Supporting Information

Copper-Catalyzed Allylation of Carbonyl Derivatives Using Allyl(2-pyridyl)silanes

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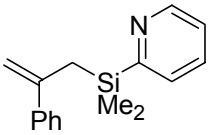
General. ^{1}H and ^{13}C NMR spectra were recorded on Varian GEMINI-2000 (^{1}H 300 MHz, ^{13}C 75 MHz) and Varian MERCURYplus-400 (^{1}H 400 MHz, ^{13}C 100 MHz) spectrometers in $CDCl_3$ or CD_3CN with chemical shifts referenced to internal standards ($CDCl_3$ 7.26 ppm ^{1}H, 77.0 ppm ^{13}C or CD_3CN 1.94 ppm ^{1}H, 118.1 ppm ^{13}C). IR spectra were recorded on Shimadzu FTIR-8100 spectrophotometer. EI and CI mass spectra were recorded on a JMS-SX102A spectrometer. FAB mass spectra were recorded on a JMS-HX110A spectrometer. Unless otherwise noted, all materials and anhydrous tetrahydrofuran (THF) were obtained from commercial suppliers and used without further purification. CuCl (Nacalai Tesque, Inc.) and CuBr (Wako Pure Chemical Industries Ltd.) were used without further purification. CuI was recrystalized from H_2O/NaI prior to use. Compound **8**,[1] β-styryl iodide,[2] α-styryl iodide,[3] (*E*)-hexenyl iodide, [4] (2-iodoethenyl)cyclohexane, [5] ethyl (*E*)-2-iodo-3-phenyl-2-propenoate [6] and acetone N-benzylimine[7] were prepared according to the literature procedure.

Allyldimethyl(2-pyridyl)silane (1)

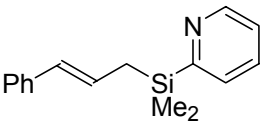
To a solution of 2-bromopyridine (3.16 g, 20 mmol) in dry Et_2O (20 mL) was added dropwise a solution of *n*-BuLi (21 mmol, 1.54 M solution in hexane) at –78 °C under argon. The mixture was stirred for additional 1 h to afford an ether solution of 2-pyridyllithium. To this solution was added allylchlorodimethylsilane (3.0 g, 22 mmol) at –78 °C. After being stirred at room temperature for 2 h, the reaction mixture was quenched with H_2O (30 mL). Aqueous phase was extracted with Et_2O (3 x 30 mL), and the combined organic phase was washed with brine (50 mL). Drying over $MgSO_4$, removal of the solvents under the reduced pressure and subsequent distillation (bp 104–105 °C/18.3 mmHg) afforded the title compound (2.45 g, 69%) as a colorless oil. ^{1}H NMR (300 MHz) δ 0.33 (s, 6H), 1.84 (dt, *J* = 8.1, 1.2 Hz, 2H), 4.83 (dm, *J* = 10.2 Hz, 1H), 4.86 (dm, *J* = 16.8 Hz, 1H), 5.78 (ddt, *J* = 16.8, 10.2, 8.1 Hz, 1H), 7.19 (ddd, *J* = 7.5, 4.8, 1.5 Hz, 1H), 7.48 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.58 (td, *J* = 7.5, 1.5 Hz, 1H), 8.77 (ddd, *J* = 5.1, 1.8, 1.2 Hz, 1H); ^{13}C NMR (75 MHz) δ –4.1, 22.7, 113.5, 122.8, 129.2, 133.9, 134.4, 150.1, 166.8; IR (neat) 2990, 2959, 1630, 1417, 1248 cm^{-1}. HRMS (CI) *m*/*z* calcd for $C_{10}H_{15}NSi$ (MH^+): 178.1052 found 178.1054.

Typical procedure for the copper-mediated cross-coupling reaction of 5 with alkenyl iodide 6 (Table 2, Figure 2, Li method). To a solution of trimethyl(2-pyridyl)silane **(**36.0 mg, 0.24 mmol) in dry Et_2O (0.3 mL) was added dropwise a solution of *t*-BuLi (0.20 mmol, 1.32 M solution in pentane) at –78 ˚C under argon. The mixture was stirred for additional 30 min to afford an orange ether solution of (2-pyridyldimethylsilyl)methyllithium (**5**). To this solution were added CuBr (17.2 mg, 0.12 mmol) and dry Et_2O (0.2 mL), and the resultant mixture was stirred at –78 °C for 0.5 h and at room temperature for 0.5 h to afford a black suspension of bis[(2-pyridyldimethylsilyl)methyl]cuprate. α-Styryl iodide (45.5 mg, 0.20 mmol) was added to this mixture. After the mixture was stirred at room temperature for 4 h, sat. *aq* NH_4Cl (2 mL) was added to the reaction mixture. The aqueous layer was extracted with EtOAc (2 mL × 3), and the combined organic phase was dried over $MgSO_4$. Removal of solvents and subsequent silica gel chromatography (hexane/EtOAc/Et_3N = 100/10/1) afforded **7** (38.7 mg, 77%).

Typical procedure for the copper-mediated cross-coupling reaction of 8 with alkenyl iodide (Scheme 2, Figure 2, Sn Method). To a solution of **8** (140.0 mg, 0.32 mmol) and α-styryl iodide (47.2 mg, 0.21 mmol) in dry dioxane (2.0 mL) was added CuCl (29.6 mg, 0.30 mmol). After the mixture was stirred at 100 ˚C (reflux) for 4 h, 1,8-diazabicyclo[5.4.0]undec-7-ene (ca. 0.1 mL) and Et_2O (1.0 mL) were added to the mixture. The copper salt and tin residue were removed by filtration through a short silica gel pad (Et_2O). Removal of solvents under reduced pressure and subsequent silica gel chromatography (hexane/EtOAc/Et_3N = 100/10/1) afforded **7** (36.4 mg, 70%).

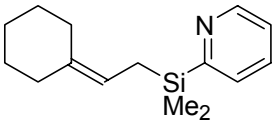


^{1}H NMR (400 MHz) δ 0.23 (s, 6H), 2.36 (s, 2H), 4.87 (d, *J* = 1.2 Hz, 1H), 5.14 (d, *J* = 1.2 Hz, 1H), 7.15 (ddd, *J* = 7.6, 4.8, 1.6 Hz, 1H), 7.18–7.25 (m, 3H), 7.34 (dm, *J* = 7.6 Hz, 2H), 7.36 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.50 (td, *J* = 7.6, 1.6 Hz, 1H), 8.74 (ddd, *J* = 5.2, 1.6, 1.2 Hz, 1H); ^{13}C NMR (100 MHz) δ –3.4, 24.3, 110.8, 122.6, 126.2, 127.0, 127.8, 129.0, 133.6, 142.2, 145.6, 149.8, 166.7. IR (neat) 3056, 2959, 1615, 1418, 1248 cm^{-1}. HRMS (EI) *m*/*z* calcd for $C_{16}H_{19}NSi$: 253.1287, found 253.1284.

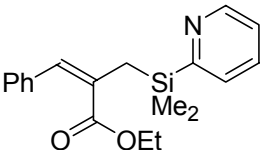


^{1}H NMR (400 MHz) δ 0.40 (s, 6H), 2.03 (dd, *J* = 4.0, 2.4 Hz, 2H), 6.19–6.29 (m, 2H), 7.16 (td, *J* = 8.8, 4.4 Hz, 1H), 7.22 (ddd, *J* = 7.6, 4.8, 1.6 Hz, 1H), 7.26 (s, 2H), 7.27 (s, 2H), 7.51 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.59 (td, *J* = 7.6, 1.6 Hz, 1H), 8.81 (ddd, *J* = 4.8, 1.6, 1.2 Hz, 1H); ^{13}C NMR (100 MHz) δ –3.7, 22.1, 122.8, 125.4, 126.1,

126.8, 128.2, 128.9, 129.1, 133.8, 138.2, 150.0, 166.5. IR (neat) 3023, 2957, 1640, 1418, 1246 cm^{-1}. HRMS (EI) *m*/*z* calcd for $C_{16}H_{19}NSi$: 253.1287, found 253.1288.

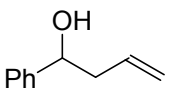


^{1}H NMR (400 MHz) δ 0.33 (s, 6H), 1.33–1.39 (m, 2H), 1.42–1.52 (m, 4H), 1.74 (d, *J* = 8.8 Hz, 2H), 2.00–2.06 (m, 4H), 5.09 (t, *J* = 8.4 Hz, 1H), 7.19 (ddd, *J* = 7.6, 4.8, 1.6 Hz, 1H), 7.48 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.56 (td, *J* = 7.6, 1.6 Hz, 1H), 8.76 (ddd, *J* = 4.8, 1.6, 1.2 Hz, 1H); ^{13}C NMR (100 MHz) δ –3.6, 16.0, 27.1, 27.6, 28.5, 28.9, 37.4, 115.6, 122.6, 129.1, 133.6, 137.8, 149.9, 167.2. IR (neat) 2926, 1576, 1447, 1418, 1246 cm^{-1}. HRMS (EI) *m*/*z* calcd for $C_{15}H_{23}NSi$: 245.1599, found 245.1592.

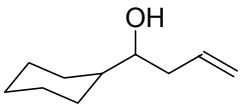


^{1}H NMR (400 MHz) δ 0.02 (s, 6H), 0.63 (t, *J* = 7.6 Hz, 3H), 1.82 (s, 2H), 3.57 (q, *J* = 7.6 Hz, 2H), 6.02 (s, 1H), 6.69 (dm, *J* = 7.6 Hz, 2H), 6.76-6.85 (m, 4H), 7.11 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.18 (td, *J* = 7.6, 1.6 Hz, 1H), 8.37 (ddd, *J* = 4.8, 1.6, 1.2 Hz, 1H); ^{13}C NMR (100 MHz) δ –3.4, 13.8, 24.0, 60.5, 122.8, 126.9, 127.76, 127.81, 129.3, 131.87, 131.92, 133.8, 136.7, 149.9, 166.3, 169.6. IR (neat) 2901, 1717, 1576, 1448, 1211 cm^{-1}. HRMS (EI) *m*/*z* calcd for $C_{19}H_{23}NO_2Si$: 325.1498, found 325.1497.

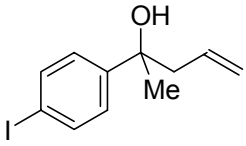
Typical procedure for the copper-catalyzed allylation of carbonyl derivatives using 1. To a suspension of CuI (4.0 mg, 0.021 mmol, 10 mol %) in dry THF (0.50 mL) were added **1** (47.5 mg, 0.26 mmol), benzaldehyde (**2a**) (23.2 mg, 0.22 mmol), CsF (78.1 mg, 0.51 mmol), and dry THF (0.5 mL). After the mixture was stirred at room tempreture for 2 h, 1N HCl aq (1 mL) was added to the reaction mixture. The aqueous layer was extracted with EtOAc (2 mL × 3), and the combined organic phase was dried over $MgSO_4$. Removal of solvents and subsequent silica gel chromatography (hexane/EtOAc = 5/2) afforded **3a** (27.5 mg, 86%) as colorless oil.



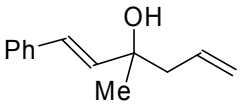
3a:[8] ^{1}H NMR (400 MHz) δ 2.05 (brs, 1H), 2.50 (dd, *J* = 14.0, 8.0 Hz, 1H), 2.57 (ddd, *J* = 14.0, 5.2, 1.2 Hz, 1H), 4.75 (ddd, *J* = 8.0, 5.2, 2.8 Hz, 1H), 5.16 (dd, *J* = 10.4, 0.8 Hz, 1H), 5.18 (dd, *J* = 16.8, 1.2 Hz, 1H), 5.82 (dddd, *J* = 16.8, 10.0, 7.2, 6.4 Hz, 1H), 7.26–7.30 (m, 1H), 7.34–7.37 (m, 4H).



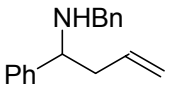
3b:[9] ^{1}H NMR (400 MHz) δ 1.01–1.17 (m, 2H), 1.19–1.42 (m, 4H), 1.60 (brs, 1H), 1.65–1.72 (m, 2H), 1.73–1.80 (m, 2H), 1.83–1.90 (m, 1H), 2.14 (dt, *J* = 14.8, 8.8 Hz, 1H), 2.35 (dm, *J* = 14.8 Hz, 1H), 3.40 (td, *J* = 9.2, 3.6 Hz, 1H), 5.14 (dm, *J* = 11.2 Hz, 1H), 5.15 (dm, *J* = 15.2 Hz, 1H), 5.84 (ddt, *J* = 16.0, 11.2, 6.0 Hz, 1H).



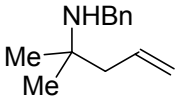
3c: ^{1}H NMR (400 MHz) δ 1.53 (s, 3H), 2.08 (brs, 1H), 2.48 (dd, *J* = 13.6, 8.0 Hz, 1H), 2.65 (dd, *J* = 13.6, 6.8 Hz, 1H), 5.137 (dm, *J* = 11.6 Hz, 1H), 5.139 (dm, *J* = 15.2 Hz, 1H), 5.59 (dddd, *J* = 15.2, 11.6, 8.4, 6.4 Hz, 1H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz) δ 29.9, 48.3, 73.4, 92.1, 119.8, 126.9, 133.0, 137.0, 147.2. IR (neat) 3460, 2977, 1483, 1393, 1005 cm^{-1}. HRMS (CI) *m*/*z* calcd for $C_{11}H_{14}OI$ (MH^+): 289.0089, found 289.0090.



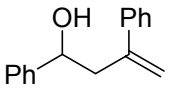
3d:[10] ^{1}H NMR (300 MHz) δ 1.40 (s, 3H), 1.79 (brs, 1H), 2.37 (dd, *J* = 13.5, 8.1 Hz, 1H), 2.46 (dd, *J* = 13.8, 6.9 Hz, 1H), 5.176 (dm, *J* = 15.9 Hz, 1H), 5.183 (dm, *J* = 9.9 Hz, 1H), 5.84 (dddd, *J* = 15.6, 11.7, 8.1, 6.6 Hz, 1H), 6.31 (d, *J* = 15.9 Hz, 1H), 6.61 (d, *J* = 15.9 Hz, 1H), 7.20–7.41 (m, 5H).



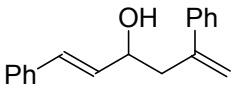
3e:[11] ^{1}H NMR (400 MHz) δ 1.81 (brs, 1H), 2.41 (dd, *J* = 14.4, 8.0 Hz, 1H), 2.47 (dd, *J* = 14.4, 6.0 Hz, 1H), 3.54 (d, *J* = 13.2 Hz, 1H), 3.69 (d, *J* = 12.8 Hz, 1H), 3.71 (dd, *J* = 7.6, 6.4 Hz, 1H), 5.05 (dm, *J* = 10.4 Hz, 1H), 5.09 (dm, *J* = 16.4 Hz, 1H), 5.71 (dddd, *J* = 16.4, 10.0, 7.6, 6.0 Hz, 2H), 7.24–7.38 (m, 10H).



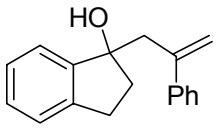
3f:[12] ^{1}H NMR (400 MHz) δ 1.16 (s, 6H), 2.18–2.19 (br, 1H), 2.26 (d, *J* = 7.6 Hz, 2H), 3.72 (s, 2H), 5.119 (d, *J* = 15.2 Hz, 1H), 5.121 (d, *J* = 10.4 Hz, 1H), 5.88 (ddt, *J* = 16.4, 10.4, 7.2 Hz, 1H), 7.23 (tt, *J* = 7.2, 1.6 Hz, 1H), 7.29–7.36 (m, 4H).



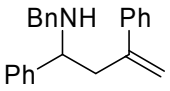
9a:[13] ^{1}H NMR (400 MHz) δ 2.08 (brs, 1H), 2.87 (dd, *J* = 14.4, 9.2 Hz, 1H), 3.04 (ddd, *J* = 14.0, 4.4, 1.2 Hz, 1H), 4.74 (ddd, *J* = 9.2, 4.4, 2.4 Hz, 1H), 5.19 (d, *J* = 1.2 Hz, 1H), 5.43 (d, *J* = 1.2 Hz, 1H), 7.26–7.47 (m, 10H).



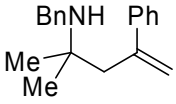
9g: ^{1}H NMR (400 MHz) δ 1.91 (brs, 1H), 2.81 (ddd, *J* = 14.0, 8.0, 0.8 Hz, 1H), 2.93 (ddd, *J* = 14.4, 4.8, 1.2 Hz, 1H), 4.37 (dd, *J* = 14.0, 6.0 Hz, 1H), 5.24 (d, *J* = 1.2 Hz, 1H), 5.45 (d, *J* = 1.2 Hz, 1H), 6.23 (dd, *J* = 16.0, 6.4 Hz, 1H), 6.55 (d, *J* = 16.0 Hz, 1H), 7.22–7.27 (m, 1H), 7.29–7.40 (m, 7H), 7.45 (dm, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz) δ 44.0, 70.7, 115.7, 126.2, 126.3, 127.4, 127.6, 128.3, 128.4, 130.1, 131.4, 136.5, 140.3, 144.6. IR (neat) 3400, 3026, 2936, 1495, 1447 cm^{-1}. HRMS (EI) *m*/*z* calcd for $C_{18}H_{18}O$: 250.1357, found 250.1357.



9h: ^{1}H NMR (400 MHz) δ 1.91 (ddd, *J* = 15.2, 8.4, 6.8 Hz, 1H), 2.11 (brs, 1H), 2.20 (ddd, *J* = 13.2, 8.0, 4.4 Hz, 1H), 2.73 (dt, *J* = 16.0, 7.6 Hz, 1H), 2.92 (ddd, *J* = 16.0, 8.4, 4.4 Hz, 1H), 3.02 (d, *J* = 14.0 Hz, 1H), 3.14 (d, *J* = 14.0 Hz, 1H), 5.18 (d, *J* = 0.8 Hz, 1H), 5.42 (d, *J* = 0.8 Hz, 1H), 7.17–7.22 (m, 3H), 7.24–7.35 (m, 4H), 7.39–7.42 (m, 2H); ^{13}C NMR (100 MHz) δ 29.6, 40.0, 45.5, 83.1, 117.4, 122.8, 124.7, 126.3, 126.4, 127.3, 128.0, 128.2, 142.1, 142.6, 145.0, 147.0. IR(neat) 3410, 3023, 2938, 1624, 1458 cm^{-1}. HRMS (EI) *m*/*z* calcd for $C_{18}H_{16}$([M–H_2O]$^+$): 232.1252, found 232.1250.

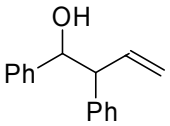


9e:[14] ^{1}H NMR (400 MHz) δ 1.68 (brs, 1H), 2.78 (dd, *J* = 14.0, 9.2 Hz, 1H), 2.91 (dd, *J* = 14.0, 4.4 Hz, 1H), 3.38 (d, *J* = 13.2 Hz, 1H), 3.62 (d, *J* = 13.2 Hz, 1H), 3.69 (dd, *J* = 9.2, 4.4 Hz, 1H), 5.08 (d, *J* = 1.2 Hz, 1H), 5.31 (d, *J* = 1.2 Hz, 1H), 7.10–7.40 (m, 15H).

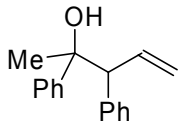


9f : ^{1}H NMR (400 MHz) δ 1.07 (s, 6H), 1.39 (brs, 1H), 2.77 (s, 2H), 3.67 (s, 2H), 5.14 (d, *J* = 0.8 Hz, 1H), 5.32 (d, *J* = 0.8 Hz, 1H), 7.15 (dm, *J* = 6.8 Hz, 2H), 7.21 (dm, *J* = 7.2 Hz, 1H), 7.24–7.35 (m, 5H), 7.41 (dm, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz) δ 27.9, 46.1, 46.7, 53.7, 117.1, 126.4, 126.5, 127.0, 127.8, 128.1, 128.2,

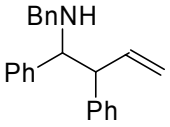
141.0, 143.3, 146.6. IR (neat) 3318, 2965, 1622, 1493, 1453 cm^{-1}. HRMS (CI) *m*/*z* calcd for $C_{19}H_{23}N$ (MH^+): 266.1909, found 226.1911.



11a:[15] ^1H NMR (400 MHz) (syn isomer) δ 2.33 (brs, 1H), 3.65 (dd, *J* = 8.4, 7.6 Hz, 1H), 4.86 (dd, *J* = 17.2, 1.6 Hz, 1H), 4.91 (dd, *J* = 8.4, 2.0 Hz, 1H), 5.01 (dd, *J* = 10.4, 1.2 Hz, 1H), 5.91 (ddd, *J* = 17.2, 10.4, 8.0 Hz, 1H), 7.05–7.40 (m, 10H); (anti isomer) δ 1.96 (brs, 1H), 3.56 (t, *J* = 8.4 Hz, 1H), 4.86 (dd, *J* = 8.4, 2.0 Hz, 1H), 5.24 (dd, *J* = 16.4, 1.2 Hz, 1H), 5.28 (dd, *J* = 10.4, 1.2 Hz, 1H), 6.26 (ddd, *J* = 17.2, 10.4, 9.2 Hz, 1H), 7.05–7.40 (m, 10H).



11i:[16] ^1H NMR (400 MHz) (syn isomer) δ 1.58 (s, 3H), 2.07 (brs, 1H), 3.59 (d, *J* = 10.4 Hz, 1H), 5.09 (ddd, *J* = 16.8, 1.6, 0.8 Hz, 1H), 5.17 (dd, *J* = 10.4, 2.0 Hz, 1H), 6.24 (dt, 17.2, 10.4 Hz, 1H), 7.10–7.32 (m, 10H); (anti isomer) δ 1.43 (s, 3H), 2.00 (brs, 1H), 3.62 (d, *J* = 8.8 Hz, 1H), 4.92 (ddd, *J* = 16.8, 1.6, 0.8 Hz, 1H), 5.04 (ddd, *J* = 10.8, 2.0, 0.8 Hz, 1H), 6.10 (ddd, 16.8, 10.8, 8.8 Hz, 1H), 6.90–6.94 (m, 1H), 7.10–7.32 (m, 9H).



11e: ^1H NMR (400 MHz) δ 1.73 (brs, 1H), 3.35 (d, *J* = 13.6 Hz, 1H), 3.55 (dd, *J* = 8.4, 8.0 Hz, 1H), 3.61 (d, *J* = 14.0 Hz, 1H), 3.84 (d, *J* = 9.2 Hz, 1H), 4.67 (d, *J* = 17.2 Hz, 1H), 4.82 (d, *J* = 10.0 Hz, 1H), 5.76 (ddd, *J* = 17.2, 10.4, 8.0 Hz, 1H), 7.01 (dm, *J* = 8.0 Hz, 2H), 7.18 (dm, *J* = 8.4 Hz, 2H), 7.21–7.37 (m, 11H); ^{13}C NMR (75 MHz) δ 51.0, 57.6, 65.9, 116.1, 126.5, 126.7, 127.1, 127.9, 127.97, 128.02, 128.3, 128.52, 128.54, 138.9, 140.1, 141.2, 141.6. IR (KBr) 3340, 3026, 1599, 1453, 698cm^{-1}. HRMS (FAB) *m*/*z* calcd for $C_{23}H_{25}N$ (MH^+): 314.1909, found 314.1909.

Synthesis of copper complex 4. To a suspension of CuI (95.4 mg, 0.50 mmol) in dry THF (1.2 mL) were added **1** (97.7 mg, 0.55 mmol) and dry THF (0.8 mL). After the mixture was stirred at room temperature for 16 h, the mixture was filtrated and washed with THF to afford **4** (128.8 mg, 73%). ^1H NMR (400 MHz, CD_3CN) δ 0.35 (s, 12H), 1.81 (d, *J* = 8.0 Hz, 4H), 4.68 (d, *J* = 16.4 Hz, 2H), 4.71 (d, *J* = 9.2 Hz, 2H), 5.57 (ddd, *J* = 17.2, 9.2, 8.0 Hz, 2H), 7.35 (t, *J* = 5.6 Hz, 2H), 7.63 (d, *J* = 7.6 Hz, 2H), 7.74 (t, *J* = 5.6

Hz, 2H), 8.82 (d, *J* = 4.8 Hz, 2H); ^{13}C NMR (100 MHz, CD_3CN) δ –3.0, 22.2, 103.5 (br), 124.5, 124.7 (br), 130.7, 135.8, 151.5, 167.0. LRMS (FAB) *m*/*z* 607 (bridged dimer – I), 430 (bridged dimer – I – allylsilane), 240 (monomer – I); HRMS (FAB) *m*/*z* calcd for $C_{20}H_{30}N_2Si_2Cu_2I$ ([M – I]$^+$): 606.9584, found 606.9580.

Reaction of 4 with benzaldehyde. To a suspension of **4** (55.4 mg, 0.16 mmol) and benzaldehyde **2a** (13.9 mg, 0.13 mmol) in dry THF (0.3 mL) were added CsF (35.7 mg, 0.24 mmol) and dry THF (0.2 mL). After the mixture was stirred at room temperature for 2 h, sat. NH_4Cl *aq* (2 mL) was added to the reaction mixture. The aqueous layer was extracted with Et_2O (2 mL × 3), and the combined organic phase was dried over $MgSO_4$. Removal of solvents and subsequent silica gel chromatography (hexane/EtOAc = 5/1) afforded **3a** (14.1 mg, 73%).

Transformation of homoallylic amine 11e to 4-acetoxypiperidine 15 (Scheme 3).

To a solution of homoallylic amine **11e** (327.3 mg, 1.00 mmol) and $Na_2WO_4{\cdot}2H_2O$ (33.0 mg, 0.1 mmol) in acetone (1 mL) was added 30% H_2O_2 *aq* (8.3 mmol, 1 mL). After the mixture was stirred at room temperature for 3 days, the mixture was poured into H_2O (10 mL) and then filtrated. The residue was washed with hexane to afford nitrone **12** as colorless solid (257.9 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.70 (dd, *J* = 11.2, 7.6 Hz, 1H), δ 4.94 (dt, *J* = 17.2, 1.6 Hz, 1H), 4.99 (dt, *J* = 10.4, 1.2 Hz, 1H), 5.05 (d, *J* = 11.2 Hz, 1H), 5.82 (d, *J* = 17.2, 10.4, 7.6 Hz, 1H), 5.82 (ddd, *J* = 17.2, 10.4, 7.6 Hz, 1H), 7.13–7.18 (m, 2H), 7.23–7.29 (m, 6H), 7.35–7.43 (m, 6H), 7.70 (dm, *J* = 7.6 Hz, 2H), 7.93–7.97 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.5, 84.3, 118.1, 126.9, 127.8, 128.0, 128.2, 128.3, 128.4, 128.8, 128.9, 129.8, 130.1, 133.5, 135.6, 136.6, 140.3; IR (KBr) 1576, 1455, 1146 cm^{-1}. HRMS (FAB) *m*/*z* calcd for $C_{23}H_{22}NO$ (MH$^+$): 328.1701, found 328.1703.

This nitrone **12** was dissolved to toluene (1 mL) and the resultant solution was heated at 110 °C (reflux) for 12 h. Removal of solvent afforded **13** which was used for the next reaction without further purification.

A suspension of Zn powder (320.0 mg, 5.0 mmol) and **13** in acetic acid (5 mL) was stirred at 60 °C for 15 h. After filtration of the resultant mixture, filtrate was poured into 10% NH_3 *aq* (25 mL). The resultant mixture was extracted with $CHCl_3$ (20 ml × 3), and the combined organic layer was washed with 5% NH_3 *aq* (20 ml × 2) and dried over $MgSO_4$. Removal of the solvents afforded **14** which was used for the next reaction without further purification.

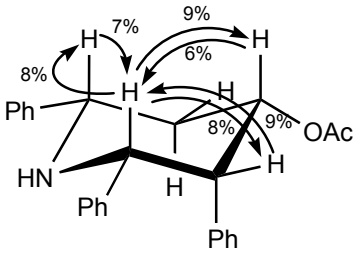
To a solution of **14** in CH_2Cl_2 were added triethylamine (0.5 mL, 3.5 mmol), acetic anhydride (0.6 mL, 2.5 mmol) and 4-dimethylaminopyridine (5 mg, 0.05 mmol). After the mixture was stirred at room temperature for 12 h, H_2O (5 mL) was added to the mixture. The mixture was extracted with CH_2Cl_2 (5 mL × 3), and combined organic layer was washed with brine (5 mL × 1) and dried with $MgSO_4$. Removal

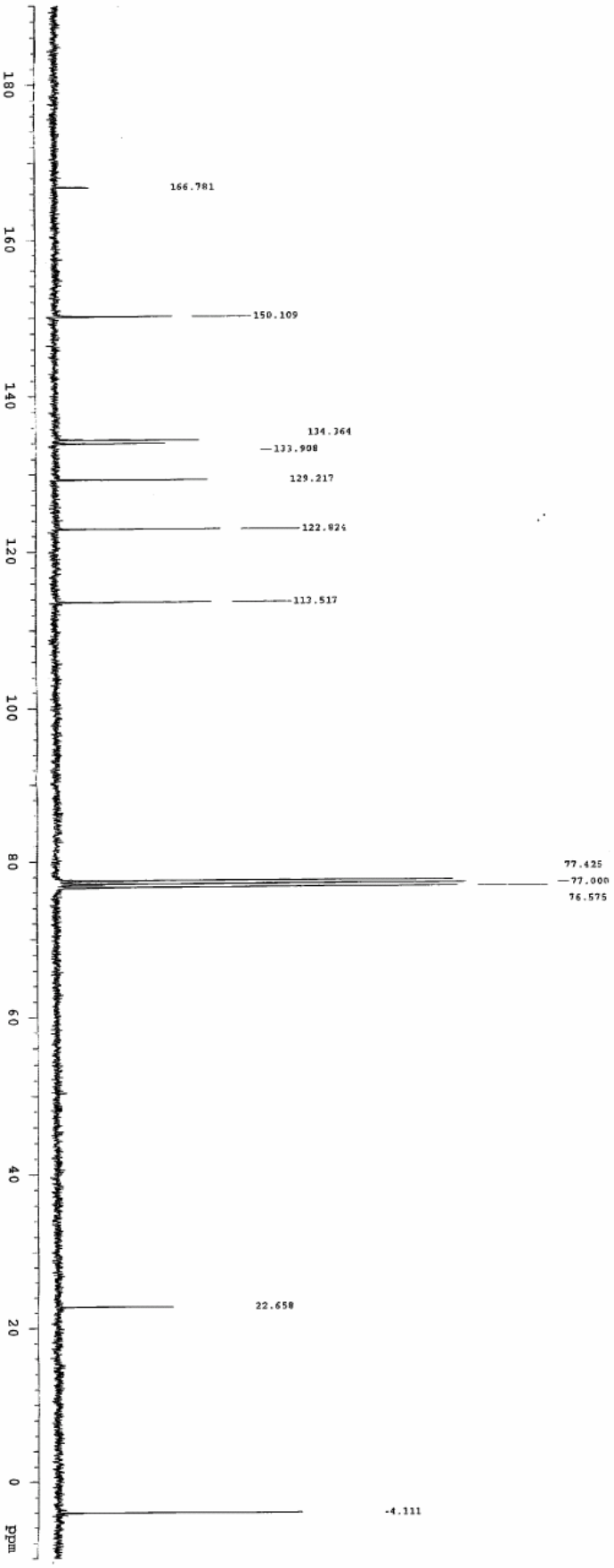
of solvents under reduced pressure and subsequent silica gel chromatography (hexane/EtOAc/Et_3N = 100/20/1) afforded **15** (158.9 mg, 49%) as a mixture of diastereomers (77/23). (Major isomer could be purified by gel permeation chromatography, but minor isomer could not be separated from major isomer)

^1H NMR (400 MHz, $CDCl_3$) (major isomer) δ 1.87 (s, 3H), 1.97 (dt, *J* = 12.8, 4.0 Hz, 1H), 2.00 (brs, 1H), 2.21 (ddd, *J* = 12.0, 12.0, 12.0 Hz, 1H), 3.62 (dd, *J* = 5.2, 3.2 Hz, 1H), 4.12 (dd, *J* = 12.0, 3.2 Hz, 1H), 4.48 (d *J* = 3.6 Hz, 1H), 5.40 (ddd, *J* = 12.4, 5.6, 5.6 Hz, 1H), 7.02–7.21 (m, 7H), 7.28 (dm, *J* = 7.2 Hz, 2H), 7.34 (tm, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.60 (dm, *J* = 7.2 Hz, 2H), 7.65 (dm, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 34.7, 49.7, 60.7, 63.3, 74.7, 126.2, 126.6, 126.70, 126.72, 127.1, 127.5, 127.7, 128.5, 131.4, 136.8, 141.5, 143.8, 170.4; IR (KBr) 3310, 3063, 1728, 1242 cm^{-1}.HRMS (EI) *m*/*z* calcd for $C_{25}H_{25}NO_2$ (M^+): 371.1885, found 371.1885.

(minor isomer) δ 1.90 (s, 3H), 2.49 (dt, *J* = 17.2, 3.6 Hz, 1H), 2.65 (ddd, *J* = 12.0, 12.0, 5.6 Hz, 1H), 3.53-3.56 (m, 1H), 4.47–4.49(m, 1H), 4.80 (dm *J* = 2.8 Hz, 1H), 5.38–5.46 (m, 1H), 7.06–7.68 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 31.7, 50.4, 54.0, 57.1, 71.4, 126.20, 126.6, 126.8, 126.9, 127.2, 127.6, 127.7, 128.6, 131.1, 136.9, 141.6, 143.7, 170.3.

The NOE data of **15** (major isomer) are as follow.

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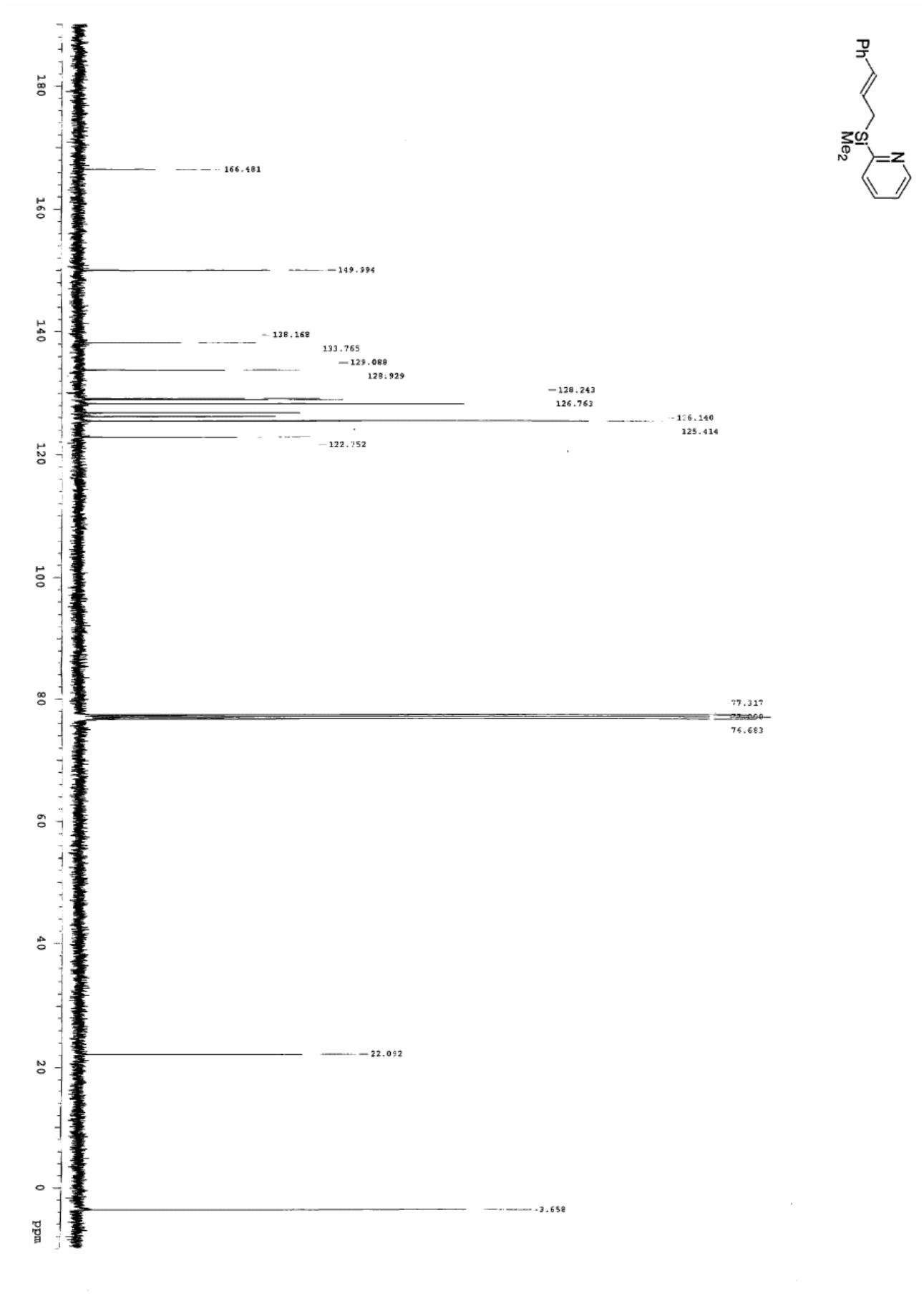
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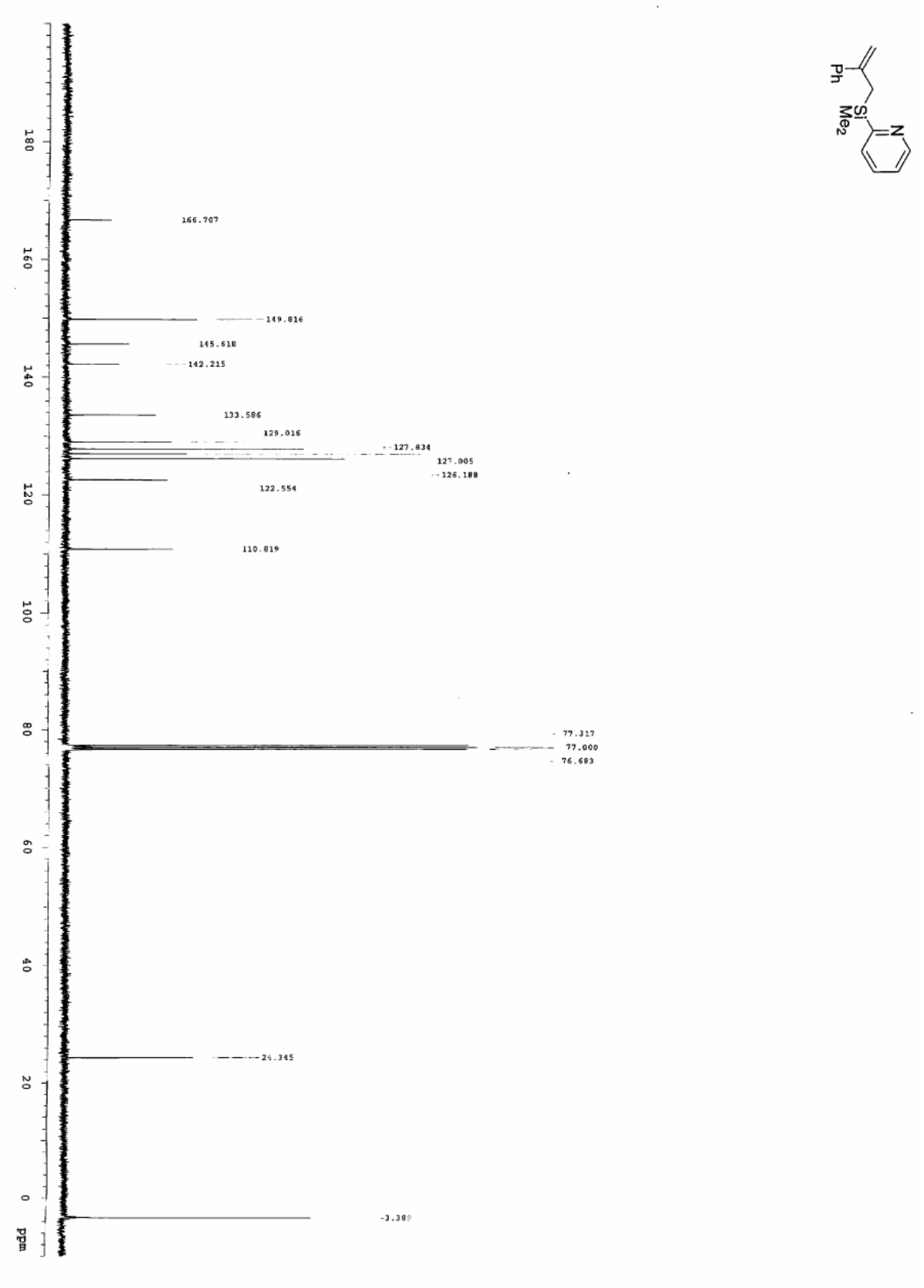
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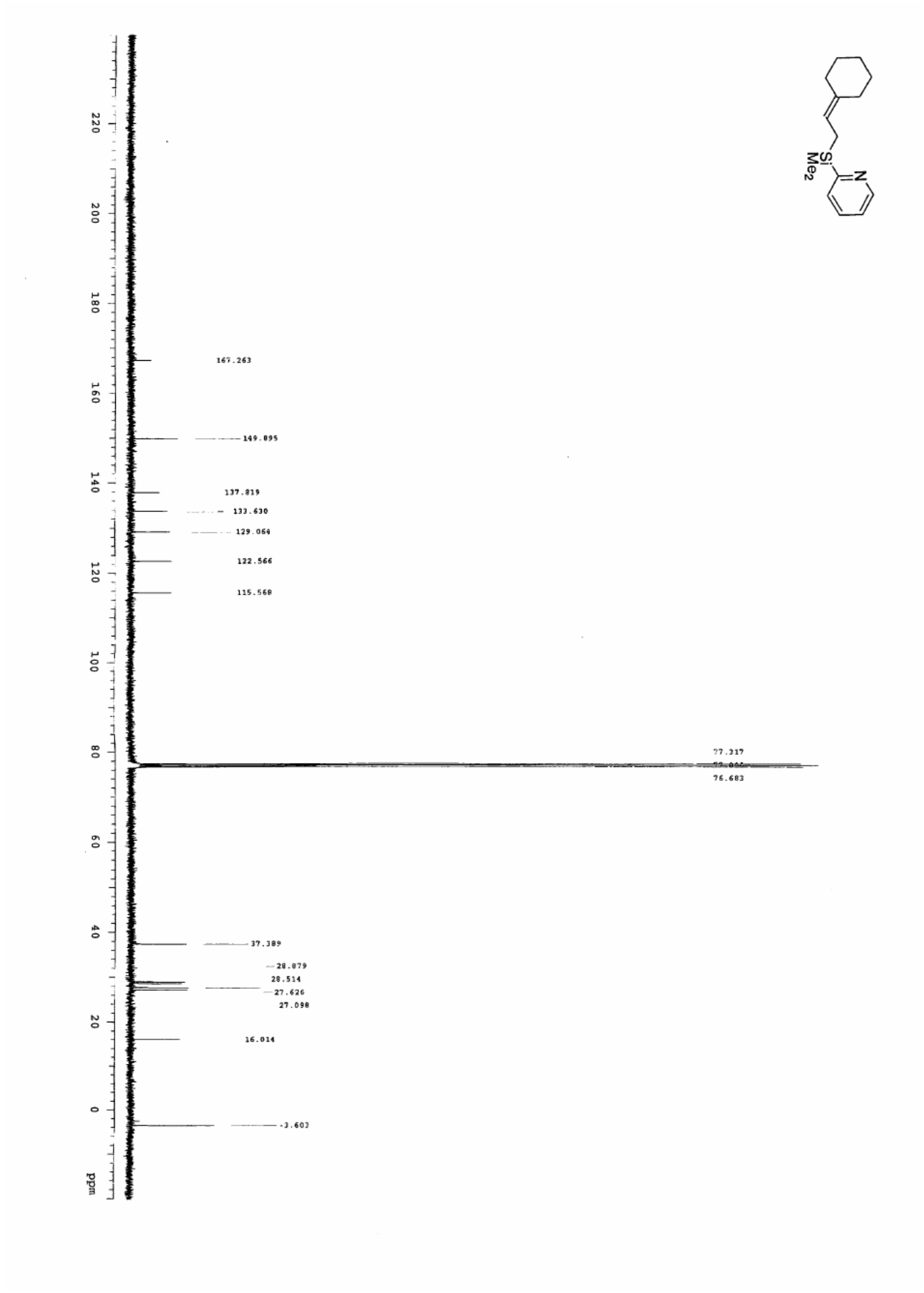
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Me2
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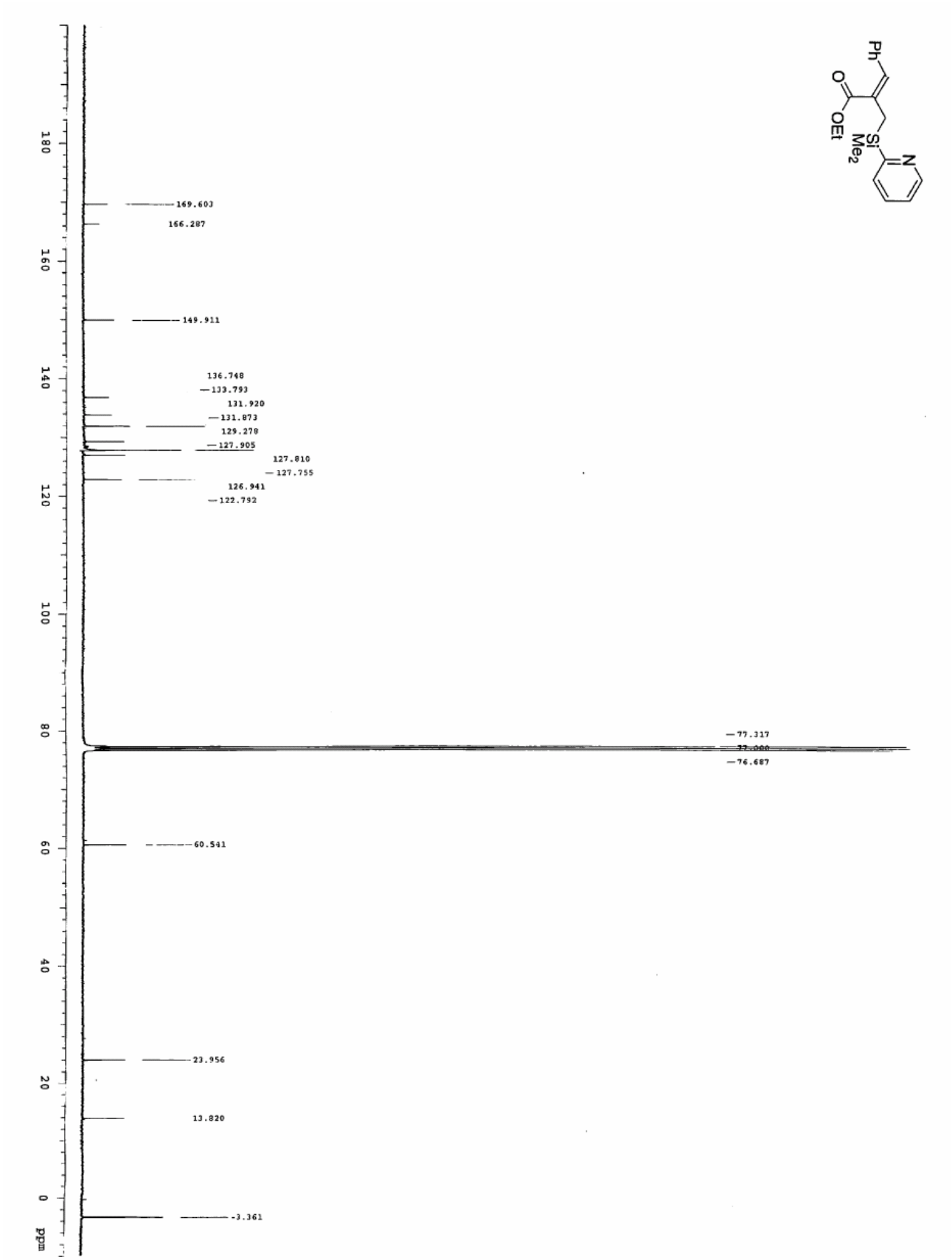
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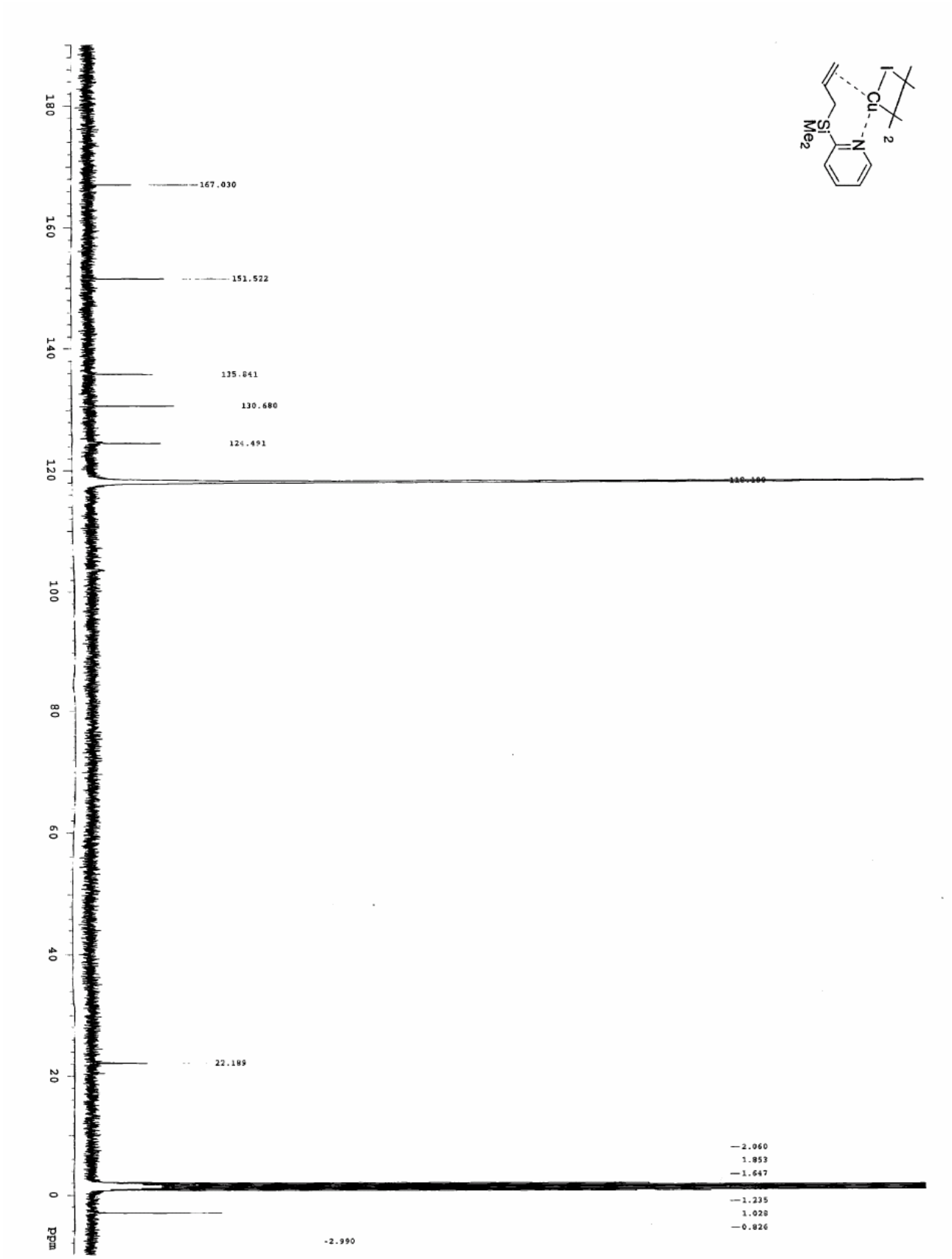
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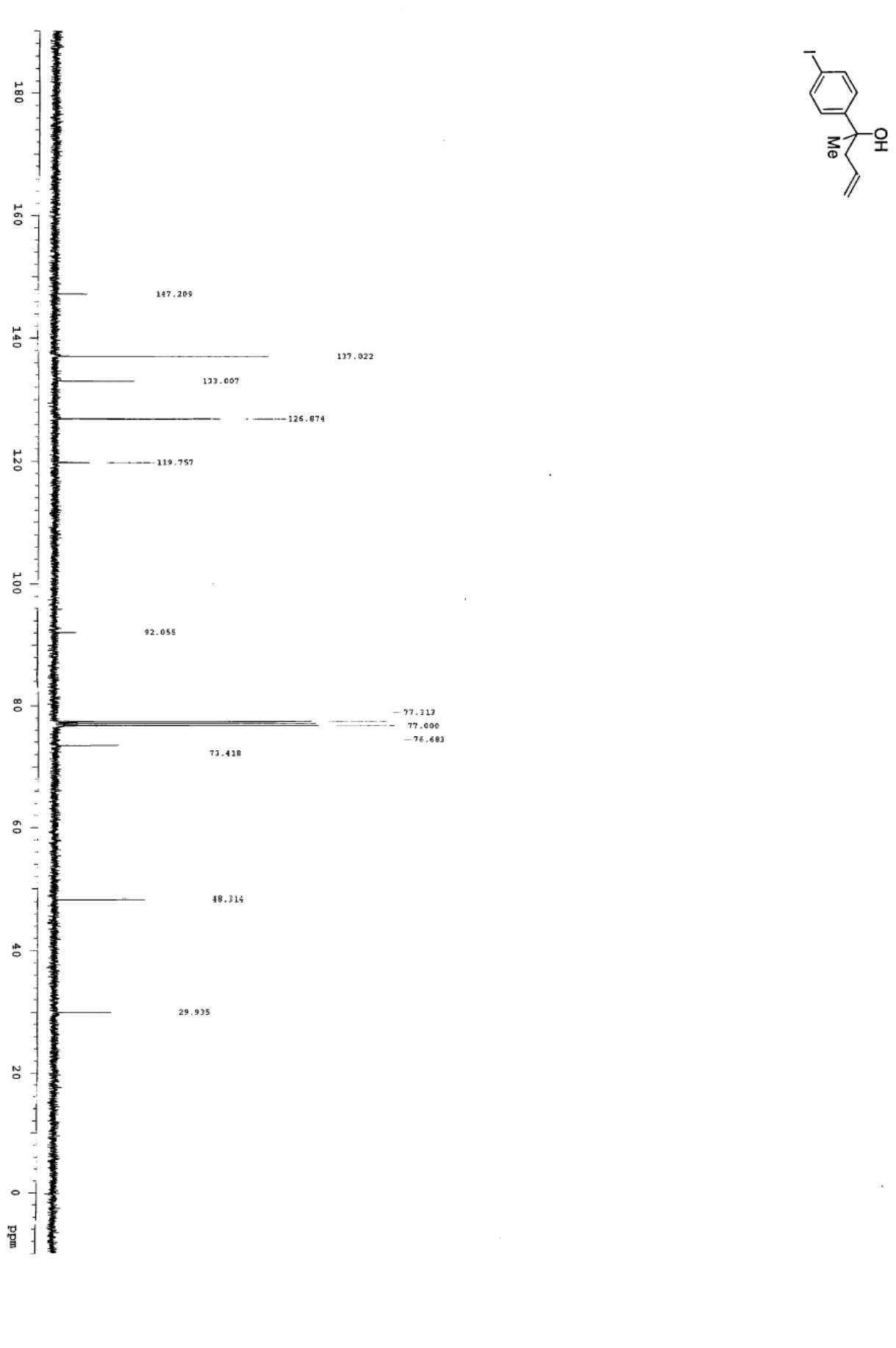
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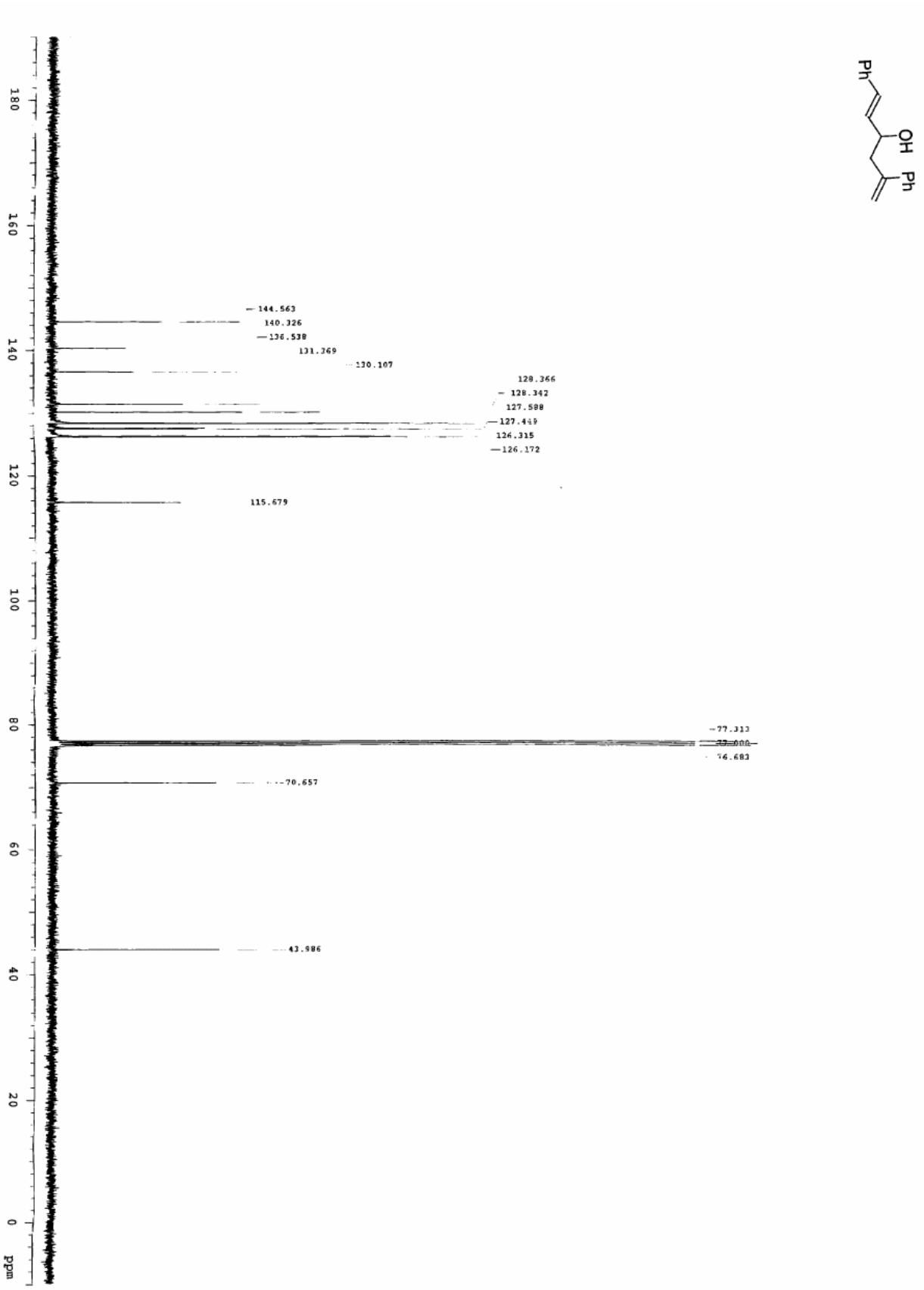
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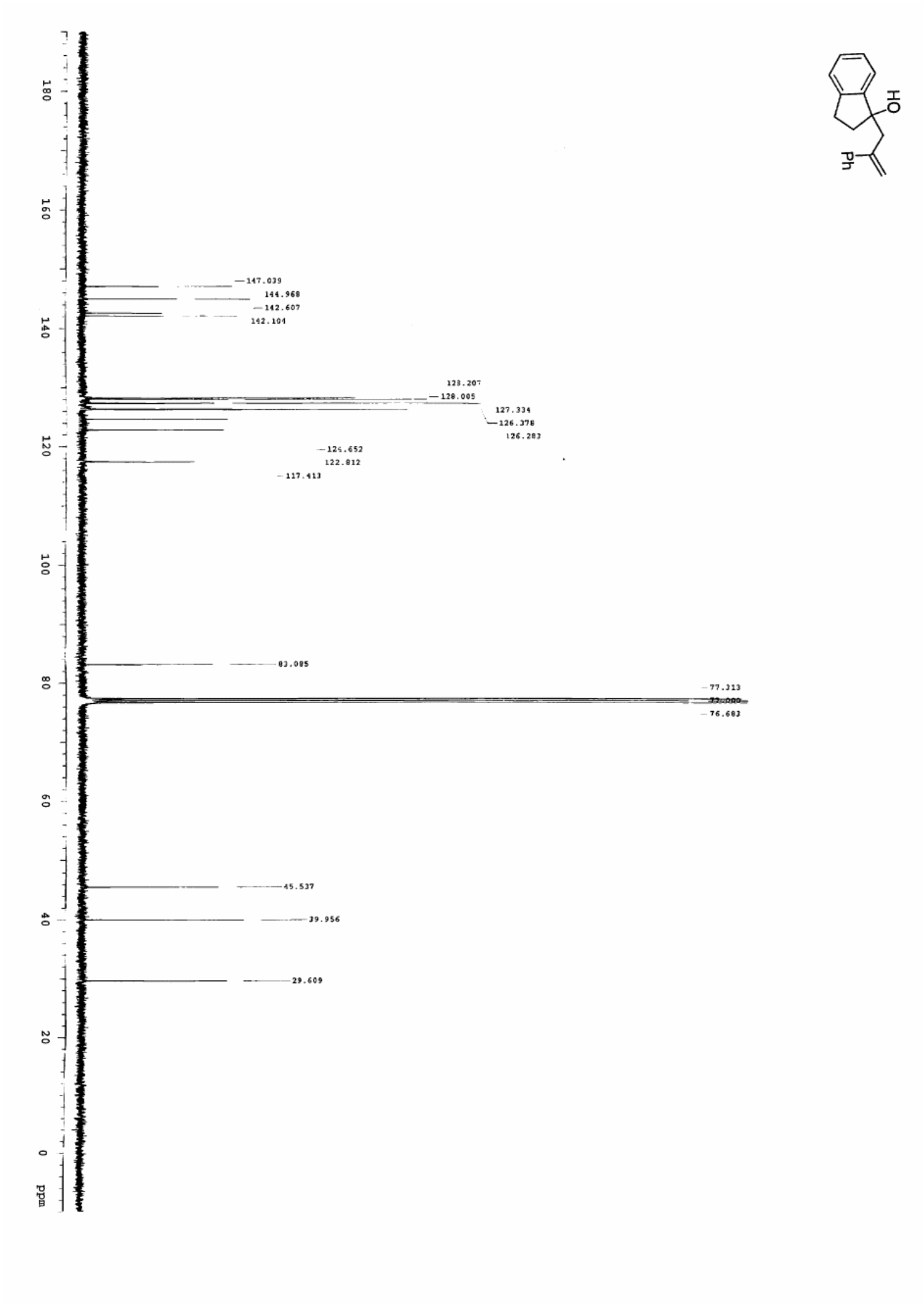
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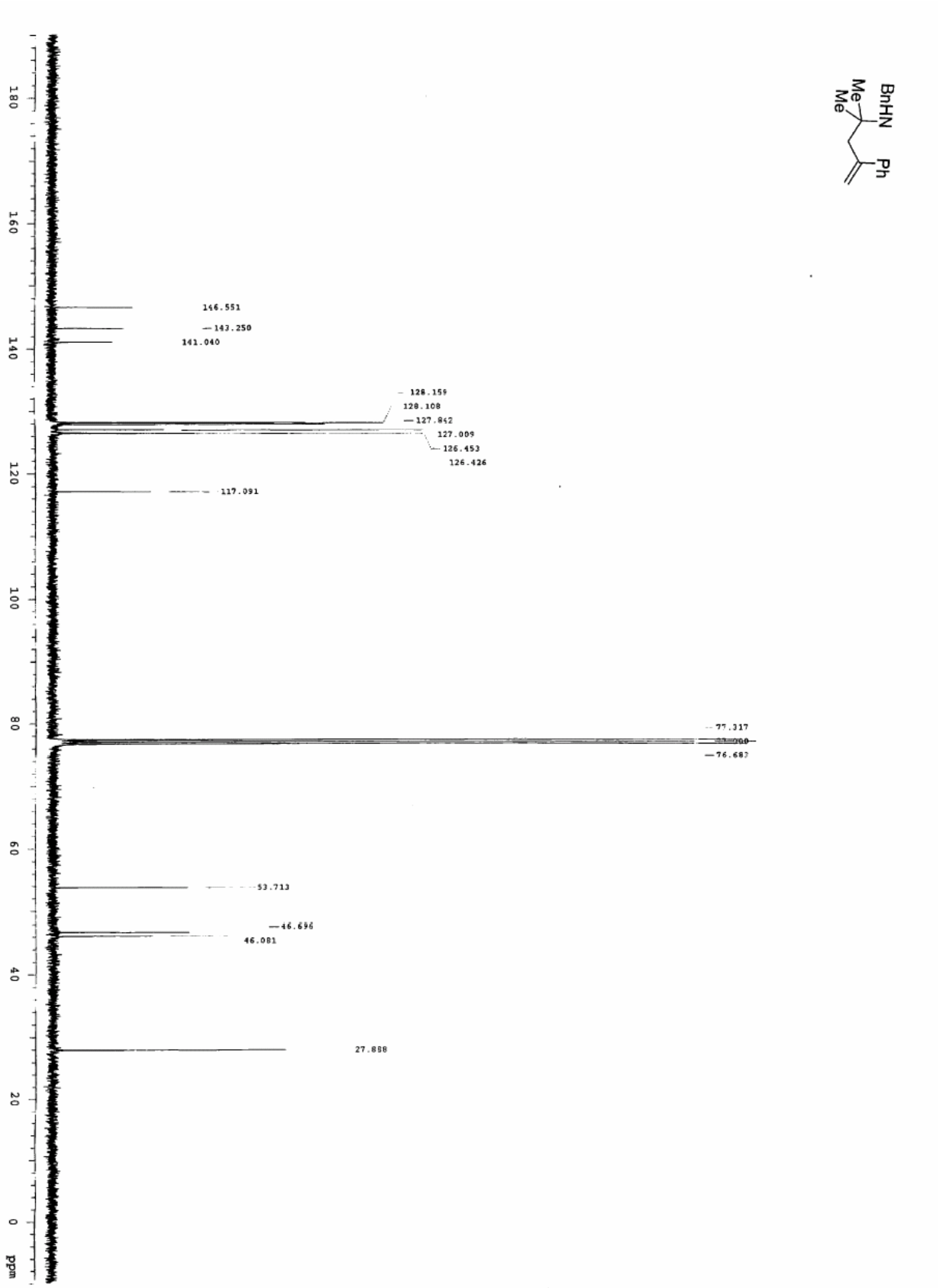
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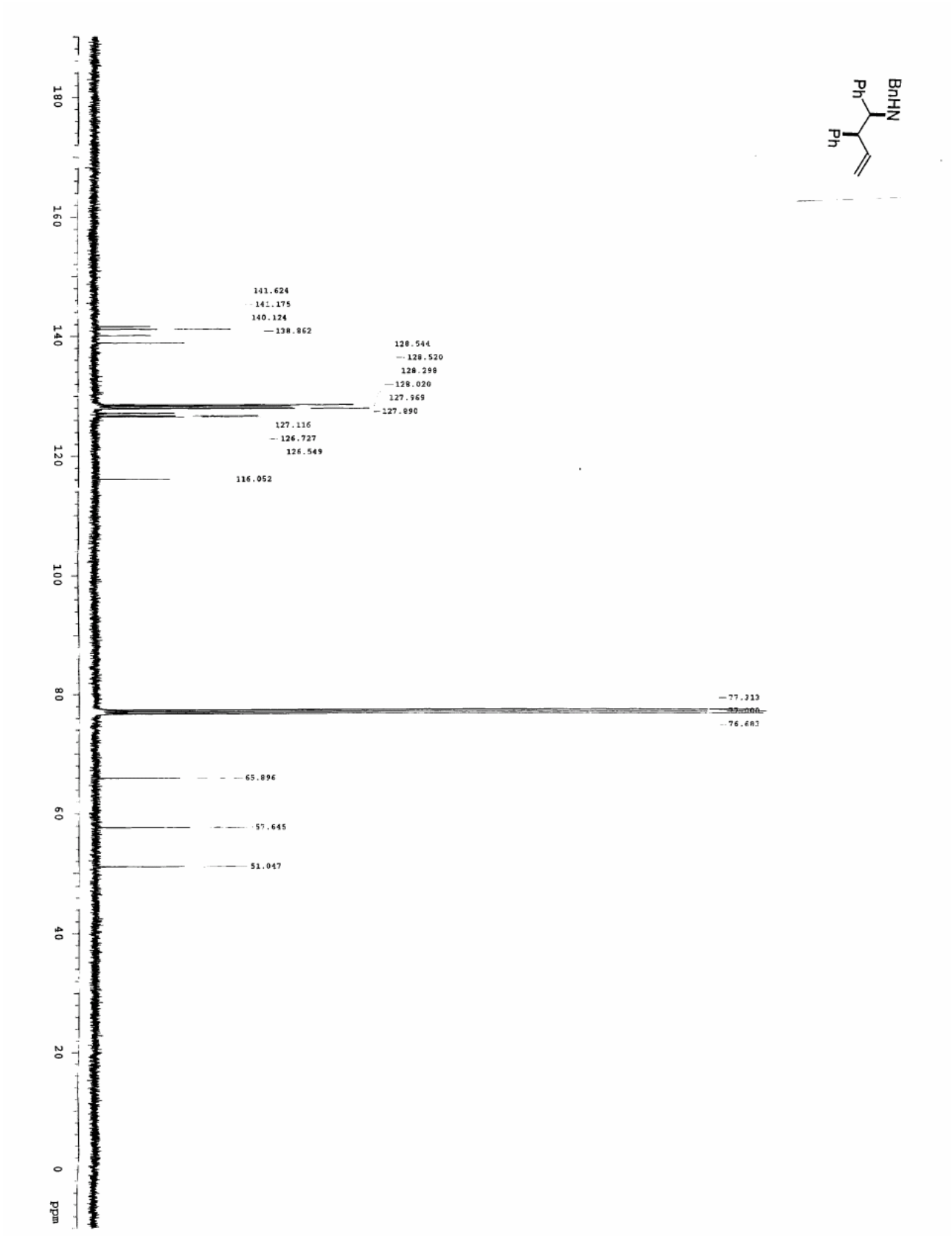
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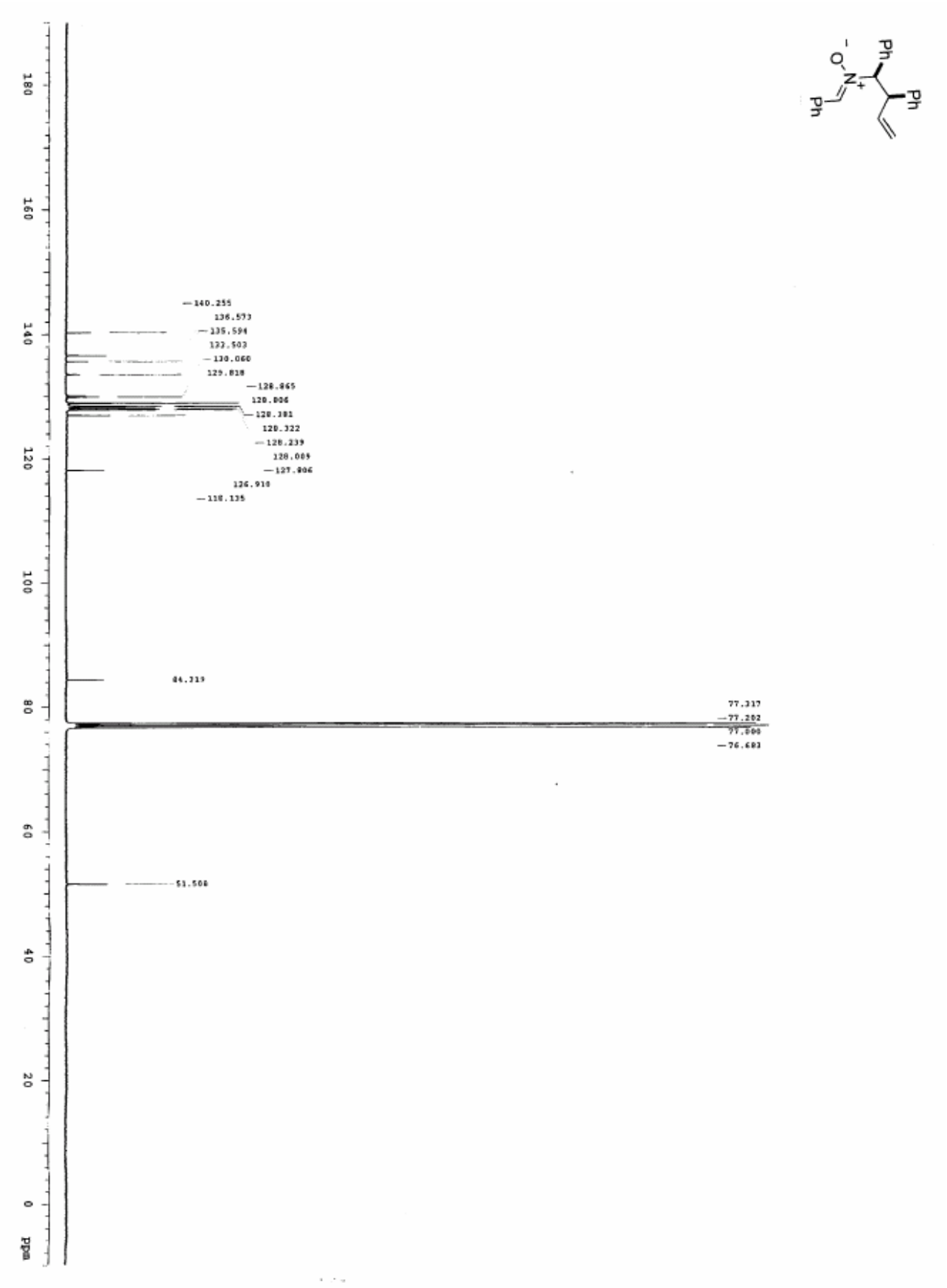
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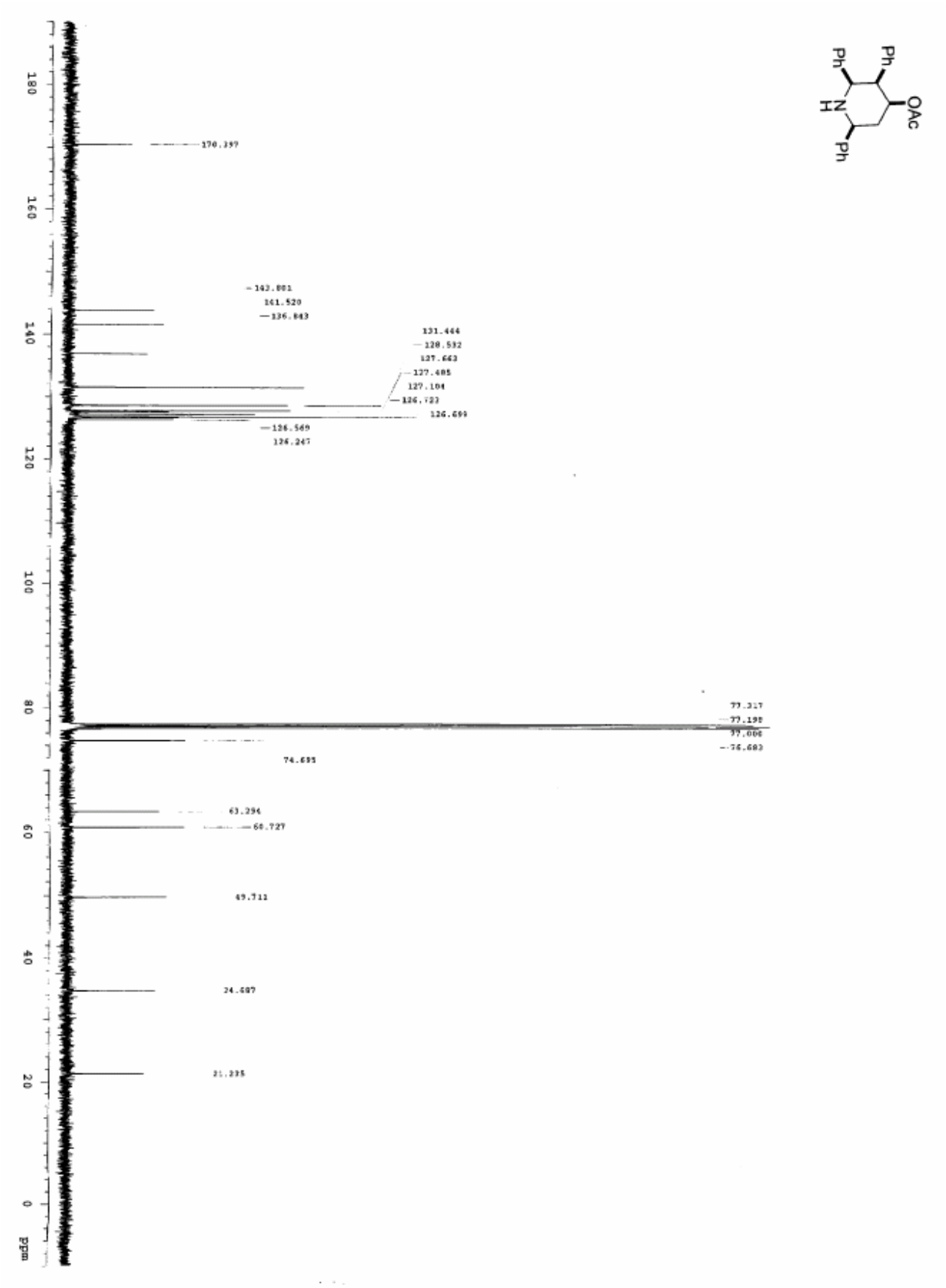
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References

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