Gallium(III) Promoted Halocyclizations of 1,6-Diynes

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SUPPORTING INFORMATION

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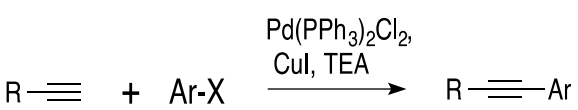
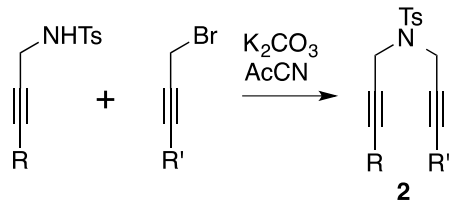
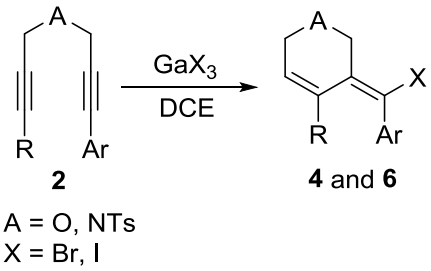
General Methods. The ^{1}H NMR and ^{13}C NMR spectra were recorded at 117.42 kG (^{1}H 500 MHz, ^{13}C 125 MHz), or 93.94 kG (^{1}H 400 MHz, ^{13}C 100 MHz) at ambient temperature as noted. Hydrogen chemical shifts are expressed in parts per million (ppm) relative to the residual protio solvent resonance: $CDCl_3$ δ 7.26, benzene-d_6 δ 7.16. For ^{13}C spectra, the centerline of the solvent signal was used as internal reference: $CDCl_3$ δ 77.23. Unless otherwise noted, each carbon resonance represents a single carbon (relative intensity). All exchangeable OH and NH hydrogen resonances were confirmed by D_2O exchange. High resolution mass spectrometric data were obtained on a QToF (hybrid quadrupolar/time-of-flight) API US system by electrospray (ESI) in the positive ion mode. Mass correction was done by an external reference using a lockspray accessory. Mobile phases were water and acetonitrile (1:9) with 0.1% formic acid. With a flow rate of 0.2 mL/min. The MS settings were: capillary voltage 3kV, cone voltage 35, source temperature 120 °C and desolvation temperature 350 °C unless otherwise noted. Flash chromatography was performed on silica gel-60 (43-60 μm). A silica gel plug refers to a short pad of silica gel through which crude materials are quickly eluted in a single fraction using a mobile phase that gives the desired compound at an Rf near 1.0. Commercially available anhydrous solvents were used as indicated.



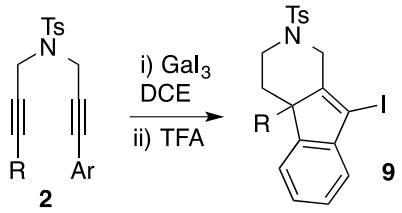
General Procedure A: Sonogashira Couplings of Terminal Alkynes. An oven dried screw cap vial, equipped with a stir bar, was purged with Ar atmosphere, then charged with $Pd(PPh_3)_2Cl_2$ (3-5 mol%) and CuI (6-10 mol%). The terminal alkyne was added to the flask dissolved in the specified solvent, followed by TEA, if not using as the solvent, and finally the aryl halide (1.2 eq). The solution was sparged with Ar for 15 min, then sealed with a teflon cap. After stirring for the specified time at rt, the reaction mixture was diluted with DCM (10 mL/0.1 mmol alkyne) and poured into 1 N HCl (20 mL/0.1 mmol alkyne). The organic layer was separated and the aqueous layer extracted with DCM (2 X 10 mL/0.1 mmol alkyne). The combined organic layers were, dried over Na_2SO_4, filtered, and then the solvent removed *in vacuo*. The crude product was purified via silica gel flash chromatography.



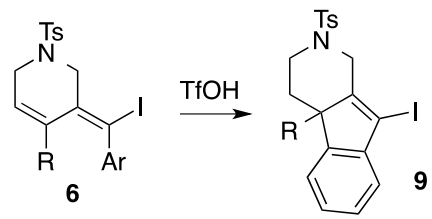
General Procedure B: S_N2 Alkylation of *N*-Tosylpropargylamines with Alkynyl Bromides: Bisalkynes 2. An oven dried round bottom flask, equipped with a stir bar and reflux condenser, was placed under Ar and charged with K_2CO_3 (4 eq). *N*-Tosylpropargylamine was added to the flask and dissolved in acetonitrile (0.2 M). Alkynyl bromide (1-2 eq) was added with stirring then the solution was brought to a reflux for the specified time. After cooling to rt, the reaction mixture was diluted with DCM (10 mL/0.1 mmol tosyl amine) and poured into 1 N HCl (20 mL/0.1 mmol tosyl amine). The aqueous layer was extracted with DCM (2 X 10 mL/0.1 mmol tosyl amine), then the organic layers were combined, dried over Na_2SO_4, filtered, and the solvent removed *in vacuo*. The crude product was purified via silica gel flash chromatography.



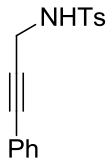
General Procedure C: Ga(III) Iodide Catalyzed Cyclizations of Diynes to Vinyl Halides 4 and 6. An oven dried thick-walled tube equipped with a stir bar was placed under an argon atmosphere. A single portion of GaX_3 was added directly to the tube, avoiding prolonged exposure to air, and the tube was capped with a septum. The mass of GaX_3 was used to set the scale for the reaction. In a separate vessel, diyne **2** (1 eq) was dissolved in anhydrous DCE to give a 0.2 M solution. This solution was added to the tube containing the GaX_3 via syringe, and the reaction allowed to stir at rt for the indicated time. Once complete, as determined by TLC, the reaction was diluted with DCM (10 mL/0.1 mmol diyne) and poured into 1 M NaOH (20 mL/0.1 mmol diyne). The aqueous layer was extracted with DCM (2 X 10 mL/0.1 mmol diyne), then the combined organic layers were dried over Na_2SO_4, filtered, and the solvent removed *in vacuo*. The crude product was used directly, or after eluting through a short plug of silica gel, as indicated. If not used immediately, the vinyl halides could be stored in a freezer at 0 °C under argon. Protection from prolonged exposure to light and acid was essential to the longevity of the compounds.



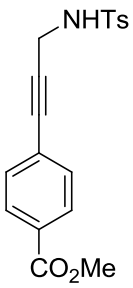
General Procedure D: Single Pot Preparation of Tricyclic Vinyl Iodides 9 from Bisalkynes 2. Bisalkynes **2** were treated with GaI_3 according to General Procedure C. Once conversion to the vinyl iodide **6** was complete as determined by TLC, TFA (1 eq) was added to the reaction mixture via syringe. The solution was brought to 50 ^{o}C, and stirred for the indicated time. After cooling to rt, the reaction was diluted with DCM (10 mL/0.1 mmol diyne) and poured into 1 M NaOH (20 mL/0.1 mmol diyne). The aqueous layer was extracted with DCM (2 X 10 mL/0.1 mmol diyne), then the combined organic layers were dried over Na_2SO_4, filtered, and the solvent removed *in vacuo*. The crude product was purified via silica gel flash chromatography. Compounds **9** were stored at 0 °C, protected from light. However, no significant decomposition was observed on the benchtop under ambient conditions over several weeks.



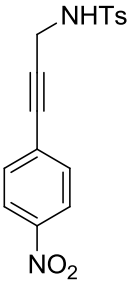
General Procedure E: Two Step Preparation of Tricyclic Vinyl Iodides 9 from Vinyl Iodides 6. Vinyl iodides **6** were prepared according to General Procedure C. Immediately following work up, the crude isolates were dissolved in anhydrous DCE to give a 0.2 M solution, transferred to a thick-walled test tube, and placed under an argon atmosphere. Triflic acid (TfOH, 1 eq) was added and the reaction mixture stirred for the indicated time at the indicated temperature. When the reaction was complete as determined by TLC, the mixture was diluted with DCM (10 mL/0.1 mmol diyne) and poured into 1 M NaOH (20 mL/0.1 mmol diyne). The aqueous layer was extracted with DCM (2 X 10 mL / 0.1 mmol diyne), then the combined organic layers were dried over Na_2SO_4, filtered, and the solvent removed *in vacuo*. The crude product was purified via silica gel flash chromatography. Compounds **9** were stored at 0 °C, protected from light. However, no significant decomposition was observed on the bench top under ambient conditions over over several weeks.



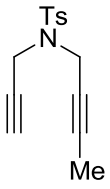
4-Methyl-*N*-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (I). Prepared according to General Procedure A: *N*-tosyl propargylamine[1] (630 mg, 3.0 mmol) was reacted with iodobenzene (400 uL, 3.6 mmol), in the presence of $Pd(PPh_3)_2Cl_2$ (60 mg, 0.09 mmol), CuI (33 mg, 0.17 mmol), and TEA (0.84 mL, 6.0 mmol), in DMF (3 mL, 1.0 M), for 1.5 hr at rt. Purification via flash chromatography gave **I** (pet ether:EtOAc, 1:1, Rf 0.75, 675 mg, 82%) as a light orange solid. The identity of **I** was confirmed by comparison to reported ^{1}H NMR data.[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.27 – 7.18 (overlap, 3H), 7.13 (m, 2H), 4.58 (br t, *J* = 6.2 Hz, N*H*), 4.08 (d, *J* = 6.2 Hz, 2H), 2.36 (s, 3H).



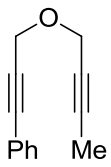
Methyl 4-(3-(4-Methylphenylsulfonamido)prop-1-yn-1-yl)benzoate (II). Prepared according to General Procedure A: *N*-tosyl propargylamine[1] (209 mg, 1.0 mmol) was reacted with methyl 4-iodobenzoate (314 mg, 1.2 mmol), in the presence of $Pd(PPh_3)_2Cl_2$ (35 mg, 0.05 mmol), CuI (19 mg, 0.1 mmol), in TEA (2 mL), for 2 hr at rt. Purification via flash chromatography gave **II** (1% MeOH in DCM, R_f 0.5, 290 mg, 84%) as an orange solid. The identity of **II** was confirmed by comparison to reported ^{1}H-NMR data.[3] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.3 Hz, 2H), 7.81 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.3 Hz, 2H), 7.16 (d, *J* = 8.3 Hz, 2H), 4.85 (br t, *J* = 6.2 Hz, N*H*), 4.09 (d, *J* = 6.2 Hz, 2H), 3.91 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.6, 144.0, 137.1, 131.7 (2C), 130.0, 129.9 (2C), 129.5 (2C), 127.7 (2C), 126.9, 86.5, 84.1, 52.5, 33.9, 21.7.



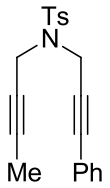
4-Methyl-*N*-(3-(4-nitrophenyl)prop-2-yn-1-yl)benzenesulfonamide (III).[4] Prepared according to General Procedure A: *N*-tosyl propargylamine (209 mg, 1.0 mmol) was reacted with 1-iodo-4-nitrobenzene (298 mg, 1.2 mmol), in the presence of $Pd(PPh_3)_2Cl_2$ (35 mg, 0.05 mmol), CuI (19 mg, 0.1 mmol), in TEA (2 mL), for 1.5 hr. Purification via flash chromatography gave **III** (pet ether:EtOAc, 3:2, R_f 0.7, 274 mg, 82%) as an orange solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.7 Hz, 2H), 7.82 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.7 Hz, 2H), 7.27 (d, *J* = 8.3 Hz, 2H), 4.91 (br t, *J* = 6.2 Hz, N*H*), 4.12 (d, *J* = 6.2 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.4, 144.1, 137.0, 132.5 (2C), 130.0 (2C), 129.1, 127.7 (2C), 123.6 (2C), 89.0, 83.0, 33.8, 21.7; HRMS compound failed to ionize under various conditions.



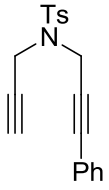
***N*-(But-2-yn-1-yl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (IV).** Prepared according to General Procedure B: *N*-tosyl propargylamine (0.50 g, 2.39 mmol) was refluxed with 1-bromobut-2-yne (0.32 g, 2.39 mmol) in acetonitrile (12 mL, 0.2 M) over K_2CO_3 (1.32 g, 9.56 mmol) for 16 hr. Purification via flash chromatography gave **IV** (pet ether:EtOAc, 9:1, Rf 0.55, 0.57 g, 91%) as a white solid. The identity of **IV** was confirmed by comparison to reported ^{1}H-NMR data.[5] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 4.14 (dt, *J* = 2.5, 0.8 Hz, 2H), 4.10 (qt, *J* = 2.4, 0.8 Hz, 2H), 2.42 (s, 3H), 2.13 (t, *J* = 2.5 Hz, 1H), 1.65 (t, *J* = 2.4 Hz, 1H).



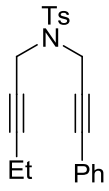
(3-(But-2-yn-1-yloxy)prop-1-yn-1-yl)benzene (2a). To an oven dried round bottom flask was added NaH (25 mg as 60% in mineral oil, 0.6 mmol), which was then purged with argon. Anhydrous THF (2.5 mL) was then added and the suspension cooled to 0 °C. 3-Phenylprop-2-yn-1-ol (60 uL, 0.5 mmol) was added dropwise with stirring, and stirring continued at 0 °C for 30 min, followed by the addition of 1-bromobut-2-yne (53 uL, 0.6 mmol). The solution was stirred at 0 °C another 30 min, then allowed to warm to rt. After 1 h, the reaction was quenched by the addition of water (100 uL), and the mixture poured into a separatory funnel containing brine (50 mL). The organic layer was separated, and the aqueous layer extracted with DCM (2 X 15 mL). The combined organic layers were dried over Na_2SO_4, filtered, and the solvent removed *in vacuo*. Purification via filtration though a silica plug gave **2a** ($CHCl_3$, R_f 0.95, 92 mg, 99%) as a colorless oil. The identity of **2a** was confirmed by comparison to reported ^{1}H-NMR data.[6] ^{1}H NMR (500 MHz, $CDCl_3$) 7.45 (m, 2H), 7.33 – 7.27 (overlap, 3H), 4.46 (s, 2H), 4.27 (q, *J* = 2.3 Hz, 2H), 1.87 (t, *J* = 2.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 131.9 (2C), 128.6, 128.4 (2C), 122.7, 86.7, 84.7, 83.3, 74.6, 57.4, 57.3, 3.8.



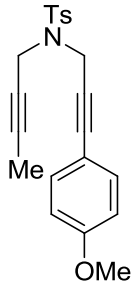
***N*-(But-2-yn-1-yl)-4-methyl-*N*-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (2b).** Prepared according to General Procedure B: tosyl amine **I** (630 mg, 2.2 mmol) was refluxed with 1-bromobut-2-yne (270 uL, 3.1 mmol) in acetonitrile (11 mL, 0.2 M) over K_2CO_3 (1.2 g, 8.8 mmol), for 4 h. Purification via flash chromatography gave **2c** (pet ether:EtOAc, 9:1, R_f 0.65, 707 mg, 95%) as a colorless oil which solidified to a white solid on standing. The identity of **2b** was confirmed by comparison to reported ^{1}H-NMR data.[7] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.35 – 7.20 (overlap, 5H), 7.17 (dd, *J* = 8.1, 1.6 Hz, 2H), 4.38 (s, 2H), 4.13 (q, *J* = 2.4 Hz, 2H), 2.36 (s, 3H), 1.69 (t, *J* = 2.4 Hz, 3H).



4-Methyl-*N*-(3-phenylprop-2-yn-1-yl)-*N*-(prop-2-yn-1-yl)benzenesulfonamide (2c). Prepared according to General Procedure B: *N*-tosyl propargylamine (0.49 g, 2.39 mmol) was refluxed with (3-bromoprop-1-yn-1-yl)benzene (0.93 g, 4.78 mmol) in acetonitrile (12 mL, 0.2 M) over K_2CO_3 (1.32 g, 9.55 mmol) for 16 hr. Purification via flash chromatography gave **2c** (pet ether:EtOAc, 9:1, R_f 0.55, 0.78 g, 99%) as a white solid. The identity of **2c** was confirmed by comparison to reported ^{1}H-NMR spectral data.[8] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.37 – 7.19 (overlap, 5H), 7.15 (dd, *J* = 7.8, 1.7 Hz, 2H), 4.41 (s, 2H), 4.19 (d, *J* = 2.5 Hz, 2H), 2.33 (s, 3H), 2.22 (t, *J* = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 135.1, 131.6 (2C), 129.7 (2C), 128.6, 128.2 (2C), 127.9 (2C), 122.1, 86.0, 81.3, 76.5, 74.2, 37.2, 36.6, 21.5.

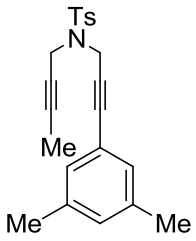


4-Methyl-*N*-(pent-2-yn-1-yl)-*N*-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (2d). Prepared according to General Procedure B: tosyl amine **I** (100 mg, 0.35 mmol) was refluxed with 1-bromopent-2-yne (77 mg, 0.53 mmol) over K_2CO_3 (194 mg, 1.4 mmol) in acetonitrile (1.75 mL, 0.2M) for 2 h. Purification via flash chromatography gave **2d** (pet ether:EtOAc, 9:1, R_f 0.65, 107 mg, 87%) as an off-white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.36 – 7.20 (overlap, 5H), 7.11 (br d, *J* = 8.1 Hz 2H), 4.39 (s, 2H), 4.17 (t, *J* = 2.2 Hz, 2H), 2.34 (s, 3H), 2.05 (qt, *J* = 7.5, 2.2 Hz, 2H), 1.00 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.8, 135.6, 131.7 (2C), 129.6 (2C), 128.6, 128.3 (2C), 128.1 (2C), 122.4, 87.9, 85.7, 81.9, 71.9, 37.20, 37.19, 21.6, 13.7, 12.4; HRMS (ESI) m/z 352.1366 ($[M+H]^+$, 100%), calc'd for $C_{21}H_{22}NO_2S$ 352.1371.

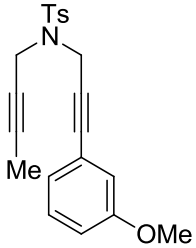


***N*-(But-2-yn-1-yl)-*N*-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (2e).** Prepared according to General Procedure A: diyne **IV** (200 mg, 0.77 mmol) was reacted with 1-iodo-4-methoxybenzene (217 mg, 0.93 mmol), in the presence of $Pd(PPh_3)_2Cl_2$ (16 mg, 0.02), CuI (9 mg, 0.05), and TEA (0.2 mL, 1.5 mmol), in DMF (0.77 mL, 1.0 M), for 3 h. Purification via flash chromatography gave **2e** (pet ether:EtOAc, 7:3, R_f 0.65, 77 mg, 27%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 8.3 Hz, 2H), 7.12 (d, *J* = 8.7 Hz, 2H), 6.77 (d, *J* = 8.7 Hz, 2H), 4.36 (s, 2H), 4.13 (q, *J* = 2.3 Hz, 2H), 3.79 (s, 3H), 2.37 (s, 3H), 1.68 (t, *J* = 2.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.9, 143.7, 135.8, 133.3 (2C), 129.6

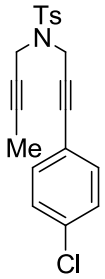
(2C), 128.2 (2C), 114.6, 114.0 (2C), 85.7, 82.0, 80.4, 71.9, 55.5, 37.4, 37.1, 21.7, 3.7; HRMS (ESI) m/z 390.1144 ([M+Na]$^+$, 100%), calc'd for $C_{21}H_{21}NO_3SNa$ 390.1140



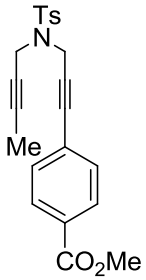
***N*-(But-2-yn-1-yl)-*N*-(3-(3,5-dimethylphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (2f)**. Prepared according to General Procedure A: diyne **IV** (116 mg, 0.44 mmol) was reacted with 1-iodo-3,5-dimethylbenzene (75 uL, 0.53 mmol), in the presence of $Pd(PPh_3)_2Cl_2$ (9 mg, 0.013 mmol) and CuI (5 mg, 0.03 mmol) in TEA (1 mL, 0.4 M) for 16 hr. Purification via flash chromatography gave **2f** (pet ether:EtOAc, 9:1, R_f 0.65, 147 mg, 91%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.28 (br d, *J* = 8.2 Hz, 2H), 6.92 (br s, 1H), 6.80 (br s, 2H), 4.38 (s, 2H), 4.13 (q, *J* = 2.3 Hz, 2H), 2.37 (s, 3H), 2.25 (s, 6H), 1.69 (t, *J* = 2.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 137.9 (2C), 135.7, 130.5, 129.6 (2C), 129.5 (2C), 128.1 (2C), 122.1, 86.2, 82.0, 81.0, 71.9, 37.3, 37.1, 21.7, 21.2 (2C), 3.7; HRMS (ESI) m/z 366.1547 ([M+H]$^+$, 100%), calc'd for $C_{22}H_{24}NO_2S$ 366.1528.



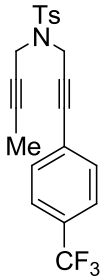
***N*-(But-2-yn-1-yl)-*N*-(3-(3-methoxyphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (2g).** Prepared according to General Procedure A: diyne **IV** (105 mg, 0.40 mmol) was reacted with 1-iodo-3-methoxybenzene (57 uL, 0.48 mmol), in the presence of $Pd(PPh_3)_2Cl_2$ (8 mg, 0.012 mmol) and CuI (5 mg, 0.024 mmol), in TEA (1 mL, 0.4 M), for 2 hr. Purification via flash chromatography gave **2g** (pet ether:EtOAc, 9:1, R_f 0.45, 140 mg, 95%) as a light orange solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.3 Hz, 1H), 7.26 (d, *J* = 8.3 Hz, 2H), 7.16 (dd, *J* = 8.4, 7.6 Hz, 1H), 6.84 (ddd, *J* = 8.4, 2.6, 1.2 Hz, 1H), 6.76 (ddd, *J* = 7.6, 1.4, 1.2 Hz, 1H), 6.71 (dd, *J* = 2.6, 1.4 Hz, 1H), 4.38 (s, 2H), 4.13 (q, *J* = 2.4 Hz, 2H), 3.77 (s, 3H), 2.36 (s, 3H), 1.68 (t, *J* = 2.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.3, 143.9, 135.6, 129.6 (2C), 129.4, 128.1 (2C), 124.3, 123.4, 117.0, 114.8, 85.7, 82.1, 81.7, 71.8, 55.4, 37.26, 37.21, 21.6, 3.6; HRMS (ESI) m/z 368.1333 ([M+H]$^+$, 100%), calc'd for $C_{21}H_{22}NO_3S$ 368.1320.



***N*-(But-2-yn-1-yl)-*N*-(3-(4-chlorophenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (2h).** Prepared according to General Procedure A: diyne **IV** (150 mg, 0.57 mmol) was reacted with 1-chloro-4-iodobenzene (165 mg, 0.69 mmol), in the presence of $Pd(PPh_3)_2Cl_2$ (12 mg, 0.02 mmol) and CuI (7 mg, 0.03 mmol) in TEA (1.5 mL, 0.4 M) for 3 hr. Purification via flash chromatography gave **2h** ($CHCl_3$, R_f 0.85, 214 mg, 99%) as an orange solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.7 Hz, 2H), 7.10 (d, *J* = 8.7 Hz, 2H), 4.36 (s, 2H), 4.12 (q, *J* = 2.4 Hz, 2H), 2.36 (s, 3H), 1.67 (t, *J* = 2.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.8, 135.7, 134.7, 133.0 (2C), 129.6 (2C), 128.7 (2C), 128.2 (2C), 120.9, 84.6, 83.0, 82.2, 71.7, 37.27, 37.22, 21.6, 3.6; HRMS (ESI) m/z 372.0818 ($[M+H]^+$, 100%), calc'd for $C_{20}H_{19}{}^{35}ClNO_2S$ 372.0825.

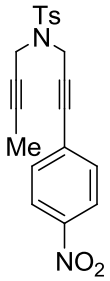


Methyl 4-(3-(*N*-(But-2-yn-1-yl)-4-methylphenylsulfonamido)prop-1-yn-1-yl)benzoate (2i). Prepared according to General Procedure B: tosyl amine **II** (75 mg, 0.22 mmol) was refluxed with 1-bromobut-2-yne (40.35 mg, 0.306 mmol) over K_2CO_3 (121 mg, 0.874 mmol) in acetonitrile (1.1 mL, 0.2M) for 0.5 h. Purification via flash chromatography gave **2i** (pet ether:EtOAc, 4:1, R_f 0.60, 85 mg, 98%) as a light yellow oil that solidified to an off-white solid upon standing. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.3 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 4.40 (s, 2H), 4.13 (q, *J* = 2.4 Hz, 2H), 3.91 (s, 3H), 2.35 (s, 3H), 1.69 (t, *J* = 2.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.6, 143.9, 135.6, 131.7 (2C), 130.0, 129.7 (2C), 129.5 (2C), 128.2 (2C), 127.1, 85.1, 85.0, 82.3, 71.7, 52.5, 37.4, 37.3, 21.7, 3.7; HRMS (ESI) m/z 396.1295 ($[M+H]^+$, 100%), calc'd for $C_{22}H_{22}NO_4S$ 396.1270.

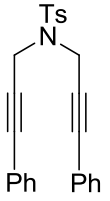


***N*-(But-2-yn-1-yl)-4-methyl-*N*-(3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-yl)benzenesulfonamide (2j).** Prepared according to General Procedure A: diyne **IV** (50 mg, 0.19 mmol) was reacted with 1-iodo-4-(trifluoromethyl)benzene (60 mg, 0.22 mmol), in the presence of $Pd(PPh_3)_2Cl_2$ (4 mg, 0.006 mmol) and CuI (2 mg, 0.01 mmol) in TEA (0.4 mL, 0.4 M) for 1 hr. Purification via flash chromatography gave **2j** (pet ether:EtOAc 4:1, R_f 0.85, 65 mg, 84%) as an orange solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 4.39 (s, 2H), 4.13 (q, *J* = 2.4 Hz, 2H), 2.35 (s, 3H), 1.68 (t, *J* = 2.4 Hz, 3H); ^{13}C NMR (125

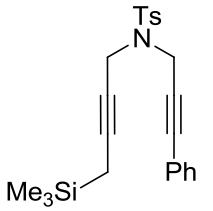
MHz, $CDCl_3$) δ 143.9, 135.6, 132.0 (2C), 130.4 (q, $^2J_{C\text{-}F}$ = 32.7 Hz), 129.6 (2C), 128.2 (2C), 126.2 (q, $^5J_{C\text{-}F}$ = 1.3 Hz), 125.2 (q, $^3J_{C\text{-}F}$ = 3.9 Hz, 2C), 123.9 (q, $^1J_{C\text{-}F}$ = 272.2 Hz) 84.7, 84.4, 82.3, 71.6, 37.3, 37.2, 21.6, 3.7; HRMS (ESI) m/z 406.1090 ([M+H]$^+$, 100%), calc'd for $C_{20}H_{19}F_3NO_2S$ 406.1089.



***N*-(But-2-yn-1-yl)-4-methyl-*N*-(3-(4-nitrophenyl)prop-2-yn-1-yl)benzenesulfonamide (2k).** Prepared according to General Procedure B: tosyl amine **III** (165 mg, 0.5 mmol) was refluxed with 1-bromobut-2-yne (60 uL, 0.7 mmol) over K_2CO_3 (276 mg, 2 mmol) in acetonitrile (2.5 mL, 0.2M) for 1 h. Purification via flash chromatography gave **2k** (pet ether:EtOAc, 4:1, R_f 0.50, 141 mg, 74%) as an orange solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.8 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.8 Hz, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 4.40 (s, 2H), 4.13 (q, *J* = 2.4 Hz, 2H), 2.36 (s, 3H), 1.67 (t, *J* = 2.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.2, 144.0, 135.5, 132.5 (2C), 129.6 (2C), 129.2, 128.1 (2C), 123.5 (2C), 87.4, 83.8, 82.4, 71.4, 37.4, 37.1, 21.6, 3.6; HRMS (ESI) m/z 383.1075 ([M+H]$^+$, 100%), calc'd for $C_{20}H_{19}N_2O_4S$ 383.1066.

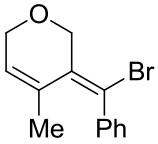


4-Methyl-*N*,*N*-bis(3-phenylprop-2-yn-1-yl)benzenesulfonamide (2l). Tosyl amine (500 mg, 2.9 mmol) and K_2CO_3 (2 g, 14.5 mmol) were added to a round bottom flask, and suspended in acetonitrile (25 mL, 0.1 M). The solution was brought to reflux with vigorous stirring, then (3-bromoprop-1-yn-1-yl)benzene (1.71 g, 8.8 mmol) was added dropwise. After refluxing 1 hr, the reaction was allowed to cool to rt, filtered, then concentrated to a brown solid. Purification via flash chromatography gave **2l** (pet ether:EtOAc, 9:1, R_f 0.6, 735 mg, 63%) as an off-white solid. The identity of **2l** was confirmed by comparison to reported ^{1}H-NMR spectral data.[9] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.27 – 7.07 (overlap, 12H), 4.37 (s, 4H), 2.23 (s, 3H).

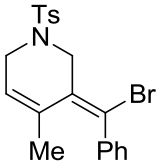


4-Methyl-*N*-(3-phenylprop-2-yn-1-yl)-*N*-(4-(trimethylsilyl)but-2-yn-1-yl)benzenesulfonamide (2m). Prepared according to General Procedure B, with modifications as noted: tosyl amine **I** (47 mg, 0.16 mmol) was reacted with (4-bromobut-2-yn-1-yl)trimethylsilane[10] (34 mg, 0.16 mmol) over K_2CO_3 (68 mg, 0.49 mmol) in acetonitrile (1 mL, 0.15 M) for 4 days at rt. Purification via flash chromatography gave **2m** (pet ether:EtOAc, 20:1, R_f 0.3, 35 mg, 52%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.33 – 7.24 (overlap, 5H), 7.17 (dd, *J* = 8.1, 1.6 Hz, 2H), 4.39

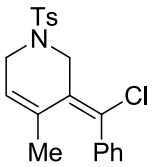
(s, 2H), 4.18 (t, *J* = 2.5 Hz, 2H), 2.35 (s, 3H), 1.37 (t, *J* = 2.5 Hz, 2H), 0.06 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.8, 135.6, 131.8 (2C), 129.7 (2C), 128.6, 128.3 (2C), 128.1 (2C), 122.5, 85.7, 84.7, 81.8, 71.1, 37.5, 37.0, 21.7, 7.3, -1.8 (3C); HRMS (ESI) m/z 410.1618 ($[M+H]^+$, 100%), calc'd for $C_{23}H_{28}NO_2SSi$ 410.1610.



(*Z*)-3-(Bromo(phenyl)methylene)-4-methyl-3,6-dihydro-2*H*-pyran (4a). Prepared according to General Procedure C: diyne **2a** (90 mg, 0.49 mmol) was reacted with $GaBr_3$ (151 mg, 0.49, 1.0 eq) in DCE (2.4 mL) for 20 min. Purification via flash chromatography gave **4a** (pet ether:EtOAc, 20:1, R_f 0.6, 56 mg, 45%) as a light yellow oil with significant loss of material. The compound began to noticeably decompose immediately after isolation. Attempts to further purify the compound resulted only in decomposition products. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.28 (overlap, 5H), 5.58 (br s, 1H), 4.55 (s, 2H), 4.21 (br s, 2H), 1.26 (br s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.3, 133.4, 130.7, 129.9 (2C), 128.8, 128.1 (2C), 128.0, 120.8, 70.9, 66.7, 22.9; HRMS (ESI) m/z 265.0225 ($[M+H]^+$, 100%), calc'd for $C_{13}H_{14}{}^{79}BrO$ 265.0228.

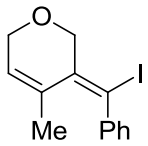


(*Z*)-3-(Bromo(phenyl)methylene)-4-methyl-1-tosyl-1,2,3,6-tetrahydropyridine (4b). Perpared according to General Procedure C: diyne **2b** (23 mg, 0.068 mmol) was reacted with $GaBr_3$ (21 mg, 0.068, 1.0 eq) in DCE (0.3 mL) for 30 min. After work-up, filtration though a silica plug gave pure **4b** (pet ether:EtOAc, 5:1, R_f 0.75, 27 mg, 95%) as a pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.30 (br d, *J* = 8.3 Hz, 2H), 7.25 – 7.19 (overlap, 3H), 6.94 (dd, *J* = 8.0, 1.6 Hz, 2H), 5.40 (tq, *J* = 3.5, 1.4 Hz, 1H), 4.30 (s, 2H), 3.93 (dq, *J* = 3.5, 2.0 Hz, 2H), 2.43 (s, 3H), 1.09 (td, *J* = 2.0, 1.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.7, 141.6, 135.7, 131.9, 131.3, 129.9 (2C), 129.8 (2C), 129.0, 128.0 (2C), 127.8 (2C), 125.4, 123.9, 50.6, 46.3, 22.8, 21.7; HRMS (ESI) m/z 418.0485 ($[M+H]^+$, 100%), calc'd for $C_{20}H_{21}{}^{79}BrNO_2S$ 418.0476.

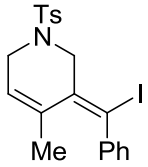


(*Z*)-3-(Chloro(phenyl)methylene)-4-methyl-1-tosyl-1,2,3,6-tetrahydropyridine (5b). Diyne **2b** (50 mg, 0.15 mmol) was added to an oven dried thick-walled tube equipped with a magnetc stir bar, purged with argon, then DCE (0.7 mL) was added. To this solution, $GaCl_3$ was then added as a 0.5 M solution in pentane (300 uL, 0.15 mmol, 1.0 eq). After 2 h the solution was diluted with DCM (10 mL) and washed with 1 M NaOH (15 mL). The organic layer was dried over Na_2SO_4, filtered, and the solvent removed. Filtration

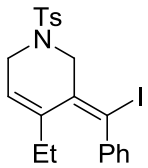
though a silica plug gave **5b** ($CHCl_3$, R_f 0.95, 31 mg, 55%) as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 7.31 – 7.27 (overlapped m, 1H), 7.25 (m, 2H), 6.97 (m, 2H), 5.43 (tq, *J* = 3.5, 1.4 Hz, 1H), 4.29 (s, 2H), 3.96 (dq, *J* = 3.5, 2.1 Hz, 2H), 2.42 (s, 3H), 1.11 (td, *J* = 2.1, 1.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.6, 139.6, 135.7, 131.5, 131.2, 129.9 (2C), 129.8 (2C), 129.1, 128.7, 128.0 (2C), 127.7 (2C), 125.2, 47.3, 46.1, 22.6, 21.7; HRMS (ESI) m/z 374.0997 ([M+H]$^+$, 100%), calc'd for $C_{20}H_{21}{}^{35}ClNO_2S$ 374.0982.



(*Z*)-3-(Iodo(phenyl)methylene)-4-methyl-3,6-dihydro-2*H*-pyran (6a). Prepared according to General Procedure C: diyne **2a** (10 mg, 0.053 mmol) was reacted with GaI_3 (24 mg, 0.053, 1.0 eq) in DCE (0.26 mL) for 30 min. After work-up, ^{1}H NMR showed the crude isolate to be 70% **6a**. Purification via flash chromatography gave pure **6a** (cyclohexanes:$CHCl_3$, 2:3, R_f 0.75, 5 mg, 30%) as a colorless oil with significant loss of material. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.27 (overlap, 4H), 7.23 (m, 1H), 5.44 (tq, *J* = 3.2, 1.4 Hz, 1H), 4.47 (s, 2H), 4.20 (dq, *J* = 3.2, 2.0 Hz, 2H), 1.25 (td, *J* = 2.0, 1.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.3, 137.9, 131.0, 129.3 (2C), 128.3, 128.1, 128.0 (2C), 99.4, 77.2, 67.1, 23.2; HRMS was unable to be obtained for this compound due to its limited stability.

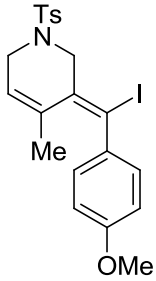


(*Z*)-3-(Iodo(phenyl)methylene)-4-methyl-1-tosyl-1,2,3,6-tetrahydropyridine (6b). Prepared according to General Procedure C: diyne **2b** (22.5 mg, 0.067 mmol) was reacted with GaI_3 (30 mg, 0.067, 1.0 eq) in DCE (0.33 mL) for 30 min. After work-up, ^{1}H NMR showed the crude isolate to be 91% **6b**. Purification via filtration through a silica plug eluting with $CHCl_3$ gave pure **6b** ($CHCl_3$, R_f 0.9, 27 mg, 88%) as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 7.23 – 7.16 (overlap, 3H), 6.90 (m, 2H), 5.29 (tq, *J* = 3.5, 1.3 Hz, 1H), 4.24 (s, 2H), 3.89 (dq, *J* = 3.5, 2.0 Hz, 2H), 2.44 (s, 3H), 1.07 (td, *J* = 2.0, 1.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.6, 143.7, 136.2, 135.7, 132.0, 129.9 (2C), 129.2 (2C), 128.5, 127.9 (4C), 125.6, 103.1, 56.9, 46.7, 23.0, 21.7; HRMS (ESI) m/z 466.0352 ([M+H]$^+$, 100%), calc'd for $C_{20}H_{21}INO_2S$ 466.0338.

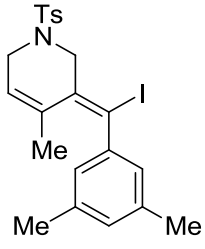


(*Z*)-4-Ethyl-3-(iodo(phenyl)methylene)-1-tosyl-1,2,3,6-tetrahydropyridine (6d). Prepared according to General Procedure C**:** diyne **2d** (145 mg, 0.41 mmol) was reacted with GaI_3 (186 mg, 0.41 mmol, 1.0 eq) in DCE (2.0 mL) for 40 min. After work-up, ^{1}H NMR showed the resulting pale yellow solid to be 80% **6d**. Purification via flash chromatography gave pure **6d** (9:1 pet ether:EtOAc, R_f 0.45, 104 mg, 53%) as an off-

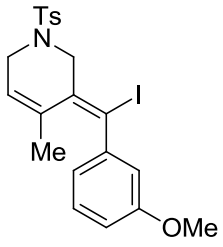
white solid with significant loss of material. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.31 (br d, *J* = 8.3 Hz, 2H), 7.21 – 7.16 (overlap, 3H), 6.91 (m, 2H), 5.34 (tt, *J* = 3.5, 1.4 Hz, 1H), 4.23 (s, 2H), 3.92 (dt, *J* = 3.5, 1.7 Hz, 2H), 2.42 (s, 3H), 1.32 (qtd, *J* = 7.4, 1.7, 1.4 Hz, 2H), 0.59 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.3, 143.7, 138.7, 135.8, 135.5, 130.0 (2C), 129.2 (2C), 128.6, 128.0 (2C), 127.9 (2C), 123.5, 102.5, 57.3, 46.8, 27.6, 21.7, 13.3; HRMS (ESI) m/z 480.0504 ($[M+H]^+$, 100%), calc'd for $C_{21}H_{23}INO_2S$ 480.0494.



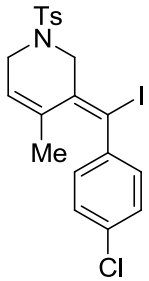
(*Z*)-3-(Iodo(4-methoxyphenyl)methylene)-4-methyl-1-tosyl-1,2,3,6-tetrahydropyridine (6e). Prepared according to General Procedure C**:** diyne **2e** (22 mg, 0.060 mmol) was reacted with GaI_3 (27 mg, 0.060, 1.0 eq) in DCE (0.30 mL) for 5 min. After work-up, ^{1}H NMR showed the resulting pale yellow solid to be 93% **6e**. Purification via filtration through a silica plug eluting with $CHCl_3$ gave pure **6e** ($CHCl_3$, R_f 0.8, 26 mg, 88%) as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 6.72 (d, *J* = 8.5 Hz, 2H), 5.28 (br s, 1H), 4.21 (s, 2H), 3.89 (br s, 2H), 3.79 (s, 3H), 2.43 (s, 3H), 1.12 (br s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.6, 143.6, 138.0, 135.9, 135.7, 132.2, 130.7 (2C), 129.9 (2C), 127.9 (2C), 125.2, 113.2 (2C), 103.6, 56.9, 55.5, 46.7, 22.9, 21.7; HRMS (ESI) m/z 496.0428 ($[M+H]^+$, 100%), calc'd for $C_{21}H_{23}INO_3S$ 496.0443.



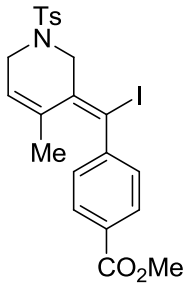
(*Z*)-3-((3,5-Dimethylphenyl)iodomethylene)-4-methyl-1-tosyl-1,2,3,6-tetrahydropyridine (6f). Prepared according to General Procedure C**:** diyne **2f** (22 mg, 0.060 mmol) was reacted with GaI_3 (27 mg, 0.060 mmol) in DCE (0.03 mL) for 10 min. After work-up, ^{1}H NMR showed the resulting pale yellow solid to be 94% **6f**. Purification via filtration through a silica plug eluting with $CHCl_3$ gave pure **6f** ($CHCl_3$, R_f 0.9, 28 mg, 93%) as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.32 (br d, *J* = 8.3 Hz, 2H), 6.82 (br s, 1H), 6.54 (br s, 2H), 5.27 (tq, *J* = 3.6, 1.3 Hz, 1H), 4.24 (s, 2H), 3.89 (dq, *J* = 3.6, 2.1 Hz, 2H), 2.44 (s, 3H), 2.23 (s, 6H), 1.10 (td, *J* = 2.1, 1.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.5, 143.5, 137.3 (2C), 135.8, 135.6, 132.2, 130.2, 129.9 (2C), 128.0 (2C), 126.9 (2C), 125.3, 103.7, 56.9, 46.7, 23.0, 21.8, 21.4 (2C); HRMS (ESI) m/z 494.0653 ($[M+H]^+$, 100%), calc'd for $C_{22}H_{25}INO_2S$ 494.0651.



(*Z*)-3-(Iodo(3-methoxyphenyl)methylene)-4-methyl-1-tosyl-1,2,3,6-tetrahydropyridine (6g). Prepared according to General Procedure C**:** diyne **2g** (16 mg, 0.044 mmol) was reacted with GaI_3 (20 mg, 0.044, 1.0 eq) in DCE (0.2 mL) for 45 min. After work-up, ^{1}H NMR showed the resulting pale yellow solid to be 94% **6g**. Filtration through a silica plug eluting with $CHCl_3$ gave pure **6g** ($CHCl_3$, R_f 0.8, 19 mg, 87%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.11 (dd, *J* = 8.3, 7.8 Hz, 1H), 6.73 (ddd, *J* = 8.3, 2.5, 0.8 Hz, 1H), 6.51 (ddd, *J* = 7.8, 1.5, 0.8 Hz, 1H), 6.47 (dd, *J* = 2.5, 1.5 Hz, 1H), 5.29 (tq, *J* = 3.4 1.4 Hz, 1H), 4.23 (s, 2H), 3.89 (dq, *J* = 3.4, 2.1 Hz, 2H), 3.77 (s, 3H), 2.44 (s, 3H), 1.14 (td, *J* = 2.1, 1.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.9, 146.8, 143.8, 136.1, 135.6, 132.1, 130.0 (2C), 128.9, 127.9 (2C), 125.5, 121.8, 115.1, 113.8, 102.6, 56.9, 55.5, 46.7, 22.9, 21.7; HRMS (ESI) m/z 496.0442 ($[M+H]^+$, 100%), calc'd for $C_{21}H_{23}INO_3S$ 496.0443.

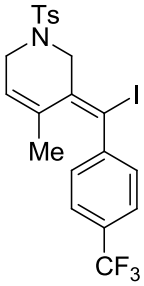


(*Z*)-3-((4-Chlorophenyl)iodomethylene)-4-methyl-1-tosyl-1,2,3,6-tetrahydropyridine (6h). Prepared according to General Procedure C**:** diyne **2h** (124 mg, 0.33 mmol) was reacted with GaI_3 (150 mg, 0.33 mmol) in DCE (1.7 mL) for 45 min. After work-up, ^{1}H NMR showed the crude isolate to be to be 92% pure **6h.** Purification via flash chromatography gave pure **6h** (9:1 pet ether:EtOAc, R_f 0.6, 128 mg, 78%) as a light yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.2 Hz, 2H), 7.31 (br d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 5.33 (tq, *J* = 3.5, 1.5 Hz, 1H), 4.21 (s, 2H), 3.89 (dq, *J* = 3.5, 1.9 Hz, 2H), 2.44 (s, 3H), 1.11 (td, *J* = 1.9, 1.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.0, 143.8, 137.0, 135.7, 134.4, 131.7, 130.6 (2C), 129.9 (2C), 128.2 (2C), 127.9 (2C), 126.2, 101.1, 56.8, 46.8, 23.2, 21.8; HRMS (ESI) m/z 499.9954 ($[M+H]^+$, 100%), calc'd for $C_{20}H_{20}{}^{35}ClINO_2S$ 499.9948.

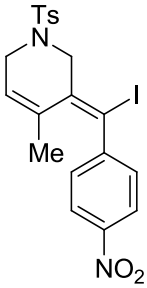


(*Z*)-Methyl-4-(Iodo(4-methyl-1-tosyl-1,6-dihydropyridin-3(2*H*)-ylidene)methyl)benzoate (6i). Prepared according to General Procedure C**:** diyne **2i** (23 mg, 0.058 mmol) was reacted with with GaI_3 (27 mg, 0.058 mmol) in DCE (0.3 mL) for 9 h at 60 °C. After work-up, the ^{1}H NMR spectrum showed the crude isolate to be 88% **6i**. Purification via flash chromatography gave pure **6i** (pet ether:EtOAc, 4:1, R_f 0.6, 11 mg, 36%) as a white solid with significant loss of material. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.3 Hz, 2H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.32

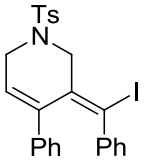
(d, *J* = 8.3 Hz, 2H), 6.97 (d, *J* = 8.3 Hz, 1H), 5.33 (tq, *J* = 3.5, 1.4 Hz, 1H), 4.24 (s, 2H), 3.92 – 3.89 (overlapped m, 2H), 3.91 (s, 3H), 2.45 (s, 3H), 1.06 (td, *J* = 1.9, 1.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.6, 150.0, 143.8, 137.2, 135.7, 131.6, 129.95 (2C), 129.94, 129.3 (2C), 129.2 (2C), 127.9 (2C), 126.3, 100.8, 56.8, 52.5, 46.8, 23.2, 21.8; HRMS (ESI) m/z 524.0400 ($[M+H]^+$, 100%), calc'd for $C_{22}H_{23}INO_4S$ 524.0393.



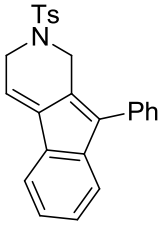
(*Z*)-3-(Iodo(4-(trifluoromethyl)phenyl)methylene)-4-methyl-1-tosyl-1,2,3,6-tetrahydropyridine (6j). Prepared according to General Procedure C**:** diyne **2j** (32 mg, 0.079 mmol) was reacted with with GaI_3 (36 mg, 0.079 mmol) in DCE (0.4 mL) for 2 h. After work-up, the ^{1}H NMR spectrum showed the crude isolate to be 88% **6j**. Purification via flash chromatography gave pure **6j** (pet ether:EtOAc, 4:1, R_f 0.55, 26 mg, 61%) as a white solid with significant loss of material. ^{1}H NMR (500 MHz, $CDCl_3$) δ; ^{13}C NMR (125 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.03 (d, *J* = 8.2 Hz, 2H), 5.35 (tq, *J* = 3.3, 1.3 Hz, 1H), 4.23 (s, 1H), 3.90 (dq, *J* = 3.3, 2.0 Hz, 1H), 2.45 (s, 3H), 1.07 (td, *J* = 2.0, 1.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.0 (q, $^5J_{CF}$ = 1.3 Hz), 143.9, 137.6, 135.6, 131.5, 130.4 (q, $^2J_{CF}$ = 32.8 Hz) 130.0 (2C), 129.6 (2C), 127.9 (2C), 126.6, 124.9 (q, $^3J_{CF}$ = 3.8 Hz, 2C), 123.9 (q, $^1J_{CF}$ = 272.4 Hz), 100.0, 56.8, 46.8, 23.4, 21.8. HRMS (ESI) m/z 534.0192 ($[M+H]^+$, 100%), calc'd for $C_{21}H_{20}F_3INO_2S$ 534.0212.



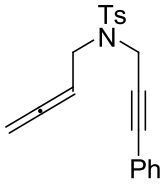
(*Z*)-3-(Iodo(4-nitrophenyl)methylene)-4-methyl-1-tosyl-1,2,3,6-tetrahydropyridine (6k). Prepared according to General Procedure C**:** diyne **2k** (35 mg, 0.092 mmol) was reacted with with GaI_3 (41 mg, 0.092 mmol) in DCE (0.5 mL) for 3 h at 50 °C. After work-up, the ^{1}H NMR spectrum showed the crude isolate to be 83% **6k**. Purification via flash chromatography gave **6k** (pet ether:EtOAc, 4:1, R_f 0.5, 21 mg, 45%) as a white solid with significant loss of material. For **6k**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 2H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 5.40 (br s, 1H), 4.24 (s, 2H), 3.91 (br s, 2H), 2.46 (s, 3H), 1.10 (br d, *J* = 1.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.8, 147.4, 143.9, 138.4, 135.5, 131.1, 130.2 (2C), 130.0 (2C), 127.9 (2C), 127.2, 123.3 (2C), 98.3, 56.7, 46.8, 23.5, 21.8; HRMS (ESI) m/z 511.0200 ($[M+H]^+$, 100%), calc'd for $C_{20}H_{20}IN_2O_4S$ 511.0189.



(*Z*)-3-(Iodo(phenyl)methylene)-4-phenyl-1-tosyl-1,2,3,6-tetrahydropyridine (6l). Prepared according to General Procedure C**:** diyne **2l** (139 mg, 0.35 mmol) was reacted with with GaI_3 (157 mg, 0.35 mmol) in DCE (1.8 mL) for 10 min. After work-up, the ^{1}H NMR spectrum showed the crude isolate to be a 6:4 mixture of **6l** and **7**. Purification via flash chromatography gave **6l** (9:1 pet ether:EtOAc, R_f 0.4, 75 mg, 41%) as a white solid and **7** (R_f 0.3, 64 mg, 46%) as a bright yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 6.85 – 6.77 (overlap, 3H), 6.78 – 6.73 (overlap, 3H), 6.68 (AA'BB'C m, 2H), 6.57 (dd, *J* = 7.7, 1.2 Hz, 2H), 5.53 (t, *J* = 3.5 Hz, 1H), 4.46 (s, 2H), 4.12 (d, *J* = 3.5 Hz, 2H), 2.39 (s, 3H)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.84, 143.79, 139.7, 138.7, 135.8, 134.9, 130.3 (2C), 130.0 (2C), 128.0, 127.89 (2C), 127.86 (2C), 127.55 (2C), 127.54, 127.2 (2C), 126.6, 106.5, 57.0, 47.3, 21.7; HRMS (ESI) m/z 528.0486 ($[M+H]^+$, 100%), calc'd for $C_{25}H_{23}INO_2S$ 528.494.

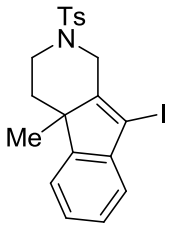


9-Phenyl-2-tosyl-2,3-dihydro-1*H*-indeno[2,1-*c*]pyridine (7). Diyne **2l** (269 mg, 0.67 mmol) was added to an oven-dried, thick-walled tube, placed under Ar atmosphere, and dissolved in anhydrous DCE (0.85 mL). A solution of $GaCl_3$ (0.5 M solution in hexanes, 135 uL, 0.067 mmol, 0.1 eq) was then added dropwise. The solution was stirred at rt overnight (12 h), then diluted with DCM (10 mL), poured into 1 M NaOH (10 mL). The organic layer was separated, dried over $NaSO_4$, filtered and concentrated to a dark brown solid. Purification via flash chromatography gave **7** (4:1, pet ether:EtOAc, R_f 0.45, 220 mg, 82%) as a bright yellow solid. The identity of **7** was confirmed by comparison to reported ^{1}H-NMR spectral data.[9] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.3 Hz, 2H), 7.51 (dd, *J* = 7.8, 7.2 Hz, 2H), 7.47 (d, *J* = 7.4 Hz, 1H), 7.45 – 7.37 (overlap, 3H), 7.31 (d, *J* = 7.5 Hz, 1H), 7.23 (ddd, *J* = 7.5, 7.4, 1.1 Hz, 1H), 7.18 (d, *J* = 7.8 Hz, 2H), 7.16 (ddd, *J* = 7.5, 7.5, 1.0 Hz, 1H), 6.62 (t, *J* = 4.1 Hz, 1H), 4.46 (s, 2H), 4.18 (d, *J* = 4.1 Hz, 2H), 2.30 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.0, 143.0, 139.1, 137.6, 134.3, 133.9, 133.8, 129.7 (2C), 129.1 (2C), 128.5 (2C), 128.3, 128.2, 127.8 (2C), 127.5, 125.4, 121.9, 120.1, 119.9, 45.5, 44.1, 21.6,

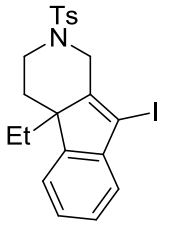


***N*-(Buta-2,3-dien-1-yl)-4-methyl-*N*-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (8).** Diyne **2m** (30 mg, 0.073 mmmol) was added to an oven-dried, thick-walled tube, placed under Ar atmosphere, and dissolved in anhydrous DCE (0.35 mL). A solution of $GaCl_3$ (0.5 M in hexanes, 30 uL, 0.015

mmol, 0.1 eq) was added dropwise. The solution was stirred at rt 1.5 h, then diluted with DCM (10 mL), then poured into 1 M NaOH (10 mL). The organic layer was separated, dried over $NaSO_4$, filtered and concentrated to a light brown solid. Purification via flash chromatography gave **8** (4:1, pet ether:EtOAc, R_f 0.65, 20 mg, 81%) as a white solid. The identity of the compound was confirmed by comparison to reported ^{1}H-NMR spectral data.[11] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.34 – 7.19 (m, 5H), 7.08 (dd, *J* = 8.1, 1.6 Hz, 2H), 5.11 (tt, *J* = 7.2, 6.7 Hz, 1H), 4.80 (dt, *J* = 6.7, 2.4 Hz, 2H), 4.37 (s, 2H), 3.93 (dt, *J* = 7.2, 2.4 Hz, 2H), 2.33 (s, 3H).

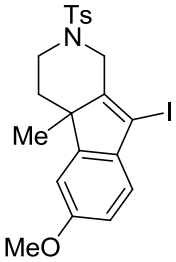


9-Iodo-4a-methyl-2-tosyl-2,3,4,4a-tetrahydro-1*H*-indeno[2,1-*c*]pyridine (9b). Prepared according to General Procedure D: diyne **2b** (65 mg, 0.19 mmol) was reacted with GaI_3 (87 mg, 0.19 mmol, 1.0 eq) for 30 min at rt, followed by the addition of TFA (0.19 mmol, 15 uL) and heating to 50 °C for 2 h. Purification via flash chromatography afforded pure **9b** (4:1 pet ether:EtOAc, R_f 0.5, 81 mg, 91%) as a pale yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.37 – 7.30 (overlap, 4H), 7.28 – 7.20 (overlap, 2H), 4.76 (dd, *J* = 13.0, 1.6 Hz, 1H), 3.79 (dddd, *J* = 12.6, 4.6, 2.5, 1.6 Hz, 1H), 3.40 (d, *J* = 13.0 Hz, 1H), 2.87 (ddd, *J* = 12.9, 12.7, 2.6 Hz, 1H), 2.42 (s, 3H), 2.01 (ddd, *J* = 13.1, 2.5, 2.5 Hz, 1H), 1.30 (ddd, *J* = 13.1, 12.9, 4.6 Hz, 1H), 1.14 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.2, 150.7, 143.9, 142.9, 134.2, 129.9 (2C), 127.9 (2C), 127.6, 126.8, 123.3, 121.2, 92.4, 50.4, 46.4, 42.2, 35.6, 21.8, 19.9. HRMS (ESI) m/z 466.0331 ($[M+H]^+$, 100%), calc'd for $C_{20}H_{21}INO_2S$ 466.0338.

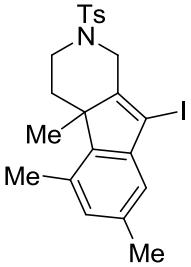


4a-Ethyl-9-iodo-2-tosyl-2,3,4,4a-tetrahydro-1*H*-indeno[2,1-*c*]pyridine (9d). Precursor vinyl iodide **6d** was prepared according to General Procedure C, then subjected General Procedure E without purification: crude **6d** (25 mg, 0.052 mmol) was dissolved in DCE (0.25 mL), treated with TfOH (5 uL, 0.052 mmol), and stirred at rt for 4 h. Purification via flash chromatography afforded pure **9e** ($CHCl_3$, R_f 0.8, 18 mg, 73%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.37 – 7.28 (overlap, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.25 (ddd, *J* = 7.2, 7.2, 1.4 Hz, 1H), 7.19 (d, *J* = 7.4 Hz, 1H), 4.75 (dd, *J* = 12.9, 1.3 Hz, 1H), 3.75 (dddd, *J* = 12.7, 4.8, 2.5, 1.3 Hz, 1H), 3.31 (d, *J* = 12.9 Hz, 1H), 2.92 (ddd, *J* = 12.8, 12.7, 2.6 Hz, 1H), 2.42 (s, 3H), 2.07 (ddd, *J* = 13.3, 2.6, 2.5 Hz, 1H), 1.82 (dq, *J* = 13.7, 7.3 Hz, 1H), 1.70 (dq, *J* = 13.7, 7.3 Hz, 1H), 1.34 (ddd, *J* = 13.3, 12.8, 4.8 Hz, 1H), 0.26 (dd, *J* = 7.3, 7.3 Hz, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 149.35, 149.26, 144.3, 143.9,

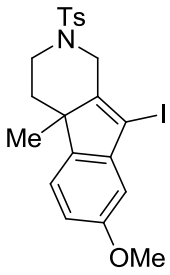
134.4, 130.0 (2C), 128.0 (2C), 127.67 126.8, 123.1, 121.3, 92.9, 54.6, 46.5, 42.0, 35.1, 26.0, 21.8, 7.6; HRMS (ESI) m/z 480.0503 ([M+H]$^+$, 100%), calc'd for $C_{21}H_{23}INO_2S$ 480.0494.



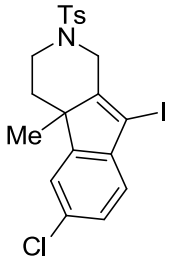
9-Iodo-6-methoxy-4a-methyl-2-tosyl-2,3,4,4a-tetrahydro-1*H*-indeno[2,1-*c*]pyridine (9e). Precursor vinyl iodide **6e** was prepared according to General Procedure C, then subjected General Procedure E without purification: crude **6e** (24 mg, 0.048 mmol) was dissolved in DCE (0.25 mL), treated with TfOH (4 uL, 0.048 mmol), and stirred at room temp for 45 min. Purification via flash chromatography afforded pure **9e** ($CHCl_3$, R_f 0.8, 14 mg, 58%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) 7.74 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 1H), 6.87 (dd, *J* = 8.3, 1.7 Hz, 1H), 6.81 (d, *J* = 1.7 Hz, 1H), 4.70 (d, *J* = 13.0 Hz, 1H), 3.83 (s, 3H), 3.78 (br d, *J* = 12.3 Hz, 1H), 3.38 (d, *J* = 13.0 Hz, 1H), 2.86 (dd, *J* = 13.1, 12.3 Hz, 1H), 2.42 (s, 3H), 1.96 (br d, *J* = 13.3 Hz, 1H), 1.32 (ddd, *J* = 13.3, 13.1, 4.4 Hz, 1H), 1.12 (s, 3H); δ ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.5, 152.7, 148.4, 143.8, 136.0, 134.2, 129.9 (2C), 127.9 (2C), 123.8, 112.4, 108.2, 91.7, 55.9, 50.5, 46.5, 42.3, 35.7, 21.8, 20.1; HRMS (ESI) m/z 496.0438 ([M+H]$^+$, 100%), calc'd for $C_{21}H_{23}INO_3S$ 496.0443.



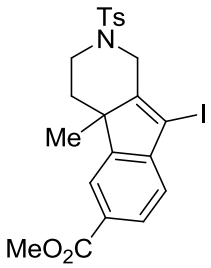
9-Iodo-4a,5,7-trimethyl-2-tosyl-2,3,4,4a-tetrahydro-1*H*-indeno[2,1-*c*]pyridine (9f). Prepared according to General Procedure D: diyne **2f** (18 mg, 0.049 mmol) was reacted with GaI_3 (22 mg, 0.049 mmol, 1.0 eq) for 10 min at rt, followed by the addition of TFA (4 uL, 0.049 mmol) and heating to 50 °C for 2 h. Purification via flash chromatography afforded pure **9f** ($CHCl_3$, R_f 0.85, 22 mg, 91%) as a pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 6.99 (s, 1H), 6.84 (s, 1H), 4.73 (dd, *J* = 13.1, 1.3 Hz, 1H), 3.76 (dddd, *J* = 12.6, 4.6, 2.6, 1.3 Hz, 1H), 3.41 (d, *J* = 13.1 Hz, 1H), 2.86 (ddd, *J* = 12.8, 12.6, 2.6 Hz, 1H), 2.43 (s, 3H), 2.37 (s, 3H), 2.36 (s, 3H), 2.27 (ddd, *J* = 13.1, 2.6, 2.6 Hz, 1H), 1.40 (ddd, *J* = 13.1, 12.8, 4.6 Hz, 1H), 1.19 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.8, 145.4, 143.9, 143.4, 137.4, 134.2, 132.4, 130.0, 129.9 (2C), 128.0 (2C), 121.9, 93.0, 50.9, 46.5, 42.1, 34.1, 21.8, 21.4, 18.6, 17.8; HRMS (ESI) m/z 494.0669 ([M+H]$^+$, 100%), calc'd for $C_{22}H_{25}INO_2S$ 494.0651.



9-Iodo-7-methoxy-4a-methyl-2-tosyl-2,3,4,4a-tetrahydro-1*H*-indeno[2,1-*c*]pyridine (9g). Precursor vinyl iodide **6g** was prepared according to General Procedure C, then subjected General Procedure E without purification: crude **6g** (29 mg, 0.058 mmol) was dissolved in DCE (0.25 mL), treated with TfOH (5 uL, 0.058 mmol), with heating to 50 °C for 40 min. Purification via flash chromatography afforded pure **9e** (CH_2Cl_2, R_f 0.8, 15 mg, 52%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 8.1 Hz, 1H), 6.88 (d, *J* = 2.4 Hz, 1H), 6.79 (dd, *J* = 8.1, 2.4 Hz, 1H), 4.74 (dd, *J* = 13.0, 1.2 Hz, 1H), 3.86 (s, 3H), 3.78 (dddd, *J* = 12.7, 4.6, 2.1, 1.2 Hz, 1H), 3.38 (d, *J* = 13.0 Hz, 1H), 2.85 (ddd, *J* = 12.8, 12.7, 2.4 Hz, 1H), 2.43 (s, 3H), 1.98 (ddd, *J* = 13.2, 2.4, 2.1 Hz, 1H), 1.29 (ddd, *J* = 13.2, 12.8, 4.6 Hz, 1H), 1.12 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.8, 151.9, 144.5, 143.9, 143.6, 134.3, 130.0 (2C), 128.0 (2C), 121.9, 112.8, 108.8, 92.3, 55.9, 49.7, 46.4, 42.3, 36.0, 21.8, 20.0; HRMS (ESI) m/z 496.0443 ($[M+H]^+$, 100%), calc'd for $C_{21}H_{23}INO_3S$ 496.0443.

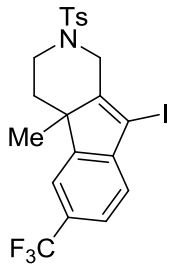


6-Chloro-9-iodo-4a-methyl-2-tosyl-2,3,4,4a-tetrahydro-1*H*-indeno[2,1-*c*]pyridine (9h) Prepared according to General Procedure D: diyne **2h** (50 mg, 0.13 mmol) was reacted with GaI_3 (61 mg, 0.13 mmol, 1.0 eq) for 30 min at rt, followed by the addition of TFA (0.13 mmol, 10 uL) and heating to 50 °C for 3 h. Purification via flash chromatography afforded pure **9h** ($CHCl_3$, R_f 0.8, 63 mg, 97%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.7 Hz, 2H), 7.32 (d, J = 7.7 Hz, 2H), 7.34 – 7.30 (overlapped m, 1H), 7.24 (br d, *J* = 8.1 Hz, 1H), 7.22 (br s, 1H), 4.73 (d, *J* = 13.1 Hz, 1H), 3.79 (br d, *J* = 12.6 Hz, 1H), 3.38 (d, *J* = 13.1 Hz, 1H), 2.86 (br dd, *J* = 12.7, 12.6 Hz, 1H), 2.42 (s, 3H), 1.98 (br d, *J* = 13.3 Hz, 1H), 1.31 (ddd, *J* = 13.3, 12.7, 3.8 Hz, 1H), 1.14 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.6, 151.3, 144.0, 141.6, 134.2, 133.1, 130.0 (2C), 127.9 (2C), 127.8, 124.3, 122.0, 91.2, 50.9, 46.4, 42.2, 35.5, 21.8, 19.9; HRMS (ESI) m/z 499.9962 ($[M+H]^+$, 100%), calc'd for $C_{20}H_{20}{}^{35}ClINO_2S$ 499.9948.

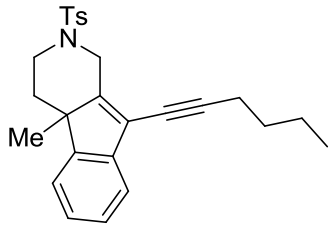


Methyl 9-Iodo-4a-methyl-2-tosyl-2,3,4,4a-tetrahydro-1*H*-indeno[2,1-*c*]pyridine-6-carboxylate (9i). Precursor vinyl iodide **6i** was prepared according to General Procedure C, then subjected General Procedure E without purification: crude **6i** (92 mg, 0.18 mmol) was dissolved in DCE (0.25 mL), treated with TfOH (16 uL, 0.18 mmol), and heated to 60 °C for 20 h. Purification

via flash chromatography afforded pure **9i** (4:1, pet ether:EtOAc, R_f 0.5, 30 mg, 33%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.90 (d, *J* = 1.3 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 2H), 4.78 (dd, *J* = 13.1, 1.1 Hz, 1H), 3.93 (s, 3H), 3.81 (dddd, *J* = 12.6, 4.5, 2.2, 1.1 Hz, 1H), 3.42 (d, *J* = 13.1 Hz, 1H), 2.89 (ddd, *J* = 12.9, 12.6, 2.3 Hz, 1H), 2.42 (s, 3H), 2.07 (ddd, *J* = 13.3, 2.3, 2.2 Hz , 1H), 1.31 (ddd, *J* = 13.3, 12.9, 4.5 Hz, 1H), 1.18 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.4, 154.4, 151.1, 147.5, 144.0, 134.2, 130.0 (2C), 129.7, 128.5, 127.9 (2C), 123.1, 122.4, 91.6, 52.4, 50.8, 46.4, 42.2, 35.5, 21.8, 19.8; HRMS (ESI) m/z 524.0388 ($[M+H]^+$, 100%), calc'd for $C_{22}H_{23}INO_4S$ 524.0393.

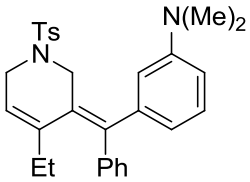


9-Iodo-4a-methyl-2-tosyl-6-(trifluoromethyl)-2,3,4,4a-tetrahydro-1I-indeno[2,1-*c*]pyridine (9j). Precursor vinyl iodide **6j** was prepared according to General Procedure C, then subjected General Procedure E without purification: crude **6j** (25 mg, 0.047 mmol) was dissolved in DCE (0.8 mL), treated with TfOH (4 uL, 0.047 mmol), and heated to 60 °C for 20 h. Purification via flash chromatography afforded pure **9j** (DCM, R_f 0.6, 12 mg, 48%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.1 Hz, 2H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.47 (s, 1H), 7.43 (d, *J* = 7.9 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 2H), 4.78 (dd, *J* = 13.1, 1.1 Hz, 1H), 3.82 (dddd, *J* = 12.6, 4.6, 2.0, 1.1 Hz, 1H), 3.41 (d, *J* = 13.1 Hz, 1H), 2.89 (ddd, *J* = 12.8, 12.6, 2.4 Hz, 1H), 2.43 (s, 3H), 2.06 (ddd, *J* = 13.3, 2.4, 2.0 Hz, 1H), 1.33 (ddd, *J* = 13.3, 12.8, 4.6 Hz, 1H), 1.18 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.9, 151.1, 146.4 (q, $^5J_{C-F}$ = 1.5 Hz), 144.1, 134.1, 130.0 (2C), 129.2 (q, $^2J_{C-F}$ = 32.1 Hz), 127.9 (2C), 126.8 (q, $^1J_{C-F}$ = 272.1 Hz), 125.2 (q, $^3J_{C-F}$ = 3.8 Hz), 123.5, 118.2 (q, $^3J_{C-F}$ = 3.9 Hz), 91.1, 50.9, 46.3, 42.1, 35.5, 21.8, 19.8; HRMS (ESI) m/z 534.0190 ($[M+H]^+$, 100%), calc'd for $C_{21}H_{20}F_3INO_2S$ 534.0212.



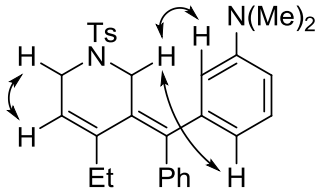
9-(Hex-1-yn-1-yl)-4a-methyl-2-tosyl-2,3,4,4a-tetrahydro-1*H*-indeno[2,1-*c*]pyridine (10b). Vinyl iodide **9b** (20 mg, 0.043 mmol), $Pd(PPh_4)_3$ (2.5 mg, 0.0022 mmol, 0.05 eq), and CuI (0.8 mg, 0.0043 mmol, 0.1 eq) were added to a round bottom flask, then the headspace was purged with argon and sealed with a septum. Piperidine (0.15 mL) was added, followed by hex-1-yne (7.4 uL, 0.064 mmol, 1.5 eq). The mixture was stirred 16 hr at 60 °C, then allowed to cool to rt, diluted with DCM (10 mL) and washed with 1 N HCl (10 mL). The organic layer was separated, dried over Na_2SO_4 and concentrated to a brown solid.

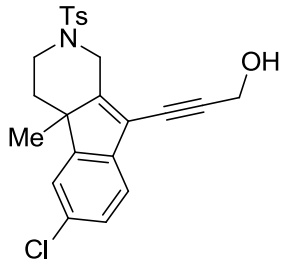
Purification by flash chromatography afforded **10b** (pet ether:EtOAc, 9:1, R_f 0.35, 8 mg, 44%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.45 (br d, *J* = 7.5 Hz, 1H), 7.32 – 7.26 (overlapped m, 1H), 7.29 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 7.0 Hz, 1H) 7.21 (dd, *J* = 7.5, 7.0 Hz, 1H), 4.93 (d *J* = 12.8 Hz, 1H), 3.76 (br d, *J* = 12.4 Hz, 1H), 3.37 (d, *J* = 12.8 Hz, 1H), 2.86 (ddd, *J* = 13.0, 12.4, 2.3 Hz, 1H), 2.52 (t, *J* = 7.0 Hz, 2H), 2.40 (s, 3H), 2.02 (ddd, *J* = 13.3, 2.3, 2.1 Hz, 1H), 1.67 (tt, *J* = 7.1, 7.0 Hz, 2H), 1.57 (qt, *J* = 7.3, 7.1 Hz, 2H), 1.25 (ddd, *J* = 13.3, 13.0, 4.6 Hz, 1H), 1.12 (s, 3H), 1.00 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.8, 148.7, 143.7, 141.9, 134.4, 129.8 (2C), 128.0 (2C), 127.3, 126.0, 121.3, 121.1, 120.1, 98.3, 72.8, 47.8, 43.6, 42.1, 35.6, 31.1, 22.3, 21.7, 19.9, 19.6, 13.9; HRMS (ESI) m/z 420.2003 ($[M+H]^+$, 100%), calc'd for $C_{26}H_{30}NO_2S$ 420.1997.



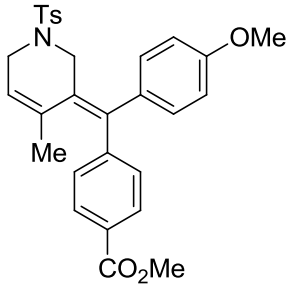
(Z)-3-((4-Ethyl-1-tosyl-1,6-dihydropyridin-3(2H)-ylidene)(phenyl)methyl)-*N*,*N*-dimethylaniline (10d). The precursor vinyl iodide **6d** was prepared according to General Procedure C, then subjected to Suzuki coupling without purification: diyne **2d** (90 mg, 0.256 mmol) was treated with GaI_3 (115 mg, 0.256 mmol) in DCE (0.9 mL) following General Procedure C. When TLC indicated all diyne had been converted to **6d**, the reaction was diluted with DCM (10 mL) and washed with 1 M NaOH (10 mL). The organic layer was separated, dried over Na_2SO_4, filtered, and the solvent removed *in vacuo* to yield a yellow solid. To this crude material in a 10 mL thick-walled vial, $Pd(PPh_4)_3$ (3.0 mg, 0.0026 mmol, 0.01 eq), K_2CO_3 (178 mg, 1.3 mmol, 5 eq), and (4-methoxyphenyl)boronic acid (53 mg, 0.32 mmol, 1.25 eq) were added. Toluene (2.4 mL), water (1.6 mL), and ethanol (250 uL) were then added and the solution was purged with Ar for 15 min, then the vial was sealed with a Teflon cap and heated to 80° C with stirring for 3 h. The reaction was then allowed to cool to rt, diluted with DCM (10 mL) and washed with water (10 mL). The organic layer was separated, dried over Na_2SO_4, and the solvent removed to provide an orange solid. Purification by flash chromatography afforded pure **10d** (DCM 0.5% formic acid, R_f 0.1, then DCM with 0.5% TEA, R_f 0.8, 65 mg, 54%) as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.17 – 7.09 (overlap, 4H), 6.72 (br d, *J* = 7.8 Hz, 2H), 6.68 (dd, *J* = 8.2, 2.3 Hz, 1H), 6.34 (br d, *J* = 2.3 Hz, 1H), 6.33 (d, *J* = 7.8 Hz, 1H), 5.50 (t, *J* = 3.1 Hz, 1H), 4.03 (br s, 2H), 4.00 (s, 2H), 2.93 (s, 6H), 2.41 (s, 3H), 1.48 (br q, *J* = 7.3 Hz, 2H), 0.68 (t, *J* = 7.3 Hz, 3H); δ ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.4, 143.2, 142.80, 142.79, 142.6, 140.8, 136.3, 130.5 (2C), 129.8 (2C), 128.9, 127.64 (2C), 127.63 (2C), 127.55, 127.45, 122.3,

119.2, 114.9, 112.2, 48.2, 46.1, 40.8 (2C), 27.7, 21.7, 13.7; HRMS (ESI) m/z 473.2271 ([M+H]$^+$, 100%), calc'd for $C_{29}H_{33}N_2O_2S$ 473.2263. The stereochemistry of the exocyclic, tetrasubstituted alkene was confirmed by an NOE (NOESY) between the dimethylaniline protons ortho to the exocyclic double bond (δ 6.34 and 6.3) and the methylene adjacent to the ring nitrogen (δ 4.00). The vinyl hydrogen (δ 5.50), in turn, showed an NOE with the other ring methylene (δ 4.03), confirming the assignments of these two methylenes (*Inset*).



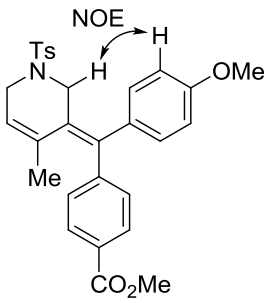


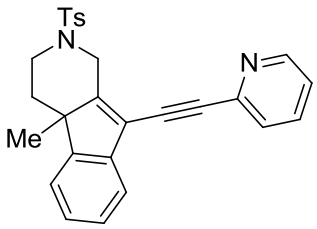
3-(6-Chloro-4a-methyl-2-tosyl-2,3,4,4a-tetrahydro-1*H*-indeno[2,1-*c*]pyridin-9-yl)prop-2-yn-1-ol (10h). Vinyl iodide **9h** (23 mg, 0.046 mmol), $Pd(PPh_4)_3$ (3 mg, 0.0023 mmol, 0.05 eq), and CuI (1 mg, 0.0046 mmol, 0.1 eq) were added to a round bottom flask, then the headspace was purged with argon and the flask sealed with a septum. Piperidine (0.15 mL) was then added, followed by propargyl alcohol (8 uL, 0.14 mmol, 3 eq). The mixture was stirred 4 h at 60 °C, then allowed to cool to rt. The reaction mixture was diluted with DCM (20 mL) and washed with 1 N HCl (20 mL). The organic layer was separated, dried over Na_2SO_4 and concentrated to a brown solid. Purification by flash chromatography afforded **10h** ($CHCl_3$:MeOH, 95:5, R_f 0.8, 16.2 mg, 82%) as a colorless glassy solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.29 (br dd, *J* = 8.1, 1.9 Hz, 1H), 7.23 (br d, *J* = 1.9 Hz, 1H), 4.90 (dd, *J* = 12.9, 1.5 Hz, 1H), 4.58 (d, *J* = 6.2, 2H), 3.78 (dddd, *J* = 12.6, 4.6, 2.4, 1.5 Hz, 1H), 3.32 (d, *J* = 12.9 Hz, 1H), 2.82 (ddd, *J* = 12.8, 12.6, 2.5 Hz, 1H), 2.42 (s, 3H), 2.02 (ddd, *J* = 13.1, 2.5, 2.4 Hz, 1H), 1.90 (t, *J* = 6.2, O*H*), 1.30 (ddd, *J* = 13.1, 12.8, 4.6 Hz, 1H), 1.12 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.2, 151.3, 144.0, 139.7, 133.9, 132.4, 130.0 (2C), 127.9 (2C), 127.7, 122.24, 122.16, 118.4, 95.3, 77.4, 51.9, 48.4, 43.5, 42.1, 35.6, 21.8, 19.8; HRMS (ESI) m/z 428.1070 ([M+H]$^+$, 100%), calc'd for $C_{23}H_{23}{}^{35}ClNO_3S$ 428.1087.



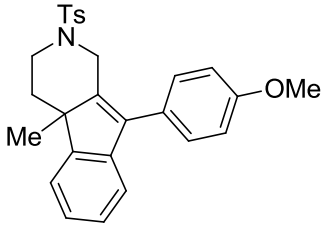
(*Z*)-Methyl 4-((4-Methoxyphenyl)(4-methyl-1-tosyl-1,6-dihydropyridin-3(2H)-ylidene)methyl)benzoate (10i). The precursor vinyl iodide **6i** was prepared according to General Procedure C, then subjected to Suzuki coupling without purification: diyne **2i** (65 mg, 0.16 mmol) was treated with GaI_3 (79 mg, 0.16 mmol) in DCE (0.9 mL) following General Procedure C. When TLC indicated all diyne had been

converted to **6i**, the reaction mixture was diluted with DCM (20 mL) and washed with 1 M NaOH (20 mL). The organic layer was separated, dried over Na_2SO_4, filtered, and the solvent removed *in vacuo* to yield a yellow solid. To this crude material in a 10 mL thick-walled vial, $Pd(PPh_4)_3$ (1.0 mg, 0.009 mmol, 0.005 eq), K_2CO_3 (121 mg, 0.22 mmol, 5 eq), and (4-methoxyphenyl)boronic acid (33 mg, 0.22 mmol, 1.25 eq) were added. Toluene (2 mL), water (1.2 mL), and ethanol (200 uL) were then added and the solution was purged with Ar for 15 min, then the vial was sealed with a Teflon cap and heated to 80° C with stirring for 4 h. After cooling to rt, the reaction mixture was diluted with DCM (20 mL) and washed with water (20 mL). The organic layer was separated, dried over Na_2SO_4, and the solvent removed to provide an orange solid. Purification by flash chromatography afforded pure **10i** (pet ether:EtOAc, 4:1, R_f 0.4, 73 mg, 88%) as a colorless solid. ^{1}H NMR (500 MHz, $CDCl_3$) 7.82 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 6.86 (s, 4H), 6.73 (d, *J* = 8.2 Hz, 2H), 5.49 (br s, 1H), 4.03 (br s, 2H), 4.01 (s, 2H), 3.90 (s, 3H), 3.84 (s, 3H), 2.42 (s, 3H), 1.18 (br s, 3H); δ ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.1, 159.5, 148.0, 143.4, 140.2, 136.4, 133.7, 133.6, 131.9 (2C), 130.9 (2C), 129.8 (2C), 129.7, 129.2, 129.0 (2C), 127.6 (2C), 125.1, 113.9 (2C), 55.5, 52.3, 47.6, 46.3, 22.9, 21.8; HRMS (ESI) m/z 504.1839 ($[M+H]^+$, 100%), calc'd for $C_{29}H_{30}NO_5S$ 504.1845. The stereochemistry of the exocyclic, tetrasubstituted alkene was confirmed by NMR experiments. An H,H-COSY spectrum enabled assignments of the sets of aromatic resonances to specific aryl rings and, together with the HSQC experiment, established that the 4H singlet at δ 6.86 was from the anisole ring. The 2H doublet at δ 7.82 for the benzoate hydrogens ortho to the carbonyl group, which showed coupling to the carbonyl carbon (δ 167.1) in the HMBC spectrum, coupled to the 2H doublet at δ 6.73 in the COSY spectrum allowing assignment of this aryl system. The 2H doublet at δ 7.52 in turn coupled to the 2H doublet at δ 7.24, with the diagnostic NOE (NOESY) to the tosyl methyl singlet, enabling assignment of the tosyl protons of the aryl ring. The 4H singlet at δ 6.86 was therefore assigned as the four aryl protons of the anisole ring which are coincident, an assignment supported by the coupling between this signal and the resonance at δ 159.5 for the oxygenated anisole carbon in the HBMC spectrum. An NOE was observed in the NOESY spectrum from the 4H aromatic singlet (δ 6.86) to the methylene singlet at δ 4.01, confirming the cis relative stereochemistry between the anisole ring and this methylene (*inset*).



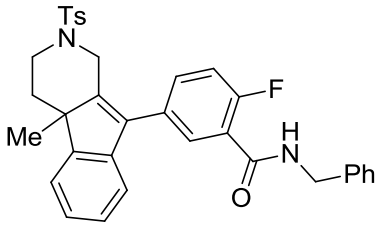


4a-Methyl-9-(pyridin-2-ylethynyl)-2-tosyl-2,3,4,4a-tetrahydro-1*H*-indeno[2,1-*c*]pyridine (11b). Vinyl iodide **9b** (45 mg, 0.97 mmol), $Pd(PPh_4)_3$ (6 mg, 0.005 mmol, 0.05 eq), and CuI (2 mg, 0.01 mmol, 0.1 eq) were added to a round bottom flask. The headspace was purged with argon and the flask sealed with a septum. Piperidine (0.3 mL) was added, followed by 2-ethynylpyridine (30 uL, 0.3 mmol, 3 eq). The mixture was stirred 1 hr at rt, then diluted with DCM (20 mL) and washed with 1 N HCl (20 mL). The organic layer was separated, dried over Na_2SO_4 and concentrated to a give black oil. Purification by flash chromatography afforded **11b** ($CHCl_3$ with 0.5% TEA and 0.5% MeOH, R_f 0.6, 30 mg, 70%) as a light brown solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 (br d, *J* = 4.9 Hz, 1H), 7.75 (d, J = 8.1 Hz, 2H), 7.74 (ddd, *J* = 7.7, 7.7, 1.8 Hz, 1H), 7.63 – 7.60 (overlap, 2H), 7.33 (ddd, *J* = 7.4, 7.2, 1.5 Hz, 1H), 7.32 – 7.26 (overlap, 2H), 7.25 (ddd, *J* = 7.4, 7.2, 0.8 Hz, 1H), 5.04 (dd, *J* = 13.0, 1.7 Hz, 1H), 3.81 (dddd, *J* = 12.7, 4.4, 2.2, 1.7 Hz, 1H), 3.45 (d, *J* = 13.0 Hz, 1H), 2.90 (ddd, *J* = 12.9, 12.7, 2.4 Hz, 1H), 2.38 (s, 3H), 2.08 (ddd, *J* = 13.3, 2.4, 2.2 Hz, 1H), 1.34 (ddd, *J* = 13.3, 12.9, 4.4 Hz, 1H), 1.17 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.5, 151.6, 150.3, 143.8, 143.3, 140.9, 136.5, 134.2, 129.9 (2C), 128.0, 127.9 (2C), 127.5, 126.4, 123.3, 121.51, 121.49, 118.9, 95.7, 81.4, 48.5, 43.7, 42.1, 35.8, 21.7, 19.9; HRMS (ESI) m/z 441.1637 ($[M+H]^+$, 100%), calc'd for $C_{27}H_{25}N_2O_2S$ 441.1637.



9-(4-Methoxyphenyl)-4a-methyl-2-tosyl-2,3,4,4a-tetrahydro-1*H*-indeno[2,1-*c*]pyridine (12b). Vinyl iodide **9b** (25 mg, 0.054 mmol), $Pd(PPh_4)_3$ (0.3 mg, 0.0003 mmol, 0.005 eq), K_2CO_3 (37.3 mg, 0.27 mmol, 5 eq), and (4-methoxyphenyl)boronic acid (10.3 mg, 0.068 mmol, 1.25 eq) were added to a 10 mL thick-walled vial. Toluene (0.5 mL), water (0.3 mL), and ethanol (50 uL) were added and the solution was then purged with Ar for 15 min. The flask was sealed with a Teflon cap and heated to 80° C with stirring for 2 h, then allowed to cool to rt. The reaction mixture was then diluted with DCM (20 mL) and washed with water (20 mL). The organic layer was separated, dried over Na_2SO_4 and the solvent removed *in vacuo* to yield an orange solid. Purification by flash chromatography afforded **12b** (pet ether:EtOAc, 3:1, R_f 0.7, 22 mg, 90%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.2 Hz, 2H), 7.35 (br d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.7 Hz, 2H), 7.30 – 7.20 (overlap, 4H), 7.02 (d, *J* = 8.7 Hz, 2H), 4.73 (dd, *J* = 12.6, 1.5 Hz, 1H), 3.89 (s, 3H), 3.81 (dddd, *J* = 12.3, 4.6, 2.4, 1.5

Hz, 1H), 3.32 (d, *J* = 12.6 Hz, 1H), 2.87 (ddd, *J* = 12.8, 12.3, 2.5 Hz, 1H), 2.43 (s, 3H), 2.13 (ddd, *J* = 13.2, 2.5, 2.4 Hz, 1H), 1.43 (ddd, *J* = 13.2, 12.8, 4.6 Hz, 1H), 1.20 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.4, 152.9, 143.6, 143.1, 141.3, 136.8, 134.2, 130.4 (2C), 129.9 (2C), 127.9 (2C), 127.1, 126.0, 125.6, 121.7, 121.3, 114.4 (2C), 55.5, 47.8, 42.8, 42.3, 36.1, 21.8, 19.9; HRMS (ESI) m/z 446.1790 ($[M+H]^+$, 100%), calc'd for $C_{27}H_{28}NO_3S$ 446.1790.



***N*-Benzyl-2-fluoro-5-(4a-methyl-2-tosyl-2,3,4,4a-tetrahydro-1*H*-indeno[2,1-*c*]pyridin-9-yl)benzamide (13b).** Vinyl iodide **9b** (20 mg, 0.043 mmol), $Pd(PPh_4)_3$ (0.25 mg, 0.0002 mmol, 0.005 eq), K_2CO_3 (29.7 mg, 0.22 mmol, 5 eq), and (3-(benzylcarbamoyl)-4-fluorophenyl)boronic acid (6 mg, 0.054 mmol, 1.25 eq) were added to a 10 mL thick-walled vial. Toluene (0.5 mL), water (0.3 mL), and ethanol (50 uL) were added and the solution was purged with Ar for 15 min. The vial was sealed with a Teflon cap and heated to 80° C with stirring for 2 h, then allowed to cool to rt. The reaction mixture was diluted with DCM (20 mL), then washed with water (20 mL). The organic layer was separated, dried over Na_2SO_4 and the solvent removed *in vacuo* to provide an orange solid. Purification by flash chromatography afforded **13b** (pet ether:EtOAc, 4:1, R_f 0.4, 24 mg, 98%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 7.4, 2.2 Hz, 1H), 7.62 (d, *J* = 8.1 Hz, 2H), 7.53 (ddd, *J* = 8.3, 4.8, 2.3 Hz, 1H), 7.46 – 7.33 (overlap, 5H), 7.32 – 7.22 (overlap, 7H), 7.18 (ddd, *J* = 11.6, 5.6, 5.6 Hz, 1H), 4.73 (d, *J* = 5.6 Hz, 2H), 4.62 (d, *J* = 12.7 Hz, 1H), 3.80 (br ddd, *J* = 12.3, 4.6, 2.1 Hz, 1H), 3.32 (d, *J* = 12.7 Hz, 1H), 2.83 (ddd, *J* = 12.8, 12.3, 2.2 Hz, 1H), 2.42 (s, 3H), 2.15 (ddd, *J* = 13.2, 2.2, 2.1 Hz, 1H), 1.46 (ddd, *J* = 13.2, 12.8, 4.6 Hz, 1H), 1.20 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.3 ($^3J_{C\text{-}F}$ = 3.3 Hz), 160.5 ($^1J_{C\text{-}F}$ = 250.3 Hz), 152.7, 143.9, 143.2, 142.3, 138.2, 135.7, 134.1 ($^2J_{C\text{-}F}$ = 9.3 Hz), 134.0, 132.7 ($^3J_{C\text{-}F}$ = 2.3 Hz), 130.7 ($^4J_{C\text{-}F}$ = 3.3 Hz) 130.0 (2C), 129.0 (2C), 128.1 (2C), 127.8 (2C), 127.7, 127.4, 126.0, 121.75 ($^2J_{C\text{-}F}$ = 12.7 Hz), 121.74, 121.1, 117.1 ($^2J_{C\text{-}F}$ = 24.9 Hz), 48.1, 44.4, 42.7, 42.3, 36.2, 21.8, 19.9; HRMS (ESI) m/z 567.2103 ($[M+H]^+$, 100%), calc'd for $C_{34}H_{32}FN_2O_3S$ 567.2118.

References

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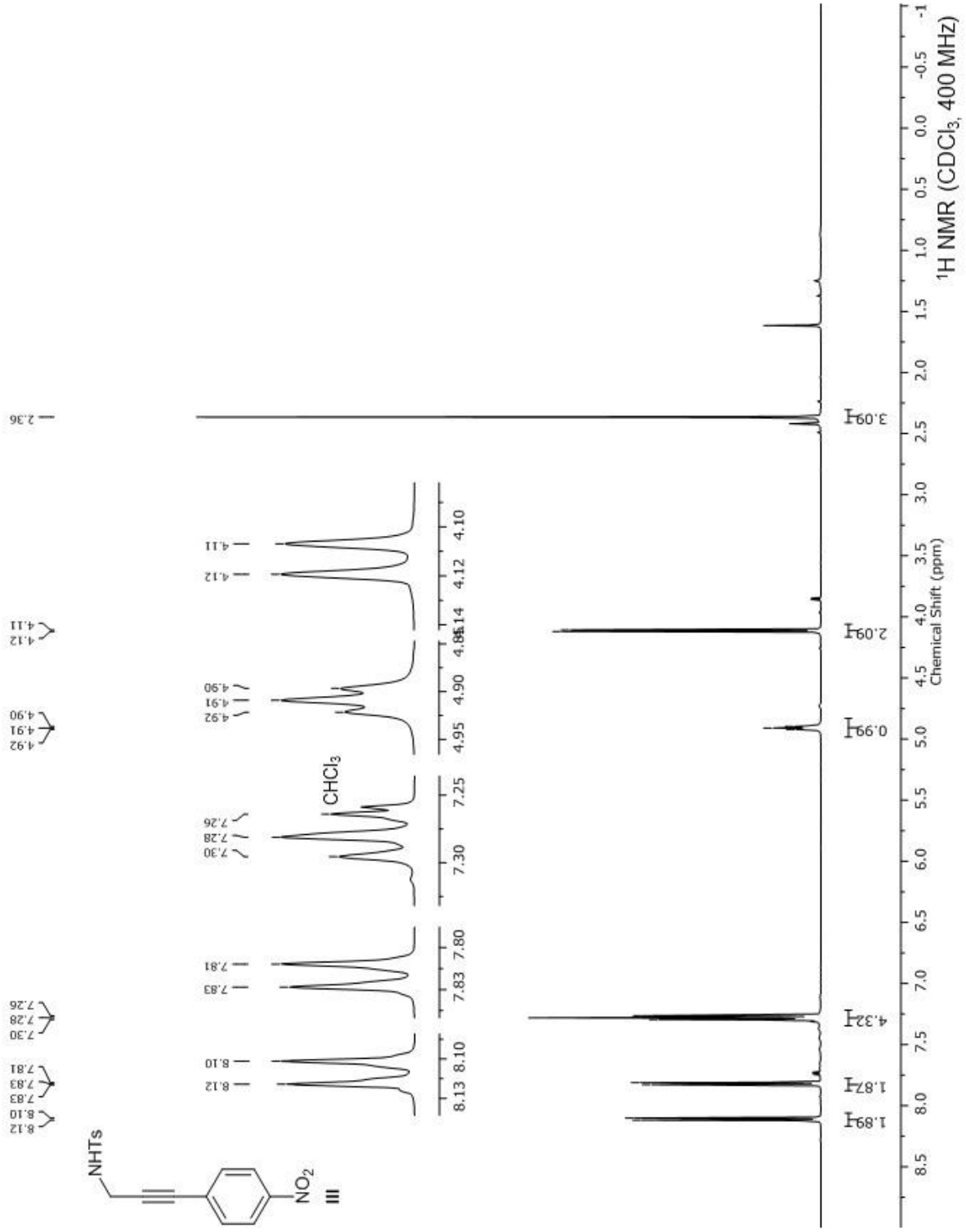
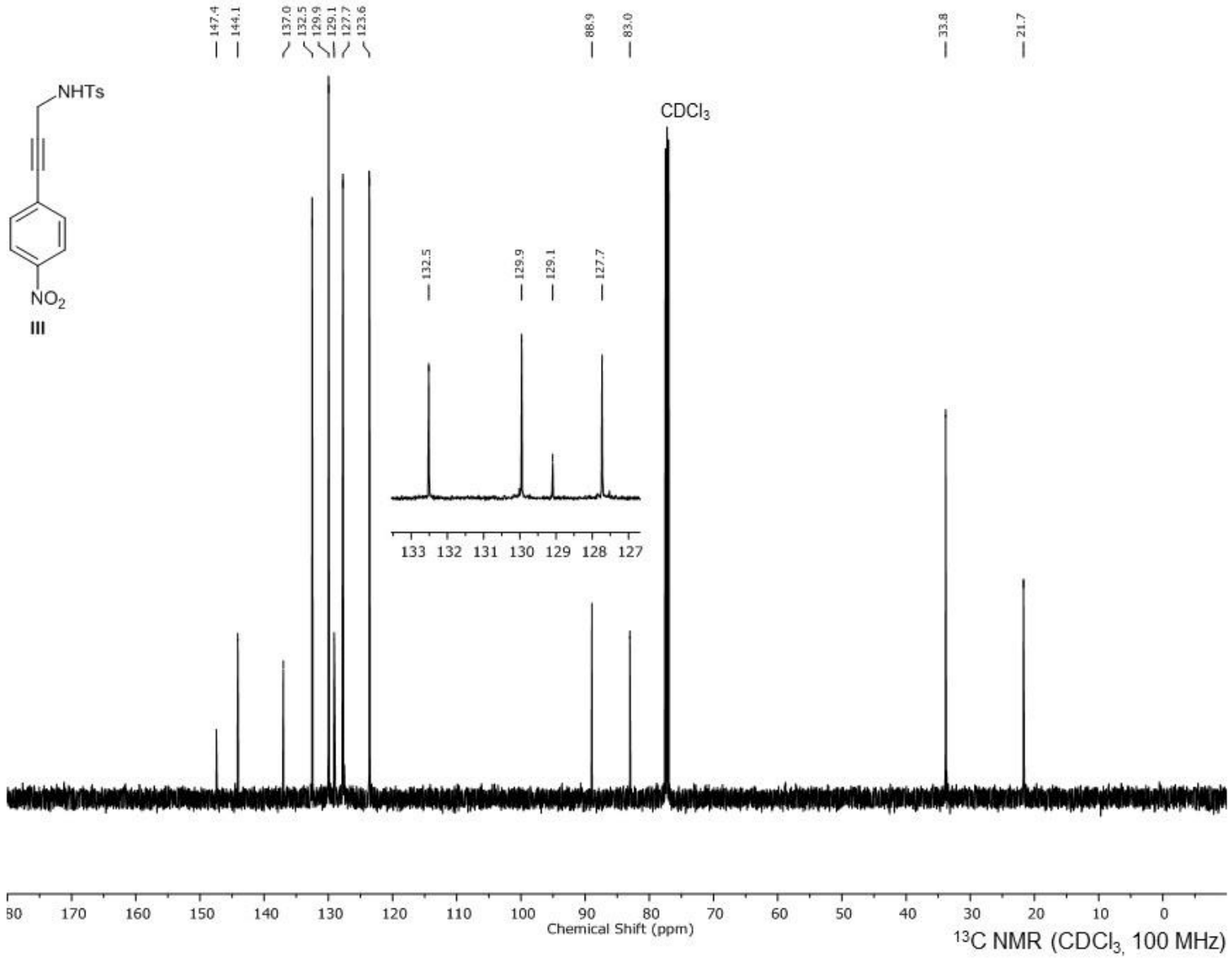
NMR Spectral Data

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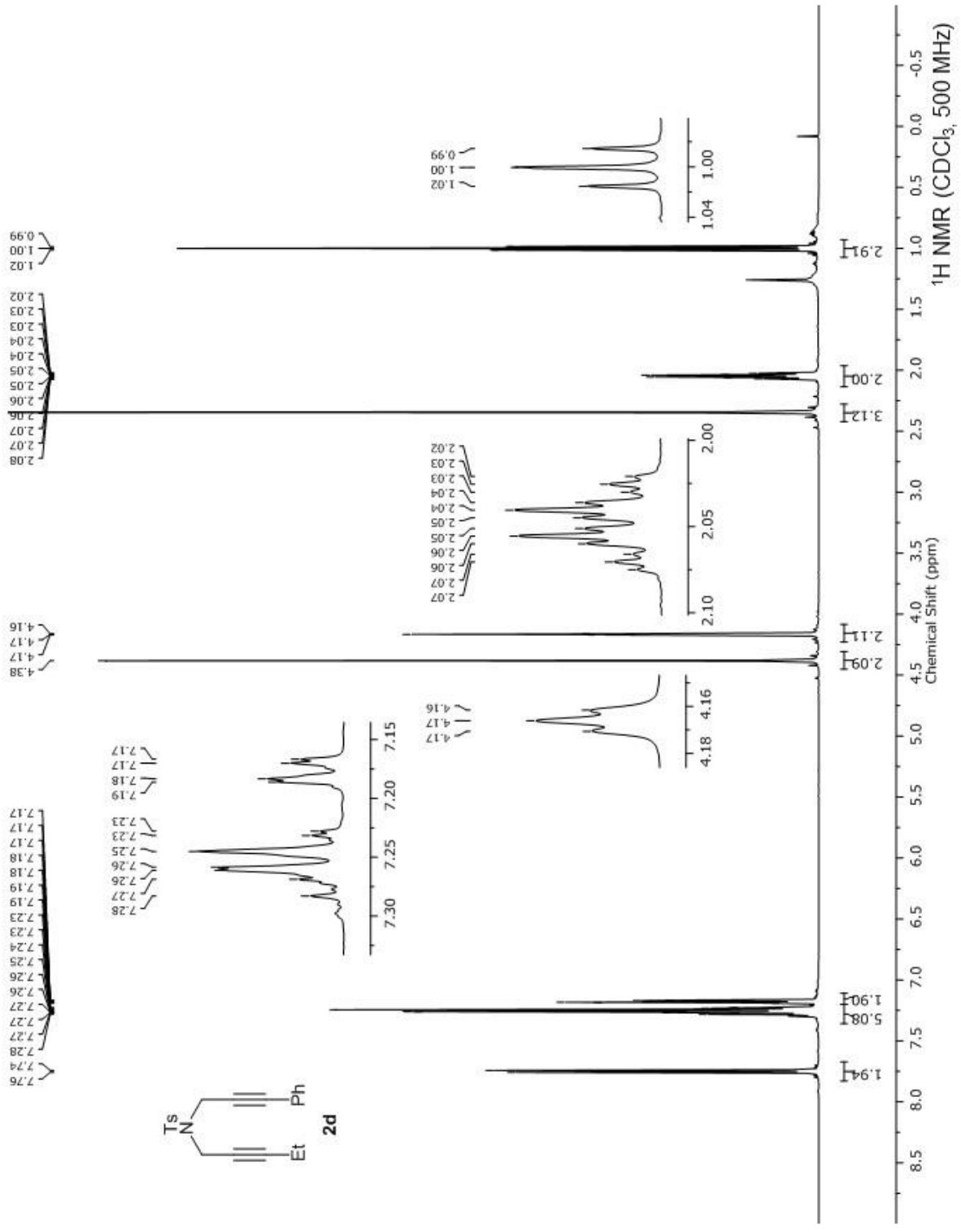
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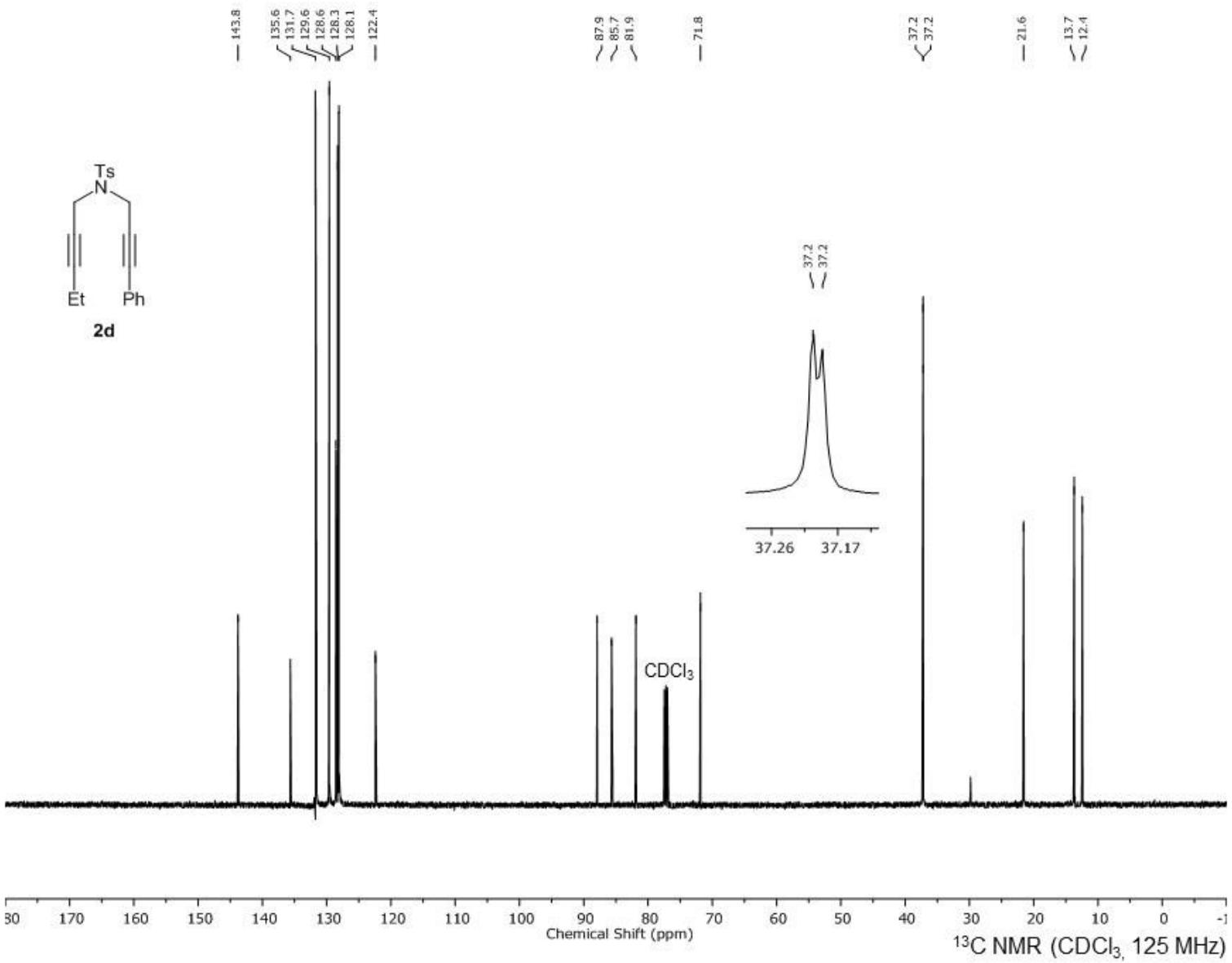
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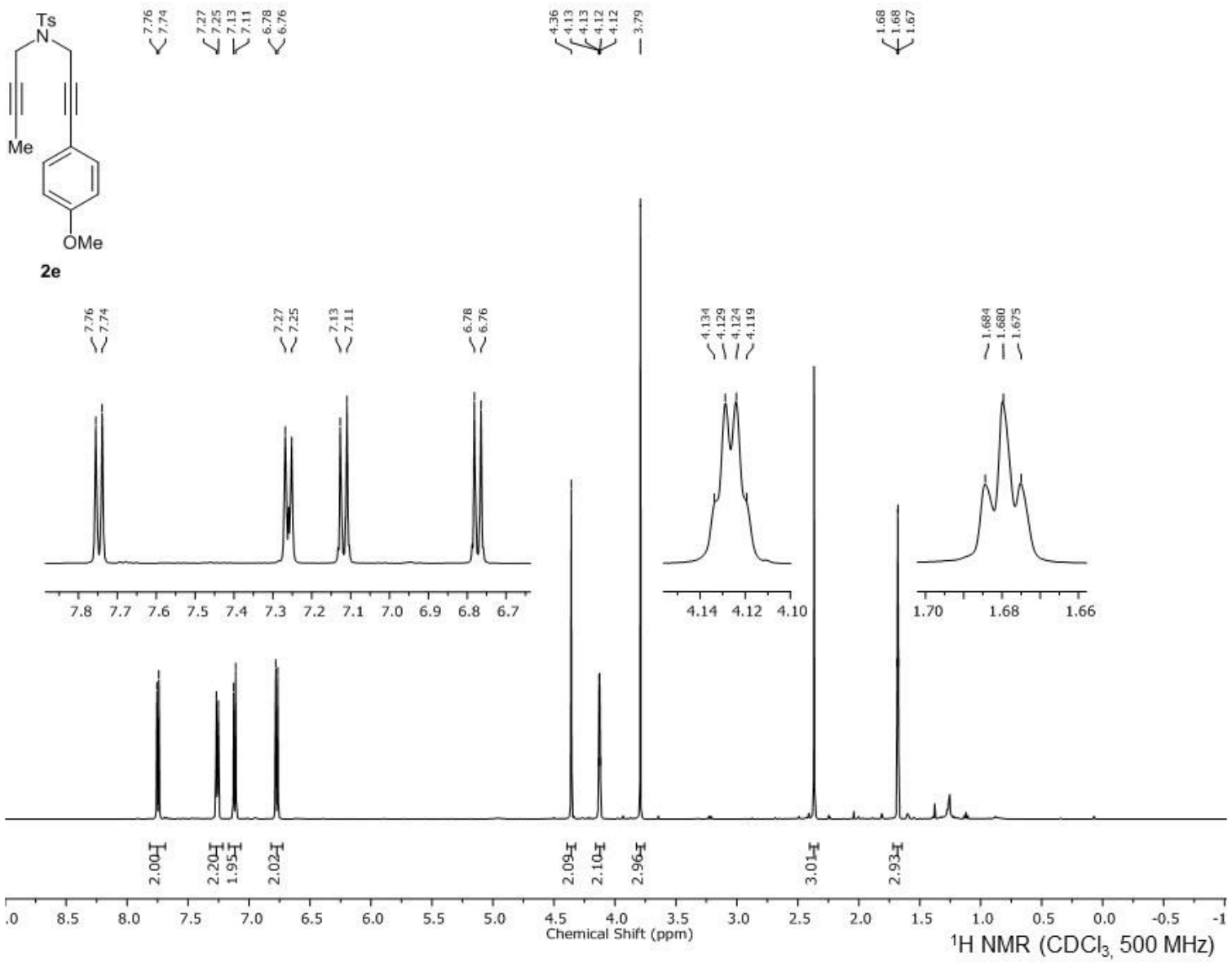
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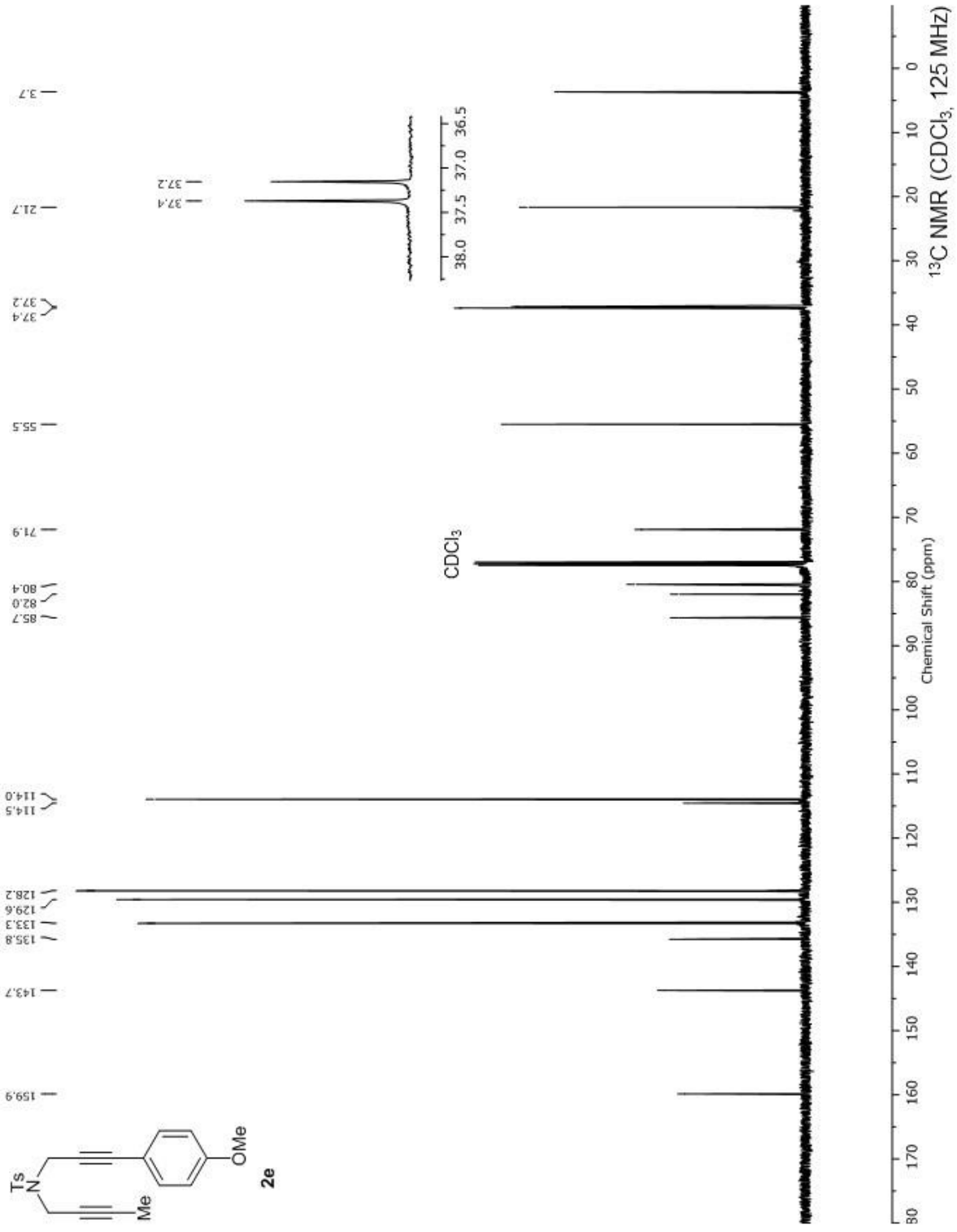
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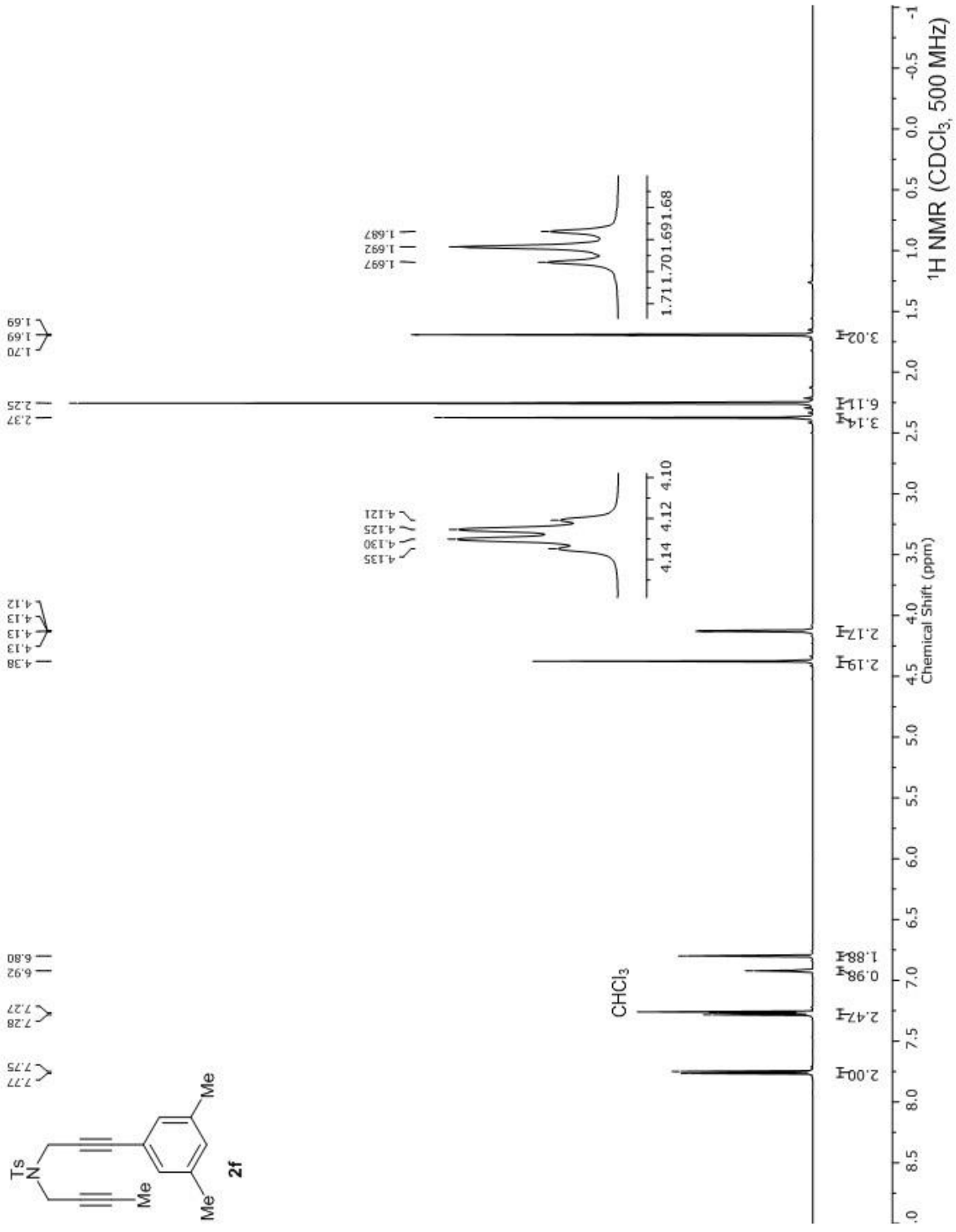
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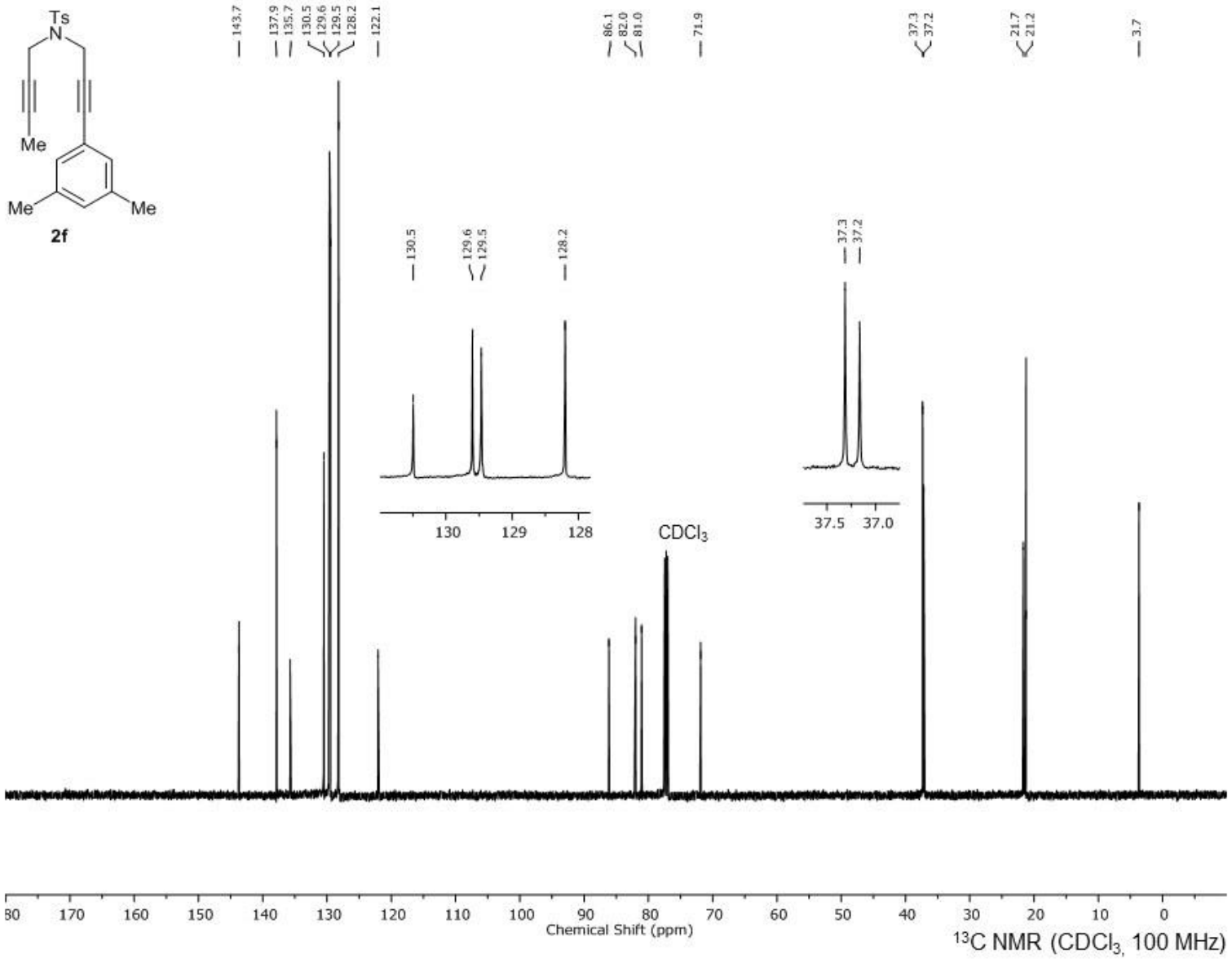
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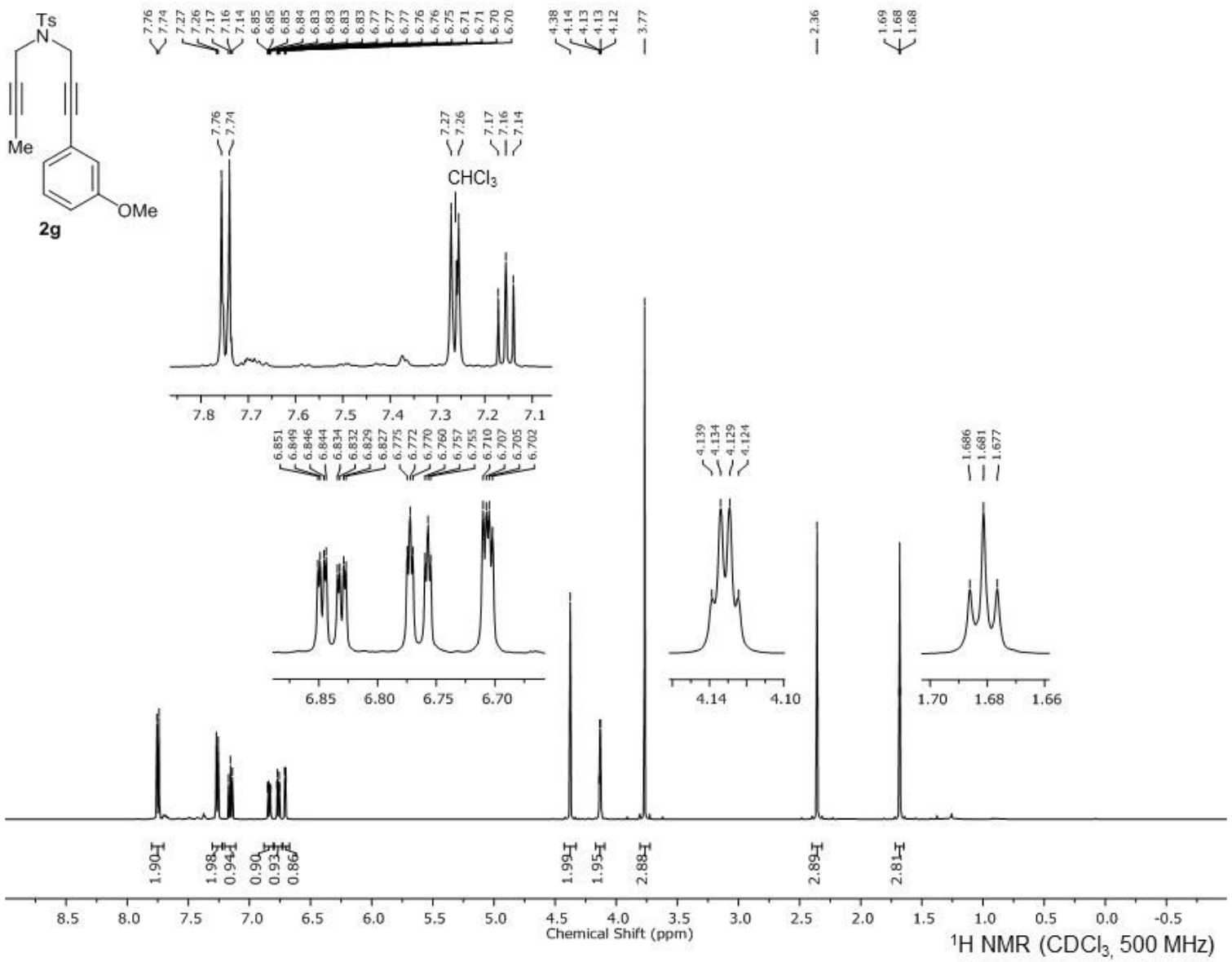
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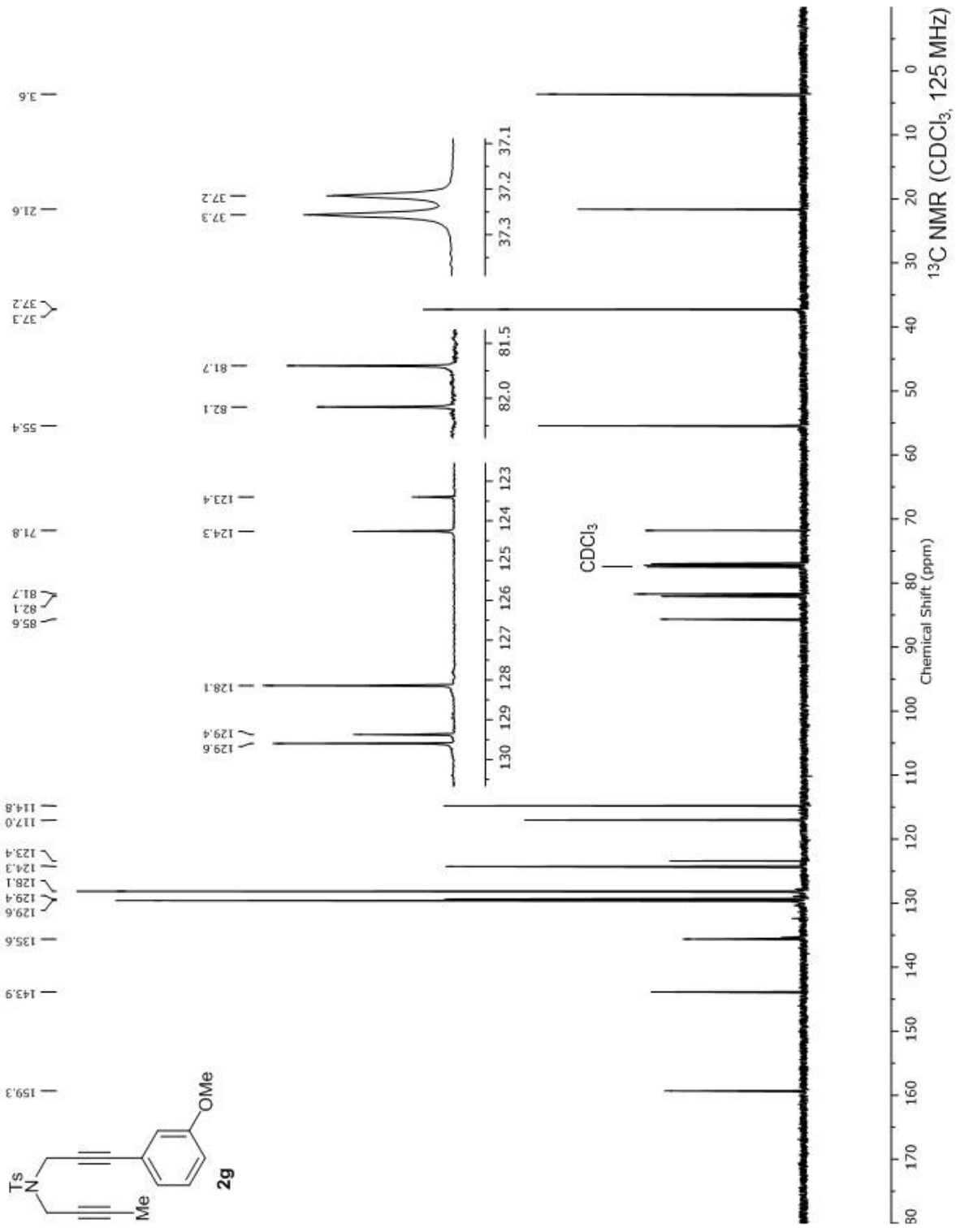
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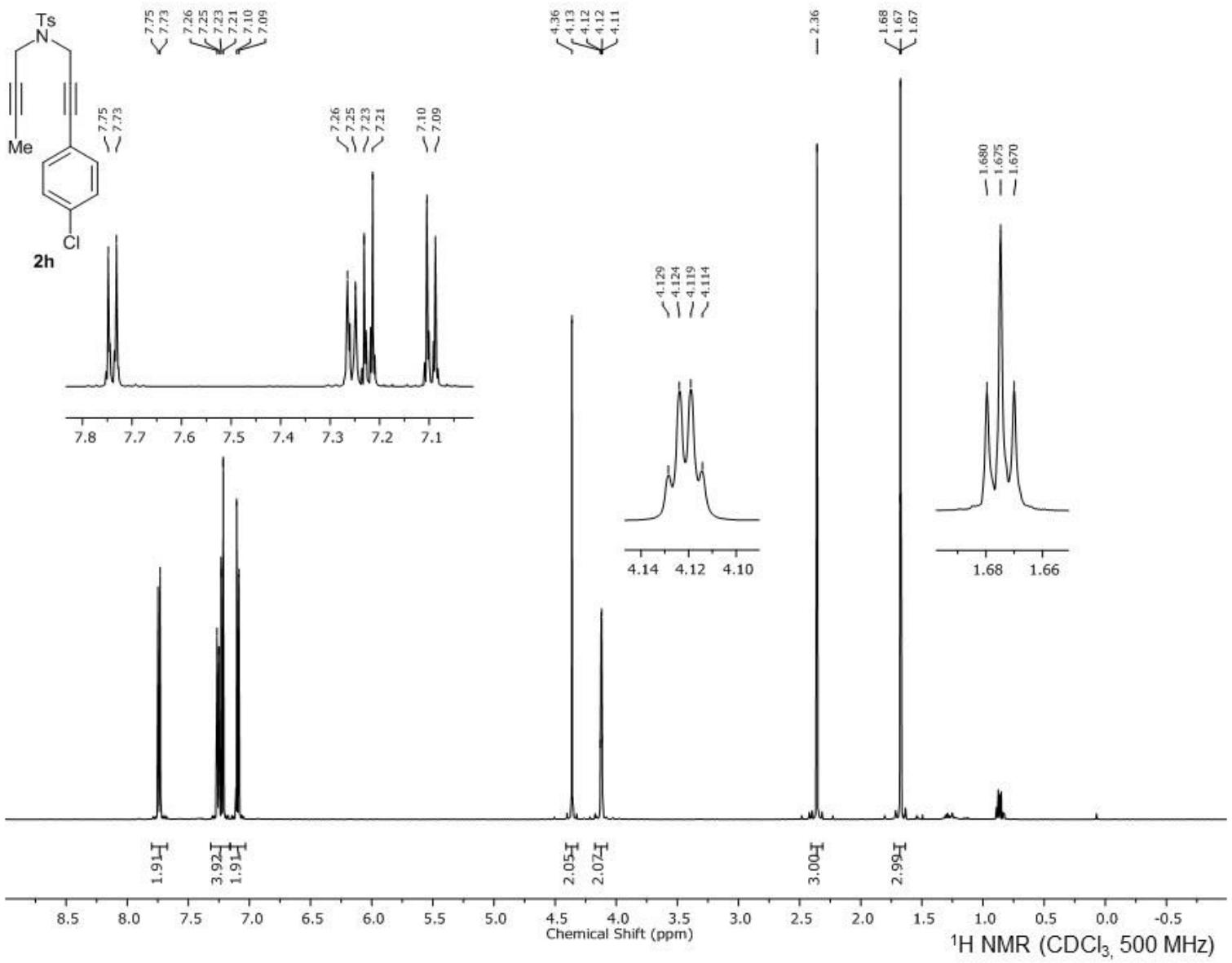
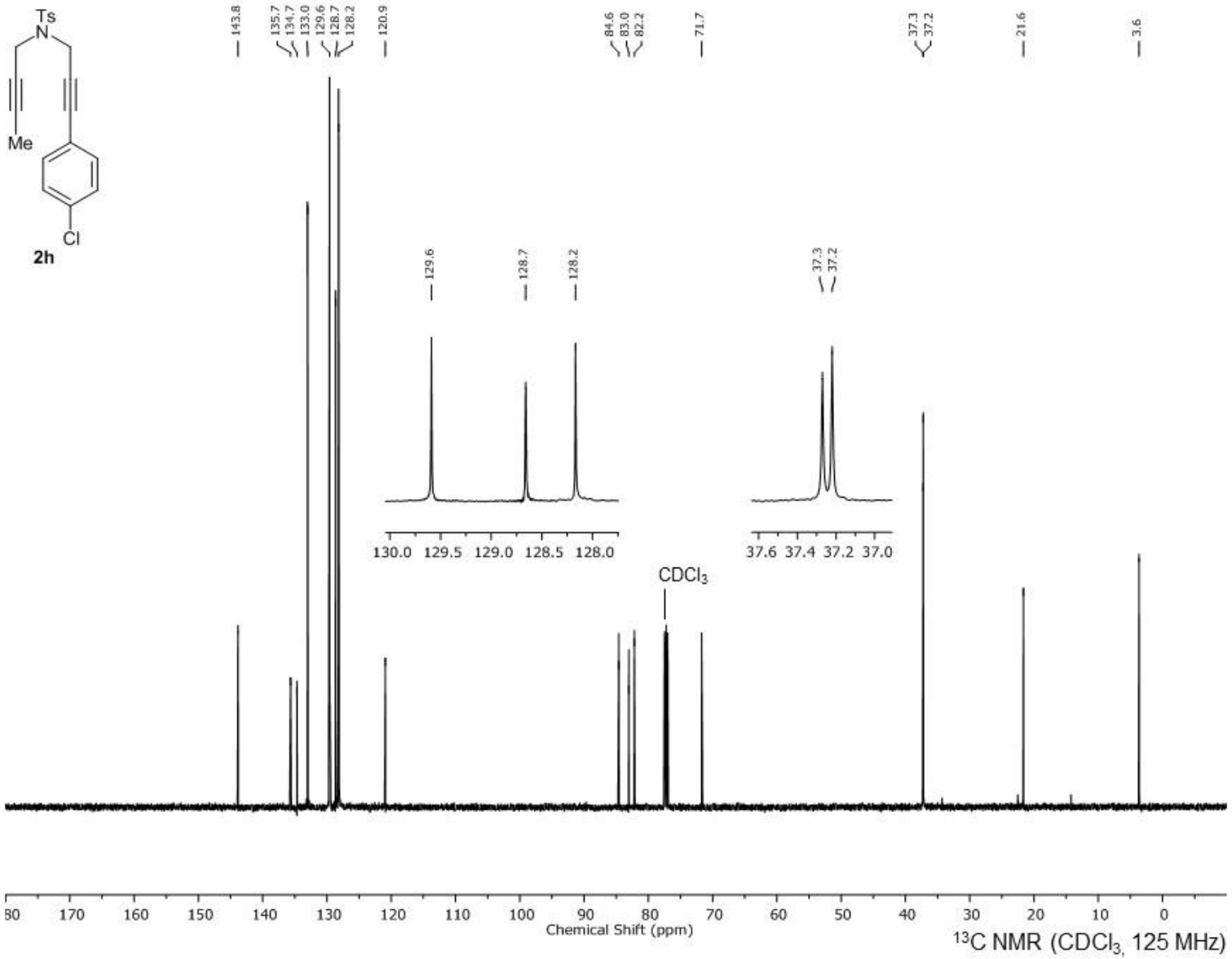
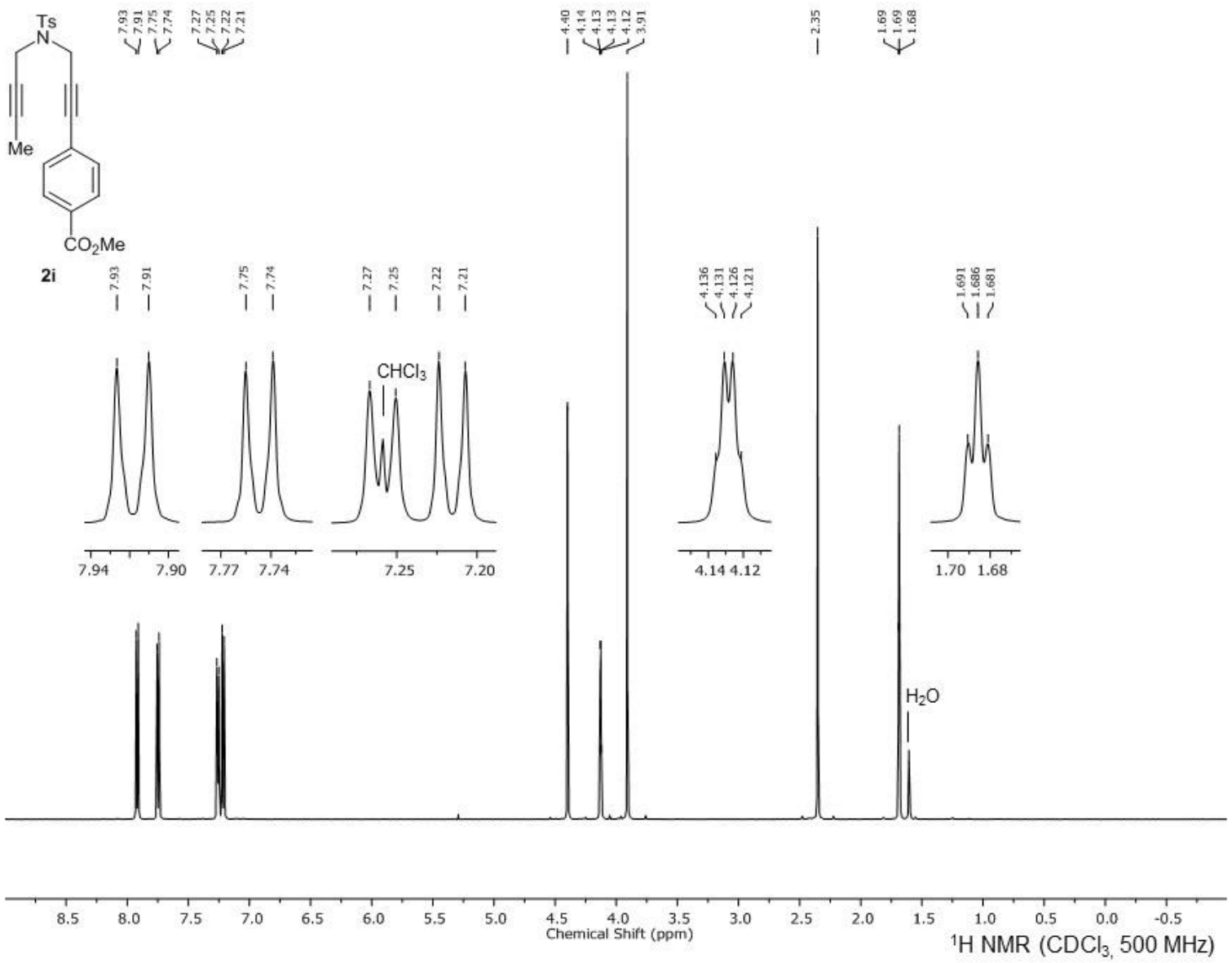
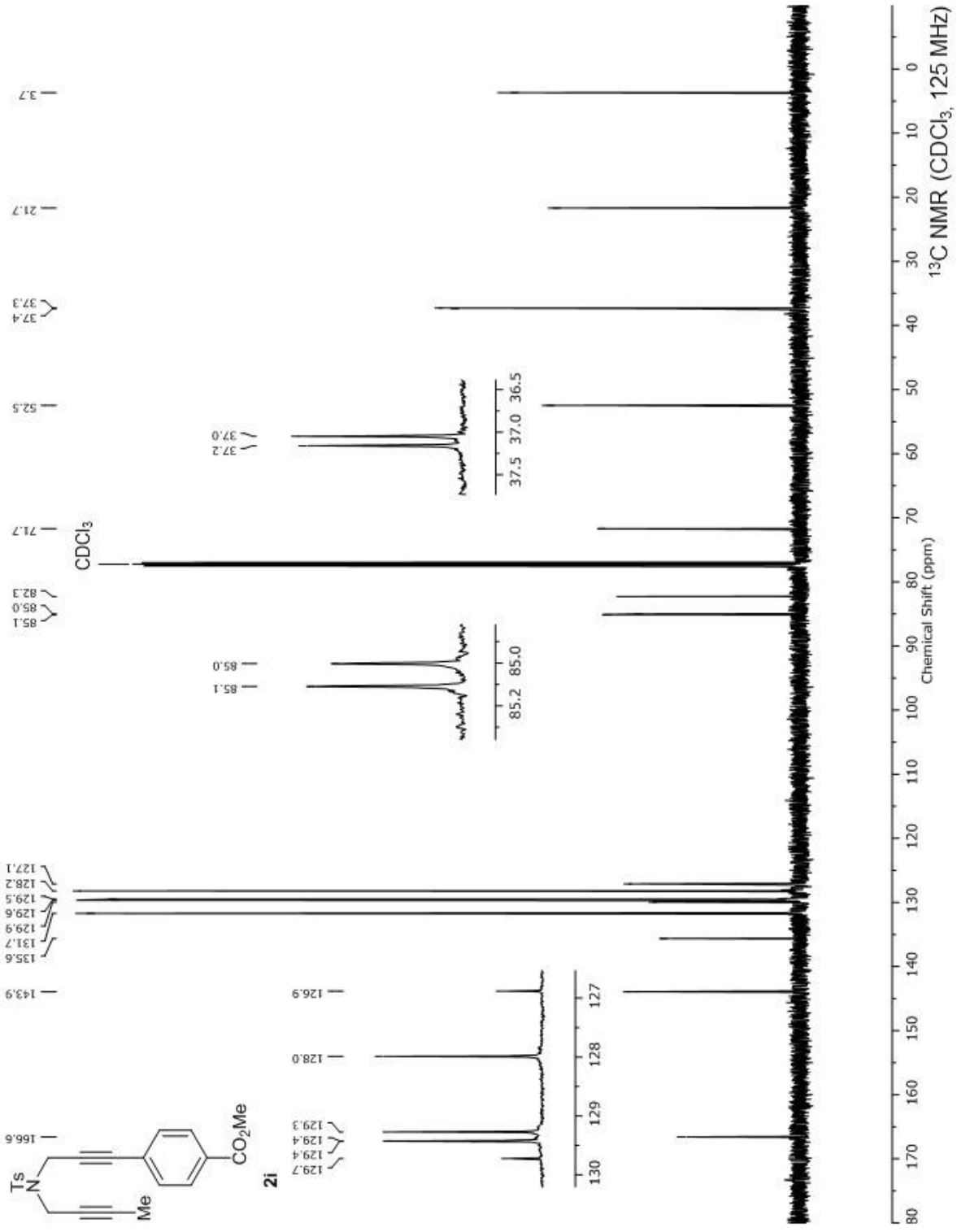
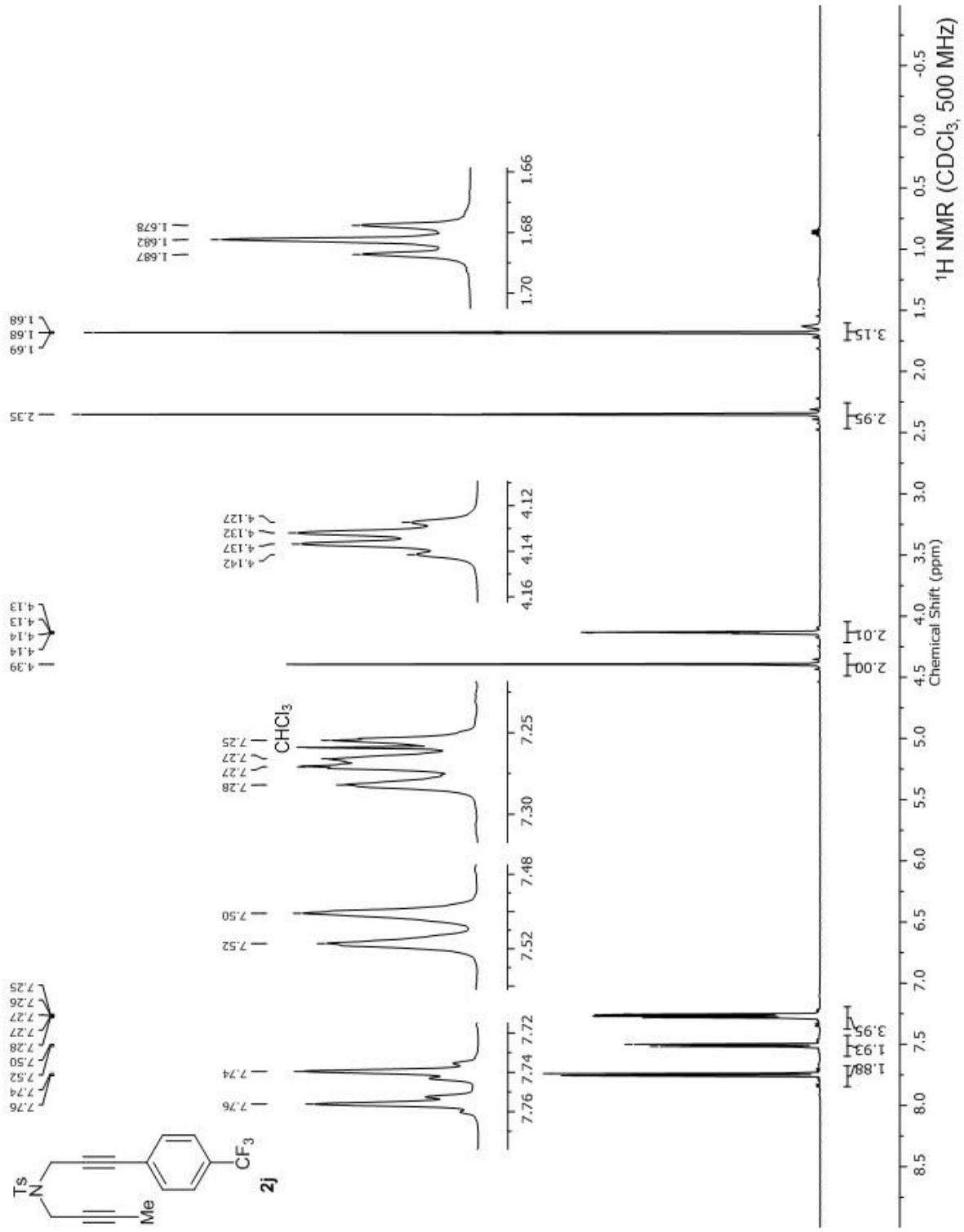
117.0
114.8
85.6
82.1
81.7
71.8
55.4
37.3
37.2
21.6
3.6
CDCl3
Chemical Shift (ppm)
13C NMR (CDCl3, 125 MHz)

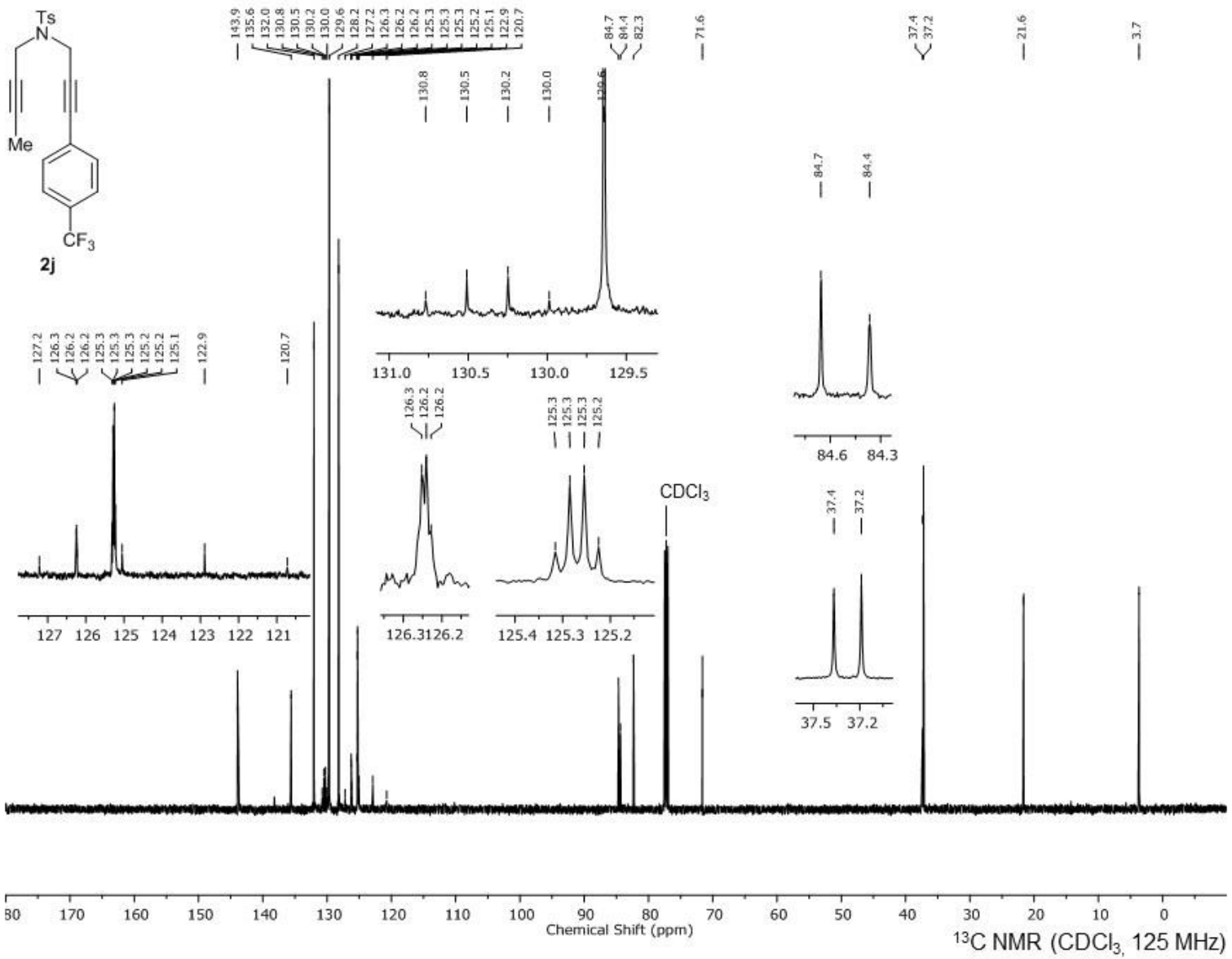

Ts
N
Me
Cl
2h
7.75
7.73
7.26
7.25
7.23
7.21
7.10
7.09
4.36
4.13
4.12
4.12
4.11
2.36
1.68
1.67
1.67
1.680
1.675
1.670
4.129
4.124
4.119
4.114
1.91
3.92
1.91
2.05
2.07
3.00
2.99
Chemical Shift (ppm)
^{1}H NMR ($CDCl_3$, 500 MHz)

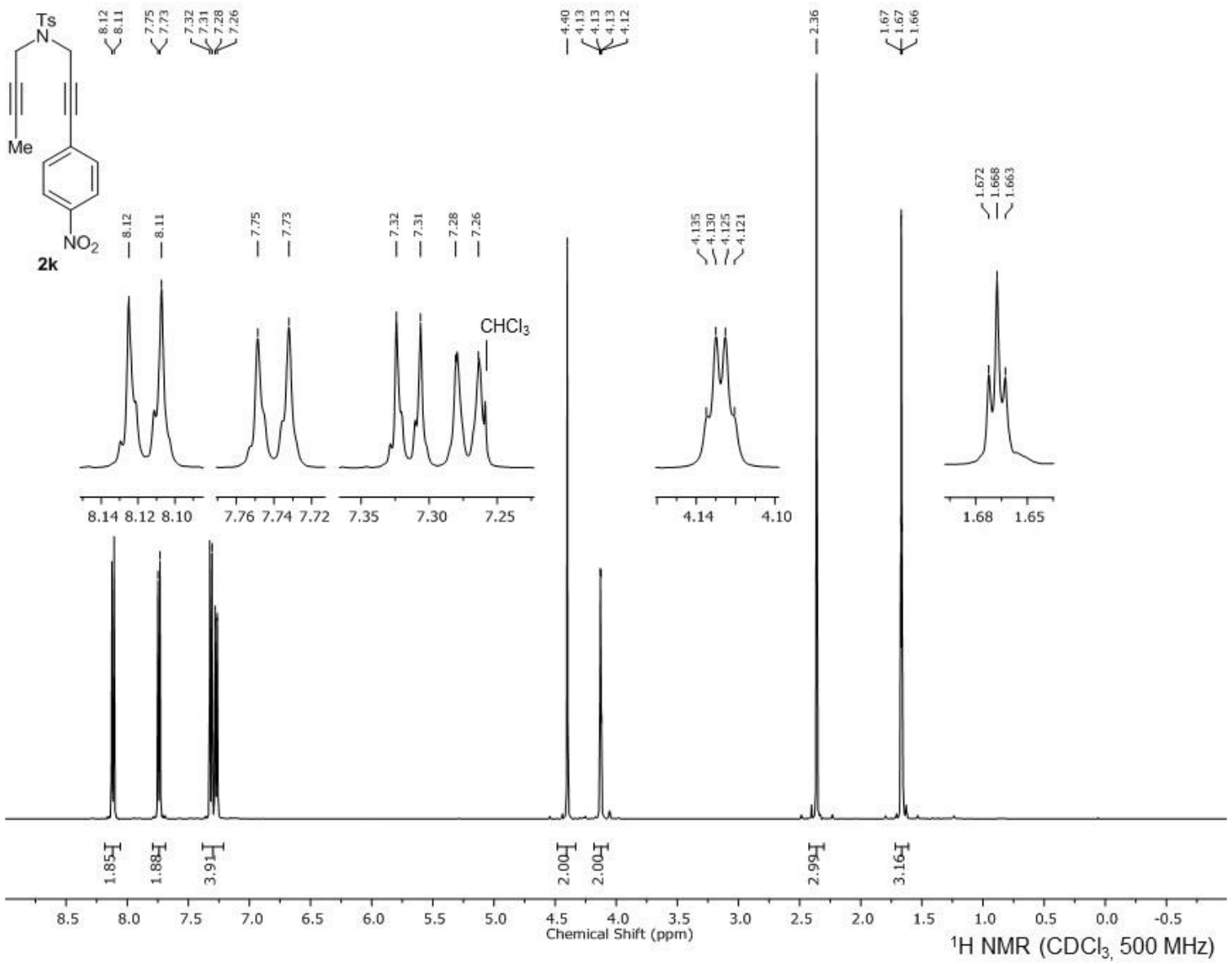

Ts
N
Me
Cl
2h
143.8
135.7
134.7
133.0
129.6
128.7
128.2
120.9
84.6
83.0
82.2
71.7
37.3
37.2
21.6
3.6
129.6
128.7
128.2
130.0 129.5 129.0 128.5 128.0
37.3
37.2
37.6 37.4 37.2 37.0
CDCl3
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift (ppm)
13C NMR (CDCl3, 125 MHz)

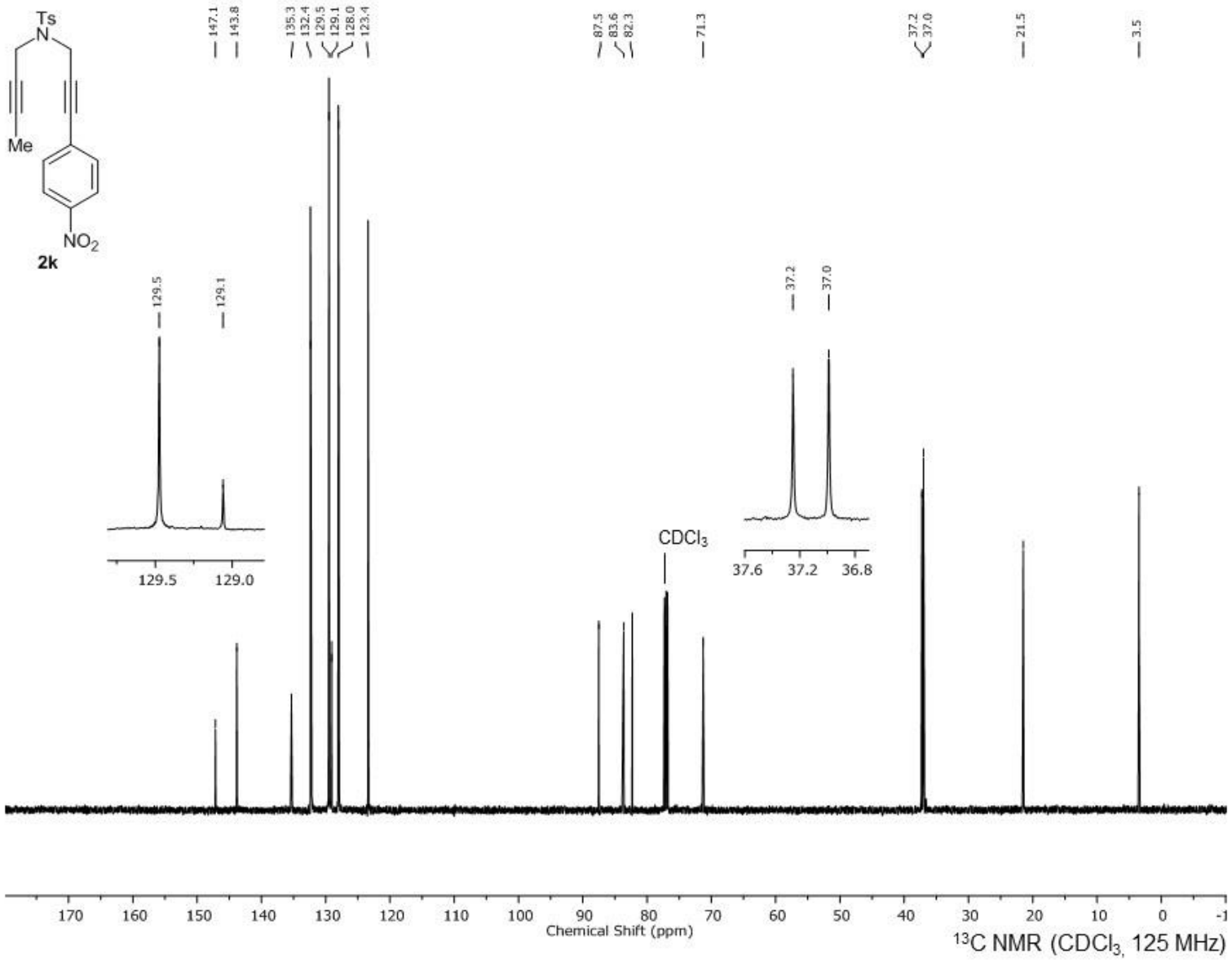

Ts
N
Me
CO2Me
2i
7.93
7.91
7.75
7.74
7.27
7.25
7.22
7.21
4.40
4.14
4.13
4.13
4.12
3.91
2.35
1.69
1.69
1.68
4.136
4.131
4.126
4.121
1.691
1.686
1.681
CHCl3
H2O
7.94
7.90
7.77
7.74
7.25
7.20
4.14 4.12
1.70 1.68
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
Chemical Shift (ppm)
1H NMR (CDCl3, 500 MHz)

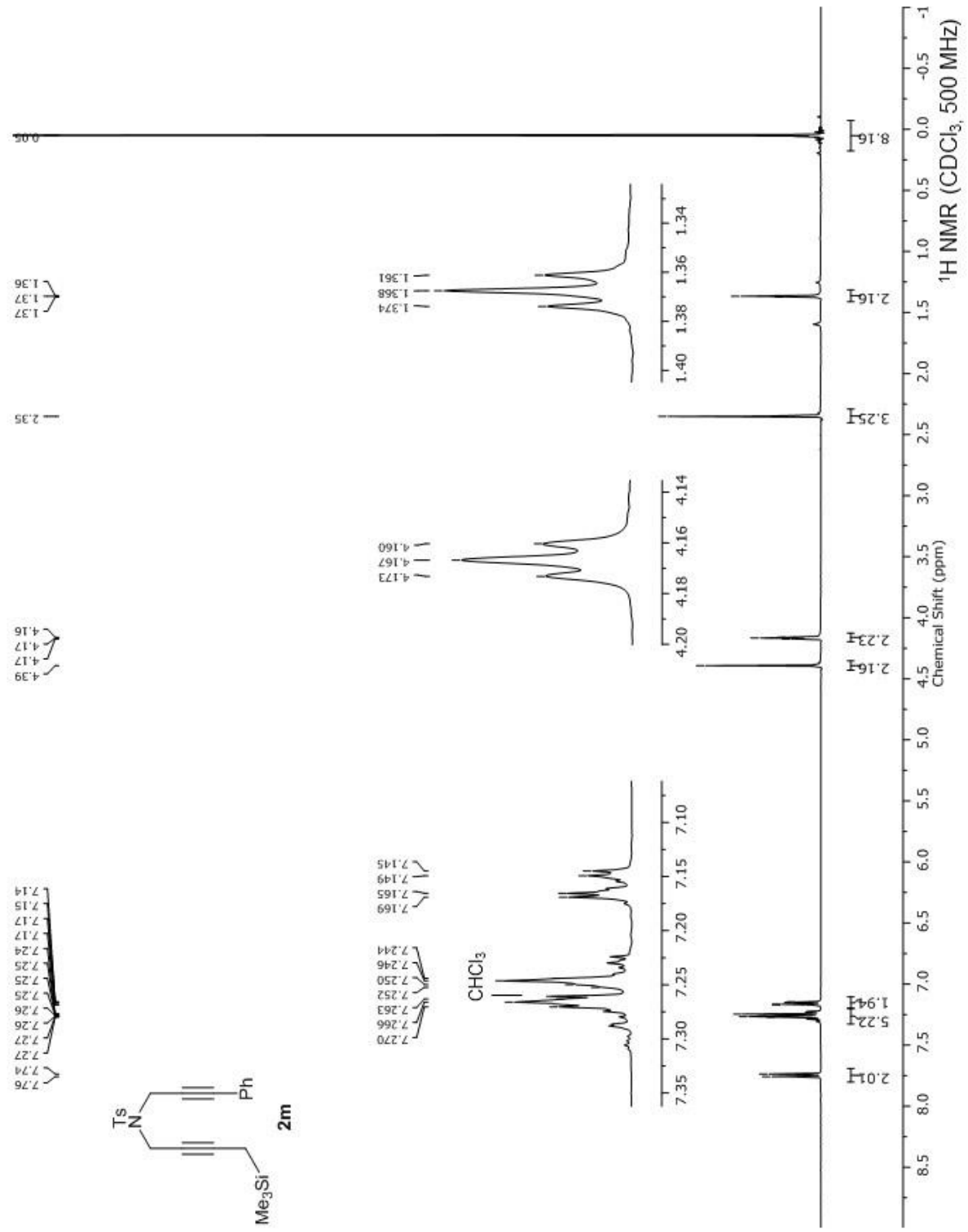

Ts
N
Me
CO2Me
2i
CDCl3
13C NMR (CDCl3, 125 MHz)
Chemical Shift (ppm)

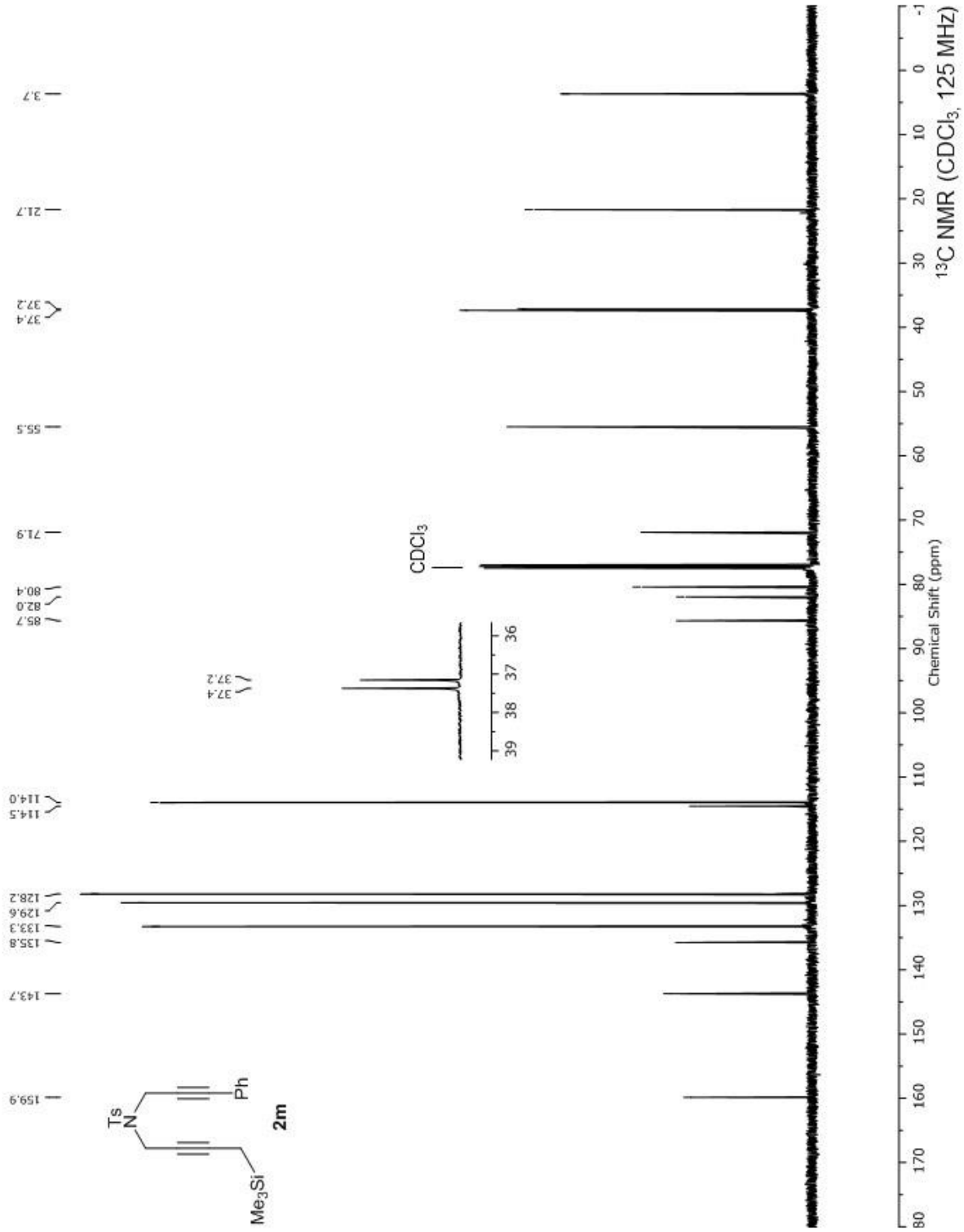

Ts
N
Me
CF3
2j
CHCl3
Chemical Shift (ppm)
1H NMR (CDCl3, 500 MHz)

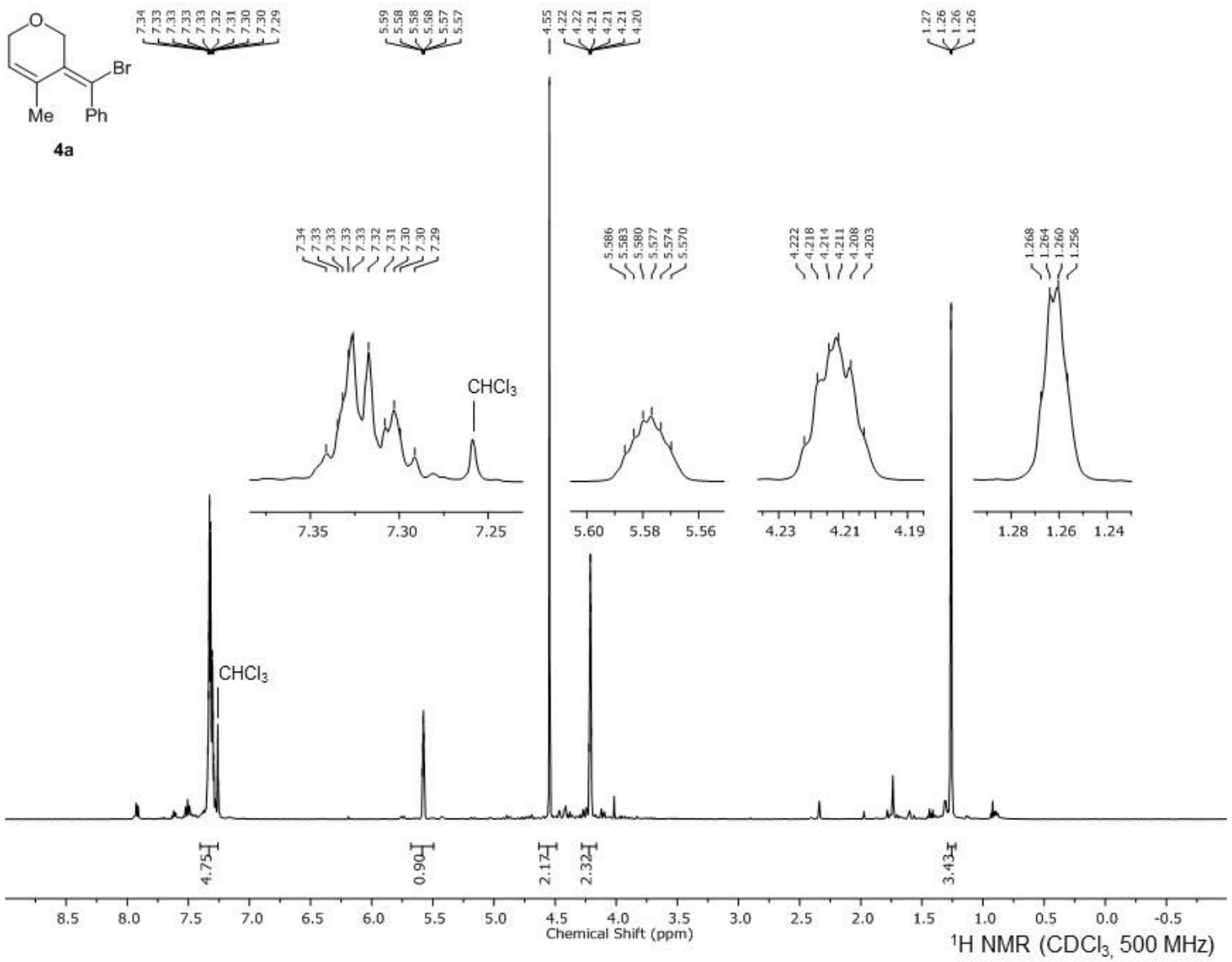

Ts
N
Me
CF3
2j
143.9
135.6
132.0
130.8
130.5
130.2
130.0
129.6
128.2
127.2
126.3
126.2
126.2
125.3
125.3
125.3
125.2
125.2
125.1
122.9
120.7
84.7
84.4
82.3
71.6
37.4
37.2
21.6
3.7
CDCl3
Chemical Shift (ppm)
13C NMR (CDCl3, 125 MHz)

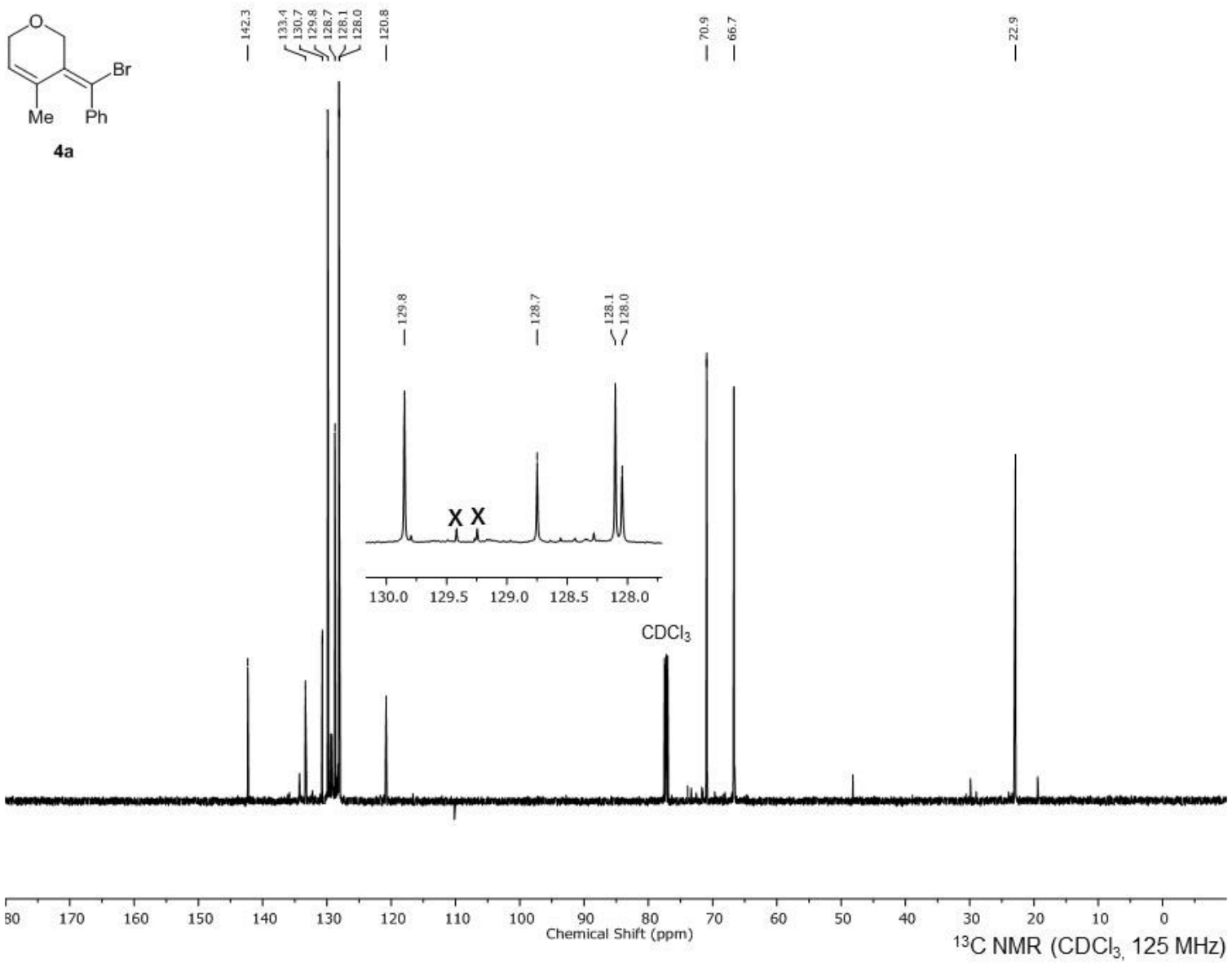

Ts
N
Me
NO2
2k
8.12
8.11
7.75
7.73
7.32
7.31
7.28
7.26
4.40
4.13
4.13
4.13
4.12
2.36
1.67
1.67
1.66
4.135
4.130
4.125
4.121
1.672
1.668
1.663
CHCl3
8.14 8.12 8.10
7.76 7.74 7.72
7.35
7.30
7.25
4.14
4.10
1.68
1.65
1.85
1.88
3.91
2.00
2.00
2.99
3.16
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
Chemical Shift (ppm)
1H NMR (CDCl3, 500 MHz)

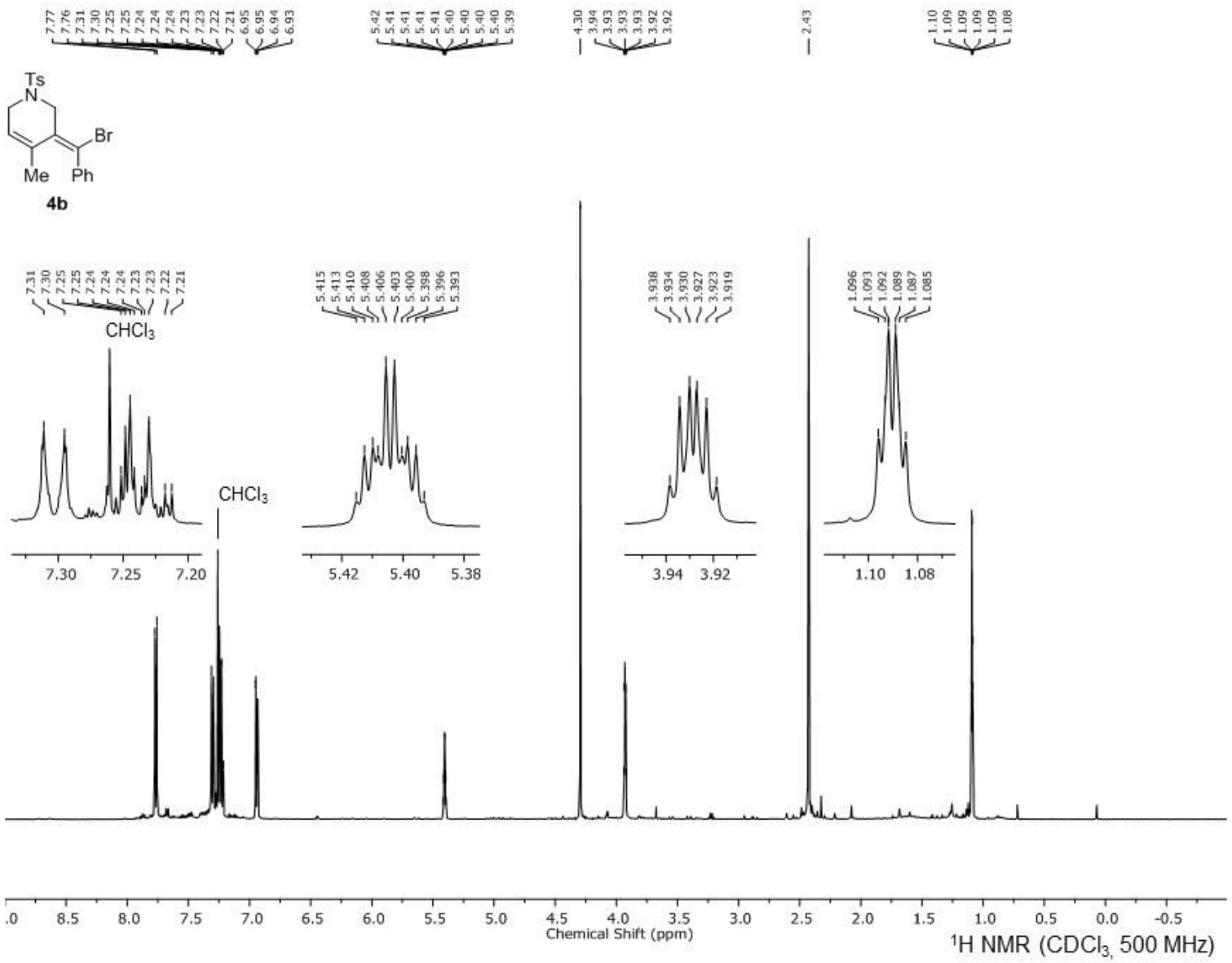

Ts
N
Me
NO2
2k
147.1
143.8
135.3
132.4
129.5
129.1
128.0
123.4
87.5
83.6
82.3
71.3
37.2
37.0
21.5
3.5
129.5
129.1
129.5
129.0
37.2
37.0
37.6
37.2
36.8
CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
Chemical Shift (ppm)
13C NMR (CDCl3, 125 MHz)

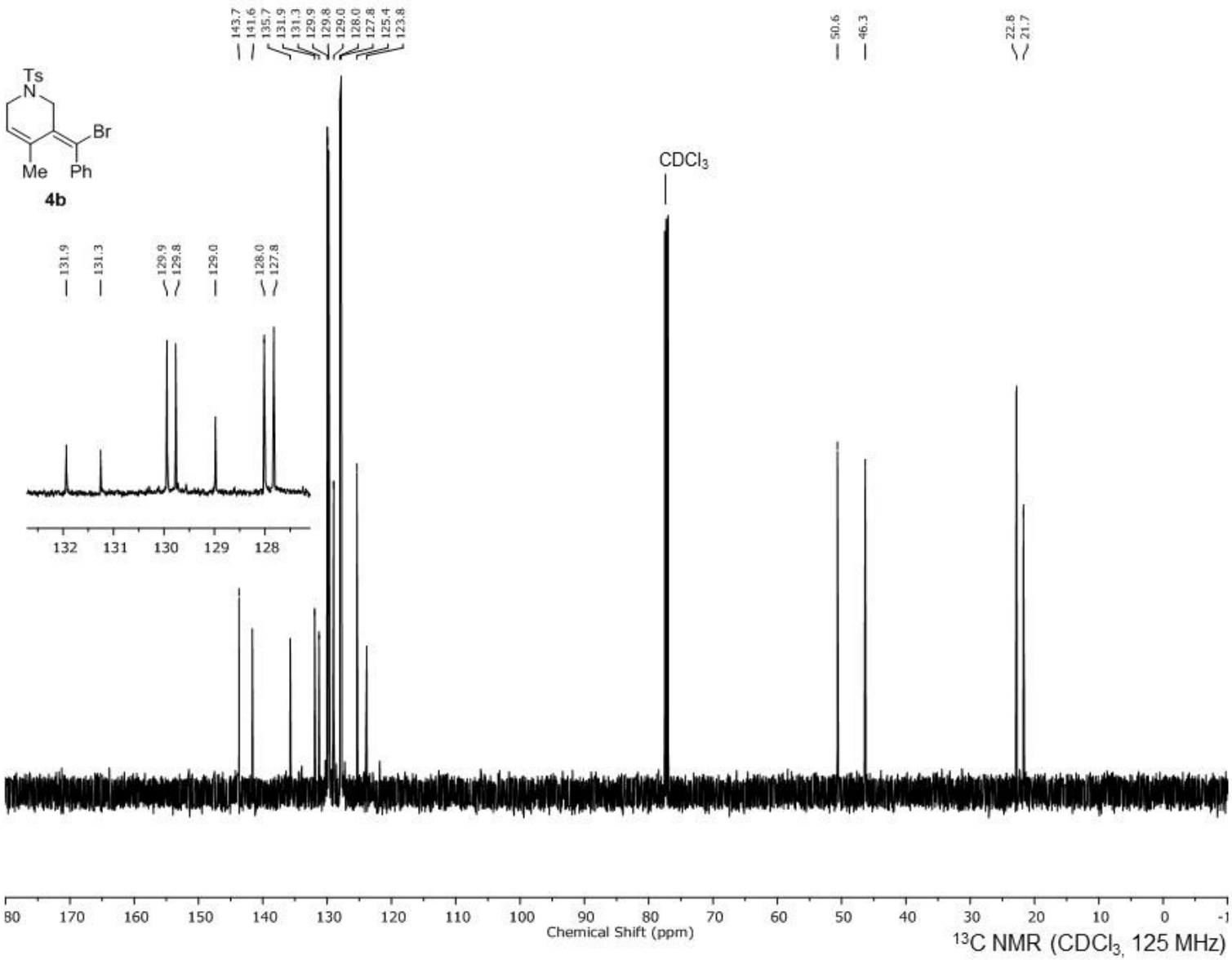

Ts
N
Ph
Me3Si
2m
CHCl3
1H NMR (CDCl3, 500 MHz)
Chemical Shift (ppm)

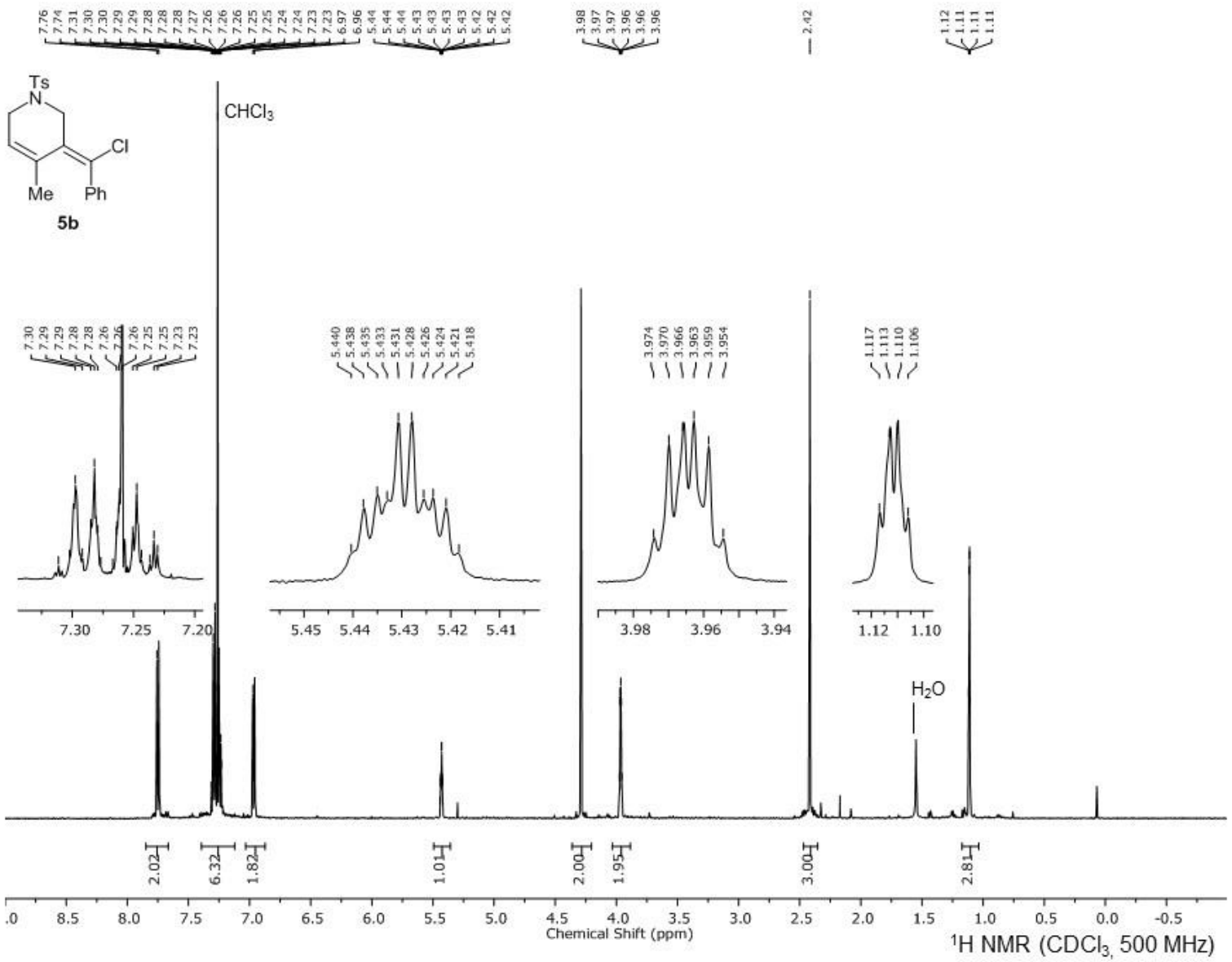

Ts
N
Ph
Me3Si
2m
159.9
143.7
135.8
133.3
129.6
128.2
114.5
114.0
85.7
82.0
80.4
71.9
55.5
37.4
37.2
21.7
3.7
CDCl3
39
38
37
36
Chemical Shift (ppm)
13C NMR (CDCl3, 125 MHz)

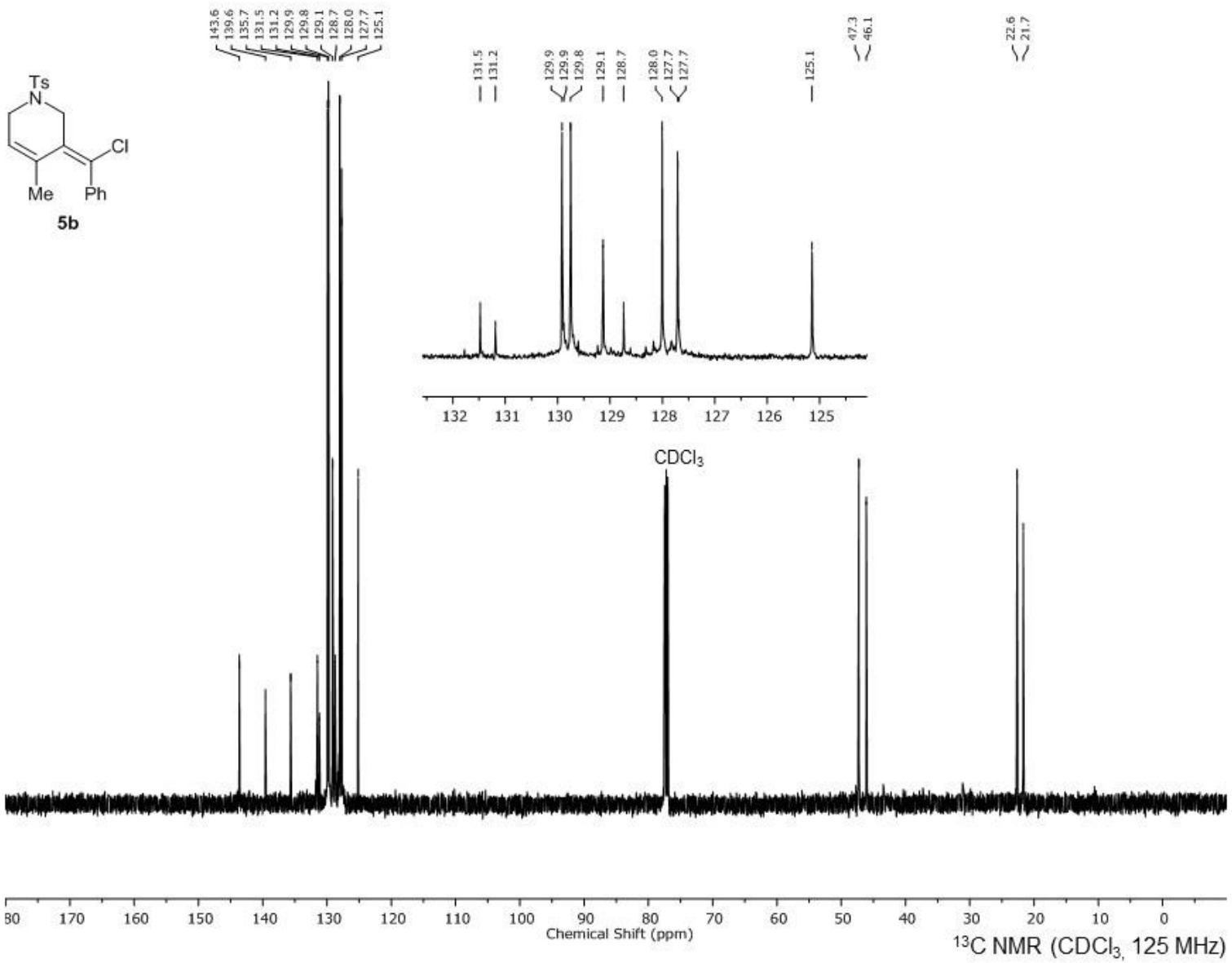

Br
Me
Ph
4a
CHCl3
CHCl3
4.75
0.90
2.17
2.32
3.43
Chemical Shift (ppm)
1H NMR (CDCl3, 500 MHz)

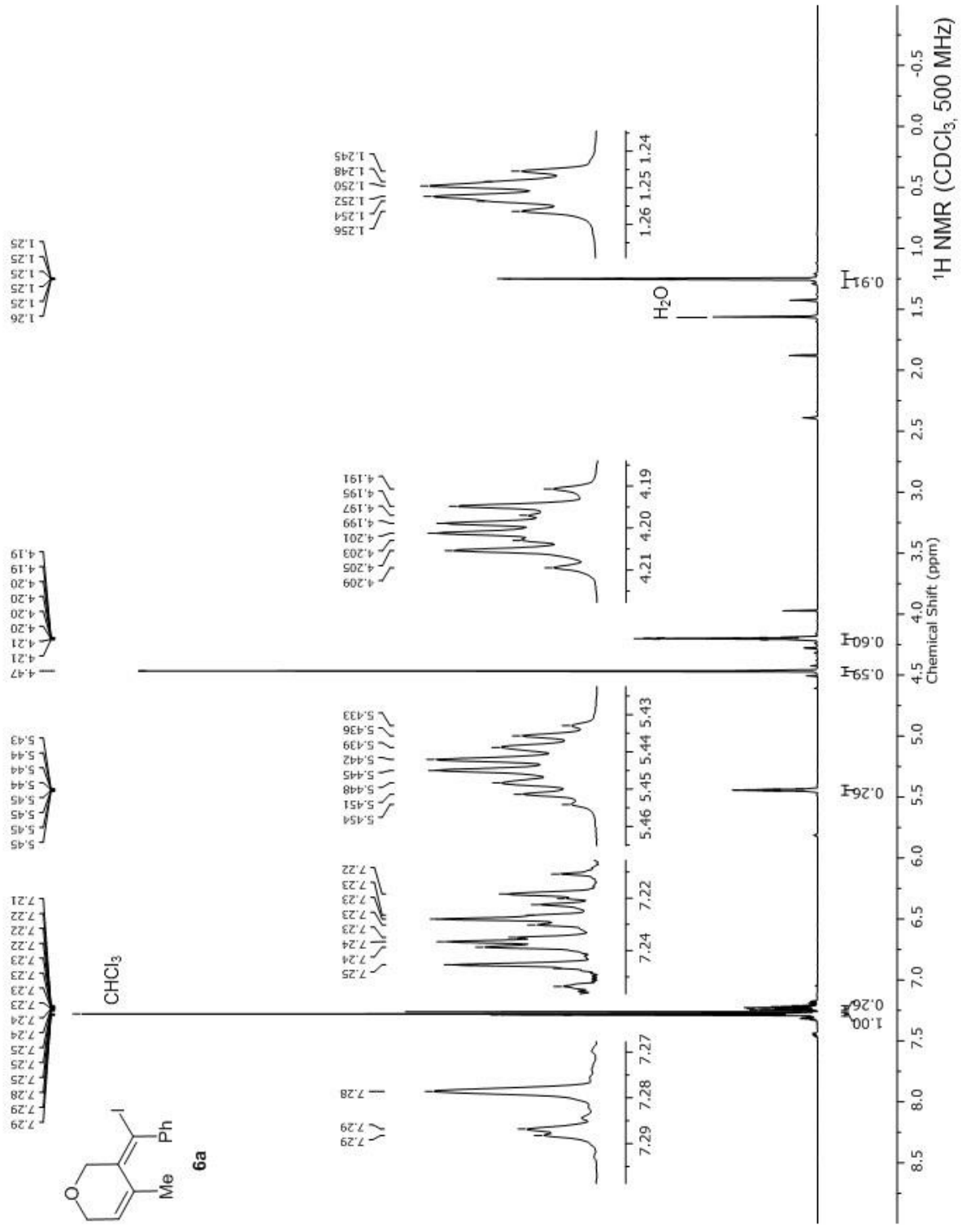

O
Br
Me
Ph
4a
142.3
133.4
130.7
129.8
128.7
128.1
128.0
120.8
70.9
66.7
22.9
129.8
128.7
128.1
128.0
X X
130.0
129.5
129.0
128.5
128.0
CDCl3
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)
13C NMR (CDCl3, 125 MHz)

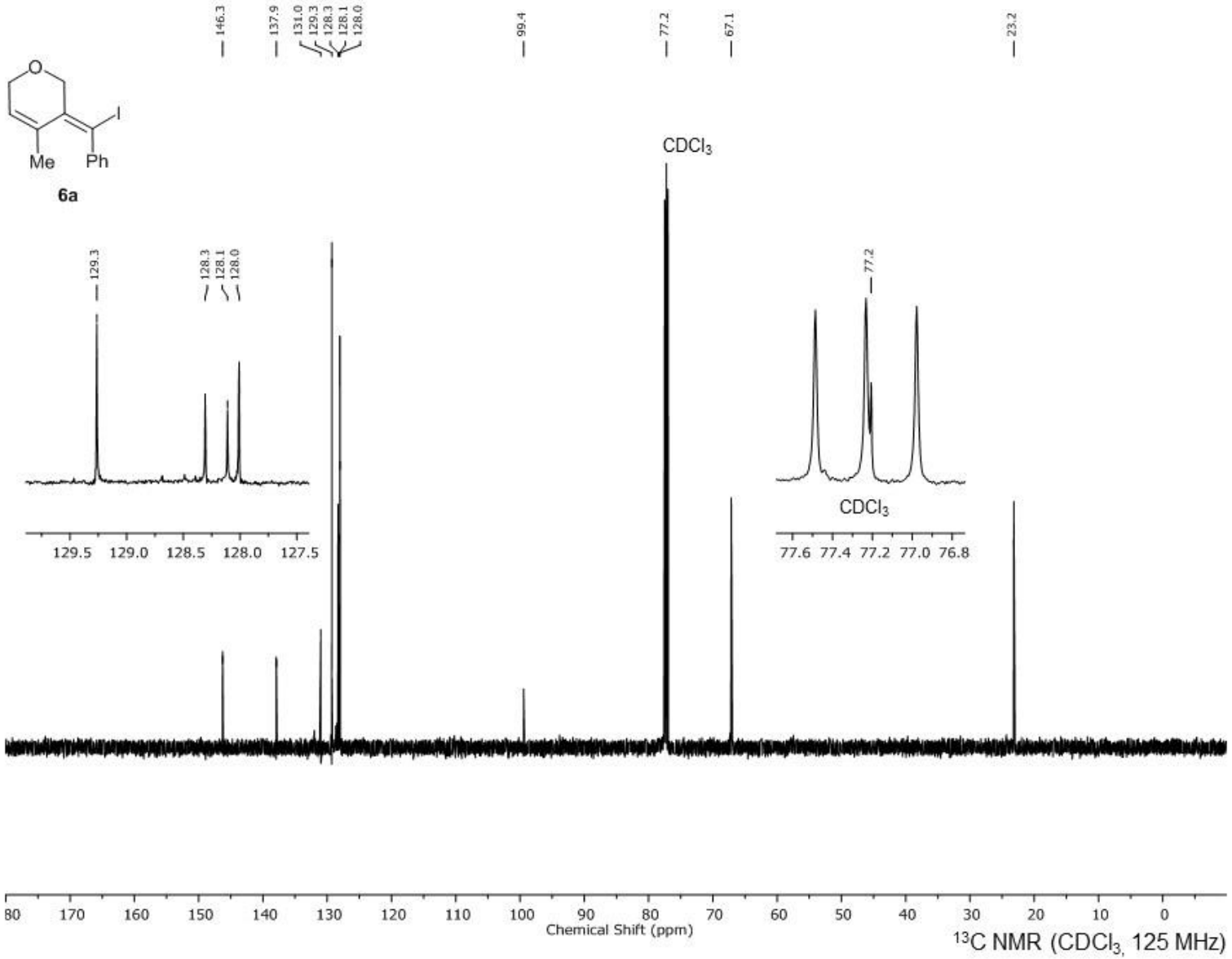

Ts
N
Br
Me
Ph
4b
CHCl3
CHCl3
Chemical Shift (ppm)
1H NMR (CDCl3, 500 MHz)

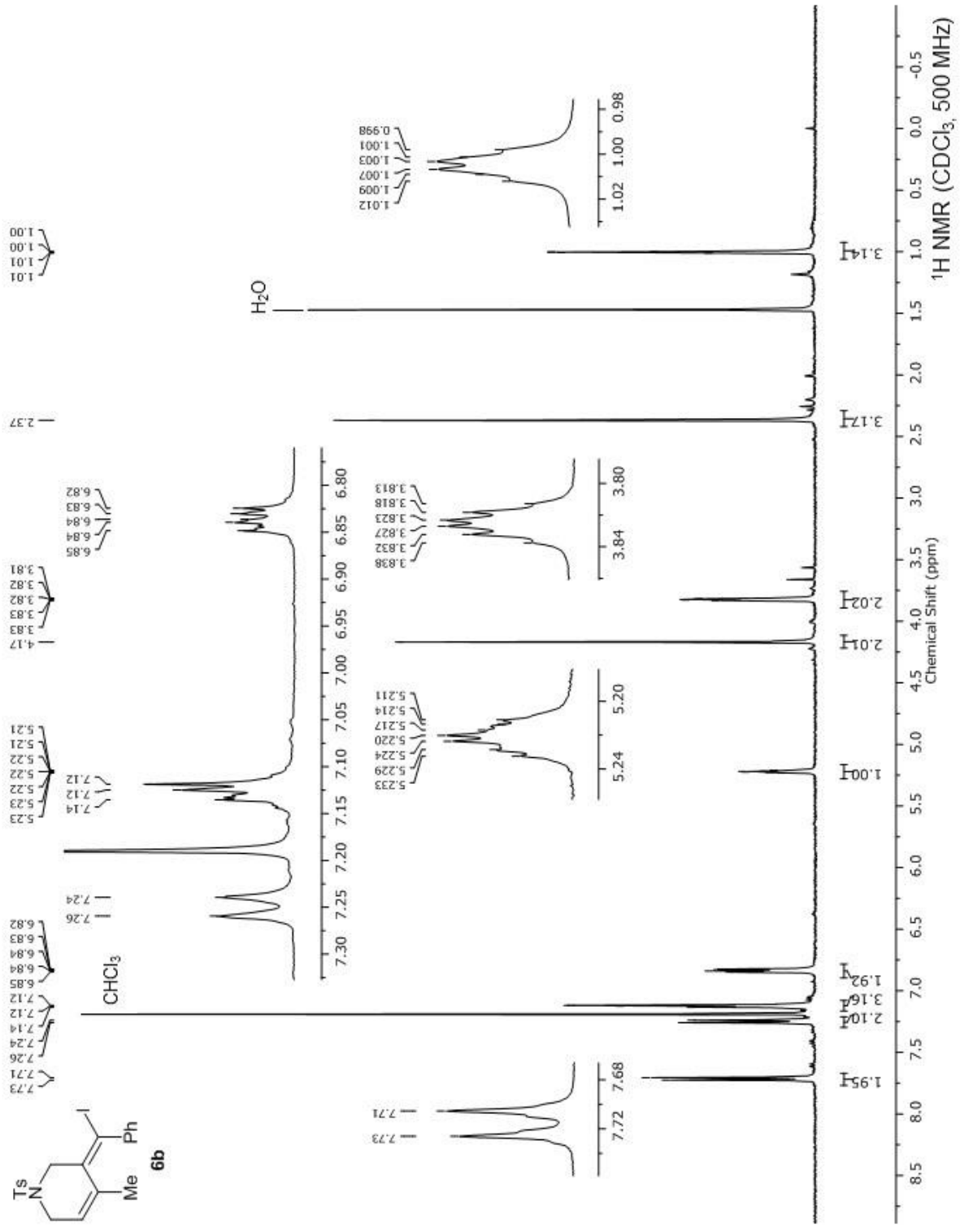

143.7
141.6
135.7
131.9
131.3
129.9
129.8
129.0
128.0
127.8
125.4
123.8
50.6
46.3
22.8
21.7
Ts
N
Br
Me
Ph
4b
CDCl3
131.9
131.3
129.9
129.8
129.0
128.0
127.8
132
131
130
129
128
Chemical Shift (ppm)
13C NMR (CDCl3, 125 MHz)

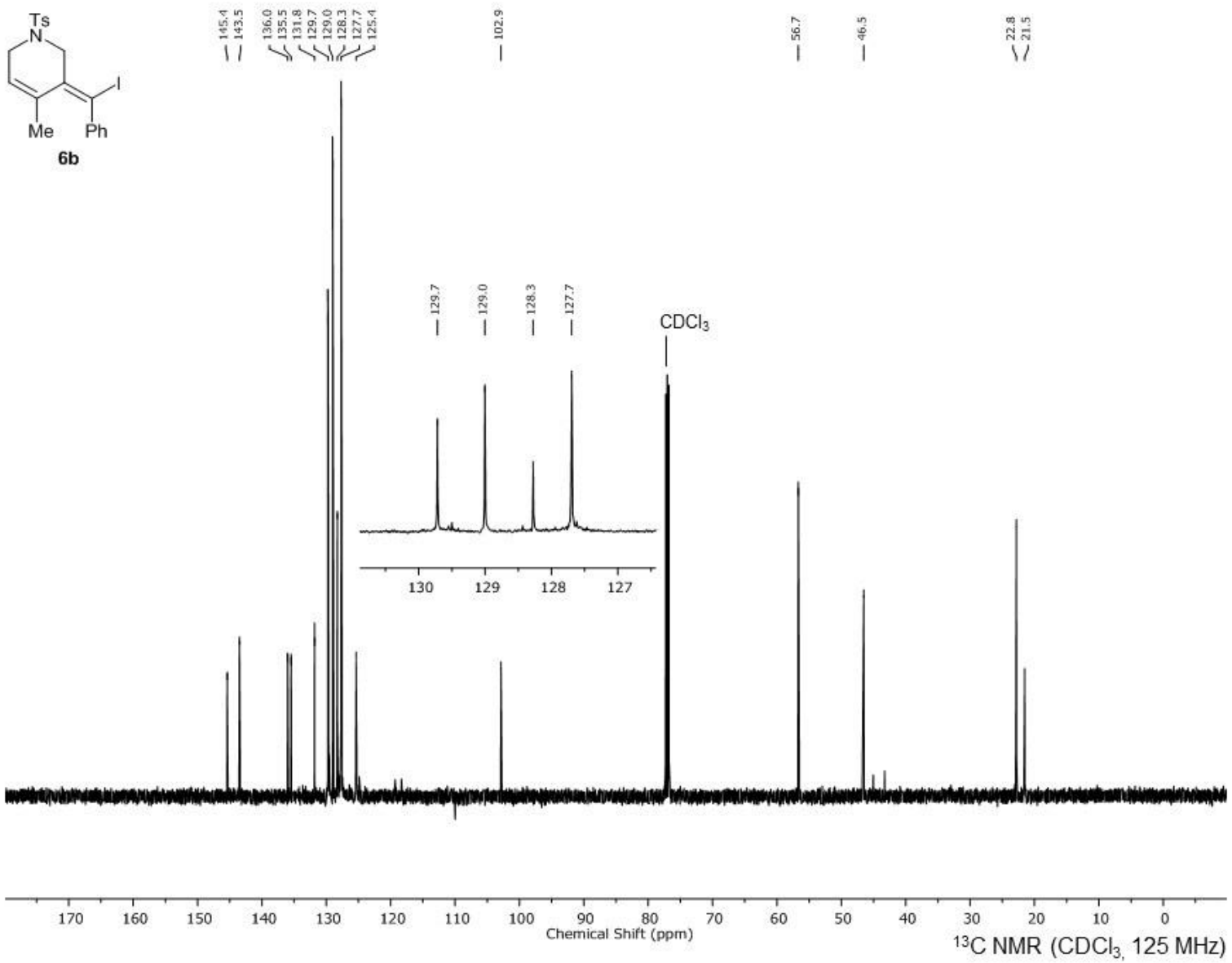

Ts
N
Cl
Me
Ph
5b
CHCl3
H2O
Chemical Shift (ppm)
1H NMR (CDCl3, 500 MHz)

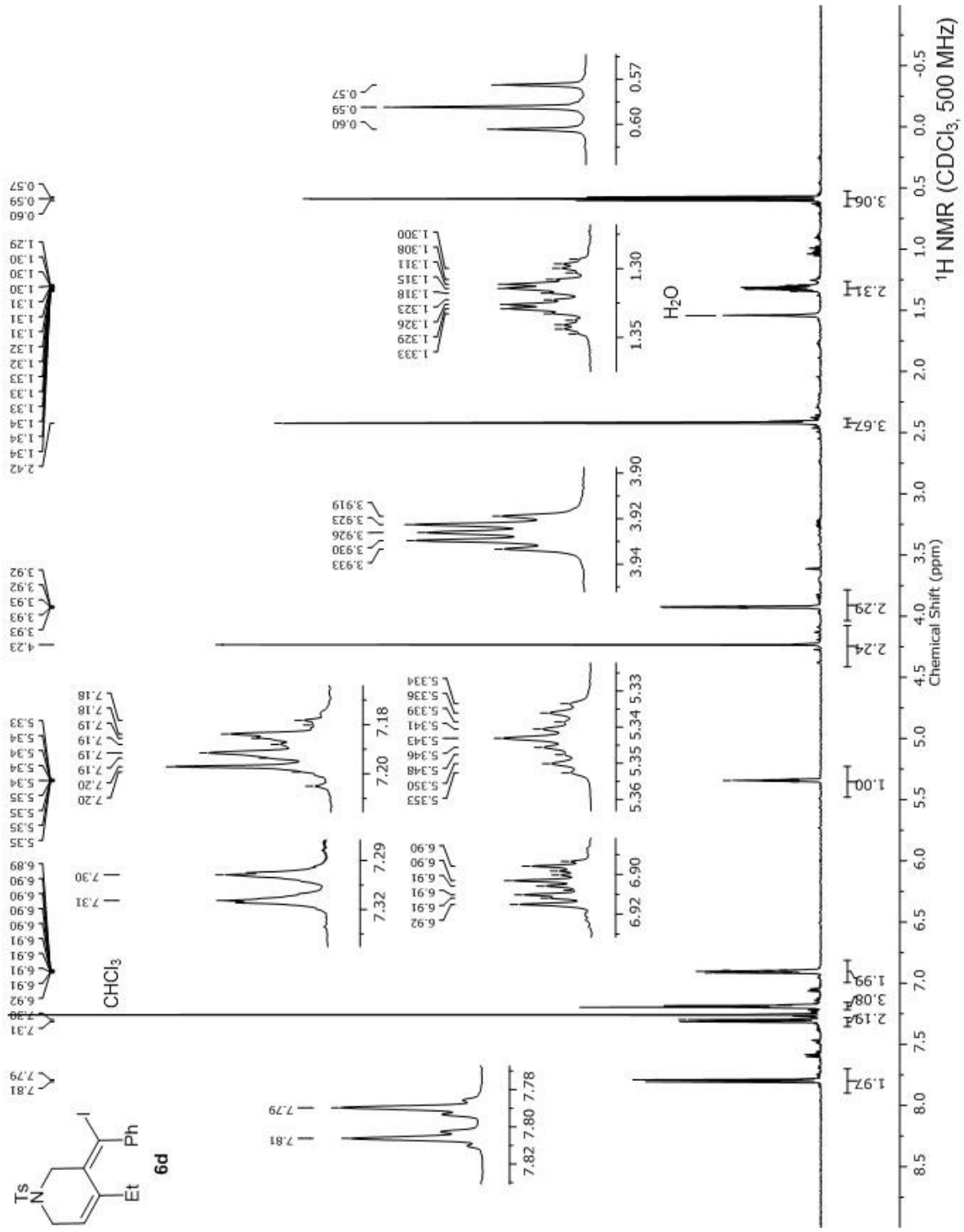

143.6
139.6
135.7
131.5
131.2
129.9
129.8
129.1
128.7
128.0
127.7
125.1
131.5
131.2
129.9
129.9
129.8
129.1
128.7
128.0
127.7
127.7
125.1
47.3
46.1
22.6
21.7
Ts
N
Cl
Me
Ph
5b
CDCl3
132
131
130
129
128
127
126
125
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)
13C NMR (CDCl3, 125 MHz)

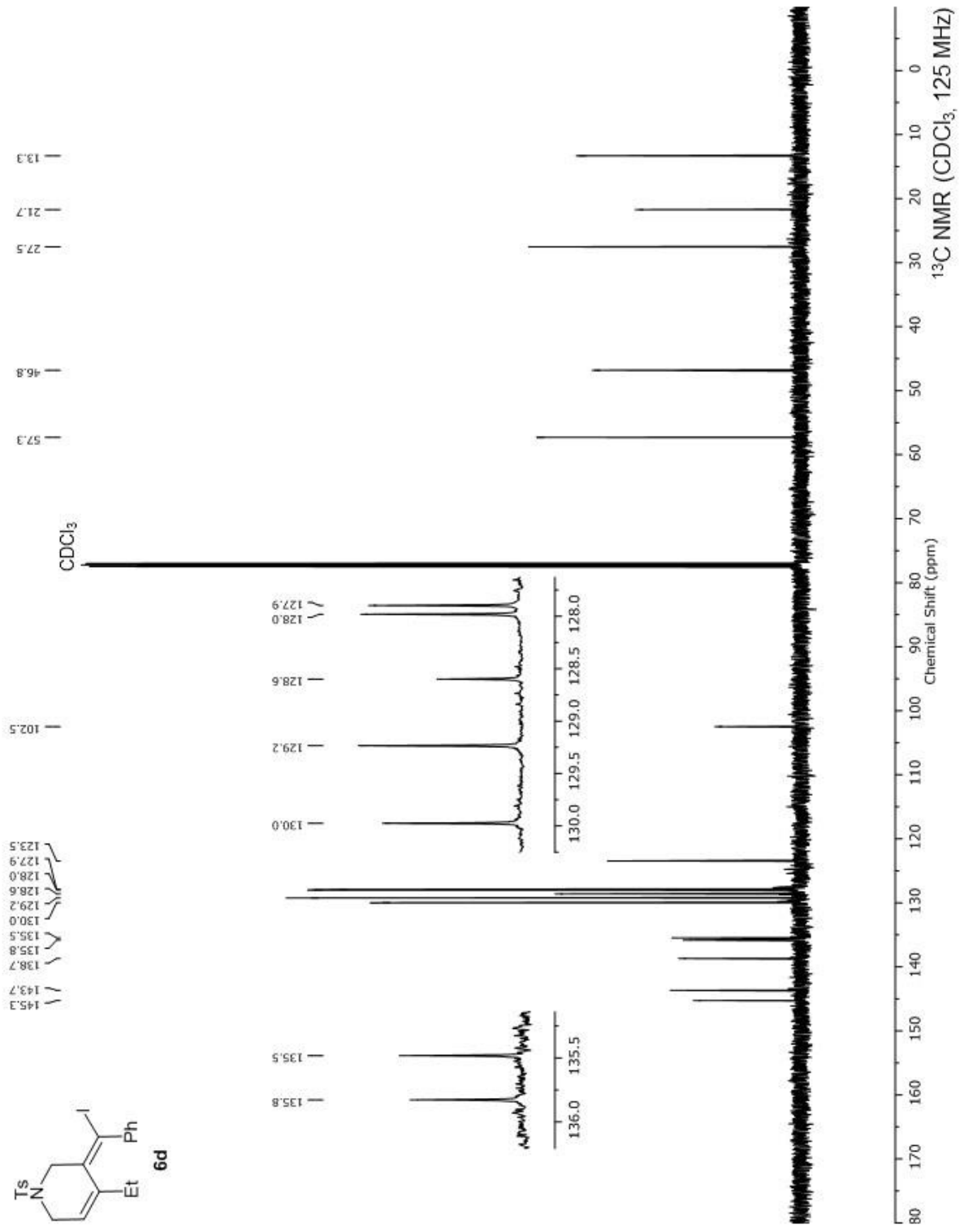

CHCl3
H2O
Me
Ph
6a
1H NMR (CDCl3, 500 MHz)
Chemical Shift (ppm)

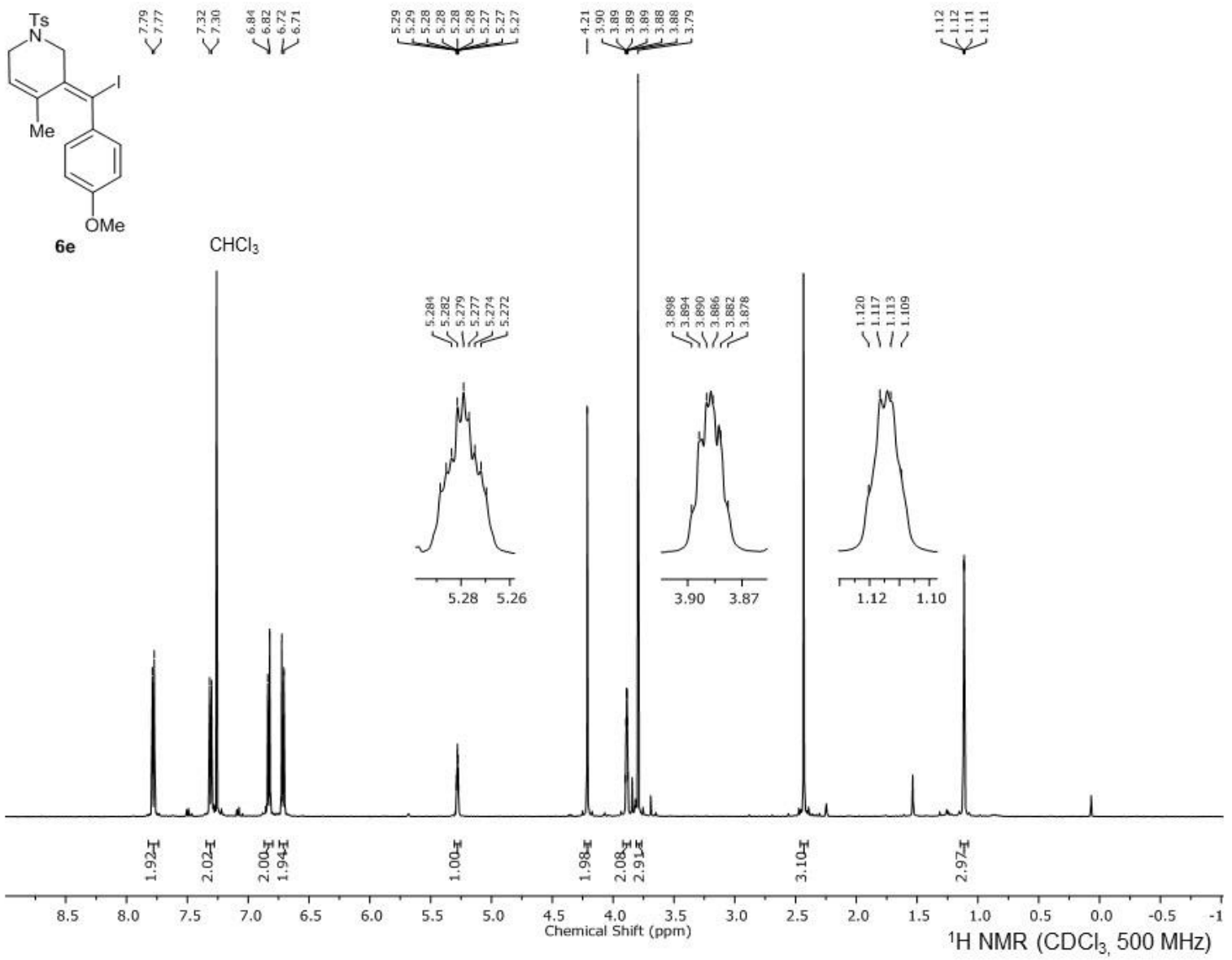

146.3
137.9
131.0
129.3
128.3
128.1
128.0
99.4
77.2
67.1
23.2
O
I
Me
Ph
6a
CDCl3
129.3
128.3
128.1
128.0
129.5 129.0 128.5 128.0 127.5
77.2
CDCl3
77.6 77.4 77.2 77.0 76.8
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift (ppm)
13C NMR (CDCl3, 125 MHz)

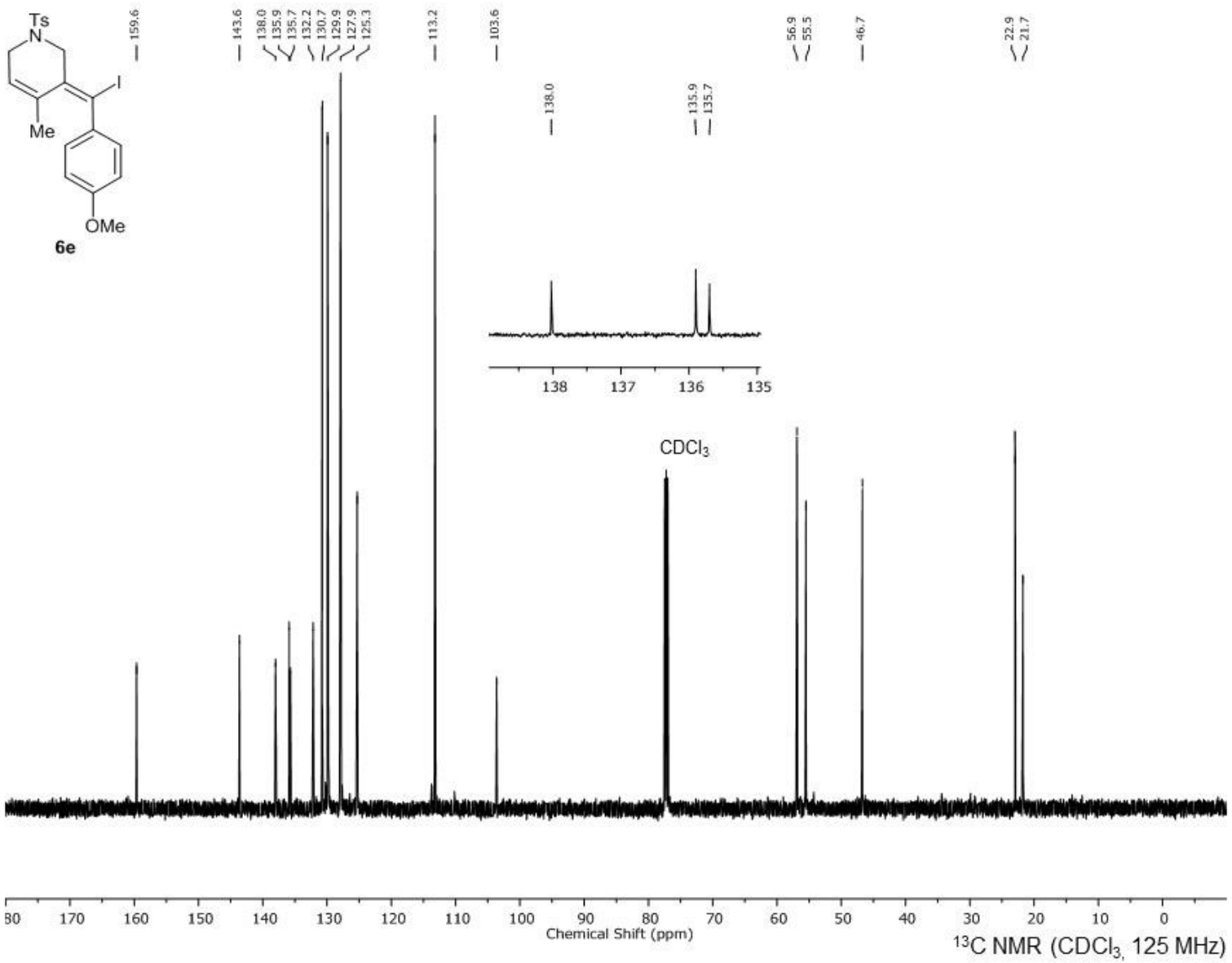

Ts
N
Me
Ph
I
6b
^{1}H NMR ($CDCl_3$, 500 MHz)
Chemical Shift (ppm)
$CHCl_3$
H_2O

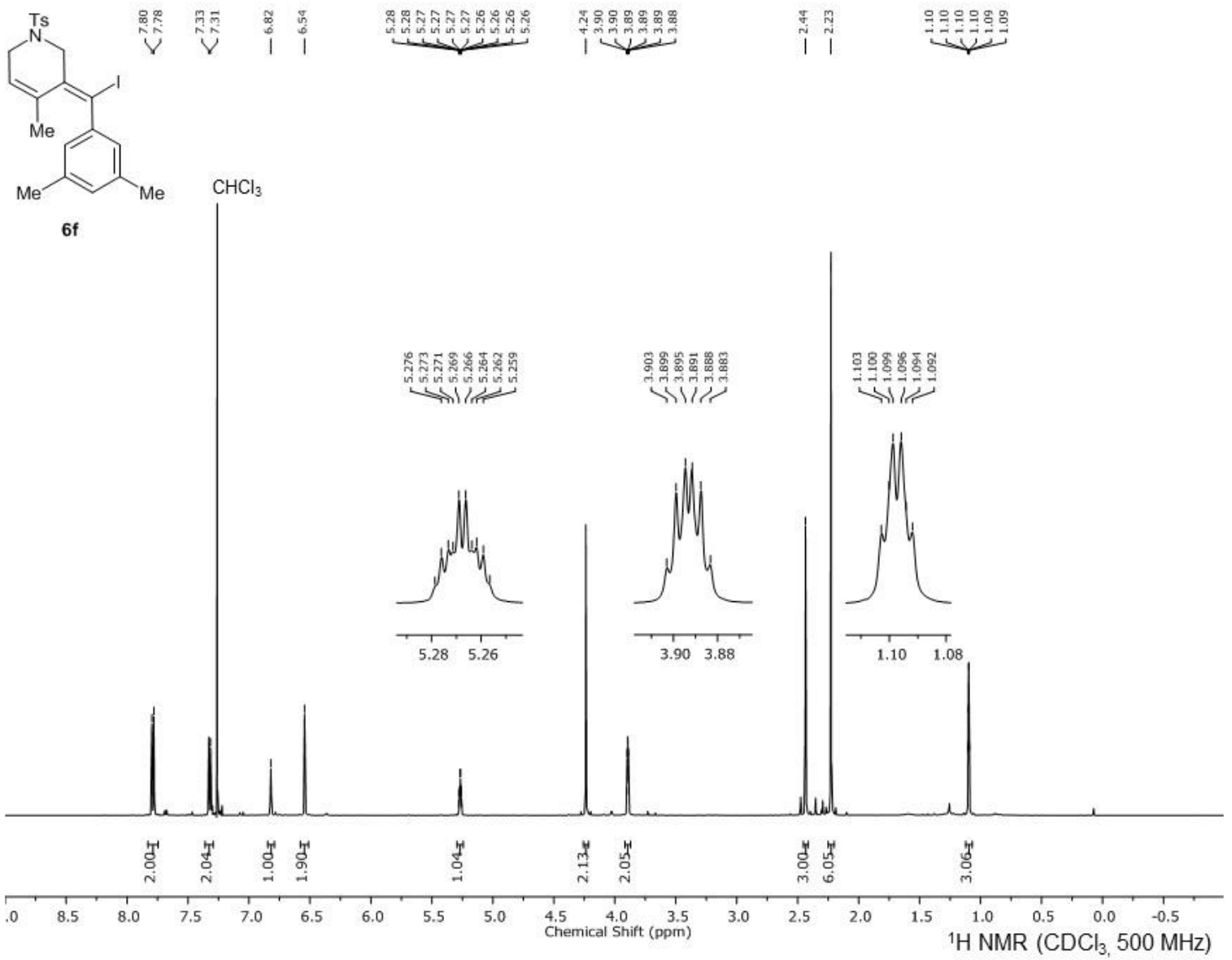

Ts
N
I
Me
Ph
6b
145.4
143.5
136.0
135.5
131.8
129.7
129.0
128.3
127.7
125.4
102.9
56.7
46.5
22.8
21.5
CDCl3
130
129
128
127
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)
13C NMR (CDCl3, 125 MHz)

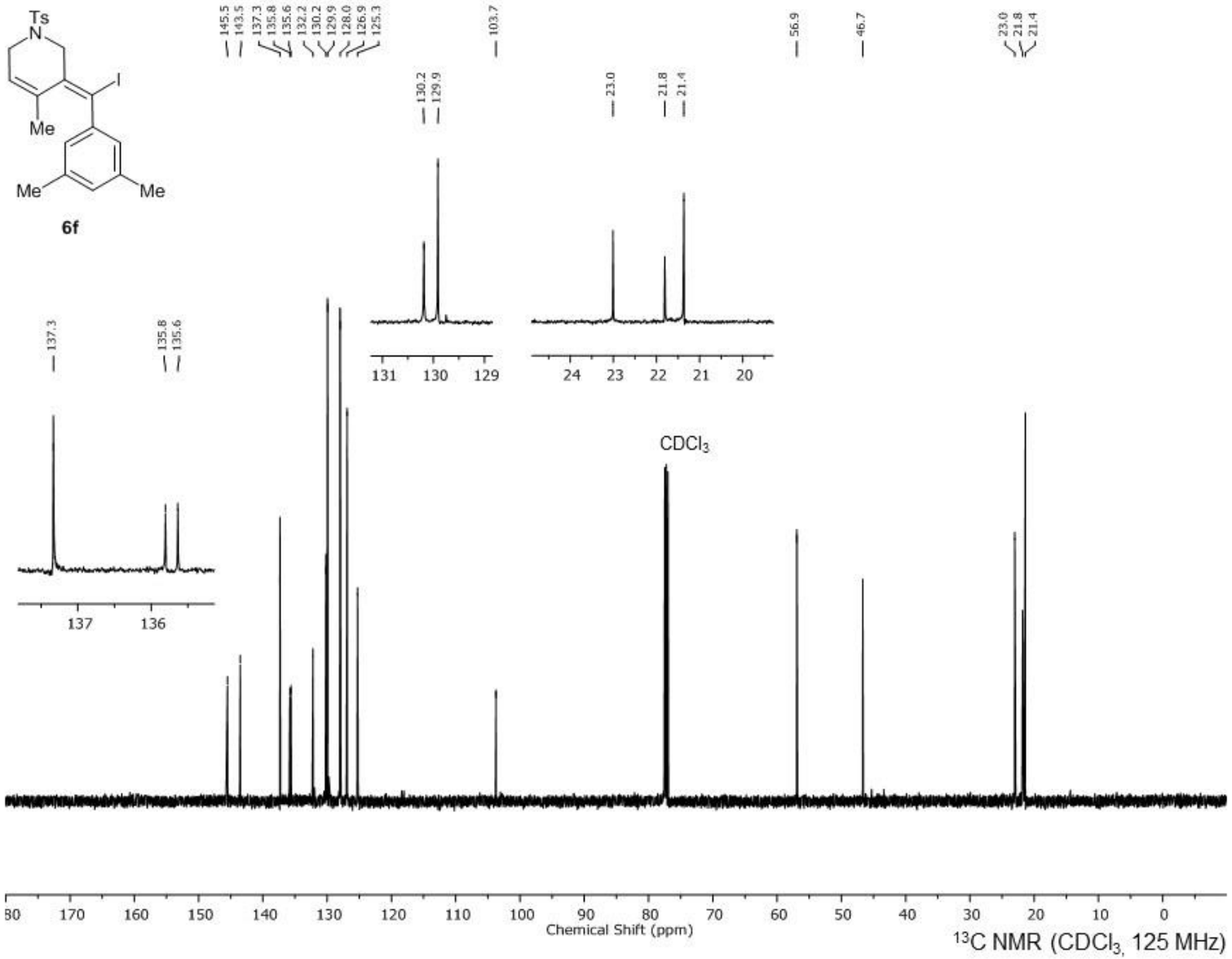

6d
Ts
N
Et
Ph
I
CHCl3
H2O
1H NMR (CDCl3, 500 MHz)
Chemical Shift (ppm)

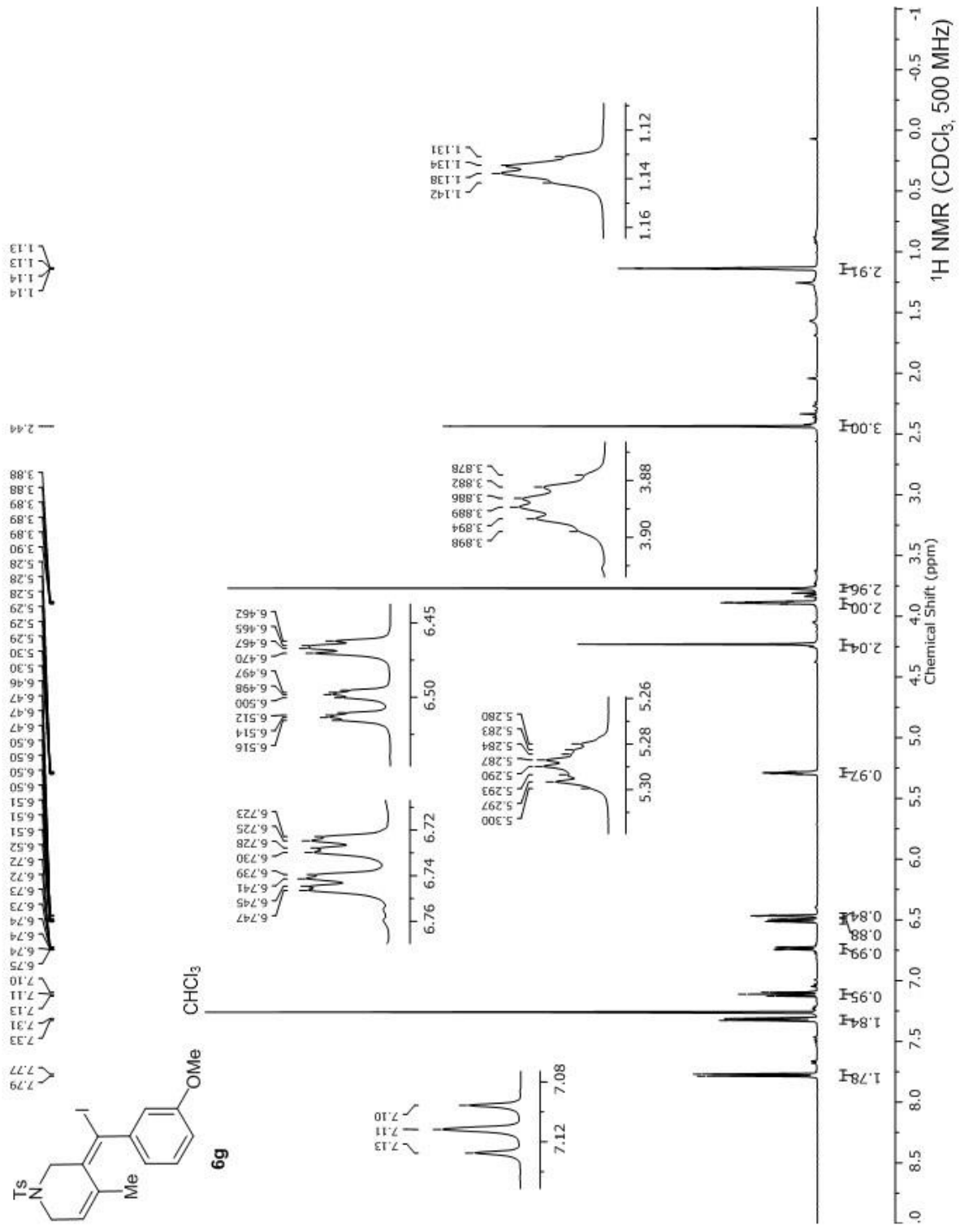

6d
Ts
N
Et
Ph
I
CDCl3
13.3
21.7
27.5
46.8
57.3
102.5
123.5
127.9
128.0
128.6
129.2
130.0
135.5
135.8
138.7
143.7
145.3
127.9
128.0
128.6
129.2
130.0
135.5
135.8
138.7
143.7
145.3
128.0 128.5 129.0 129.5 130.0
135.5 136.0
Chemical Shift (ppm)
13C NMR (CDCl3, 125 MHz)

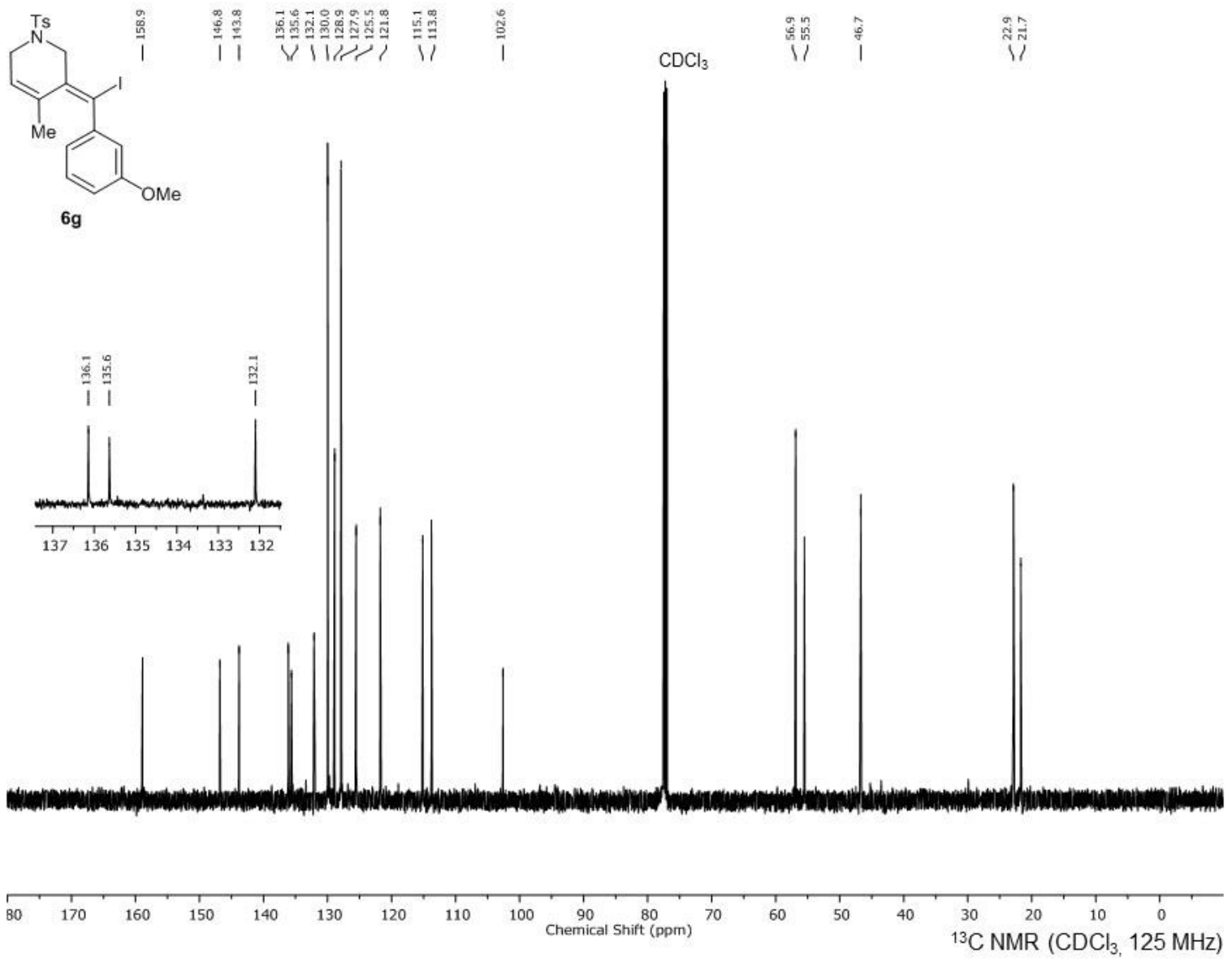

Ts
N
I
Me
OMe
6e
CHCl3
7.79
7.77
7.32
7.30
6.84
6.82
6.72
6.71
5.29
5.28
5.27
4.21
3.90
3.89
3.88
3.79
1.12
1.11
5.284
5.282
5.279
5.277
5.274
5.272
3.898
3.894
3.890
3.886
3.882
3.878
1.120
1.117
1.113
1.109
5.28
5.26
3.90
3.87
1.12
1.10
1.92
2.02
2.00
1.94
1.00
1.98
2.08
2.91
3.10
2.97
Chemical Shift (ppm)
1H NMR (CDCl3, 500 MHz)

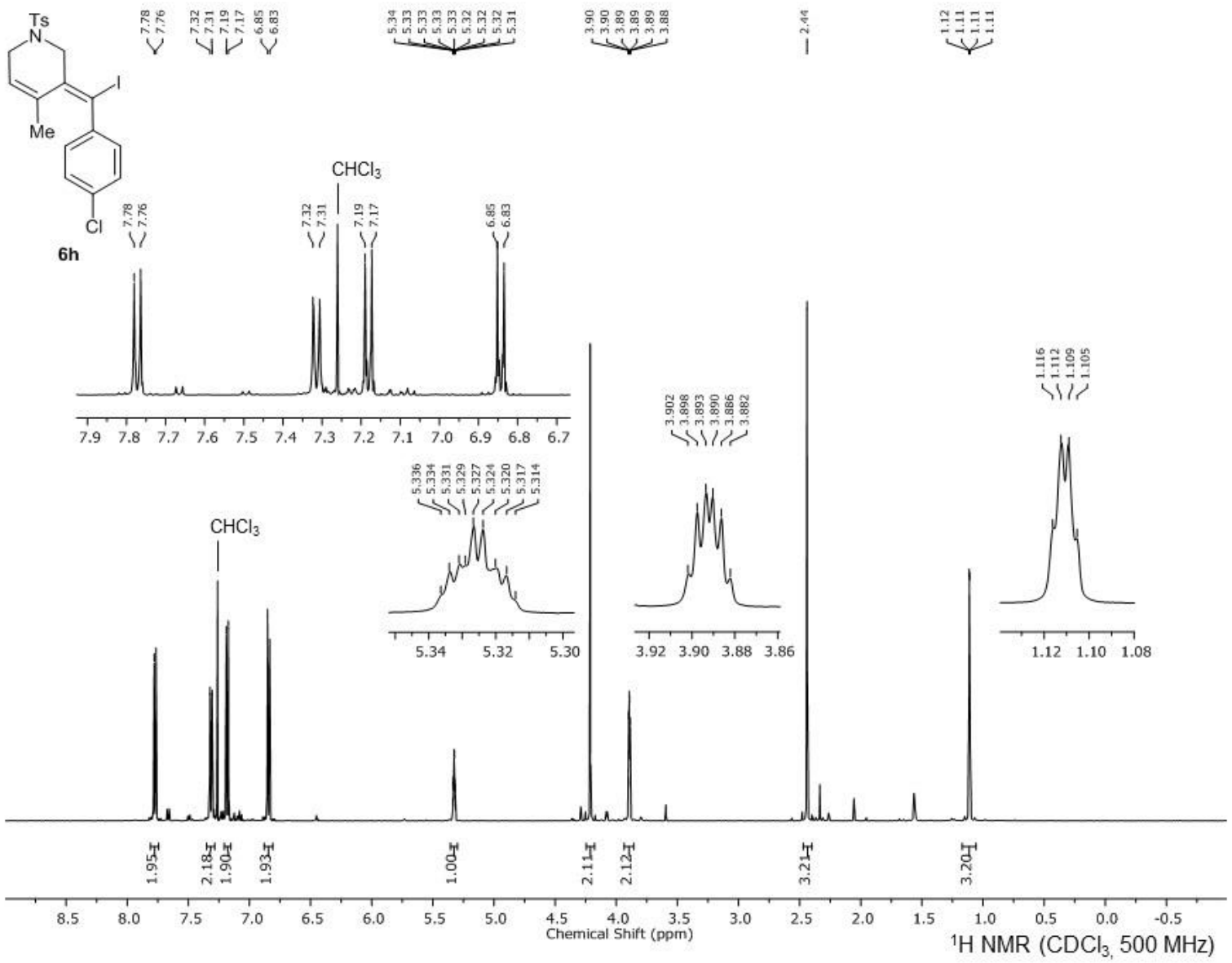

Ts
N
I
Me
OMe
6e
159.6
143.6
138.0
135.9
135.7
132.2
130.7
129.9
127.9
125.3
113.2
103.6
56.9
55.5
46.7
22.9
21.7
CDCl3
138
137
136
135
Chemical Shift (ppm)
13C NMR (CDCl3, 125 MHz)

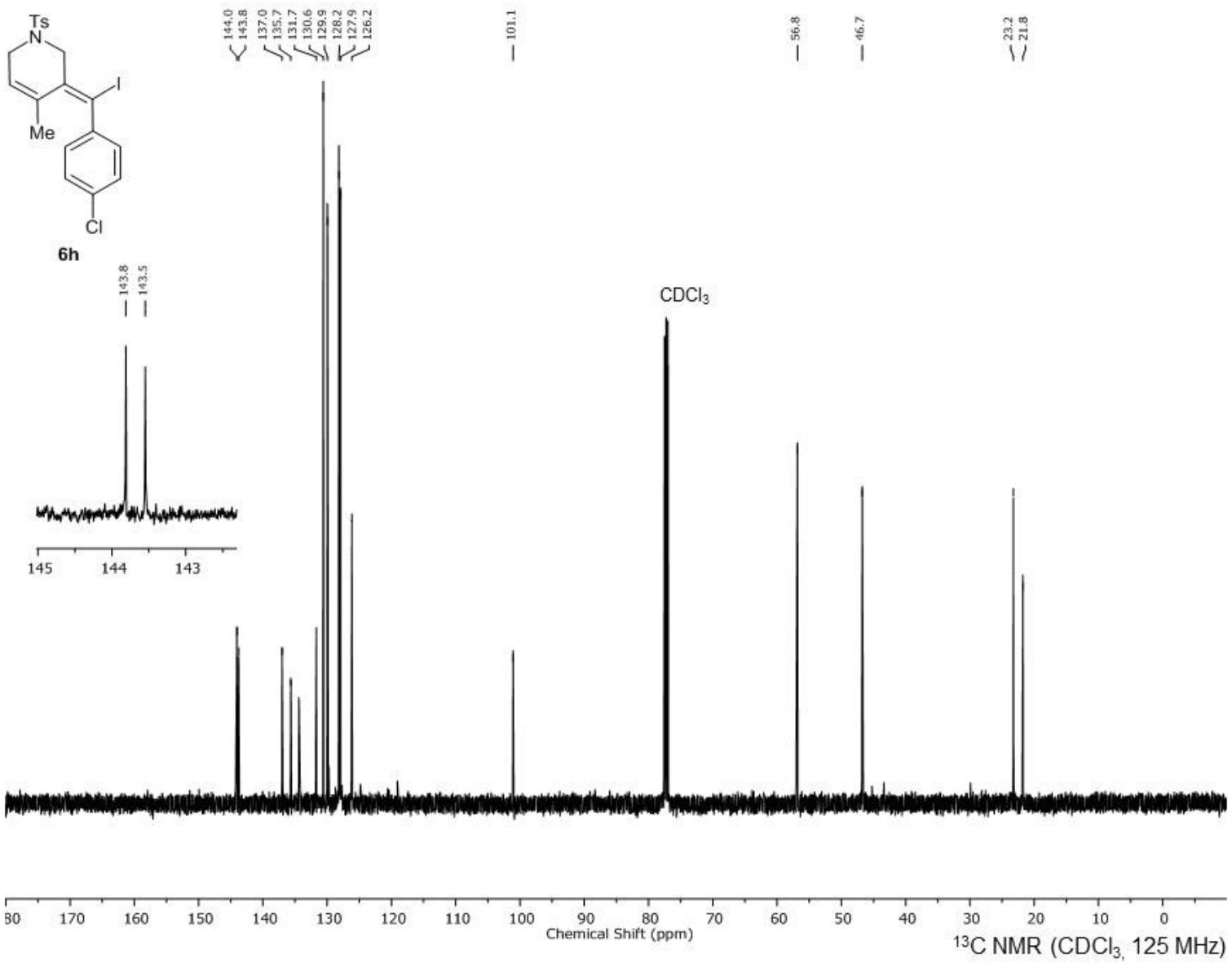

Ts
N
I
Me
Me
Me
6f
CHCl3
7.80
7.78
7.33
7.31
6.82
6.54
5.28
5.28
5.27
5.27
5.27
5.27
5.26
5.26
5.26
5.26
4.24
3.90
3.90
3.89
3.89
3.89
3.88
2.44
2.23
1.10
1.10
1.10
1.10
1.09
1.09
5.276
5.273
5.271
5.269
5.266
5.264
5.262
5.259
3.903
3.899
3.895
3.891
3.888
3.883
1.103
1.100
1.099
1.096
1.094
1.092
5.28 5.26
3.90 3.88
1.10 1.08
2.00
2.04
1.00
1.90
1.04
2.13
2.05
3.00
6.05
3.06
.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 -0.5
Chemical Shift (ppm)
1H NMR (CDCl3, 500 MHz)


Ts
N
I
Me
Me
Me
6f
145.5
143.5
137.3
135.8
135.6
132.2
130.2
129.9
128.0
126.9
125.3
103.7
56.9
46.7
23.0
21.8
21.4
CDCl3
Chemical Shift (ppm)
13C NMR (CDCl3, 125 MHz)

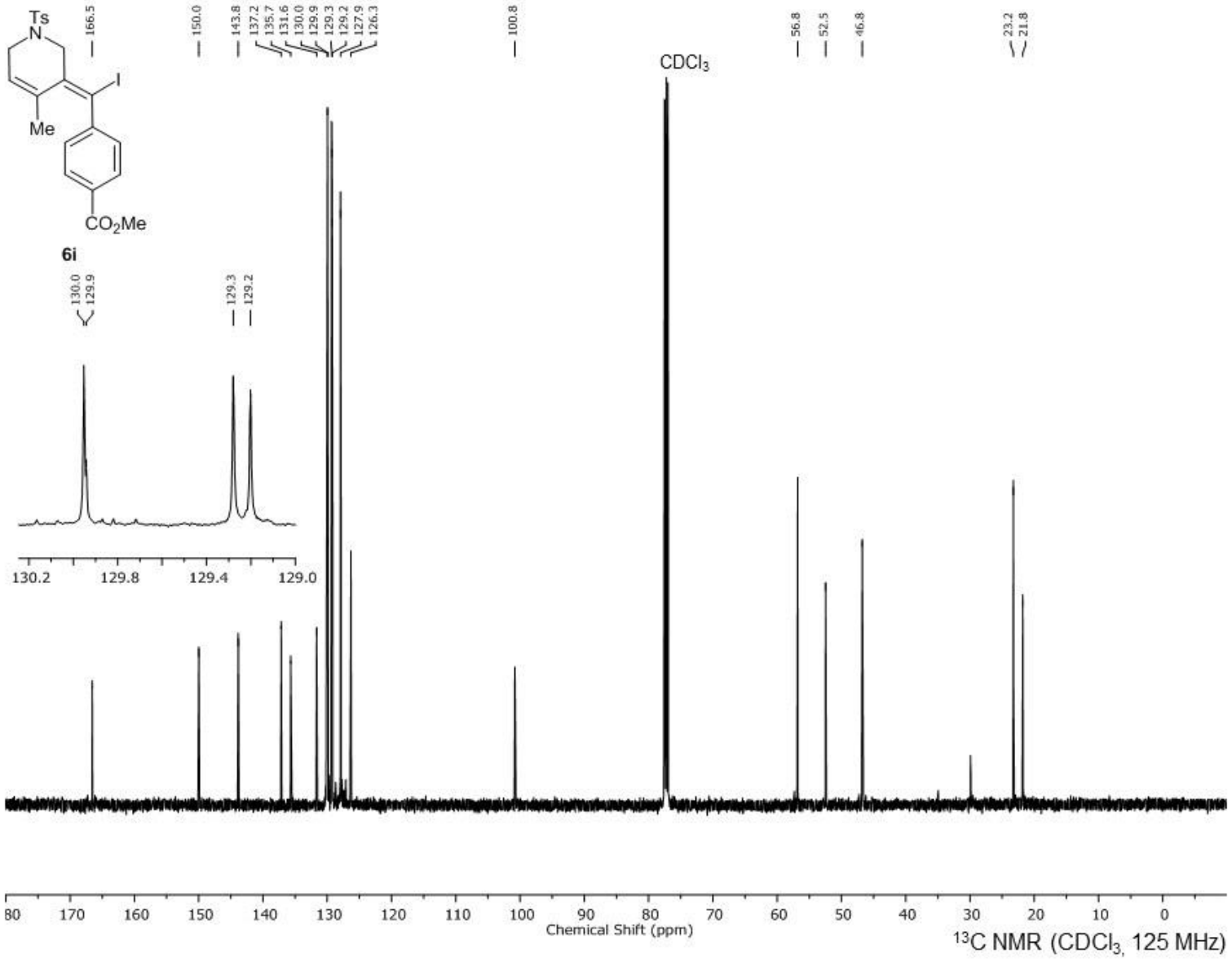

Ts
N
Me
I
OMe
6g
CHCl3
1H NMR (CDCl3, 500 MHz)
Chemical Shift (ppm)

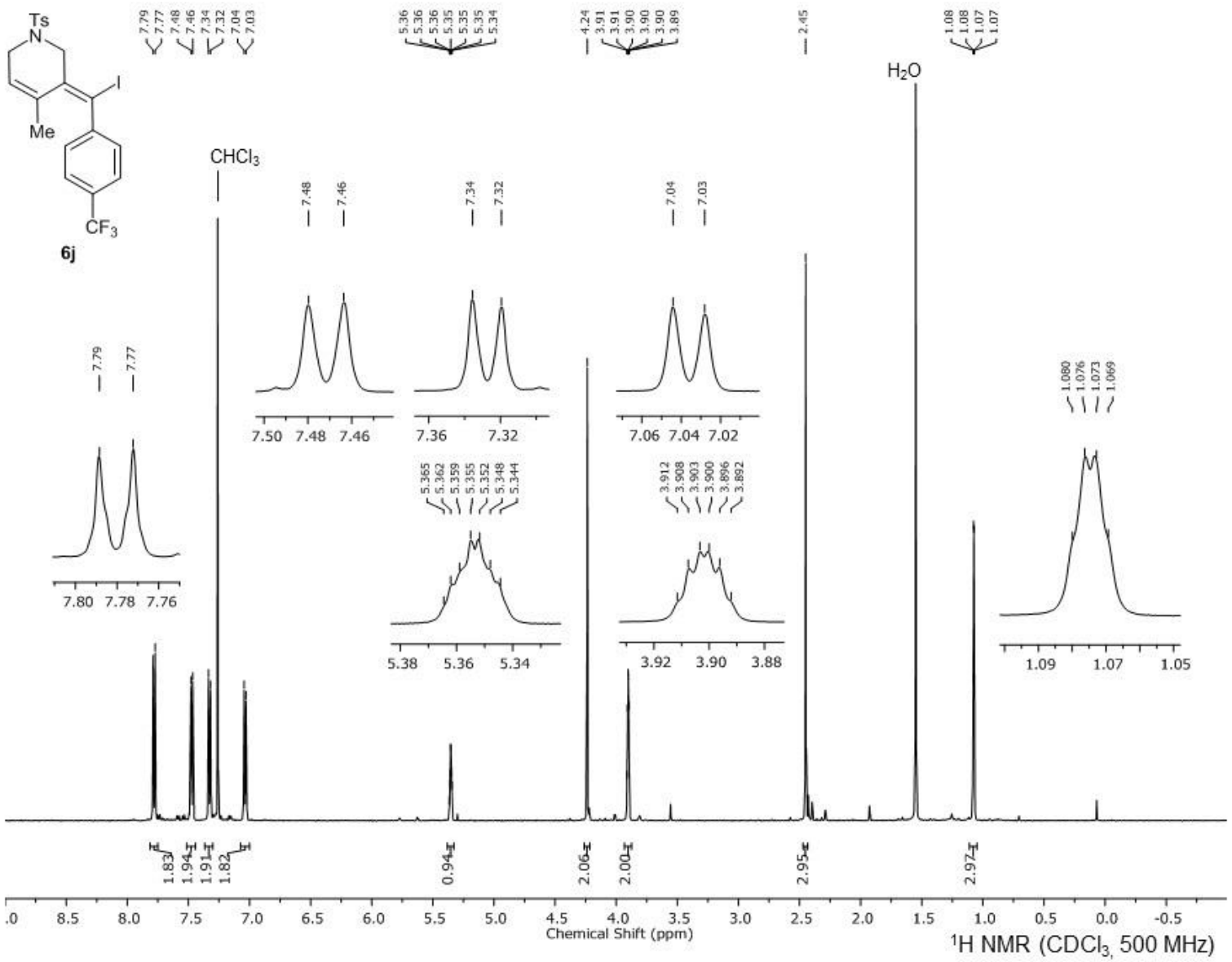

Ts
N
I
Me
OMe
6g
158.9
146.8
143.8
136.1
135.6
132.1
130.0
128.9
127.9
125.5
121.8
115.1
113.8
102.6
CDCl3
56.9
55.5
46.7
22.9
21.7
136.1
135.6
132.1
137 136 135 134 133 132
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift (ppm)
13C NMR (CDCl3, 125 MHz)

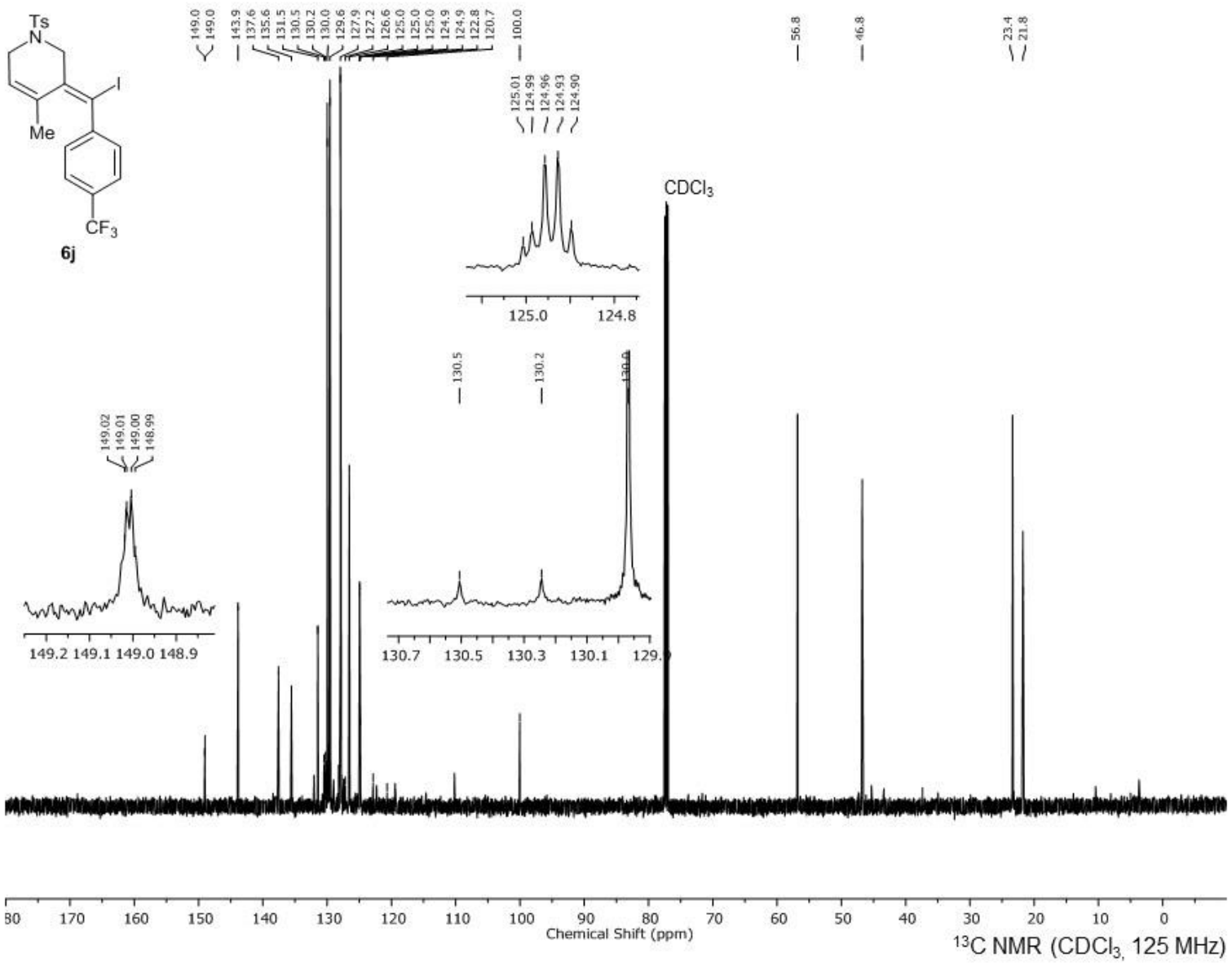

Ts
N
I
Me
Cl
6h
7.78
7.76
7.32
7.31
7.19
7.17
6.85
6.83
5.34
5.33
5.33
5.33
5.32
5.32
5.31
3.90
3.90
3.89
3.89
3.89
3.88
2.44
1.12
1.11
1.11
1.11
CHCl3
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7
5.336
5.334
5.331
5.329
5.327
5.324
5.320
5.317
5.314
5.34 5.32 5.30
3.902
3.898
3.893
3.890
3.886
3.882
3.92 3.90 3.88 3.86
1.116
1.112
1.109
1.105
1.12 1.10 1.08
1.95
2.18
1.90
1.93
1.00
2.11
2.12
3.21
3.20
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 -0.5
Chemical Shift (ppm)
1H NMR (CDCl3, 500 MHz)

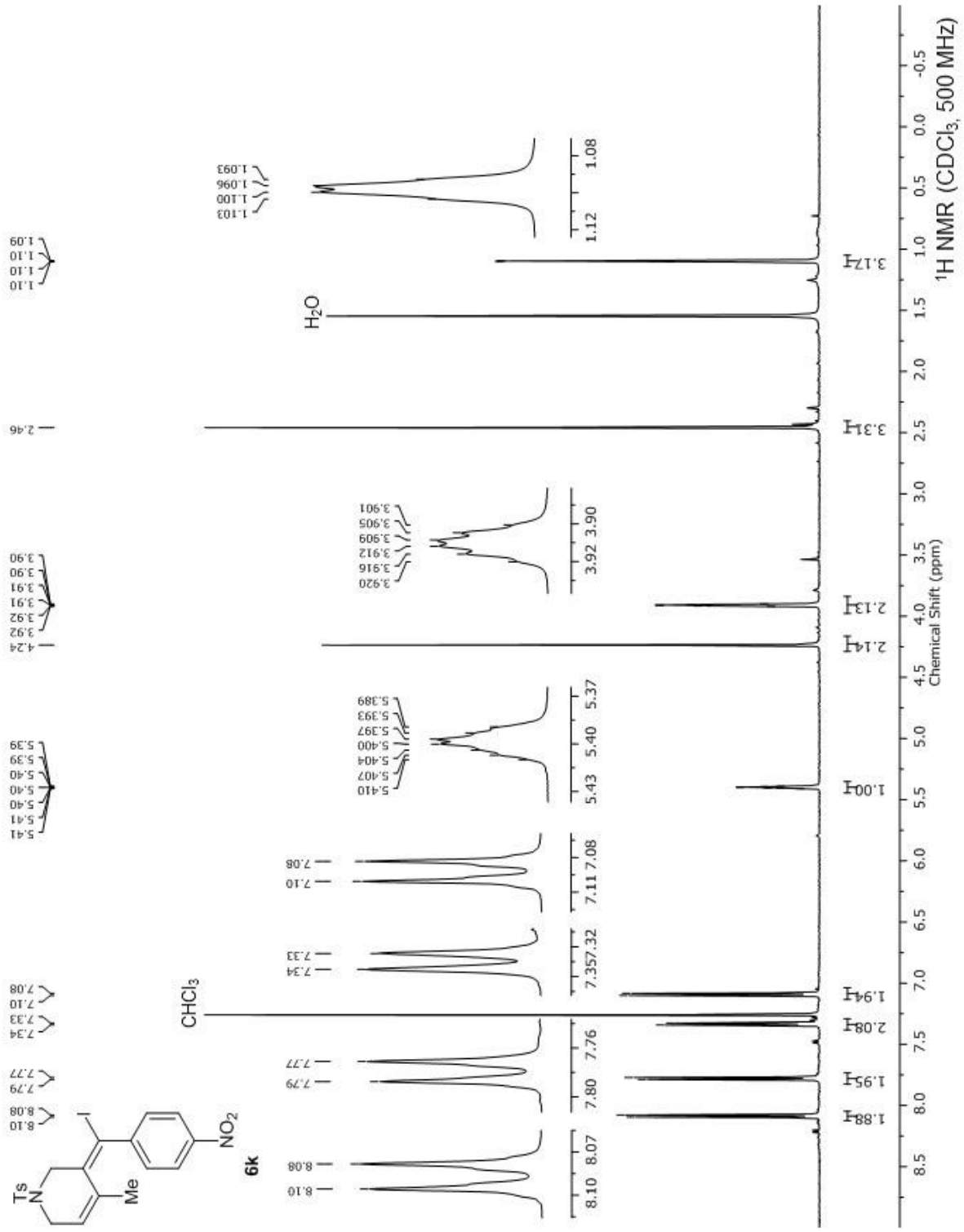

Ts
N
I
Me
Cl
6h
144.0
143.8
137.0
135.7
131.7
130.6
129.9
128.2
127.9
126.2
101.1
56.8
46.7
23.2
21.8
143.8
143.5
145
144
143
CDCl3
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)
13C NMR (CDCl3, 125 MHz)

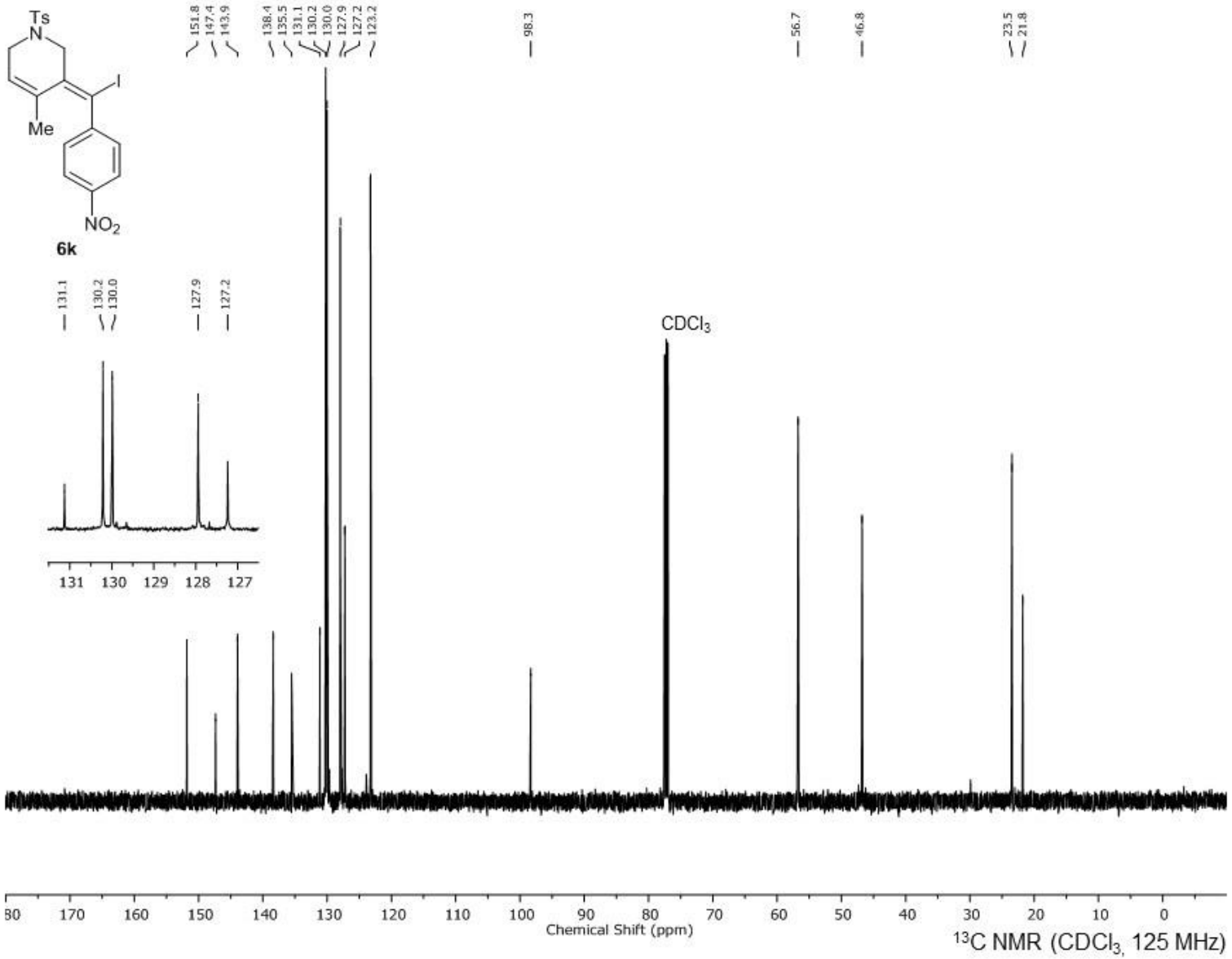
6i
Ts
N
Me
I
CO2Me
CHCl3
1H NMR (CDCl3, 500 MHz)
Chemical Shift (ppm)

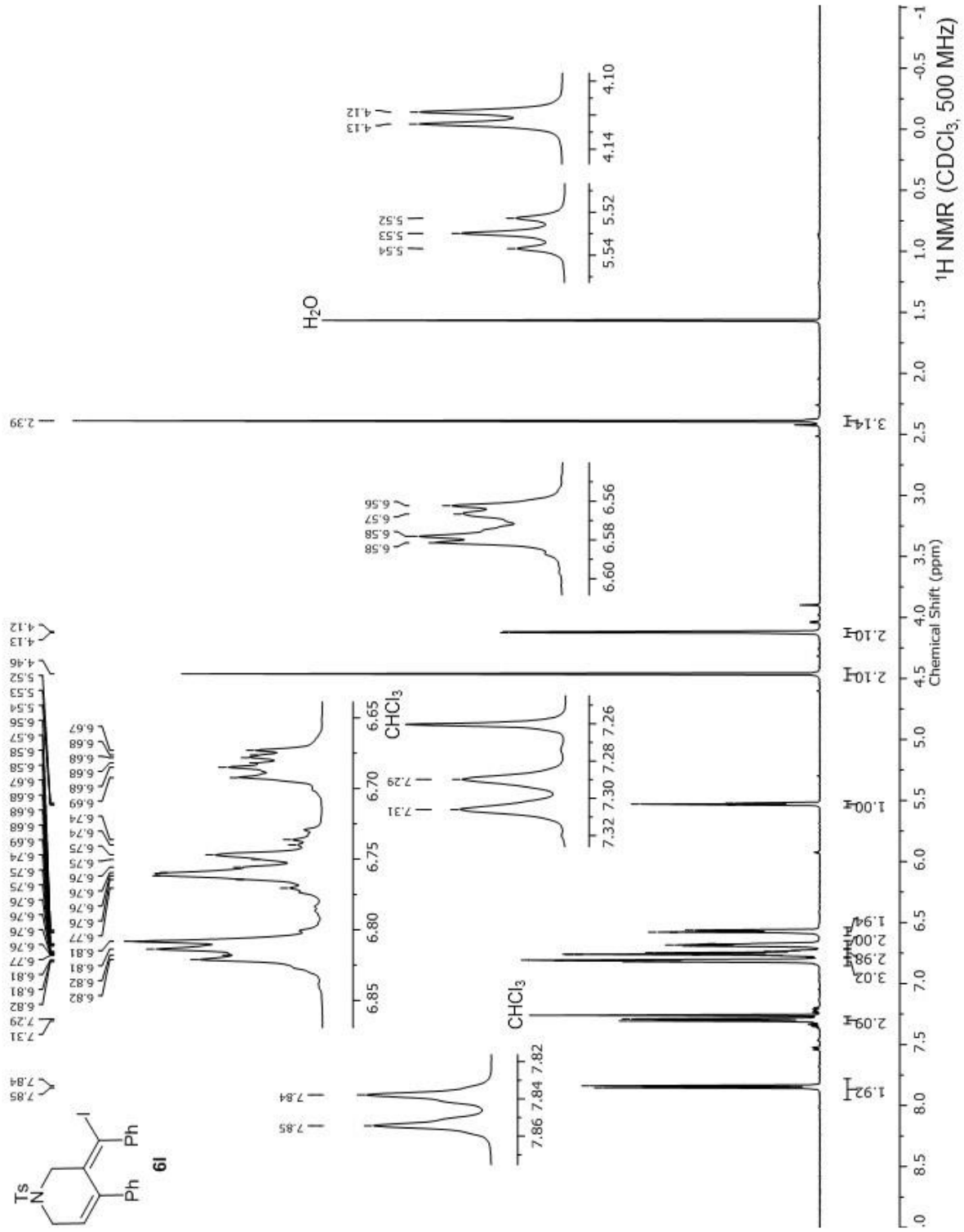

Ts
N
I
Me
CO2Me
6i
166.5
150.0
143.8
137.2
135.7
131.6
130.0
129.9
129.3
129.2
127.9
126.3
100.8
CDCl3
56.8
52.5
46.8
23.2
21.8
130.0
129.9
129.3
129.2
130.2
129.8
129.4
129.0
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)
13C NMR (CDCl3, 125 MHz)

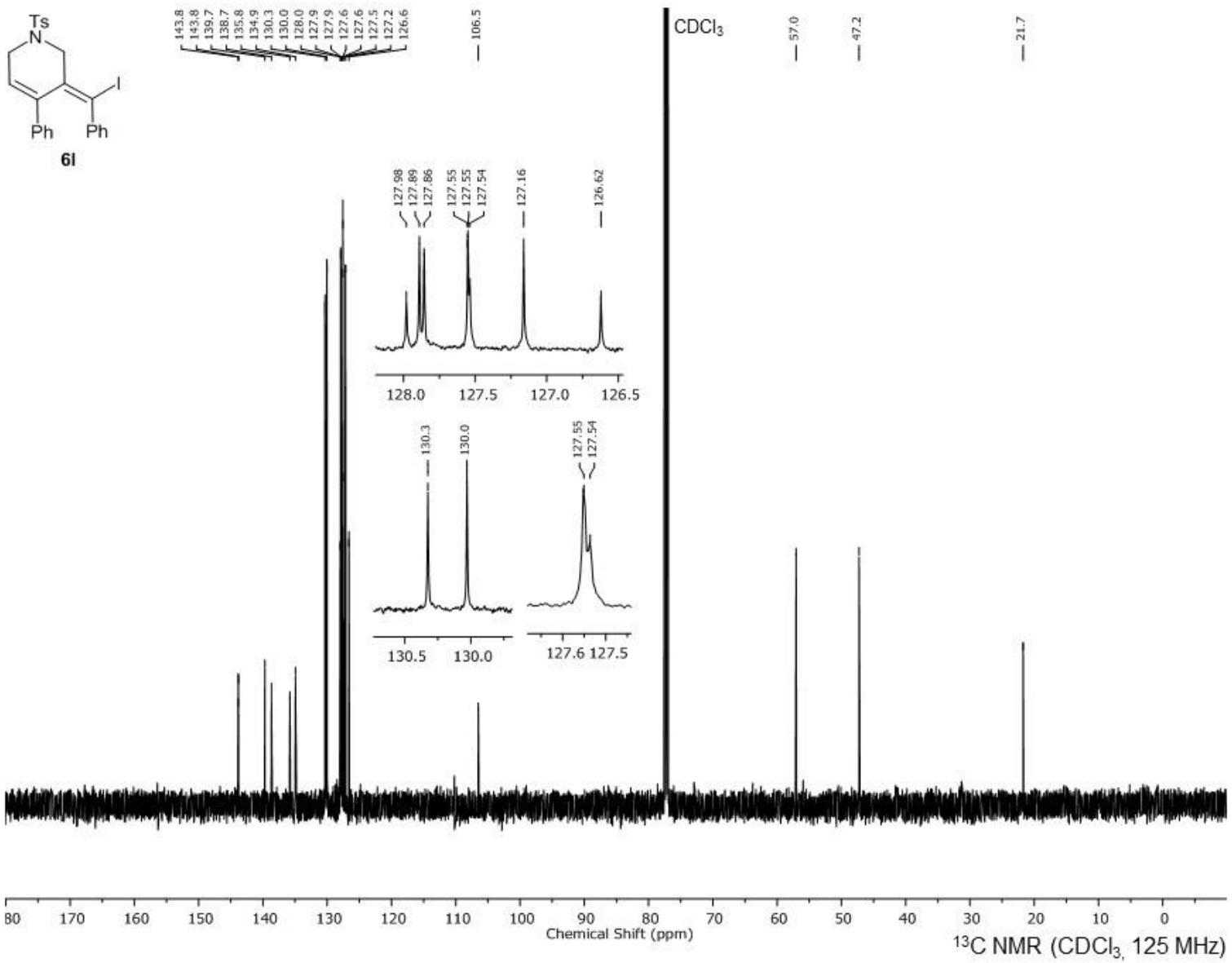

Ts
N
Me
I
CF3
6j
CHCl3
H2O
7.79
7.77
7.48
7.46
7.34
7.32
7.04
7.03
5.36
5.35
4.24
3.91
3.90
3.89
2.45
1.08
1.07
5.365
5.362
5.359
5.355
5.352
5.348
5.344
3.912
3.908
3.903
3.900
3.896
3.892
1.080
1.076
1.073
1.069
7.80 7.78 7.76
7.50 7.48 7.46
7.36 7.32
7.06 7.04 7.02
5.38 5.36 5.34
3.92 3.90 3.88
1.09 1.07 1.05
1.83
1.94
1.91
1.82
0.94
2.06
2.00
2.95
2.97
Chemical Shift (ppm)
1H NMR (CDCl3, 500 MHz)

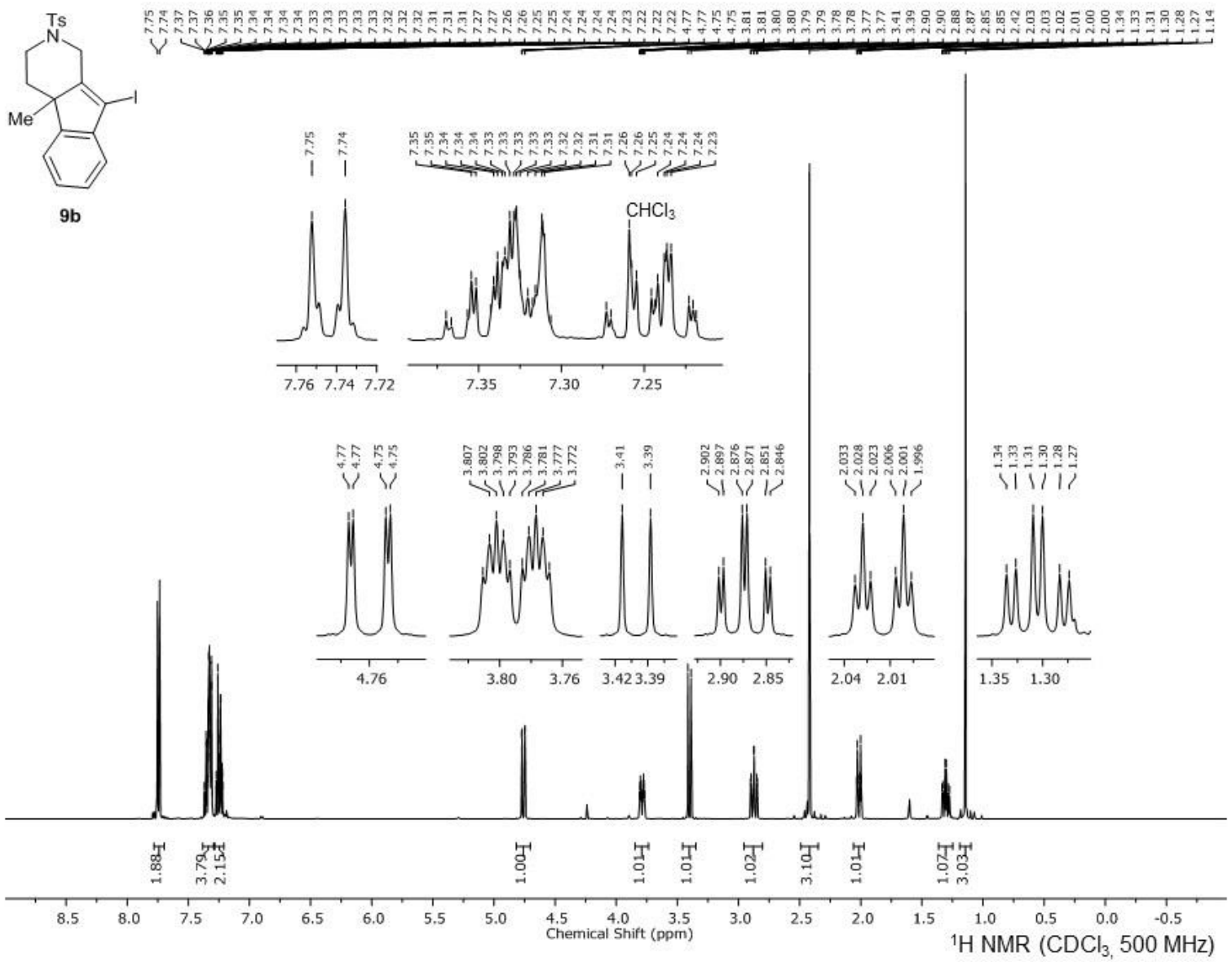

Ts
N
I
Me
CF3
6j
149.0
149.0
143.9
137.6
135.6
131.5
130.5
130.2
130.0
129.6
127.9
127.2
126.6
125.0
125.0
125.0
124.9
124.9
122.8
120.7
100.0
56.8
46.8
23.4
21.8
125.01
124.99
124.96
124.93
124.90
CDCl3
125.0
124.8
130.5
130.2
130.0
149.02
149.01
149.00
148.99
149.2 149.1 149.0 148.9
130.7 130.5 130.3 130.1
Chemical Shift (ppm)
13C NMR (CDCl3, 125 MHz)

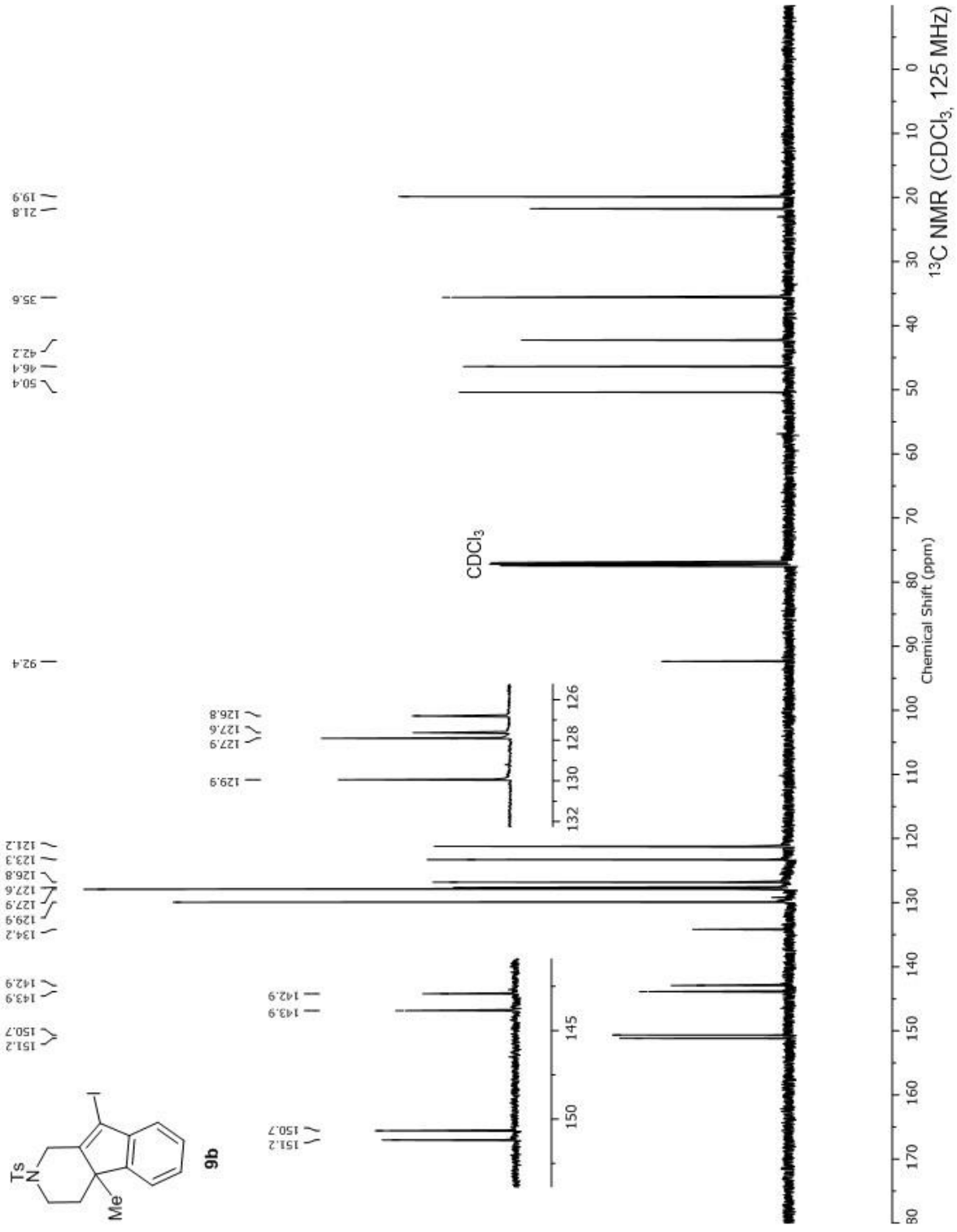

6k
Ts
N
Me
I
NO2
CHCl3
H2O
1H NMR (CDCl3, 500 MHz)
Chemical Shift (ppm)

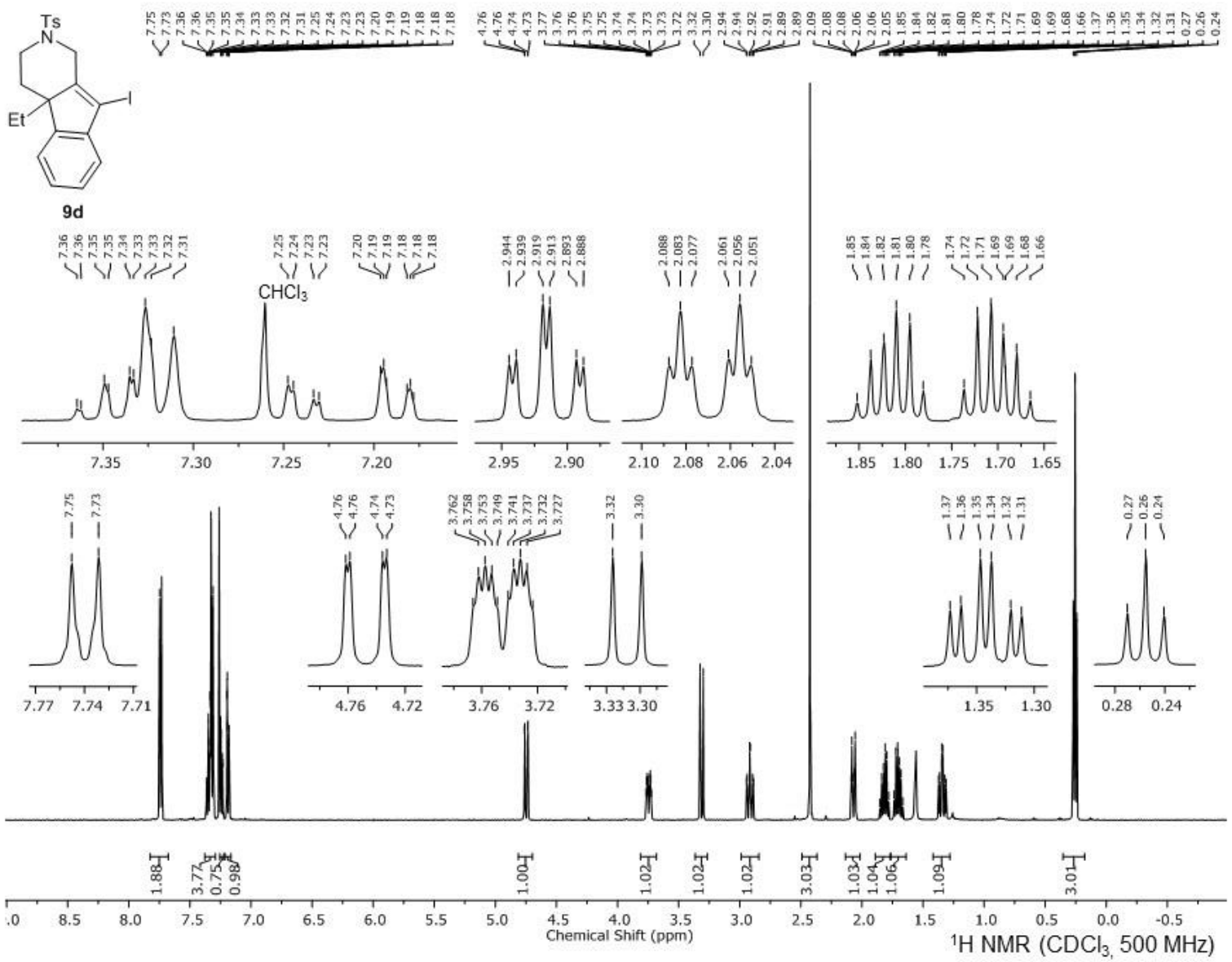

Ts
N
I
Me
NO2
6k
151.8
147.4
143.9
138.4
135.5
131.1
130.2
130.0
127.9
127.2
123.2
98.3
56.7
46.8
23.5
21.8
CDCl3
131.1
130.2
130.0
127.9
127.2
131
130
129
128
127
Chemical Shift (ppm)
13C NMR (CDCl3, 125 MHz)

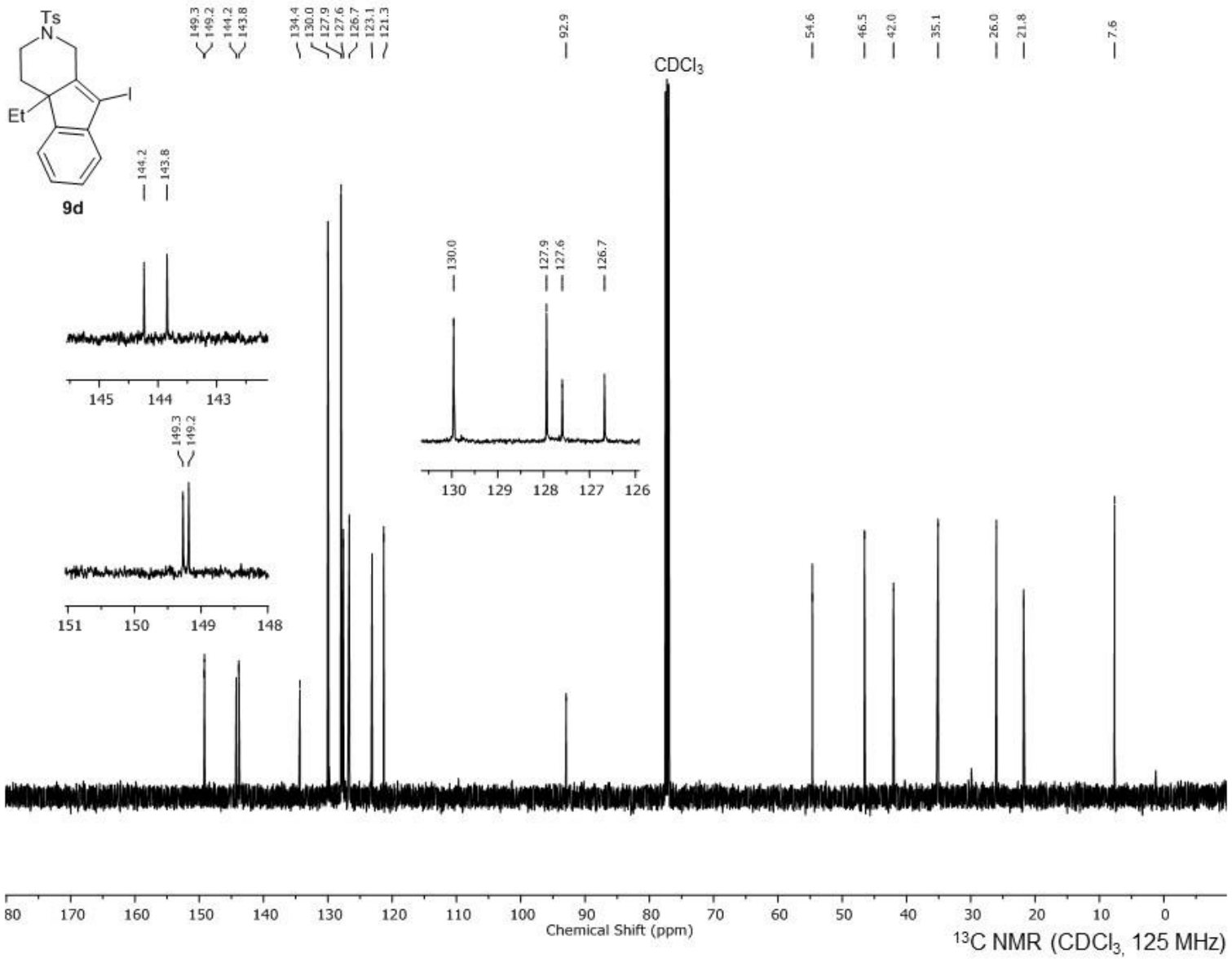

Ts
N
Ph
Ph
I
6l
^{1}H NMR ($CDCl_3$, 500 MHz)
Chemical Shift (ppm)
H_2O
$CHCl_3$
$CHCl_3$

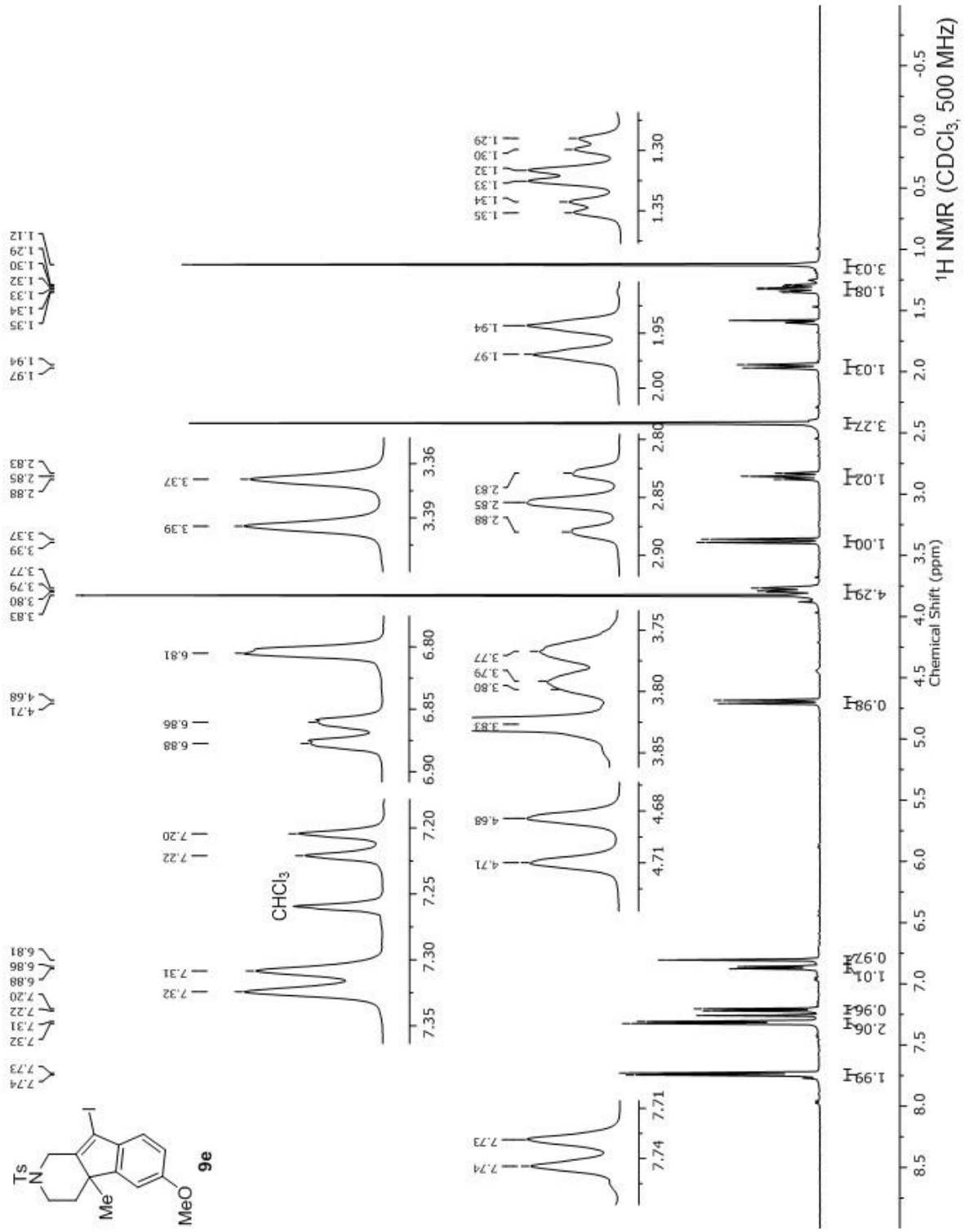

Ts
N
I
Ph
Ph
6l
143.8
143.8
139.7
138.7
135.8
134.9
130.3
130.0
128.0
127.9
127.9
127.6
127.6
127.5
127.2
126.6
106.5
CDCl3
57.0
47.2
21.7
127.98
127.89
127.86
127.55
127.55
127.54
127.16
126.62
128.0
127.5
127.0
126.5
130.3
130.0
127.55
127.54
130.5
130.0
127.6
127.5
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)
13C NMR (CDCl3, 125 MHz)

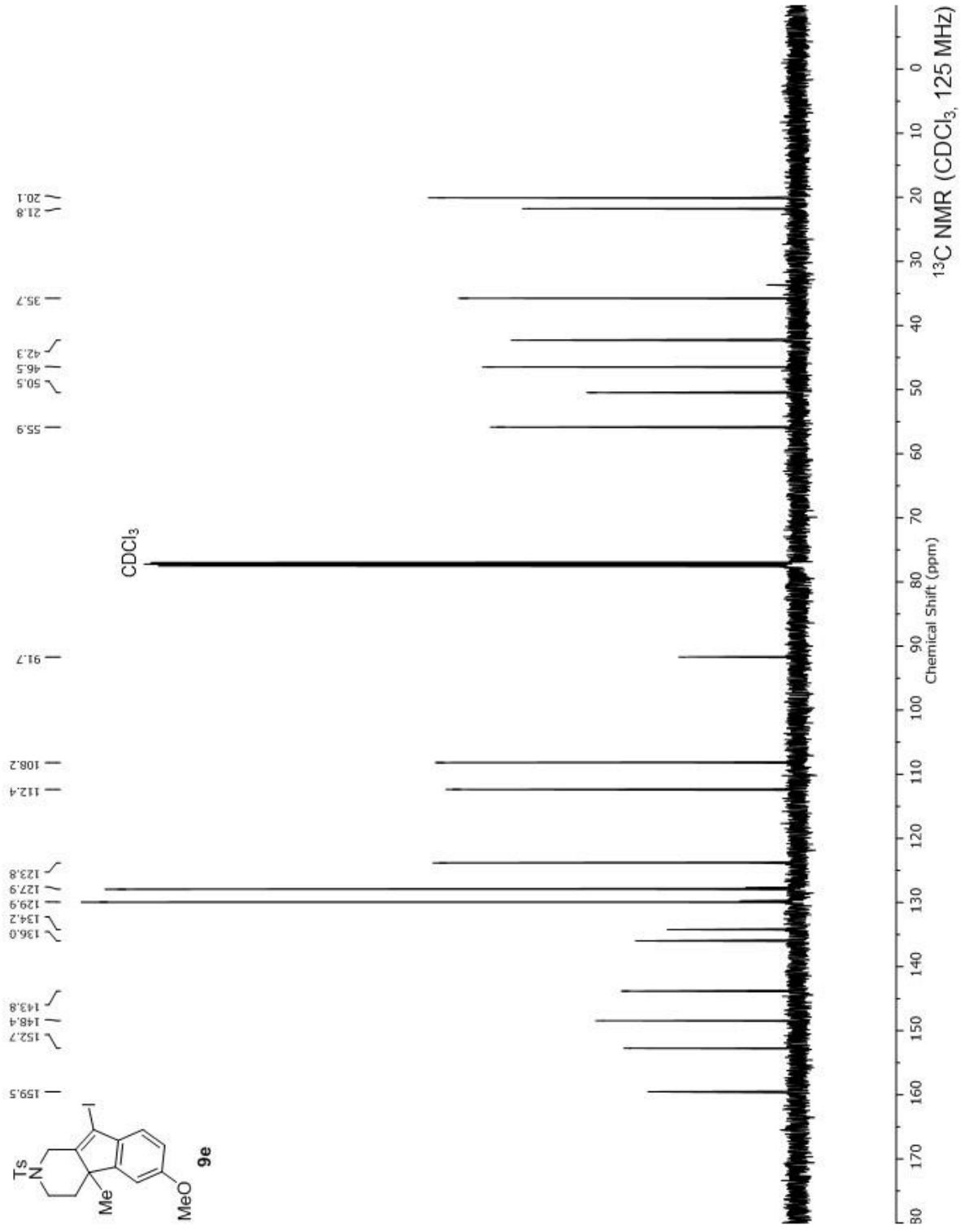

Ts
N
Me
I
9b
CHCl3
Chemical Shift (ppm)
1H NMR (CDCl3, 500 MHz)

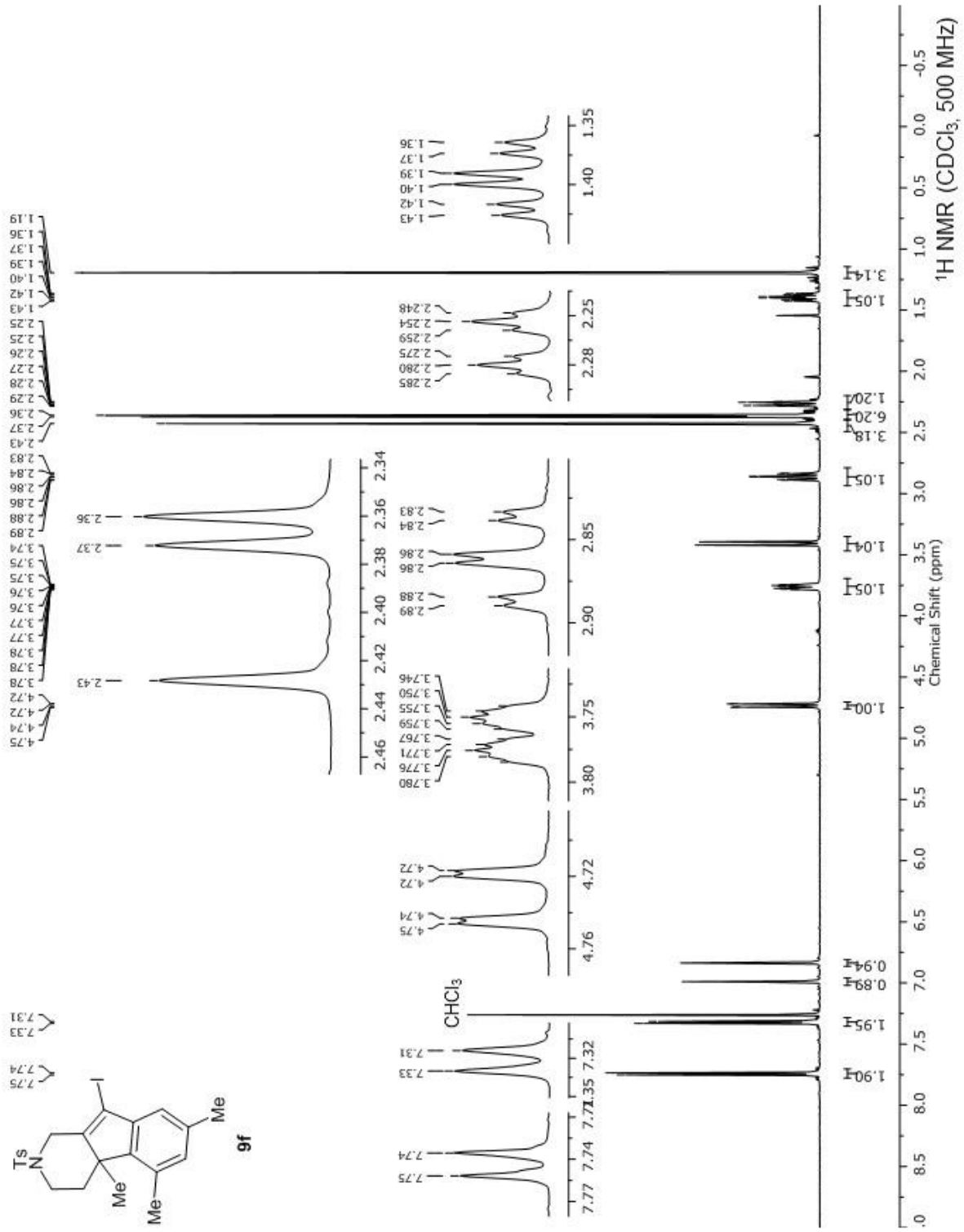

Ts
N
Me
9b
151.2
150.7
143.9
142.9
134.2
129.9
127.9
127.6
126.8
123.3
121.2
92.4
129.9
127.9
127.6
126.8
151.2
150.7
143.9
142.9
CDCl3
50.4
46.4
42.2
35.6
21.8
19.9
13C NMR (CDCl3, 125 MHz)
Chemical Shift (ppm)

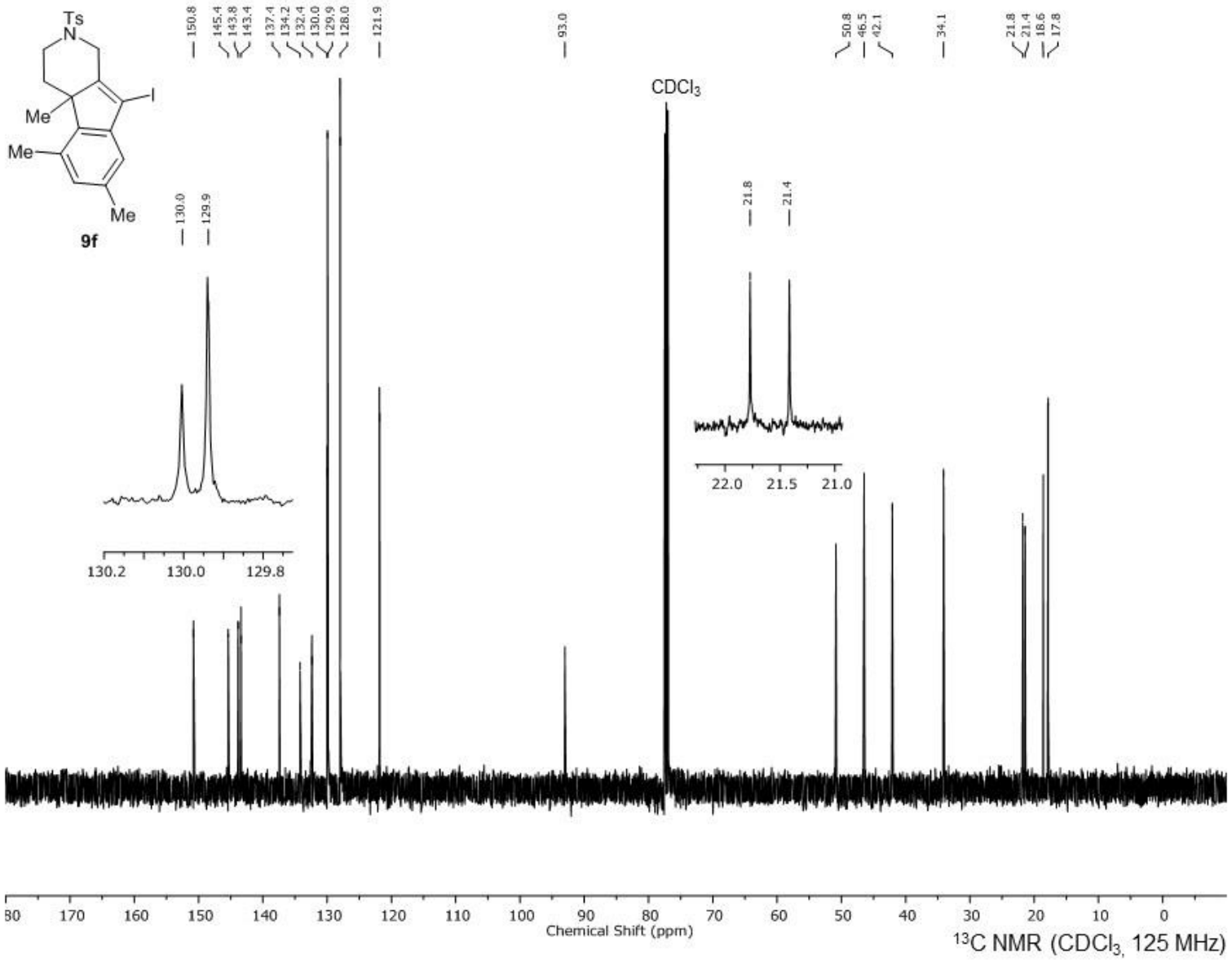

Ts
N
Et
I
9d
CHCl3
Chemical Shift (ppm)
1H NMR (CDCl3, 500 MHz)

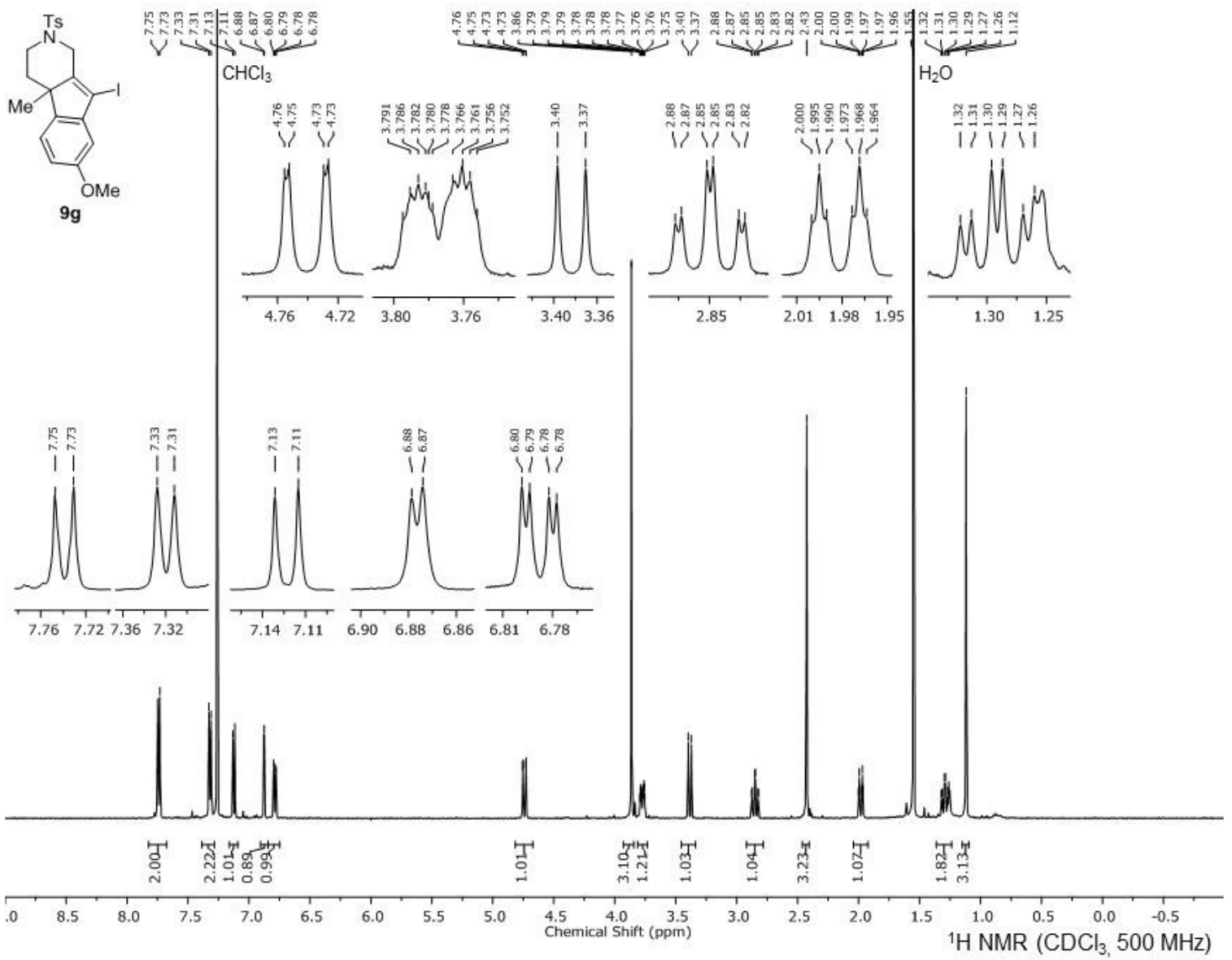

Ts
N
Et
I
9d
149.3
149.2
144.2
143.8
134.4
130.0
127.9
127.6
126.7
123.1
121.3
92.9
CDCl3
54.6
46.5
42.0
35.1
26.0
21.8
7.6
145
144
143
130
129
128
127
126
151
150
149
148
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)
13C NMR (CDCl3, 125 MHz)

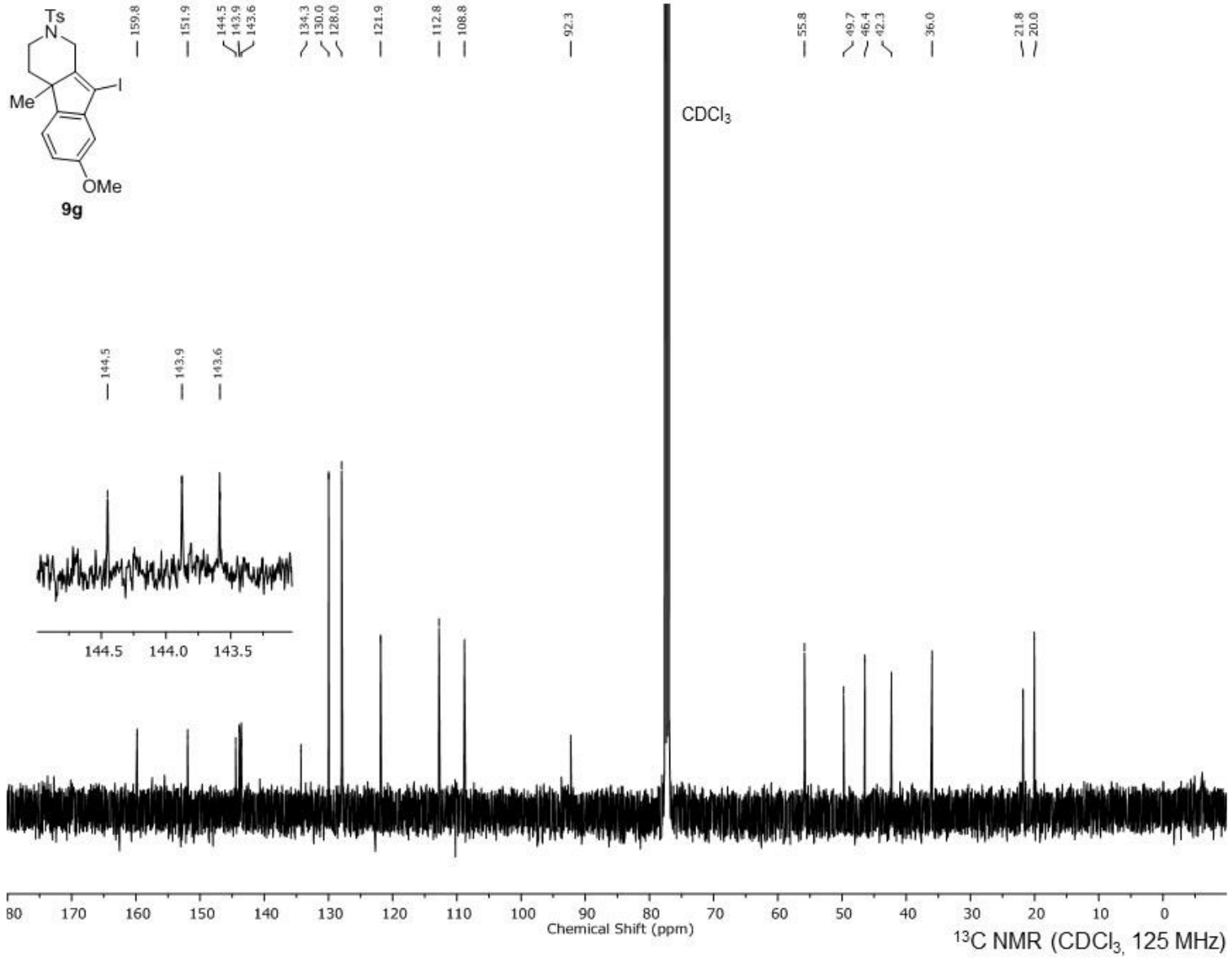

Ts
N
Me
MeO
9e
CHCl3
Chemical Shift (ppm)
1H NMR (CDCl3, 500 MHz)

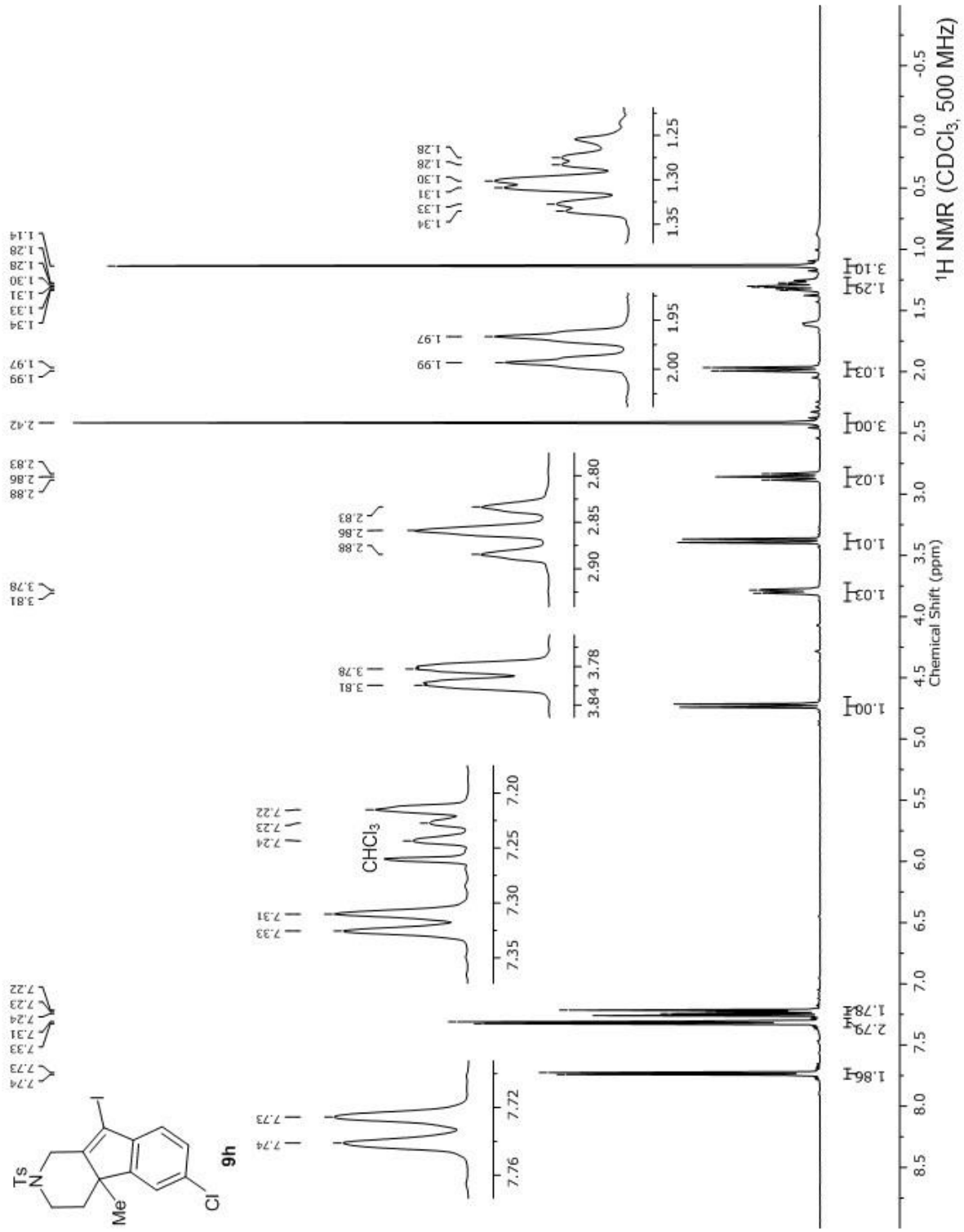

159.5
152.7
148.4
143.8
136.0
134.2
129.9
127.9
123.8
112.4
108.2
91.7
CDCl3
55.9
50.5
46.5
42.3
35.7
21.8
20.1
Ts
N
Me
MeO
9e
13C NMR (CDCl3, 125 MHz)
Chemical Shift (ppm)

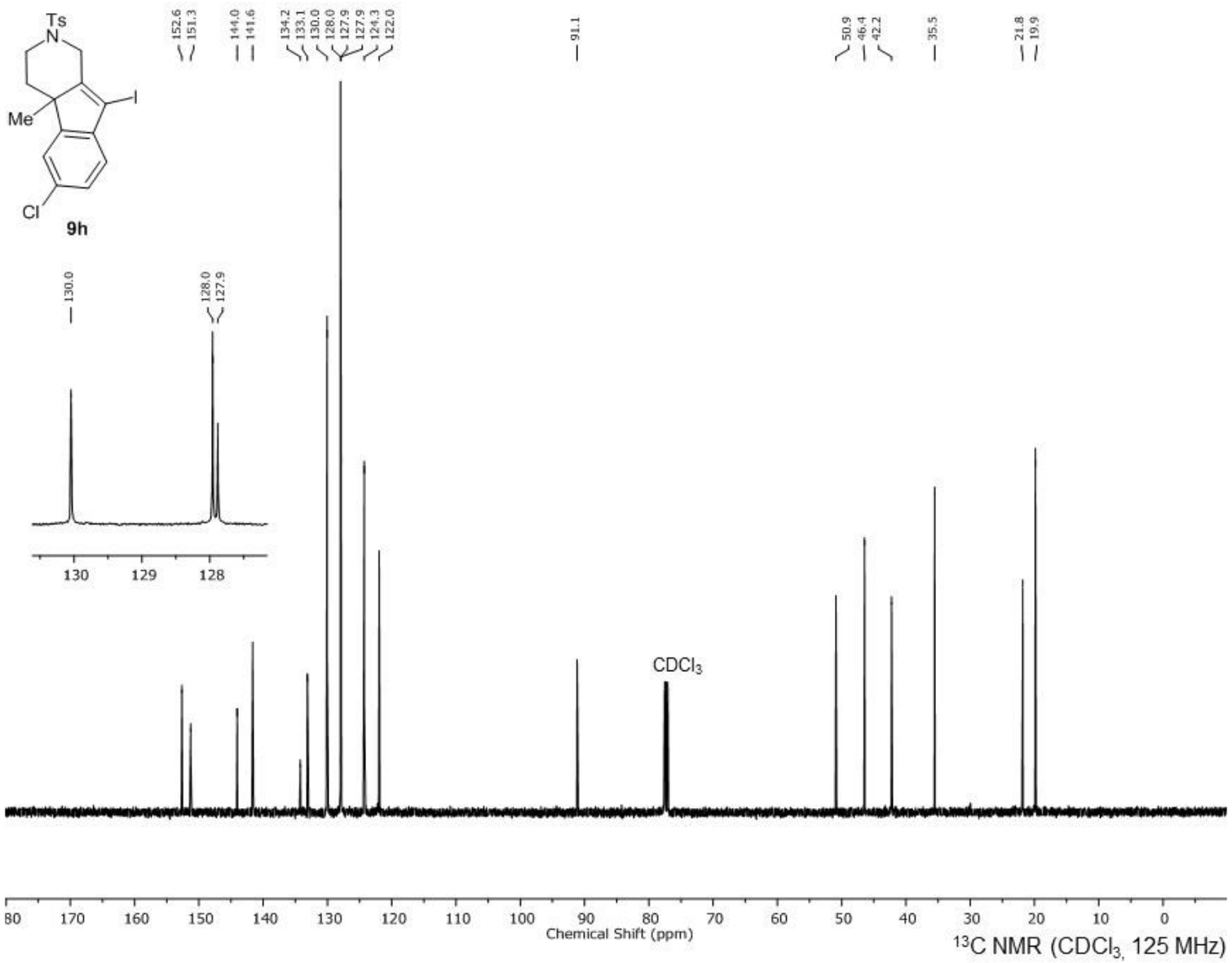

Ts
N
Me
Me
Me
I
9f
CHCl3
Chemical Shift (ppm)
1H NMR (CDCl3, 500 MHz)

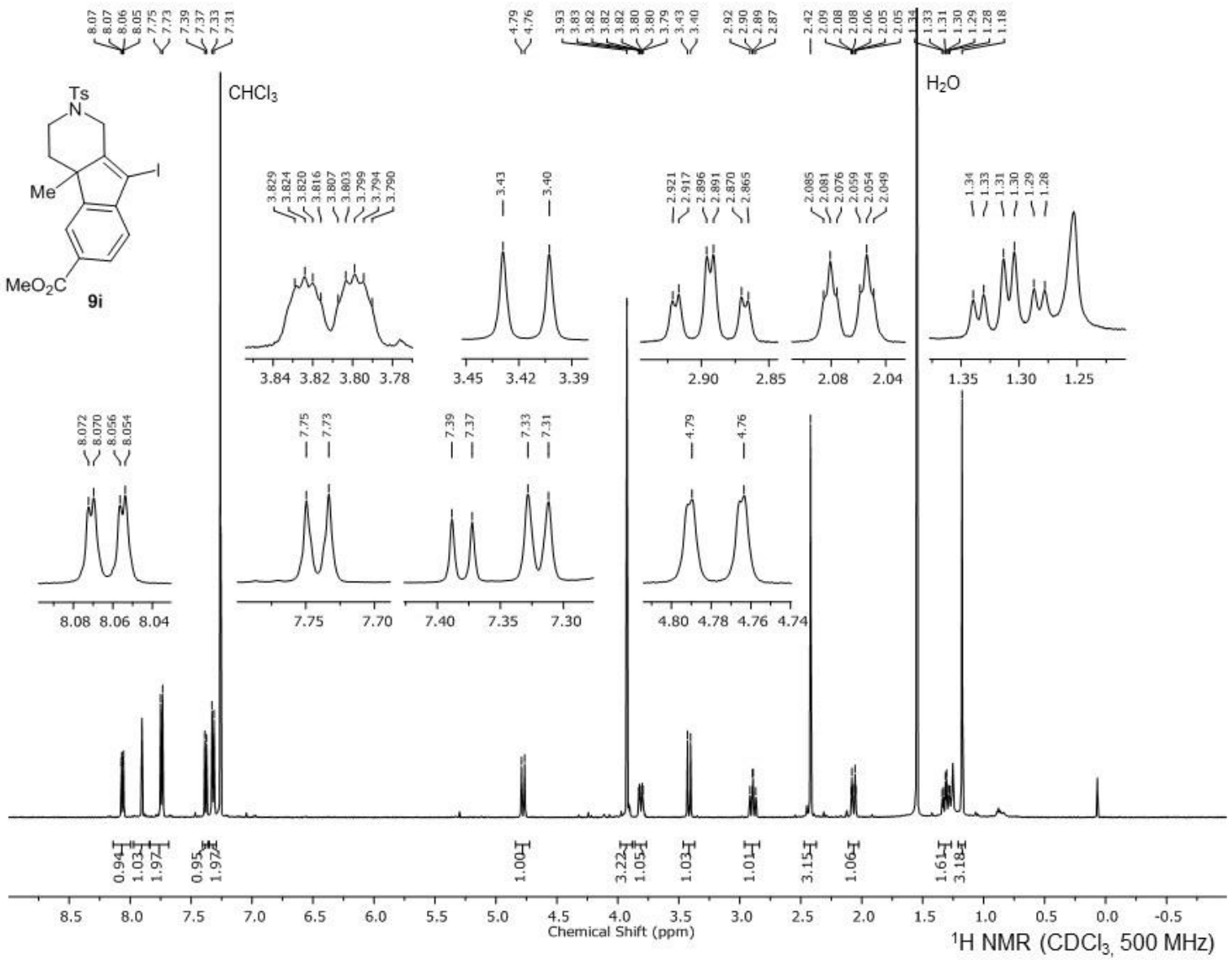

Ts
N
I
Me
Me
Me
9f
150.8
145.4
143.8
143.4
137.4
134.2
132.4
130.0
129.9
128.0
121.9
93.0
CDCl3
50.8
46.5
42.1
34.1
21.8
21.4
18.6
17.8
130.0
129.9
130.2
130.0
129.8
21.8
21.4
22.0
21.5
21.0
Chemical Shift (ppm)
13C NMR (CDCl3, 125 MHz)

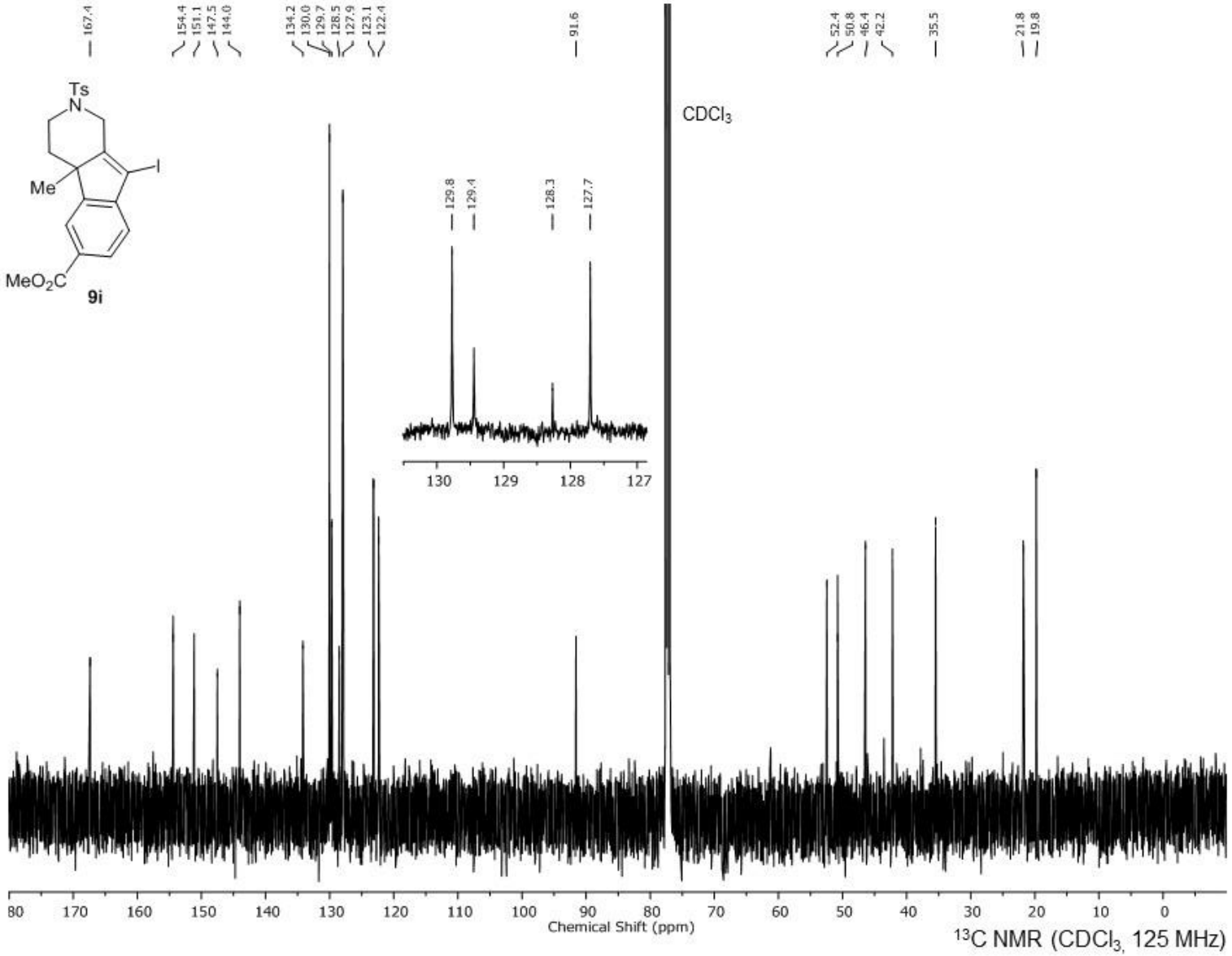

Ts
N
Me
I
OMe
9g
CHCl3
H2O
Chemical Shift (ppm)
1H NMR (CDCl3, 500 MHz)

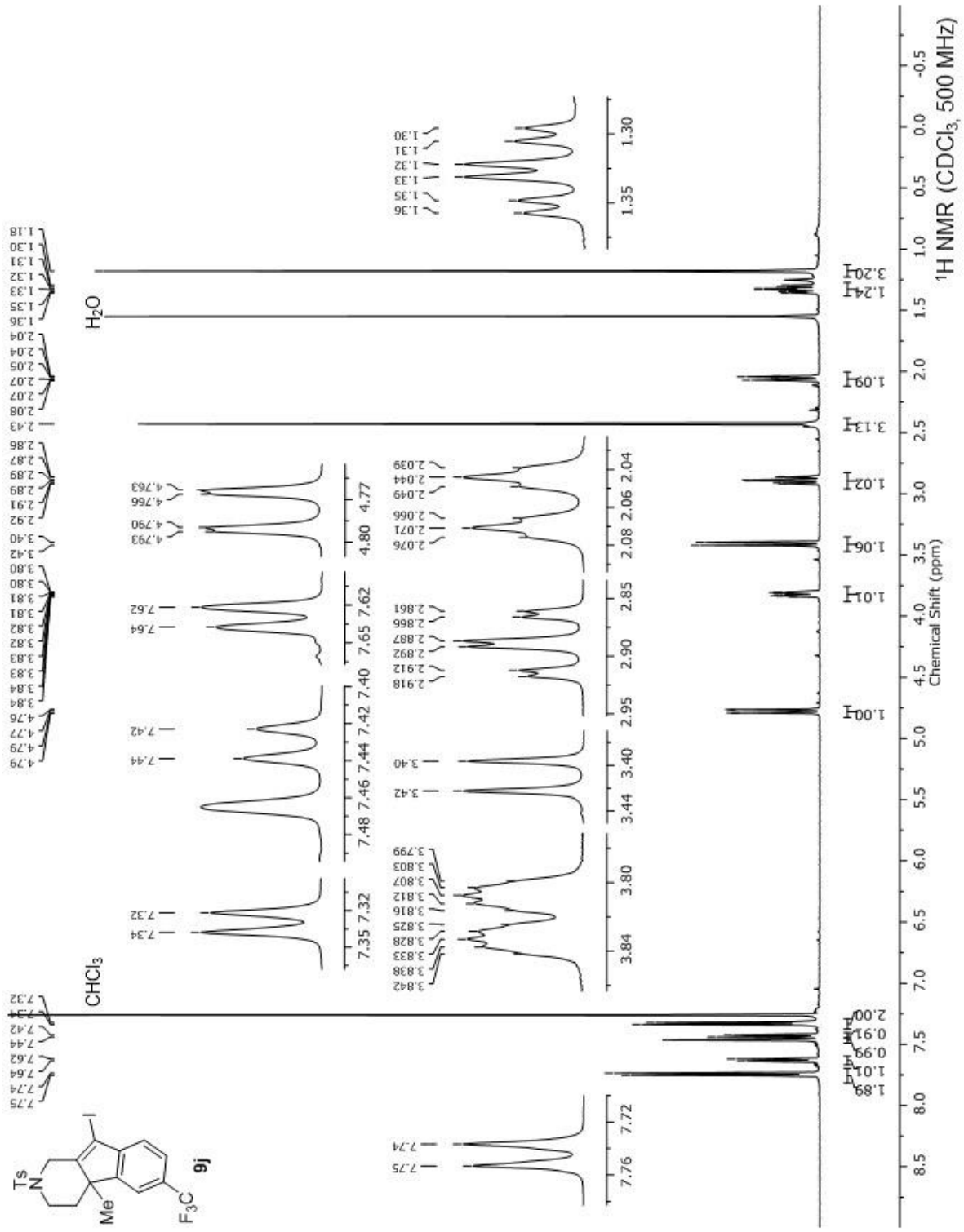

Ts
N
Me
I
OMe
9g
159.8
151.9
144.5
143.9
143.6
134.3
130.0
128.0
121.9
112.8
108.8
92.3
CDCl3
55.8
49.7
46.4
42.3
36.0
21.8
20.0
144.5
144.0
143.5
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)
13C NMR (CDCl3, 125 MHz)

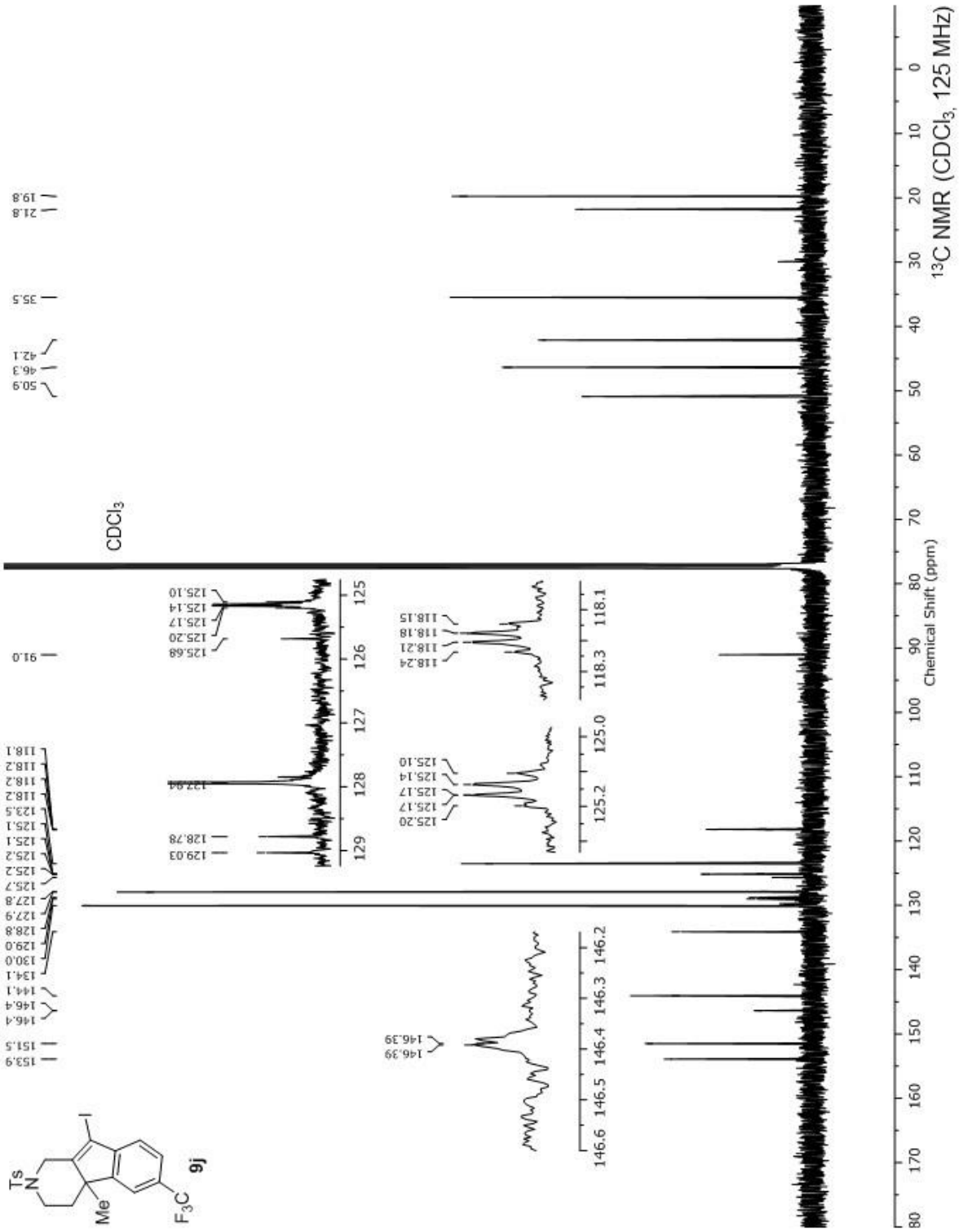

Ts
N
Me
Cl
9h
CHCl3
Chemical Shift (ppm)
1H NMR (CDCl3, 500 MHz)

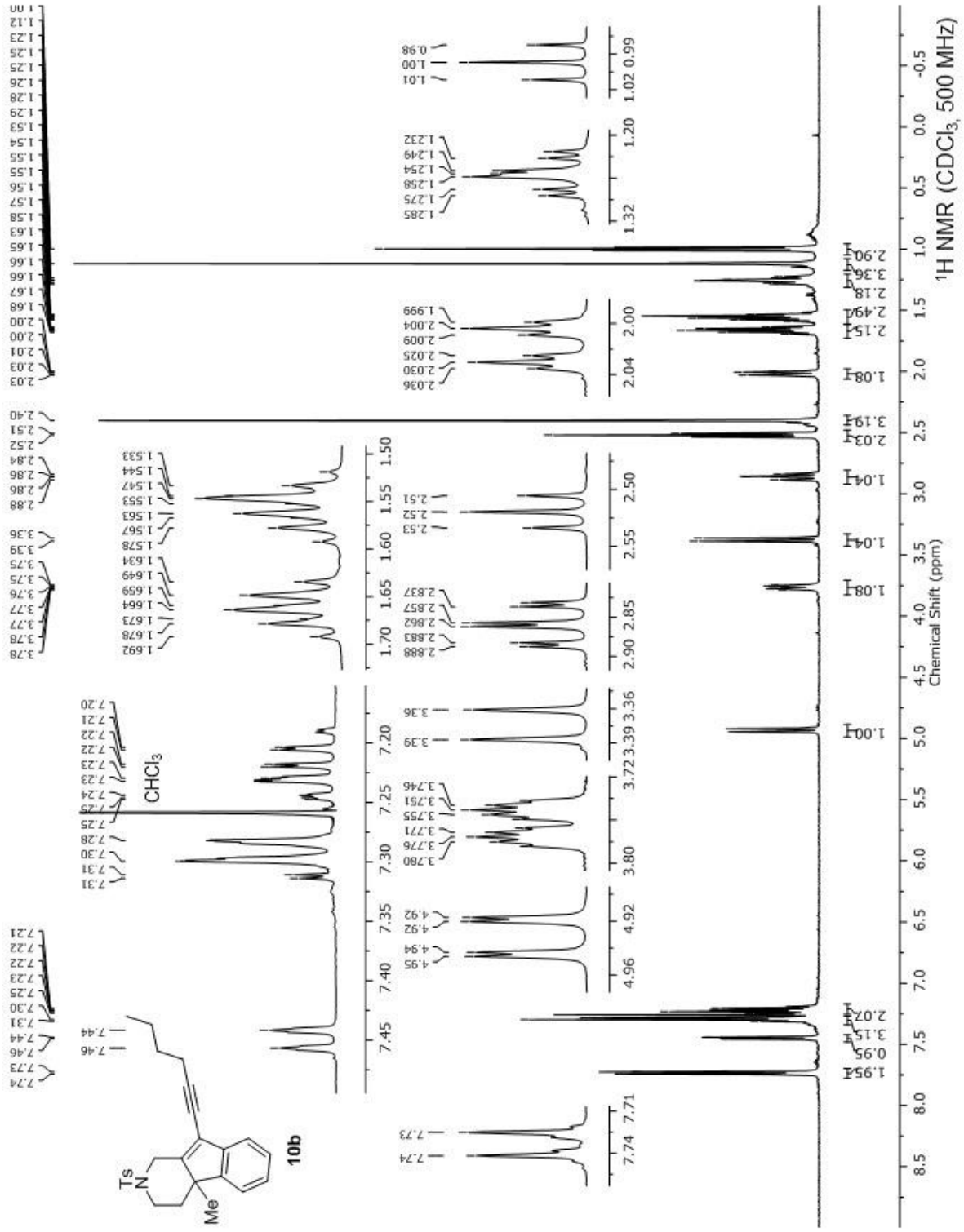

Ts
N
Me
I
Cl
9h
152.6
151.3
144.0
141.6
134.2
133.1
130.0
128.0
127.9
127.9
124.3
122.0
91.1
50.9
46.4
42.2
35.5
21.8
19.9
CDCl3
130.0
128.0
127.9
130
129
128
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)
13C NMR (CDCl3, 125 MHz)

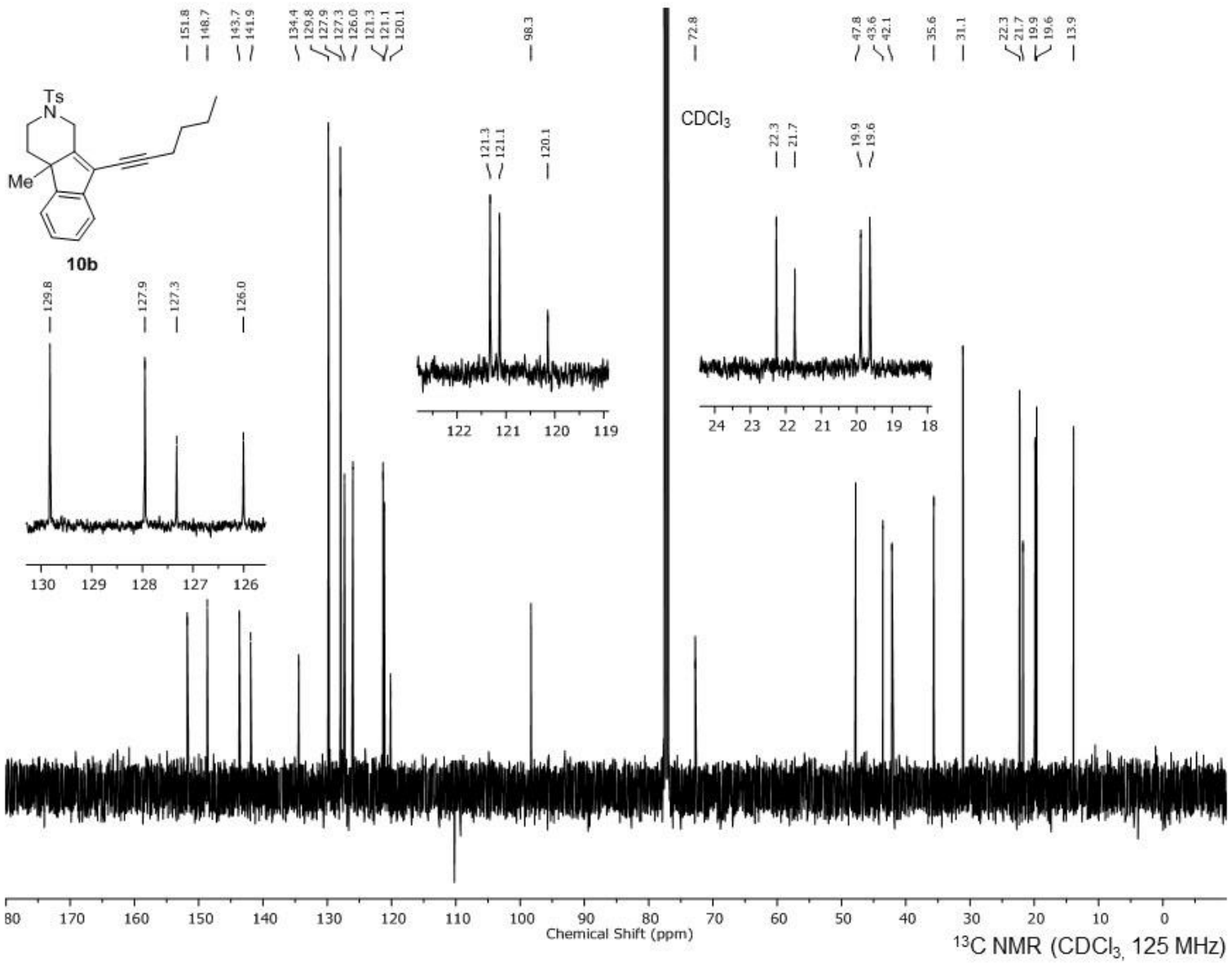

Ts
N
Me
I
MeO2C
9i
CHCl3
H2O
Chemical Shift (ppm)
1H NMR (CDCl3, 500 MHz)

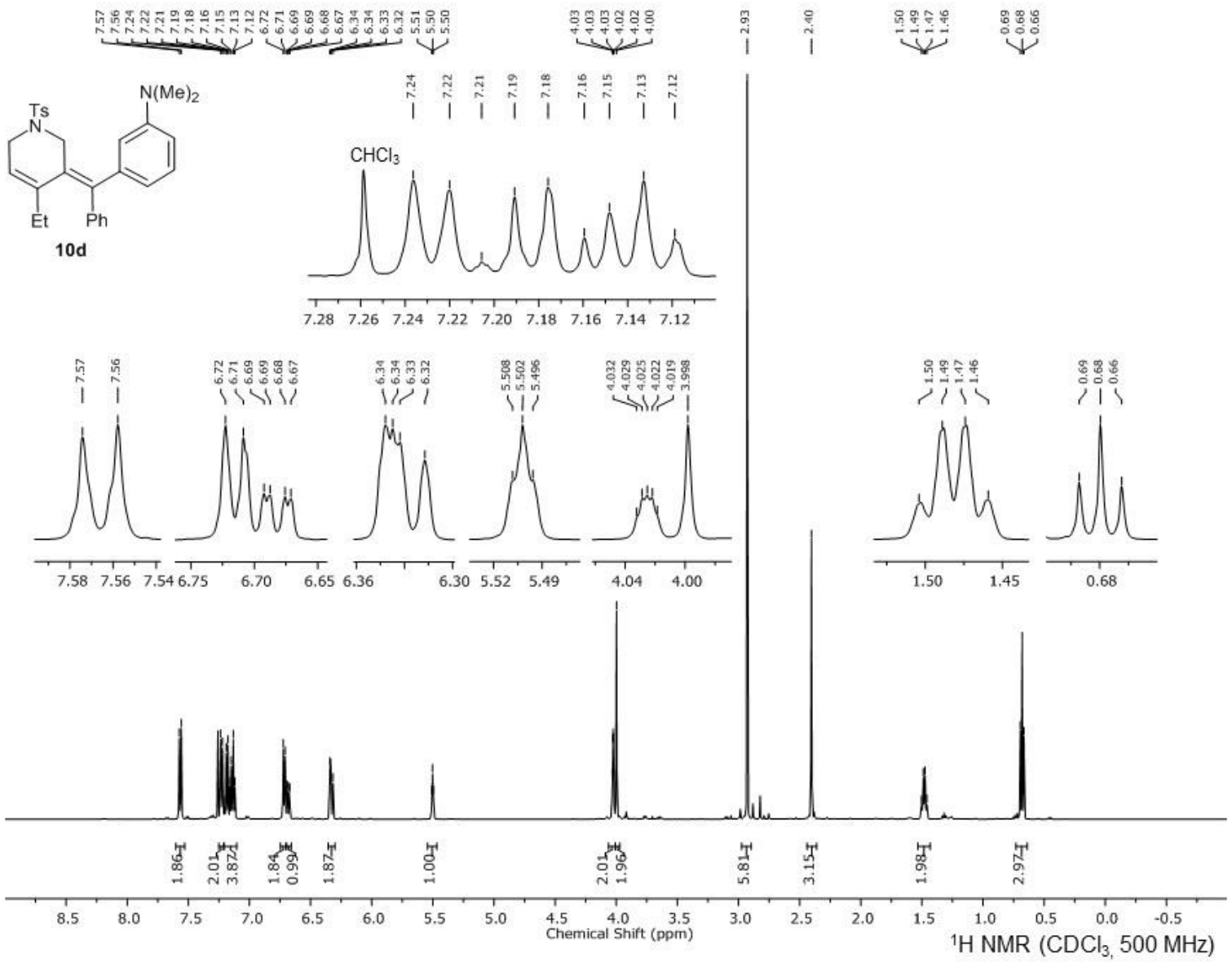

167.4
154.4
151.1
147.5
144.0
134.2
130.0
129.7
128.5
127.9
123.1
122.4
91.6
52.4
50.8
46.4
42.2
35.5
21.8
19.8
CDCl3
Ts
N
Me
I
MeO2C
9i
129.8
129.4
128.3
127.7
130
129
128
127
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)
13C NMR (CDCl3, 125 MHz)

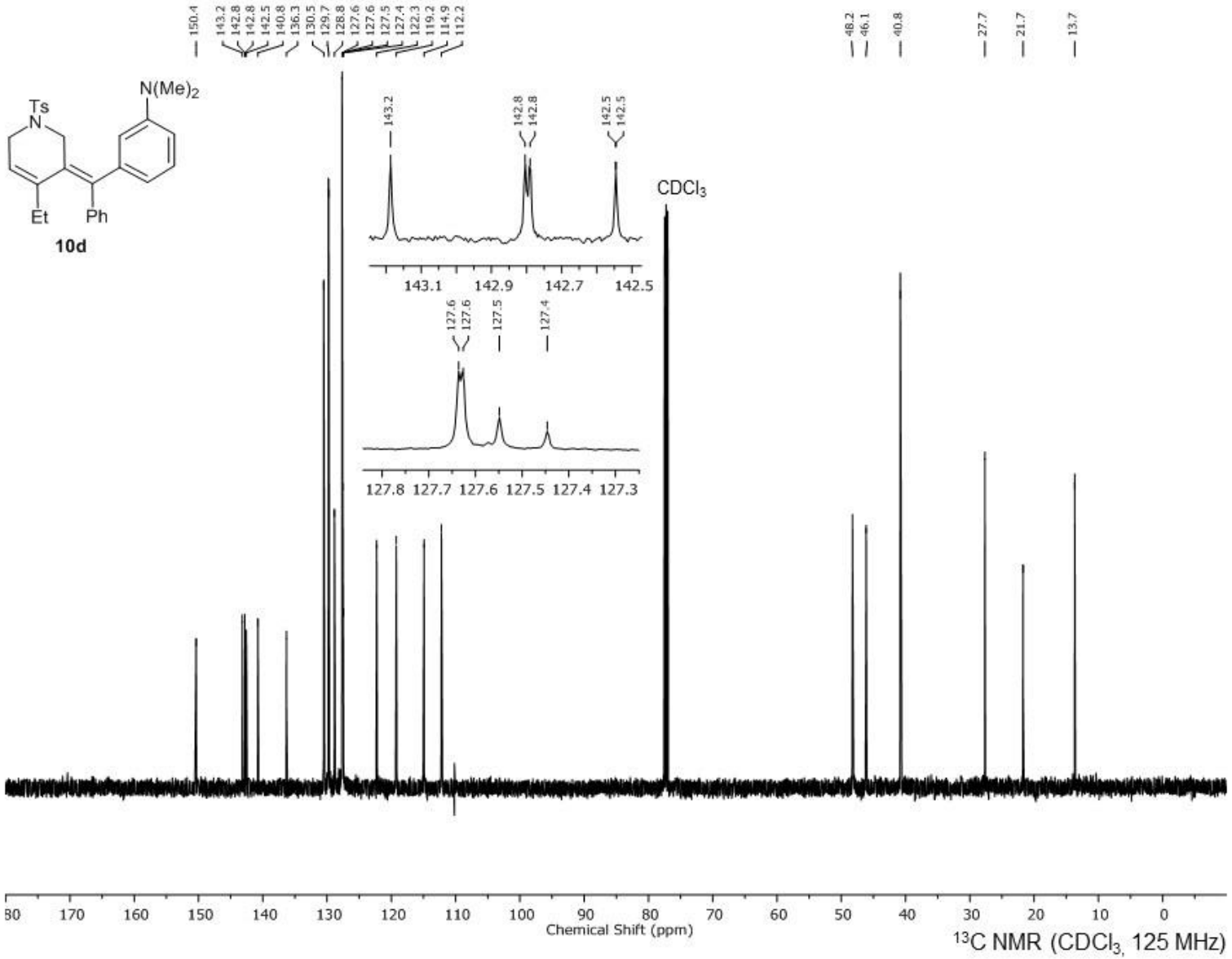

Ts
N
Me
I
F3C
9j
CHCl3
H2O
1H NMR (CDCl3, 500 MHz)
Chemical Shift (ppm)

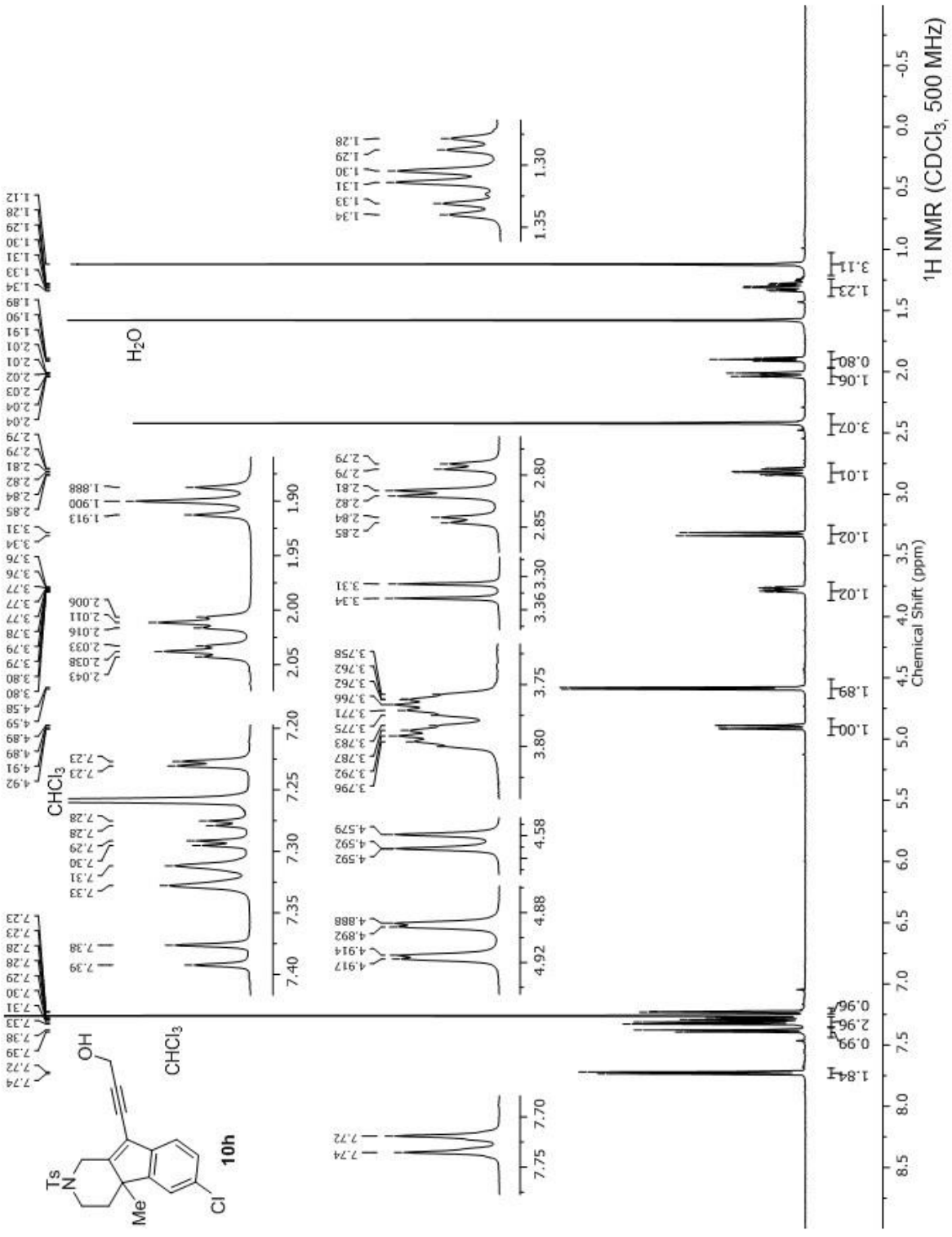

Ts
N
Me
I
F3C
9j
CDCl3
153.9
151.5
146.4
144.1
134.1
130.0
129.0
128.8
127.9
127.8
125.7
125.2
125.2
125.1
125.1
123.5
118.2
118.2
118.2
118.1
91.0
50.9
46.3
42.1
35.5
21.8
19.8
129.03
128.78
127.94
125.68
125.20
125.17
125.14
125.10
118.24
118.21
118.18
118.15
125.20
125.17
125.17
125.14
125.10
146.39
146.39
Chemical Shift (ppm)
13C NMR (CDCl3, 125 MHz)

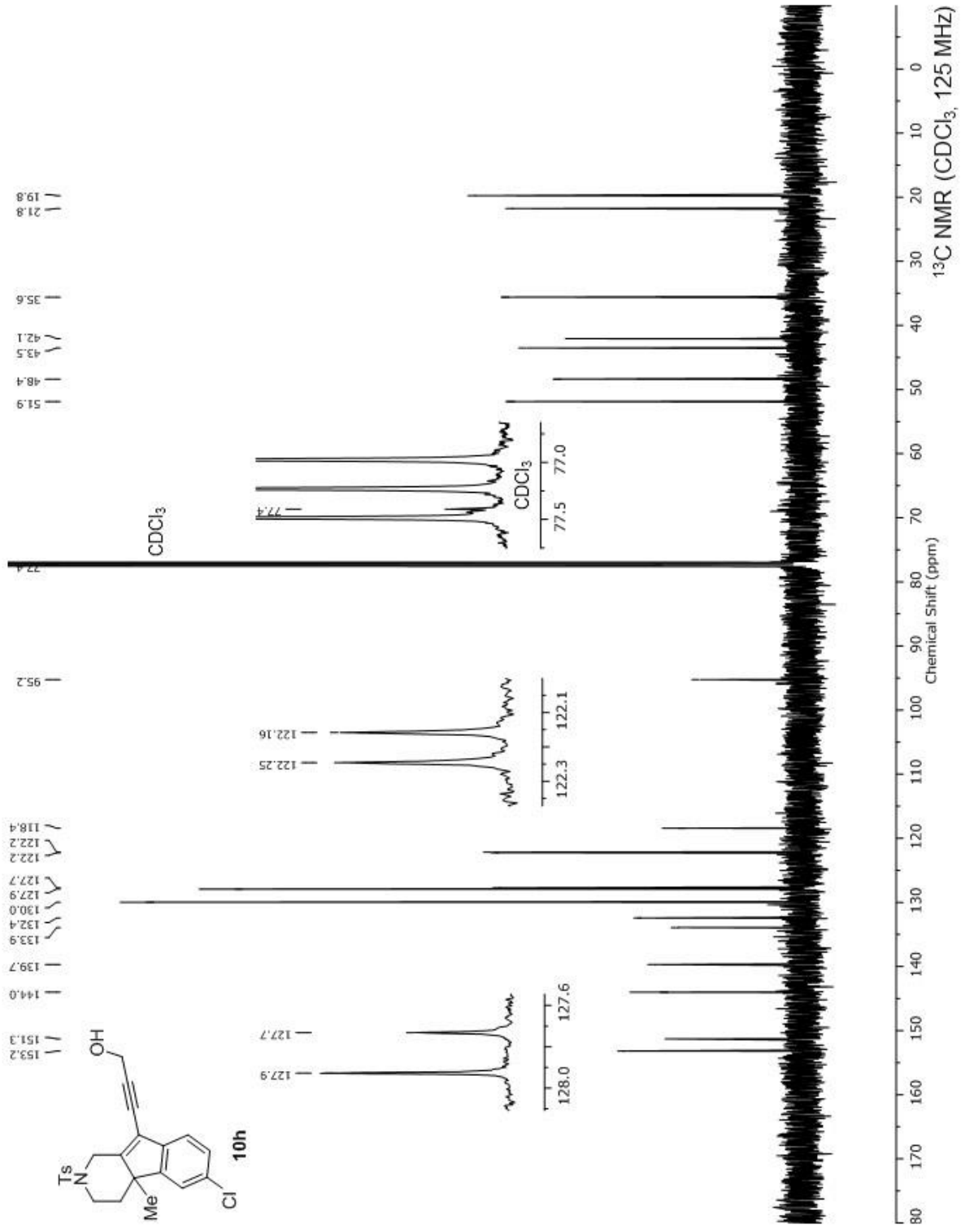

10b
Ts
N
Me
CHCl3
1H NMR (CDCl3, 500 MHz)
Chemical Shift (ppm)

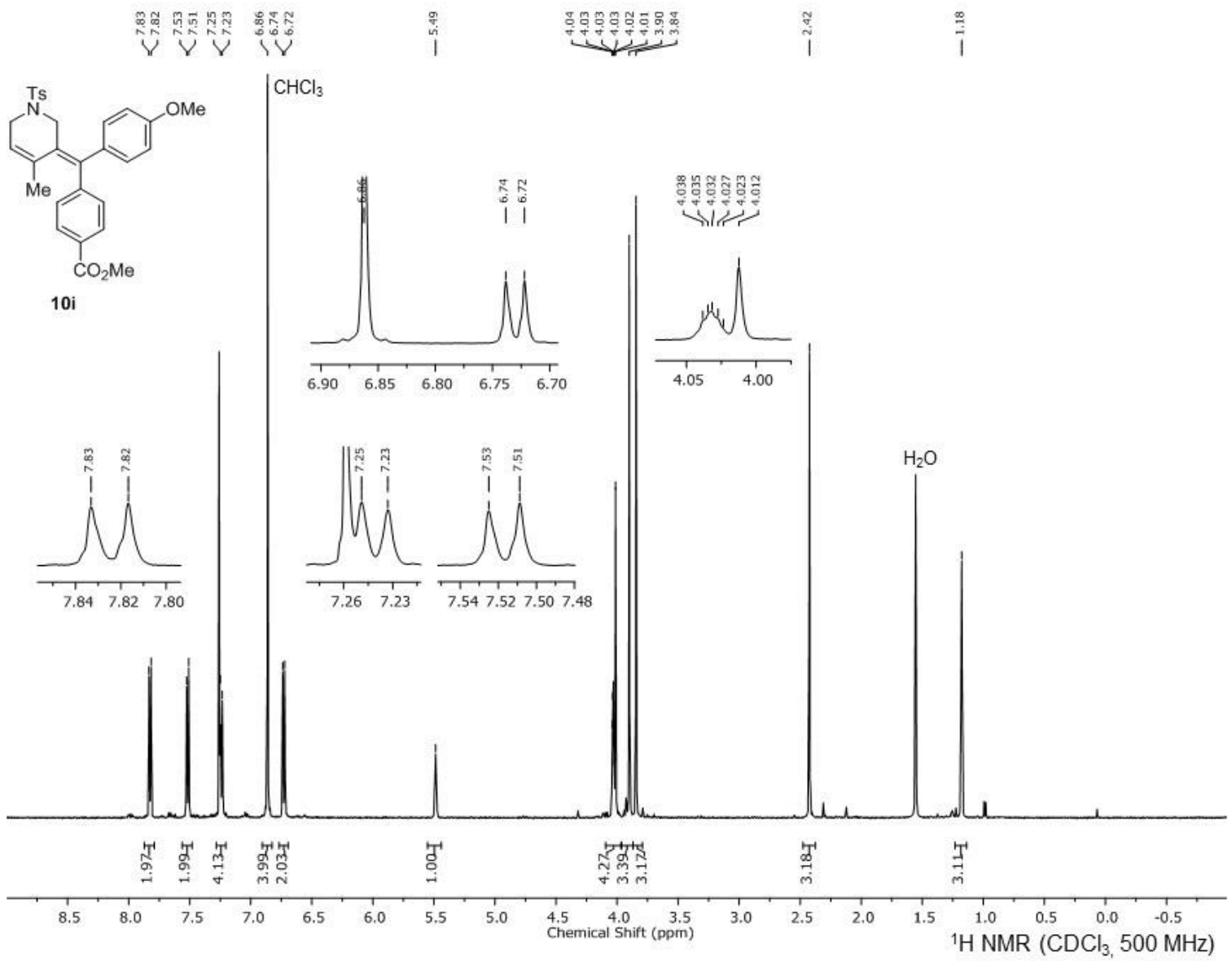

151.8
148.7
143.7
141.9
134.4
129.8
127.9
127.3
126.0
121.3
121.1
120.1
98.3
72.8
47.8
43.6
42.1
35.6
31.1
22.3
21.7
19.9
19.6
13.9
CDCl3
Ts
N
Me
10b
129.8
127.9
127.3
126.0
130 129 128 127 126
121.3
121.1
120.1
122 121 120 119
22.3
21.7
19.9
19.6
24 23 22 21 20 19 18
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift (ppm)
13C NMR (CDCl3, 125 MHz)

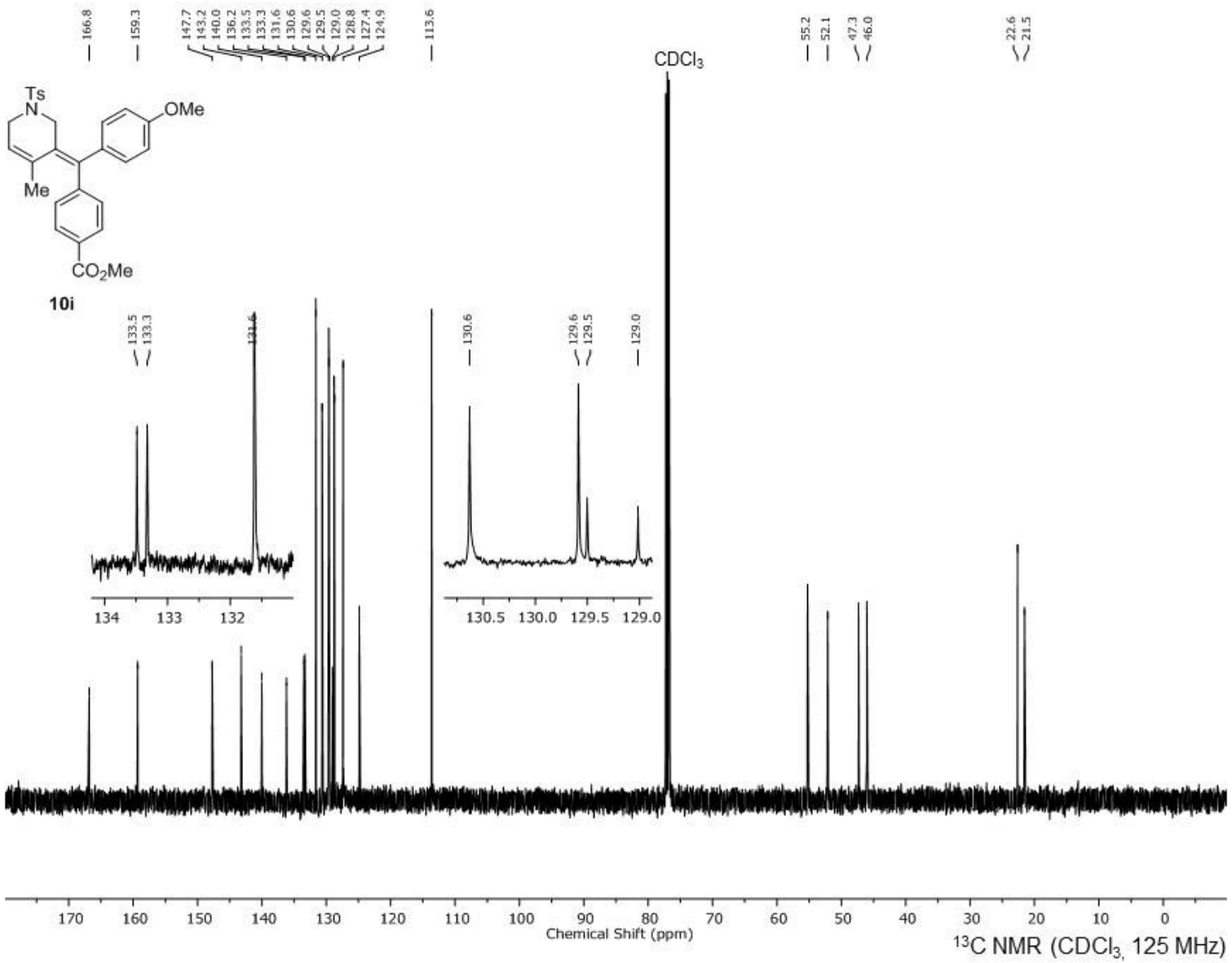

N(Me)2
Ts
N
Et
Ph
10d
CHCl3
Chemical Shift (ppm)
1H NMR (CDCl3, 500 MHz)

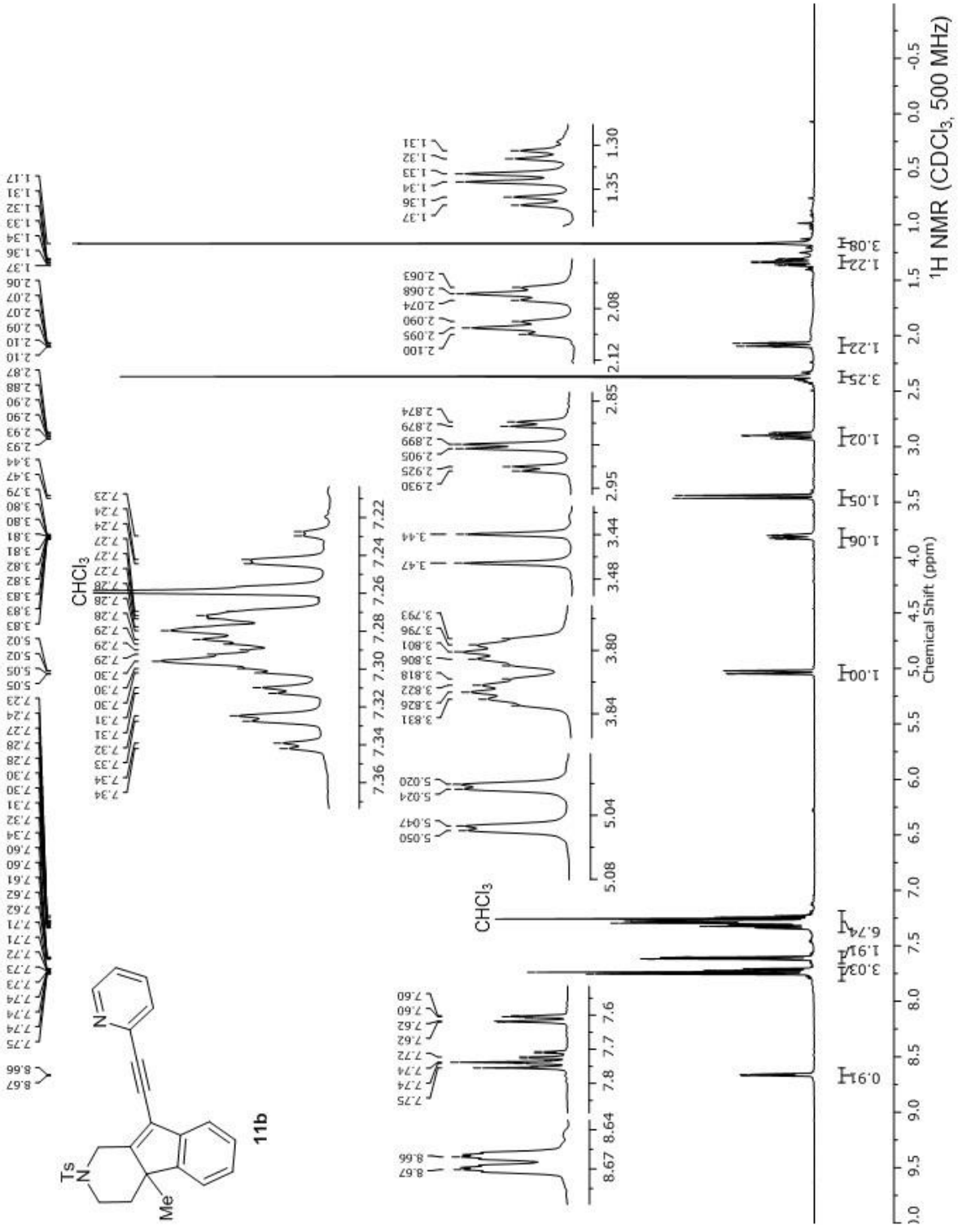

150.4
143.2
142.8
142.8
142.5
140.8
136.3
130.5
129.7
128.8
127.6
127.6
127.5
127.4
122.3
119.2
114.9
112.2
48.2
46.1
40.8
27.7
21.7
13.7
N(Me)2
Ts
N
Et
Ph
10d
CDCl3
143.2
142.8
142.8
142.5
142.5
143.1
142.9
142.7
142.5
127.6
127.6
127.5
127.4
127.8 127.7 127.6 127.5 127.4 127.3
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift (ppm)
13C NMR (CDCl3, 125 MHz)

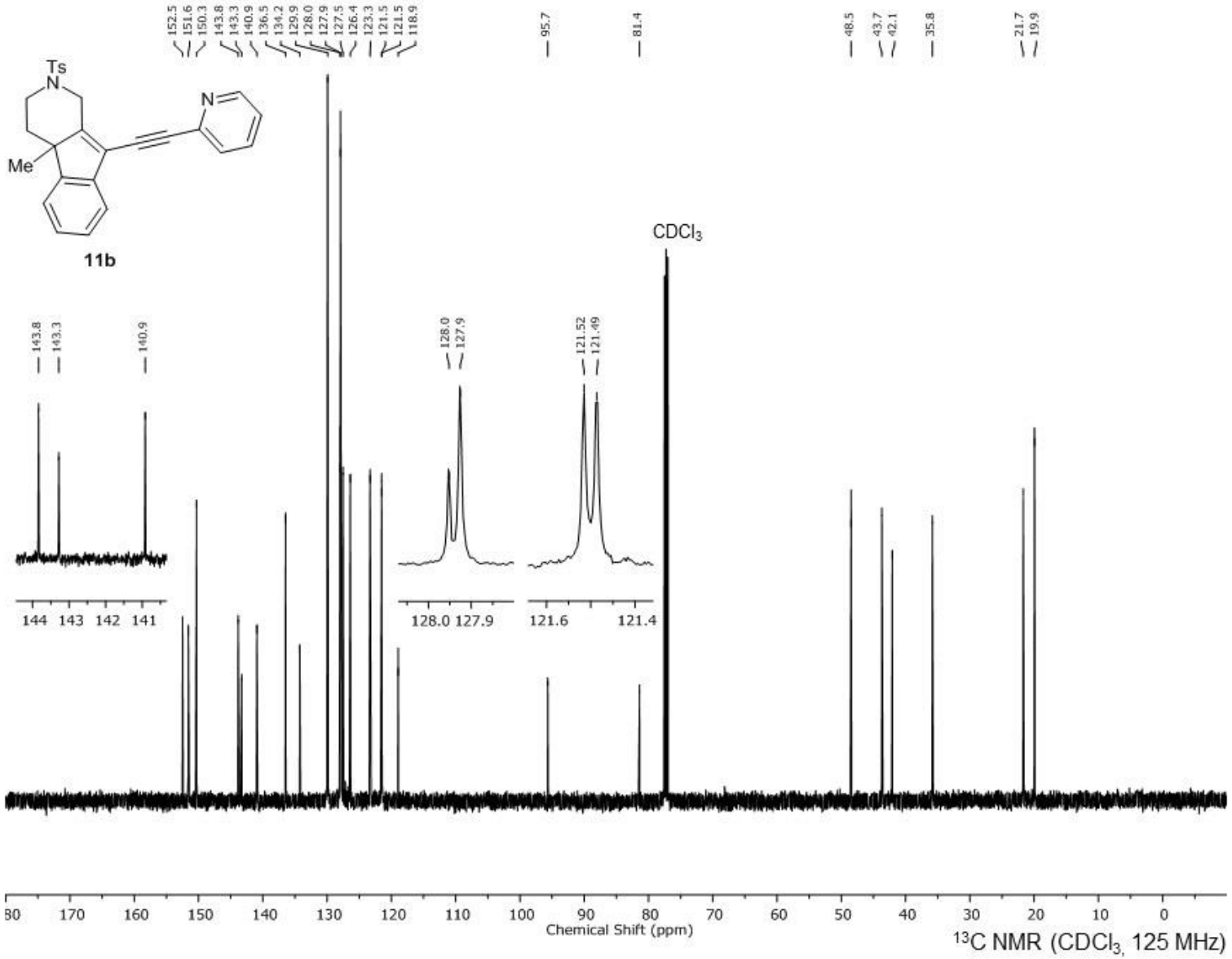

Ts
N
Me
OH
Cl
10h
CHCl3
H2O
1H NMR (CDCl3, 500 MHz)
Chemical Shift (ppm)

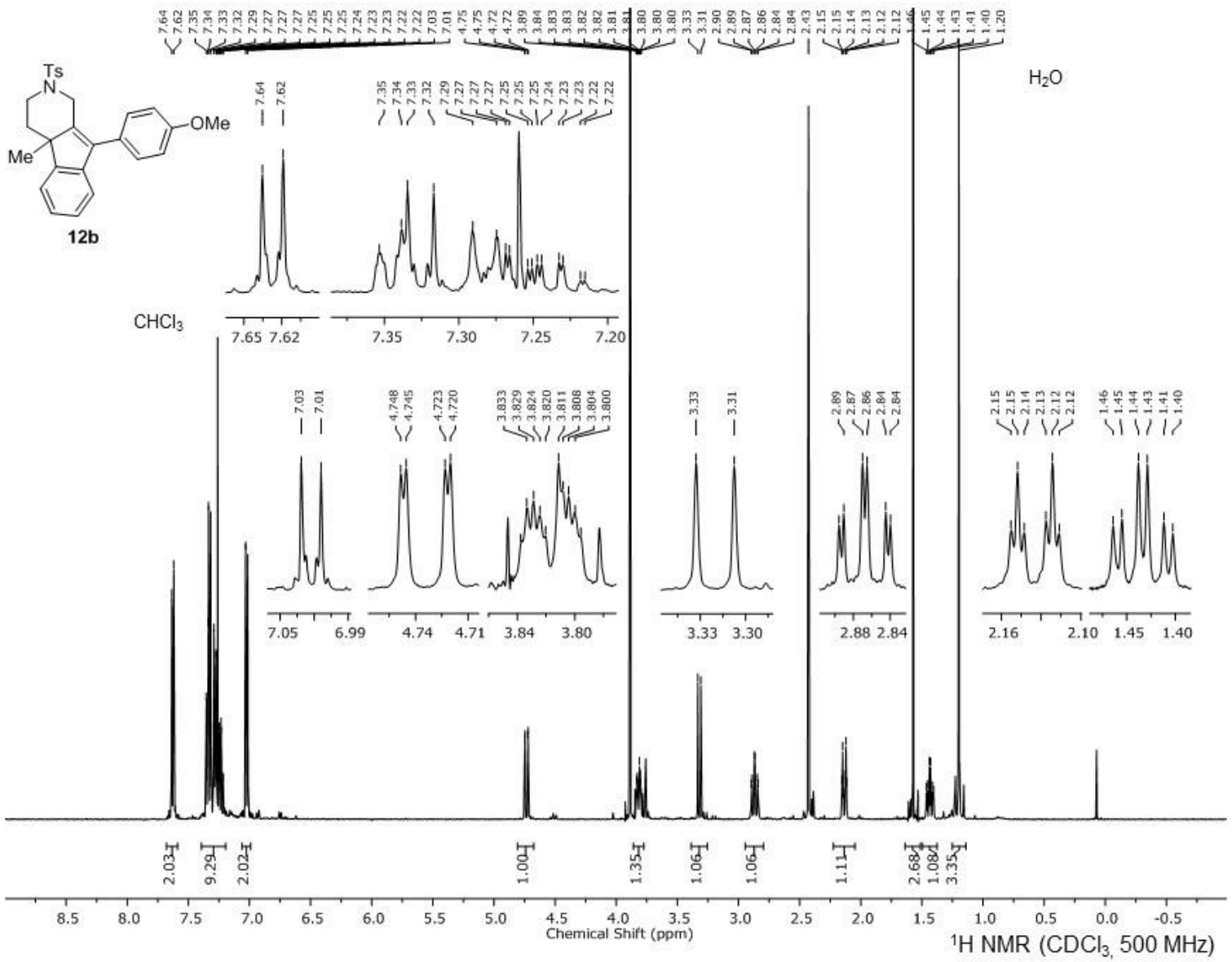

OH
Ts
N
Me
Cl
10h
153.2
151.3
144.0
139.7
133.9
132.4
130.0
127.9
127.7
122.2
122.2
118.4
95.2
77.4
CDCl3
51.9
48.4
43.5
42.1
35.6
21.8
19.8
127.9
127.7
128.0
127.6
122.25
122.16
122.3
122.1
77.4
CDCl3
77.5
77.0
Chemical Shift (ppm)
13C NMR (CDCl3, 125 MHz)

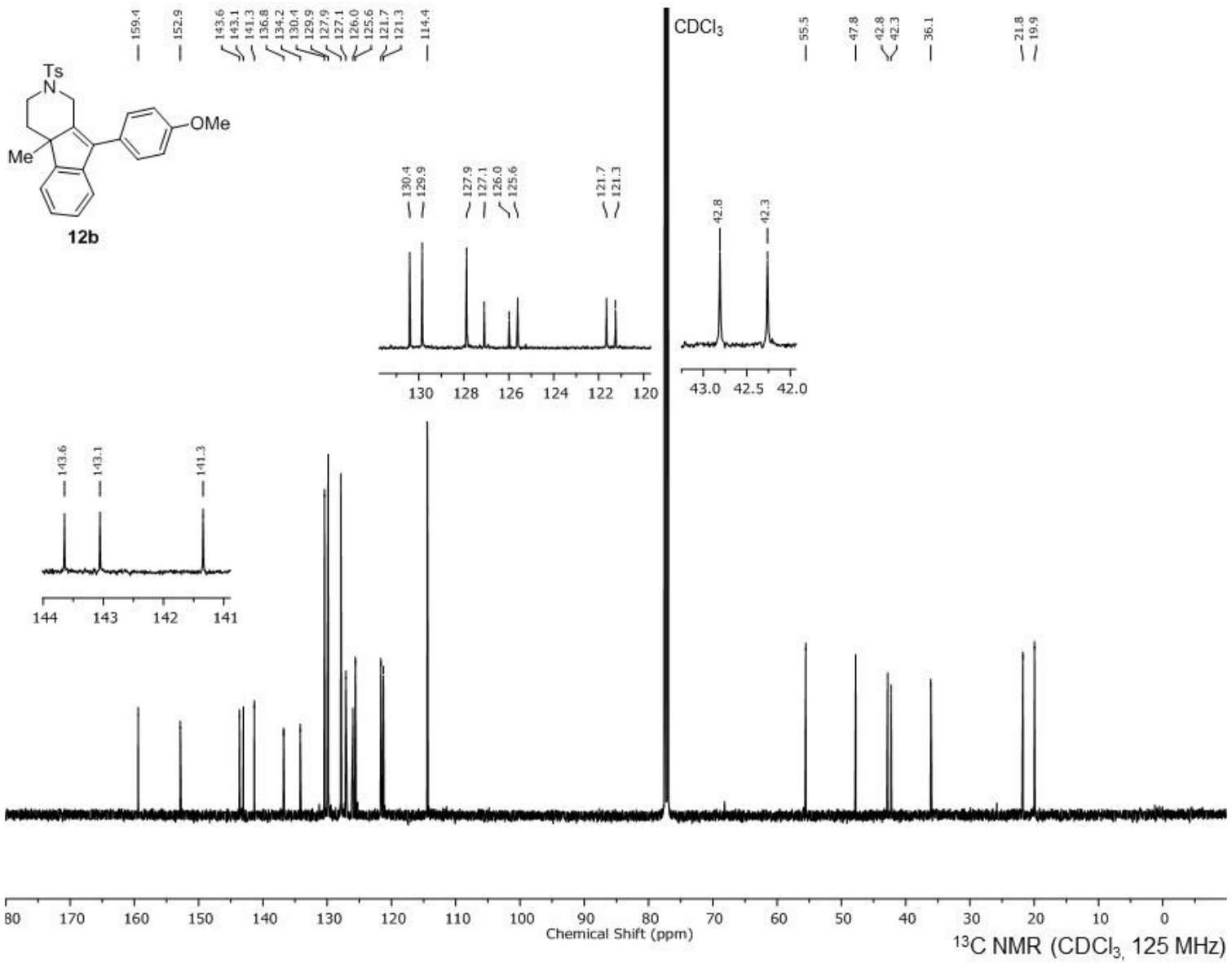

Ts
N
OMe
Me
CO2Me
10i
CHCl3
H2O
7.83
7.82
7.53
7.51
7.25
7.23
6.86
6.74
6.72
5.49
4.04
4.03
4.03
4.03
4.02
4.01
3.90
3.84
2.42
1.18
4.038
4.035
4.032
4.027
4.023
4.012
1.97
1.99
4.13
3.99
2.03
1.00
4.27
3.39
3.17
3.18
3.11
Chemical Shift (ppm)
1H NMR (CDCl3, 500 MHz)

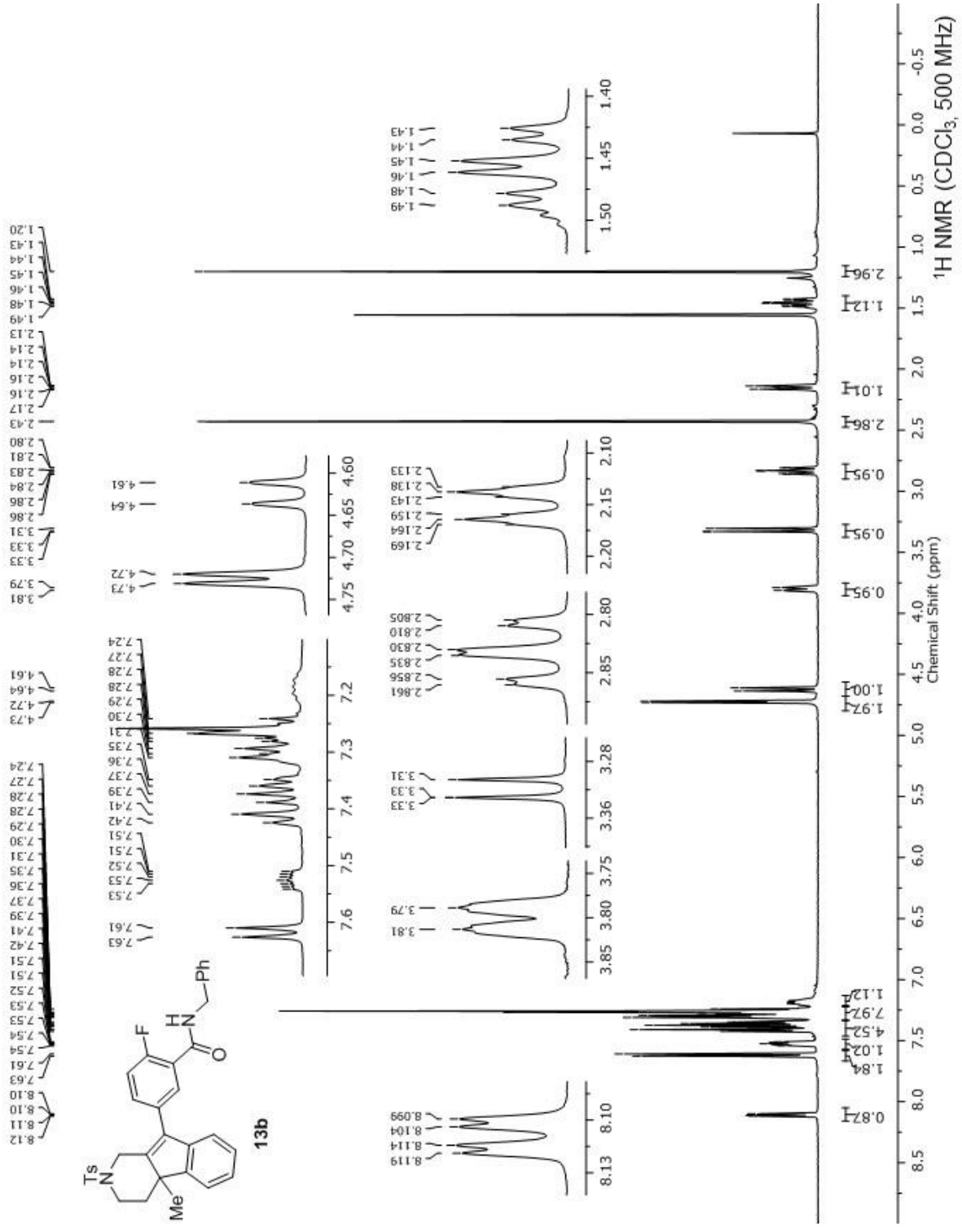

166.8
159.3
147.7
143.2
140.0
136.2
133.5
133.3
131.6
130.6
129.6
129.5
129.0
128.8
127.4
124.9
113.6
CDCl3
55.2
52.1
47.3
46.0
22.6
21.5
Ts
N
OMe
Me
CO2Me
10i
133.5
133.3
131.6
130.6
129.6
129.5
129.0
134
133
132
130.5
130.0
129.5
129.0
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)
13C NMR (CDCl3, 125 MHz)

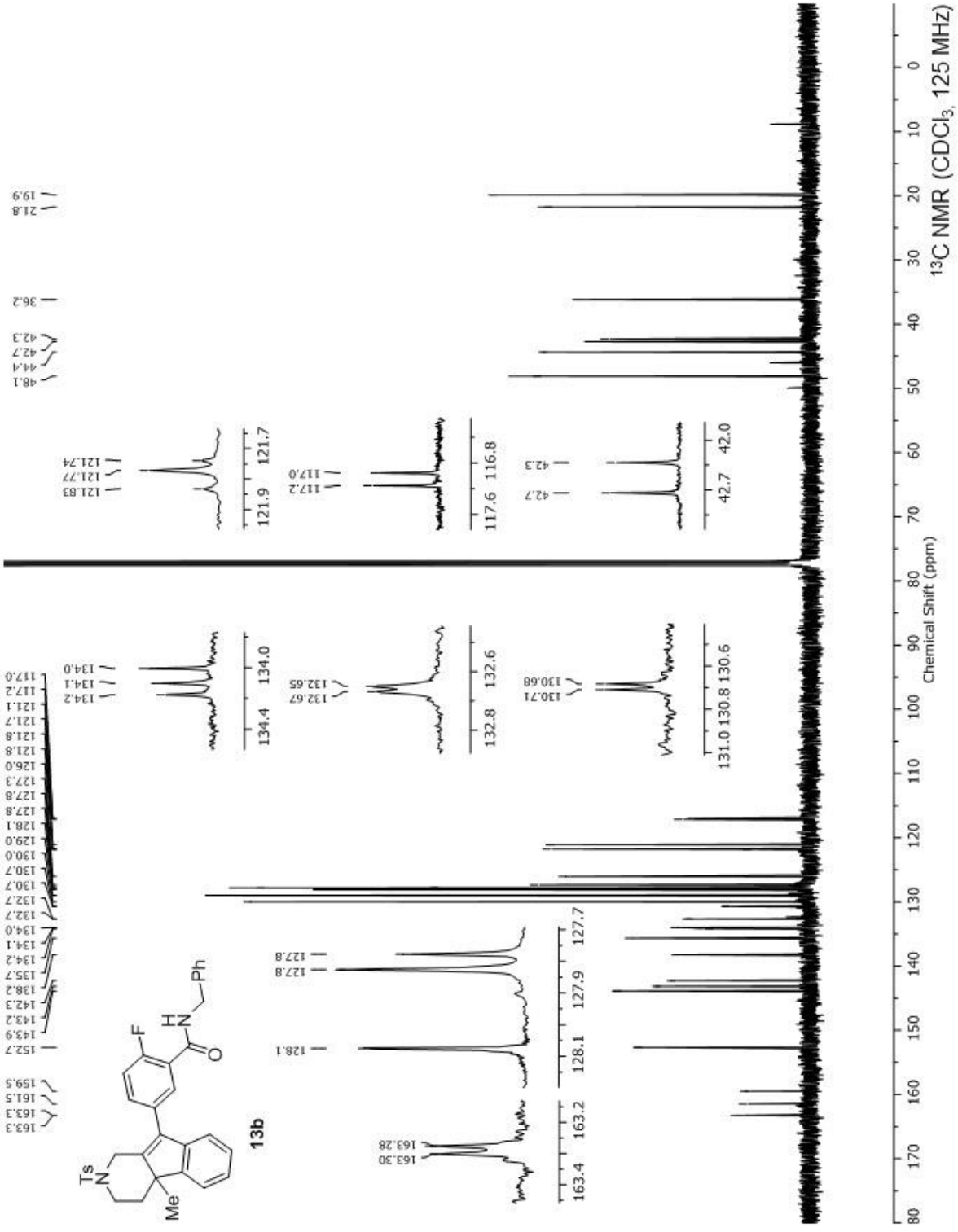

11b
Ts
N
Me
CHCl3
CHCl3
1H NMR (CDCl3, 500 MHz)
Chemical Shift (ppm)


Ts
N
N
Me
11b
152.5
151.6
150.3
143.8
143.3
140.9
136.5
134.2
129.9
128.0
127.9
127.5
126.4
123.3
121.5
121.5
118.9
95.7
81.4
48.5
43.7
42.1
35.8
21.7
19.9
CDCl3
143.8
143.3
140.9
128.0
127.9
121.52
121.49
144 143 142 141
128.0 127.9
121.6 121.4
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift (ppm)
13C NMR (CDCl3, 125 MHz)


Ts
N
OMe
Me
12b
CHCl3
H2O
Chemical Shift (ppm)
1H NMR (CDCl3, 500 MHz)


159.4
152.9
143.6
143.1
141.3
136.8
134.2
130.4
129.9
127.9
127.1
126.0
125.6
121.7
121.3
114.4
CDCl3
55.5
47.8
42.8
42.3
36.1
21.8
19.9
Ts
N
OMe
Me
12b
130.4
129.9
127.9
127.1
126.0
125.6
121.7
121.3
130
128
126
124
122
120
42.8
42.3
43.0
42.5
42.0
143.6
143.1
141.3
144
143
142
141
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)
13C NMR (CDCl3, 125 MHz)


13b
Ts
N
Me
F
H
N
O
Ph
^{1}H NMR ($CDCl_3$, 500 MHz)
Chemical Shift (ppm)


13b
Ts
N
Me
F
H
N
O
Ph
Chemical Shift (ppm)
^{13}C NMR ($CDCl_3$, 125 MHz)