Synthesis and Kinetics of Disassembly for Silyl-Containing Ethoxycarbonyls using Fluoride Ions

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Supporting Information

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General Experimental Information:

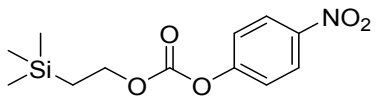
Materials for synthesis of the silyl-containing molecules include: trimethylsilylethanol, diphenylmethylsilyl ethanol, 4-methoxyisocyanate, 4-tolyl isocyanate, phenyl isocyanate, 3-trifluoromethyl isocyanate, 4-nitrophenyl isocyanate, 4-methoxychloroformate, 4-tolyl chloroformate, phenyl chlorofomate, 4-nitrophenyl chloroformate, 4-nitrophenyl (2-(trimethylsilyl)ethyl) carbonate, disuccinimidyl carbonate, ethanolamine, N-methylethanolamine, sodium hydroxide, 9-borabicyclo[3.3.1]nonane (9-BBN, 0.5 M in THF), hydrogen peroxide (30 wt.% in water) and vinyl magnesium bromide (1 M in THF). All were readily available through Sigma-Aldrich. Dimethyldivinyl silane and diphenyldichlorosilane were available through Gelest. Fluoride salts, such as tetrabutylammonium fluoride trihydrate, tetrabutylammonium fluoride (1 M in THF), cesium fluoride, sodium fluoride, potassium fluoride and stannous fluoride, were also purchased from Sigma-Aldrich. All chemicals were used as received.

NMR spectra were performed on a 300 MHz NMR spectrometer and subsequently worked-up on Spinworks Version 4.2.3.0. ^{13}C NMR spectra were correspondingly recorded at 75 MHz. Chemical shifts (δ) for ^{1}H and ^{13}C are presented in ppm against tetramethylsilane as an internal standard reference. *J* values are reported in Hz. Deuterated solvents, such as chloroform-*d* and acetone-d_6, were purchased from Sigma Aldrich. NMR data is reported as follows: chemical shift, multiplicity (bs = broad singlet, bt = broad triplet, s = singlet, d = doublet, t = triplet, q = quartet), coupling constant(s) in Hz, and integration. Thin layer chromatography (TLC) was used in conjunction with column chromatography to determine the species formed post-TBAF exposure. TLC was performed on EMD silica gel 60 F_{254} plates and column chromatography was performed using flash grade silica gel (SiO_2, 32-63μm). UV-Vis spectra were obtained on an Agilent 8453 UV-Visible spectrophotometer, and subsequently analyzed with Chemstation software. A typical preparation involved dissolving the silyl-containing molecule in tetrahydrofuran (THF) to achieve a 0.1 mM concentration. Four equivalents of tetrabutylammonium fluoride (TBAF, 1.0 M in THF) were added to per UV-detectable group of the silyl-containing molecule and the reaction was monitored with UV-Vis spectroscopy until the absorbance of the starting material ceased to decrease. The molar absorptivity of each sample was determined for the λ_{max} allowing kinetic comparisons between different molecules.

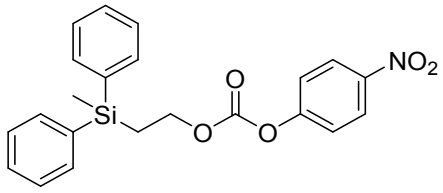
GC-MS was utilized for confirmation of molecular disassembly. Samples exposed to TBAF were tested on an Agilent 7890A gas chromatograph equipped with an Agilent 5975C mass selective detector and an Agilent 7693A auto injector. The column used for separation was a Restek Rxi-5ms. The GC method run started at 55 °C, was held for 3 min, then a 5 °C ramp to 150 °C followed by a 10 °C ramp to 300 °C with a flow of 1.25 mL/min. The inlet, quadrupole and ion source temperatures were 250, 150, and 230 °C, respectively. The MS was run in scan mode with a range of 35-500 amu. High resolution mass spectrometry (HRMS) was performed on a Bruker FT-ICR Apex IV qQ equipped with a 12T superconductor magnet and run with ESI source in positive mode with a capillary voltage of 3 KV, drying gas flow of 8 L/min at 220 °C, and was infused at 10 μL/min. The MS was run in scan mode with a range of 100-1000 amu.

Procedures for Synthesis of Silyl-Terminated Carbonates

To a solution of the corresponding silyl alcohol in THF, the corresponding isocyanate or chloroformate was added at room temperature and allowed to stir for overnight. The reaction mixture was extracted with dichloromethane and brine, dried with magnesium sulfate, and then concentrated *in vacuo*. The resulting mixture was purified using column chromatography to furnish the product.



4-nitrophenyl (2-(trimethylsilyl)ethyl) carbonate (1a): To a solution of trimethylsilyl ethanol (1.4 mL, 9.92 mmol) in THF (25 mL), 4-nitrophenyl chloroformate (1 g, 4.96 mmol) was added at room temperature and let stir for overnight. The reaction mixture was extracted with dichloromethane and brine, dried with magnesium sulfate, and then concentrated *in vacuo*. The resulting mixture was purified using column chromatography (ethyl acetate/hexane: 20/80) to furnish the product (2.05 g) as a solid in 73% yield. The NMR spectra matched the reported literature spectra.[1]



2-(methyldiphenylsilyl)ethyl (4-nitrophenyl) carbonate (1c): To a solution of diphenylmethylsilyl ethanol (958 mg, 4.12 mmol) in THF (10 mL), 4-nitrophenyl chloroformate (915 mL, 4.54 mmol) was added at room temperature and let stir for overnight. The reaction mixture was extracted with dichloromethane and brine, dried with magnesium sulfate, and then concentrated *in vacuo*. The resulting mixture was purified using column chromatography (ethyl acetate/hexane: 20/80) to furnish the product (1.44 g) as a solid in 86% yield. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ = 8.28 (d, *J* = 9.4 Hz, 2H), 7.61 (m, 4H), 7.44 (m, 6H), 7.35 (d, *J* = 8.9 Hz, 2H), 4.48 (t, *J* = 8.8 Hz , 2H), 1.79 (t, *J* = 8.8 Hz, 2H), 0.71 (s, 3H) ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ = 155.62, 152.45, 145.34, 135.39, 134.40, 129.80, 128.20, 125.31, 121.88, 67.76, 15.56, -4.03. HRMS (EIC) *m/z* calculated for $C_{22}H_{21}NO_5Si$ $[M]^-$ 407.1189, found 407.1140.

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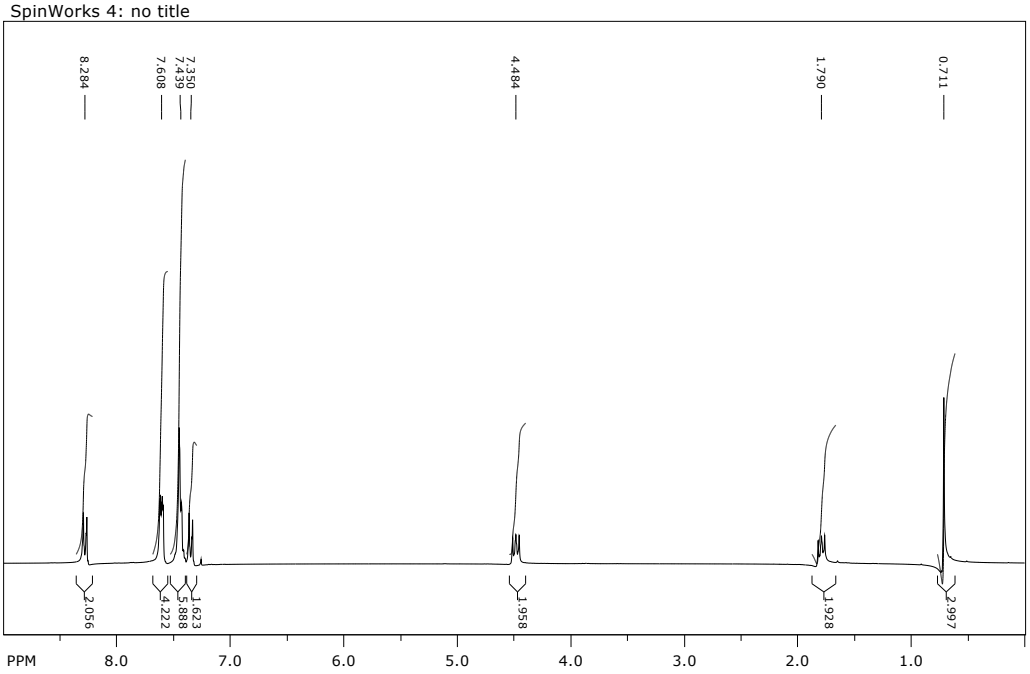

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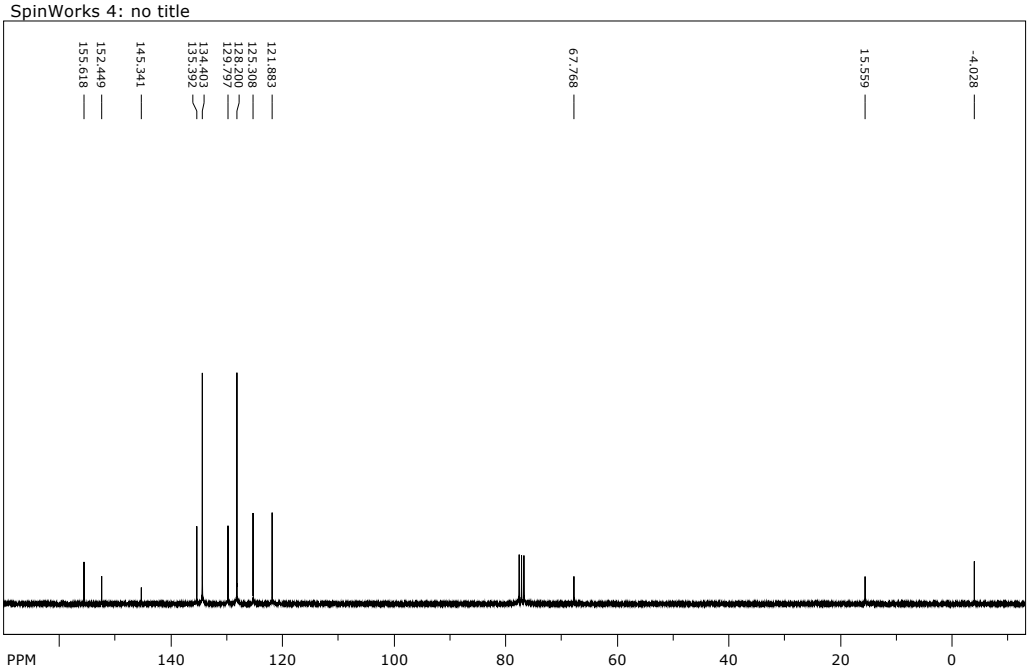

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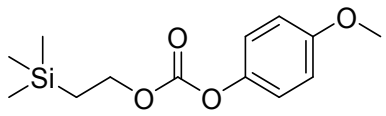
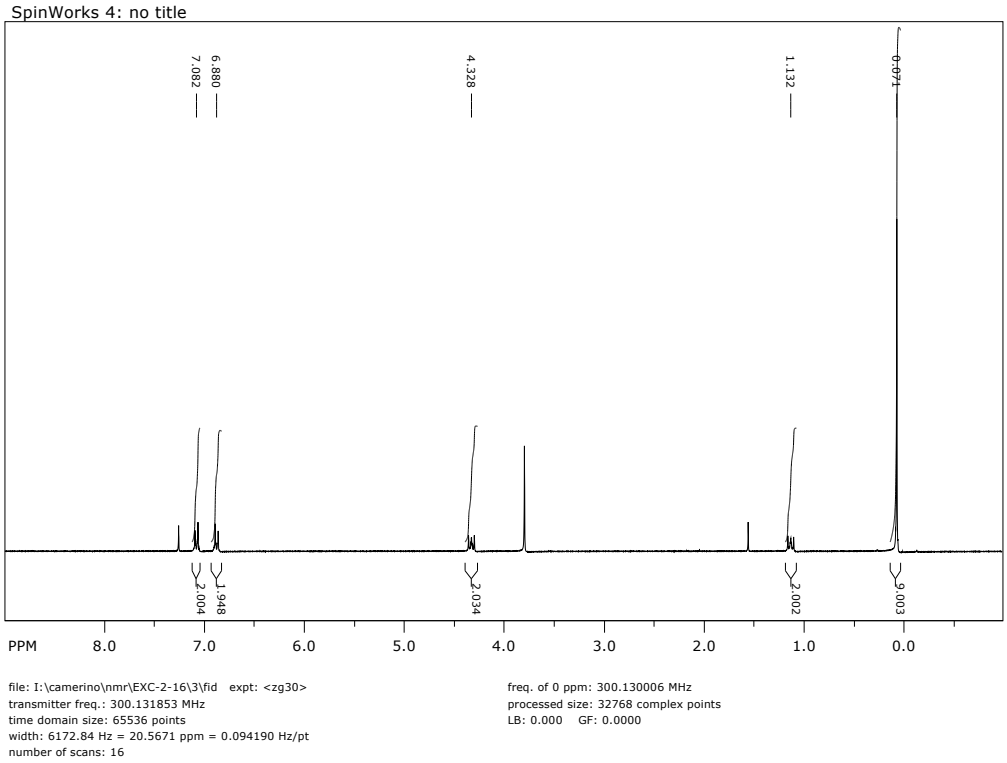
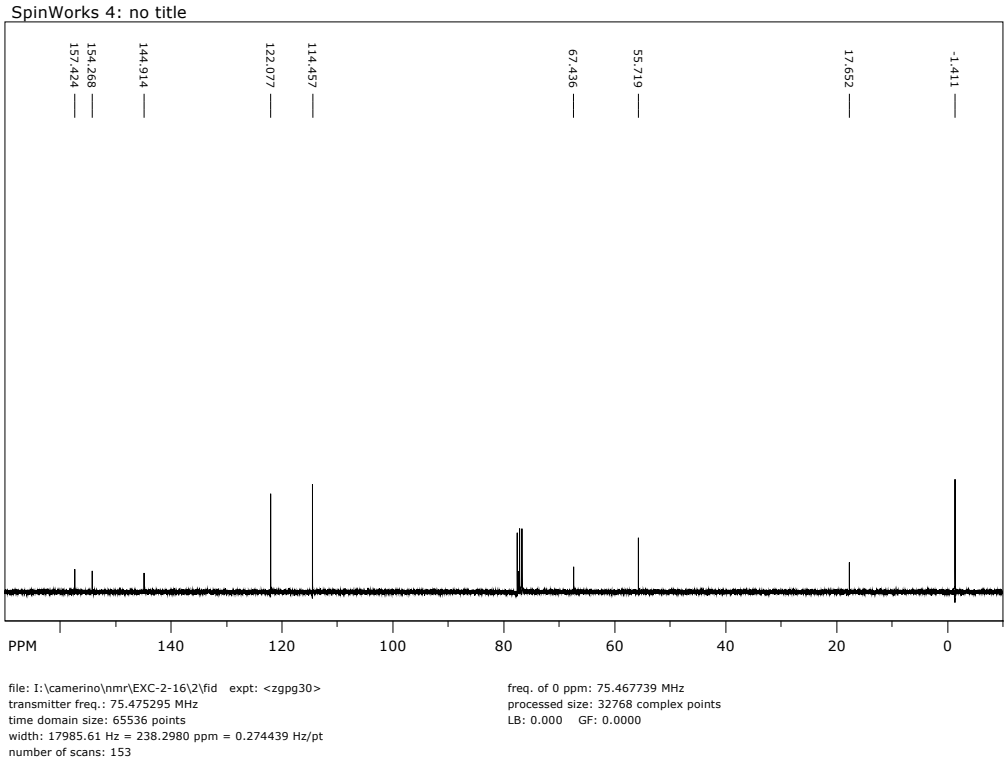
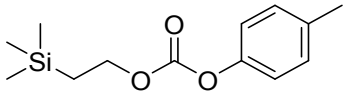


4-methoxyphenyl (2-(trimethylsilyl)ethyl) carbonate: To a solution of trimethylsilyl ethanol (0.63 mL, 4.31 mmol) in THF (10 mL), 4-methoxyphenyl chloroformate (0.62 mL, 4.19 mmol) was added at room temperature and let stir for overnight. The reaction mixture was extracted with dichloromethane and brine, dried with magnesium sulfate, and then concentrated *in vacuo*. The resulting mixture was purified using column chromatography (ethyl acetate/hexane: 3/97) to furnish the product (1.7 g) as a clear liquid in 95% yield. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ = 7.08 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 9 Hz, 2H), 4.33 (t, *J* = 9 Hz, 2H), 1.13 (t, *J* = 8.7 Hz, 2H), 0.07 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ = 157.42, 154.27, 144.91, 122.08, 114.46, 67.44, 55.72, 17.65, -1.41. HRMS (EIC) *m/z* calculated for $C_{13}H_{20}O_4SiNa$ [M + Na]$^+$ 291.3904, found 291.3946.







***p*-tolyl (2-(trimethylsilyl)ethyl) carbonate:** To a solution of trimethylsilyl ethanol (0.63 mL, 4.31 mmol) in THF (10 mL), p-tolyl chloroformate (0.60 mL, 4.19 mmol) was added at room temperature and let stir for overnight. The reaction mixture was extracted with dichloromethane and brine, dried with magnesium sulfate, and then concentrated *in vacuo*. The resulting mixture was purified using column chromatography (ethyl acetate/hexane: 0/100) to furnish the product (0.14g) as a clear liquid in 13% yield. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ = 7.17 (d, *J* = 8.5 Hz, 2H), 7.05 (d, *J* = 8.5Hz, 2H), 4.34 (t, *J* = 8.8 Hz, 2H), 2.34 (s, 3H), 1.14 (t, *J* = 8.8 Hz, 2H), 0.08 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ = 154.06, 149.14, 135.72, 130.04, 120.93, 67.42, 20.96, 17.60, -1.41. HRMS (ESI) *m/z* calculated for $C_{13}H_{20}O_3SiNa$ $[M + Na]^+$ 275.1074, found 275.1074.

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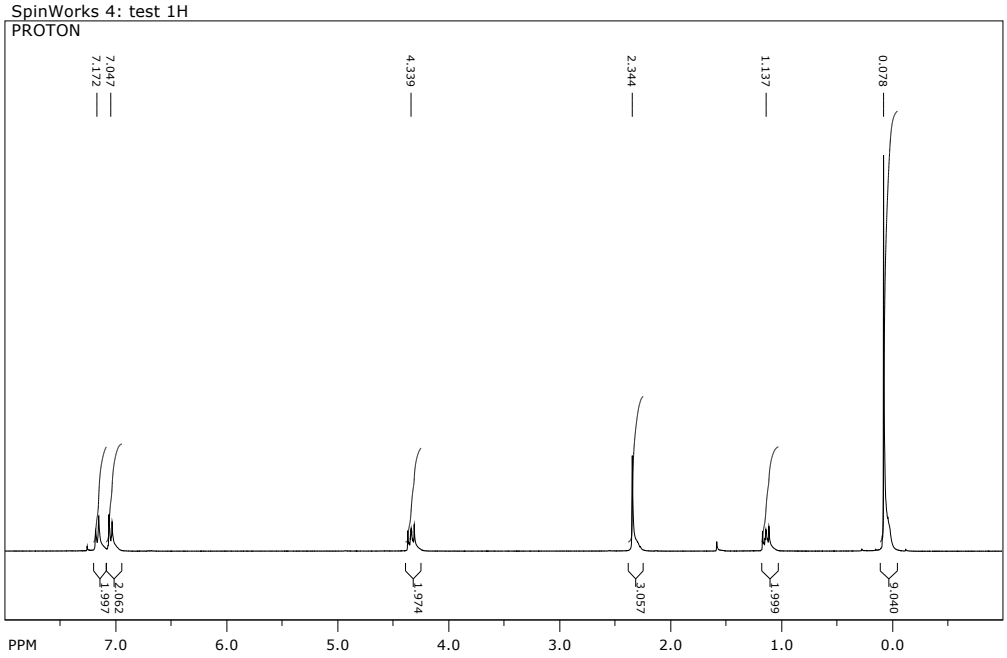

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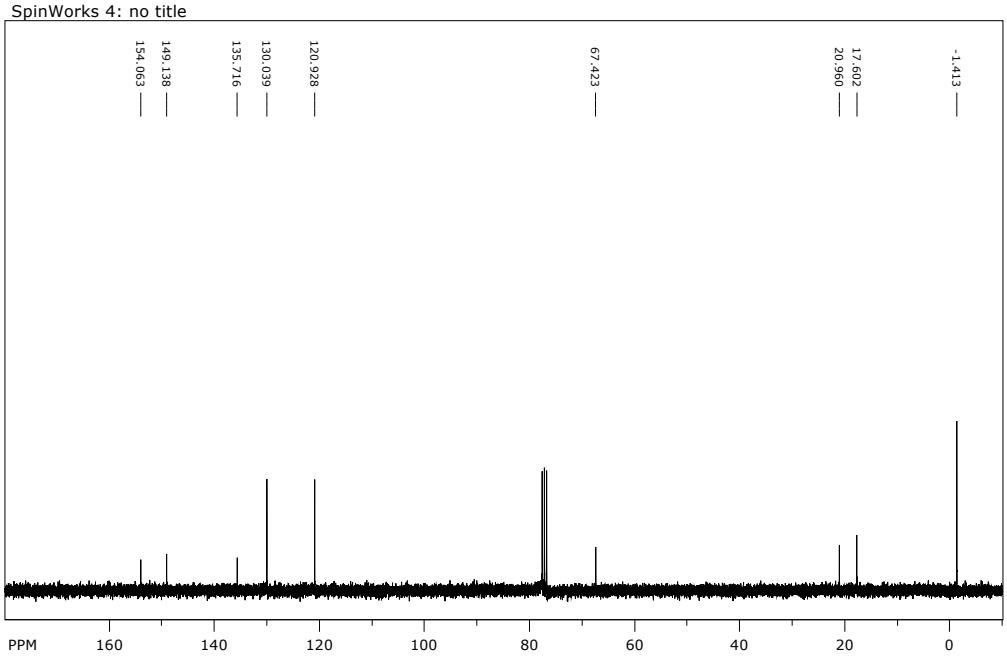

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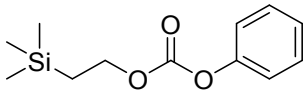
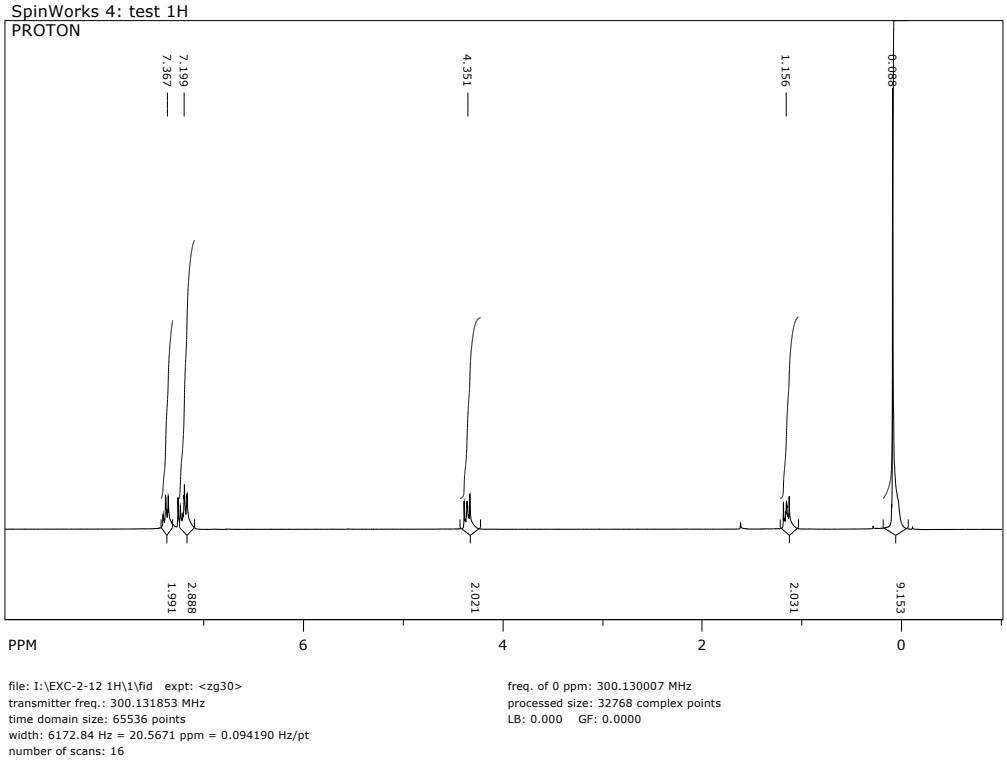
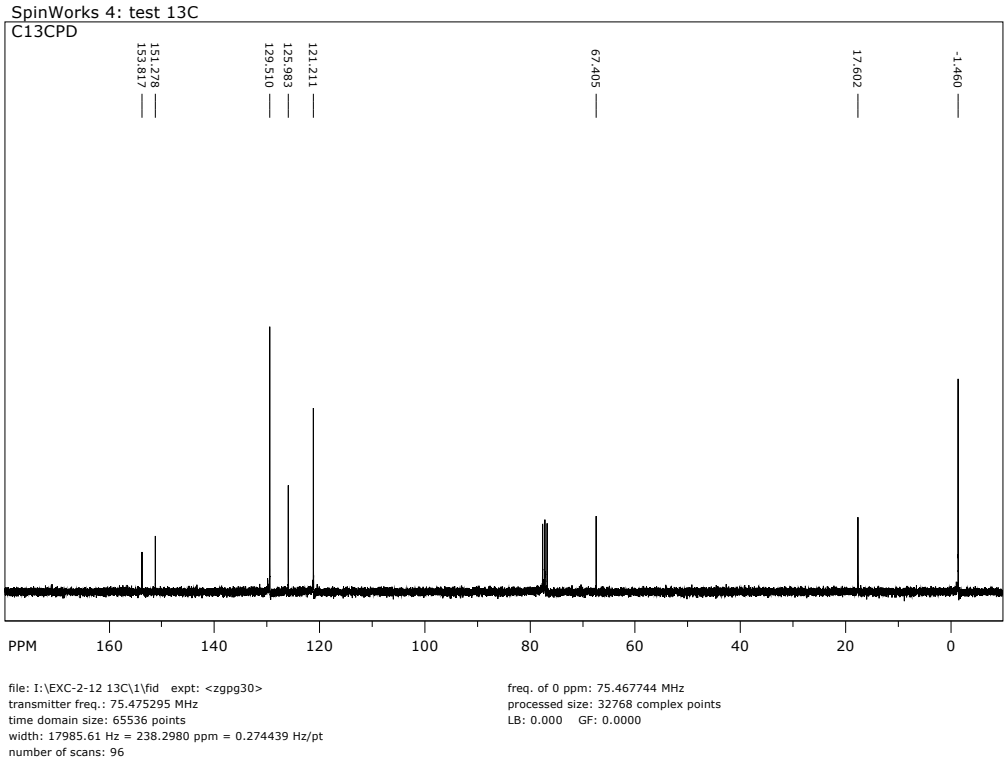
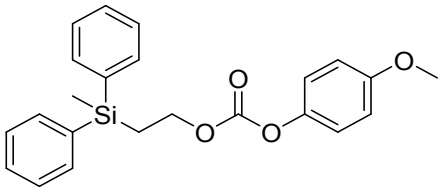


Phenyl (2-(trimethylsilyl)ethyl) carbonate: To a solution of trimethylsilyl ethanol (0.63 mL, 4.31 mmol) in THF (10 mL), phenyl chloroformate (0.53 mL, 4.19 mmol) was added at room temperature and let stir for overnight. The reaction mixture was extracted with dichloromethane and brine, dried with magnesium sulfate, and then concentrated *in vacuo*. The resulting mixture was purified using column chromatography (ethyl acetate/hexane: 0/100) to furnish the product (0.89 g) as a liquid in 90% yield. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ = 7.37 (d, *J* = 7.5 Hz, 2H), 7.20 (m, 3H), 4.35 (t, *J* = 8.9 Hz, 2H), 1.16 (t, *J* = 8.3 Hz, 2H), 0.09 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ = 151.28, 153.82, 129.51, 125.98, 121.21, 67.41, 17.60, -1.46. HRMS (ESI) *m/z* calculated for $C_{12}H_{18}O_3SiNa$ $[M + Na]^+$ 261.0917, found 261.0918.







4-methoxyphenyl (2-(methyldiphenylsilyl)ethyl) carbonate: To a solution of diphenylmethylsilyl ethanol (0.19 mL, 0.83 mmol) in THF (10 mL), 4-methoxyphenyl chloroformate (0.12 mL, 0.83 mmol) was added at room temperature and let stir for overnight. The reaction mixture was extracted with dichloromethane and brine, dried with magnesium sulfate, and then concentrated *in vacuo*. The resulting mixture was purified using column chromatography (ethyl acetate/hexane: 5/95) to furnish the product (0.26 g) as a clear liquid in 81% yield. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ = 7.54 (m, 4H), 7.39 (m, 6H), 7.05 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.4Hz, 2H), 4.36 (t, *J* = 8.4Hz, 2H), 3.80 (s, 3H), 1.71 (t, *J* = 8.4Hz, 2H), 0.63 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ = 157.37, 154.10, 144.78, 135.59, 134.41, 129.68, 128.13, 121.98, 114.45, 66.84, 55.62, 15.56, -4.01. HRMS (ESI) *m/z* calculated for $C_{23}H_{24}O_4SiNa$ $[M + Na]^+$ 415.1336, found 415.1329.

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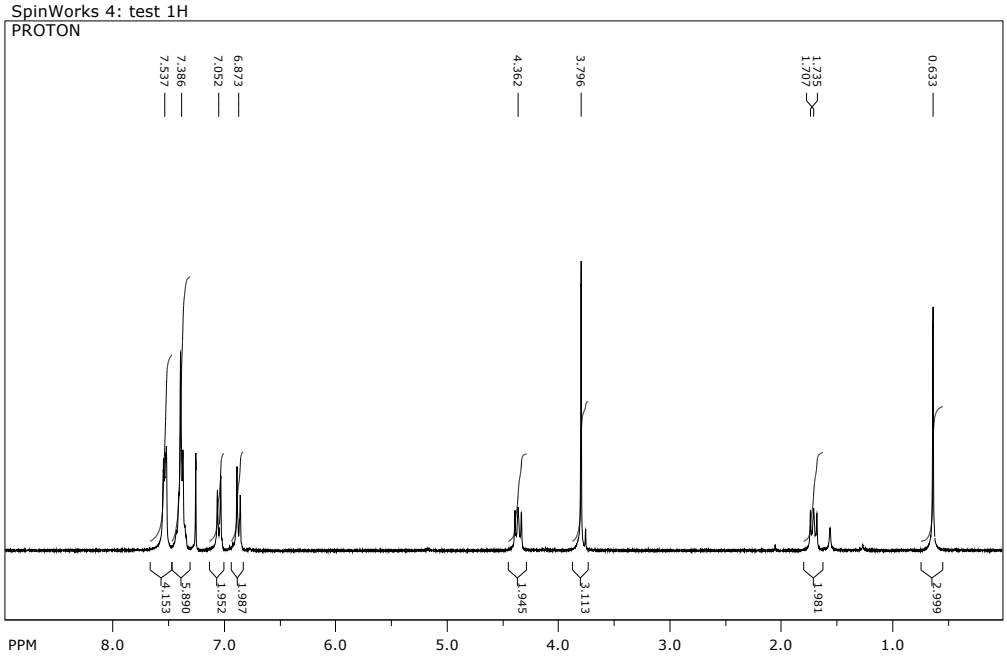

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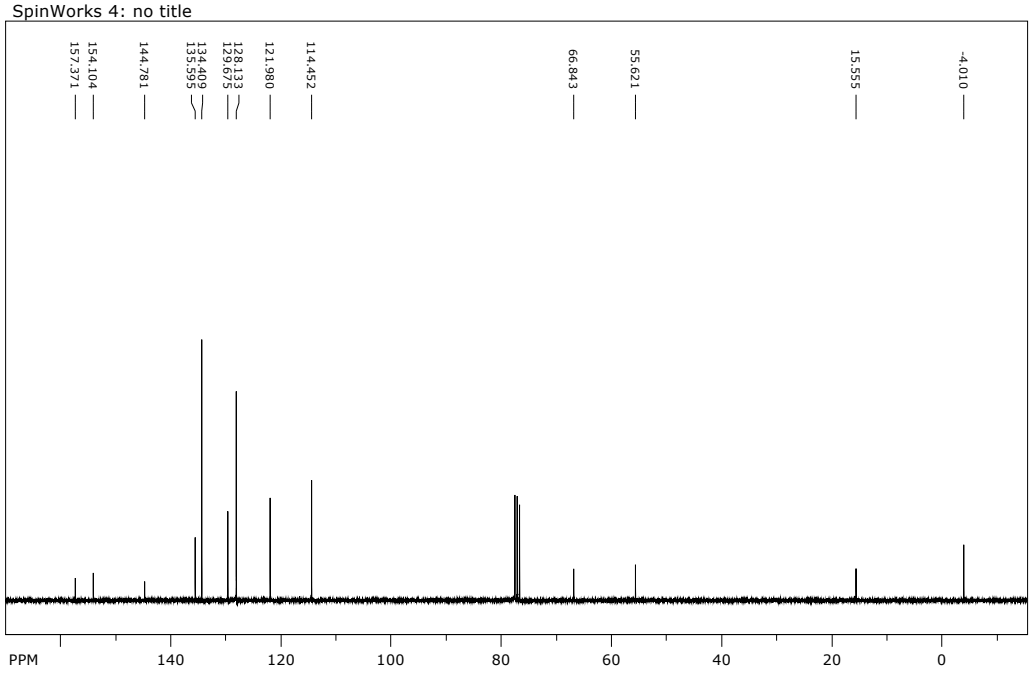

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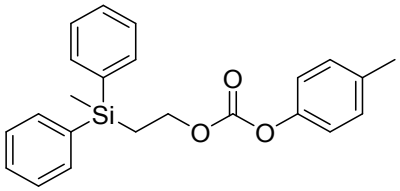
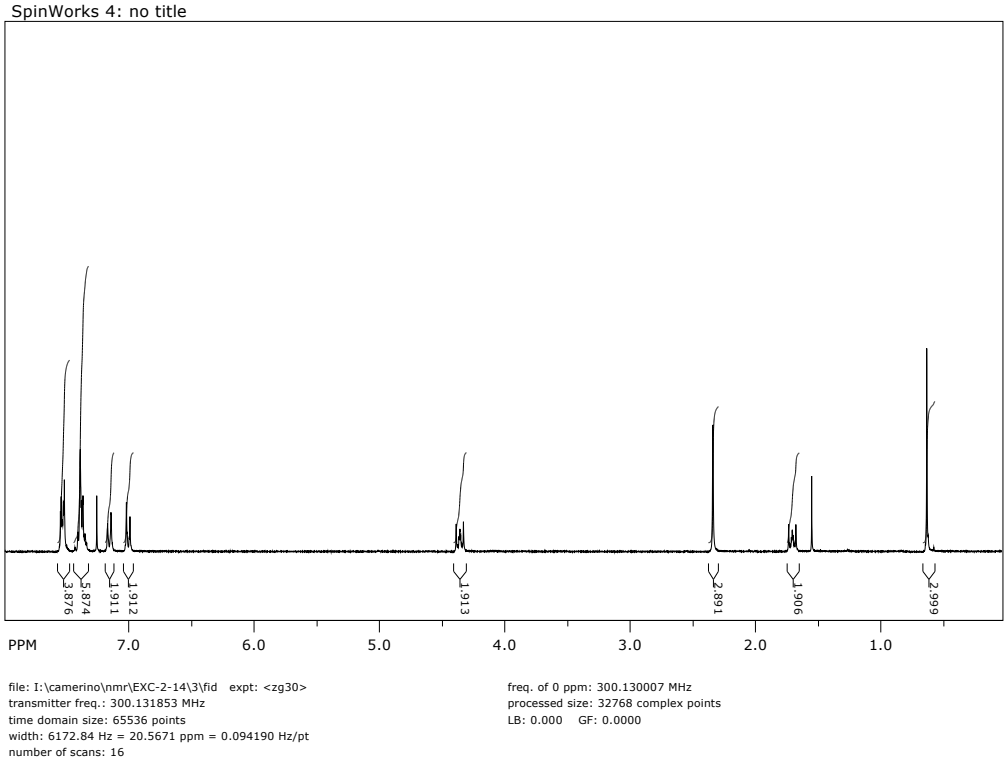
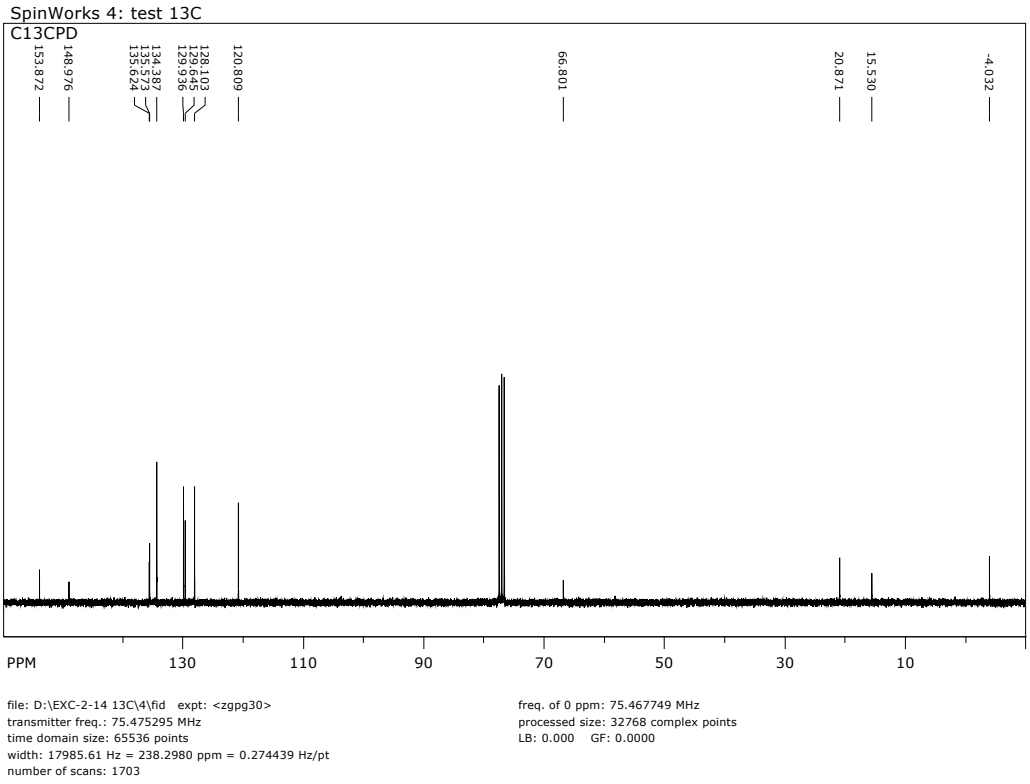
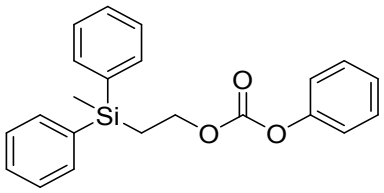


2-(methyldiphenylsilyl)ethyl *p*-tolyl carbonate: To a solution of diphenylmethylsilyl ethanol (0.19 mL, 0.83 mmol) in THF (10 mL), p-tolyl chloroformate (0.12 mL, 0.83 mmol) was added at room temperature and let stir for overnight. The reaction mixture was extracted with dichloromethane and brine, dried with magnesium sulfate, and then concentrated *in vacuo*. The resulting mixture was purified using column chromatography (ethyl acetate/hexane: 20/80) to furnish the product (0.15g) as a liquid in 65% yield. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ = 7.54 (m, 4H), 7.38 (m, 2H), 7.16 (d, J = 8.1 Hz), 7.01 (d, J = 8.4 Hz), 4.36 (t, J = 9 Hz, 2H), 2.34 (s, 3H), 1.70 (d, J = 9 Hz, 2H), 0.63 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ = 153.87, 148.98, 135.62, 135.57, 134.39, 129.94, 129.65, 128.10, 120.81, 66.80, 20.87, 15.53, -4.03. HRMS (ESI) *m/z* calculated for $C_{23}H_{24}O_3SiNa$ $[M + Na]^+$ 399.1387, found 399.1307.

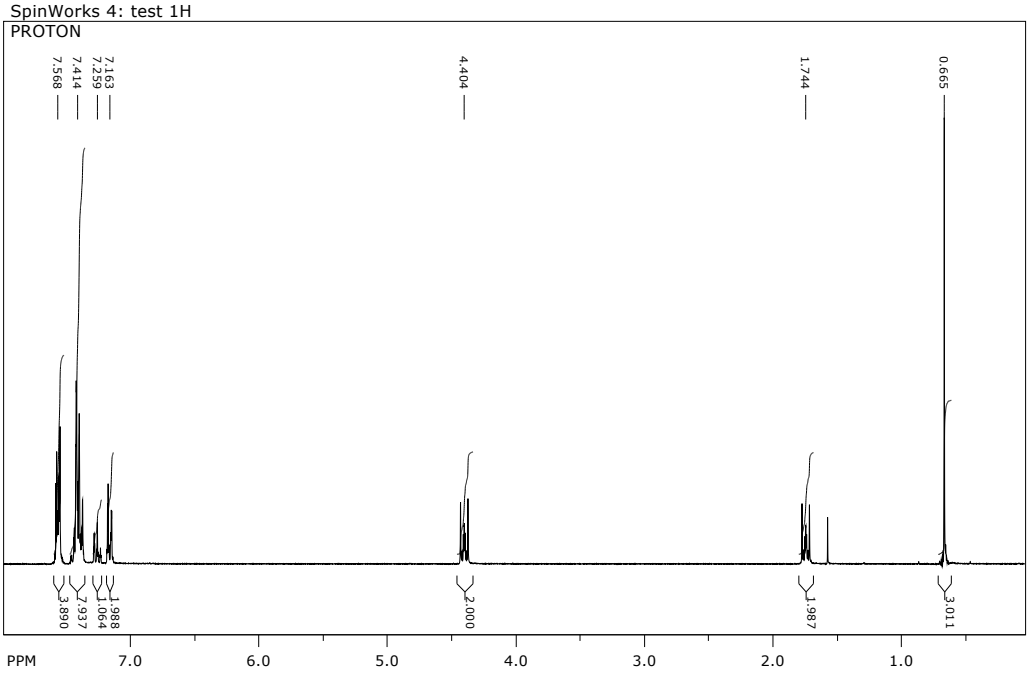






2-(methyldiphenylsilyl)ethyl phenyl carbonate: To a solution of diphenylmethylsilyl ethanol (0.19 mL, 0.83mmol) in THF (10 mL), phenyl chloroformate (0.10 mL, 0.83 mmol) was added at room temperature and let stir for overnight. The reaction mixture was extracted with dichloromethane and brine, dried with magnesium sulfate, and then concentrated *in vacuo*. The resulting mixture was purified using column chromatography (ethyl acetate/hexane: 25/75) to furnish the product (0.15 g) as a liquid in 50% yield. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ = 7.55 (m, 4H), 7.4 (m, 8H), 7.25 (tt, J = 7.0 Hz, 1.6 Hz, 1H), 7.15 (dq, J = 8.4 Hz, 1.4 Hz, 2H), 4.39 (t, J = 8.6 Hz, 2H), 1.73 (t, J = 8.7 Hz, 2H), 0.65 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ = 153.78, 151.23, 135.65, 134.49, 129.77, 129.57, 128.22, 126.09, 121.24, 61.02, 15.63, -3.92. HRMS (ESI) *m/z* calculated for $C_{22}H_{22}O_3SiNa$ $[M + Na]^+$ 385.1230, found 385.1227.

SpinWorks 4: test 1H



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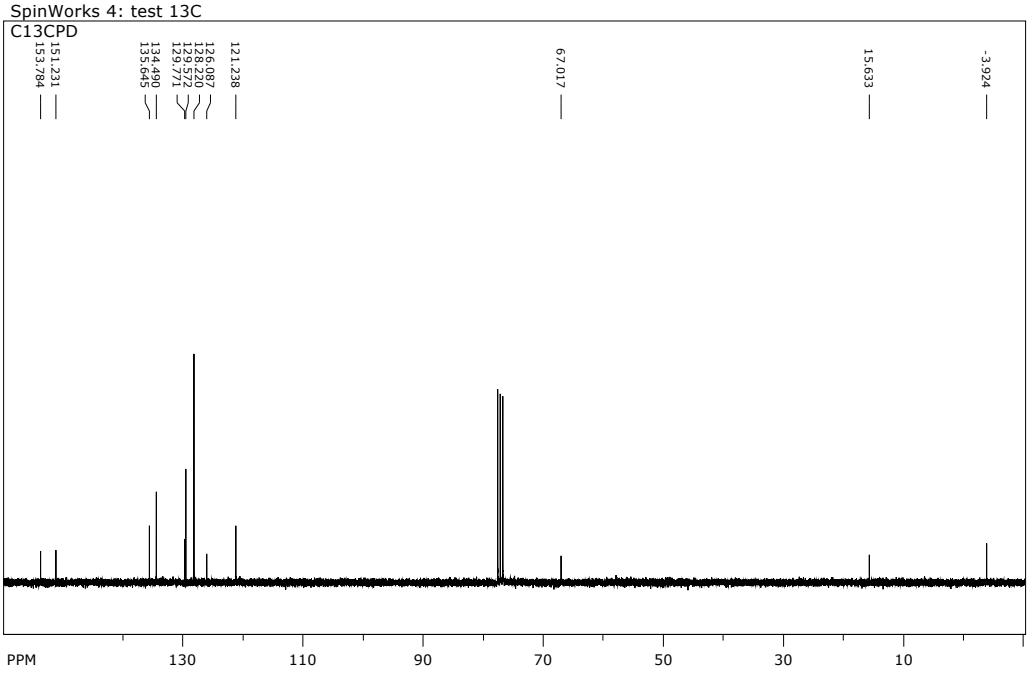

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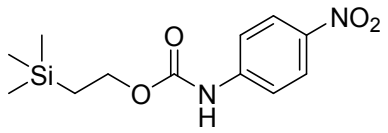
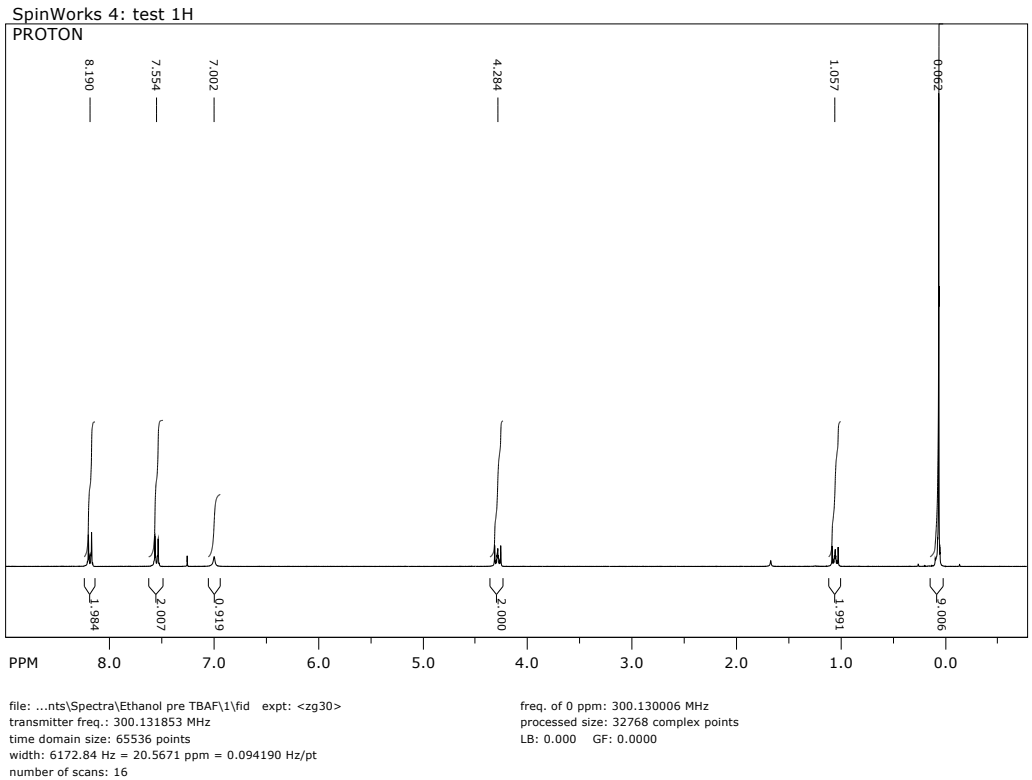
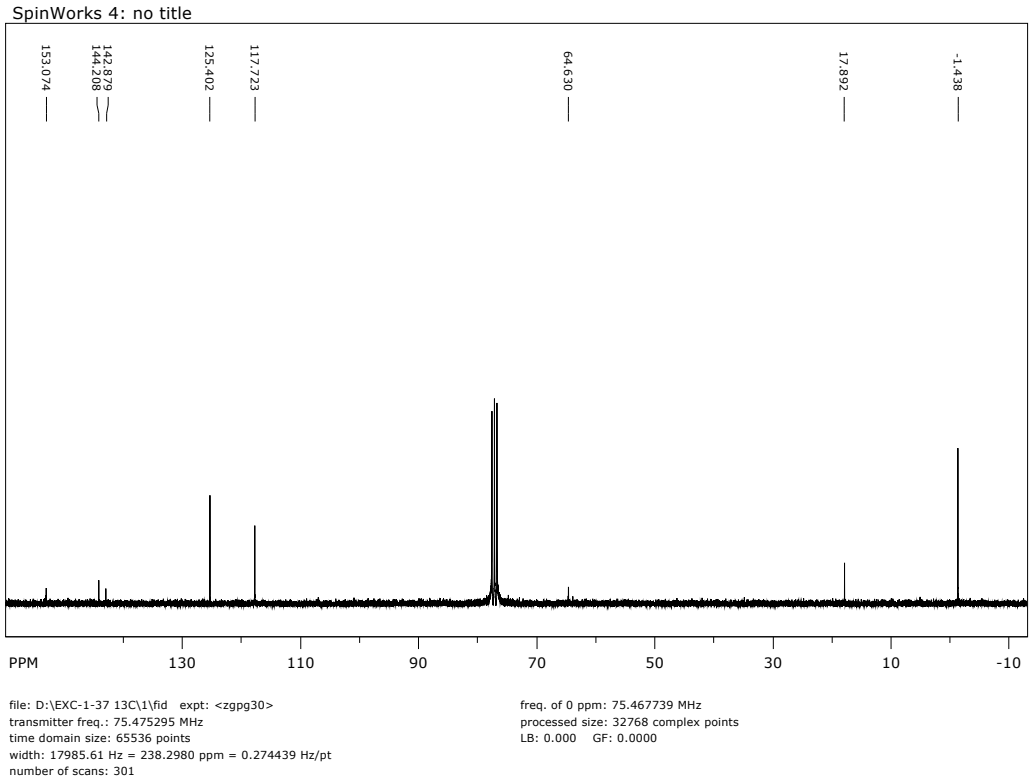
Procedures for Synthesis of Silyl-Terminated Carbamates:

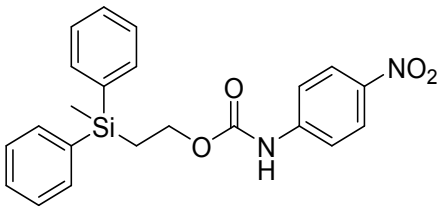
To a solution of the silyl alcohol in THF, the isocyanate was added at room temperature and allowed to stir for overnight. The reaction mixture was extracted with dichloromethane and brine, dried with magnesium sulfate, and then concentrated *in vacuo*. The resulting mixture was purified using column chromatography to furnish the product.



2-(trimethylsilyl)ethyl (4-nitrophenyl)carbamate (1b): To a solution of trimethylsilyl ethanol (0.4 g, 3.35 mmol) in THF (10 mL), 4-nitrophenyl isocyanate (0.5 g, 3.05 mmol) was added at room temperature and let stir for overnight. The reaction mixture was extracted with dichloromethane and brine, dried with magnesium sulfate, and then concentrated *in vacuo*. The resulting mixture was purified using column chromatography (dichloromethane/hexane: 90/10) to furnish the product (0.67 g) as a solid in 78% yield. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ = 8.19 (d, *J* = 9.1 Hz, 2H), 7.55 (d, *J* = 9.1 Hz, 2H), 7.00 (s, 1H), 4.28 (t, *J* = 8.5Hz, 2H), 1.06 (t, *J* = 8.5 Hz, 2H), 0.06 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ = 153.07, 144.21, 142.88, 125.40, 117.72, 64.63, 17.89, -1.44. HRMS (EIC) *m/z* calculated for $C_{12}H_{18}N_2O_4SiNa$ $[M - H]^-$ 305.0928, found 305.0926.

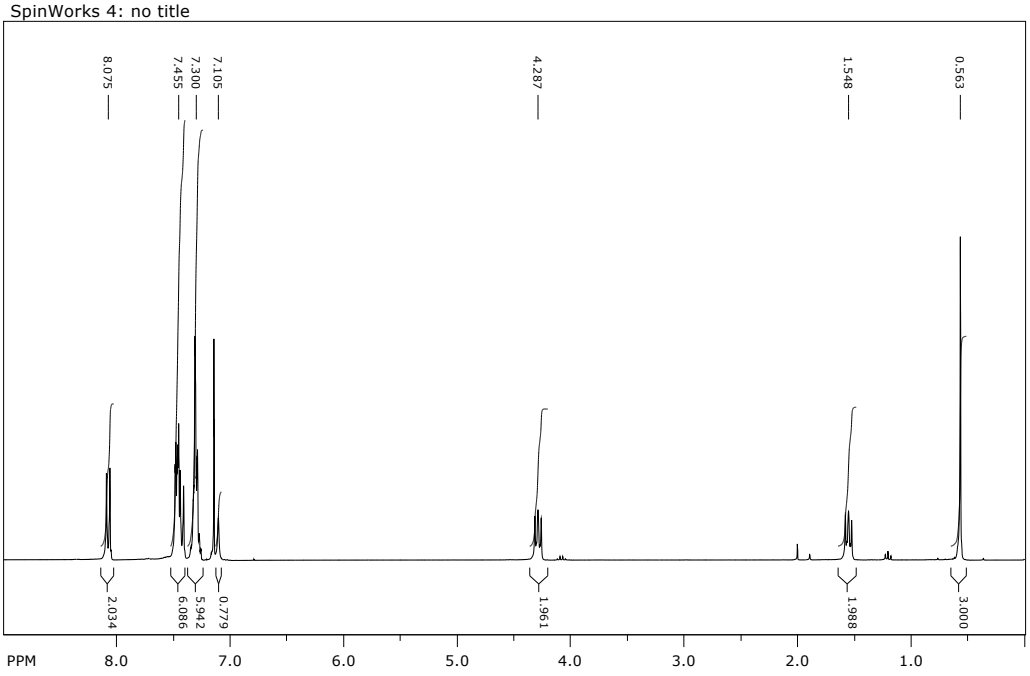






2-(methyldiphenylsilyl)ethyl (4-nitrophenyl)carbamate (1d): To a solution of diphenylmethylsilyl ethanol (0.82 mL, 3.6 mmol) in THF (10 mL), 4-nitrophenyl isocyanate (0.54 mg, 3.27 mmol) was added at room temperature and let stir for overnight. The reaction mixture was extracted with dichloromethane and brine, dried with magnesium sulfate, and then concentrated *in vacuo*. The resulting mixture was purified using column chromatography (ethyl acetate/hexane: 30/70) to furnish the product (0.73 g) as a white solid in 51% yield. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ = 8.08 (d, *J* = 9.3Hz), 7.46 (m, 6H), 7.30 (m, 6H), 7.11 (s, 1H), 4.29 (t, *J* = 8.5Hz), 1.55 (t, *J* = 8.5Hz), 0.56 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ = 153.14, 144.46, 142.77, 135.88, 134.44, 129.72, 128.17, 125.22, 117.82, 63.95, 15.76, -4.14. HRMS (ESI) *m/z* calculated for $C_{22}H_{23}N_2O_4Si$ $[M + H]^+$, 407.1422 found 407.1420.

SpinWorks 4: no title



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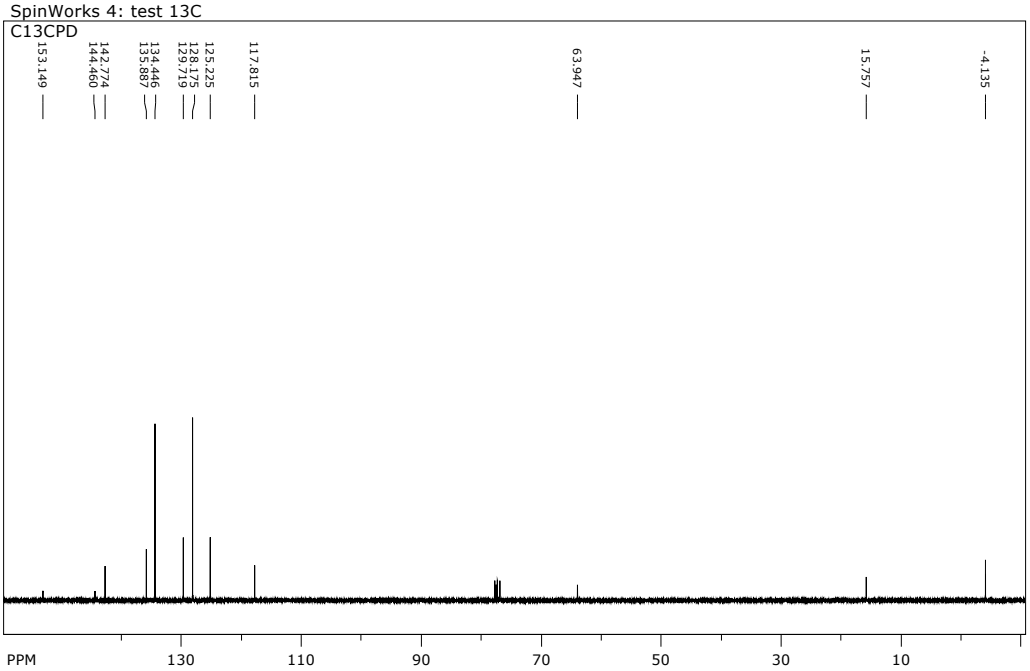
number of scans: 16

freq. of 0 ppm: 300.130041 MHz
processed size: 32768 complex points
LB: 0.000 GF: 0.0000

SpinWorks 4: test 13C



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number of scans: 1991

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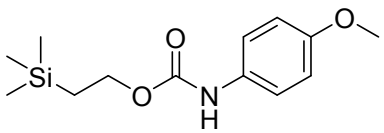
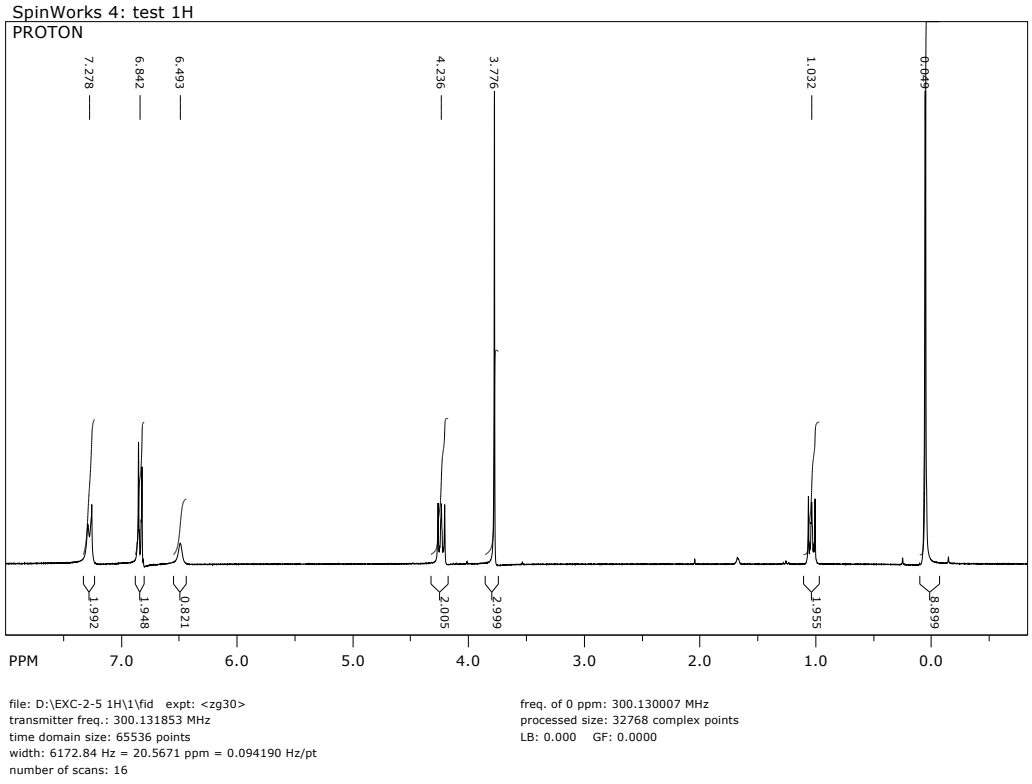
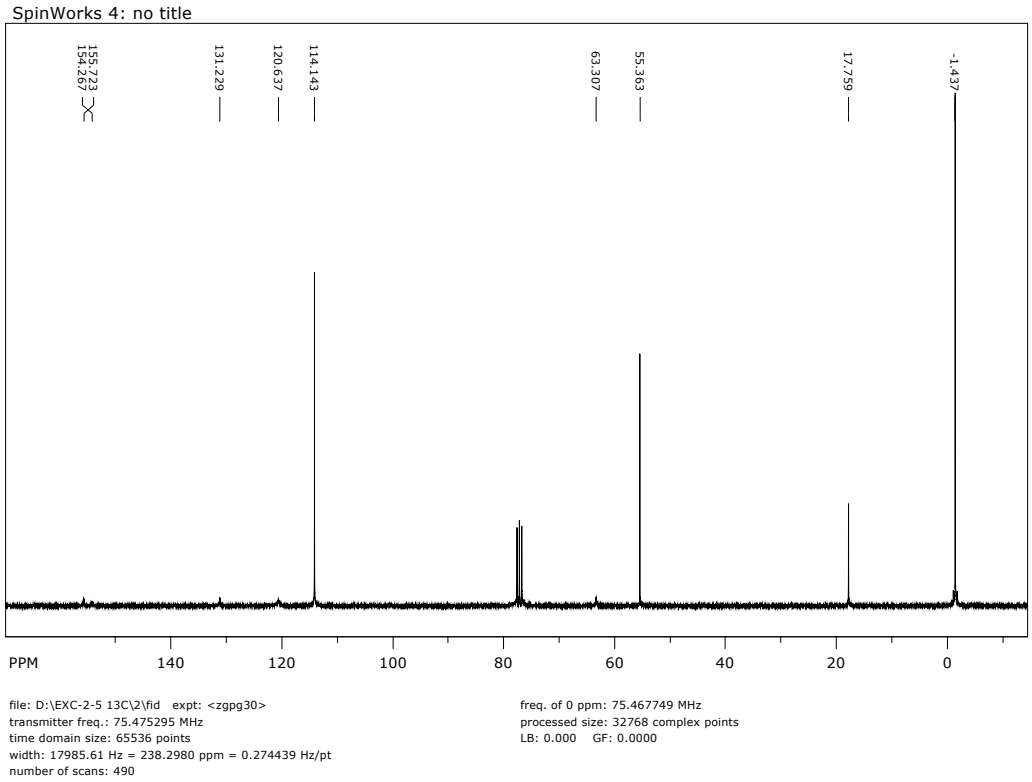
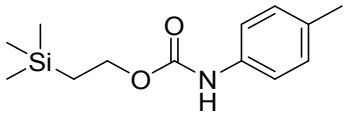
processed size: 32768 complex points
LB: 0.000 GF: 0.0000



2-(trimethylsilyl)ethyl (4-methoxyphenyl)carbamate: To a solution of trimethylsilyl ethanol (0.63 mL, 4.31 mmol) in THF (10 mL), 4-methoxyphenyl isocyanate (0.54 mL, 4.19 mmol) was added at room temperature and let stir for overnight. The reaction mixture was extracted with dichloromethane and brine, dried with magnesium sulfate, and then concentrated *in vacuo*. The resulting mixture was purified using column chromatography (ethyl acetate/hexane: 20/80) to furnish the product (0.95 g) as a liquid in 82% yield. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ = 7.28(d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 6.49 (s, 1H), 4.24 (t, *J* = 8.4 Hz, 2H), 3.78 (s, 3H), 1.03 (t, *J* = 8.4 Hz, 2H), 0.05 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ = 155.72, 154.27, 131.23, 120.64, 114.14, 63.31, 55.37, 17.76, -1.44. HRMS (ESI) *m/z* calculated for $C_{13}H_{21}NO_3SiNa$ $[M + Na]^+$ 290.1183, found 290.1181.

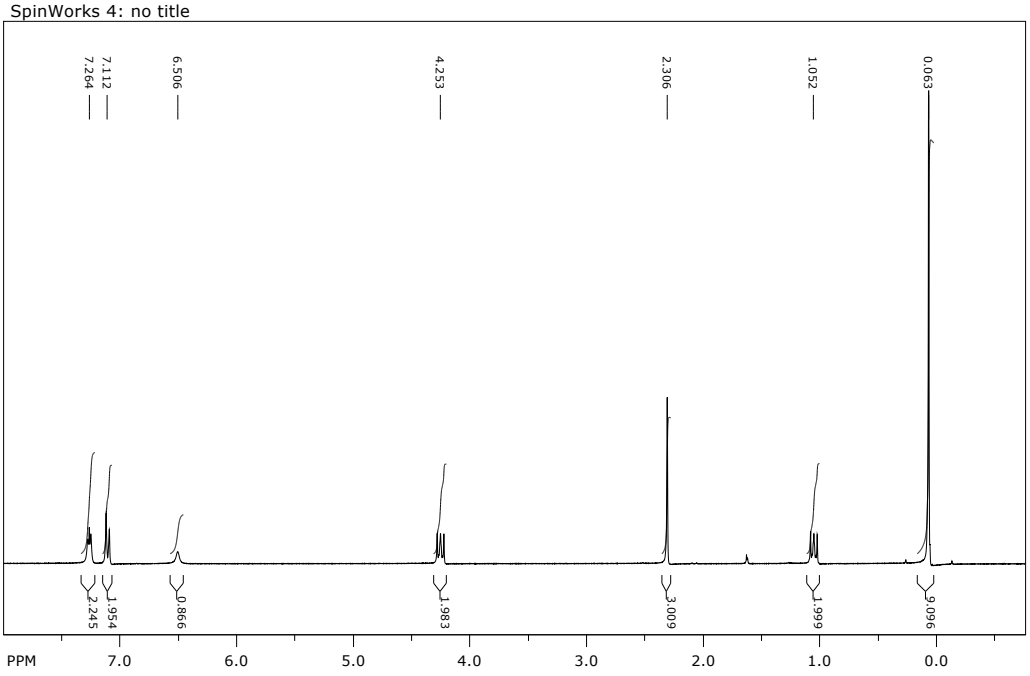






2-(trimethylsilyl)ethyl *p*-tolylcarbamate: To a solution of trimethylsilyl ethanol (0.63 mL, 4.41 mmol) in THF (10 mL), *p*-tolyl isocyanate (0.58 mL, 4.19 mmol) was added at room temperature and let stir for overnight. The reaction mixture was extracted with dichloromethane and brine, dried with magnesium sulfate, and then concentrated *in vacuo*. The resulting mixture was purified using column chromatography (ethyl acetate/hexane: 20/80) to furnish the product (1.1 g) as a liquid in 80% yield. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ = 7.26 (t, *J* = 4.2 Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 6.51 (s, 1H), 4.25 (t, *J* = 8.9 Hz, 2H), 2.31 (s, 3H), 1.05 (t, *J* = 8.4 Hz, 2H), 0.06 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ = 154.10, 135.58, 132.58, 129.38, 118.86, 63.26, 20.68, 17.71, -1.56. HRMS (ESI) *m/z* calculated for $C_{13}H_{21}NO_2SiNa$ $[M + Na]^+$ 274.1234, found 274.1231.

SpinWorks 4: no title



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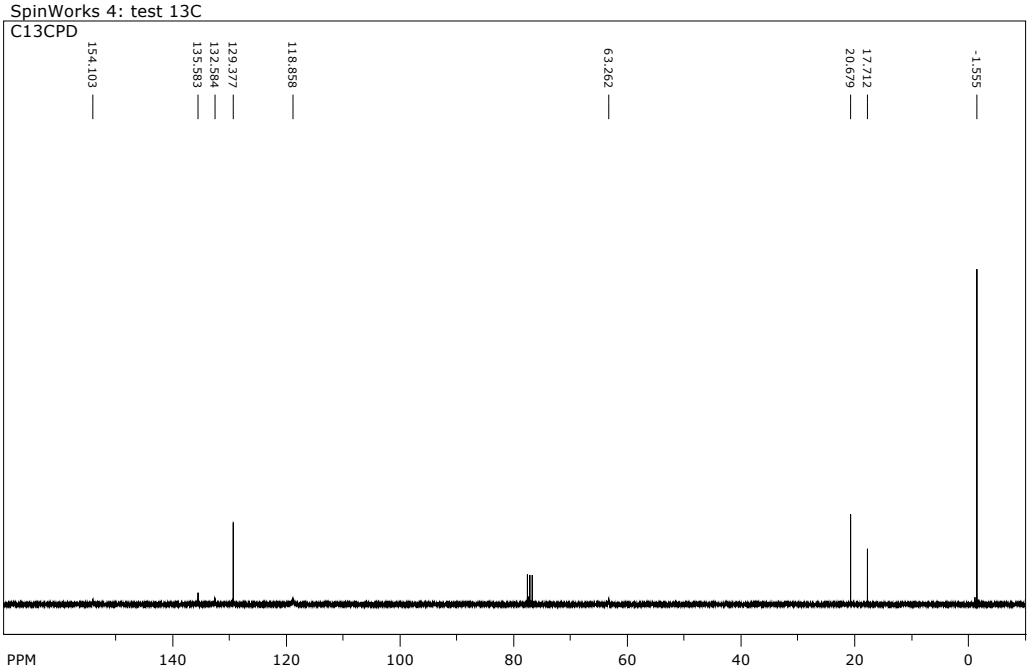
number of scans: 16

freq. of 0 ppm: 300.130005 MHz
processed size: 32768 complex points
LB: 0.000 GF: 0.0000

SpinWorks 4: test 13C



file: D:\EXC-2-4 13C\2\fid expt: <zgpg30>
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time domain size: 65536 points
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number of scans: 500

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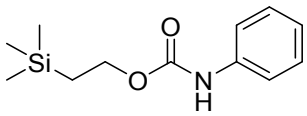
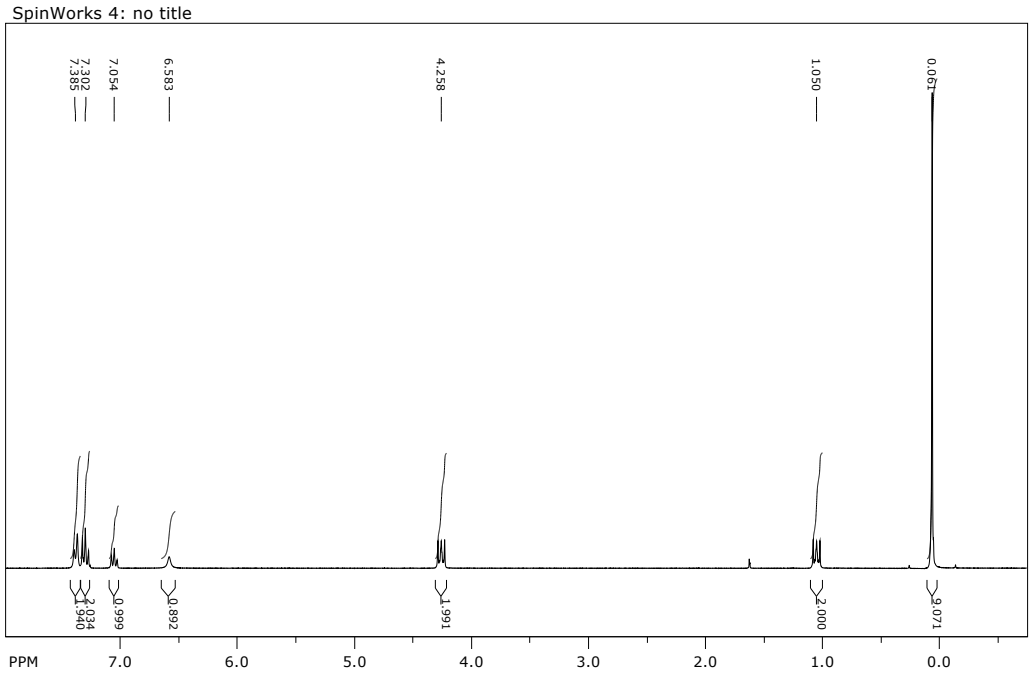
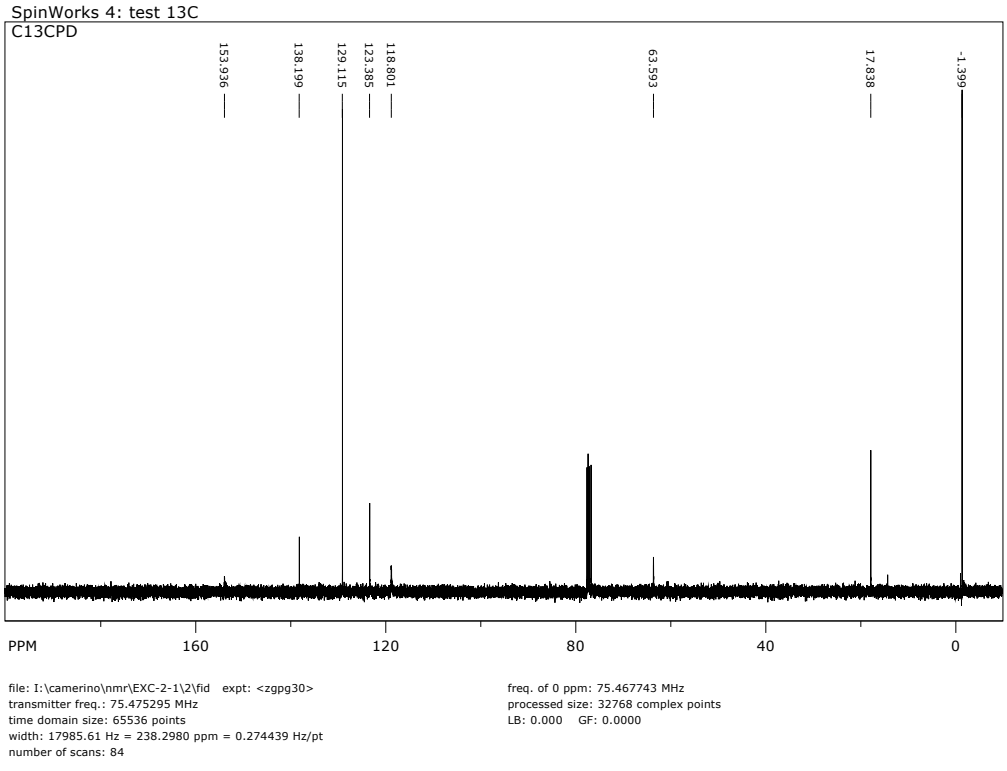
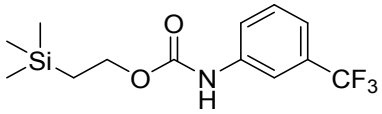
LB: 0.000 GF: 0.0000



2-(trimethylsilyl)ethyl phenylcarbamate: To a solution of trimethylsilyl ethanol (0.63 mL, 4.41 mmol) in THF (10 mL), phenyl isocyanate (0.46 mL, 4.19 mmol) was added at room temperature and let stir for overnight. The reaction mixture was extracted with dichloromethane and brine, dried with magnesium sulfate, and then concentrated *in vacuo*. The resulting mixture was purified using column chromatography (ethyl acetate/hexane: 20/80) to furnish the product (0.5 g) as a solid in 48% yield. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ = 7.38 (d, *J* = 8.1 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.05 (t, *J* =7.4 Hz, 1H), 6.58 (s, 1H), 4.26 (t, *J* = 8.7 Hz, 2H), 1.05 (t, *J* = 8.7 Hz, 2H), 0.6 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ = 138.16, 129.09, 123.36, 118.75, 63.59, 17.84, -1.40. HRMS (ESI) *m/z* calculated for $C_{12}H_{19}NO_2SiNa$ [M + Na]$^+$ 260.1077, found 260.1077.

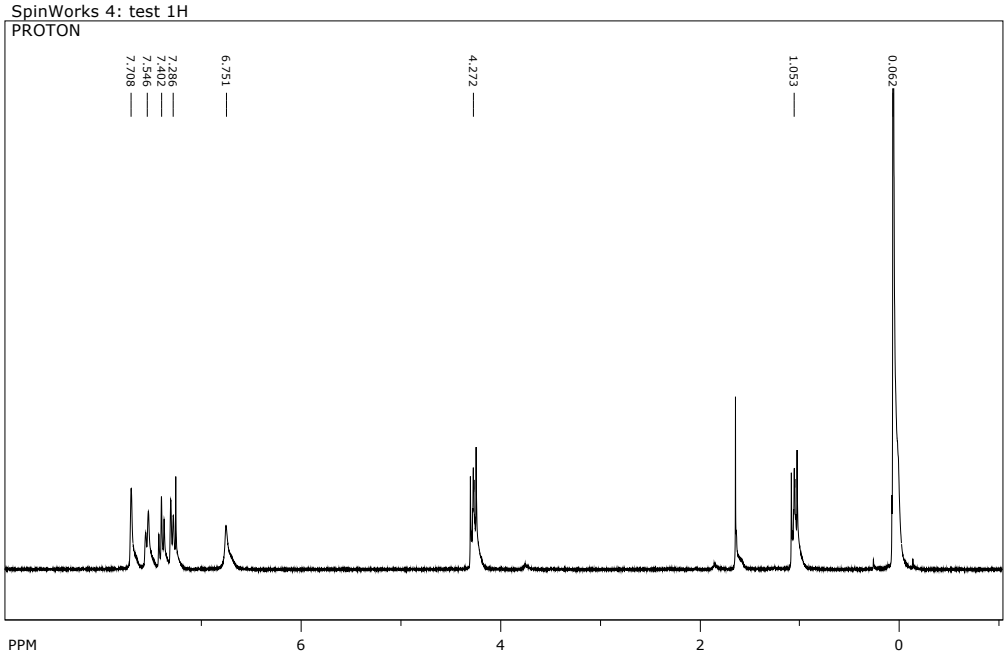






2-(trimethylsilyl)ethyl) (3-(trifluoromethyl)phenyl)carbamate: To a solution of trimethylsilyl ethanol (0.63 mL, 4.31 mmol) in THF (10 mL), 3-(trifluoromethyl)phenyl isocyanate (0.58 mL, 4.19 mmol) was added at room temperature and let stir for overnight. The reaction mixture was extracted with dichloromethane and brine, dried with magnesium sulfate, and then concentrated *in vacuo*. The resulting mixture was purified using column chromatography (ethyl acetate/hexane: 25/75) to furnish the product (0.78 g) as a liquid in 61% yield. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ = 7.71 (s, 1H), 7.55 (d, J = 8.3 Hz, 1H), 7.40 (t, J = 7.8 Hz, 1H), 7.29 (d, J = 8.7 Hz, 1H), 6.75 (s, 1H), 4.27 (t, J = 8.3 Hz, 2H), 1.05 (t, J = 8.6 Hz, 2H), 0.06 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ = 153.74 (q, $^{3}J_{CF}$ = 3.9 Hz), 138.78, 131.59(q, $^{2}J_{CF}$ = 32.3 Hz), 129.66, 123.94 (q, $^{1}J_{CF}$ = 272.8 Hz), 121.71 (q, $^{3}J_{CF}$ = 2.1 Hz), 119.94, 115.44, 64.11, 17.89, -1.4. HRMS (ESI) *m/z* calculated for $C_{13}H_{18}F_3NO_3SiNa$ $[M + Na]^+$ 328.0951, found 328.0950.

SpinWorks 4: test 1H



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number of scans: 16

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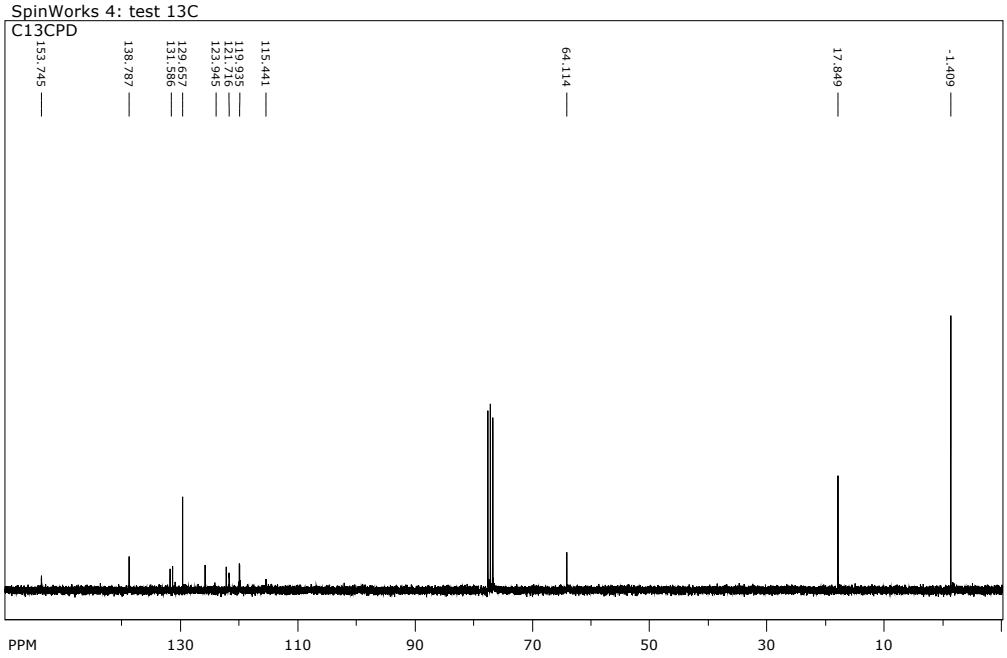
SpinWorks 4: test 13C



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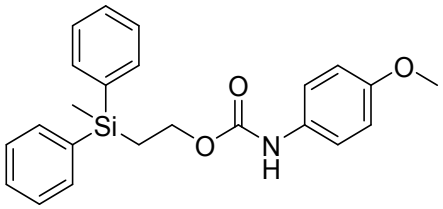
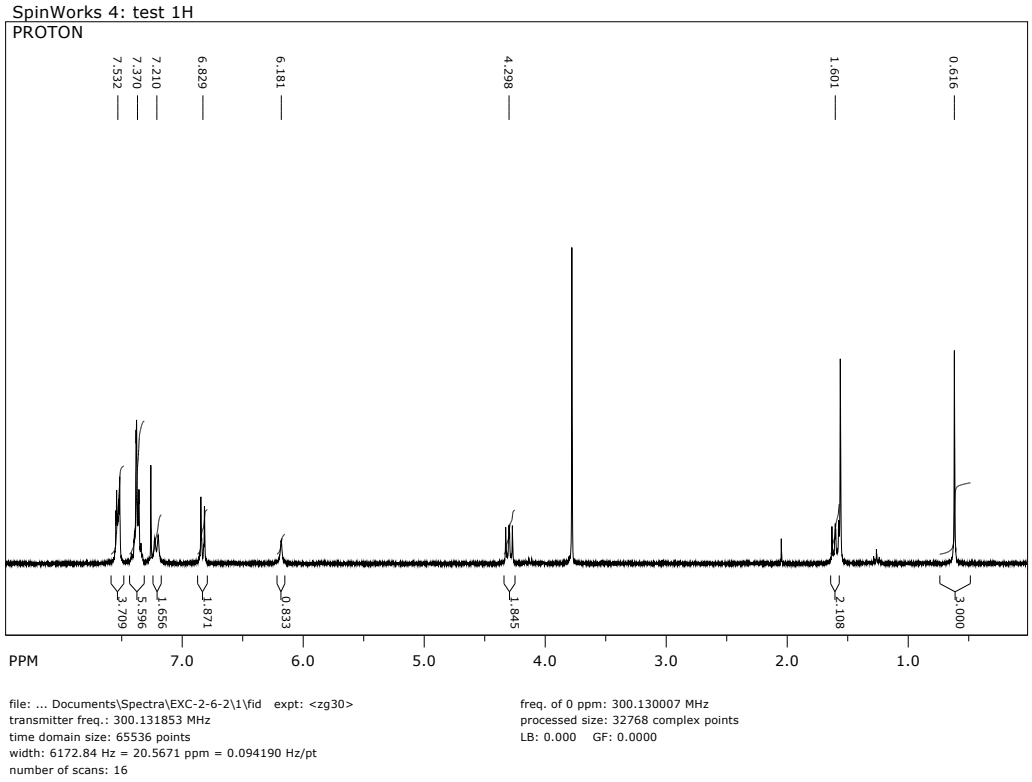
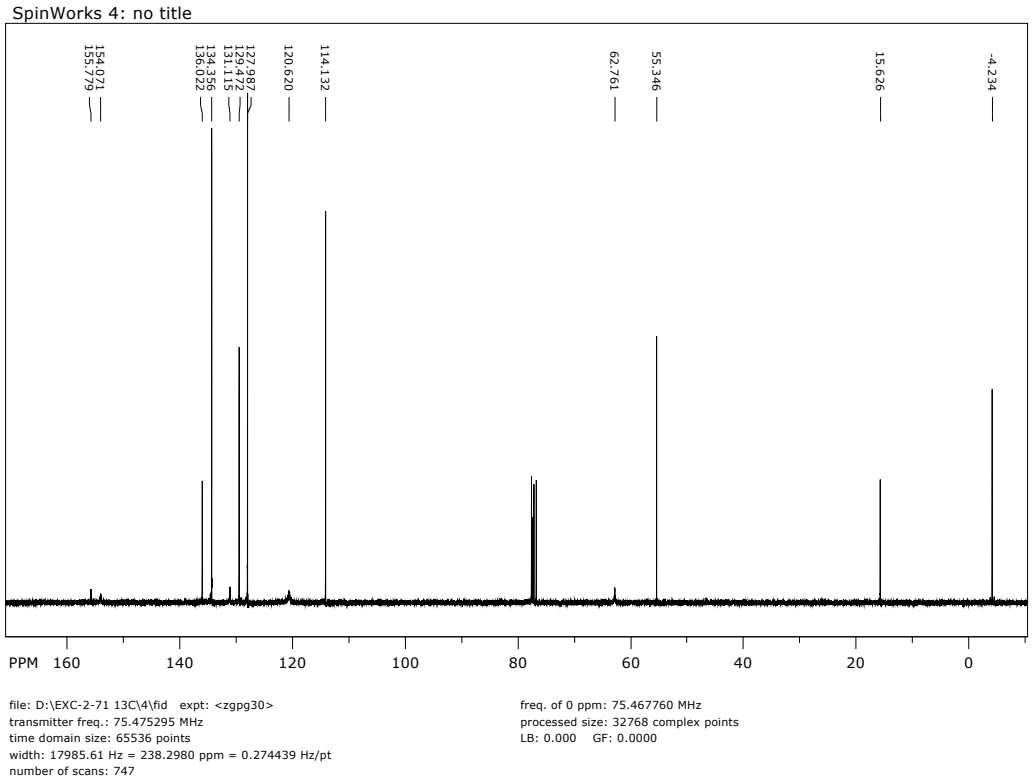
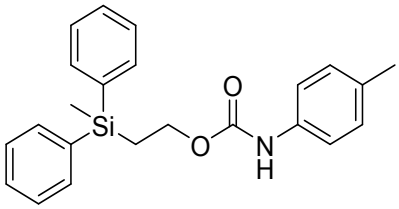


2-(methyldiphenylsilyl)ethyl (4-methoxyphenyl)carbamate: To a solution of diphenylmethylsilyl ethanol (0.19 mL, 0.83 mmol) in THF (10 mL), 4-methoxyphenyl isocyanate (0.11 mL, 0.83 mmol) was added at room temperature and let stir for overnight. The reaction mixture was extracted with dichloromethane and brine, dried with magnesium sulfate, and then concentrated *in vacuo*. The resulting mixture was purified using column chromatography (ethyl acetate/hexane: 20/80) to furnish the product (0.12 g) as a solid in 38% yield. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ = 7.53 (m, 4H), 7.37 (m, 6H), 7.21 (d, *J* = 8.3 Hz, 2H), 6.83 (d, *J* = 8.9Hz, 1H), 6.18 (s, 1H), 4.23 (t, *J* = 8.3 Hz, 2H) 1.60 (t, *J* = 8.3 Hz, 2H), 0.62 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ = 155.78, 154.07, 136.02, 134.35, 131.12, 129.47, 127.99, 120.62, 114.13, 62.76, 55, 35, 15.63, -4.23. HRMS (ESI) *m/z* calculated for $C_{23}H_{25}NO_3SiNa$ [M + Na]$^+$ 414.1496, found 414.1493.

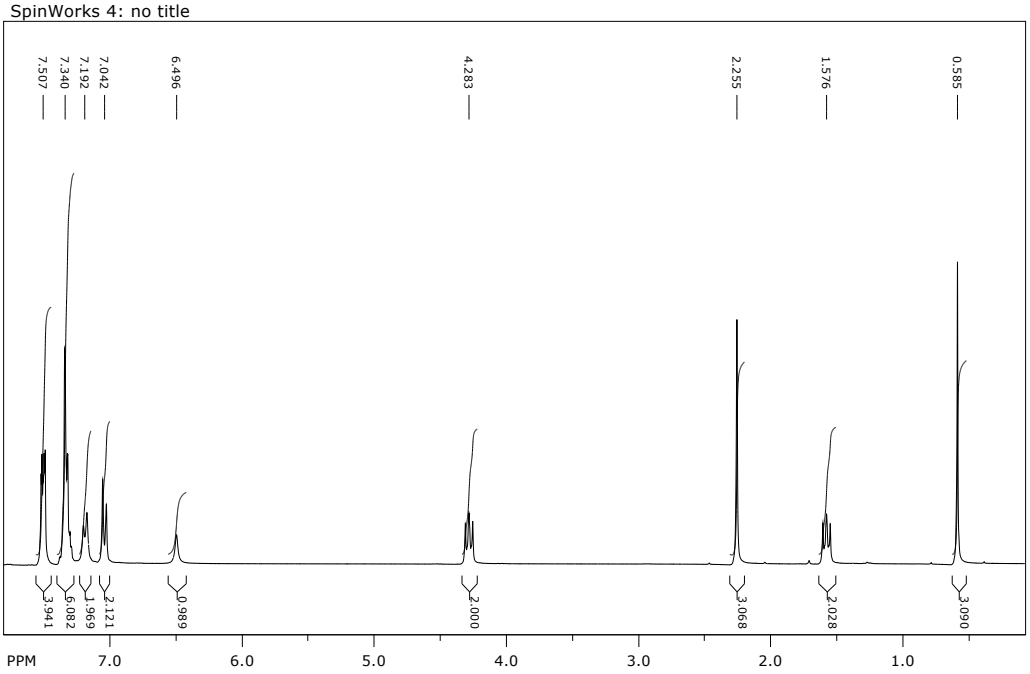






2-(methyldiphenylsilyl)ethyl *p*-tolylcarbamate: To a solution of diphenylmethylsilyl ethanol (0.19 mL, 0.83 mmol) in THF (10 mL), *p*-tolyl isocyanate (0.11 mL, 0.83 mmol) was added at room temperature and let stir for overnight. The reaction mixture was extracted with dichloromethane and brine, dried with magnesium sulfate, and then concentrated *in vacuo*. The resulting mixture was purified using column chromatography (ethyl acetate/hexane: 20/80) to furnish the product (0.29 g) as a liquid in 97% yield. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ = 7.51 (m, 4H), 7.34 (m, 6H), 7.19 (d, J= 8.3 Hz, 2H), 7.04 (d, J= 8.3 Hz, 2H), 6.49 (s, 1H), 4.28 (t, J= 8.3 Hz, 2H), 2.26 (3H, s), 1.58 (t, J= 8.3 Hz, 2H), 0.59 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ = 153.81, 136.10, 135.42, 134.43, 132.79, 129.53, 129.51, 128.05, 118.87, 62.95, 20.79, 15.73, -4.12. HRMS (EIC) *m/z* calculated for $C_{23}H_{25}NO_2SiNa$ $[M + Na]^+$ 398.1547, found 398.1542.

SpinWorks 4: no title



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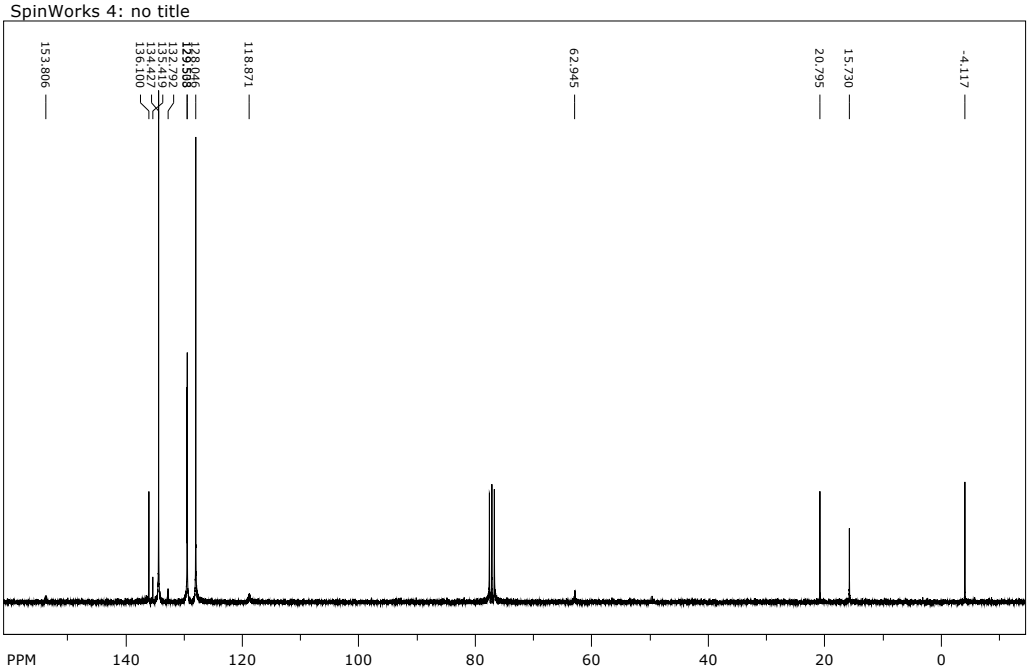
SpinWorks 4: no title



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number of scans: 250

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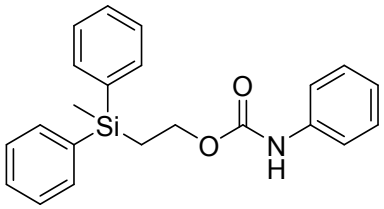
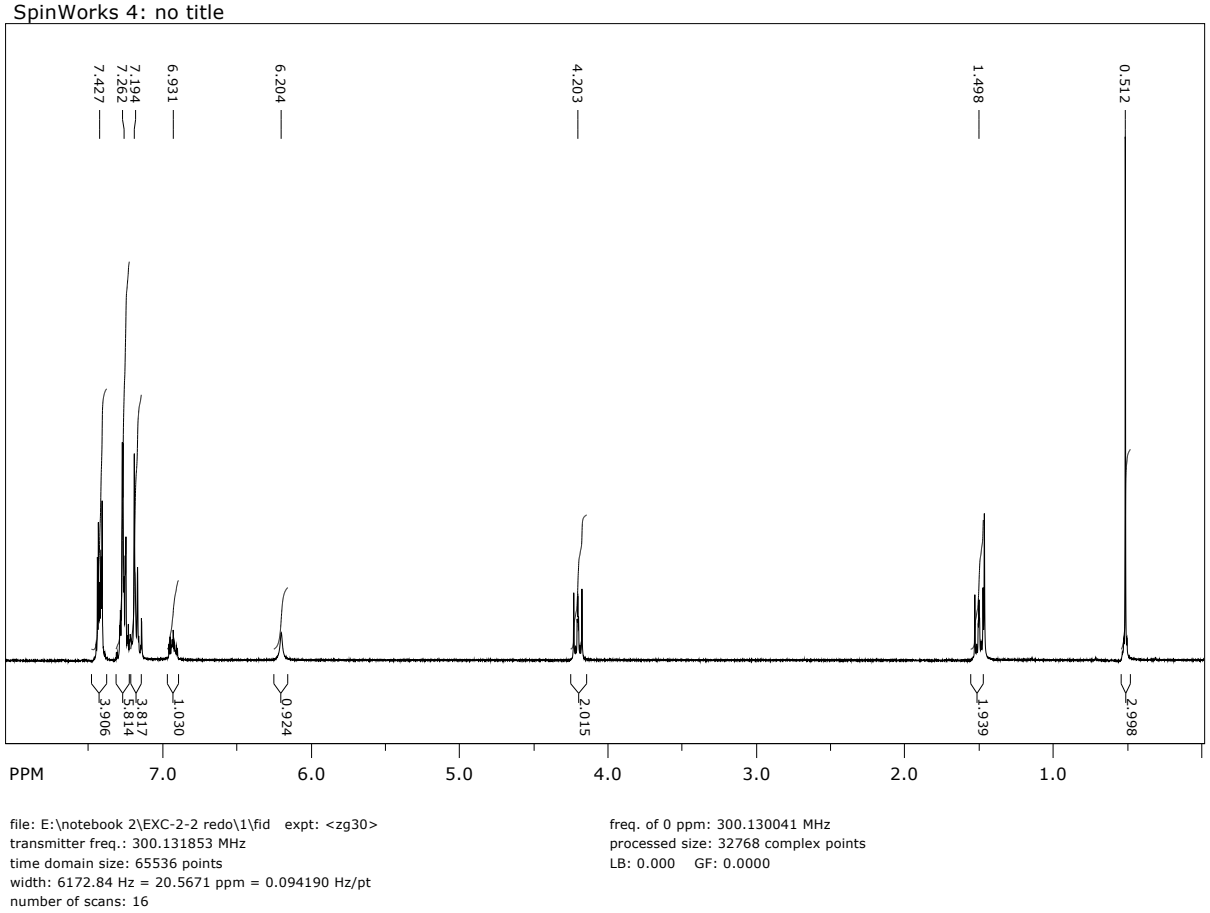
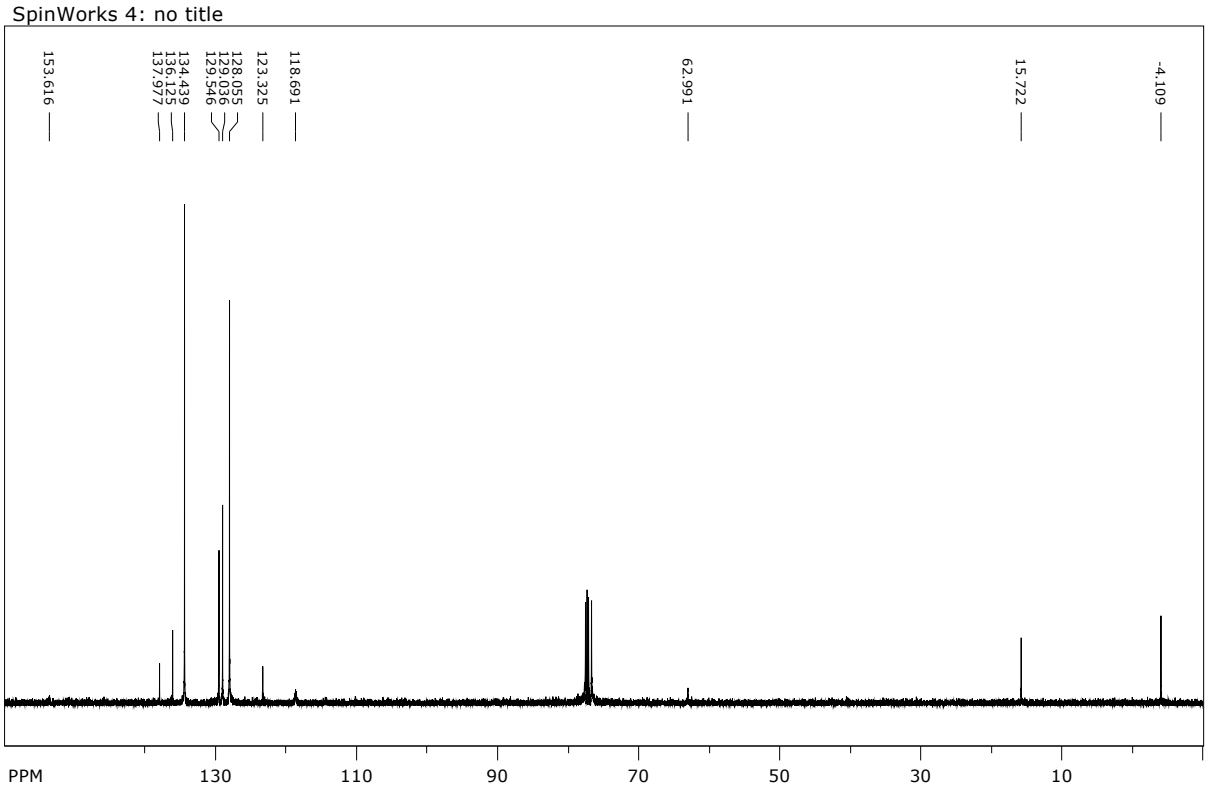
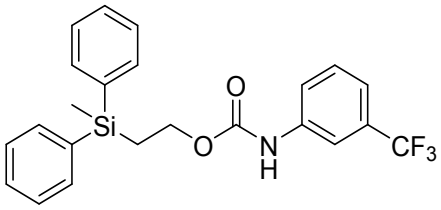


2-(methyldiphenylsilyl)ethyl) phenylcarbamate: To a solution of trimethylsilyl ethanol (0.19 mL, 0.83 mmol) in THF (10 mL), phenyl isocyanate (0.09 mL, 0.83 mmol) was added at room temperature and let stir for overnight. The reaction mixture was extracted with dichloromethane and brine, dried with magnesium sulfate, and then concentrated *in vacuo*. The resulting mixture was purified using column chromatography (ethyl acetate/hexane: 20/80) to furnish the product (0.21 g) as a clear liquid in 70% yield. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ = 7.43 (m, 4H), 7.26 (m, 6H), 7.19 (m, 4H), 6.9 (m, 1H), 6.2 (s, 1H), 4.02 (t, *J* = 8.2 Hz, 2H), 1.49 (t, *J* = 8.6 Hz, 3H), 0.51 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ = 153.62, 137.97, 136.13, 134.44, 129.55, 129.04, 128.06, 123.33, 118.69, 62.99, 15.72, -4.11. HRMS (ESI) *m/z* calculated for $C_{22}H_{23}NO_2SiNa$ $[M + Na]^+$ 384.1390, found 384.1389.

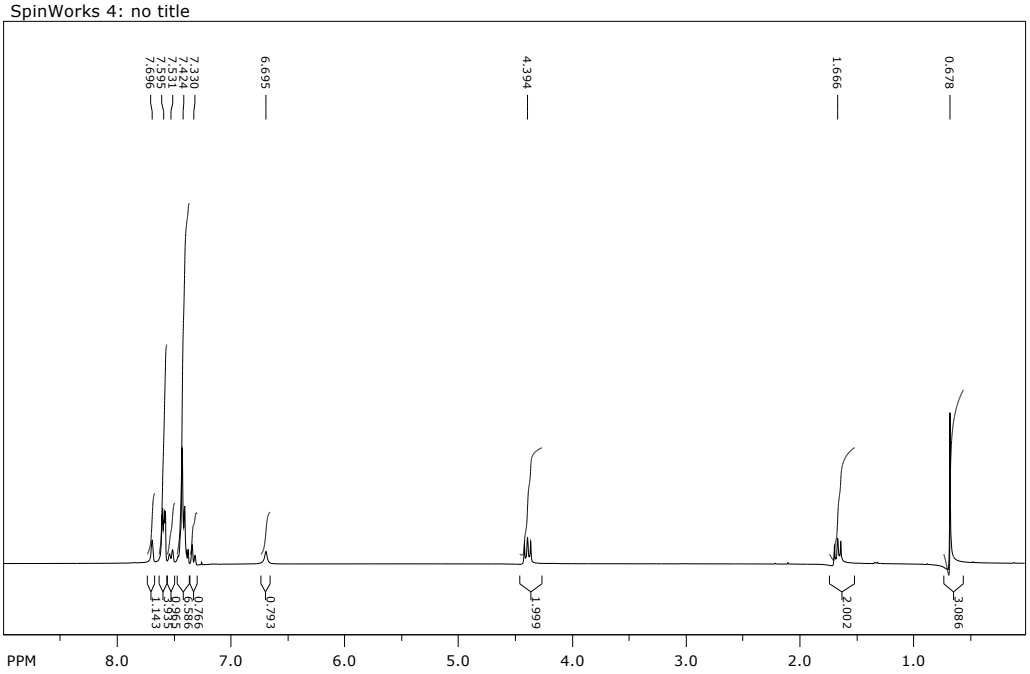






2-(methyldiphenylsilyl)ethyl (3-(trifluoromethyl)phenyl)carbamate: To a solution of diphenylmethylsilyl ethanol (0.19 mL, 0.83 mmol) in THF (10 mL), 3-(trifluoromethyl)phenyl isocyanate (0.11 mL, 0.83 mmol) was added at room temperature and let stir for overnight. The reaction mixture was extracted with dichloromethane and brine, dried with magnesium sulfate, and then concentrated *in vacuo*. The resulting mixture was purified using column chromatography (ethyl acetate/hexane: 25/75) to furnish the product (0.32 g) as a liquid in 92% yield. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ = 7.70 (s, 1H), 7.59 (m, 4H), 7.53 (d, *J* = 8.3 Hz, 1H), 7.42 (m, 7H) 7.33 (d, *J* = 7.9 Hz, 1H), 6.69 (s, 1H), 4.39 (t, *J* = 8.3Hz, 2H), 1.67 (t, *J* = 8.3 Hz, 2H), 0.68 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ = 153.46, 138.64, 134.46, 131.41(q, $^{2}J_{CF}$ = 32.6 Hz), 129.64, 129.57, 128.13, 124.13(q, $^{1}J_{CF}$ = 271 Hz), 121.59, 119.87(q, $^{3}J_{CF}$ = 3.9 Hz), 115.28, 63.46, 15.74, -4.15. HRMS (ESI) *m/z* calculated for $C_{23}H_{22}F_3NO_2SiNa$ $[M + Na]^+$ 452.1264, found 452.1261.

SpinWorks 4: no title



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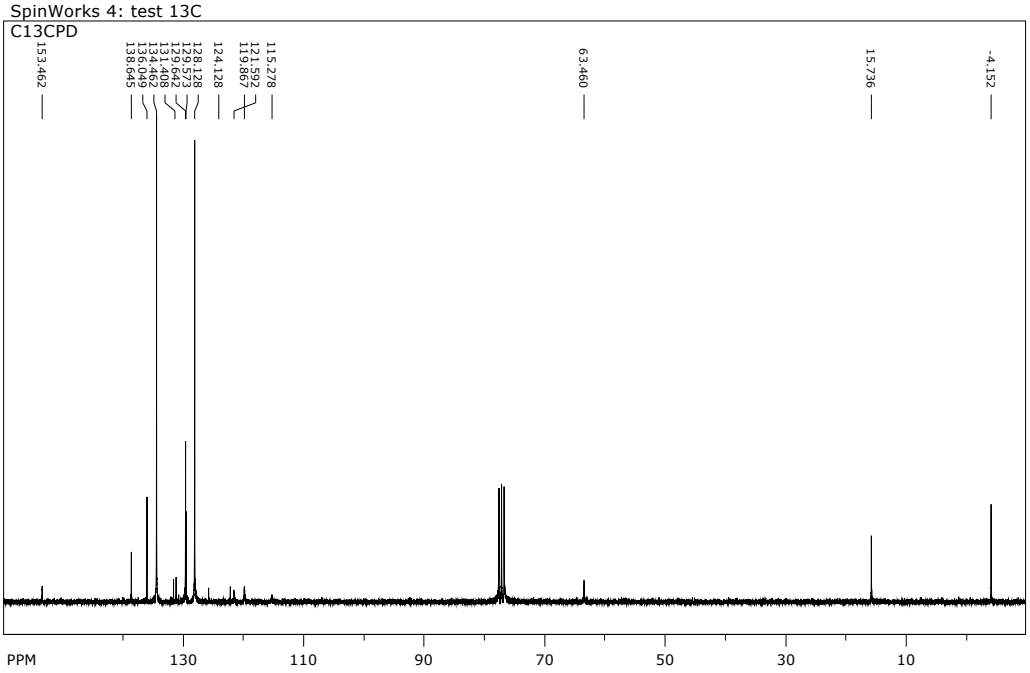
number of scans: 16

freq. of 0 ppm: 300.130006 MHz
processed size: 32768 complex points
LB: 0.000 GF: 0.0000

SpinWorks 4: test 13C



file: D:\EXC-2-10 13C\1\fid expt: <zgpg30>
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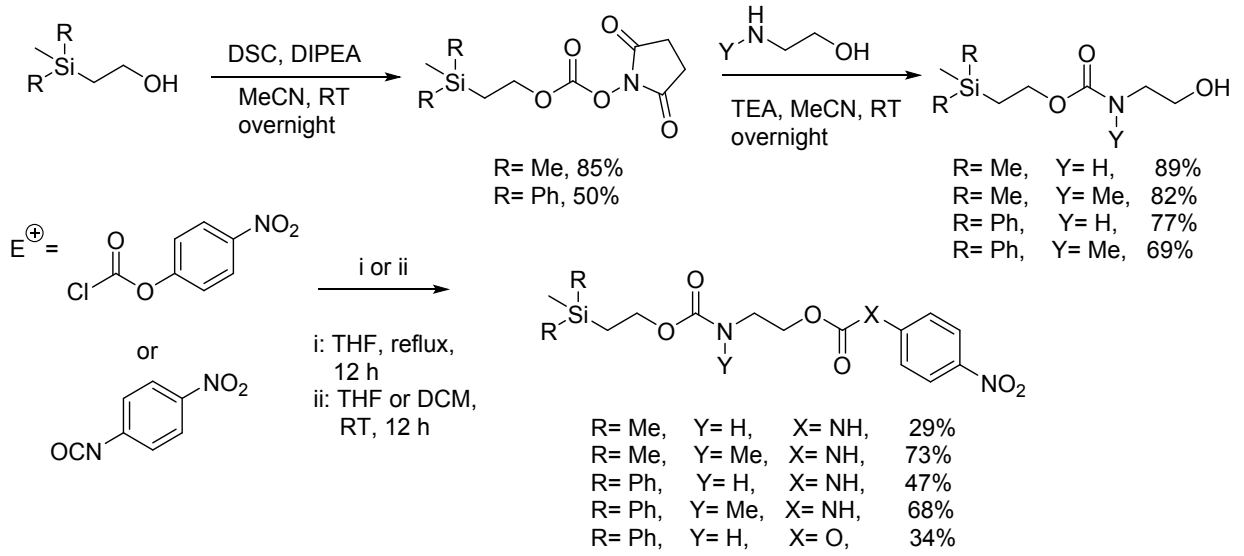
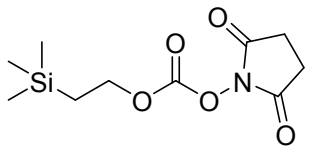


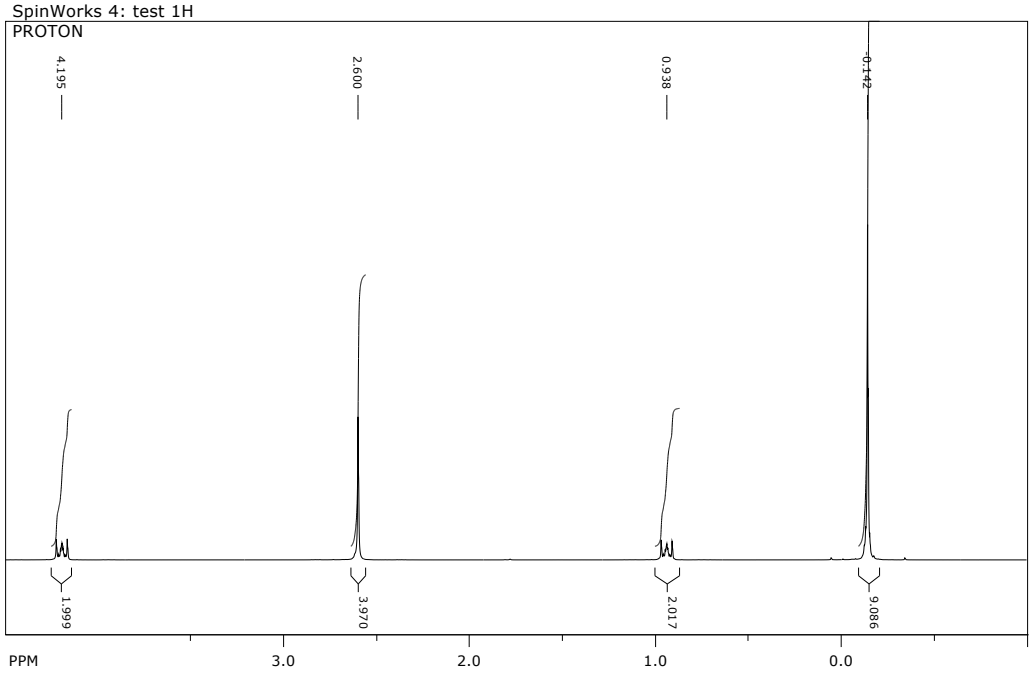
Scheme S1: Synthesis of Silyl-Terminated Extended Chain Molecules.

Procedures for Synthesis of Silyl-Terminated Extended Chain Molecules:



2,5-dioxopyrrolidin-1-yl (2-(trimethylsilyl)ethyl) carbonate: Triethylamine (10.7 mL, 77.8 mmol) was added to 2-trimethylsilylethanol (3.7 mL, 25.94 mmol) in 130 mL acetonitrile, followed by di-succinimidyl carbonate (10 g). The reaction was stirred at room temperature for overnight. The reaction was concentrated and extracted using ethyl acetate and saturated sodium bicarbonate. The organic layer was concentrated after dried over magnesium sulfate. The resulting mixture was purified using column chromatography (ethyl acetate/hexane: 40/60) to furnish the product (5.6 g) as a white solid in 85% yield. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ = 4.19 (t, *J* = 8.2Hz, 2H), 2.60 (s, 4H), 0.94 (t, *J* = 8.2Hz, 2H), -0.14 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ = 169.04, 151.40, 70.44, 25.39, 17.37, -1.68. The NMR spectra matched the reported literature spectra.

SpinWorks 4: test 1H



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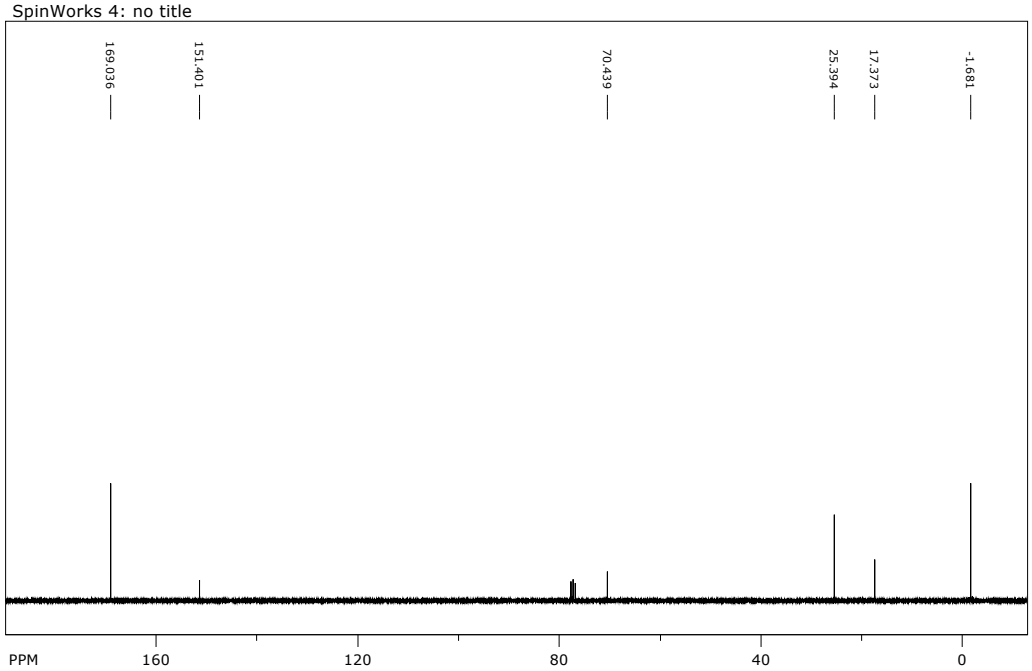
SpinWorks 4: no title



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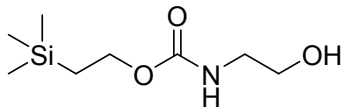
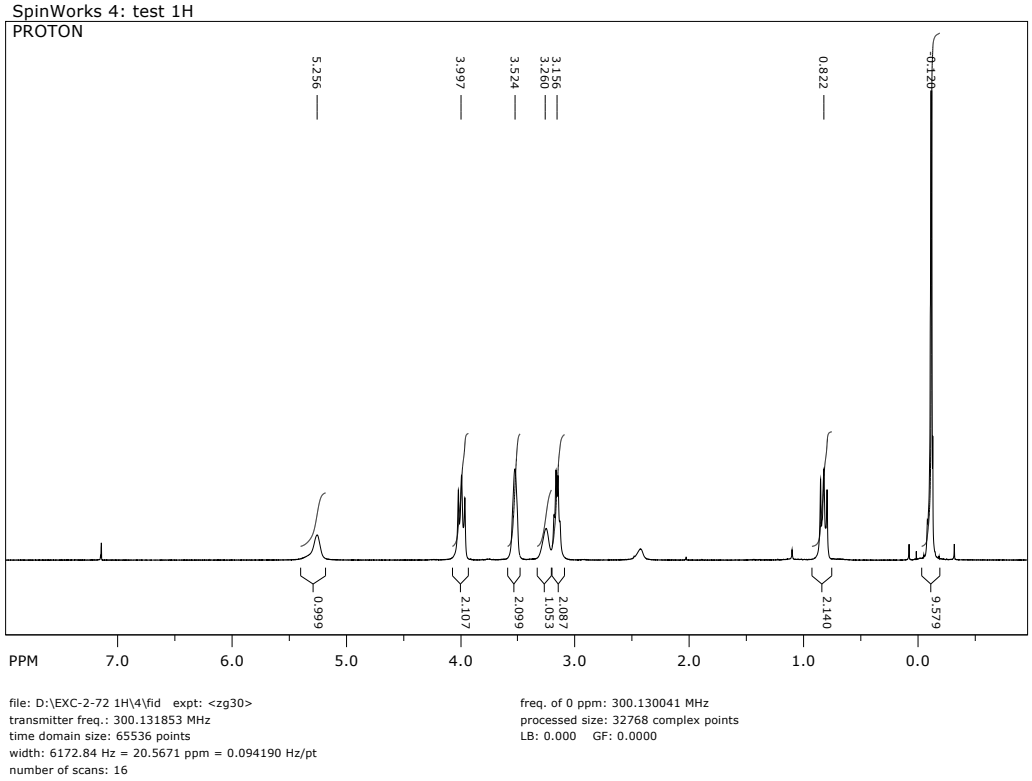
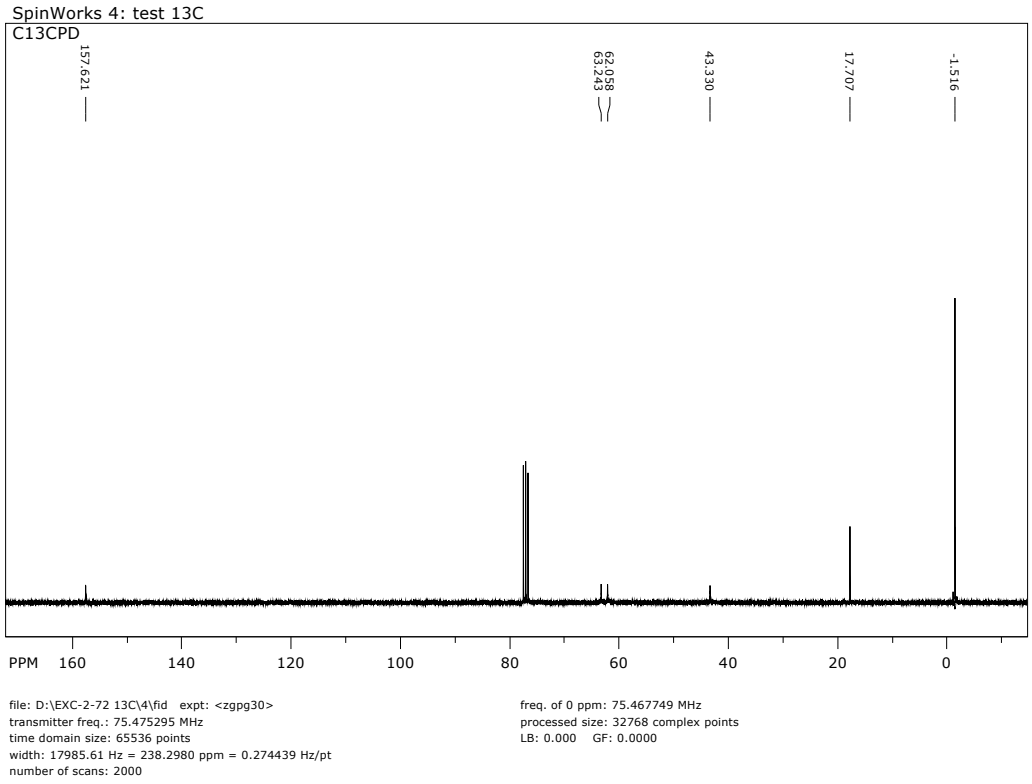
number of scans: 1024

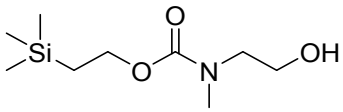
freq. of 0 ppm: 75.467749 MHz
processed size: 32768 complex points
LB: 0.000 GF: 0.0000



2-(trimethylsilyl)ethyl (2-hydroxyethyl)carbamate: A solution of ethanolamine (0.5 mL, 8.3 mmol) and diisopropylethylamine (2.8 mL, 16.6 mmol) was prepared in acetonitrile (30 mL). 2,5-dioxopyrrolidin-1-yl (2-(trimethylsilyl)ethyl) carbonate (4.29 g, 8.3 mmol) was then added to the solution, at which point a precipiate appeared, and was stirred for overnight at room temperature. The reaction mixture was concentrated, dissolved in dichloromethane, and washed with sodium bicarbonate, 3M sodium hydroxide, and brine. The organic layer was concentrated after dried over magnesium sulfate. The resulting mixture was purified using column chromatography (ethyl acetate/hexane: 60/40) to furnish the product (3.0 g) as a clear liquid in 89% yield. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ = 5.26 (s, 1H), 3.99 (t, *J* = 8.76 Hz, 2H), 3.52 (bt, 2H), 3.26 (s, 1H), 3.16 (q, *J* =5.0 Hz), 0.82 (t, *J* = 8.5 Hz, 2H), -0.12 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ = 157.62, 63.24, 62.06, 43.33, 17.71, -1.52. HRMS (ESI) *m/z* calculated for $C_8H_{19}NO_3SiNa$ $[M + Na]^+$ 228.1026, found 228.107.

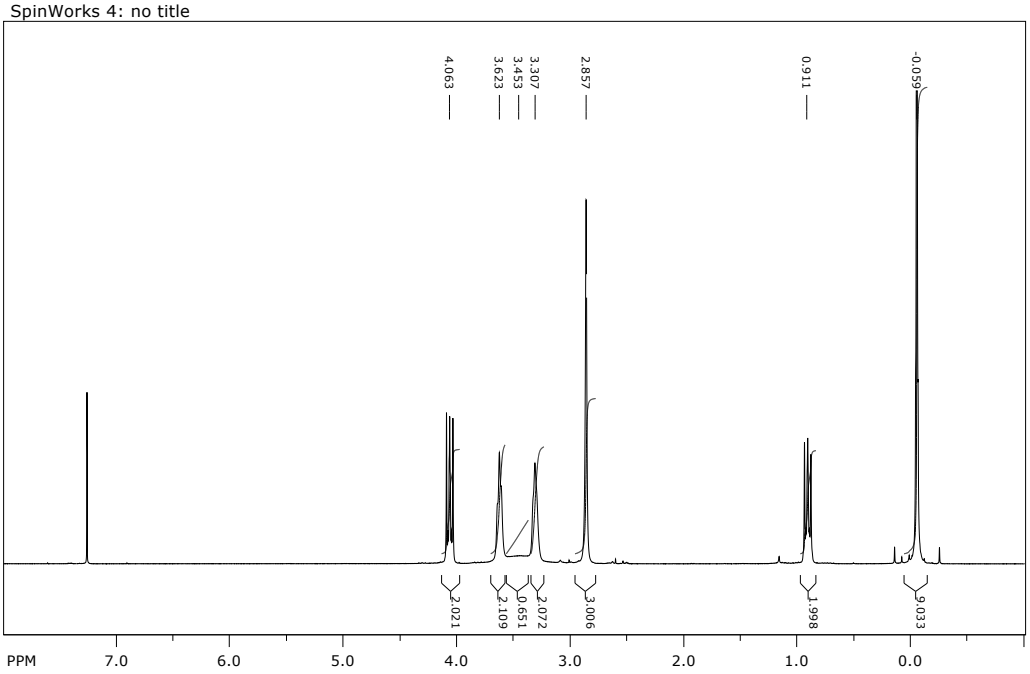






2-(trimethylsilyl)ethyl (2-hydroxyethyl)(methyl)carbamate: A solution of N-methyl ethanolamine (1.0 mL, 12.4 mmol) and diisopropylethylamine (2.8 mL, 12.4 mmol) was prepared in acetonitrile (30 mL). 2,5-dioxopyrrolidin-1-yl (2-(trimethylsilyl)ethyl) carbonate (3.2 g, 12.3 mmol) was then added to the solution, at which point a precipiate appeared, and was stirred for overnight at room temperature. The reaction mixture was concentrated, dissolved in dichloromethane, and washed with sodium bicarbonate, 3M sodium hydroxide, and brine. The organic layer was concentrated after dried over magnesium sulfate. The resulting mixture was purified using column chromatography (ethyl acetate/hexane: 60/40) to furnish the product (2.4 g) as a clear liquid in 82% yield. (^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ = 4.06 (t, J = 8.2 Hz, 2H), 3.62 (t, J = 4.5 Hz, 2H), 3.45 (bs, 1H), 3.31 (t, J = 4.5 Hz, 2H), 2.86 (s, 3H), 0.91 (t, J = 8.2 Hz, 2H), -0.06 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ = 157.71, 63.55, 60.63, 51.59, 35.09, 17.81, -1.61. The material was found to be unstable at the inlet during MS analysis, and thus the partent ion could not be obtained.

SpinWorks 4: no title



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freq. of 0 ppm: 300.130006 MHz
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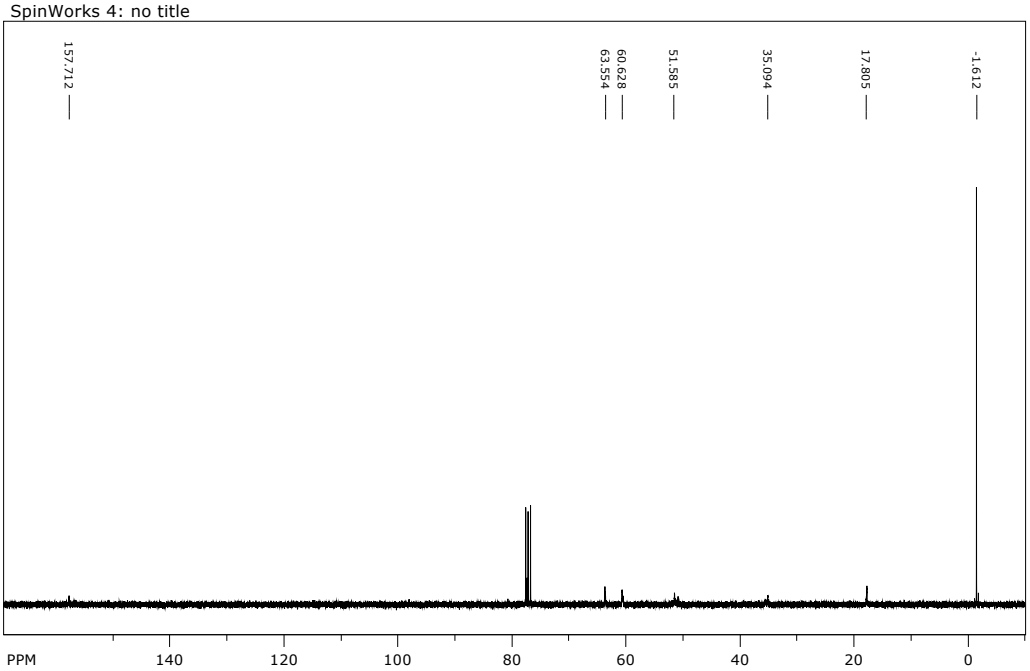
SpinWorks 4: no title



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number of scans: 250

freq. of 0 ppm: 75.467749 MHz
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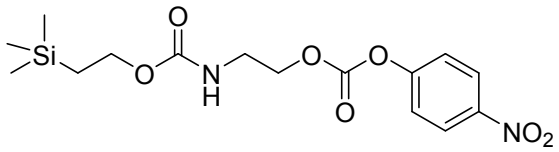
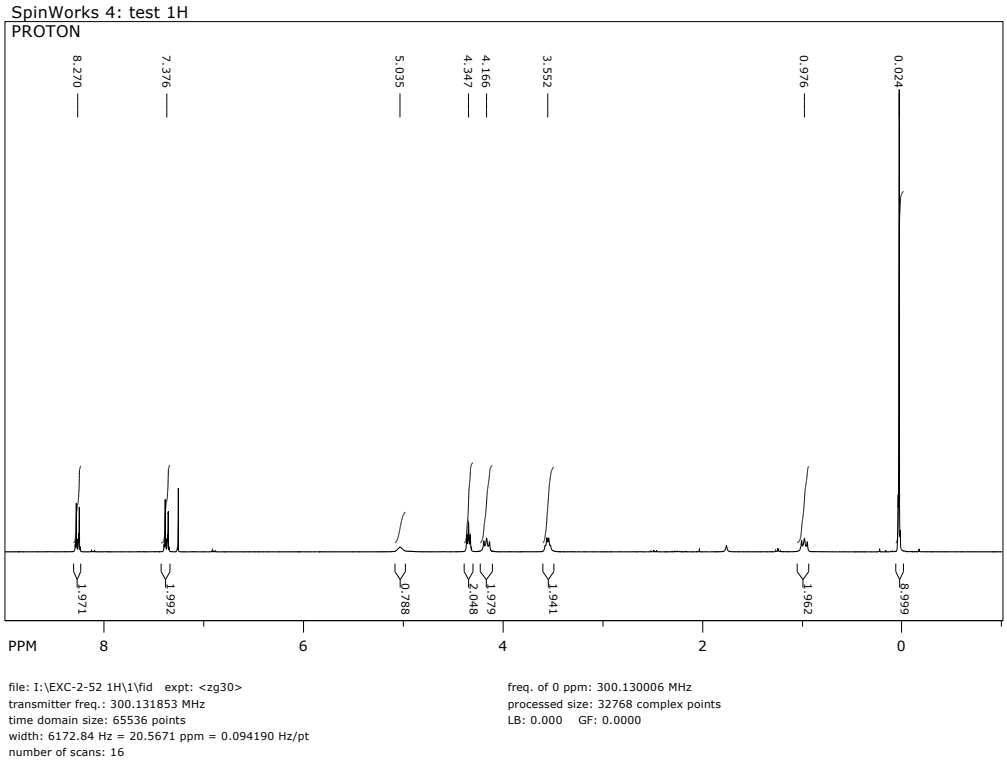
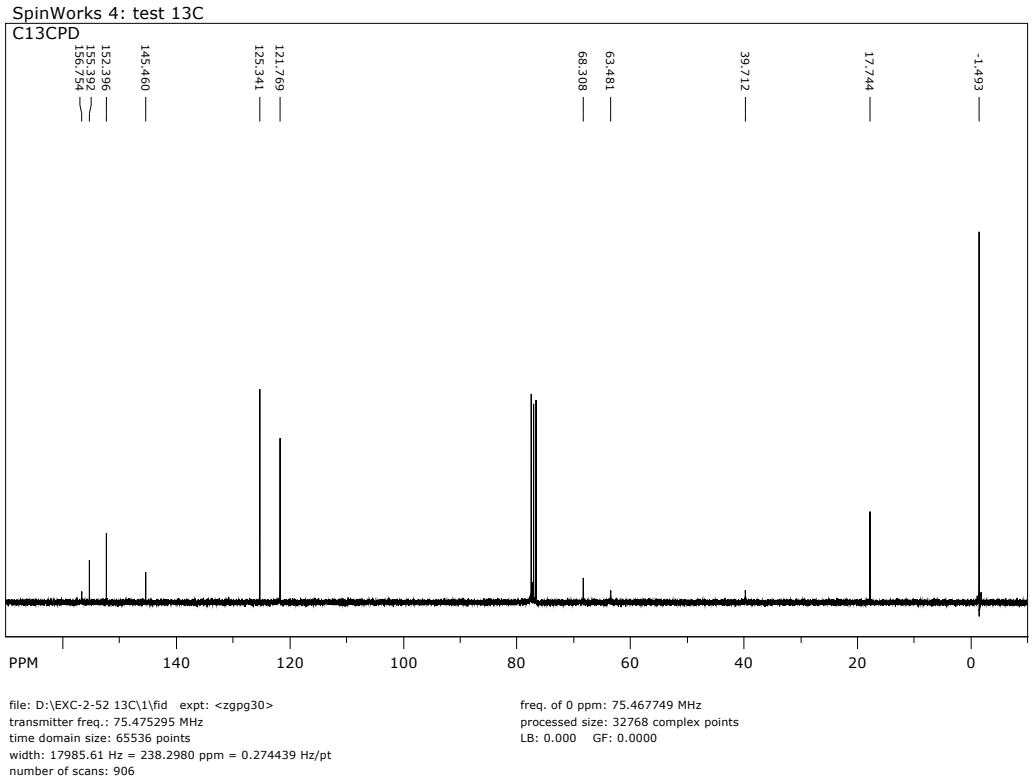
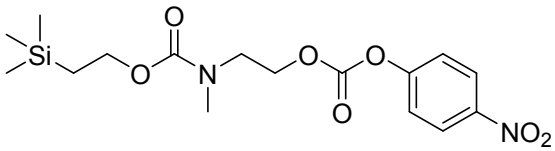


2-(trimethylsilyl)ethyl (2-(((4-nitrophenoxy)carbonyl)oxy)ethyl)carbamate (3a): To a solution of 2-(trimethylsilyl)ethyl (2-hydroxyethyl)carbamate (1 g, 4.87 mmol) in THF (20 mL), 4-nitrophenyl isocyanate (0.76 mg, 4.63 mmol) was added at room temperature and let stir for overnight. The reaction mixture was extracted with dichloromethane and brine, dried with magnesium sulfate, and then concentrated *in vacuo*. The resulting mixture was purified using column chromatography (hexane/ dichloromethane/ ethyl acetate: 8/7/1) to furnish the product (0.2 g) as an off-white solid in 62% yield. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ = 8.27 (d, *J* = 9.3 Hz, 2H), 7.38 (d, *J* = 9.3Hz, 2H), 5.03 (s, 1H), 4.35 (t, *J* = 5.0Hz, 2H), 4.17 (t, *J* = 8.8Hz, 2H), 3.55 (q, *J* = 5.3Hz, 2H), 0.98 (t, *J* = 8.5Hz, 2H), 0.02 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ = 156.75, 155.39, 152.39, 145.46, 125.34, 121.77, 68.31, 63.48, 39.71, 17.74, -1.49. HRMS (EIC) *m/z* calculated for $C_{15}H_{22}N_2O_7SiNa$ $[M + Na]^+$ 393.1088, found 393.1087.

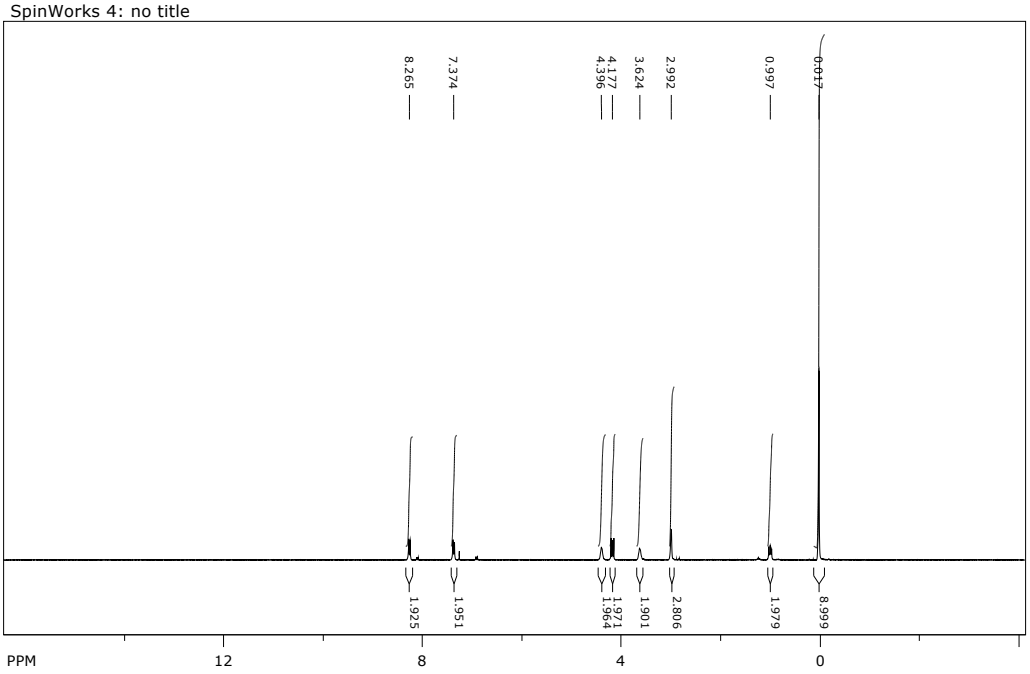






2-(trimethylsilyl)ethyl methyl(2-(((4-nitrophenoxy)carbonyl)oxy)ethyl)carbamate (3b): To a solution of 2-(trimethylsilyl)ethyl (2-hydroxyethyl)(methyl)carbamate (0.4 g, 1.82 mmol) in MeCN (20 mL), 4-nitrophenyl chloroformate (0.4 mg, 2.00 mmol) was added at room temperature and let stir for overnight. The reaction mixture was extracted with dichloromethane and brine, dried with magnesium sulfate, and then concentrated *in vacuo*. The resulting mixture was purified using column chromatography (ethyl acetate/hexane: 3/17) to furnish the product (0.38 g) as an off-white solid in 54% yield. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ = 8.27 (d, *J* = 8.9Hz), 7.37 (d, *J* = 8.9Hz), 4.39 (bs, 2H), 4.18 (t, *J* = 8.7Hz), 3.62 (bs, 2H), 2.99 (s, 3H), 0.99(t, *J* = 8.7Hz), 0.02 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ = 152.50, 145.53, 126.22, 125.41, 121.93, 115.71, 67.12, 64.08, 47.79, 35.35, 17.87, -1.46. HRMS (EIC) *m/z* calculated for $C_{16}H_{24}N_2O_7SiNa$ $[M + Na]^+$ 407.1245, found 407.1243.

SpinWorks 4: no title



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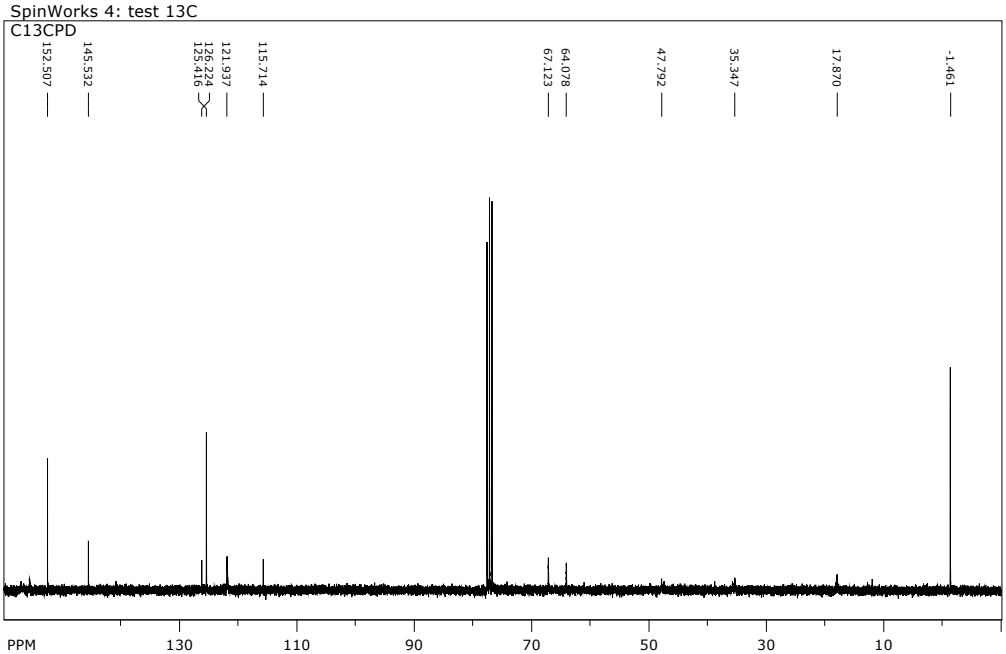
SpinWorks 4: test 13C

C13CPD



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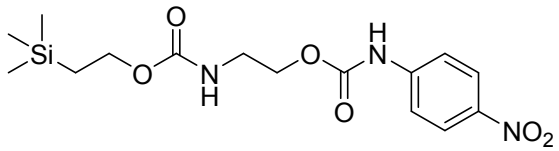
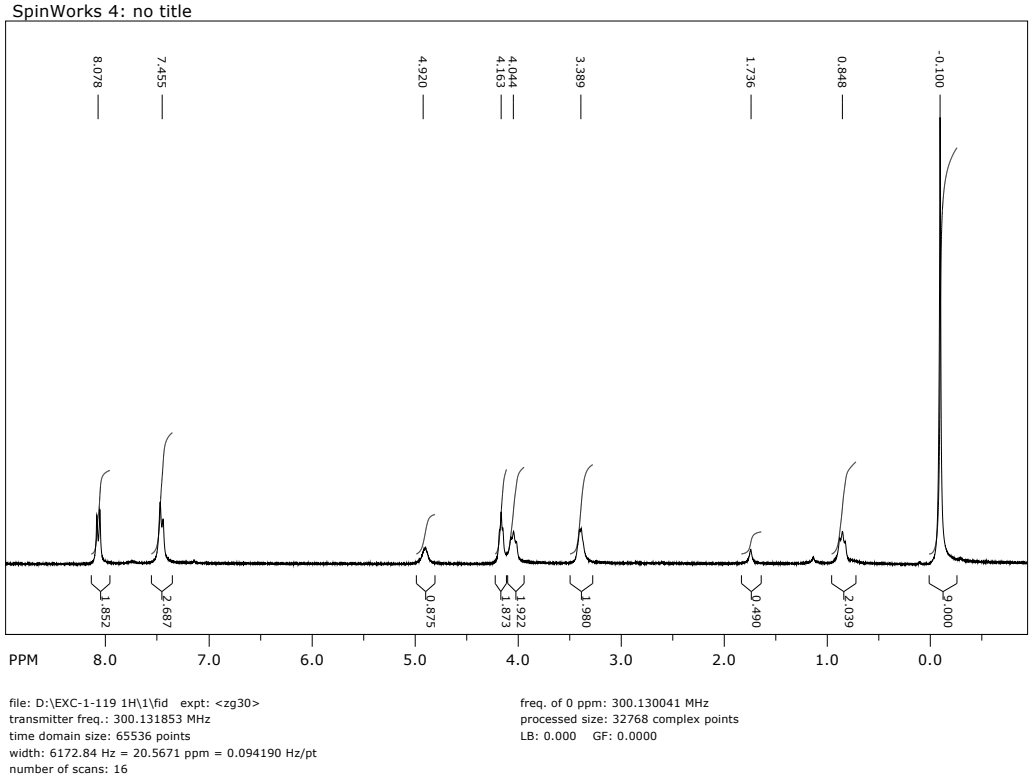
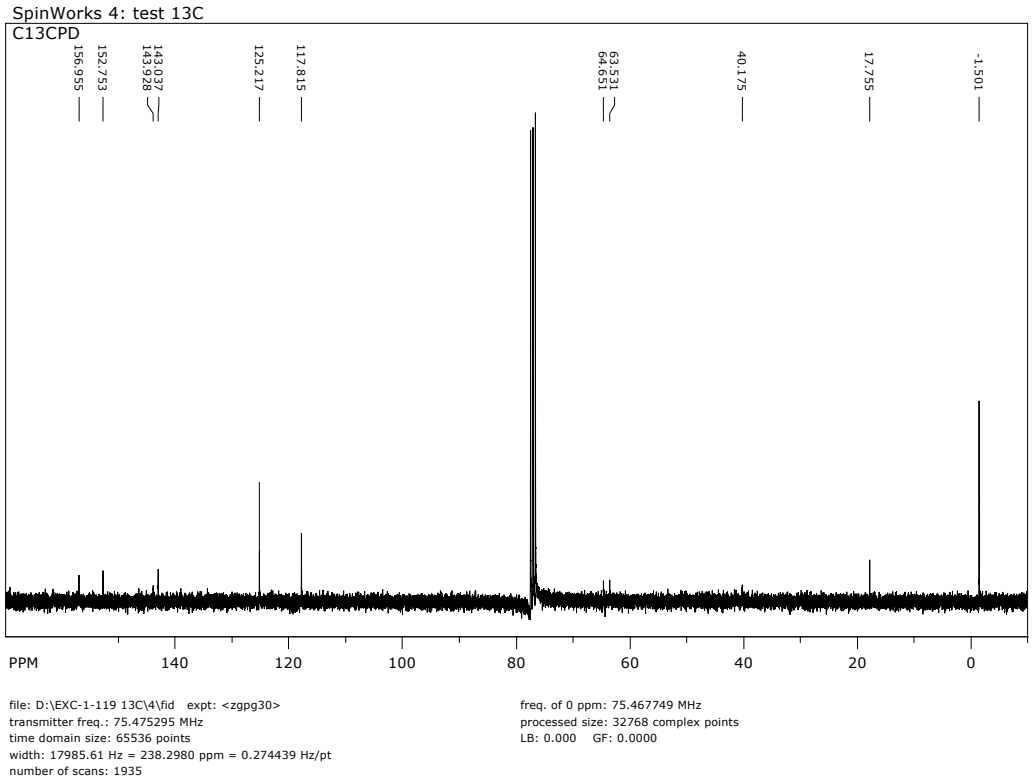
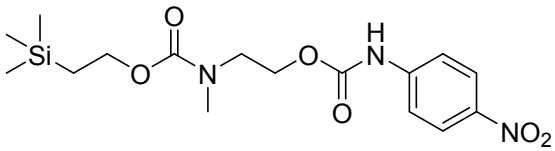


2-(trimethylsilyl)ethyl (2-(((4-nitrophenyl)carbamoyl)oxy)ethyl)carbamate (3e): To a solution of 2-(trimethylsilyl)ethyl (2-hydroxyethyl)carbamate (1 g, 4.87 mmol) in THF (20 mL), 4-nitrophenyl isocyanate (0.76 mg, 4.63 mmol) was added at room temperature and let stir for overnight. The reaction mixture was extracted with dichloromethane and brine, dried with magnesium sulfate, and then concentrated *in vacuo*. The resulting mixture was purified using column chromatography (ethyl acetate/dichloromethane: 10/90) to furnish the product (0.49 g) as an off-white solid in 29% yield. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ = 8.08 (d, *J* = 8.8 Hz, 2H), 7.45 (d, *J* = 8.8 Hz, 2H), 4.92 (s, 1H), 4.16 (t, *J* = 4.8 Hz, 2H), 4.04 (t, *J* = 7.9 Hz, 2H), 3.39 (q, 4.8 Hz, 2H), 1.74, (s, 1H), 0.84 (t, *J* = 7.9 Hz, 2H), -0.10 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ = 156.96, 152.75, 143.92, 143.04, 125.22, 11.82, 64.65, 63.53, 40.18, 17.76, -1.50. HRMS (EIC) *m/z* calculated for $C_{15}H_{23}N_3O_6SiNa$ $[M + Na]^+$ 392.1248, found 392.1246.

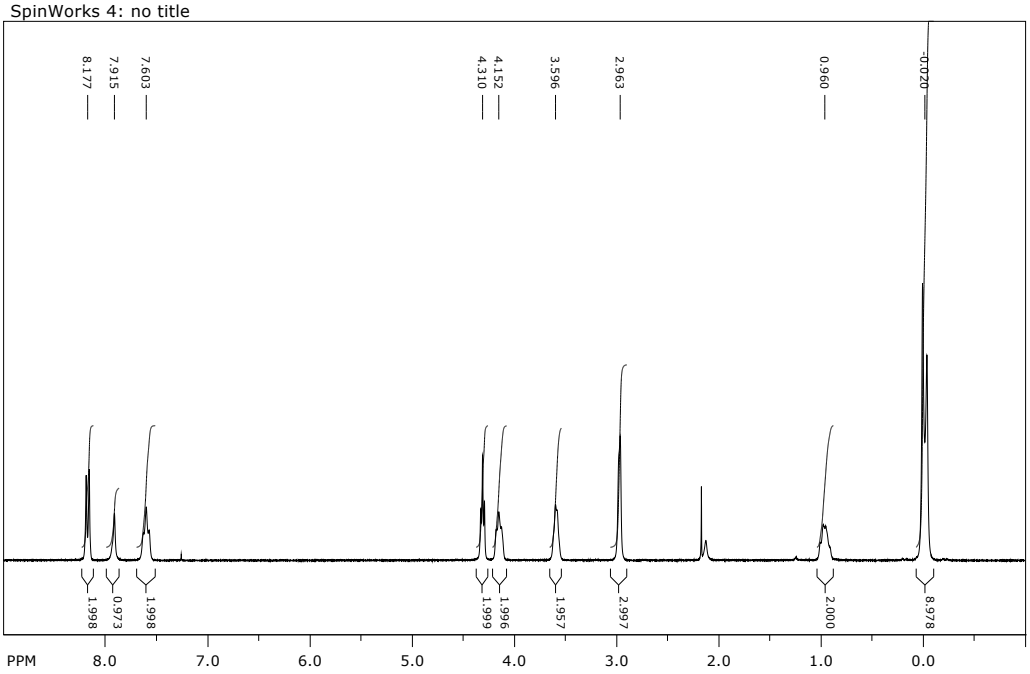






2-(trimethylsilyl)ethyl methyl(2-(((4-nitrophenyl)carbamoyl)oxy)ethyl)carbamate (3f): To a solution of 2-(trimethylsilyl)ethyl (2-hydroxyethyl)(methyl)carbamate (1 g, 4.56 mmol) in THF (20 mL), 4-nitrophenyl isocyanate (0.71 mg, 4.34 mmol) was added at room temperature and let stir for overnight. The reaction mixture was extracted with dichloromethane and brine, dried with magnesium sulfate, and then concentrated *in vacuo*. The resulting mixture was purified using column chromatography (100% dichloromethane) to furnish the product (1.08 g) as an off-white solid in 73% yield. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ = 8.18 (d, *J* = 8.7 Hz, 2H), 7.92 (s, 1H), 7.60 (t, *J* = 8.7 Hz, 2H), 4.31 (t, *J* = 5.6 Hz, 2H), 4.15 (t, *J* = 7.3 Hz, 2H), 3.60 (t, *J* = 5.6 Hz, 2H), 2.96 (s, 3H), 0.96 (t, *J* = 7.3 Hz, 2H), -0.02 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ = 171.42, 157.03, 156.78, 153.01, 144.79, 144.69, 142.61, 124.97, 117.84, 63.98, 63.41, 62.63, 60.46, 47.89, 47.79, 35.43, 34.91, 21.01, 17.72, 17.68, 14.42, -1.57, -1.69. HRMS (ESI) *m/z* calculated for $C_{16}H_{25}N_3O_6SiNa$ $[M + Na]^+$ 406.1405, found 406.1401.

SpinWorks 4: no title



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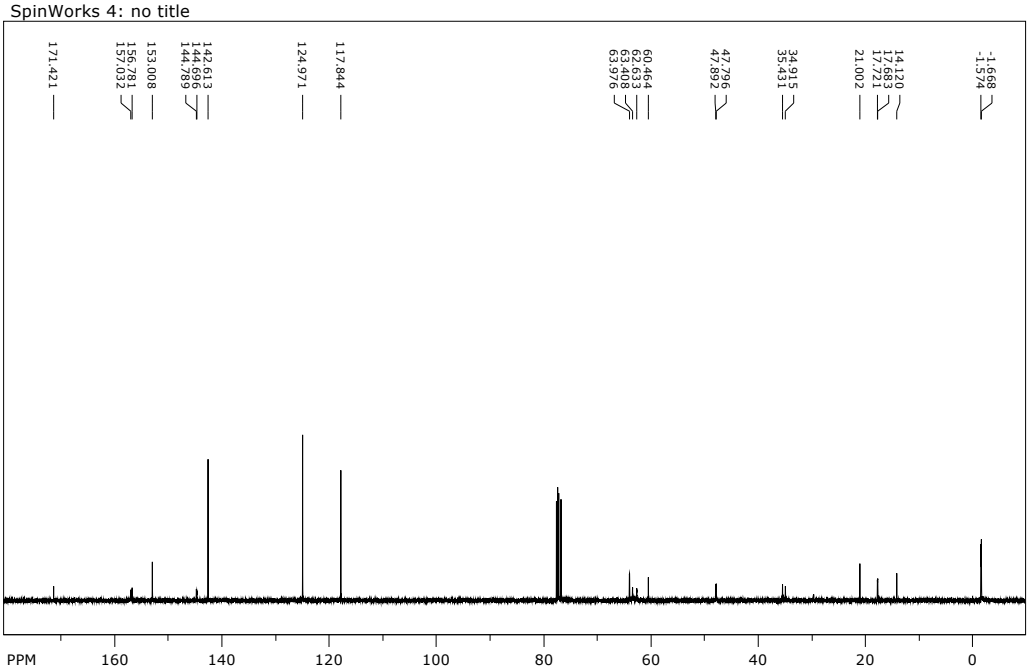
SpinWorks 4: no title



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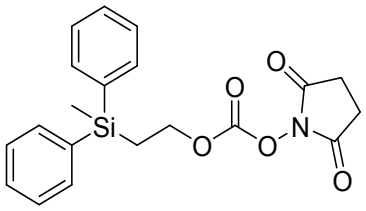
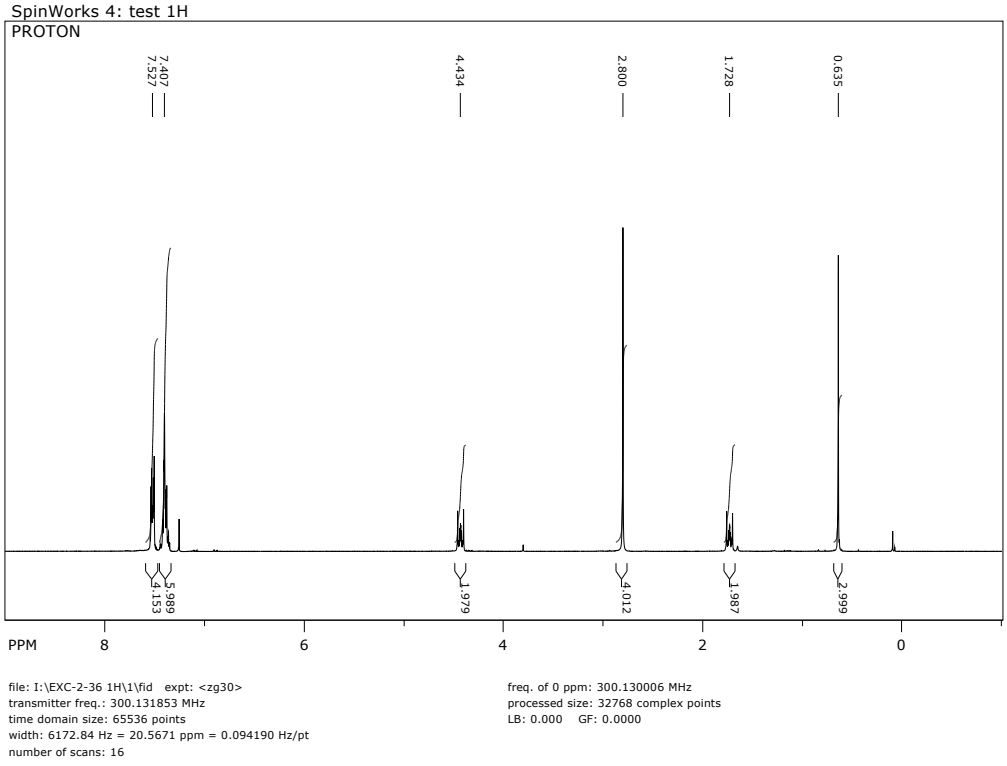
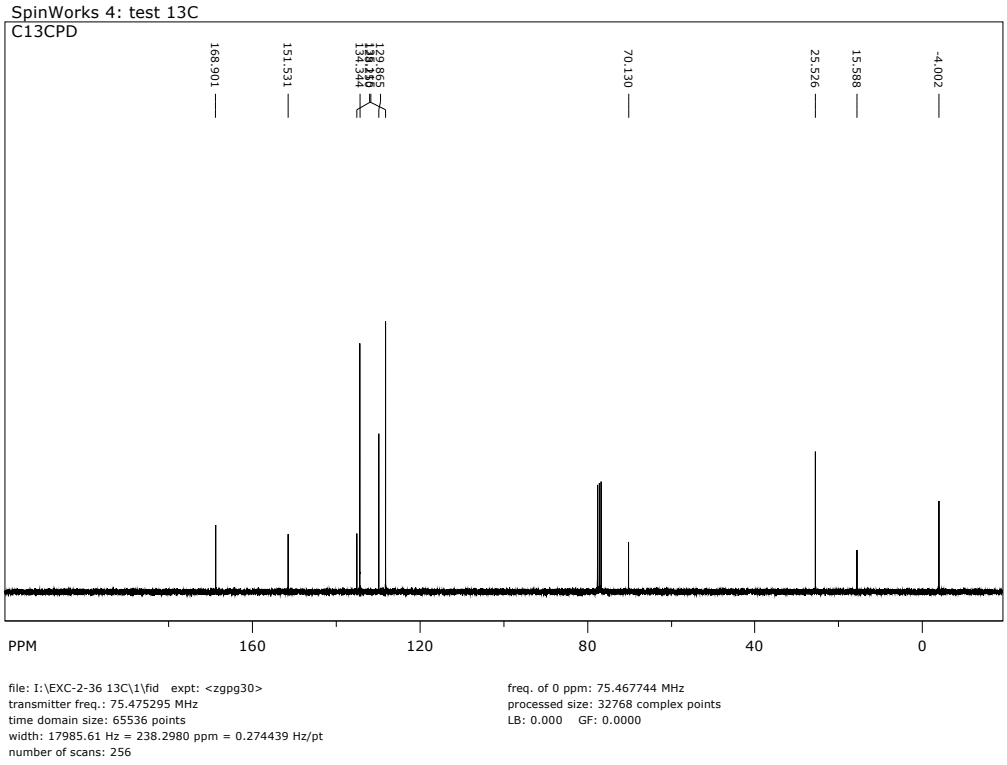
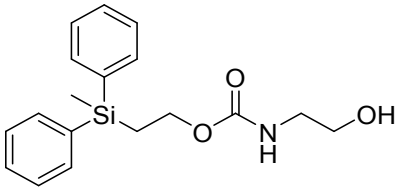


2,5-dioxopyrrolidin-1-yl (2-(methyldiphenylsilyl)ethyl) carbonate: Diisopropylethylamine (3.19 g, 24.8 mmol) was added to 2-diphenlmethylsilylethanol (2.0 g , 8.25 mmol) in 40 mL acetonitrile, followed by di-succinimidyl carbonate (3.17g, 12.38mmol). The reaction was stirred at room temperature for overnight. The reaction was concentrated and extracted using ethyl acetate and saturated sodium bicarbonate. The organic layer was concentrated after dried over magnesium sulfate. The resulting mixture was purified using column chromatography (ethyl acetate/hexane: 60/40) to furnish the product (1.6 g) as a clear crystal in 50% yield. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ = 7.57 (m, 4H), 7.41 (m, 6H), 4.43 (t, *J* = 8.5 Hz, 2H), 2.80 (s, 4H), 1.73 (t, *J* = 8.7Hz, 2H), 0.64 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ = 168.90, 151.53, 135.12, 134.34, 129.87, 128.25, 70.13, 25.53, 15.59, -4.00. HRMS (ESI) *m/z* calculated for $C_{20}H_{21}NO_5SiNa$ $[M + Na]^+$ 406.1081, found 406.1079.

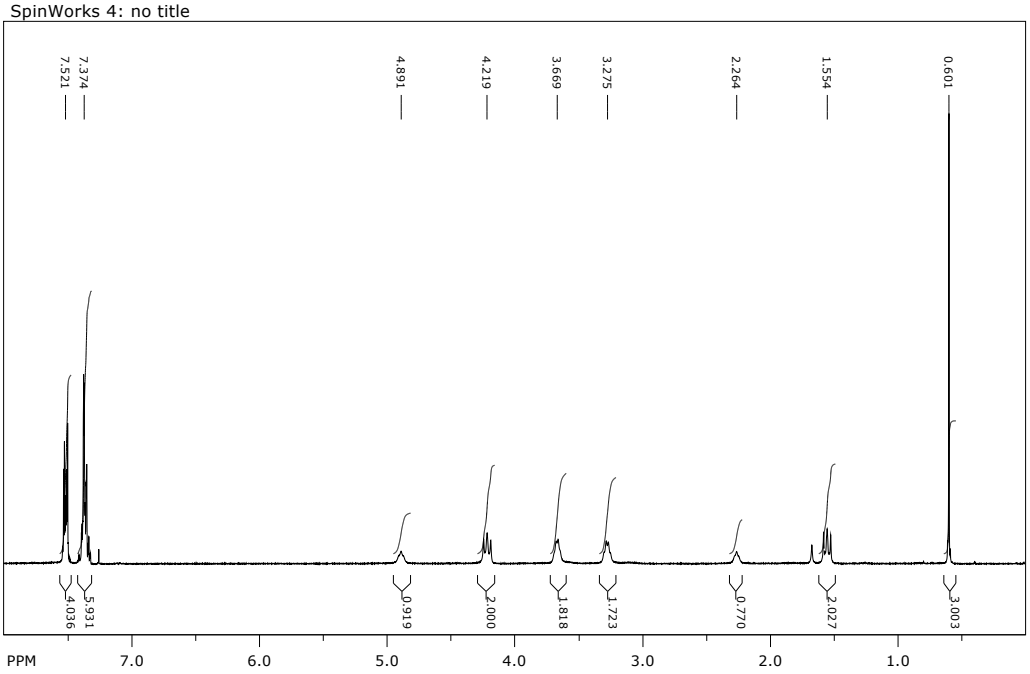






2-(methyldiphenylsilyl)ethyl (2-hydroxyethyl)carbamate: A solution of ethanolamine (0.07 mL, 1.22 mmol) and diisopropylethylamine (0.34 mL, 2.44 mmol) was prepared in acetonitrile (30 mL). 2,5-dioxopyrrolidin-1-yl (2-(trimethylsilyl)ethyl) carbonate (0.47 g, 1.22 mmol) was then added to the solution, at which point a precipiate appeared, and was stirred for overnight at room temperature. The reaction mixture was concentrated, dissolved in dichloromethane, and washed with sodium bicarbonate, 3M sodium hydroxide, and brine. The organic layer was concentrated after dried over magnesium sulfate. The resulting mixture was purified using column chromatography (ethyl acetate/hexane: 50/50) to furnish the product (0.3 g) as a clear liquid in 77% yield. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ = 7.52 (m, 4H), 7.37(m, 6H), 4.89 (s, 1H), 4.22 (t, *J* = 8.2Hz, 2H), 3.67 (q, *J* = 4.3Hz, 2H), 3.28 (q, *J* = 4.3Hz, 2H), 2.26(s, 1H), 1.55 (t, *J* = 8.2Hz, 2H), 0.60 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ = 136.13, 134.39, 132.27, 129.45, 127.98, 73.83, 62.79, 43.38, 15.66, -4.13. HRMS (EIC) *m/z* calculated for $C_{18}H_{23}NO_3SiNa$ $[M + Na]^+$ 352.1339, found 352.1337.

SpinWorks 4: no title



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number of scans: 16

freq. of 0 ppm: 300.130006 MHz
processed size: 32768 complex points
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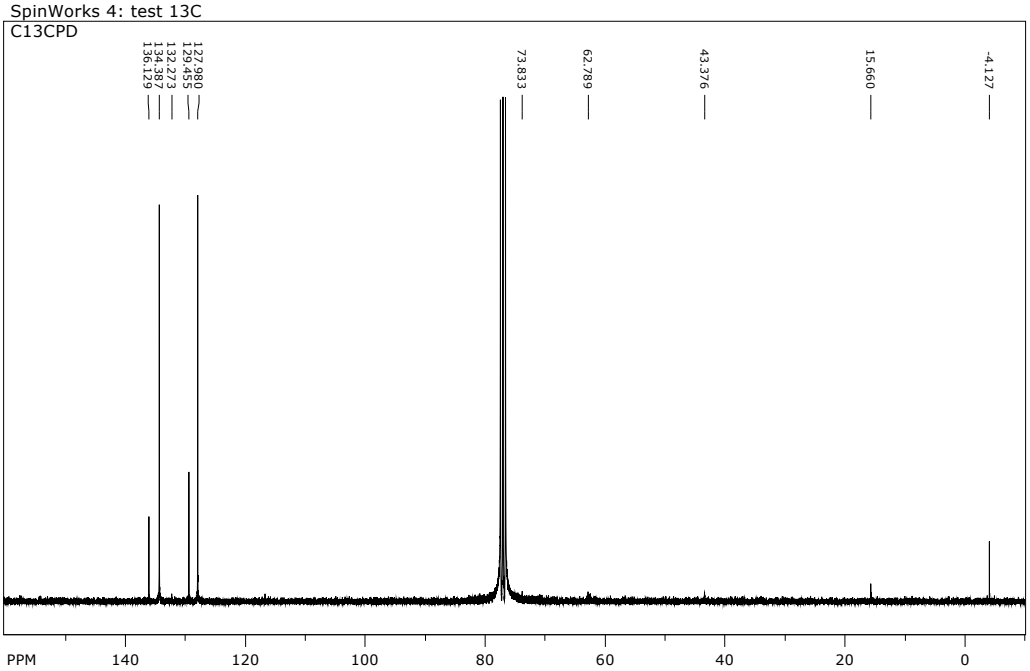
SpinWorks 4: test 13C
C13CPD



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number of scans: 1984

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processed size: 32768 complex points
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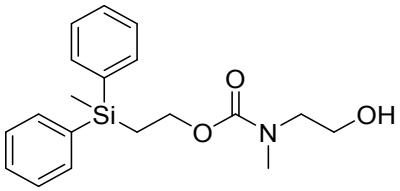
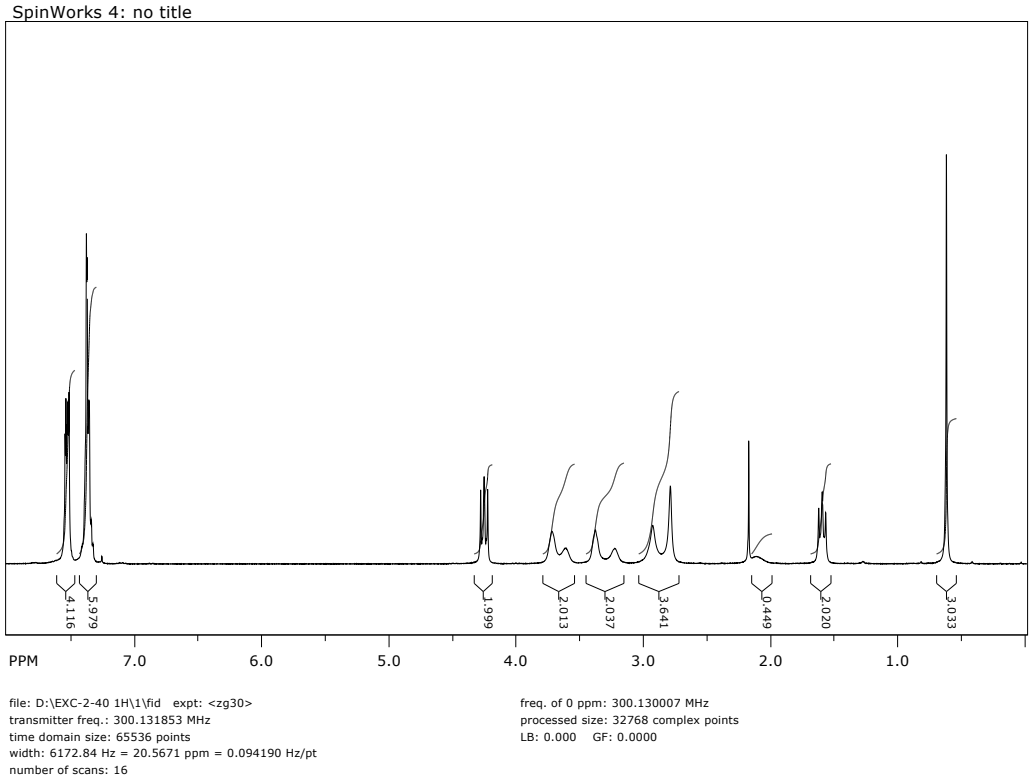
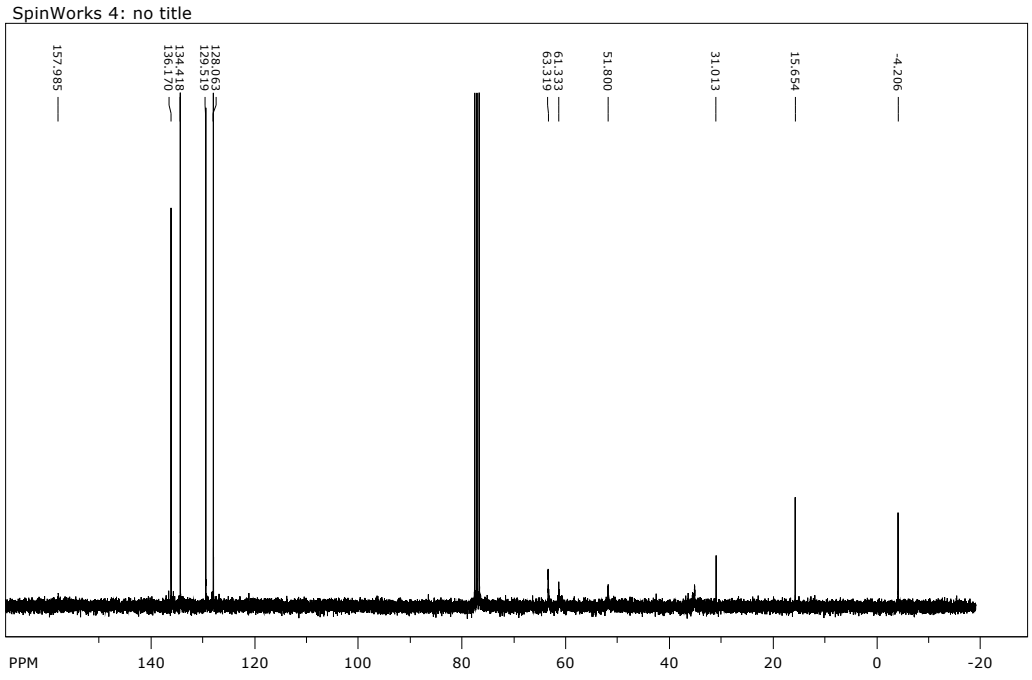
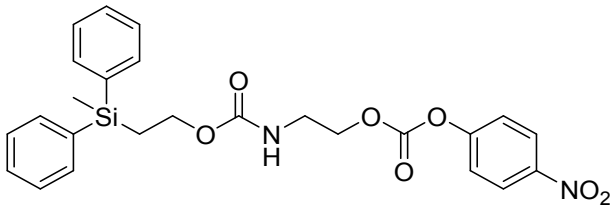


2-(methyldiphenylsilyl)ethyl (2-hydroxyethyl)(methyl)carbamate: A solution of N-methyl ethanolamine (0.2 mL, 2.62 mmol) and triethylamine (0.7 mL, 5.24 mmol) was prepared in acetonitrile (20 mL). 2,5-dioxopyrrolidin-1-yl (2-(diphenylmethylsilyl)ethyl) carbonate (1 g, 2.62 mmol) was then added to the solution, at which point a precipiate appeared, and was stirred for overnight at room temperature. The reaction mixture was concentrated, dissolved in dichloromethane, and washed with sodium bicarbonate, 3M sodium hydroxide, and brine. The organic layer was concentrated after dried over magnesium sulfate. The resulting mixture was purified using column chromatography (ethyl acetate/hexane: 50/50) to furnish the product (2.4 g) as an off-yellow liquid in 69% yield. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ = 7.53 (m, 4H), 7.38 (m, 6H), 4.25 (t, J = 8.4 Hz, 2H), 3.66 (bt, 2H), 3.30 (bt, 2H), 2.86 (s, 3H), 2.11 (s, 1H), 1.59 (t, J = 8.4 Hz, 2H), 0.62(s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ = 157.99, 136.17, 134.42, 129.52, 128.06, 63.32, 61.33, 51.80, 31.01, 15.65, -4.21. HRMS (EIC) *m/z* calculated for $C_{19}H_{25}NO_3SiNa$ $[M + Na]^+$ 366.1496, found 366.1491.

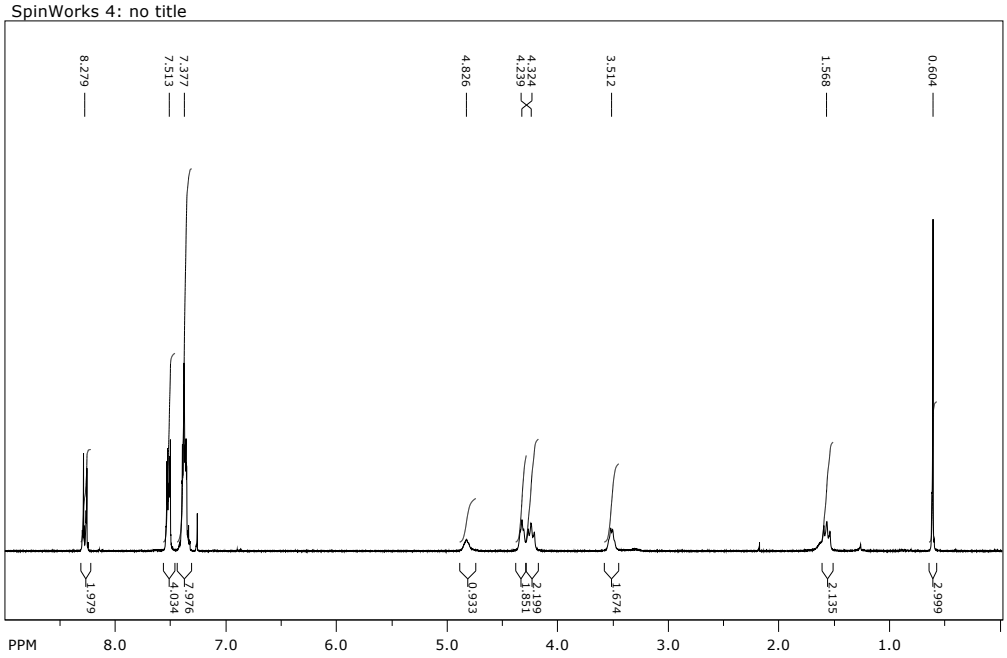






2-(methyldiphenylsilyl)ethyl (2-(((4-nitrophenoxy)carbonyl)oxy)ethyl)carbamate (3c): To a solution of 2-(methyldiphenylsilyl)ethyl (2-hydroxyethyl)carbamate (0.4 g, 1.21 mmol) in THF (20 mL), 4-nitrophenyl chloroformate (0.27 mg, 1.33 mmol), and triethylamine (0.25 mL, 1.82 mmol) was added at room temperature and let stir for overnight. The reaction mixture was extracted with dichloromethane and brine, dried with magnesium sulfate, and then concentrated *in vacuo*. The resulting mixture was purified using column chromatography (100% dichloromethane) to furnish the product (0.2 g) as an off-white solid in 34% yield. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ = 8.27 (d, *J* = 9.2 Hz, 2H), 7.51 (m, 4H), 7.37 (m, 8H), 4.83 (bs, 1H), 4.32 (t, *J* = 5.2 Hz, 2H), 4.24 (t, *J* = 7.7 Hz, 2H), 3.51 (q, *J* = 5.9 Hz, 2H), 1.57 (t, *J* = 9.1 Hz), 0.60 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ = 156.52, 155.33, 152.43, 145.54, 136.01, 134.42, 129.49, 128.06, 125.41, 121.71, 68.22, 63.05, 39.75, 15.65, -4.07. HRMS (EIC) *m/z* calculated for $C_{25}H_{26}N_2O_7SiNa$ $[M + Na]^+$ 517.1401, found 517.1399.

SpinWorks 4: no title



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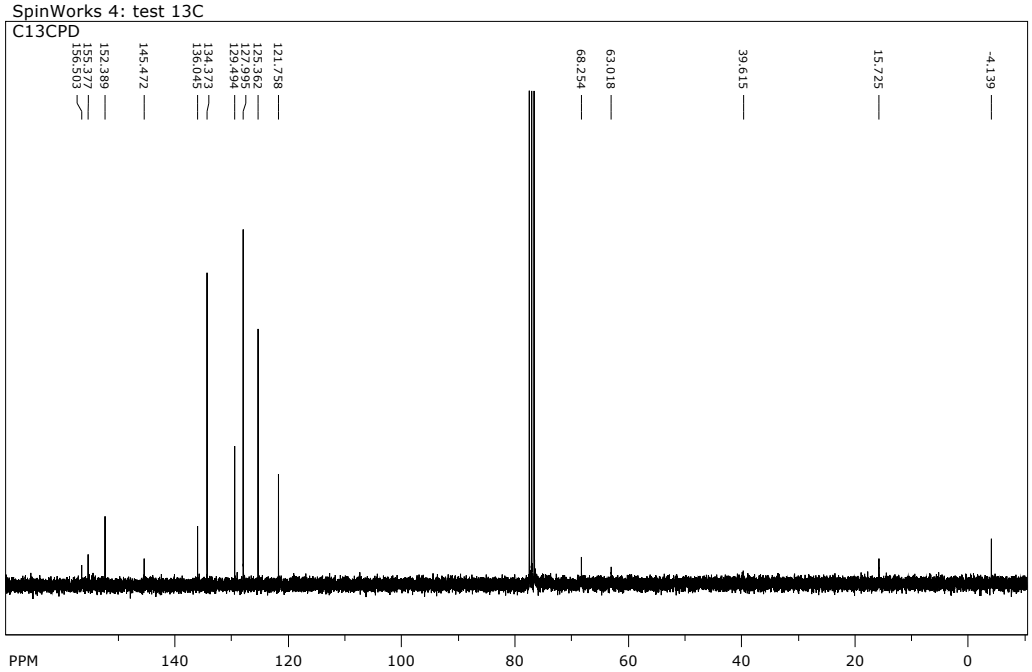
number of scans: 16

freq. of 0 ppm: 300.130006 MHz
processed size: 32768 complex points
LB: 0.000 GF: 0.0000

SpinWorks 4: test 13C

C13CPD



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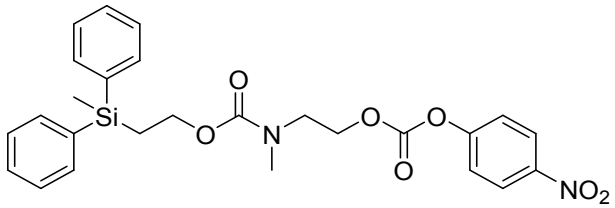
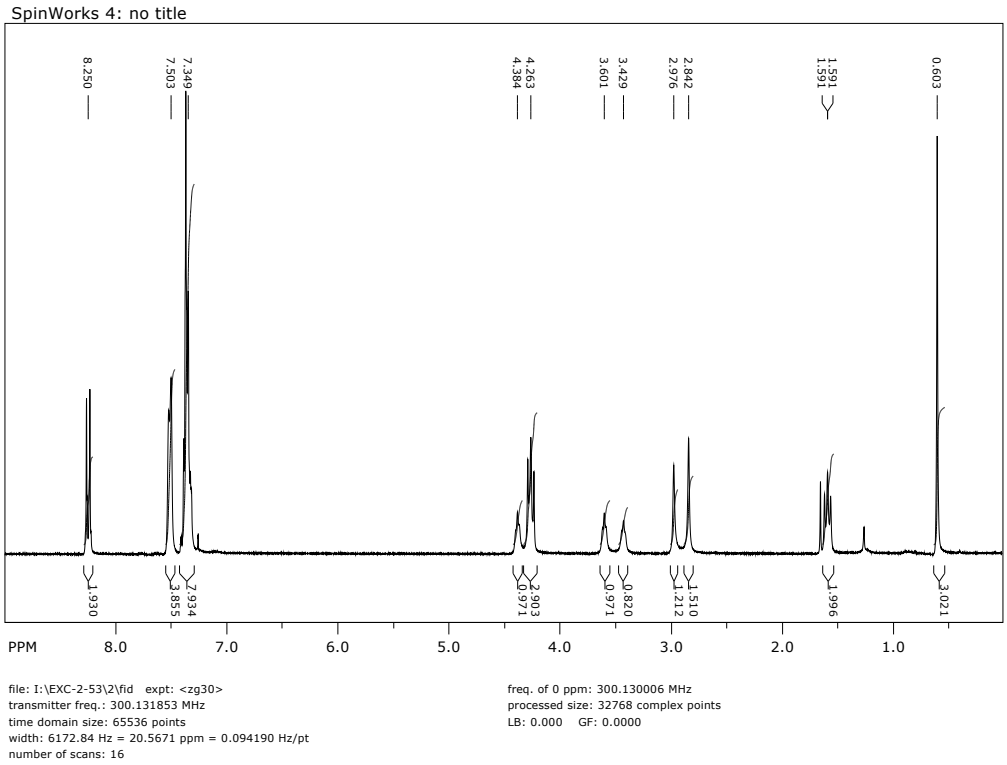
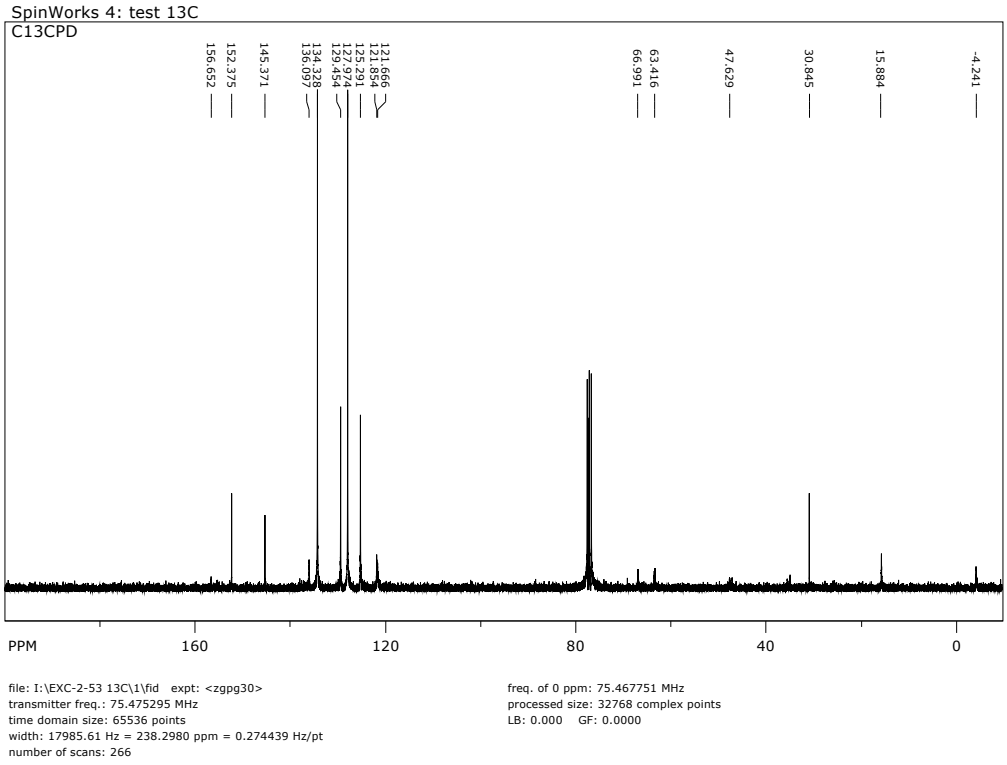
number of scans: 887

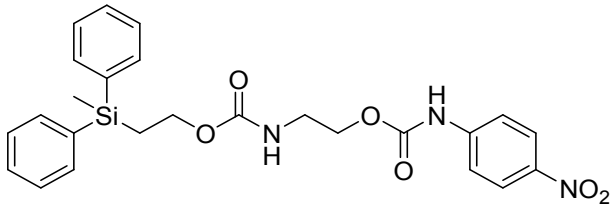
freq. of 0 ppm: 75.467749 MHz
processed size: 32768 complex points
LB: 0.000 GF: 0.0000



2-(methyldiphenylsilyl)ethyl methyl(2-(((4-nitrophenoxy)carbonyl)oxy)ethyl)carbamate (3d): To a solution of 2-(methyldiphenylsilyl)ethyl (2-hydroxyethyl)(methyl)carbamate (0.3 g, 0.87 mmol) in THF (20 mL), 4-nitrophenyl chloroformate (0.26 mg, 1.31 mmol), and triethylamine (0.82 mL, 2.62 mmol) was added at room temperature and let stir for overnight. The reaction mixture was extracted with dichloromethane and brine, dried with magnesium sulfate, and then concentrated *in vacuo*. The resulting mixture was purified using column chromatography (hexane/dichloromethane/ethyl acetate: 8/7/1) to furnish the product (0.18 g) as an off-white solid in 41% yield. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ = 8.25 (d, *J* = 9.1 Hz, 2H), 7.50 (d, *J* = 6.2, 4H), 7.35 (m, 8H), 4.38 (t, *J* = 4.87 Hz, 1H), 4.26 (t, *J* = 8.23, 3H), 3.60 (t, *J* = 4.7 Hz, 1H), 3.43 (t, 4.7 Hz, 1H), 2.98 (s, 1.4H), 2.84 (s, 1.6H), 1.59 (t, *J* = 8.2 Hz), 0.60 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ = 156.65, 152.37, 145.37, 136.10, 134.32, 129.45, 127.97, 125.29, 121.85, 121.67, 66.91, 63.42, 47.63, 30.85, 15.88, -4.24. HRMS (EIC) *m/z* calculated for CHNOSiNa $[M+Na]^+$ 531.1558, found 531.1556.

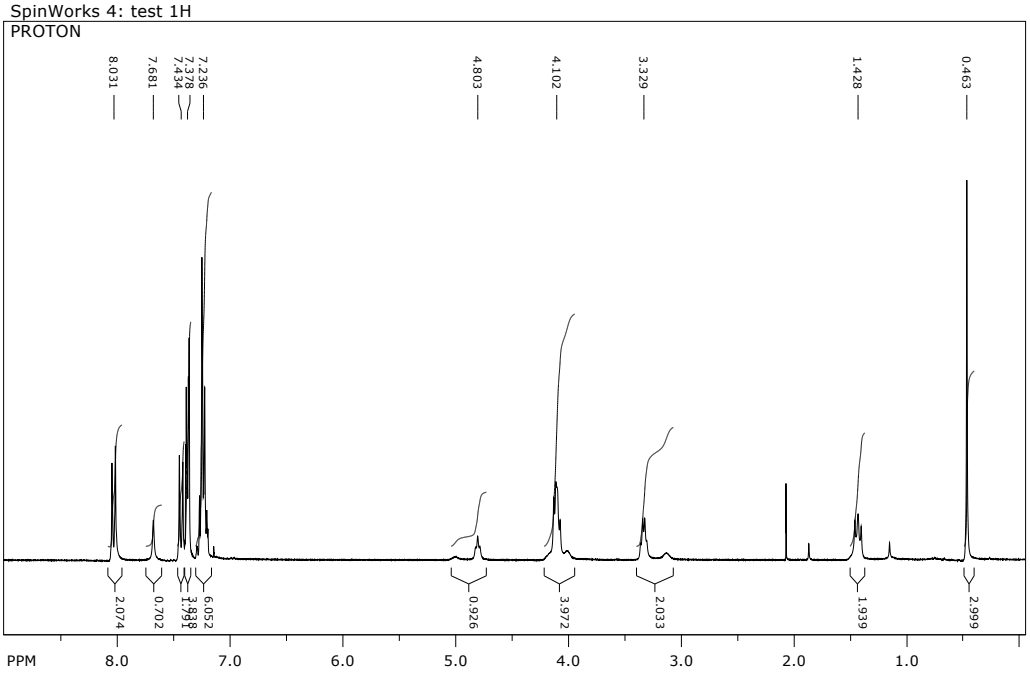






2-(methyldiphenylsilyl)ethyl (2-(((4-nitrophenyl)carbamoyl)oxy)ethyl)carbamate (3g): To a solution of 2-(methyldiphenylsilyl)ethyl (2-hydroxyethyl)carbamate (0.47 g, 4.87 mmol) in THF (20 mL), 4-nitrophenyl isocyanate (0.22 mg, 1.34 mmol) was added at room temperature and let stir for overnight. The reaction mixture was extracted with dichloromethane and brine, dried with magnesium sulfate, and then concentrated *in vacuo*. The resulting mixture was purified using column chromatography (dichloromethane/ ethyl acetate: 4/96) to furnish the product (0.27 g) as an off-white solid in 39% yield. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ = 8.03 (d, *J* = 8.8 Hz, 2H), 7.68 (s, 1H), 7.43 (d, *J* = 8.8 Hz, 2H), 7.38 (m, 4H), 7.24 (m, 6H), 4.80 (t, *J* = 6.2 Hz, 2H), 4.10 (t, *J* = 5.9 Hz, 2H), 3.33 (q, *J* = 5.7 Hz, 2H), 1.43 (t, *J* = 8.4 Hz, 2H), 0.46 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ = 156.90, 152.79, 144.07, 142.94, 135.87, 134.34, 129.57, 128.04, 125.19, 117.79, 64.39, 63.11, 40.18, 15.74, -4.14. HRMS (EIC) *m/z* calculated for $C_{25}H_{27}N_3O_6SiNa$ $[M+Na]^+$ 516.1561, found 516.1558.

SpinWorks 4: test 1H



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number of scans: 16

freq. of 0 ppm: 300.130041 MHz
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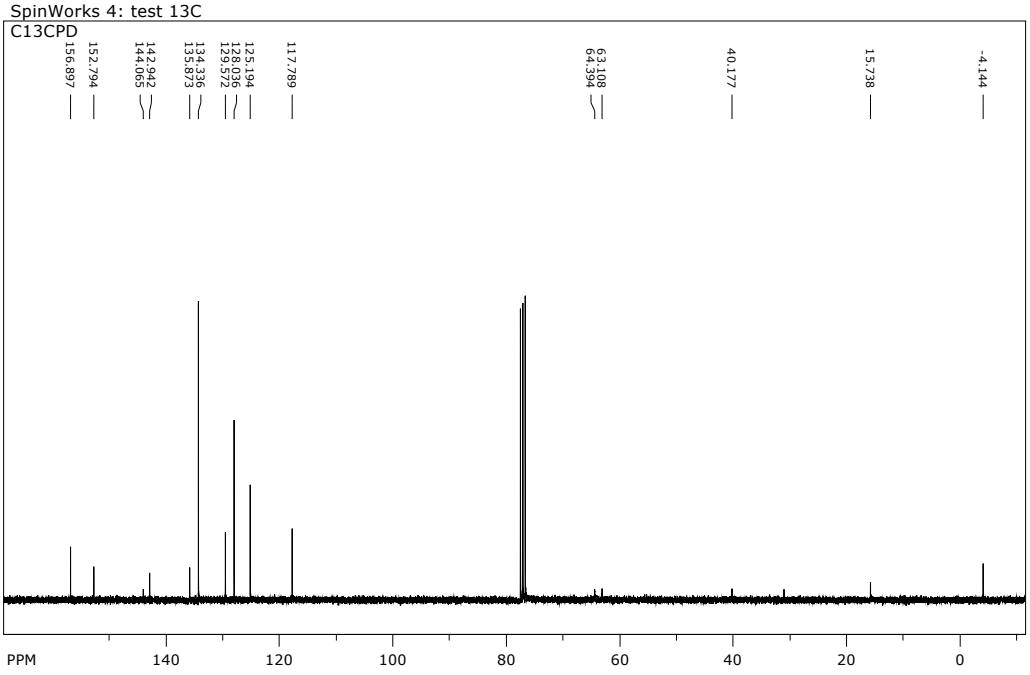
SpinWorks 4: test 13C



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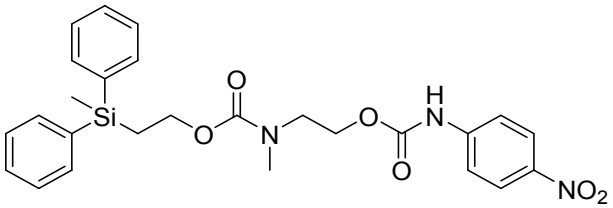
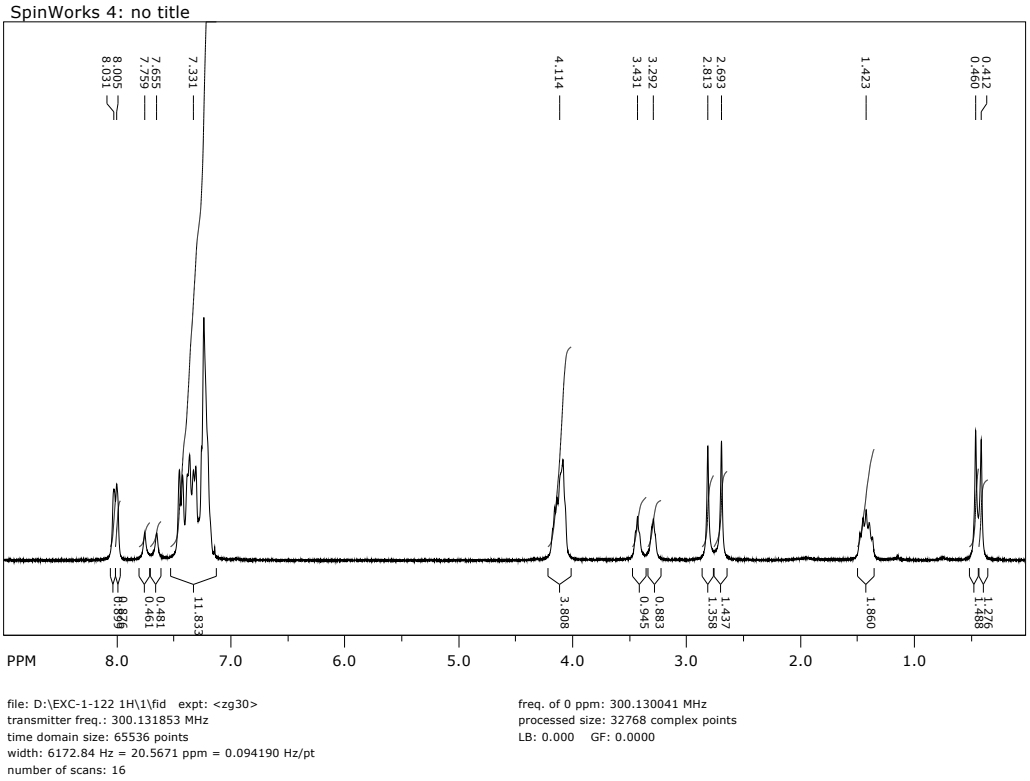
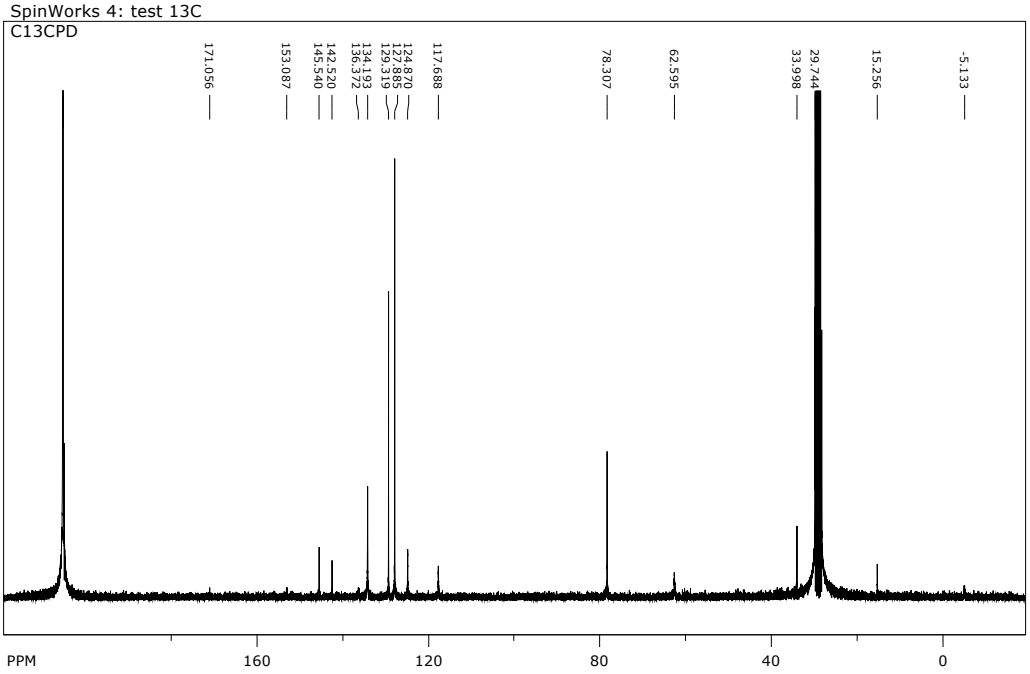


2-(methyldiphenylsilyl)ethyl methyl(2-(((4-nitrophenyl)carbamoyl)oxy)ethyl)carbamate (3h): To a solution of 2-(methyldiphenylsilyl)ethyl (2-hydroxyethyl)(methyl)carbamate (0.62 g, 1.8 mmol) in THF (20 mL), 4-nitrophenyl isocyanate (0.28 mg, 1.71 mmol) was added at room temperature and let stir for overnight. The reaction mixture was extracted with dichloromethane and brine, dried with magnesium sulfate, and then concentrated *in vacuo*. The resulting mixture was purified using column chromatography (100% dichloromethane) to furnish the product (0.62 g) as an off-white solid in 68% yield. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ = 8.03 (s, 1H), 8.01 (s, 1H), 7.76, (s, 0.5H), 7.66 (s, 0.5H), 7.33 (m, 12H), 4.11 (m, 4H), 3.43 (t, *J* = 4.5Hz, 1H), 3.29 (t, *J* = 4.5Hz, 1H), 2.81 (s, 1.5H), 2.69 (s, 1.5H), 1.42 (m, 2H), 0.46 (s, 1.5H), 0.41 (s, 1.5H). The doubling of peaks suggests the presence of rotational isomers. ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ = 171.06, 153.09, 145.54, 142.52, 136.37, 134.19, 129.32, 127.88, 124.87, 117.69, 78.31, 62.59, 33.99, 29.74, 15.56, -5.13. HRMS (EIC) *m/z* calculated for $C_{26}H_{29}N_3O_6SiNa$ $[M+Na]^+$ 530.1718, found 530.1714.



SpinWorks 4: test 13C



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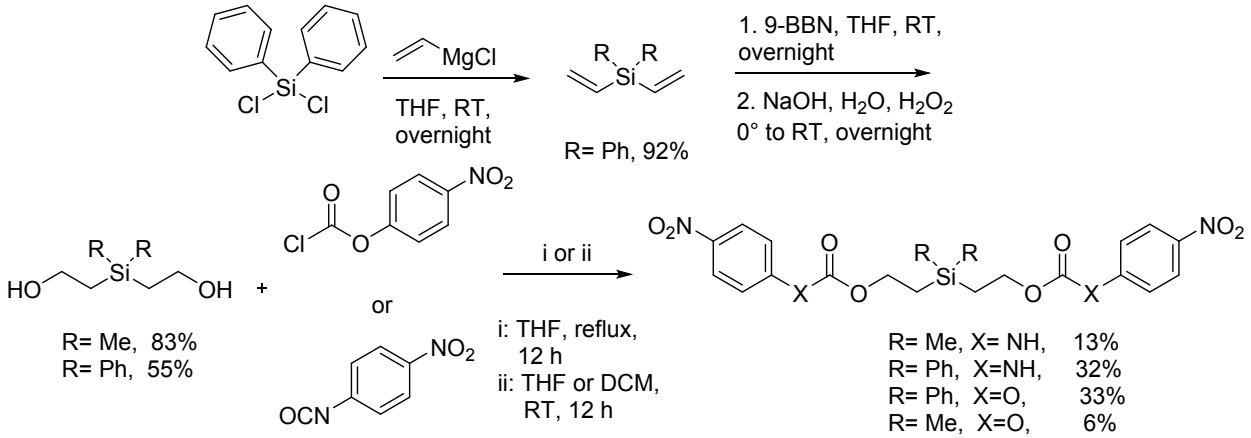
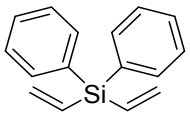
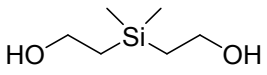


Scheme S2: Synthesis of Silyl-Centered Carbonates and Carbamates.

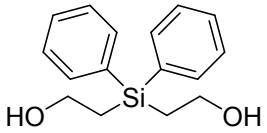
Procedures for Synthesis of Silyl-Centered Carbonates and Carbamates



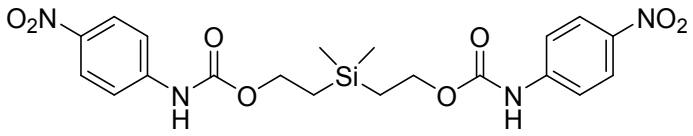
Diphenyldivinylsilane: Diphenyldichlorosilane (1.9 mL, 9.1 mmol) was added to vinylmagnesium bromide (20 mL, 1M solution in THF, 20 mmol) at 0° C. After10 min the cooling bath was removed and the mixture stirred at room temperature for 15 h. Aqueous ammonium chloride (30 mL) was added followed by water and the organic layer separated. The aqueous layer was extracted with dichloromethane (100 mL). The combined organics were dried with $MgSO_4$ and concentrated to give a tallow oil. The resulting mixture was purified using column chromatography (100% hexane) to furnish the product (1.97 g) as an oil in 92% yield. The NMR spectra matched the reported literature spectra.[2]



2,2'-(dimethylsilanediyl)bis(ethan-1-ol): A solution of dimethyldivinylsilane (1 g, 8.9 mmol) in 30 mL of THF was added dropwise to a 0.5 M solution of 9-borabicyclo[3.3.1]nonane in THF (35.6 mL, 17.8 mmol) and the resulting mixture was stirred at room temperature for 4 h, followed by the addition of water (30 mL) and 3 M aqueous sodium hydroxide solution (30 mL). Subsequently aqueous, hydrogen peroxide solution (30 wt.%, 30 mL) was added dropwise at 0 °C within 15 minutes and the reaction mixture was heated to reflux for 3 h. Upon cooling to room temperature, the aqueous layer was saturated with potassium carbonate, the organic layer was removed and the aqueous layer was extracted with ethyl acetate (100 mL). The organic layer was concentrated after dried over magnesium sulfate. The resulting mixture was purified using column chromatography (100% ethyl acetate) to furnish the product (1.1 g) as an oil in 83% yield. The NMR spectra matched the reported literature spectra.[3]

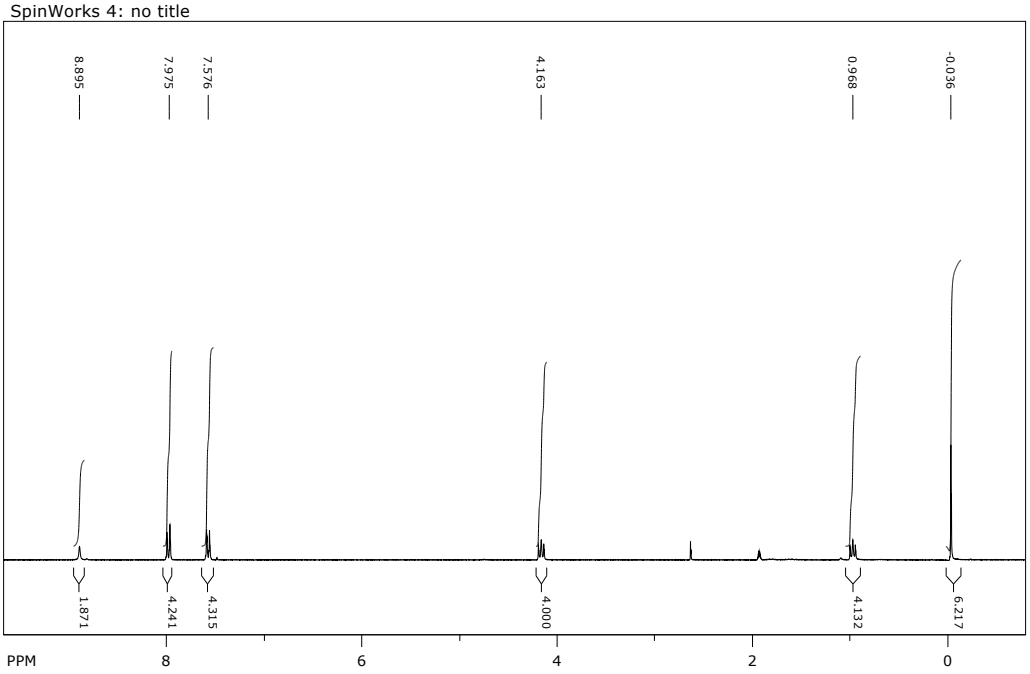


2,2'-(diphenylsilanediyl)bis(ethan-1-ol): A solution of diphenyldivinylsilane (2.2 g, 9.4 mmol) in 15mL of THF was added dropwise to a 0.5 M solution of 9-borabicyclo[3.3.1]nonane in THF (47.2 mL, 23.6 mmol) and the resulting mixture was stirred at room temperature for 4 h, followed by the addition of water (30 mL) and 3 M aqueous sodium hydroxide solution (30 mL). Subsequently aqueous, hydrogen peroxide solution (30 wt.%, 30 mL) was added dropwise at 0 °C within 15 minutes and the reaction mixture was heated to reflux for 3 h. Upon cooling to room temperature, the aqueous layer was saturated with potassium carbonate, the organic layer was removed and the aqueous layer was extracted with ethyl acetate (100 mL). The organic layer was concentrated after dried over magnesium sulfate. The resulting mixture was purified using column chromatography (100% ethyl acetate) to furnish the product (1.4 g) as a clear crystal in 83% yield. The NMR spectra matched the reported literature spectra.[4]



(dimethylsilanediyl)bis(ethane-2,1-diyl) bis((4-nitrophenyl)carbamate) (5a): To a solution of 2,2'-(dimethylsilanediyl)bis(ethan-1-ol) (0.9 g, 6.06 mmol) in THF (35 mL), 4-nitrophenyl isocyanate (0.76 mg, 4.63 mmol) was added at room temperature and let stir for overnight. The reaction mixture was extracted with dichloromethane and brine, dried with magnesium sulfate, and then concentrated *in vacuo*. The resulting mixture was purified using column chromatography (tetrahydrofuran/ hexane: 1/1) to furnish the product (0.35 g) as an off-white solid in 12% yield. ^{1}H NMR (300 MHz, d_6-acetone/$CDCl_3$, Me_4Si): δ = 8.89 (s, 2H), 7.97 (d, J = 9.2 Hz, 4H), 7.57 (d, J = 9.2 Hz, 4H), 4.16 (t, J = 8.9 Hz, 4H), 0.97 (t, J = 8.9 Hz, 4H), -0.04(s, 6H). ^{13}C NMR (75 MHz, d_6-acetone/$CDCl_3$, Me_4Si): δ = 153.54, 145.28, 142.48, 124.77, 117.84, 62.23, 16.31, -3.39. HRMS (ESI) *m/z* calculated for $C_{20}H_{24}N_4O_8SiNa$ $[M+Na]^+$ 499.1256, found 499.1255.

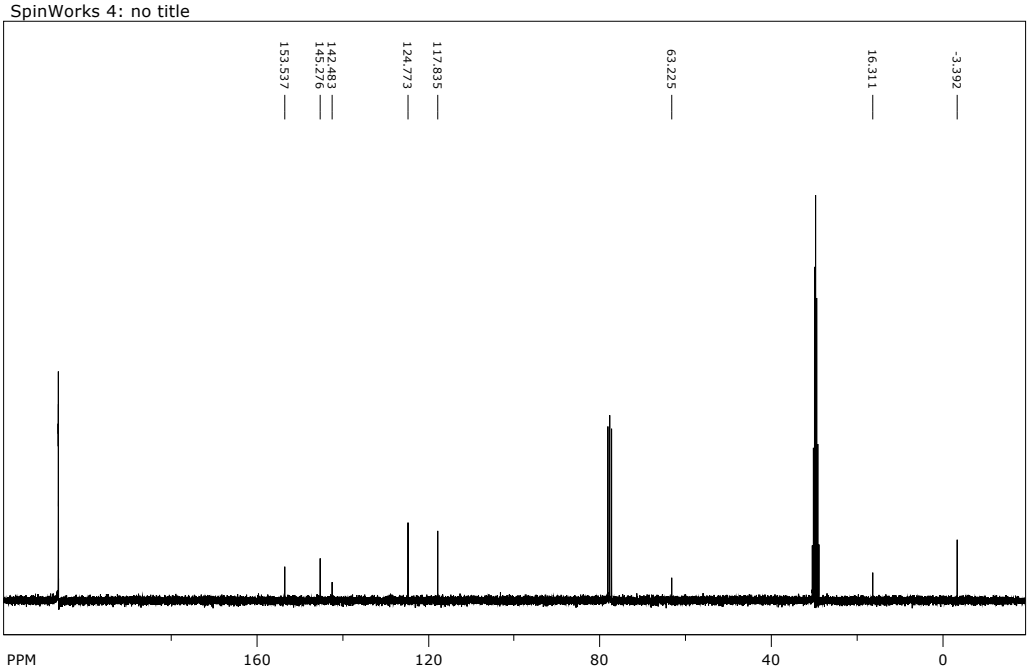
SpinWorks 4: no title



file: D:\EXC-1-36 1H\4\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6172.84 Hz = 20.5671 ppm = 0.094190 Hz/pt
number of scans: 16

freq. of 0 ppm: 300.130041 MHz
processed size: 32768 complex points
LB: 0.000 GF: 0.0000

SpinWorks 4: no title



file: D:\EXC-1-36 13C\4\fid expt: <zgpg30>
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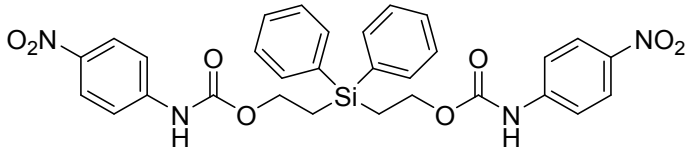
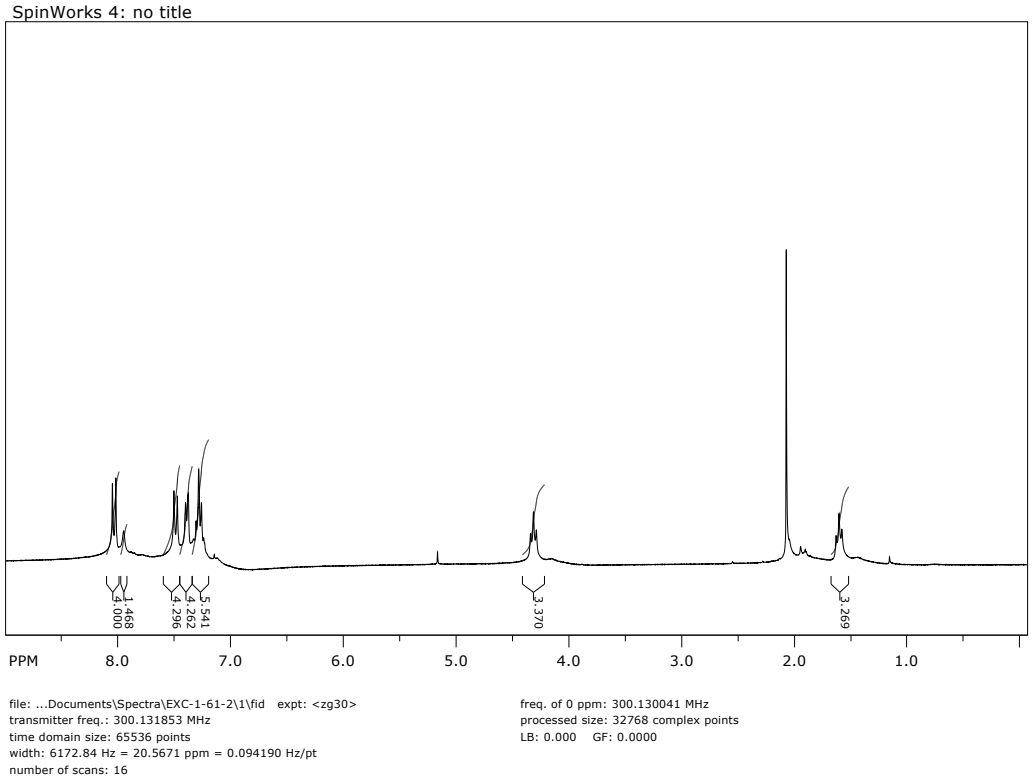
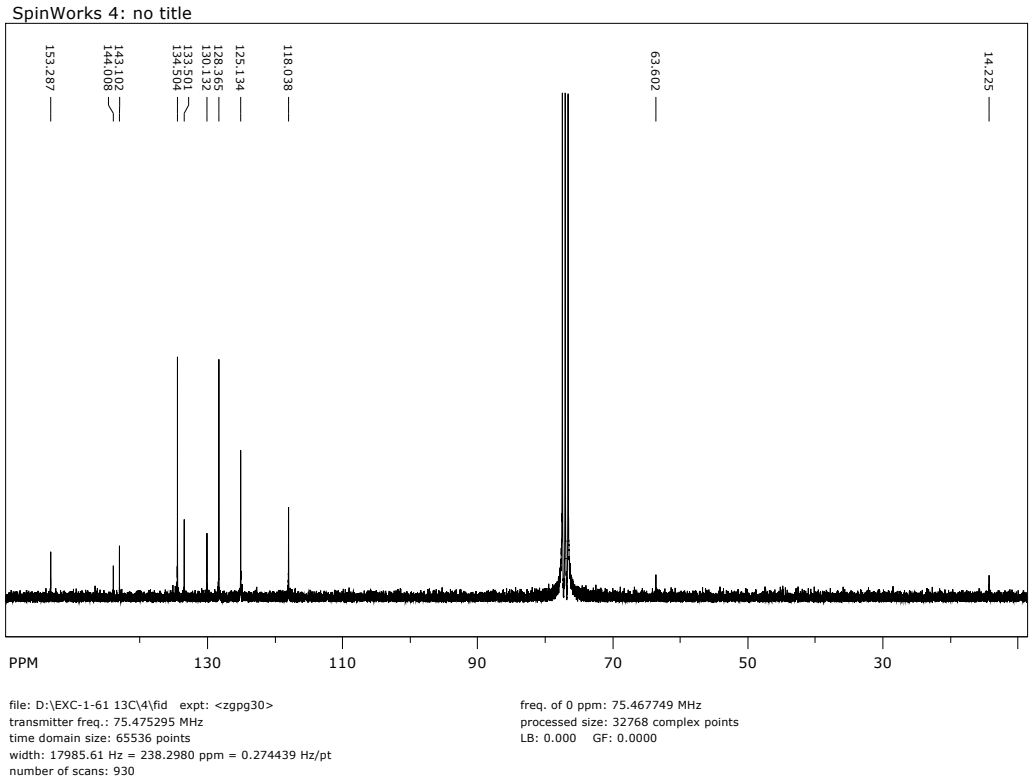
time domain size: 65536 points
width: 17985.61 Hz = 238.2980 ppm = 0.274439 Hz/pt
number of scans: 1110

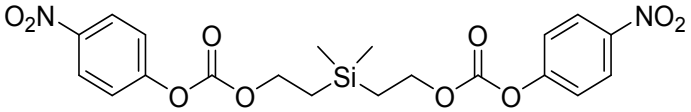
freq. of 0 ppm: 75.467749 MHz
processed size: 32768 complex points
LB: 0.000 GF: 0.0000



(diphenylsilanediyl)bis(ethane-2,1-diyl) bis((4-nitrophenyl)carbamate) (5b): To a solution of 2,2'-(diphenylsilanediyl)bis(ethan-1-ol) (0.3 g, 1.09 mmol) in THF (10 mL), 4-nitrophenyl isocyanate (0.33 mg, 1.98 mmol) was added at room temperature and let stir for overnight. The reaction mixture was extracted with dichloromethane and brine, dried with magnesium sulfate, and then concentrated *in vacuo*. The resulting mixture was purified using column chromatography (100% dichloromethane) to furnish the product (0.21 g) as an off-white solid in 32% yield. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ = 8.04 (d, *J* = 9.1 Hz, 4H), 7.95 (s, 1H), 7.49 (d, *J* = 9.1Hz, 4H), 7.38 (m, 4H), 7.28 (m, 6H), 4.31 (t, *J* = 7.7Hz, 4H), 1.61 (t, *J* = 7.7 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ = 153.29, 144.01, 143.10, 134.50, 133.50, 128.67, 125.13, 118.04, 63.60, 14.23. HRMS (ESI) *m/z* calculated for $C_{30}H_{28}N_4O_8SiNa$ $[M+Na]^+$ 623.1569, found 623.1564.

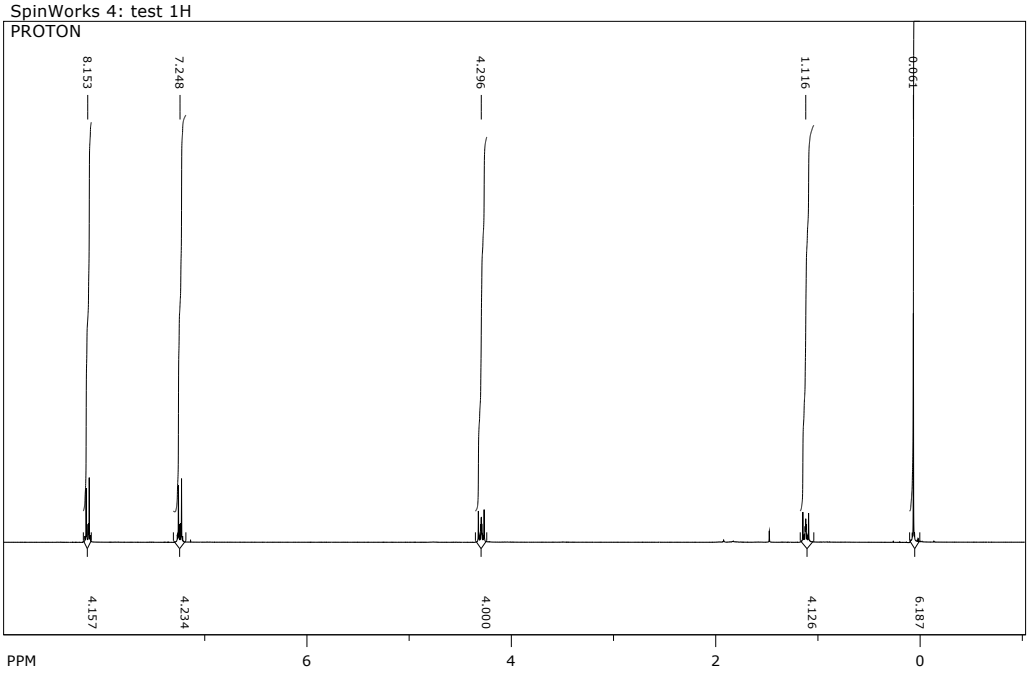






(dimethylsilanediyl)bis(ethane-2,1-diyl) bis((4-nitrophenyl) bis(carbonate) (5c): To a solution of 2,2'-(dimethylsilanediyl)bis(ethan-1-ol) (0.4 g, 2.70 mmol) in THF (20 mL), 4-nitrophenyl chloroformate (1.1 g, 5.53 mmol) was added at room temperature and let stir for overnight. The reaction mixture was extracted with dichloromethane and brine, dried with magnesium sulfate, and then concentrated *in vacuo*. The resulting mixture was purified using column chromatography (ethyl acetate/hexane: 1/1) to furnish the product (0.08 g) as an off-white solid in 6% yield. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ = 8.15 (d, *J* = 9.4Hz, 4H), 7.25 (d, *J* = 9.4Hz, 4H), 4.29 (t, *J* = 8.6Hz, 4H), 1.12 (t, *J* = 8.6Hz, 4H), 0.06 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ = 155.53, 152.43, 145.39, 125.30, 121.82, 67.35, 16.15, -3.06. HRMS (ESI) *m/z* calculated for $C_{20}H_{22}N_2O_{10}SiNa$ $[M + Na]^+$ 501.0936, found 501.0933.

SpinWorks 4: test 1H



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time domain size: 65536 points
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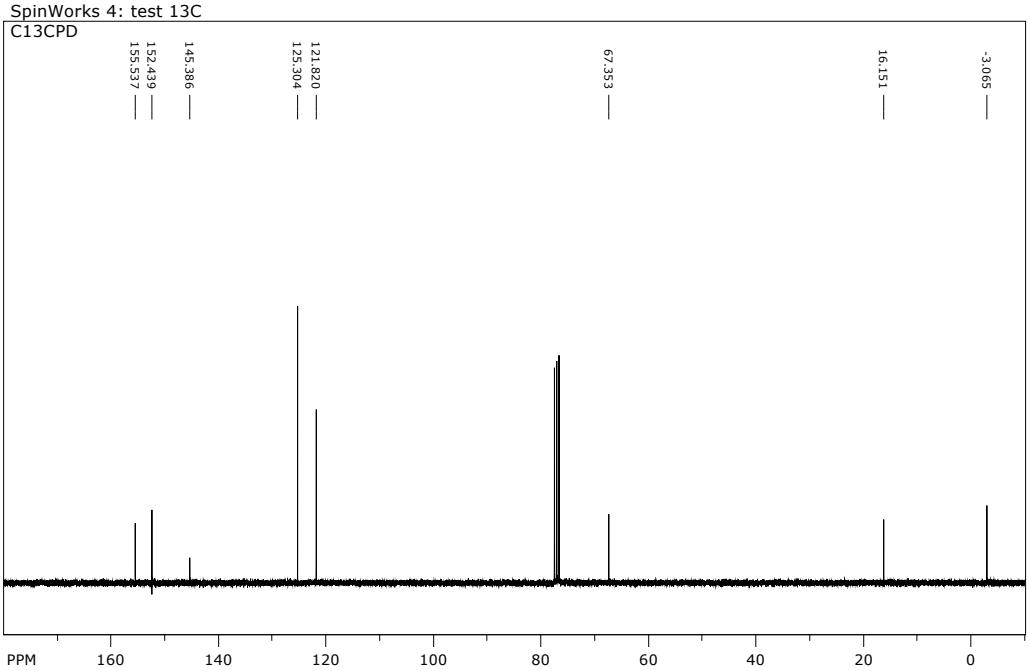
number of scans: 16

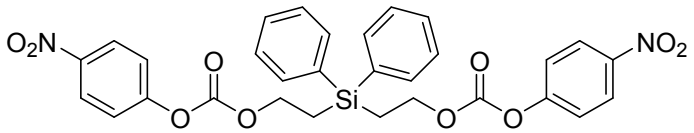
freq. of 0 ppm: 300.130041 MHz
processed size: 32768 complex points
LB: 0.000 GF: 0.0000

SpinWorks 4: test 13C

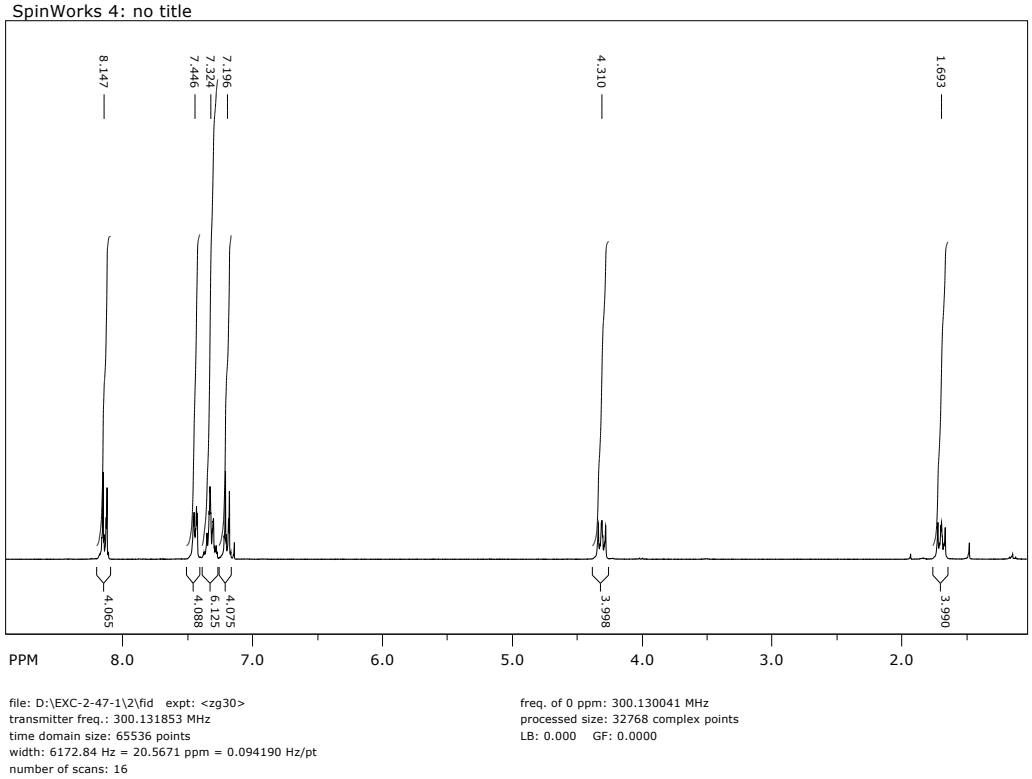


file: D:\notebook 2\EXC-2-38 13C\4\fid expt: <zgpg30>
transmitter freq.: 75.475295 MHz
time domain size: 65536 points
width: 17985.61 Hz = 238.2980 ppm = 0.274439 Hz/pt
number of scans: 1459

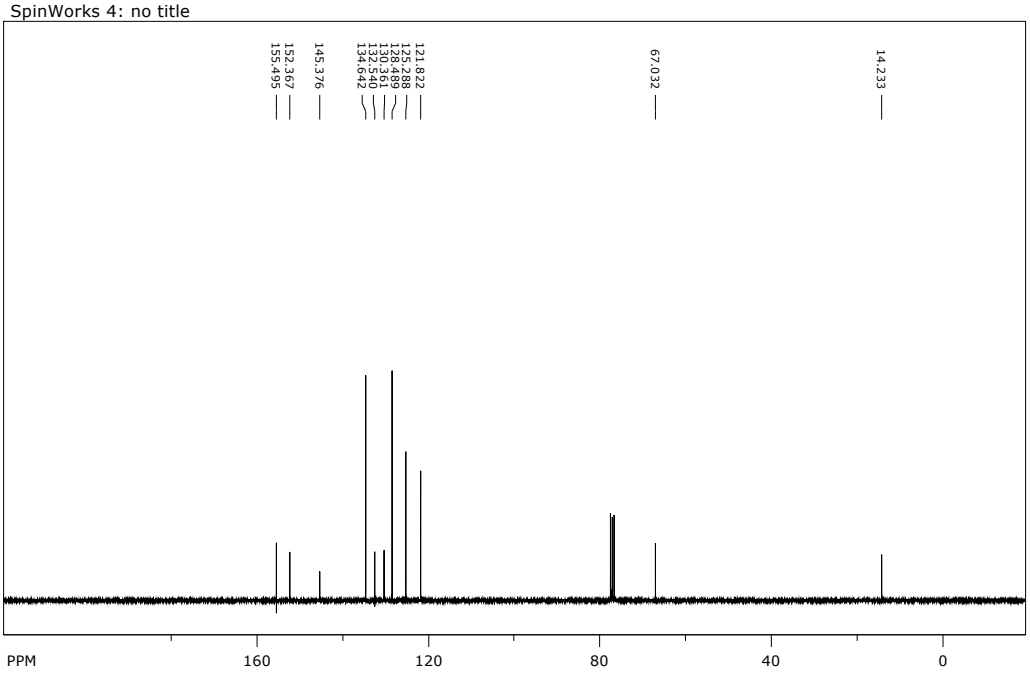
freq. of 0 ppm: 75.467749 MHz
processed size: 32768 complex points
LB: 0.000 GF: 0.0000



(diphenylsilanediyl)bis(ethane-2,1-diyl) bis(4-nitrophenyl) bis(carbonate) (5d): To a solution of 2,2'-(diphenylsilanediyl)bis(ethan-1-ol) (0.4 g, 1.47 mmol) in acetonitrile (20 mL), 4-nitrophenyl chloroformate (0.62 mg, 3.09 mmol) was added at room temperature and let stir for overnight. The reaction mixture was extracted with dichloromethane and brine, dried with magnesium sulfate, and then concentrated *in vacuo*. The resulting mixture was purified using column chromatography (dichloromethane/hexane: 1/1) to furnish the product (0.29 g) as an off-white solid in 33% yield. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ = 8.15 (d, *J* = 9.2, 4H), 7.45 (dd, *J* = 7.4 Hz, 1.8 Hz, 4H), 7.32 (m, 6H), 7.19 (d, *J* =8.9 Hz, 4H), 4.31 (t, *J*=8.29 Hz, 4H), 1.69 (t, *J* = 8.27, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ = 155.49, 152.37, 145.38, 134.64, 132.54, 130.36, 128.49, 125.29, 121.82, 67.03, 14.23. HRMS (EIC) *m/z* calculated for $C_{30}H_{26}N_2O_{10}SiNa$ $[M + Na]^+$ 625.1249, found 625.1245.



SpinWorks 4: no title



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time domain size: 65536 points
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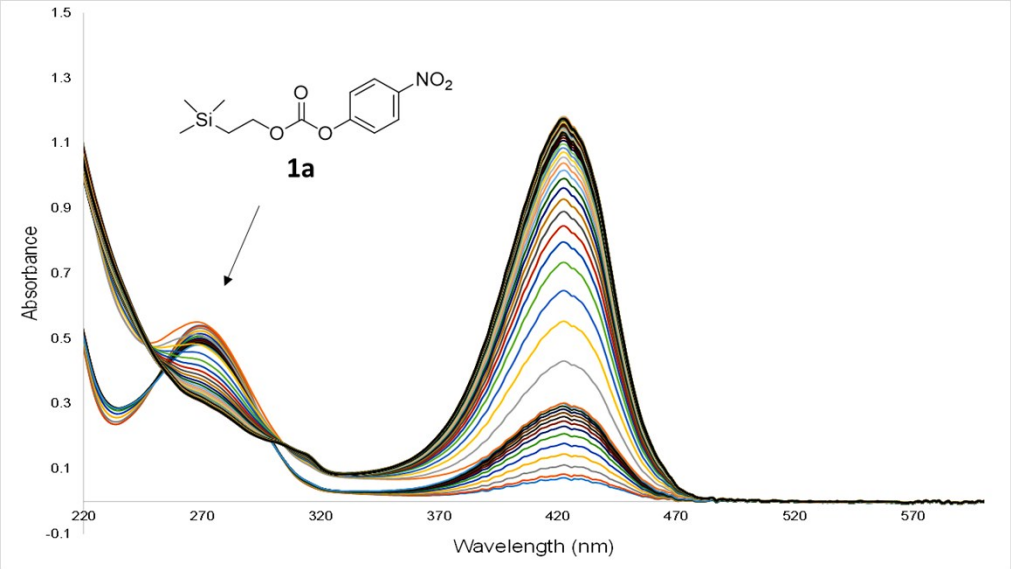
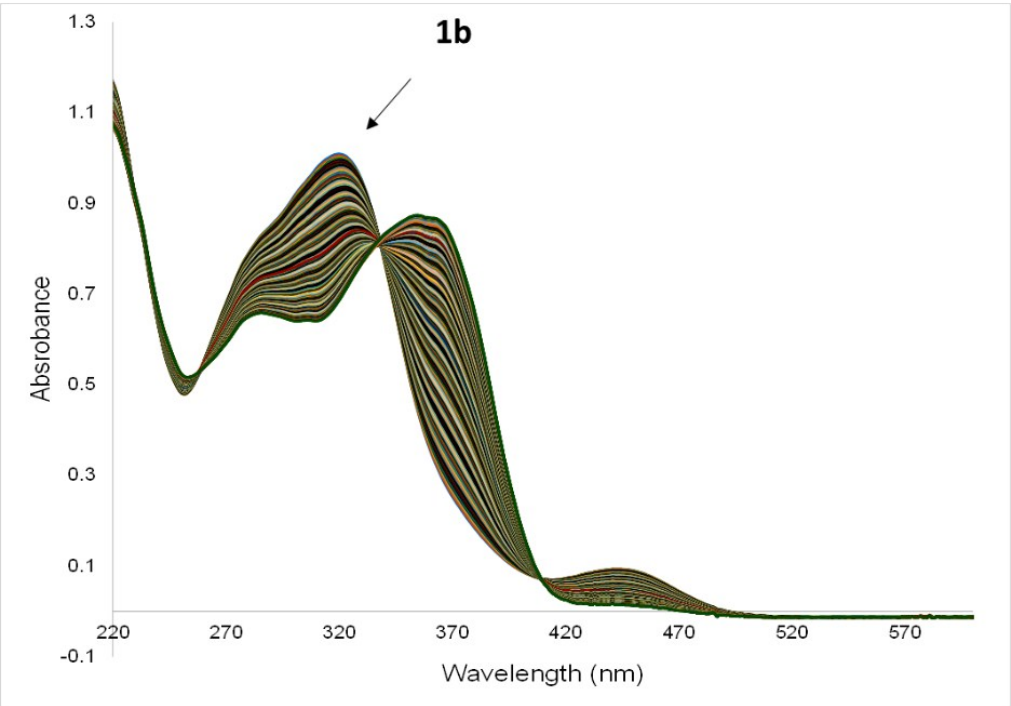
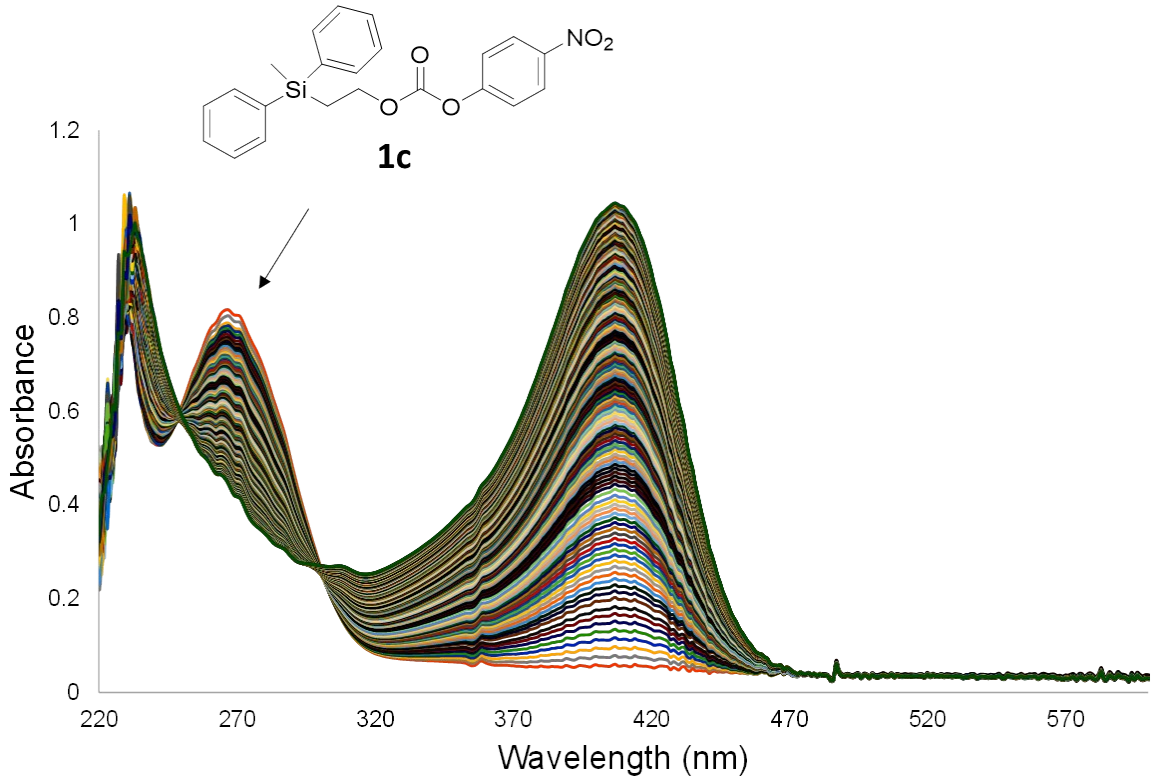
number of scans: 1024

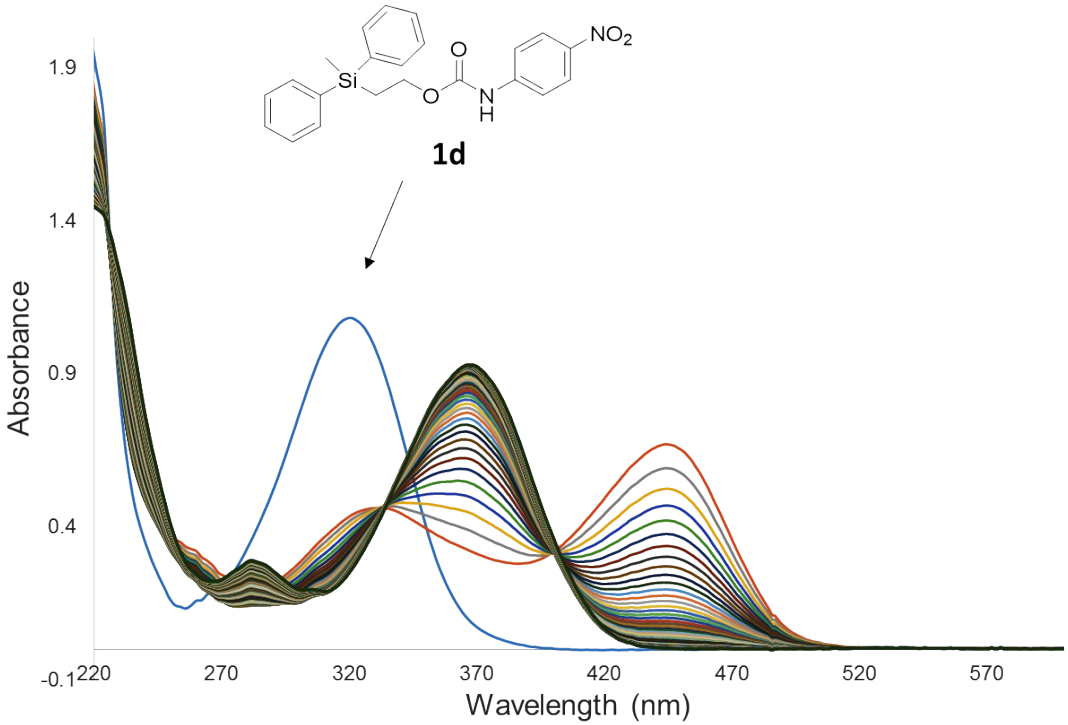
freq. of 0 ppm: 75.467749 MHz
processed size: 32768 complex points
LB: 0.000 GF: 0.0000

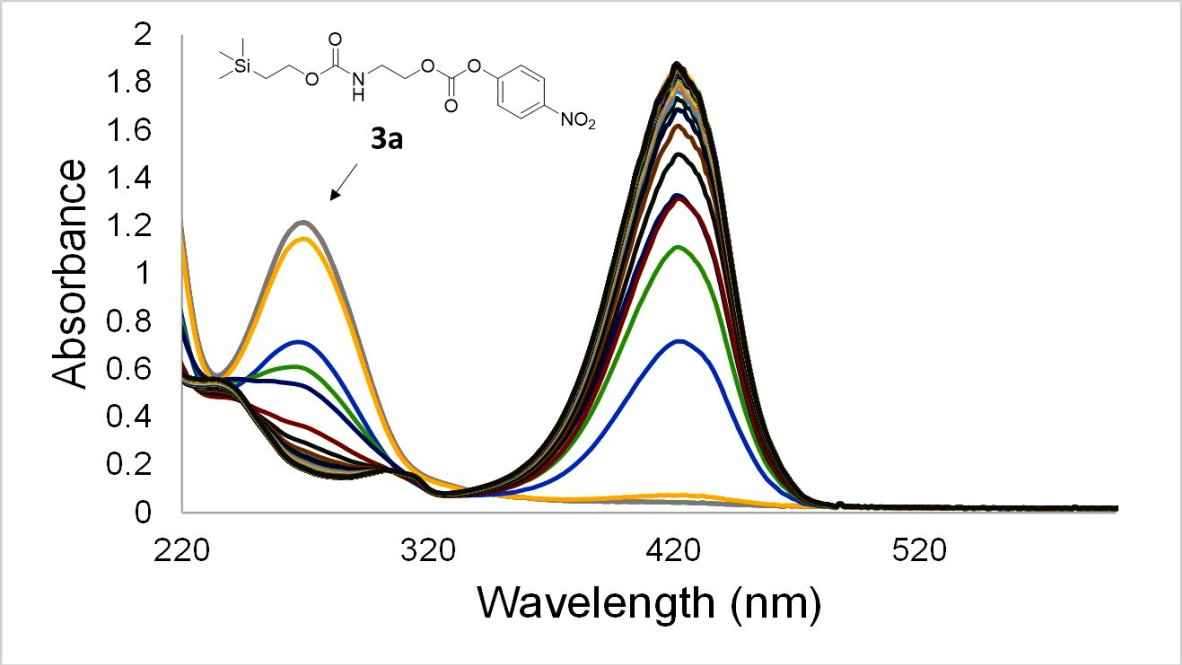
UV-Visible Spectra of Molecules upon Treatment with TBAF

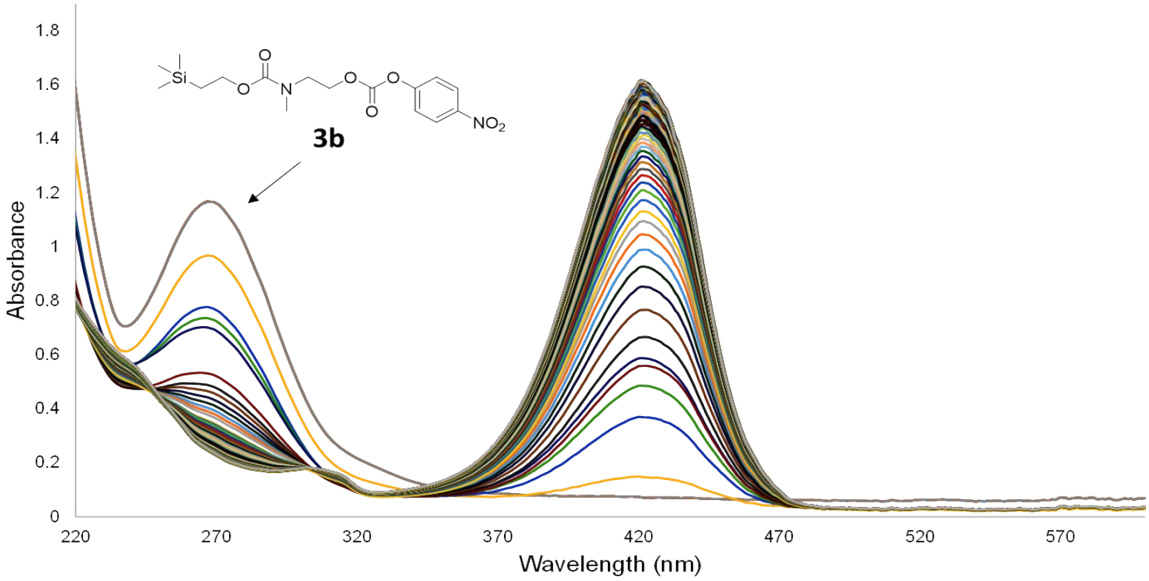


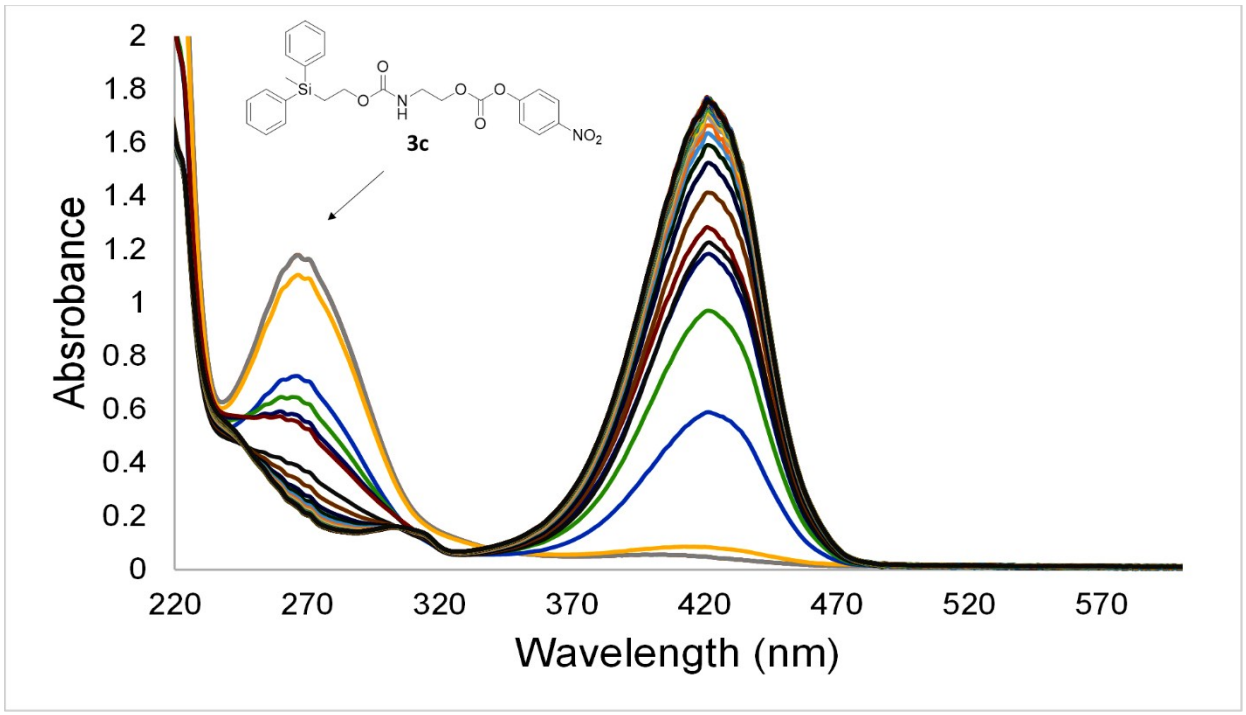


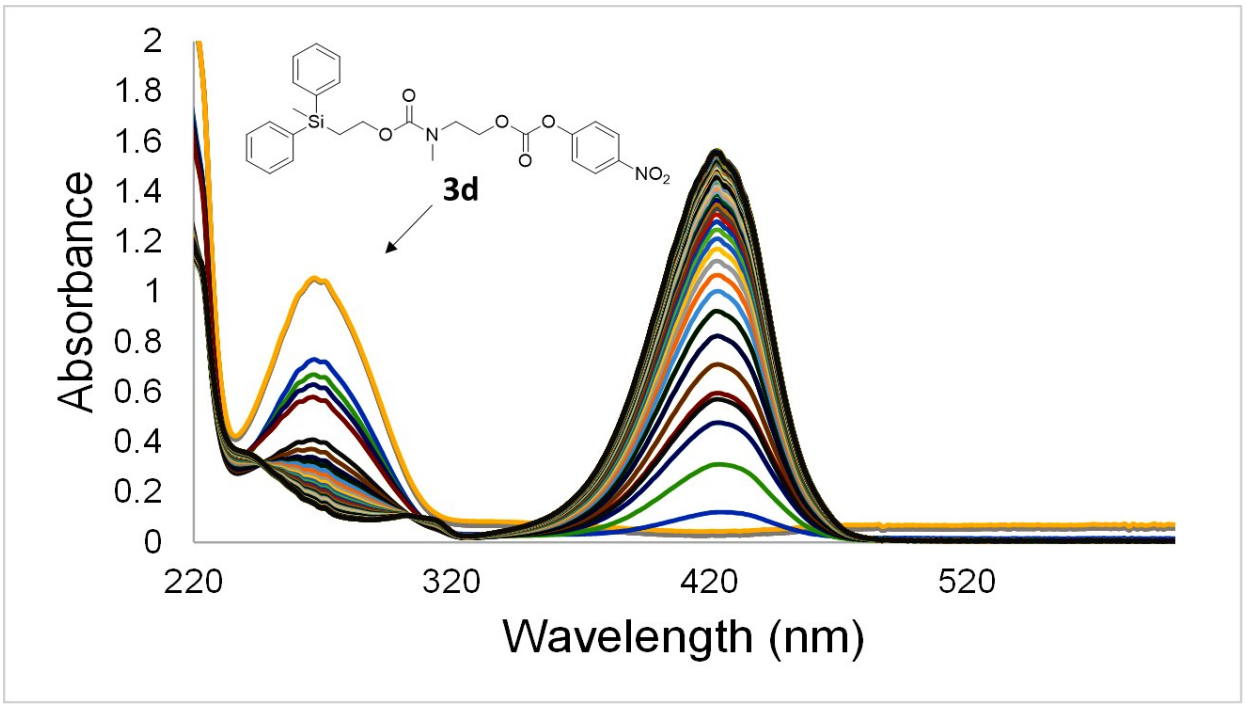

NO2
Si
O
O
O
1c
1.2
1
0.8
0.6
0.4
0.2
0
Absorbance
220
270
320
370
420
470
520
570
Wavelength (nm)

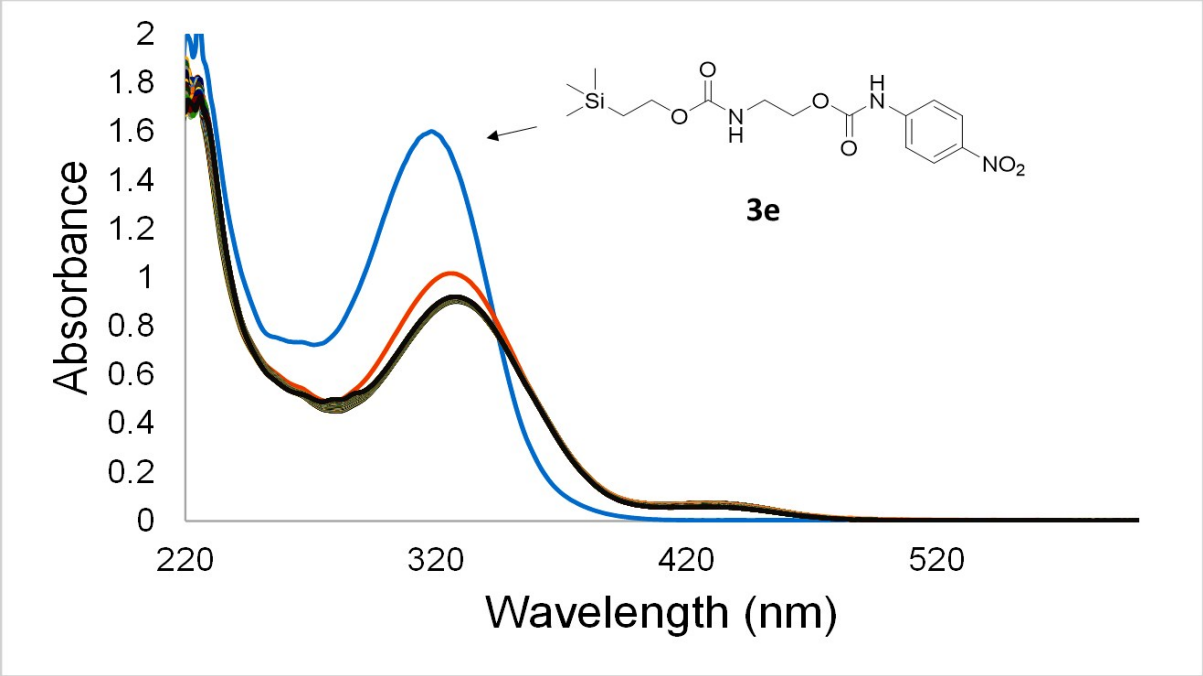

NO2
Si
O
O
N
H
1d
1.9
1.4
0.9
0.4
-0.1
Absorbance
220
270
320
370
420
470
520
570
Wavelength (nm)

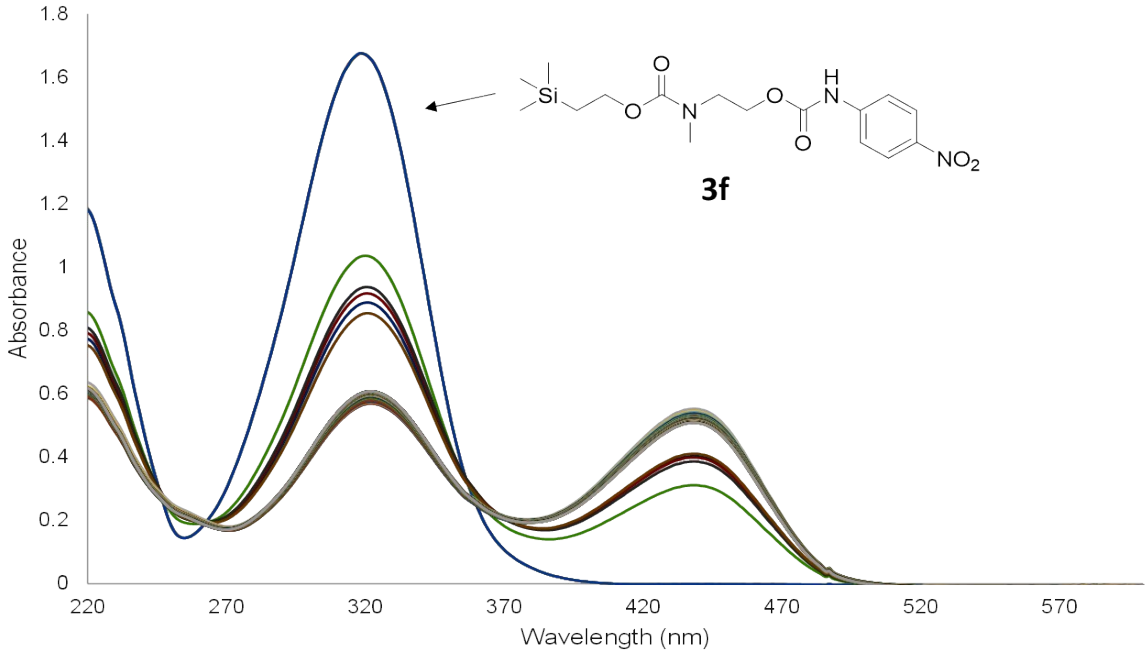

Absorbance
Wavelength (nm)
3a
NO2

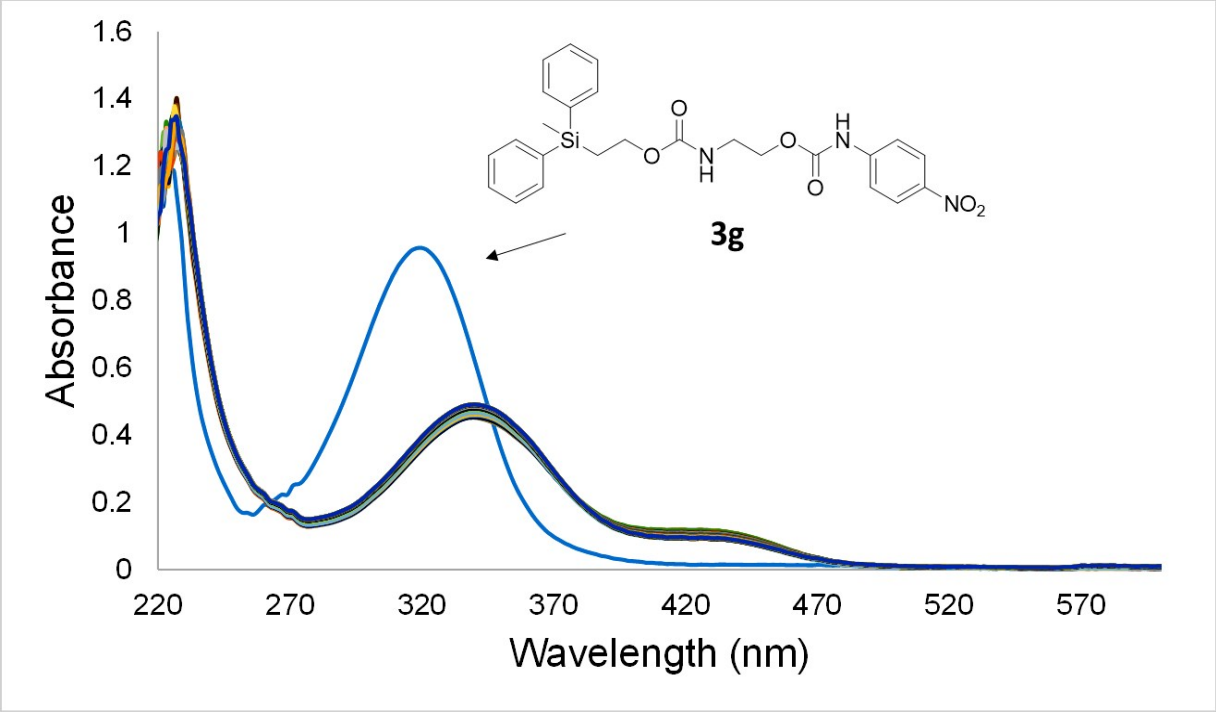

Absorbance
Wavelength (nm)
3b
NO2


Absrobance
Wavelength (nm)
3c
NO2


Absorbance
Wavelength (nm)
3d
NO2


Absorbance
Wavelength (nm)
3e


Absorbance
Wavelength (nm)
3f


1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
Absorbance
220
270
320
370
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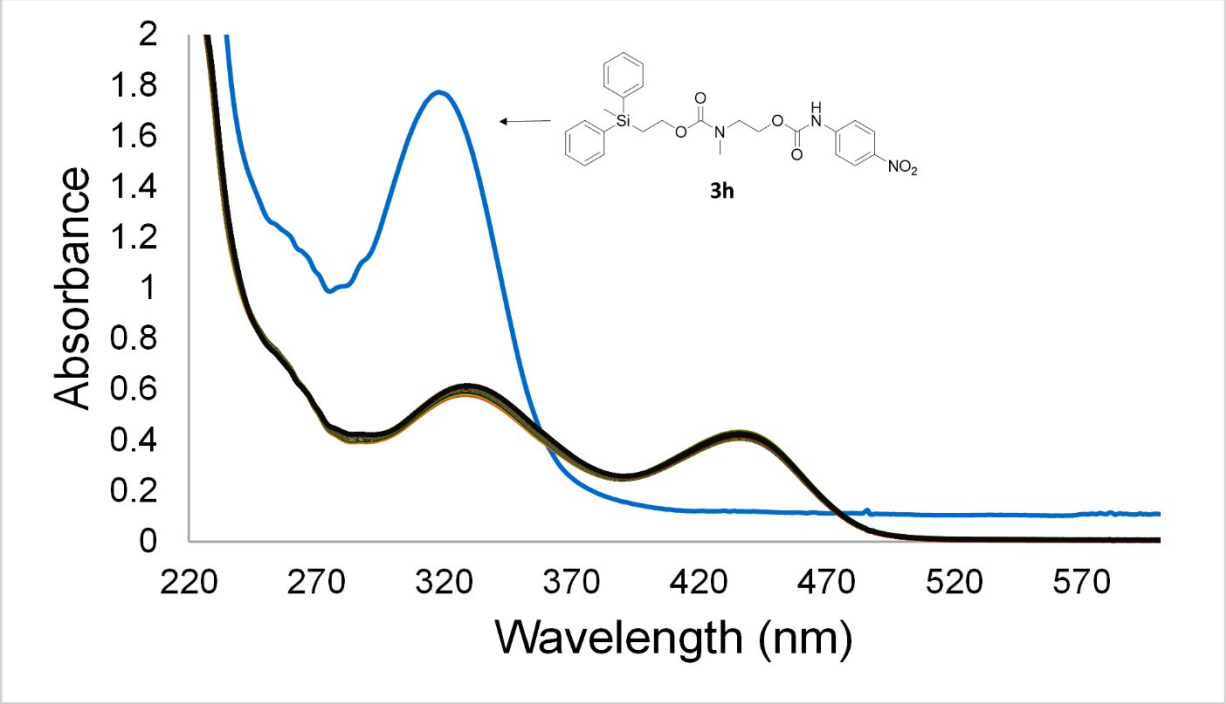
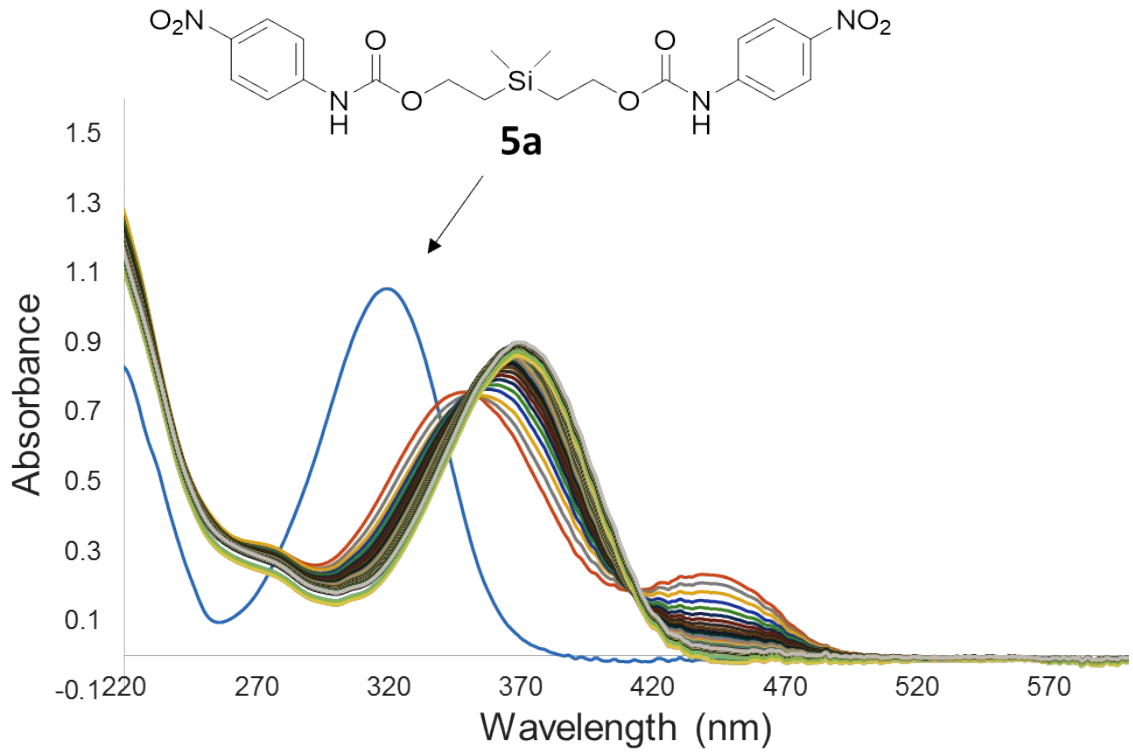
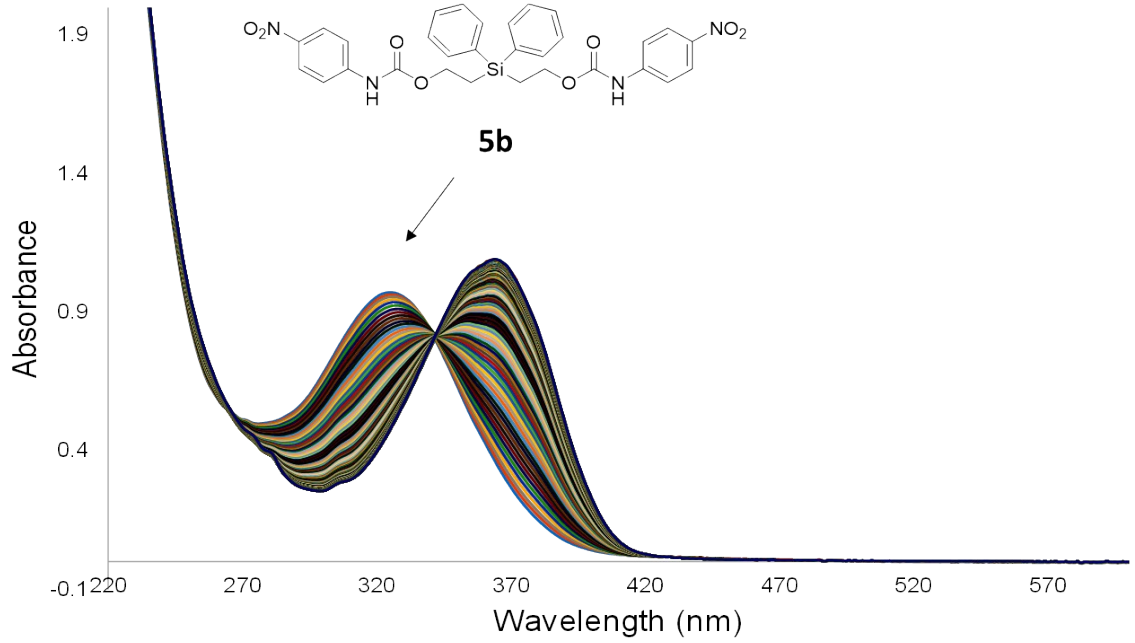
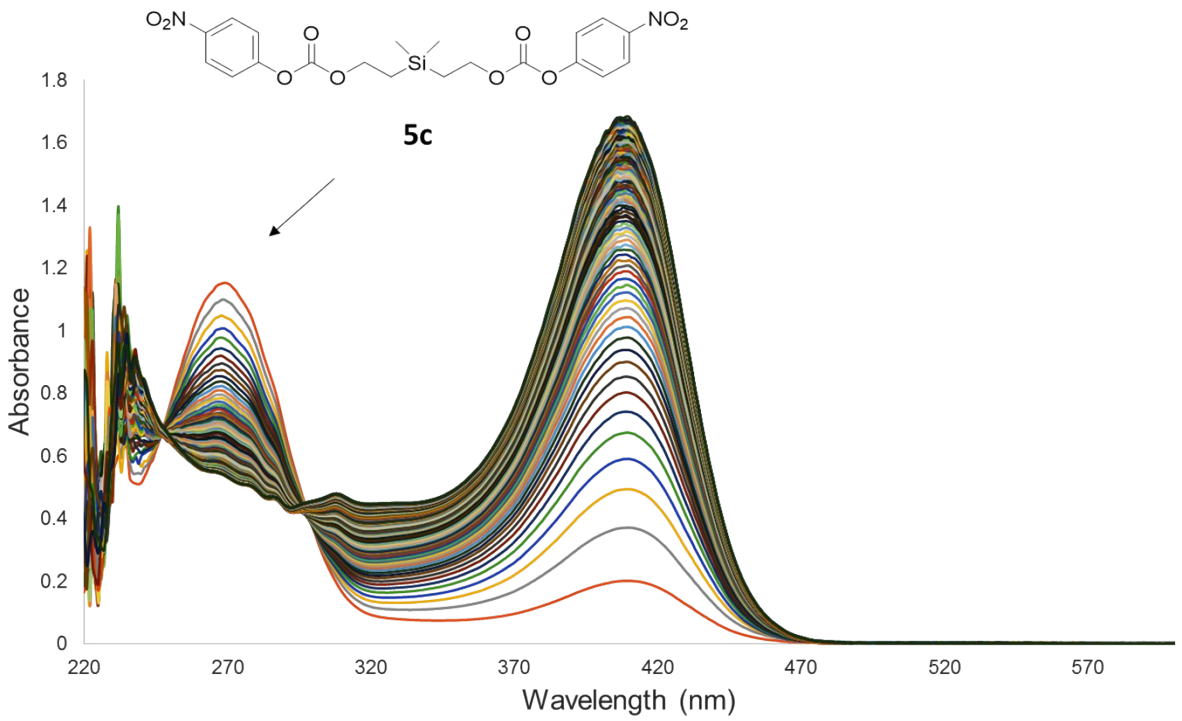
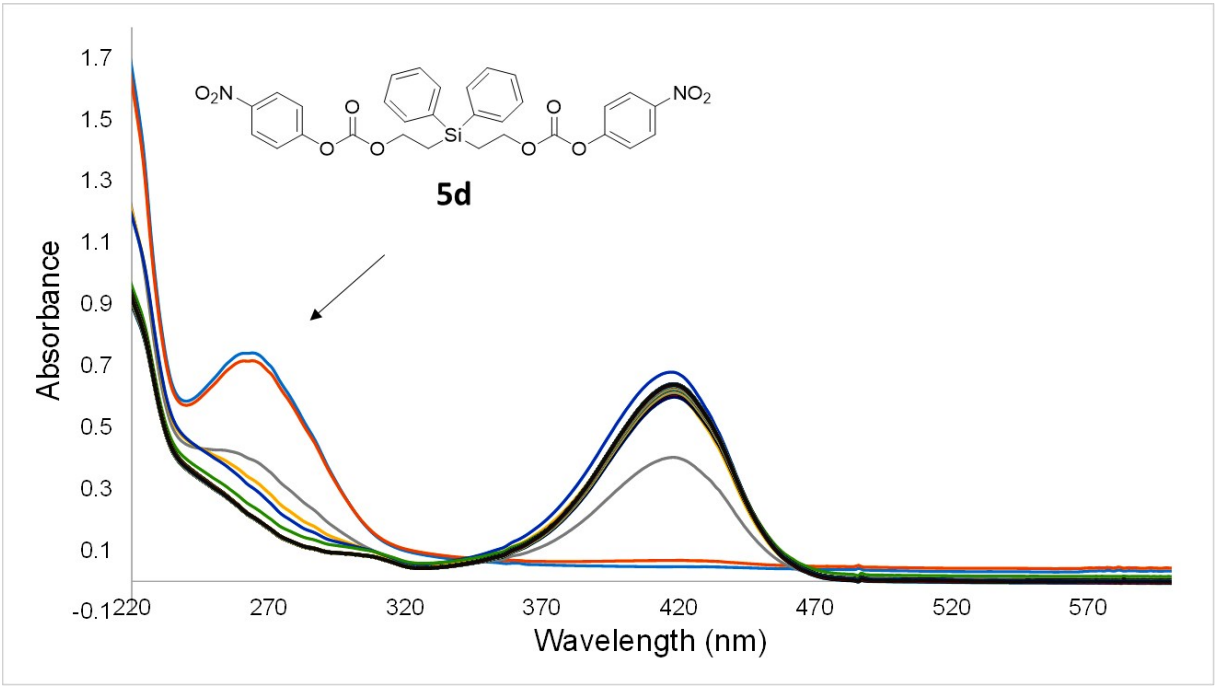
470
520
570
Wavelength (nm)
Si
O
N
H
O
O
N
H
O
NO2
3g


2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
Absorbance
220
270
320
370
420
470
520
570
Wavelength (nm)
Si
O
N
O
O
N
H
O
NO2
3h

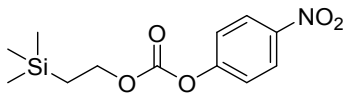

5a
Absorbance
Wavelength (nm)
1.5
1.3
1.1
0.9
0.7
0.5
0.3
0.1
-0.1
220
270
320
370
420
470
520
570


5b
Absorbance
Wavelength (nm)
1.9
1.4
0.9
0.4
-0.1
220
270
320
370
420
470
520
570

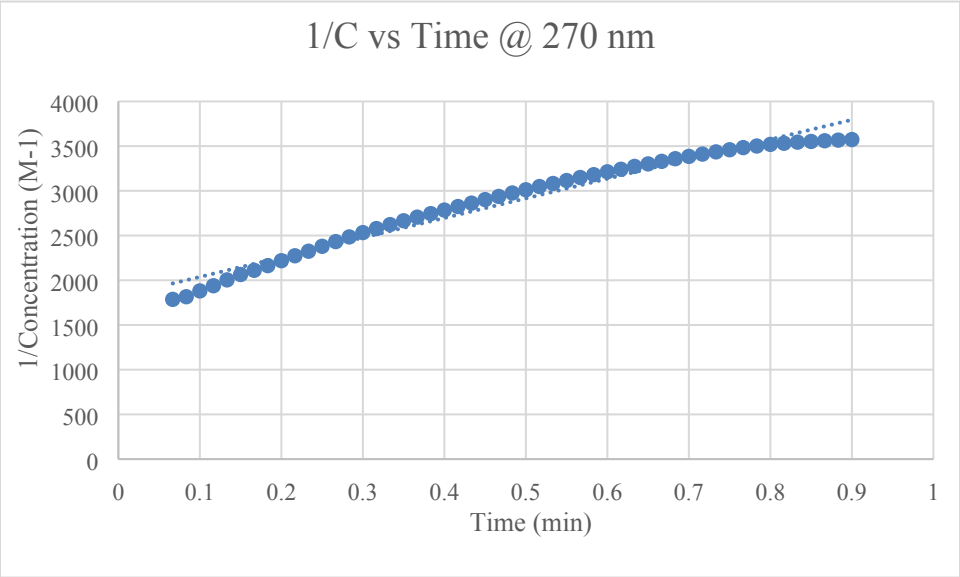

5c
Absorbance
Wavelength (nm)

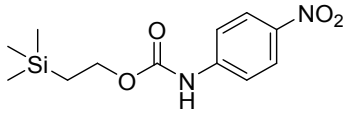

5d
Absorbance
Wavelength (nm)

Kinetic Plots for Disassembled Molecules

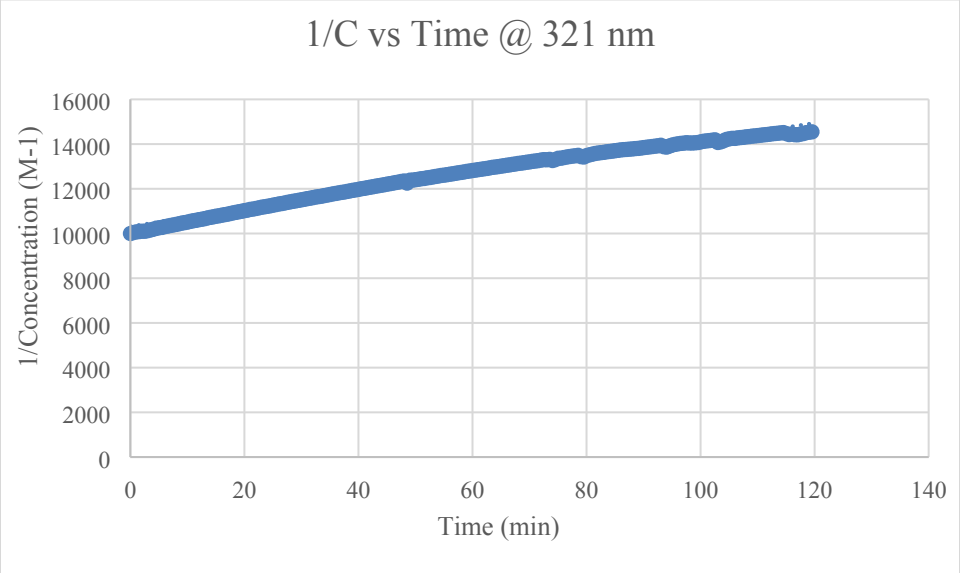


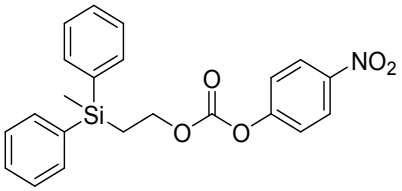
1a



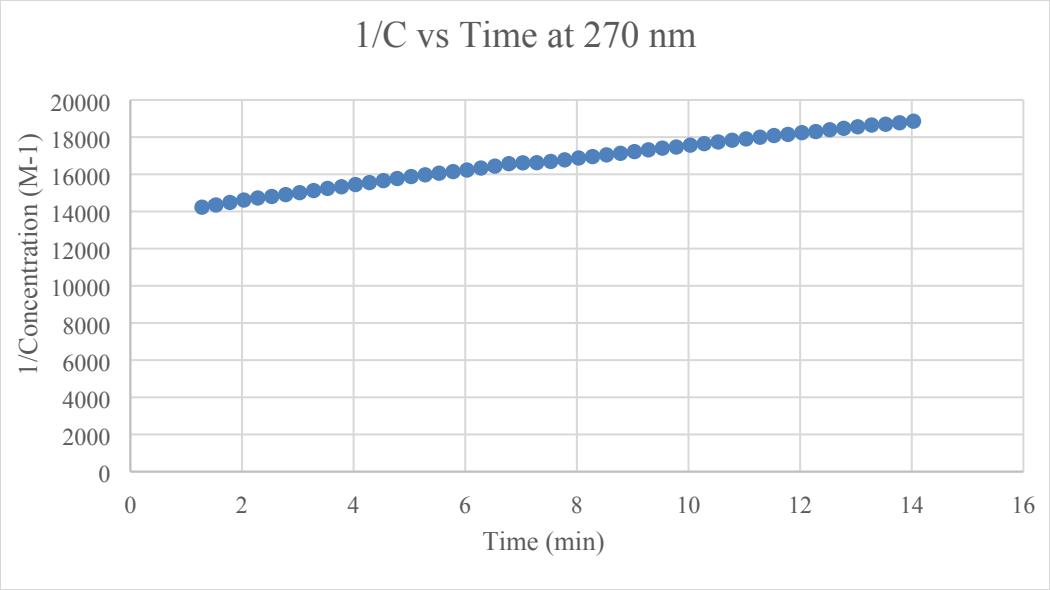


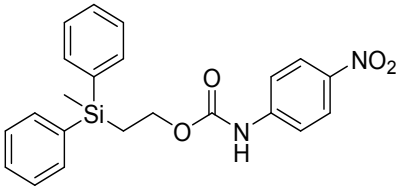
1b



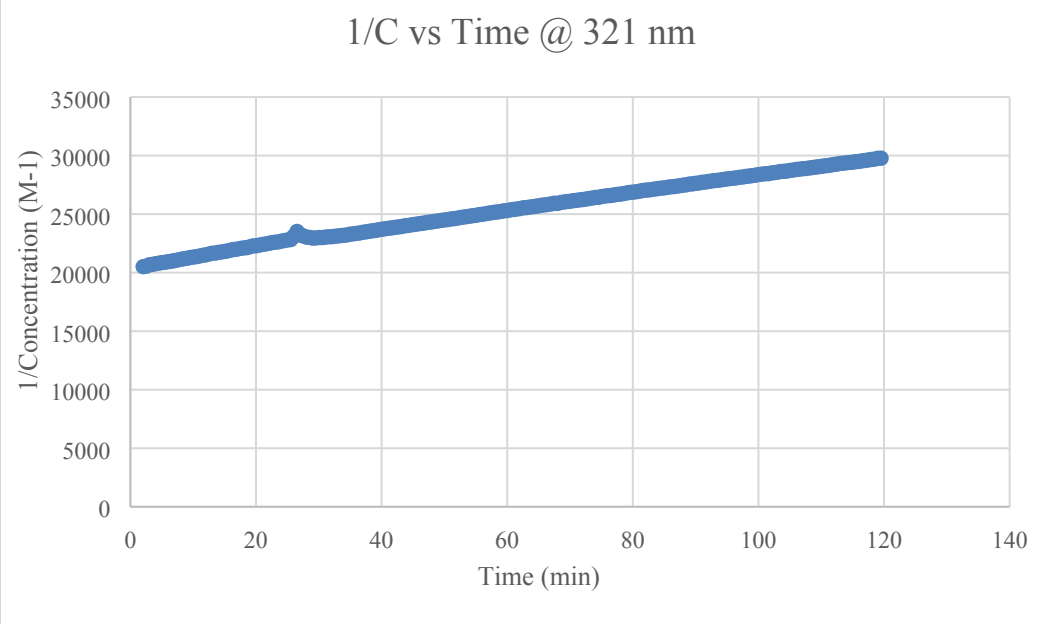

NO2
O
Si
O
O

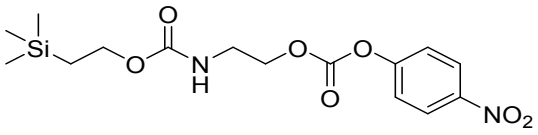
1c


1/C vs Time at 270 nm
1/Concentration (M-1)
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
0
2
4
6
8
10
12
14
16
Time (min)

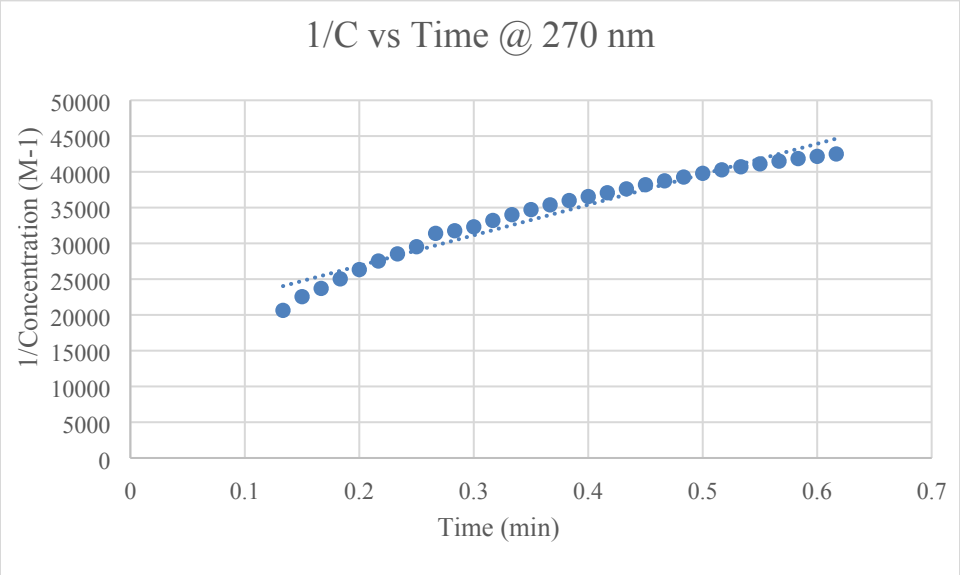

NO2
O
Si
O
N
H

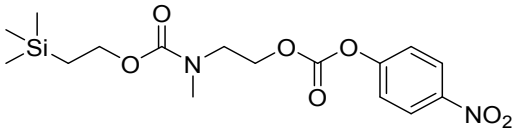
1d


1/C vs Time @ 321 nm
1/Concentration (M-1)
35000
30000
25000
20000
15000
10000
5000
0
0
20
40
60
80
100
120
140
Time (min)

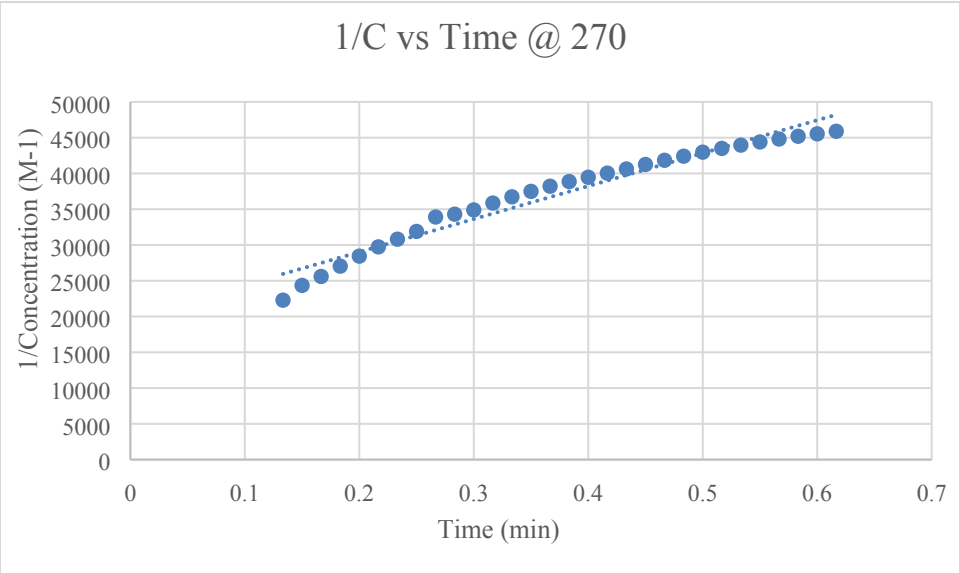


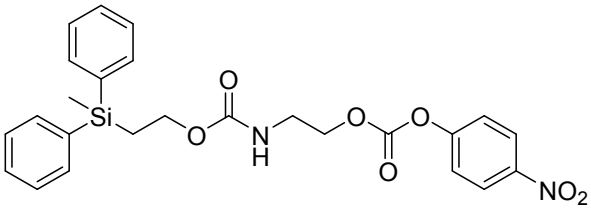
3a


1/C vs Time @ 270 nm
1/Concentration (M-1)
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
Time (min)

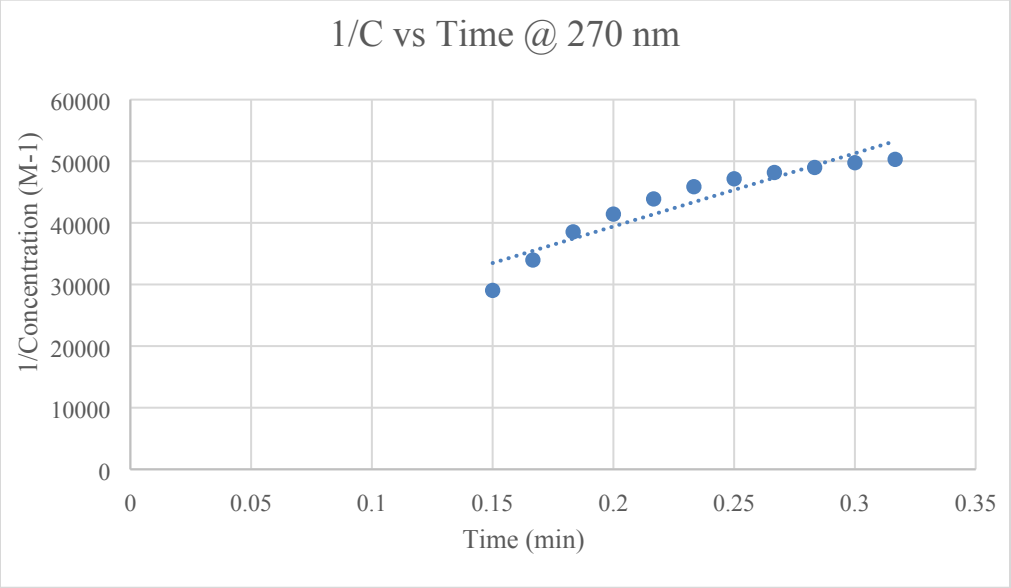


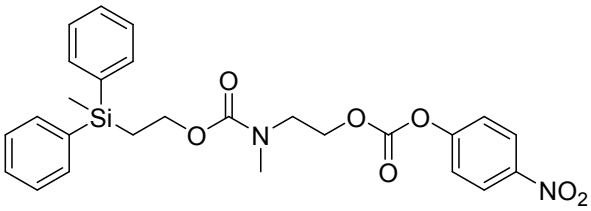
3b


1/C vs Time @ 270
1/Concentration (M-1)
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
Time (min)

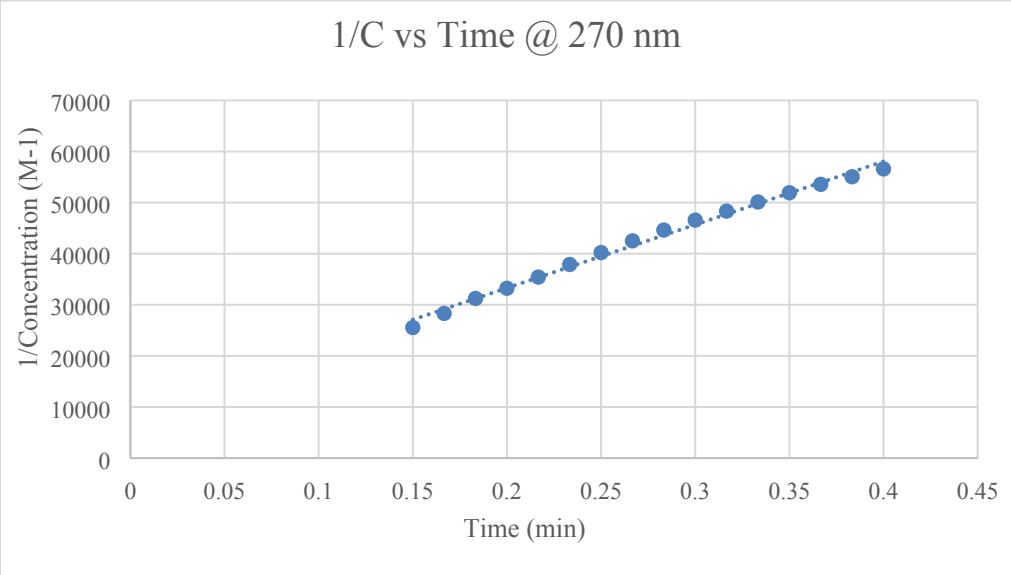

Si
O
O
N
H
O
O
O
O
NO2

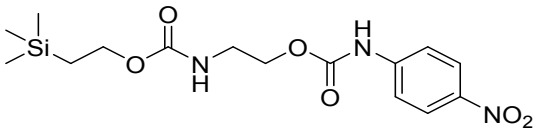
3c


1/C vs Time @ 270 nm
1/Concentration (M-1)
60000
50000
40000
30000
20000
10000
0
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
Time (min)

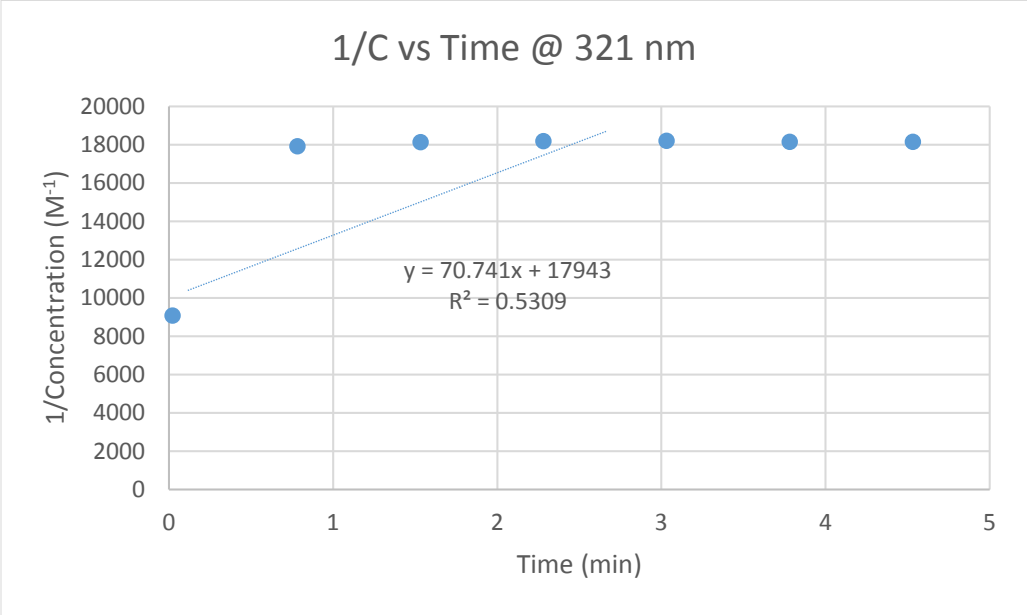

Si
O
O
N
O
O
O
O
NO2

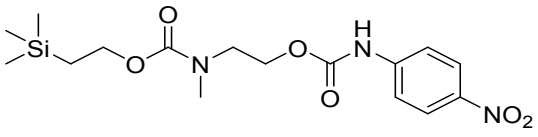
3d


1/C vs Time @ 270 nm
1/Concentration (M-1)
70000
60000
50000
40000
30000
20000
10000
0
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
0.4
0.45
Time (min)

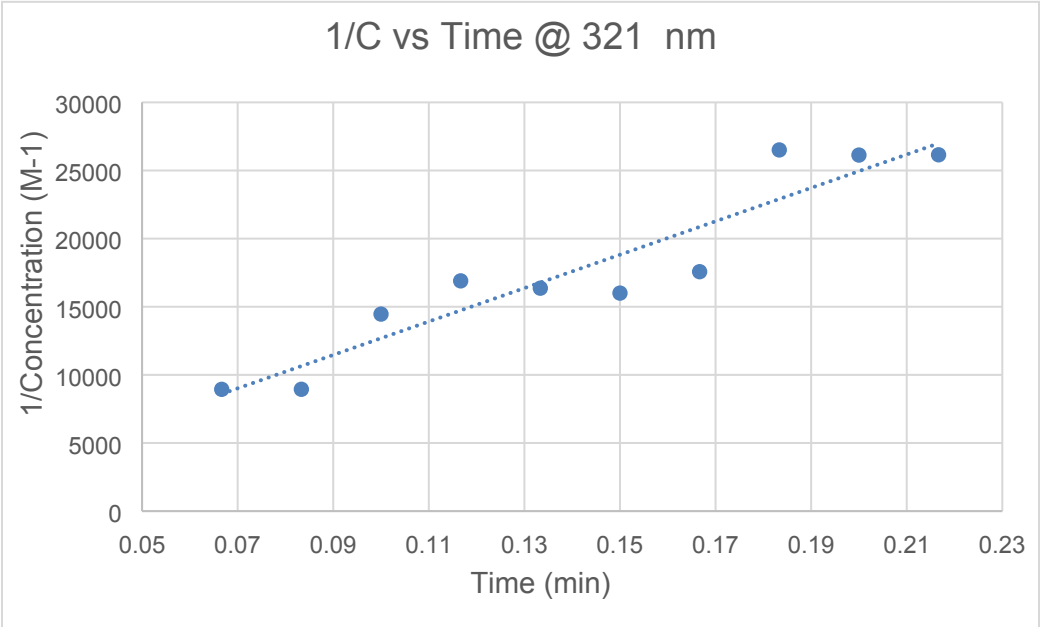


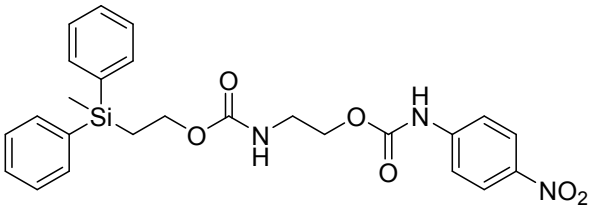
3e


1/C vs Time @ 321 nm
1/Concentration (M-1)
Time (min)
y = 70.741x + 17943
R² = 0.5309
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
0
1
2
3
4
5

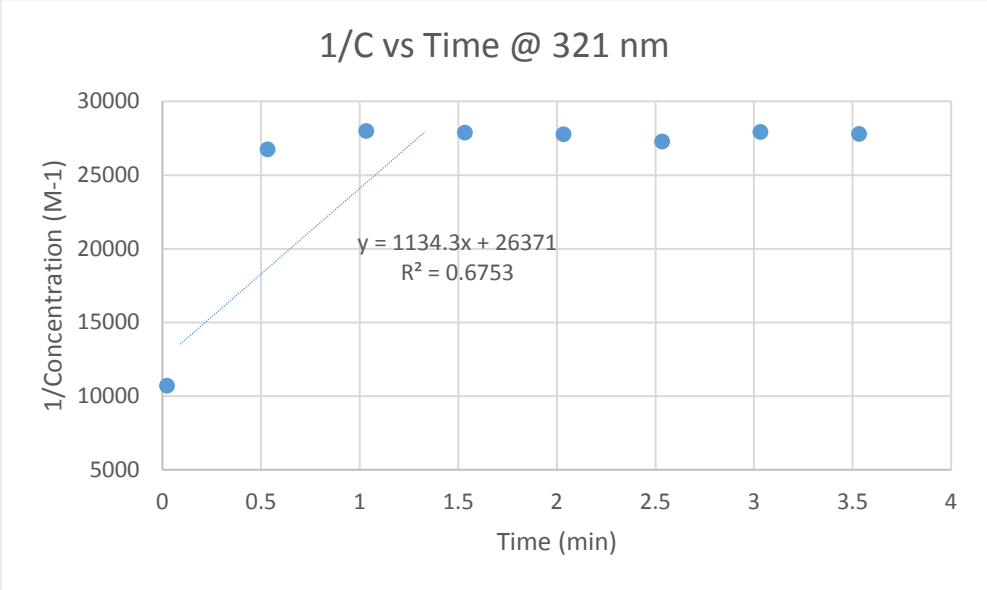


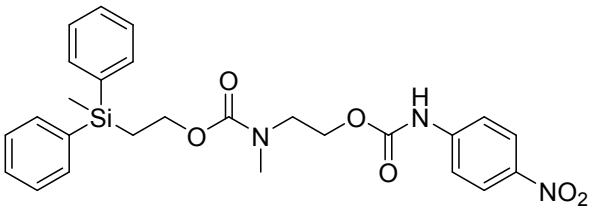
3f


1/C vs Time @ 321 nm
1/Concentration (M-1)
Time (min)
30000
25000
20000
15000
10000
5000
0
0.05
0.07
0.09
0.11
0.13
0.15
0.17
0.19
0.21
0.23

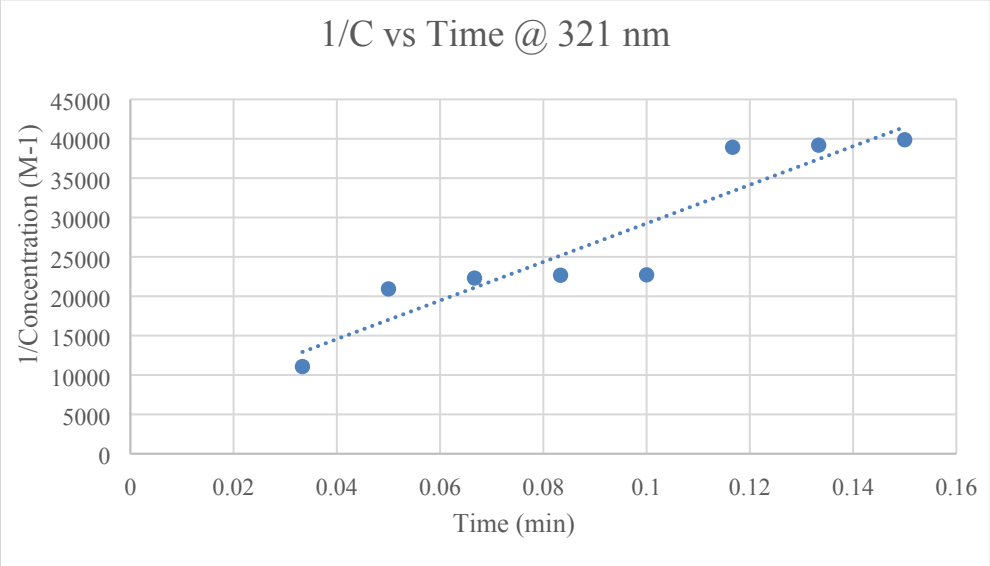

Si
O
O
N
H
O
O
H
N
NO2

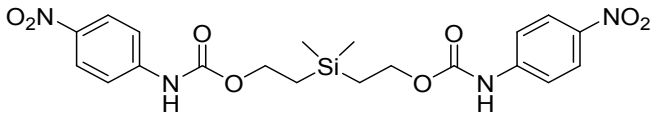
3g


1/C vs Time @ 321 nm
1/Concentration (M-1)
30000
25000
20000
15000
10000
5000
y = 1134.3x + 26371
R² = 0.6753
0
0.5
1
1.5
2
2.5
3
3.5
4
Time (min)

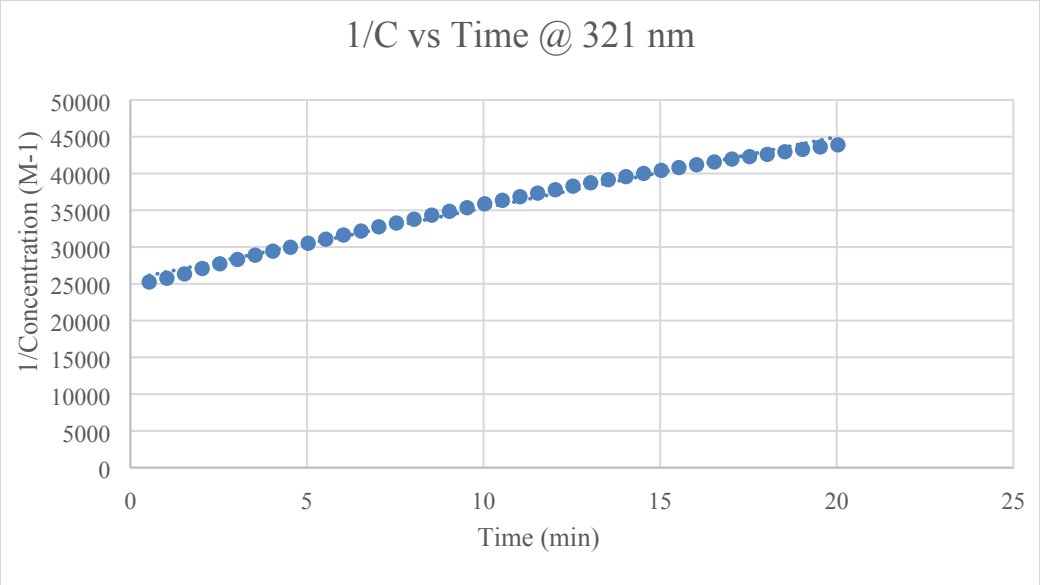

Si
O
O
N
O
O
H
N
NO2

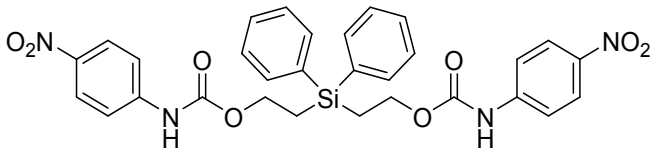
3h


1/C vs Time @ 321 nm
1/Concentration (M-1)
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
0.16
Time (min)

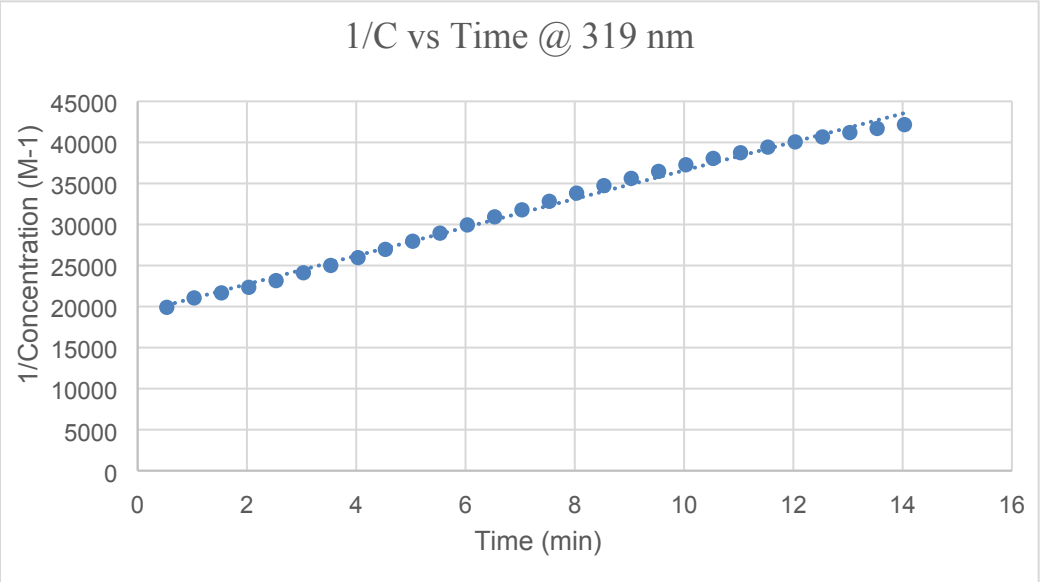

O2N
NO2
O
N
H
O
Si
O
O
N
H

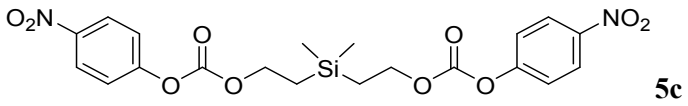
5a


1/C vs Time @ 321 nm
1/Concentration (M-1)
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
0
5
10
15
20
25
Time (min)

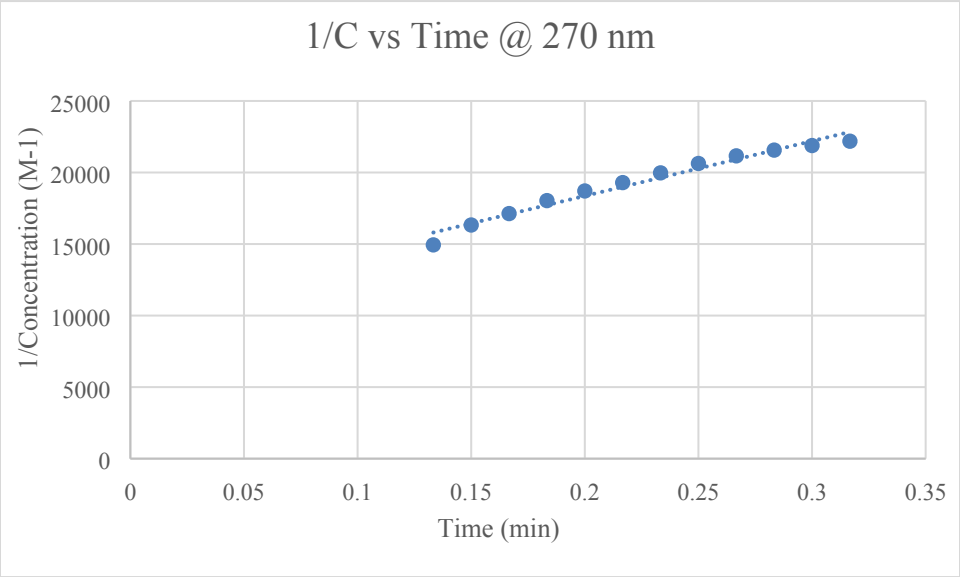

O2N
NO2
O
N
H
O
Si
O
O
N
H

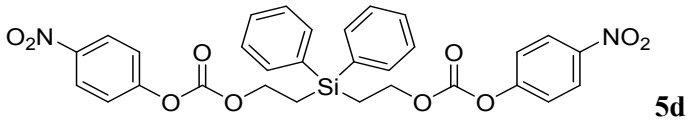
5b


1/C vs Time @ 319 nm
1/Concentration (M-1)
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
0
2
4
6
8
10
12
14
16
Time (min)

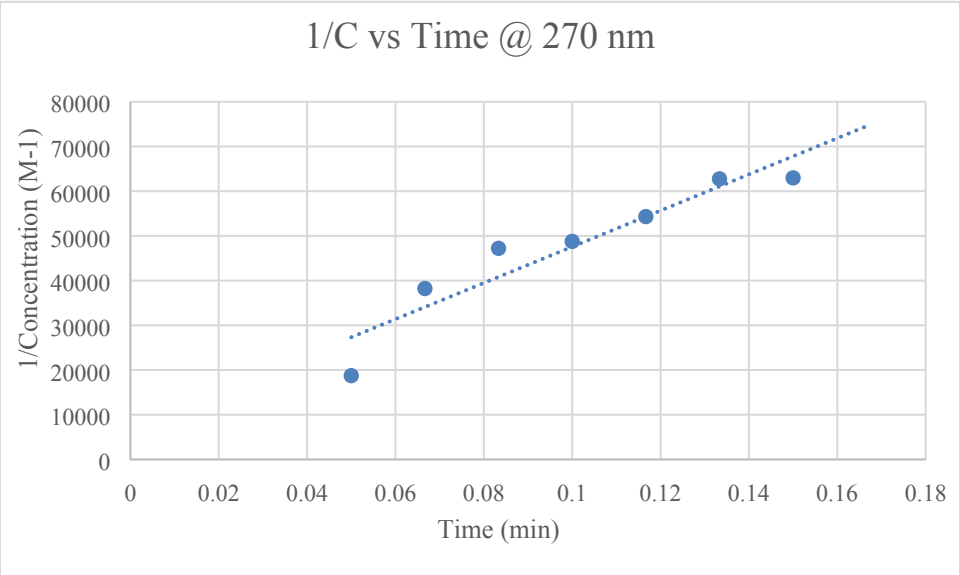

O2N
NO2
O
Si

5c

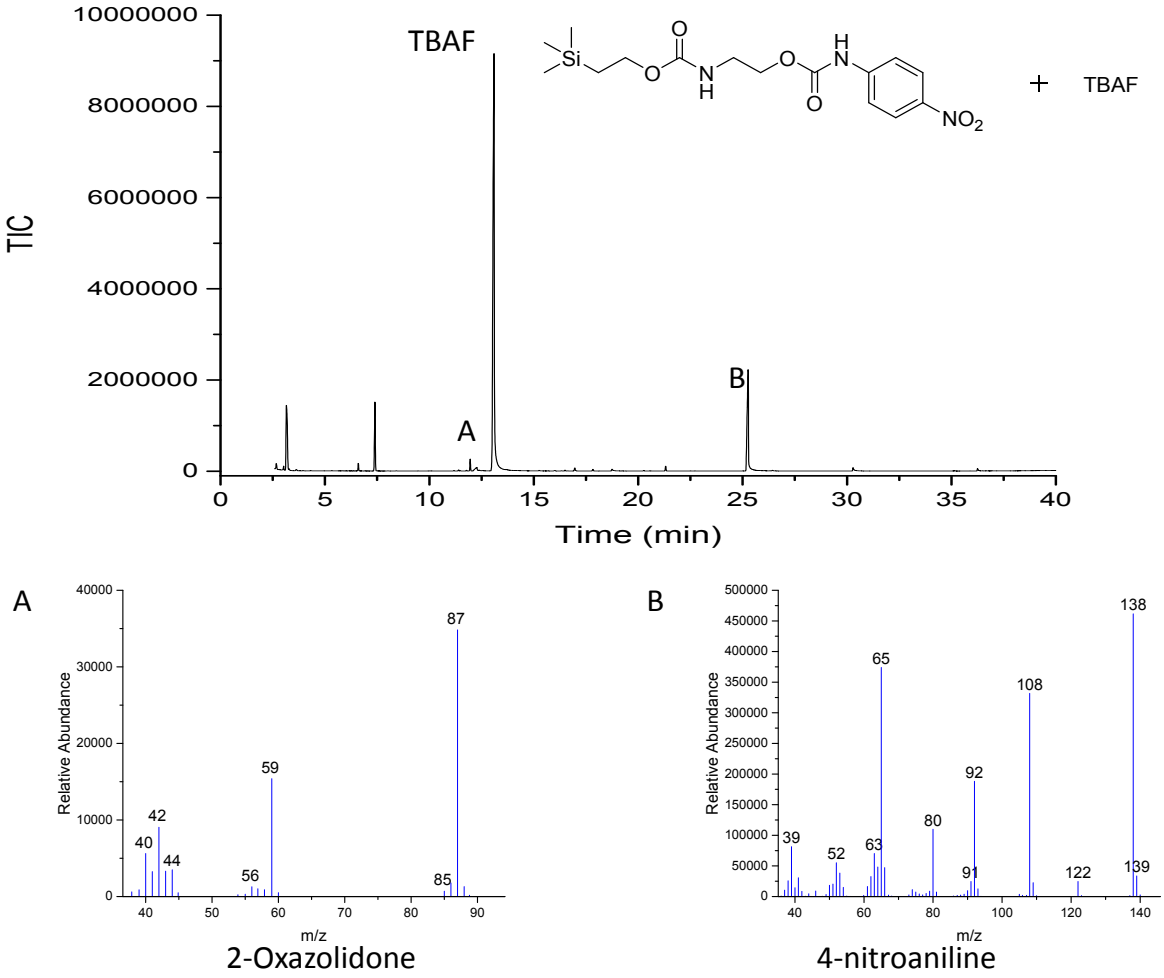

1/C vs Time @ 270 nm
1/Concentration (M-1)
25000
20000
15000
10000
5000
0
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
Time (min)


O2N
NO2
O
Si

5d


1/C vs Time @ 270 nm
1/Concentration (M-1)
80000
70000
60000
50000
40000
30000
20000
10000
0
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
0.16
0.18
Time (min)

GC-MS Spectra Confirming Complete Disassembly of Entry 3e



Works Cited:

1. C. A. Olsen, M. Witt, J. W. Jaroszewski and H. Franzyk, *Org. Lett.*, 2003, **5**, 4183-4185.
2. B. Marciniec and E. Malecka, *J. Phys. Org. Chem.*, 2003, **16**, 818-823.
3. J. A. Soderquist and A. Hassner, *J. Org. Chem.*, 1983, **48**, 1801-1810.
4. A. Chiotellis, S. V. Selivanova, B. Schweizer, R. Schibli and S. M. Ametamey, *J. Fluor. Chem.*, 2014, **160**, 20-28.