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Electronic Supplementary Information

Atom-Economic Synthesis of Bicyclo[3.1.0]hexane Silanes by Gold-Catalyzed Si-H Bond Insertion Reaction of 1,6-Enynes with Hydrosilanes

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Table of Contents

1. General Information

Unless otherwise noted, all reactions were carried out in a flame-dried, sealed Schlenk reaction tube under an atmosphere of nitrogen with magnetic stirring. The oil bath acts as heat source for reactions that require heating. Reactions were monitored by analytical thin-layer chromatography (TLC). TLC was performed using Huanghai 8 ±0.2 μm precoated glass plates (0.25 mm 230-400 mesh silica gel) and visualized by UV fluorescence quenching, $KMnO_4$, or phosphomolybdic acid staining. Visualization was accomplished by exposure to a UV lamp. All the products in this article are compatible with standard silica gel chromatography. Column chromatography was performed on silica gel (200-300 mesh) using standard methods.

Melting points are recorded using DBK programmable melting point apparatus in capillary tubes and are uncorrected. ^{1}H NMR and proton decoupled ^{13}C NMR spectra were recorded on Bruker Avance 500 MHz spectrometers or Bruker Avance III HD 400 MHz at ambient temperature. NMR standards were used as follows: ^{1}H NMR spectroscopy: δ = 7.26 ppm ($CDCl_3$). ^{13}C NMR spectroscopy: δ = 77.16 ppm ($CDCl_3$). Data for ^{1}H NMR were reported as chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration) using standard abbreviations for multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, dt = doublet of triplet, m = multiplet, and bs = broad signal. Data for ^{13}C NMR were reported in terms of chemical shifts (δ ppm). High resolution mass spectra (HRMS) were recorded on Bruker 15T SolariX FTICR or Advion Mass Expression CMS mass spectrometer instrument in an electrospray ionization mode (ESI+). X-ray diffraction analysis was recorded on an Agilent Gemini E X-ray single crystal diffractometer.

Petroleum ester (PE, 60~90 ^{o}C) and ethyl acetate (EA) were used as eluent for silica gel chromatography. Solvents were distilled under nitrogen from calcium hydride or sodium/benzophenone. Enynes **1** were prepared according to literature procedures[1-3]. Hydrosilanes **2** and tributylgermane **4** were commercially available. Other reagents were purchased commercially and used without further purification unless otherwise noted.

2. Preparation of Enynes

1,6-Enynes (**1a-1x**)[1], 1,5-enyne (**1y**)[2] and 1,7-enyne (**1z**)[3] were prepared according to literature procedures.

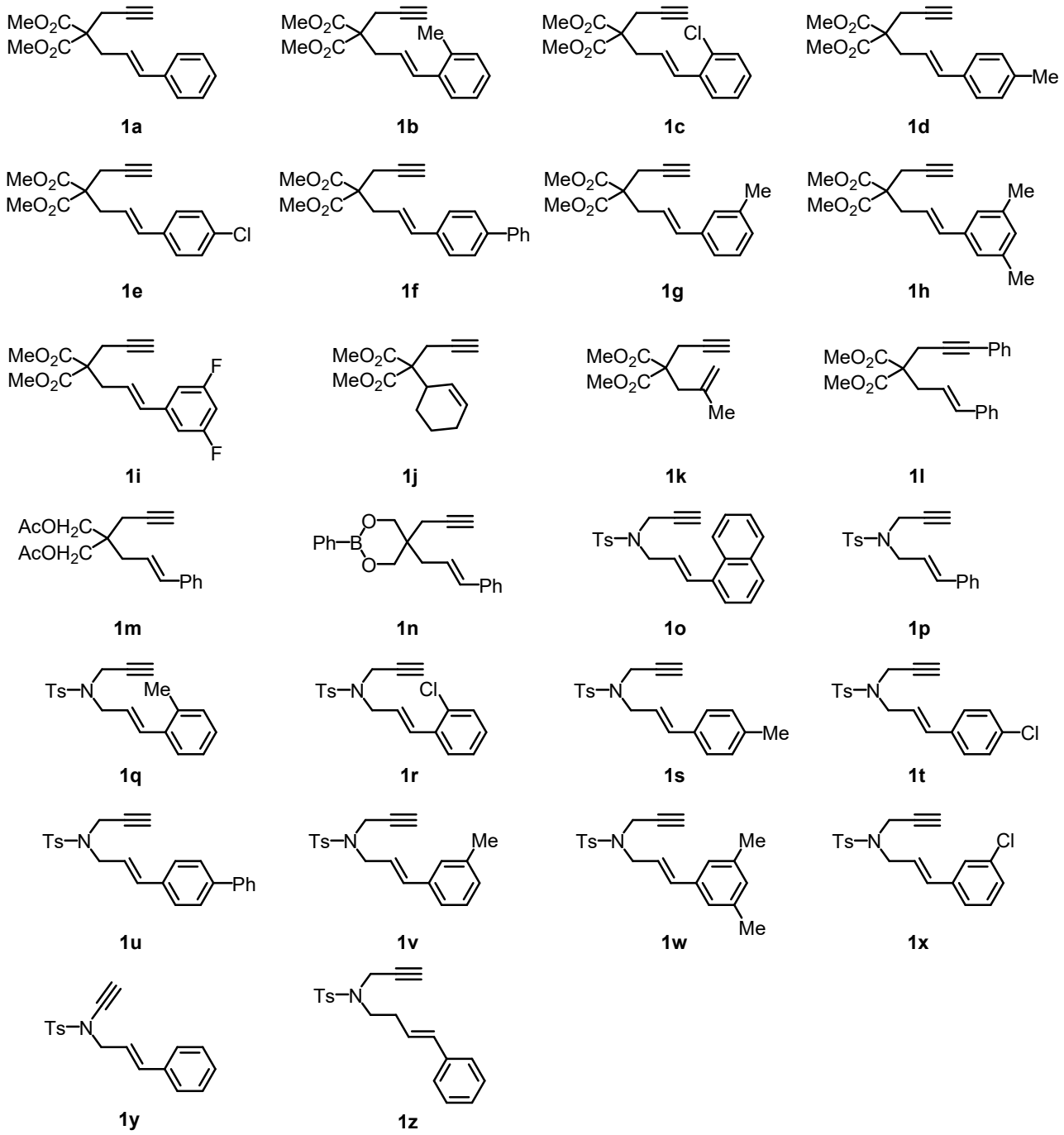


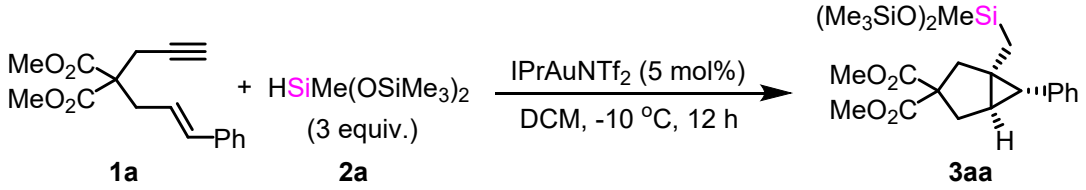
Figure S1. Enynes used in this work

Analytical Data of Unkown Enynes:

(*E*)-*N*-(3-([1,1'-biphenyl]-4-yl)allyl)-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide (1u). Colorless solid, m.p. 110-111 °C (262.5 mg, 65% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.78 (d, J = 8.4 Hz, 2H), 7.66-7.51 (m, 4H), 7.49-7.38 (m, 4H), 7.38-7.28 (m, 3H), 6.61 (d, J = 15.8 Hz, 1H), 6.08 (dt, J = 15.8, 6.8 Hz, 1H), 4.15 (d, J = 2.4 Hz, 2H), 4.00 (d, J = 6.4

Hz, 2H), 2.44 (s, 3H), 2.06 (t, J = 2.4 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 143.8, 141.0, 140.7, 136.2, 135.3, 134.6, 129.7, 129.0, 128.0, 127.6, 127.5, 127.14, 127.09, 123.2, 74.0, 48.8, 36.1, 21.7. **HRMS** (ESI, m/z) Calculated for $[C_{24}H_{40}O_6Si_3Na, M + Na]^+$: 424.1342, found: 424.1340.

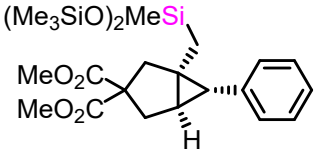
3. Typical Procedure for Bicyclo[3.1.0]hexane Silanes



1a **2a** **3aa**

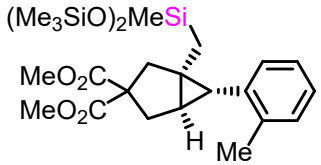
Typical procedure: A pre-dried 10.0 mL Schlenk tube was charged with stirring bar and $IPrAuNTf_2$ (8.7 mg, 0.01 mmol, 0.05 eq.), and then vacuumed and replaced with nitrogen three times. DCM was added under nitrogen atmosphere and the mixture was stirred at room temperature for 10 minutes. The solution was reduced down to -10 °C and added successively with **2a** (133.3 mg, 0.6 mmol, 3.0 eq.) and **1a** (57.2 mg, 0.2 mmol, 1.0 eq.). Then, the reaction mixture was stirred at -10 °C for 12 h. Subsequently, solvent was removed by rotary evaporation instrument and 1,3,5-trimethoxybenzene as the internal reference was added to measure the ^{1}HNMR yield. Finally, the mixture was transferred to a column and purified by flash chromatography on silica gel (PE/EA = 10:1, R_f = 0.20) to give the analytical pure products **3aa** (colorless oil, 78.3 mg, 77% yield).

4. Characterization of Bicyclo[3.1.0]hexane Silanes and Germanes



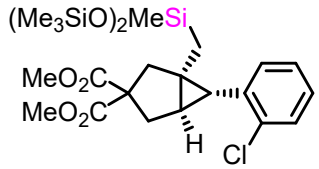
3aa

Dimethyl(1S,5R,6S)-1-((1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)methyl)-6-phenylbicyclo[3.1.0]hexane-3,3-dicarboxylate (3aa), colorless oil (78.3 mg, 77% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.24 (t, J = 7.5 Hz, 2H), 7.17-7.10 (m, 1H), 7.07-7.00 (m, 2H), 3.76 (s, 3H), 3.71 (s, 3H), 2.82 (d, J = 14.2 Hz, 1H), 2.78-2.71 (m, 1H), 2.68 (d, J = 13.7, 1H), 2.56 (d, J = 14.2 Hz, 1H), 1.65 (s, 2H), 0.59 (d, J = 15.4 Hz, 1H), 0.47 (d, J = 15.4 Hz, 1H), 0.08-0.02 (m, 18H), -0.04--0.10 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 173.7, 172.6, 139.2, 128.8, 128.0, 125.6, 60.0, 53.03, 53.00, 43.4, 37.3, 33.7, 31.6, 29.3, 17.3, 1.96, 1.95, 1.1. **HRMS** (ESI, m/z) Calculated for $[C_{24}H_{40}O_6Si_3Na, M + Na]^+$: 531.2025, found: 531.2028.



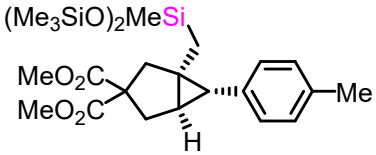
3ab

Dimethyl(1S,5R,6S)-1-((1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)methyl)-6-(o-tolyl)bicyclo[3.1.0]hexane-3,3-dicarboxylate (3ab), colorless oil (94.0 mg, 90% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.16-7.12 (m, 1H), 7.11-7.03 (m, 2H), 6.94-6.86 (m, 1H), 3.74 (s, 3H), 3.71 (s, 3H), 2.88 (d, J = 14.0 Hz, 1H), 2.81 (dd, J = 13.6 Hz, J = 5.0 Hz, 1H), 2.69 (d, J = 13.8 Hz, 1H), 2.59 (d, J = 14.0 Hz, 1H), 2.26 (s, 3H), 1.74 (t, J = 4.6 Hz, 1H), 1.53 (d, J = 4.3 Hz, 1H), 0.62 (d, J = 15.4 Hz, 1H), 0.08-0.01 (m, 19H), -0.03 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 173.7, 172.4, 138.5, 137.6, 129.7, 127.5, 125.9, 125.6, 60.1, 53.0, 52.96, 42.7, 37.3, 32.4, 29.3, 27.6, 20.0, 16.8. 2.0, 1.9, 1.1. **HRMS** (ESI, m/z) Calculated for $[C_{25}H_{42}O_6Si_3Na, M + Na]^+$: 545.2181, found: 545.2183.



3ac

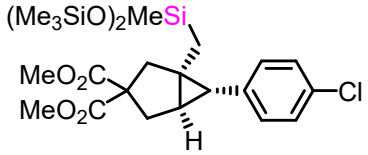
Dimethyl(1S,5R,6R)-6-(2-chlorophenyl)-1-((1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)methyl)bicyclo[3.1.0]hexane-3,3-dicarboxylate (3ac), colorless oil (92.2 mg, 85% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.39-7.29 (m, 1H), 7.18-7.07 (m, 2H), 7.00-6.92 (m, 1H), 3.76 (s, 3H), 3.71 (s, 3H), 2.94-2.85 (m, 1H), 2.79-2.69 (m, 2H), 2.69-2.60 (m, 1H), 1.79-1.69 (m, 2H), 0.84-0.68 (m, 1H), 0.08-0.02 (m, 19H), 0.01--0.04 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 173.5, 172.4, 137.4, 136.3, 129.2, 129.1, 127.0, 126.3, 60.0, 53.0, 42.6, 37.3, 33.3, 29.5, 28.4, 17.0, 2.0, 1.9, 1.0. **HRMS** (ESI, m/z) Calculated for $[C_{24}H_{39}ClO_6Si_3Na, M + Na]^+$: 565.1635, found: 565.1639.



3ad

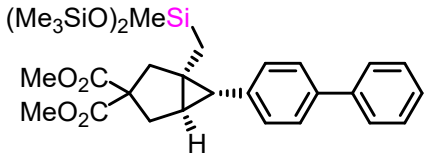
Dimethyl(1S,5R,6S)-1-((1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)methyl)-6-(p-tolyl)bicyclo[3.1.0]hexane-3,3-dicarboxylate (3ad), colorless oil (47.0 mg, 45% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.04 (d, J = 8.0 Hz, 2H), 6.93 (d, J = 8.0 Hz, 2H), 3.75 (s, 3H), 3.71 (s, 3H), 2.84-2.78 (m, 1H), 2.76-2.65 (m, 2H), 2.60-2.52 (m, 1H), 2.29 (s, 3H), 1.65-1.58 (m, 2H), 0.57 (d, J = 15.4 Hz, 1H), 0.47 (d, J = 15.4 Hz, 1H), 0.10-0.01 (m, 18H), -0.01--0.10 (m, 3H). **^{13}C NMR**

(125 MHz, $CDCl_3$): δ 173.7, 172.6, 136.0, 135.0, 128.7, 128.6, 60.0, 53.01, 52.98, 43.4, 37.3, 33.4, 31.2, 29.2, 21.1, 17.3. 1.97, 1.95, 1.1. **HRMS** (ESI, m/z) Calculated for $[C_{25}H_{42}O_6Si_3Na, M + Na]^+$: 545.2181, found: 545.2180.



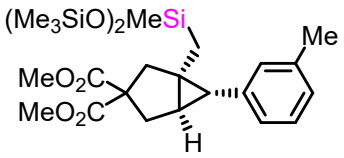
3ae

Dimethyl(1S,5R,6S)-6-(4-chlorophenyl)-1-((1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)methyl)bicyclo[3.1.0]hexane-3,3-dicarboxylate (3ae), colorless oil (60.7 mg, 56% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.20 (d, J = 8.4 Hz, 2H), 6.97 (d, J = 8.4 Hz, 2H), 3.75 (s, 3H), 3.71 (s, 3H), 2.83-2.77 (m, 1H), 2.77-2.71 (m, 1H), 2.70-2.64 (m, 1H), 2.60-2.53 (m, 1H), 1.65-1.58 (m, 2H), 0.64-0.51 (m, 1H), 0.51-0.38 (m, 1H), 0.11-0.02 (m, 18H), 0.00--0.10 (m, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 173.7, 172.4, 137.8, 131.3, 130.1, 128.13, 128.10, 128.0, 59.8, 53.0, 43.3, 37.2, 33.8, 31.0, 29.6, 17.3, 2.0, 1.1. **HRMS** (ESI, m/z) Calculated for $[C_{24}H_{39}ClO_6Si_3Na, M + Na]^+$: 565.1635, found: 565.1637.



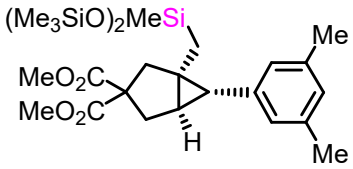
3af

Dimethyl(1S,5R,6S)-6-([1,1'-biphenyl]-4-yl)-1-((1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)methyl)bicyclo[3.1.0]hexane-3,3-dicarboxylate (3af), colorless oil (72.5 mg, 62% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.57 (d, J = 7.2 Hz, 2H), 7.48 (d, J = 8.2 Hz, 2H), 7.42 (t, J = 7.6 Hz, 2H), 7.32 (t, J = 7.4 Hz, 1H), 7.12 (d, J = 8.2 Hz, 2H), 3.78 (s, 3H), 3.72 (s, 3H), 2.89-2.81 (m, 1H), 2.80-2.67 (m, 2H), 2.64-2.53 (m, 1H), 1.69 (s, 2H), 0.70-0.59 (m, 1H), 0.59-0.46 (m, 1H), 0.12-0.02 (m, 18H), 0.00--0.10 (m, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 173.7, 172.6, 141.2, 138.5, 138.4, 129.1, 128.8, 127.10, 127.07, 126.7, 59.9, 53.05, 53.04, 43.4, 37.3, 34.0, 31.4, 29.6, 17.4, 1.98, 1.96, 1.2. **HRMS** (ESI, m/z) Calculated for $[C_{30}H_{44}O_6Si_3Na, M + Na]^+$: 607.2338, found: 607.2338.



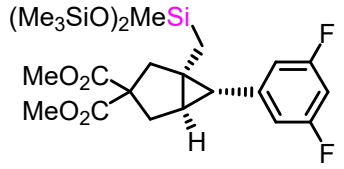
3ag

Dimethyl(1S,5R,6S)-1-((1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)methyl)-6-(m-tolyl)bicyclo[3.1.0]hexane-3,3-dicarboxylate (3ag), colorless oil (68.9 mg, 66% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.12 (t, J = 7.6 Hz, 1H), 6.95 (d, J = 7.5 Hz, 1H), 6.86 (s, 1H), 6.82 (d, J = 7.6 Hz, 1H), 3.75 (s, 3H), 3.71 (s, 3H), 2.87-2.78 (m, 1H), 2.77-2.71 (m, 1H), 2.70-2.64 (m, 1H), 2.60-2.52 (m, 1H), 2.30 (s, 3H), 1.69-1.59 (m, 2H), 0.68-0.44 (m, 2H), 0.11-0.02 (m, 18H), 0.01--0.10 (m, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 173.7, 172.6, 139.0, 137.4, 129.6, 127.8, 126.4, 125.6, 59.9, 53.02, 53.01, 43.4, 37.3, 33.6, 31.5, 29.3, 21.5, 17.2, 2.0, 1.9, 1.1. **HRMS** (ESI, m/z) Calculated for $[C_{25}H_{42}O_6Si_3Na, M + Na]^+$: 545.2181, found: 545.2183.



3ah

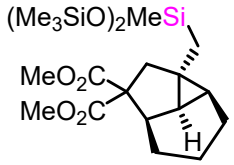
Dimethyl(1S,5R,6S)-6-(3,5-dimethylphenyl)-1-((1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)methyl)bicyclo[3.1.0]hexane-3,3-dicarboxylate (3ah), colorless oil (80.5 mg, 75% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 6.78 (s, 1H), 6.65 (s, 2H), 3.76 (s, 3H), 3.71 (s, 3H), 2.84-2.78 (m, 1H), 2.77-2.71 (m, 1H), 2.70-2.63 (m, 1H), 2.59-2.52 (m, 1H), 2.26 (s, 6H), 1.64-1.56 (m, 2H), 0.66-0.56 (m, 1H), 0.55-0.45 (m, 1H), 0.09-0.02 (m, 18H), 0.00--0.08 (m, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 173.7, 172.6, 138.9, 137.3, 127.3, 126.6, 59.9, 53.0, 52.98, 43.4, 37.3, 33.5, 31.5, 29.2, 21.4, 17.2, 2.0, 1.9, 1.1. **HRMS** (ESI, m/z) Calculated for $[C_{26}H_{44}O_6Si_3Na, M + Na]^+$: 559.2338, found: 559.2338.



3ai

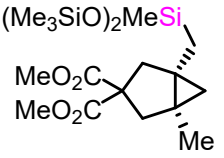
Dimethyl (1S,5R,6S)-6-(3,5-difluorophenyl)-1-((1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)methyl)bicyclo[3.1.0]hexane-3,3-dicarboxylate (3ai), colorless oil (55.5 mg, 51% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 6.64-6.52 (m, 3H), 3.76 (s, 3H), 3.71 (s, 3H), 2.84-2.77 (m, 1H), 2.76-2.70 (m, 1H), 2.70-2.63 (m, 1H), 2.60-2.52 (m, 1H), 1.66-1.58 (m, 2H), 0.65-0.53 (m, 1H), 0.53-0.42 (m, 1H), 0.10-0.04 (m, 18H), 0.01--0.06 (m, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ

173.6, 172.3, 163.8 (d, J = 13.5 Hz), 161.9 (d, J = 13.5 Hz), 143.7 (t, J = 9.5 Hz), 111.6 (d, J = 5.7 Hz), 111.4 (d, J = 5.7 Hz), 101.1 (t, J = 25.4 Hz), 59.7, 53.1, 43.3, 37.1, 34.5, 31.5, 30.0, 17.3, 1.9, 1.1. **HRMS** (ESI, m/z) Calculated for $[C_{24}H_{38}F_2O_6Si_3Na, M + Na]^+$: 567.1836, found: 567.1838.



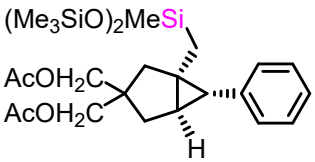
3aj

Dimethyl(2aR,2a1R,2bS,5aR)-2a-((1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)methyl)octahydro-1H-cyclopropa[cd]indene-1,1-dicarboxylate (3aj), colorless oil (72.8 mg, 77% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 3.74 (s, 3H), 3.67 (s, 3H), 3.03 (s, 1H), 2.76-2.65 (m, 1H), 2.16-2.08 (m, 1H), 2.00-1.82 (m, 2H), 1.42-1.23 (m, 5H), 1.07-0.95 (m, 1H), 0.87-0.75 (m, 1H), 0.12-0.06 (m, 20H), 0.04-0.01 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 173.7, 170.7, 72.4, 52.7, 52.2, 39.9, 38.6, 30.6, 28.6, 28.2, 25.4, 24.1, 19.0, 17.6, 2.05, 2.03, 1.0. **HRMS** (ESI, m/z) Calculated for $[C_{21}H_{40}O_6Si_3Na, M + Na]^+$: 495.2025, found: 495.2029.



3ak

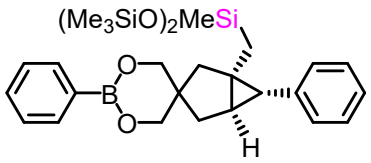
Dimethyl(1S,5R)-1-((1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)methyl)-5-methylbicyclo[3.1.0]hexane-3,3-dicarboxylate (3ak), colorless oil (31.2 mg, 35% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.72 (s, 6H), 3.06-2.84 (m, 4H), 2.08-1.93 (m, 2H), 1.59 (s, 3H), 0.60-0.42 (m, 2H), 0.15-0.02 (m, 18H), -0.01 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 173.2, 134.8, 126.8, 57.3, 52.8, 46.1, 43.3, 21.3, 16.0, 13.3, 2.0, -0.3. **HRMS** (ESI, m/z) Calculated for $[C_{19}H_{38}O_6Si_3Na, M + Na]^+$: 469.1868, found: 469.1868.



3am

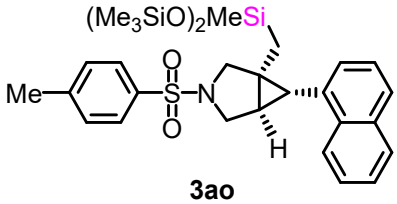
1,1'-((1S,5R,6S)-1-((1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)methyl)-6-phenylbicyclo[3.1.0]hexane-3,3-diyl)bis(propane-1,2-dione) (3am), colorless oil (34.2 mg, 32% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.28-7.20 (m, 2H), 7.14 (t, J = 7.4 Hz, 1H), 7.08-7.00 (m, 2H), 4.08-3.92 (m, 4H), 2.10-2.00 (m, 8H), 1.91-1.83 (m, 1H), 1.79-1.75 (m, 1H), 1.74-1.68 (m, 1H), 1.67-

1.63 (m, 1H), 0.67-0.52 (m, 2H), 0.08--0.02 (m, 18H), -0.12--0.22 (m, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 171.30, 171.26, 139.4, 128.3, 128.0, 125.6, 68.4, 68.1, 49.4, 44.0, 39.4, 37.0, 36.2, 31.5, 21.1, 21.0, 18.7, 2.0, 1.9, 1.1. **HRMS** (ESI, m/z) Calculated for $[C_{26}H_{44}O_6Si_3Na, M + Na]^+$: 559.2338, found: 559.2345.



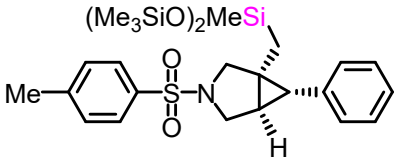
3an

3-(((1S,5R,6S)-2',6-diphenylspiro[bicyclo[3.1.0]hexane-3,5'-[1,3,2]dioxaborinan]-1-yl)methyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane (**3an**), colorless oil (53.8 mg, 50% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.86-7.72 (m, 2H), 7.45-7.38 (m, 1H), 7.37-7.31 (m, 2H), 7.29-7.22 (m, 2H), 7.18-7.13 (m, 1H), 7.09-7.02 (m, 2H), 3.97-3.83 (m, 4H), 2.16-2.03 (m, 2H), 2.00-1.91 (m, 1H), 1.89-1.78 (m, 1H), 1.76-1.64 (m, 2H), 0.70-0.55 (m, 1H), 0.53-0.39 (m, 1H), 0.08-0.02 (m, 18H), -0.05--0.12 (m, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 139.4, 134.0, 130.8, 128.5, 128.1, 128.0, 127.7, 125.7, 72.7, 72.6, 46.0, 44.1, 38.0, 37.4, 35.6, 31.0, 18.1, 2.0, 1.8, 1.2. **HRMS** (ESI, m/z) Calculated for $[C_{28}H_{43}BO_4Si_3Na, M + Na]^+$: 561.2454, found: 561.2454.



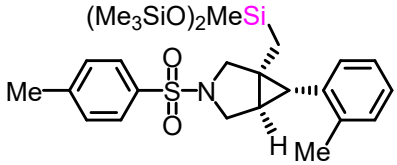
3ao

(1R,5R,6S)-1-((1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)methyl)-6-(naphthalen-1-yl)-3-tosyl-3-azabicyclo[3.1.0]hexane (3ay), colorless oil (93.2 mg, 78% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.94-7.87 (m, 1H), 7.87-7.80 (m, 1H), 7.78 (d, J = 8.1 Hz, 2H), 7.71 (d, J = 8.2 Hz, 1H), 7.54-7.46 (m, 2H), 7.40-7.30 (m, 3H), 7.11 (d, J = 7.1 Hz, 1H), 3.87-3.76 (m, 2H), 3.41 (dd, J = 9.1, 3.8 Hz, 1H), 3.38-3.32 (m, 1H), 2.40 (s, 3H), 2.37 (d, J = 4.2 Hz, 1H), 1.93 (t, J = 4.0 Hz, 1H), 0.58-0.44 (m, 1H), 0.02-0.00 (m, 1H), -0.02--0.10 (m, 18H), -0.28--0.39 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.6, 134.25, 134.21 133.7, 133.6, 129.9, 128.6, 127.6, 127.0, 126.1, 125.9, 125.5, 125.3, 124.6, 54.8, 51.1, 31.5, 27.6, 26.2, 21.6, 15.0, 1.9, 0.9. **HRMS** (ESI, m/z) Calculated for $[C_{30}H_{43}NO_4SSi_3Na, M + Na]^+$: 620.2113, found: 620.2116.



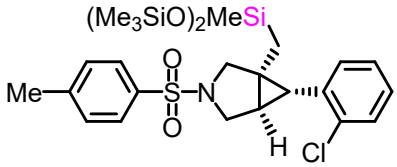
3ap

(1R,5R,6S)-1-((1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)methyl)-6-phenyl-3-tosyl-3-azabicyclo [3.1.0]hexane (3ap), white solid, m.p. 71-72 °C (71.1 mg, 65% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.72 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.25 (t, J = 7.4 Hz, 2H), 7.17 (t, J = 7.4 Hz, 1H), 6.99 (t, J = 7.4 Hz, 2H), 3.71-3.60 (m, 2H), 3.26 (dd, J = 9.1, 3.8 Hz, 1H), 3.18-3.08 (m, 1H), 2.44 (s, 3H), 2.05-1.99 (m, 1H), 1.73-1.65 (m, 1H), 0.60-0.40 (m, 2H), 0.08--0.06 (m, 18H), -0.20--0.32 (m, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 143.6, 137.8, 134.0, 129.8, 128.6, 128.1, 127.7, 126.0, 55.3, 50.9, 31.9, 29.9, 27.2, 21.7, 14.9, 2.0, 1.9, 0.8. **HRMS** (ESI, m/z) Calculated for $[C_{26}H_{41}NO_4SSi_3Na, M + Na]^+$: 570.1956, found: 570.1956.



3aq

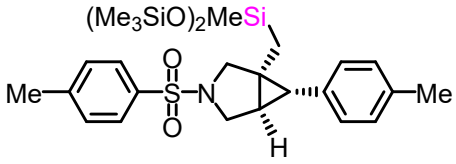
(1R,5R,6S)-1-((1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)methyl)-6-(o-tolyl)-3-tosyl-3-azabicyclo [3.1.0]hexane (3aq), colorless oil (83.1 mg, 74% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.73 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 7.18-7.03 (m, 3H), 6.90-6.83 (m, 1H), 3.73-3.57 (m, 2H), 3.37 (dd, J = 9.2, 3.8 Hz, 1H), 3.32-3.22 (m, 1H), 2.42 (s, 3H), 2.17 (s, 3H), 1.86-1.74 (m, 2H), 0.62-0.46 (m, 1H), 0.06-0.04 (m, 1H), 0.03--0.07 (m, 18H), -0.20--0.30 (m, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 143.5, 138.4, 136.0, 134.4, 129.9, 129.8, 127.61, 127.58, 126.3, 125.7, 55.1, 51.1, 30.9, 28.5, 26.1, 21.6, 20.0, 14.6, 1.9, 0.9. **HRMS** (ESI, m/z) Calculated for $[C_{27}H_{43}NO_4SSi_3Na, M + Na]^+$: 584.2113, found: 584.2116.



3ar

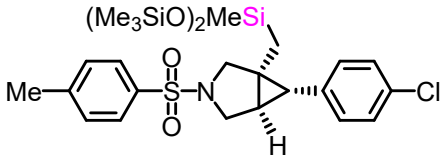
(1R,5R,6R)-6-(2-chlorophenyl)-1-((1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)methyl)-3-tosyl-3-azabicyclo[3.1.0]hexane (3ar), colorless oil (67.5 mg, 58% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.73 (d, J = 8.1 Hz, 2H), 7.40-7.28 (m, 3H), 7.18-7.10 (m, 2H), 6.98-6.90 (m, 1H), 3.76-3.63 (m, 2H), 3.36 (dd, J = 9.1, 3.9 Hz, 1H), 3.32-3.22 (m, 1H), 2.42 (s, 3H), 2.05 (d, J = 4.3 Hz, 1H), 1.80-1.72 (m, 1H), 0.78-0.60 (m, 1H), 0.06-0.05 (m, 1H), 0.04--0.07 (m, 18H), -

0.17--0.30 (m, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 143.5, 136.3, 136.0, 134.3, 129.8, 129.4, 129.3, 127.6, 127.5, 126.4, 54.9, 50.9, 31.6, 28.6, 26.6, 21.6, 14.8, 1.91, 1.90, 0.9. **HRMS** (ESI, m/z) Calculated for $[C_{26}H_{40}ClNO_4SSi_3Na, M + Na]^+$: 604.1566, found: 604.1568.



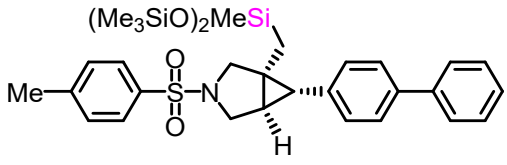
3as

(1R,5R,6S)-1-((1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)methyl)-6-(p-tolyl)-3-tosyl-3-azabicyclo[3.1.0]hexane (3as), white solid, m.p. 67-69 °C (70.6 mg, 63% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.72 (t, J = 8.2 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.05 (t, J = 7.8 Hz, 2H), 6.88 (t, J = 8.0 Hz, 2H), 3.72-3.56 (m, 2H), 3.26 (dd, J = 9.1, 3.8 Hz, 1H), 3.19-3.08 (m, 1H), 2.44 (s, 3H), 2.30 (s, 3H), 2.00-1.92 (m, 1H), 1.69-1.61 (m, 1H), 0.63-0.35 (m, 2H), 0.10--0.05 (m, 18H), -0.20--0.30 (m, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 143.5, 135.5, 134.6, 134.1, 129.8, 128.8, 128.4, 127.7, 55.3, 50.9, 31.6, 29.5, 27.2, 21.6, 21.1, 14.9, 2.0, 1.9, 0.9. **HRMS** (ESI, m/z) Calculated for $[C_{27}H_{43}NO_4SSi_3Na, M + Na]^+$: 584.2113, found: 584.2113.



3at

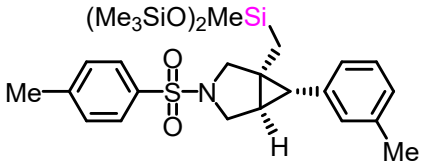
(1R,5R,6S)-6-(4-chlorophenyl)-1-((1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)methyl)-3-tosyl-3-azabicyclo[3.1.0]hexane (3at), white solid, m.p. 65-66 °C (40.6 mg, 35% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.71 (t, J = 8.2 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 6.93 (d, J = 8.4 Hz, 2H), 3.74-3.57 (m, 2H), 3.23 (dd, J = 9.1, 3.8 Hz, 1H), 3.17-3.05 (m, 1H), 2.44 (s, 3H), 2.07-1.98 (m, 1H), 1.68-1.62 (m, 1H), 0.57-0.35 (m, 2H), 0.08--0.04 (m, 18H), -0.18--0.28 (m, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 143.7, 136.5, 134.0, 131.9, 130.0, 129.9, 128.3, 127.8, 55.2, 50.8, 32.0, 29.3, 27.5, 21.7, 15.0, 2.05, 1.98, 1.0. **HRMS** (ESI, m/z) Calculated for $[C_{26}H_{40}ClNO_4SSi_3Na, M + Na]^+$: 604.1566, found: 604.1567.



3au

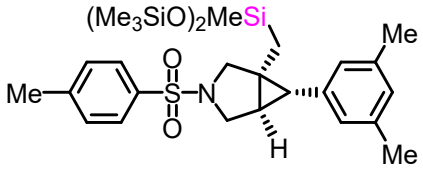
(1R,5R,6S)-6-([1,1'-biphenyl]-4-yl)-1-((1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)methyl)-3-tosyl

-3-azabicyclo[3.1.0]hexane (3au), white solid, m.p. 86-87 °C (58.6 mg, 47% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.73 (d, J = 8.2 Hz, 2H), 7.56 (d, J = 7.3 Hz, 2H), 7.49 (d, J = 8.2 Hz, 2H), 7.43 (t, J = 7.6 Hz, 2H), 7.38-7.29 (m, 3H), 7.07 (d, J = 8.2 Hz, 2H), 3.74-3.62 (m, 2H), 3.28 (dd, J = 9.1, 3.8 Hz, 1H), 3.20-3.06 (m, 1H), 2.45 (s, 3H), 2.09-2.02 (m, 1H), 1.76-1.70 (m, 1H), 0.68-0.38 (m, 2H), 0.08--0.05 (m, 18H), -0.16--0.28 (m, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 143.6, 141.0, 139.0, 137.0, 134.0, 129.8, 129.0, 128.9, 127.7, 127.2, 127.1, 126.8, 55.3, 50.9, 32.1, 29.6, 27.5, 21.7, 15.0, 2.0, 1.9, 0.9. **HRMS** (ESI, m/z) Calculated for $[C_{32}H_{45}NO_4SSi_3Na, M + Na]^+$: 646.2269, found: 646.2269.



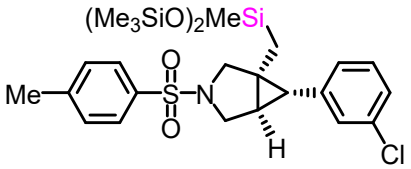
3av

(1R,5R,6S)-1-((1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)methyl)-6-(o-tolyl)-3-tosyl-3-azabicyclo [3.1.0]hexane (3av), white solid, m.p. 72-74 °C (67.5 mg, 60% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.73 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.13 (t, J = 7.5 Hz, 1H), 6.98 (d, J = 7.5 Hz, 1H), 6.84-6.73 (m, 2H), 3.74-3.55 (m, 2H), 3.26 (dd, J = 9.1, 3.8 Hz, 1H), 3.21-3.05 (m, 1H), 2.44 (s, 3H), 2.30 (s, 3H), 1.99-1.92 (m, 1H), 1.71-1.64 (m, 1H), 0.61-0.40 (m, 2H), 0.08--0.06 (m, 18H), -0.19--0.30 (m, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 143.5, 137.7, 137.6, 134.1, 129.8, 129.4, 128.0, 127.7, 126.8, 125.5, 55.3, 50.9, 31.8, 29.8, 27.2, 21.7, 21.6, 14.9, 2.0, 1.9, 0.9. **HRMS** (ESI, m/z) Calculated for $[C_{27}H_{44}NO_4SSi_3, M + H]^+$: 562.2293, found: 562.2290.



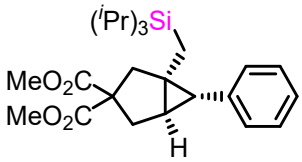
3aw

(1R,5R,6S)-6-(2,6-dimethylphenyl)-1-((1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)methyl)-3-tosyl -3-azabicyclo[3.1.0]hexane (3aw), colorless oil, (80.5 mg, 70% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.1 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 6.80 (s, 1H), 6.58 (s, 2H), 3.73-3.53 (m, 2H), 3.26 (dd, J = 9.1, 3.8 Hz, 1H), 3.19-3.06 (m, 1H), 2.45 (s, 3H), 2.26 (s, 6H), 1.93-1.84 (m, 1H), 1.71-1.62 (m, 1H), 0.64-0.37 (m, 2H), 0.06--0.05 (m, 18H), -0.17--0.29 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.5, 137.6, 137.5, 134.0, 129.8, 127.70, 127.67, 126.4, 55.3, 51.0, 31.7, 29.8, 27.2, 21.7, 21.4, 14.8, 2.0, 1.9, 0.9. **HRMS** (ESI, m/z) Calculated for $[C_{28}H_{45}NO_4SSi_3Na, M + Na]^+$: 598.2269, found: 598.2274.



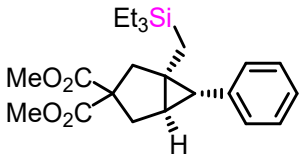
3ax

(1R,5R,6S)-6-(3-chlorophenyl)-1-((1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)methyl)-3-tosyl-3-azabicyclo[3.1.0]hexane (3ax), white solid, m.p. 97-98 °C (32.5 mg, 28% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.71 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 7.22-7.11 (m, 2H), 6.96 (s, 1H), 6.89 (d, J = 7.2 Hz, 1H), 3.74-3.57 (m, 2H), 3.24 (dd, J = 9.2, 3.8 Hz, 1H), 3.17-3.04 (m, 1H), 2.45 (s, 3H), 2.02-1.90 (m, 1H), 1.72-1.64 (m, 1H), 0.60-0.34 (m, 2H), 0.07--0.07 (m, 18H), -0.19--0.29 (m, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 143.7, 140.1, 134.1, 133.9, 129.9, 129.3, 128.6, 127.7, 126.9, 126.2, 55.2, 50.8, 32.1, 29.5, 27.4, 21.7, 14.9, 2.0, 1.9, 0.9. **HRMS** (ESI, m/z) Calculated for $[C_{26}H_{40}ClNO_4SSi_3Na, M + Na]^+$: 604.1566, found: 604.1568.



3ay

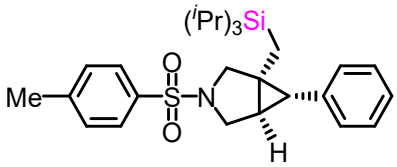
Dimethyl(1S,5R,6S)-6-phenyl-1-((triisopropylsilyl)methyl)bicyclo[3.1.0]hexane-3,3-dicarboxylate (3bc), colorless oil (67.8 mg, 77% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.23 (t, J = 7.5 Hz, 2H), 7.13 (t, J = 7.3 Hz, 1H), 7.05 (d, J = 7.3 Hz, 2H), 3.76 (s, 3H), 3.72 (s, 3H), 2.82 (d, J = 14.0 Hz, 1H), 2.75-2.65 (m, 2H), 2.58 (d, J = 14.0 Hz, 1H), 1.74-1.68 (m, 1H), 1.66-1.62 (m, 1H), 0.99-0.88 (m, 21H), 0.75 (d, J = 15.5 Hz, 1H), 0.67 (d, J = 15.5 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 173.5, 172.8, 139.0, 128.6, 128.0, 125.7, 60.4, 53.2, 53.0, 44.1, 37.4, 35.2, 33.3, 31.2, 19.0, 11.6, 9.5. **HRMS** (ESI, m/z) Calculated for $[C_{26}H_{40}O_4SiNa, M + Na]^+$: 467.2588, found: 467.2588.



3az

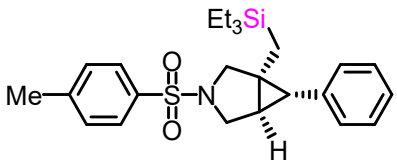
Dimethyl(1S,5R,6S)-6-phenyl-1-((triethylsilyl)methyl)bicyclo[3.1.0]hexane-3,3-dicarboxylate (3ba), colorless oil (40.2 mg, 50% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.24 (t, J = 7.6 Hz, 2H), 7.14 (t, J = 7.3 Hz, 1H), 7.04 (d, J = 7.2 Hz, 2H), 3.76 (s, 3H), 3.73 (s, 3H), 2.78 (d, J = 14.0 Hz, 1H), 2.75-2.66 (m, 2H), 2.49 (d, J = 14.0 Hz, 1H), 1.67-1.61 (m, 2H), 0.82 (t, J

= 8.0 Hz, 9H), 0.69 (d, *J* = 15.3 Hz, 1H), 0.56 (d, *J* = 15.3 Hz, 1H), 0.50-0.35 (m, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$): *δ* 173.6, 172.9, 139.1, 128.6, 128.0, 125.7, 60.4, 53.2, 53.0, 44.1, 37.6, 35.3, 32.5, 30.2, 11.4, 7.5, 4.2. **HRMS** (ESI, m/z) Calculated for $[C_{23}H_{34}O_4SiNa, M + Na]^+$: 425.2118, found: 425.2119.



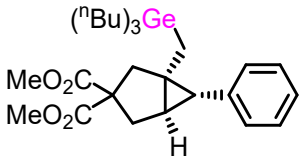
3bb

(1R,5R,6S)-6-phenyl-3-tosyl-1-((triisopropylsilyl)methyl)-3-azabicyclo[3.1.0]hexane (3bf), white solid, m.p. 91-92 °C (88.0 mg, 91% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* 7.72 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.25 (t, *J* = 7.5 Hz, 2H), 7.16 (t, *J* = 7.3 Hz, 1H), 7.01 (d, *J* = 7.3 Hz, 2H), 3.65 (t, *J* = 8.8 Hz, 2H), 3.25 (dd, *J* = 9.2, 3.8 Hz, 1H), 3.08 (d, *J* = 9.4 Hz, 1H), 2.46 (s, 3H), 2.07 (d, *J* = 4.2 Hz, 1H), 1.70 (t, *J* = 4.0 Hz, 1H), 0.86-0.76 (m, 18H), 0.76-0.64 (m, 4H), 0.50 (d, *J* = 15.7 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): *δ* 143.8, 137.6, 133.0, 129.7, 128.6, 128.2, 127.9, 126.2, 55.9, 51.1, 33.1, 31.2, 28.8, 21.7, 18.8, 18.7, 11.6, 7.0. **HRMS** (ESI, m/z) Calculated for $[C_{28}H_{41}NO_2SSiNa, M + Na]^+$: 506.2519, found: 506.2520.



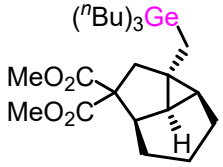
3bc

(1R,5R,6S)-6-phenyl-3-tosyl-1-((triethylsilyl)methyl)-3-azabicyclo[3.1.0]hexane (3bg), white solid, m.p. 112-113 °C (20.4 mg, 23% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* 7.73 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.30-7.21 (m, 2H), 7.20-7.12 (m, 1H), 6.99 (d, *J* = 7.2 Hz, 2H), 3.66 (d, *J* = 9.2 Hz, 1H), 3.61 (d, *J* = 9.2 Hz, 1H), 3.25 (dd, *J* = 9.1, 3.9 Hz, 1H), 2.99 (d, *J* = 9.4 Hz, 1H), 2.46 (s, 3H), 2.05 (d, *J* = 4.2 Hz, 1H), 1.63 (t, *J* = 4.0 Hz, 1H), 0.71 (t, *J* = 8.0 Hz, 9H), 0.62 (d, *J* = 15.6 Hz, 1H), 0.43 (d, *J* = 15.6 Hz, 1H), 0.33-0.15 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): *δ* 143.7, 137.7, 133.1, 129.8, 128.5, 128.2, 127.8, 126.1, 55.8, 51.1, 33.2, 30.6, 27.8, 21.7, 8.9, 7.4, 4.1. **HRMS** (ESI, m/z) Calculated for $[C_{25}H_{35}NO_2SSiNa, M + Na]^+$: 464.2050, found: 464.2051.



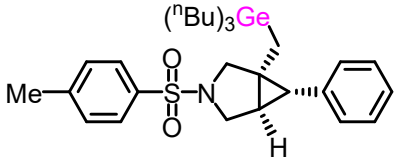
5a

Dimethyl(1S,5R,6S)-6-phenyl-1-((tributylgermyl)methyl)bicyclo[3.1.0]hexane-3,3-dicarboxylate (5a), colorless oil (61.7 mg, 58% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.23 (t, J = 7.6 Hz, 2H), 7.14 (t, J = 7.3 Hz, 1H), 7.03 (d, J = 7.4 Hz, 2H), 3.76 (s, 3H), 3.72 (s, 3H), 2.82-2.62 (m, 3H), 2.42 (d, J = 14.0 Hz, 1H), 1.70-1.60 (m, 2H), 1.30-1.12 (m, 12H), 0.90-0.80 (m, 10H), 0.76 (d, J = 14.4 Hz, 1H), 0.67-0.52 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 173.5, 172.8, 139.0, 128.6, 128.0, 125.7, 60.4, 53.1, 53.0, 44.1, 37.6, 36.3, 32.9, 30.4, 27.4, 26.7, 13.9, 13.4, 13.2. **HRMS** (ESI, m/z) Calculated for $[C_{29}H_{46}GeO_4Na, M + Na]^+$: 555.2500, found: 555.2502.



5b

Dimethyl(2aR,2a1R,2bS,5aR)-2a-((tributylgermyl)methyl)octahydro-1H-cyclopropa[cd]indene-1,1-dicarboxylate (5b), colorless oil (56.6 mg, 57% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.75 (s, 3H), 3.67 (s, 3H), 3.12-3.00 (m, 1H), 2.68 (d, J = 14.6 Hz, 1H), 2.04-1.83 (m, 3H), 1.38-1.23 (m, 18H), 0.88 (t, J = 6.8 Hz, 9H), 0.77-0.67 (m, 7H), 0.30 (d, J = 13.8 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 173.5, 170.7, 72.6, 52.7, 52.3, 39.8, 38.8, 31.5, 30.6, 27.6, 26.8, 26.5, 24.4, 24.1, 19.0, 17.7, 13.9, 13.4. **HRMS** (ESI, m/z) Calculated for $[C_{26}H_{46}GeO_4Na, M + Na]^+$: 519.2500, found: 519.2502.



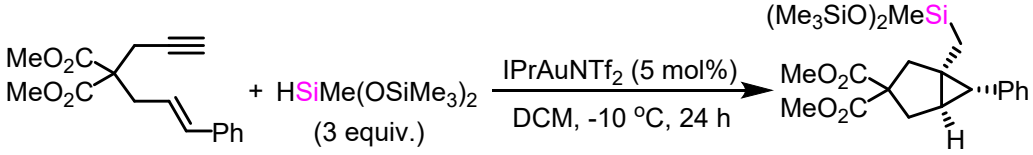
5c

(1R,5R,6S)-6-phenyl-3-tosyl-1-((tributylgermyl)methyl)-3-azabicyclo[3.1.0]hexane (5c), white solid, m.p. 42-43 °C (22.8 mg, 20% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.2 Hz, 2H), 7.35 (t, J = 8.0 Hz, 2H), 7.28-7.22 (m, 2H), 7.17 (t, J = 7.3 Hz, 1H), 6.99 (t, J = 7.3 Hz, 2H), 3.67 (d, J = 9.1 Hz, 1H), 3.60 (d, J = 9.3 Hz, 1H), 3.23 (dd, J = 9.1, 3.8 Hz, 1H), 2.95 (d, J = 9.3 Hz, 1H), 2.45 (s, 3H), 2.09 (d, J = 4.1 Hz, 1H), 1.62 (t, J = 4.0 Hz, 1H), 1.23-1.13 (m, 6H), 1.13-1.01 (m, 6H), 0.83 (t, J = 7.2 Hz, 9H), 0.77 (d, J = 14.6 Hz, 1H), 0.63 (d, J = 14.6 Hz, 1H),

0.54-0.32 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.7, 137.7, 133.2, 129.8, 128.5, 128.2, 127.8, 126.1, 60.3, 55.7, 51.1, 34.1, 30.7, 28.0, 27.3, 26.6, 21.7, 13.9, 13.4, 10.6. **HRMS** (ESI, m/z) Calculated for $[C_{31}H_{47}GeNO_2SNa, M + Na]^+$: 594.2431, found: 594.2434.

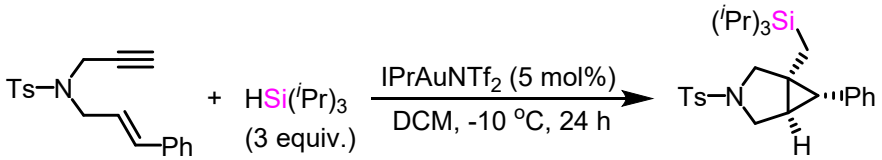
5. Large-Scale Experiment and Product Transformations

(a) Large-scale experiments



1a, 2 mmol **2a** **3aa**, 65%, 0.66 g

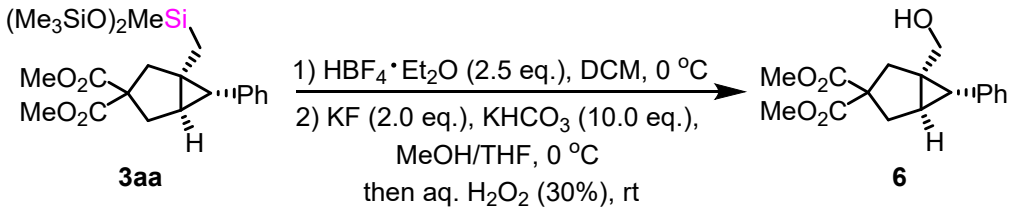
A pre-dried 10.0 mL Schlenk tube was charged with stirring bar and $IPrAuNTf_2$ (86.6 mg, 0.1 mmol, 0.05 eq.). DCM was added and the mixture was stirred at room temperature for 10 minutes. The solution was reduced down to -10 °C and added successively with **2a** (1332.6 mg, 6.0 mmol, 3.0 eq.) and **1a** (572.2 mg, 2.0 mmol, 1.0 eq.). Then, the reaction mixture was stirred at -10 °C for 24 h. Finally, the mixture was transferred to a column and purified by flash chromatography on silica gel (PE/EA = 10:1, R_f = 0.20) to give the analytical pure products **3aa** (0.66 g, 65% yield).



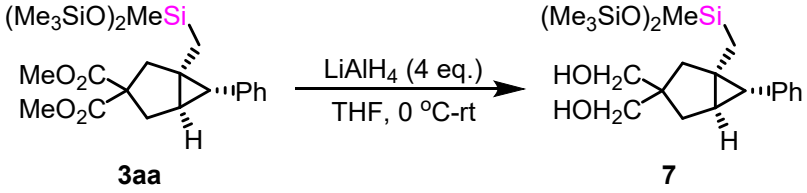
1p, 2 mmol **2b** **3bb**, 90%, 0.87 g

A pre-dried 10.0 mL Schlenk tube was charged with stirring bar and $IPrAuNTf_2$ (86.6 mg, 0.1 mmol, 0.05 eq.). DCM was added and the mixture was stirred at room temperature for 10 minutes. The solution was reduced down to -10 °C and added successively with **2b** (948.9 mg, 6.0 mmol, 3.0 eq.) and **1p** (651.0 mg, 2.0 mmol, 1.0 eq.). Then, the reaction mixture was stirred at -10 °C for 24 h. Finally, the mixture was transferred to a column and purified by flash chromatography on silica gel (PE/EA = 10:1, R_f = 0.20) to give the analytical pure products **3bb** (0.87 g, 90% yield).

(b) Product transformations



Tetrafluoroboric acid diethyl ether complex (92.0 mg, 0.5 mmol, 2.5 eq.) was added dropwise to a solution of **3aa** (101.6 mg, 0.2 mmol, 1.0 eq.) in DCM (1.0 mL) at 0 °C. The mixture stirred for 1 hour at 0 °C and then the solvent was removed under vacuum. The residue was dissolved in MeOH (1.0 mL) and THF (1.0 mL). Then, KF (23.2 mg, 0.40 mmol, 2.0 eq.) and $KHCO_3$ (200.0 mg, 2.0 mmol, 10.0 eq.) were added to this solution at 0 °C. After stirring for 15 minutes at 0 °C, H_2O_2 (272.0 mg, 2.4 mmol, 13.0 eq., 30% in water) was added, and the mixture was stirred for 12 h at room temperature. The reaction was quenched with $Na_2S_2O_3$ (10.0 mL, 2M aqueous) and then poured into HCl (0.5 M aqueous). DCM (20.0 mL) was added for extraction and the organic phase was washed with brine (20.0 mL) and water (20.0 mL). The aqueous phase was extracted with DCM (2 × 20.0 mL). The combined organic phases were dried over anhydrous $MgSO_4$, filtered and evaporated under reduced pressure. Purification of the residue by flash column chromatography on silica gel using PE/EA = 10/1 as eluent afforded **6** (59.0 mg, 97% yield). Known compound.[1] **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.26 (t, J = 7.9 Hz, 2H), 7.21-7.10 (m, 3H), 3.75 (s, 3H), 3.73 (s, 3H), 3.47 (q, J = 24.8 Hz, 2H), 2.80 (d, J = 14.3 Hz, 1H), 2.76-2.66 (m, 2H), 2.59 (d, J = 13.9 Hz, 1H), 2.00 (d, J = 4.0 Hz, 1H), 1.94 (t, J = 4.7 Hz, 1H), 1.43-1.29 (m, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 172.94, 172.87, 137.4, 128.6, 128.5, 126.4, 63.5, 61.9, 53.2, 53.0, 41.0, 39.7, 37.4, 34.5, 27.4.



$LiAlH_4$ (30.4 mg, 0.8 mmol) was suspended in anhydrous THF (1.0 mL), and the slurry was cooled to 0 °C. A solution of **3aa** (101.6 mg, 0.2 mmol) in anhydrous THF (1.0 mL) was added dropwise at 0 °C. When effervescence had ceased, the mixture was allowed to warm to room temperature for overnight. The mixture was diluted with wet ethyl acetate (EA, 5.0 mL) and quenched by addition of sodium sulfate decahydrate (36.2 mg) slowly, to control the effervescence. After stirring for 1 h under room temperature, a few drops of saturated aqueous NH_4Cl were added, until the suspension became white. The solids were filtered off over Celite, and the cake was washed thoroughly with EA (10 mL). The filtrate was concentrated in vacuo, and the residue was purified by column chromatography on silica gel eluting with PE/EA 2:1 to afford a colorless solid (m.p. 72-74

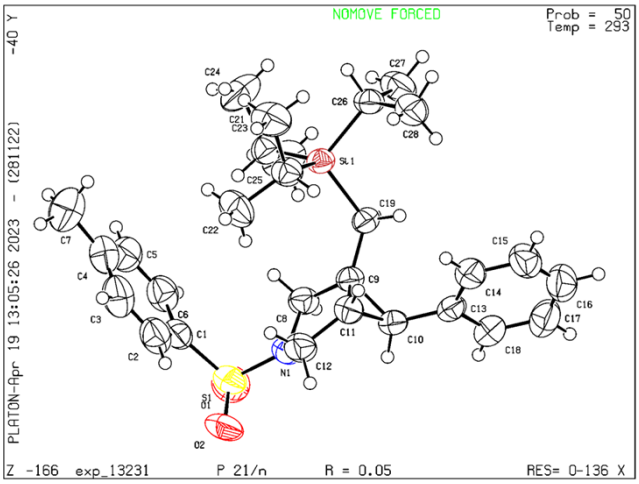
°C, 77.8 mg, 86%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 (t, J = 7.6 Hz, 2H), 7.14 (t, J = 7.3 Hz, 1H), 7.05 (d, J = 7.2 Hz, 2H), 3.80-3.55 (m, 4H), 2.34 (bs, 2H), 2.06 (dd, J = 13.8, 6.0 Hz, 1H), 1.97 (d, J = 14.2 Hz, 1H), 1.83 (d, J = 14.2 Hz, 1H), 1.74-1.65 (m, 3H), 0.59 (d, J = 15.3 Hz, 1H), 0.48 (d, J = 15.3 Hz, 1H), 0.09-0.01 (m, 18H), -0.10 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.7, 128.4, 128.0, 125.5, 71.8, 71.7, 52.0, 43.2, 39.2, 36.4, 35.8, 31.4, 18.6, 2.03, 1.98, 1.3. **HRMS** (ESI, m/z) Calculated for $[C_{22}H_{40}O_4Si_3Na, M + Na]^+$: 475.2127, found: 475.2126.

6. References

1. Wang, G. H.; Wang, Y. Q.; Li, Z. Z.; Li, H. T.; Yu, M. W.; Pang, M. F.; Zhao, X. M. *Org. Lett.* **2022**, 2*4*, 9425.
2. Liu R.; Winston-McPherson G. N.; Yang, Z-Y.; Zhou, X.; Song, W.; Guzei, L. A.; Xu, X., Tang, W. *J. Am. Chem. Soc.* **2013**, *135*, 8201.
3. Zhao, S.; Zang, Z-L.; Li, S.; Wen, X.; Wang, C.; Guo, J.; He, Y. *J. Org. Chem.* **2020**, *85*, 9321.

7. Crystal Data and Structure Refinement for 3bb.

ORTEP drawing of **3bb** (thermal ellipsoids set at 50% probability). Recrystallization from *n*-hexane/DCM afforded the single crystal suitable for X-ray diffraction analysis. X-ray diffraction measurements were performed using an Agilent Diffraction Gemini E Diffractometer equipped with an Eos CCD detector and a Cu Kα (λ = 1.54184 Å) incident beam at the school of chemistry and chemical engineering, state key laboratory of crystal materials at Liaocheng University. A crystal was mounted on a glass fibre. The CCD data were integrated and scaled using the *CrystAlis*^{Pro} software suite, and the structure was solved using the charge-flipping algorithm, as implemented in the program XS and refined by full-matrix least-squares techniques against Fo^2 using the SHELXL program through the Shelxtl interface.



Bond precision:	C-C = 0.0051 A	Wavelength=1.54184	
Cell:	a=14.8440(19)	b=9.8188(11)	c=18.983(2)
	alpha=90	beta=92.132(10)	gamma=90
Temperature:	293 K		

	Calculated	Reported
Volume	2764.9(6)	2764.8(6)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Moiety formula	C28 H41 N O2 S Si	?
Sum formula	C28 H41 N O2 S Si	C28 H41 N O2 S Si
Mr	483.77	483.77
Dx,g cm-3	1.162	1.162
Z	4	4
Mu (mm-1)	1.630	1.630
F000	1048.0	1048.0
F000'	1052.77	
h,k,lmax	17,11,22	17,11,22
Nref	4966	4960
Tmin,Tmax	0.864,0.878	0.969,1.000
Tmin'	0.864	

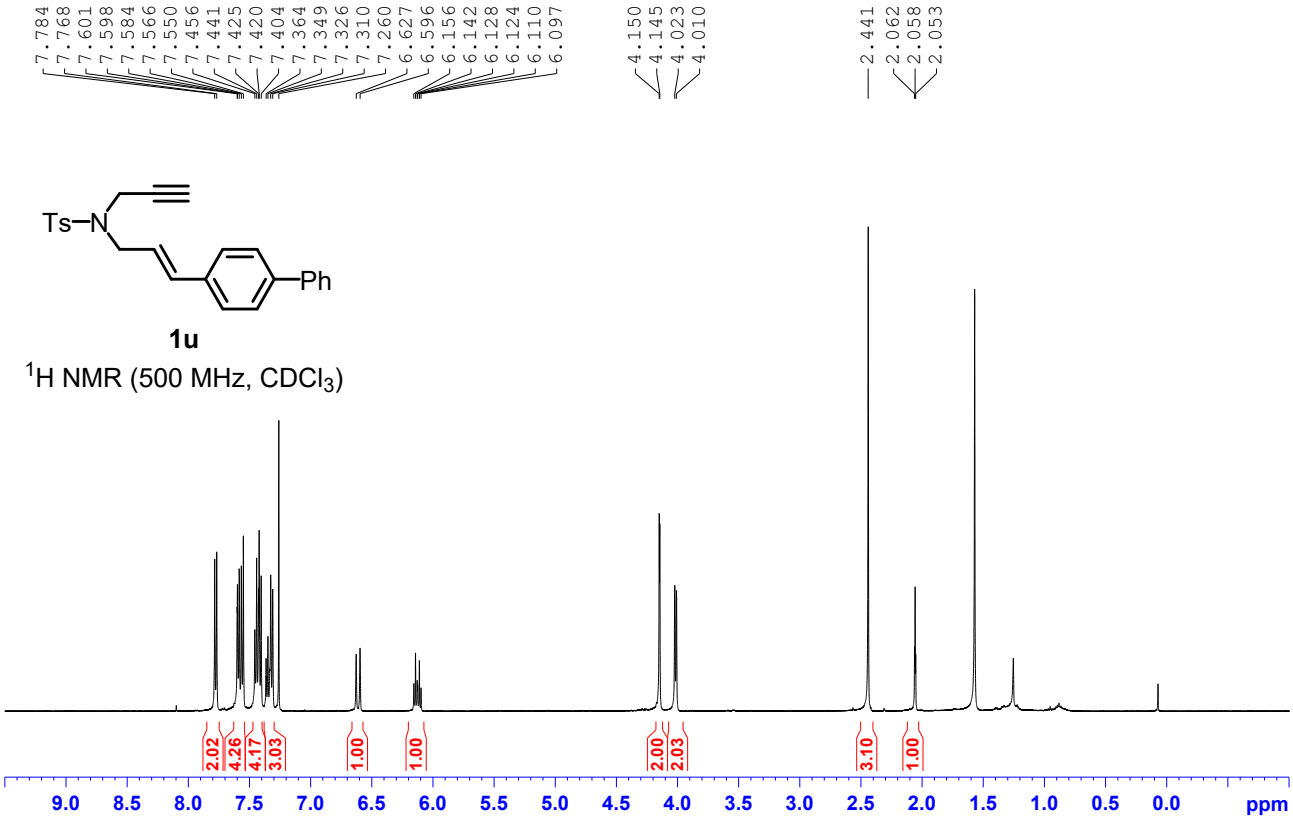
Correction method= # Reported T Limits: Tmin=0.969 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.999 Theta(max)= 67.240

R(reflections)= 0.0511(2717) wR2(reflections)= 0.1334(4960)

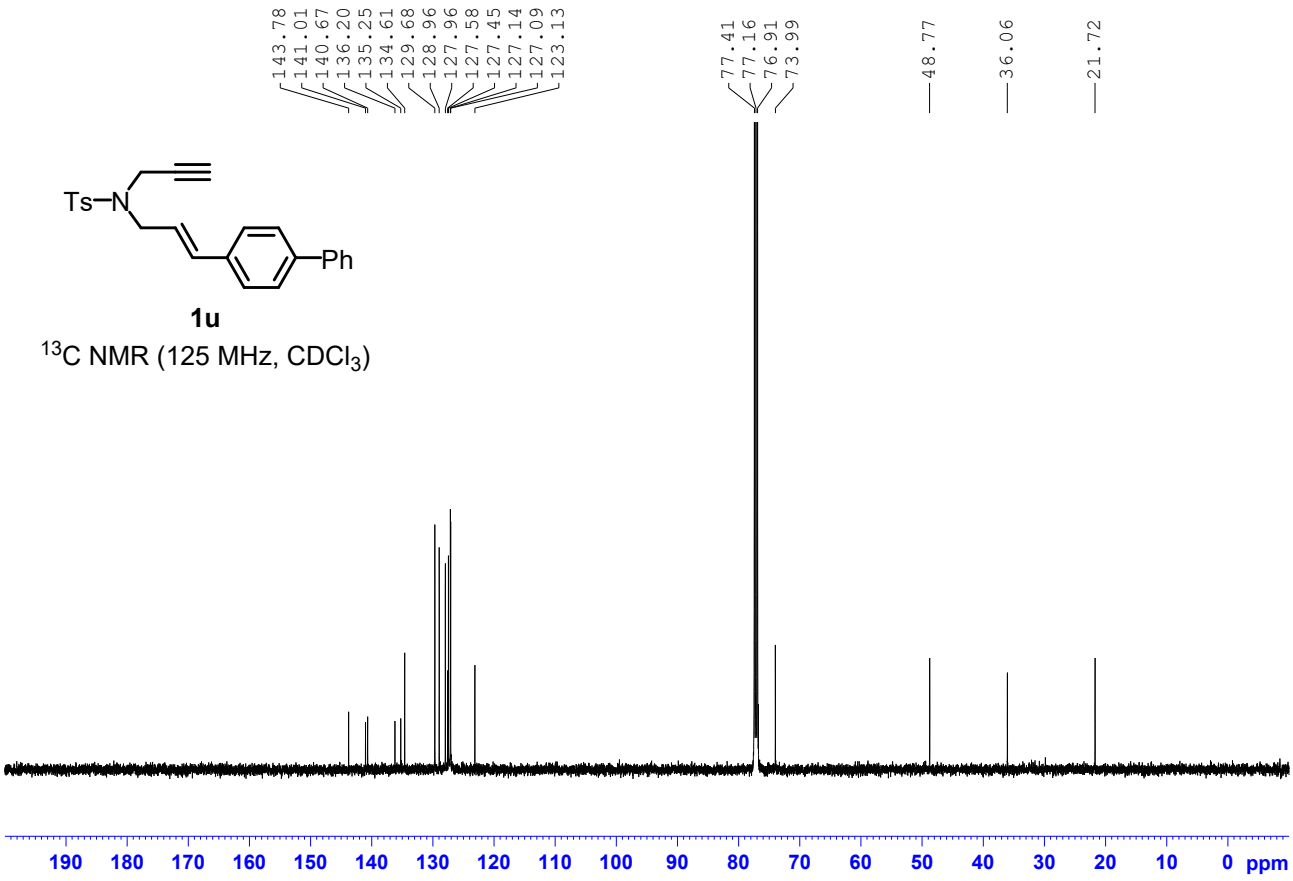
S = 1.002 Npar= 306

8. NMR Spectra



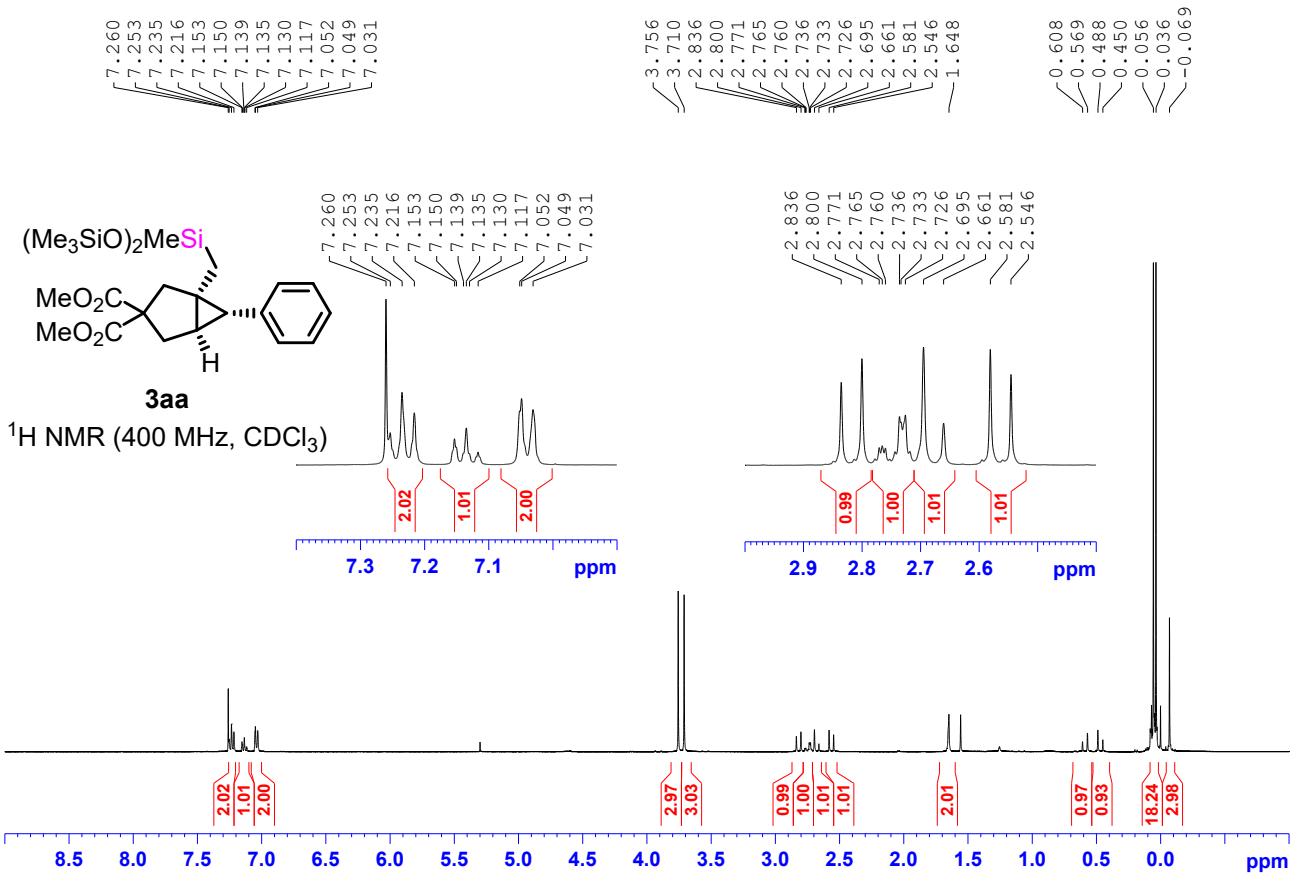
1u

^{1}H NMR (500 MHz, $CDCl_3$)



1u

^{13}C NMR (125 MHz, $CDCl_3$)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7.216
7.153
7.150
7.139
7.135
7.130
7.117
7.052
7.049
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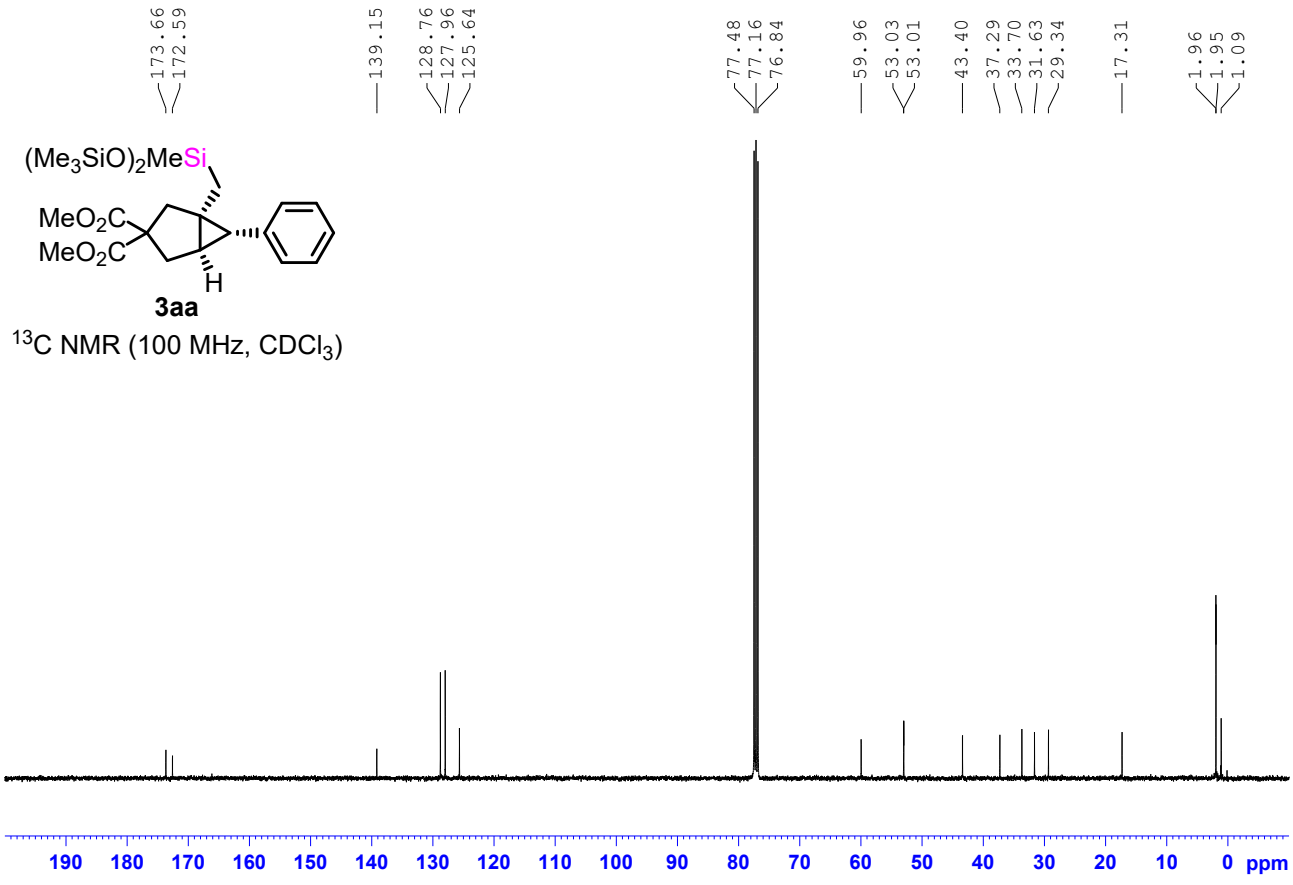
3.756
3.710
2.836
2.800
2.771
2.765
2.760
2.736
2.733
2.726
2.695
2.661
2.581
2.546
1.648
0.608
0.569
0.488
0.450
0.056
0.036
-0.069
(Me3SiO)2MeSi
MeO2C
MeO2C
H
3aa
1H NMR (400 MHz, CDCl3)
2.02
1.01
2.00
0.99
1.00
1.01
1.01
2.97
3.03
2.01
0.97
0.93
18.24
2.98
ppm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172.59
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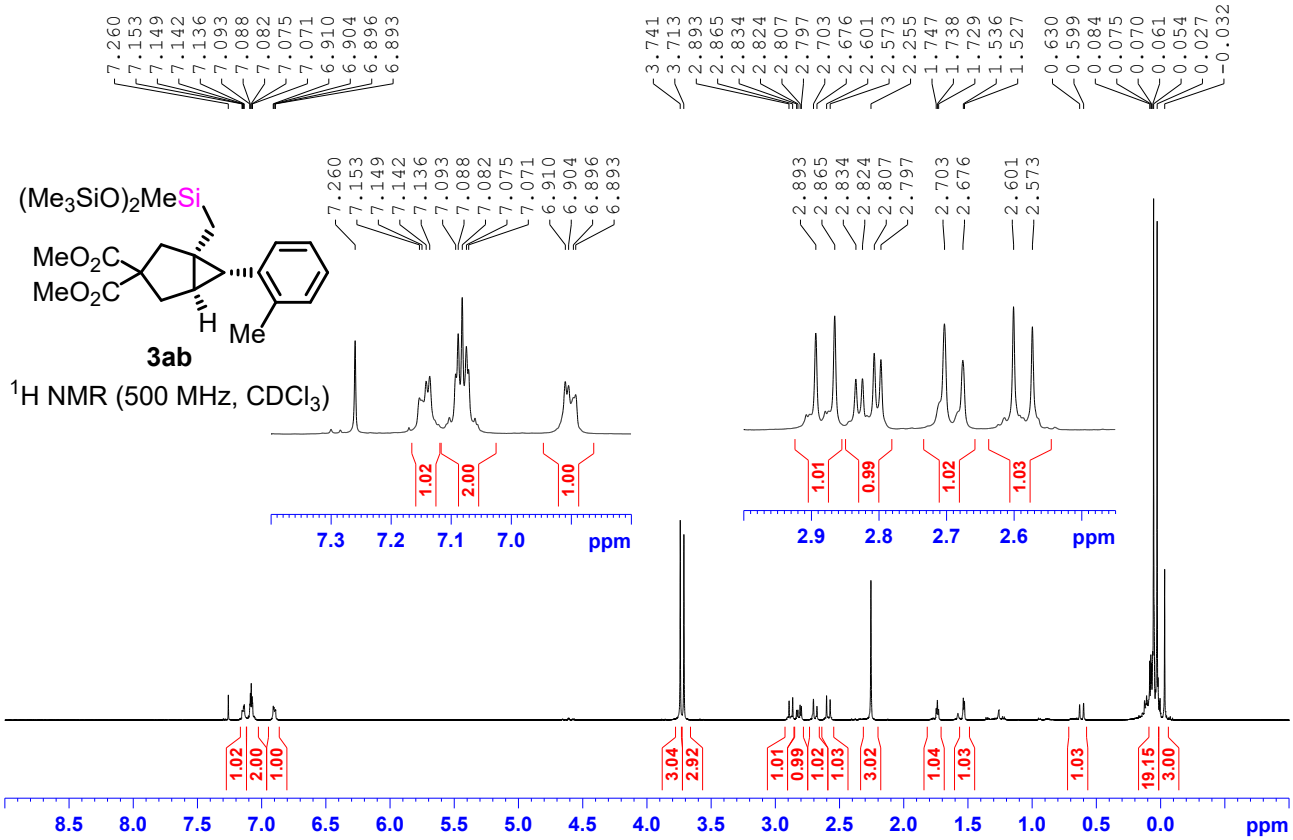
128.76
127.96
125.64
77.48
77.16
76.84
59.96
53.03
53.01
43.40
37.29
33.70
31.63
29.34
17.31
1.96
1.95
1.09
(Me3SiO)2MeSi
MeO2C
MeO2C
H
3aa
13C NMR (100 MHz, CDCl3)
ppm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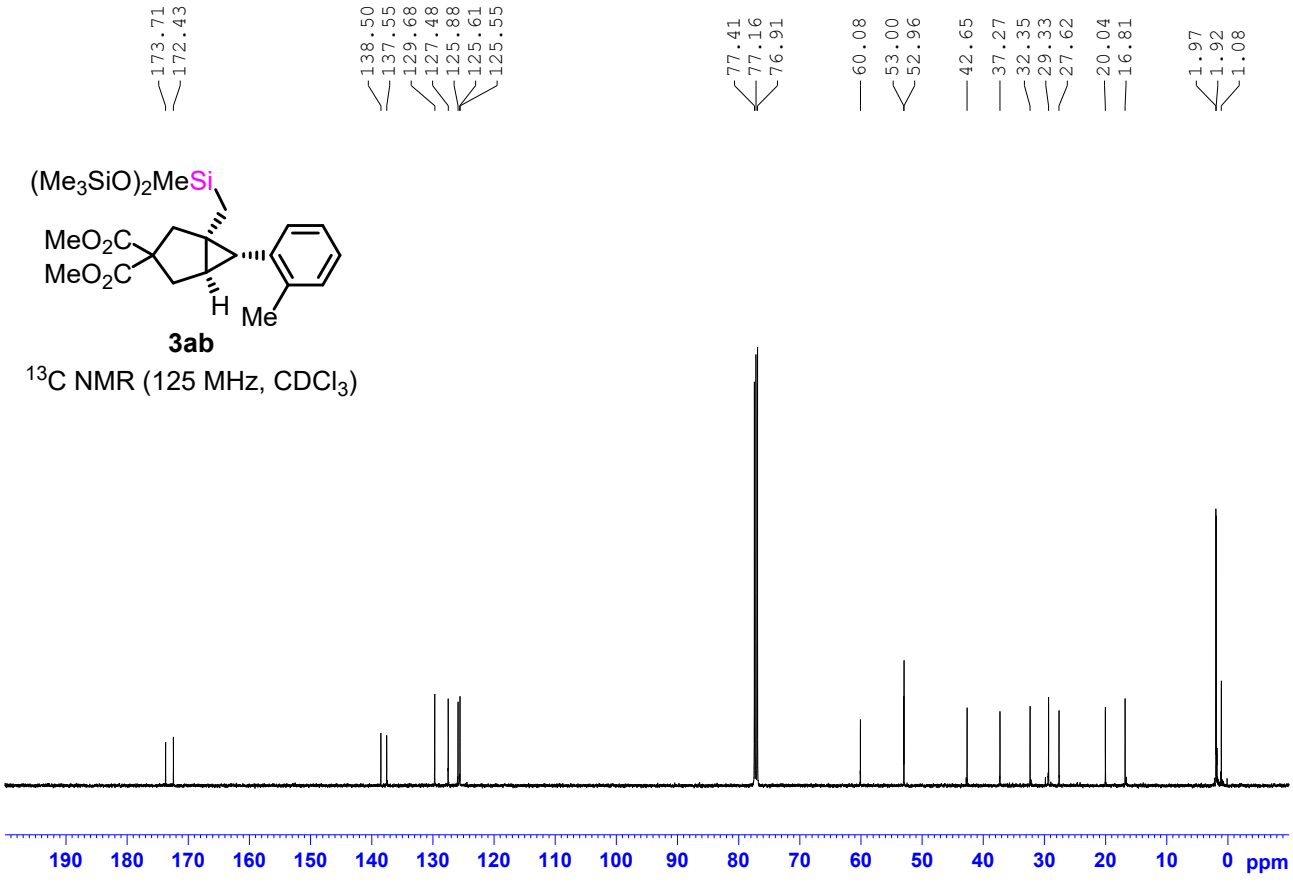
MeO2C
MeO2C
H
Me
3ab
1H NMR (500 MHz, CDCl3)
ppm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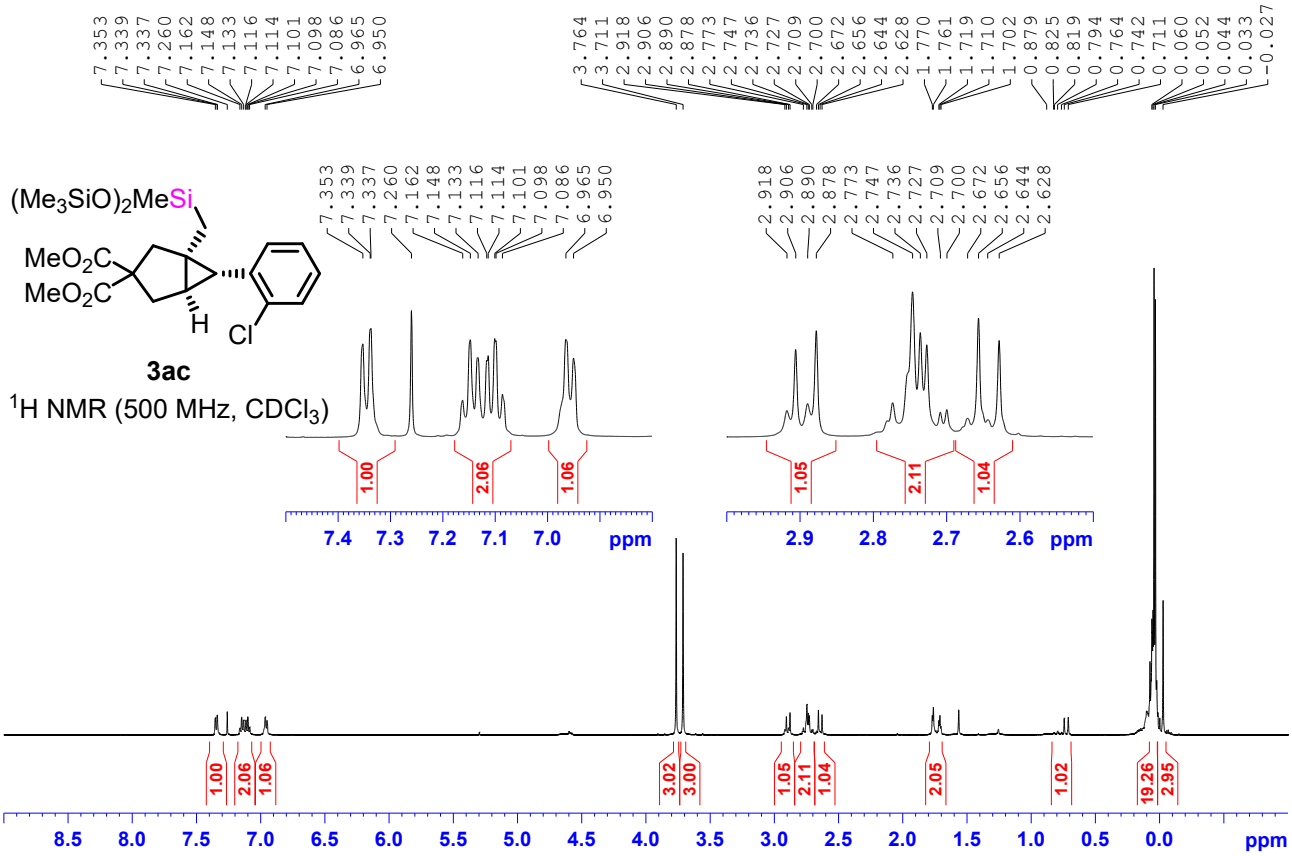
MeO2C
MeO2C
H
Me
3ab
13C NMR (125 MHz, CDCl3)
ppm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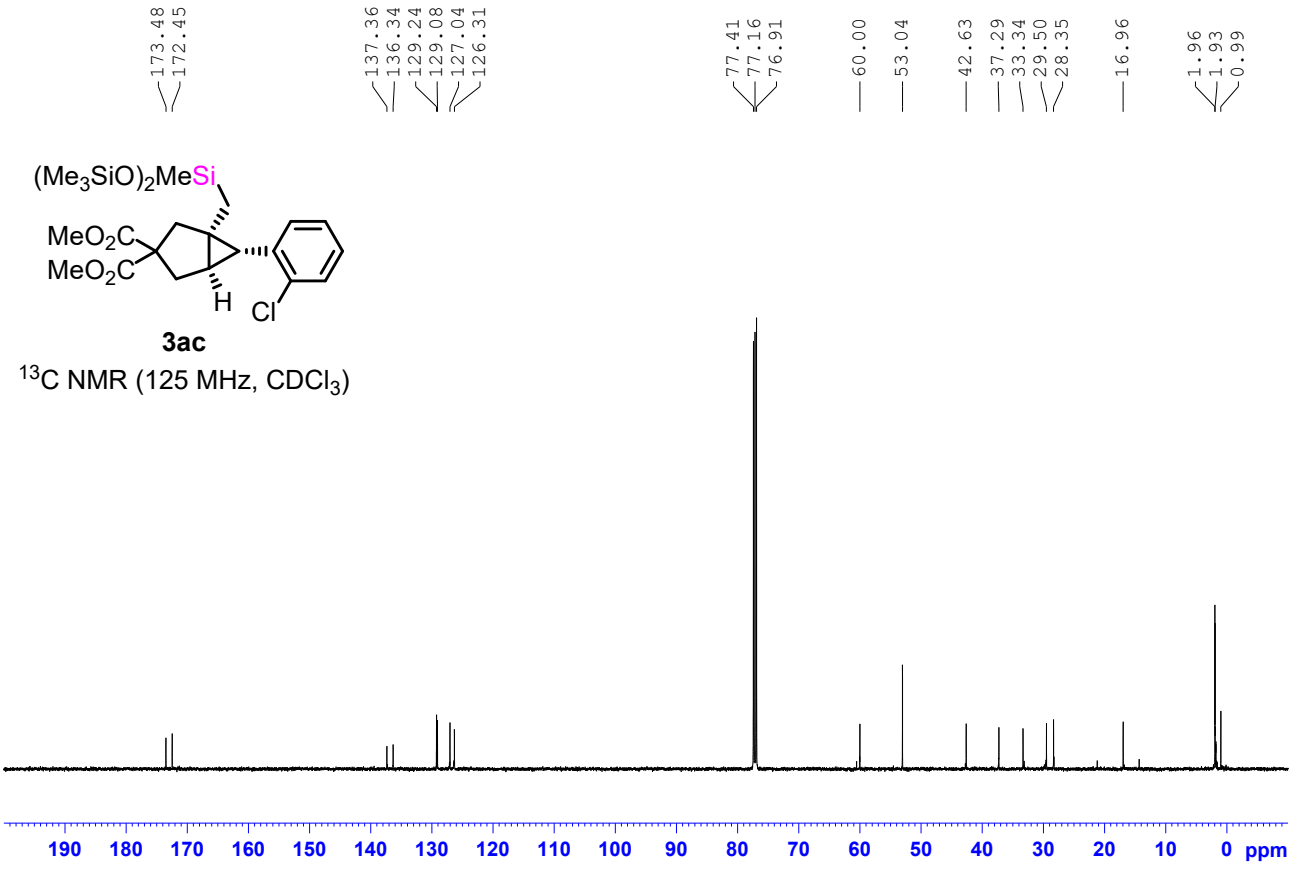
MeO2C
H
Cl
3ac
1H NMR (500 MHz, CDCl3)
ppm


(Me3SiO)2MeSi
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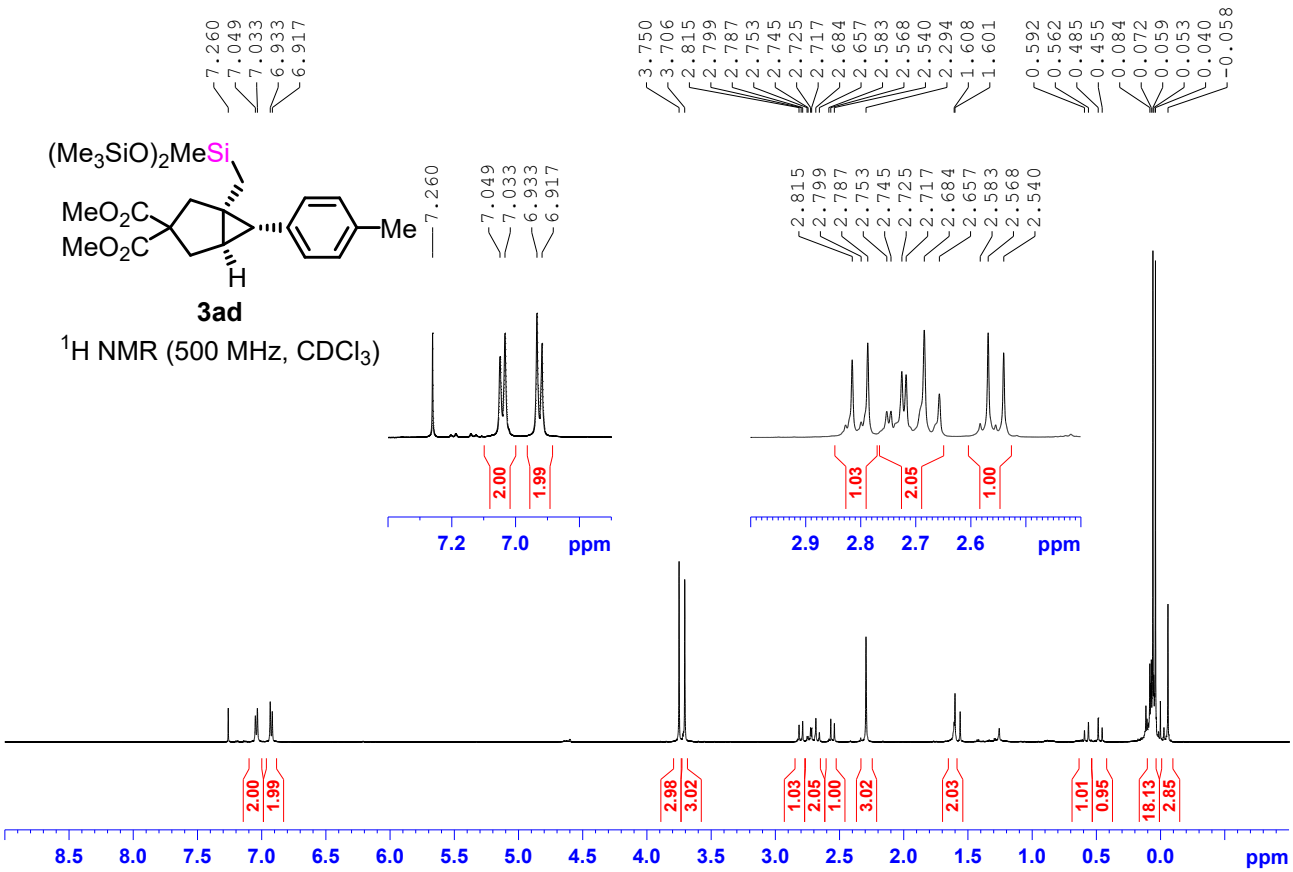
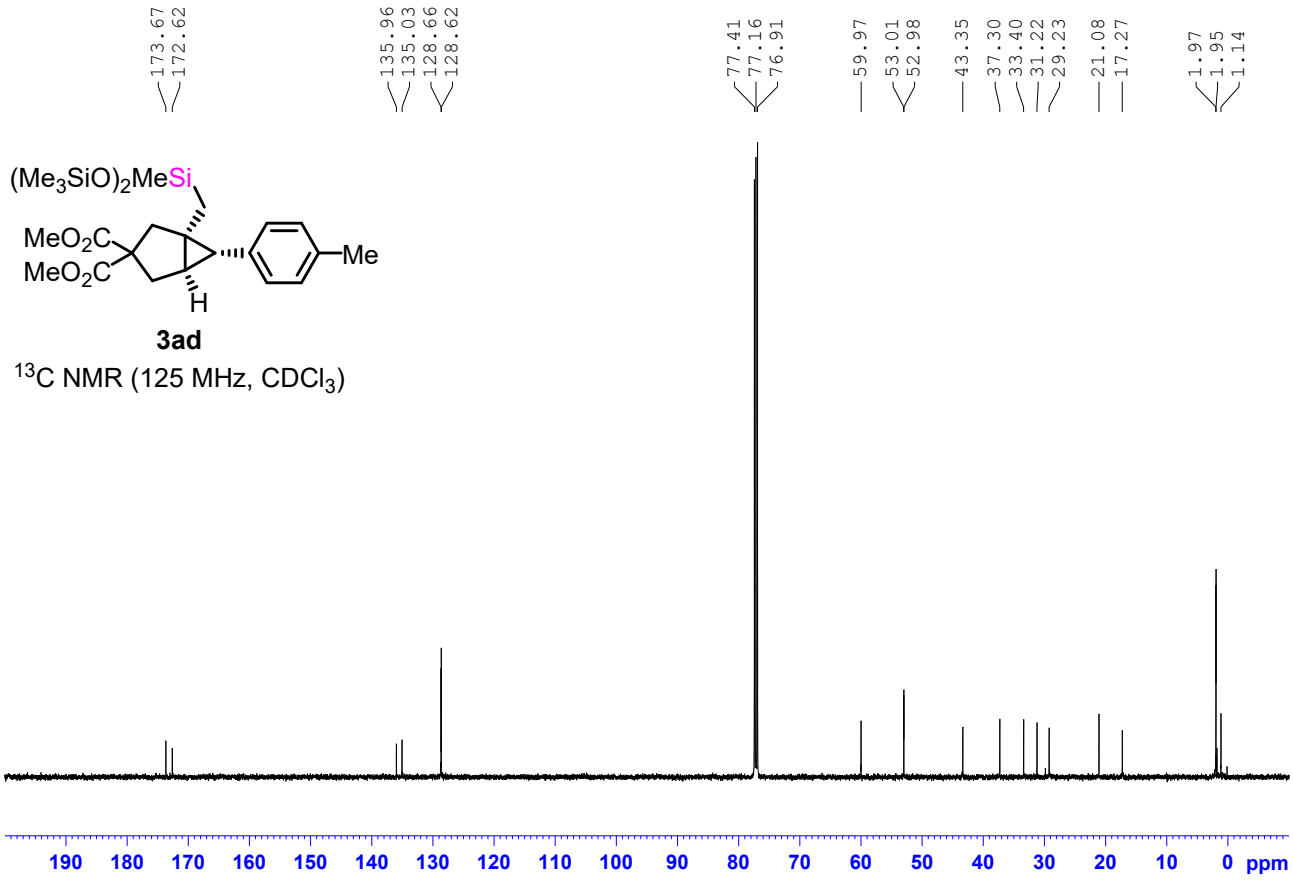
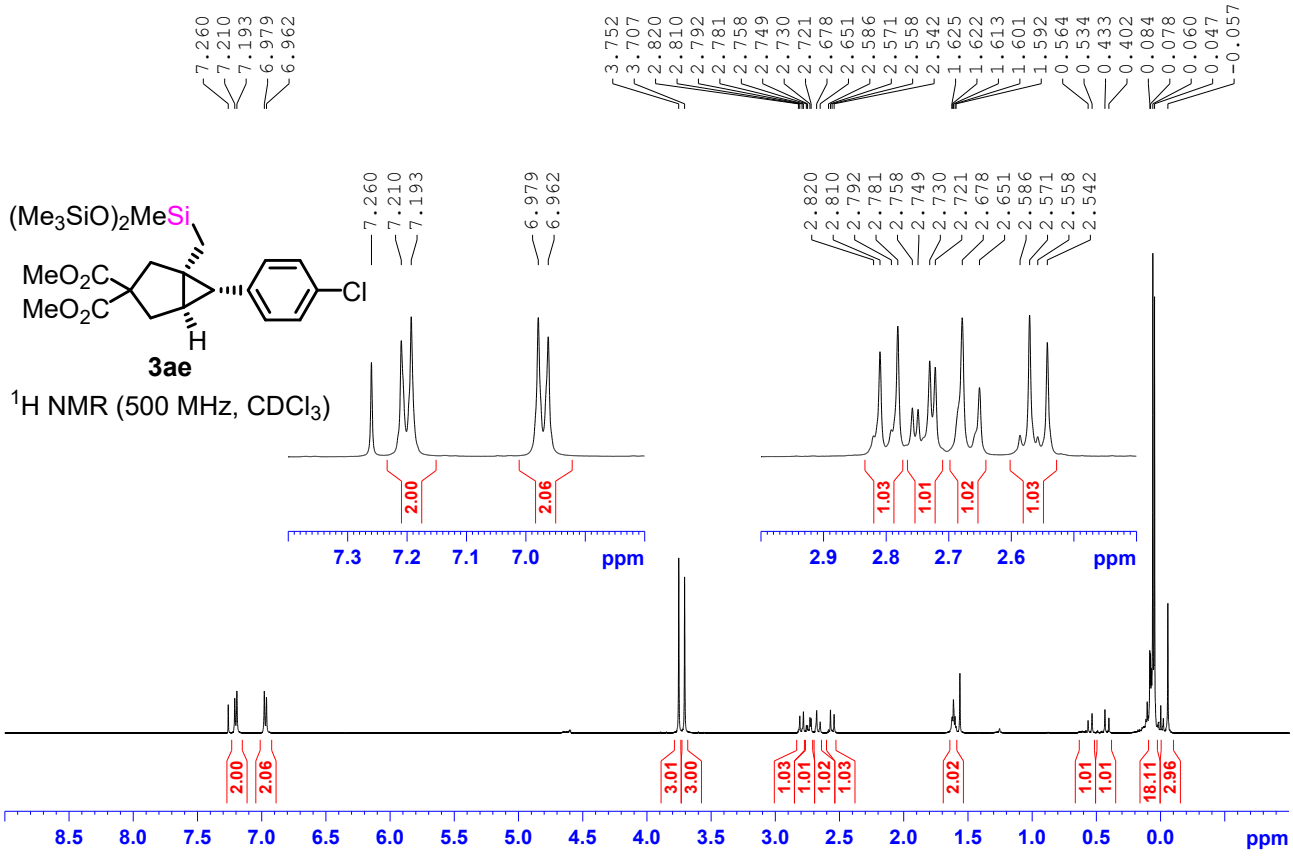
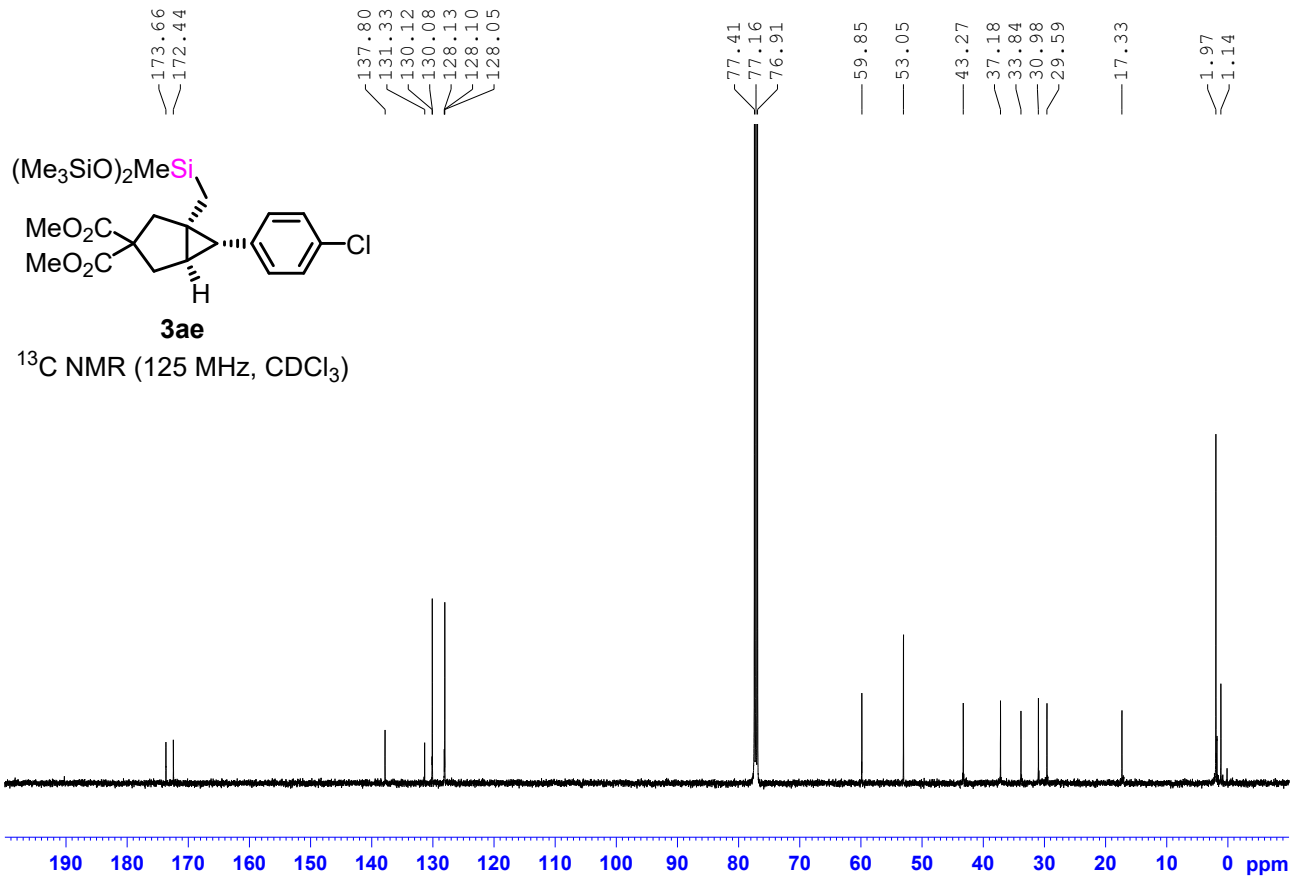
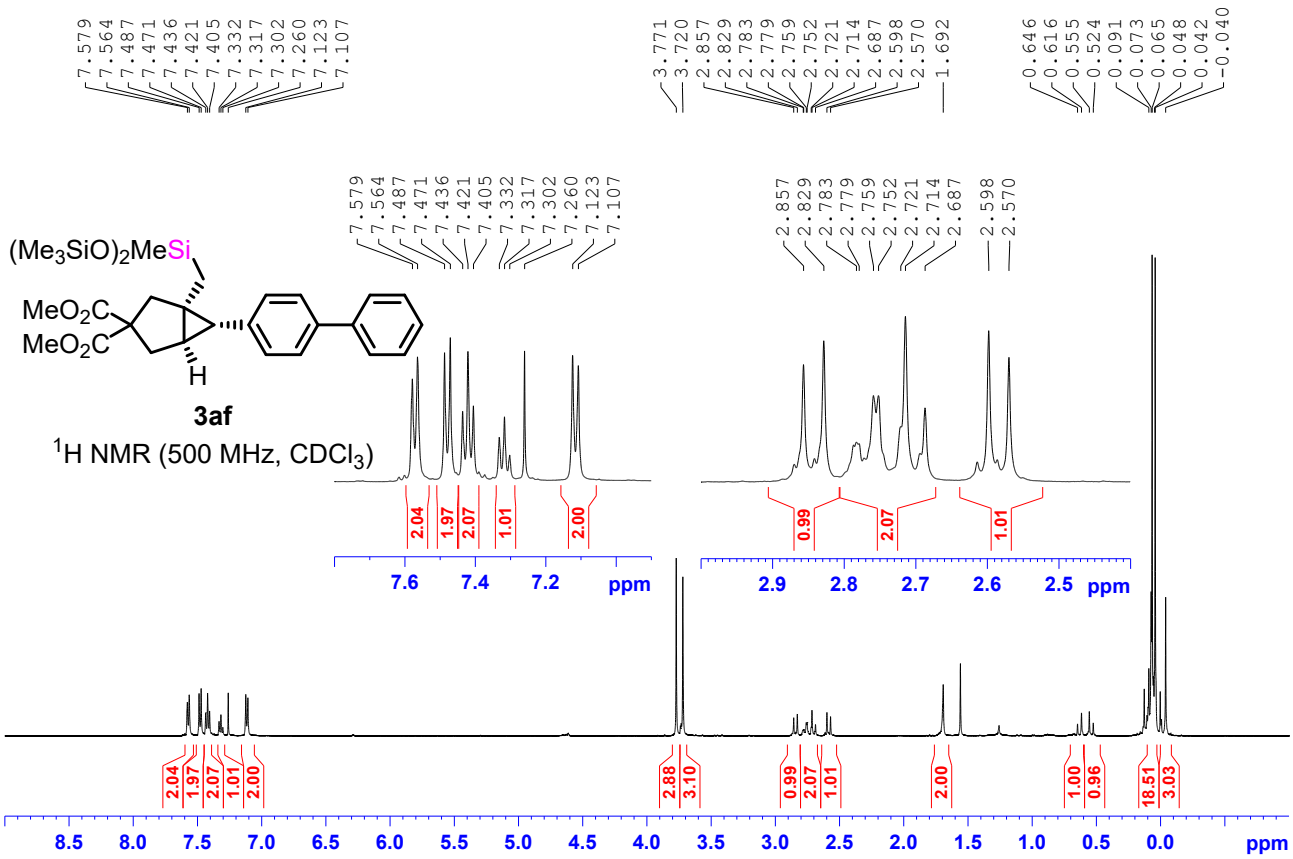
MeO2C
H
Cl
3ac
13C NMR (125 MHz, CDCl3)
ppm

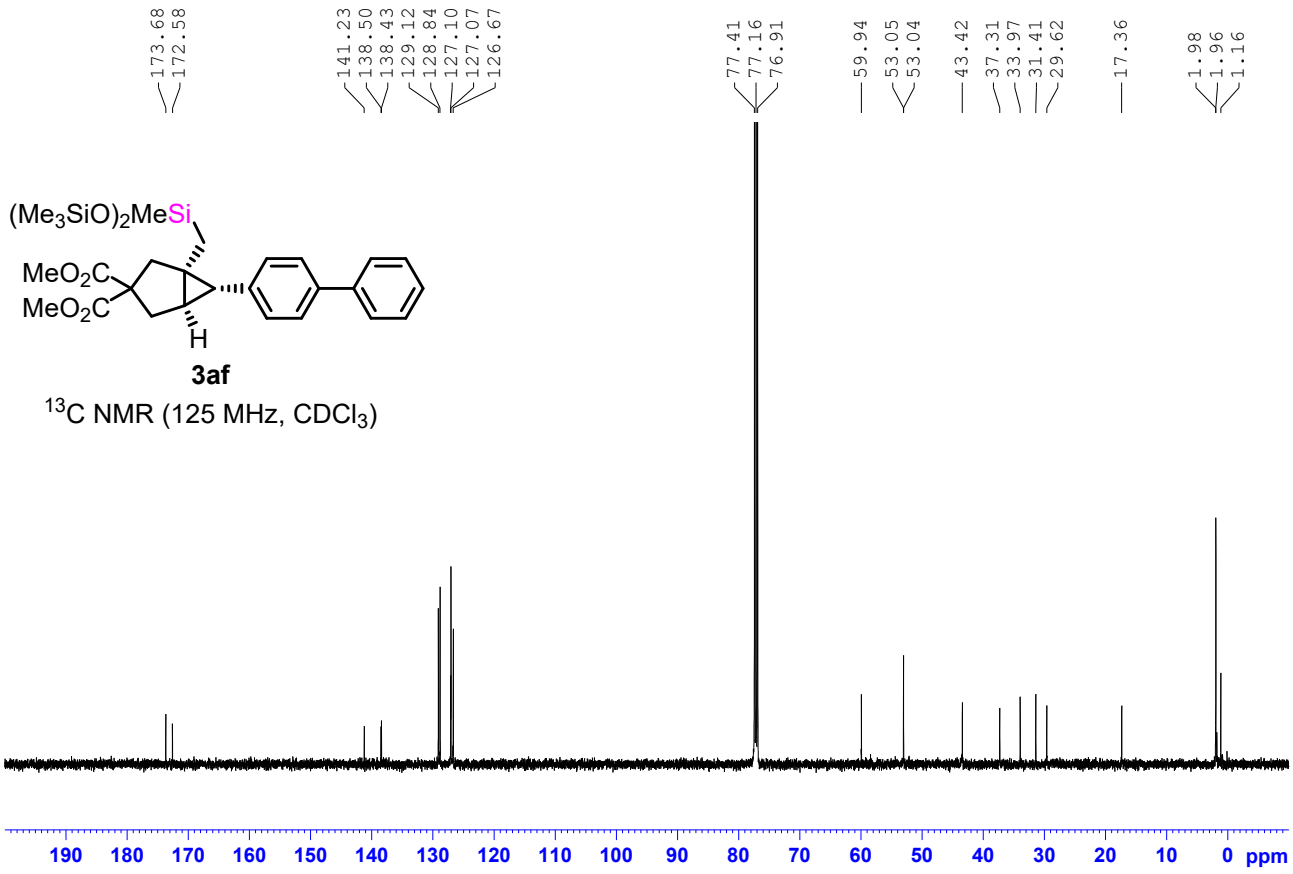

(Me3SiO)2MeSi
MeO2C
MeO2C
Me
H
3ad
1H NMR (500 MHz, CDCl3)
7.260
7.049
7.033
6.933
6.917
3.750
3.706
2.815
2.799
2.787
2.753
2.745
2.725
2.717
2.684
2.657
2.583
2.568
2.540
2.294
1.608
1.601
0.592
0.562
0.485
0.455
0.084
0.072
0.059
0.053
0.040
-0.058
2.00
1.99
1.03
2.05
1.00
2.98
3.02
1.03
2.05
1.00
3.02
2.03
1.01
0.95
18.13
2.85
ppm

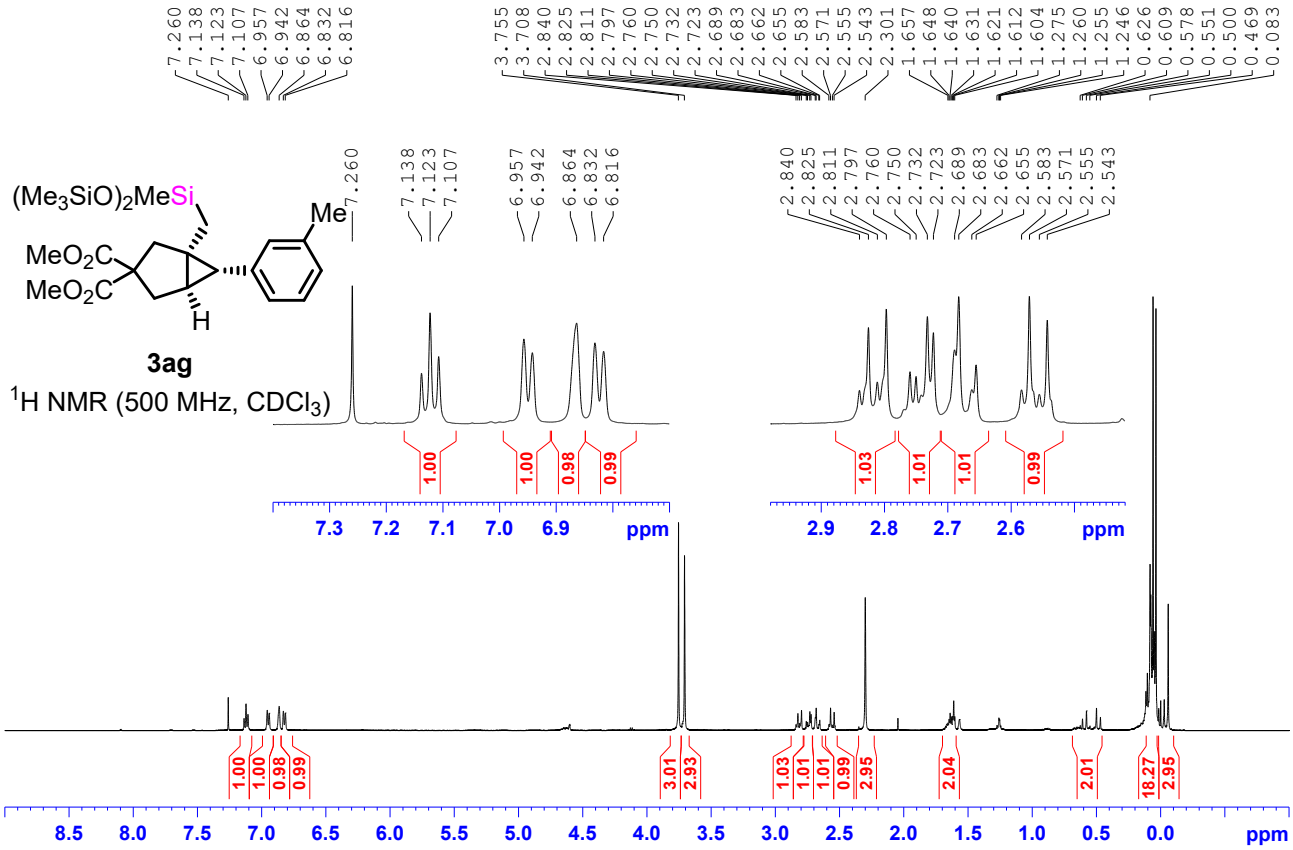

(Me3SiO)2MeSi
MeO2C
MeO2C
Me
H
3ad
13C NMR (125 MHz, CDCl3)
173.67
172.62
135.96
135.03
128.66
128.62
77.41
77.16
76.91
59.97
53.01
52.98
43.35
37.30
33.40
31.22
29.23
21.08
17.27
1.97
1.95
1.14
ppm

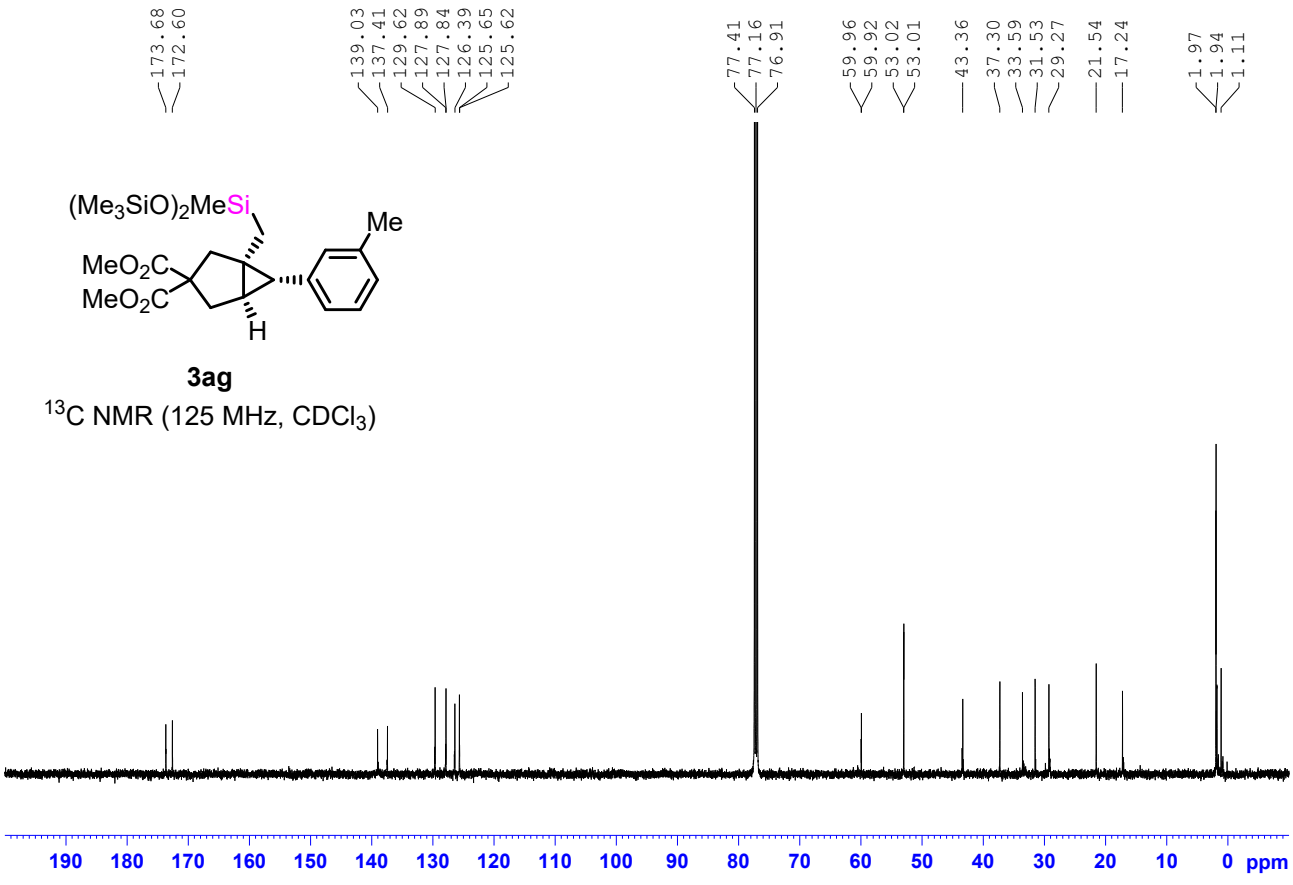

7.260
7.210
7.193
6.979
6.962
3.752
3.707
2.820
2.810
2.792
2.781
2.758
2.749
2.730
2.721
2.678
2.651
2.586
2.571
2.558
2.542
1.625
1.622
1.613
1.601
1.592
0.564
0.534
0.433
0.402
0.084
0.078
0.060
0.047
-0.057
(Me3SiO)2MeSi
MeO2C
MeO2C
Cl
H
3ae
1H NMR (500 MHz, CDCl3)
2.00
2.06
1.03
1.01
1.02
1.03
7.3
7.2
7.1
7.0
ppm
2.9
2.8
2.7
2.6
ppm
3.01
3.00
2.02
1.01
1.01
18.11
2.96
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
ppm

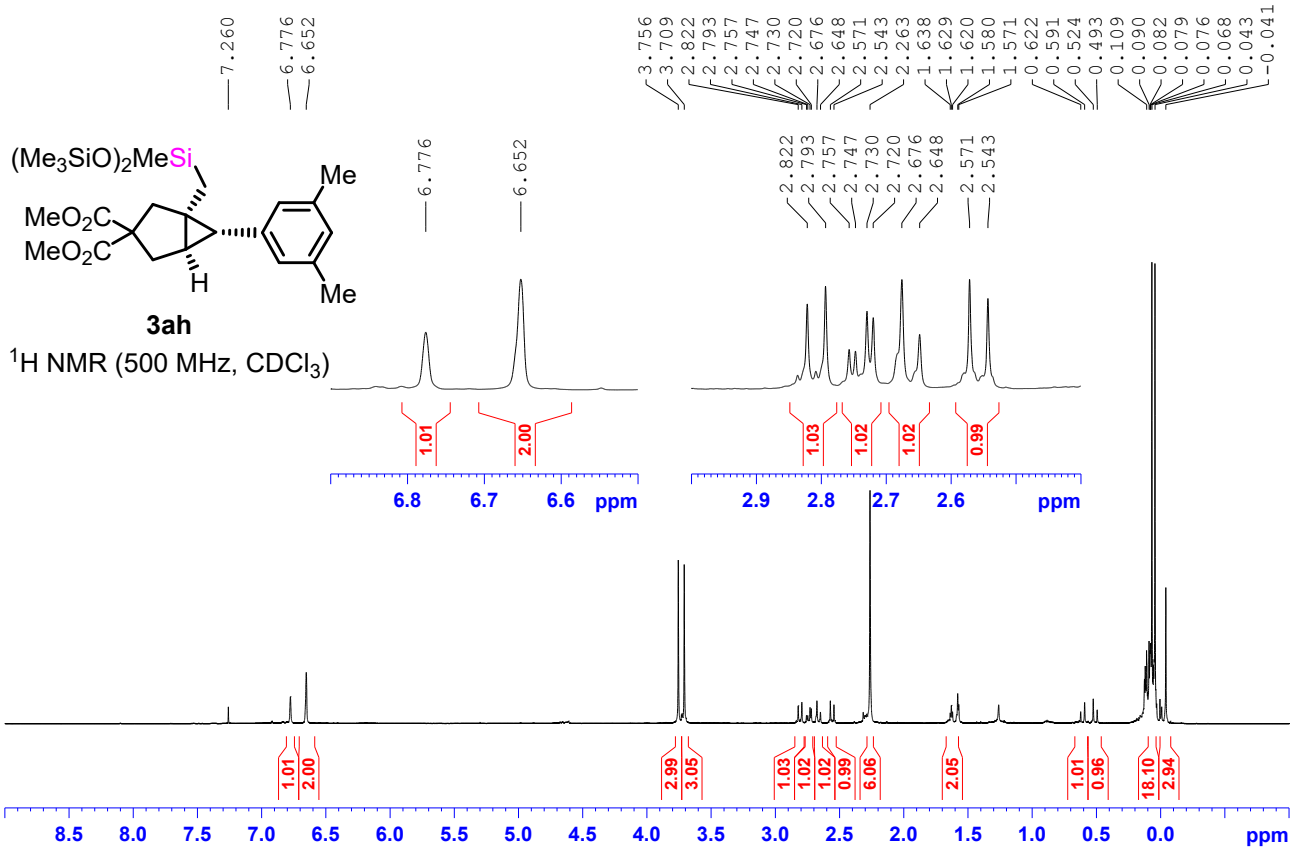

173.66
172.44
137.80
131.33
130.12
130.08
128.13
128.10
128.05
77.41
77.16
76.91
59.85
53.05
43.27
37.18
33.84
30.98
29.59
17.33
1.97
1.14
(Me3SiO)2MeSi
MeO2C
MeO2C
Cl
H
3ae
13C NMR (125 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

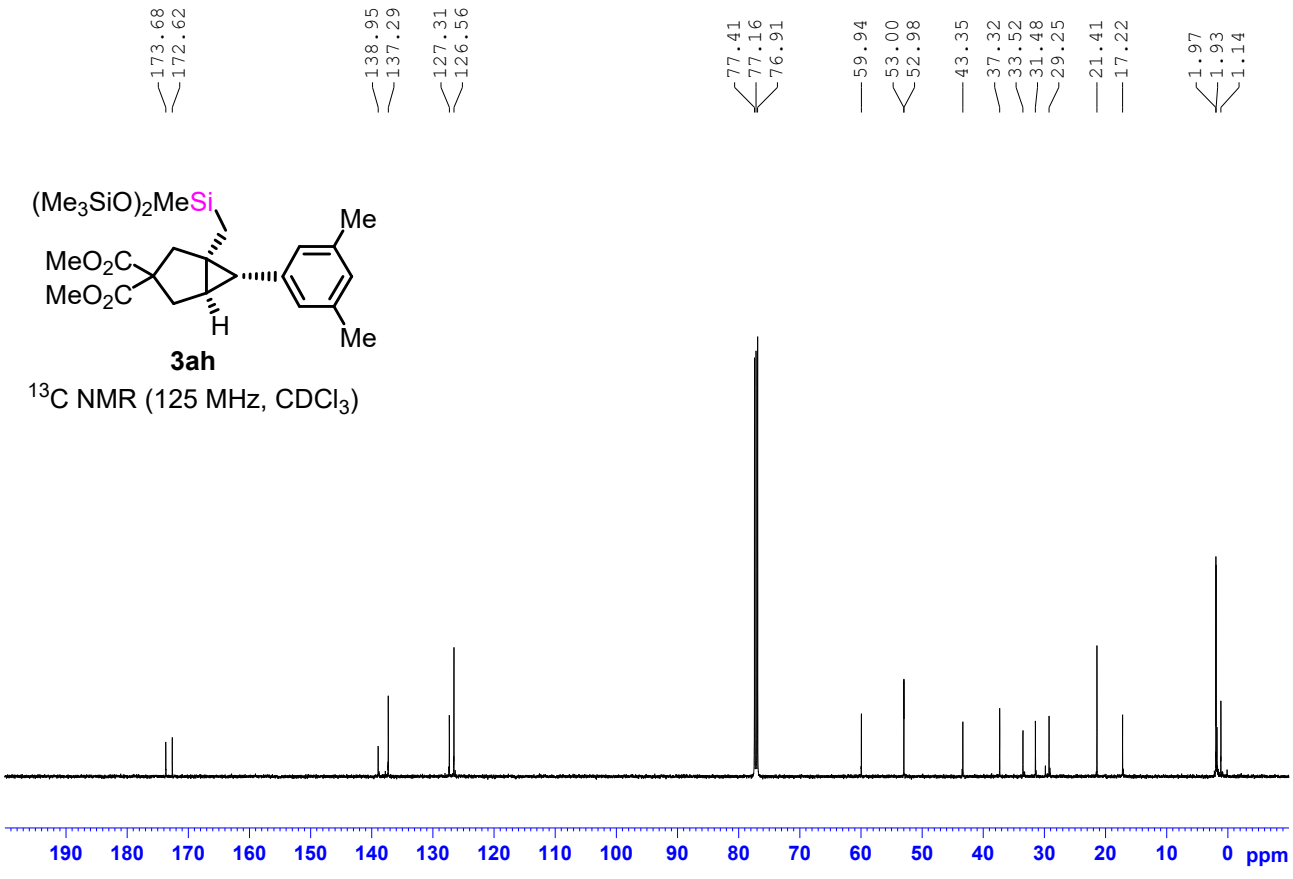

(Me3SiO)2MeSi
MeO2C
MeO2C
H
3af
1H NMR (500 MHz, CDCl3)
ppm

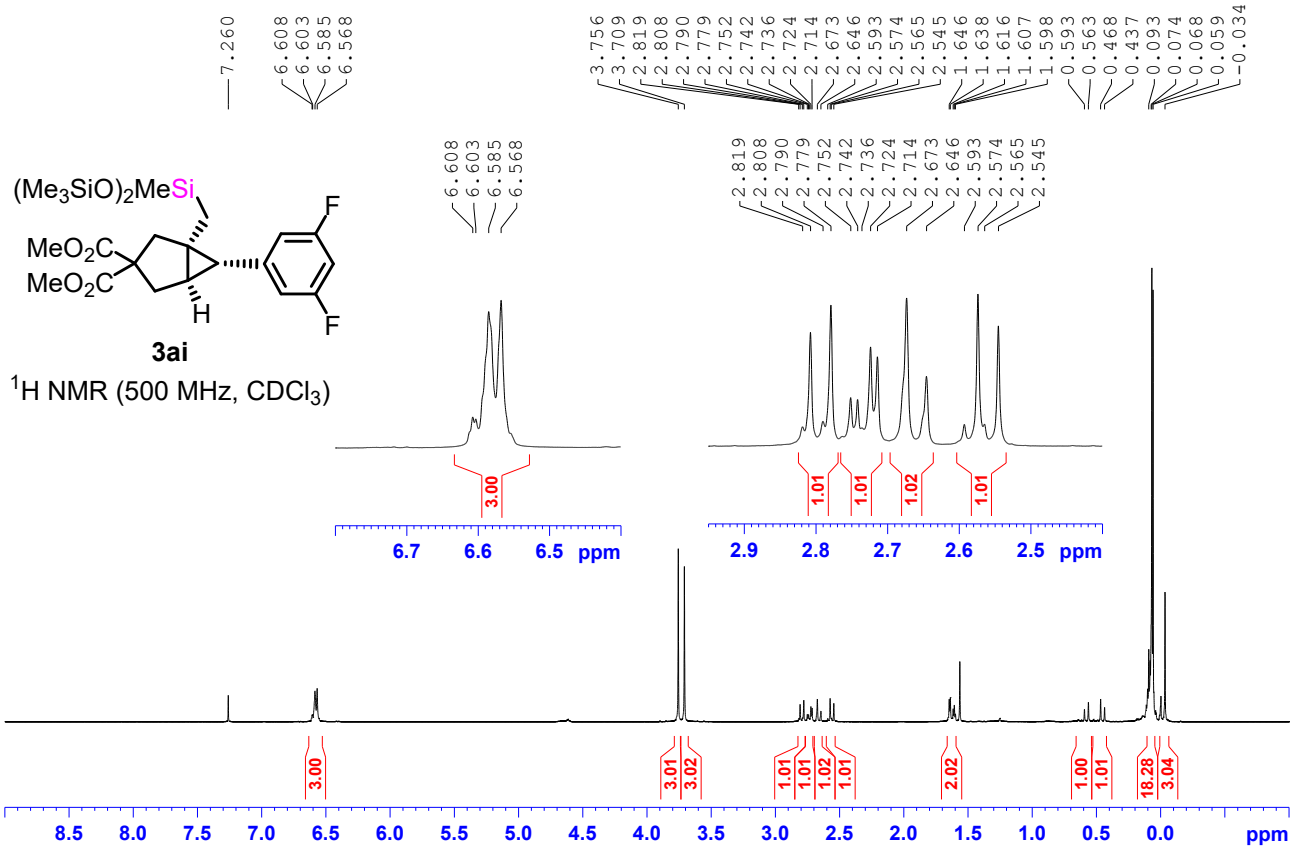

(Me3SiO)2MeSi
MeO2C
MeO2C
H
3af
13C NMR (125 MHz, CDCl3)
ppm

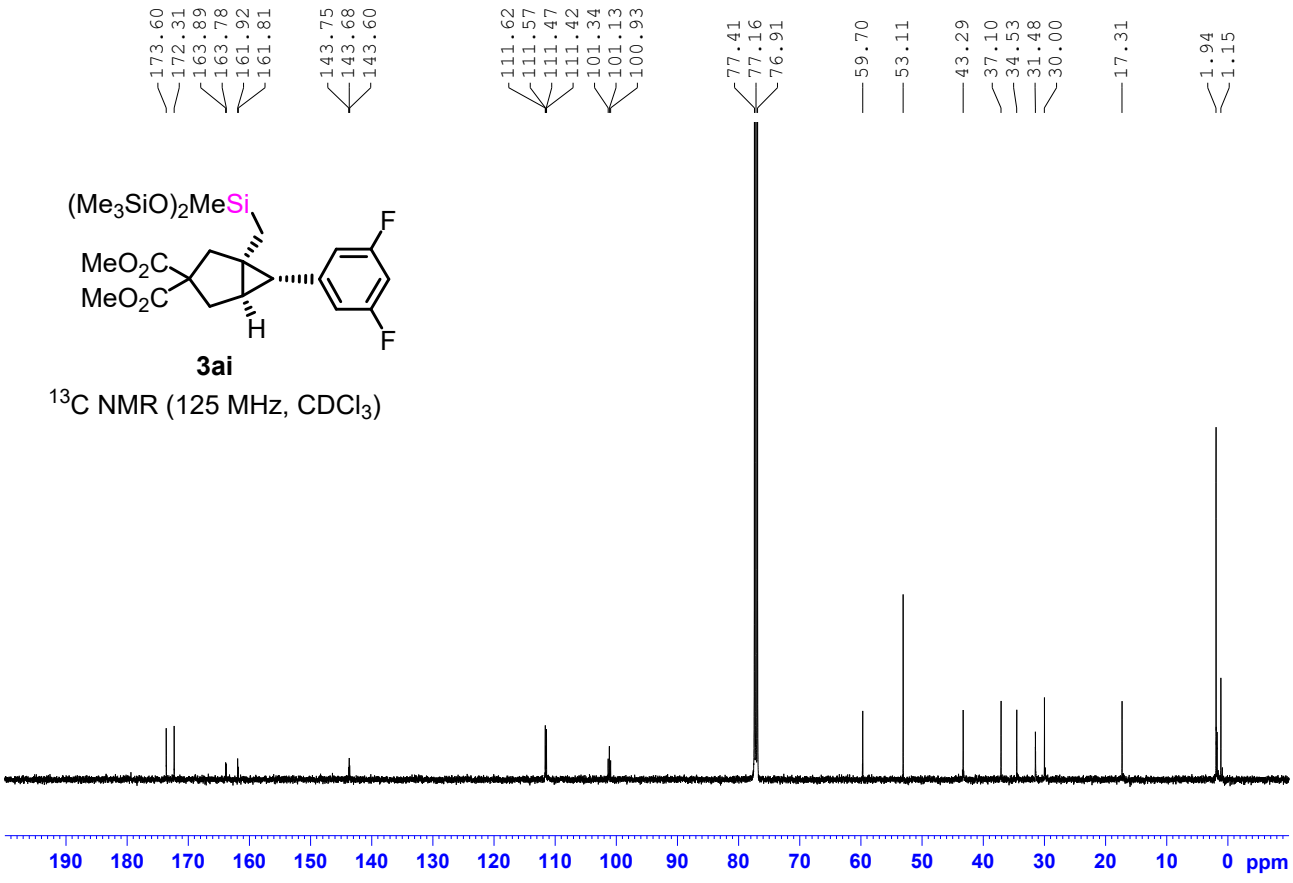

(Me3SiO)2MeSi
Me
MeO2C
MeO2C
H
3ag
1H NMR (500 MHz, CDCl3)
ppm

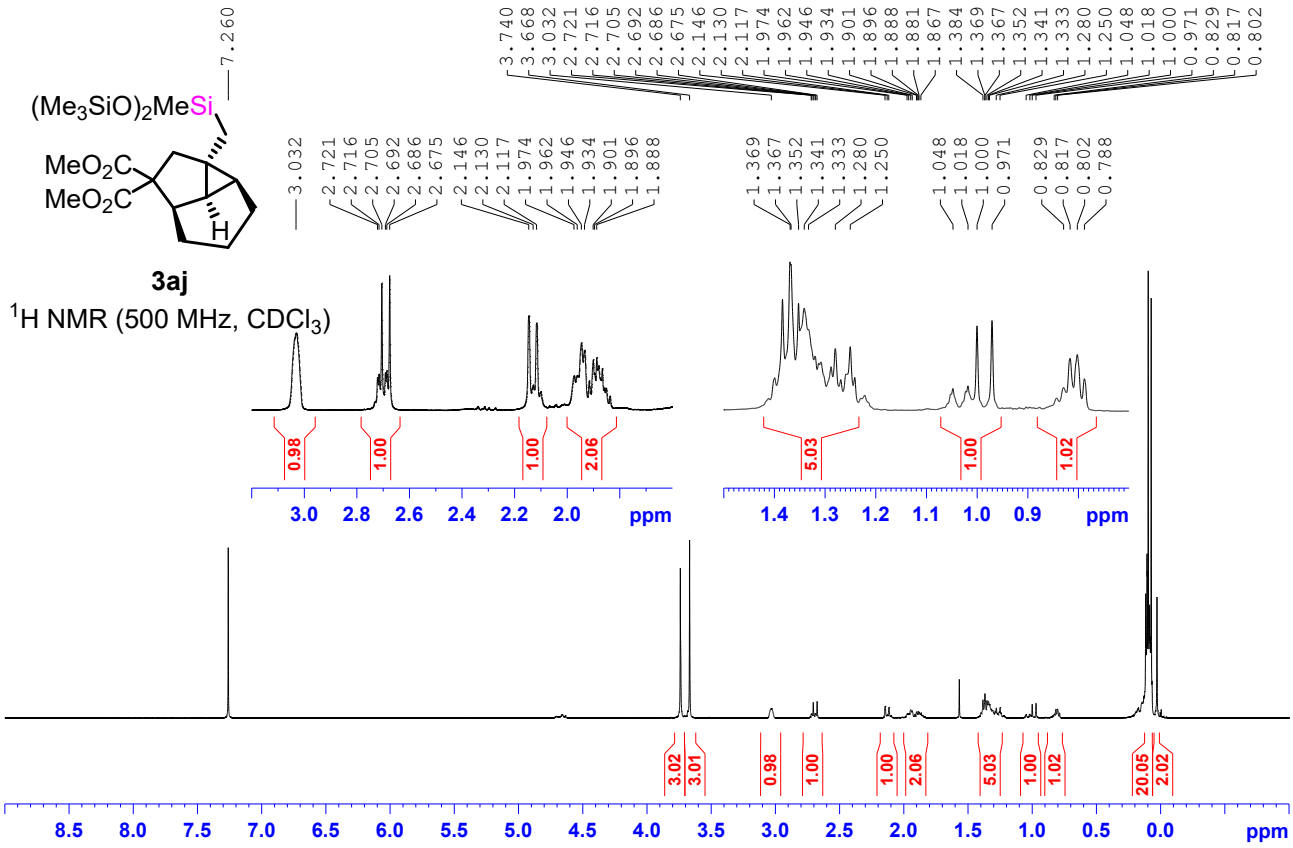

(Me3SiO)2MeSi
Me
MeO2C
MeO2C
H
3ag
13C NMR (125 MHz, CDCl3)
ppm

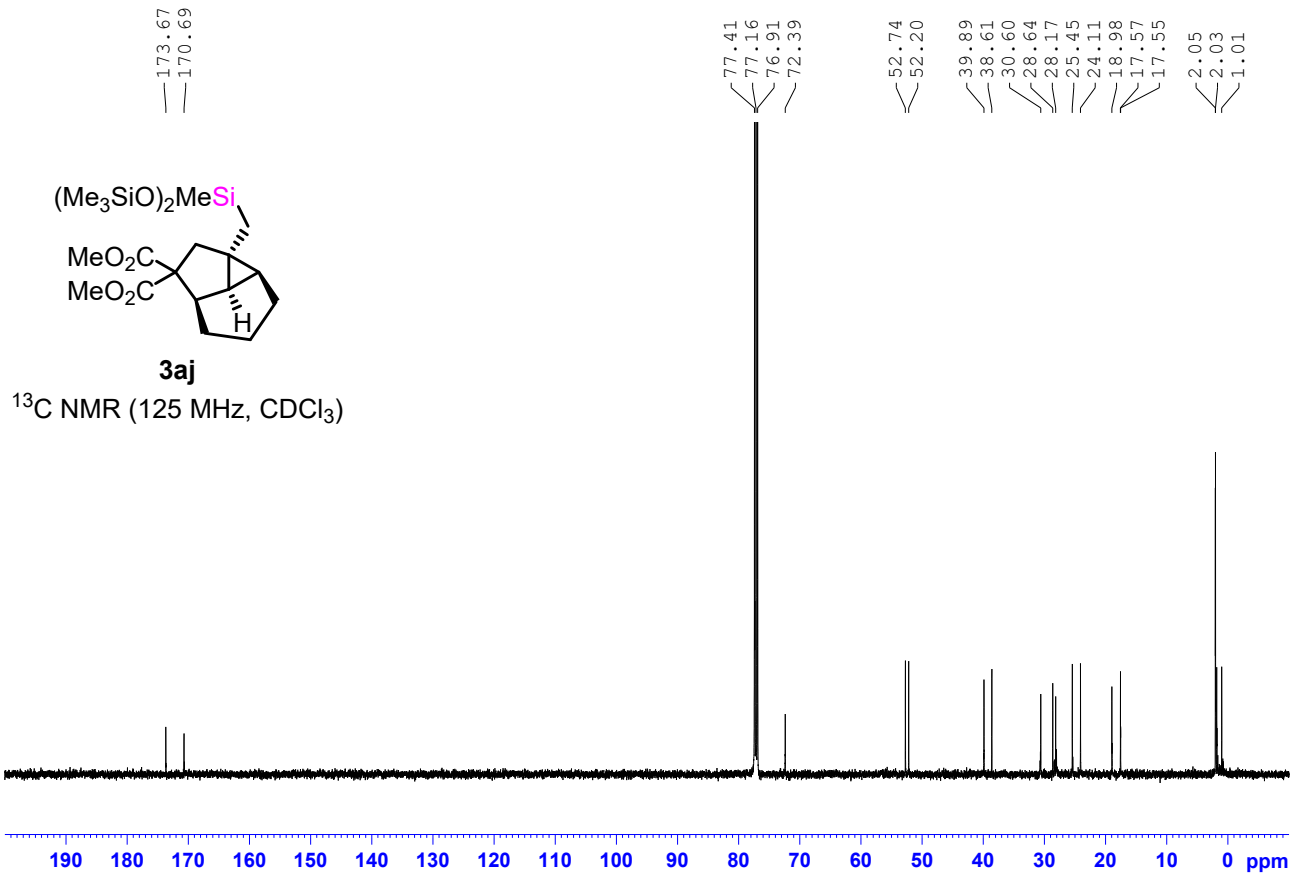

7.260
6.776
6.652
3.756
3.709
2.822
2.793
2.757
2.747
2.730
2.720
2.676
2.648
2.571
2.543
2.263
1.638
1.629
1.620
1.580
1.571
0.622
0.591
0.524
0.493
0.109
0.090
0.082
0.079
0.076
0.068
0.043
-0.041
(Me3SiO)2MeSi
MeO2C
MeO2C
Me
Me
H
3ah
1H NMR (500 MHz, CDCl3)
1.01
2.00
1.03
1.02
1.02
0.99
6.8
6.7
6.6
ppm
2.9
2.8
2.7
2.6
ppm
2.99
3.05
1.03
1.02
1.02
0.99
6.06
2.05
1.01
0.96
18.10
2.94
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
ppm

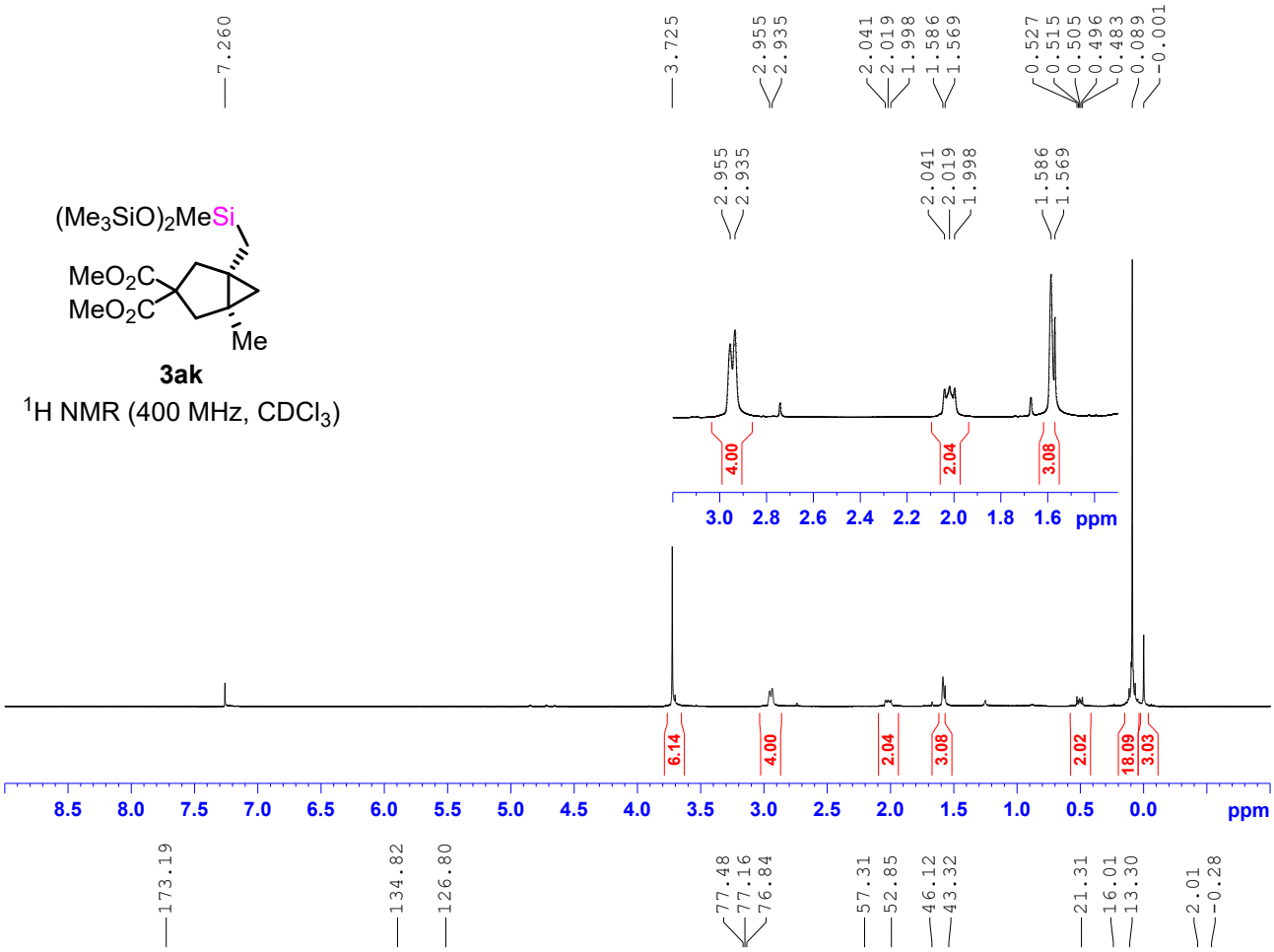

173.68
172.62
138.95
137.29
127.31
126.56
77.41
77.16
76.91
59.94
53.00
52.98
43.35
37.32
33.52
31.48
29.25
21.41
17.22
1.97
1.93
1.14
(Me3SiO)2MeSi
MeO2C
MeO2C
Me
Me
H
3ah
13C NMR (125 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.260
6.608
6.603
6.585
6.568
3.756
3.709
2.819
2.808
2.790
2.779
2.752
2.742
2.736
2.724
2.714
2.673
2.646
2.593
2.574
2.565
2.545
1.646
1.638
1.616
1.607
1.598
0.593
0.563
0.468
0.437
0.093
0.074
0.068
0.059
-0.034
(Me3SiO)2MeSi
MeO2C
MeO2C
F
F
H
3ai
1H NMR (500 MHz, CDCl3)
3.00
1.01
1.01
1.02
1.01
6.7
6.6
6.5 ppm
2.9
2.8
2.7
2.6
2.5 ppm
3.00
3.01
3.02
1.01
1.01
1.02
1.01
2.02
1.00
1.01
18.28
3.04
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
ppm


173.60
172.31
163.89
163.78
161.92
161.81
143.75
143.68
143.60
111.62
111.57
111.47
111.42
101.34
101.13
100.93
77.41
77.16
76.91
59.70
53.11
43.29
37.10
34.53
31.48
30.00
17.31
1.94
1.15
(Me3SiO)2MeSi
MeO2C
MeO2C
F
F
H
3ai
13C NMR (125 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

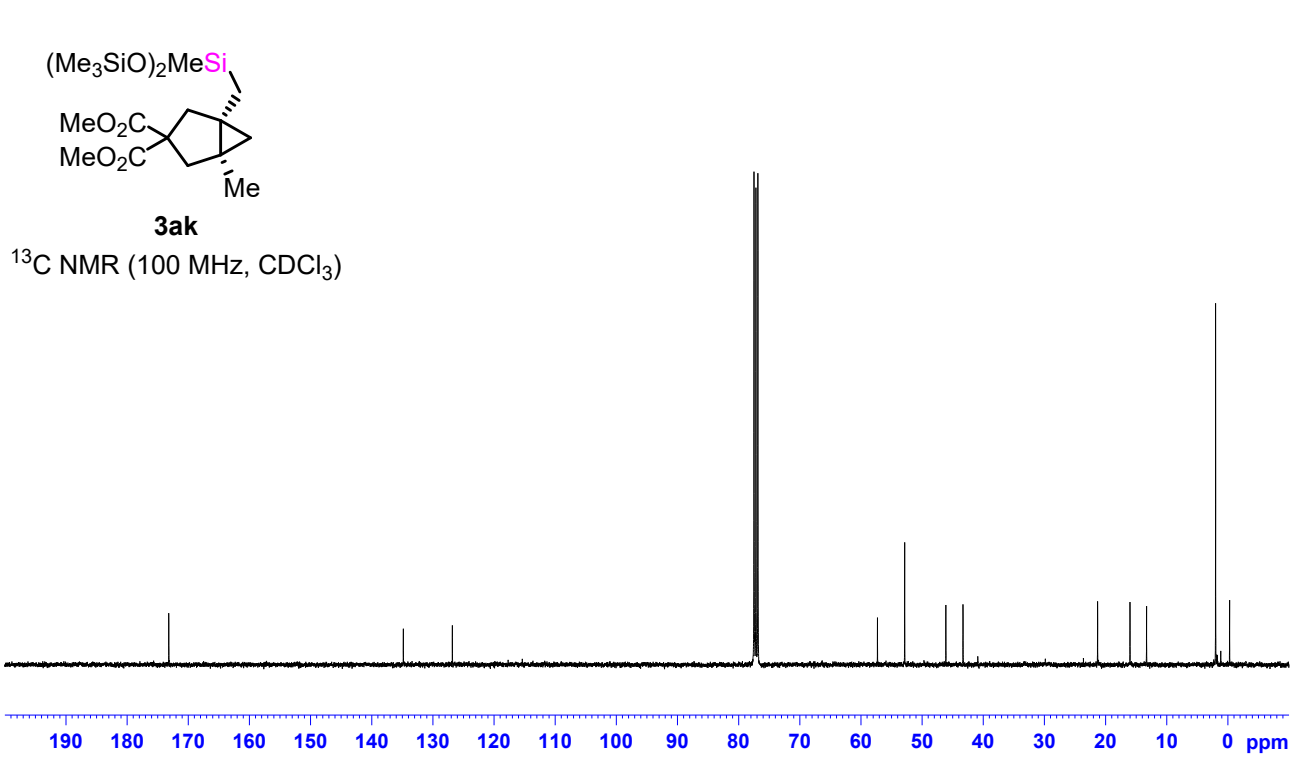

(Me3SiO)2MeSi
MeO2C
MeO2C
H
3aj
1H NMR (500 MHz, CDCl3)
ppm


(Me3SiO)2MeSi
MeO2C
MeO2C
H
3aj
13C NMR (125 MHz, CDCl3)
ppm



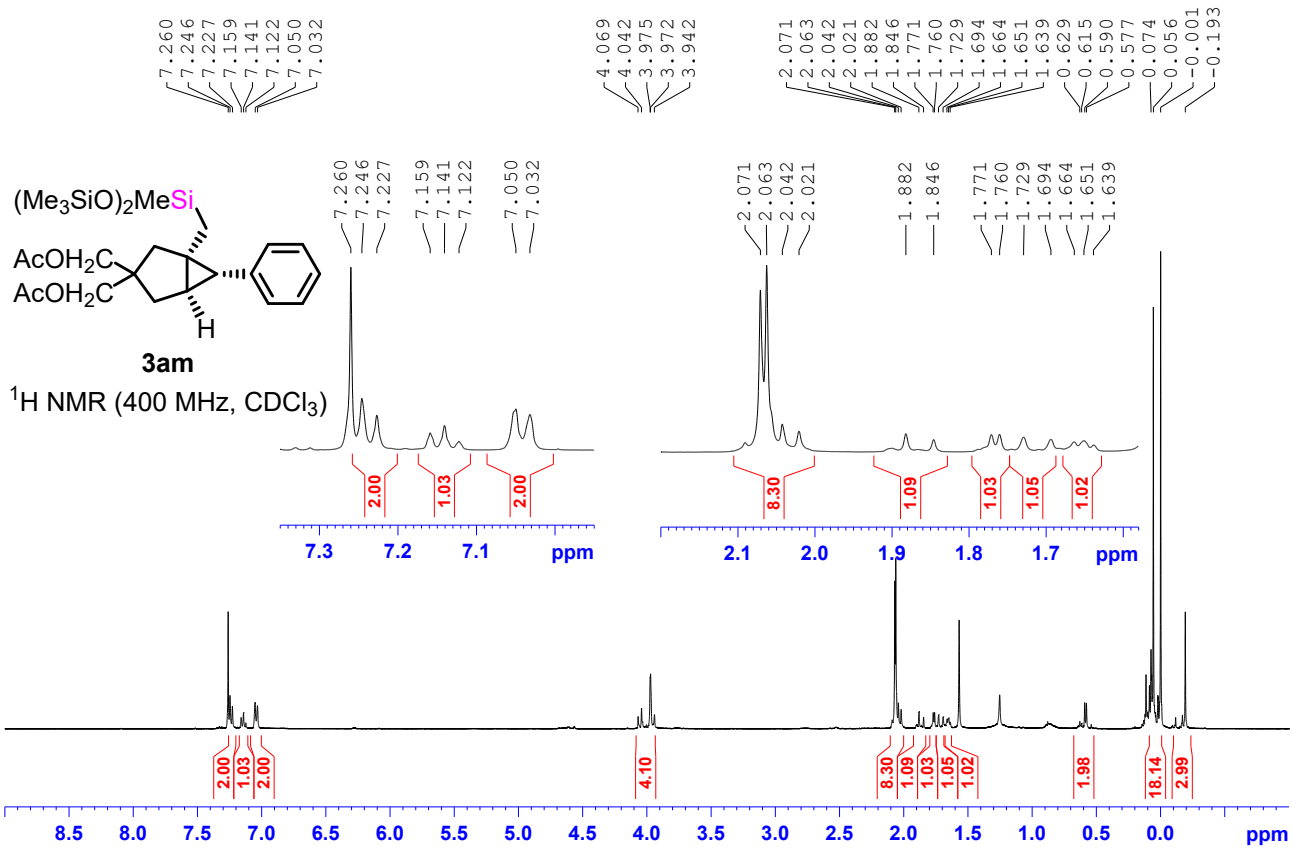
3ak

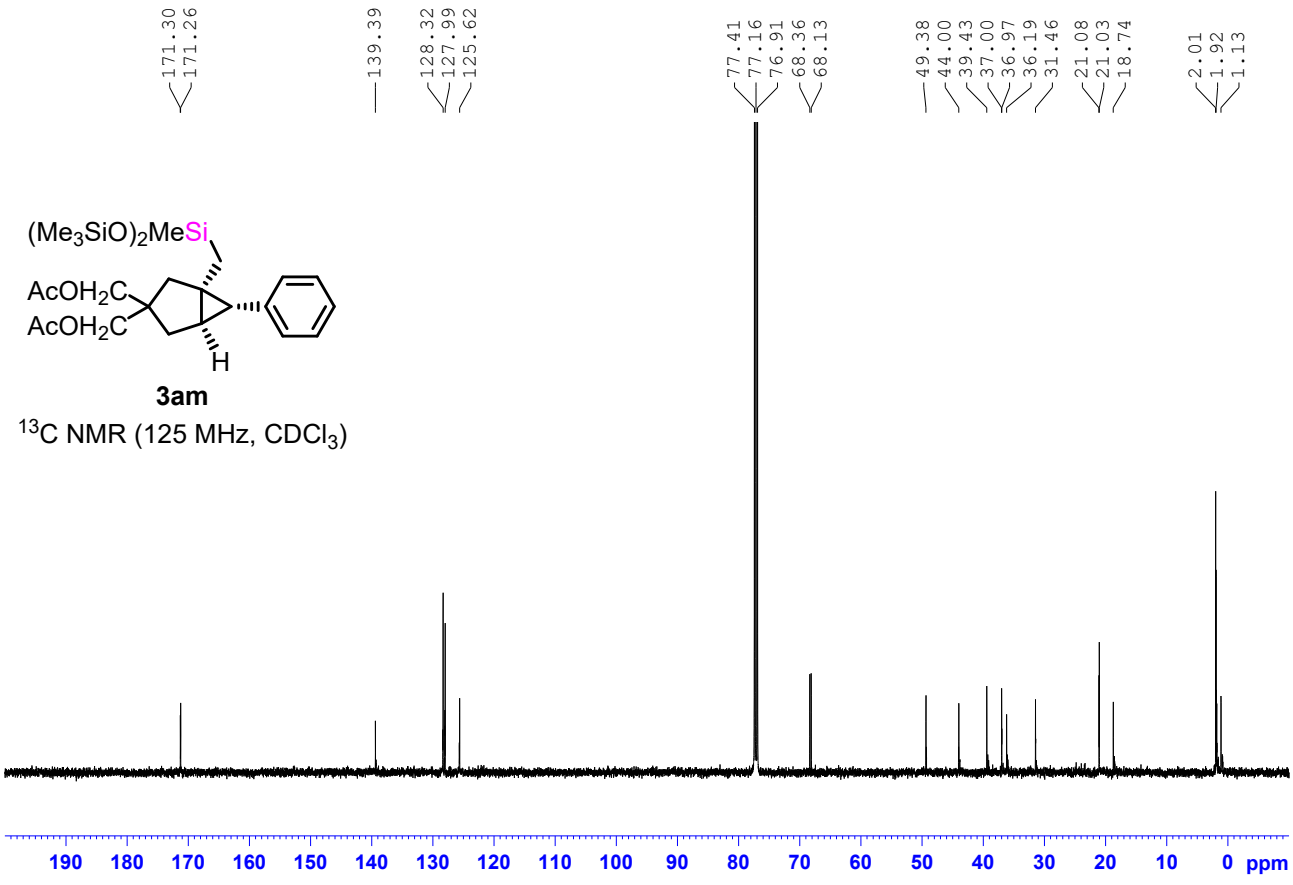
^{1}H NMR (400 MHz, $CDCl_3$)

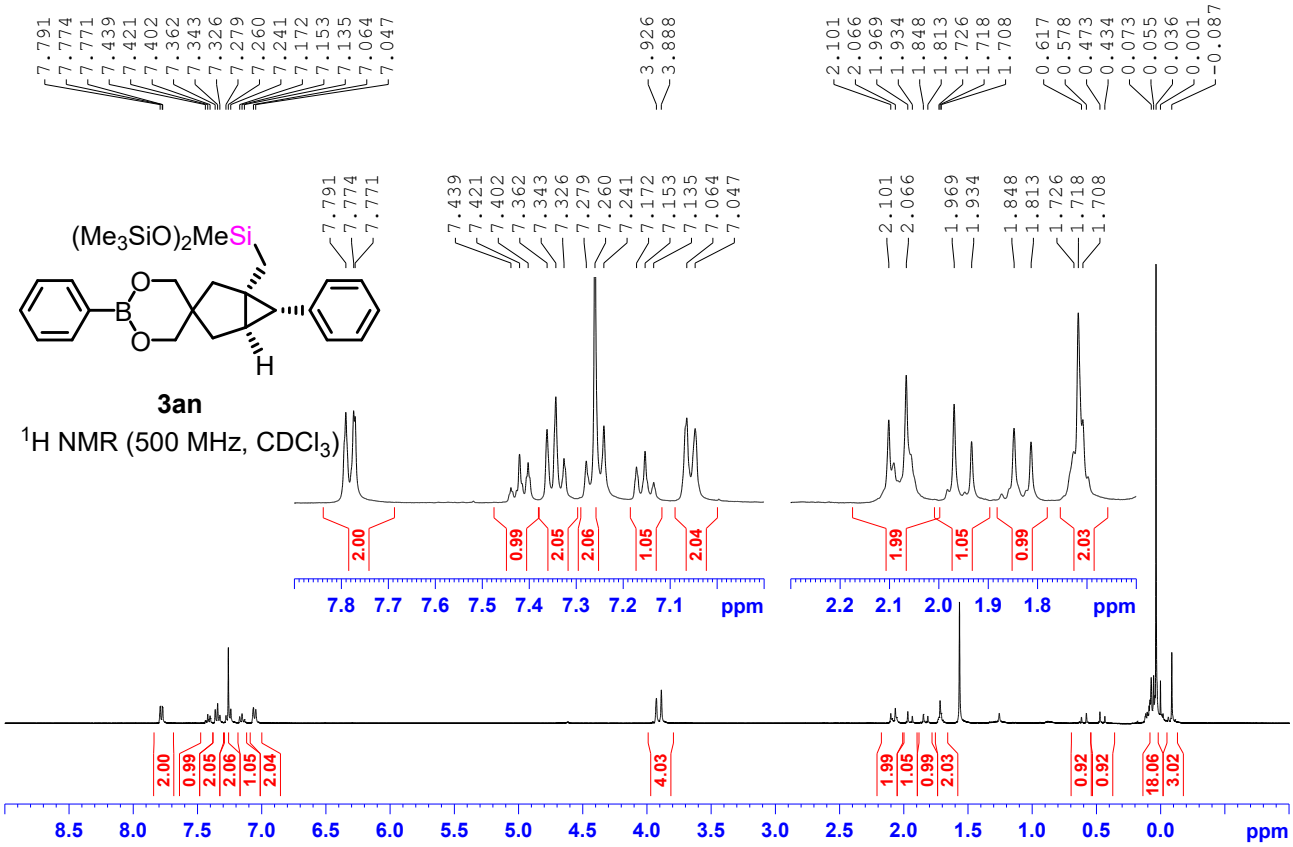


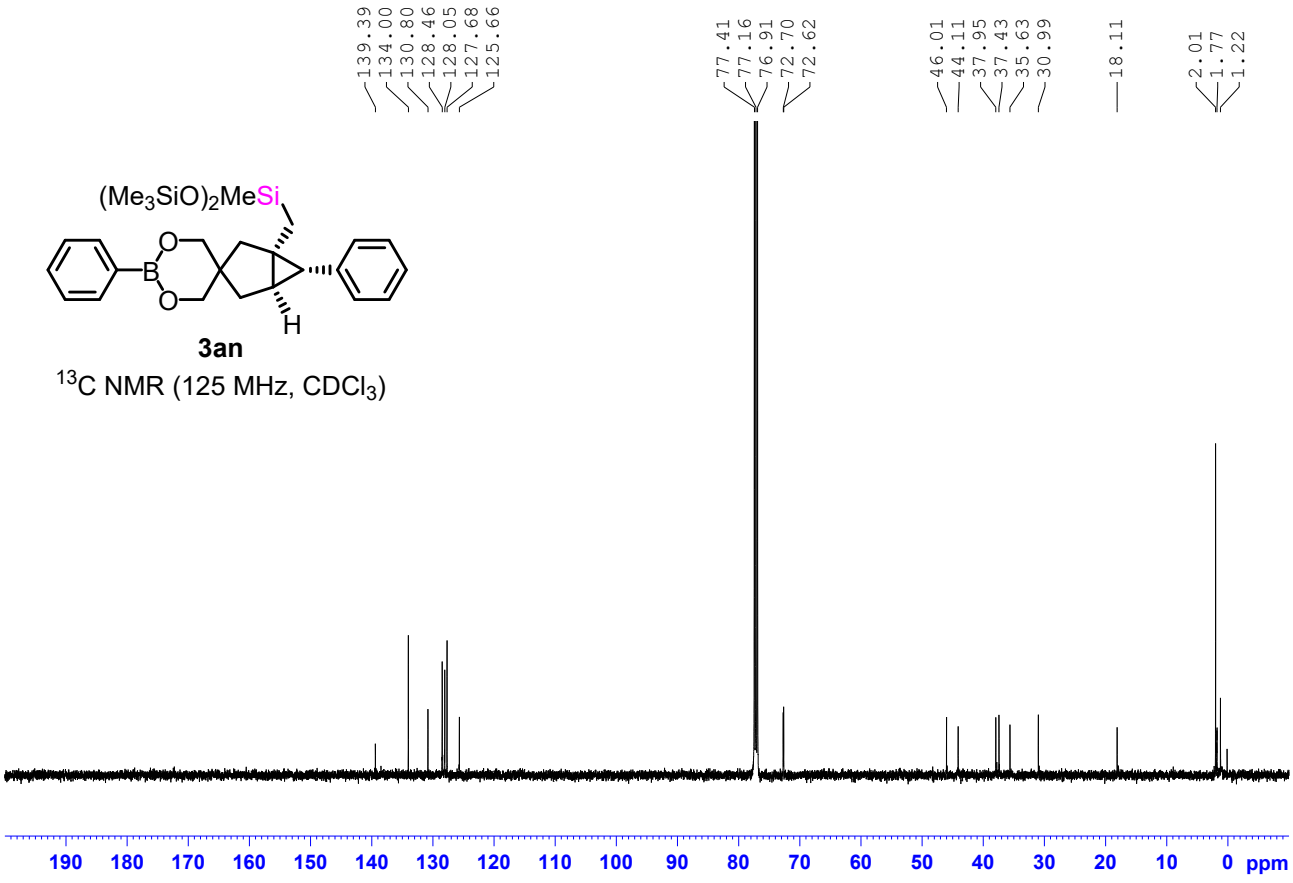
3ak

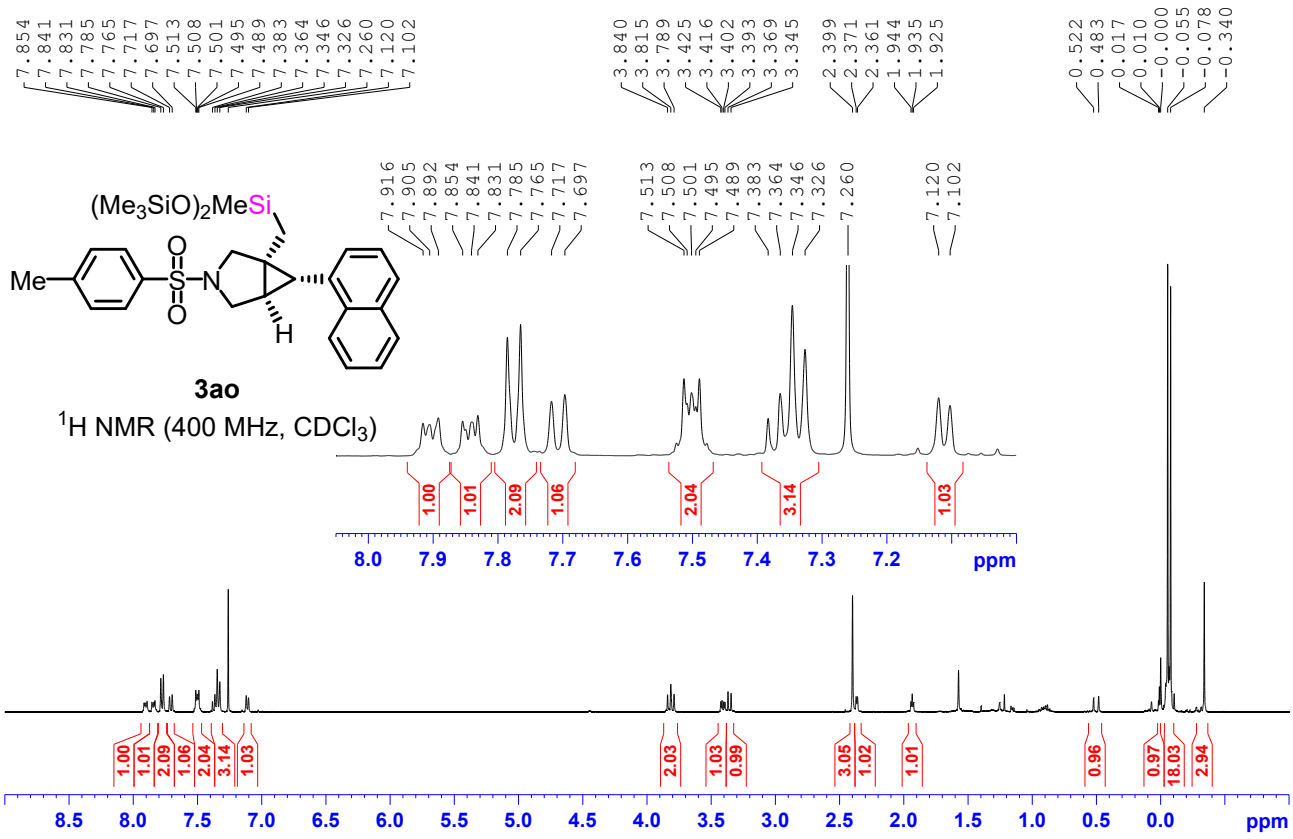
^{13}C NMR (100 MHz, $CDCl_3$)

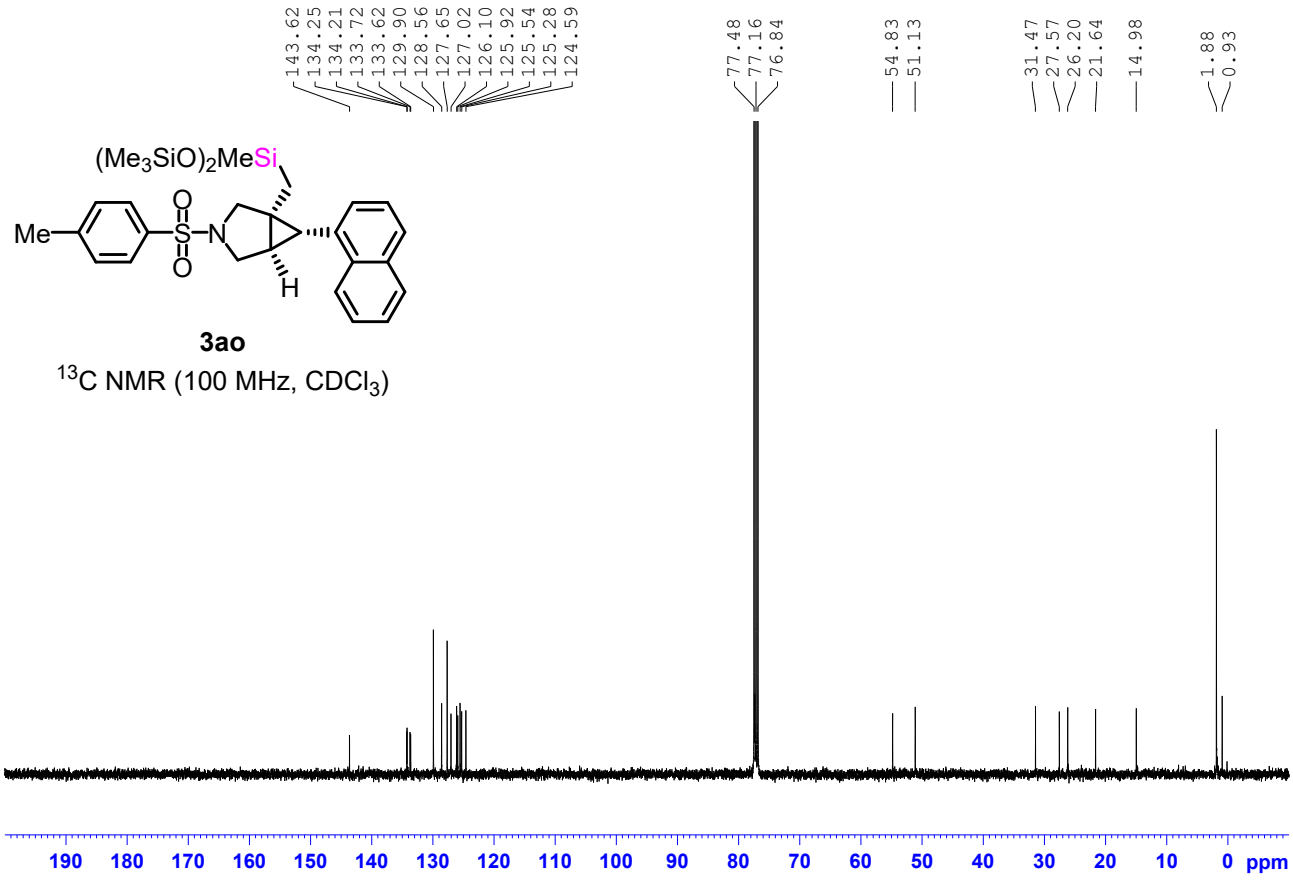

7.260
7.246
7.227
7.159
7.141
7.122
7.050
7.032
4.069
4.042
3.975
3.972
3.942
2.071
2.063
2.042
2.021
1.882
1.846
1.771
1.760
1.729
1.694
1.664
1.651
1.639
0.629
0.615
0.590
0.577
0.074
0.056
-0.001
-0.193
(Me3SiO)2MeSi
AcOH2C
AcOH2C
H
3am
1H NMR (400 MHz, CDCl3)
2.00
1.03
2.00
4.10
8.30
1.09
1.03
1.05
1.02
1.98
18.14
2.99
ppm

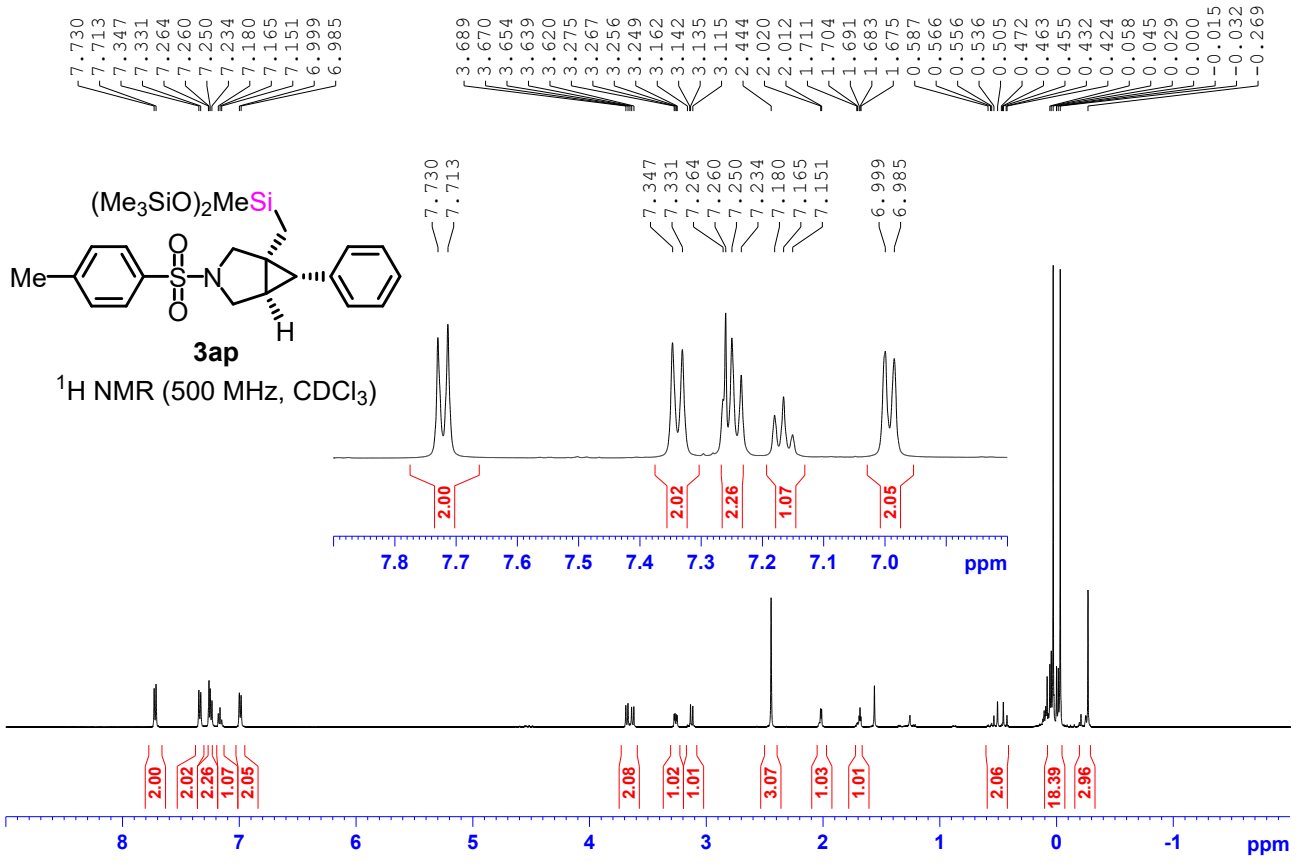

171.30
171.26
139.39
128.32
127.99
125.62
77.41
77.16
76.91
68.36
68.13
49.38
44.00
39.43
37.00
36.97
36.19
31.46
21.08
21.03
18.74
2.01
1.92
1.13
(Me3SiO)2MeSi
AcOH2C
AcOH2C
H
3am
13C NMR (125 MHz, CDCl3)
ppm

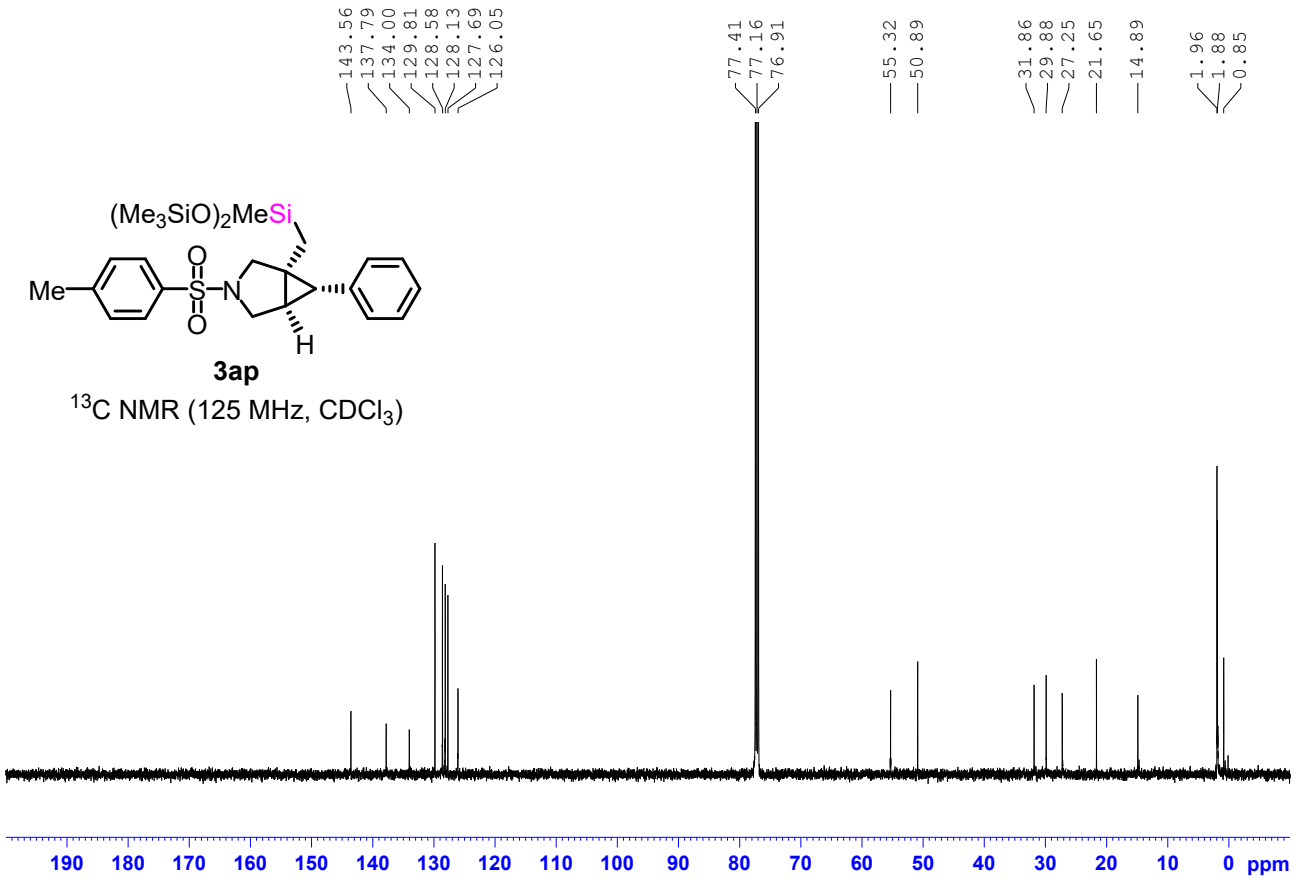

7.791
7.774
7.771
7.439
7.421
7.402
7.362
7.343
7.326
7.279
7.260
7.241
7.172
7.153
7.135
7.064
7.047
3.926
3.888
2.101
2.066
1.969
1.934
1.848
1.813
1.726
1.718
1.708
0.617
0.578
0.473
0.434
0.073
0.055
0.036
0.001
-0.087
(Me3SiO)2MeSi
O
B
O
H
3an
1H NMR (500 MHz, CDCl3)
2.00
0.99
2.05
2.06
1.05
2.04
4.03
1.99
1.05
0.99
2.03
0.92
0.92
18.06
3.02
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 ppm
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 ppm
2.2 2.1 2.0 1.9 1.8 ppm

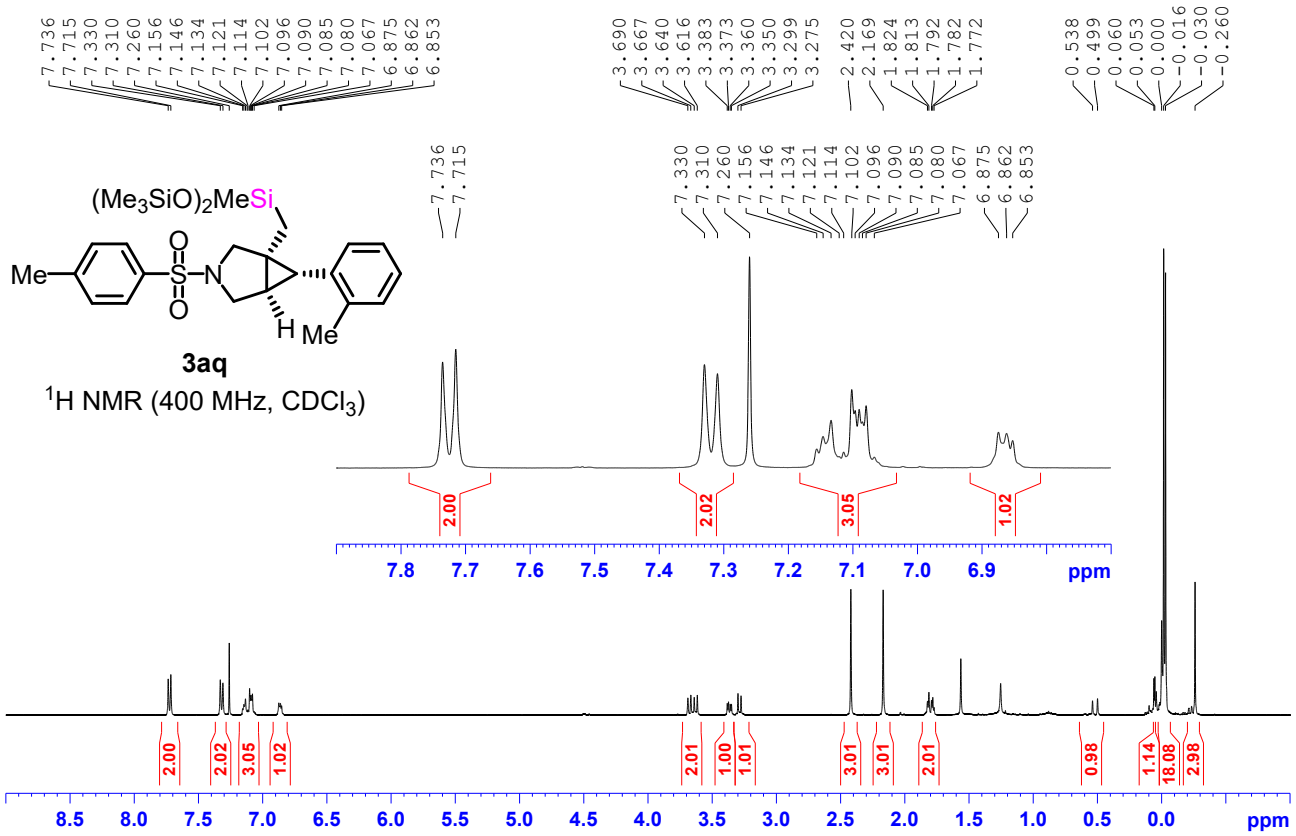

139.39
134.00
130.80
128.46
128.05
127.68
125.66
77.41
77.16
76.91
72.70
72.62
46.01
44.11
37.95
37.43
35.63
30.99
18.11
2.01
1.77
1.22
(Me3SiO)2MeSi
O
B
O
H
3an
13C NMR (125 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

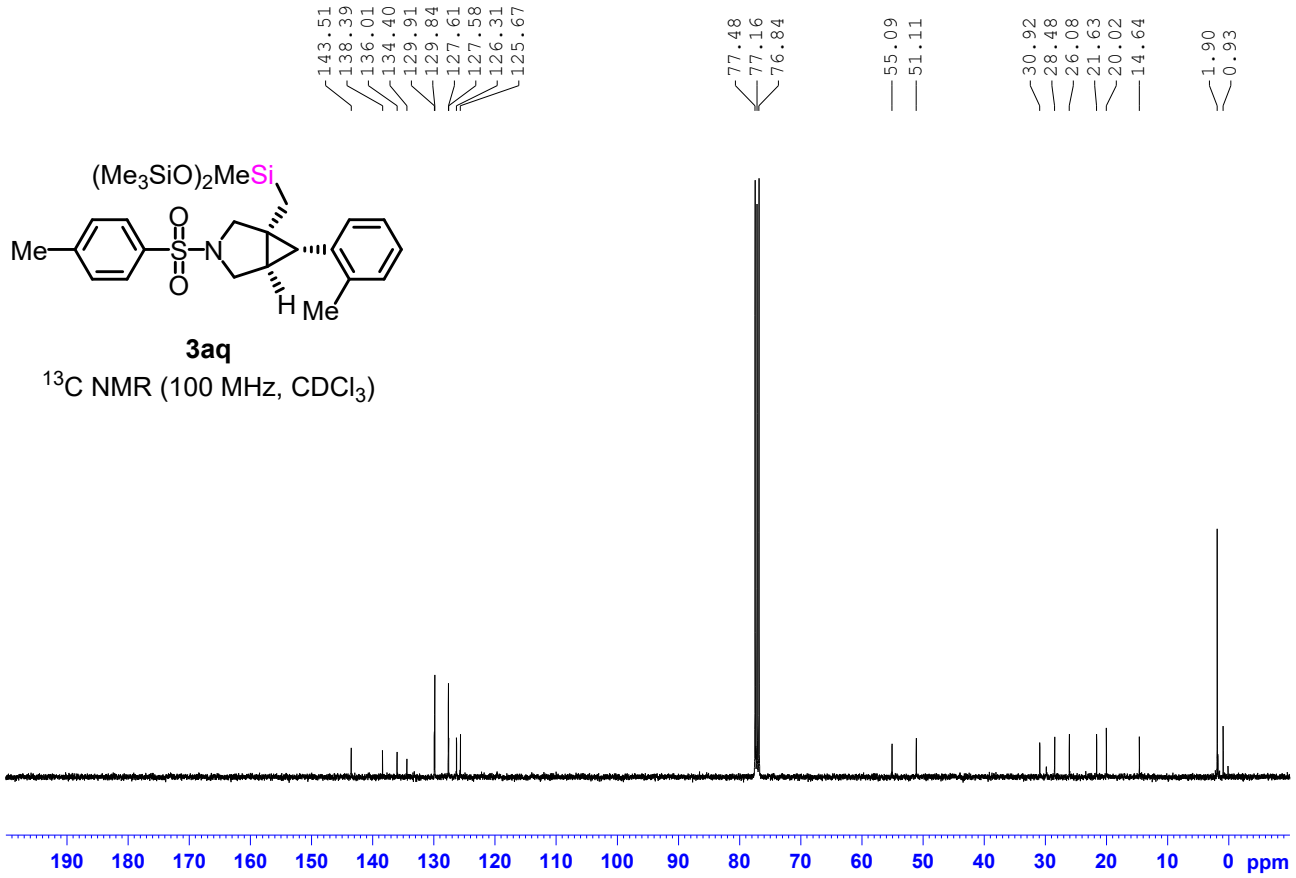

7.854
7.841
7.831
7.785
7.765
7.717
7.697
7.513
7.508
7.501
7.495
7.489
7.383
7.364
7.346
7.326
7.260
7.120
7.102
3.840
3.815
3.789
3.425
3.416
3.402
3.393
3.369
3.345
2.399
2.371
2.361
1.944
1.935
1.925
0.522
0.483
0.017
0.010
-0.000
-0.055
-0.078
-0.340
(Me3SiO)2MeSi
Me
N
H
3ao
1H NMR (400 MHz, CDCl3)
1.00
1.01
2.09
1.06
2.04
3.14
1.03
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
ppm
2.03
1.03
0.99
3.05
1.02
1.01
0.96
0.97
18.03
2.94
8.5
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


143.62
134.25
134.21
133.72
133.62
129.90
128.56
127.65
127.02
126.10
125.92
125.54
125.28
124.59
77.48
77.16
76.84
54.83
51.13
31.47
27.57
26.20
21.64
14.98
1.88
0.93
(Me3SiO)2MeSi
Me
N
H
3ao
13C NMR (100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


(Me3SiO)2MeSi
Me
O
S
N
H
3ap
1H NMR (500 MHz, CDCl3)
7.730
7.713
7.347
7.331
7.264
7.260
7.250
7.234
7.180
7.165
7.151
6.999
6.985
2.00
2.02
2.26
1.07
2.05
2.08
1.02
1.01
3.07
1.03
1.01
2.06
18.39
2.96
ppm


(Me3SiO)2MeSi
Me
O
S
N
H
3ap
13C NMR (125 MHz, CDCl3)
143.56
137.79
134.00
129.81
128.58
128.13
127.69
126.05
77.41
77.16
76.91
55.32
50.89
31.86
29.88
27.25
21.65
14.89
1.96
1.88
0.85
ppm


7.736
7.715
7.330
7.310
7.260
7.156
7.146
7.134
7.121
7.114
7.102
7.096
7.090
7.085
7.080
7.067
6.875
6.862
6.853
3.690
3.667
3.640
3.616
3.383
3.373
3.360
3.350
3.299
3.275
2.420
2.169
1.824
1.813
1.792
1.782
1.772
0.538
0.499
0.060
0.053
0.000
-0.016
-0.030
-0.260
(Me3SiO)2MeSi
Me
N
H
Me
3aq
1H NMR (400 MHz, CDCl3)
2.00
2.02
3.05
1.02
2.01
1.00
1.01
3.01
3.01
2.01
0.98
1.14
18.08
2.98
ppm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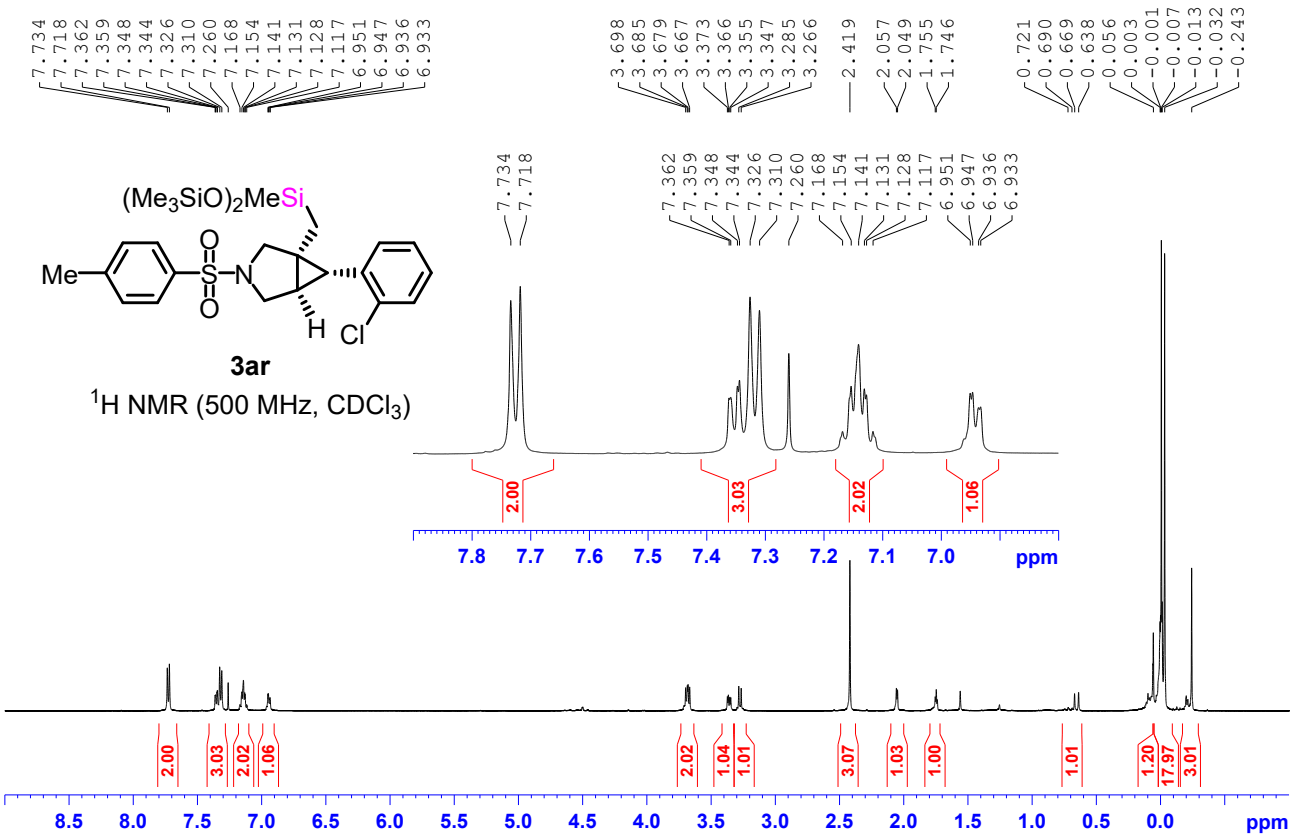
138.39
136.01
134.40
129.91
129.84
127.61
127.58
126.31
125.67
77.48
77.16
76.84
55.09
51.11
30.92
28.48
26.08
21.63
20.02
14.64
1.90
0.93
(Me3SiO)2MeSi
Me
N
H
Me
3aq
13C NMR (100 MHz, CDCl3)
ppm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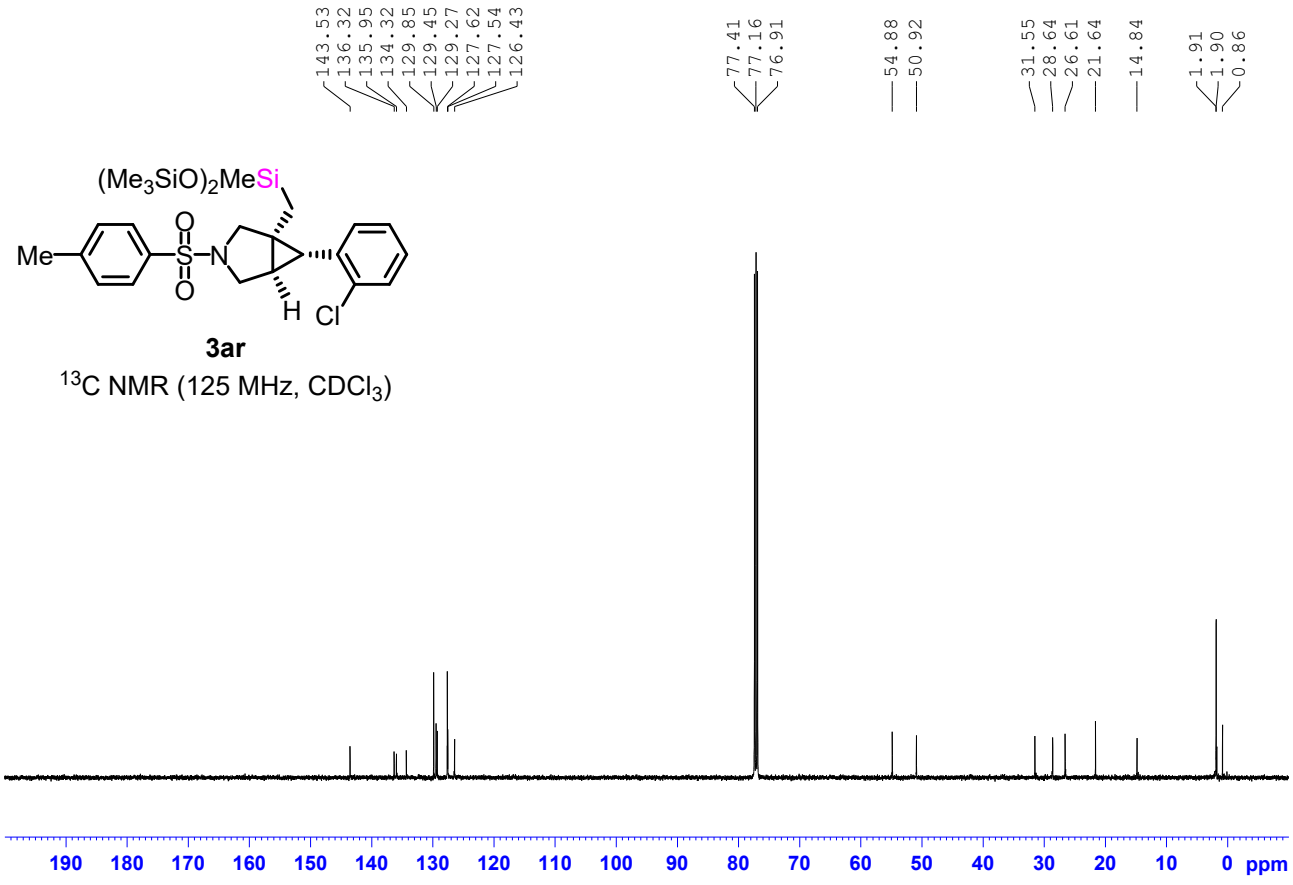
7.718
7.362
7.359
7.348
7.344
7.326
7.310
7.260
7.168
7.154
7.141
7.131
7.128
7.117
6.951
6.947
6.936
6.933
3.698
3.685
3.679
3.667
3.373
3.366
3.355
3.347
3.285
3.266
2.419
2.057
2.049
1.755
1.746
0.721
0.690
0.669
0.638
0.056
0.003
-0.001
-0.007
-0.013
-0.032
-0.243
(Me3SiO)2MeSi
Me
S
N
H
Cl
3ar
1H NMR (500 MHz, CDCl3)
2.00
3.03
2.02
1.06
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
ppm
2.00
3.03
2.02
1.06
2.02
1.04
1.01
3.07
1.03
1.00
1.01
1.20
17.97
3.01
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
ppm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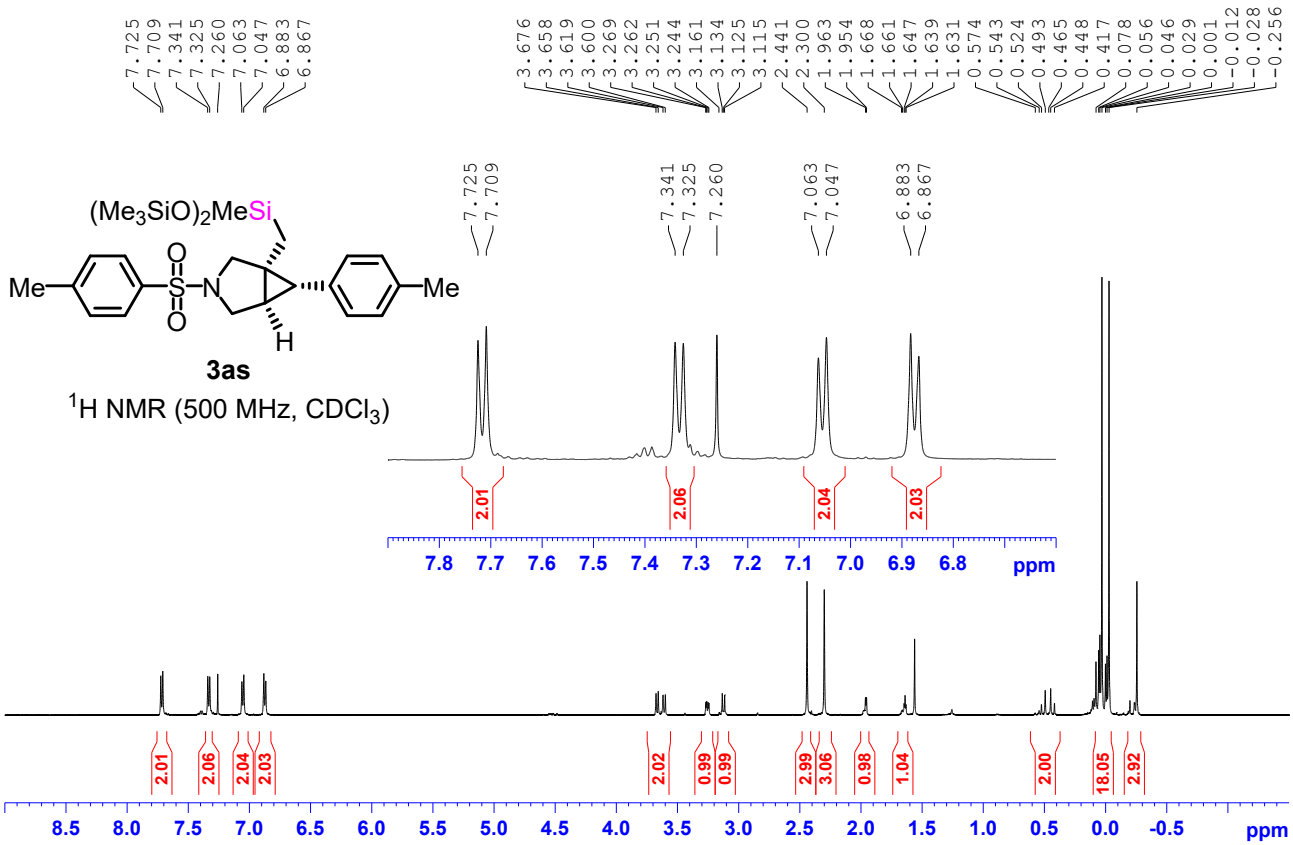
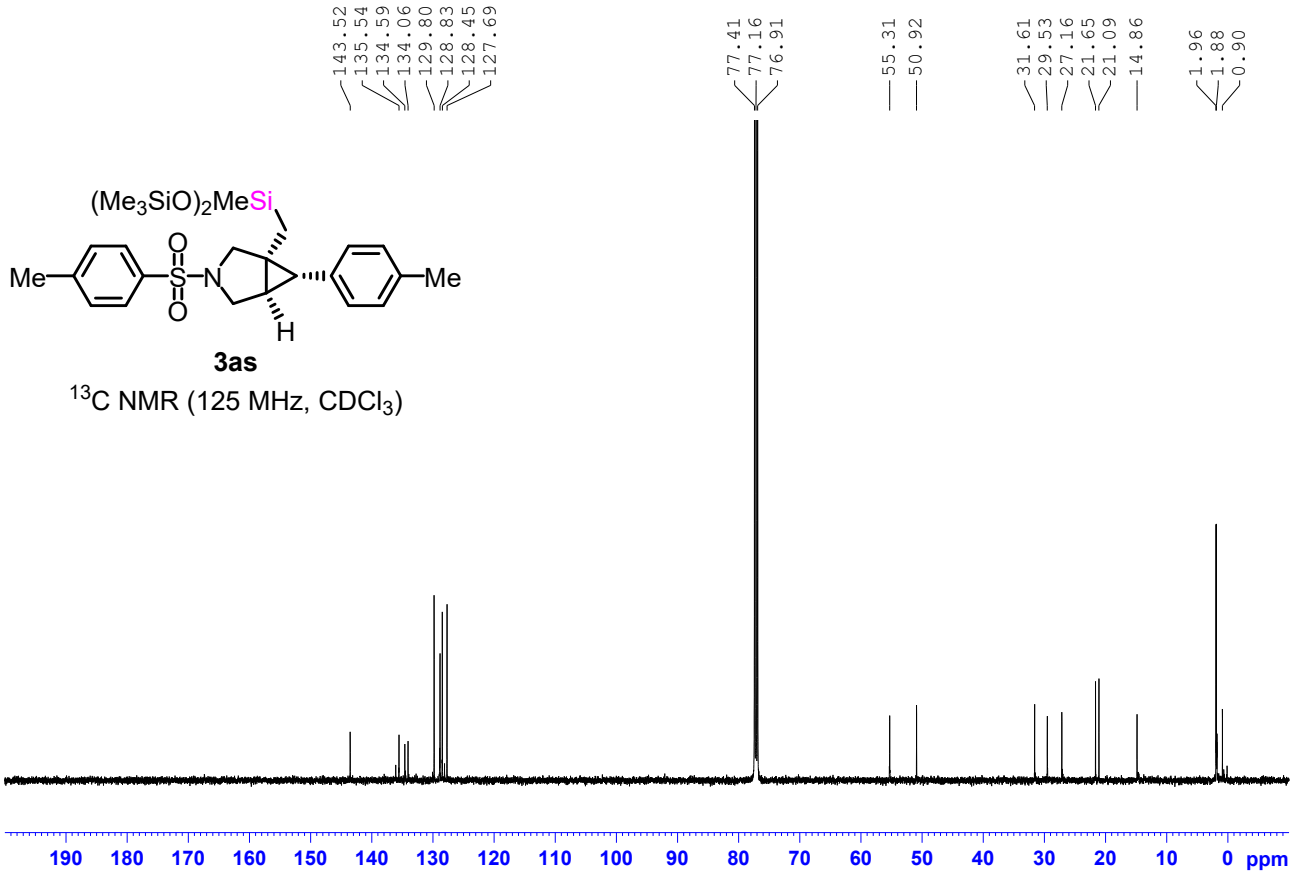
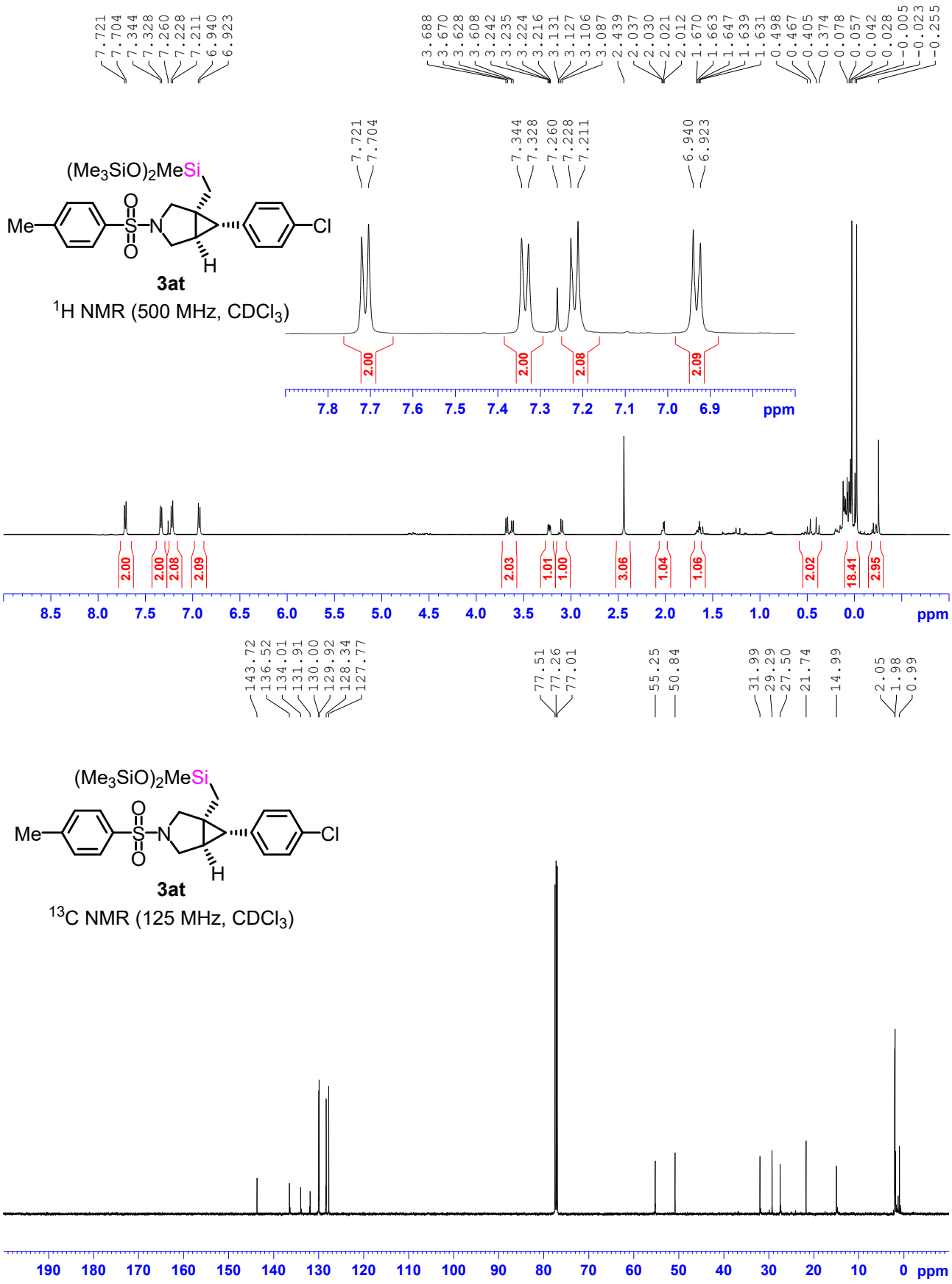
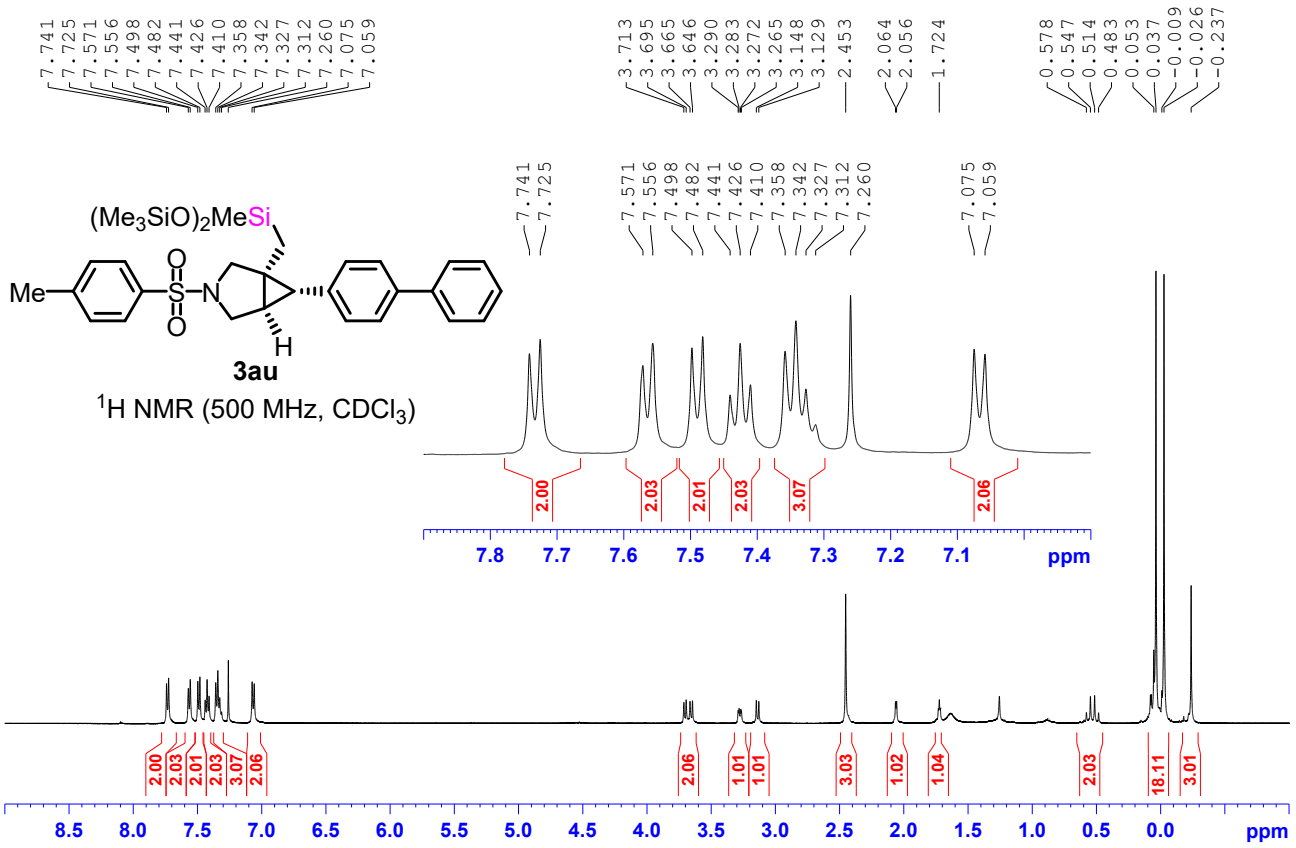
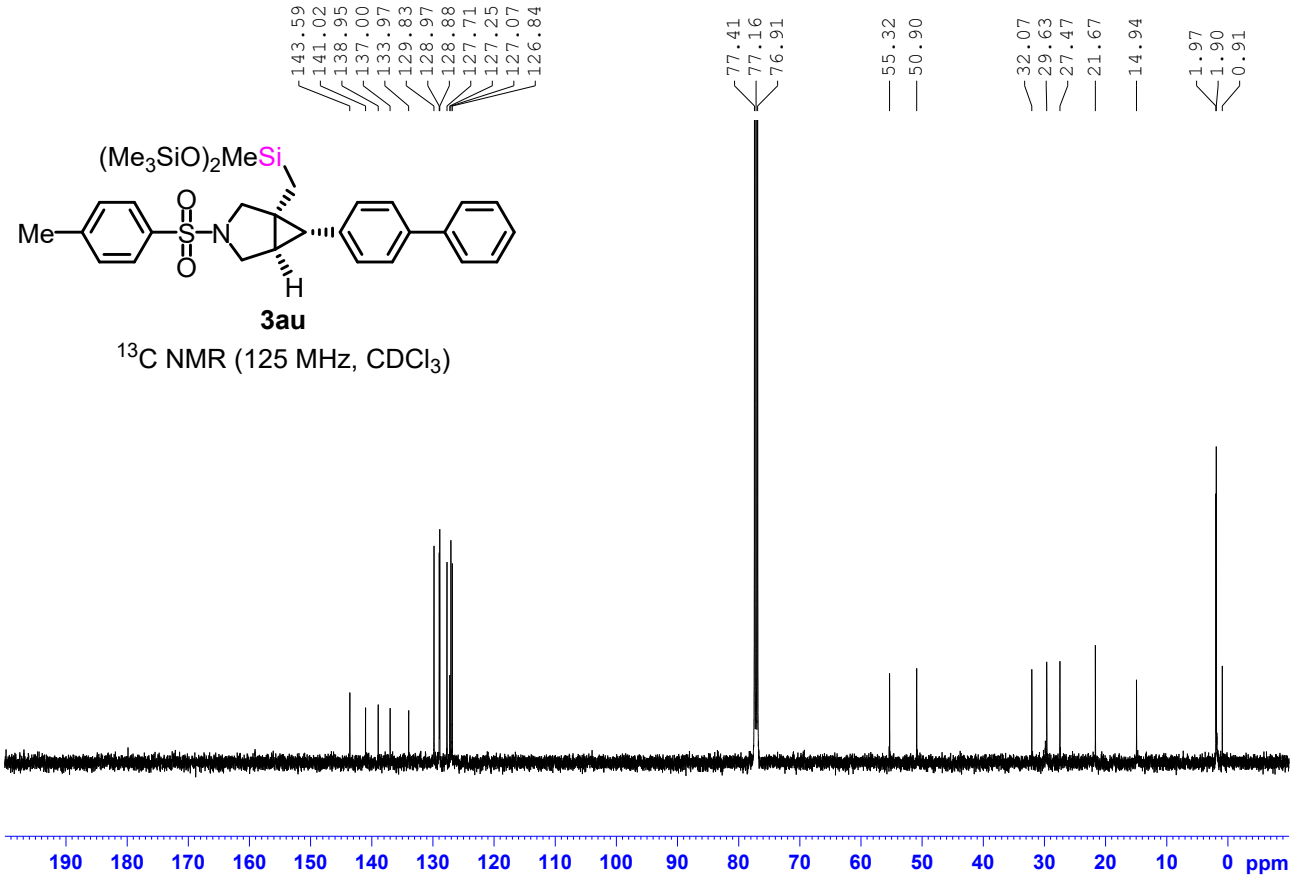
136.32
135.95
134.32
129.85
129.45
129.27
127.62
127.54
126.43
77.41
77.16
76.91
54.88
50.92
31.55
28.64
26.61
21.64
14.84
1.91
1.90
0.86
(Me3SiO)2MeSi
Me
S
N
H
Cl
3ar
13C NMR (125 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

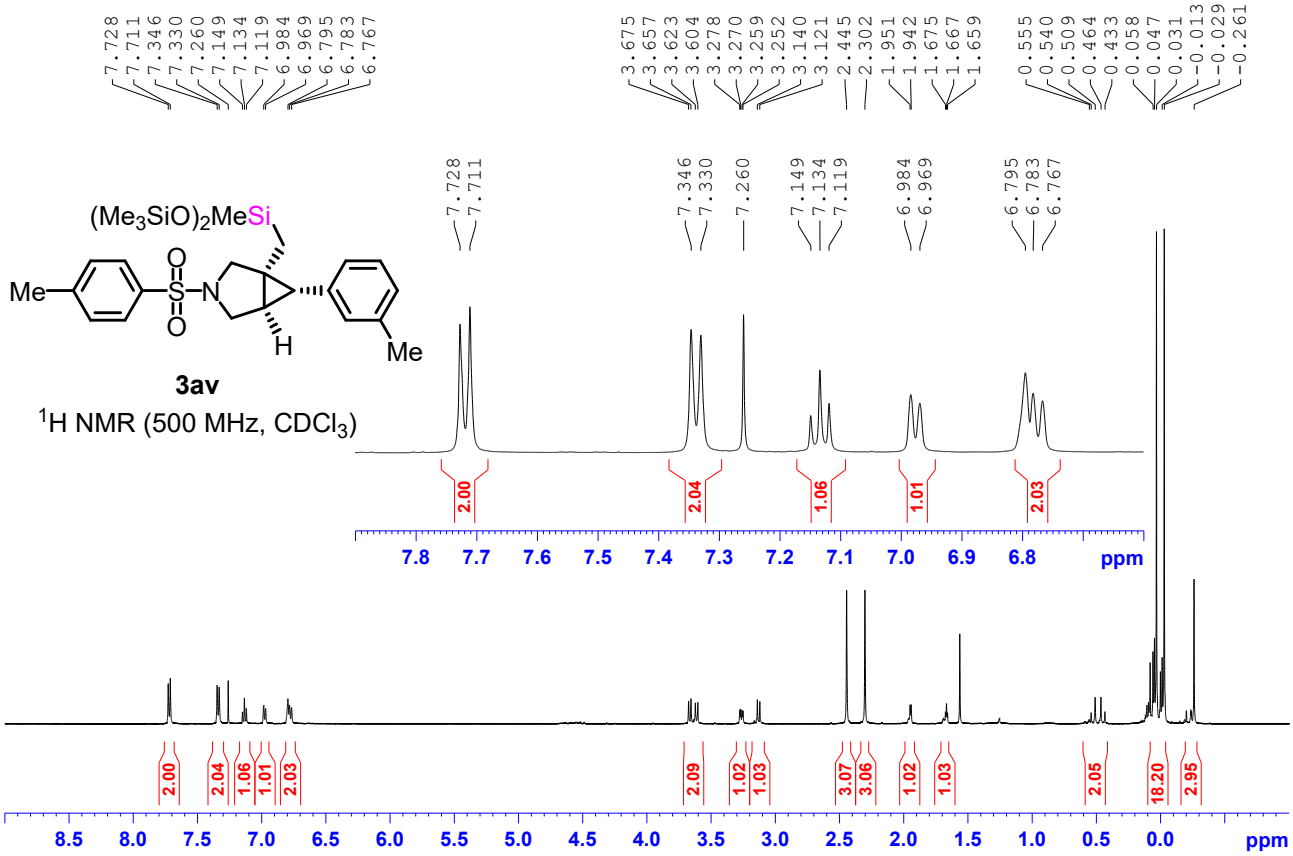

7.725
7.709
7.341
7.325
7.260
7.063
7.047
6.883
6.867
3.676
3.658
3.619
3.600
3.269
3.262
3.251
3.244
3.161
3.134
3.125
3.115
2.441
2.300
1.963
1.954
1.668
1.661
1.647
1.639
1.631
0.574
0.543
0.524
0.493
0.465
0.448
0.417
0.078
0.056
0.046
0.029
0.001
-0.012
-0.028
-0.256
(Me3SiO)2MeSi
Me
Me
H
3as
1H NMR (500 MHz, CDCl3)
2.01
2.06
2.04
2.03
2.02
0.99
0.99
2.99
3.06
0.98
1.04
2.00
18.05
2.92
ppm


143.52
135.54
134.59
134.06
129.80
128.83
128.45
127.69
77.41
77.16
76.91
55.31
50.92
31.61
29.53
27.16
21.65
21.09
14.86
1.96
1.88
0.90
(Me3SiO)2MeSi
Me
Me
H
3as
13C NMR (125 MHz, CDCl3)
ppm


(Me3SiO)2MeSi
Me
Cl
H
3at
1H NMR (500 MHz, CDCl3)
13C NMR (125 MHz, CDCl3)
ppm


(Me3SiO)2MeSi
Me
O
S
N
O
H
3au
1H NMR (500 MHz, CDCl3)
7.741
7.725
7.571
7.556
7.498
7.482
7.441
7.426
7.410
7.358
7.342
7.327
7.312
7.260
7.075
7.059
3.713
3.695
3.665
3.646
3.290
3.283
3.272
3.265
3.148
3.129
2.453
2.064
2.056
1.724
0.578
0.547
0.514
0.483
0.053
0.037
-0.009
-0.026
-0.237
2.00
2.03
2.01
2.03
3.07
2.06
1.01
1.01
3.03
1.02
1.04
2.03
18.11
3.01
ppm


(Me3SiO)2MeSi
Me
O
S
N
O
H
3au
13C NMR (125 MHz, CDCl3)
143.59
141.02
138.95
137.00
133.97
129.83
128.97
128.88
127.71
127.25
127.07
126.84
77.41
77.16
76.91
55.32
50.90
32.07
29.63
27.47
21.67
14.94
1.97
1.90
0.91
ppm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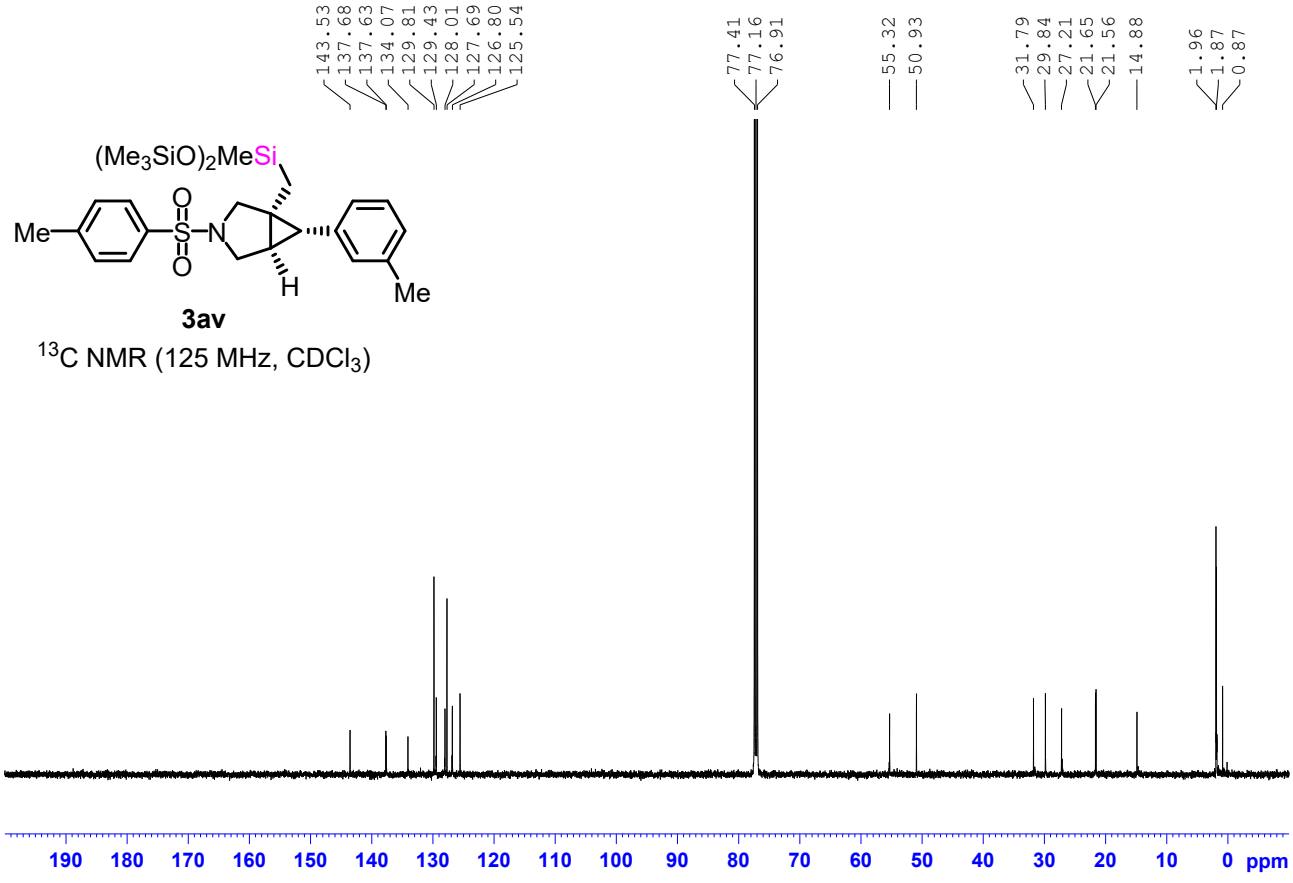
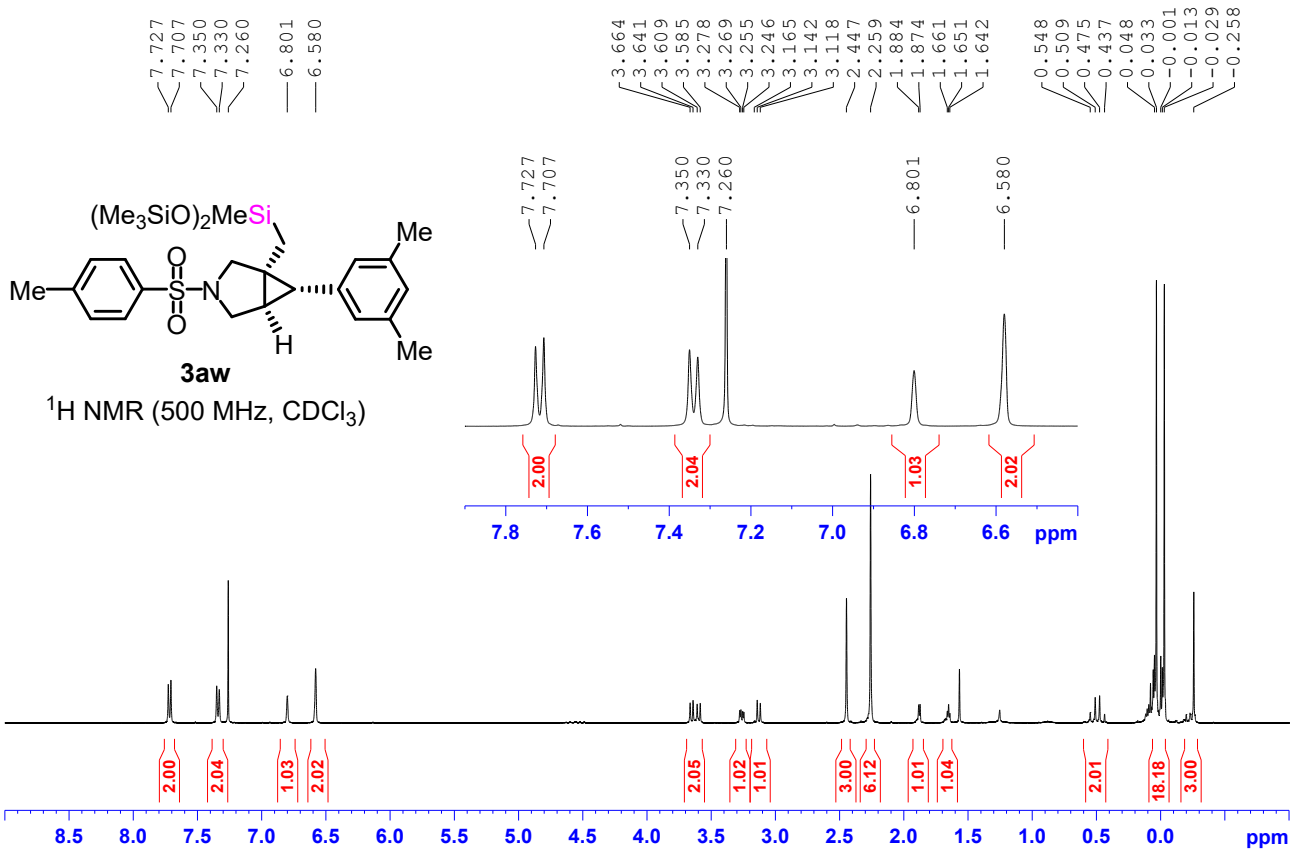
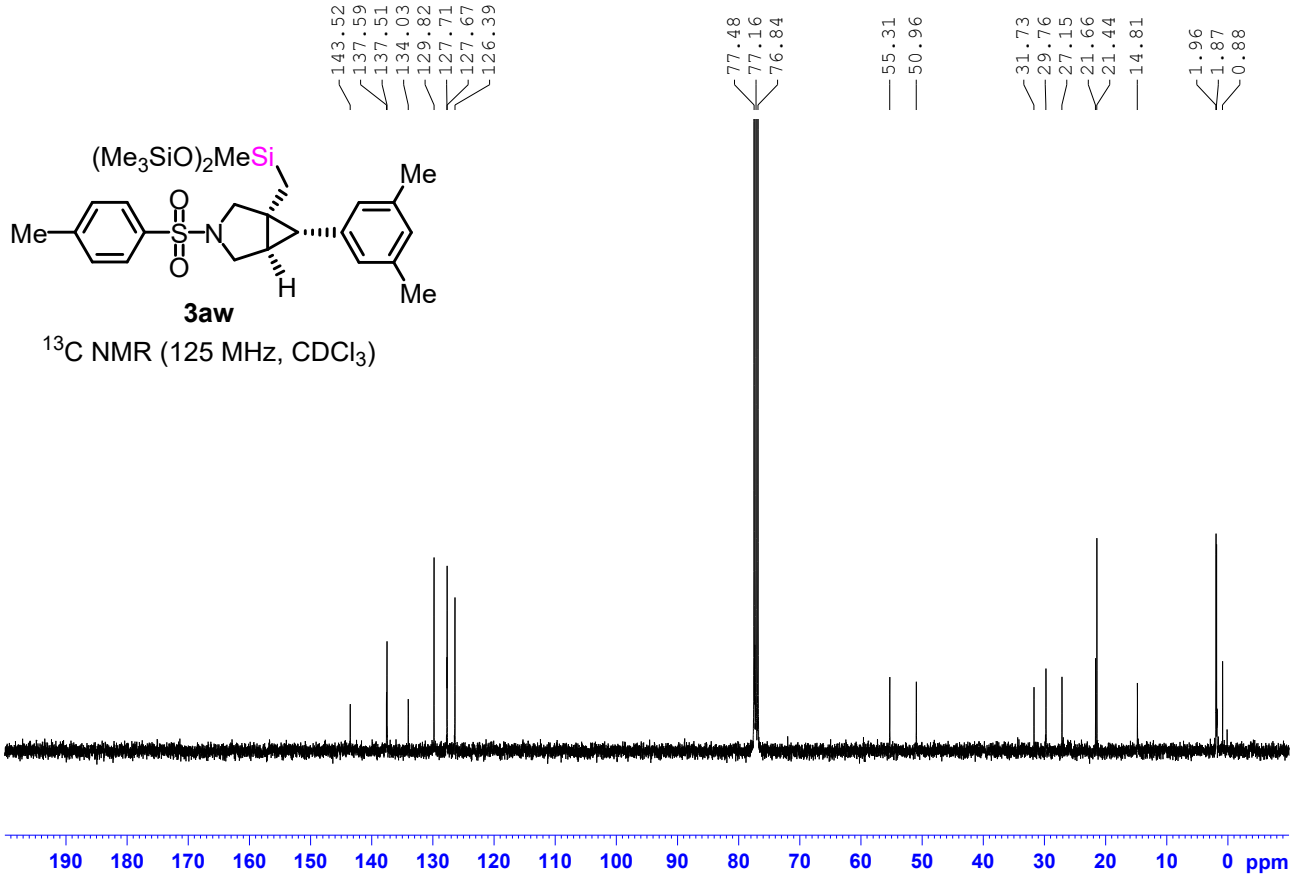
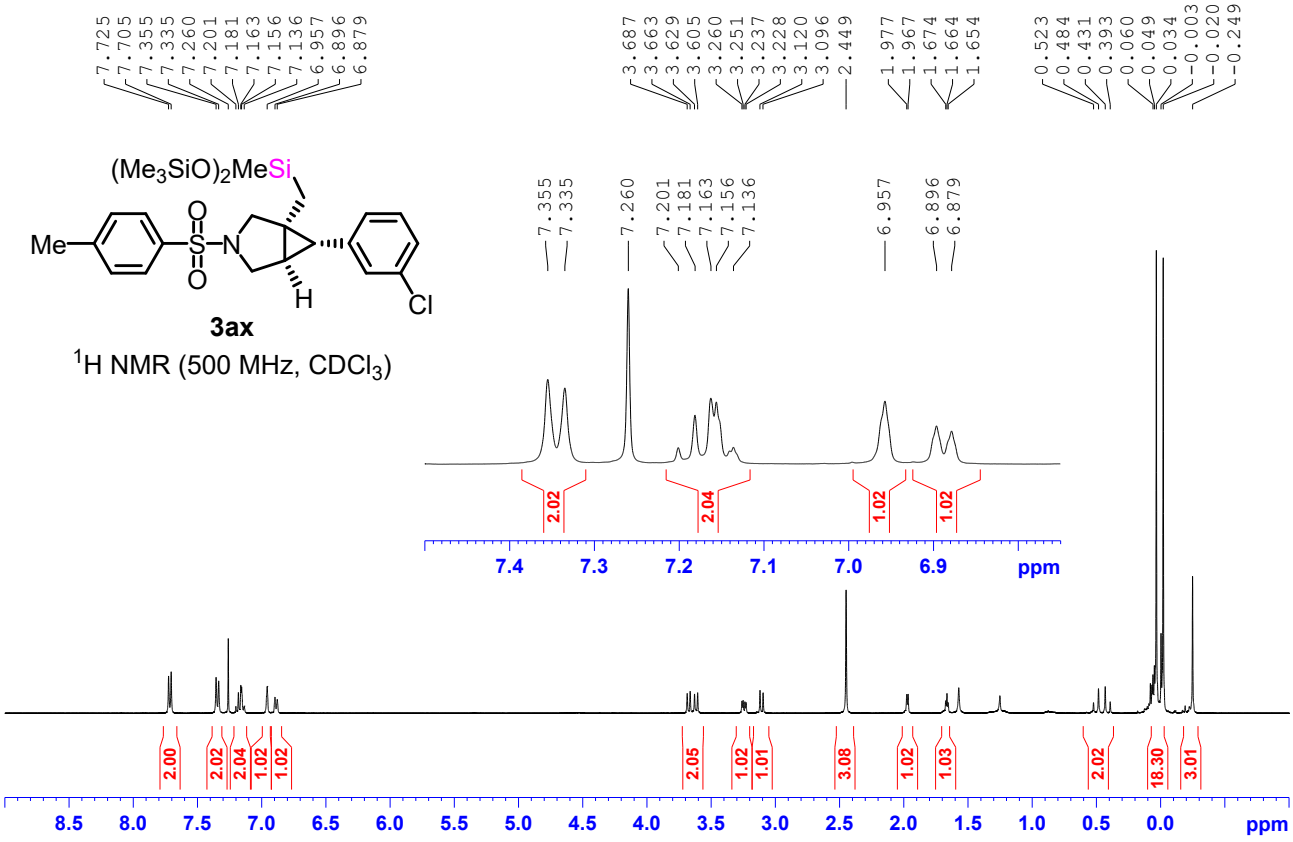
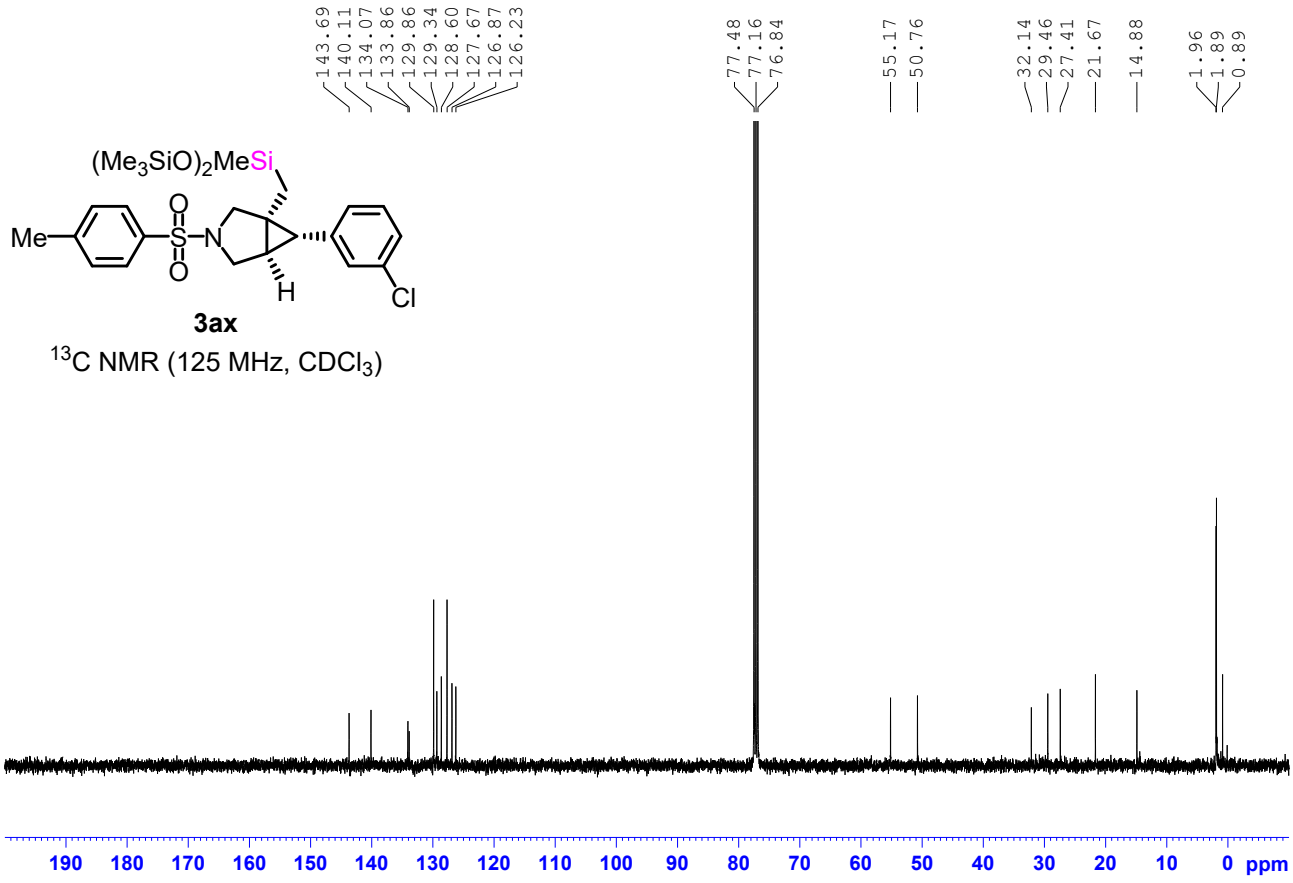
7.711
7.346
7.330
7.260
7.149
7.134
7.119
6.984
6.969
6.795
6.783
6.767
3.675
3.657
3.623
3.604
3.278
3.270
3.259
3.252
3.140
3.121
2.445
2.302
1.951
1.942
1.675
1.667
1.659
0.555
0.540
0.509
0.464
0.433
0.058
0.047
0.031
-0.013
-0.029
-0.261
(Me3SiO)2MeSi
Me
N
H
Me
3av
1H NMR (500 MHz, CDCl3)
2.00
2.04
1.06
1.01
2.03
2.09
1.02
1.03
3.07
3.06
1.02
1.03
2.05
18.20
2.95
ppm

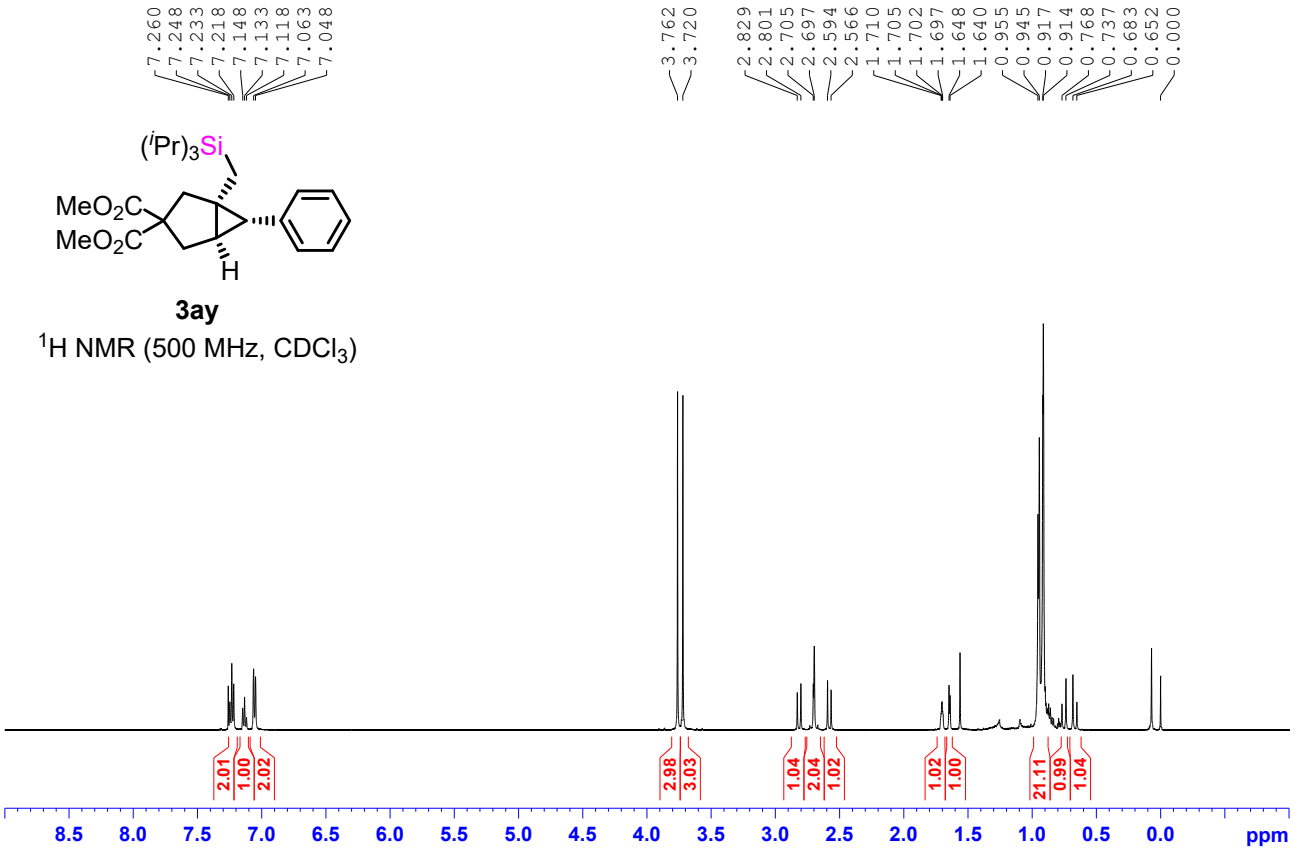

143.53
137.68
137.63
134.07
129.81
129.43
128.01
127.69
126.80
125.54
77.41
77.16
76.91
55.32
50.93
31.79
29.84
27.21
21.65
21.56
14.88
1.96
1.87
0.87
(Me3SiO)2MeSi
Me
N
H
Me
3av
13C NMR (125 MHz, CDCl3)
ppm


7.727
7.707
7.350
7.330
7.260
6.801
6.580
3.664
3.641
3.609
3.585
3.278
3.269
3.255
3.246
3.165
3.142
3.118
2.447
2.259
1.884
1.874
1.661
1.651
1.642
0.548
0.509
0.475
0.437
0.048
0.033
-0.001
-0.013
-0.029
-0.258
(Me3SiO)2MeSi
Me
Me
Me
O
S
N
O
H
3aw
1H NMR (500 MHz, CDCl3)
2.00
2.04
1.03
2.02
2.05
1.02
1.01
3.00
6.12
1.01
1.04
2.01
18.18
3.00
ppm


143.52
137.59
137.51
134.03
129.82
127.71
127.67
126.39
77.48
77.16
76.84
55.31
50.96
31.73
29.76
27.15
21.66
21.44
14.81
1.96
1.87
0.88
(Me3SiO)2MeSi
Me
Me
Me
O
S
N
O
H
3aw
13C NMR (125 MHz, CDCl3)
ppm

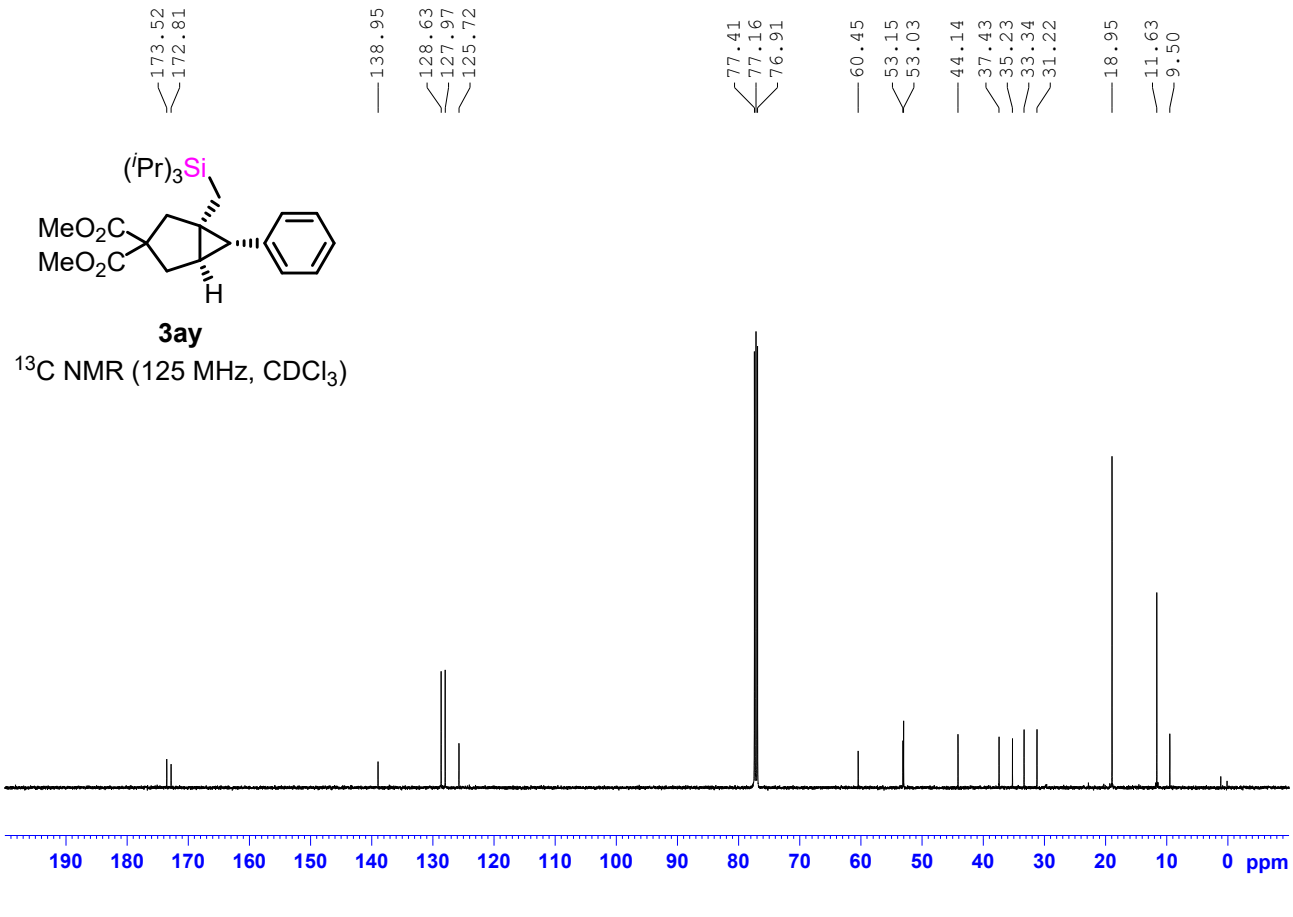

7.725
7.705
7.355
7.335
7.260
7.201
7.181
7.163
7.156
7.136
6.957
6.896
6.879
3.687
3.663
3.629
3.605
3.260
3.251
3.237
3.228
3.120
3.096
2.449
1.977
1.967
1.674
1.664
1.654
0.523
0.484
0.431
0.393
0.060
0.049
0.034
-0.003
-0.020
-0.249
(Me3SiO)2MeSi
Me
S
N
O
O
H
Cl
3ax
1H NMR (500 MHz, CDCl3)
2.02
2.04
1.02
1.02
2.00
2.02
2.04
1.02
1.02
2.05
1.02
1.01
3.08
1.02
1.03
2.02
18.30
3.01
ppm


143.69
140.11
134.07
133.86
129.86
129.34
128.60
127.67
126.87
126.23
77.48
77.16
76.84
55.17
50.76
32.14
29.46
27.41
21.67
14.88
1.96
1.89
0.89
(Me3SiO)2MeSi
Me
S
N
O
O
H
Cl
3ax
13C NMR (125 MHz, CDCl3)
ppm



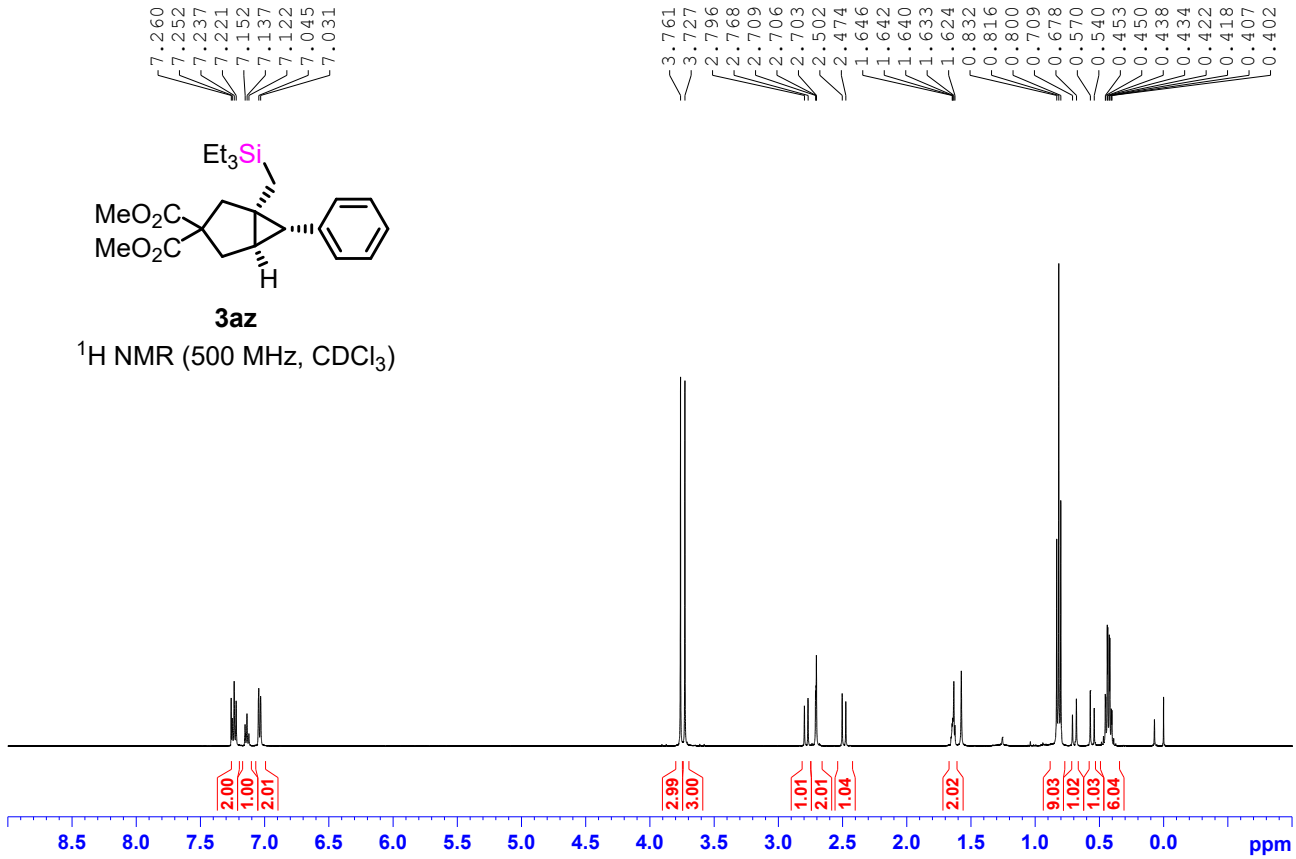
3ay

^{1}H NMR (500 MHz, $CDCl_3$)



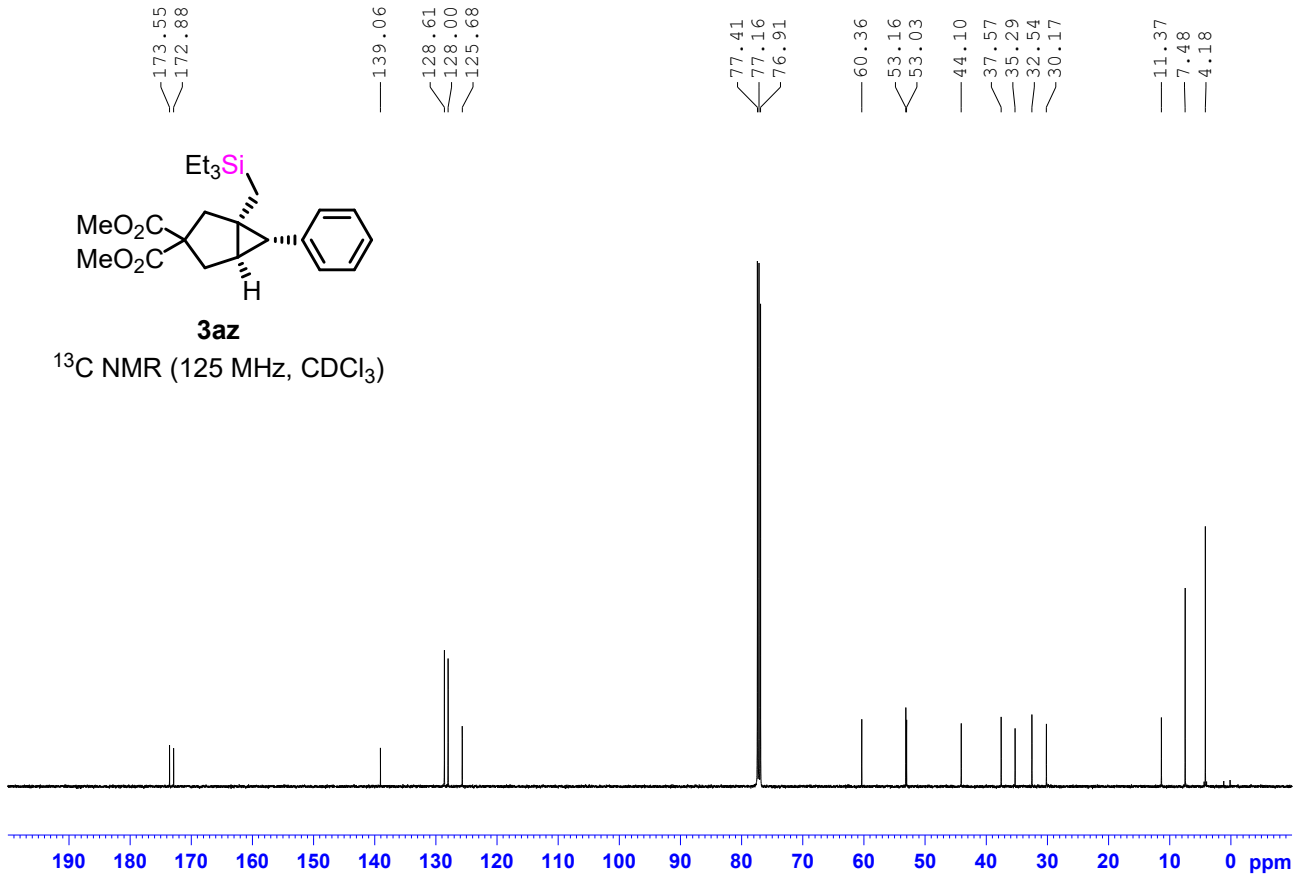
3ay

^{13}C NMR (125 MHz, $CDCl_3$)



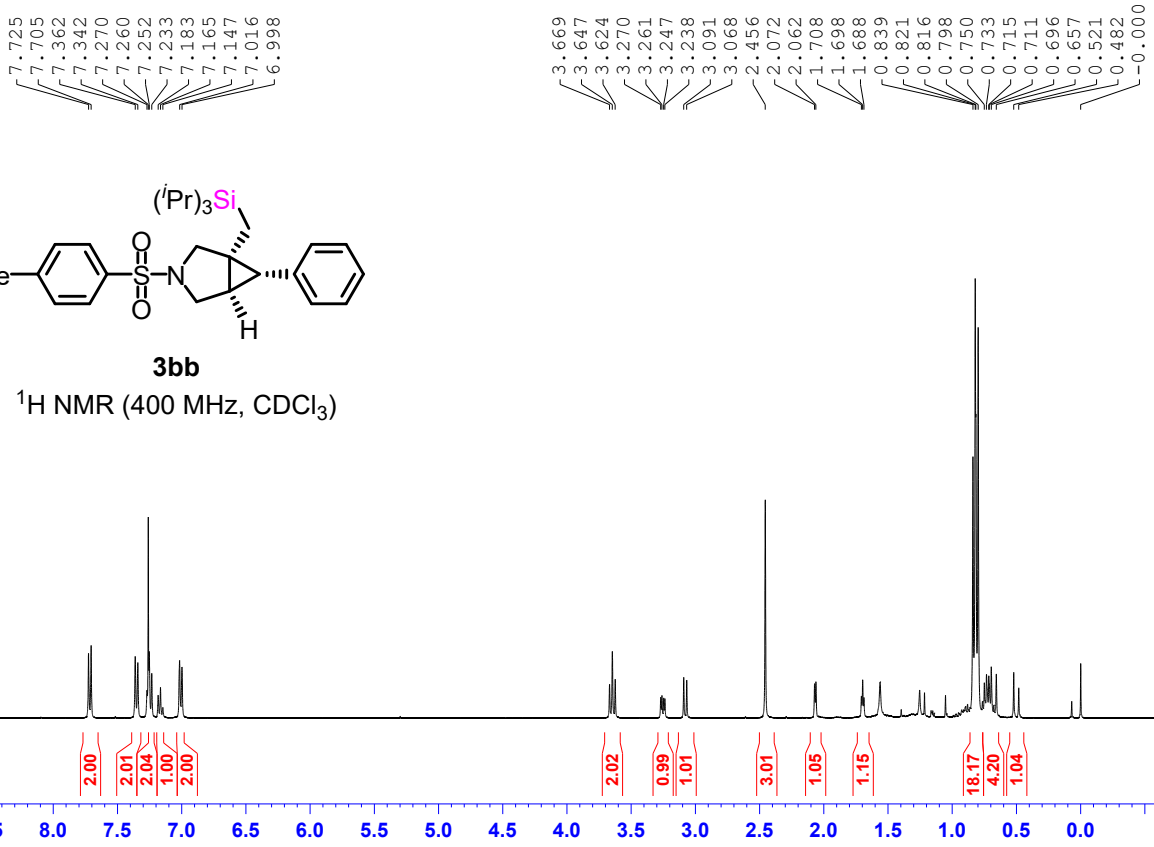
3az

^{1}H NMR (500 MHz, $CDCl_3$)



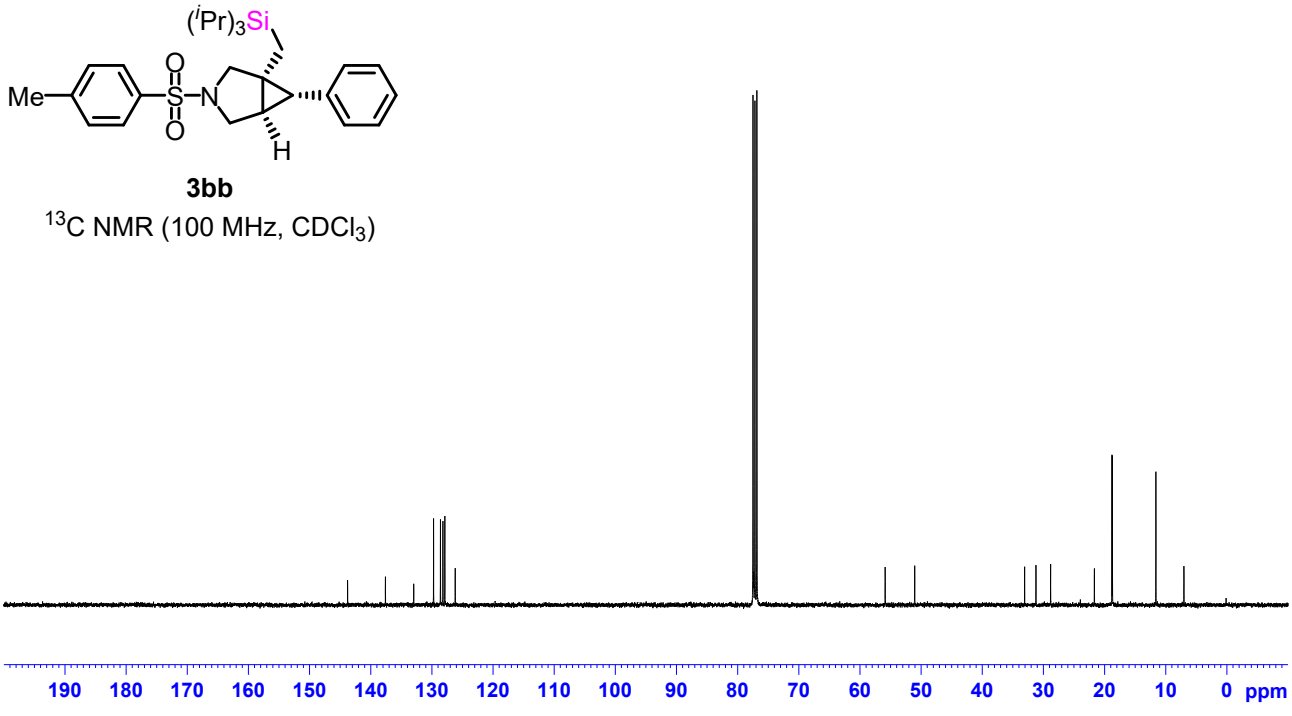
3az

^{13}C NMR (125 MHz, $CDCl_3$)



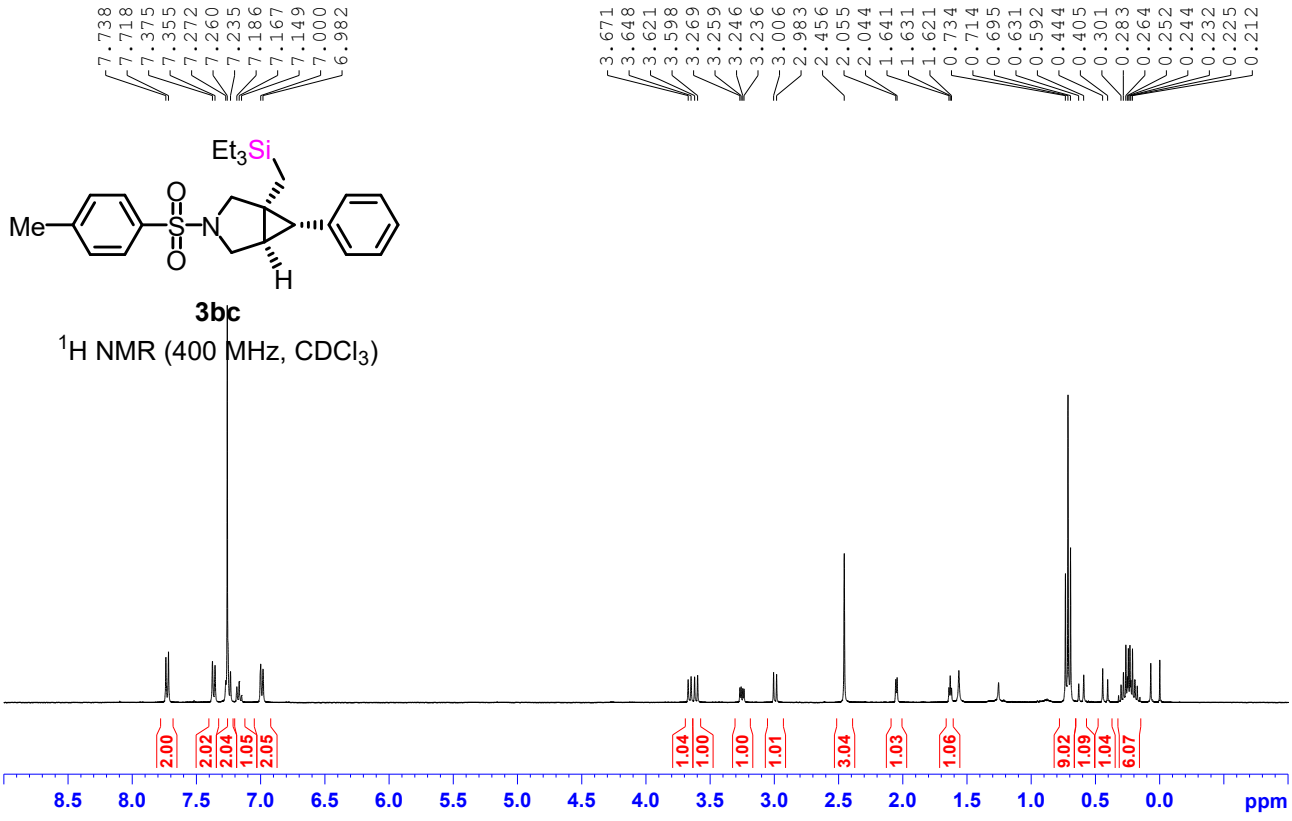
3bb

^{1}H NMR (400 MHz, $CDCl_3$)



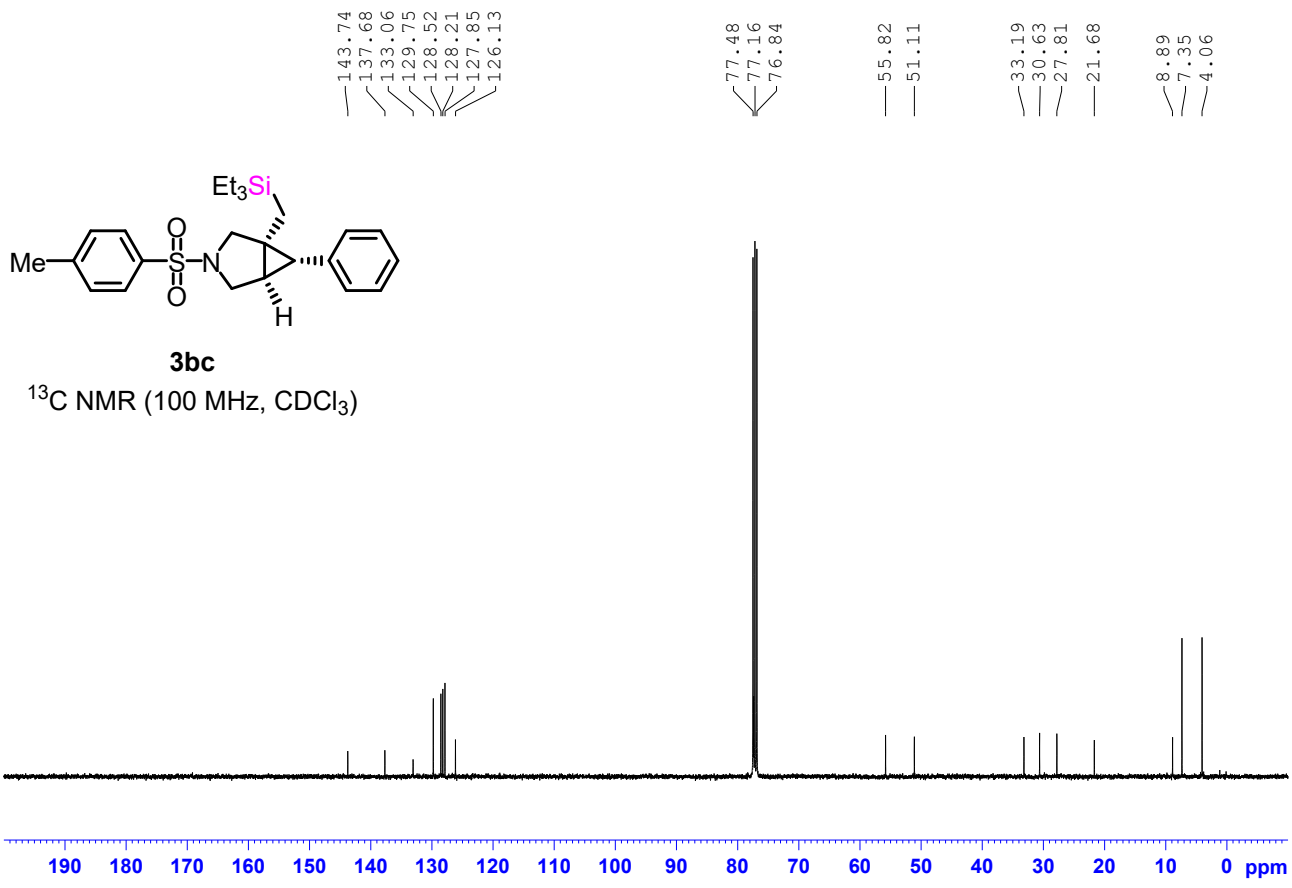
3bb

^{13}C NMR (100 MHz, $CDCl_3$)



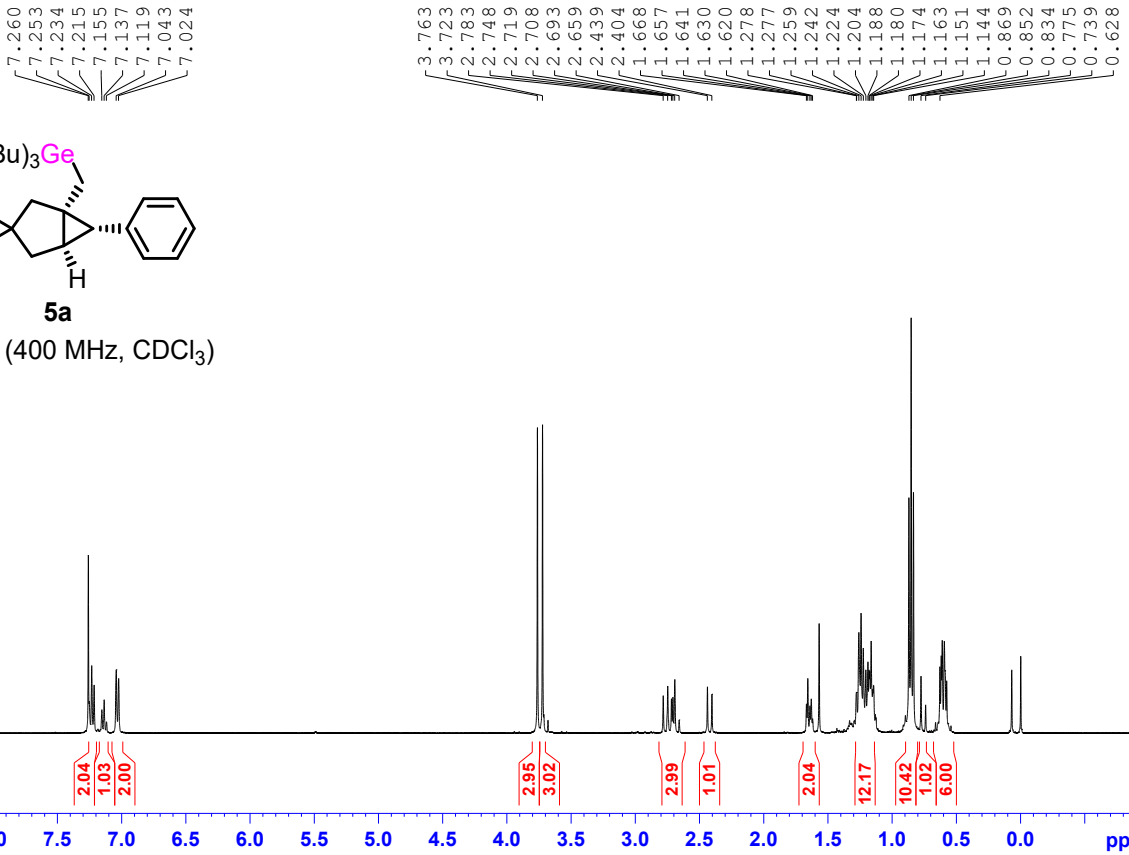
3bc

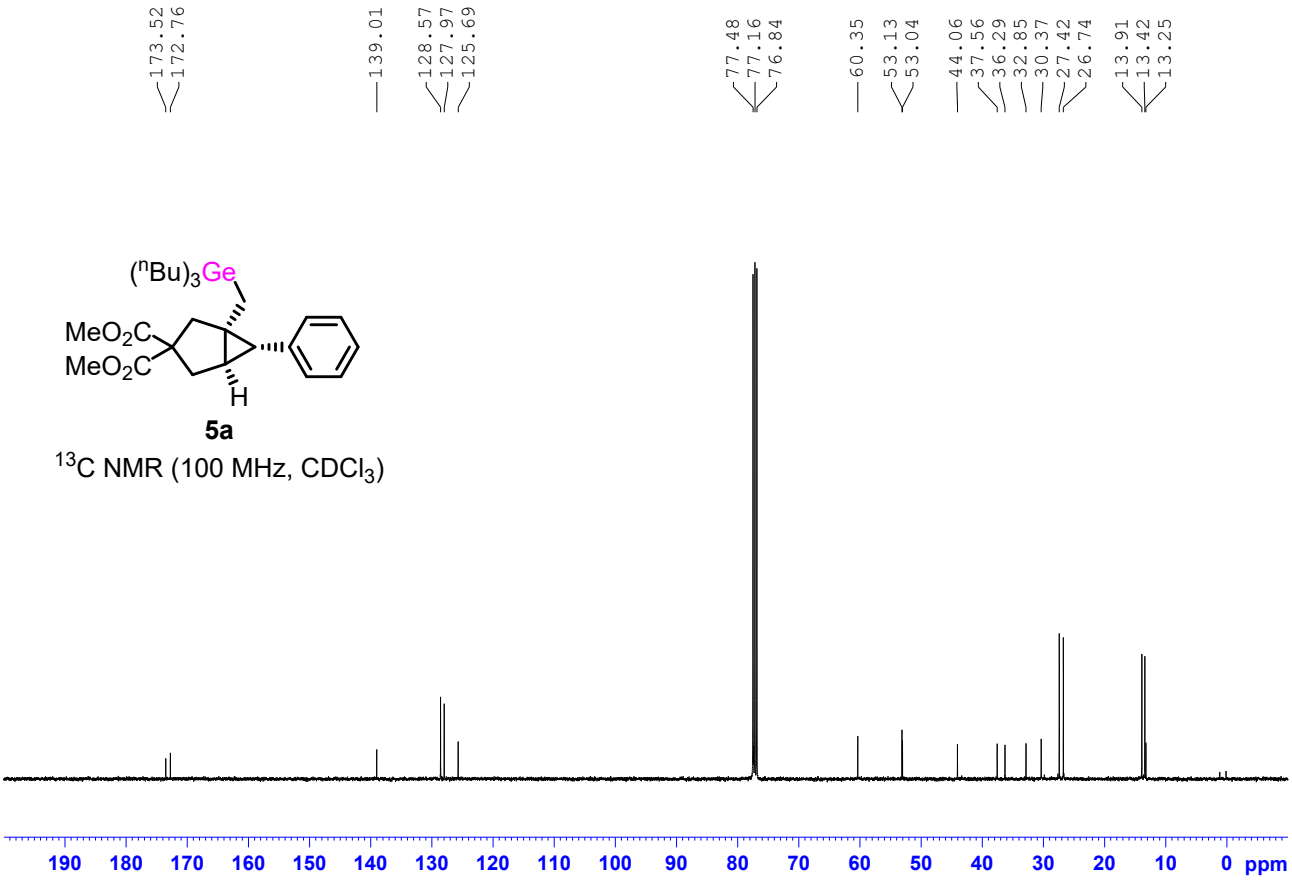
^{1}H NMR (400 MHz, $CDCl_3$)

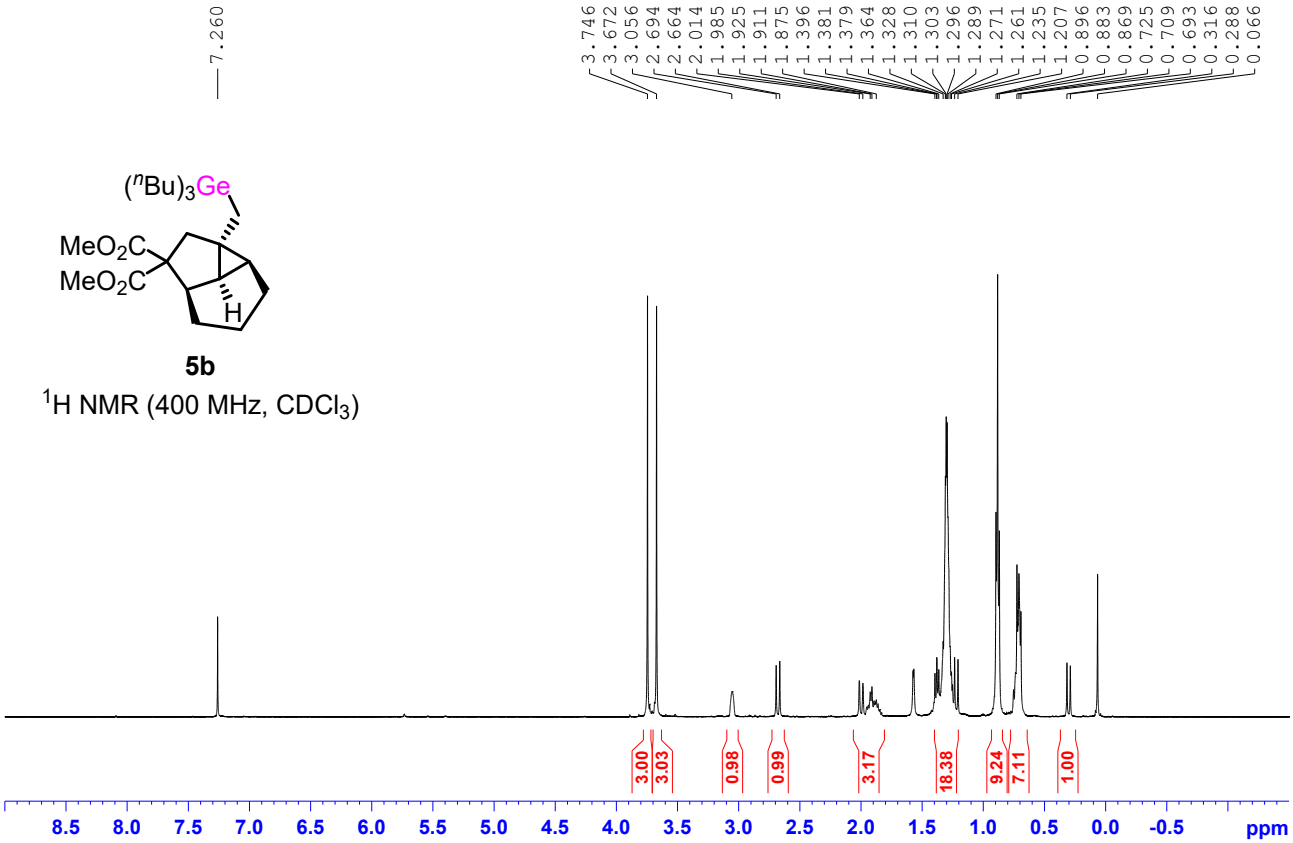


3bc

^{13}C NMR (100 MHz, $CDCl_3$)

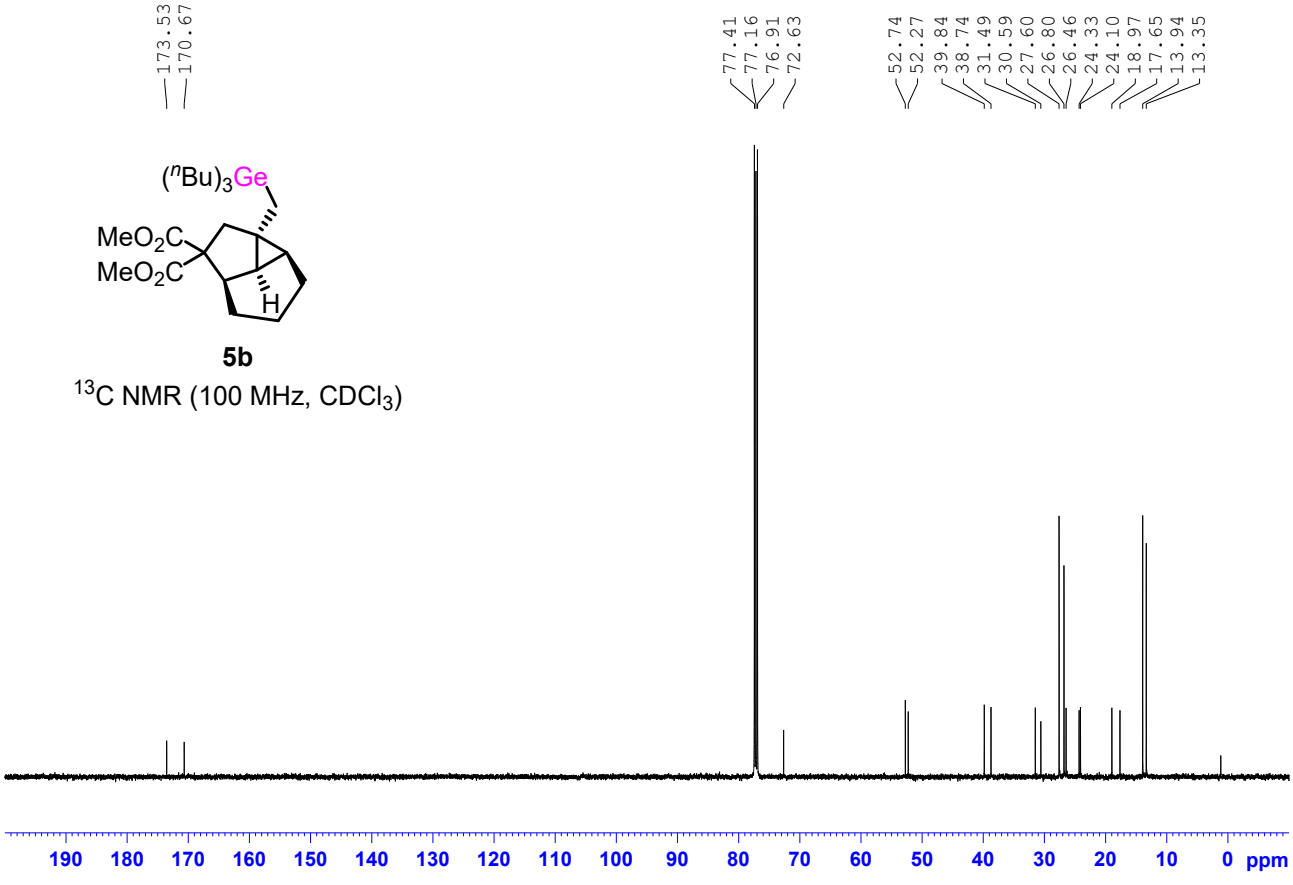

7.260
7.253
7.234
7.215
7.155
7.137
7.119
7.043
7.024
3.763
3.723
2.783
2.748
2.719
2.708
2.693
2.659
2.439
2.404
1.668
1.657
1.641
1.630
1.620
1.278
1.277
1.259
1.242
1.224
1.204
1.188
1.180
1.174
1.163
1.151
1.144
0.869
0.852
0.834
0.775
0.739
0.628
(nBu)3Ge
MeO2C
MeO2C
H
5a
1H NMR (400 MHz, CDCl3)
2.04
1.03
2.00
2.95
3.02
2.99
1.01
2.04
12.17
10.42
1.02
6.00
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
ppm


173.52
172.76
139.01
128.57
127.97
125.69
77.48
77.16
76.84
60.35
53.13
53.04
44.06
37.56
36.29
32.85
30.37
27.42
26.74
13.91
13.42
13.25
(nBu)3Ge
MeO2C
MeO2C
H
5a
13C NMR (100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



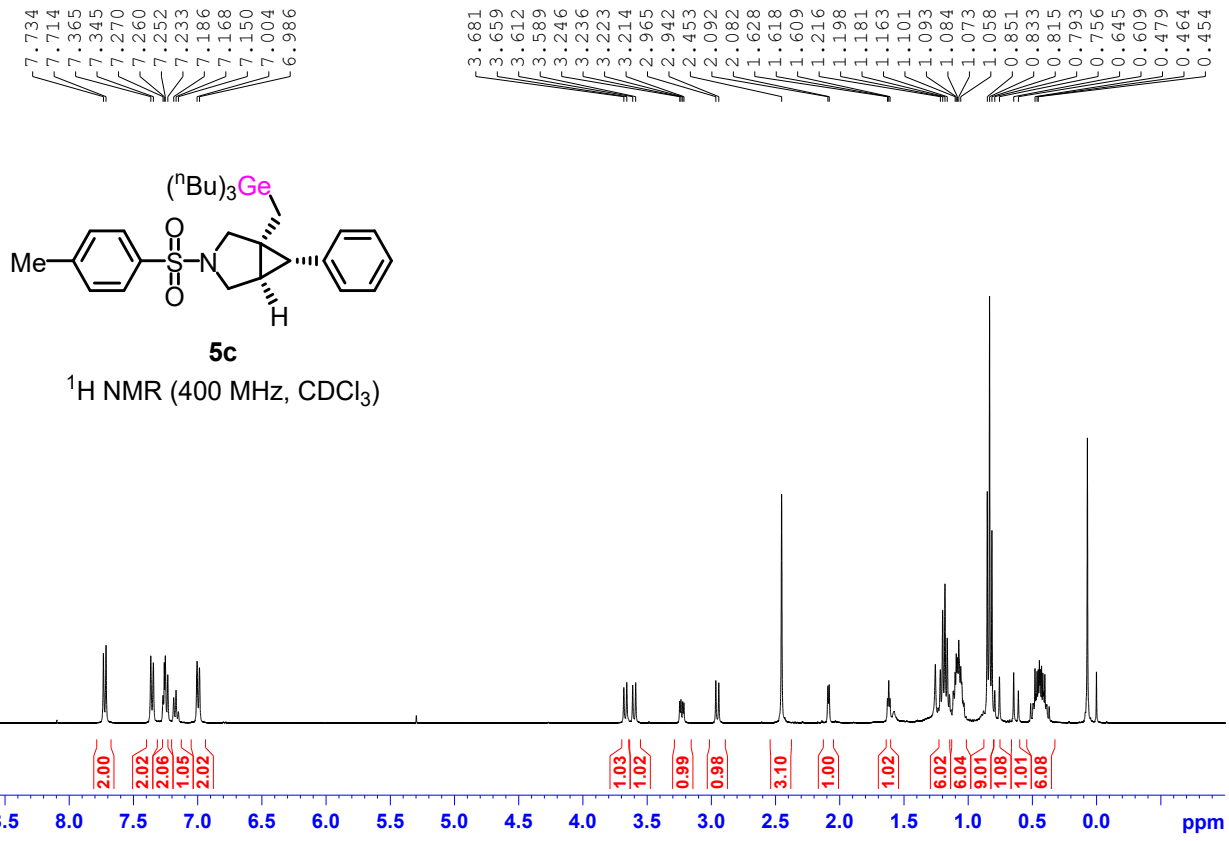
5b

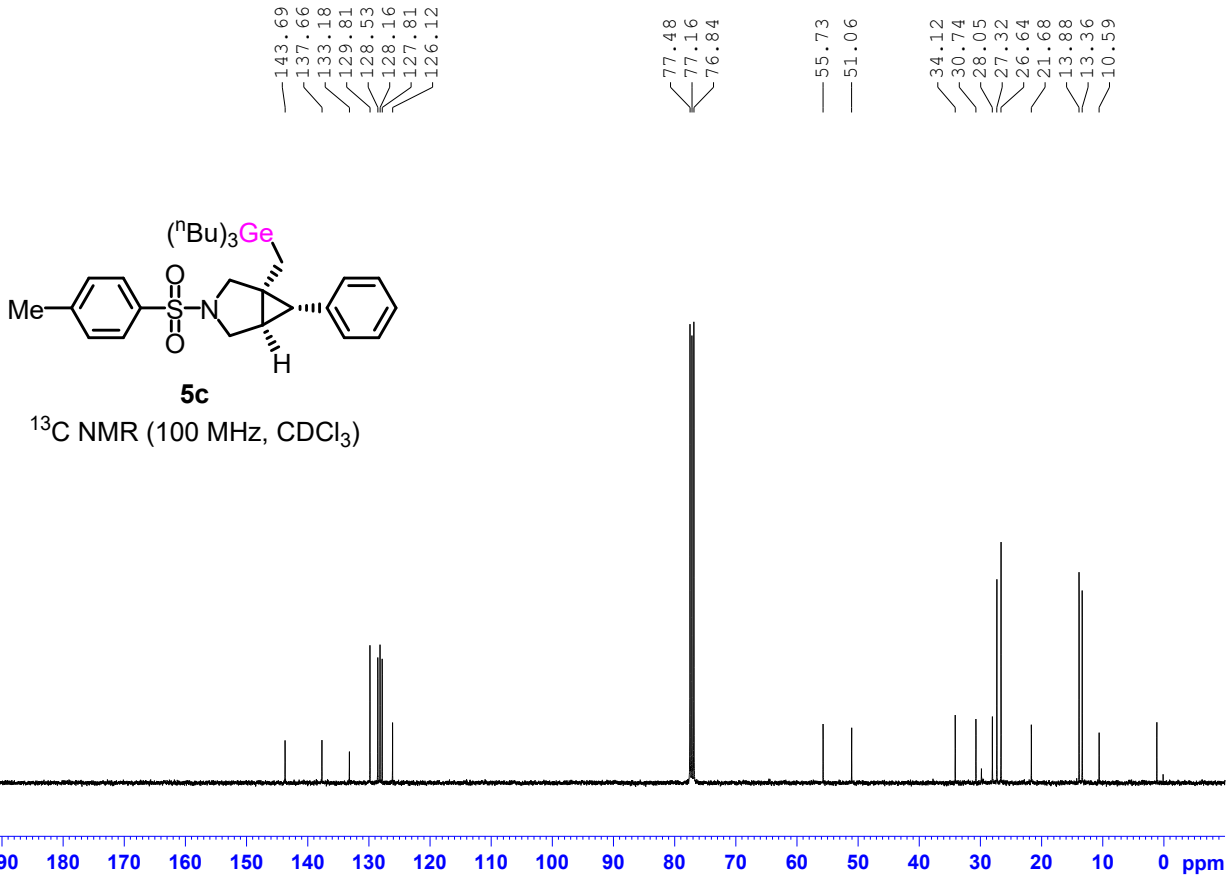
^{1}H NMR (400 MHz, $CDCl_3$)

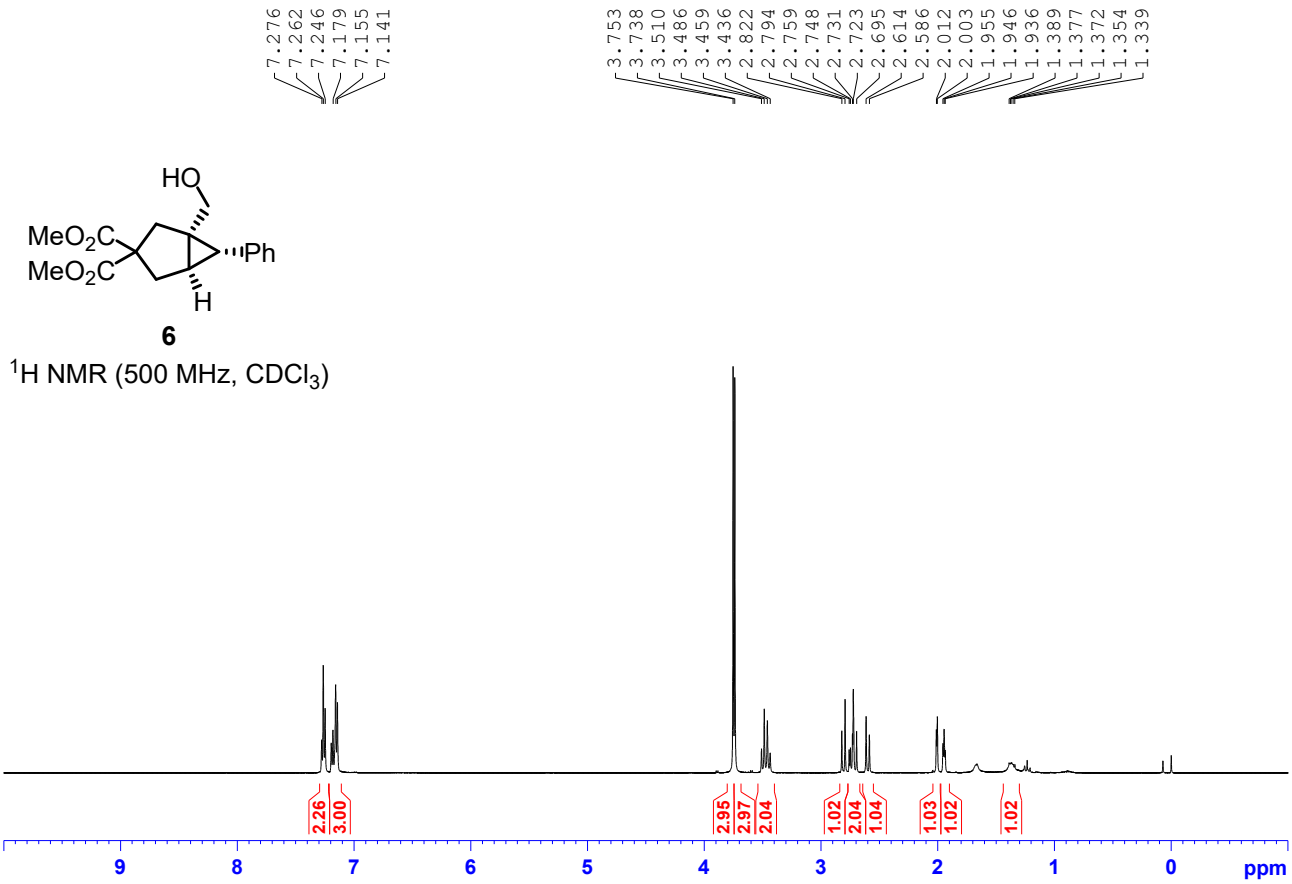


5b

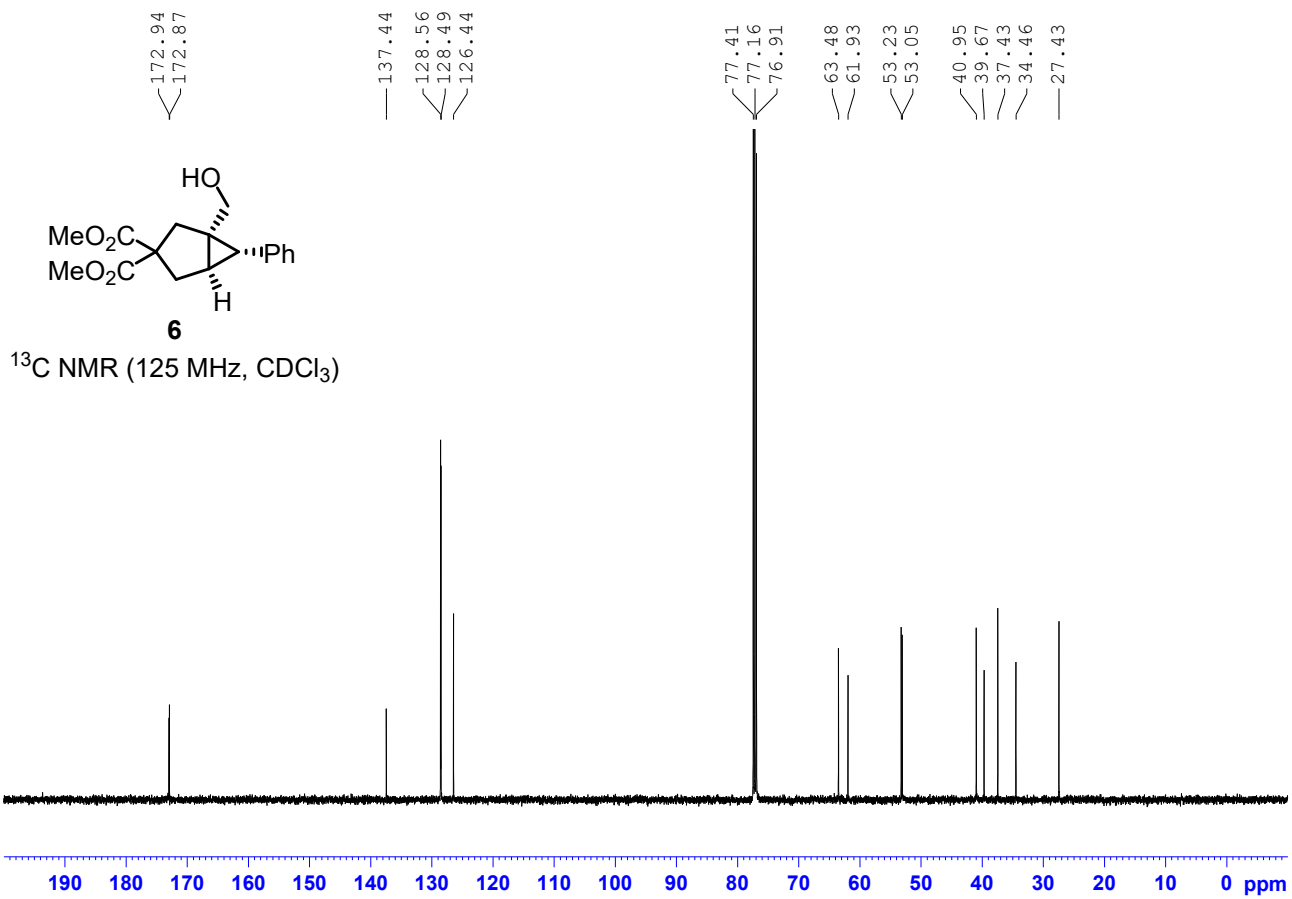
^{13}C NMR (100 MHz, $CDCl_3$)


7.734
7.714
7.365
7.345
7.270
7.260
7.252
7.233
7.186
7.168
7.150
7.004
6.986
3.681
3.659
3.612
3.589
3.246
3.236
3.223
3.214
2.965
2.942
2.453
2.092
2.082
1.628
1.618
1.609
1.216
1.198
1.181
1.163
1.101
1.093
1.084
1.073
1.058
0.851
0.833
0.815
0.793
0.756
0.645
0.609
0.479
0.464
0.454
(nBu)3Ge
Me
O
S
N
O
H
5c
1H NMR (400 MHz, CDCl3)
2.00
2.02
2.06
1.05
2.02
1.03
1.02
0.99
0.98
3.10
1.00
1.02
6.02
6.04
9.01
1.08
1.01
6.08
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
ppm

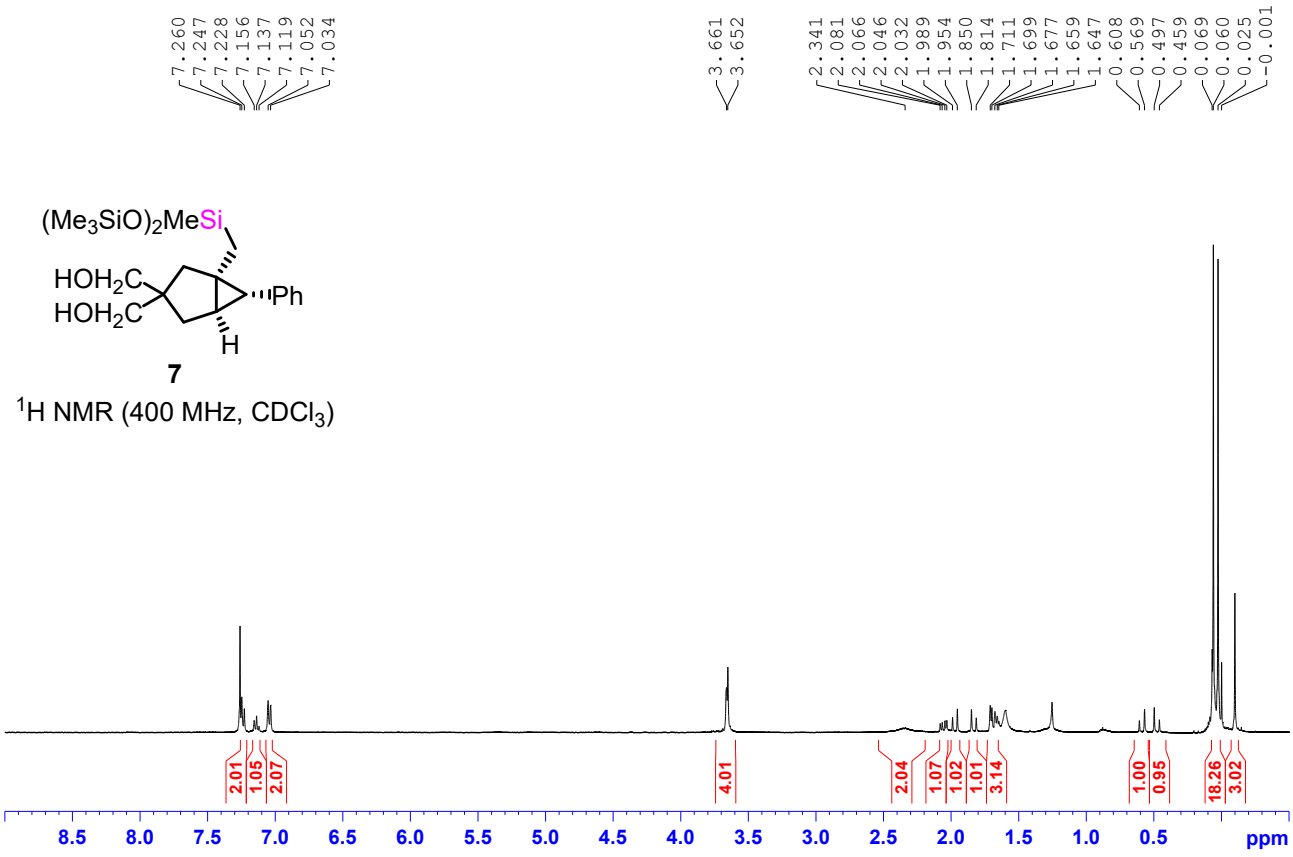

143.69
137.66
133.18
129.81
128.53
128.16
127.81
126.12
77.48
77.16
76.84
55.73
51.06
34.12
30.74
28.05
27.32
26.64
21.68
13.88
13.36
10.59
(nBu)3Ge
Me
O
S
N
O
H
5c
13C NMR (100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



^{1}H NMR (500 MHz, $CDCl_3$)

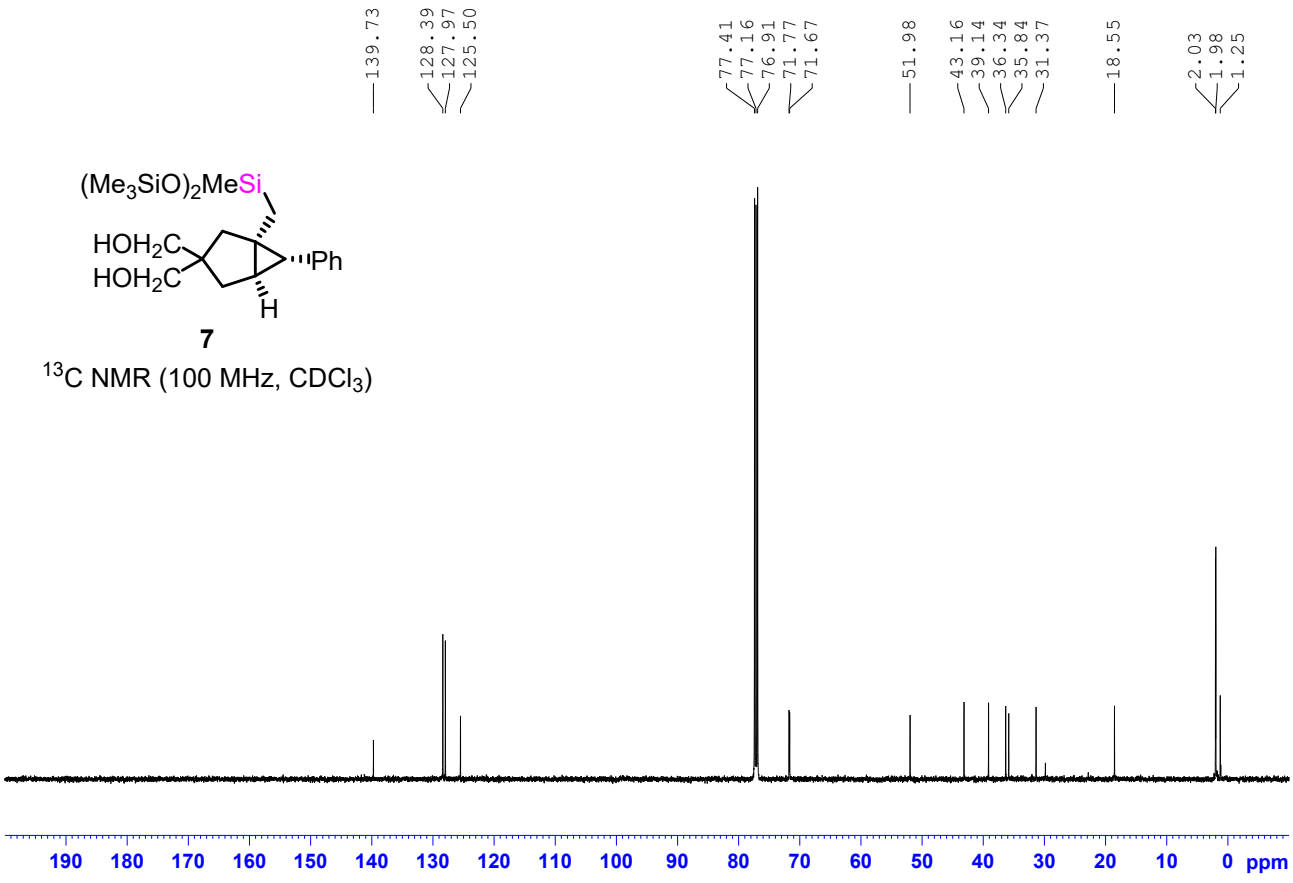


^{13}C NMR (125 MHz, $CDCl_3$)



7

^{1}H NMR (400 MHz, $CDCl_3$)



7

^{13}C NMR (100 MHz, $CDCl_3$)