Supporting Information for

Aminoboration: Addition of B–N σ Bonds Across C–C π Bonds

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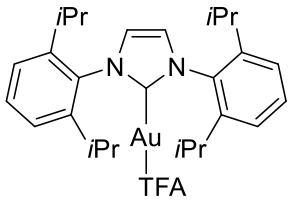
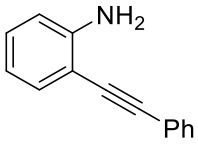
General Methods and Materials

Unless stated otherwise, reactions were performed in oven-dried or flame-dried glassware using a Schlenk line or a glovebox under a nitrogen atmosphere. Toluene, CH_2Cl_2, THF and NEt_3 were purified by passage through an alumina column under argon pressure on a push-still solvent system. d_8-Toluene was dried over sodium-benzophenone ketyl and vacuum transferred before use. All chemicals were used as received from commercial sources unless otherwise noted. Catecholborane (HBcat) was purified by distillation at reduced pressure. Sodium trifluoroacetate (NaTFA) was dried at 130 °C at 10 mTorr for 18 h before use. Analytical thin layer chromatography (TLC) was performed using Merck F_{250} plates. TLC plates were visualized under UV irradiation (254 nm) and/or by staining with iodine on silica gel. Flash chromatography was conducted using a Teledyne Isco Combiflash® Rf 200 Automated Flash Chromatography System, and Teledyne Isco Redisep® 35–70 μm silica gel. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX-500 spectrometer outfitted with a cryoprobe, or a Bruker AVANCE-600 spectrometer. ^{11}B NMR spectra were recorded on a Bruker AVANCE-600 spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) and coupling constants (J) are given in Hertz (Hz), and referenced to the residual protio solvent (δ = 7.26 ppm for $CDCl_3$, δ = 5.32 ppm for CD_2Cl_2 and δ = 2.08 ppm for d_8-toluene in ^{1}H NMR spectra; δ = 77.16 ppm for $CDCl_3$ in ^{13}C NMR spectra). The following abbreviations are used to indicate signal multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad. ^{11}B NMR spectroscopy experiments are referenced to the absolute frequency of 0 ppm in the ^{1}H dimension according to the Xi scale. High-resolution mass spectrometry (HRMS) data were obtained at the University of California, Irvine. The ipso carbon (C directly bound to quadrupolar B) could not be observed in the ^{13}C NMR spectra of indole boronic esters **3**. Broad features in the ^{11}B NMR spectra are due to the boron materials of the NMR tube.



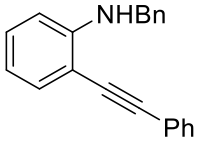
IPrAuTFA. The preparation of IPrAuTFA was adapted from a literature procedure.[1] A mixture of IPrAuCl (0.497 g, 0.800 mmol) and AgTFA (0.186 g, 0.840 mmol) in CH_2Cl_2 (10 mL) in a 20 mL vial, wrapped with aluminum foil, was stirred for 17 h at room temperature. The reaction mixture was filtered through a Celite plug to remove AgCl. The filtrate was concentrated and dried in vacuo to yield IPrAuTFA as a white solid (0.548 g, 98% yield), which was used directly in catalytic reactions.

^{1}H NMR (600 MHz, CD_2Cl_2): δ 7.57 (t, J = 7.8 Hz, 2H), 7.36 (d, J = 7.8 Hz, 4H), 7.27 (s, 2H), 2.55 (septet, J = 6.9 Hz, 4H), 1.35 (d, J = 6.9 Hz, 12H), 1.24 (d, J = 6.9 Hz, 12H). This spectrum is in agreement with literature spectral data.[1]



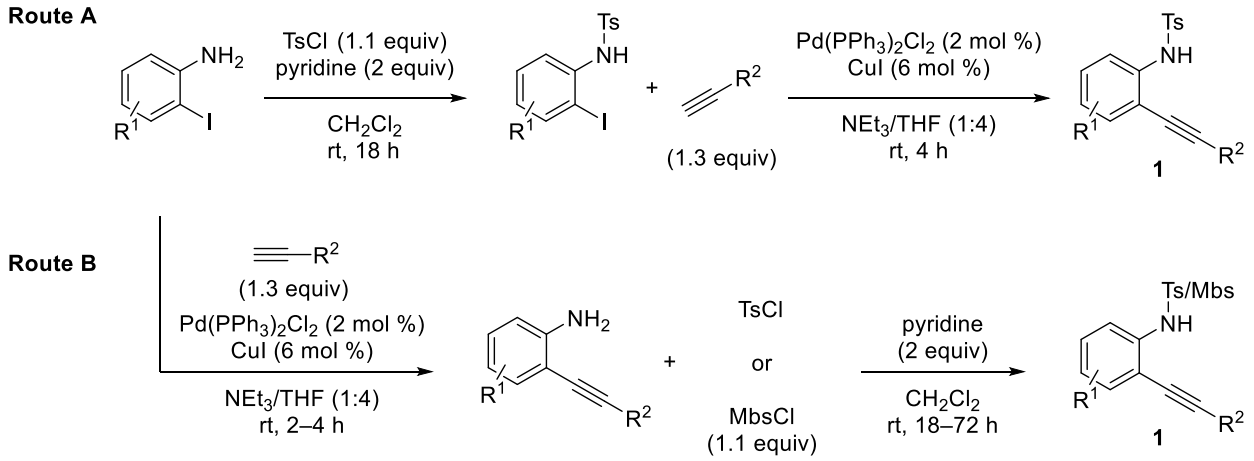
2-(Phenylethynyl)aniline (1a) was prepared according to a literature procedure.[2]

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.55-7.50 (m, 2H), 7.38-7.32 (m, 4H), 7.17-7.12 (m, 1H), 6.75-6.70 (m, 2H), 4.28 (br s, 2H). This spectrum is in agreement with literature spectral data.[2]



***N*-Benzyl-2-(phenylethynyl)aniline (1b)**. The procedure for *N*-alkylation of aniline was adapted from a literature procedure.[3] A mixture of **1a** (0.464 g, 2.40 mmol), benzyl bromide (0.342 g, 2.00 mmol) and $NaHCO_3$ (0.336 g, 4.00 mmol) in EtOH (10 mL) in a 25 mL round-bottom flask was stirred at room temperature for 20 h. The resulting mixture was diluted with water (10 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The resulting crude residue was purified by flash chromatography (elution gradient from 0-10% CH_2Cl_2 in hexanes) to give title compound as a yellow oil (0.219 g, 39% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.51-7.47 (m, 2H), 7.42-7.26 (m, 9H), 7.19-7.14 (m, 1H), 6.67 (t, J = 7.4 Hz, 1H), 6.60 (d, J = 8.3 Hz, 1H), 5.14 (br t, J = 5.3 Hz, 1H), 4.48 (d, J = 5.8 Hz, 2H). This spectrum is in agreement with literature spectral data.[4]



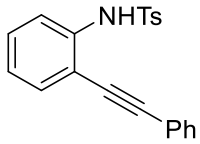
Route A and Route B were used to synthesize substrates **1**. Route A sometimes resulted in self-cyclization of **1** in the Sonogashira cross-coupling step and, thus, route B was alternatively used.

General Procedure for *N*-Sulfonyl Anilines

A solution of aniline (1.00 equiv, 0.2–0.5 M in CH_2Cl_2) and TsCl (1.10 equiv) or MbsCl (1.10 equiv), pyridine (2.00 equiv) in CH_2Cl_2 was stirred at room temperature overnight. The reaction was monitored by TLC. When the reaction was complete or no further reactivity seen, water was added and extracted with CH_2Cl_2 (3×). The combined organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The resulting crude residue was purified by flash chromatography.

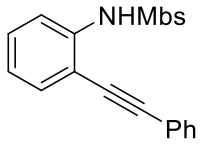
General Procedure for Sonogashira Cross-Coupling

To a stirring suspension containing 2-iodoaniline (1.00 equiv, 0.2 M in NEt_3/THF), $Pd(PPh_3)_2Cl_2$ (2 mol %), CuI (6 mol %) in NEt_3/THF (1:4) under N_2 atmosphere, alkyne (1.30 equiv) was added and stirred at room temperature. The reaction was monitored by TLC. When the reaction was complete, the reaction mixture was diluted with EtOAc and filtered through a pad of silica gel. The filtrate was concentrated in vacuo and purified by flash chromatography.



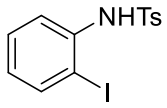
4-Methyl-*N*-(2-(phenylethynyl)phenyl)benzenesulfonamide (1c) was synthesized from **1a** (0.386 g, 2.00 mmol) using the general procedure for *N*-sulfonyl anilines with a reaction time of 18.5 h. Purification by flash chromatography (elution gradient from 5-10% EtOAc in hexanes) gave the title compound as a faint yellow solid (0.436 g, 63% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.68 (d, J = 8.3 Hz, 2H), 7.63 (d, J = 8.3 Hz, 1H), 7.49-7.45 (m, 2H), 7.42-7.36 (m, 4H), 7.32-7.27 (m, 1H), 7.20 (br s, 1H), 7.17 (d, J = 8.2 Hz, 2H), 7.07 (t, J = 7.6 Hz, 1H), 2.34 (s, 3H). This spectrum is in agreement with literature spectral data.[5]



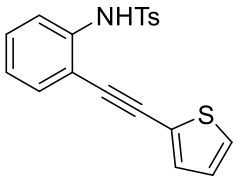
4-Methoxy-*N*-(2-(phenylethynyl)phenyl)benzenesulfonamide (1d) was synthesized from **1a** (0.386 g, 2.00 mmol) using the general procedure for *N*-sulfonyl anilines with a reaction time of 19.5 h. Purification by flash chromatography (elution gradient from 10-20% EtOAc in hexanes) gave the title compound as a white solid (0.720 g, 99% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.73-7.69 (m, 2H), 7.63 (d, J = 8.2 Hz, 1H), 7.49-7.46 (m, 2H), 7.41-7.36 (m, 4H), 7.32-7.27 (m, 1H), 7.18 (br s, 1H), 7.00-7.05 (m, 1H), 6.85-6.81 (m, 2H), 3.78 (s, 3H). This spectrum is in agreement with literature spectral data.[5]



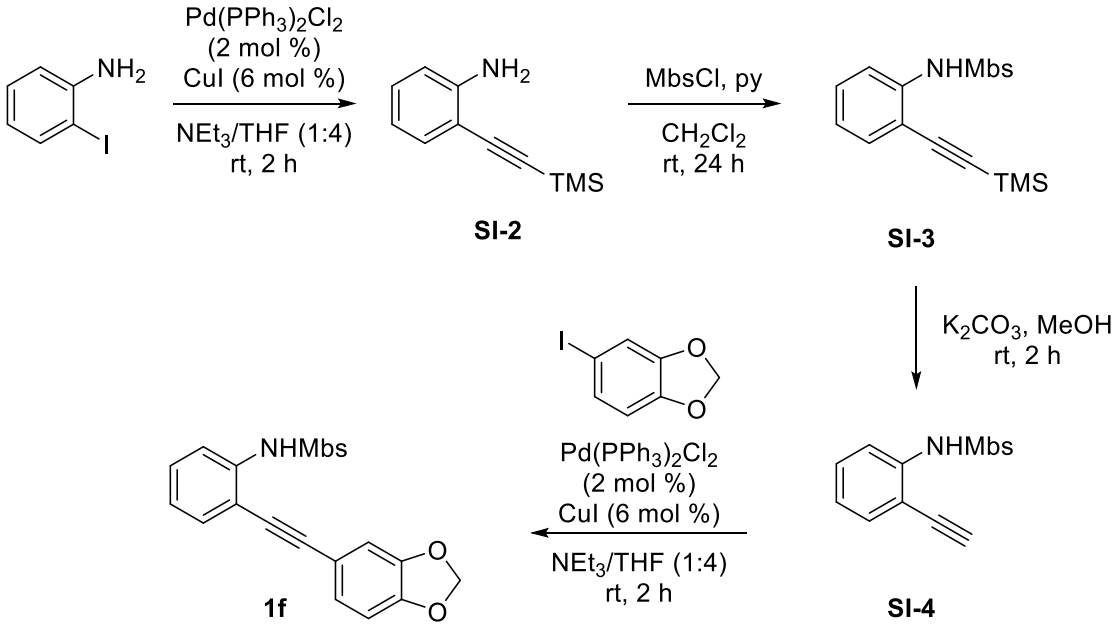
***N*-(2-Iodophenyl)-4-methylbenzenesulfonamide (SI-1)** was synthesized from 2-iodoaniline (5.48 g, 25.0 mmol) using the general procedure for *N*-sulfonyl anilines with a reaction time of 18 h. Purification by chromatography (elution gradient from 10-20% EtOAc in hexanes) gave the title compound as an off-white solid (8.06 g, 86% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.67-7.61 (m, 4H), 7.33-7.28 (m, 1H), 7.22 (d, J = 8.1 Hz, 2H), 6.83 (td, J = 7.8, 1.3 Hz, 1H), 6.79 (br s, 1H), 2.38 (s, 3H). This spectrum is in agreement with literature spectral data.[6]



4-Methyl-*N*-(2-(thiophen-2-ylethynyl)phenyl)benzenesulfonamide (1e) was synthesized from **SI-1** (0.746 g, 2.00 mmol) and 2-ethynylthiophene (0.281 g, 2.60 mmol) using the general procedure for Sonogashira cross-coupling with a reaction time of 4 h. Purification by flash chromatography (elution gradient from 5-10% EtOAc in hexanes) gave the title compound as a brown solid (0.482 g, 68% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.67-7.62 (m, 3H), 7.39-7.26 (m, 4H), 7.19 (d, J = 8.1 Hz, 2H), 7.10-7.04 (m, 3H), 2.35 (s, 3H). This spectrum is in agreement with literature spectral data.[7]



2-((Trimethylsilyl)ethynyl)aniline (SI-2) was synthesized from 2-iodoaniline (1.10 g, 5.00 mmol) and trimethylsilylacetylene (0.92 mL, 6.5 mmol) using the general procedure for Sonogashira cross-coupling with a reaction time of 2 h. Purification by flash chromatography (elution gradient from 0-10% EtOAc in hexanes) gave the title compound as a brown liquid (0.862 g, 91% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.31-7.27 (m, 1H), 7.13-7.09 (m, 1H), 6.70-6.63 (m, 2H), 4.22 (br s, 2H), 0.26 (s, 9H). This spectrum is in agreement with literature spectral data.[8]

4-Methoxy-*N*-(2-((trimethylsilyl)ethynyl)phenyl)benzenesulfonamide (SI-3) was synthesized from **SI-2** (0.862 g, 4.55 mmol) using the general procedure for *N*-sulfonyl anilines with a reaction time of 24 h. Purification by flash chromatography (20% EtOAc in hexanes), followed by recrystallization from hexanes gave the title compound as a colourless crystalline solid (1.30 g, 79% yield).

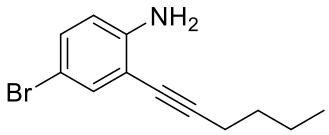
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71-7.66 (m, 2H), 7.60 (d, J = 8.1 Hz, 1H), 7.31-7.24 (m, 2H), 7.17 (br s, 1H), 7.00 (td, J = 7.6, 1.0 Hz, 1H), 6.88-6.83 (m, 2H), 3.81 (s, 3H), 0.27 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 163.3, 138.3, 132.1, 130.7, 129.9, 129.6, 124.4, 119.9, 114.4, 114.3, 102.4, 99.7, 55.7, 0.04. **HRMS** (ESI): *m/z* calcd for $C_{18}H_{21}NO_3SSiNa$ $[M+Na]^+$: 382.0909. Found: 382.0897.

***N*-(2-Ethynylphenyl)-4-methoxybenzenesulfonamide (SI-4).** A suspension of **SI-3** (0.560 g, 1.56 mmol) and K_2CO_3 (0.323 g, 2.34 mmol) in MeOH (4 mL) was stirred vigorously at room temperature for 2 h. The reaction mixture was dried over $MgSO_4$, filtered through a Celite plug, and concentrated in vacuo. The crude residue was purified by flash chromatography (20% EtOAc in hexanes) to give the title compound as a pink oil (0.320 g, 71% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76-7.71 (m, 2H), 7.59 (dd, J = 8.4, 0.6 Hz), 7.34 (dd, J = 7.7, 1.5 Hz), 7.31-7.26 (m, 1H), 7.21 (br s, 1H), 7.01 (td, J = 7.7, 1.1 Hz, 1H), 6.90-6.85 (m, 2H), 3.82 (s, 3H), 3.37 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 163.4, 138.7, 132.6, 130.5, 130.3, 129.7, 124.3, 119.5, 114.3, 112.8, 84.5, 78.8, 55.7. **HRMS** (ESI): *m/z* calcd for $C_{15}H_{13}NO_3SNa$ $[M+Na]^+$: 310.0514. Found: 310.0504.

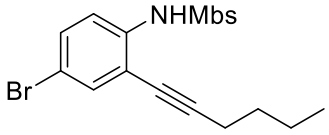
***N*-(2-(Benzo[*d*][1,3]dioxol-5-ylethynyl)phenyl)-4-methoxybenzenesulfonamide (1f).** To a mixture of 1-iodo-3,4-methylenedioxybenzene (0.372 g, 1.50 mmol), $Pd(PPh_3)_2Cl_2$ (10.5 mg, 0.0150 mmol), CuI (8.6 mg, 0.045 mmol) in THF/NEt_3 (3 mL: 1 mL) under N_2 atmosphere, a solution of **SI-4** (0.215 g, 0.748 mmol) in THF (1 mL) was added and stirred at room temperature. After 2 h, the reaction mixture was diluted with EtOAc, filtered through a pad of Celite, and concentrated in vacuo. Purification by flash column chromatography (20% EtOAc in hexanes), followed by trituration with minimal cold Et_2O gave the title compound as an off-white solid (0.201 g, 66% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72-7.68 (m, 2H), 7.61 (d, J = 8.2 Hz, 1H), 7.34 (dd, J = 7.7, 1.4 Hz, 1H), 7.28 (td, J = 7.9, 1.5 Hz, 1H), 7.14 (br s, 1H), 7.06 (td, J = 7.6, 1.0 Hz, 1H), 7.00 (dd, J = 8.0, 1.6 Hz, 1H), 6.89 (d, J = 1.6 Hz, 1H), 6.86-6.80 (m, 3H), 6.03 (s, 2H), 3.79 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 163.3, 148.7, 147.8, 137.6, 132.0, 130.7, 129.6, 126.6, 124.7, 120.5, 115.3, 115.0, 114.3, 111.5, 108.8, 101.7, 96.2, 82.3, 55.7. **HRMS** (ESI): *m/z* calcd for $C_{22}H_{17}NO_5SNa$ $[M+Na]^+$: 430.0725. Found: 430.0725.



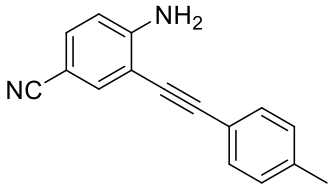
4-Bromo-2-(hex-1-yn-1-yl)aniline (SI-5) was synthesized from 4-bromo-2-iodoaniline (1.49 g, 5.00 mmol) and 1-hexyne (0.75 mL, 6.5 mmol) using the general procedure for Sonogashira cross-coupling with a reaction time of 2 h. Purification by flash column chromatography (elution gradient from 5-10% EtOAc in hexanes) gave the title compound as a brown oil (1.20 g, 95% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 (d, J = 2.3 Hz, 1H), 7.15 (dd, J = 8.6, 2.3 Hz, 1H), 6.56 (d, J = 8.6 Hz, 1H), 4.16 (br s, 2H), 2.46 (t, J = 7.0 Hz, 2H), 1.64-1.55 (m, 2H), 1.52-1.43 (m, 2H), 0.95 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 146.8, 134.3, 131.7, 115.7, 111.0, 109.0, 97.2, 75.9, 31.0, 22.2, 19.4, 13.8. **HRMS** (ESI): *m/z* calcd for $C_{12}H_{13}BrN$ $[M–H]^-$: 250.0231. Found: 250.0228.



***N*-(4-Bromo-2-(hex-1-yn-1-yl)phenyl)-4-methoxybenzenesulfonamide (1g)** was synthesized from **SI-5** (1.20 g, 4.76 mmol) using the general procedure for *N*-sulfonyl anilines with a reaction time of 19 h. Purification by flash column chromatography (elution gradient from 5-10% EtOAc in hexanes) gave the title compound as a yellow oil (1.34 g, 67% yield).

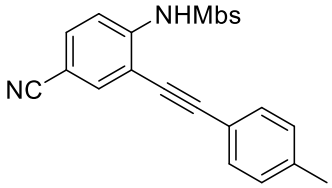
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.70-7.67 (m, 2H), 7.44 (d, J = 8.8 Hz, 1H), 7.37 (d, J = 2.3 Hz, 1H), 7.31 (dd, J = 8.7, 2.3 Hz, 1H), 7.12 (br s, 1H), 6.89-6.86 (m, 2H), 3.82 (s, 3H), 2.41 (t, J = 7.1 Hz, 2H), 1.60-1.53 (m, 2H), 1.49-1.41 (m, 2H), 0.97 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 163.5, 136.9, 134.5, 131.9, 130.5, 129.5, 121.0, 117.0, 117.0, 114.3, 99.4, 74.4, 55.7, 30.6, 22.2, 19.3, 13.7. **HRMS** (ESI): *m/z* calcd for $C_{19}H_{20}BrNO_3SNa$ $[M+Na]^+$: 444.0245. Found: 444.0247.



4-Amino-3-(*p*-tolylethynyl)benzonitrile (SI-6) was synthesized from 4-cyano-2-iodoaniline (1.22 g, 5.00 mmol) and 4-ethynyltoluene (0.824 mL, 6.50 mmol) using the general procedure for Sonogashira cross-coupling with a reaction time of 4 h. Purification by flash column chromatography (elution gradient from 10-30% EtOAc in hexanes) gave the title compound as a tan solid (0.992 g, 86% yield).

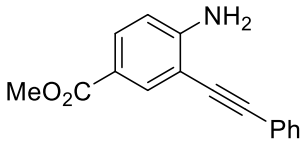
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 (d, J = 1.9 Hz, 1H), 7.42 (d, J = 8.1 Hz, 2H), 7.36 (dd, J = 8.5, 2.0 Hz, 1H), 7.18 (d, J = 7.9 Hz, 2H), 6.71 (d, J = 8.5 Hz, 1H), 4.78 (br s, 2H), 2.39 (s, 3H). **^{13}C NMR** (125

MHz, $CDCl_3$): δ 151.0, 139.3, 136.4, 133.2, 131.6, 129.4, 119.6, 119.3, 114.0, 108.6, 100.3, 96.6, 82.8, 21.7. **HRMS** (ESI): *m/z* calcd for $C_{16}H_{12}N_2Na$ $[M+Na]^+$: 255.0898. Found: 255.0896.



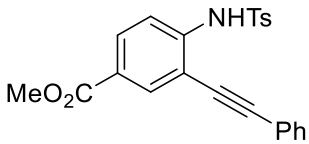
***N*-(4-Cyano-2-(*p*-tolylethynyl)phenyl)-4-methoxybenzenesulfonamide (1h)** was synthesized from **SI-6** (0.978 g, 4.21 mmol) using the general procedure for *N*-sulfonyl anilines with a reaction time of 72 h. Purification by flash column chromatography (elution gradient from 10-20% EtOAc in hexanes) gave the title compound as a white solid (0.693 g, 41% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81-7.76 (m, 2H), 7.68-7.63 (m, 2H), 7.53-7.49 (m, 2H) 7.42 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 6.94-6.89 (m, 2H), 3.83 (s, 3H), 2.42 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 163.8, 141.4, 140.4, 135.8, 132.9, 131.8, 130.1, 129.6, 118.4, 118.1, 118.0, 114.7, 107.6, 99.1, 81.0, 55.8, 21.8. **HRMS** (ESI): *m/z* calcd for $C_{23}H_{18}N_2O_3SNa$ $[M+Na]^+$: 425.0936. Found: 425.0937.



Methyl 4-amino-3-(phenylethynyl)benzoate (SI-7) was synthesized from methyl 4-amino-3-iodobenzoate (0.554 g, 2.00 mmol) and phenylacetylene (0.29 mL, 2.6 mmol) using the general procedure for Sonogashira cross-coupling with a reaction time of 3 h. Purification by flash column chromatography (elution gradient from 20-30% EtOAc in hexanes) gave the title compound as a brown solid (0.499 g, 99% yield).

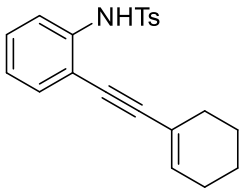
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.09 (d, *J* = 2.0 Hz, 1H), 7.82 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.54-7.51 (m, 2H), 7.39-7.34 (m, 3H), 6.71 (d, *J* = 8.5 Hz, 1H), 4.69 (br s, 2H), 3.87 (s, 3H). This spectrum is in agreement with literature spectral data.[9]



Methyl 4-((4-methylphenyl)sulfonamido)-3-(phenylethynyl)benzoate (1i) was synthesized from **SI-7** (0.499 g, 1.99 mmol) using general the procedure for *N*-sulfonyl anilines with a reaction time of 72 h.

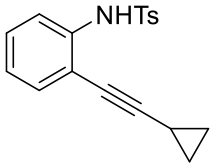
Purification by flash column chromatography (elution gradient from 5-10% EtOAc in hexanes) gave the title compound as a white solid (0.490 g, 61% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.08 (d, J = 1.5 Hz, 1H), 7.93 (dd, J = 8.7, 1.5 Hz, 1H), 7.73 (d, J = 8.2 Hz, 2H), 7.64 (d, J = 8.7 Hz, 1H), 7.53-7.50 (m, 2H), 7.48 (s, 1H), 7.43-7.40 (m, 3H), 7.22 (d, J = 8.0 Hz, 2H), 3.88 (s, 3H), 2.36 (s, 3H). This spectrum is in agreement with literature spectral data.[10]



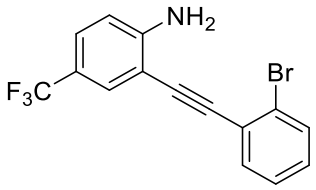
***N*-(2-(Cyclohex-1-en-1-ylethynyl)phenyl)-4-methylbenzenesulfonamide (1j)** was synthesized from **SI-1** (0.746 g, 2.00 mmol) and 1-ethynylcyclohexene (0.31 mL, 2.6 mmol) using the general procedure for Sonogashira cross-coupling with a reaction time of 4 h. Purification by flash column chromatography (5% EtOAc in hexanes) gave the title compound as a yellow orange solid (0.543 g, 77% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.66 (d, J = 8.2 Hz, 2H), 7.57 (d, J = 8.2 Hz, 1H), 7.26-7.18 (m, 4H), 7.15 (br s, 1H), 7.00 (t, J = 7.6 Hz, 1H), 6.22-6.19 (m, 1H), 2.36 (s, 3H), 2.20-2.15 (m, 4H), 1.73-1.68 (m, 2H), 1.67-1.62 (m, 2H). This spectrum is in agreement with literature spectral data.[7]



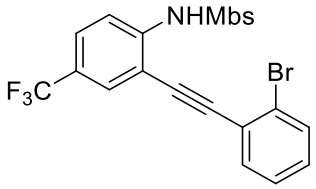
***N*-(2-(Cyclopropylethynyl)phenyl)-4-methylbenzenesulfonamide (1k)** was synthesized from **SI-1** (0.746 g, 2.00 mmol) and cyclopropylacetylene (0.22 mL, 2.6 mmol) using the general procedure for Sonogashira cross-coupling with a reaction time of 4 h. Purification by flash column chromatography (elution gradient from 5-10% EtOAc in hexanes) gave the title compound as a yellow solid (0.192 g, 31% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.65 (d, J = 8.3 Hz, 2H), 7.54 (d, J = 8.1 Hz, 1H), 7.23-7.18 (m, 4H), 7.15 (br s, 1H), 6.97 (td, J = 7.6, 1.1 Hz, 1H), 2.37 (s, 3H), 1.46-1.41 (m, 1H), 0.95-0.90 (m, 2H), 0.78-0.74 (m, 2H). This spectrum is in agreement with literature spectral data.[7]



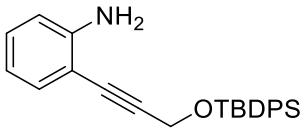
2-((2-Bromophenyl)ethynyl)-4-(trifluoromethyl)aniline (SI-8) was synthesized from 2-iodo-4-(trifluoromethyl)aniline (0.718 g, 2.50 mmol) and 1-bromo-2-ethynylbenzene (0.588 g, 3.25 mmol) using the general procedure for Sonogashira cross-coupling with a reaction time of 2.5 h. Purification by flash column chromatography (elution gradient from 5-10% EtOAc in hexanes) gave the title compound as a tan solid (0.785 g, 92% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66-7.61 (m, 2H), 7.58 (d, J = 7.8 Hz, 1H), 7.70-7.30 (m, 2H), 7.24-7.18 (m, 1H), 6.76 (d, J = 8.6 Hz, 1H), 4.82 (br s, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 150.9, 133.2, 132.5, 129.8, 129.5 (q, J = 3.9 Hz), 127.5, 127.1 (q, J = 3.6 Hz), 125.2, 125.1, 123.5 (q, J = 270.8 Hz), 119.8 (q, J = 33.0 Hz), 113.8, 106.9, 94.3, 89.6. **HRMS** (ESI): *m/z* calcd for $C_{15}H_{10}BrF_3N$ $[M+H]^+$: 339.9949. Found: 339.9944.



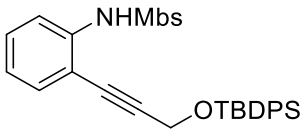
***N*-(2-((2-Bromophenyl)ethynyl)-4-(trifluoromethyl)phenyl)-4-methoxybenzenesulfonamide (1l)** was synthesized from **SI-8** (0.776 g, 2.28 mmol) using the general procedure for *N*-sulfonyl anilines with a reaction time of 24 h. Purification by flash column chromatography (elution gradient from 10-20% EtOAc in hexanes) gave the title compound as a white solid (0.754 g, 65% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.09 (br s, 1H), 7.86-7.82 (m, 2H), 7.76 (d, J = 8.7 Hz, 1H), 7.71-7.67 (m, 2H), 7.56 (dd, J = 7.7, 1.6 Hz, 1H), 7.52 (dd, J = 8.7, 1.7 Hz, 1H), 7.37 (td, J = 7.5, 1.0 Hz, 1H), 7.29 (td, J = 8.0, 1.7 Hz, 1H), 6.92-6.87 (m, 2H), 3.81 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 163.6, 141.5, 133.2, 132.6, 130.7, 130.4, 129.8, 129.0 (q, J = 3.8 Hz), 127.6, 126.9 (q, J = 3.6 Hz), 125.81, 125.8 (q, J = 33.3 Hz), 124.0, 123.7 (q, J = 271.9 Hz), 117.6, 114.6, 112.8, 96.5, 87.4, 55.7. **HRMS** (ESI): *m/z* calcd for $C_{22}H_{15}BrF_3NO_3SNa$ $[M+Na]^+$: 531.9806. Found: 531.9794.



2-(3-((*t*-Butyldiphenylsilyl)oxy)prop-1-yn-1-yl)aniline (SI-9) was synthesized from 2-iodoaniline (1.09 g, 5.00 mol) and *t*-butyldiphenyl(prop-2-yn-1-yloxy)silane (1.91 g, 6.50 mmol) using the general procedure for Sonogashira cross-coupling with a reaction time of 4 h. Purification by flash column chromatography (elution gradient from 0-5% EtOAc in hexanes) gave the title compound as an orange oil (1.09 g, 56% yield).

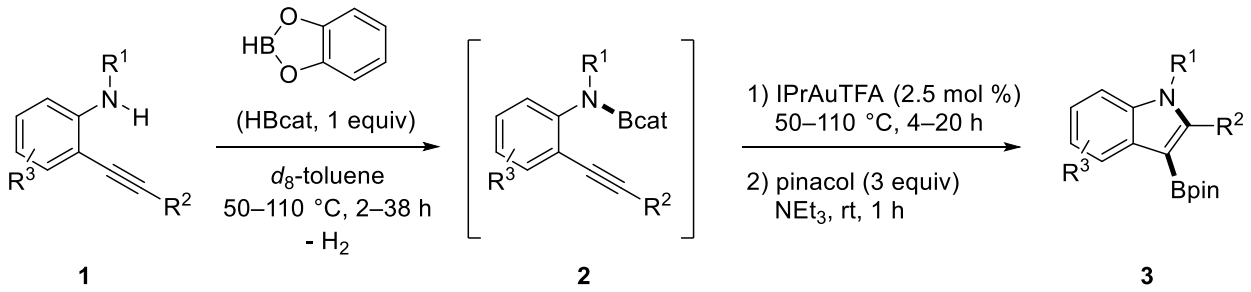
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79-7.75 (m, 4H), 7.48-7.38 (m, 6H), 7.21 (dd, J = 7.9, 1.4 Hz, 1H), 7.11 (td, J = 7.8, 1.4 Hz, 1H), 6.69-6.64 (m, 2H), 4.62 (s, 2H), 4.06 (br s, 2H), 1.10 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 148.1, 135.8, 133.3, 132.5, 130.0, 129.7, 127.9, 117.8, 114.3, 107.7, 93.0, 81.8, 53.5, 26.9, 19.3. **HRMS** (ESI): *m/z* calcd for $C_{25}H_{27}NOSiNa$ $[M+Na]^+$: 408.1760. Found: 408.1761.



***N*-(2-(3-((*t*-Butyldiphenylsilyl)oxy)prop-1-yn-1-yl)phenyl)-4-methoxybenzenesulfonamide (1m)** was synthesized from **SI-9** (0.524 g, 1.36 mmol) using the general procedure for *N*-sulfonyl anilines with a reaction time of 18 h. Purification by flash column chromatography (elution gradient from 10-20% EtOAc in hexanes) gave the title compound as a pale yellow gum (0.580 g, 77% yield).

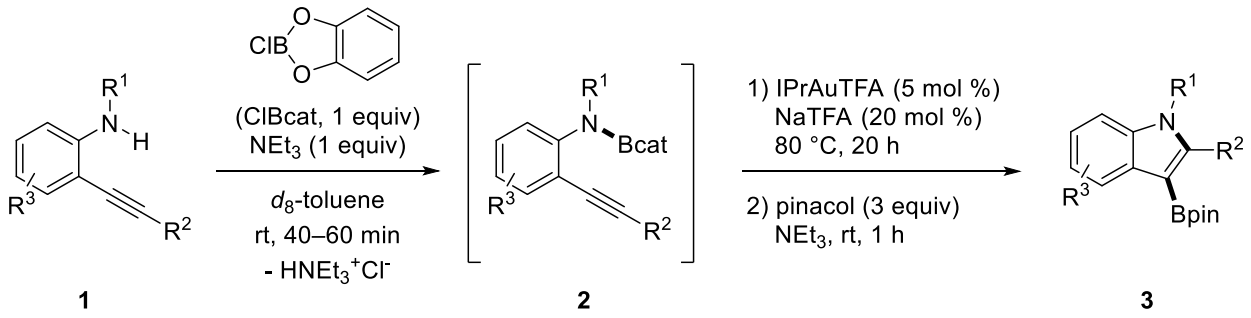
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76-7.72 (m, 4H), 7.70-7.66 (m, 2H), 7.57 (d, J = 8.2 Hz, 1H), 7.50-7.40 (m, 6H), 7.28-7.23 (m, 1H), 7.18 (dd, J = 7.7, 1.3 Hz, 1H), 7.06 (br s, 1H), 6.99 (td, J = 7.6, 1.2 Hz, 1H), 6.82-6.78 (m, 2H), 4.52 (s, 2H), 3.76 (s, 3H), 1.11 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 163.3, 138.0, 135.7, 132.9, 132.4, 130.6, 130.2, 129.7, 129.6, 128.0, 124.3, 119.9, 114.2, 114.0, 94.7, 79.8, 55.6, 53.1, 26.9, 19.3. **HRMS** (ESI): *m/z* calcd for $C_{32}H_{33}NO_4SSiNa$ $[M+Na]^+$: 578.1797. Found: 578.1787.

General Procedure from HBcat (Table 1)



Inside a nitrogen-filled glovebox, to a solution of amine **1** (0.100 mmol) in d_8-toluene (0.6 mL) in a J. Young NMR tube, HBcat (10.7 μL, 0.100 mmol) was added using a gastight syringe. The J. Young NMR tube was sealed with a Teflon cap and heated to the specified temperature (50–110 °C) and time (2–38 h) outside the glovebox. The B–N bond formation and release of H_2 was monitored by ^{1}H and ^{11}B NMR spectroscopy for the formation of **2** (66-83% conv). Then the J. Young NMR tube was brought back into a glovebox, IPrAuTFA (1.7 mg, 0.0025 mmol) in d_8-toluene (0.2 mL) was added to the tube. Outside the glovebox, the reaction was heated to specified temperatures (50–110 °C) and time (4–20 h). Once full consumption of **2** was observed by ^{1}H and ^{11}B NMR spectroscopy, the J. Young NMR tube was brought into a glovebox, and the reaction contents were poured into a dram vial containing a solution of pinacol (35.5 mg, 0.300 mmol) in NEt_3 (0.21 mL, 1.5 mmol). Toluene (3 × 0.2 mL) rinses were used to ensure full transfer from the NMR tube to the vial. The vial was sealed with a Teflon cap and stirred for 1 h outside the glovebox. The reaction mixture was then concentrated in vacuo and purified by flash chromatography.

General Procedure from ClBcat (Chart 1)



Inside a nitrogen-filled glovebox, to a mixture of amine **1** (0.200 mmol) and ClBcat (30.9 mg, 0.200 mmol) in d_8-toluene (0.4 mL) in a dram vial, NEt_3 (28 μL, 0.20 mmol) was added using a gastight syringe. The vial was sealed with a Teflon cap and stirred for 40–60 min at room temperature, during which $HNEt_3Cl$ salt was formed. The resulting slurry was filtered through a plug of Celite (~2 cm in a Pasteur pipette), and additional d_8-toluene (2 × 0.2 mL) rinses were used to ensure full transfer. The filtrate was mixed with IPrAuTFA (7.0 mg, 0.010 mmol) and NaTFA (5.4 mg, 0.040 mmol) and transferred to a J. Young NMR tube with one rinse of d_8-toluene (0.2 mL) to aid the transfer to make a total reaction volume of 1 mL. The J. Young NMR tube was sealed with a Teflon cap and heated to 80 °C for 20 h outside the glovebox. Once the reaction was complete (>95% conversion) as monitored by ^{1}H and ^{11}B NMR spectroscopy, the J. Young NMR tube was brought into a glovebox, and the reaction contents were poured into a dram vial containing a solution of pinacol (70.9 mg, 0.600 mmol) in NEt_3 (0.42 mL, 3.0 mmol). Toluene (3 × 0.2 mL) rinses were used to ensure full transfer from the NMR tube to the vial. The vial was sealed with a Teflon cap and stirred for 1 h outside the glovebox. The reaction mixture was then concentrated in vacuo and purified by flash chromatography.

A control experiment using NaTFA additive. Following the general procedure from ClBcat, the reaction of in situ prepared **2d** (0.200 mmol) and NaTFA (20 mol %, 5.4 mg, 0.040 mmol) in d_8-toluene (1 mL) for 20 h at 80 °C in a J. Young NMR tube showed no reactivity, as monitored by ^{1}H and ^{11}B NMR spectroscopy.

An example of in situ monitoring of the aminoboration reaction by NMR spectroscopy for the synthesis of **3d** from **1d** is shown in Figure S1 and Figure S2 below.

Figure S1. Stacked ^{1}H NMR (600 MHz, d_8-toluene) Spectra of 1d (top), 2d (middle), and 3d-Bcat (bottom)

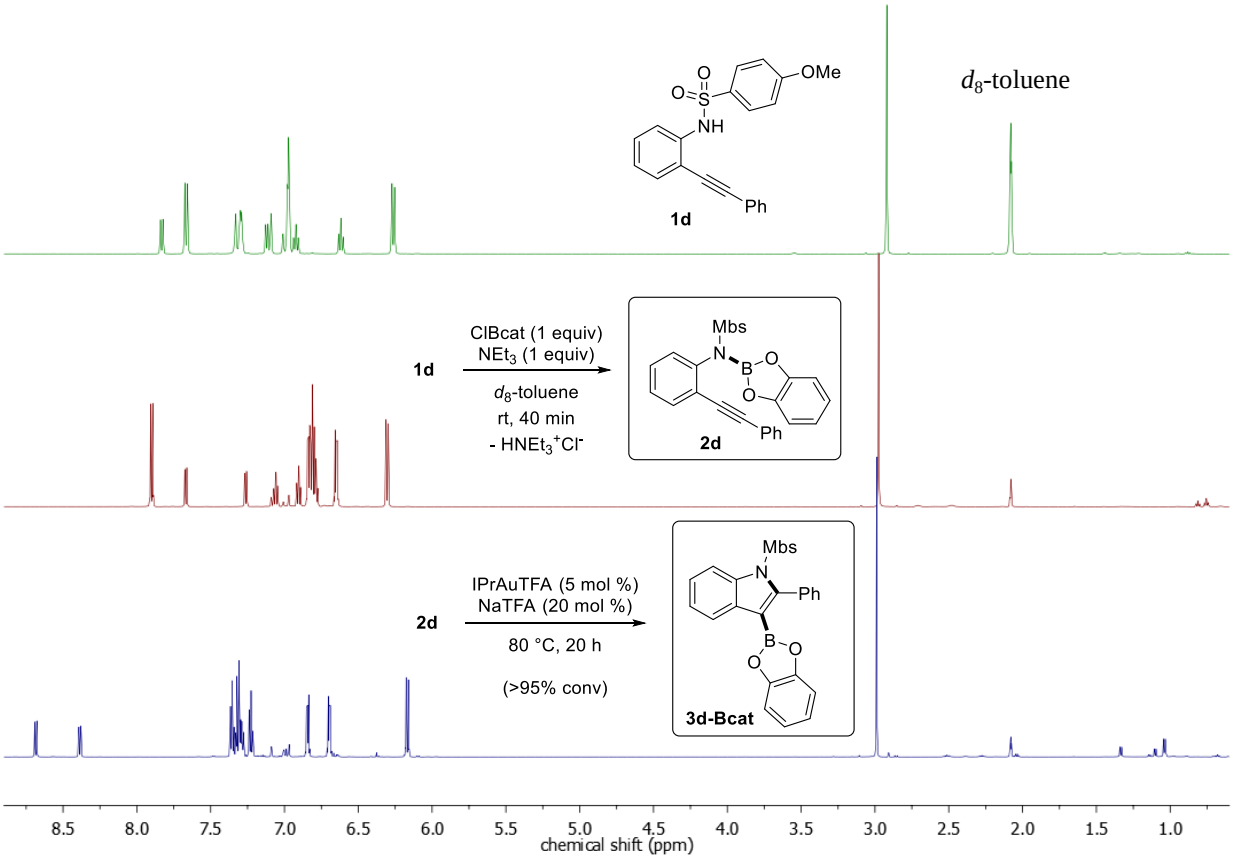
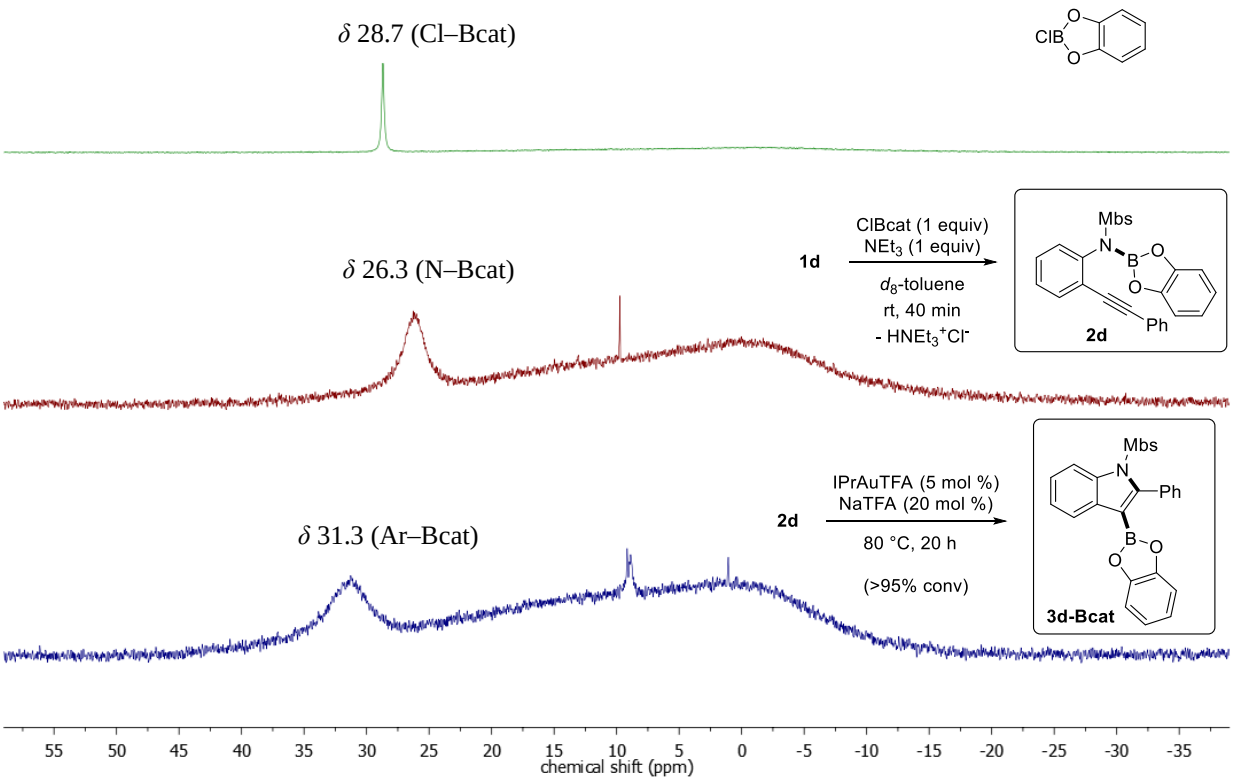
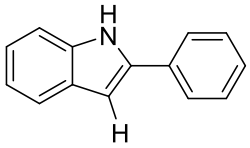


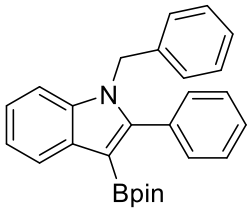
Figure S2. Stacked ^{11}B NMR (193 MHz, d_8-toluene) Spectra of ClBcat (top), 2d (middle), and 3d-Bcat (bottom)





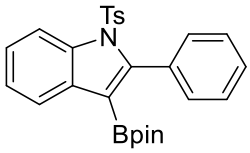
2-Phenyl-1*H*-indole (3a-H). Following the general procedure from HBcat (50 °C, 2 h for B–N bond formation step; 50 °C, 15.5 h for cyclization step), purification by flash column chromatography (elution gradient from 10-30% CH_2Cl_2 in hexanes) gave the title compound as a white solid (13.4 mg, 69% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.33 (br s, 1H), 7.68 (d, J = 7.5 Hz, 2H), 7.64 (d, J = 7.9 Hz, 1H), 7.45 (t, J = 7.7 Hz, 2H), 7.41 (d, J = 8.1 Hz, 1H), 7.33 (t, J = 7.4 Hz, 1H), 7.20 (t, J = 7.6 Hz, 1H), 7.13 (t, J = 7.5 Hz, 1H), 6.84 (s, 1H). This spectrum is in agreement with literature spectral data.[11]



1-Benzyl-2-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (3b). Following the general procedure from HBcat (110 °C, 38 h for B–N bond formation step; 110 °C, 17 h for cyclization step), purification by flash column chromatography (elution gradient from 10-50% CH_2Cl_2 in hexanes) gave the title compound as a colorless oil (22.6 mg, 55% yield).

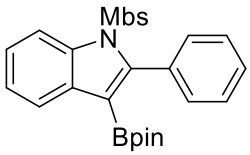
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.13 (d, J = 7.8 Hz, 1H), 7.43-7.33 (m, 5H), 7.27-7.14 (m, 6H), 6.98 (d, J = 6.9 Hz, 2H), 5.28 (s, 2H), 1.27 (s, 12H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 150.3, 138.02, 137.99, 133.0, 132.6, 131.0, 128.7, 128.4, 127.7, 127.2, 126.2, 122.5, 122.1, 120.9, 110.5, 82.6, 47.8, 24.9. **^{11}B NMR** (193 MHz, $CDCl_3$): δ 30.4. **HRMS** (ESI): *m/z* calcd for $C_{27}H_{28}BNO_2Na$ $[M+Na]^+$: 432.2116. Found: 432.2113.



2-Phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-tosyl-1*H*-indole (3c). Following the general procedure from HBcat (110 °C, 20 h for B–N bond formation step; 80 °C, 20 h for cyclization step), purification by flash column chromatography (elution gradient from 10-50% CH_2Cl_2 in hexanes) gave the title compound as a white solid (30.4 mg, 64% yield, average of two runs).

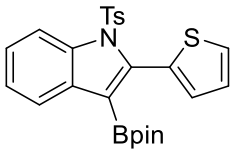
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.30 (d, J = 8.3 Hz, 1H), 7.86 (d, J = 7.7 Hz, 1H), 7.44-7.40 (m, 1H), 7.38-7.27 (m, 8H), 7.06 (d, J = 8.2 Hz, 2H), 2.30 (s, 3H), 1.16 (s, 12H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ

148.9, 144.7, 137.8, 135.9, 133.5, 132.4, 131.8, 129.5, 128.8, 127.0, 126.7, 124.7, 124.1, 122.3, 115.7, 83.4, 24.7, 21.7. **^{11}B NMR** (193 MHz, $CDCl_3$): δ 29.8. These spectra are in agreement with literature spectral data.[12]



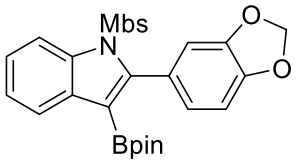
1-((4-Methoxyphenyl)sulfonyl)-2-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (3d). Following the general procedure from HBcat (110 °C, 20 h for B–N bond formation step; 80 °C, 20 h for cyclization step), purification by flash column chromatography (elution gradient from 10-50% CH_2Cl_2 in hexanes) gave the title compound as a white solid (32.4 mg, 66% yield). Following the general procedure from ClBcat, purification by flash column chromatography (elution gradient from 10-50% CH_2Cl_2 in hexanes) gave the title compound as a white solid (78.2 mg, 80% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.31 (d, J = 8.4 Hz, 1H), 7.87 (d, J = 7.7 Hz, 1H), 7.46-7.40 (m, 1H), 7.38-7.32 (m, 7H), 7.29 (t, J = 7.5 Hz, 1H), 6.71 (d, J = 9.0 Hz, 2H), 3.76 (s, 3H), 1.16 (s, 12H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 163.7, 148.8, 137.8, 133.5, 132.4, 131.8, 130.4, 129.2, 128.7, 126.7, 124.7, 124.1, 122.3, 115.7, 114.0, 83.4, 55.7, 24.7. **^{11}B NMR** (193 MHz, $CDCl_3$): δ 30.1. These spectra are in agreement with literature spectral data.[12]



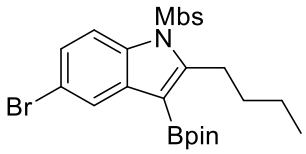
3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(thiophen-2-yl)-1-tosyl-1*H*-indole (3e). Following the general procedure from ClBcat, purification by flash column chromatography (elution gradient from 10-50% CH_2Cl_2 in hexanes) gave the title compound as a pale yellow solid (68.1 mg, 71% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.30 (d, J = 8.4 Hz, 1H), 7.86 (d, J = 7.7 Hz, 1H), 7.45-7.34 (m, 4H), 7.29 (t, J = 7.5 Hz, 1H), 7.14-7.04 (m, 4H), 2.32 (s, 3H), 1.20 (s, 12H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 144.8, 140.0, 138.0, 135.9, 132.9, 132.0, 131.8, 129.6, 127.8, 127.1, 126.0, 125.2, 124.0, 122.4, 115.4, 83.5, 24.8, 21.7. **^{11}B NMR** (193 MHz, $CDCl_3$): δ 29.9. **HRMS** (ESI): *m/z* calcd for $C_{25}H_{26}BNO_4S_2Na$ $[M+Na]^+$: 501.1330. Found: 501.1336.



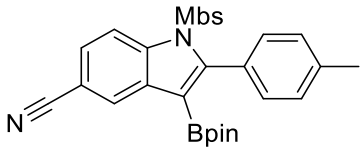
2-(Benzo[d][1,3]dioxol-5-yl)-1-((4-methoxyphenyl)sulfonyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (3f). Following the general procedure from ClBcat, purification by flash column chromatography (elution gradient from 10-60% CH_2Cl_2 in hexanes) gave the title compound as a white solid (83.4 mg, 78% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.29 (d, J = 8.3 Hz, 1H), 7.85 (d, J = 7.7 Hz, 1H), 7.39 (d, J = 9.0 Hz, 2H), 7.34 (t, J = 7.2 Hz, 1H), 7.28 (t, J = 7.3 Hz, 1H), 6.89 (s, 1H), 6.80 (s, 2H), 6.73 (d, J = 8.9 Hz, 2H), 6.04 (s, 2H), 3.76 (s, 3H), 1.20 (s, 12H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 163.7, 148.5, 148.2, 146.3, 137.8, 133.5, 130.2, 129.2, 126.0, 125.8, 124.7, 124.1, 122.2, 115.8, 114.0, 112.5, 106.8, 101.3, 83.4, 55.7, 24.8. **^{11}B NMR** (193 MHz, $CDCl_3$): δ 30.1. **HRMS** (ESI): *m/z* calcd for $C_{28}H_{28}BNO_7SNa$ $[M+Na]^+$: 556.1583. Found: 556.1568.



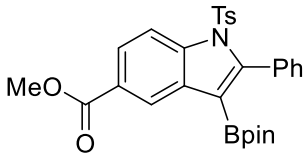
5-Bromo-2-butyl-1-((4-methoxyphenyl)sulfonyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (3g). Following the general procedure from ClBcat, purification by flash column chromatography (elution gradient from 10-20% CH_2Cl_2 in hexanes) gave the title compound as a white solid (87.0 mg, 79% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05 (d, J = 1.9 Hz, 1H), 8.01 (d, J = 8.9 Hz, 1H), 7.70-7.65 (m, 2H), 7.33 (dd, J = 8.9, 2.1 Hz, 1H), 6.87-6.81 (m, 2H), 3.78 (s, 3H), 3.28 (t, J = 7.7 Hz, 2H), 1.68 (pentet, J = 7.6 Hz, 2H), 1.43 (sextet, J = 7.4 Hz, 2H), 1.34 (s, 12H), 0.95 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 163.8, 154.3, 136.0, 135.4, 130.7, 128.7, 126.5, 124.8, 117.2, 116.0, 114.6, 83.4, 55.8, 34.3, 28.2, 25.0, 22.8, 13.9. **^{11}B NMR** (193 MHz, $CDCl_3$): δ 30.1. **HRMS** (ESI): *m/z* calcd for $C_{25}H_{31}BBrNO_5SNa$ $[M+Na]^+$: 570.1102. Found: 570.1103.



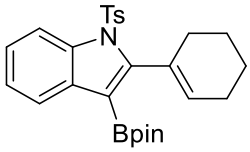
1-((4-Methoxyphenyl)sulfonyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(*p*-tolyl)-1*H*-indole-5-carbonitrile (3h). Following the general procedure from ClBcat, purification by flash column chromatography (elution gradient from 10-50% CH_2Cl_2 in hexanes) gave the title compound as a white solid (69.0 mg, 65% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.40 (dd, J = 8.7, 0.5 Hz, 1H), 8.25 (dd, J = 1.7, 0.5 Hz, 1H), 7.59 (dd, J = 8.7, 1.7 Hz, 1H), 7.33-7.28 (m, 2H), 7.20-7.14 (m, 4H), 6.76-6.71 (m, 2H), 3.79 (s, 3H), 2.45 (s, 3H), 1.17 (s, 12H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 164.1, 151.3, 139.6, 139.2, 133.5, 131.7, 129.9, 129.4, 128.2, 127.54, 127.47, 127.4, 120.0, 116.3, 114.2, 107.3, 83.7, 55.8, 24.7, 21.7. **^{11}B NMR** (193 MHz, $CDCl_3$): δ 29.5. **HRMS** (ESI): *m/z* calcd for $C_{29}H_{29}BN_2O_5SNa$ $[M+Na]^+$: 551.1793. Found: 551.1804.



Methyl 2-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-tosyl-1*H*-indole-5-carboxylate (3i). Following the general procedure from ClBcat, purification by flash column chromatography (elution gradient from 10-60% CH_2Cl_2 in hexanes) gave the title compound as a white solid (73.1 mg, 69% yield).

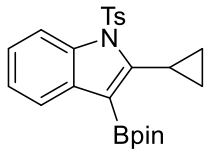
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.55 (d, J = 1.4 Hz, 1H), 8.36 (d, J = 8.8 Hz, 1H), 8.05 (dd, J = 8.8, 1.7 Hz, 1H), 7.47-7.41 (m, 1H), 7.38-7.27 (m, 6H), 7.06 (d, J = 8.2 Hz, 2H), 3.94 (s, 3H), 2.30 (s, 3H), 1.17 (s, 12H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 167.6, 149.9, 145.1, 140.4, 135.5, 133.1, 131.7, 129.6, 129.0, 127.0, 126.7, 126.0, 125.9, 124.5, 115.2, 83.5, 52.2, 24.7, 21.6. **^{11}B NMR** (193 MHz, $CDCl_3$): δ 30.2. **HRMS** (ESI): *m/z* calcd for $C_{29}H_{30}BNO_6SNa$ $[M+Na]^+$: 554.1790. Found: 554.1789.



2-(Cyclohex-1-en-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-tosyl-1*H*-indole (3j). Following the general procedure from ClBcat, purification by flash column chromatography (elution gradient from 10-40% CH_2Cl_2 in hexanes) gave the title compound as a white solid (70.1 mg, 73% yield).

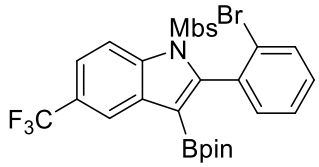
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.18 (d, J = 8.3 Hz, 1H), 7.81 (d, J = 7.6 Hz, 1H), 7.61 (d, J = 8.2 Hz, 2H), 7.30-7.20 (m, 2H), 7.12 (d, J = 8.2 Hz, 2H), 5.40 (br s, 1H), 2.63 (br s, 2H), 2.31 (s, 3H), 2.15 (br s, 2H), 1.85-1.80 (m, 2H), 1.74 (br s, 2H), 1.29 (s, 12H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 152.1, 144.6, 137.2,

136.3, 133.5, 132.2, 130.5, 129.5, 127.0, 124.2, 123.7, 122.2, 114.9, 83.2, 31.0, 25.9, 25.0, 22.9, 22.0, 21.7. **^{11}B NMR** (193 MHz, $CDCl_3$): δ 30.6. **HRMS** (ESI): *m/z* calcd for $C_{27}H_{32}BNO_4SNa$ $[M+Na]^+$: 500.2048. Found: 500.2035.



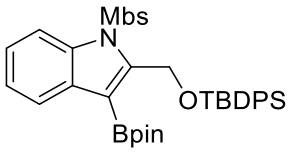
2-Cyclopropyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-tosyl-1*H*-indole (3k). Following the general procedure from ClBcat, purification by flash column chromatography (elution gradient from 10-50% CH_2Cl_2 in hexanes) gave the title compound as a white solid (58.4 mg, 67% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.19 (d, *J* = 8.2 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.30-7.25 (m, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 8.1 Hz, 2H), 2.35 (s, 3H), 2.32-2.25 (m, 1H), 1.39 (s, 12H), 1.03-0.97 (m, 2H), 0.67-0.62 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 151.0, 144.7, 137.6, 137.1, 132.9, 129.8, 126.7, 124.3, 123.4, 122.0, 114.3, 83.8, 25.1, 21.7, 10.6, 9.4. **^{11}B NMR** (193 MHz, $CDCl_3$): δ 30.8. **HRMS** (ESI): *m/z* calcd for $C_{24}H_{28}BNO_4SNa$ $[M+Na]^+$: 460.1734. Found: 460.1736.



2-(2-Bromophenyl)-1-((4-methoxyphenyl)sulfonyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(trifluoromethyl)-1*H*-indole (3l). Following the general procedure from ClBcat (cyclization temperature 110 °C), purification by flash column chromatography (elution gradient from 10-40% CH_2Cl_2 in hexanes) gave the title compound as a white solid (76.3 mg, 60% yield).

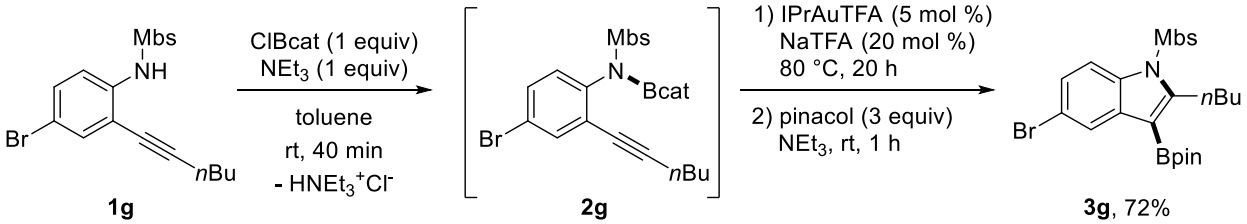
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.38 (d, *J* = 8.9 Hz, 1H), 8.25 (s, 1H), 7.61 (dd, *J* = 8.9, 1.7 Hz, 1H), 7.58 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.55-7.51 (m, 2H), 7.38-7.27 (m, 3H), 6.83-6.79 (m, 2H), 3.80 (s, 3H), 1.15 (s, 6H), 1.14 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 164.2, 147.9, 138.5, 133.6, 133.4, 132.4, 131.8, 130.5, 130.3, 129.8, 126.2, 126.0 (q, *J* = 32.1 Hz), 125.9, 125.0 (q, *J* = 262.5 Hz), 121.5 (q, *J* = 3.4 Hz), 120.4 (q, *J* = 4.1 Hz), 115.1, 114.4, 83.4, 55.9, 24.9, 24.6. **^{11}B NMR** (193 MHz, $CDCl_3$): δ 29.6. **HRMS** (ESI): *m/z* calcd for $C_{28}H_{26}BBrF_3NO_5SNa$ $[M+Na]^+$: 658.0663. Found: 658.0672.



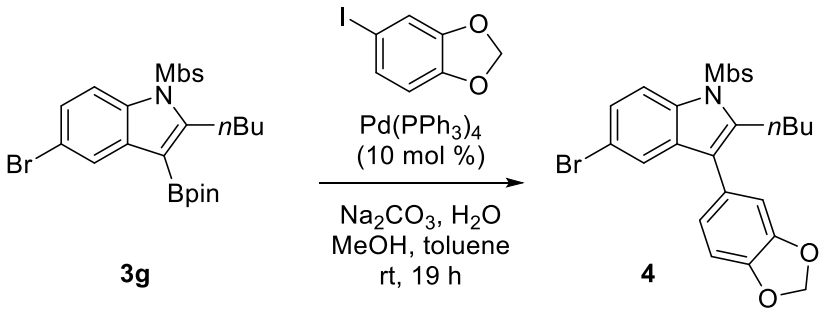
2-(((*t*-Butyldiphenylsilyl)oxy)methyl)-1-((4-methoxyphenyl)sulfonyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (3m). Following the general procedure from ClBcat (cyclization temperature 110 °C), purification by flash column chromatography (elution gradient from 10-40% CH_2Cl_2 in hexanes) gave the title compound as a white solid (74.5 mg, 55% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.05 (d, J = 7.5 Hz, 1H), 7.97 (d, J = 8.2 Hz, 1H), 7.92 (d, J = 9.0 Hz, 2H), 7.77 (d, J = 6.8 Hz, 4H), 7.43-7.39 (m, 2H), 7.35 (t, J = 7.4 Hz, 4H), 7.28-7.21 (m, 2H), 6.62 (d, J = 9.0 Hz, 2H), 5.51 (s, 2H), 3.70 (s, 3H), 1.15 (s, 12H), 1.13 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 163.5, 148.2, 137.0, 136.1, 134.4, 132.8, 131.0, 129.6, 129.5, 127.6, 124.7, 123.34, 123.32, 114.4, 114.1, 83.4, 58.5, 55.6, 27.3, 24.9, 20.0. **^{11}B NMR** (193 MHz, $CDCl_3$): δ 30.1. **HRMS** (ESI): *m/z* calcd for $C_{38}H_{44}BNO_6SSiNa$ $[M+Na]^+$: 704.2656. Found: 704.2667.

Gram-Scale Preparation of 3g (Scheme 1)

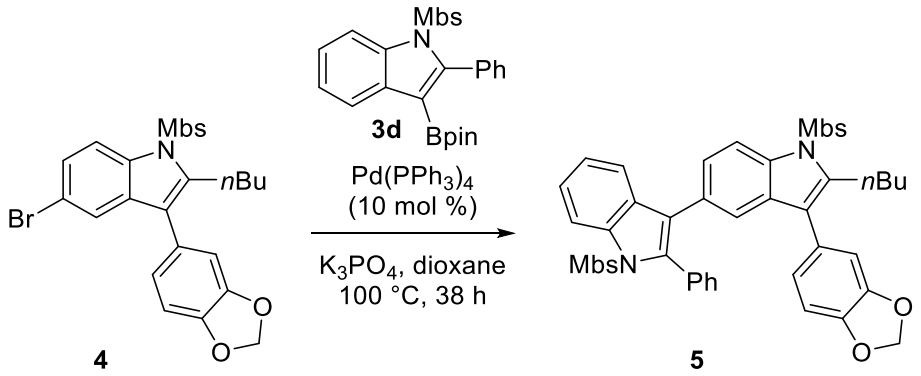


Inside a nitrogen-filled glovebox, to a mixture of **1a** (1.09 g, 2.58 mmol) and ClBcat (0.398 g, 2.58 mmol) in toluene (6 mL) in a 20 mL vial, NEt_3 (360 µL, 2.58 mmol) was added using a gastight syringe. The vial was sealed with a cap and stirred for 40 min at room temperature, during which $HNEt_3Cl$ salt was formed. The resulting slurry was filtered through a plug of Celite, and additional toluene (3 × 1 mL) rinses were used to ensure full transfer. The filtrate was mixed with IPrAuTFA (90.1 mg, 0.129 mmol) and NaTFA (70.2 mg, 0.516 mmol) and transferred to a 25 mL Schlenk tube, containing a magnetic stir bar, with toluene (2 × 2 mL) rinses to aid the transfer to make a total reaction volume of 13 mL. The Schlenk tube was sealed with a Teflon cap and heated to the 80 °C for 20 h outside the glovebox. The reaction was allowed to cool to room temperature and brought into a glovebox. A solution of pinacol (0.915 g, 7.74 mmol) in NEt_3 (5.4 mL, 39 mmol) was added to the Schlenk tube and stirred for 1 h outside the glovebox. The resulting mixture was concentrated in vacuo and purified by flash chromatography (elution gradient from 10-30% CH_2Cl_2 in hexanes) to give the title compound as a white solid (1.02 g, 72% yield). Spectral data were identical to those previously obtained for this compound (see page S19). Single crystals suitable for X-ray crystallography were grown in hexanes by storing at 3 °C in a fridge overnight.



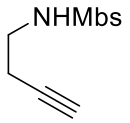
3-(Benzo[*d*][1,3]dioxol-5-yl)-5-bromo-2-butyl-1-((4-methoxyphenyl)sulfonyl)-1*H*-indole (4). The Suzuki cross-coupling reaction was adapted from a literature procedure.[13] A mixture of **3g** (82.2 mg, 0.150 mmol), 1-iodo-3,4-methylenedioxybenzene (44.6 mg, 0.180 mmol), Na_2CO_3 aq (0.25 mL, 2M, 0.50 mmol), toluene/MeOH (4 mL:1 mL) in a 10 mL round bottom flask, sealed with a septa, was deoxygenated by bubbling a stream of N_2 into the reaction mixture for 5 min. To this reaction mixture, $Pd(PPh_3)_4$ (17.3 mg, 0.0150 mmol) was added, and the system was further purged with N_2. The reaction mixture was stirred for 19 h at room temperature. Then the reaction was quenched with the addition of $MgSO_4$ (500 mg), stirred for 15 min, and filtered through a Celite plug. The filtrate was concentrated in vacuo and purified by flash chromatography (elution gradient from 10-30% CH_2Cl_2 in hexanes) to give the title compound as an off-white solid (70.5 mg, 87% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.08 (d, J = 8.8 Hz, 1H), 7.67-7.63 (m, 2H), 7.40 (d, J = 1.9 Hz, 1H), 7.37 (dd, J = 8.8, 2.0 Hz, 1H), 6.90 (d, J = 7.8 Hz, 1H), 6.87-6.83 (m, 2H), 6.75-6.71 (m, 2H), 6.03 (s, 2H), 3.80 (s, 3H), 2.95 (t, J = 7.8 Hz, 2H), 1.71-1.64 (m, 2H), 1.32-1.24 (m, 2H), 0.84 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 163.8, 148.0, 147.3, 140.1, 135.4, 132.8, 130.3, 128.7, 127.2, 126.3, 123.6, 122.8, 122.1, 117.4, 116.9, 114.5, 110.3, 108.8, 101.4, 55.8, 33.4, 26.8, 22.7, 13.8. **HRMS** (ESI): *m/z* calcd for $C_{26}H_{24}BrNO_5SNa$ $[M+Na]^+$: 564.0457. Found: 564.044.



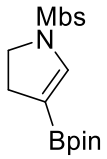
3'-(Benzo[*d*][1,3]dioxol-5-yl)-2'-butyl-1,1'-bis((4-methoxyphenyl)sulfonyl)-2-phenyl-1*H*,1'*H*-3,5'-biindole (5). The Suzuki cross-coupling reaction was adapted from a literature procedure.[14] A Schlenk tube was charged with **4** (43.4 mg, 0.0800 mmol), **3d** (50.9 mg, 0.104 mmol), $Pd(PPh_3)_4$ (9.2 mg, 0.0080 mmol), K_3PO_4 (50.9 mg, 0.240 mmol) and dioxane (2 mL) and degassed by three cycles of freeze-pump-thaw. Then the Schlenk tube was placed under N_2 atmosphere, sealed, and heated to 100 °C for 38 h. For workup, the reaction mixture was diluted with EtOAc (10 mL) and washed with water and brine (3 mL each). The organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification by flash chromatography (elution gradient from 30-50% CH_2Cl_2 in hexanes) gave the title compound as a white solid (30.9 mg, 47% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.40 (d, J = 8.4 Hz, 1H), 8.08 (d, J = 8.7 Hz, 1H), 7.68-7.63 (m, 2H), 7.50 (d, J = 7.8 Hz, 1H), 7.42-7.36 (m, 4H), 7.31-7.26 (m, 3H), 7.23-7.20 (m, 2H), 7.12 (dd, J = 8.7, 1.7 Hz, 1H), 6.96 (d, J = 1.4 Hz, 1H), 6.87-6.83 (m, 2H), 6.79 (d, J = 7.8 Hz, 1H), 6.75-6.71 (m, 2H), 6.48 (d, J = 1.4 Hz, 1H), 6.46 (dd, J = 7.9, 1.6 Hz, 1H), 6.00 (s, 2H), 3.81 (s, 3H), 3.76 (s, 3H), 2.93 (t, J = 7.8 Hz, 2H), 1.68-1.61 (m, 2H), 1.29-1.23 (m, 2H), 0.83 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 163.7, 147.8, 147.0, 138.9, 137.3, 136.9, 135.5, 132.4, 131.3, 130.8, 130.6, 130.4, 130.2, 129.3, 128.7, 128.6, 128.2, 127.5, 126.6, 126.1, 125.2, 124.6, 124.2, 123.4, 123.3, 120.9, 120.1, 116.2, 115.1, 114.4, 114.0, 110.2, 108.6, 101.2, 55.74, 55.69, 33.4, 26.7, 22.7, 13.8. **HRMS** (ESI): *m/z* calcd for $C_{47}H_{40}N_2O_8S_2Na$ $[M+Na]^+$: 847.2124. Found: 847.2117.



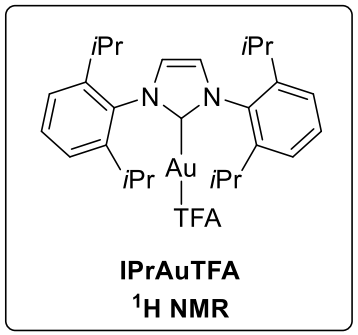
***N*-(But-3-yn-1-yl)-4-methoxybenzenesulfonamide (6).** To a cooled solution of 3-butynylamine (0.600 mL, 7.33 mmol) in pyridine (6 mL) at 0 °C, MbsCl (1.67 g, 8.06 mmol) was added and stirred at room temperature for 24 h. The resulting reaction mixture was diluted with CH_2Cl_2 (50 mL) and washed sequentially with 1M HCl (50 mL), saturated $NaHCO_3$ solution, and brine. Then the organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification by flash column chromatography (30% EtOAc in hexanes) gave the title compound as a white solid (1.35 g, 77% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83-7.78 (m, 2H), 7.01-6.96 (m, 2H), 4.79 (br t, J = 5.9 Hz, 1H), 3.87 (s, 3H), 3.10 (q, J = 6.5 Hz, 2H), 2.35 (td, J = 6.5, 2.6 Hz, 2H), 2.00 (t, J = 2.6 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 163.1, 131.6, 129.4, 114.5, 80.5, 71.1, 55.8, 41.7, 19.9. **HRMS** (ESI): *m/z* calcd for $C_{11}H_{13}NO_3SNa$ $[M+Na]^+$: 262.0514. Found: 262.0520.

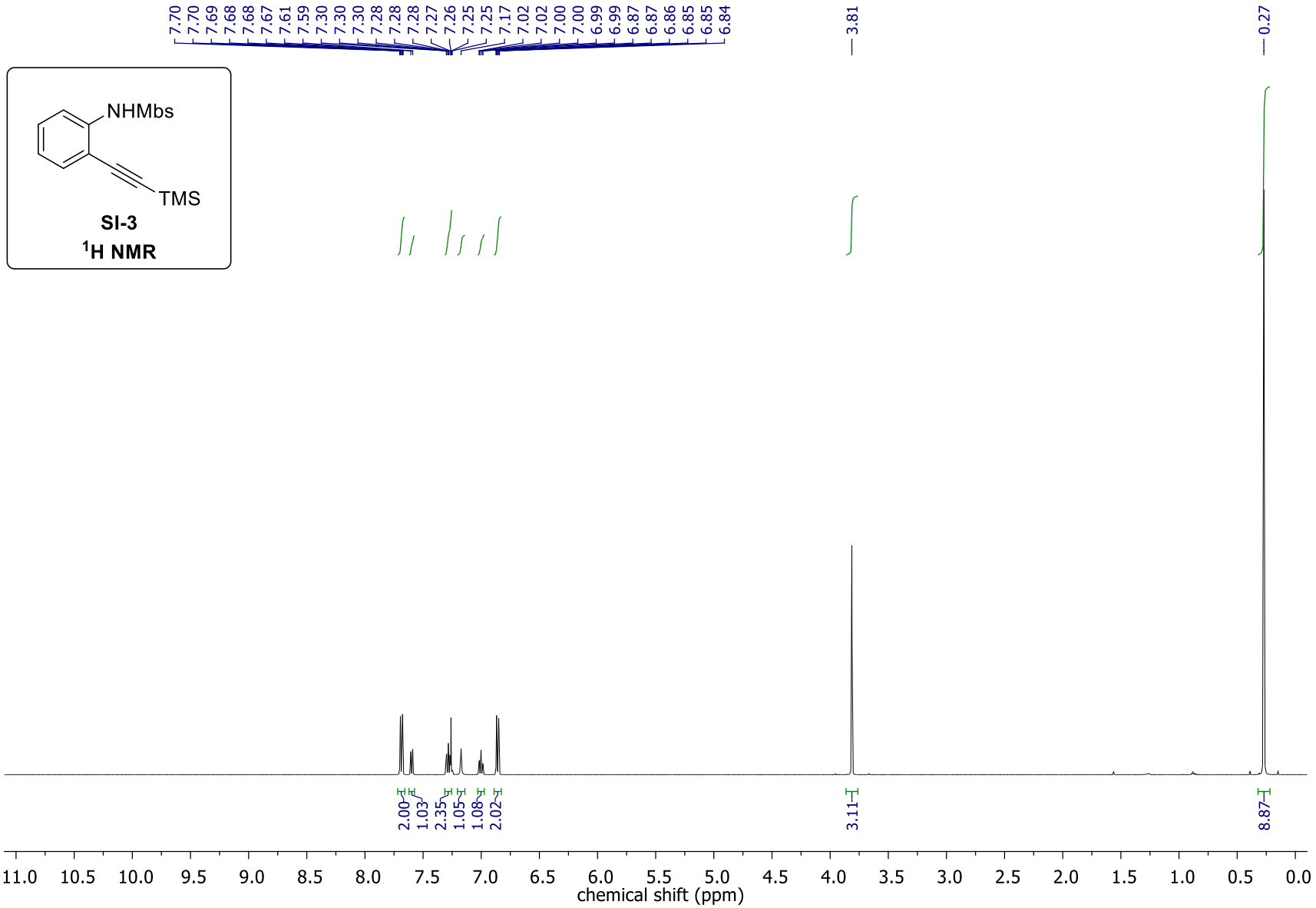


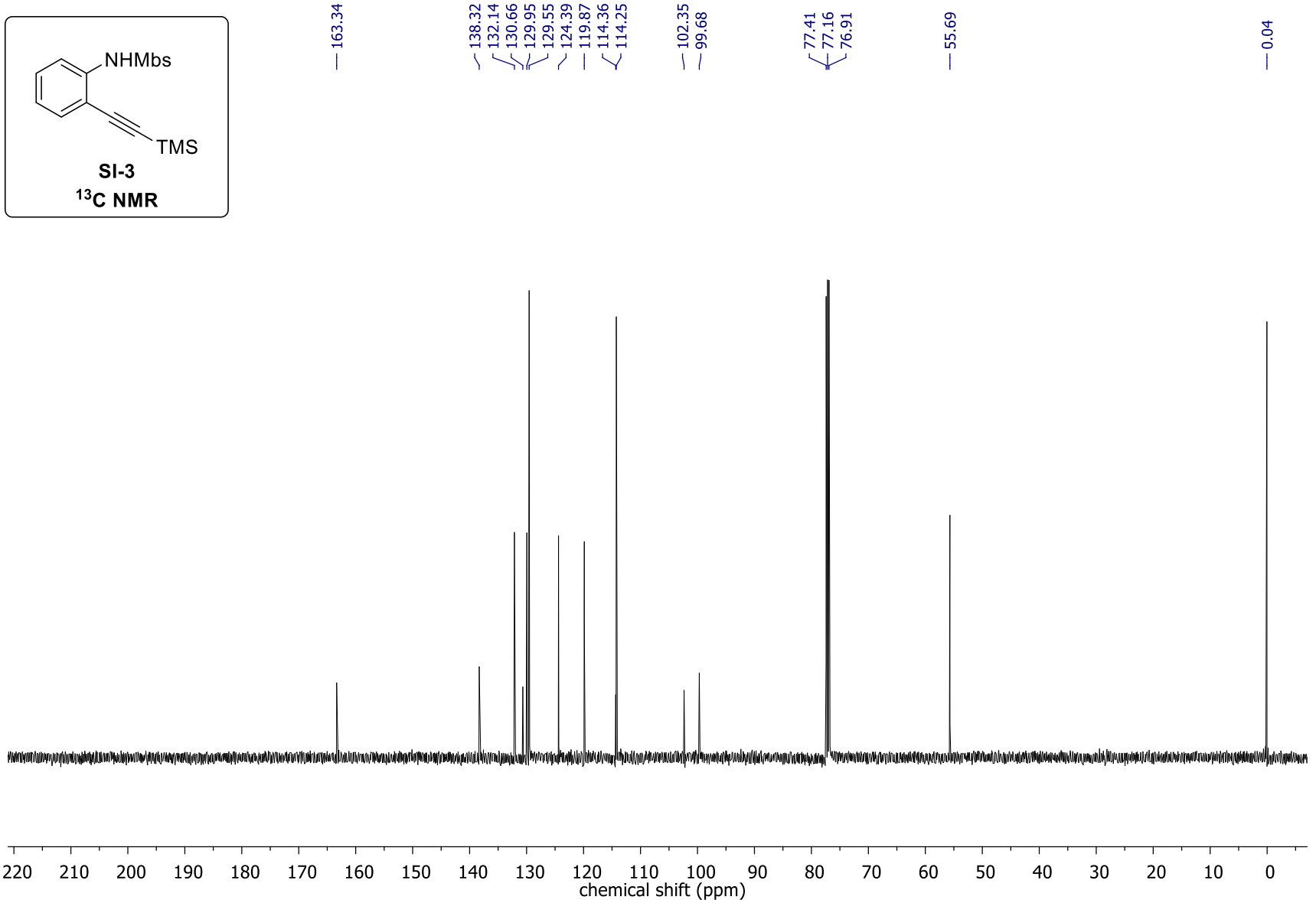
1-((4-Methoxyphenyl)sulfonyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydro-1*H*-pyrrole (8a). Following the general procedure from ClBcat (80 °C, 24 h for cyclization step) and analysis of the crude reaction mixture by ^{1}H NMR spectroscopy showed that the ratio of **8a**:**8b**[15] was 56:44. Purification by flash column chromatography (30% CH_2Cl_2/5% EtOAc in hexanes) gave the title compound as a white solid (20.1 mg, 27% yield).

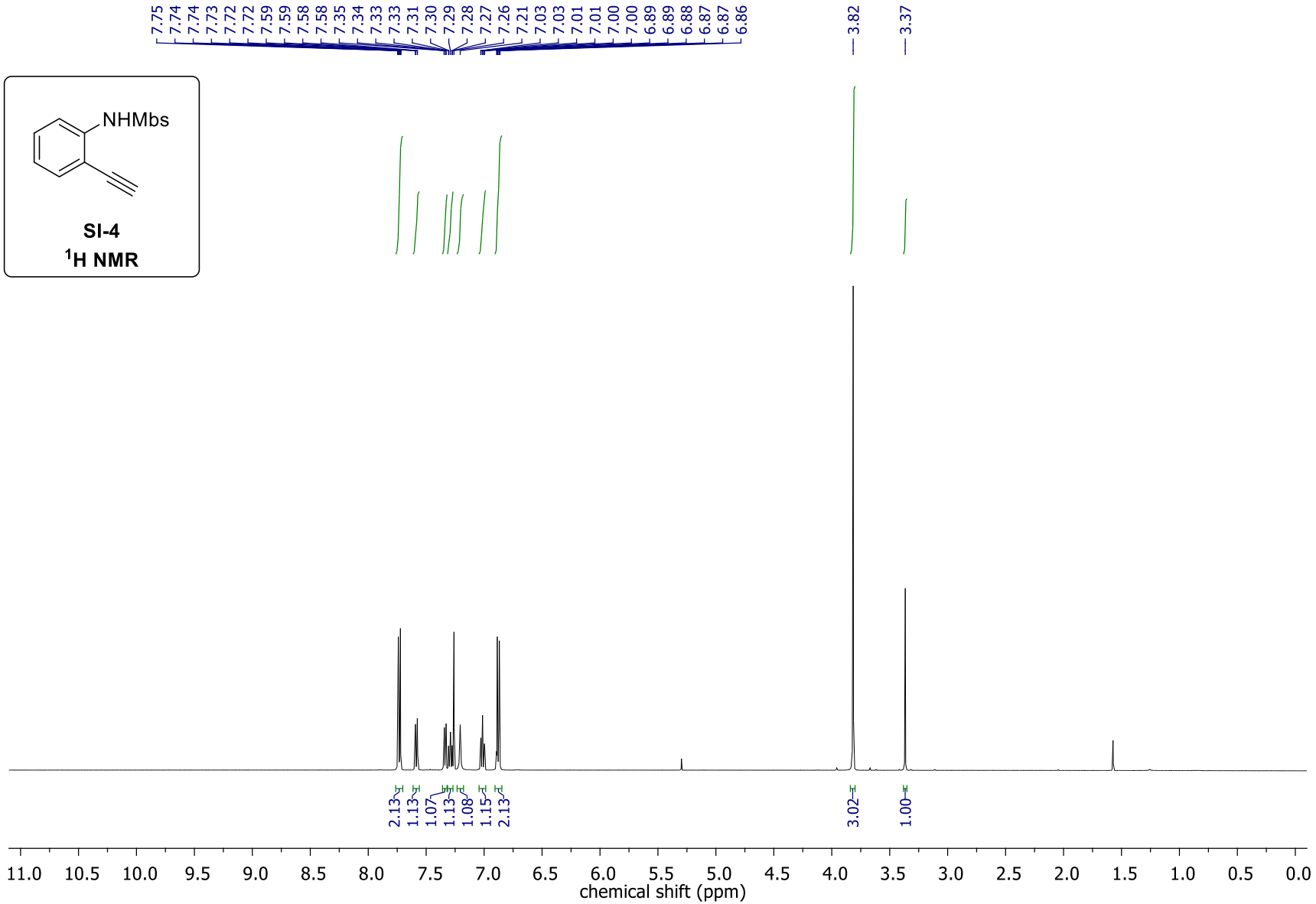
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75-7.71 (m, 2H), 7.00-6.96 (m, 2H), 6.94 (t, J = 1.8 Hz, 1H), 3.86 (s, 3H), 3.50 (t, J = 9.2 Hz, 2H), 2.61 (td, J = 9.2, 1.8 Hz, 2H), 1.24 (s, 12H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 163.3, 142.4, 129.8, 128.3, 114.5, 83.4, 55.8, 48.3, 31.1, 24.9. **^{11}B NMR** (193 MHz, $CDCl_3$): δ 29.5. **HRMS** (ESI): *m/z* calcd for $C_{17}H_{24}BNO_5SNa$ $[M+Na]^+$: 388.1369. Found: 388.1362.

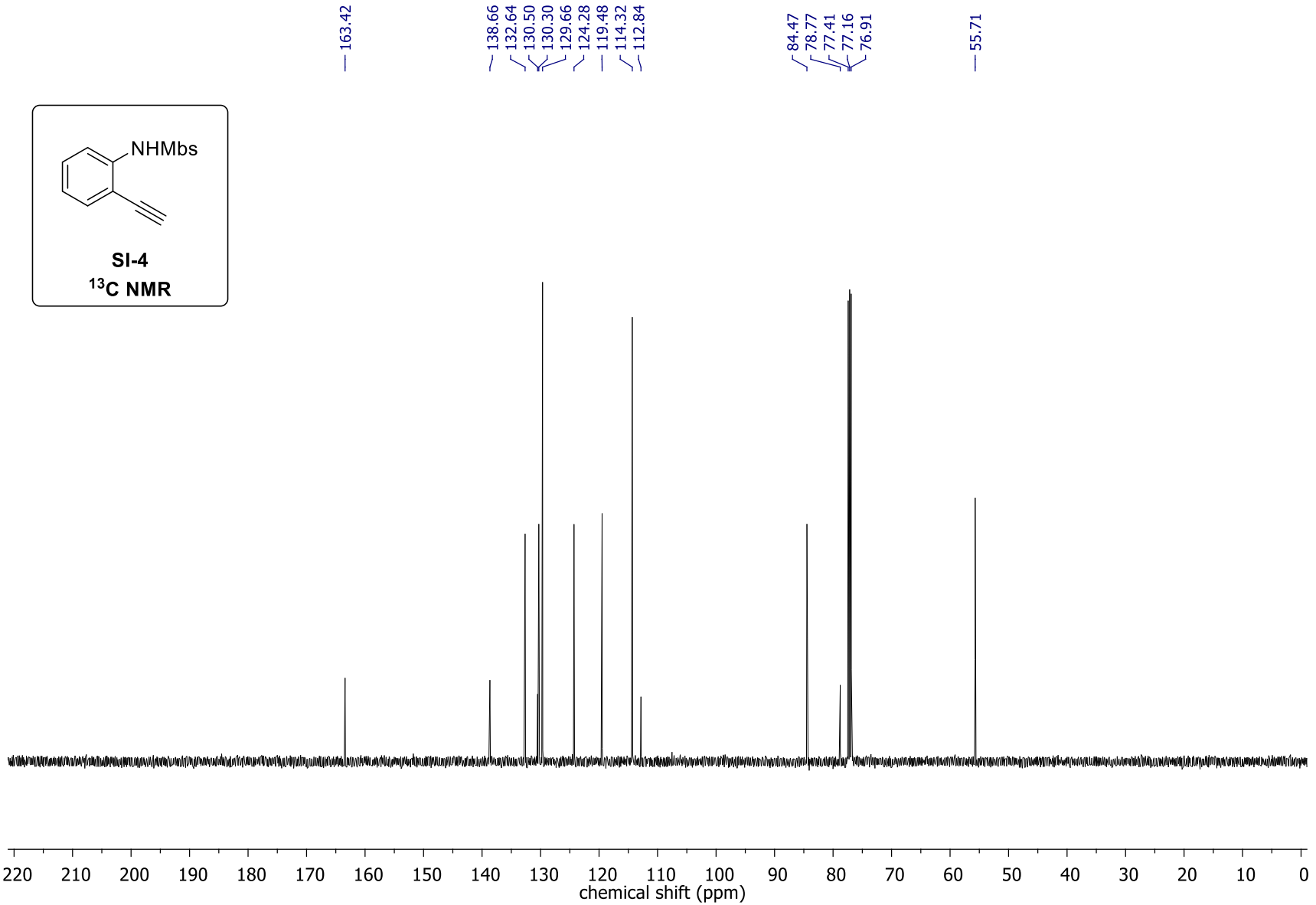


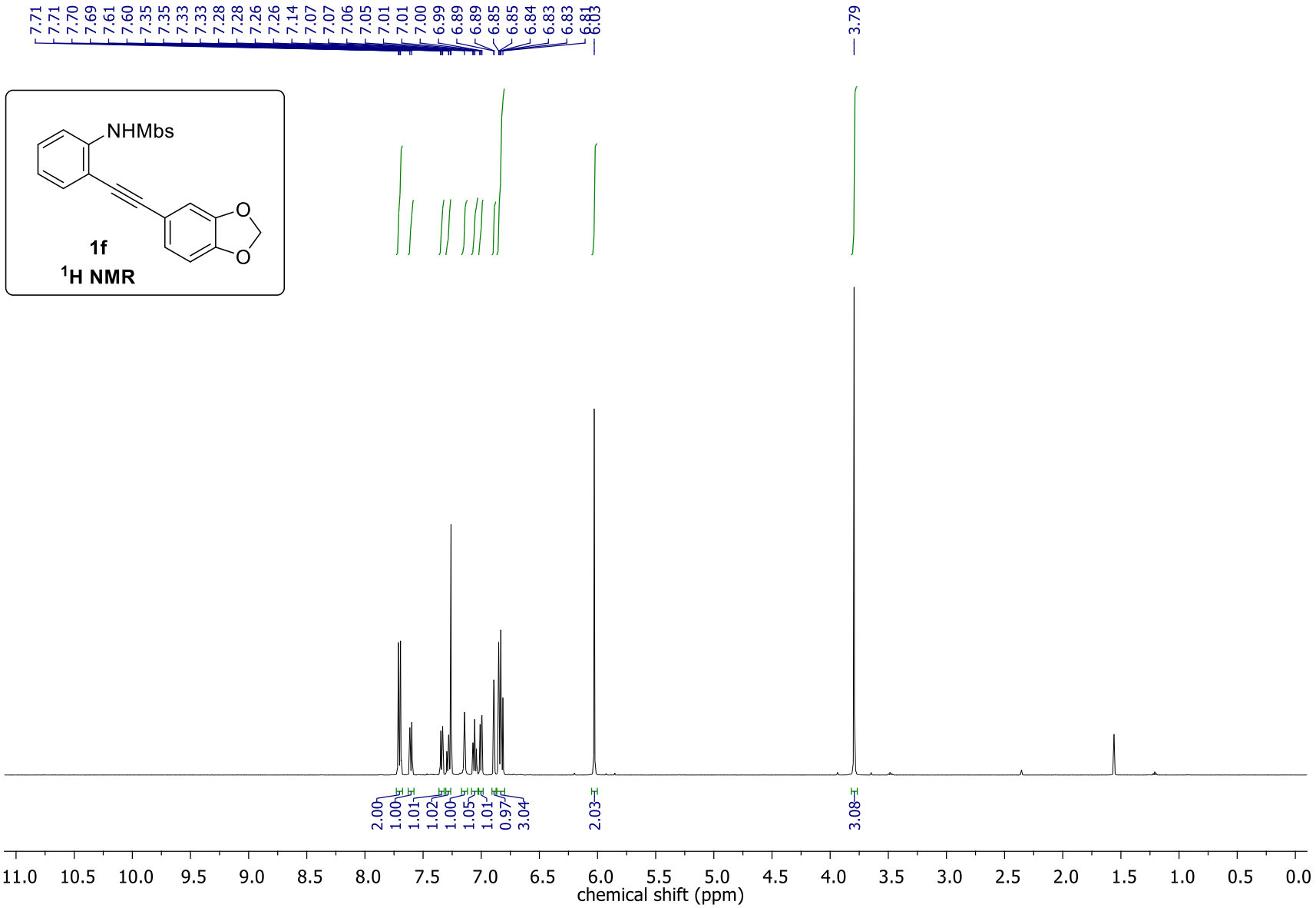
IPrAuTFA
^{1}H NMR

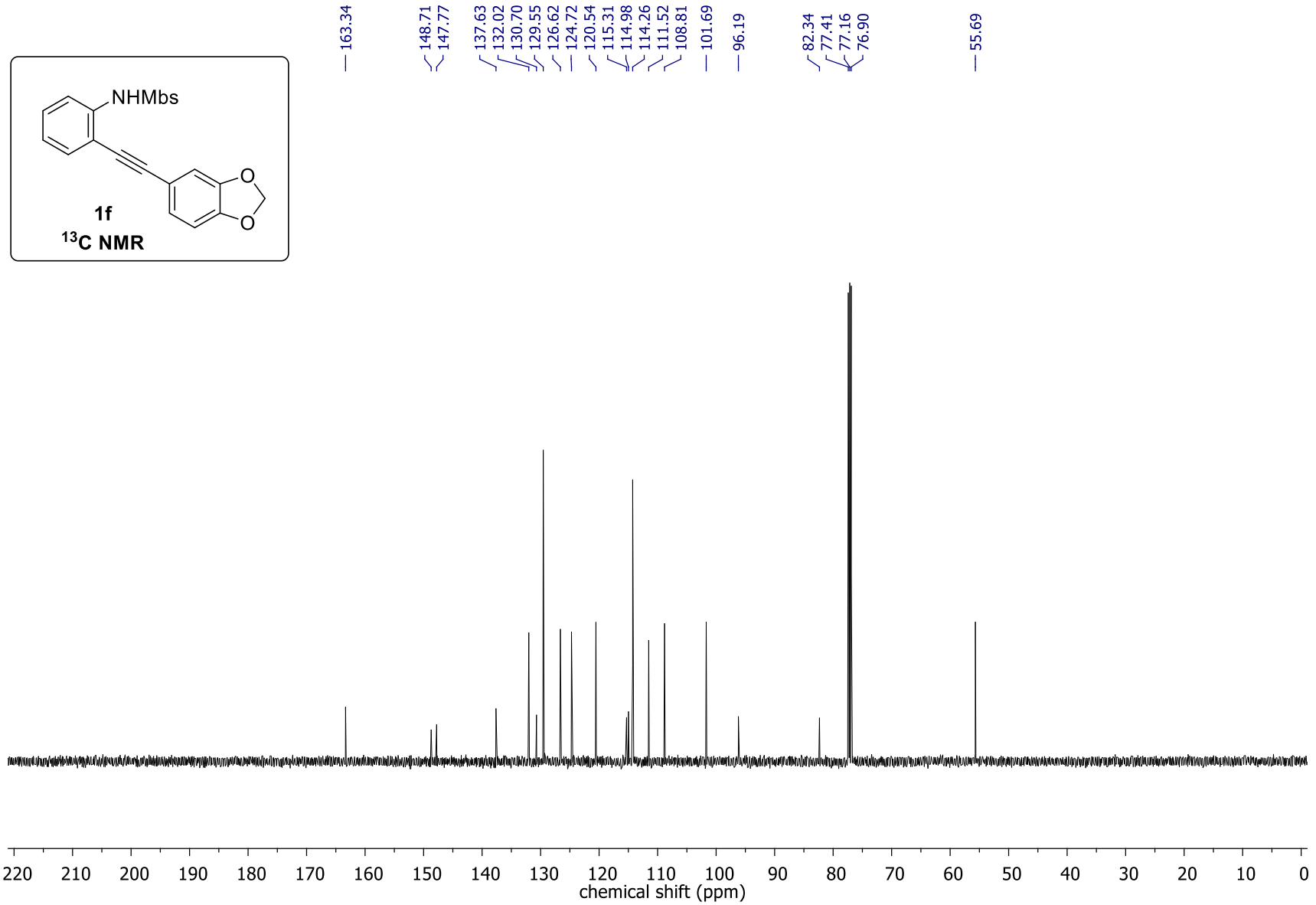

NHMbs
TMS
SI-3
1H NMR
7.70
7.70
7.69
7.68
7.68
7.67
7.61
7.59
7.30
7.30
7.30
7.28
7.28
7.28
7.27
7.26
7.25
7.25
7.17
7.02
7.02
7.00
7.00
6.99
6.99
6.87
6.87
6.86
6.85
6.84
3.81
0.27
2.00
1.03
2.35
1.05
1.08
2.02
3.11
8.87
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)

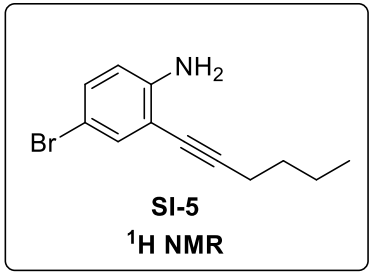

NHMbs
TMS
SI-3
13C NMR
163.34
138.32
132.14
130.66
129.95
129.55
124.39
119.87
114.36
114.25
102.35
99.68
77.41
77.16
76.91
55.69
0.04
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
chemical shift (ppm)


NHMbs
SI-4
^{1}H NMR
7.75
7.74
7.74
7.73
7.72
7.72
7.59
7.59
7.58
7.58
7.35
7.34
7.33
7.33
7.31
7.30
7.29
7.28
7.27
7.26
7.21
7.03
7.03
7.01
7.01
7.00
7.00
6.89
6.89
6.88
6.87
6.87
6.86
3.82
3.37
2.13
1.13
1.07
1.13
1.08
1.15
2.13
3.02
1.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)


163.42
138.66
132.64
130.50
130.30
129.66
124.28
119.48
114.32
112.84
84.47
78.77
77.41
77.16
76.91
55.71
NHMbs
SI-4
13C NMR
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
chemical shift (ppm)


7.71
7.71
7.70
7.69
7.61
7.60
7.35
7.35
7.33
7.33
7.28
7.28
7.26
7.26
7.14
7.07
7.07
7.06
7.05
7.01
7.01
7.00
6.99
6.89
6.89
6.85
6.85
6.84
6.83
6.83
6.81
6.81
3.79
NHMbs
O
O
1f
1H NMR
2.00
1.00
1.01
1.02
1.00
1.05
1.01
0.97
3.04
2.03
3.08
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)

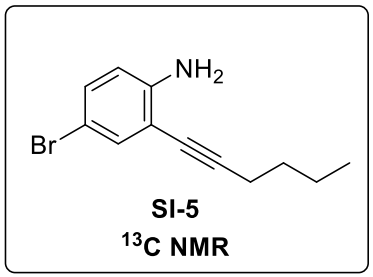

NHMbs
O
O
1f
13C NMR
163.34
148.71
147.77
137.63
132.02
130.70
129.55
126.62
124.72
120.54
115.31
114.98
114.26
111.52
108.81
101.69
96.19
82.34
77.41
77.16
76.90
55.69
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
chemical shift (ppm)


NH2
Br

SI-5

^{1}H NMR

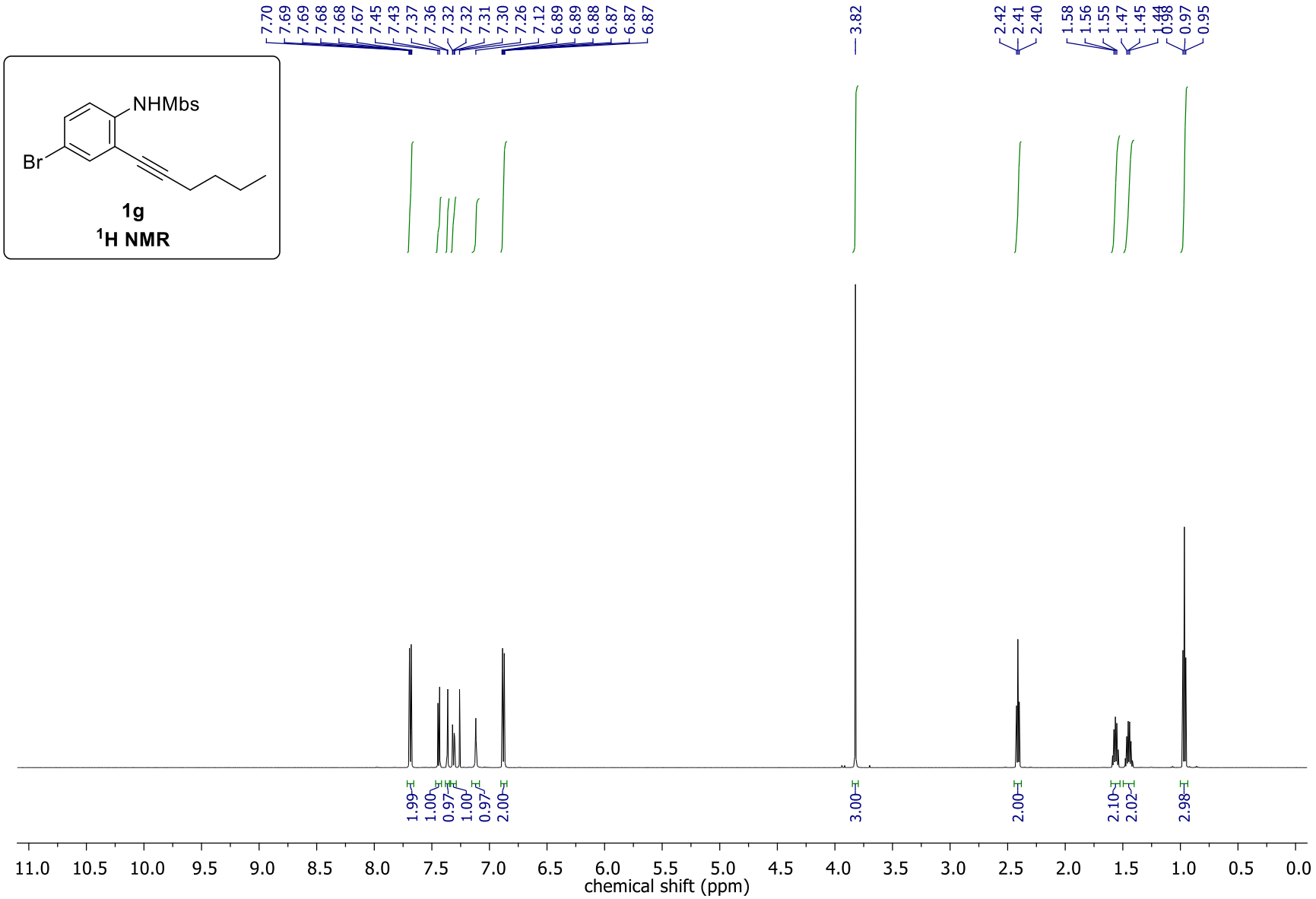
7.34
7.34
7.26
7.16
7.15
7.14
7.14
6.56
6.55
4.16
2.48
2.46
2.45
1.61
1.60
1.58
1.50
1.49
1.47
0.97
0.95
0.94
1.00
1.01
1.04
2.03
2.13
2.26
2.18
3.22
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)

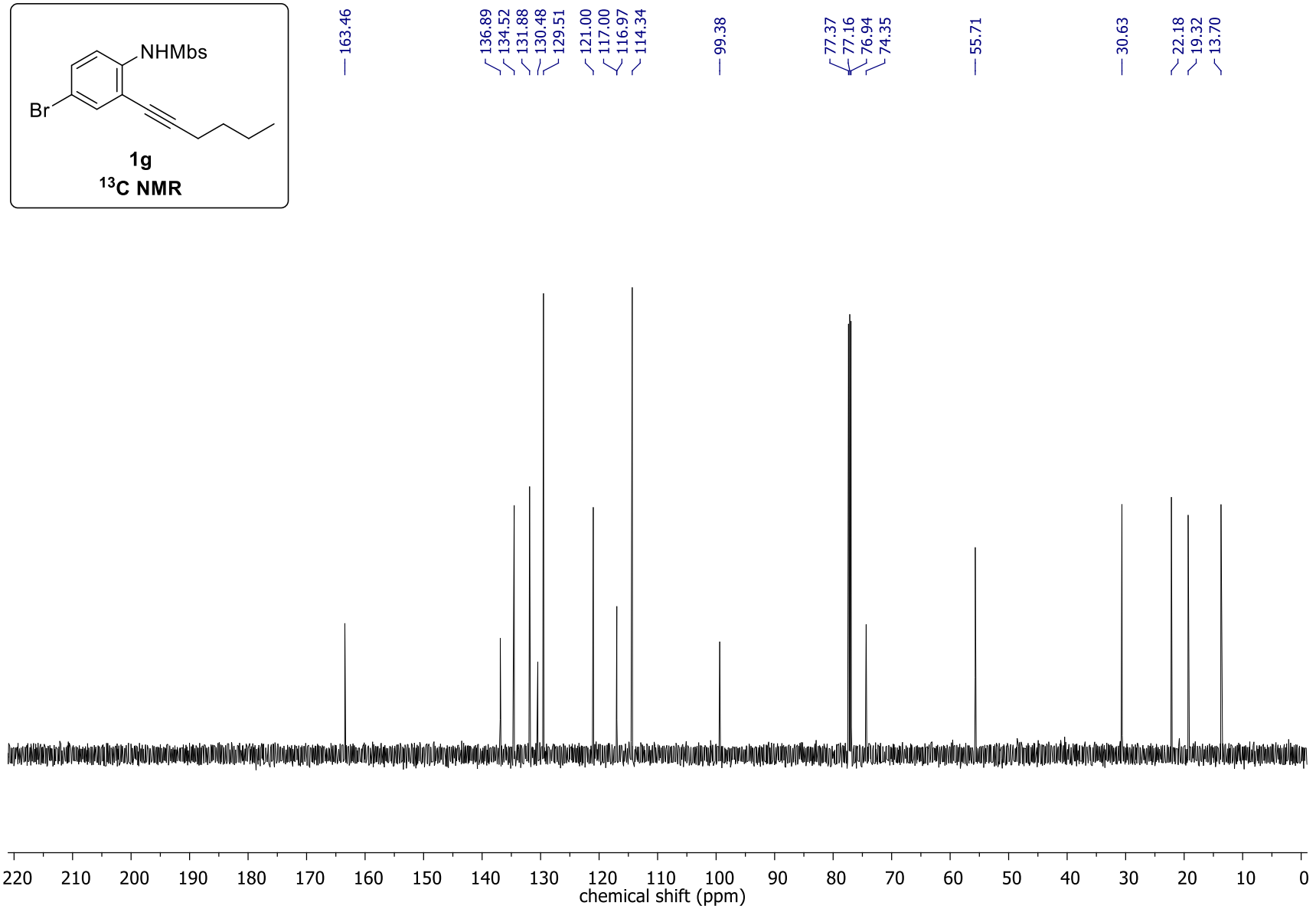

NH2
Br

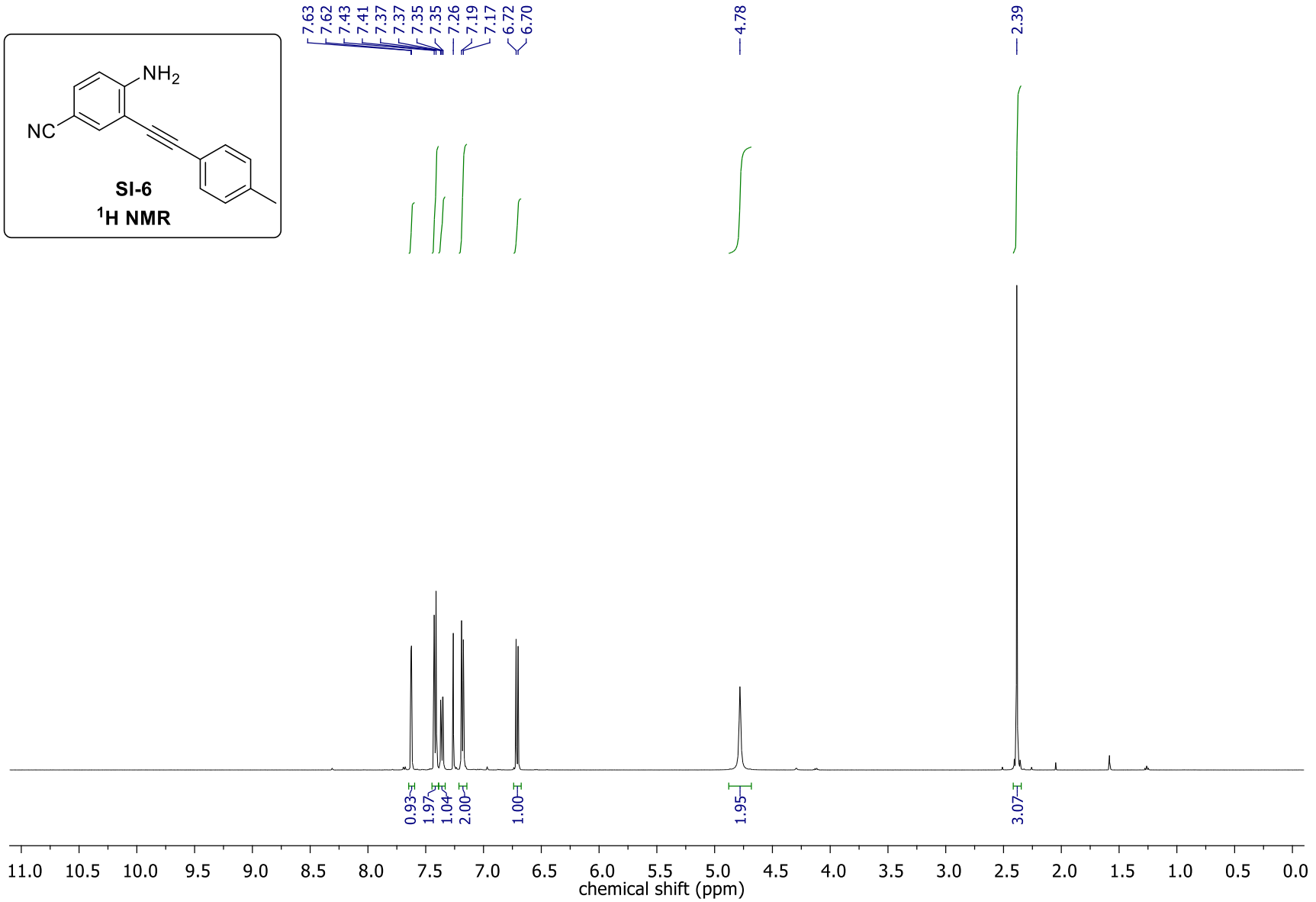
SI-5

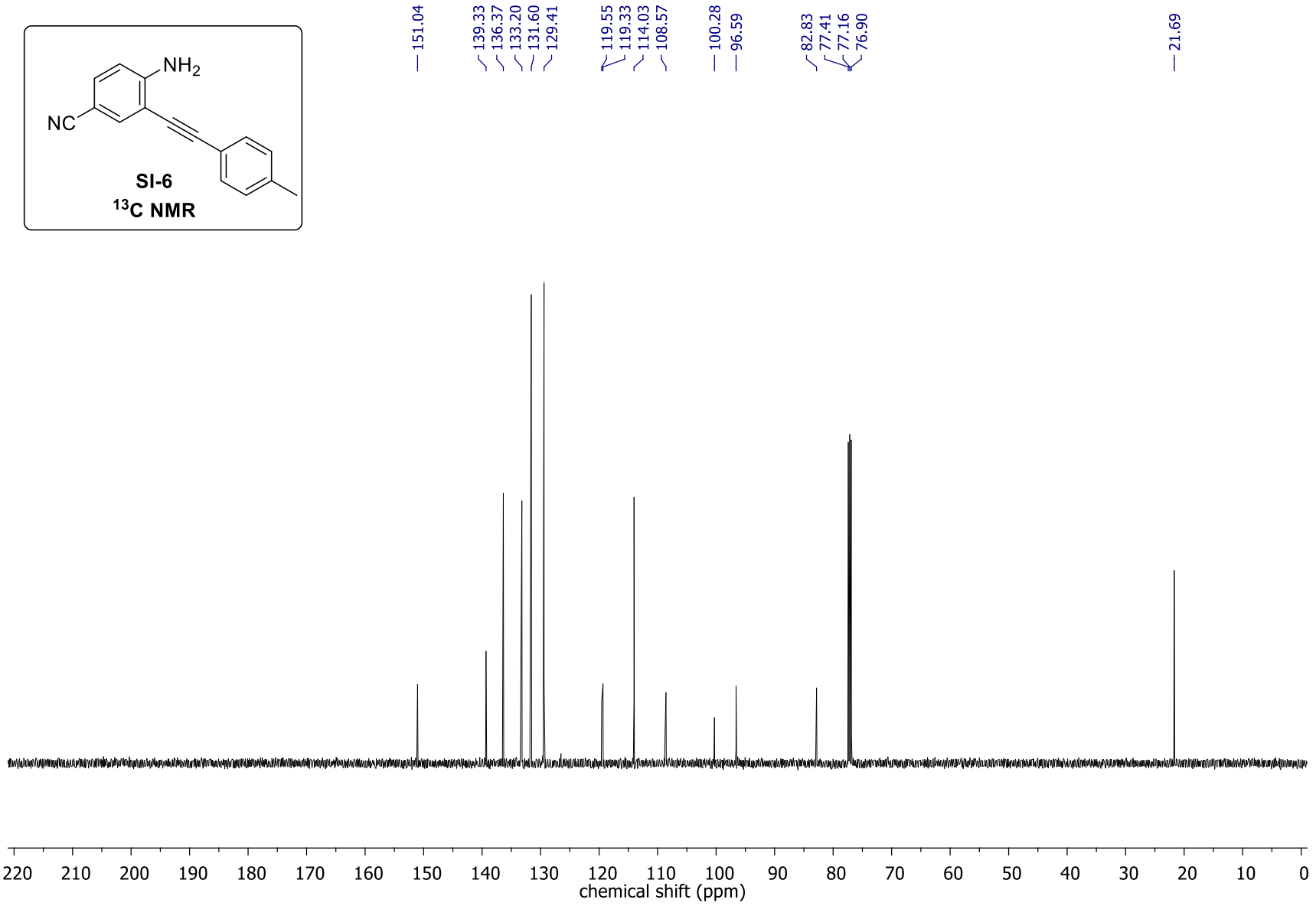
^{13}C NMR

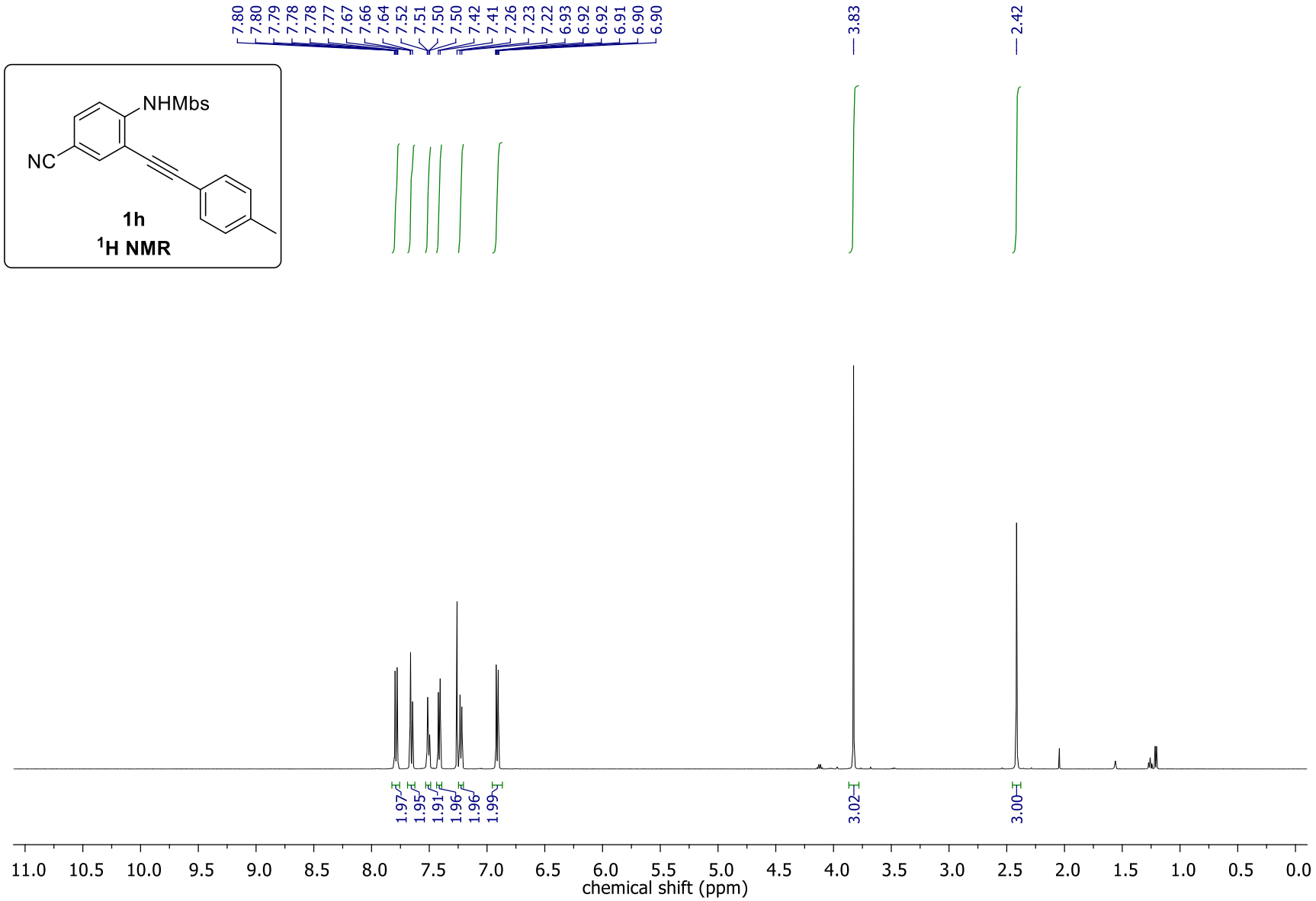
146.76
134.32
131.66
115.66
111.02
109.00
97.19
77.41
77.16
76.90
75.94
31.00
22.17
19.42
13.76
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
chemical shift (ppm)

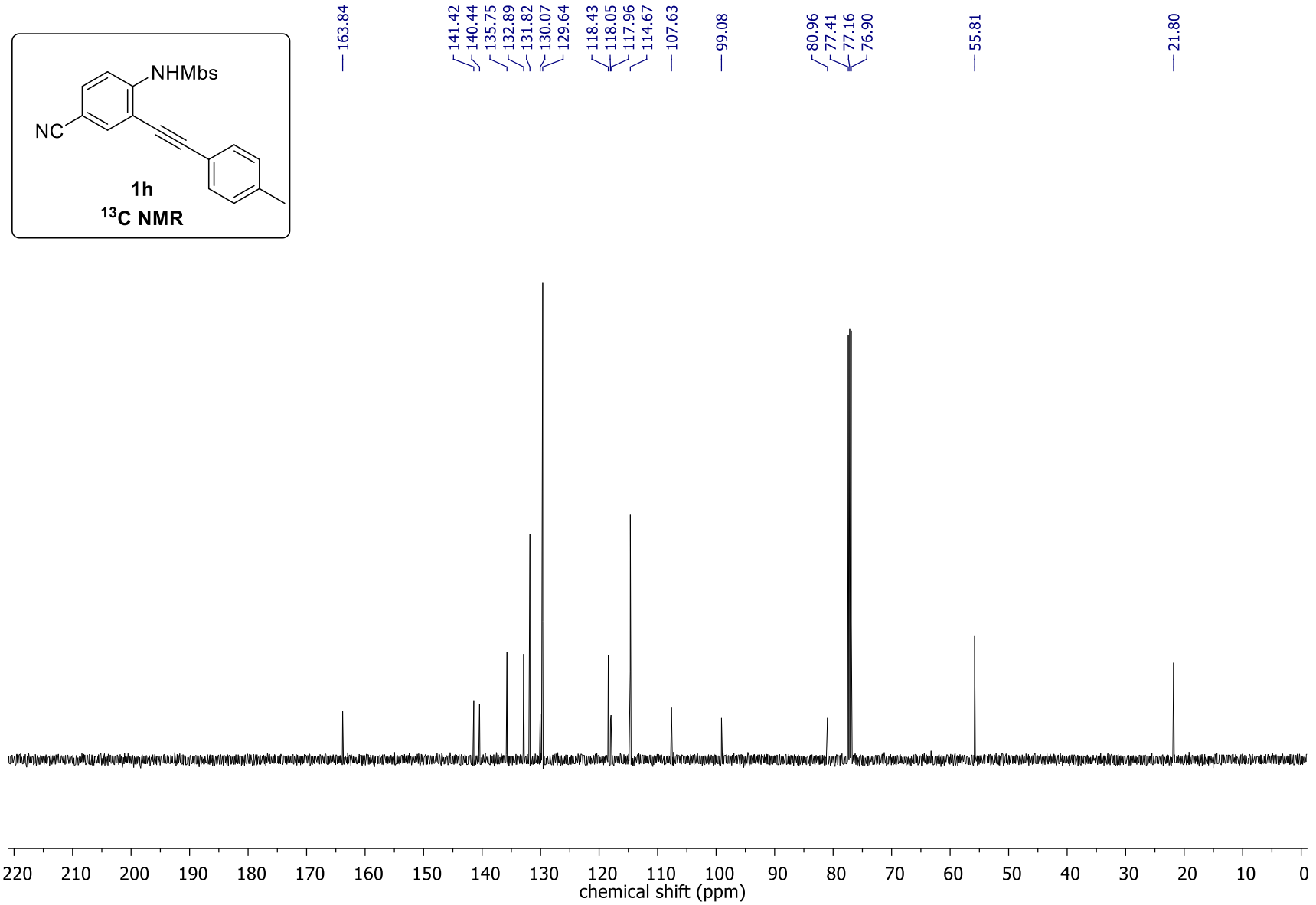

NHMbs
Br
1g
1H NMR
chemical shift (ppm)

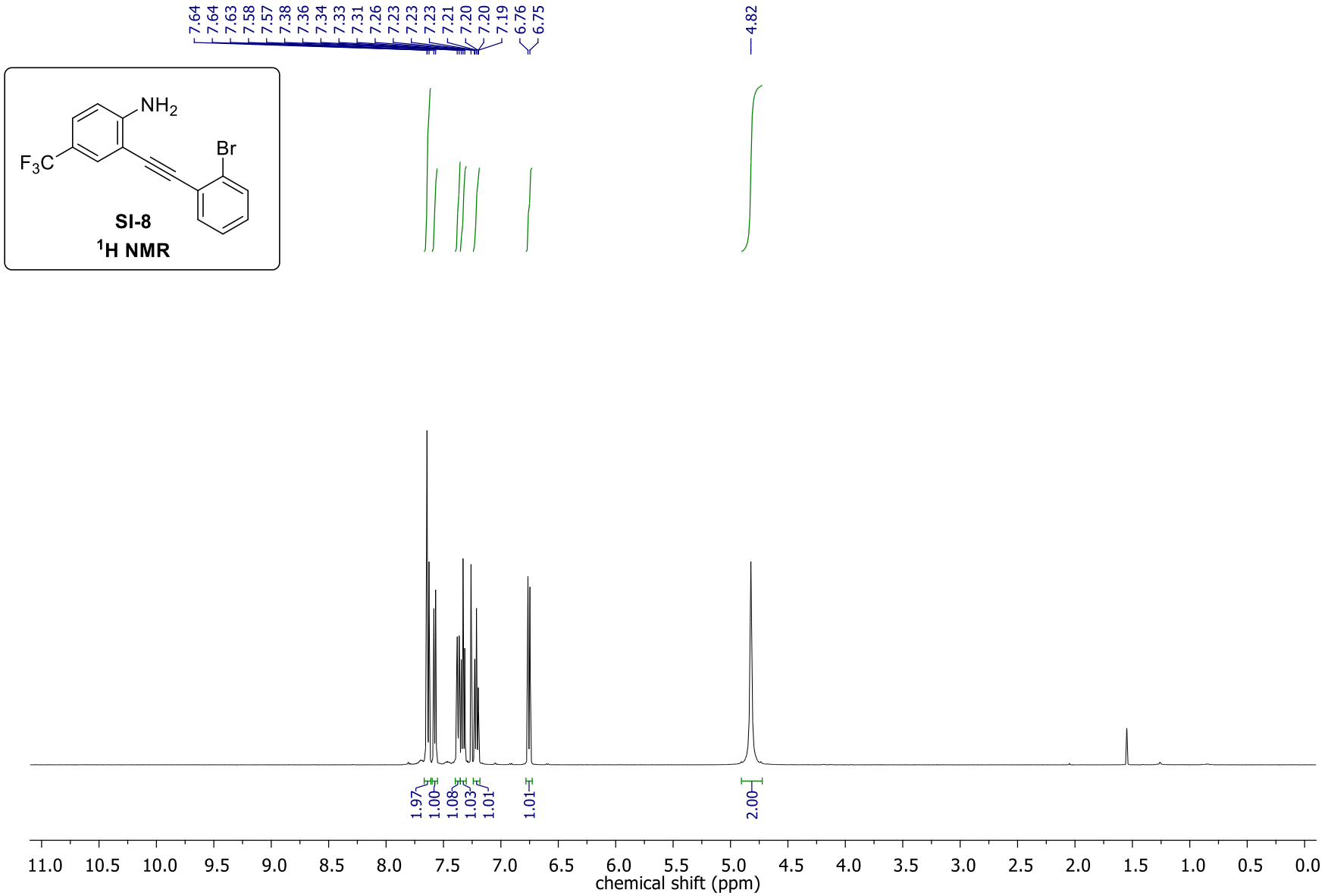

NHMbs
Br
1g
13C NMR
163.46
136.89
134.52
131.88
130.48
129.51
121.00
117.00
116.97
114.34
99.38
77.37
77.16
76.94
74.35
55.71
30.63
22.18
19.32
13.70
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
chemical shift (ppm)

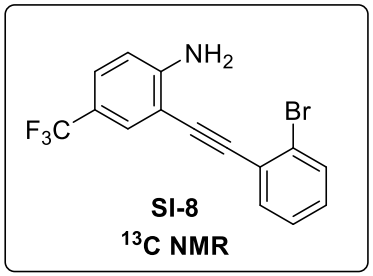

NH2
NC
SI-6
1H NMR
7.63
7.62
7.43
7.41
7.37
7.37
7.35
7.35
7.26
7.19
7.17
6.72
6.70
4.78
2.39
0.93
1.97
1.04
2.00
1.00
1.95
3.07
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)


NH2
NC
SI-6
13C NMR
151.04
139.33
136.37
133.20
131.60
129.41
119.55
119.33
114.03
108.57
100.28
96.59
82.83
77.41
77.16
76.90
21.69
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
chemical shift (ppm)


NHMbs
NC
1h
1H NMR
7.80
7.80
7.79
7.78
7.78
7.77
7.67
7.66
7.64
7.52
7.51
7.50
7.50
7.42
7.41
7.26
7.23
7.22
6.93
6.92
6.92
6.91
6.90
6.90
3.83
2.42
1.97
1.95
1.91
1.96
1.96
1.99
3.02
3.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)


NHMbs
NC
1h
13C NMR
163.84
141.42
140.44
135.75
132.89
131.82
130.07
129.64
118.43
118.05
117.96
114.67
107.63
99.08
80.96
77.41
77.16
76.90
55.81
21.80
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
chemical shift (ppm)

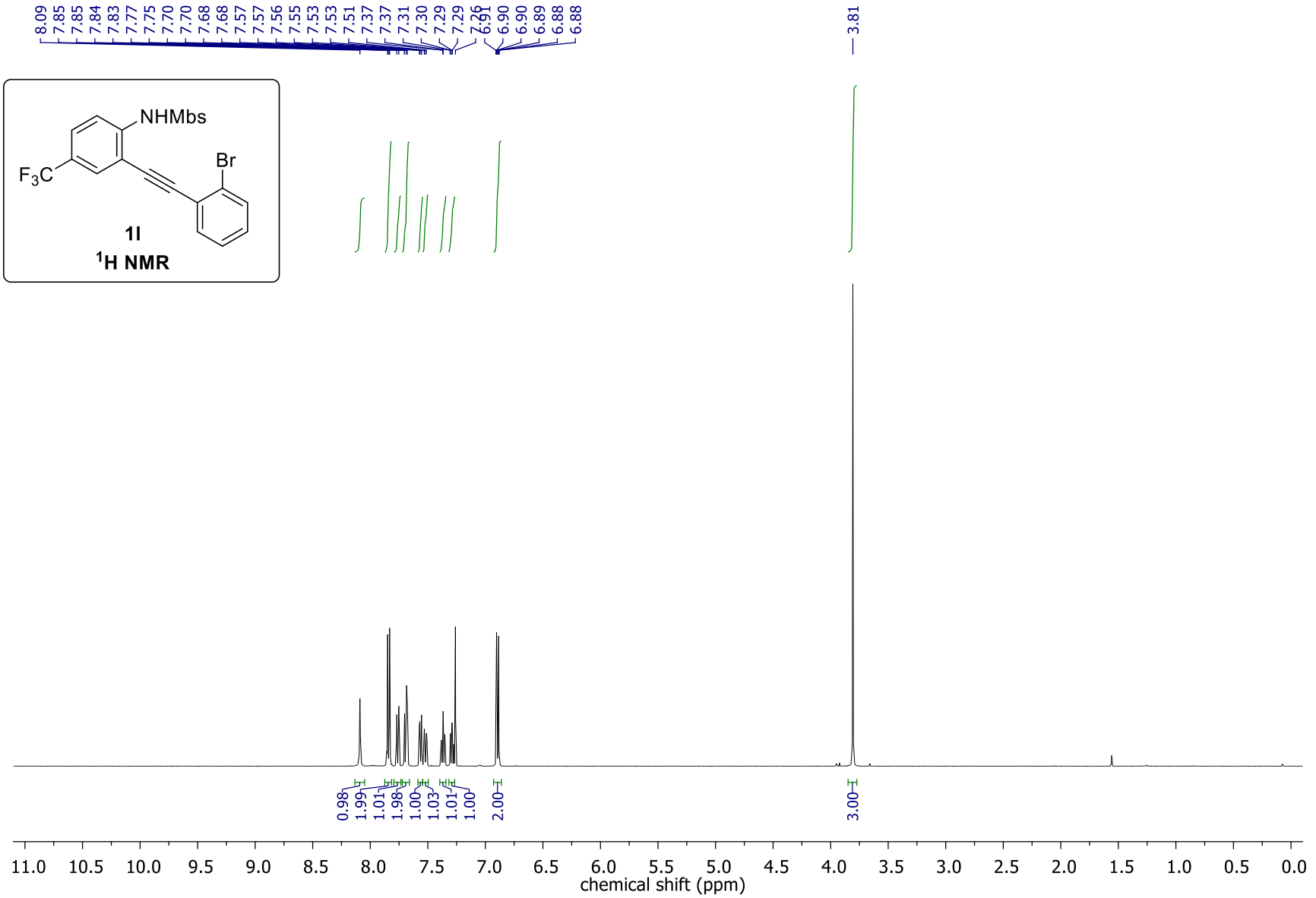

7.64
7.64
7.63
7.58
7.57
7.38
7.36
7.34
7.33
7.31
7.26
7.23
7.23
7.21
7.20
7.20
7.19
6.76
6.75
4.82
NH2
F3C
Br
SI-8
1H NMR
1.97
1.00
1.08
1.03
1.01
1.01
2.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)

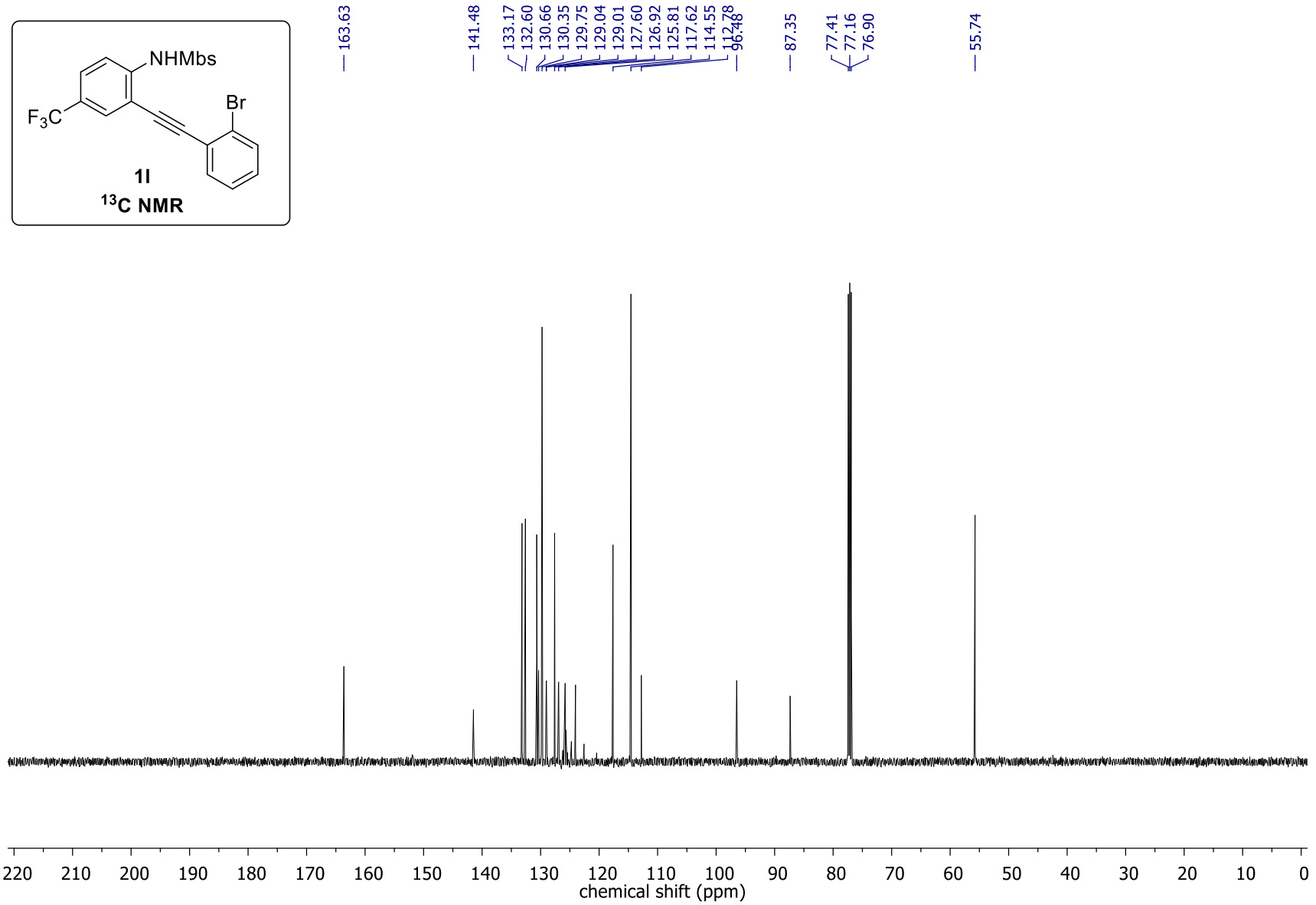

NH2
F3C
Br

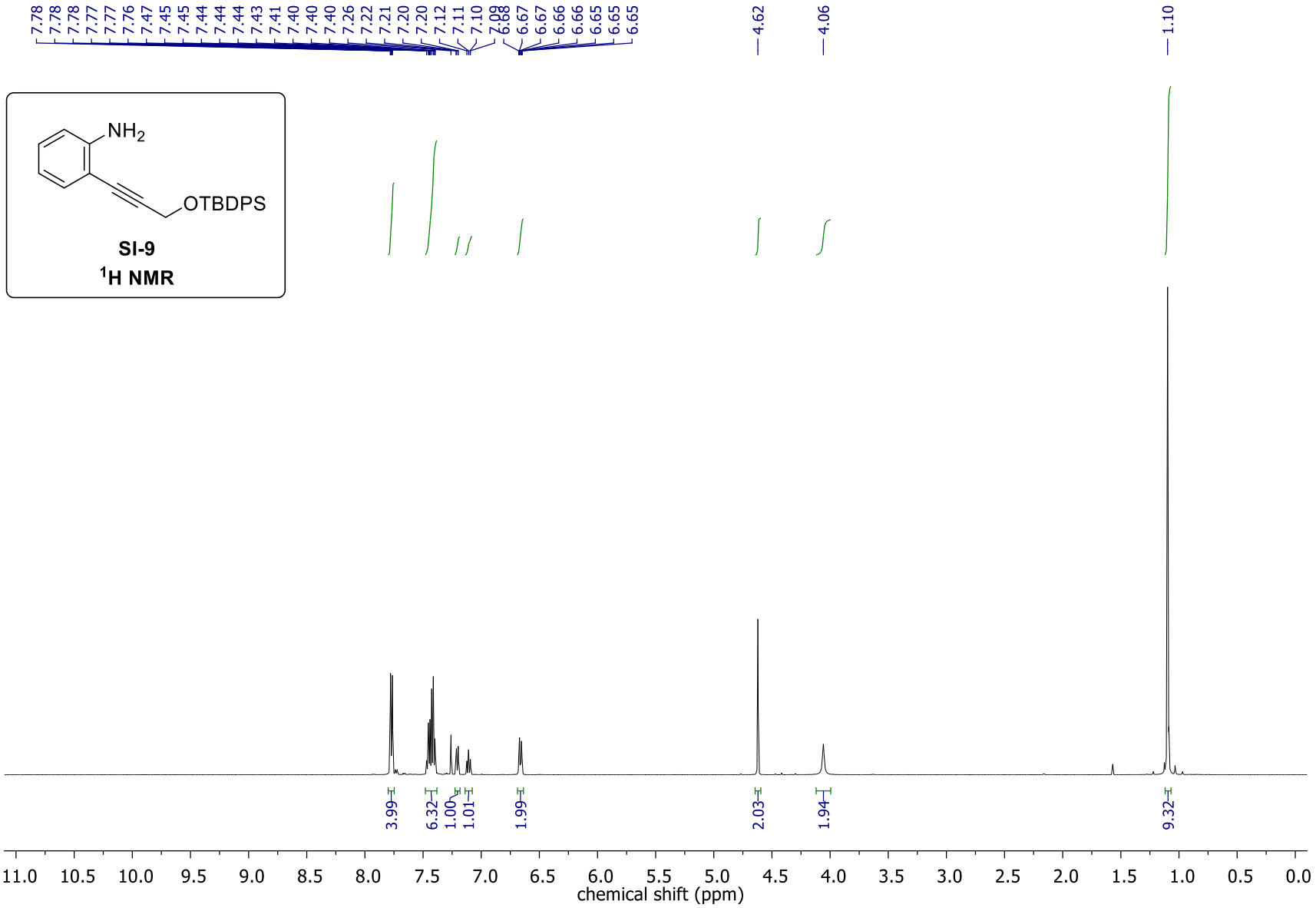
SI-8

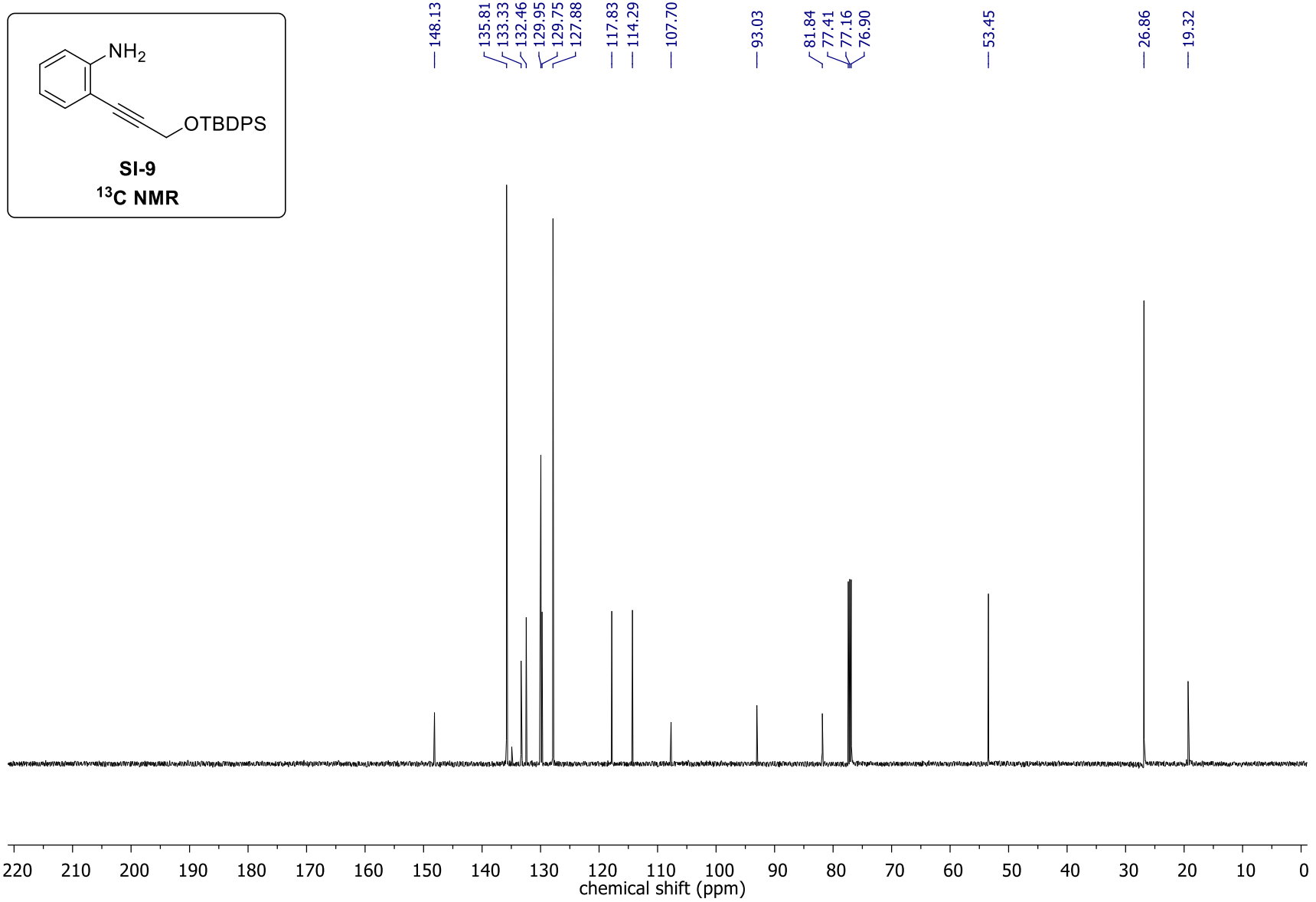
^{13}C NMR

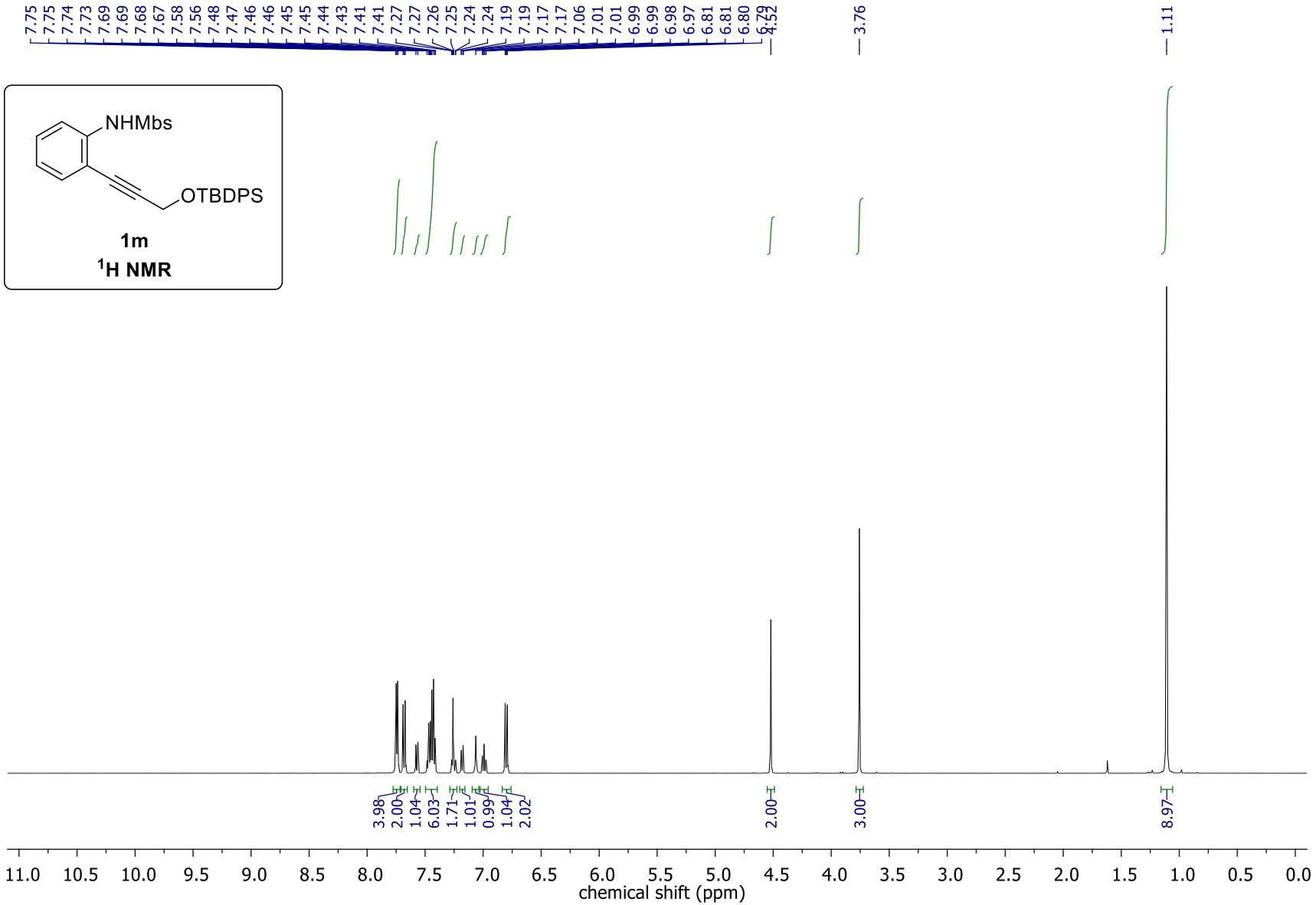
150.90
133.20
132.52
129.79
129.58
129.55
129.51
127.45
127.16
127.13
127.10
125.21
125.10
113.83
106.92
94.30
89.57
77.41
77.16
76.90
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
chemical shift (ppm)

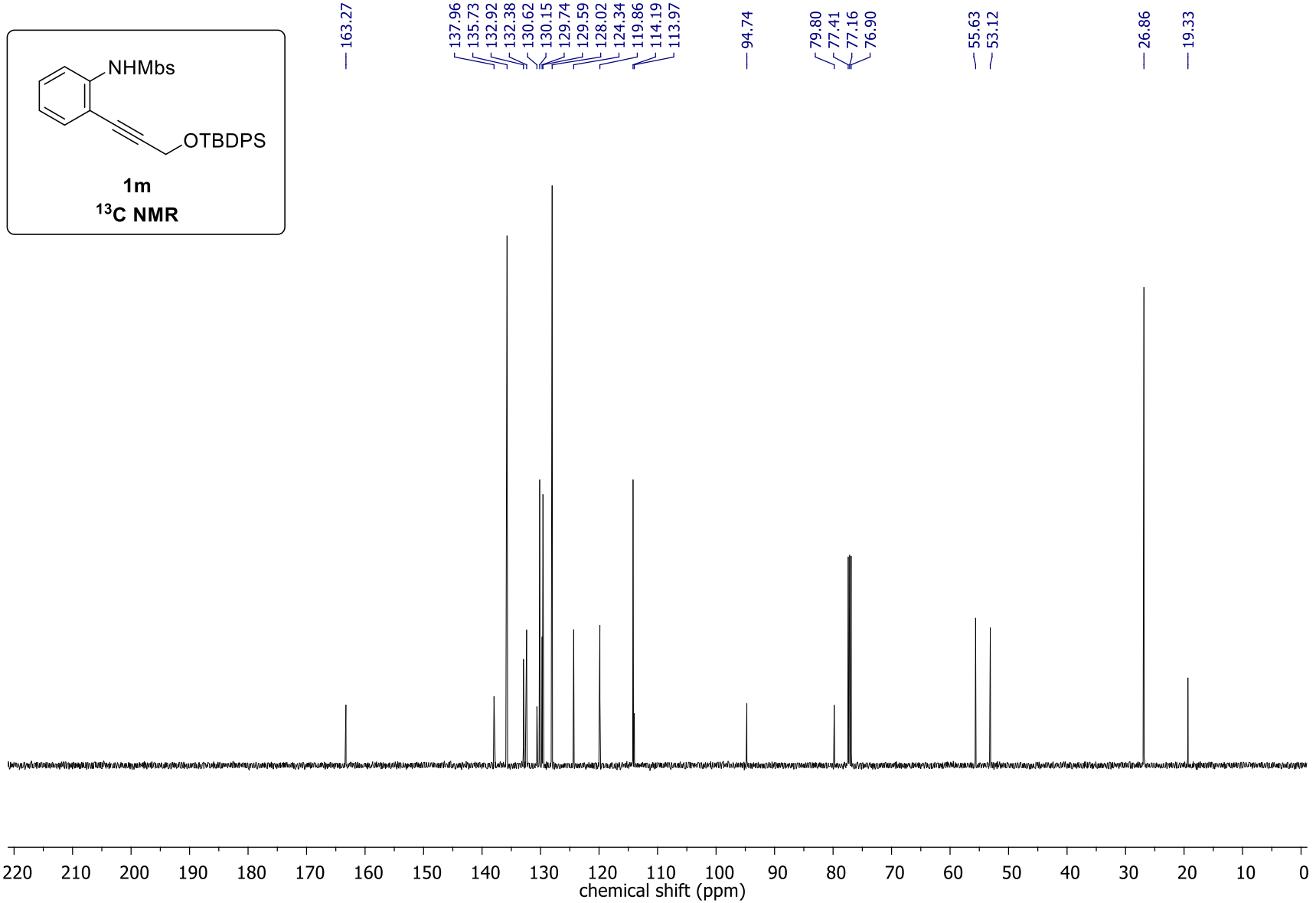

8.09
7.85
7.85
7.84
7.83
7.77
7.75
7.70
7.70
7.68
7.68
7.57
7.57
7.56
7.55
7.53
7.53
7.51
7.37
7.37
7.31
7.30
7.29
7.29
6.91
6.90
6.90
6.89
6.88
6.88
3.81
NHMbs
Br
F3C
1l
1H NMR
0.98
1.99
1.01
1.98
1.00
1.03
1.01
1.00
2.00
3.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)

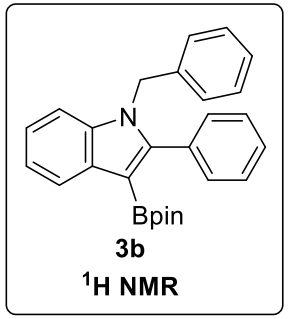

NHMbs
Br
F3C
1l
13C NMR
163.63
141.48
133.17
132.60
130.66
130.35
129.75
129.04
129.01
127.60
126.92
125.81
117.62
114.55
112.78
96.48
87.35
77.41
77.16
76.90
55.74
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
chemical shift (ppm)


7.78
7.78
7.78
7.77
7.77
7.76
7.47
7.45
7.45
7.44
7.44
7.44
7.43
7.41
7.40
7.40
7.40
7.26
7.22
7.21
7.20
7.20
7.12
7.11
7.10
7.09
7.08
6.67
6.67
6.66
6.66
6.65
6.65
6.65
4.62
4.06
1.10
NH2
OTBDPS
SI-9
1H NMR
3.99
6.32
1.00
1.01
1.99
2.03
1.94
9.32
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
chemical shift (ppm)


NH2
OTBDPS
SI-9
13C NMR
148.13
135.81
133.33
132.46
129.95
129.75
127.88
117.83
114.29
107.70
93.03
81.84
77.41
77.16
76.90
53.45
26.86
19.32
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
chemical shift (ppm)


NHMbs
OTBDPS
1m
1H NMR
chemical shift (ppm)

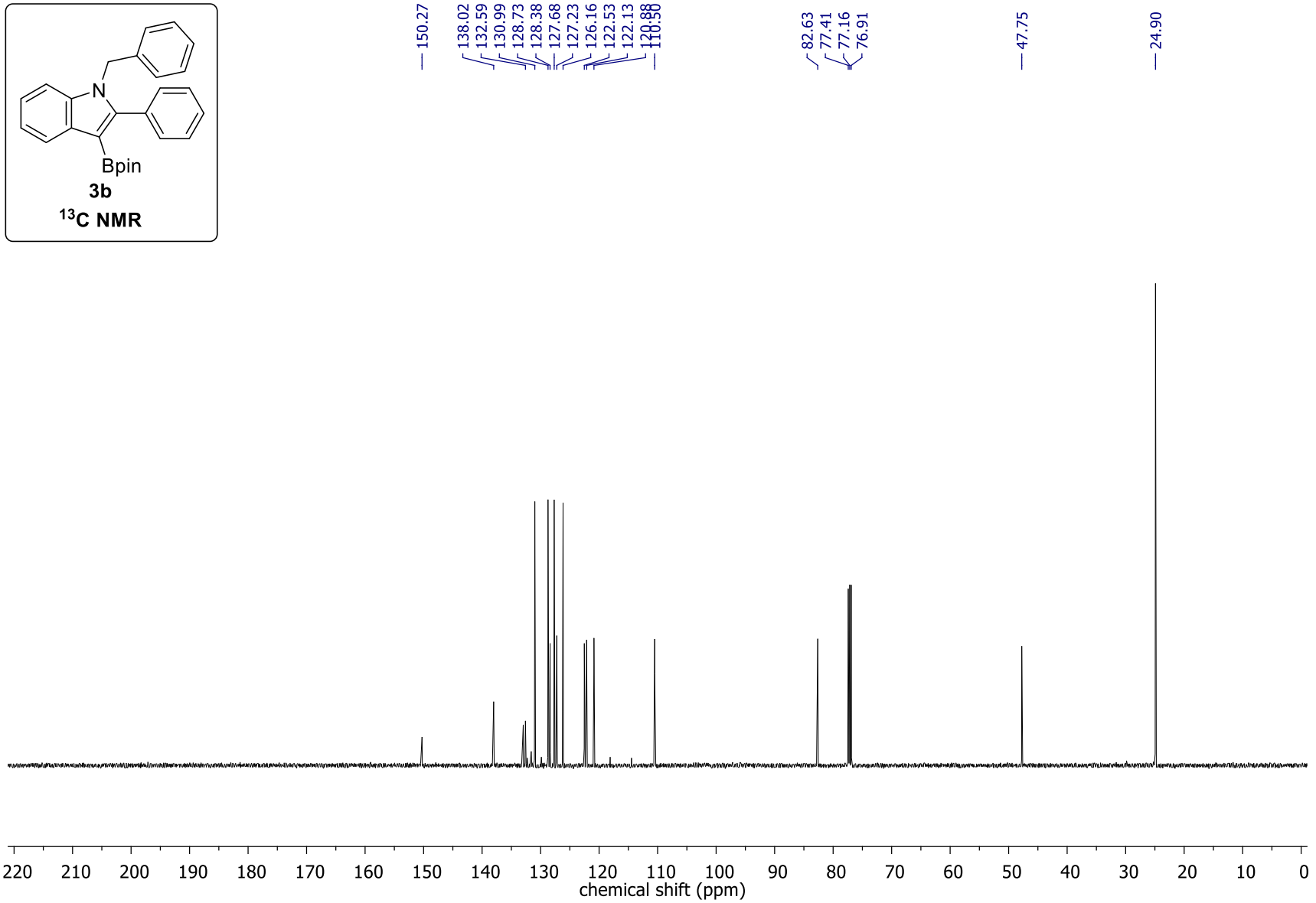

NHMbs
OTBDPS
1m
13C NMR
163.27
137.96
135.73
132.92
132.38
130.62
130.15
129.74
129.59
128.02
124.34
119.86
114.19
113.97
94.74
79.80
77.41
77.16
76.90
55.63
53.12
26.86
19.33
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
chemical shift (ppm)

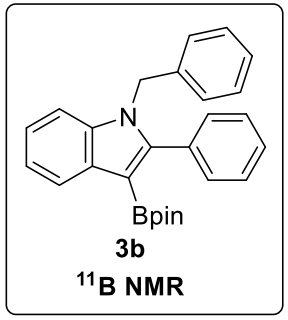

N
Bpin

3b

^{1}H NMR

8.14
8.12
7.41
7.40
7.40
7.39
7.37
7.36
7.35
7.35
7.26
7.24
7.22
7.21
7.17
7.16
6.97
6.96
6.96
1.27
1.00
5.08
6.08
1.93
2.07
11.83
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)

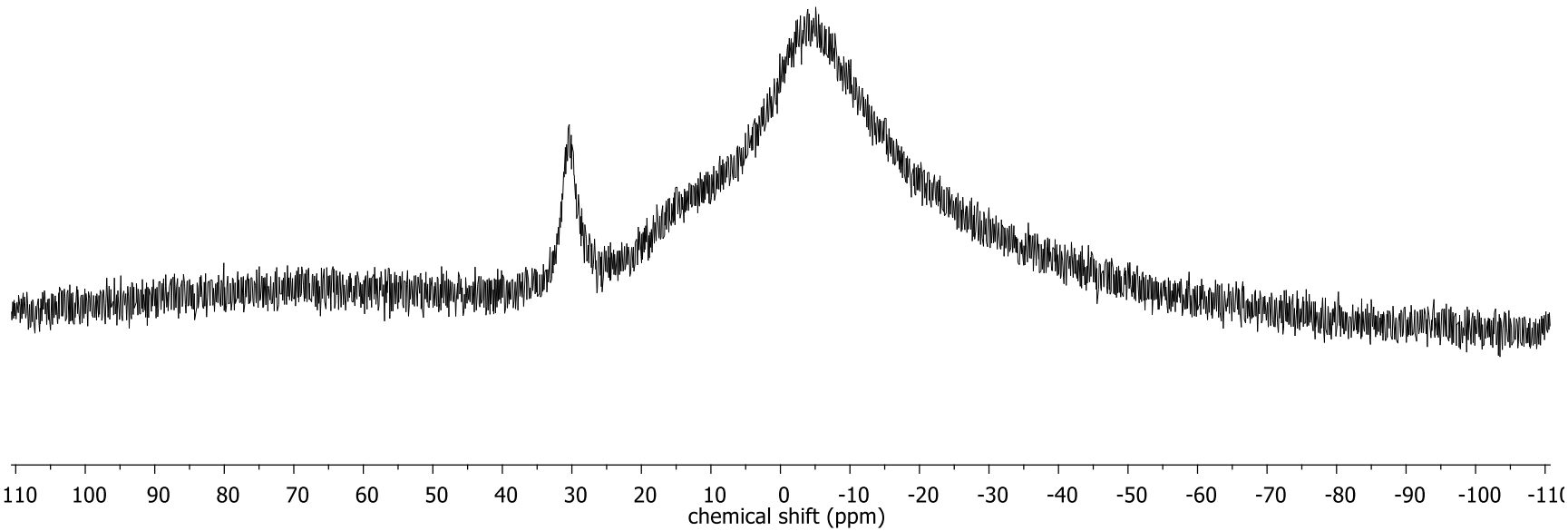

N
Bpin
3b
13C NMR
150.27
138.02
132.59
130.99
128.73
128.38
127.68
127.23
126.16
122.53
122.13
110.88
110.50
82.63
77.41
77.16
76.91
47.75
24.90
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
chemical shift (ppm)

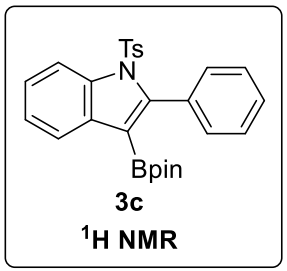


3b

^{11}B NMR

30.37

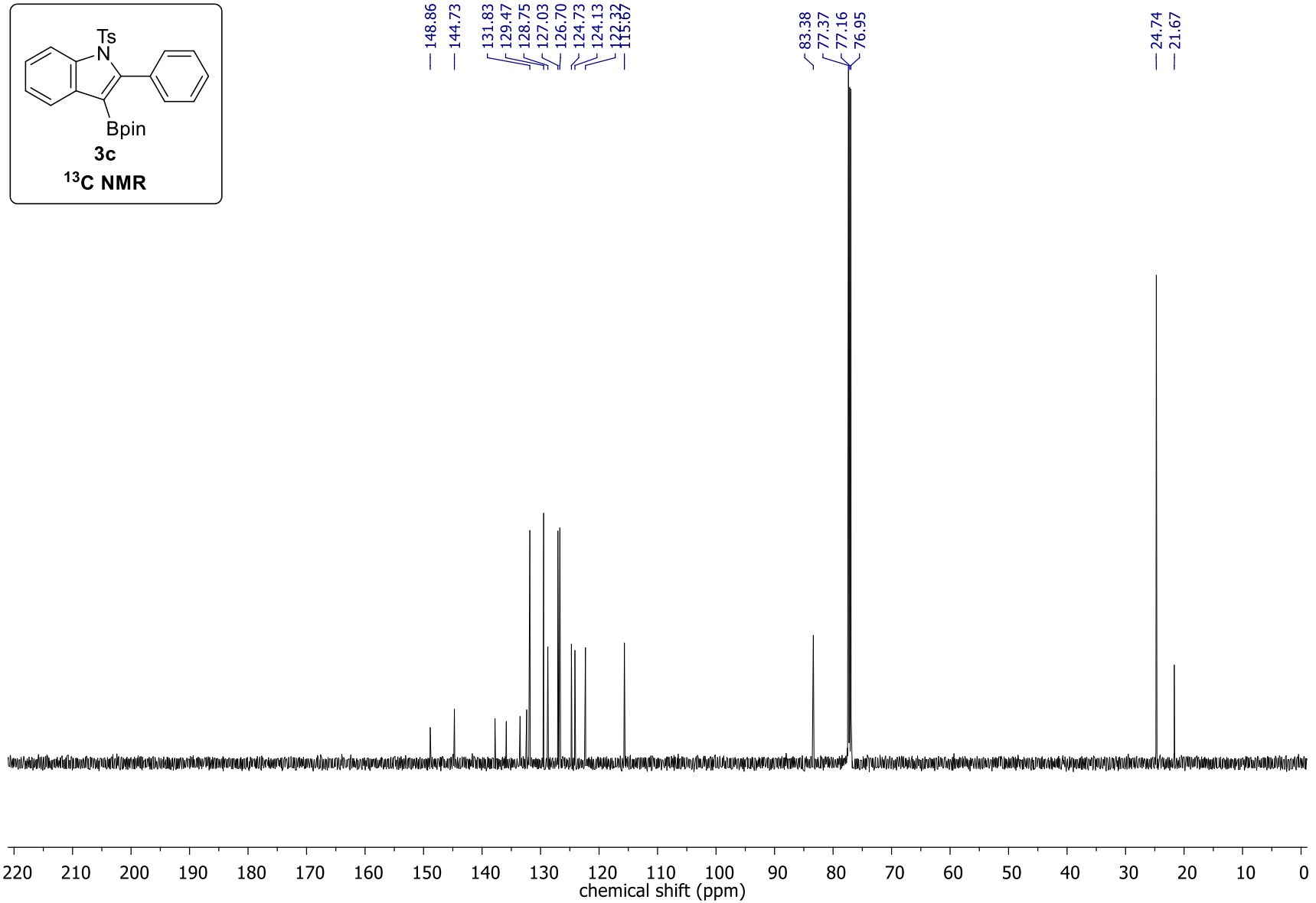


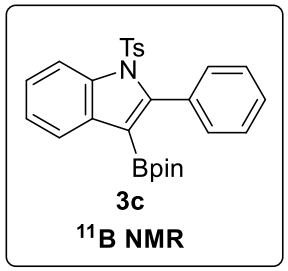

Ts
N
Bpin

3c

^{1}H NMR

8.31
8.29
7.87
7.85
7.44
7.43
7.43
7.42
7.42
7.41
7.41
7.40
7.36
7.35
7.34
7.32
7.30
7.29
7.28
7.26
7.06
7.05
2.30
1.16
1.00
0.99
1.10
7.95
1.98
3.00
12.05
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)

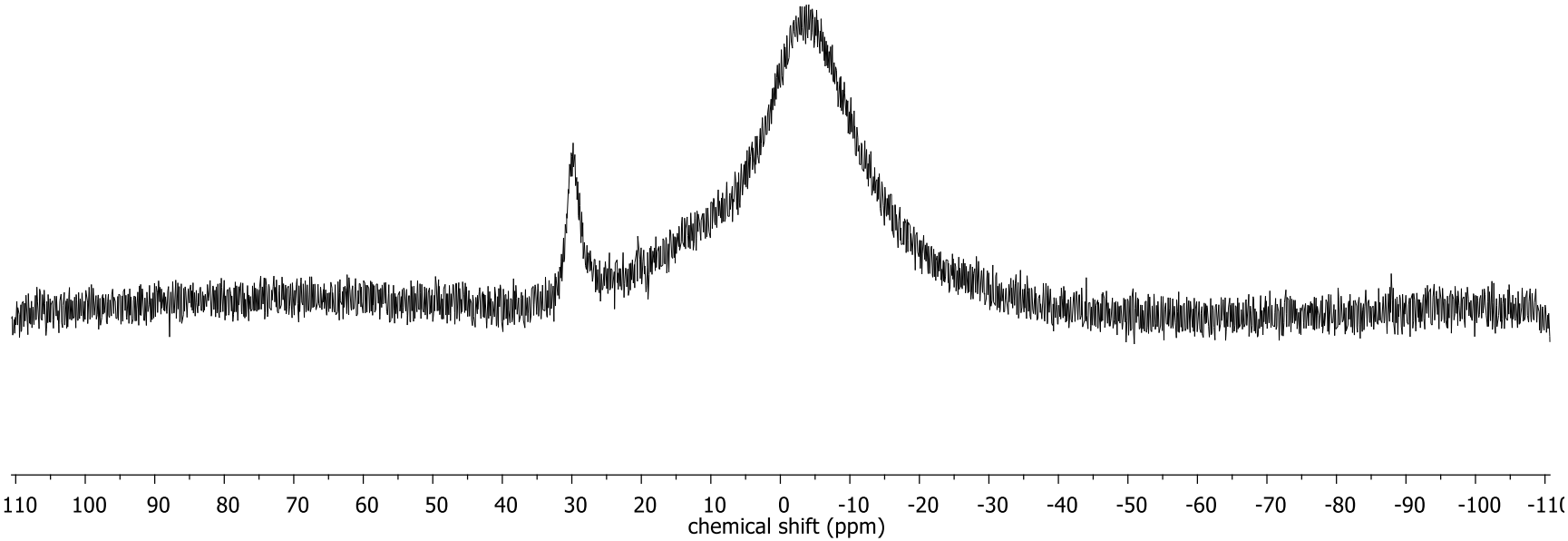

Ts
N
Bpin
3c
13C NMR
148.86
144.73
131.83
129.47
128.75
127.03
126.70
124.73
124.13
122.32
115.67
83.38
77.37
77.16
76.95
24.74
21.67
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
chemical shift (ppm)

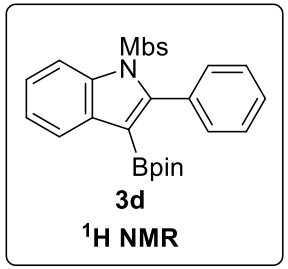


3c

^{11}B NMR

29.81

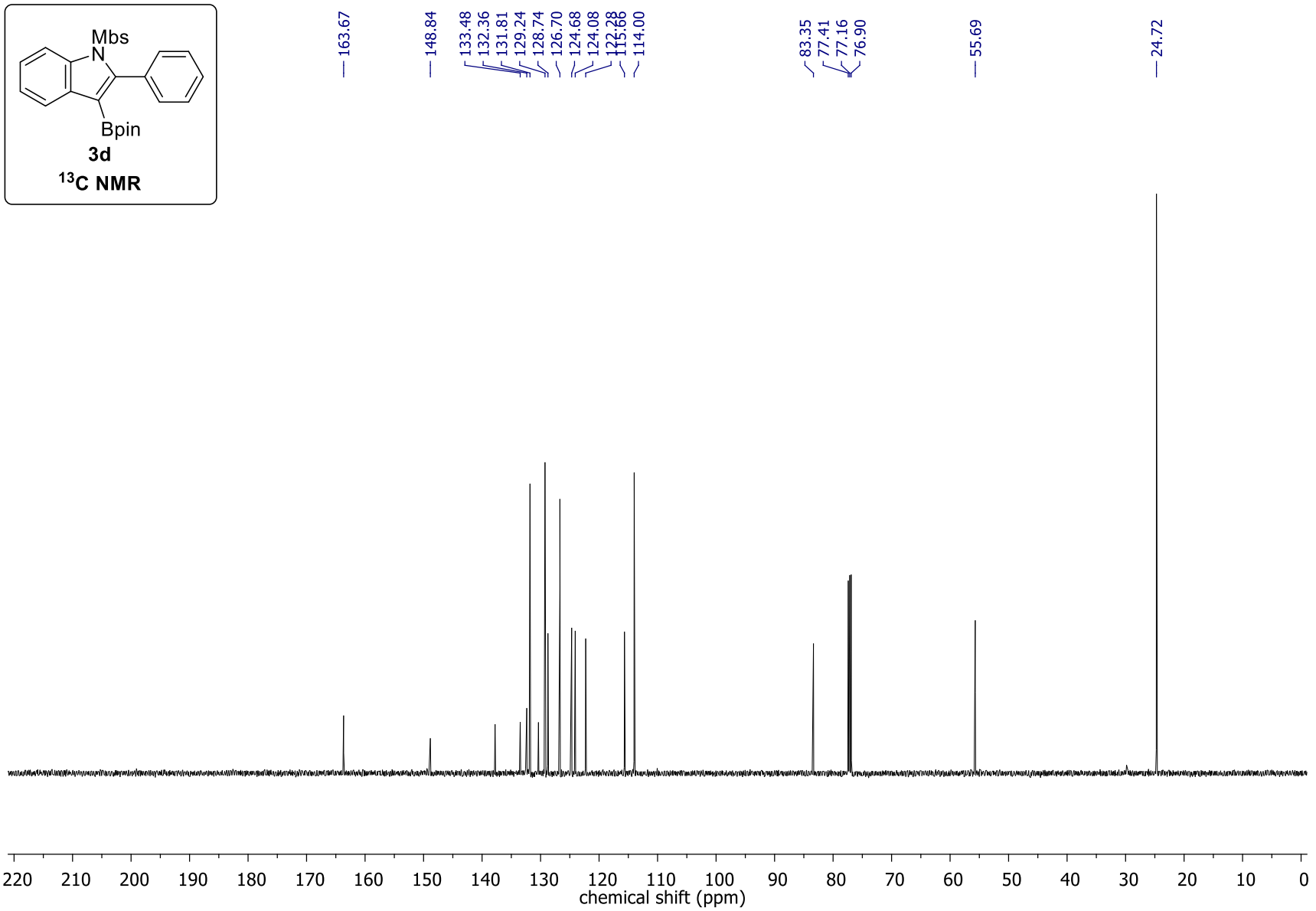


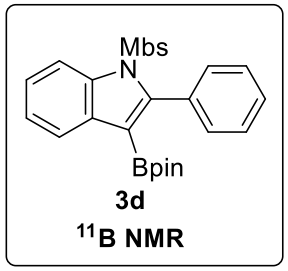

Mbs
N
Bpin

3d

^{1}H NMR

8.32
8.30
7.88
7.86
7.36
7.35
7.34
7.29
7.26
6.72
6.70
3.76
1.16
1.03
1.02
1.09
6.68
1.04
2.04
3.00
11.83
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
chemical shift (ppm)

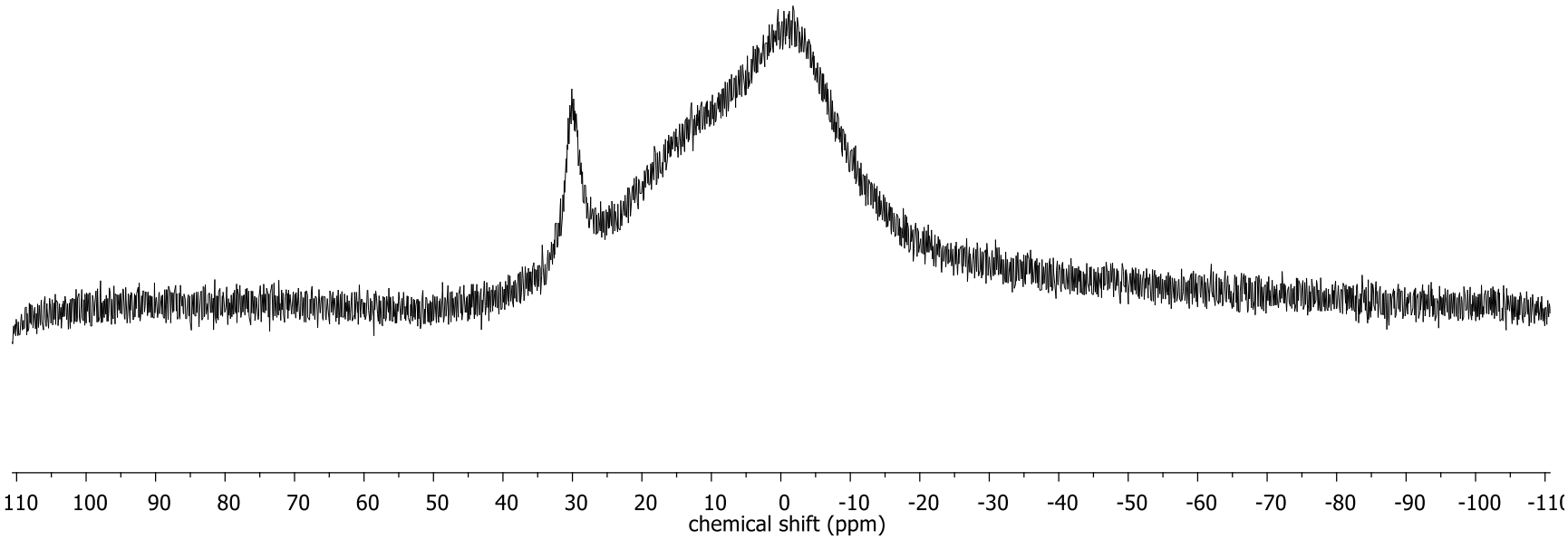

Mbs
N
Bpin
3d
13C NMR
163.67
148.84
133.48
132.36
131.81
129.24
128.74
126.70
124.68
124.08
122.28
115.66
114.00
83.35
77.41
77.16
76.90
55.69
24.72
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
chemical shift (ppm)

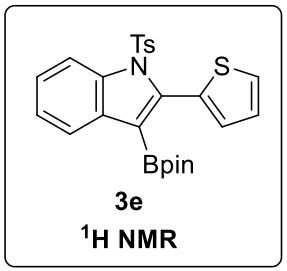


3d

^{11}B NMR

30.09

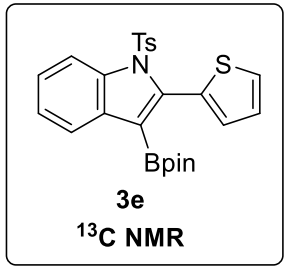



Ts
N
S
Bpin

3e

^{1}H NMR

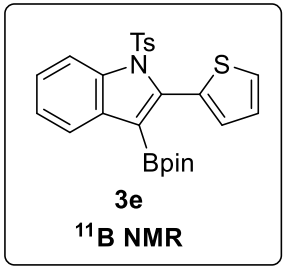
8.31
8.29
7.87
7.85
7.44
7.43
7.41
7.39
7.38
7.36
7.35
7.31
7.29
7.28
7.26
7.13
7.12
7.09
7.08
7.07
7.06
7.06
7.05
2.32
1.20
1.00
1.00
4.11
1.10
4.23
3.00
12.11
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)


Ts
N
S
Bpin

3e

^{13}C NMR

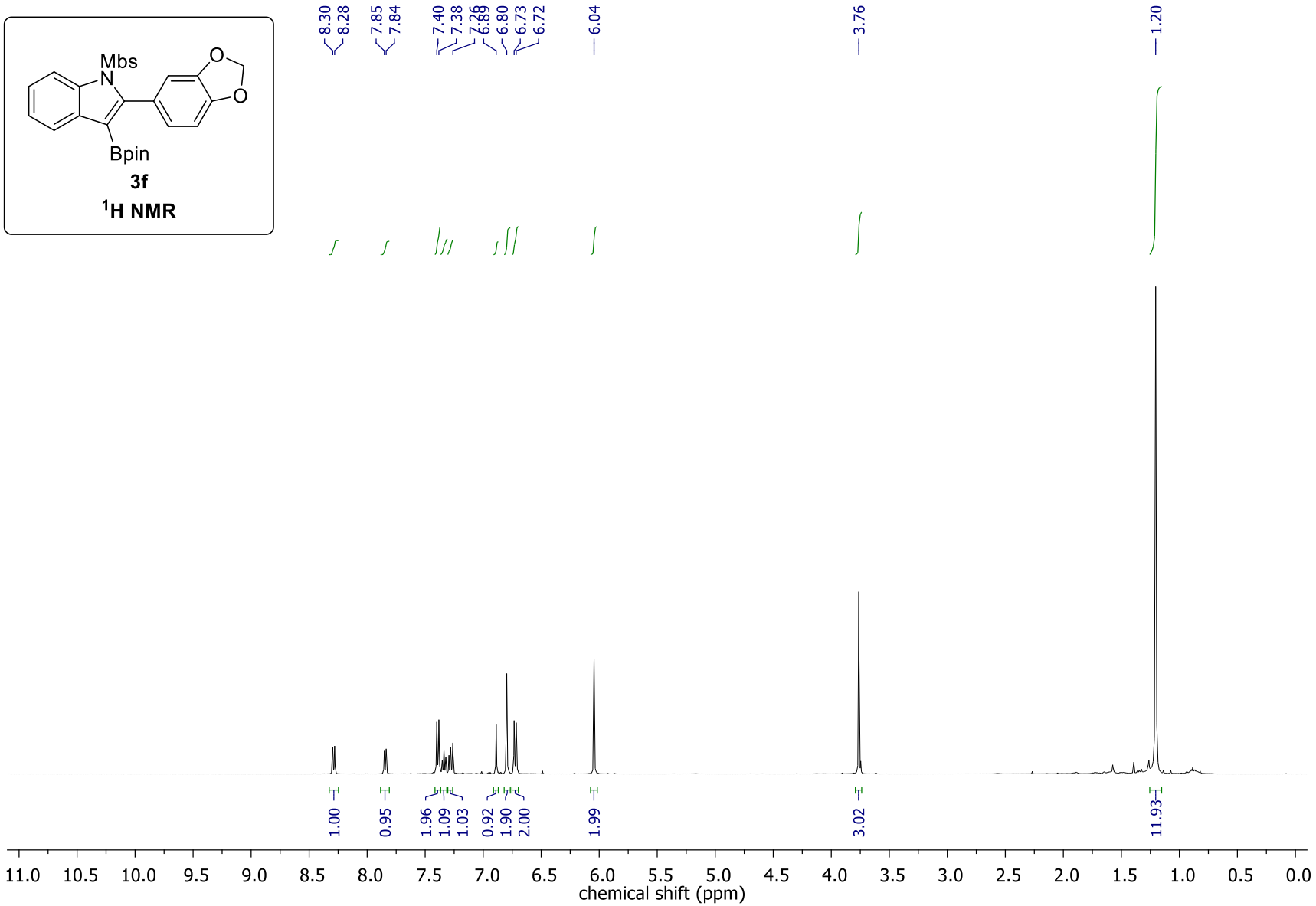
144.79
139.95
137.98
135.90
132.86
131.96
131.80
129.56
127.76
127.05
125.99
125.18
124.03
122.41
115.44
83.51
77.41
77.16
76.90
24.78
21.70
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
chemical shift (ppm)

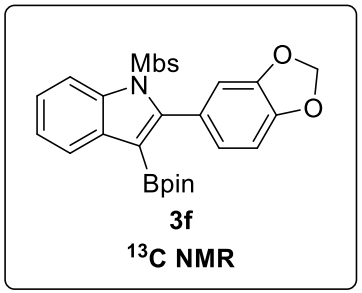

Ts
N
S
Bpin

3e

^{11}B NMR

29.90
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
chemical shift (ppm)

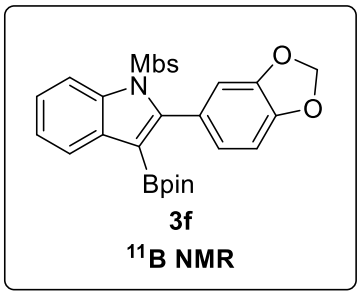

Mbs
N
O
O
Bpin
3f
1H NMR
8.30
8.28
7.85
7.84
7.40
7.38
6.80
6.73
6.72
6.04
3.76
1.20
1.00
0.95
1.96
1.09
1.03
0.92
1.90
2.00
1.99
3.02
11.93
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
chemical shift (ppm)


Mbs
N
O
O
Bpin

3f

^{13}C NMR

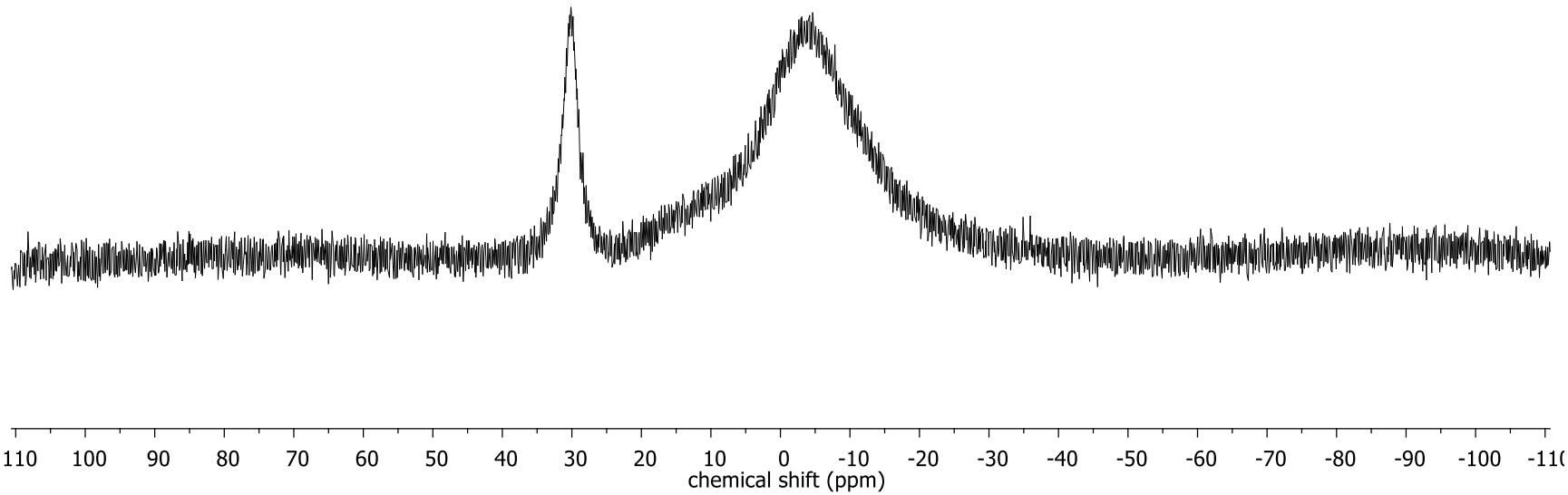
163.69
148.48
148.17
146.31
137.78
130.21
129.22
125.99
125.82
124.67
124.14
122.23
115.79
114.00
112.49
106.82
101.26
83.40
77.41
77.16
76.90
55.69
24.78
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
chemical shift (ppm)

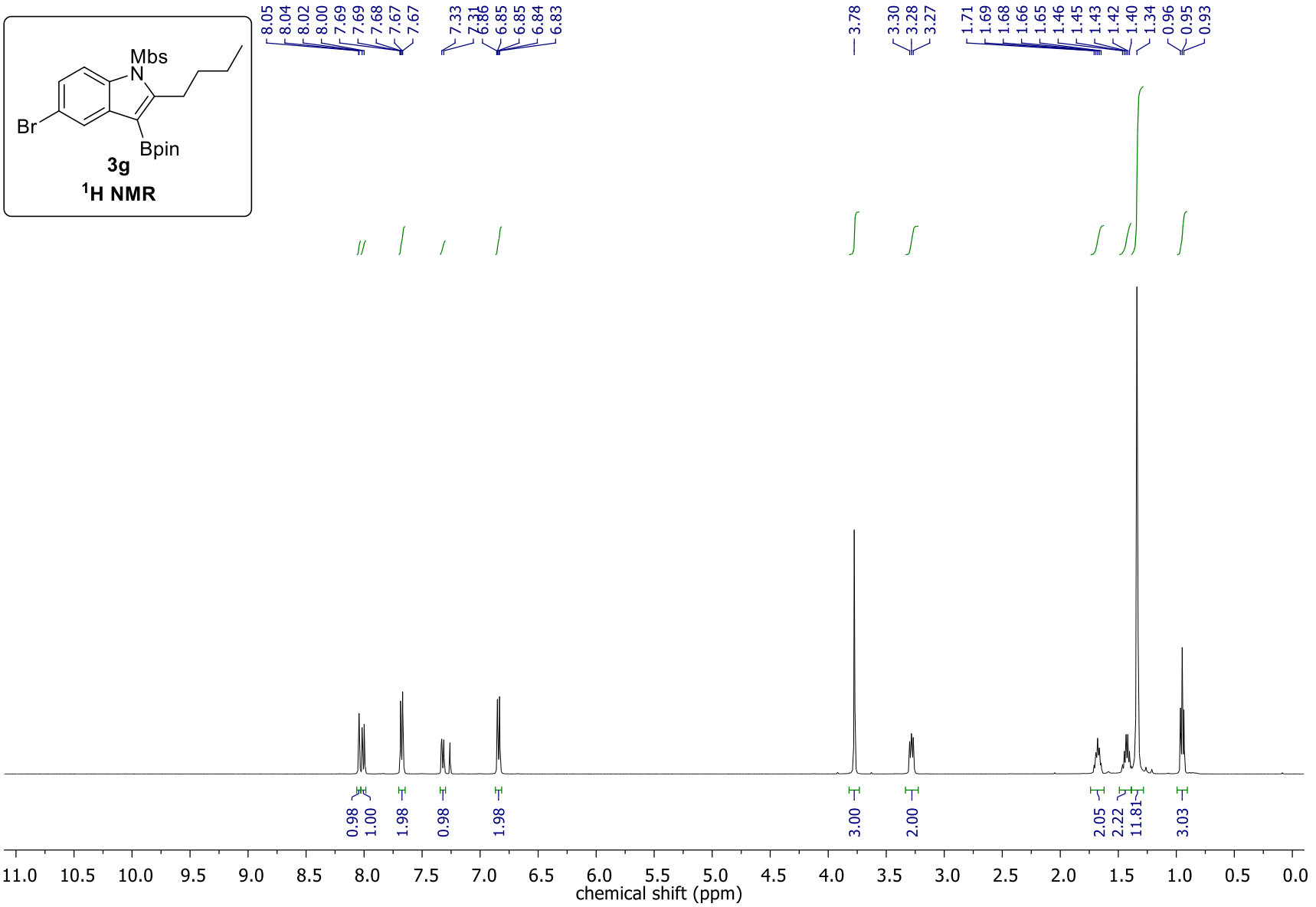


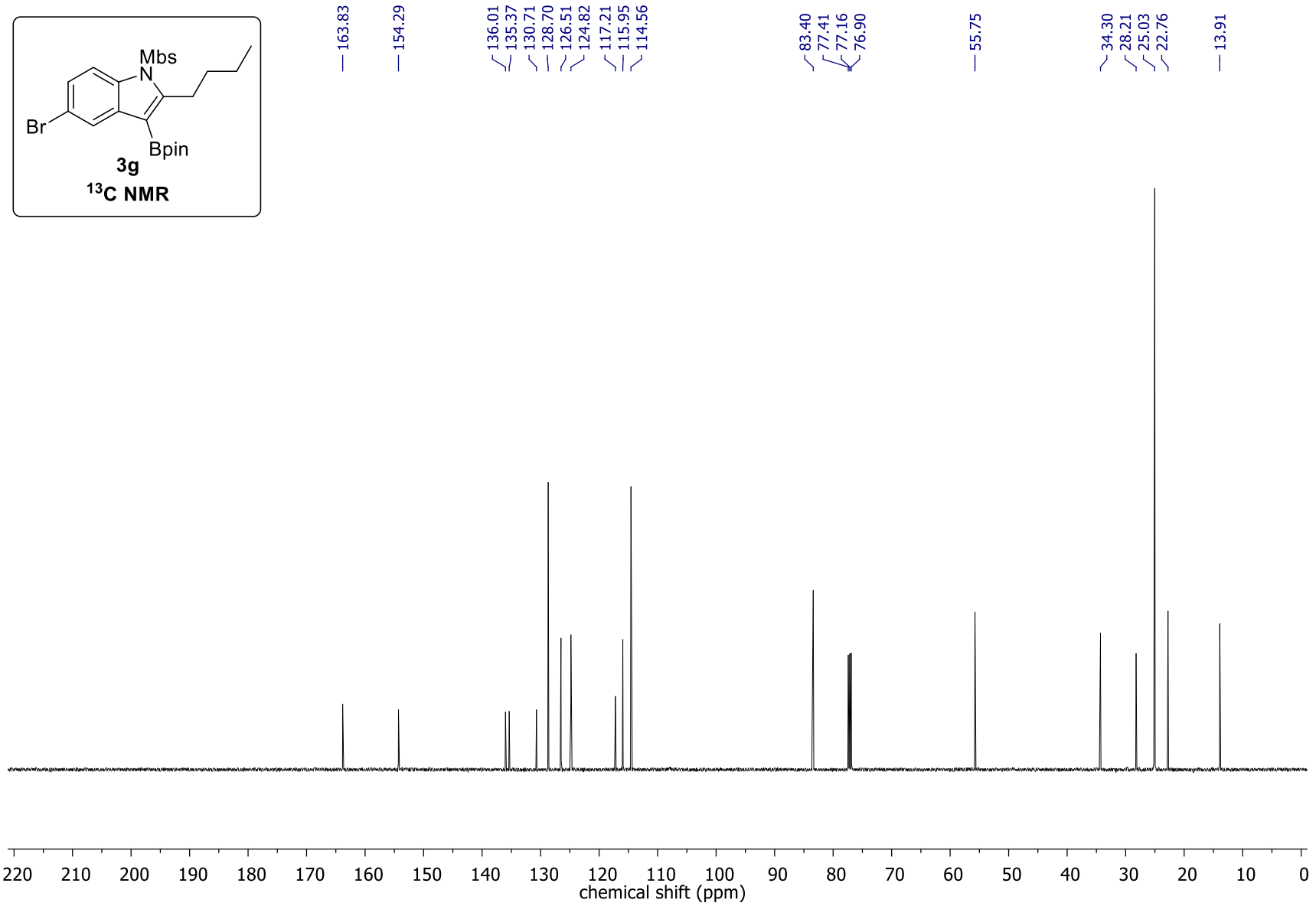
3f

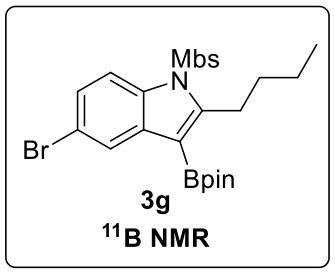
^{11}B NMR

30.14




Mbs
N
Br
Bpin
3g
^{1}H NMR
8.05
8.04
8.02
8.00
7.69
7.69
7.68
7.67
7.67
7.33
7.31
7.30
6.85
6.85
6.84
6.83
3.78
3.30
3.28
3.27
1.71
1.69
1.68
1.66
1.65
1.46
1.45
1.43
1.42
1.40
1.34
0.96
0.95
0.93
0.98
1.00
1.98
0.98
1.98
3.00
2.00
2.05
2.22
11.81
3.03
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)

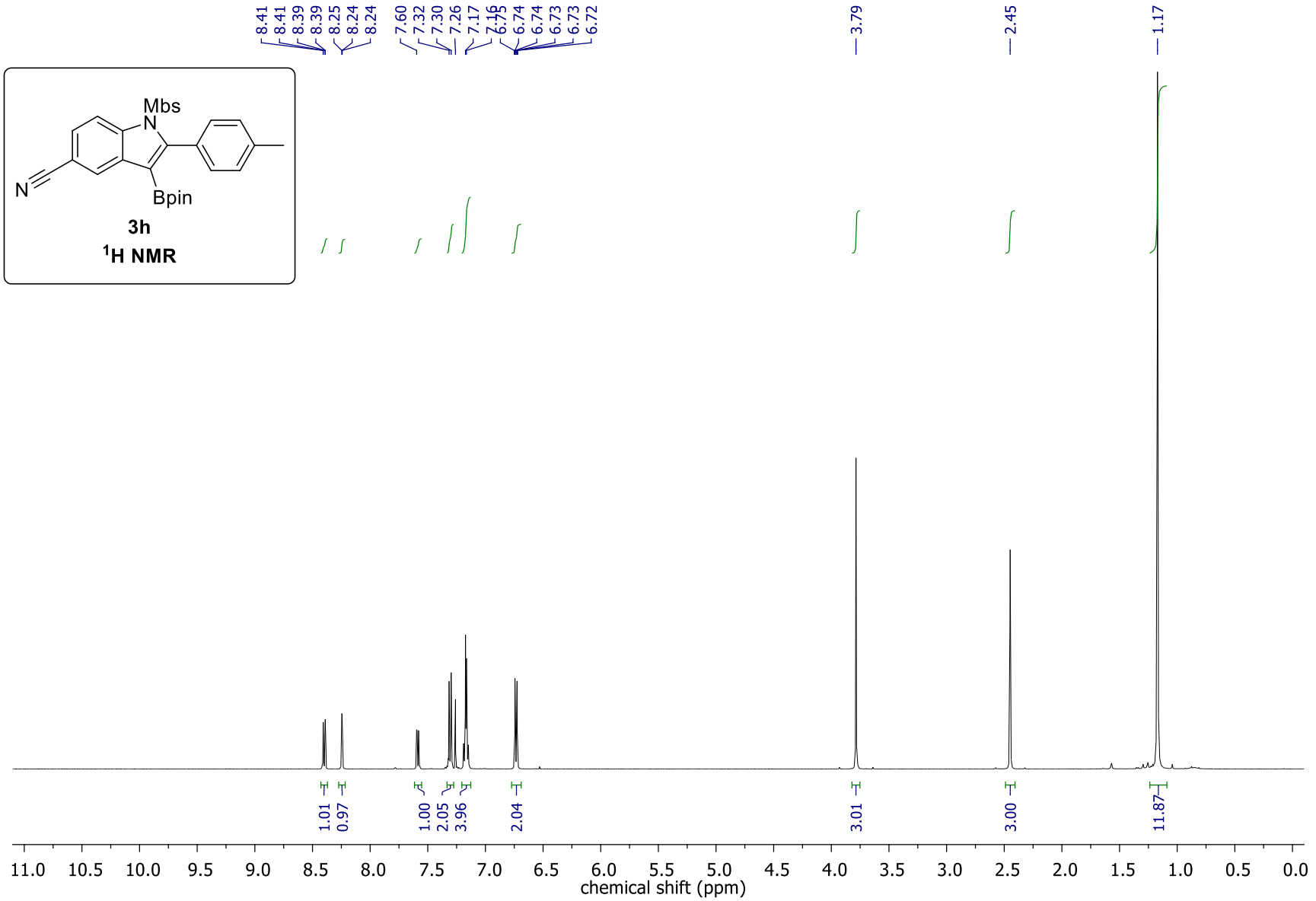

Mbs
N
Br
Bpin
3g
13C NMR
163.83
154.29
136.01
135.37
130.71
128.70
126.51
124.82
117.21
115.95
114.56
83.40
77.41
77.16
76.90
55.75
34.30
28.21
25.03
22.76
13.91
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
chemical shift (ppm)

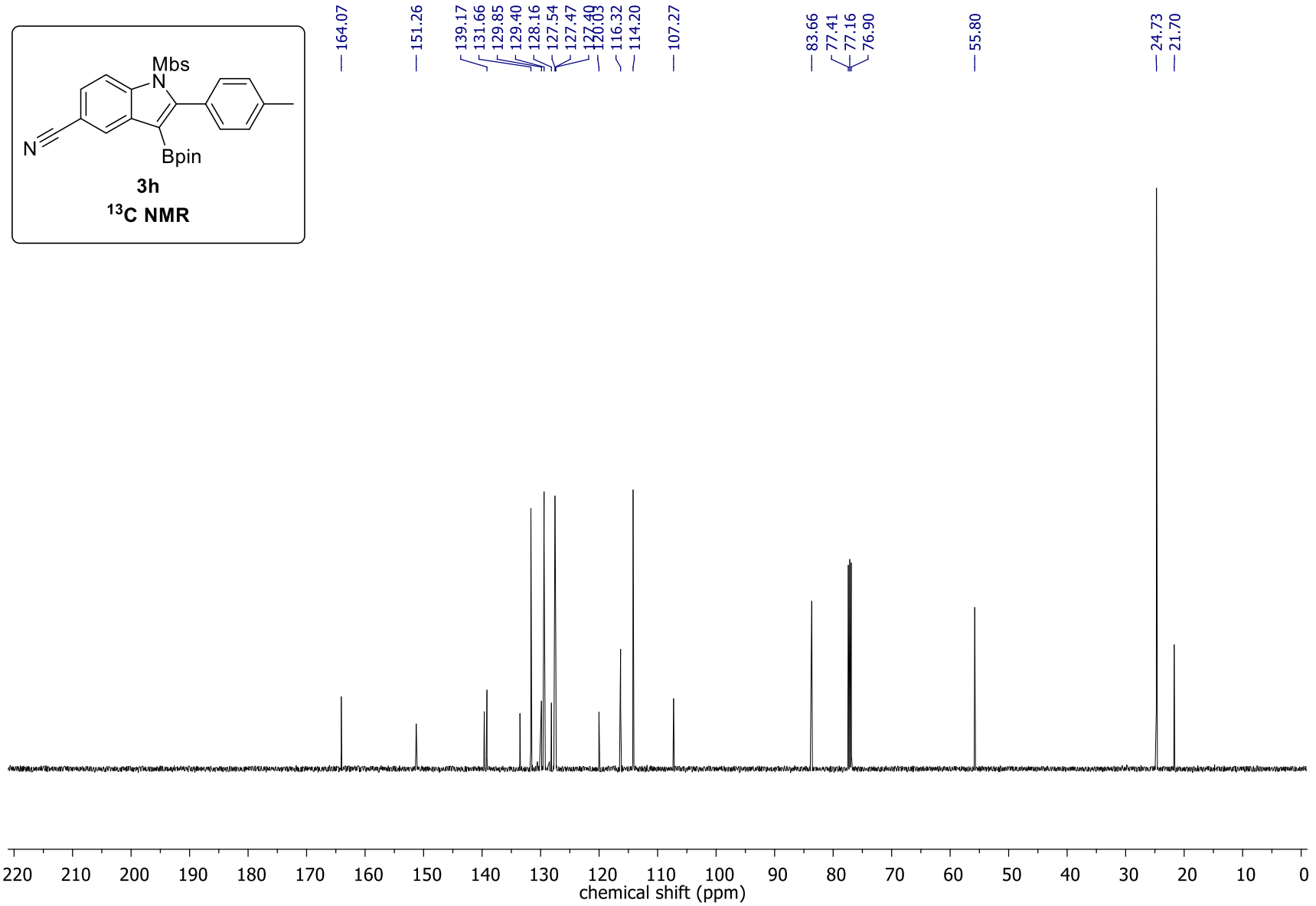

Mbs
N
Br
Bpin

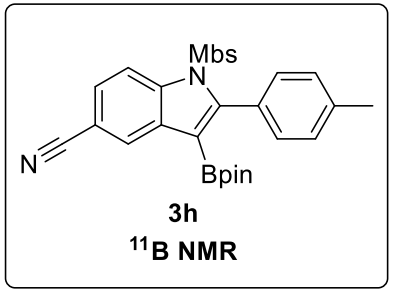
3g

^{11}B NMR

30.08
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
chemical shift (ppm)


Mbs
N
N
Bpin
3h
1H NMR
8.41
8.41
8.39
8.39
8.25
8.24
8.24
7.60
7.32
7.30
7.26
7.17
7.16
6.75
6.74
6.74
6.73
6.73
6.72
3.79
2.45
1.17
1.01
0.97
1.00
2.05
3.96
2.04
3.01
3.00
11.87
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)

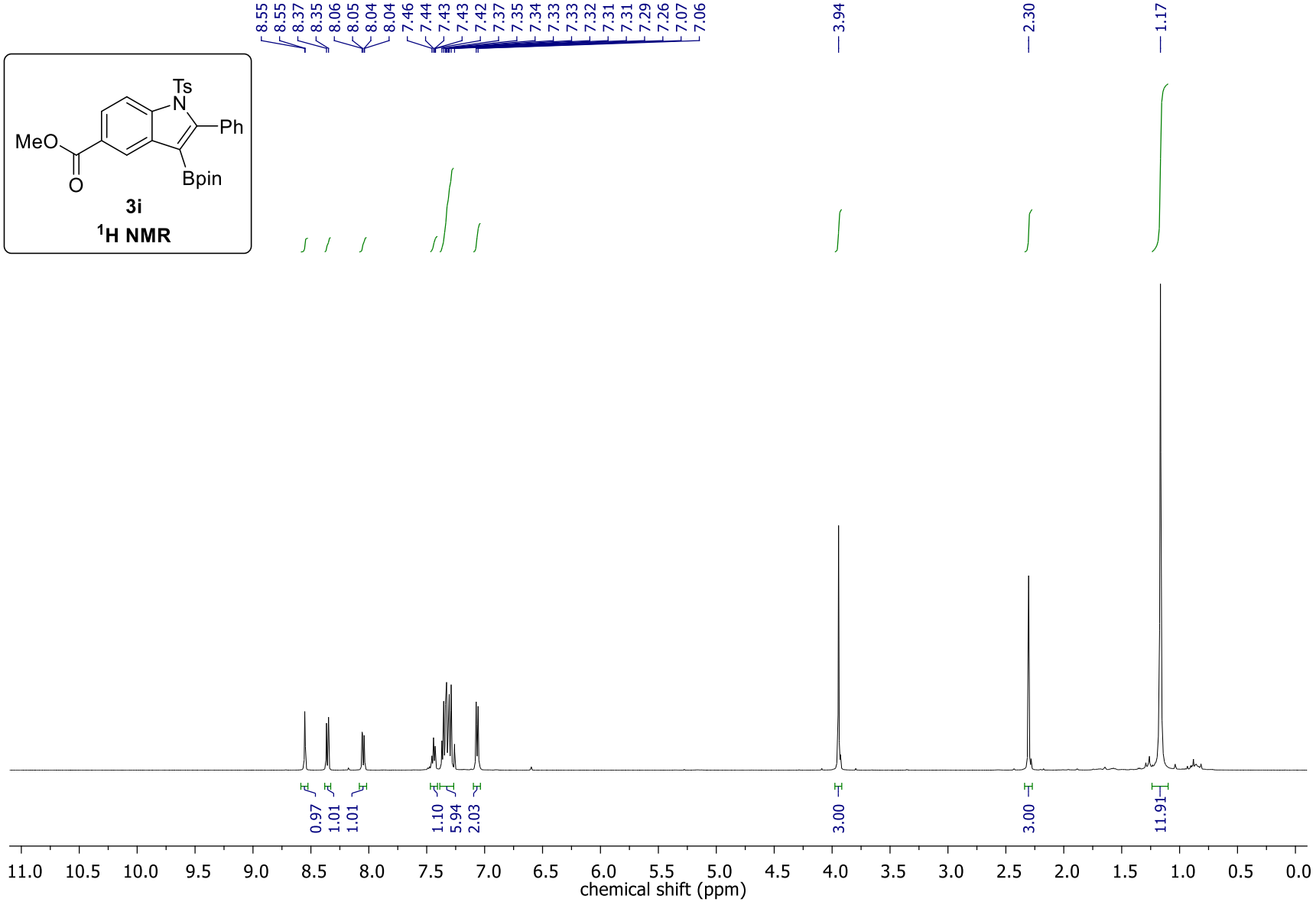

Mbs
N
N
Bpin
3h
13C NMR
164.07
151.26
139.17
131.66
129.85
129.40
128.16
127.54
127.47
127.49
120.03
116.32
114.20
107.27
83.66
77.41
77.16
76.90
55.80
24.73
21.70
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
chemical shift (ppm)

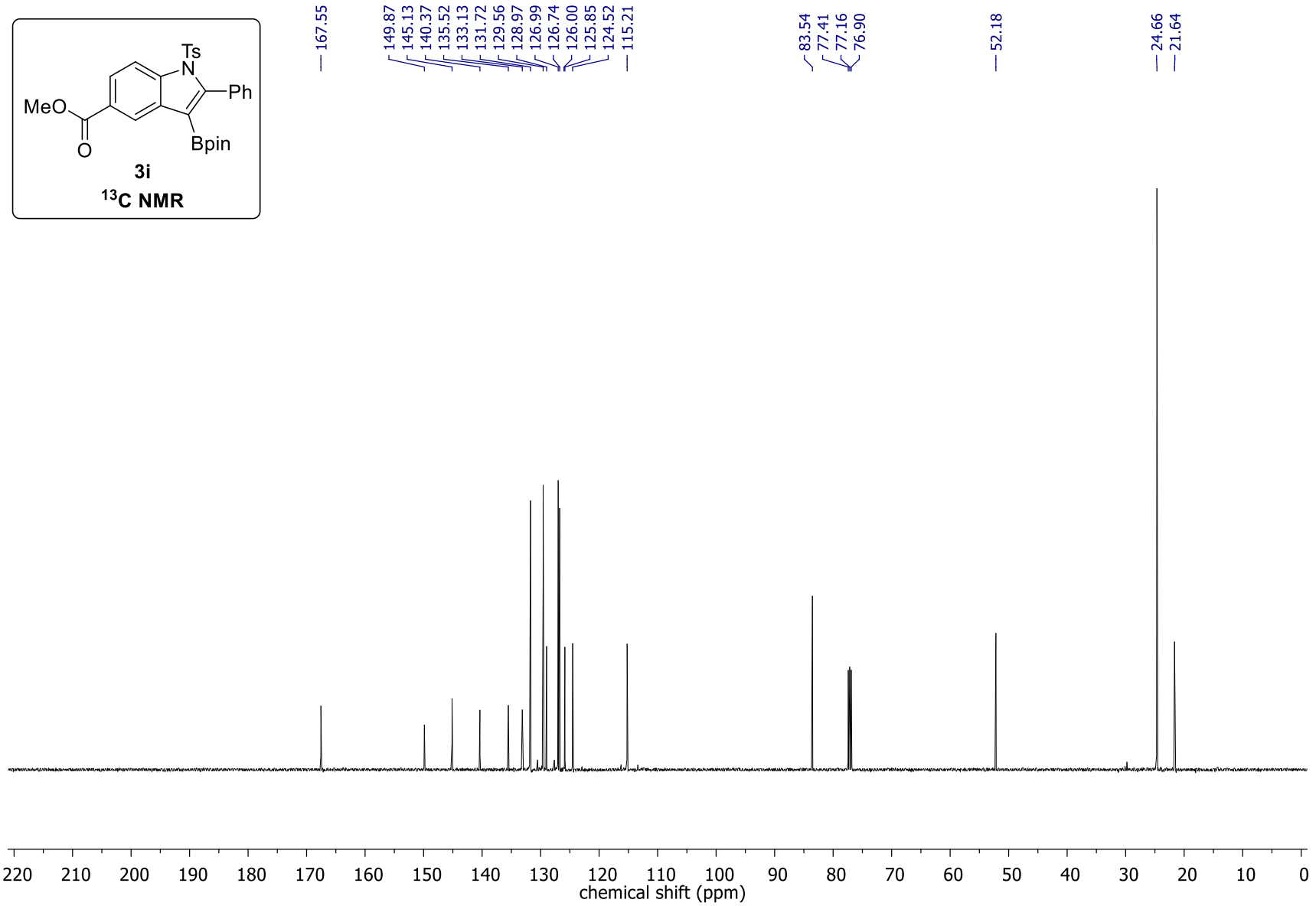

Mbs
N
N
Bpin

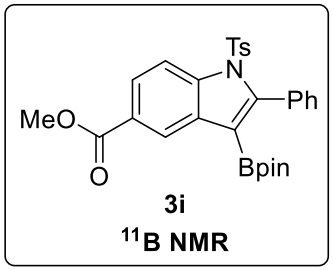
3h

^{11}B NMR

29.53
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
chemical shift (ppm)


Ts
N
Ph
MeO
O
Bpin
3i
1H NMR
8.55
8.55
8.37
8.35
8.06
8.05
8.04
8.04
7.46
7.44
7.43
7.43
7.42
7.37
7.35
7.34
7.33
7.33
7.32
7.31
7.29
7.26
7.07
7.06
3.94
2.30
1.17
0.97
1.01
1.01
1.10
5.94
2.03
3.00
3.00
11.91
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)

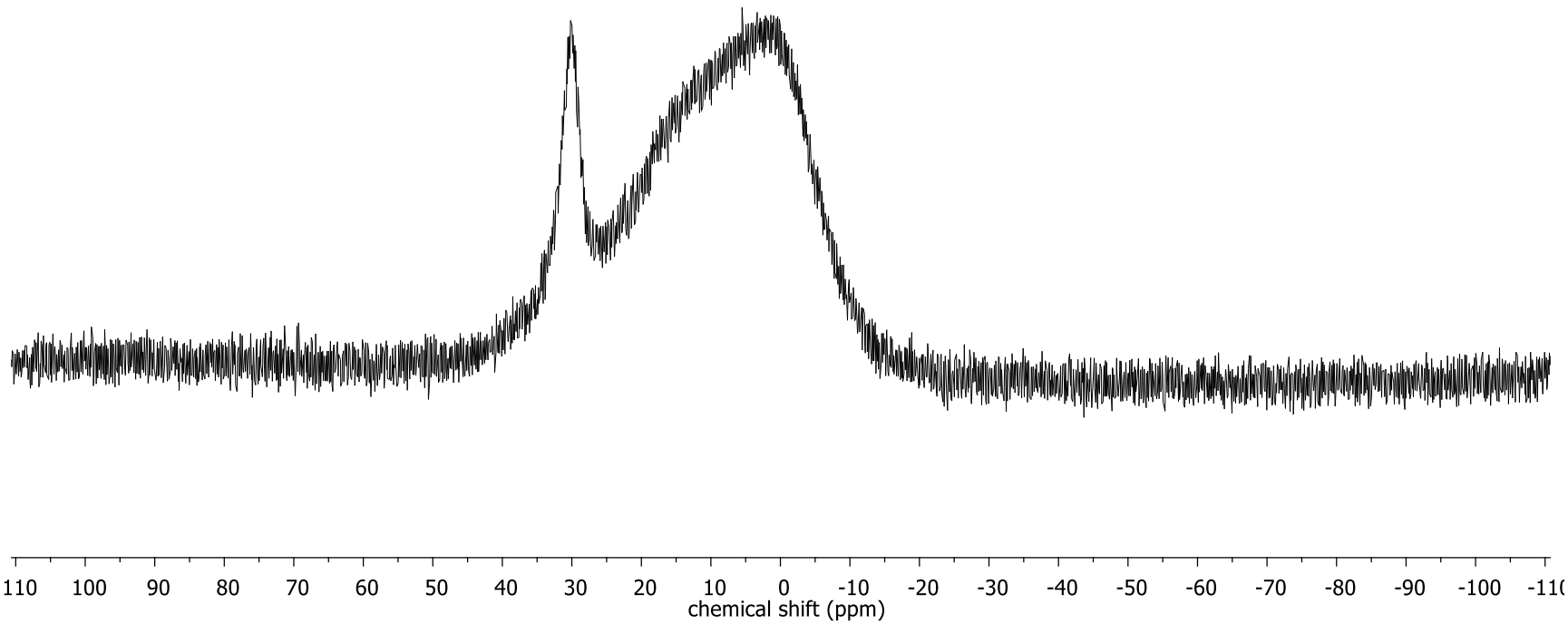

Ts
N
Ph
MeO
O
Bpin
3i
13C NMR
167.55
149.87
145.13
140.37
135.52
133.13
131.72
129.56
128.97
126.99
126.74
126.00
125.85
124.52
115.21
83.54
77.41
77.16
76.90
52.18
24.66
21.64
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
chemical shift (ppm)

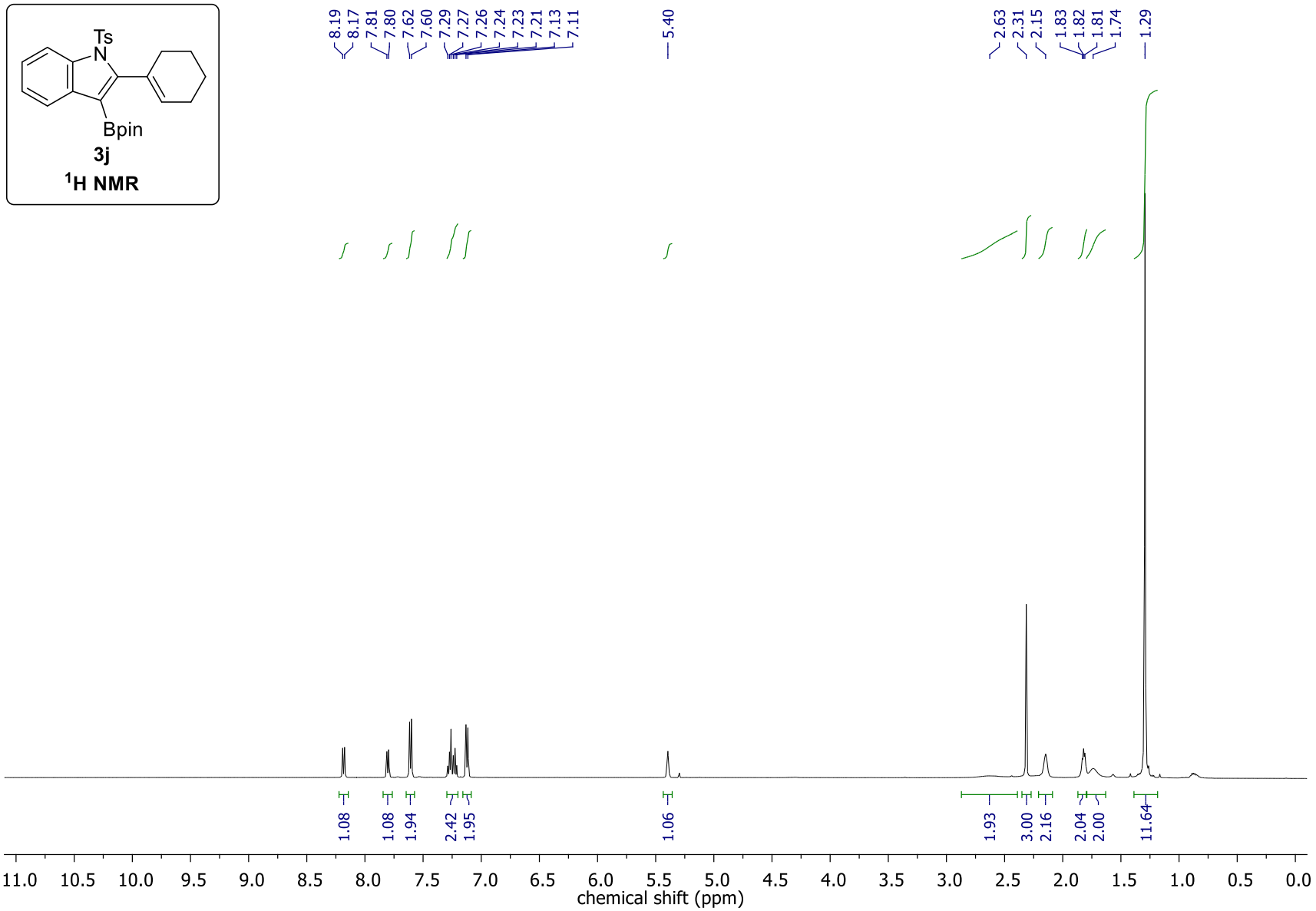


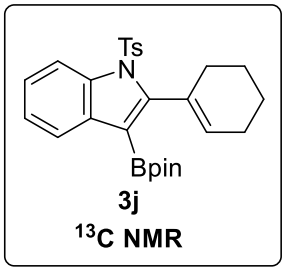
3i

^{11}B NMR

30.19



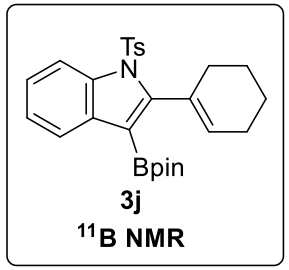

Ts
N
Bpin
3j
1H NMR
8.19
8.17
7.81
7.80
7.62
7.60
7.29
7.27
7.26
7.24
7.23
7.21
7.13
7.11
5.40
2.63
2.31
2.15
1.83
1.82
1.81
1.74
1.29
1.08
1.08
1.94
2.42
1.95
1.06
1.93
3.00
2.16
2.04
2.00
11.64
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)


Ts
N
Bpin

3j

^{13}C NMR

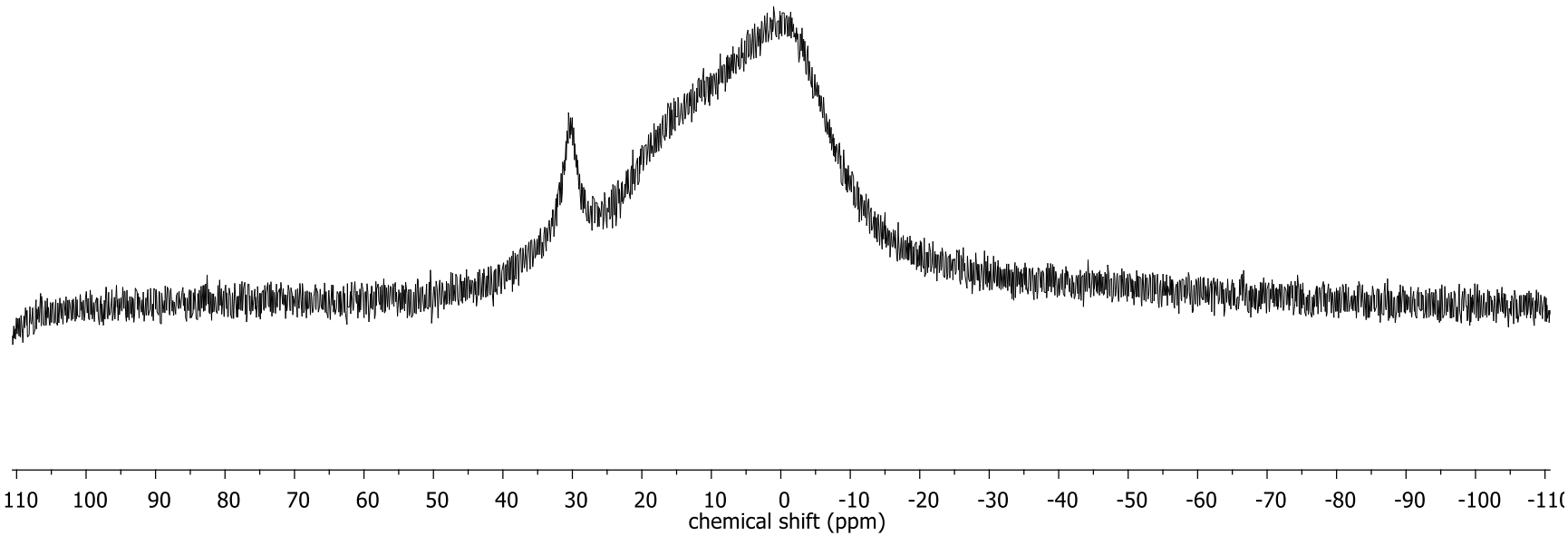
152.07
144.64
133.51
132.20
130.48
129.47
126.99
124.21
123.72
83.15
77.41
77.16
76.90
31.03
25.86
25.03
22.91
22.01
21.67
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
chemical shift (ppm)

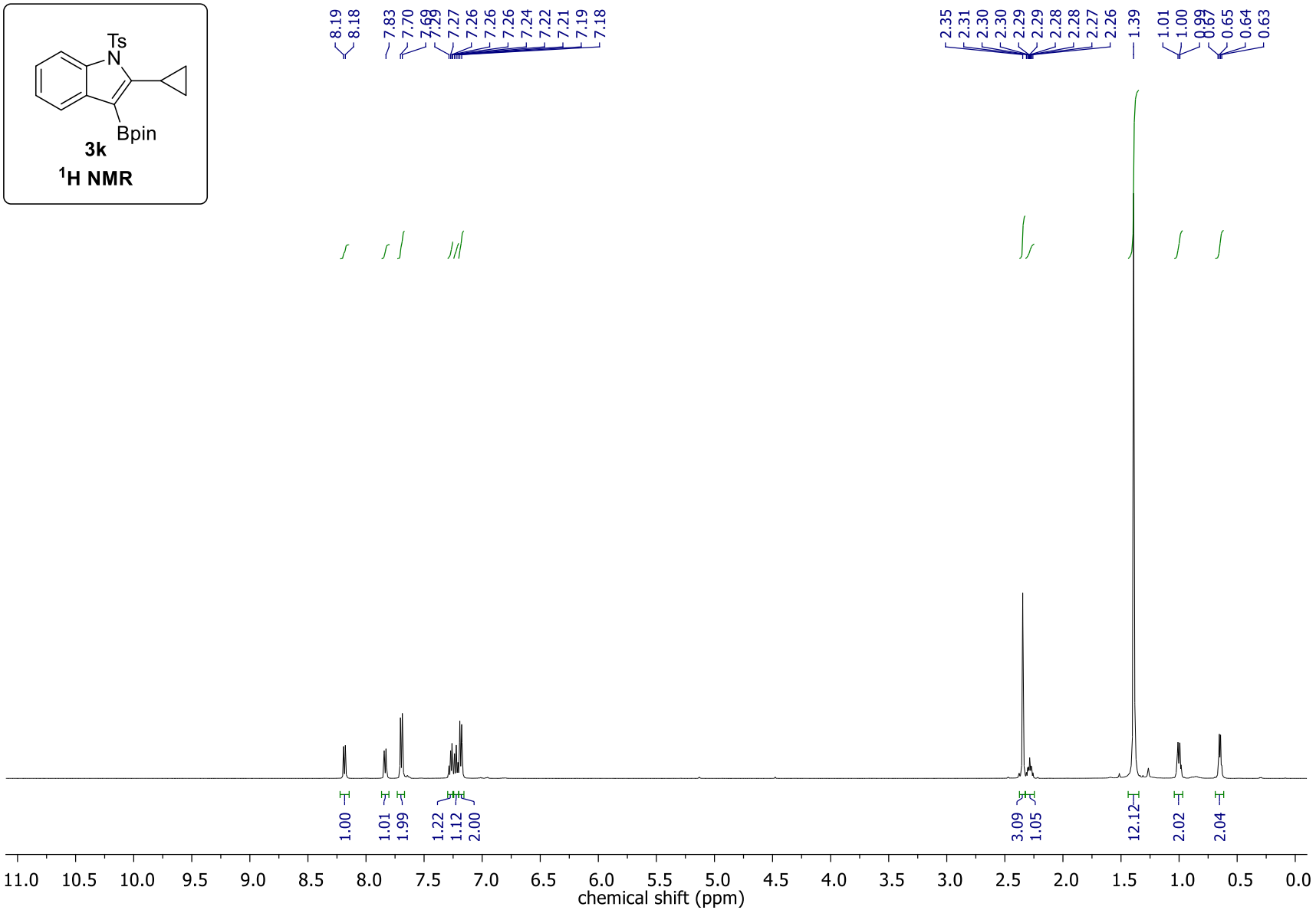


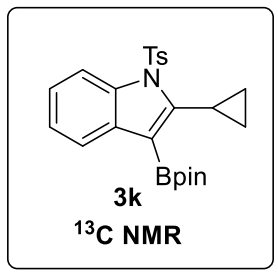
3j

^{11}B NMR

30.56



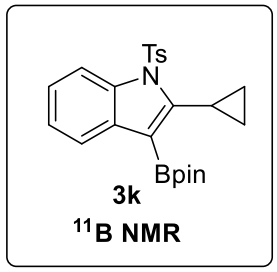

Ts
N
Bpin
3k
1H NMR
8.19
8.18
7.83
7.70
7.69
7.29
7.27
7.26
7.26
7.26
7.24
7.22
7.21
7.19
7.18
2.35
2.31
2.30
2.30
2.29
2.29
2.28
2.28
2.27
2.26
1.39
1.01
1.00
0.99
0.67
0.65
0.64
0.63
1.00
1.01
1.99
1.22
1.12
2.00
3.09
1.05
12.12
2.02
2.04
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)


Ts
N
Bpin

3k

^{13}C NMR

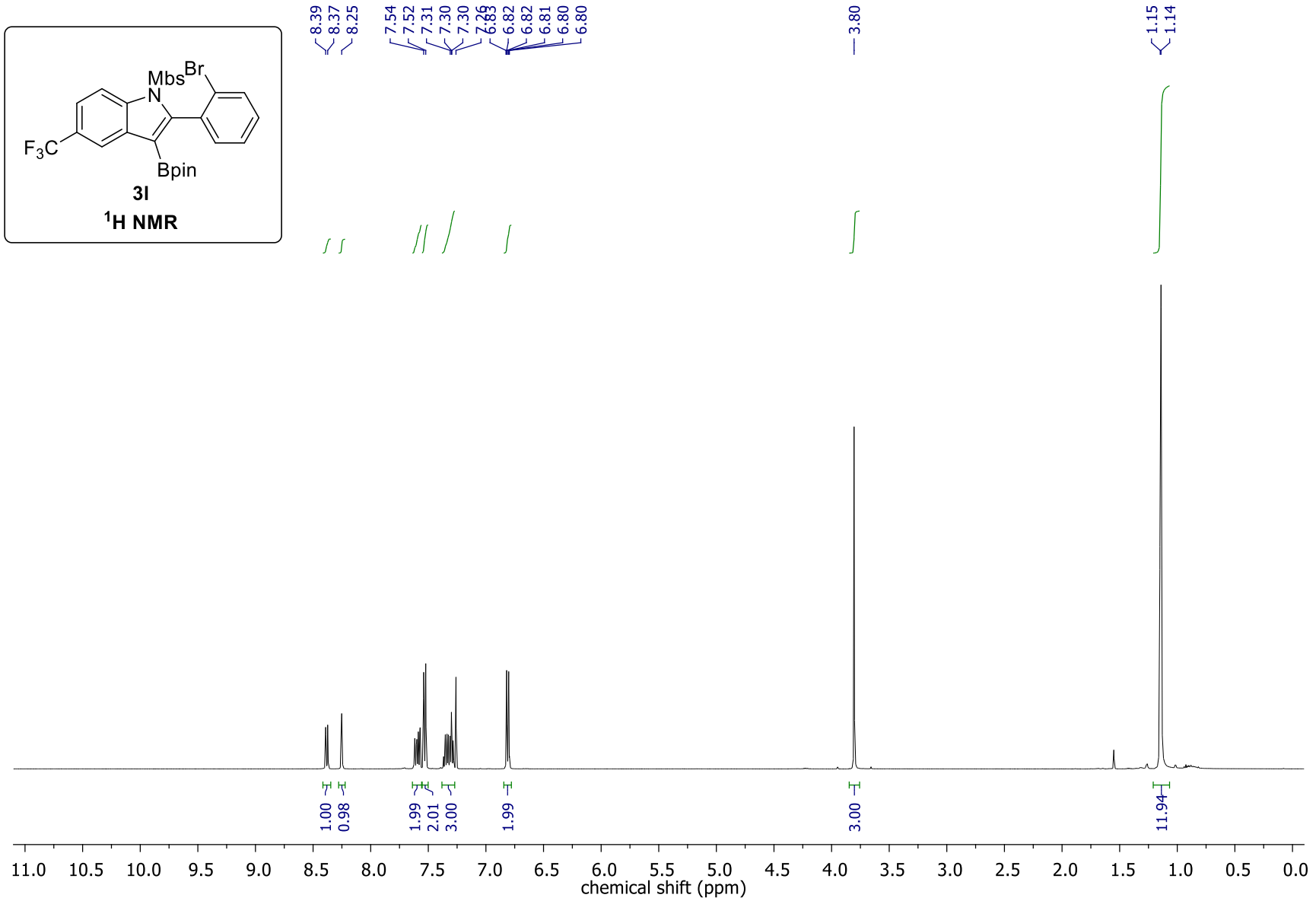
151.03
144.65
137.63
137.11
132.89
129.76
126.68
124.25
123.42
121.98
114.28
83.75
77.41
77.16
76.90
25.08
21.67
10.59
9.41
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
chemical shift (ppm)

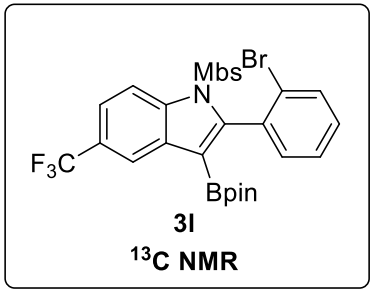

Ts
N
Bpin

3k

^{11}B NMR

30.83
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
chemical shift (ppm)

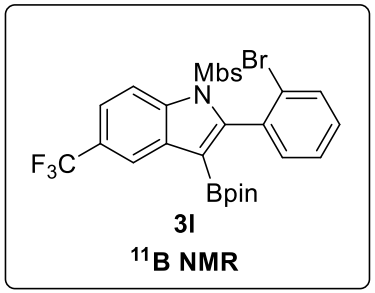

Mbs
Br
N
F3C
Bpin
3l
1H NMR
8.39
8.37
8.25
7.54
7.52
7.31
7.30
7.30
7.26
6.83
6.82
6.82
6.81
6.80
6.80
3.80
1.15
1.14
1.00
0.98
1.99
2.01
3.00
1.99
3.00
11.94
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)


Mbs
Br
N
F3C
Bpin

3l

^{13}C NMR

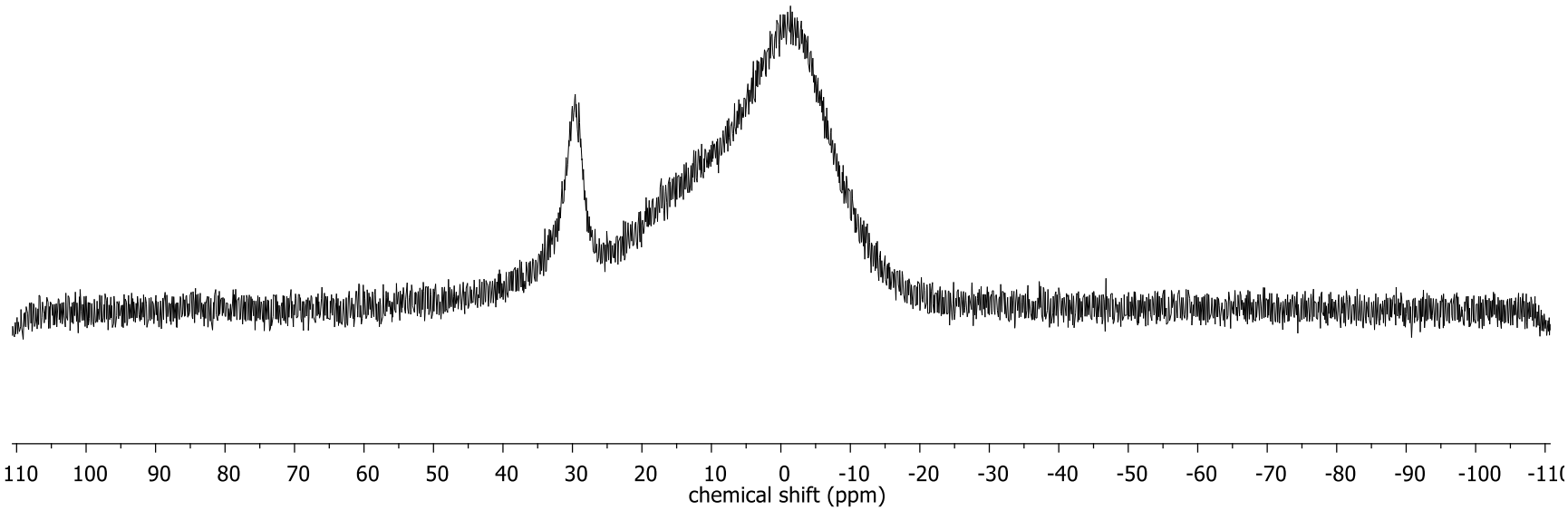
164.20
147.94
138.46
133.57
133.40
132.44
131.83
130.46
130.28
129.78
126.13
121.54
121.51
121.48
121.46
120.42
120.39
120.35
120.32
115.06
114.38
83.43
77.41
77.16
76.90
55.85
24.92
24.63
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
chemical shift (ppm)

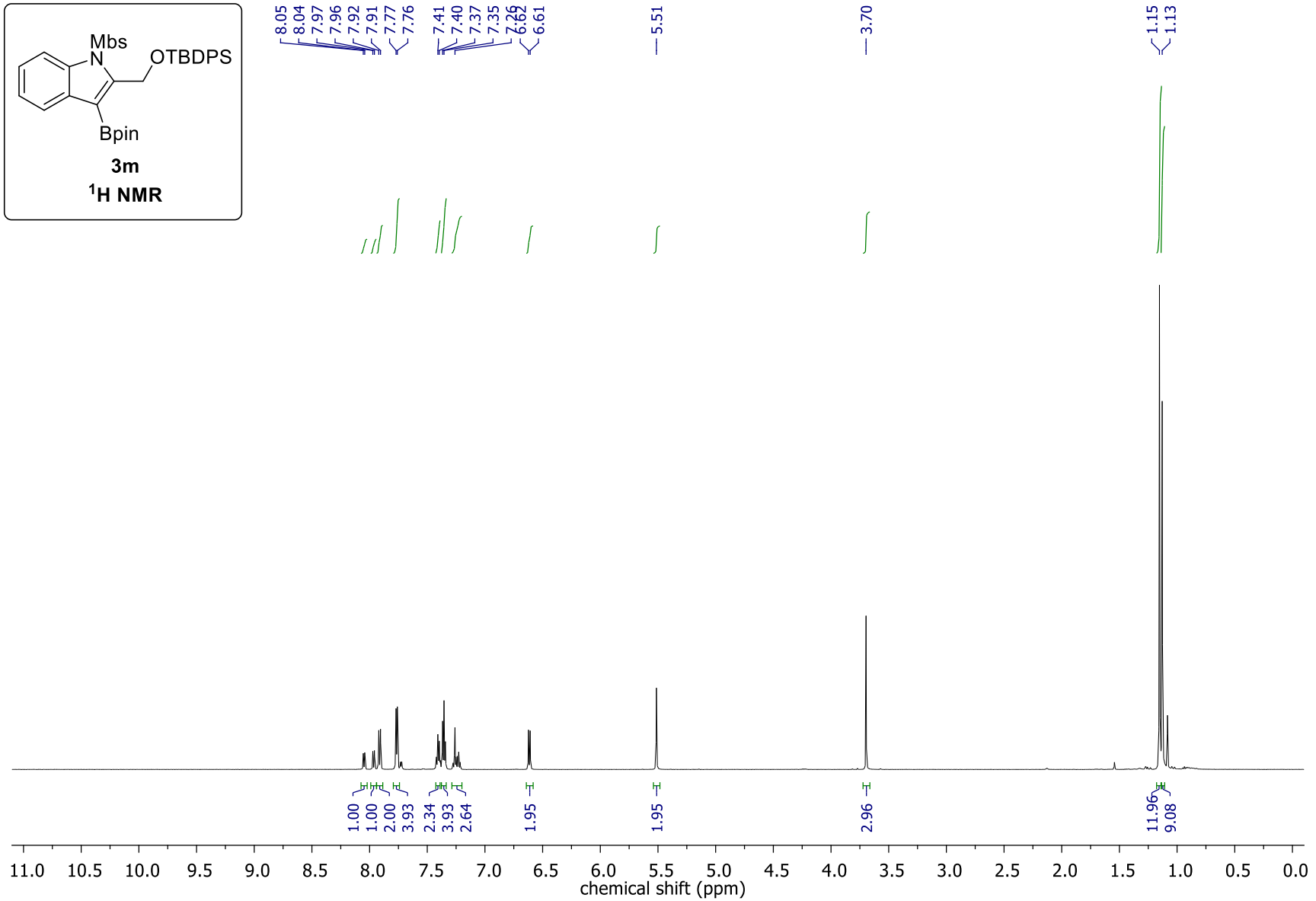


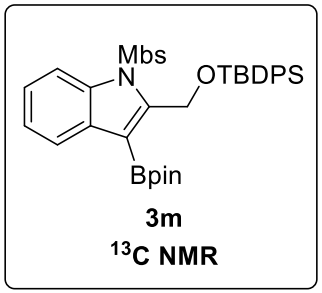
3l

^{11}B NMR

29.60



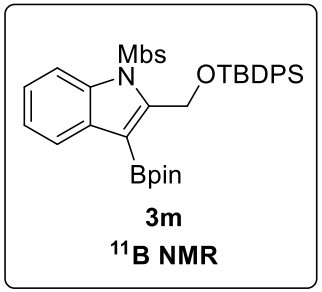

Mbs
N
OTBDPS
Bpin
3m
1H NMR
8.05
8.04
7.97
7.96
7.92
7.91
7.77
7.76
7.41
7.40
7.37
7.35
7.26
6.62
6.61
5.51
3.70
1.15
1.13
1.00
1.00
2.00
3.93
2.34
3.93
2.64
1.95
1.95
2.96
11.96
9.08
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)


Mbs
N
OTBDPS
Bpin

3m

^{13}C NMR

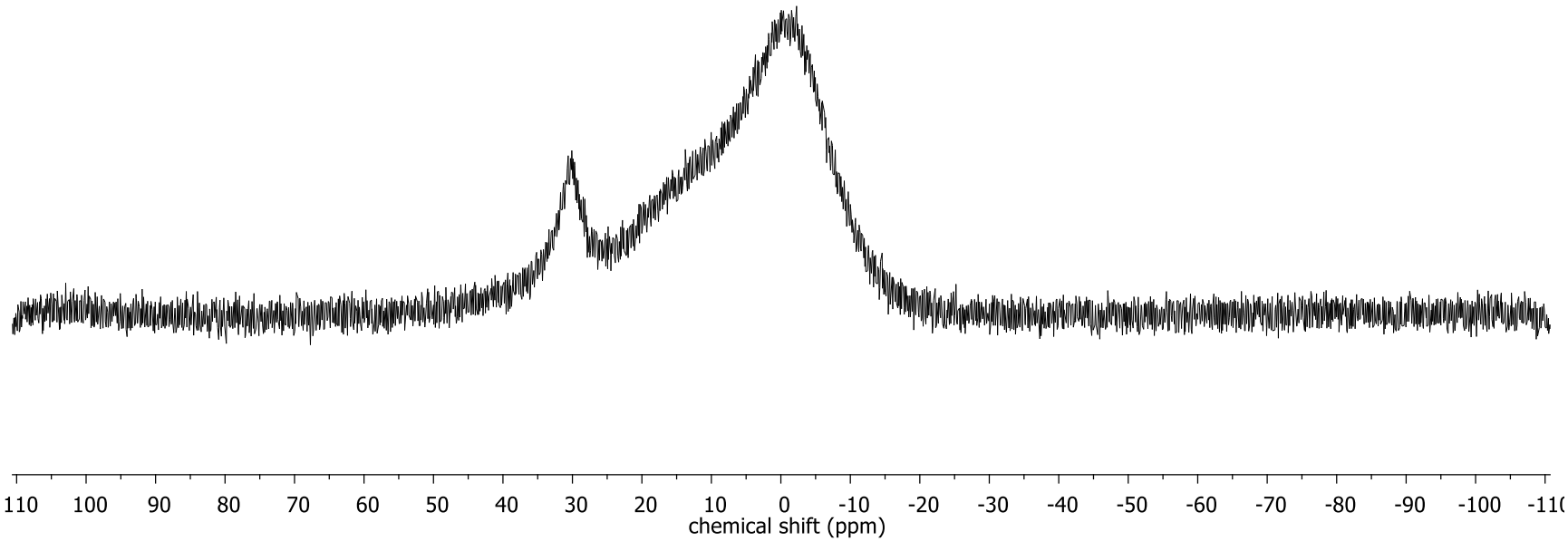
163.48
148.21
136.14
134.36
131.02
129.59
129.52
127.58
124.69
123.34
114.13
83.39
77.37
77.16
76.95
58.52
55.62
27.34
24.89
19.95
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
chemical shift (ppm)

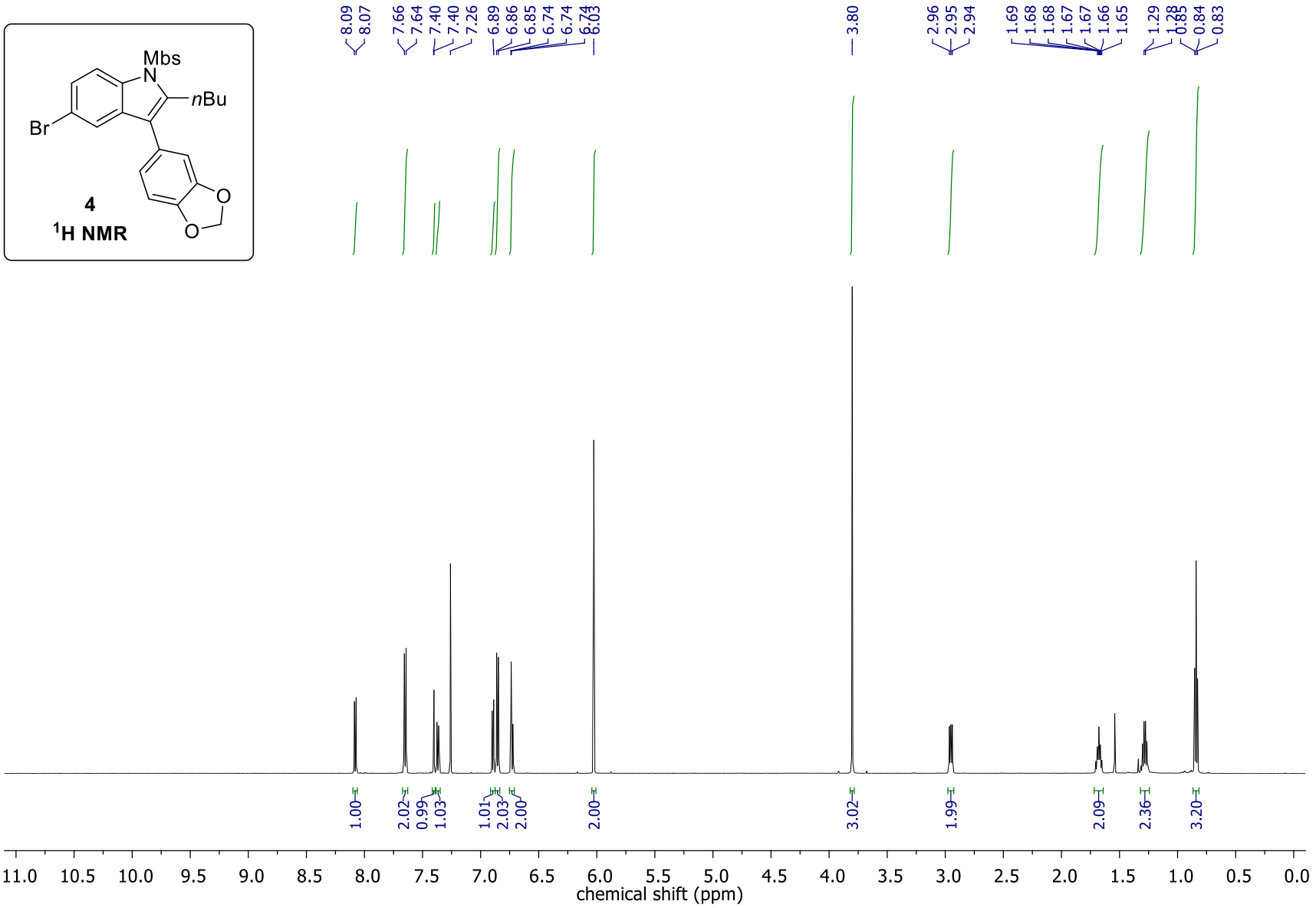


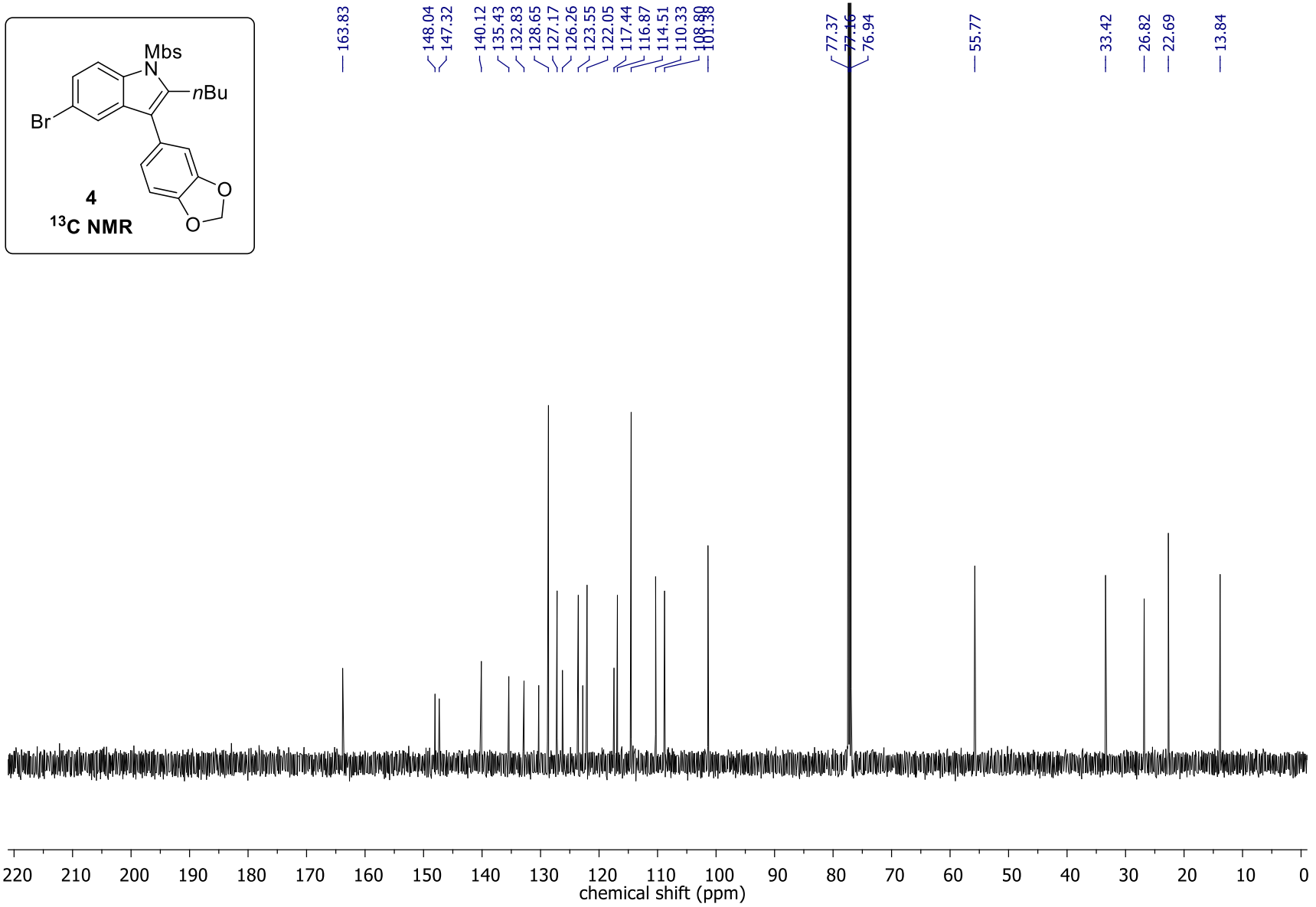
3m

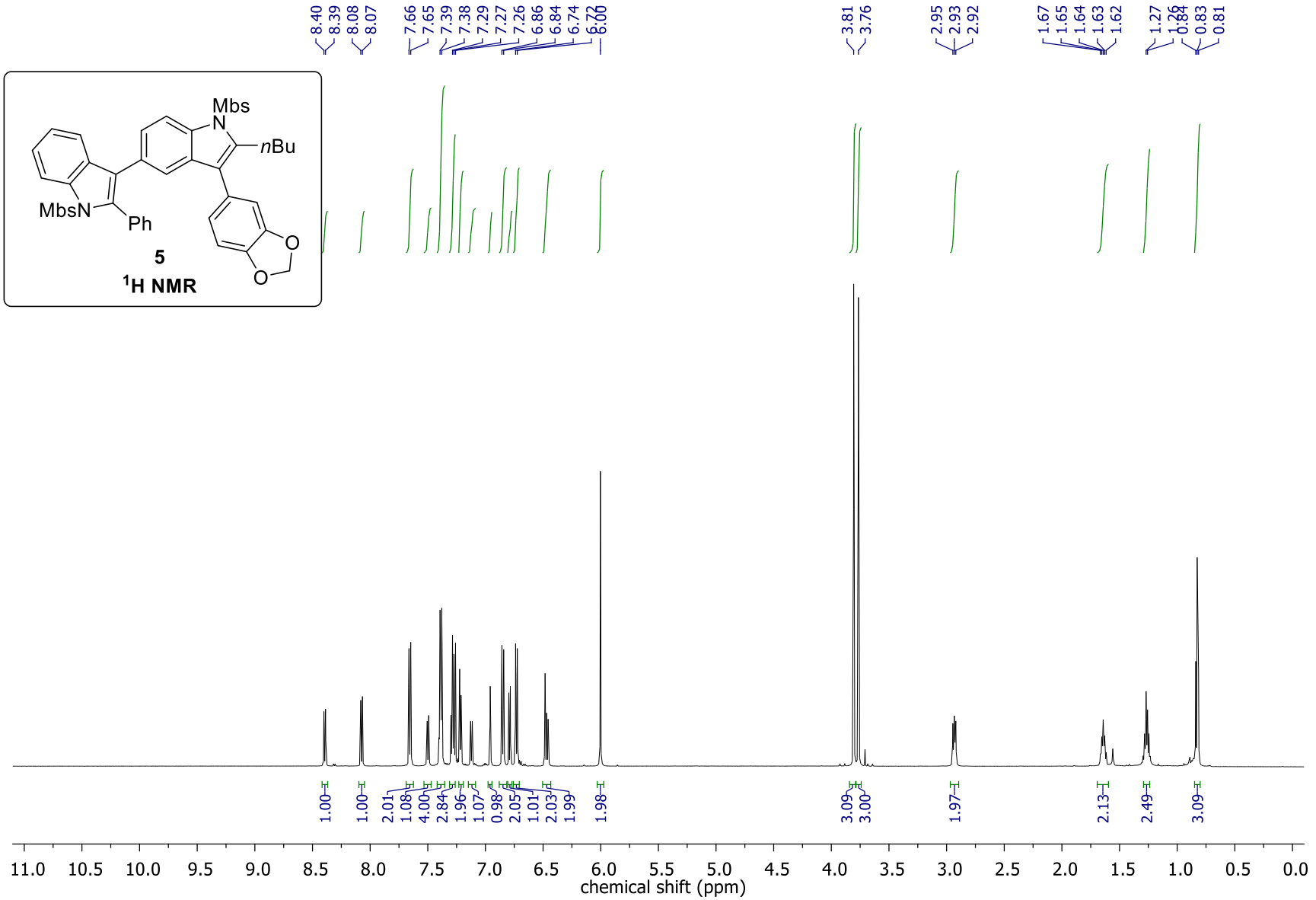
^{11}B NMR

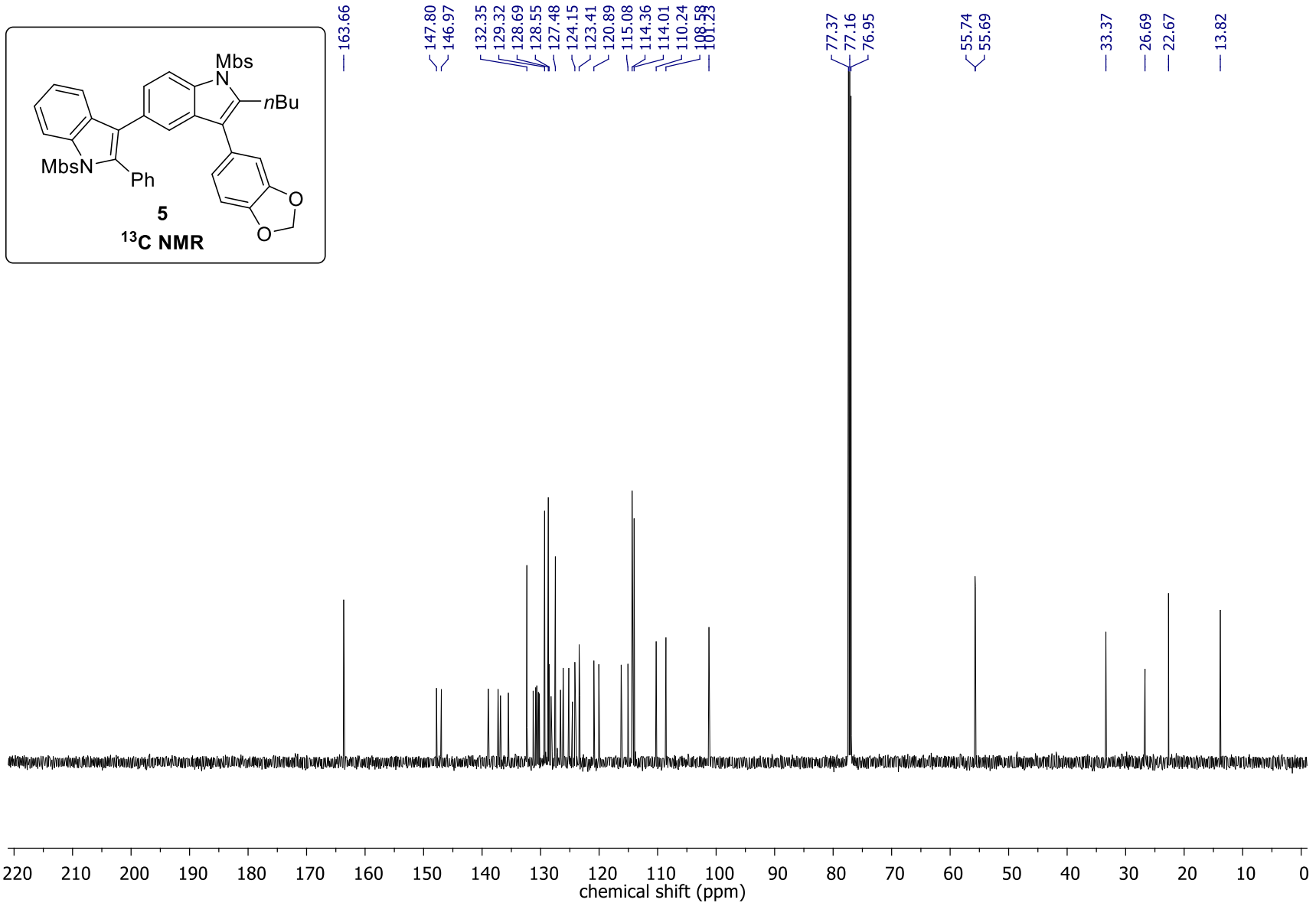
30.09

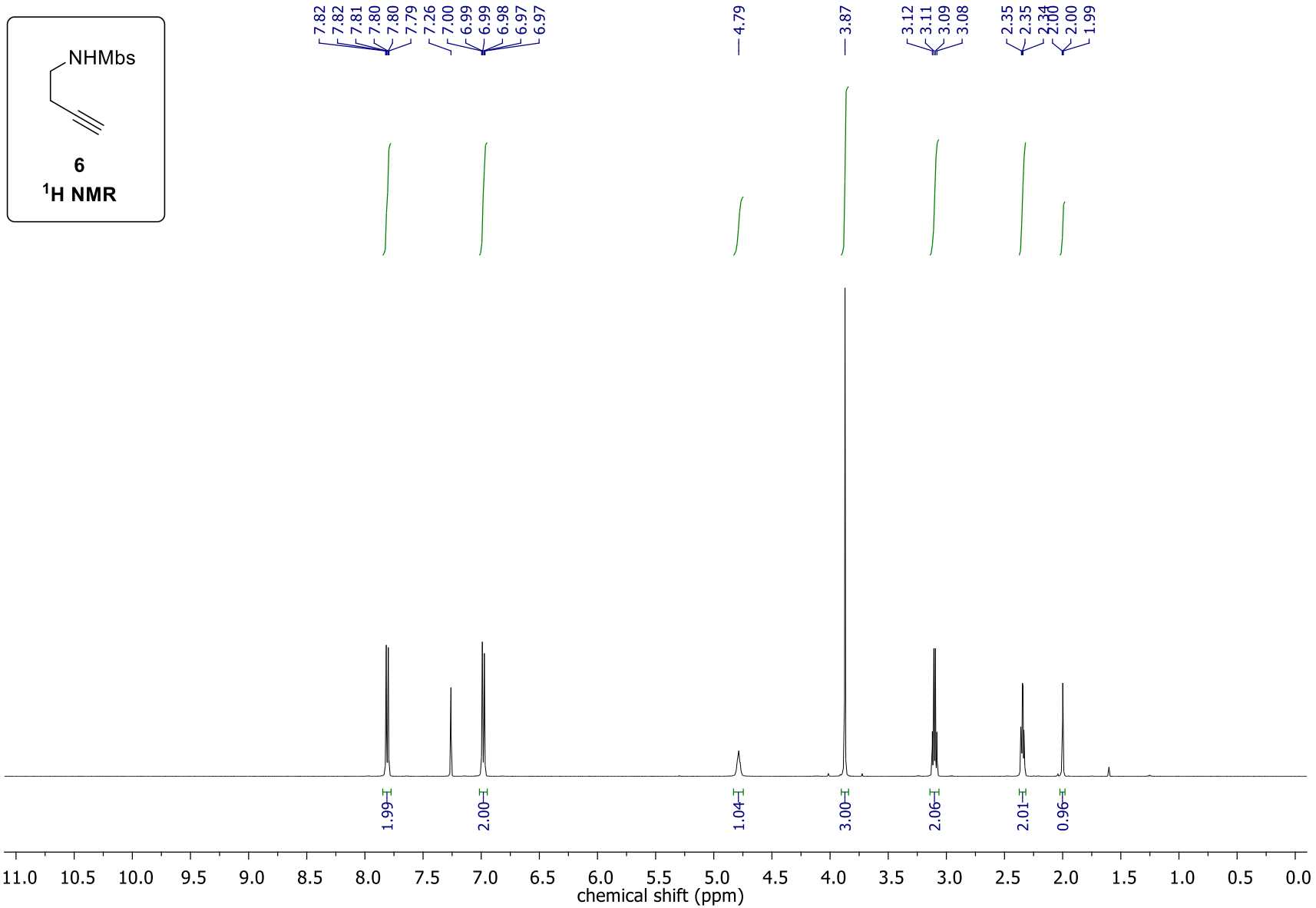


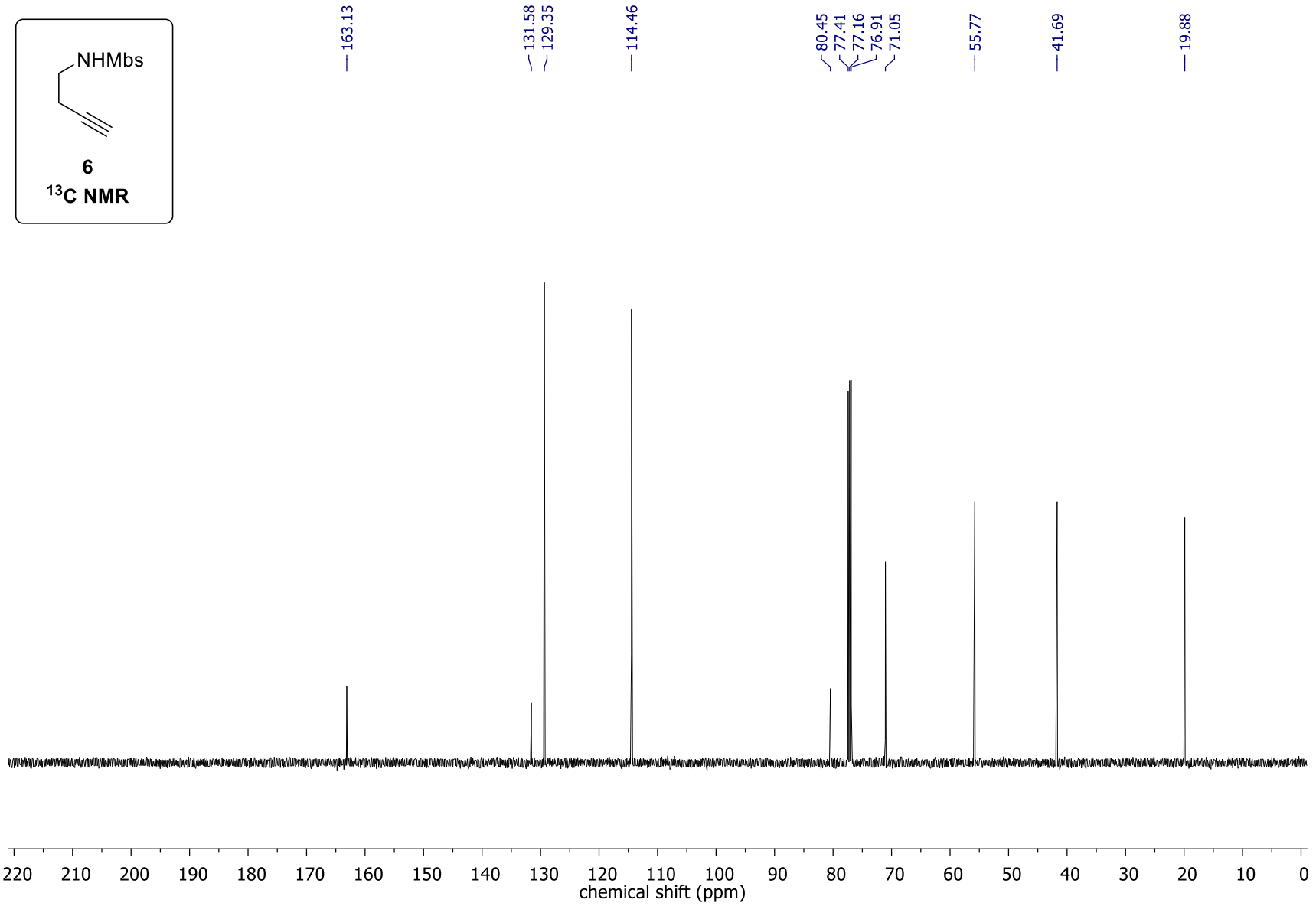

Mbs
N
nBu
Br
O
O
4
1H NMR
8.09
8.07
7.66
7.64
7.40
7.40
7.26
6.89
6.86
6.85
6.74
6.74
6.73
6.03
3.80
2.96
2.95
2.94
1.69
1.68
1.68
1.67
1.67
1.66
1.65
1.29
1.28
0.85
0.84
0.83
1.00
2.02
0.99
1.03
1.01
2.03
2.00
2.00
3.02
1.99
2.09
2.36
3.20
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)

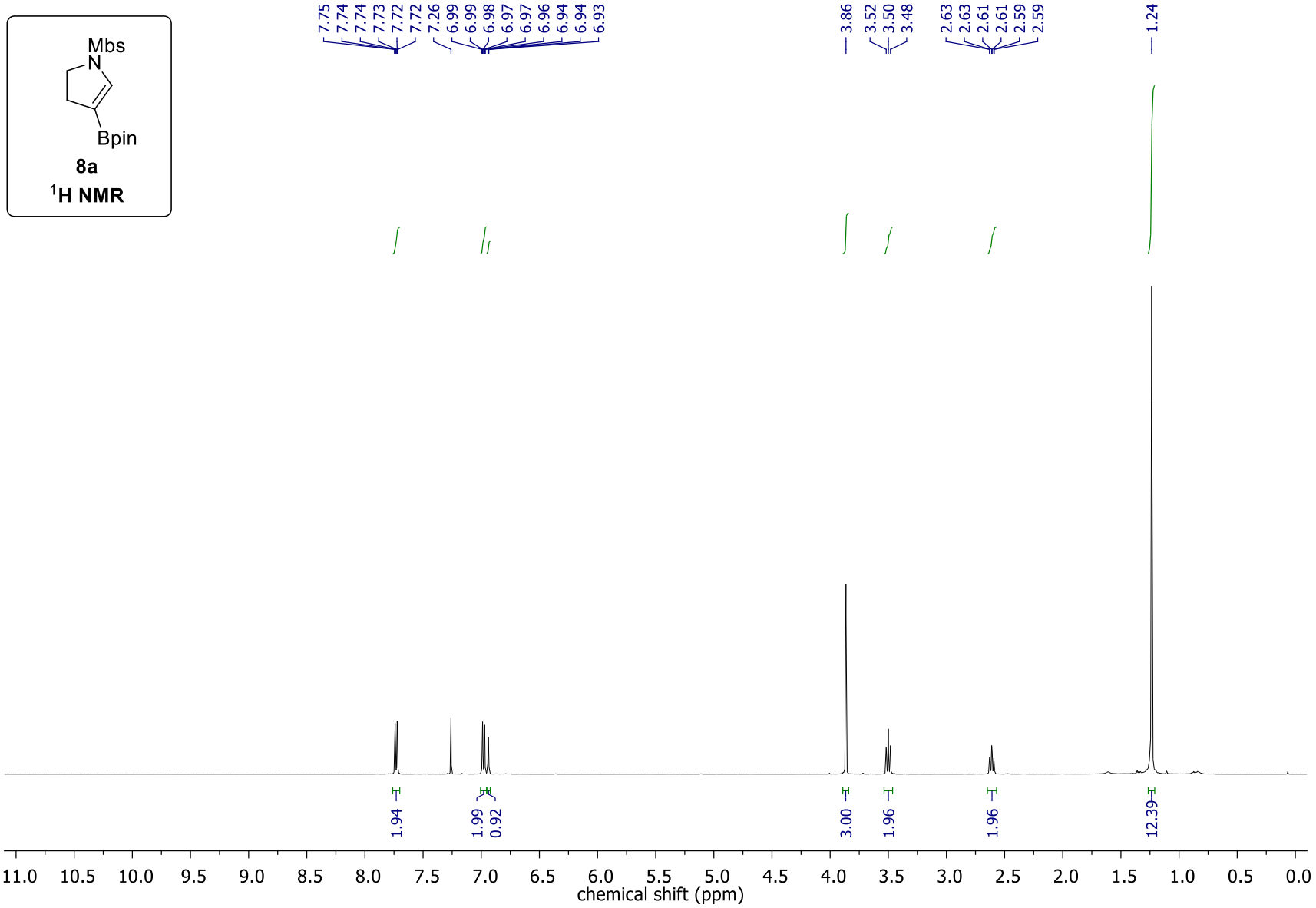

Mbs
N
nBu
Br
O
O
4
13C NMR
163.83
148.04
147.32
140.12
135.43
132.83
128.65
127.17
126.26
123.55
122.05
117.44
116.87
114.51
110.33
101.38
77.37
77.16
76.94
55.77
33.42
26.82
22.69
13.84
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
chemical shift (ppm)

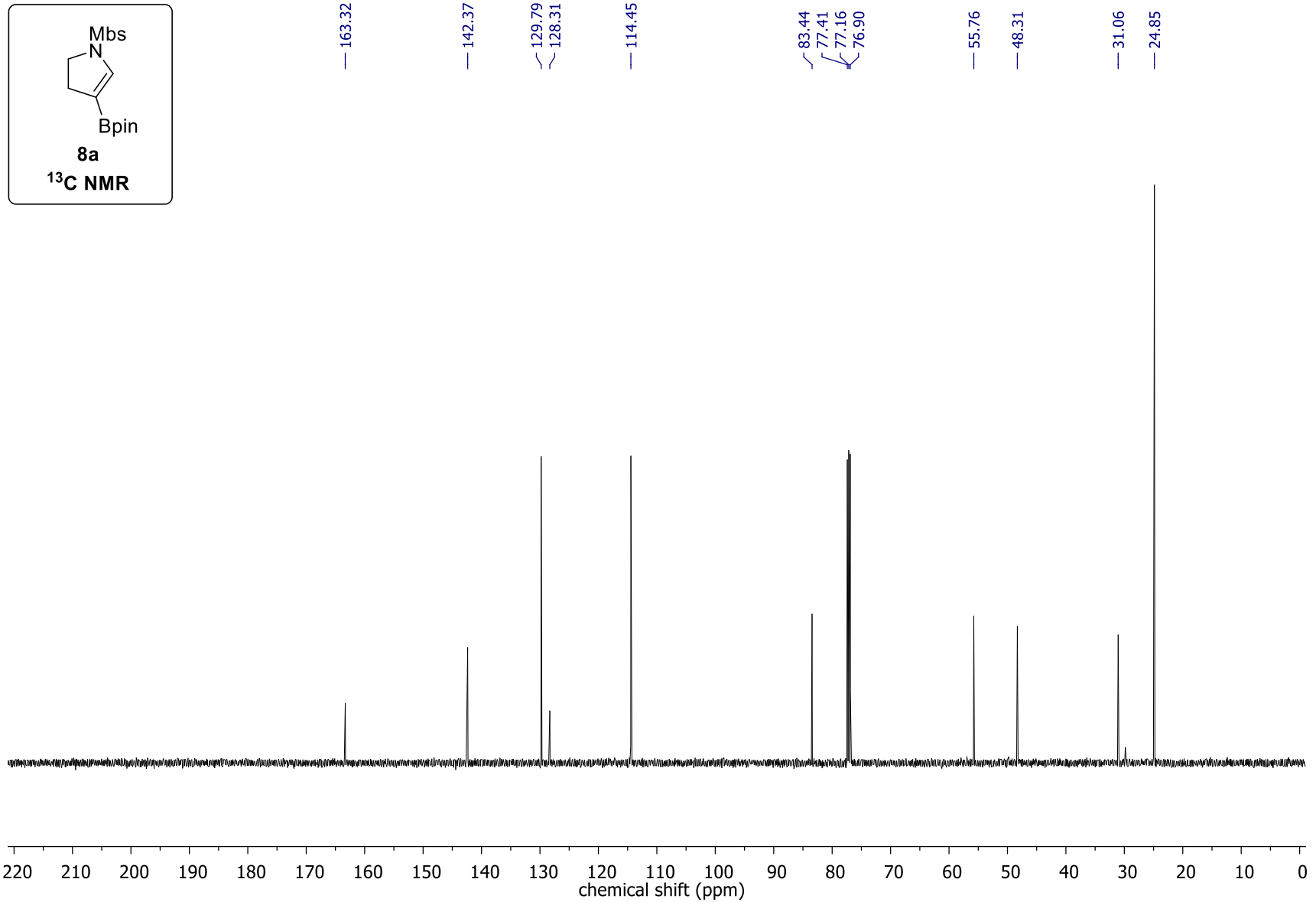

Mbs
N
nBu
MbsN
Ph
O
O
5
1H NMR
8.40
8.39
8.08
8.07
7.66
7.65
7.39
7.38
7.29
7.27
7.26
6.86
6.84
6.74
6.72
6.00
3.81
3.76
2.95
2.93
2.92
1.67
1.65
1.64
1.63
1.62
1.27
1.26
0.84
0.83
0.81
1.00
1.00
2.01
1.08
4.00
2.84
1.96
1.07
0.98
2.05
1.01
2.03
1.99
1.98
3.09
3.00
1.97
2.13
2.49
3.09
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)

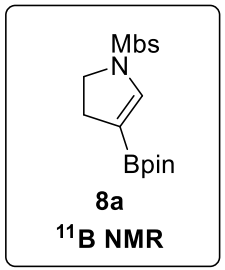

Mbs
N
nBu
MbsN
Ph
O
O
5
13C NMR
163.66
147.80
146.97
132.35
129.32
128.69
128.55
127.48
124.15
123.41
120.89
115.08
114.36
114.01
110.24
108.58
101.23
77.37
77.16
76.95
55.74
55.69
33.37
26.69
22.67
13.82
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
chemical shift (ppm)


NHMbs
6
1H NMR
7.82
7.82
7.81
7.80
7.80
7.79
7.26
7.00
6.99
6.99
6.98
6.97
6.97
4.79
3.87
3.12
3.11
3.09
3.08
2.35
2.35
2.34
2.00
2.00
1.99
1.99
2.00
1.04
3.00
2.06
2.01
0.96
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)


NHMbs
6
13C NMR
163.13
131.58
129.35
114.46
80.45
77.41
77.16
76.91
71.05
55.77
41.69
19.88
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
chemical shift (ppm)


Mbs
N
Bpin
8a
1H NMR
7.75
7.74
7.74
7.73
7.72
7.72
7.26
6.99
6.99
6.98
6.97
6.97
6.96
6.94
6.94
6.93
3.86
3.52
3.50
3.48
2.63
2.63
2.61
2.61
2.59
2.59
1.24
1.94
1.99
0.92
3.00
1.96
1.96
12.39
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)


Mbs
N
Bpin
8a
13C NMR
163.32
142.37
129.79
128.31
114.45
83.44
77.41
77.16
76.90
55.76
48.31
31.06
24.85
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
chemical shift (ppm)


Mbs
N
Bpin

8a

^{11}B NMR

29.48
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
chemical shift (ppm)

References

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