne. Preparation of 10-methyl-12-trimethylstannanyl-dodec-11-ene-1,10-diol (Control Experiment). Apply the above conditions to 10-methyl-dodec-11-yne-1,10-diol (**25**) (2.06 g, 9.7 mmol) afforded after column chromatography [silica gel; 50:50 hexane/EtOAc, 1% TEA] 10-methyl-12-trimethylstannanyl-dodec-11-ene-1,10-diol (3.13 g, 86%) as a thick waxy oil.

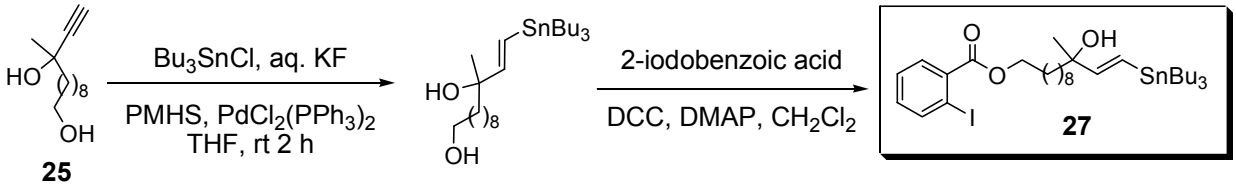


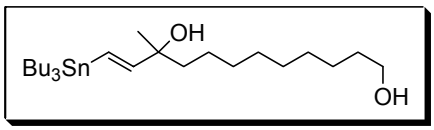
IR (neat) 3304 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.11 (s, 9 H), 1.20-1.40 (m, 17 H), 1.43-1.61 (m, 2 H), 1.64 (br s, 2 H), 3.63 (t, *J* = 6.5 Hz, 2 H), 6.02 (d, *J* = 19.3 Hz, 1 H), 6.15 (d, *J* = 19.3 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -9.5, 23.8, 25.7, 27.5, 29.3, 29.4, 29.5, 30.0, 32.7, 42.2, 63.0, 74.4, 124.1, 154.2 HRMS (EI) *m/z* 363.1344 $[(M\text{-}Me)^+$ calcd. for $C_{15}H_{31}O_2Sn$ 363.1346].



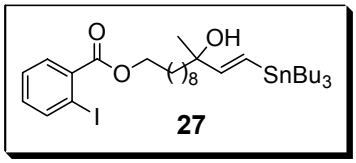
Procedure for a DCC mediated coupling. Preparation of 2-iodo-benzoic acid 10-hydroxy-10-methyl-12-trimethylstannanyl-dodec-11-enyl ester (Control Experiment). 2-Iodobenzoic acid (1.56 g, 6.31 mmol), 10-methyl-12-trimethylstannanyl-dodec-11-ene-1,10-diol (2.50 g, 6.63 mmol), DCC (6.63 mL of a 1 M solution in CH_2Cl_2, 6.63 mmol), DMAP (154 mg, 1.26 mmol) were added to dry CH_2Cl_2 (65 mL) at room temperature. The mixture was allowed to stir until complete by TLC (5 h). Once complete the reaction was filtered through a plug of celite and the filtrate was concentrated. The resulting residue was purified by column chromatography [silica gel; 90:10 hexane/EtOAc] to afford 2-iodo-benzoic acid 10-hydroxy-10-

methyl-12-trimethylstannanyl-dodec-11-enyl ester (**28**) (2.46 g, 64%) as an oil. For spectroscopic data see above.





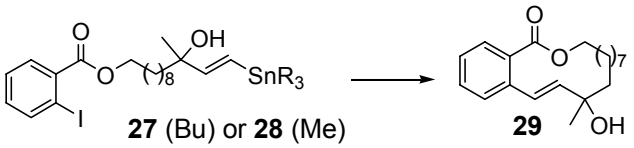
Procedure for the preparation of 10-methyl-12-tributylstannanyl-dodec-11-ene-1,10-diol (Control experiment). $PdCl_2(PPh_3)_2$ (174 mg, 0.19 mmol) was added to a flask containing THF (150 mL). 10-methyl-dodec-11-yne-1,10-diol (**25**) (4.0 g, 18.84 mmol), Bu_3SnCl (6.10 mL, 22.61 mmol), KF (3.28 g, 56.52 mmol), H_2O (10 mL) and PMHS (2.54 mL, 28.26 mmol) were added successively. This mixture was stirred at room temperature for 2 h. The reaction was then diluted with Ether and washed with brine. The aqueous phase was extracted with Ether and the combined organics were dried ($MgSO_4$), filtered, and concentrated. The resulting residue was purified by column chromatography [silica gel; 75:25 hexane/EtOAc, 1% TEA] to afford 10-methyl-12-tributylstannanyl-dodec-11(*E*)-ene-1,10-diol (8.64 g, 91%) as an oil. IR (neat) 3447 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.80-0.95 (m, 15 H), 1.20 –1.40 (m, 23 H), 1.43-1.60 (m, 10 H), 3.62 (q, J = 6.7 Hz, 2 H), 6.00 (d, J = 19.2 Hz, 1 H), 6.06 (d, J = 19.2 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 9.5, 13.7, 23.9, 25.7, 27.2, 27.8, 29.1, 29.4, 29.5, 30.0, 32.8, 42.3, 63.0, 74.6, 123.0, 154.8; HRMS (EI) *m/z* 504.2991 [(M^+), calcd. for $C_{25}H_{52}O_2Sn$ 504.2989].



27

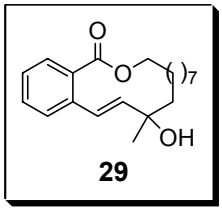
Procedure for the preparation of 2-iodo-benzoic acid 10-hydroxy-10-methyl-12-tributylstannanyl-dodec-11-enyl ester (Control experiment). 2-Iodobenzoic acid (40) (714 mg, 2.88 mmol), 10-methyl-12-tributylstannanyl-dodec-11(*E*)-ene-1,10-diol (1.52 g, 3.02 mmol), DCC (3.02 mL of a 1M THF solution, 3.02 mmol) and DMAP (73 mg, 0.60 mmol) were dissolved in CH_2Cl_2 (33 mL). This mixture was stirred at 25 °C for 5 h. Once the reaction was complete it was filtered through a plug of celite and the plug washed with CH_2Cl_2. The filtrate was concentrated and the resulting residue was purified by column chromatography [silica gel; 95:5 hexane/EtOAc, 1% TEA] to afford 2-iodo-benzoic acid 10-hydroxy-10-methyl-12-tributylstannanyl-dodec-11-enyl ester (**27**) (1.32 g, 65%) as a clear oil. See above for spectroscopic data.

Survey of Catalyst/Ligand Combinations and Conditions (Scheme 5, a-h)



27 (Bu) or **28** (Me) **29**

Entry	R	Catalyst	Solvent	Temp/time	Isolated Yield
1	Bu	$Pd_2dba_3/AsPh_3$ (1:4)	NMP (0.005 M)	60 °C/22 h	60%
2	Bu	$Pd_2dba_3/AsPh_3$ (1:4)	THF (0.005 M)	70 °C/28 h	52%
3	Bu	Pd_2dba_3/TFP (1:4)	NMP (0.005 M)	60 °C/24 h	61%
4	Bu	Pd_2dba_3/TFP (1:4)	THF (0.005 M)	70 °C/27 h	63%
5	Me	$Pd_2dba_3/AsPh_3$ (1:4)	NMP (0.005 M)	60 °C/14 h	72%
6	Me	$Pd_2dba_3/AsPh_3$ (1:4)	THF (0.005 M)	70 °C/15 h	63%
7	Me	Pd_2dba_3/TFP (1:4)	NMP (0.005 M)	60 °C/10h	74%
8	Me	Pd_2dba_3/TFP (1:4)	THF (0.005 M)	70 °C/12 h	73%



29

General procedure for the intramolecular Stille coupling control. Preparation of 16-hydroxy-16-methyl-7,8,9,10,11,12,13,14,15,16-

decahydro-6-oxa-benzocyclohexadecen-5-one (29) (entry 1). To 100 mL of degassed (Ar) NMP (0.005 M) was added Pd_2dba_3 (14 mg, 0.015 mmol) and $AsPh_3$ (19 mg, 0.06 mmol). This mixture was stirred for 10 min while Ar was bubbled through the solution. 2-Iodo-benzoic acid 10-hydroxy-10-methyl-12-tributylstannanyl-dodec-11-enyl ester (**27**) (354 mg, 0.5 mmol) was added in one portion. The mixture was then heated at ~60 °C for 22 h. The reaction was then cooled to room temperature and diluted with Et_2O. After washing with water and separation, the aqueous phase was extracted with Et_2O (3x). The combined organics were dried ($MgSO_4$), filtered, and concentrated. The resulting residue was purified by column chromatography [silica gel; 80:20 hexane/EtOAc] to afford 16-hydroxy-16-methyl-7,8,9,10,11,12,13,14,15,16-decahydro-6-oxa-benzocyclohexadecen-5-one (**29**) (90 mg, 60 %) as an oil. IR (neat) 3487 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.21-1.51 (m, 15 H), 1.65-1.91 (m, 5 H), 4.47 (t, *J* = 4.9 Hz, 2 H), 6.12 (d, *J* = 16.2 Hz, 1 H), 7.23-7.37 (m, 2 H), 7.45 (t, *J* = 8.8 Hz, 1 H), 7.56 (d, *J* = 7.7 Hz, 1 H), 7.78 (d, *J* = 8.9 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.5, 24.3, 26.4, 26.8, 26.9, 27.7, 28.4, 29.1, 41.6, 63.8, 73.7, 126.1, 126.9, 129.8, 129.9, 131.5, 137.9, 139.4, 168.2; HRMS (EI) *m/z* 316.2038 [(M^+) calcd. for $C_{20}H_{28}O_3$ 316.2038].

Intramolecular Stille coupling control. Use of tributylstannane with $AsPh_3$ and THF. Preparation of 16-hydroxy-16-methyl-7,8,9,10,11,12,13,14,15,16-decahydro-6-oxa-benzocyclohexadecen-5-one (29) (entry 2). Applying the above conditions using 2-iodo-benzoic acid 10-hydroxy-10-methyl-12-tributylstannanyl-dodec-11-enyl ester (**27**) (354 mg, 0.5 mmol) and $AsPh_3$ (19 mg, .06 mmol) in THF (0.005 M) at 70 °C for 28 h after column chromatography [silica gel; 80:20 hexane/EtOAc] afforded 16-hydroxy-16-methyl-7,8,9,10,11,12,13,14,15,16-decahydro-6-oxa-benzocyclohexadecen-5-one (**29**) (79 mg, 52 %) as an oil. For spectroscopic data see above.

Intramolecular Stille coupling control. Use of tributylstannane with TFP and NMP. Preparation of 16-hydroxy-16-methyl-7,8,9,10,11,12,13,14,15,16-decahydro-6-oxa-benzocyclohexadecen-5-one (29) (entry 3). Applying the above conditions using 2-iodo-benzoic acid 10-hydroxy-10-methyl-12-tributylstannanyl-dodec-11-enyl ester (**27**) (354 mg, 0.48 mmol) and TFP (14 mg, 0.06 mmol) in NMP (0.005 M) at 60 °C for 24 h after column chromatography [silica gel; 80:20 hexane/EtOAc] afforded 16-hydroxy-16-methyl-7,8,9,10,11,12,13,14,15,16-decahydro-6-oxa-benzocyclohexadecen-5-one (**29**) (92 mg, 61 %) as an oil. For spectroscopic data see above.

Intramolecular Stille coupling control. Use of tributylstannane with TFP and THF. Preparation of 16-hydroxy-16-methyl-7,8,9,10,11,12,13,14,15,16-decahydro-6-oxa-benzocyclohexadecen-5-one (29) (entry 4). Applying the above conditions using 2-iodo-benzoic acid 10-hydroxy-10-methyl-12-tributylstannanyl-dodec-11-enyl ester (**27**) (367 mg, 0.24 mmol) and TFP (14 mg, 0.06 mmol) in THF (0.005 M) at 70 °C for 27 h after column chromatography [silica gel; 80:20 hexane/EtOAc] afforded 16-hydroxy-16-methyl-7,8,9,10,11,12,13,14,15,16-decahydro-6-oxa-benzocyclohexadecen-5-one (**29**) (99 mg, 63 %) as an oil. For spectroscopic data see above.

Intramolecular Stille coupling control. Use of trimethylstannane with $AsPh_3$ and NMP. Preparation of 16-hydroxy-16-methyl-7,8,9,10,11,12,13,14,15,16-decahydro-6-oxa-benzocyclohexadecen-5-one (29) (entry 5). Applying the above conditions using 2-iodo-benzoic acid 10-hydroxy-10-methyl-12-trimethylstannanyl-dodec-11-enyl ester (**28**) (304 mg, 0.5 mmol) and $AsPh_3$ (19 mg, 0.06 mmol) in NMP (0.005 M) at 60 °C for 14 h after column chromatography [silica gel; 80:20 hexane/EtOAc] afforded 16-hydroxy-16-methyl-

7,8,9,10,11,12,13,14,15,16-decahydro-6-oxa-benzocyclohexadecen-5-one (**29**) (114 mg, 72 %) as an oil. For spectroscopic data see above.

Intramolecular Stille coupling control. Use of trimethylstannane with $AsPh_3$ and THF. Preparation of 16-hydroxy-16-methyl-7,8,9,10,11,12,13,14,15,16-decahydro-6-oxa-benzocyclohexadecen-5-one (29) (entry 6). Applying the above conditions using 2-iodo-benzoic acid 10-hydroxy-10-methyl-12-trimethylstannanyl-dodec-11-enyl ester (**28**) (304 mg, 0.5 mmol) and $AsPh_3$ (19 mg, 0.06 mmol) in THF (0.005 M) at 70 °C for 15 h after column chromatography [silica gel; 80:20 hexane/EtOAc] afforded 16-hydroxy-16-methyl-7,8,9,10,11,12,13,14,15,16-decahydro-6-oxa-benzocyclohexadecen-5-one (**29**) (100 mg, 63 %) as an oil. For spectroscopic data see above.

Intramolecular Stille coupling control. Use of trimethylstannane with TFP and NMP. Preparation of 16-hydroxy-16-methyl-7,8,9,10,11,12,13,14,15,16-decahydro-6-oxa-benzocyclohexadecen-5-one (44) (entry 7). Applying the above conditions using 2-iodo-benzoic acid 10-hydroxy-10-methyl-12-trimethylstannanyl-dodec-11-enyl ester (**28**) (304 mg, 0.5 mmol) and TFP (14 mg, 0.06 mmol) in NMP (0.005 M) at 60 °C for 10 h after column chromatography [silica gel; 80:20 hexane/EtOAc] afforded 16-hydroxy-16-methyl-7,8,9,10,11,12,13,14,15,16-decahydro-6-oxa-benzocyclohexadecen-5-one (**29**) (117 mg, 74 %) as an oil. For spectroscopic data see above.

Intramolecular Stille coupling control. Use of trimethylstannane with TFP and THF. Preparation of 16-hydroxy-16-methyl-7,8,9,10,11,12,13,14,15,16-decahydro-6-oxa-benzocyclohexadecen-5-one (44) (entry 8). Applying the above conditions using 2-iodo-benzoic acid 10-hydroxy-10-methyl-12-trimethylstannanyl-dodec-11-enyl ester (**28**) (304 mg, 0.5 mmol) and TFP (14 mg, 0.06 mmol) in THF (0.005 M) at 70 °C for 12 h after column

chromatography [silica gel; 80:20 hexane/EtOAc] afforded 16-hydroxy-16-methyl-7,8,9,10,11,12,13,14,15,16-decahydro-6-oxa-benzocyclohexadecen-5-one (**29**) (115 mg, 73 %) as an oil. For spectroscopic data see above.

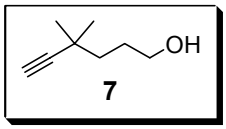
Representative procedure for a one-pot hydrostannation/intra-molecular Stille. Use of the "Sn-F" route with everything added at once under high dilution. Preparation of 16-hydroxy-16-methyl-7,8,9,10,11,12,13,14,15,16-decahydro-6-oxa-benzocyclo-hexadecen-5-one (29) (Scheme 5, entry i). Pd_2dba_3 (27 mg, 0.03 mmol) and TFP (28 mg, .12 mmol) were added to degassed THF (200 mL). At this time Me_3SnCl (0.05 mL of a 1 M solution in THF, 0.05 mmol), KF (87 mg, 1.5 mmol), water (1 mL), PMHS (0.09 mL, 1.5 mmol) and 2-iodo-benzoic acid 10-hydroxy-10-methyl-dodec-11-ynyl ester (**26**) (431 mg, 1.0 mmol) were all added. This mixture was stirred for 14 h at 70 °C. The reaction was then diluted with Et_2O and washed with water. After separation of the phases, the aqueous phase was extracted with Et_2O. The combined organics were dried ($MgSO_4$), filtered, and concentrated. The resulting residue was purified by column chromatography [silica gel; 80:20 hexane/EtOAc] to afford 16-hydroxy-16-methyl-7,8,9,10,11,12,13, 14,15,16-decahydro-6-oxa-benzocyclohexadecen-5-one (**29**) (70 mg, 23%) as an oil. For spectroscopic data see above.

Representative procedure for a one-pot hydrostannation/intra-molecular Stille. Use of syringe pump addition. Preparation of 16-hydroxy-16-methyl-7,8,9,10,11,12,13,14,15,16-decahydro-6-oxa-benzocyclohexadecen -5-one (29) (Scheme 5, entry j). Applying the conditions noted above except that 2-iodo-benzoic acid 10-hydroxy-10-methyl-dodec-11-ynyl ester (**26**) (431 mg, 1.0 mmol) was added via syringe pump over 8 h at 70 °C. After column chromatography [silica gel; 80:20 hexane/EtOAc] 16-hydroxy-16-methyl-

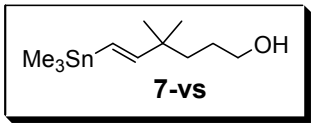
7,8,9,10,11,12,13,14,15,16-decahydro-6-oxa-benzocyclohexadecen-5-one (**29**) (93 mg, 29%) was obtained as an oil. For spectroscopic data see above.

Representative procedure for a one-pot hydrostannation/intra-molecular Stille. Use of the "Sn-F" route in conjunction with the "Sn-O" route with everything added at once under high dilution. Preparation of 16-hydroxy-16-methyl-7,8,9,10,11,12,13,14,15,16-decahydro-6-oxa-benzocyclohexadecen-5-one (29) (Scheme 5, entry k). Pd_2dba_3 (27 mg, 0.03 mmol) and TFP (28 mg, .12 mmol) were added to degassed THF (200 mL). At this time Me_3SnF (9.1 mg, 0.05 mmol), Na_2CO_3 (159 mg, 1.5 mmol), water (1 mL), PMHS (0.09 mL, 1.5 mmol) and 2-iodo-benzoic acid 10-hydroxy-10-methyl-dodec-11-ynyl ester (**26**) (431 mg, 1.0 mmol) were all added. This mixture was stirred for 12 h at 70 °C. The reaction was then diluted with Et_2O and washed with water. After separation of the phases, the aqueous phase was extracted with Et_2O. The combined organics were dried ($MgSO_4$), filtered, and concentrated. The resulting residue was purified by column chromatography [silica gel; 80:20 Hexane/EtOAc] to afford 16-hydroxy-16-methyl-7,8,9,10,11,12,13,14,15,16-decahydro-6-oxa-benzocyclohexadecen-5-one (**29**) (130 mg, 41%) as an oil. For spectroscopic data see above.

Representative procedure for a one-pot hydrostannation/intramolecular Stille. Use of the "Sn-F" route in conjunction with the "Sn-O" route with syringe pump addition. Preparation of 16-hydroxy-16-methyl-7,8,9,10,11,12,13,14,15,16-decahydro-6-oxa-benzo-cyclohexa decen-5-one (29) (Scheme 5, entry l). Applying the conditions noted above except that 2-iodo-benzoic acid 10-hydroxy-10-methyl-dodec-11-ynyl ester (**26**) (431 mg, 1.0 mmol) was added via syringe pump over 8 h at 70 °C. After column chromatography [silica gel; 80:20 hexane/EtOAc] 16-hydroxy-16-methyl-7,8,9,10,11,12,13,14,15,16-decahydro-6-oxa-benzocyclo-hexadecen-5-one (**44**) (150 mg, 47%) was obtained as an oil. For spectroscopic data see above.

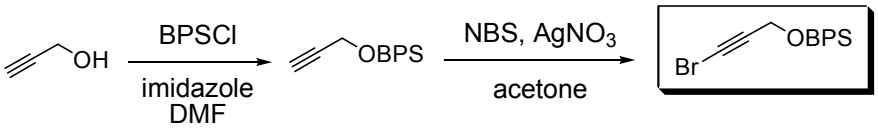


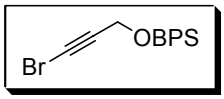
Representative Procedure for the preparation of 4,4-dimethyl-hex-5-yn-1-ol (7) (Table 2, entry 1). Isopropyl acetylene (**33**) (7.51 mL, 73.4 mmol) was added to 50 mL of dry Et_2O in a flame dried 500 mL round bottom flask under N_2 and the solution was cooled to 0 °C. *n*-BuLi (92 mL of 1.6 M solution in hexanes, 147 mmol) was then added dropwise via an addition funnel. When the addition was complete the solution had a clear yellow appearance. Upon addition of *N*,*N*,*N*',*N*'-tetramethylethylenediamine (11.65 mL, 77.1 mmol) in one portion, the solution turned to a thick white slurry within minutes. This solution was then placed in a 60 °C oil bath and gently refluxed for 15 hours to produce a deep red solution (the dianion). The dianion solution was then allowed to cool to room temperature and then cooled to –78°C. Oxetane (4.75 mL, 73.4 mmol) was then added followed by addition of BF_3•OEt_2 (9.31 mL, 73.4 mmol) via a syringe pump over 6 hours. The solution was then warmed to room temperature and diluted with 1 M HCl and stirred for 30 minutes. The mixture was then diluted with Et_2O and the phases separated. The aqueous phase was extracted with Et_2O (3x) and the combined organics were washed with brine, dried over $MgSO_4$, filtered and concentrated. The resulting residue was purified by column chromatography [silica gel; 90:10 to 80:20 hexane/EtOAc] to afford 4,4-dimethyl-hex-5-yn-1-ol[15] (**7**) (2.58 g, 35%) as a pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.24 (s, 6 H), 1.43-1.53 (m, 2 H), 1.69-1.83 (m, 3 H), 2.11 (s, 1 H), 3.70 (t, *J* = 6.46 Hz, 2 H); ^{13}C (75 MHz, $CDCl_3$) δ 28.7, 29.1, 30.7, 39.3, 63.2, 67.9, 91.6.



Procedure for the palladium catalyzed hydrostannation of 4,4-dimethyl-hex-5-yn-1-ol Preparation of 4,4-dimethyl-6-trimethylstannanyl-hex-5-en-1-ol (7-vs) (Control Experiment). To 50 mL of THF was added $PdCl_2(PPh_3)_2$ (0.029 g, 0.041 mmol), 4,4-dimethyl-hex-5-yn-1-ol (**7**) (0.5213 g, 4.13 mmol), Me_3SnCl (5 mL of a 1M solution in THF, 4.96 mmol), KF (.7199 g, 12.4 mmol; 3 mL H_2O),

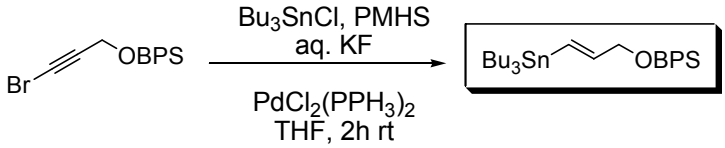
PMHS (0.37 mL, 6.2 mmol) and TBAF (1 drop of a 1M solution in THF, ca. 0.8 mol %). This mixture was then stirred for 1 hour. The reaction was then separated and the aqueous phase extracted with Et_2O (2x). The combined organics were then washed with brine, dried over $MgSO_4$, filtered, and concentrated. The resulting residue was purified by column chromatography [silica gel; 90:10 hexane/EtOAc, 1% NEt_3] to afford 4,4-dimethyl-6-trimethylstannanyl-hex-5-en-1-ol (**7-vs**) (1.05 g, 88%) as a light yellow oil. IR (neat) 3327 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.11 (m, 9 H), 0.99 (s, 6 H), 1.28-1.36 (m, 2 H), 1.42-1.56 (m, 3 H), 3.61 (m, 2 H), 5.87 (m, 2 H); ^{13}C (75 MHz, $CDCl_3$) δ -9.6, 26.6, 28.0, 38.3, 38.5, 63.7, 122.9, 157.7; HRMS (EI) m/z 277.0613 [(M^+-CH_3) calcd. for $C_{10}H_{21}OSn$ 277.0616].

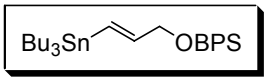




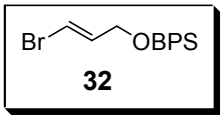
Preparation of (3-bromo-prop-2-ynyloxy)-*t*-butyldiphenylsilane (Scheme 7). To a solution of propargyl alcohol (1.40 g, 25 mmol) and imidazole (3.74 g, 55 mmol) in DMF (25 mL) was added BPSCl (7.15 mL, 27.5 mmol) dropwise at room temperature and stirred for 5 h. The reaction was then partitioned between sat. aq. NH_4Cl (100 mL) and hexane (100 mL) and the aqueous phase extracted with hexane (2x). The combined organics were washed with brine, dried over $MgSO_4$, filtered, and concentrated. The resulting residue was purified by column chromatography [silica gel; 95:5 hexane/EtOAc] to afford *t*-butyl-diphenyl-prop-2-ynyloxy-silane (7.36 g, 100%). The silylated propargyl alcohol was then dissolved in 75 mL of dry acetone. *N*-Bromosuccinimide (4.90 g, 27.5 mmol) and $AgNO_3$ (375 mg, 2.2 mmol) were added and the reaction was allowed to stir for 8 hours. The reaction was then diluted with ether and washed with H_2O. The aqueous phase was extracted with ether. The combined organics were washed with brine, dried over $MgSO_4$, filtered, and concentrated. The

resulting residue was then purified by column chromatography [silica, 95:5 hexane/EtOAc] to afford (3-bromo-prop-2-ynyloxy)-*t*-butyldiphenylsilane (7.93 g, 85%) as a yellow oil. IR (neat) 3071, 2221 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.11 (s, 9 H), 4.38 (s, 2 H), 7.40-7.50 (m, 6 H), 7.70-7.80 (m, 4 H); ^{13}C (75 MHz, $CDCl_3$) δ 19.1, 26.7, 44.7, 53.5, 78.3, 127.7, 129.8, 132.8, 135.6; HRMS (EI) m/z 314.9851 [$(M-t\text{-}Bu)^+$ calcd for $C_{15}H_{12}BrOSi$ 314.9841].



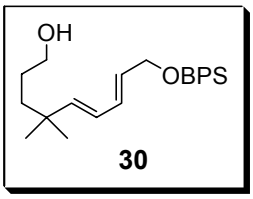


Preparation of *t*-butyl-diphenyl-(3-tributylstannanyl-allyloxy)-silane (Scheme 7). To 100 mL of THF was added (3-bromo-prop-2-ynyloxy)-*t*-butyl-diphenyl-silane (7.55 g, 20.2 mmol), Bu_3SnCl (6.60 ml, 24.3 mmol), KF (3.55 g, 61 mmol), H_2O (6 mL), PMHS (1.82 mL, 30.3 mmol), TBAF (1 drop of a 1M solution in THF, ca. 0.8 mol %), and $PdCl_2(PPh_3)_2$. The reaction was stirred at room temperature until complete by TLC (2 hours). Once complete, the reaction was diluted with ether. The phases were separated and the aqueous phase extracted with ether. The combined organics were washed with brine, dried over $MgSO_4$, filtered, and concentrated. The resulting residue was purified by column chromatography [silica gel, hexane, 1% NEt_3] to afford (*E*)-*t*-butyl-diphenyl-(3-tributylstannanyl-allyloxy)-silane (8.27 g, 70%) as a clear oil. IR (neat) 2956, 1112 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.94 (m, 15 H), 1.12 (s, 9 H), 1.37 (m, 6 H), 1.56 (m, 6 H), 4.30 (dd, J = 1.8, 4.2 Hz, 2 H), 6.02-6.43 (m, 2 H), 7.38-7.48 (m, 6 H), 7.71-7.77 (m, 4 H); ^{13}C (125 MHz, $CDCl_3$) δ 9.4, 13.7, 19.3, 26.9, 27.2, 29.1, 67.2, 126.9, 127.5, 129.5, 133.9, 135.6, 146.7; HRMS (EI) m/z 529.1950 [$(M-Bu)^+$ calcd. for $C_{27}H_{41}OSiSn$ 529.1953].



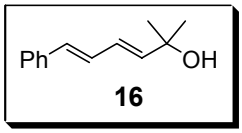
32

Preparation of (3-bromo-allyloxy)-*t*-butyl-diphenyl-silane (32) (Scheme 7). *N*-Bromosuccinimide (3.07 g, 17.23 mmol) was added to a cold solution of (*E*)-t-butyl-diphenyl-(3-tributylstannanyl-allyloxy)-silane (9.61 g, 16.41 mmol) in dry CH_2Cl_2 (100 mL). Upon completion (TLC, 1 hr), the reaction was quenched by the addition of sat. aq. $Na_2S_2O_3$ (25 mL). CH_2Cl_2 was added and the aqueous phase extracted with CH_2Cl_2 (3X). The combined organics were washed with brine, dried over Na_2SO_4, filtered, and concentrated. The resulting residue was purified by column chromatography [silica gel; hexanes] to afford (*E*)-(3-bromo-allyloxy)-*t*-butyl-diphenyl-silane (**32**) (6.01 g, 97%) as a clear liquid. IR 2959, 2857, 1112 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.10 (s, 9 H), 4.17 (m, 2 H), 6.30 (m, 1 H), 6.38 (m, 1 H), 7.44 (m, 6 H), 7.70 (m, 4 H); ^{13}C (75 MHz, $CDCl_3$) δ 19.2, 26.8, 64.0, 105.9, 127.8, 129.8, 133.1, 135.5, 136.3; HRMS (EI) m/z 316.9998 [$(M\text{-}Bu)^+$ calcd. for $C_{15}H_{14}BrOSi$ 316.9997].



30

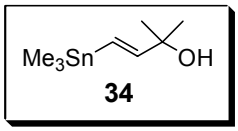
Preparation of 9-(*t*-butyldiphenylsilanyloxy)-4,4-dimethyl-nona-5,7-dien-1-ol (30) (Scheme 7). Applying the above "Sn-F" one-pot catalytic Stille conditions to 4,4-dimethyl-hex-5-yn-1-ol (**7**) (126.2 mg, 1 mmol) and (*E*)-(3-bromo-allyloxy)-*t*-butyl-diphenyl-silane (**32**) (563.1 mg, 1.5 mmol) afforded after column chromatography [silica gel; 80:20 hexane/EtOAc] 9-(t-butyl-diphenyl-silanyloxy)-4,4-dimethyl-nona-5,7-dien-1-ol (**30**) (336 mg, 80%) as an oil. IR (neat) 3352, 3071 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.04 (s, 6 H), 1.08 (s, 9 H), 1.37 (m, 3 H), 1.51 (m, 2 H), 3.61 (t, J = 6.4 Hz, 2 H), 4.25 (dd, J = 1.1, 5.1 Hz, 2 H), 5.61 (d, J = 15.5 Hz, 1 H), 5.70 (dt, J = 5.1, 15.2 Hz, 1 H), 5.98 (dd, J = 10.4, 15.5 Hz, 1 H), 6.24 (dd, J = 10.4, 15.2, 1 H), 7.36-7.45 (m, 6 H), 7.68-7.72 (m, 4 H); ^{13}C (125 MHz, $CDCl_3$) δ 19.2, 26.8, 27.1, 28.0, 35.7, 38.9, 63.5, 64.2, 126.0, 127.6, 129.5, 129.9, 130.5, 133.7, 135.5, 143.7; HRMS (EI) m/z 365.1923 [$(M\text{-}Bu\text{-}t)^+$ calcd. for $C_{23}H_{29}O_2Si$ 365.1937].



Representative procedure for the use of Me_3SnF as the tin source. Preparation of 2-methyl-6-phenyl-hexa-3,5-dien-2-ol (16) (Control Experiment). Tri-2-furylphosphine (9.3 mg, 0.04 mmol) was added to a solution of Pd_2bda_3 (9.2 mg, 0.01 mmol) in Et_2O (5 mL). After stirring at room temperature for 15 min, (*E*)-β-bromostyrene (274.5 mg, 1.5 mmol), Me_3SnF (11 mg, 0.06 mmol), aq. KF (0.1743 g, 3 mmol; 1 mL H_2O), TBAF (1 drop of a 1M solution in THF, ca. 0.8 mol %) and $PdCl_2(PPh_3)_2$ (7.0 mg, 0.01 mmol) were all added to the solution. The solution was heated to reflux and then a solution of 2-methyl-but-3-yn-2-ol (**1**) (0.10 mL, 1 mmol) and PMHS (0.09 mL, 1.5 mmol) in Et_2O (4mL) was added via a syringe pump over 11 hrs. The phases were separated and the organics washed with brine, dried over $MgSO_4$, filtered, and concentrated. The resulting residue was purified by column chromatography [silica gel, 90:10 hexane/EtOAc] to afford 2-methyl-6-phenyl-hexa-3,5-dien-2-ol (**16**) (152 mg, 81%) as an oil. For spectroscopic data see above.

Preparation of Me_3SnH. A solution of Me_3SnCl (36.87 mL of a 1M solution in THF, 36.87 mmol), KF (4.71 g, 81.11 mmol), H_2O (5-10 mL) and PMHS (2.43 mL, 40.56 mmol) were added to a flask containing THF (50 mL). This mixture was then allowed to stir at room temperature until the initially formed Me_3SnF precipitate disappeared. After 4-5 hours the reaction was complete, and the layers were separated. Me_3SnH was distilled as a 2.74 M solution in THF.

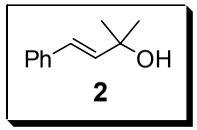
Representative procedure for the use of 6 mol% Me_3SnH as the tin source. Preparation of 2-methyl-6-phenyl-hexa-3,5-dien-2-ol (16) (Control Experiment). Following the above procedure outlined for Table 1, Me_3SnH (0.11 mL of a 2.74 M solution in THF, 0.30 mmol), (*E*)-β-bromostyrene (1.37 g, 7.5 mmol) and 2-methyl-but-3-yn-2-ol (**1**) (0.50 mL, 5 mmol) after column chromatography [silica gel, 90:10 hexane/EtOAc] 2-methyl-6-phenyl-hexa-3,5-dien-2-ol (**16**) (846 mg, 90%) was afforded as an oil. For spectroscopic data see above.



34

Preparation of *E*)-2-methyl-4-(trimethylstannyl)but-3-en-2-ol (34). A flask containing THF (50 mL) was charged with Me_3SnCl (18 mL, 18 mmol; 1M solution in THF), 2-methyl-3-butyn-2-ol (**1**) (2.43 mL, 15 mmol), KF (36 mmol), water (5 mL) and $PdCl_2(PPh_3)_2$ (126 mg, 0.18 mmol) and TBAF (1 drop of a 1 M solution in THF, ca. 0.8 mol %). After stirring at 25 °C for 2 h, column chromatography [silica; 70:30 hexane/Ether, 1% TEA] afforded (*E*)-2-methyl-4-(trimethylstannyl)-3-buten-2-ol (**34**) (3.17 g, 85%) as a yellow oil. IR (neat): 3362 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.10 (s, 9 H), 1.27 (s, 6 H), 1.64 (br s, 1 H), 6.1 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.9, 123.4, 72.2, 30.0, -9.3; HRMS (EI) *m/z* 235.1037 [(M^+-CH_3) calcd for $C_7H_{15}O^{116}Sn$ 235.1046].

Representative procedure for the use of 6 mol% (*E*)-2-methyl-4-(trimethylstannyl)but-3-en-2-ol as the tin source. Preparation of 2-methyl-6-phenyl-hexa-3,5-dien-2-ol (16) (Control Experiment). Following the above procedure outlined for Table 1, (*E*)-2-methyl-4-(trimethylstannyl)but-3-en-2-ol (**34**) (15.0 mg, 0.06 mmol), (*E*)-β-bromostyrene (275 mg, 1.5 mmol) and 2-methyl-but-3-yn-2-ol (**1**) (0.094 mL, 0.94 mmol) after column chromatography [silica gel, 90:10 hexane/EtOAc] 2-methyl-6-phenyl-hexa-3,5-dien-2-ol (**16**) (181 mg, 96%) was afforded as an oil. For spectroscopic data see above.



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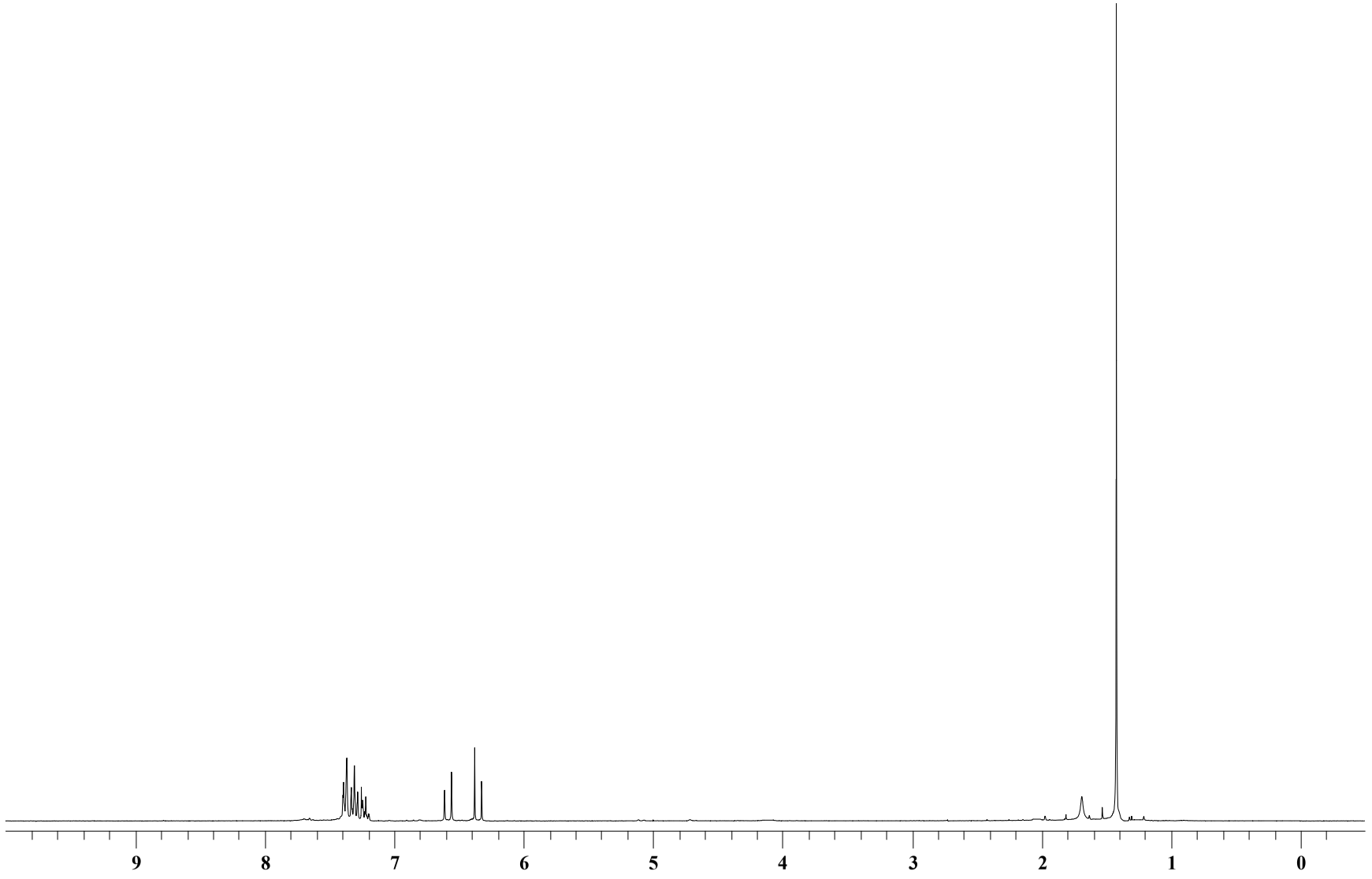

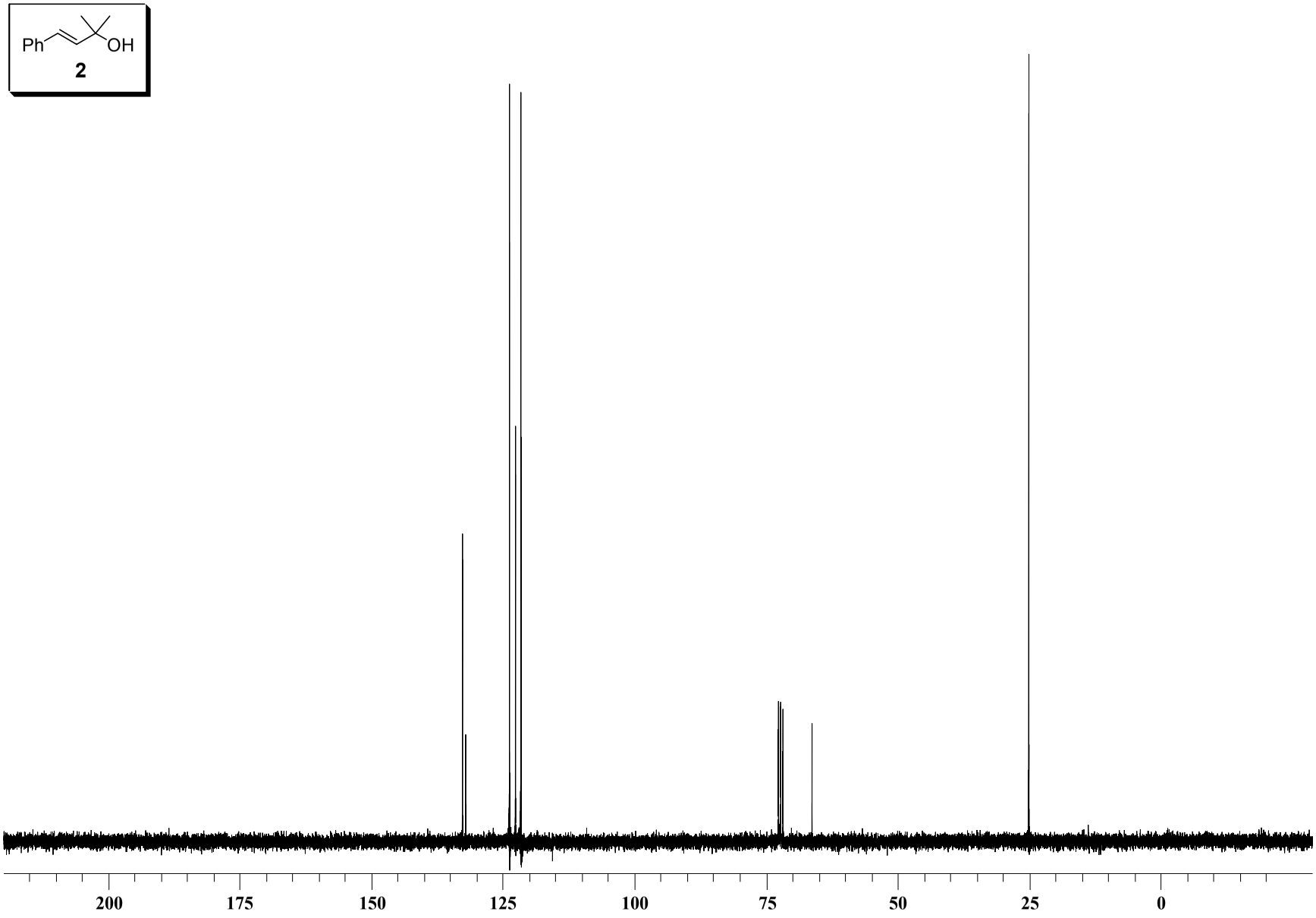
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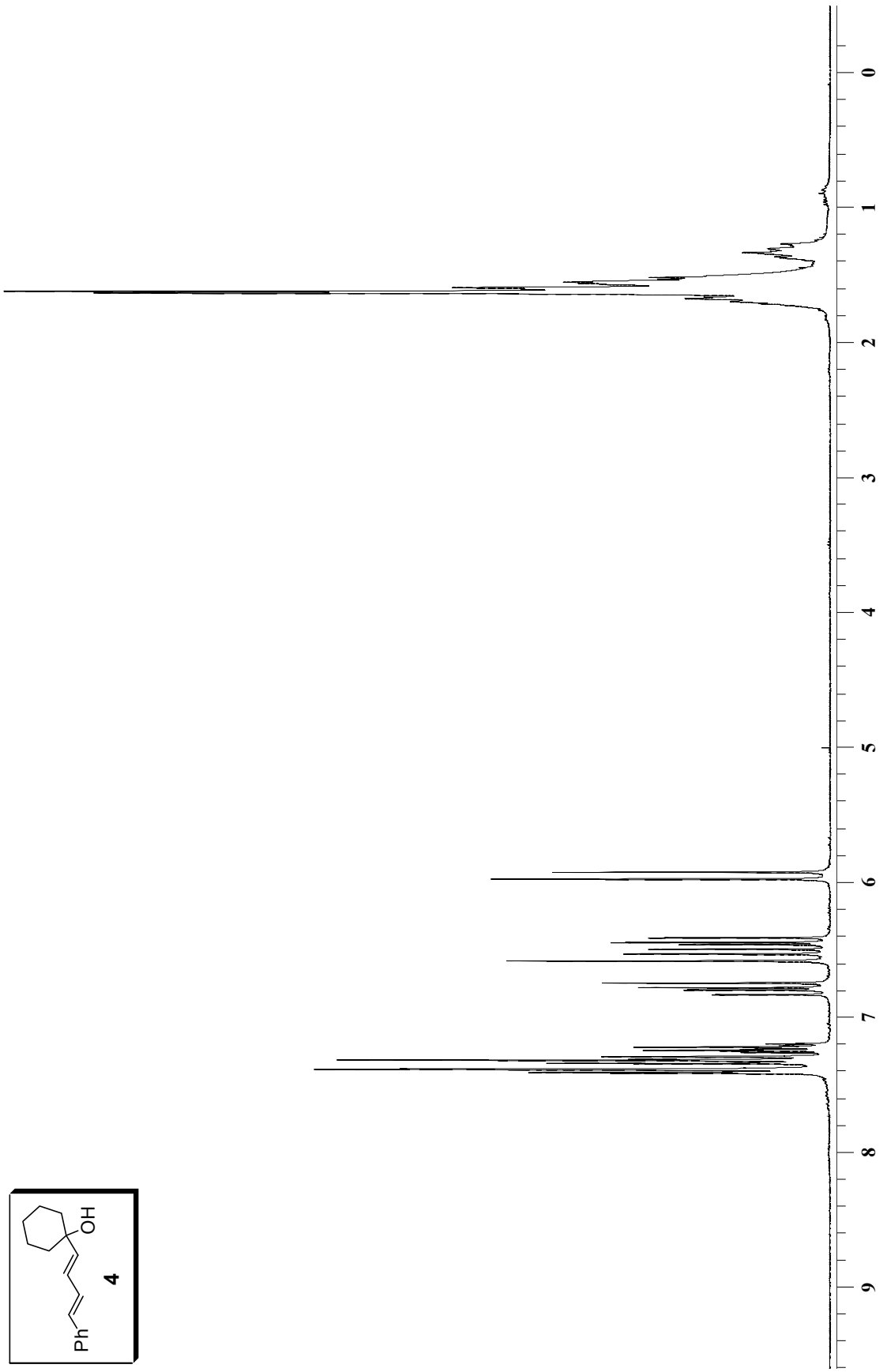
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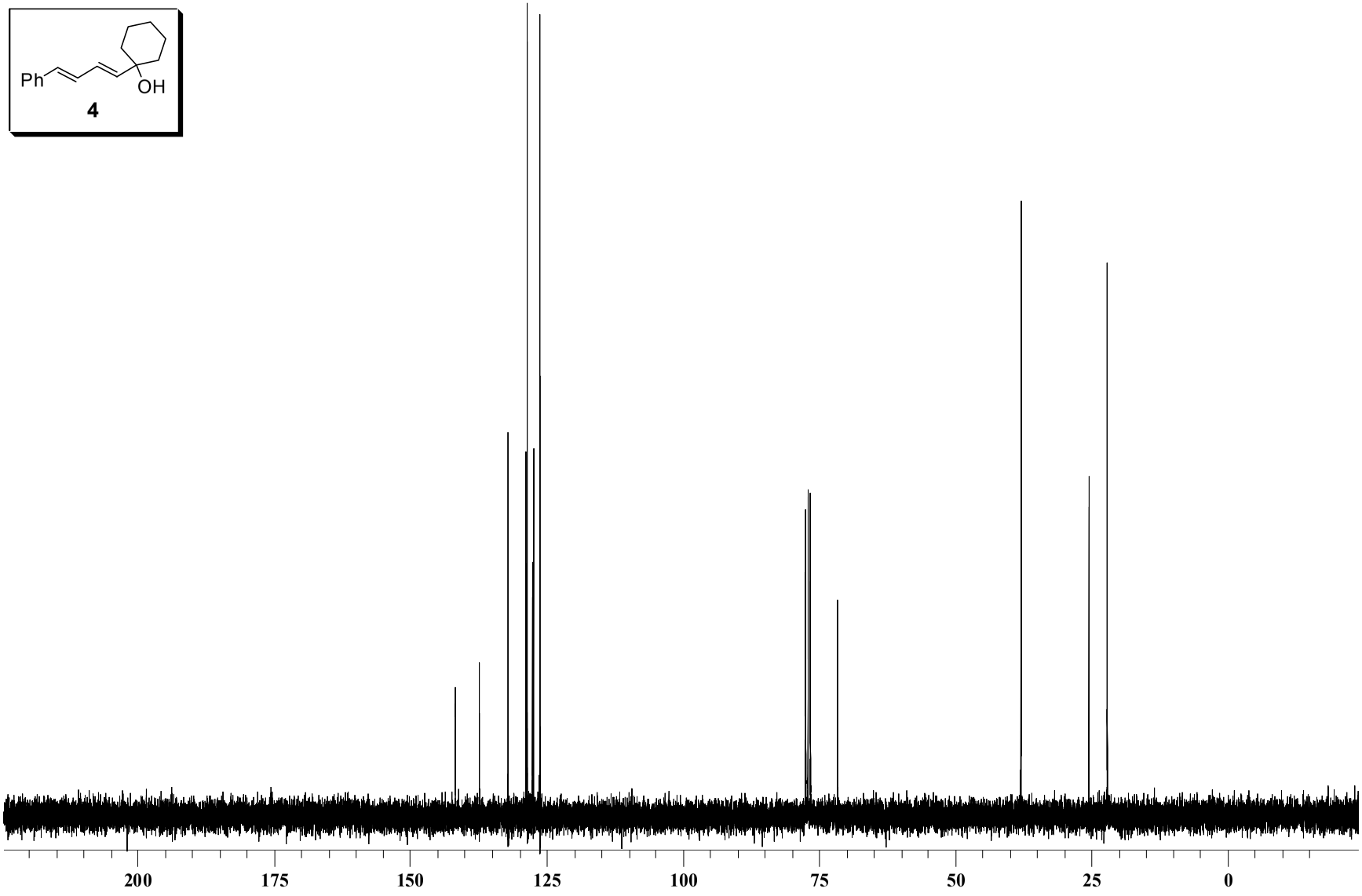
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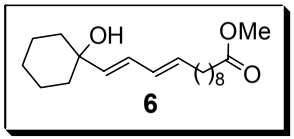

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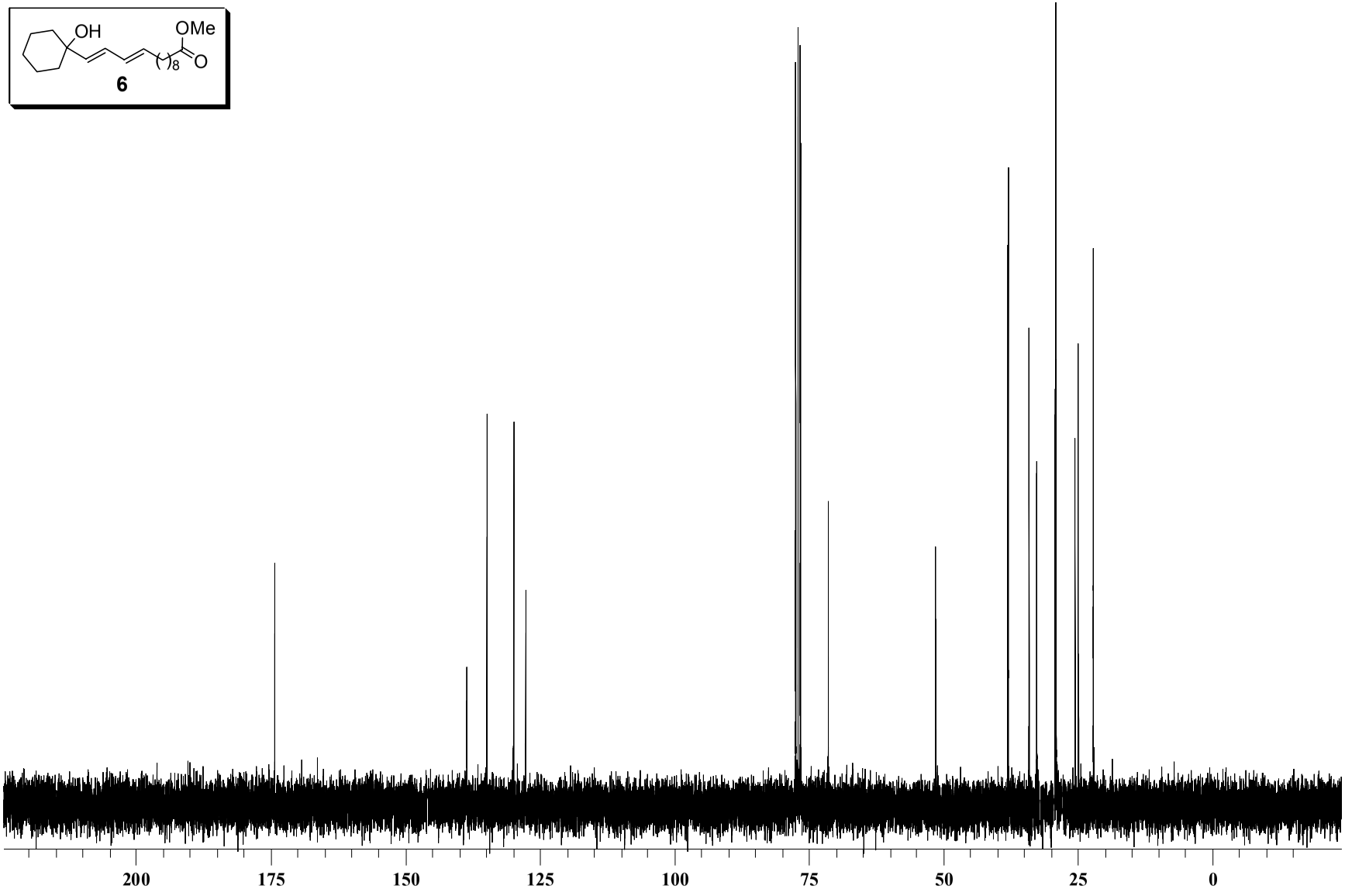
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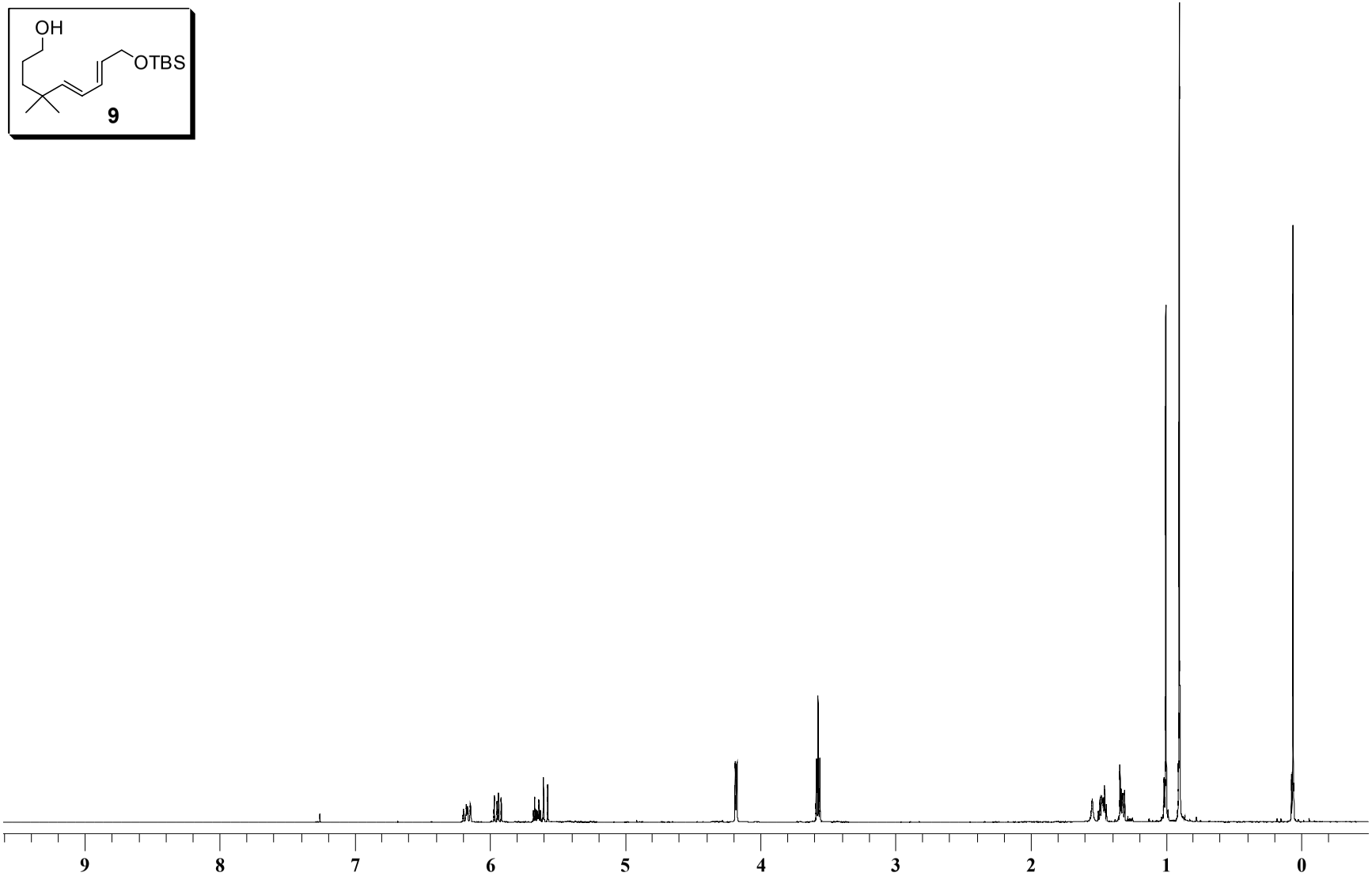
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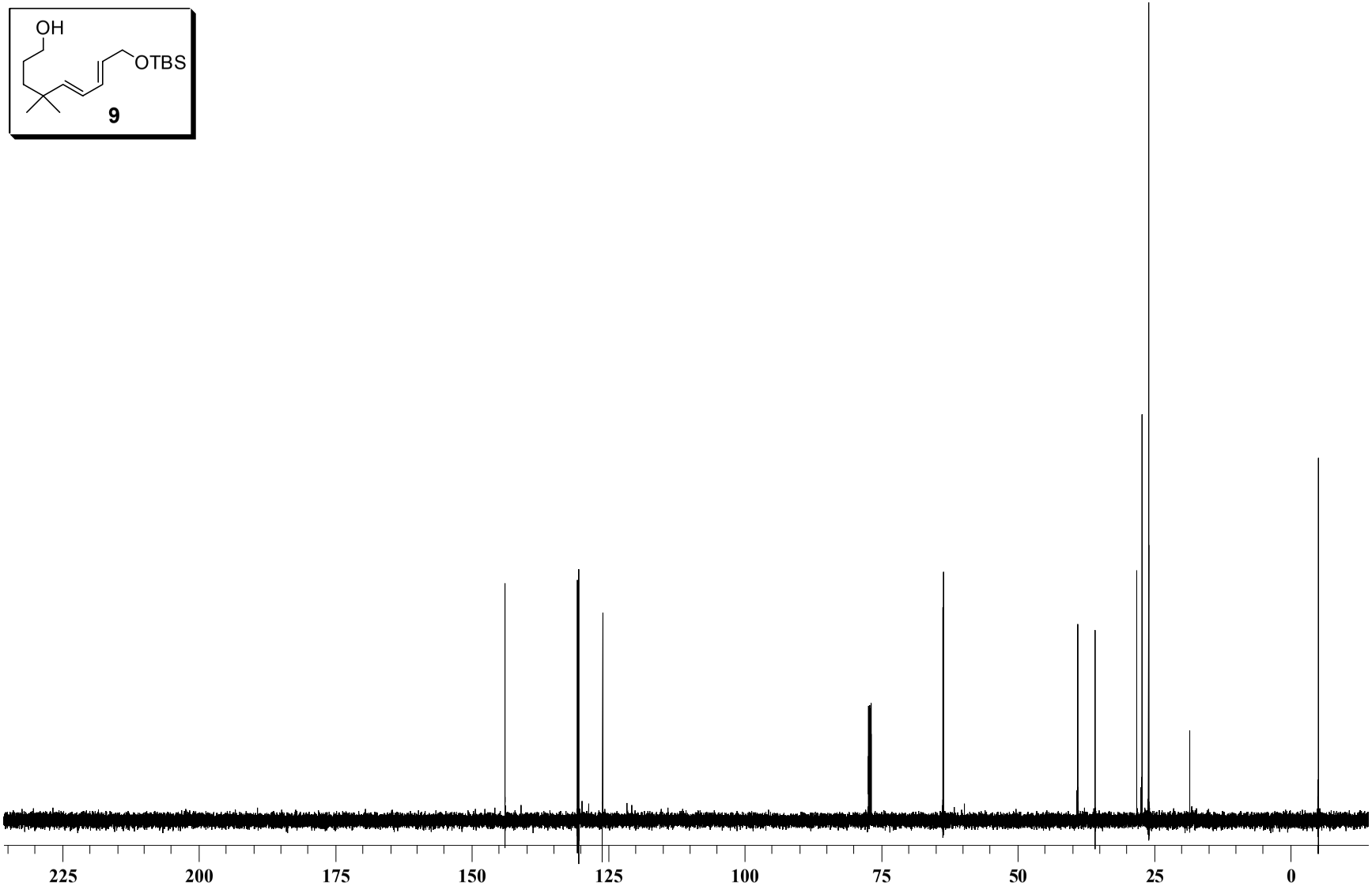
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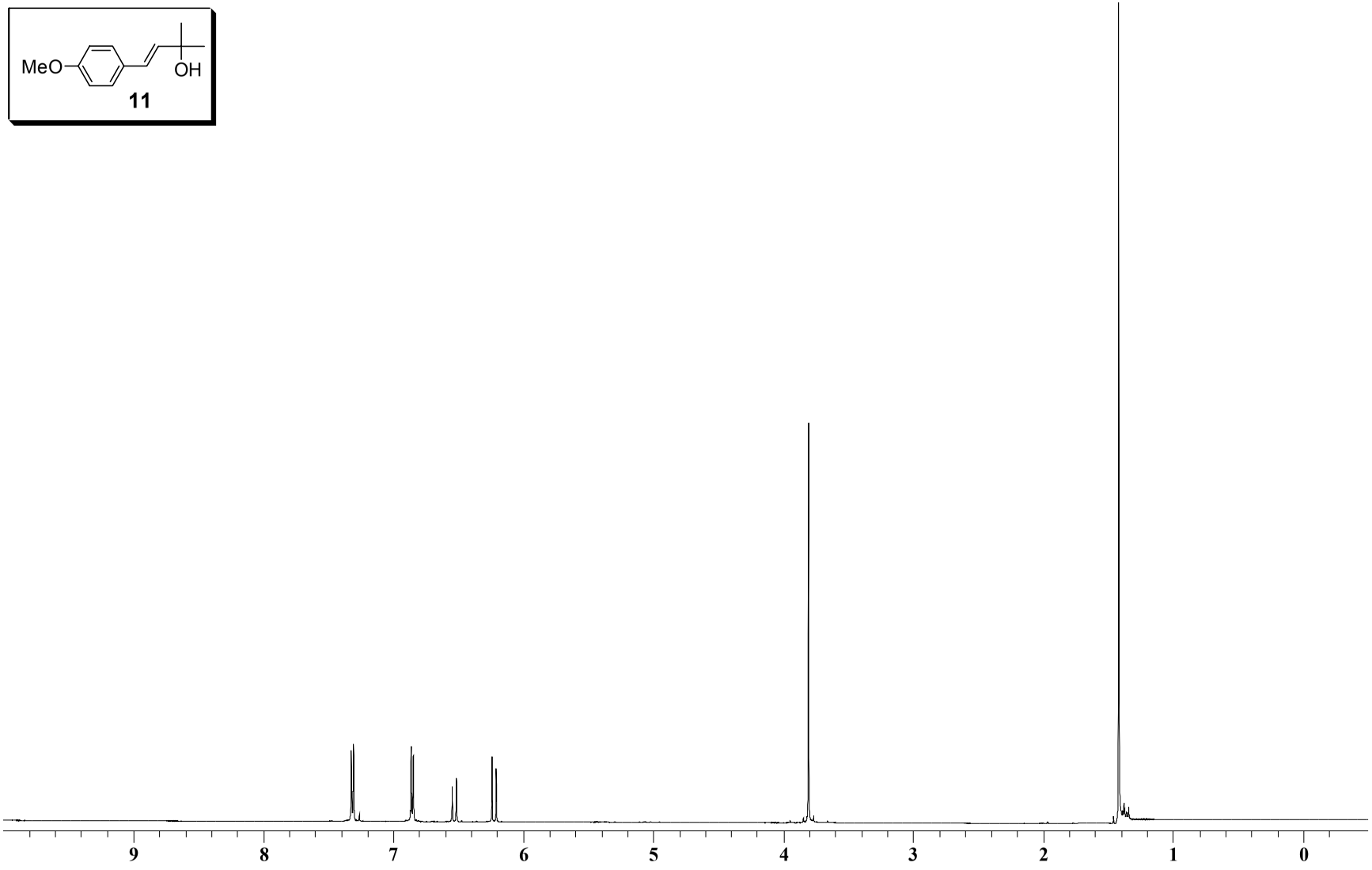
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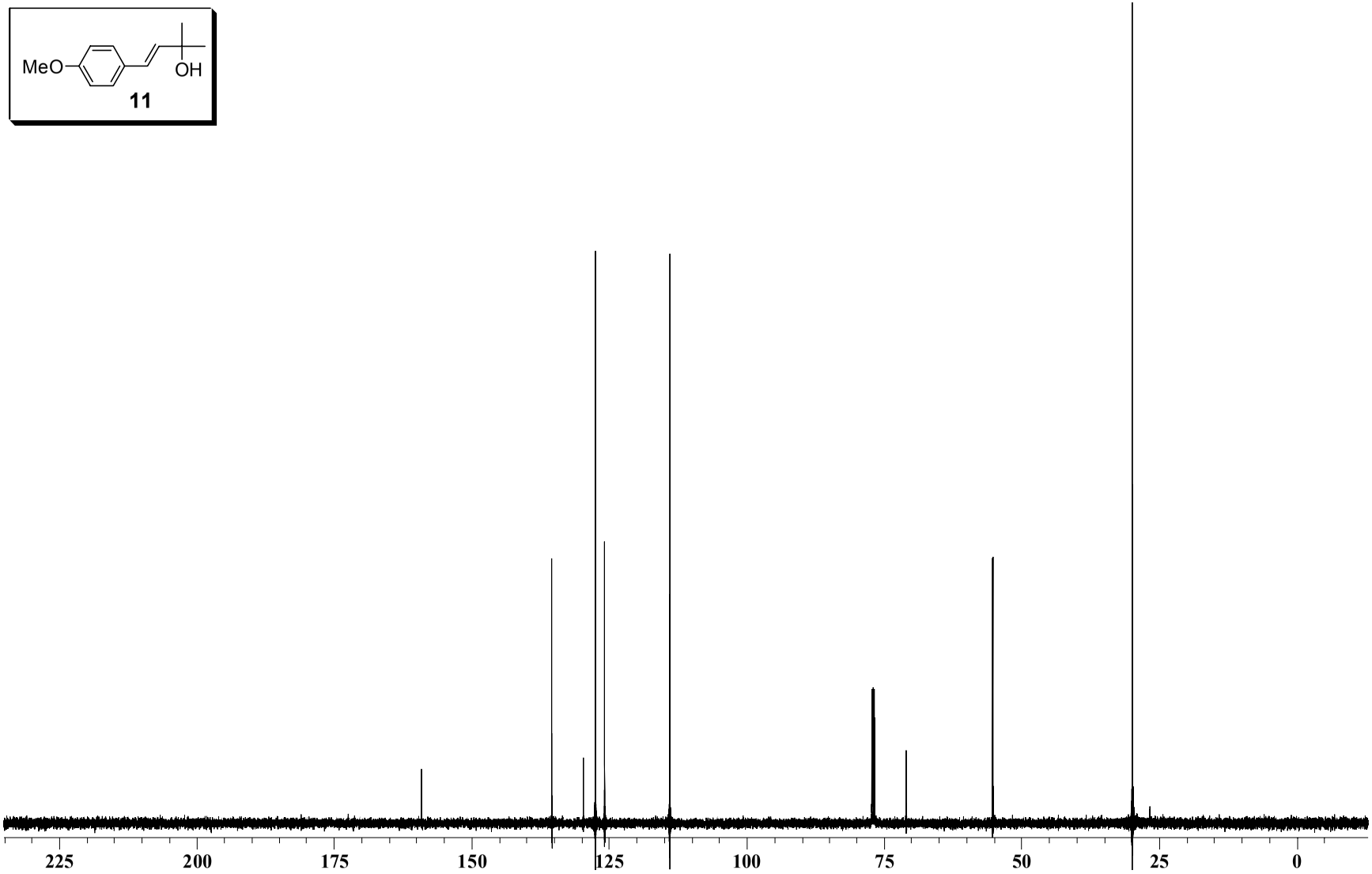
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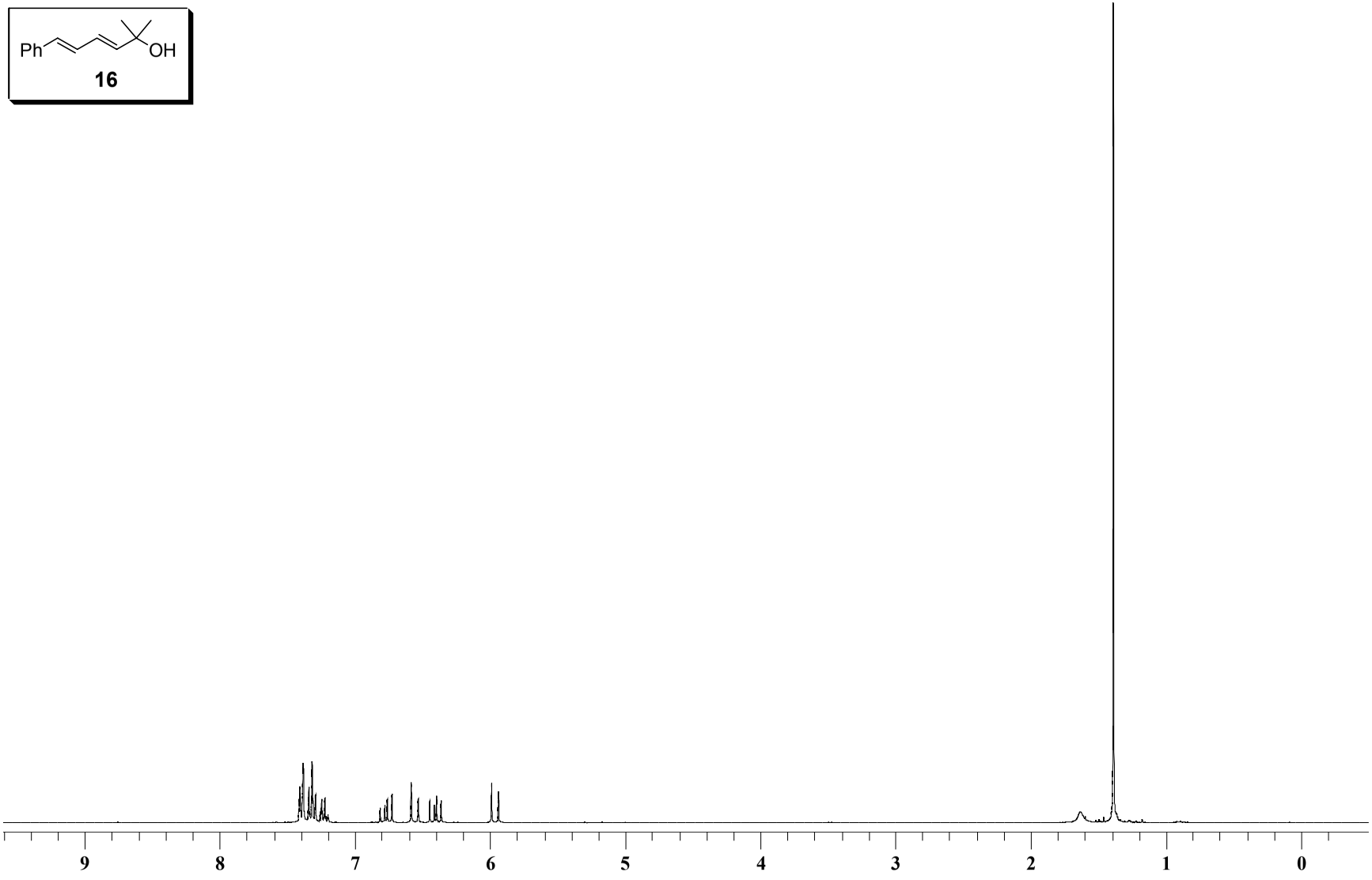
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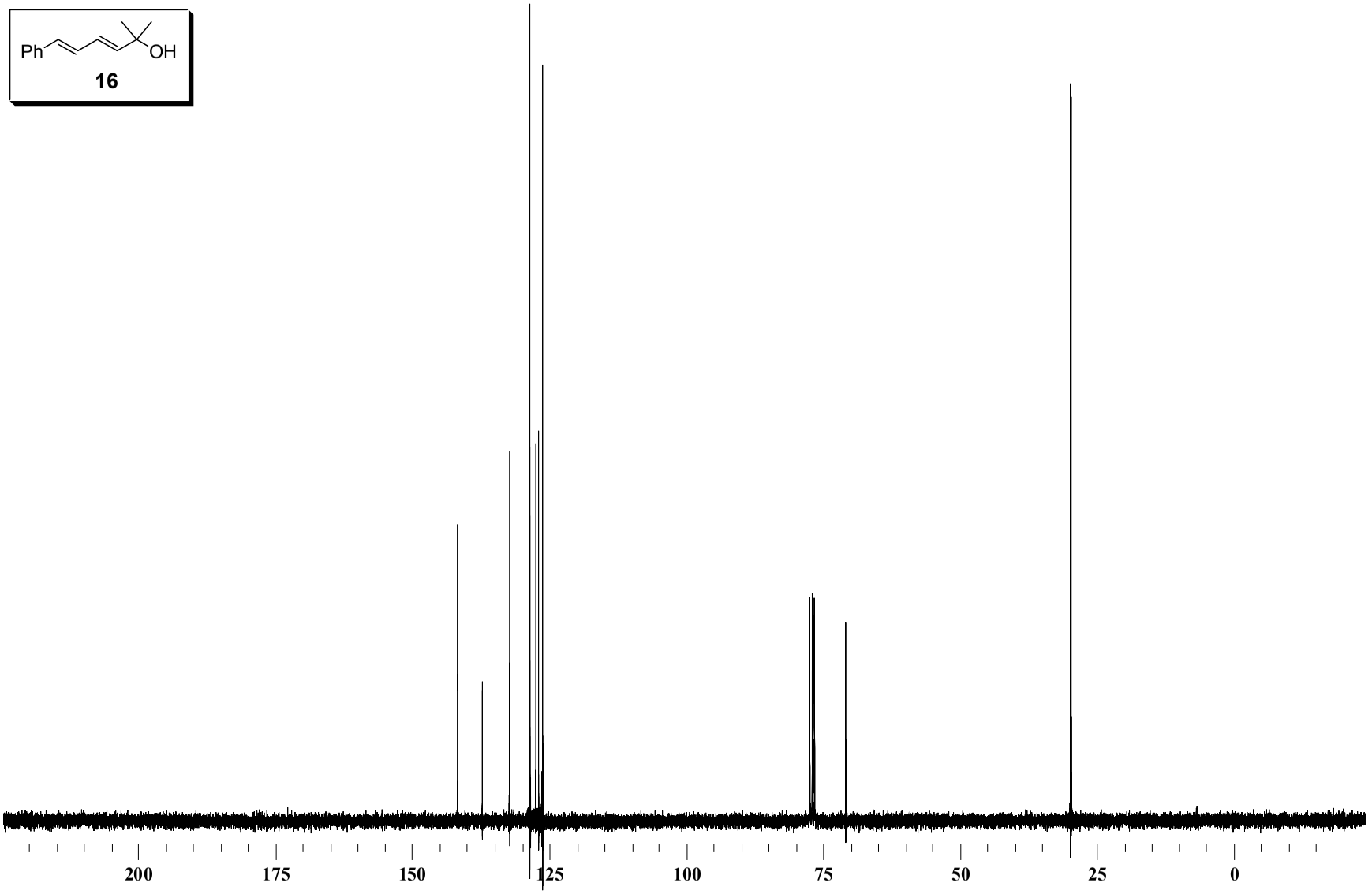
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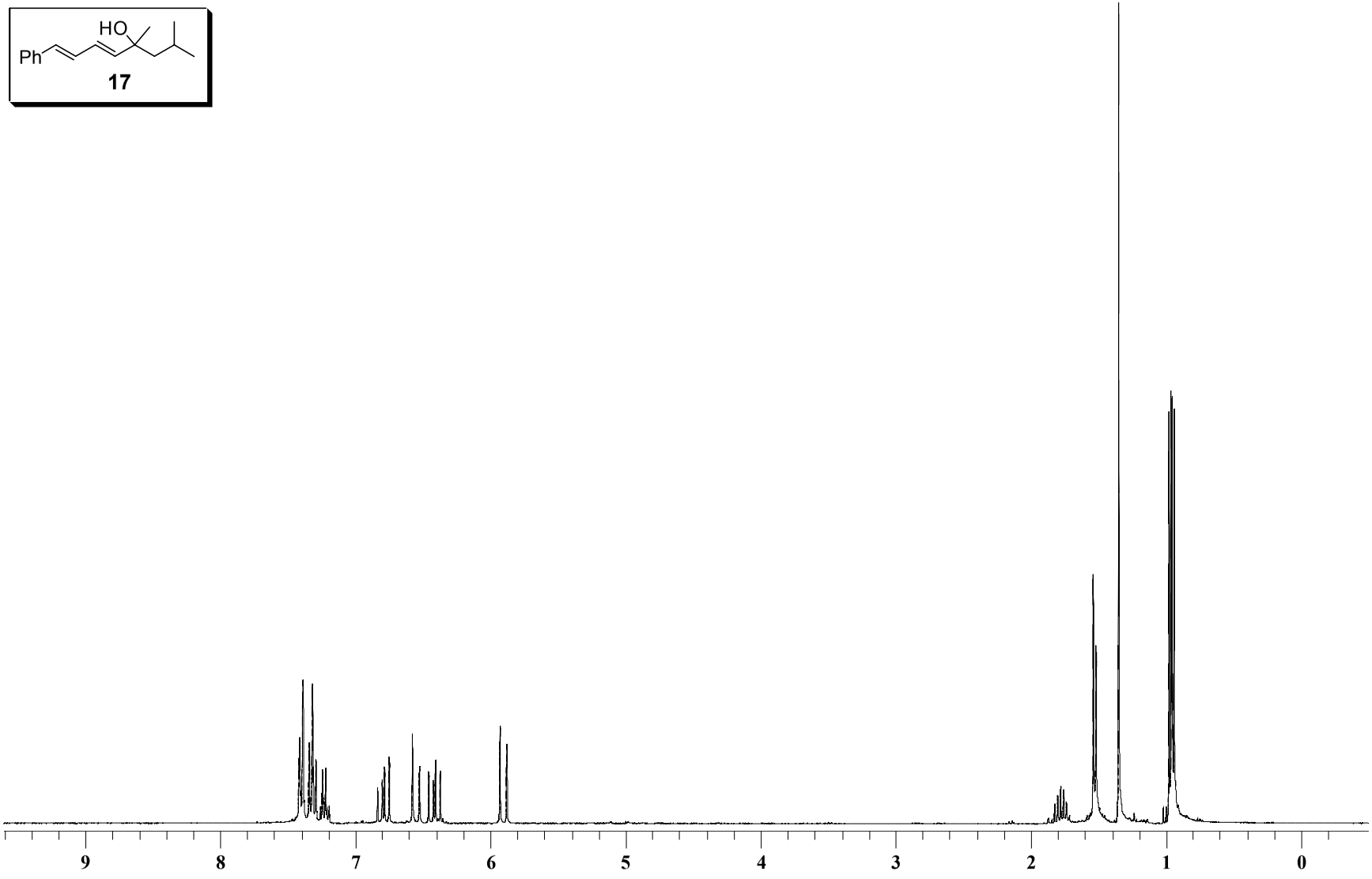
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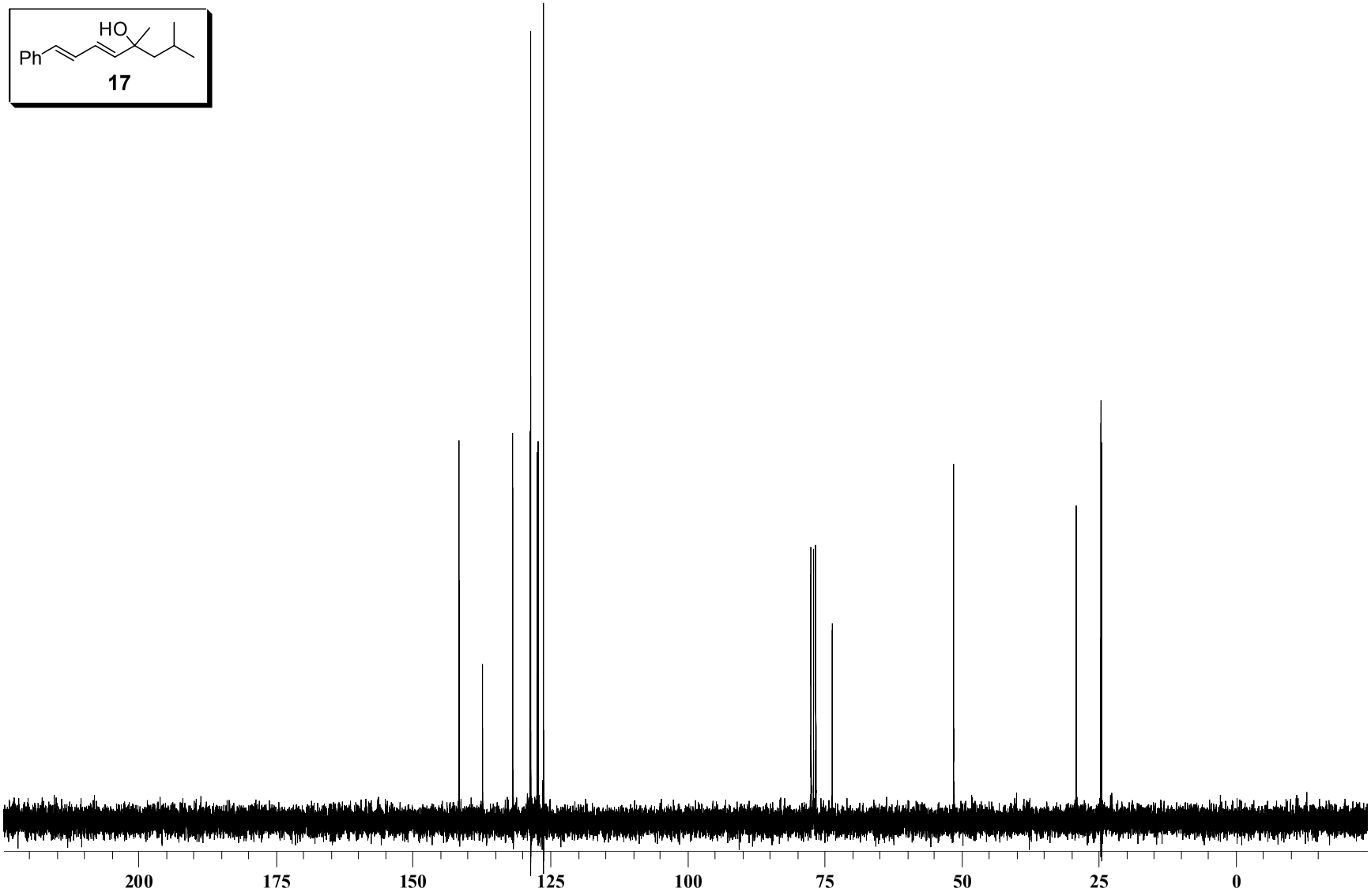
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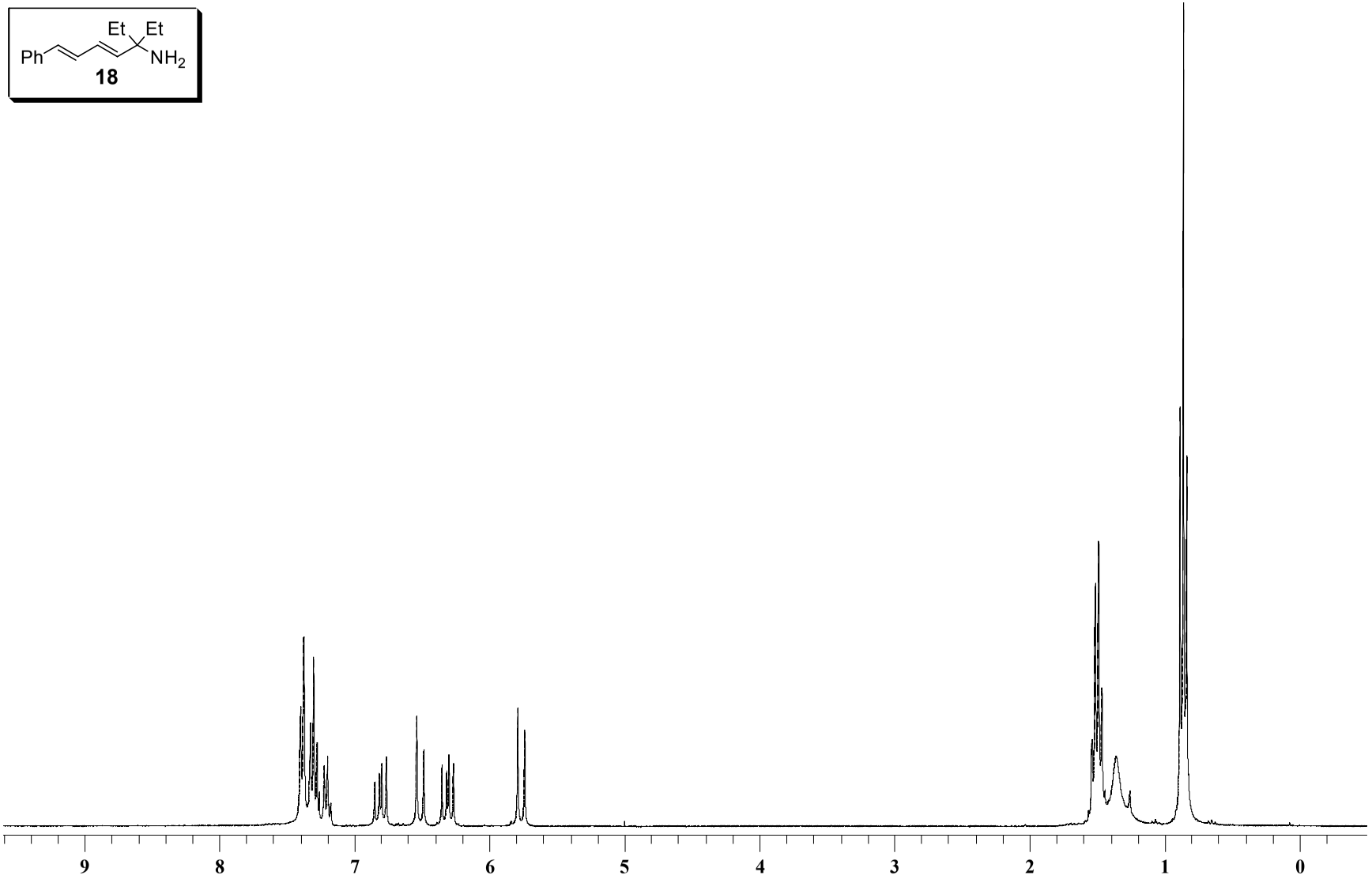
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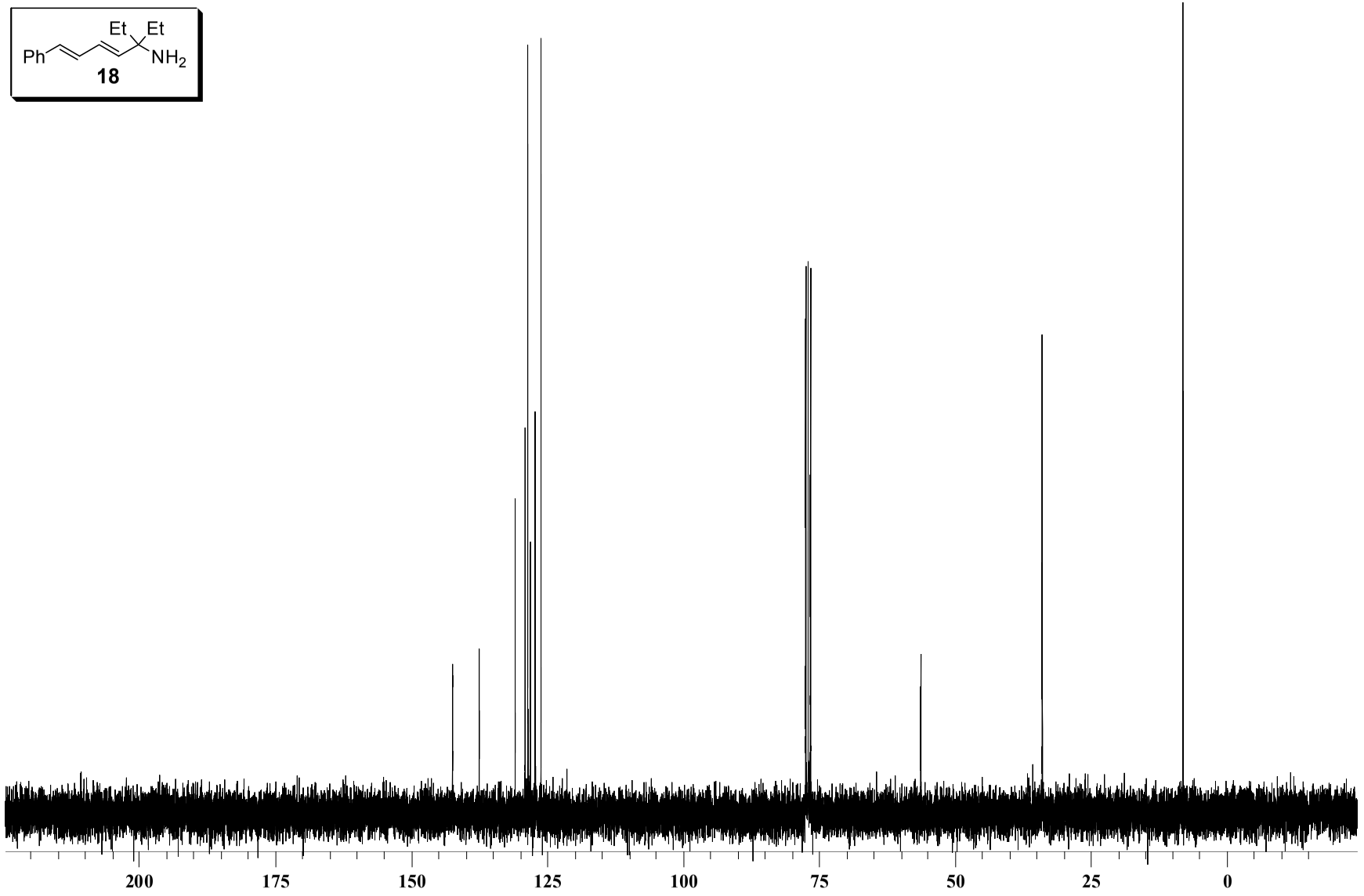
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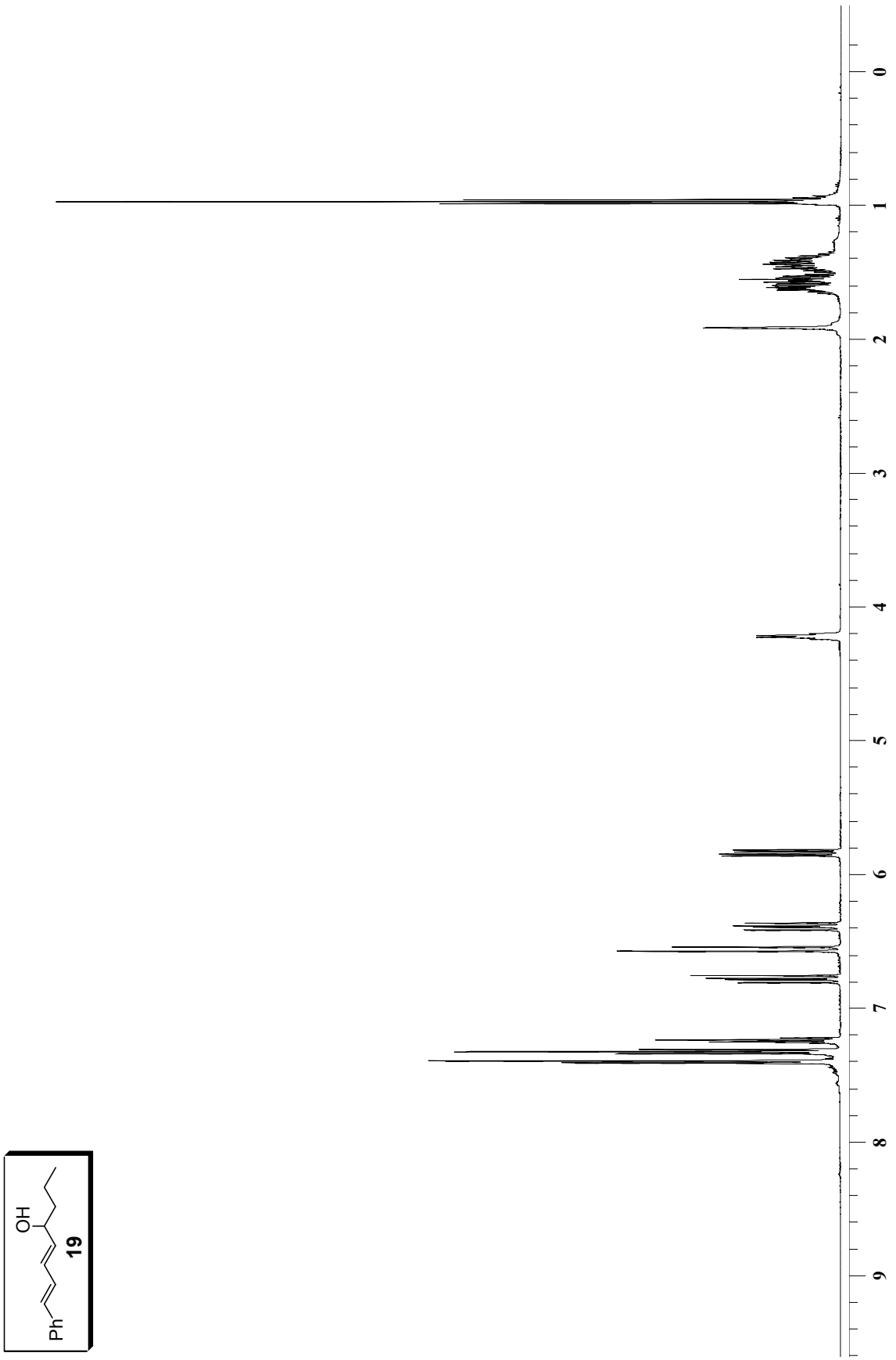
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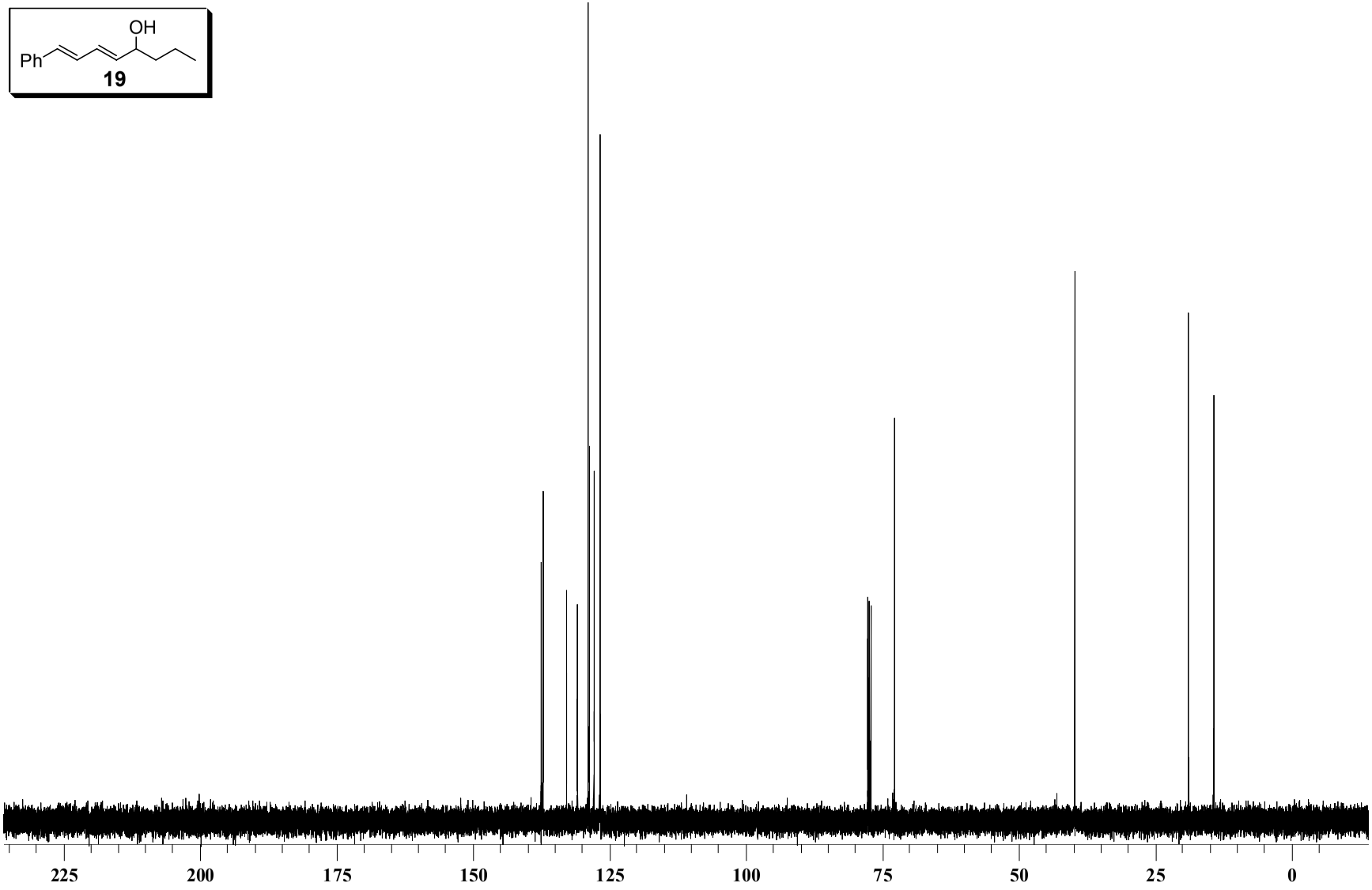
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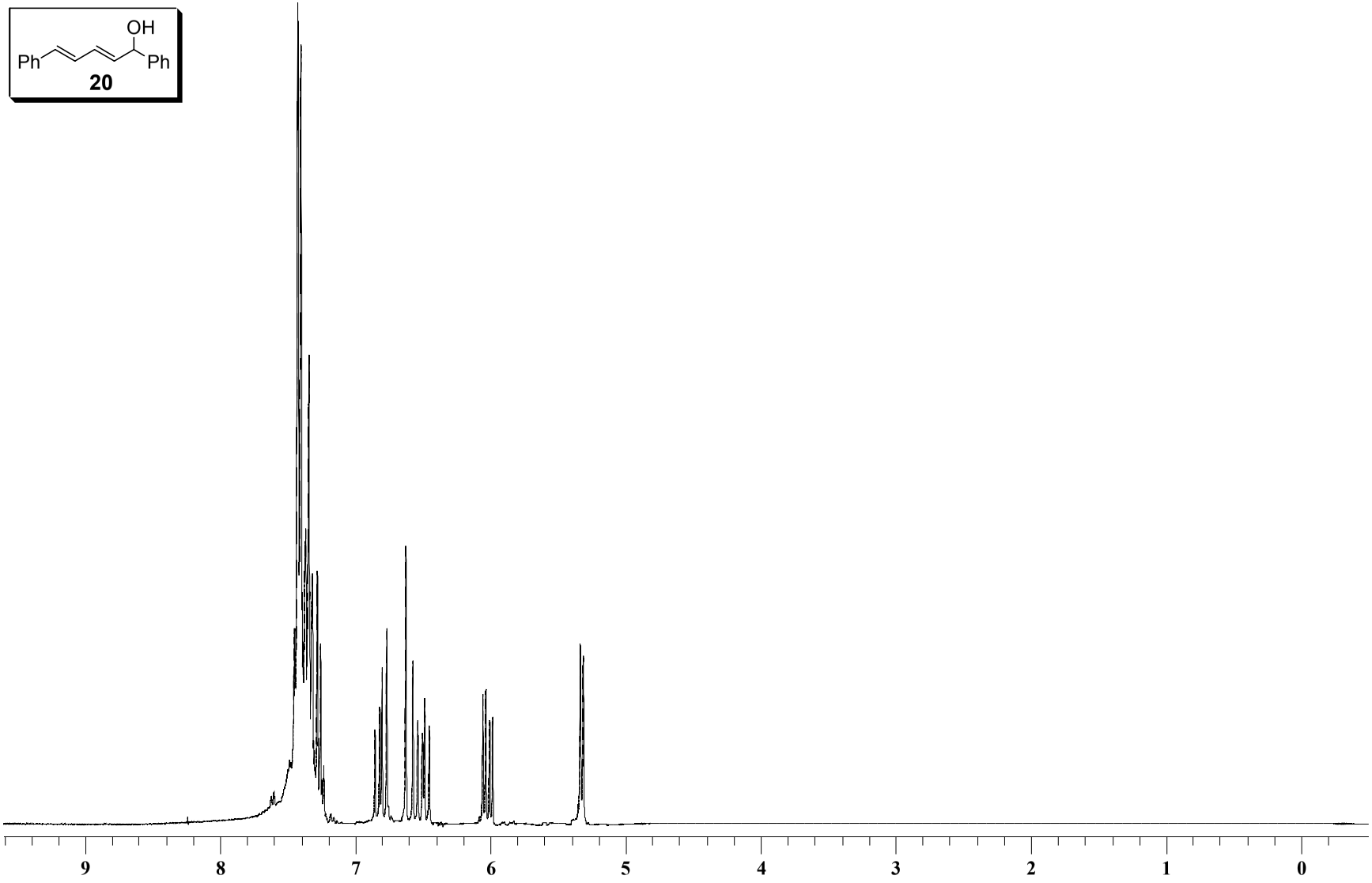
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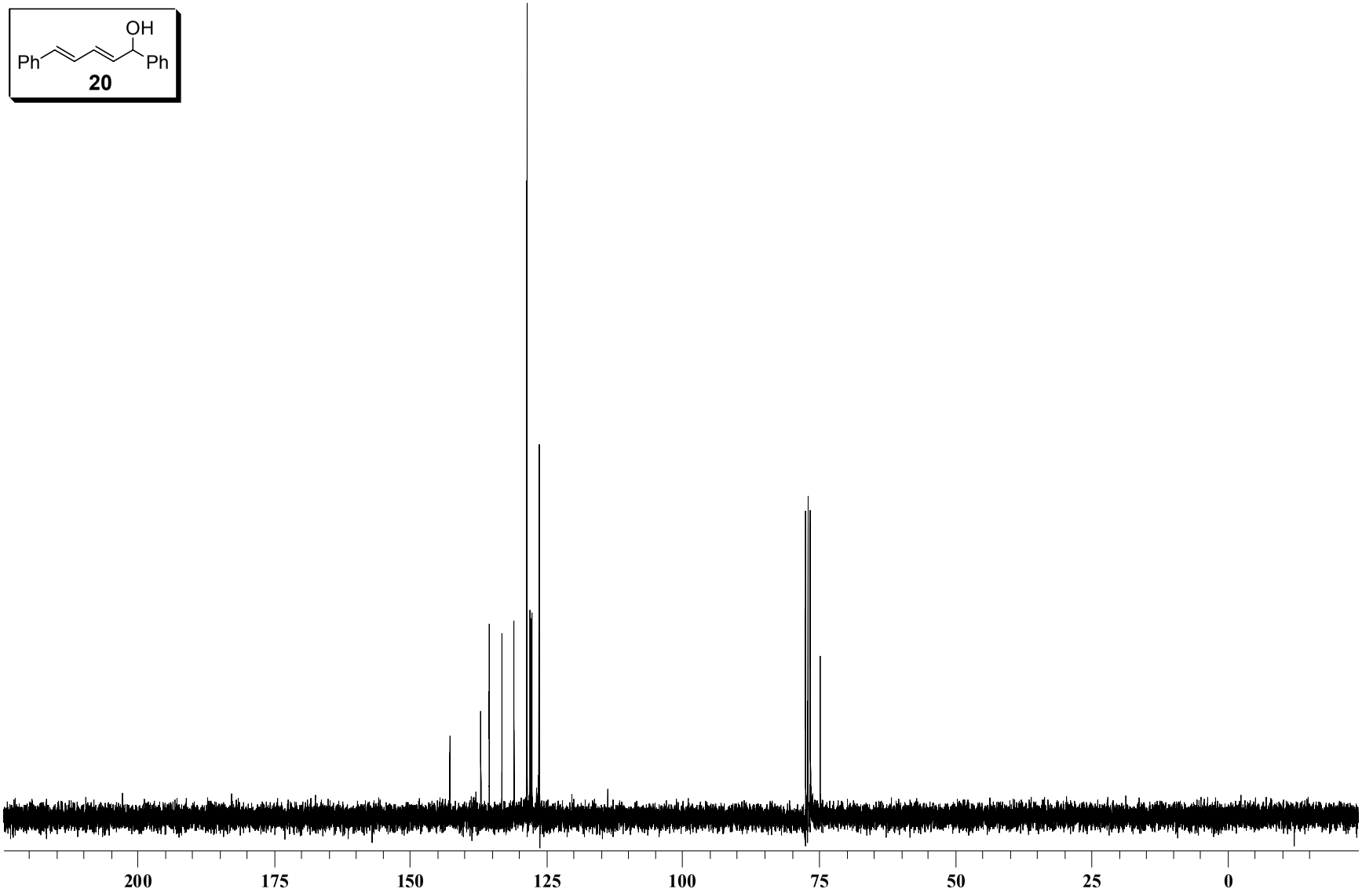
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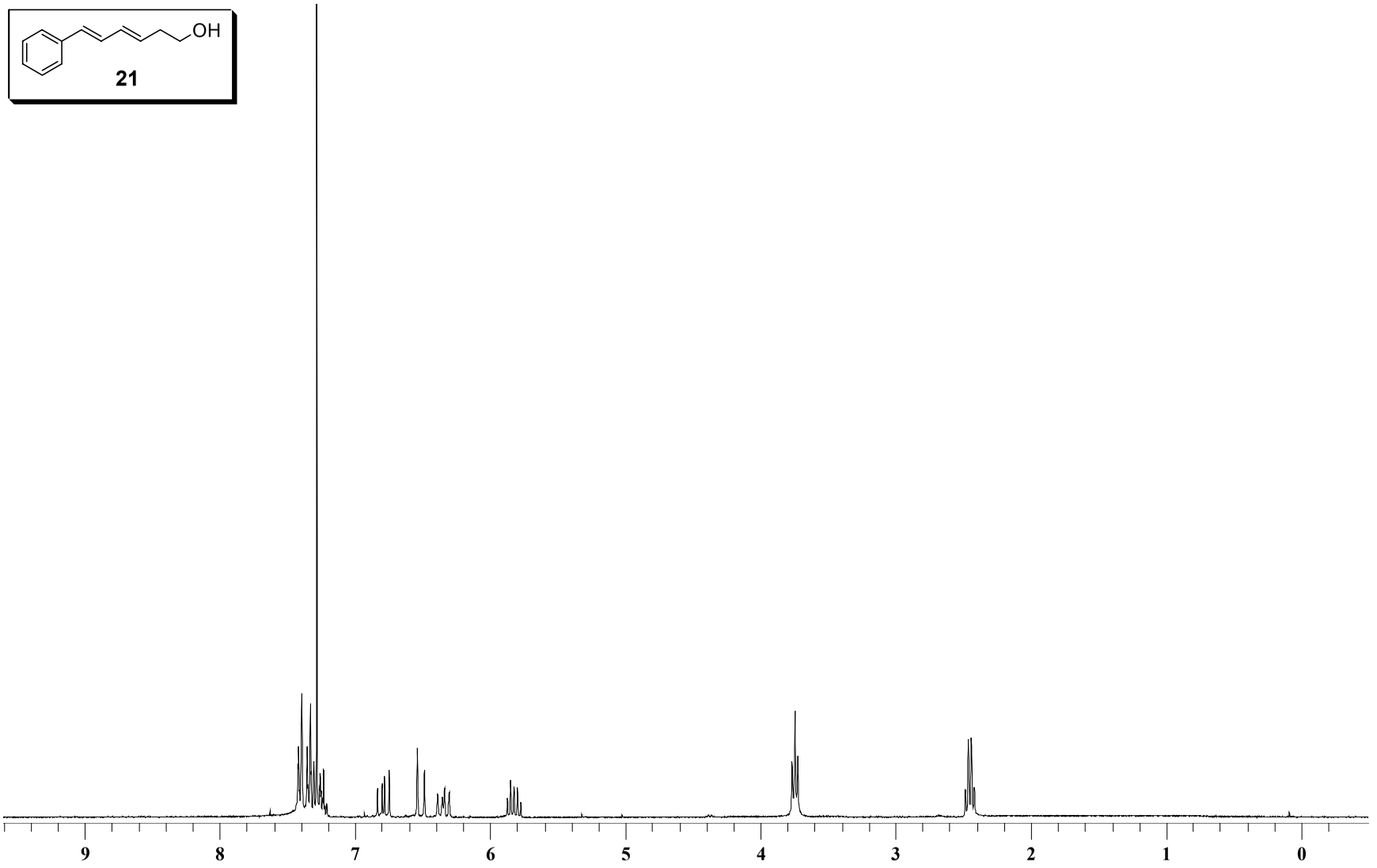
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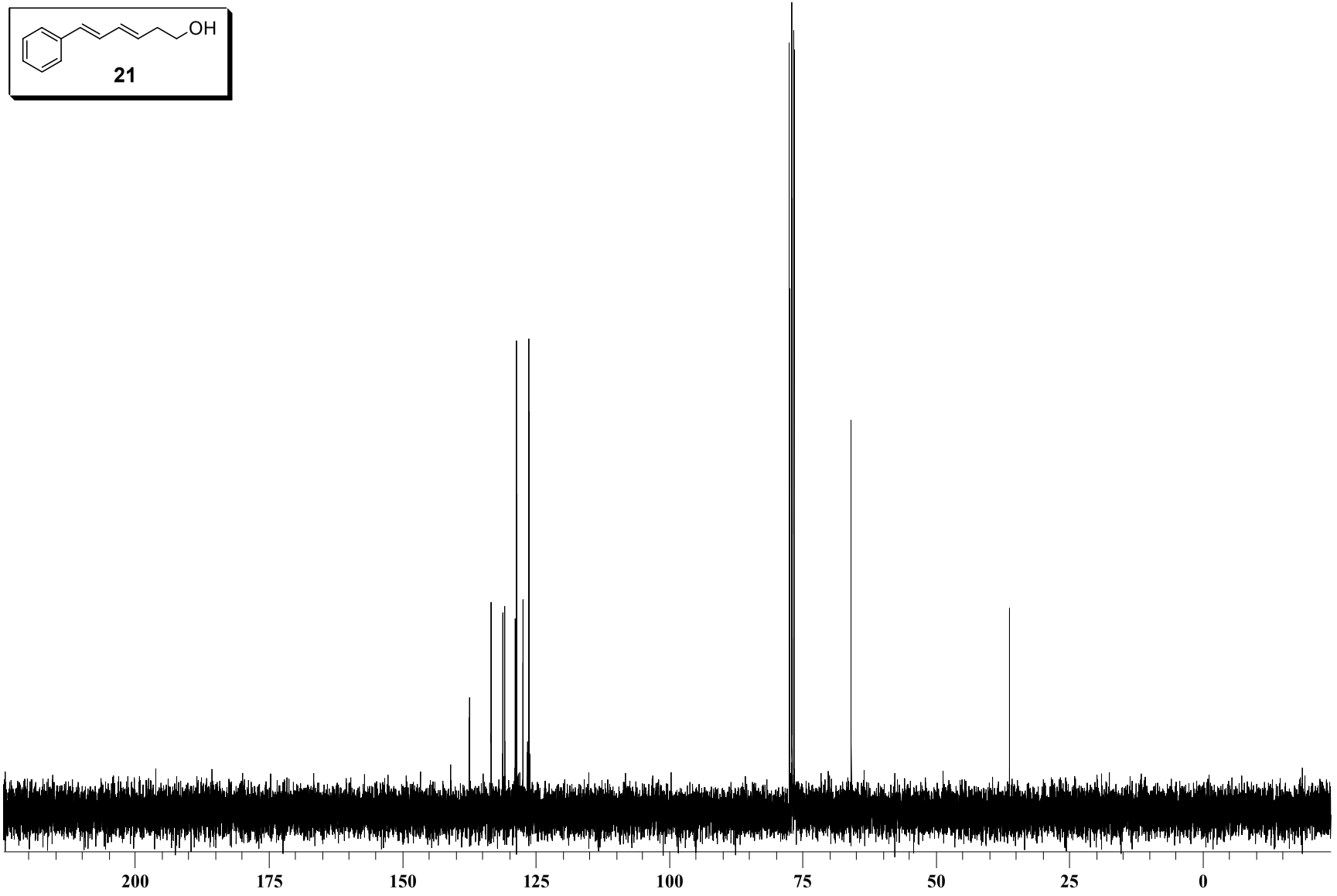
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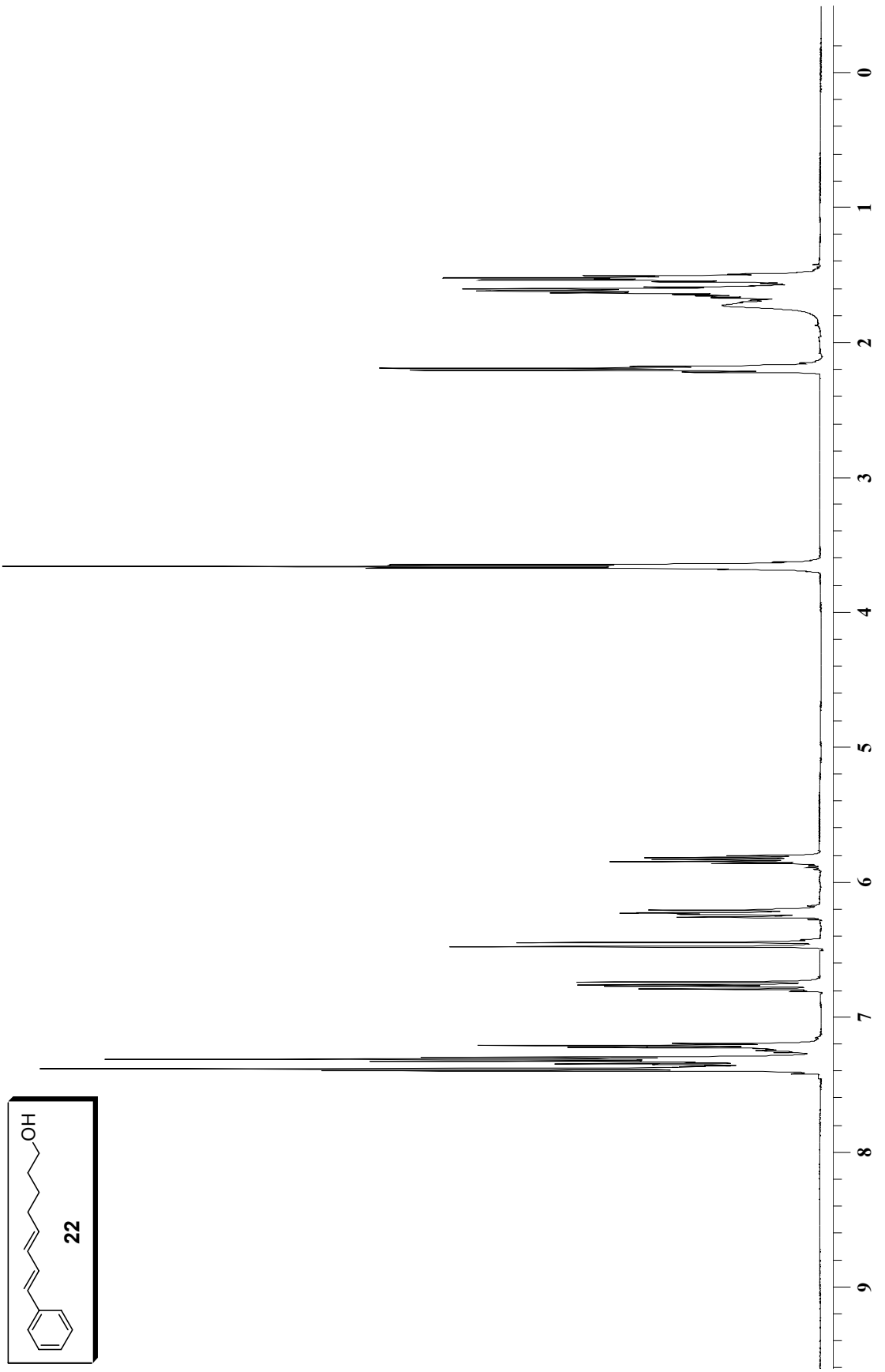
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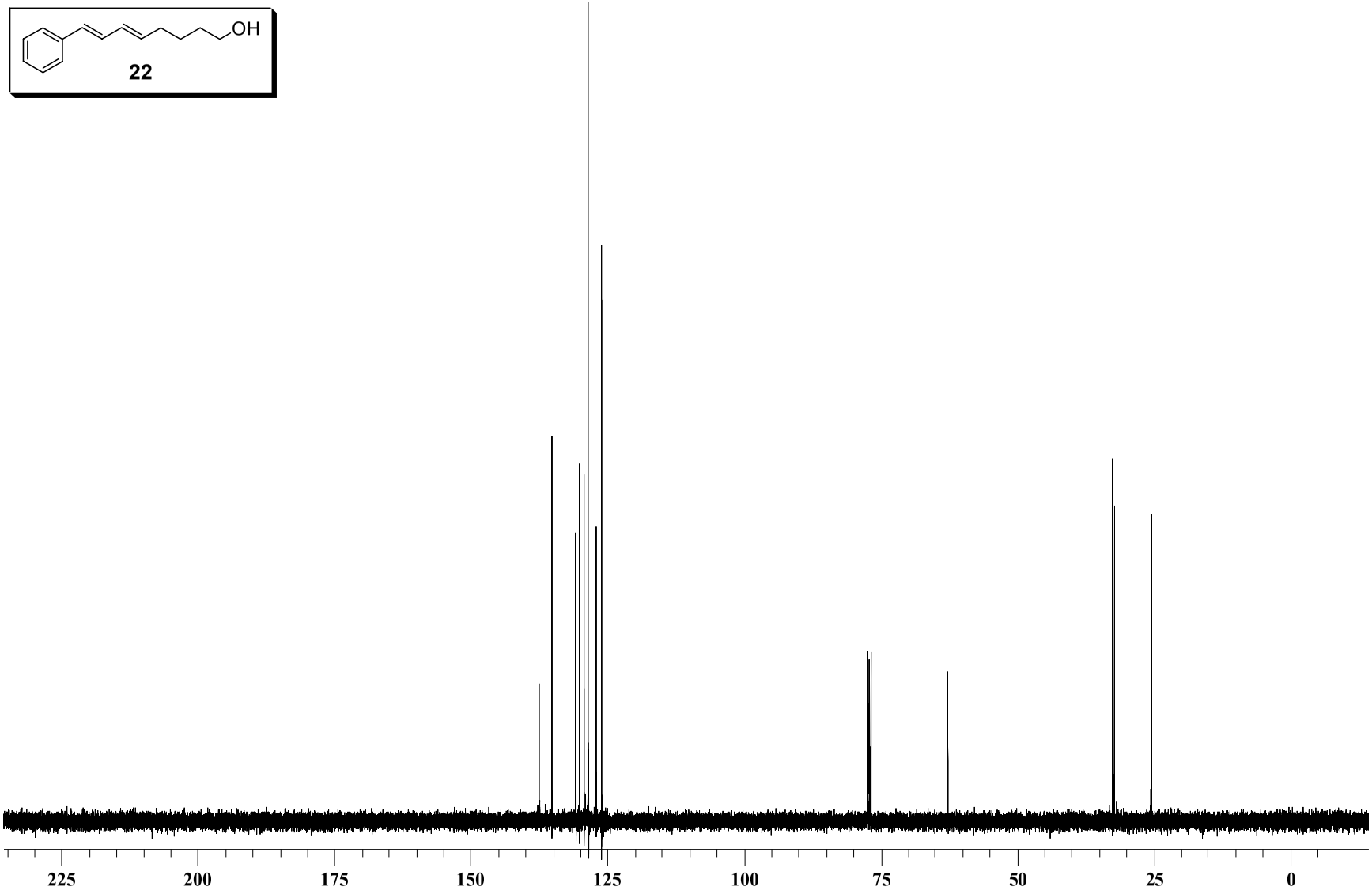
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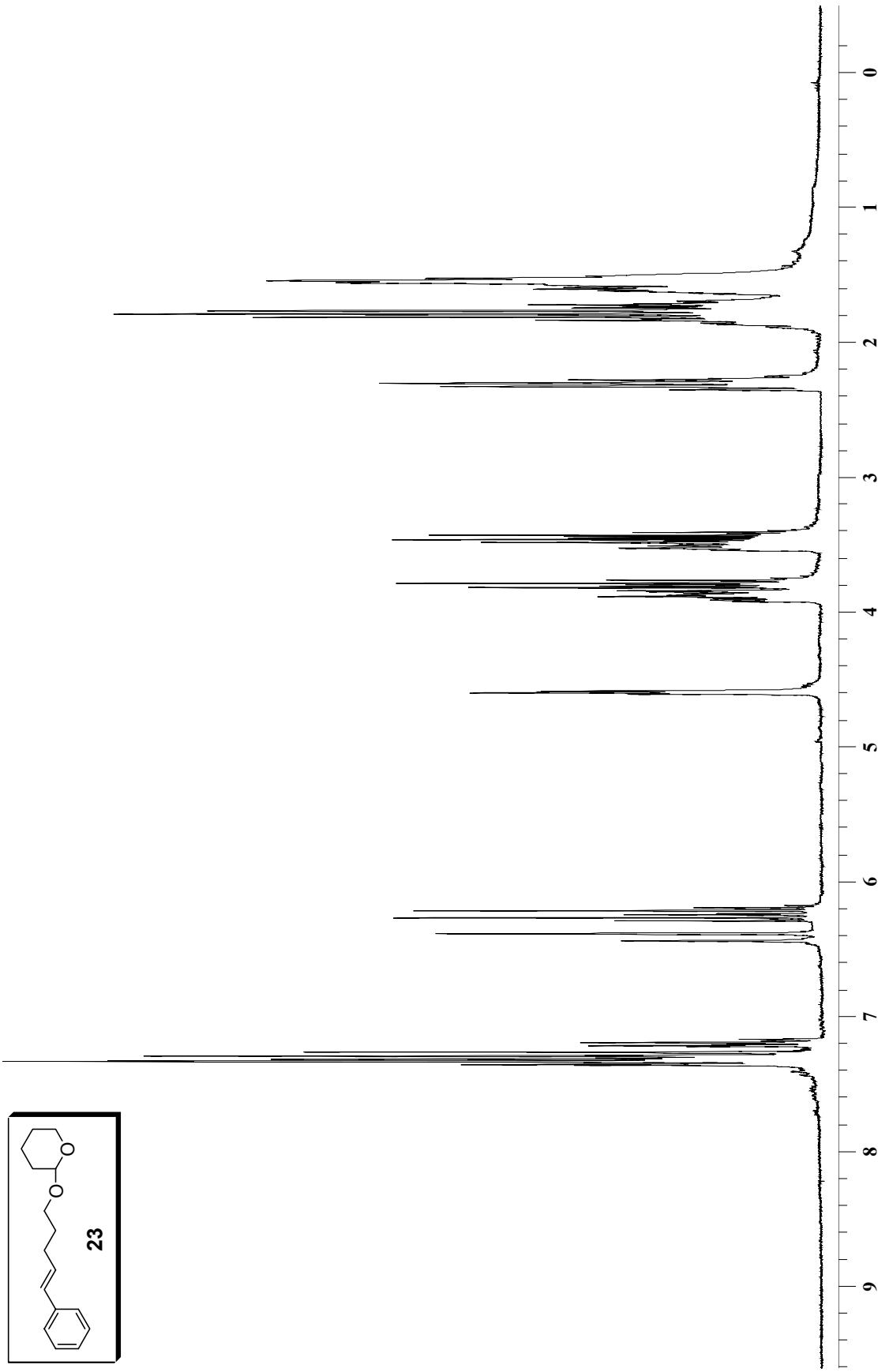
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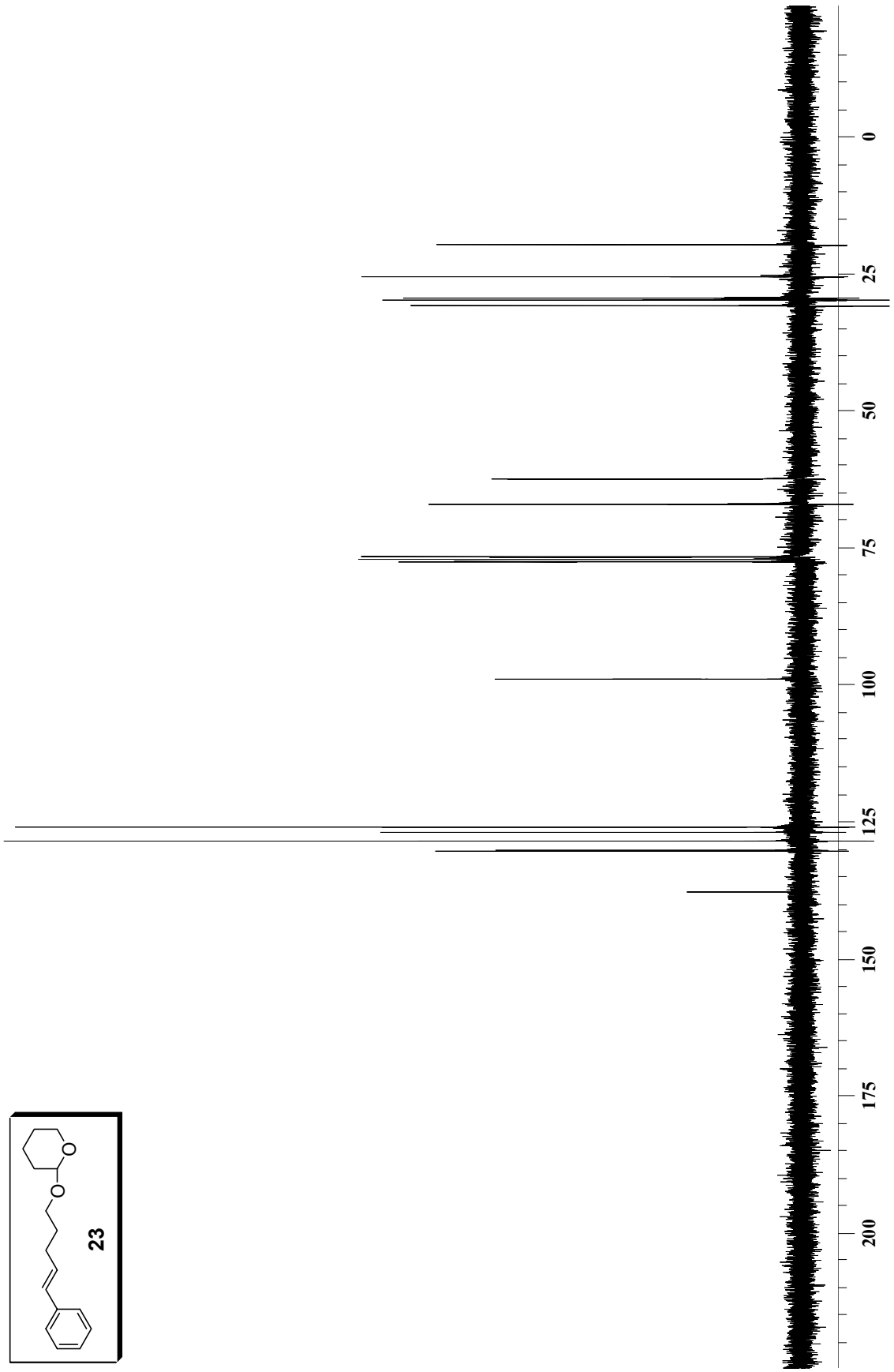
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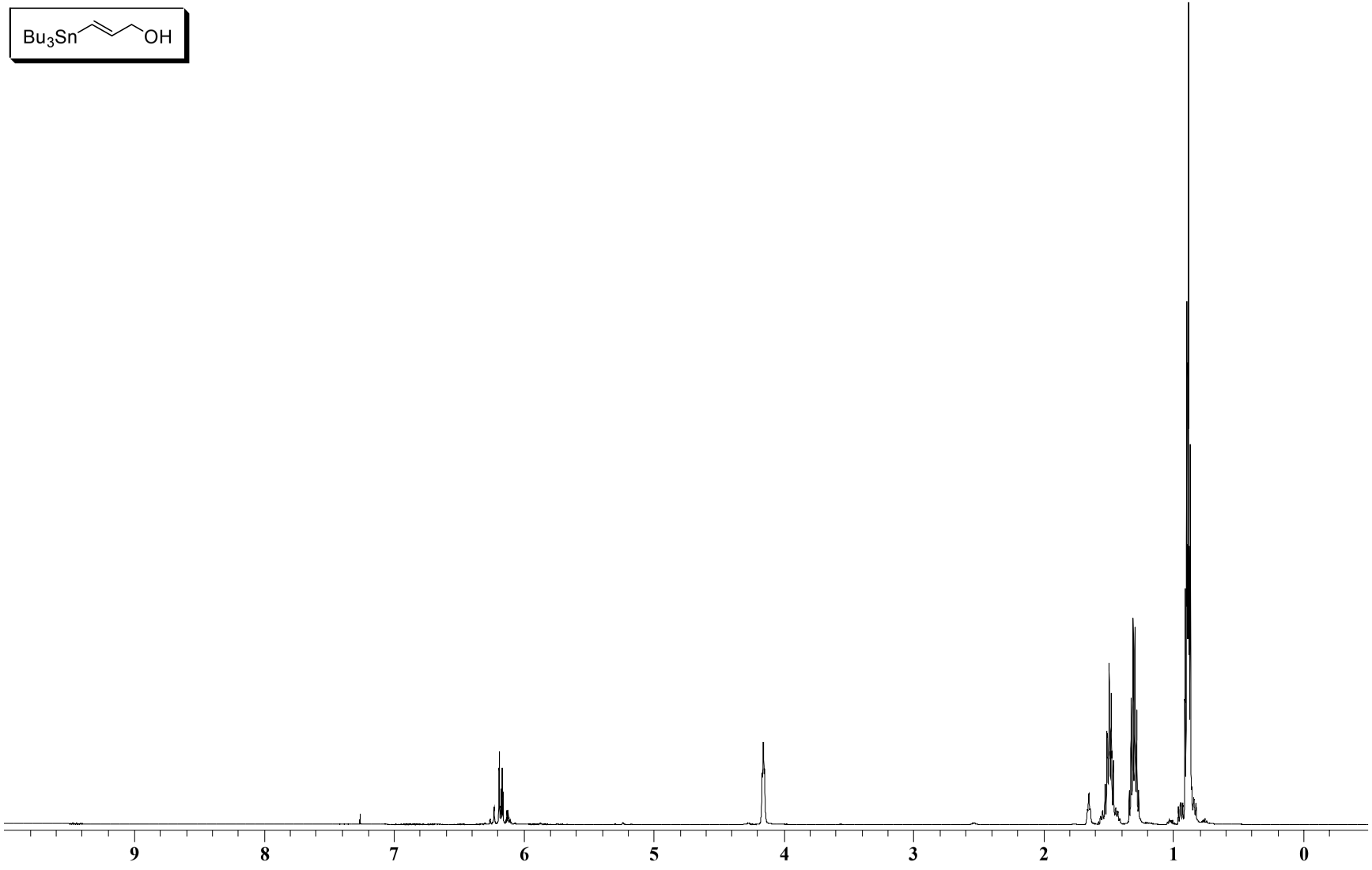
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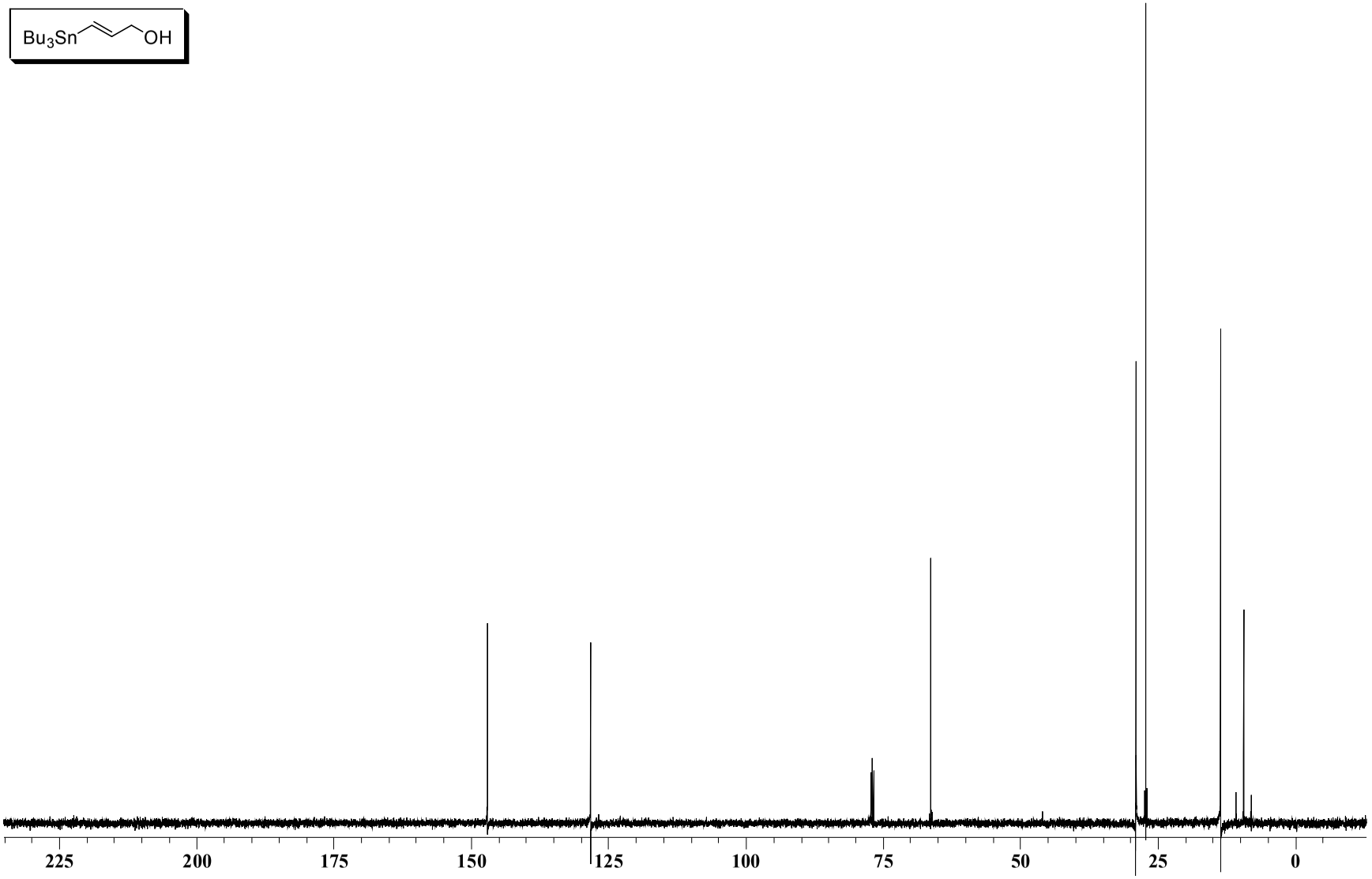
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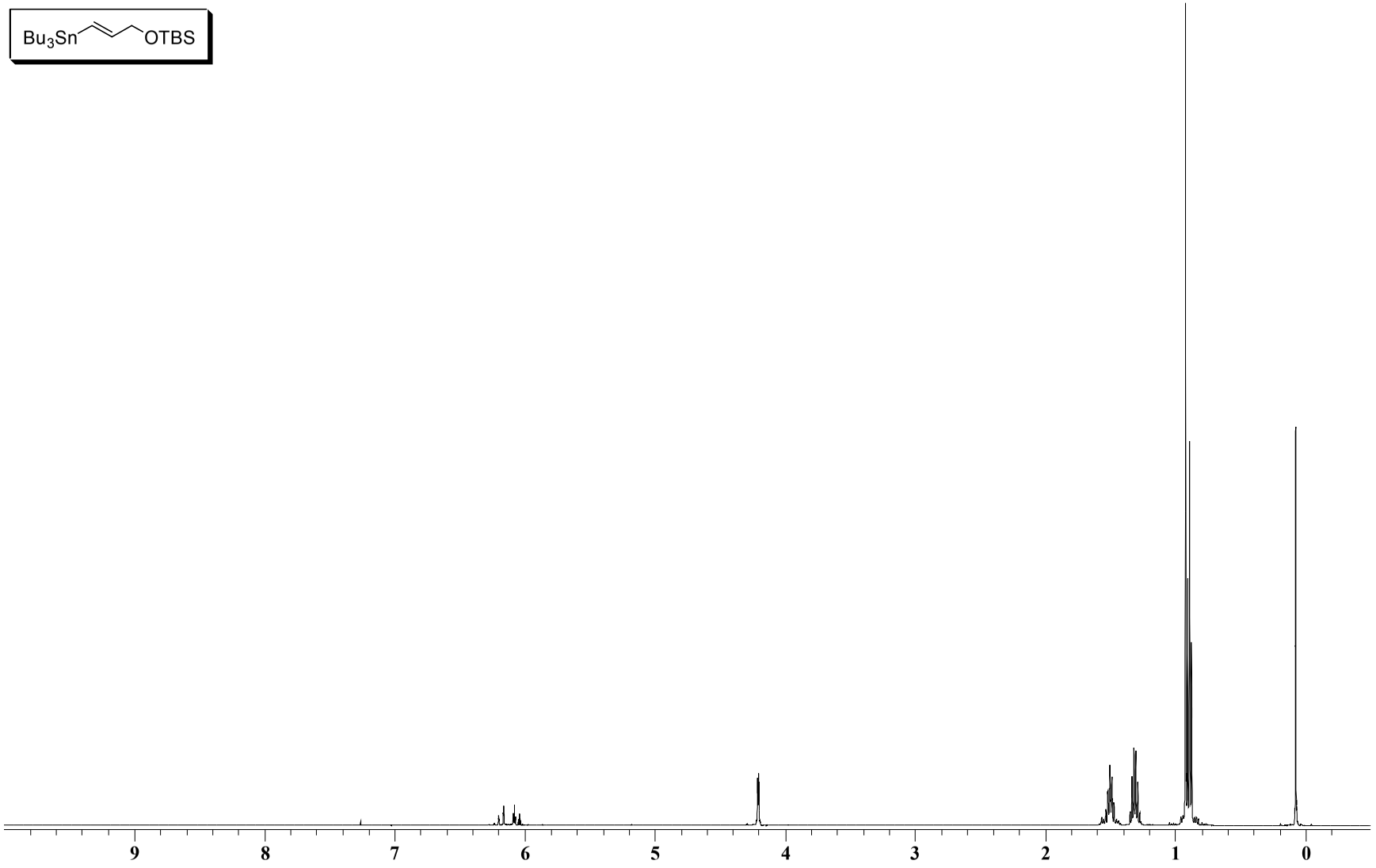
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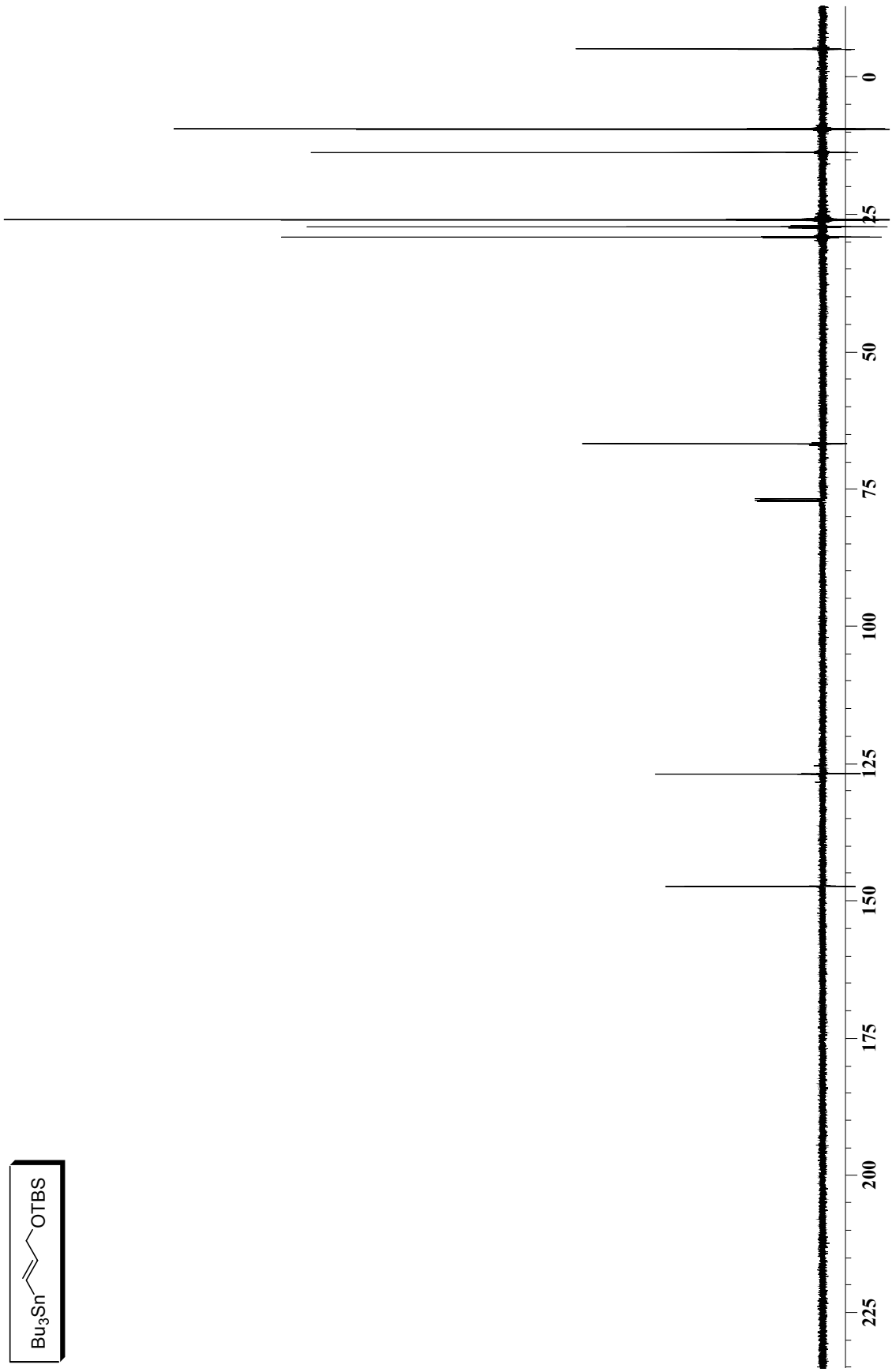
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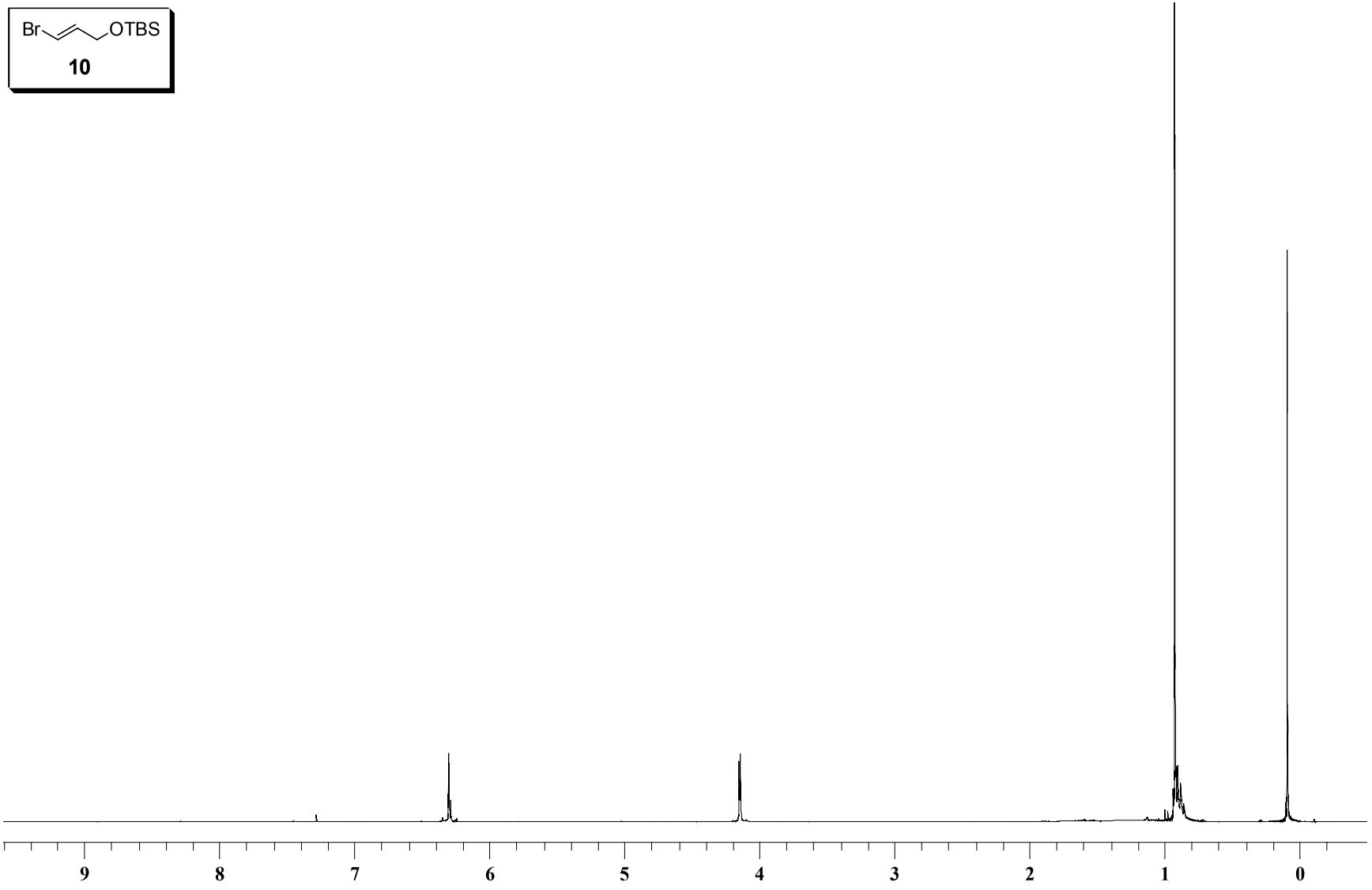
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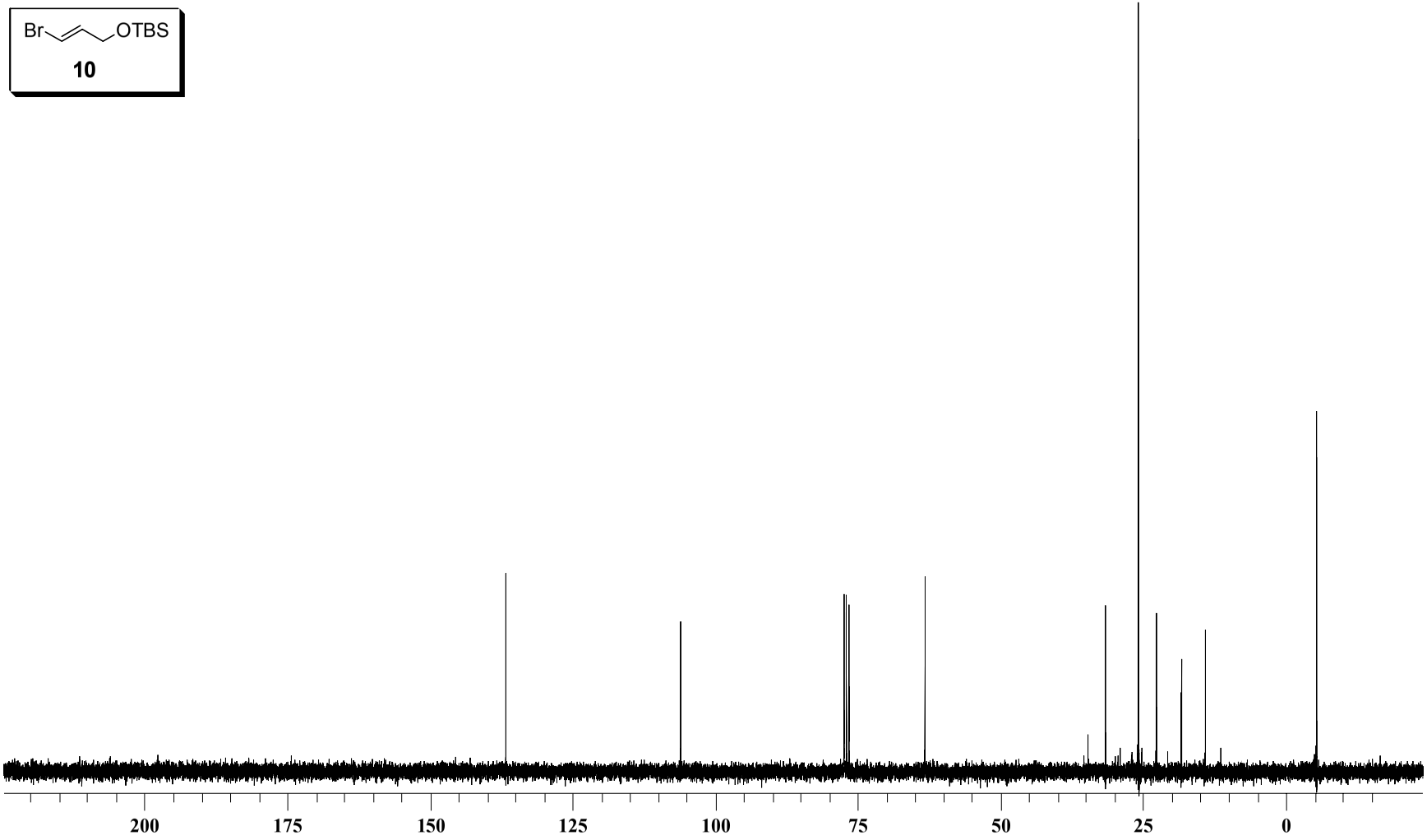
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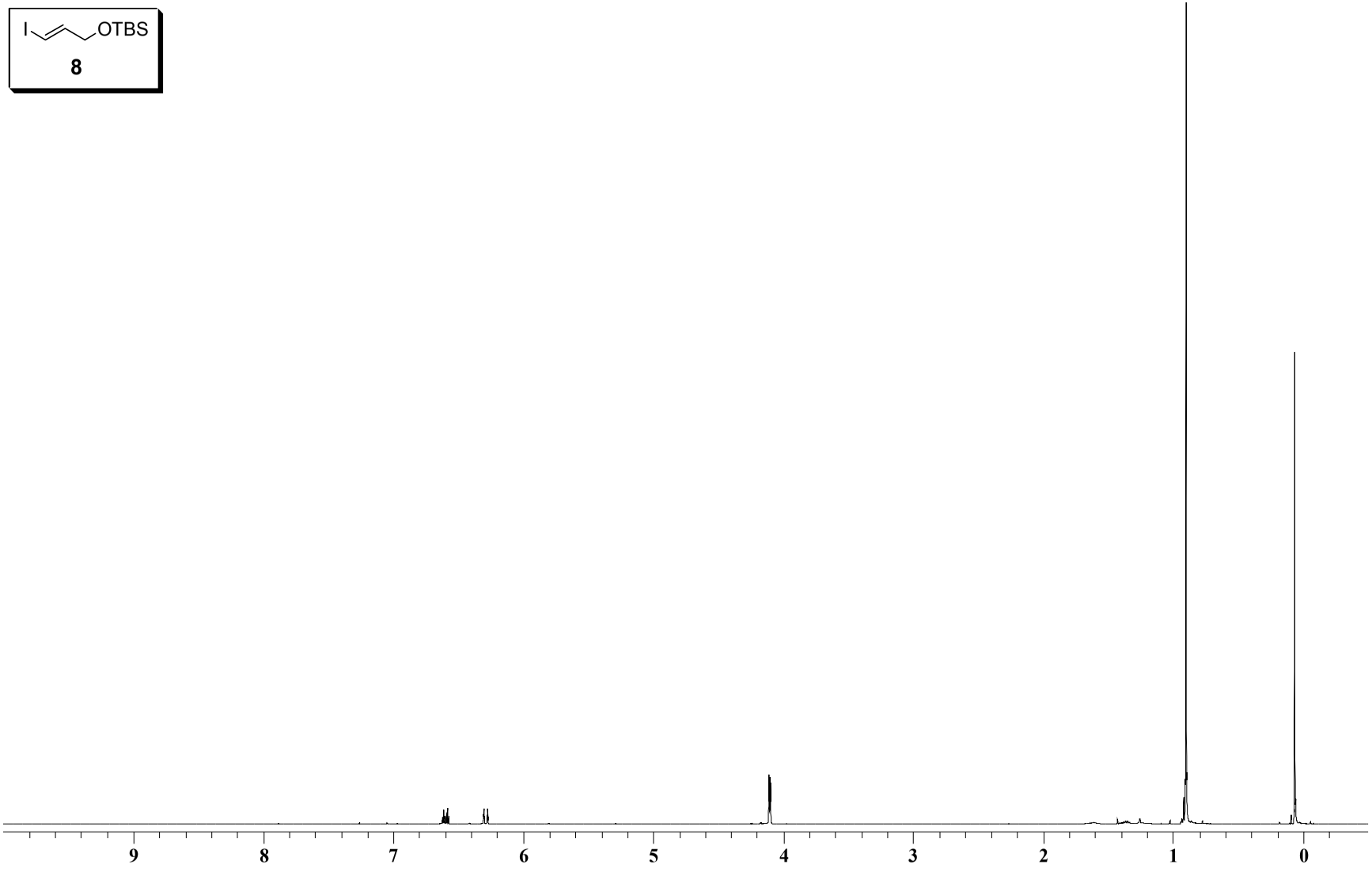
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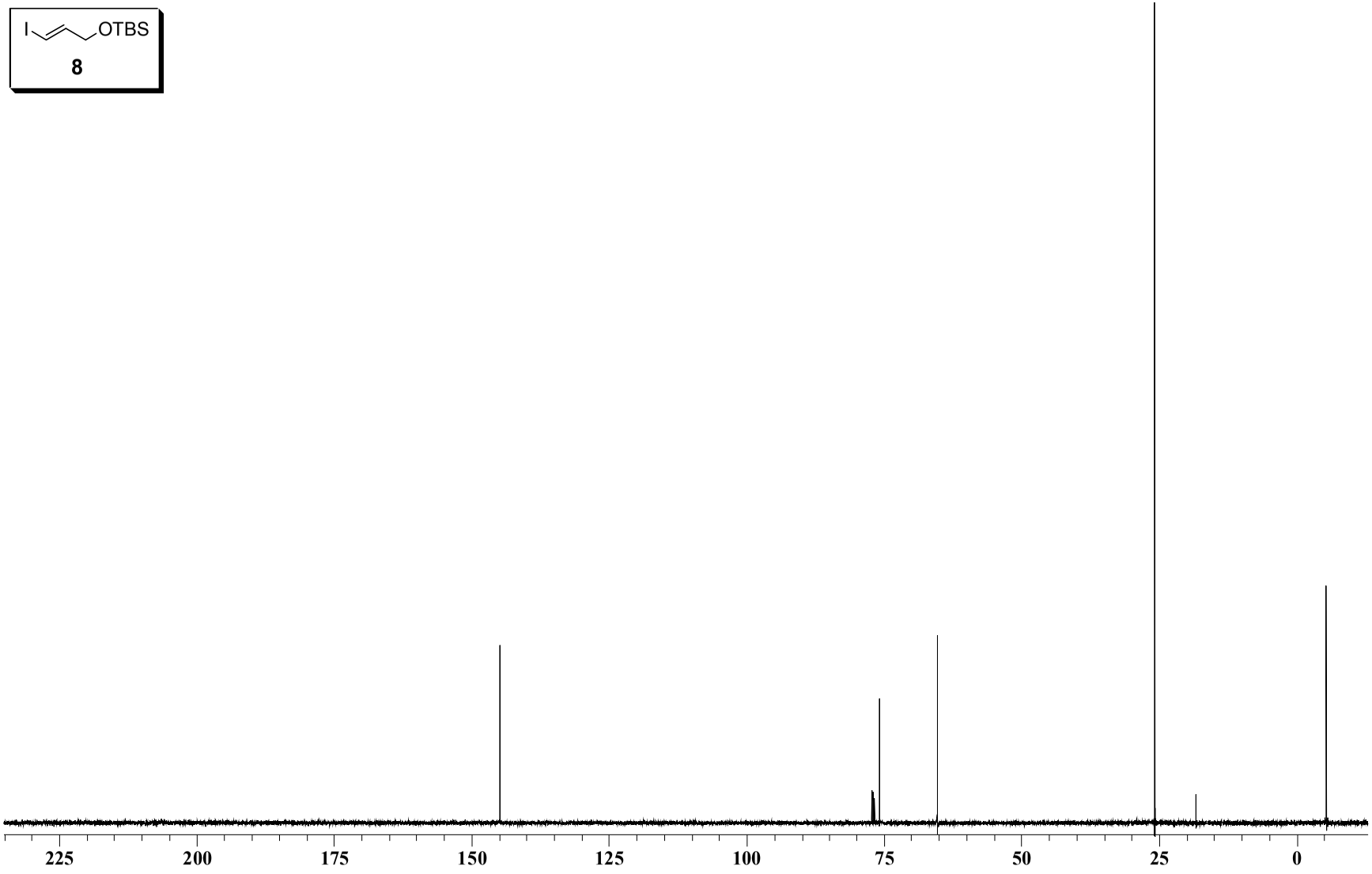
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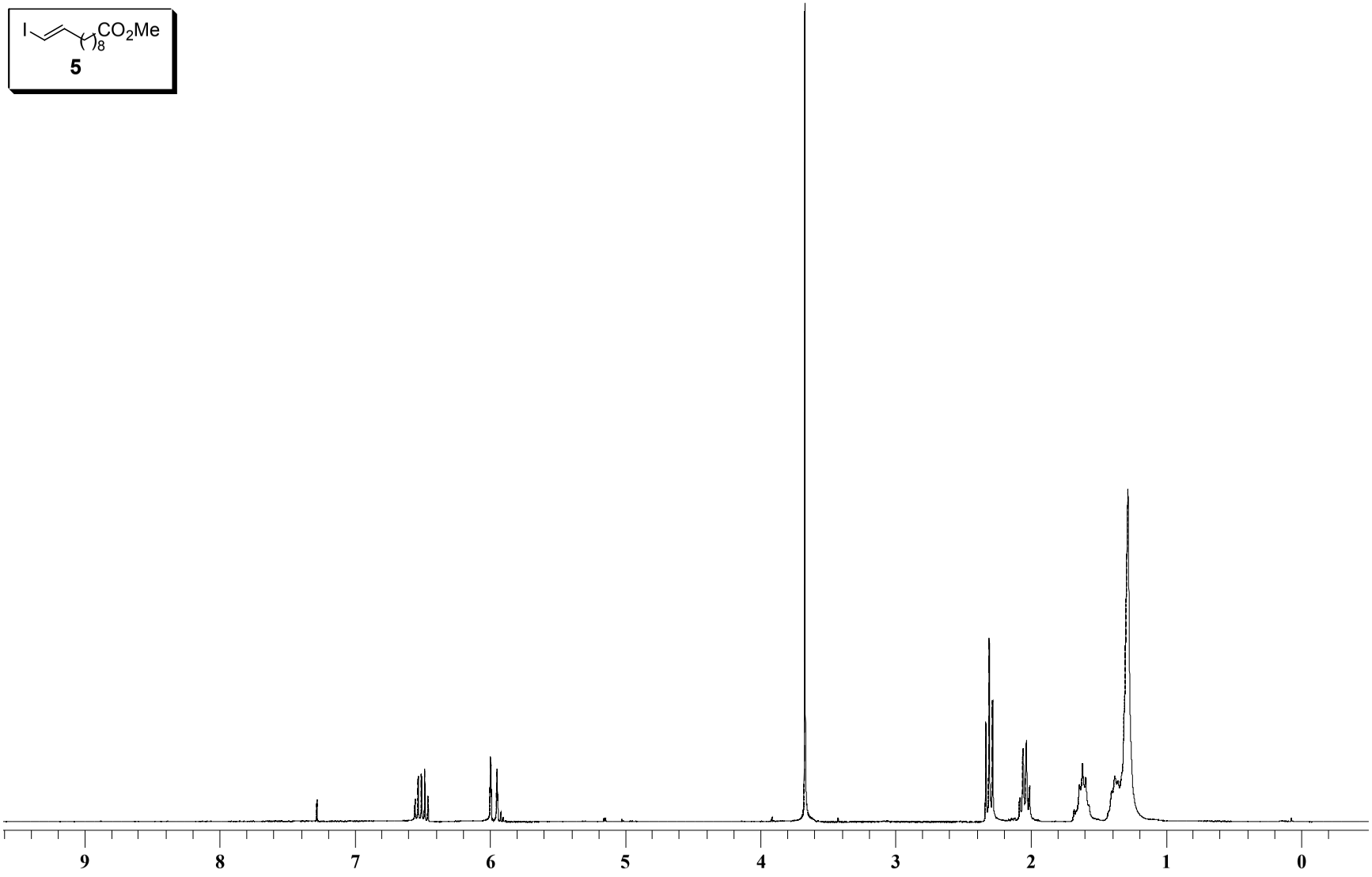
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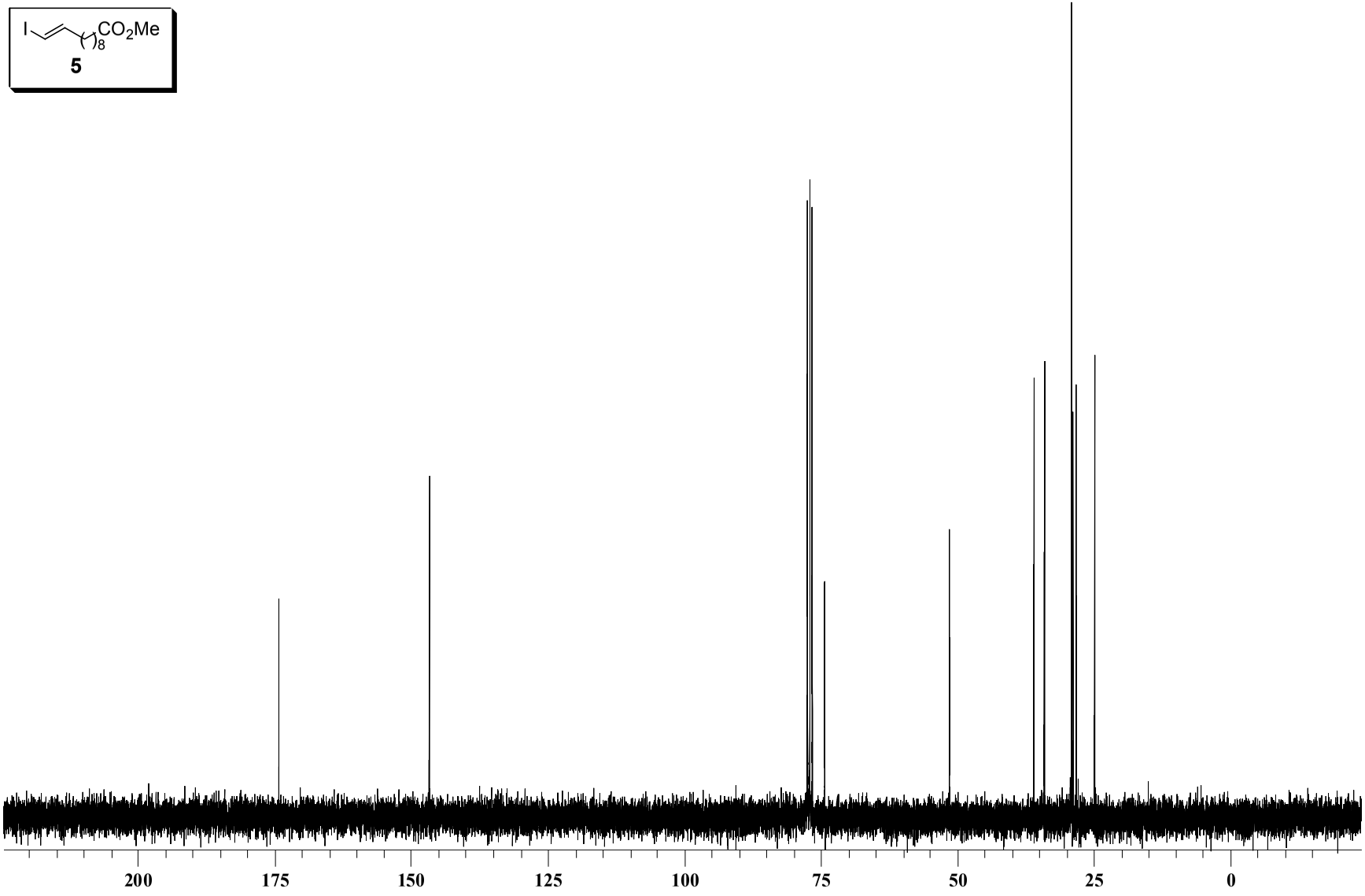
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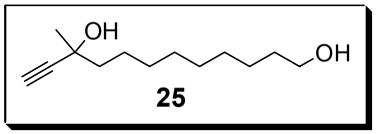

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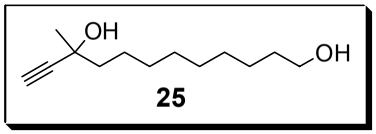

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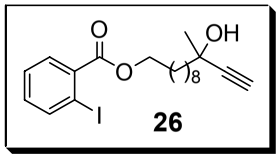

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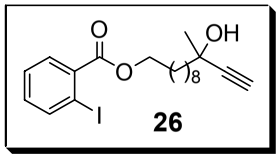

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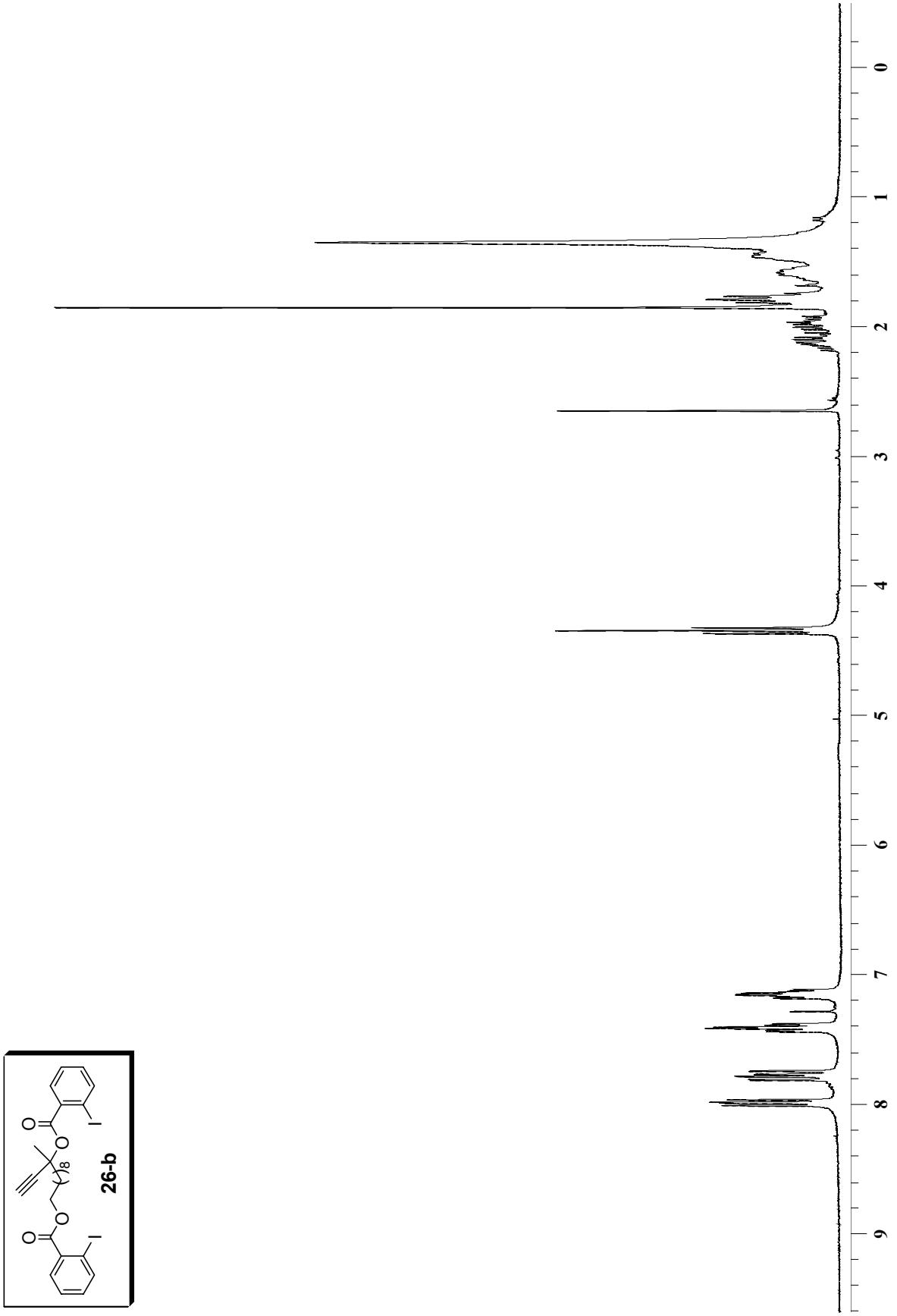
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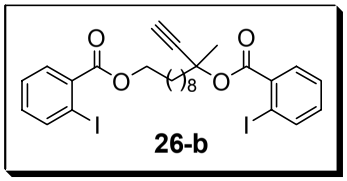

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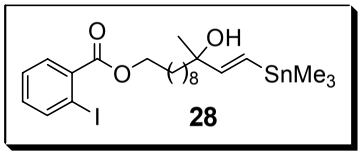

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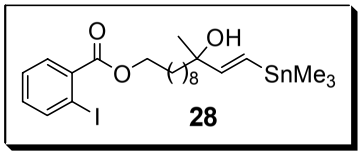

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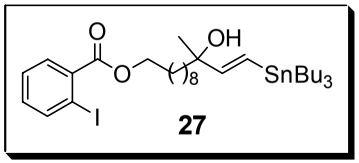

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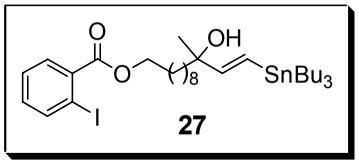

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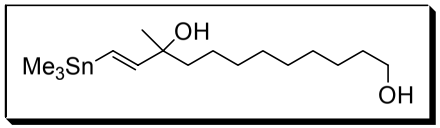
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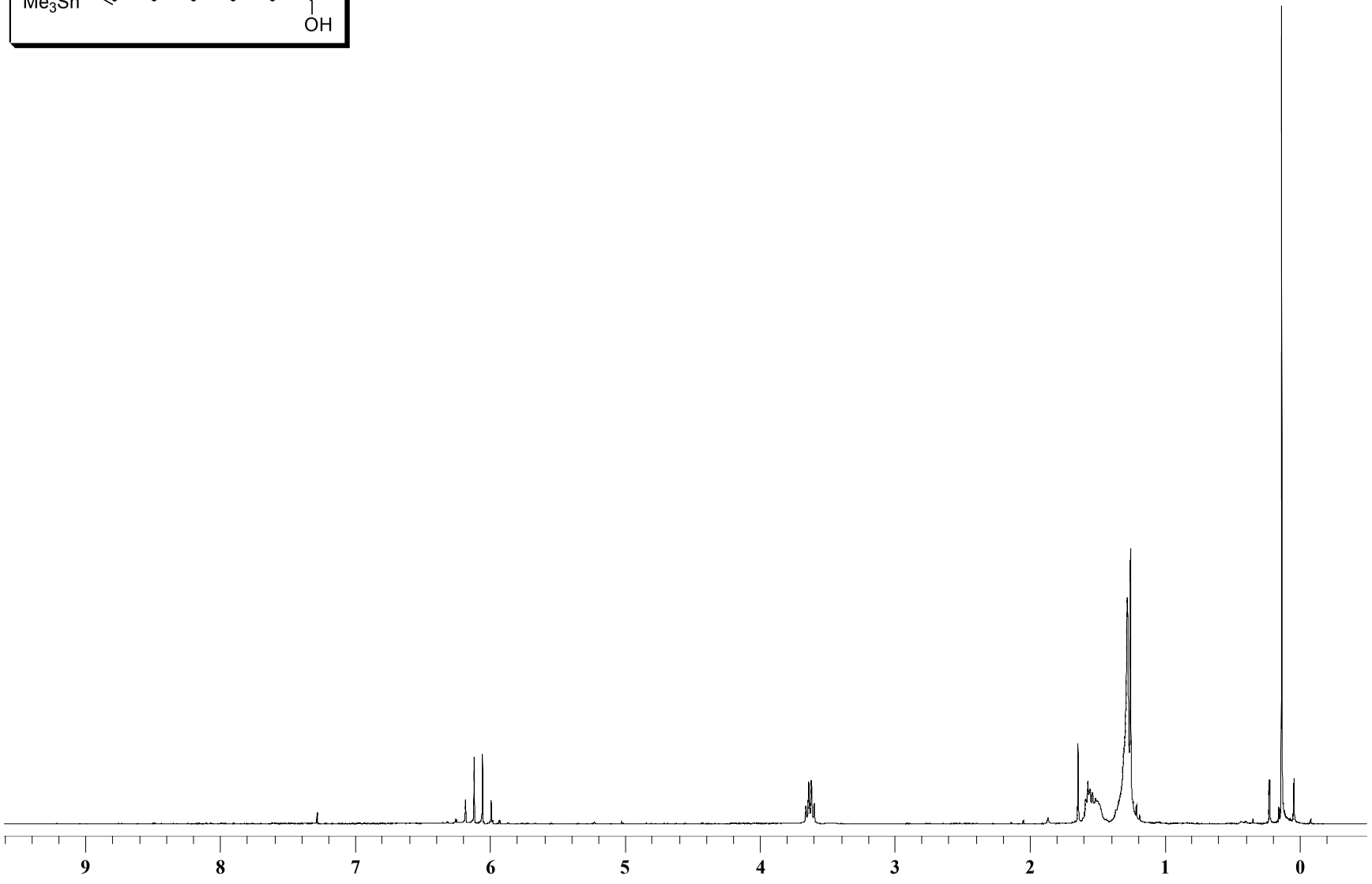
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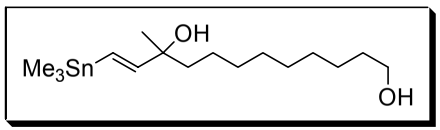

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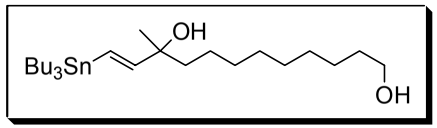
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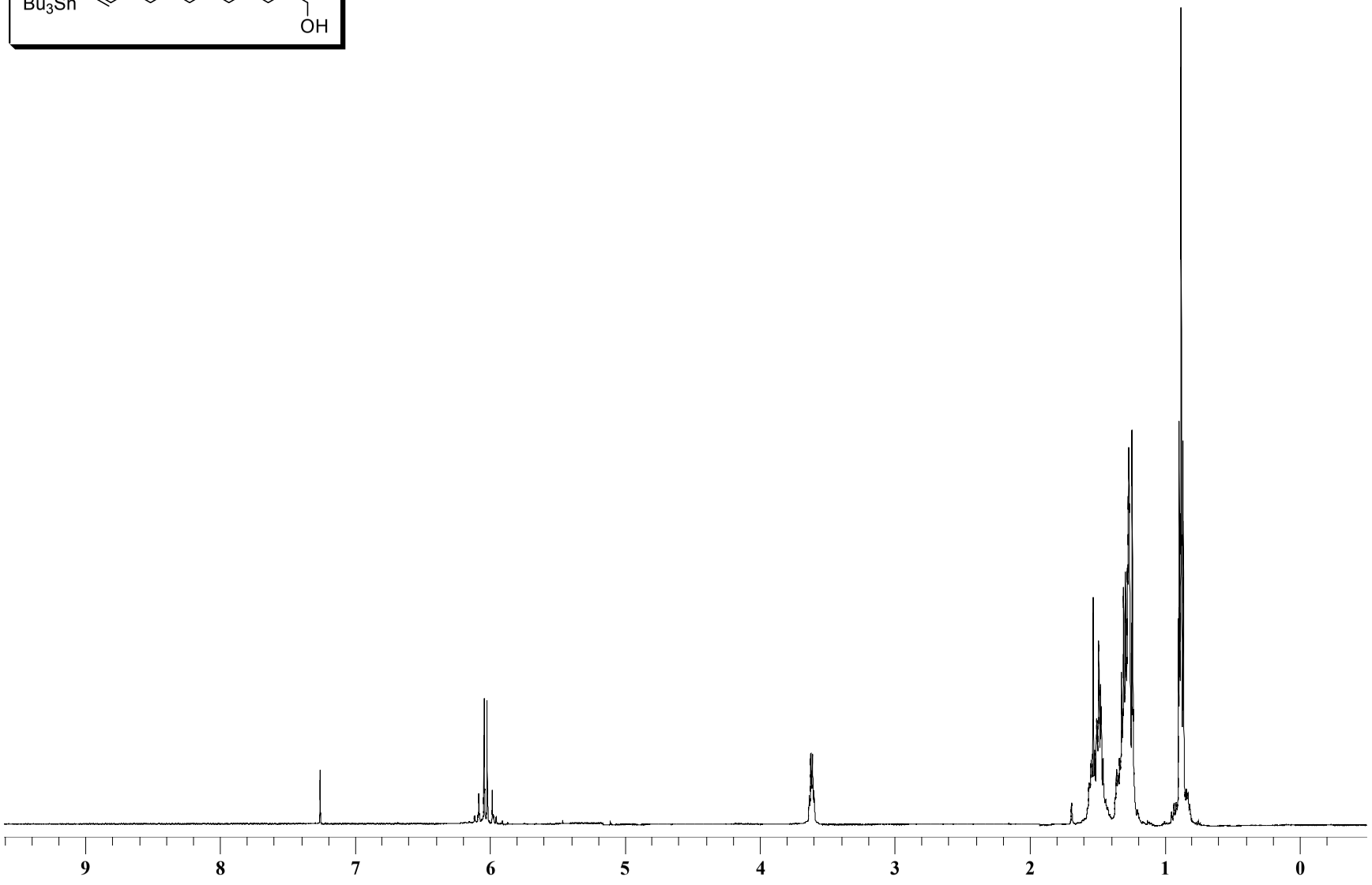
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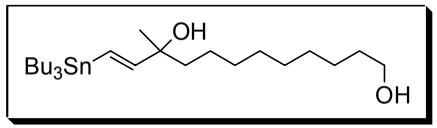
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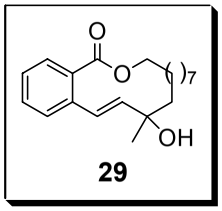

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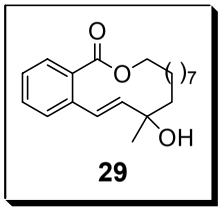

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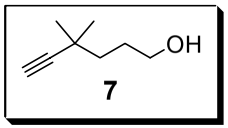

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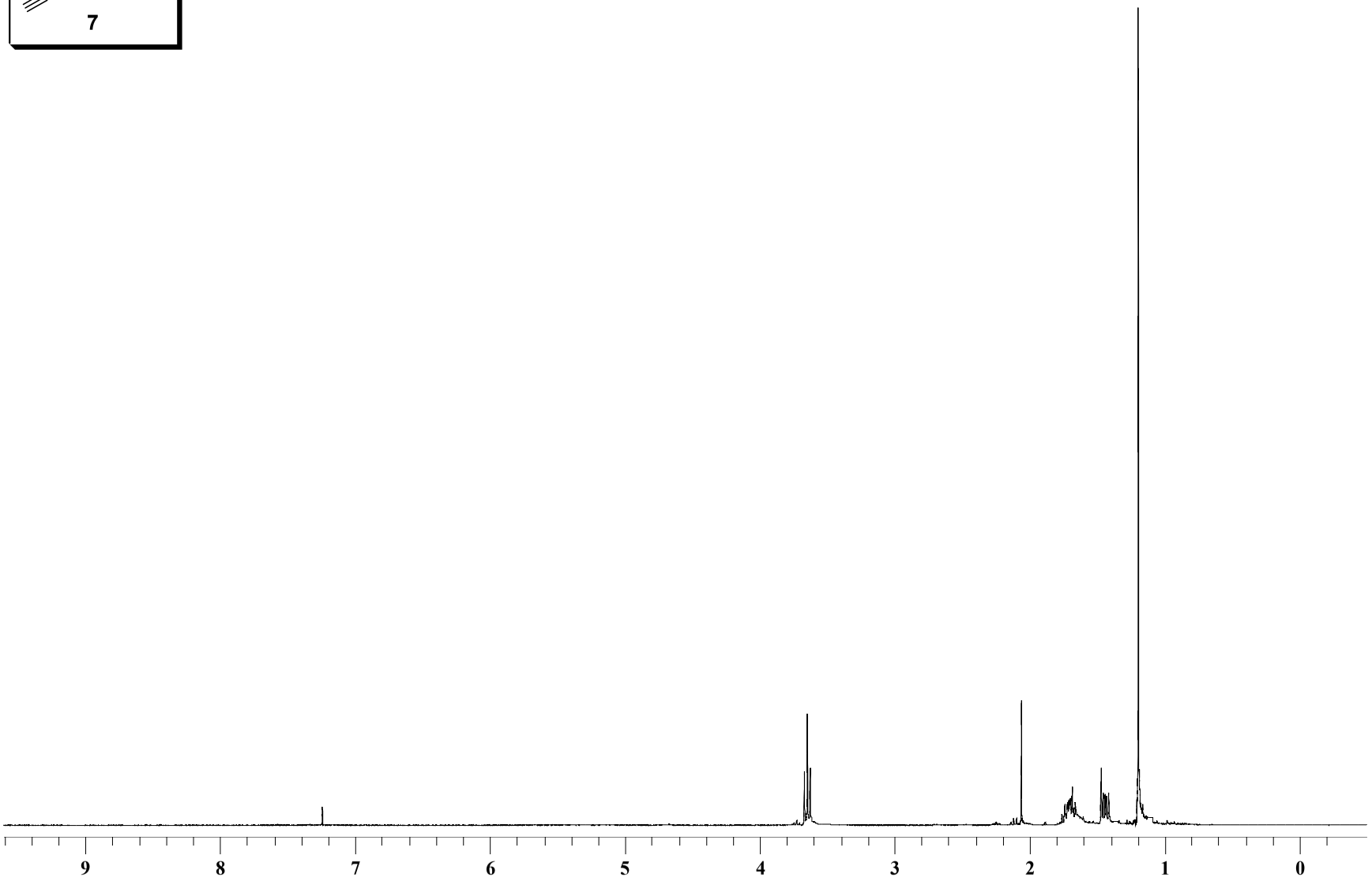

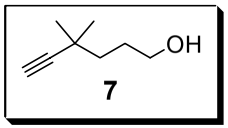

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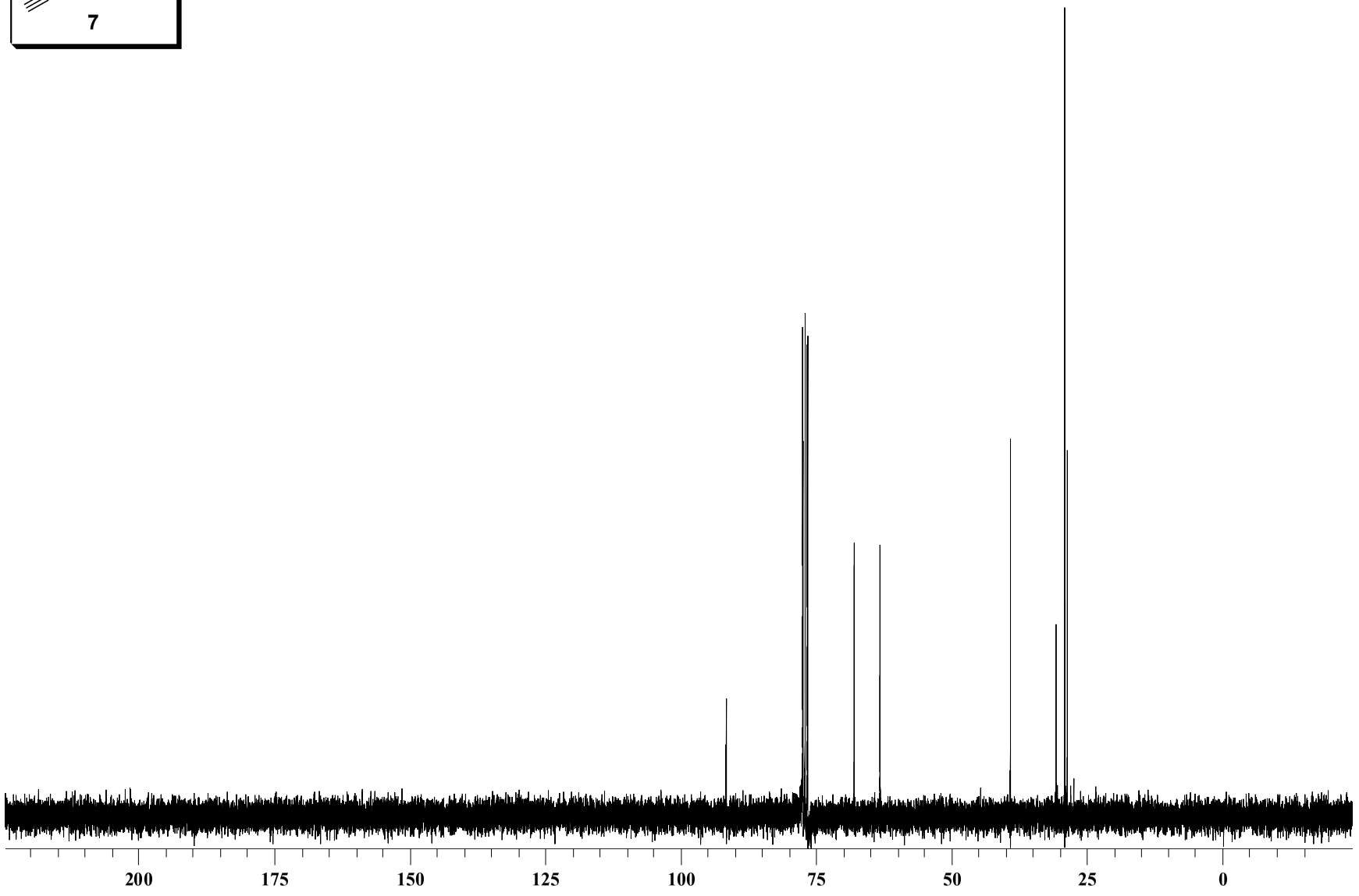

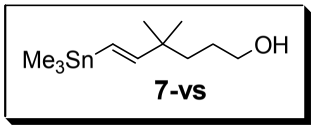

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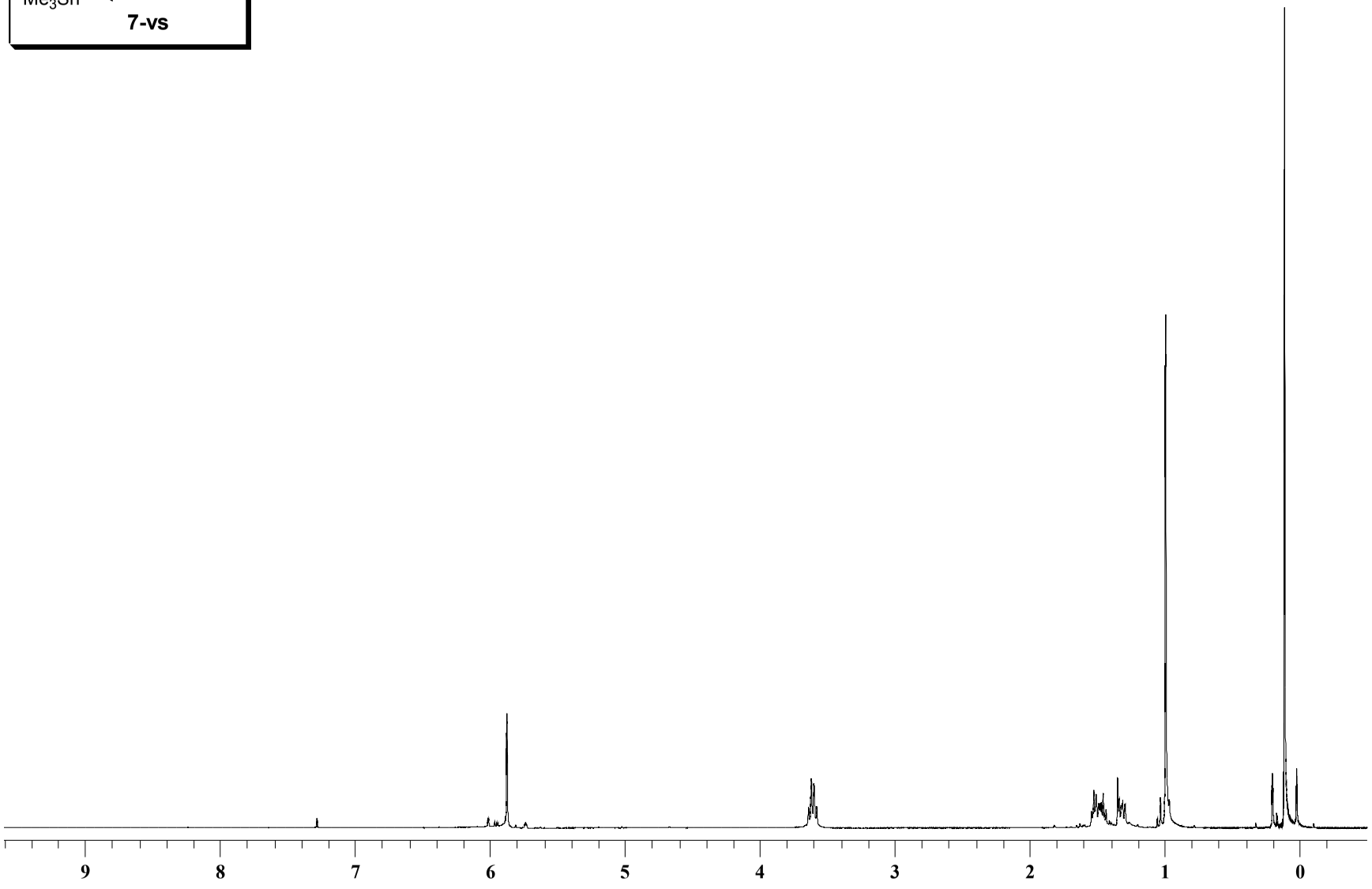

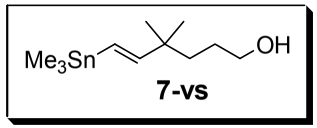

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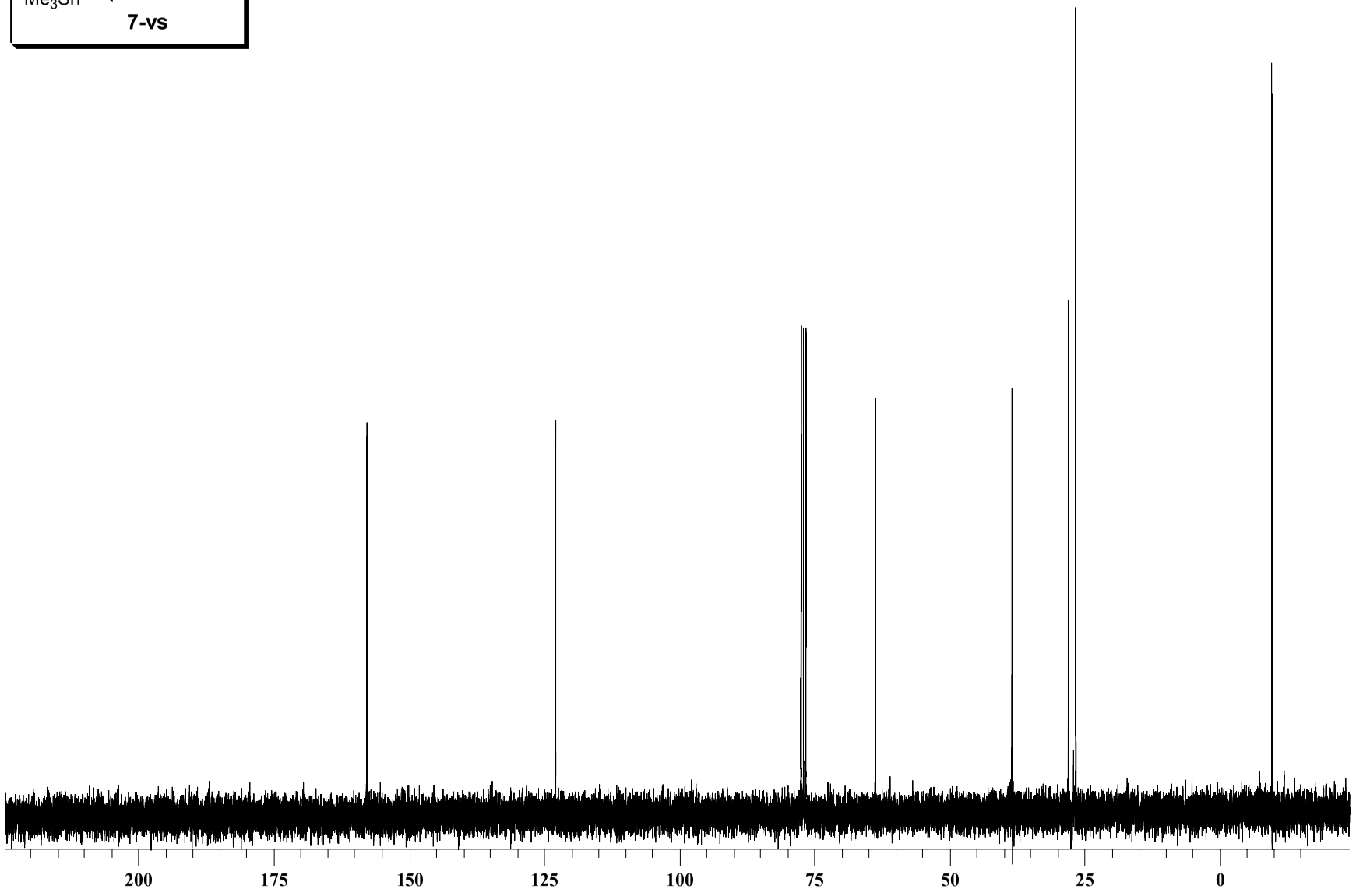

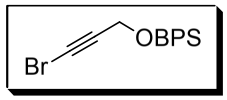

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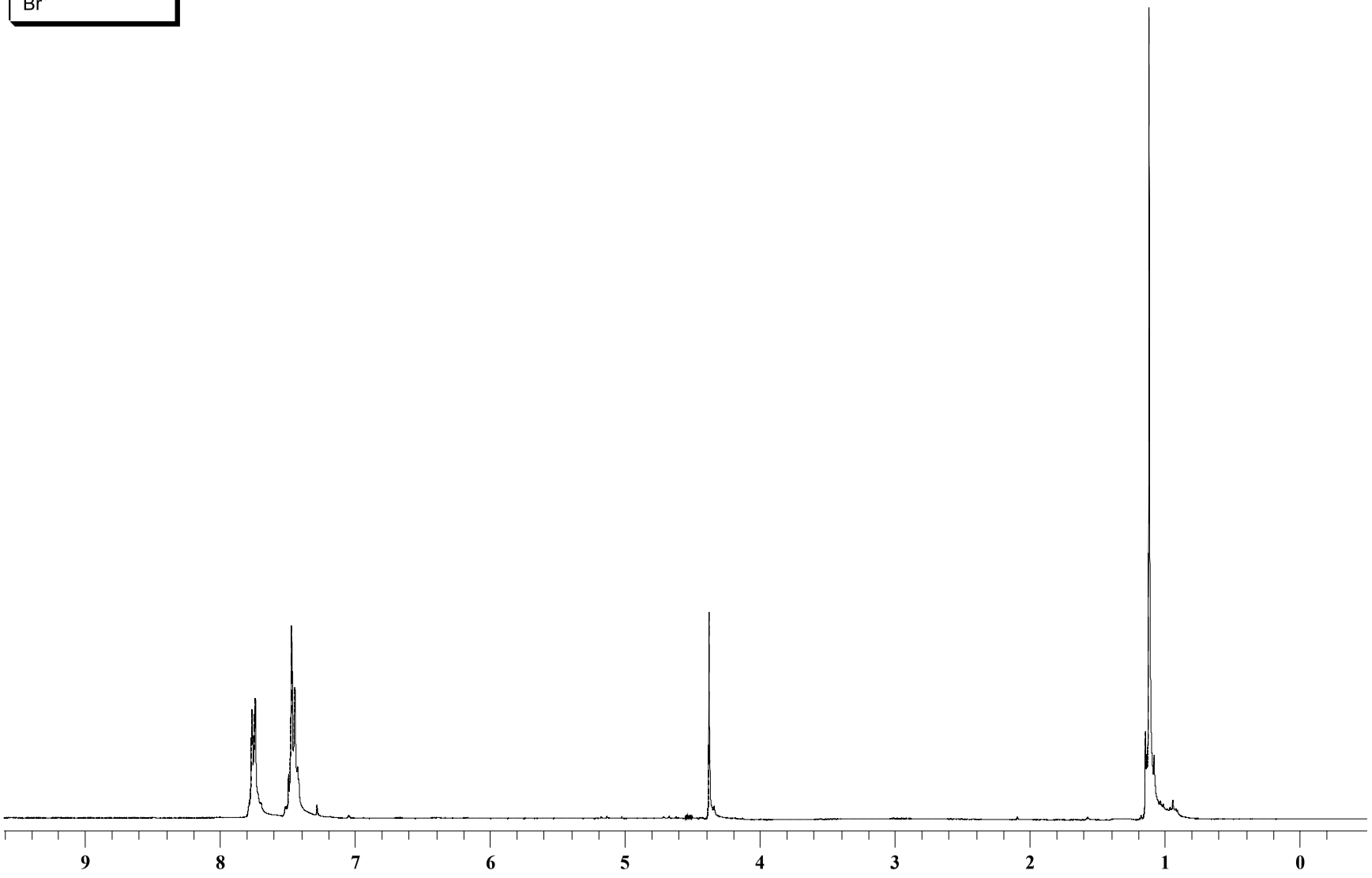

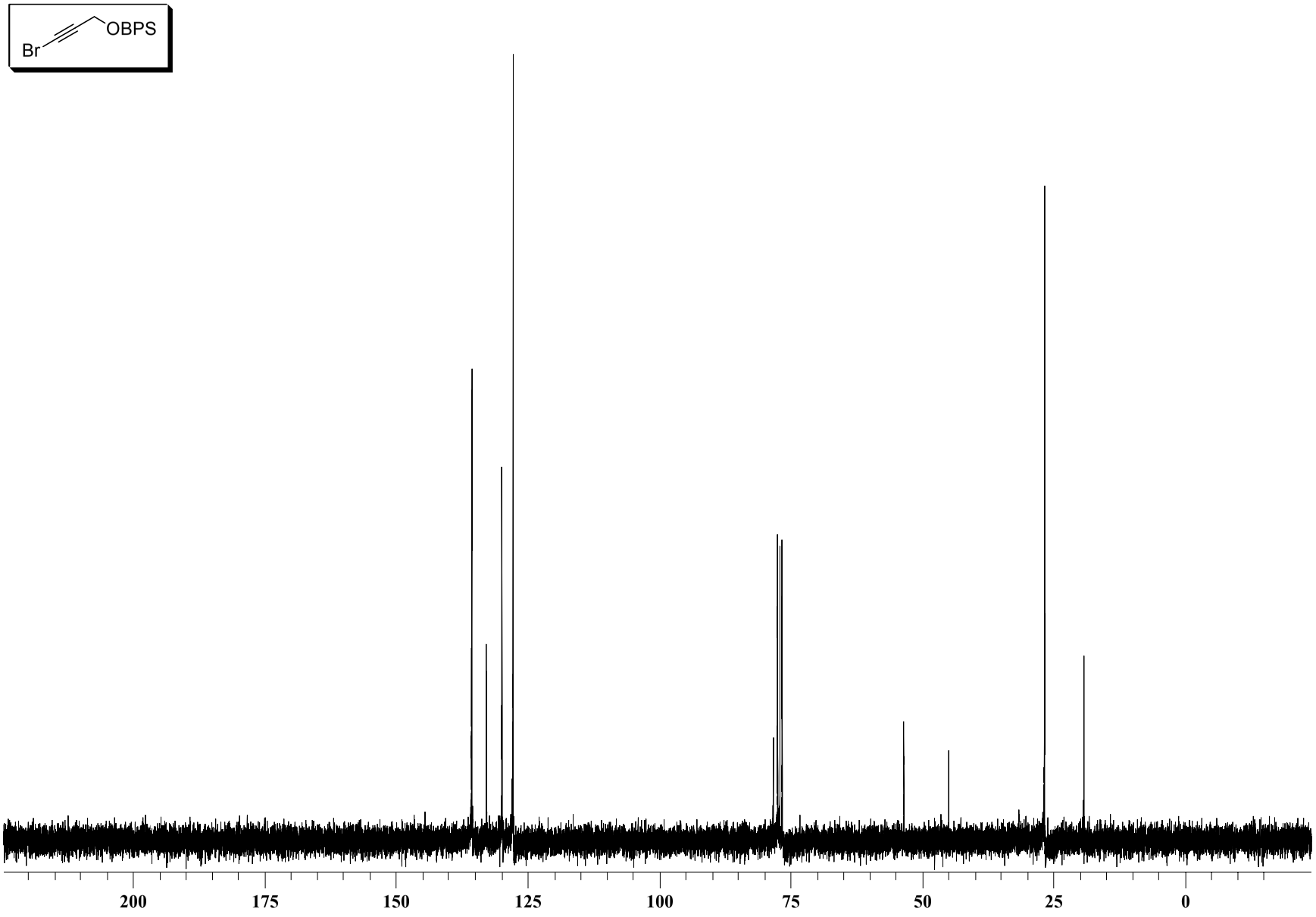
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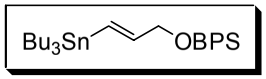
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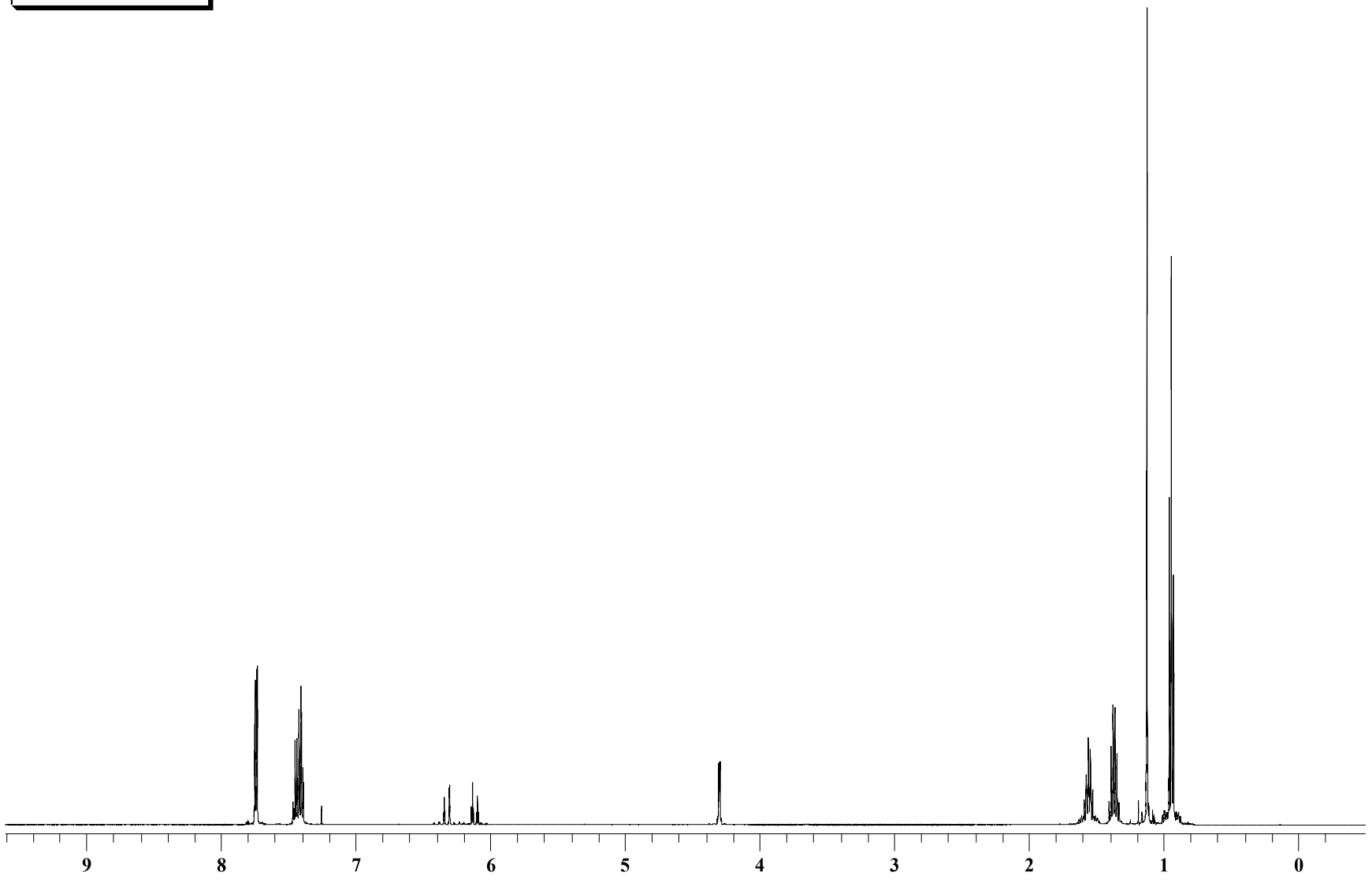
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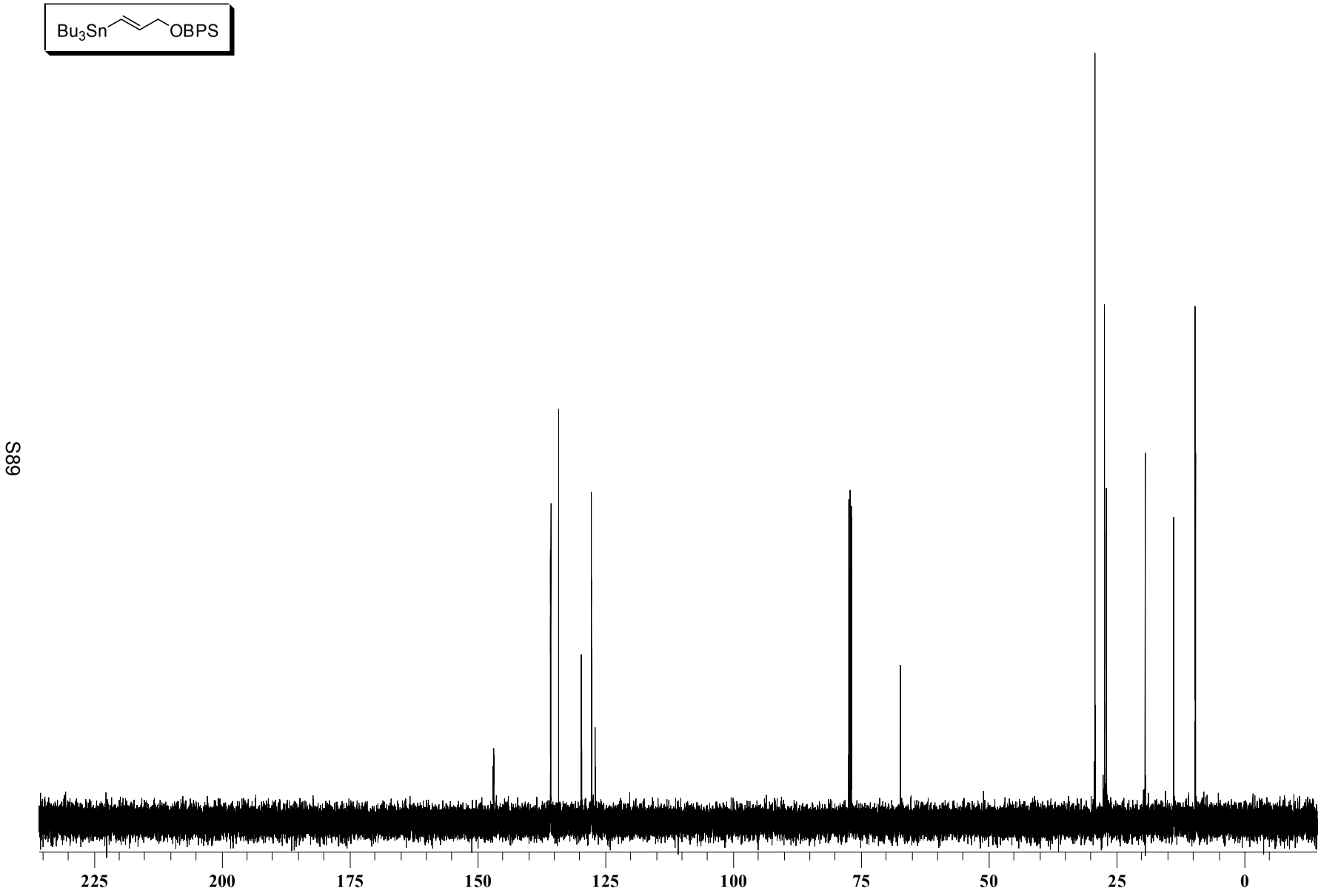
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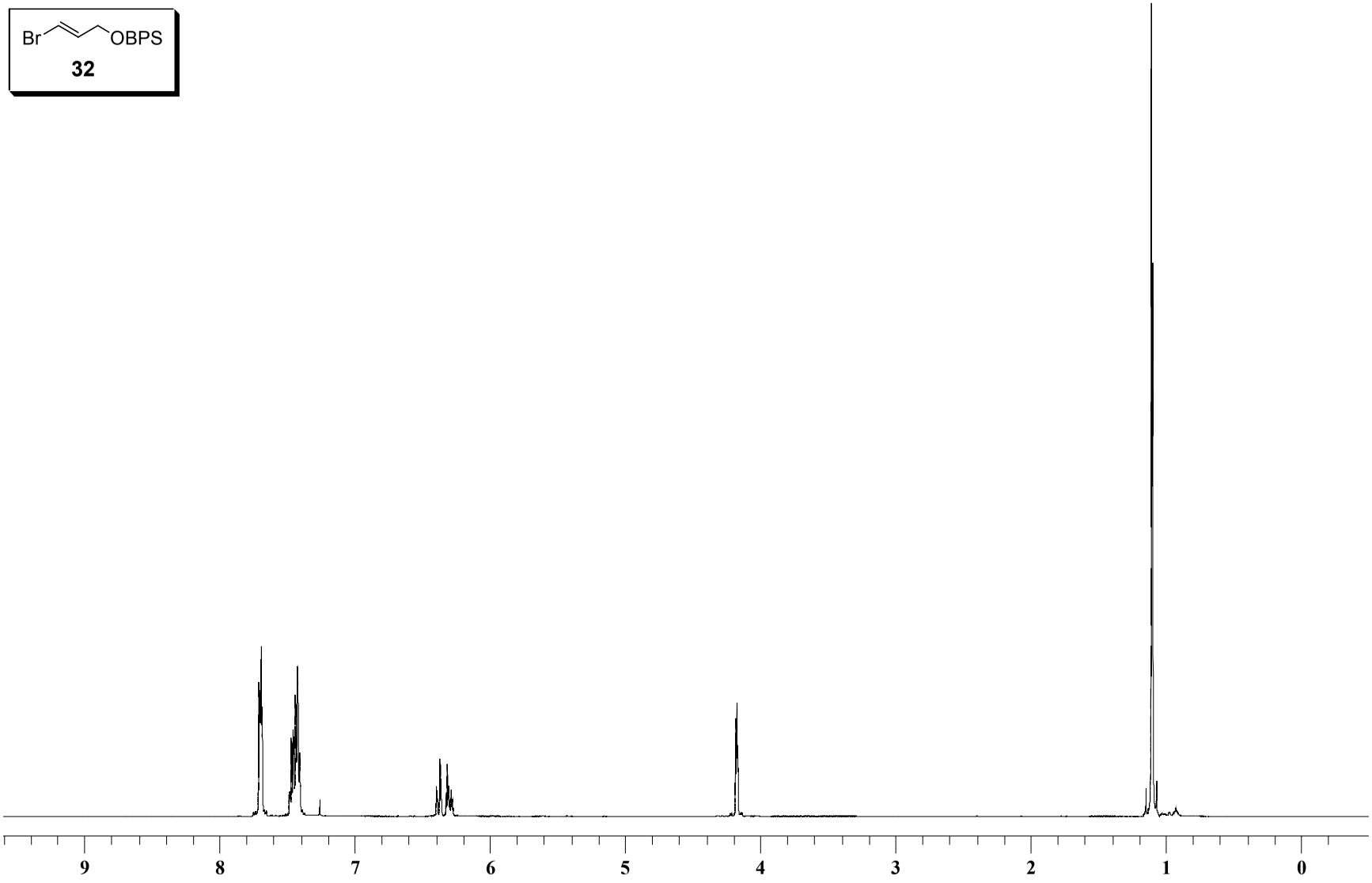
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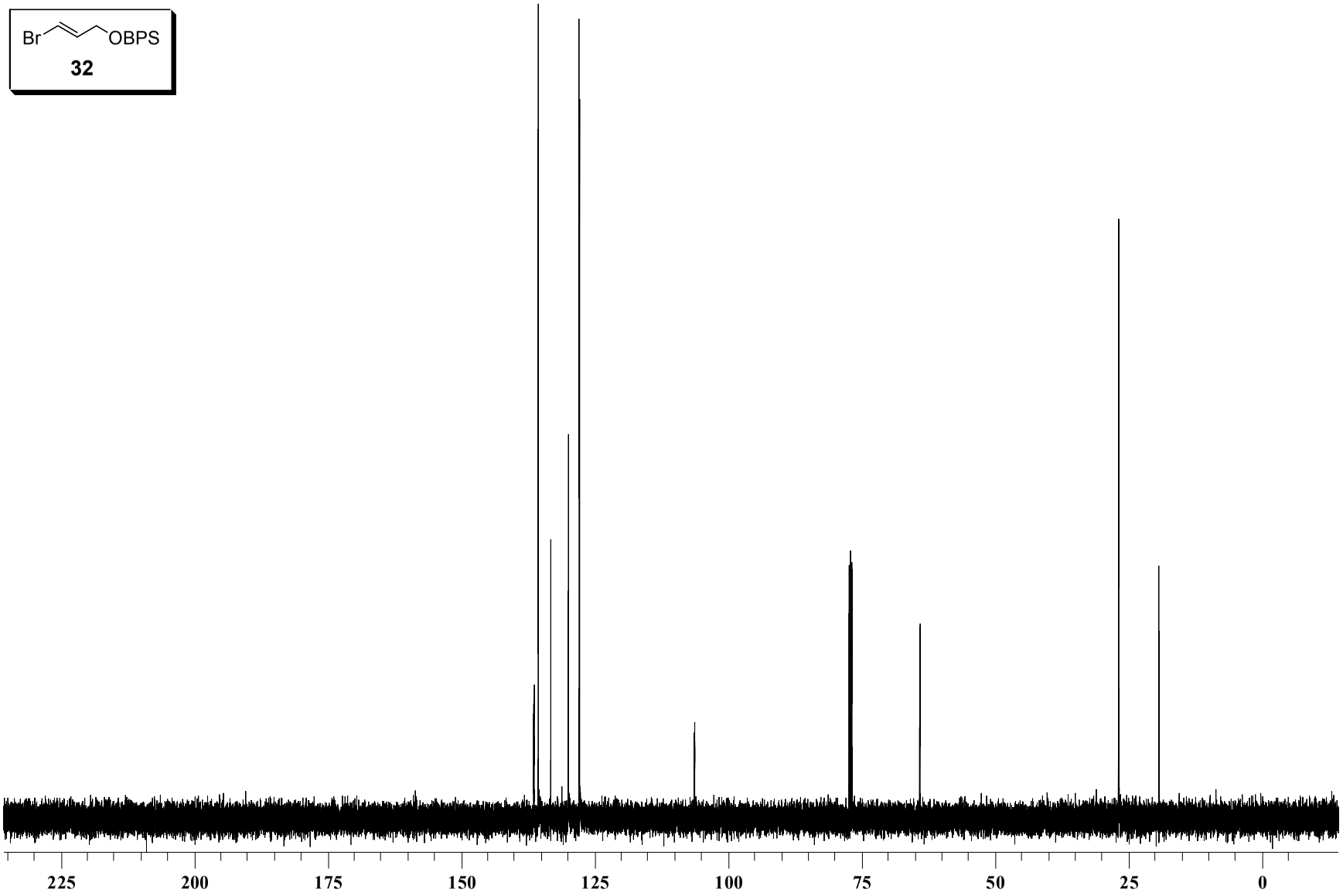
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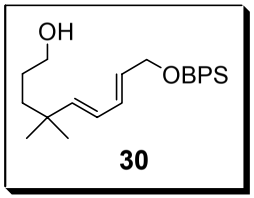

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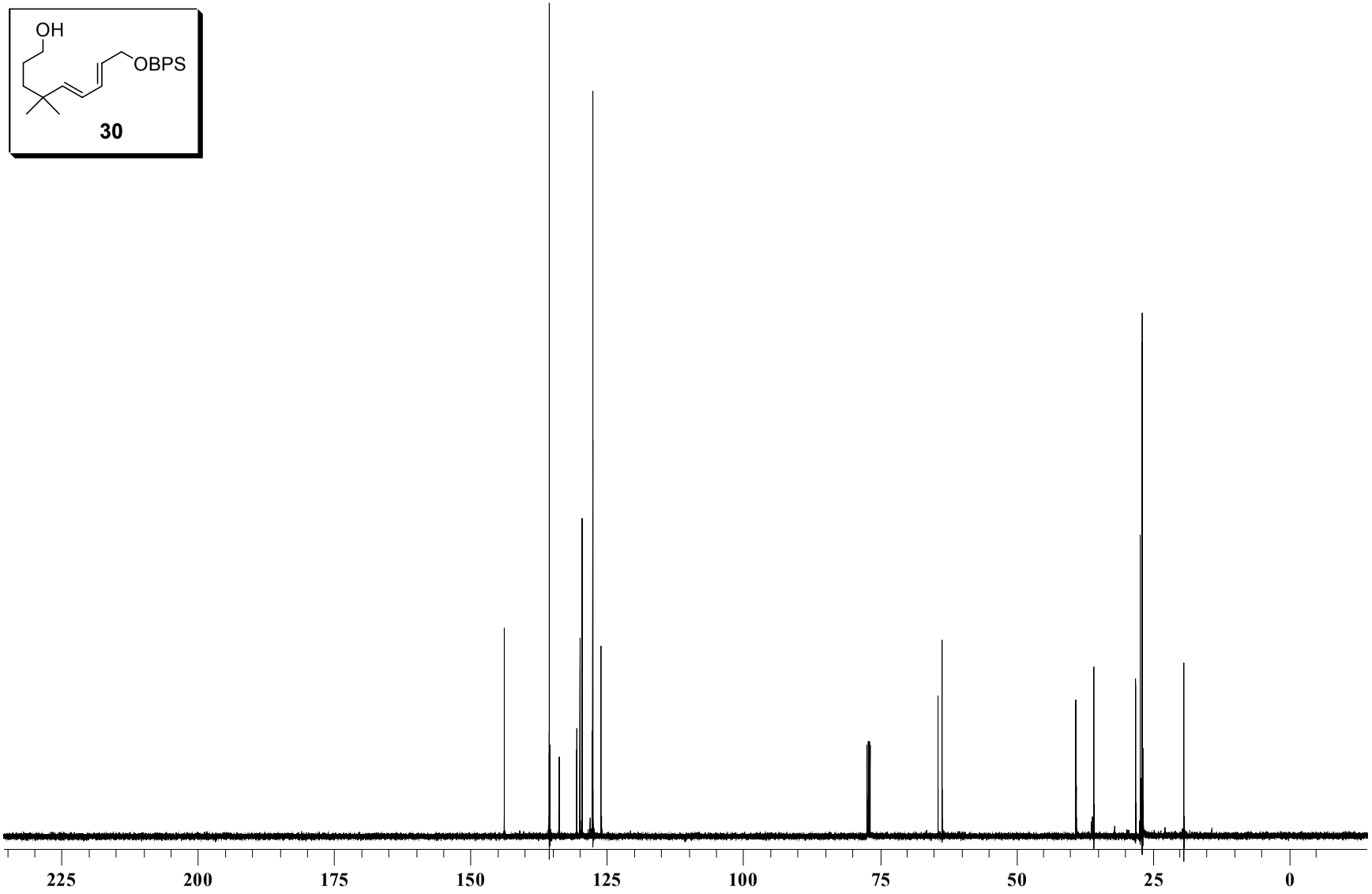
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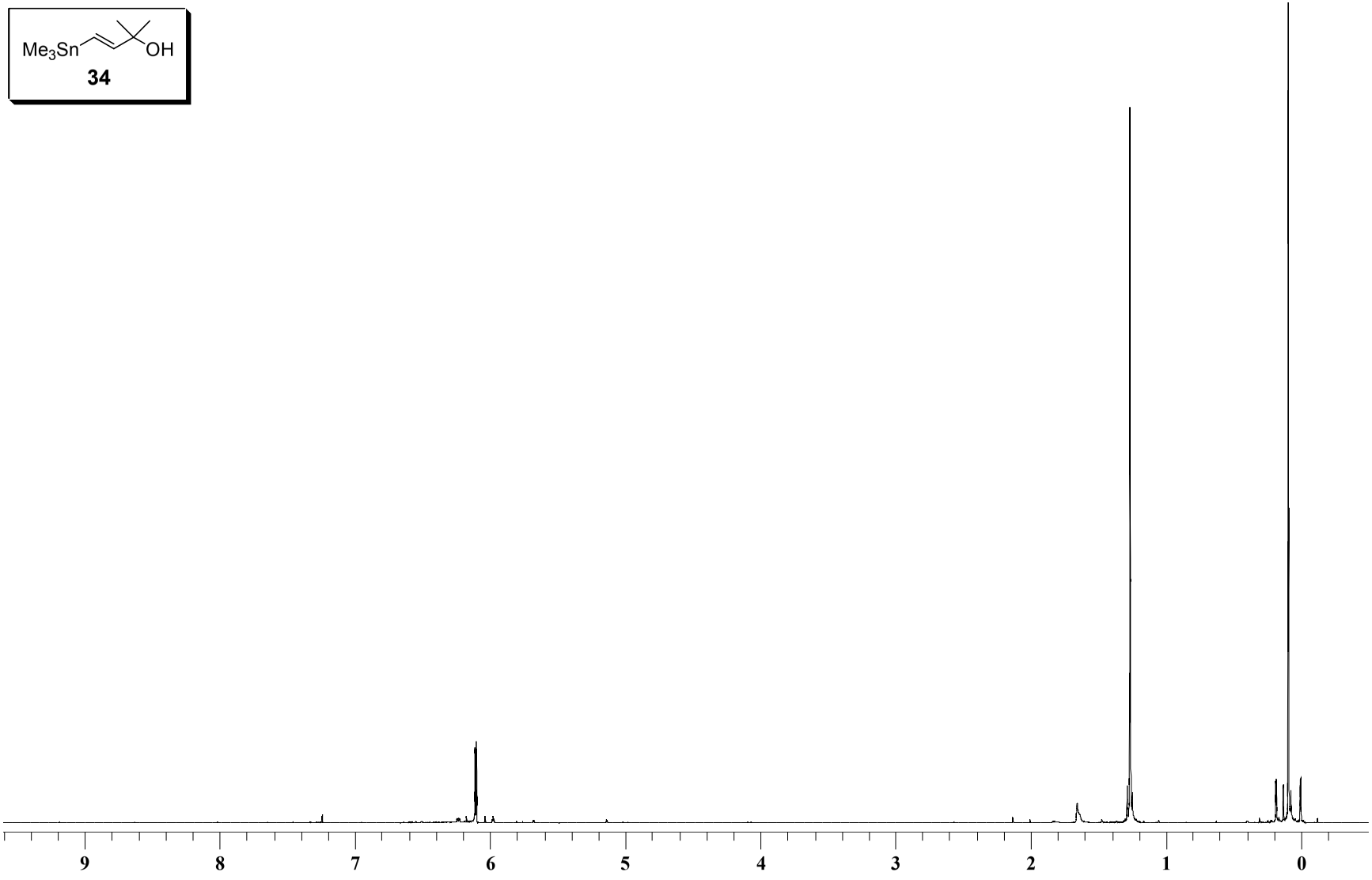
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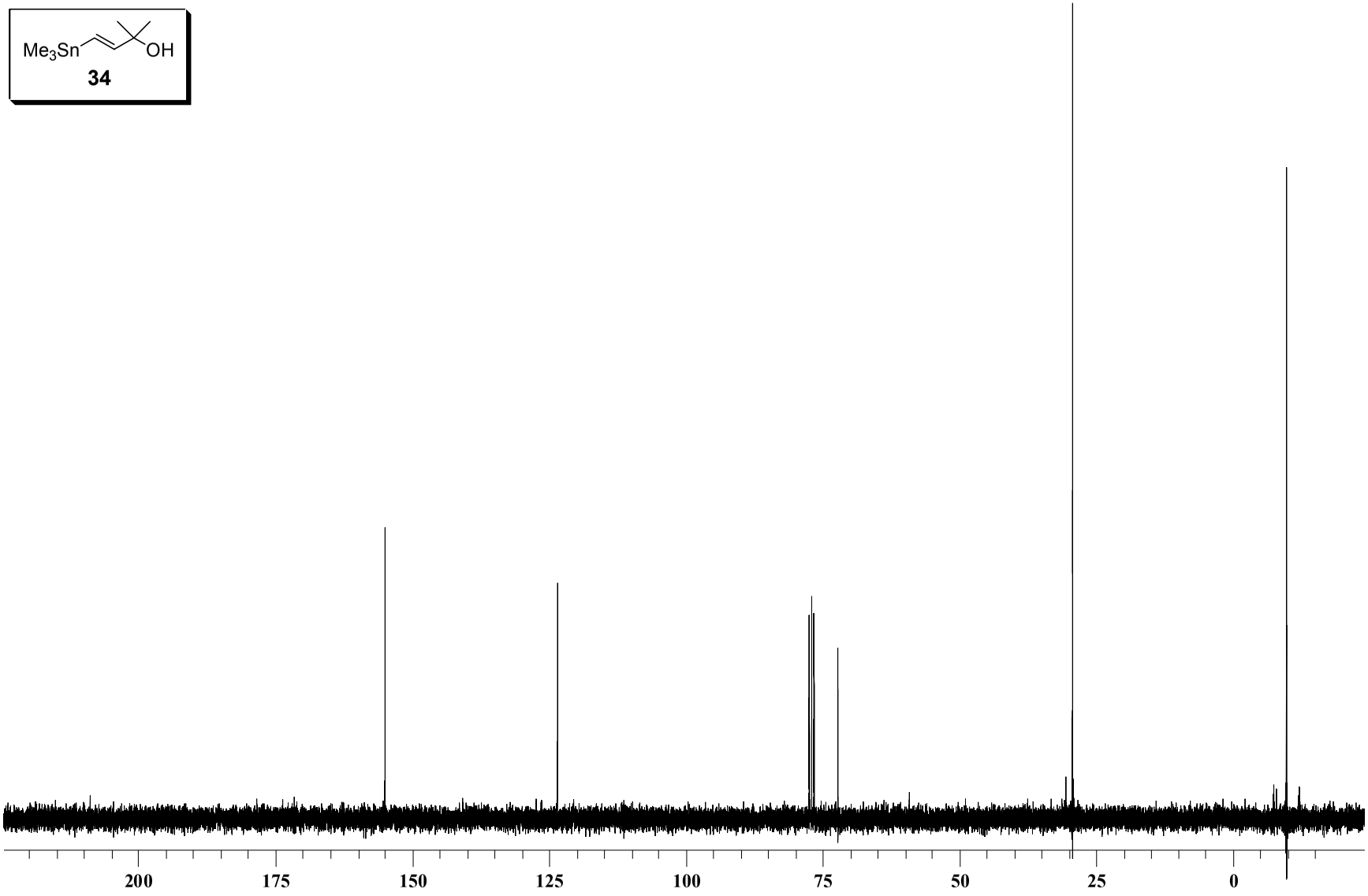
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References and Notes

(1) For a prior preparation and spectroscopic data see: Marko, I. E.; Leung, C. W. *J. Am. Chem. Soc.* **1994**, *116*, 371-372.

(2) For prior preparation and spectroscopic data see: Prakash, G. K. S.; Krishnamurthy, V. V.; Olah, G. A.; Farnum, D. G. *J. Am. Chem. Soc.* **1985**, *107*, 3928-3935.

(3) For prior preparation and spectroscopic data see: Reich, H. J.; Shah, S. K.; Chow, F. *J. Am. Chem. Soc*. **1979**, *101*, 6648-6656.

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