Enyne [4+4] Photocycloaddition with Polycyclic Aromatics

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SUPPORTING INFORMATION

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General Techniques

Instrumentation. For all compounds, ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 400, Bruker Avance III 500 or Bruker DRX 500 spectrometer. Chemical shifts were measured relative to the residual solvent resonance for ^1H and ^{13}C NMR. Coupling constants, *J*, are reported in hertz (Hz). The following abbreviations were used to designate signal multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublet; ddt, doublet of doublet of triplet; m, multiplet; br, broad.

IR spectra were recorded on Mattson 4020 GALAXY Series FT-IR. UV spectra were recorded on a Hewlett-Packard 8450 UV/VIS. Mass spectra were obtained from the Mass Spectrometry Facility of University of California at Riverside and also on an Agilent QTOF-HRMS at Temple University Chemistry Department. A Thomas Hoover UNI-MELT capillary melting point apparatus was used for melting point measurement; melting points are uncorrected. Reactions were monitored by TLC using a hexane / ethyl acetate, dichloromethane / methanol as solvent system unless otherwise stated. Glassware was oven-dried at 120 °C or flame dried under vacuum, assembled while hot, and cooled to ambient temperature under an inert atmosphere. Unless noted otherwise, reactions involving air sensitive reagents and/or requiring anhydrous conditions were performed an under argon atmosphere.

Reagents and solvents. Reagents and solvents were purchased from Aldrich Chemical Company, Gelest Inc, Fisher Scientific, Strem, Alfa Aesar, Acros Organics or TCI. Liquid reagents such as triethylamine or diisopropylethylamine were purified by distillation when necessary. Unless otherwise noted, solid reagents were used without further purification. Organolithium reagents were titrated using menthol / 2,2`-bipyridine.[1] Reaction solvents (THF, dichloromethane, DMF, and diethyl ether) were taken from a “Grubbs-style” Solvent Dispensing System purchased from Glass Contour or distilled as described in the literature.[2]

Chromatography. Combiflash R_f 200 using silica redi sep *Rf* high performance gold columns were used for purification. Also, 60 Å Silica gel (170–400 mesh) or basic alumina (aluminum oxide, 50–200 micron, activated) was used for flash column chromatography. Analytical and preparative thin layer chromatography (TLC) was performed using Analtech UniplateTM Silica Gel GF(250 micron) pre-coated glass plates. Spots were detected by 254 nm UV lamp, iodine and phosphomolybdic acid solution.

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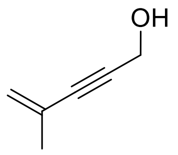
[1] Lin, H.-S.; Paquette, L. A. "A Convenient Method for Determining the Concentration of Grignard Reagents," *Synth. Commun.***1994**, *24*, 2503-2506.

[2] Armarego, W.; Chai, C. *Purification of Laboratory Chemicals*; 5 ed.; Elsevier, 2004.

Synthesis of Photosubstrates

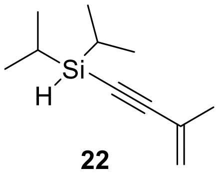
4-Methyl-4-enten-2-yn-1-ol 18[3]



18

n-Butyllithium in hexanes (1.36 M, 35 mL, 0.0473 mol) was added dropwise to a -78 °C solution of 2-methylbut-1-en-3-yne (5 mL, 0.0526 mol) in THF (100 mL) over 20 minutes. The resulting mixture was stirred and warmed to 0 °C over 1 hour. The reaction mixture was then re-cooled to -78 °C and paraformaldehyde (1.74 g, 0.0578 mol) was added in one portion. The resulting suspension was stirred andslowly warmed to room temperature. After 12 h the crude reaction mixture was quenched at 0 °C with saturated aqueous ammonium chloride (30 mL) and extracted with ether (3 × 15 mL). The combined organic layers were washed with brine, dried over anhydrous magnesium sulfate and concentrated, giving 5.5 g of crude product. Purification by Kugelrohr distillation at 95-100 °C / 3 mmHg afforded 3.85 g (84%) of pure **18** as a colorless liquid. 1H NMR (400 MHz, $CDCl_3$): δ 5.30 (s br, 1H), 5.24 (dq, *J* = 1.5, 1.4 Hz; 1H), 4.38 (s, 2H), 1.83 (dd, *J* = 1.4, 1.3 Hz; 3H), 1.76 (s br, OH).

Diisopropyl(3-methyl-3-buten-1-yn-1-yl)silane 22.[4]



22

n-Butyllithium (2.61 mL of 1.54 M solution in hexanes, 4.03 mmol) was slowly added to the solution of 2-methylbut-1-en-3-yne (0.4 mL, 4.2 mmol) in THF (6 mL) at -78 °C. The reaction mixture was stirred at the same temperature for 30 min. Diispropylchlorosilane (0.72 mL, 4.2 mmol) was then added dropwise. The reaction was slowly warmed to the rt and stirred overnight. Reaction was quenched with aqueous saturated ammonium chloride solution (5 mL) and extracted with ether (3x5 mL). The combined organics were washed with brine and concentrated to give the title compound (0.758 g, 100%) as a colorless oil that required no further purification. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.37 (dd, *J* = 2.0, 1.0 Hz, 1H), 5.31 – 5.21 (m, 1H), 3.75 (t, *J* = 2.3 Hz, 1H), 1.90 (dd, *J* = 1.5, 1.1 Hz, 3H), 1.13 – 0.89 (m, 14H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 126.9, 123.0, 109.3, 86.8, 23.2, 18.5, 18.2, 10.9 ppm. **IR** (neat): 3097, 2944, 2865, 2153, 2119, 1615 cm^{-1}. **Exact Mass** Calculated For $C_{11}H_{20}Si^+$ (M+) 180.1329, Found 180.1334.

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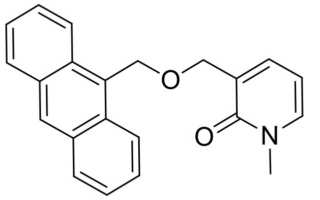
[3] M. S. Newman, W. S. Fones and W. T. Booth *J. Am. Chem. Soc.* 1945, **67,** 1053.

[4] P. P. Choudhury, C. S. Junker, R. R. Pidaparthi and M. E. Welker *J. Organomet. Chem*. **2014**, *754*, 88.

Photosubstrate 16

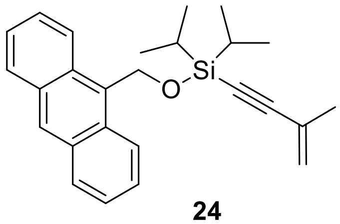


16

To sodium hydride (38 mg, 60% suspension in mineral oil, 0.97 mmol) suspended in THF (3 mL) at 0 °C was added hydroxymethyl anthracene (150 mg, 0.72 mmol). The mixture was stirred for 1 h at the same temperature and then 3-(bromomethyl)-1-methylpyridin-2(1*H*)-one (160 mg, 0.80 mmol) in THF (3 mL) was added dropwise. The reaction mixture was slowly allowed to warm to rt and stirred for additional 3 h before quenching with saturated aqueous ammonium chloride. After extraction with ethyl acetate the combined organics were washed with brine, concentrated in *vacuo* and purified by column chromatography using 3 % MeOH in DCM to get title compound as yellow solid (200 mg, 84 %).

mp 119 °C. R_f = 0.25 (methanol / dichloromethane; 1:33). **^{1}H NMR** (500 MHz, C_6D_6) δ 8.41 (d, *J* = 8.9 Hz, 2H), 8.17 (s, 1H), 7.79 (d, *J* = 8.3 Hz, 2H), 7.35 – 7.30 (m, 2H), 7.28 – 7.22 (m, 2H), 7.20 (d, *J* = 6.3 Hz, 1H), 6.06 (d, *J* = 6.5 Hz, 1H), 5.40 (s, 2H), 5.38 (t, *J* = 6.8 Hz, 1H), 4.89 (s, 2H), 2.86 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.91, 136.65, 136.01, 131.57, 131.15, 129.90, 129.10, 128.86, 128.53, 126.34, 125.07, 124.55, 105.77, 67.75, 65.50, 37.60. **IR** (neat): 3448, 3059, 2925, 2865, 2233, 1653, 1594, 1564, 1091, 733 cm^{-1}. **Exact mass** calculated for $C_{22}H_{19}NO_2Na^+$ (M+Na) 352.1314, found 352.1305.

Photosubstrate 24

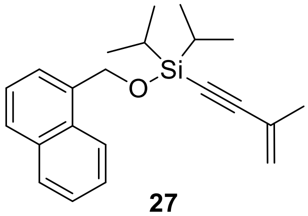


24

To the solution of diisopropyl(3-methylbut-3-en-1-yn-1-yl)silane **22** (190 mg, 1.06 mmol), in 5 mL of DCM was added NBS (205 mg, 1.15 mmol) in two portions and the mixture was stirred for 25 min before being transferred by cannula to a flask containing triethylamine (147 µl, 1.06 mmol), DMAP (11.7 mg, 0.09 mmol) and 9-anthracenemethanol (200 mg, 0.96 mmol) in 5 mL DCM. The reaction mixture was stirred for additional 4 h and then transferred to a separatory funnel with 10 mL DCM, washed with saturated aqueous ammonium chloride and brine, dried over anhydrous sodium sulfate and concentrated in *vacuo*. The product was purified by column chromatography using pure hexanes as elutant to furnish (anthracen-9-ylmethoxy)diisopropyl(3-methylbut-3-en-1-yn-1-yl)silane as a yellow solid (250 mg, 67%).

mp 53 °C, R_f = 0.46 (ethyl acetate / hexanes; 1:40). **^{1}H NMR** (500 MHz, C_6D_6) δ 8.73 (d, *J* = 8.9 Hz, 2H), 8.17 (s, 1H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.46 – 7.34 (m, 2H), 7.26 (dd, *J* = 7.7, 7.2 Hz, 2H), 5.90 (s, 2H), 5.52 (d, *J* = 0.8 Hz, 1H), 5.12 (d, *J* = 1.4 Hz, 1H), 1.82 (s, 3H), 1.16 – 0.91 (m, 14H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 131.82, 131.65, 130.80, 129.03, 128.02, 126.94, 125.90, 125.07, 125.01, 123.62, 109.41, 88.00, 59.32, 23.46, 17.47, 17.31, 13.53, 13.45. **IR** (neat): 2943, 2864, 2362, 2149, 1461, 1080, 1031, 883, 850 cm^{-1}.

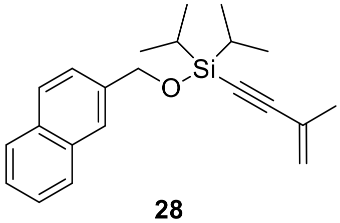
Photosubstrate 27



27

Prepared as described for compound **24** to give **27** as a colorless liquid, 73% yield, R_f = 0.40 (ethyl acetate / hexanes; 1:33). **^{1}H NMR** (400 MHz, C_6D_6) δ 8.13 (d, *J* = 8.3 Hz, 1H), 7.69 (d, *J* = 7.1 Hz, 1H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.59 (d, *J* = 8.1 Hz), 7.25 – 7.35 (m, 3H), 5.41 – 5.42 (m, 3H), 5.02 (m, 1H), 1.72 – 1.73 (dd, *J* = 1.5, 1.0 Hz, 3H), 1.12 – 1.20 (m, 14H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.48, 133.69, 131.19, 128.65, 127.91, 126.75, 125.96, 125.68, 125.56, 124.70, 123.85, 123.68, 108.94, 87.50, 64.81, 23.47, 17.46, 17.32, 13.36, 12.27. **IR** (neat): 2954, 2944, 2865, 2149, 1462, 1088, 847, 791, 759 cm^{-1}. **Exact mass c**alculated for $C_{22}H_{29}OSi$ $(M+H)^+$ 337.1987, found 337.1987

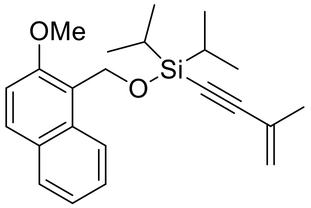
Photosubstrate 28



28

Prepared as described for compound **24** to give **28** as a colorless liquid, 77 % yield. R_f = 0.40 (ethyl acetate / hexanes; 1:33) **^{1}H NMR** (400 MHz, C_6D_6) δ 7.82 (s, 1H), 7.62 – 7.69 (m, 3H), 7.50 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.24 – 7.27 (m, 2H), 5.41 – 5.40 (dd, *J* = 2.0, 1.0 Hz, 1H), 5.08 (s, 2H), 5.01 – 5.04 (m, 1H), 1.71 – 1.72 (m, 3H), 1.15 – 1.24 (m, 14H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 138.66, 133.51, 132.91, 128.02, 127.97, 127.80, 126.71, 126.03, 125.64, 125.19, 125.06, 123.66, 108.88, 87.48, 66.54, 23.42, 17.45, 17.32, 13.36. **IR** (neat): 2943, 2864, 2149, 1462, 1092, 848, 811, 749 cm^{-1}. **Exact mass c**alculated for $C_{22}H_{29}OSi$ $(M+H)^+$ 337.1987, found 337.2003

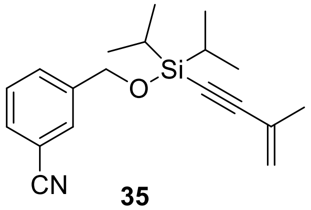
Photosubstrate 29



29

Prepared as described for compound **24** to give **29** as a colorless solid in 70 % yield. $R_f = 0.31$ (ethyl acetate / hexanes; 1:40). mp 56 °C. **^{1}H NMR** (500 MHz, C_6D_6) δ 8.56 (d, *J* = 8.6 Hz, 1H), 7.65 (d, *J* = 8.2 Hz, 1H), 7.56 (d, *J* = 9.0 Hz, 1H), 7.44 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 7.22 (ddd, *J* = 8.0, 6.8, 1.1 Hz, 1H) 6.88 (d,*J* = 9.1 Hz, 1H), 5.62 (s, 2H), 5.42– 5.47 (m, 1H), 5.05 – 5.07 (m, 1H), 3.44 (s, 3H), 1.78 (dd, *J* = 1.6, 1.1 Hz, 3H), 1.71 – 1.72 (m, 3H), 1.16 – 1.21 (m, 14H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.95, 133.91, 130.00, 129.40, 128.20, 126.96, 126.54, 124.71, 123.60, 123.37, 121.47, 113.91, 108.55, 88.03, 57.04, 56.92, 23.55, 17.44, 17.30, 13.29, 13.20. **IR** (neat): 2942, 2864, 2149, 1596, 1514, 1462, 1269, 1250, 1069, 1045, 847, 802 cm^{-1}. **Exact mass** calculated for $C_{23}H_{31}O_2Si$ $(M+H)^+$ 367.2093, found 367.2090

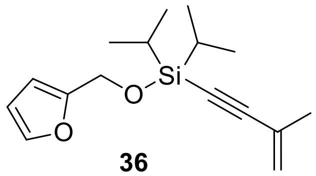
Photosubstrate 35



35

Prepared as described for compound **24** to give **35** as a colorless liquid in 83 % yield. $R_f = 0.25$ (ethyl acetate / hexanes; 1:40) **^{1}H NMR** (500 MHz, C_6D_6) δ 7.67 (m, 1H), 7.54 – 7.59 (m, 2H), 7.43 (t, *J* = 7.7 Hz, 1H), 5.39 – 5.40 (m, 1H), 5.31 (p, *J* = 1.7 Hz, 1H), 4.88 (s, 2H), 1.90 (dd, *J* = 1.6, 1.1 Hz, 3H), 1.07 – 1.09 (m, 14H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.73, 130.86, 130.80, 130.04, 129.08, 126.50, 124.01, 119.20, 112.38, 109.22, 86.80, 65.26, 23.37, 17.37, 17.21, 13.21. **IR** (neat): 2944, 2866, 2230, 2150, 1464, 1106, 1086, 848, 686 cm^{-1}. **Exact mass** calculated for $C_{19}H_{26}NOSi^+$ $(M+Na)^+$ 312.1783, found 312.1774

Photosubstrate 36



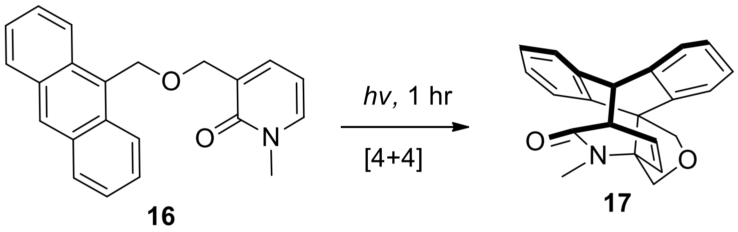
36

Prepared as described for compound **24** to give **36** as a colorless liquid in 79% yield. R_f = 0.46 (ethyl acetate / hexanes; 1:40) ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 1.8, 0.9 Hz, 1H), 6.32 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.28 (ddd, *J* = 3.2, 1.4, 0.6 Hz, 1H), 6.28 (ddd, *J* = 3.2, 1.4, 0.6 Hz, 1H), 5.42 (dq, *J* = 2.1, 1.0 Hz, 1H), 5.31 (dq, *J* = 3.3, 1.6 Hz, 1H),, 4.78 (s, 2H), 1.93 (dd, *J* = 1.6, 1.1 Hz, 3H), 1.08 – 0.98 (m, 14H). ^{13}**C NMR** (125 MHz, $CDCl_3$) δ 154.21, 142.23, 126.72, 123.64, 110.29, 108.98, 107.73, 87.10, 59.28, 23.42, 17.23, 17.11, 13.24. **IR** (neat): 2945, 2925, 2866, 2150, 1463, 1275, 1151, 1061, 848, 740 cm^{-1}.

Photocycloadditions:

General Procedure: A solution of the photosubstrate in benzene-d_6 or toluene (c = 0.025 – 0.030 M) was degassed for 30 min, transferred to NMR tubes and irradiated for 1 – 15 hours at 4 – 8 °C with a water-cooled Pyrex-filtered 450 W medium pressure mercury lamp. Progress of the reaction was periodically monitored by ^{1}H-NMR or TLC. After the reaction was complete, the solvent was evaporated and purified by column chromatography using the specified solvent mixtures.

Photocycloaddition of substrate 16

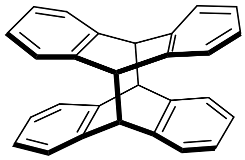


Reaction was complete within one hour and the photoproduct was isolated in quantitative yield as a colorless solid. R_f = 0.18 (ethylacetate / hexanes; 1:33). mp 56 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.48 (dd, J = 7.7, 0.6 Hz, 1H), 7.37 (dd, J = 7.5, 0.8 Hz, 1H), 7.25 - 7.10 (m, 6H), 5.93 (dd, J = 8.3, 6.8 Hz, 1H), 5.47 (dd, J = 8.3, 1.4 Hz, 1H), 4.86 (d, J = 9.1 Hz, 1H), 4.70 (q, J = 10.2 Hz, 2H), 4.46 (d, J = 10.0 Hz, 1H), 4.17 (ddd, J = 10.0, 6.8, 1.4 Hz, 1H), 3.78 (d, J = 9.1 Hz, 1H), 2.44 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.81, 144.31, 142.72, 142.11, 142.08, 135.93, 133.08, 127.24, 127.06, 127.03, 126.67, 126.57, 124.78, 124.36, 75.96, 71.60, 64.89, 64.14, 61.36, 53.75, 34.79. **IR** (neat): 3467, 2921, 2247, 1656, 1473, 1081, 911, 727 cm^{-1}. **Exact mass** calculated for $C_{22}H_{19}NO_2Na^+$ (M+Na) 352.1314, found 352.1302.

Photocycloaddition of anthracene and enyne alcohol 18

A mixture of anthracene (30 mg, 0.17 mmol) and 4-methyl-4-penten-2-yn-1-ol **18** (0.78 mL, 8.43 mmol) in benzene or methanol (2.6 mL) was irradiated for 2 h at rt with a water-cooled, Pyrex filtered 450W medium-pressure mercury lamp. Anthracene dimer **15** (~50% yield) was filtered off and the filtrate was concentrated *in vacuo*. The resulting mixture of products were separated by repetitive preparative thin layer chromatography using ethyl acetate / hexanes and chloroform / methanol as mobile phases to give products **19** (5 mg, 17%) and **21** (0.8 mg, 3%) which were partially characterized.

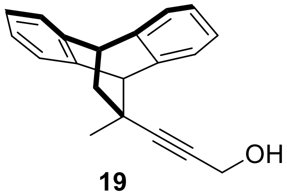
Anthracene photodimer 15.



15

^{1}H NMR (500 MHz, CDCl3) δ 6.93 (m, 8H), 6.82 (m,8H), 4.56 (s, 4H).

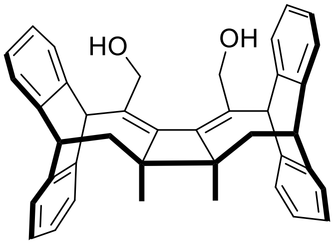
[4+2] Cycloaddition product 19



19

Colorless solid, 17% yield. R*f* = 0.72 (hexane / ethyl acetate 2:1); **^{1}H NMR** (500 MHz, CDCl3) _ 7.32 – 7.28 (m, 1H), 7.27 – 7.20 (m, 3H), 7.14 – 7.06 (m,4H), 4.24 (dd, *J* = 2.9, 2.5 Hz, 1H), 4.06 (s, 1H), 4.03 (s, 2H), 2.12 (dd, *J* = 12.3, 2.9 Hz,1H), 1.62 (dd, *J* = 12.3, 2.5 Hz, 1H), 1.05 (s, 3H). **^{13}C NMR** (125 MHz, CDCl3) _ 142.7, 142.7, 142.5, 140.6, 126.3, 125.9, 125.8, 125.6, 125.4, 125.3, 123.2, 123.2, 94.0, 78.4, 55.8, 51.2, 44.4, 44.3, 35.6, 29.2.

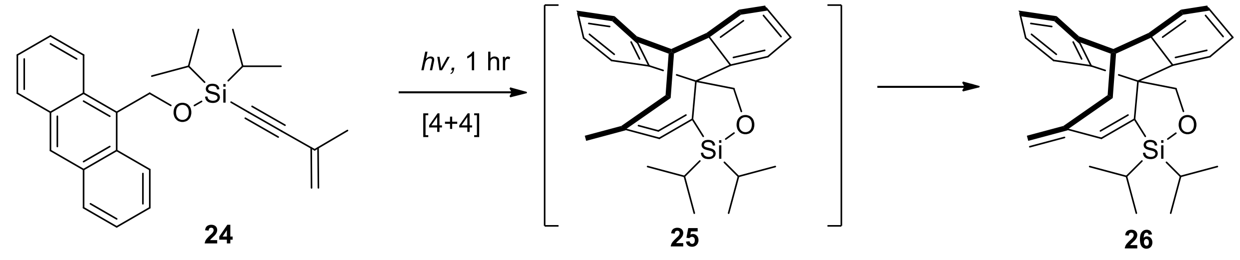
Symmetric dimer 21



21

Colorless solid, R*f* = 0.55 (dichloromethane / methanol 20:1); **^{1}H NMR** (500 MHz, CDCl3) _ 7.20 (m, 4H), 7.10 (m, 4H), 4.47 (s, 1H), 4.32 (m, 1H), 4.19 (m, 2H), 2.48 (s, OH), 2.18 (d, *J* = 14.5 Hz, 1H), 1.93 (dd, *J* = 14.5, 8.2 Hz, 1H), 1.55 (s, 2H). **^{13}C NMR** (125 MHz, CDCl3) _ 142.7, 142.5, 140.4, 140.0, 139.8, 136.6, 127.9, 127.8, 127.4, 126.6, 126.6, 126.4, 126.0, 125.6, 63.5, 51.4, 48.7, 45.4, 44.5, 29.7. **Exact mass** calculated For $C_{40}H_{40}NO_2^+$ (MNH_4+) 566.3054, Found 566.3041.

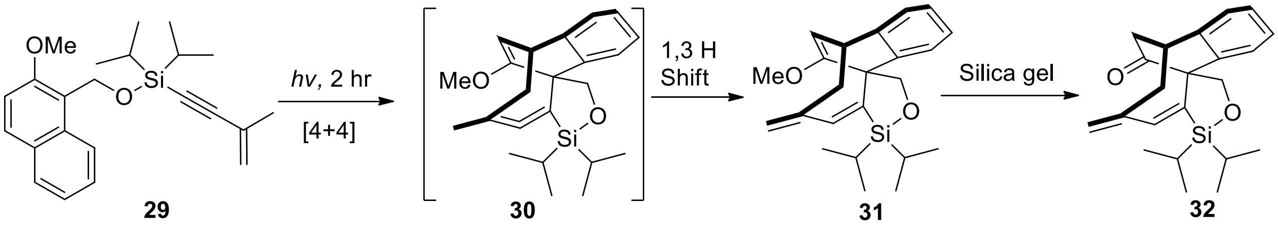
Photocycloaddition of substrate 24



This reaction was complete in 1 h. The crude reaction mixture was concentrated and purified by column chromatography using 5% ethylacetate in hexanes.

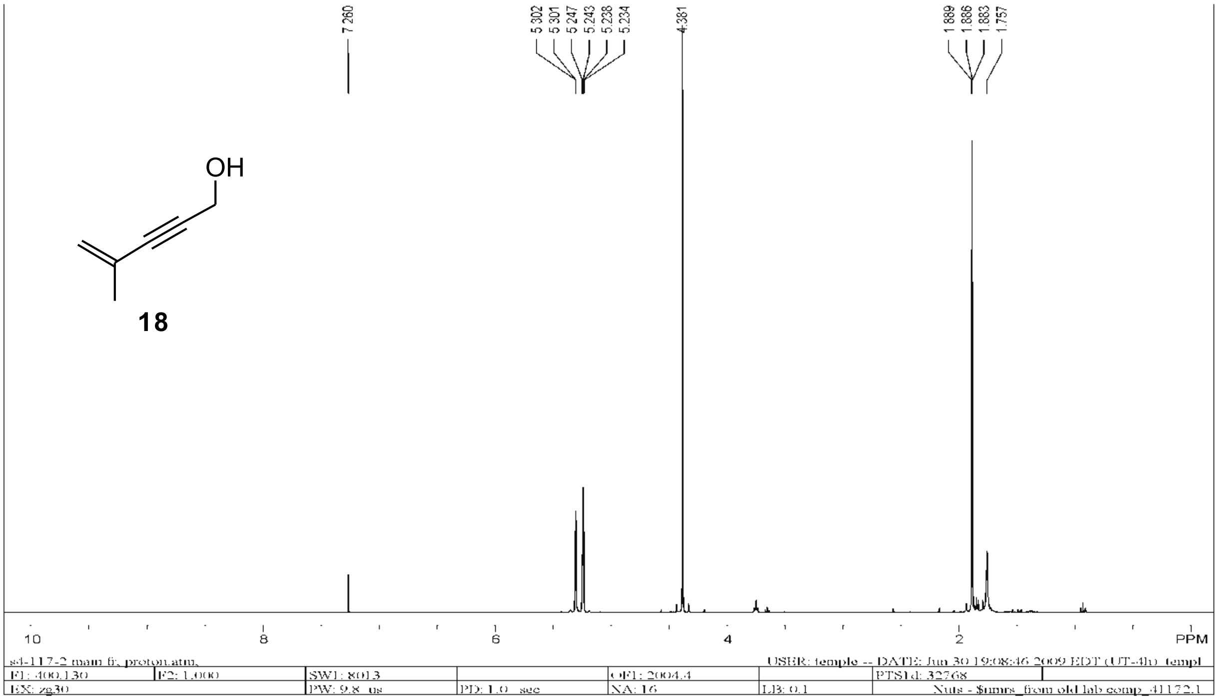
Colorless solid, 67% yield, R_f = 0.7 (ethyl acetate / hexanes; 1:100). mp = 82 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 5.6, 3.6 Hz, 2H), 7.29 – 7.27 (m, 2H), 7.20 – 7.22 (m, 4H), 6.20 (t, *J* = 1.3 Hz, 1H), 4.90 (s, 2H), 4.71 – 4.72 (m, 1H), 4.56 (t, *J* = 1.7 Hz, 1H), 4.34 (t, *J* = 4.9 Hz, 1H), 2.98 (d, *J* = 4.9 Hz, 2H), 1.07 – 1.11 (m, 8H), 1.00 – 1.02 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.54, 144.69, 142.00, 141.16, 136.71, 127.53, 126.89, 126.60, 126.41, 119.86, 74.46, 53.77, 49.54, 46.02, 17.86, 17.64, 13.94. **IR** (neat): 2941, 2863, 2362, 1480, 1456, 1032, 993, 881, 789, 745 cm^{-1}. **Exact mass** calculated for $C_{26}H_{31}OSi$ $(M+H)^+$ 387.2144, found 387.2129

Photocycloaddition of substrate 29

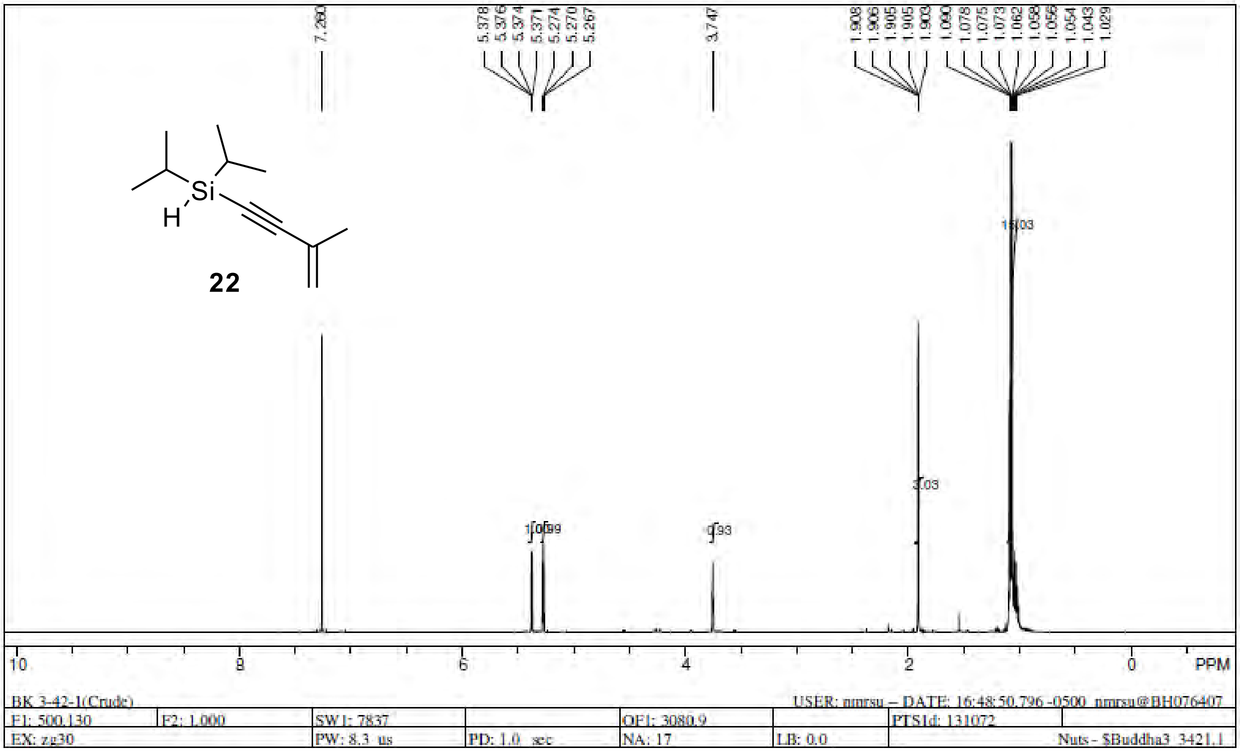


This reaction was complete in 2 h. The crude reaction mixture was concentrated and column chromatography purification using 2.5% ethyl acetate in hexanes gave **32** as a colorless oil, 74%. R_f = 0.30 (ethyl acetate / hexanes; 1:20) **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 7.1, 1.8 Hz, 1H), 7.19 – 7.26 (m, 3H), 6.43 (s, 1H), 5.18 (m, 1H), 4.93 (dd, *J* = 3.0, 1.4 Hz, 1H), 4.90 (d, *J* = 10.3 Hz, 1H), 4.48 (d, *J* = 10.3 Hz, 1H), 3.45 – 3.48 (m, 1H), 2.87 (dd, *J* = 14.4, 8.1 Hz, 1H), 2.83 (dd, *J* = 17.9, 1.6 Hz, 1H), 2.63 (dd, *J* = 14.4, 0.9 Hz, 1H), 2.58 (ddd, *J* = 17.9, 6.4, 1.0 Hz, 1H), 1.13 – 1.19 (m, 4H), 1.09 (d, *J* = 6.0 Hz, 3H), 0.96 – 1.01 (m, 1H), 0.94 (d, *J* = 6.8 Hz, 3H), 0.90 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 211.84, 147.59, 143.51, 141.41, 140.67, 138.27, 128.43, 127.24, 127.17, 126.52, 121.91, 74.45, 62.85, 43.91, 42.91, 36.72, 17.81, 17.52, 13.62, 13.00. **IR** (neat): 2942, 2864, 1706, 1462, 1077, 1004, 881, 793, 763 cm^{-1}. **Exact mass** calculated for $C_{22}H_{29}O_2Si$ $(M+H)^+$ 353.1937, found 353.1952

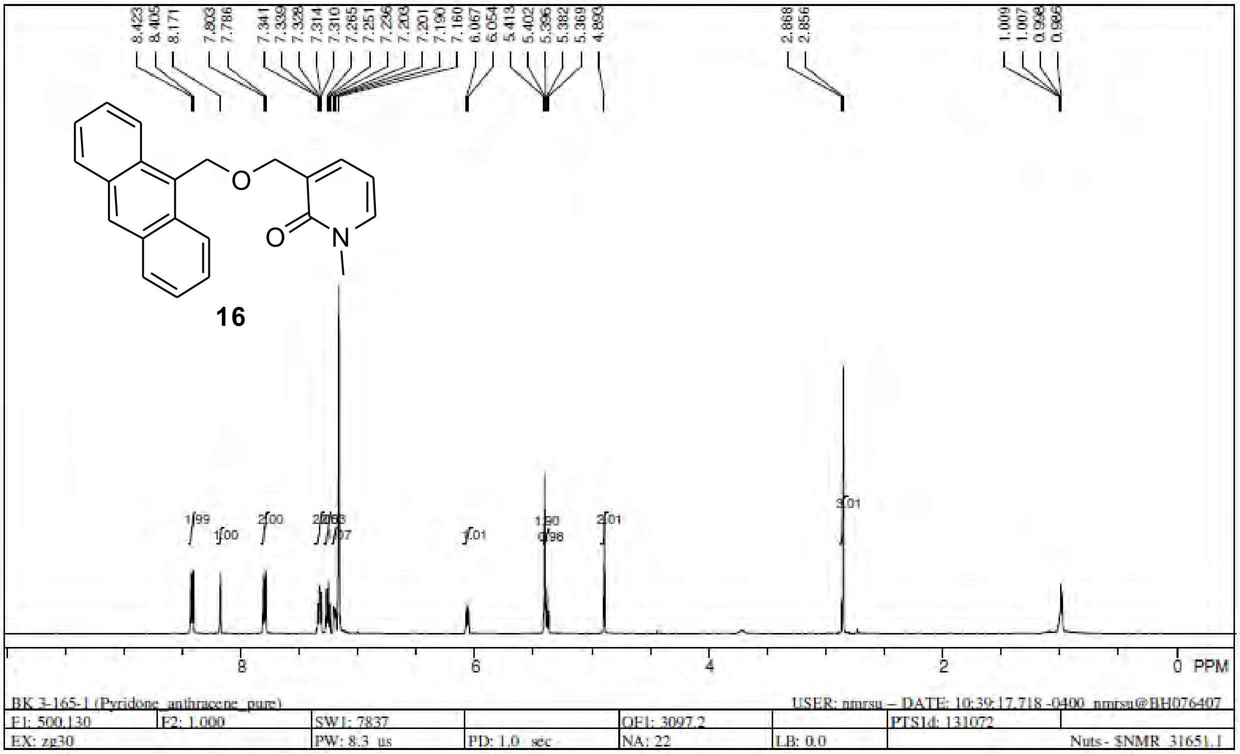
^{1}H NMR, ^{13} C NMR and 2D Spectra

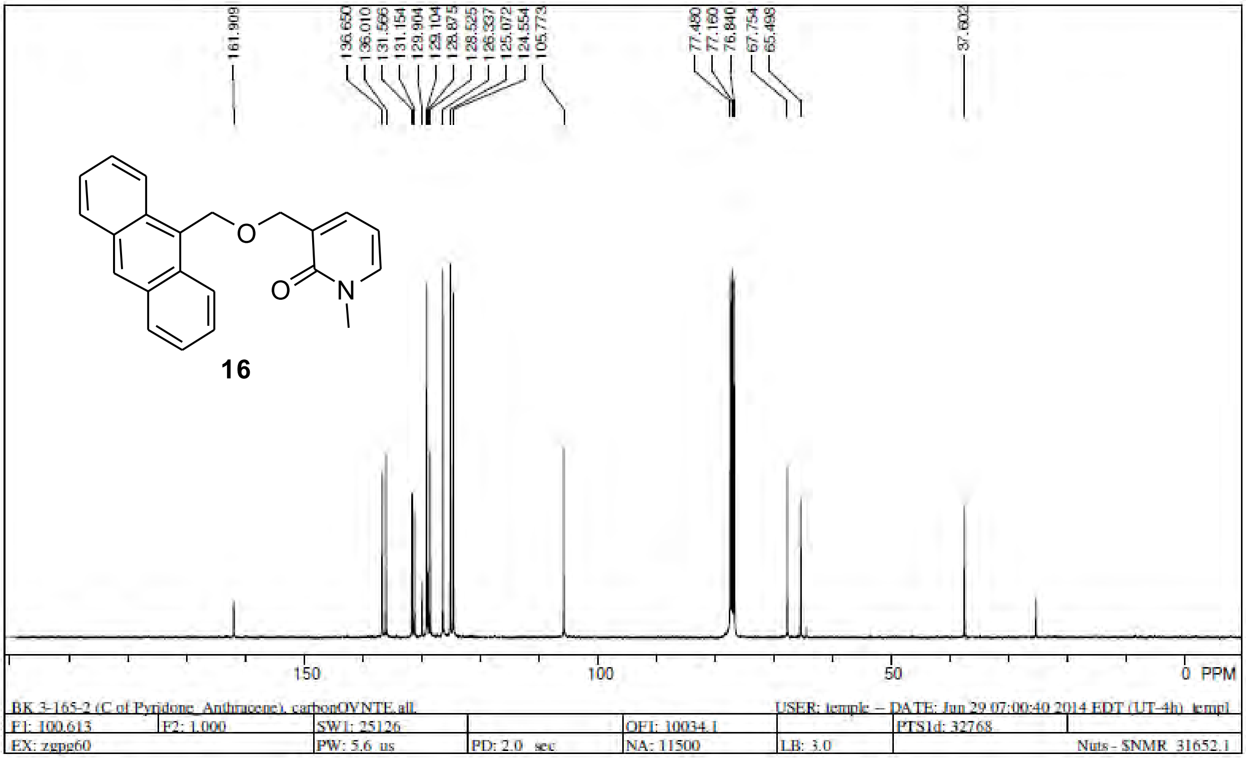


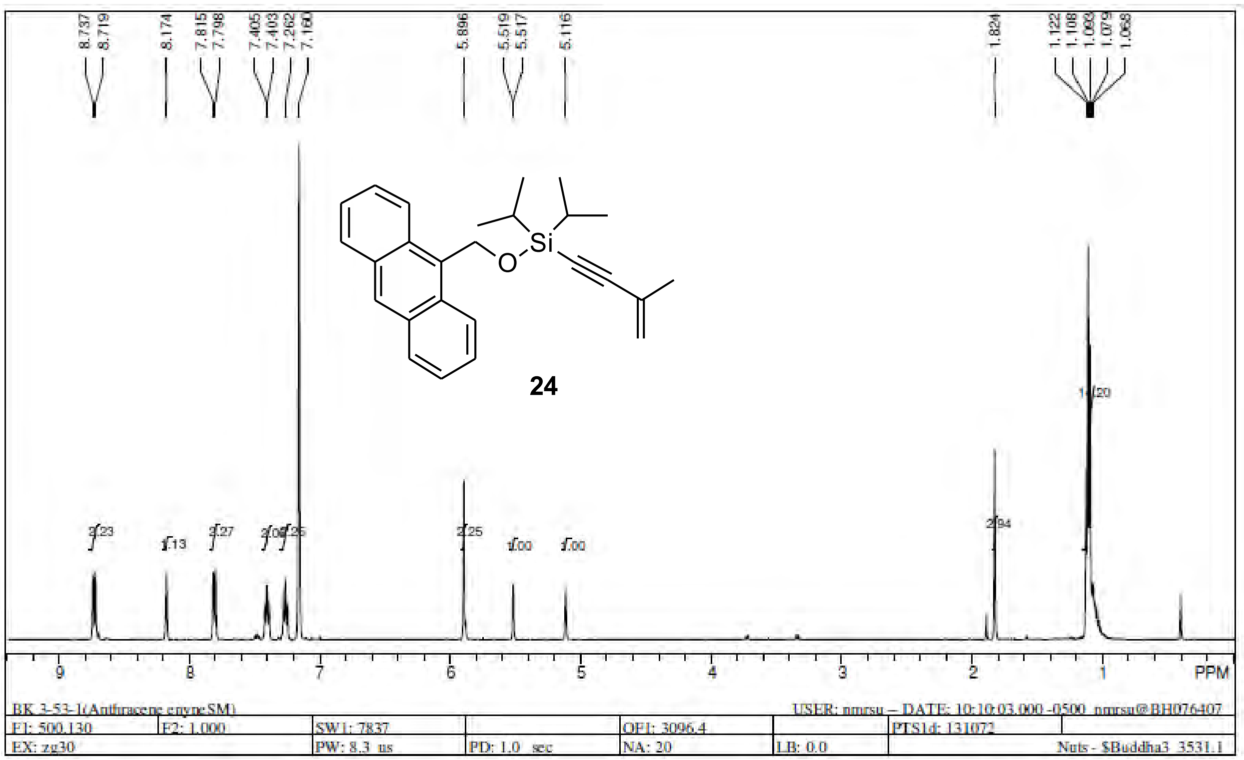
18

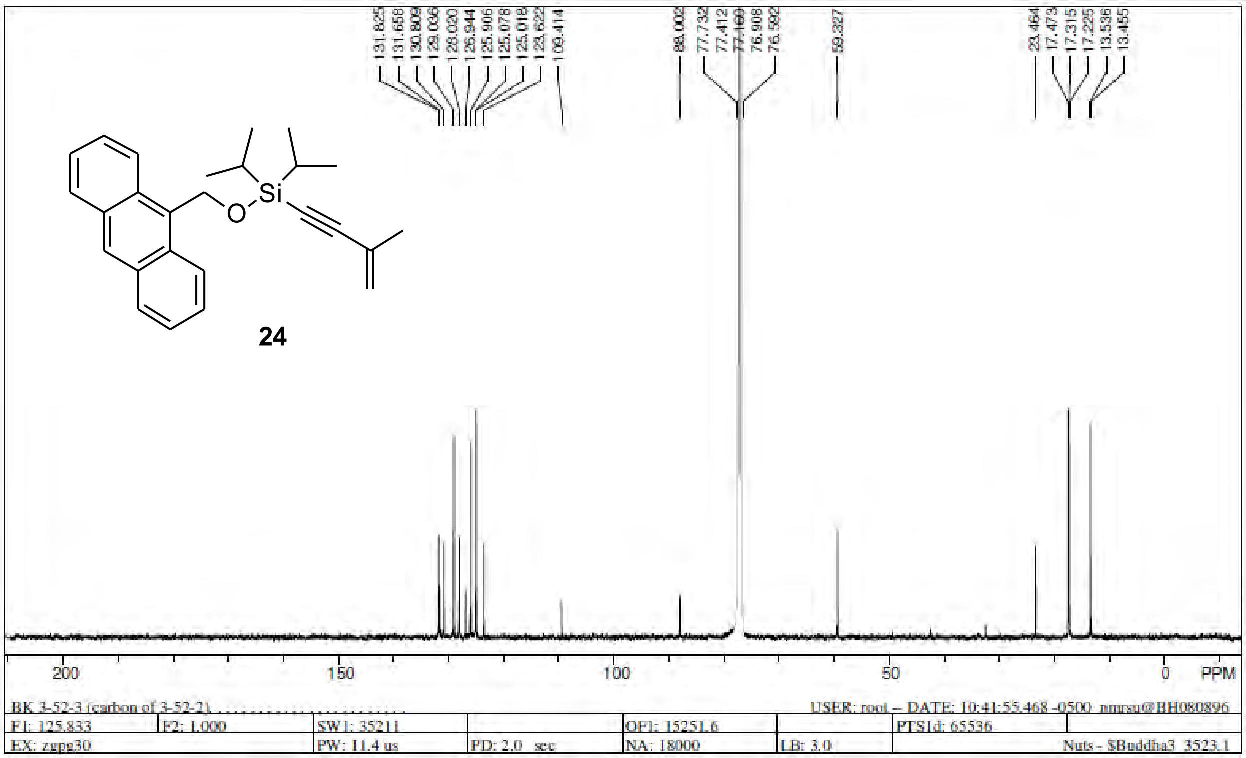


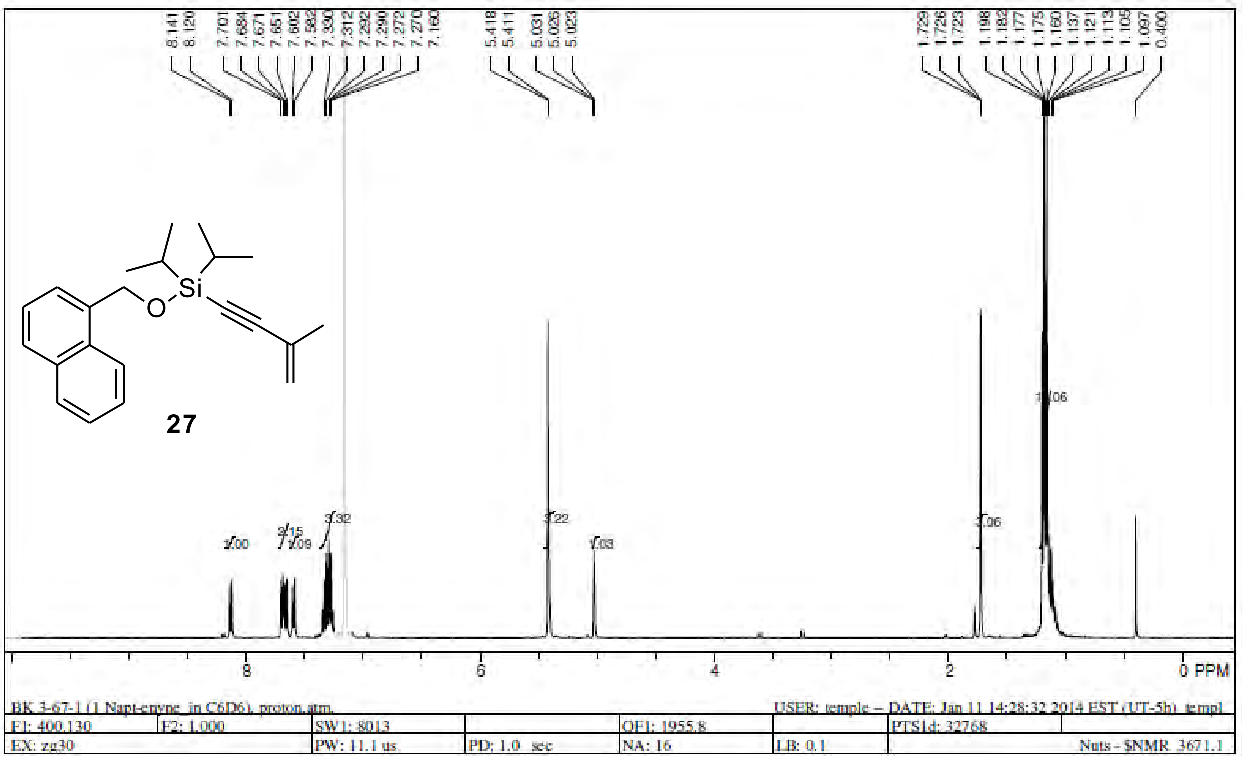
22


8.423
8.405
8.171
7.803
7.786
7.341
7.339
7.328
7.314
7.310
7.265
7.251
7.236
7.203
7.201
7.190
7.160
6.067
6.054
5.413
5.402
5.396
5.382
5.369
4.893
2.868
2.856
1.009
1.007
0.998
0.986
O
O
N
16
1.99
1.00
2.00
2.03
2.03
1.07
1.01
1.90
0.98
2.01
3.01
8
6
4
2
0 PPM
BK 3-165-1 (Pyridone_anthracene_pure)
USER: nmrsu – DATE: 10:39:17.718 -0400 nmrsu@BH076407
F1: 500.130
F2: 1.000
SW1: 7837
OF1: 3097.2
PTS1d: 131072
EX: zg30
PW: 8.3 us
PD: 1.0 sec
NA: 22
LB: 0.0
Nuts - $NMR_31651.1


161.909
136.650
136.010
131.566
131.154
129.904
129.104
128.875
128.525
126.337
125.072
124.554
105.773
77.480
77.160
76.840
67.754
65.498
37.602
O
O
N
16
150
100
50
0 PPM
BK 3-165-2 (C of Pyridone_Anthracene), carbonOVNTE.all
USER: temple – DATE: Jun 29 07:00:40 2014 EDT (UT-4h) templ
F1: 100.613
F2: 1.000
SW1: 25126
OF1: 10034.1
PTS1d: 32768
EX: zgpg60
PW: 5.6 us
PD: 2.0 sec
NA: 11500
LB: 3.0
Nuts - $NMR_31652.1

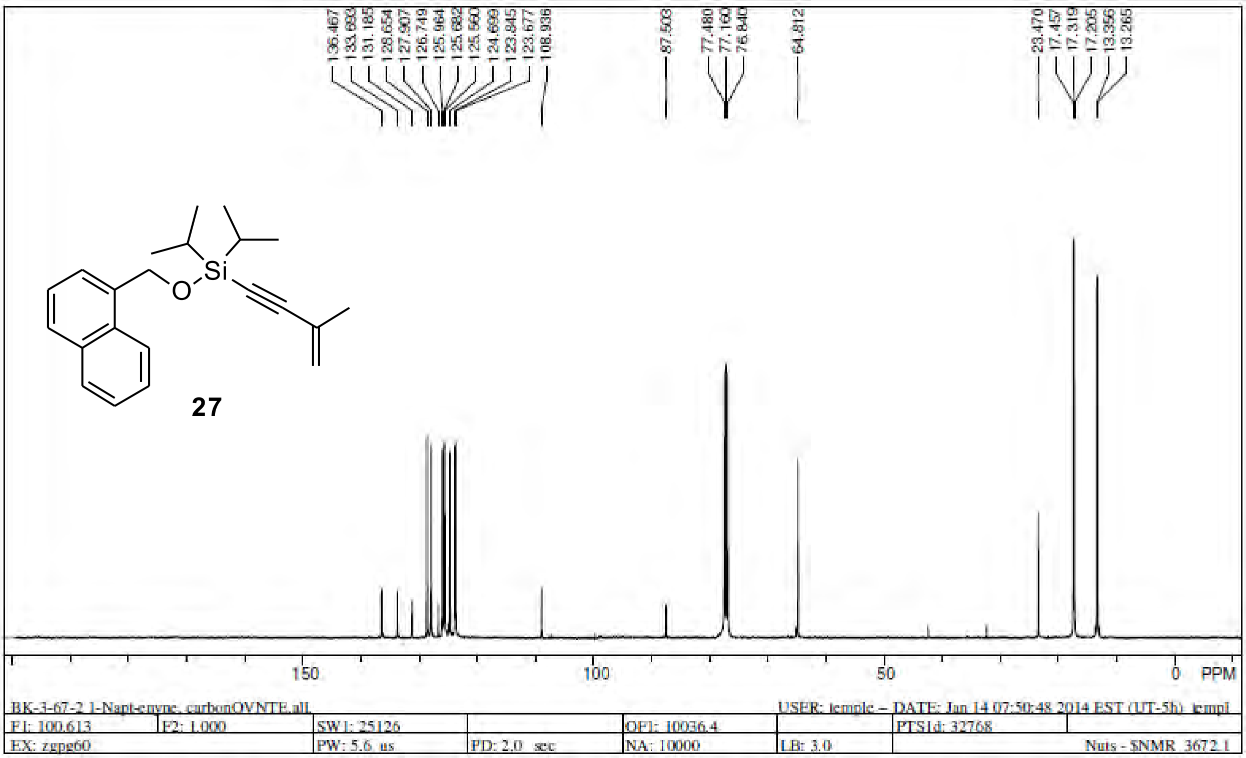

8.737
8.719
8.174
7.815
7.798
7.405
7.403
7.262
7.160
5.896
5.519
5.517
5.116
1.824
1.122
1.108
1.093
1.079
1.068
O
Si
24
2.23
1.13
2.27
2.08
2.25
2.25
1.00
1.00
2.94
14.20
9
8
7
6
5
4
3
2
1
PPM
BK 3-53-1(Anthracene enyneSM)
USER: nmrsu – DATE: 10:10:03.000 -0500 nmrsu@BH076407
F1: 500.130
F2: 1.000
SW1: 7837
OF1: 3096.4
PTS1d: 131072
EX: zg30
PW: 8.3 us
PD: 1.0 sec
NA: 20
LB: 0.0
Nuts - $Buddha3_3531.1


131.825
131.658
130.809
129.036
128.020
126.944
125.906
125.078
125.018
123.622
109.414
88.002
77.732
77.412
77.160
76.908
76.592
59.327
23.464
17.473
17.315
17.225
13.536
13.455
O
Si
24
200
150
100
50
0
PPM
BK 3-52-3 (carbon of 3-52-2)
USER: root – DATE: 10:41:55.468 -0500 nmrsu@BH080896
F1: 125.833
F2: 1.000
SW1: 35211
OF1: 15251.6
PTS1d: 65536
EX: zgpg30
PW: 11.4 us
PD: 2.0 sec
NA: 18000
LB: 3.0
Nuts - $Buddha3_3523.1



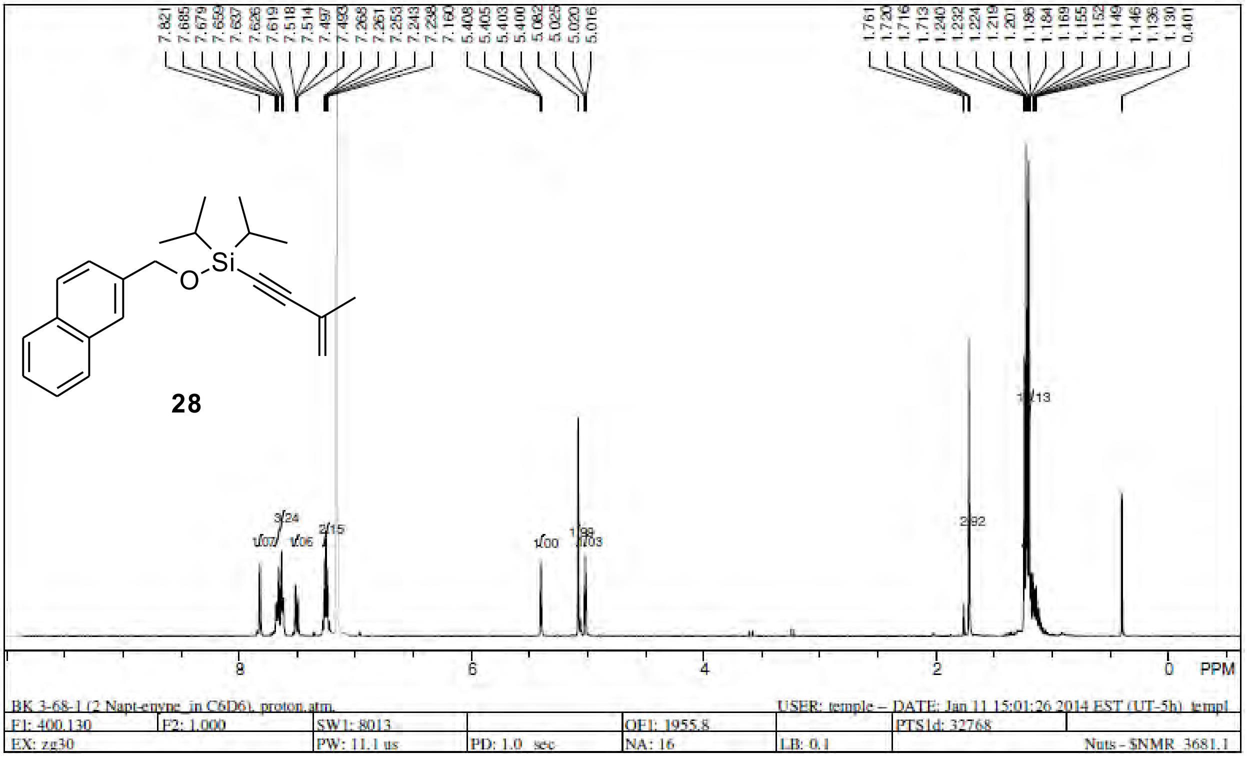
27

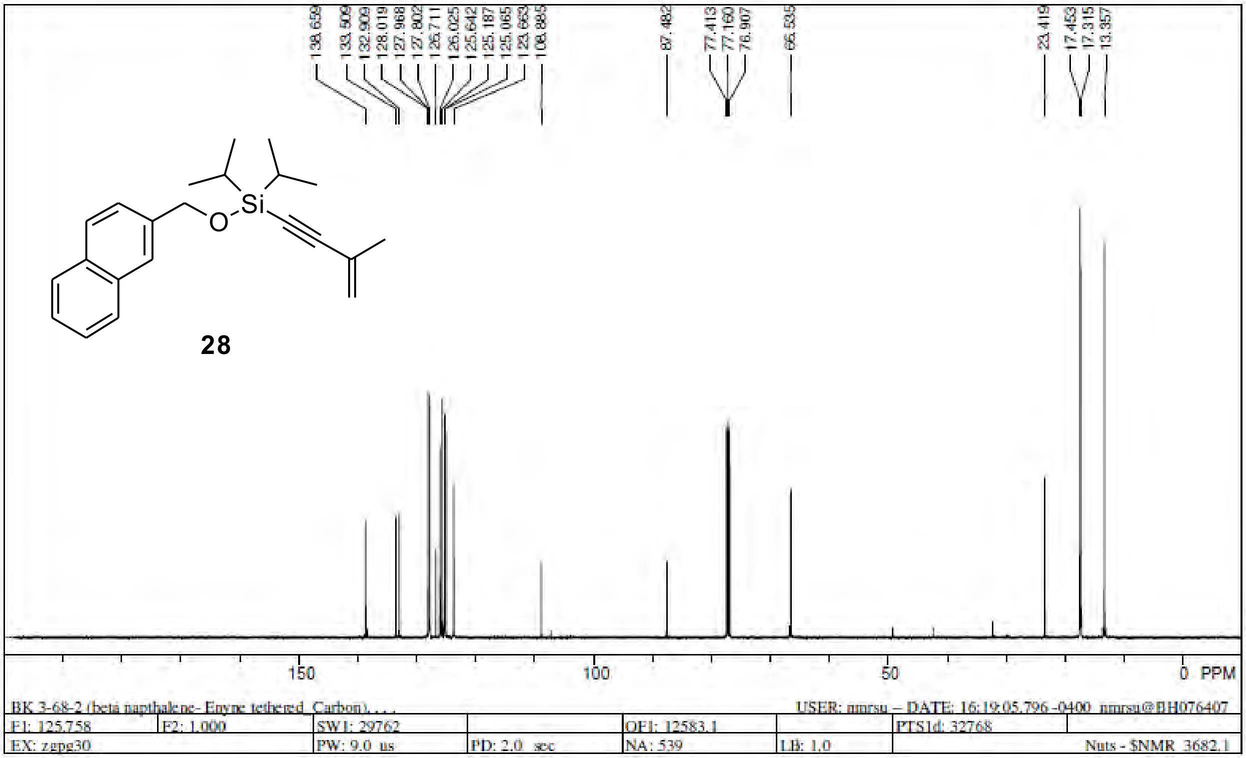
8.141
8.120
7.701
7.684
7.671
7.651
7.602
7.582
7.330
7.312
7.292
7.290
7.272
7.270
7.160
5.418
5.411
5.031
5.026
5.023
1.729
1.726
1.723
1.198
1.182
1.177
1.175
1.160
1.137
1.121
1.113
1.105
1.097
0.400
1.00
2.15
1.09
3.32
3.22
1.03
3.06
1 06
8
6
4
2
0 PPM
BK 3-67-1 (1 Napt-enyne_in C6D6). proton.atm.
USER: temple – DATE: Jan 11 14:28:32 2014 EST (UT-5h) templ
F1: 400.130
F2: 1.000
SW1: 8013
OF1: 1955.8
PTS1d: 32768
EX: zg30
PW: 11.1 us
PD: 1.0 sec
NA: 16
LB: 0.1
Nuts - $NMR 3671.1

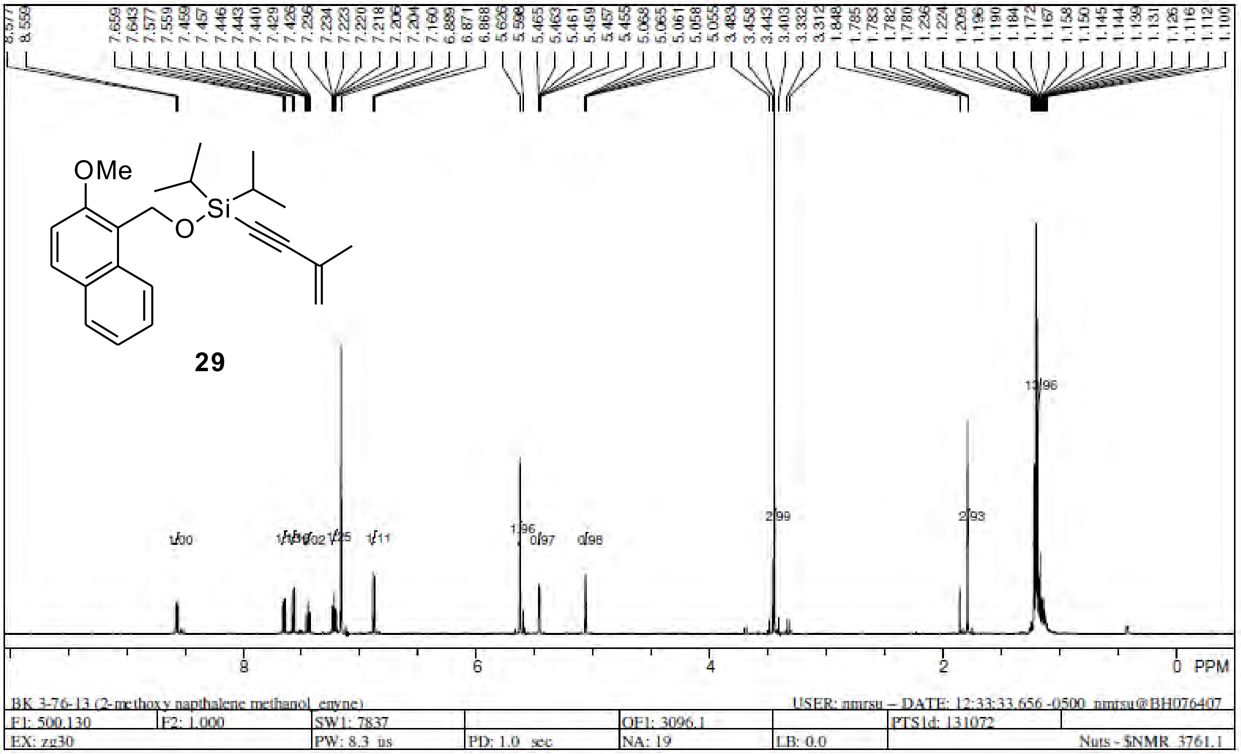


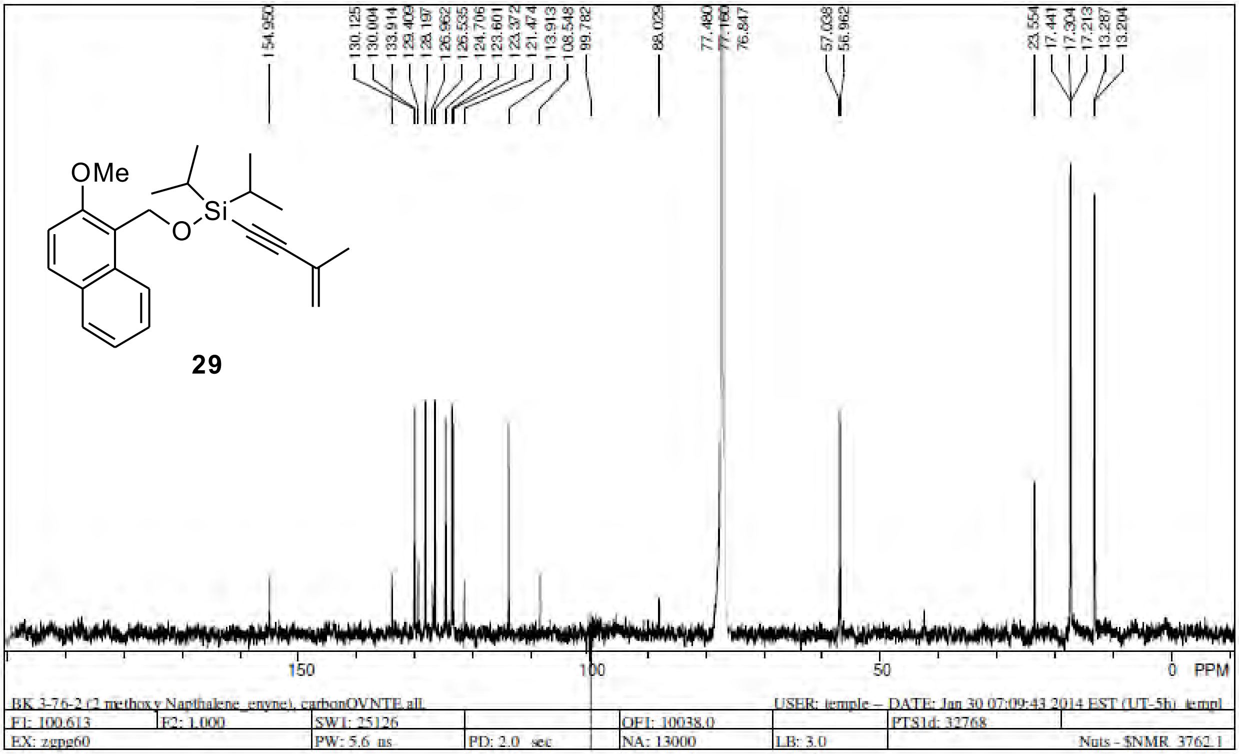
27

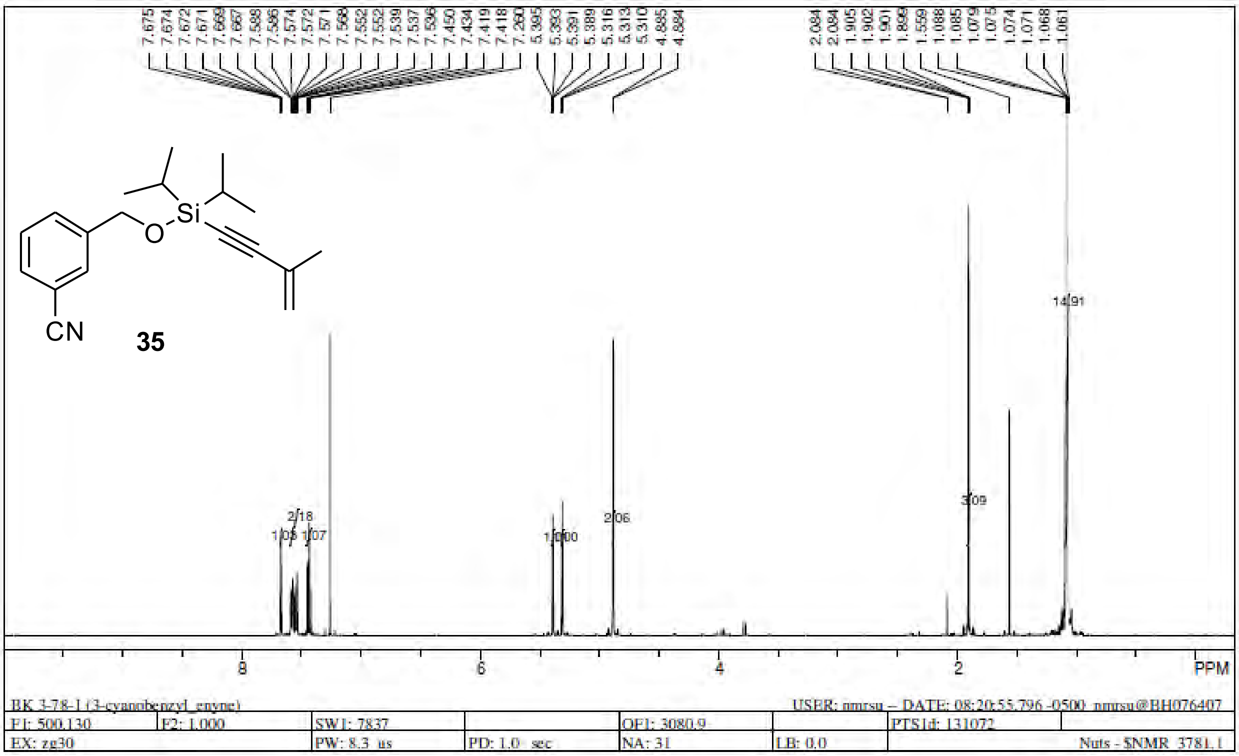
136.467
133.693
131.185
128.654
127.907
126.749
125.964
125.682
125.560
124.699
123.845
123.677
108.936
87.503
77.480
77.160
76.840
64.812
23.470
17.457
17.319
17.205
13.356
13.265
150
100
50
0 PPM
BK-3-67-2 1-Napt-enyne. carbonOVNTE.all.
USER: temple – DATE: Jan 14 07:50:48 2014 EST (UT-5h) templ
F1: 100.613
F2: 1.000
SW1: 25126
OF1: 10036.4
PTS1d: 32768
EX: zgpg60
PW: 5.6 us
PD: 2.0 sec
NA: 10000
LB: 3.0
Nuts - $NMR 3672.1

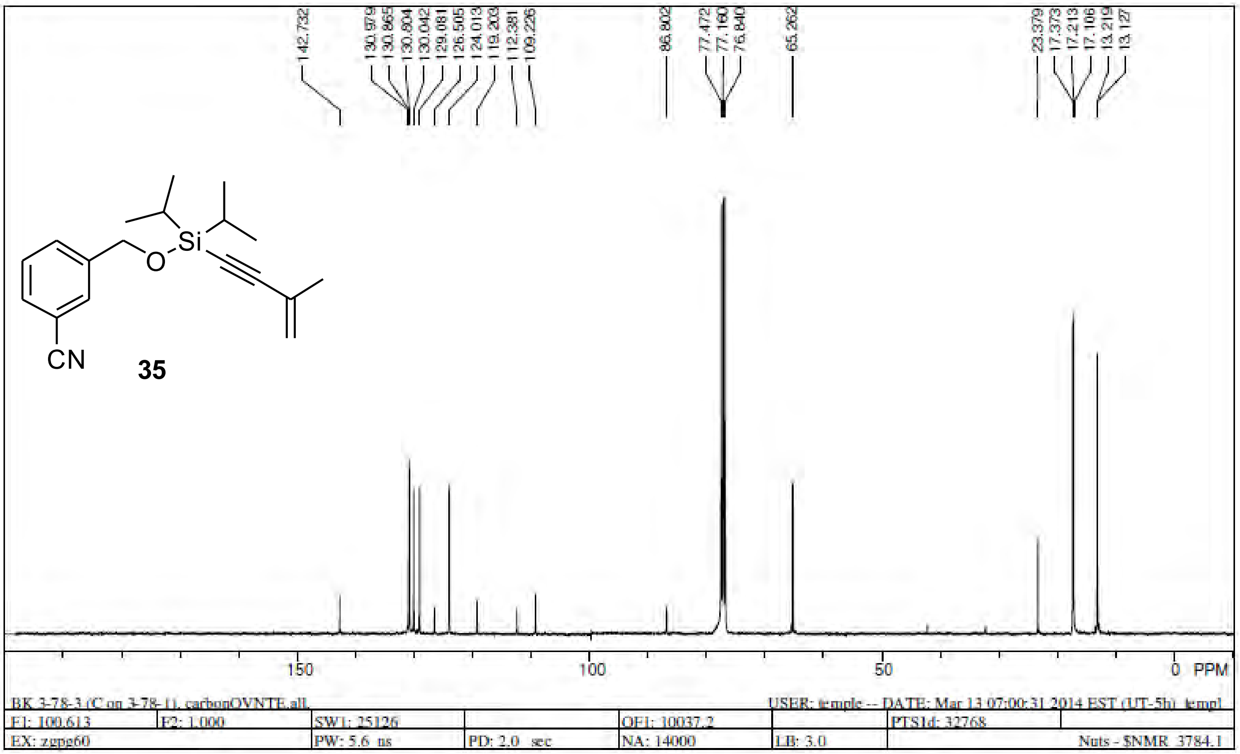

7.821
7.685
7.679
7.659
7.637
7.626
7.619
7.518
7.514
7.497
7.493
7.268
7.261
7.253
7.243
7.238
7.160
5.408
5.405
5.403
5.400
5.082
5.025
5.020
5.016
1.761
1.720
1.716
1.713
1.240
1.232
1.224
1.219
1.201
1.186
1.184
1.169
1.155
1.152
1.149
1.146
1.136
1.130
0.401
O
Si
28
1.07
3.24
1.06
2.15
1.00
1.99
1.03
2.92
14.13
8
6
4
2
0
PPM
BK 3-68-1 (2 Napt-enyne_in C6D6), proton.atm.
USER: temple – DATE: Jan 11 15:01:26 2014 EST (UT-5h) templ
F1: 400.130
F2: 1.000
SW1: 8013
OF1: 1955.8
PTS1d: 32768
EX: zg30
PW: 11.1 us
PD: 1.0 sec
NA: 16
LB: 0.1
Nuts - $NMR 3681.1

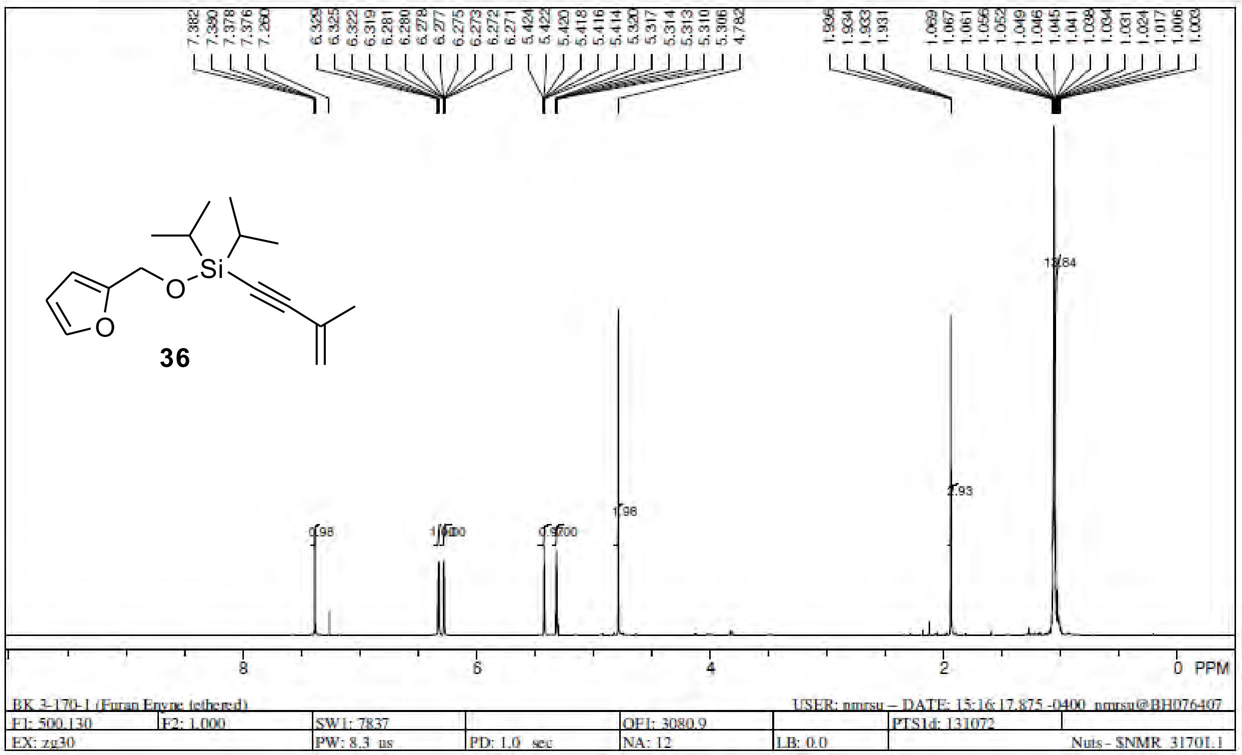

138.659
133.509
132.909
128.019
127.968
127.802
126.711
126.025
125.642
125.187
125.065
123.663
108.885
87.482
77.413
77.160
76.907
66.535
23.419
17.453
17.315
13.357
O
Si
28
150
100
50
0
PPM
BK 3-68-2 (beta napthalene- Enyne tethered_Carbon), . . .
USER: nmrsu – DATE: 16:19:05.796 -0400 nmrsu@BH076407
F1: 125.758
F2: 1.000
SW1: 29762
OF1: 12583.1
PTS1d: 32768
EX: zgpg30
PW: 9.0 us
PD: 2.0 sec
NA: 539
LB: 1.0
Nuts - $NMR 3682.1


8.577
8.559
7.659
7.643
7.577
7.559
7.459
7.457
7.446
7.443
7.440
7.429
7.426
7.296
7.234
7.223
7.220
7.218
7.206
7.204
7.160
6.889
6.871
6.868
5.626
5.598
5.465
5.463
5.461
5.459
5.457
5.455
5.068
5.065
5.061
5.058
5.055
3.483
3.458
3.443
3.403
3.332
3.312
1.848
1.785
1.783
1.782
1.780
1.236
1.224
1.209
1.196
1.190
1.184
1.172
1.167
1.158
1.150
1.145
1.144
1.139
1.131
1.126
1.116
1.112
1.100
OMe
O
Si
29
1.00
1.02
1.25
1.11
1.96
0.97
0.98
2.99
2.93
12.96
8
6
4
2
0 PPM
BK 3-76-13 (2-methoxy napthalene methanol_enyne)
USER: nmrsu – DATE: 12:33:33.656 -0500 nmrsu@BH076407
F1: 500.130
F2: 1.000
SW1: 7837
OF1: 3096.1
PTS1d: 131072
EX: zg30
PW: 8.3 us
PD: 1.0 sec
NA: 19
LB: 0.0
Nuts - $NMR 3761.1


154.950
130.125
130.004
133.914
129.409
128.197
126.962
126.535
124.706
123.601
123.372
121.474
113.913
108.548
99.782
88.029
77.480
77.160
76.847
57.038
56.962
23.554
17.441
17.304
17.213
13.287
13.204
OMe
O
Si
29
150
100
50
0 PPM
BK 3-76-2 (2 methoxy Napthalene_enyne), carbonOVNTE.all
USER: temple – DATE: Jan 30 07:09:43 2014 EST (UT-5h) templ
F1: 100.613
F2: 1.000
SW1: 25126
OF1: 10038.0
PTS1d: 32768
EX: zgpg60
PW: 5.6 us
PD: 2.0 sec
NA: 13000
LB: 3.0
Nuts - $NMR 3762.1

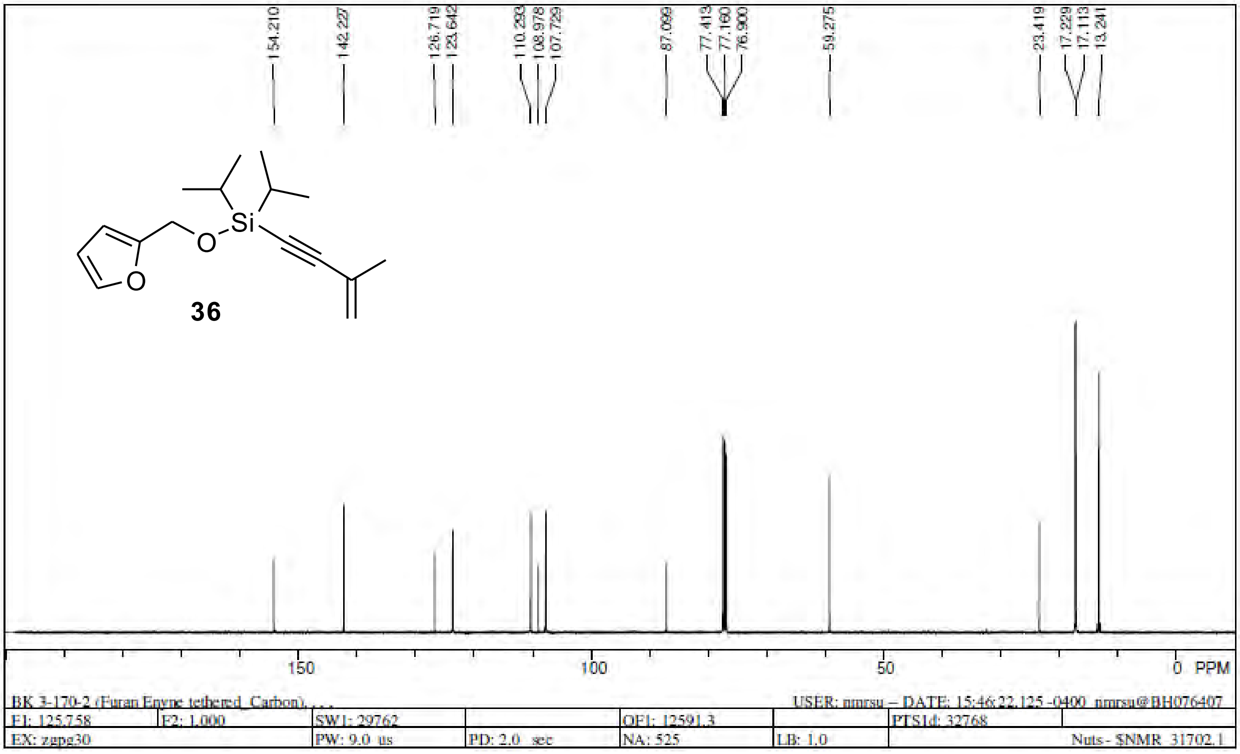

7.675
7.674
7.672
7.671
7.669
7.667
7.588
7.586
7.574
7.572
7.571
7.568
7.552
7.552
7.539
7.537
7.536
7.450
7.434
7.419
7.418
7.260
5.395
5.393
5.391
5.389
5.316
5.313
5.310
4.885
4.884
2.084
2.084
1.905
1.902
1.901
1.899
1.559
1.088
1.085
1.079
1.075
1.074
1.071
1.068
1.061
Si
O
CN
35
14.91
3.09
2.06
2.18
1.05
1.07
1.000
8
6
4
2
PPM
BK 3-78-1 (3-cyanobenzyl_enyne)
USER: nmrsu -- DATE: 08:20:55.796 -0500 nmrsu@BH076407
F1: 500.130
F2: 1.000
SW1: 7837
OF1: 3080.9
PTS1d: 131072
EX: zg30
PW: 8.3 us
PD: 1.0 sec
NA: 31
LB: 0.0
Nuts - $NMR 3781.1


142.732
130.979
130.865
130.804
130.042
129.081
126.505
124.013
119.203
112.381
109.226
86.802
77.472
77.160
76.840
65.262
23.379
17.373
17.213
17.106
13.219
13.127
Si
O
CN
35
150
100
50
0
PPM
BK 3-78-3 (C on 3-78-1), carbonOVNTE.all
USER: temple -- DATE: Mar 13 07:00:31 2014 EST (UT-5h) templ
F1: 100.613
F2: 1.000
SW1: 25126
OF1: 10037.2
PTS1d: 32768
EX: zgpg60
PW: 5.6 us
PD: 2.0 sec
NA: 14000
LB: 3.0
Nuts - $NMR 3784.1



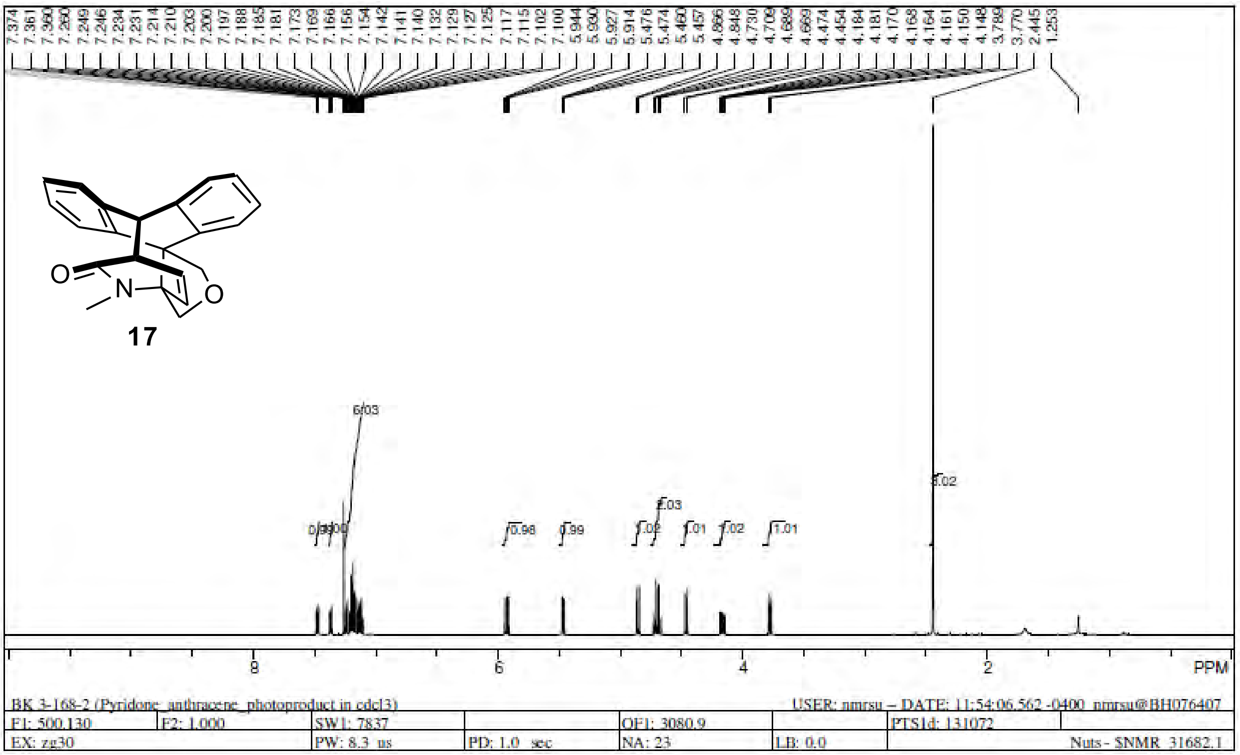
36

7.382
7.380
7.378
7.376
7.260
6.329
6.325
6.322
6.319
6.281
6.280
6.278
6.277
6.275
6.273
6.272
6.271
5.424
5.422
5.420
5.418
5.416
5.414
5.320
5.317
5.314
5.313
5.310
5.306
4.782
1.935
1.934
1.933
1.931
1.069
1.067
1.061
1.056
1.052
1.049
1.046
1.045
1.041
1.038
1.034
1.031
1.024
1.017
1.006
1.003
0.98
1.00
1.00
0.97
1.00
1.98
2.93
13.84
O
O
Si
8
6
4
2
0 PPM
BK 3-170-1 (Furan Enyne tethered)
USER: nmrsu – DATE: 15:16:17.875 -0400 nmrsu@BH076407
F1: 500.130
F2: 1.000
SW1: 7837
OF1: 3080.9
PTS1d: 131072
EX: zg30
PW: 8.3 us
PD: 1.0 sec
NA: 12
LB: 0.0
Nuts - $NMR 31701.1



36

154.210
142.227
126.719
123.642
110.293
108.978
107.729
87.099
77.413
77.160
76.900
59.275
23.419
17.229
17.113
13.241
O
O
Si
150
100
50
0 PPM
BK 3-170-2 (Furan Enyne tethered_Carbon), . . .
USER: nmrsu – DATE: 15:46:22.125 -0400 nmrsu@BH076407
F1: 125.758
F2: 1.000
SW1: 29762
OF1: 12591.3
PTS1d: 32768
EX: zgpg30
PW: 9.0 us
PD: 2.0 sec
NA: 525
LB: 1.0
Nuts - $NMR 31702.1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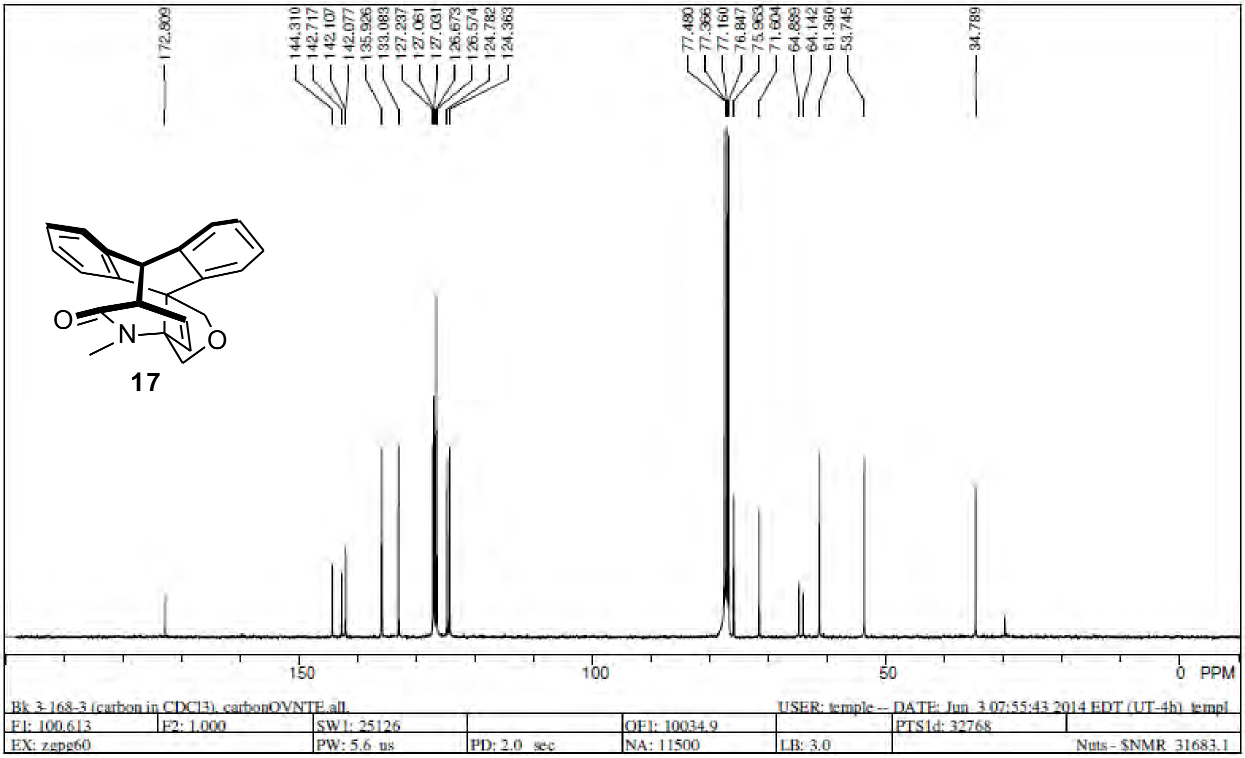
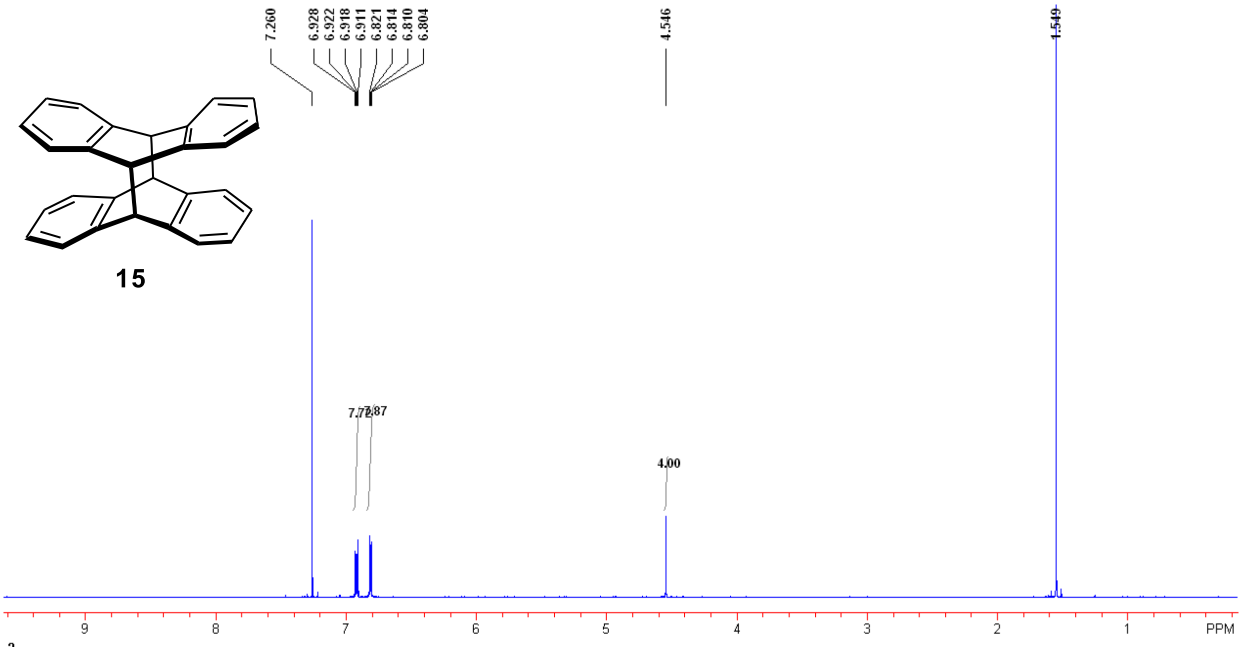
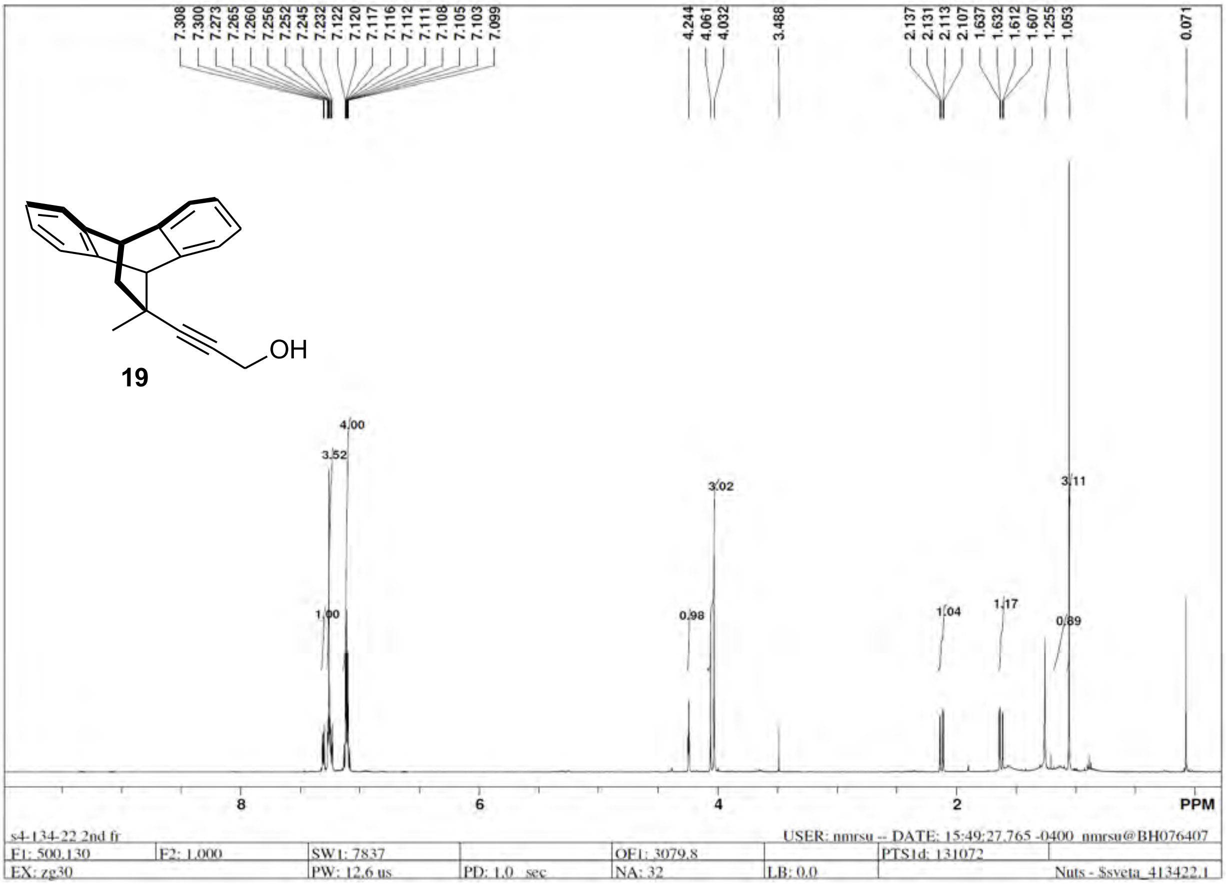
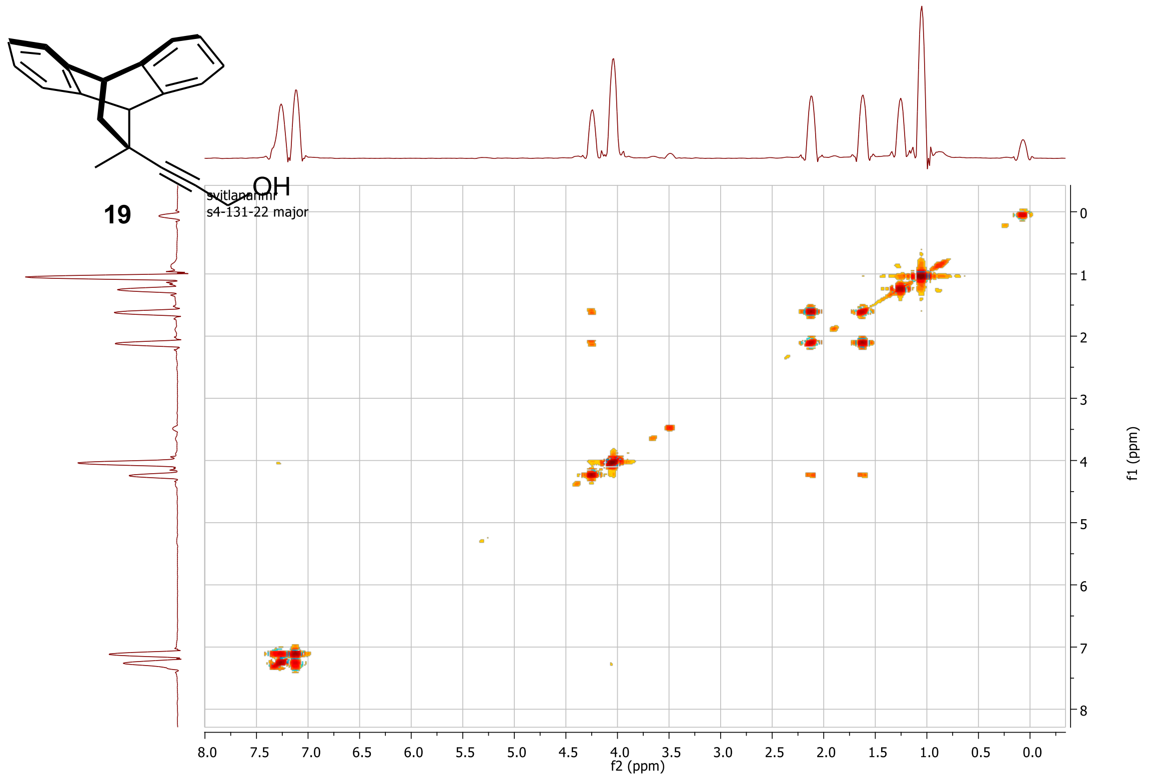
7.360
7.260
7.249
7.246
7.234
7.231
7.214
7.210
7.203
7.200
7.197
7.188
7.185
7.181
7.173
7.169
7.166
7.156
7.154
7.142
7.141
7.140
7.132
7.129
7.127
7.125
7.117
7.115
7.102
7.100
5.944
5.930
5.927
5.914
5.476
5.474
5.460
5.457
4.866
4.848
4.730
4.709
4.689
4.669
4.474
4.454
4.184
4.181
4.170
4.168
4.164
4.161
4.150
4.148
3.789
3.770
2.445
1.253
O
N
O
17
0.99
1.00
6.03
0.98
0.99
1.02
2.03
1.01
1.02
1.01
3.02
8
6
4
2
PPM
BK 3-168-2 (Pyridone_anthracene_photoproduct in cdcl3)
USER: nmrsu – DATE: 11:54:06.562 -0400 nmrsu@BH076407
F1: 500.130
F2: 1.000
SW1: 7837
OF1: 3080.9
PTS1d: 131072
EX: zg30
PW: 8.3 us
PD: 1.0 sec
NA: 23
LB: 0.0
Nuts - $NMR 31682.1

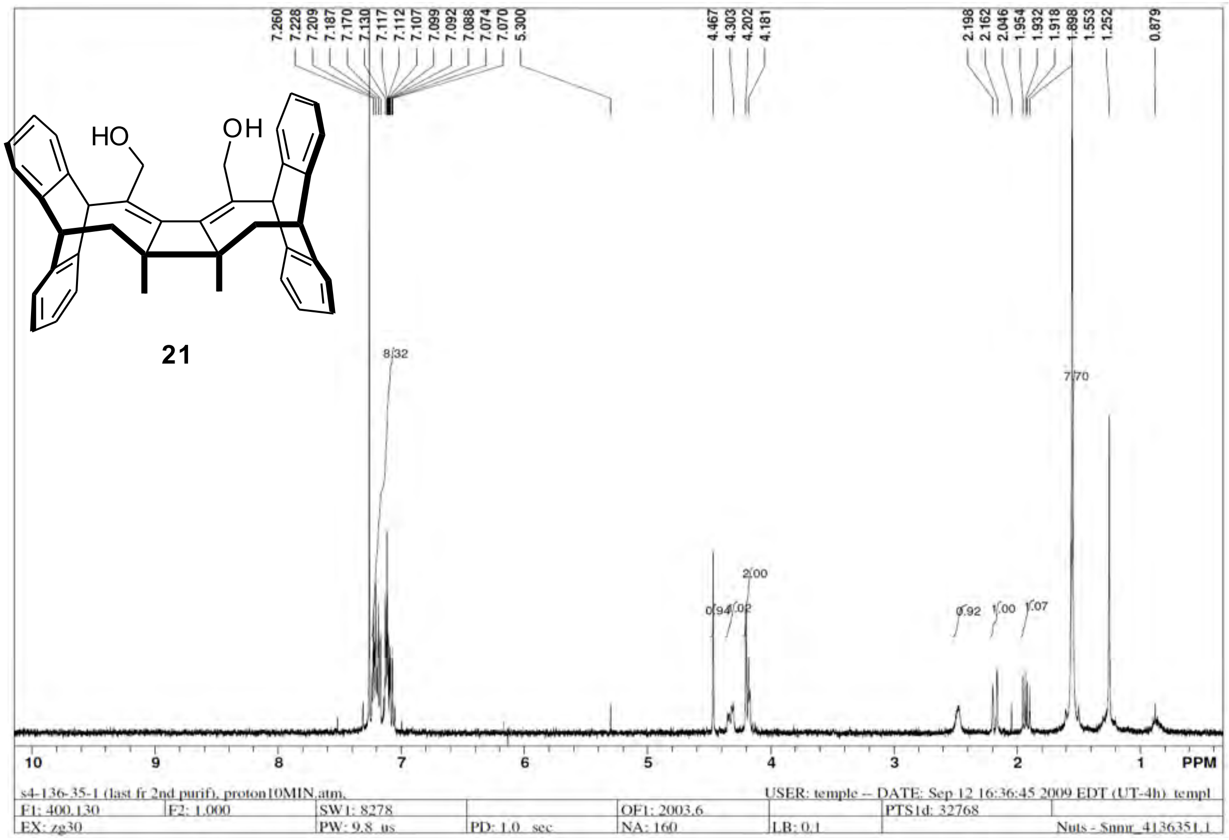

172.809
144.310
142.717
142.107
142.077
135.926
133.083
127.237
127.061
127.031
126.673
126.574
124.782
124.363
77.480
77.366
77.160
76.847
75.963
71.604
64.889
64.142
61.360
53.745
34.789
O
N
O
17
150
100
50
0 PPM
Bk 3-168-3 (carbon in CDCl3), carbonOVNTE.all.
USER: temple -- DATE: Jun 3 07:55:43 2014 EDT (UT-4h) templ
F1: 100.613
F2: 1.000
SW1: 25126
OF1: 10034.9
PTS1d: 32768
EX: zgpg60
PW: 5.6 us
PD: 2.0 sec
NA: 11500
LB: 3.0
Nuts - $NMR 31683.1


15
7.260
6.928
6.922
6.918
6.911
6.821
6.814
6.810
6.804
4.546
1.549
7.72
7.87
4.00
9
8
7
6
5
4
3
2
1
PPM

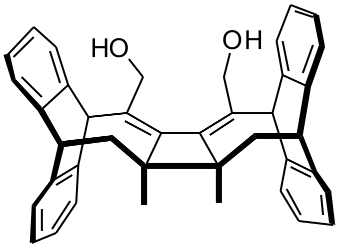

19
OH
7.308
7.300
7.273
7.265
7.260
7.256
7.252
7.245
7.232
7.122
7.120
7.117
7.116
7.112
7.111
7.108
7.105
7.103
7.099
4.244
4.061
4.032
3.488
2.137
2.131
2.113
2.107
1.637
1.632
1.612
1.607
1.255
1.053
0.071
1.00
3.52
4.00
0.98
3.02
1.04
1.17
0.89
3.11
8
6
4
2
PPM
s4-134-22 2nd fr
USER: nmrsu -- DATE: 15:49:27.765 -0400 nmrsu@BH076407
F1: 500.130
F2: 1.000
SW1: 7837
OF1: 3079.8
PTS1d: 131072
EX: zg30
PW: 12.6 us
PD: 1.0 sec
NA: 32
LB: 0.0
Nuts - $sveta_413422.1


OH
svitlananmr
s4-131-22 major
f2 (ppm)
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
0 1 2 3 4 5 6 7 8

19

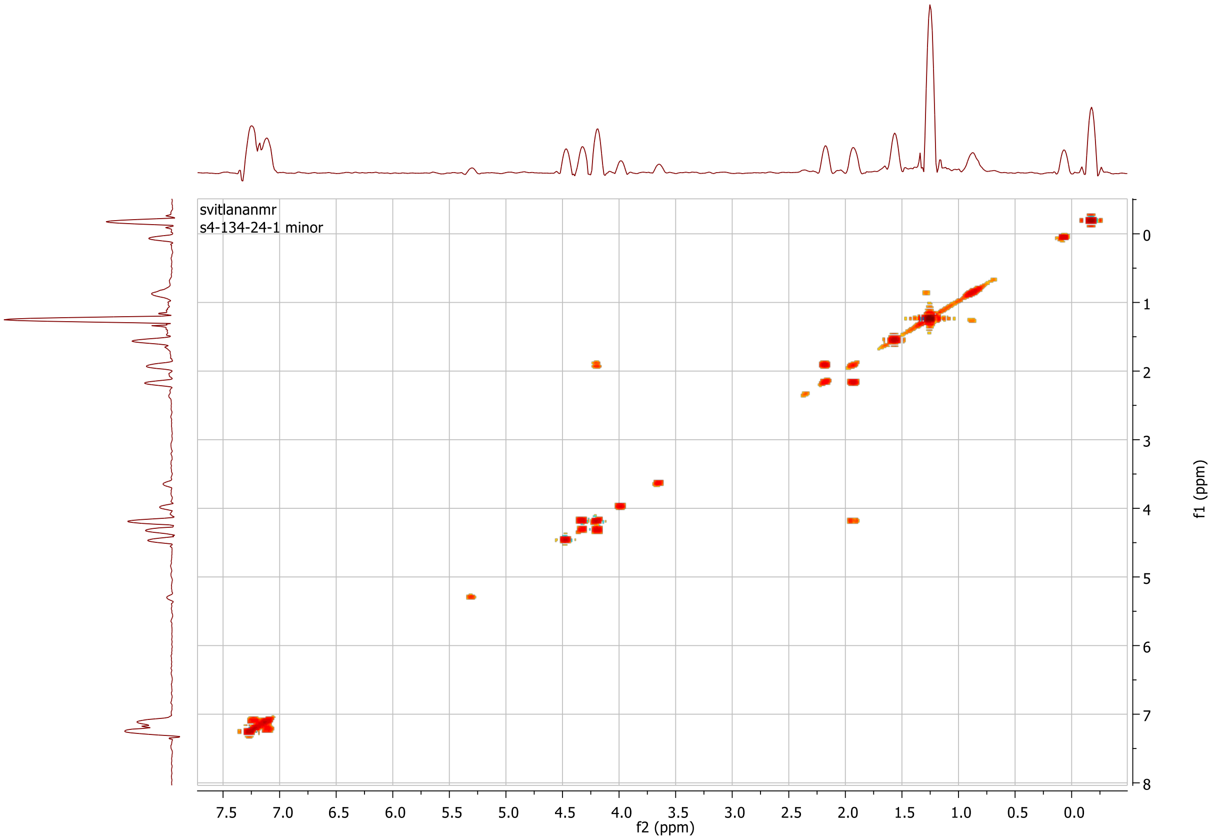

7.260 7.228 7.209 7.187 7.170 7.130 7.117 7.112 7.107 7.099 7.092 7.088 7.074 7.070 5.300
4.467 4.303 4.202 4.181
2.198 2.162 2.046 1.954 1.932 1.918 1.898 1.553 1.252 0.879
HO
OH
8.32
7.70
2.00
0.94
1.02
0.92
1.00
1.07
10 9 8 7 6 5 4 3 2 1 PPM
s4-136-35-1 (last fr 2nd purif), proton10MIN.atm.
USER: temple -- DATE: Sep 12 16:36:45 2009 EDT (UT-4h) templ
F1: 400.130
F2: 1.000
SW1: 8278
OF1: 2003.6
PTS1d: 32768
EX: zg30
PW: 9.8 us
PD: 1.0 sec
NA: 160
LB: 0.1
Nuts - $nmr_4136351.1

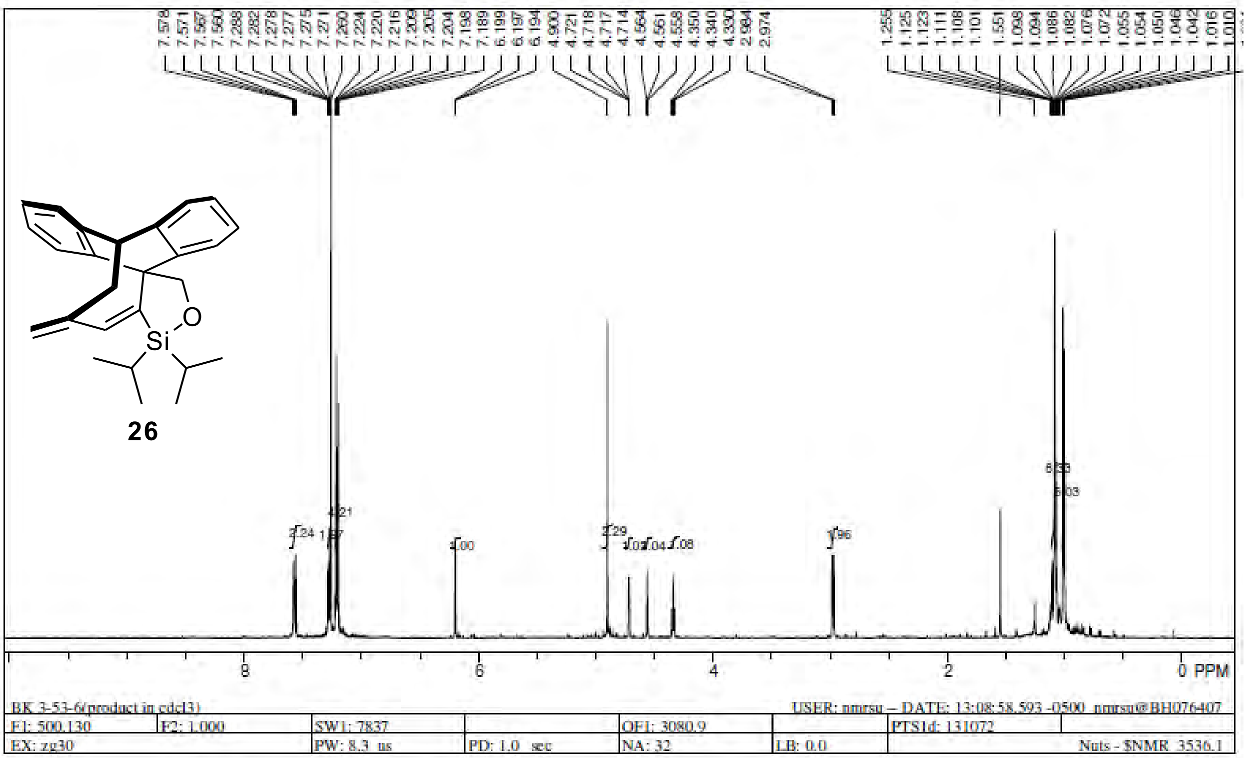
21

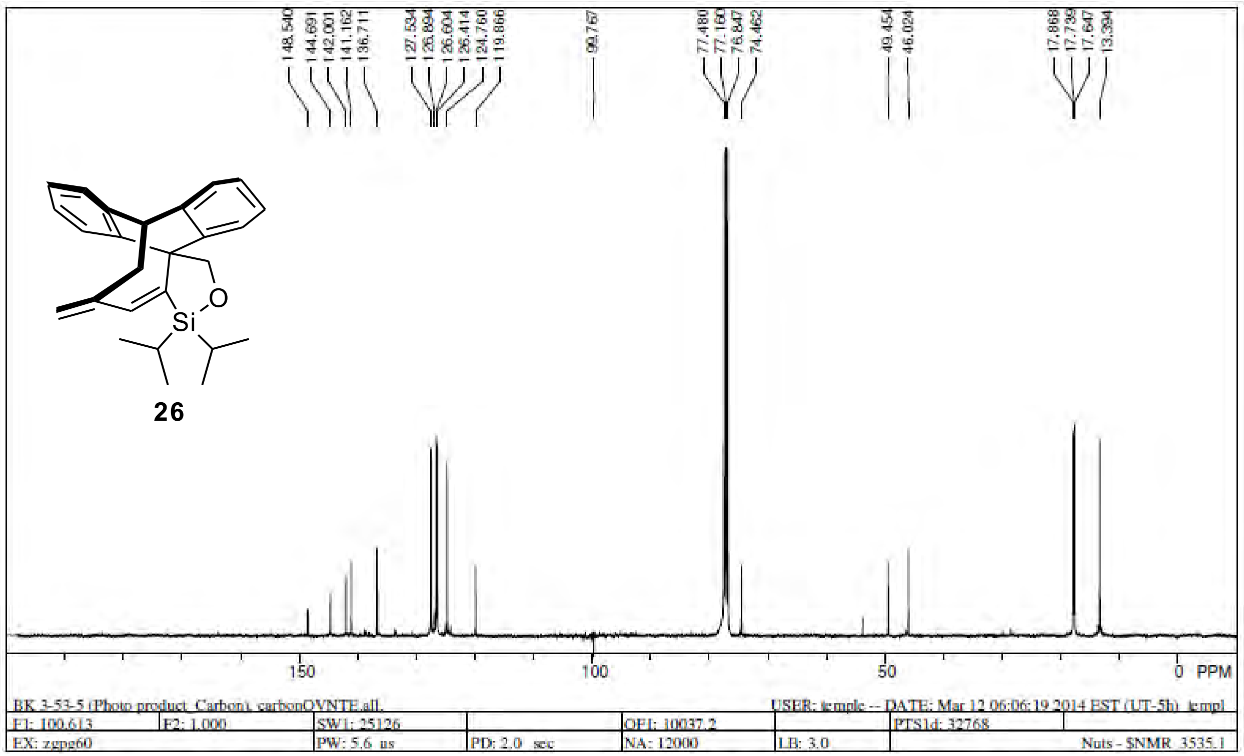


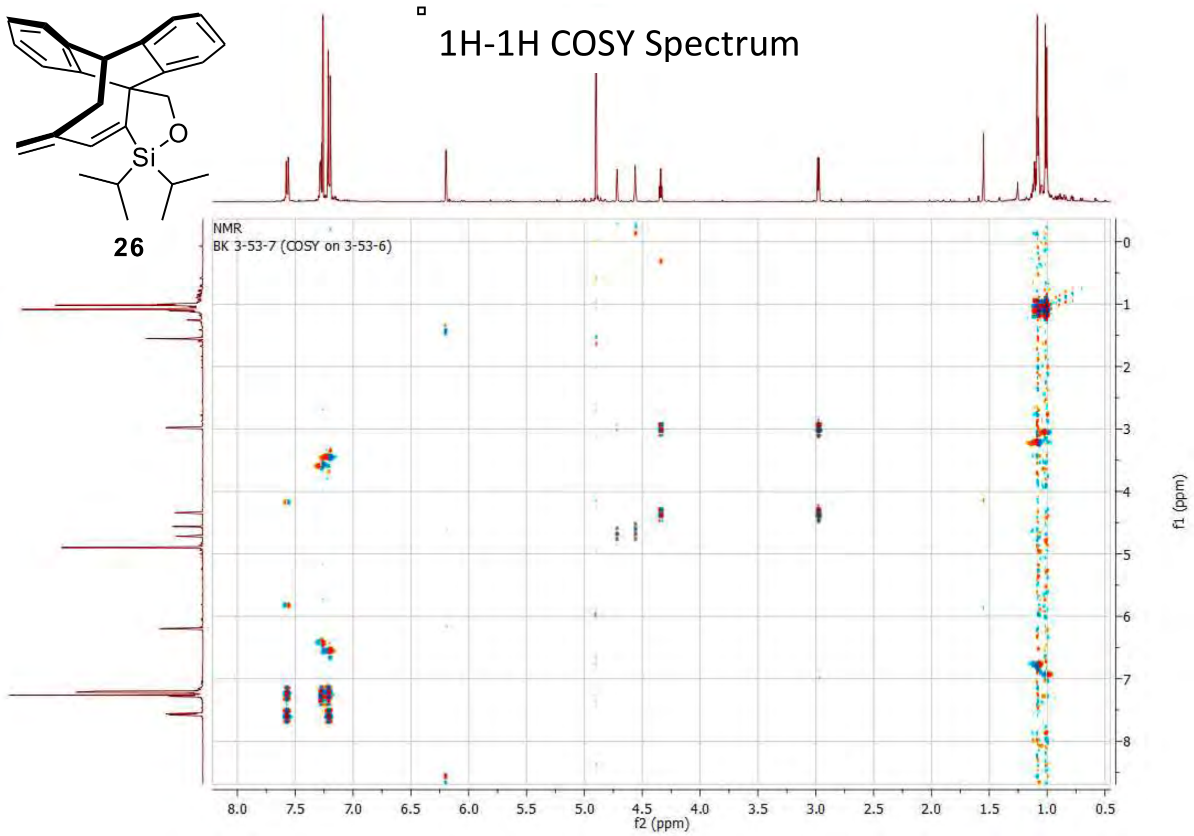
21

1H-1H COSY Spectrum

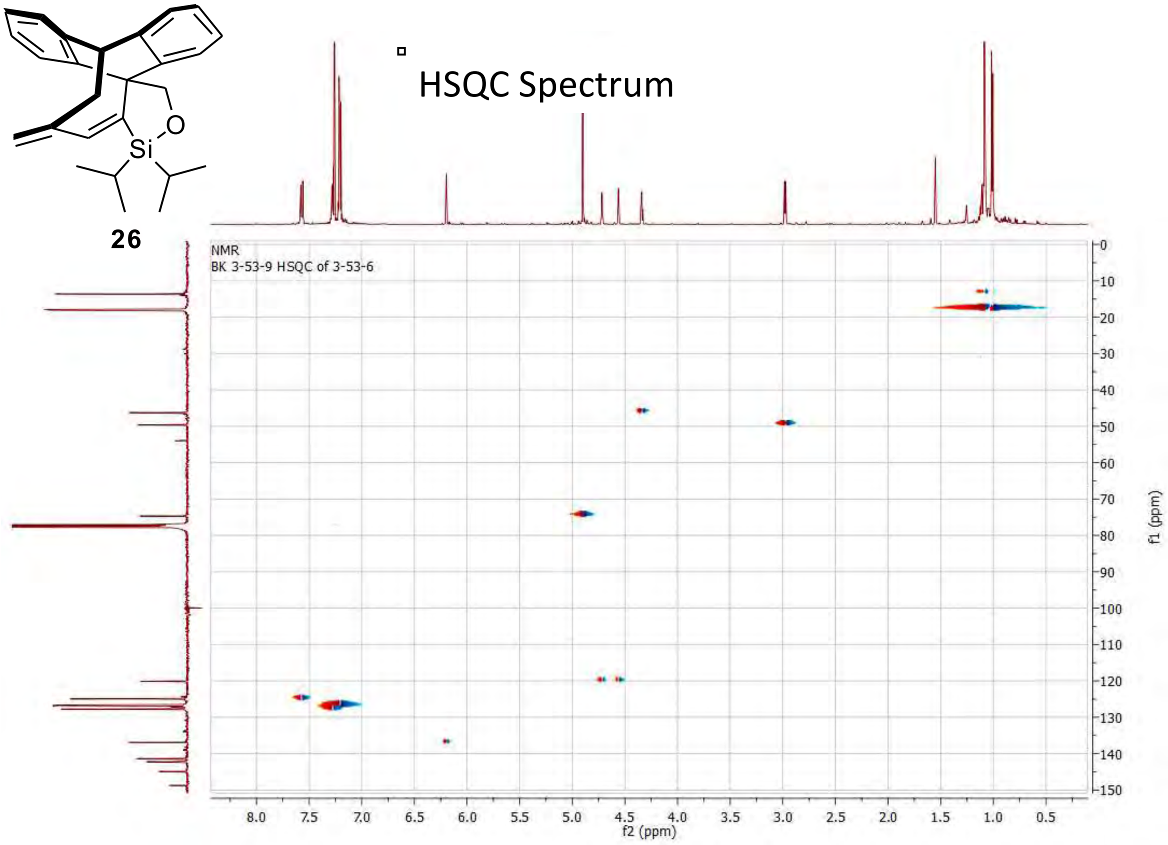



7.578
7.571
7.567
7.560
7.288
7.282
7.278
7.277
7.275
7.271
7.260
7.224
7.220
7.216
7.209
7.205
7.204
7.198
7.189
6.199
6.197
6.194
4.900
4.721
4.718
4.717
4.714
4.564
4.561
4.558
4.350
4.340
4.330
2.984
2.974
1.255
1.125
1.123
1.111
1.108
1.101
1.551
1.098
1.094
1.086
1.082
1.076
1.072
1.055
1.054
1.050
1.046
1.042
1.016
1.010
26
2.24
1.87
4.21
1.00
2.29
1.02
1.04
1.08
1.96
6.33
6.03
8
6
4
2
0 PPM
BK 3-53-6(product in cdcl3)
USER: nmrsu -- DATE: 13:08:58.593 -0500 nmrsu@BH076407
F1: 500.130
F2: 1.000
SW1: 7837
OF1: 3080.9
PTS1d: 131072
EX: zg30
PW: 8.3 us
PD: 1.0 sec
NA: 32
LB: 0.0
Nuts - $NMR 3536.1

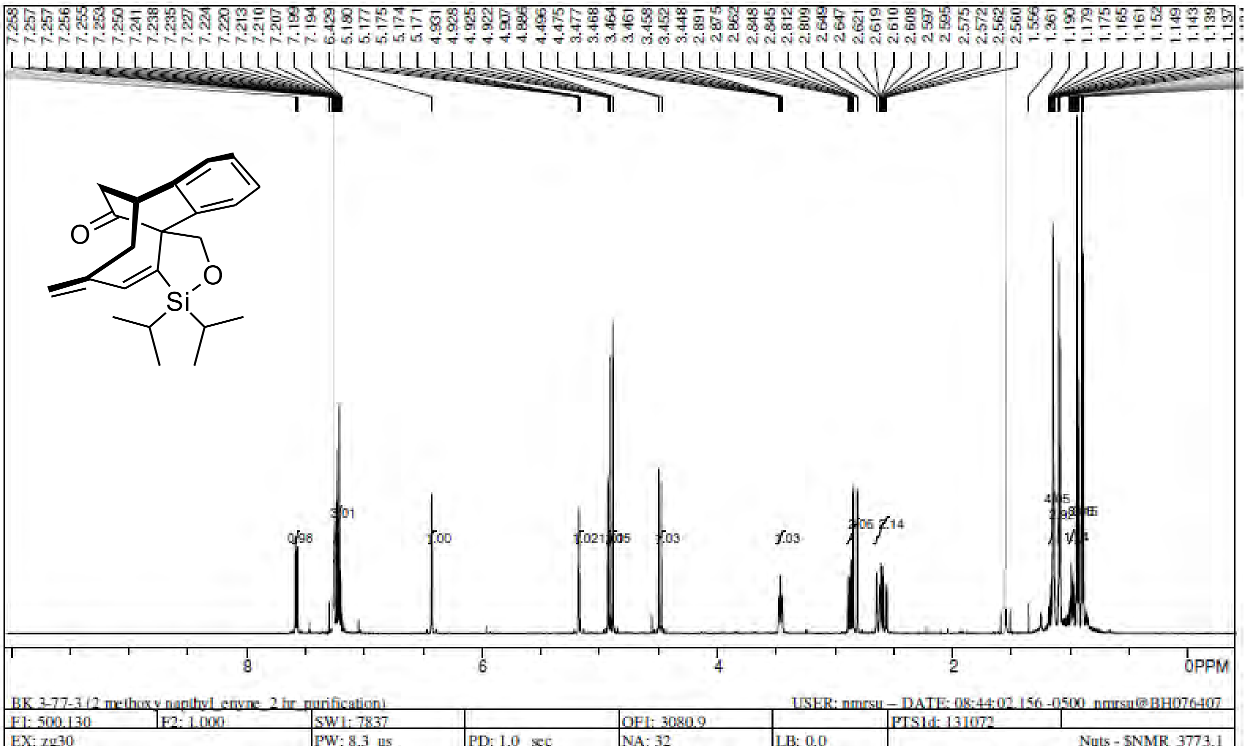

148.540
144.691
142.001
141.162
136.711
127.534
126.894
126.604
126.414
124.760
119.866
99.767
77.480
77.160
76.847
74.462
49.454
46.024
17.868
17.739
17.647
13.394
26
150
100
50
0 PPM
BK 3-53-5 (Photo product_Carbon), carbonOVNTE.all.
USER: temple -- DATE: Mar 12 06:06:19 2014 EST (UT-5h) templ
F1: 100.613
F2: 1.000
SW1: 25126
OF1: 10037.2
PTS1d: 32768
EX: zgpg60
PW: 5.6 us
PD: 2.0 sec
NA: 12000
LB: 3.0
Nuts - $NMR 3535.1

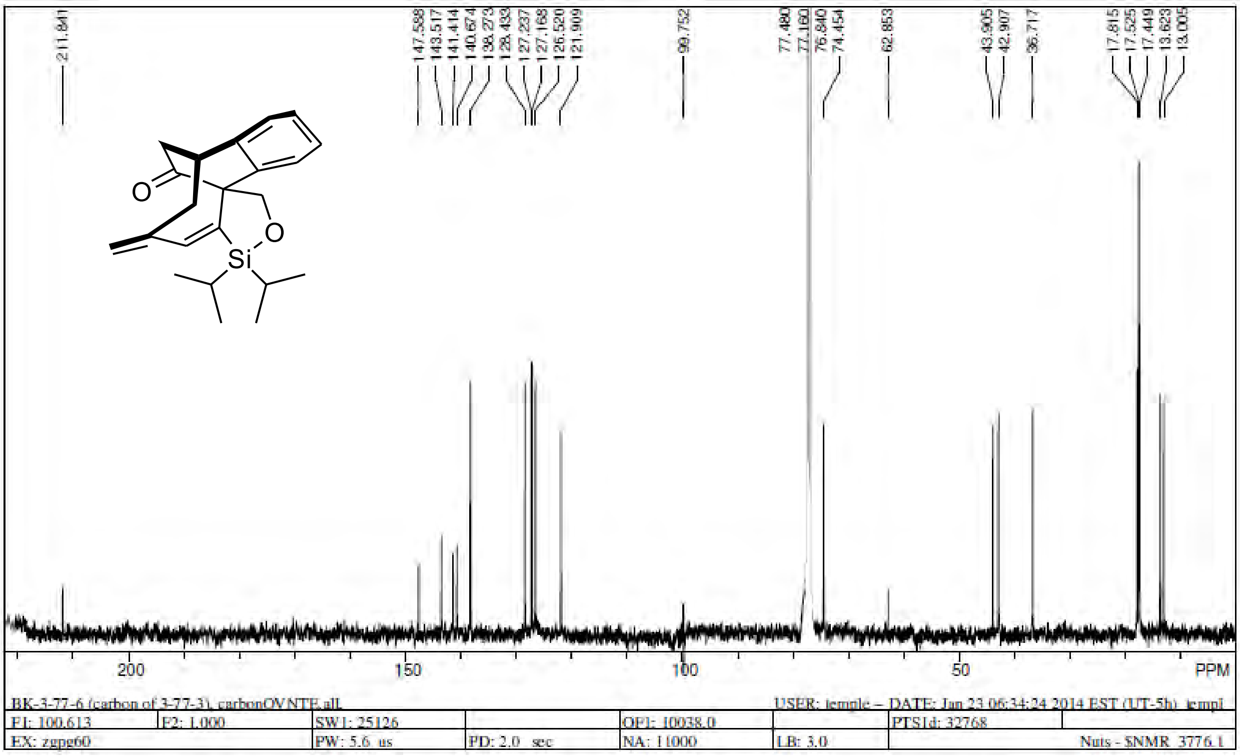

1H-1H COSY Spectrum

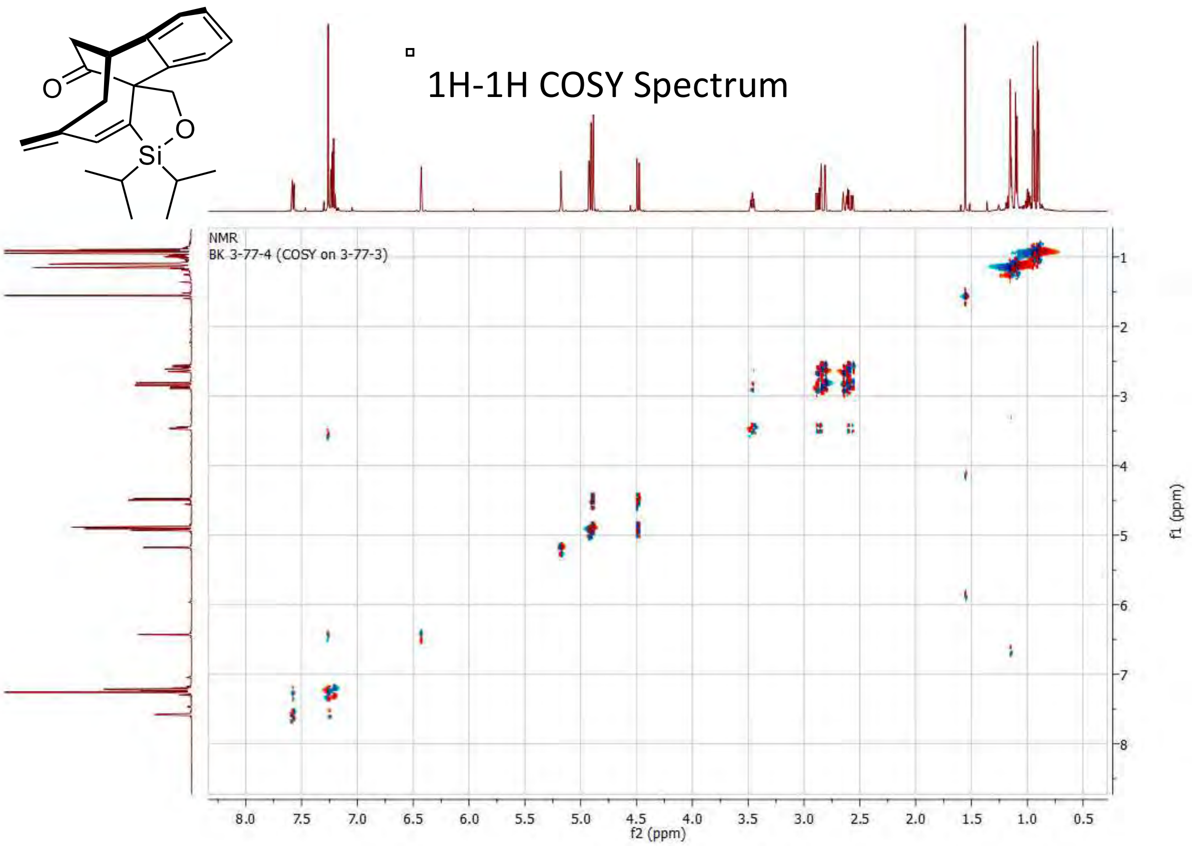
26


HSQC Spectrum

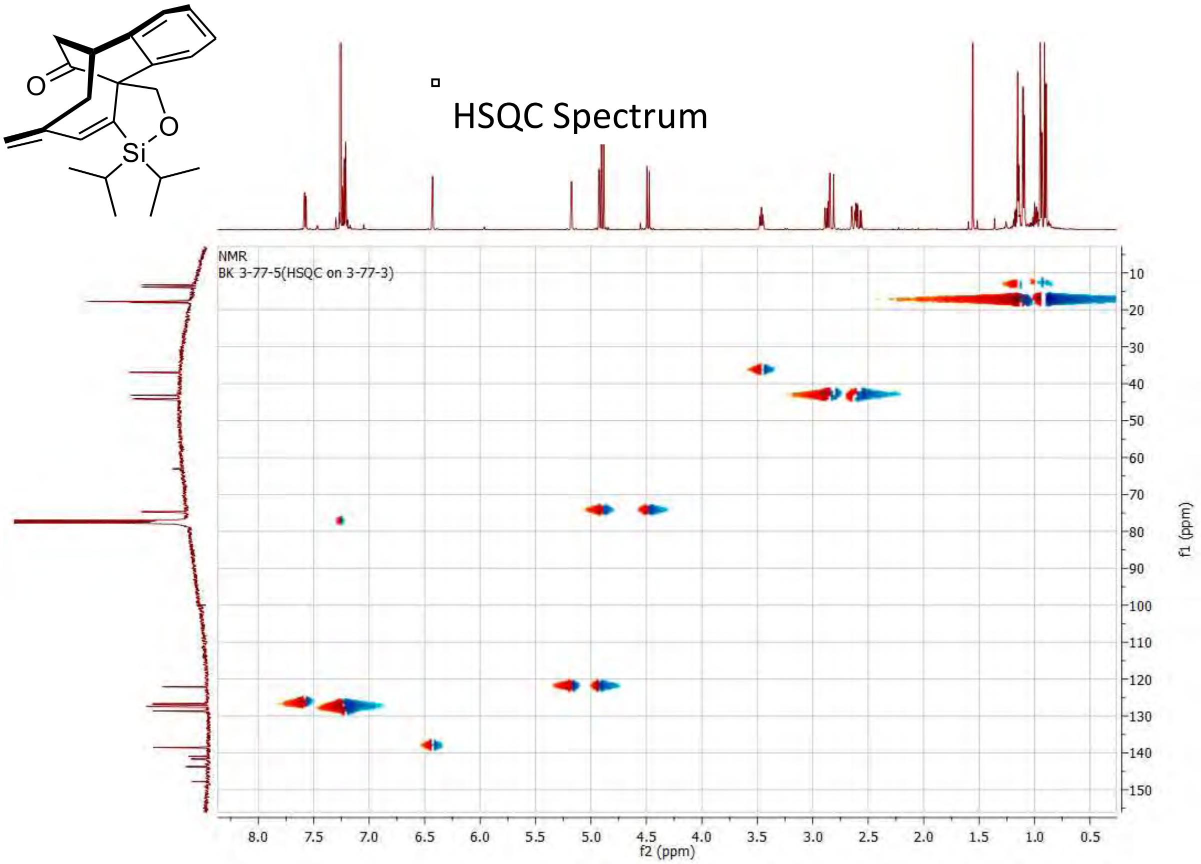
26


7.258
7.257
7.257
7.256
7.255
7.253
7.250
7.241
7.238
7.235
7.227
7.224
7.220
7.213
7.210
7.207
7.199
7.194
6.429
5.180
5.177
5.175
5.174
5.171
4.931
4.928
4.925
4.922
4.907
4.896
4.496
4.475
3.477
3.468
3.464
3.461
3.458
3.452
3.448
2.891
2.875
2.862
2.848
2.845
2.812
2.809
2.649
2.647
2.621
2.619
2.610
2.608
2.597
2.595
2.575
2.572
2.562
2.560
1.556
1.361
1.190
1.179
1.175
1.165
1.161
1.152
1.149
1.143
1.139
1.137
O
O
Si
0.98
3.01
1.00
1.02
1.05
1.03
1.03
2.06
2.14
4.05
2.98
5.96
1.04
8
6
4
2
0PPM
BK 3-77-3 (2 methoxy napthyl_enyne_2 hr_purification)
USER: nmrsu – DATE: 08:44:02.156 -0500 nmrsu@BH076407
F1: 500.130
F2: 1.000
SW1: 7837
OF1: 3080.9
PTS1d: 131072
EX: zg30
PW: 8.3 us
PD: 1.0 sec
NA: 32
LB: 0.0
Nuts - $NMR 3773.1


211.841
147.588
143.517
141.414
140.674
138.273
128.433
127.237
127.168
126.520
121.909
99.752
77.480
77.160
76.840
74.454
62.853
43.905
42.907
36.717
17.815
17.525
17.449
13.623
13.005
O
O
Si
200
150
100
50
PPM
BK-3-77-6 (carbon of 3-77-3), carbonOVNTE.all
USER: temple – DATE: Jan 23 06:34:24 2014 EST (UT-5h) templ
F1: 100.613
F2: 1.000
SW1: 25126
OF1: 10038.0
PTS1d: 32768
EX: zgpg60
PW: 5.6 us
PD: 2.0 sec
NA: 11000
LB: 3.0
Nuts - $NMR 3776.1



1H-1H COSY Spectrum



HSQC Spectrum