Supplementary Information for

Silicon as a Powerful Element in HDDA Chemistry: Redirection of Innate Cyclization Preferences, Functionalizable Tethers, and Formal Bimolecular HDDA Reactions

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Table of Contents

I. General Experimental Information

^{1}H and **^{13}C NMR** spectra were recorded on Bruker Avance spectrometers 500 or 400 MHz. Chemical shifts for proton NMR spectra recorded in $CDCl_3$ are referenced to TMS (δ 0.00 ppm). NMR chemical shifts for carbon spectra taken in $CDCl_3$ are referenced to TMS (δ 0.00 ppm). In some instances, the $CDCl_3$ did not contain TMS; in those cases the residual C*H*Cl_3 was referenced to δ 7.26 and the *C*DCl_3 to 77.16 ppm. Non-first order multiplets and non-first order doublets in the ^{1}H NMR spectra are designated as "nfom" and "nfod", respectively. Resonances for protons are reported in the following format: chemical shift in ppm [multiplicity, coupling constant(s) (*J*) in Hz, integration (to the nearest whole integer), and assignment (italicized "*H*")]. Proton NMR assignments are designated by the substructure environment with neighboring atoms, e.g., CHCH$_a$*H*$_b$. Previously reported protocols were used to guide coupling constant analysis.[1]

Infrared (IR) spectra were taken of thin film samples on a Bruker Alpha II spectrometer. The most intense and/or diagnostic peaks are reported [in wavenumbers (cm^{-1})]. IR spectra were collected in attenuated total reflectance (ATR) mode.

High-resolution mass spectrometry (HRMS) data were primarily collected on a Thermo Orbitrap Velos instrument in the electrospray ionization (ESI) positive mode and calibrated relative to an external standard (Pierce^{TM} LTQ); the mass accuracy of the instrument is < 3 ppm. Samples were injected directly as a dilute solution in acetonitrile or methanol MeCN (<10^{-5} M).

Medium pressure liquid chromatography (MPLC) was done at 25-100 psi using glass columns hand-packed with silica gel (20–40 μm, 60 Å pore size, Teledyne RediSep Rf Gold® normal-phase). The eluent was pumped with a FMI lab pump (model QSY, Fluid Metering Inc.) at flow rates of around 5–6 mL/min. Detection was done with a differential refractive index (RI) detector (Waters R401).

Flash chromatography was performed on columns packed with Agela silica gel (40-60 μm, 60 Å pore size). Thin layer chromatography was done on plastic-backed plates of silica gel. TLC visualization was done by UV detection or dipping into a solution of $KMnO_4$ stain following by heating.

Reactions requiring anhydrous conditions were performed using oven-dried glassware under an atmosphere of nitrogen. Diispropylamine and triethylamine were distilled from CaH_2 and stored over KOH. MeCN was distilled from CaH_2 and stored over 3Å molecular sieves. Et_2O, CH_2Cl_2 and $CHCl_3$ were dried over 3 Å molecular sieves for at least 24 h prior to use. Anhydrous THF (containing 250 ppm BHT) and DMF (Sigma-Aldrich) were used as received. The decalins reaction solvent was distilled over sodium and benzophenone and stored in a Schlenk flask. The reaction temperature refers to the temperature of the external heating or cooling bath. Reactions carried out at temperatures above the boiling point of the solvent were performed in round-bottomed, threaded culture tubes that were capped with inert, Teflon®-lined screw closures.

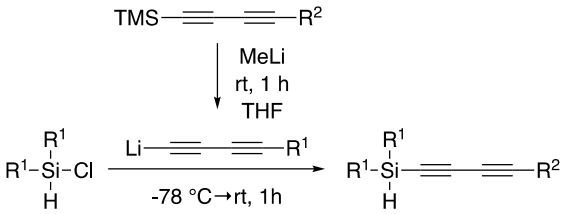
GC-MS data were obtained using an Agilent 5975 mass spectrometer (electron ionization (EI) mode at 70 eV). The column (15 m×0.25 mm) had a DB5 stationary phase (25 μM film thickness). The temperature program was: isothermal 50 °C for 1.5 min and then a 20 °C/min ramp to 250 °C final temperature.

High resolution GCMS (HR-GC-MS) data were obtained for two compounds using an Agilent 7890B mass spectrometer (EI mode at 70 eV). The column (30 m×0.25 mm×0.25 μM) had a DB5 stationary phase. The temperature program was: injection at 120 °C and then a 30 °C/min ramp to 320 °C final temperature and isothermal at 320 °C for 10 min.

LCMS (Agilent 1100 LC and G1956 MSD, dual ESI/APCI ionization source) data were obtained on a 3.5 μM, 50 mm x 4.6 mm Zorbax column™ with a flow rate of 0.5 mL/min using a gradient from 15% Phase A (95:5 water:MeOH, 0.08 wt% NH_4OAc) / 85% Phase B (98:2 MeOH:water, 0.08 wt% NH_4OAc) to 100% Phase B (from 0 to 10 min).

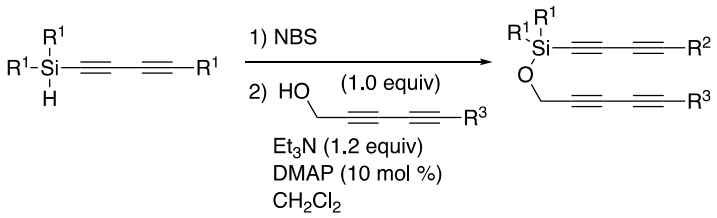
II. General Experimental Procedures

General Procedure A: Preparation of diynyl silane



To a solution of diynyl trimethylsilane (1.0 equiv) in THF (0.2 M) in an ambient temperature water bath was added MeLi (1.10 equiv, 1.6 M in Et_2O) dropwise over 5 to 10 min. The reaction mixture (dark brown solution) was stirred at rt for 1 h and then cooled to -78 °C to provide a grey-brown slurry. Diisopropylchlorosilane or dimethylchlorosilane (1.15 equiv) was added dropwise by syringe. After being stirred at -78 °C for 30 min, the reaction mixture was allowed to warm gradually to rt to afford a yellow solution. After 30 min, saturated aqueous NH_4Cl solution was added, and this mixture was extracted with hexanes. The organic extracts were combined, washed with brine, dried with $MgSO_4$, and concentrated under reduced pressure. The crude material was purified by passage through a silica gel column using hexanes as eluent to afford the corresponding diynyl silane, which was immediately used for the next step.

General Procedure B: Preparation of HDDA substrates



To a solution of diynyl silane (1.2 equiv relative to the diynyl alcohol) in CH_2Cl_2 (0.2 M) at rt was added solid *N*-bromosuccinimide (1.2 equiv) in ca. 10 portions. The mixture was stirred at rt until completion of the reaction (typically ca. 1 h) was observed by TLC. The resulting yellow solution was added to a solution of diynyl alcohol (1.0 equiv), Et_3N (1.2 equiv), and DMAP (0.1 equiv) in CH_2Cl_2 (0.1 M) at 0 °C. The cooling bath was removed, and the mixture was stirred for 1 h at rt. After completion of the reaction (TLC, again, ca. 1 h), saturated aqueous NH_4Cl solution was added and the resulting mixture was extracted with CH_2Cl_2. The organic extracts were combined, washed with brine, dried with $MgSO_4$, and concentrated under reduced pressure. The crude product was

purified by passage through a small silica plug (10-20% EtOAc in hexanes) and the residue was further purified by medium pressure liquid chromatography.

General Procedure C: HDDA Reaction

To a culture tube of appropriate size under N_2 was added a solution of silicon tethered triyne or tetrayne substrate (1.0 equiv) in dry $CHCl_3$ (0.02M) or dry *o*-dichlorobenzene (0.02 M) followed by addition of a trapping reagent (amount as specified). The culture tube was fitted with an inert, Teflon®-lined cap, firmly sealed, and heated in an oil bath that had been pre-equilibrated to the indicated temperature. After 3-6 h (as specified), the reaction mixture was cooled to rt and concentrated. The crude product was purified by passage through a small silica plug and the residue was further purified medium pressure liquid chromatography.

General Procedure D: Synthesis of Naphthalene Derivatives by Deoxygenation

To a suspension of the benzoxanorbornadiene derivative (1.0 equiv) and NaI (5.0 equiv) in dry MeCN (0.03 M) at 0 ºC was added TMSCl (5.0 equiv) dropwise by syringe. The mixture was stirred at 0 ºC and the reaction progress was monitored by TLC. After completion of the reaction, an orange-brown suspension was obtained, which was quenched by dropwise addition of aqueous $Na_2S_2O_3$ solution at 0 ºC. The resulting mixture was then extracted with Et_2O. The organic extracts were combined, washed with brine, dried with $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by passage through a small silica gel plug followed by further purification by medium pressure liquid chromatography.

General Procedure E: Halogenation Reactions

To a suspension of the benzoxanorbornadiene derivative or naphthalene derivative (1.0 equiv) in dry MeCN (0.07 M) in a glass vial was added AgF (4.0 equiv) and NBS or NIS (4.0 equiv) in the glovebox. After the addition, the vial was wrapped with aluminum foil and the mixture was stirred at rt for 3 to 5 h. The mixture was then diluted with CH_2Cl_2, filtered through a small column of Celite®, and rinsed with additional CH_2Cl_2. The filtrate was concentrated to dryness. The crude product was purified by a small silica gel plug and the residue was further purified by medium pressure liquid chromatography.

General procedure F: HDDA reaction with dihydrogen transfer in decalins

The tetrayne substrate was dissolved in anhydrous decalins (100 mL/mmol tetrayne, mixture of *cis* and *trans* isomers, distilled under vacuum from Na/benzophenone). The solution was placed in a borosilicate pressure vessel and sparged with N_2. The vessel was sealed and then heated to the reaction temperature. After the reaction was complete and the vessel had cooled to rt, the solution was passed through a plug of silica gel to separate the product from the decalin. The plug was washed with hexanes, and the crude product was eluted with 9:1 hexanes/ethyl acetate.

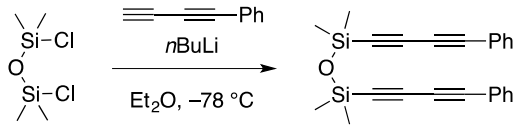
General procedure G: Desilylation of HDDA products 5a-c

The compound was dissolved in a minimal amount of THF in a vial under N_2. A solution of TBAF (1 M in THF, 8 equivalents) was added and the reaction was allowed to proceed overnight. Sat. aq. NH_4Cl and EtOAc were added to the cooled reaction solution. The organic layer was removed, washed with brine, dried ($MgSO_4$), and evaporated to yield the crude product.

III. Experimental Procedures and Characterization Data for All Compounds

(a) Preliminary result (4a-c to 5a-c)

1,1,3,3-Tetramethyl-1,3-bis(phenylbuta-1,3-diyn-1-yl)disiloxane (**4a**)



4a

Phenylbutadiyne[2] (749.6 mg, 5.94 mmol) was dissolved in anhydrous Et_2O (10 mL) under N_2 and cooled to –78 °C. n-BuLi (2.5 M in hexanes, 2.00 mL, 5.00 mmol) was added with stirring. After 15 minutes, 1,3-dichlorotetramethyldisiloxane (0.49 mL, 0.51 g, 2.5 mmol) was added over 2 minutes. After an additional 2 hours of stirring at -78 °C, the reaction mixture was quenched by the addition of MeOH (1 mL). The mixture was warmed to rt, and sat. aq. NH_4Cl (5 mL) and water (5 mL) were added. The organic phase was removed, washed with brine (5 mL), dried ($MgSO_4$), and concentrated to give the crude product (997 mg). This was purified by flash chromatography (hexanes) to yield the tetrayne **4a** (828 mg, 2.16 mmol, 87%) as a waxy beige solid.

A sample of **4a** was crystallized by dissolving it in a minimal amount of methanol at rt, then slowly cooling to -78 °C.

mp: 63–66 °C.

TLC (hexanes): Rf 0.40.

^{1}H NMR (500 MHz; $CDCl_3$): δ 0.36 (s, 12H), 7.30 (nfodd, *J* = 7.4, 7.1 Hz, 6H, PhH_m), 7.36 (tt, *J* = 7.4, 1.4 Hz, 2H, PhH_p) and 7.48 (nfodd, *J* = 7, 1.5 Hz, 4H, PhH_o).

^{13}C NMR (126 MHz; $CDCl_3$) δ 2.1, 74.2, 77.7, 87.3, 88.9, 121.3, 128.6, 129.6, and 132.9.

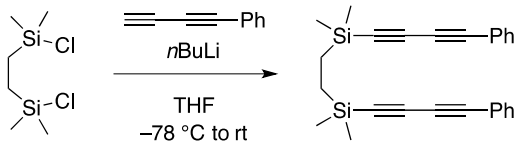
HRMS: Expected $C_{24}H_{22}NaOSi_2^+$ $[M + Na]^+$ *m/z* 405.1101, found 405.1112.

GC-MS: t_R = 12.96 min, *m/z* 382 ($M^{+\bullet}$), fragments 367, 293, 250, 183, and 126.

IR: 3059, 2962, 2901, 2205, 2105, 1490, 1442, 1403, 1278, 1258, 1046, 1021, 1009, 992, 965, 944, 912, 834, and 800 cm^{-1}.

UV (λ_{max}): peaks 252.1, 265.4, 281.0, and 298.1 nm.

1,2-bis(Dimethyl(phenylbuta-1,3-diyn-1-yl)silyl)ethane (**4b**)



4b

Phenylbutadiyne[2] (876 mg, 6.94 mmol) was dissolved in anhydrous THF (25 mL) under N_2 and cooled to –78 °C. n-BuLi (2.5 M in hexanes, 2.75 mL, 6.88 mmol) was added with stirring. After 15 minutes, a solution of 1,2-bis(chlorodimethylsilyl)ethane (725 mg, 3.37 mmol) in anhydrous THF (2 mL) was added. The reaction mixture was allowed slowly warming to rt and to stir overnight. Sat. aq. NH_4Cl (5 mL) and water (5 mL) were added. The organic phase was removed, washed with brine (5 mL), dried ($MgSO_4$), and concentrated to yield crude product (1.50 g). This was recrystallized from hexanes (3 mL) to yield crystals of tetrayne **4b** (466 mg). The non-volatile contents of the supernatant were purified by flash chromatography (99:1 hexanes/ethyl acetate) to yield a further 680 mg of **4b**. Total yield: 1.15 g, 2.90 mmol, 86%.

mp (from hexanes): 108–109 °C.

TLC (19:1 hexanes/ethyl acetate) Rf 0.39.

^{1}H NMR (400 MHz; $CDCl_3$): δ 0.23 (s, 12H), 0.68 (s, 4H), 7.31 (nfodd, *J* = 7.6, 6.9 Hz, 6H, PhH_m), 7.36 (tt, *J* = 7.2, 1.6 Hz, 2H, PhH_p), and 7.49 (nfodd, *J* = 6.7, 1.7 Hz, 4H, PhH_o).

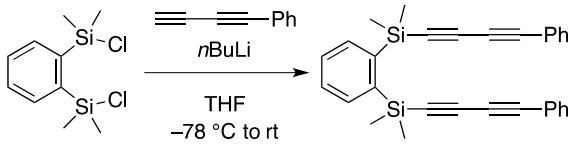
^{13}C NMR (101 MHz, $CDCl_3$, referenced to *C*DCl_3 at 77.16 ppm): δ –2.4, 8.4, 74.4, 76.8, 88.5, 90.0, 121.5, 128.6, 129.5, and 132.9.

HRMS: Expected $C_{26}H_{26}NaSi_2^+$ $[M + Na]^+$ *m/z* 417.1465, found 417.1468

GC-MS: t_R = 14.19 min, *m/z* 394 ($M^{+\bullet}$), fragments 379, 351, 293, 183, 169, 153, and 126.

IR: 3059, 2958, 2909, 2205, 2103, 1489, 1442, 1405, 1251, 1135, 1056, 1019, 1007, 990, 836, 815, and 784 cm^{-1}.

1,2-bis(Dimethyl(phenylbuta-1,3-diyn-1-yl)silyl)benzene (**4c**)



4c

Phenylbutadiyne[2] (885 mg, 7.02 mmol) was dissolved in anhydrous THF (25 mL) under N_2 and cooled to –78 °C. n-BuLi (2.5 M in hexanes, 2.8 mL, 7.0 mmol) was added with stirring. After 15 minutes, 1,2-bis(chlorodimethylsilyl)benzene[3] (805 mg, 3.06 mmol) was added dropwise by syringe. The reaction mixture was allowed slowly warm to rt and then to stir overnight. Sat. aq. NH_4Cl (5 mL) and water (5 mL) were added. The organic phase was removed, washed with brine (5 mL), dried ($MgSO_4$), and concentrated to yield crude product (2.07 g). This was purified by flash chromatography (49:1 hexanes/ethyl acetate) to give tetrayne **4c** (1.086 g, 2.45 mmol, 80%) as a tan waxy solid.

TLC (49:1 hexanes/ethyl acetate) Rf 0.15.

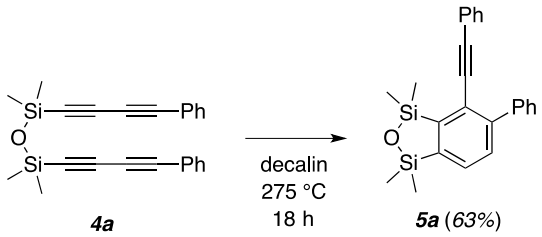
^{1}H-NMR (400 MHz, $CDCl_3$): δ 0.65 (s, 12H), 7.29 (nfodd, *J* = 7.6, 7.0 Hz, 4H, PhH_m), 7.35 (tt, *J* = 7.2, 1.5 Hz, 2H, PhH_p), 7.44–7.39 (nfom, 2H), 7.48 (nfodd, *J* = 6.8, 1.5 Hz, 4H, PhH_o), and 7.88–7.84 (nfom, 2H).

^{13}C NMR (101 MHz, $CDCl_3$, referenced to *C*DCl_3 at 77.16 ppm): δ 1.9, 74.6, 77.8, 90.4, 90.8, 121.5, 128.5, 128.9, 129.5, 132.9, 136.1, and 142.0.

HRMS: Expected $C_{30}H_{27}Si_2^+$ $[M + H]^+$ *m/z* 443.1646, found 443.1636.

IR: 3045, 2957, 2900, 2203, 2103, 1488, 1441, 1414, 1293, 1279, 1249, 1117, 1055, 1039, 1019, 1007, 837, 814, 779, 752, 731, 686, 661, and 640 cm^{-1}.

1,1,3,3-Tetramethyl-5-phenyl-4-(phenylethynyl)-1,3-dihydrobenzo[*c*][1,2,5]oxadisilole (**5a**)



4a ***5a*** (*63%*)

Tetrayne **4a** (161 mg, 0.421 mmol) was heated in decalin at 275 °C for 18 hours according to the general procedure. The crude mass after elution was 204.3 mg, still containing some dihydro- and tetrahydronaphthalenes. This was purified by MPLC (49:1 hexanes/ethyl acetate) to yield **5a** as a viscous pale yellow oil (102 mg, 0.265 mmol, 63%).

TLC (hexanes): Rf 0.17.

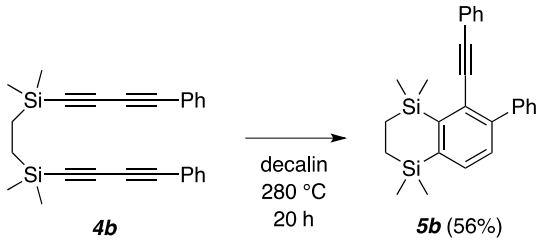
^{1}H-NMR (400 MHz, $CDCl_3$, referenced to residual $CHCl_3$ at 7.26 ppm): δ 0.44 (s, 6H), 0.60 (s, 6H), 7.30–7.37 (m, 5H, ≡CPh*H*), 7.43 (tt, *J* = 7.3, 1.3 Hz, 1H, PhH_p), 7.50 (nfodd, *J* = 7.7, 6.5 Hz, 2H, PhH_m), 7.52 (d, *J* = 7.5 Hz, 1H, Ar$H^{\cdot}$), 7.62 (d, *J* = 7.5 Hz, 1H, Ar*H*), and 7.72 (nfodd, *J* = 7.2, 1.4, Hz, 2H, ArPhH_o).

^{13}C NMR (101 MHz, $CDCl_3$, referenced to *C*DCl_3 at 77.16 ppm): δ 0.6, 1.2, 90.4, 94.1, 123.6, 124.4, 127.7, 128.0, 128.4, 128.5, 129.6, 130.5, 130.9, 131.1, 140.7, 144.4, 147.2, and 152.3.

HRMS: Expected $C_{24}H_{25}OSi_2^+$ $[M + H]^+$ *m/z* 385.1438, found 385.1430.

IR: 3080, 3057, 3028, 2956, 2923, 2854, 1597, 1571, 1490, 1442, 1425, 1397, 1363, 1249, 1160, 1070, 1053, 1024, 928, 873, 840, 789, 753, 732, 697, 635, and 605 cm^{-1}.

1,1,4,4-Tetramethyl-6-phenyl-5-(phenylethynyl)-1,2,3,4-tetrahydrobenzo[*b*][1,4]disiline (**5b**)



Tetrayne **4b** (99.2 mg, 0.251 mmol) was heated in decalin at 280 °C for 20 hours according to the general procedure. The crude mass after elution was 122.2 mg, still containing some dihydro- and tetrahydronaphthalenes. This was purified by MPLC (hexanes) to yield **5b** as a pale yellow crystalline solid (56.1 mg, 0.141 mmol, 56%).

mp: 123–126 °C.

TLC (49:1 hexanes/ethyl acetate) Rf 0.39.

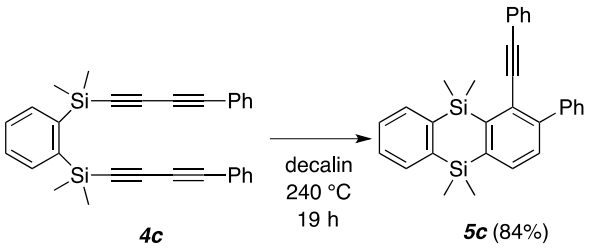
^{1}H-NMR (400 MHz, $CDCl_3$, referenced to residual $CHCl_3$ at 7.26 ppm): δ 0.31 (s, 6H), 0.53 (s, 6H), 1.05–1.01 (nfom, 2H), 1.12–1.08 (nfom, 2H), 7.33–7.24 (m, ca. 5H), 7.40 (overlapped tt, *J* = 7.2, 1.3 Hz, 1H, PhH_p), 7.41 (d, *J* = 7.7 Hz, 1H, Ar*H*), 7.47 (nfodd, *J* = 7.6, 7.0 Hz, 2H, PhH_m), 7.57 (d, *J* = 7.7 Hz, 1H, Ar*H'*), and 7.64 (nfodd, *J* = 7.0, 1.3 Hz, 2H, PhH_o).

^{13}C NMR (101 MHz, $CDCl_3$, referenced to *C*DCl_3 at 77.16 ppm): δ –1.4, –1.2, 7.0, 9.6, 91.5, 96.3, 123.9, 126.9, 127.4, 127.8, 128.1, 128.4, 129.1, 129.8, 131.0, 133.7, 141.4, 145.1, 145.6, and 148.4.

HRMS: Expected $C_{26}H_{29}Si_2^+$ $[M + H]^+$ *m/z* 397.1802, found 397.1794.

IR: 3080, 3056, 3025, 2949, 2920, 2898, 2802, 1598, 1490, 1443, 1423, 1407, 1352, 1245, 1169, 1129, 1050, 1023, 894, 829, 812, 773, 754, 698, 666, 621, and 600 cm^{-1}.

5,5,10,10-Tetramethyl-2-phenyl-1-(phenylethynyl)-5,10-dihydrosilanthrene (**5c**)



Tetrayne **4c** (111 mg, 0.251 mmol) was heated in decalin at 240 °C for 19 hours according to the general procedure. The crude product was purified by MPLC (49:1 hexanes/ethyl acetate) to yield **5c** as a yellow wax (93.4 mg, 0.210 mmol, 84%).

TLC (9:1 hexanes/ethyl acetate): Rf 0.53.

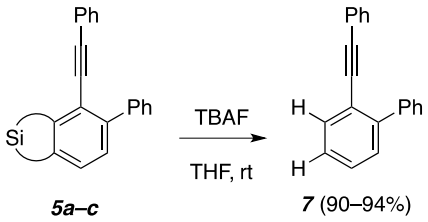
^{1}H-NMR (400 MHz, $CDCl_3$, referenced to residual $CHCl_3$ at 7.26 ppm): δ 0.51 (s, 6H), 0.79 (s, 6H), 7.34–7.28 (m, 5H, ArPh*H*), 7.52–7.40 (m, 5H, overlapped Ar*H7*, Ar*H8*, ≡CPhH_m, and ≡CPhH_p), 7.50 (d, *J* = 7.6 Hz, 1H, Ar*H3*), 7.67 (nfodd, *J* = 7.0, 1.7 Hz, 1H, ≡CPhH_o), 7.70–7.68 (overlapped m, 1H, Ar*H6*), 7.73 (d, *J* = 7.6 Hz, 1H, Ar*H4*), and 7.75 (dd, *J* = 7, 1.6 Hz, 1H, Ar*H9*).

^{13}C NMR (101 MHz, $CDCl_3$, referenced to *C*DCl_3 at 77.16 ppm): δ 0.7, 0.9, 91.4, 97.2, 123.7, 127.1, 127.6, 127.9, 128.2, 128.3, 128.5, 128.8, 129.5, 129.8, 131.0, 133.1, 133.4, 134.1, 141.3, 143.1, 144.0, 145.6, 146.1, and 146.7.

HRMS: Expected $C_{30}H_{29}Si_2^+$ $[M + H]^+$ *m/z* 445.1802, found 445.1791.

IR: 3101, 3055, 2953, 2897, 2247, 1597, 1572, 1489, 1443, 1408, 1352, 1246, 1169, 1132, 1118, 1071, 1052, 1023, 907, 895, 828, 811, 772, 752, 736, 698, 687, and 646 cm^{-1}.

2-(Phenylethynyl)biphenyl (**7**)



5a–c ***7*** (90–94%)

Compounds **5a** (38.6 mg, 0.100 mmol), **5b** (40.2 mg, 0.101 mmol), and **5c** (43.0 mg, 0.097 mmol) were each deprotected according to the general procedure. The crude product was purified by MPLC (49:1 hexanes/ethyl acetate) to yield **7** as a pale brown oil. From **5a**: 22.9 mg, 0.090 mmol, 90%. From **5b**: 24.2 mg, 0.095 mmol, 94%. From **5c**: 22.4 mg, 0.088 mmol, 91%.

The spectral data for **7** are in agreement with those previously reported.[4]

TLC (49:1 hexanes/ethyl acetate) Rf 0.31.

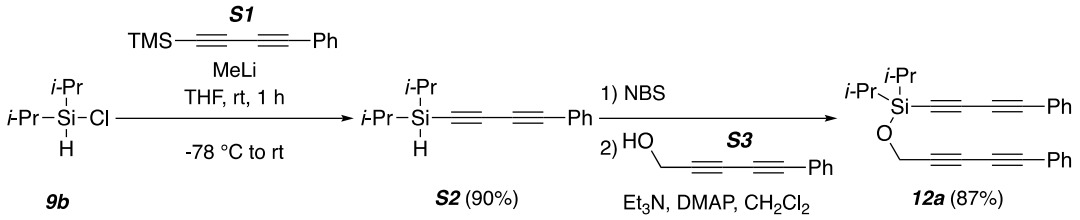
^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.28–7.26 (m, 3H), 7.34–7.30 (m, 3H), 7.47–7.37 (m, 5H), 7.68–7.64 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$, referenced to *C*DCl_3 at 77.16 ppm): δ 89.5, 92.4, 121.7, 123.6, 127.2, 127.6, 128.0, 128.2, 128.4, 128.6, 129.5, 129.6, 131.5, 133.0, 140.7, and 144.1.

IR: 3055, 3020, 1946, 1597, 1571, 1489, 1473, 1442, 1432, 1179, 1157, 1071, 1006, 914, 753, 734, and 694 cm^{-1}.

(b) Preparation of Tetrayne and triyne substrates 12a-g

Diisopropyl(phenylbuta-1,3-diyn-1-yl)((5-phenylpenta-2,4-diyn-1-yl)oxy)silane (12a)



The diynylsilane ***S2*** was prepared following general procedure A from trimethyl(phenylbuta-1,3-diyn-1-yl)silane ***S1***[2] (363 mg, 1.83 mmol), MeLi (1.26 mL, 1.6 M in Et_2O, 2.01 mmol), and diisopropylchlorosilane (0.34 mL, 2.01 mmol) to give the diynylsilane ***S2*** (396 mg, 90%) as a yellow oil.

Data for *S2*

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (br d, *J* = 7.1 Hz, 2H, ArH_o), 7.37 (br t, *J* = 7.4 Hz, 1H, ArH_p), 7.32 (br dd, *J* = 7.2, 7.2 Hz, 2H, ArH_m), 3.79 (br s, 1H, Si*H*), and 1.14–1.07 (m, 14H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 132.8, 129.4, 128.4, 121.3, 90.3, 85.0, 76.3, 74.3, 18.5, 18.2, and 10.9.

IR (neat) 3062, 2943, 2890, 2863, 2205 (sharp), 2122 (br), 2104 (sharp), 1460, 1443, 1002, 880, 782, 752, and 686 cm^{-1}.

GC-MS (EI, 70 eV): t_R = 8.87 min. Calc for $C_{16}H_{20}Si^+$ [M^+] 240, found 240.

The tetrayne **12a** was prepared following general procedure B from diynyl silane ***S2*** (255 mg, 1.06 mmol), NBS (189 mg, 1.06 mmol), the diynyl alcohol ***S3***[8] (138 mg, 0.88 mmol), Et_3N (0.15 mL, 1.1 mmol), and DMAP (11 mg, 0.090 mmol). The crude material was purified by being passed through a small plug of silica gel (5% EtOAc/hexanes eluant) and then purified by medium pressure liquid chromatography (5% EtOAc/hexanes) to give the tetrayne **12a** (319 mg, 92%) as a slightly yellow oil, which solidified after storing in the freezer.

Data for 12a

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (br d, *J* = 7.2 Hz, 2H, ArH_o), 7.49 (br d, *J* = 7.2 Hz, 2H, ArH_o'), 7.40–7.28 (overlapping m, 6H), 4.63 (s, 2H, SiOCH_2), and 1.12 [br s, 14H, Si(*i-Pr*)$_2$].

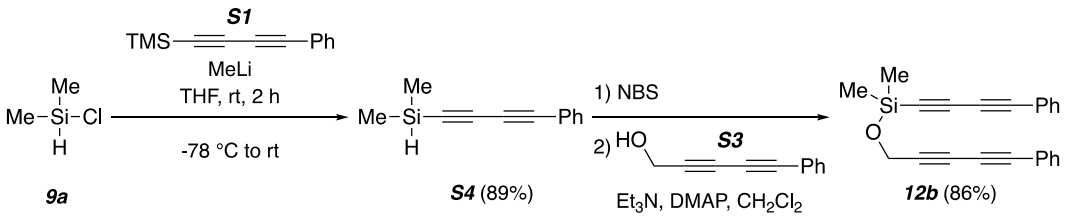
^{13}C NMR (126 MHz, $CDCl_3$) δ 132.8, 132.6, 129.6, 129.2, 128.5, 128.4, 121.6, 121.0, 90.4, 84.2, 80.5, 78.1, 77.2, 74.1, 73.6, 69.9, 53.6, 17.0, 16.9, and 13.2.

IR (neat) 2947, 2866, 2247, 2204, 2103, 1490, 1462, 1443, 1370, 1111, 1068, 882, 754, and 688 cm^{-1}.

HRMS (ESI-Orbitrap) Calc for [$(C_{27}H_{27}OSi)^+$] [$(M+H)^+$] 395.1826; found: 395.1820.

mp 67–70 °C.

Dimethyl(phenylbuta-1,3-diyn-1-yl)((5-phenylpenta-2,4-diyn-1-yl)oxy)silane (12b)



Diynylsilane ***S4*** was prepared following general procedure A from trimethyl(phenylbuta-1,3-diyn-1-yl)silane ***S1***[2] (1.52 g, 7.66 mol), MeLi (5.26 mL, 1.6 M in Et_2O, 8.42 mol), and dimethylchlorosilane (0.96 mL, 8.8 mol) to give the diyne ***S4*** (1.26 g, 89%) as a yellow oil.

Data for S4

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (br d, *J* = 7.2 Hz, 2H, ArH_o), 7.40 (br t, *J* = 7.2 Hz, 1H, ArH_p), 7.34 (br dd, *J* = 7.2, 7.2 Hz, 2H, ArH_m), 4.24 (sept, *J* = 3.8 Hz, 1H, Si*H*), and 0.33 [d, *J* = 3.8 Hz, 6H, Si(CH_3)$_2$].

^{13}C NMR (126 MHz, $CDCl_3$) δ 132.7, 129.5, 128.4, 121.2, 89.1, 87.5, 74.0, 71.3, and -3.3.

IR (neat) 3065, 2963, 2205 (sharp), 2142 (br), 2105 (sharp), 1442, 1251, 871, 837, 752, 726, and 685 cm^{-1}.

GC-MS (EI, 70 eV): t_R = 6.89 min. Calc for $C_{12}H_{12}Si^+$ [M^+] 184, found 184.

Tetrayne **12b** was prepared following general procedure B from diynylsilane ***S4*** (301 mg, 1.63 mmol), NBS (345 mg, 1.94 mmol), diynylalcohol ***S3***[8] (190 mg, 1.03 mmol), Et_3N (0.16 mL, 1.1 mmol), and DMAP (12 mg, 0.10 mmol). The crude material was purified by passage through a small silica plug (100% CH_2Cl_2) and the residue was further purified by medium pressure liquid chromatography (2% EtOAc/hexanes) to give the tetrayne **12b** (300 mg, 86%) as a yellow oil.

Data for 12b

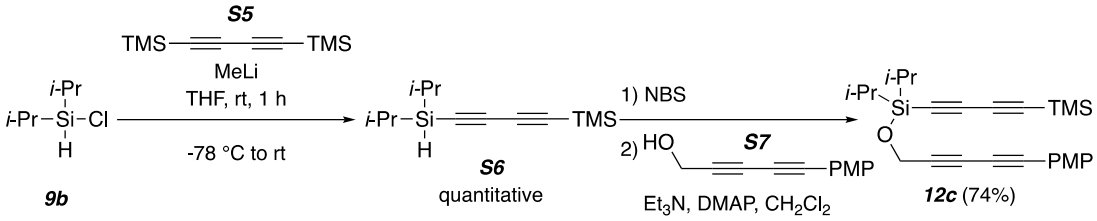
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52–7.46 (m, 4H, ArH_o and ArH_o*'*), 7.41–7.35 (m, 2H, ArH_p and ArH_p*'*), 7.35–7.27 (m, 4H, ArH_m and ArH_m*'*), 4.57 (s, 2H, SiOCH_2), and 0.40 [s, 6H, Si(CH_3)$_2$].

^{13}C NMR (126 MHz, $CDCl_3$) δ 132.8, 132.6, 129.6, 129.2, 128.44, 128.36, 121.5, 120.9, 88.9, 86.5, 80.0, 78.3, 78.0, 73.8, 73.4, 70.4, and 52.5.

IR (neat) 3058, 2962, 2244 (sharp), 2204 (sharp), 2104 (sharp), 1489, 1442, 1371, 1256, 1106, 1067, 825, 796, 753, and 687 cm $^{-1}$.

HRMS (ESI-Orbitrap) Calc for [$(C_{23}H_{19}OSi)^+$] [$(M+H)^+$] 339.1200; found: 339.1190.

((Diisopropyl((5-(4-methoxyphenyl)penta-2,4-diyn-1-yl)oxy)silyl)buta-1,3-diyn-1-yl)trimethylsilane (12c)



Diynylsilane ***S6*** was prepared following general procedure A from 1,4-bis(trimethylsilyl)buta-1,3-diyne ***S5***[5] (339 mg, 2.0 mmol), MeLi (1.38 mL, 1.6 M in Et_2O, 2.20 mmol), and diisopropylchlorosilane (0.38 mL, 2.20 mmol) to give diynylsilane ***S6*** (471 mg, quantitative) as a colorless oil.

Data for *S6*

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.72 (br s, 1H, Si*H*), 1.11–1.03 [m, 14H, Si(*i-Pr*)$_2$], and 0.20 [s, 9H, Si(C*H*$_3$)$_3$].

^{13}C NMR (126 MHz, $CDCl_3$) δ 90.5, 88.1, 85.5, 80.3, 18.4, 18.2, 10.8, and -0.5.

IR (neat) 2945m 2866, 2125 (br), 2067 (sharp), 1461, 1250, 841, 782, 758, and 644 cm^{-1}.

GC-MS (EI, 70 eV): t_R = 6.25 min. Calc for $C_{13}H_{24}Si_2^+$ [M^+] 236, found 236.

Tetrayne **12c** was prepared following general procedure B from diynylsilane ***S6*** (431 mg, 1.82 mmol), NBS (324 mg, 1.82 mmol), diynyl alcohol ***S7***[6] (283 mg, 1.52 mmol), Et_3N (0.25 mL, 1.8 mmol) and DMAP (18 mg, 0.15 mmol). The crude material was purified by passage through a small silica plug and the residue was further purified by medium pressure liquid chromatography (5% EtOAc/hexanes) to give the tetrayne **12c** (474 mg, 74%) as a yellow oil.

Data for 2c

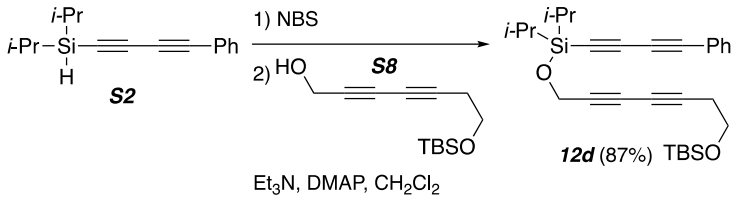
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (nfod, *J* = 8.8 Hz, 2H, *H*C$_o$=C-C≡C), 6.84 (nfod, *J* = 8.8 Hz, 2H, *H*C$_o$=C-OMe), 4.58 (s, 2H, SiOC*H*$_2$), 3.81 (s, 3H, OC*H*$_3$), 1.08 [m, 14H, Si(*i-Pr*)$_2$], and 0.21 [s, 9H, Si(C*H*$_3$)$_3$].

^{13}C NMR (126 MHz, $CDCl_3$) δ 160.4, 134.2, 114.1, 113.5, 90.4, 87.8, 86.7, 79.8, 79.5, 78.3, 72.4, 70.1, 55.3, 53.6, 17.0, 16.9, 13.1, and -0.5.

IR (neat) 2949, 2867, 2243 (sharp), 2066 (sharp), 1604, 1509, 1463, 1371, 1251, 1173, 1111, 1064, 846, and 683 cm^{-1}.

HRMS (ESI-Orbitrap) Calc for $[(C_{25}H_{33}O_2Si_2)^+]$ $[(M+H)^+]$ 421.2014; found: 421.2012.

13,13-Diisopropyl-2,2,3,3-tetramethyl-17-phenyl-4,12-dioxa-3,13-disilaseptadeca-7,9,14,16-tetrayne (12d)



Tetrayne **12d** was prepared following general procedure B from diynylsilane ***S2*** (330 mg, 1.37 mmol), NBS (265 mg, 1.49 mmol), diynyl alcohol ***S8***[7] (273 mg, 1.14 mmol), Et_3N (0.19 mL, 1.37 mmol), and DMAP (13 mg, 0.11 mmol). The crude material was purified by passage through a small silica plug and the residue was further purified by medium pressure liquid chromatography (5% EtOAc/hexanes) to give the tetrayne **12d** (443 mg, 87%) as a yellow oil.

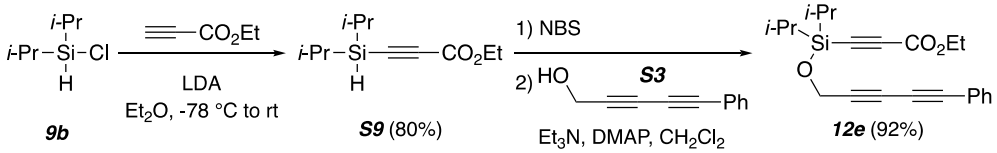
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (br d, *J* = 7.1 Hz, 2H, ArH_o), 7.39 (tt, *J* = 7.3, 1.5 Hz, 1H, ArH_p), 7.33 (br dd, *J* = 7.0, 7.01 Hz, 2H, ArH_m), 4.52 (s, 2H, SiOCH_2), 3.74 (t, *J* = 7.0 Hz, 2H, CH_2CH_2OTBS), 2.49 (t, *J* = 7.0 Hz, 2H, CH_2CH_2OTBS), 1.11–1.07 (m, 14H), 0.89 [s, 9H, OSiC(CH_3)$_3$], and 0.07 [s, 6H, OSi(CH_3)$_2$].

^{13}C NMR (126 MHz, $CDCl_3$) δ 132.8, 129.6, 128.5, 121.1, 90.2, 84.2, 78.1, 77.1, 74.1, 73.8, 70.1, 65.8, 61.3, 53.4, 25.9, 23.7, 18.3, 17.0, 16.9, 13.2, and -5.3.

IR (neat) 2948, 2865, 2259 (sharp), 2205 (sharp), 2103 (sharp), 1463, 1254, 1086, 835, 775, 754, and 686 cm $^{-1}$.

HRMS (ESI-Orbitrap) Calc for [($C_{29}H_{41}O_2Si_2$)$^+$] [(M+H)$^+$] 477.2640; found: 477.2646.

Ethyl 3-(diisopropyl((5-phenylpenta-2,4-diyn-1-yl)oxy)silyl)propiolate (12e)



To a solution of diisopropylamine (0.33 mL, 2.4 mmol) in Et_2O (20 mL) at -78 ºC was added *n*-BuLi (2.5 M in hexanes, 1.0 mL, 2.5 mmol) dropwise by syringe. After an additional 20 min at -78 °C, ethyl propiolate (0.23 mL, 2.3 mmol) was added to provide a light yellow slurry. After another 30 min at -78 °C, diisopropylchlorosilane (0.39 mL, 2.3 mmol) was added dropwise. The reaction mixture was warmed to rt and the completion of reaction was confirmed by TLC. The mixture was diluted with Et_2O (15 mL), quenched with saturated aqueous NH_4Cl solution, and extracted with additional Et_2O. The organic extracts were combined, washed with brine, dried with $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by flash chromatography (5% EtOAc/hexanes) to provide alkynyl silane ***S9*** (382 mg, 80%) as a slightly yellow oil, which was immediately used for the subsequent step.

Data for *S9*

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.24 (q, *J* = 7.1 Hz, 2H, OC*H*$_2$CH$_3$), 3.77 (br s, 1H, Si*H*), 1.32 (t, *J* = 7.1 Hz, 3H, OCH$_2$C*H*$_3$), and 1.10 [br s, 14H, Si(*i-Pr*)$_2$].

^{13}C NMR (126 MHz, $CDCl_3$) δ 152.8, 97.2, 88.2, 62.1, 18.3, 18.2, 14.0, and 10.5.

IR (neat) 2946, 2867, 2131 (br), 1711, 1462, 1218, 1003, 881, 782, and 752 cm^{-1}.

GC-MS (EI, 70 eV): t_R = 5.65 min. Calc for $C_{11}H_{20}O_2Si^+$ [M^+] 212, found 212.

The triyne **12e** was prepared following general procedure B from alkynyl silane ***S9*** (400 mg, 1.88 mmol), NBS (335 mg, 1.88 mmol), diynyl alcohol ***S3***[8] (245 mg, 1.57 mmol), Et_3N (0.26 mL, 1.88 mmol), and DMAP (19 mg, 0.16 mmol). The crude material was purified by flash column chromatography (5% EtOAc/hexanes) to give triyne **12e** (503 mg, 87%) as a slightly yellow oil.

Data for 12e

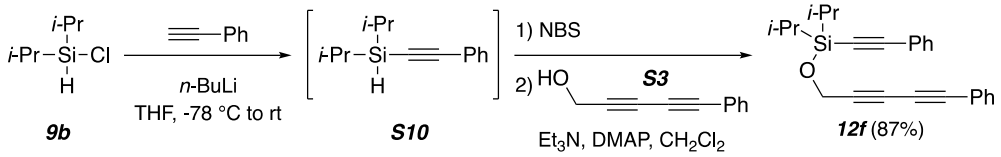
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (br d, *J* = 7.4 Hz, 2H, ArH_o), 7.36 (t, *J* = 7.0 Hz, 1H, ArH_p), 7.32 (br dd, *J* = 7.4 Hz, 2H, ArH_m), 4.60 (s, 2H, SiOCH_2), 4.25 (q, *J* = 7.2 Hz, 2H, OC$H_2$$CH_3$), 1.32 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3), and 1.11 [br s, 14H, Si(*i*-*Pr*)$_2$].

^{13}C NMR (126 MHz, $CDCl_3$) δ 152.7, 132.6, 129.3, 128.4, 121.5, 96.9, 87.0, 80.0, 78.3, 73.4, 70.2, 62.2, 53.7, 16.9, 16.8, 14.0, and 12.9.

IR (neat) 3061, 2948, 2868, 2245, 1711, 1463, 1368, 1225, 1110, 1065, 754, and 689 cm^{-1}.

HRMS (ESI-Orbitrap) Calc for [$(C_{22}H_{27}O_3Si)^+$] [$(M+H)^+$] 367.1724; found: 367.1729.

Diisopropyl(phenylethynyl)((5-phenylpenta-2,4-diyn-1-yl)oxy)silane (12f)



To a solution of phenylacetylene (269 mg, 2.64 mmol) in THF (10 mL) at -78 °C was added *n*-BuLi (2.5 M in hexanes, 1.10 mL, 2.77 mmol) dropwise by syringe. After an additional 30 min at -78 °C, diisopropylchlorosilane (0.45 mL, 2.64 mmol) was added. The reaction mixture was then warmed to rt and complete reaction was observed by TLC. After 1 h the mixture was diluted with Et_2O (10 mL), quenched with saturated aqueous NH_4Cl solution, and extracted with Et_2O. The organic extracts were combined, washed with brine, dried with $MgSO_4$, and concentrated under reduced pressure. The crude product alkynyl silane ***S10*** was directly used without purification.

Triyne **12f** was prepared following general procedure B from the crude alkynyl silane ***S10*** (240 mg, 1.11 mmol), NBS (197 mg, 1.11 mmol), diynyl alcohol ***S3***[8] (157 mg, 1.00 mmol), Et_3N (0.15 mL, 1.10 mmol) and DMAP (12 mg, 0.10 mmol). The crude product mixture was purified by passage through a small silica plug (5% hexanes/EtOAc eluant) and the residue was further purified by medium pressure liquid chromatography (5% EtOAc/hexanes) to give triyne **12f** (321 mg, 87%) as a slightly yellow oil.

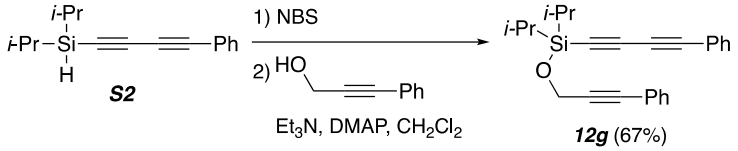
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55–7.51 (m, 2H), 7.50–7.46 (m, 2H), 7.38–7.28 (m, 6H), 4.65 (s, 2H, SiOC*H*$_2$), and 1.13 [br s, 14H, Si(*i-Pr*)$_2$].

^{13}C NMR (126 MHz, $CDCl_3$) δ 132.6, 132.3, 129.2, 129.0, 128.4, 128.3, 122.5, 121.7, 108.0, 87.5, 80.9, 78.0, 73.7, 69.7, 53.5, 17.2, 17.0, and 13.1.

IR (neat) 3059, 2944, 2865, 2245, 2155, 1489, 1462, 1442, 1370, 1108, 1063, 830, 753, and 689 cm $^{-1}$.

HRMS (ESI-Orbitrap) Calc for [($C_{25}H_{27}OSi)^+$] [$(M+H)^+$] 371.1826; found: 371.1823.

Diisopropyl(phenylbuta-1,3-diyn-1-yl)((3-phenylprop-2-yn-1-yl)oxy)silane (12g)



Triyne **12g** was prepared following general procedure B from diynylsilane ***S2*** (120 mg, 0.65 mmol), NBS (126 mg, 0.71 mmol), 3-phenyl-2-propyn-1-ol (101 mg, 0.54 mmol), Et_3N (0.11 mL, 0.78 mmol), and DMAP (7 mg, 0.05 mmol). The crude material was purified by passage through a small silica plug (100% CH_2Cl_2) and the residue was further purified by medium pressure liquid chromatography (2% EtOAc/hexanes) to give the tetrayne **12g** (134 mg, 67%) as a slightly yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (nfod, *J* = 7.5 Hz, 2H, PhH_o), 7.46 (nfom, 2H, PhH_o'), 7.38 (br t, *J* = 7.5 Hz, 1H, PhH_p), 7.33 (br dd, *J* = 7.2, 7.2 Hz, 2H, PhH_m), 7.32–7.28 (m, 3H, PhH_m' + PhH_p'), 4.70 (s, 2H, SiOCH_2), and 1.13 [s, 6H, Si(CH_3)$_2$].

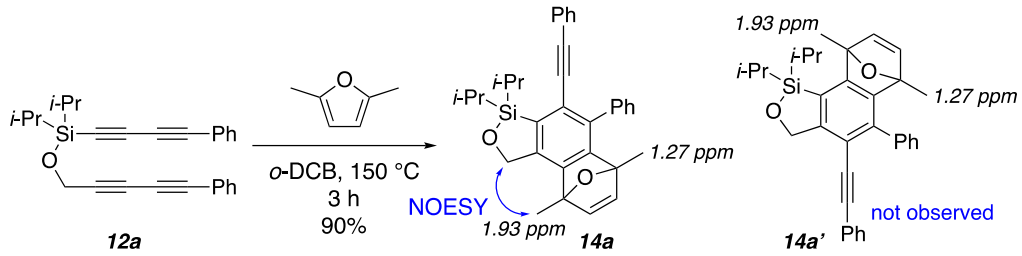
^{13}C NMR (126 MHz, $CDCl_3$) δ 132.8, 131.7, 129.6, 128.5, 128.3, 128.2, 122.9, 121.1, 90.1, 87.3, 85.3, 84.7, 77.1, 74.2, 53.6, 17.1, 17.0, and 13.2.

IR (neat) 3060, 2945, 2865, 2204 (sharp), 2103 (sharp), 1489, 1462, 1084, 754 and 688 cm $^{-1}$.

HRMS (GCMS, EI, 70 eV): t_R =7.18 min. Calc for $C_{25}H_{26}OSi^+$ [M^+] 370.1747, found 370.1756.

(c) Products (14a–n) obtained from HDDA cascade reactions

3,3-Diisopropyl-6,9-dimethyl-5-phenyl-4-(phenylethynyl)-1,3,6,9-tetrahydro-6,9-epoxynaphtho[2,1-*c*][1,2]oxasilole (14a)



Compound **14a** was prepared following general procedure C from tetrayne **12a** (23 mg, 0.058 mmol) and 2,5–dimethylfuran (0.13 mL, 1.2 mmol) in *o*-DCB (3.0 mL, 0.02 M) at 150 ºC for 3 h. The reaction mixture was passed through a silica gel column and eluted with hexanes to remove *o*-DCB and the residue was purified by flash chromatography (4% to 20% EtOAc/hexanes) to give compound **14a** (26 mg, 90%) as an off-white foamy crystalline solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (br d, *J* = 7.5 Hz, 1H), 7.50–7.45 (m, 1H), 7.44–7.40 (m, 2H), 7.24–7.18 (m, 3H), 7.09–7.05 (m, 1H), 7.04–6.99 (m, 2H), 6.842 (br d, *J* = 5 Hz, 1H, C*H*=CH), 6.839 (br d, *J* = 5 Hz, 1H, CH=C*H*), 5.35 (d, *J* = 13.9 Hz, 1H, SiOCH_AH_B), 5.14 (d, *J* = 13.9 Hz, 1H, SiOCH_AH_B), 1.93 (br s, 3H, CH_3), 1.383 [sept, *J* = 7.6 Hz, 1H, OSiC*H*$(CH_3)_2$], 1.375 [sept, *J* = 7.6 Hz, 1H, OSiC*H*$(CH_3)_2$], 1.27 (br s, 3H, CH_3), 1.11 [d, *J* = 7.6 Hz, 9H, OSiCH$(CH_3)_2$ and OSiCHCH_3CH_3], and 1.06 [d, *J* = 7.6 Hz, 3H, OSiCHCH_3CH_3).

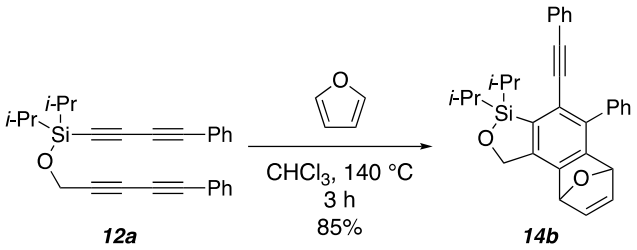
^{13}C NMR (126 MHz, $CDCl_3$) δ 152.7, 146.9, 146.7, 145.0, 140.5, 138.4, 136.5, 134.8, 131.1, 130.6, 129.5, 128.2, 127.9, 127.7, 127.6, 127.5, 123.8, 123.4, 92.4, 91.3, 90.3, 88.5, 69.7, 17.62, 17.59, 17.23, 17.20, 17.1, 16.8, 13.6, and 13.4.

IR (neat) 3056, 2934, 2863, 1490, 1461, 1442, 1382, 1296, 1133, 1056, 883, 764, 689, 674, and 648 cm^{-1}.

HRMS (ESI-Orbitrap) Calc for $[(C_{33}H_{35}O_2Si)^+]$ $[(M+H)^+]$ 491.2401; found: 491.2402.

mp 175–178 °C.

3,3-Diisopropyl-5-phenyl-4-(phenylethynyl)-1,3,6,9-tetrahydro-6,9-epoxynaphtho[2,1-*c*][1,2]oxasilole (14b)



Compound **14b** was prepared following general procedure C from tetrayne **12a** (28 mg, 0.071 mmol) and furan (0.15 mL, 2.1 mmol) in $CHCl_3$ (3.5 mL, 0.02 M) at 140 ºC for 3 h. The crude material was purified by passage through a small plug of silica gel (15% EtOAc/hexanes as eluent) and the residue was purified by medium pressure liquid chromatography (20% EtOAc/hexanes) to give compound **14b** (28 mg, 85%) as a pale-yellow, crystalline solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52–7.45 (m, 4H), 7.45–7.39 (m, 1H), 7.29–7.23 (m, 3H), 7.22–7.17 (m, 2H), 7.14 (br d, *J* = 5.6 Hz, 1H, C*H*=CH), 7.07 (br d, *J* = 5.6 Hz, 1H, CH=C*H*), 5.76 (s, 1H, OC*H*), 5.62 (s, 1H, OC*H*), 5.26 (d, *J* = 14.0 Hz, 1H, OSiCH_AH_B), 5.08 (d, *J* = 14.0 Hz, 1H, OSiCH_AH_B), 1.41 [sept, *J* = 7.6 Hz, 1H, OSiC*H*$(CH_3)_2$], 1.39 [sept, *J* = 7.6 Hz, 1H, OSiC*H*$(CH_3)_2$], 1.12 [2 overlapped d, 6H, OSiCH(CH_3)$_2$], 1.10 [d, 3H, OSiCH(CH_3)$_2$] and 1.08 [d, 3H, OSiCH(CH_3)$_2$].

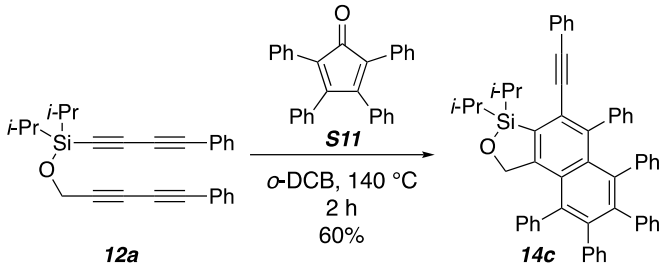
^{13}C NMR (126 MHz, $CDCl_3$) δ 150.2, 143.2, 142.3, 141.7, 140.8, 138.0, 136.1, 135.5, 131.1, 129.8, 128.3, 128.1, 128.0, 127.6, 123.4, 122.3, 91.8, 91.4, 81.9, 80.9, 69.9, 17.6, 17.20 (2x), 17.19, 13.53, and 13.51.

IR (neat) 3053, 3019, 2942, 2862, 1491, 1461, 1443, 1278, 1057, 868, 833, 755, 700, 689, 657, and 645 cm $^{-1}$.

HRMS (ESI-Orbitrap) Calc for [$(C_{31}H_{31}O_2Si)^+$] [$(M+H)^+$] 463.2088; found: 463.2078.

mp 131–133 °C.

3,3-Diisopropyl-5,6,7,8,9-pentaphenyl-4-(phenylethynyl)-1,3-dihydronaphtho[2,1-*c*][1,2]oxasilole (14c)



The naphthalene derivative **14c** was prepared following general procedure C from tetrayne **12a** (19 mg, 0.048 mmol) and 2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-one ***S11*** (28 mg, 0.074 mmol) in *o*-DCB (1.0 mL, 0.05 M) at 140 ºC for 2 h. The reaction mixture was passed through a small silica gel column and eluted with hexanes to remove the *o*-DCB and then eluted with 20% EtOAc/hexanes. The crude material was then purified by medium pressure liquid chromatography (3% EtOAc/hexanes) to remove the excess of ***S11***. Subsequent recrystallization from CH_2Cl_2/MeOH gave compound **14c** (22 mg, 60%) as a white crystalline solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23–7.17 (m, 5H), 7.17–7.12 (m, 3H), 7.04–7.00 (m, 2H), 6.95 (br s, 5H), 6.82–6.75 (m, 3H), 6.75–6.70 (m, 5H), 6.70–6.66 (m, 1H), 6.65–6.61 (m, 2H), 6.60–6.57 (m, 2H), 6.53–6.49 (m, 2H), 4.48 (s, 2H, SiOCH_2), 1.38 [sept, *J* = 7.6 Hz, 2H, OSiC*H*$(CH_3)_2$], 1.09 [d, *J* = 7.5 Hz, 6H, OSiCH(CH_3)$_2$], and 1.06 [d, *J* = 7.5 Hz, 6H, OSiCH(CH_3)$_2$].

^{13}C NMR (126 MHz, $CDCl_3$) δ 148.8, 143.7, 142.5, 141.8, 141.4, 141.3, 140.8, 140.3, 140.1, 139.8, 136.8, 133.8, 133.5, 132.0, 131.6, 131.2, 131.1, 131.0, 130.9, 128.9, 128.2, 127.9, 127.19, 127.17, 126.6, 126.3, 126.22, 126.17, 125.4, 125.1, 125.0, 124.9, 124.1, 123.5, 93.4, 92.1, 74.0, 17.7, 17.2, and 13.6.

IR (neat) 3055, 3025, 2940, 2862, 1597, 1491, 1461, 1443, 1051, 881, 794, 784, 754, 694, 674, and 652 cm $^{-1}$.

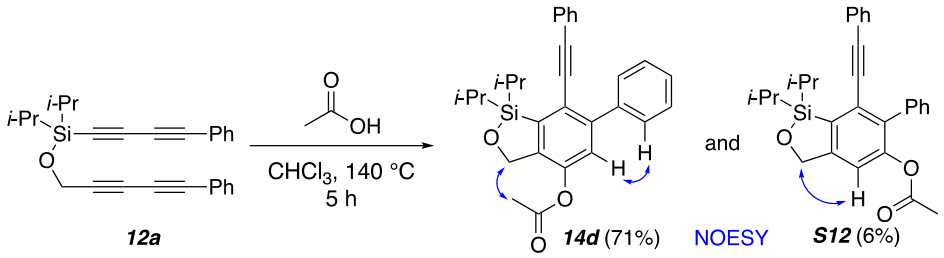
HRMS (ESI-Orbitrap) Calc for $[(C_{55}H_{47}OSi)^+]$ $[(M+H)^+]$ 751.3391; found: 751.3397.

mp 282–284 °C.

1,1-Diisopropyl-6-phenyl-7-(phenylethynyl)-1,3-dihydrobenzo[*c*][1,2]oxasilol-4-yl acetate (14d)

and

1,1-Diisopropyl-6-phenyl-7-(phenylethynyl)-1,3-dihydrobenzo[*c*][1,2]oxasilol-5-yl acetate (*S12*)



Compounds **14d** and ***S12*** were prepared following general procedure C from the tetrayne **12a** (50 mg, 0.13 mmol) and AcOH (70 μL, 1.3 mmol) in $CHCl_3$ (6.5 mL, 0.02 M) at 140 ºC for 5 h. The crude material was purified by passage through a small silica plug (10% EtOAc/hexanes as eluent) and the residue was further purified by medium pressure liquid chromatography (6% EtOAc/hexanes) to give compound **14d** (42 mg, 71%) as a light yellow foamy crystalline solid followed by ***S12*** (3 mg, 6%) as a light yellow oil.

Data for 14d

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (br d, *J* = 7.5 Hz, 2H, ArPhH_o), 7.46 (br dd, *J* = 7.5, 7.5 Hz, 2H, ArPhH_m), 7.39 (t, *J* = 7.4 Hz, 1H, ArPhH_p), 7.31-7.26 (m, 5H, C≡CPhH_5), 7.23 (s, 1H, Ar*H5*), 5.07 (s, 2H, SiOCH_2), 2.31 [s, 3H, C(O)CH_3], 1.42 [sept, *J* = 7.5 Hz, 2H, OSiC*H*$(CH_3)_2$], 1.13 [d, *J* = 7.5 Hz, 6H, OSiCH(CH_3)$_2$], and 1.11 [d, *J* = 7.5 Hz, 6H, OSiCH(CH_3)$_2$].

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.5, 145.0, 144.8, 141.2, 140.2, 139.8, 131.1, 129.5, 128.4, 128.2, 127.9, 127.7, 124.3, 123.3, 121.9, 92.3, 90.8, 69.3, 20.9, 17.5, 17.1, and 13.5.

IR (neat) 3059, 2943, 2863, 1765, 1491, 1462, 1427, 1194, 1155, 1054, 773, 755, 699, and 660 cm $^{-1}$.

HRMS (ESI-Orbitrap) Calc for $[(C_{29}H_{31}O_3Si)^+]$ $[(M+H)^+]$ 455.2037; found: 455.2046.

mp 96–97 °C.

Data for *S12*

^{1}H NMR (500 MHz, CDCl3) δ 7.46–7.42 (m, 4H), 7.42–7.36 (nfom, 1H, ArPh*H$_p$*), 7.26–7.22 (m, 3H), 7.11 (br d, *J* = 7.4 Hz, 2H, C≡CPh*H$_o$*), 6.97 (s, 1H, Ar*H4*), 5.15 (s, 2H, SiOC*H$_2$*), 1.98 [s, 3H, C(O)C*H$_3$*], 1.40 [sept, *J* = 7.5 Hz, 2H, OSiC*H*(CH$_3$)$_2$], 1.13 [d, *J* = 6.9 Hz, 6H, OSiCH(C*H$_3$*)(CH$_3$)], and 1.11 [d, *J* = 6.9 Hz, 6H, OSiCH(CH$_3$)(C*H$_3$*)].

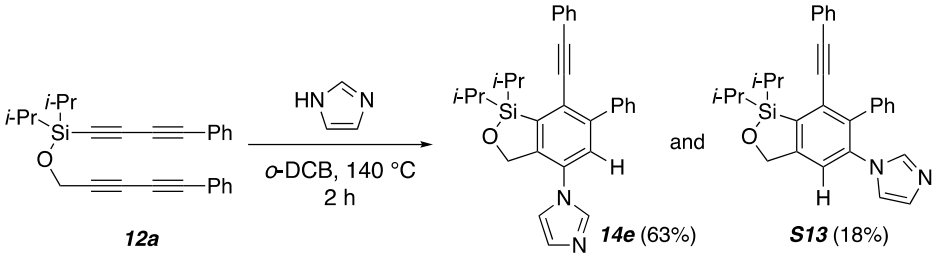
^{13}C NMR (126 MHz, CDCl$_3$) δ 169.2, 151.3, 149.8, 136.3, 135.9, 134.1, 131.2, 130.2, 128.33, 128.29, 127.7, 127.6, 127.3, 123.0, 115.9, 93.4, 90.5, 71.9, 20.7, 17.5, 17.2, and 13.5.

IR (neat) 3059, 2944, 2864, 1770, 1491, 1462, 1444, 1194, 1058, 1031, 882, 781, 755, and 689 cm $^{-1}$.

HRMS (ESI-Orbitrap) Calc for [(C$_{29}$H$_{31}$O$_3$Si)$^+$] [(M+H)$^+$] 455.2037; found: 455.2045.

1-(1,1-Diisopropyl-6-phenyl-7-(phenylethynyl)-1,3-dihydrobenzo[*c*][1,2]oxasilol-4-yl)-1*H*-imidazole (14e) and

1-(1,1-Diisopropyl-6-phenyl-7-(phenylethynyl)-1,3-dihydrobenzo[*c*][1,2]oxasilol-5-yl)-1*H*-imidazole (*S13*)



Compounds **14e** and ***S13*** were prepared following general procedure C from the tetrayne **12a** (20 mg, 0.051 mmol) and imidazole (17 mL, 0.25 mmol) in *o*-DCB (2.5 mL, 0.02 M) at 140 ºC for 2 h. The reaction mixture was passed through a small silica gel column and eluted with 100% hexanes to remove *o*-DCB and then eluted with 10:10:1 hexanes/EtOAc/MeOH. The residue was further purified by medium pressure liquid chromatography (10:10:1 hexanes/EtOAc/MeOH) to give compound **14e** (15 mg, 63%) as a yellow oil and ***S13*** (4 mg, 18%) as a yellow oil.

Data for 14e

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (s, 1H, Im*H2*), 7.70 (nfod, *J* = 7.2 Hz, 2H, ArPhH_o), 7.49 (br dd, *J* = 7.7, 7.2 Hz, 2H, ArPhH_m), 7.44 (tt, *J* = 7.4, 2.0 Hz, 1H, ArPhH_p), 7.38 (s, 1H, Ar*H5*), 7.34–7.27 (m, 5H, C≡CPhH_5), 7.24 (br s, 1H, Im*H4*), 7.17 (br s, 1H, Im*H5*), 5.11 (s, 2H, SiOCH_2), 1.46 [sept, *J* = 7.5 Hz, 2H, OSiC*H*$(CH_3)_2$], 1.16 [d, *J* = 7.5 Hz, 6H, OSiCH(CH_3)(CH_3)], and 1.13 [d, *J* = 7.5 Hz, 6H, OSiCH(CH_3)(CH_3)].

^{13}C NMR (126 MHz, $CDCl_3$) δ 144.6, 143.6, 140.9, 139.1, 136.9 (br), 131.9, 131.2, 130.2 (br), 129.4, 128.6, 128.5, 128.13, 128.10, 127.7, 124.7, 122.9, 119.6 (br), 93.8, 90.2, 70.1, 17.6, 17.1, and 13.5.

IR (neat) 3057, 2944, 2864, 1493, 1462, 1430, 1054, 785, 757, 700, 690, and 653 cm $^{-1}$.

HRMS (ESI-Orbitrap) Calc for [$(C_{30}H_{31}N_2OSi)^+$] [$(M+H)^+$] 463.2200; found: 463.2204.

Data for *S13*

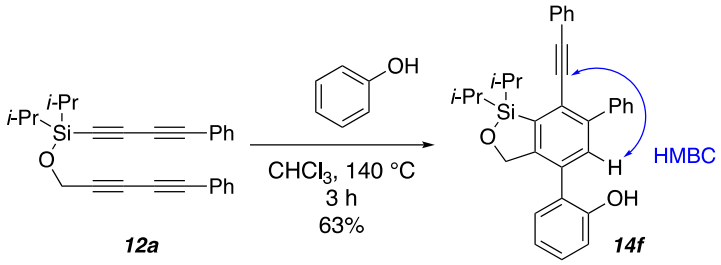
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (br s, 1H, Im*H2*), 7.36–7.32 (m, 3H), 7.30–7.23 (m, 5H, overlapped with $CDCl_3$), 7.19 (s, 1H, Ar*H4*), 7.12 (dd, *J* = 7.4, 1.8 Hz, 2H, C≡CPhH_o), 6.96 (br s, 1H, Im*H4*), 6.82 (br s, 1H, Im*H5*), 5.20 (s, 2H, SiOCH_2), 1.43 [sept, *J* = 7.5 Hz, 2H, OSiC*H*$(CH_3)_2$], 1.16 [d, *J* = 7.4 Hz, 6H, OSiCH(CH_3)(CH_3)], and 1.14 [d, *J* = 7.4 Hz, 6H, OSiCH(CH_3)(CH_3)].

^{13}C NMR (126 MHz, $CDCl_3$) δ 151.4, 138.6, 137.5 (br), 137.4, 137.0, 136.3, 131.3, 129.7, 129.2 (br), 128.6, 128.4, 128.1, 127.94, 127.93, 122.7, 120.5 (br), 118.8, 94.1, 90.3, 71.8, 17.5, 17.1, and 13.5.

IR (neat) 3058, 2943, 2863, 1583, 1490, 1462, 1444, 1054, 881, 780, 756, 700, 689, 658, and 648 cm^{-1}.

HRMS (ESI-Orbitrap) Calc for $[(C_{30}H_{31}N_2OSi)^+]$ $[(M+H)^+]$ 463.2200; found: 463.2201.

2-(1,1-Diisopropyl-6-phenyl-7-(phenylethynyl)-1,3-dihydrobenzo[*c*][1,2]oxasilol-4-yl)phenol (14f)



Compound **14f** was prepared following general procedure C from tetrayne **12a** (20 mg, 0.051 mmol) and phenol (48 mg, 0.51 mmol) in $CHCl_3$ (2.5 mL, 0.02 M) at 140 ºC for 3 h. The crude material was purified by passage through a small silica plug (10% EtOAc/hexanes as eluent) and the residue was further purified by medium pressure liquid chromatography (8% EtOAc/hexanes) to give compound **14f** (16 mg, 63%) as a light yellow foamy crystalline solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (br d, *J* = 7.4 Hz, 2H, ArPh*H*$_o$), 7.47 (br dd, *J* = 7.4, 7.4 Hz, 2H, ArPh*H*$_m$), 7.41 (s, 1H, Ar*H5*), 7.40 (t, *J* = 7.4 Hz, 1H, ArPh*H*$_p$), 7.31 (br s, 5H, C***CPh*H**$_5$), 7.30–7.26 (ddd, *J* = 7.9, 7.9, 1.8, 1H, Ar*H4'*), 7.19 (dd, *J* = 8.0, 1.6 Hz, 1H, Ar*H6'*), 7.00 (ddd, *J* = 8.1, 6.1, 1.3 Hz, 1H, Ar*H5'*), 6.98 (d, *J* = 8.0 Hz, 1H, Ar*H3'*), 5.05 (br s, 1H, ArO*H*), 5.00 (s, 2H, SiOC*H*$_2$), 1.46 [sept, *J* = 7.5 Hz, 2H, OSiC*H*$(CH_3)_2$], 1.15 [d, *J* = 7.5 Hz, 6H, OSiCH(C*H*$_3)_2$], and 1.14 [d, *J* = 7.5 Hz, 6H, OSiCH(C*H*$_3)_2$].

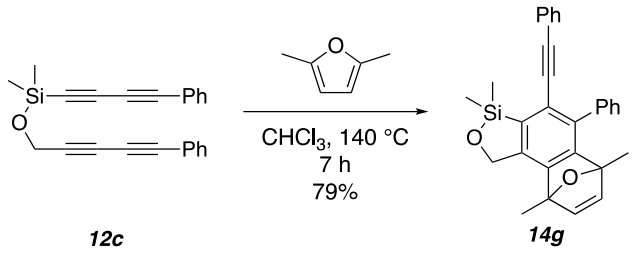
^{13}C NMR (126 MHz, $CDCl_3$) δ 152.3, 149.0, 143.4, 140.0, 132.8, 131.2, 130.0, 129.66, 129.57, 129.6, 128.4, 128.3, 127.9, 127.6, 125.6, 124.2, 123.3, 120.8, 115.8, 115.3, 92.9, 91.2, 71.6, 17.6, 17.2, and 13.6.

IR (neat) 3239, 3058, 2944, 2864, 1595, 1491, 1447, 1426, 1054, 1025, 881, 770, 752, 699, and 661 cm $^{-1}$.

HRMS (ESI-Orbitrap) Calc for $[(C_{33}H_{33}O_2Si)^+]$ $[(M+H^+)]$ 489.2244; found: 489.2308 (minor). Calc for $[(C_{33}H_{31}O_2Si)^+]$ $[(M+H^+-H_2$ (i.e., a pyrylium ion)] 487.2088; found: 487.2095 (major). Calc for $[(C_{33}H_{31}OSi)^+]$ $[(M+H^+-H_2O)]$ 471.2139; found: 471.2145 (minor).

mp 77–79 °C.

3,3,6,9-Tetramethyl-5-phenyl-4-(phenylethynyl)-1,3,6,9-tetrahydro-6,9-epoxynaphtho[2,1-*c*][1,2]oxasilole (14g)



12c *14g*

0.5 mmol scale: Compound **14g** was prepared following general procedure C with slight modifications. A solution of tetrayne **12c** (160 mg, 0.48 mmol) and 2,5-dimethylfuran (1.0 mL, 9.5 mmol) in $CHCl_3$ (24 mL, 0.02 M) was divided equally into three portions and then transferred into three culture tubes of the same size. The culture tubes were heated at 140 ºC for 7 h. The crude material was purified by passage through a small silica gel flash column (20% hexanes/EtOAc) and the residue was purified by medium pressure liquid chromatography (10% hexanes/EtOAc) to give compound **14g** (164 mg, 79%) as a slightly beige crystalline solid.

1.5 mmol scale: A solution of tetrayne **12c** (500 mg, 1.50 mmol) and 2,5-dimethylfuran (3.2 mL, 29.6 mmol) in $CHCl_3$ (75 mL, 0.02 M) was heated at 140 ºC for 6 h. The crude material was purified by passage through a small silica gel flash column (20% hexanes/EtOAc) and the residue was purified by medium pressure liquid chromatography (10% hexanes/EtOAc) to give compound **14g** (507 mg, 78%) as a slightly beige crystalline solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (br d, *J* = 7.4 Hz, 1H, ArPhH_o), 7.51–7.39 (m, 3H), 7.25–7.20 (m, 3H), 7.13–7.07 (m, 2H), 7.07–7.02 (nfom, 1H), 6.85 (s, 2H, C*H*=C*H*), 5.38 (d, *J* = 14.0 Hz, 1H, SiOCH_AH$_B$), 5.16 (d, *J* = 14.0 Hz, 1H, SiOCH$_A$$H_B$), 1.94 (s, 3H, C$H_3$), 1.28 (s, 3H, C$H_3$), and 0.50 [s, 6H, OSi(CH_3)$_2$].

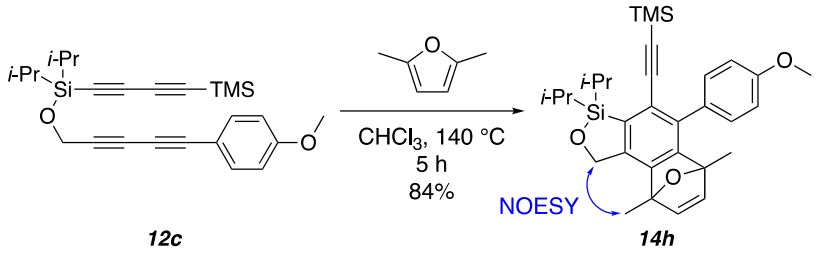
^{13}C NMR (126 MHz, $CDCl_3$; this spectrum referenced to the $CDCl_3$ shift at 77.16 ppm) δ 153.3, 147.1, 146.9, 145.6, 139.6, 138.1, 137.5, 136.2, 131.2, 130.6, 129.5, 128.4, 128.2, 127.9, 127.78, 127.76, 123.7, 123.4, 93.0, 90.5, 89.7, 88.6, 69.1, 17.2, 16.9, 0.2, and 0.1.

IR (neat) 3056, 2969, 1598, 1492, 1442, 1248, 1134, 1049, 854, 826, 790, 758, 691 and 757 cm^{-1}.

HRMS (ESI-Orbitrap) Calc for [($C_{29}H_{27}O_2Si$)$^+$] [(M+H)$^+$] 435.1775; found: 435.1777.

mp 182–183 °C.

3,3-Diisopropyl-5-(4-methoxyphenyl)-6,9-dimethyl-4-((trimethylsilyl)ethynyl)-1,3,6,9-tetrahydro-6,9-epoxynaphtho[2,1-*c*][1,2]oxasilole (14h)



Compound **14h** was prepared following general procedure C from the tetrayne **12c** (20 mg, 0.048 mmol) and 2,5–dimethylfuran (0.10 mL, 0.95 mmol) in $CHCl_3$ (2.5 mL, 0.02 M) at 140 ºC for 5 h. The crude material was purified by passage through a small plug of silica gel and the residue was purified by flash chromatography (6–12% EtOAc/hexanes) to give compound **14h** (21 mg, 84%) as an off-white crystalline solid.

^{1}H NMR (500 MHz, $CDCl_3$; this spectrum referenced to the $CDCl_3$ shift at 7.26 ppm) δ 7.40 (br d, *J* = 8.0 Hz, 1H, Ar'Ar*H*$_o$), 6.93 (br d, *J* = 8.5 Hz, 1H, Ar'Ar*H*$_o$'), 6.91–6.87 (m, 2H, Ar'Ar*H*$_m$ and Ar'Ar*H*$_m$'), 6.82 (d, *J* = 5.5 Hz, 1H, C*H*=CH), 6.81 (d, *J* = 5.5 Hz, 1H, CH=C*H*), 5.30 (d, *J* = 13.9 Hz, 1H, SiOC*H*$_A$H$_B$), 5.09 (d, *J* = 14.0 Hz, 1H, SiOCH$_A$*H*$_B$), 3.86 (s, 3H, OC*H*$_3$), 1.90 (s, 3H, C9C*H*$_3$), 1.30 [two overlapped sept, *J* = 7.5 Hz, 2H, SiC*H*(CH$_3$)$_2$], 1.29 (s, 3H, C6C*H*$_3$), 1.07 [d, *J* = 7.5 Hz, 3H, OSiCH(C*H*$_3$)$_2$], 1.063 [d, *J* = 7.5 Hz, 3H, OSiCH(C*H*$_3$)$_2$], 1.056 [d, *J* = 7.5 Hz, 3H, OSiCH(C*H*$_3$)$_2$], and 1.02 [d, *J* = 7.5 Hz, 3H, OSiCH(C*H*$_3$)$_2$], 0.00 ppm [s, 9 H, Si(C*H*$_3$)$_3$].

^{13}C NMR (126 MHz, $CDCl_3$, this spectrum referenced to the $CDCl_3$ shift at 77.16 ppm) δ 159.2, 152.8, 147.0, 146.8, 145.2, 140.3, 136.5, 135.6, 131.8, 130.53, 130.51, 124.3, 113.07, 113.06, 106.6, 97.5, 90.5, 88.6, 69.7, 55.5, 17.80, 17.76, 17.33(2x), 17.31, 17.0, 13.7, 13.5, and -0.3.

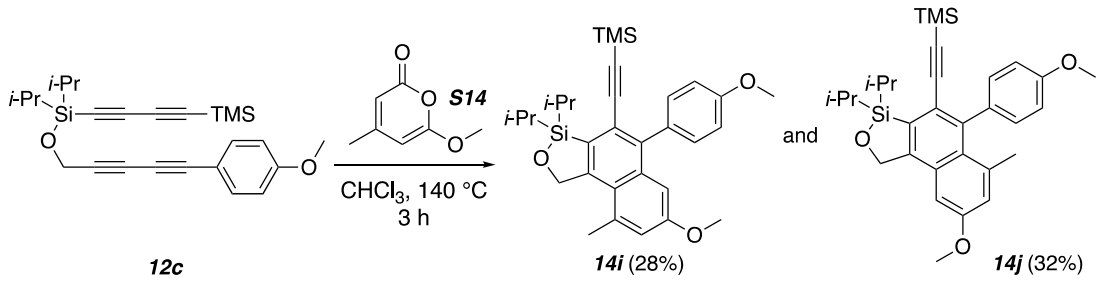
IR (neat) 2940, 2863, 2150 (sharp), 1610, 1509, 1462, 1384, 1242, 1153, 1137, 843, 761, 670, and 638 cm $^{-1}$.

HRMS (ESI-Orbitrap) Calc for [($C_{31}H_{41}O_3Si_2$)$^+$] [(M+H)$^+$] 517.2589; found: 517.2595.

mp 157–159 °C.

3,3-Diisopropyl-8-methoxy-5-(4-methoxyphenyl)-9-methyl-4-((trimethylsilyl)ethynyl)-1,3-dihydronaphtho[2,1-*c*][1,2]oxasilole (14i) and

3,3-Diisopropyl-7-methoxy-5-(4-methoxyphenyl)-6-methyl-4-((trimethylsilyl)ethynyl)-1,3-dihydronaphtho[2,1-*c*][1,2]oxasilole (14j)



Compounds ***14i*** and ***14j*** were prepared following general procedure C from the tetrayne ***12c*** (20 mg, 0.048 mmol) and 6-methoxy-4-methyl-2*H*-pyran-2-one ***S14*** (33 mg, 0.24 mmol) in $CHCl_3$ (2.5 mL, 0.02 M) at 140 ºC for 3 h. The crude material was purified by passage through a small plug of silica gel (10% hexanes/EtOAc), and the residue was further purified by medium pressure liquid chromatography (10% hexanes/EtOAc) to give compound ***14i*** (7 mg, 28%) as a yellow oil and ***14j*** (8 mg, 32%) as a yellow oil. Both samples of these compounds crystallized after being stored in the cold.

Data for compound 14i

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (nfod, *J* = 8.5 Hz, 2H, Ar'Ar*H*$_o$), 7.01 (nfod, *J* = 8.5 Hz, 2H, Ar'Ar*H*$_m$), 6.96 (d, *J* = 2.7 Hz, 1H, *H6* or *H8*), 6.90 (d, *J* = 2.7 Hz, 1H, *H6* or *H8*), 5.74 (s, 2H, SiOC*H*$_2$), 3.89 (s, 3H, Ar'ArOC*H*$_3$), 3.67 (s, 3H, C7OC*H*$_3$), 2.76 (s, 3H, ArC*H*$_3$), 1.37 [sept, *J* = 7.6 Hz, 2H, OSiC*H*(CH$_3$)$_2$], 1.11 [d, *J* = 7.6 Hz, 6H, OSiCH(C*H*$_3$)$_2$], 1.05 [d, *J* = 7.6 Hz, 6H, OSiCH(C*H*$_3$)$_2$], and 0.03 [s, 9H, Si(C*H*$_3$)$_3$].

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.8, 157.1, 148.6, 142.3, 136.8, 136.6, 132.3, 131.7, 130.4, 125.0, 122.2, 121.3, 113.4, 107.1, 105.2, 98.3, 74.7, 55.4, 55.0, 24.4, 17.8, 17.2, 13.6, and -0.4.

IR (neat) 2955, 2864, 2152 (sharp), 1611, 1513, 1461, 1398, 1246, 1071, 1047, 838, and 759 cm $^{-1}$.

HRMS (ESI-Orbitrap) Calc for [($C_{31}H_{41}O_3Si_2$)$^+$] [(M+H)$^+$] 517.2589; found: 517.2584.

mp 123–126 °C.

Data for compound 14j

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (nfod, *J* = 8.5 Hz, 2H, Ar'Ar*H*$_o$), 6.933 (d, *J* = 1.8 Hz, 1H, Ar*H9*), 6.928 (d, *J* = 8.6 Hz, 2H, Ar'Ar*H*$_m$), 6.75 (d, *J* = 2.7 Hz, 1H, Ar*H7*), 5.48 (s, 2H, SiOC*H*$_2$), 3.91 (s, 1H, OC*H*$_3$), 3.87 (s, 3H, OC*H*$_3$), 1.99 (s, 3H, ArC*H*$_3$), 1.36 [sept, *J* = 7.5 Hz, 2H, OSiC*H*$(CH_3)_2$], 1.09 [d, *J* = 7.5 Hz, 6H, OSiCH(C*H*$_3)_2$], 1.06 [d, *J* = 7.5 Hz, 6H, OSiCH(C*H*$_3)_2$], and -0.01 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.8, 157.4, 146.7, 142.8, 139.2, 135.6, 132.5, 131.3, 130.2, 127.7, 122.5, 121.9, 112.9, 107.6, 100.3, 97.9, 72.1, 55.4, 55.3, 25.7, 17.6, 17.2, 13.5, and -0.4.

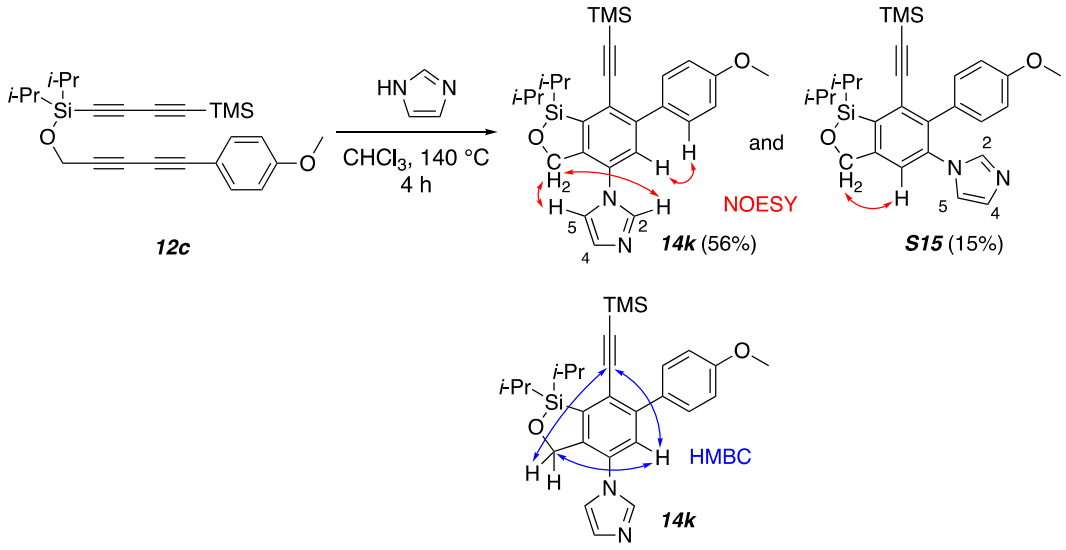
IR (neat) 2955, 2864, 2148 (sharp), 1611, 1514, 1462, 1247, 1223, 1060, 782 and 648 cm $^{-1}$.

HRMS (ESI-Orbitrap) Calc for $[(C_{31}H_{41}O_3Si_2)^+]$ $[(M+H)^+]$ 517.2589; found: 517.2590.

mp 111–113 °C.

1-(1,1-Diisopropyl-6-(4-methoxyphenyl)-7-((trimethylsilyl)ethynyl)-1,3-dihydrobenzo[*c*][1,2]oxasilol-4-yl)-1*H*-imidazole (14k) and

1-(1,1-Diisopropyl-6-(4-methoxyphenyl)-7-((trimethylsilyl)ethynyl)-1,3-dihydrobenzo[*c*][1,2]oxasilol-5-yl)-1*H*-imidazole (*S15*)



Compounds **14k** and ***S15*** were prepared following general procedure C from the tetrayne **12c** (50 mg, 0.12 mmol) and imidazole (40 mg, 0.59 mmol) in $CHCl_3$ (6.0 mL, 0.02 M) at 140 ºC for 3 h. The crude material was purified by passage through a small column of silica gel (10:10:1 hexanes/EtOAc/MeOH) and the residue was purified by medium pressure liquid chromatography (10:10:1 hexanes/EtOAc/MeOH) to give compound **14k** (33 mg, 56%) as a slightly yellow oil that slowly crystallized upon storage in the cold and ***S15*** (9 mg, 15%) as a slightly yellow oil.

Data for compound 14k

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (br s, 1H, Im*H2*), 7.61 (nfod, *J* = 8.7 Hz, 2H, Ar'ArH_o), 7.31 (s, 1H, Ar*H5*), 7.22 (br s, 1H, Im*H4*), 7.14 (br s, 1H, Im*H5*), 6.96 (nfod, *J* = 8.7 Hz, 2H, Ar'ArH_m), 5.05 (s, 2H, SiOCH_2), 3.87 (s, 3H, OCH_3), 1.40 [sept, *J* = 7.5 Hz, 2H, OSiC*H*$(CH_3)_2$], 1.12 [d, *J* = 7.5 Hz, 6H, OSiCH(CH_3)$_2$], 1.09 [d, *J* = 7.5 Hz, 6H, OSiCH(CH_3)$_2$], and 0.16 [s, 9H, Si(CH_3)$_3$].

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.6, 144.3, 142.9, 141.7, 136.9 (br), 132.0 (br), 131.2, 130.6, 130.1, 127.4, 124.2, 119.6 (br), 113.4, 105.6, 99.6, 69.9, 55.4, 17.6, 17.1, 13.5, and -0.5.

IR (neat) 2940, 2863, 2150 (sharp), 1610, 1509, 1462, 1384, 1242, 1153, 1137, 843, 761, 670, and 638 cm^{-1}.

HRMS (ESI-Orbitrap) Calc for [$(C_{28}H_{37}N_2O_2Si_2)^+$] [$(M+H)^+$] 489.2388; found: 489.2386.

mp 130–132 °C.

Data for *S15*

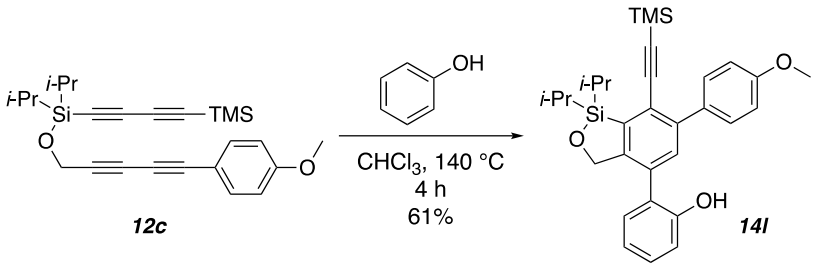
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (br s, 1H, Im*H2*), 7.14 (s, 1H, Ar*H5*), 7.09 (nfod, *J* = 8.6 Hz, 2H, Ar'ArH_o), 6.96 (br s, 1H, Im*H4*), 6.80 (nfod, *J* = 8.6 Hz, 2H, Ar'ArH_m), 6.79 (br s, 1H, Im*H5*), 5.15 (s, 2H, SiOCH_2), 3.79 (s, 3H, OCH_3), 1.37 [sept, *J* = 7.5 Hz, 2H, OSiC*H*$(CH_3)_2$], 1.11 [d, *J* = 7.5 Hz, 6H, OSiCH(CH_3)$_2$], 1.09 [d, *J* = 7.5 Hz, 6H, OSiCH(CH_3)$_2$], and 0.06 [s, 9H, Si(CH_3)$_3$].

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.2, 150.9, 138.4, 137.7, 137.5 (br), 137.4, 130.8, 129.2 (br), 128.04, 127.96, 120.4 (br), 119.0, 113.5, 105.5, 99.8, 71.7, 55.2, 17.6, 17.1, 13.5, and -0.6.

IR (neat) 2955, 2864, 2154, 1610, 1514, 1466, 1248, 1054, 859, 841, 776, 760, 663 and 642 cm^{-1}.

HRMS (ESI-Orbitrap) Calc for [$(C_{28}H_{37}N_2O_2Si_2)^+$] [$(M+H)^+$] 489.2388; found: 489.2395.

2-(1,1-Diisopropyl-6-(4-methoxyphenyl)-7-((trimethylsilyl)ethynyl)-1,3-dihydrobenzo[*c*][1,2]oxasilol-4-yl)phenol (14l)



Compound **14l** was prepared following general procedure C from the tetrayne **12c** (22 mg, 0.056 mmol) and phenol (52 mg, 0.56 mmol) in $CHCl_3$ (2.8 mL, 0.02 M) at 140 ºC for 4 h. The crude material was purified by passage through a small plug of silica gel (10% EtOAc/hexanes) and the residue was purified by medium pressure liquid chromatography (8% EtOAc/hexanes) to give compound **14l** (18 mg, 61%) as yellow foamy crystalline solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (nfod, *J* = 8.7 Hz, 2H, Ar'Ar*H*$_o$), 7.34 (s, 1H, Ar*H5*), 7.28 (ddd, *J* = 7.8, 7.8, 1.7 Hz, 1H, Ar*H4'*), 7.16 (dd, *J* = 7.8, 1.7 Hz, 1H, Ar*H6'*), 7.02–6.95 (m, 2H, Ar*H3'* and Ar*H5'*), 6.94 (nfod, *J* = 8.7 Hz, 2H, Ar'Ar*H*$_m$), 5.05 (br s, 1H, ArO*H*), 4.94 (s, 2H, SiOC*H*$_2$), 3.85 (s, 3H, C*H*$_3$), 1.39 [sept, *J* = 7.5 Hz, 2H, OSiC*H*$(CH_3)_2$], 1.11 [d, *J* = 7.0 Hz, 6H, OSiCH(C*H*$_3$)(CH_3)], 1.09 [d, *J* = 7.0 Hz, 6H, OSiCH(CH_3)(C*H*$_3$)] and 0.16 [s, 9H, Si(C*H*$_3)_3$].

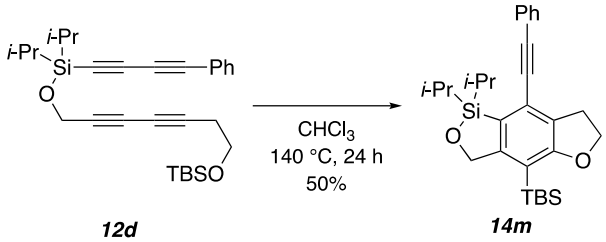
^{13}C NMR (126 MHz, $CDCl_3$) δ 159.2, 152.3, 148.4, 143.0, 139.3, 132.5, 132.1, 131.3, 130.7, 129.9, 129.7, 125.6, 123.9, 120.7, 115.8, 113.2, 106.5, 98.6, 71.4, 55.3, 17.7, 17.2, 13.6, and -0.4.

IR (neat) 3029 (br), 2955, 2865, 2144 (sharp), 1608, 1513, 1247, 1030, 833, 756, 733, and 641 cm $^{-1}$.

HRMS (ESI-Orbitrap) Calc for $[(C_{31}H_{39}O_3Si_2)^+]$ [(M+H$^+$)] 515.2432; found: 515.2422 (major ion). Calc for $[(C_{31}H_{37}O_2Si_2)^+]$ [(M+H$^+$-H_2O)] 497.2327; found: 497.2323 (minor ion).

mp 68–70 °C.

4-(*tert*-Butyldimethylsilyl)-1,1-diisopropyl-8-(phenylethynyl)-1,3,6,7-tetrahydro-[1,2]oxasilolo[3,4-*f*]benzofuran (14m)



12d ***14m***

Compound **14m** was prepared following general procedure C from tetrayne **12d** (40 mg, 0.084 mmol) in $CHCl_3$ (4.0 mL, 0.02 M) at 140 ºC for 24 h. The crude material was purified by passage through a small silica plug (10% EtOAc/hexanes) and the residue was further purified by medium pressure liquid chromatography (2% EtOAc/hexanes) to give compound **14m** (20 mg, 50%) as a slightly yellow crystalline solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50–7.45 (nfom, 2H), 7.39–7.34 (m, 3H), 5.08 (s, 2H, SiOC*H*$_2$), 4.54 (t, *J* = 8.6 Hz, 2H, ArOC*H*$_2$CH$_2$), 3.30 (t, *J* = 8.6 Hz, 2H, ArOCH$_2$C*H*$_2$), 1.32 [sept, *J* = 7.5 Hz, 2H, OSiC*H*(CH$_3$)$_2$], 1.074 [d, *J* = 7.5 Hz, 6H, OSiCH(C*H*$_3$)$_2$], 1.068 [d, *J* = 7.5 Hz, 6H, OSiCH(C*H*$_3$)$_2$], 0.87 [s, 9H, OSi(CH$_3$)$_2$C(C*H*$_3$)$_3$], and 0.34 [s, 6H, OSi(C*H*$_3$)$_2$C(CH$_3$)$_3$].

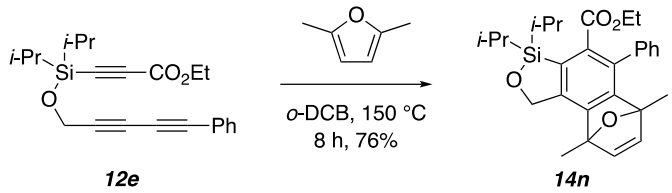
^{13}C NMR (126 MHz, $CDCl_3$) δ 168.1, 158.4, 131.4, 128.46, 128.45, 128.0, 125.0, 123.3, 123.2, 111.6, 92.9, 89.4, 74.4, 70.4, 29.1, 26.7, 18.8, 17.5, 17.1, 13.6, and -2.4.

IR (neat) 2926, 2891, 2861, 1559, 1462, 1380, 1214, 1071, 1005, 865, 840, 822, 812, 777, 754, 689, and 673 cm $^{-1}$.

HRMS (ESI-Orbitrap) Calc for [($C_{29}H_{41}O_2Si_2$)$^+$] [(M+H)$^+$] 477.2640; found: 477.2647.

mp 131–134 °C.

Ethyl 3,3-Diisopropyl-6,9-dimethyl-5-phenyl-1,3,6,9-tetrahydro-6,9-epoxynaphtho[2,1-*c*][1,2]oxasilole-4-carboxylate (14n)



Compound **14n** was prepared following general procedure C from tetrayne **12e** (21 mg, 0.057 mmol) and 2,5-dimethylfuran (0.12 mL, 1.1 mmol) in *o*-DCB (3.0 mL, 0.02 M) at 150 ºC for 8 h. The reaction mixture was purified by flash column chromatography by eluting first with hexanes to remove *o*-DCB and then with 5–15% EtOAc/hexanes to give compound **14n** (20 mg, 76%) as an off-white crystalline solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.32 (m, 3H), 7.28–7.24 (nfom, 1H), 7.05–6.99 (nfom, 1H), 6.82 (d, *J* = 5.3 Hz, 1H, CH_A=CH_B), 6.79 (d, *J* = 5.3 Hz, 1H, CH_A=CH_B), 5.33 (d, *J* = 14.2 Hz, 1H, OSiCH_AH$_B$), 5.11 (d, *J* = 14.1 Hz, 1H, OSiCH$_A$$H_B$), 3.91 (q, *J* = 7.2 Hz, 2H, OCH_2CH$_3$), 1.93 (s, 3H, C9CH_3), 1.37 [sept, *J* = 7.5 Hz, 1H, OSiCH(CH$_3$)$_2$], 1.29 [sept, *J* = 7.5 Hz, 1H, OSiCH(CH$_3$)$_2$], 1.12 (s, 3H, C6CH_3), 1.11 [d, *J* = 7.5 Hz, 3H, OSiCH(CH_3)$_2$], 1.06 [d, *J* = 7.5 Hz, 3H, OSiCH(CH_3)$_2$], 0.89 [d, *J* = 7.5 Hz, 3H, OSiCH(CH_3)$_2$], 0.84 [d, *J* = 7.4 Hz, 3H, OSiCH(CH_3)$_2$], and 0.76 (t, *J* = 7.1 Hz, 3H, OCH$_2$CH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.1, 154.1, 149.0, 147.5, 146.5, 140.7, 139.5, 136.9, 134.4, 131.3, 129.8, 128.5, 127.4, 127.3, 127.0, 90.6, 88.4, 69.0, 60.8, 18.2, 18.1, 17.62, 17.60, 17.0, 16.7, 14.0, 13.5, and 13.3.

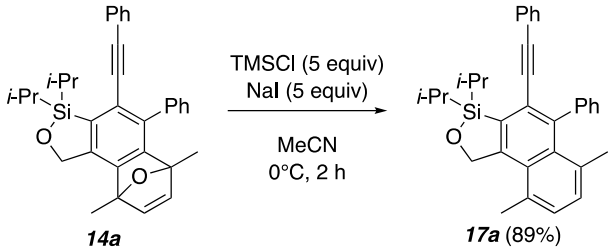
IR (neat) 2940, 2863, 1678, 1465, 1375, 1297, 1234, 1072, 1026, 862, and 649 cm $^{-1}$.

HRMS (ESI-Orbitrap) Calc for [($C_{28}H_{35}O_4Si$)$^+$] [(M+H)$^+$] 463.2299; found: 463.2302.

mp 160–162 °C.

(d) Products (17a–e) obtained from deoxygenation reactions

3,3-Diisopropyl-6,9-dimethyl-5-phenyl-4-(phenylethynyl)-1,3-dihydronaphtho[2,1-*c*][1,2]oxasilole (17a)



Compound **17a** was prepared following general procedure D from the benzoxanorbornadiene **14a** (57 mg, 0.12 mmol), NaI (87 mg, 0.58 mmol), and TMSCl (70 μL, 0.58 mmol) in MeCN (4.6 mL, 0.03 M) at 0 ºC for 2 h. The crude material was purified by passage through a small silica plug (10% EtOAc/hexanes) and the residue was further purified by medium pressure liquid chromatography (3% EtOAc/hexanes) to give compound **17a** (51 mg, 89%) as a foamy off-white crystalline solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47–7.42 (m, 3H), 7.42–7.38 (m, 2H), 7.25–7.22 (m, 3H), 7.20 (d, *J* = 7.3 Hz, 1H, *H7* or *H8*), 7.12 (d, *J* = 7.3 Hz, 1H, *H7* or *H8*), 7.08–7.03 (m, 2H), 5.83 (s, 2H), 2.80 (s, 3H, C9C*H*$_3$), 1.93 (s, 3H, C6CH_3), 1.45 [sept, *J* = 7.5 Hz, 2H, OSiC*H*(CH_3)$_2$], 1.15 [d, *J* = 7.5 Hz, 6H, OSiCH(C*H*$_3$)$_2$], and 1.09 [d, *J* = 7.5 Hz, 6H, OSiCH(C*H*$_3$)$_2$].

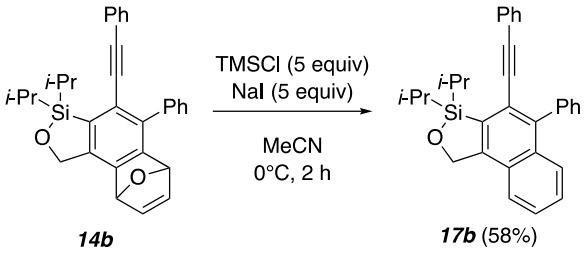
^{13}C NMR (126 MHz, $CDCl_3$) δ 149.6, 143.9, 142.8, 134.7, 134.1, 132.9, 132.0, 131.2, 130.88, 130.86, 130.0, 128.2, 128.0, 127.4, 126.9, 123.50, 123.48, 93.9, 92.2, 75.2, 26.0, 24.9, 17.7, 17.2, and 13.6. (one quaternized aromatic carbon resonance not observed)

IR (neat) 3057, 3025, 2940, 2863, 1596, 1491, 1457, 1445, 1070, 881, 792, 754, 700, 689, 670, and 653 cm $^{-1}$.

HRMS (ESI-Orbitrap) Calc for [($C_{33}H_{35}OSi$)$^+$] [(M+H)$^+$] 475.2452; found: 475.2454.

mp 47–50 °C.

3,3-Diisopropyl-5-phenyl-4-(phenylethynyl)-1,3-dihydronaphtho[2,1-*c*][1,2]oxasilole (17b)



14b ***17b*** (58%)

Compound **17b** was prepared following general procedure D from the benzoxanorbornadiene **14b** (16 mg, 0.035 mmol), NaI (26 mg, 0.17 mmol), and TMSCl (22 μL, 0.17 mmol) in MeCN (1.5 mL, 0.03 M) at 0 ºC for 2 h. The crude material was purified by flash chromatography (5 to 10% EtOAc/hexanes) to give compound **17b** (9 mg, 58%) as a yellow oil.

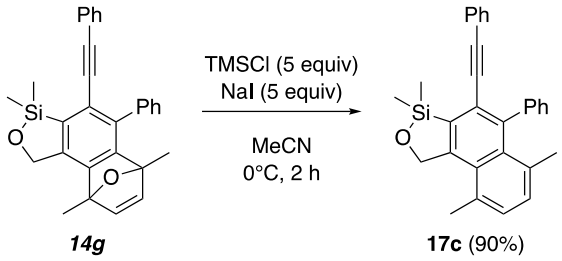
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.9 Hz, 1H, *H6* or *H9*), 7.72 (d, *J* = 7.9 Hz, 1H, *H6* or *H9*), 7.58–7.52 (m, 3H), 7.52–7.49 (m, 3H), 7.46 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H, *H7* or *H8*), 7.26–7.23 (overlapping m, 3H), 7.13–7.09 (m, 2H), 5.62 (s, 2H, SiOCH_2), 1.45 [sept, *J* = 7.5 Hz, 2H, OSiC*H*$(CH_3)_2$], 1.15 [d, *J* = 7.5 Hz, 6H, OSiCH(CH_3)$_2$], and 1.13 [d, *J* = 7.5 Hz, 6H, OSiCH(CH_3)$_2$].

^{13}C NMR (126 MHz, $CDCl_3$) δ 147.8, 142.5, 139.2, 133.1, 132.2, 131.2, 130.9, 128.3, 128.1, 128.0, 127.6, 127.5, 127.4, 127.0, 126.6, 123.4, 123.0, 121.5, 93.2, 91.9, 71.8, 17.6, 17.2, and 13.6.

IR (neat) 3058, 3022, 2941, 2862, 1596, 1492, 1461, 1442, 1075, 1048, 1029, 881, 779, 754, 700, 688, 667, and 648 cm $^{-1}$.

HRMS (ESI-Orbitrap) Calc for [$(C_{31}H_{31}OSi)^+$] [$(M+H)^+$] 447.2139; found: 447.2143.

3,3,6,9-Tetramethyl-5-phenyl-4-(phenylethynyl)-1,3-dihydronaphtho[2,1-*c*][1,2]oxasilole (17c)



14g **17c** (90%)

Compound **17c** was prepared following general procedure D from the benzoxanorbornadiene **14g** (142 mg, 0.327 mmol), NaI (244 mg, 1.63 mmol), and TMSCl (0.21 mL, 1.63 mmol) in MeCN (11 mL, 0.03 M) at 0 ºC for 2 h. The crude material was purified by flash chromatography (5 to 10% EtOAc/hexanes) to give compound **17c** (125 mg, 90%) as a slightly yellow crystalline solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47–7.38 (m, 5H), 7.27–7.23 (overlapping with $CDCl_3$, ca. 3H), 7.20 (br d, *J* = 7.2 Hz, 1H, *H7* or *H8*), 7.13–7.09 (m, 3H), 5.85 (s, 2H, SiOC*H*$_2$), 2.80 (s, 3H, C9C*H*$_3$), 1.93 (s, 3H, C6C*H*$_3$), and 0.57 [s, 6H, OSi(C*H*$_3$)$_2$].

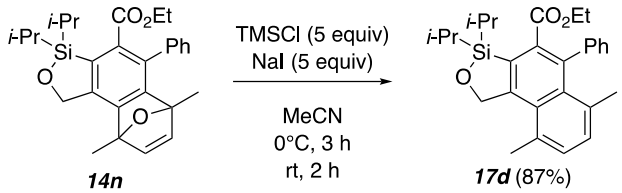
^{13}C NMR (126 MHz, $CDCl_3$) δ 148.4, 143.6, 142.4, 134.8, 134.21, 134.16, 132.9, 131.1, 130.9, 130.9, 130.7, 130.0, 128.3, 128.1, 127.5, 127.0, 123.4, 123.2, 94.2, 90.9, 74.4, 25.9, 24.7, and 0.5.

IR (neat) 3056, 3028, 2966, 2926, 1598, 1487, 1445, 1243, 1060, 1049, 833, 784, 745, 702, 683, and 665 cm $^{-1}$.

HRMS (ESI-Orbitrap) Calc for [($C_{29}H_{27}OSi)^+$] [$(M+H)^+$] 419.1826; found: 419.1814.

mp 205–206 °C.

Ethyl 3,3-Diisopropyl-6,9-dimethyl-5-phenyl-1,3-dihydronaphtho[2,1-*c*][1,2]oxasilole-4-carboxylate (17d)



Compound **17d** was prepared following general procedure D from the benzoxanorbornadiene **14n** (19 mg, 0.041 mmol), NaI (31 mg, 0.21 mmol), and TMSCl (30 μL, 0.24 mmol) in MeCN (2 mL, 0.03 M) at 0 ºC for 3 h and at rt for 2 h. The crude material was purified by passage through a small silica plug (10% EtOAc/hexanes) and the residue was further purified by medium pressure liquid chromatography (5% EtOAc/hexanes) to give compound **17d** (16 mg, 87%) as a clear colorless oil.

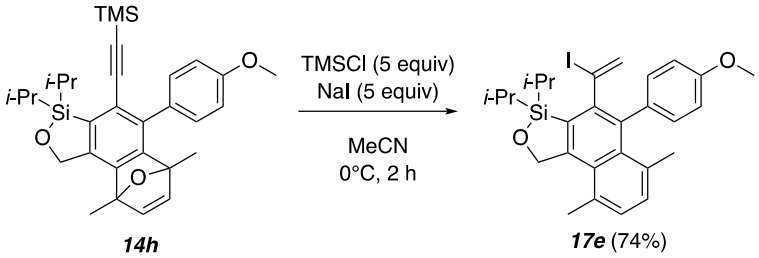
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.31 (m, 3H), 7.31–7.27 (m, 2H), 7.24 (d, *J* = 7.4 Hz, 1H, *H7* or *H8*), 7.12 (d, *J* = 7.4 Hz, 1H, *H7* or *H8*), 5.79 (s, 2H, SiOC*H*$_2$), 3.86 (q, *J* = 7.1 Hz, 2H, OC*H*$_2$CH$_3$), 2.79 (s, 3H, C9C*H*$_3$), 1.85 (s, 3H, C6C*H*$_3$), 1.33 [sept, *J* = 7.4 Hz, 2H, OSiC*H*(CH$_3$)$_2$], 1.11 [d, *J* = 7.4 Hz, 6H, OSiCH(C*H*$_3$)$_2$], 0.90 [d, *J* = 7.4 Hz, 6H, OSiCH(C*H*$_3$)$_2$], and 0.79 (t, *J* = 7.1 Hz, 3H, OCH$_2$C*H*$_3$).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.7, 150.0, 142.9, 139.0, 135.9, 134.3, 132.9, 132.7, 132.4, 131.1, 130.63, 130.55, 129.8, 127.3, 127.1, 74.6, 61.0, 25.7, 24.8, 17.9, 17.5, 13.9, and 13.5.

IR (neat) 3059, 3025, 2937, 2863, 1702, 1591, 1458, 1377, 1348, 1320, 1240, 1179, 1074, 1026, 880, 822, 702, 673, and 648 cm $^{-1}$.

HRMS (ESI-Orbitrap) Calc for [($C_{28}H_{35}O_3Si$)$^+$] [(M+H)$^+$] 447.2350; found: 447.2352.

4-(1-Iodovinyl)-3,3-diisopropyl-5-(4-methoxyphenyl)-6,9-dimethyl-1,3-dihydronaphtho[2,1-*c*][1,2]oxasilole (17e)



Compound **17e** was prepared following general procedure D from the benzoxanorbornadiene **14h** (57 mg, 0.11 mmol), NaI (82 mg, 0.55 mmol), and TMSCl (80 μL, 0.55 mmol) in MeCN (3.5 mL, 0.03 M) at 0 ºC for 2 h. The crude material was purified by passage through a small silica plug (10% EtOAc/hexanes) and the residue was further purified by medium pressure liquid chromatography (2% EtOAc/hexanes) to give compound **17e** (40 mg, 74%) as a tan-yellow crystalline solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (dd, *J* = 8.4, 2.3 Hz, 1H, Ar'ArH_o), 7.18 (d, *J* = 7.3 Hz, 1H, *H7* or *H8*), 7.13 (dd, *J* = 8.4, 2.3 Hz, 1H, Ar'ArH_o'), 7.09 (d, *J* = 7.3 Hz, 1H, *H7* or *H8*), 6.93 (dd, *J* = 8.4, 2.7 Hz, 1H, Ar'ArH_m), 6.88 (dd, *J* = 8.4, 2.7 Hz, 1H, Ar'ArH_m'), 6.16 (d, *J* = 1.0 Hz, 1H, =CH_AH$_B$), 6.00 (d, *J* = 1.0 Hz, 1H, =CH$_A$$H_B$), 5.88 (d, *J* = 14.6 Hz, 1H, SiOCH_AH$_B$), 5.73 (d, *J* = 14.6 Hz, 1H, SiOCH$_A$$H_B$), 3.89 (s, 6H, ArOC$H_3$), 2.78 (s, 3H, C9C$H_3$), 1.88 (s, 3H, C6C$H_3$), 1.57 [sept, *J* = 7.5 Hz, 1H, OSiC*H*(CH$_3$)$_2$], 1.24 [d, *J* = 7.5 Hz, 3H, OSiCH(CH_3)$_2$], 1.22 (sept, *J* = 7.5 Hz, 1H, OSiC'*H*(CH$_3$)$_2$], 1.11 [d, *J* = 7.5 Hz, 3H, OSiCH(CH_3)$_2$], 1.09 [d, *J* = 7.5 Hz, 3H, OSiCH(CH_3)$_2$], and 0.89 [d, *J* = 7.5 Hz, 3H, OSiCH(CH_3)$_2$].

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.8, 149.9, 142.3, 136.8, 135.3, 135.2, 133.9, 133.8, 132.7, 132.0, 131.2, 130.9, 130.1, 129.9, 129.6, 112.8, 112.7, 109.0, 75.0, 55.2, 25.6, 25.1, 17.8, 17.6, 17.4, 17.3, 14.3, and 14.1.

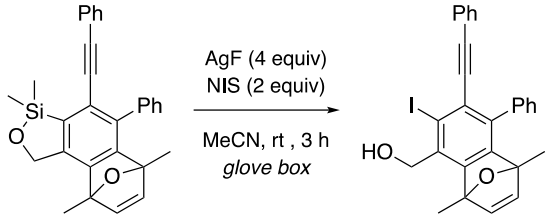
IR (neat) 2926, 2863, 1608, 1510, 1443, 1285, 1242, 1172, 1063, 1032, 904, 880, 837, 823, 792, 775, 651, and 633 cm $^{-1}$.

HRMS (ESI-Orbitrap) Calc for [($C_{28}H_{34}IO_2Si$)$^+$] [(M+H)$^+$] 557.1367; found: 557.1373.

mp 149–152 °C.

(e) Products (18–25) obtained from functionalization of C–Si bonds

(6-Iodo-1,4-dimethyl-8-phenyl-7-(phenylethynyl)-1,4-dihydro-1,4-epoxynaphthalen-5-yl)methanol (18a)



14g ***18a*** (58%)

Compound **18a** was prepared following general procedure E from the benzoxanorbornadiene derivative **14g** (15 mg, 0.035 mmol), AgF (18 mg, 0.14 mmol), and NIS (16 mg, 0.071 mmol) in MeCN (0.5 mL) at rt for 3 h. The crude material was purified by passage through a silica gel plug (40% EtOAc/hexanes) and the residue was further purified by medium pressure liquid chromatography (40% EtOAc/hexanes) to give compound **18a** (10 mg, 58%) as an off-white crystalline solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49–7.46 (m, 2H), 7.45–7.39 (nfom, 2H), 7.25–7.19 (m, 3H), 7.13–7.09 (nfodd, *J* = 7.7. 1.6 Hz, 2H, ≡CPhH_o), 7.01–6.97 (br d, *J* = 7.6 Hz, 1H, PhH_o'), 6.82 (d, *J* = 5.3 Hz, 1H, CH_A=CH_B), 6.76 (d, *J* = 5.3 Hz, 1H, CH_A=CH_B), 4.97 (d, *J* = 6.7 Hz, 2H, ArCH_2OH), 2.12 (s, 3H, C4CH_3), 2.02 (t, *J* = 6.7 Hz, 1H, ArCH$_2$O*H*), and 1.20 (s, 3H, C1CH_3).

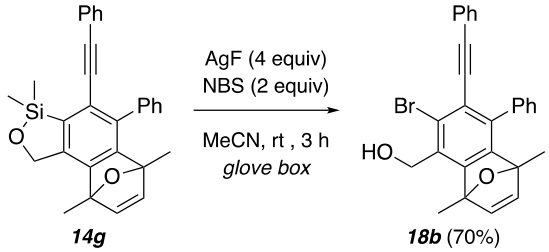
^{13}C NMR (126 MHz, $CDCl_3$) δ 152.5, 151.3, 146.9, 146.8, 138.3, 137.6, 134.9, 131.2, 130.2, 128.8, 128.5, 128.4, 128.2, 127.88, 127.91, 127.8, 123.0, 105.4, 96.8, 92.6, 89.9, 89.3, 66.1, 17.7, and 16.9.

IR (neat) 3401 (br), 3055, 2977, 2934, 2211, 1490, 1442, 1131, 1016, 862, 755, 735, 702 and 689 cm $^{-1}$.

HRMS (ESI-Orbitrap) Calc for [($C_{27}H_{20}IO)^+$] [(M+H^+-H_2O)] 487.0553; found: 487.0543.

mp 189–191 °C.

(6-Bromo-1,4-dimethyl-8-phenyl-7-(phenylethynyl)-1,4-dihydro-1,4-epoxynaphthalen-5-yl)methanol (18b)



14g ***18b*** (70%)

Compound **18b** was prepared following general procedure E from the benzoxanorbornadiene derivative **14g** (18 mg, 0.041 mmol), AgF (18 mg, 0.17 mmol), and NBS (15 mg, 0.084 mmol) in MeCN (0.5 mL) at rt for 3 h. The crude material was purified by passage through a silica gel plug (40% EtOAc/hexanes) and the residue was further purified by medium pressure liquid chromatography (40% EtOAc/hexanes) to give compound **18b** (13 mg, 70%) as light crystalline yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51–7.38 (m, 4H), 7.25–7.19 (m, 3H), 7.09 (d, *J* = 7.2 Hz, 2H, ≡CPhH_o), 7.00 (br d, *J* = 6.9 Hz, 1H, PhH_o'), 6.83 (d, *J* = 5.3 Hz, 1H, CH_A=CH_B), 6.77 (d, *J* = 5.3 Hz, 1H, CH_A=CH_B), 4.99 (dd, *J* = 12.5, 6.0 Hz, ArCH_AH$_B$OH), 4.95 (dd, *J* = 12.5, 7.0 Hz, ArCH$_A$$H_B$OH), 2.12 (s, 3H, C4C$H_3$), 2.03–1.95 (m, 1H, CH$_AH_B$O*H*), and 1.21 (s, 3H, C1CH_3).

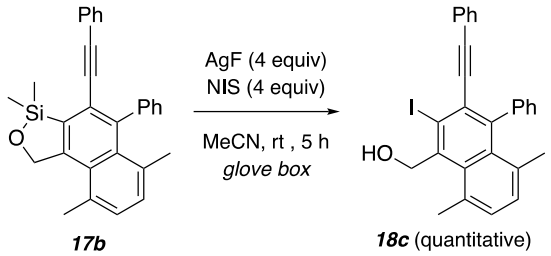
^{13}C NMR (126 MHz, $CDCl_3$) δ 153.1, 150.1, 146.9, 146.8, 137.93, 137.88, 132.0, 131.4, 130.2, 128.9, 128.4, 128.1, 127.93, 127.91, 127.8, 125.3, 123.4, 123.0, 97.6, 89.9, 89.3, 88.5, 61.1, 17.6, and 16.9.

IR (neat) 3434 (br), 3056, 2978, 2932, 1490, 1443, 1381, 1132, 1025, 862, 809, 757, 732, 702, and 682 cm $^{-1}$.

HRMS (ESI-Orbitrap) Calc for [($C_{27}H_{21}{}^{79}BrO)^+$] [(M+$H^+$-$H_2O$)] 439.0692; found: 439.0681.

mp 174–177 °C.

(2-Iodo-5,8-dimethyl-4-phenyl-3-(phenylethynyl)naphthalen-1-yl)methanol (18c)



17b ***18c*** (quantitative)

Compound **18c** was prepared following general procedure E from the naphthalene derivative **17b** (20 mg, 0.048 mmol), AgF (24 mg, 0.19 mmol), and NIS (43 mg, 0.19 mmol) in MeCN (1.0 mL) at rt for 6 h. The crude material was purified by passage through a silica gel plug (CH_2Cl_2 as eluent) and the residue was further purified by medium pressure liquid chromatography (10% EtOAc/hexanes) to give compound **18c** (23 mg, quantitative) as an off-white crystalline solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45–7.41 (m, 3H), 7.36–7.31 (m, 2H), 7.27 (d, *J* = 7.1 Hz, 1H, *H7*), 7.26–7.21 (m, overlapped with $CDCl_3$, ca. 3H), 7.17–7.12 (m, 2H), 7.10 (d, *J* = 7.1 Hz, 1H, *H6*), 5.18 (d, *J* = 7.2 Hz, 2H, ArC*H*$_2$OH), 2.97 (s, 3H, C8C*H*$_3$), 2.80 (t, *J* = 7.2 Hz, 1H, ArCH$_2$O*H*), and 1.84 (s, 3H, C5C*H*$_3$).

^{13}C NMR (126 MHz, $CDCl_3$) δ 144.4, 143.5, 139.5, 136.1, 134.2, 133.1, 132.6, 131.2, 131.0, 130.6, 130.4, 128.3, 128.1, 127.7, 127.5, 127.3, 123.2, 109.5, 97.8, 93.5, 69.1, 25.1, and 24.4.

IR (neat) 3364 (br), 3051, 2959, 2927, 1596, 1488, 1467, 1442, 1126, 1068, 1026, 1013, 998, 826, 755, 740, 704, and 689 cm $^{-1}$.

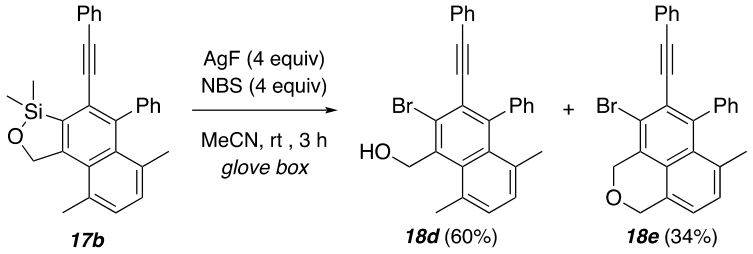
HRMS (ESI-Orbitrap) Calc for [($C_{27}H_{20}I)^+$] [(M+H^+-H_2O)] 471.0604; found: 471.0590.

mp 163–165 °C.

(2-Bromo-5,8-dimethyl-4-phenyl-3-(phenylethynyl)naphthalen-1-yl)methanol (18d)

and

4-Bromo-7-methyl-6-phenyl-5-(phenylethynyl)-1*H*,3*H*-benzo[*de*]isochromene (18e)



Compounds **18d** and **18e** were prepared following general procedure E from the naphthalene derivative **17b** (22 mg, 0.053 mmol), AgF (27 mg, 0.21 mmol), and NBS (37 mg, 0.21 mmol) in MeCN (0.70 mL) at rt for 3 h. The crude material was purified by passage through a silica gel plug (CH_2Cl_2 as eluent) and the residue was purified by medium pressure liquid chromatography (10% EtOAc/hexanes) to give **18e** (8 mg, 34%) as a yellow crystalline solid followed by compound **18d** (14 mg, 60%) as a yellow crystalline solid.

Data for compound 18d

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46–7.40 (m, 3H), 7.37–7.32 (m, 2H), 7.28 (d, *J* = 7.2 Hz, 1H, *H7*), 7.25–7.21 (m, 3H), 7.15–7.11 (m, 2H), 7.10 (d, *J* = 7.3 Hz, 1H, *H6*), 5.21 (s, 2H, ArC*H*$_2$OH), 2.99 (s, 3H, C8C*H*$_3$), 2.64 (br s, 1H, ArCH$_2$O*H*), and 1.85 (s, 3H, C5C*H*$_3$).

^{13}C NMR (126 MHz, $CDCl_3$) δ 145.3, 143.1, 135.9, 135.6, 134.3, 132.7, 132.5, 131.4, 131.2, 130.6, 130.3, 128.3, 128.1, 127.9, 127.7, 127.5, 123.6, 123.2, 98.4, 89.3, 64.1, 25.2, and 24.2.

IR (neat) 3357 (br), 3053, 3020, 2925, 1596, 1489, 1470, 1442, 1323, 1128, 1026, 1013, 998, 976, 904, 755, 738, 704 and 688 cm $^{-1}$.

HRMS (ESI-Orbitrap) Calc for [($C_{27}H_{20}Br)^+$] [(M+H^+-H_2O)] 423.0743; found: 423.0736.

mp 105–107 °C.

Data for compound 18e

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50–7.44 (m, 3H), 7.40–7.34 (m, 2H), 7.25–7.20 (m, 3H), 7.19 (d, *J* = 7.1 Hz, 1H, *H8*), 7.12 (d, *J* = 7.1 Hz, 1H, *H9*), 7.11–7.07 (m, 2H), 5.16 (s, 2H, OC*H*$_2$Ar), 5.01 (s, 2H, OC*H*$_2$Ar), and 1.94 (s, 3H, C7C*H*$_3$).

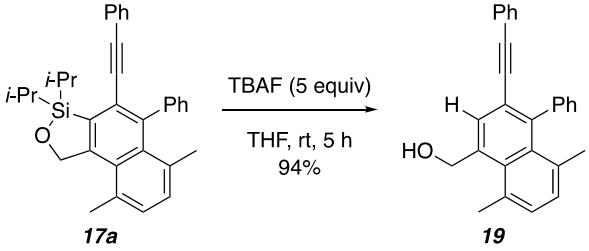
^{13}C NMR (126 MHz, $CDCl_3$) δ 143.7, 143.0, 135.1, 131.8, 131.5, 130.4, 130.1, 129.8, 129.7, 128.6, 128.3, 128.1, 127.7, 127.5, 124.2, 123.1, 121.7, 118.2, 99.1, 88.9, 70.7, 69.3, and 25.2.

IR (neat) 3055, 3025, 2965, 2932, 2822, 2210, 1597, 1450, 1443, 1111, 1065, 1030, 836, 815, 755, 735, 703, and 689 cm^{-1}.

HRMS (ESI-Orbitrap) Calc for [($C_{27}H_{20}BrO)^+$] [$(M+H)^+$] 439.0692; found: 439.0687.

mp 103–106 °C.

(5,8-Dimethyl-4-phenyl-3-(phenylethynyl)naphthalen-1-yl)methanol (19)



17a *19*

To a solution of the naphthalene derivative **17a** (17 mg, 0.036 mmol) in THF (0.2 mL) was added TBAF (1.0M solution in THF, 0.18 mL, 0.18 mmol) at rt under N_2. After 5 h, saturated aqueous NH_4Cl solution was added to the reaction mixture and extracted with Et_2O. The organic extracts were combined, washed with brine, dried with $MgSO_4$, and concentrated under reduced pressure. The crude material was purified by passage through a silica gel plug (30% EtOAc/hexanes) and the residue was further purified by medium pressure liquid chromatography (30% EtOAc/hexanes) to give compound **19** (12 mg, 94%) as a white crystalline solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.45–7.41 (m, 3H), 7.40–7.35 (nfom, 2H), 7.25–7.21 (m, 4H), 7.15–7.11 (nfom, 2H), 7.11 (d, *J* = 7.2 Hz, 1H, *H6*), 5.25 (d, *J* = 5.8 Hz, 2H, C*H*$_2$OH), 2.97 (s, 3H, C8C*H*$_3$), 1.91 (s, 3H, C5C*H*$_3$), and 1.73 (t, *J* = 6.0 Hz, 1H, CH$_2$O*H*).

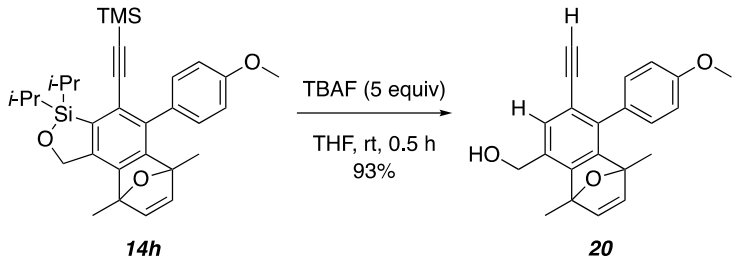
^{13}C NMR (126 MHz, $CDCl_3$) δ 143.9, 143.4, 137.5, 134.8, 133.8, 133.0, 132.9, 131.4, 130.7, 130.6, 130.3, 130.0, 128.1, 128.0, 127.5, 127.1, 123.4, 121.4, 93.8, 89.9, 66.4, 25.8, and 24.6.

IR (neat) 3288 (br), 2931, 2866, 2205, 1596, 1489, 1458, 1442, 1024, 1010, 824, 753, 701, and 688 cm $^{-1}$.

HRMS (ESI-Orbitrap) Calc for [$(C_{27}H_{21})^+$] [$(M\text{-}OH)^+$] 345.1638; found: 345.1640.

mp 184–185 °C.

(7-Ethynyl-8-(4-methoxyphenyl)-1,4-dimethyl-1,4-dihydro-1,4-epoxynaphthalen-5-yl)methanol (20)



To a solution of the benzoxanorbornadiene derivative **14h** (22 mg, 0.042 mmol) in THF (0.5 mL) was added TBAF (1.0M solution in THF, 0.21 mL, 0.21 mmol) at rt under N_2. After 0.5 h, saturated aqueous NH_4Cl solution was added and the resulting mixture was extracted Et_2O. The organic extracts were combined, washed with brine, dried with $MgSO_4$, and concentrated under reduced pressure. The crude material was purified by flash chromatography (40% to 50% EtOAc/hexanes) to give compound **20** (13 mg, 93%) as a white crystalline solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 8.4, 2.2 Hz, 1H, ArPh*H*$_o$), 7.22 (s, 1H, *H6*), 6.96 (dd, *J* = 8.5, 2.6 Hz, 1H, ArPh*Ho'*), 6.93 (dd, *J* = 8.3, 2.6 Hz, 1H, MeOPh*H*$_o$), 6.87 (dd, *J* = 8.3, 2.2 Hz, 1H, MeOPh*H*$_{o'}$), 6.83 (d, *J* = 5.3 Hz, 1H, C*H*=CH), 6.78 (d, *J* = 5.3 Hz, 1H, CH=C*H*), 4.86 (dd, *J* = 12.6, 5.1 Hz, 1H, SiOC*H*$_A$H$_B$), 4.65 (br d, *J* = 12.6 Hz, 1H, SiOCH$_A$*H*$_B$) 3.86 (s, 3H, ArOC*H*$_3$), 2.85 (s, 1H, C≡C–*H*), 2.07 (s, 3H, C1C*H*$_3$), 1.67–1.55 (br s, 1H, C*H*$_2$O*H*), and 1.24 (s, 3H, C4C*H*$_3$).

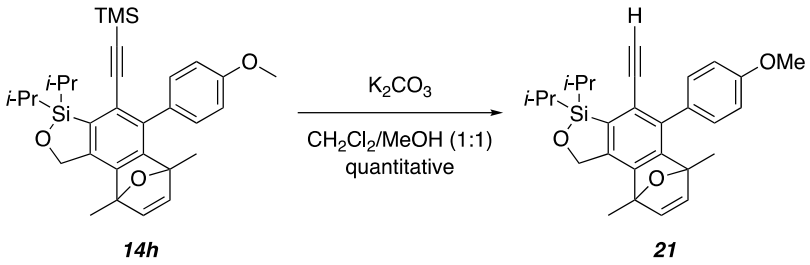
^{13}C NMR (126 MHz, $CDCl_3$) δ 159.2, 151.7, 151.4, 147.1, 146.9, 136.6, 131.8, 131.2, 130.9, 130.0, 129.8, 119.8, 113.23, 113.18, 89.6, 89.3, 82.6, 79.6, 62.0, 55.2, 17.1, and 16.9.

IR (neat) 3444 (br), 3274 (sharp), 2973, 2934, 2869, 2838, 1612, 1515, 1452, 1439, 1244, 1182, 1131, 1033, 1022, 859, 830, 723, 654, and 627 cm $^{-1}$.

HRMS (ESI-Orbitrap) Calc for [$(C_{22}H_{19}O_2)^+$] [(M+H^+-H_2O)] 315.1380; found: 315.1387. Calc for [$(C_{22}H_{21}O_3)^+$] [(M+H)$^+$] 333.1485; found: 333.1491.

mp 181–183 °C.

4-Ethynyl-3,3-diisopropyl-5-(4-methoxyphenyl)-6,9-dimethyl-1,3,6,9-tetrahydro-6,9-epoxynaphtho[2,1-*c*][1,2]oxasilole (21)



14h ***21***

To a solution of the benzoxanorbornadiene derivative **14h** (20 mg, 0.039 mmol) in CH_2Cl_2/MeOH (1:1 v/v, 0.6 mL) was added K_2CO_3 (18 mg, 0.12 mmol) at rt. After being stirred at rt for 17 h, the reaction mixture was quenched by the addition of saturated aqueous NH_4Cl solution. The resulting mixture was extracted with CH_2Cl_2. The organic extracts were combined, washed with brine, dried with $MgSO_4$, and concentrated under reduced pressure. The crude material was purified by passage through a silica gel plug (30% EtOAc/hexanes) and the residue was further purified by medium pressure liquid chromatography (20% EtOAc/hexanes) to give compound **21** (17 mg, quantitative) as a white crystalline solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.3 Hz, 1H, ArPhH_o), 6.96 (d, *J* = 8.5 Hz, 1H, MeOPhH_o), 6.94–6.89 (m, 2H, MeOPh$H_{o'}$ and ArPh$H_{o'}$), 6.82 (d, *J* = ca. 5.5 Hz, 1H, C*H*=CH), 6.81 (d, *J* = ca. 5.5 Hz, 1H, CH=C*H*), 5.31 (d, *J* = 14.1 Hz, 1H, SiOCH_ACH$_B$), 5.10 (dd, *J* = 13.9, Hz, 1H, SiOCH$_A$CH_B), 3.87 (s, 3H, ArOCH_3), 2.87 (s, 1H, C≡C–*H*), 1.91 (s, 3H, C9CH_3), 1.39–1.28 [m, 2H, OSiC*H*$(CH_3)_2$], 1.25 (s, 3H, C6CH_3), 1.08 [two overlapped d's, *J* = 7.5 Hz, 6H, OSiCH(C$H_3)_2$], 1.05 [d, *J* = 7.5 Hz, 3H, OSiCH(C$H_3)_2$], and 0.99 [d, *J* = 7.5 Hz, 3H, OSiCH(C$H_3)_2$].

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.1, 153.0, 146.9, 146.7, 145.6, 140.3, 136.5, 136.3, 131.4, 130.3, 130.2, 122.8, 113.2, 113.1, 90.3, 88.5, 84.8, 80.2, 69.6, 55.2, 17.64, 17.59, 17.2, 17.1, 17.0, 16.8, 13.5, and 13.2.

IR (neat) 3292 (sharp), 2937, 2864, 1610, 1509, 1461, 1384, 1243, 1052, 1035, 834, 782, 766, 735, 699, 663, 639, and 609 cm $^{-1}$.

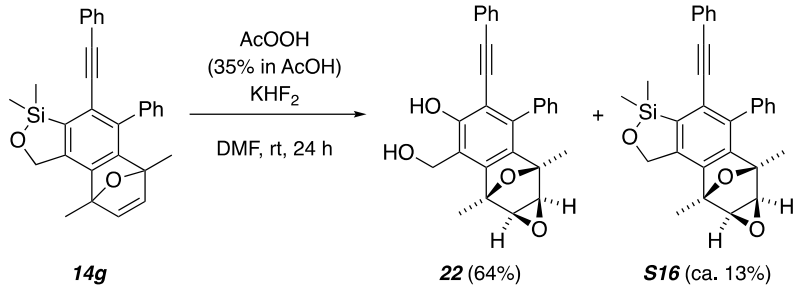
HRMS (ESI-Orbitrap) Calc for $[(C_{28}H_{33}O_3Si)^+]$ $[(M+H)^+]$ 445.2193; found: 445.2182.

mp 149–151 °C.

(±)-(1a*R*,2*S*,7*R*,7a*S*)-3-(Hydroxymethyl)-2,7-dimethyl-6-phenyl-5-(phenylethynyl)-1a,2,7,7a-tetrahydro-2,7-epoxynaphtho[2,3-*b*]oxiren-4-ol (22)

and

(±) (6*R*,6a*S*,7a*R*,8*S*)-3,3,6,8-tetramethyl-5-phenyl-4-(phenylethynyl)-1,3,6,6a,7a,8-hexahydro-6,8-epoxyoxireno[2',3':6,7]naphtho[2,1-*c*][1,2]oxasilole (*S16*)



14g ***22*** (64%) ***S16*** (ca. 13%)

To a solution of the benzoxanorbornadiene derivative **14g** (20 mg, 0.046 mmol) in DMF (0.5 mL) was added AcOOH (35% in AcOH, 0.10 mL, 0.52 mmol) and KHF_2 (7 mg, 0.092 mmol). The resulting solution was stirred at rt for 24 h. 5% Aqueous $NaHCO_3$ solution was added and the resulting mixture was extracted with Et_2O. The organic extracts were combined, washed with brine, dried with $MgSO_4$, and concentrated under reduced pressure. The crude material was purified by passage through a silica gel plug (50% EtOAc/hexanes) and the residue was further purified by medium pressure liquid chromatography (50% EtOAc/hexanes) to give compound **22** (12 mg, 64%) as a yellow crystalline solid. A small amount of a second compound, the epoxide ***S16***, was isolated in a faster eluting fraction. It was resubjected to the original reaction conditions described above and observed to give rise to the Tamao-Fleming product **22** (^{1}H NMR).

Data for 22

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49–7.41 (m, 4H), 7.31–7.21 (m, overlapped with $CDCl_3$, ca. 3H), 7.15 (dd, *J* = 7.9, 1.4 Hz, 2H, ≡CPh*H*$_o$), 7.13–7.10 (m, 1H), 6.45 (s, 1H, ArO*H*), 5.01 (d, *J* = 12.3 Hz, 1H, ArC*H*$_A$CH$_B$OH), 4.84 (br d, *J* = 12.3 Hz, 1H, ArCH$_A$C*H*$_B$OH), 3.52 (d, *J* = 3.5 Hz, 1H, C*H*$_A$OCH$_B$), 3.42 (d, *J* = 3.5 Hz, 1H, CH$_A$OC*H*$_B$), 2.21 (br s, ArCH$_A$CH$_B$O*H*), 2.01 (s, 3H, C2C*H*$_3$), and 1.16 (s, 3H, C7C*H*$_3$).

^{13}C NMR (126 MHz, $CDCl_3$) δ 154.1, 149.1, 138.9, 138.0, 137.3, 131.2, 129.9, 128.74, 128.69, 128.4, 128.1, 128.0, 127.9, 122.2, 121.0, 108.4, 100.0, 84.1, 83.6, 82.5, 59.3, 59.0, 55.9, 15.7, and 15.2.

IR (neat) 3391 (br), 3056, 2892, 2935, 1592, 1490, 1444, 1384, 1265, 1136, 1014, 968, 900, 870, 756, 735, and 690 cm $^{-1}$.

HRMS (ESI-Orbitrap) Calc for $[(C_{27}H_{21}O_3)^+]$ $[(M+H^+-H_2O)]$ 393.1485; found: 393.1480.

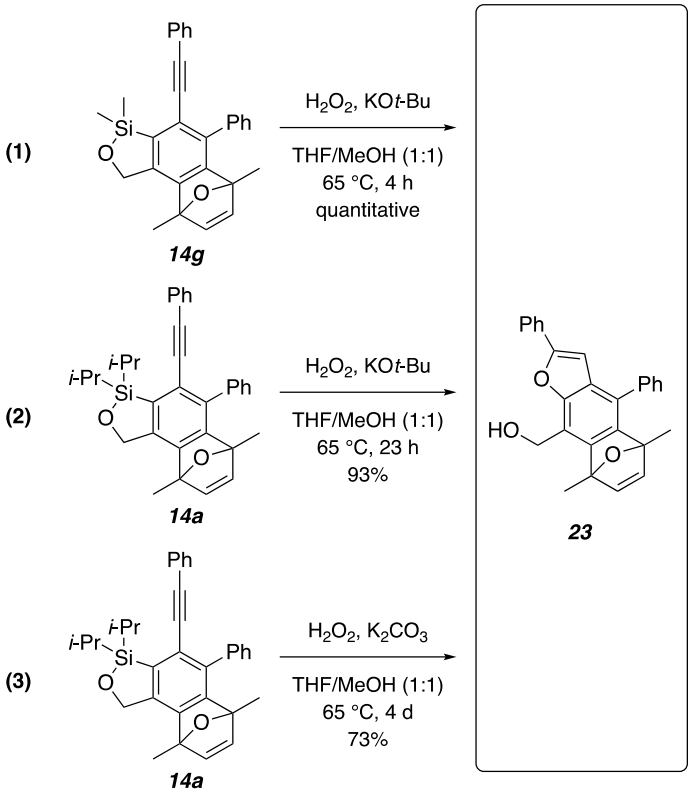
mp 130–133 °C.

Data for *S16*

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53–7.43 (m, 5H), 7.29–7.21 (m, overlapping with $CHCl_3$), 7.17–7.13 (m, 1H), 7.13–7.07 (m, 2H), 5.38 (d, J = 14.2 Hz, 1H, SiOCH_ACH$_B$), 5.20 (d, J = 14.2 Hz, 1H, SiOCH$_A$CH_B), 3.49 (d, J = 3.5 Hz, 1H, CH_AOCH$_B$), 3.48 (d, J = 3.5 Hz, 1H, CH$_A$OCH_B), 1.86 (s, 3H, C8CH_3), 1.20 (s, 3H, C6CH_3), 0.52 (s, 3H, OSiCH_3CH$_{3'}$), and 0.51 (s, 3H, OSiCH$_3$C$H_{3'}$).

LCMS: t_R = 3.72 min. Calc for $[(C_{29}H_{30}NO_3Si)^+][M+NH_4^+]$ 468.2; found 468.1. Calc for $[(C_{29}H_{27}O_3Si)^+][M+H^+]$ 451.2; found 451.0.

(5,8-Dimethyl-2,4-diphenyl-5,8-dihydro-5,8-epoxynaphtho[2,3-*b*]furan-9-yl)methanol (23)



Reaction (1). To a solution of the benzoxanorbornadiene derivative **14g** (22 mg, 0.051mmol) in THF/MeOH (2 mL, 1:1 v/v) was added 30% H_2O_2 (50 μL, 0.49 mmol) and *t*-BuOK (20 mg, 0.18 mmol). The resulting suspension was stirred in a 65 °C oil bath for 4 h to provide a clear, slightly yellow solution. The mixture was cooled to 0 °C in an ice water bath. 20% Aqueous $NaHSO_3$ solution was added, and the resulting mixture was extracted with Et_2O. The organic extracts were combined, washed with brine, dried with $MgSO_4$, and concentrated under reduced pressure. The crude material was purified by passage through a silica gel plug (40% EtOAc/hexanes) and the residue was further purified by medium pressure liquid chromatography (40% EtOAc/hexanes) to give compound **23** (20 mg, quantitative) as a foamy white crystalline solid.

Reaction (2). Compound **23** was prepared following the procedure in **Reaction (1)** from the di-isopropyl-containing benzoxanorbornadiene derivative **14a** (20 mg, 0.041mmol), 30% H_2O_2 (40 μL, 0.39 mmol), and *t*-BuOK (14 mg, 0.41 mmol) in THF/MeOH (2 mL, 1:1 v/v) at 65 °C for 23 h. After purification, compound **23** (15 mg, 93%) was obtained as a foamy crystalline white solid.

Reaction (3). Compound **23** was prepared following the procedure in **Reaction (1)** from the diisopropyl-containing benzoxanorbornadiene derivative **14a** (22 mg, 0.045 mmol), 30% H_2O_2 (50 μL, 0.49 mmol), and K_2CO_3 (37 mg, 0.27 mmol) in THF/MeOH (2 mL, 1:1 v/v) at 65 °C for 2 d. Unreacted starting material was observed by TLC. More K_2CO_3 (25 mg, 0.18 mmol) was added and the mixture was stirred at 65 °C for 2 d. After purification, compound **23** (13 mg, 73%) was obtained as a foamy crystalline white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (nfod, *J* = 7.5 Hz, 2H, FurPh*H*$_o$), 7.51 (br s, 2H, ArPh*H*$_o$ or ArPh*H*$_m$), 7.47–7.41 (br s, 2H, ArPh*H*$_o$ or ArPh*H*$_m$), 7.38 (nfodd, *J* = 7.5, 7.5 Hz, 2H, FurPh*H*$_m$), 7.29 (tt, *J* = 7.5, 1.3 Hz, 1H, ArPh*H*$_m$), 7.10 (br s, 1H, ArPh*H*$_p$), 6.89 (d, *J* = 5.2 Hz, 1H, C*H*$_A$=CH$_B$), 6.86 (d, *J* = 5.2 Hz, 1H, CH$_A$=C*H*$_B$), 6.68 (s, 1H, PhC=C*H*), 5.23 (d, *J* = 12.2 Hz, 1H, ArC*H*$_A$H$_B$OH) 5.10 (dd, *J* = 12.2, 5.2 Hz, 1H, ArCH$_A$*H*$_B$OH), 2.17 (s, 3H, C8C*H*$_3$), and 1.88 (br s, 1H, ArCH$_A$H$_B$O*H*), and 1.38 (s, 3H, C5C*H*$_3$).

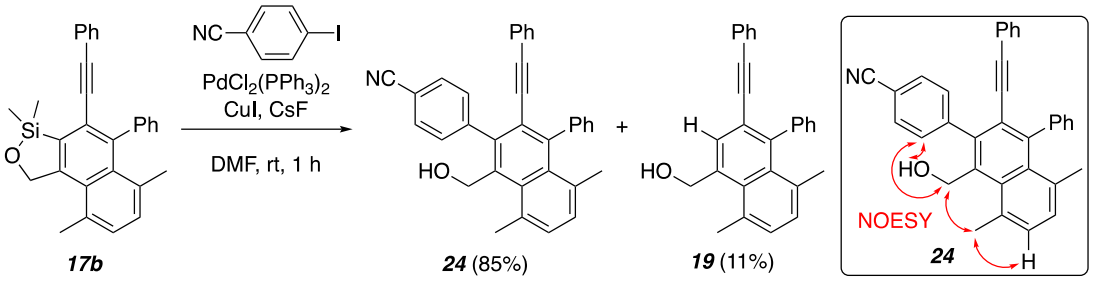
^{13}C NMR (126 MHz, $CDCl_3$) δ 156.2, 150.8, 148.1, 147.1, 147.0, 145.1, 137.4, 130.4, 129.6 (br), 129.4 (br), 128.7, 128.4 (br), 128.3, 128.1 (br), 127.74, 127.71, 126.4, 124.4, 117.9, 101.6, 89.3, 89.2, 55.7, 17.5, and 17.3.

IR (neat) 3408 (br) 3050, 2976, 1603, 1566, 1472, 1446, 1381, 1350, 1187, 1130, 1002, 859, 760, and 689 cm $^{-1}$.

HRMS (ESI-Orbitrap) Calc for [($C_{27}H_{23}O_3$)$^+$] [(M+H)$^+$] 395.1642; found: 395.1639.

mp 118–121 °C.

4-(1-(Hydroxymethyl)-5,8-dimethyl-4-phenyl-3-(phenylethynyl)naphthalen-2-yl)benzonitrile (24)



To a small culture tube under N_2 was added the naphthalene derivative **17b** (20 mg, 0.048 mmol), $Pd(PPh_3)_2Cl_2$ (3 mg, 0.004 mmol), CuI (1 mg, 0.005 mmol), 4-iodobenzonitrile (18 mg, 0.079 mmol), and CsF (17 mg, 0.11 mmol). DMF (1.0 mL) was added and the mixture (yellow-orange suspension) was stirred at rt for 1 h. Saturated aqueous NH_4Cl solution was added and the resulting mixture was extracted with EtOAc. The organic extracts were combined, washed with water, washed with brine, dried with $MgSO_4$, and concentrated under reduced pressure. The crude material was purified by passage through a silica gel plug (30% EtOAc/hexanes) and the residue was further purified by medium pressure liquid chromatography (15% EtOAc/hexanes) to give compound **24** (19 mg, 85%) as a white solid that crystallized when allowed to concentrate from a methanol solution at ambient temperature. A small amount of a second compound, the epoxide **19** (2 mg, 11%), was isolated in a faster eluting fraction.

Data for compound 24

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.2 Hz, 2H, NCPh*H*$_o$), 7.62 (d, *J* = 8.2 Hz, 2H, NCPh*H*$_m$), 7.45–7.41 (m, 3H, Ph*H*s), 7.41–7.36 (m, 2H, Ph*H*s), 7.32 (d, *J* = 7.2 Hz, 1H, Ar*H7*), 7.15 (d, *J* = 7.2 Hz, 1H, Ar*H6*), 7.19–7.09 (m, 3H, C≡C–Ph*H*$_m$ and C≡C–Ph*H*$_p$), 6.56–6.51 (m, 2H, C≡C–Ph*H*$_o$), 4.90 (d, *J* = 5.0 Hz, 2H, ArC*H*$_2$OH), 3.06 (s, 3H, C7C*H*$_3$), 1.93 (s, 3H, C6C*H*$_3$), and 1.57 (t, *J* = 5.2 Hz, 1H, ArCH$_2$O*H*).

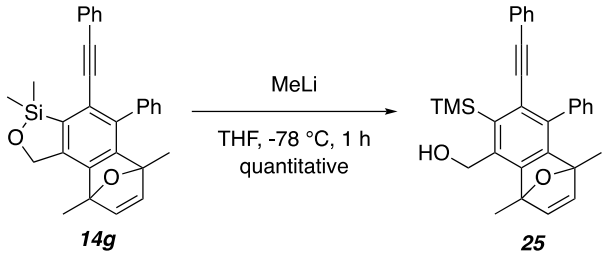
^{13}C NMR (126 MHz, $CDCl_3$) δ 146.1, 144.2, 143.2, 141.0, 134.7, 133.9, 133.8, 133.4, 133.2, 131.7, 131.6, 131.3, 130.9, 130.7, 130.5, 128.12, 128.10, 127.6, 127.3, 122.8, 121.5, 118.9, 111.2, 99.0, 89.0, 61.1, 25.6, and 24.5.

IR (neat) 3386 (br), 3053, 2956, 2926, 2227 (sharp), 1592, 1490, 1443, 1033, 1016, 994, 974, 844, 823, 753, 701, and 688 cm^{-1}.

HRMS (ESI-Orbitrap) Calc for [($C_{34}H_{24}N)^+$] [(M+H$^+$-H_2O)] 446.1903; found: 446.1896.

mp 227–229 °C.

(1,4-Dimethyl-8-phenyl-7-(phenylethynyl)-6-(trimethylsilyl)-1,4-dihydro-1,4-epoxynaphthalen-5-yl)methanol (25)



14g *25*

To a solution of the benzoxanorbornadiene derivative **14g** (21 mg, 0.048 mmol) in THF (0.5 mL) at -78 ºC was added MeLi (1.6M solution in Et_2O, 40 μL, 0.064 mmol). After being stirred at -78 ºC for 1 h, saturated aqueous NH_4Cl solution was added and the resulting mixture was extracted with Et_2O. The organic extracts were combined, washed with brine, dried with $MgSO_4$, and concentrated under reduced pressure. The crude material was purified by passage through a silica gel plug (15% EtOAc/hexanes) and the residue was further purified by medium pressure liquid chromatography (20% EtOAc/hexanes) to give compound **25** (21 mg, quantitative) as a white crystalline solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50–7.37 (m, 4H), 7.22–7.15 (m, 3H), 6.99 (br d, *J* = 6.3 Hz, 1H), 6.95–6.88 (m, 2H), 6.85 (d, *J* = 5.2 Hz, 1H, C*H*=CH), 6.73 (d, *J* = 5.2 Hz, 1H, CH=C*H*), 4.90 (dd, *J* = 12.1, 6.5 Hz, HOCH_ACH$_B$), 4.85 (dd, *J* = 12.2, 3.8 Hz, 1H, SiOCH$_A$CH_B), 2.14 (s, 3H, C4CH_3), 1.44 (br t, *J* = 5.5 Hz, 1H, *H*OCH$_A$CH$_B$), 1.19 (s, 3H, C1CH_3), and 0.55 [s, 9H, ArSi(CH_3)$_3$].

^{13}C NMR (126 MHz, $CDCl_3$) δ 151.6, 151.3, 147.1, 146.5, 139.5, 139.0, 137.9, 137.6, 130.8, 130.7, 129.0, 128.1, 127.9, 127.8, 127.6, 127.4, 127.3, 123.5, 98.0, 91.5, 90.0, 89.1, 60.8, 17.6, 16.9, and 3.0.

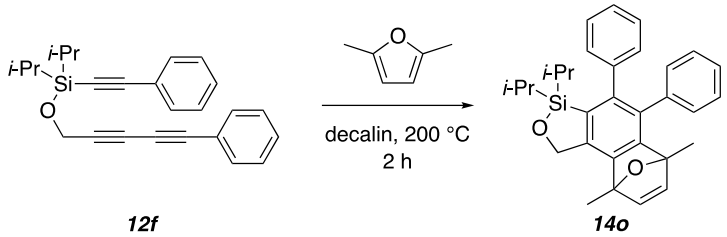
IR (neat) 3452 (br), 3054, 2933, 2896, 1487, 1442, 1380, 1242, 1153, 1024, 857, 838, 763, 749, 740, 698, and 685 cm $^{-1}$.

HRMS (ESI-Orbitrap) Calc for [($C_{30}H_{29}OSi)^+$] [(M+H^+-H_2O)] 433.1982; found: 433.1981.

mp 233–235 °C.

(f) Products (14o–p) obtained from HDDA and TDDA reactions

3,3-Diisopropyl-6,9-dimethyl-4,5-diphenyl-1,3,6,9-tetrahydro-6,9-epoxynaphtho[2,1-*c*][1,2]oxasilole (14o)



12f *14o*

Compound **14o** was prepared following general procedure C from the triyne **12f** (20 mg, 0.054 mmol) and dimethylfuran (0.12 mL, 1.1 mmol) in decalin (2.7 mL, 0.02 M) at 200 ºC for 2 h. The reaction mixture was purified by flash column chromatography by eluting first with hexanes to remove decalin and then with 50% EtOAc/hexanes. The resulting crude material was then purified by medium pressure liquid chromatography (10% EtOAc/hexanes) to give compound **14o** (22 mg, 87%) as a slightly yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$, ca. 20 °C) δ 7.24 (ddd, *J* = 7.5, 7.5, 1.4 Hz, 1H), 7.14 (tt, *J* = 7.5, 1.4 Hz, 1H), 7.09–7.05 (m, 2H), 7.04 (ddd, *J* = 7.5, 7.5, 1.4 Hz, 1H), 6.99 (ddd, *J* = 7.6, 1.6, 1.6 Hz, 1H), 6.89 (d, *J* = 5.3 Hz, 1H, C*H*$_A$=CH$_B$), 6.91–6.85 (m, 1H), 6.87 (d, *J* = 5.3 Hz, 1H, CH$_A$=C*H*$_B$), 5.40 (d, *J* = 14.0 Hz, 1H, SiOC*H*$_A$H$_B$), 5.16 (d, *J* = 14.0 Hz, 1H, SiOCH$_A$*H*$_B$), 1.97 (s, 3H, C*H*$_3$), 1.16 (s, 3H, C*H*$_3$), 1.08–0.99 [m, 4H, OSiC*H*(CH$_3$)$_2$ and OSiCH(C*H*$_3$)(CH$_3$)], 0.88 [d, *J* = 6.5 Hz, 3H, OSiCH(C*H*$_3$)(CH$_3$)], 0.79 [sept, *J* = 7.5 Hz, 1H, OSiC'*H*(CH$_3$)$_2$], 0.69 [d, *J* = 7.3 Hz, 3H, OSiC'H(C*H*$_3$)(CH$_3$)], and 0.36 [d, *J* = 7.5 Hz, 3H, OSiC'H(CH$_3$)(C*H*$_3$)]. Because of hindered rotation about *both* of the biaryl bonds, not two protons are equivalent and three were so broad that they could not be discerned in the baseline. Hence, spectra were recorded at higher temperature in C_6D_6.

^{1}H NMR (500 MHz, C_6D_6, ca. 57 °C, referenced to C_6D_5H at 7.15 ppm) δ 7.15–7.07 (v br s, 2H), 7.03 (br dd, *J* = 7.3, 7.3 Hz, 1H), 7.00–6.85 (m, ca. 6H), 6.83 (br dd, *J* = 7.7, 7.7 Hz, 1H), 6.63 (d, *J* = 5.3 Hz, 1H, C*H*$_a$=CH$_b$), 6.57 (d, *J* = 5.3 Hz, 1H, CH$_a$=C*H*$_b$), 5.45 (d, *J* = 14.1 Hz, 1H, SiOC*H*$_a$H$_b$), 5.19 (d, *J* = 14.1 Hz, 1H, SiOCH$_a$*H*$_b$), 1.76 (s, 3H, C9C*H*$_3$), 1.26 (s, 3H, C6C*H*$_3$), 1.19–1.12 [m, 4H, OSiC*H*(CH$_3$)$_2$ and OSiCH(C*H*$_3$)(CH$_3$)], 1.01 [br d, *J* = 6.4 Hz, 3H,

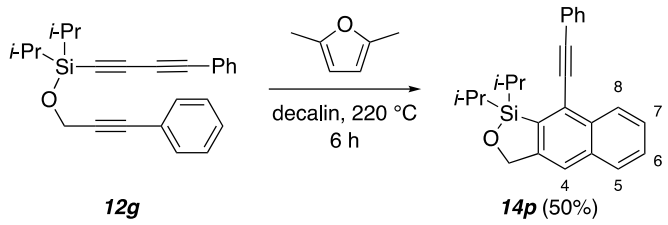
OSiCH(C*H*$_3$)(CH$_3$)], 0.95–0.85 [m, 4H, OSiC'*H*(CH$_3$)$_2$ and OSiC'H(C*H*$_3$)(CH$_3$)], and 0.62 [d, *J* = 7.1 Hz, 3H, OSiC'H(CH$_3$)(C*H*$_3$)].

^{13}C NMR (126 MHz, CDCl$_3$) δ 153.2, 147.0, 146.9, 143.9, 143.4, 142.7, 140.3, 138.5, 133.4, 131.2, 130.8, 130.1, 127.3, 127.2, 126.6, 126.5, 90.5, 88.5, 69.7, 17.091, 17.087 17.03, 16.97, 16.8, 15.9, 14.4, and 13.1. (Very broad resonances at ca. 129.8 and 127.4 were observed; these correspond to the ortho and meta carbons on each of the two phenyl rings.)

IR (neat) 3057, 2941, 2864, 1461 1443, 1388, 1152, 1059, 791, 702, and 649 cm $^{-1}$.

HRMS (ESI-Orbitrap) Calc for [($C_{31}H_{35}O_2Si$)$^+$] [(M+H)$^+$] 467.2401 found: 467.2393.

1,1-Diisopropyl-9-(phenylethynyl)-1,3-dihydronaphtho[2,3-*c*][1,2]oxasilole (14p)



12g ***14p*** (50%)

Compound **14p** was prepared following general procedure C from the triyne **12g** (24 mg, 0.065 mmol) and dimethylfuran (0.15 mL, 1.4 mmol) in decalin (3.4 mL, 0.02 M) at 220 ºC for 6 h. The reaction mixture was purified by eluting through a silica gel column first with hexanes to remove decalin and then with 20% EtOAc/hexanes. The resulting crude material was then purified by medium pressure liquid chromatography (2% EtOAc/hexanes) to give compound **14p** (12 mg, 50%) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (d, *J* = 8.3, 1H, ArC8*H*), 7.83 (d, *J* = 7.7 Hz, 1H, ArC5*H*), 7.65 (s, 1H, ArC4*H*), 7.62 (br dd, *J* = 7.8, 1.8 Hz, 2H, PhH_o), 7.60–7.52 (m, *2*H, ArC6*H* and ArC7*H*), 7.44–7.36 (m, 3H, PhH_p + PhH_m), 5.30 (d, *J* = 1.2 Hz, 2H, SiOCH_2), 1.46 [sept, *J* = 7.5 Hz, 2H, OSiC*H*(CH_3)$_2$], 1.12 [d, *J* = 7.5 Hz, 6H, OSiC*H*(CH_3)(CH_3)], and 1.11 [d, *J* = 7.5 Hz, 6H, OSiC*H*(CH_3)(CH_3)].

^{13}C NMR (126 MHz, $CDCl_3$) δ 146.5, 136.4, 134.2, 132.8, 131.5, 128.55, 128.52, 128.2, 127.0, 126.4, 126.3, 124.9, 123.4, 120.2, 94.7, 89.6, 71.8, 17.5, 17.1, and 13.5.

IR (neat) 3060, 2941, 2862, 1596, 1491, 1461, 1069, 880, 779, 751, 685 and 648 cm^{-1}.

HRMS (GCMS, EI, 70 eV): t_R = 7.87 min. Calc for $C_{25}H_{26}OSi^+$ [M^+] 370.1747, found 370.1756.

VI. DFT Calculations

The DFT calculations were carried out using Gaussian 09[9]. Structures were first optimized and characterized by a frequency calculation (performed at 413 K) in the gas phase at the (U)M06-2X/6-311+G(d,p) level of theory. Each of these gas phase optimized geometries was subsequently subjected to a single-point energy calculation at the B3LYP-D3BJ/6-311+G(d,p) level of theory with chloroform solvation treatment (SMD[10]).

More explicitly, model tetrayne **15a** was subjected to an initial conformational search in Maestro (Version 10.1.013, MMshare Version 2.9.013, Release 2015-1, Platform Linux-x86_64) in the Schrödinger software package. The lowest energy conformer was then subjected to a DFT geometry optimization and frequency calculation using the above level of theory.

For all open-shell calculations (i.e., for the diradical **15b** and stepwise transition state structures **TS1**, **TS2**, and **TS2'**), spin symmetry was broken using the keyword "guess=(mix,always)." To correct for spin contamination, the method of Yamaguchi et al.[11] for spin purification was used to extract the pure singlet state energy for the diradical and the transition state structures.

On the following pages the electronic energy value, the free energy value, and the Cartesian coordinates from the output files are listed for each of species **15a-d**, **TS1**, **TS2**, **TS2'**, and the concerted TSs leading to **15c-d**. The spin expectation values (<S2>) for **15b**, **TS1**, **TS2**, and **TS2'**; the imaginary frequency value for each transition structure; and a 3D structure (generated from coordinates using PYMOL) for **15b** are also given.

Optimized geometry for tetrayne 15a

E(RM062X) = -789.6340843 Hartree/Particle
Sum of electronic and thermal Free Energies = -789.538260 Hartree/Particle

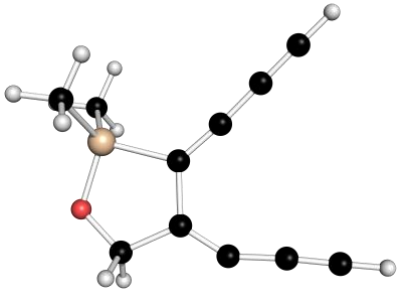
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.695236	-0.151175	0.196249
2	6	0	-2.366028	-1.161678	0.153131
3	6	0	-3.12306	-2.308512	0.106939
4	6	0	-3.785934	-3.31218	0.067062
5	1	0	-4.371091	-4.200405	0.033623
6	14	0	-0.663282	1.382972	0.262552
7	8	0	0.161538	1.460211	-1.184364
8	6	0	0.744501	0.360704	-1.846366
9	6	0	1.85426	-0.236224	-1.093832
10	6	0	2.765155	-0.718673	-0.468678
11	6	0	3.791441	-1.264837	0.266521
12	6	0	4.687477	-1.740674	0.913231
13	1	0	5.479529	-2.162428	1.484652
14	6	0	-1.749258	2.886399	0.315185
15	6	0	0.472513	1.262036	1.730513
16	1	0	-0.006374	-0.415678	-2.037609
17	1	0	1.116403	0.716472	-2.809466
18	1	0	-1.138167	3.792132	0.303817
19	1	0	-2.414388	2.910417	-0.549586
20	1	0	-2.358444	2.895263	1.221701
21	1	0	1.173878	2.100205	1.736783
22	1	0	-0.109461	1.294974	2.655397
23	1	0	1.046765	0.334639	1.720149

TS1

Imaginary frequency: -838.0722 cm^{-1}
E(UM062X) = -789.5753219 Hartree/Particle
Sum of electronic and thermal Free Energies = -789.482212 Hartree/Particle
<S**2>= 0.347468

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.010882	0.377302	-0.101613
2	6	0	0.704207	1.428023	-0.140122
3	8	0	-1.84837	-1.483424	-0.439643
4	6	0	-0.660685	-1.943342	-1.051113
5	1	0	-0.569288	-3.016002	-0.884539
6	1	0	-0.699352	-1.751795	-2.129643
7	6	0	0.551883	-1.247542	-0.469133
8	6	0	1.733133	-1.597748	-0.181783
9	6	0	3.003178	-1.433151	0.258447
10	6	0	1.562963	2.467831	-0.214147
11	14	0	-1.816882	0.050595	0.213198
12	6	0	-2.878552	1.239325	-0.742067
13	1	0	-2.754652	2.253462	-0.354119
14	1	0	-2.602412	1.240871	-1.79818
15	1	0	-3.934258	0.969212	-0.66084
16	6	0	-2.221565	0.012064	2.024574
17	1	0	-2.133658	1.009312	2.462006
18	1	0	-3.243788	-0.341087	2.182222
19	1	0	-1.540932	-0.65865	2.552088
20	6	0	2.310417	3.421895	-0.278418
21	1	0	2.972739	4.252516	-0.334434
22	6	0	4.147429	-1.32144	0.646842
23	1	0	5.149181	-1.21808	0.989014

Optimized geometry for diradical 15b



E(UM062X) = -789.5825314 Hartree/Particle
Sum of electronic and thermal Free Energies = -789.489207 Hartree/Particle
<S**2>= 0.945036

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.573401	-1.261143	-0.029898
2	6	0	-1.843933	-1.590945	-0.00366
3	6	0	-3.138169	-1.226012	0.030374
4	6	0	-0.757766	1.263951	-0.021757
5	6	0	-0.071758	0.157113	-0.013573
6	6	0	-1.371043	2.439786	-0.031771
7	14	0	1.818392	0.037246	0.024237
8	8	0	1.818469	-1.632454	0.067534
9	6	0	0.569895	-2.278316	-0.088005
10	1	0	0.449126	-3.019811	0.704299
11	1	0	0.545218	-2.795784	-1.052056
12	6	0	-4.329649	-0.968104	0.060217
13	1	0	-5.365643	-0.727372	0.086241
14	6	0	-1.937708	3.527296	-0.042752
15	1	0	-2.442701	4.463273	-0.052318
16	6	0	2.598101	0.714781	-1.523406
17	1	0	2.154025	0.264865	-2.413243
18	1	0	2.448328	1.796503	-1.577389
19	1	0	3.673429	0.521155	-1.538331
20	6	0	2.576992	0.766535	1.555838
21	1	0	3.649403	0.560287	1.595129
22	1	0	2.441343	1.851245	1.565271
23	1	0	2.112895	0.354162	2.453166

TS2

Imaginary frequency: -158.9858 cm^{-1}
E(UM062X) = -789.5785412 Hartree/Particle
Sum of electronic and thermal Free Energies = -789.479800 Hartree/Particle
<S**2>= 0.380694

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.263195	-1.619645	-0.000064
2	6	0	1.438085	-2.212958	-0.000112
3	6	0	2.648762	-1.610517	-0.00011
4	6	0	1.174819	0.779783	0.000019
5	6	0	0.228097	-0.098691	-0.000002
6	6	0	1.758465	1.997442	0.000062
7	14	0	-1.621072	0.341999	0.000034
8	8	0	-2.123744	-1.246083	-0.000031
9	6	0	-1.12281	-2.248128	-0.000059
10	1	0	-1.242458	-2.87636	-0.886565
11	1	0	-1.242437	-2.876391	0.886427
12	6	0	3.574135	-0.816727	-0.000093
13	1	0	4.447309	-0.207053	-0.000083
14	6	0	2.311473	3.081113	0.0001
15	1	0	2.792378	4.029913	0.000134
16	6	0	-2.117329	1.247322	1.544309
17	1	0	-1.819547	0.687869	2.432806
18	1	0	-1.635047	2.227987	1.577302
19	1	0	-3.198868	1.399872	1.577663
20	6	0	-2.11736	1.247449	-1.544158
21	1	0	-3.198899	1.399999	-1.57748
22	1	0	-1.63508	2.228118	-1.57708
23	1	0	-1.819592	0.688068	-2.432705

TS2'

Imaginary frequency: -311.8719 cm^{-1}
E(UM062X) = -789.5698847 Hartree/Particle
Sum of electronic and thermal Free Energies = -789.470252 Hartree/Particle
<S**2>= 0.515775

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.008255	-0.320618	0.000015
2	6	0	1.41264	2.337762	0.000017
3	6	0	0.124588	1.938673	0.000028
4	6	0	-0.313349	0.692868	0.000025
5	6	0	0.701676	-0.432035	0.00003
6	6	0	3.230642	-0.907977	-0.000007
7	14	0	-2.014758	-0.104404	-0.000008
8	8	0	-1.397574	-1.659436	-0.000001
9	6	0	0.005732	-1.806005	0.000047
10	1	0	0.312901	-2.365459	-0.887423
11	1	0	0.312853	-2.365403	0.887568
12	6	0	4.354463	-1.372724	-0.000033
13	1	0	5.329277	-1.798219	-0.000063
14	6	0	2.629901	2.22148	-0.000006
15	1	0	3.693954	2.285624	-0.00002
16	6	0	-2.997673	0.245419	-1.540174
17	1	0	-3.910282	-0.355284	-1.564979
18	1	0	-3.286199	1.299256	-1.576678
19	1	0	-2.411671	0.019516	-2.432842
20	6	0	-2.997744	0.245426	1.540107
21	1	0	-3.286383	1.299233	1.576539
22	1	0	-3.910291	-0.355371	1.564924
23	1	0	-2.411744	0.019638	2.432806

Optimized geometry for benzyne 15c

E(RM062X) = -789.6932378 Hartree/Particle
Sum of electronic and thermal Free Energies = -789.584308 Hartree/Particle

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.497583	-1.617476	0.000007
2	6	0	-1.822955	-2.012126	0.000026
3	6	0	-2.822817	-1.277611	0.000006
4	6	0	-1.530557	0.620949	-0.000001
5	6	0	-0.39156	-0.212794	0.000009
6	6	0	-1.345796	2.044636	0.000013
7	14	0	1.449589	0.163222	0.000004
8	8	0	1.871579	-1.465969	0.000156
9	6	0	0.799981	-2.38963	0.000014
10	1	0	0.862968	-3.029672	0.885689
11	1	0	0.863045	-3.029517	-0.885772
12	6	0	-2.849638	0.101133	-0.00003
13	1	0	-3.713212	0.751743	-0.000023
14	6	0	-1.175855	3.234823	-0.000002
15	1	0	-1.034875	4.289465	0.000015
16	6	0	2.046783	1.023003	-1.537731
17	1	0	3.138117	1.076517	-1.556346
18	1	0	1.712629	0.495476	-2.433042
19	1	0	1.656298	2.043418	-1.574888
20	6	0	2.046826	1.023247	1.53758
21	1	0	3.138149	1.077027	1.556024
22	1	0	1.656105	2.043573	1.574723
23	1	0	1.71293	0.495699	2.432973

Optimized geometry for benzyne 15d

E(RM062X) = -789.6912623 Hartree/Particle
Sum of electronic and thermal Free Energies = -789.586261 Hartree/Particle

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.071605	0.248013	0.00005
2	6	0	-1.383806	2.482504	0.000097
3	6	0	-0.219622	2.050401	0.000074
4	6	0	0.351498	0.805313	0.000022
5	6	0	-0.709773	-0.133219	-0.000006
6	6	0	-3.074213	-0.775711	-0.000041
7	14	0	1.963685	-0.155912	-0.000031
8	8	0	1.162346	-1.625349	-0.000667
9	6	0	-0.25336	-1.580748	-0.000125
10	1	0	-0.636909	-2.099624	0.884215
11	1	0	-0.637552	-2.099702	-0.884129
12	6	0	-3.900449	-1.648713	-0.000168
13	1	0	-4.637914	-2.415411	0.000167
14	6	0	-2.46315	1.607518	0.000117
15	1	0	-3.512353	1.875705	0.000097
16	6	0	2.982606	0.072282	1.538651
17	1	0	3.423019	1.072154	1.570163
18	1	0	2.37013	-0.060808	2.43218
19	1	0	3.798679	-0.653742	1.571296
20	6	0	2.983265	0.073287	-1.538108
21	1	0	3.422608	1.073644	-1.569271
22	1	0	3.800145	-0.651839	-1.570346
23	1	0	2.371428	-0.060375	-2.431986

Concerted TS to benzyne15c

Imaginary frequency: -457.6482 cm^{-1}

E(RM062X) = -789.5752265 Hartree/Particle

Sum of electronic and thermal Free Energies =-789.475309 Hartree/Particle

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.235604	-0.093504	0.022334
2	6	0	-1.367071	-0.629325	0.033293
3	8	0	2.244581	0.922029	-0.349231
4	6	0	1.521561	2.052959	0.072696
5	1	0	1.778399	2.304629	1.109005
6	1	0	1.788727	2.899552	-0.562003
7	6	0	0.041104	1.842048	-0.01362
8	6	0	-1.091426	2.379072	-0.065803
9	6	0	-2.354679	1.93315	-0.059558
10	6	0	-3.194818	1.043338	-0.03312
11	1	0	-4.092364	0.46662	-0.02553
12	6	0	-2.284746	-1.656519	0.055292
13	6	0	-3.090248	-2.554744	0.074488
14	1	0	-3.785576	-3.359489	0.091579
15	14	0	1.562779	-0.5689	-0.031565
16	6	0	1.952649	-1.728896	-1.42348
17	1	0	3.031764	-1.883114	-1.500816
18	1	0	1.479447	-2.69969	-1.259047
19	1	0	1.592795	-1.323759	-2.370507
20	6	0	2.075361	-1.215435	1.637407
21	1	0	1.522915	-2.125259	1.883945
22	1	0	3.143388	-1.446545	1.652748
23	1	0	1.872454	-0.477451	2.416805

Concerted TS to benzyne15d

Imaginary frequency: -450.1050 cm^{-1}

E(RM062X) = -789.5685061 Hartree/Particle

Sum of electronic and thermal Free Energies =-789.467772 Hartree/Particle

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.875415	-0.628551	-0.002814
2	6	0	-2.091118	-0.338599	-0.001682
3	8	0	1.381091	-1.518807	-0.40504
4	6	0	0.578148	0.991984	0.050106
5	6	0	-0.210685	1.950701	0.078453
6	6	0	-1.490943	2.311757	0.075748
7	6	0	-2.619118	1.803363	0.050219
8	1	0	-3.689182	1.776406	0.035235
9	6	0	-3.40467	-0.785273	-0.050806
10	6	0	-4.557653	-1.134812	-0.092025
11	1	0	-5.56382	-1.477143	-0.131117
12	6	0	0.07442	-1.783144	0.052221
13	1	0	-0.335028	-2.583537	-0.567702
14	1	0	0.103713	-2.136592	1.090356
15	14	0	2.09639	-0.064322	-0.030527
16	6	0	3.24056	0.420644	-1.405432
17	1	0	4.038147	-0.318596	-1.512048
18	1	0	2.697392	0.478758	-2.349841
19	1	0	3.700406	1.391468	-1.208253
20	6	0	2.919701	-0.101079	1.638099
21	1	0	3.779025	-0.775892	1.631625
22	1	0	3.2697	0.894921	1.919806
23	1	0	2.222106	-0.440784	2.407112

Optimized geometry for benzyne 16a

E(RM062X) = -1408.9405065 Hartree/Particle
Sum of electronic and thermal Free Energies =-1408.588043 Hartree/Particle

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.582279	-2.869026	0.025844
2	6	0	0.5399	-3.778856	0.042189
3	6	0	-0.674233	-3.534629	0.008761
4	6	0	-1.300308	-2.299838	-0.087768
5	6	0	-0.302715	-1.272501	-0.09704
6	6	0	1.083278	-1.557269	-0.0658
7	6	0	-0.680612	0.106863	-0.048984
8	6	0	-0.959907	1.27832	0.039326
9	6	0	-1.345025	2.652014	0.119494
10	6	0	-2.702862	2.997367	0.086838
11	6	0	-0.380055	3.661136	0.228375
12	6	0	-3.082545	4.33019	0.156854
13	1	0	-3.44459	2.210513	0.011601
14	6	0	-0.768866	4.991804	0.298704
15	1	0	0.668975	3.391312	0.25653
16	6	0	-2.11856	5.329703	0.261436
17	1	0	-4.133989	4.590849	0.132083
18	1	0	-0.016978	5.767141	0.384787
19	1	0	-2.419363	6.369106	0.316485
20	14	0	2.594538	-0.435735	-0.101597
21	8	0	3.664098	-1.732331	0.052088
22	6	0	3.081591	-3.020905	0.095642
23	1	0	3.369231	-3.524146	1.024616
24	1	0	3.448411	-3.622084	-0.742853
25	6	0	2.906436	0.435139	-1.743392
26	1	0	2.414057	-0.188415	-2.500355
27	6	0	2.704812	0.690486	1.397233
28	1	0	1.955441	1.480738	1.257774
29	6	0	2.285552	1.836826	-1.797575
30	1	0	2.733971	2.492257	-1.043231
31	1	0	2.461112	2.298558	-2.774118
32	1	0	1.206352	1.815331	-1.627279

33	6	0	4.406911	0.479257	-2.074758
34	1	0	4.562299	0.894719	-3.075228
35	1	0	4.952447	1.113269	-1.370077
36	1	0	4.856701	-0.514611	-2.039559
37	6	0	2.34925	-0.093071	2.668009
38	1	0	1.333984	-0.49495	2.625017
39	1	0	3.040001	-0.930508	2.809422
40	1	0	2.421724	0.549184	3.550873
41	6	0	4.093381	1.335338	1.521582
42	1	0	4.324997	1.98487	0.674081
43	1	0	4.154512	1.941409	2.430831
44	1	0	4.873374	0.570029	1.580742
45	6	0	-2.759441	-2.080965	-0.132223
46	6	0	-3.594614	-2.923935	0.607244
47	6	0	-3.334999	-1.082267	-0.92301
48	6	0	-4.972527	-2.75633	0.579956
49	1	0	-3.150468	-3.708267	1.210667
50	6	0	-4.715008	-0.920655	-0.95437
51	1	0	-2.703683	-0.445817	-1.530488
52	6	0	-5.537195	-1.750516	-0.1987
53	1	0	-5.606	-3.411315	1.166314
54	1	0	-5.149737	-0.151548	-1.582232
55	1	0	-6.612613	-1.620756	-0.223958

VI. References for the Supplementary Information

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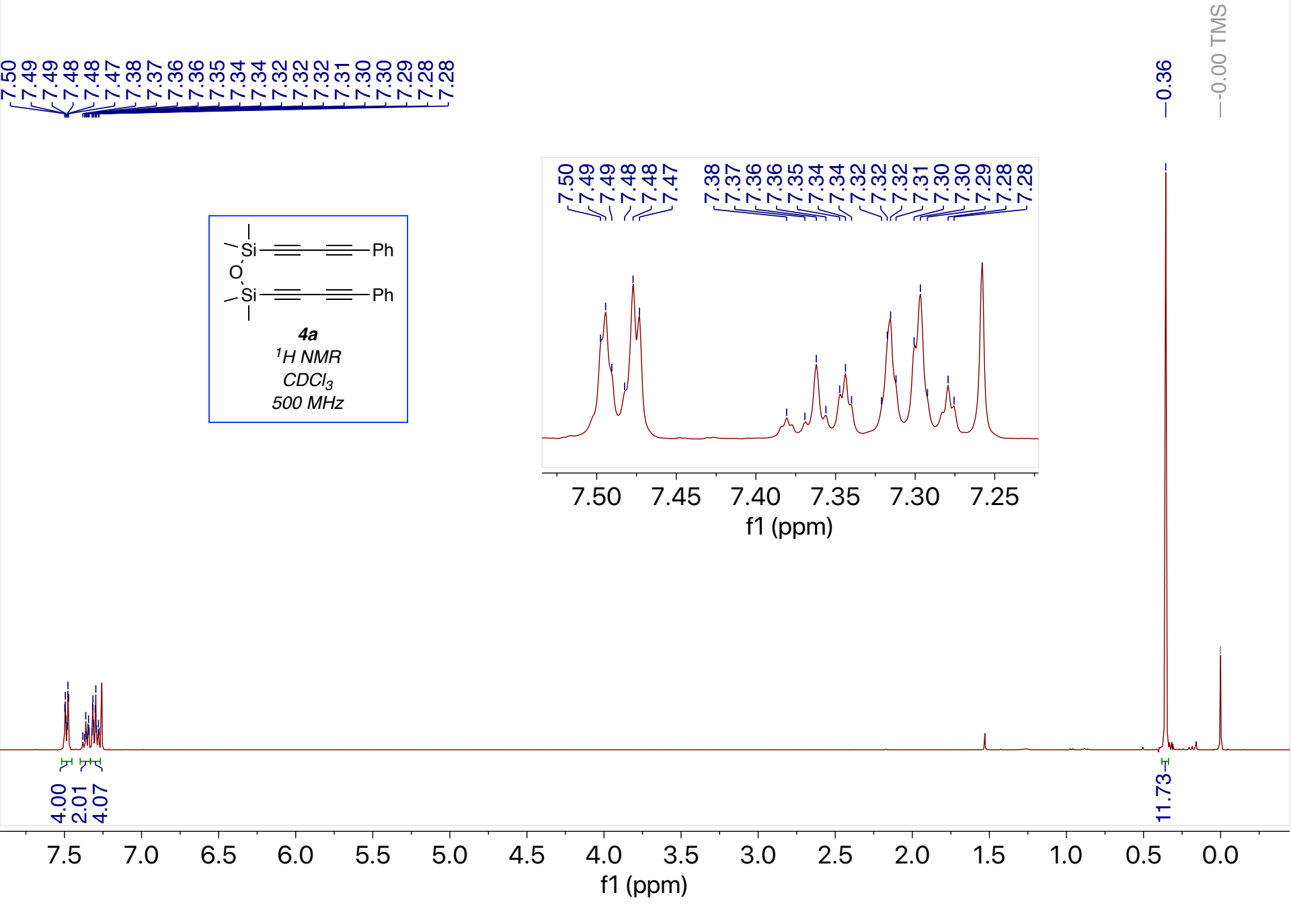
VII. Copies of NMR spectra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0.36
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Si
O
Si
Ph
Ph
4a
1H NMR
CDCl3
500 MHz
7.50 7.45 7.40 7.35 7.30 7.25
f1 (ppm)
4.00
2.01
4.07
11.73
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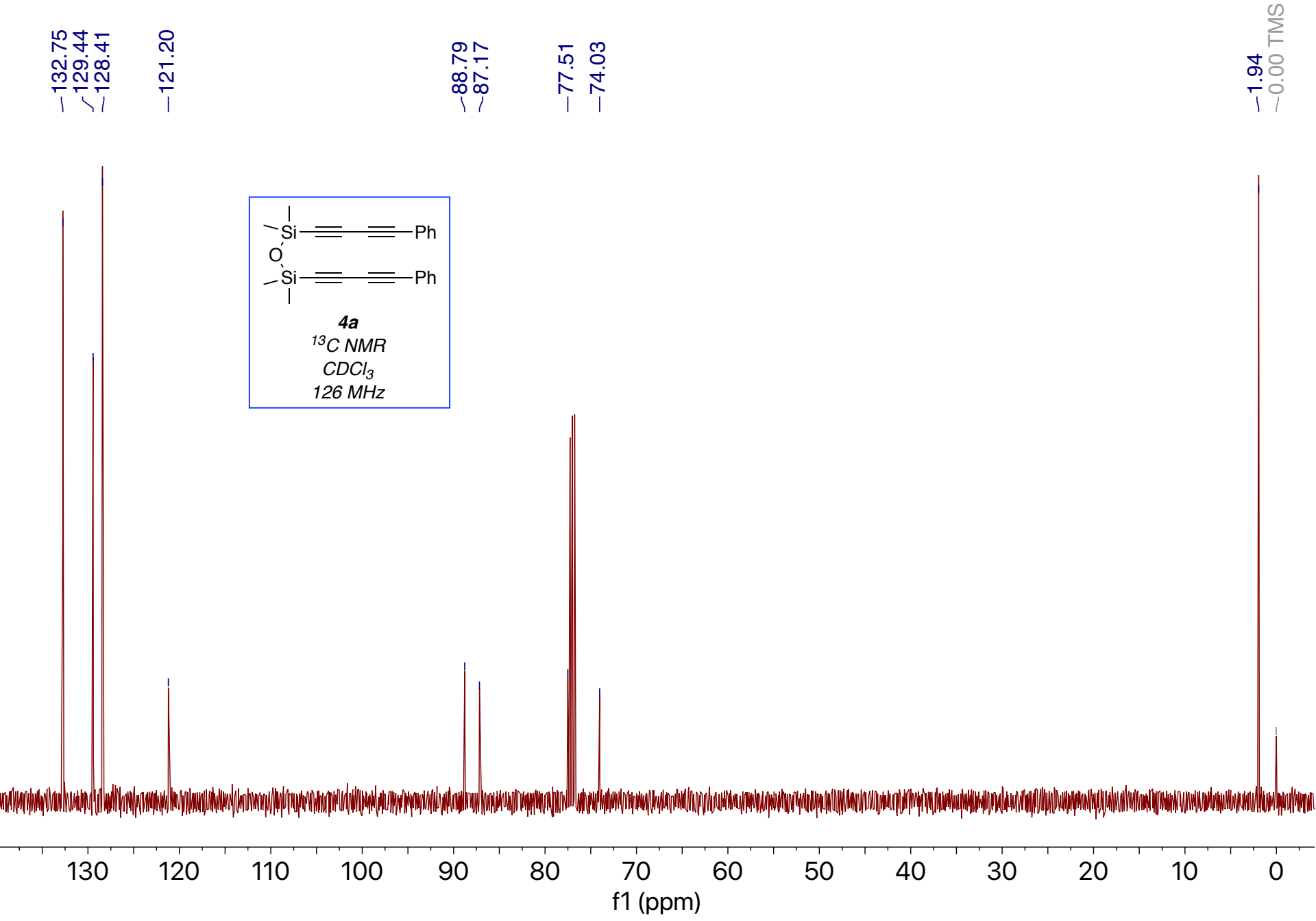
f1 (ppm)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O
Si
Ph
Ph
4a
13C NMR
CDCl3
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130
120
110
100
90
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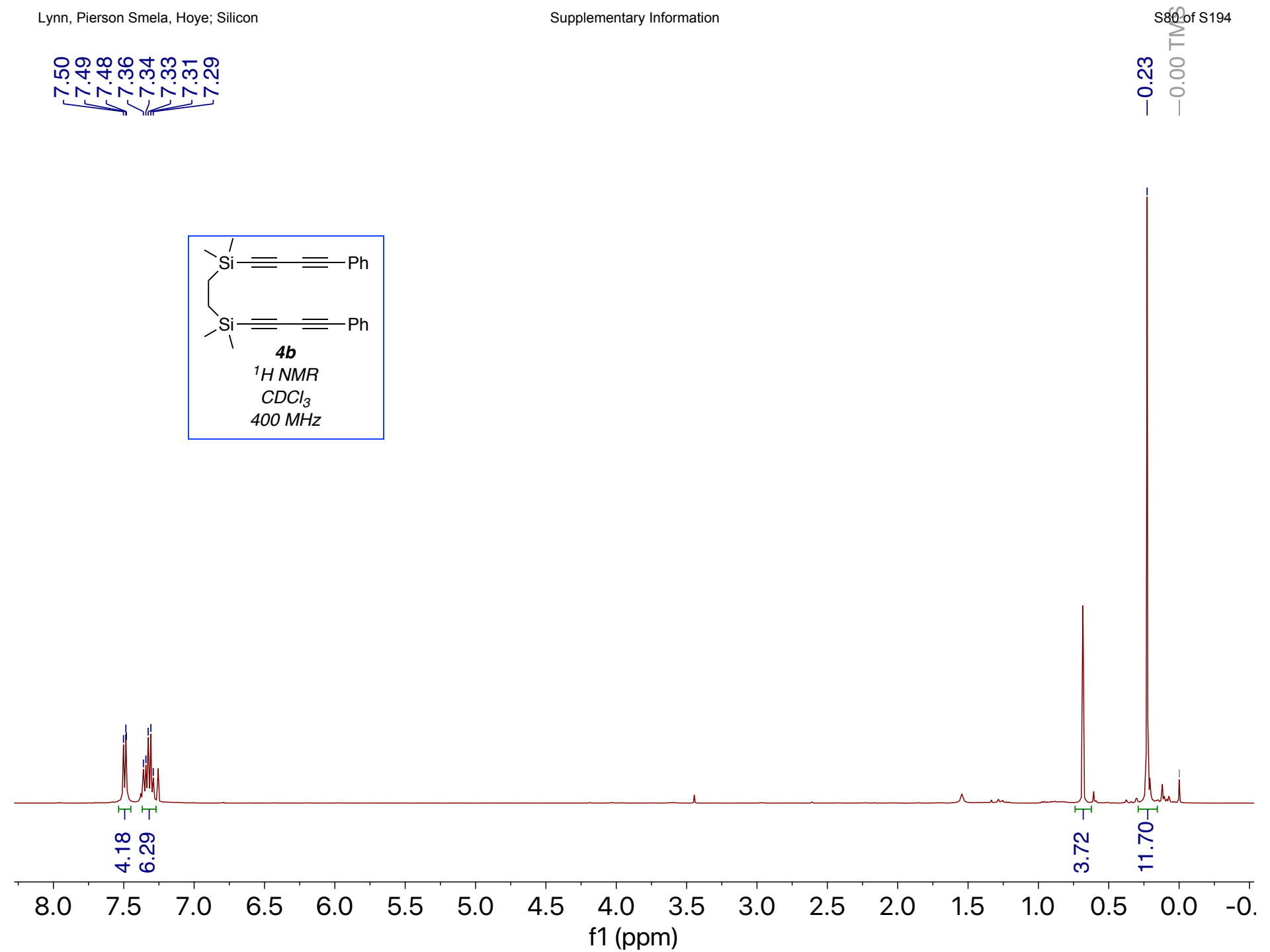
70
60
50
40
30
20
10
0
f1 (ppm)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Ph
Si
Ph
4b
1H NMR
CDCl3
400 MHz
4.18
6.29
3.72
11.70
8.0
7.5
7.0
6.5
6.0
5.5
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3.5
3.0
2.5
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1.0
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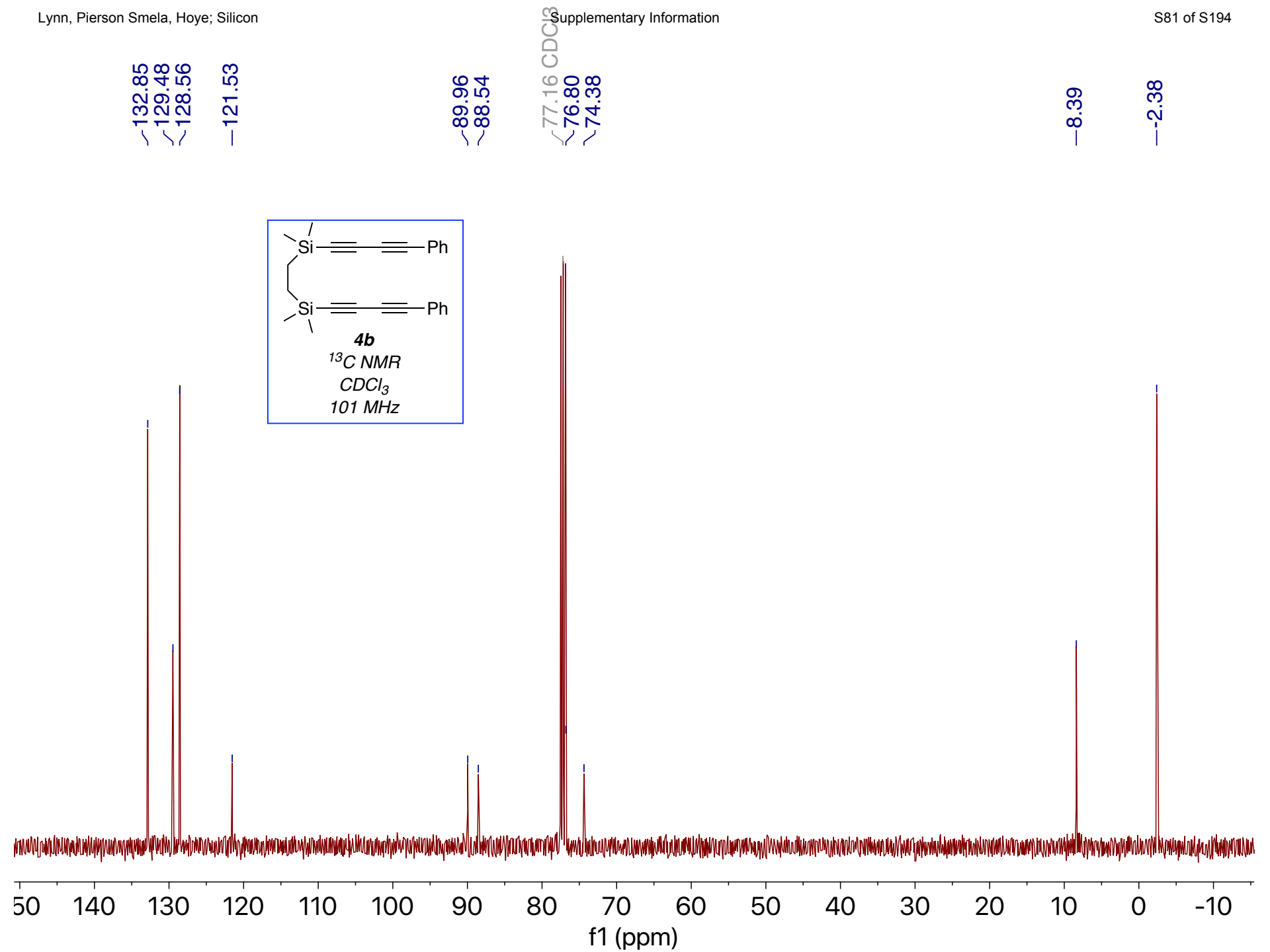
f1 (ppm)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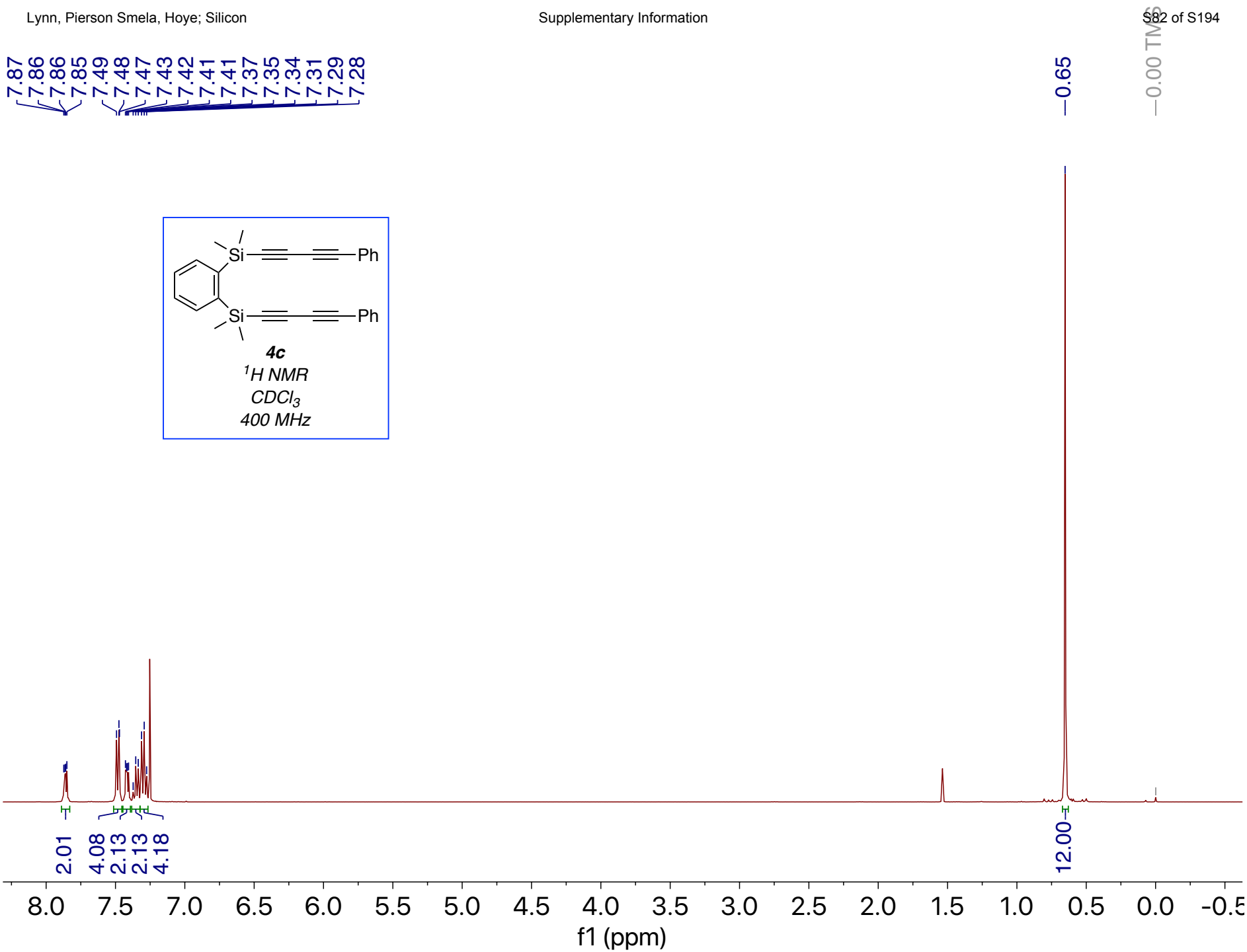
Si
Ph
Si
Ph
4b
13C NMR
CDCl3
101 MHz
f1 (ppm)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7.48
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7.41
7.41
7.37
7.35
7.34
7.31
7.29
7.28
0.65
0.00 TMS
Si
Ph
Si
Ph
4c
1H NMR
CDCl3
400 MHz
2.01
4.08
2.13
2.13
4.18
12.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
2.0
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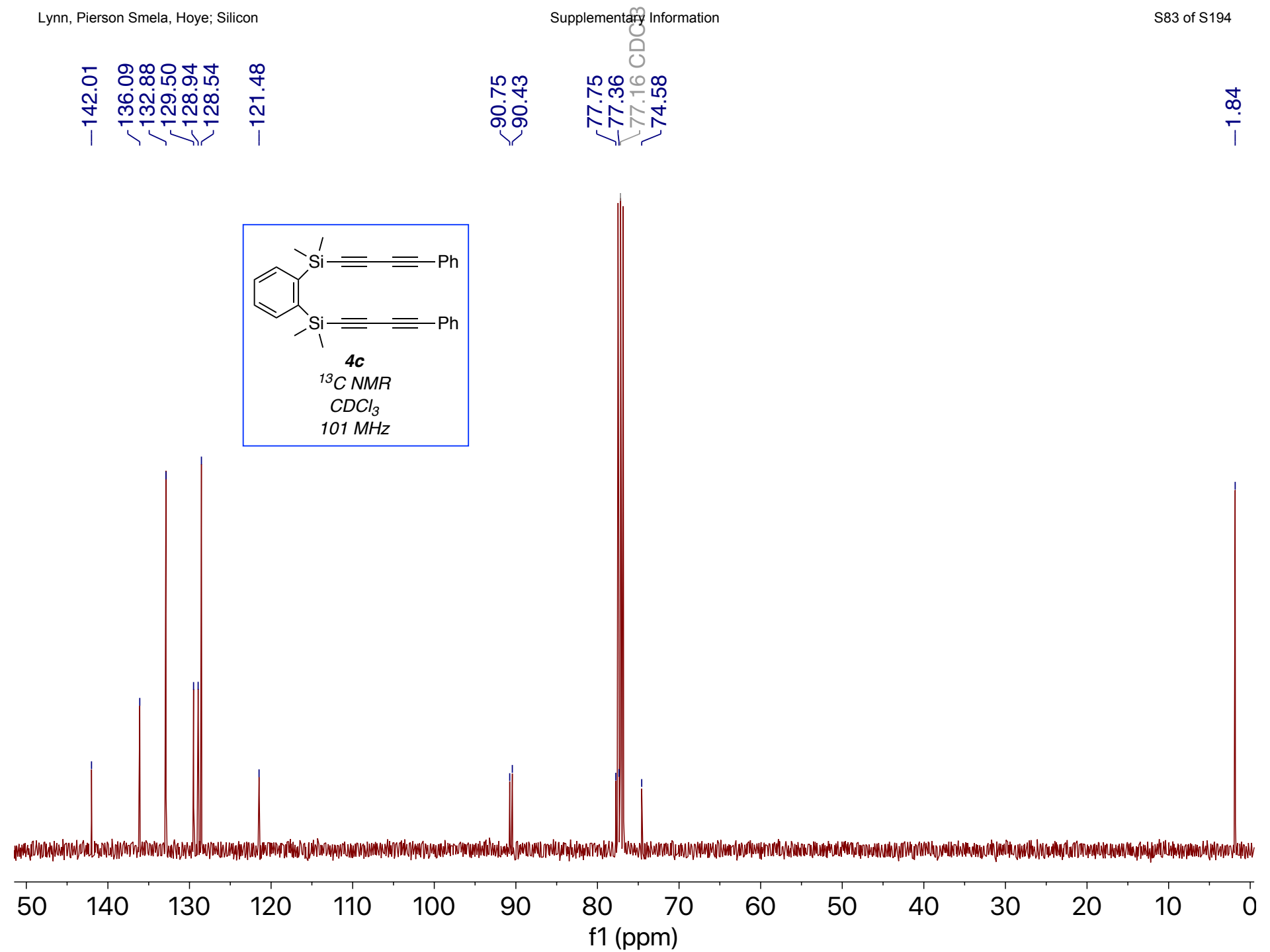
1.0
0.5
0.0
-0.5
f1 (ppm)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74.58
1.84
Si
Ph
Si
Ph
4c
13C NMR
CDCl3
101 MHz
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130
120
110
100
90
80
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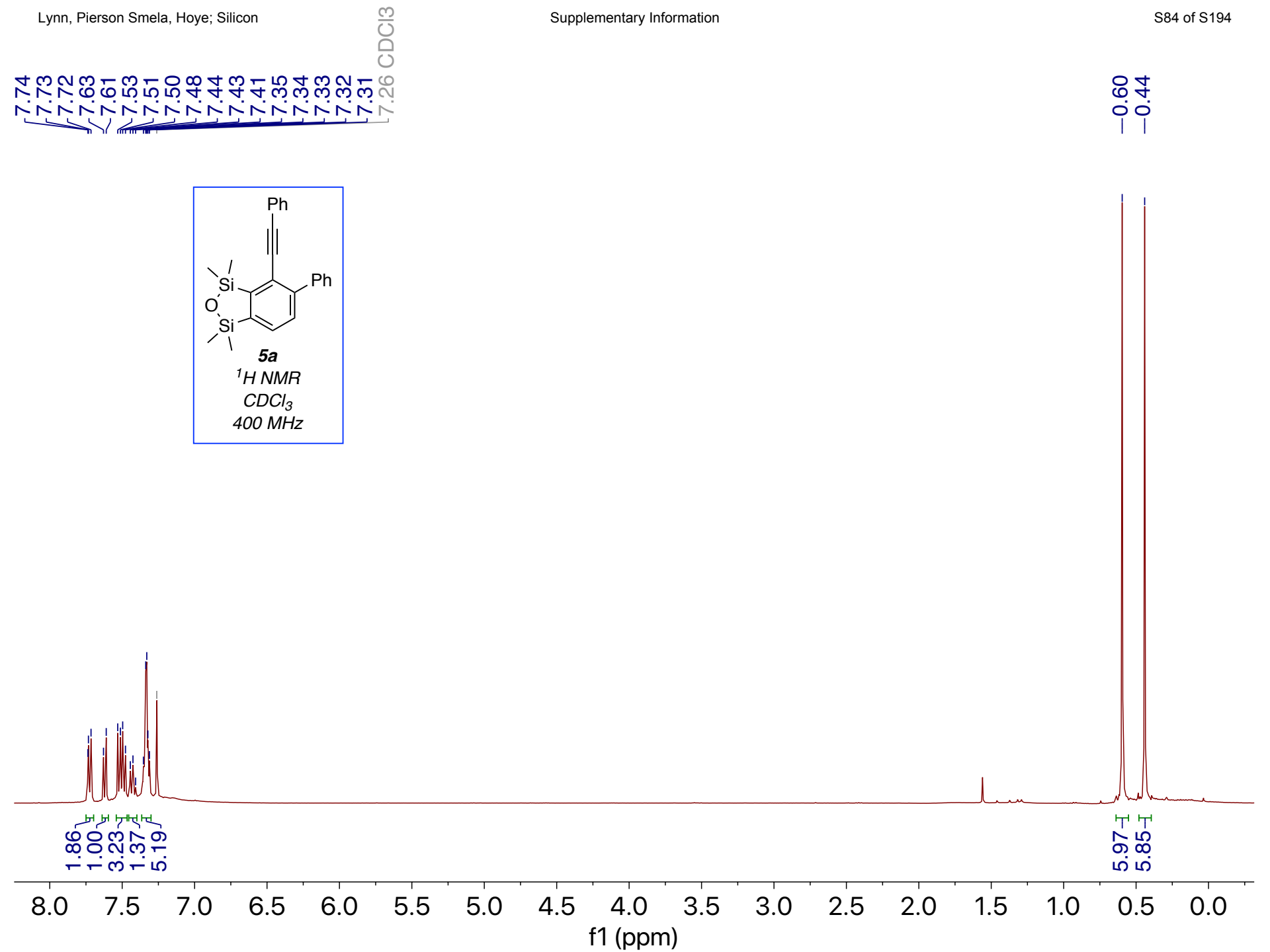
60
50
40
30
20
10
0
f1 (ppm)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7.34
7.33
7.32
7.31
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O
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Ph
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CDCl3
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1.37
5.19
5.97
5.85
8.0
7.5
7.0
6.5
6.0
5.5
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3.5
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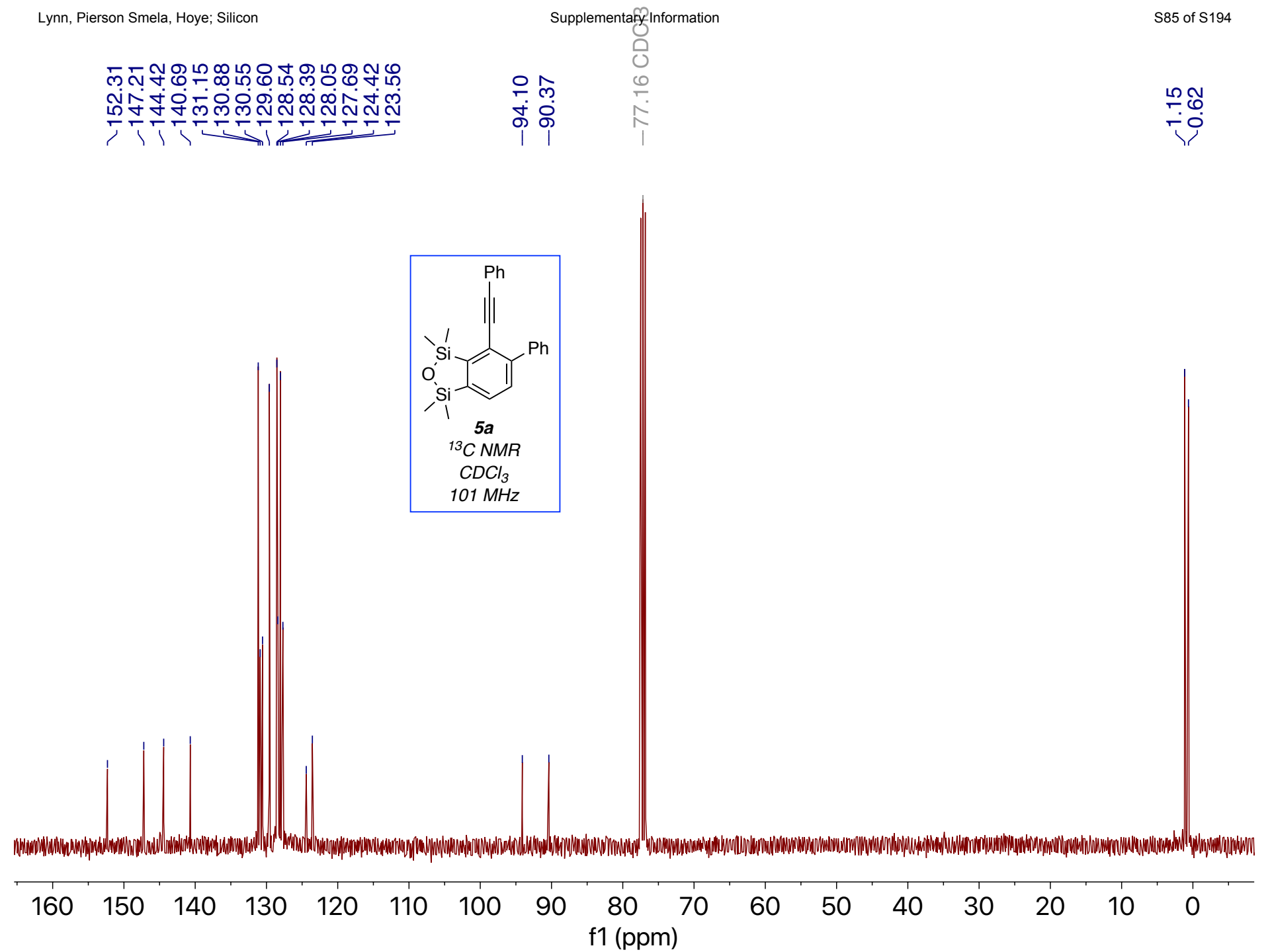
f1 (ppm)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124.42
123.56
94.10
90.37
77.16 CDCl3
1.15
0.62
Ph
Ph
Si
O
Si
5a
13C NMR
CDCl3
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120
110
100
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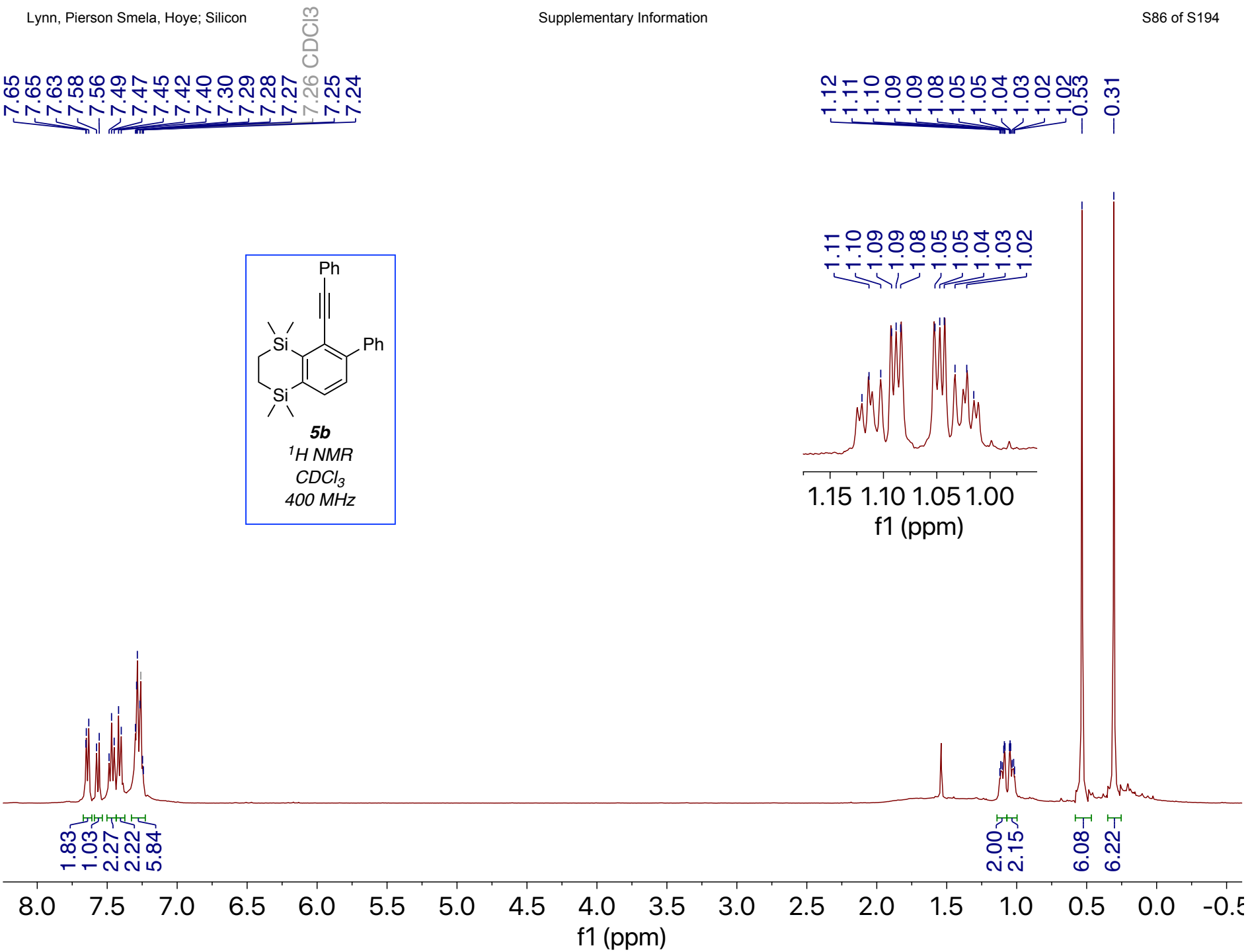
50
40
30
20
10
0
f1 (ppm)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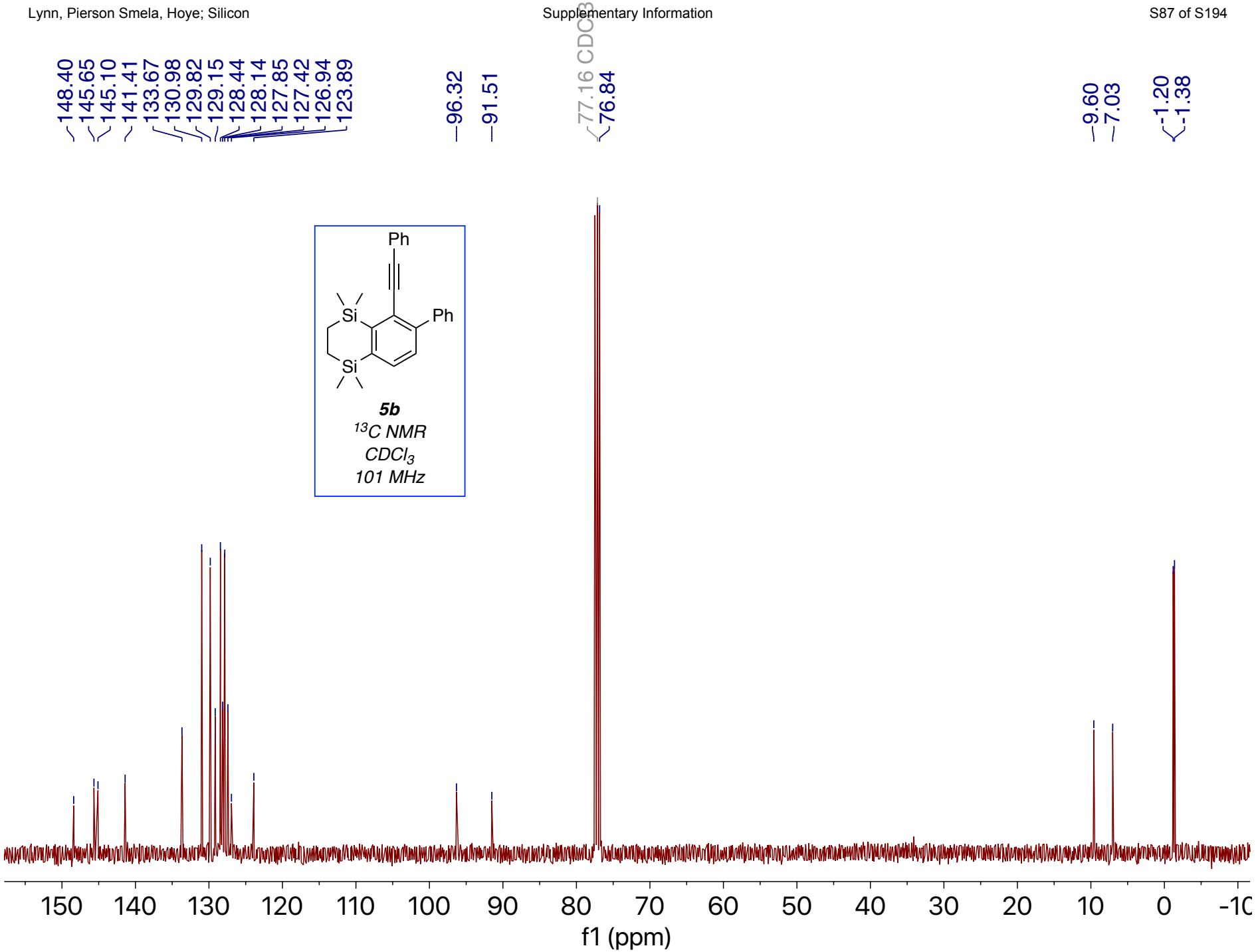
7.28
7.27
CDCl3
7.26
7.25
7.24
1.12
1.11
1.10
1.09
1.09
1.08
1.05
1.05
1.04
1.03
1.02
1.02
0.53
0.31
Ph
Si
Si
Ph
5b
1H NMR
CDCl3
400 MHz
1.11
1.10
1.09
1.09
1.08
1.05
1.05
1.04
1.03
1.02
1.15 1.10 1.05 1.00
f1 (ppm)
1.83
1.03
2.27
2.22
5.84
2.00
2.15
6.08
6.22
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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123.89
96.32
91.51
77.16 CDCl3
76.84
9.60
7.03
1.20
1.38
Ph
Si
Si
Ph
5b
13C NMR
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101 MHz
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100
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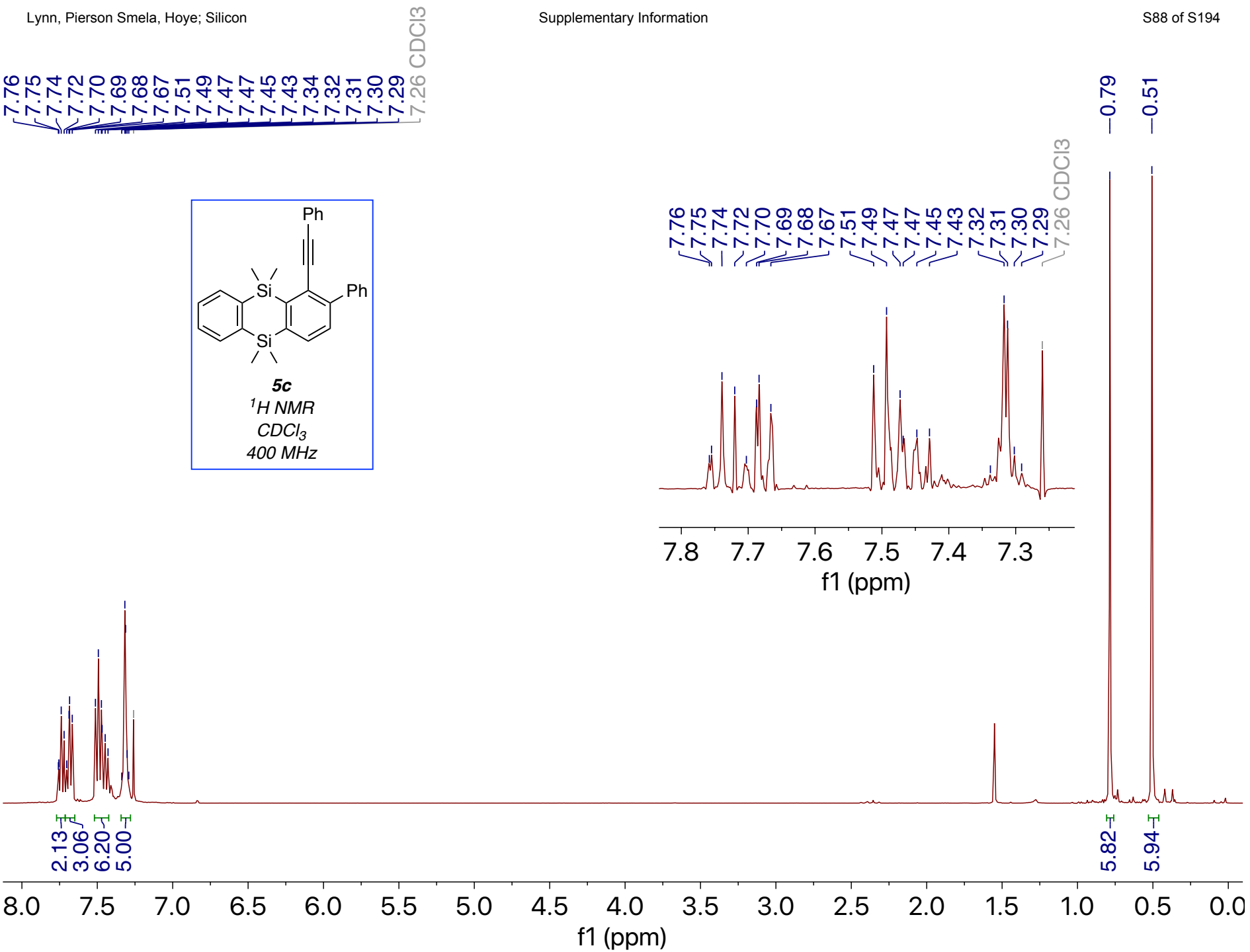
40
30
20
10
0
-10
f1 (ppm)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7.32
7.31
7.30
7.29
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Ph
Si
Si
Ph
5c
1H NMR
CDCl3
400 MHz
—0.79
—0.51
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7.7
7.6
7.5
7.4
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f1 (ppm)
2.13
3.06
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5.00
5.82
5.94
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7.5
7.0
6.5
6.0
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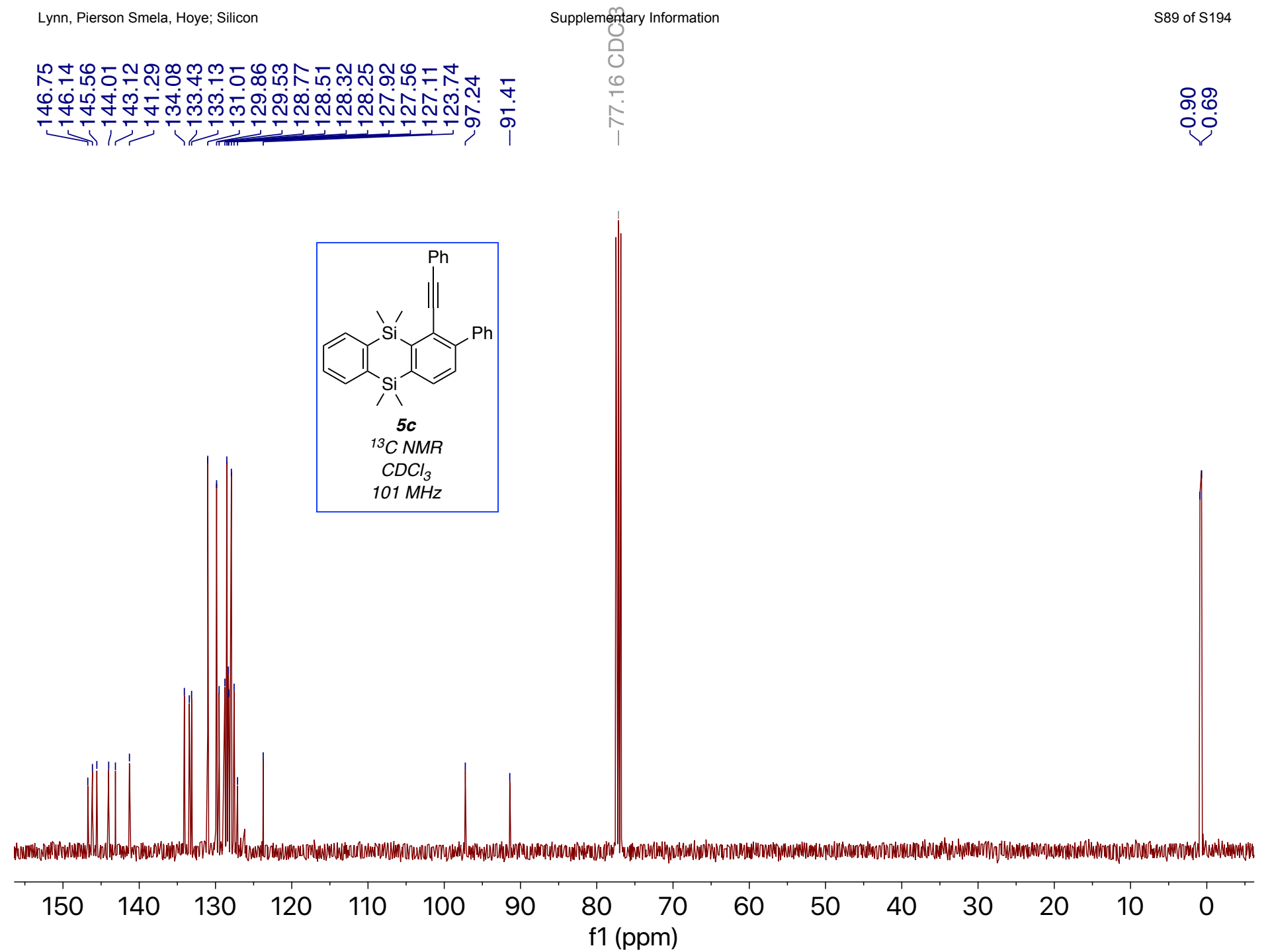
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128.51
128.32
128.25
127.92
127.56
127.11
123.74
97.24
91.41
77.16 CDCl3
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0.69
Ph
Si
Si
Ph
5c
13C NMR
CDCl3
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90
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50
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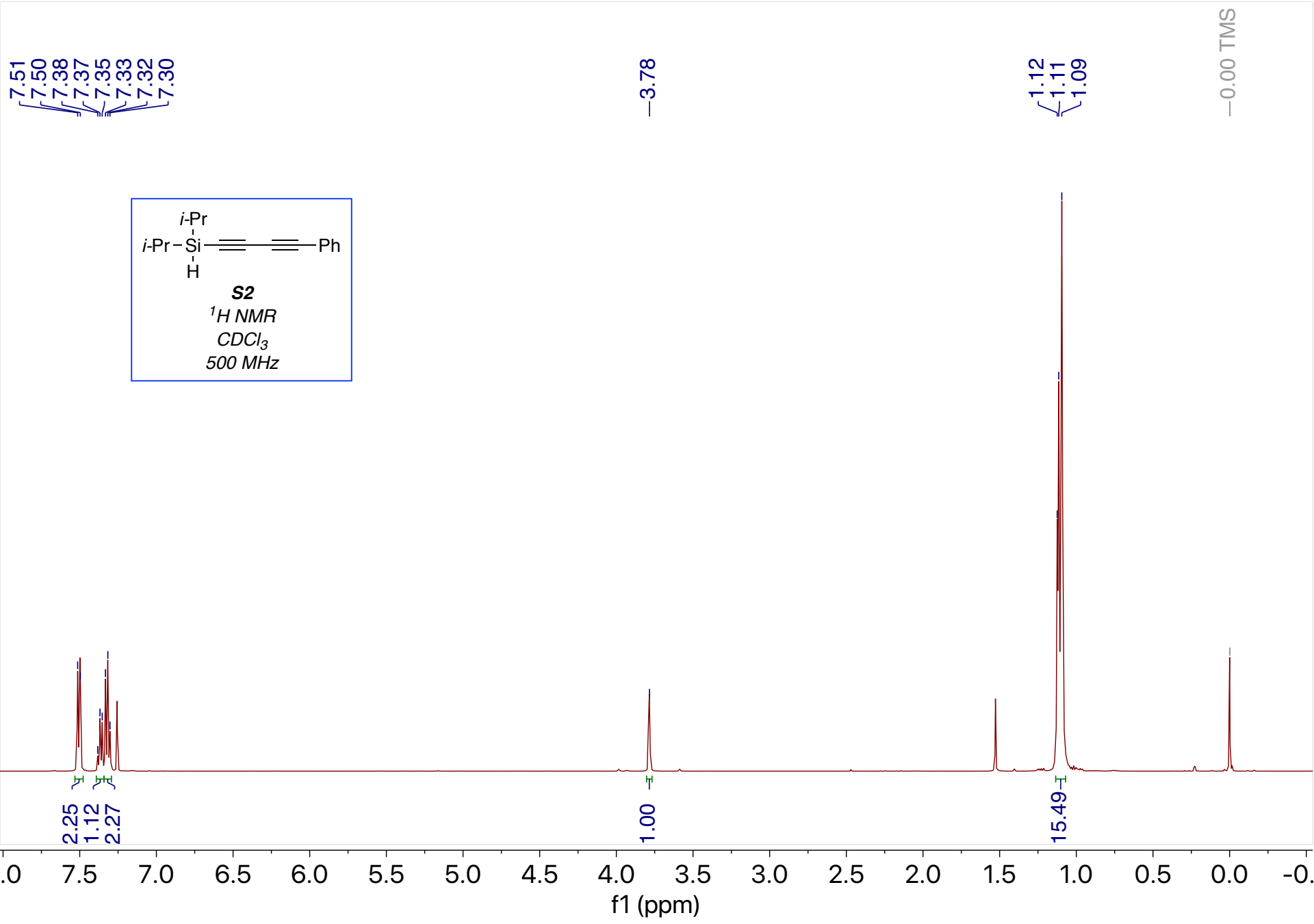
10
0
f1 (ppm)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i-Pr
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H
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1H NMR
CDCl3
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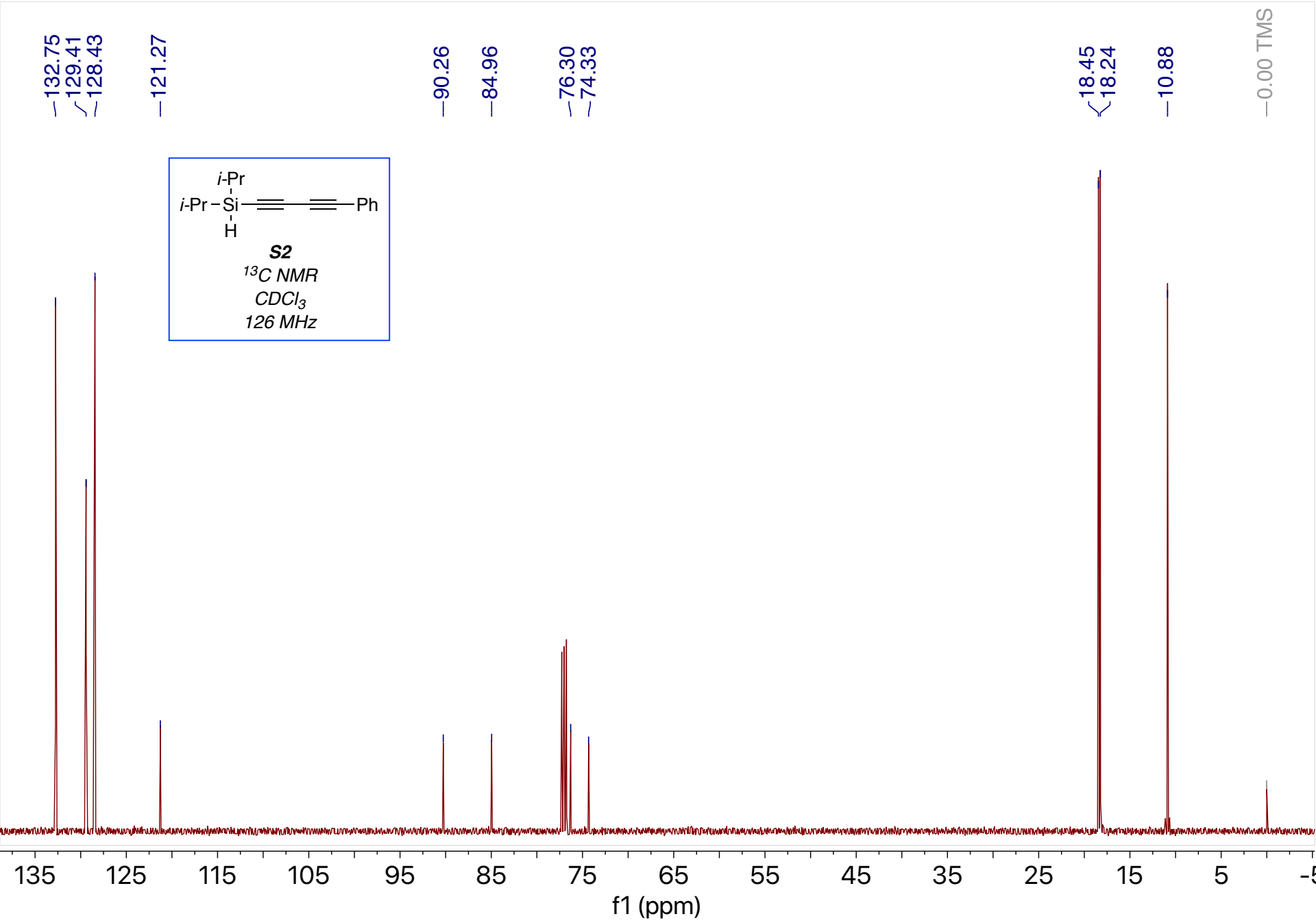
1.12
2.27
1.00
15.49
f1 (ppm)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18.45
18.24
10.88
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i-Pr
i-Pr
Si
H
Ph
S2
13C NMR
CDCl3
126 MHz
135
125
115
105
95
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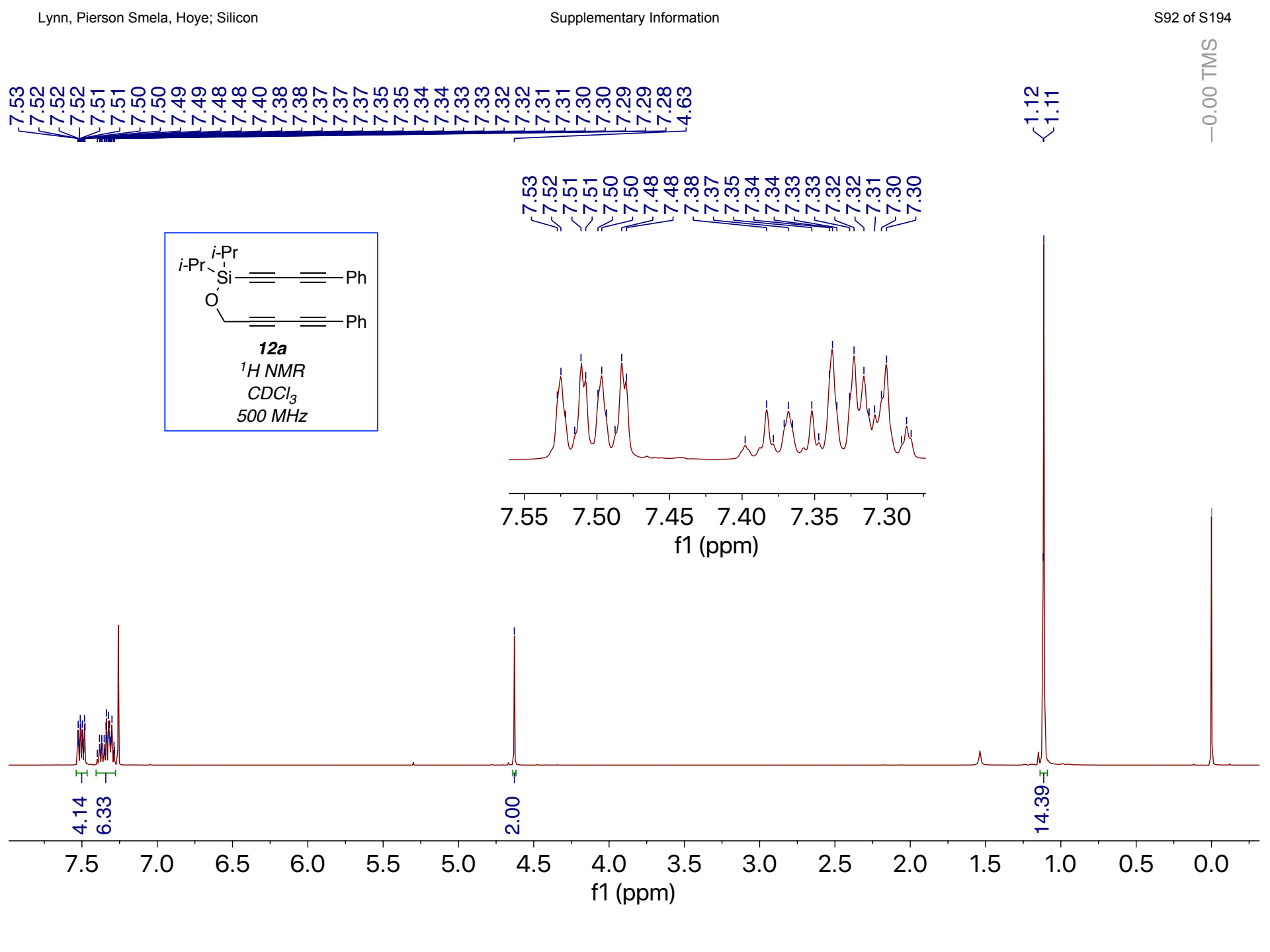
75
65
55
45
35
25
15
5
f1 (ppm)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1.12 1.11
0.00 TMS
i-Pr
i-Pr
Si
O
Ph
Ph
12a
1H NMR
CDCl3
500 MHz
7.53 7.52 7.51 7.51 7.50 7.50 7.48 7.48 7.38 7.37 7.35 7.34 7.34 7.33 7.33 7.32 7.32 7.31 7.30 7.30
7.55 7.50 7.45 7.40 7.35 7.30
f1 (ppm)
4.14 6.33 2.00 14.39
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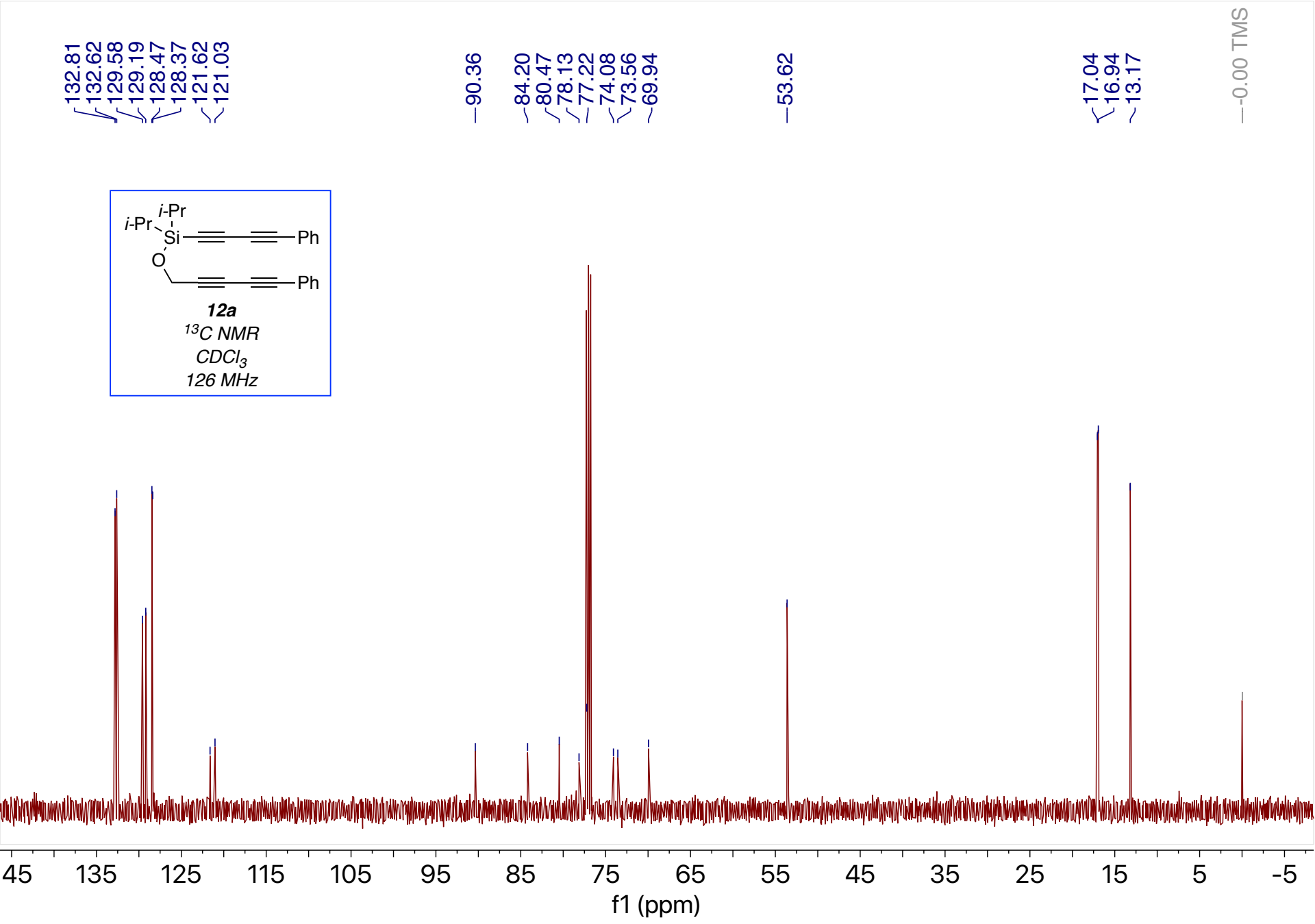
f1 (ppm)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Ph
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CDCl3
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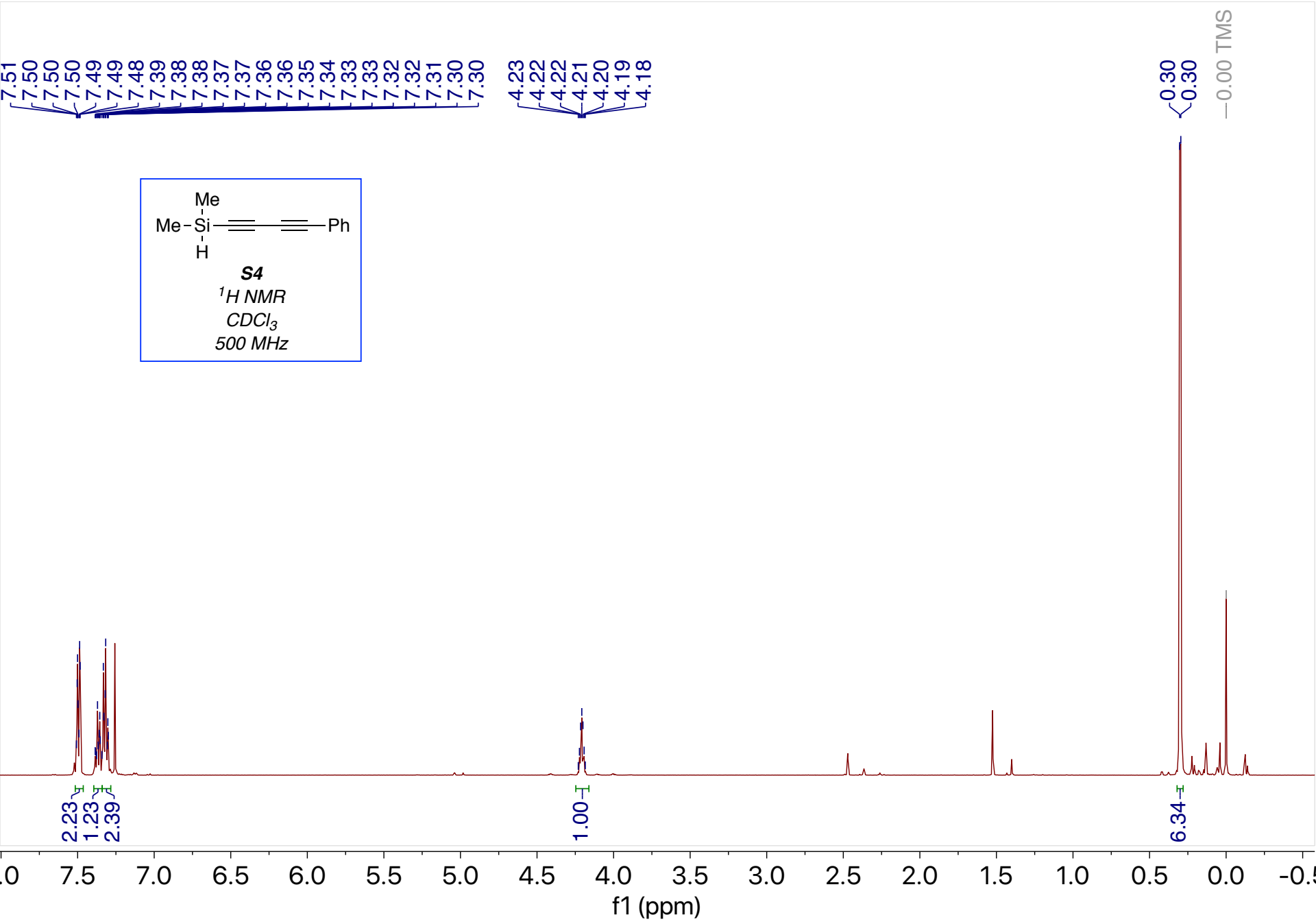
f1 (ppm)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7.30
7.30
4.23
4.22
4.22
4.21
4.20
4.19
4.18
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0.30
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Me
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6.34
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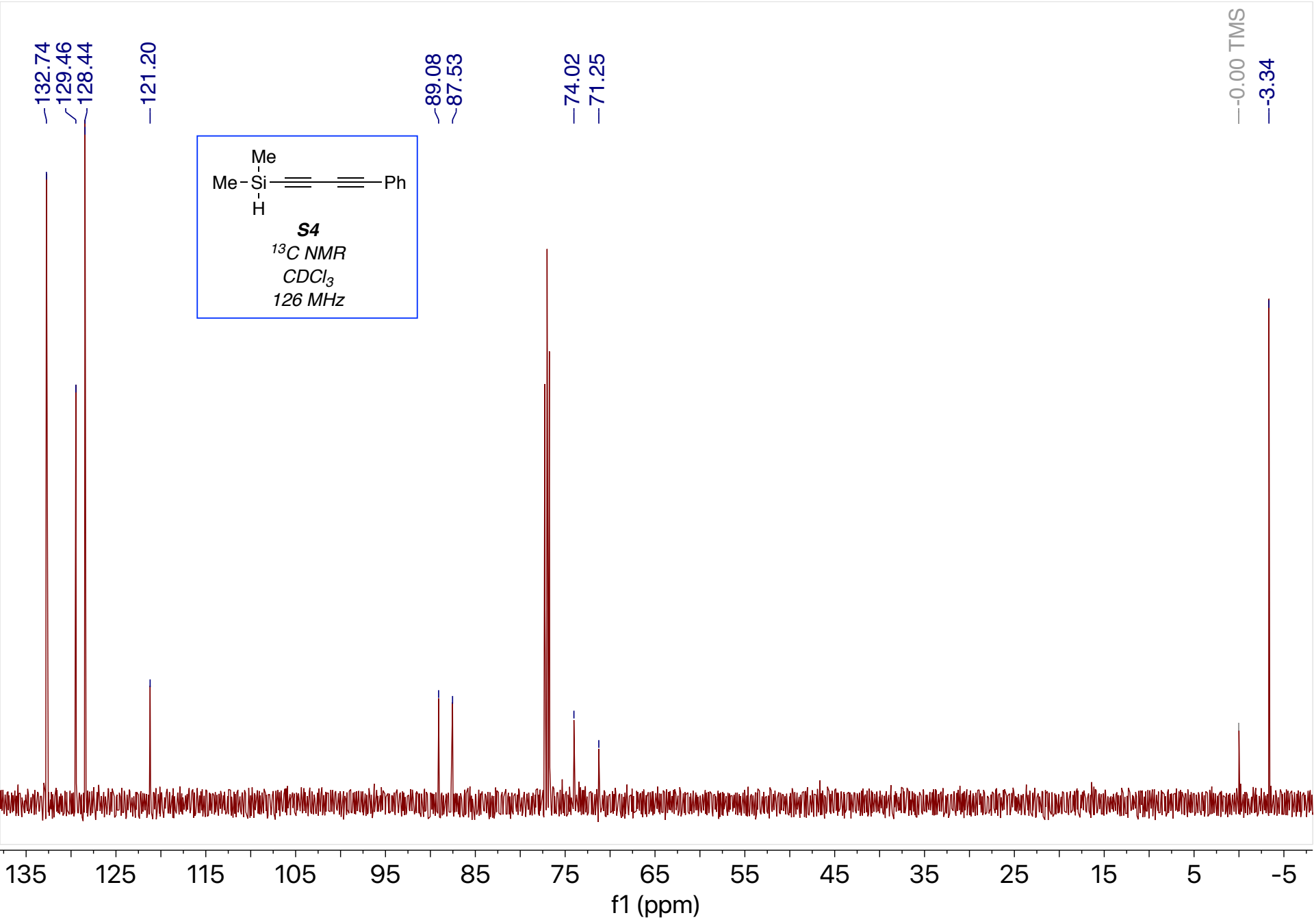
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H
Ph
S4
13C NMR
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125
115
105
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85
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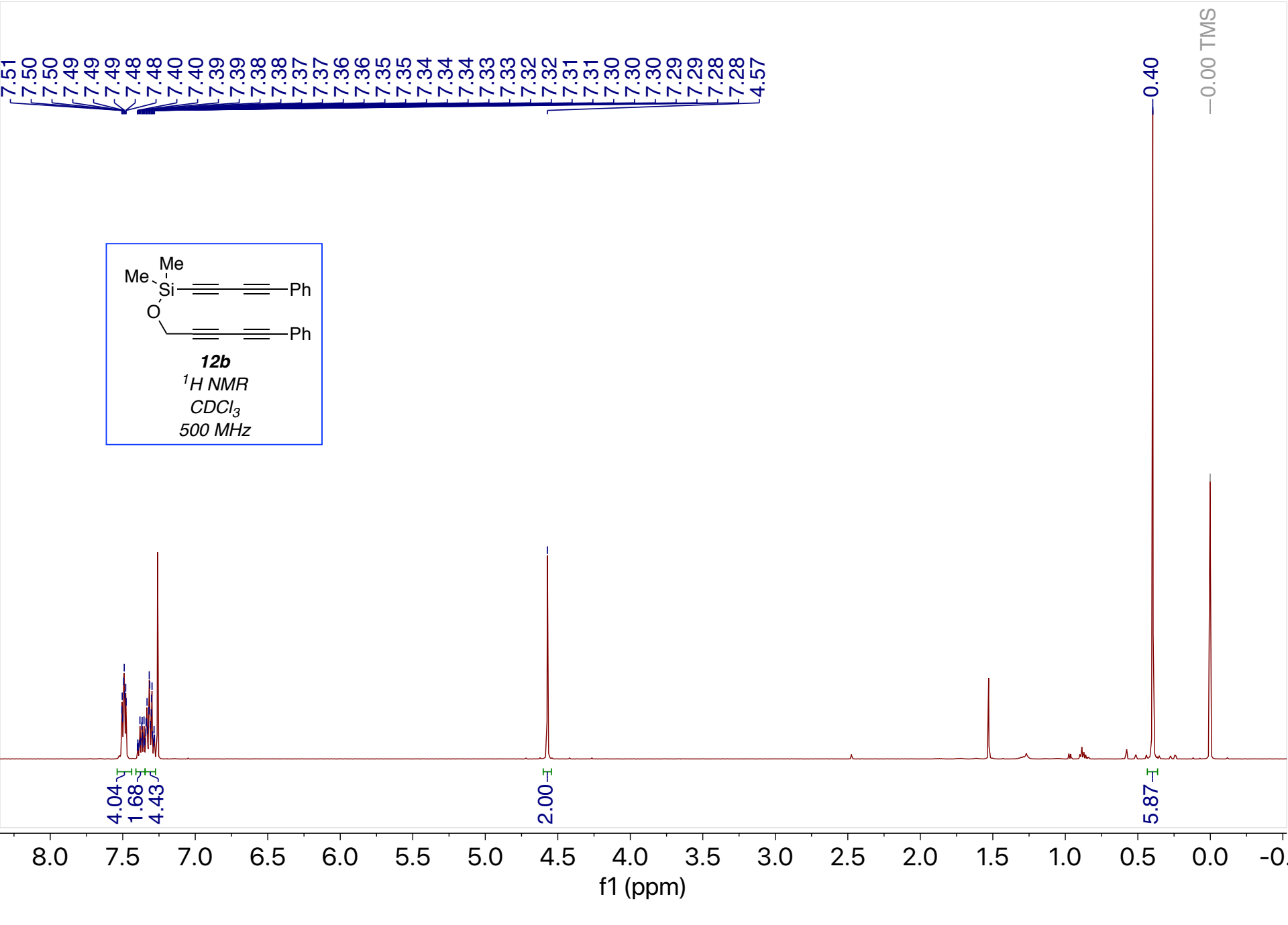
5
-5
f1 (ppm)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7.33
7.32
7.31
7.31
7.30
7.30
7.30
7.29
7.29
7.28
7.28
4.57
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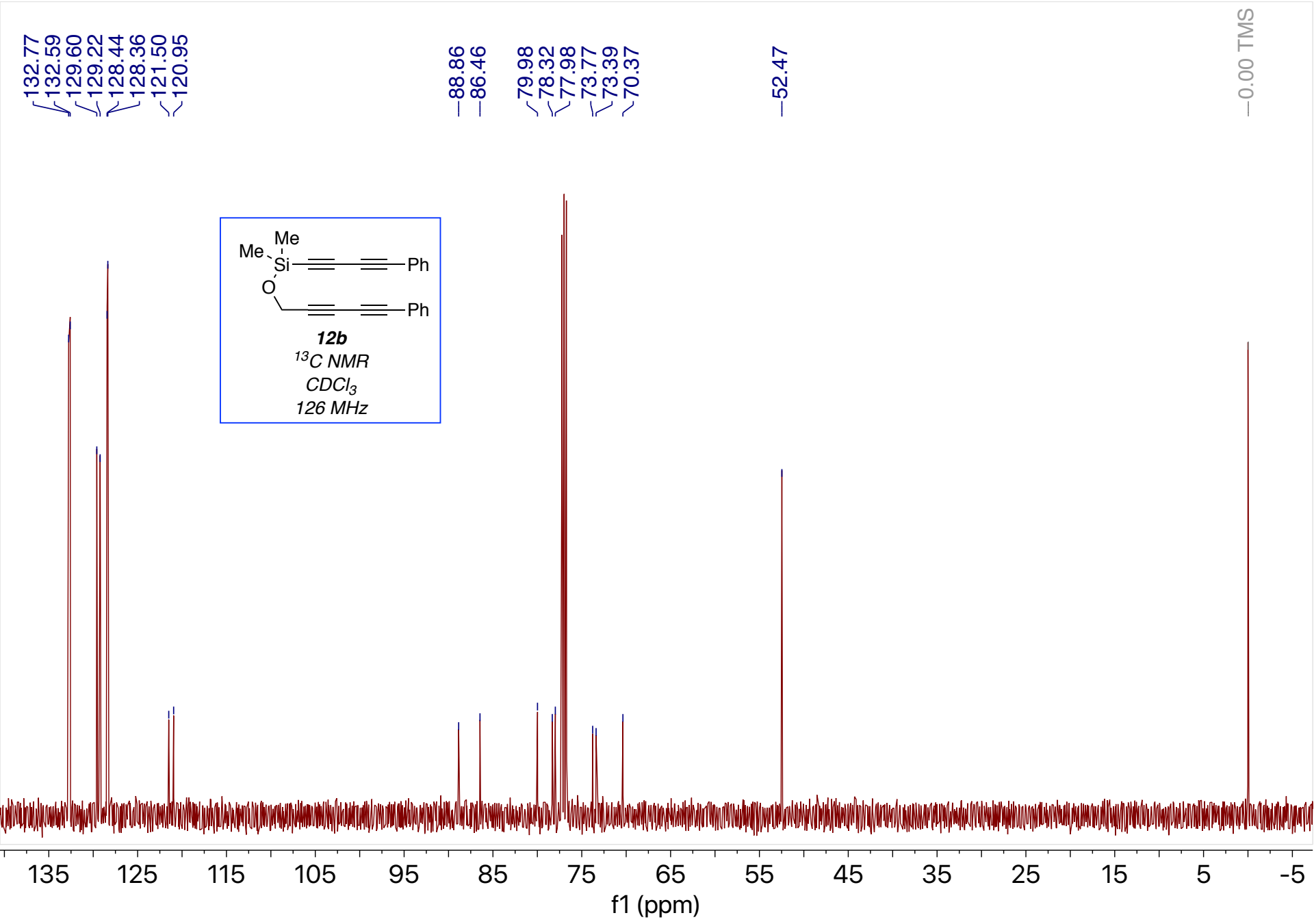
Me
Me
Si
O
Ph
Ph
12b
1H NMR
CDCl3
500 MHz
4.04
1.68
4.43
2.00
5.87
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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77.98
73.77
73.39
70.37
52.47
0.00 TMS
Me
Me
Si
O
Ph
Ph
12b
13C NMR
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125
115
105
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45
35
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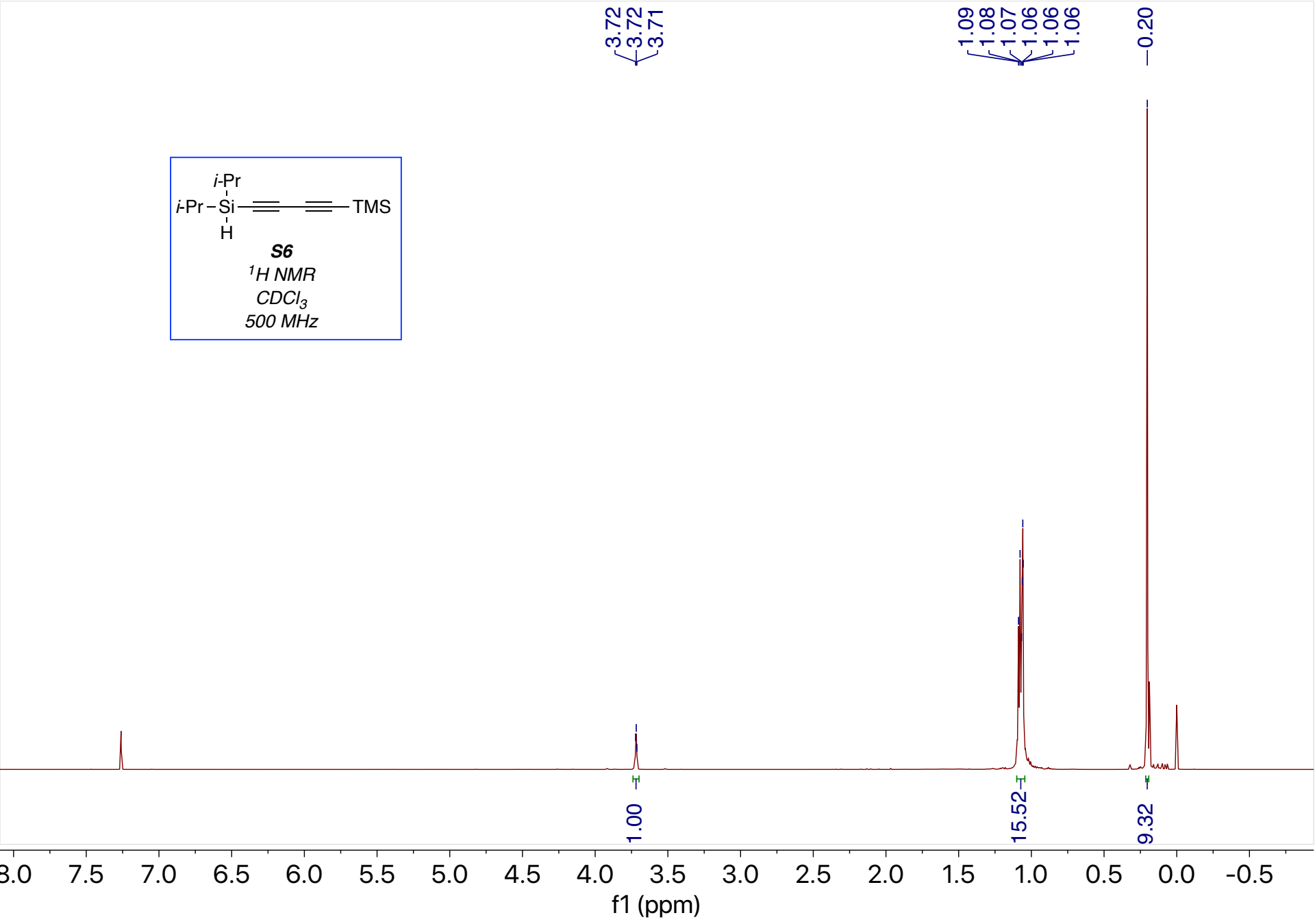
15
5
-5
f1 (ppm)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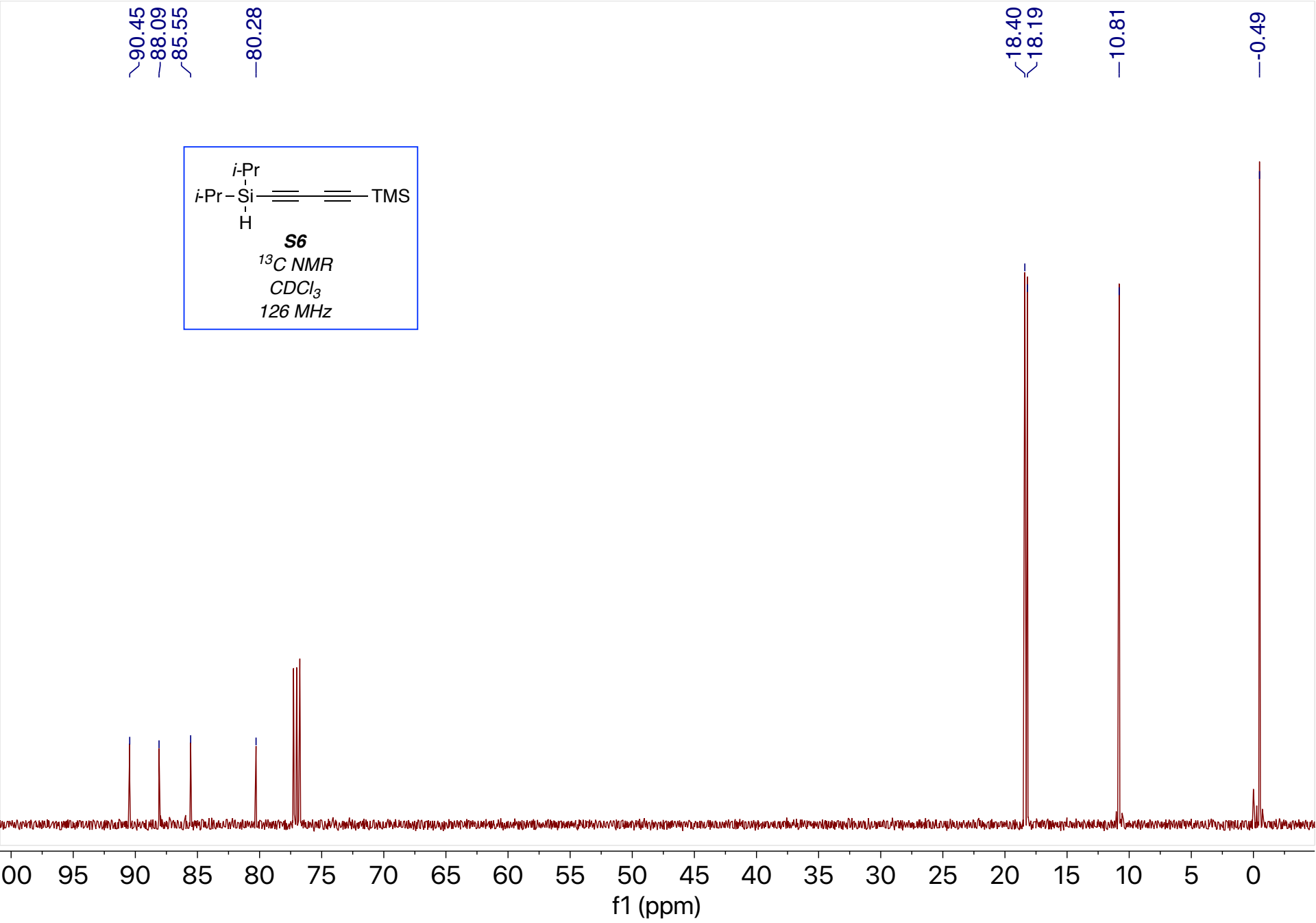
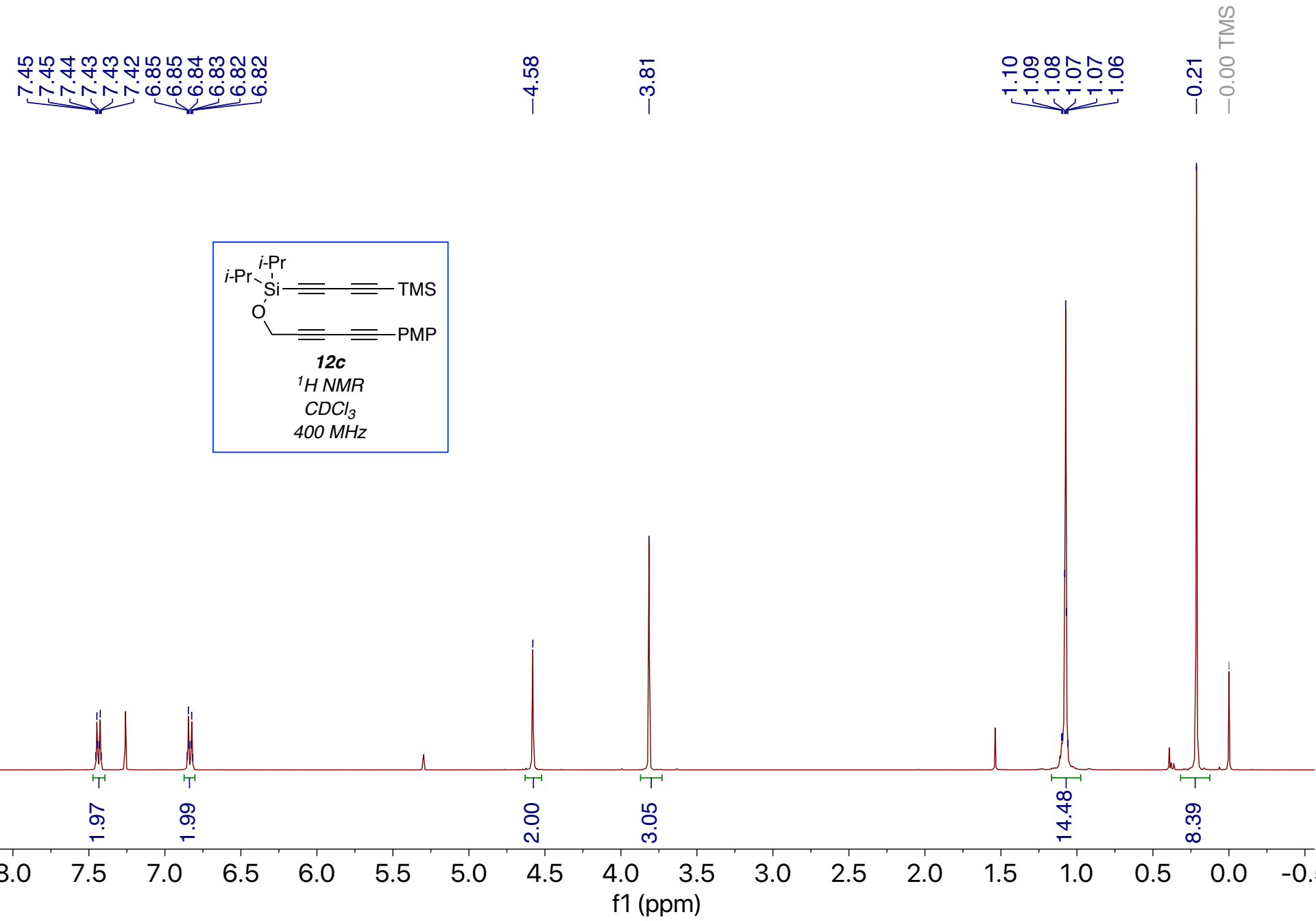
3.71
1.09
1.08
1.07
1.06
1.06
1.06
0.20
i-Pr
i-Pr – Si – TMS
H
S6
1H NMR
CDCl3
500 MHz
1.00
15.52
9.32
f1 (ppm)


90.45
88.09
85.55
80.28
18.40
18.19
10.81
-0.49
i-Pr
i-Pr – Si
H
TMS
S6
13C NMR
CDCl3
126 MHz
00 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)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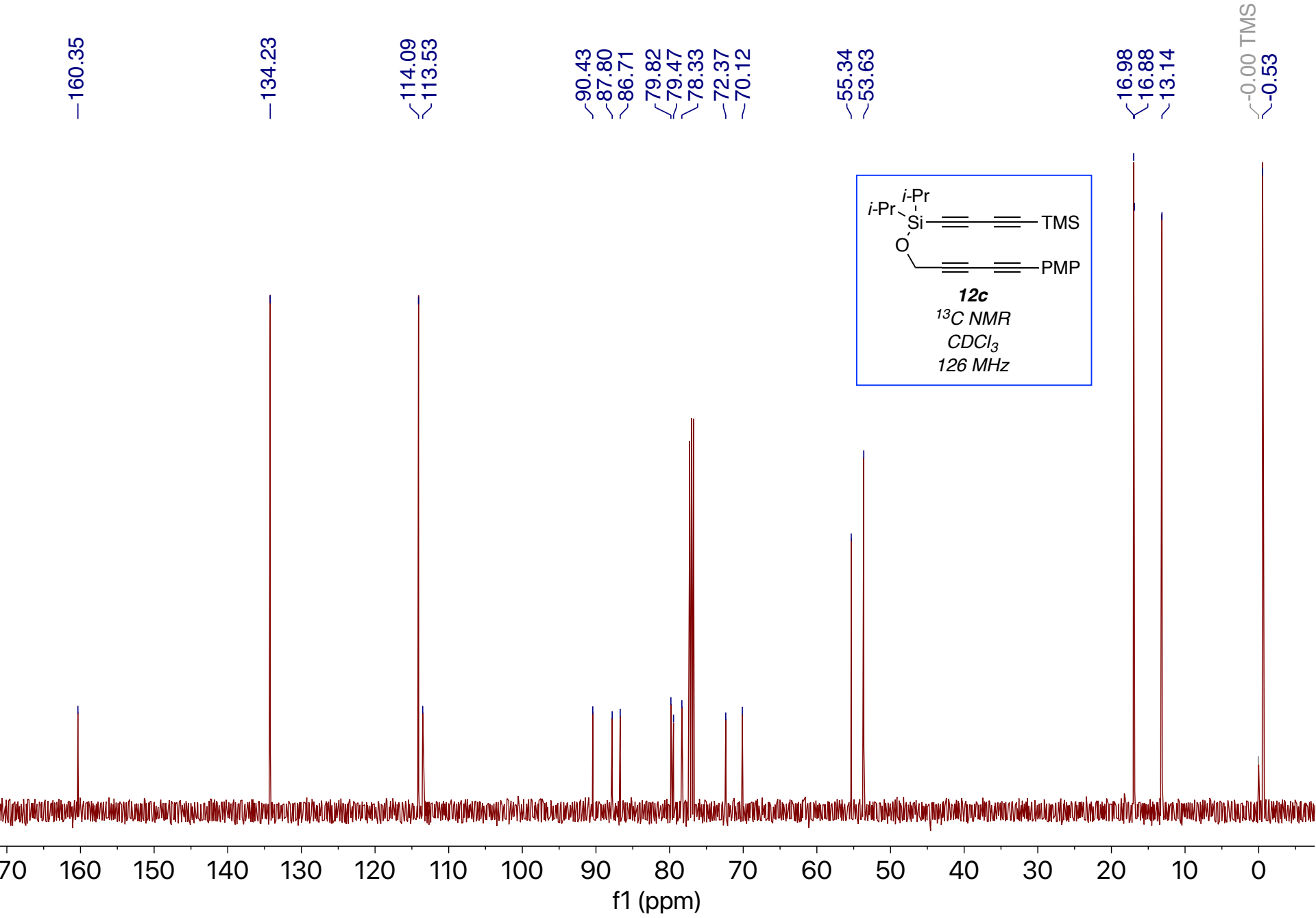
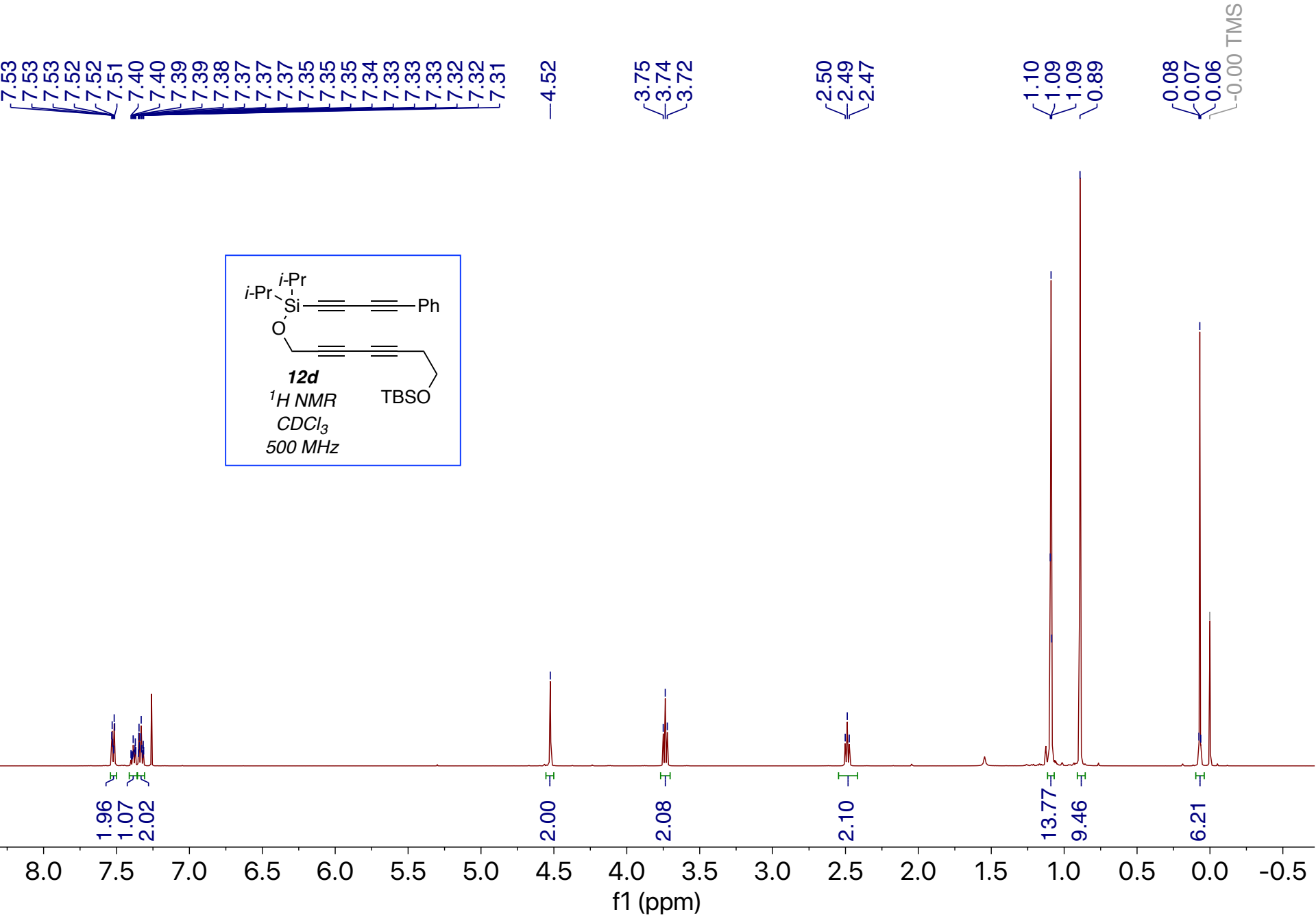
7.45
7.44
7.43
7.43
7.42
6.85
6.85
6.84
6.83
6.82
6.82
4.58
3.81
1.10
1.09
1.08
1.07
1.07
1.06
0.21
0.00 TMS
i-Pr
i-Pr
Si
TMS
O
PMP
12c
1H NMR
CDCl3
400 MHz
1.97
1.99
2.00
3.05
14.48
8.39
f1 (ppm)


160.35
134.23
114.09
113.53
90.43
87.80
86.71
79.82
79.47
78.33
72.37
70.12
55.34
53.63
16.98
16.88
13.14
-0.00 TMS
-0.53
i-Pr
i-Pr
Si
O
TMS
PMP
12c
13C NMR
CDCl3
126 MHz
f1 (ppm)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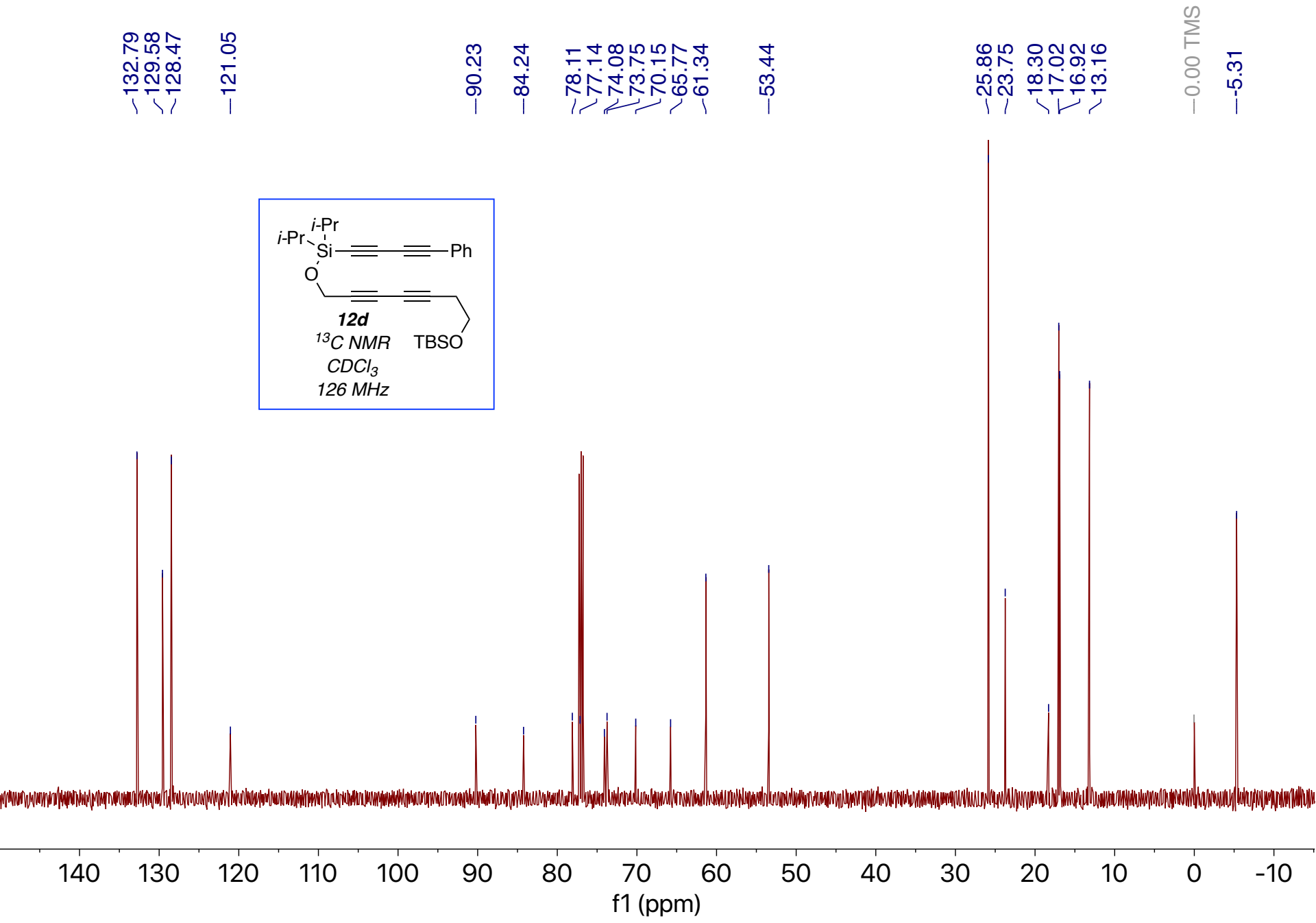
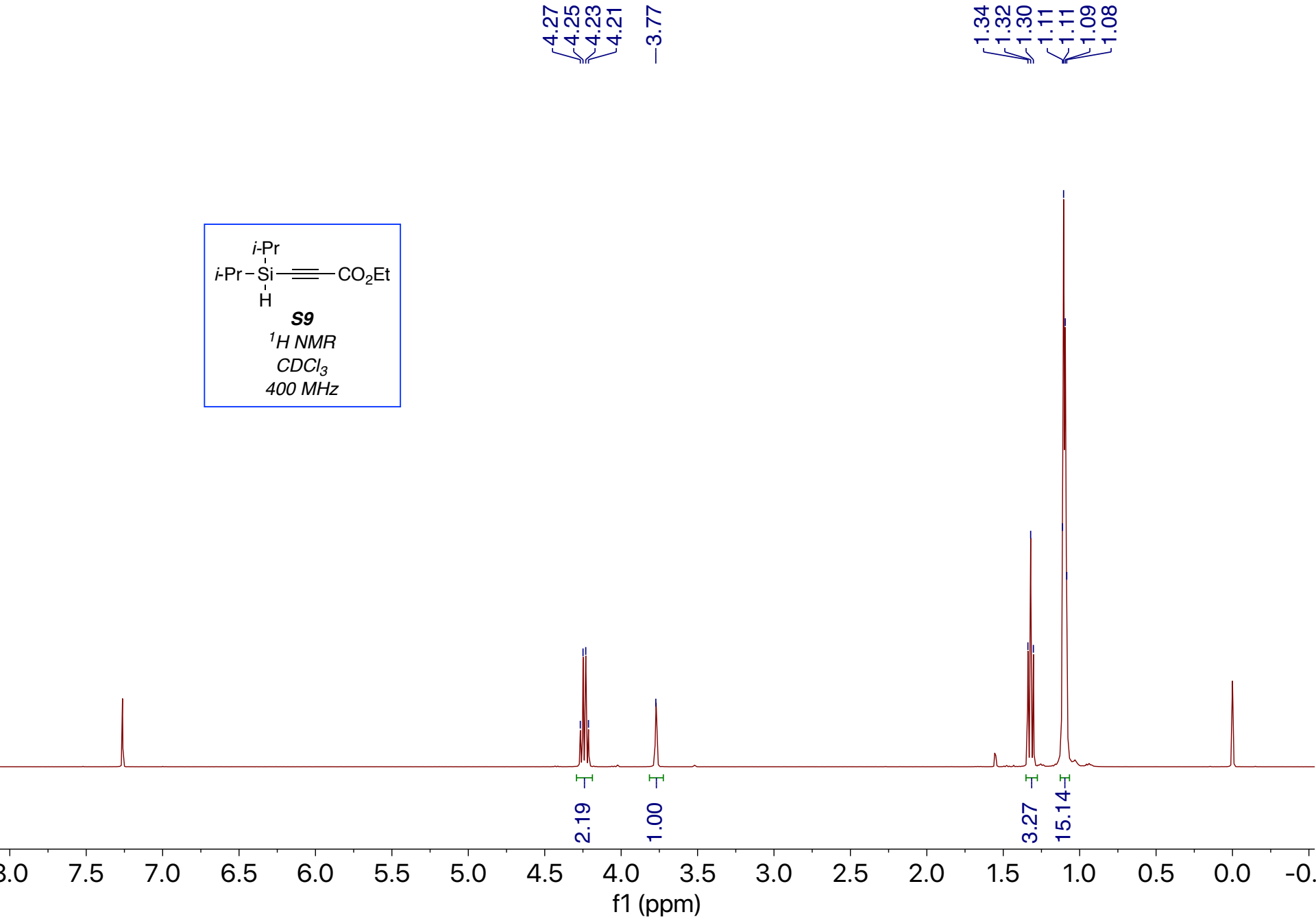
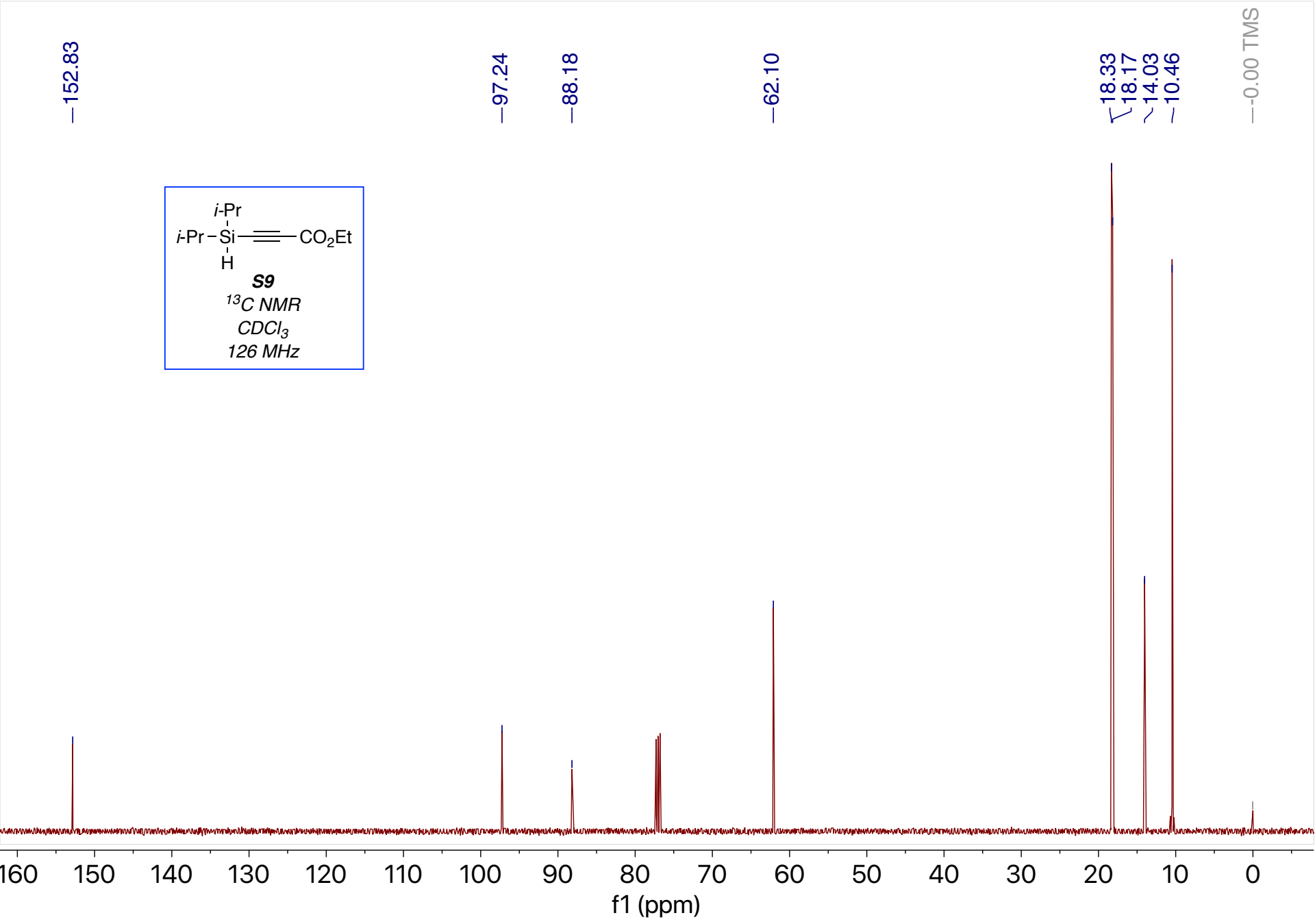
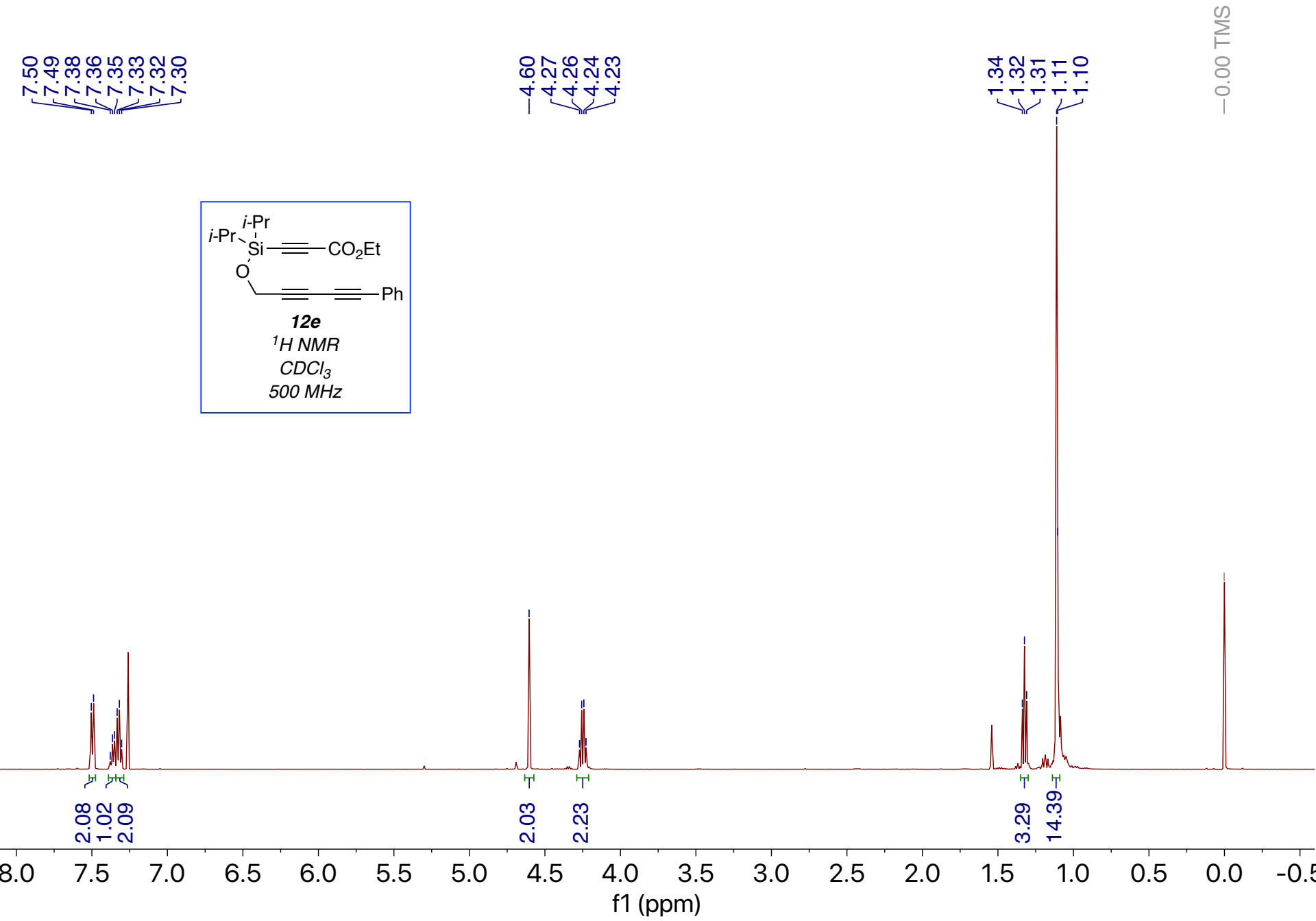
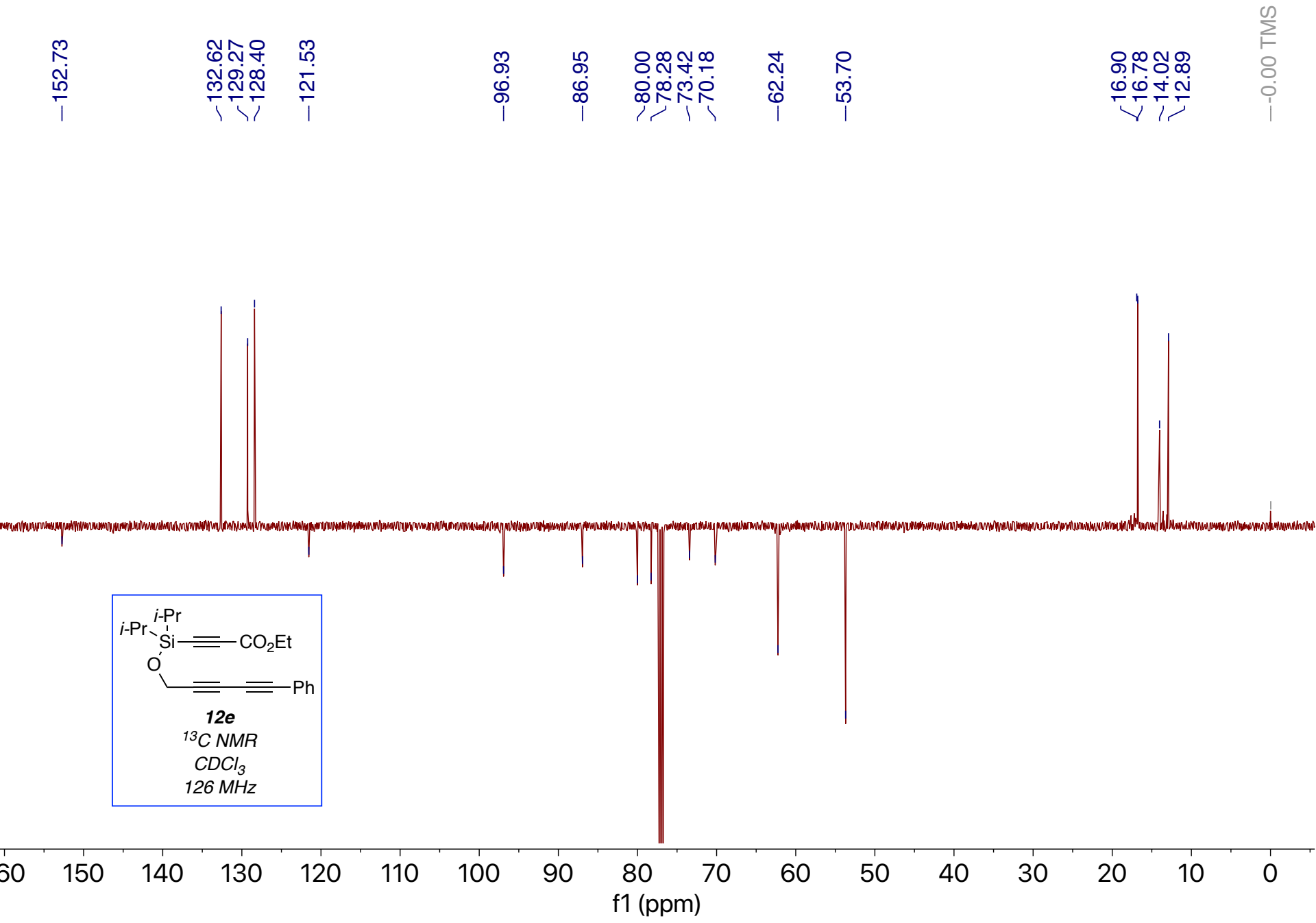
7.53
7.53
7.52
7.52
7.51
7.40
7.40
7.39
7.39
7.38
7.37
7.37
7.37
7.35
7.35
7.35
7.34
7.33
7.33
7.33
7.32
7.32
7.31
4.52
3.75
3.74
3.72
2.50
2.49
2.47
1.10
1.09
1.09
0.89
0.08
0.07
0.06
-0.00 TMS
i-Pr
i-Pr
Si
Ph
O
12d
1H NMR
CDCl3
500 MHz
TBSO
1.96
1.07
2.02
2.00
2.08
2.10
13.77
9.46
6.21
8.0
7.5
7.0
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
f1 (ppm)

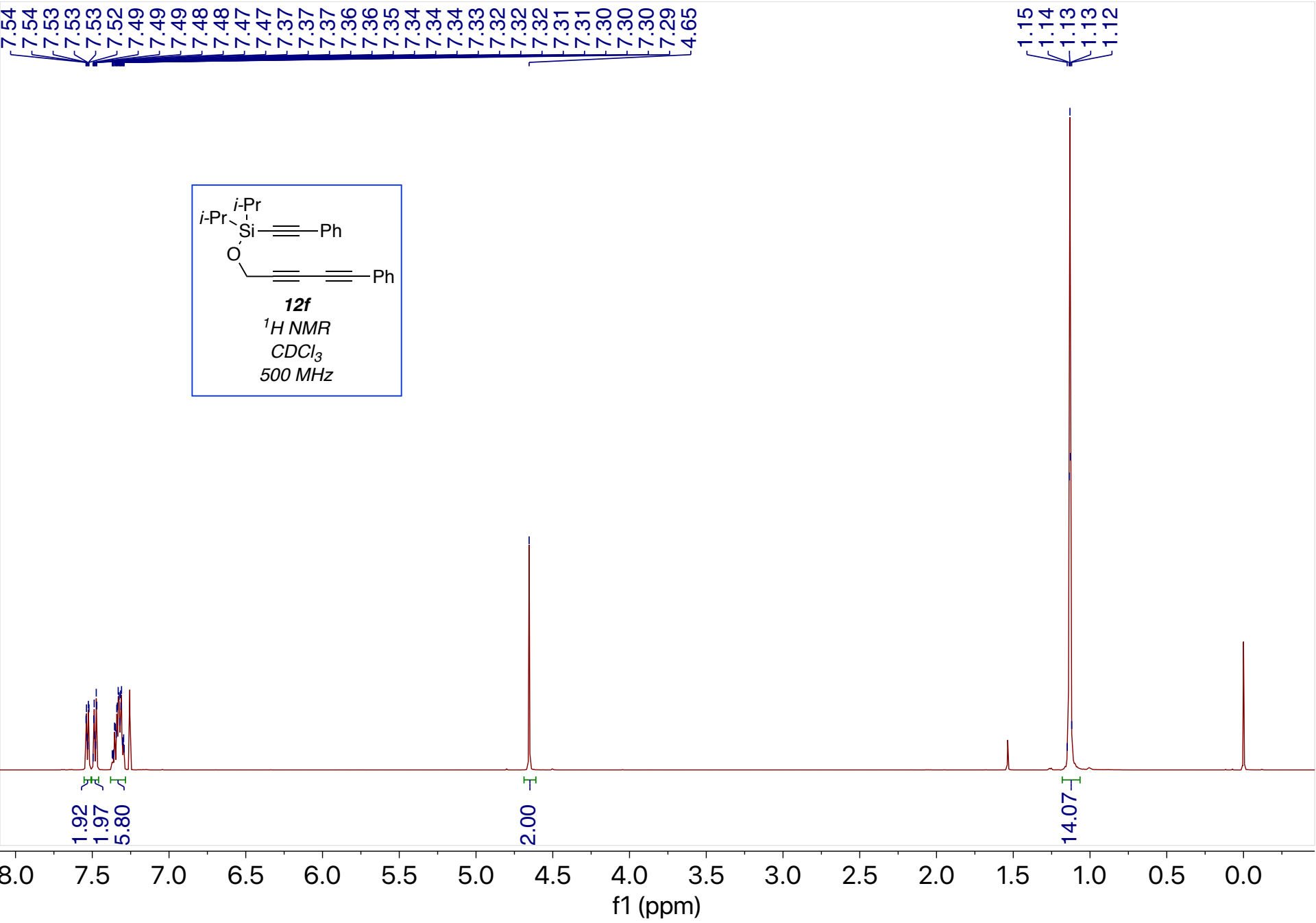

132.79
129.58
128.47
121.05
90.23
84.24
78.11
77.14
74.08
73.75
70.15
65.77
61.34
53.44
25.86
23.75
18.30
17.02
16.92
13.16
0.00 TMS
-5.31
i-Pr
i-Pr
Si
Ph
O
12d
13C NMR
CDCl3
126 MHz
TBSO
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


4.27
4.25
4.23
4.21
3.77
1.34
1.32
1.30
1.11
1.11
1.09
1.08
i-Pr
i-Pr – Si — ≡ — CO2Et
H
S9
1H NMR
CDCl3
400 MHz
2.19
1.00
3.27
15.14
f1 (ppm)


152.83
97.24
88.18
62.10
18.33
18.17
14.03
10.46
-0.00 TMS
i-Pr
i-Pr
Si
H
CO2Et
S9
13C NMR
CDCl3
126 MHz
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.50
7.49
7.38
7.36
7.35
7.33
7.32
7.30
4.60
4.27
4.26
4.24
4.23
1.34
1.32
1.31
1.11
1.10
0.00 TMS
i-Pr
i-Pr
Si
CO2Et
O
Ph
12e
1H NMR
CDCl3
500 MHz
2.08
1.02
2.09
2.03
2.23
3.29
14.39
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
f1 (ppm)


152.73
132.62
129.27
128.40
121.53
96.93
86.95
80.00
78.28
73.42
70.18
62.24
53.70
16.90
16.78
14.02
12.89
0.00 TMS
i-Pr
i-Pr
Si
CO2Et
O
Ph
12e
13C NMR
CDCl3
126 MHz
60
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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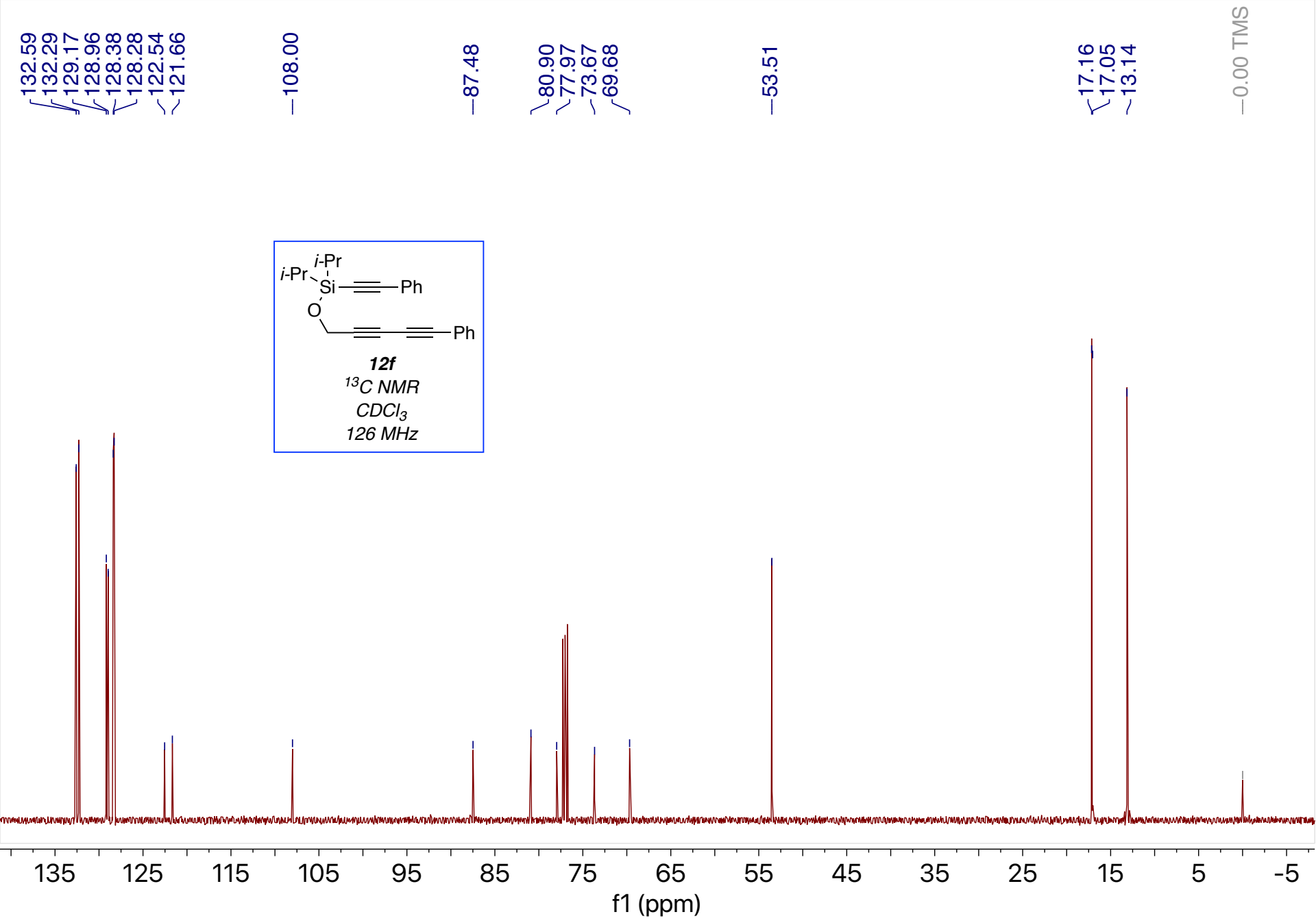
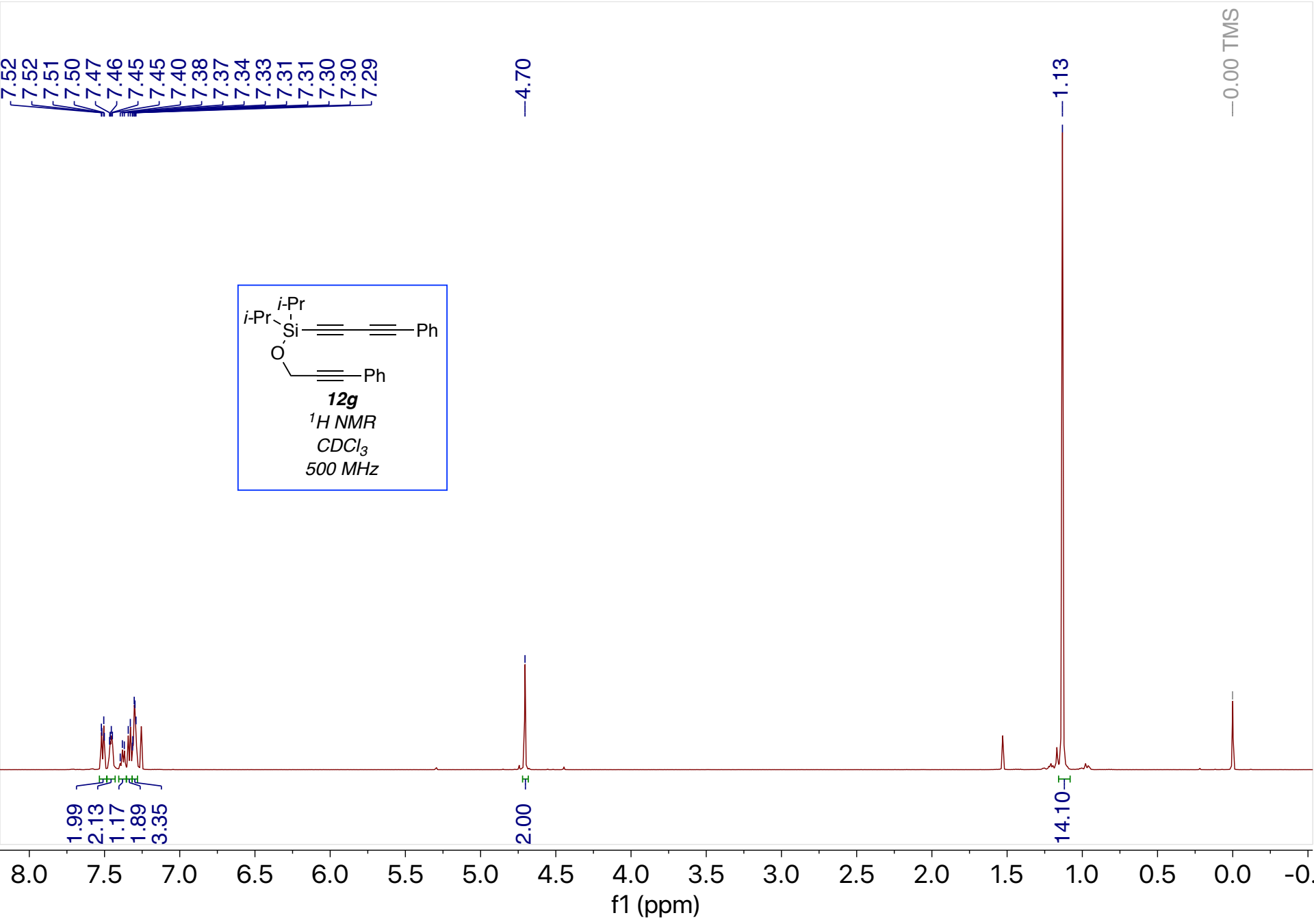
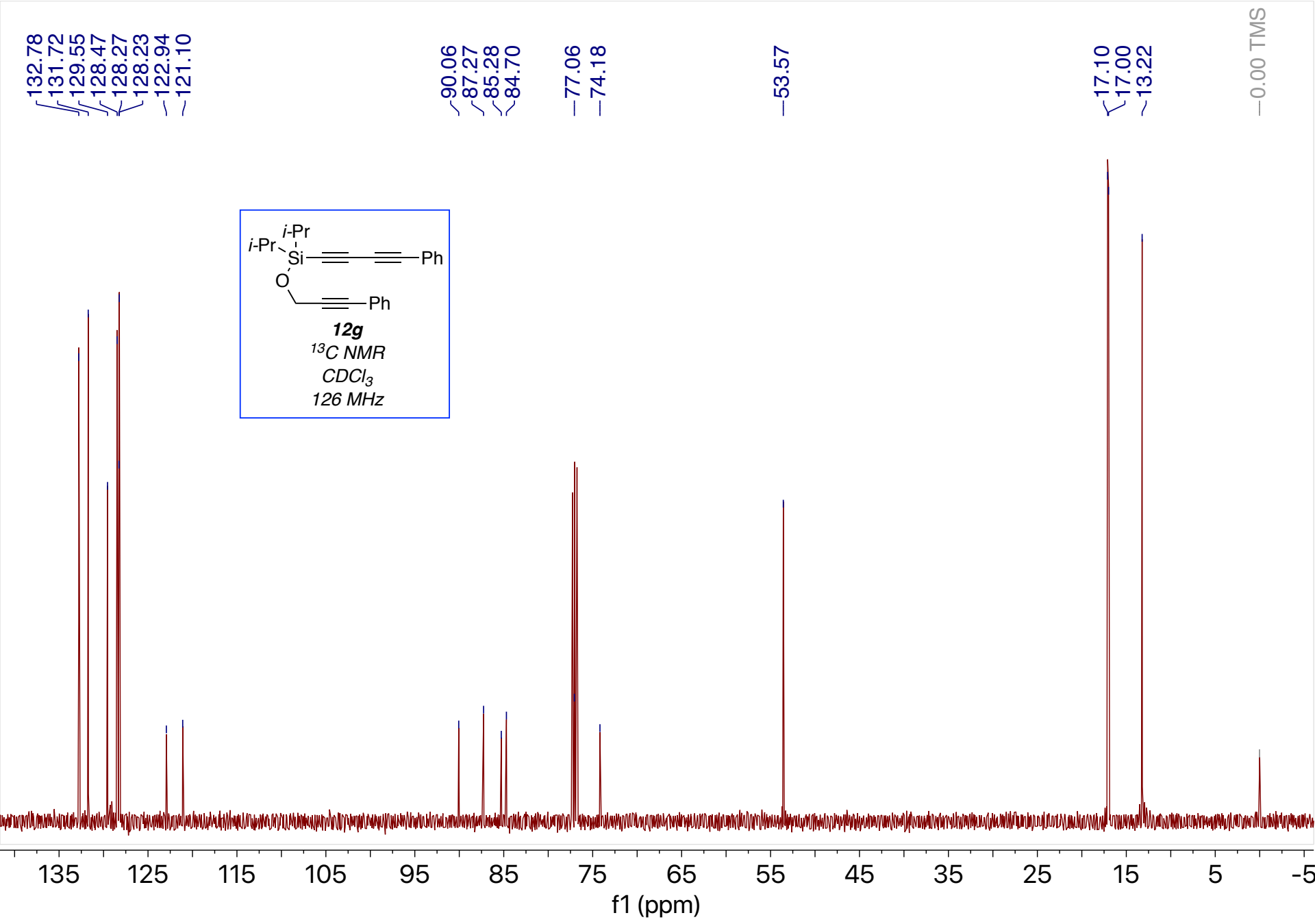
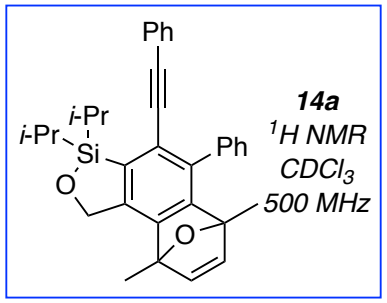
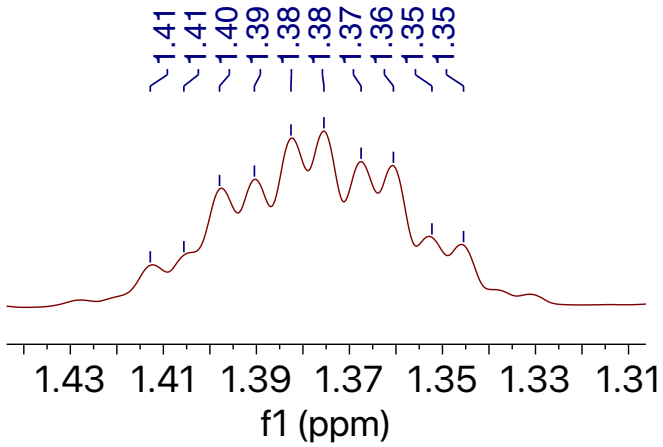
7.54
7.53
7.53
7.53
7.52
7.49
7.49
7.49
7.48
7.48
7.47
7.47
7.37
7.37
7.37
7.36
7.36
7.35
7.34
7.34
7.34
7.33
7.32
7.32
7.32
7.31
7.31
7.30
7.30
7.30
7.29
4.65
1.15
1.14
1.13
1.13
1.12
i-Pr
i-Pr
Si
Ph
O
Ph
12f
1H NMR
CDCl3
500 MHz
1.92
1.97
5.80
2.00
14.07
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


132.59
132.29
129.17
128.96
128.38
128.28
122.54
121.66
108.00
87.48
80.90
77.97
73.67
69.68
53.51
17.16
17.05
13.14
0.00 TMS
i-Pr
i-Pr
Si
Ph
O
Ph
12f
13C NMR
CDCl3
126 MHz
135
125
115
105
95
85
75
65
55
45
35
25
15
5
-5
f1 (ppm)

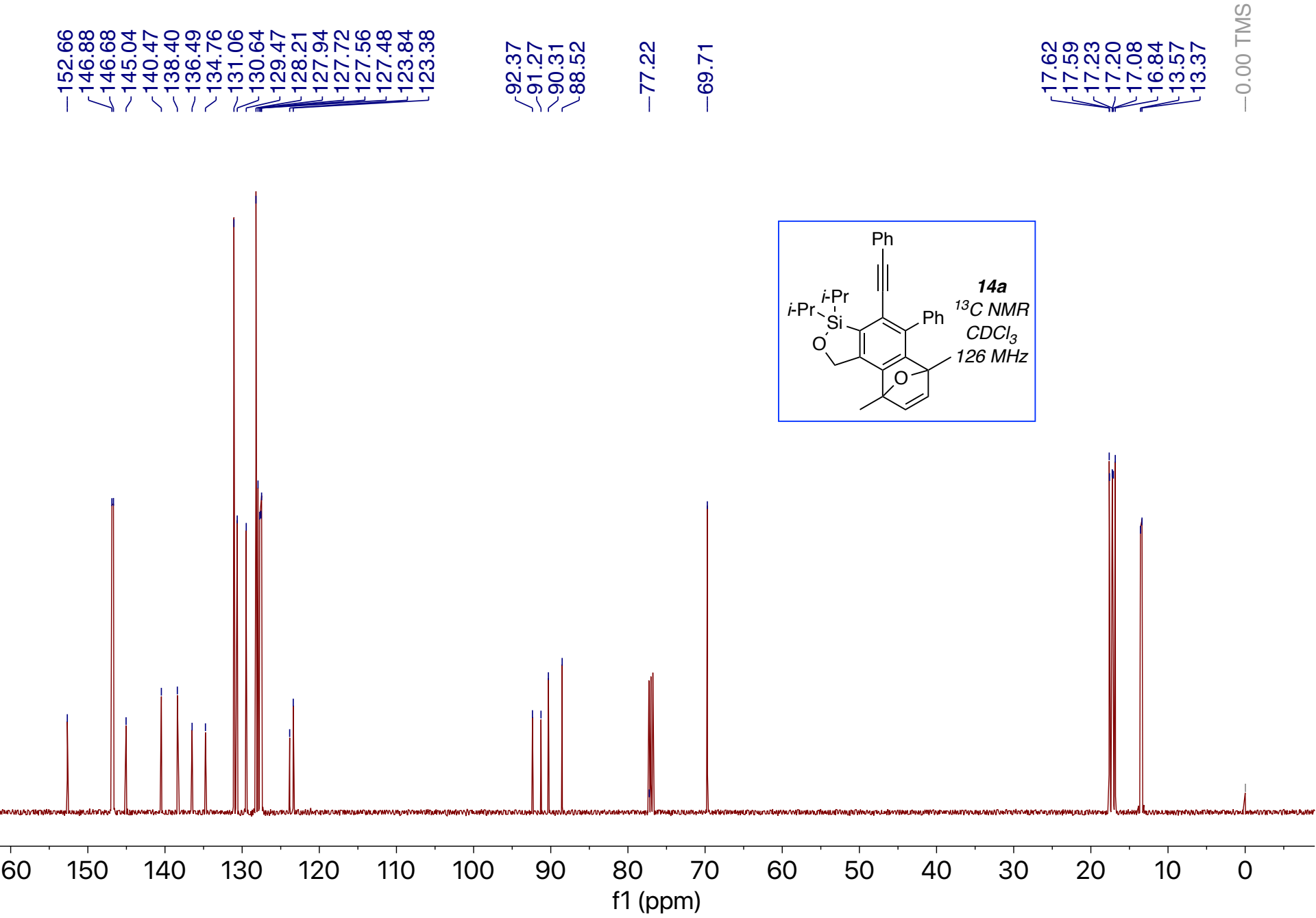

7.52
7.52
7.51
7.50
7.47
7.46
7.45
7.45
7.40
7.38
7.37
7.34
7.33
7.31
7.31
7.30
7.30
7.29
4.70
1.13
0.00 TMS
i-Pr
i-Pr
Si
Ph
O
Ph
12g
1H NMR
CDCl3
500 MHz
1.99
2.13
1.17
1.89
3.35
2.00
14.10
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

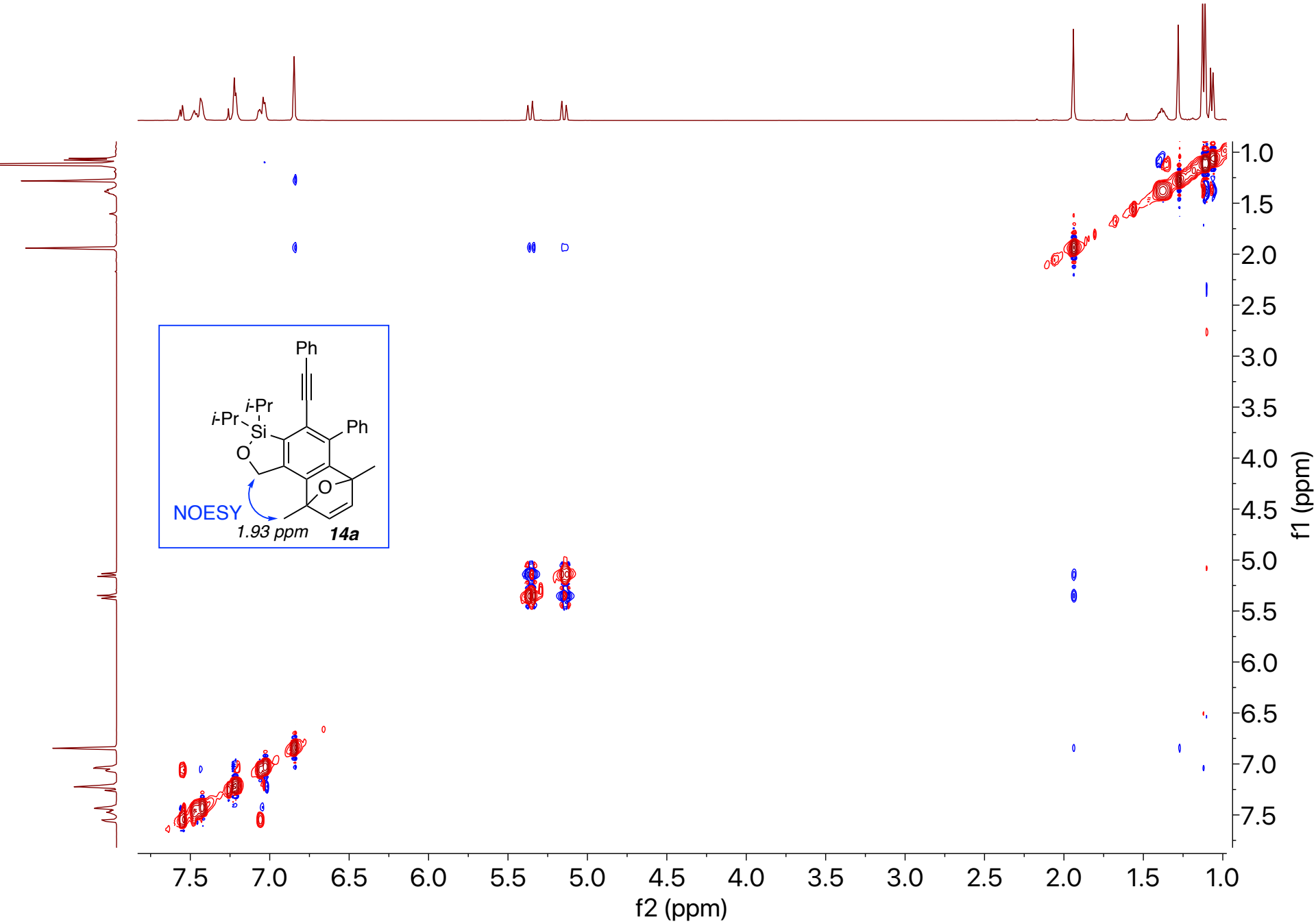

132.78
131.72
129.55
128.47
128.27
128.23
122.94
121.10
90.06
87.27
85.28
84.70
77.06
74.18
53.57
17.10
17.00
13.22
0.00 TMS
i-Pr
i-Pr
Si
Ph
O
Ph
12g
13C NMR
CDCl3
126 MHz
135
125
115
105
95
85
75
65
55
45
35
25
15
5
-5
f1 (ppm)

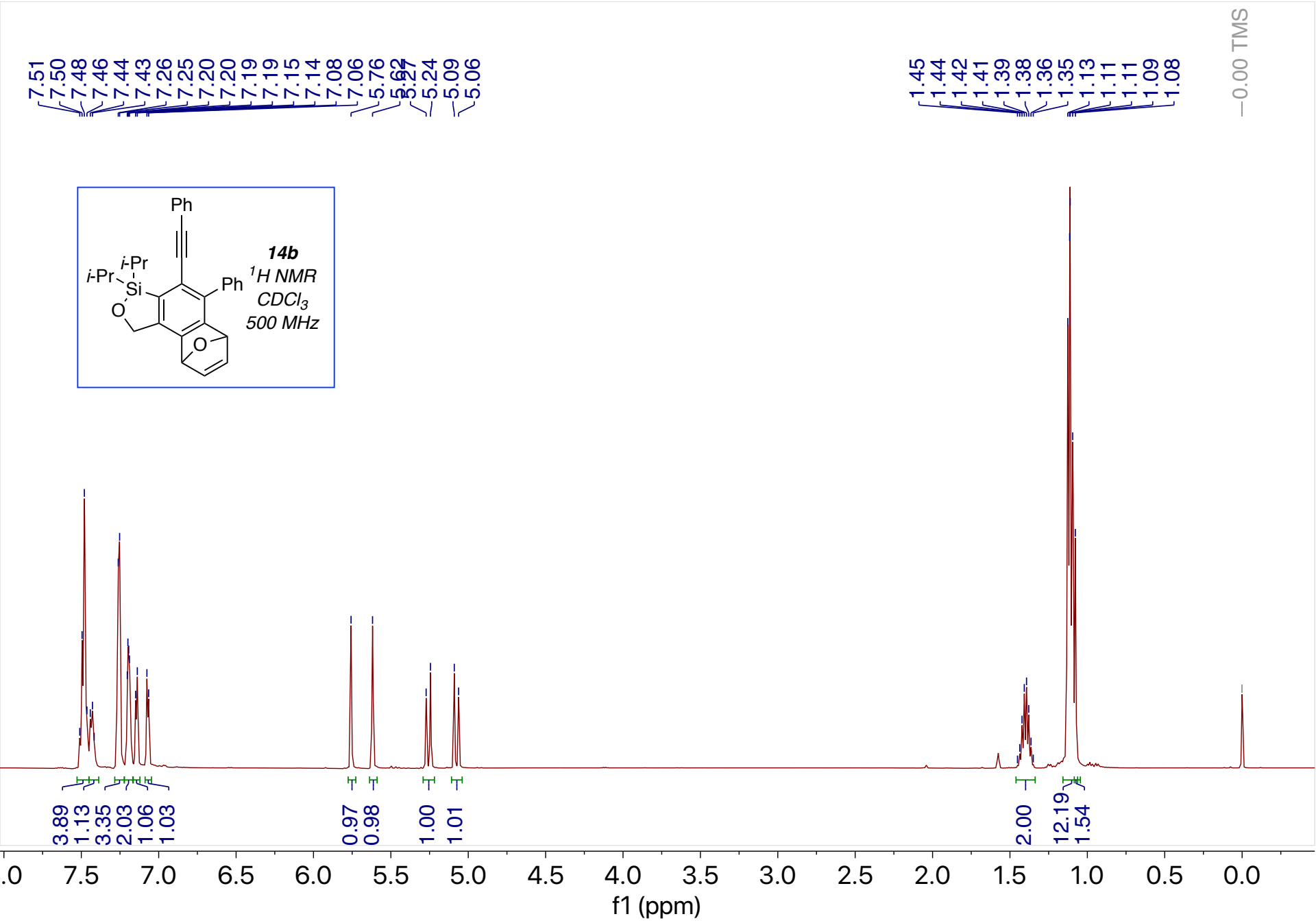

Ph
i-Pr
i-Pr
Si
Ph
O
O
14a
1H NMR
CDCl3
500 MHz

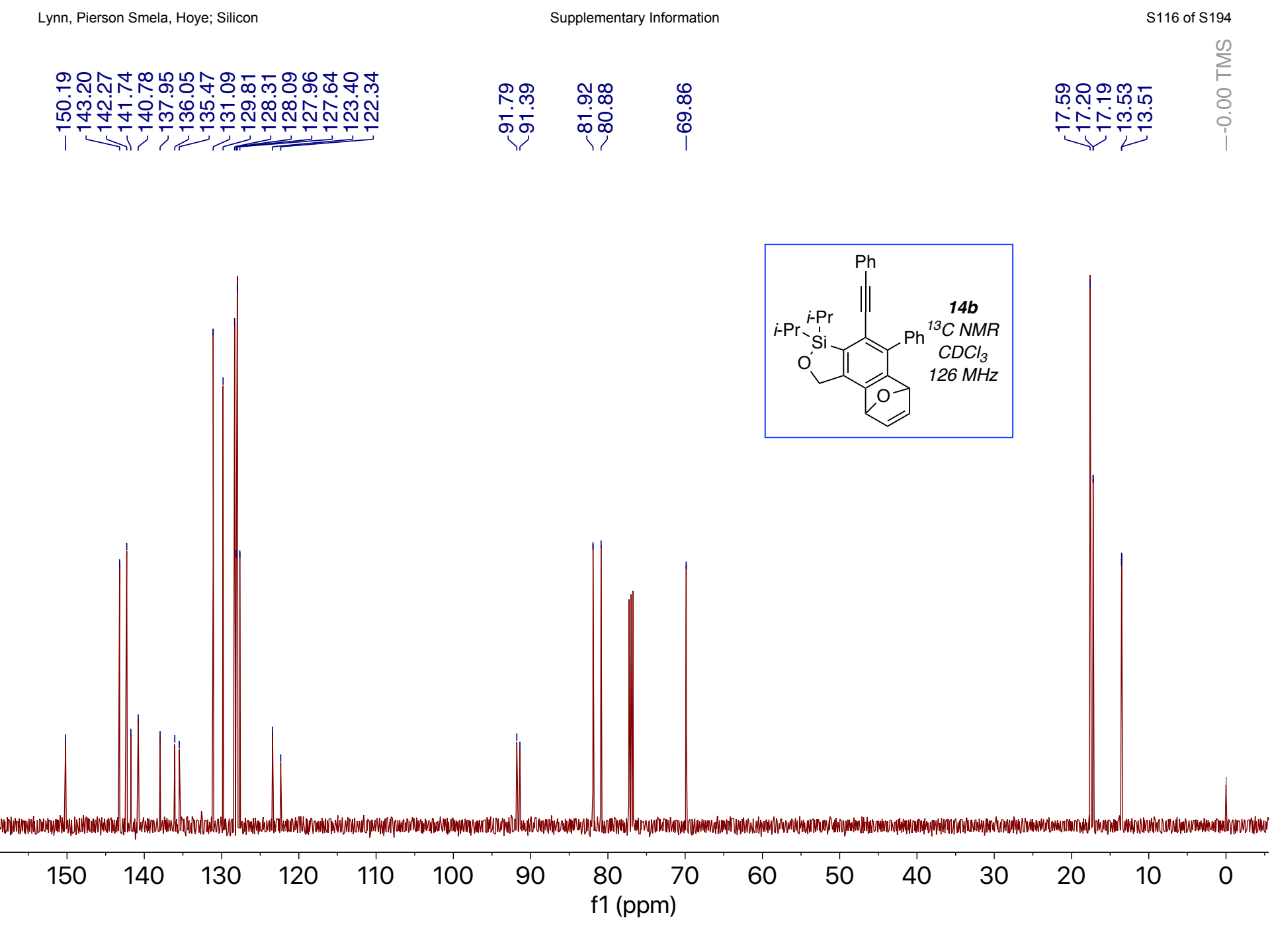

1.43 1.41 1.39 1.37 1.35 1.33 1.31
f1 (ppm)

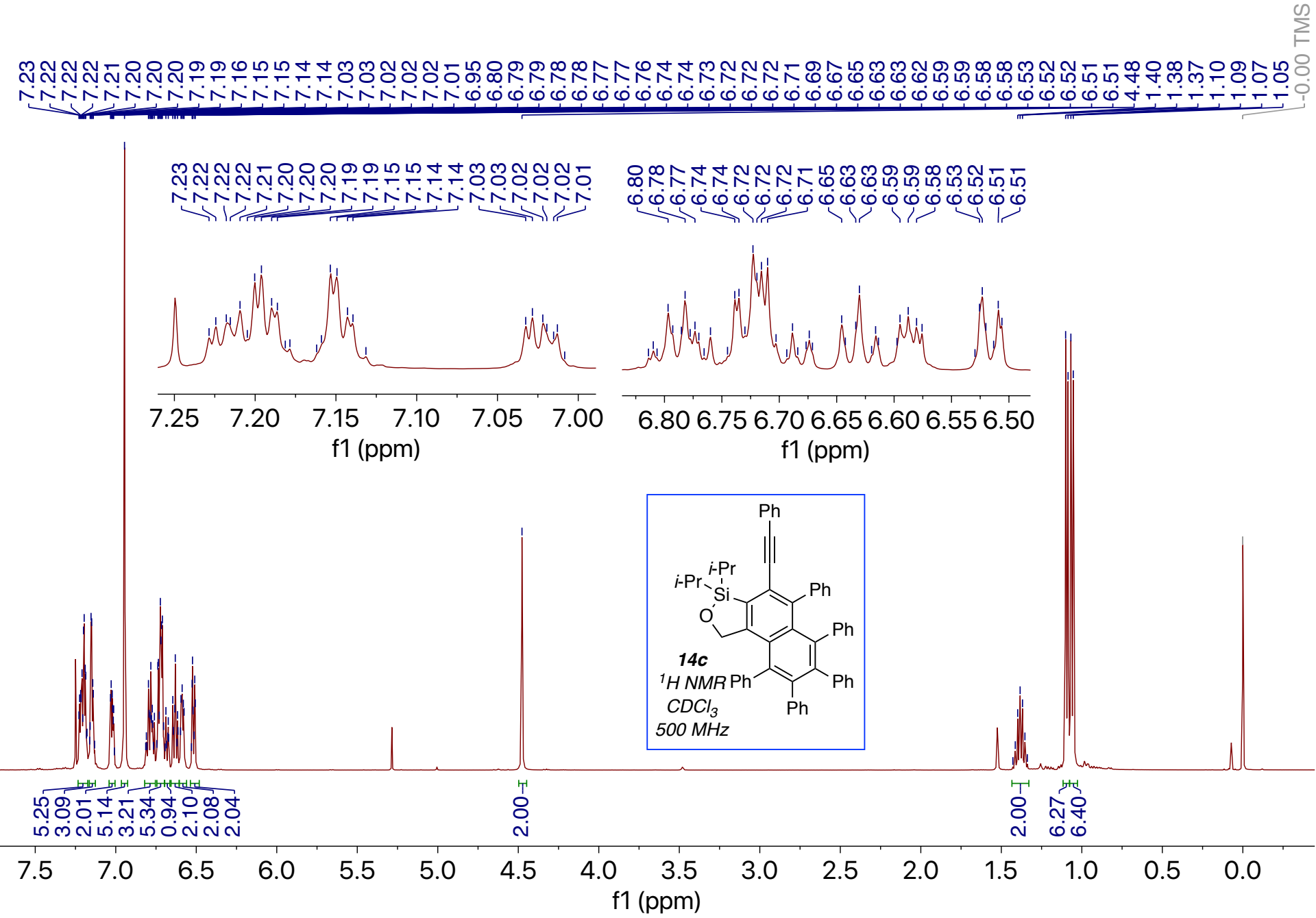
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

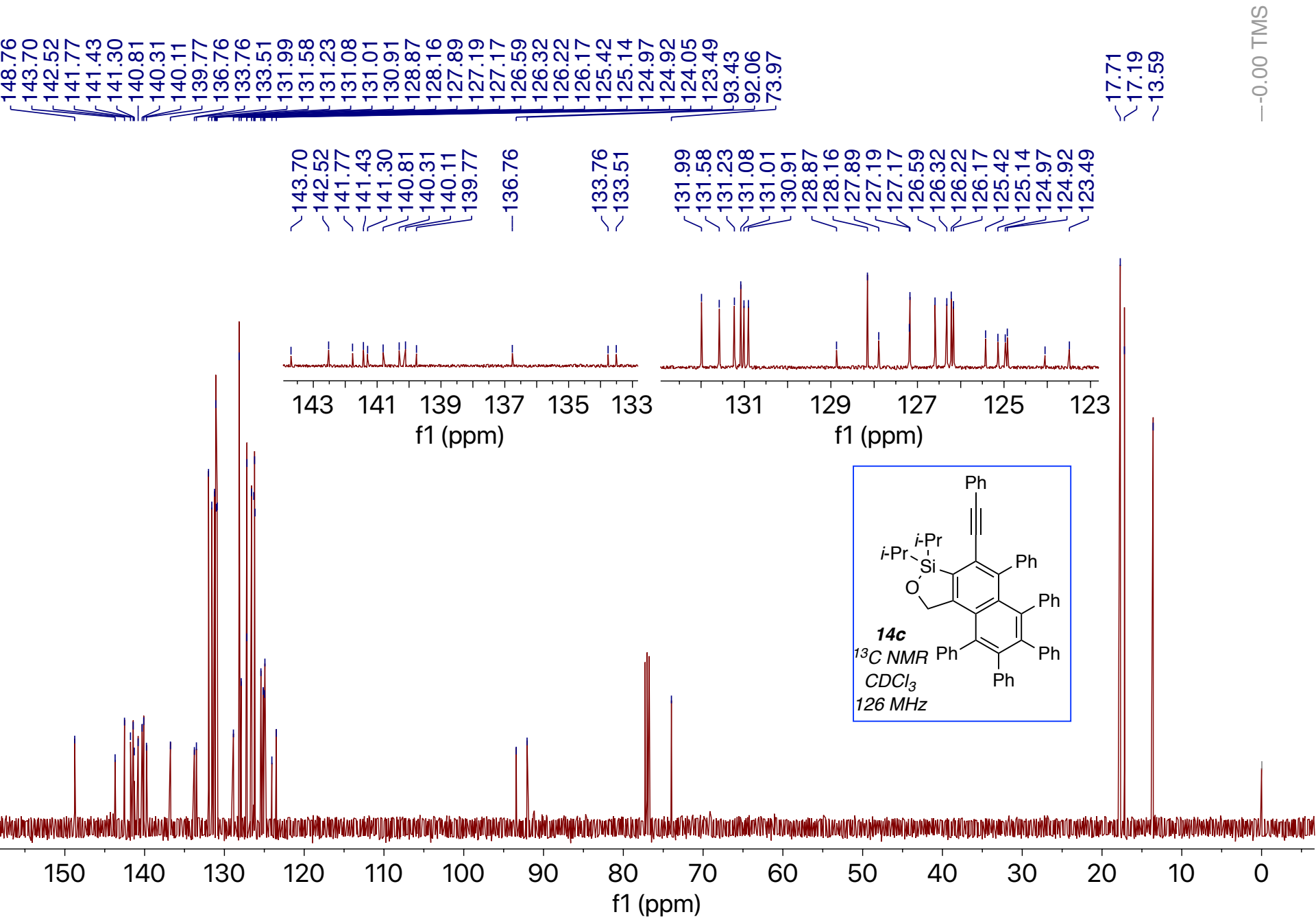

152.66
146.88
146.68
145.04
140.47
138.40
136.49
134.76
131.06
130.64
129.47
128.21
127.94
127.72
127.56
127.48
123.84
123.38
92.37
91.27
90.31
88.52
77.22
69.71
17.62
17.59
17.23
17.20
17.08
16.84
13.57
13.37
0.00 TMS
Ph
i-Pr
i-Pr
Si
O
Ph
O
14a
13C NMR
CDCl3
126 MHz
60
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

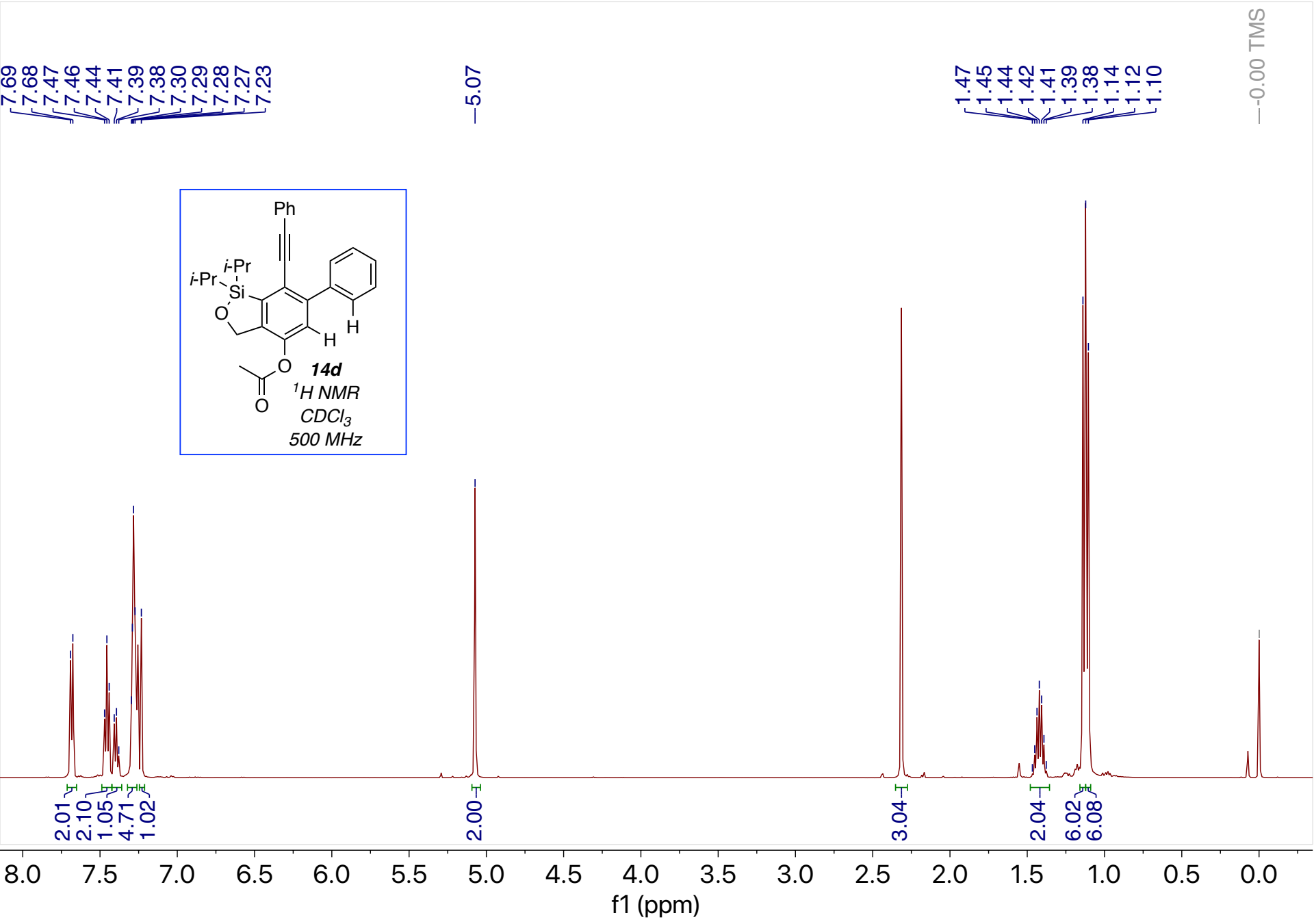

Ph
i-Pr
i-Pr
Si
Ph
O
O
NOESY
1.93 ppm
14a
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
f1 (ppm)

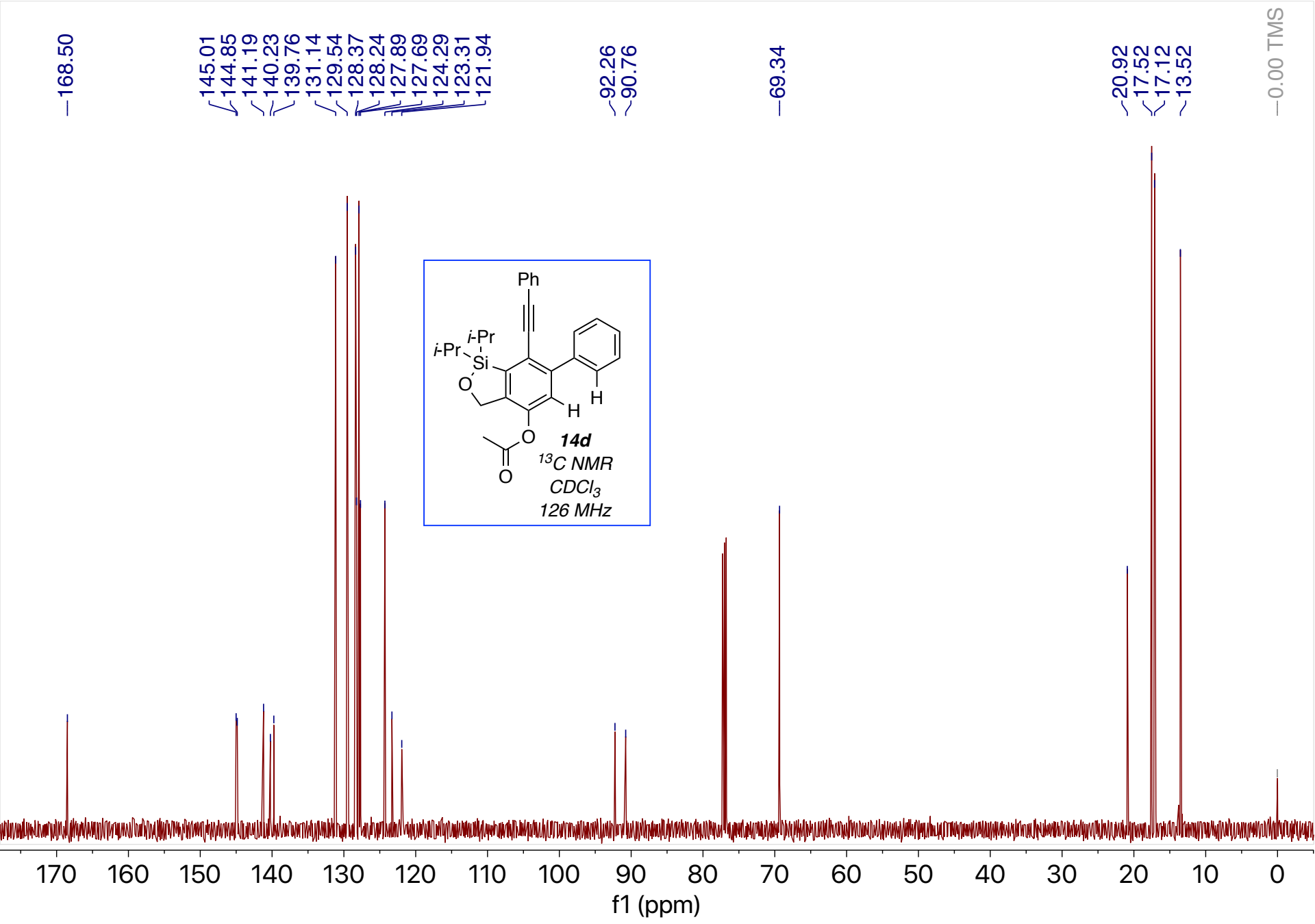

7.51
7.50
7.48
7.46
7.44
7.43
7.26
7.25
7.20
7.20
7.19
7.19
7.15
7.14
7.08
7.06
5.76
5.62
5.27
5.24
5.09
5.06
1.45
1.44
1.42
1.41
1.39
1.38
1.36
1.35
1.13
1.11
1.11
1.09
1.08
0.00 TMS
Ph
i-Pr
i-Pr
Si
O
Ph
O
14b
1H NMR
CDCl3
500 MHz
3.89
1.13
3.35
2.03
1.06
1.03
0.97
0.98
1.00
1.01
2.00
12.19
1.54
f1 (ppm)

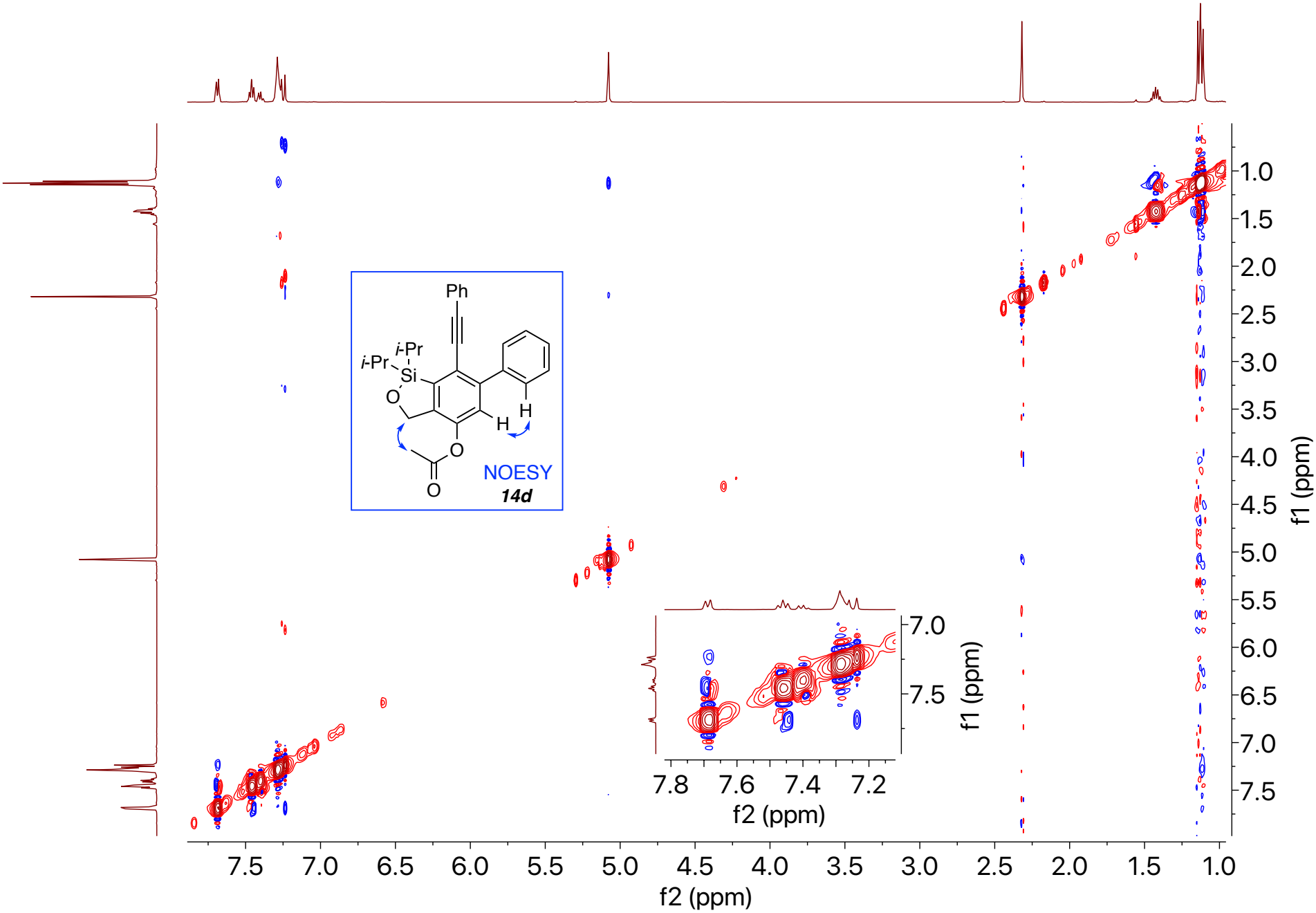

150.19
143.20
142.27
141.74
140.78
137.95
136.05
135.47
131.09
129.81
128.31
128.09
127.96
127.64
123.40
122.34
91.79
91.39
81.92
80.88
69.86
17.59
17.20
17.19
13.53
13.51
0.00 TMS
Ph
i-Pr
i-Pr
Si
O
Ph
O
14b
13C NMR
CDCl3
126 MHz
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

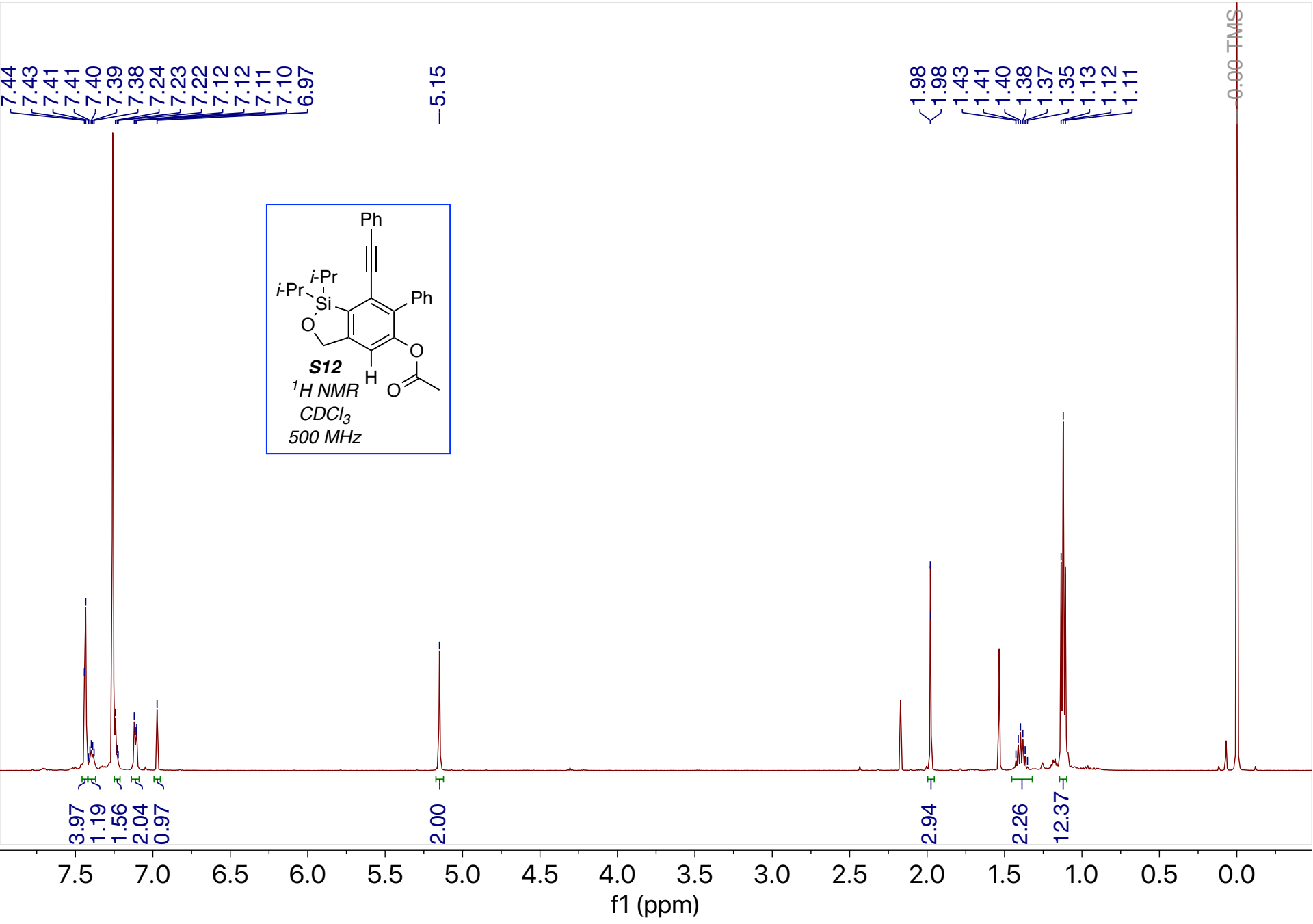

7.23 7.22 7.22 7.22 7.21 7.20 7.20 7.20 7.19 7.19 7.16 7.15 7.15 7.14 7.14 7.03 7.03 7.02 7.02 7.02 7.01 6.95 6.80 6.79 6.79 6.78 6.78 6.77 6.77 6.76 6.74 6.74 6.73 6.72 6.72 6.72 6.71 6.69 6.67 6.65 6.63 6.63 6.62 6.59 6.59 6.58 6.58 6.53 6.52 6.52 6.51 6.51 4.48 1.40 1.38 1.37 1.10 1.09 1.07 1.05 -0.00 TMS
7.25 7.20 7.15 7.10 7.05 7.00
f1 (ppm)
6.80 6.75 6.70 6.65 6.60 6.55 6.50
f1 (ppm)
Ph
i-Pr
i-Pr
Si
O
Ph
Ph
Ph
Ph
Ph
14c
1H NMR
CDCl3
500 MHz
5.25 3.09 2.01 5.14 3.21 5.34 0.94 2.10 2.08 2.04
2.00
2.00 6.27 6.40
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
f1 (ppm)

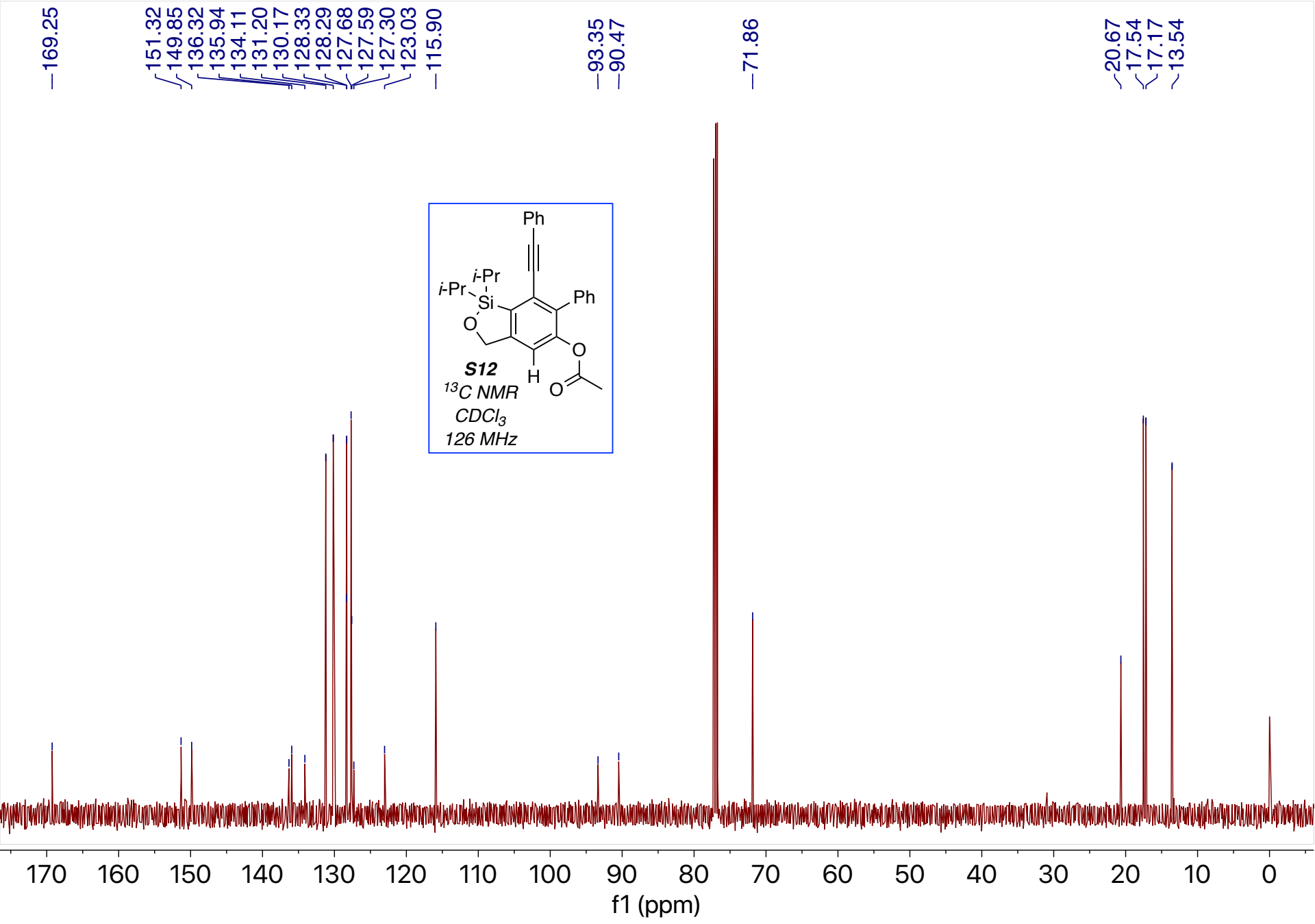

148.76
143.70
142.52
141.77
141.43
141.30
140.81
140.31
140.11
139.77
136.76
133.76
133.51
131.99
131.58
131.23
131.08
131.01
130.91
128.87
128.16
127.89
127.19
127.17
126.59
126.32
126.22
126.17
125.42
125.14
124.97
124.92
124.05
123.49
93.43
92.06
73.97
17.71
17.19
13.59
0.00 TMS
f1 (ppm)
Ph
i-Pr
i-Pr
Si
O
Ph
Ph
Ph
Ph
Ph
14c
13C NMR
CDCl3
126 MHz

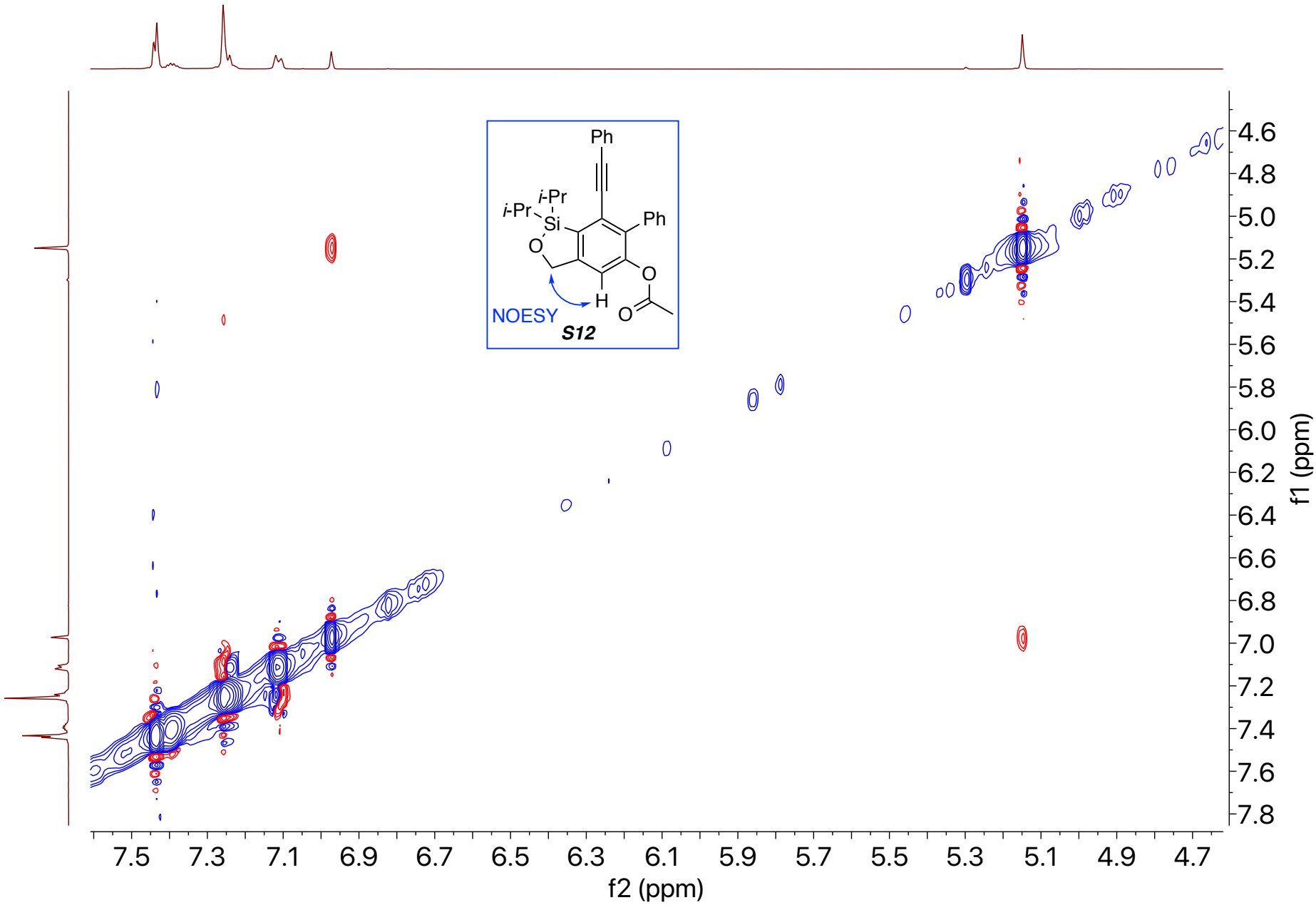

7.69
7.68
7.47
7.46
7.44
7.41
7.39
7.38
7.30
7.29
7.28
7.27
7.23
5.07
1.47
1.45
1.44
1.42
1.41
1.39
1.38
1.14
1.12
1.10
0.00 TMS
Ph
i-Pr
i-Pr
Si
O
H
H
O
O
14d
1H NMR
CDCl3
500 MHz
2.01
2.10
1.05
4.71
1.02
2.00
3.04
2.04
6.02
6.08
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

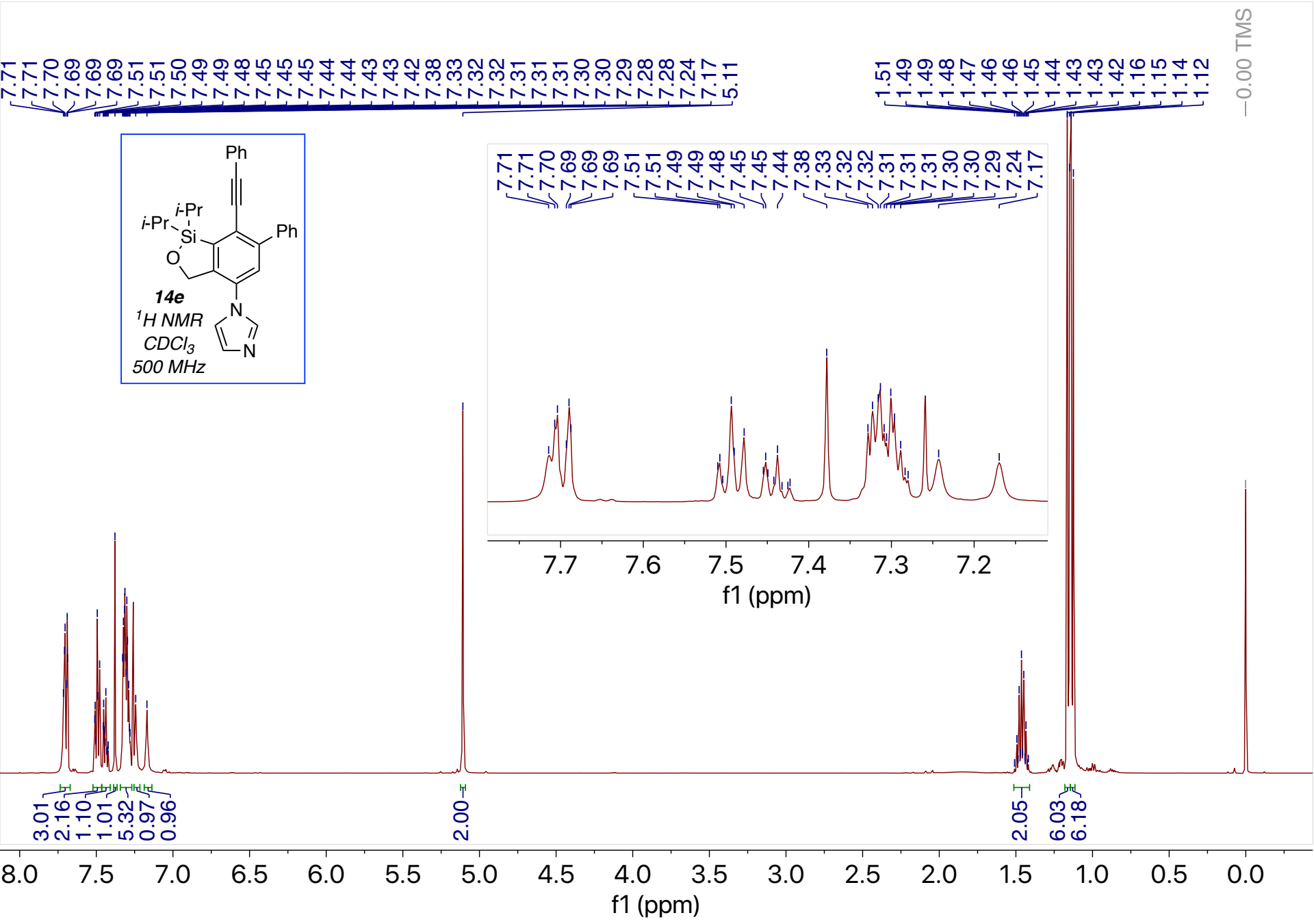

168.50
145.01
144.85
141.19
140.23
139.76
131.14
129.54
128.37
128.24
127.89
127.69
124.29
123.31
121.94
92.26
90.76
69.34
20.92
17.52
17.12
13.52
0.00 TMS
Ph
i-Pr
i-Pr
Si
O
H
H
O
O
14d
13C NMR
CDCl3
126 MHz
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

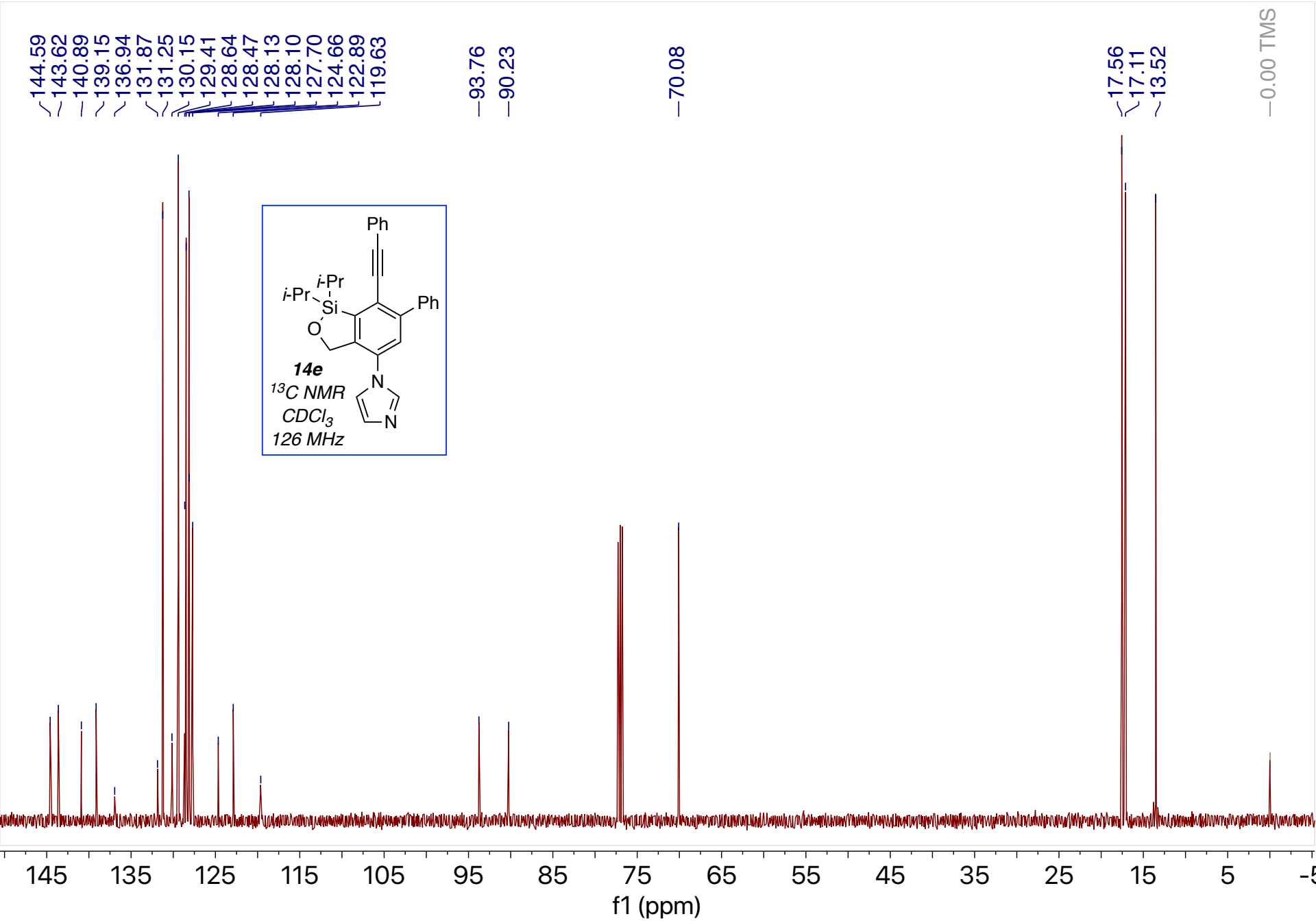

Ph
i-Pr
i-Pr
Si
O
O
H
H
O
O
NOESY
14d
7.8
7.6
7.4
7.2
f2 (ppm)
7.0
7.5
f1 (ppm)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
f1 (ppm)

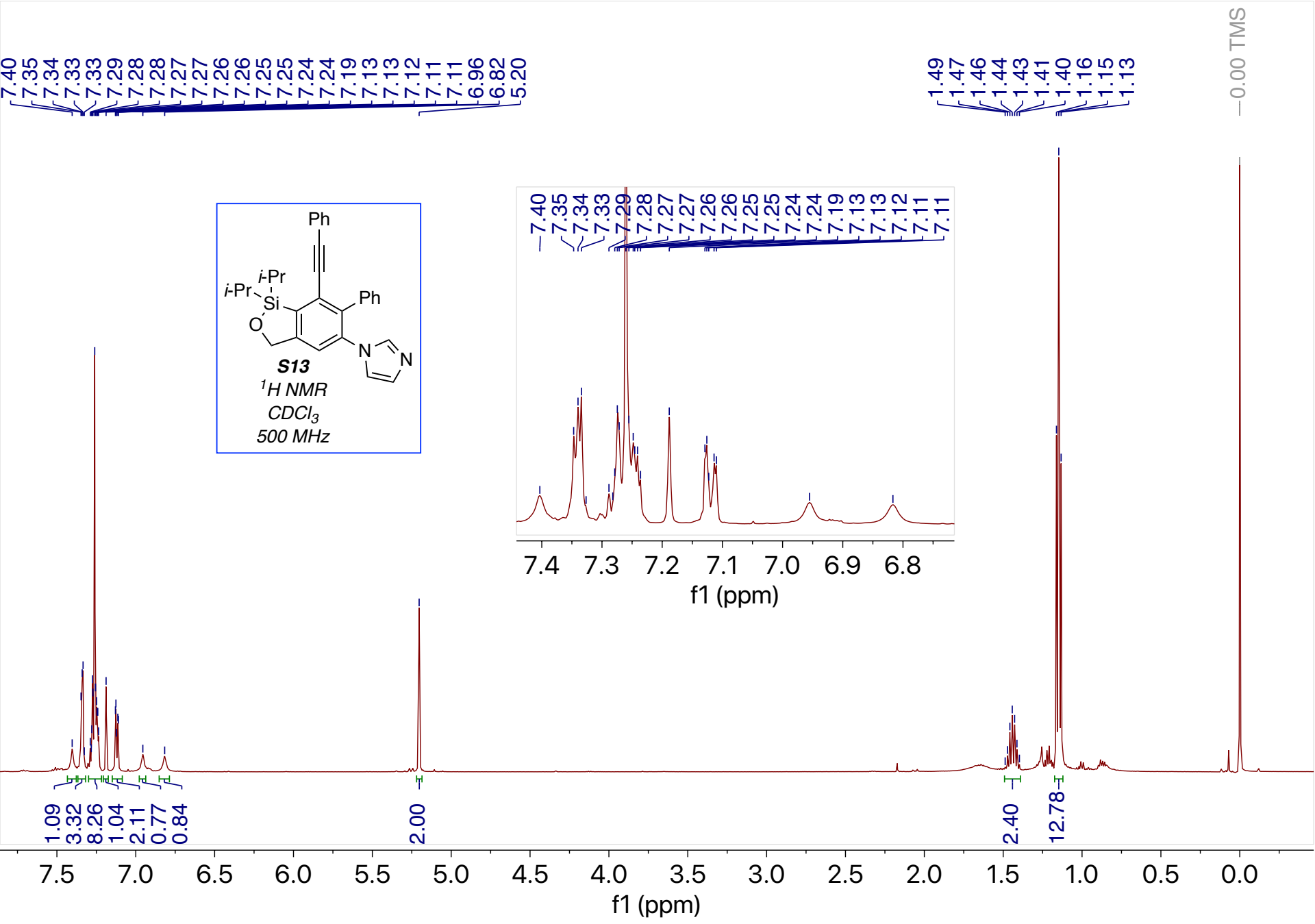

7.44
7.43
7.41
7.41
7.40
7.39
7.38
7.24
7.23
7.22
7.12
7.12
7.11
7.10
6.97
5.15
1.98
1.98
1.43
1.41
1.40
1.38
1.37
1.35
1.13
1.12
1.11
0.00 TMS
Ph
i-Pr
i-Pr
Si
Ph
O
O
H
O
S12
1H NMR
CDCl3
500 MHz
3.97
1.19
1.56
2.04
0.97
2.00
2.94
2.26
12.37
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

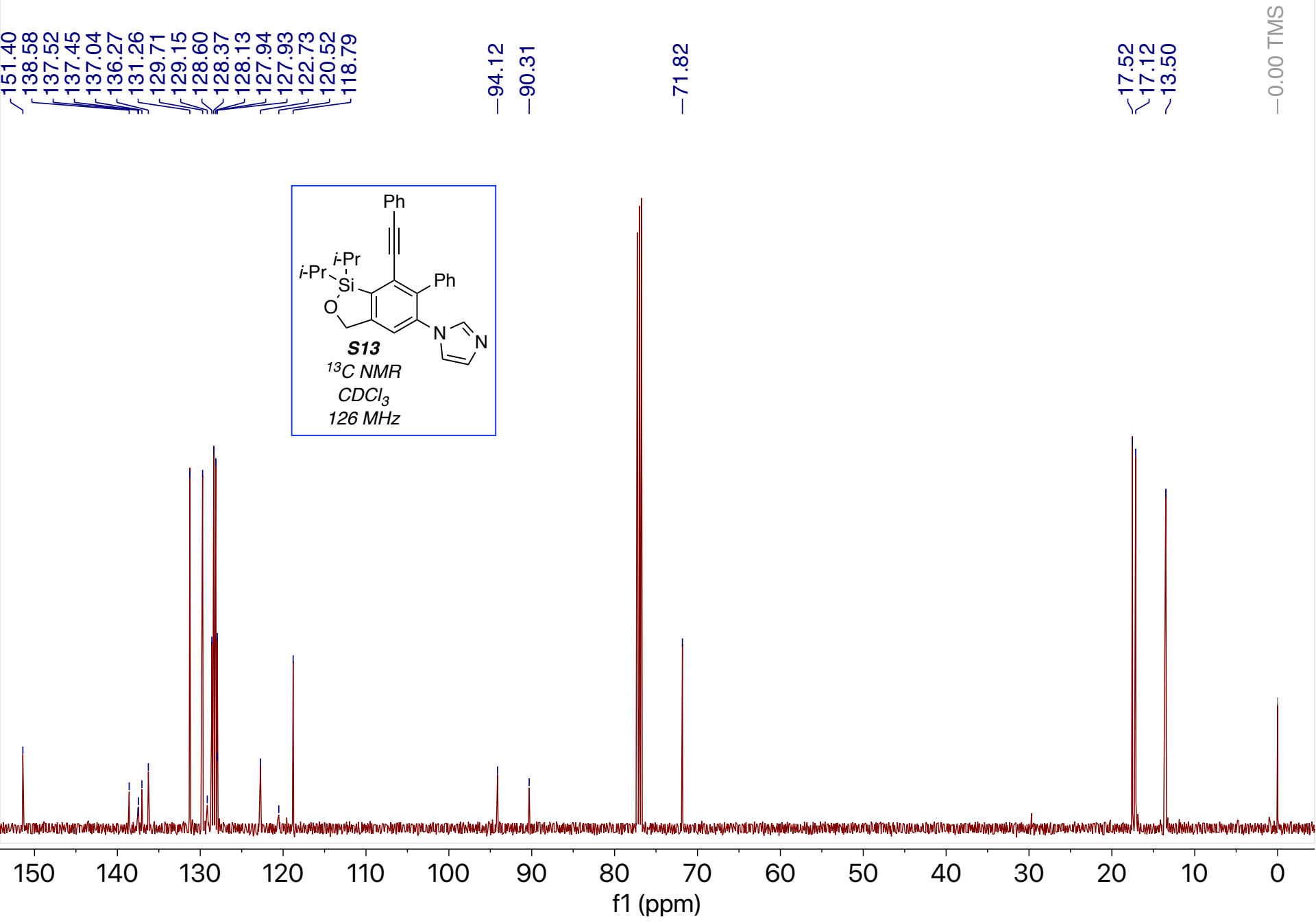

169.25
151.32
149.85
136.32
135.94
134.11
131.20
130.17
128.33
128.29
127.68
127.59
127.30
123.03
115.90
93.35
90.47
71.86
20.67
17.54
17.17
13.54
Ph
i-Pr
i-Pr
Si
O
Ph
O
H
O
S12
13C NMR
CDCl3
126 MHz
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

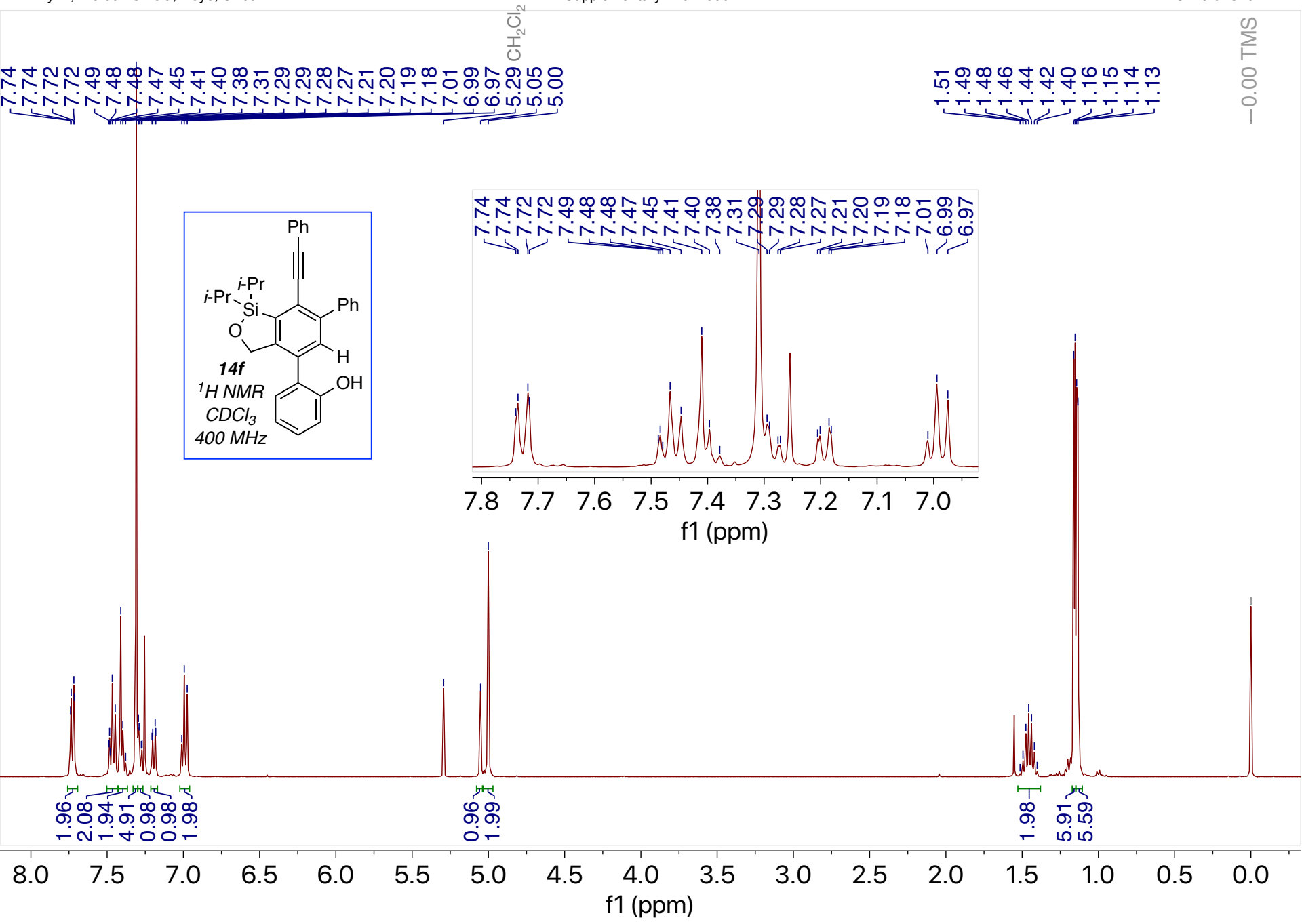

Ph
i-Pr
i-Pr
Si
O
Ph
O
H
O
NOESY
S12
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.2
6.4
6.6
6.8
7.0
7.2
7.4
7.6
7.8
f1 (ppm)
7.5
7.3
7.1
6.9
6.7
6.5
6.3
6.1
5.9
5.7
5.5
5.3
5.1
4.9
4.7
f2 (ppm)

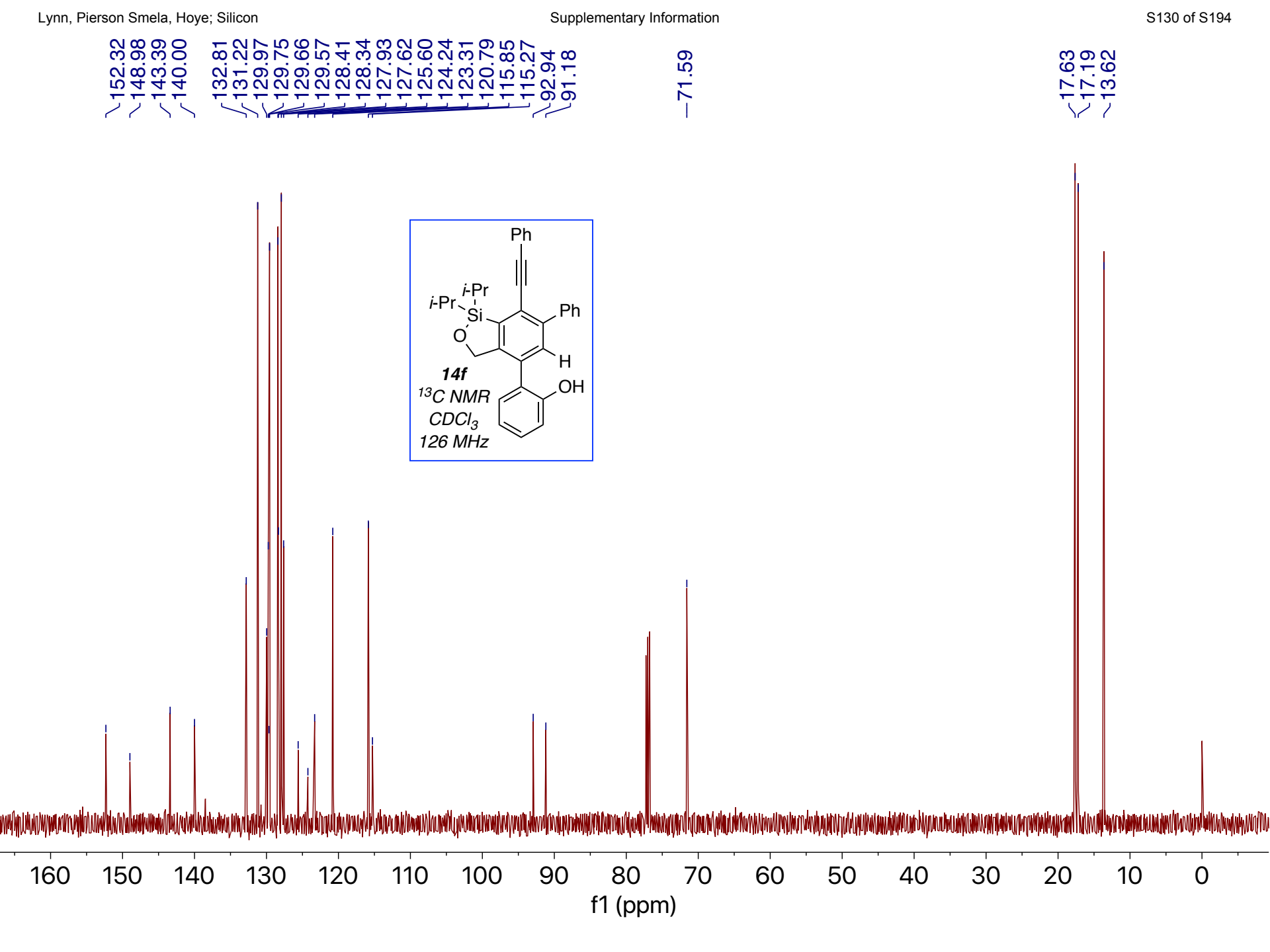

7.71 7.71 7.70 7.69 7.69 7.69 7.51 7.51 7.50 7.49 7.49 7.48 7.45 7.45 7.45 7.44 7.44 7.43 7.43 7.42 7.38 7.33 7.32 7.32 7.31 7.31 7.31 7.30 7.30 7.29 7.28 7.28 7.24 7.17 5.11
1.51 1.49 1.49 1.48 1.47 1.46 1.46 1.45 1.44 1.43 1.43 1.42 1.16 1.15 1.14 1.12
0.00 TMS
Ph
i-Pr
i-Pr
Si
O
Ph
N
N
14e
1H NMR
CDCl3
500 MHz
7.7
7.6
7.5
7.4
7.3
7.2
f1 (ppm)
3.01 2.16 1.10 1.01 5.32 0.97 0.96
2.00
2.05 6.03 6.18
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
f1 (ppm)

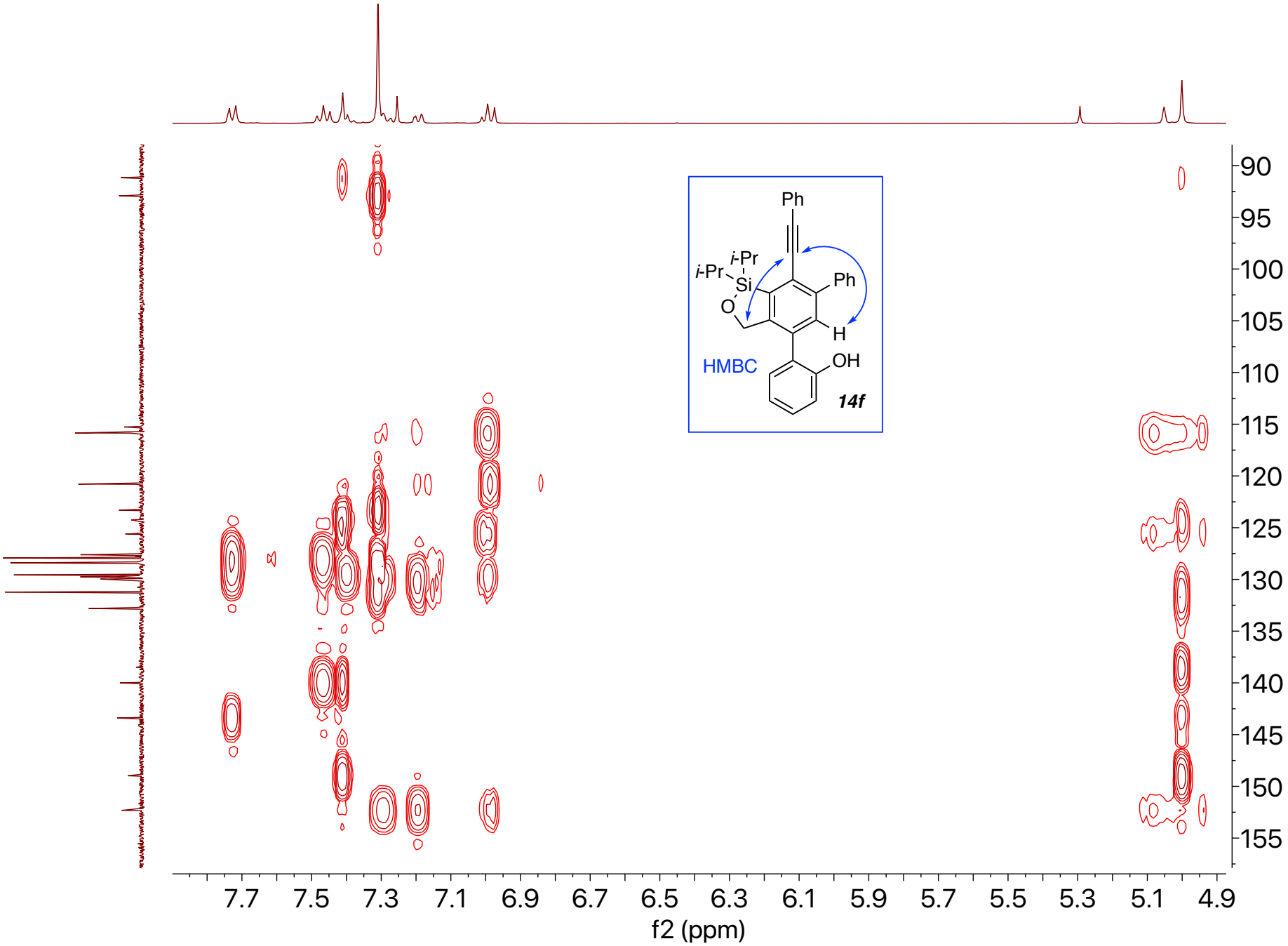

144.59
143.62
140.89
139.15
136.94
131.87
131.25
130.15
129.41
128.64
128.47
128.13
128.10
127.70
124.66
122.89
119.63
93.76
90.23
70.08
17.56
17.11
13.52
0.00 TMS
Ph
i-Pr
i-Pr
Si
O
Ph
N
N
14e
13C NMR
CDCl3
126 MHz
145
135
125
115
105
95
85
75
65
55
45
35
25
15
5
f1 (ppm)

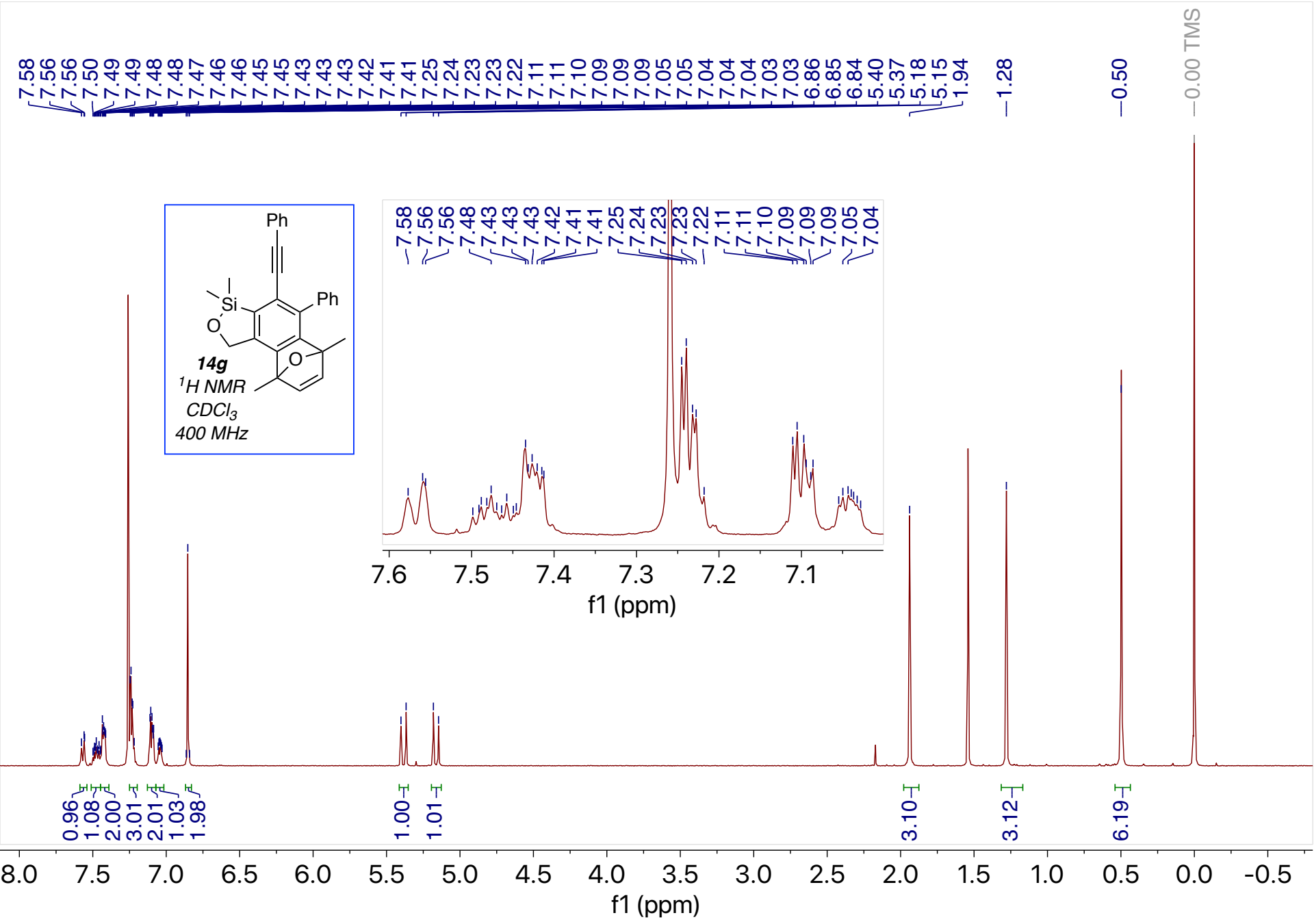

7.40 7.35 7.34 7.33 7.33 7.29 7.28 7.28 7.27 7.27 7.26 7.26 7.25 7.25 7.24 7.24 7.19 7.13 7.13 7.12 7.11 7.11 6.96 6.82 5.20
1.49 1.47 1.46 1.44 1.43 1.41 1.40 1.16 1.15 1.13
0.00 TMS
Ph
i-Pr
i-Pr
Si
O
Ph
N
N
S13
1H NMR
CDCl3
500 MHz
7.4 7.3 7.2 7.1 7.0 6.9 6.8
f1 (ppm)
1.09 3.32 8.26 1.04 2.11 0.77 0.84
2.00
2.40
12.78
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
f1 (ppm)

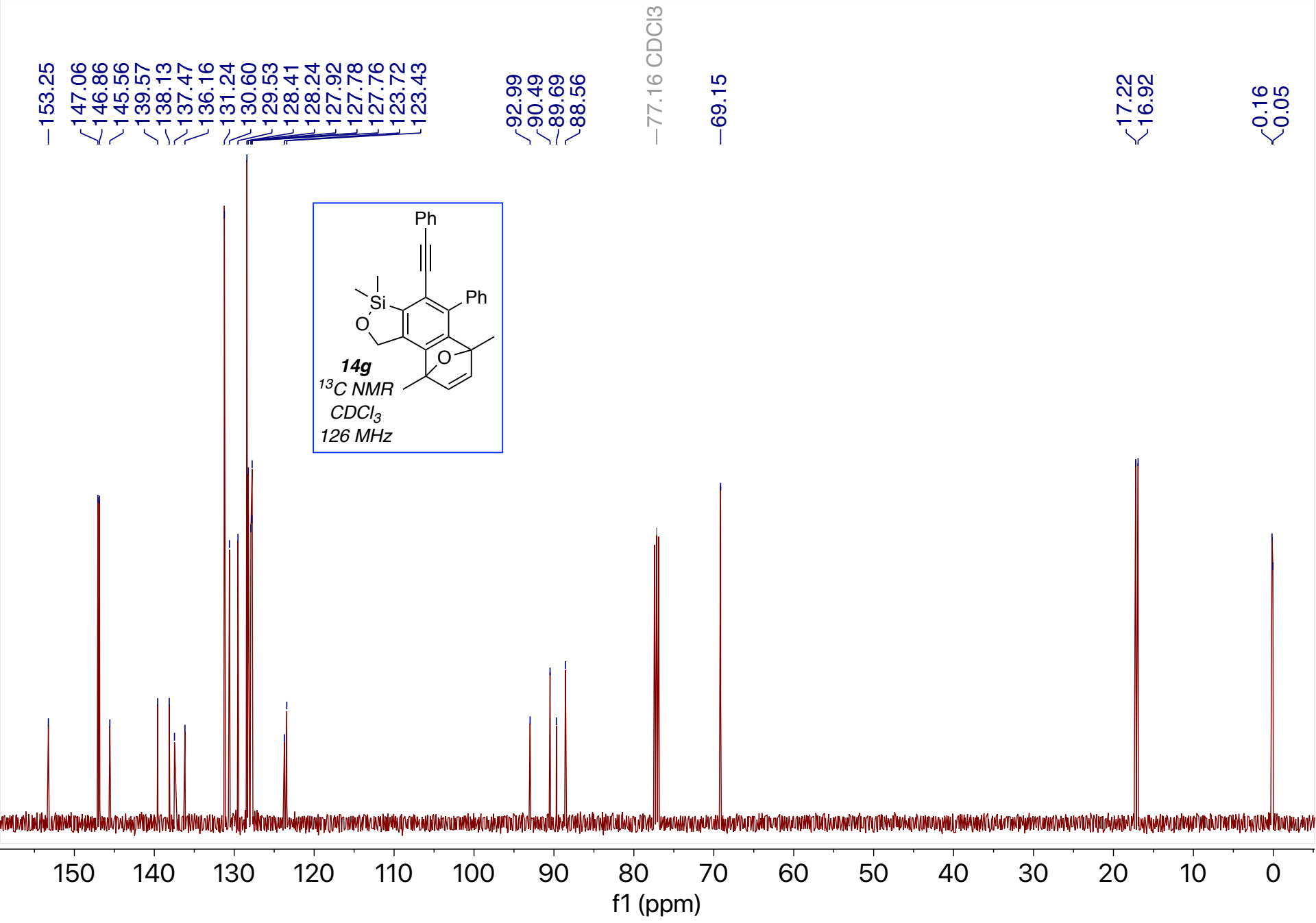

151.40
138.58
137.52
137.45
137.04
136.27
131.26
129.71
129.15
128.60
128.37
128.13
127.94
127.93
122.73
120.52
118.79
94.12
90.31
71.82
17.52
17.12
13.50
0.00 TMS
Ph
i-Pr
i-Pr
Si
O
Ph
N
N
S13
13C NMR
CDCl3
126 MHz
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

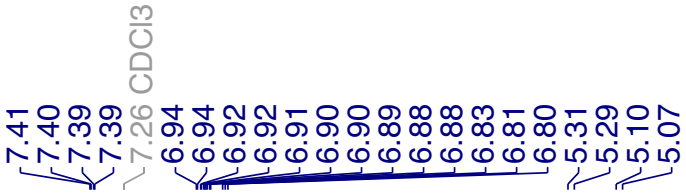

7.74 7.74 7.72 7.72 7.49 7.48 7.48 7.47 7.45 7.41 7.40 7.38 7.31 7.29 7.29 7.28 7.27 7.21 7.20 7.19 7.18 7.01 6.99 6.97 5.29 5.05 5.00
CH2Cl2
1.51 1.49 1.48 1.46 1.44 1.42 1.40 1.16 1.15 1.14 1.13
0.00 TMS
Ph
i-Pr
i-Pr
Si
O
Ph
H
OH
14f
1H NMR
CDCl3
400 MHz
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0
f1 (ppm)
1.96 2.08 1.94 4.91 0.98 0.98 1.98 0.96 1.99 1.98 5.91 5.59
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
f1 (ppm)

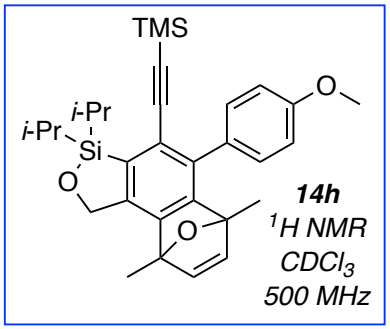

152.32
148.98
143.39
140.00
132.81
131.22
129.97
129.75
129.66
129.57
128.41
128.34
127.93
127.62
125.60
124.24
123.31
120.79
115.85
115.27
92.94
91.18
71.59
17.63
17.19
13.62
Ph
i-Pr
i-Pr
Si
O
Ph
H
OH
14f
13C NMR
CDCl3
126 MHz
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

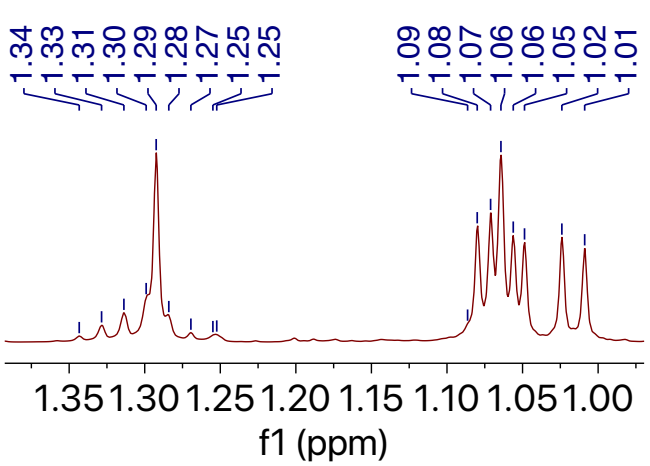

Ph
i-Pr
i-Pr
Si
O
Ph
H
OH
HMBC
14f
90
95
100
105
110
115
120
125
130
135
140
145
150
155
f1 (ppm)
7.7
7.5
7.3
7.1
6.9
6.7
6.5
6.3
6.1
5.9
5.7
5.5
5.3
5.1
4.9
f2 (ppm)


7.58 7.56 7.56 7.50 7.49 7.49 7.48 7.48 7.47 7.46 7.46 7.45 7.45 7.43 7.43 7.43 7.42 7.41 7.41 7.25 7.24 7.23 7.23 7.22 7.11 7.11 7.10 7.09 7.09 7.09 7.05 7.05 7.04 7.04 7.04 7.03 7.03 6.86 6.85 6.84 5.40 5.37 5.18 5.15 1.94
1.28
0.50
0.00 TMS
Ph
Si
Ph
O
O
14g
1H NMR
CDCl3
400 MHz
7.6 7.5 7.4 7.3 7.2 7.1
f1 (ppm)
0.96 1.08 2.00 3.01 2.01 1.03 1.98
1.00 1.01
3.10
3.12
6.19
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
f1 (ppm)

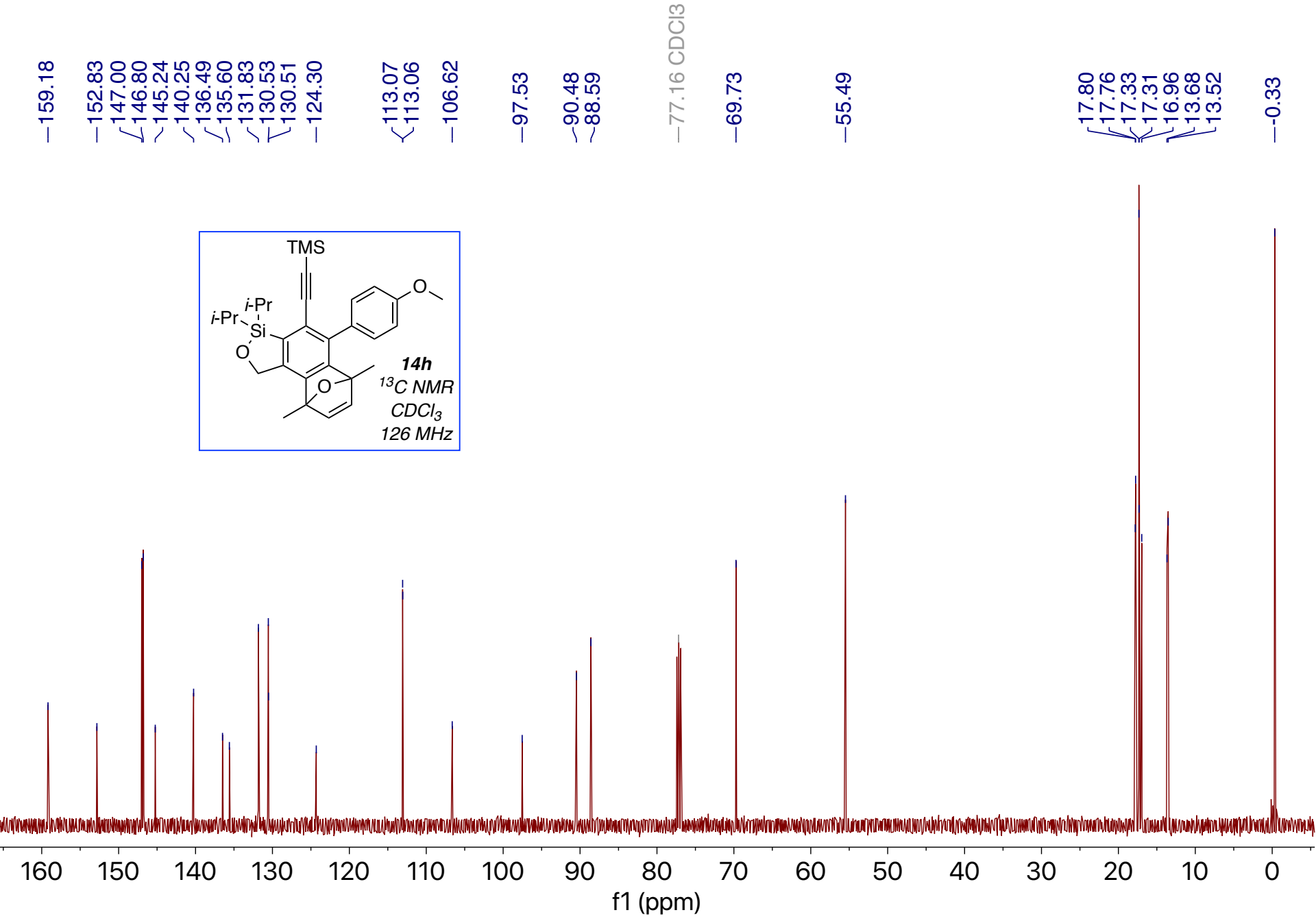

153.25
147.06
146.86
145.56
139.57
138.13
137.47
136.16
131.24
130.60
129.53
128.41
128.24
127.92
127.78
127.76
123.72
123.43
92.99
90.49
89.69
88.56
77.16 CDCl3
69.15
17.22
16.92
0.16
0.05
Ph
Si
O
Ph
O
14g
13C NMR
CDCl3
126 MHz
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

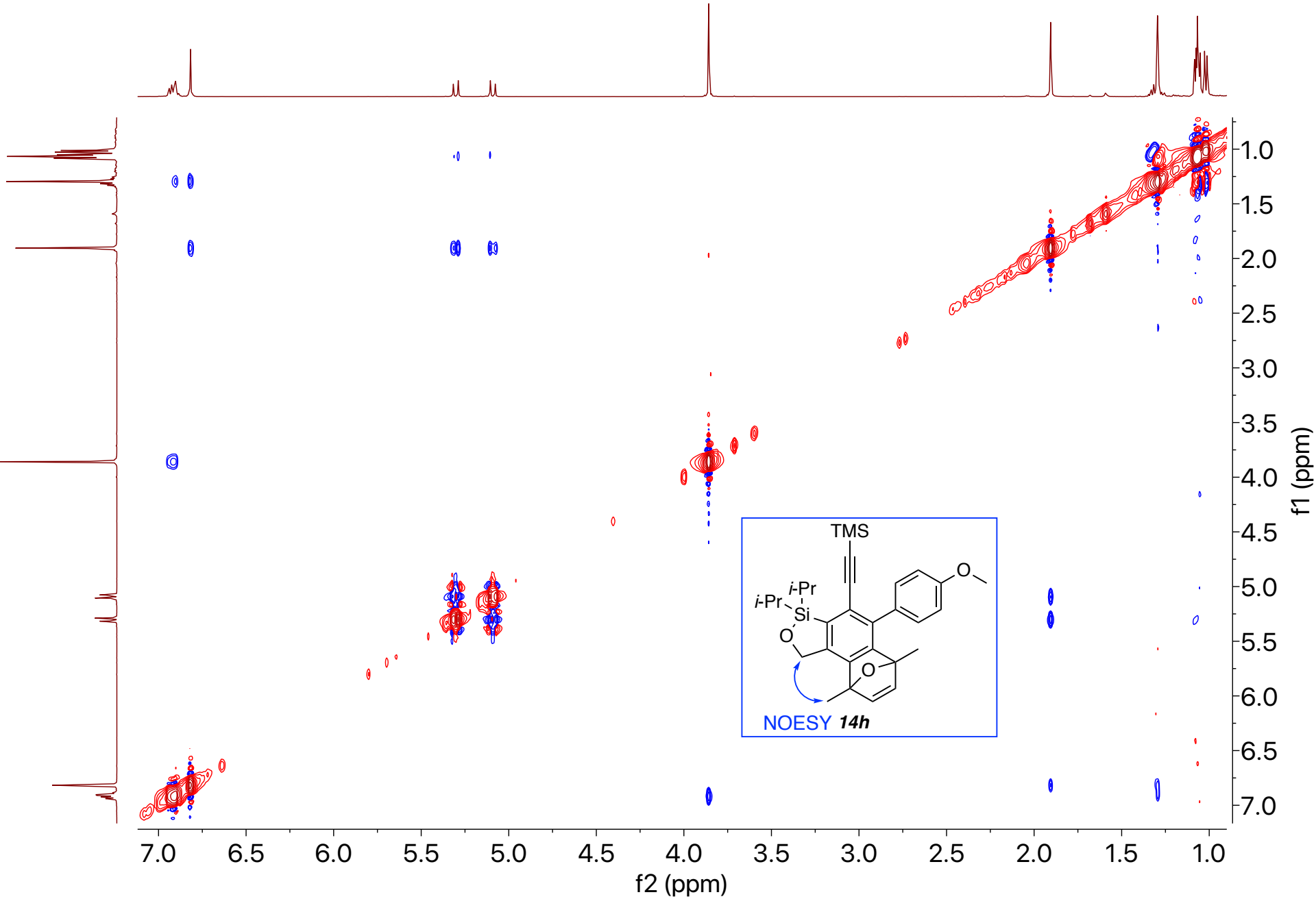

7.41
7.40
7.39
7.39
7.26 CDCl3
6.94
6.94
6.92
6.92
6.91
6.90
6.90
6.89
6.88
6.88
6.83
6.81
6.80
5.31
5.29
5.10
5.07
3.86
1.90
1.33
1.31
1.30
1.29
1.28
1.27
1.25
1.25
1.09
1.08
1.07
1.06
1.06
1.05
1.02
1.01

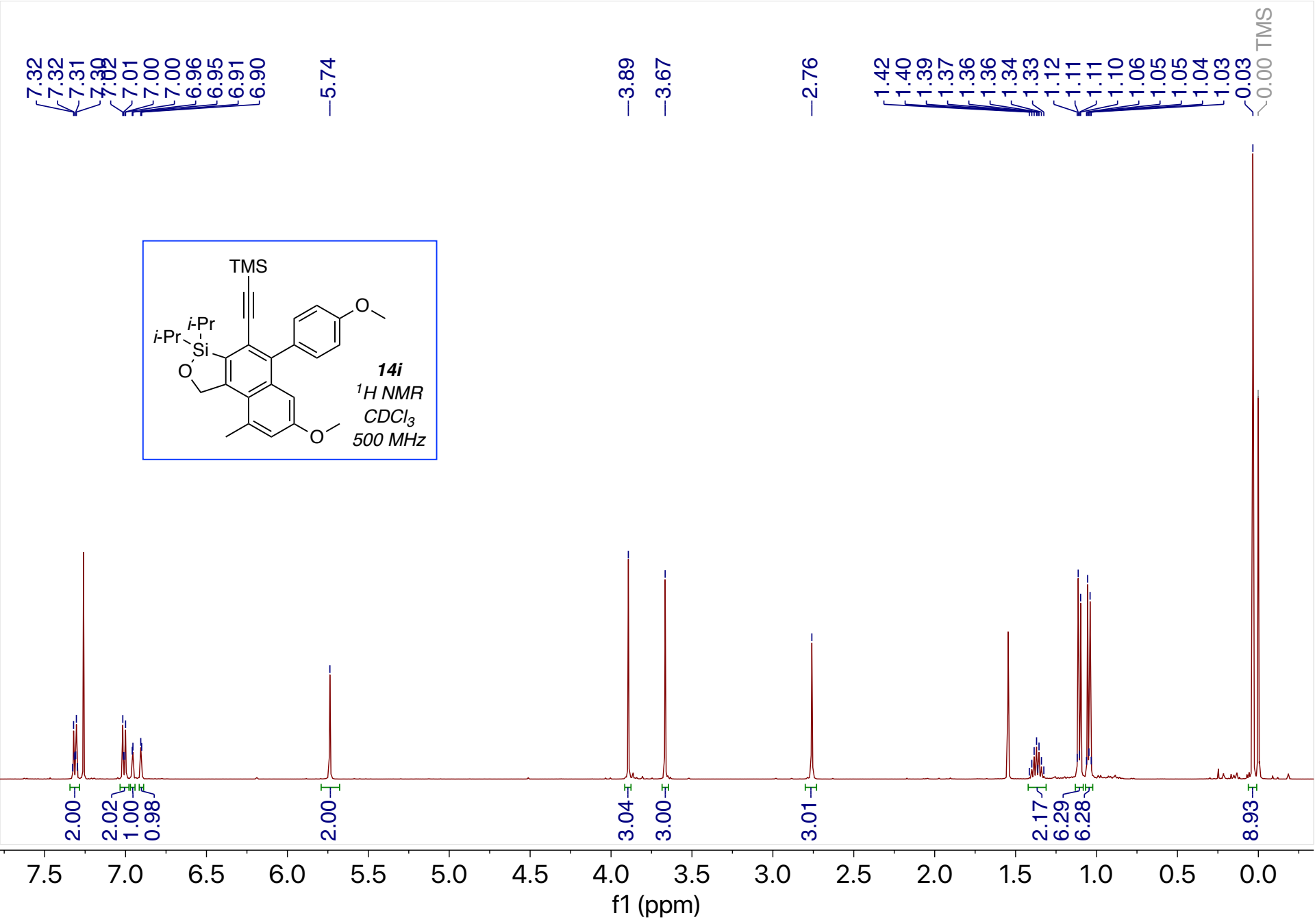

TMS
i-Pr
i-Pr
Si
O
O
O
14h
1H NMR
CDCl3
500 MHz

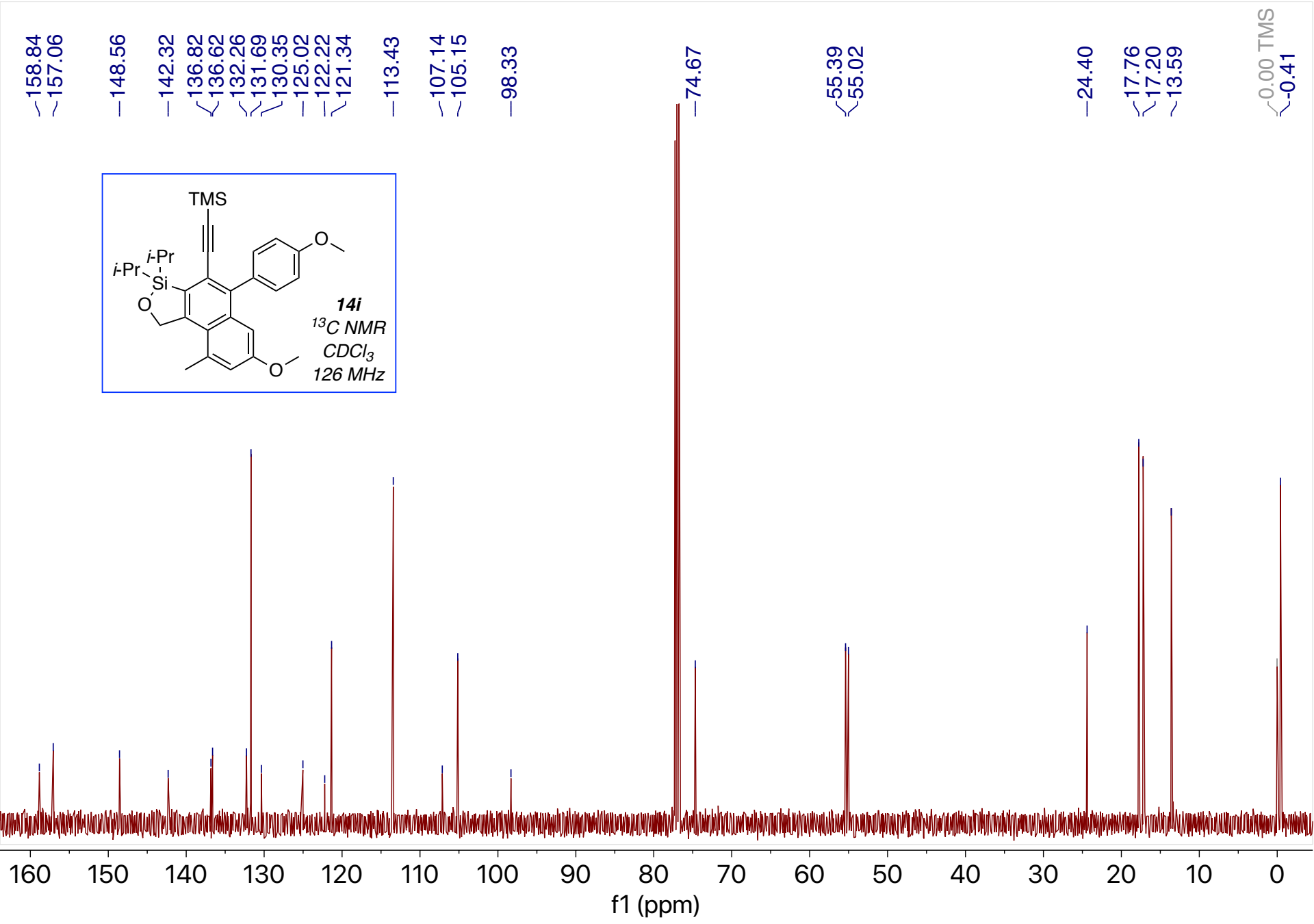

1.34 1.33 1.31 1.30 1.29 1.28 1.27 1.25 1.25
1.09 1.08 1.07 1.06 1.06 1.05 1.02 1.01
1.35 1.30 1.25 1.20 1.15 1.10 1.05 1.00
f1 (ppm)

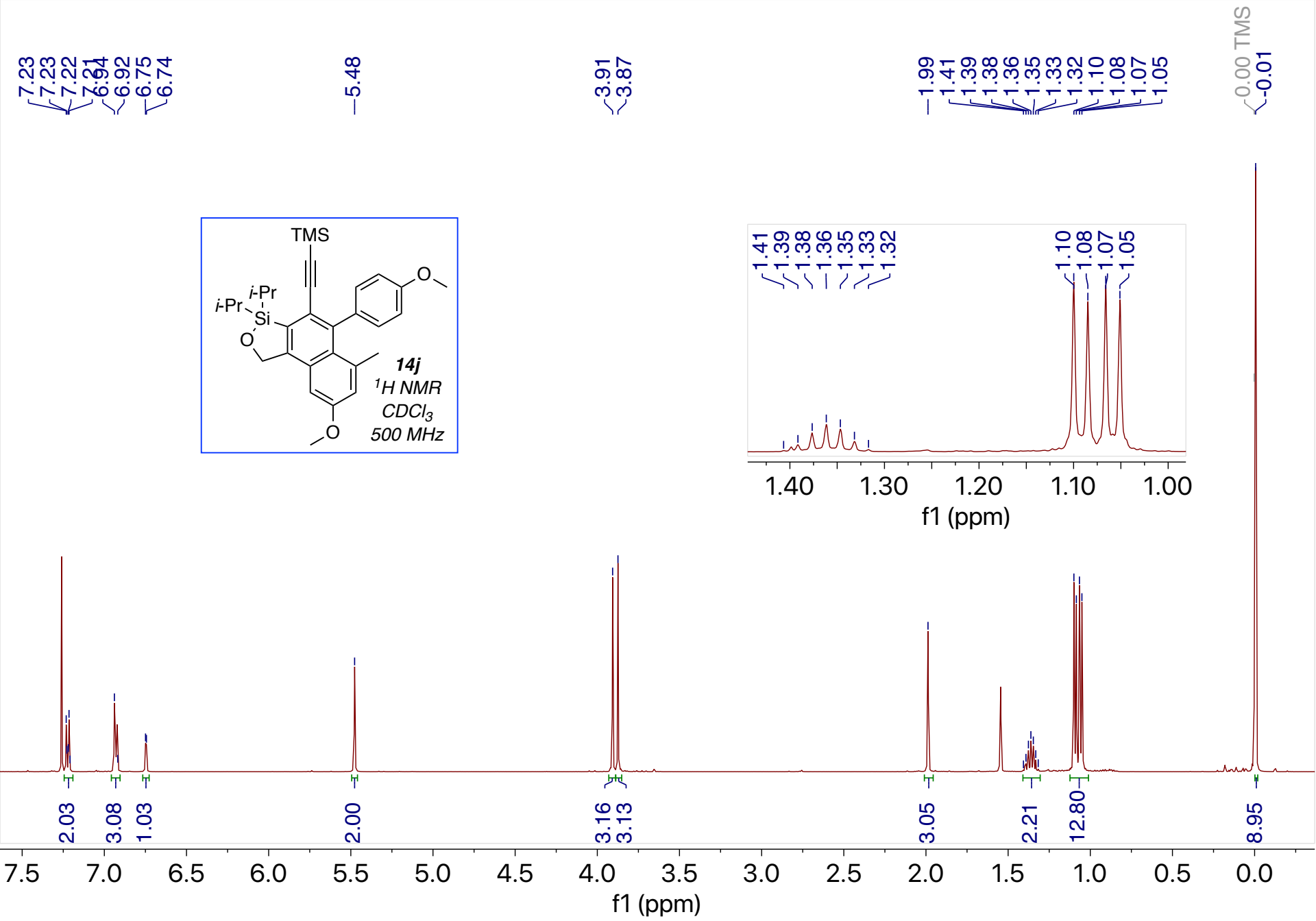
0.93
2.92
1.95
0.99
1.02
3.01
2.93
5.03
8.52
2.96
8.70
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

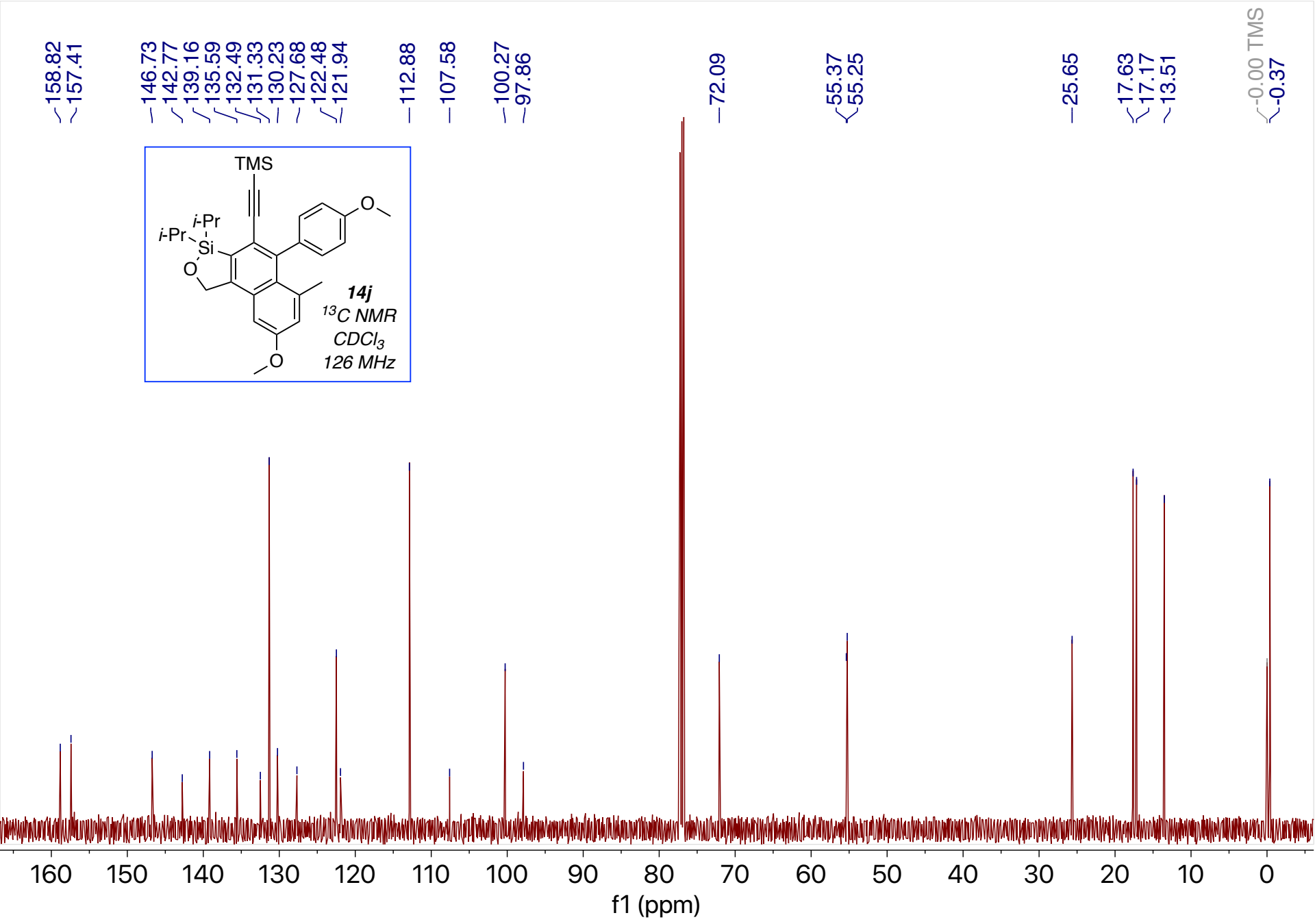

159.18
152.83
147.00
146.80
145.24
140.25
136.49
135.60
131.83
130.53
130.51
124.30
113.07
113.06
106.62
97.53
90.48
88.59
77.16 CDCl3
69.73
55.49
17.80
17.76
17.33
17.31
16.96
13.68
13.52
-0.33
TMS
i-Pr
i-Pr
Si
O
O
O
14h
13C NMR
CDCl3
126 MHz
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

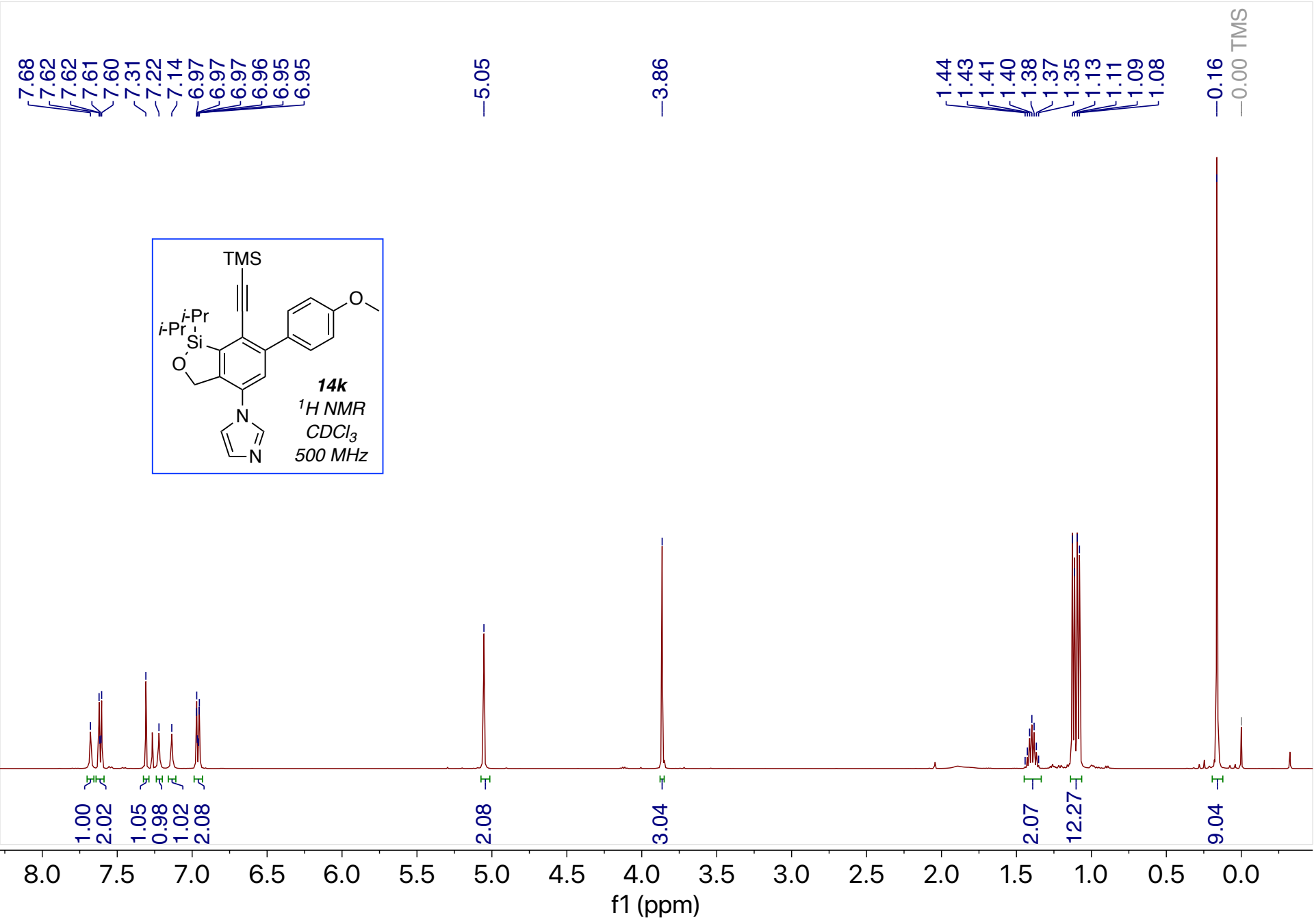

TMS
i-Pr
i-Pr
Si
O
O
O
NOESY 14h
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
f1 (ppm)


7.32
7.32
7.31
7.30
7.02
7.01
7.00
7.00
6.96
6.95
6.91
6.90
5.74
3.89
3.67
2.76
1.42
1.40
1.39
1.37
1.36
1.36
1.34
1.33
1.12
1.11
1.11
1.10
1.06
1.05
1.05
1.04
1.03
0.03
0.00 TMS
TMS
i-Pr
i-Pr
Si
O
O
O
14i
1H NMR
CDCl3
500 MHz
2.00
2.02
1.00
0.98
2.00
3.04
3.00
3.01
2.17
6.29
6.28
8.93
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
f1 (ppm)


158.84
157.06
148.56
142.32
136.82
136.62
132.26
131.69
130.35
125.02
122.22
121.34
113.43
107.14
105.15
98.33
74.67
55.39
55.02
24.40
17.76
17.20
13.59
0.00 TMS
-0.41
TMS
i-Pr
i-Pr
Si
O
O
O
14i
13C NMR
CDCl3
126 MHz
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.23
7.23
7.22
7.21
6.94
6.92
6.75
6.74
5.48
3.91
3.87
1.99
1.41
1.39
1.38
1.36
1.35
1.33
1.32
1.10
1.08
1.07
1.05
0.00 TMS
-0.01
TMS
i-Pr
i-Pr
Si
O
O
O
14j
1H NMR
CDCl3
500 MHz
1.40
1.30
1.20
1.10
1.00
f1 (ppm)
2.03
3.08
1.03
2.00
3.16
3.13
3.05
2.21
12.80
8.95
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
f1 (ppm)


158.82
157.41
146.73
142.77
139.16
135.59
132.49
131.33
130.23
127.68
122.48
121.94
112.88
107.58
100.27
97.86
72.09
55.37
55.25
25.65
17.63
17.17
13.51
0.00 TMS
-0.37
TMS
i-Pr
i-Pr
Si
O
O
O
14j
13C NMR
CDCl3
126 MHz
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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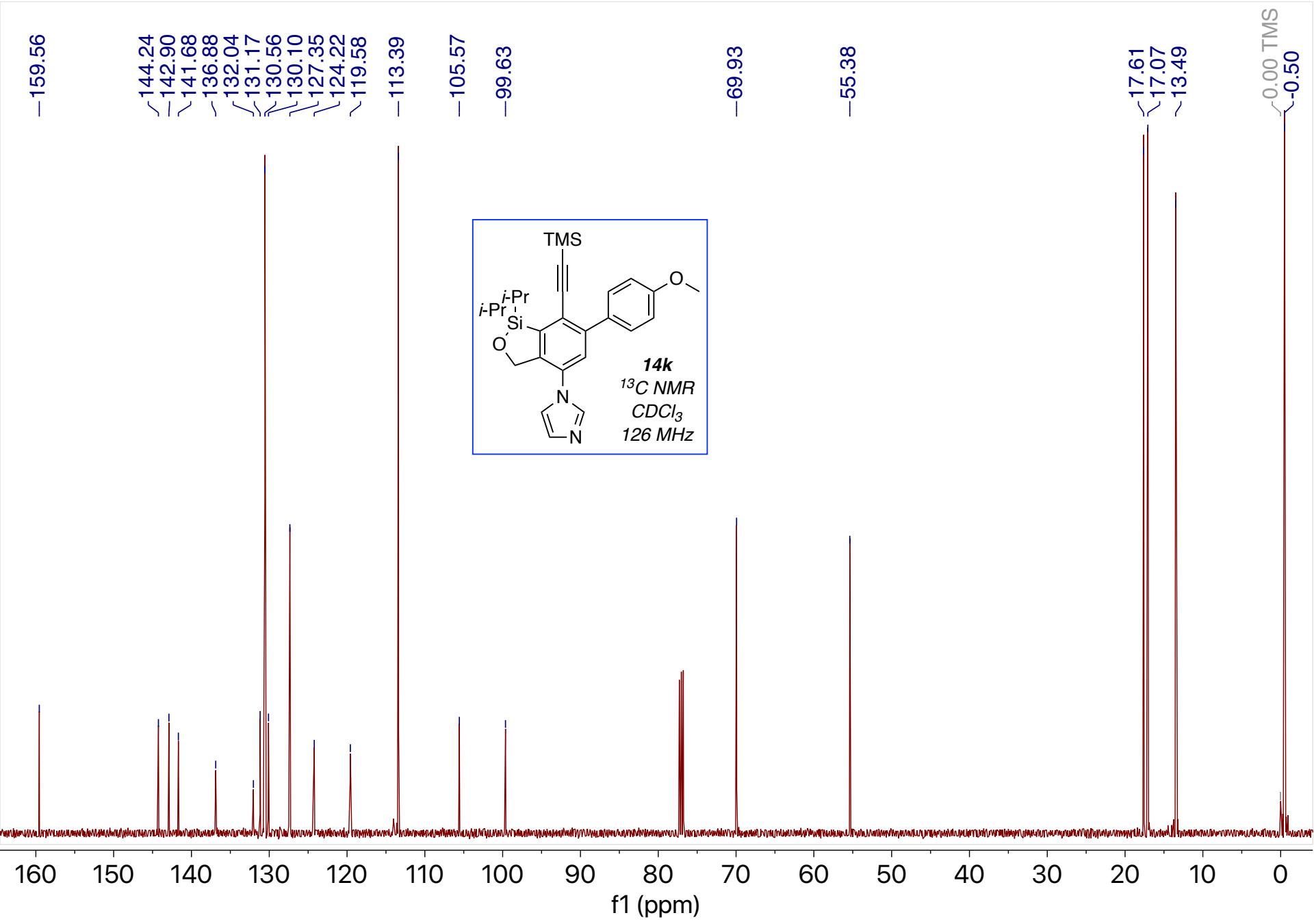
7.62
7.62
7.61
7.60
7.31
7.22
7.14
6.97
6.97
6.97
6.96
6.95
6.95
5.05
3.86
1.44
1.43
1.41
1.40
1.38
1.37
1.35
1.13
1.11
1.09
1.08
0.16
0.00 TMS
TMS
i-Pr
i-Pr
Si
O
O
N
N
14k
1H NMR
CDCl3
500 MHz
1.00
2.02
1.05
0.98
1.02
2.08
2.08
3.04
2.07
12.27
9.04
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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144.24
142.90
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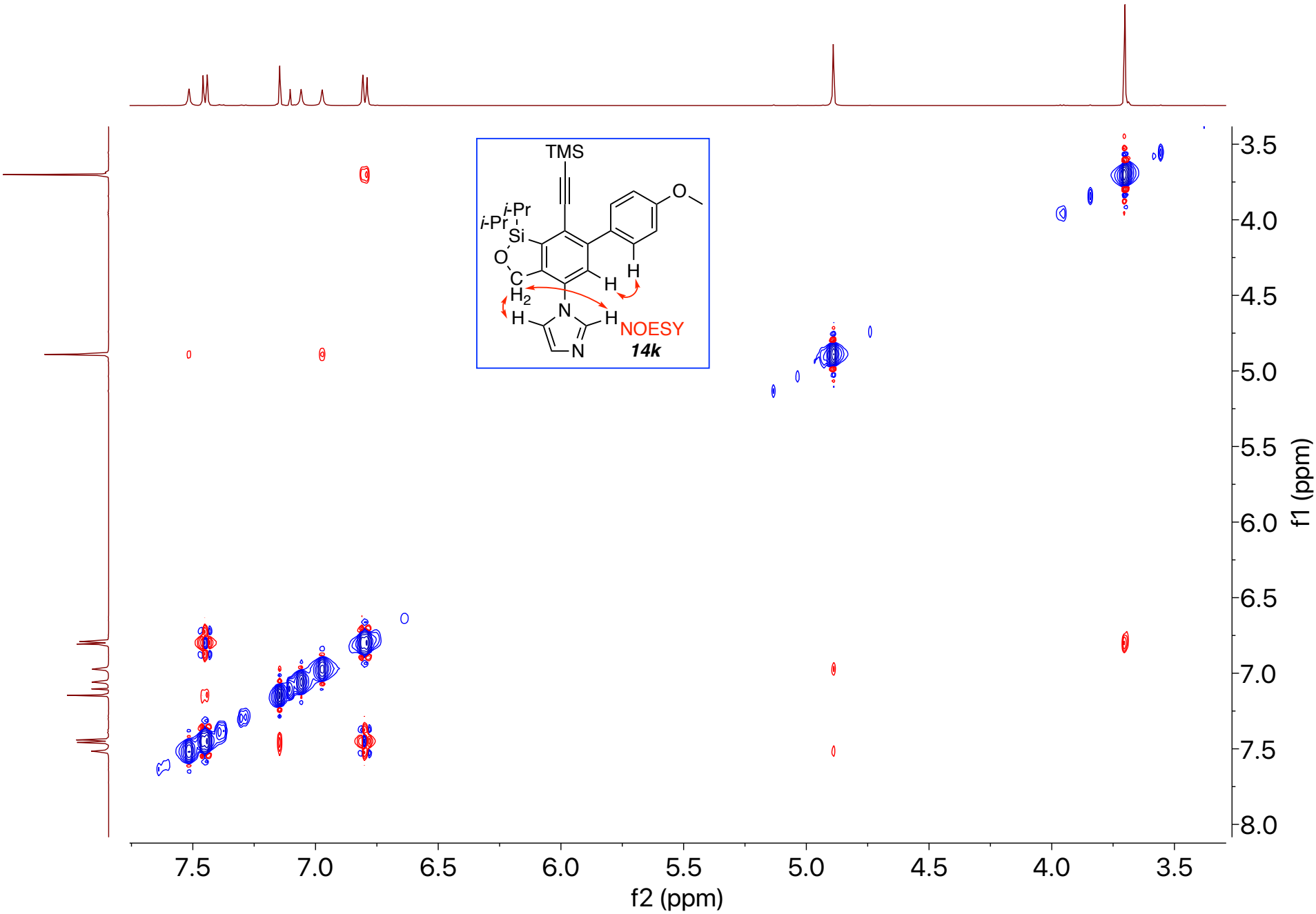
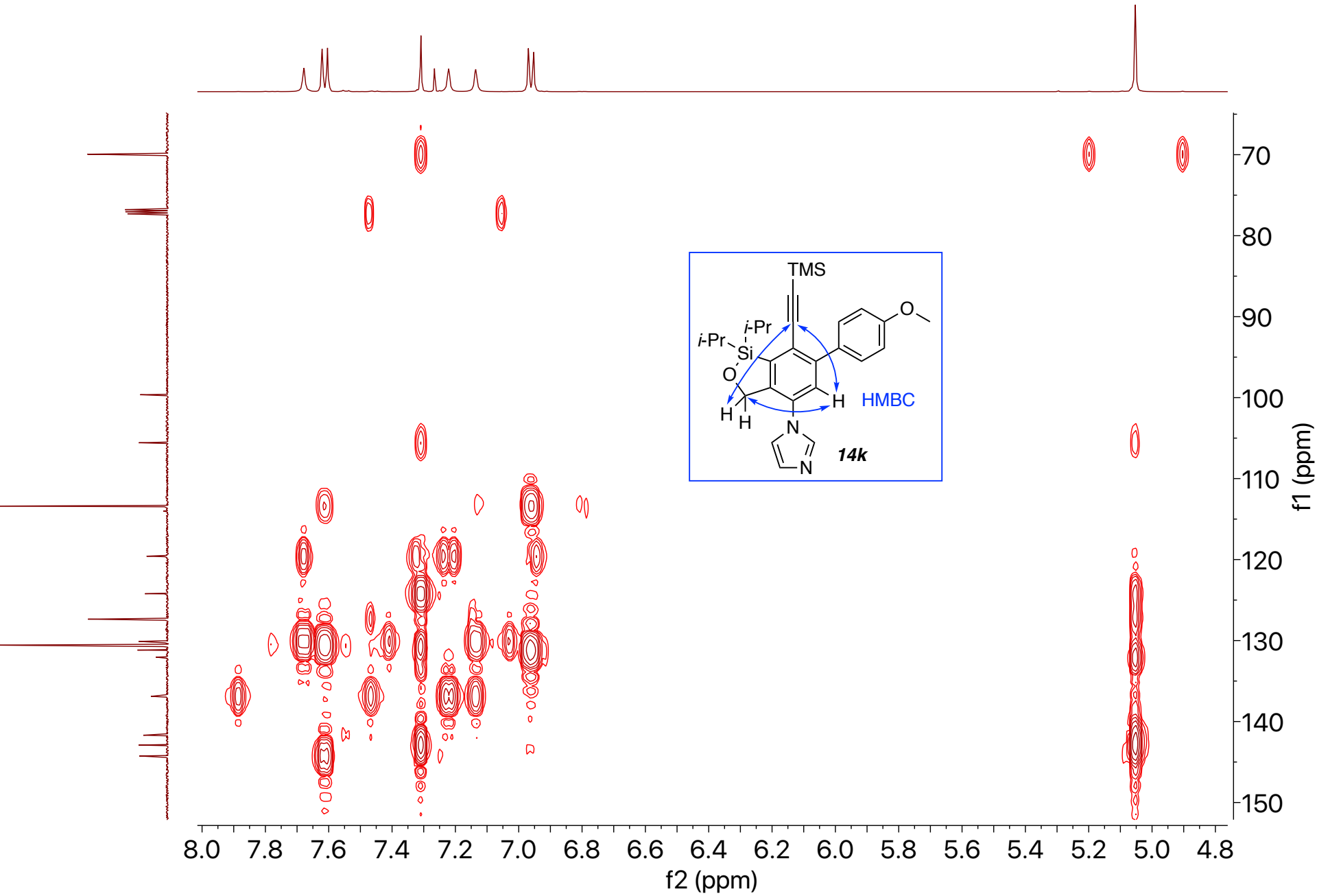
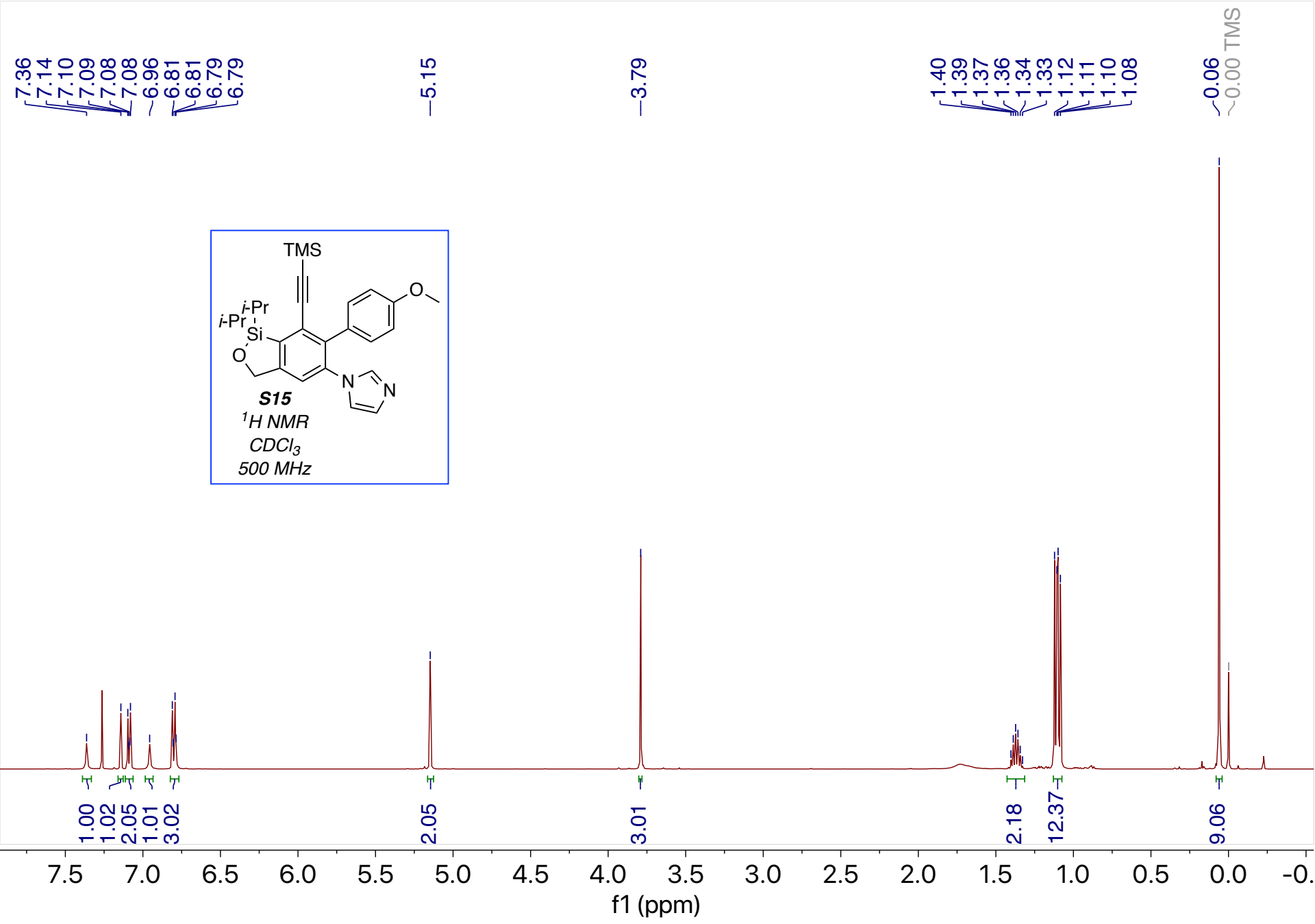
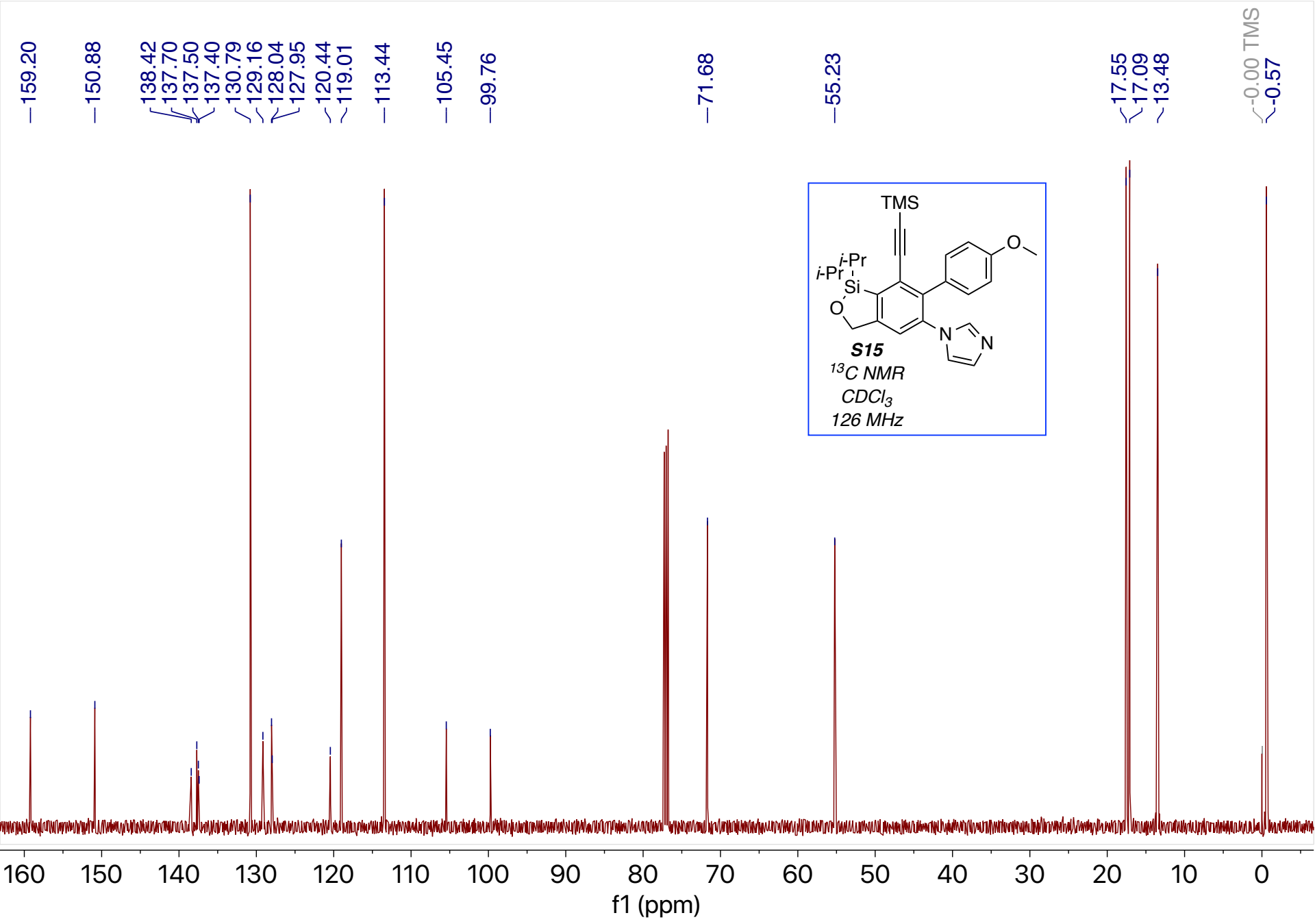
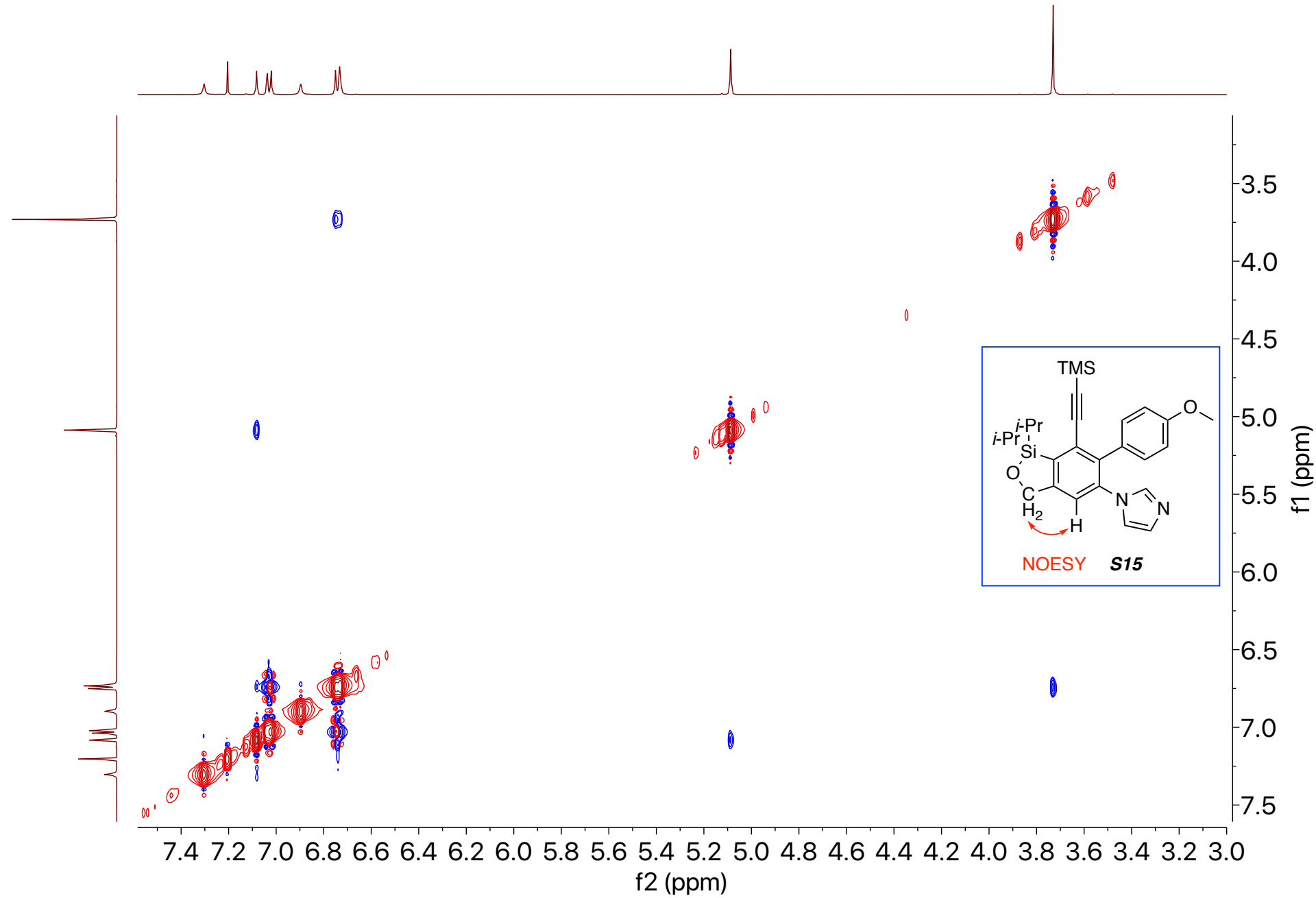
136.88
132.04
131.17
130.56
130.10
127.35
124.22
119.58
113.39
105.57
99.63
69.93
55.38
17.61
17.07
13.49
0.00 TMS
-0.50
TMS
i-Pr
i-Pr
Si
O
O
N
N
14k
13C NMR
CDCl3
126 MHz
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

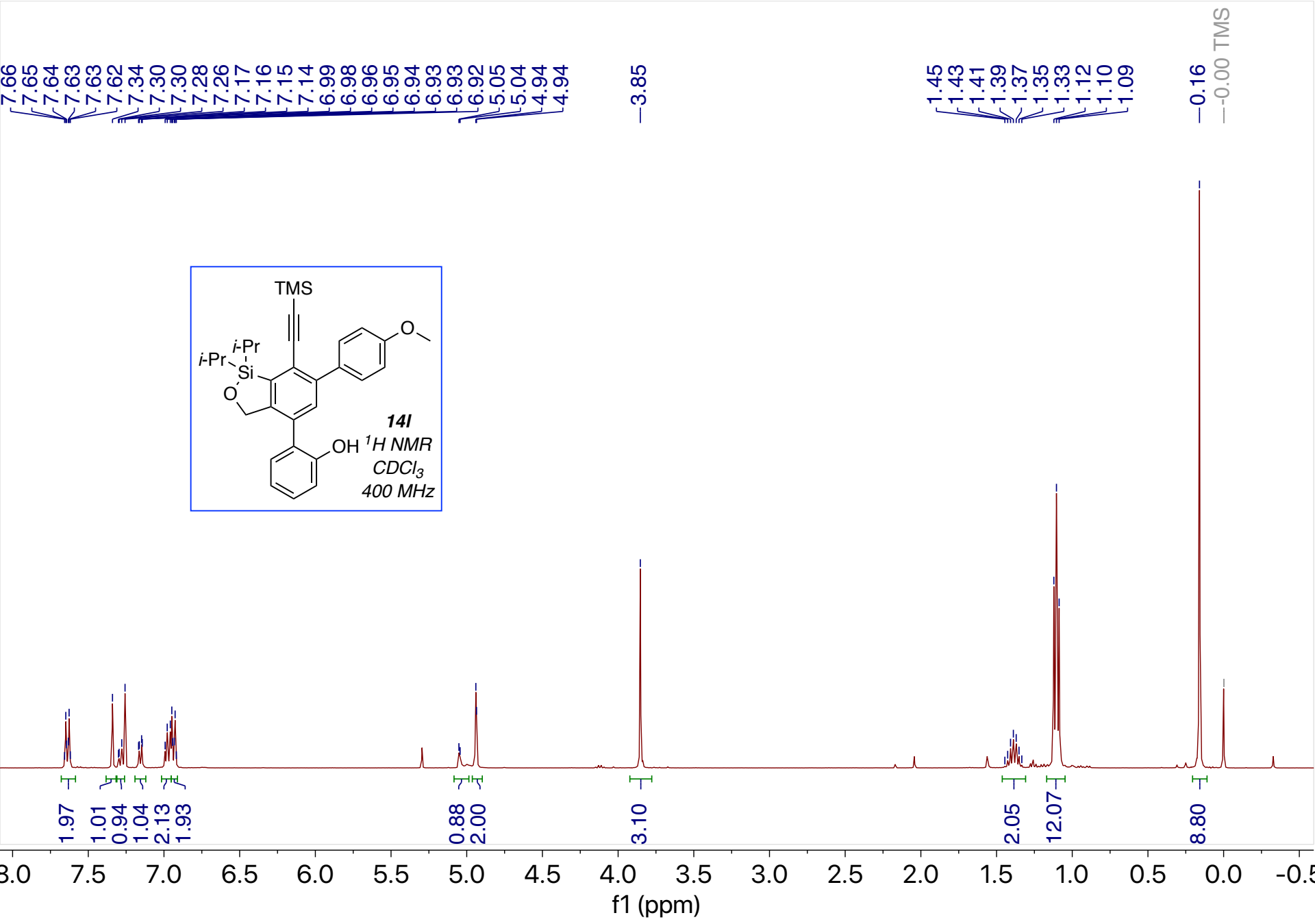

TMS
i-Pr
i-Pr
Si
O
C
H2
H
H
N
H
N
O
H
NOESY
14k
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
f1 (ppm)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
f2 (ppm)

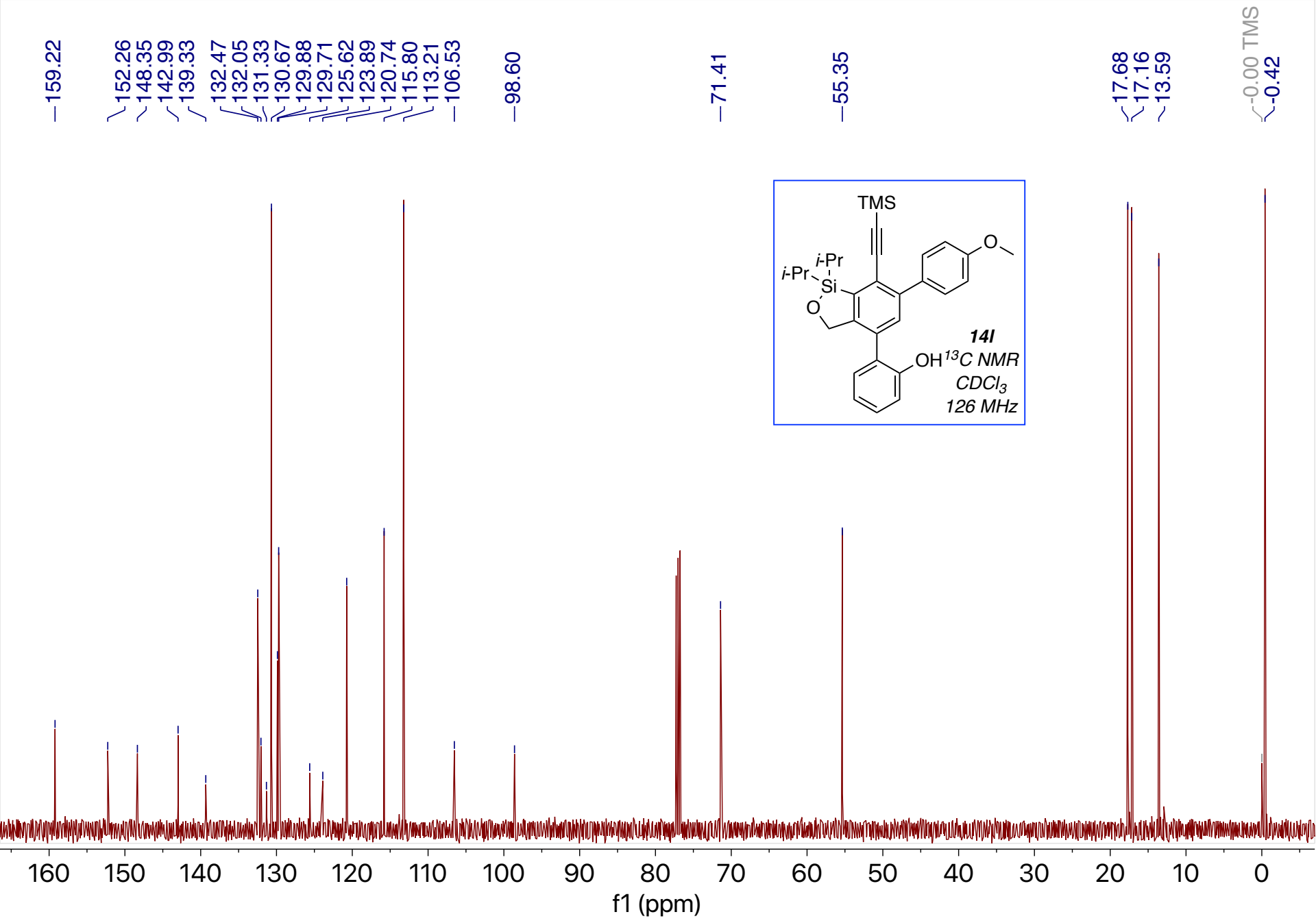

TMS
i-Pr
i-Pr
Si
O
O
H
H
H
N
N
HMBC
14k
f2 (ppm)
f1 (ppm)
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
70
80
90
100
110
120
130
140
150

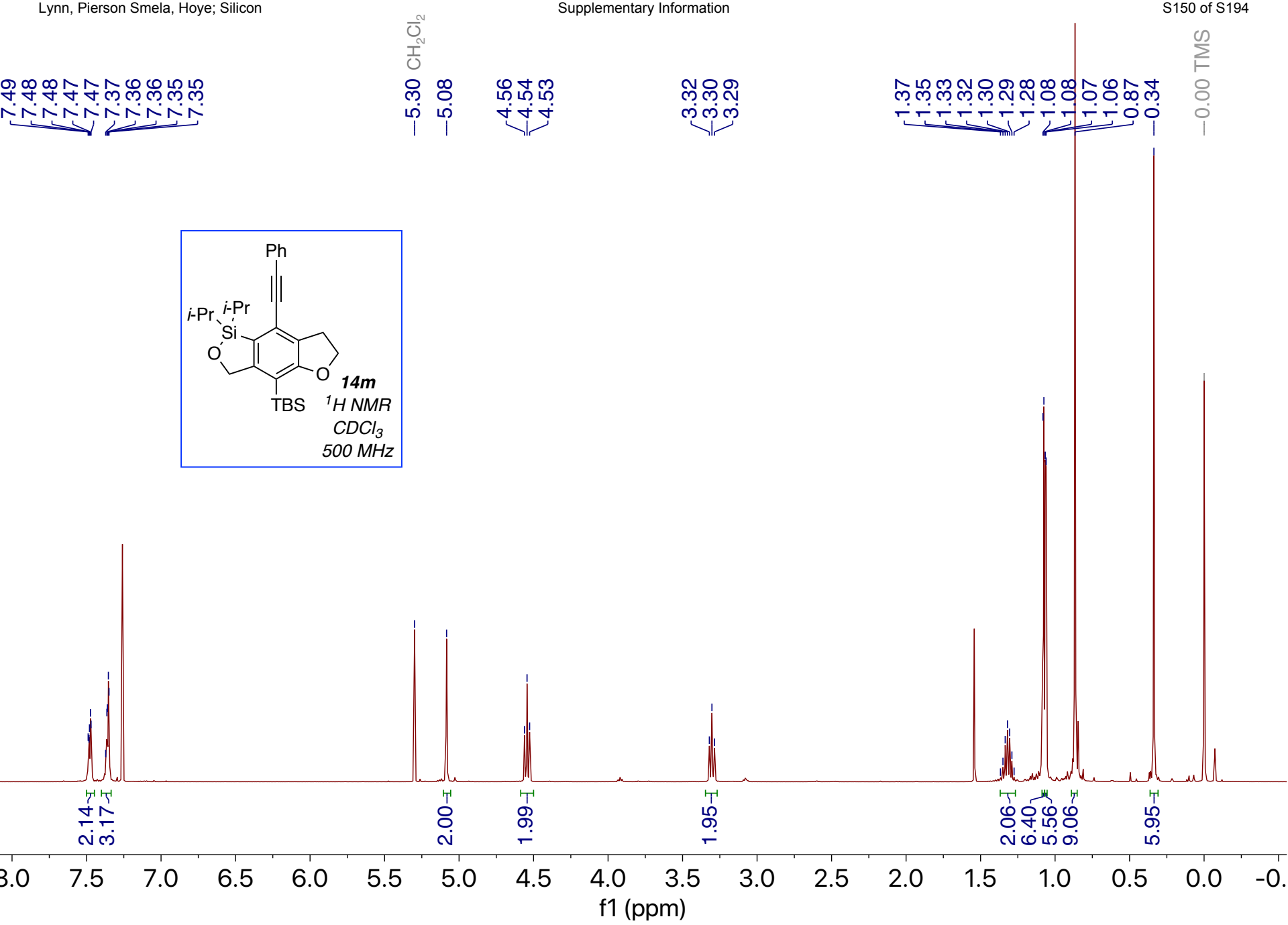

7.36
7.14
7.10
7.09
7.08
7.08
6.96
6.81
6.81
6.79
6.79
5.15
3.79
1.40
1.39
1.37
1.36
1.34
1.33
1.12
1.11
1.10
1.08
0.06
0.00 TMS
TMS
i-Pr
i-Pr
Si
O
O
N
N
S15
1H NMR
CDCl3
500 MHz
1.00
1.02
2.05
1.01
3.02
2.05
3.01
2.18
12.37
9.06
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

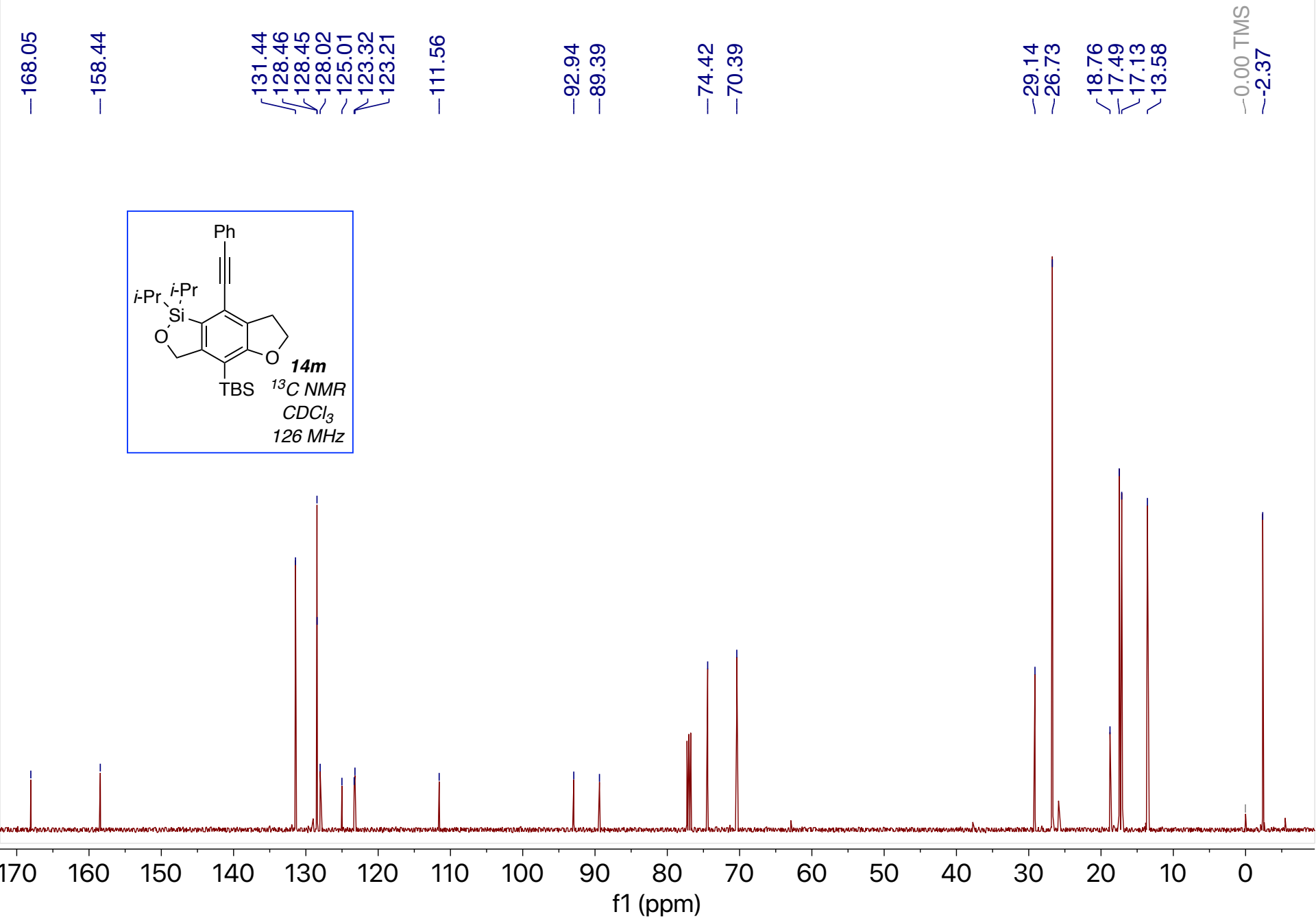

159.20
150.88
138.42
137.70
137.50
137.40
130.79
129.16
128.04
127.95
120.44
119.01
113.44
105.45
99.76
71.68
55.23
17.55
17.09
13.48
0.00 TMS
-0.57
TMS
i-Pr
i-Pr
Si
O
O
N
N
S15
13C NMR
CDCl3
126 MHz
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

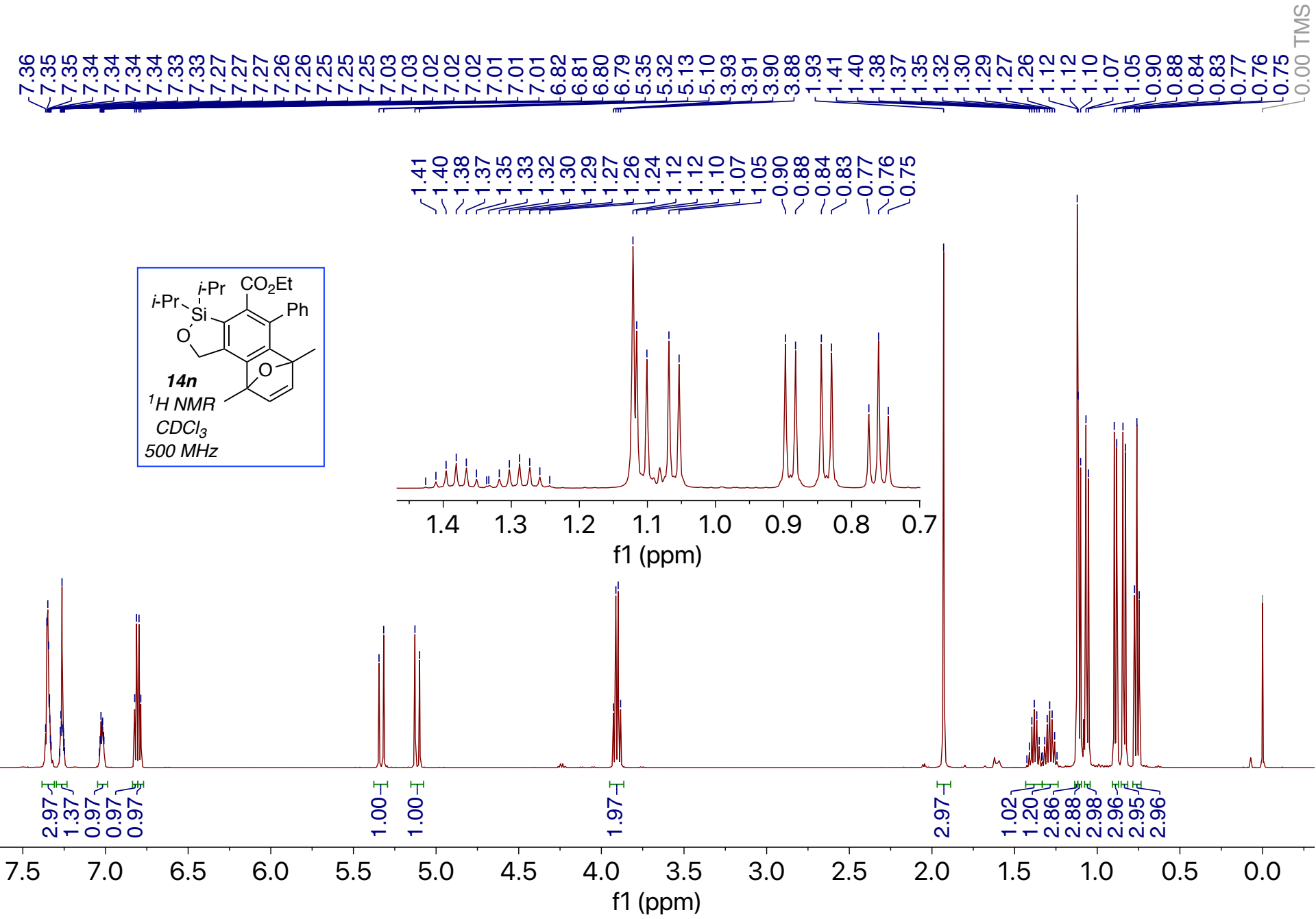

TMS
i-Pr
i-Pr
Si
O
C
H2
H
N
N
O
NOESY S15
f1 (ppm)
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0
f2 (ppm)

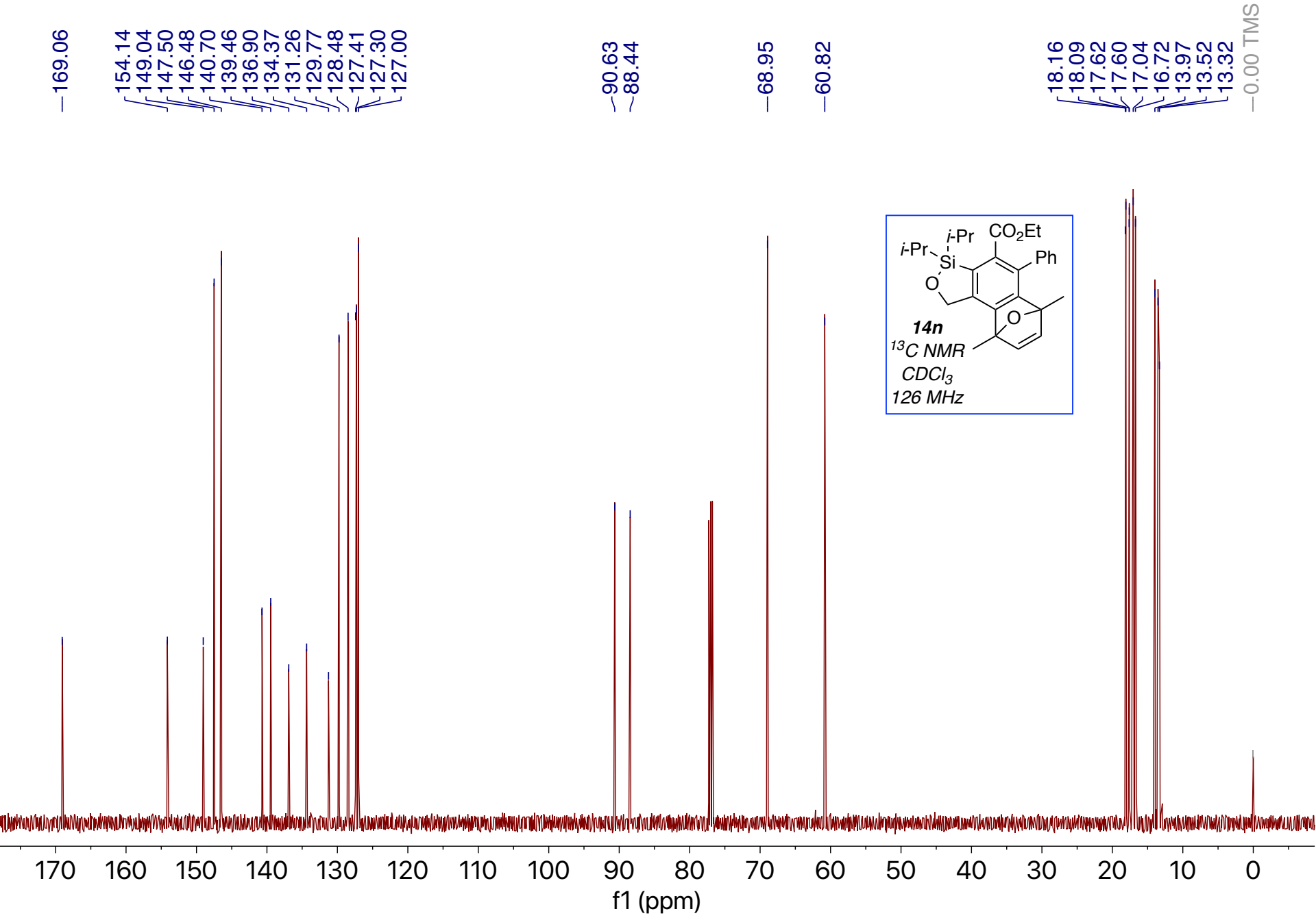

7.66
7.65
7.64
7.63
7.63
7.62
7.34
7.30
7.30
7.28
7.26
7.17
7.16
7.15
7.14
6.99
6.98
6.96
6.95
6.94
6.93
6.93
6.92
5.05
5.04
4.94
4.94
3.85
1.45
1.43
1.41
1.39
1.37
1.35
1.33
1.12
1.10
1.09
0.16
-0.00 TMS
TMS
i-Pr
i-Pr
Si
O
O
OH
14l
1H NMR
CDCl3
400 MHz
1.97
1.01
0.94
1.04
2.13
1.93
0.88
2.00
3.10
2.05
12.07
8.80
f1 (ppm)


159.22
152.26
148.35
142.99
139.33
132.47
132.05
131.33
130.67
129.88
129.71
125.62
123.89
120.74
115.80
113.21
106.53
98.60
71.41
55.35
17.68
17.16
13.59
-0.00 TMS
-0.42
TMS
i-Pr
i-Pr
Si
O
O
OH
14l
13C NMR
CDCl3
126 MHz
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.49
7.48
7.48
7.47
7.47
7.37
7.36
7.36
7.35
7.35
5.30 CH_2Cl_2
5.08
4.56
4.54
4.53
3.32
3.30
3.29
1.37
1.35
1.33
1.32
1.30
1.29
1.28
1.08
1.08
1.07
1.06
0.87
0.34
0.00 TMS
Ph
i-Pr
i-Pr
Si
O
O
TBS
14m
^1H NMR
$CDCl_3$
500 MHz
2.14
3.17
2.00
1.99
1.95
2.06
6.40
5.56
9.06
5.95
f1 (ppm)


168.05
158.44
131.44
128.46
128.45
128.02
125.01
123.32
123.21
111.56
92.94
89.39
74.42
70.39
29.14
26.73
18.76
17.49
17.13
13.58
0.00 TMS
-2.37
Ph
i-Pr
i-Pr
Si
O
O
TBS
14m
13C NMR
CDCl3
126 MHz
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.36 7.35 7.35 7.34 7.34 7.34 7.34 7.33 7.33 7.27 7.27 7.27 7.26 7.26 7.25 7.25 7.25 7.03 7.03 7.02 7.02 7.02 7.01 7.01 7.01 6.82 6.81 6.80 6.79 5.35 5.32 5.13 5.10 3.93 3.91 3.90 3.88 1.93 1.41 1.40 1.38 1.37 1.35 1.32 1.30 1.29 1.27 1.26 1.12 1.12 1.10 1.07 1.05 0.90 0.88 0.84 0.83 0.77 0.76 0.75 0.00 TMS
i-Pr
i-Pr
Si
O
CO2Et
Ph
O
14n
1H NMR
CDCl3
500 MHz
1.41 1.40 1.38 1.37 1.35 1.33 1.32 1.30 1.29 1.27 1.26 1.24 1.12 1.12 1.10 1.07 1.05 0.90 0.88 0.84 0.83 0.77 0.76 0.75
1.4 1.3 1.2 1.1 1.0 0.9 0.8 0.7
f1 (ppm)
2.97 1.37 0.97 0.97 0.97 1.00 1.00 1.97 2.97 1.02 1.20 2.86 2.88 2.98 2.96 2.95 2.96
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
f1 (ppm)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154.14
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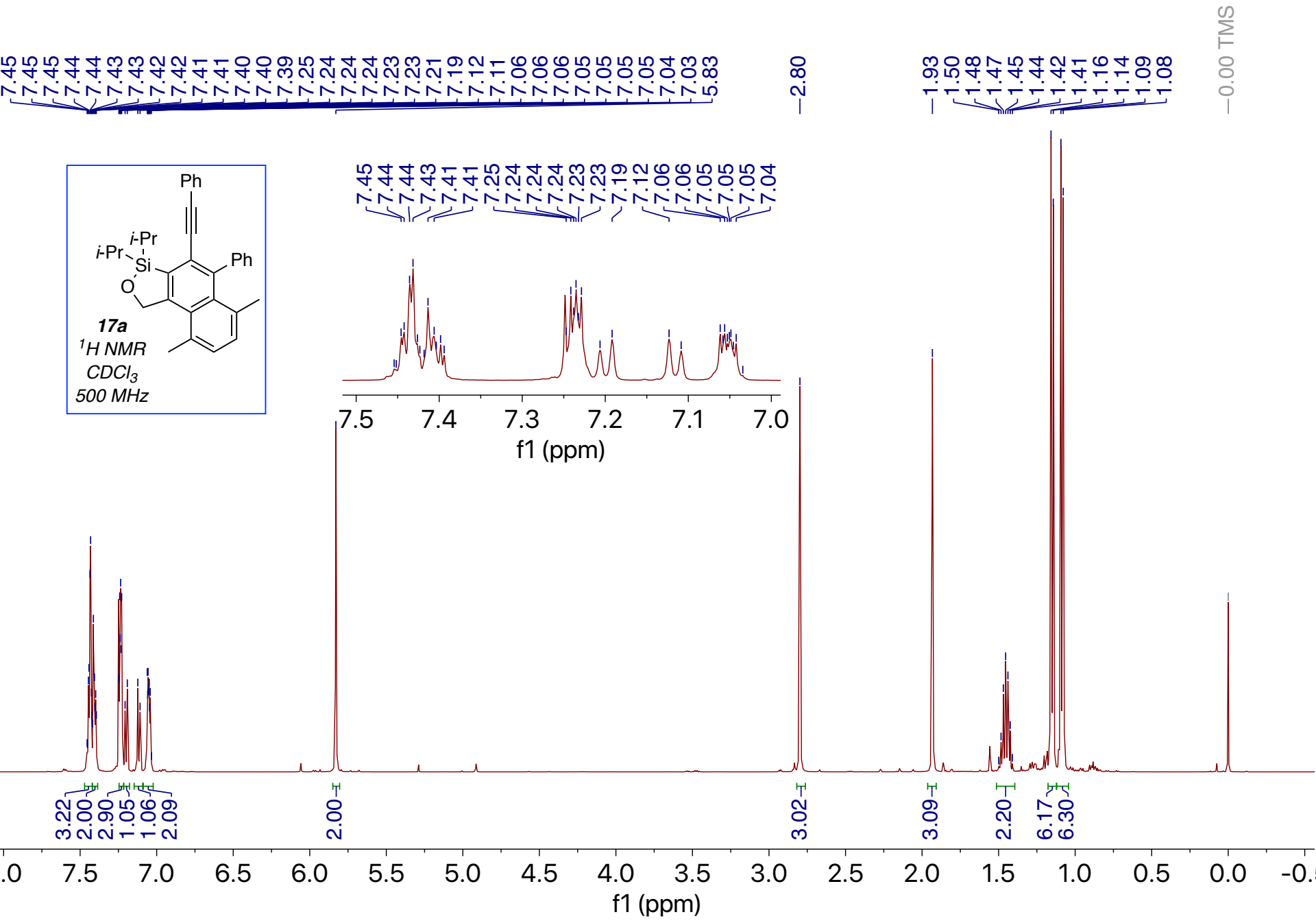
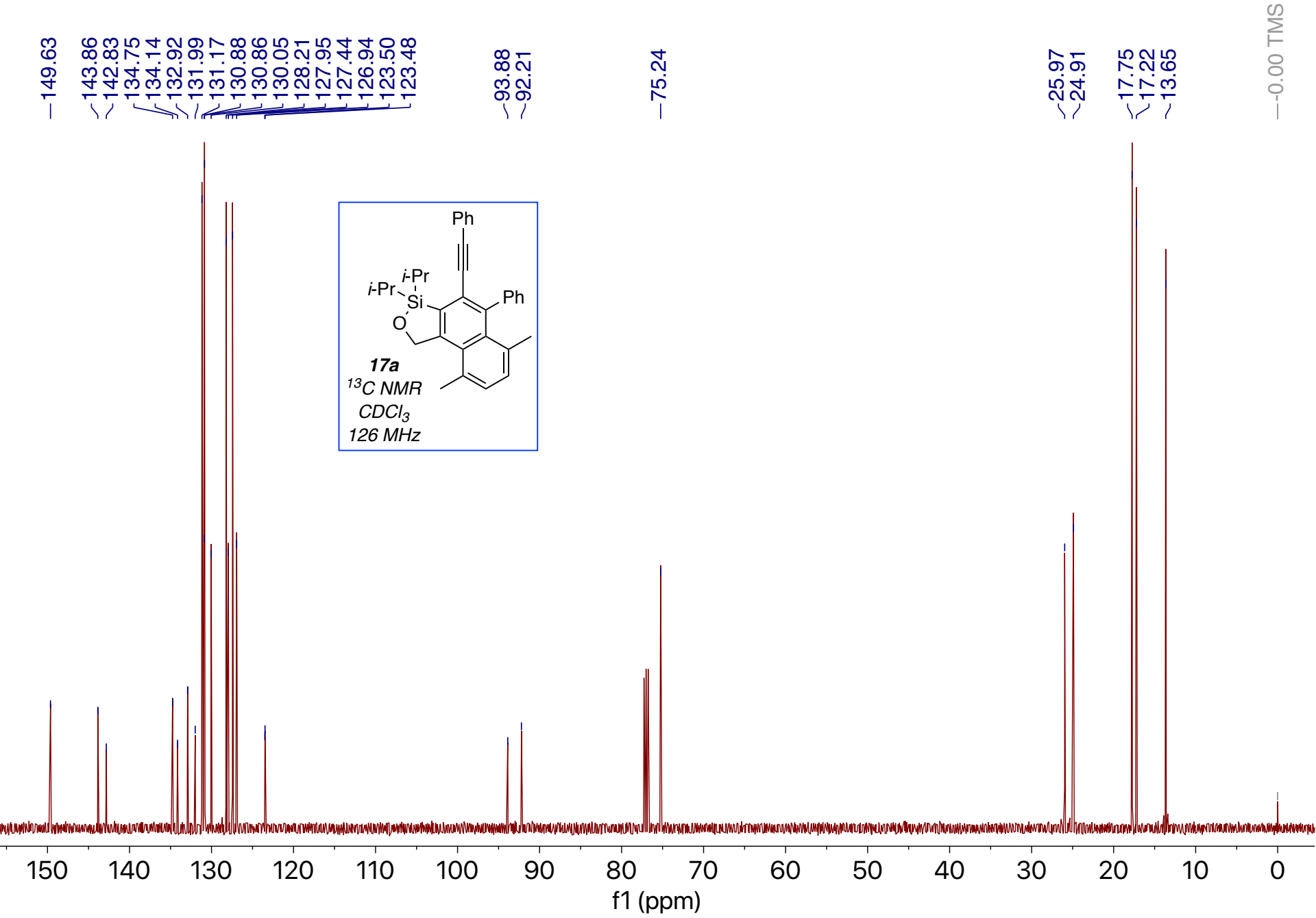
140.70
139.46
136.90
134.37
131.26
129.77
128.48
127.41
127.30
127.00
90.63
88.44
68.95
60.82
18.16
18.09
17.62
17.60
17.04
16.72
13.97
13.52
13.32
0.00 TMS
i-Pr
i-Pr
Si
O
CO2Et
Ph
O
14n
13C NMR
CDCl3
126 MHz
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.45 7.45 7.45 7.44 7.44 7.43 7.43 7.42 7.42 7.41 7.41 7.40 7.40 7.39 7.25 7.24 7.24 7.24 7.23 7.23 7.21 7.19 7.12 7.11 7.06 7.06 7.06 7.05 7.05 7.05 7.05 7.04 7.03 5.83
2.80
1.93 1.50 1.48 1.47 1.45 1.44 1.42 1.41 1.16 1.14 1.09 1.08
0.00 TMS
Ph
i-Pr
i-Pr
Si
O
Ph
17a
1H NMR
CDCl3
500 MHz
7.45 7.44 7.44 7.43 7.41 7.41 7.25 7.24 7.24 7.24 7.23 7.23 7.19 7.12 7.06 7.06 7.05 7.05 7.05 7.04
7.5 7.4 7.3 7.2 7.1 7.0
f1 (ppm)
3.22 2.00 2.90 1.05 1.06 2.09
2.00
3.02
3.09
2.20
6.17
6.30
.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.
f1 (ppm)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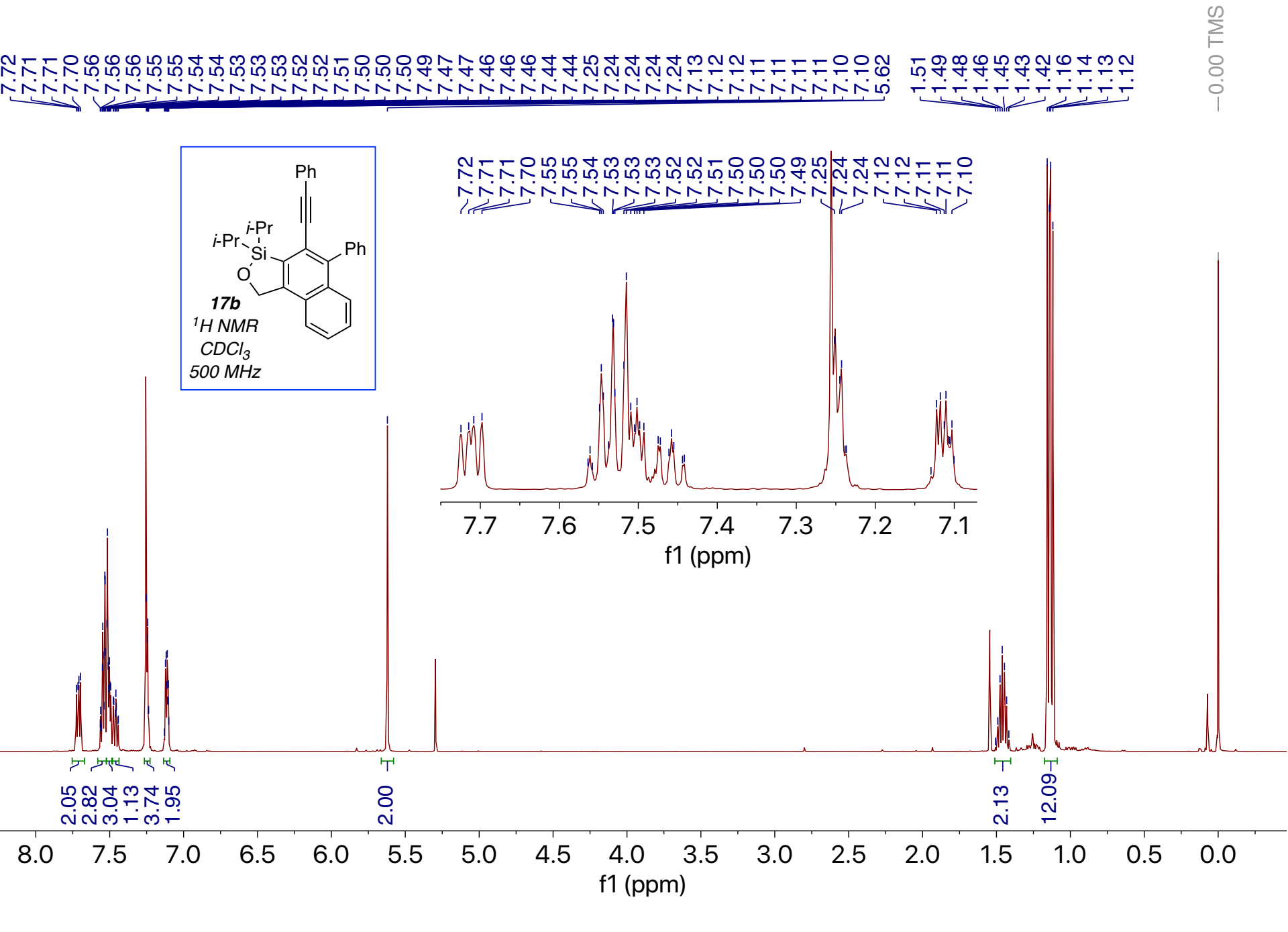
131.17
130.88
130.86
130.05
128.21
127.95
127.44
126.94
123.50
123.48
93.88
92.21
75.24
25.97
24.91
17.75
17.22
13.65
-0.00 TMS
Ph
i-Pr
i-Pr
Si
O
Ph
17a
13C NMR
CDCl3
126 MHz
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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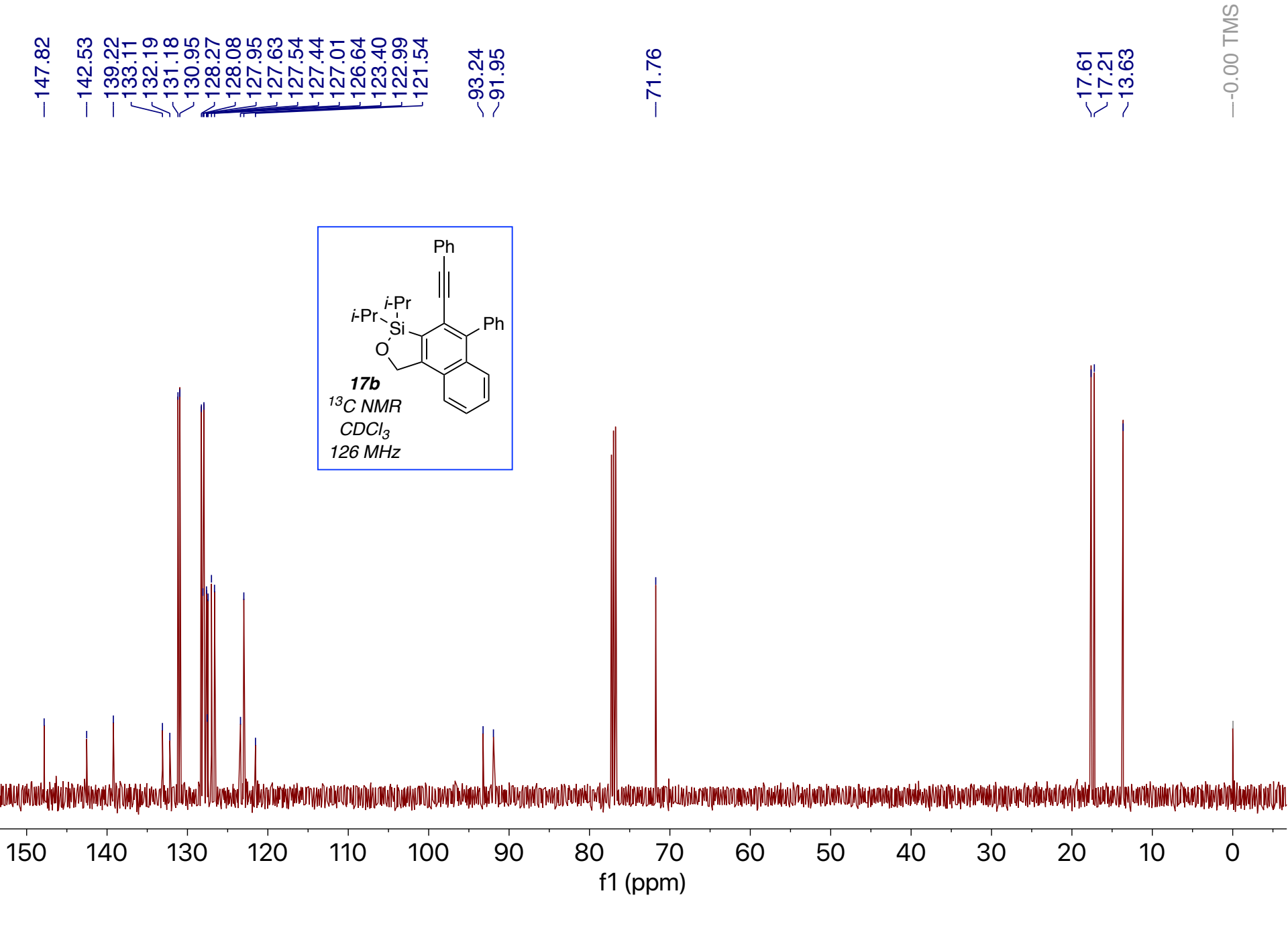
1.51 1.49 1.48 1.46 1.45 1.43 1.42 1.16 1.14 1.13 1.12
0.00 TMS
Ph
i-Pr
i-Pr
Si
O
Ph
17b
1H NMR
CDCl3
500 MHz
7.72 7.71 7.71 7.70 7.55 7.55 7.54 7.53 7.53 7.53 7.52 7.52 7.51 7.50 7.50 7.50 7.49 7.25 7.24 7.24 7.12 7.12 7.11 7.11 7.10
7.7 7.6 7.5 7.4 7.3 7.2 7.1
f1 (ppm)
2.05 2.82 3.04 1.13 3.74 1.95 2.00 2.13 12.09
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
f1 (ppm)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131.18
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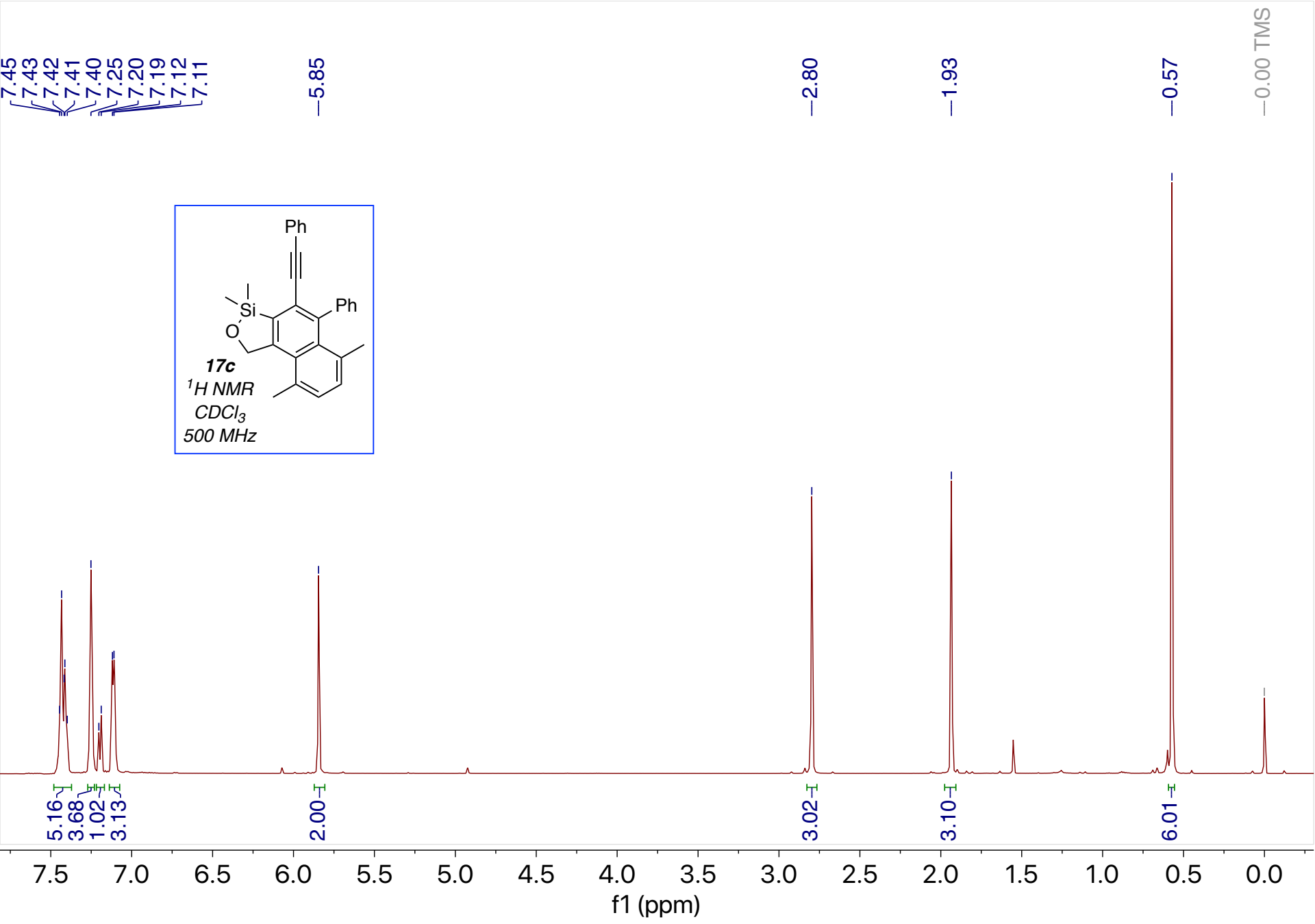
128.27
128.08
127.95
127.63
127.54
127.44
127.01
126.64
123.40
122.99
121.54
93.24
91.95
71.76
17.61
17.21
13.63
0.00 TMS
Ph
i-Pr
i-Pr
Si
O
Ph
17b
13C NMR
CDCl3
126 MHz
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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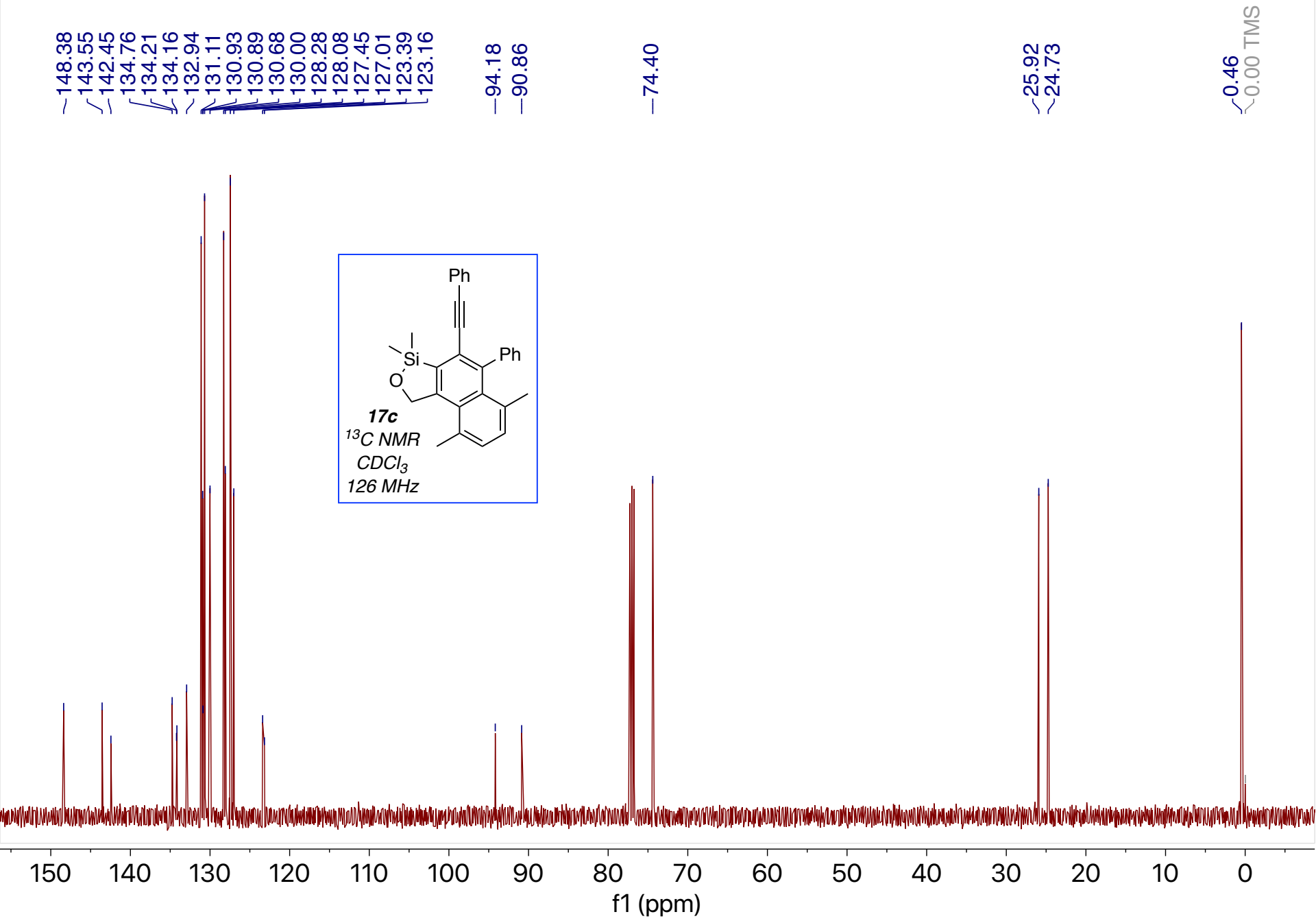
7.41
7.40
7.25
7.20
7.19
7.12
7.11
5.85
2.80
1.93
0.57
0.00 TMS
Ph
Si
O
Ph
17c
1H NMR
CDCl3
500 MHz
5.16
3.68
1.02
3.13
2.00
3.02
3.10
6.01
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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131.11
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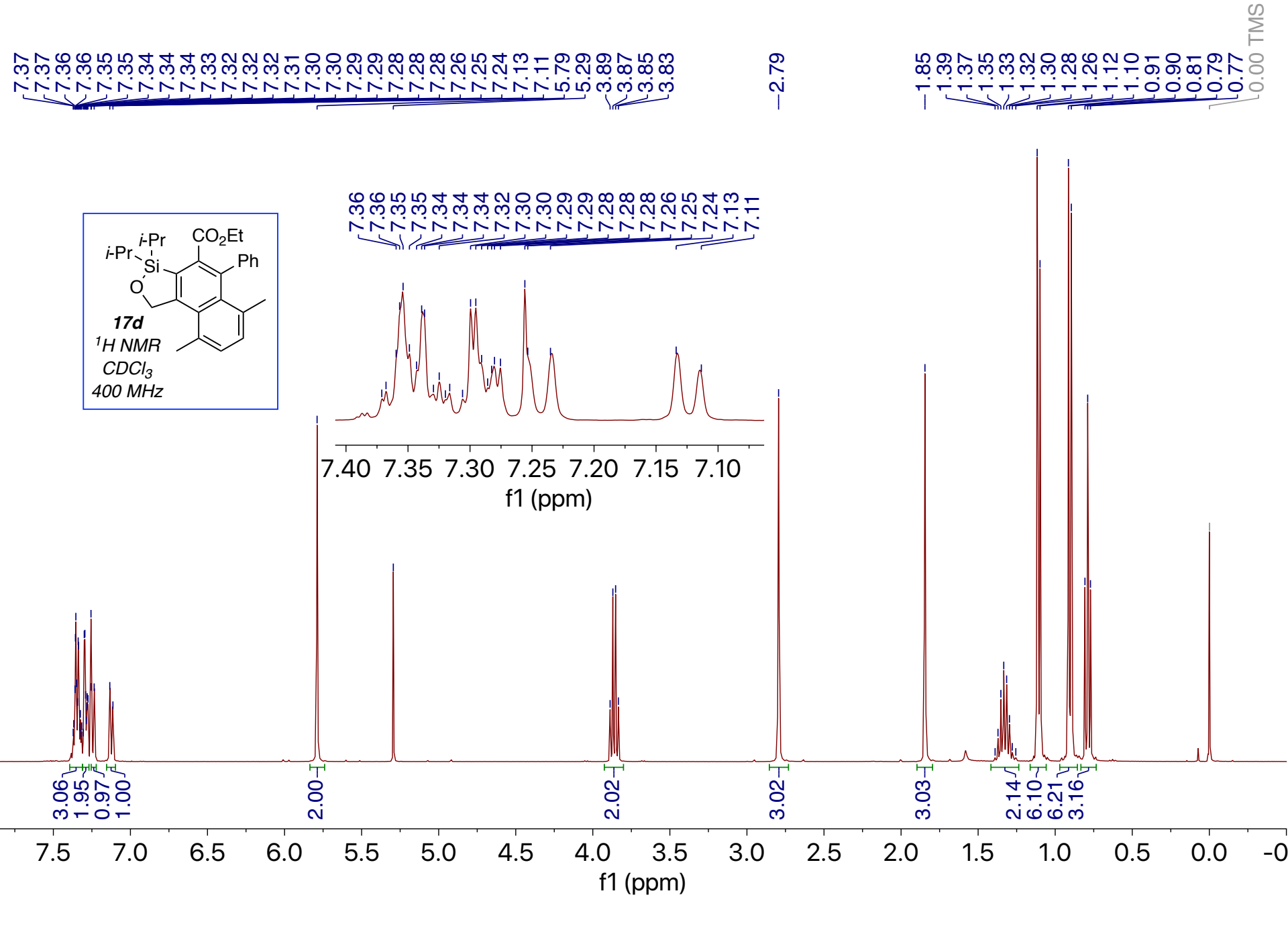
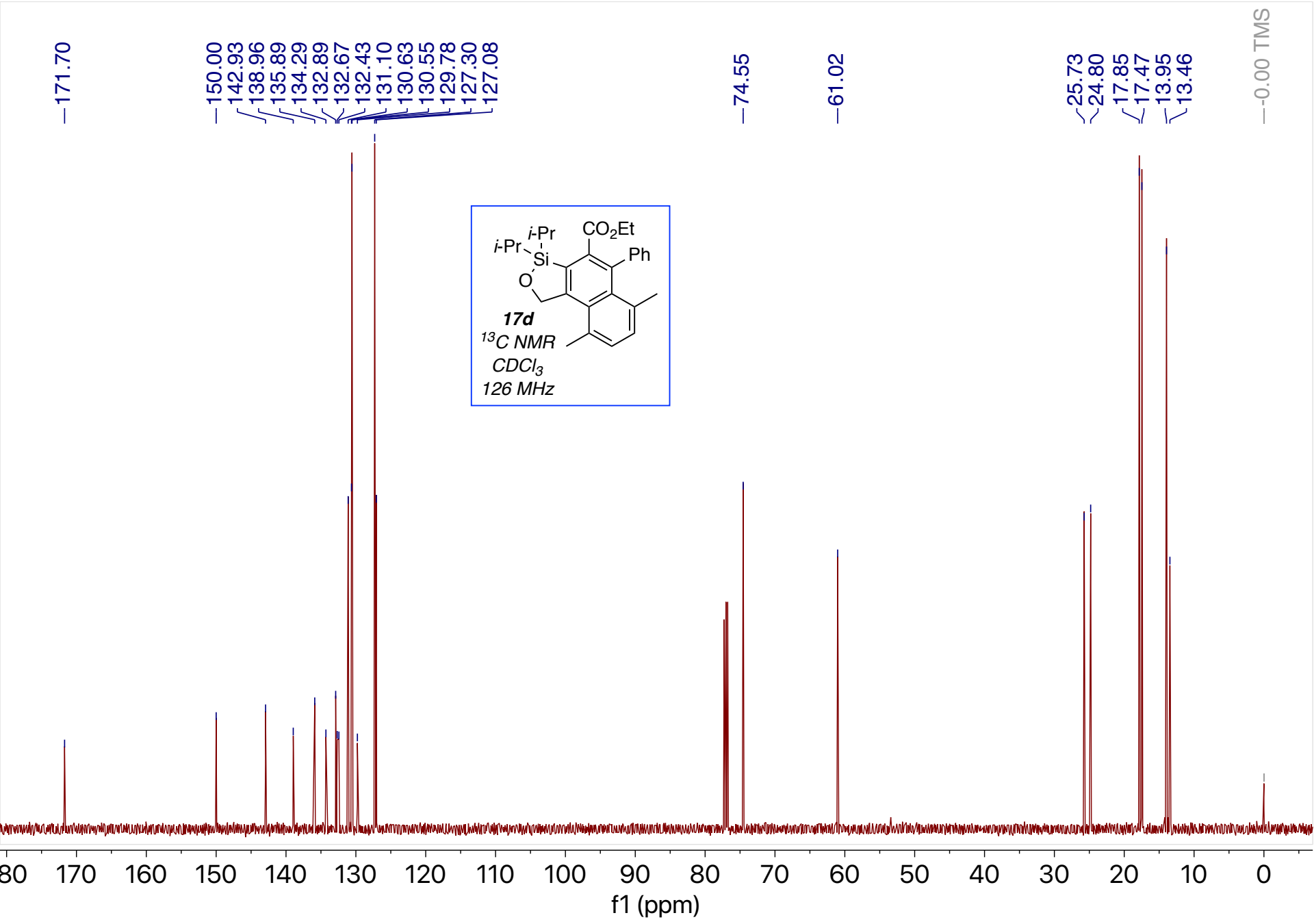
130.89
130.68
130.00
128.28
128.08
127.45
127.01
123.39
123.16
94.18
90.86
74.40
25.92
24.73
0.46
0.00 TMS
Ph
Si
O
Ph
17c
13C NMR
CDCl3
126 MHz
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.37 7.37 7.36 7.36 7.35 7.35 7.34 7.34 7.34 7.33 7.32 7.32 7.32 7.31 7.30 7.30 7.29 7.29 7.28 7.28 7.28 7.26 7.25 7.24 7.13 7.11 5.79 5.29 3.89 3.87 3.85 3.83
2.79
1.85 1.39 1.37 1.35 1.33 1.32 1.30 1.28 1.26 1.12 1.10 0.91 0.90 0.81 0.79 0.77 0.00 TMS
i-Pr
i-Pr
Si
O
CO2Et
Ph
17d
1H NMR
CDCl3
400 MHz
7.36 7.36 7.35 7.35 7.34 7.34 7.34 7.32 7.30 7.30 7.29 7.29 7.28 7.28 7.28 7.26 7.25 7.24 7.13 7.11
7.40 7.35 7.30 7.25 7.20 7.15 7.10
f1 (ppm)
3.06 1.95 0.97 1.00 2.00 2.02 3.02 3.03 2.14 6.10 6.21 3.16
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
f1 (ppm)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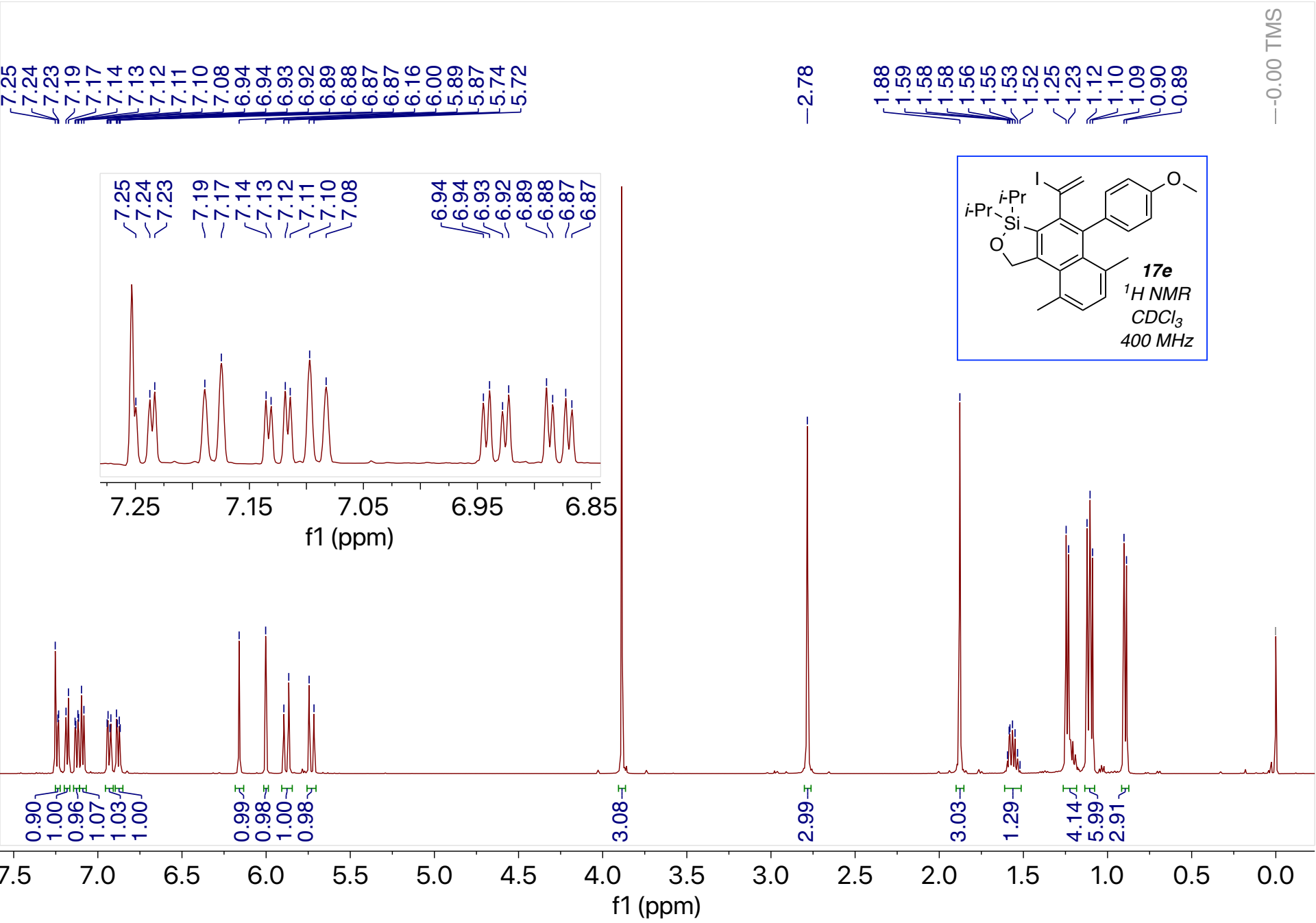
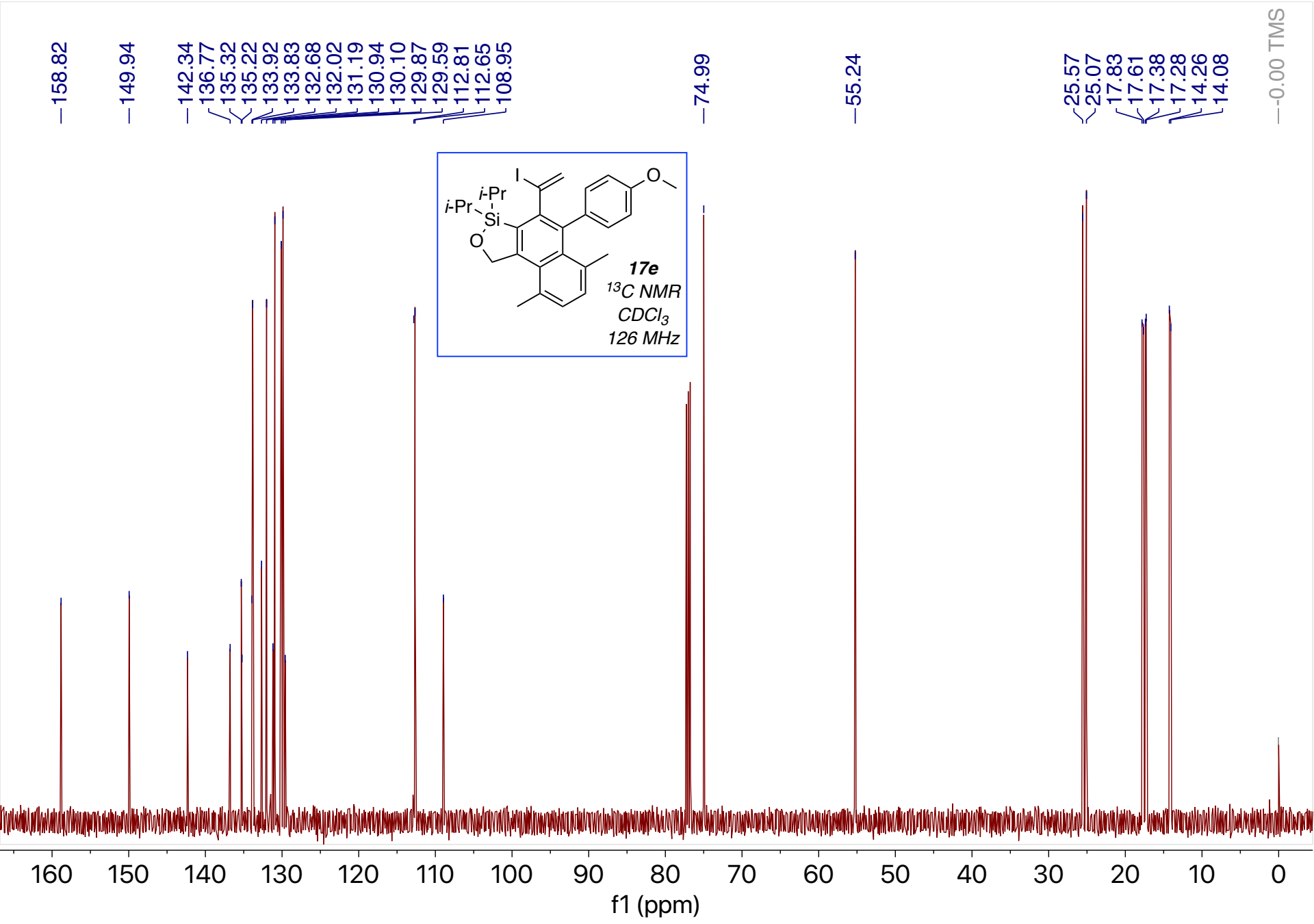
134.29
132.89
132.67
132.43
131.10
130.63
130.55
129.78
127.30
127.08
74.55
61.02
25.73
24.80
17.85
17.47
13.95
13.46
0.00 TMS
i-Pr
i-Pr
Si
O
CO2Et
Ph
17d
13C NMR
CDCl3
126 MHz
f1 (ppm)


7.25
7.24
7.23
7.19
7.17
7.14
7.13
7.12
7.11
7.10
7.08
6.94
6.94
6.93
6.92
6.89
6.88
6.87
6.87
6.16
6.00
5.89
5.87
5.74
5.72
2.78
1.88
1.59
1.58
1.58
1.56
1.55
1.53
1.52
1.25
1.23
1.12
1.10
1.09
0.90
0.89
0.00 TMS
i-Pr
i-Pr
Si
O
I
O
17e
1H NMR
CDCl3
400 MHz
7.25
7.15
7.05
6.95
6.85
f1 (ppm)
0.90
1.00
0.96
1.07
1.03
1.00
0.99
0.98
1.00
0.98
3.08
2.99
3.03
1.29
4.14
5.99
2.91
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
f1 (ppm)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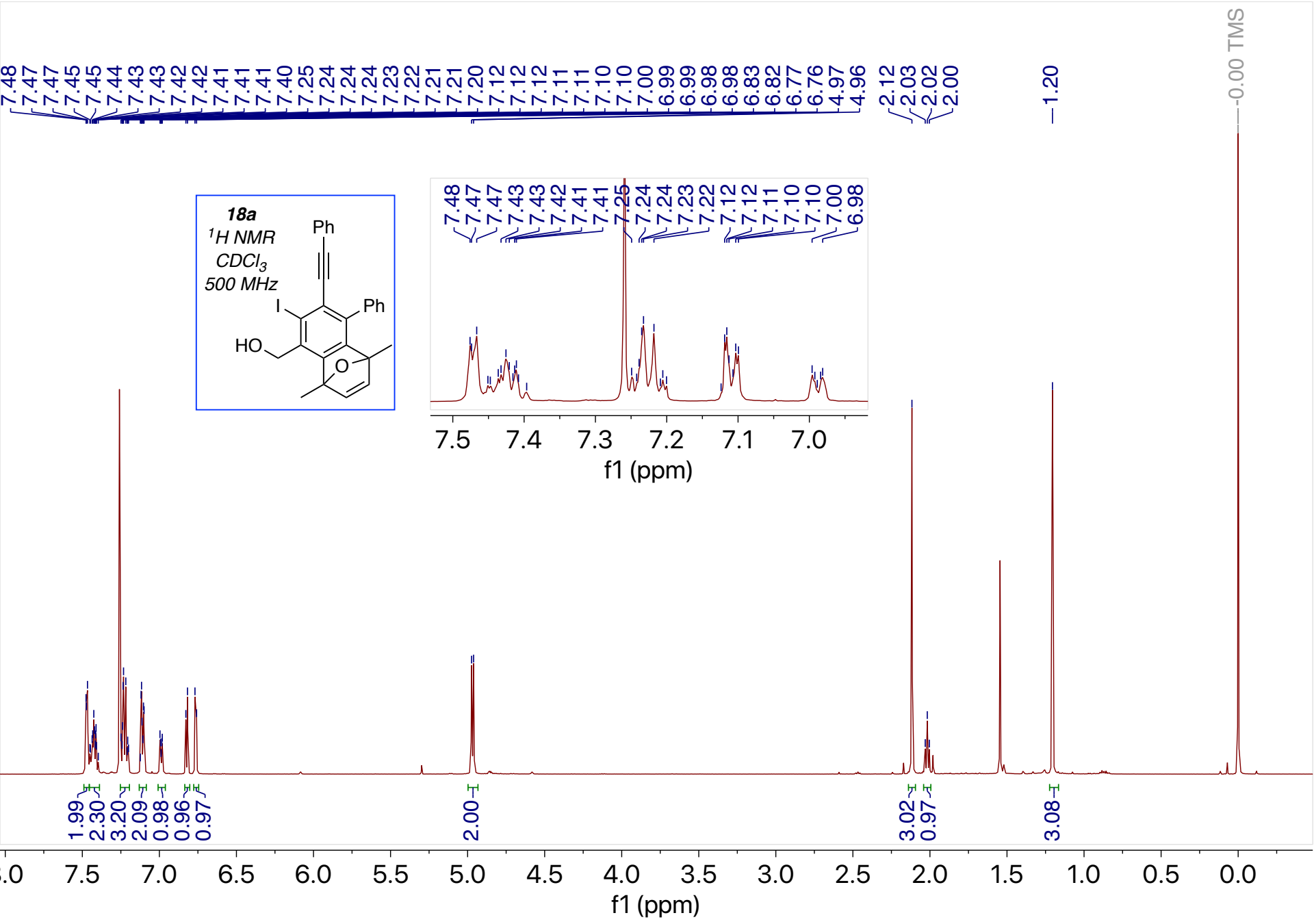
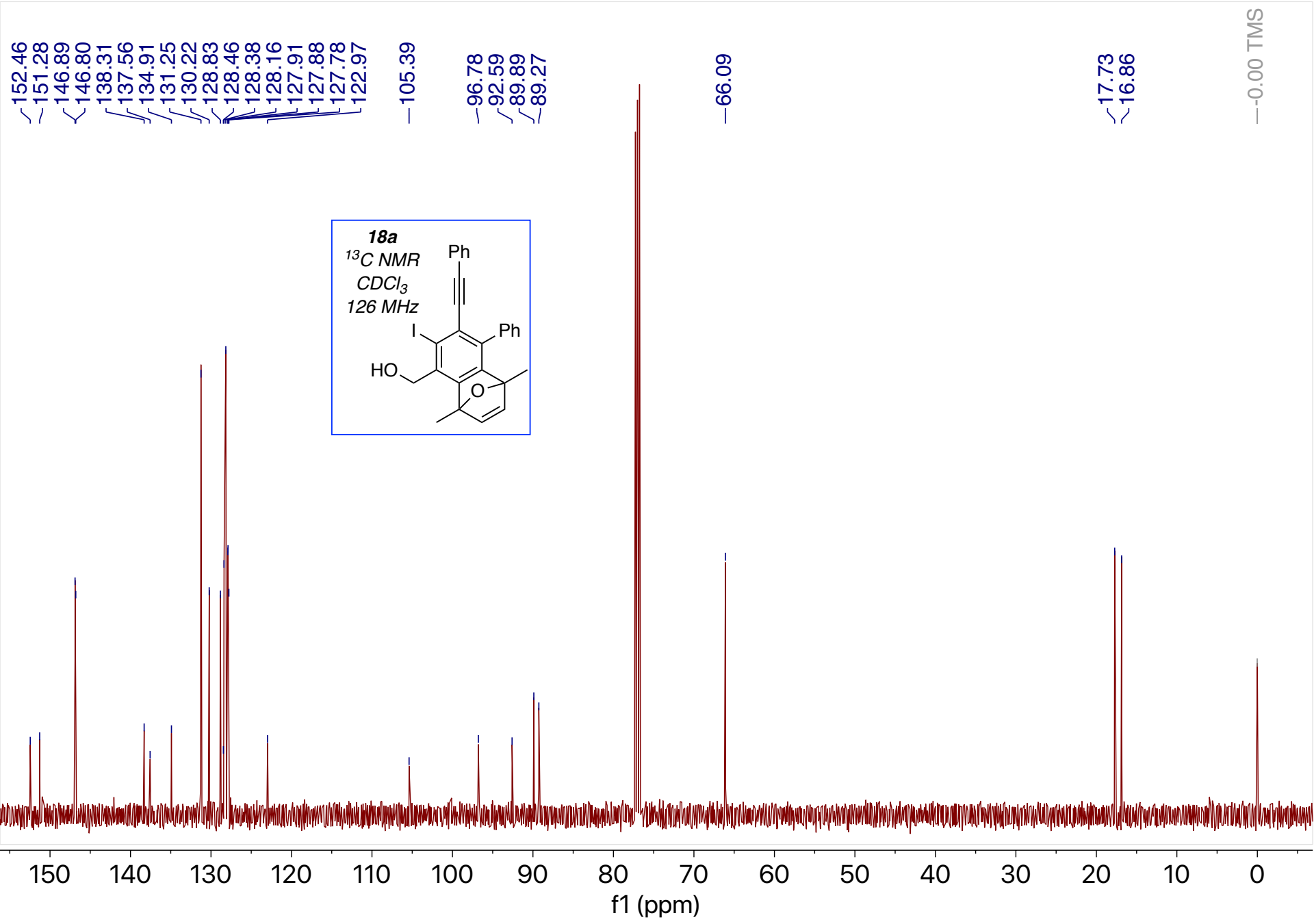
133.83
132.68
132.02
131.19
130.94
130.10
129.87
129.59
112.81
112.65
108.95
74.99
55.24
25.57
25.07
17.83
17.61
17.38
17.28
14.26
14.08
0.00 TMS
I
O
i-Pr
i-Pr
Si
O
17e
13C NMR
CDCl3
126 MHz
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


18a
1H NMR
CDCl3
500 MHz
Ph
I
Ph
HO
O
7.48 7.47 7.47 7.45 7.45 7.44 7.43 7.43 7.42 7.42 7.41 7.41 7.41 7.40 7.25 7.24 7.24 7.24 7.23 7.22 7.21 7.21 7.20 7.12 7.12 7.12 7.11 7.11 7.10 7.10 7.00 6.99 6.99 6.98 6.98 6.83 6.82 6.77 6.76 4.97 4.96 2.12 2.03 2.02 2.00 1.20 -0.00 TMS
7.5 7.4 7.3 7.2 7.1 7.0
f1 (ppm)
1.99 2.30 3.20 2.09 0.98 0.96 0.97 2.00 3.02 0.97 3.08
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
f1 (ppm)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134.91
131.25
130.22
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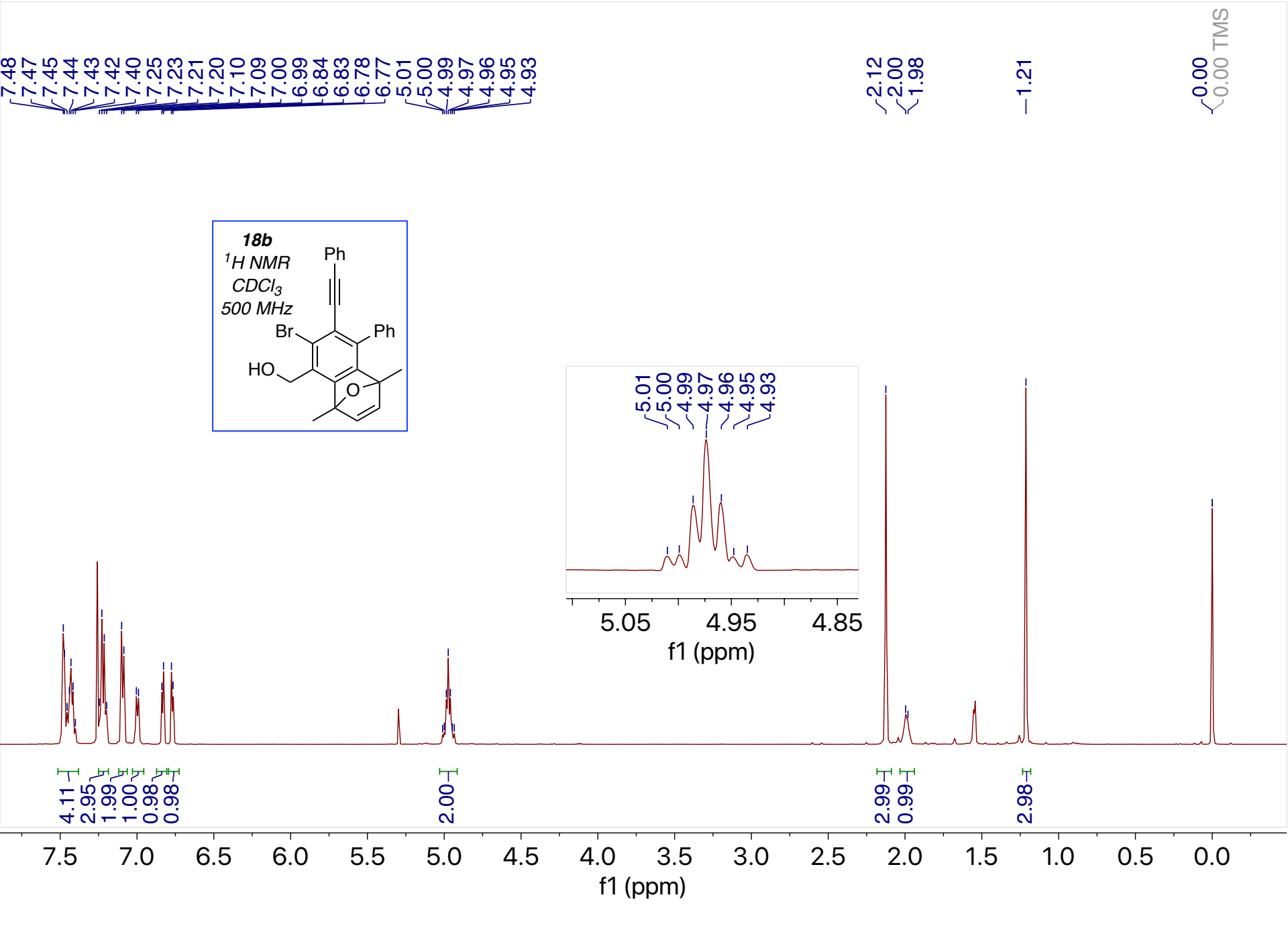
128.46
128.38
128.16
127.91
127.88
127.78
122.97
105.39
96.78
92.59
89.89
89.27
66.09
17.73
16.86
-0.00 TMS
18a
13C NMR
CDCl3
126 MHz
Ph
I
Ph
HO
O
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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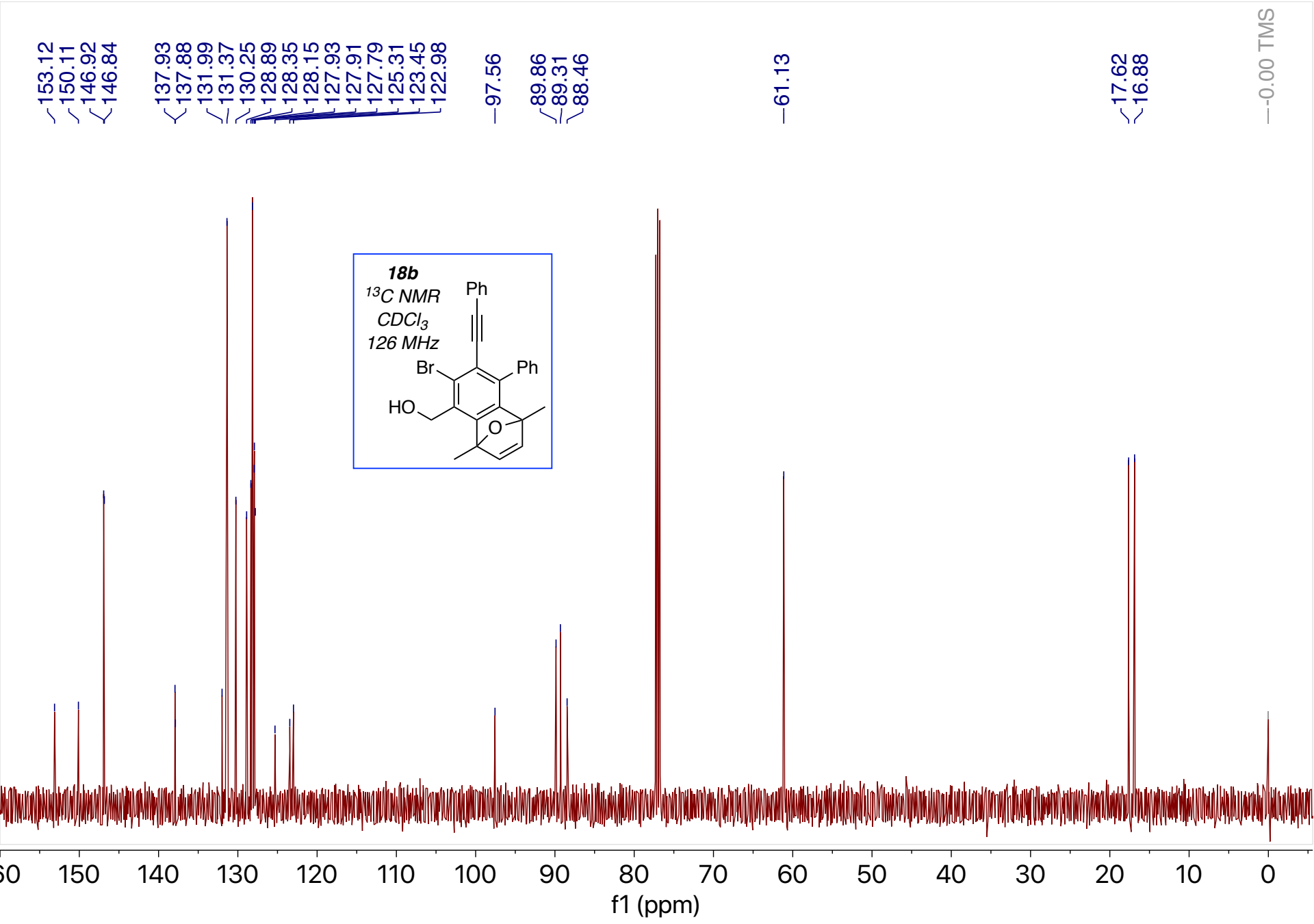
7.47
7.45
7.44
7.43
7.42
7.40
7.25
7.23
7.21
7.20
7.10
7.09
7.00
6.99
6.84
6.83
6.78
6.77
5.01
5.00
4.99
4.97
4.96
4.95
4.93
2.12
2.00
1.98
1.21
0.00
0.00 TMS
18b
1H NMR
CDCl3
500 MHz
Ph
Br
Ph
HO
O
5.01
5.00
4.99
4.97
4.96
4.95
4.93
5.05
4.95
4.85
f1 (ppm)
4.11
2.95
1.99
1.00
0.98
0.98
2.00
2.99
0.99
2.98
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
f1 (ppm)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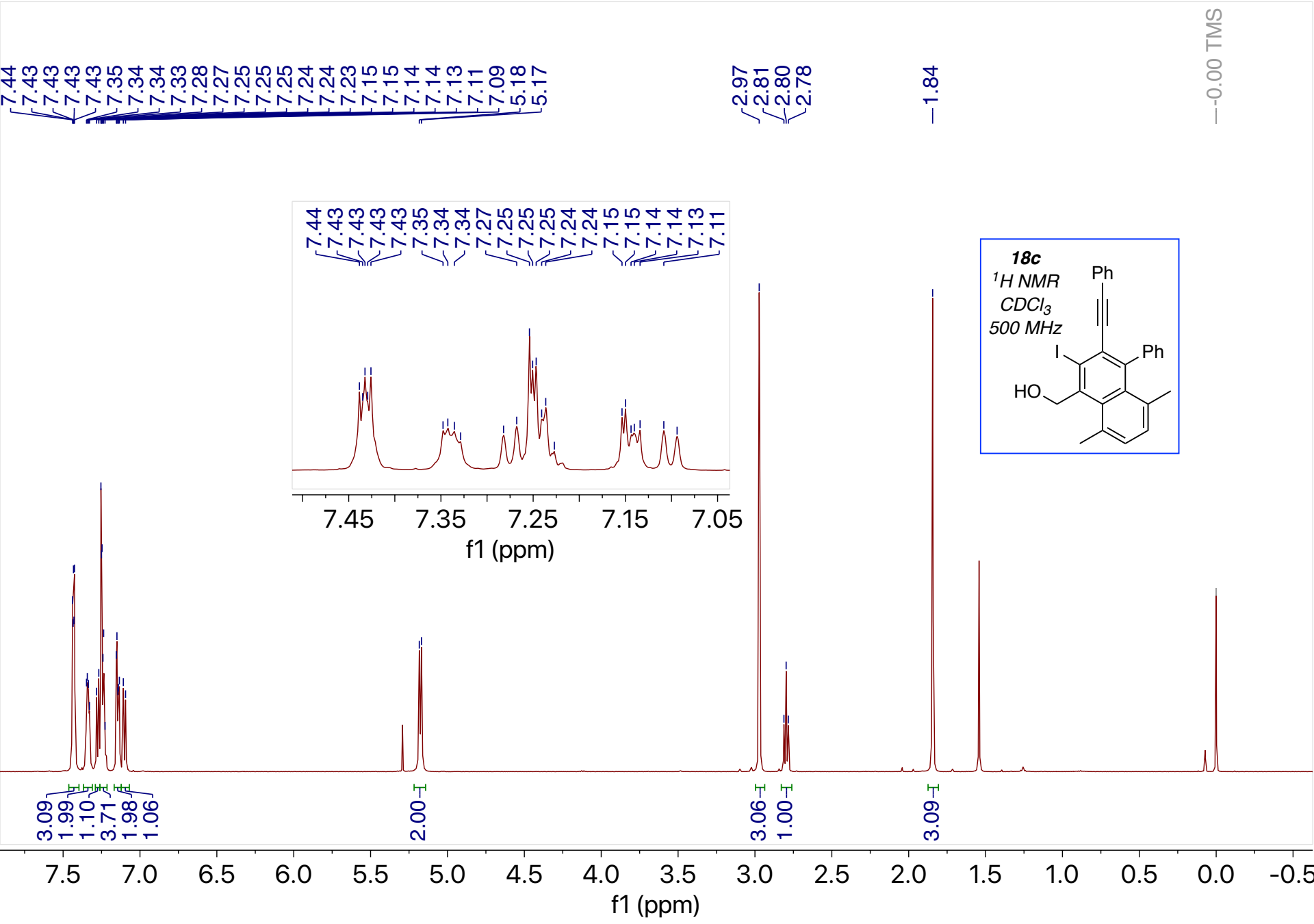
150.11
146.92
146.84
137.93
137.88
131.99
131.37
130.25
128.89
128.35
128.15
127.93
127.91
127.79
125.31
123.45
122.98
97.56
89.86
89.31
88.46
61.13
17.62
16.88
0.00 TMS
18b
13C NMR
CDCl3
126 MHz
Ph
Br
Ph
HO
O
f1 (ppm)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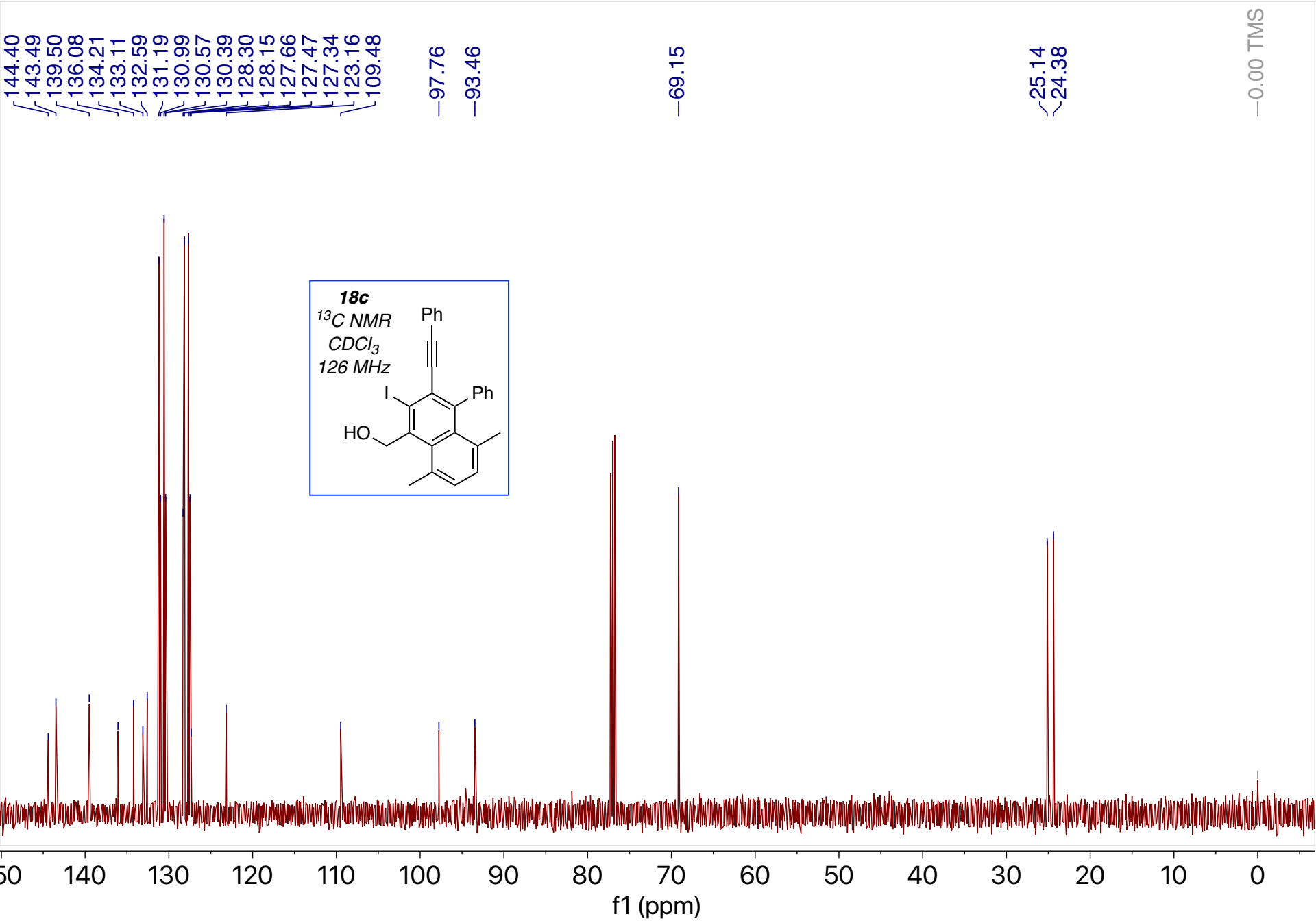
7.43
7.43
7.43
7.43
7.35
7.34
7.34
7.33
7.28
7.27
7.25
7.25
7.25
7.24
7.24
7.23
7.15
7.15
7.14
7.14
7.13
7.11
7.09
5.18
5.17
2.97
2.81
2.80
2.78
1.84
-0.00 TMS
18c
1H NMR
CDCl3
500 MHz
Ph
I
Ph
HO
7.45
7.35
7.25
7.15
7.05
f1 (ppm)
3.09
1.99
1.10
3.71
1.98
1.06
2.00
3.06
1.00
3.09
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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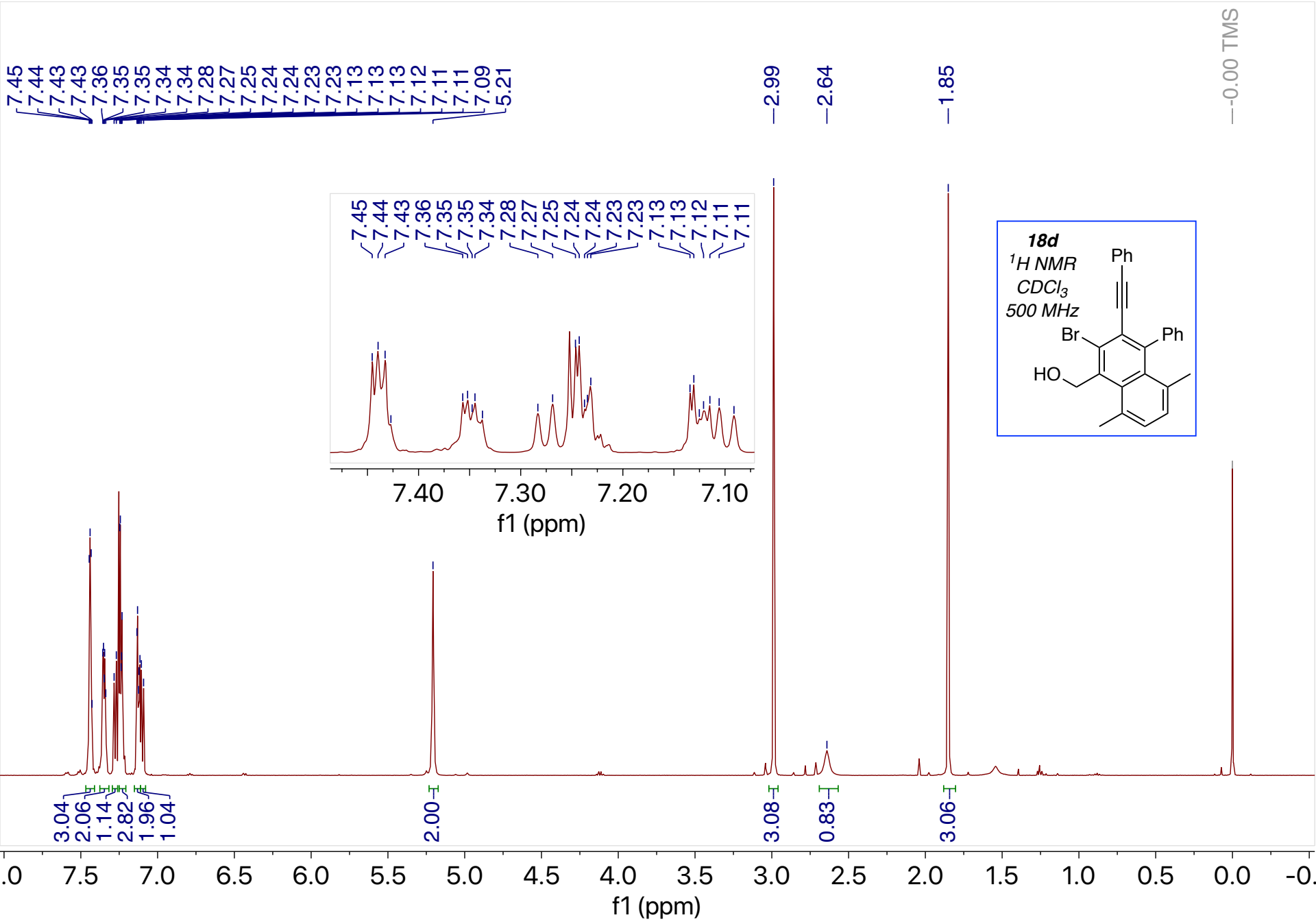
143.49
139.50
136.08
134.21
133.11
132.59
131.19
130.99
130.57
130.39
128.30
128.15
127.66
127.47
127.34
123.16
109.48
97.76
93.46
69.15
25.14
24.38
0.00 TMS
18c
13C NMR
CDCl3
126 MHz
Ph
I
Ph
HO
f1 (ppm)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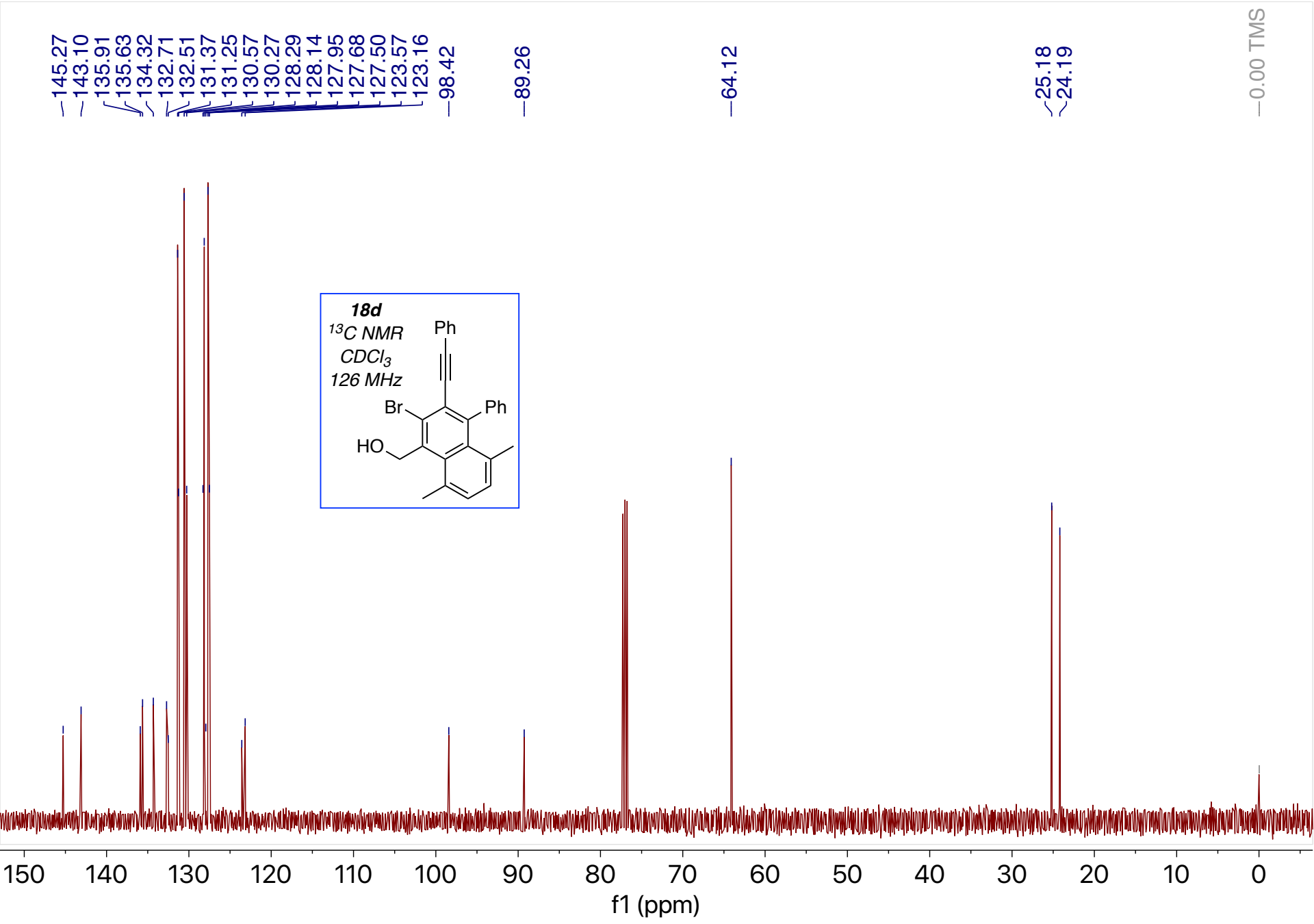
7.44
7.43
7.43
7.36
7.35
7.35
7.34
7.34
7.28
7.27
7.25
7.24
7.24
7.23
7.23
7.13
7.13
7.13
7.12
7.11
7.11
7.09
5.21
2.99
2.64
1.85
-0.00 TMS
18d
1H NMR
CDCl3
500 MHz
Ph
Br
Ph
HO
7.40
7.30
7.20
7.10
f1 (ppm)
3.04
2.06
1.14
2.82
1.96
1.04
2.00
3.08
0.83
3.06
f1 (ppm)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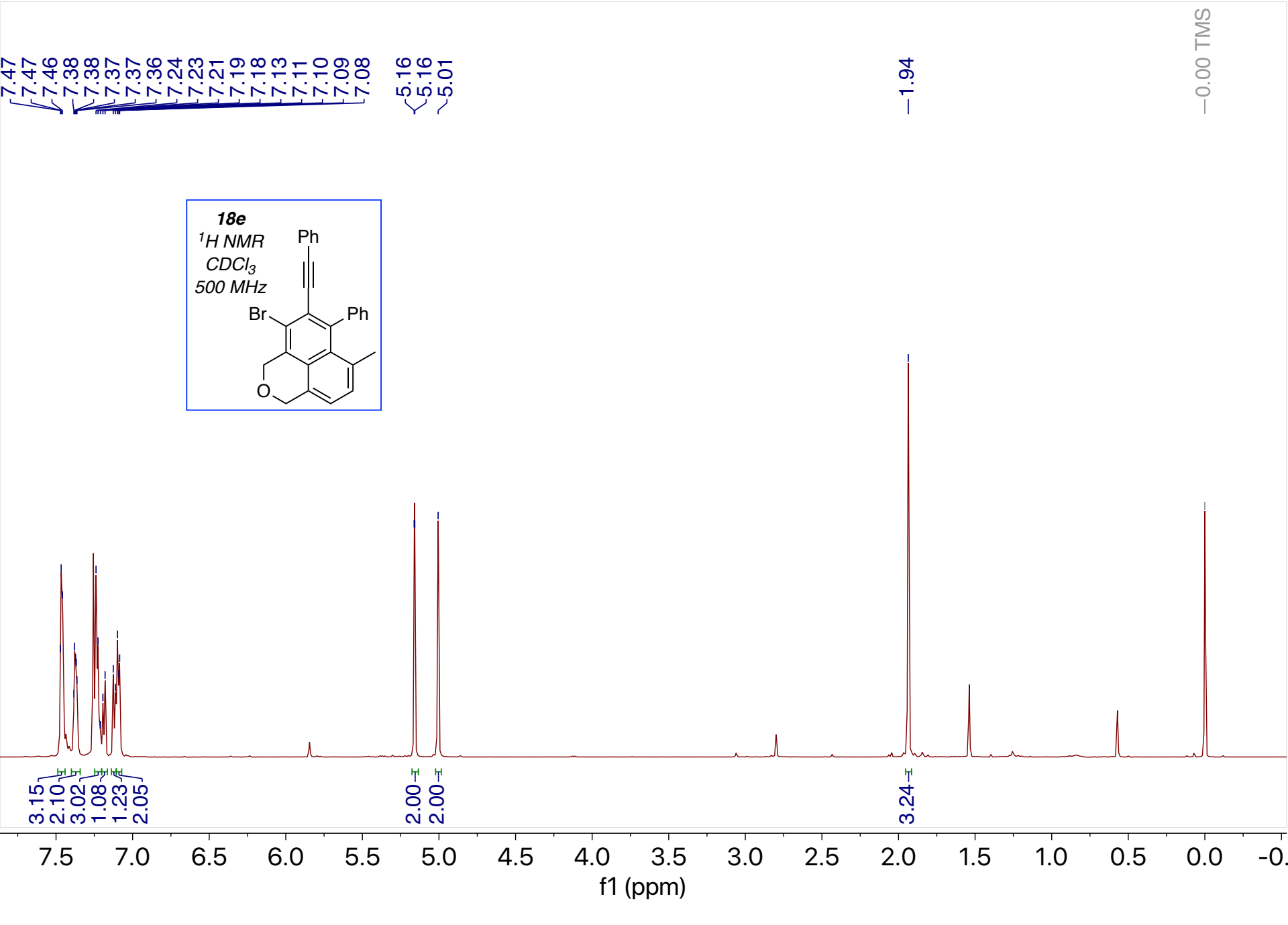
143.10
135.91
135.63
134.32
132.71
132.51
131.37
131.25
130.57
130.27
128.29
128.14
127.95
127.68
127.50
123.57
123.16
98.42
89.26
64.12
25.18
24.19
0.00 TMS
18d
13C NMR
CDCl3
126 MHz
Ph
Br
Ph
HO
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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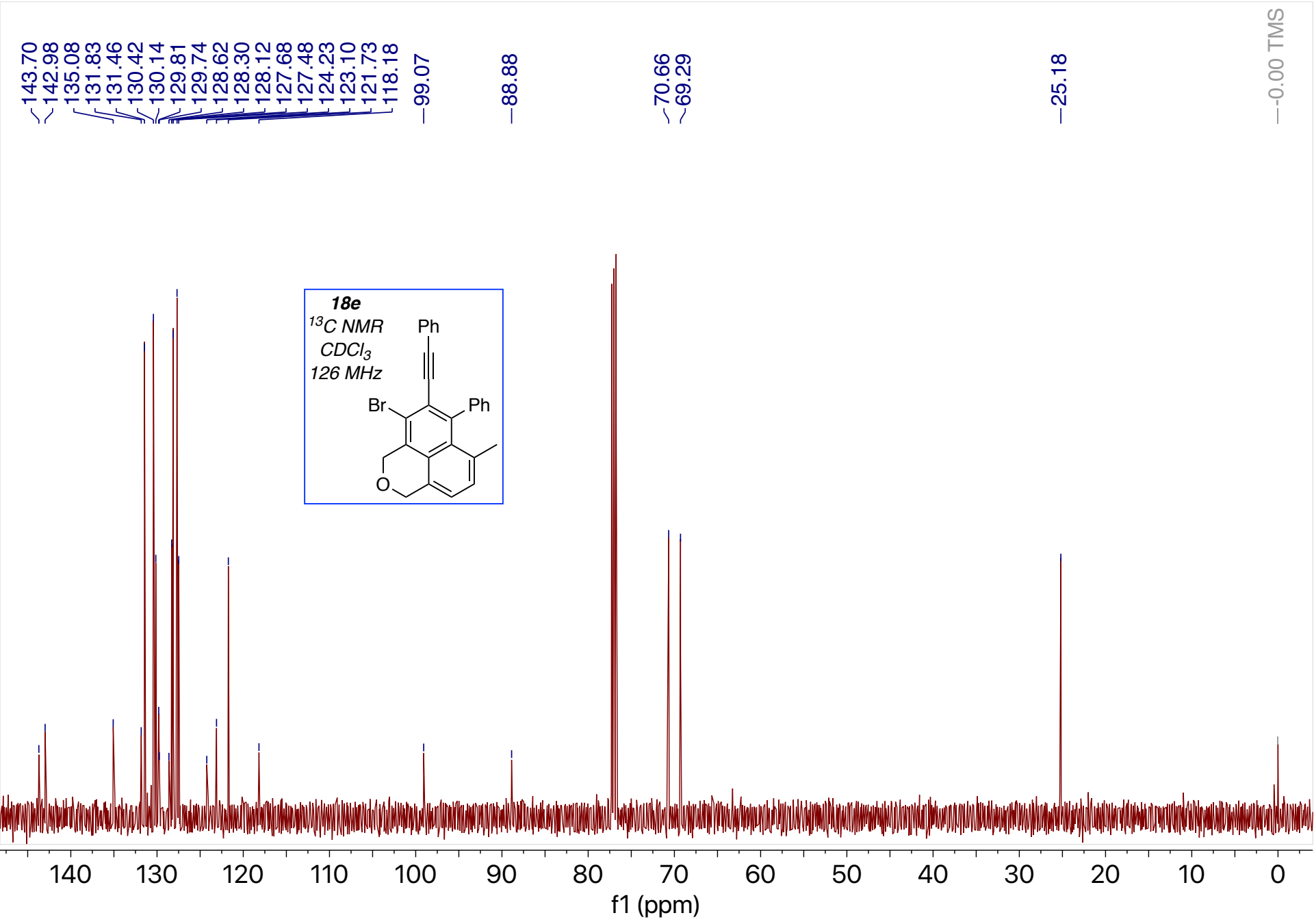
7.47
7.46
7.38
7.38
7.37
7.37
7.36
7.24
7.23
7.21
7.19
7.18
7.13
7.11
7.10
7.09
7.08
5.16
5.16
5.01
1.94
0.00 TMS
18e
1H NMR
CDCl3
500 MHz
Ph
Br
Ph
O
3.15
2.10
3.02
1.08
1.23
2.05
2.00
2.00
3.24
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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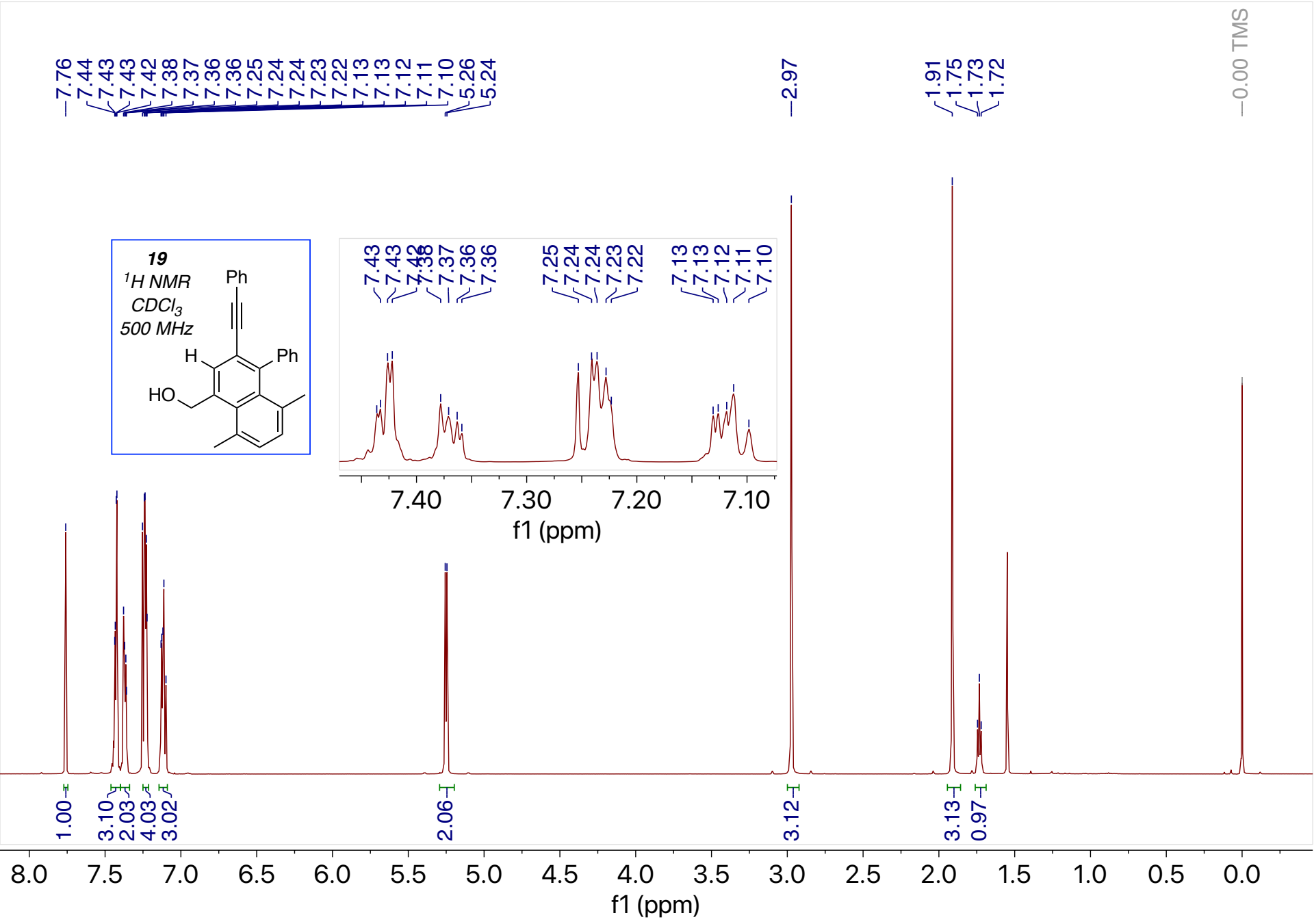
129.81
129.74
128.62
128.30
128.12
127.68
127.48
124.23
123.10
121.73
118.18
99.07
88.88
70.66
69.29
25.18
-0.00 TMS
18e
13C NMR
CDCl3
126 MHz
Ph
Br
Ph
O
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.43
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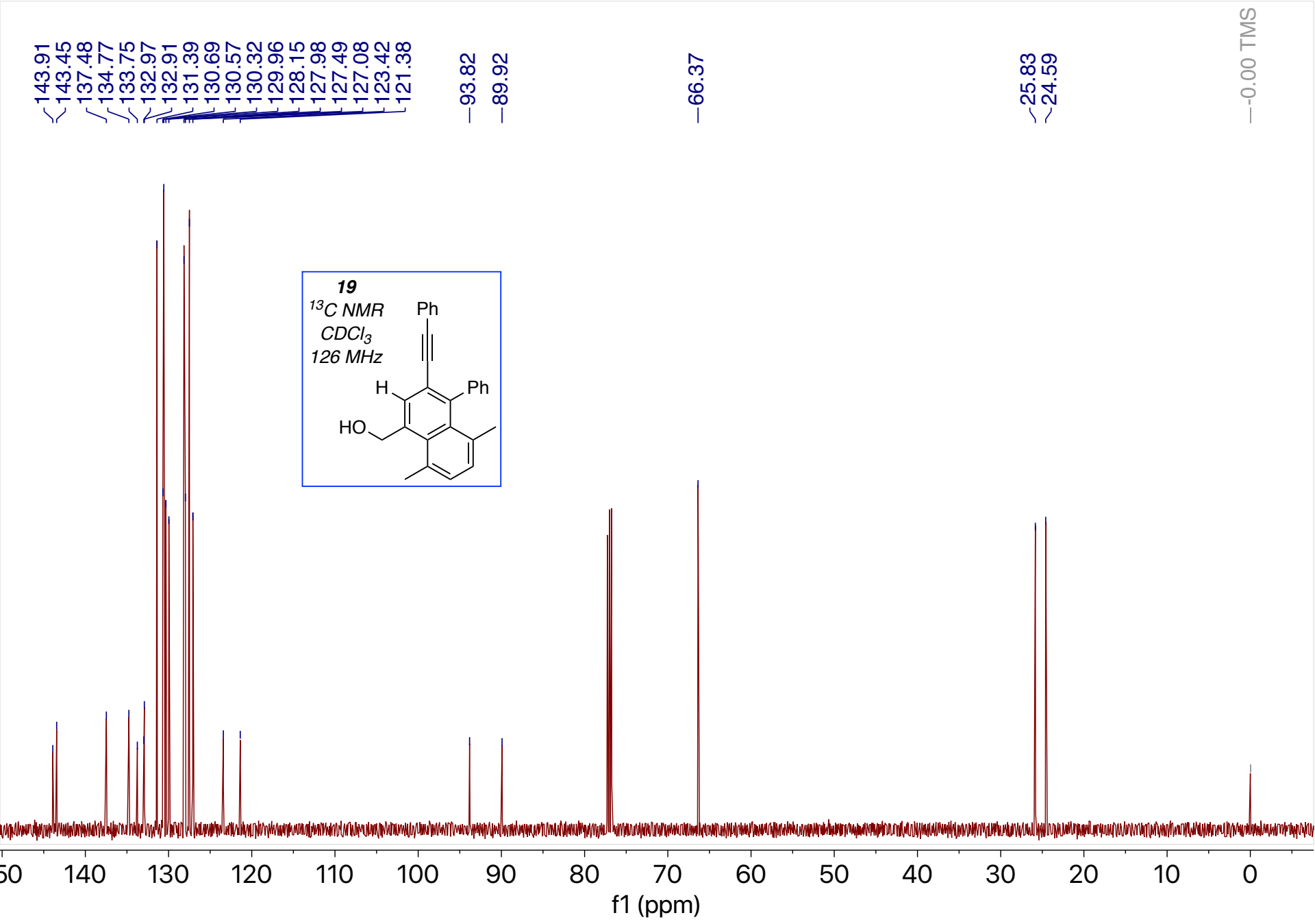
7.37
7.36
7.36
7.25
7.24
7.24
7.23
7.22
7.13
7.13
7.12
7.11
7.10
5.26
5.24
2.97
1.91
1.75
1.73
1.72
0.00 TMS
19
1H NMR
CDCl3
500 MHz
Ph
H
Ph
HO
7.40
7.30
7.20
7.10
f1 (ppm)
1.00
3.10
2.03
4.03
3.02
2.06
3.12
3.13
0.97
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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131.39
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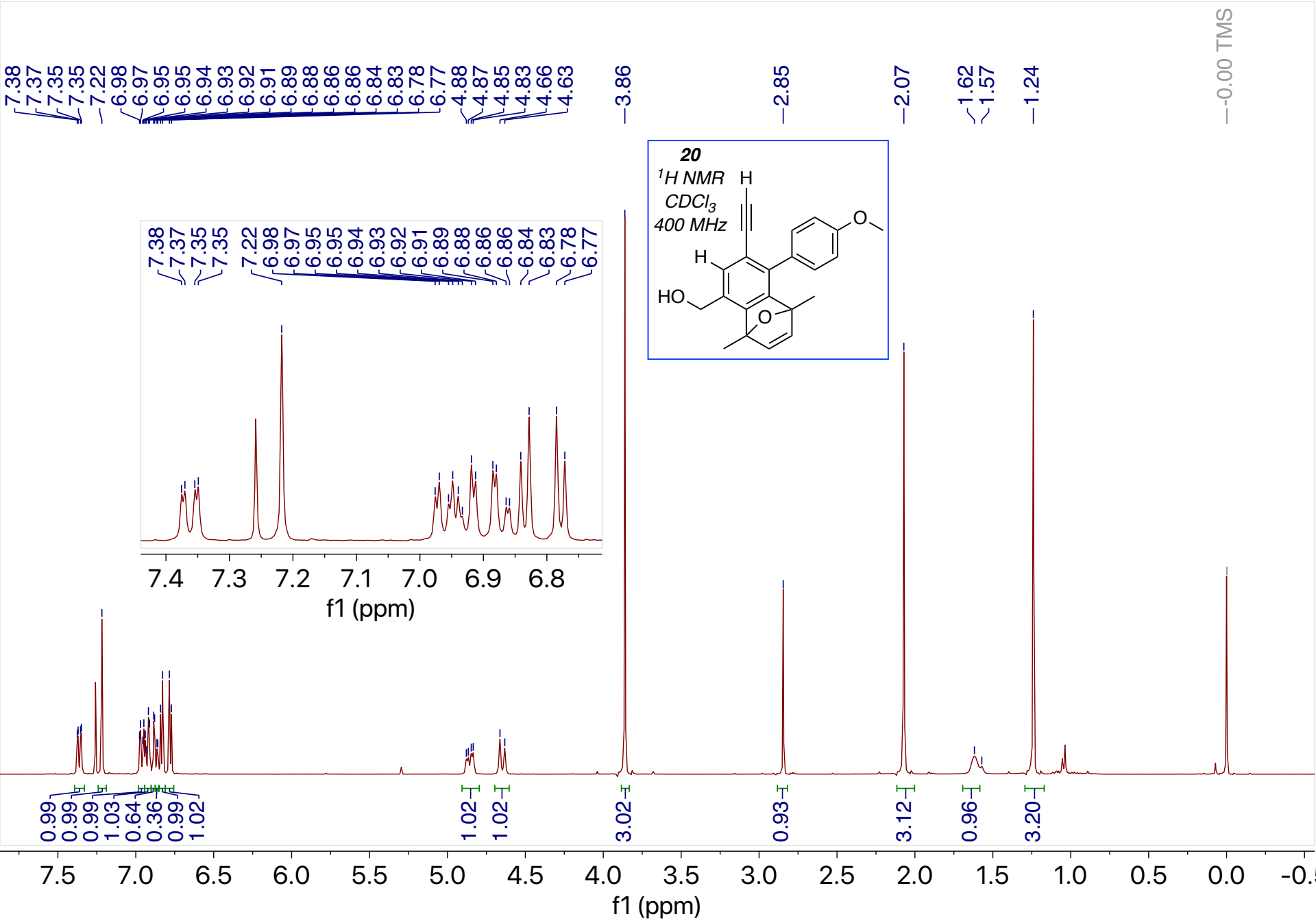
130.32
129.96
128.15
127.98
127.49
127.08
123.42
121.38
93.82
89.92
66.37
25.83
24.59
-0.00 TMS
19
13C NMR
CDCl3
126 MHz
Ph
H
Ph
HO
50
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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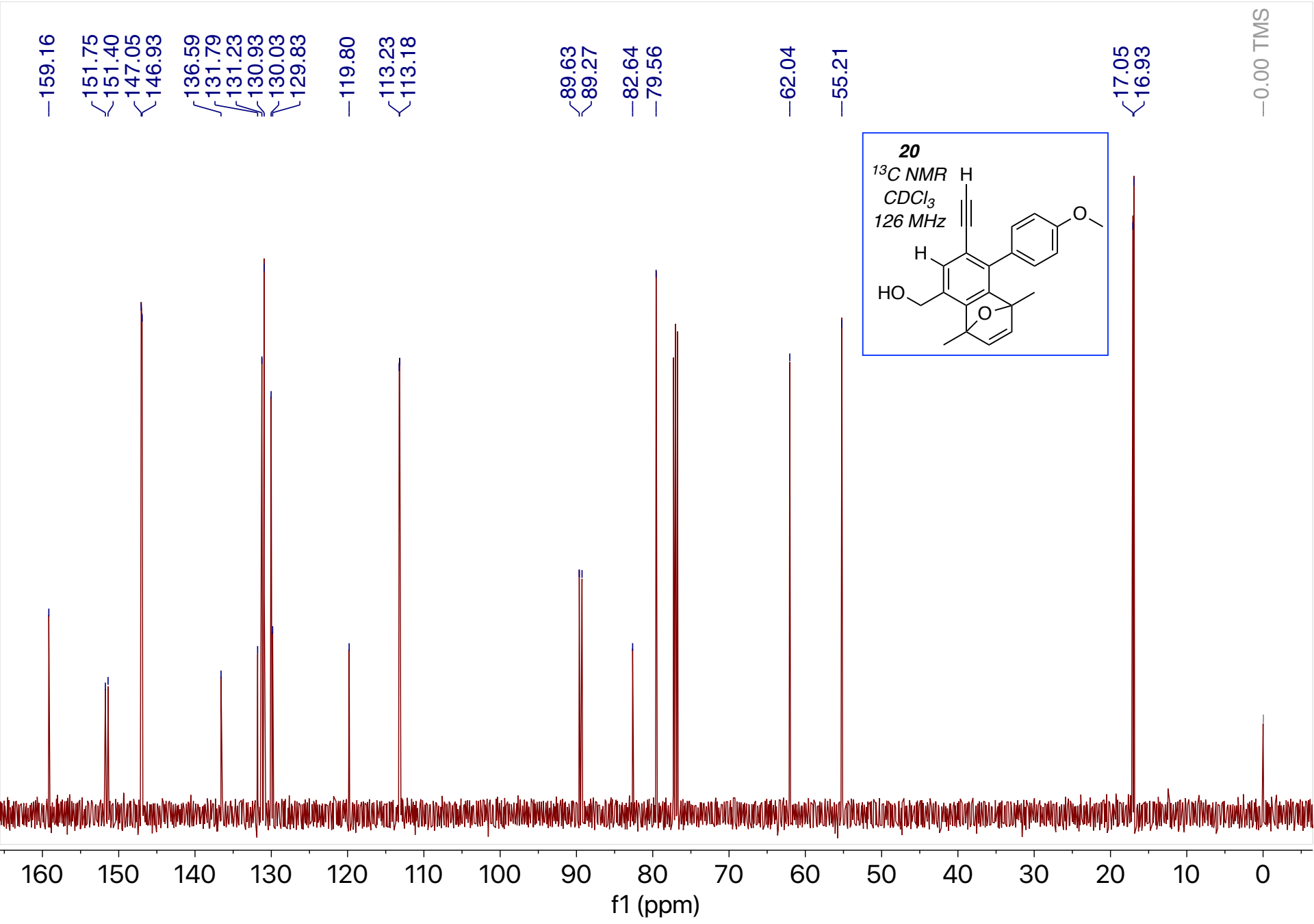
7.37
7.35
7.35
7.22
6.98
6.97
6.95
6.95
6.94
6.93
6.92
6.91
6.89
6.88
6.86
6.86
6.84
6.83
6.78
6.77
4.88
4.87
4.85
4.83
4.66
4.63
3.86
2.85
2.07
1.62
1.57
1.24
-0.00 TMS
20
1H NMR
CDCl3
400 MHz
H
H
HO
O
O
7.4
7.3
7.2
7.1
7.0
6.9
6.8
f1 (ppm)
0.99
0.99
0.99
1.03
0.64
0.36
0.99
1.02
1.02
1.02
3.02
0.93
3.12
0.96
3.20
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
f1 (ppm)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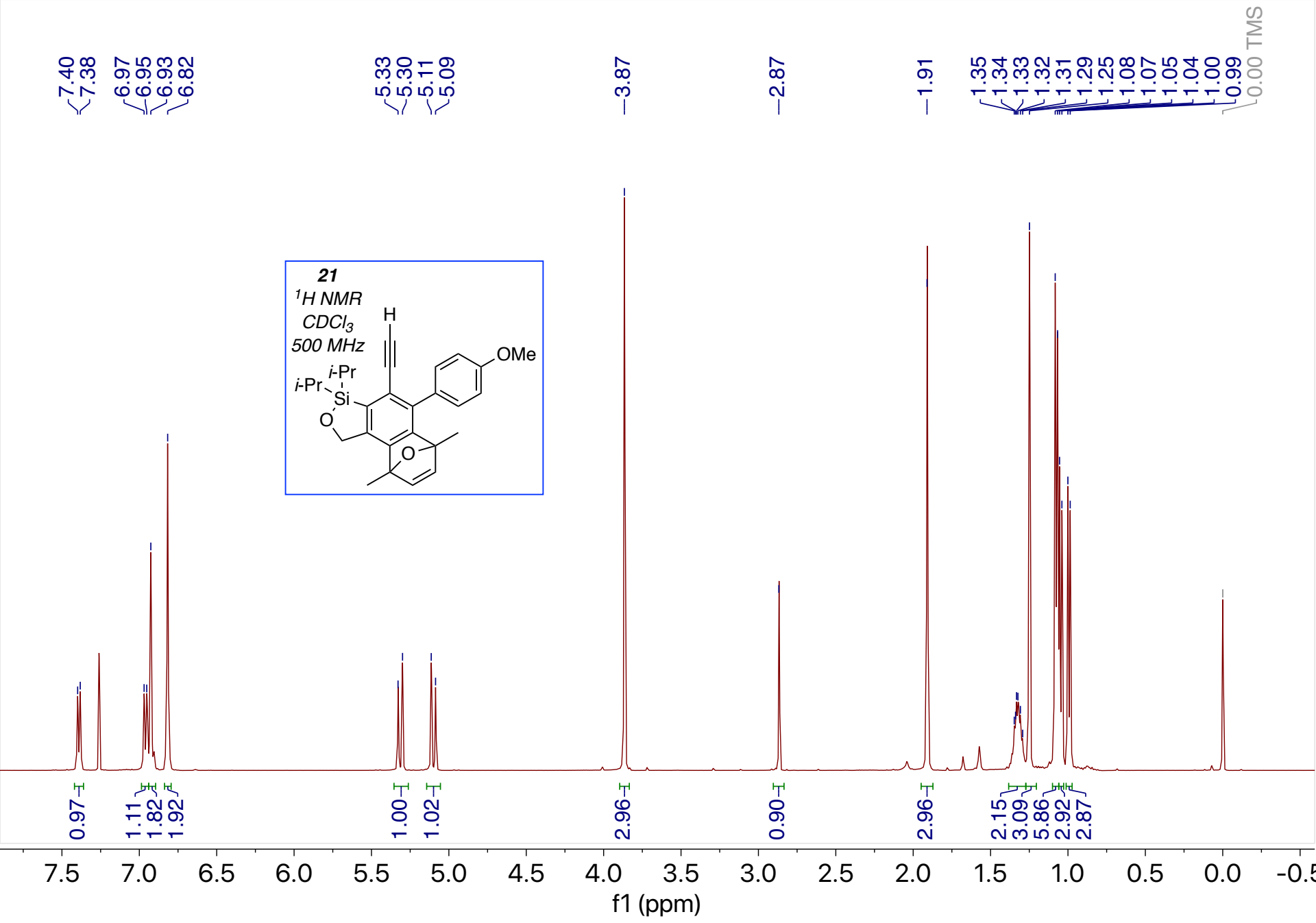
119.80
113.23
113.18
89.63
89.27
82.64
79.56
62.04
55.21
17.05
16.93
0.00 TMS
20
13C NMR
CDCl3
126 MHz
H
O
H
HO
O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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6.97
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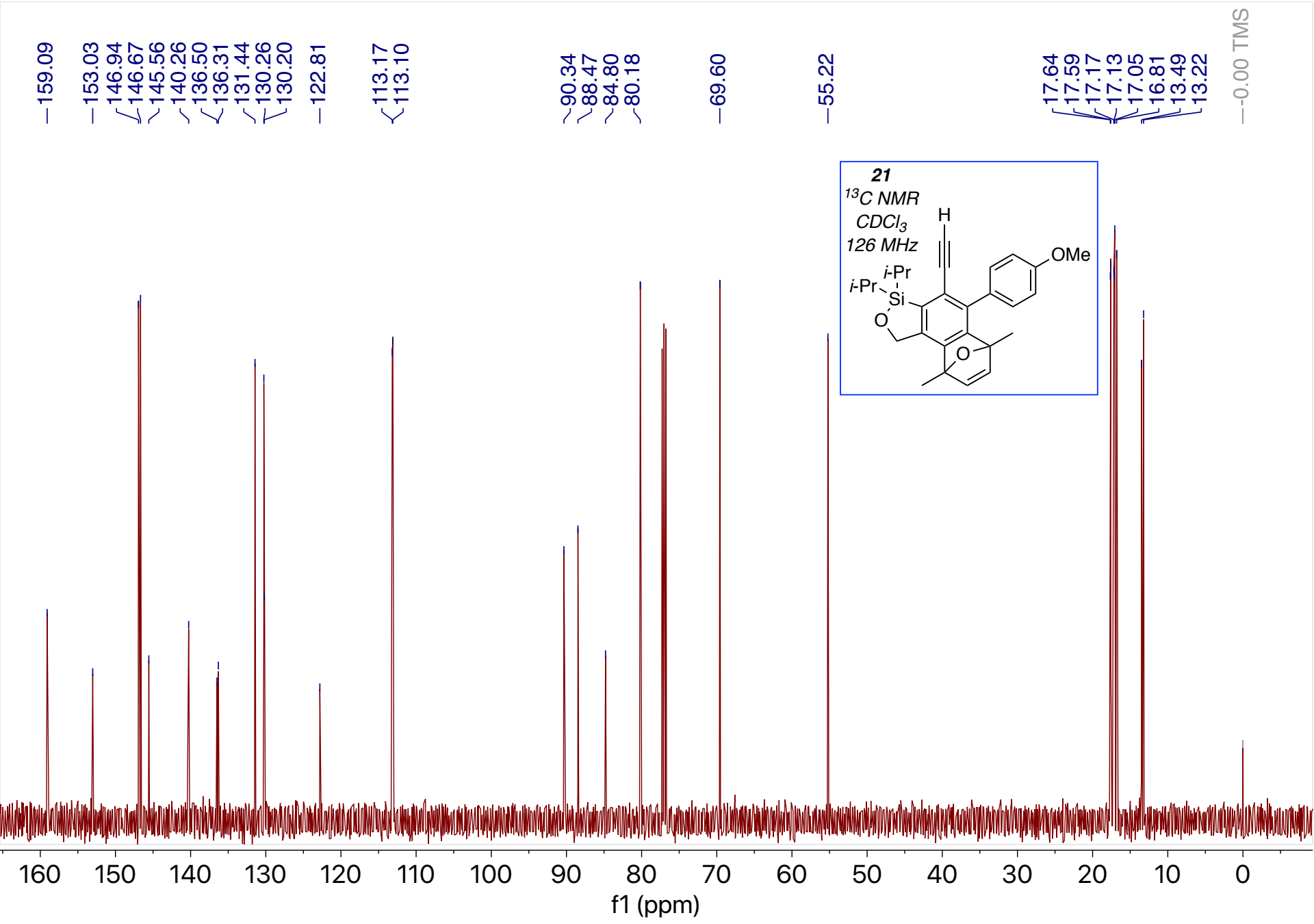
6.82
5.33
5.30
5.11
5.09
3.87
2.87
1.91
1.35
1.34
1.33
1.32
1.31
1.29
1.25
1.08
1.07
1.05
1.04
1.00
0.99
0.00 TMS
21
1H NMR
CDCl3
500 MHz
H
OMe
i-Pr
i-Pr
Si
O
O
0.97
1.11
1.82
1.92
1.00
1.02
2.96
0.90
2.96
2.15
3.09
5.86
2.92
2.87
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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136.31
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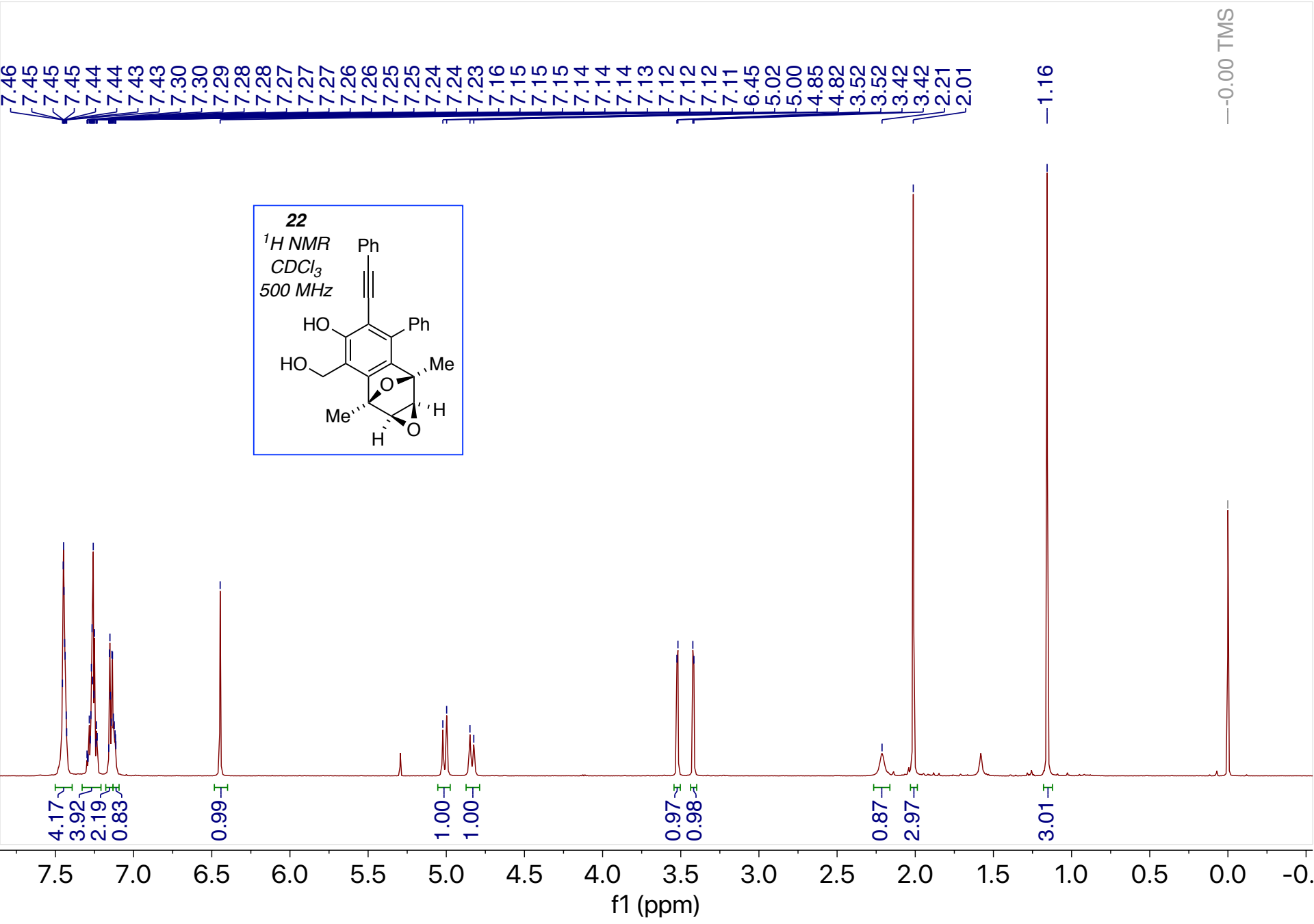
130.26
130.20
122.81
113.17
113.10
90.34
88.47
84.80
80.18
69.60
55.22
17.64
17.59
17.17
17.13
17.05
16.81
13.49
13.22
0.00 TMS
21
13C NMR
CDCl3
126 MHz
H
OMe
i-Pr
i-Pr
Si
O
O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.45
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7.43
7.43
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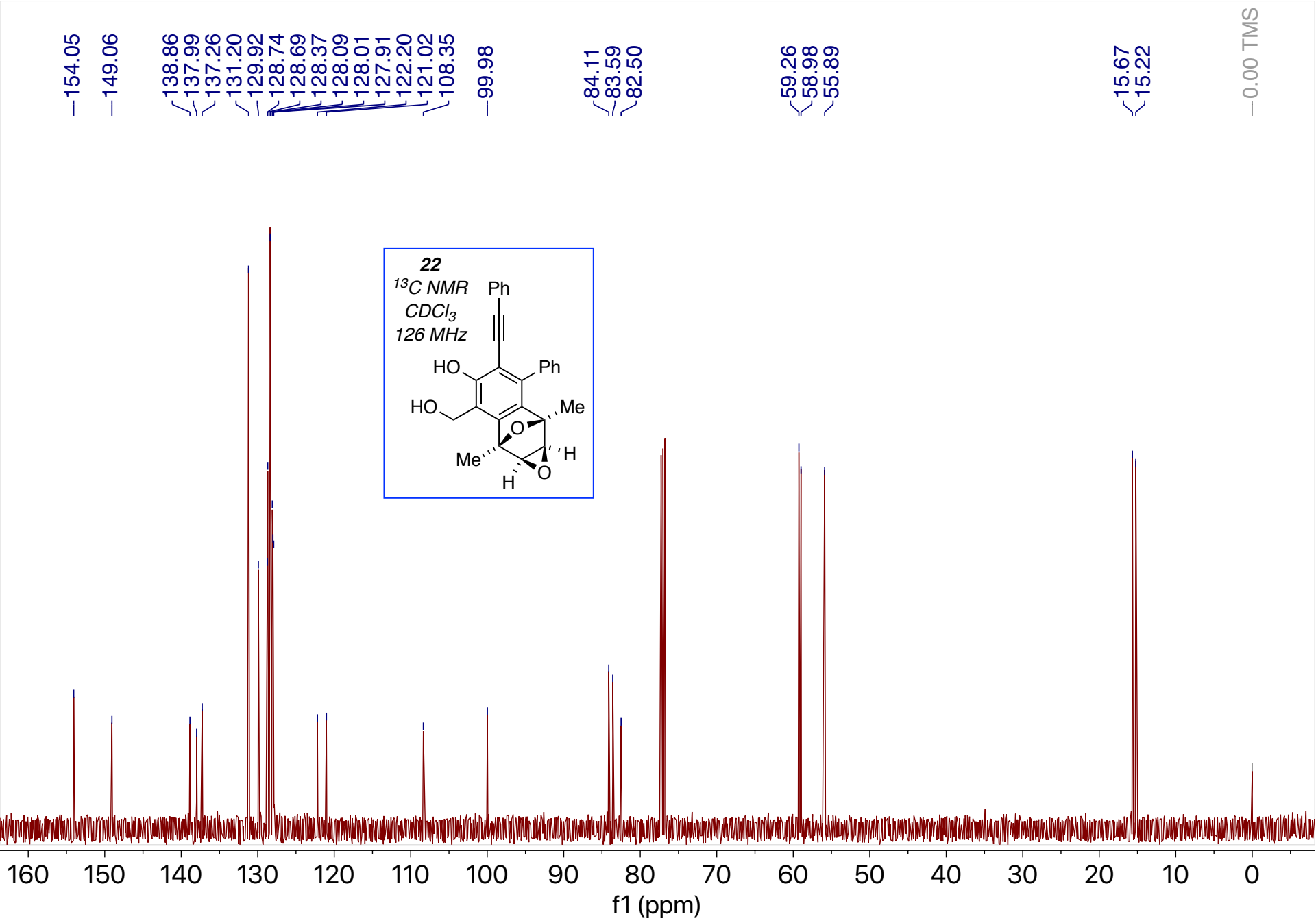
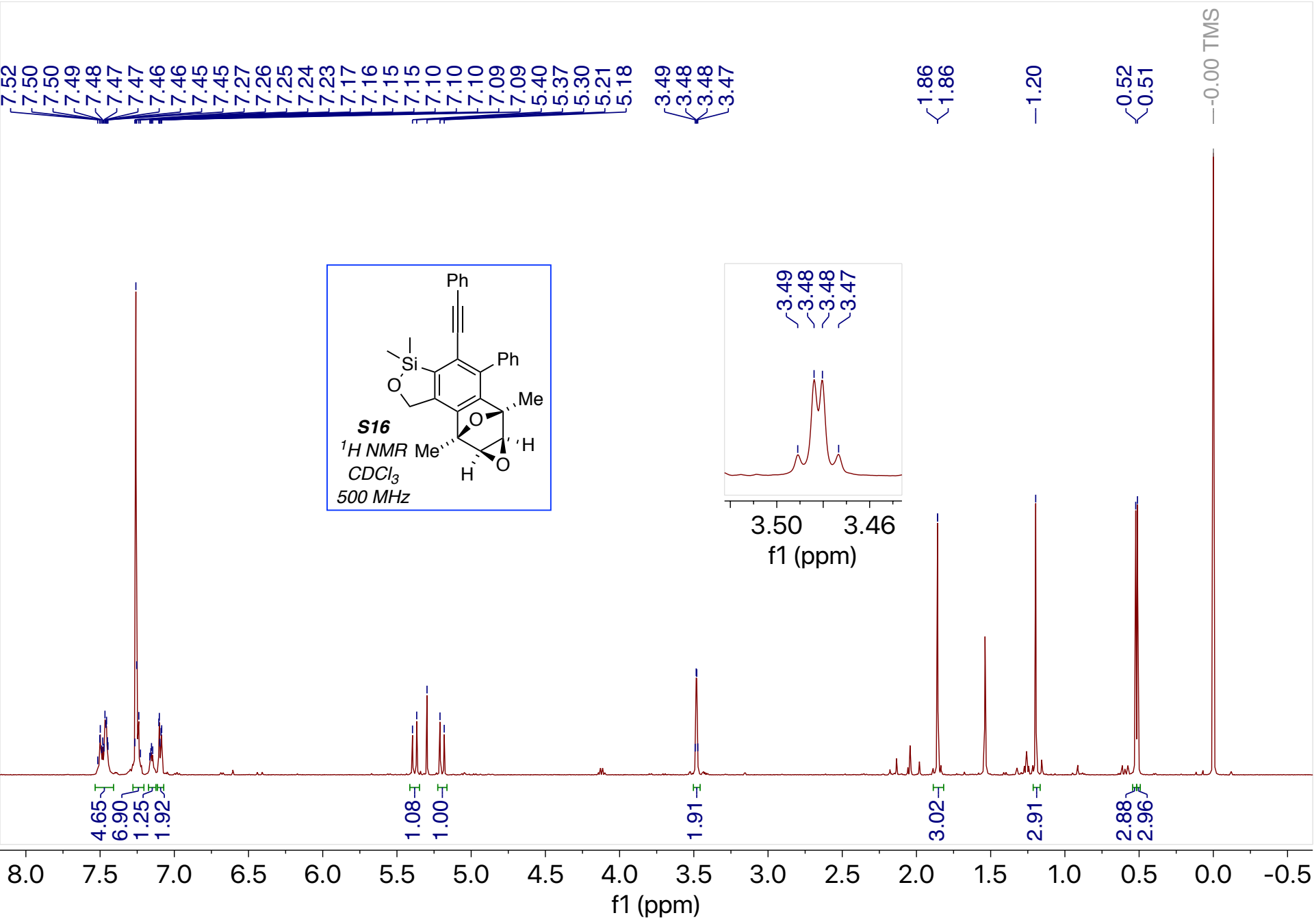
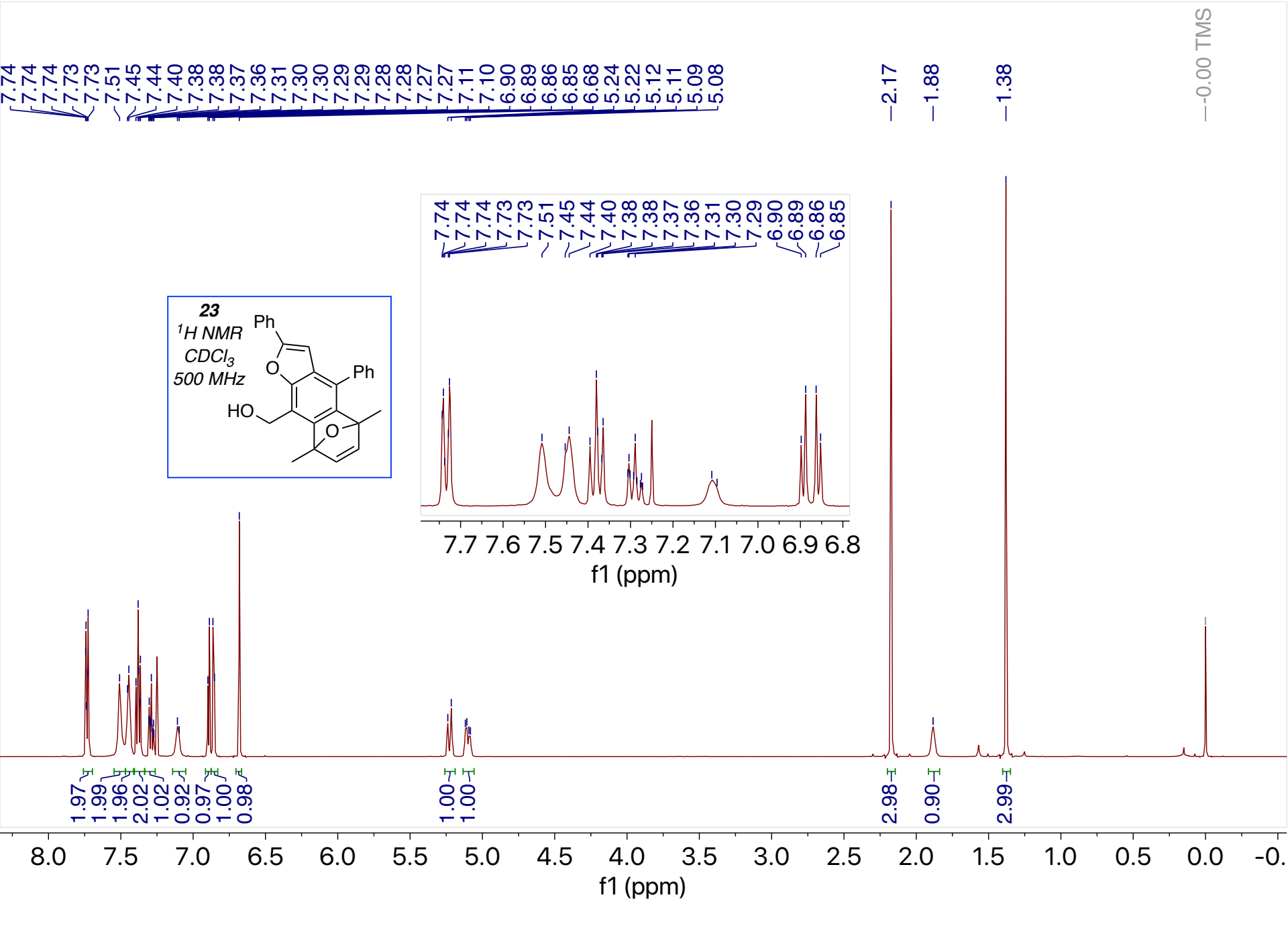
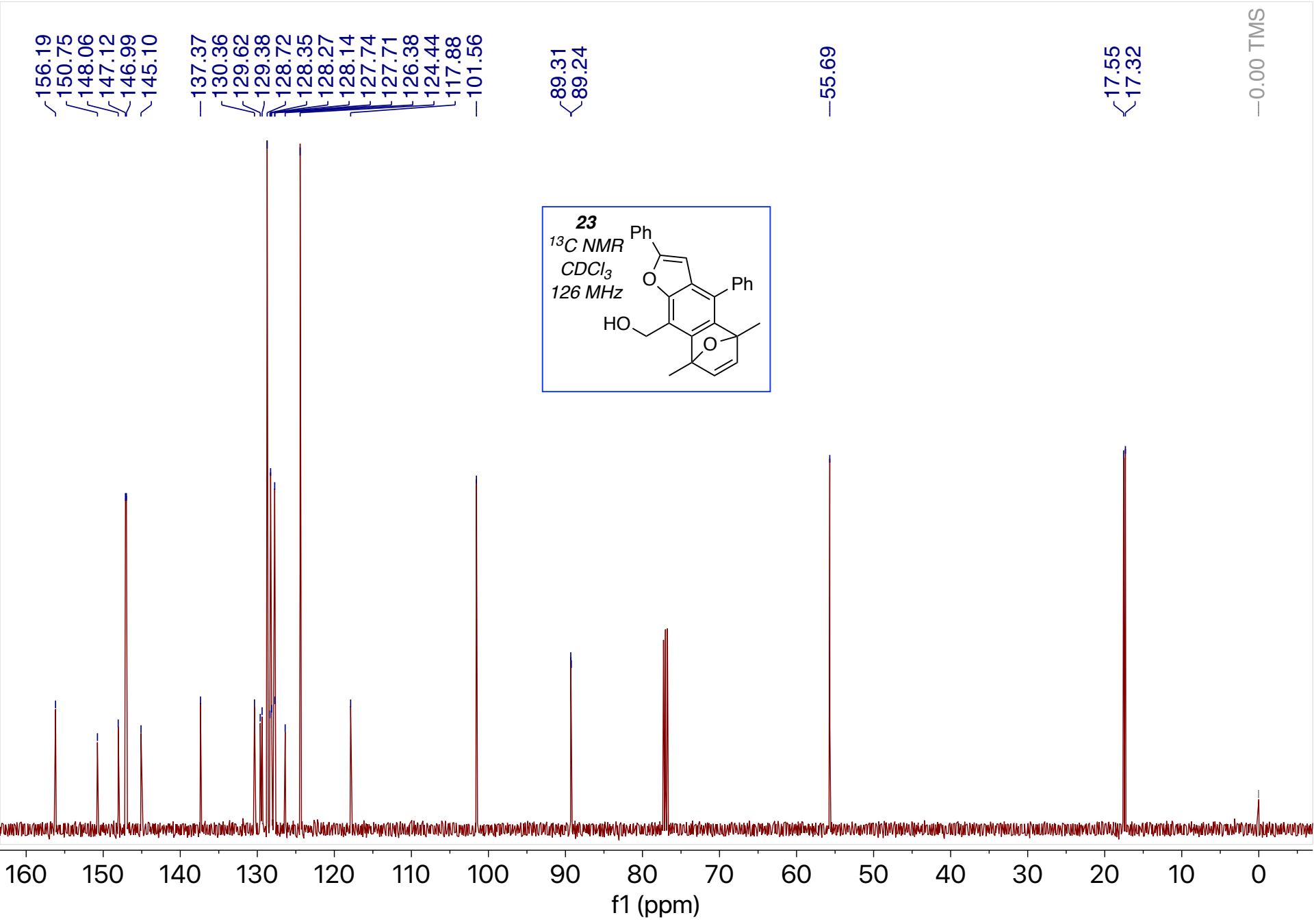
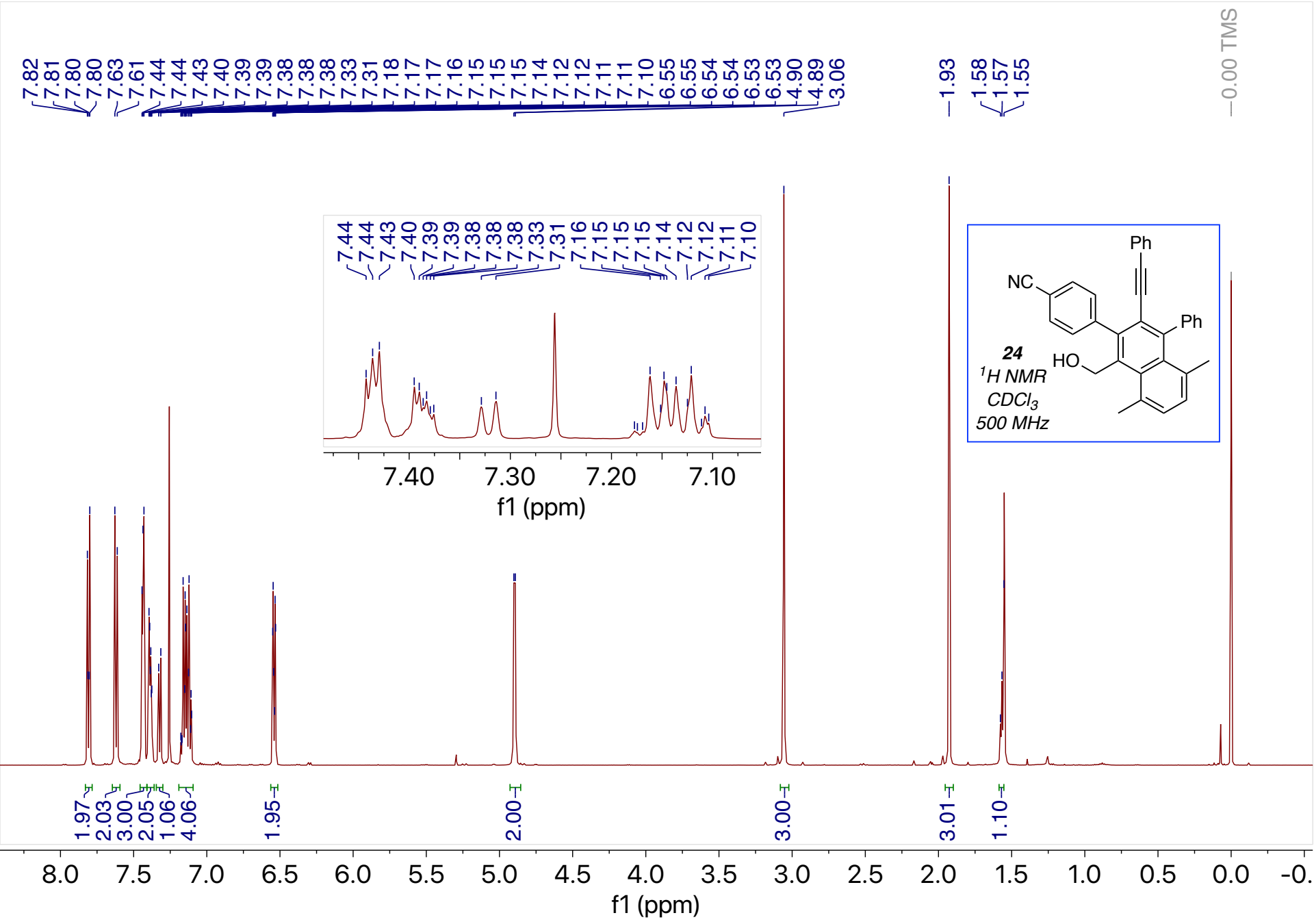
7.27
7.27
7.27
7.26
7.26
7.25
7.25
7.24
7.24
7.23
7.16
7.15
7.15
7.15
7.14
7.14
7.14
7.13
7.12
7.12
7.12
7.11
6.45
5.02
5.00
4.85
4.82
3.52
3.52
3.42
3.42
2.21
2.01
1.16
-0.00 TMS
22
1H NMR
CDCl3
500 MHz
Ph
HO
Ph
HO
Me
O
Me
H
H
O
4.17
3.92
2.19
0.83
0.99
1.00
1.00
0.97
0.98
0.87
2.97
3.01
7.5
7.0
6.5
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
f1 (ppm)

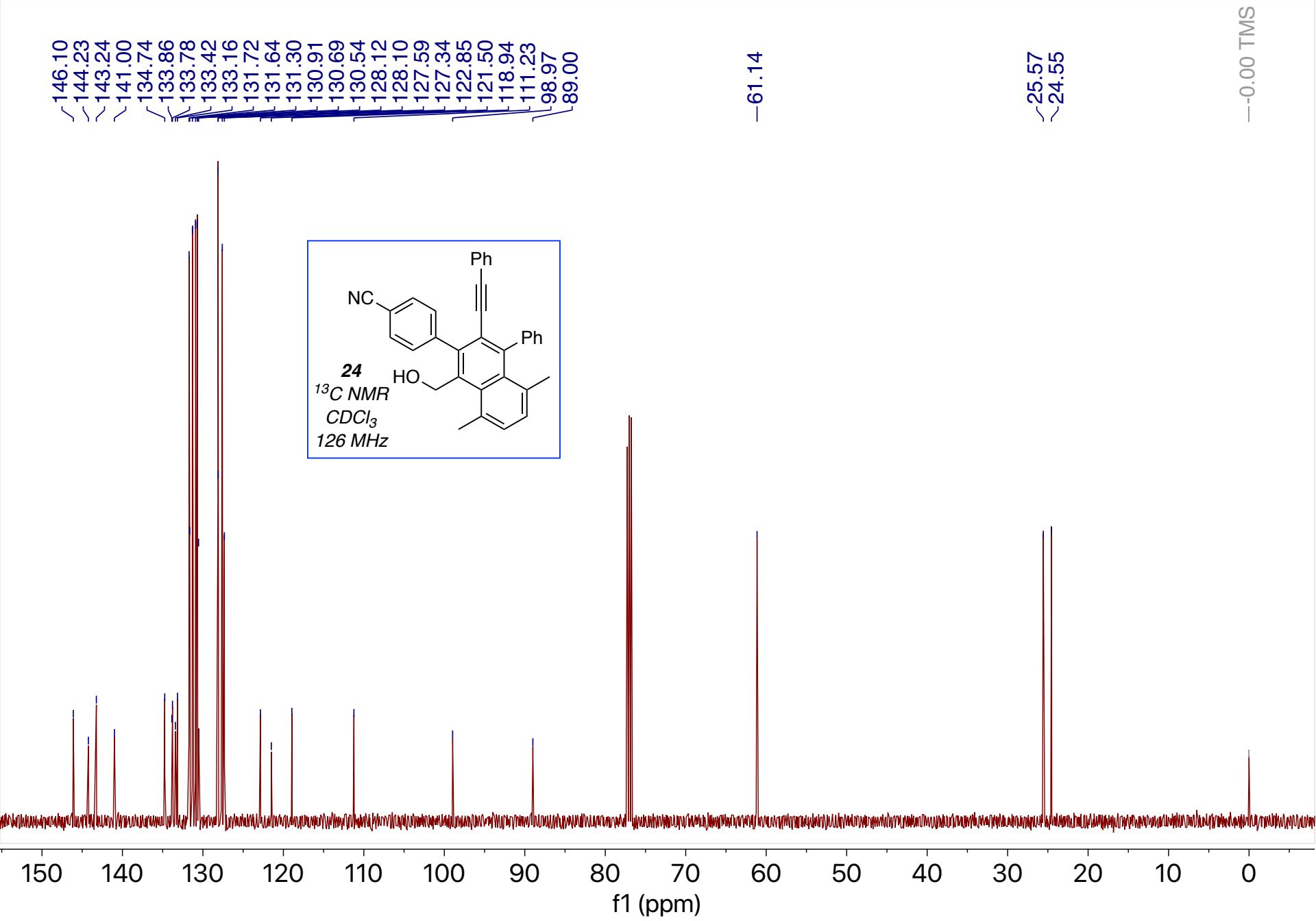

154.05
149.06
138.86
137.99
137.26
131.20
129.92
128.74
128.69
128.37
128.09
128.01
127.91
122.20
121.02
108.35
99.98
84.11
83.59
82.50
59.26
58.98
55.89
15.67
15.22
0.00 TMS
22
13C NMR
CDCl3
126 MHz
Ph
HO
Ph
HO
Me
O
Me
H
O
H
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

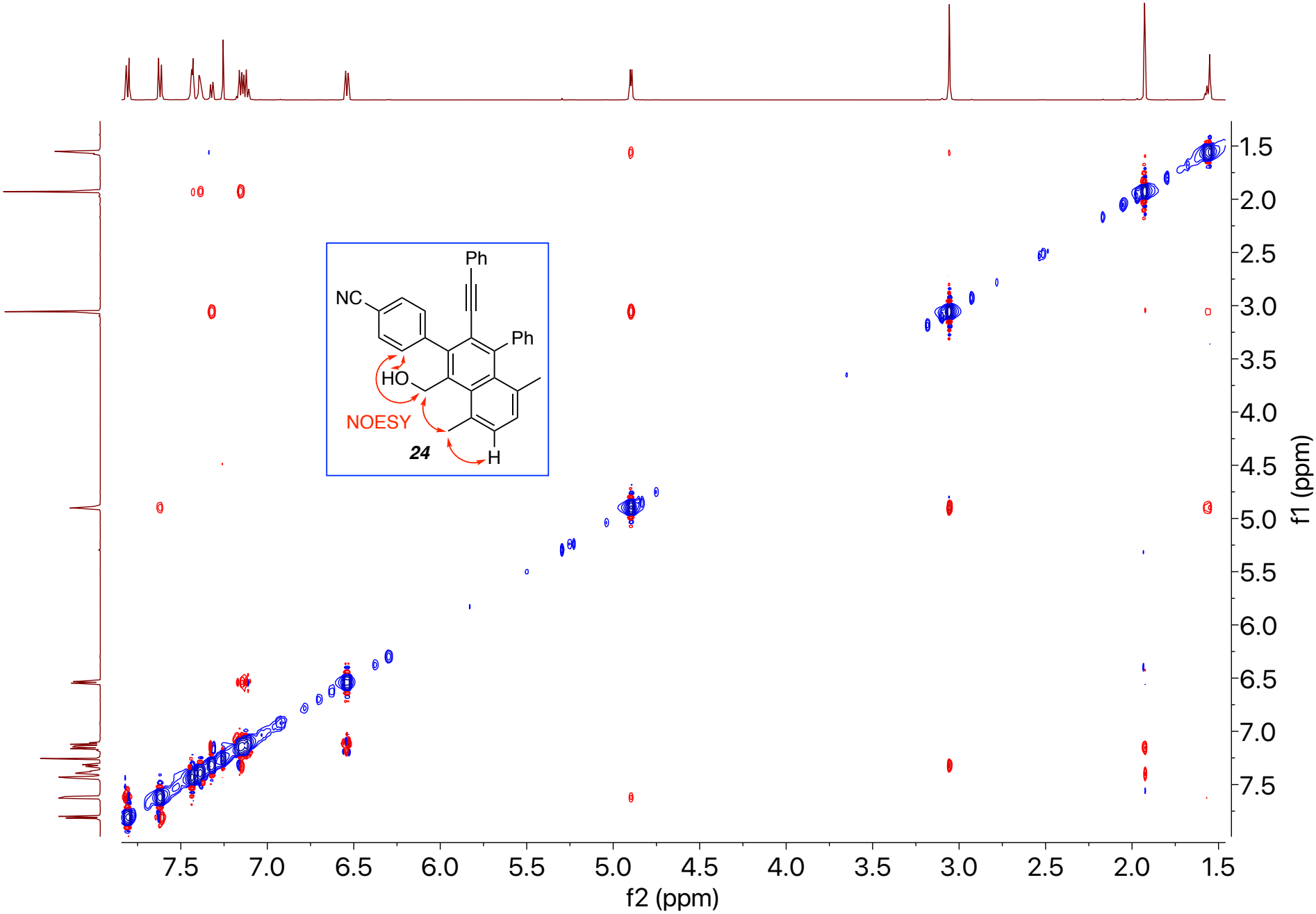

7.52
7.50
7.50
7.49
7.48
7.47
7.47
7.46
7.46
7.45
7.45
7.27
7.26
7.25
7.24
7.23
7.17
7.16
7.15
7.15
7.10
7.10
7.10
7.09
7.09
5.40
5.37
5.30
5.21
5.18
3.49
3.48
3.48
3.47
1.86
1.86
1.20
0.52
0.51
-0.00 TMS
Ph
Si
O
Ph
Me
O
S16
1H NMR
CDCl3
500 MHz
Me
H
O
H
3.49
3.48
3.48
3.47
3.50
3.46
f1 (ppm)
4.65
6.90
1.25
1.92
1.08
1.00
1.91
3.02
2.91
2.88
2.96
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
f1 (ppm)

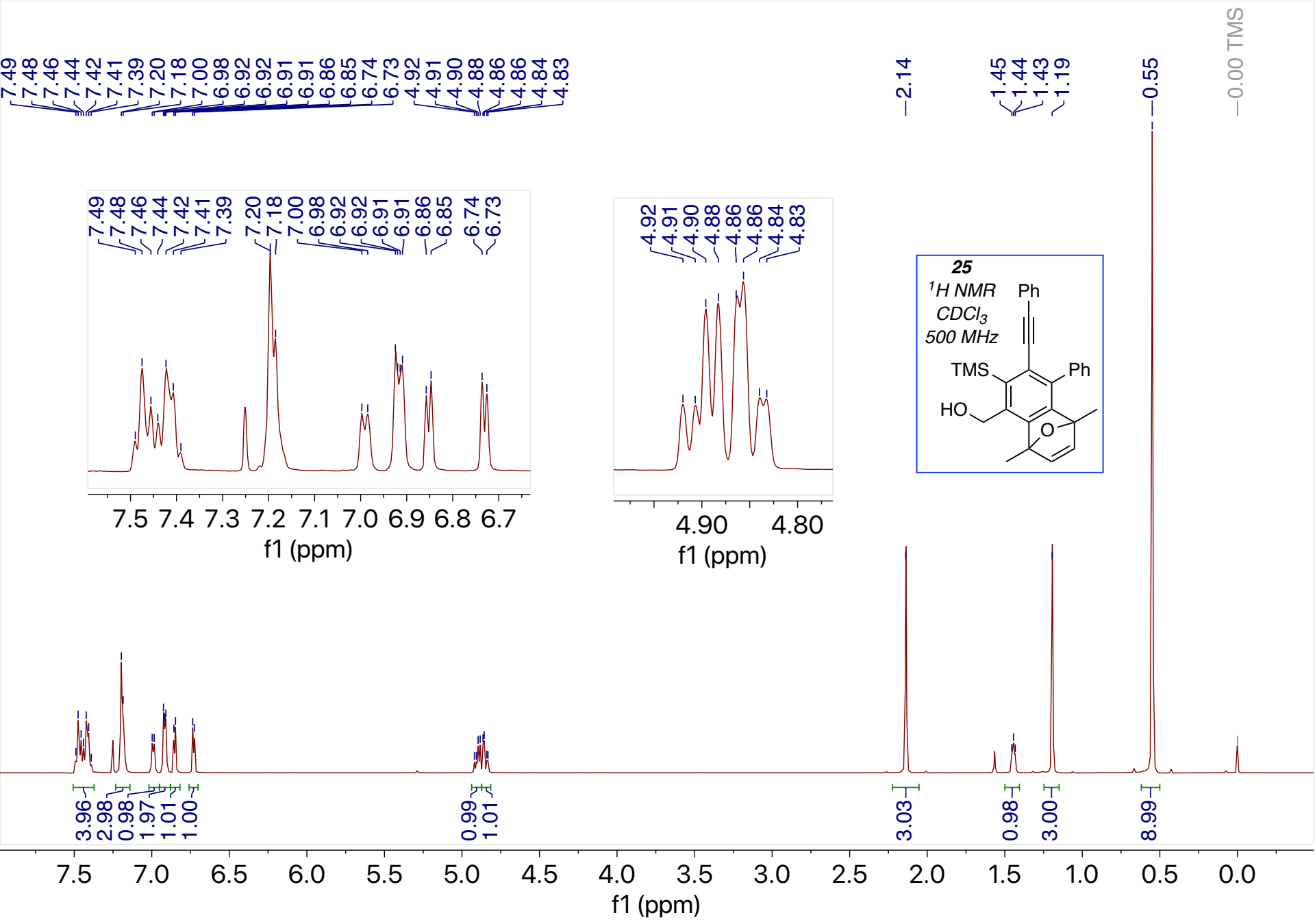

7.74 7.74 7.74 7.73 7.73 7.51 7.45 7.44 7.40 7.38 7.38 7.37 7.36 7.31 7.30 7.30 7.29 7.29 7.28 7.28 7.27 7.27 7.11 7.10 6.90 6.89 6.86 6.85 6.68 5.24 5.22 5.12 5.11 5.09 5.08
2.17
1.88
1.38
-0.00 TMS
23
1H NMR
CDCl3
500 MHz
Ph
O
Ph
HO
O
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8
f1 (ppm)
1.97 1.99 1.96 2.02 1.02 0.92 0.97 1.00 0.98
1.00 1.00
2.98 0.90 2.99
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
f1 (ppm)

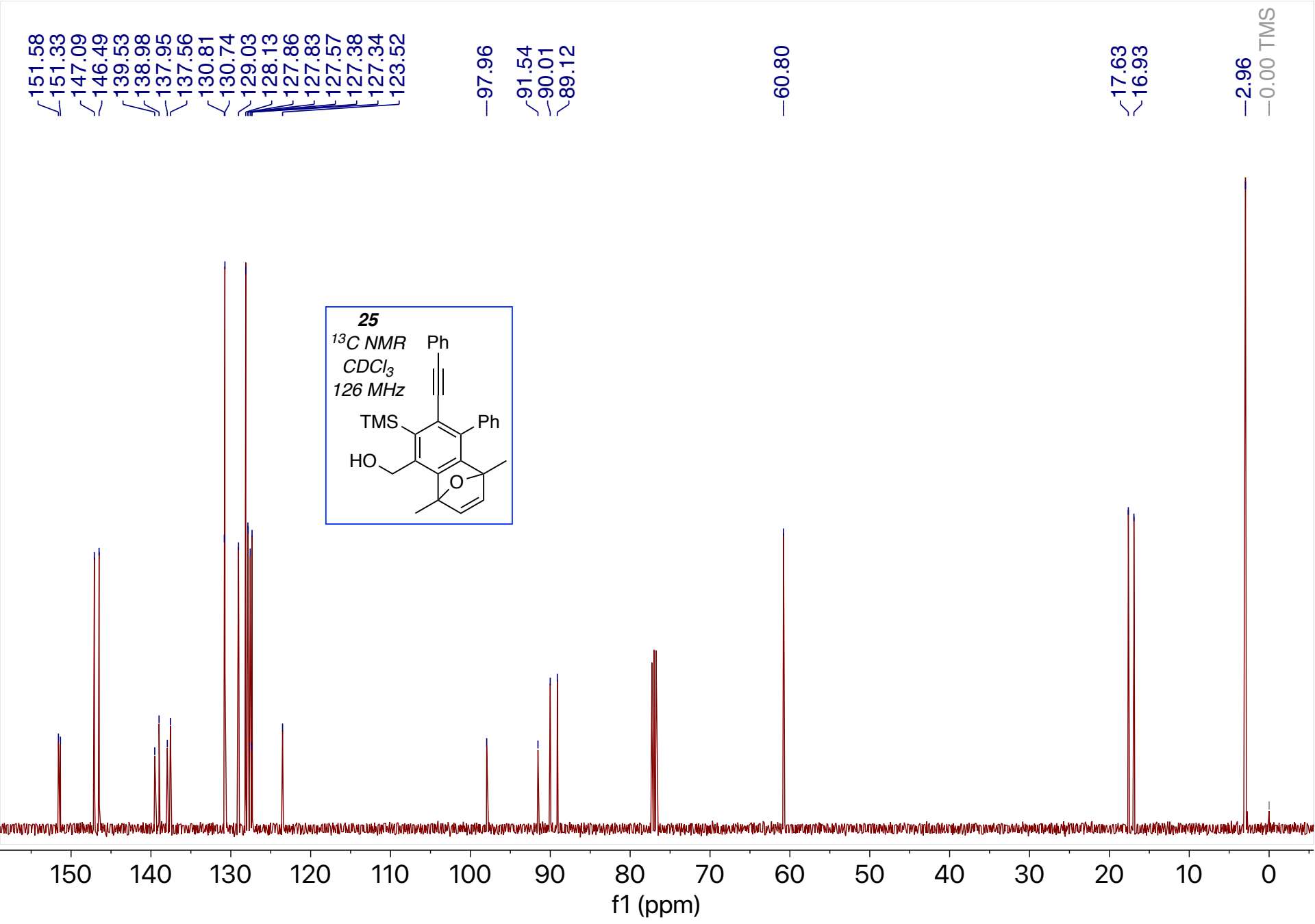

156.19
150.75
148.06
147.12
146.99
145.10
137.37
130.36
129.62
129.38
128.72
128.35
128.27
128.14
127.74
127.71
126.38
124.44
117.88
101.56
89.31
89.24
55.69
17.55
17.32
0.00 TMS
23
13C NMR
CDCl3
126 MHz
Ph
O
Ph
HO
O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

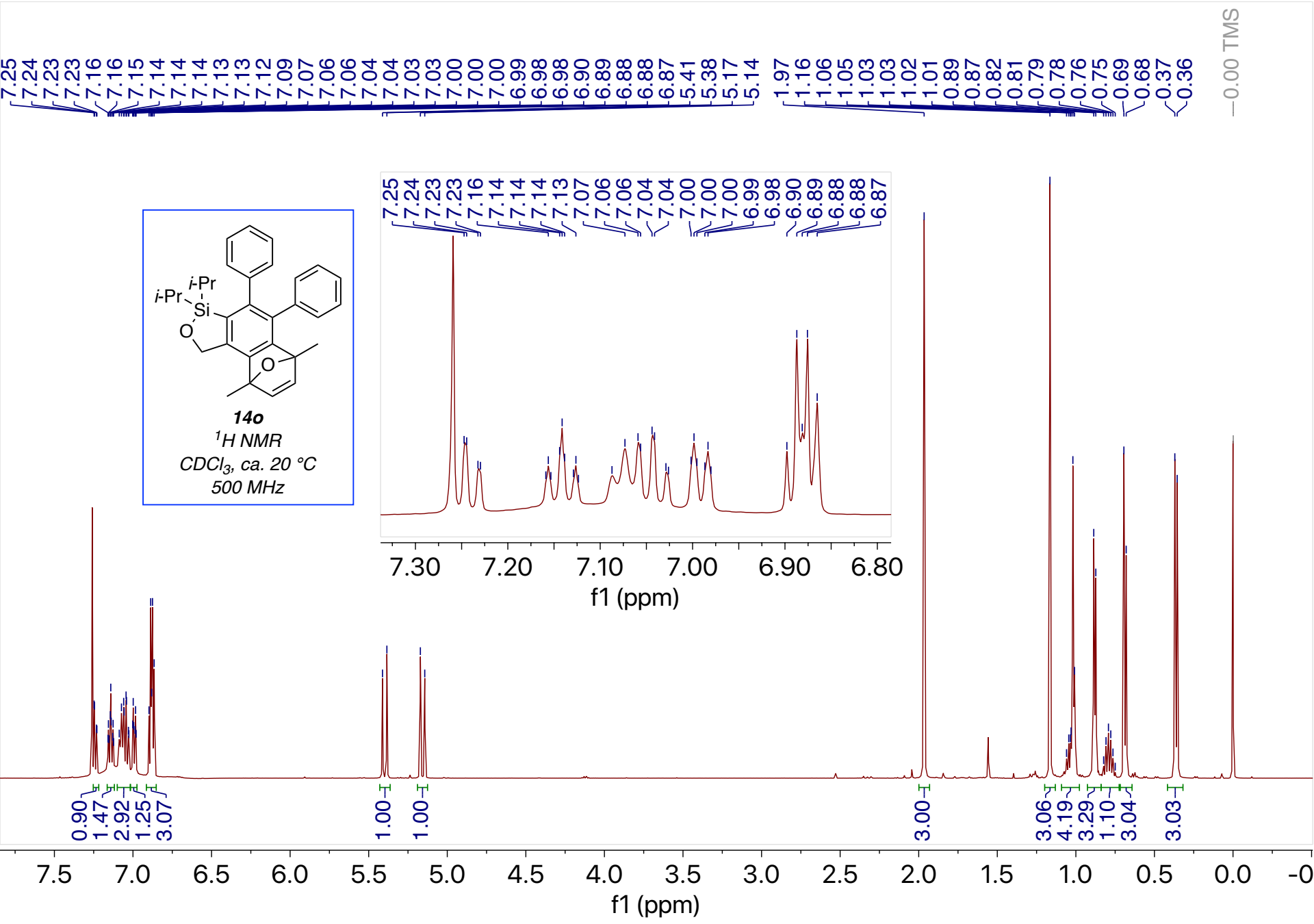

7.82 7.81 7.80 7.80 7.63 7.61 7.44 7.44 7.43 7.40 7.39 7.39 7.38 7.38 7.38 7.33 7.31 7.18 7.17 7.17 7.16 7.15 7.15 7.15 7.14 7.12 7.12 7.11 7.11 7.10 6.55 6.55 6.54 6.54 6.53 6.53 4.90 4.89 3.06
1.93 1.58 1.57 1.55
0.00 TMS
7.44 7.44 7.43 7.40 7.39 7.39 7.38 7.38 7.38 7.33 7.31 7.16 7.15 7.15 7.15 7.14 7.12 7.12 7.11 7.10
7.40 7.30 7.20 7.10
f1 (ppm)
Ph
NC
Ph
HO
24
1H NMR
CDCl3
500 MHz
1.97 2.03 3.00 2.05 1.06 4.06 1.95 2.00 3.00 3.01 1.10
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
f1 (ppm)

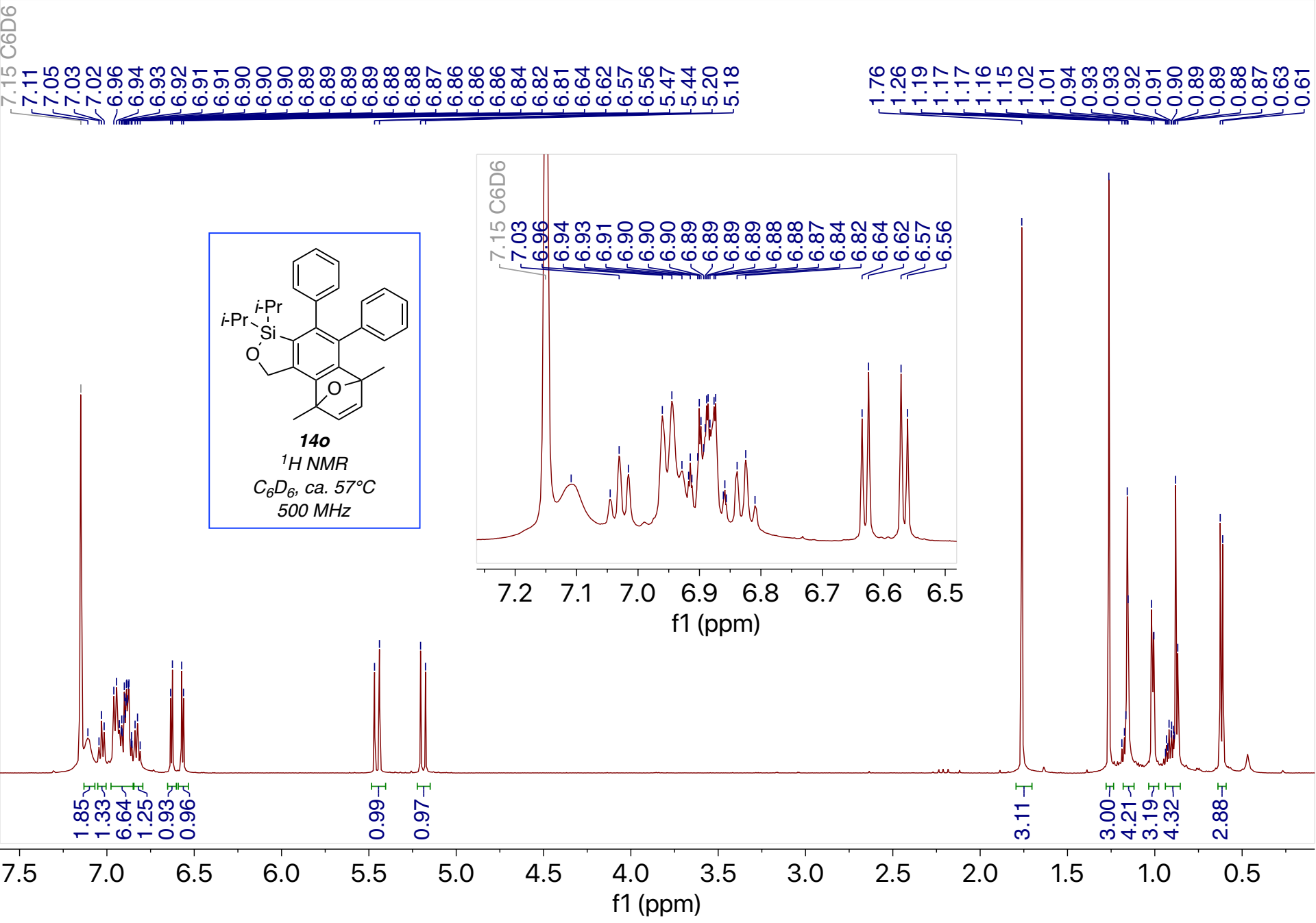

146.10
144.23
143.24
141.00
134.74
133.86
133.78
133.42
133.16
131.72
131.64
131.30
130.91
130.69
130.54
128.12
128.10
127.59
127.34
122.85
121.50
118.94
111.23
98.97
89.00
61.14
25.57
24.55
-0.00 TMS
Ph
NC
Ph
HO
24
13C NMR
CDCl3
126 MHz
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

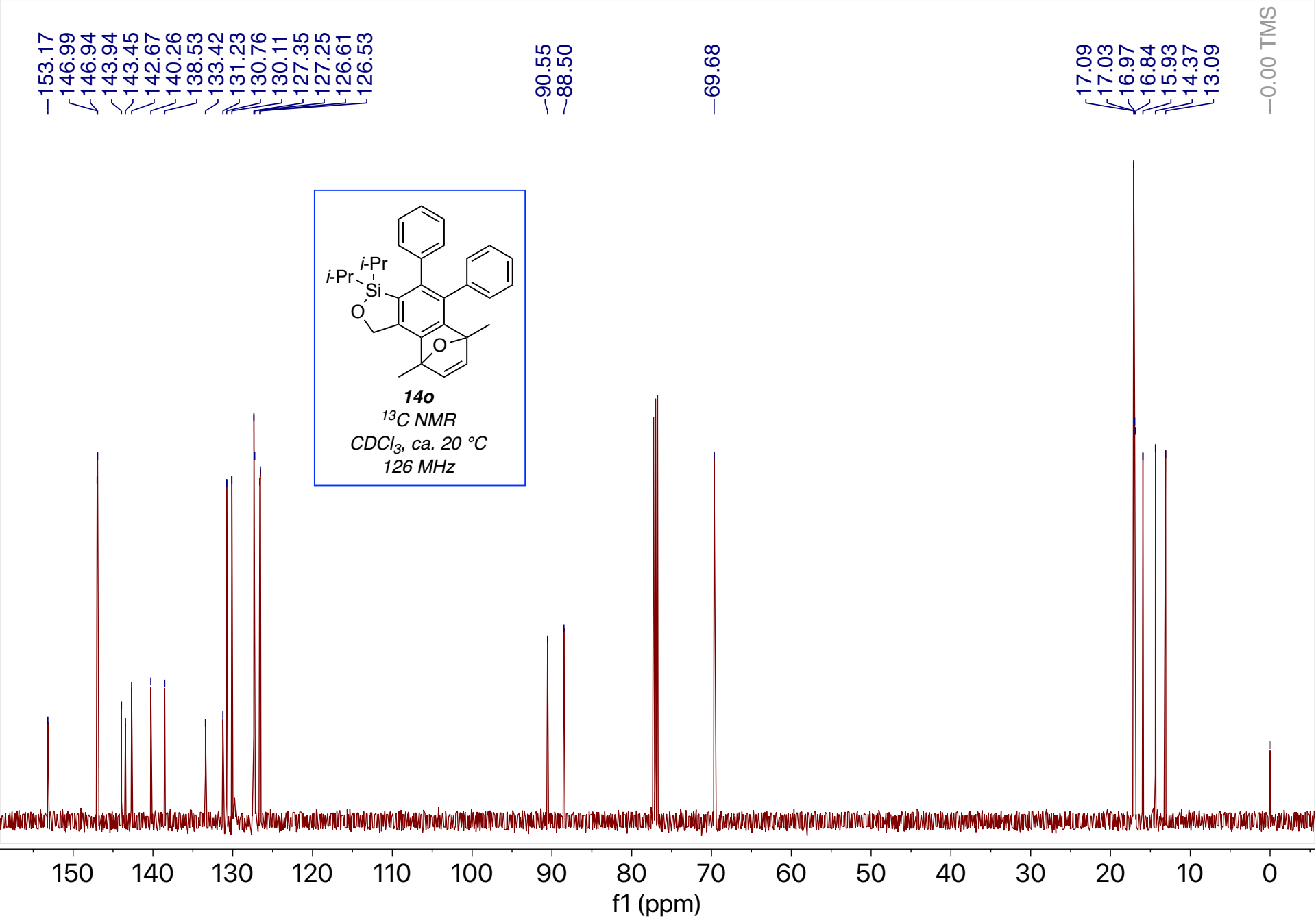

Ph
NC
Ph
HO
NOESY
24
H
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)
f1 (ppm)

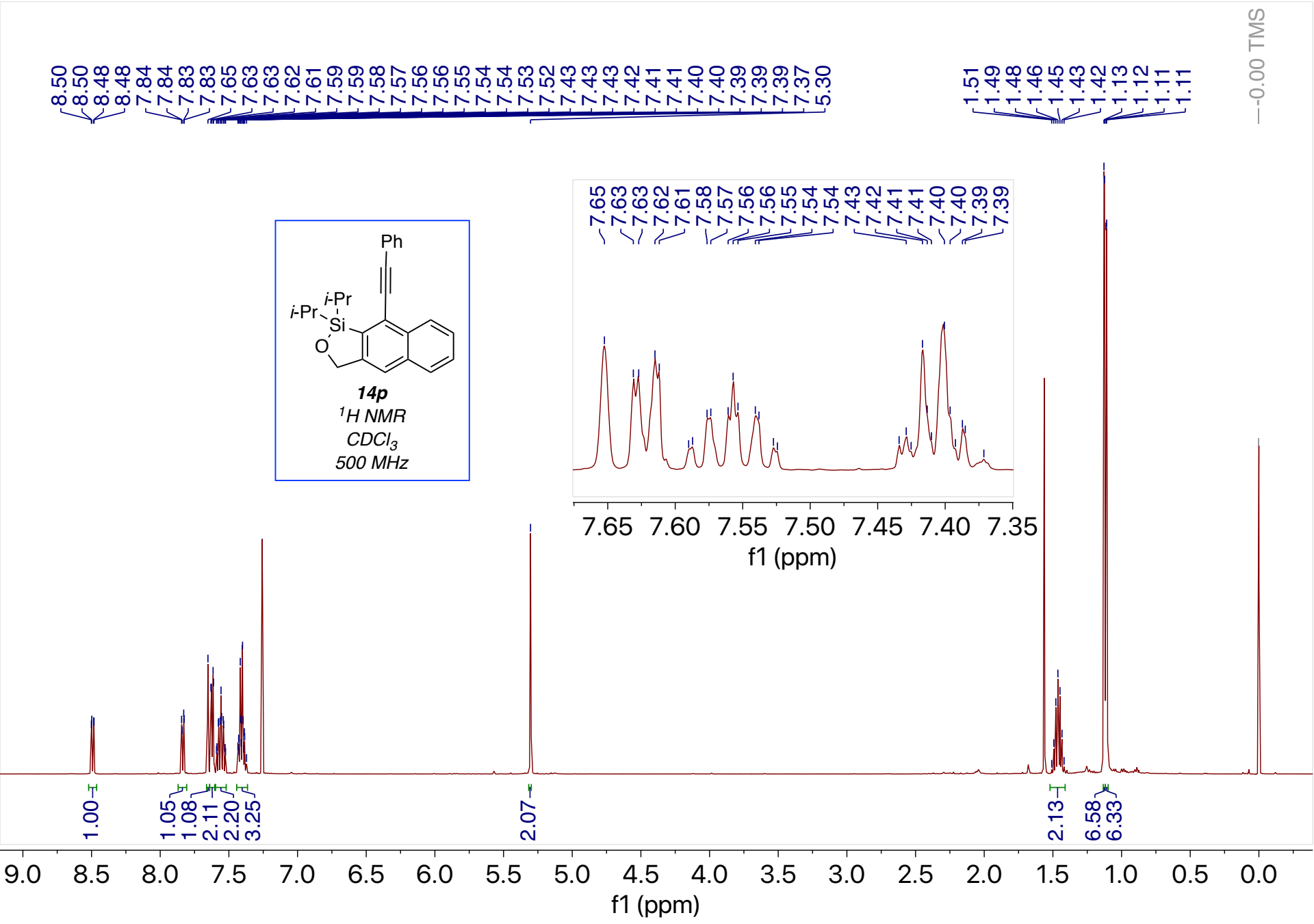

7.49
7.48
7.46
7.44
7.42
7.41
7.39
7.20
7.18
7.00
6.98
6.92
6.92
6.91
6.91
6.86
6.85
6.74
6.73
4.92
4.91
4.90
4.88
4.86
4.86
4.84
4.83
2.14
1.45
1.44
1.43
1.19
0.55
0.00 TMS
7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7
f1 (ppm)
4.90 4.80
f1 (ppm)
25
1H NMR
CDCl3
500 MHz
Ph
TMS
Ph
HO
O
3.96
2.98
0.98
1.97
1.01
1.00
0.99
1.01
3.03
0.98
3.00
8.99
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
f1 (ppm)

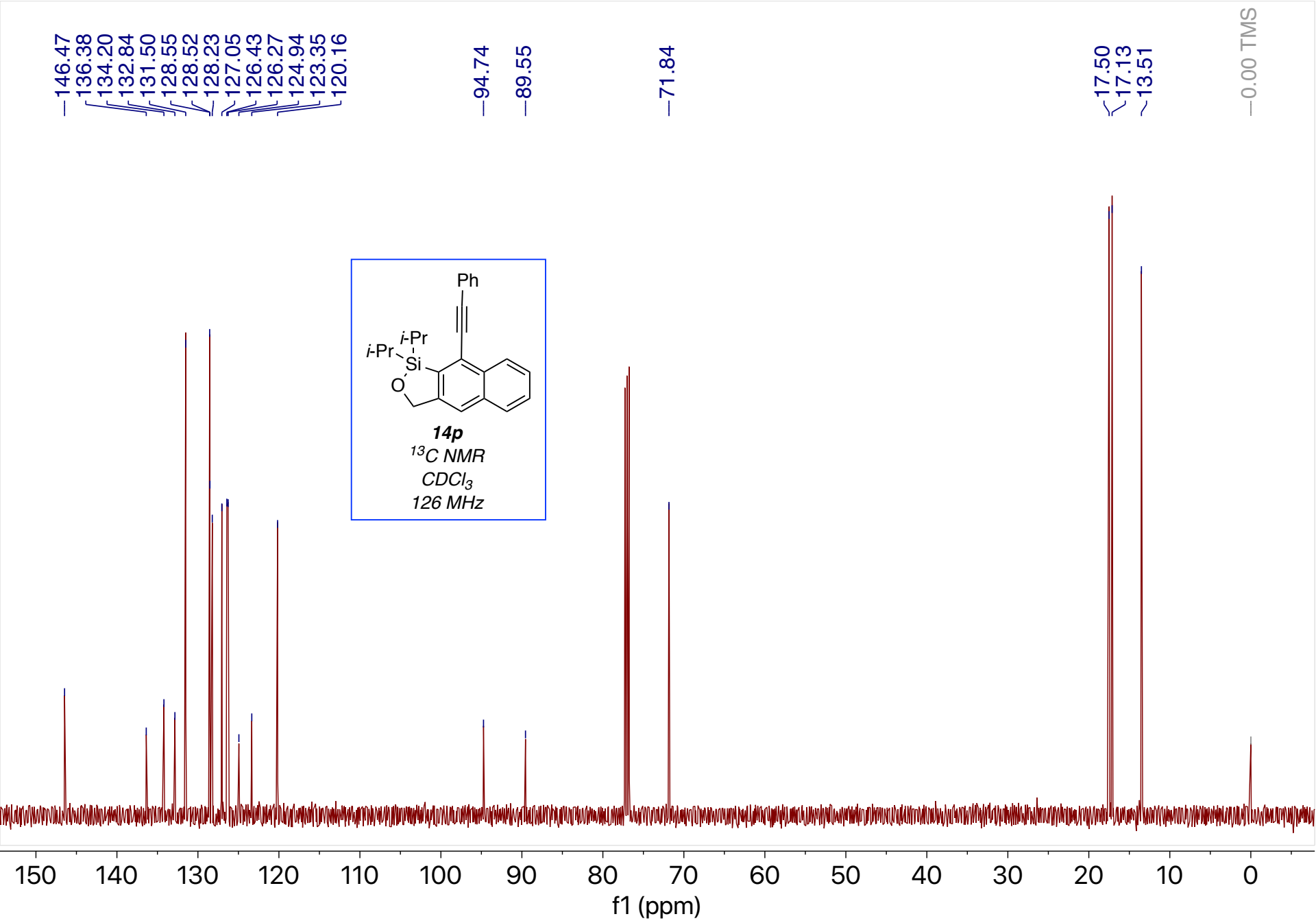

151.58
151.33
147.09
146.49
139.53
138.98
137.95
137.56
130.81
130.74
129.03
128.13
127.86
127.83
127.57
127.38
127.34
123.52
97.96
91.54
90.01
89.12
60.80
17.63
16.93
2.96
0.00 TMS
25
13C NMR
CDCl3
126 MHz
Ph
TMS
Ph
HO
O
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.25 7.24 7.23 7.23 7.16 7.16 7.15 7.14 7.14 7.14 7.13 7.13 7.12 7.09 7.07 7.06 7.06 7.04 7.04 7.03 7.03 7.00 7.00 7.00 6.99 6.98 6.98 6.90 6.89 6.88 6.88 6.87 5.41 5.38 5.17 5.14 1.97 1.16 1.06 1.05 1.03 1.03 1.02 1.01 0.89 0.87 0.82 0.81 0.79 0.78 0.76 0.75 0.69 0.68 0.37 0.36
—0.00 TMS
i-Pr
i-Pr
Si
O
O
14o
1H NMR
CDCl3, ca. 20 °C
500 MHz
7.30 7.20 7.10 7.00 6.90 6.80
f1 (ppm)
0.90 1.47 2.92 1.25 3.07 1.00 1.00 3.00 3.06 4.19 3.29 1.10 3.04 3.03
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
f1 (ppm)


7.15 C6D6
7.11 7.05 7.03 7.02 6.96 6.94 6.93 6.92 6.91 6.91 6.90 6.90 6.90 6.89 6.89 6.89 6.89 6.88 6.88 6.87 6.86 6.86 6.86 6.84 6.82 6.81 6.64 6.62 6.57 6.56 5.47 5.44 5.20 5.18
1.76 1.26 1.19 1.17 1.17 1.16 1.15 1.02 1.01 0.94 0.93 0.93 0.92 0.91 0.90 0.89 0.89 0.88 0.87 0.63 0.61
i-Pr
i-Pr
Si
O
O
14o
1H NMR
C6D6, ca. 57°C
500 MHz
7.15 C6D6
7.03 6.96 6.94 6.93 6.91 6.90 6.90 6.90 6.89 6.89 6.89 6.88 6.88 6.87 6.84 6.82 6.64 6.62 6.57 6.56
7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5
f1 (ppm)
1.85 1.33 6.64 1.25 0.93 0.96 0.99 0.97 3.11 3.00 4.21 3.19 4.32 2.88
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
f1 (ppm)


153.17
146.99
146.94
143.94
143.45
142.67
140.26
138.53
133.42
131.23
130.76
130.11
127.35
127.25
126.61
126.53
90.55
88.50
69.68
17.09
17.03
16.97
16.84
15.93
14.37
13.09
0.00 TMS
i-Pr
i-Pr
Si
O
O
14o
13C NMR
CDCl3, ca. 20 °C
126 MHz
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.50 8.50 8.48 8.48 7.84 7.84 7.83 7.83 7.65 7.63 7.63 7.62 7.61 7.59 7.59 7.58 7.57 7.56 7.56 7.55 7.54 7.54 7.53 7.52 7.43 7.43 7.43 7.42 7.41 7.41 7.40 7.40 7.39 7.39 7.39 7.37 5.30
1.51 1.49 1.48 1.46 1.45 1.43 1.42 1.13 1.12 1.11 1.11
0.00 TMS
Ph
i-Pr
i-Pr
Si
O
14p
1H NMR
CDCl3
500 MHz
7.65 7.63 7.63 7.62 7.61 7.58 7.57 7.56 7.56 7.55 7.54 7.54 7.43 7.42 7.41 7.41 7.40 7.40 7.39 7.39
7.65 7.60 7.55 7.50 7.45 7.40 7.35
f1 (ppm)
1.00 1.05 1.08 2.11 2.20 3.25 2.07 2.13 6.58 6.33
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


146.47
136.38
134.20
132.84
131.50
128.55
128.52
128.23
127.05
126.43
126.27
124.94
123.35
120.16
94.74
89.55
71.84
17.50
17.13
13.51
0.00 TMS
Ph
i-Pr
i-Pr
Si
O
14p
13C NMR
CDCl3
126 MHz
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)