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Supplementary Information

Synthesis of Structurally Diverse Silicon-Incorporated Indolines via Silyl Radical-Triggered Radical Cascade Reactions

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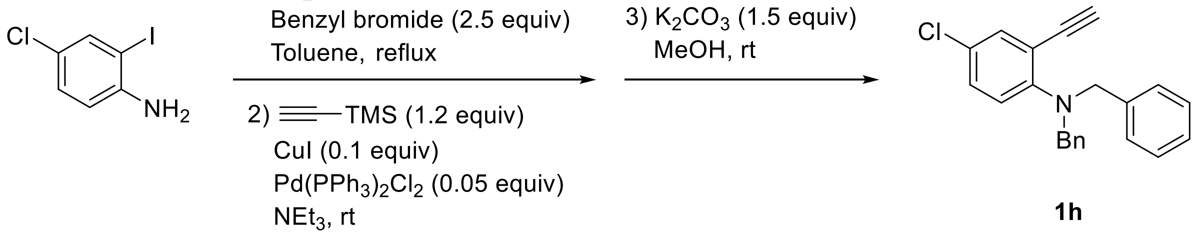
1. General

^{1}H NMR (400 MHz) (500 MHz) spectra were recorded on a Bruker Avance 400 or 500 spectrometer in $CDCl_3$ [using $CDCl_3$ (for ^{1}H, $\delta = 7.26$). ^{13}C NMR (100 MHz) (125 MHz) spectra on a Bruker Avance 400 or 500 spectrometer in $CDCl_3$ [using $CDCl_3$ (for ^{13}C, $\delta = 77.0$) as internal standard]. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, ddd = doublet of doublet of doublet, dt = doublet of triplet, m = multiplet, s br = single broad. High-resolution mass spectra were obtained with a Water XEVO G2 Q-Tof (Waters Corporation). X-ray crystallography analysis was performed on Bruker X8 APEX X-ray diffractionmeter. Melting points were uncorrected and were recorded on a Buchi B-54 melting point apparatus. Flash column chromatography was performed using Merck silica gel 60 with distilled solvents. Commercially available reagents were purchased from Energy Chemical, J & K Scientific, Adamas-beta and Sigma-Aldrich Co., Inc.

Substrates **1a**[1], **1b**[1], **1aa**[2], **1ab**[2], **1ac**[2], **1ad**[2], **1ae**[2], **1af**[2], **1ag**[2], **1ah**[2], **1ai**[2], **1aj**[2] were known compounds and prepared according to the literature procedures.

2. Synthesis of starting materials

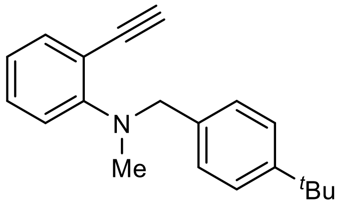
General procedure A:



1h

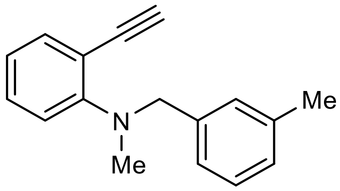
To a solution of 4-chloro-2-iodoaniline (5.069 g, 20.00 mmol) in toluene was added $i$$Pr_2NEt$ (8.3 mL, 50.22 mmol) and benzyl bromide (5.9 mL, 49.68 mmol). The reaction mixture was refluxed under nitrogen atmosphere for 72 h. The white solid precipitant was filtered off and the solvent was removed under *vacuo* to afford orange crude product. The crude material was dissolved in NEt_3, then ethynyltrimethylsilane (3.4 mL, 24.05 mmol), $Pd(PPh_3)_2Cl_2$ (702.0 mg, 1.00 mmol) and CuI (381.0 mg, 2 mmol) were added. The reaction mixture was stirred overnight under nitrogen atmosphere followed by filtration through celite and washed with Et_2O (100.0 mL). The filtrate was concentrated in *vacuo* to give brown crude mixture which was then dissolved in MeOH (50.0 mL), and K_2CO_3 (4.146 g, 30.00 mmol) was added subsequently. The reaction mixture was stirred at room temperature for 1 h and quenched with water. The aqueous layer was extracted with CH_2Cl_2 three times. The combined organic extracts were dried over Na_2SO_4, and concentrated in *vacuo*. The crude residue was purified by flash column chromatography on silica gel (petroleum ether) to give **1h** (4.618 g) in 70% yield as orange oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.40 (s, 1H), 4.35 (s, 4H), 6.71 (d, *J* = 8.0 Hz, 1H), 7.05 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.19-7.29 (m, 10H), 7.45 (d, *J* = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.1, 81.4, 83.7, 117.6, 121.9, 126.1, 127.0, 128.1, 128.3, 129.3, 134.2, 138.0, 151.6; ESI-HRMS (*m/z*): $(M+H)^+$ Calcd for $C_{22}H_{19}ClN$, 332.1201; Found: 332.1203.

N-(4-(tert-butyl)benzyl)-2-ethynyl-*N*-methylaniline (1c)



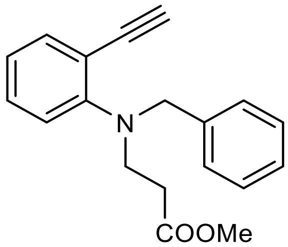
Following general procedure A, **1c** was obtained in 82% yield (1.140 g, 4.10 mmol) from the reaction of *N*-(4-(tert-butyl)benzyl)-2-iodo-*N*-methylaniline[3] (1.900 g, 5.00 mmol) as pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (s, 9H), 2.73 (s, 3H), 3.36 (s, 1H), 4.44 (s, 2H), 6.87-6.94 (m, 2H), 7.23-7.34 (m, 5H), 7.49 (dd, *J* = 7.6, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.4, 34.4, 39.3, 59.9, 82.7, 82.8, 114.6, 118.3, 120.7, 125.0, 128.0, 129.7, 135.0, 135.6, 149.8, 154.8; ESI-HRMS (*m/z*): $(M+H)^+$ Calcd for $C_{20}H_{24}N$, 278.1903; Found: 278.1906.

2-Ethynyl-*N*-methyl-*N*-(3-methylbenzyl)aniline (1d)



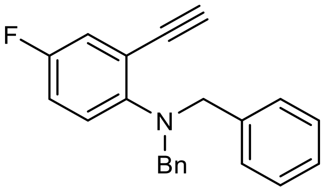
Following general procedure A, **1d** was obtained in 68% yield (1.592 g, 6.77 mmol) from the reaction of 2-iodo-*N*-methyl-*N*-(3-methylbenzyl)aniline (according to the first step of general procedure B, prepared from the reaction of 2-iodo-*N*-methylaniline (2.320 g, 9.95 mmol), K_2CO_3 (2.752 g, 19.91 mmol) and 1-(bromomethyl)-3-methylbenzene (1.8 mL, 13.41 mmol) in toluene at 120 °C for 48 h) as pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3H), 2.73 (s, 3H), 3.35 (s, 1H), 4.44 (s, 2H), 6.87-6.93 (m, 2H), 7.07 (d, *J* = 6.8 Hz, 1H), 7.16-7.28 (m, 4H), 7.49 (dd, *J* = 7.6, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 39.2. 60.2, 82.6, 82.8, 114.5, 118.3, 120.7, 125.3, 127.7, 128.0, 129.0, 129.7, 135.0, 137.7, 138.6, 154.7; ESI-HRMS (*m/z*): $(M+H)^+$ Calcd for $C_{17}H_{18}N$, 236.1434; Found: 236.1433.

Methyl 3-(benzyl(2-ethynylphenyl)amino)propanoate (1e)



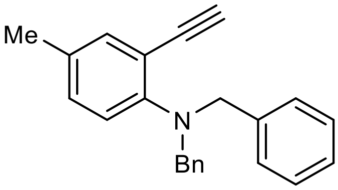
Following general procedure A, **1e** was obtained in 70% yield (1.098 g, 3.74 mmol) from the reaction of methyl 3-(benzyl(2-iodophenyl)amino)propanoate (prepared from the reaction of methyl 3-((2-iodophenyl)amino)propanoate[4] (1.632 g, 5.35 mmol), *i*Pr_2NEt (1.3 mL, 7.87 mmol) and benzyl bromide (0.8 mL, 6.74 mmol) in toluene) as yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.52 (t, *J* = 7.2 Hz, 2H), 3.35 (s, 1H), 3.54 (t, *J* = 7.2 Hz, 2H), 3.57 (s, 3H), 4.41 (s, 2H), 6.88-6.93 (m, 2H), 7.18-7.33 (m, 6H), 7.47 (dd, *J* = 7.6, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.4, 47.1, 51.4, 57.4, 82.3, 82.6, 116.6, 120.6, 121.7, 127.0, 128.1, 128.2, 129.3, 135.0, 138.3, 152.3, 172.6; ESI-HRMS (*m/z*): $(M+H)^+$ Calcd for $C_{19}H_{20}NO_2$, 294.1489; Found: 294.1492.

N,N-dibenzyl-2-ethynyl-4-fluoroaniline (1f)



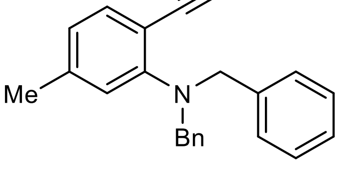
Following general procedure A, **1f** was obtained in 71% yield (4.478 g, 14.20 mmol) from the reaction of 4-fluoro-2-iodoaniline (4.740 g, 20.00 mmol) as yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.42 (s, 1H), 4.29 (s, 4H), 6.74 (dd, J = 8.8, 4.8 Hz, 1H), 6.82 (ddd, J = 8.8, 8.8, 2.8 Hz, 1H), 7.17-7.32 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.7, 81.5 (J = 2.7 Hz), 83.3, 116.2 (J = 21.8 Hz), 118.4 (J = 9.4 Hz), 120.7 (J = 24.4 Hz), 122.6 (J = 8.5 Hz), 127.0, 128.2, 128.3, 138.1, 149.4 (J = 2.4 Hz), 157.3 (J = 240.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -121.55—121.50 (m, 1F); ESI-HRMS (m/z): $(M+H)^+$ Calcd for $C_{22}H_{19}FN$, 316.1496; Found: 316.1504.

N,N-dibenzyl-2-ethynyl-4-methylaniline (1g)



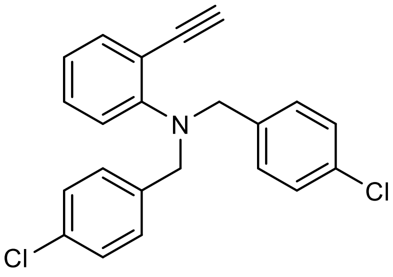
Following general procedure A, **1g** was obtained in 70% yield (4.676 g, 15.01 mmol) from the reaction of 2-iodo-4-methylaniline (5.000 g, 21.45 mmol) as yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.22 (s, 3H), 3.36 (s, 1H), 4.33 (s, 4H), 6.72 (d, J = 8.4 Hz, 1H), 6.92 (dd, J = 8.4, 1.6 Hz, 1H), 7.19-7.33 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.3, 56.3, 82.1, 82.9, 116.3, 120.8, 126.8, 128.1, 128.2, 130.1, 130.9, 135.1, 138.6, 150.7; ESI-HRMS (m/z): $(M+H)^+$ Calcd for $C_{23}H_{22}N$, 312.1752; Found: 312.1751.

N,N-dibenzyl-2-ethynyl-5-methylaniline (1i)



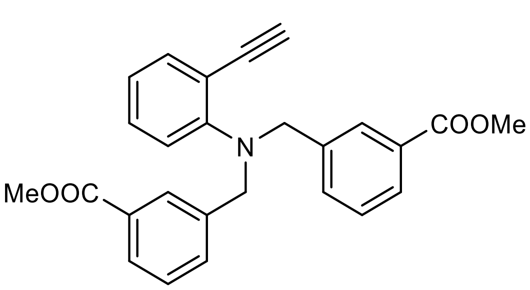
Following general procedure A, **1i** was obtained in 78% yield (5.211 g, 16.73 mmol) from the reaction of 2-iodo-5-methylaniline (5.000 g, 21.45 mmol) as yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.19 (s, 3H), 3.32 (s, 1H), 4.37 (s, 4H), 6.64 (s, 1H), 6.68 (d, *J* = 6.4 Hz, 1H), 7.18-7.21 (m, 2H), 7.25-7.31 (m, 8H), 7.38 (d, *J* = 6.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.7, 55.9, 81.8, 83.0, 113.0, 121.4, 122.2, 126.8, 128.1, 128.2, 134.7, 138.5, 139.5, 153.1; ESI-HRMS (*m/z*): $(M+H)^+$ Calcd for $C_{23}H_{22}N$, 312.1747; Found: 312.1744.

***N,N*-bis(4-chlorobenzyl)-2-ethynylaniline (1j)**



Following general procedure A, **1j** was obtained in 78% yield (1.178 g, 4.17 mmol) from the reaction of 2-iodoaniline (4.380 g, 20.00 mmol) and 1-(bromomethyl)-4-chlorobenzene (6.6 mL, 50.43 mmol) as pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.39 (s, 1H), 4.31 (s, 4H), 6.78 (dd, *J* = 8.0, 0.8 Hz, 1H), 6.92 (ddd, *J* = 7.6, 7.6, 0.8 Hz, 1H), 7.15 (ddd, *J* = 8.0, 7.6, 1.6 Hz, 1H), 7.21-7.25 (m, 8H), 7.51 (dd, *J* = 7.6, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.5, 82.5, 82.7, 116.5, 120.8, 122.0, 128.4, 129.4, 129.5, 132.7, 135.0, 136.7, 152.5; ESI-HRMS (*m/z*): $(M+H)^+$ Calcd for $C_{22}H_{18}Cl_2N$, 366.0811; Found: 366.0817.

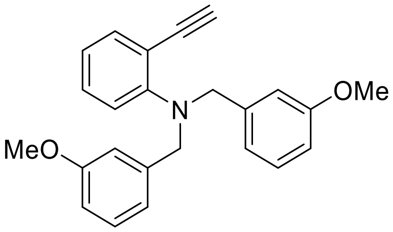
Dimethyl 3,3'-(((2-ethynylphenyl)azanediyl)bis(methylene))dibenzoate (1k)



Following general procedure A, **1k** was obtained in 70% yield (1.178 g, 4.17 mmol) from the reaction of 2-iodoaniline (4.380 g, 20.00 mmol) and methyl 3-

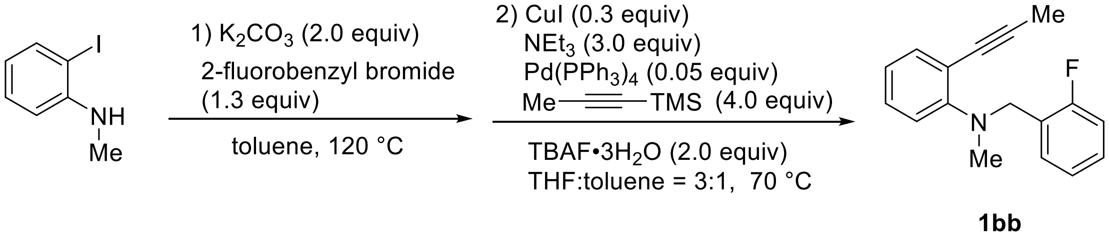
(bromomethyl)benzoate (7.8 mL, 50.05 mmol) as yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.41 (s, 1H), 3.90 (s, 6H), 4.41 (s, 4H), 6.84 (dd, *J* = 8.0, 0.8 Hz, 1H), 6.91 (ddd, *J* = 7.2, 7.2, 0.8 Hz, 1H), 7.14 (ddd, *J* = 8.0, 7.2, 1.6 Hz, 1H), 7.35 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.50 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.56 (ddd, *J* = 7.6, 1.2, 1.2 Hz, 2H), 7.89 (ddd, *J* = 7.6, 1.2, 1.2 Hz, 2H), 7.99 (dd, *J* = 1.2, 1.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.1, 56.1, 82.5, 82.8, 116.7, 120.9, 122.1, 128.3, 128.4, 129.4 (overlapped), 130.1, 132.7, 134.9, 138.7, 152.5, 167.1; ESI-HRMS (*m/z*): $(M+H)^+$ Calcd for $C_{26}H_{24}NO_4$, 414.1700; Found: 414.1701.

2-Ethynyl-*N,N*-bis(3-methoxybenzyl)aniline (1l)



Following general procedure A, **1l** was obtained in 58% yield (4.146 g, 11.60 mmol) from the reaction of 2-iodoaniline (4.380 g, 20.00 mmol) and 1-(bromomethyl)-3-methoxybenzene (7.0 mL, 50.00 mmol) as pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.41 (s, 1H), 3.76 (s, 6H), 4.38 (s, 4H), 6.76-6.79 (m, 2H), 6.86-6.95 (m, 6H), 7.14-7.22 (m, 3H), 7.52 (dd, *J* = 7.6, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.0, 56.0, 82.4, 82.8, 112.6, 113.4, 116.2, 120.5, 120.7, 121.5, 129.1, 129.3, 134.8, 140.1, 153.1, 159.6; ESI-HRMS (*m/z*): $(M+H)^+$ Calcd for $C_{24}H_{24}NO_2$, 358.1802; Found: 358.1808.

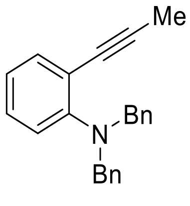
General procedure B:



1bb

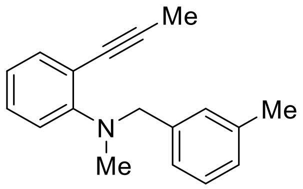
To a solution of 2-iodo-*N*-methylaniline (724.7 mg, 3.11 mmol) in toluene was added potassium carbonate (859.6 mg, 6.22 mmol) and 2-fluorobenzyl bromide (0.5 mL, 4.15 mmol). The mixture was stirred at 120 °C overnight under N_2 atmosphere. Then the reaction mixture was cooled to room temperature and Et_2NH (5.0 mL) was added, which was followed by filtration through celite and washed with Et_2O (20.0 mL). The filtrate was concentrated in *vacuo* to give white crude mixture. The crude product was dissolved in toluene and THF (v:v = 1:3), then $TBAF\cdot 3H_2O$ (1.96 g, 6.22 mmol), NEt_3 (1.3 mL, 9.33 mmol), CuI (177.7 mg, 0.93 mmol), $Pd(PPh_3)_4$ (179.7 mg, 0.16 mmol), and trimethyl(prop-1-ynyl)silane (1.8 mL, 12.44 mmol) were added. The mixture was stirred at 70 °C overnight under N_2 atmosphere. Quenched with water and the aqueous layer was extracted with CH_2Cl_2 three times. The combined organic extracts were dried over Na_2SO_4, and concentrated in *vacuo*. The crude residue was purified by flash column chromatography on silica gel (petroleum ether) to give **1bb** (393.9 mg) in 50% yield as yellow solid, mp: 53-54 °C (a trace amount of unidentified impurity was remained in the product); ^1H NMR (400 MHz, $CDCl_3$) δ 1.82 (s, 3H), 2.76 (s, 3H), 4.55 (s, 2H), 6.84-6.89 (m, 2H), 7.00 (dd, *J* = 9.6, 8.8 Hz, 1H), 7.08 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.15-7.22 (m, 2H), 7.37 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.53 (dd, *J* = 7.2, 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.4, 39.0, 52.9 (d, *J* = 3.2 Hz), 78.6, 91.3, 114.7 (d, *J* = 21.8 Hz), 116.4, 117.8, 120.8, 123.7 (d, *J* = 3.0 Hz), 126.0 (d, *J* = 14.1 Hz), 128.1 (d, *J* = 8.0 Hz), 128.3, 129.9 (d, *J* = 4.6 Hz), 134.0, 153.8, 161.0 (d, *J* = 243.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -119.1--119.0 (m, 1F); ESI-HRMS (*m/z*): $(M+H)^+$ Calcd for $C_{17}H_{17}FN$, 254.1340; Found: 254.1342.

N,N-dibenzyl-2-(prop-1-yn-1-yl)aniline (1ba)



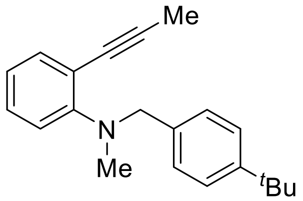
Following general procedure B, **1ba** was obtained in 58% yield (780.0 mg, 2.50 mmol) from the reaction of *N,N*-dibenzyl-2-iodoaniline[1] (1.725 g, 4.32 mmol) as white solid, mp: 92-94 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.93 (s, 3H), 4.42 (s, 4H), 6.79-6.85 (m, 2H), 7.05 (ddd, *J* = 8.4, 8.4, 1.6 Hz, 1H), 7.18-7.22 (m, 2H), 7.26-7.30 (m, 4H), 7.36-7.40 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.6, 56.0, 78.7, 91.2, 117.6, 120.0, 121.0, 126.7, 127.9, 128.0, 128.1, 134.0, 138.9, 152.3; ESI-HRMS (*m/z*): $(M+H)^+$ Calcd for $C_{23}H_{22}N$, 312.1752; Found: 312.1745.

N-methyl-*N*-(3-methylbenzyl)-2-(prop-1-yn-1-yl)aniline (1bc)



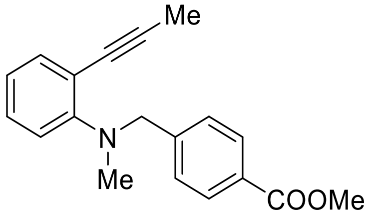
Following general procedure B, **1bc** was obtained in 51% yield (286.7 mg, 1.15 mmol) from the reaction of 2-iodo-*N*-methylaniline (525.5 mg, 2.25 mmol) as yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ 1.94 (s, 3H), 2.36 (s, 3H), 2.72 (s, 3H), 4.42 (s, 2H), 6.89 (ddd, *J* = 9.5, 9.0, 1.5 Hz, 1H), 6.93 (d, *J* = 10.5 Hz, 1H), 7.08-7.10 (m, 1H), 7.19-7.24 (m, 3H), 7.29 (s, 1H), 7.41 (dd, *J* = 9.5, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.6, 21.4, 38.8, 60.1, 78.6, 91.4, 116.6, 117.9, 120.8, 125.2, 127.6, 128.0, 128.4, 128.8, 134.1, 137.6, 139.2, 154.2; ESI-HRMS (*m/z*): $(M+H)^+$ Calcd for $C_{18}H_{20}N$, 250.1590; Found: 250.1596.

N-(4-(tert-butyl)benzyl)-*N*-methyl-2-(prop-1-yn-1-yl)aniline (1bd)



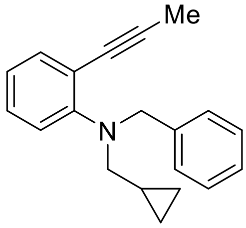
Following general procedure B, **1bd** was obtained in 58% yield (324.3 mg, 1.11 mmol) from the reaction of 2-iodo-*N*-methylaniline (447.5 mg, 1.92 mmol) as colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 1.35 (s, 9H), 1.94 (s, 3H), 2.75 (s, 3H), 4.45 (s, 2H), 6.89 (dd, *J* = 7.6, 7.6 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 7.22 (ddd, *J* = 8.0, 7.6, 1.6 Hz, 1H), 7.37 (s, 4H), 7.42 (dd, *J* = 7.6, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.6, 31.4, 34.4, 38.9, 60.1, 78.7, 91.3, 116.5, 117.8, 120.6, 124.9, 127.7, 128.4, 134.1, 136.2, 149.7, 154.2; ESI-HRMS (*m/z*): $(M+H)^+$ Calcd for $C_{21}H_{26}N$, 292.2060; Found: 292.2064.

Methyl-4-((methyl(2-(prop-1-yn-1-yl)phenyl)amino)methyl)benzoate (1be)



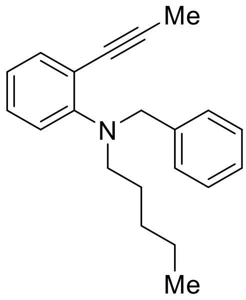
Following general procedure B, **1be** was obtained in 59% yield (287.4 mg, 0.87 mmol) from the reaction of 2-iodo-*N*-methylaniline (344.9 mg, 1.48 mmol) as colorless oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.83 (s, 3H), 2.73 (s, 3H), 3.91 (s, 3H), 4.51 (s, 2H), 6.87-6.93 (m, 2H), 7.21 (dd, *J* = 7.2, 7.2 Hz, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 2H), 8.02 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 4.4, 38.9, 51.9, 60.2, 78.5, 91.4, 116.4, 117.6, 120.9, 127.7, 128.4, 128.7, 129.4, 134.0, 145.0, 153.8, 167.0; ESI-HRMS (*m/z*): (M+H)$^+$ Calcd for $C_{22}H_{20}NO_2$, 330.1494; Found: 330.1496.

***N*-benzyl-*N*-(cyclopropylmethyl)-2-(prop-1-yn-1-yl)aniline (1bf)**



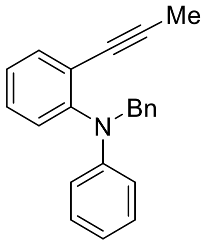
Following general procedure B, **1bf** was obtained in 62% yield (154.5 mg, 0.56 mmol) from the reaction of *N*-(cyclopropylmethyl)-2-iodoaniline[5] (247.2 g, 0.905 mmol) as yellow oil; ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.09-0.12 (m, 2H), 0.47-0.50 (m, 2H), 1.03-1.09 (m, 1H), 2.03 (s, 3H), 3.17 (d, *J* = 6.5 Hz, 2H), 4.63 (s, 2H), 6.91 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.07 (d, *J* = 8.5 Hz, 1H), 7.21 (ddd, *J* = 8.5, 7.5, 1.5 Hz, 1H), 7.27 (dd, *J* = 7.0, 7.0 Hz, 1H), 7.34-7.37 (m, 2H), 7.45 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.51 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 3.8, 4.6, 8.7, 56.1, 56.4, 78.9, 90.7, 117.5, 119.8, 120.7, 126.6, 127.8, 128.0 (overlapped), 134.1, 139.6, 153.1; ESI-HRMS (*m/z*): (M+H)$^+$ Calcd for $C_{20}H_{22}N$, 276.1747; Found: 276.1750.

***N*-benzyl-*N*-pentyl-2-(prop-1-yn-1-yl)aniline (1bg)**



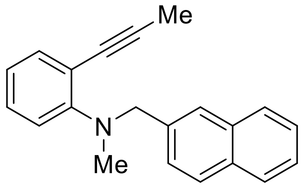
Following general procedure B, **1bg** was obtained in 45% yield (236.9 mg, 0.81 mmol) from the reaction of 2-iodo-*N*-pentylaniline[6] (523.4 mg, 1.81 mmol) as colorless oil; ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.85 (t, *J* = 7.0 Hz, 3H), 1.21-1.27 (m, 4H), 1.51-1.57 (m, 2H), 1.96 (s, 3H), 3.09-3.12 (m, 2H), 4.43 (s, 2H), 6.84 (dd, *J* = 7.5, 7.5 Hz, 1H), 6.89 (d, *J* = 8.5 Hz, 1H), 7.15 (ddd, *J* = 8.5, 7.5, 1.5 Hz, 1H), 7.22 (dd, *J* = 7.5, 7.0 Hz, 1H), 7.30 (dd, *J* = 7.5, 7.5 Hz, 2H), 7.37-7.40 (m, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 4.6, 14.1, 22.5, 26.9, 29.3, 51.0, 57.9, 78.9, 90.1, 117.7, 119.5, 120.7, 126.6, 127.9 (overlapped), 128.0, 134.2, 139.7, 152.7; ESI-HRMS (*m/z*): (M-H)$^+$ Calcd for $C_{21}H_{26}N$, 292.2060; Found: 292.2065.

_N_-benzyl-_N_-phenyl-2-(prop-1-yn-1-yl)aniline (1bh)



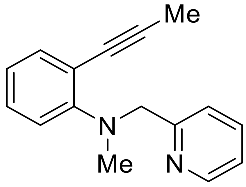
Following general procedure B, **1bh** was obtained in 43% yield (254.5 g, 0.86 mmol) from the reaction of 2-iodo-*N*-phenylaniline[7] (587.3 mg, 1.99 mmol) as yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.83 (s, 3H), 4.97 (s, 2H), 6.66 (d, *J* = 8.0 Hz, 2H), 6.73 (dd, *J* =7.6, 7.2 Hz, 1H), 7.09-7.13 (m, 3H), 7.18-7.30 (m, 5H), 7.42-7.47 (m, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 4.4, 56.2, 77.6, 91.6, 115.5, 118.1, 122.8, 125.2, 126.6, 126.8, 128.3, 128.5, 128.6, 128.7, 134.0, 139.4, 148.6, 149.5; ESI-HRMS (*m/z*): (M+H)$^+$ Calcd for $C_{22}H_{20}N$, 298.1590; Found: 298.1592.

_N_-methyl-_N_-(naphthalen-1-ylmethyl)-2-(prop-1-yn-1-yl)aniline (1bi)



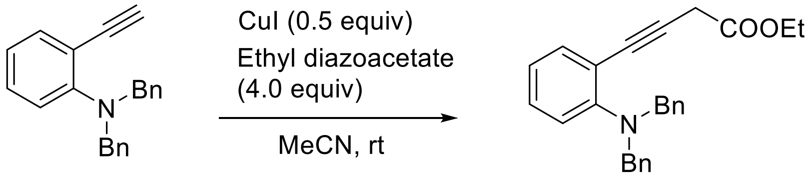
Following general procedure B, **1bi** was obtained in 70% yield (410.5 mg, 1.44 mmol) from the reaction of 2-iodo-*N*-methylaniline (480.0 mg, 2.06 mmol) as yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.80 (s, 3H), 2.68 (s, 3H), 4.55 (s, 2H), 6.85 (dd, *J* = 7.6, 7.6 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 1H), 7.15 (ddd, *J* = 8.4, 8.4, 1.2 Hz, 1H), 7.37-7.43 (m, 3H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.73-7.77 (m, 3H), 7.83 (s, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 4.5, 38.7, 60.6, 78.7, 91.4, 116.5, 117.7, 120.7, 125.3, 125.7, 126.2, 126.4, 127.5, 127.55, 127.59, 128.4, 132.6, 133.3, 134.0, 136.9, 154.0; ESI-HRMS (*m/z*): $(M+H)^+$ Calcd for $C_{21}H_{20}N$, 286.1590; Found: 286.1595.

N-methyl-2-(prop-1-yn-1-yl)-*N*-(pyridin-2-ylmethyl)aniline (1bj)



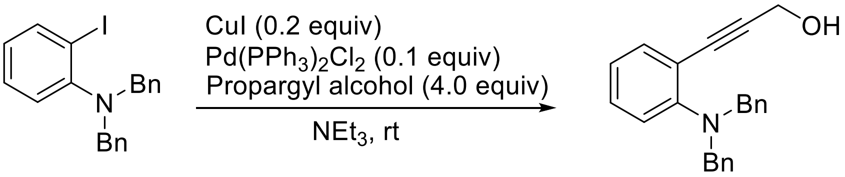
Following general procedure B, **1bj** was obtained in 66% yield (313.5 mg, 1.33 mmol) from the reaction of 2-iodo-*N*-methylaniline (468.4 mg, 2.01 mmol) as colorless solid, mp: 60-61 °C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.75 (s, 3H), 2.82 (s, 3H), 4.62 (s, 2H), 6.86 (dd, *J* = 7.5, 7.5 Hz, 1H), 6.93 (d, *J* = 8.5 Hz, 1H), 7.15-7.21 (m, 2H), 7.37 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.65-7.66 (m, 2H), 8.55 (d, *J* = 4.5 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 4.4, 39.5, 62.1, 78.6, 91.3, 115.9, 117.4, 120.6, 121.7, 121.8, 128.4, 134.1, 136.3, 148.8, 153.8, 160.2; ESI-HRMS (*m/z*): $(M+H)^+$ Calcd for $C_{16}H_{17}N_2$, 237.1386; Found: 237.1388.

Ethyl 4-(2-(dibenzylamino)phenyl)but-3-ynoate (1bk)



To a mixture of *N,N*-dibenzyl-2-ethynylaniline (946.9 mg, 3.18 mmol) in MeCN was added CuI (302.8 mg, 1.59 mmol) and ethyl diazoacetate (340 μL, 3.23 mmol). The mixture was stirred at room temperature overnight under N_2 atmosphere. Quenched with water and the aqueous layer was extracted with CH_2Cl_2 three times. The combined organic extracts were dried over Na_2SO_4, and concentrated in *vacuo*. The crude residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10 : 1) to give **1bk** (244.1 mg) in 20% yield as yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26 (t, *J* = 7.2 Hz, 3H), 3.34 (s, 2H), 4.15 (q, *J* = 7.2 Hz, 2H), 4.46 (s, 4H), 6.82 (d, *J* = 8.4 Hz, 1H), 6.85 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1H), 7.10 (ddd, *J* = 7.6, 7.6, 2.0 Hz, 1H), 7.19-7.23 (m, 2H), 7.26-7.30 (m, 4H), 7.34-7.36 (m, 4H), 7.45 (dd, *J* = 7.6, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 27.0, 56.0, 61.4, 82.5, 86.5, 116.2, 119.9, 120.9, 126.7, 127.9, 128.1, 128.7, 134.4, 138.8, 152.6, 168.2; ESI-HRMS (*m/z*): $(M+H)^+$ Calcd for $C_{26}H_{26}NO_2$, 384.1958; Found: 384.1964.

3-(2-(Dibenzylamino)phenyl)prop-2-yn-1-ol (1bl)

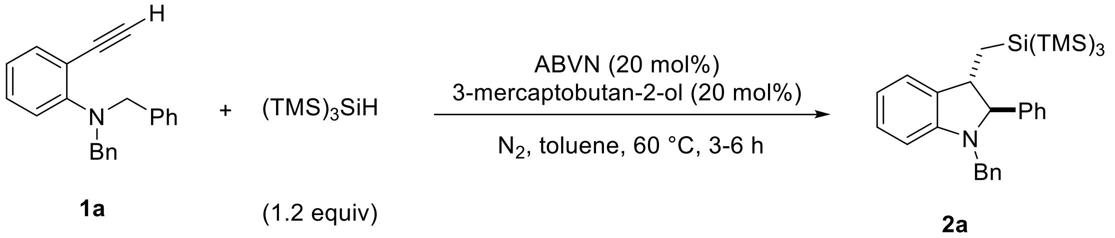


To a mixture of *N,N*-dibenzyl-2-iodoaniline[1] (2.940 g, 7.36 mmol) in NEt_3 was added CuI (280.3 mg, 1.47 mmol), $Pd(PPh_3)_2Cl_2$ (516.6 mg, 0.74 mmol), and propargyl alcohol (1.7 mL, 29.44 mmol). The mixture was stirred at room temperature overnight under N_2 atmosphere. Quenched with water and the aqueous layer was extracted with CH_2Cl_2 three times. The combined organic extracts were dried over Na_2SO_4, and concentrated in *vacuo*. The crude residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5 : 1) to give **1bl** (1.566 g) in 65% yield as yellow solid, mp: 63-64 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22 (s, 1H), 4.21 (s, 2H), 4.48 (s, 4H), 6.80-6.83 (m, 2H), 7.08 (ddd, *J* = 8.8, 8.4, 1.6 Hz, 1H), 7.19-7.23 (m, 2H), 7.29 (dd, *J* = 7.6, 7.2 Hz, 4H), 7.36 (d, *J* = 7.2 Hz, 4H), 7.40 (dd, *J* = 8.4, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.7, 56.1, 84.8, 92.5, 115.1, 119.4, 120.7, 126.8, 127.5, 128.3, 129.0, 134.3, 138.8, 152.5; ESI-HRMS (*m/z*): $(M+H)^+$ Calcd for $C_{23}H_{22}NO$, 328.1696; Found: 328.1701.

3. Synthesis of structurally diverse silicon-incorporated indolines via silyl radical-triggered radical cascades reactions

3.1 Synthesis of alkylsilicon-containing indolines

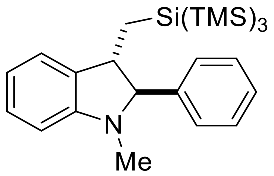
General procedure C:



A solution of **1a** (76.0 mg, 0.256 mmol), $(TMS)_3SiH$ (103 μL, 0.339 mmol), ABVN (8.9 mg, 0.051 mmol) and 3-mercaptobutan-2-ol (5 μL, 0.048 mmol) in toluene (2.5 mL) was stirred at 60 °C for 6 h under nitrogen atmosphere. After evaporation of solvent, the crude mixture was purified by flash column chromatography (silica gel; petroleum ether) to give product **2a** (126.2 mg) in 90% yield as pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.13 (s, 27H), 1.29 (dd, J = 15.0, 8.0 Hz, 1H), 1.34 (dd, J = 15.0, 4.5 Hz, 1H), 3.38 (ddd, J = 9.0, 8.0, 4.5 Hz, 1H), 3.94 (d, J = 15.5 Hz, 1H), 4.10 (d, J = 9.0 Hz, 1H), 4.32 (d, J = 15.5 Hz, 1H), 6.43 (d, J = 8.0 Hz, 1H), 6.78 (dd, J = 7.5, 7.5 Hz, 1H), 7.09 (dd, J = 8.0, 7.5 Hz, 1H), 7.19 (d, J = 7.5 Hz, 1H), 7.26-7.39 (m, 8H), 7.46-7.48 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 1.2, 10.5, 49.7, 51.1, 79.7, 107.4, 117.8, 123.3, 126.8, 127.6 (overlapped), 128.0, 128.4 (overlapped), 128.6, 134.9, 138.5, 141.0, 151.4; ESI-HRMS (*m/z*): $(M+H)^+$ Calcd for $C_{31}H_{48}NSi_4$, 546.2858; Found: 546.2870.

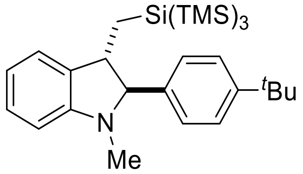
Gram-scale up synthesis: According to general procedure C , **2a** was afforded in 85% yield (1.206 g) from the reaction of **1a** (773.0 mg, 2.600 mmol), $(TMS)_3SiH$ (960 μL, 3.120 mmol), ABVN (130.0 mg, 0.520 mmol) and 3-mercaptobutan-2-ol (70 μL, 0.526 mmol) in toluene (20.0 mL) at 60 °C for 6 h under nitrogen atmosphere.

(2*S**,3*S**)-3-((1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methyl)-1-methyl-2-phenylindoline (2b)



According to general procedure C, the reaction of *N*-benzyl-2-ethynyl-*N*-methylaniline (61.2 mg, 0.277 mmol), $(TMS)_3SiH$ (103 μL, 0.334 mmol), ABVN (13.9 mg, 0.056 mmol) and 3-mercaptobutan-2-ol (7.5 μL, 0.056 mmol) in toluene (2.8 mL) was stirred at 60 °C for 3 h under nitrogen atmosphere. After evaporation of solvent, the crude mixture was purified by flash column chromatography (silica gel; petroleum ether : ethyl acetate = 500 : 1) to give product **2b** (96.0 mg) in 74% yield as white oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.08 (s, 27H), 1.23 (dd, *J* = 15.2, 8.0 Hz, 1H), 1.28 (dd, *J* = 15.2, 3.2 Hz, 1H), 2.55 (s, 3H), 3.24 (ddd, *J* = 10.0, 8.0, 3.2 Hz, 1H), 3.78 (d, *J* = 10.0 Hz, 1H), 6.52 (d, *J* = 7.6 Hz, 1H), 6.76 (ddd, *J* = 7.6, 7.6, 0.8 Hz, 1H), 7.13-7.18 (m, 2H), 7.31-7.38 (m, 3H), 7.44-7.46 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 1.2, 9.3, 34.1, 49.7, 82.6, 107.0, 117.9, 123.2, 127.7, 128.0, 128.2, 128.6, 134.6, 141.0, 152.4; ESI-HRMS (*m/z*): $(M+H)^+$ Calcd for $C_{25}H_{44}NSi_4$, 470.2545; Found: 470.2553.

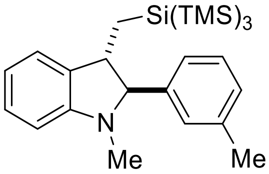
(2*S**,3*S**)-2-(4-(tert-butyl)phenyl)-3-((1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methyl)-1-methylindoline (2c)



According to general procedure C, the reaction of *N*-(4-(tert-butyl)benzyl)-2-ethynyl-N-methylaniline (85.0 mg, 0.306 mmol), $(TMS)_3SiH$ (114 μL, 0.370 mmol), ABVN (15.2 mg, 0.061 mmol) and 3-mercaptobutan-2-ol (6.5 μL, 0.062 mmol) in toluene (3.0 mL) was stirred at 60 °C for 4 h under nitrogen atmosphere. After evaporation of solvent, the crude mixture was purified by flash column chromatography (silica gel; petroleum ether) to give product **2c** (135.5 mg) in 84% yield as yellow oil; ^{1}H NMR

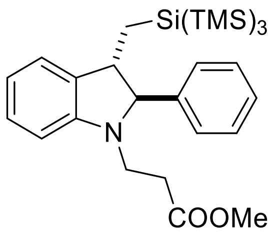
(400 MHz, $CDCl_3$) δ 0.05 (s, 27H), 1.22 (d, *J* = 5.6 Hz, 2H), 1.32 (s, 9H), 2.54 (s, 3H), 3.24 (ddd, *J* = 10.4, 5.6, 5.6 Hz, 1H), 3.71 (d, *J* = 10.4 Hz, 1H), 6.52 (d, *J* = 7.6 Hz, 1H), 6.75 (dd, *J* = 7.2, 7.2, Hz, 1H), 7.11-7.17 (m, 2H), 7.37 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 1.2, 8.7, 31.4, 34.3, 34.5, 49.7, 82.7, 107.2, 117.9, 123.1, 125.5, 127.6, 127.9, 134.8, 137.7, 150.9, 152.5; ESI-HRMS (m/z): $(M+H)^+$ Calcd for $C_{29}H_{52}NSi_4$, 526.3171; Found: 526.3185.

(2*S,3*S**)-3-((1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methyl)-1-methyl-2-(m-tolyl)indoline (2d)**



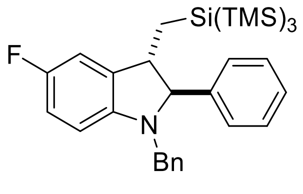
According to general procedure C, the reaction of 2-ethynyl-*N*-methyl-*N*-(3-methylbenzyl)aniline (60.2 mg, 0.256 mmol), $(TMS)_3SiH$ (95 μL, 0.308 mmol), ABVN (12.7 mg, 0.051 mmol) and 3-mercaptobutan-2-ol (5.5 μL, 0.052 mmol) in toluene (2.5 mL) was stirred at 60 °C for 3 h under nitrogen atmosphere. After evaporation of solvent, the crude mixture was purified by flash column chromatography (silica gel; petroleum ether) to give product **2d** (93.4 mg) in 74% yield as pale yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ 0.06 (s, 27H), 1.21 (dd, *J* = 15.0, 7.5 Hz, 1H), 1.25 (dd, *J* = 15.0, 3.5 Hz, 1H), 2.35 (s, 3H), 2.54 (s, 3H), 3.22 (ddd, *J* = 10.5, 7.5, 3.5 Hz, 1H), 3.71 (d, *J* = 10.5 Hz, 1H), 6.51 (d, *J* = 7.5 Hz, 1H), 6.75 (dd, *J* = 7.5, 7.0 Hz, 1H), 7.11-7.16 (m, 3H), 7.23-7.26 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 1.2, 8.9, 21.4, 34.2, 49.7, 82.8, 107.1, 117.9, 123.2, 125.4, 127.7, 128.5, 128.7, 128.9, 134.6, 138.1, 140.9, 152.5; ESI-HRMS (m/z): $(M+H)^+$ Calcd for $C_{26}H_{46}NSi_4$, 484.2702; Found: 484.2707.

Methyl 3-((2*S,3*S**)-3-((1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methyl)-2-phenylindolin-1-yl)propanoate (2e)**



According to general procedure C, the reaction of methyl 3-(benzyl(2-ethynylphenyl)amino)propanoate (68.3 mg, 0.233 mmol), $(TMS)_3SiH$ (105 μL, 0.340 mmol), ABVN (11.6 mg, 0.047 mmol) and 3-mercaptobutan-2-ol (6 μL, 0.045 mmol) in toluene (2.5 mL) was stirred at 60 °C for 3 h under nitrogen atmosphere. After evaporation of solvent, the crude mixture was purified by flash column chromatography (silica gel; petroleum ether : ethyl acetate = 50 : 1) to give product **2e** (113.7 mg) in 90% yield as pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.08 (s, 27H), 1.21 (dd, *J* = 15.0, 7.0 Hz, 1H), 1.25 (dd, *J* = 15.0, 4.0 Hz, 1H), 2.39-2.44 (m, 2H), 3.22-3.29 (m, 2H), 3.34-3.40 (m, 1H), 3.60 (s, 3H), 4.01 (d, *J* = 9.5 Hz, 1H), 6.53 (d, *J* = 7.5 Hz, 1H), 6.74 (ddd, *J* = 7.5, 7.0, 1.0 Hz, 1H), 7.12-7.16 (m, 2H), 7.30-7.36 (m, 3H), 7.40-7.42 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 1.2, 10.0, 31.1, 42.4, 49.9, 51.6, 79.6, 106.6, 117.8, 123.4, 127.7, 128.2 (overlapped), 128.7, 134.5, 141.0, 150.3, 172.6; ESI-HRMS (m/z): $(M+H)^+$ Calcd for $C_{28}H_{48}NO_2Si_4$, 542.2757; Found: 564.2762.

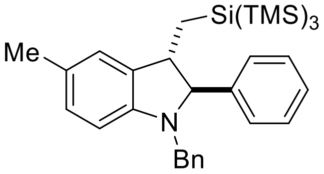
(2*S,3*S**)-1-benzyl-5-fluoro-3-((1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methyl)-2-phenylindoline (2f)**



According to general procedure C, the reaction of *N*,*N*-dibenzyl-2-ethynyl-4-fluoroaniline (67.1 mg, 0.213 mmol), $(TMS)_3SiH$ (79 μL, 0.256 mmol), ABVN (7.4 mg, 0.042 mmol) and 3-mercaptobutan-2-ol (4.4 μL, 0.043 mmol) in toluene (2.1 mL) was stirred at 60 °C for 3 h under nitrogen atmosphere. After evaporation of solvent, the crude mixture was purified by flash column chromatography (silica gel; petroleum ether) to give product **2f** (84.0 mg) in 70% yield as yellow oil; ^{1}H NMR (400 MHz,

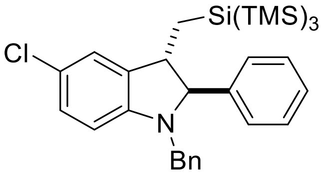
$CDCl_3$) δ 0.07 (s, 27H), 1.18 (dd, *J* = 15.2, 8.4 Hz, 1H), 1.27 (dd, *J* = 15.2, 3.6 Hz, 1H), 3.28 (ddd, *J* = 9.2, 8.4, 3.6 Hz, 1H), 3.83 (d, *J* = 15.6 Hz, 1H), 4.02 (d, *J* = 9.2 Hz, 1H), 4.19 (d, *J* = 15.6 Hz, 1H), 6.21 (dd, *J* = 8.4, 4.4 Hz, 1H), 6.69 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.87 (ddd, *J* = 8.4, 2.8, 1.2 Hz, 1H), 7.21-7.36 (m, 8H), 7.42-7.44 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 1.2, 9.9, 49.6, 51.9, 80.5, 107.6 (d, *J* = 7.9 Hz), 111.1 (d, *J* = 23.0 Hz), 113.0 (d, *J* = 22.3 Hz), 126.9, 127.5, 128.2, 128.36, 128.42, 128.6, 136.5 (d, *J* = 7 Hz), 138.4, 140.6, 147.7, 156.7 (d, *J* = 233.9 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -127.2--127.1 (1F, m); ESI-HRMS (*m/z*): $(M+H)^+$ Calcd for $C_{31}H_{47}FNSi_4$, 564.2764; Found: 564.2769.

(2*S**,3*S**)-1-benzyl-3-((1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methyl)-5-methyl-2-phenylindoline (2g)



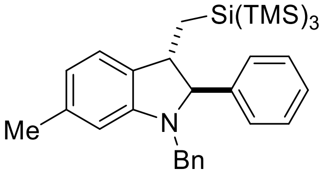
According to general procedure C, the reaction of *N*,*N*-dibenzyl-2-ethynyl-4-methylaniline (65.1 mg, 0.209 mmol), $(TMS)_3SiH$ (77 μL, 0.250 mmol), ABVN (10.4 mg, 0.042 mmol) and 3-mercaptobutan-2-ol (5.6 μL, 0.042 mmol) in toluene (2.1 mL) was stirred at 60 °C for 3 h under nitrogen atmosphere. After evaporation of solvent, the crude mixture was purified by flash column chromatography (silica gel; petroleum ether) to give product **2g** (84.8 mg) in 73% yield as white oil; ^1H NMR (400 MHz, $CDCl_3$) δ 0.07 (s, 27H), 1.18 (dd, *J* = 14.8, 7.6 Hz, 1H), 1.27 (dd, *J* = 14.8, 3.6 Hz, 1H), 2.27 (s, 3H), 3.28 (ddd, *J* = 9.6, 7.6, 3.6 Hz, 1H), 3.85 (d, *J* = 15.2 Hz, 1H), 3.98 (d, *J* = 9.6 Hz, 1H), 4.20 (d, *J* = 15.2 Hz, 1H), 6.26 (d, *J* = 8.0 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.98 (s, 1H), 7.17-7.34 (m, 8H), 7.44-7.46 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 1.3, 9.8, 20.6, 49.7, 51.8, 80.6, 107.7, 124.2, 126.8, 127.4, 127.6, 127.7, 128.0, 128.3, 128.5, 128.6, 135.1, 138.6, 140.9, 149.3; ESI-HRMS (*m/z*): $(M+H)^+$ Calcd for $C_{32}H_{50}NSi_4$, 560.3015; Found: 560.3024.

(2*S**,3*S**)-1-benzyl-5-chloro-3-((1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methyl)-2-phenylindoline (2h)



According to general procedure C, the reaction of *N*,*N*-dibenzyl-4-chloro-2-ethynylaniline (70.5 mg, 0.212 mmol), $(TMS)_3SiH$ (80.0 μL, 0.260 mmol), ABVN (10.6 mg, 0.043 mmol) and 3-mercaptobutan-2-ol (5.6 μL, 0.042 mmol) in toluene (2.1 mL) was stirred at 60 °C for 3 h under nitrogen atmosphere. After evaporation of solvent, the crude mixture was purified by flash column chromatography (silica gel; petroleum ether) to give product **2h** (103.6 mg) in 84% yield as white oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.08 (s, 27H), 1.17 (dd, *J* = 14.8, 8.4 Hz, 1H), 1.26 (dd, *J* = 14.8, 3.6 Hz, 1H), 3.28 (ddd, *J* = 9.2, 8.4, 3.6 Hz, 1H), 3.85 (d, *J* = 15.6 Hz, 1H), 4.04 (d, *J* = 9.2 Hz, 1H), 4.24 (d, *J* = 15.6 Hz, 1H), 6.25 (d, *J* = 8.0 Hz, 1H), 6.96 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.08 (s, 1H), 7.20-7.33 (m, 8H), 7.40 (d, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 1.3, 10.2, 49.7, 51.0, 79.7, 108.1, 122.5, 123.5, 127.0, 127.2, 127.6, 128.2 (overlapped), 128.5, 128.7, 136.7, 137.9, 140.4, 150.0; ESI-HRMS (*m/z*): $(M+H)^+$ Calcd for $C_{31}H_{47}ClNSi_4$, 580.2469; Found: 580.2466.

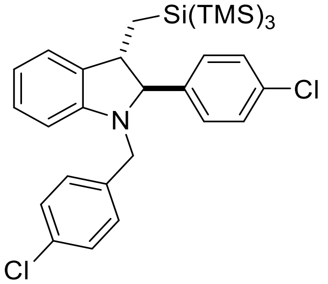
(2*S**,3*S**)-1-benzyl-3-((1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methyl)-6-methyl-2-phenylindoline (2i)



According to general procedure C, the reaction of *N*,*N*-dibenzyl-2-ethynyl-5-methylaniline (95.1 mg, 0.305 mmol), $(TMS)_3SiH$ (113 μL, 0.260 mmol), ABVN (15.2 mg, 0.061 mmol) and 3-mercaptobutan-2-ol (6.4 μL, 0.061 mmol) in toluene (3.0 mL) was stirred at 60 °C for 4 h under nitrogen atmosphere. After evaporation of solvent, the crude mixture was purified by flash column chromatography (silica gel; petroleum ether) to give product **2i** (130.3 mg) in 76% yield as yellow oil; ^{1}H NMR (400 MHz,

$CDCl_3$) δ 0.06 (s, 27H), 1.20 (dd, *J* = 14.8, 7.6 Hz, 1H), 1.26 (dd, *J* = 14.8, 4.4 Hz, 1H), 2.24 (s, 3H), 3.27 (ddd, *J* = 8.4, 7.6, 4.4 Hz, 1H), 3.87 (d, *J* = 15.6 Hz, 1H), 4.01 (d, *J* = 8.4 Hz, 1H), 4.25 (d, *J* = 15.6 Hz, 1H), 6.21 (s, 1H), 6.55 (d, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 7.2 Hz, 1H), 7.20-7.32 (m, 8H), 7.37-7.39 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 1.2, 10.8, 21.8, 49.4, 50.9, 79.8, 108.2, 118.3, 123.0, 126.8, 127.5, 128.0, 128.32, 128.34, 128.5, 132.2, 137.5, 138.6, 141.0, 151.6; ESI-HRMS (*m/z*): $(M+H)^+$ Calcd for $C_{32}H_{50}NSi_4$, 560.3015; Found: 560.3018.

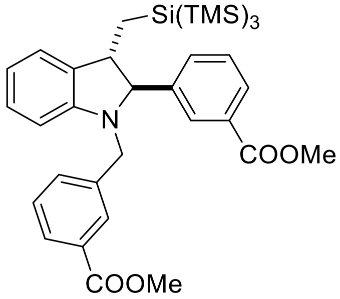
(2*S**,3*S**)-1-(4-chlorobenzyl)-2-(4-chlorophenyl)-3-((1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methyl)indoline (2j)



According to general procedure C, the reaction of *N,N*-bis(4-chlorobenzyl)-2-ethynylaniline (111.4 mg, 0.304 mmol), $(TMS)_3SiH$ (113 μL, 0.260 mmol), ABVN (15.6 mg, 0.063 mmol) and 3-mercaptobutan-2-ol (8 μL, 0.060 mmol) in toluene (3.0 mL) was stirred at 60 °C for 6 h under nitrogen atmosphere. After evaporation of solvent, the crude mixture was purified by flash column chromatography (silica gel; petroleum ether) to give product **2j** (165.0 mg) in 88% yield as yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.07 (s, 27H), 1.23 (d, *J* = 5.6 Hz, 2H), 3.26 (ddd, *J* = 8.8, 5.6, 5.6 Hz, 1H), 3.84 (d, *J* = 15.6 Hz, 1H), 3.98 (d, *J* = 8.8 Hz, 1H), 4.18 (d, *J* = 15.6 Hz, 1H), 6.35 (d, *J* = 7.6 Hz, 1H), 6.75 (ddd, *J* = 7.6, 7.6, 0.8 Hz, 1H), 7.05 (dd, *J* = 7.6, 7.6 Hz, 1 H), 7.13-7.15 (m, 3H), 7.22-7.24 (m, 2H), 7.28-7.33 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 1.2, 10.6, 49.7, 50.5, 78.7, 107.5, 118.3, 123.4, 127.7, 128.6, 128.8, 128.9, 129.5, 132.7, 133.9, 134.7, 136.7, 139.4, 150.9; ESI-HRMS (*m/z*): $(M+H)^+$ Calcd for $C_{31}H_{46}Cl_2NSi_4$, 614.2079; Found: 614.2092.

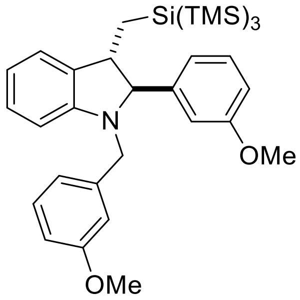
Methyl 3-((2*S**,3*S**)-3-((1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)me-

thyl)-1-(3-(methoxycarbonyl)benzyl)indolin-2-yl)benzoate (2k)



According to general procedure C, the reaction of dimethyl 3,3'-(((2-ethynylphenyl)azanediyl)bis(methylene))dibenzoate (80.6 mg, 0.195 mmol), $(TMS)_3SiH$ (72 μL, 0.233 mmol), ABVN (10.6 mg, 0.043 mmol) and 3-mercaptobutan-2-ol (5.5 μL, 0.041 mmol) in toluene (2.0 mL) was stirred at 60 °C for 6 h under nitrogen atmosphere. After evaporation of solvent, the crude mixture was purified by flash column chromatography (silica gel; petroleum ether : ethyl acetate = 25 : 1) to give product **2k** (113.6 mg) in 88% yield as yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.06 (s, 27H), 1.26-1.27 (m, 2H), 3.34 (ddd, *J* = 9.2, 6.4, 5.2 Hz, 1H), 3.89 (s, 3H), 3.39 (s, 3H), 4.01 (d, *J* = 15.6 Hz, 1H), 4.10 (d, *J* = 9.2 Hz, 1H), 4.21 (d, *J* = 15.6 Hz, 1H), 6.39 (d, *J* = 7.6 Hz, 1H), 6.77 (ddd, *J* = 7.6, 7.6, 0.8 Hz, 1H), 7.07 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.33 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.41 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.65 (ddd, *J* = 8.0, 1.6, 1.2 Hz, 1H), 7.86-7.89 (m, 2H), 7.96 (ddd, *J* = 8.0, 1.6, 1.6 Hz, 1H), 8.09 (dd, *J* = 1.6, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 1.2, 10.4, 49.8, 51.5, 52.07, 52.08, 79.8, 107.6, 118.4, 123.5, 127.8, 128.3, 128.5, 128.8, 128.9, 129.4, 129.8, 130.3, 130.4, 132.2, 132.6, 134.5, 138.7, 141.5, 151.1, 166.7, 167.0; ESI-HRMS (*m/z*): $(M+H)^+$ Calcd for $C_{25}H_{44}NSi_4$, 662.2968; Found: 662.2971.

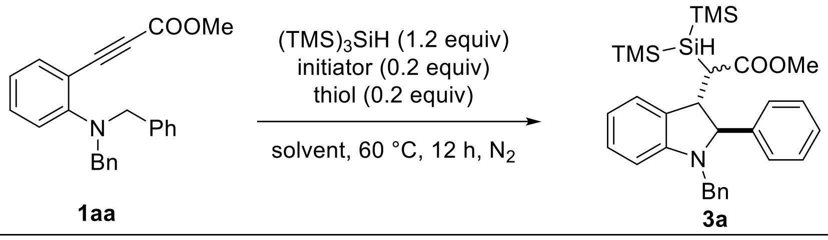
(2*S**,3*S**)-3-((1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methyl)-1-(3-methoxybenzyl)-2-(3-methoxyphenyl)indoline (2l)

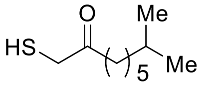
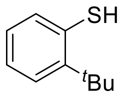


According to general procedure C, the reaction of 2-ethynyl-*N*,*N*-bis(3-methoxybenzyl)aniline (59.9 mg, 0.168 mmol), $(TMS)_3SiH$ (62 μL, 0.200 mmol), ABVN (8.2 mg, 0.033 mmol) and 3-mercaptobutan-2-ol (4.5 μL, 0.034 mmol) in toluene (1.7 mL) was stirred at 60 °C for 6 h under nitrogen atmosphere. After evaporation of solvent, the crude mixture was purified by flash column chromatography (silica gel; petroleum ether) to give product **2l** (81.3 mg) in 80% yield as yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.08 (s, 27H), 1.23 (dd, J = 15.0, 7.5 Hz, 1H), 1.28 (dd, J = 15.0, 4.0 Hz, 1H), 3.32 (ddd, J = 9.0, 7.5, 4.0 Hz, 1H), 3.74 (s, 3H), 3.75 (s, 3H), 3.88 (d, J = 15.5 Hz, 1H), 4.01 (d, J = 9.0 Hz, 1H), 4.22 (d, J = 15.5 Hz, 1H), 6.39 (d, J = 8.0 Hz, 1H), 6.71-6.76 (m, 2 H), 6.80-6.83 (m, 2H), 6.87 (d, J = 8.0 Hz, 1H), 6.99-7.05 (m, 3H), 7.12-7.22 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 1.2, 10.3, 49.6, 55.5, 55.08, 55.14, 80.0, 107.5, 112.2, 113.18, 113.22, 114.0, 117.9, 119.9, 120.9, 123.2, 127.6, 129.3, 129.5, 134.8, 140.3, 142.6, 151.4, 159.7, 159.8; ESI-HRMS (*m/z*): $(M+H)^+$ Calcd for $C_{33}H_{52}NO_2Si_4$, 606.3070; Found: 606.3077.

3.2 Synthesis of α-silyl ester-containing indolines

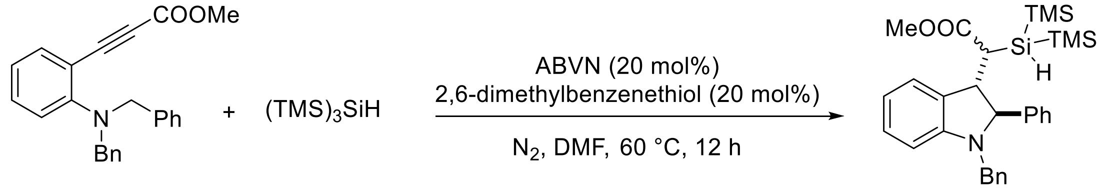
Table S1 Optimization[a]



entry	thiol	initiator	solvent	yield/%[b]
1	---	ABVN	toluene	trace
2		ABVN	toluene	trace
3	3-mercaptobutan-2-ol	ABVN	toluene	trace
4	PhSH	ABVN	toluene	67% dr (4:1)
5	PhSH	ABVN	THF	71% dr (1:1)
6	PhSH	ABVN	1,4-dioxane	61% dr (1.6:1)
7	PhSH	ABVN	DMF	82% dr (2:1)
8		ABVN	DMF	70% dr (2:1)
9	**2,6-dimethylbenzenethiol**	**ABVN**	**DMF**	**84% dr (1.3:1)**
10[c]	2,6-dimethylbenzenethiol	AIBN	DMF	62% dr (1:1)
11[d]	2,6-dimethylbenzenethiol	ACCN	DMF	55% dr (1.5:1)
12[e]	2,6-dimethylbenzenethiol	ABVN	DMF	trace
13[f]	2,6-dimethylbenzenethiol	ABVN	DMF	trace
14[g]	2,6-dimethylbenzenethiol	ABVN	DMF	trace

[a]Reaction conditions: **1aa** (0.2-0.3 mmol), $(TMS)_3SiH$ (1.2 equiv), radical initiator (0.2 equiv), RSH (0.2 equiv), solvent (2-3 mL), 60 °C for 12 h. [b] Isolated yield. [c]The reaction was run at 80 °C. [d]The reaction was run at 95 °C. [e] Et_3SiH was used instead of $(TMS)_3SiH$. [f] Ph_3SiH was used instead of $(TMS)_3SiH$. [g] Ph_2MeSiH used instead of $(TMS)_3SiH$.

General procedure D:



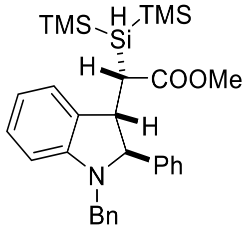
1aa (1.2 equiv) **3a**

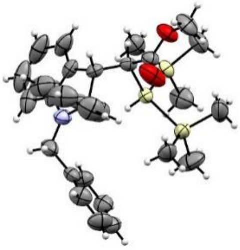
A solution of **1aa** (90.0 mg, 0.253 mmol), $(TMS)_3SiH$ (94 μL, 0.305 mmol), ABVN (12.6 mg, 0.050 mmol) and 2,6-dimethylbenzenethiol (6.7 μL, 0.051 mmol) in DMF (2.5 mL) was stirred at 60 °C for 12 h under nitrogen atmosphere. The reaction was quenched with water and the aqueous layer was extracted with ethyl acetate three times. The combined organic extracts were extracted with water three times and brine, dried over Na_2SO_4 and concentrated in *vacuo*. The crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 50 : 1) to give **3a** (113.0 mg) as a mixture of diastereoisomers in 84% yield (dr = 1.3:1) as orange oil; ^1H NMR (400 MHz, $CDCl_3$) δ 0.07 (s, 9Hx2), 0.11 (s, 9Hx1+9Hx1), 0.13 (s, 9Hx2), 2.75-2.80 (m, 1Hx1+1Hx2), 3.30 (d, J = 2.0 Hz, 1Hx1), 3.52 (s, 1Hx2), 3.54 (s, 3Hx1), 3.60 (s, 3Hx2), 3.68 (dd, J = 9.6, 3.2 Hz, 1Hx2), 3.78 (dd, J = 6.4, 6.0 Hz, 1Hx1), 3.90-3.97 (m, 1Hx1+1Hx2), 4.37-4.42 (m, 1Hx1+1Hx1+1Hx2), 4.60 (d, J = 3.2 Hz, 1Hx2), 6.35-6.39 (m, 1Hx1+1Hx2), 6.58-6.60 (m, 1Hx1+1Hx2), 7.04-7.29 (m, 12Hx1+12Hx2); ^{13}C NMR (100 MHz, $CDCl_3$) δ -0.2, 0.0, 0.3, 0.5, 35.0, 36.7, 48.9, 49.8, 50.5, 50.9, 51.2, 51.3, 71.4, 73.8, 105.1, 105.8, 116.8, 116.9, 125.1, 126.1, 126.88, 126.92, 127.1, 127.4, 127.5, 127.6 (overlapped, overlapped), 128.3 (overlapped), 128.36, 128.43, 128.5 (overlapped), 129.5, 131.1, 138.4, 138.5, 142.1, 142.3, 150.9, 151.8, 174.8, 175.3.

The two diastereoisomers were difficult to be separated by the flash column chromatography on silica gel but could be separated slightly by running the Pre-TLC (petroleum ether : ethyl ether = 100 : 3) several times. Collecting the upper part on the Pre-TLC plate and recrystallization from petroleum ether/ethyl acetate gave colorless crystal **3aa**; CCDC: 2234919; The structure of the crystal was shown below, and it was the major one according to the analysis of ^1H NMR spectrum.

Methyl (*S)-2-((2*S**,3*S**)-1-benzyl-2-phenylindolin-3-yl)-2-(1,1,1,3,3,3-hexamethy**

-ltrisilan-2-yl)acetate (3aa)





^{1}H NMR (400 MHz, CDCl$_3$) δ 0.07 (s, 9H), 0.14 (s, 9H), 2.77 (dd, *J* = 9.6, 1.6 Hz, 1H), 3.52 (s, 1H), 3.59 (s, 3H), 3.68 (dd, *J* = 9.6, 3.2 Hz, 1H), 3.92 (d, *J* = 15.6 Hz, 1H), 4.39 (d, *J* = 15.6 Hz, 1H), 4.60 (d, *J* = 3.2 Hz, 1H), 6.36 (d, *J* = 8.0 Hz, 1H), 6.60 (ddd, *J* = 7.6, 7.2, 0.8 Hz, 1H), 7.04-7.09 (m, 2H), 7.14-7.28 (m, 10H); ^{13}C NMR (100 MHz, CDCl$_3$) δ -0.2, 0.4, 36.7, 48.9, 50.5, 51.2, 71.4, 105.2, 116.8, 125.1, 126.9, 127.1, 127.4, 127.6, 128.36, 128.43, 128.5, 131.1, 138.5, 142.1, 150.9, 174.8; ESI-HRMS (m/z): (M+H)$^+$ Calcd for $C_{30}H_{42}NO_2Si_3$, 532.2518; Found: 532.2521.

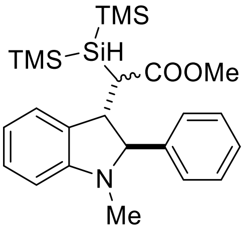
Gram-scale up synthesis: According to general procedure, **3a** was afforded in 74% yield (1.107 g) from the reaction of **1aa** (1.000 g, 2.813 mmol), (TMS)$_3$SiH (1.1 mL, 3.566 mmol), ABVN (140.0 mg, 0.560 mmol) and 2,6-dimethylbenzenethiol (75 μL, 0.563 mmol) in toluene (20.0 mL) at 60 °C for 12 h under nitrogen atmosphere.

Table S2. Crystal data and structure refinement for **3aa**.

Empirical formula	$C_{30}H_{41}NO_2Si_3$
Formula weight	531.91
Temperature/K	291(2)
Crystal system	triclinic
Space group	P-1
a/Å	10.4395(3)
b/Å	11.2727(3)
c/Å	14.3163(4)
α/°	87.569(2)
β/°	85.699(2)
γ/°	68.070(3)
Volume/Å^3	1558.26(8)
Z	2
ρ_{calc}g/cm^3	1.134
μ/mm^{-1}	1.593

F(000)	572.0
Crystal size/mm^3	0.25 × 0.21 × 0.2
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.456 to 147.852
Index ranges	$-12 \leq h \leq 12$, $-14 \leq k \leq 12$, $-17 \leq l \leq 16$
Reflections collected	10646
Independent reflections	6107 [R_{int} = 0.0206, R_{sigma} = 0.0251]
Data/restraints/parameters	6107/0/332
Goodness-of-fit on F^2	1.019
Final R indexes [I>=2σ (I)]	R_1 = 0.0458, wR_2 = 0.1027
Final R indexes [all data]	R_1 = 0.0496, wR_2 = 0.1053
Largest diff. peak/hole / e Å^{-3}	0.40/-0.44

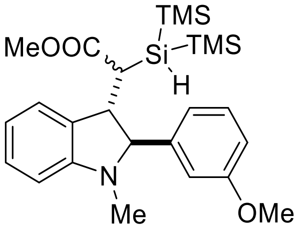
Methyl 2-(1,1,1,3,3,3-hexamethyltrisilan-2-yl)-2-((2*S,3*S**)-1-methyl-2-phenylindolin-3-yl)acetate (3b)**



According to general procedure D, the reaction of methyl 3-(2-(benzyl(methyl)amino)phenyl)propiolate (79.8 mg, 0.286 mmol), $(TMS)_3SiH$ (110 μL, 0.357 mmol), ABVN (15.0 mg, 0.060 mmol), 2,6-dimethylbenzenethiol (7.6 μL, 0.058 mmol) in DMF (2.5 mL) was stirred at 60 °C for 6 h under nitrogen atmosphere. Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 80 : 1) afforded **3b** (90.2 mg) in 69% yield as an inseparable mixture of diastereomers (dr = 1.8:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.10 (s, 9Hx2.2), 0.12 (s, 9Hx1), 0.13 (s, 9Hx2.2), 0.14 (s, 9Hx1), 2.62 (s, 3Hx1+3Hx2.2), 2.74 (dd, *J* = 8.4, 2 Hz, 1Hx2.2), 2.78 (dd, *J* = 6.4, 2 Hz, 1Hx1), 3.39 (d, *J* = 2 Hz, 1Hx1), 3.50 (d, *J* = 1.6 Hz, 1Hx2.2), 3.54 (s, 3Hx1), 3.61 (s, 3Hx2.2), 3.67 (dd, *J* = 8.4, 4.4 Hz, 1Hx2.2), 3.74 (dd, *J* = 6.8, 6.4 Hz, 1Hx1), 4.26 (d, *J* = 6.8 Hz, 1Hx1), 4.42 (d, *J* = 6.4 Hz, 1Hx2.2), 6.38 (d, *J* = 8.0 Hz, 1Hx2.2), 6.42 (d, *J* = 2.0 Hz, 1Hx1), 6.60 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1Hx2.2), 6.65 (ddd, *J* = 7.6, 7.2, 0.8 Hz, 1Hx1), 7.05 (d, *J* = 7.2 Hz, 1Hx2.2), 7.10-7.15 (m, 1Hx1+1Hx2.2), 7.15-7.28

(m, 5Hx2.2+6Hx1); ^{13}C NMR (100 MHz, $CDCl_3$) δ -0.1, 0.1, 0.4, 0.4, 0.6, 32.2, 33.0, 34.7, 35.8, 50.6, 51.2, 51.3, 74.2, 76.1, 105.1, 105.6, 116.7, 116.9, 124.6, 125.7, 127.2, 127.51, 127.55, 127.6, 128.3 (overlapped), 128.43, 128.44, 129.8, 131.1, 142.0, 142.2, 151.7, 152.6, 174.9, 175.2; ESI-HRMS (m/z): $(M+H)^+$ Calcd for $C_{24}H_{38}NO_2Si_3$, 456.2205; Found: 456.2202.

Methyl 2-(1,1,1,3,3,3-hexamethyltrisilan-2-yl)-2-((2*S,3*S**)-2-(3-methoxyphenyl) -1-methylindolin-3-yl)acetate (3c)**



According to general procedure D, **3c** was obtained in 65% combined yield (dr = 1:1) from the reaction of methyl 3-(2-((3-methoxybenzyl)(methyl)amino)phenyl)propiolate (93.5 mg, 0.302 mmol), $(TMS)_3SiH$ (112 μL, 0.363 mmol), ABVN (15.0 mg, 0.060 mmol), 2,6-dimethylbenzenethiol (8 μL, 0.060 mmol) in DMF (3.0 mL). The two diastereomers could be separated by flash column chromatography (silica gel; petroleum ether : ethyl ether = 200 : 1) to afford diastereomer 1 (49.8 mg) and diastereomer 2 (50.0 mg).

Diastereomer 1:

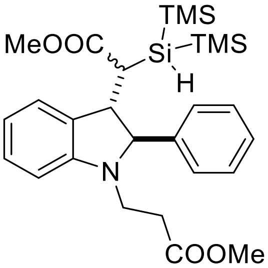
White oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.09 (s, 9H), 0.14 (s, 9H), 2.60 (s, 3H), 2.77 (d, *J* = 9.5 Hz, 1H), 3.53 (s, 1H), 3.61 (s, 3H), 3.64 (dd, *J* = 9.5, 4.5 Hz, 1H), 3.78 (s, 3H), 4.37 (d, *J* = 4.5 Hz, 1H), 6.37 (d, *J* = 9 Hz, 1H), 6.60 (dd, *J* = 9, 9 Hz, 1H), 6.81 (d, *J* = 11 Hz, 2H), 7.05 (d, *J* = 9 Hz, 1H), 7.11, (dd, *J* = 9, 9 Hz, 1H), 7.15 (d, *J* = 11 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ -0.1, 0.4, 32.2, 35.7, 50.6, 51.2, 55.2, 73.7, 105.1, 113.7, 116.6, 124.5, 128.3, 128.4, 131.2, 134.1, 151.7, 159.0, 175.0; ESI-HRMS (m/z): $(M+H)^+$ Calcd for $C_{25}H_{40}NO_3Si_3$, 486.2311; Found: 486.2308.

Diastereomer 2:

White oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.12 (s, 9H), 0.15 (s, 9H), 2.59 (s, 3H), 2.76

(dd, *J* = 6.4, 2.4 Hz, 1H), 3.38 (d, *J* = 2.4 Hz, 1H), 3.54 (s, 3H), 3.72 (dd, *J* = 6.4, 6.4 Hz, 1H), 3.79 (s, 3H), 4.19 (d, *J* = 7.2 Hz, 1H), 6.41 (d, *J* = 7.6 Hz, 1H), 6.65 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1H), 6.84 (ddd, *J* = 9.6, 4.8, 2.8 Hz, 2H), 7.13 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.19 (ddd, *J* = 9.6, 4.8, 2.8 Hz, 2H), 7.24 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 0.15, 0.58, 33.0, 34.4, 50.6, 51.3, 55.2, 75.7, 105.7, 113.8, 117.0, 125.6, 128.3, 128.7, 130.0, 134.2, 152.6, 159.1, 175.3; ESI-HRMS (m/z): $(M+H)^+$ Calcd for $C_{25}H_{40}NO_3Si_3$, 486.2311; Found: 486.2309.

Methyl 3-((2*S**,3*S**)-3-((*S**)-1-(1,1,1,3,3,3-hexamethyltrisilan-2-yl)-2-methoxy-2-oxoethyl)-2-phenylindolin-1-yl)propanoate (3d)



According to general procedure D, **3d** was obtained in 76% combined yield (dr = 1.4:1) from the reaction of methyl 3-(2-(benzyl(3-methoxy-3-oxopropyl)amino)phenyl)propiolate (96.0 mg, 0.273 mmol), $(TMS)_3SiH$ (102 μL, 0.330 mmol), ABVN (14.2 mg, 0.057 mmol) and 2,6-dimethylbenzenethiol (7.3 μL, 0.055 mmol) in DMF (2.5 mL). The two diastereomers could be separated by flash column chromatography (silica gel; petroleum ether : ethyl acetate = 30 : 1) to afford diastereomer 1 (61.9 mg) and diastereomer 2 (47.6 mg).

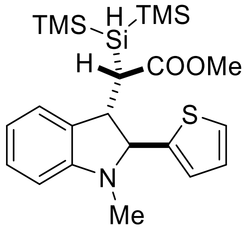
Diastereomer 1:

White oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.10 (s, 9H), 0.15 (s, 9H), 2.38-2.54 (m, 2H), 2.70 (dd, *J* = 9.2, 1.2 Hz, 1H), 3.23 (ddd, *J* = 14.4, 7.6, 6.4 Hz, 1H), 3.46 (ddd, *J* = 14.4, 7.6, 7.2 Hz, 1H), 3.60-3.64 (m, 8H), 4.61 (d, *J* = 3.6 Hz, 1H), 6.43 (d, *J* = 8.0 Hz, 1H), 6.59 (ddd, *J* = 7.6, 7.6, 0.8 Hz, 1H), 7.04 (d, *J* = 6.4 Hz, 1H), 7.11 (ddd, *J* = 7.6, 7.6, 0.4 Hz, 1H), 7.19-7.26 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -0.18, 0.43, 32.5, 36.6, 41.2, 50.7, 51.2, 51.6, 71.7, 104.7, 116.8, 125.0, 127.0, 127.6, 128.4, 128.5, 130.8, 142.4, 150.2, 172.4, 174.8; ESI-HRMS (m/z): $(M+H)^+$ Calcd for $C_{27}H_{42}NO_4Si_3$, 528.2416; Found: 528.2427 .

Diastereomer 2:

White oil; ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.11 (s, 9H), 0.12 (s, 9H), 2.41-2.54 (m, 2H), 2.74 (dd, *J* = 6.5, 2.5 Hz, 1H), 3.26 (ddd, *J* = 14.5, 8.5, 7.5 Hz, 1H), 3.36 (d, *J* = 2.5 Hz, 1H), 3.50 (ddd, *J* = 14.5, 8.0, 6.0 Hz, 1H), 3.58 (s, 3H), 3.62 (s, 3H), 3.66 (dd, *J* = 6.0, 6.0 Hz, 1H), 4.48 (d, *J* = 4.5 Hz, 1H), 6.46 (d, *J* = 8.0 Hz, 1H), 6.64 (dd, *J* = 7.0, 7.0 Hz, 1H), 7.12 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.20-7.30 (m, 6H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 0.05, 0.46, 31.9, 35.0, 41.6, 51.0, 51.3, 51.6, 73.2, 105.1, 116.9, 126.1, 127.2, 127.6, 128.4, 128.5, 129.3, 142.7, 150.9, 172.6, 175.2； ESI-HRMS (m/z): (M+H)$^+$ Calcd for $C_{27}H_{42}NO_4Si_3$, 528.2416; Found: 528.2425.

Methyl (*S)-2-(1,1,1,3,3,3-hexamethyltrisilan-2-yl)-2-((2*S**,3*S**)-1-methyl-2-(thiophen-2-yl)indolin-3-yl)acetate (3e)**



According to general procedure D, **3e** was obtained in 61% combined yield (dr = 1:1) from the reaction of methyl 3-(2-(methyl(thiophen-2-ylmethyl)amino)phenyl)propiolate (60.5 mg, 0.212 mmol), (TMS)$_3$SiH (79 μL, 0.256 mmol), ABVN (10.5 mg, 0.042 mmol), 2,6-dimethylbenzenethiol (5.6 μL, 0.042 mmol) in DMF (2.0 mL). The two diastereomers could be separated by flash column chromatography (silica gel; petroleum ether : ethyl ether = 200 : 1) to afford diastereomer 1 (31.3 mg) and diastereomer 2 (34.5 mg).

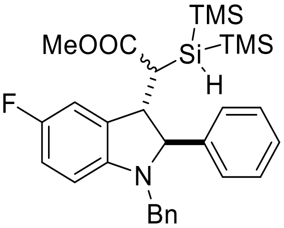
Diastereomer 1:

White oil; ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.15 (s, 9H), 0.16 (s, 9H), 2.64 (s, 3H), 2.76 (dd, *J* = 9.0, 1.5 Hz, 1H), 3.49 (d, *J* = 1.5 Hz, 1H), 3.61 (s, 3H), 3.69 (dd, *J* = 9.0, 3.5 Hz, 1H), 4.73 (d, *J* = 3.5 Hz, 1H), 6.42 (d, *J* = 7.5 Hz, 1H), 6.66 (dd, *J* = 7.5, 7.5 Hz, 1H), 6.90 (dd, *J* = 5.0, 4.0 Hz, 1H), 6.95 (d, *J* = 3.0 Hz, 1H), 7.11-7.15 (m, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ -0.1, 0.4, 32.5, 35.0, 51.0, 51.2, 70.1, 106.6, 117.6, 124.3, 124.9, 125.5, 126.0, 128.4, 129.5, 131.2, 144.6, 174.8; ESI-HRMS (m/z): $(M+Na)^+$ Calcd for $C_{22}H_{35}NNaO_2SSi_3$, 484.1589; Found: 484.1593.

Diastereomer 2:

White oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.13 (s, 9H), 0.16 (s, 9H), 2.65 (s, 3H), 2.81 (d, *J* = 6.0 Hz, 1H), 3.35 (s, 1H), 3.59 (s, 3H), 3.78 (dd, *J* = 6.4, 6.4 Hz, 1H), 4.52 (d, *J* = 6.8 Hz, 1H), 6.45 (d, *J* = 8.0 Hz, 1H), 6.70 (dd, *J* = 3.2, 3.2 Hz, 1H), 6.93-6.96 (m, 2H), 7.14 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.18-7.24 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.09, 0.56, 33.4, 33.8, 51.2, 51.4, 71.8, 106.7, 117.7, 124.8, 125.68, 125.74, 126.2, 128.3, 129.7, 145.8, 151.8, 175.2; ESI-HRMS (m/z): $(M+Na)^+$ Calcd for $C_{22}H_{35}NNaO_2SSi_3$, 484.1589; Found: 484.1587.

Methyl (*S)-2-((2*S**,3S*)-1-benzyl-5-fluoro-2-phenylindolin-3-yl)-2-(1,1,1,3,3,3-hexamethyltrisilan-2-yl)acetate (3f)**



According to general procedure D, **3f** was obtained in 68% combined yield (dr = 2.5:1) from the reaction of methyl 3-(2-(dibenzylamino)-5-fluorophenyl)propiolate (91.9 mg, 0.246 mmol), $(TMS)_3SiH$ (95 μL, 0.308 mmol), ABVN (13.0 mg, 0.052 mmol), 2,6-dimethylbenzenethiol (6.6 μL, 0.049 mmol) in DMF (2.5 mL). The two diastereomers could be separated by flash column chromatography (silica gel; petroleum ether : ethyl ether = 200 : 1) to afford diastereomer 1 (26.2 mg) and diastereomer 2 (65.6 mg).

Diastereomer 1:

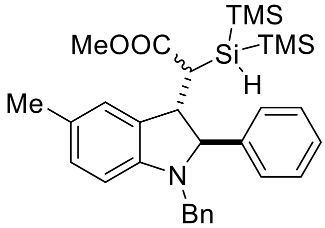
White oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.08 (s, 9H), 0.14 (s, 9H), 2.76 (dd, *J* = 9.6, 1.6 Hz, 1H), 3.53 (s, 1H), 3.60-3.63 (m, 4H), 3.92 (d, *J* = 15.6 Hz, 1H), 4.30 (d, *J* = 15.6 Hz, 1H), 4.59 (d, *J* = 3.6 Hz, 1H), 6.20 (dd, *J* = 8.4, 4.0 Hz, 1H), 6.74 (ddd, *J* = 8.4, 8.4, 2.8 Hz, 1H), 6.88 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.14-7.30 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -0.2, 0.3, 36.0, 49.7, 50.5, 51.3, 72.3, 105.1 (d, *J* = 8.0 Hz), 113.0 (d, *J* = 24.5 Hz), 113.9 (d, *J* = 23.0 Hz), 127.0, 127.1, 127.3, 127.7, 128.47, 128.54, 132.7

(d, $J = 7.5$ Hz), 138.3, 141.7, 147.3, 156.0 (d, $J = 232.4$ Hz), 174.6; ^{19}F NMR (376 MHz, CDCl$_3$): δ -128.5—128.4 (1F, m); ESI-HRMS (m/z): (M+H)$^+$ Calcd for $C_{30}H_{41}FNO_2Si_3$, 550.2424; Found: 550.2436.

Diastereomer 2:

White oil; ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.10 (s, 9H), 0.13 (s, 9H), 2.76 (d, $J = 5.0$ Hz, 1H), 3.25 (s, 1H), 3.57 (s, 3H), 3.79 (dd, $J = 6.0$, 6.0 Hz, 1H), 3.93 (d, $J = 16.0$ Hz, 1H), 4.33 (d, $J = 16.0$ Hz, 1H), 4.38 (d, $J = 6.5$ Hz, 1H), 6.23 (dd, $J = 8.5$, 4.0 Hz, 1H), 6.74 (ddd, $J = 9.0$, 7.5, 1.5 Hz, 1H), 7.04 (d, $J = 7.5$ Hz, 1H), 7.20-7.31 (m, 10H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 0.0, 0.5, 34.0, 50.60, 50.63, 51.4, 74.3, 105.9 (d, $J = 8.0$ Hz), 113.9 (d, $J = 23.5$ Hz) (overlapped), 127.0, 127.60, 127.63, 127.8, 128.4, 128.6, 131.2 (d, $J = 8.1$ Hz), 138.2, 141.9, 148.3, 156.0 (d, $J = 232.0$ Hz), 175.3; ^{19}F NMR (470 MHz, CDCl$_3$): δ -128.1—128.0 (1F, m); ESI-HRMS (m/z): (M+H)$^+$ Calcd for $C_{30}H_{41}FNO_2Si_3$, 550.2424; Found: 550.2431.

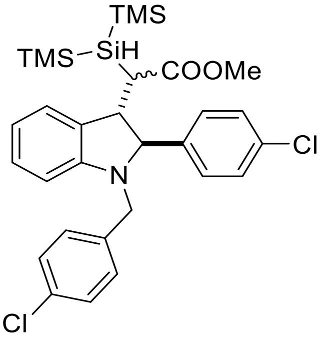
Methyl 2-((2*S,3*S**)-1-benzyl-5-methyl-2-phenylindolin-3-yl)-2-(1,1,1,3,3,3-hexamethyltrisilan-2-yl)acetate (3g)**



According to general procedure D, the reaction of methyl 3-(2-(dibenzylamino)-5-methylphenyl)propiolate (113.3 mg, 0.307 mmol), (TMS)$_3$SiH (114 μL, 0.370 mmol), ABVN (16.0 mg, 0.064 mmol), 2,6-dimethylbenzenethiol (8.2 μL, 0.062 mmol) in DMF (3.1 mL) was stirred at 60 °C for 6 h under nitrogen atmosphere. Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 100 : 1) afforded **3g** (118.9 mg) in 71% yield as an inseparable mixture of diastereomers (dr = 1.4:1); ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.07 (s, 9Hx1.4), 0.09 (s, 9Hx1), 0.12 (s, 9Hx1), 0.13 (s, 9Hx1.4), 2.22 (s, 3Hx1.4), 2.24 (s, 3Hx1), 2.76-2.78 (m, 1Hx1+1Hx1.4), 3.26 (d, $J = 1.5$ Hz, 1Hx1), 3.50 (s, 1Hx1.4), 3.55 (s, 3Hx1), 3.60 (s, 3Hx1.4), 3.65 (dd, $J = 9.0$, 3.0 Hz, 1Hx1.4), 3.79 (dd, $J = 6.5$, 6.0 Hz, 1Hx1), 3.89-3.94 (m, 1Hx1+1Hx1.4), 4.33-4.38

(m, 1Hx1+1Hx1+1Hx1.4), 4.58 (d, *J* = 3.0 Hz, 1Hx1.4), 6.25 (d, *J* = 8.0 Hz, 1Hx1.4), 6.29 (d, *J* = 8.0 Hz, 1Hx1), 6.86 (d, *J* = 7.5 Hz, 1Hx1+1Hx1.4), 6.91 (s, 1Hx1.4), 7.09 (s, 1Hx1), 7.15-7.28 (m, 10Hx1+10Hx1.4); ^{13}C NMR (100 MHz, $CDCl_3$) δ -0.2, 0.1, 0.3, 0.5, 20.8, 20.9, 34.4, 36.5, 49.3, 50.2, 50.6, 50.8, 51.1, 51.3, 71.7, 73.9, 105.0, 105.9, 125.9, 126.0, 126.1, 126.80, 126.83, 126.9, 127.2, 127.4, 127.5, 127.56, 127.64, 127.7, 128.3, 128.38, 128.43, 128.45, 128.5, 129.8, 131.4, 138.5, 138.7, 142.3, 142.4, 148.9, 149.8, 174.9, 175.4; ESI-HRMS (m/z): $(M+H)^+$ Calcd for $C_{31}H_{44}NO_2Si_3$, 546.2674; Found: 546.2682.

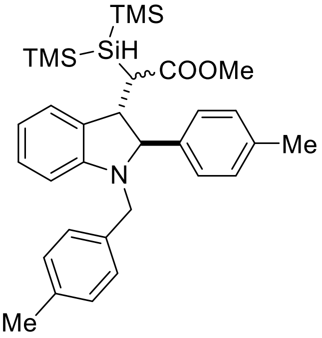
Methyl 2-((2*S,3*S**)-1-(4-chlorobenzyl)-2-(4-chlorophenyl)indolin-3-yl)-2-(1,1,1,3,3,3-hexamethyltrisilan-2-yl)acetate (3h)**



According to general procedure D, the reaction of methyl 3-(2-(bis(4-chlorobenzyl)amino)phenyl)propiolate (106.5 mg, 0.251 mmol), $(TMS)_3SiH$ (100 μL, 0.324 mmol), ABVN (13.5 mg, 0.054 mmol), 2,6-dimethylbenzenethiol (6.7 μL, 0.050 mmol) in DMF (2.2 mL) was stirred at 60 °C for 12 h under nitrogen atmosphere. Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 100 : 1) afforded **3h** (101.6 mg) in 78% yield as an inseparable mixture of diastereomers (dr = 3.2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.08 (s, 9Hx5.3), 0.11 (s, 9Hx1), 0.12 (s, 9Hx1), 0.14 (s, 9Hx5.3), 2.73-2.76 (m, 1Hx1+1Hx5.3), 3.28 (d, *J* = 2 Hz, 1Hx1), 3.43 (s, 1Hx5.3), 3.56 (s, 3Hx1), 3.60 (s, 3Hx5.3), 3.63-3.70 (m, 1Hx1+1Hx5.3), 3.84 (d, *J* = 16 Hz, 1Hx5.3), 3.91 (d, *J* = 15.6 Hz, 1Hx1), 4.32-4.38 (m, 1Hx1+1Hx1+1Hx5.3), 4.53 (d, *J* = 3.2 Hz, 1Hx5.3), 6.34-6.37 (m, 1Hx1+1Hx5.3), 6.61-6.89 (m, 1Hx1+1Hx5.3), 7.06-7.14 (m, 6Hx1+6Hx5.3), 7.21-7.26 (m, 4Hx1+4Hx5.3); ^{13}C NMR (100 MHz, $CDCl_3$) δ -0.2, 0, 0.4, 0.5, 34.9, 36.4, 48.5, 49.3, 50.4, 51.0, 51.3, 51.4, 70.8, 72.9, 105.3, 105.9, 117.4

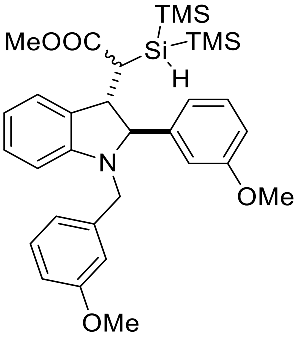
(overlapped), 125.2, 126.2, 128.46 (overlapped), 128.51 (overlapped), 128.6, 128.7 (overlapped, overlapped), 128.8, 128.9, 130.8 (overlapped), 132.7, 132.8, 133.3 (overlapped), 136.6, 136.7, 140.5, 140.7, 150.5, 151.3, 174.7, 175.2; ESI-HRMS (m/z): $(M+H)^+$ Calcd for $C_{30}H_{40}Cl_2NO_2Si_3$, 600.1738; Found: 600.1741.

Methyl 2-(1,1,1,3,3,3-hexamethyltrisilan-2-yl)-2-((2*S**,3*S**)-1-(3-methylbenzyl)-2-(m-tolyl)indolin-3-yl)acetate (3i)



According to general procedure D, the reaction of methyl 3-(2-(bis(4-methylbenzyl)amino)phenyl)propiolate (81.3 mg, 0.212 mmol), $(TMS)_3SiH$ (80 μL, 0.259 mmol), ABVN (10.5 mg, 0.042 mmol), 2,6-dimethylbenzenethiol (6.0 μL, 0.045 mmol) in DMF (2.0 mL) was stirred at 60 °C for 12 h under nitrogen atmosphere. Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 80 : 1) afforded **3i** (86.6 mg) in 73% yield as an inseparable mixture of diastereomers (dr = 1.3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.07 (s, 9Hx1.2), 0.10 (s, 9Hx1), 0.12 (s, 9Hx1), 0.14 (s, 9Hx1.2), 2.27-2.30 (m, 6Hx1+6Hx1.2), 2.74-2.79 (m, 1Hx1+1Hx1.2), 3.28 (s, 1Hx1), 3.54-3.55 (m, 3Hx1+1Hx1.2), 3.60 (s, 3Hx1.2), 3.67 (dd, *J* = 10, 3.2 Hz, 1Hx1.2), 3.80 (dd, *J* = 6.4, 6 Hz, 1Hx1), 3.91 (m, 1Hx1+1Hx1.2), 4.32-4.38 (m, 1Hx1+1Hx1+1Hx1.2), 4.57 (d, *J* = 2.8 Hz, 1Hx1.2), 6.34-6.39 (m, 1Hx1+1Hx1.2), 6.57-6.65 (m, 1Hx1+1Hx1.2), 6.93-7.18 (m, 9Hx1+9Hx1.2), 7.24-7.26 (m, 1Hx1+1Hx1.2); ^{13}C NMR (100 MHz, $CDCl_3$) δ -0.2, 0, 0.4, 0.6, 21.4, 21.5, 34.7, 36.9, 49.0, 49.6, 50.5, 50.7, 51.2, 51.3, 71.5, 73.6, 105.1, 105.7, 116.6, 116.8, 124.2, 124.4, 124.6, 124.7, 125.0, 126.1, 127.56, 127.62, 127.9, 128.15, 128.25, 128.3, 129.6, 131.2, 137.8, 137.9, 137.98, 138.04, 138.3, 138.5, 142.1, 142.3, 151.0, 151.9, 174.8, 175.3; ESI-HRMS (m/z): $(M+H)^+$ Calcd for $C_{32}H_{46}NO_2Si_3$, 560.2831; Found: 560.2840.

Methyl 2-(1,1,1,3,3,3-hexamethyltrisilan-2-yl)-2-((2S,3S)-1-(3-methoxybenzyl)-2-(3-methoxyphenyl)indolin-3-yl)acetate (3j)



According to general procedure D, **3j** was obtained in 76% combined yield (dr = 1.3:1) from the reaction of methyl 3-(2-(bis(3-methoxybenzyl)amino)phenyl)propiolate (110.0 mg, 0.265 mmol), $(TMS)_3SiH$ (100 μL, 0.318 mmol), ABVN (13.2 mg, 0.053 mmol), 2,6-dimethylbenzenethiol (7.0 μL, 0.053 mmol) in DMF (2.6 mL) was stirred at 60 °C for 12 h under nitrogen atmosphere. The two diastereomers could be separated by flash column chromatography (silica gel; petroleum ether : ethyl ether = 200 : 1) to afford diastereomer 1 (63.6 mg) and diastereomer 2 (48.9 mg).

Diastereomer 1

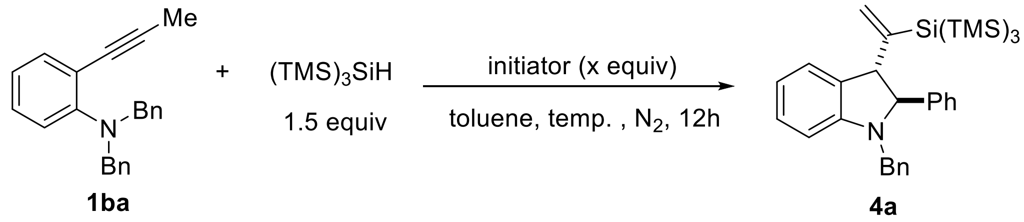
Pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.09 (s, 9H), 0.14 (s, 9H), 2.77 (d, *J* = 9.5, 1H), 3.53 (s, 1H), 3.60 (s, 3H), 3.69 (dd, *J* = 9.5, 3.5 Hz, 1H), 3.73 (s, 3H), 3.74 (s, 3H), 3.94 (d, *J* = 16.0 Hz, 1H), 4.36 (d, *J* = 16.0 Hz, 1H), 4.57 (d, *J* = 3.5 Hz, 1H), 6.36 (d, *J* = 8.0 Hz, 1H), 6.60 (dd, *J* = 7.5, 7.0 Hz, 1H), 6.73-6.83 (m, 6H), 7.04-7.09 (m, 2H), 7.17-7.22 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ -0.2, 0.4, 36.5, 49.2, 50.5, 51.2, 55.06, 55.09, 71.7, 105.4, 112.5, 112.78, 112.80 (overlapped), 116.9, 119.6 (overlapped), 125.0, 128.3, 129.4, 129.5, 131.1, 140.3, 143.7, 150.9, 159.6, 159.7, 174.8; ESI-HRMS (m/z): $(M+H)^+$ Calcd for $C_{32}H_{46}NO_4Si_3$, 592.2729; Found: 592.2739.

Diastereomer 2

Pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.11 (s, 9H), 0.12 (s, 9H), 2.78 (dd, *J* = 6.0, 1.0, 1H), 3.29 (d, *J* = 1.0 Hz, 1H), 3.56 (s, 3H), 3.72 (s, 3H), 3.74 (s, 3H), 3.79 (dd, *J* = 6.0, 6.0 Hz, 1H), 3.95 (d, *J* = 16.0 Hz, 1H), 4.38 (d, *J* = 16.0 Hz, 1H), 4.40 (d, *J* = 6.5 Hz, 1H), 6.39 (d, *J* = 8.0 Hz, 1H), 6.64 (dd, *J* = 7.5, 7.0 Hz, 1H), 6.74-6.82 (m, 6H), 7.06 (dd, *J* = 8.0, 7.5 Hz, 1H), 7.15-7.25 (m, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 0.0, 0.6, 34.8, 50.0, 50.7, 51.3, 55.0, 55.1, 73.7, 105.9, 112.6, 112.76, 112.79, 113.2, 117.0, 119.9, 120.0, 126.0, 128.3, 129.3, 129.5, 129.6, 140.1, 144.0, 151.8, 159.7 (overlapped), 175.3; ESI-HRMS (m/z): (M+H)$^+$ Calcd for C$_{32}$H$_{46}$NO$_4$Si$_3$, 592.2729; Found: 592.2733.

3.3 Synthesis of alkenylsilicon-containing indolines

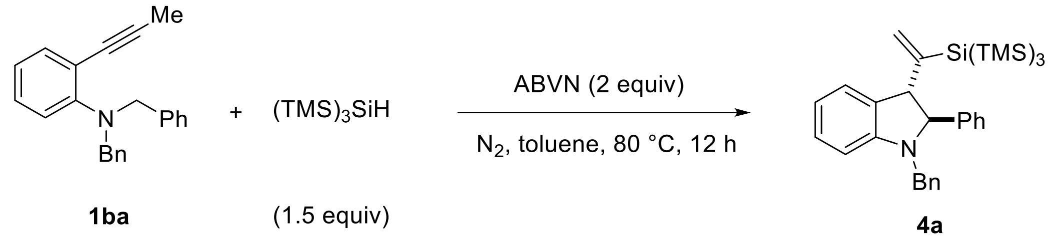
Table S3 Optimization[a]



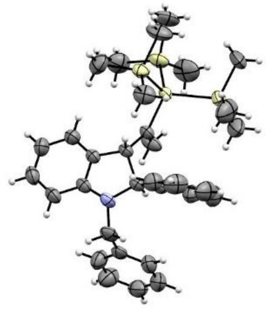
entry	Initiator (x equiv)	Temp.	Si-source	yield[b]
1	ABVN (0.2)	60 °C	(TMS)$_3$SiH	11%
2	ABVN (2.0)	60 °C	(TMS)$_3$SiH	79%
3	BPO (2.0)	110 °C	(TMS)$_3$SiH	0 (48%)[c]
4	DTBP (2.0)	120 °C	(TMS)$_3$SiH	33%
5	AIBN (2.0)	80 °C	(TMS)$_3$SiH	85%
6	AIBN (3.0)	80 °C	(TMS)$_3$SiH	79%
7	**AIBN (2.0)**	**80 °C**	**(TMS)$_3$SiH**	**93%[d]**
8	AIBN (1.5)	80 °C	(TMS)$_3$SiH	78%
9	AIBN (2.0)	80 °C	(Et)$_3$SiH	0 (98%)[c]
10	AIBN (2.0)	80 °C	Ph$_3$SiH	0 (78%)[c]
11	AIBN (2.0)	80 °C	Ph$_2$MeSiH	0 (87%)[c]
12	AIBN (2.0)	80 °C	(EtO)$_3$SiH	0 (94%)[c]

[a] Reaction conditions: **1ba** (0.1-0.2 mmol), Si-source (1.5 equiv), radical initiator (x equiv), toluene (1-2 mL) under N$_2$ for 12 h. [b] NMR yield using tetrachloroethane as an internal standard. [c] Recovery yield of **1ba** is shown in parentheses. [d] Isolated yield.

General procedure E:



A solution of *N,N*-dibenzyl-2-(prop-1-yn-1-yl)aniline (57.6 mg, 0.185 mmol), AIBN (66.9 mg, 0.407 mmol) and (TMS)$_3$SiH (85 μL, 0.277 mmol) in toluene (1.9 mL) was stirred at 80 °C for 12 h under nitrogen atmosphere. After evaporation of solvent, the crude mixture was purified by flash column chromatography (silica gel; petroleum ether) to give product **4a** (96.2 mg) in 93% yield as colorless solid; Recrystallization from petroleum ether/ethyl acetate gave colorless crystals.



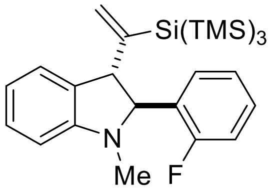
CCDC: 2234920; mp: 76-77 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.10 (s, 27H), 3.96 (d, *J* = 16.0 Hz, 1H), 4.12 (d, *J* = 9.6 Hz, 1H), 4.30 (d, *J* = 16.0 Hz, 1H), 4.54 (d, *J* = 9.6 Hz, 1H), 5.66 (d, *J* = 1.6 Hz, 1H), 5.86 (d, *J* = 1.6 Hz, 1H), 6.39 (d, *J* = 7.6 Hz, 1H), 6.70 (ddd, *J* = 7.6, 7.2, 0.8 Hz, 1H), 6.93 (d, *J* = 7.2 Hz, 1H), 7.03 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.20-7.32 (m, 8H), 7.38-7.41 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 1.4, 50.9, 58.9, 78.0, 107.3, 118.0, 124.2, 126.6, 127.5, 127.6, 127.9, 128.3, 128.4, 128.5, 131.8, 134.0, 138.4, 141.3, 148.0, 151.4; ESI-HRMS (*m/z*): (M+H)$^+$ Calcd for $C_{32}H_{48}NSi_4$, 558.2858; Found: 558.2851.

Gram-scale up synthesis: According to general procedure E, the reaction of *N,N*-dibenzyl-2-(prop-1-yn-1-yl)aniline (799.2 mg, 2.50 mmol), AIBN (822.9 mg, 5.00 mmol) and (TMS)$_3$SiH (1.1 mL,3.75 mmol) in toluene (20.0 mL) was stirred at 80 °C for 12 h under nitrogen atmosphere. After evaporation of solvent, the crude mixture was purified by flash column chromatography (silica gel; petroleum ether) to give product **4a** (1.255 g) in 90% yield as colorless solid.

Table S4. Crystal data and structure refinement for **4a**.

Empirical formula	$C_{32}H_{47}NSi_4$
Formula weight	558.07
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	21.8655(2)
b/Å	8.98117(9)
c/Å	17.4043(2)
α/°	90.00
β/°	92.1965(10)
γ/°	90.00
Volume/Å^3	3415.31(6)
Z	4
ρ_{calc}g/cm^3	1.085
μ/mm^{-1}	1.752
F(000)	1208.0
Crystal size/mm^3	0.25 × 0.24 × 0.22
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.1 to 140.12
Index ranges	$-26 \leq h \leq 26$, $-9 \leq k \leq 10$, $-17 \leq l \leq 20$
Reflections collected	12334
Independent reflections	6311 [R_{int} = 0.0196, R_{sigma} = 0.0218]
Data/restraints/parameters	6311/0/343
Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0453, wR_2 = 0.1204
Final R indexes [all data]	R_1 = 0.0495, wR_2 = 0.1253
Largest diff. peak/hole / e Å^{-3}	0.27/-0.38

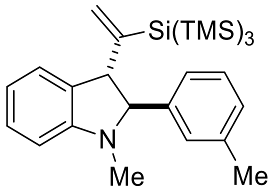
(2*S**,3*S**)-2-(2-fluorophenyl)-3-(1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)vinyl)-1-methylindoline (4b)



According to general procedure E, the reaction of *N*-(2-fluorobenzyl)-*N*-methyl-2-

(prop-1-yn-1-yl)aniline (52.5 mg, 0.207 mmol), AIBN (68.2 mg, 0.414 mmol) and $(TMS)_3SiH$ (96 μL, 0.311 mmol) in toluene (2.0 mL) was stirred at 80 °C for 12 h under nitrogen atmosphere. After evaporation of solvent, the crude mixture was purified by flash column chromatography (silica gel; petroleum ether) to give product **4b** (95.2 mg) in 92% yield as white solid, mp: 102-103 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.11 (s, 27H), 2.59 (s, 3H), 4.08 (d, *J* = 10.0 Hz, 1H), 4.74 (d, *J* = 10.0 Hz, 1H), 5.67 (d, *J* = 1.6 Hz, 1H), 5.95 (d, *J* = 1.6 Hz, 1H), 6.51 (d, *J* = 7.6 Hz, 1H), 6.73 (ddd, *J* = 7.6, 7.2, 0.8 Hz, 1H), 6.92 (d, *J* = 7.2 Hz, 1H), 7.02 (ddd, *J* = 7.6, 7.6, 0.8 Hz, 1H), 7.11-7.16 (m, 2H), 7.22-7.28 (m, 1H), 7.57 (ddd, *J* = 7.2, 7.2, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 1.3, 33.9, 57.8, 71.7, 106.9, 115.5 (d, *J* = 22.1 Hz), 118.3, 124.1, 124.4 (d, *J* = 3.5 Hz), 127.7, 128.2 (d, *J* = 12.3 Hz), 129.1 (d, *J* = 8.2 Hz), 129.3 (d, *J* = 4.2 Hz), 131.9, 133.8, 146.6, 152.0, 161.4 (d, *J* = 245.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.4 (1F); ESI-HRMS (*m/z*): $(M+H)^+$ Calcd for $C_{26}H_{43}FNSi_4$, 500.2451; Found: 500.2454.

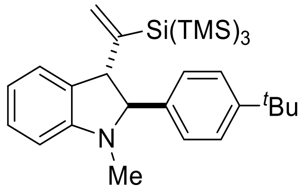
(2*S,3*S**)-3-(1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)vinyl)-1-methyl-2-(m-tolyl)indoline (4c)**



According to general procedure E, the reaction of *N*-methyl-*N*-(3-methylbenzyl)-2-(prop-1-yn-1-yl)aniline (53.7 mg, 0.215 mmol), AIBN (70.9 mg, 0.431 mmol) and $(TMS)_3SiH$ (99 μL, 0.323 mmol) in toluene (2.1 mL) was stirred at 80 °C for 12 h under nitrogen atmosphere. After evaporation of solvent, the crude mixture was purified by flash column chromatography (silica gel; petroleum ether) to give product **4c** (105.5 mg) in 98% yield as colorless solid, mp: 73-74 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.10 (s, 27H), 2.33 (s, 3H), 2.58 (s, 3H), 3.99 (d, *J* = 10.5 Hz, 1H), 4.25 (d, *J* = 10.5 Hz, 1H), 5.65 (d, *J* = 1.5 Hz, 1H), 5.90 (d, *J* = 1.5 Hz, 1H), 6.50 (d, *J* = 7.5 Hz, 1H), 6.70 (dd, *J* = 7.5, 7.0 Hz, 1H), 6.89 (d, *J* = 7.0 Hz, 1H), 7.07-7.14 (m, 2H), 7.20-7.21 (m, 3H); ^{13}C

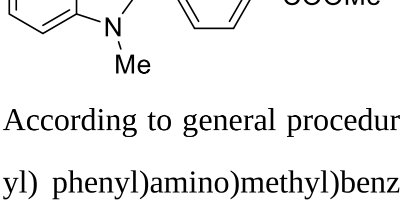
NMR (100 MHz, CDCl$_3$) δ 1.4, 21.3, 33.9, 59.7, 80.0, 106.8, 118.1, 124.0, 125.2, 127.7, 128.3, 128.5, 129.0, 132.0, 133.7, 137.9, 141.2, 147.0, 152.2; ESI-HRMS (*m/z*): $(M+H)^+$ Calcd for $C_{27}H_{46}NSi_4$, 496.2702; Found: 496.2707.

(2*S**,3*S**)-2-(4-(tert-butyl)phenyl)-3-(1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)vinyl)-1-methylindoline (4d)



According to general procedure E, the reaction of *N*-(4-(tert-butyl)benzyl)-*N*-methyl-2-(prop-1-yn-1-yl)aniline (52.5 mg, 0.180 mmol), AIBN (59.2 mg, 0.360 mmol) and $(TMS)_3SiH$ (96 μL, 0.271 mmol) in toluene (1.8 mL) was stirred at 80 °C for 12 h under nitrogen atmosphere. After evaporation of solvent, the crude mixture was purified by flash column chromatography (silica gel; petroleum ether) to give product **4d** (78.2 mg) in 81% yield as colorless solid, mp: 120-121 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.11 (s, 27H), 1.34 (s, 9H), 2.60 (s, 3H), 4.00 (d, J = 10.8 Hz, 1H), 4.29 (d, J = 10.8 Hz, 1H), 5.70 (s, 1H), 5.97 (s, 1H), 6.53 (d, J = 7.6 Hz, 1H), 6.72 (dd, J = 7.6, 7.2 Hz, 1H), 6.91 (d, J = 7.2 Hz, 1H), 7.14 (dd, J = 7.6, 7.6 Hz, 1H), 7.35 (d, J = 1.6 Hz, 4H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 1.5, 31.4, 34.0, 34.5, 59.1, 80.0, 106.8, 118.1, 124.0, 125.3, 127.6, 127.8, 131.8, 134.0, 138.0, 147.2, 150.6, 152.3; ESI-HRMS (*m/z*): $(M+H)^+$ Calcd for $C_{30}H_{52}NSi_4$, 538.3171; Found: 538.3179.

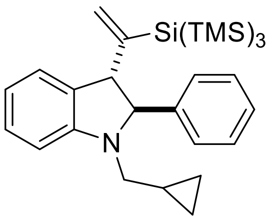
Methyl 4-((2*S**,3*S**)-3-(1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)vinyl)-1-methylindolin-2-yl)benzoate (4e)



According to general procedure E, the reaction of methyl 4-((methyl(2-(prop-1-yn-1-yl) phenyl)amino)methyl)benzoate (55.5 mg, 0.189 mmol), AIBN (62.0 mg, 0.378

mmol) and $(TMS)_3SiH$ (87 μL, 0.284 mmol) in toluene (1.9 mL) was stirred at 80 °C for 12 h under nitrogen atmosphere. After evaporation of solvent, the crude mixture was purified by flash column chromatography (silica gel; petroleum ether/ethyl acetate = 10 : 1) to give product **4e** (99.9 mg) in 98% yield as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.11 (s, 27H), 2.60 (s, 3H), 3.93 (s, 3H), 3.99 (d, *J* = 10.4 Hz, 1H), 4.38 (d, *J* = 10.4 Hz, 1H), 5.66 (s, 1H), 5.89 (s, 1H), 6.54 (d, *J* = 7.6 Hz, 1H), 6.74 (dd, *J* = 7.6, 7.2 Hz, 1H), 6.91 (d, *J* = 7.2 Hz, 1H), 7.15 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 2H), 8.03 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 1.5, 33.9, 52.0, 60.1, 79.2, 106.9, 118.4, 124.0, 127.9, 128.1, 129.6, 129.8, 132.2, 133.1, 146.6, 146.8, 151.9, 166.8; ESI-HRMS (*m/z*): $(M+H)^+$ Calcd for $C_{28}H_{46}NO_2Si_4$, 540.2600; Found: 540.2606.

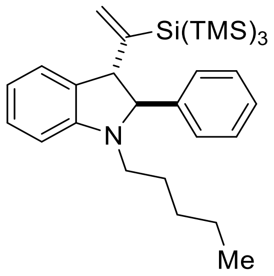
(2*S,3*S**)-1-(cyclopropylmethyl)-3-(1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)vinyl)-2-phenylindoline (4f)**



According to general procedure E, the reaction of *N*-benzyl-*N*-(cyclopropylmethyl)-2-(prop-1-yn-1-yl)aniline (51.9 mg, 0.188 mmol), AIBN (62.1 mg, 0.377 mmol) and $(TMS)_3SiH$ (87 μL, 0.282 mmol) in toluene (1.9 mL) was stirred at 80 °C for 12 h under nitrogen atmosphere. After evaporation of solvent, the crude mixture was purified by flash column chromatography (silica gel; petroleum ether) to give product **4f** (93.6 mg) in 95% yield as white solid, mp: 104-105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ -0.16--0.10 (m, 1H), 0.02-0.06 (m, 1H), 0.10 (s, 27H), 0.29-0.36 (m, 1H), 0.41-0.48 (m, 1H), 0.87-0.95 (m, 1H), 2.52 (dd, *J* = 14.8, 8.0 Hz, 1H), 3.25 (dd, *J* = 14.8, 8.0 Hz, 1H), 4.00 (d, *J* = 10.4 Hz, 1H), 4.77 (d, *J* = 10.4 Hz, 1H), 5.67 (s, 1H), 5.94 (s, 1H), 6.58 (d, *J* = 7.6 Hz, 1H), 6.68 (dd, *J* = 7.6, 7.2 Hz, 1H), 6.90 (d, *J* = 7.2 Hz, 1H), 7.12 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.27-7.33 (m, 3H), 7.41 (d, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 1.4, 2.4, 5.0, 7.8, 50.6, 59.6, 77.2, 106.6, 117.6, 124.2, 127.6, 127.7, 128.3 (overlapped), 131.8, 133.7, 141.7, 147.8, 151.1; ESI-HRMS (*m/z*): $(M+H)^+$ Calcd for

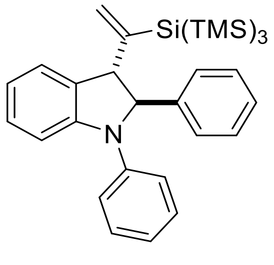
$C_{29}H_{48}NSi_4$, 522.2858; Found: 522.2863.

(2*S**,3*S**)-3-(1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)vinyl)-1-pentyl-2-phenylindoline (4g)



According to general procedure E, the reaction of *N*-benzyl-*N*-pentyl-2-(prop-1-yn-1-yl)aniline (41.7 mg, 0.143 mmol), AIBN (47.1 mg, 0.286 mmol) and $(TMS)_3SiH$ (66 μL, 0.214 mmol) in toluene (1.5 mL) was stirred at 80 °C for 12 h under nitrogen atmosphere. After evaporation of solvent, the crude mixture was purified by flash column chromatography (silica gel; petroleum ether) to give product **4g** (70.8 mg) in 92% yield as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.13 (s, 27H), 0.85 (t, *J* = 7.2 Hz, 3H), 1.16-1.31 (m, 4H), 1.43-1.51 (m, 2H), 2.86-3.08 (m, 2H), 4.02 (d, *J* = 9.6 Hz, 1H), 4.54 (d, *J* = 9.6 Hz, 1H), 5.67 (d, *J* = 1.2 Hz, 1H), 5.89 (d, *J* = 1.2 Hz, 1H), 6.48 (d, *J* = 7.6 Hz, 1H), 6.68 (dd, *J* = 7.6, 7.2 Hz, 1H), 6.91 (d, *J* = 7.2 Hz, 1H), 7.12 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.28-7.35 (m, 3H), 7.40 (d, *J* = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 1.4, 14.0, 22.4, 26.1, 29.4, 46.5, 59.3, 77.7, 106.0, 117.2, 124.1, 127.7, 127.8, 128.2, 128.4, 131.7, 133.7, 142.0, 148.2, 151.4; ESI-HRMS (*m/z*): $(M+H)^+$ Calcd for $C_{30}H_{52}NSi_4$, 538.3171; Found: 538.3178.

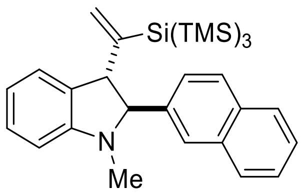
(2*S**,3*S**)-3-(1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)vinyl)-1,2-diphenyl indoline (4h)



According to general procedure E, the reaction of *N*-benzyl-*N*-phenyl-2-(prop-1-yn -1-

yl)aniline (54.4 mg, 0.183 mmol), AIBN (60.1 mg, 0.366 mmol) and $(TMS)_3SiH$ (85 μL, 0.274 mmol) in toluene (2.0 mL) was stirred at 80 °C for 12 h under nitrogen atmosphere. After evaporation of solvent, the crude mixture was purified by flash column chromatography (silica gel; petroleum ether) to give product **4h** (84.1 mg) in 84% yield as white solid, mp: 120-121 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.17 (s, 27H), 4.02 (d, J = 10.5 Hz, 1H), 5.11 (d, J = 10.5 Hz, 1H), 5.63 (s, 1H), 5.82 (s, 1H), 6.80 (dd, J = 7.2, 7.2 Hz, 1H), 6.93 (dd, J = 7.2, 7.2 Hz, 1H), 7.02 (d, J = 7.2 Hz, 1H), 7.06-7.24 (m, 9H), 7.31 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 1.5, 60.0, 76.7, 108.4, 119.4, 120.4 (overlapped), 122.1, 124.9, 127.0, 127.5, 128.5, 128.9, 131.7, 134.4, 142.5, 143.2, 147.6, 148.6; ESI-HRMS (m/z): $(M+H)^+$ Calcd for $C_{31}H_{46}NSi_4$, 544.2702; Found: 544.2701.

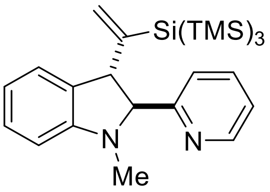
(2*S**,3*S**)-3-(1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)vinyl)-1-methyl-2-(naphthalen-2-yl)indoline (4i)



According to general procedure E, the reaction of *N*-methyl-*N*-(naphthalen-1-ylmethyl)-2-(prop-1-yn-1-yl)aniline (58.3 mg, 0.204 mmol), AIBN (67.3 mg, 0.408 mmol) and $(TMS)_3SiH$ (95 μL, 0.306 mmol) in toluene (2.0 mL) was stirred at 80 °C for 12 h under nitrogen atmosphere. After evaporation of solvent, the crude mixture was purified by flash column chromatography (silica gel; petroleum ether) to give product **4i** (97.7 mg) in 90% yield as white solid, mp: 114-116 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.09 (s, 27H), 2.65 (s, 3H), 4.14 (d, J = 10.8 Hz, 1H), 4.51 (d, J = 10.8 Hz, 1H), 5.69 (s, 1H), 5.93 (s, 1H), 6.56 (d, J = 7.6 Hz, 1H), 6.76 (dd, J = 7.6, 7.2 Hz, 1H), 6.94 (d, J = 7.2 Hz, 1H), 7.18 (ddd, J = 7.6, 7.6, 0.8 Hz, 1H), 7.47-7.52 (m, 2H), 7.66 (d, J = 8.4 Hz, 1H), 7.81-7.87 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 1.5, 33.8, 60.0, 80.0, 106.8, 118.2, 124.1, 125.4, 125.7, 126.0, 127.67, 127.69, 127.7, 127.8, 128.4, 132.3, 133.3, 133.4, 133.5, 138.7, 147.0, 152.2; ESI-HRMS (m/z): $(M+H)^+$ Calcd for

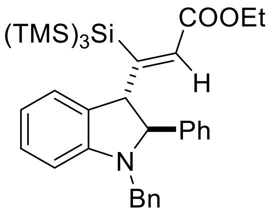
$C_{30}H_{46}NSi_4$, 532.2702; Found: 532.2709.

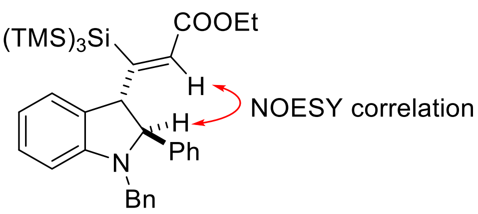
(2*S**,3*S**)-3-(1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)vinyl)-1-methyl-2-(pyridin-2-yl)indoline (4j)



According to general procedure E, the reaction of *N*-methyl-2-(prop-1-yn-1-yl)-*N*-(pyridin-2-ylmethyl)aniline (53.6 mg, 0.227 mmol), AIBN (74.9 mg, 0.455 mmol) and $(TMS)_3SiH$ (105 µL, 0.341 mmol) in toluene (2.3 mL) was stirred at 80 °C for 12 h under nitrogen atmosphere. After evaporation of solvent, the crude mixture was purified by flash column chromatography (silica gel; petroleum ether/ethyl acetate = 20 : 1) to give product **4j** (99.5 mg) in 91% yield as yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 0.11 (s, 27H), 2.63 (s, 3H), 4.22 (d, *J* = 10.4 Hz, 1H), 4.51 (d, *J* = 10.4 Hz, 1H), 5.64 (d, *J* = 1.6 Hz, 1H), 5.90 (d, *J* = 1.6 Hz, 1H), 6.51 (d, *J* = 7.6 Hz, 1H), 6.72 (dd, *J* = 7.2, 7.2 Hz, 1H), 6.91 (d, *J* = 7.2 Hz, 1H), 7.12 (dd, *J* = 7.6, 7.2 Hz, 1H), 7.18-7.22 (m, 1H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.65 (ddd, *J* = 8.0, 8.0, 1.2 Hz, 1H), 8.59 (d, *J* = 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 1.4, 34.1, 58.4, 80.8, 107.1, 118.3, 122.6, 122.7, 124.0, 127.7, 132.1, 133.6, 136.4, 146.7, 149.4, 151.9, 160.9; ESI-HRMS (*m/z*): $(M+H)^+$ Calcd for $C_{25}H_{43}N_2Si_4$, 483.2498; Found: 483.2499.

Ethyl-(*Z*)-3-((2*S**,3*S**)-1-benzyl-2-phenylindolin-3-yl)-3-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)acrylate (4k)

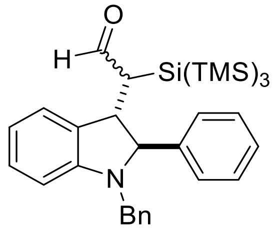




According to general procedure E, the reaction of ethyl 4-(2-(dibenzylamino)phenyl)but-3-ynoate (79.1 mg, 0.206 mmol), AIBN (68.2 mg, 0.413

mmol) and $(TMS)_3SiH$ (96 μl, 0.309 mmol) in toluene (2.0 mL) was stirred at 80 °C for 12 h under nitrogen atmosphere. After evaporation of solvent, the crude mixture was purified by flash column chromatography (silica gel; petroleum ether/ethyl acetate = 10 : 1) to give product **4k** (41.5 mg) in 32% yield as yellow oil; The *Z* configuration of the alkene was determined by NOESY interactions; ^1H NMR (400 MHz, $CDCl_3$) δ 0.07 (s, 27H), 1.25 (t, *J* = 7.2 Hz, 3H), 3.94 (d, *J* = 15.6 Hz, 1H), 4.09 (q, *J* = 7.2 Hz, 2H), 4.31 (d, *J* = 7.2 Hz, 1H), 4.37 (d, *J* = 15.6 Hz, 1H), 4.61 (d, *J* = 7.2 Hz, 1H), 6.44 (d, *J* = 8.0 Hz, 1H), 6.58 (s, 1H), 6.65 (dd, *J* = 7.6, 7.2 Hz, 1H), 6.86 (d, *J* = 7.2 Hz, 1H), 7.05 (dd, *J* = 8.0, 7.6 Hz, 1H), 7.23-7.30 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 2.7, 14.4, 50.3, 59.8, 60.1, 78.4, 106.9, 117.7, 124.7, 127.0, 127.6 (overlapped), 127.9, 128.1, 128.4, 128.7, 133.1, 133.8, 138.1, 141.4, 151.2, 167.0, 171.0; ESI-HRMS (*m/z*): $(M+H)^+$ Calcd for $C_{35}H_{52}NO_2Si_4$, 630.3070; Found: 630.3071.

(*S**)-2-((2*S**,3*S**)-1-benzyl-2-phenylindolin-3-yl)-2-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)acetaldehyde (4l)

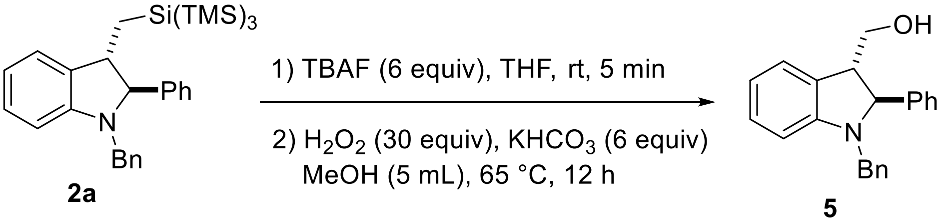


According to general procedure E, the reaction of 3-(2-(dibenzylamino)phenyl)prop-2-yn-1-ol (64.0 mg, 0.195 mmol), AIBN (64.9 mg, 0.391 mmol) and $(TMS)_3SiH$ (90 μL, 0.293 mmol) in toluene (2.0 mL) was stirred at 80 °C for 12 h under nitrogen atmosphere. ^1H NMR analysis of the crude product showed that dr = 2.5:1. After evaporation of solvent, the crude mixture was purified by flash column chromatography (silica gel; petroleum ether/ethyl acetate = 20 : 1) to give product **4l** (41.5 mg) in 40% yield as an inseparable mixture of diastereomers (dr = 1.2:1); ^1H NMR (400 MHz, $CDCl_3$) δ 0.13 (s, 27H×1), 0.14 (s, 27H×1.2), 2.93-2.97 (m, 1H×1+1H×1.2), 3.62 (d, *J* = 10.4 Hz, 1H×1.2), 3.84 (m, 1H×1+ 1H×1.2), 3.96 (d, *J* = 15.6 Hz, 1H×1.2), 4.11 (d, *J* = 10.0 Hz, 1H×1), 4.25-4.32 (m, 1H×1+1H×1.2), 4.52 (d, *J* = 5.2 Hz, 1H×1), 6.36 (d, *J* = 8.0 Hz, 1H×1), 6.46 (d, *J* = 8.0 Hz, 1H×1.2), 6.70-6.77 (m, 1H×1+1H×1.2), 7.03-

7.09 (m, 1H×1+1H×1.2), 7.18-7.41 (m, 11H×1+11H×1.2), 9.68 (d, *J* = 4.4 Hz, 1H×1), 9.77 (d, *J* = 5.6 Hz, 1H×1.2); ^{13}C NMR (100 MHz, CDCl$_3$) δ 1.7, 2.0, 41.7, 48.8, 49.8, 49.9, 51.4, 52.2, 71.0, 78.4, 107.0, 108.5, 117.6, 118.2, 124.1, 124.6, 127.0, 127.1, 127.5, 127.7, 127.9 (overlapped, overlapped), 128.0, 128.2 (overlapped), 128.4 (overlapped), 128.48, 128.53, 128.8, 133.0, 137.9, 138.0, 140.2, 140.6, 150.5, 152.3, 200.37, 200.40; ESI-HRMS (*m/z*): (M+H)$^+$ Calcd for $C_{32}H_{48}NOSi_4$, 574.2807; Found: 574.2811.

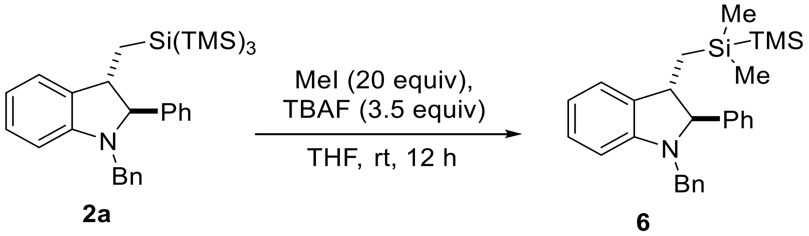
4. Synthetic applications

4.1 Synthesis of alcohol 5



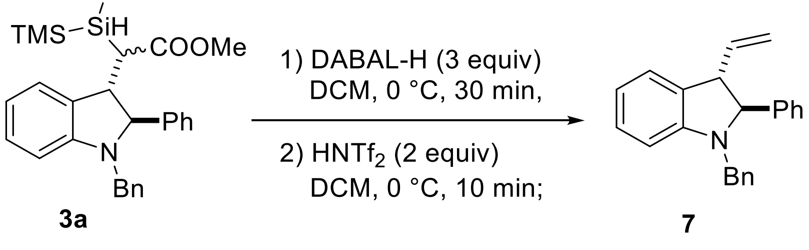
To a solution of **2a** (113.0 mg, 0.207 mmol) in THF (2.0 mL) was slowly added TBAF (1.24 mL, 1.0 M in THF) at room temperature under nitrogen atmosphere. The reaction mixture was stirred at this temperature for 5 min. Then H_2O_2 (30% aq, 0.704 g), $KHCO_3$ (124.3 mg, 1.242 mmol) and MeOH (5 mL) was added. The mixture was stirred at 65 °C for 12 h and was quenched with 1.0 M $Na_2S_2O_3$ (10.0 mL). The reaction mixture was extracted three times with dichloromethane. The combined extracts were dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by flash column chromatography (silica gel; petroleum ether : ethyl acetate = 10 : 1) to give **5** in 85% yield (55.5 mg) as white oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.38 (ddd, *J* = 8.8, 4.8, 4.8 Hz, 1H), 3.81 (dd, *J* = 11.2, 4.8 Hz, 1H), 3.96-4.01 (m, 2H), 4.39 (d, *J* = 15.6 Hz, 1H), 4.55 (d, *J* = 8.8 Hz, 1H), 6.42 (d, *J* = 7.6 Hz, 1H), 6.71 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1H), 7.06-7.12 (m, 2H), 7.20-7.35 (m, 8H), 7.38-7.41 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 50.4, 53.5, 63.1, 71.2, 107.1, 117.7, 123.5, 126.9, 127.5, 127.61, 127.64, 127.8, 128.4, 128.5, 128.7, 138.1, 142.1, 152.4; ESI-HRMS (m/z): (M+H)$^+$ Calcd for $C_{22}H_{22}NO$, 316.1696; Found: 316.1705.

4.2 Synthesis of disilane 6



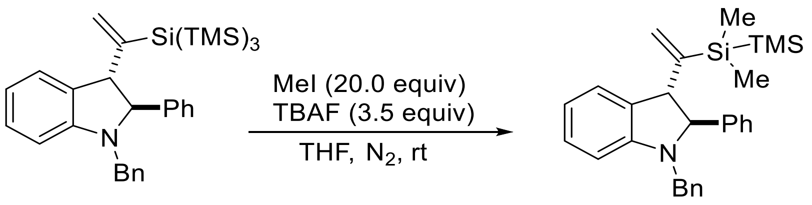
To a solution of **2a** (153.0 mg, 0.280 mmol) and MeI (350 μL, 5.622 mmol) in anhydrous THF (3.0 mL) was slowly added TBAF (980 μL, 1.0 M in THF) using syringe pump during 6 h at room temperature under nitrogen atmosphere. The reaction mixture was stirred at this temperature for 12 h and was quenched with water. The reaction mixture was extracted three times with dichloromethane. The combined extracts were dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by flash column chromatography (silica gel; petroleum ether : dichloromethane = 10 : 1) to give **6** in 58% yield (69.8 mg) as yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ -0.02 (s, 3H), 0.04 (s, 9H), 0.07 (s, 3H), 1.15 (dd, *J* = 15.5, 6.0 Hz, 1H), 1.25 (dd, *J* = 15.5, 6.0 Hz, 1H), 3.42 (ddd, *J* = 9.0, 6.0, 6.0 Hz, 1H), 4.02 (d, *J* = 15.5 Hz, 1H), 4.22 (d, *J* = 9.0 Hz, 1H), 4.43 (d, *J* = 15.5 Hz, 1H), 6.50 (d, *J* = 6.0 Hz, 1H), 6.83 (dd, *J* = 5.6, 5.6 Hz, 1H), 7.12-7.16 (m, 2H), 7.32-7.45 (m, 8H), 7.51-7.53 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -3.3, -3.3, -2.4, 18.2, 47.3, 50.9, 78.9, 107.3, 118.0, 123.2, 126.8, 127.5, 127.6, 127.9, 128.1, 128.3, 128.5, 134.6, 138.4, 141.3, 151.4; ESI-HRMS (m/z): $(M+H)^+$ Calcd for $C_{27}H_{36}NSi_2$, 430.2381; Found: 430.2389.

4.3 Synthesis of alkene 7



To a solution of **3a** (97.3 mg, 0.183 mmol) in anhydrous DCM (2.0 mL) was slowly added DIBAL-H (370 μL, 1.5 M in toluene) at 0 °C under nitrogen atmosphere. The reaction mixture was stirred at this temperature for 30 min. The reaction was quenched with potassium sodium tartrate salts solutions followed by filtration through celite and washed with ethyl acetate (30.0 mL). The solvent was evaporated and the residue was dissolved in DCM (2.0 mL), then $HNTf_2$ (102.8 mg, 0.366 mmol) was added and stirred at 0 °C for 10 min. The reaction quenched with water and was extracted three times with dichloromethane. The combined extracts were dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by flash column chromatography (silica gel; petroleum ether : ethyl ether = 100 : 1) to give **7** (34.2 mg) in 60% yield as yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.79 (dd, *J* = 10.4, 9.2 Hz, 1H), 3.97 (d, *J* = 15.6 Hz, 1H), 4.31 (d, *J* = 10.4 Hz, 1H), 4.36 (d, *J* = 15.6 Hz, 1H), 5.00 (d, *J* = 17.2 Hz, 1H), 5.14 (d, *J* = 10.0 Hz, 1H), 5.88 (ddd, *J* = 17.2, 10.4, 9.2 Hz, 1H), 6.43 (d, *J* = 7.6 Hz, 1H), 6.74 (dd, *J* = 7.2, 7.2 Hz, 1H), 6.99 (d, *J* = 7.2 Hz, 1H), 7.07 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.21-7.36 (m, 8H), 7.42-7.44 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.3, 56.5, 76.1, 108.0, 117.8, 118.3, 124.0, 126.9, 127.6, 127.7, 127.9, 128.1, 128.4, 128.5, 130.7, 137.0, 138.1, 140.8, 151.8； ESI-HRMS (m/z): $(M+H)^+$ Calcd for $C_{23}H_{22}N$, 312.1474; Found: 312.1755.

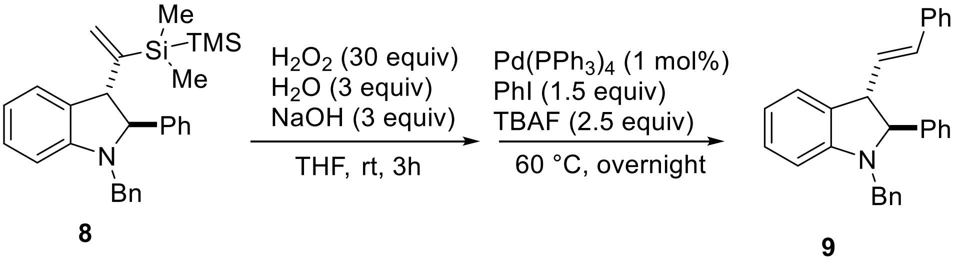
4.4 Synthesis of disilane 8



4a **8**

To a solution of **4a** (141.5 mg, 0.254 mmol) and MeI (320 μL, 5.140 mmo) in anhydrous THF (3.0 mL) was slowly added TBAF (887 μL, 1.0 M in THF) using syringe pump during 6 h at room temperature under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 12 h and was quenched with water. The reaction mixture was extracted three times with dichloromethane. The combined extracts were dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by flash column chromatography (silica gel; hexane / dichloromethane = 20 : 1) to give **8** in 60% yield (67.2 mg) as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.13 (s, 3H), 0.25 (s, 3H), 0.35 (s, 9H), 4.28-4.36 (m, 2H), 4.68-4.76 (m, 2H), 5.90 (s, 1H), 6.03 (s, 1H), 6.79 (d, *J* = 7.6 Hz, 1H), 7.04 (dd, *J* = 6.8, 6.4 Hz, 1H), 7.21 (d, *J* = 6.4 Hz, 1H), 7.39 (dd, *J* = 6.8, 6.4 Hz, 1H), 7.56-7.76 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -3.5, -3.3, -2.0, 51.1, 58.8, 77.7, 107.5, 118.1, 124.2, 126.9, 127.7, 127.76, 127.79, 128.0, 128.3, 128.4, 129.9, 132.6, 138.2, 141.3, 151.4, 151.9; ESI-HRMS (*m/z*): $(M+H)^+$ Calcd for $C_{28}H_{36}NSi_2$, 442.2381; Found: 442.2384.

4.5 Synthesis of compound 9



To a solution of **8** (75 mg, 0.170 mmol) in THF (2.0 mL) was added 30% H_2O_2 (0.6 mL, 6.1 mmol), NaOH (20.4 mg, 0.510 mmol), and H_2O (0.5 mL). The reaction mixture was stirred at room temperature for 3 h under nitrogen atmosphere, followed by addition of iodobenzene (28 μL, 0.255 mmol), $Pd(PPh_3)_4$ (2.0 mg, 0.0017 mmol) and TBAF (420 μL, 1.0 M in THF), then this reaction mixture was stirred at 60 °C overnight under nitrogen atmosphere. The reaction mixture was quenched with water and extracted three times with ethyl acetate. The combined extracts were dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by flash column chromatography (silica gel; hexane / dichloromethane = 20 : 1) to give **9** in 44% yield (29.2 mg) as yellow solid, mp: 72-74 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.96 (dd, *J* = 9.6, 7.2 Hz, 1H), 4.00 (d, *J* = 16.4 Hz, 1H), 4.38-4.42 (m, 2H), 6.28 (dd, *J* = 15.6, 7.2 Hz, 1H), 6.33 (d, *J* = 15.6 Hz, 1H), 6.47 (d, *J* = 8.0 Hz, 1H), 6.73 (dd, *J* = 7.2, 7.2 Hz, 1H), 7.02 (d, *J*

= 7.2 Hz, 1H), 7.08 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.19-7.35 (m, 13H), 7.43-7.45 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.3, 55.8, 76.3, 108.1, 118.3, 124.2, 126.3, 126.9, 127.4, 127.6, 127.7, 127.9, 128.2, 128.4, 128.50, 128.53, 128.6, 130.9, 132.8, 137.0, 138.2, 140.7, 151.8; ESI-HRMS (*m/z*): $(M+H)^+$ Calcd for $C_{29}H_{26}N$, 388.2060; Found: 388.2067.

5. References

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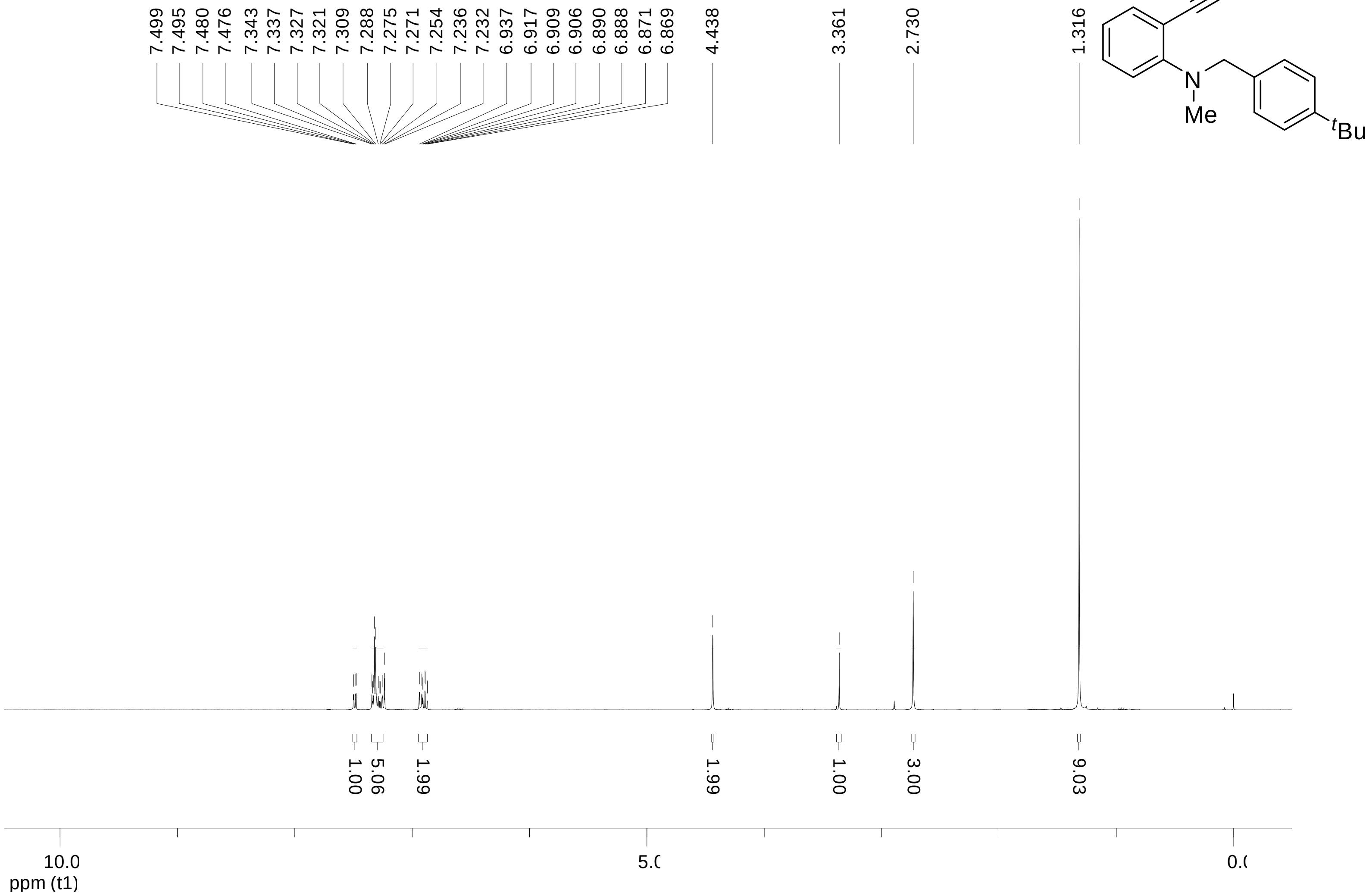
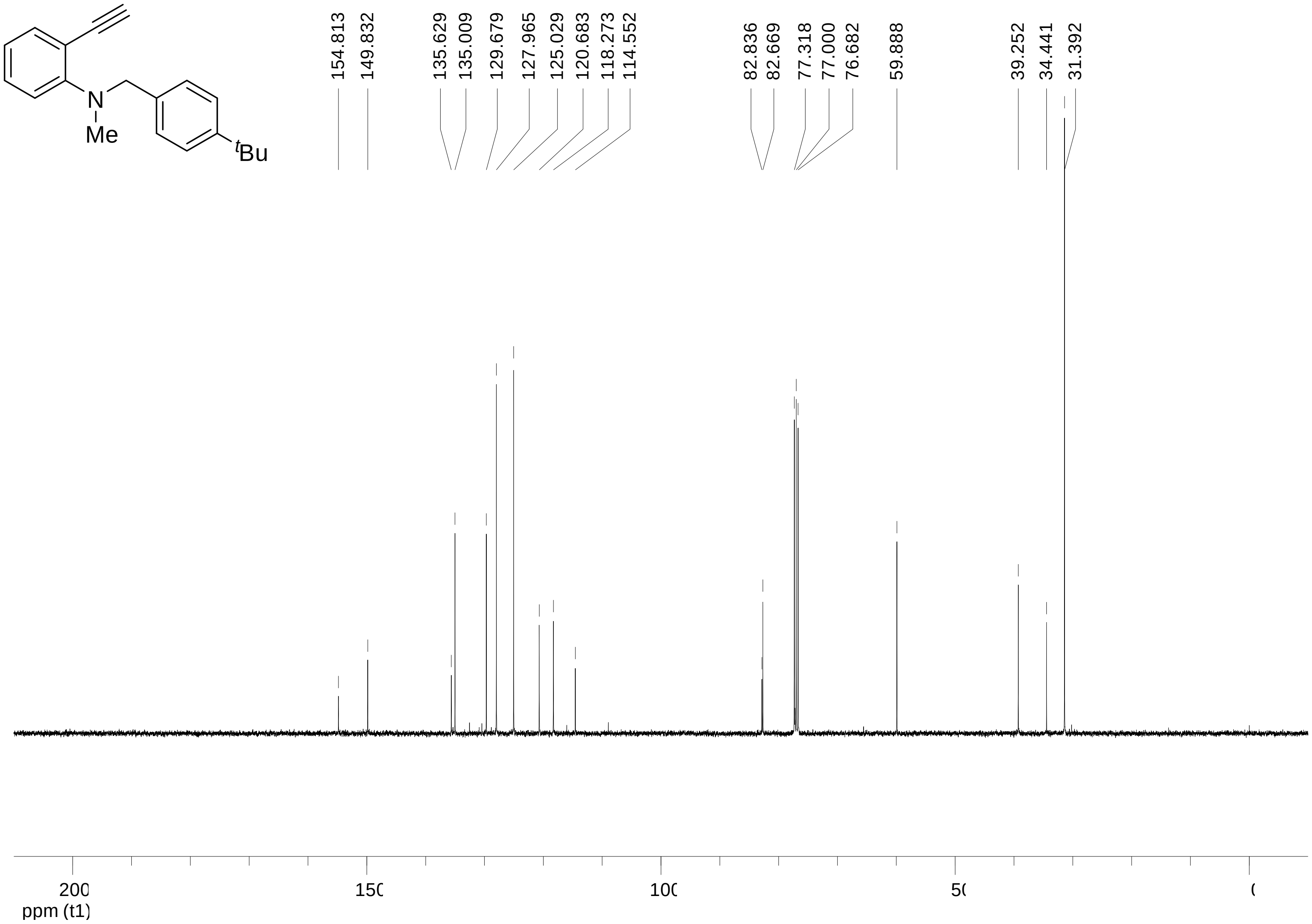
7. Dang, P.; Zeng, W.; Liang, Y., Copper-Catalyzed Three-Component Synthesis of Benzothiazolethiones from o-Iodoanilines, Isocyanide, and Potassium Sulfide. *Org. Lett.* **2015**, *17*, 34-37.

6. Copies of 1H NMR, 13C NMR and 19F NMR spectra

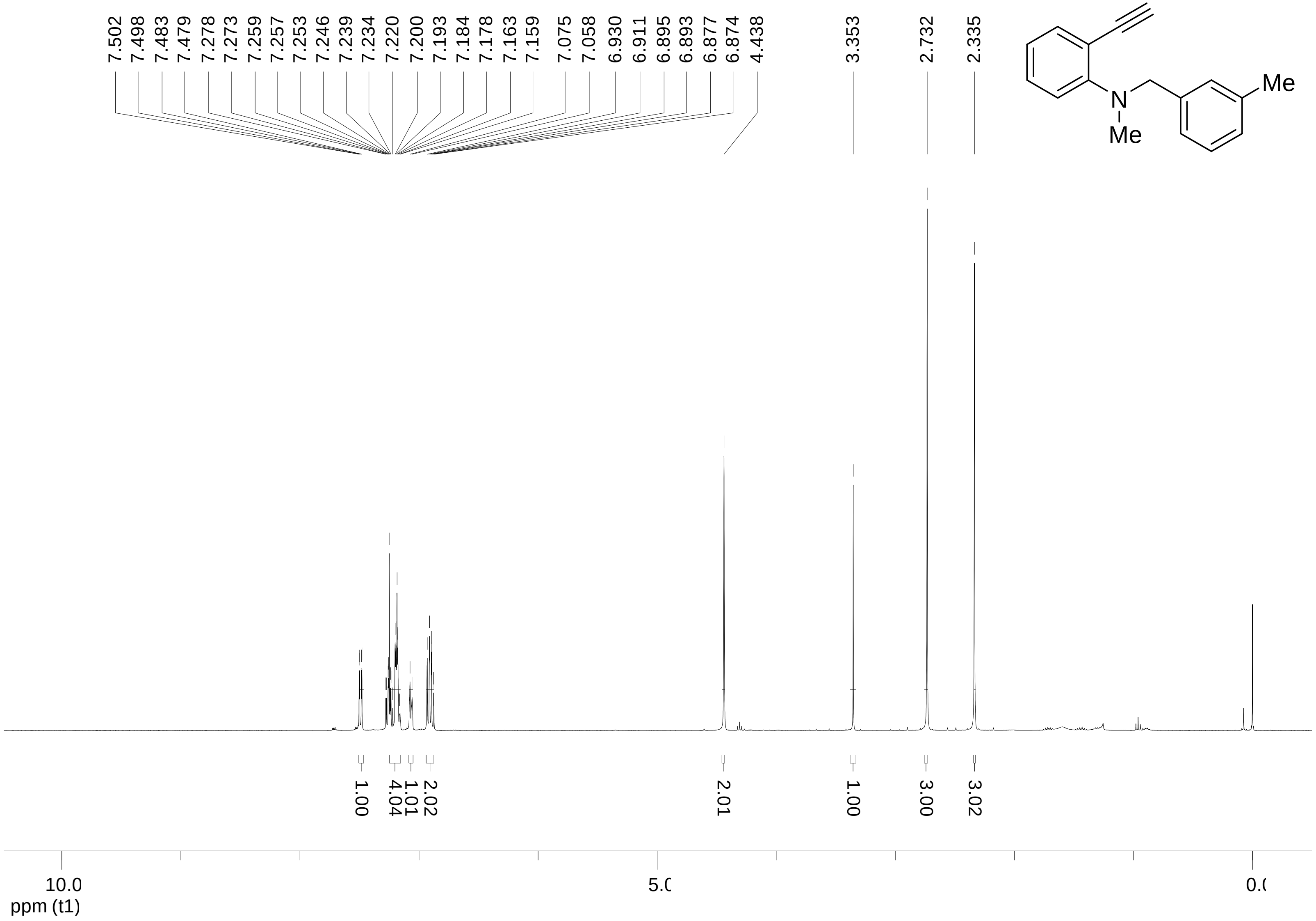
^{1}H NMR spectrum of **1c** (400 MHz, $CDCl_3$)



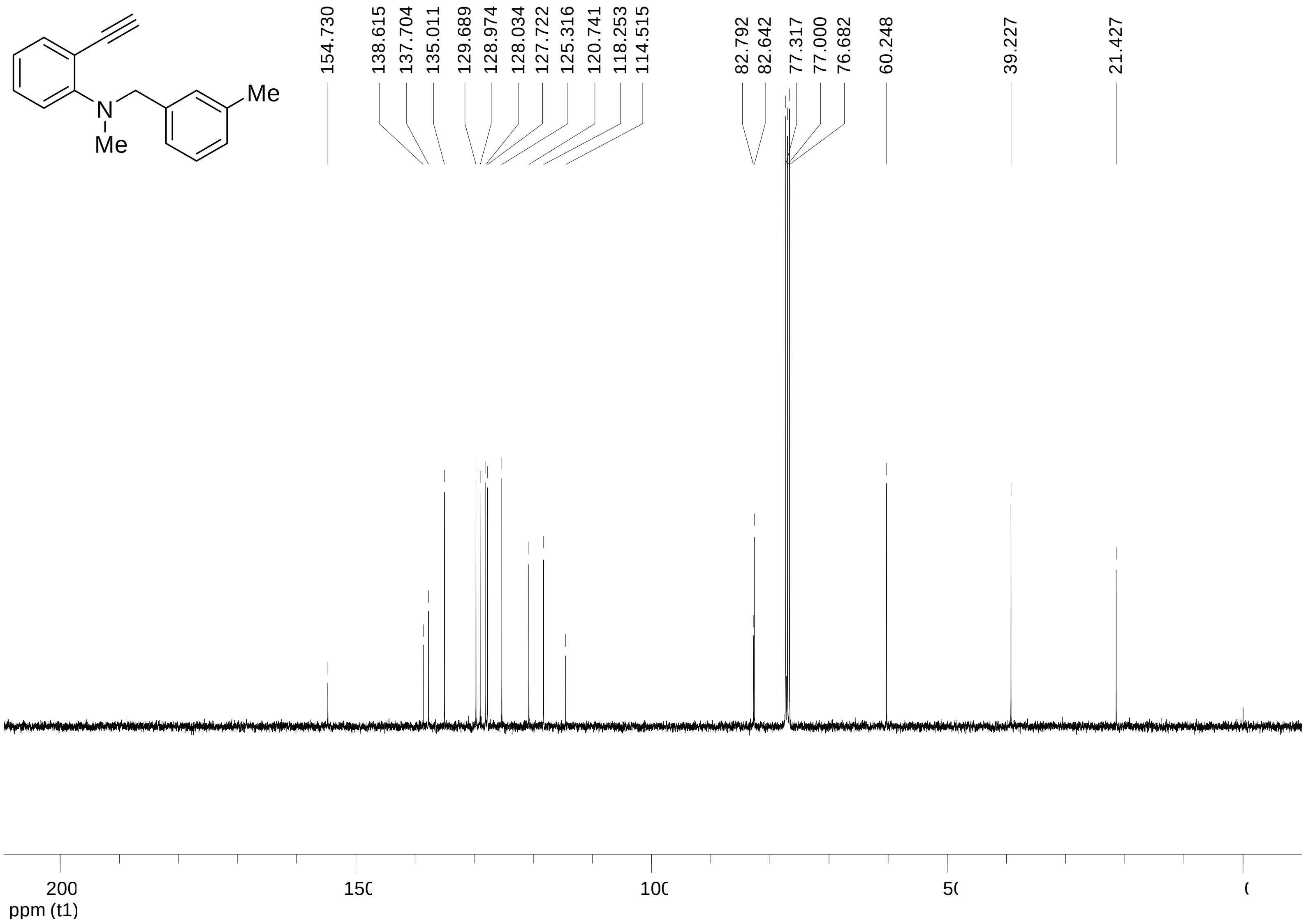
^{13}C NMR spectrum of **1c** (100 MHz, CDCl$_3$)



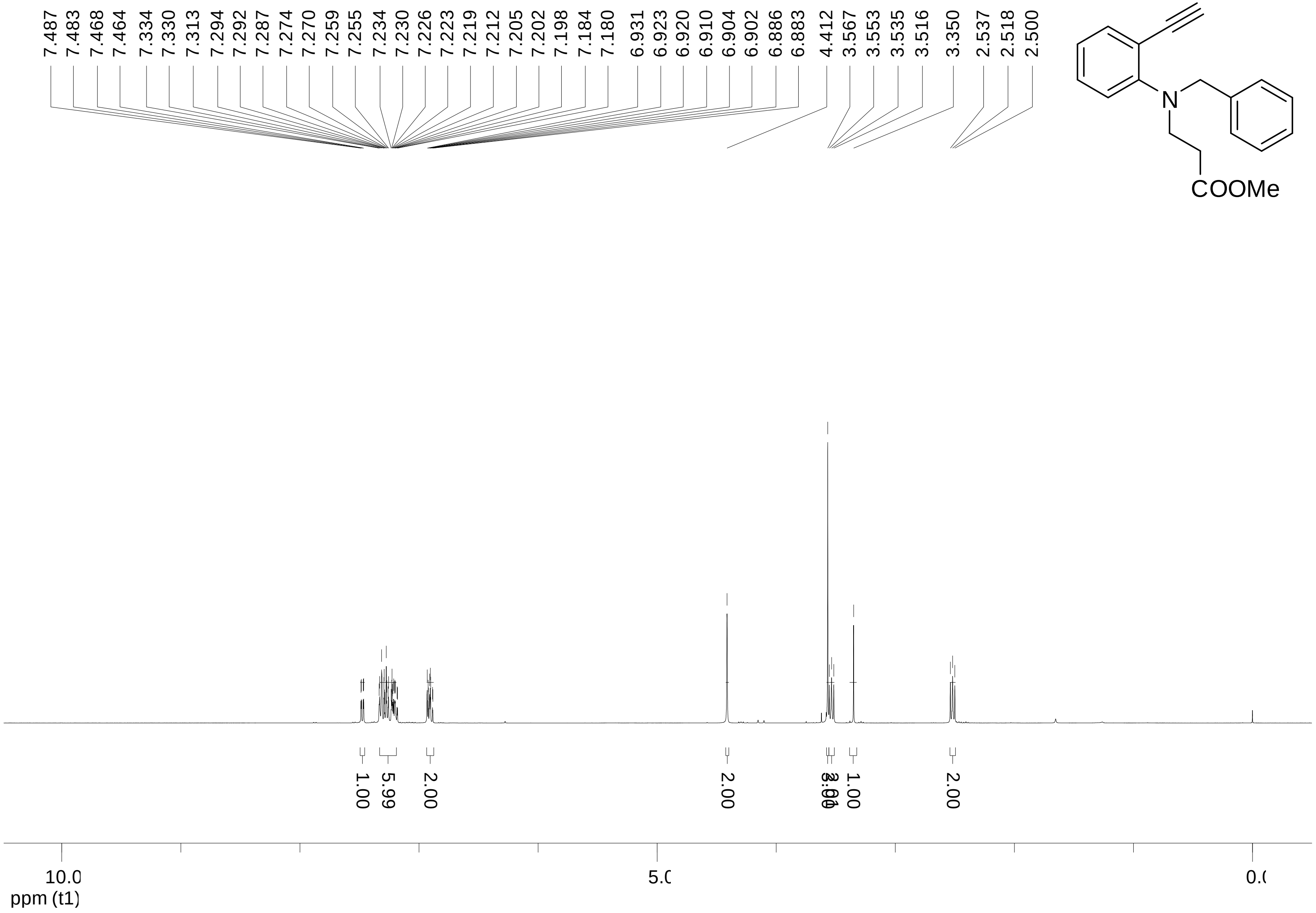
^{1}H NMR spectrum of **1d** (400 MHz, CDCl$_3$)



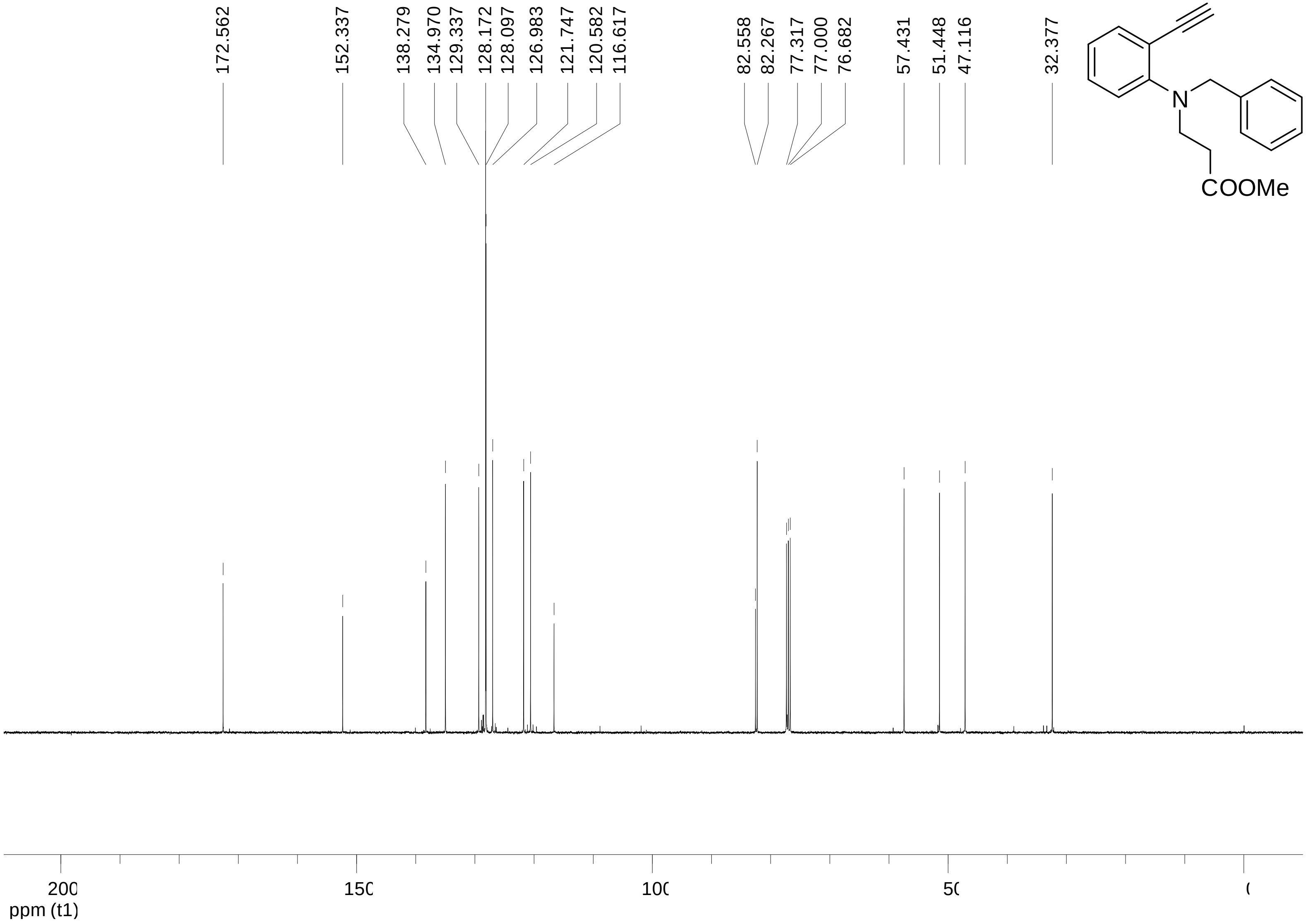
^{13}C NMR spectrum of **1d** (100 MHz, $CDCl_3$)



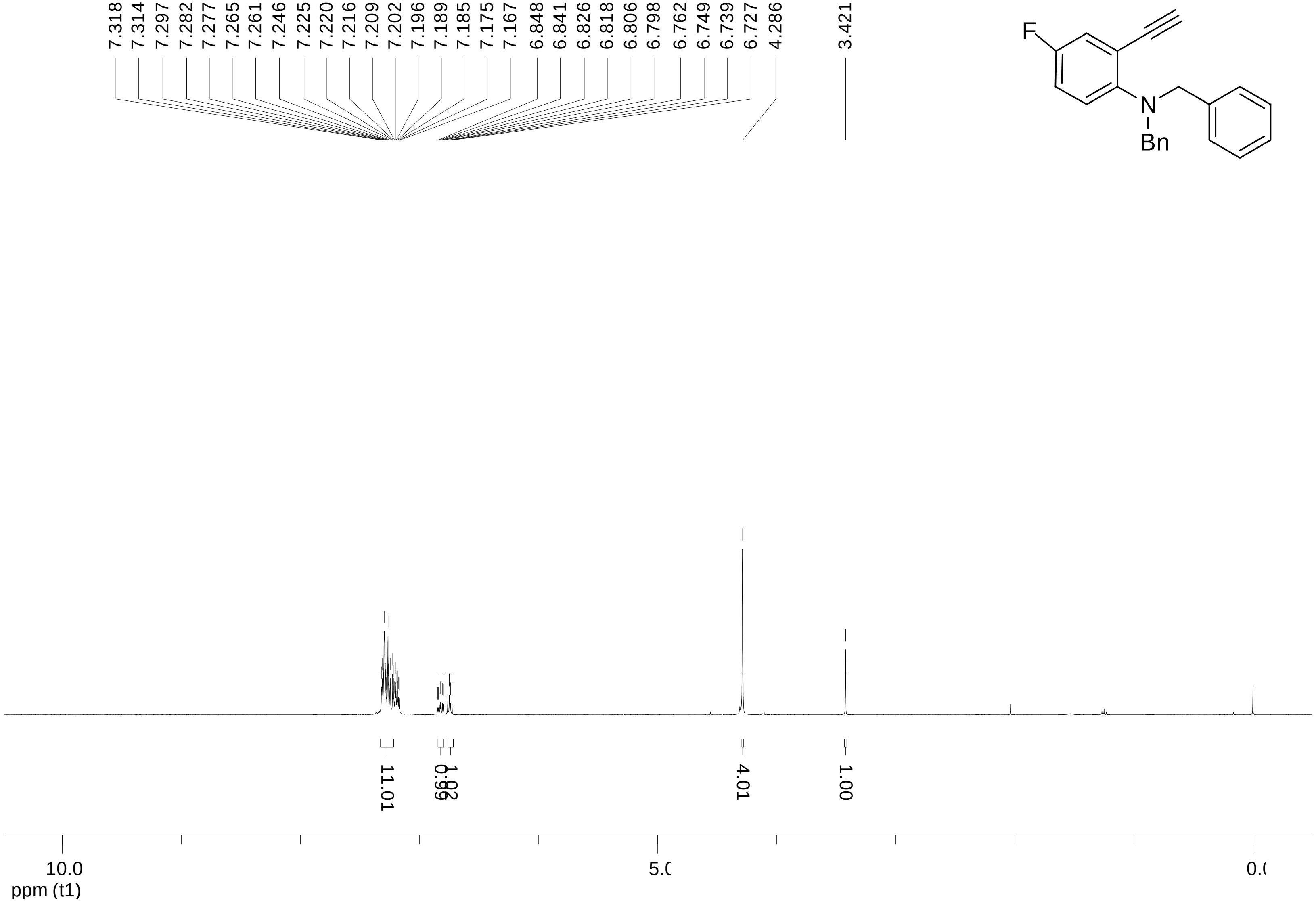
^{1}H NMR spectrum of **1e** (400 MHz, $CDCl_3$)



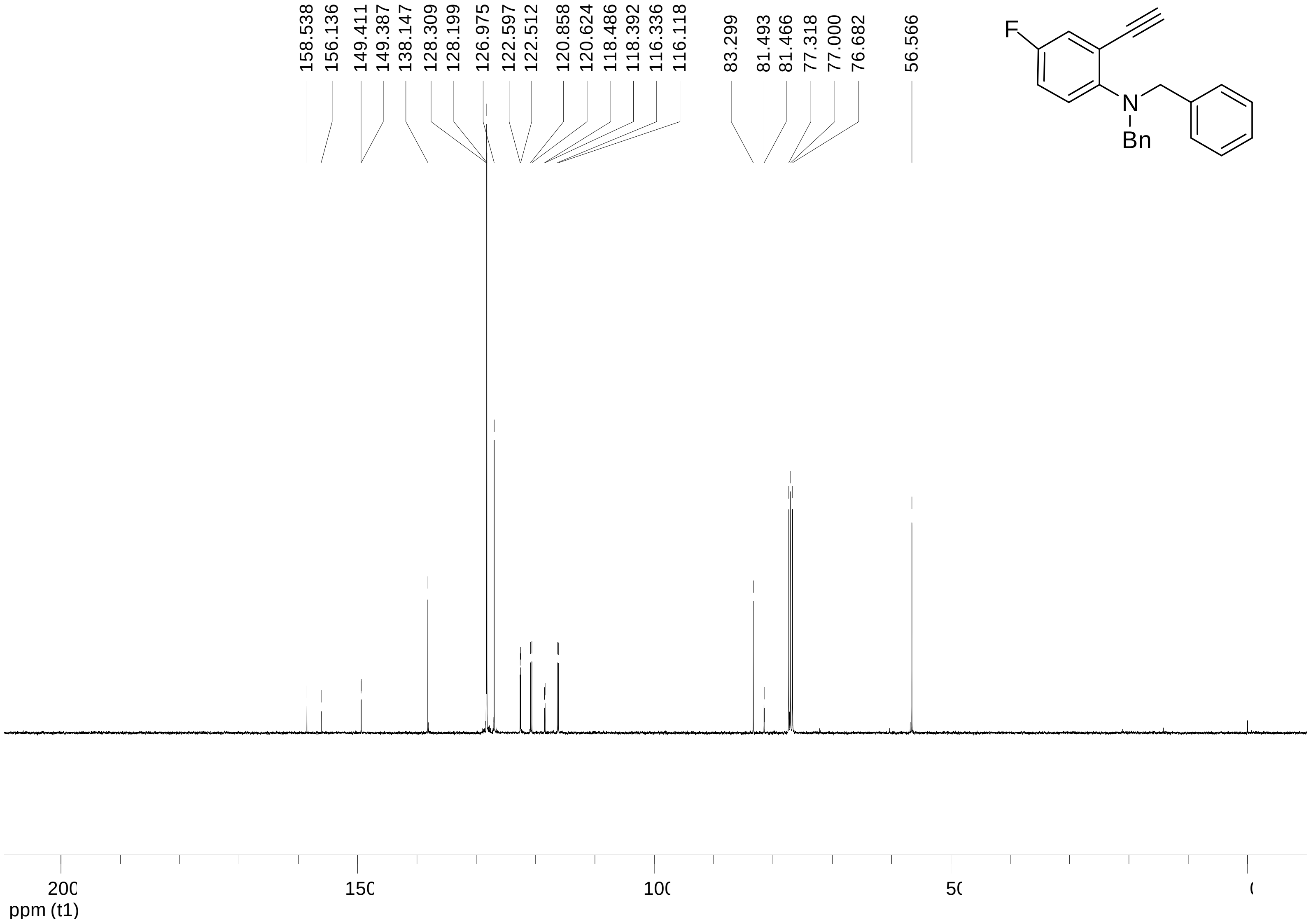
^{13}C NMR spectrum of **1e** (100 MHz, $CDCl_3$)



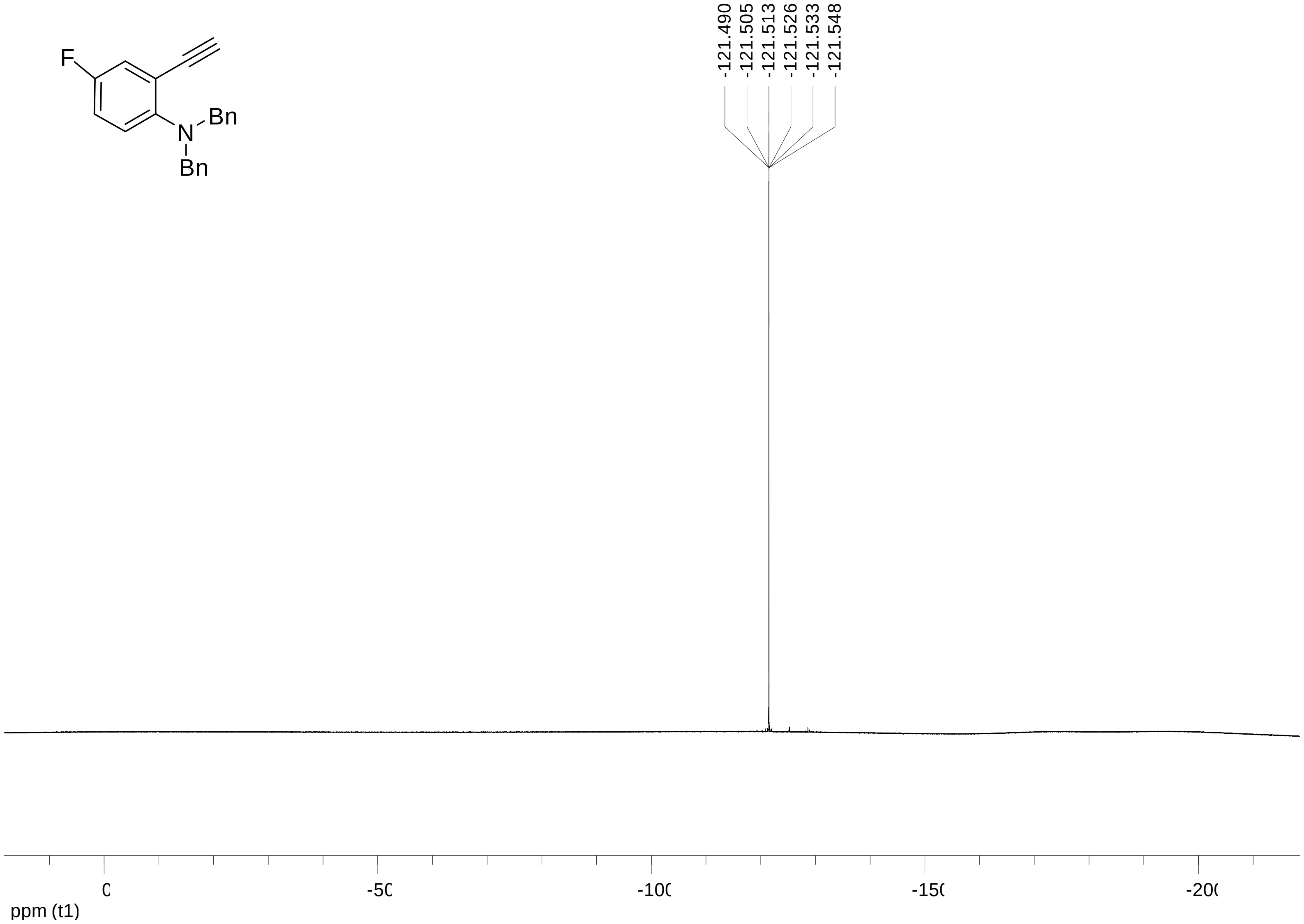
^{1}H NMR spectrum of **1f** (400 MHz, $CDCl_3$)



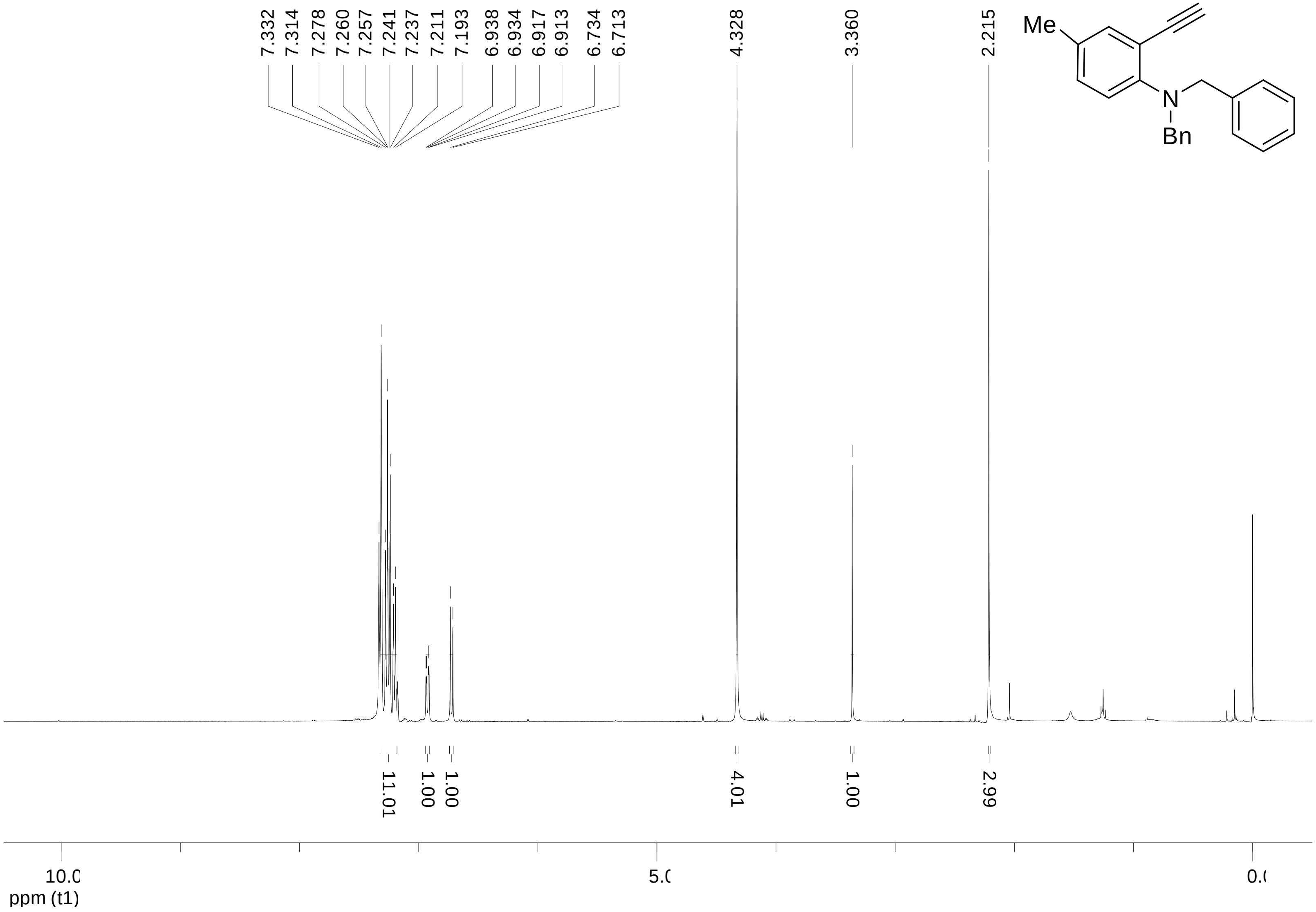
^{13}C NMR spectrum of **1f** (100 MHz, CDCl$_3$)



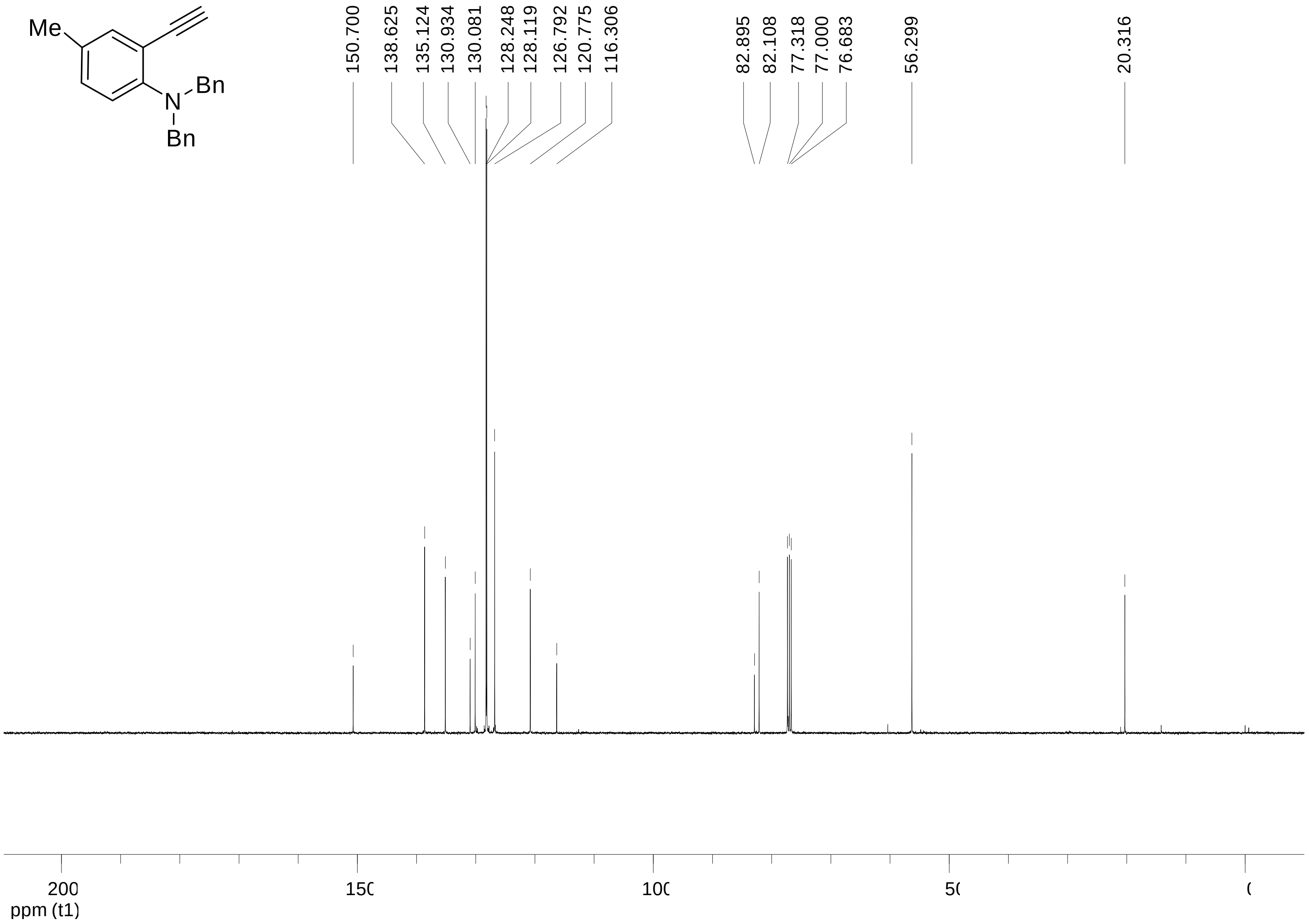
^{19}F NMR spectrum of **1f** (376 MHz, $CDCl_3$)



^{1}H NMR spectrum of **1g** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of **1g** (100 MHz, $CDCl_3$)



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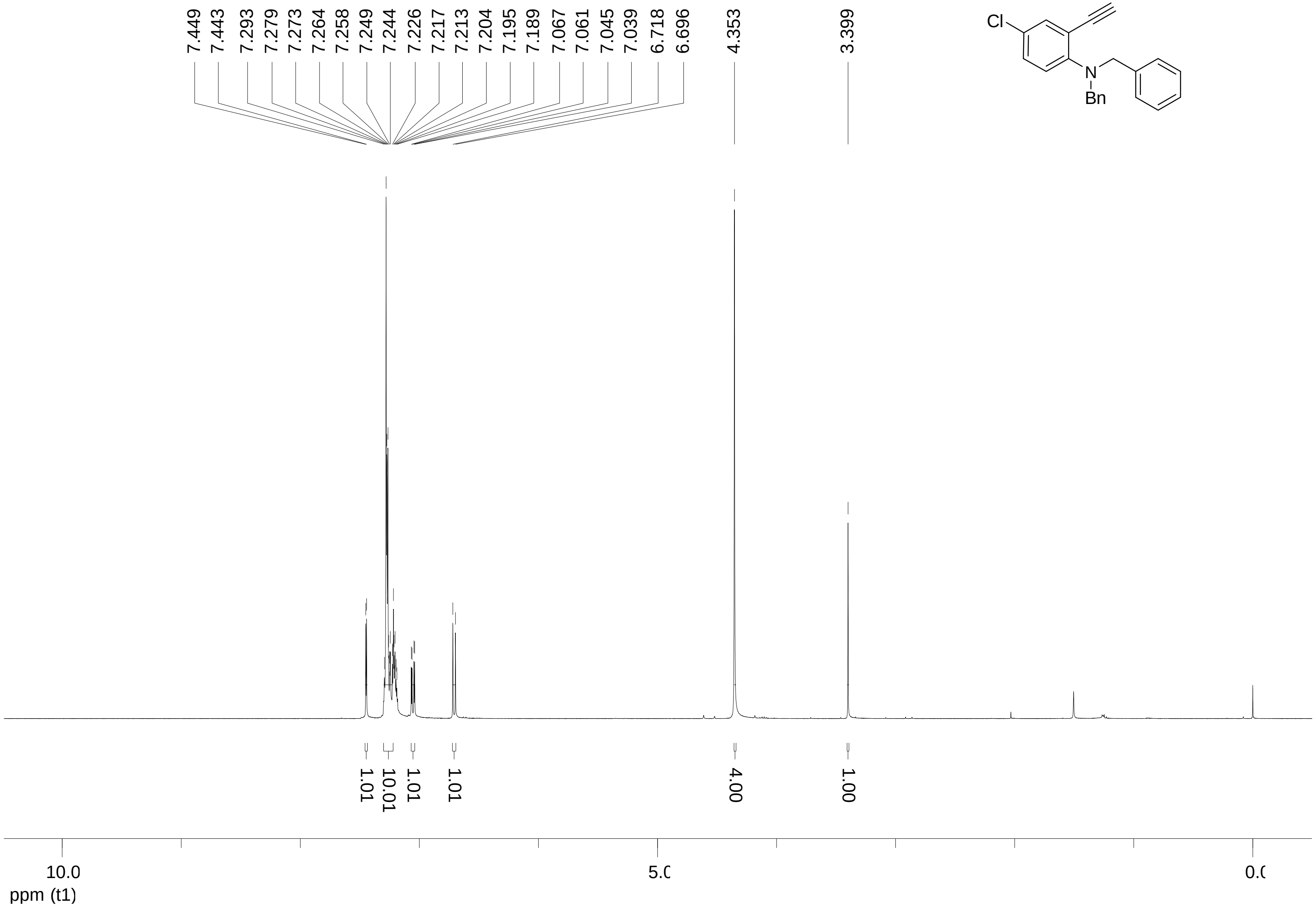
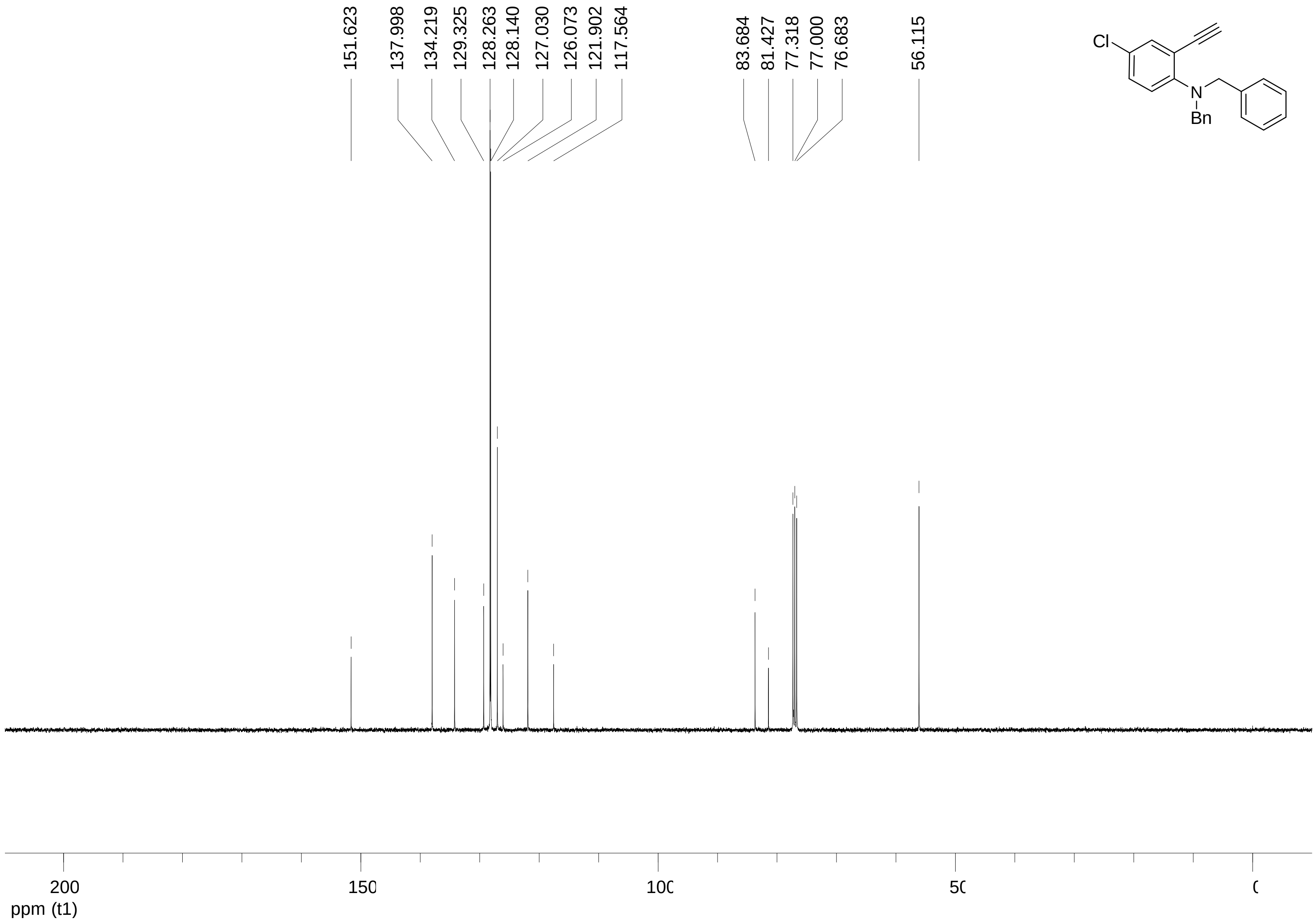
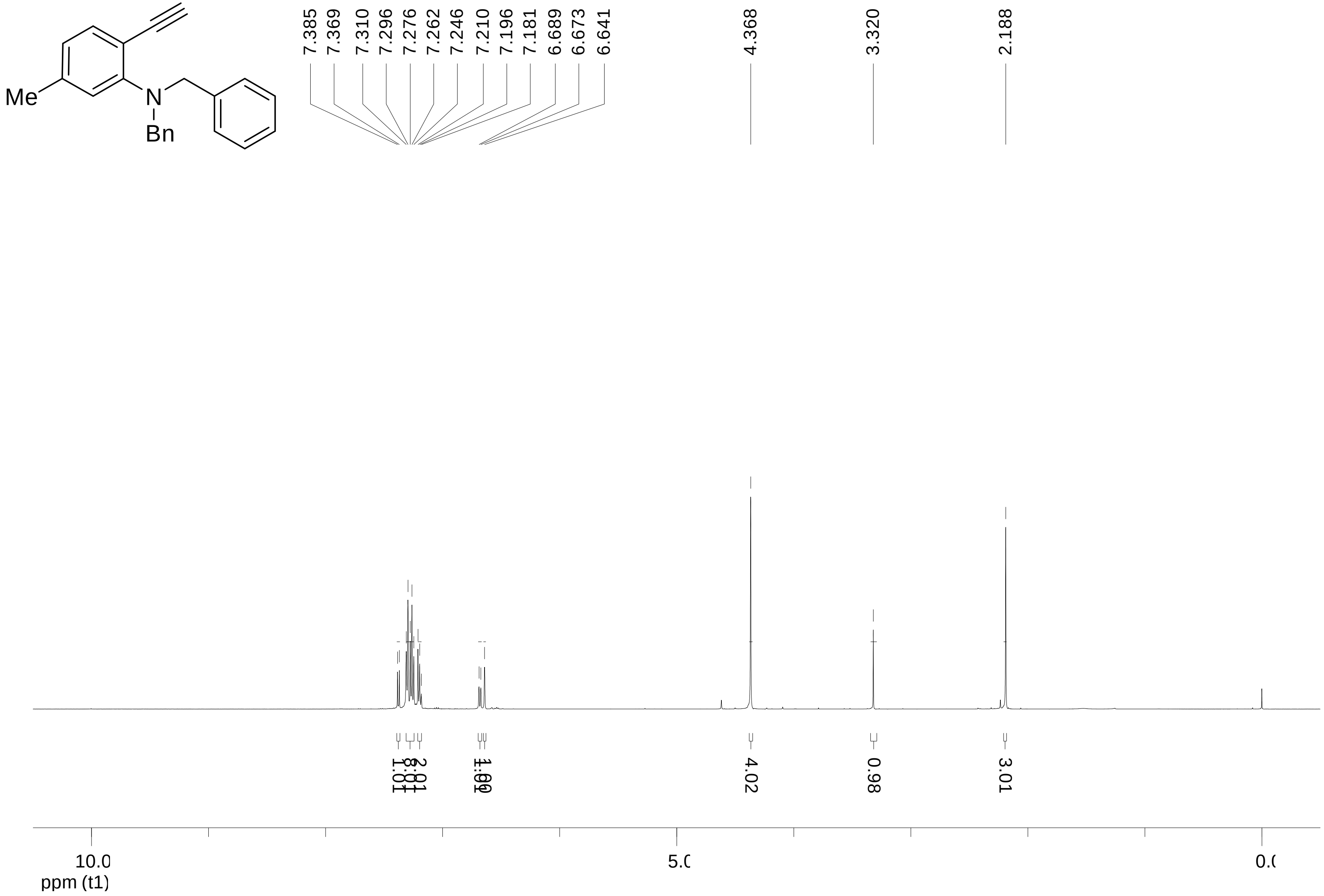


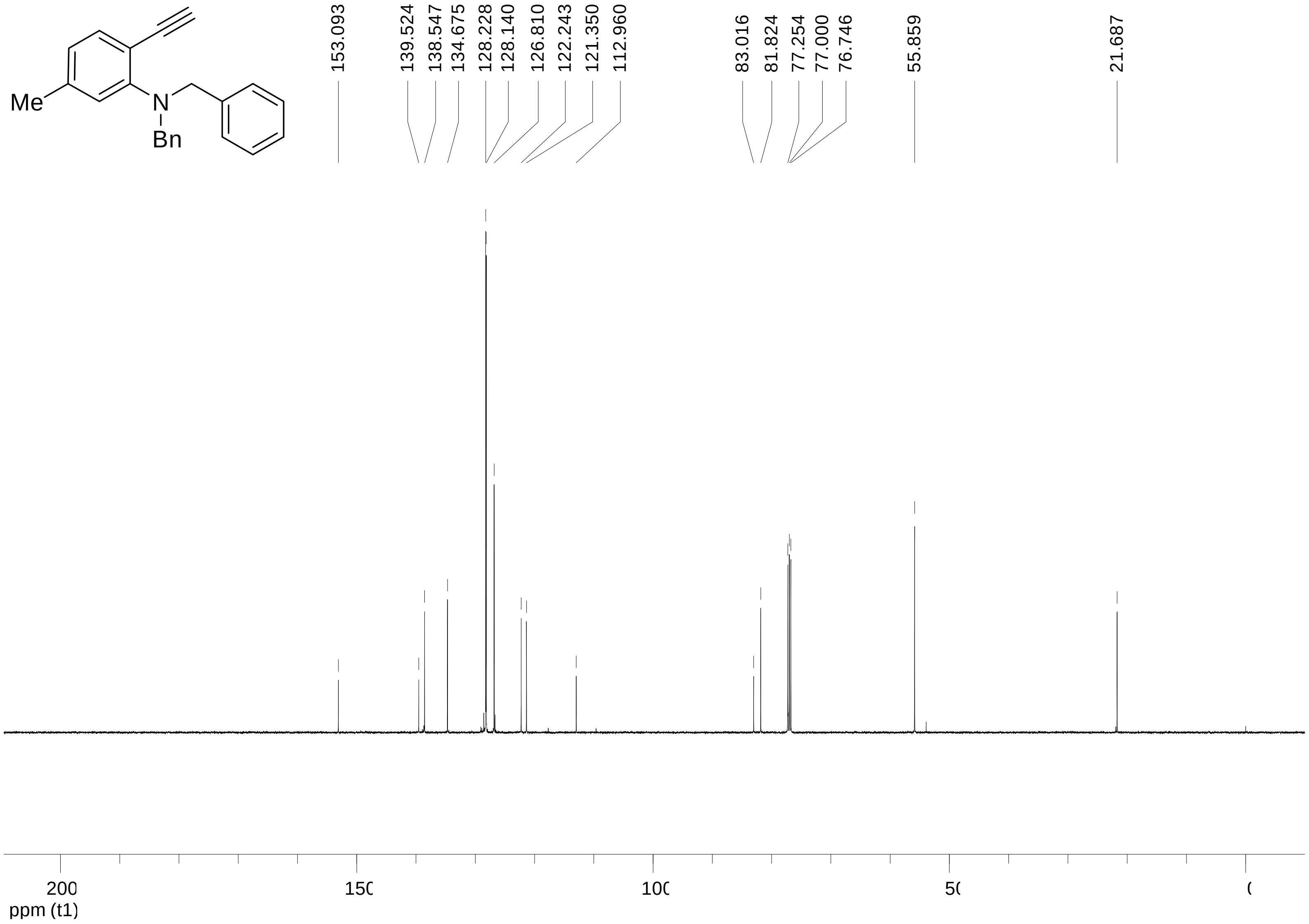
^{13}C NMR spectrum of **1h** (100 MHz, $CDCl_3$)



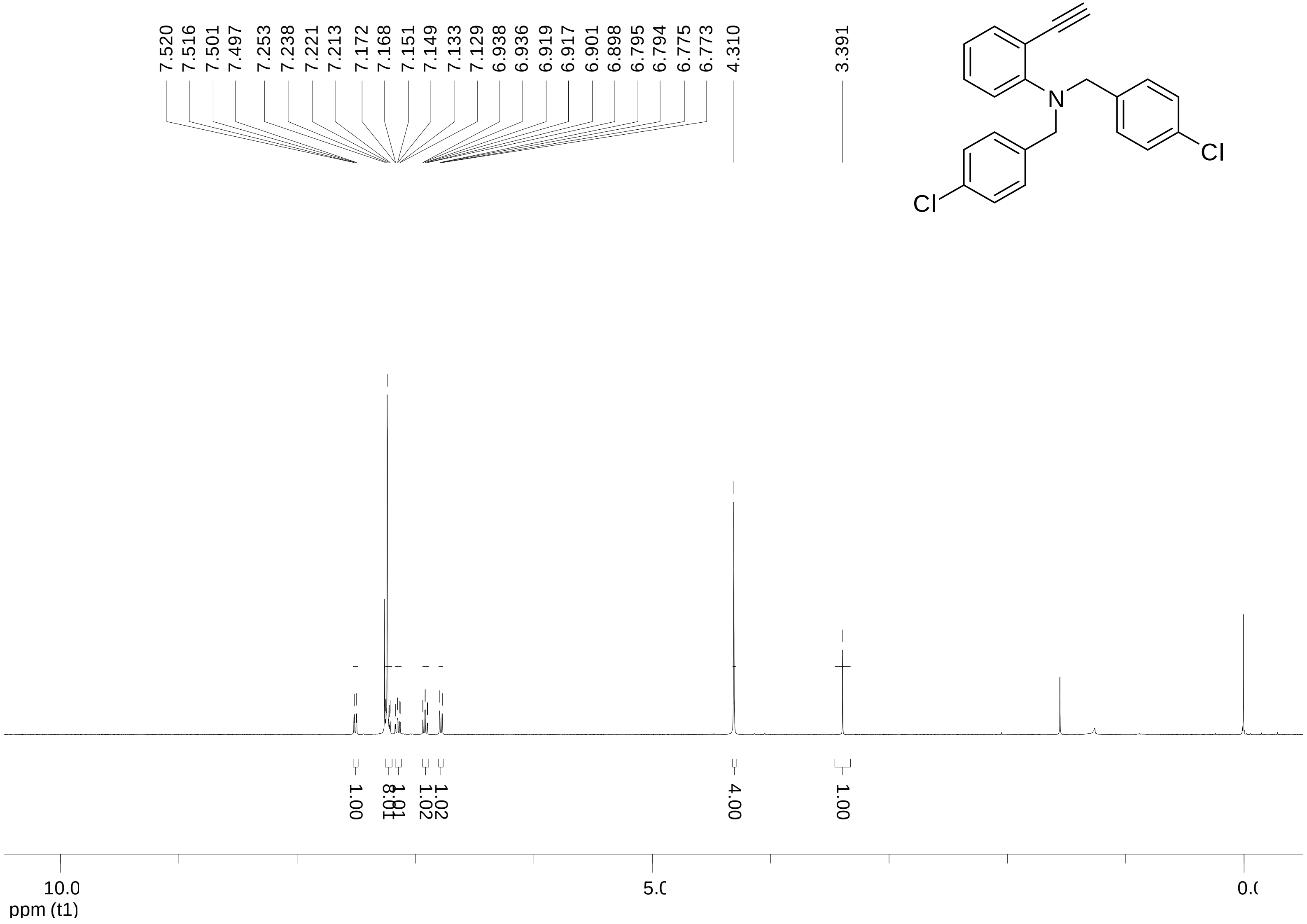
^{1}H NMR spectrum of **1i** (500 MHz, $CDCl_3$)



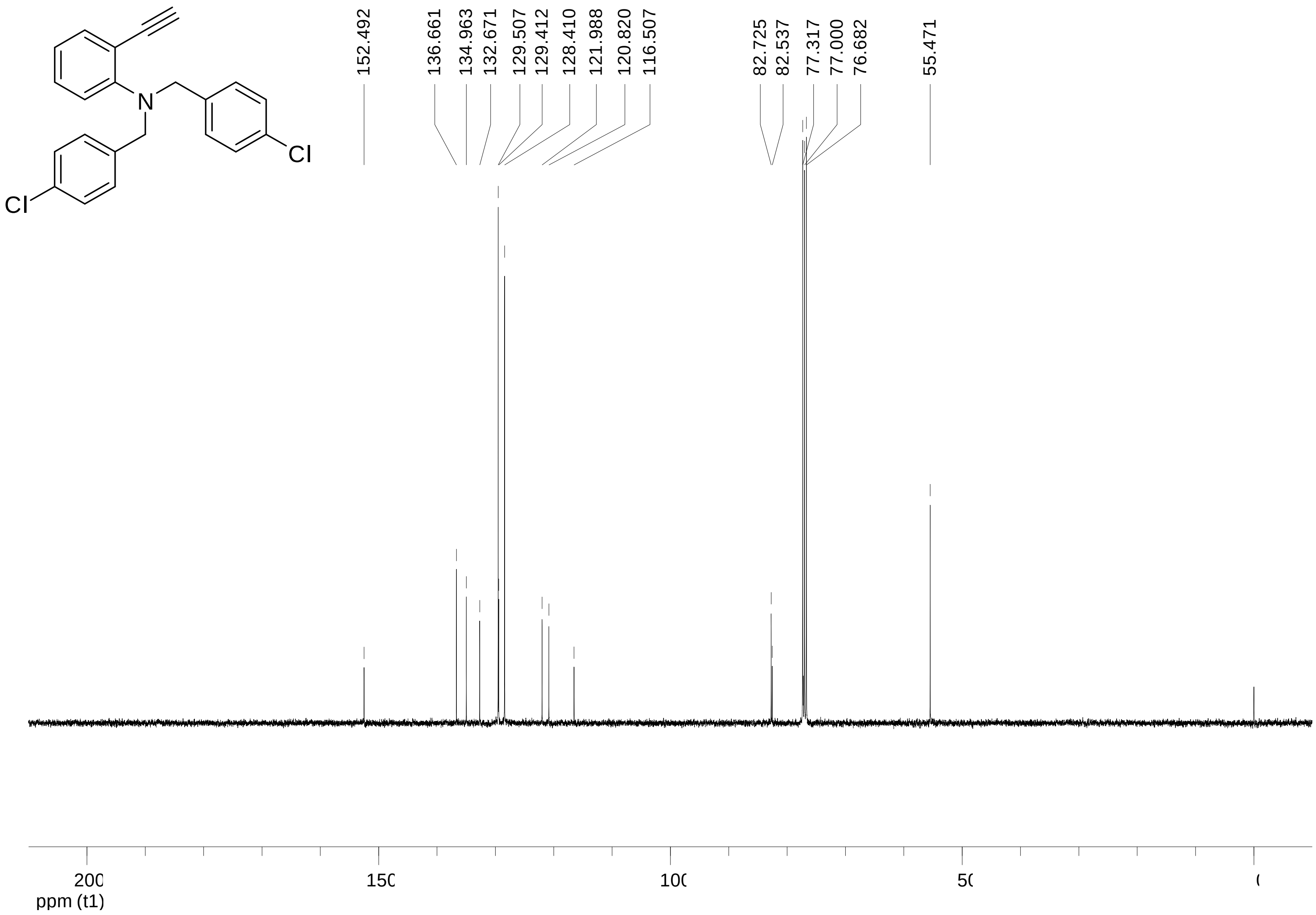
^{13}C NMR spectrum of **1i** (125 MHz, $CDCl_3$)



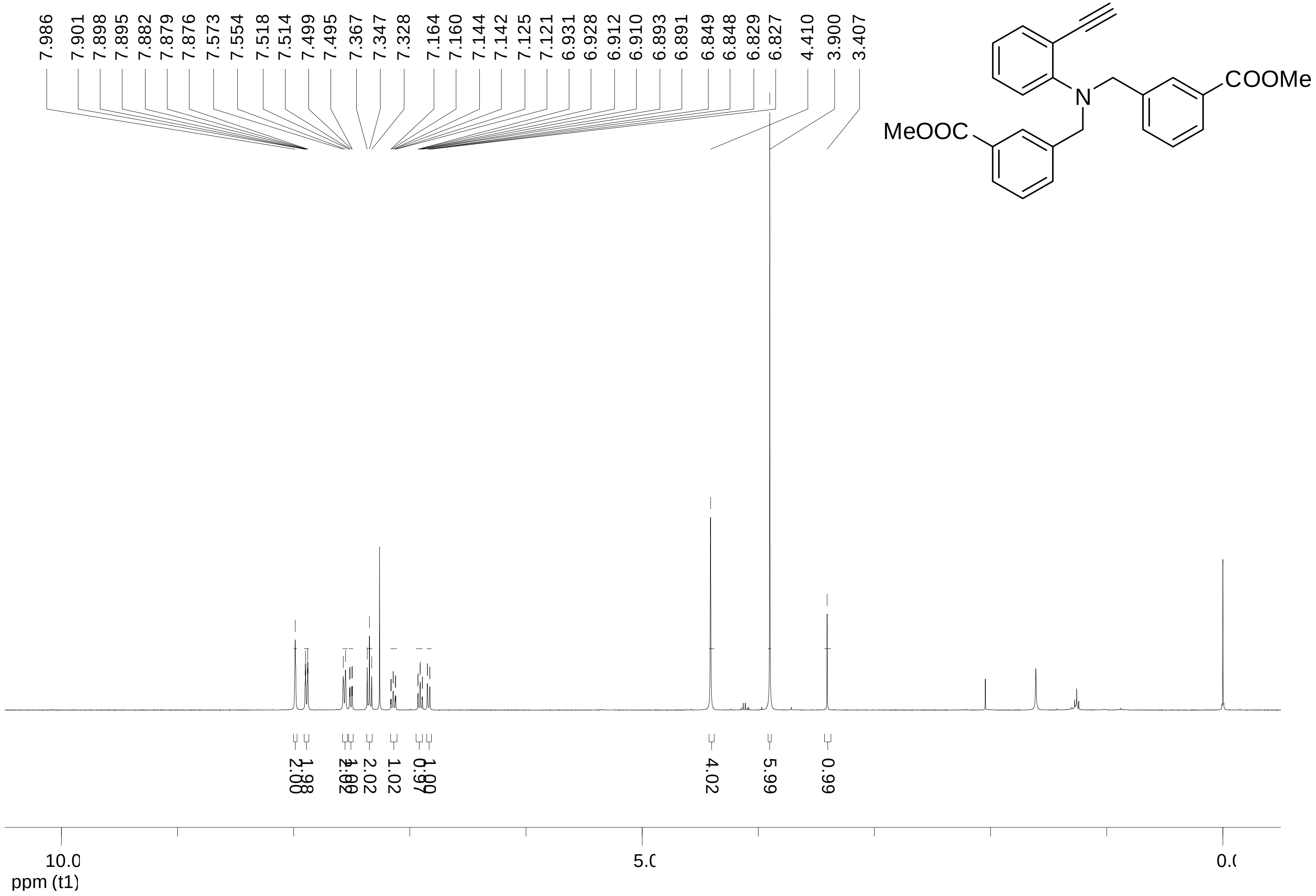
^{1}H NMR spectrum of **1j** (400 MHz, $CDCl_3$)



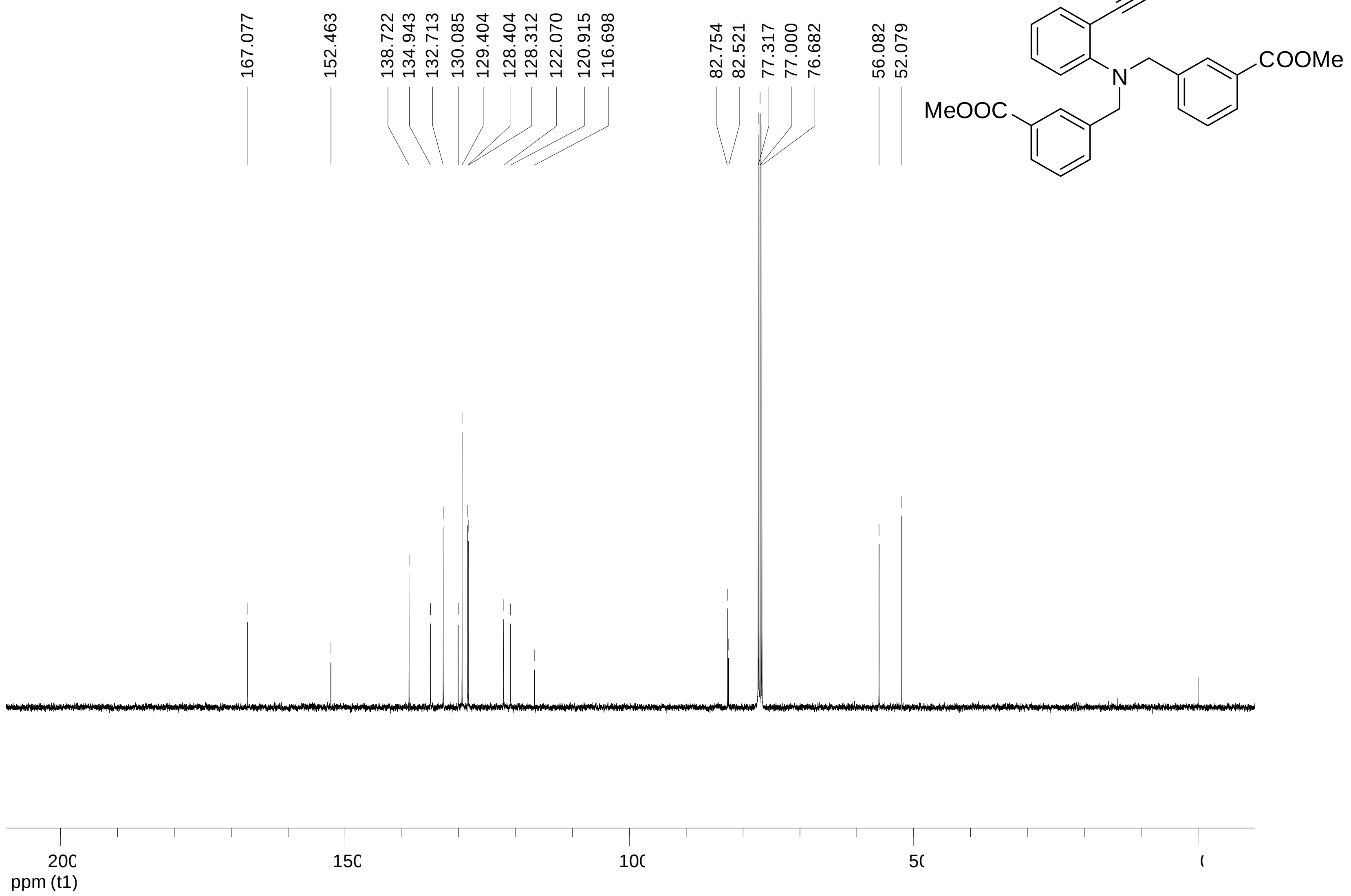
^{13}C NMR spectrum of **1j** (100 MHz, CDCl$_3$)



^{1}H NMR spectrum of **1k** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of **1k** (100 MHz, $CDCl_3$)



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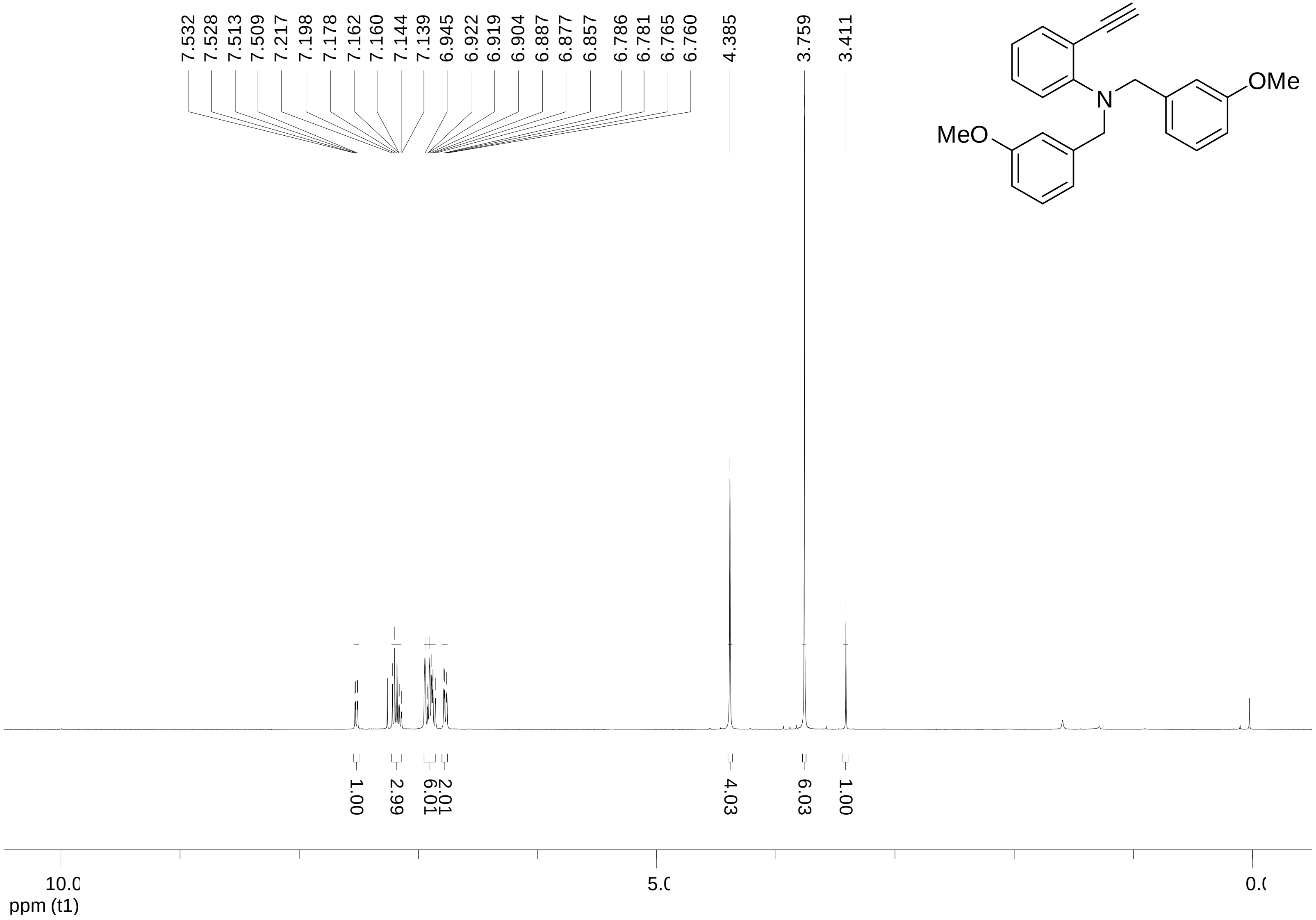
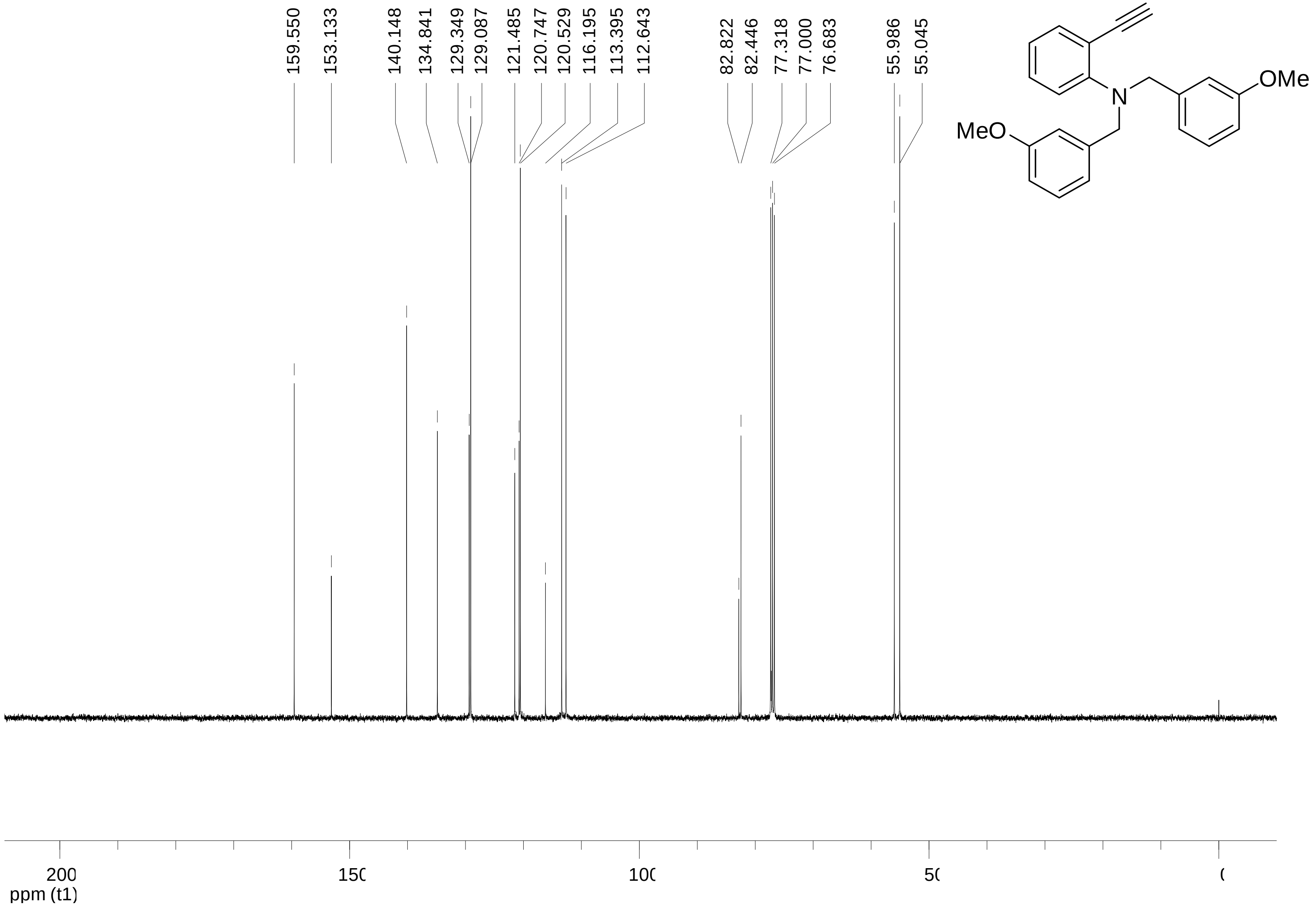
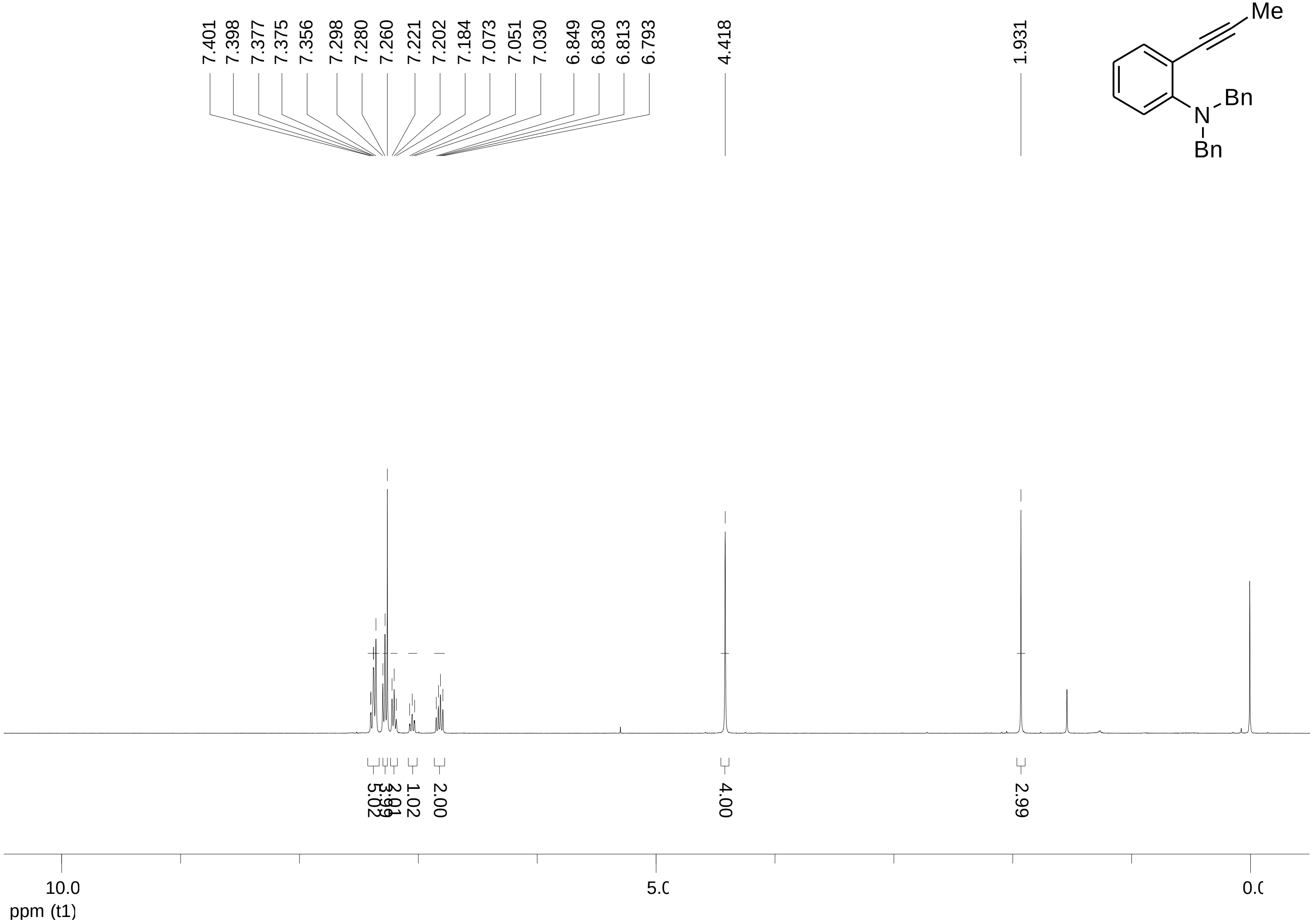


^{13}C NMR spectrum of **1l** (100 MHz, $CDCl_3$)



^{1}H NMR spectrum of **1ba** (400 MHz, $CDCl_3$)



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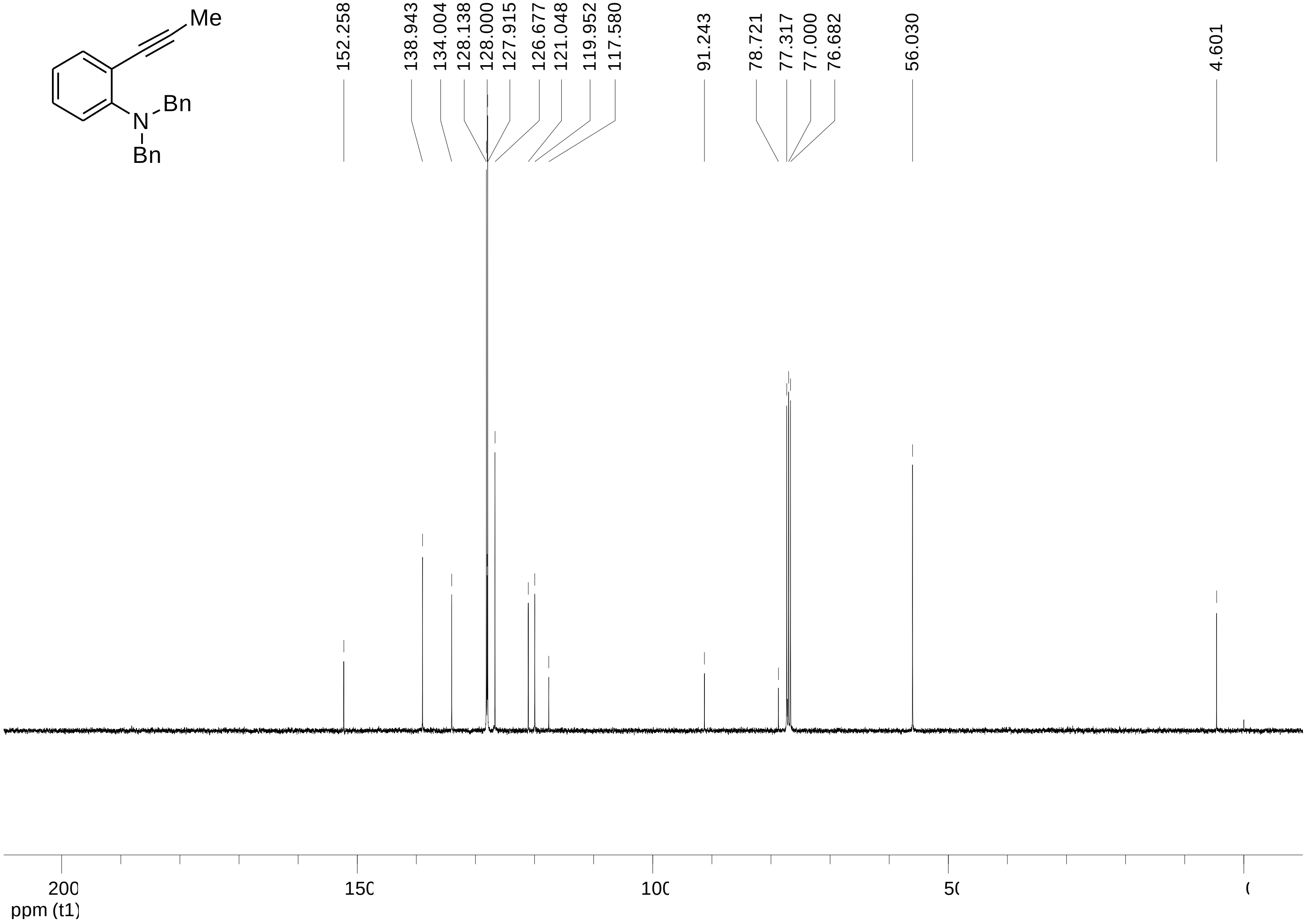

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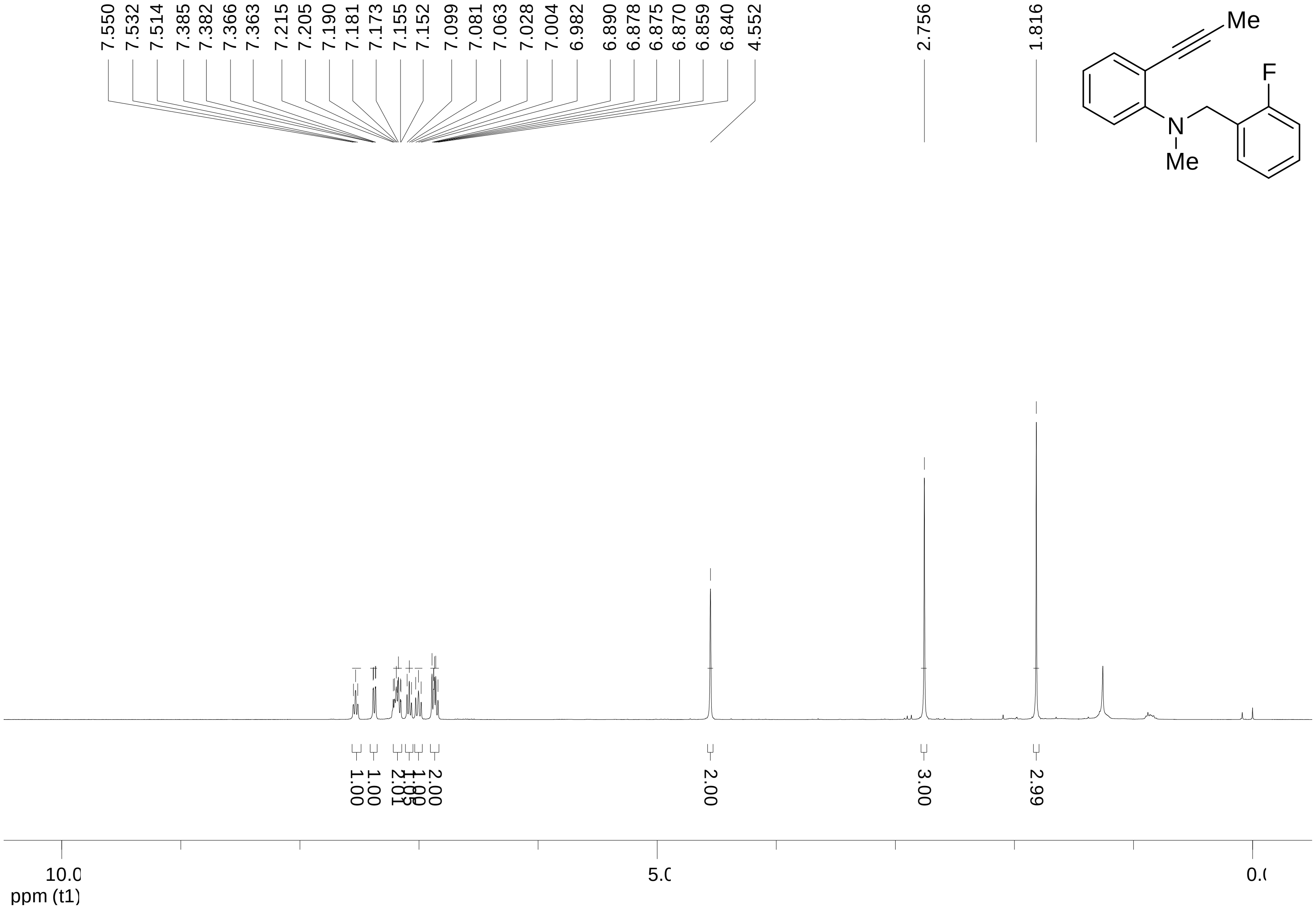

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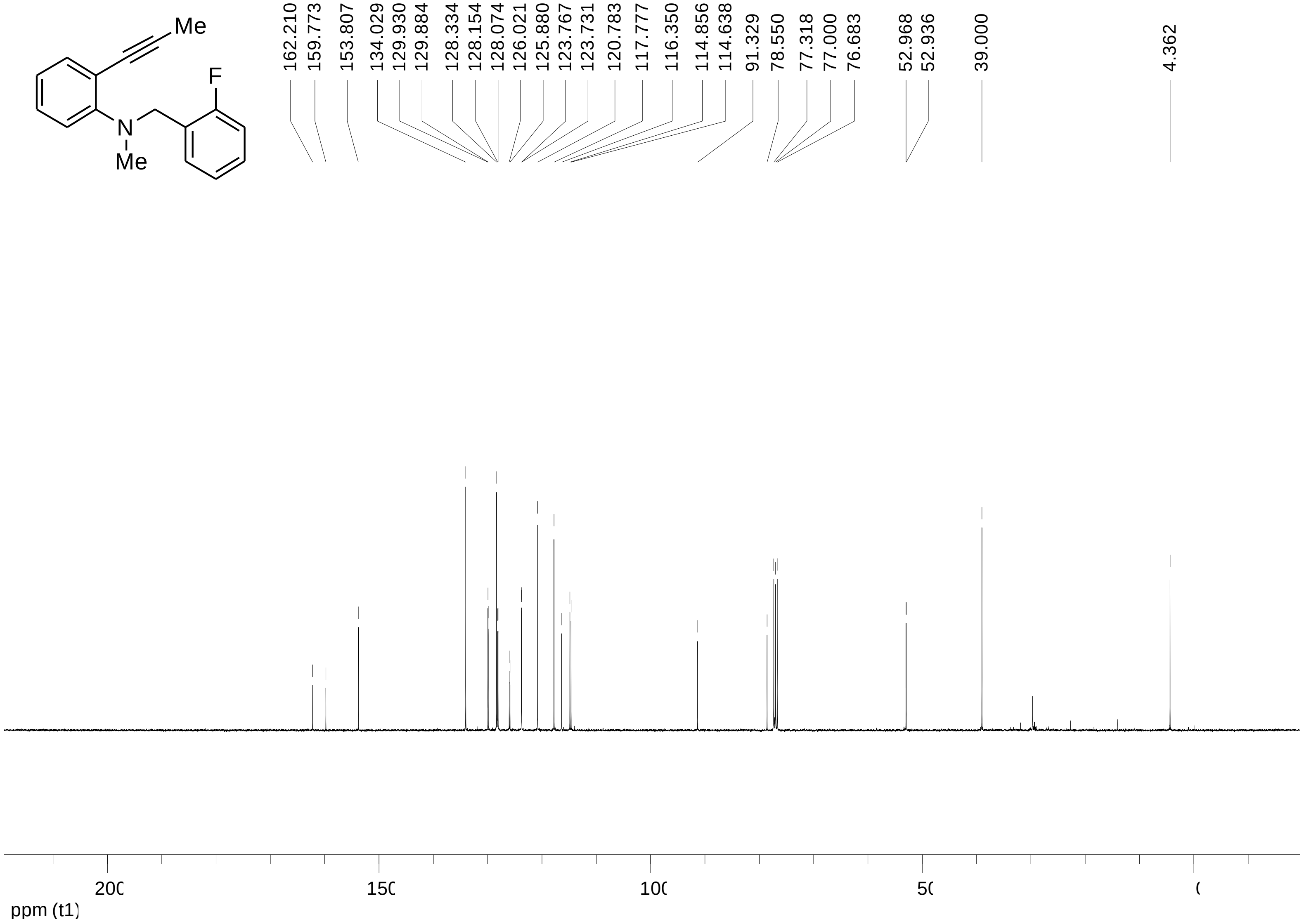
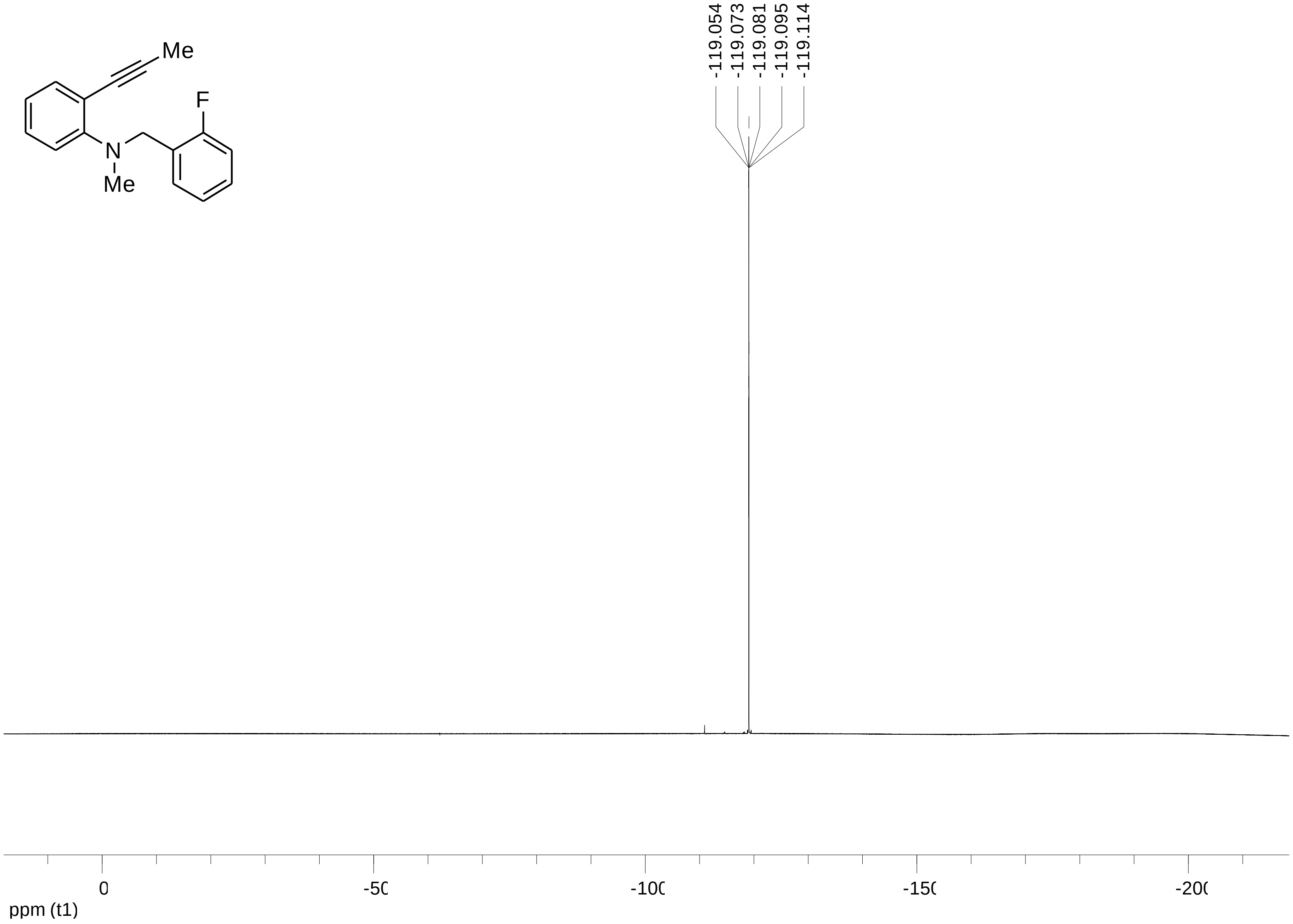


^{19}F NMR spectrum of **1bb** (376 MHz, $CDCl_3$)



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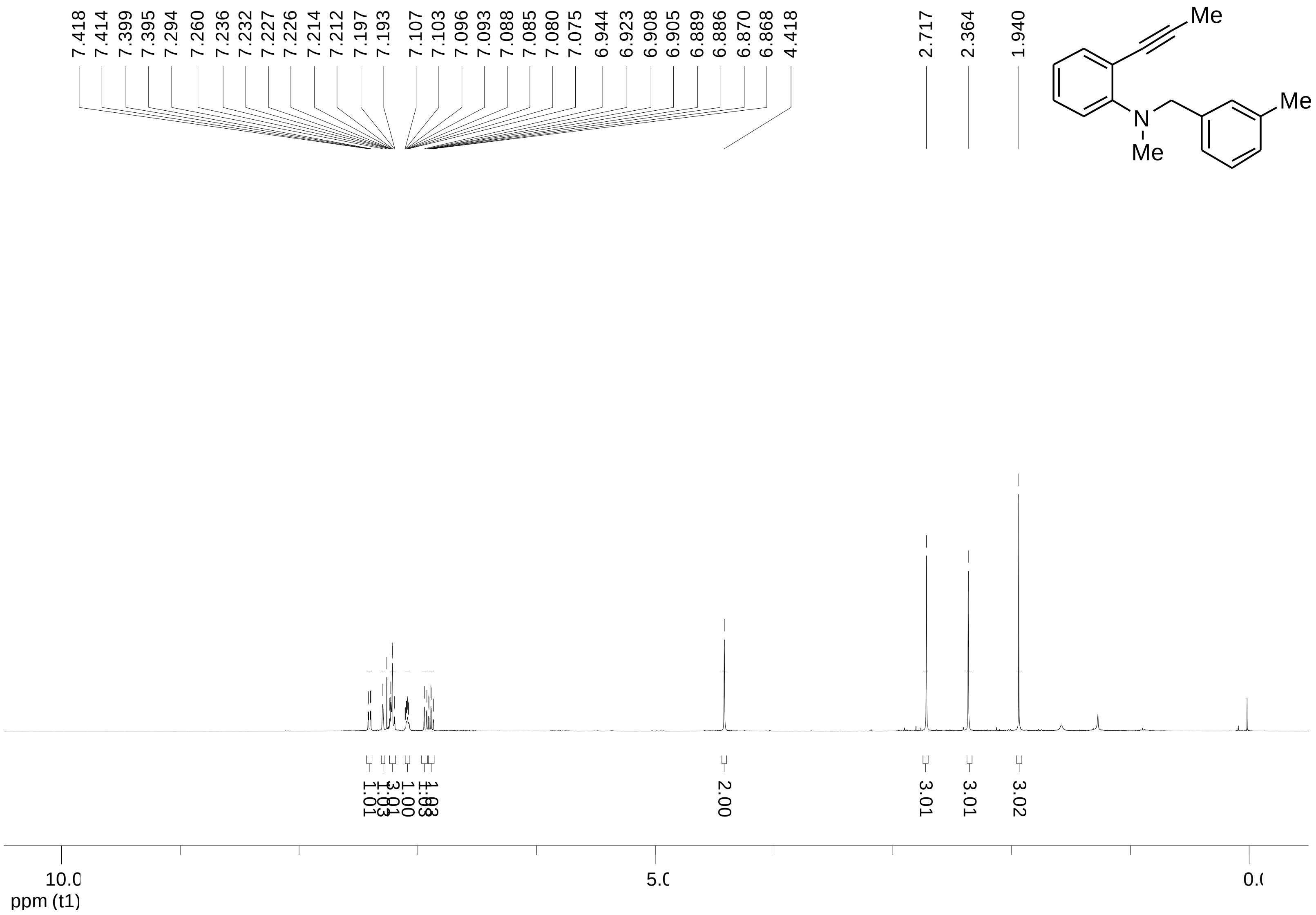
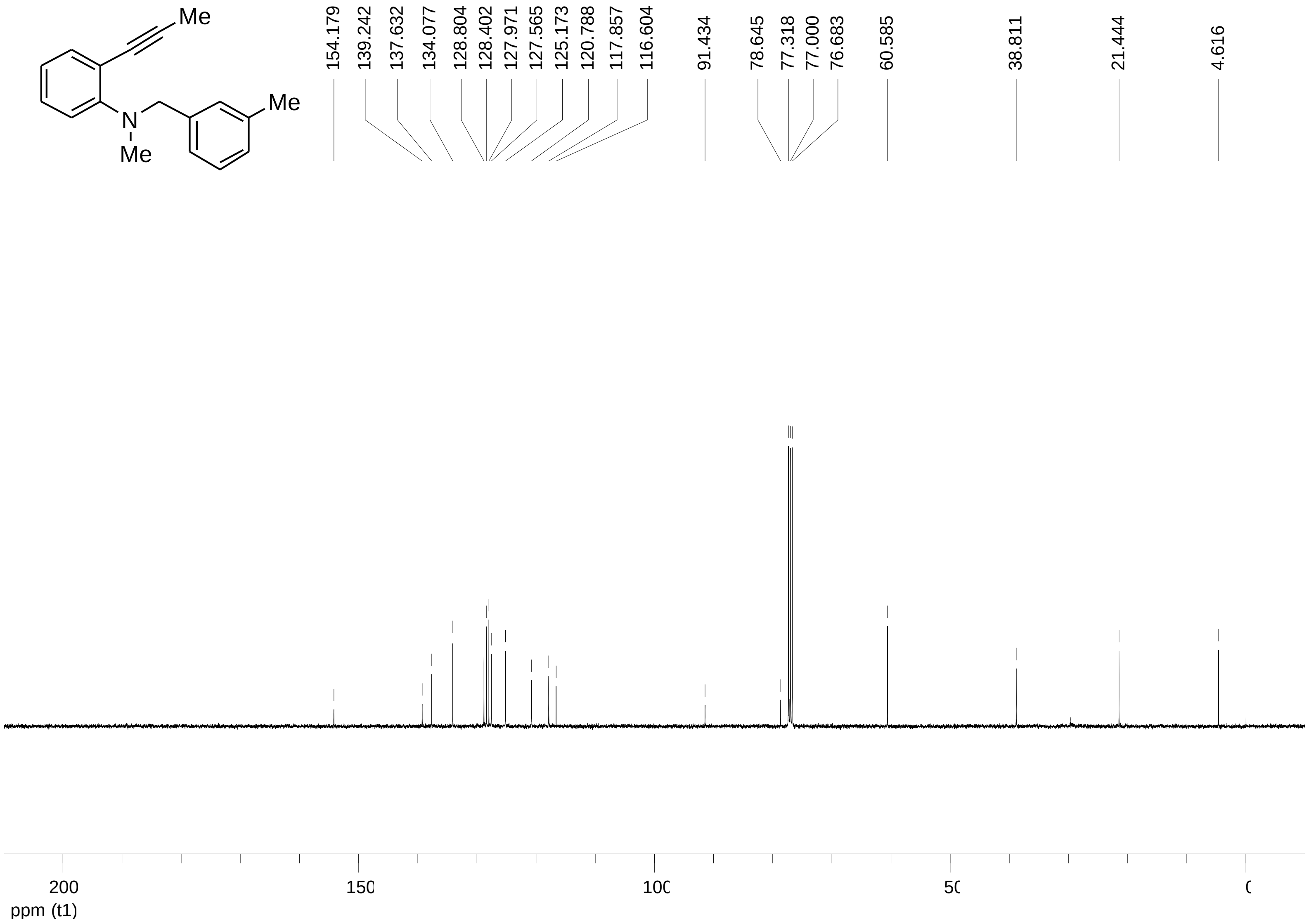


^{13}C NMR spectrum of **1bc** (125 MHz, $CDCl_3$)



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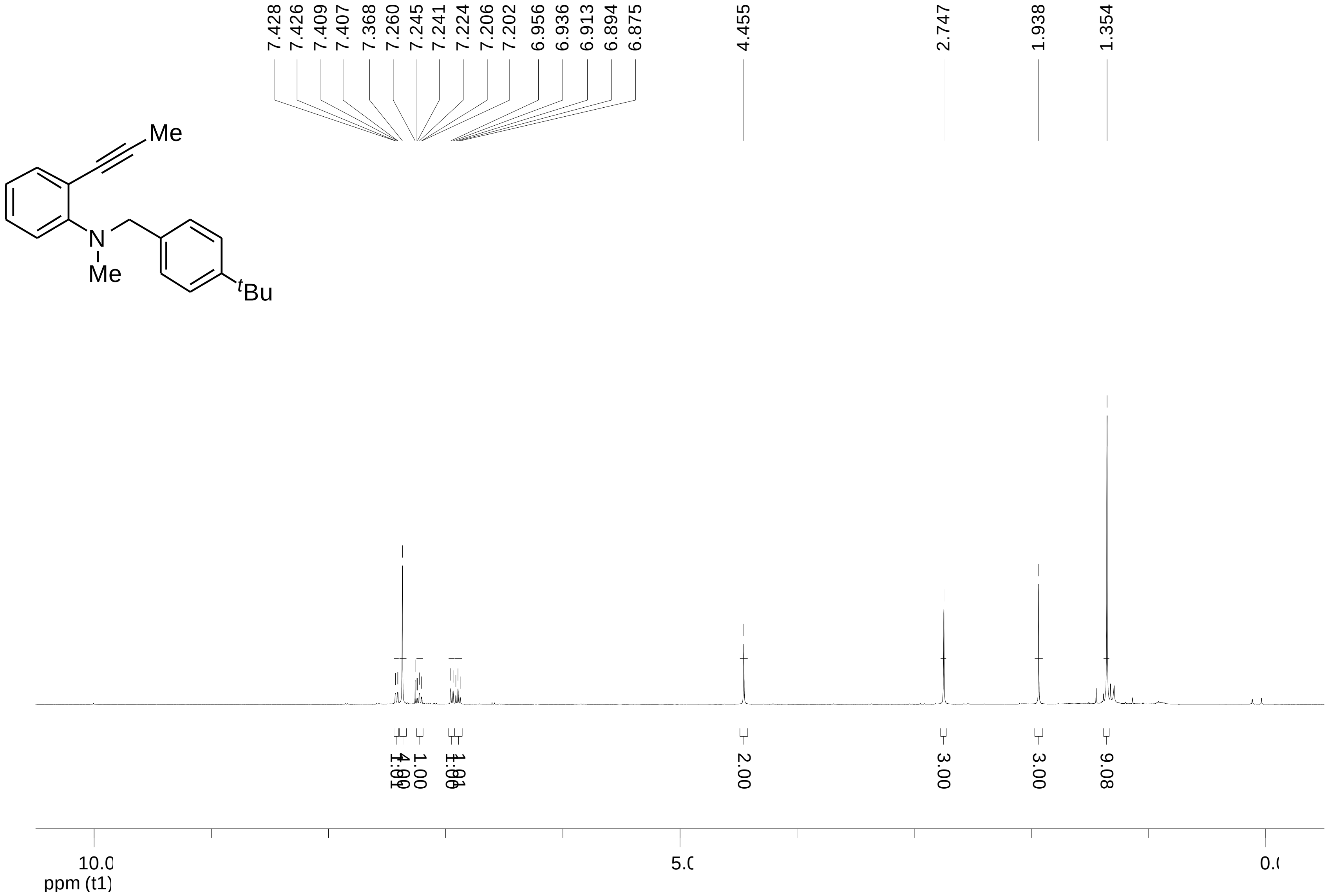

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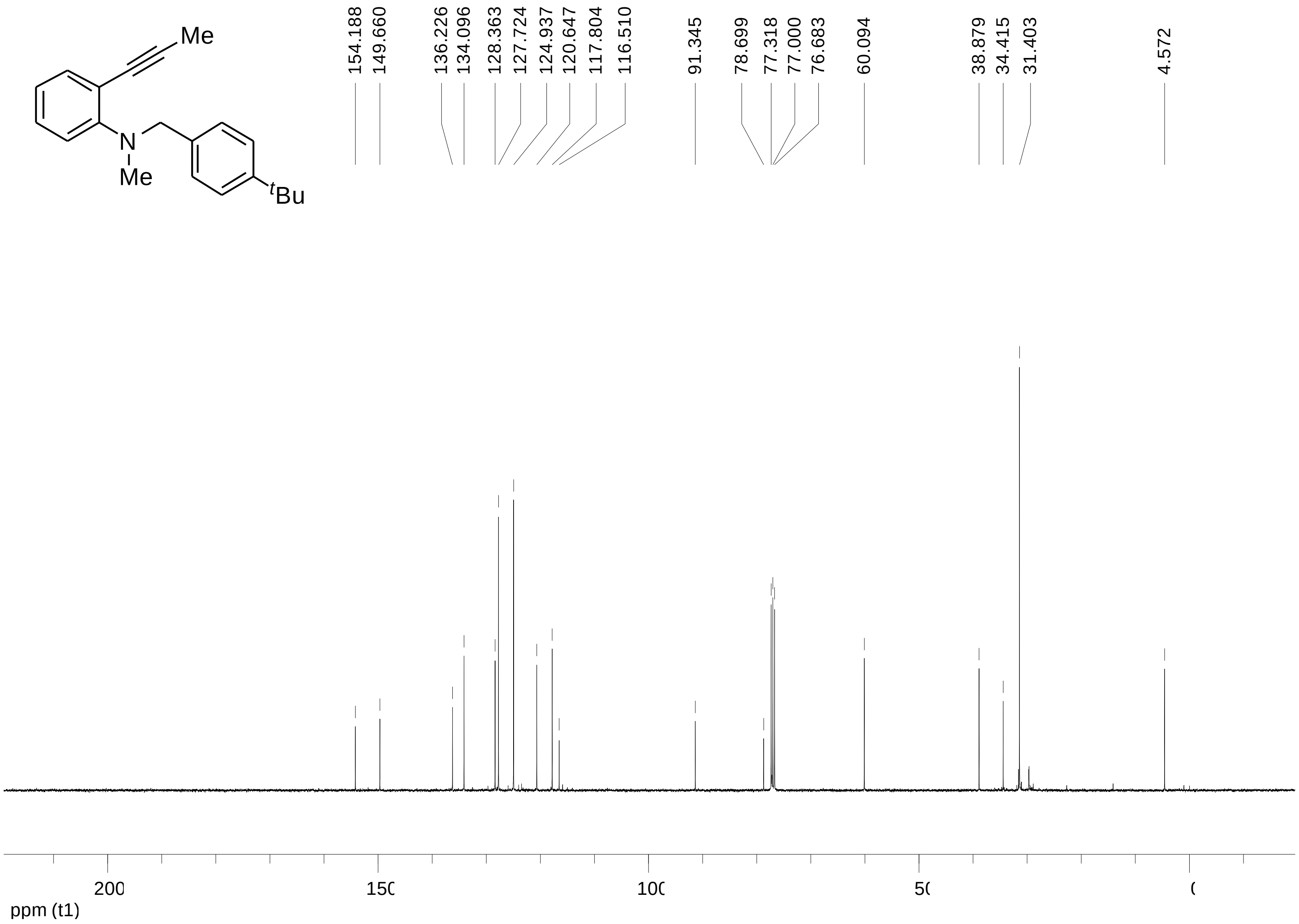

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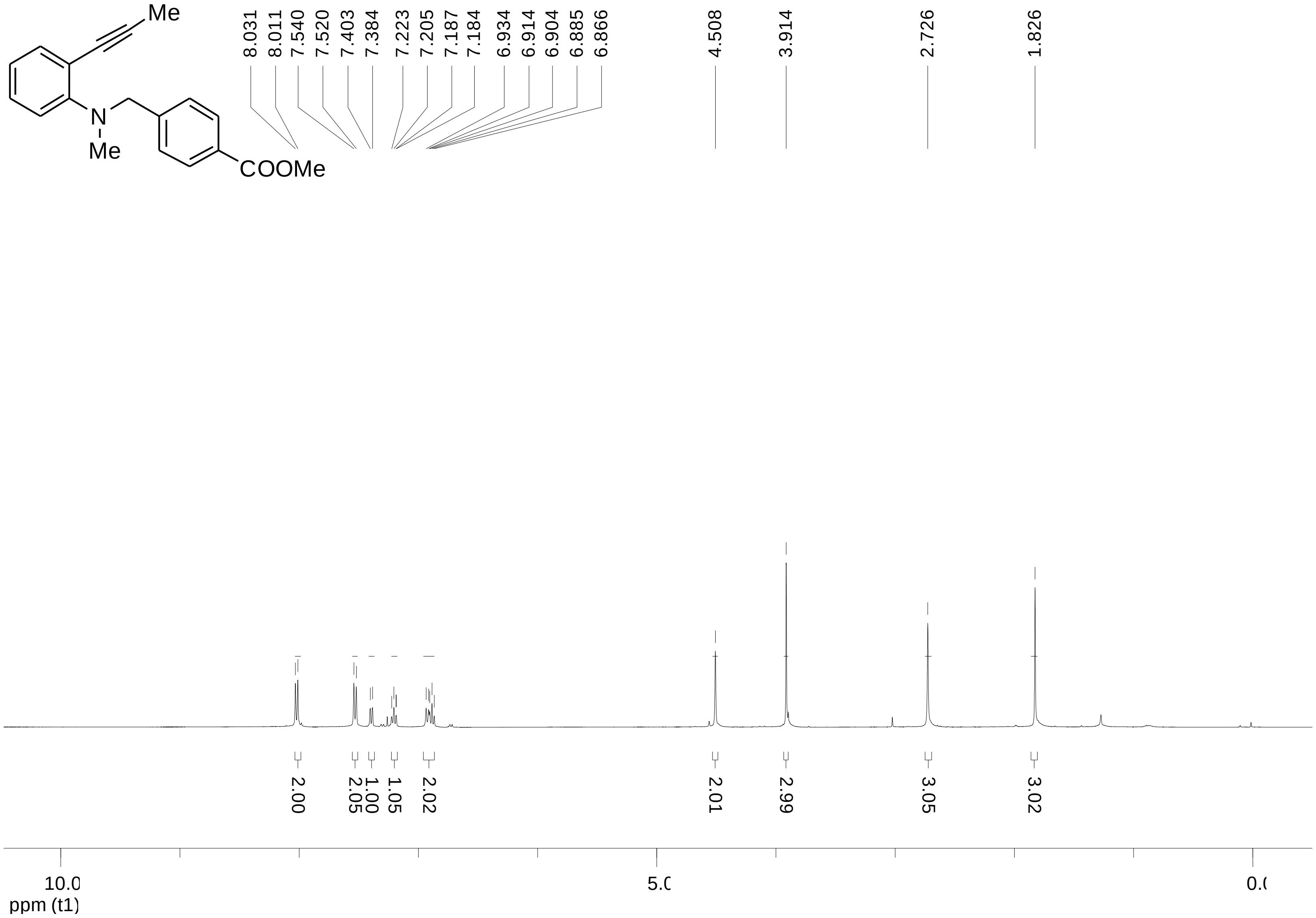

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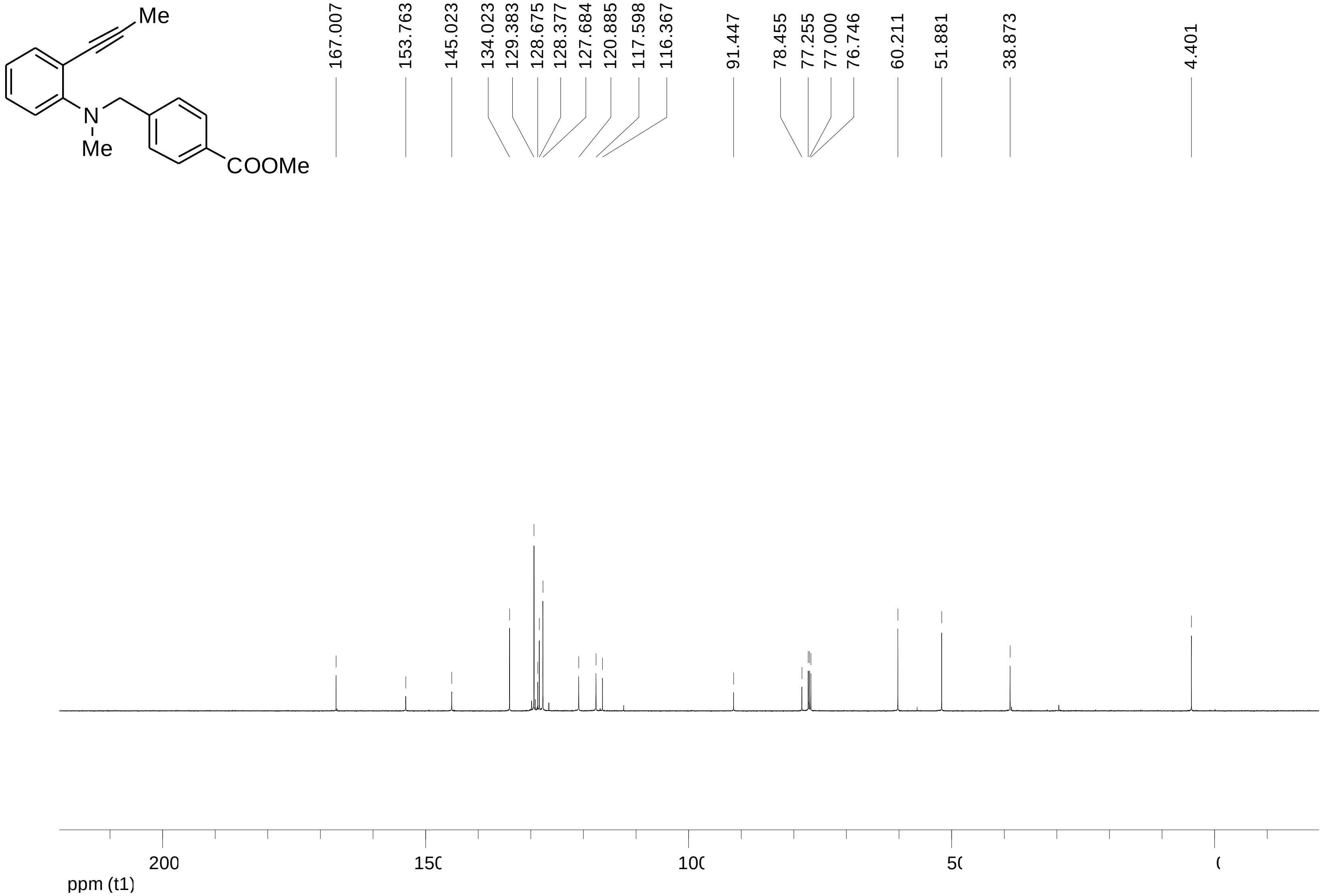

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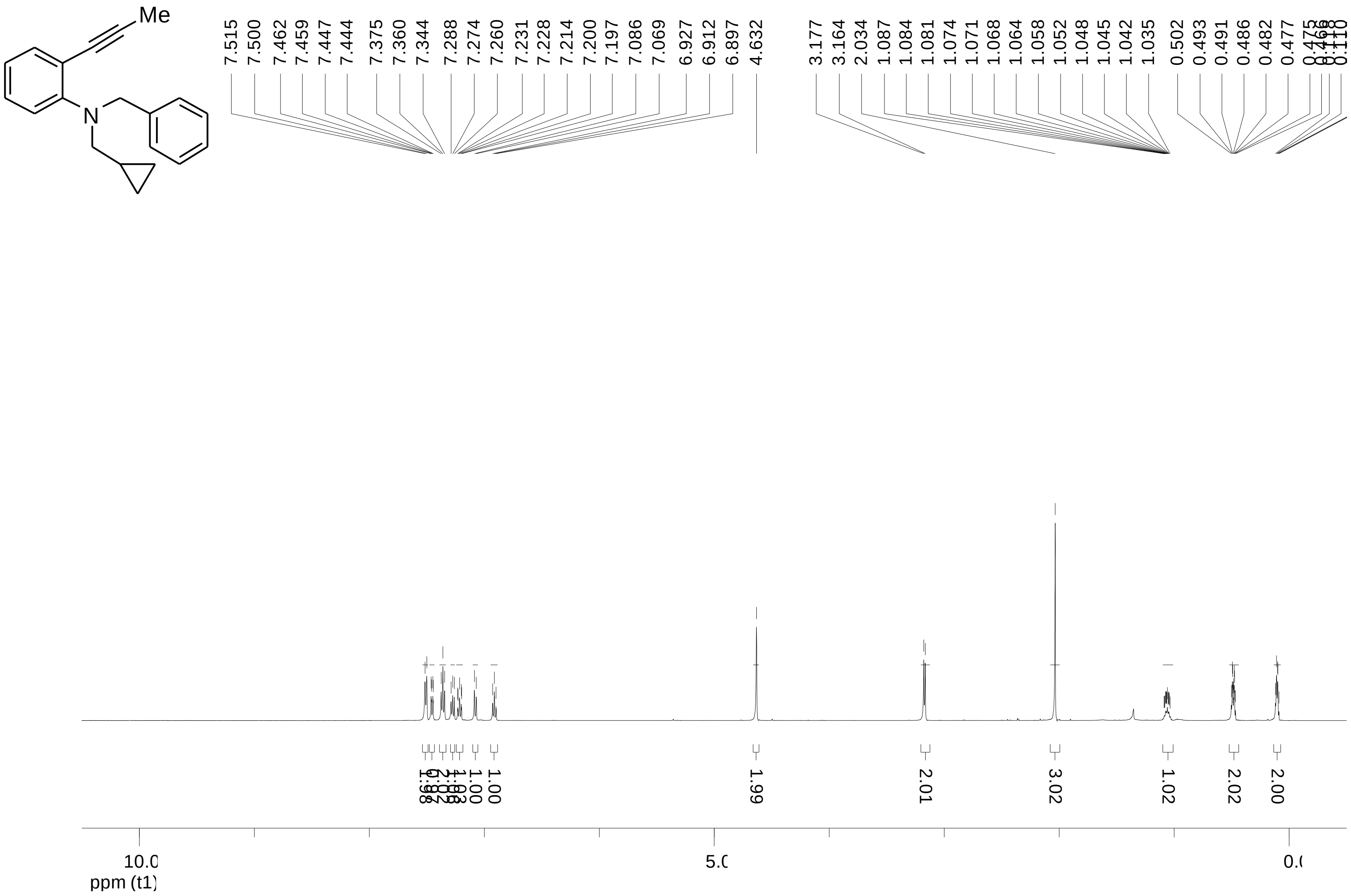
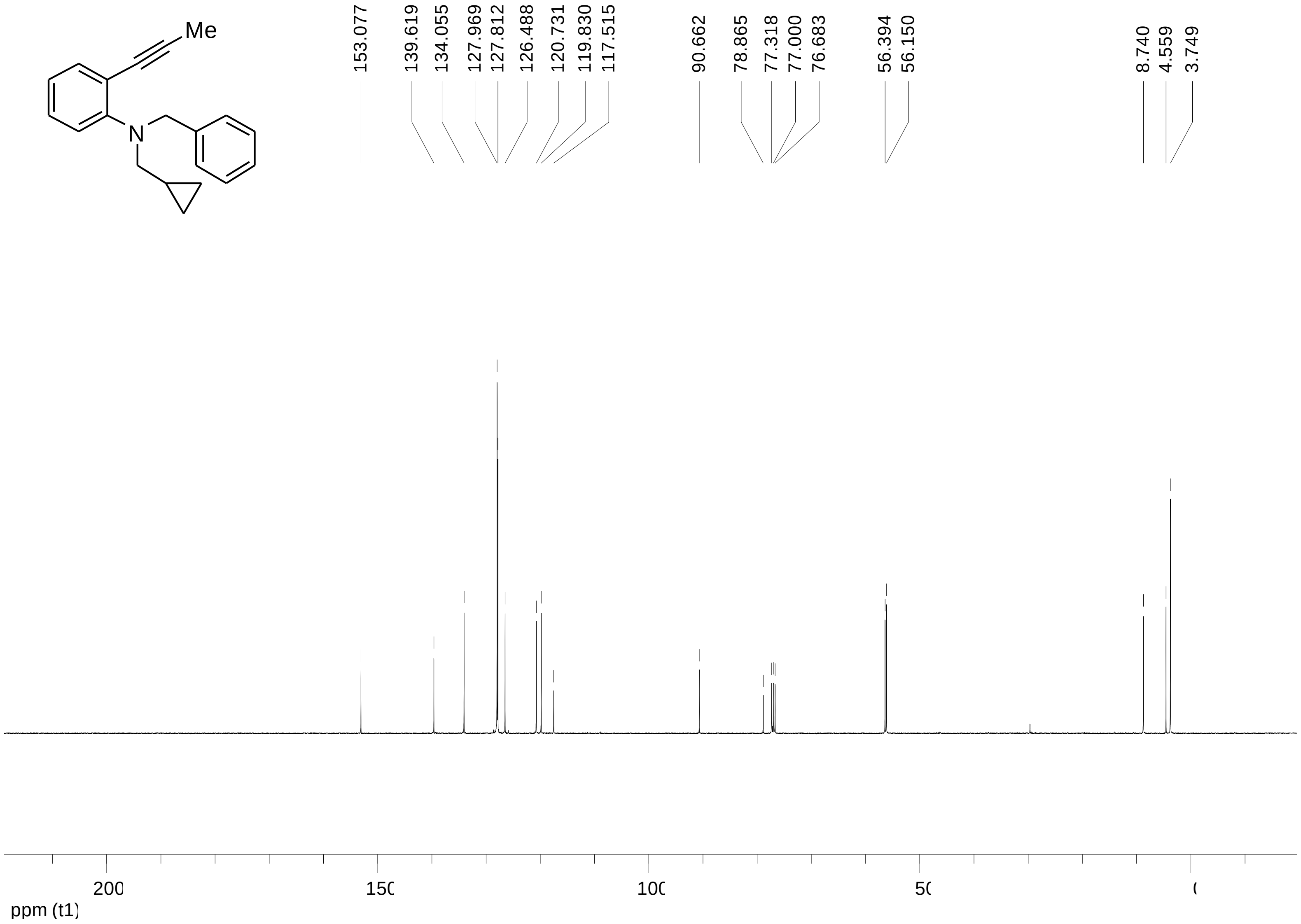


^{13}C NMR spectrum of **1bf** (125 MHz, $CDCl_3$)



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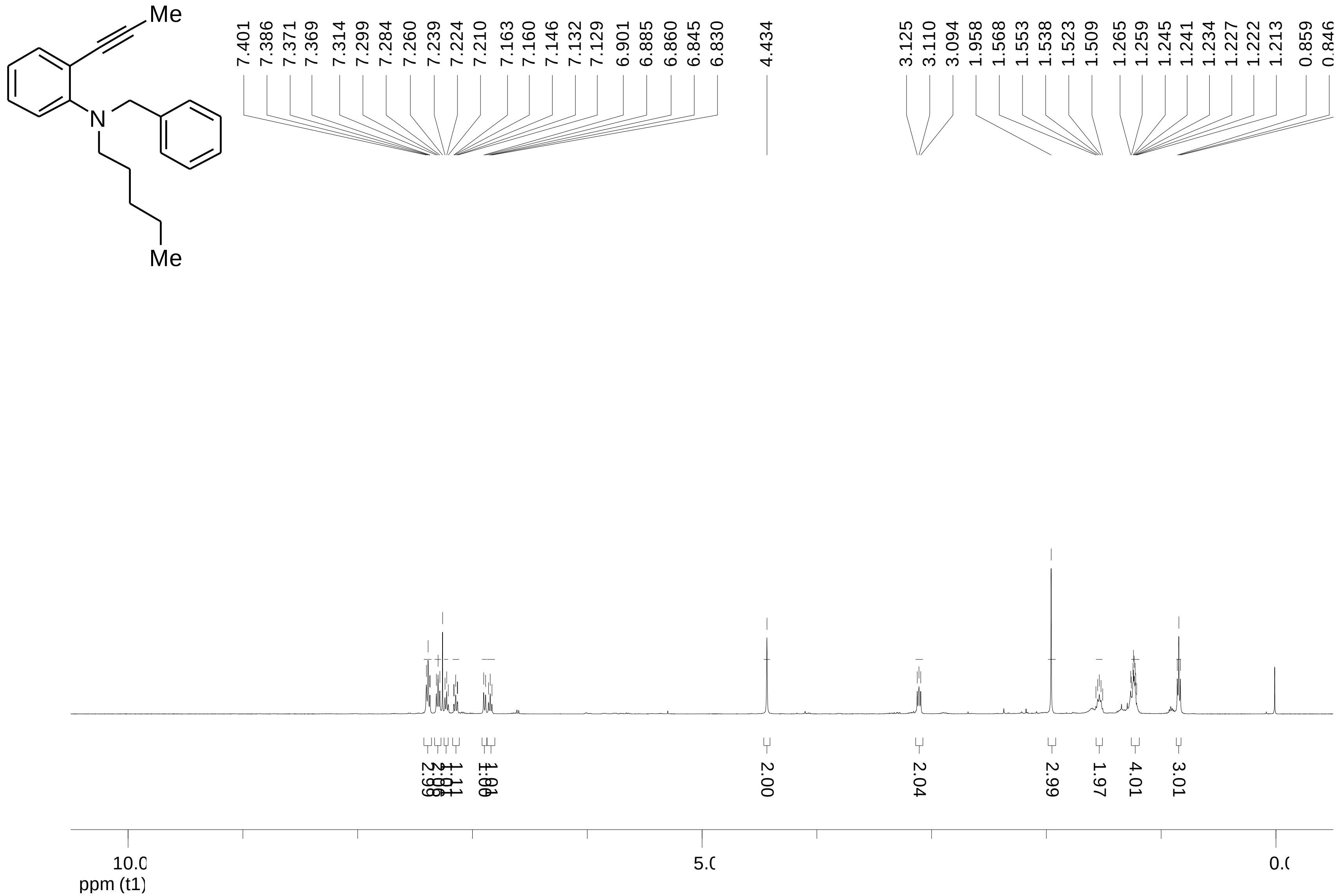

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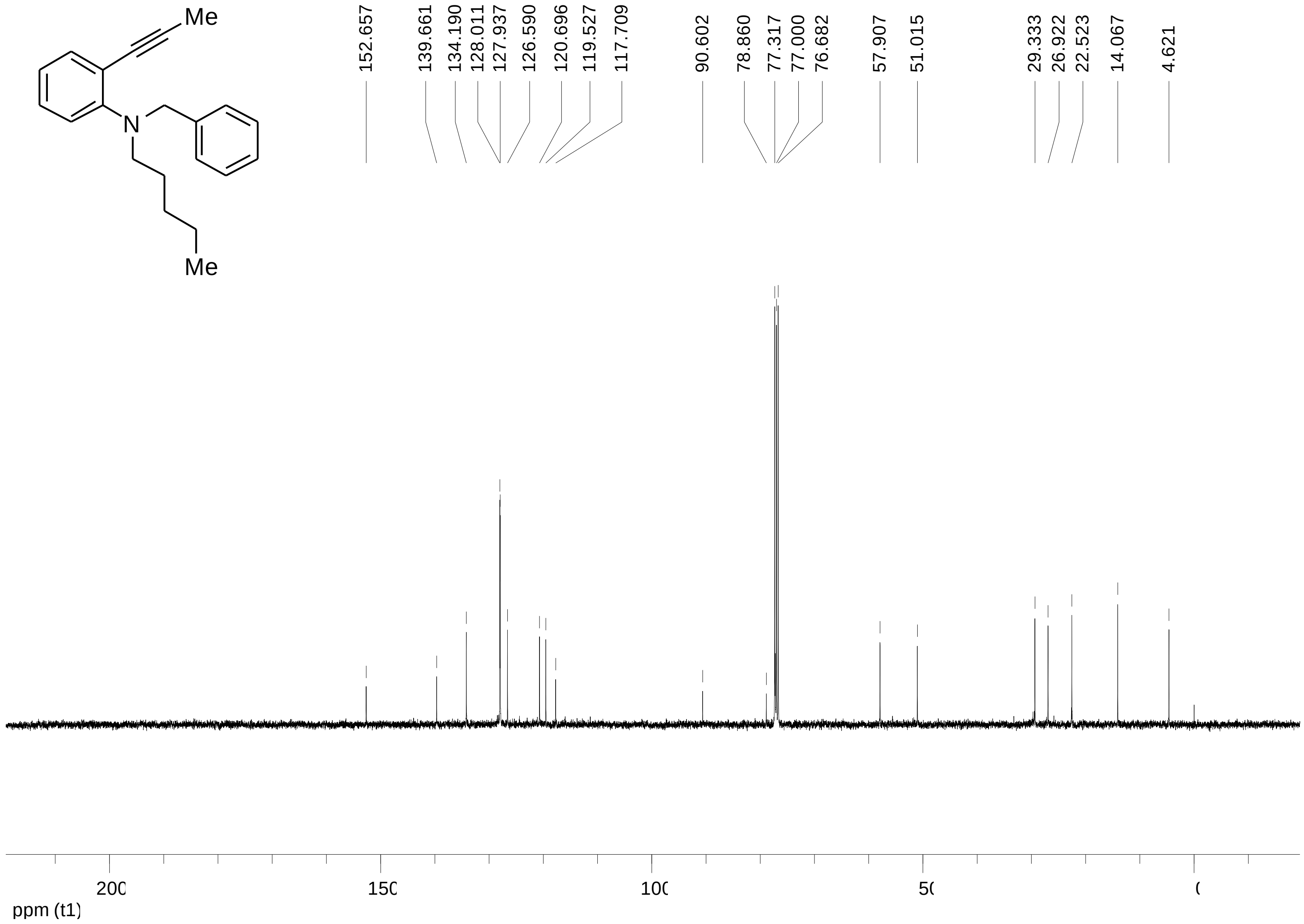

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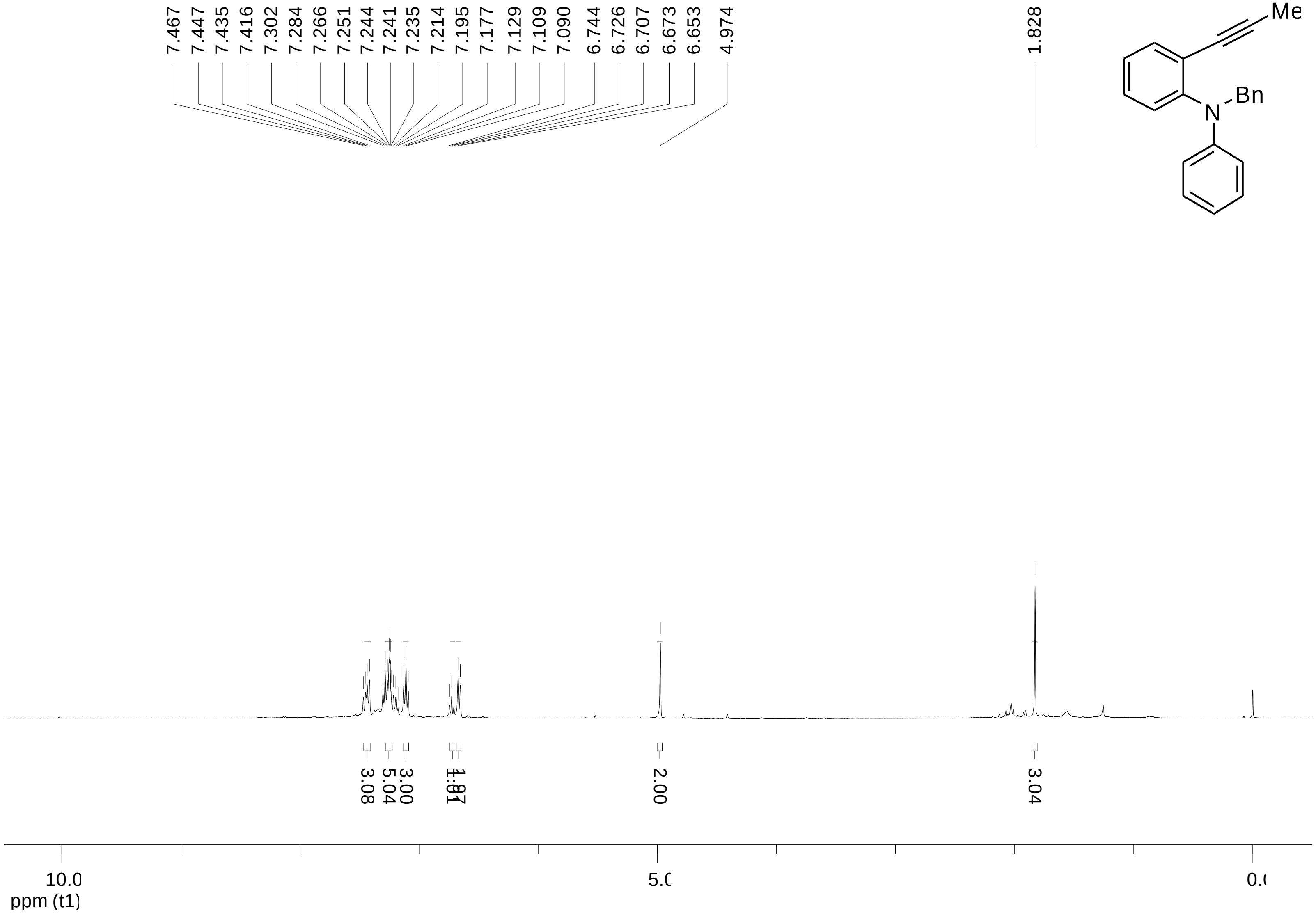

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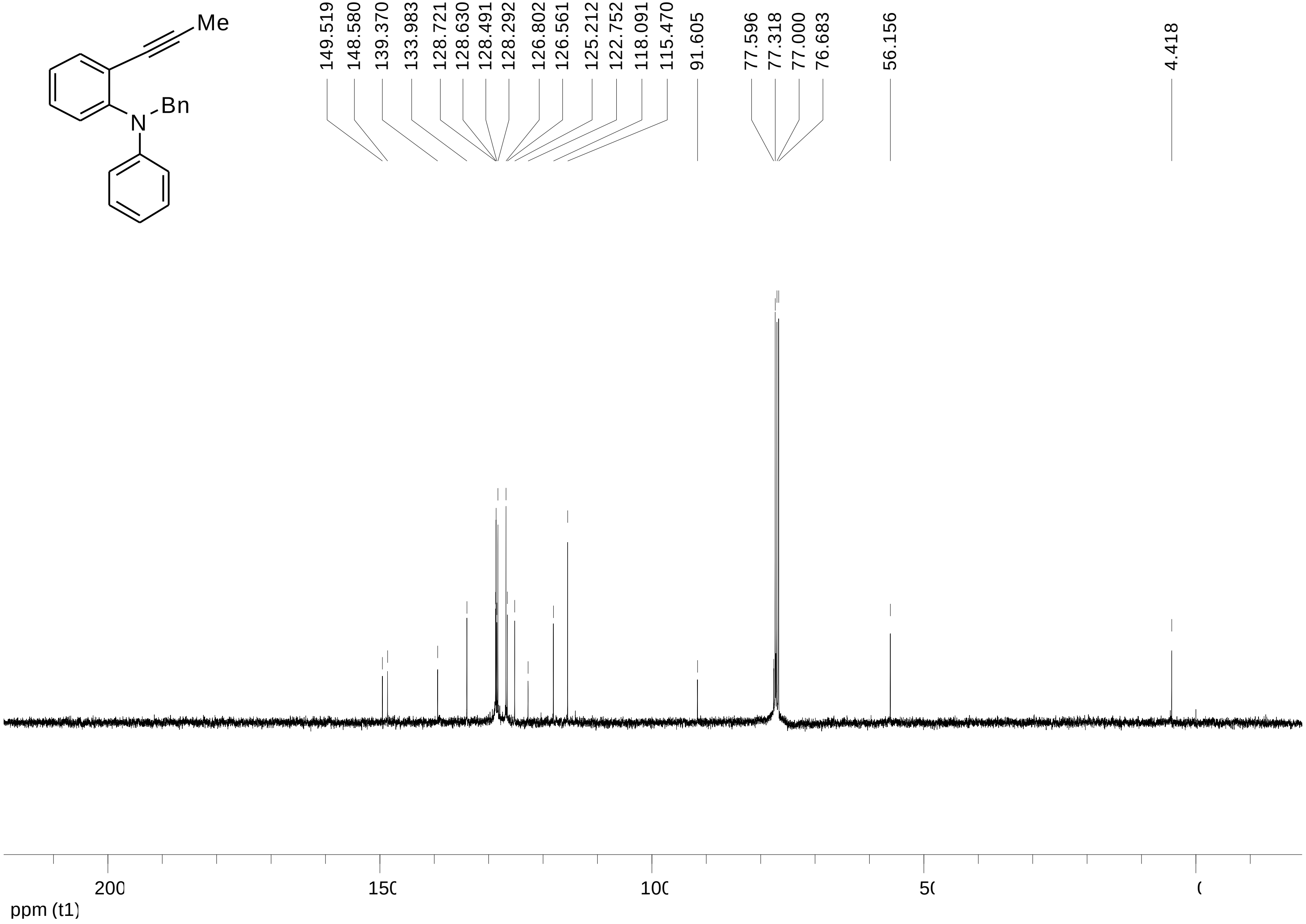

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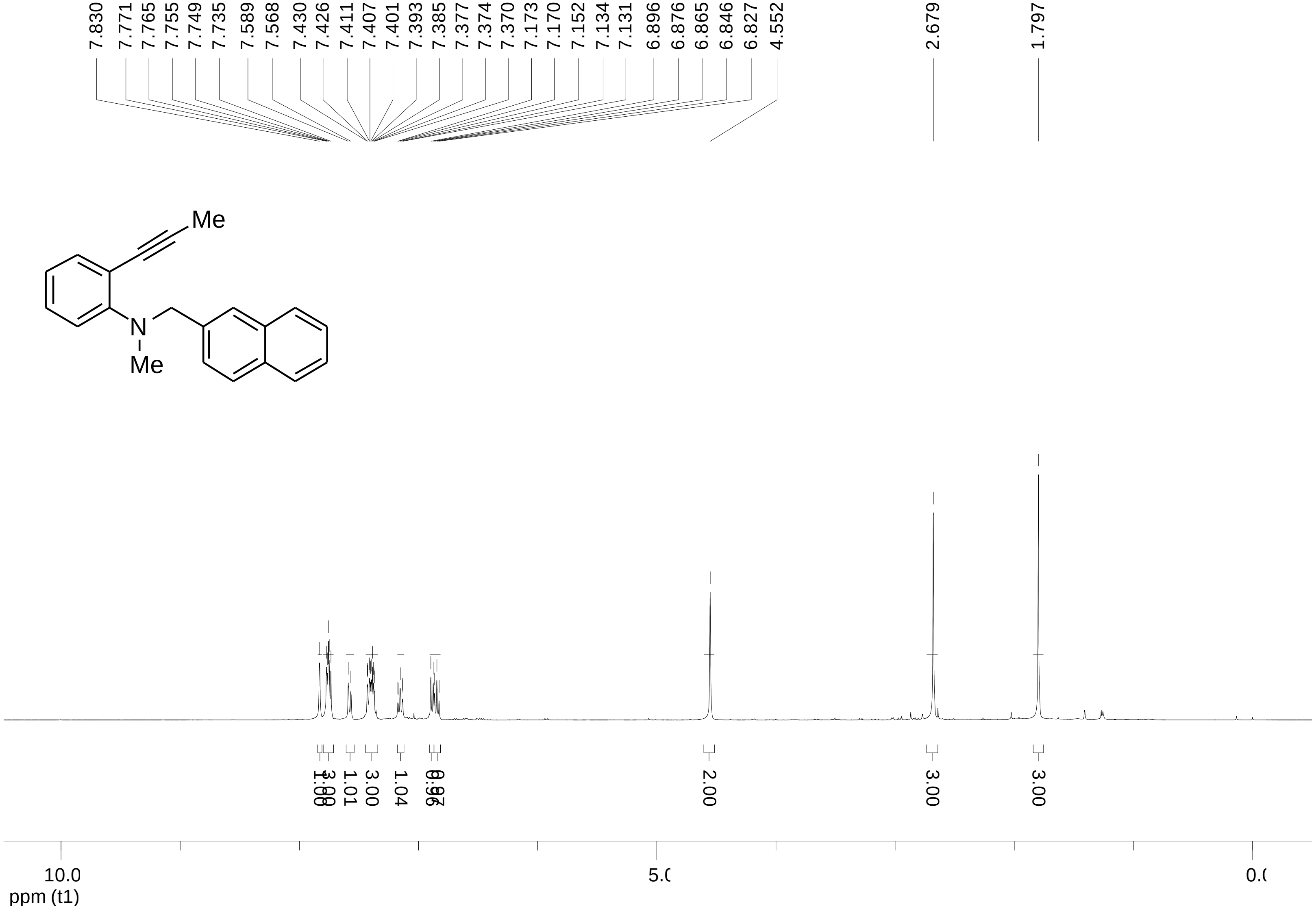

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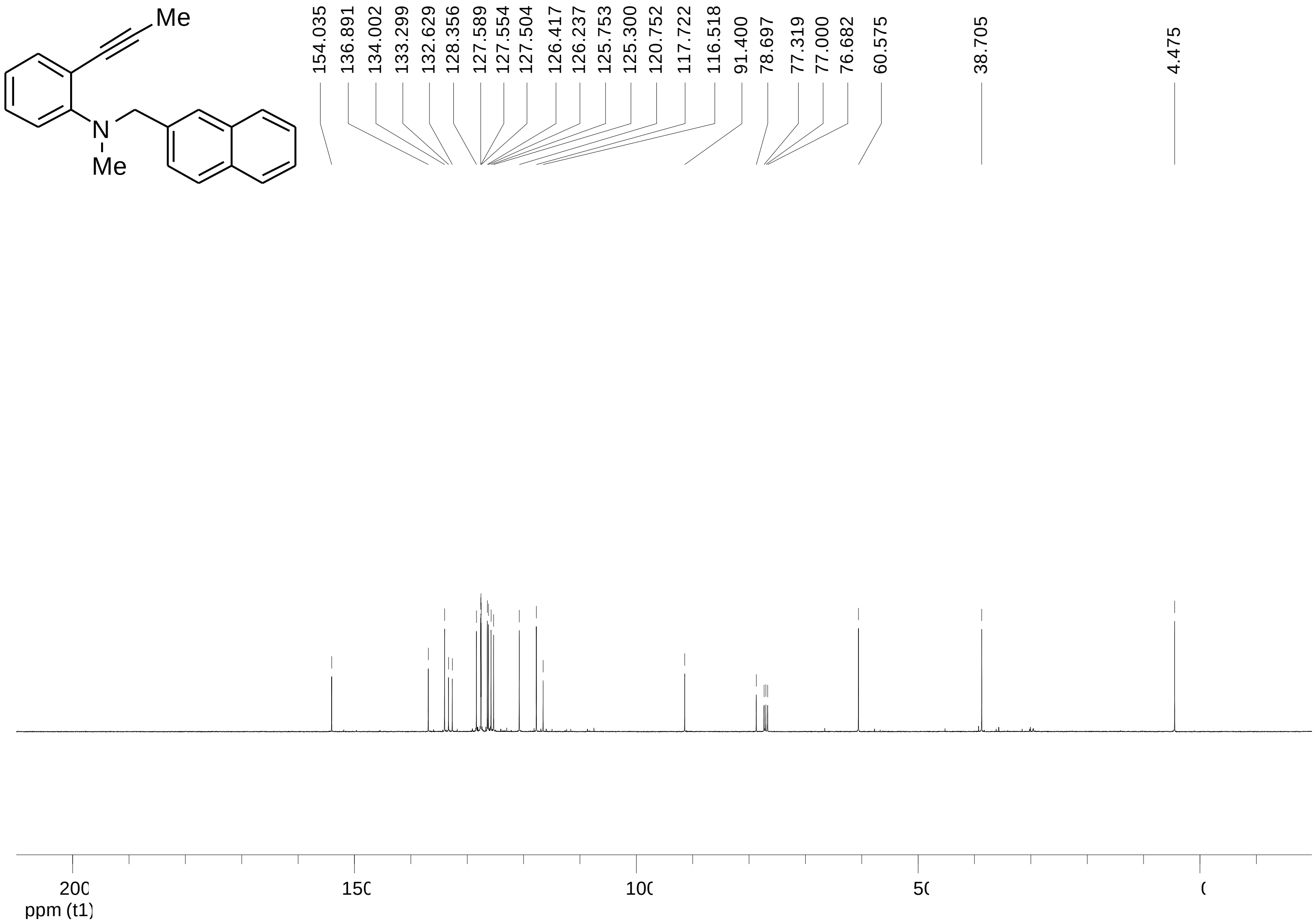

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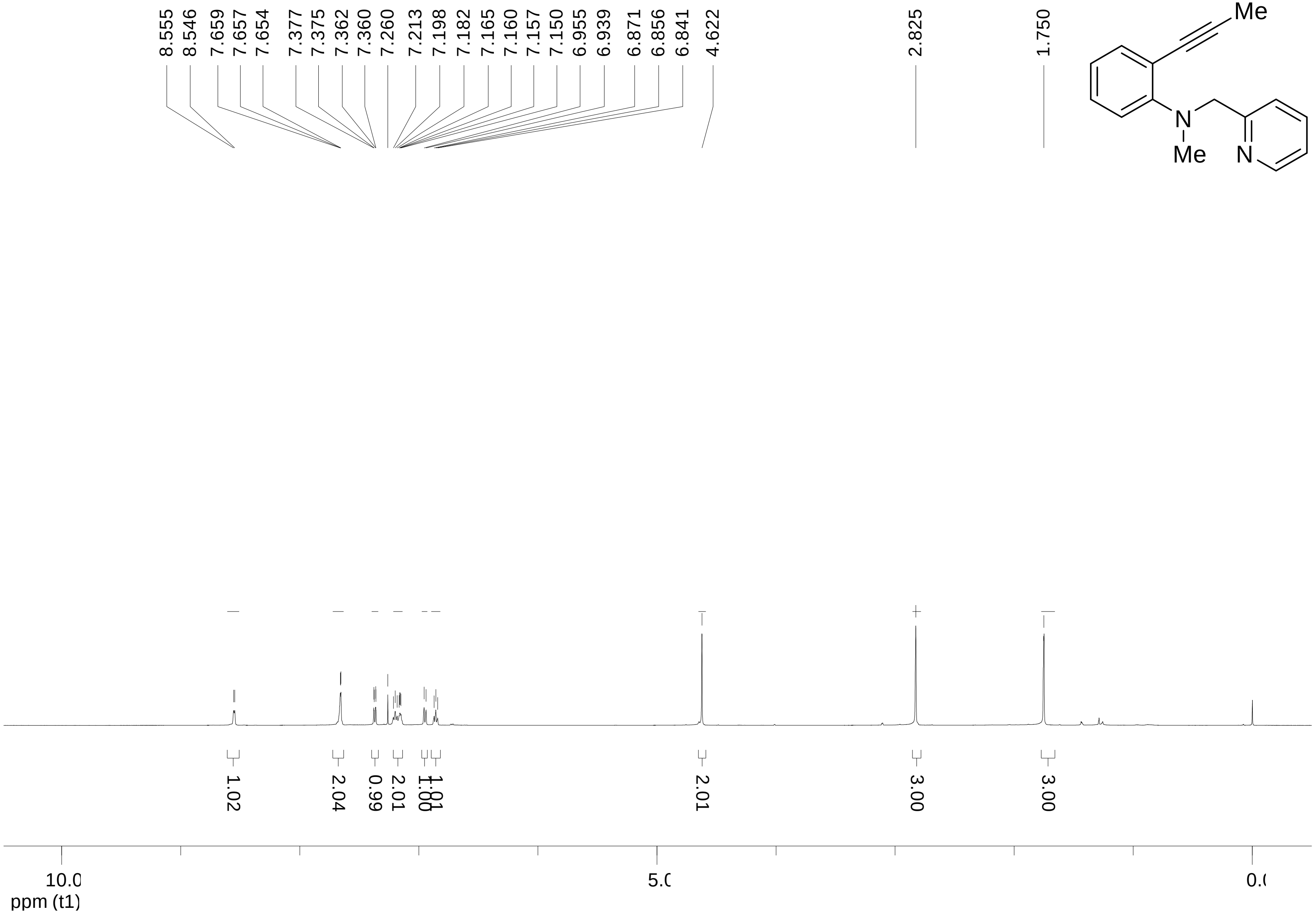
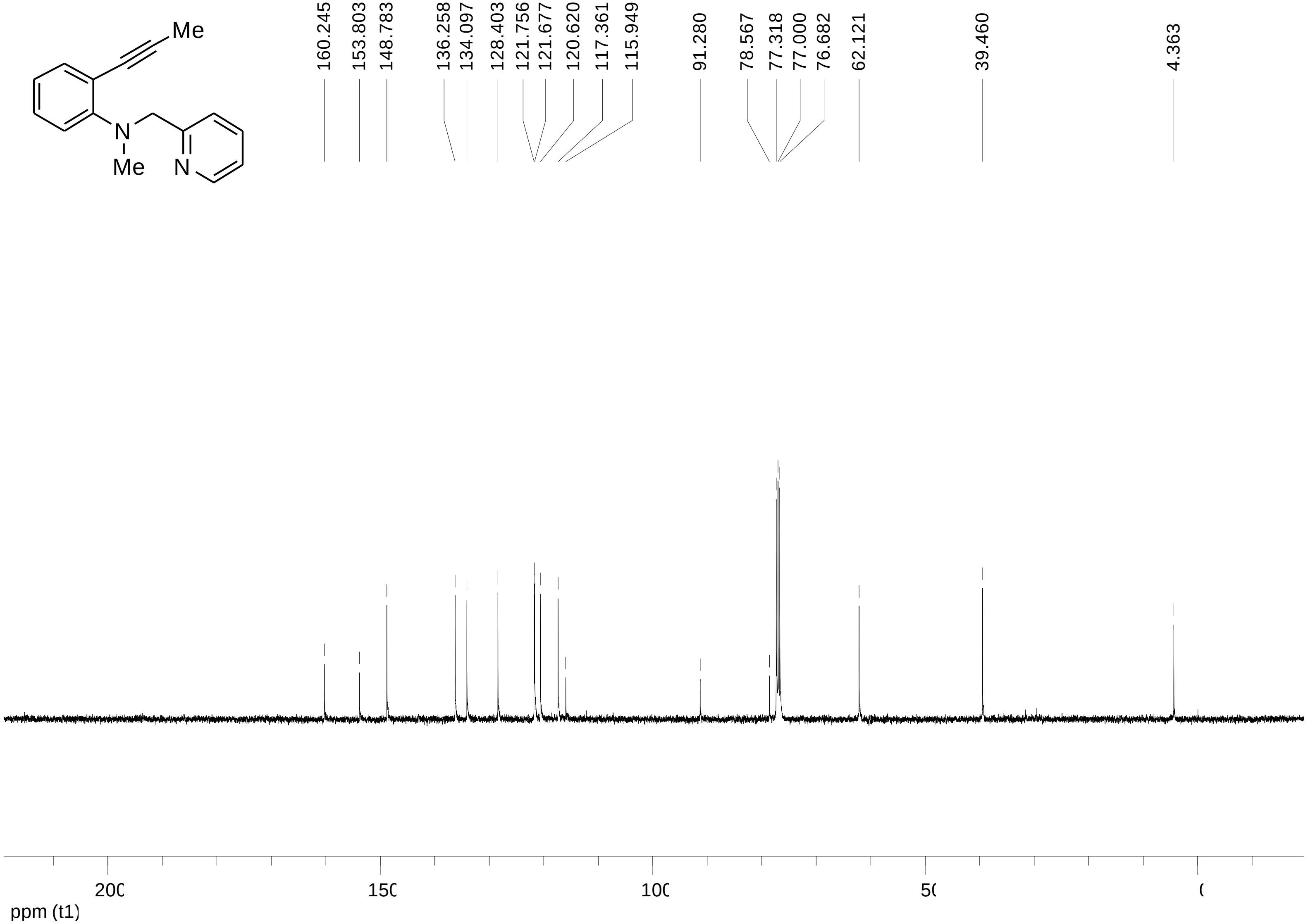


^{13}C NMR spectrum of **1bj** (125 MHz, CDCl$_3$)



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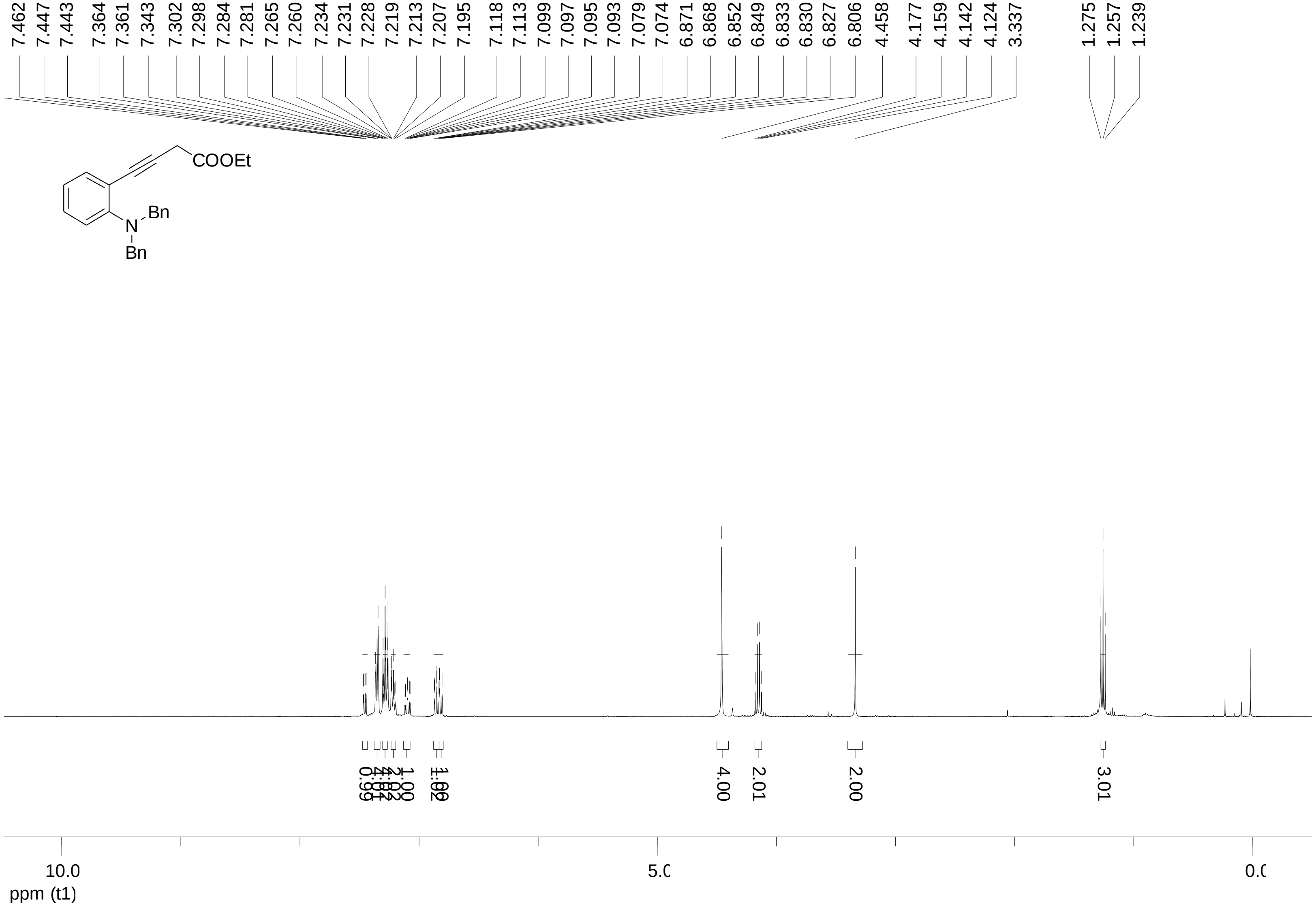

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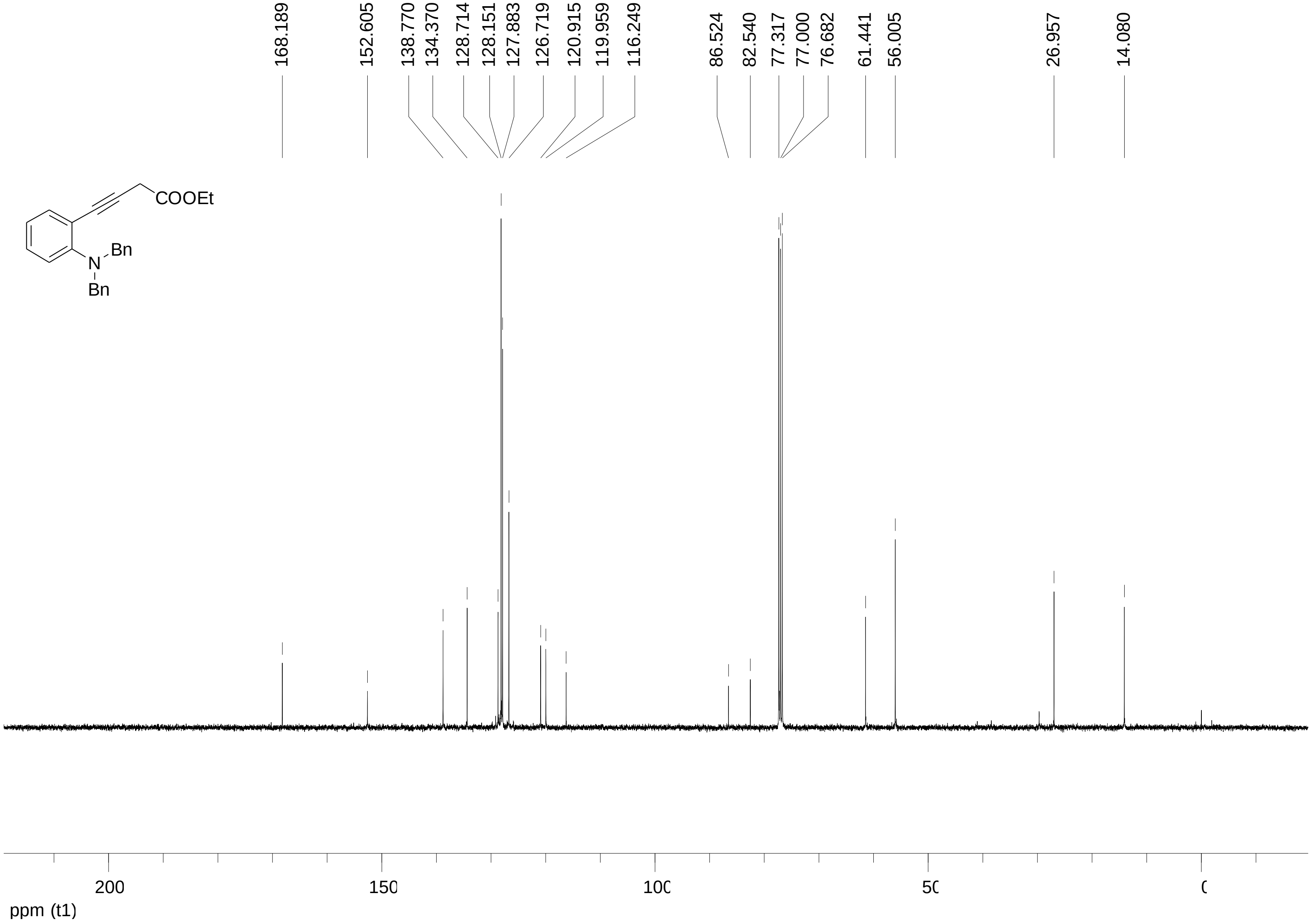

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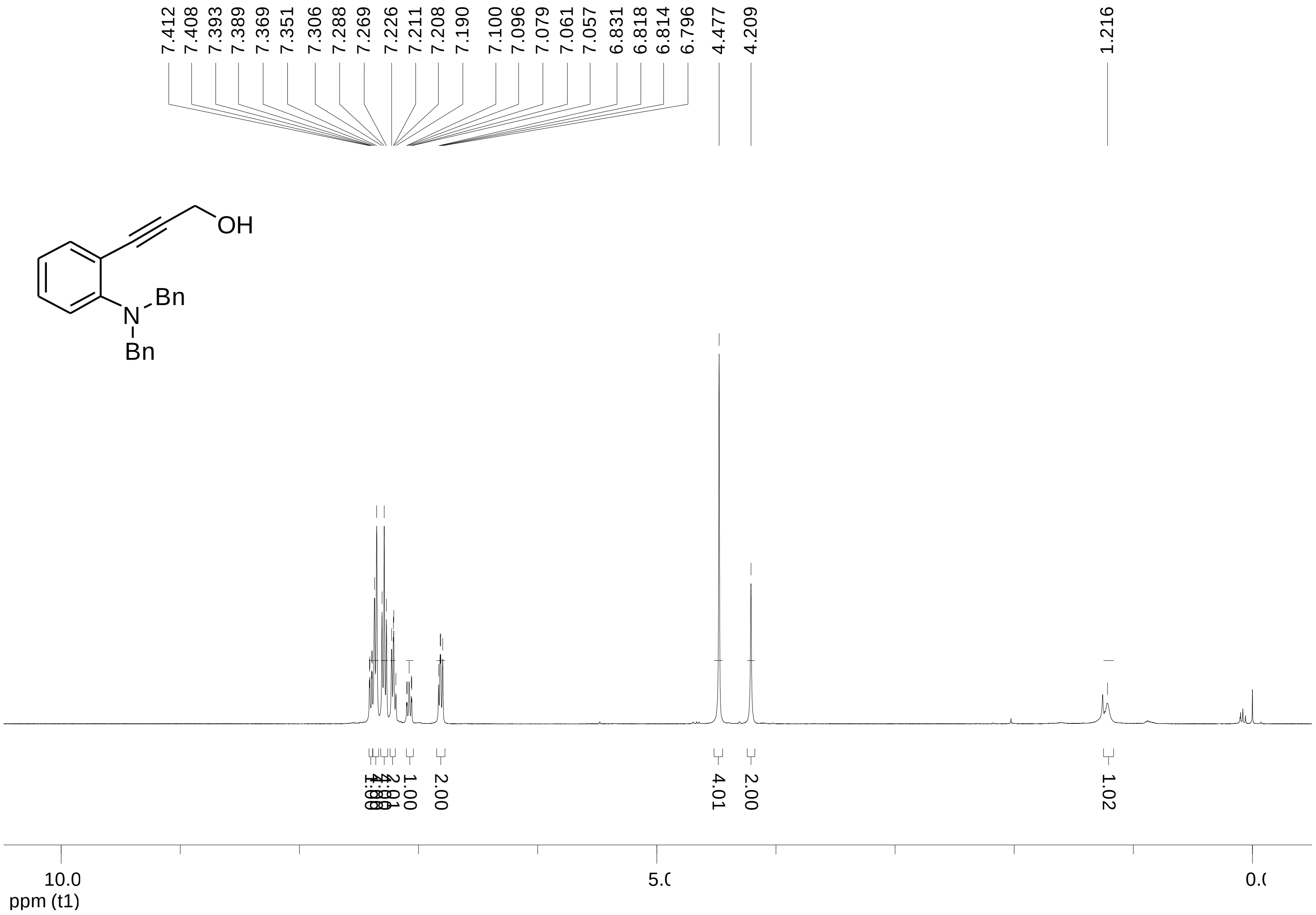

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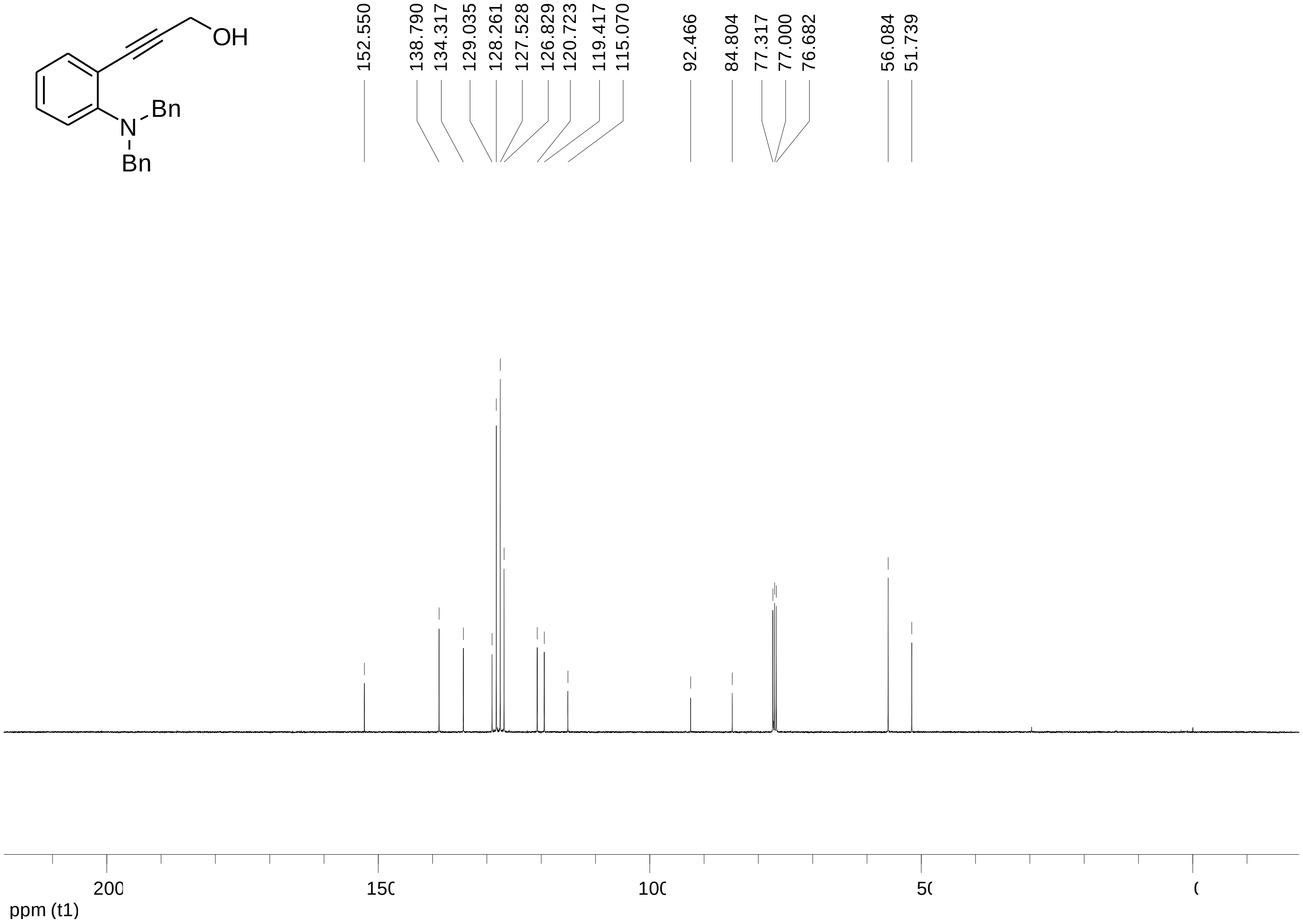
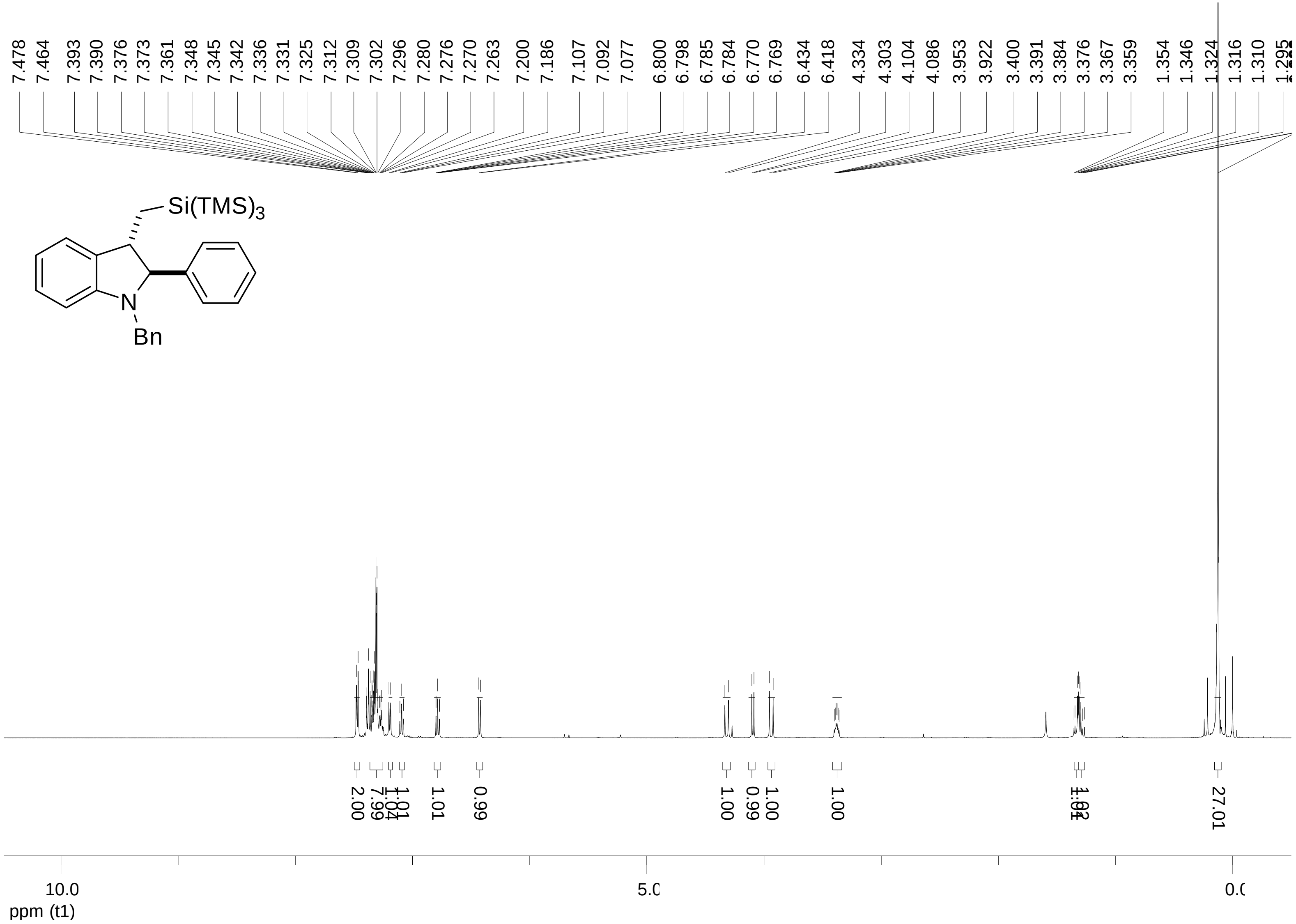
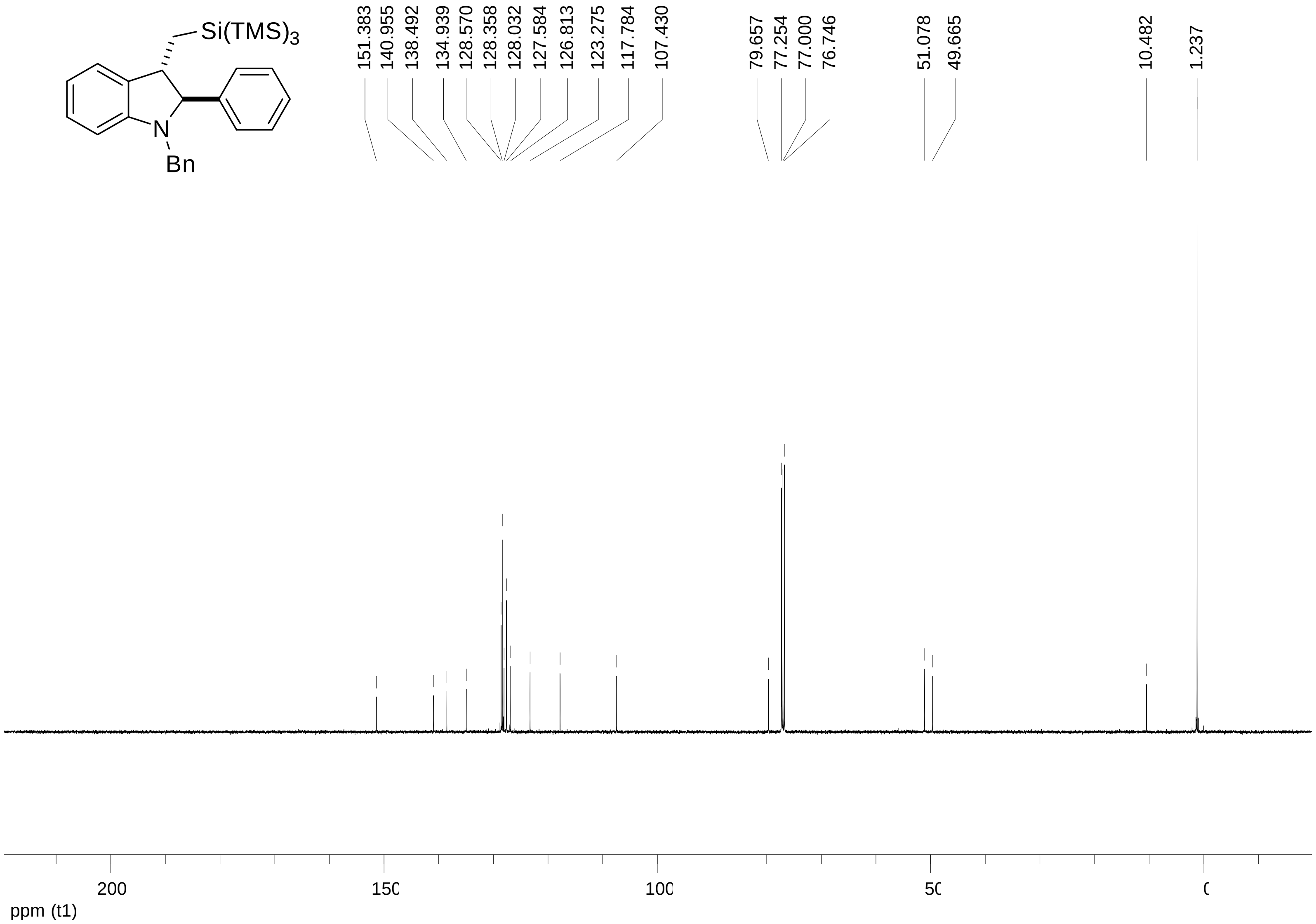


^{1}H NMR spectrum of **2a** (500 MHz, $CDCl_3$)



^{13}C NMR spectrum of **2a** (125 MHz, $CDCl_3$)



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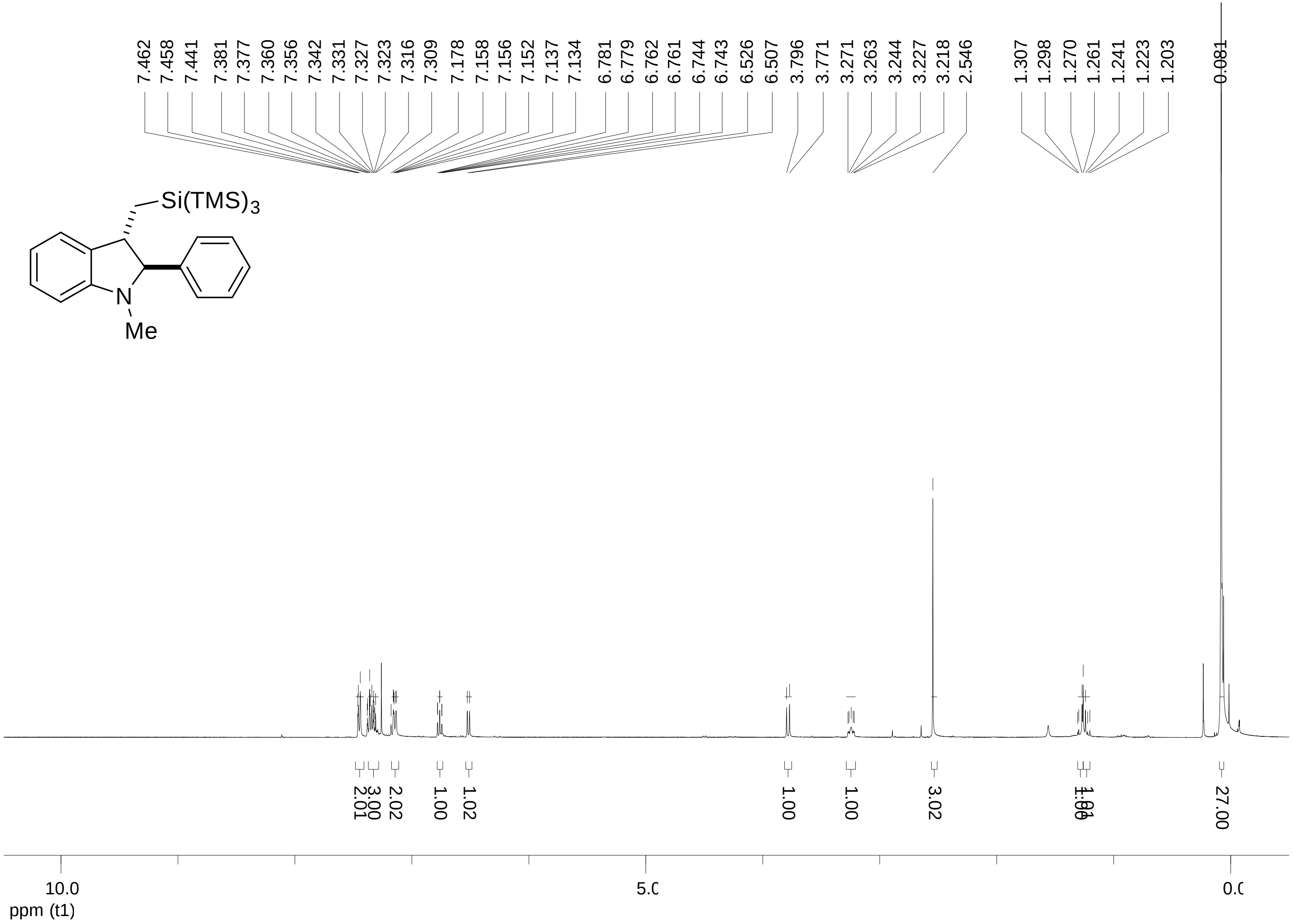
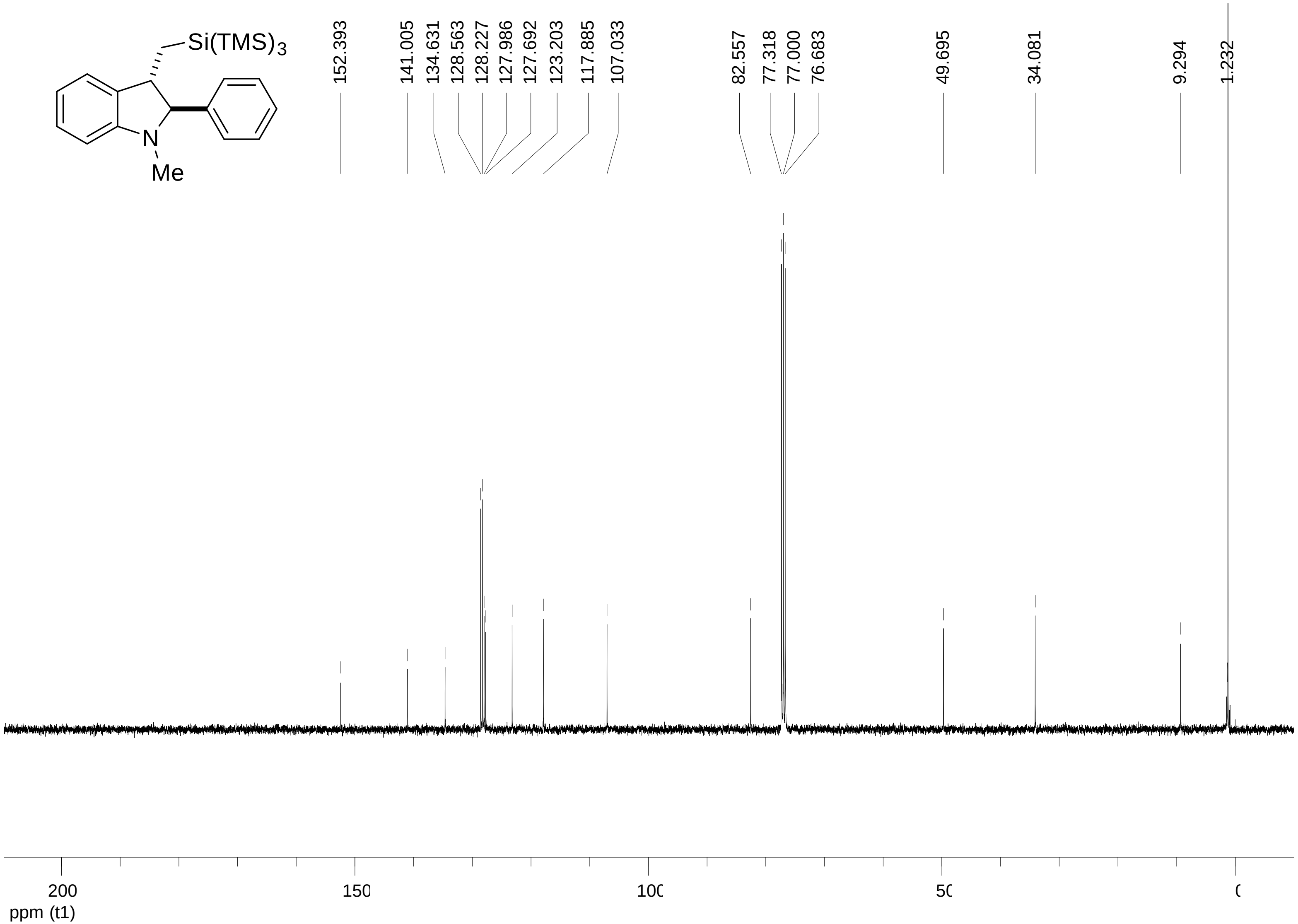
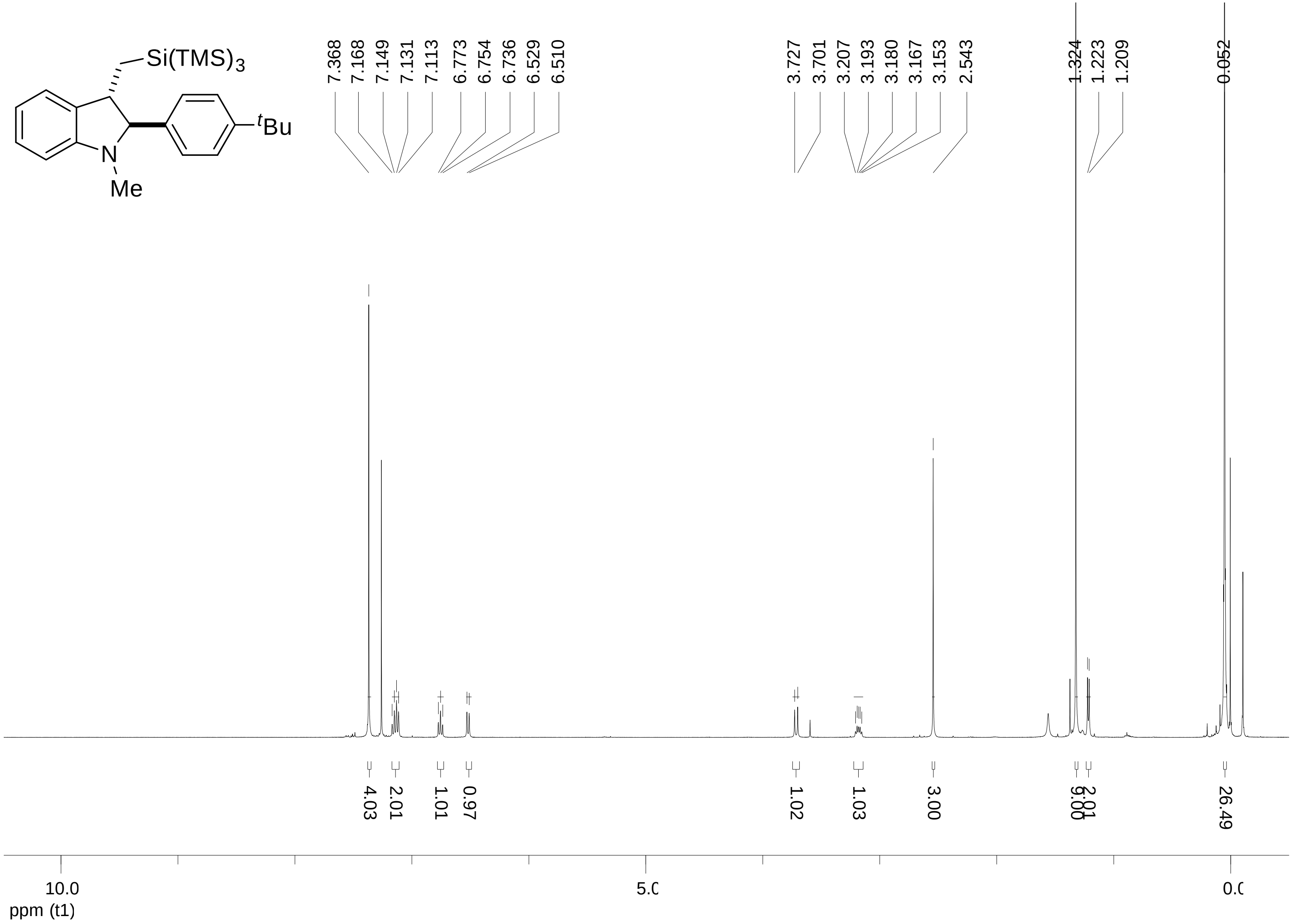


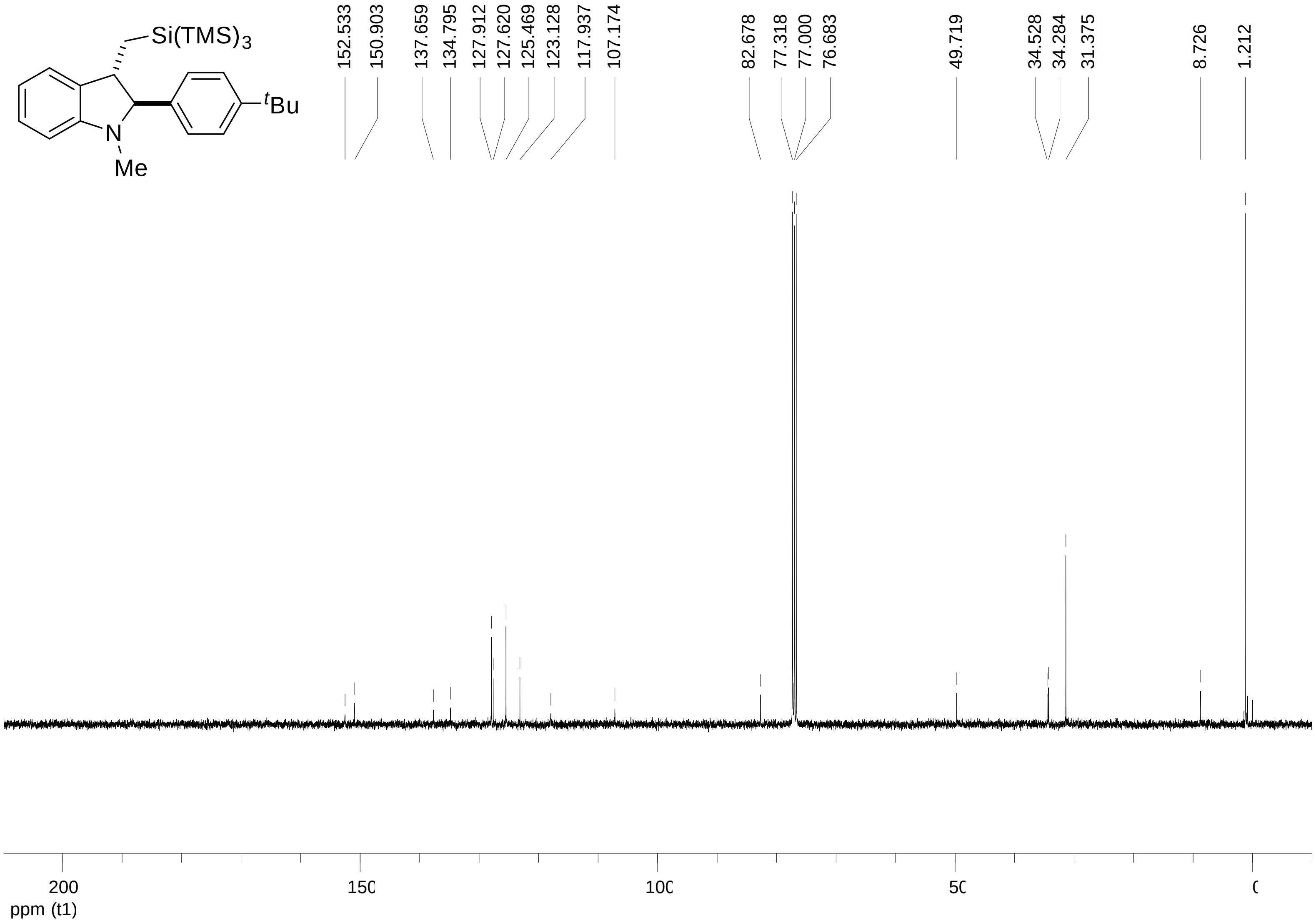
^{13}C NMR spectrum of **2b** (100 MHz, CDCl$_3$)



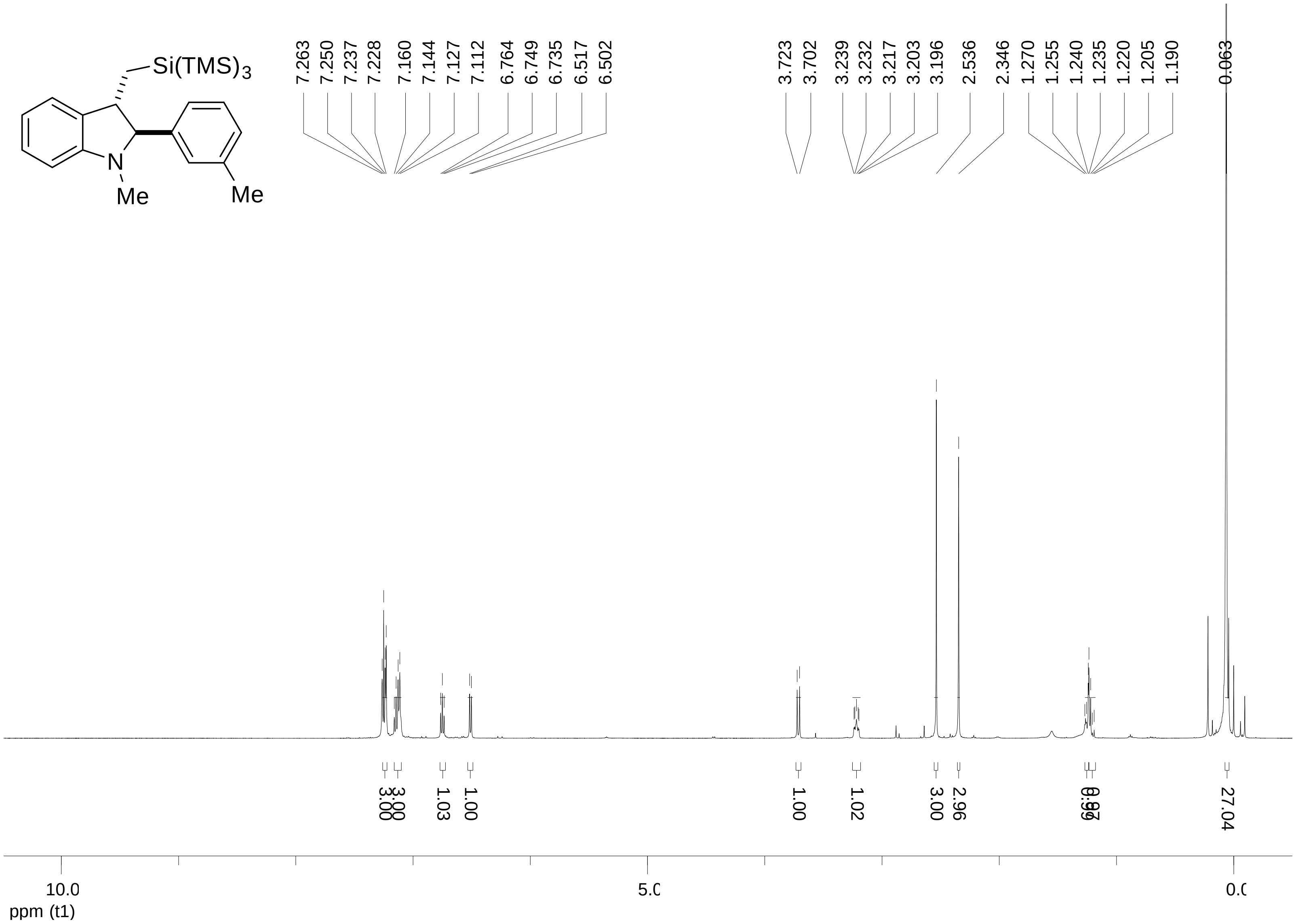
^{1}H NMR spectrum of **2c** (400 MHz, CDCl$_3$)



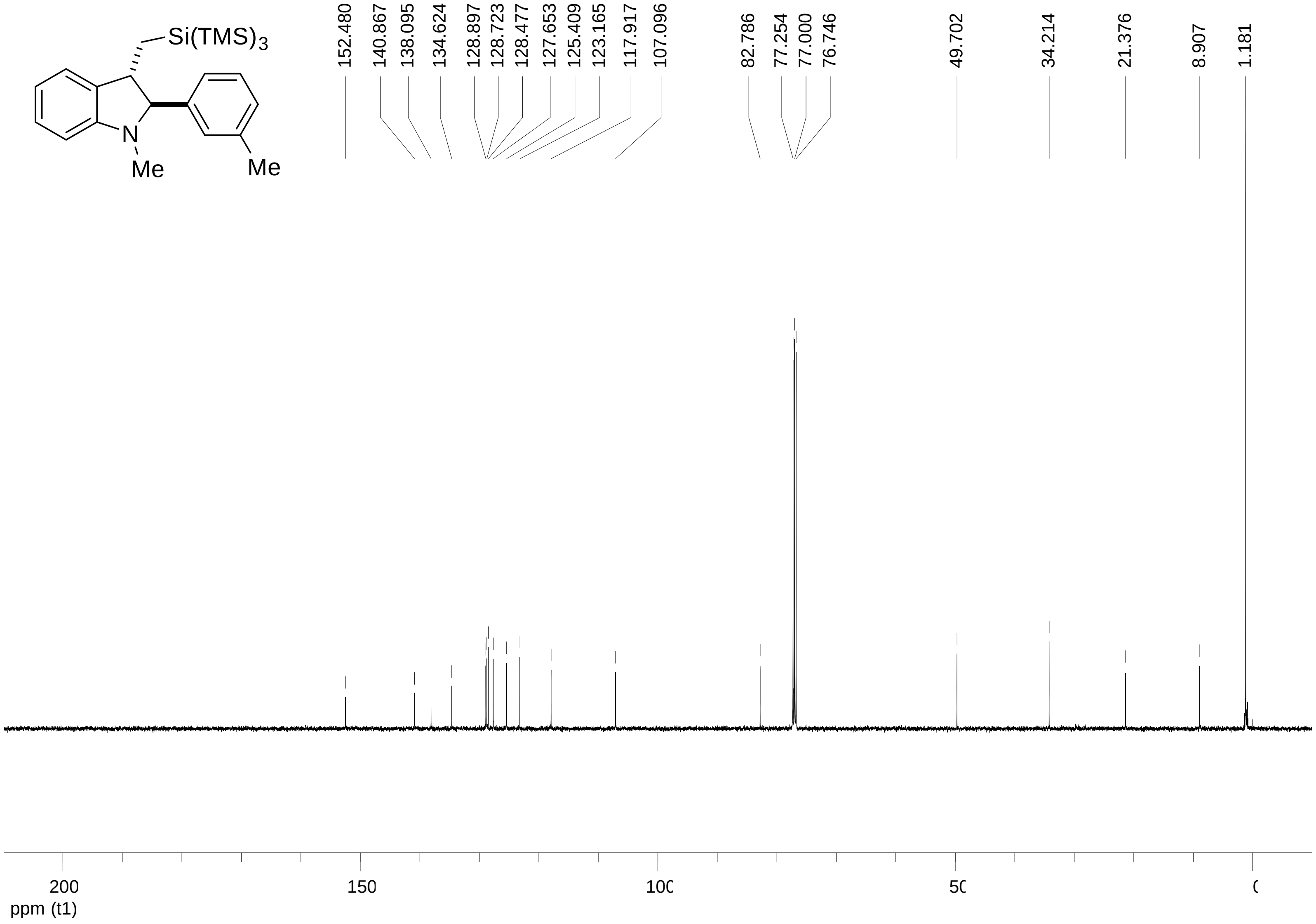
^{13}C NMR spectrum of **2c** (100 MHz, $CDCl_3$)



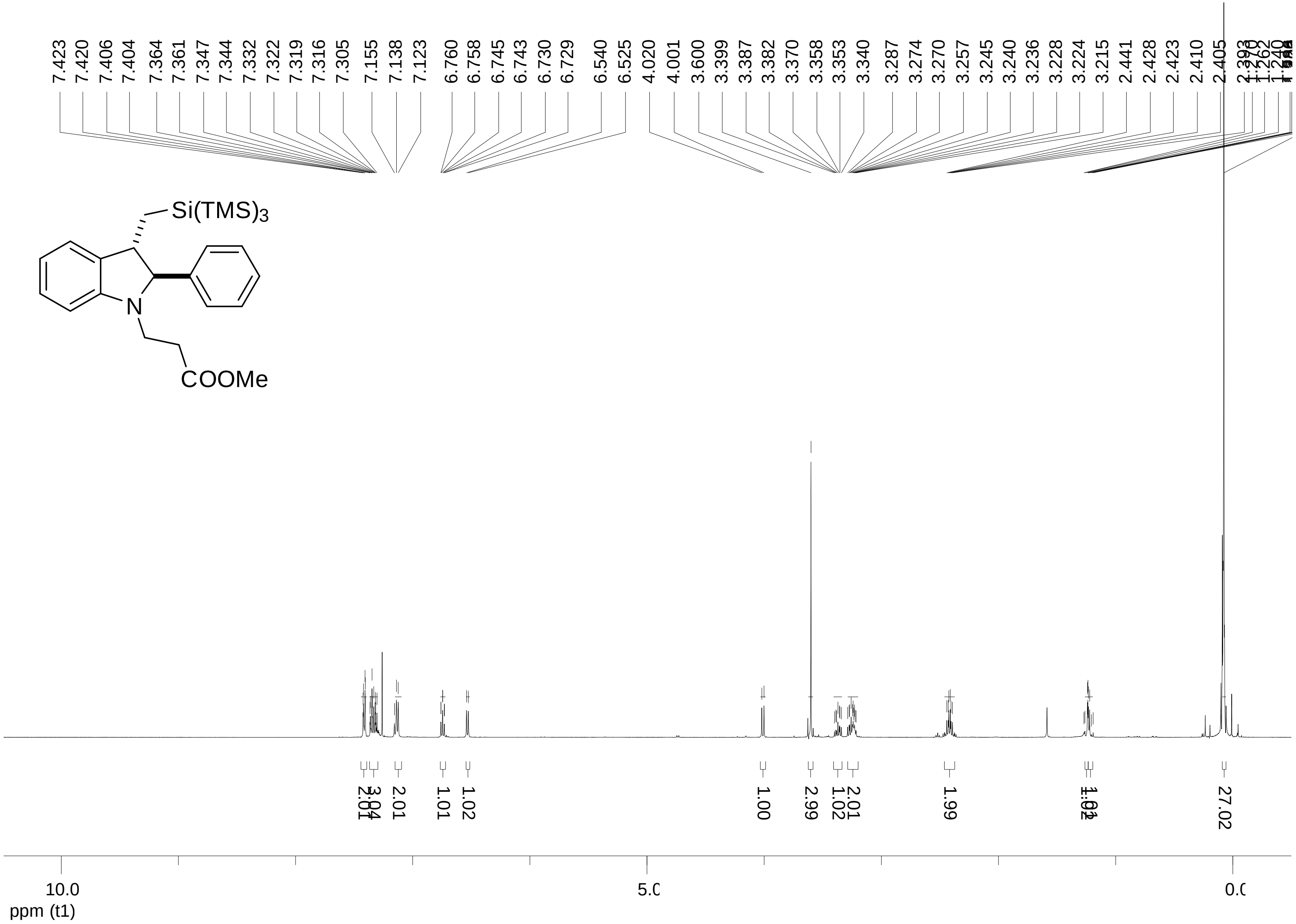
^{1}H NMR spectrum of **2d** (500 MHz, $CDCl_3$)



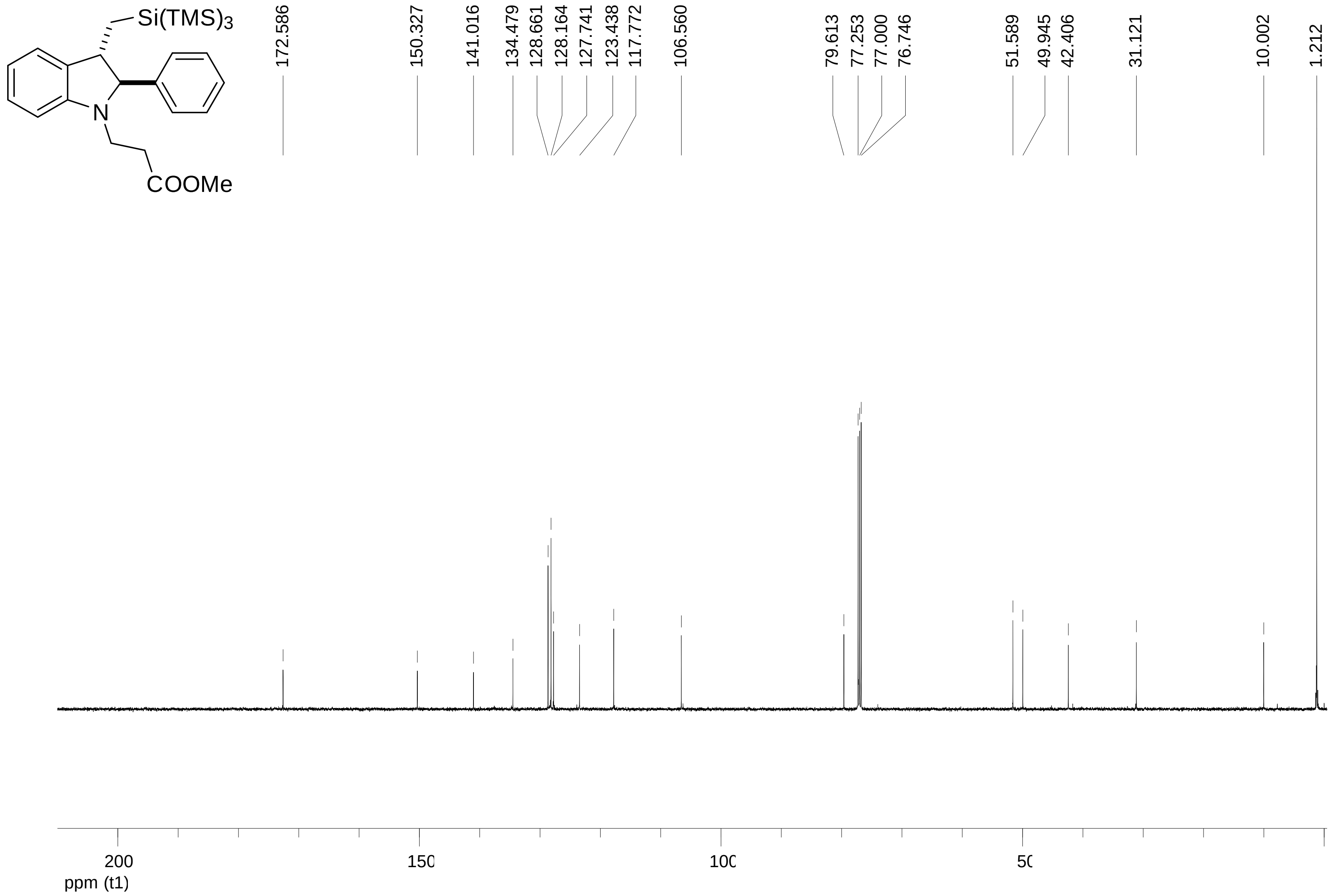
^{13}C NMR spectrum of **2d** (125 MHz, CDCl$_3$)



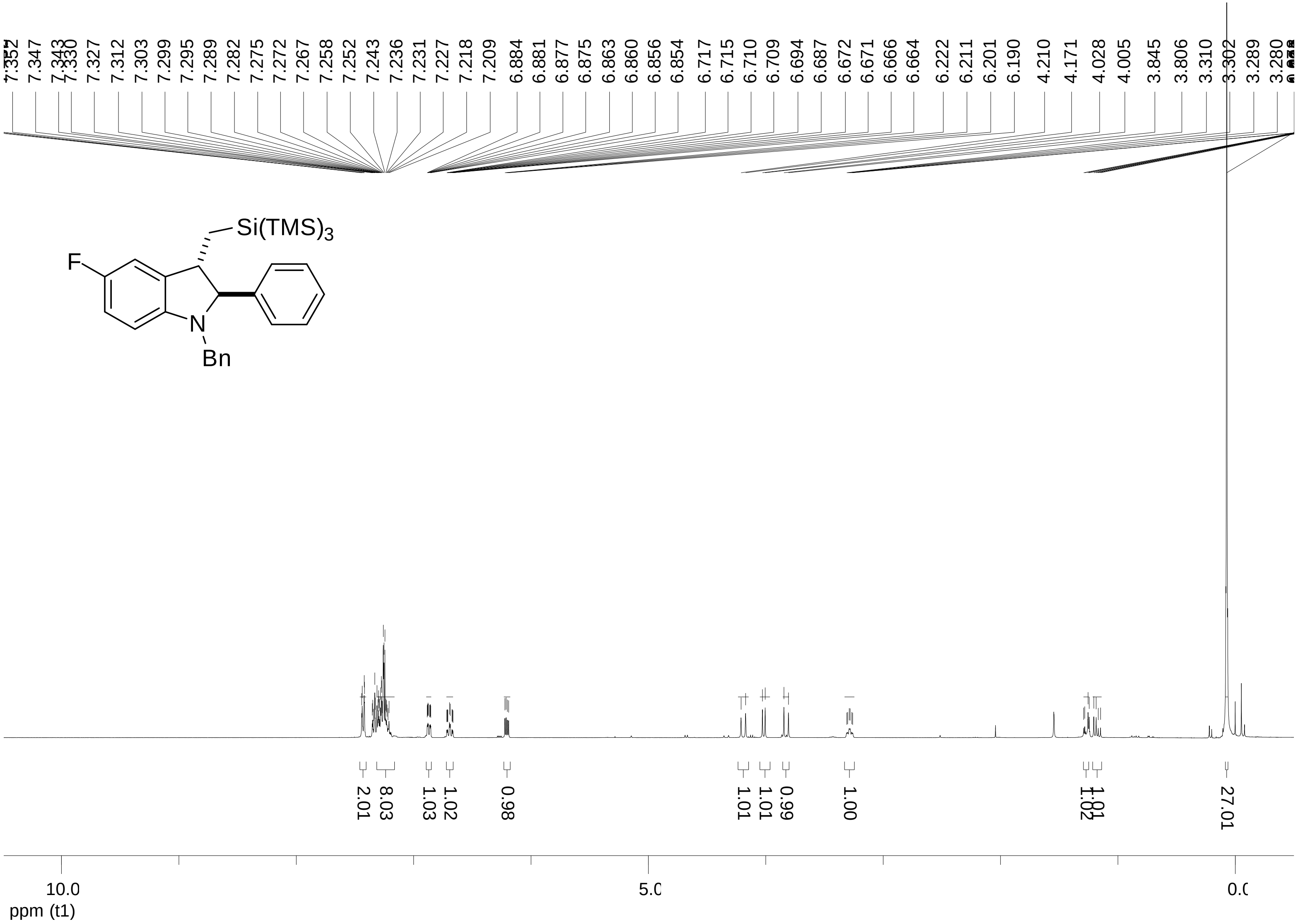
^{1}H NMR spectrum of **2e** (500 MHz, CDCl$_3$)



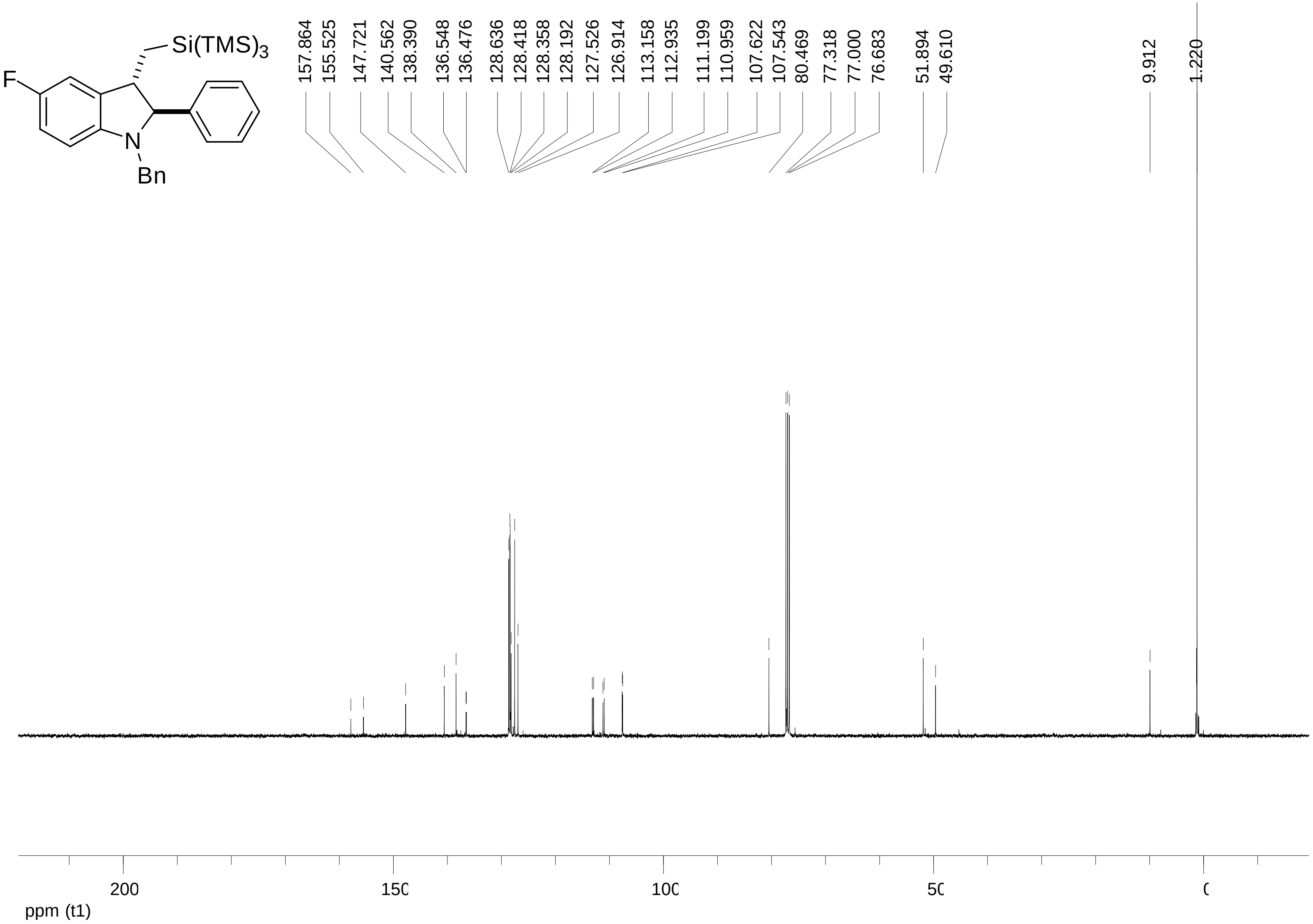
^{13}C NMR spectrum of **2e** (125 MHz, $CDCl_3$)



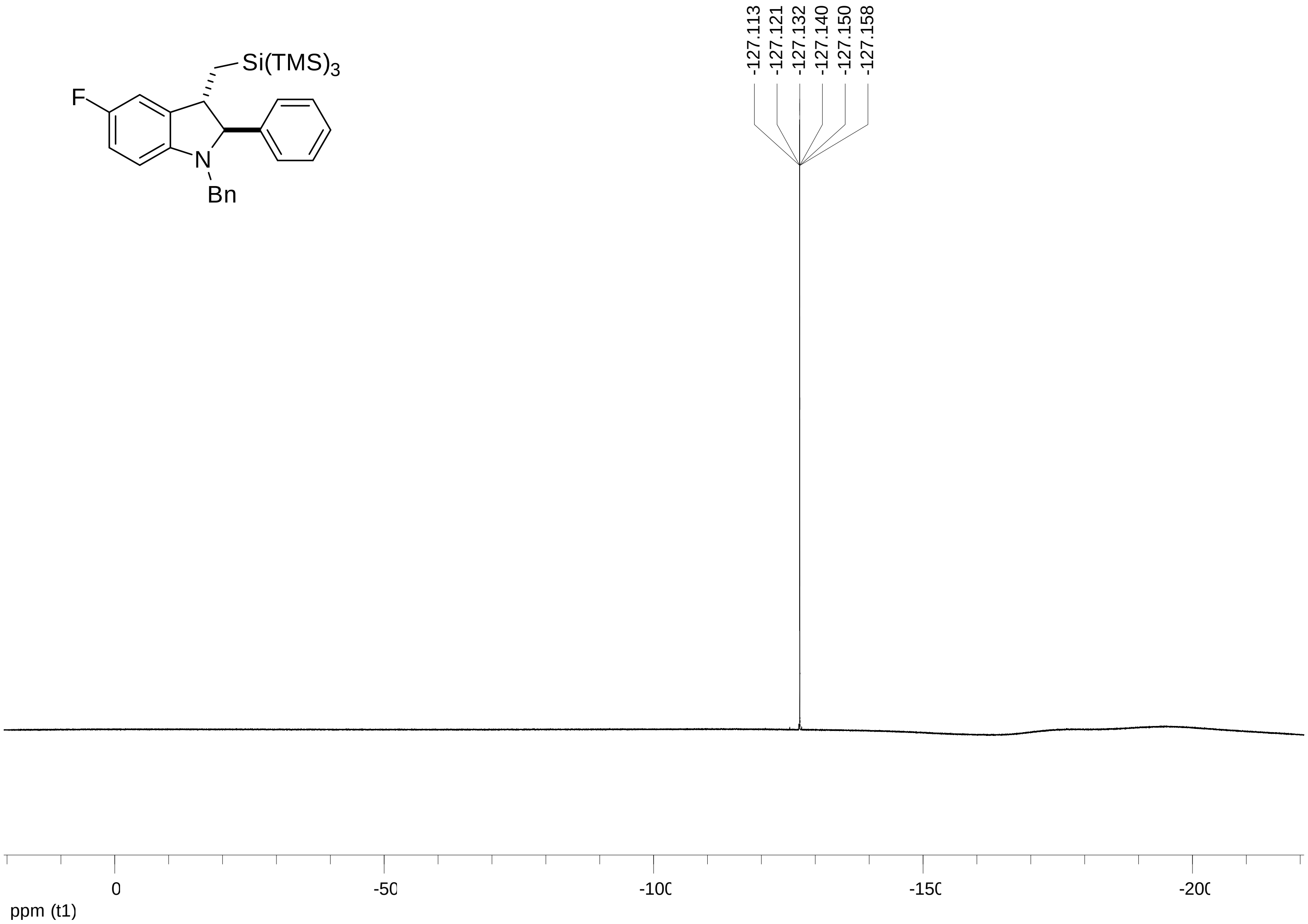
^{1}H NMR spectrum of **2f** (400 MHz, $CDCl_3$)



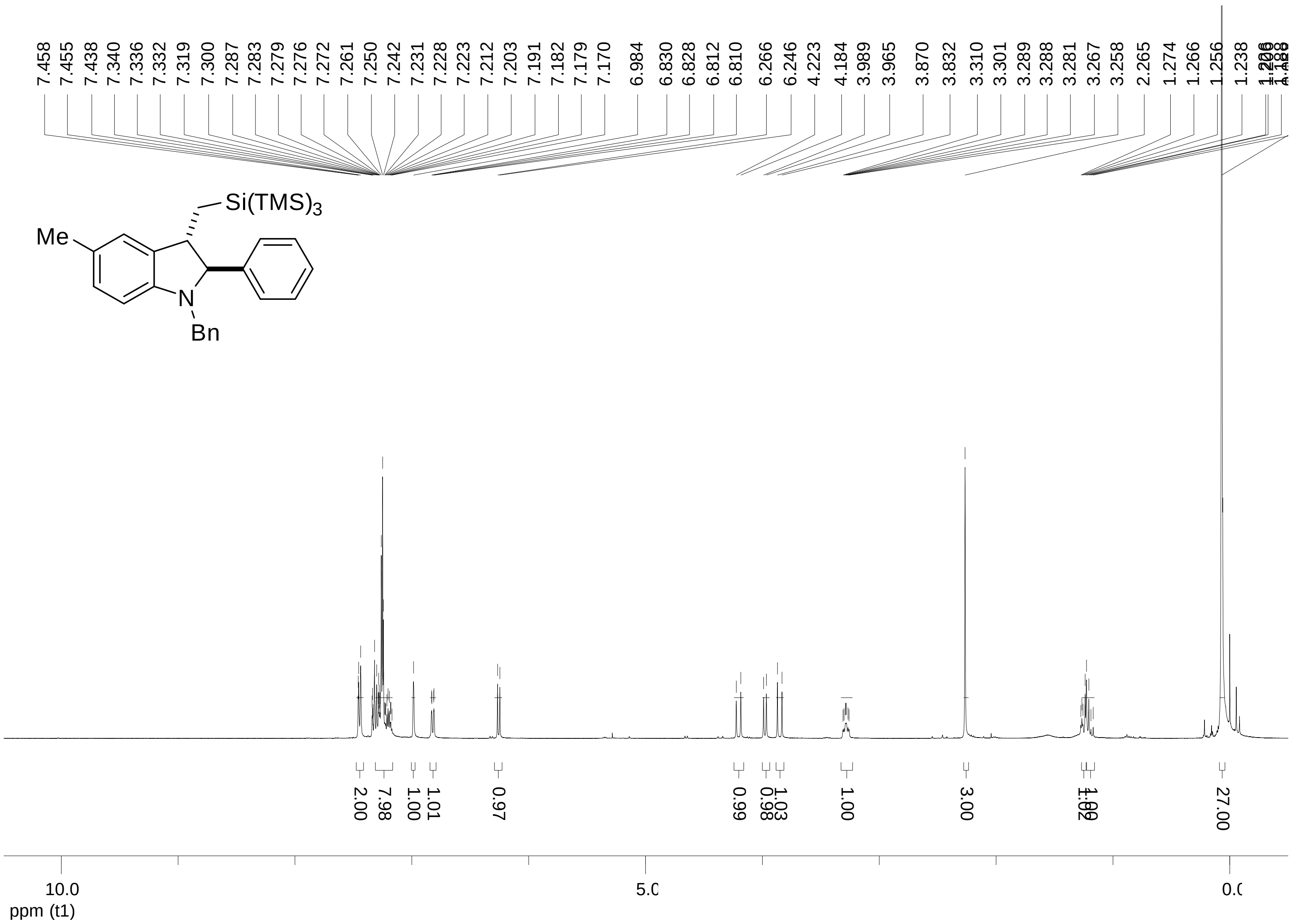
^{13}C NMR spectrum of **2f** (100 MHz, $CDCl_3$)



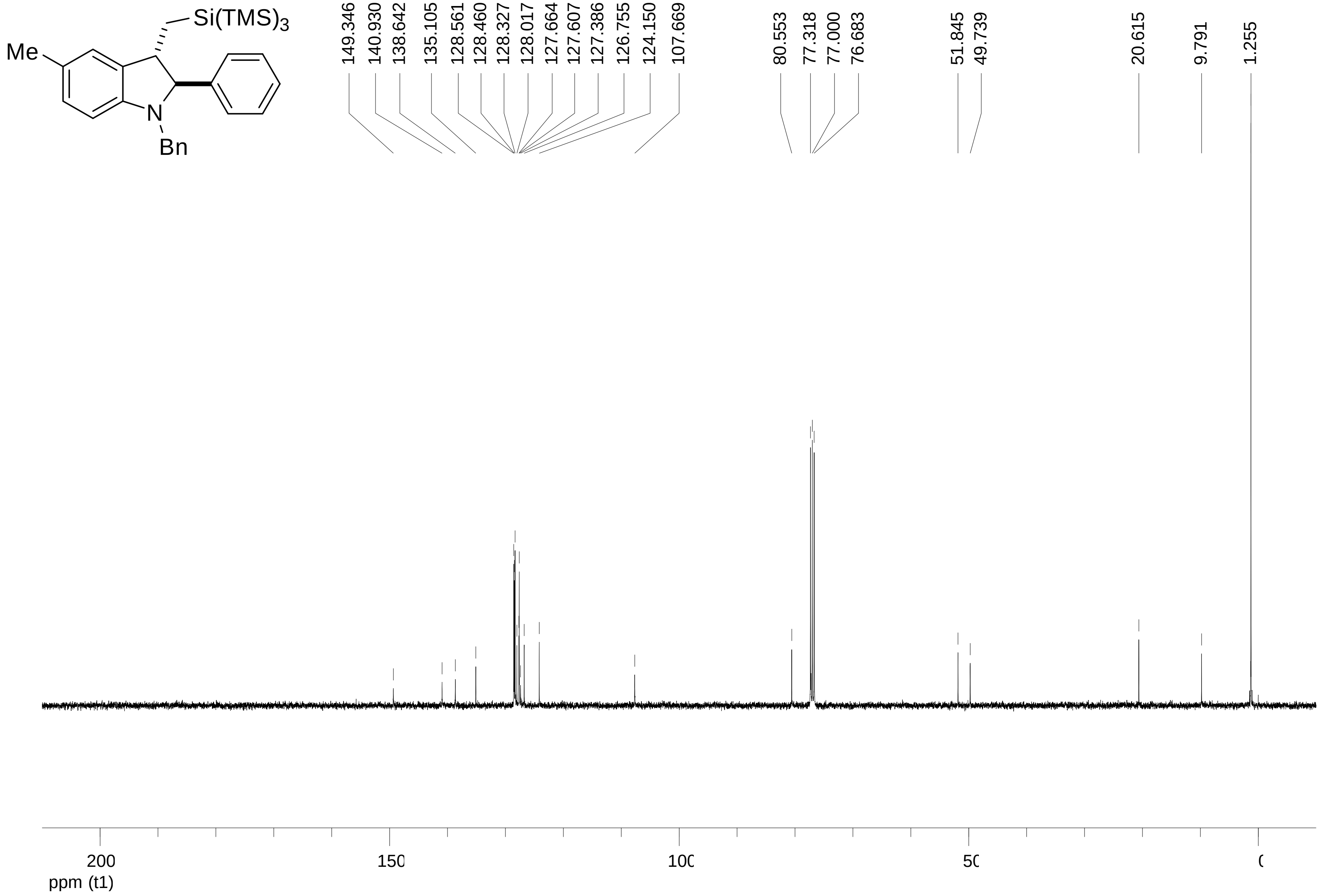
^{19}F NMR spectrum of **2f** (376 MHz, $CDCl_3$)



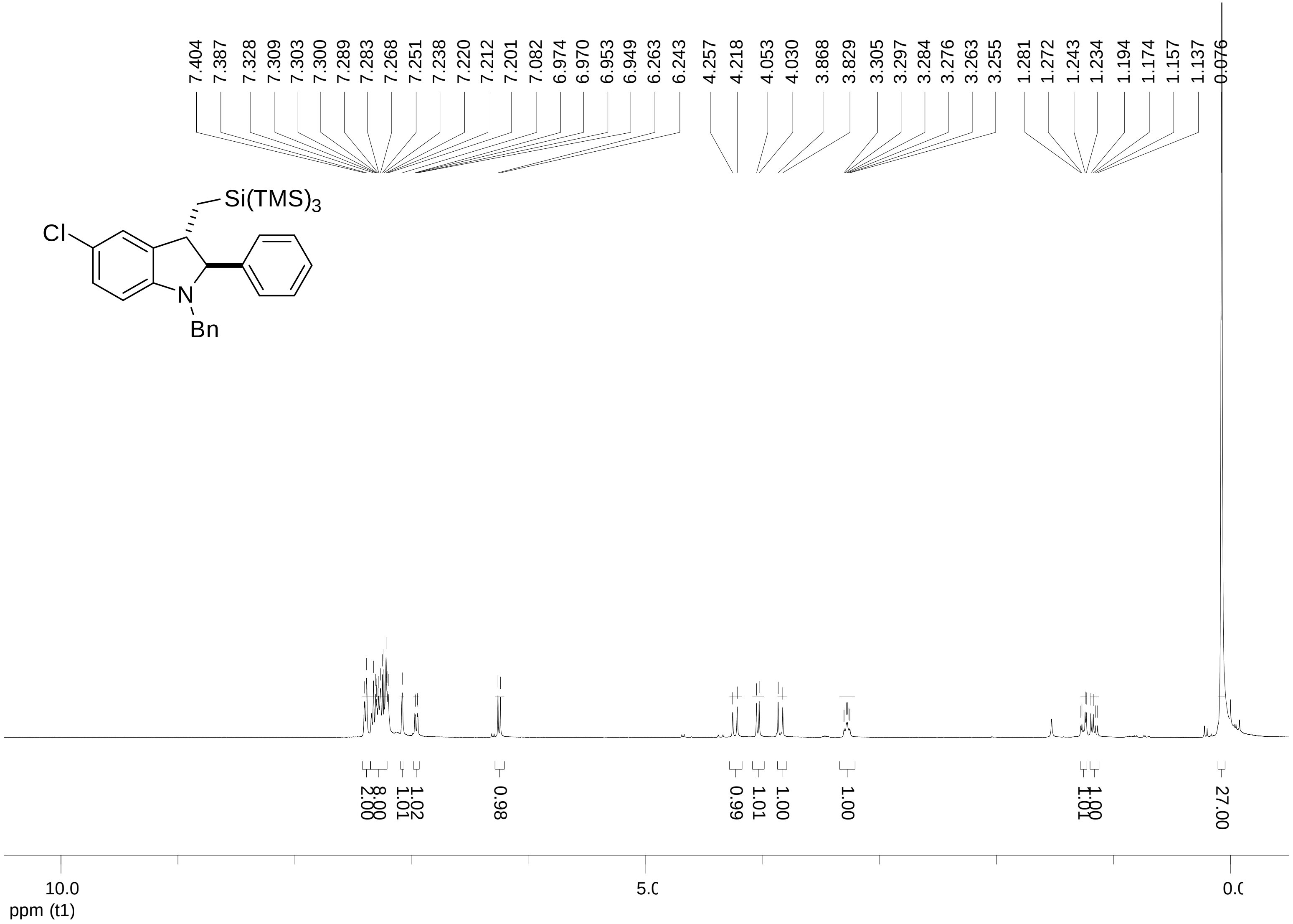
^{1}H NMR spectrum of **2g** (400 MHz, $CDCl_3$)



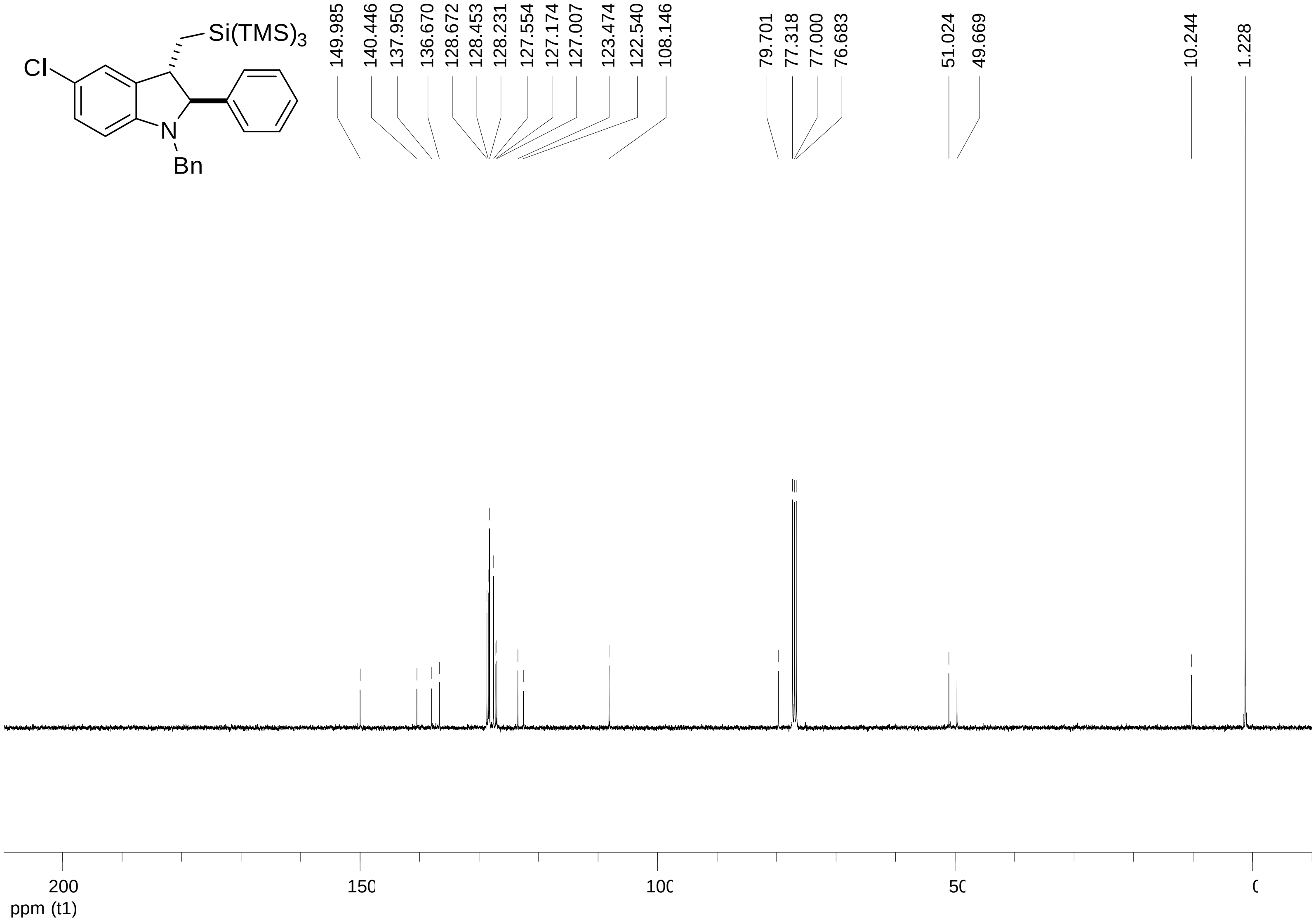
^{13}C NMR spectrum of **2g** (100 MHz, $CDCl_3$)



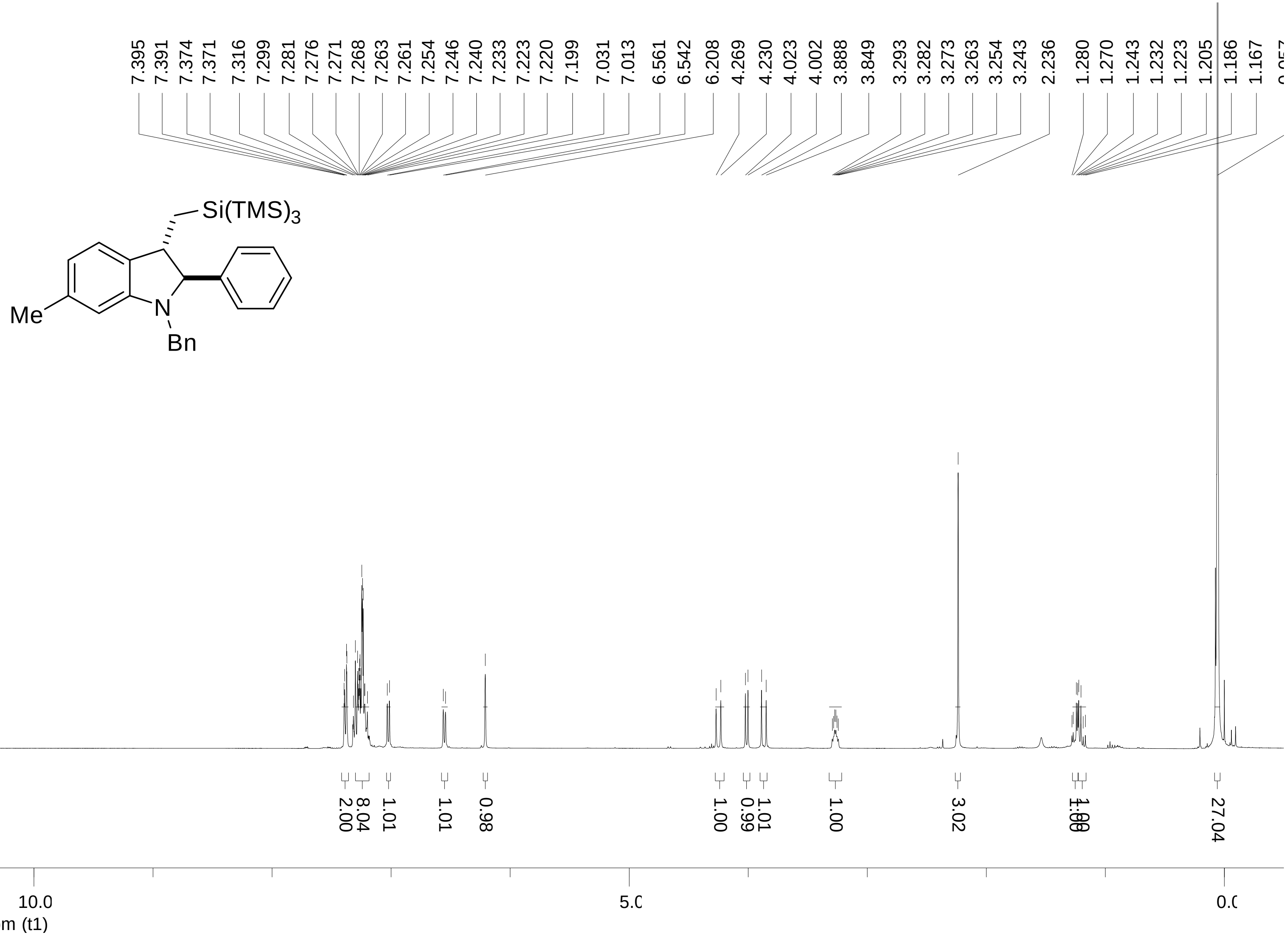
^{1}H NMR spectrum of **2h** (400 MHz, CDCl$_3$)



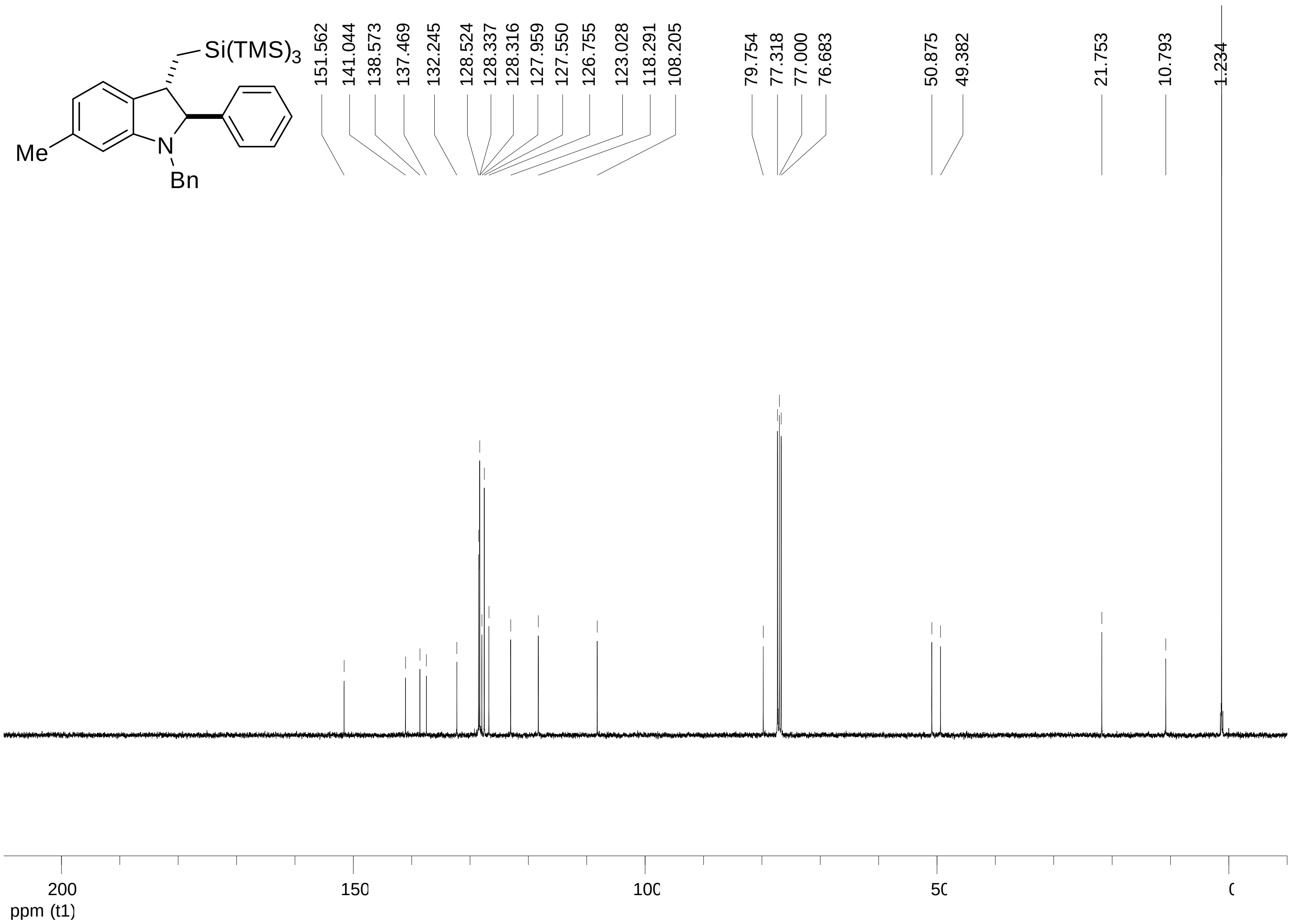
^{13}C NMR spectrum of **2h** (100 MHz, $CDCl_3$)



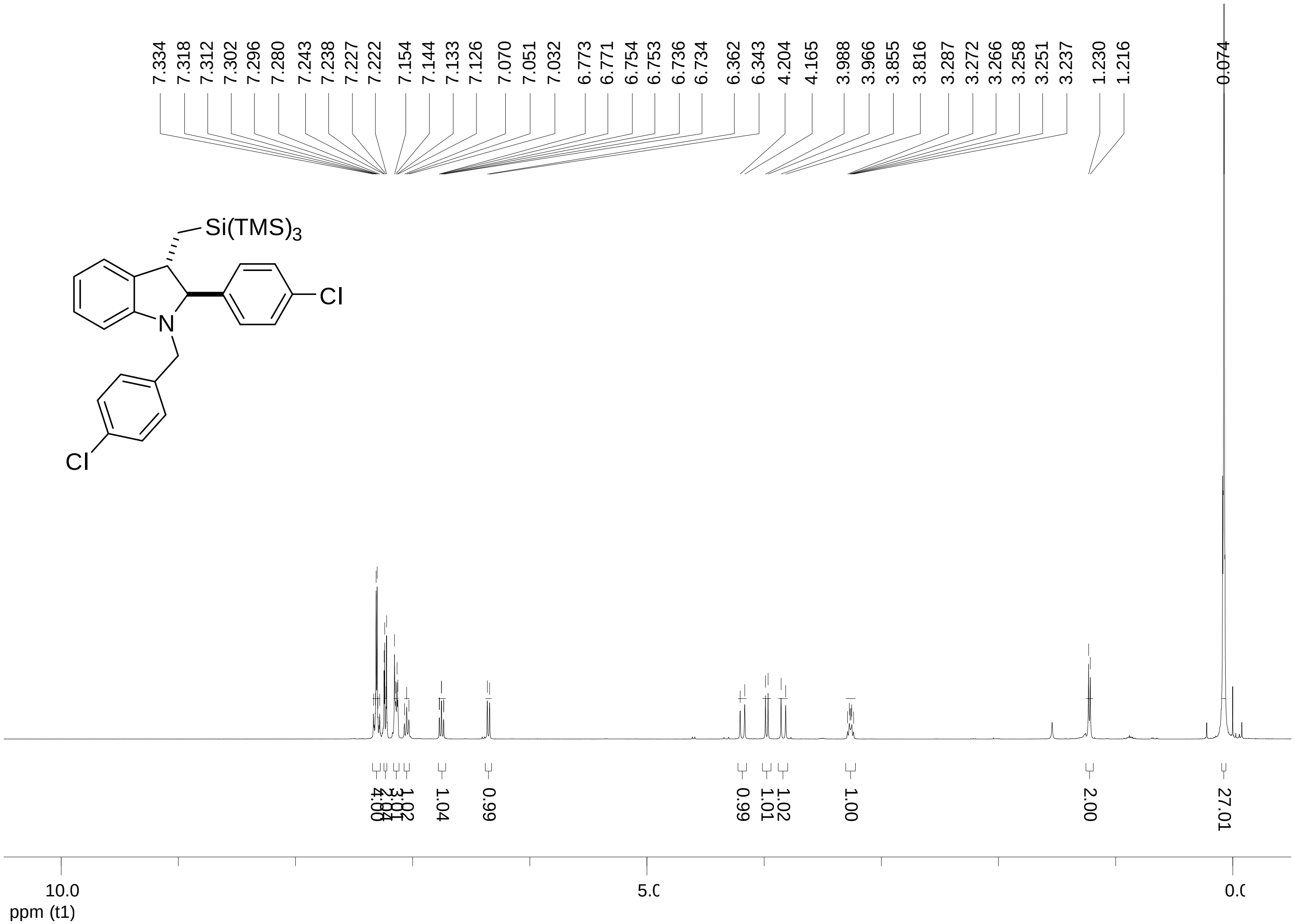
^{1}H NMR spectrum of **2i** (400 MHz, $CDCl_3$)



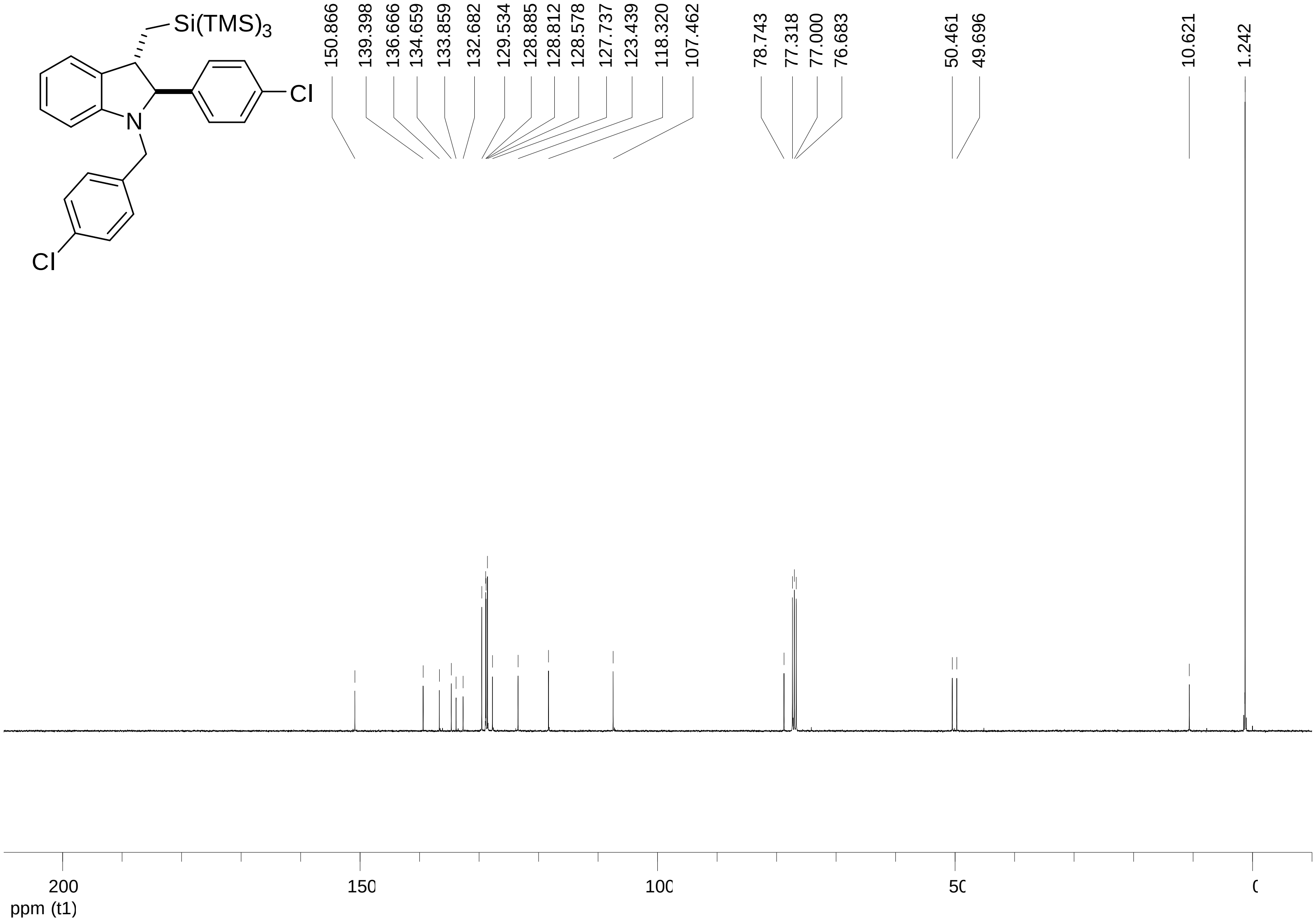
^{13}C NMR spectrum of **2i** (100 MHz, $CDCl_3$)



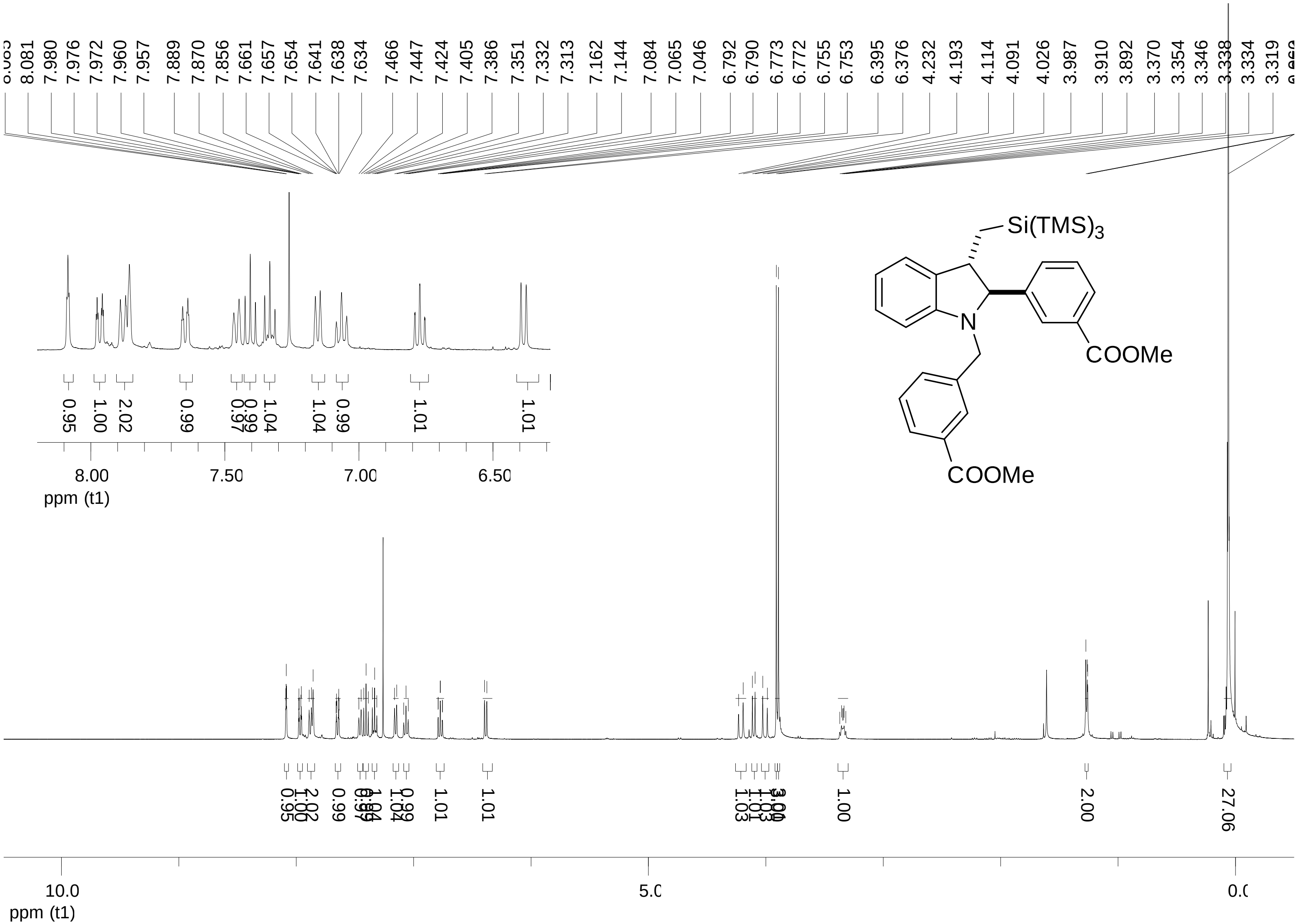
^{1}H NMR spectrum of **2j** (400 MHz, $CDCl_3$)



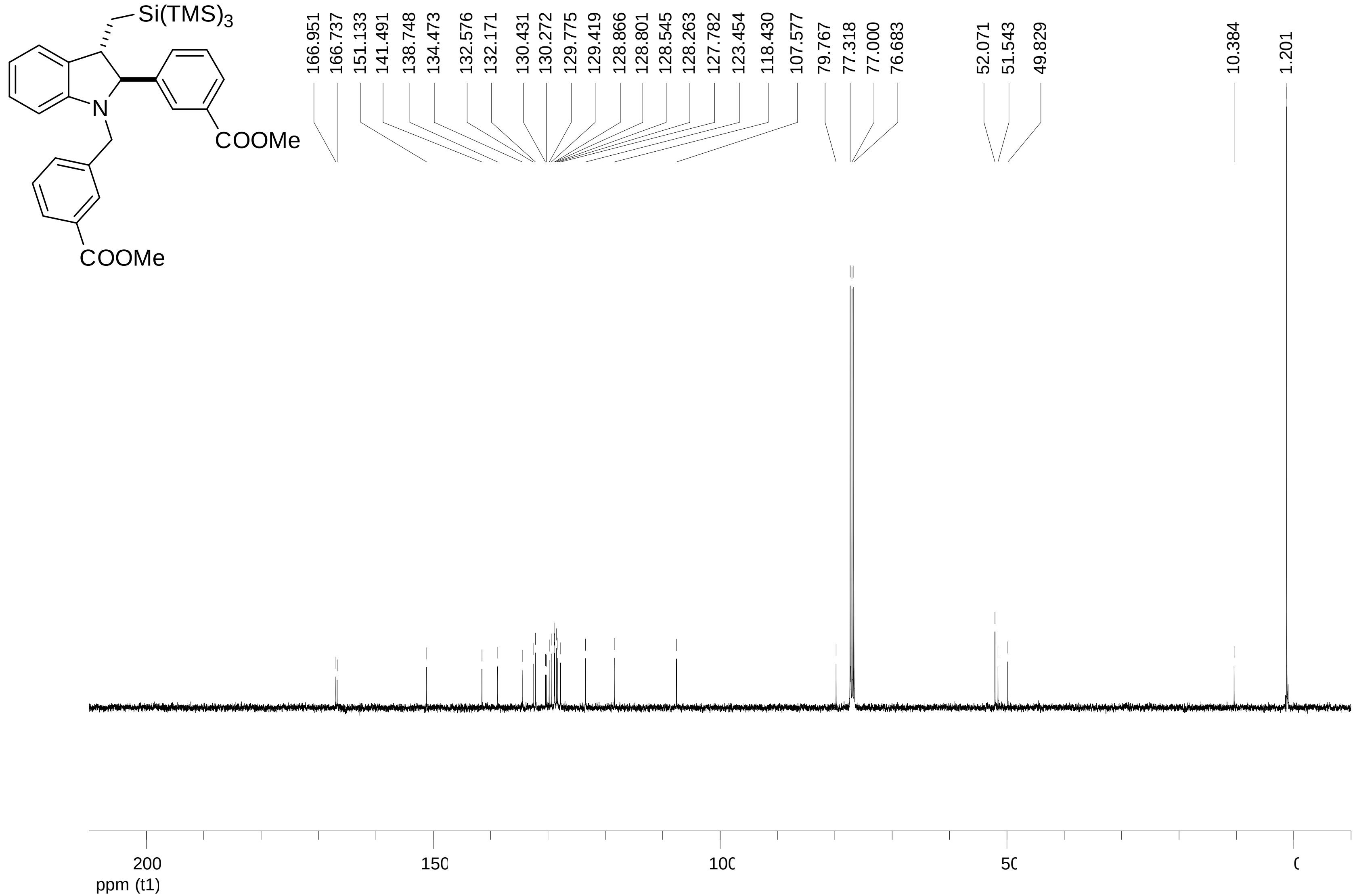
^{13}C NMR spectrum of **2j** (100 MHz, $CDCl_3$)



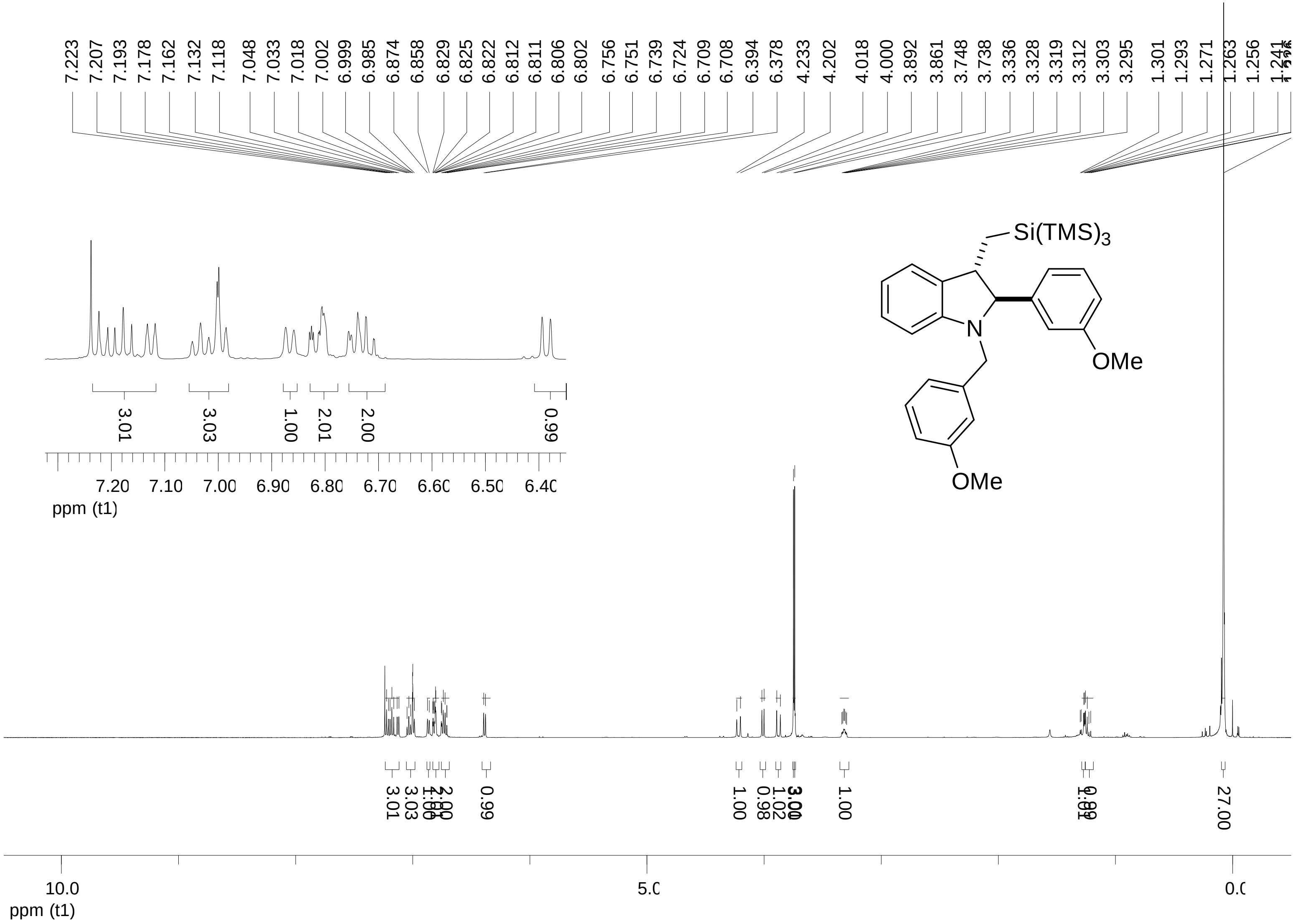
^{1}H NMR spectrum of **2k** (400 MHz, $CDCl_3$)



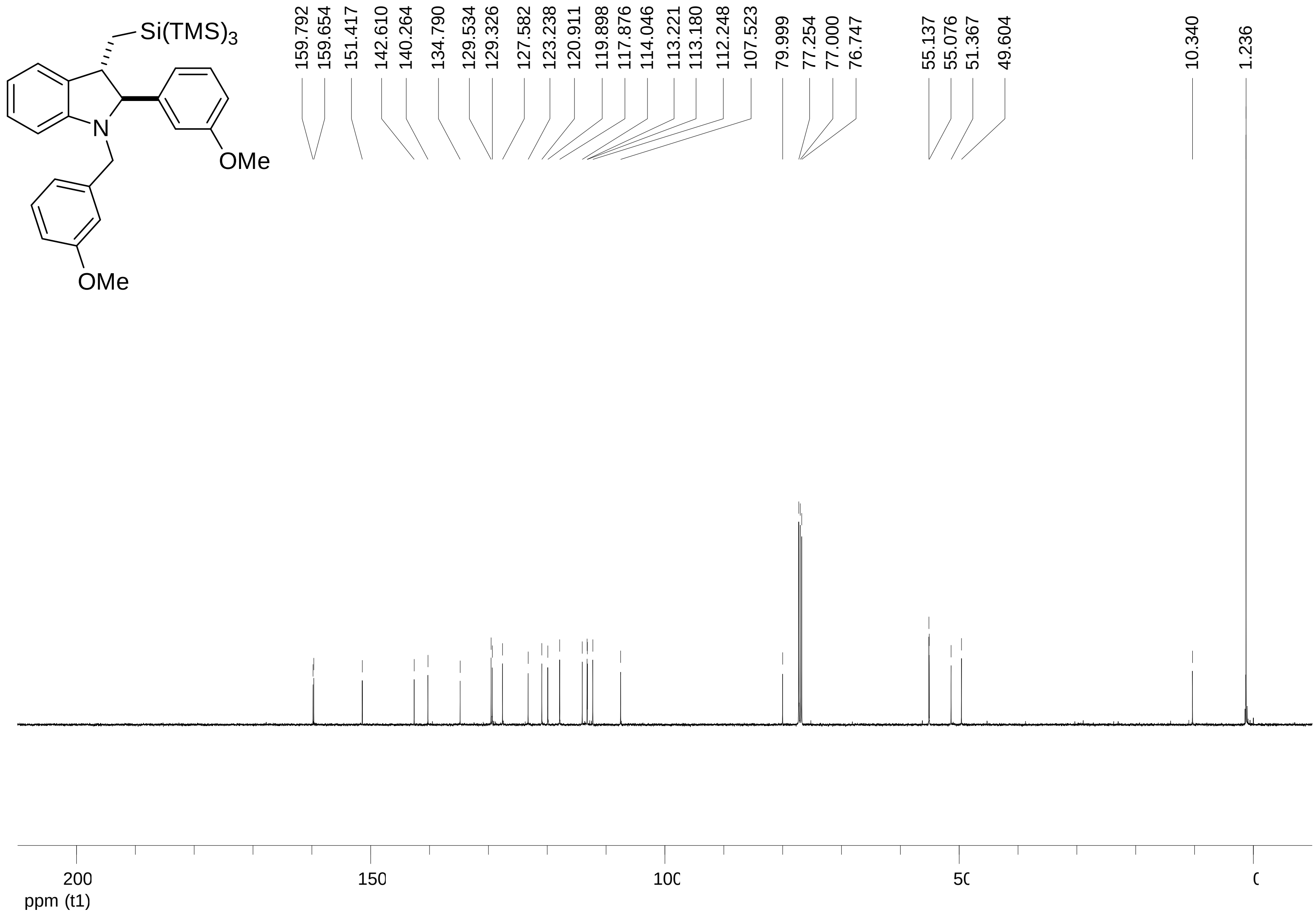
^{13}C NMR spectrum of **2k** (100 MHz, CDCl$_3$)



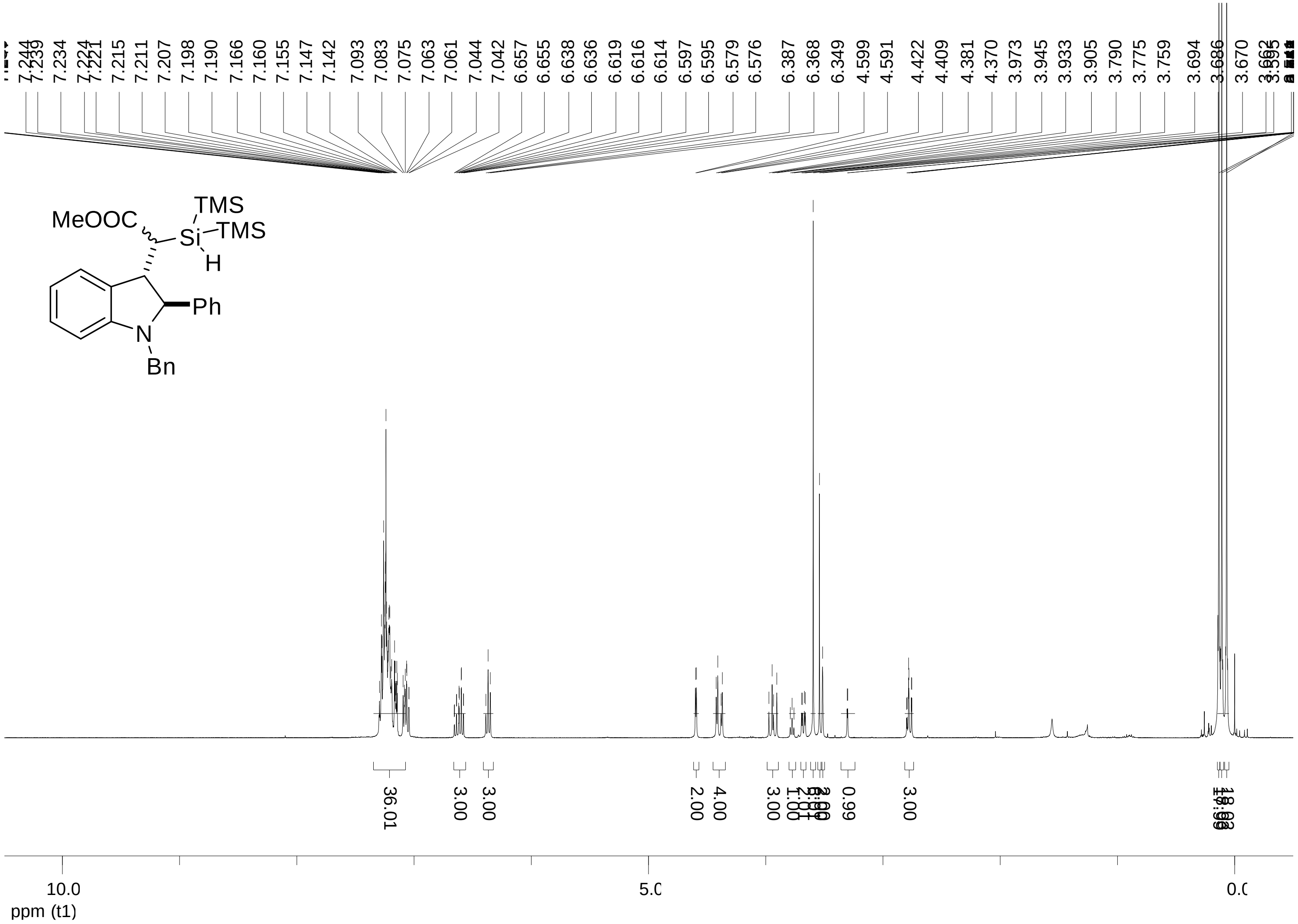
^{1}H NMR spectrum of **2l** (500 MHz, $CDCl_3$)



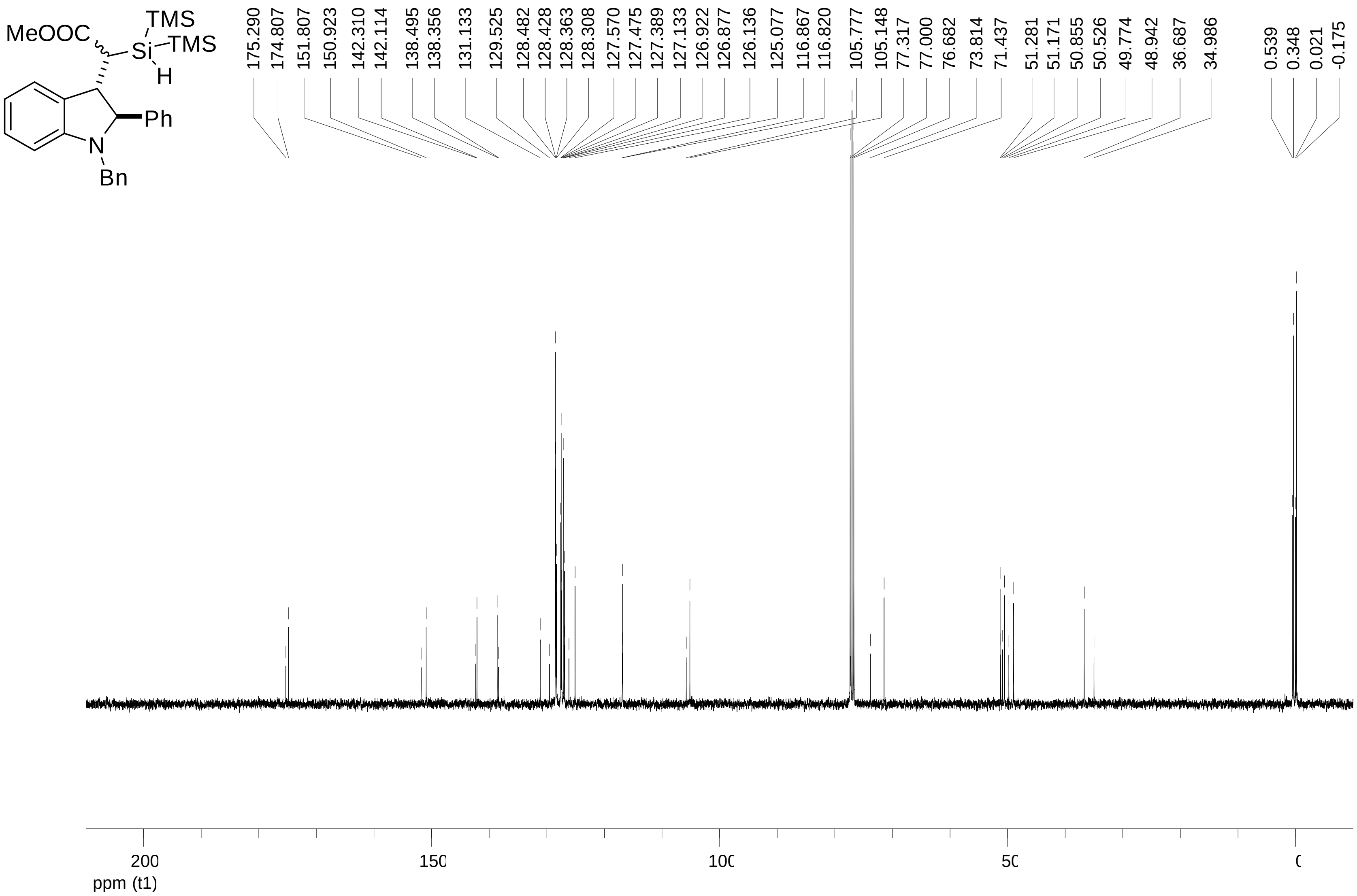
^{13}C NMR spectrum of **2l** (125 MHz, CDCl$_3$)



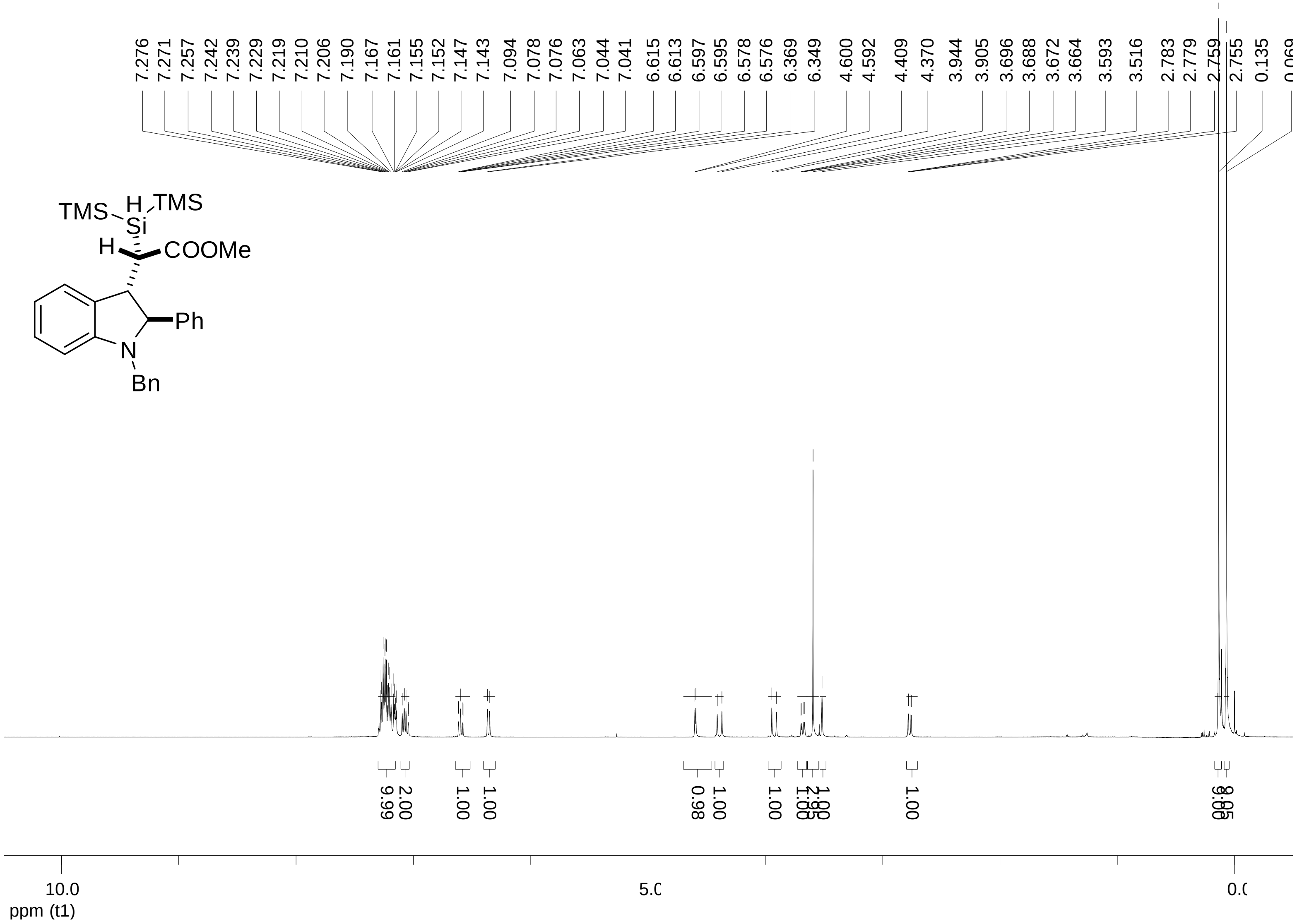
^{1}H NMR spectrum of **3a** (400 MHz, $CDCl_3$)



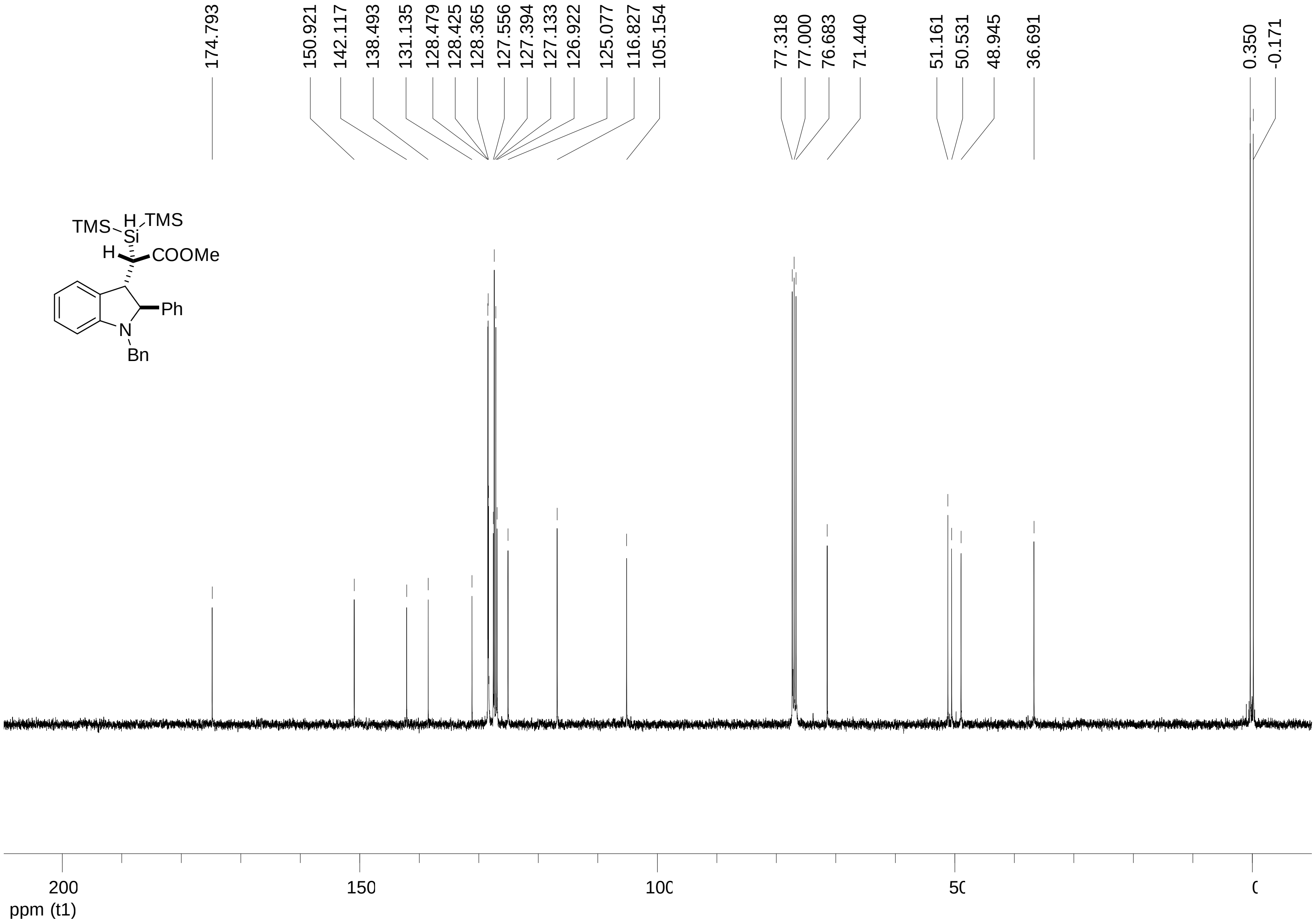
^{13}C NMR spectrum of **3a** (100 MHz, CDCl$_3$)



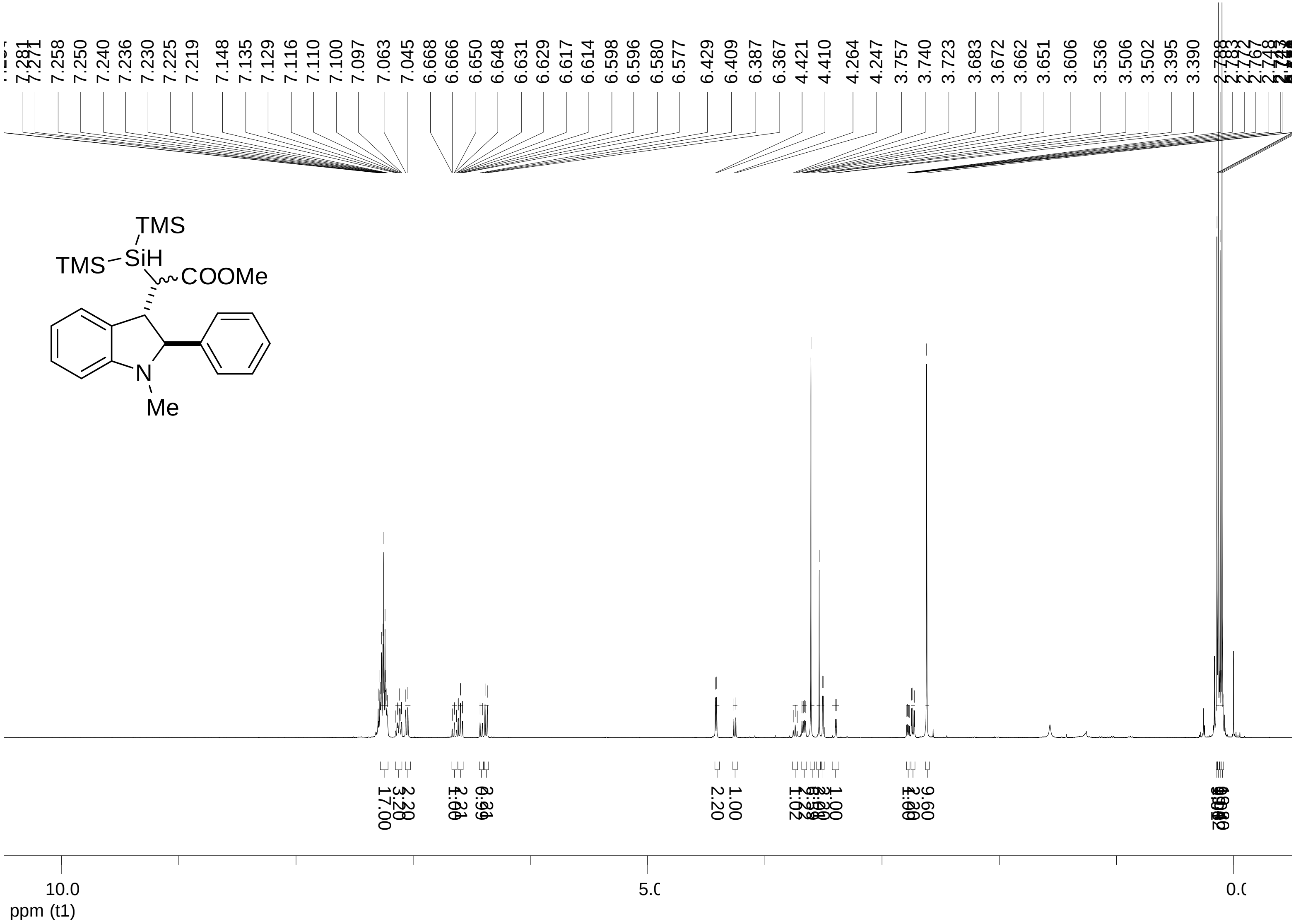
^{1}H NMR spectrum of **3aa** (400 MHz, $CDCl_3$)



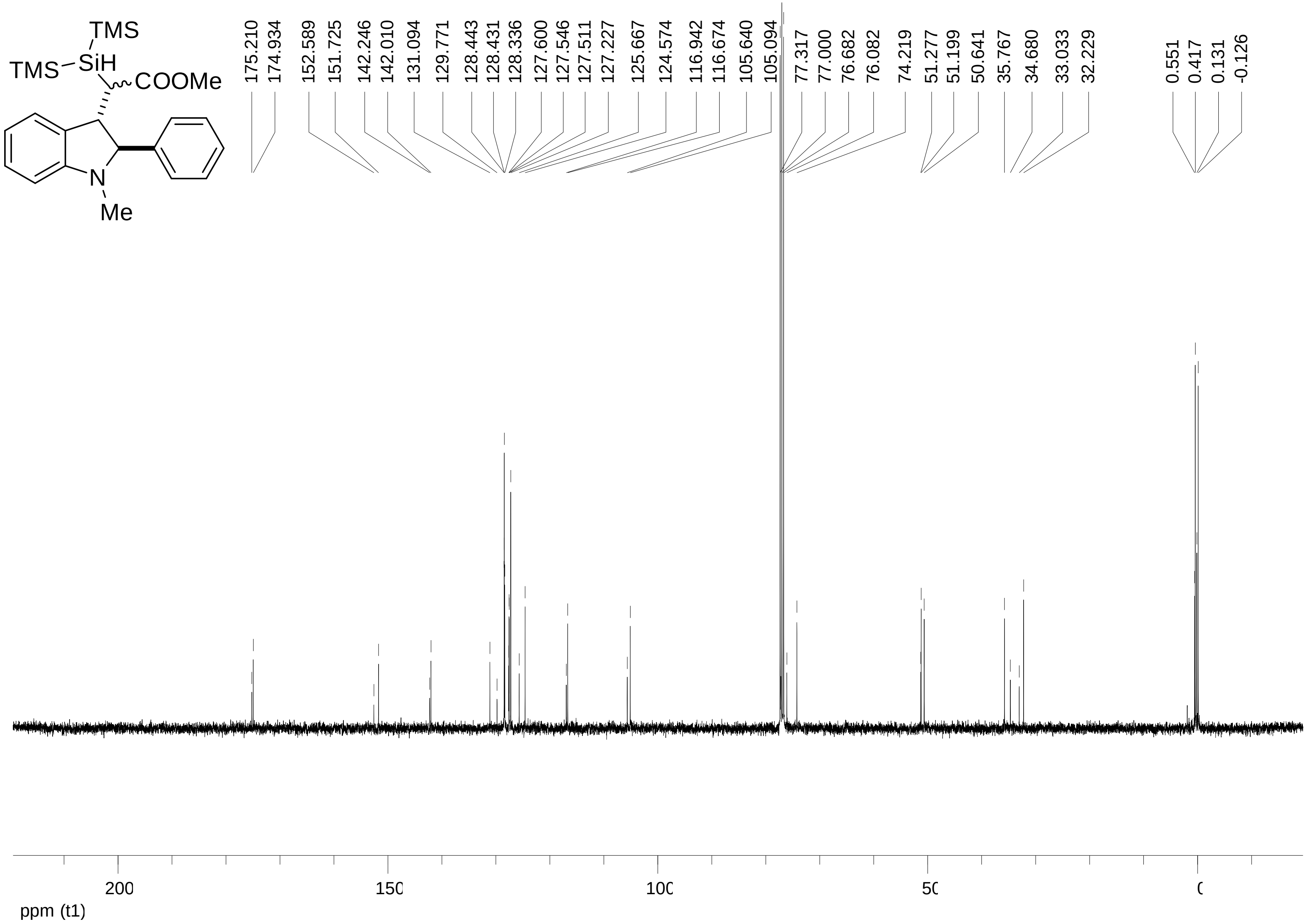
^{13}C NMR spectrum of **3aa** (100 MHz, $CDCl_3$)



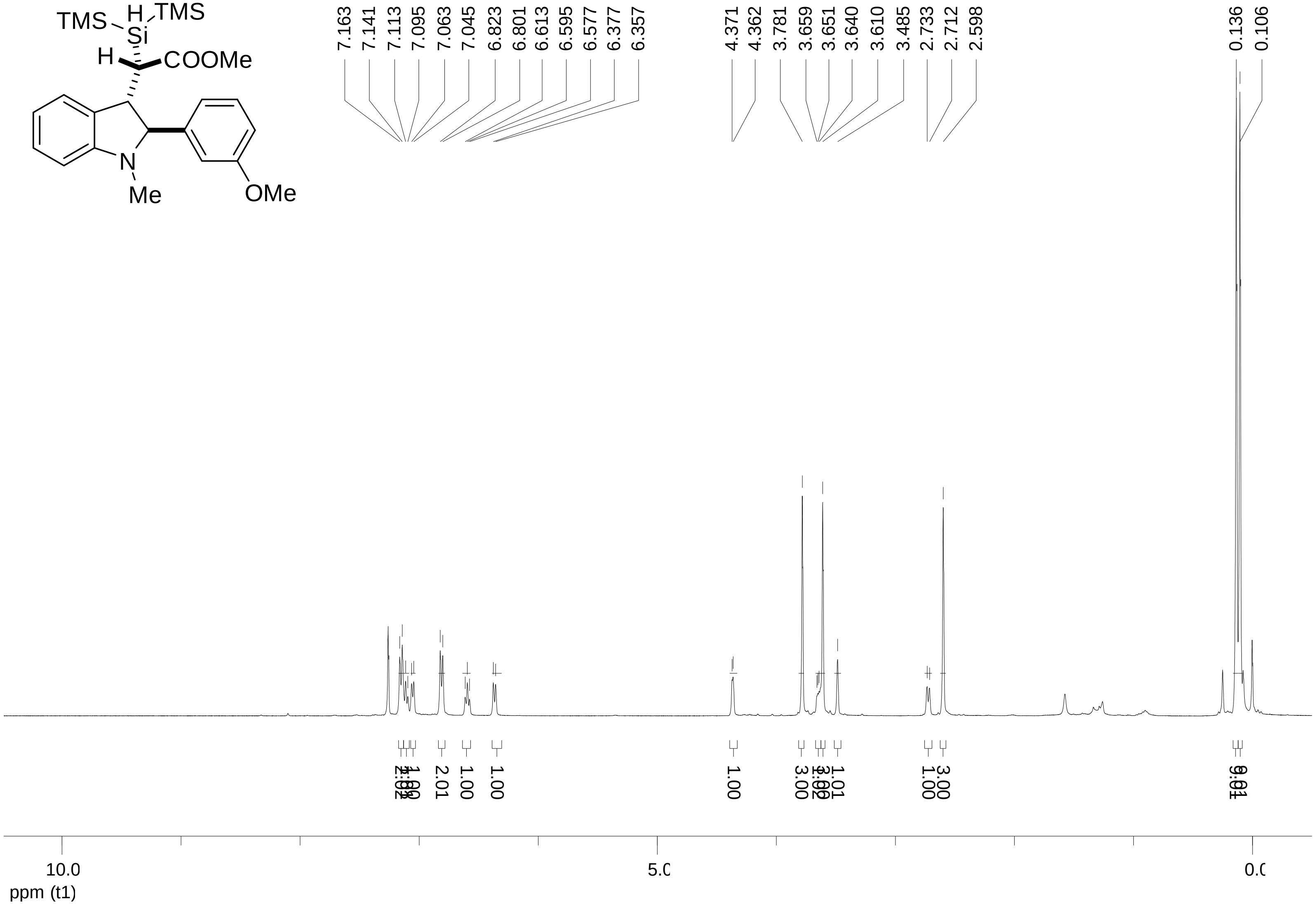
^{1}H NMR spectrum of **3b** (400 MHz, $CDCl_3$)



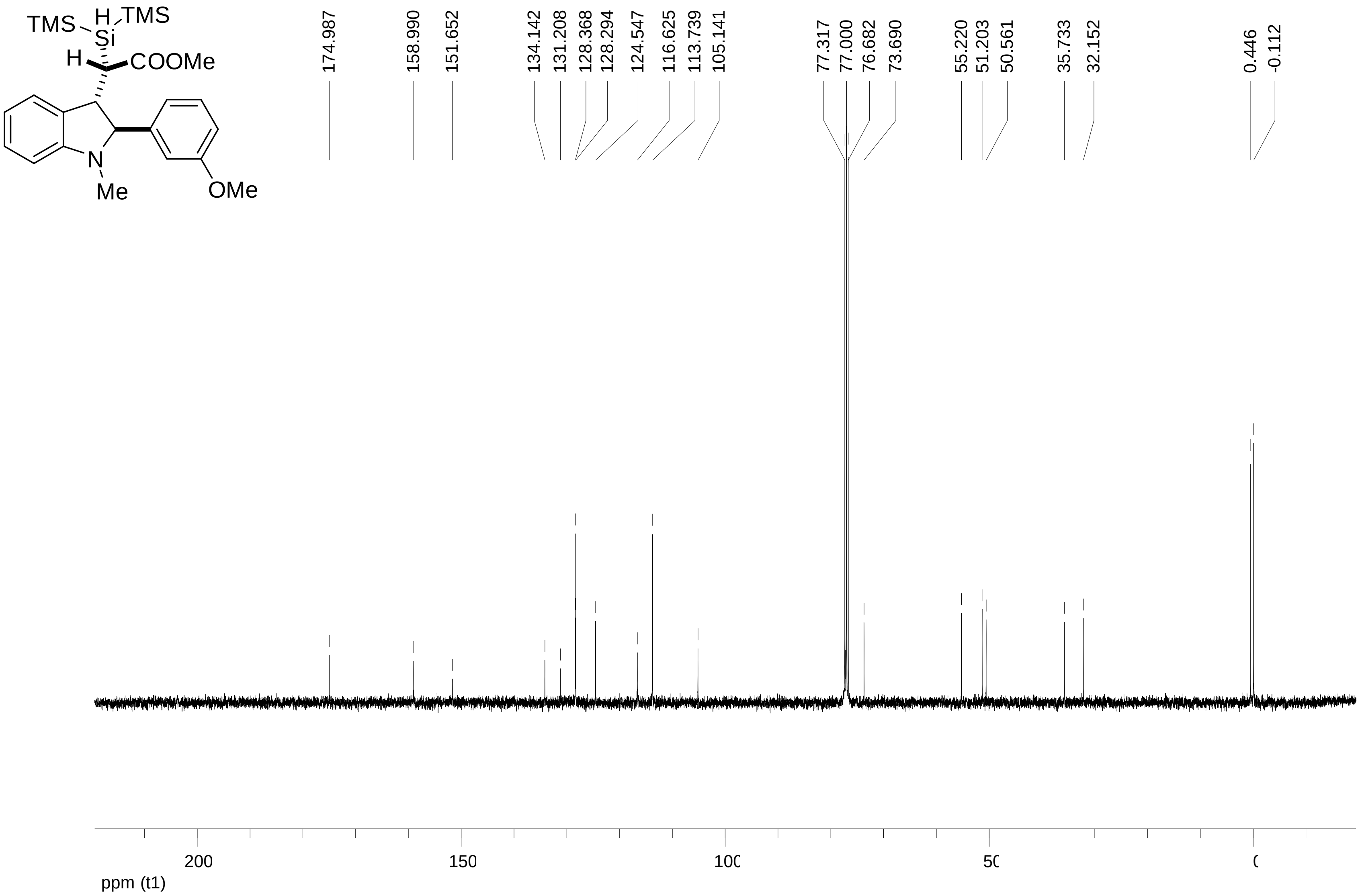
^{13}C NMR spectrum of **3b** (100 MHz, $CDCl_3$)



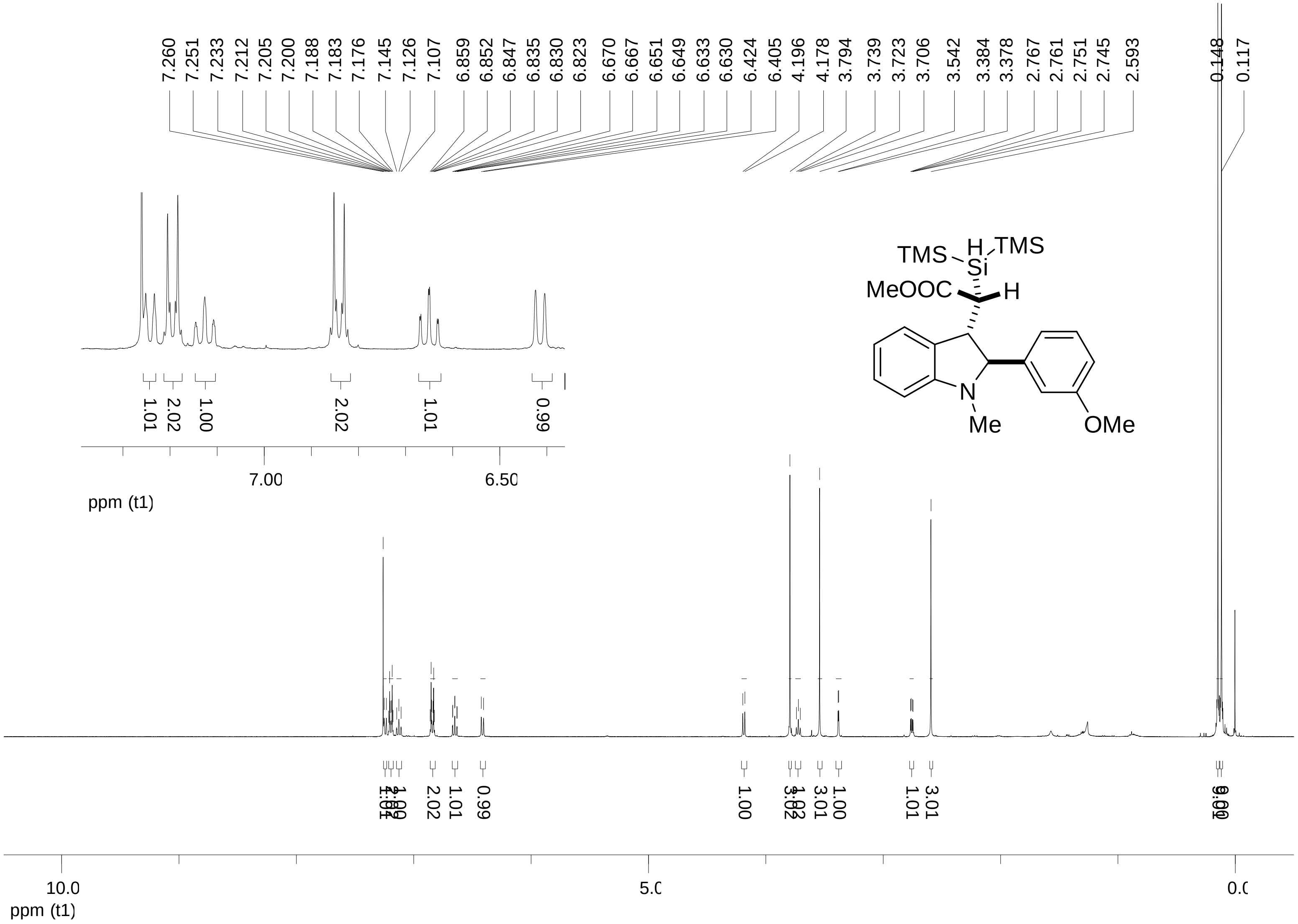
^{1}H NMR spectrum of **3c** diastereomer 1 (500 MHz, CDCl$_3$)



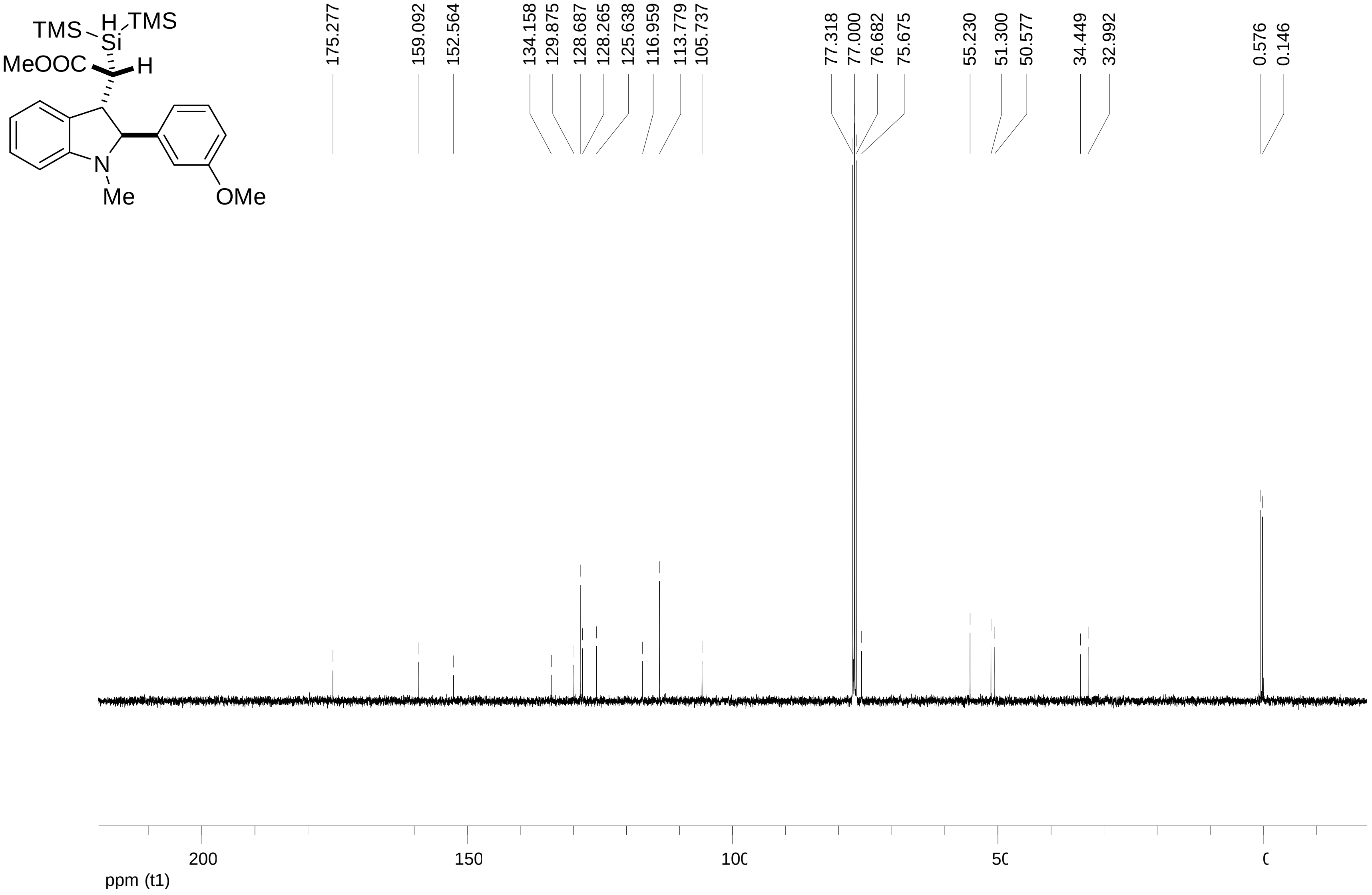
^{13}C NMR spectrum of **3c** diastereomer 1 (125 MHz, $CDCl_3$)



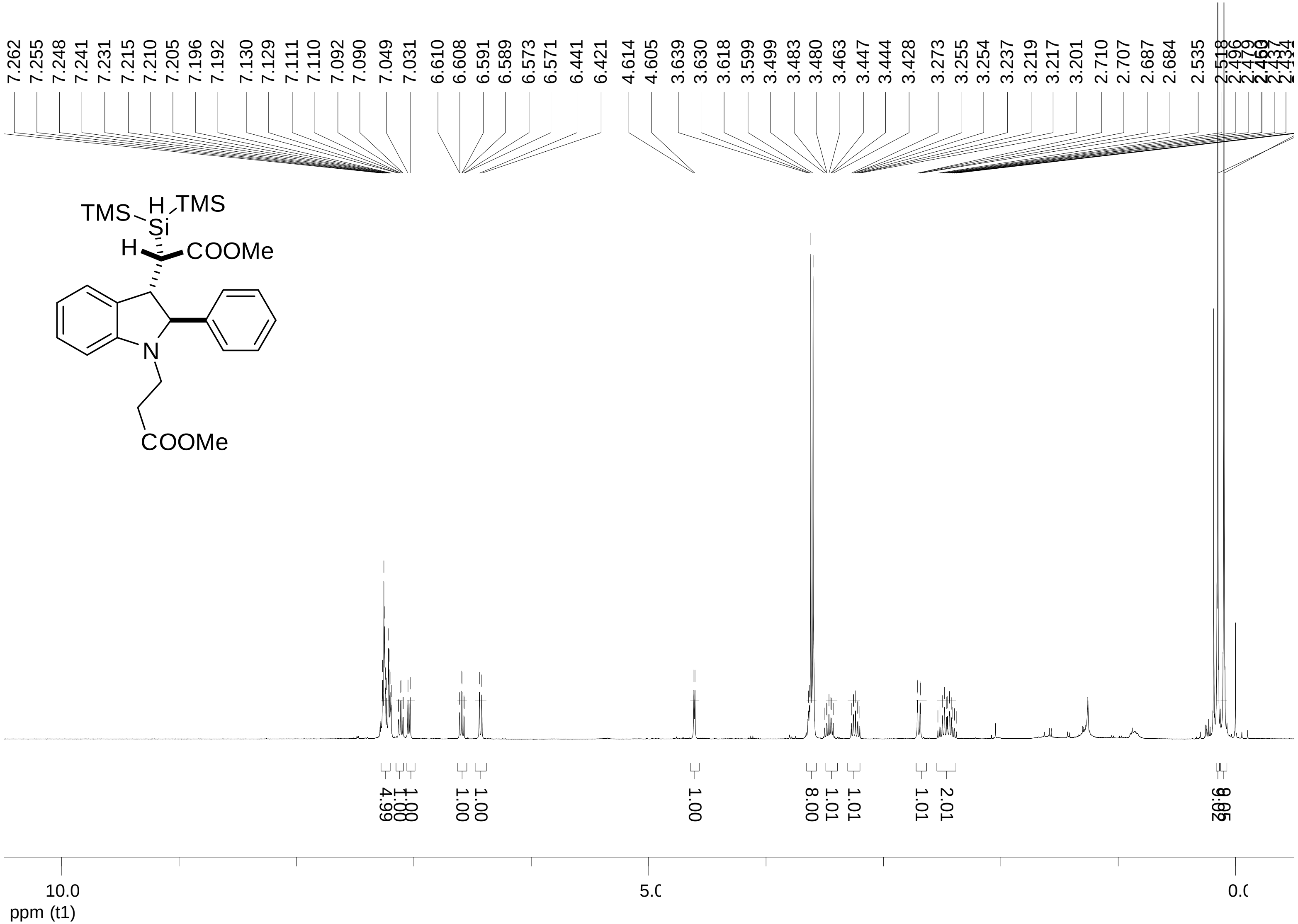
^{1}H NMR spectrum of **3c** diastereomer 2 (400 MHz, CDCl$_3$)



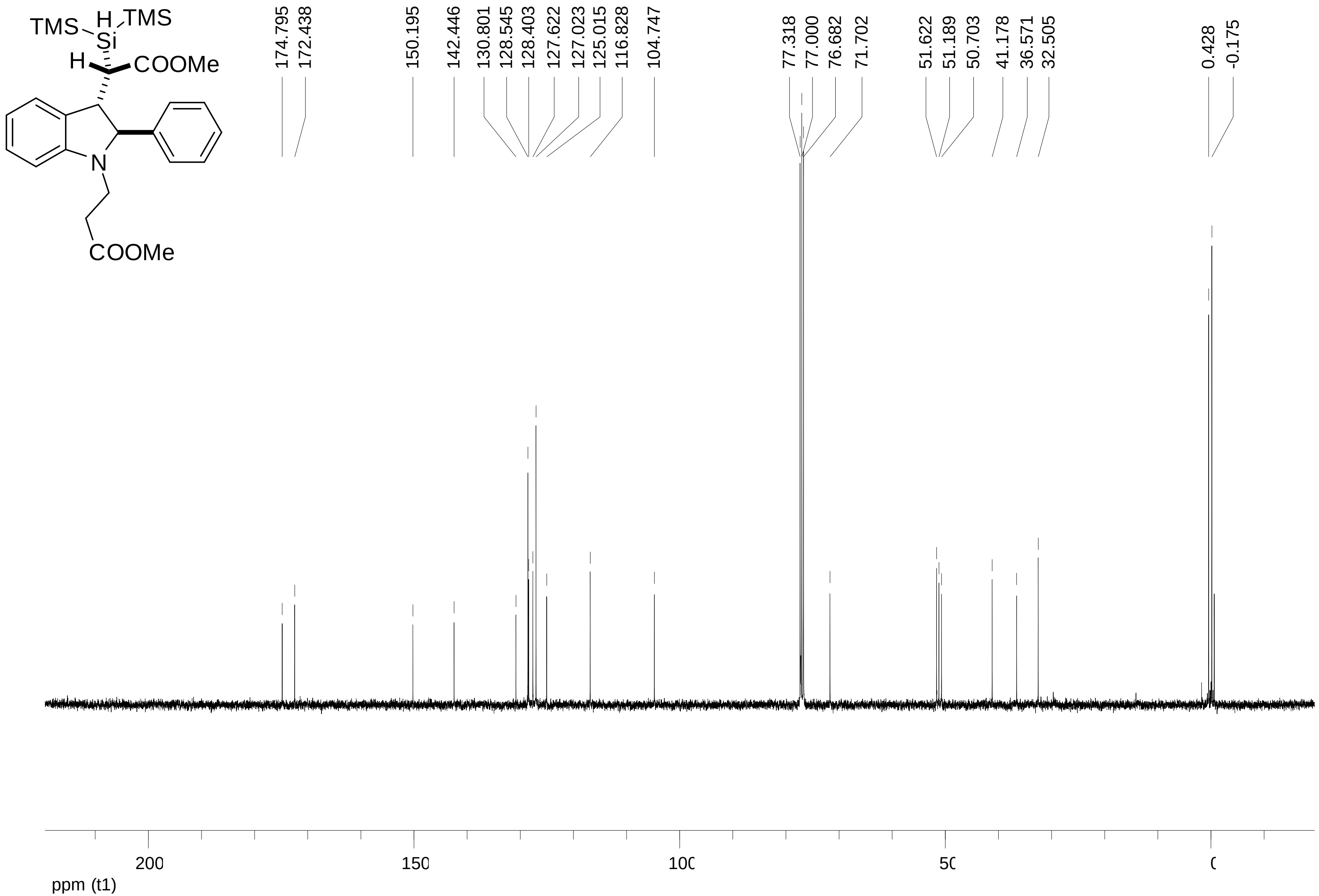
^{13}C NMR spectrum of **3c** diastereomer 2 (100 MHz, CDCl$_3$)



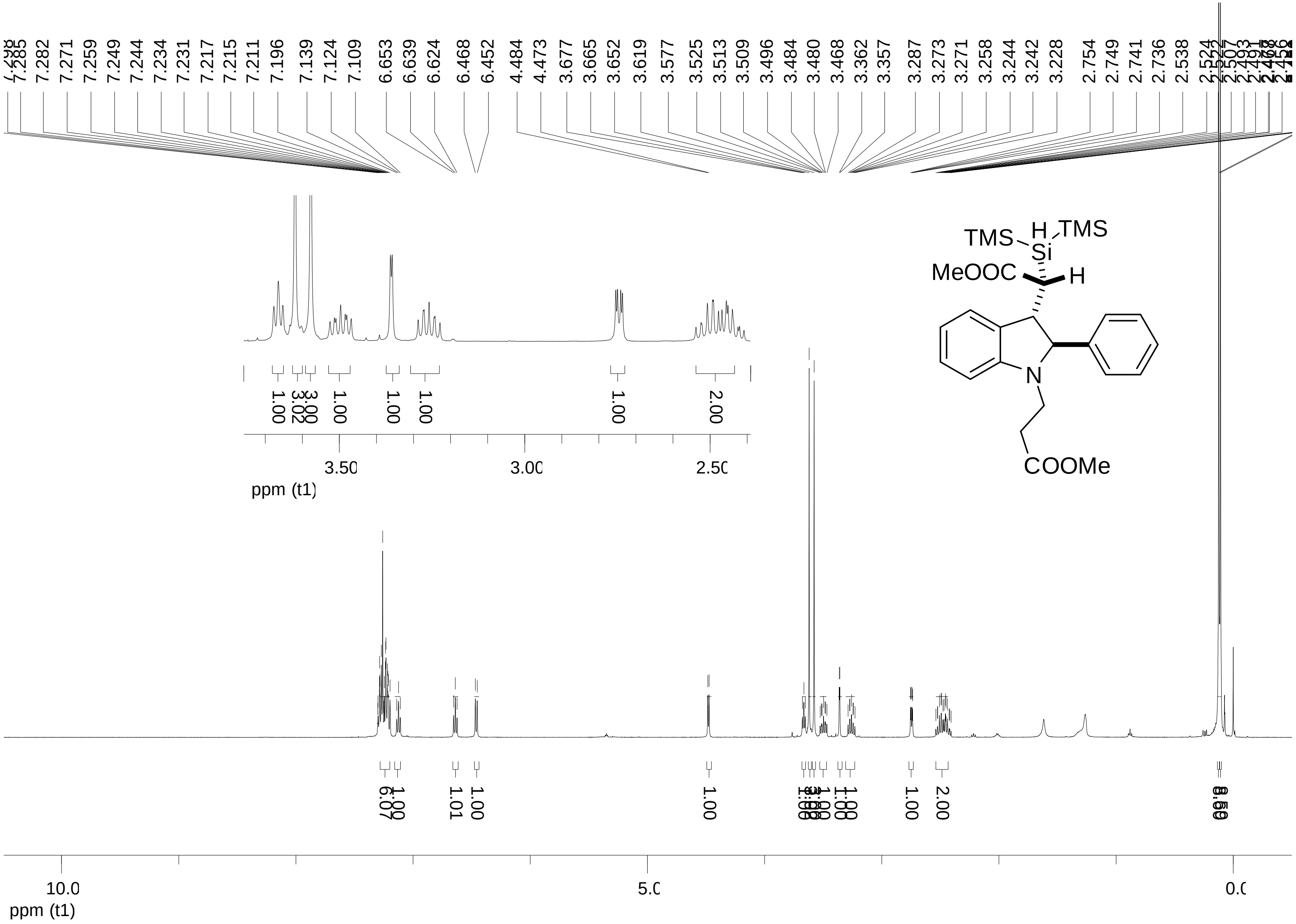
^{1}H NMR spectrum of **3d** diastereomer 1 (400 MHz, $CDCl_3$)



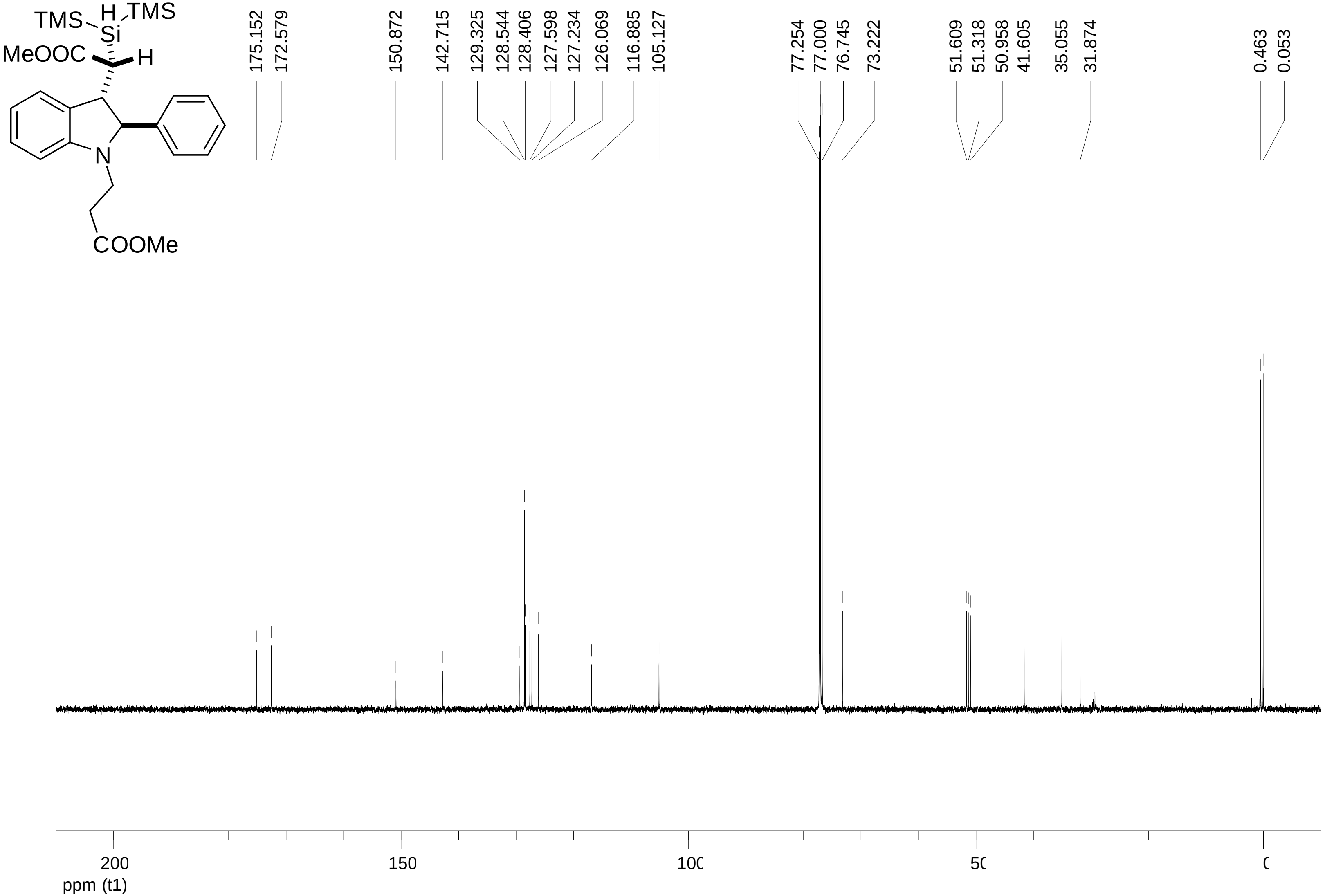
^{13}C NMR spectrum of **3d** diastereomer 1 (100 MHz, $CDCl_3$)



^{1}H NMR spectrum of **3d** diastereomer 2 (500 MHz, $CDCl_3$)



^{13}C NMR spectrum of **3d** diastereomer 2 (125 MHz, CDCl$_3$)



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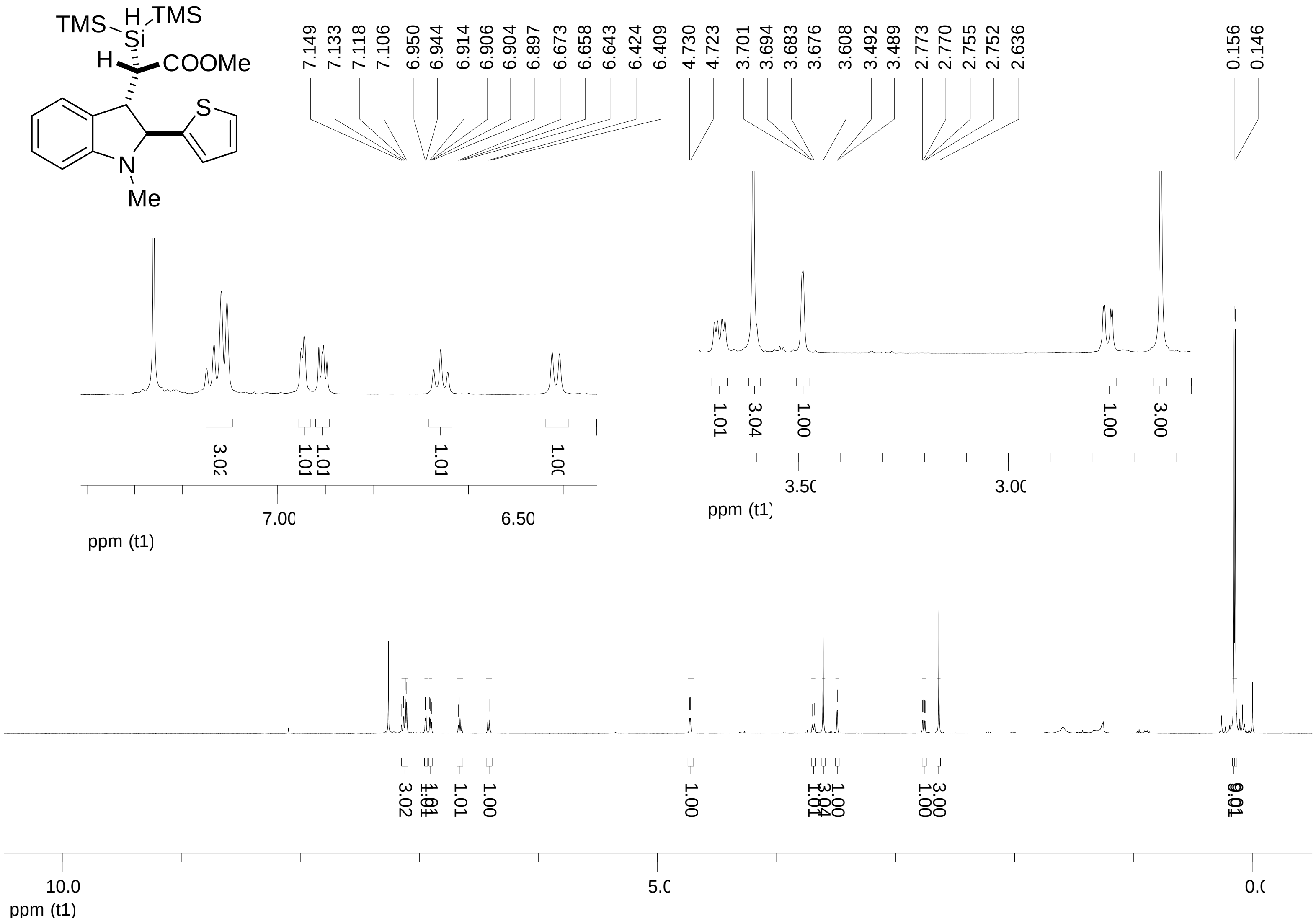
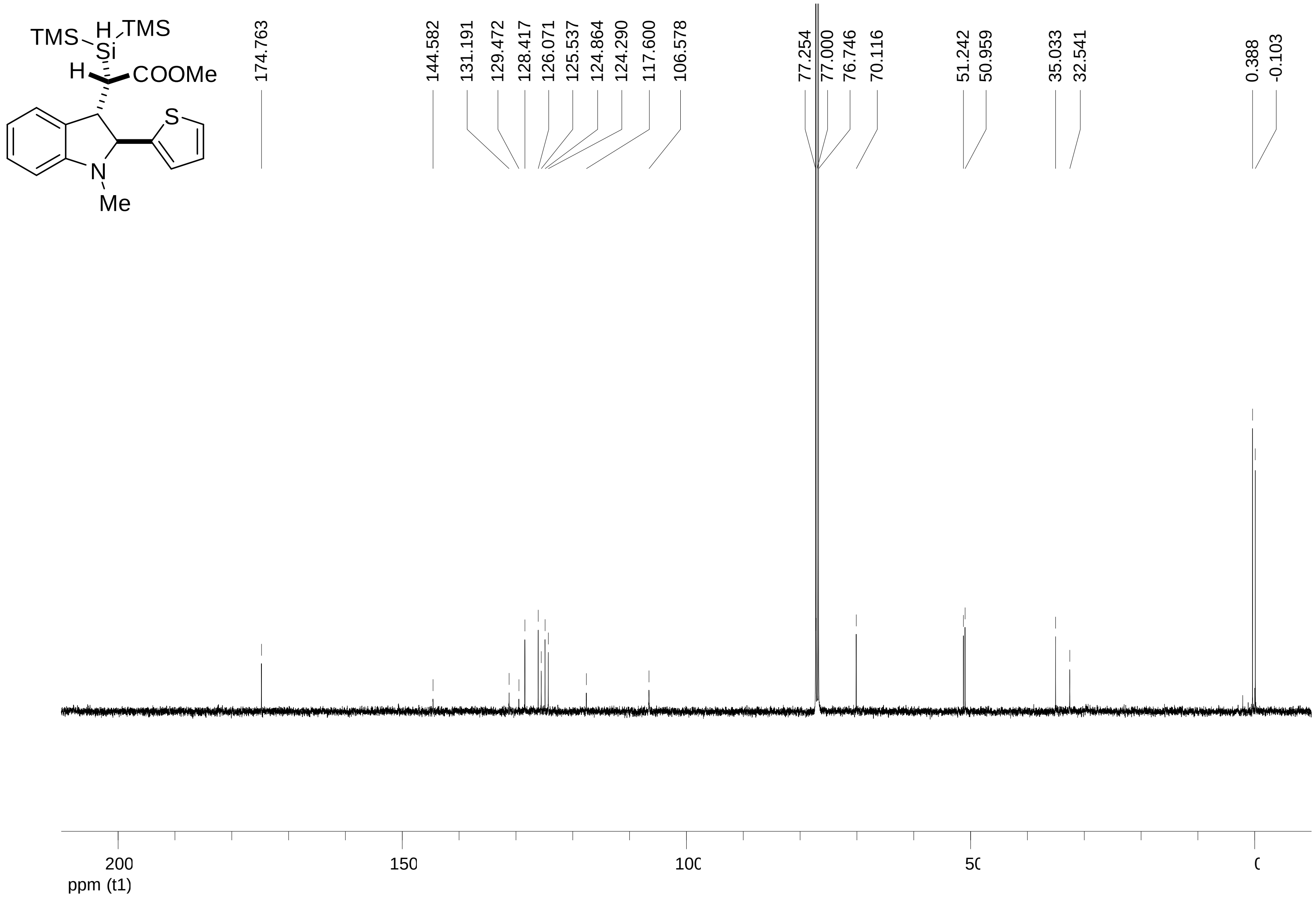
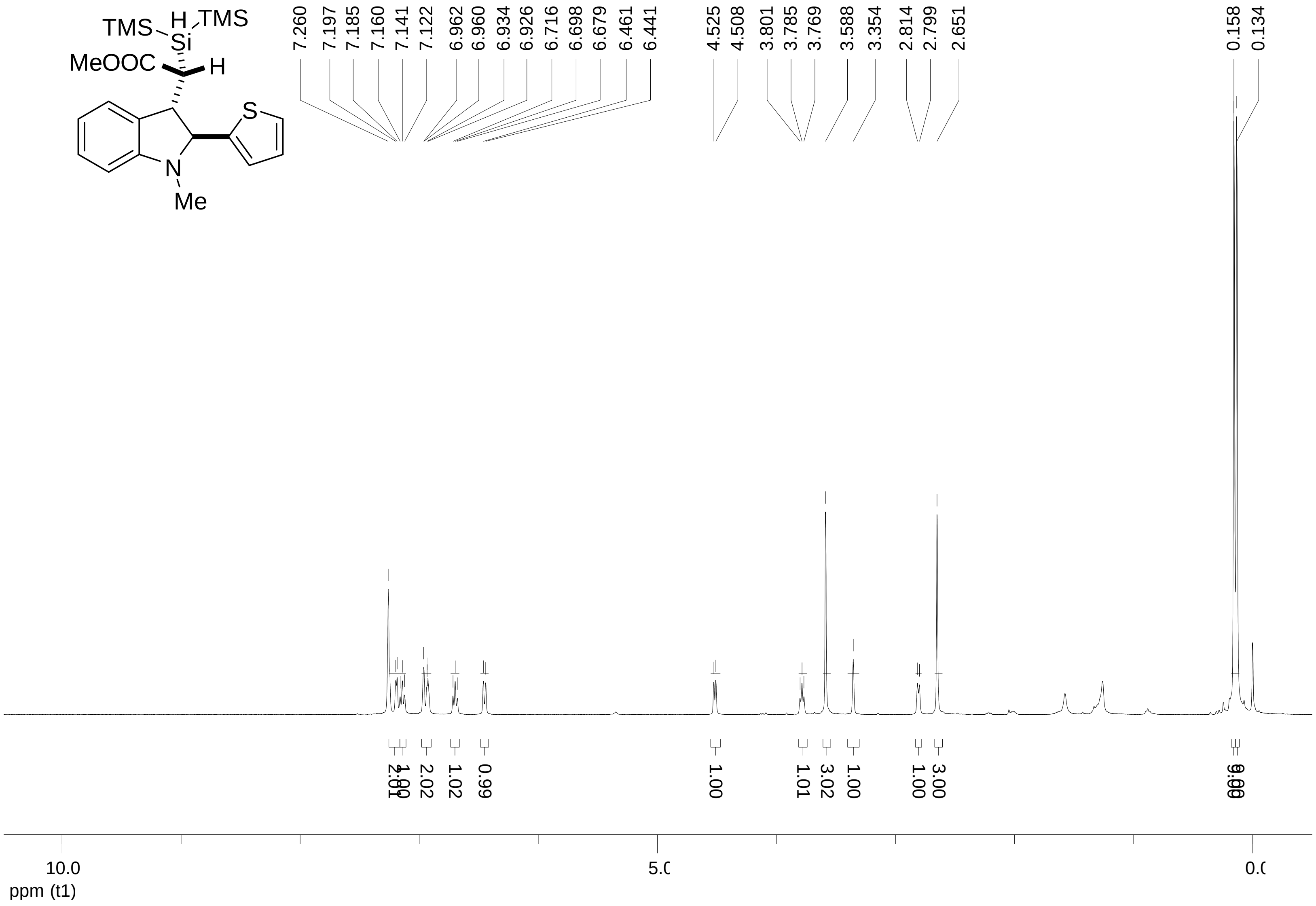


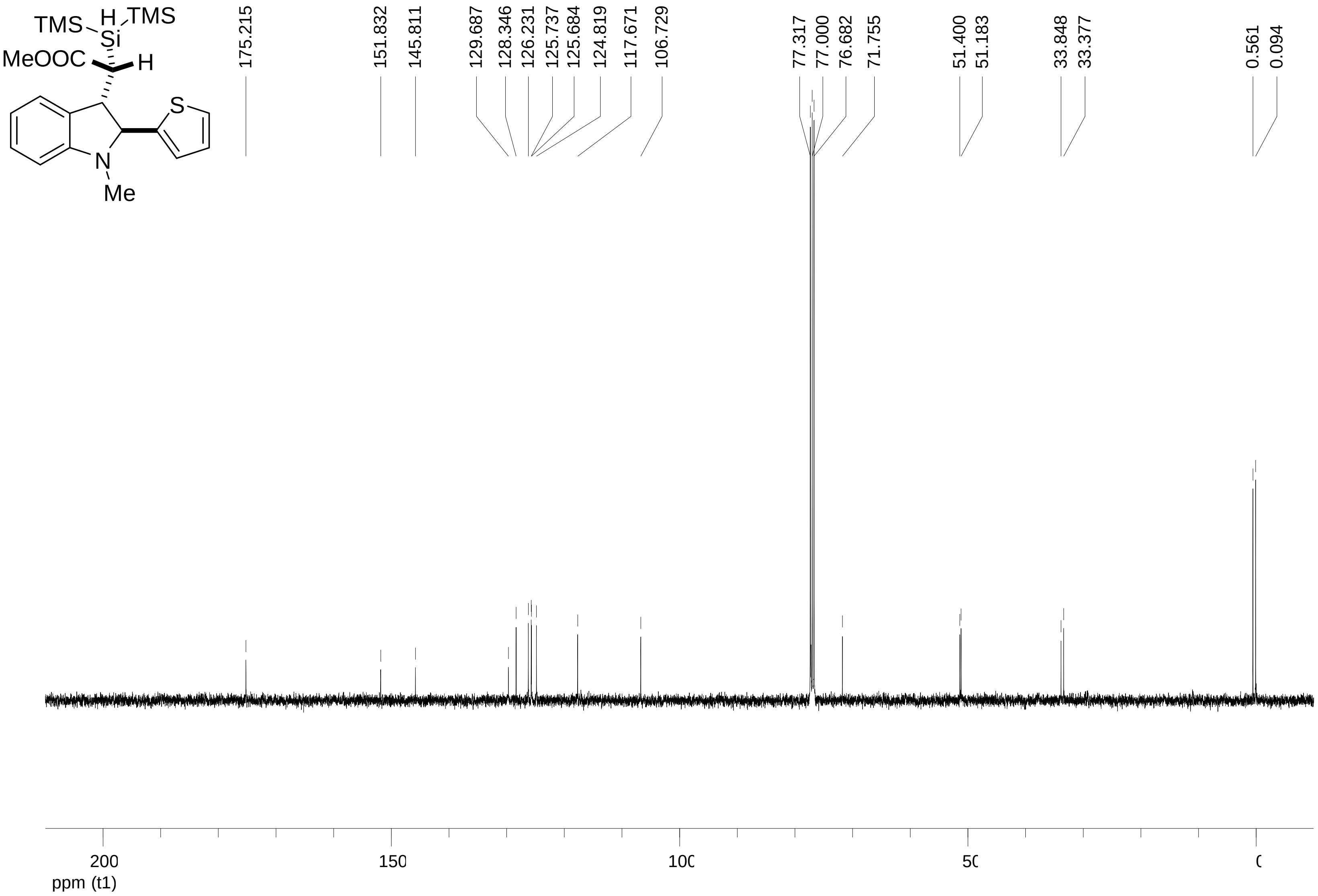
^{13}C NMR spectrum of **3e** diastereomer 1 (125 MHz, $CDCl_3$)



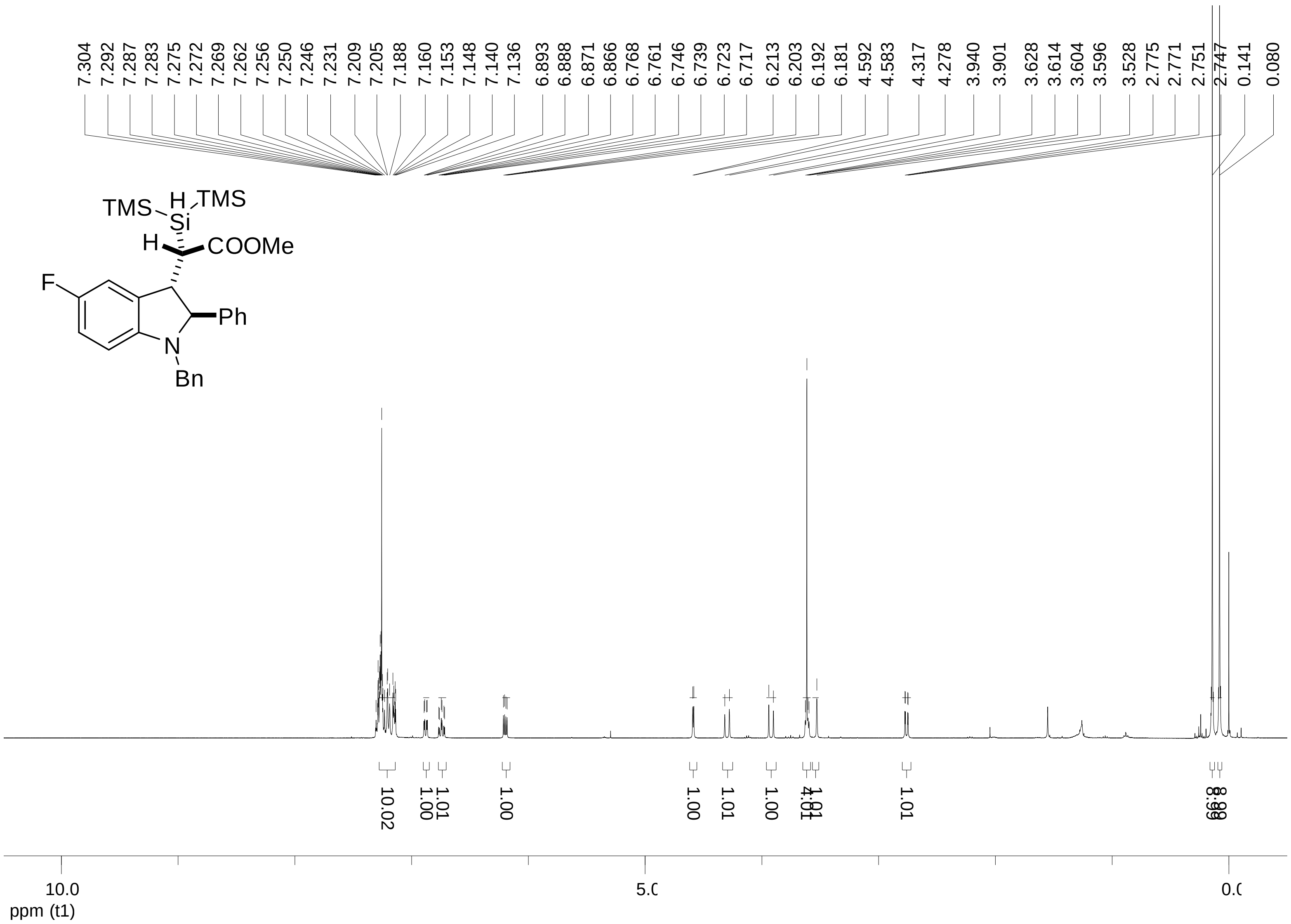
^{1}H NMR spectrum of **3e** diastereomer 2 (400 MHz, $CDCl_3$)



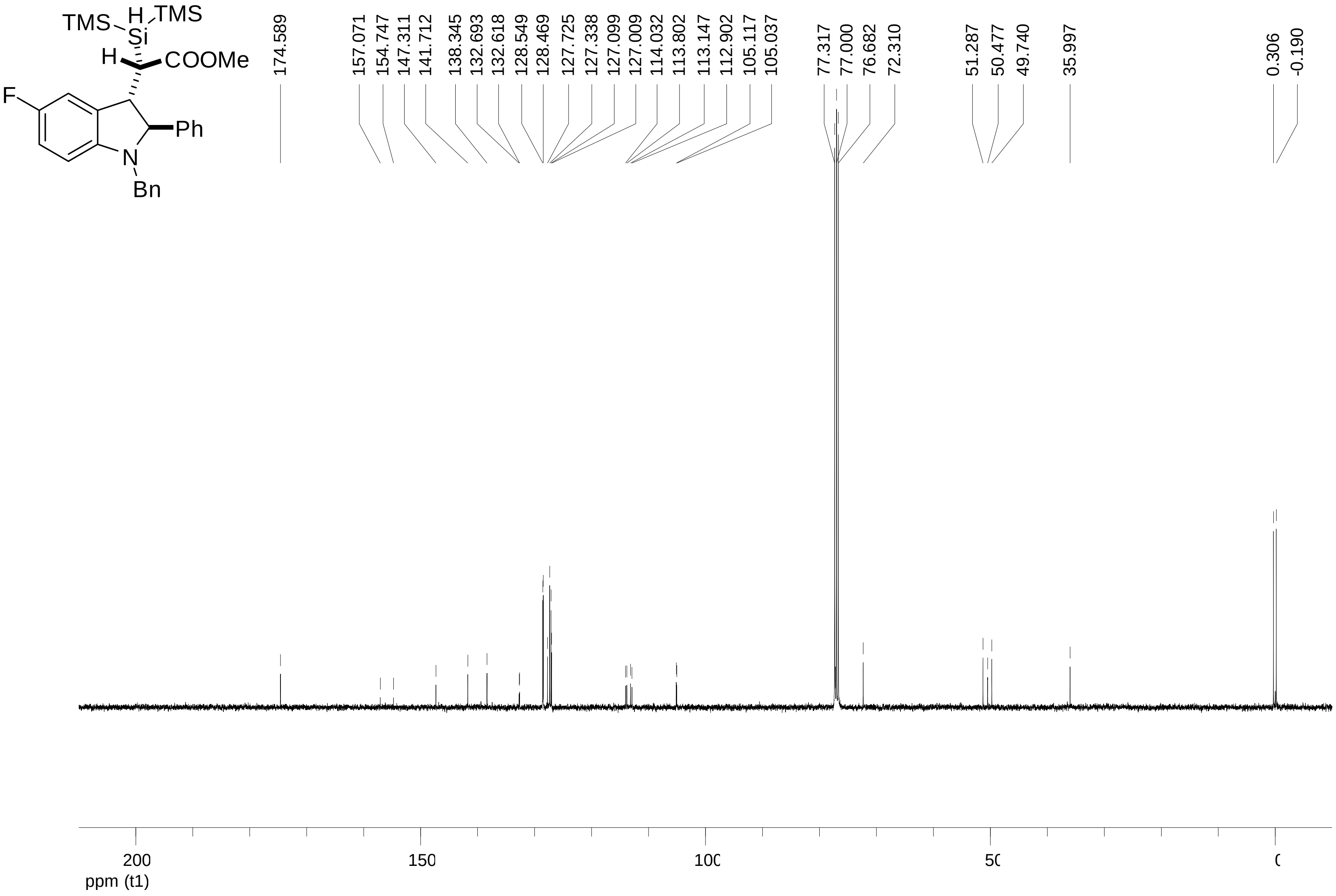
^{13}C NMR spectrum of **3e** diastereomer 2 (100 MHz, $CDCl_3$)



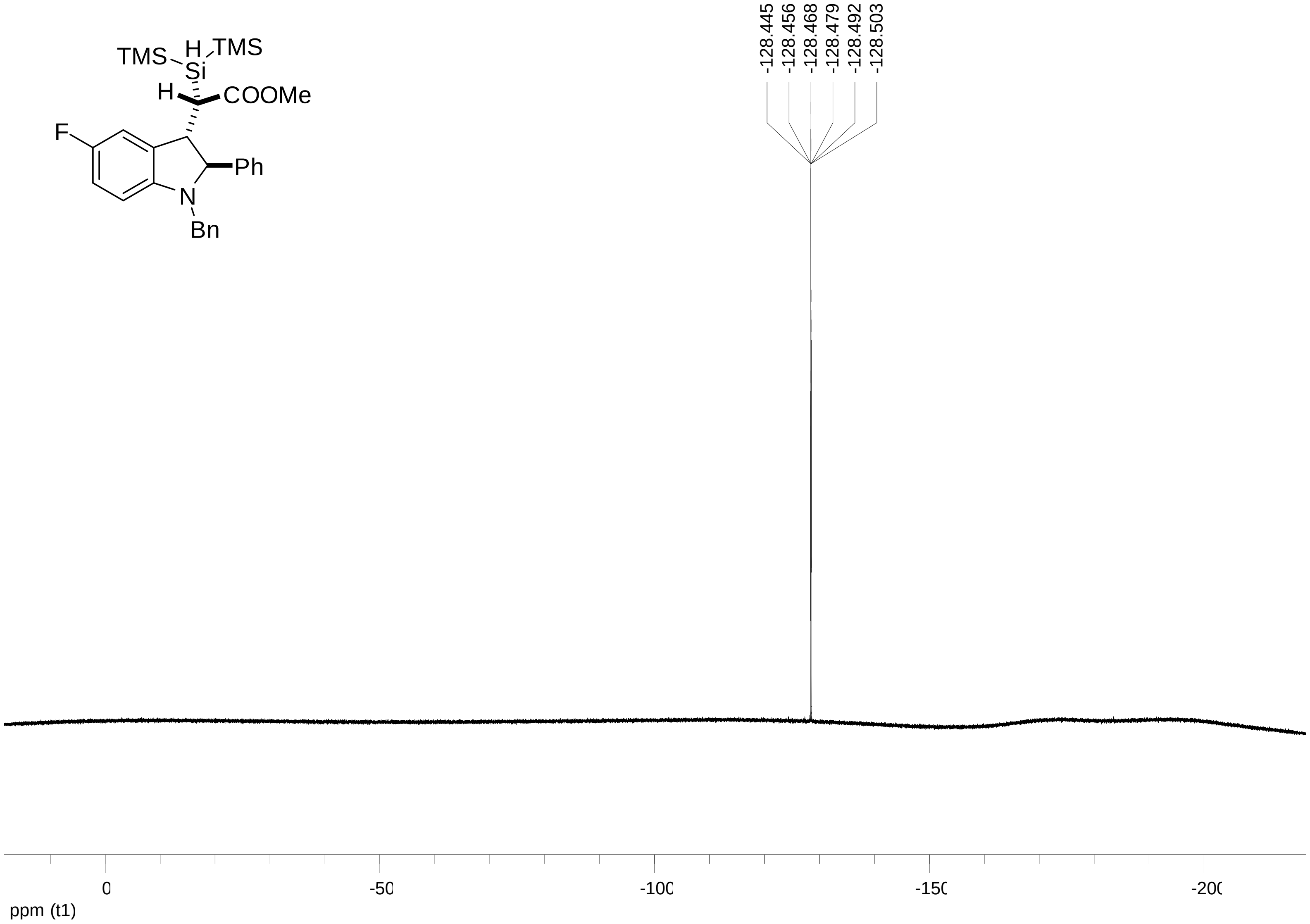
^{1}H NMR spectrum of **3f** diastereomer 1 (400 MHz, $CDCl_3$)



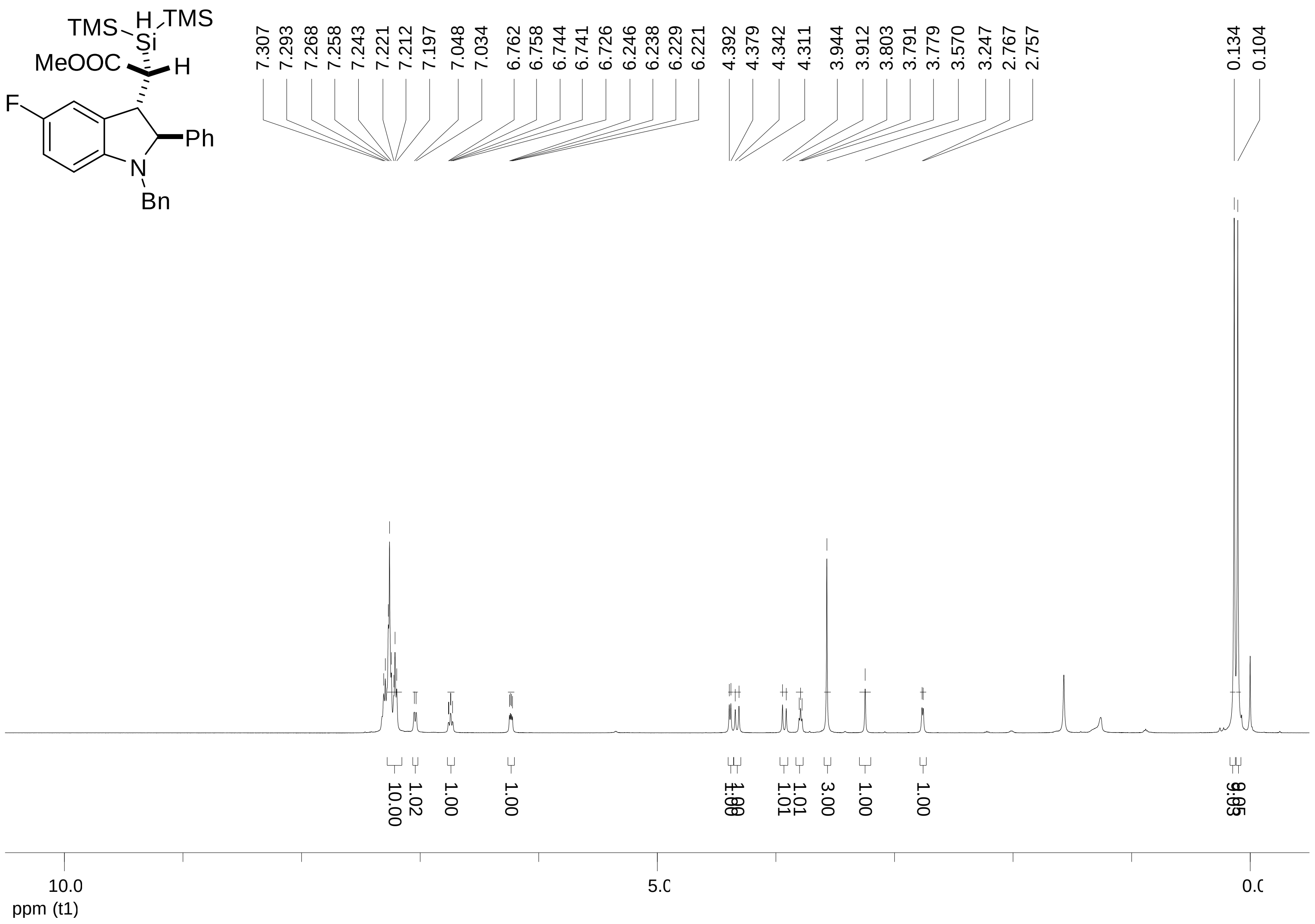
^{13}C NMR spectrum of **3f** diastereomer 1 (100 MHz, CDCl$_3$)



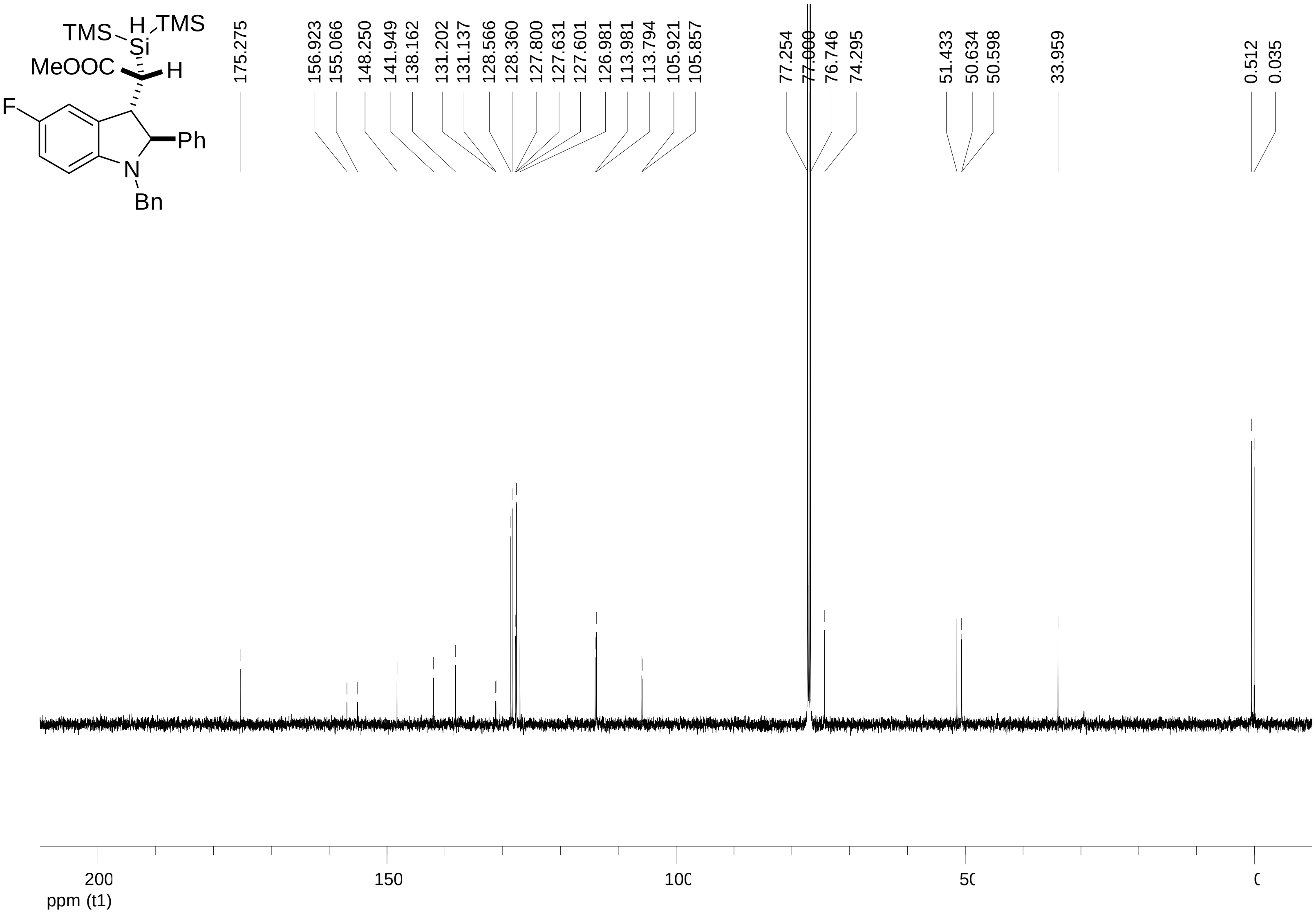
^{19}F NMR spectrum of **3f** diastereomer 1 (376 MHz, $CDCl_3$)



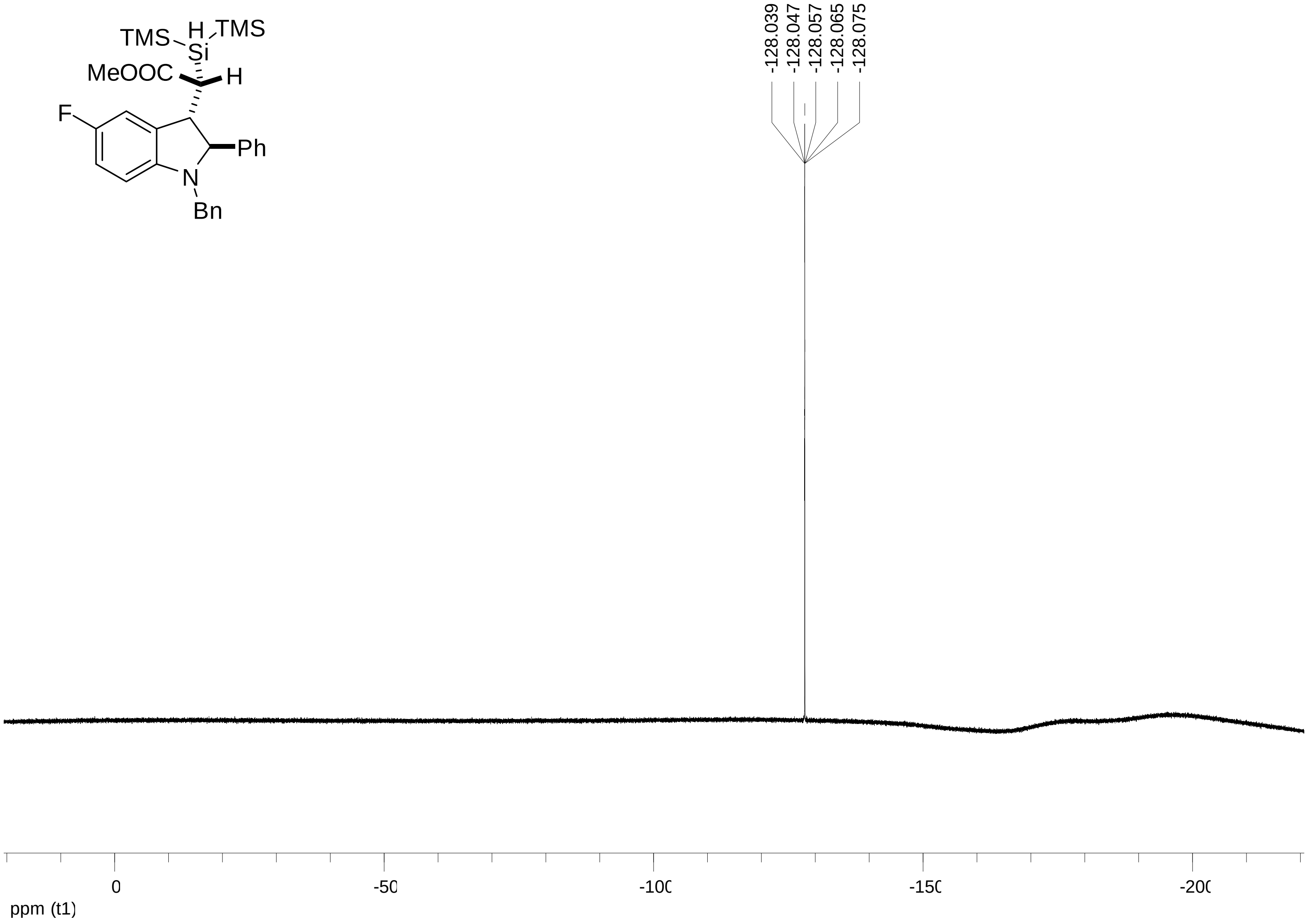
^{1}H NMR spectrum of **3f** diastereomer 2 (500 MHz, $CDCl_3$)



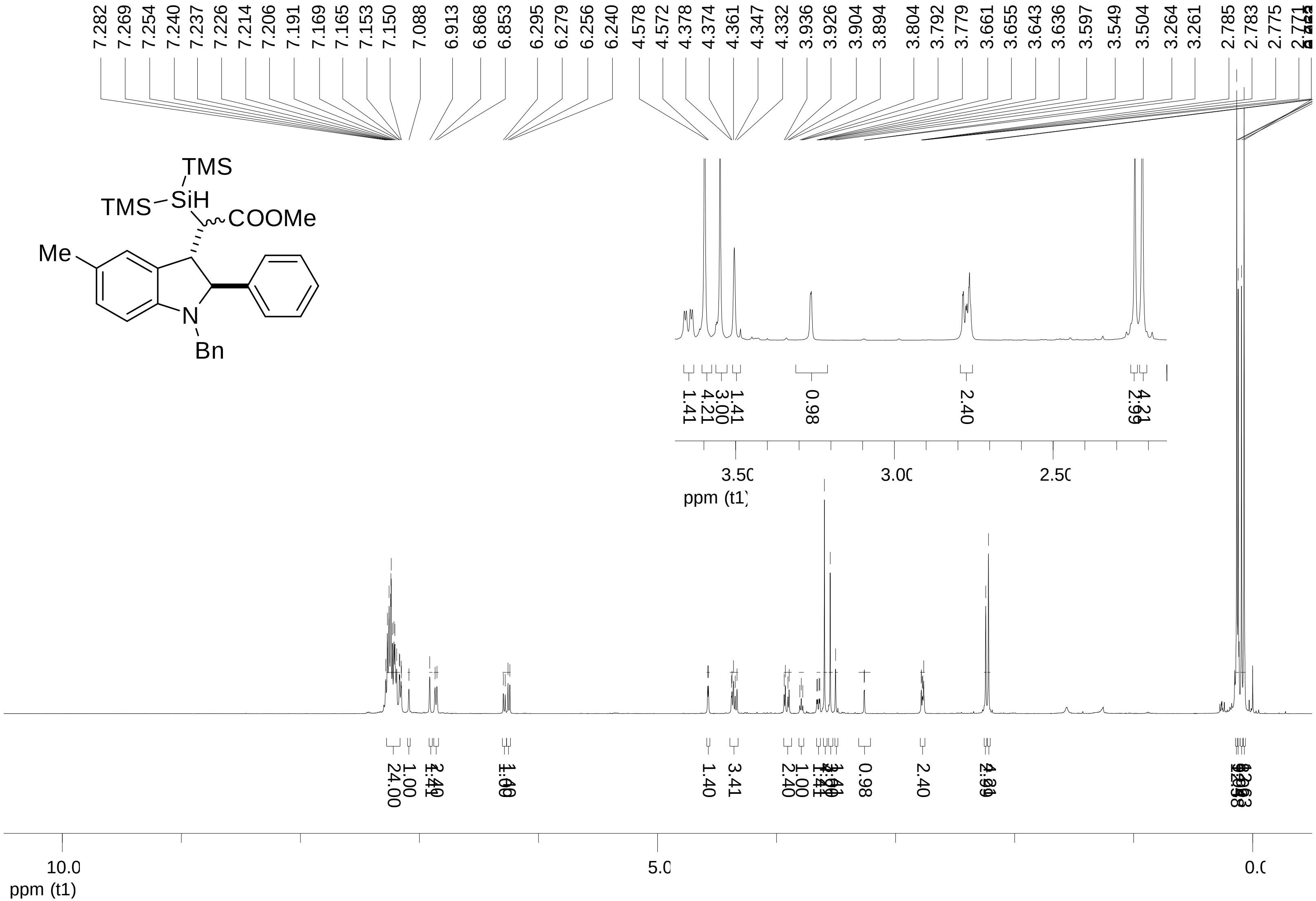
^{13}C NMR spectrum of **3f** diastereomer 2 (125 MHz, $CDCl_3$)



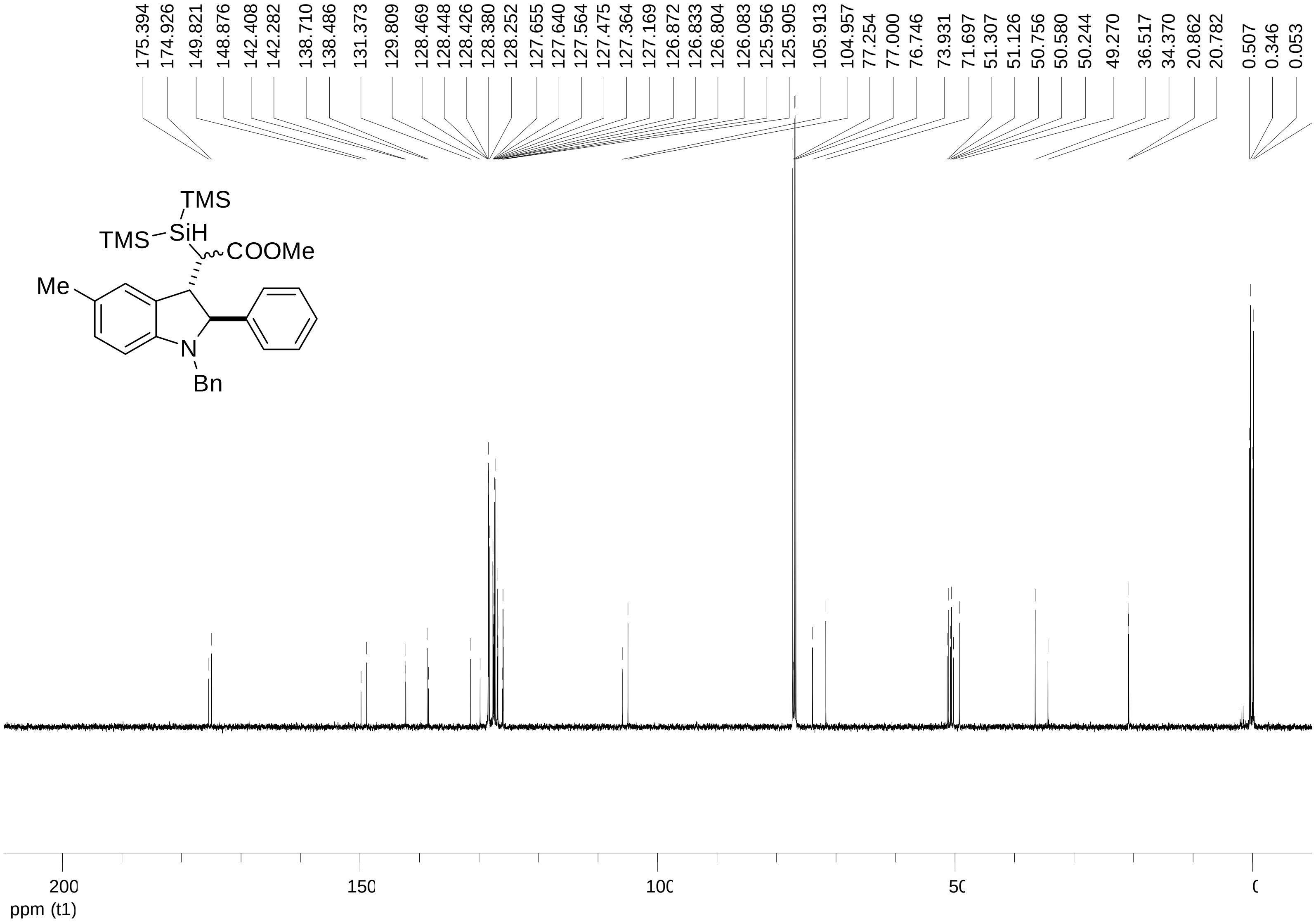
^{19}F NMR spectrum of **3f** diastereomer 2 (376 MHz, CDCl$_3$)



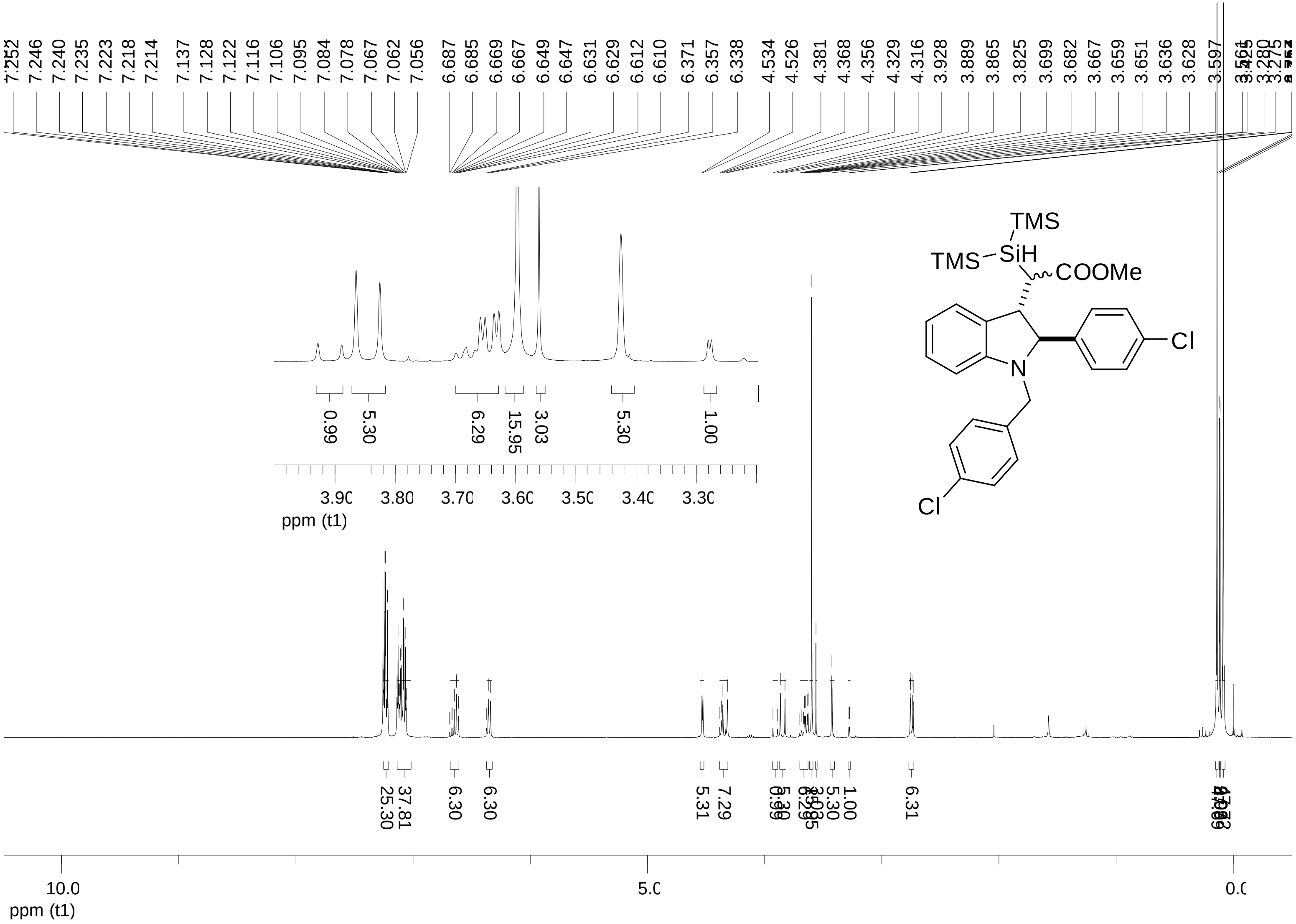
^{1}H NMR spectrum of **3g** (400 MHz, $CDCl_3$)



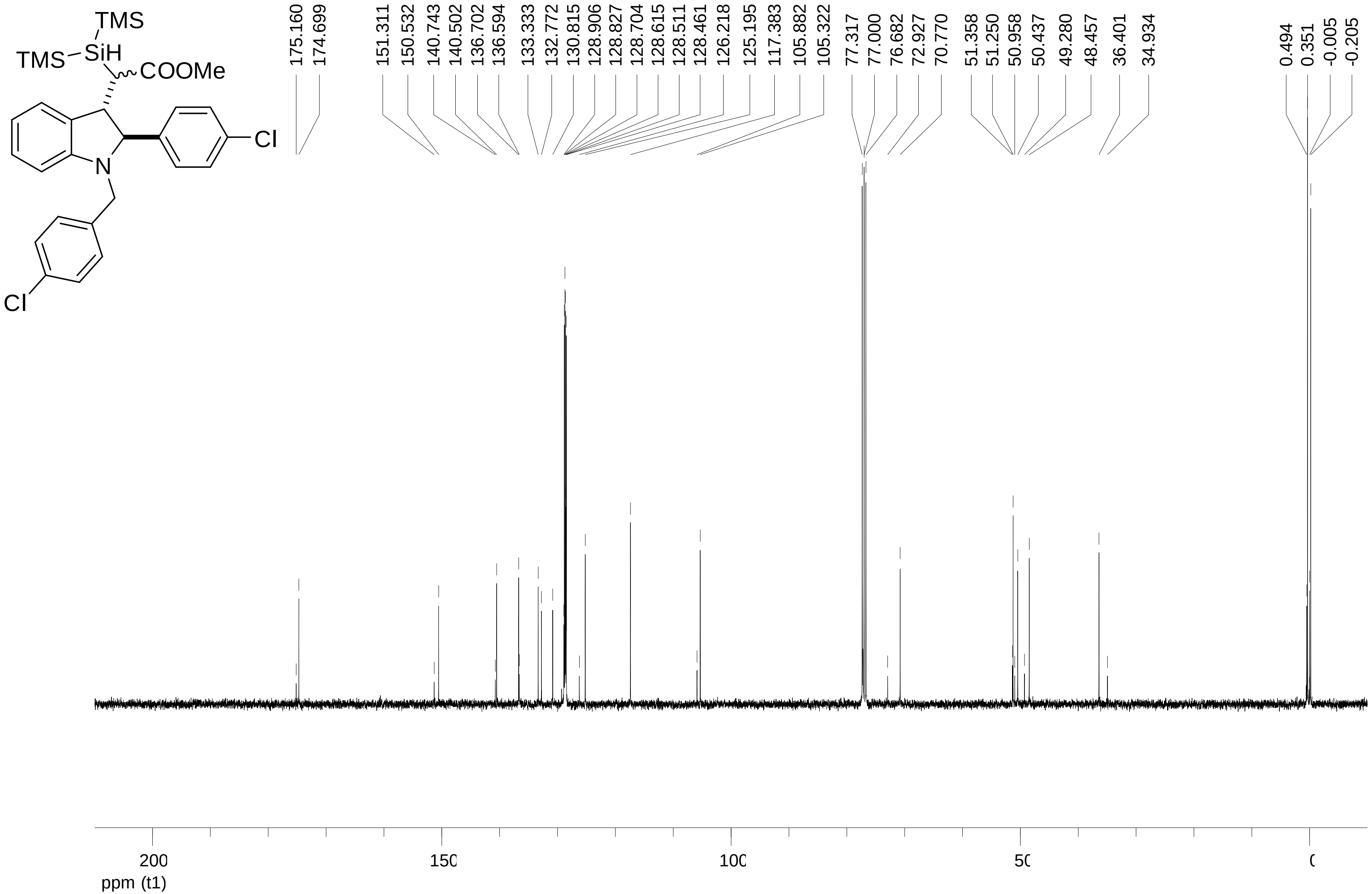
^{13}C NMR spectrum of **3g** (100 MHz, CDCl$_3$)



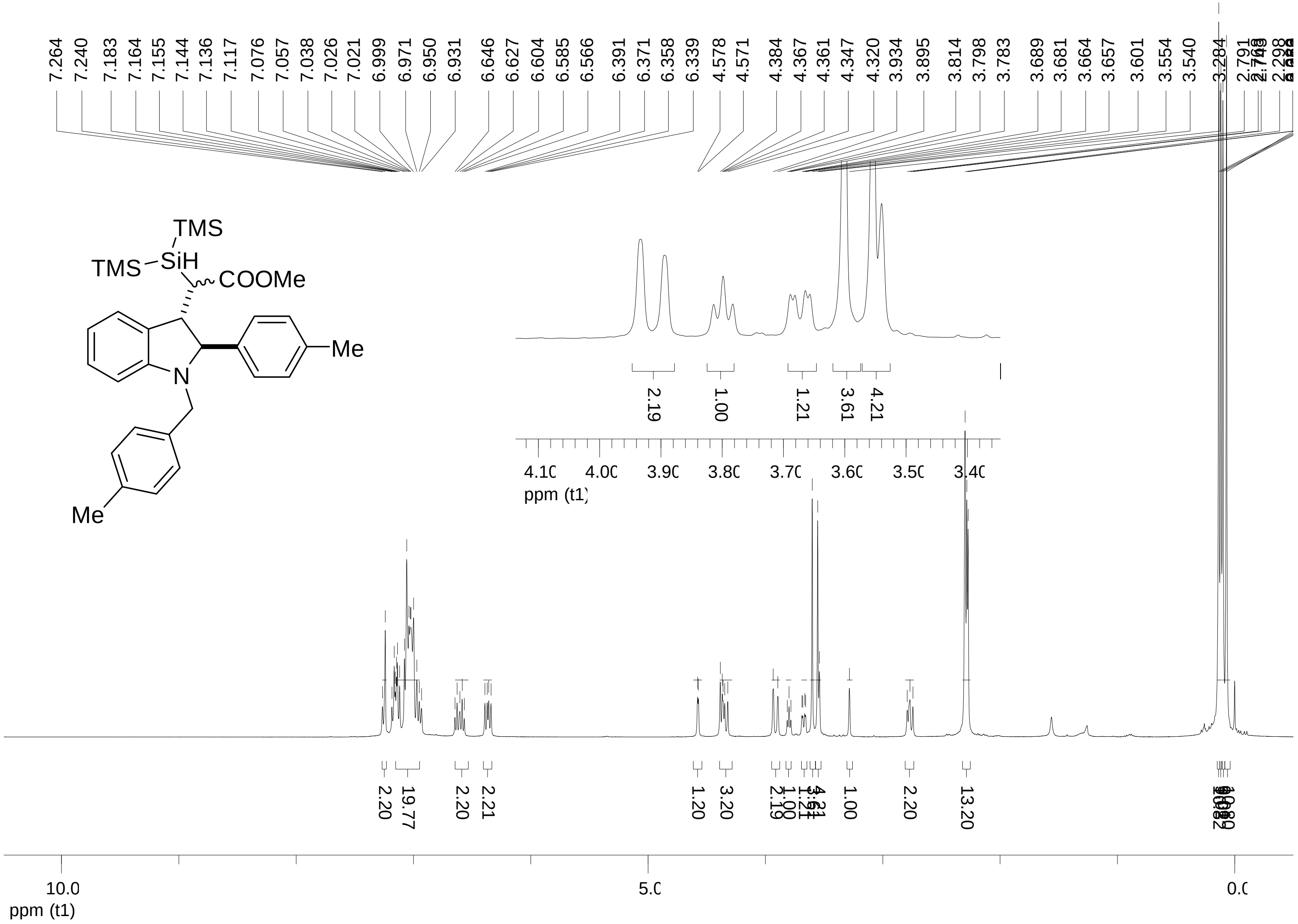
^{1}H NMR spectrum of **3h** (400 MHz, $CDCl_3$)



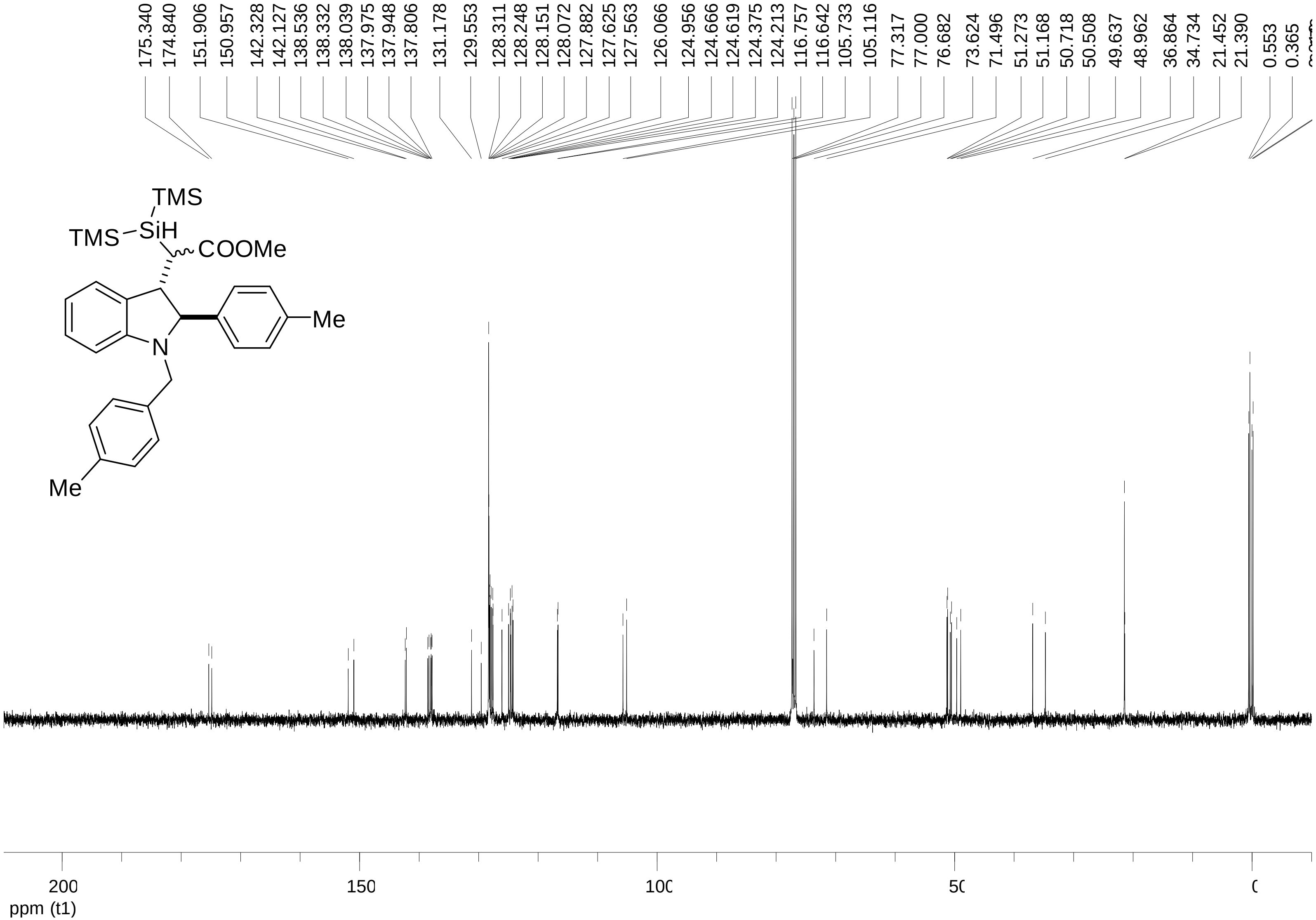
^{13}C NMR spectrum of **3h** (100 MHz, $CDCl_3$)



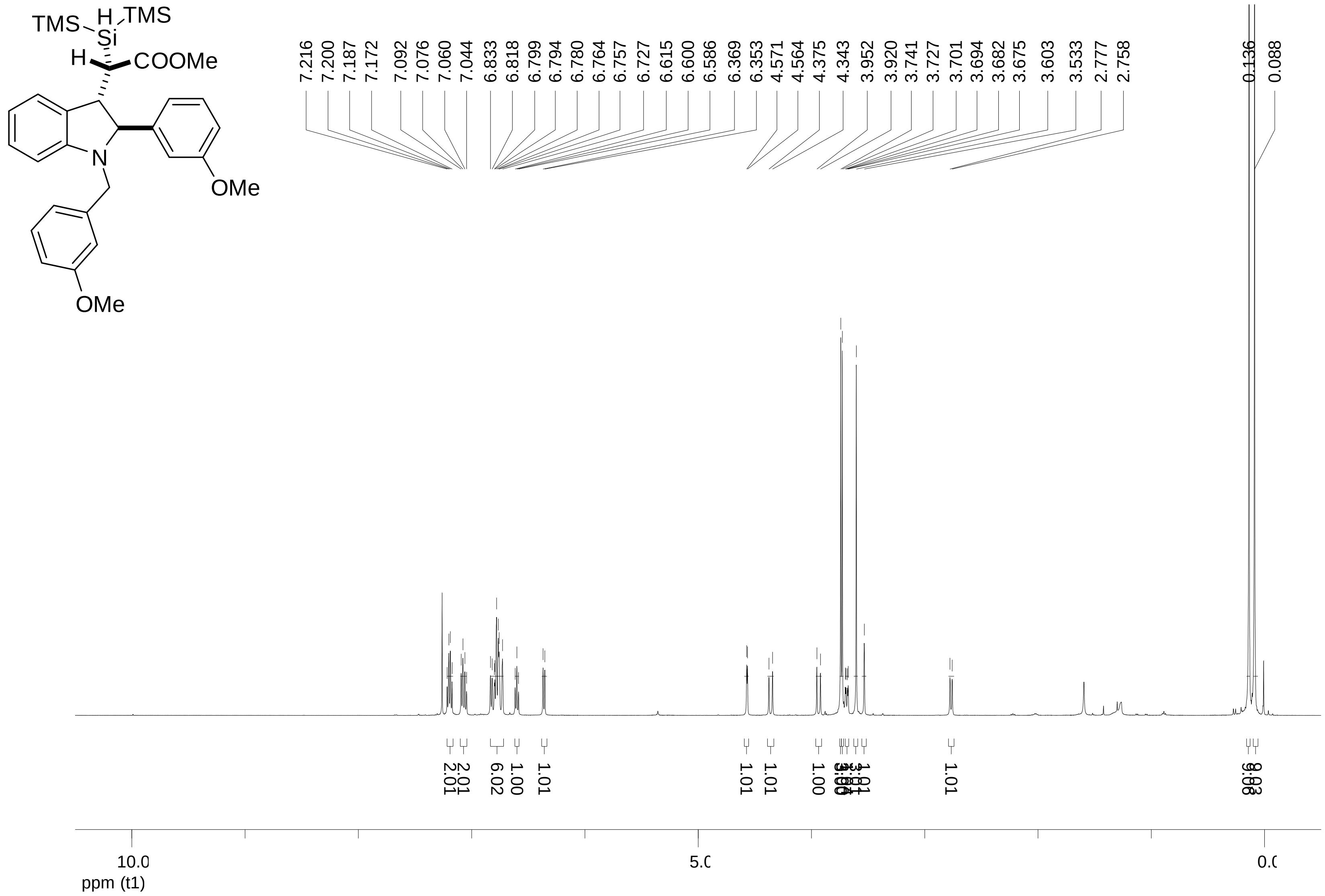
^{1}H NMR spectrum of **3i** (400 MHz, CDCl$_3$)



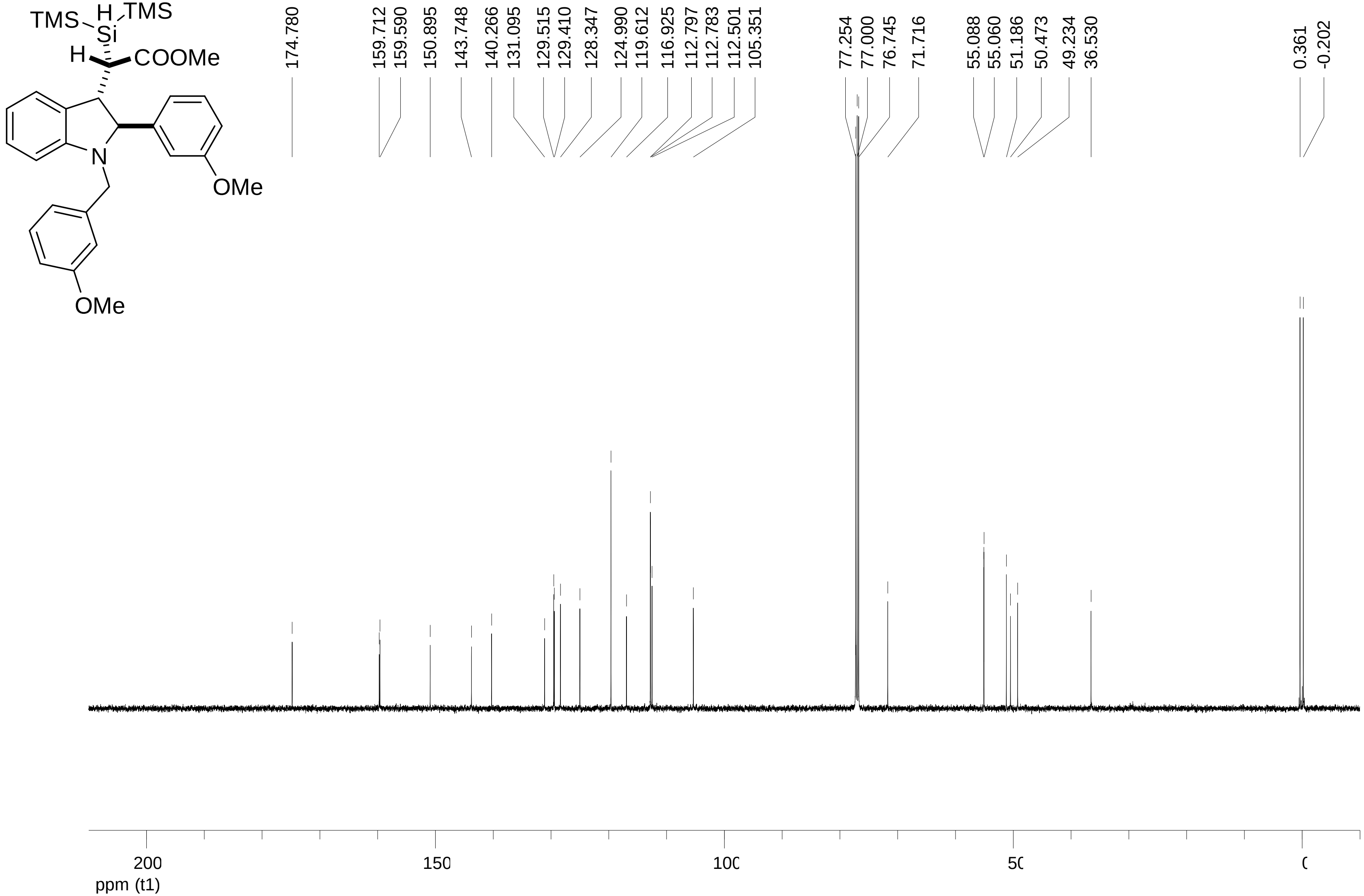
^{13}C NMR spectrum of **3i** (100 MHz, CDCl$_3$)



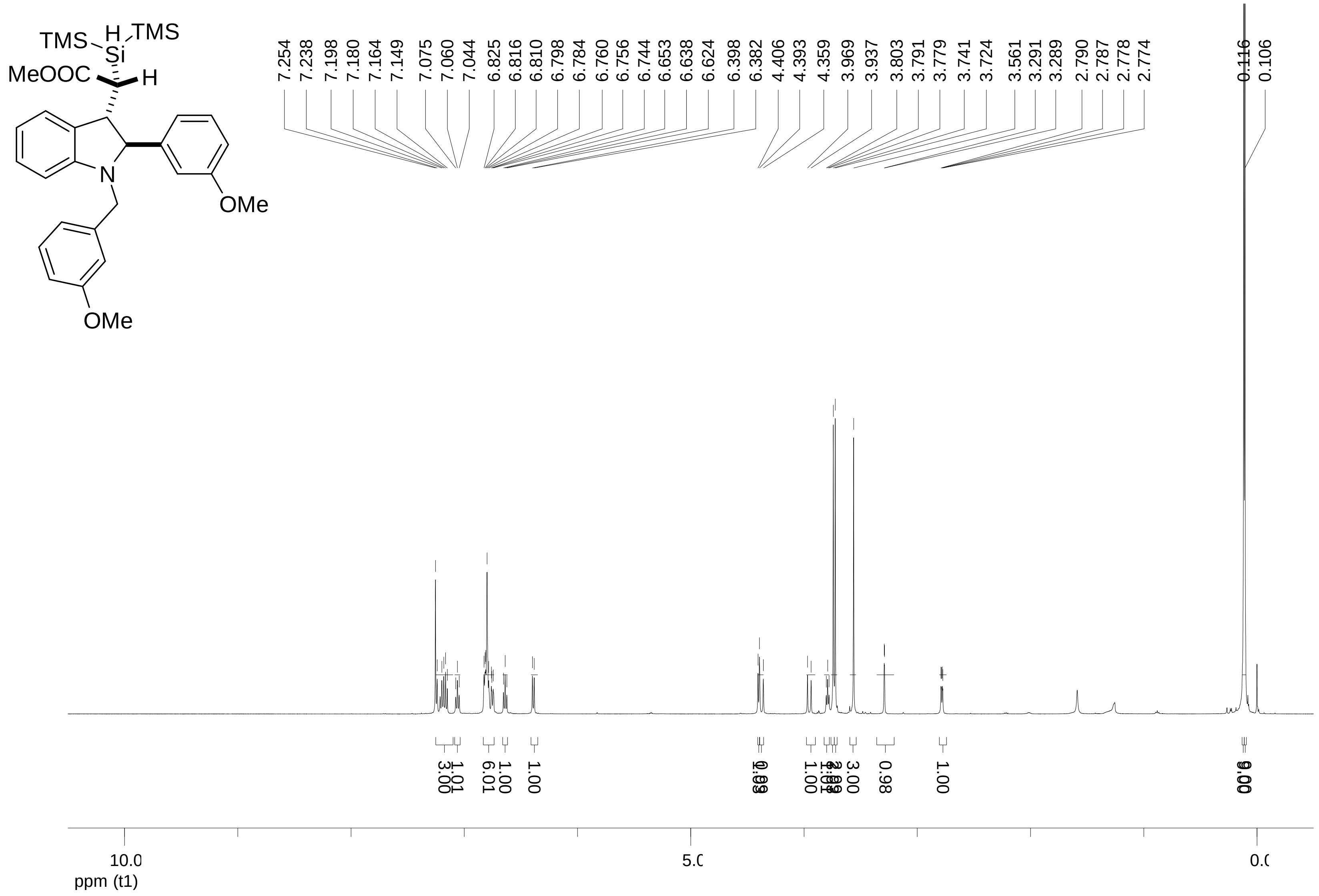
^{1}H NMR spectrum of **3j** diastereomer 1 (500 MHz, $CDCl_3$)



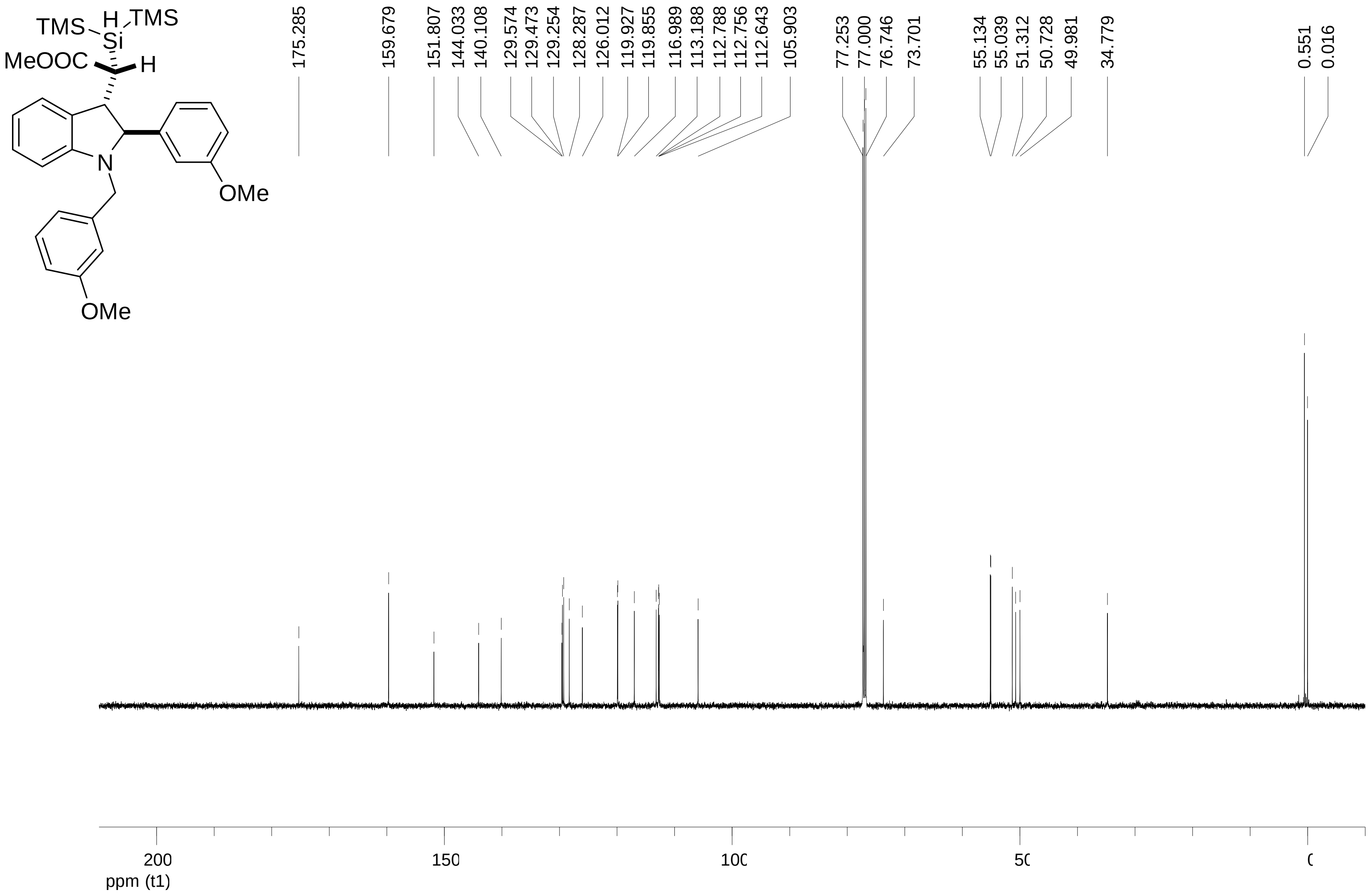
^{13}C NMR spectrum of **3j** diastereomer 1 (125 MHz, $CDCl_3$)



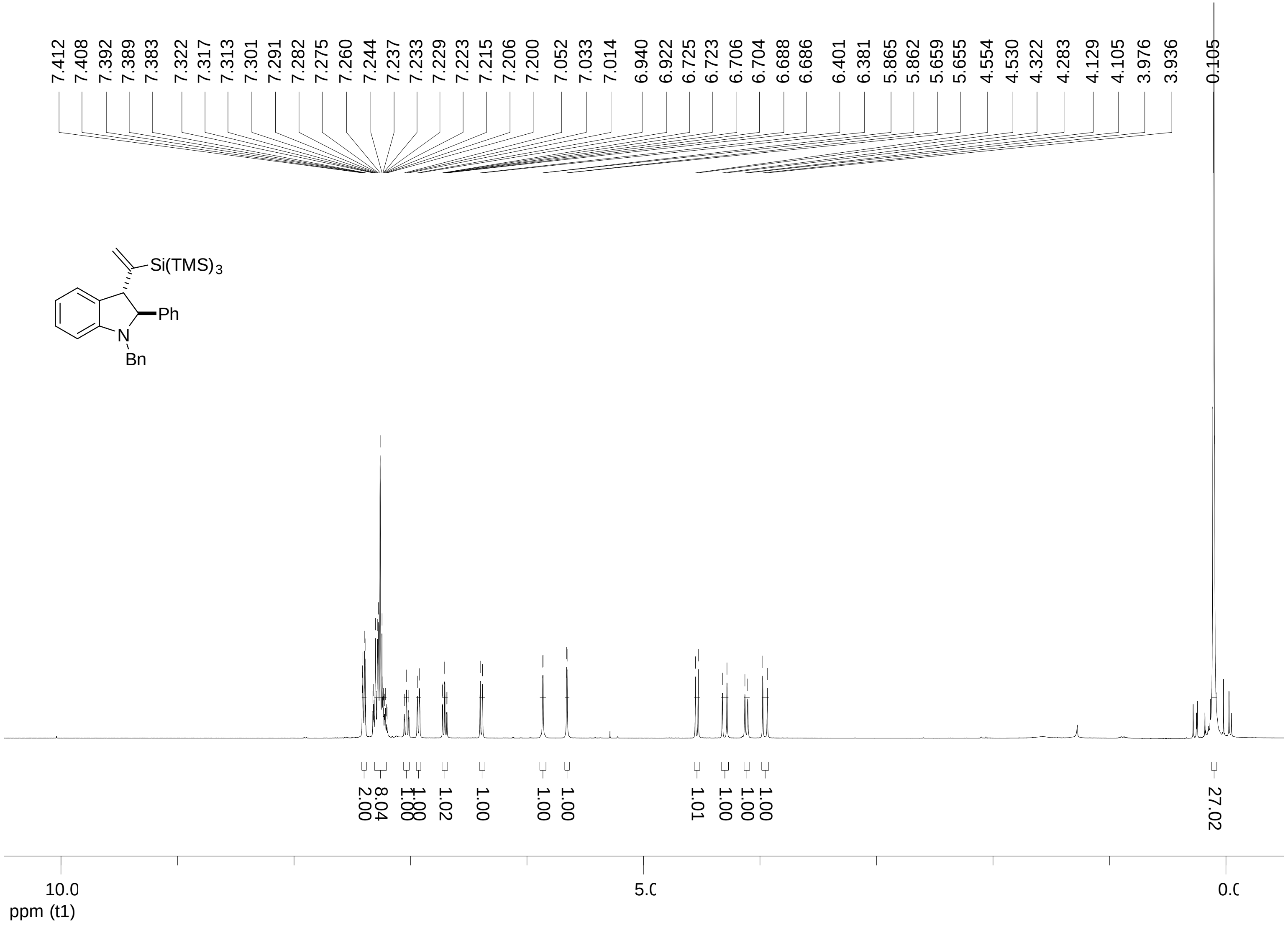
^{1}H NMR spectrum of **3j** diastereomer 2 (500 MHz, $CDCl_3$)



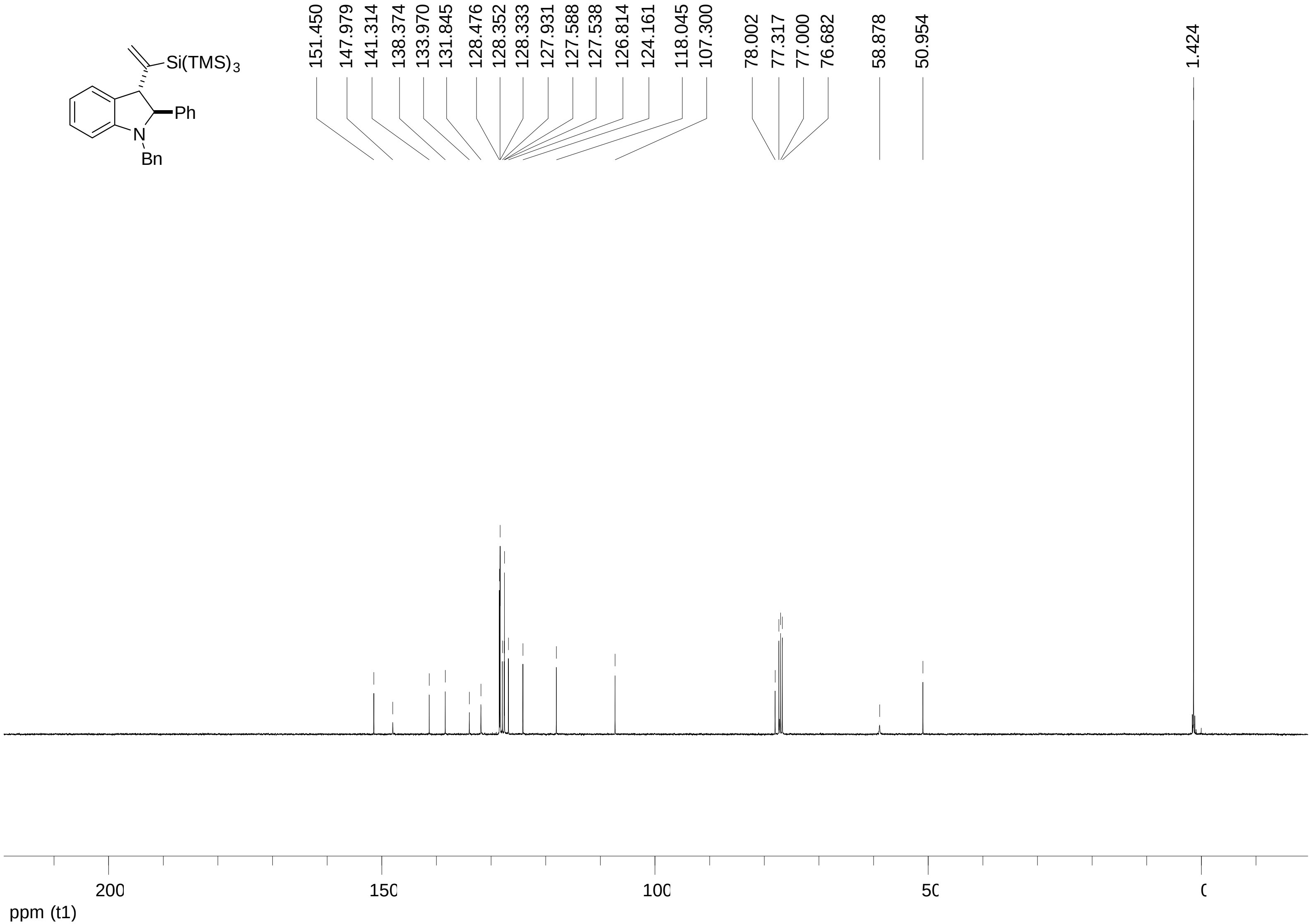
^{13}C NMR spectrum of **3j** diastereomer 2 (125 MHz, CDCl$_3$)



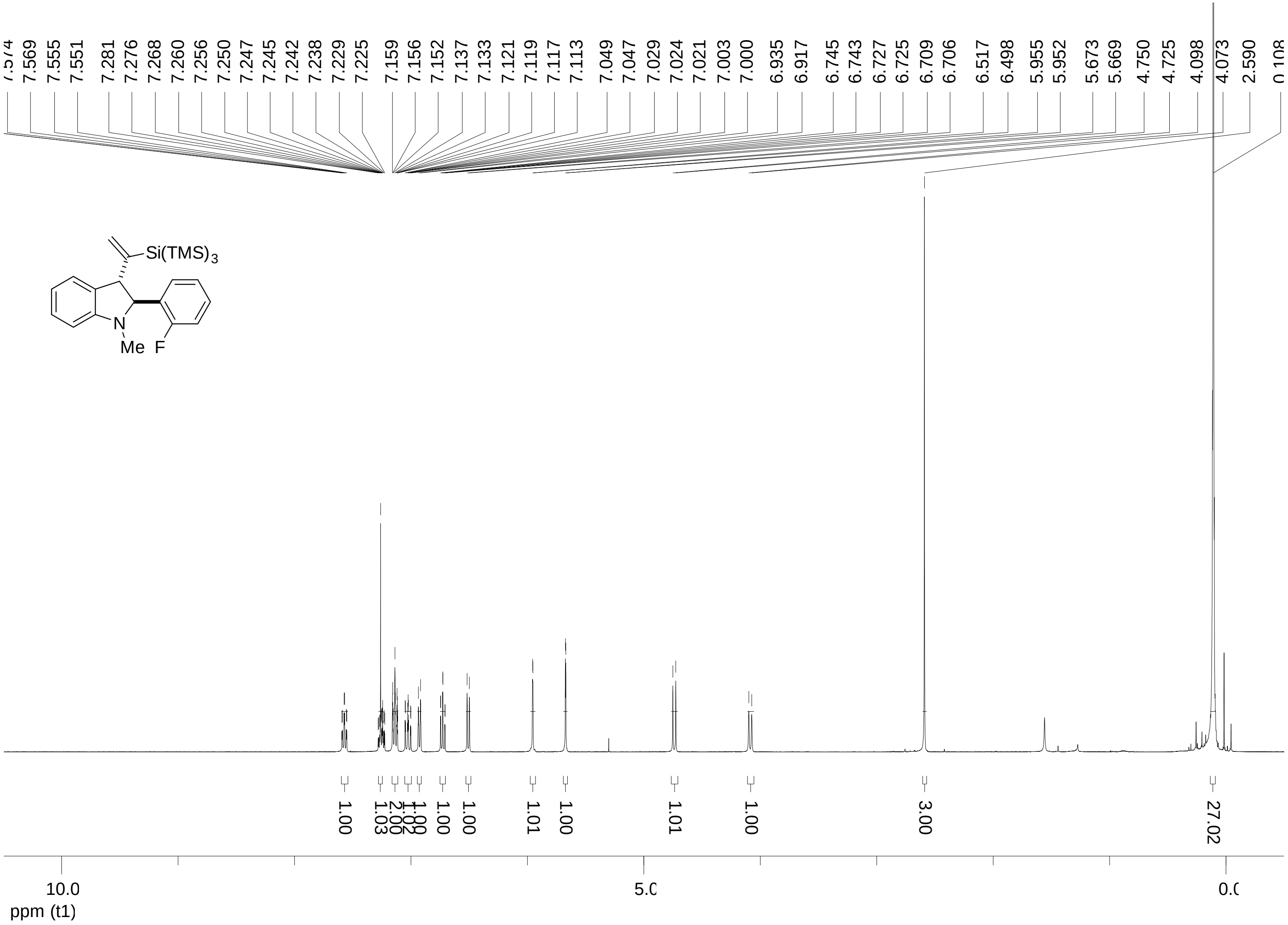
^{1}H NMR spectrum of **4a** (400 MHz, $CDCl_3$)



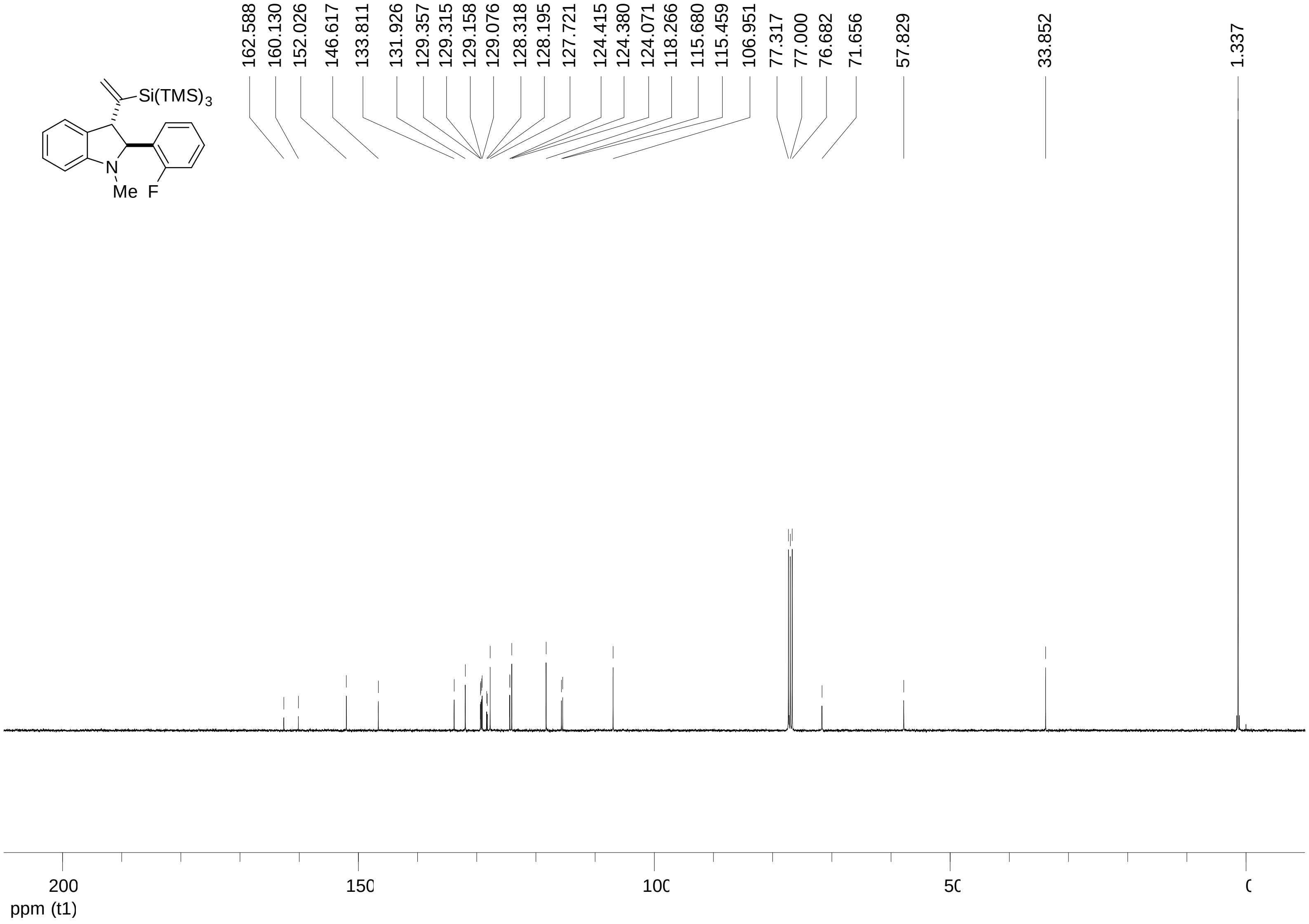
^{13}C NMR spectrum of **4a** (100 MHz, $CDCl_3$)



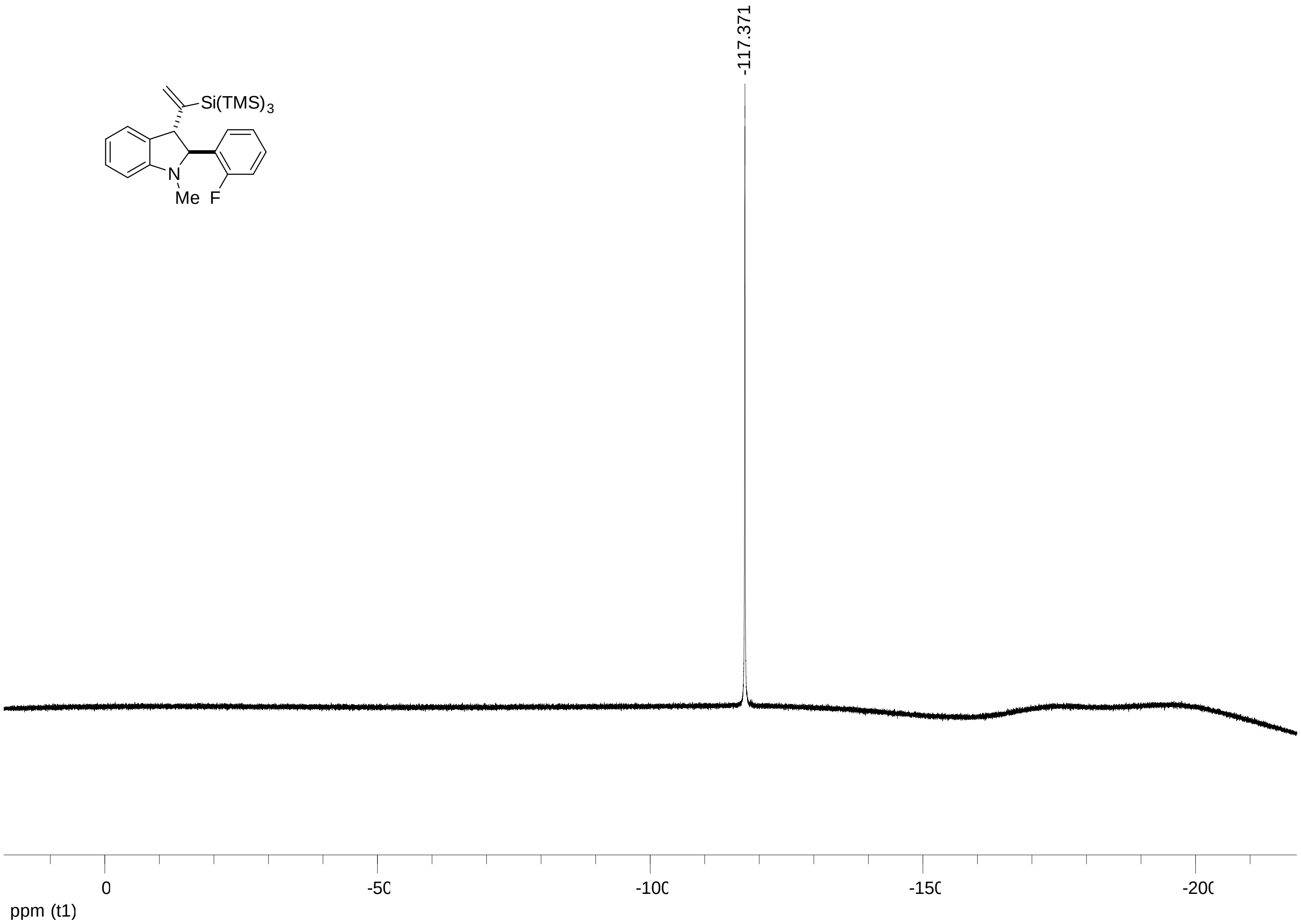
^{1}H NMR spectrum of **4b** (400 MHz, $CDCl_3$)



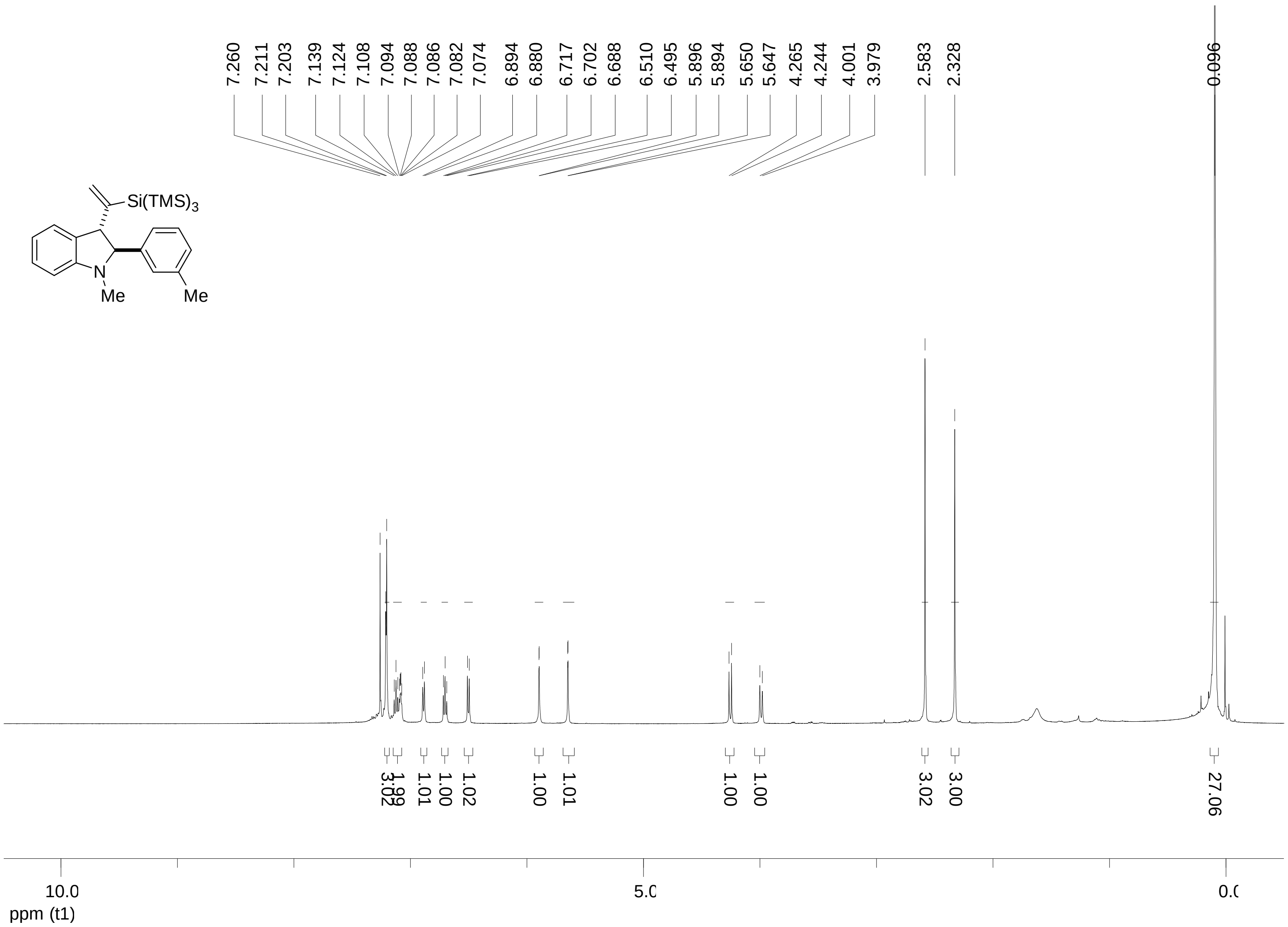
^{13}C NMR spectrum of **4b** (100 MHz, $CDCl_3$)



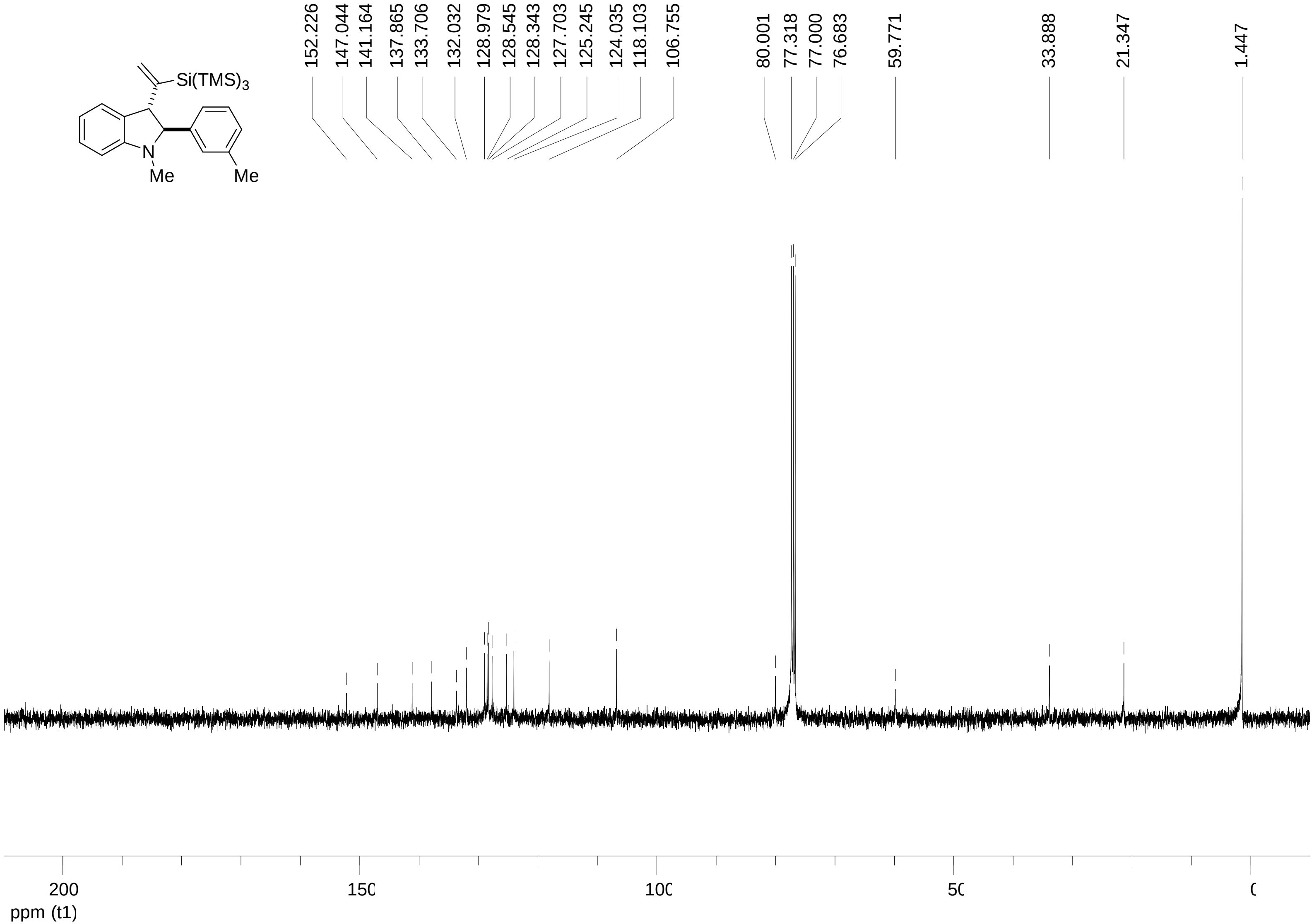
^{19}F NMR spectrum of **4b** (376 MHz, $CDCl_3$)



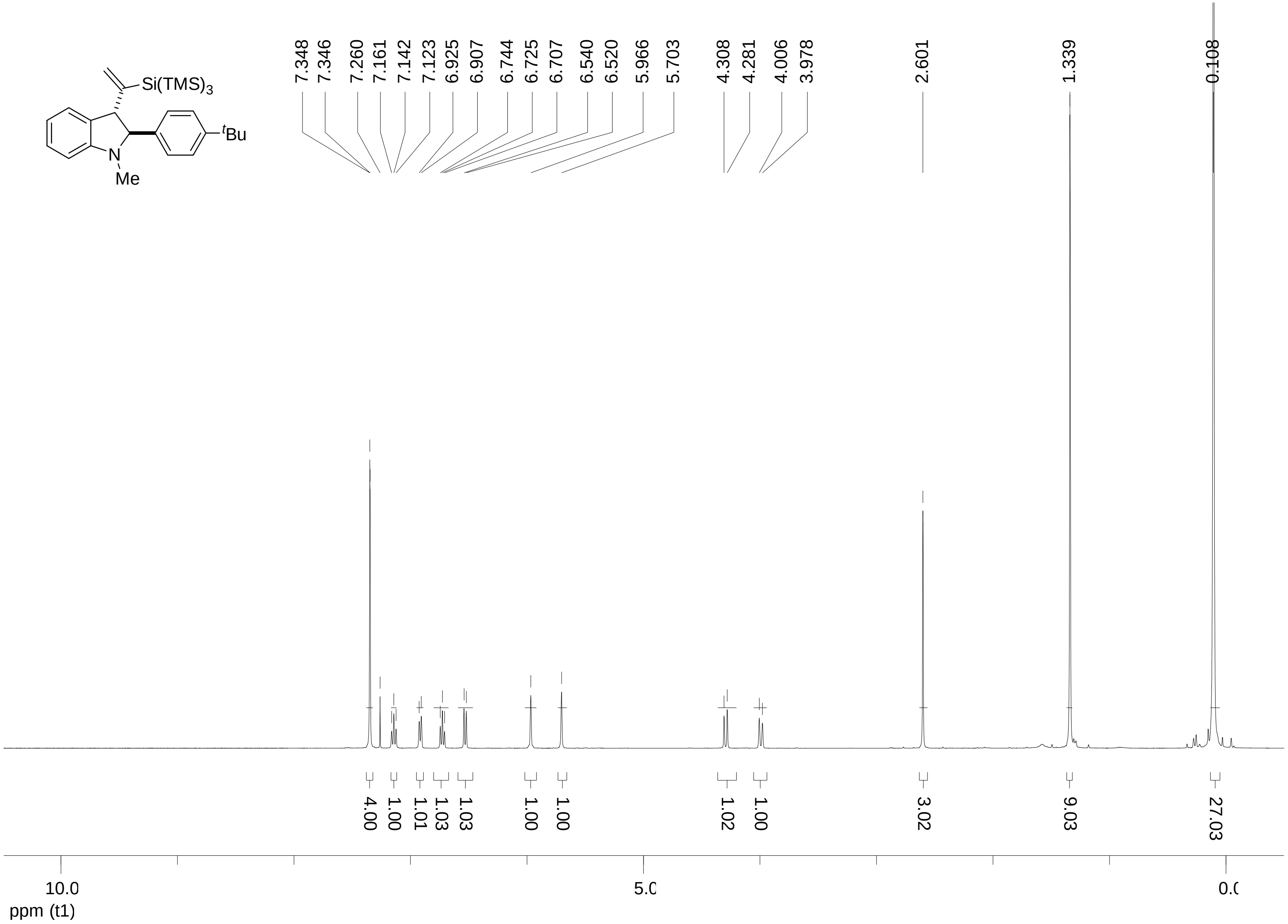
^{1}H NMR spectrum of **4c** (400 MHz, $CDCl_3$)



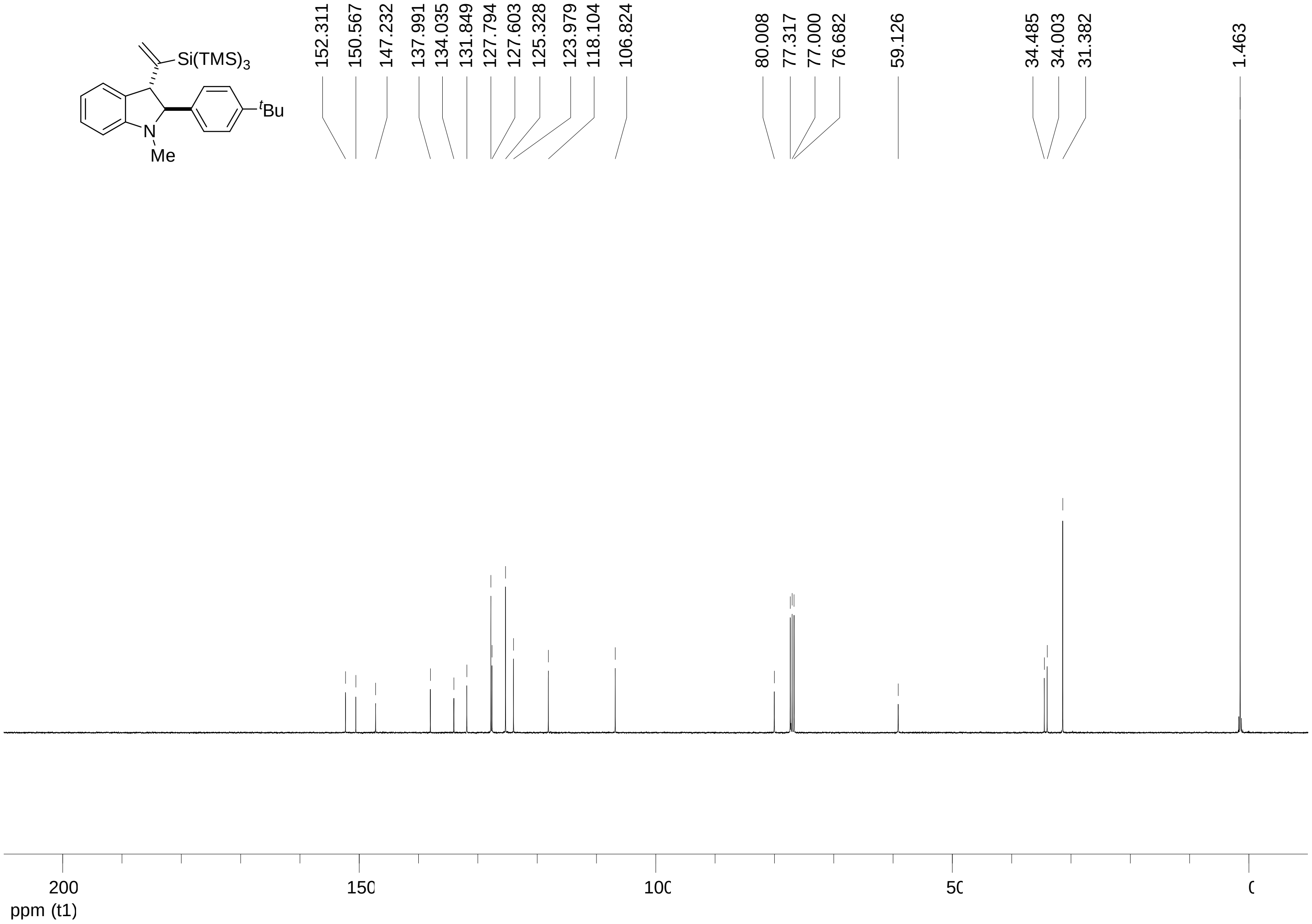
^{13}C NMR spectrum of **4c** (100 MHz, $CDCl_3$)



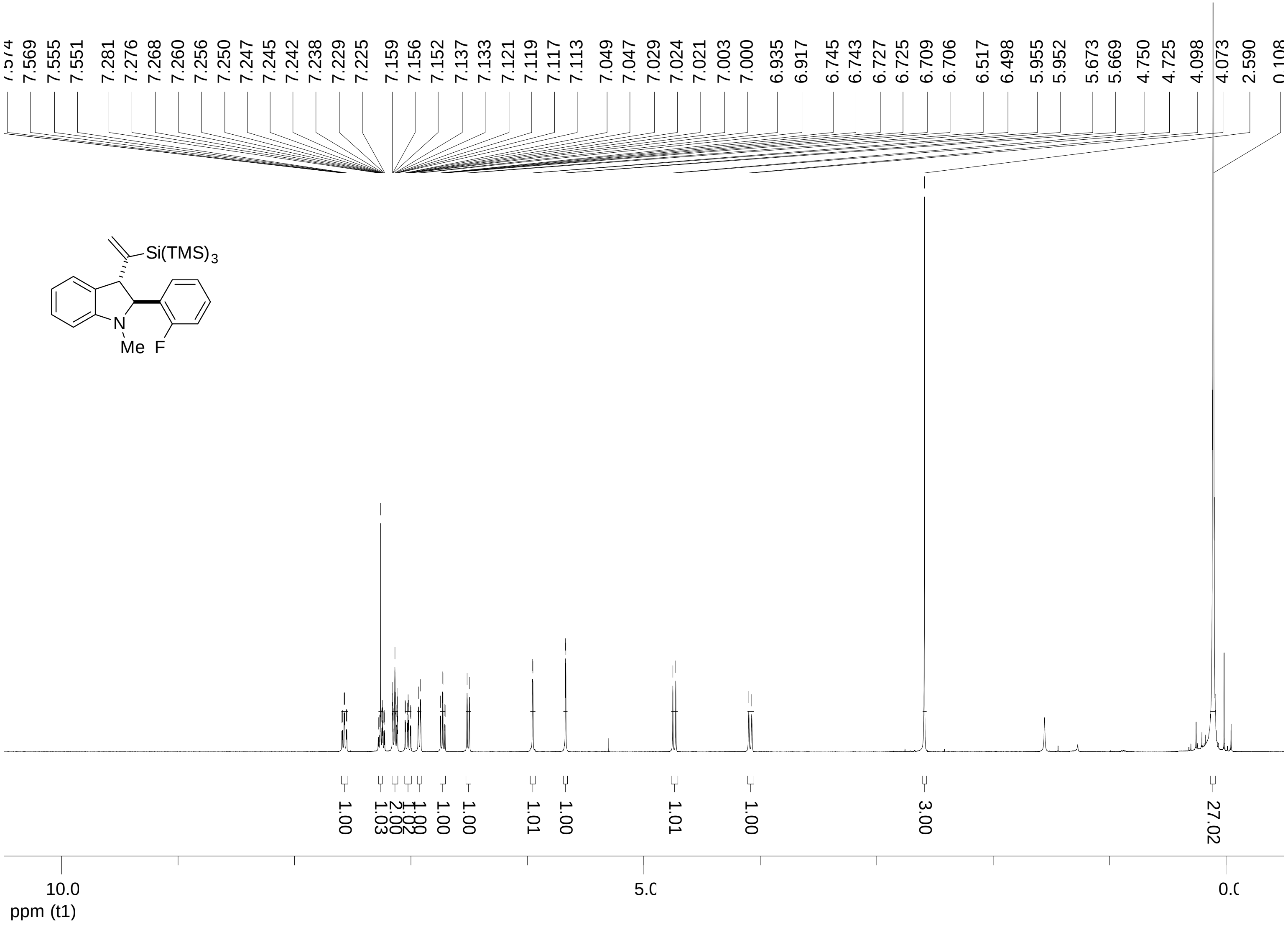
^{1}H NMR spectrum of **4d** (400 MHz, $CDCl_3$)



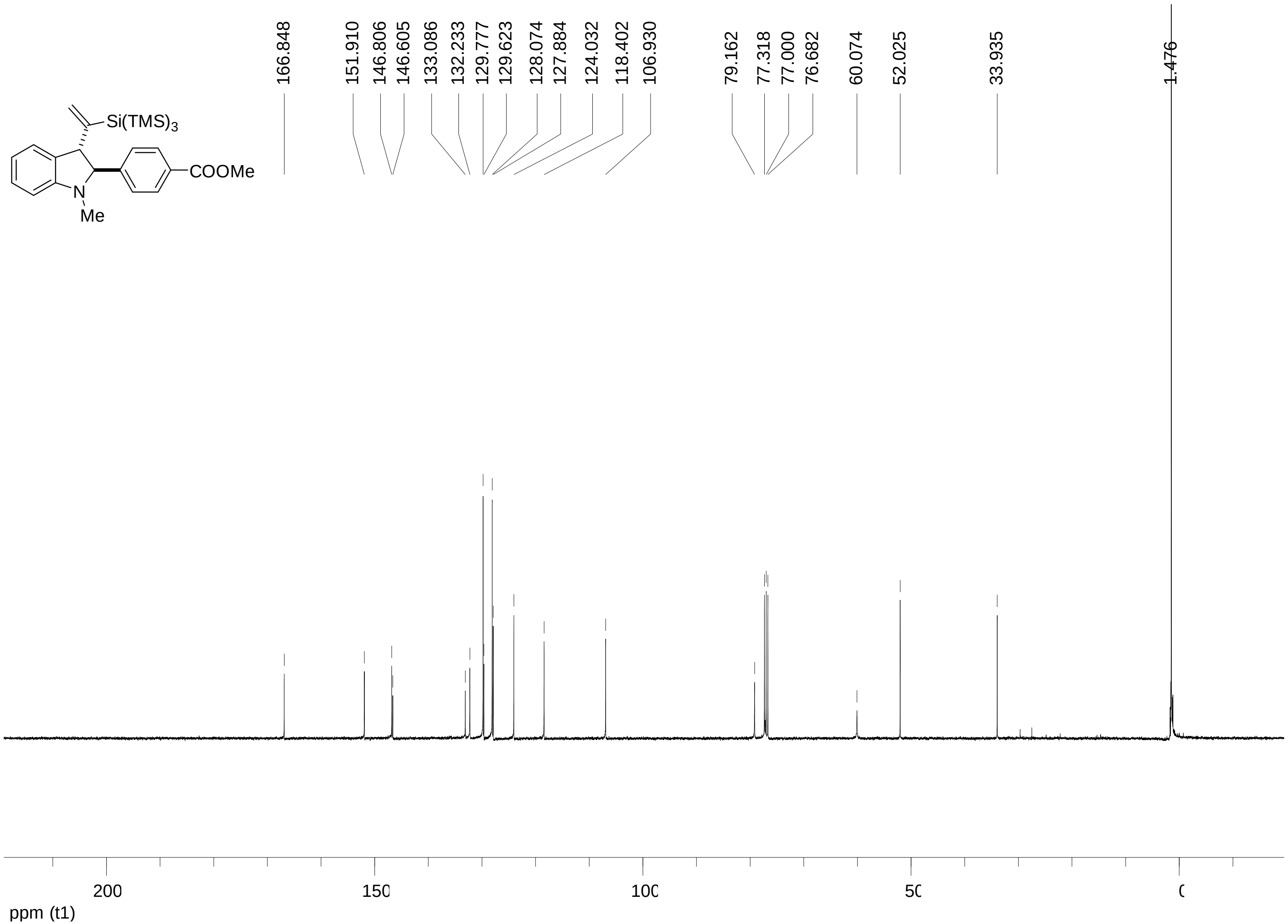
^{13}C NMR spectrum of **4d** (100 MHz, $CDCl_3$)



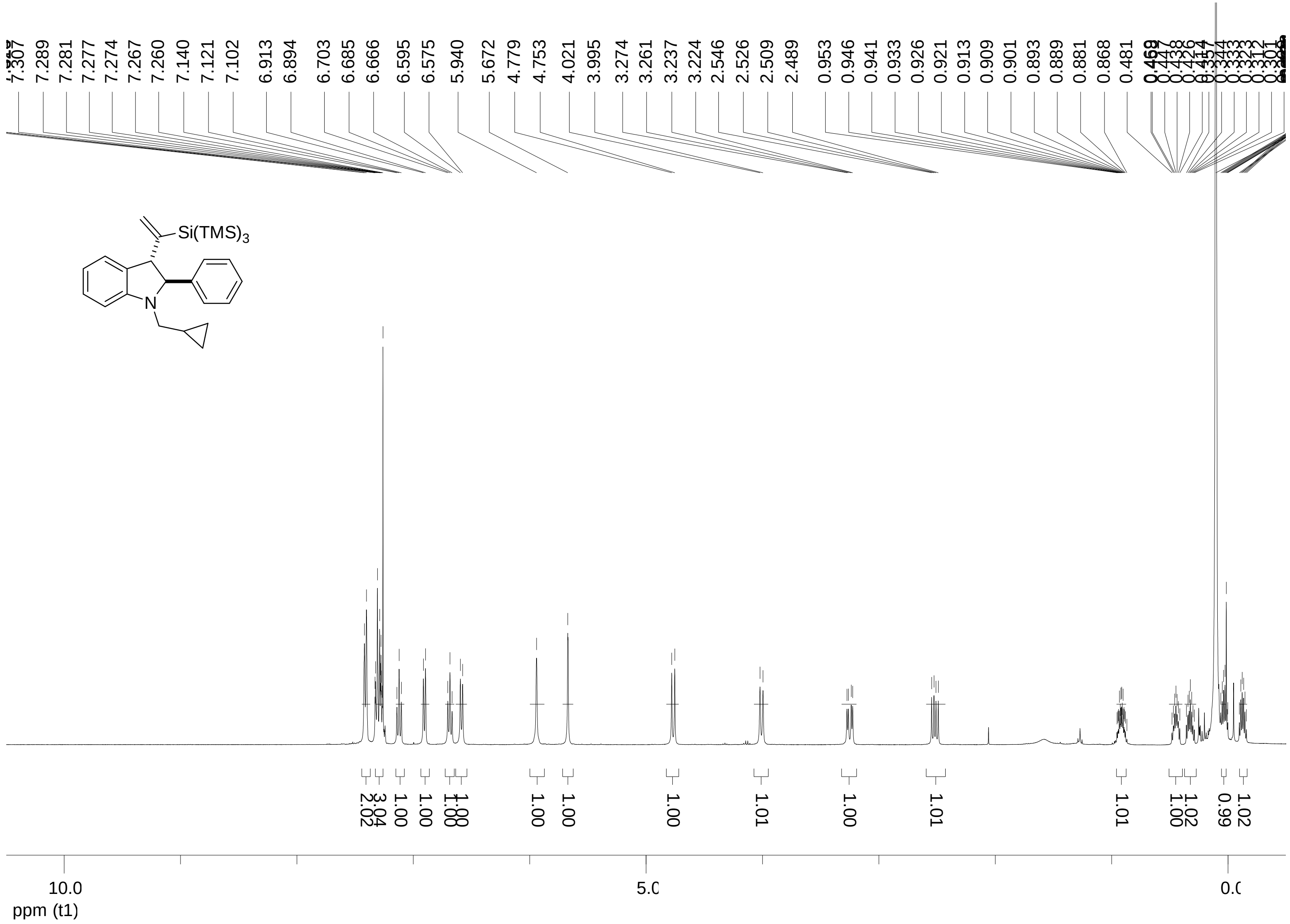
^{1}H NMR spectrum of **4e** (400 MHz, CDCl$_3$)



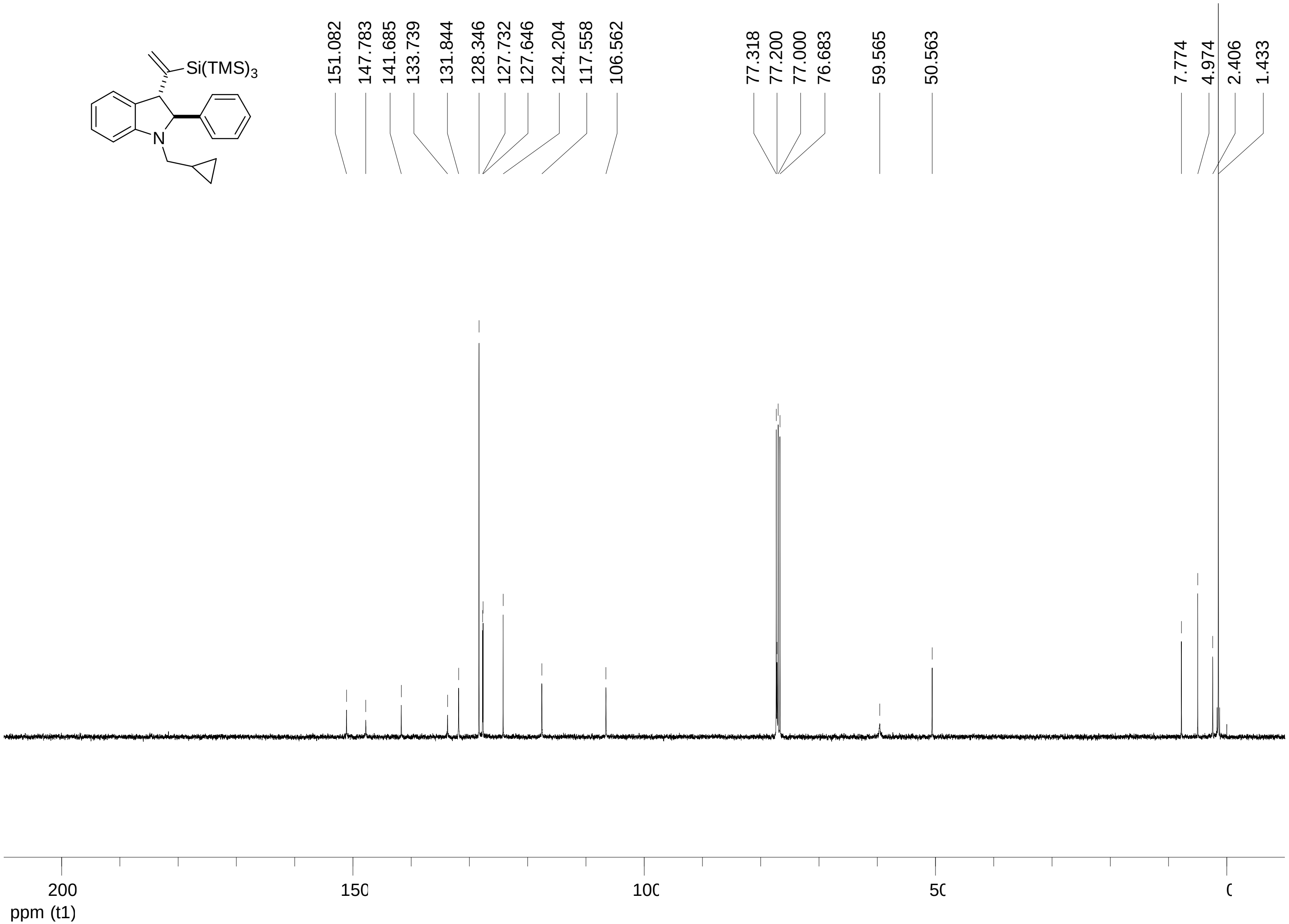
^{13}C NMR spectrum of **4e** (100 MHz, $CDCl_3$)



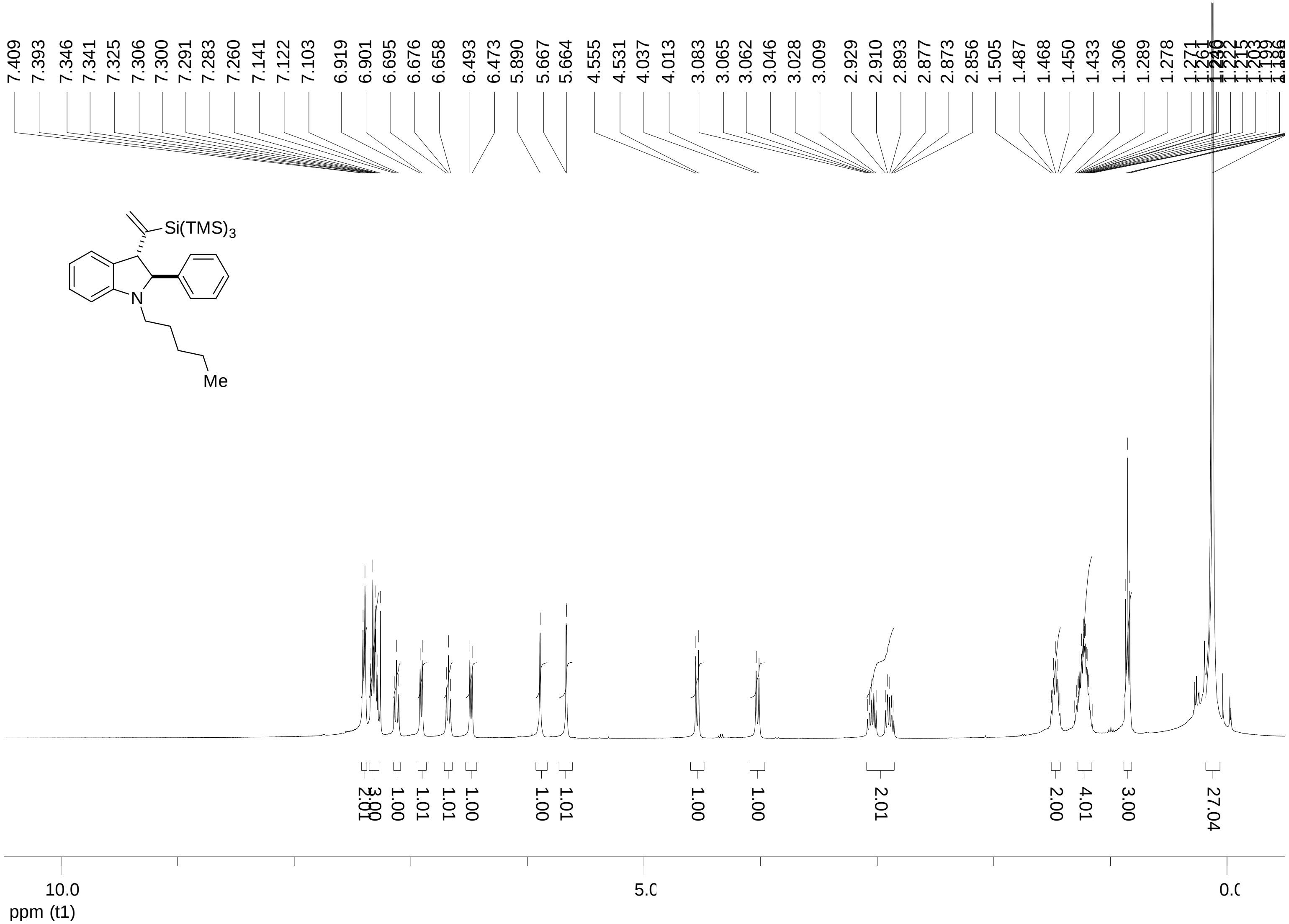
^{1}H NMR spectrum of **4f** (400 MHz, CDCl$_3$)



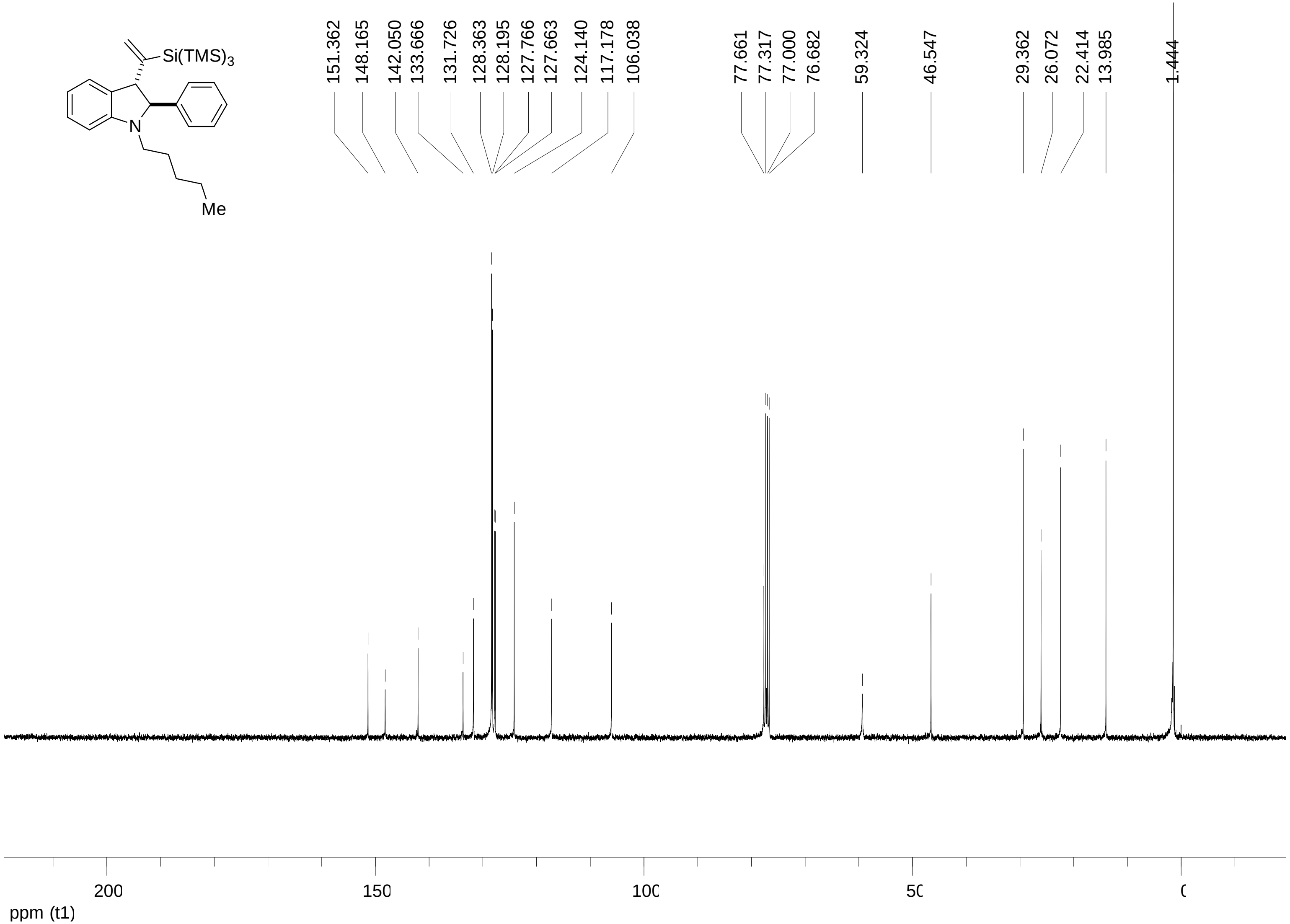
^{13}C NMR spectrum of **4f** (100 MHz, $CDCl_3$)



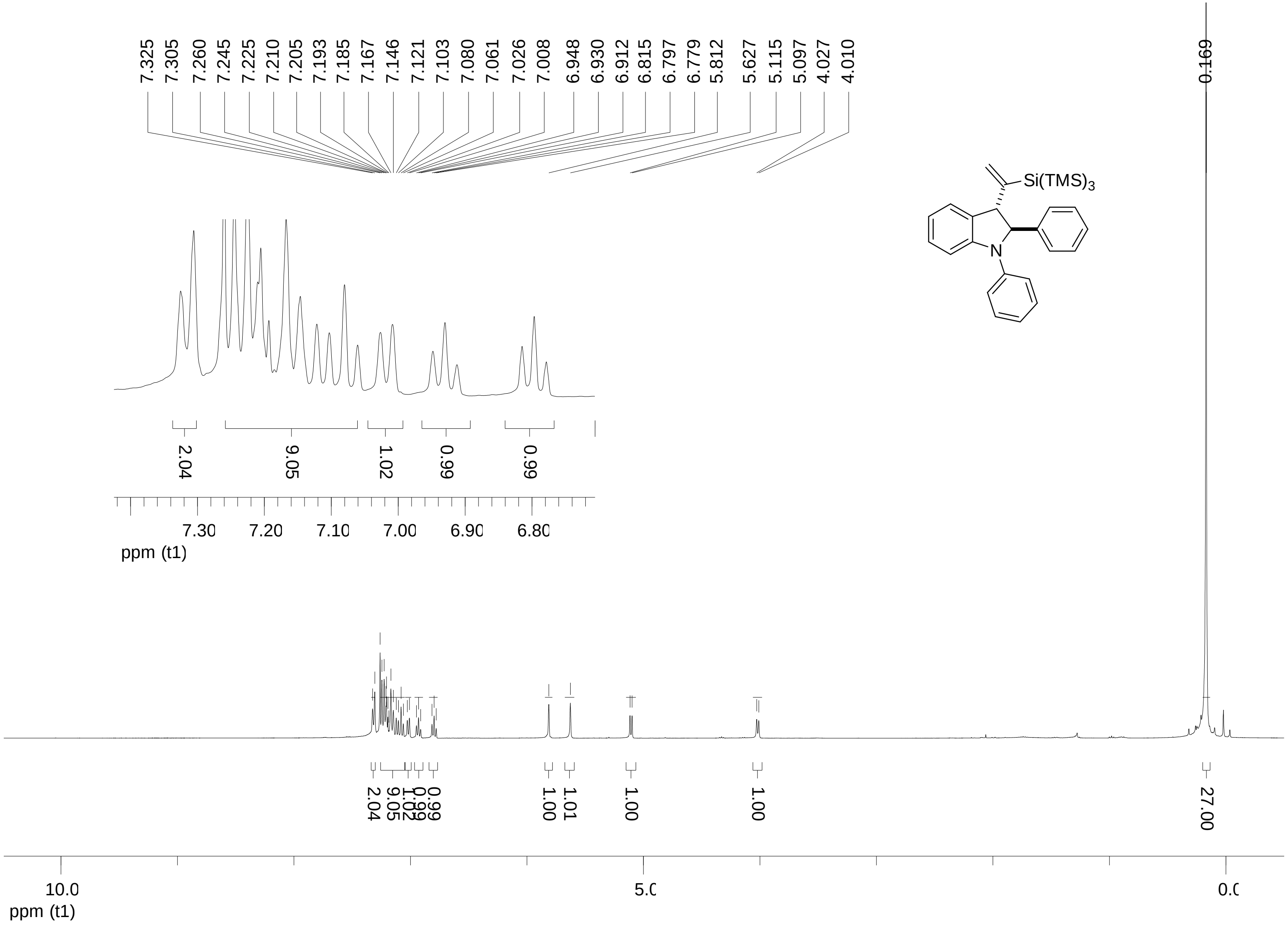
^{1}H NMR spectrum of **4g** (400 MHz, $CDCl_3$)



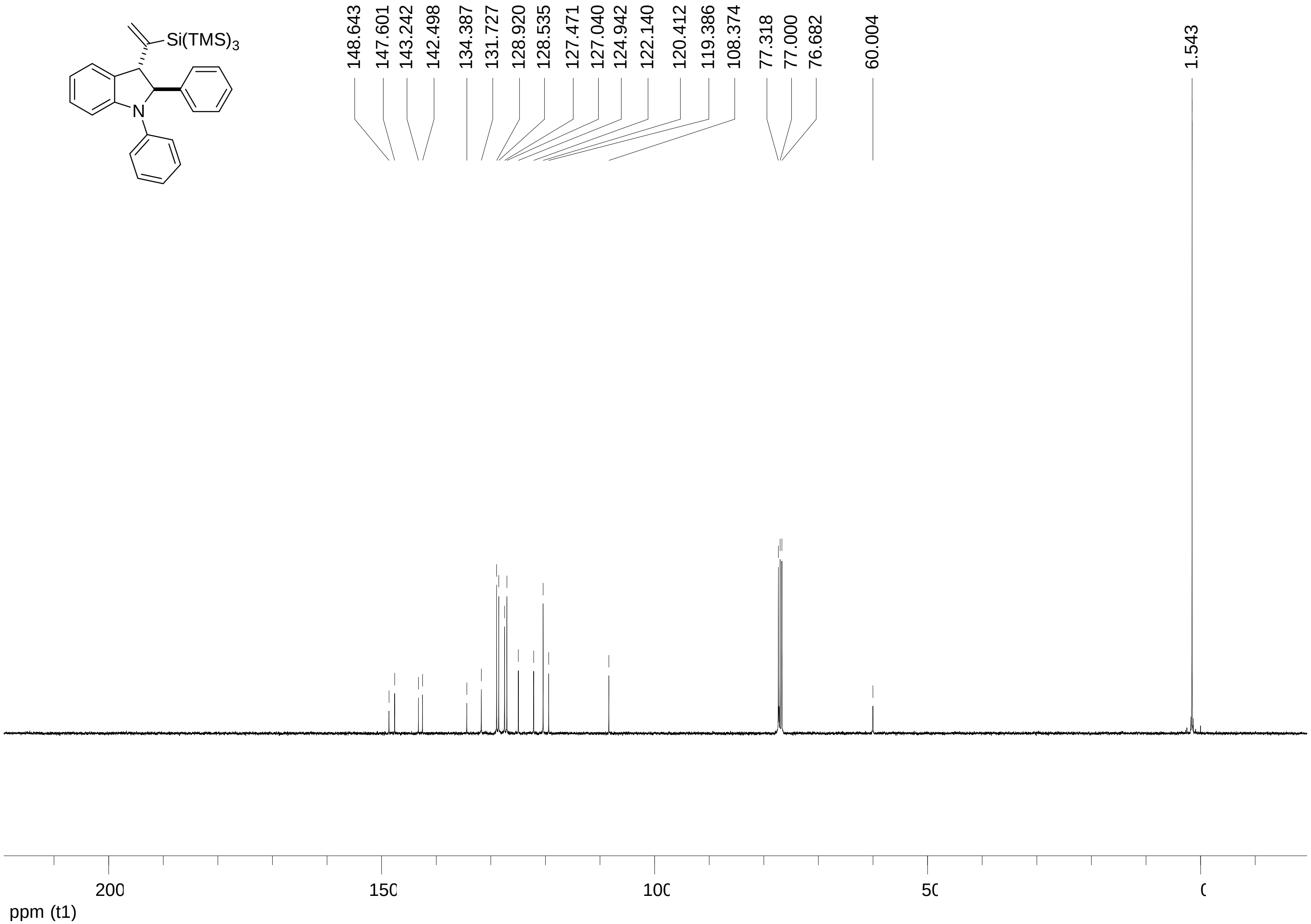
^{13}C NMR spectrum of **4g** (100 MHz, $CDCl_3$)



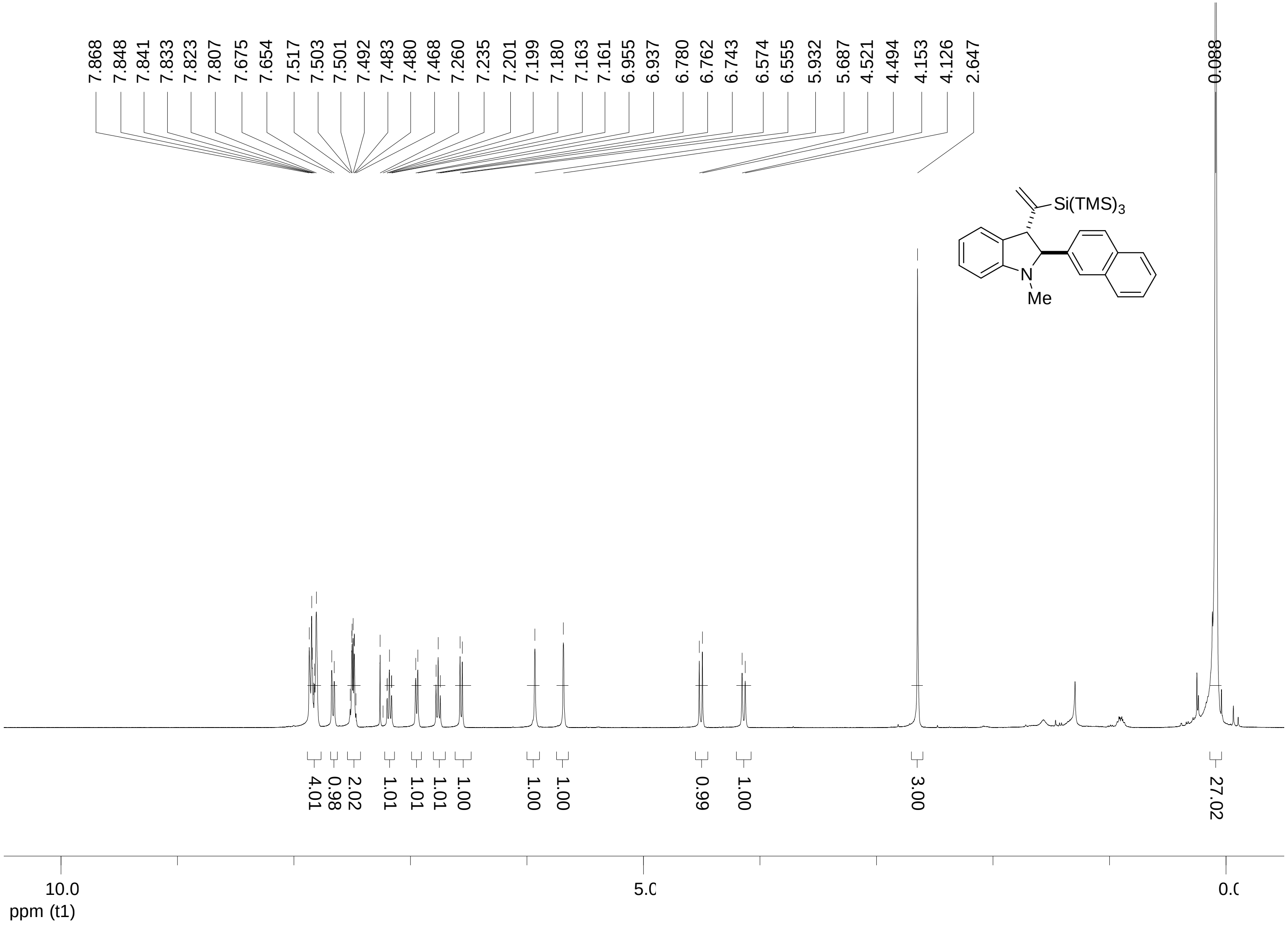
^{1}H NMR spectrum of **4h** (400 MHz, $CDCl_3$)



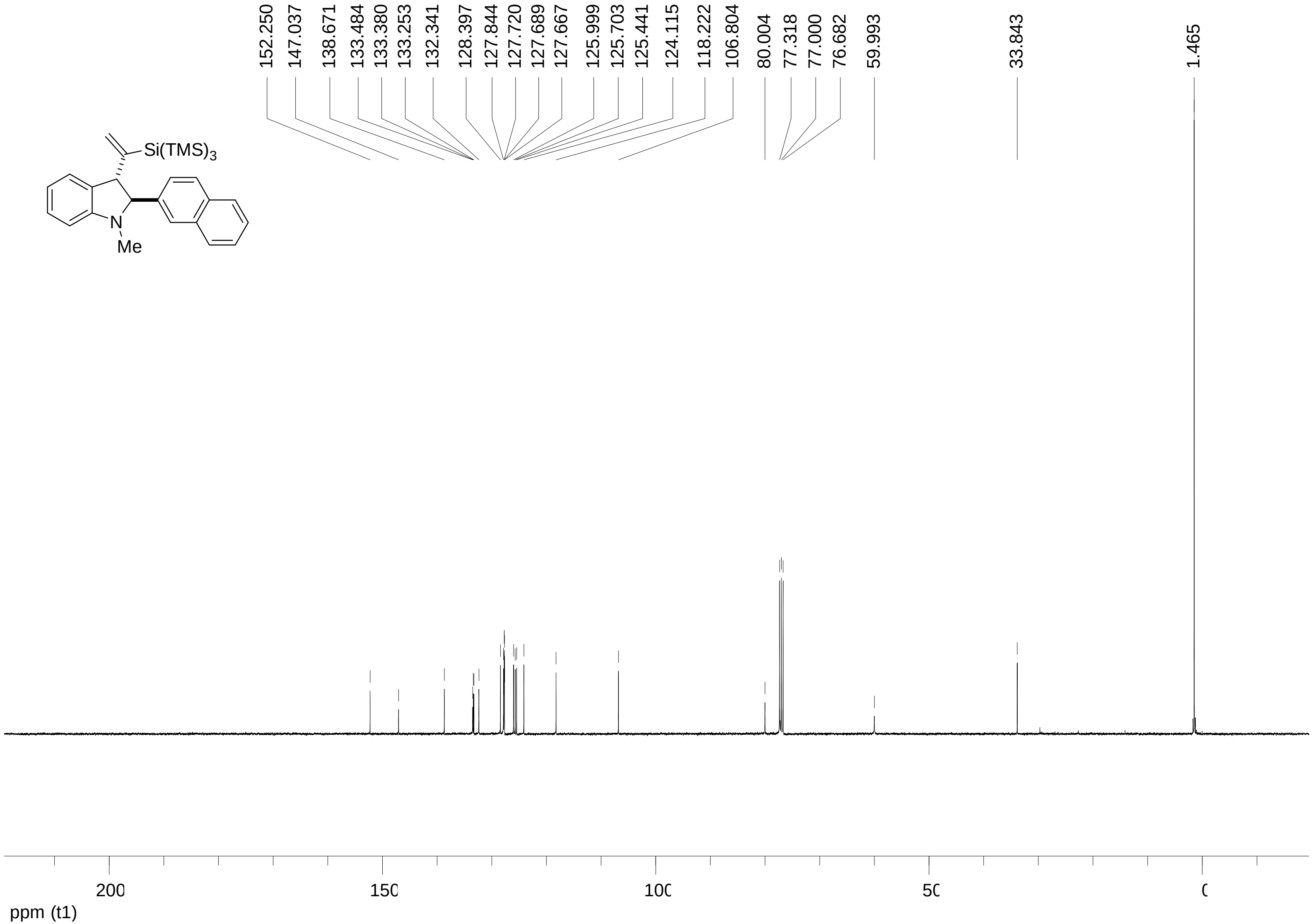
^{13}C NMR spectrum of **4h** (100 MHz, $CDCl_3$)



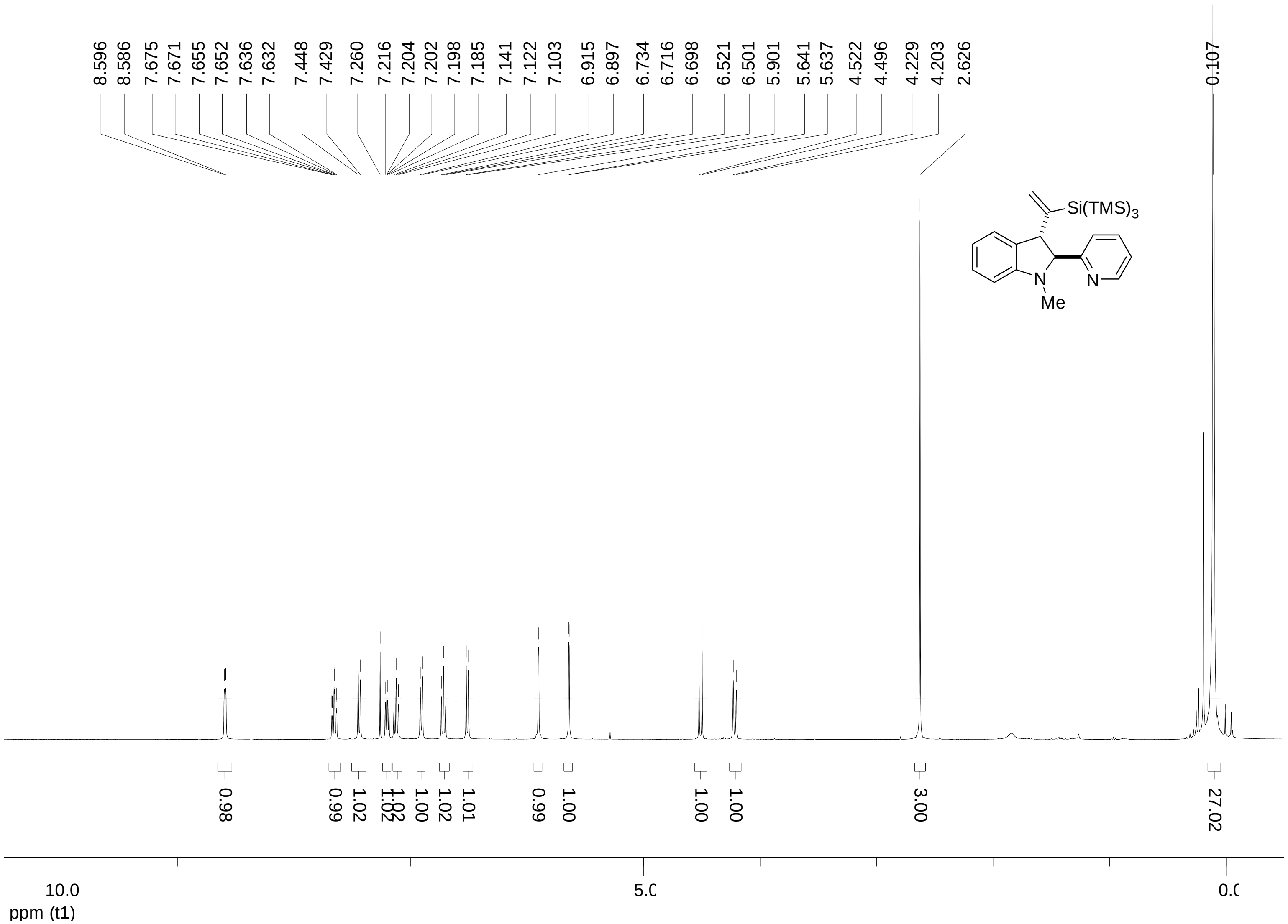
^{1}H NMR spectrum of **4i** (400 MHz, $CDCl_3$)



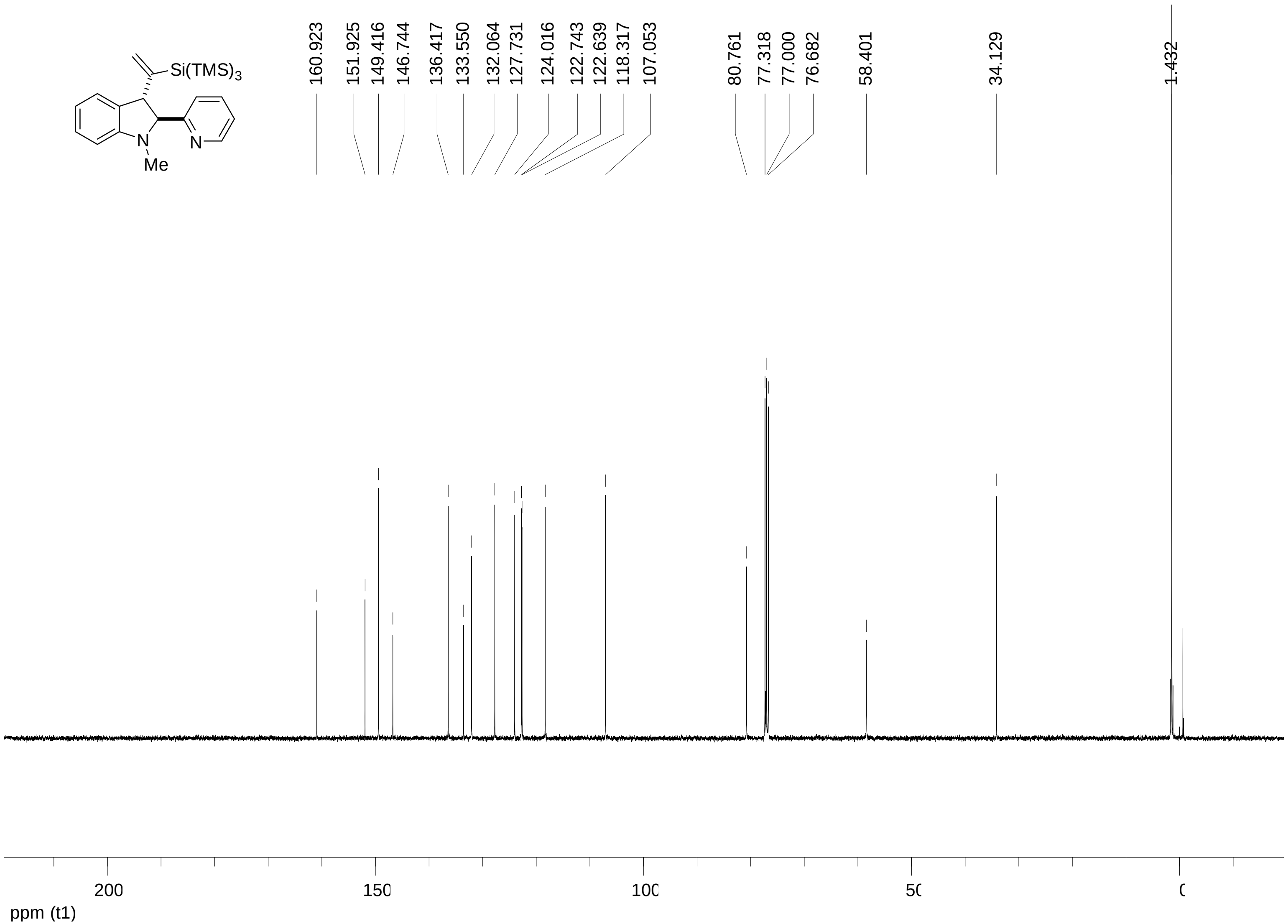
^{13}C NMR spectrum of **4i** (100 MHz, CDCl$_3$)



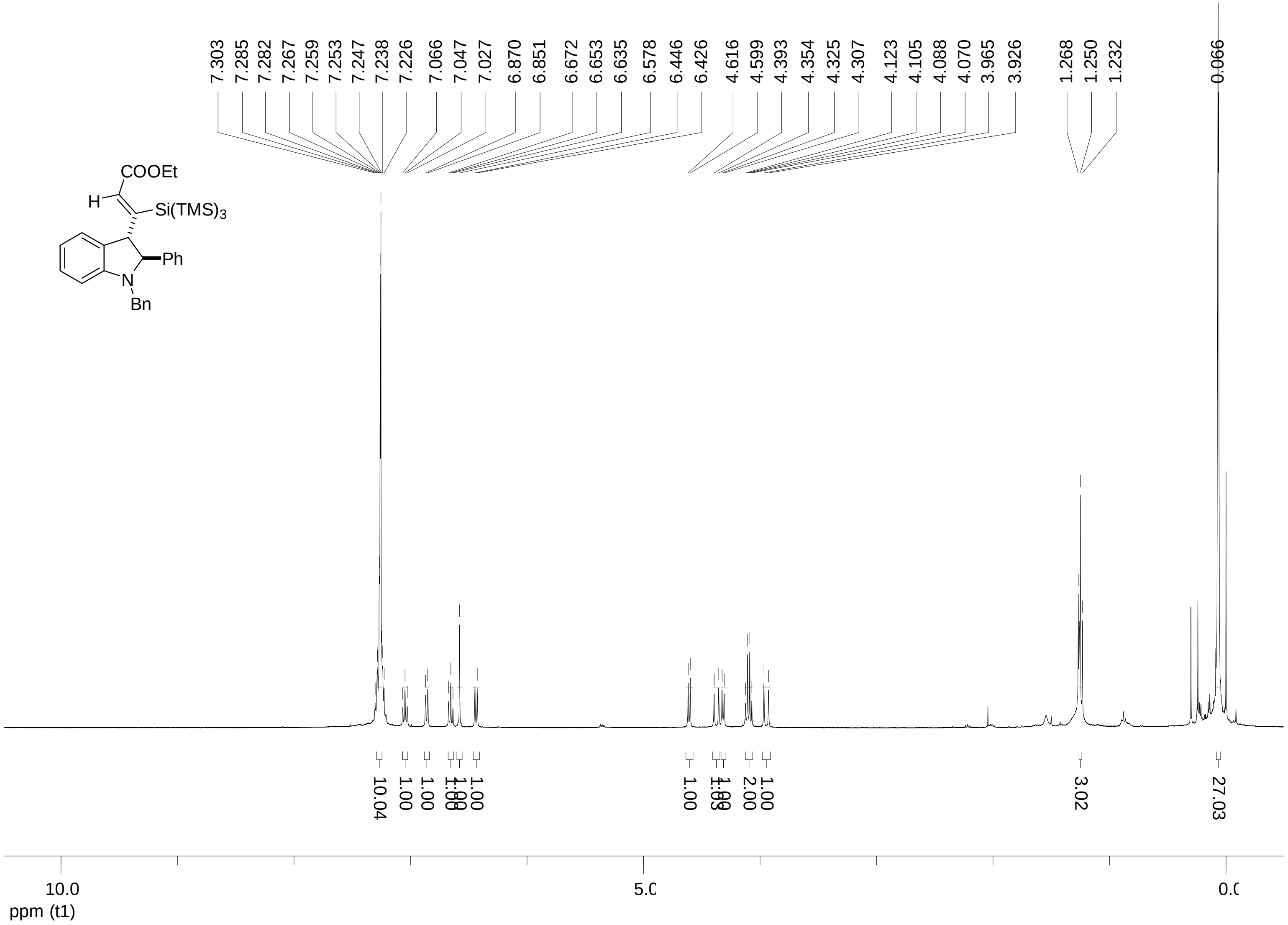
^{1}H NMR spectrum of **4j** (400 MHz, $CDCl_3$)



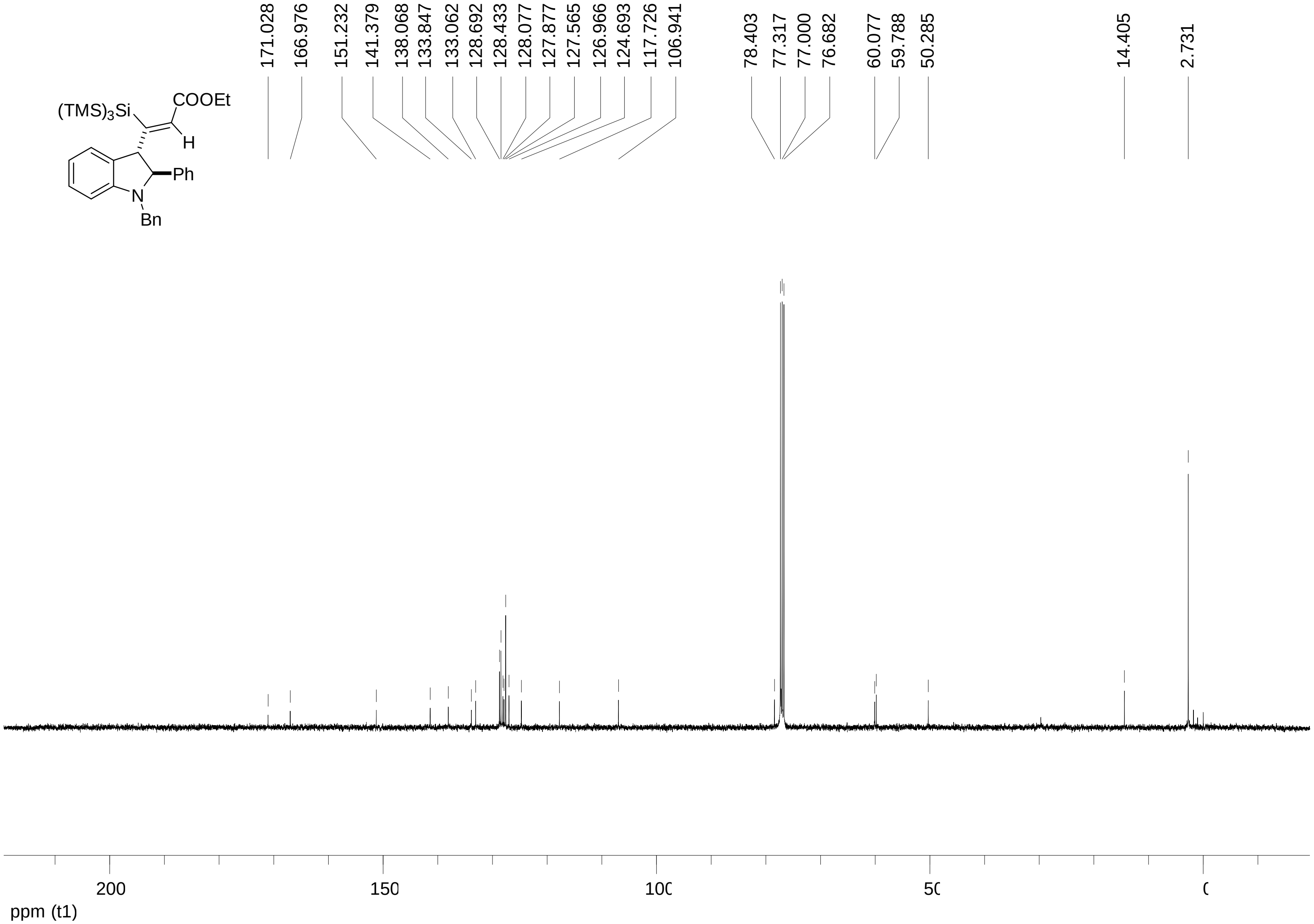
^{13}C NMR spectrum of **4j** (100 MHz, $CDCl_3$)



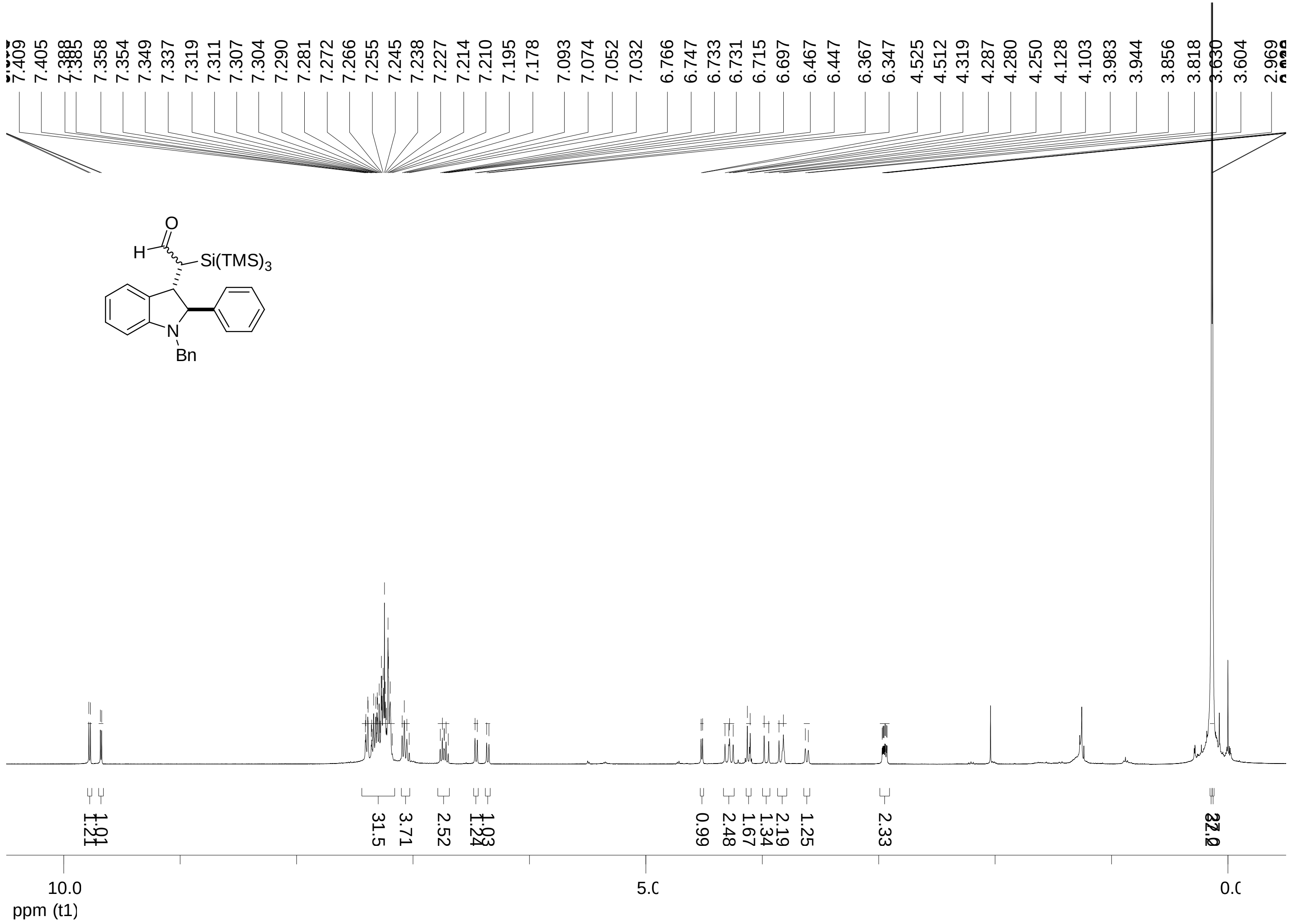
^{1}H NMR spectrum of **4k** (400 MHz, $CDCl_3$)



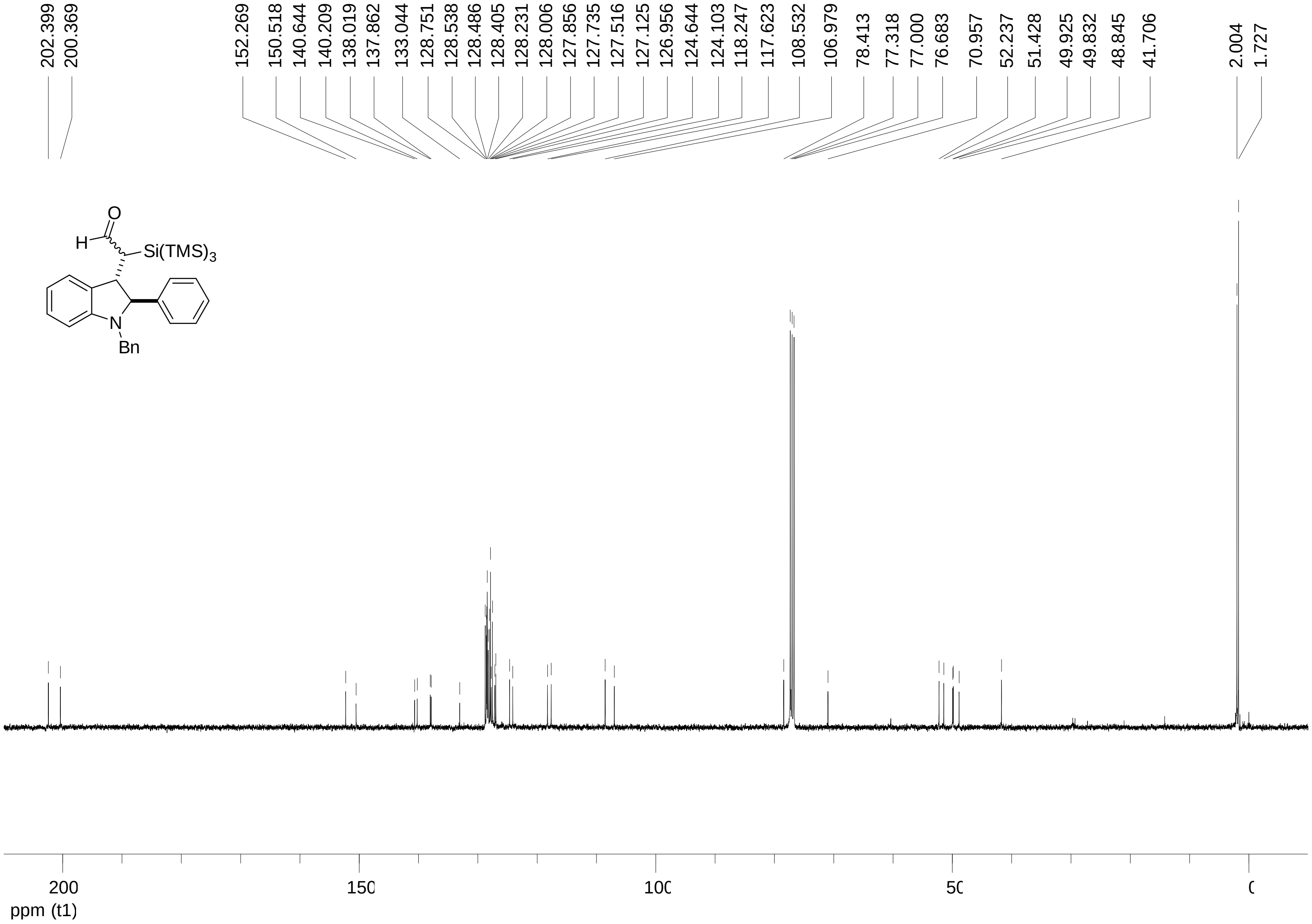
^{13}C NMR spectrum of **4k** (100 MHz, $CDCl_3$)



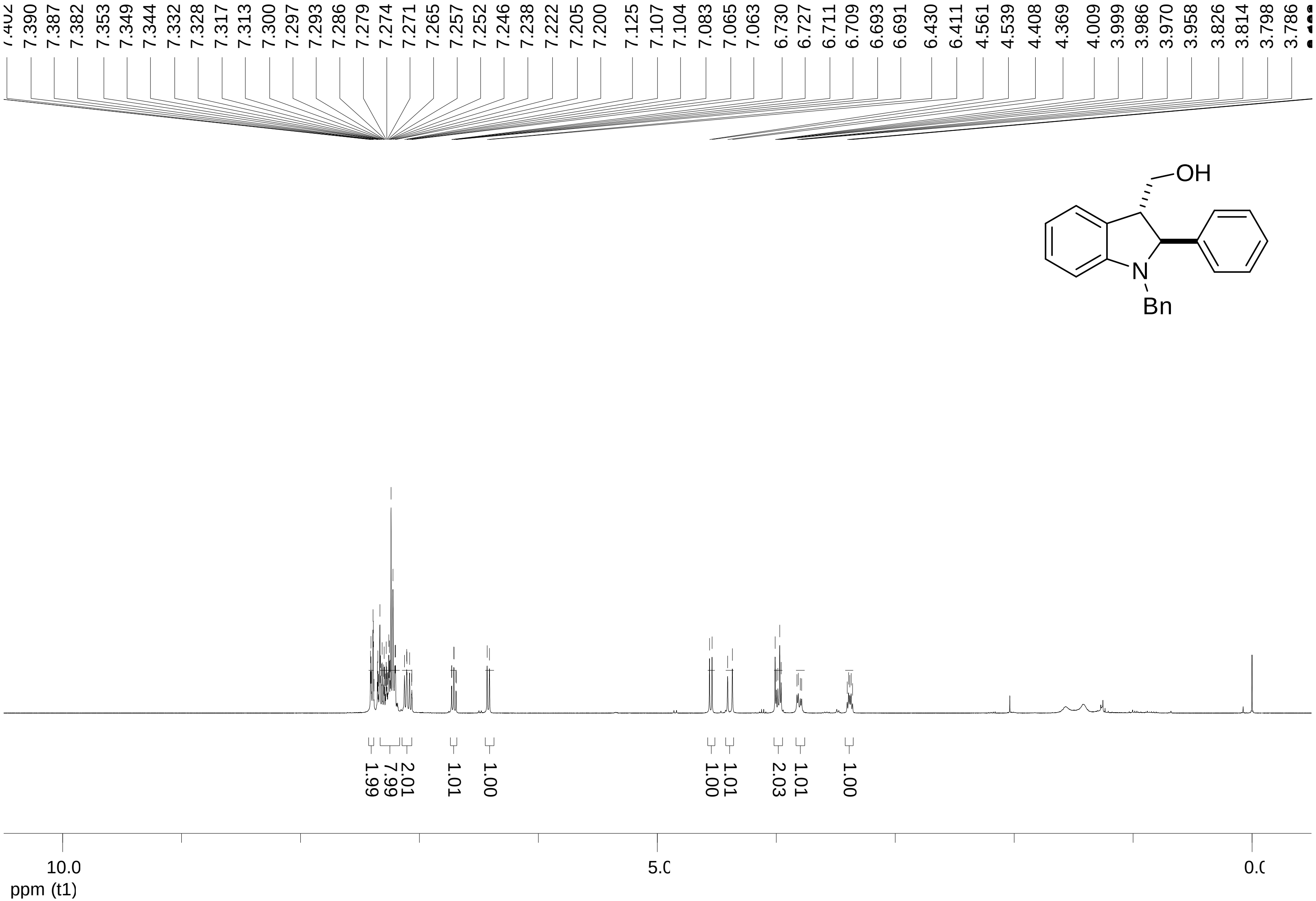
^{1}H NMR spectrum of **4l** (400 MHz, $CDCl_3$)



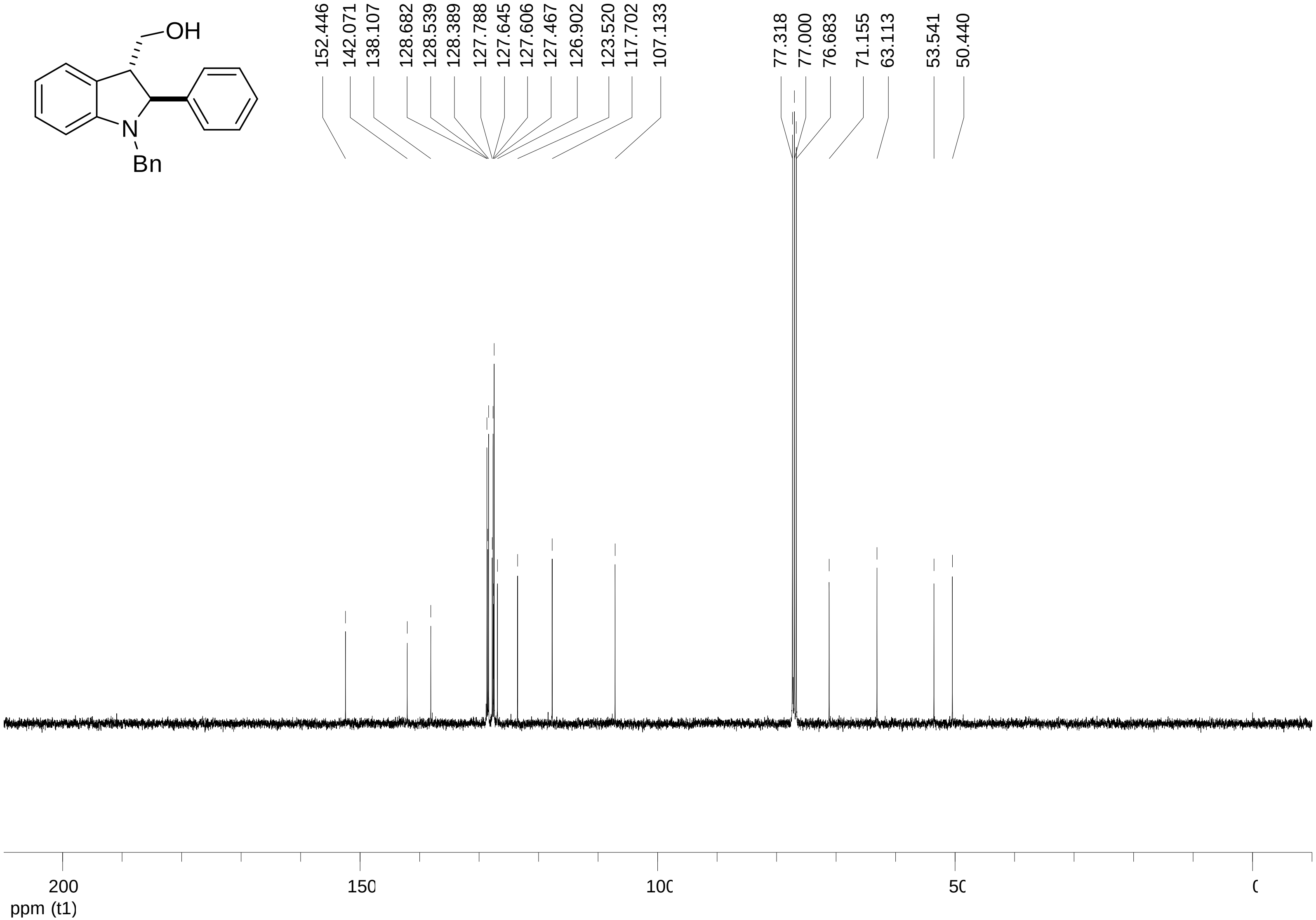
^{13}C NMR spectrum of **4l** (100 MHz, $CDCl_3$)



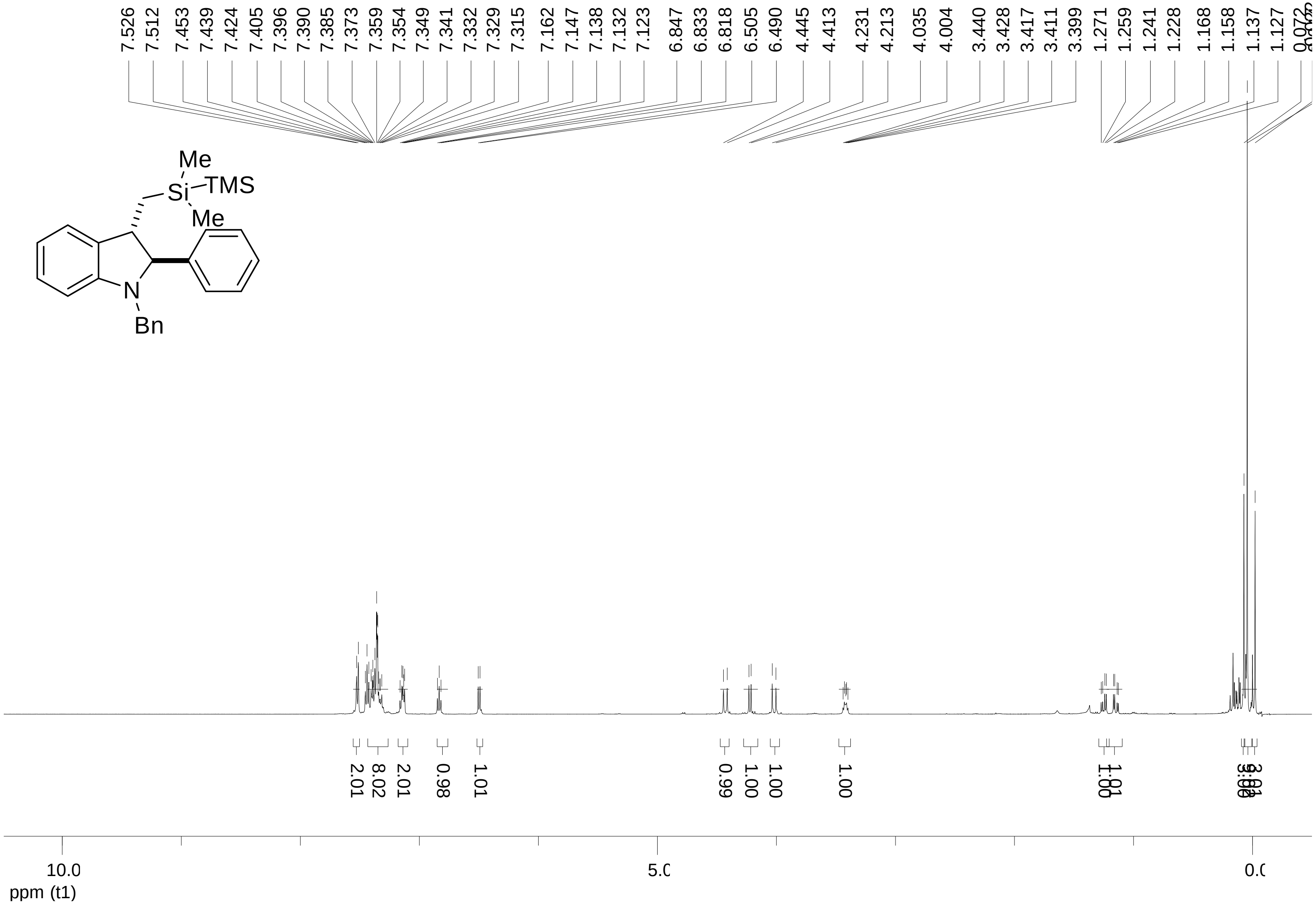
^{1}H NMR spectrum of **5** (400 MHz, CDCl$_3$)



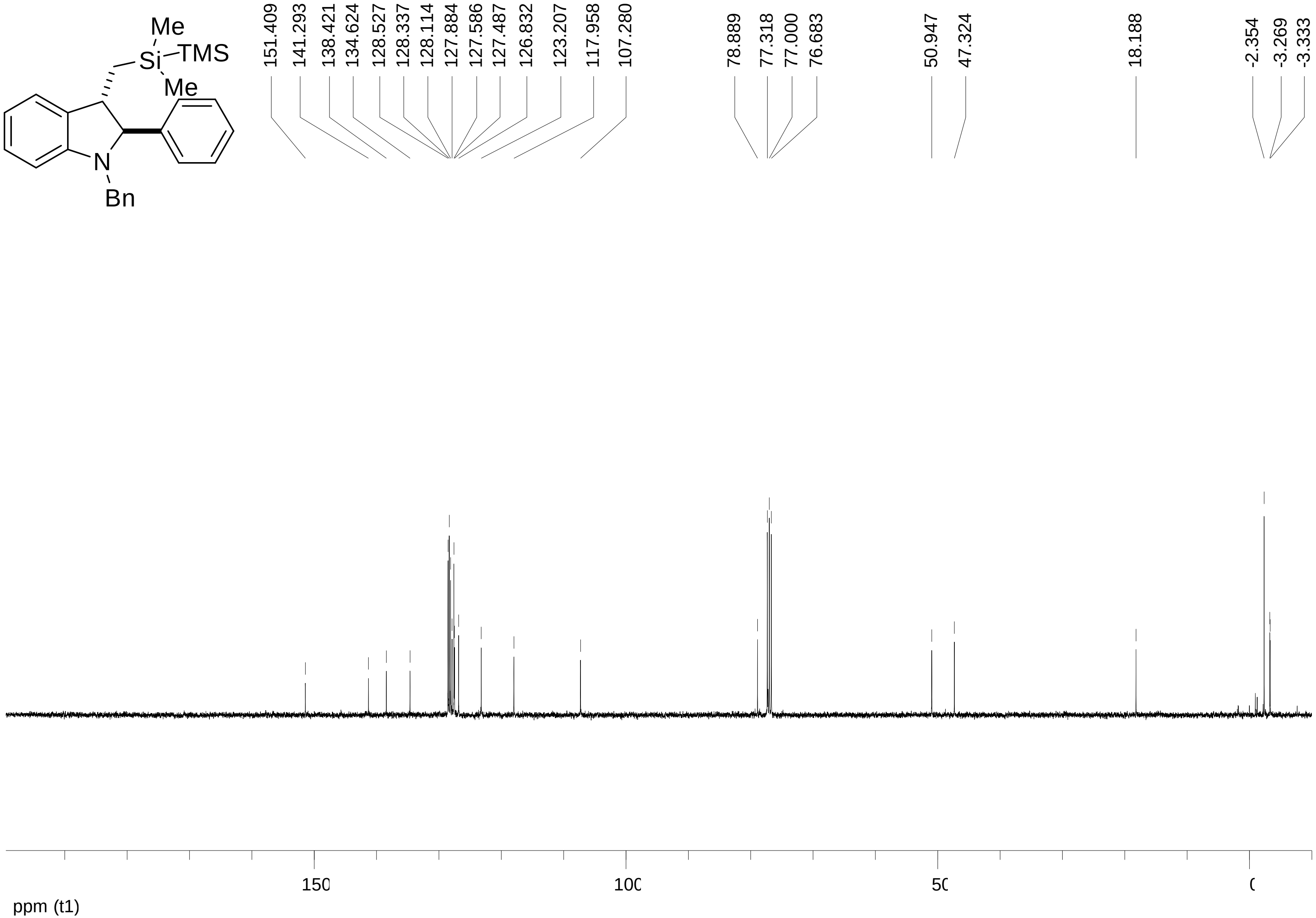
^{13}C NMR spectrum of **5** (100 MHz, CDCl$_3$)



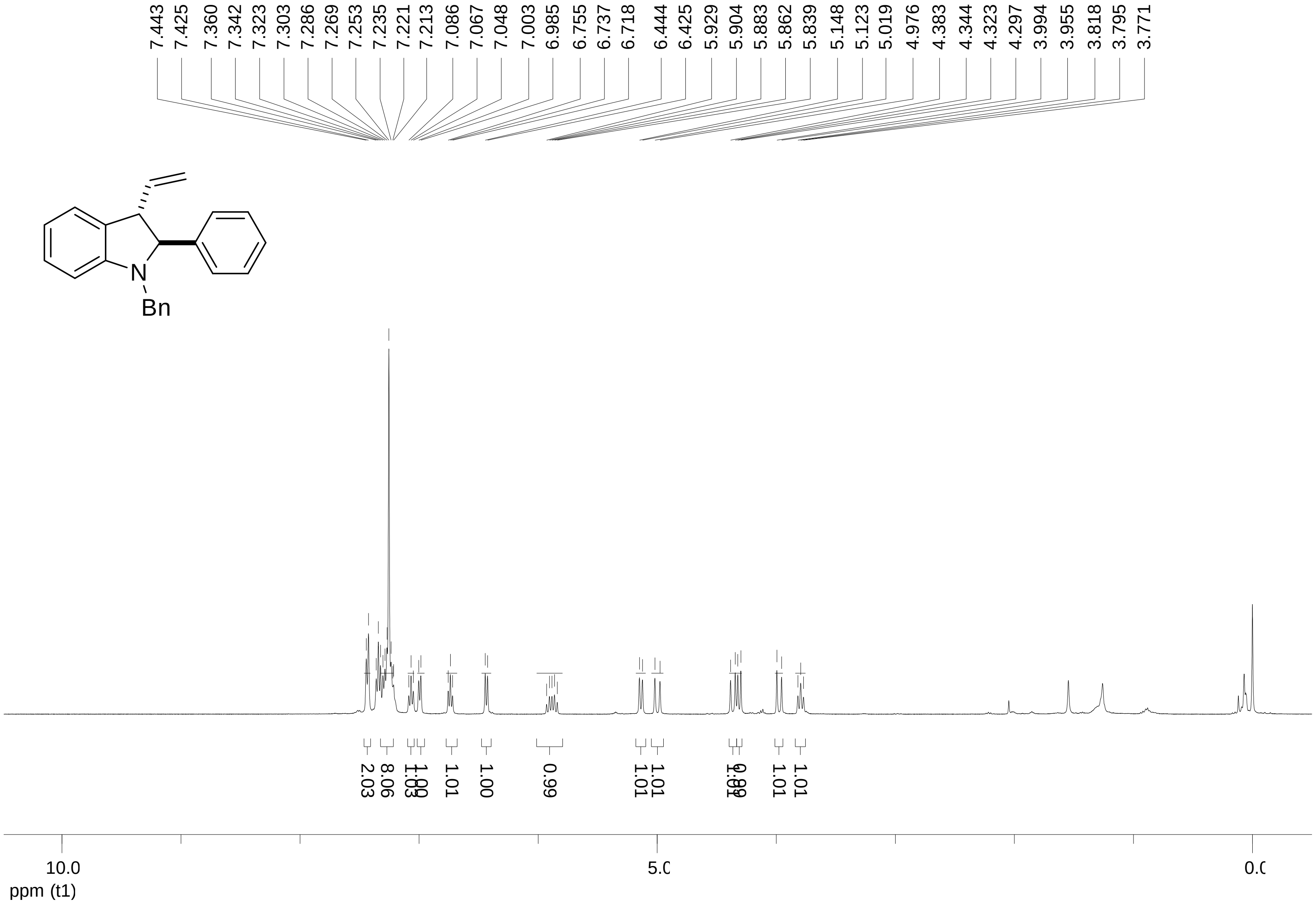
^{1}H NMR spectrum of **6** (400 MHz, $CDCl_3$)



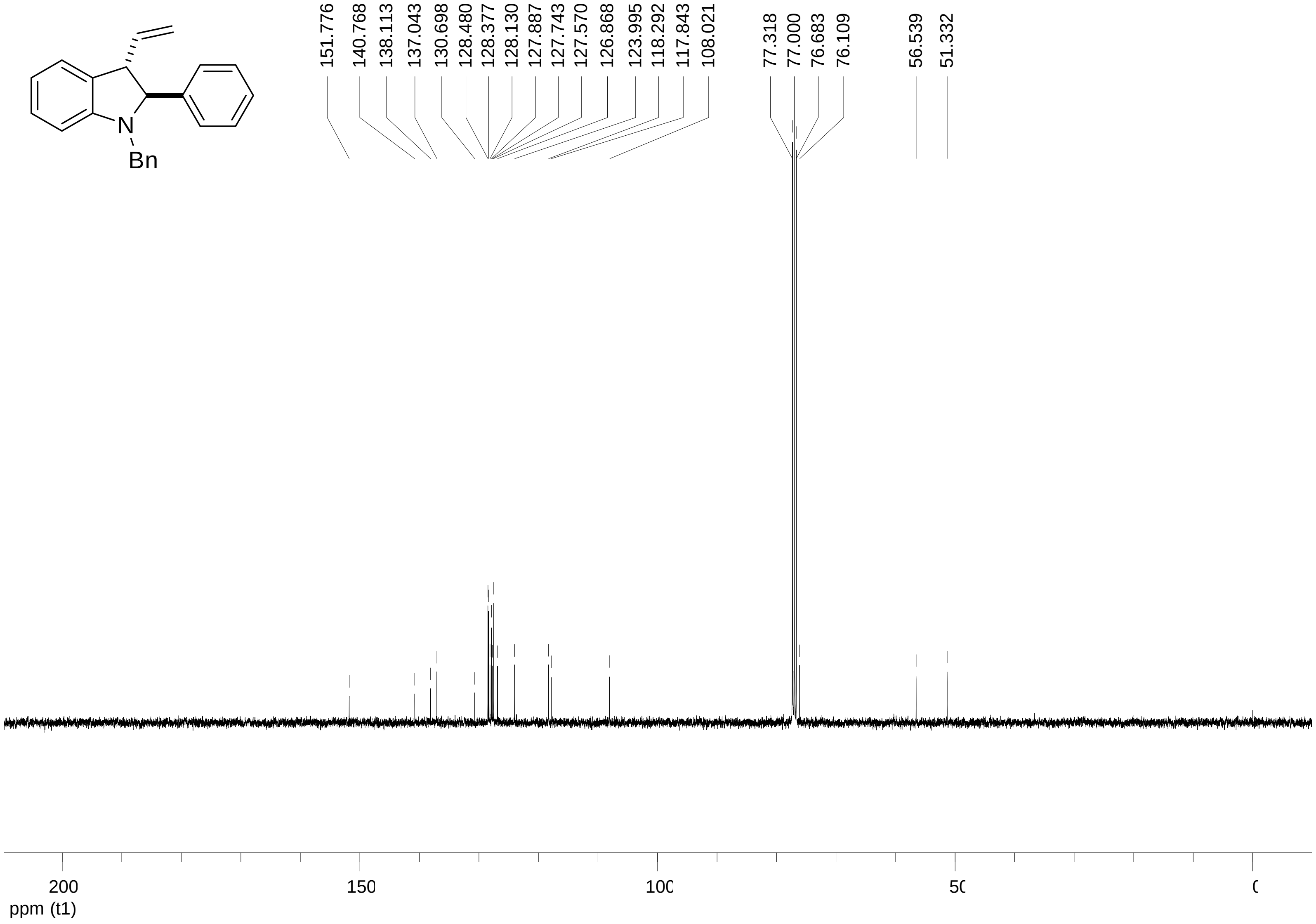
^{13}C NMR spectrum of **6** (100 MHz, $CDCl_3$)



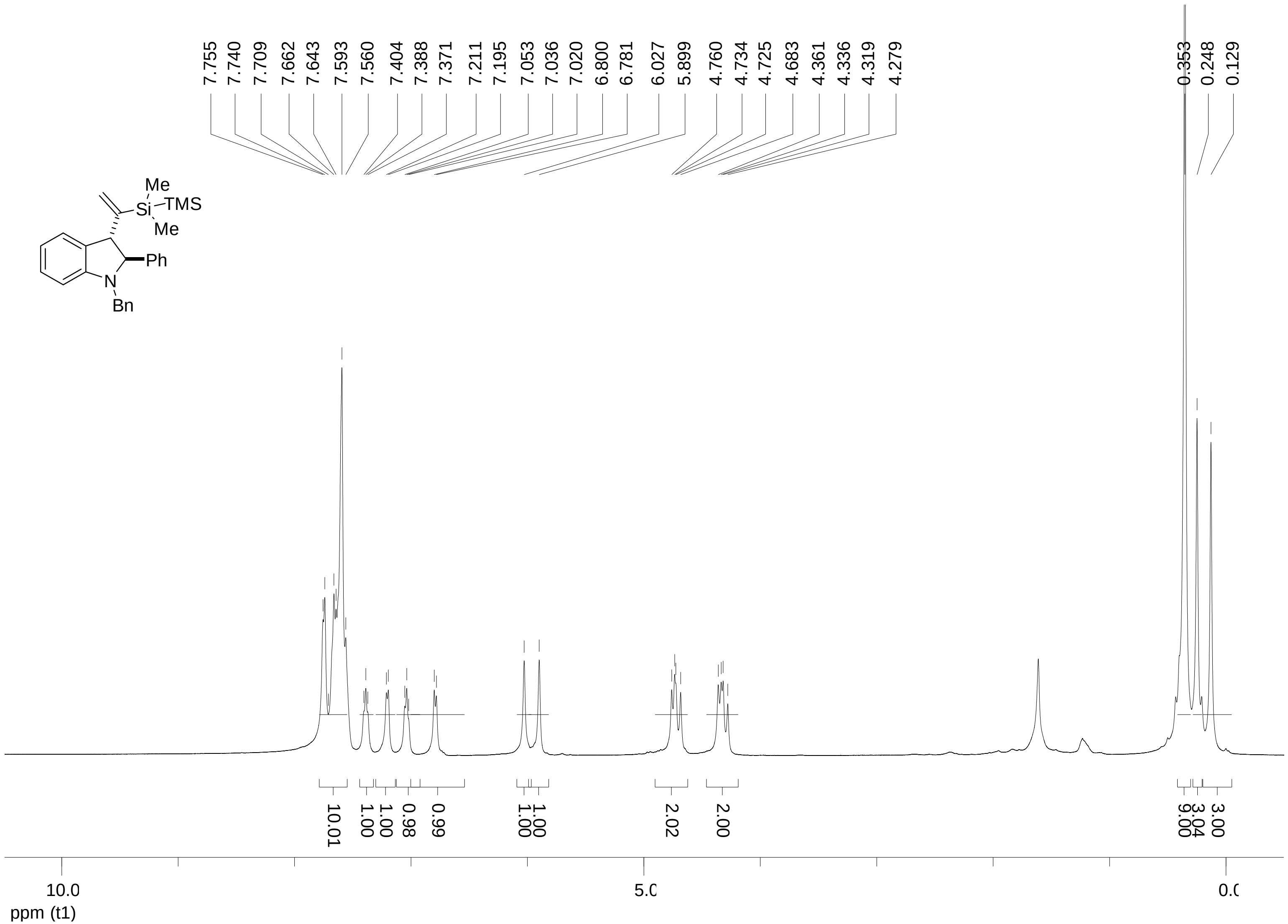
^{1}H NMR spectrum of **7** (400 MHz, $CDCl_3$)



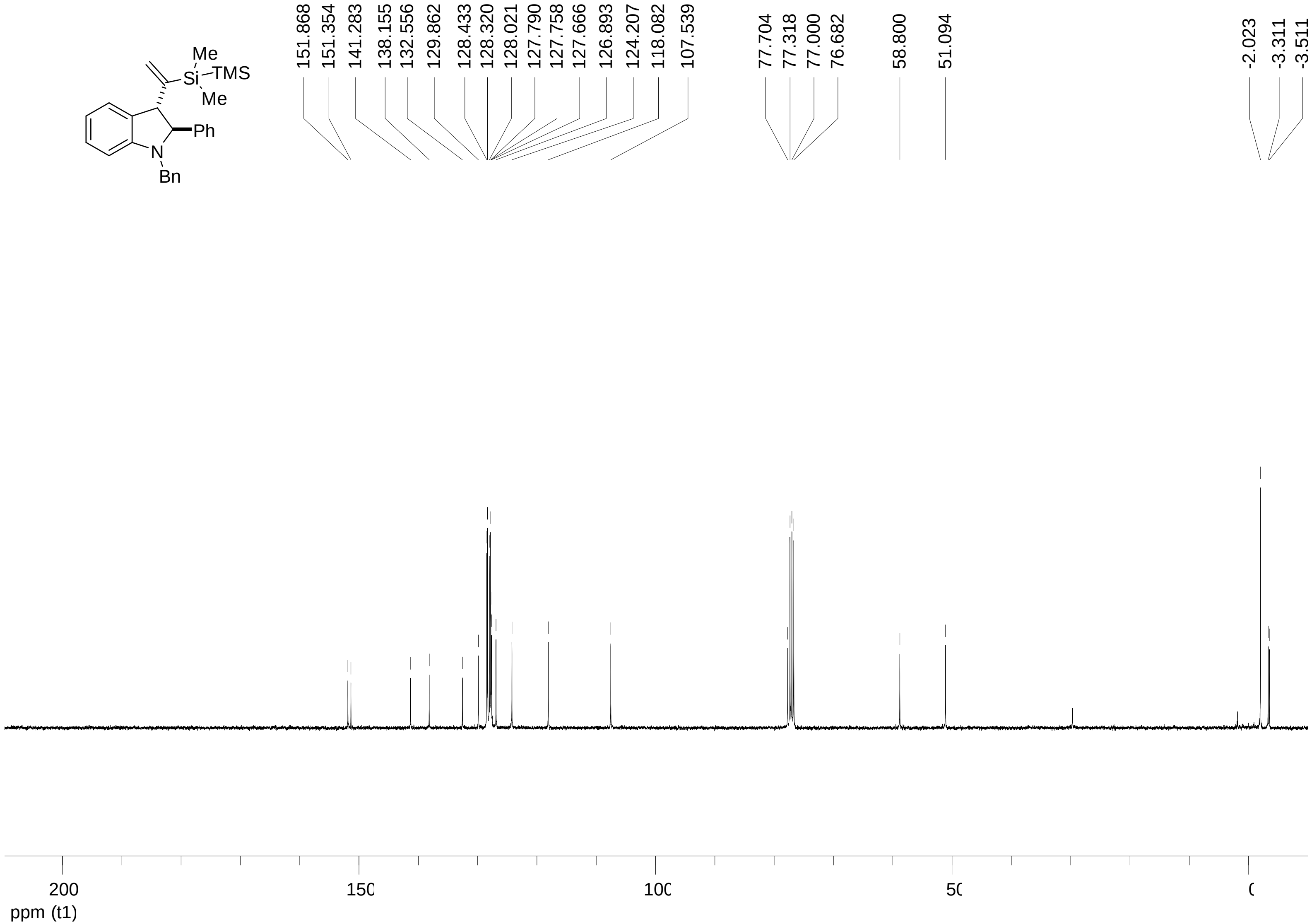
^{13}C NMR spectrum of **7** (100 MHz, CDCl$_3$)



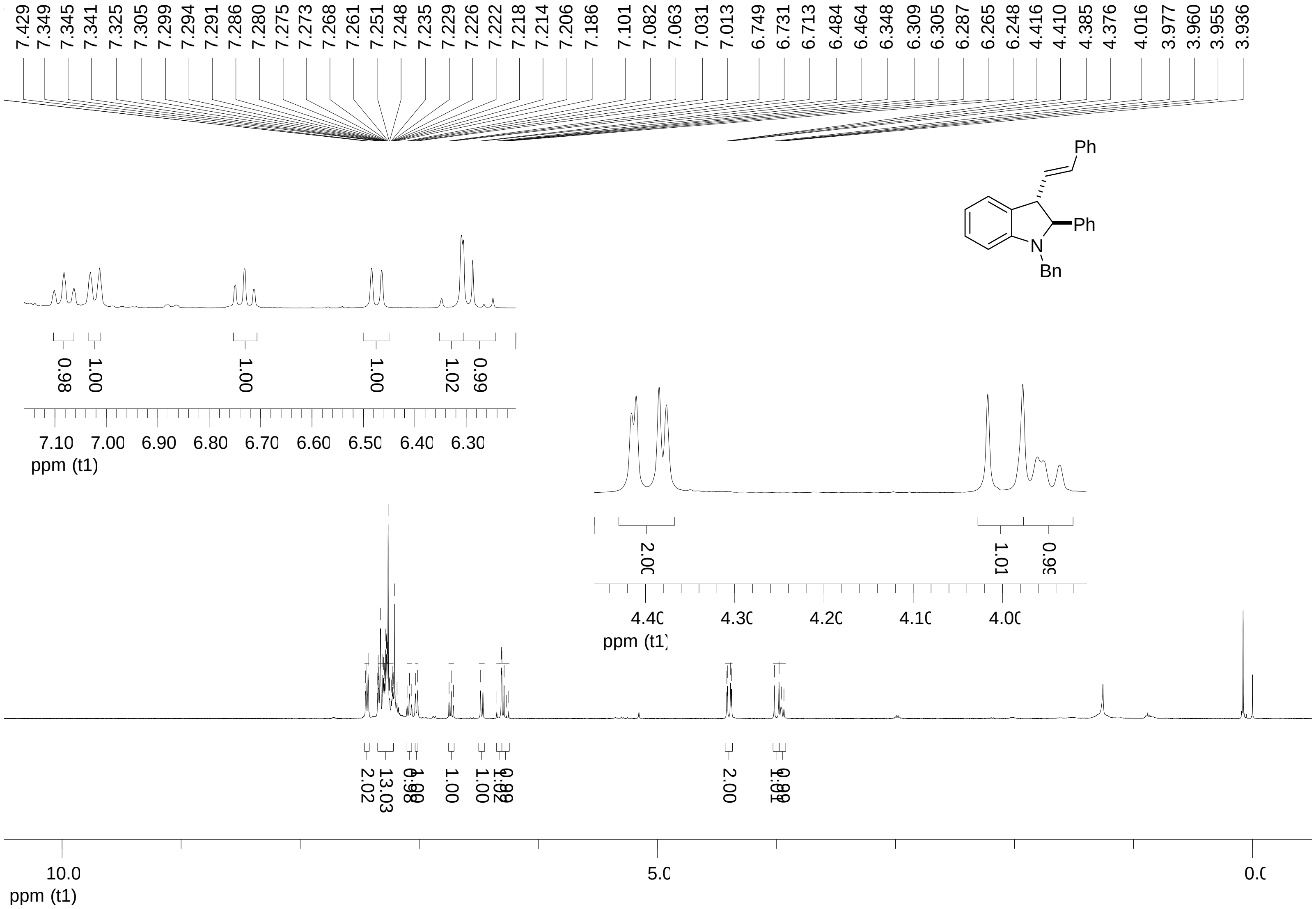
^{1}H NMR spectrum of **8** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of **8** (100 MHz, $CDCl_3$)



^{1}H NMR spectrum of **9** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of **9** (100 MHz, CDCl$_3$)