Supporting Information

I. General Information

Reagents

All compounds were used as received unless otherwise noted.

Metals: *All metal catalysts and metal reductants, unless otherwise noted, were stored and handled in a nitrogen-filled glovebox.* Nickel(II) bromide 2-methoxyethyl ether ($NiBr_2$•diglyme) was purchased from Strem and used as received. Other sources explored for the optimization and stoichiometric experiments of the nickel precursor were $NiCl_2$• diglyme (Strem) and $Ni(cod)_2$ (Strem Chemicals). The reductants used were zinc flake, -325 mesh, 97% (Alfa Aesar) and manganese powder -325 mesh (Alfa Aesar). Silver nitrate, used for bromoalkyne synthesis, was purchased from Alfa Aesar.

Ligand: The ligand used for the nickel catalyst, 4-4'-di-*tert*-butyl-2,2'-bipyridine (dtbbpy), was purchased from Sigma Aldrich.

Additives: Lithium bromide (99.5%) was purchased from Acros. Other additives tested were lithium chloride (anhydrous, 99%) (Alfa Aesar), potassium fluoride (anhydrous, 98%) (Aldrich), potassium bromide (Acros), and sodium iodide (Stem).

Solvents: The solvent *N*-methyl-2-pyrrolidone (NMP, anhydrous, 99.5%) was purchased from Sigma Aldrich. Commercial low-amine *N,N*-dimethylformamide (DMF) was degassed with argon, purified by passage through a commercial solvent drying column (PPT), and stored under nitroen before use. The water content of solvents was routinely measured with a Metrohm Karl-Fischer apparatus and were less than 40 ppm in all cases. Solvents used for kinetic studies were further degassed by 3-6 freeze-pump-thaw cycles.

Bromoalkynes: Bromoalkynes were prepared according the reported procedures from terminal alkynes.[1,2,3] 1-Octyne (Alfa Aesar), phenylacetylene (Aldrich), 1-ethynylcyclohexene (Aldrich), N-(4-pentynyl)phthalimide (Fisher Scientific), 5-hexynenitrile (Fisher Scientific), *N*-bromosuccinimide (NBS) was purchased from Alfa Aesar.

Other Reagents*:* Dodecane (Aldrich), *N*-(*tert*-butoxycarbonyl)proline (Alfa Aesar), N,N'-dicyclohexylcarbodiimide (Alfa Aesar), *N*,*N*'-diisopropylcarbodiimide (Chem-Impex), *N*-hydroxyphthalimide (Alfa Aesar), DMAP (Alfa Aesar), 4-phenylbutyric acid (Aldrich), 3,3-dimethylbutyric acid (Alfa Aesar), cyclopentane carboxylic acid (Combi-Blocks), Boc-AspO*t*Bu (Combi-Blocks), Boc-Glu-O*t*Bu (Combi-Blocks), N-Boc-Pro-OH (Alfa Aesar), 4-acetylbutyric acid (Combi-Blocks), 5-oxoheptanoic acid (Aldrich), 4-oxoheptanoic acid (Alfa Aesar), 5-bromopentanoic acid (Alfa Aesar), adipic acid monoethyl ester (Aldrich), γ-Aminobutyric acid (Aldirch), piperidine-3-

[1] Wang. Y., Chen. C., Zhang, S., Lou, Z., Su, X., Wen, L., Li, M., *Org. Lett.*, **2013**, *15*, 4794-4797.
[2] Cherney, A. H., Reisman, S. E., *J. Am. Chem., Soc*., **2014**, *136*, 14365-14368.
[3] Jiménez-Núñez, E., Claverie, C. K., Bour, C., Cárdenas, D. J., Echavarren, A. M., *Angew. Chem. Int. Ed.*, **2008**, *47*, 7892-7895.

carboxylic acid (Comb-Blocks), linolenic acid (Aldrich), and tetrahydrofuran-3-carboxylic acid (Comb-Blocks) were used as received.

NMR Spectroscopy

^{1}H nuclear magnetic resonance (NMR) spectroscopy chemical shifts are reported in ppm and referenced to TMS (tetramethylsilane) in $CDCl_3$ (δ = 0 ppm) or the residual solvent peak for $CDCl_3$ (δ = 7.26 ppm). For ^{13}C NMR and ^{19}F NMR chemical shifts, the residual solvent peak ($CDCl_3$, δ = 77.00 ppm) and the external standard, α,α,α-trifluorotoluene (δ = 0 ppm) were used as references. NMR spectra were recorded on Avance Bruker NMR spectrometers operating at either 400.13 MHz or 500.13 MHz and data analysis was performed using the iNMR software package (www.inmr.net). Chemical shifts are reported in parts per million (ppm), multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). Coupling constants (J) are reported in Hertz.

Gas Chromatography

GC analyses were performed on an Agilent 7890A GC equipped with dual DB-5 columns (20 m × 180 μm × 0.18 μm), dual FID detectors, and hydrogen as the carrier gas. A sample volume of 1 μL was injected at a temperature of 300 °C and a 100:1 split ratio. The initial inlet pressure was 20.3 psi but varied as the column flow was held constant at 1.8 mL/min for the duration of the run. The initial oven temperature of 50 °C was held for 0.46 min followed by a temperature ramp of 65 °C/min up to 300 °C. The temperature was held at 300 °C for 3 min. The total run time was ~7.3 min and the FID temperature was 325 °C.

GC/MS Analysis

GC/MS analyses were performed on a Shimadzu GCMS-QP2010 equipped with an RTX-XLB column (30 m × 0.25 mm × 0.28 μm) with a quadrupole mass analyzer using helium as the carrier gas. The analysis method used in all cases was 5 μL injection of sample, an injection temp of 225 ºC, and a 25:1 split ratio. The initial inlet pressure was 7.8 psi, but varied as the column flow was held constant at 1.0 mL/min for the duration of the run. The interface temperature was held at 250 ºC, and the ion source (EI+, 30 eV) was held at 250 ºC. The initial oven temperature was held at 50 ºC for 2 min with the detector off, followed by a temperature ramp, with the detector on, to 280 ºC at 40 º C/min. The temperature was held at 280 ºC for 3 min. Total run time was 11.75 min.

High Resolution Mass Spectrometry

High resolution mass spectra (HRMS) under electron impact (EI+) or electrospray (ESI+) ionization methods were obtained from Mass Spectrometry Laboratory at University of Illinois at Urbana-Champaign. The 70-VSE mass spectrometer (EI+ HRMS) was purchased in part with a grant from the Division of Research Resources, National Institutes of Health (RR 04648). The Q-TOF Ultima (ESI HRMS) mass spectrometer was purchased in part with a grant from the National Science Foundation, Division of Biological Infrastructure (DBI-0100085).

Low Resolution Mass Spectrometry (LRMS) Analysis

LRMS analyses were performed on a Shimadzu LCMS-2010A equipped with an ESI or ACPI probe with a quadrupole mass analyzer. Direct injection analysis was employed in all cases with 5 μL of sample solution in methanol. The ion source (electron spray ionization, ESI) was held at 250 ºC or 400 °C when atmospheric-pressure chemical ionization (APCI) was used. And the sample flow rate was 1 mL/min.

Infrared Spectroscopy

Infrared (IR) spectra were recorded on a Shimadzu IRAffinity-1 Fourier Transform Infrared Spectrophotometer and are reported in wavenumbers (cm^{-1}).

UV-Vis Spectroscopy

UV-Vis spectra (300-900 nm) and kinetic data were recorded on a HP 8452A spectrometer coupled to an HP Hewlett Packard 89090A for temperature control. Samples were prepared in a glove box under argon atmosphere using glass, screw-cap cuvettes to exclude oxygen.

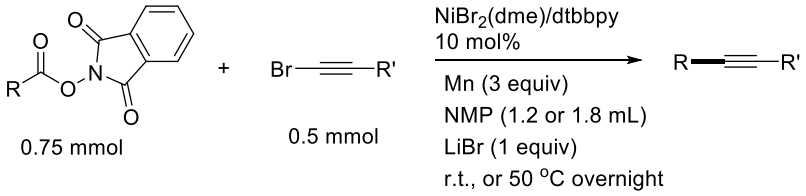
Thin Layer / Column Chromatography

Thin layer chromatography was performed on EMD Chemicals TLC Silica Gel 60 F254 plates. Visualization was accomplished with potassium permanganate after inspection under UV light. Flash chromatography was performed using EMD silica gel 60, particle size 0.040-0.063 mm using standard flash techniques.

II. General Procedures

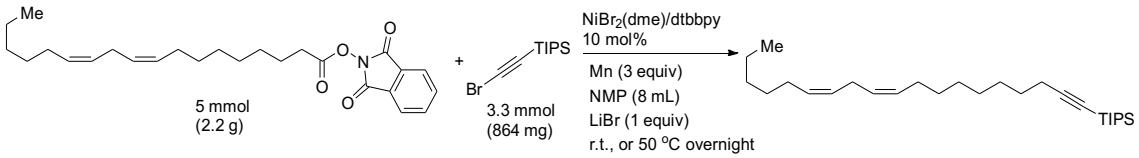
Decarboxylative coupling of NHP esters with bromoalkynes

Reaction setup for 0.5 mmol scale in nitrogen-filled glove box



To an oven-dried 1-dram vial fitted with a Teflon-coated stir-bar was added $NiBr_2$(diglyme) (16.0 mg, 0.05 mmol, 0.1 equiv), 4-4′ -di-*tert*-butyl-2,2′ -bipyridine (13.4 mg, 0.05 mmol, 0.1 equiv), LiBr (43 mg, 0.5 mmol, 1 equiv), NHP ester (0.75 mmol, 1.5 equiv), manganese (82 mg, 1.5 equiv, 3.0 equiv), dodecane (internal standard, 20-40 mg), NMP (1.2 or 1.8 mL) and bromoalkyne (0.5 mmol, 1.0 equiv). The vial was closed with a screw cap fitted with a PTFE-faced silicone septum, removed from the glove box, and heated in a reaction block (r.t. or 50 °C) on the benchtop with stirring at 1195 rpm for 12–14 h ("overnight").

Reaction setup for preparative scale on bench top



To a 25 mL round-bottom flask containing a Teflon-coated stir-bar was added $NiBr_2$(diglyme) (106 mg, 0.33 mmol, 0.1 equiv), 4-4′ -di-*tert*-butyl-2,2′ -bipyridine (88.5 mg, 0.33 mmol, 0.1 equiv). The reaction flask was sealed with a rubber septum, and the septum was fitted with a needle connected to an oil bubbler and a needle connected to an Ar manifold. The headspace of the flask was purged with Ar gas for about ten minutes and then the needle to the bubbler was removed. NMP (8 mL), was added via syringe and the resulting mixture was stirred on the benchtop (~1200 rpm) at rt under Ar. The color of the reaction mixture became blue-green. 1,3-dioxoisoindolin-2-yl (10Z,13Z)-nonadeca-10,13-dienoate (2200 mg, 5 mmol, 1.5 equiv), (bromoethynyl)triisopropylsilane (864 mg, 3.3 mmol, 1 equiv), LiBr (284 mg, 3.3 mmol, 1 equiv), and manganese (541 mg, 9.9 mmol, 3.0 equiv) were added in one portion to the reaction vessel by quickly removing the septum and replacing it. The reaction mixture was stirred at room temperature under Ar for 14 h.

GC-Analysis.

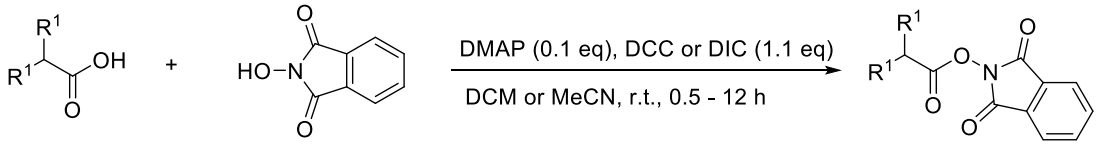
The reaction was vented to an oil bubbler before removing a 25 μL aliquot of the reaction mixture with a 50 μL gas-tight syringe. The aliquot was diluted with diethyl ether (1.5 mL) and filtered through a

short silica pad (1.5 cm) in a pipette packed with glass wool. The filtrate was analyzed by gas chromatography and percent yield was calculated versus dodecane as the internal standard.

Isolation and Purification

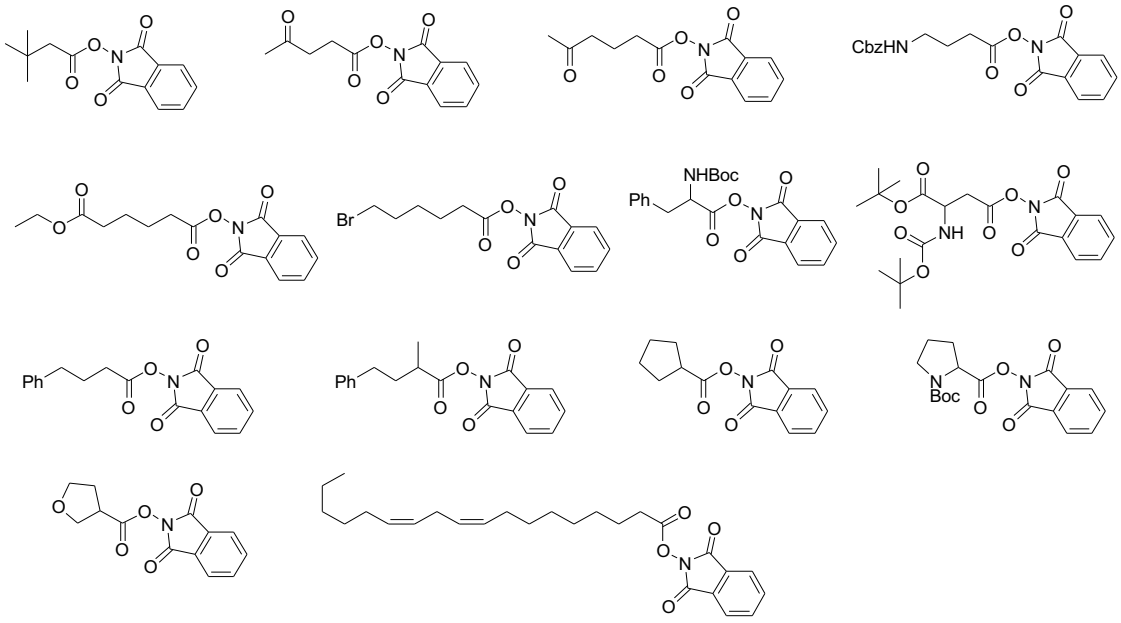
When the reaction was judged complete, the reaction mixture was filtered through a short plug of silica gel (1.5 cm wide × 2 cm high) to remove metal salts and the pad was washed with diethyl ether (50-75 mL). No aqueous work-up is needed. The filtrate was concentrated under reduced pressure. The resulting residue was purified by column chromatography on silica gel to afford the pure product.

III. Synthesis of *N*-Hydroxyphthalimide esters (NHP esters)



NHP esters were prepared according to the previously reported procedures.[4] In short, a round-bottom flask or culture tube was charged with (if solid) carboxylic acid (1.0 equiv), *N*-hydroxyphthalimide, 1.0 – 1.1 equiv.) and DMAP (0.1 equiv). Dichloromethane was added (0.1 – 0.2 M), and the mixture was stirred vigorously. Carboxylic acid (1.0 equiv) was added via syringe (if liquid). DCC (1.1 equiv) was then added and the mixture allowed to stir until the acid was consumed (determined by TLC). Typical reaction times were between 0.5 h and 12 h. The mixture was cooled down in a freezer (– 20 ^{o}C) for 2 to 12 h and then filtered through filter paper and rinsed with additional cold Et_2O. The solvent was removed from the filtrate under reduced pressure, and purification of the resulting residue by column chromatography afforded the desired NHP ester.

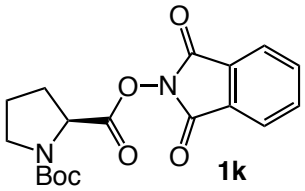
We and others have previously reported the synthesis of redox-active esters shown below. Please see ref. 1-4 for graphical supporting information on the synthesis of NHP esters.[5]



[4] a) Pratsch, G.; Lackner, G. L.; Overman, L. E. *J. Org. Chem.* **2015**, *80*, 6025–6036; Saljoughian, M.; Morimoto, H.; b) Williams, P. G.; Than, C.; Seligman, S. *J. J. Org. Chem.* **1996**, *61*, 9625–9628.

[5] a) Huihui, K. M. M., Caputo, J. A., Melchor, Z., Olivares, A. M., Spiewak, A. M., Jonhson, K. A., DiBenedetto, T. A., Kim, S., Ackerman, L., K. G., Weix, D. J., *J. Am. Chem. Soc.* **2016**, *138*, 5016; b) Cornella, J., Edwards, J. T., Qin, T., Kawamura, S., Wang, J., Pan, C.-M., Gianatassio, R., Schmidt, R., Eastgate, M. D., Baran, P. S., *J. Am. Chem. Soc.* **2016**, *138*, 2174.

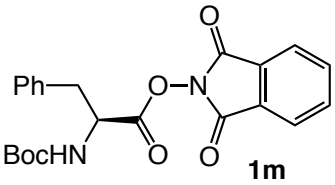
1-(*tert*-butyl) 2-(1,3-dioxoisoindolin-2-yl) (*S*)-pyrrolidine-1,2-dicarboxylate (1k)



1k

Following a modified literature procedure,[6] a round bottom flask containing a teflon-coated magnetic stir bar was charged with (*tert*-butoxycarbonyl)-*L*-proline (5.0 g, 23.2 mmol, 1.0 equiv) and reagent grade acetonitrile (50 mL). To this solution was sequentially added dicyclohexylcarbodiimide (4.8 g, 23.2 mmol, 1.0 equiv), N-hydroxyphthalimide (3.8 g, 23.2 mmol, 1.0 equiv), and dimethylaminopyridine (280 mg, 2.3 mmol, 0.1 equiv) at room temperature. The flask was capped with a septa pierced with a needle to prevent pressure buildup and allowed to stir at room temperature (~22 °C) for 18 h. The solution was filtered to remove insoluble cyclohexylurea byproducts and the filtrate concentrated under reduced pressure to an off-white slurry. The product was purified by silica gel chromatography (10:1 hexanes/EtOAc) and the solvent removed by rotary evaporation to provide a white powder. This powder was further purified by recrystallization from EtOAc and pentane to yield **1k** (5.2 g, 14.1 mmol, 62%) as white crystalline needles. NMR spectroscopy matched reported literature data.[1]

1,3-dioxoisoindolin-2-yl (*tert*-butoxycarbonyl)-*L*-phenylalaninate (1m)

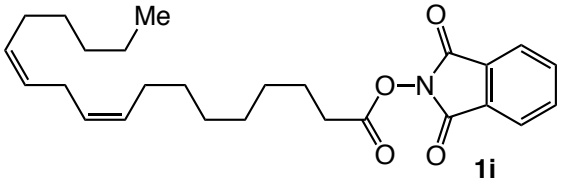


1m

Following a modified literature procedure,[6] a round bottom flask containing a teflon-coated magnetic stir bar was charged with (*tert*-butoxycarbonyl)-*L*-phenylalanine (4.0 g, 15.1 mmol, 1.0 equiv) and reagent grade acetonitrile (30 mL). To this solution was sequentially added dicyclohexylcarbodiimide (3.1 g, 15.1 mmol, 1.0 equiv), N-hydroxyphthalimide (2.5 g, 15.1 mmol, 1.0 equiv), and dimethylaminopyridine (180 mg, 1.5 mmol, 0.1 equiv) at room temperature. The flask was capped with a septa pierced with a needle to prevent pressure buildup and allowed to stir at room temperature (~22 °C) for 18 h. The solution was filtered to remove insoluble cyclohexylurea byproducts and the filtrate concentrated under reduced pressure. The resulting slurry was purified by silica gel chromatography (10:1 to 5:1 hexanes/EtOAc) and the solvent removed by rotary evaporation to provide a light yellow semi-solid. This semi-solid was dried overnight under vacuum to provide **1m** (4.9 g, 11.9 mmol, 79%) as a yellow, gooey solid. NMR spectroscopy matched reported literature data.[2] ^{1}H-NMR (400 MHz; $CDCl_3$): δ (rotamers are present for peaks near the tertiary amide) 7.96-7.90 (m, 2H), 7.86-7.81 (m, 2H), 7.39-7.30 (m, 5H), 5.05-4.95 (m, 1H), 3.40-3.35 (m, 1H), 3.30-3.28 (m, 1H), 1.44-1.40 (m, 9H).

[6] Schwarz, J.; König, B. *Green Chem.* **2016**, *18*, 4743.

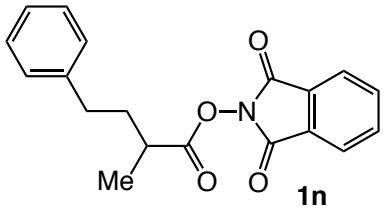
1,3-dioxoisoindolin-2-yl (9*Z*,12*Z*)-octadeca-9,12-dienoate (1i)



1i

Following a modified literature procedure,[6] a round bottom flask containing a teflon-coated magnetic stir bar was charged with (9*Z*,12*Z*)-octadeca-9,12-dienoic acid (5.0 g, 17.8 mmol, 1.0 equiv) and reagent grade acetonitrile (30 mL). To this solution was sequentially added dicyclohexylcarbodiimide (3.7 g, 17.8 mmol, 1.0 equiv), N-hydroxyphthalimide (2.9 g, 17.8 mmol, 1.0 equiv), and dimethylaminopyridine (220 mg, 1.8 mmol, 0.1 equiv) at room temperature. The flask was capped with a septa pierced with a needle to prevent pressure buildup and allowed to stir at room temperature (~22 °C) for 18 h. The solution was filtered to remove insoluble cyclohexylurea byproducts and the filtrate concentrated under reduced pressure to a yellow oil. The product was purified by silica gel chromatography (20:1 hexanes/EtOAc) and the solvent removed by rotary evaporation. The resulting oil was dried overnight under vacuum to provide **1i** (6.3 g, 14.8 mmol, 83%) as a slightly yellow oil. NMR spectroscopy matched reported literature data.[2] ^{1}H-NMR (400 MHz; $CDCl_3$): δ 7.9 (td, *J* = 4.4, 3.4 Hz, 2H), 7.83-7.80 (m, 2H), 5.44-5.32 (m, 4H), 2.80 (t, *J* = 6.2 Hz, 2H), 2.72-2.67 (m, 2H), 2.09-2.05 (m, 4H), 1.84-1.80 (m, 2H), 1.52-1.26 (m, 14H), 0.91 (t, *J* = 5.9 Hz, 3H).

1,3-dioxoisoindolin-2-yl 2-methyl-4-phenylbutanoate (1n)



1n

Following a literature procedure,[7] a round bottom flask containing a teflon-coated magnetic stir bar in a glove box was charged with solid lithium diisopropylamide (8.2 g, 76.3 mmol, 2.5 equiv) and sealed with a septa. After being removed from the glove box, the septa was pierced with an inlet nitrogen needle and dry tetrahydrofuran (120 mL) was added via syringe. The reaction was cooled to -20 °C and methyl iodide (4.2 mL, 67.1 mmol, 2.2 equiv) was added. The reaction was allowed to stir for 30 minutes at -20 °C before being allowed to warm to room temperature for 4 h. The solution was acidified to a pH of 1 with 2M HCl and extracted three times with EtOAc before being dried with Na_2SO_4, filtered, and concentrated to a yellow oil. The oil was purified by column chromatography (4:1 hexanes/EtOAc to provide 2-methyl-4-phenylbutanoic acid (1.5 g, 8.4 mmol, 28%), which matched reported NMR spectra and was used without further purification.[8] ^{1}H-NMR (400 MHz; $CDCl_3$): 7.35-7.31 (m, 2H), 7.24-7.20 (m, 3H), 2.69 (t, *J* = 7.9 Hz, 2H), 2.59-2.49 (m, 1H), 2.13-1.97 (m, 1H), 1.82-1.71 (m, 1H), 1.26 (d, *J* = 7.0 Hz, 3H).

[7] Hu, J.; Lan, T.; Sun, Y.; Chen, H.; Yao, J.; Rao, Y. *Chem. Commun.* **2015**, *51*, 14929.
[8] Wang, Z.; Zhu, L.; Yin, F.; Su, Z.; Li, Z.; Li, C. *J. Am. Chem. Soc.* **2012**, *134*, 4258.

A round bottom flask containing a teflon-coated magnetic stir bar was charged with the 2-methyl-4-phenylbutanoic acid prepared above (1.0 g, 5.3 mmol, 1.0 equiv) and reagent grade acetonitrile (10 mL). To this solution was sequentially added dicyclohexylcarbodiimide (1.1 g, 5.3 mmol, 1.0 equiv), N-hydroxyphthalimide (870 mg, 5.3 mmol, 1.0 equiv), and dimethylaminopyridine (12 mg, 0.5 mmol, 0.1 equiv) at room temperature. The flask was capped with a septa pierced with a needle to prevent pressure buildup and allowed to stir at room temperature (~22 °C) for 18 h. The solution was filtered to remove insoluble cyclohexylurea byproducts and the filtrate concentrated under reduced pressure to an off-white slurry. The product was purified by silica gel chromatography (10:1 hexanes/EtOAc) and the solvent removed by rotary evaporation. The resulting semi-solid was dried overnight under vacuum to provide **1n** (0.8 g, 2.5 mmol, 47%) as a white solid. ^{1}H-NMR (400 MHz; $CDCl_3$): δ 7.94-7.87 (m, 2H), 7.86-7.74 (m, 2H), 7.35-7.15 (m, 5H), 2.92-2.68 (m, 4H), 2.24-2.10 (m, 1H), 1.99-1.86 (m, 1H), 1.42 (d, J = 7.0, 3H).

IV. Mechanstic Studies

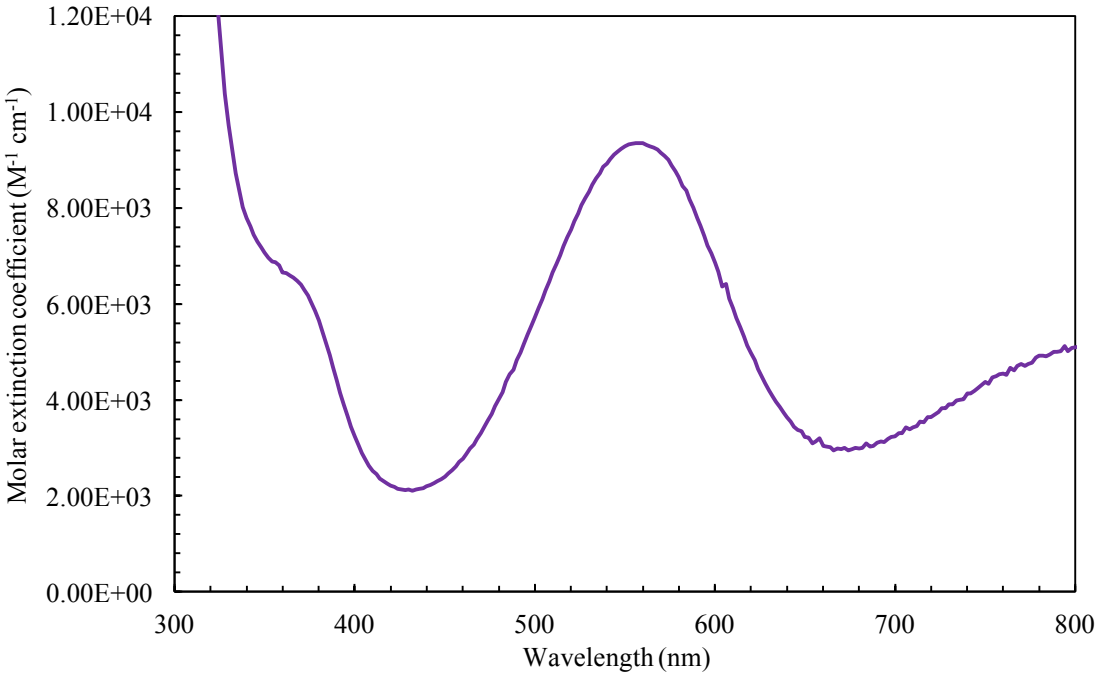


Figure 1. UV-vis spectra of (dtbbpy)Ni^0(cod) recorded in NMP at 24 °C, ϵ = 9350 M^{-1}cm^{-1}.

Reduction of (dtbbpy)NiBr$_2$(dme) to (dtbbpy)Ni^0(cod)

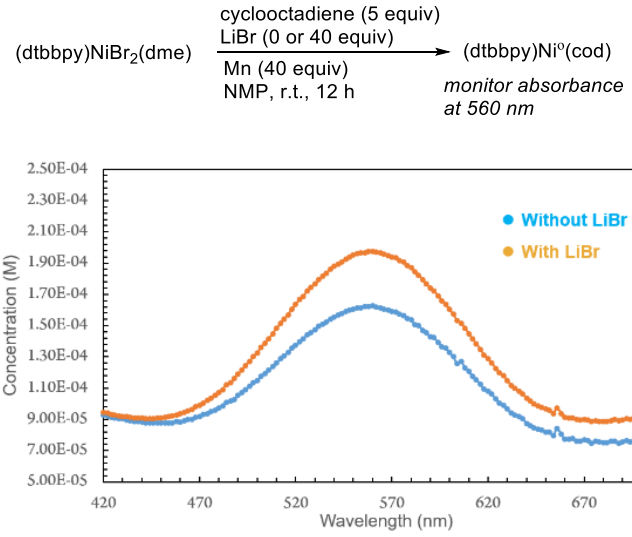


Figure 2. Nickel complex reduction by manganese with and without added LiBr, monitored by UV-vis. Calculated conversions: (dtbbpy)NiBr$_2$(dme) with LiBr (53%), without LiBr (43%).

Reduction of (dtbbpy)NiBr$_2$ with Mn: In an argon filled glovebox, NiBr$_2$·diglyme (8.8 mg, 0.025 mmol, 1 equiv), dtbbpy (6.7 mg, 0.025 mmol, 1 equiv), 1,5-cyclooctadiene (cod) (13.5 mg, 15.3 μL, 0.125 mmol, 5 equiv), Mn powder (55.0 mg, 1.0 mmol, 40 equiv), and 1 mL of NMP were added to a an oven dried 1-dram vial fitted with a Teflon-coated stir-bar. The mixture was stirred overnight at room

temperature for a total of 12 h. To measure the UV-vis spectrum, a 30 μL aliquot of the solution was filtered (oven-dried glass microfiber filters) and diluted to 2 mL total volume with NMP. A feature was observed at 560 nm, indicating that (dtbbpy)$NiBr_2$ was reduced to (dtbbpy)Ni^0(cod) by Mn.

NOTE: due to the instability of nickel(0) complexes, the glove-box was purged for 30 mins before an aliquot was taken.

Sample calculation:

$A = \varepsilon \times C \times \ell$ A = absorbance in AU, C = concentration in M, ℓ = path-length in cm, ε = extinction coefficient in M^{-1} cm^{-1}.

$$C = \frac{A}{\varepsilon \times \ell}$$

$$C = \frac{1.5195}{(9350\ M^{-1}cm^{-1}) \times (1\ cm^{-1})}$$

$$C = 0.1625\ mM$$

$$Percent\ Yield = \frac{0.1625\ mM}{0.3750\ mM} \times 100 = 43\%$$

This corresponds to a 43% yield of reduced (dtbbpy)Ni^0(cod).

Reduction of (dtbbpy)$NiBr_2$ with Mn in the presence of LiBr: In an argon filled glovebox, $NiBr_2$·diglyme (8.8 mg, 0.025 mmol, 1 equiv), dtbbpy (6.7 mg, 0.025 mmol, 1 equiv), LiBr (86.8 mg, 1.0 mmol, 40 equiv), 1,5-cyclooctadiene (cod) (13.5 mg, 15.3 μL, 0.125 mmol, 5 equiv), Mn powder (55.0 mg, 1.0 mmol, 40 equiv), and 1 mL of NMP were added to a an oven dried 1-dram vial fitted with a Teflon-coated stir-bar. The mixture was stirred overnight at room temperature for a total of 12 h. To measure the UV-vis spectrum, a 30 μL aliquot of the solution was filtered (oven-dried glass microfiber filters) and diluted to 2 mL total volume with NMP. A feature was observed at 560 nm, indicating that (dtbbpy)$NiBr_2$ was reduced to (dtbbpy)Ni^0(cod) by Mn. The concentration of (dtbbpy)Ni^0(cod) was calculated to be 0.1974 mM, corresponding to a 53% yield of (dtbbpy)Ni^0(cod).

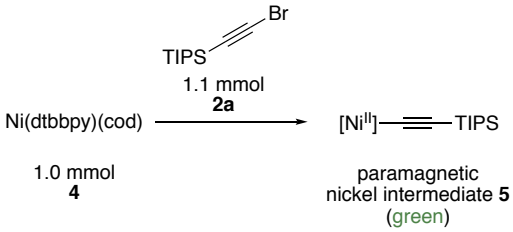
NOTE: due to the instability of nickel(0) complexes, the glove-box was purged with argon for 30 mins before an aliquot was taken.

Results. LiBr does not appear to have a dramatic effect on the reduction of nickel bromide to nickel(0).

Synthesis, Characterization and Reactivity of Potential Nickel Intermediates

1 Synthesis, Characterization and Reactivity of Potential Nickel Complex 5

1.1 Synthesis and Characterization of Nickel Complex 5



A solution of (dtbbpy)Ni(cod) was generated by stirring $Ni(COD)_2$ (275 mg, 1.0 mmol), dtbbpy (282 mg, 1.1 mmol), and 1,5-cyclooctadiene (108 mg, 123 µL, 1.0 mmol) in 5 mL of toluene overnight at room temperature in an argon-filled glovebox. Upon dissolution of the solids, the reaction mixture became dark purple. To this purple mixture was added (bromoethynyl)triisopropylsilane (287 mg, 1.1 mmol) in 5 mL of toluene. Upon the addition of electrophile, a precipitate began to form crashing out of solution. Upon the complete addition of electrophile, the precipitate was collected and triturated with dry, degassed pentane three times to remove residual reagents. The precipitate was dried under vacuum overnight to provide 271 mg of a green powder, corresponding to a ~46% yield if the product is (dtbbpy)Ni($CCSiMe_3$)Br. Although crystals could be obtained, attempts to characterize this product by X-ray diffraction have suffered from desolvation, even at low temperature.

IR (cm^{-1}) of **5**: 3280, 2961, 2867, 1613, 1550, 1483, 1464, 1409, 1367, 1251, 1203, 1020, 896, 846, 666, 637, 625, 607.

The carbon-carbon triple bond present in **2a** has a characteristic IR stretch at 2120 cm^{-1}. This distinct alkyne characteristic is not present in **5**, even though other alkynylnickel complexes have been reported to have a stretch between 2000 and 2100 cm^{-1}.[9] However, reactions of NHP ester **1a** with complex **5** yield desired product **3a** (vide infra), proving that alkyne must be present in **5**.

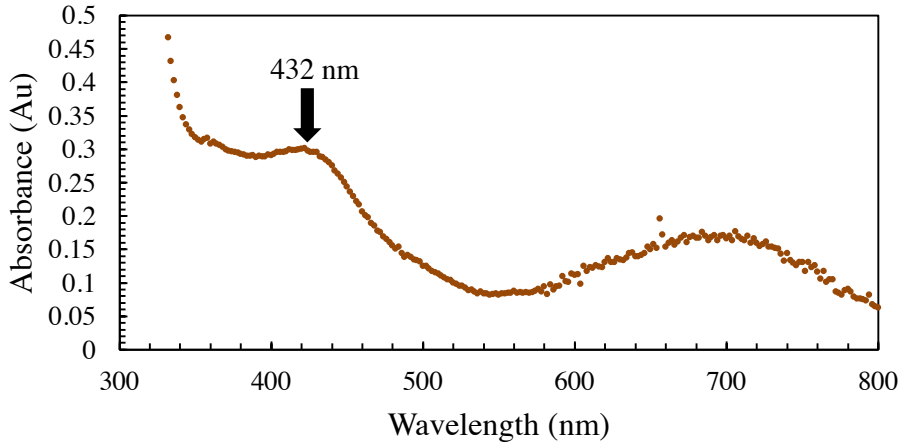


Figure 3. UV-Vis spectra of 5 in DMF at room temperature.

^{1}H NMR of **5**: 58.18 (br s, 1H), 41.80 (br s, 2H), 1.56-1.20 (overlapping m and s, 39H expected, 82 observed).

[9] For example, H.-F. Klein, A. Peterman, *Inorg. Chim. Acta* **1997**, *261*, 187-195.

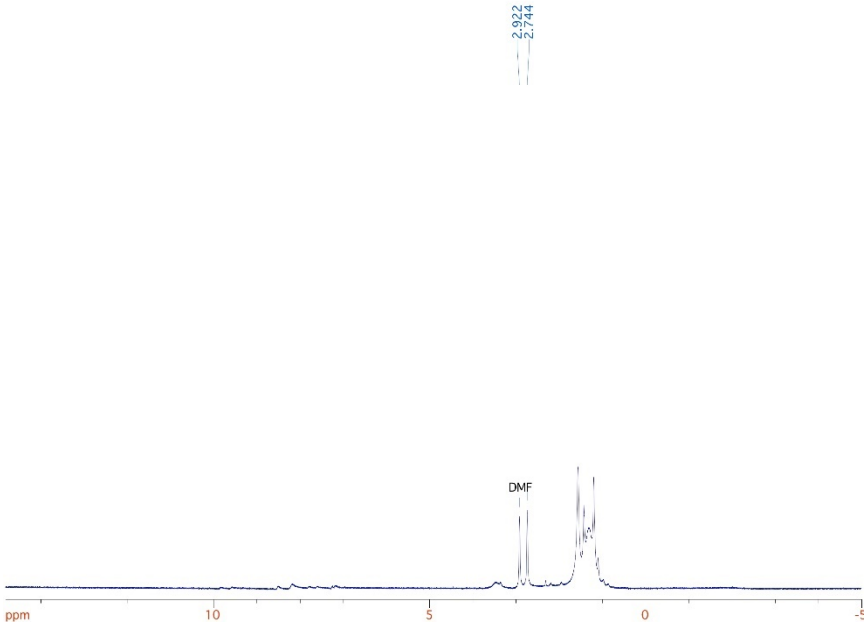


Figure 4. Diamagnetic NMR of 5.

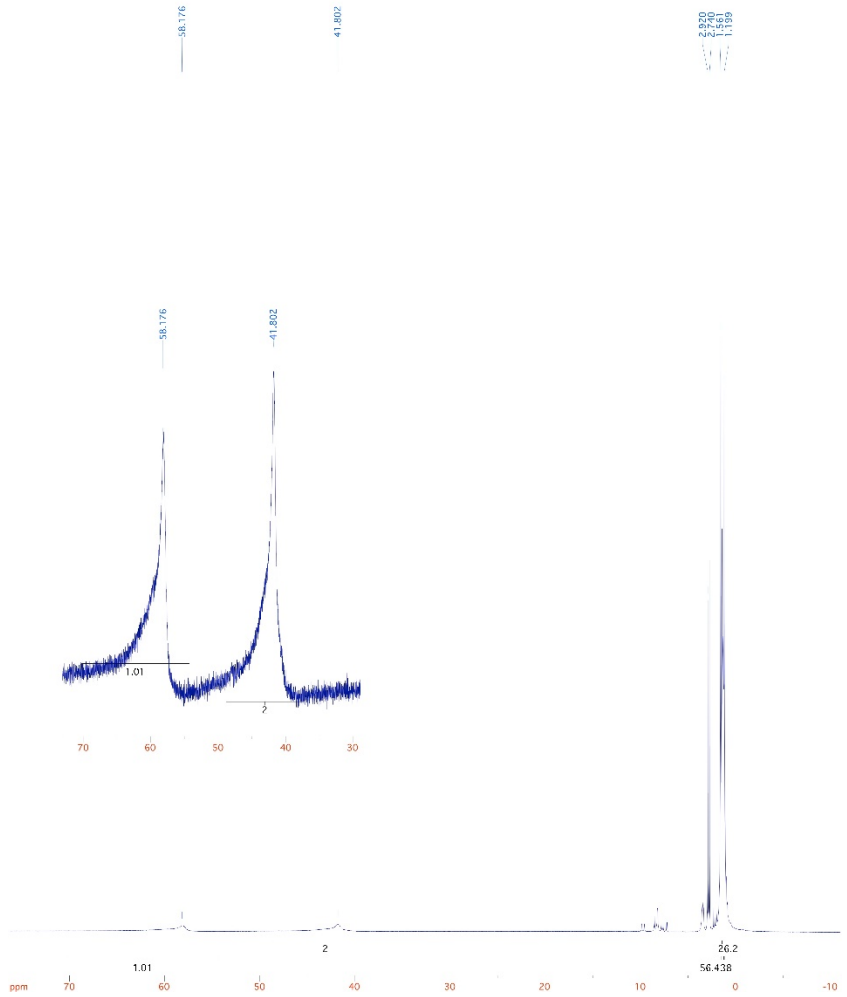


Figure 5. Paramagnetic NMR of 5.

Electron Paramagnetic Resonance (EPR) spectroscopy of 5

All samples for EPR spectroscopy were prepared in an argon atmosphere glovebox. Samples were capped and frozen to 77 K immediately after being removed from the box. EPR samples were prepared in 4 mm OD suprasil quartz EPR tubes from Wilmad Labglass. Samples for spin integration utilized high precision suprasil quartz tubes to allow for direct comparsion of intensities between different samples. X-band EPR spectra were recorded on a Bruker EMXplus spectrometer equipped with a 4119HS cavity and an Oxford ESR-900 helium flow cryostat. The instrumental parameters employed for all samples were as follows: 0.001292 mW power; time constant 0.01 ms; modulation amplitude 8 G; 9.38 GHz; modulation frequency 100 kHz. Samples exhibiting S = ½ EPR spectra were spin integrated using a 3 mM $CuSO_4$ standard under non-saturating conditions. Using a $CuSO_4 \cdot 5H_2O$ standard, the observed EPR spectra of nickel complex **5** corresponds to <5% or less of the sample. Ruling out the possibility of a Ni^{I} or Ni^{III} intermediate.

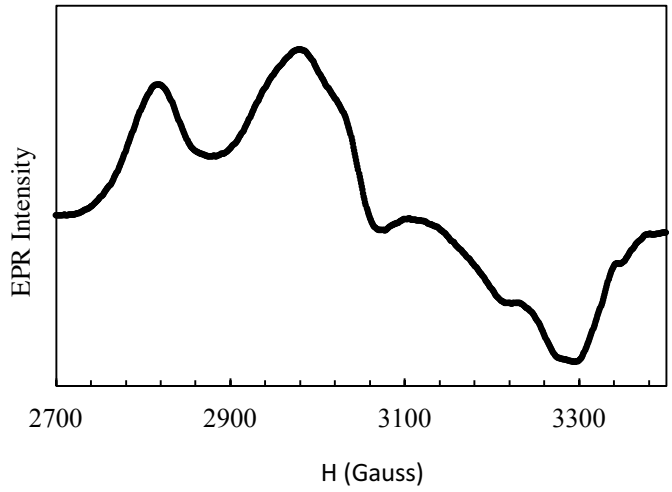
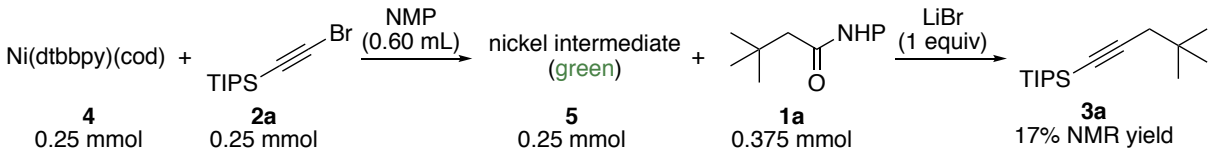


Figure 6. 10 K EPR spectra of solid 5.

1.2 Reactions with nickel complex 5 in the *absence* of Mn.



In an argon-filled glovebox, a solution of (dtbbpy)Ni(cod) was generated by stirring $Ni(cod)_2$ (68.8 mg, 0.25 mmol) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (67.1 mg, 0.25 mmol) in NMP (0.6 mL) overnight. Upon dissolution of the solids, the reaction mixture became dark purple, but the reaction was allowed to stir overnight for complete conversion. To this purple solution was added **2a** (65.5 mg, 0.25 mmol), whereupon the solution turned green in color. This solution was allowed to stir for 15 min. In a separate 1-dram vial was added LiBr (13.0 mg, 0.25 mmol) and **1a** (98.0 mg, 0.375 mmol). The green nickel solution was transferred to the solution of **1a** and the resulting mixture was stirred at rt overnight. The reaction mixture was filtered through a short plug of silica gel (2.0 cm wide × 5.0 cm high) and eluted with hexane (30 mL). The filtrate was concentrated under reduced pressure. To the resulting residue was added $CDCl_3$ for proton NMR with 1,2-dichloromethane (20 μL, 0.25 mmol) as

the internal standard. The NMR yield of product **3a** was 17% (vs 1,2-dichloromethane as an internal standard).

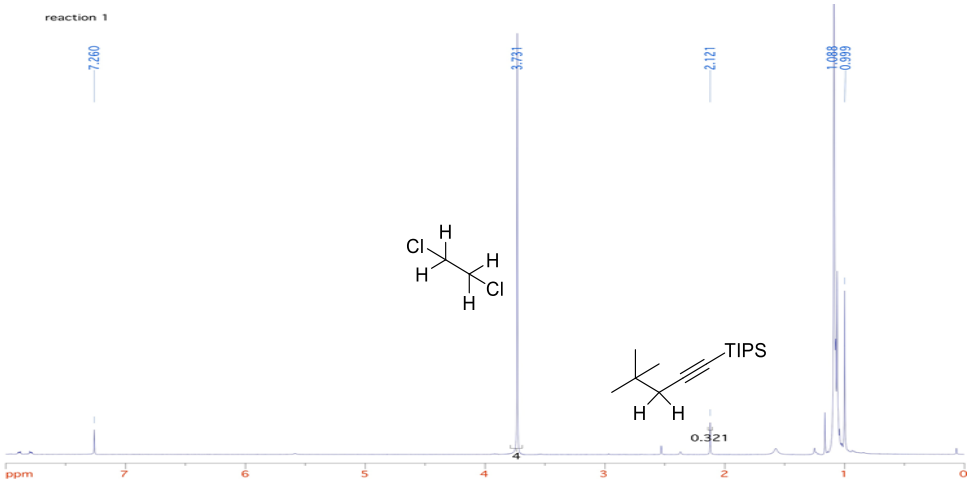


Figure 7. NMR spectra of the reaction between 5 and 1a in the absence of Mn.

A reaction of washed complex **5**, prepared as above, with **2a** and LiBr also produced cross product **3a** and diyne (Figure 8) in similar ratios.

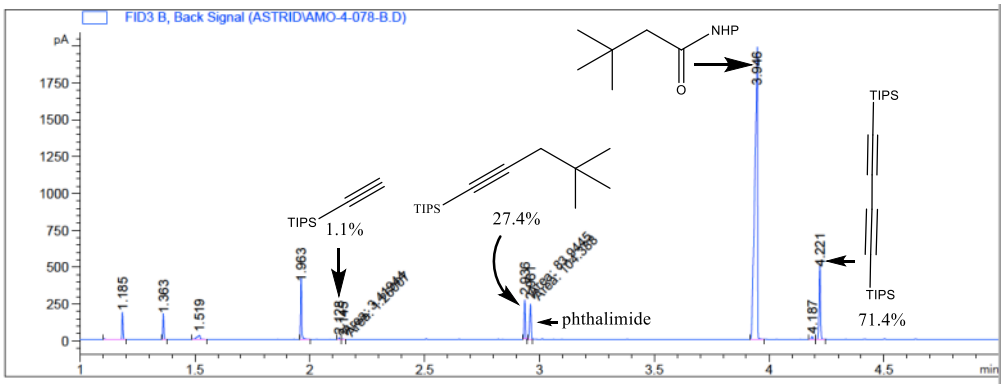
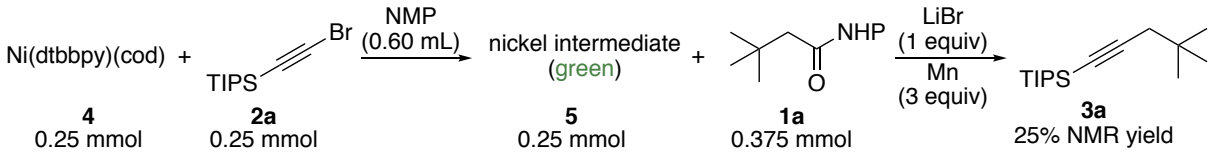


Figure 8. GC spectra of the reaction between 5 and 1a in the absence of Mn. Percentages are area% data for materials derived from the bromoalkyne.

1.3 Reactions with nickel complex 5 in the *presence* of Mn.



In an argon-filled glovebox, a solution of (dtbbpy)Ni(cod) was generated by stirring $Ni(cod)_2$ (68.8 mg, 0.25 mmol) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (67.1 mg, 0.25 mmol) in NMP (0.6 mL) overnight. Upon dissolution of the solids, the reaction mixture became dark purple, but the reaction was allowed to stir overnight for complete conversion. To this purple solution was added **2a** (65.5 mg, 0.25 mmol), whereupon the solution turned green in color. This solution was allowed to stir for 15 min. In a separate 1-dram vial was added LiBr (13.0 mg, 0.25 mmol), **1a** (98.0 mg, 0.375 mmol), and Mn (41.3 mg, 0.75 mmol). The green nickel solution was transferred to the solution of **1a** and the resulting mixture was stirred at rt overnight. The reaction mixture was filtered through a short plug of silica gel (2.0 cm

wide × 5.0 cm high) and eluted with hexane (30 mL). The filtrate was concentrated under reduced pressure. To the resulting residue was added $CDCl_3$ for proton NMR with 1,2-dichloromethane (20 μL, 0.25 mmol) as the internal standard. The NMR yield of product **3a** was 25% (vs 1,2-dichloromethane as an internal standard).

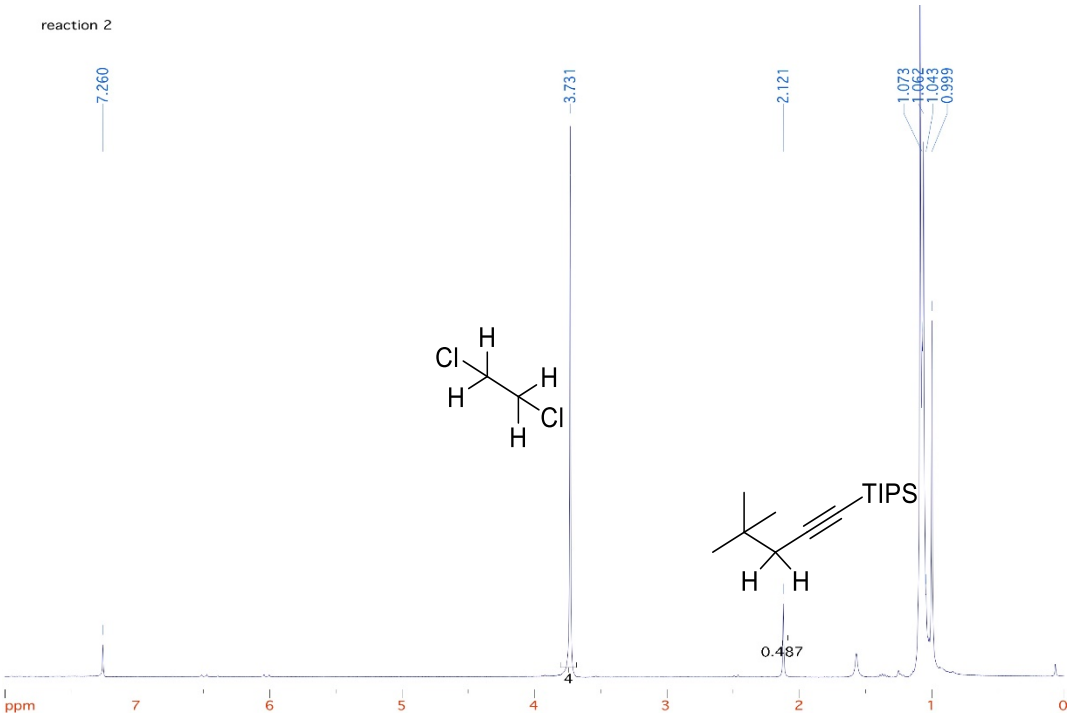


Figure 9. NMR spectra of the reaction between 5 and 1a in the presence of Mn.

A reaction of washed complex **5**, prepared as above, with **2a**, LiBr, and Mn also produced cross product **3a** and diyne (Figure 10) in similar ratios.

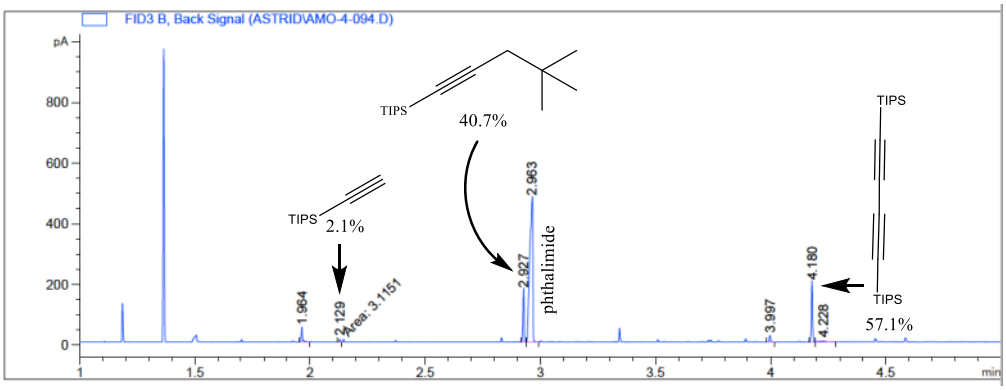
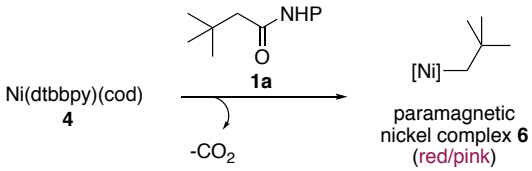


Figure 10. GC spectra of the reaction between 5 and 1a in the presence of Mn. Percentages are area% data for materials derived from the bromoalkyne.

Conclusions. Catalytic reaction with nickel intermeditate **5** and **1a** in the *presence* of Mn formed a relatively larger amount of cross-coupled product when compared to the reaction without added Mn. This mirrors results observed in our previous report with NHP esters.[5a]

2 Synthesis, Characterization and Reactvivity of Nickel Complex 6

2.1 Synthesis and Characterization of Nickel Complex 6



A solution of (dtbbpy)Ni(cod) was generated by stirring $Ni(COD)_2$ (275 mg, 1.0 mmol), dtbbpy (282 mg, 1.1 mmol), and 1,5-cyclooctadiene (108 mg, 123 μL, 1.0 mmol) in 5 mL of toluene overnight at room temperature in an argon-filled glovebox. Upon dissolution of the solids, the reaction mixture became dark purple. To this purple mixture was added 2-(4,4-dimethyl-2-oxopentyl)isoindoline-1,2-dione (262 mg, 1.0 mmol) in 5 mL of toluene and the color rapidly changed to red, indicating the formation of a new nickel intermediate. The solution was stirred for 30 minutes before the solvent was removed under vacuum. The solid was triturated with dry, degassed pentane three times to remove residual reagents and the obtained powder was dried under vacuum overnight to provide 469 mg of a red/pink solid. By ^{1}H NMR, this material was impure, but was analyzed and used in the subsequent reactions without further purification.

IR (cm^{-1}) of 6: 3344, 2960, 2869, 1724, 1631, 1594, 1552, 1466, 1408, 1369, 1296, 1250, 1179, 1116, 895, 846, 727, 607.

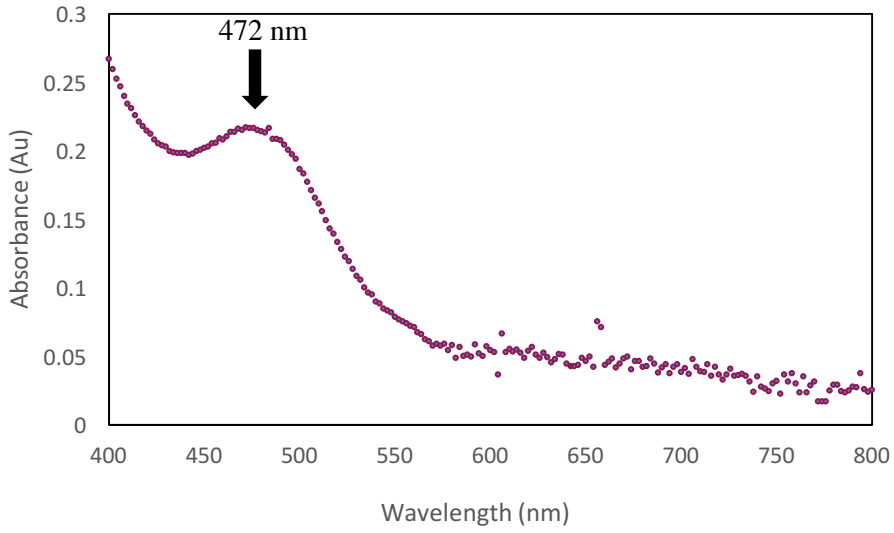


Figure 11. UV-Vis spectra of nickel complex 6 in DMF at room temperature.

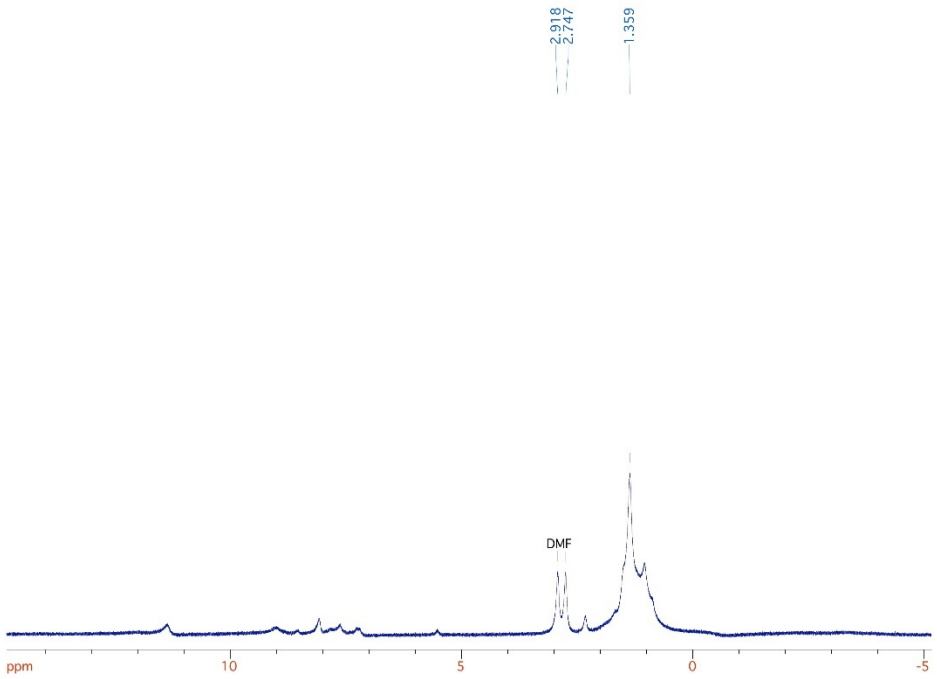


Figure 12. Diamagnetic NMR of 6.

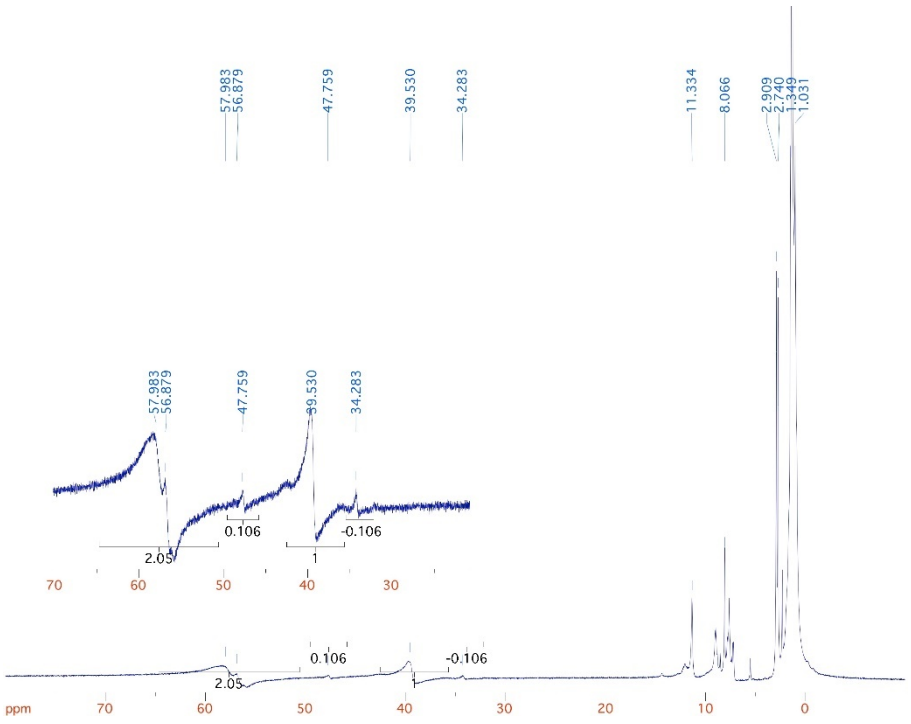
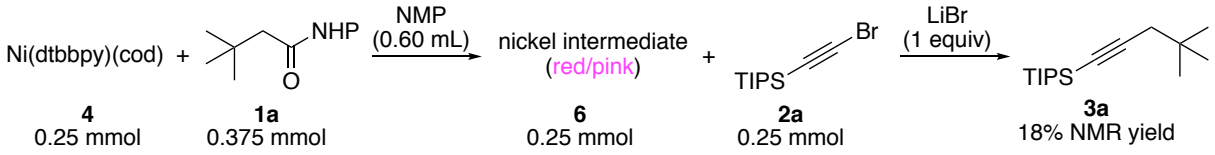


Figure 13. Paramagnetic NMR of 6.

Electron Paramagnetic Resonance (EPR) spectroscopy of nickel complex 6

No EPR signal was observed for nickel complex **6**. This rules out the possibility of a ½-integer spin complex, such as a Ni^{I} or Ni^{III} complex, and suggests an integer-spin paramagnetic complex, such as tetrahedral or octahedral Ni^{II}.

2.2 Reactions with nickel complex 6 in the *absence* of Mn.



In an argon-filled glovebox, a solution of (dtbbpy)Ni(cod) was generated by stirring $Ni(cod)_2$ (68.8 mg, 0.25 mmol) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (67.1 mg, 0.25 mmol) in NMP (0.6 mL) overnight. Upon dissolution of the solids, the reaction mixture became dark purple, but the reaction was allowed to stir overnight for complete conversion. To the resulting purple solution was added **1a** (98.0 mg, 0.375 mmol) and the solution turned to a light red or pink color. This mixture was allowed to stir for 15 minutes. In a separate 1-dram vial was added LiBr (13.0 mg, 0.25 mmol), and **2a** (65.5 mg, 0.25 mmol). The red/pink nickel complex solution was transferred to the vial containing **2a** and the resulting mixture was stirred at rt overnight. The reaction mixture was filtered through a short plug of silica gel (2.0 cm wide × 5.0 cm high) and eluted with hexane (30 mL). The filtrate was concentrated under reduced pressure. To the resulting residue was added $CDCl_3$ for proton NMR with 1,2-dichloromethane (20 μL, 0.25 mmol) as the internal standard. The NMR yield of the desired product **3a** was 18% (vs 1,2-dichloromethane as an internal standard).

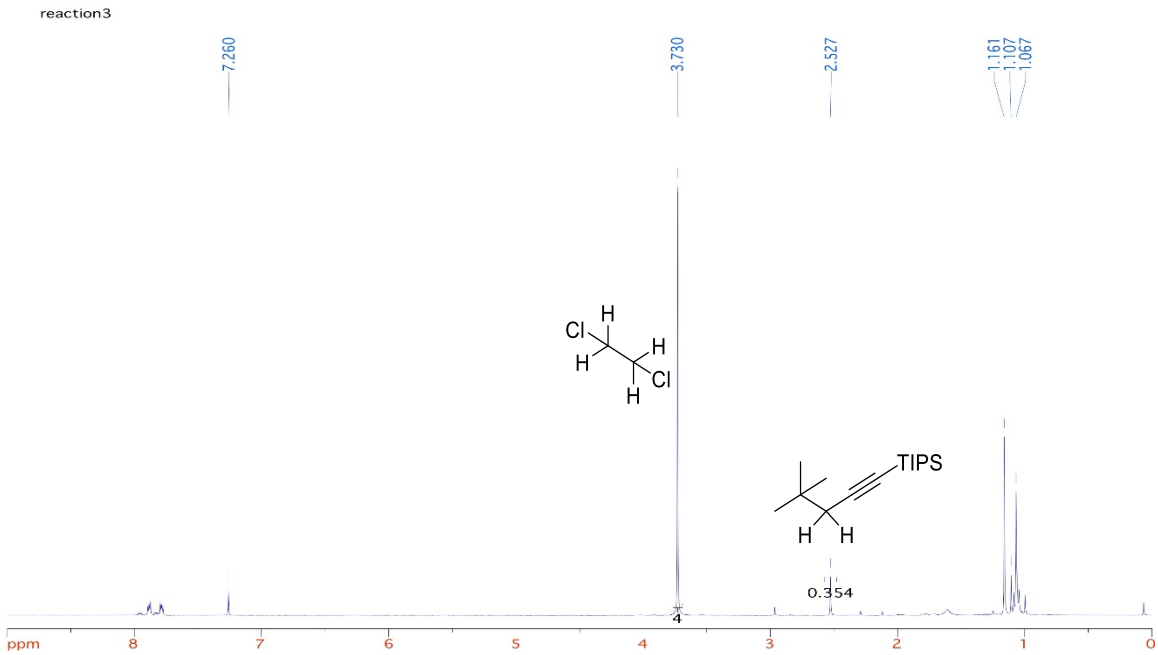


Figure 14. GCMS spectrum of the reaction between 6 and 2a in the *absence* of Mn.

A reaction of washed complex **6**, prepared as above, with **1a** and LiBr also produced cross product **3a** and diyne (Figure 15) in similar ratios.

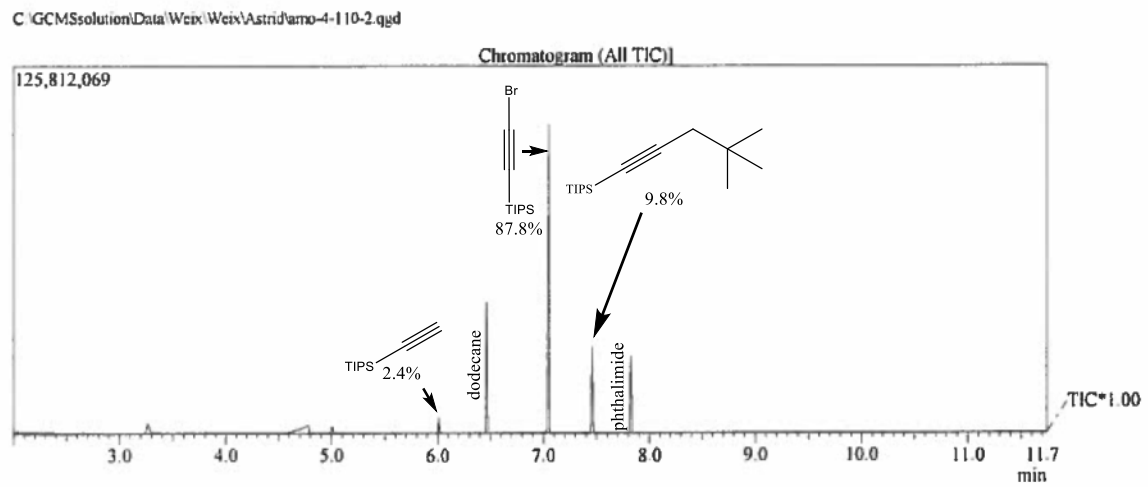
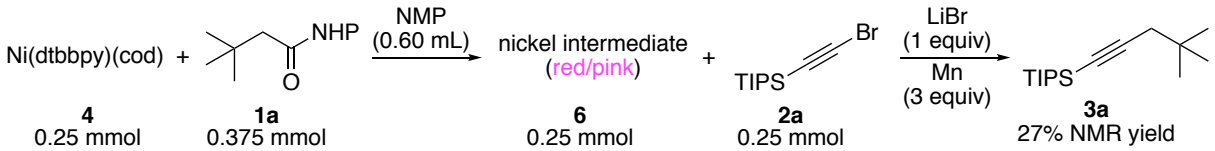


Figure 15. GCMS spectrum of the reaction between 6 and 2a in the *absence* of Mn. Percentages are area% data for materials derived from the bromoalkyne.

2.3 Reactions with nickel complex 6 in the *presence* of Mn.



In an argon-filled glovebox, a solution of (dtbbpy)Ni(cod) was generated by stirring $Ni(cod)_2$ (68.8 mg, 0.25 mmol) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (67.1 mg, 0.25 mmol) in NMP (0.6 mL) overnight. Upon dissolution of the solids, the reaction mixture became dark purple, but the reaction was allowed to stir overnight for complete conversion. To the resulting purple solution was added **1a** (98.0 mg, 0.375 mmol) and the solution turned to a light red or pink color. This mixture was allowed to stir for 15 minutes. In a separate 1-dram vial was added LiBr (13.0 mg, 0.25 mmol), **2a** (65.5 mg, 0.25 mmol), and Mn (41.3 mg, 0.75 mmol). The red/pink nickel complex solution was transferred to the vial containing **2a** and the resulting mixture was stirred at rt overnight. The reaction mixture was filtered through a short plug of silica gel (2.0 cm wide × 5.0 cm high) and eluted with hexane (30 mL). The filtrate was concentrated under reduced pressure. To the resulting residue was added $CDCl_3$ for proton NMR with 1,2-dichloromethane (20 μL, 0.25 mmol) as the internal standard. The NMR yield of the desired product **3a** was 27% (vs 1,2-dichloromethane as an internal standard).

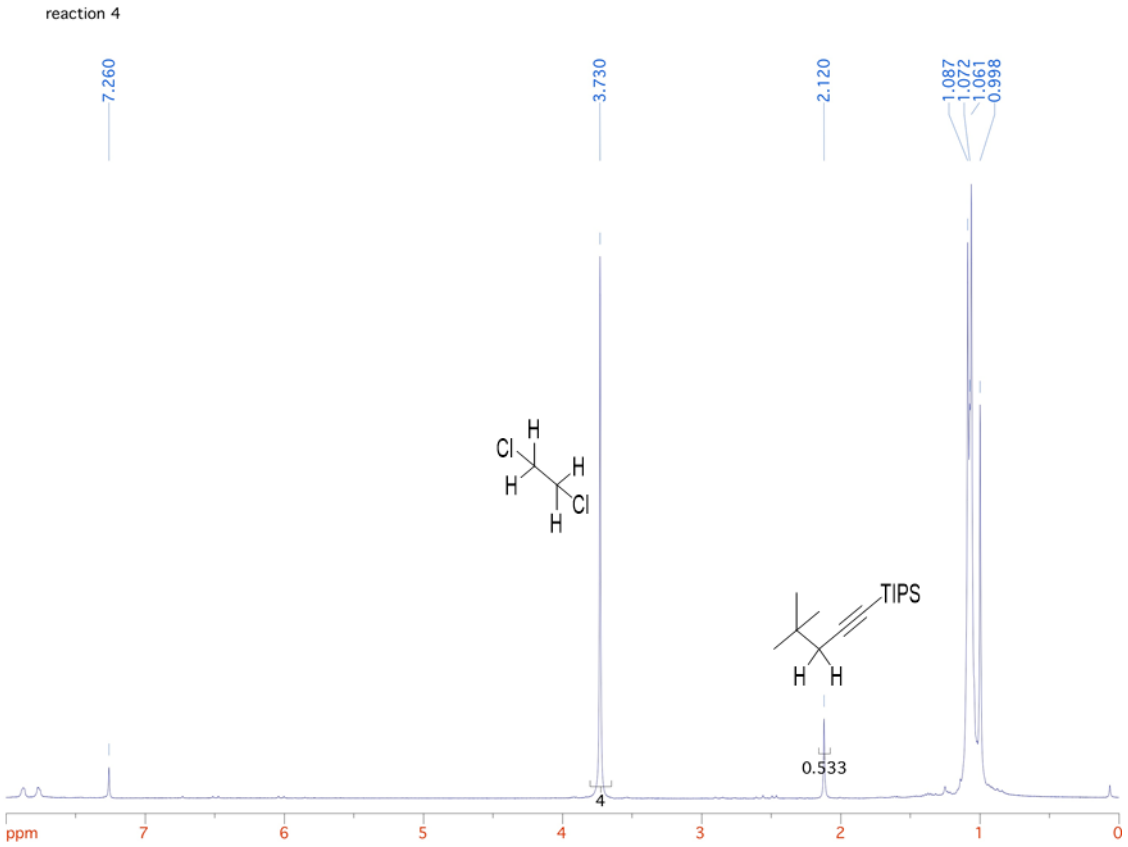


Figure 16. GCMS spectrum of the reaction between 6 and 2a in the *presence* of Mn.

A reaction of washed complex **6**, prepared as above, with **1a**, LiBr, and Mn also produced cross product **3a** and diyne (Figure 17) in similar ratios.

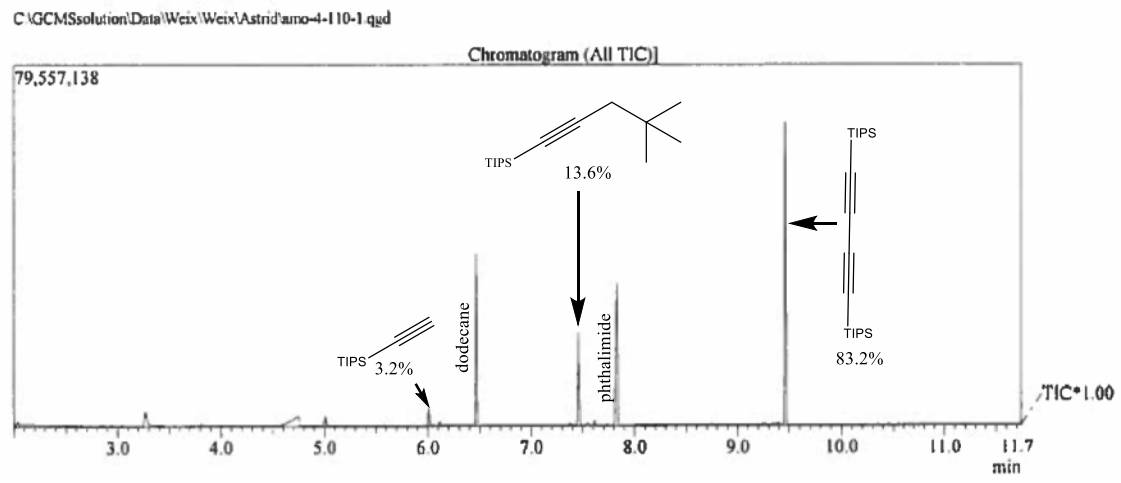
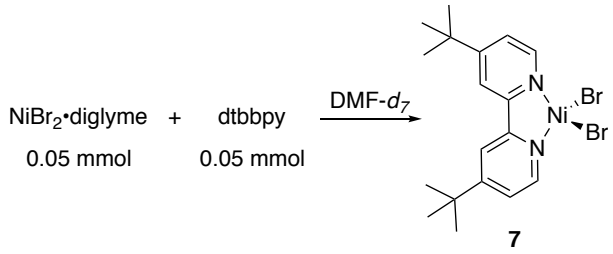


Figure 17. GCMS spectrum of the reaction between 6 and 2a in the *presence* of Mn. Percentaes are area% data from materials derived from the bromoalkyne.

Conclusions. Both reactions formed cross-coupled product. The formation of diyne in the presence of Mn is not indicative of a selectivity difference because (dtbbpy)Ni complexes rapidly form diyne from **1a** in the presence of Mn. Diyne could have been formed on subsequent turnovers.

3 Synthesis and Characterization of Nickel Complex 7.



A solution of (dtbbpy)$NiBr_2$ was generated by stirring $NiBr_2$·diglyme (17.6 mg, 0.05 mmol, 1 equiv) and dtbbpy (13.4 mg, 0.05 mmol, 1 equiv) in 0.5 mL of DMF-d_7. After 30 minutes, a homogenous green solution was observed indicating the formation of **7**.

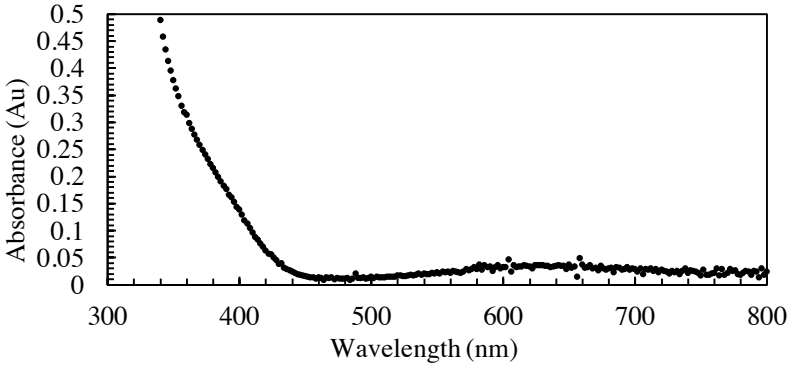


Figure 18. UV-Vis spectra of 7 in DMF at room temperature.

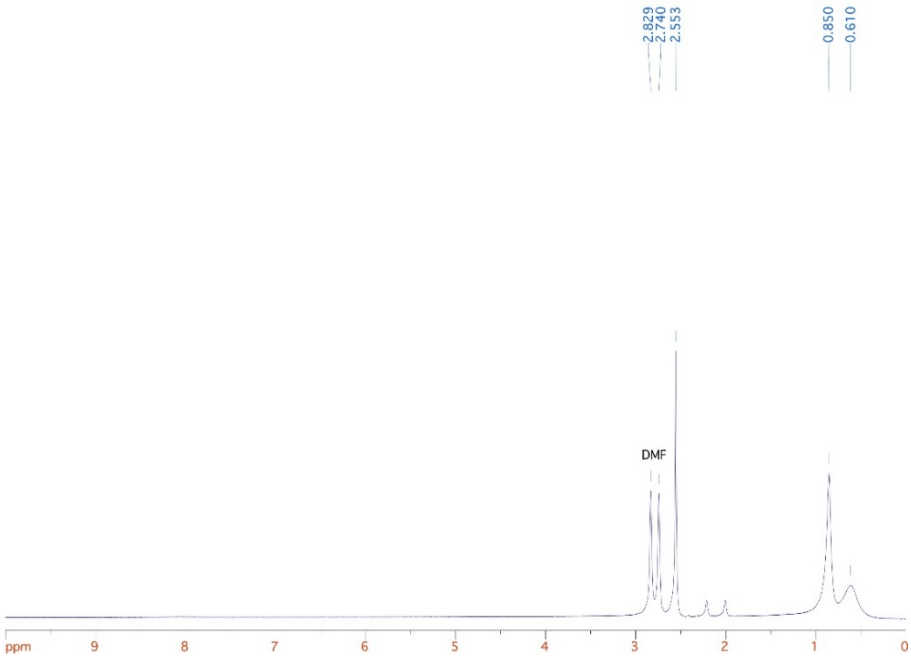


Figure 19. Diamagnetic NMR of intermidate 7

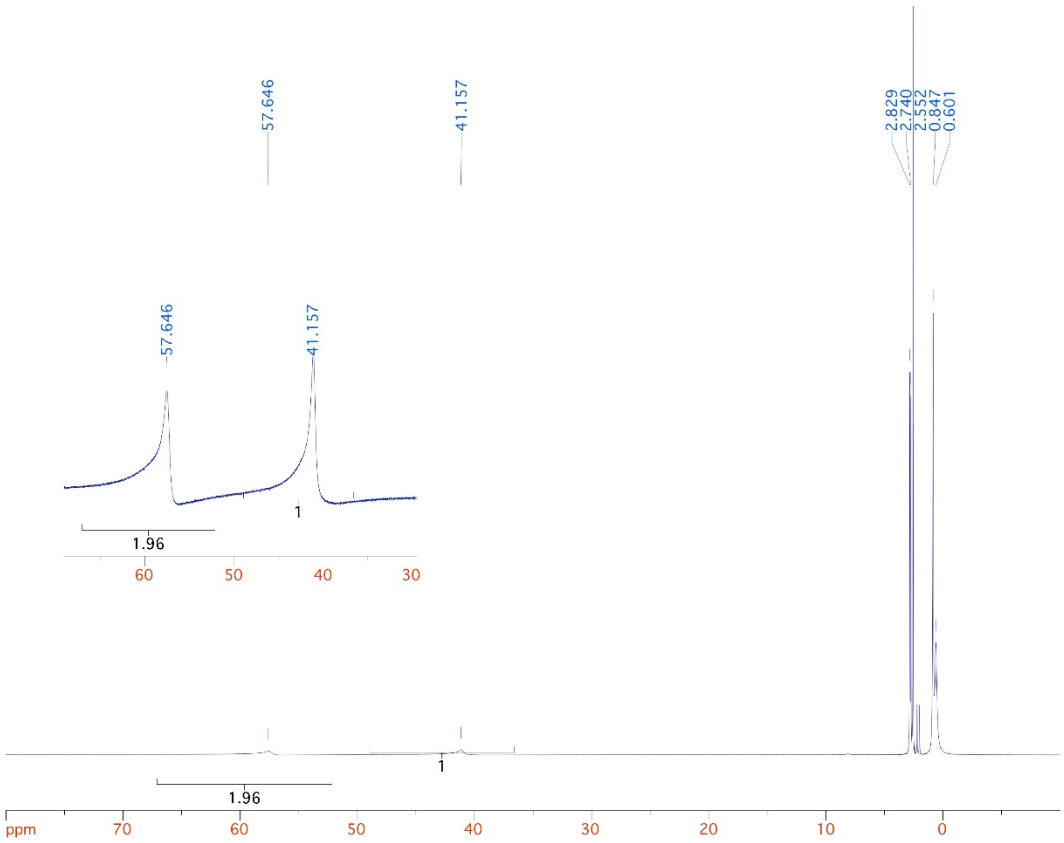
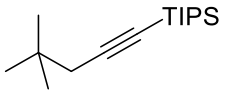


Figure 20. Paramagnetic NMR of intermediate 7.

Conclusions. Complex **7** was made for comparison with paramagnetic intermediates **5** and **6**. Products **5** and **6** appear to be different from **7**. This, coupled with the reactivity data, strongly suggest that **5** and **6** are organometallic species containing alkyne and alkyl ligands, respectively.

V. Preparative Experiments.

(4,4-Dimethylpent-1-yn-1-yl)triisopropylsilane (3a) (cas: 1367368-73-7)[10]



Compound **3a** was prepared following the general procedure, starting from $NiBr_2$(diglyme) (16.0 mg, 0.05 mmol, 0.1 equiv), 4-4′ -di-*tert*-butyl-2,2′ -bipyridine (13.4 mg, 0.05 mmol, 0.1 equiv), LiBr (43 mg, 0.5 mmol, 1 equiv), manganese (82 mg, 1.5 equiv, 3.0 equiv), 1,3-dioxoisoindolin-2-yl 3,3-dimethylbutanoate (196 mg, 0.75 mmol, 1.5 equiv), (bromoethynyl)triisopropylsilane (131 mg, 0.5 mmol, 1 equiv) and NMP (1.2 mL). After stirring at room temperatue for 14 h, the reaction mixture was worked up and purified by flash chromatography (hexane), **3a** was obtained as colorless liquid (108.4 mg, 86% isolated yield).

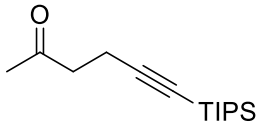
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.13 (s, 2H), 1.10 – 1.05(m, 21H), 1.01 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 107.4, 81.5, 35.0, 31.2, 29.0, 18.7, 11.4.

GCMS, m/z (% relative intensity, ion): 252.30[M^+] (3), 209.20 (100), 181.20 (42), 167.20 (43), 153.15 (88), 139.15 (96), 97.10 (18), 83.05 (22), 73.10 (17), 59.10 (17).

IR: $\tilde{\nu}$ = 2943, 2866 cm^{-1}.

6-(Triisopropylsilyl)hex-5-yn-2-one (3b) (cas: 764652-77-9)[11]



Compound **3b** was prepared following the general procedure, starting from $NiBr_2$(diglyme) (16.0 mg, 0.05 mmol, 0.1 equiv), 4-4′ -di-*tert*-butyl-2,2′ -bipyridine (13.4 mg, 0.05 mmol, 0.1 equiv), LiBr (43 mg, 0.5 mmol, 1 equiv), manganese (82 mg, 1.5 mmol, 3.0 equiv), 1,3-dioxoisoindolin-2-yl 4-oxopentanoate (196 mg, 0.75 mmol, 1.5 equiv), (bromoethynyl)triisopropylsilane (131 mg, 0.5 mmol, 1 equiv) and NMP (1.2 mL). After stirring at room temperature for 14 h, the reaction mixture was worked up and purified by flash chromatography (ethyl acetate / hexane = 1:100), **3b** was obtained as colorless liquid (53.0 mg, 42% isolated yield).

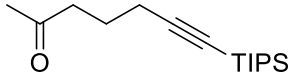
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.67 (t, J = 7.6 Hz, 2H), 2.50 (t, J = 7.6 Hz, 2H), 2.17 (s, 3H), 1.04 – 1.01 (m, 21H).

^{13}C NMR (100 MHz, $CDCl_3$): 206.6, 107.2, 80.9, 42.8, 29.9, 18.5, 14.6, 11.2.

GCMS, m/z (% relative intensity, ion): 209.15 (100), 167.10 (57), 139.05 (47), 125.05 (15), 111.05 (13), 99.05 (11), 85.05 (12), 75.05 (26), 61.05 (19).

IR: $\tilde{\nu}$ = 2943, 2866, 2172, 1720, 1462, 1366, 1161, 883, 660 cm^{-1}.

7-(Triisopropylsilyl)hept-6-yn-2-one (3c)



[10] Ye, F., Ma, X., Xiao, Q., Li, H., Zhang, Y., Wang, J., *J. Am. Chem. Soc*., **2012**, *134*, 5742–5745
[11] Villarino, L., Rebeca García-Fandiño, R., López, F., Mascareñas, J. L., *Org. Lett.*, **2012**, *14*, 2996–2999

Compound **3c** was prepared following the general procedure, starting from $NiBr_2$(diglyme) (16.0 mg, 0.05 mmol, 0.1 equiv), 4-4′ -di-*tert*-butyl-2,2′ -bipyridine (13.4 mg, 0.05 mmol, 0.1 equiv), LiBr (43 mg, 0.5 mmol, 1 equiv), manganese (82 mg, 1.5 mmol, 3.0 equiv), 1,3-dioxoisoindolin-2-yl 5-oxohexanoate (206 mg, 0.75 mmol, 1.5 equiv), (bromoethynyl)triisopropylsilane (131 mg, 0.5 mmol, 1 equiv) and NMP (1.2 mL). After stirring at room temperature for 14 h, the reaction mixture was worked up and purified by flash chromatography (ethyl acetate / hexane = 1: 100), **3c** was obtained as colorless liquid (86.5 mg, 65% isolated yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.59 (t, J = 7.2 Hz, 2H), 2.27 (d, J = 6.8 Hz, 2H), 2.12 (s, 3H), 1.76 (quintet, J = 7.2 Hz, 2H), 1.04 – 1.01 (m, 21H).

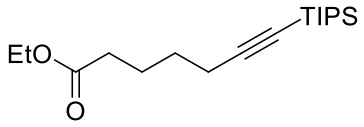
^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.3, 107.9, 81.1, 42.0, 23.0, 22.6, 19.1, 18.5, 11.2.

LRMS (ESI+) m/z: 267.0 [$M+H^+$].

HRMS (ESI+): $[M+H]^+$ Calc. for $C_{16}H_{31}OSi$: 267.2144; found: 267.2143.

IR: $\tilde{\nu}$ = 2943, 2866, 2172, 1717, 1462, 883 cm^{-1}.

Ethyl 7-(triisopropylsilyl)hept-6-ynoate (3d) (cas: 1394826-35-7)[12]



Compound **3d** was prepared following the general procedure, starting from $NiBr_2$(diglyme) (16.0 mg, 0.05 mmol, 0.1 equiv), 4-4′ -di-*tert*-butyl-2,2′ -bipyridine (13.4 mg, 0.05 mmol, 0.1 equiv), LiBr (43 mg, 0.5 mmol, 1 equiv), manganese (82 mg, 1.5 mmol, 3.0 equiv), 1,3-dioxoisoindolin-2-yl ethyl adipate (239 mg, 0.75 mmol, 1.5 equiv), (bromoethynyl)triisopropylsilane (131 mg, 0.5 mmol, 1 equiv) and NMP (1.2 mL). After stirring at room temperature for 14 h, the reaction mixture was worked up and purified by flash chromatography (ethyl acetate / hexane = 3:100), **3d** was obtained as colorless liquid (141.2 mg, 91% isolated yield).

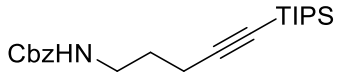
^{1}H NMR (400 MHz, $CDCl_3$): δ 4.09 (q, J = 6.4 Hz, 2H), 2.31 – 2.23 (m, 4H), 1.74 (quintet, J = 7.2 Hz, 2H), 1.54 (quintet, J = 7.2 Hz, 2H), 1.24 – 1.20 (m, 3H), 1.04 – 0.99 (m, 21H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.3, 108.3, 80.5, 60.1, 33.7, 28.1, 24.0, 19.5, 18.5, 14.2, 11.2.

GCMS, m/z (% relative intensity, ion): 267.20 (100), 223.15 (78), 197.10 (6), 181.15 (6), 153.10 (10), 131.10 (10), 109.05 (12), 103.05 (19), 89.05 (15), 75.05 (16), 59.10 (12).

IR: $\tilde{\nu}$ = 2940, 2866, 1736, 1462, 1373, 883 cm^{-1}.

Benzyl (5-(triisopropylsilyl)pent-4-yn-1-yl)carbamate (3e)



Compound **3e** was prepared following the general procedure, starting from $NiBr_2$(diglyme) (16.0 mg, 0.05 mmol, 0.1 equiv), 4-4′ -di-*tert*-butyl-2,2′ -bipyridine (13.4 mg, 0.05 mmol, 0.1 equiv), LiBr (43 mg, 0.5 mmol, 1 equiv), manganese (82 mg, 1.5 mmol, 3.0 equiv), 1,3-dioxoisoindolin-2-yl 4-(((benzyloxy)carbonyl)amino)butanoate (287 mg, 0.75 mmol, 1.5 equiv), (bromoethynyl)triisopropylsilane (131 mg, 0.5 mmol, 1 equiv) and NMP (1.2 mL). After stirring at room temperature for 14 h, the reaction mixture was worked up and purified by flash chromatography (ethyl acetate / hexane = 1:10), **3e** was obtained as colorless liquid (102.8 mg, 55% isolated yield).

[12] Liu, X., Wang, Z., Cheng, X., Li, C., *J. Am. Chem. Soc.*, **2012**, *134*, 14330–14333

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 – 7.31 (m, 4H), 5.09 (s, 2H), 5.05 (s, 1H), 3.33 (d, J = 6.0 Hz, 2H), 2.32 (t, J = 6.4 Hz, 2H), 1.75 (t, J = 6.0 Hz, 2H), 1.06 – 1.05 (m, 21H).

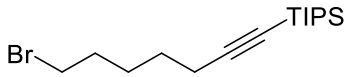
^{13}C NMR (100 MHz, $CDCl_3$): δ 156.3, 136.5, 128.4, 128.1, 128.0, 107.6, 81.3, 66.6, 40.2, 28.7, 18.6, 17.4, 11.2.

LRMS (ESI+) m/z: [M+H$^+$]373.90.

HRMS (ESI+): [M+H]$^+$ Calc. for $C_{22}H_{36}O_2SiN$: 374.2515; found: 374.2506.

IR: $\tilde{\nu}$ = 3333, 2943, 2862, 2361, 2342, 1701, 1531, 1258, 748 cm^{-1}.

(7-Bromohept-1-yn-1-yl)triisopropylsilane (3f)



Compound **3f** was prepared following the general procedure, starting from $NiBr_2$(diglyme) (16.0 mg, 0.05 mmol, 0.1 equiv), 4-4′ -di-*tert*-butyl-2,2′ -bipyridine (13.4 mg, 0.05 mmol, 0.1 equiv), LiBr (43 mg, 0.5 mmol, 1 equiv), manganese (82 mg, 1.5 mmol, 3.0 equiv), 1,3-dioxoisoindolin-2-yl 6-bromohexanoate (255 mg, 0.75 mmol, 1.5 equiv), (bromoethynyl)triisopropylsilane (131 mg, 0.5 mmol, 1 equiv) and NMP (1.2 mL). After stirring at room temperature for 14 h, the reaction mixture was worked up and purified by flash chromatography (ethyl acetate / hexane = 1:50), **3f** was obtained as colorless liquid (81.3 mg, 49% isolated).

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.41 (t, J = 6.4 Hz, 2H), 2.29 – 2.25 (m, 2H), 1.90 – 1.87(m, 2H), 1.57 – 1.56 (m, 4H), 1.05 – 0.99 (m, 21H).

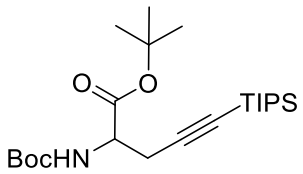
^{13}C NMR (100 MHz, $CDCl_3$): δ 108.5, 80.5, 33.6, 32.3, 27.9, 27.3, 19.7, 18.6, 11.3.

GCMS, m/z (% relative intensity, ion): 289.15 (8), 287.10 (8), 247.05 (25), 245.05 (24), 195.00 (13), 193.00 (14), 167.00 (84), 165.05 (100), 138.95 (75), 137.00 (84), 123.00 (33), 109.05 (30), 95.05 (23), 59.10 (20).

HRMS (ESI+): [M-*i*Pr]$^+$ Calc. for $C_{13}H_{24}SiBr$: 287.0831; found: 287.0827.

IR: $\tilde{\nu}$ = 2940, 2862, 2172, 1462, 883 cm^{-1}.

***tert*-Butyl 2-((tert-butoxycarbonyl)amino)-5-(triisopropylsilyl)pent-4-ynoate (3g)**



Compound **3g** was prepared following the general procedure, starting from $NiBr_2$(diglyme) (16.0 mg, 0.05 mmol, 0.1 equiv), 4-4′ -di-*tert*-butyl-2,2′ -bipyridine (13.4 mg, 0.05 mmol, 0.1 equiv), LiBr (43 mg, 0.5 mmol, 1 equiv), manganese (82 mg, 1.5 mmol, 3.0 equiv), 1-(*tert*-butyl)-3-(1,3-dioxoisoindolin-2-yl)-2-((*tert*-butoxycarbonyl)amino)malonate (315 mg, 0.75 mmol, 1.5 equiv) and NMP (1.2 mL). After stirring at room temperature for 14 h, the reaction mixture was worked up and purified by flash chromatography (ethyl acetate / hexane = 1: 10), **3g** was obtained as yellow liquid (110.8 mg, 52% isolated yield).

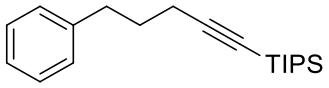
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.31 (d, J = 8.0 Hz, 1H), 4.26 (quintet, J = 8.0Hz, 1H), 2.83 (dd, J = 5.2 Hz, J = 16.8 Hz, 1H), 2.73 (dd, J = 3.6 Hz, J = 16.4 Hz, 1H), 1.45 (s, 9H), 1.42 (s, 9H), 1.04 – 1.01 (m, 21H).

^{13}C NMR (100 MHz, $CDCl_3$): 169.7, 155.0, 102.4, 84.1, 82.1, 79.6, 52.2, 28.2, 27.9, 24.0, 18.5, 11.1.
LRMS (ESI+) m/z: 426.1 [M+H$^+$], 449.2 [M+Na$^+$].

HRMS (ESI+): [M+H]$^+$ Calc. for $C_{23}H_{43}NO_4Si$: 426.3029; found: 426.3032.

IR: $\tilde{\nu}$ = 3441, 2943, 2866, 2361, 1717, 1497, 1354, 1153, 999, 883 cm^{-1}.

Triisopropyl(5-phenylpent-1-yn-1-yl)silane (3h)



Compound **3h** was prepared following the general procedure, starting from $NiBr_2$(diglyme) (16.0 mg, 0.05 mmol, 0.1 equiv), 4-4′ -di-*tert*-butyl-2,2′ -bipyridine (13.4 mg, 0.05 mmol, 0.1 equiv), LiBr (43 mg, 0.5 mmol, 1 equiv), manganese (82 mg, 1.5 mmol, 3.0 equiv), 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate (232 mg, 0.75 mmol, 1.5 equiv), (bromoethynyl)triisopropylsilane (131 mg, 0.5 mmol, 1 equiv) and NMP (1.2 mL). After stirring at room temperature for 14 h, the reaction mixture was worked up and purified by flash chromatography (hexane), **3h** was obtained as colorless liquid (138.9 mg, 92% isolated yield).

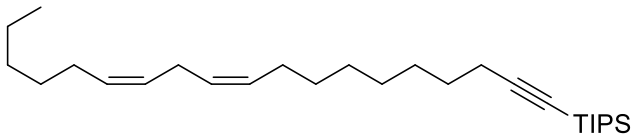
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 – 7.36 (m, 2H), 7.30 – 7.26 (m, 3H), 2.86 (t, J = 7.6 Hz, 2H), 2.36 (t, J = 6.8 Hz, 2H), 1.97 – 1.90 (m, 2H), 1.20 – 1.19 (m, 21H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 141.8, 128.6, 128.3, 125.9, 108.6, 80.7, 34.7, 30.7, 19.3, 18.7, 11.3.
LRMS (ESI+) m/z: 300.9 [M+H$^+$].

HRMS (ESI+): [M]$^+$ Calc. for $C_{20}H_{32}Si$: 300.2273; found: 300.2262.

IR: $\tilde{\nu}$ = 2940, 2862, 2361, 2342, 2172, 1462, 883, 660, 621 cm^{-1}.

Triisopropyl((9Z,12Z)-nonadeca-9,12-dien-1-yn-1-yl)silane (3i)



Compound **3i** was prepared following the general procedure, starting from $NiBr_2$(diglyme) (16.0 mg, 0.05 mmol, 0.1 equiv), 4-4′ -di-*tert*-butyl-2,2′ -bipyridine (13.4 mg, 0.05 mmol, 0.1 equiv), LiBr (43 mg, 0.5 mmol, 1 equiv), manganese (82 mg, 1.5 mmol, 3.0 equiv), 1,3-dioxoisoindolin-2-yl (10Z,13Z)-nonadeca-10,13-dienoate (330 mg, 0.75 mmol, 1.5 equiv), (bromoethynyl)triisopropylsilane (131 mg, 0.5 mmol, 1 equiv) and NMP (1.2 mL). After stirring at room temperature for 14 h, the reaction mixture was worked up and purified by flash chromatography (hexane), **3i** was obtained as colorless liquid (202.9 mg, 95% isolated yield).

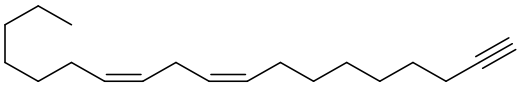
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.40 – 5.31 (m, 4H), 2.78 (t, J = 6.0 Hz, 2H), 2.25 (t, J = 6.8 Hz, 2H), 2.06(dd, J = 6.4 Hz, J = 13.2 Hz, 4H), 1.57 – 1.50 (m, 2H), 1.45 – 1.41 (m, 2H), 1.38 – 1.31 (m, 12H), 1.08 – 1.04 (m, 21H), 0.90 (t, J = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 130.2, 130.1, 128.0, 127.9, 109.3, 80.0, 31.5, 29.6, 29.4, 29.2, 29.0, 28.8, 28.7, 27.2, 25.6, 22.6, 19.8, 18.6, 14.1, 11.3.

HRMS (ESI+): [M]$^+$ Calc. for $C_{28}H_{52}Si$: 426.3838; found: 416.3823.

IR: $\tilde{\nu}$ = 2928, 2862, 2361, 2342, 1462 cm^{-1}.

(9Z,12Z)-Nonadeca-9,12-dien-1-yne (4i)



To a 25 mL round-bottom flask containing a Teflon-coated stir-bar was added $NiBr_2$(diglyme) (106 mg, 0.33 mmol, 0.1 equiv), 4-4′ -di-*tert*-butyl-2,2′ -bipyridine (88.5 mg, 0.33 mmol, 0.1 equiv). The reaction flask was sealed with a rubber septum, and the septum was fitted with a needle connected to an oil bubbler and a needle connected to an Ar manifold. The headspace of the flask was purged with Ar gas for about ten minutes and then the needle to the bubbler was removed. NMP (8 mL), was added via syringe and the resulting mixture was stirred on the benchtop (~1200 rpm) at rt under Ar. The color of the reaction mixture became blue-green. 1,3-dioxoisoindolin-2-yl (10Z,13Z)-nonadeca-10,13-dienoate (2200 mg, 5 mmol, 1.5 equiv), (bromoethynyl)triisopropylsilane (864 mg, 3.3 mmol, 1 equiv) LiBr (284 mg, 3.3 mmol, 1 equiv), and manganese (541 mg, 9.9 mmol, 3.0 equiv) were added in one portion to the reaction vessel by quickly removing the septum and replacing it. The reaction mixture was stirred at room temperature under Ar. After the reaction was judged complete by GC analysis (~14 h), the reaction mixture was filtered through a plug of silica. The pad was washed with hexane (150 mL) and concentrated. The solution was concentrated by reduced pressure. 8.5 mL of *n*-Bu_4NF(1M in THF) was added into the residue and stirred at room temperature for 24 h. The reaction mixture was filtered through a plug of silica. The pad was washed with hexane (150 mL). The resulting residue was purificated by fresh column chromatography (hexane) **4i** was obtained as colorless liquid (720 mg, 84% isolated yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.51 – 4.30 (m, 4H), 2.77 (t, J = 6.0 Hz, 2H), 2.20 – 2.16 (m, 2H), 2.05 (q, J = 6.4 Hz, 4H), 1.93 – 1.92 (m, 1H), 1.52 (quintet, J = 7.2 Hz, 2H), 1.39 – 1.31(m, 14H), 0.91 – 0.88 (m, 3H).

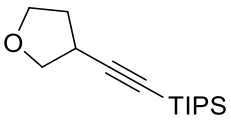
^{13}C NMR (100 MHz, $CDCl_3$): δ 130.1, 130.0, 128.0, 127.9, 84.6, 68.0, 31.5, 29.6, 29.3, 29.1, 29.0, 28.7, 28.5, 27.2, 25.6, 22.6, 18.4, 14.0.

GCMS, m/z (% relative intensity, ion): 231.25 (1), 189.20 (4), 147.15 (8), 135.10 (8), 121.10 (16), 110.15 (12), 1105.10 (31), 93.10 (39), 81.10 (59), 67.10 (100), 55.10 (41).

HRMS (ESI+): $[M]^+$ Calc. for $C_{19}H_{32}$: 260.2504; found: 260.2501.

IR: $\tilde{\nu}$ = 3310, 3009, 2924, 2855, 1462, 629 cm^{-1}.

Triisopropyl((tetrahydrofuran-3-yl)ethynyl)silane (3j)



Compound **3j** was prepared following the general procedure, starting from $NiBr_2$(diglyme) (16.0 mg, 0.05 mmol, 0.1 equiv), 4-4′ -di-*tert*-butyl-2,2′ -bipyridine (13.4 mg, 0.05 mmol, 0.1 equiv), LiBr (43 mg, 0.5 mmol, 1 equiv), manganese (82 mg, 1.5 mmol, 3.0 equiv), 1,3-dioxoisoindolin-2-yl tetrahydrofuran-3-carboxylate (196 mg, 0.75 mmol), (bromoethynyl)triisopropylsilane (131 mg, 0.5 mmol, 1 equiv) and NMP (1.2 mL). After stirring at 50 ^{o}C for 12 h, the reaction mixture was worked up and purified by flash chromatography (ethyl acetate / hexane = 1:100), **3j** was obtained as colorless liquid (91.2 mg, 73% isolated yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.02 (t, J = 8.4 Hz, 1H), 3.92 – 3.80 (m, 2H), 3.63 (d, J = 8.0 Hz, 1H), 3.01 (quintet, J = 7.6 Hz, 1H), 2.20 (sextet, J = 7.6 Hz, 1H), 1.97 (sextet, J = 6.8 Hz, 1H), 1.04 – 0.99 (m, 21H).

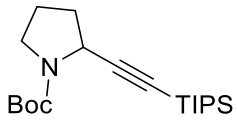
^{13}C NMR (100 MHz, $CDCl_3$): δ 109.1, 81.5, 73.6, 68.0, 34.1, 31.2, 18.6, 11.2.

GCMS, m/z (% relative intensity, ion): 252.20[M^+] (6), 209.15 (100), 181.15 (40), 153.10 (35), 139.10 (63), 123.05 (16), 109.10 (33), 183.05 (14), 75.05 (20).

HRMS (ESI+): $[M]^+$ Calc. for $C_{15}H_{28}OSi$: 252.1910; found: 252.1915.

IR: $\tilde{\nu}$ = 2943, 2866, 2164, 1462, 1069, 883, 675 cm^{-1}.

tert-Butyl 2-((triisopropylsilyl)ethynyl)pyrrolidine-1-carboxylate (3k) (cas : 1818354-91-4)[13]



Compound **3k** was prepared following the general procedure, starting from $NiBr_2$(diglyme) (16.0 mg, 0.05 mmol, 0.1 equiv), 4-4′ -di-*tert*-butyl-2,2′ -bipyridine (13.4 mg, 0.05 mmol, 0.1 equiv), LiBr (43 mg, 0.5 mmol, 1 equiv), manganese (82 mg, 1.5 mmol, 3.0 equiv), 1-(tert-butyl) 2-(1,3-dioxoisoindolin-2-yl) pyrrolidine-1,2-dicarboxylate (270 mg, 0.75 mmol, 1.5 equiv), (bromoethynyl)triisopropylsilane (131 mg, 0.5 mmol, 1 equiv) and NMP (1.2 mL). After stirring at 50 ^oC for 12 h, the reaction mixture was worked up and purified by flash chromatography (ethyl acetate / hexane = 1:10), **3k** was obtained as yellow liquid (82.8 mg, 47% isolated yield).

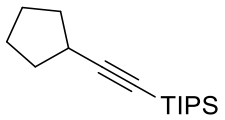
^1H NMR (400 MHz, $CDCl_3$): δ 4.55 – 4.42 (m, 1H), 3.50 – 3.45 (m, 1H), 3.35 – 3.25 (m, 1H), 2.05 – 2.00 (m, 3H), 1.92 - 1.84 (m, 1H), 1.46 (s, 9H), 1.04 – 0.98 (m, 21H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.1, 108.5, 81.5, 79.5, 48.8, 45.3, 34.2, 28.4, 23.6, 18.6, 11.1.

GCMS, m/z (% relative intensity, ion): 278.25 (4), 252.15 (100), 208.15 (14), 131.05 (15), 103.10 (9), 183.05 (7), 57.10 (9).

IR: $\tilde{\nu}$ = 2943, 2866, 2168, 1701, 1462, 1389, 1366, 1165, 1119, 1092, 952, 914, 880, 667 cm^{-1}.

(Cyclopentylethynyl)triisopropylsilane (3l) (cas: 1035794-01-4)[10]



Compound **3l** was prepared following the general procedure, starting from $NiBr_2$(diglyme) (16.0 mg, 0.05 mmol, 0.1 equiv), 4-4′ -di-*tert*-butyl-2,2′ -bipyridine (13.4 mg, 0.05 mmol, 0.1 equiv), LiBr (43 mg, 0.5 mmol, 1 equiv), manganese (82 mg, 1.5 mmol, 3.0 equiv), 1,3-dioxoisoindolin-2-yl cyclopentanecarboxylate (195 mg, 0.75 mmol, 1.5 equiv), (bromoethynyl)triisopropylsilane (131 mg, 0.5 mmol, 1 equiv) and NMP (1.2 mL). After stirring at 50 ^oC for 12 h, the reaction mixture was worked up and purified by flash chromatography (hexane), **3l** was obtained as colorless liquid (80.2 mg, 64% isolated yield).

^1H NMR (400 MHz, $CDCl_3$): δ 2.67 (quintet, J = 6.8 Hz, 1H), 1.92 – 1.87 (m, 2H), 1.77 – 1.71 (m, 2H), 1.68 – 1.63 (m, 2H), 1.59 – 1.55 (m, 2H), 1.09 – 1.02 (m, 21H).

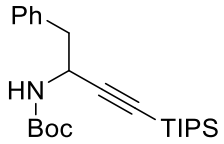
^{13}C NMR (100 MHz, $CDCl_3$): δ 114.1, 79.0, 34.2, 31.2, 24.9, 18.6, 11.3.

GCMS, m/z (% relative intensity, ion): 250.20[M^+] (100), 207.20 (74), 179.15 (30), 165.15 (49), 151.10 (62), 137.10 (100), 123.10 (13), 109.10 (19), 95.10 (21), 83.10 (18), 59.10 (21).

IR: $\tilde{\nu}$ = 2943, 2866, 2172, 1462, 675 cm^{-1}.

tert-Butyl (1-phenyl-4-(triisopropylsilyl)but-3-yn-2-yl)carbamate (3m)

[13] Vaillant, F., Courant, T., Waser, J., *Angew. Chem. Int. Ed*., **2015**, *54*, 11200–11204



Compound **3m** was prepared following the general procedure, starting from $NiBr_2$(diglyme) (16.0 mg, 0.05 mmol, 0.1 equiv), 4-4′ -di-*tert*-butyl-2,2′ -bipyridine (13.4 mg, 0.05 mmol, 0.1 equiv), LiBr (43 mg, 0.5 mmol, 1 equiv), manganese (82 mg, 1.5 mmol, 3.0 equiv), 1,3-dioxoisoindolin-2-yl (tert-butoxycarbonyl)phenylalaninate (308 mg, 0.75 mmol, 1.5 equiv), (bromoethynyl)triisopropylsilane (131 mg, 0.5 mmol, 1 equiv) and NMP (1.2 mL). After stirring at 50 °C for 12 h, the reaction mixture was worked up and purified by flash chromatography (ethyl acetate / hexane = 1:10), **3m** was obtained as light yellow liquid (82.4 mg, 41% isolated yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 – 7.22 (m, 5H), 4.68 (s, 1H), 3.01 (dd, J = 3.6 Hz, J = 12.8 Hz, 1H), 3.01 (dd, J = 3.6 Hz, J = 12.8 Hz, 1H), 2.91 (dd, J = 7.6 Hz, J = 12.8 Hz, 1H), 1.44 (s, 9H), 1.05 – 0.99 (m, 21H).

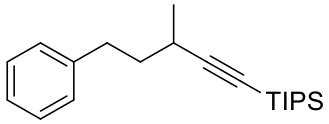
^{13}C NMR (100 MHz, $CDCl_3$): δ 154.6, 136.6, 129.9, 128.1, 126.7, 106.3, 84.8, 79.8, 44.9, 41.9, 28.3, 18.5, 11.1.

LRMS (ESI+) m/z: 424.0 [M+Na^+].

HRMS (ESI+): $[M]^+$ Calc. for $C_{24}H_{39}NO_2Si$: 402.2835; found: 402.2828.

IR: $\tilde{\nu}$ = 3333, 2943, 2866, 2361, 2342, 1705, 1489, 1466, 1366, 1339, 1242, 1165, 1018, 883, 675 cm^{-1}.

Triisopropyl(3-methyl-5-phenylpent-1-yn-1-yl)silane (3n) (cas: 1394826-25-5)[14]



Compound **3n** was prepared following the general procedure, starting from $NiBr_2$(diglyme) (16.0 mg, 0.05 mmol, 0.1 equiv), 4-4′ -di-*tert*-butyl-2,2′ -bipyridine (13.4 mg, 0.05 mmol, 0.1 equiv), LiBr (43 mg, 0.5 mmol, 1 equiv), manganese (82 mg, 1.5 mmol, 3.0 equiv), 1,3-dioxoisoindolin-2-yl 2-methyl-4-phenylbutanoate (242 mg, 0.75 mmol, 1.5 equiv), (bromoethynyl)triisopropylsilane (131 mg, 0.5 mmol, 1 equiv) and NMP (1.2 mL). After stirring at 50 °C for 12 h, the reaction mixture was worked up and purified by flash chromatography (hexane), **3n** were obtained as colorless liquid (110.3 mg, 70% isolated yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 – 7.31 (m, 2H), 7.26 – 7.21 (m, 3H), 2.95 – 2.88 (m, 1H), 2.82 – 2.75 (m, 1H), 2.56 – 2.47 (m, 1H), 1.77 (q, J = 7.6 Hz, 2H), 1.25 (d, J = 6.8 Hz, 3H), 1.15 – 1.14 (m, 21H).

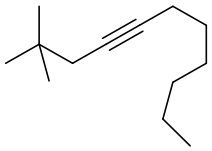
^{13}C NMR (100 MHz, $CDCl_3$): δ 142.2, 128.5, 128.3, 125.7, 113.4, 80.3, 39.1, 33.7, 26.5, 21.3, 18.7, 11.3.

GCMS, m/z (% relative intensity, ion): 271.20 (100), 243.15 (19), 229.15 (34), 201.10 (22), 125.10 (7), 109.05 (8), 91.05 (16), 73.05 (11), 59.05 (16).

IR: $\tilde{\nu}$ = 3939, 2862, 2361, 2342, 2164, 1458, 748 cm^{-1}.

2,2-Dimethylundec-4-yne (3o)

[14] Cheung, C. W., Ren, P., Hu, X., *Org. Lett.,* **2014**, *16*, 2566–2569



Compound **3o** was prepared following the general procedure, starting from $NiBr_2$(diglyme) (16.0 mg, 0.05 mmol, 0.1 equiv), 4-4′ -di-*tert*-butyl-2,2′ -bipyridine (13.4 mg, 0.05 mmol, 0.1 equiv), LiBr (43 mg, 0.5 mmol, 1 equiv), manganese (82 mg, 1.5 mmol, 3.0 equiv), 1,3-dioxoisoindolin-2-yl 3,3-dimethylbutanoate (197 mg, 0.75 mmol, 1.5 equiv), 1-bromooct-1-yne (94 mg, 0.5 mmol, 1 equiv) and NMP (1.8 mL). After stirring at room temperature for 12 h, the reaction mixture was worked up and purified by flash chromatography (hexane), **3o** was obtained as colorless liquid (63.4 mg, 71% isolated yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.16 (t, J = 5.2 Hz, 1H), 2.01 (s, 2H), 1.49 (quintet, J = 6.8 Hz, 2H), 1.39 (quintet, J = 6.8 Hz, 2H), 1.32 – 1.25 (m, 4H), 0.97 (s, 9H), 0.89 (t, J = 6.8 Hz, 3H).

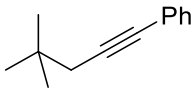
^{13}C NMR (100 MHz, $CDCl_3$): δ 81.7, 78.4, 33.9, 31.4, 31.1, 29.2, 28.9, 28.5, 22.6, 18.8, 14.0.

GCMS, m/z (% relative intensity, ion): 180.25[M^+] (0.1), 137.15 (2), 110.15 (13), 95.15 (16), 81.10 (9), 57.15 (100).

HRMS (ESI+): $[M-H]^+$ Calc. for $C_{13}H_{23}$: 179.1800; found: 179.1801.

IR: $\tilde{\nu}$ = 2924, 2855 cm^{-1}.

(4,4-Dimethylpent-1-yn-1-yl)benzene (3p) (cas: 42497-81-4)[15]



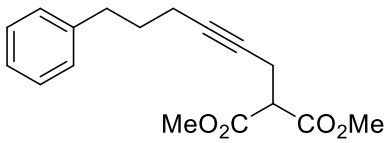
Compound **3p** was prepared following the general procedure, starting from $NiBr_2$(diglyme) (16.0 mg, 0.05 mmol, 0.1 equiv), 4-4′ -di-*tert*-butyl-2,2′ -bipyridine (13.4 mg, 0.05 mmol, 0.1 equiv), LiBr (43 mg, 0.5 mmol, 1 equiv), manganese (82 mg, 1.5 mmol, 3.0 equiv), 1,3-dioxoisoindolin-2-yl 3,3-dimethylbutanoate (197 mg, 0.75 mmol, 1.5 equiv), (bromoethynyl)benzene (90 mg, 0.5 mmol, 1 equiv) and NMP (1.8 mL). After stirring at room temperature for 12 h, the reaction mixture was worked up and purified by flash chromatography (hexane), **3p** was obtained as colorless liquid (53.7 mg, 62% isolated yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 – 7.41 (m, 2H), 7.29 – 7.28 (m, 3H), 2.29 (s, 2H), 1.07 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 131.5, 128.2, 127.4, 124.2, 88.8, 82.1, 34.4, 31.4, 29.1.

GCMS, m/z (% relative intensity, ion): 172.15[M^+] (28), 157.10 (18), 116.10 (68), 89.05 (8), 57.10 (100).

IR: $\tilde{\nu}$ = 2955, 2928, 2904, 2870, 2827, 691 cm^{-1}.

Dimethyl 2-(6-phenylhex-2-yn-1-yl)malonate (3q)



Compound **3q** was prepared following the general procedure, starting from $NiBr_2$(diglyme) (16.0 mg, 0.05 mmol, 0.1 equiv), 4-4′ -di-*tert*-butyl-2,2′ -bipyridine (13.4 mg, 0.05 mmol, 0.1 equiv), LiBr (43

[15] Inoue, H., Tsubouchi, H., Nagaoka, Y., Tomioka, K., *Tetrahedron*, **2002**, *58*, 83-90

mg, 0.5 mmol, 1 equiv), manganese (82 mg, 1.5 mmol, 3.0 equiv), 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate (232 mg, 0.75 mmol, 1.5 equiv), dimethyl 2-(3-bromoprop-2-yn-1-yl)malonate (124 mg, 0.5 mmol, 1 equiv) and NMP (1.8 mL). After stirring at room temperature for 14 h, the reaction mixture was worked up and purified by flash chromatography (ethyl acetate / hexane = 1:20), **3q** was obtained as colorless liquid (102.6 mg, 71% isolated yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 – 7.26 (m, 2H), 7.19 – 7.17 (m, 3H), 3.76 (s, 6H), 3.59 (t, J = 7.6 Hz, 1H), 2.78 (d, J = 8.0 Hz, 2H), 2.68 (t, J = 7.2 Hz, 2H), 2.15 – 2.12 (m, 2H), 1.80 – 1.73 (m, 2H).

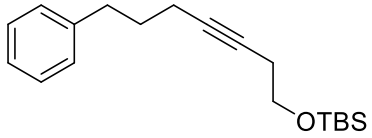
^{13}C NMR (100 MHz, $CDCl_3$): δ 168.6, 141.6, 128.5, 128.3, 125.8, 82.2, 76.0, 52.7, 51.5, 34.5, 30.3, 18.9, 18.0.

GCMS, m/z (% relative intensity, ion): 288[M^+] (2), 260.10 (8), 229.15 (9), 184.10 (19), 169.10 (38), 156.15 (43), 141.10 (29), 129.10 (24), 104.10 (100), 91.10 (58), 77.05 (17), 65.10 (21), 59.05 (10).

HRMS (ESI+): $[M]^+$ Calc. for $C_{17}H_{20}O_4$: 288.1362; found: 288.1362.

IR: $\tilde{\nu}$ = 2361, 2342, 1736, 748 cm^{-1}.

tert-Butyldimethyl((7-phenylhept-3-yn-1-yl)oxy)silane (3r) (cas: 1208491-82-0)[16]



Compound **3r** was prepared following the general procedure, starting from $NiBr_2$(diglyme) (16.0 mg, 0.05 mmol, 0.1 equiv), 4-4′ -di-*tert*-butyl-2,2′ -bipyridine (13.4 mg, 0.05 mmol, 0.1 equiv), LiBr (43 mg, 0.5 mmol, 1 equiv), manganese (82 mg, 1.5 mmol, 3.0 equiv), 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate (232 mg, 0.75 mmol, 1.5 equiv), ((4-bromobut-3-yn-1-yl)oxy)(tert-butyl)dimethylsilane (131 mg, 0.5 mmol, 1 equiv) and NMP (1.8 mL). After stirring at room temperature for 14 h, the reaction mixture was worked up and purified by flash chromatography (ethyl acetate / hexane = 1: 100), **3r** was obtained as colorless liquid (114.2 mg, 76% isolated yield).

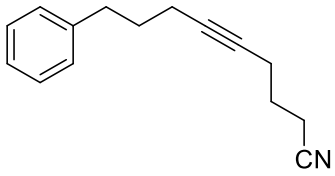
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 – 7.28 (m, 2H), 7.22 – 7.20 (m, 3H), 3.75 – 3.70 (m, 2H), 2.75 – 2.72 (m, 2H), 1.86 – 1.78 (m, 2H), 1.74 – 1.71 (m, 2H), 0.93 – 0.92 (m, 9H), 0.09 – 0.08 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 141.8, 128.5, 128.3, 125.8, 80.2, 79.8, 61.7, 34.8, 32.2, 30.7, 25.9, 18.3, 18.2, 15.2, -5.3.

GCMS, m/z (% relative intensity, ion): 259.20 (51), 183.15 (69), 157.10 (43), 141.10 (21), 129.10 (18), 117.10 (10), 105.10 (10), 101.05 (35), 91.10 (54), 75.05 (100), 59.10 (17).

IR: $\tilde{\nu}$ = 2928, 2858, 2361, 2342, 1462, 1254, 1103, 833, 775, 744, 698 cm^{-1}.

9-Phenylnon-5-ynenitrile (3s) (cas: 1360871-38-0)[17]



Compound **3s** was prepared following the general procedure, starting from $NiBr_2$(diglyme) (16.0 mg, 0.05 mmol, 0.1 equiv), 4-4′ -di-*tert*-butyl-2,2′ -bipyridine (13.4 mg, 0.05 mmol, 0.1 equiv), LiBr (43 mg, 0.5 mmol, 1 equiv), manganese (82 mg, 1.5 mmol, 3.0 equiv), 1,3-dioxoisoindolin-2-yl 4-

[16] Smith, S. M., Takacs, J. M., *J. Am. Chem. Soc.,* **2010**, 132, 1740–1741
[17] Vechorkin, O., Godinat, A., Scopelliti, R., Hu, X., *Angew. Chem. Int. Ed.*, **2011**, *50*, 11777-11781

phenylbutanoate (232 mg, 0.75 mmol, 1.5 equiv), 6-bromohex-5-ynenitrile (86 mg, 0.5 mmol, 1 equiv) and NMP (1.8 mL). After stirring at room temperature for 14 h, the reaction mixture was worked up and purified by flash chromatography (ethyl acetate / hexane = 1:50), **3s** was obtained as colorless liquid (66.1 mg, 62% isolated yield).

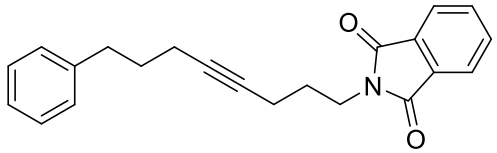
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 – 7.28 (m, 2H), 7.21 – 7.18 (m, 3H), 2.71 (t, J = 7.6 Hz, 2H), 2.49 (t, J = 7.2 Hz, 2H), 2.36 (t, J = 6.4 Hz, 2H), 2.18 (t, J = 7.2 Hz, 2H), 1.88 – 1.78 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 141.5, 128.4, 128.3, 125.8, 119.3, 81.9, 77.6, 34.8, 30.4, 24.9, 18.1, 17.9, 16.0.

LRMS (ESI+) m/z: 211.8 [M+H$^+$].

IR: $\tilde{\nu}$ = 2361, 2342 cm^{-1}.

2-(8-Phenyloct-4-yn-1-yl)isoindoline-1,3-dione (3t) (cas: 1473424-50-8)[18]



Compound **3t** was prepared following the general procedure, starting from $NiBr_2$(diglyme) (16.0 mg, 0.05 mmol, 0.1 equiv), 4-4′ -di-*tert*-butyl-2,2′ -bipyridine (13.4 mg, 0.05 mmol, 0.1 equiv), LiBr (43 mg, 0.5 mmol, 1 equiv), manganese (82 mg, 1.5 mmol, 3.0 equiv), 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate (232 mg, 0.75 mmol, 1.5 equiv), 2-(5-bromopent-4-yn-1-yl)isoindoline-1,3-dione (146 mg, 0.5 mmol, 1 equiv) and NMP (1.8 mL). After stirring at room temperature for 14 h, the reaction mixture was worked up and purified by flash chromatography (ethyl acetate / hexane = 1:10), **3t** was obtained as yellow liquid (81.0 mg, 49% isolated yield).

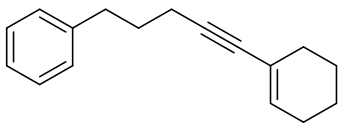
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09 – 7.07 (m 2H), 6.99 – 6.92 (m, 2H), 6.53 (t, J = 7.6 Hz, 2H), 6.44 – 6.42 (m, 3H), 3.06 (t, J = 7.2 Hz, 2H), 1.92 (t, J = 7.6 Hz, 2H), 1.52 (t, J = 6.4 Hz, 2H), 1.28 (t, J = 6.4 Hz, 2H), 1.92 (t, J = 7.6 Hz, 2H), 1.19 – 1.26 (m, 2H), 1.00 – 0.93 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 141.7, 133.8, 132.1, 128.5, 128.2, 125.7, 123.1, 80.5, 79.2, 37.3, 34.7, 30.4, 27.7, 18.0, 16.6.

LRMS (ESI+) m/z: 331.8 [M+H$^+$], 363.9 [M+Na$^+$].

IR: $\tilde{\nu}$ = 2936, 2361, 2342, 1771, 1709, 1396, 1026, 718 cm^{-1}.

(5-(Cyclohex-1-en-1-yl)pent-4-yn-1-yl)benzene (3u)



Compound **3u** was prepared following the general procedure, starting from $NiBr_2$(diglyme) (16.0 mg, 0.05 mmol, 0.1 equiv), 4-4′ -di-*tert*-butyl-2,2′ -bipyridine (13.4 mg, 0.05 mmol, 0.1 equiv), LiBr (43 mg, 0.5 mmol, 1 equiv), manganese (82 mg, 1.5 mmol, 3.0 equiv), 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate (232 mg, 0.75 mmol, 1.5 equiv), 1-(bromoethynyl)cyclohex-1-ene (92 mg, 0.5 mmol, 1 equiv) and NMP (1.8 mL). After stirring at room temperature for 14 h, the reaction mixture was worked up and purified by flash chromatography (hexane), **3u** was obtained as colorless liquid (75.7 mg, 67% isolated yield).

[18] Shu, C., Chen, C.-B., Chen, W.-X., Ye, L.-W., *Org. Lett.,* **2013**, *15*, 5542–5545

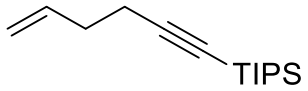
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (q, J = 7.6 Hz, 2H), 7.30 – 7.26 (m, 3H), 6.13 (s, 1H), 2.83 (t, J = 7.6 Hz, 2H), 2.41 (t, J = 6.8 Hz, 2H), 2.22 – 2.17 (m, 4H), 1.97 – 1.90 (m, 2H), 1.74 – 1.64 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.7, 133.3, 128.5, 128.3, 125.8, 121.0, 86.8, 82.9, 34.8, 30.5, 29.6, 25.5, 22.4, 21.6, 18.7.

LRMS (ESI+) m/z: 224.9 [M+H$^+$].

HRMS (ESI+): [M]$^+$ Calc. for $C_{17}H_{20}$: 224.1565; found: 224.1563.

IR: $\tilde{\nu}$ = 3024, 2928, 2859, 2835, 2361, 2342, 1450, 1346, 741, 698 cm^{-1}.

Hex-5-en-1-yn-1-yltriisopropylsilane (3v) (CAS: 1786446-56-7)[19]



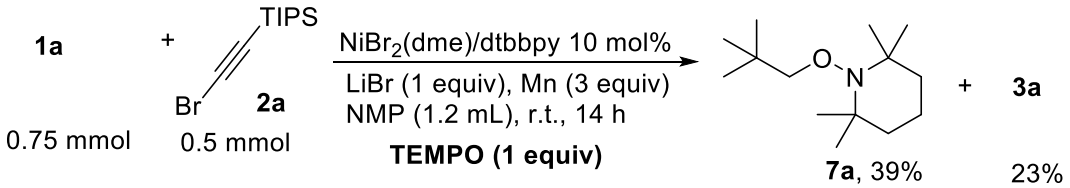
Compound **3v** was prepared following the general procedure, starting from $NiBr_2$(diglyme) (16.0 mg, 0.05 mmol, 0.1 equiv), 4-4′ -di-*tert*-butyl-2,2′ -bipyridine (13.4 mg, 0.05 mmol, 0.1 equiv), LiBr (43 mg, 0.5 mmol, 1 equiv), manganese (82 mg, 1.5 mmol, 3.0 equiv), 1,3-dioxoisoindolin-2-yl 2-cyclopropylacetate (184 mg, 0.75 mmol, 1.5 equiv), (bromoethynyl)triisopropylsilane (131 mg, 0.5 mmol, 1 equiv) and NMP (1.2 mL). After stirring at room temperature for 14 h, the reaction mixture was worked up and purified by flash chromatography (hexane), **3v** was obtained as colorless liquid (77.2 mg, 65% isolated yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.88 (ddt, J = 6.7, 10.3, 17.1 Hz, 1H), 5.10 – 5.05 (dd, J = 0.8, 16.8 Hz, 1H), 5.01 – 5.00 (m, 1H), 2.36 – 2.25 (m, 4H), 1.08 – 1.03 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.3 (3C), 18.6 (6C), 19.8, 33.2, 80.6, 108.3, 115.6, 139.6.

GCMS, m/z (% relative intensity, ion): 236.20 (1), 193.20 (100), 165.20 (35), 151.15 (20), 137.15 (34), 123.10 (62), 109.10 (36), 95.10 (37), 83.05 (18), 73.10 (16), 59.10 (44).

IR: $\tilde{\nu}$ = 2944, 2866, 2361, 2341, 2172, 1462, 1242, 995, 914, 883, 660 cm^{-1}.

2,2,6,6-Tetramethyl-1-(neopentyloxy)piperidine (7a)



Compound **7a** was prepared following the general procedure, starting from $NiBr_2$(diglyme) (16.0 mg, 0.05 mmol, 0.1 equiv), 4-4′ -di-*tert*-butyl-2,2′ -bipyridine (13.4 mg, 0.05 mmol, 0.1 equiv), LiBr (43 mg, 0.5 mmol, 1 equiv), manganese (82 mg, 1.5 mmol, 3.0 equiv), 1,3-dioxoisoindolin-2-yl 3,3-dimethylbutanoate (196 mg, 0.75 mmol, 1.5 equiv), (bromoethynyl)triisopropylsilane (131 mg, 0.5 mmol, 1 equiv), TEMPO (78 mg, 0.5 mmol, 1 equiv) and NMP (1.2 mL). After stirring at room temperature for 14 h, the reaction mixture was worked up and purified by flash chromatography (hexane). Product **7a** was obtained as colorless liquid (43 mg, 39% isolated yield) and **3a** (29 mg, 23% isolated yield) was also isolated.

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.45 (s, 2H), 1.47 – 1.42 (m, 2H), 1.30 – 1.26 (m, 4H), 1.15 (s, 6H), 1.12 – 1.03 (s, 6H), 0.94 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 88.7, 60.0, 39.7, 33.1, 27.0, 20.2, 17.1, 14.1.

[19] Nakagawa, N., Hatakeyama, T., Nakamura, M., *Chem. Lett*, **2015**, *44*, 486–488.

GCMS, m/z (% relative intensity, ion): 227.25 (2), 219.05 (8), 212.25 (9), 163.00 (9), 148.95 (11), 142.20 (100), 109.15 (8), 69.10 (8), 55.10 (8).

IR: $\tilde{\nu}$ = 2947, 2931, 2870, 2361, 2342, 1466, 1362, 1261, 1134, 1069, 1014, 918 cm^{-1}.

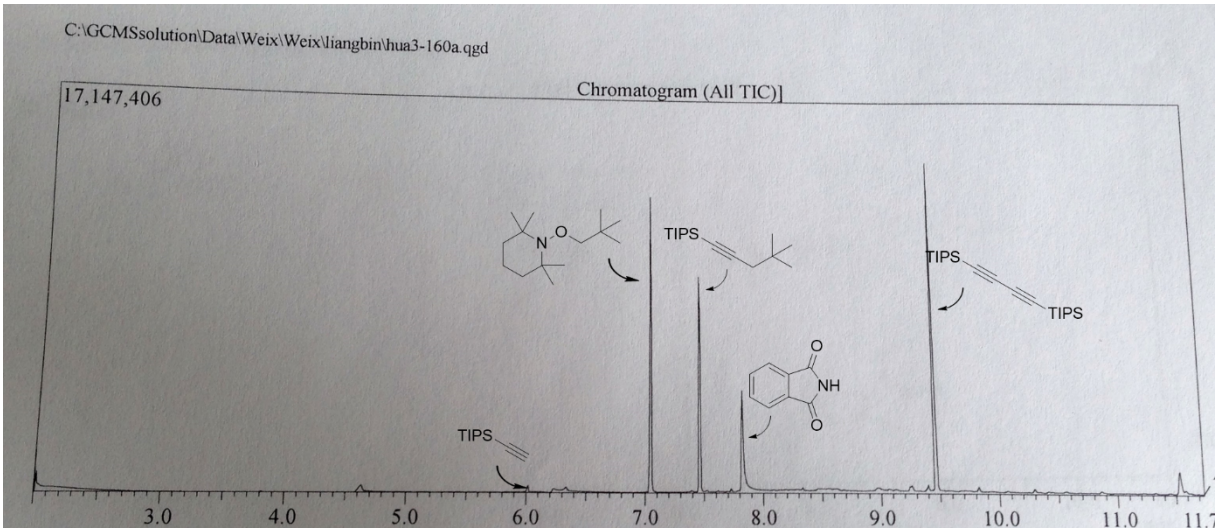
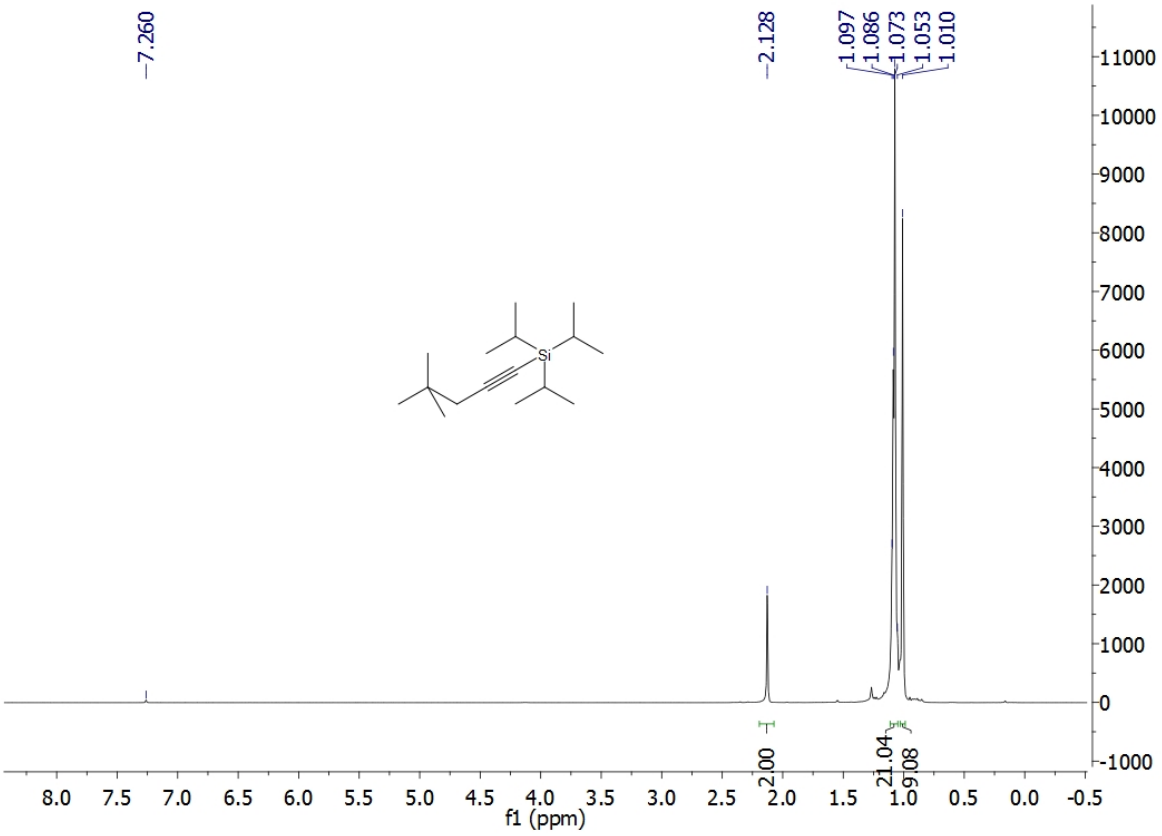


Figure 21. Gas chromatogram from the TEMPO control experiment.

VI. Copies of NMR Spectra

3a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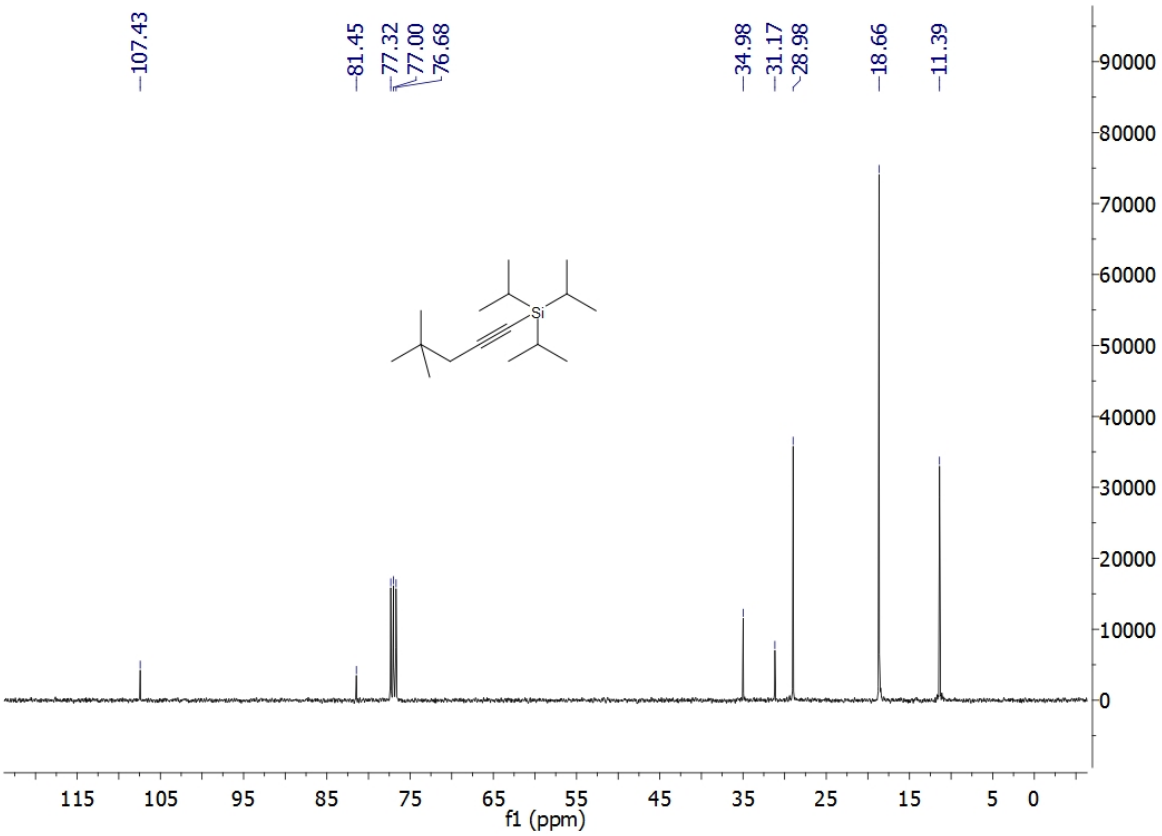
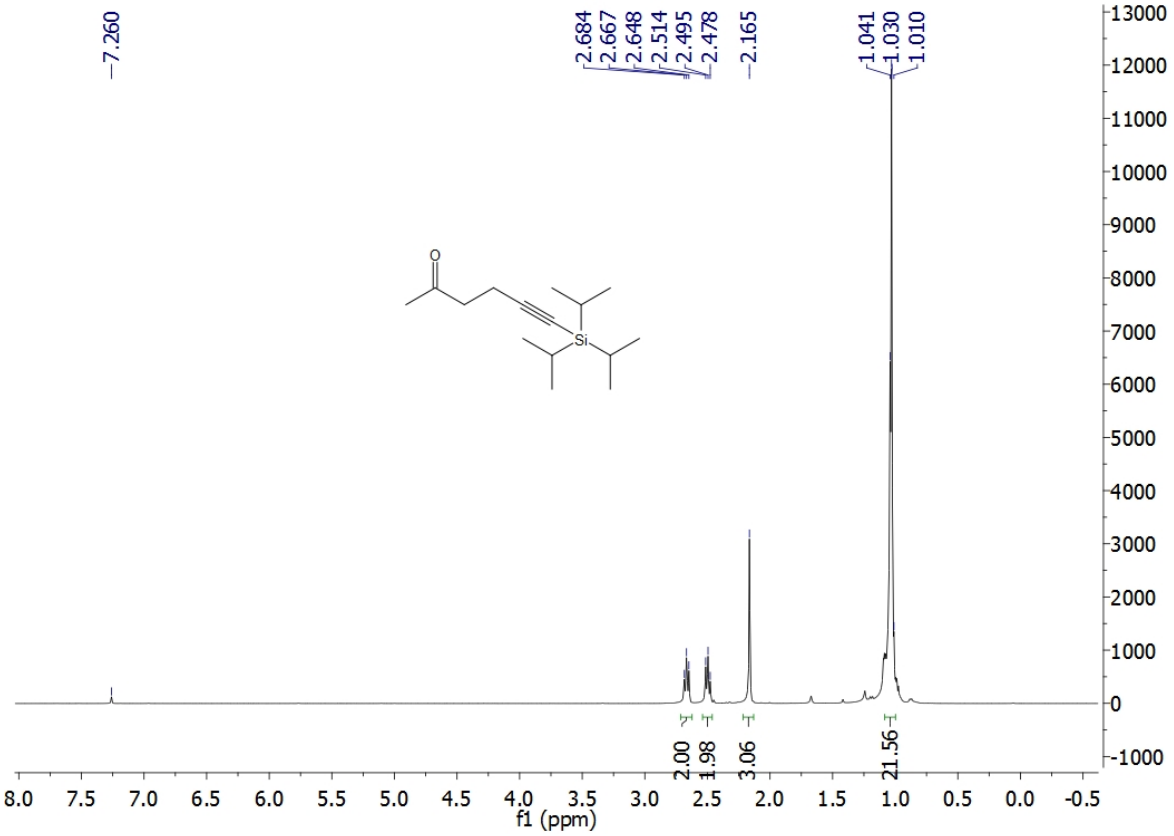
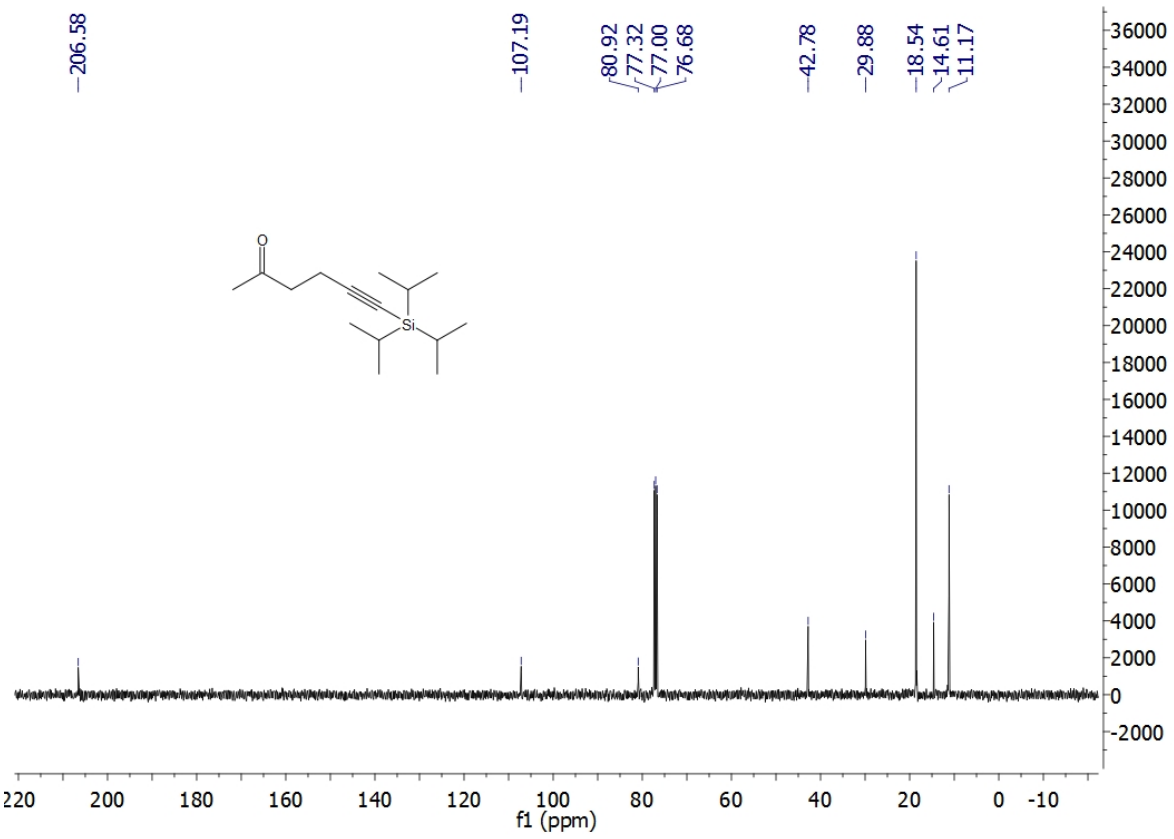
2.128
1.097
1.086
1.073
1.053
1.010
Si
2.00
21.04
9.08
f1 (ppm)

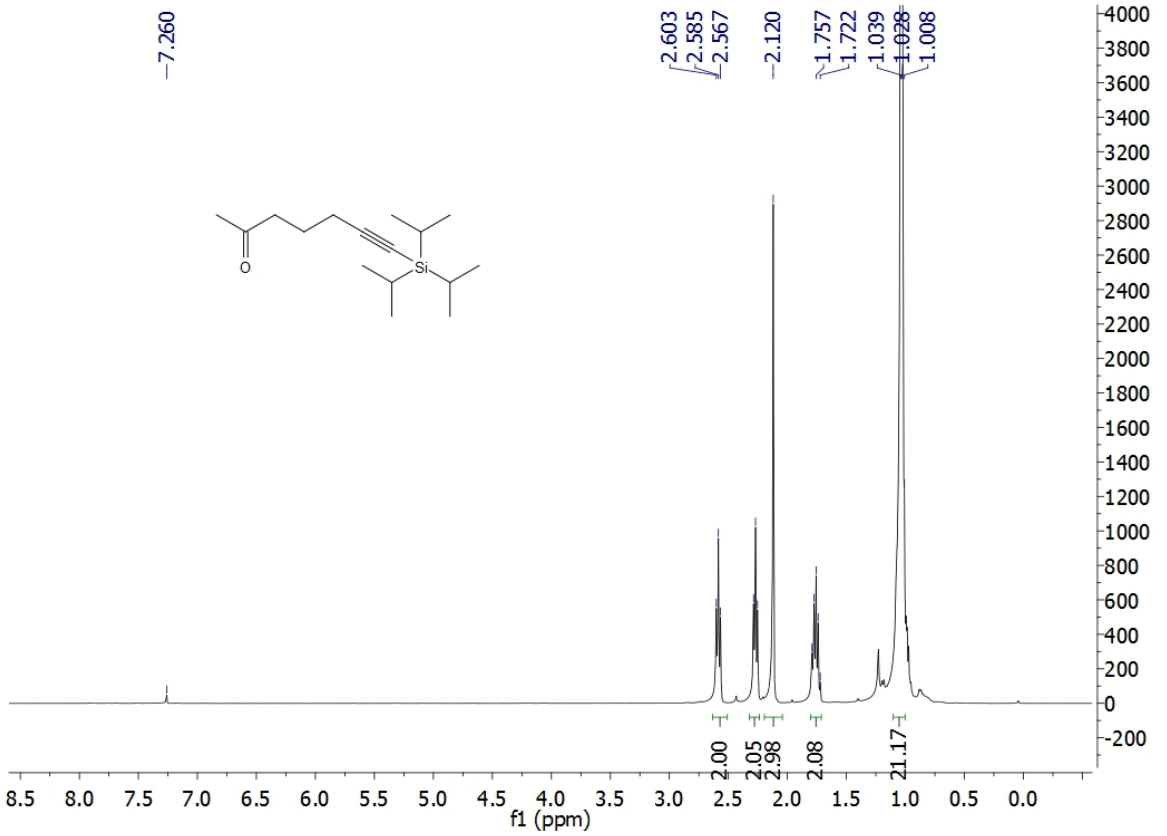

107.43
81.45
77.32
77.00
76.68
34.98
31.17
28.98
18.66
11.39
Si
f1 (ppm)

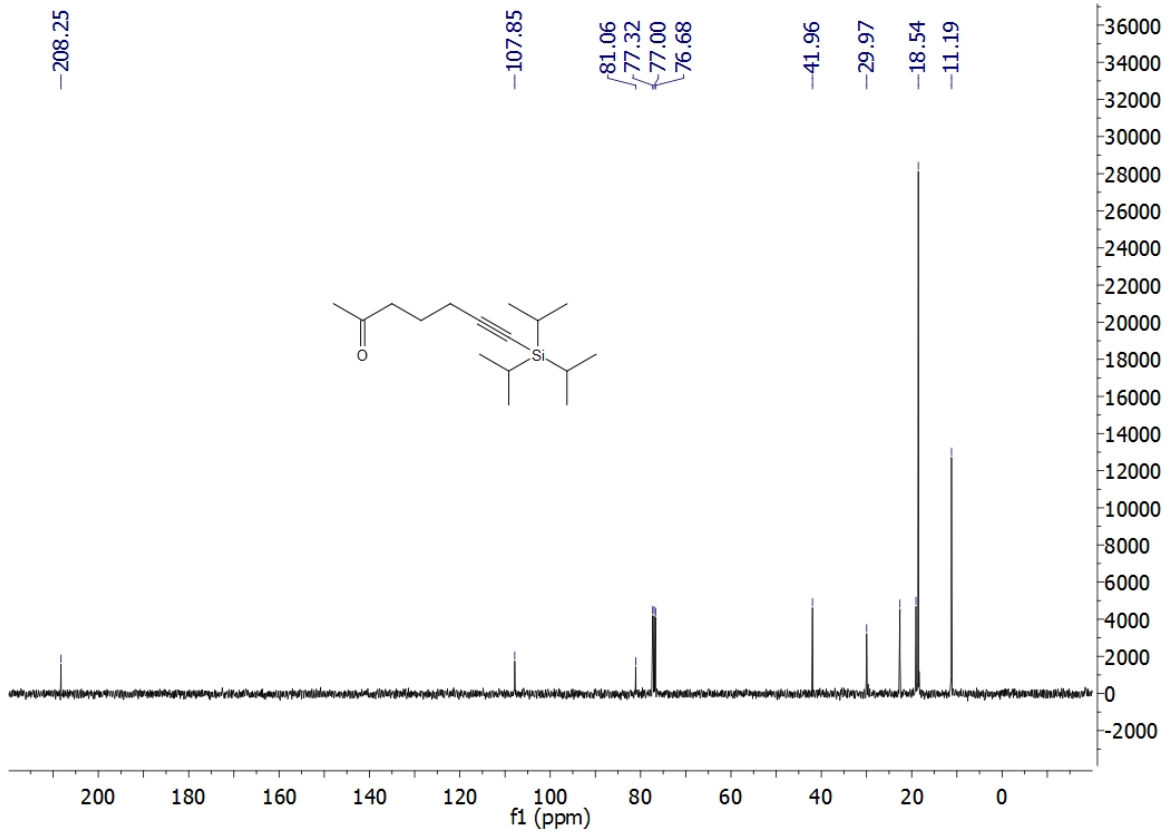
3b


7.260
2.684
2.667
2.648
2.514
2.495
2.478
2.165
1.041
1.030
1.010
2.00
1.98
3.06
21.56
f1 (ppm)

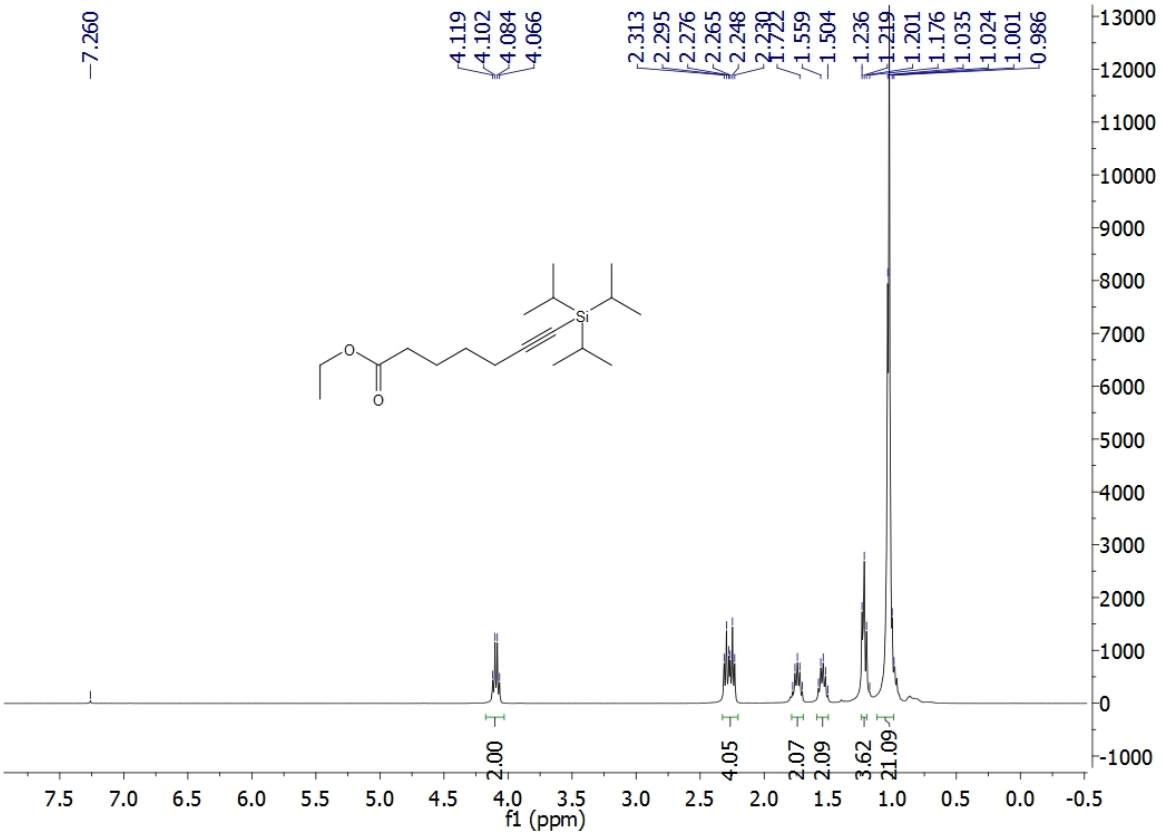

206.58
107.19
80.92
77.32
77.00
76.68
42.78
29.88
18.54
14.61
11.17
f1 (ppm)

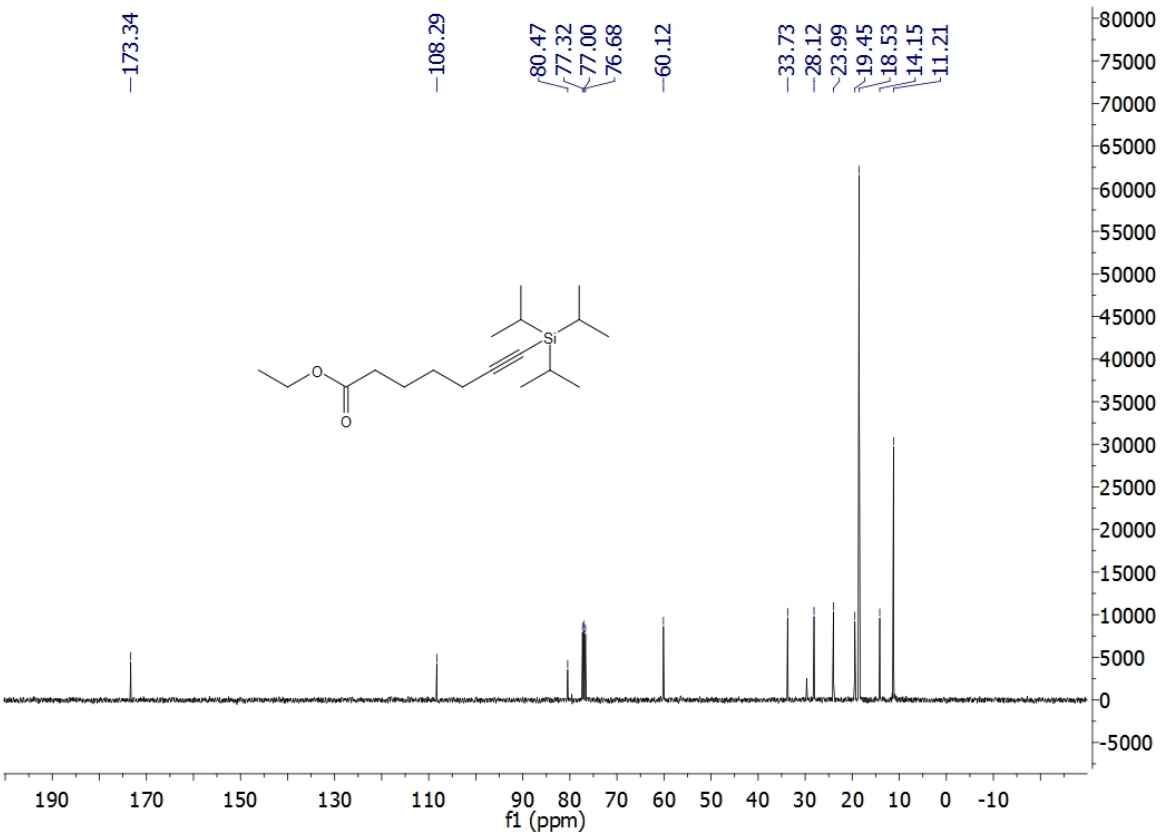
3c


7.260
2.603
2.585
2.567
2.120
1.757
1.722
1.039
1.028
1.008
O
Si
2.00
2.05
2.98
2.08
21.17
f1 (ppm)

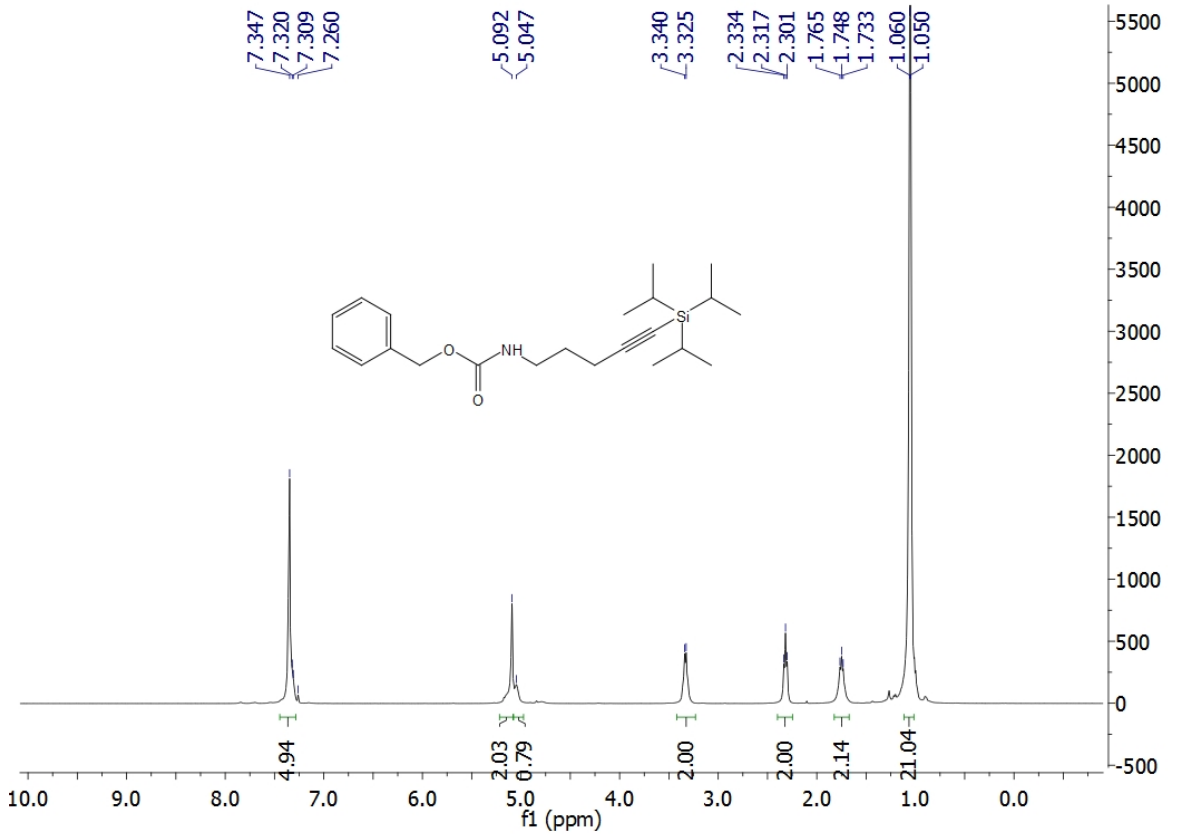

208.25
107.85
81.06
77.32
77.00
76.68
41.96
29.97
18.54
11.19
O
Si
f1 (ppm)

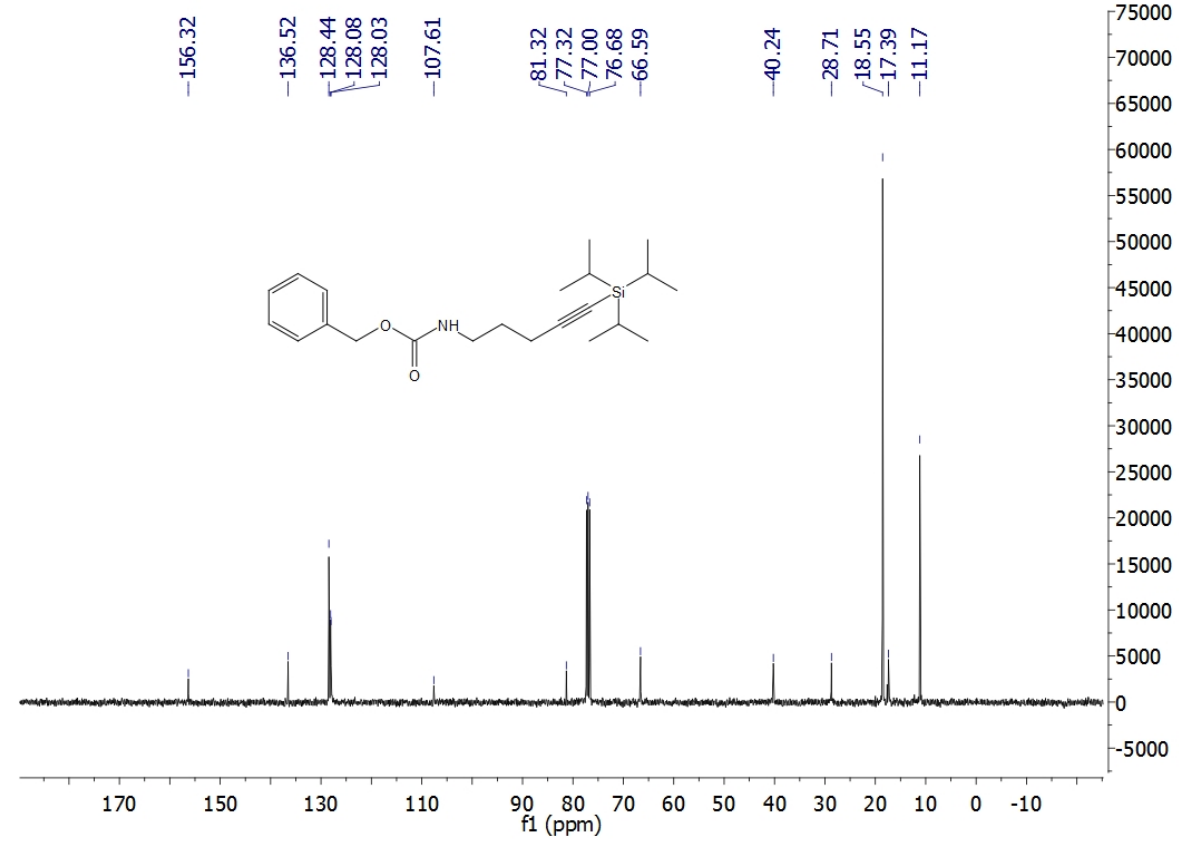
3d


7.260
4.119
4.102
4.084
4.066
2.313
2.295
2.276
2.265
2.248
2.230
1.722
1.559
1.504
1.236
1.219
1.201
1.176
1.035
1.024
1.001
0.986
2.00
4.05
2.07
2.09
3.62
21.09
f1 (ppm)

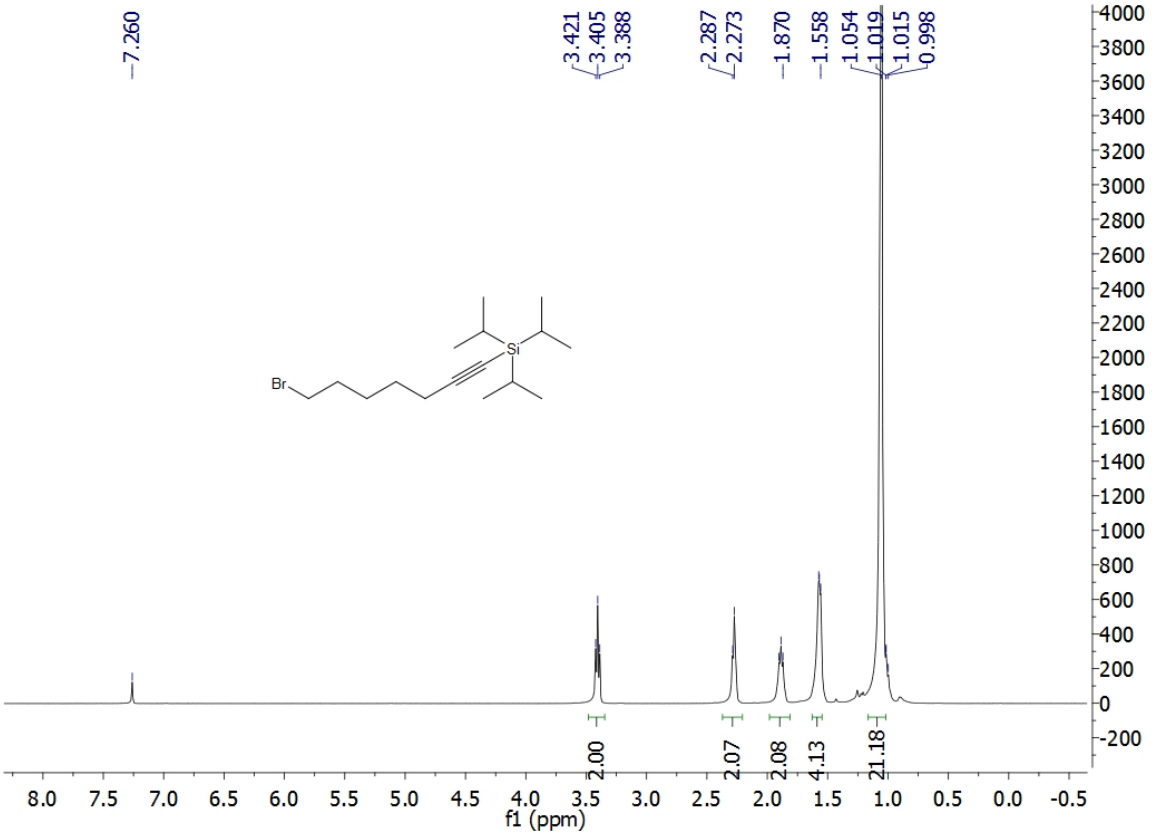

173.34
108.29
80.47
77.32
77.00
76.68
60.12
33.73
28.12
23.99
19.45
18.53
14.15
11.21
f1 (ppm)

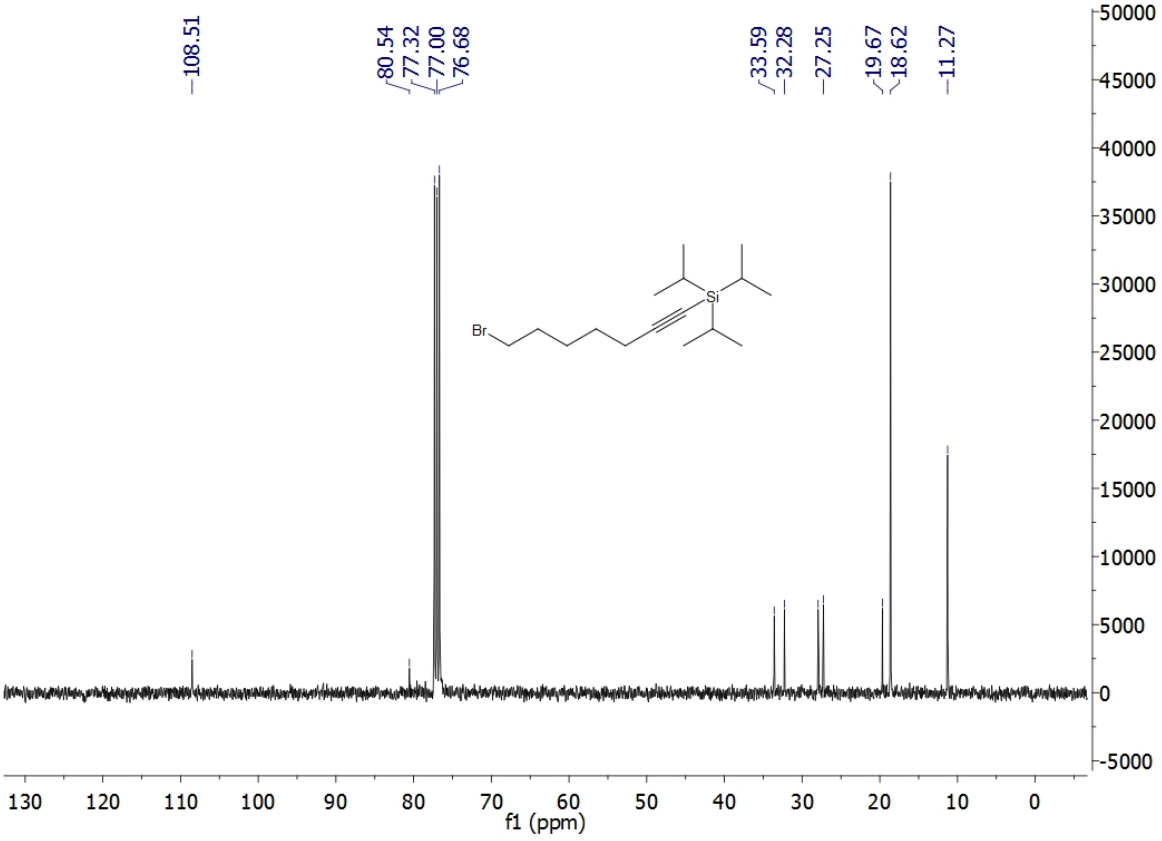
3e


7.347
7.320
7.309
7.260
5.092
5.047
3.340
3.325
2.334
2.317
2.301
1.765
1.748
1.733
1.060
1.050
Si
NH
O
4.94
2.03
6.79
2.00
2.00
2.14
21.04
f1 (ppm)

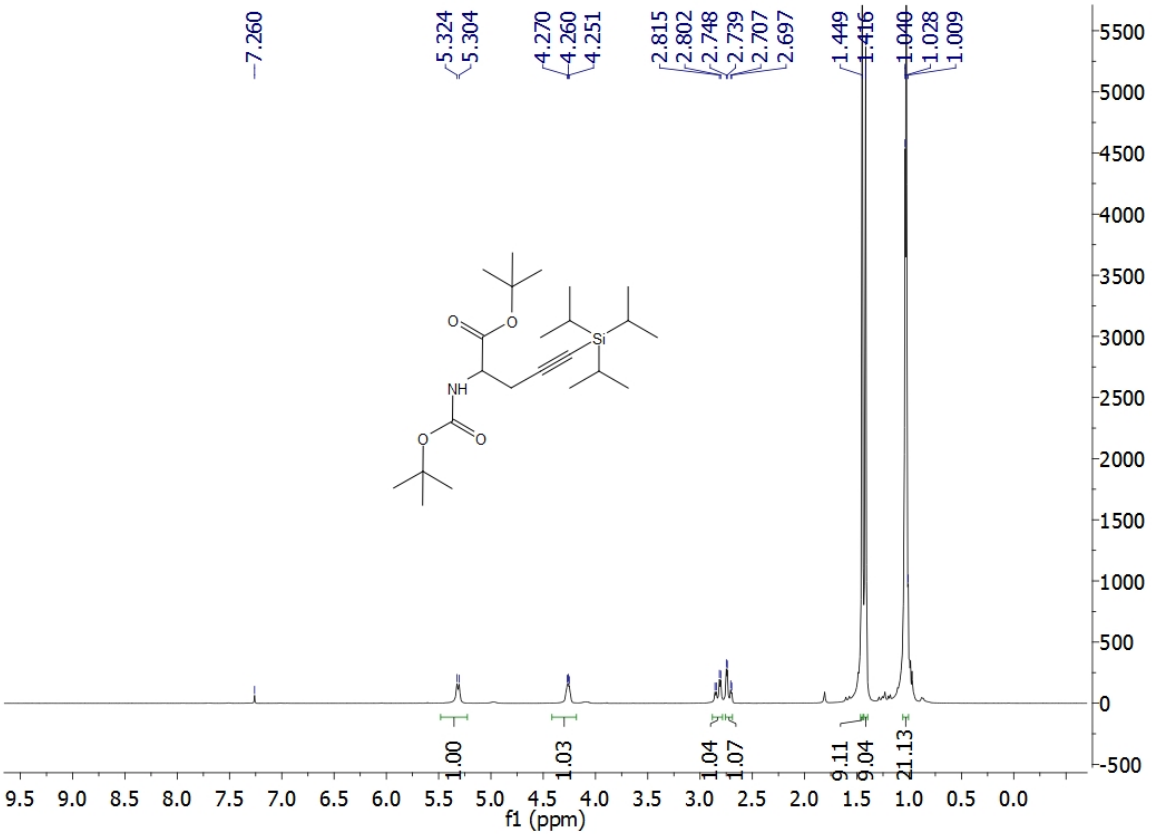

156.32
136.52
128.44
128.08
128.03
107.61
81.32
77.32
77.00
76.68
66.59
40.24
28.71
18.55
17.39
11.17
Si
NH
O
f1 (ppm)

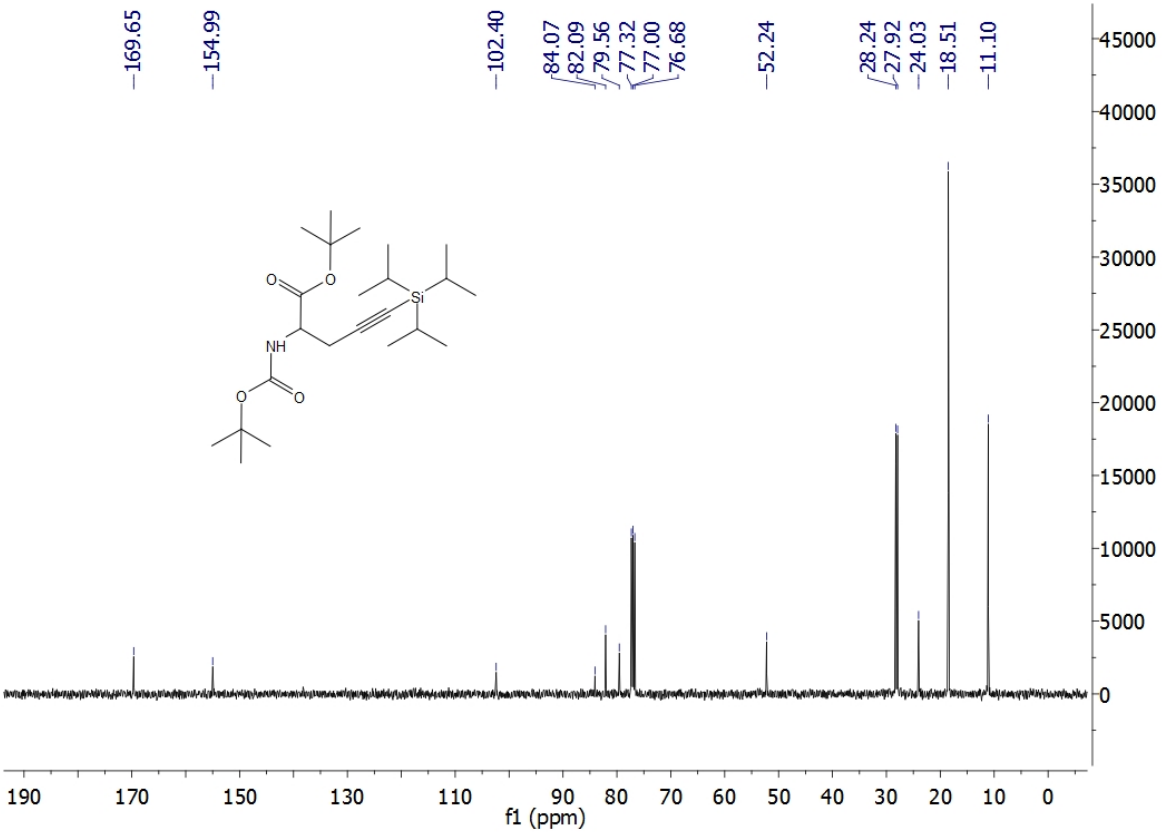
3f


7.260
3.421
3.405
3.388
2.287
2.273
1.870
1.558
1.054
1.019
1.015
0.998
Br
Si
2.00
2.07
2.08
4.13
21.18
f1 (ppm)

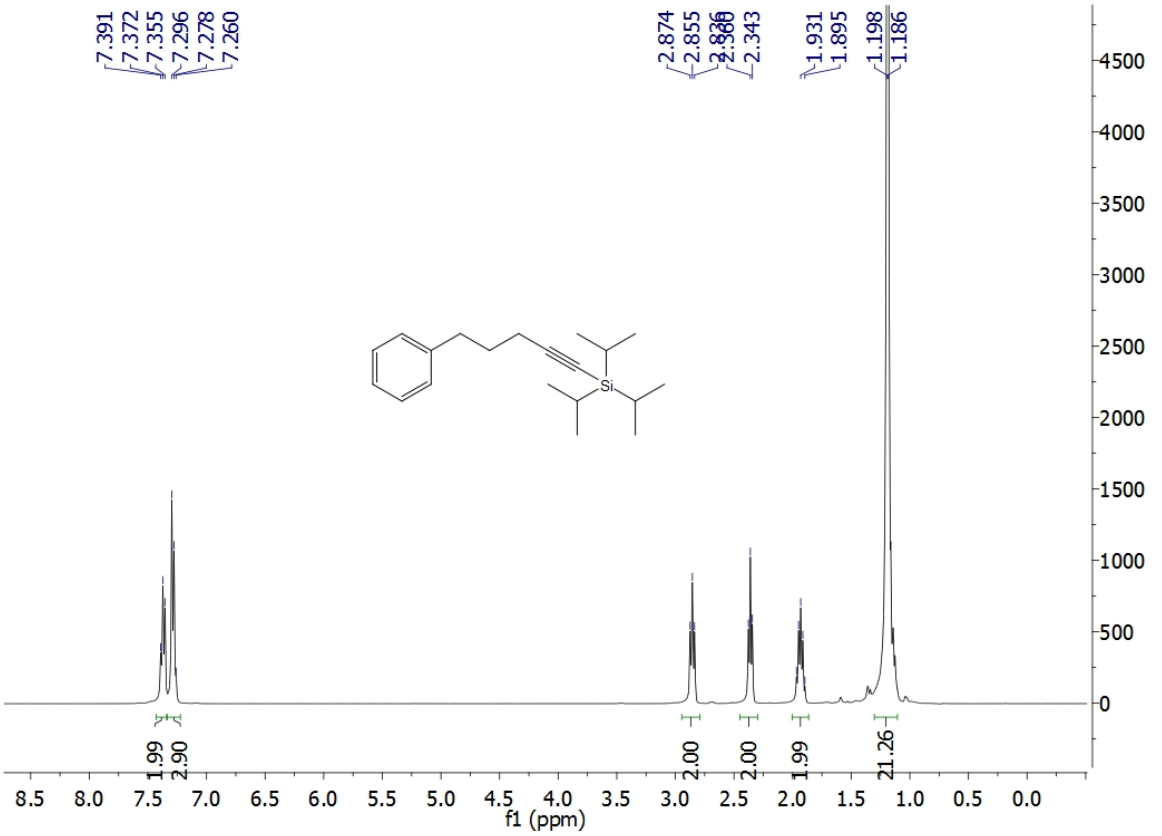

108.51
80.54
77.32
77.00
76.68
33.59
32.28
27.25
19.67
18.62
11.27
Br
Si
f1 (ppm)

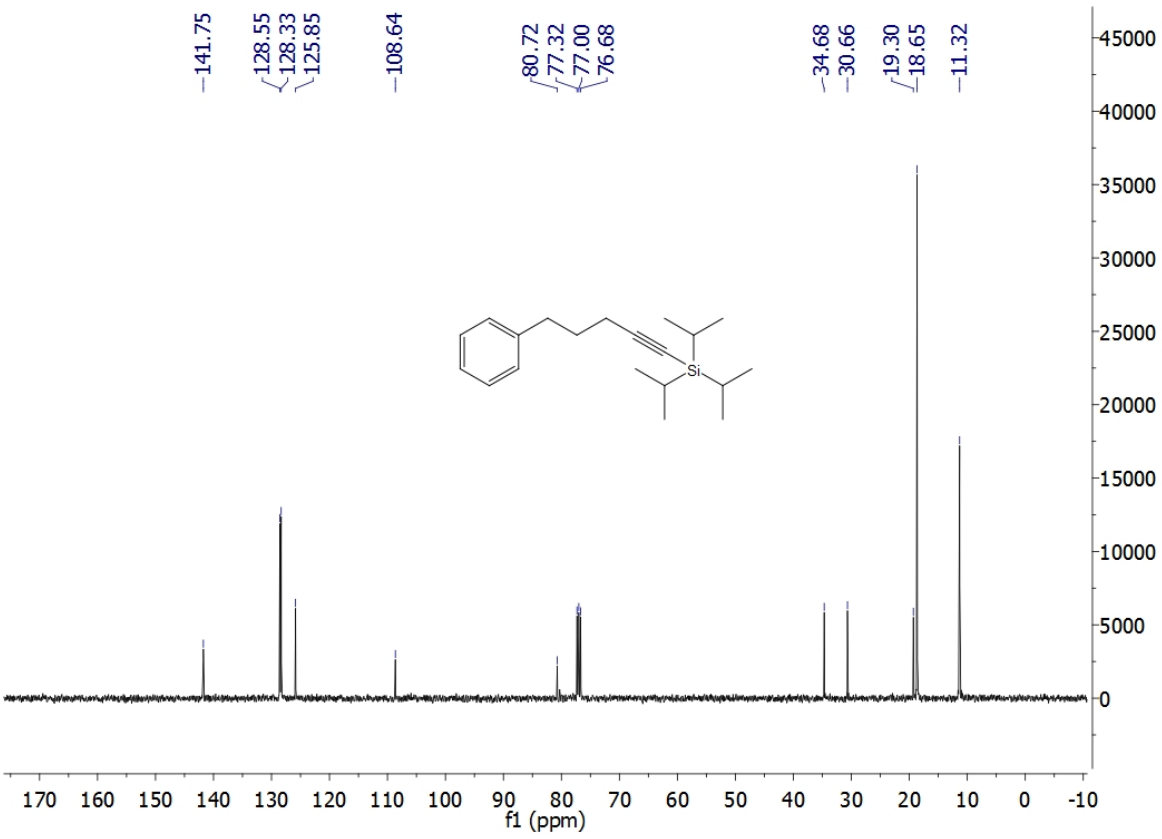
3g


7.260
5.324
5.304
4.270
4.260
4.251
2.815
2.802
2.748
2.739
2.707
2.697
1.449
1.416
1.040
1.028
1.009
1.00
1.03
1.04
1.07
9.11
9.04
21.13
f1 (ppm)

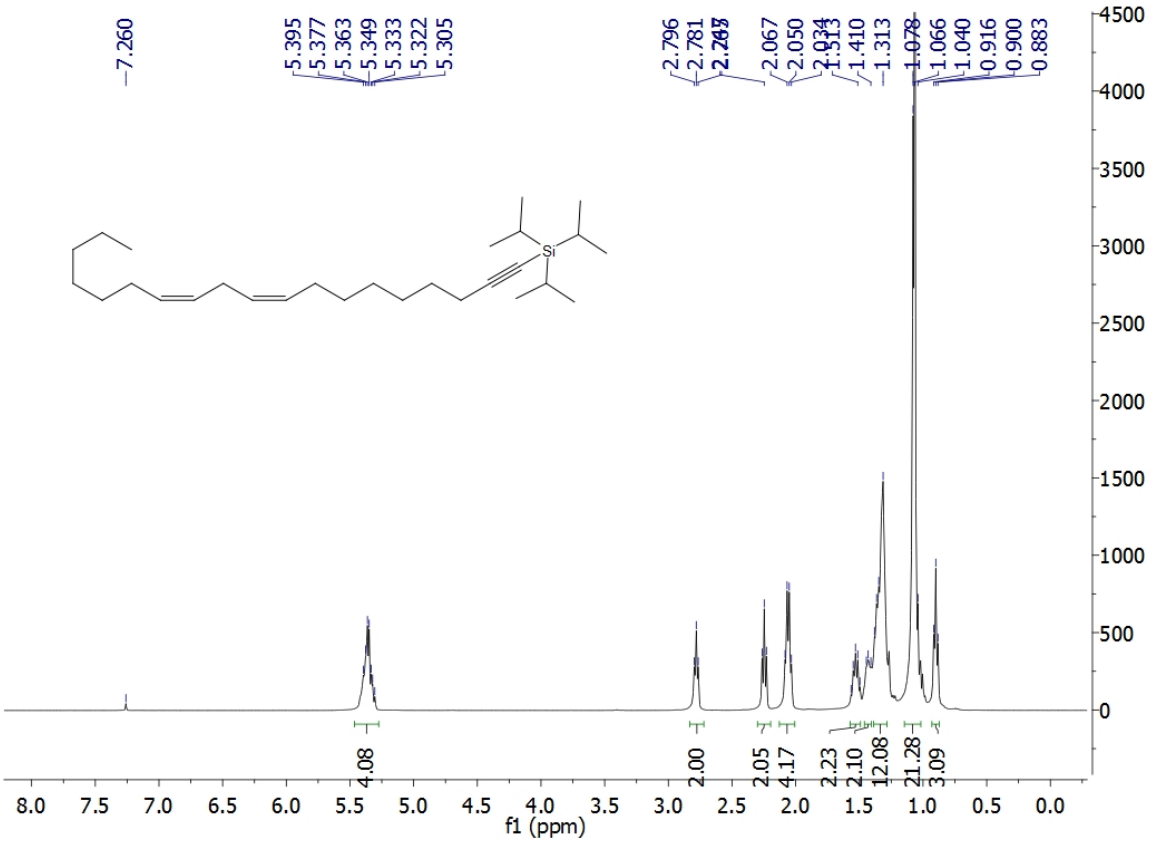

169.65
154.99
102.40
84.07
82.09
79.56
77.32
77.00
76.68
52.24
28.24
27.92
24.03
18.51
11.10
f1 (ppm)

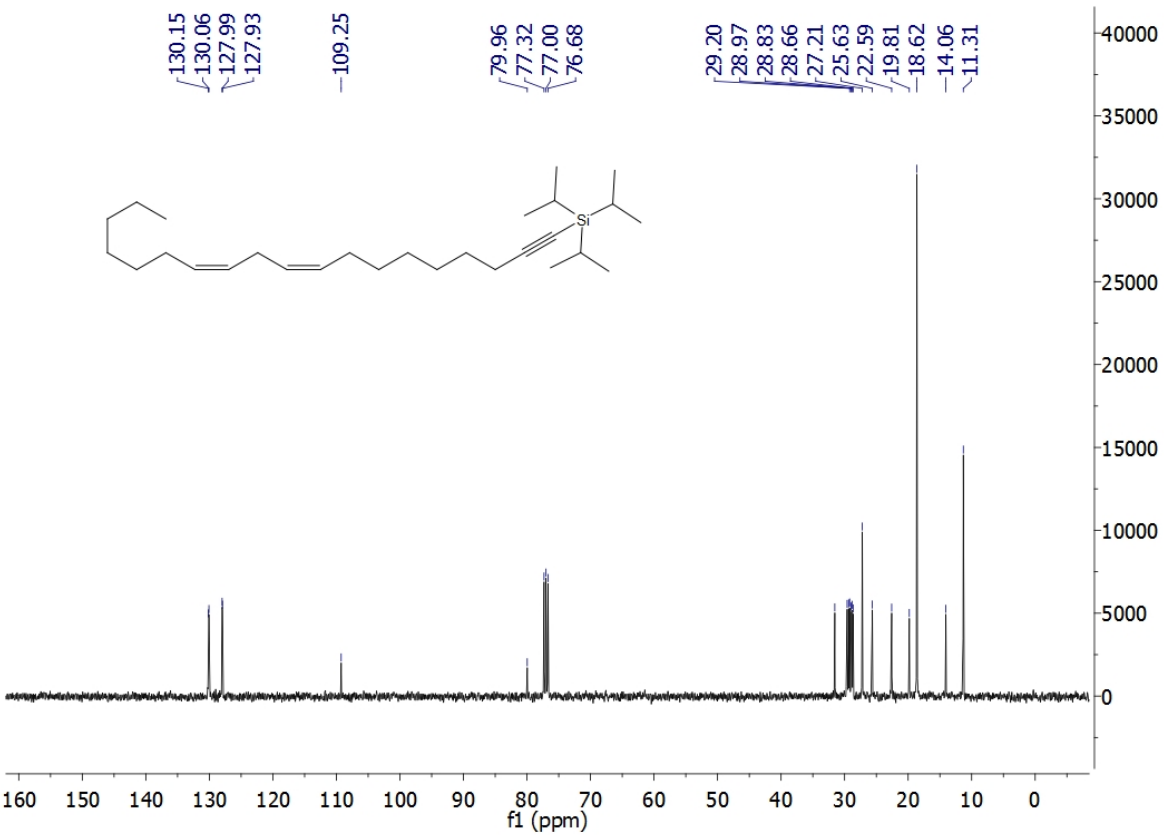
3h


7.391
7.372
7.355
7.296
7.278
7.260
2.874
2.855
2.836
2.343
1.931
1.895
1.198
1.186
Si
1.99
2.90
2.00
2.00
1.99
21.26
f1 (ppm)

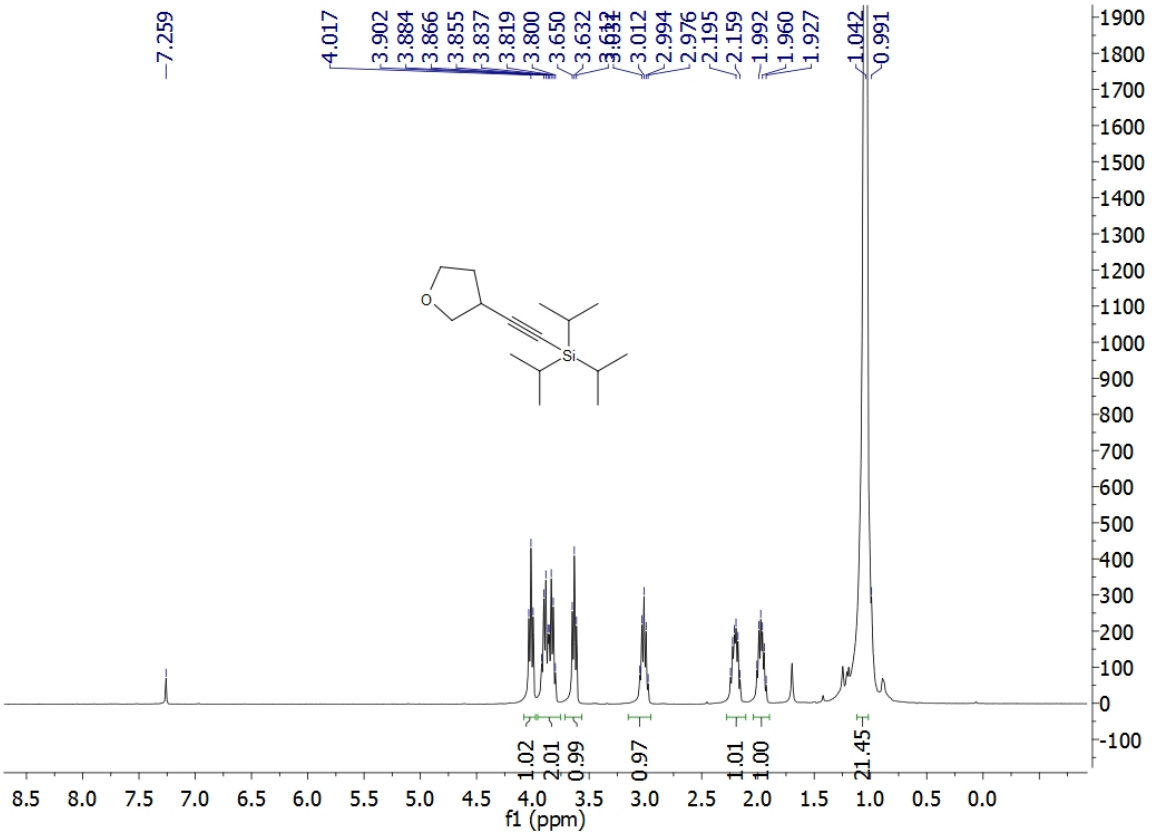

141.75
128.55
128.33
125.85
108.64
80.72
77.32
77.00
76.68
34.68
30.66
19.30
18.65
11.32
Si
f1 (ppm)

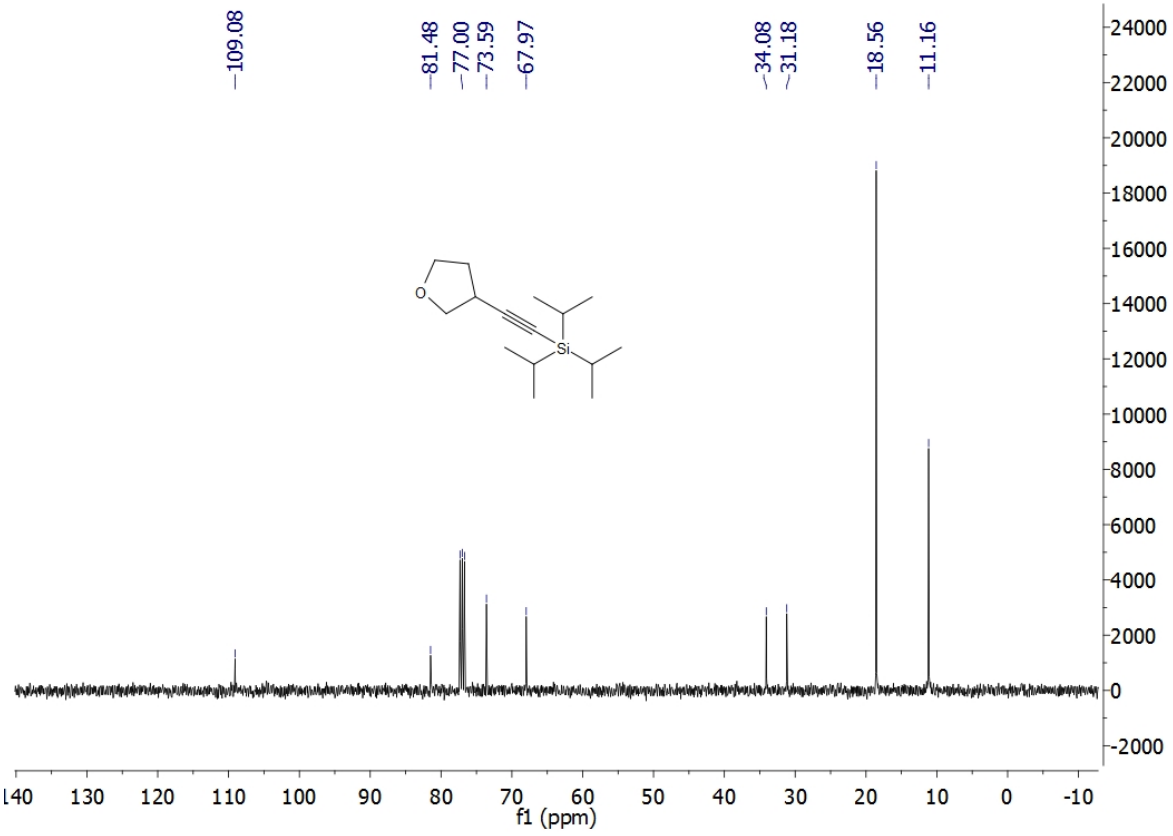
3i


7.260
5.395
5.377
5.363
5.349
5.333
5.322
5.305
2.796
2.781
2.067
2.050
1.410
1.313
1.078
1.066
1.040
0.916
0.900
0.883
Si
4.08
2.00
2.05
4.17
2.23
2.10
12.08
21.28
3.09
f1 (ppm)

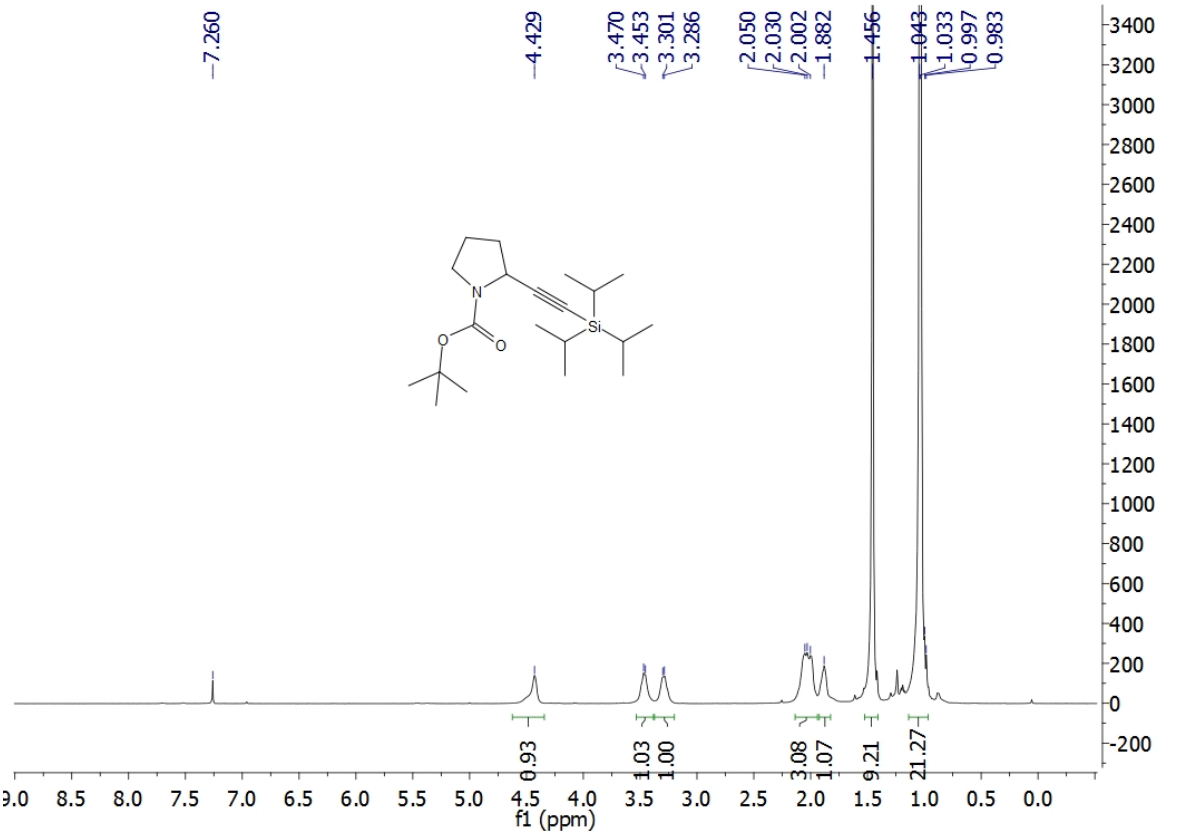

130.15
130.06
127.99
127.93
109.25
79.96
77.32
77.00
76.68
29.20
28.97
28.83
28.66
27.21
25.63
22.59
19.81
18.62
14.06
11.31
Si
f1 (ppm)

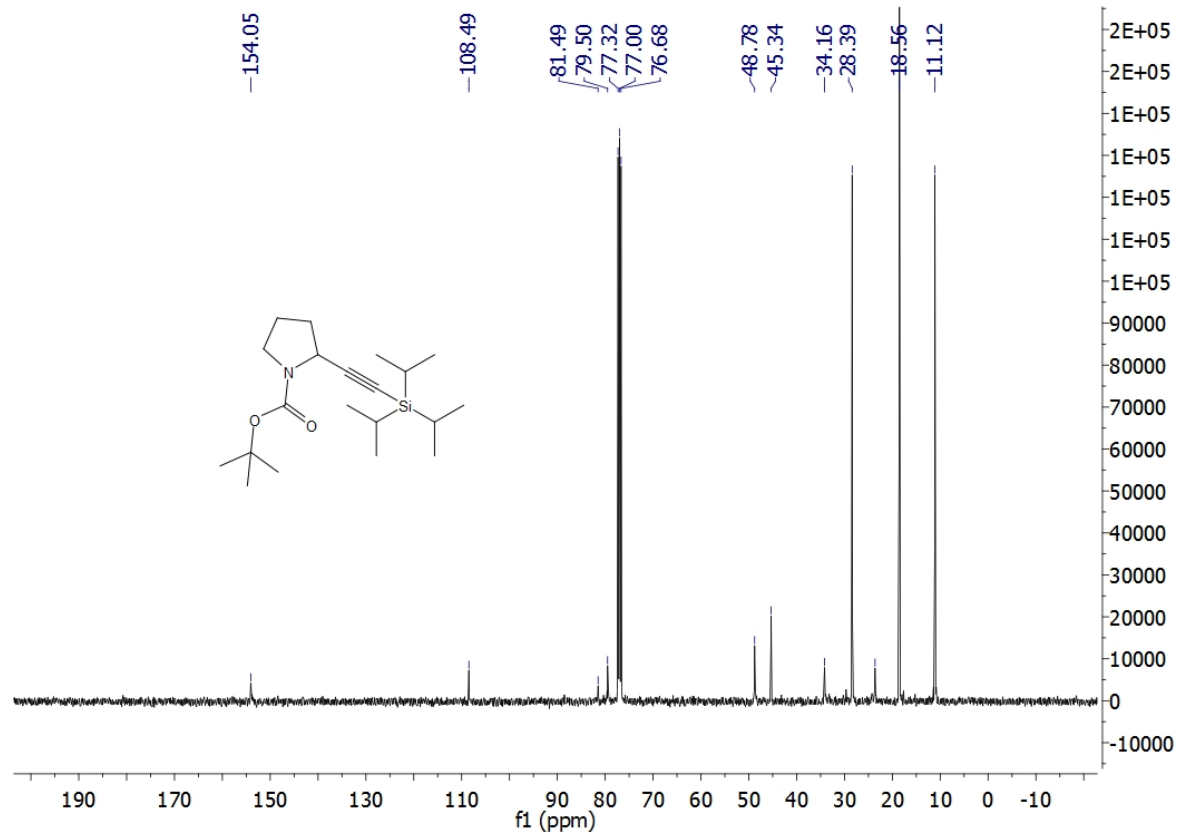
3j


7.259
4.017
3.902
3.884
3.866
3.855
3.837
3.819
3.800
3.650
3.632
3.012
2.994
2.976
2.195
2.159
1.992
1.960
1.927
1.042
0.991
O
Si
1.02
2.01
0.99
0.97
1.01
1.00
21.45
f1 (ppm)

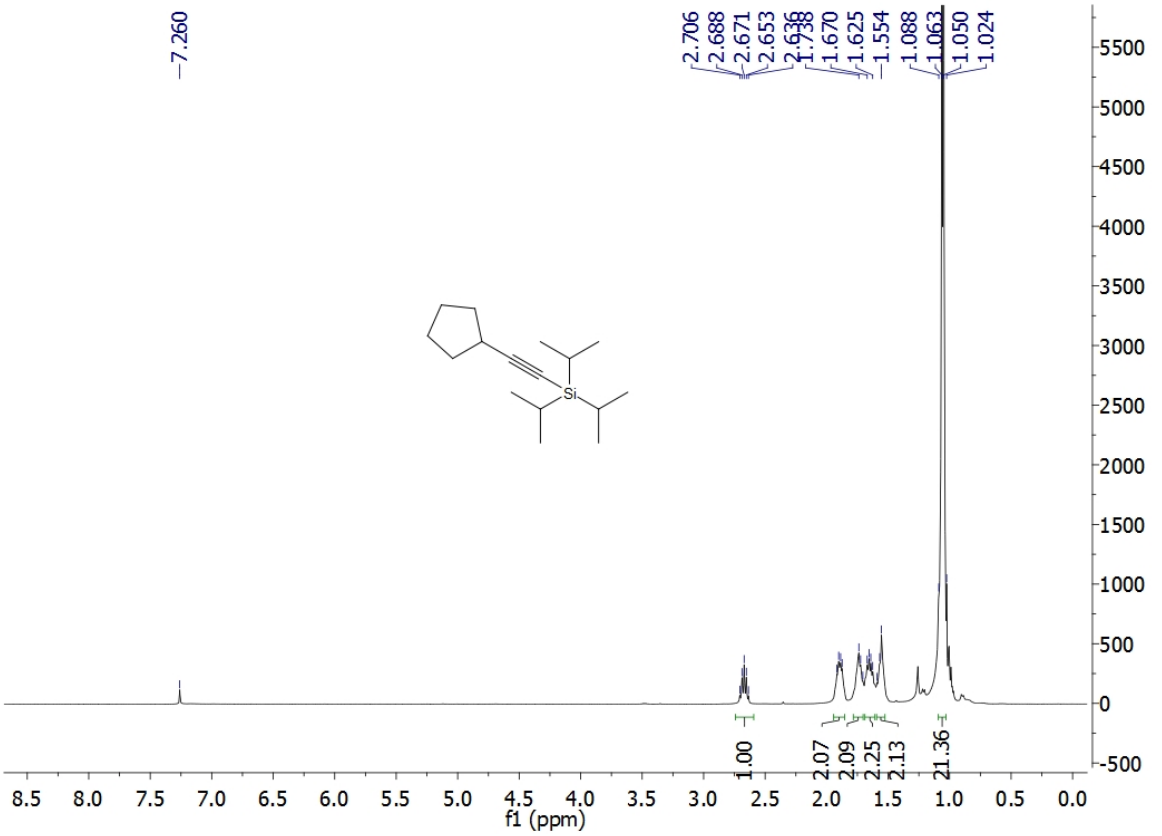

109.08
81.48
77.00
73.59
67.97
34.08
31.18
18.56
11.16
O
Si
f1 (ppm)

3k


7.260
4.429
3.470
3.453
3.301
3.286
2.050
2.030
2.002
1.882
1.456
1.043
1.033
0.997
0.983
0.93
1.03
1.00
3.08
1.07
9.21
21.27
f1 (ppm)


154.05
108.49
81.49
79.50
77.32
77.00
76.68
48.78
45.34
34.16
28.39
18.56
11.12
f1 (ppm)

3l


7.260
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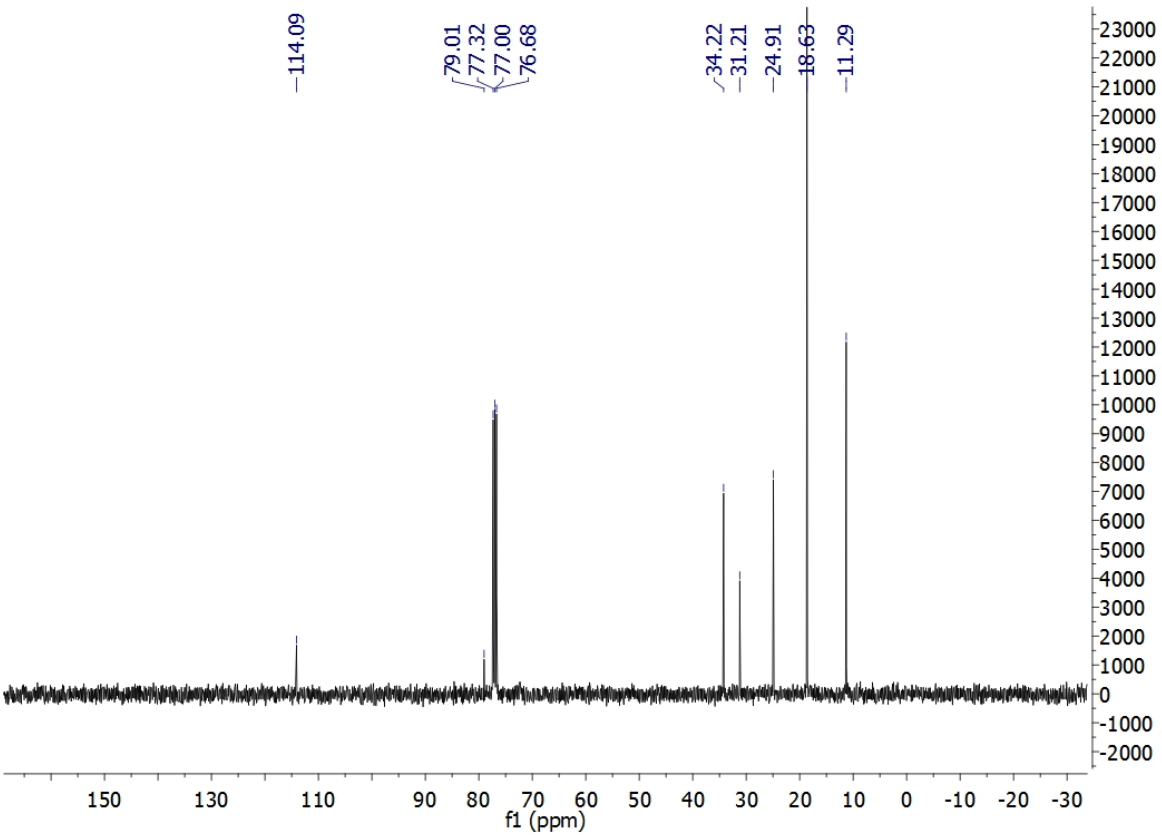
2.671
2.653
2.636
1.738
1.670
1.625
1.554
1.088
1.063
1.050
1.024
Si
1.00
2.07
2.09
2.25
2.13
21.36
f1 (ppm)


114.09
79.01
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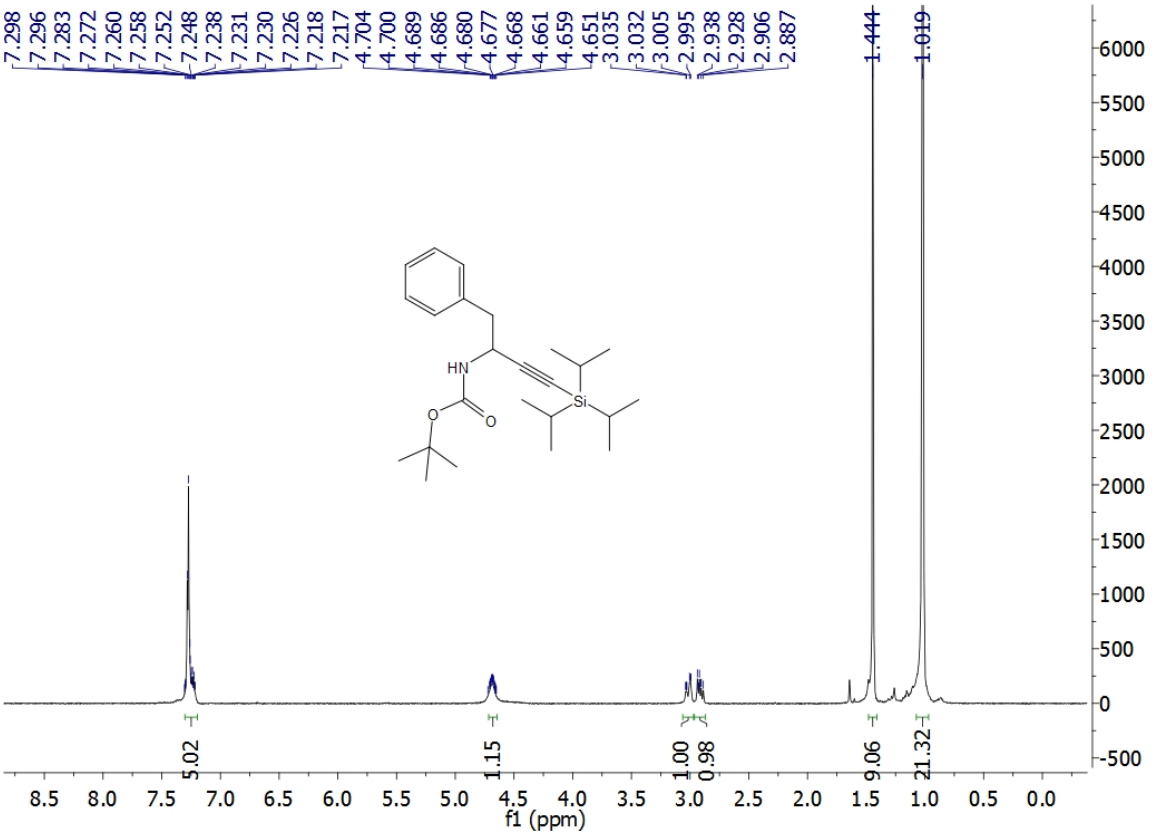
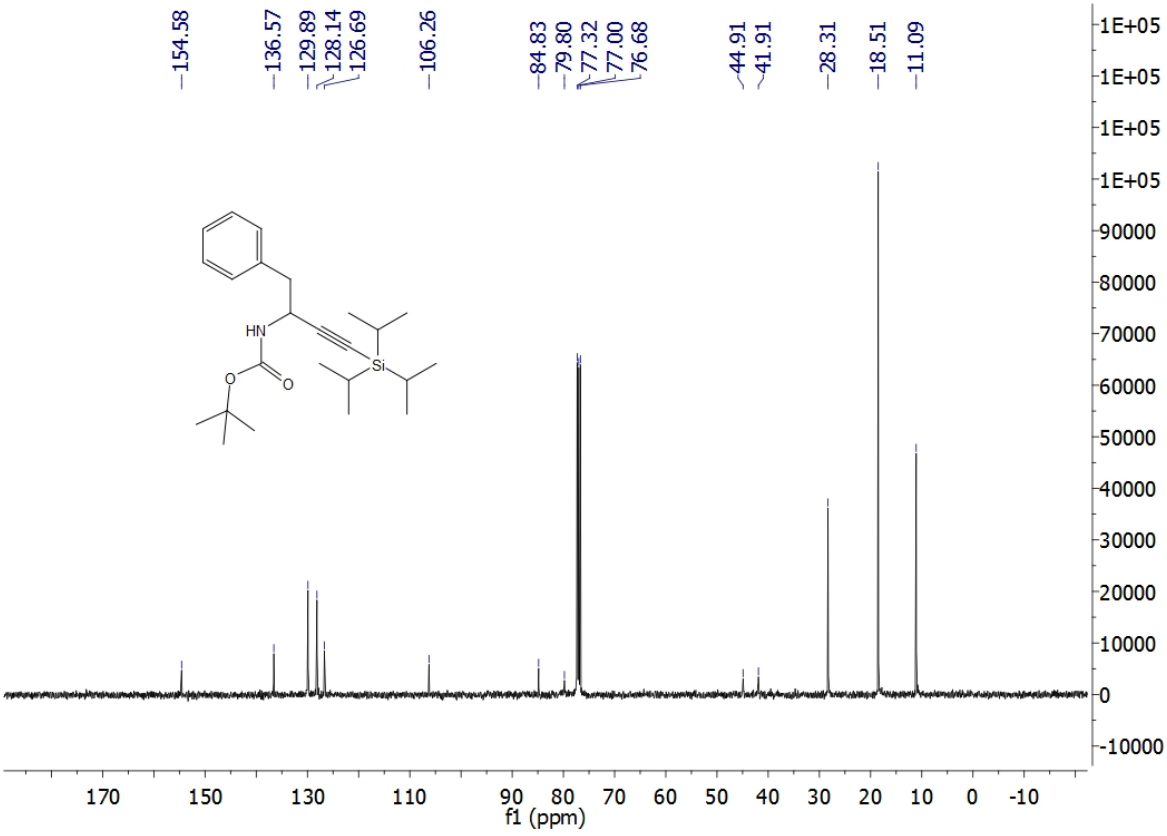
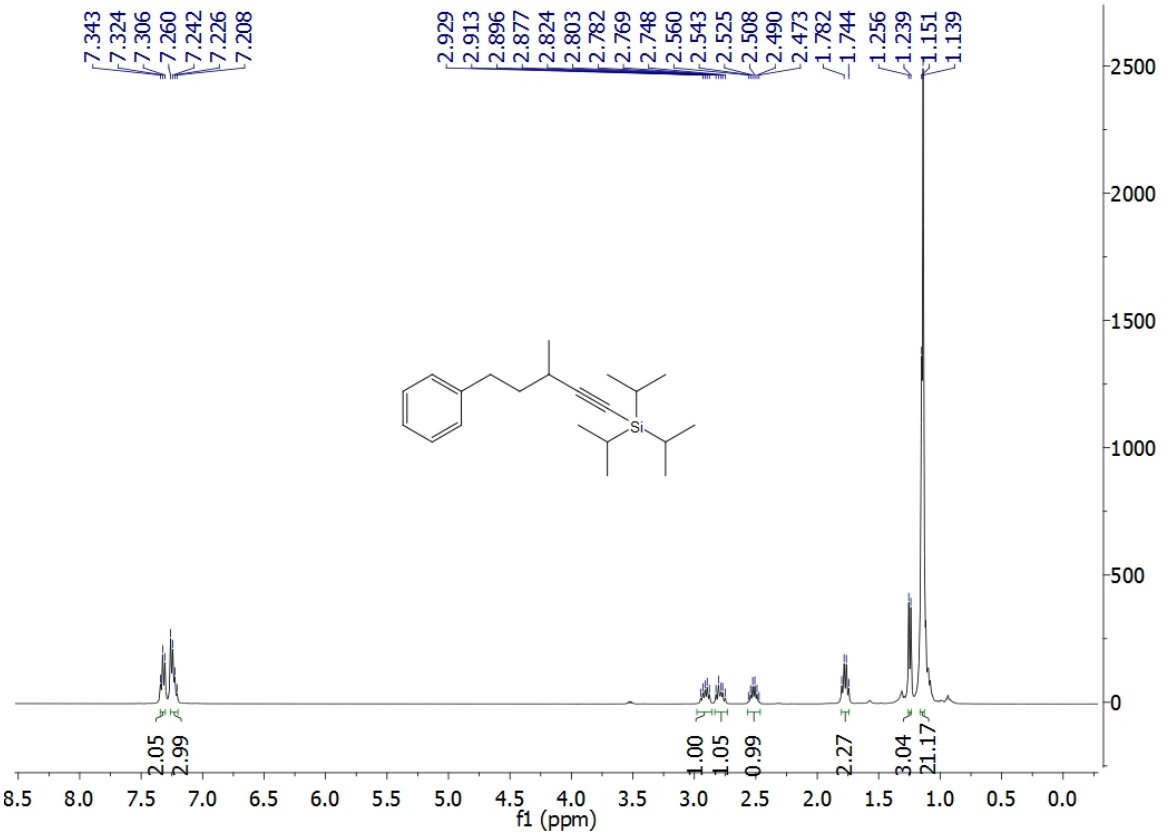
77.00
76.68
34.22
31.21
24.91
18.63
11.29
f1 (ppm)

3m


7.298
7.296
7.283
7.272
7.260
7.258
7.252
7.248
7.238
7.231
7.230
7.226
7.218
7.217
4.704
4.700
4.689
4.686
4.680
4.677
4.668
4.661
4.659
4.651
3.035
3.032
3.005
2.995
2.938
2.928
2.906
2.887
1.444
1.019
HN
O
O
Si
5.02
1.15
1.00
0.98
9.06
21.32
f1 (ppm)


154.58
136.57
129.89
128.14
126.69
106.26
84.83
79.80
77.32
77.00
76.68
44.91
41.91
28.31
18.51
11.09
HN
O
O
Si
f1 (ppm)

3n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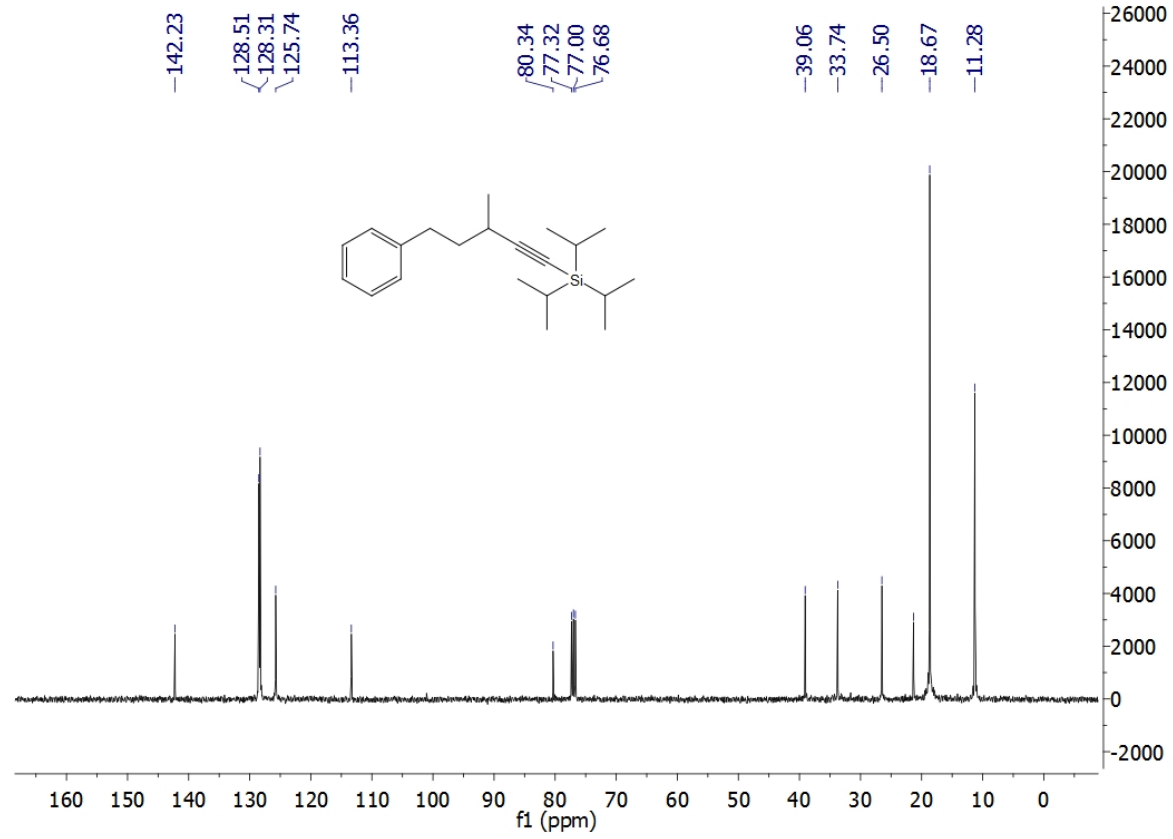
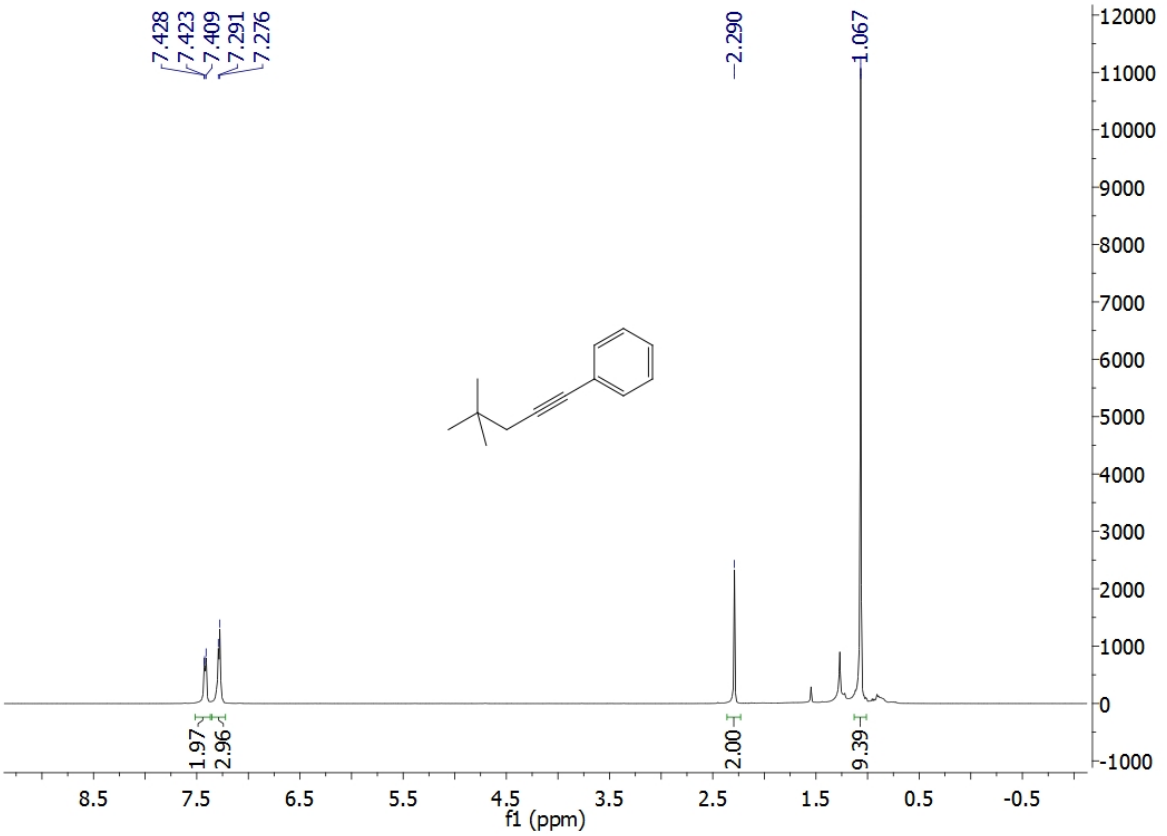
7.260
7.242
7.226
7.208
2.929
2.913
2.896
2.877
2.824
2.803
2.782
2.769
2.748
2.560
2.543
2.525
2.508
2.490
2.473
1.782
1.744
1.256
1.239
1.151
1.139
Si
2.05
2.99
1.00
1.05
0.99
2.27
3.04
21.17
f1 (ppm)


142.23
128.51
128.31
125.74
113.36
80.34
77.32
77.00
76.68
39.06
33.74
26.50
18.67
11.28
Si
f1 (ppm)

3p


7.428
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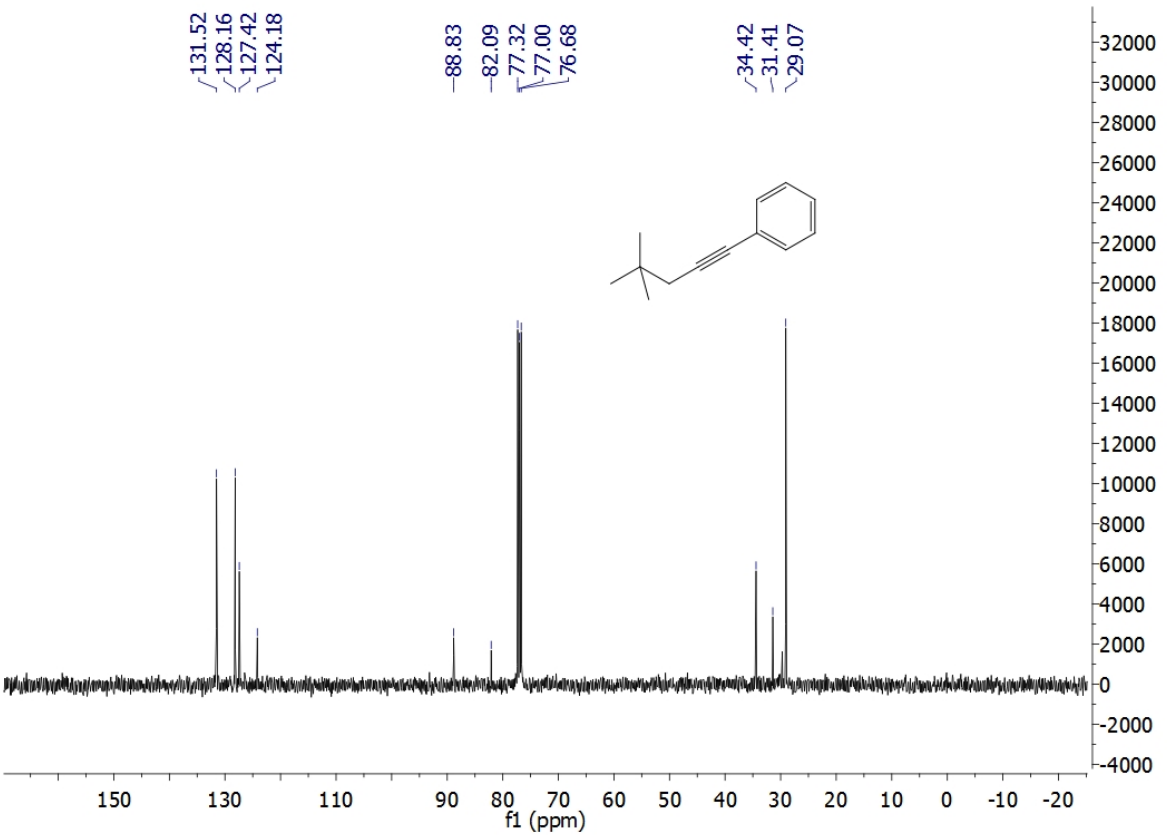
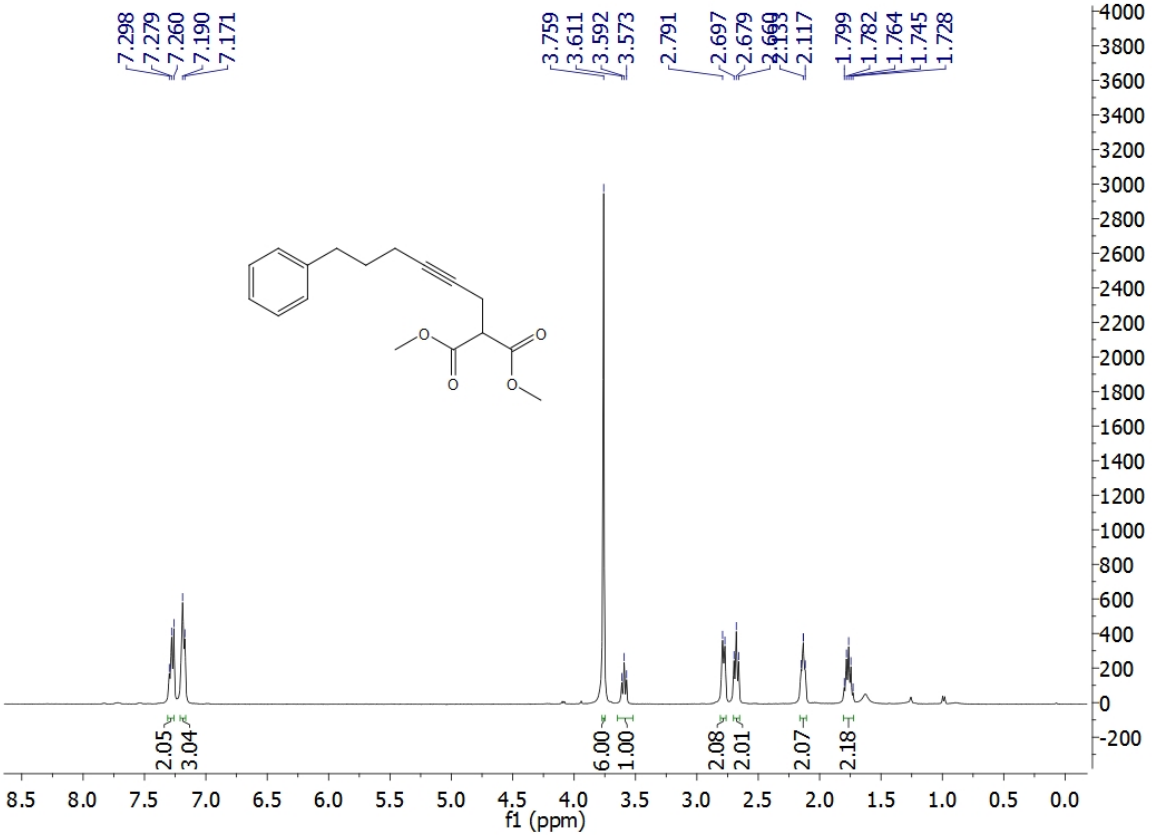
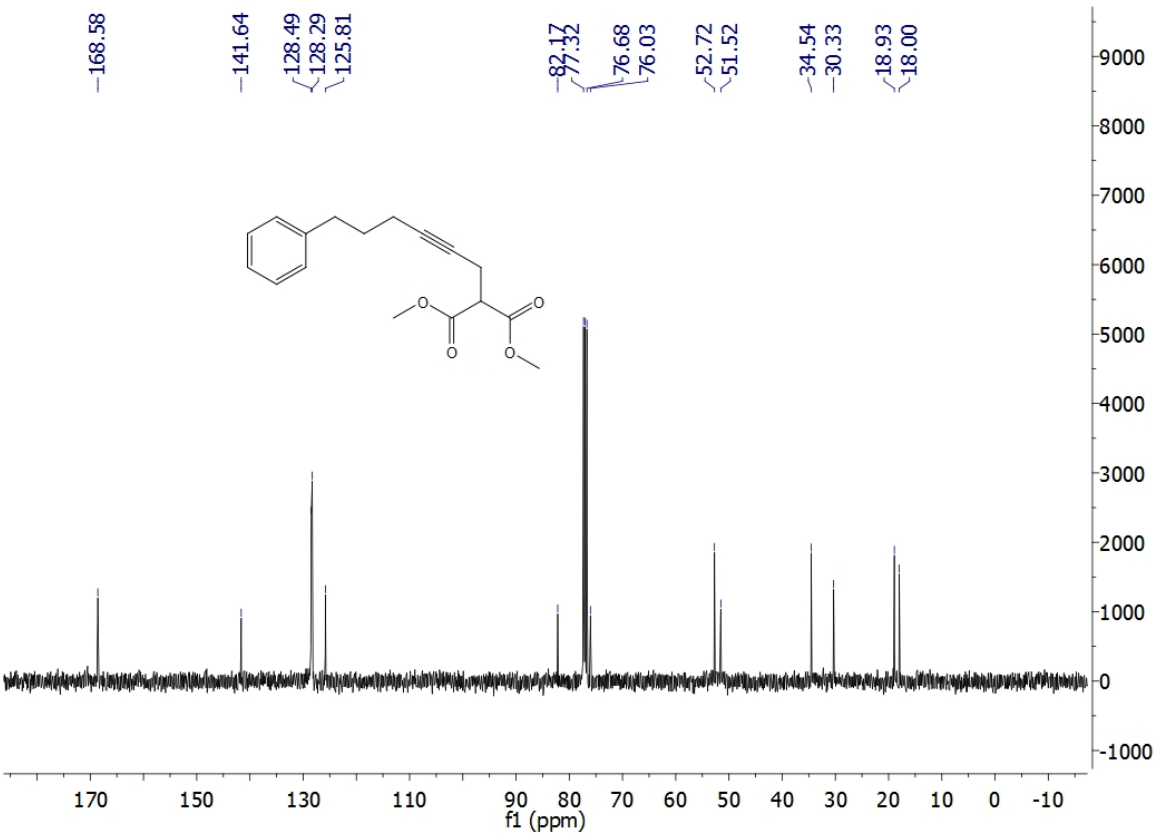
7.409
7.291
7.276
2.290
1.067
1.97
2.96
2.00
9.39
f1 (ppm)

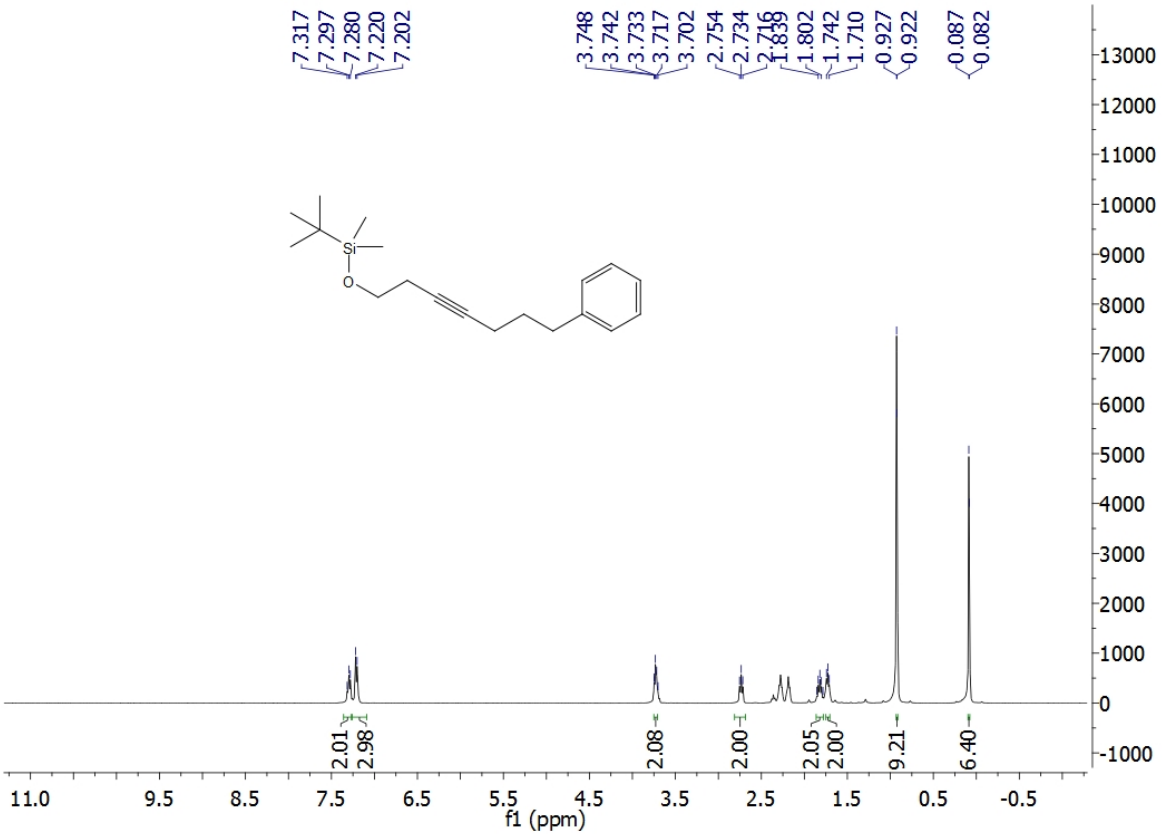

131.52
128.16
127.42
124.18
88.83
82.09
77.32
77.00
76.68
34.42
31.41
29.07
f1 (ppm)

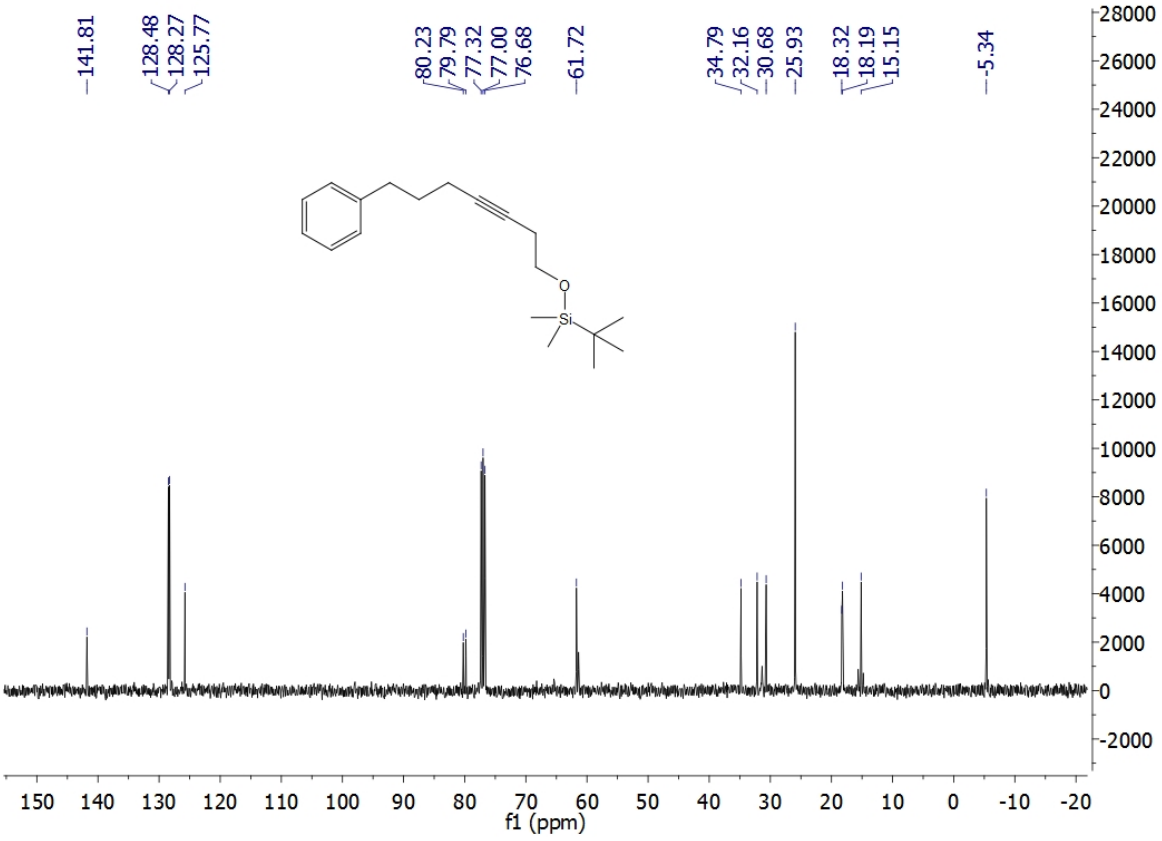
3q


7.298
7.279
7.260
7.190
7.171
3.759
3.611
3.592
3.573
2.791
2.697
2.679
2.117
1.799
1.782
1.764
1.745
1.728
2.05
3.04
6.00
1.00
2.08
2.01
2.07
2.18
f1 (ppm)

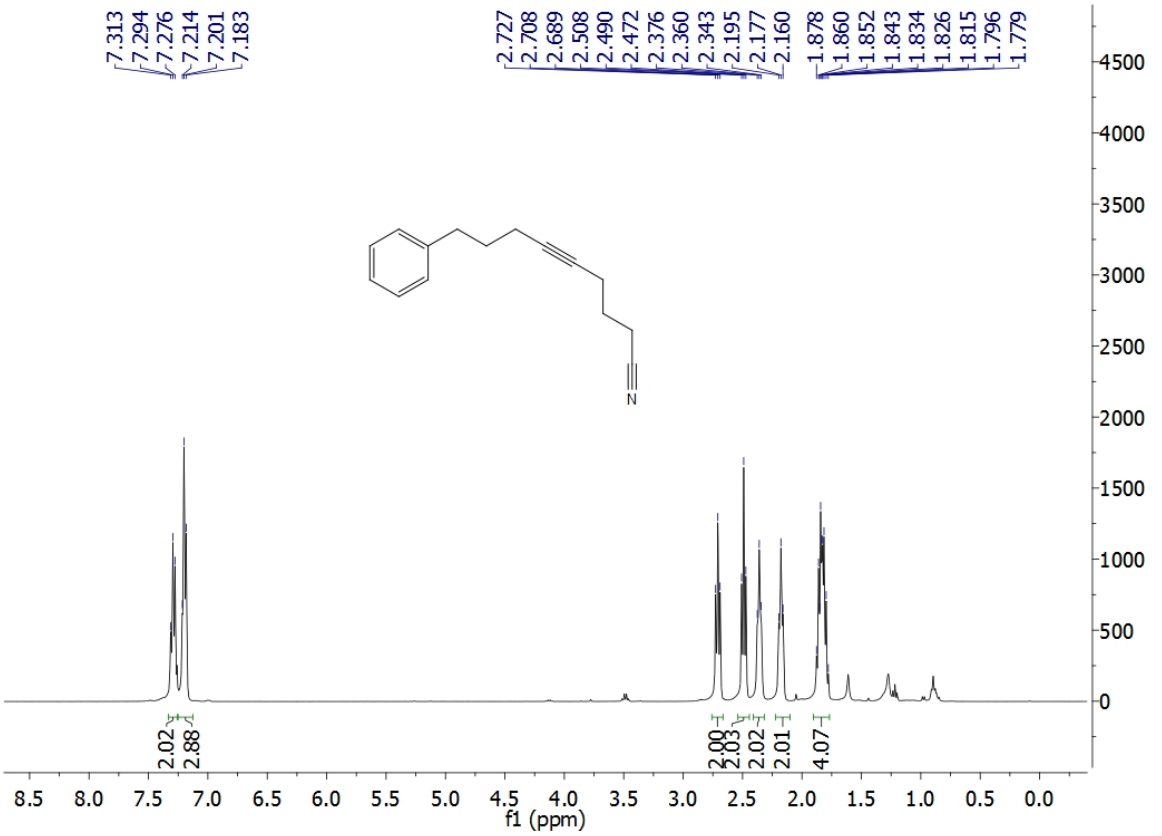

168.58
141.64
128.49
128.29
125.81
82.17
77.32
76.68
76.03
52.72
51.52
34.54
30.33
18.93
18.00
f1 (ppm)

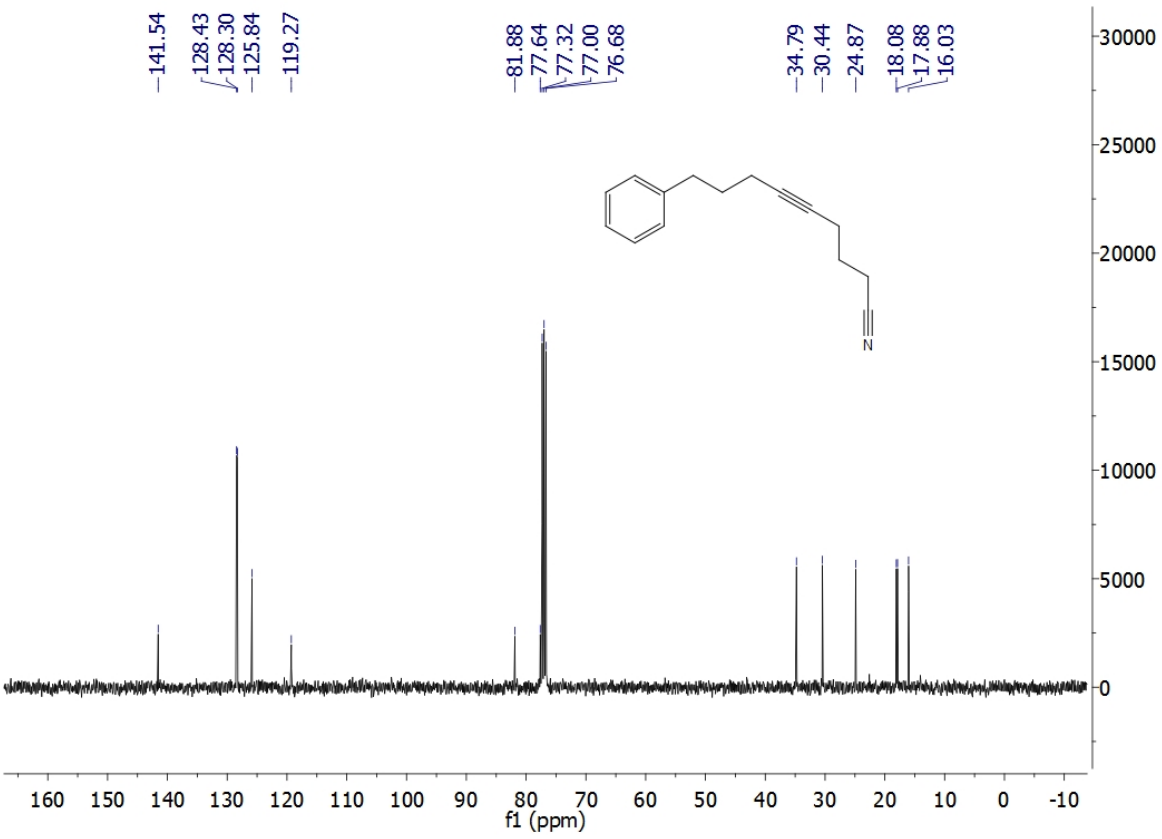
3r


7.317
7.297
7.280
7.220
7.202
3.748
3.742
3.733
3.717
3.702
2.754
2.734
2.716
1.838
1.802
1.742
1.710
0.927
0.922
0.087
0.082
Si
O
2.01
2.98
2.08
2.00
2.05
2.00
9.21
6.40
f1 (ppm)

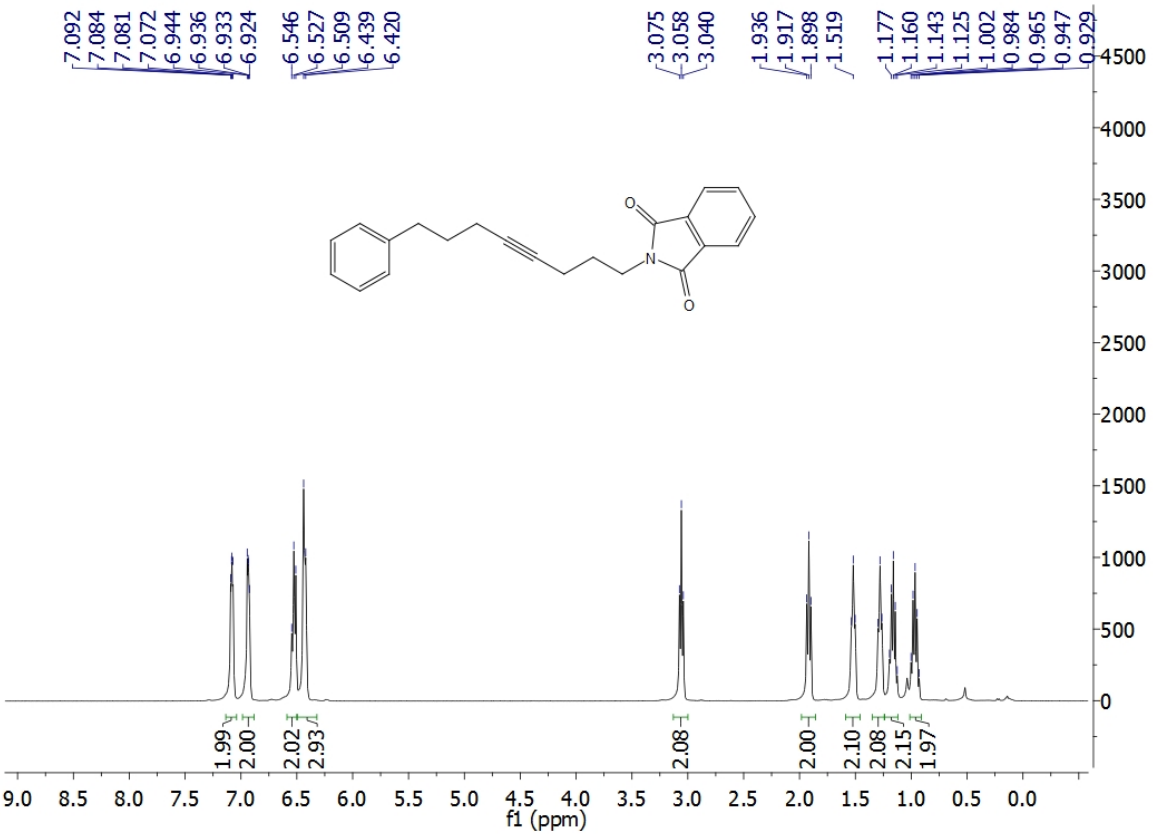

141.81
128.48
128.27
125.77
80.23
79.79
77.32
77.00
76.68
61.72
34.79
32.16
30.68
25.93
18.32
18.19
15.15
-5.34
O
Si
f1 (ppm)

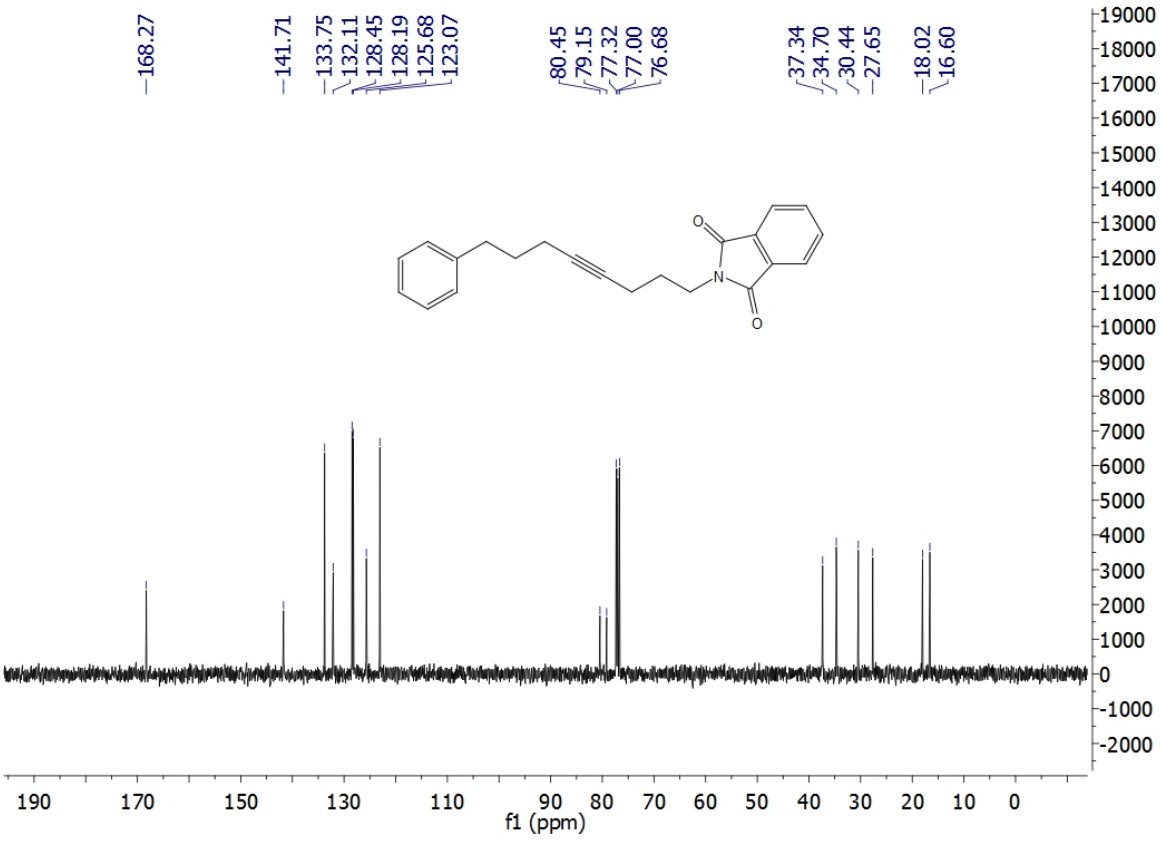
3s


7.313
7.294
7.276
7.214
7.201
7.183
2.727
2.708
2.689
2.508
2.490
2.472
2.376
2.360
2.343
2.195
2.177
2.160
1.878
1.860
1.852
1.843
1.834
1.826
1.815
1.796
1.779
2.02
2.88
2.00
2.03
2.02
2.01
4.07
f1 (ppm)

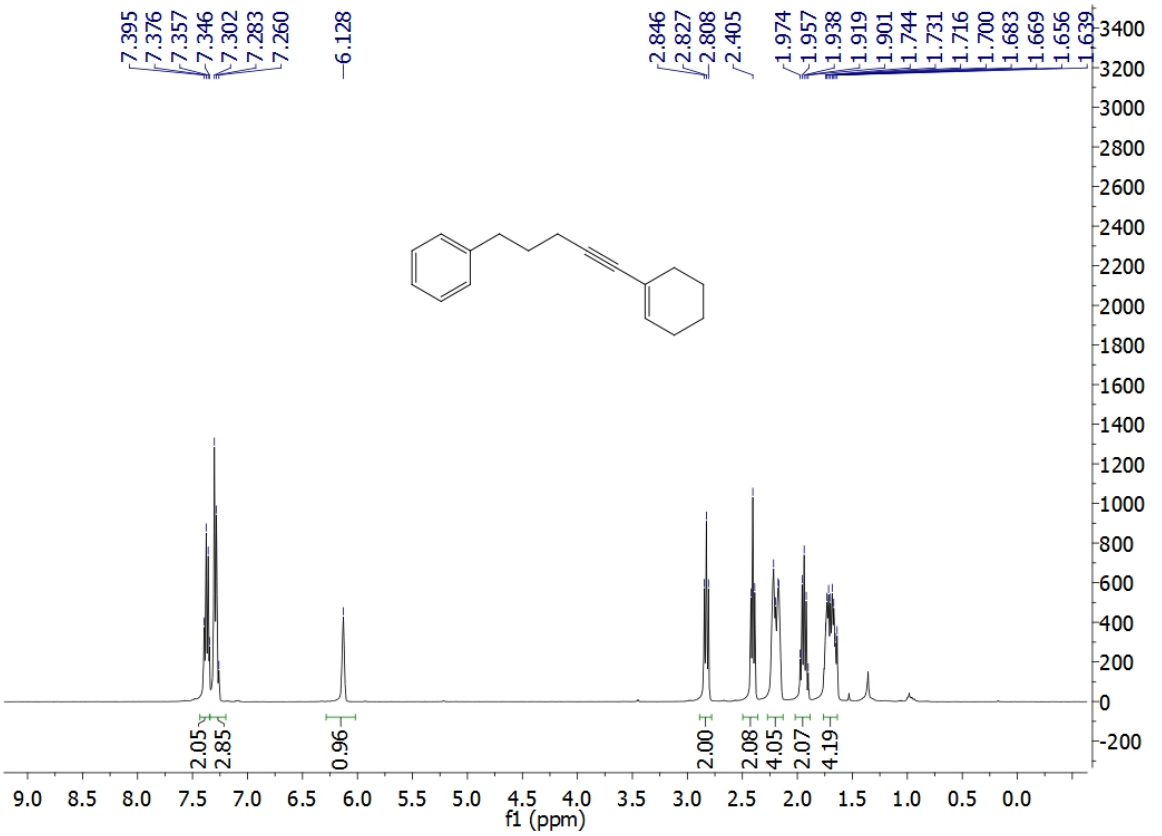

141.54
128.43
128.30
125.84
119.27
81.88
77.64
77.32
77.00
76.68
34.79
30.44
24.87
18.08
17.88
16.03
f1 (ppm)

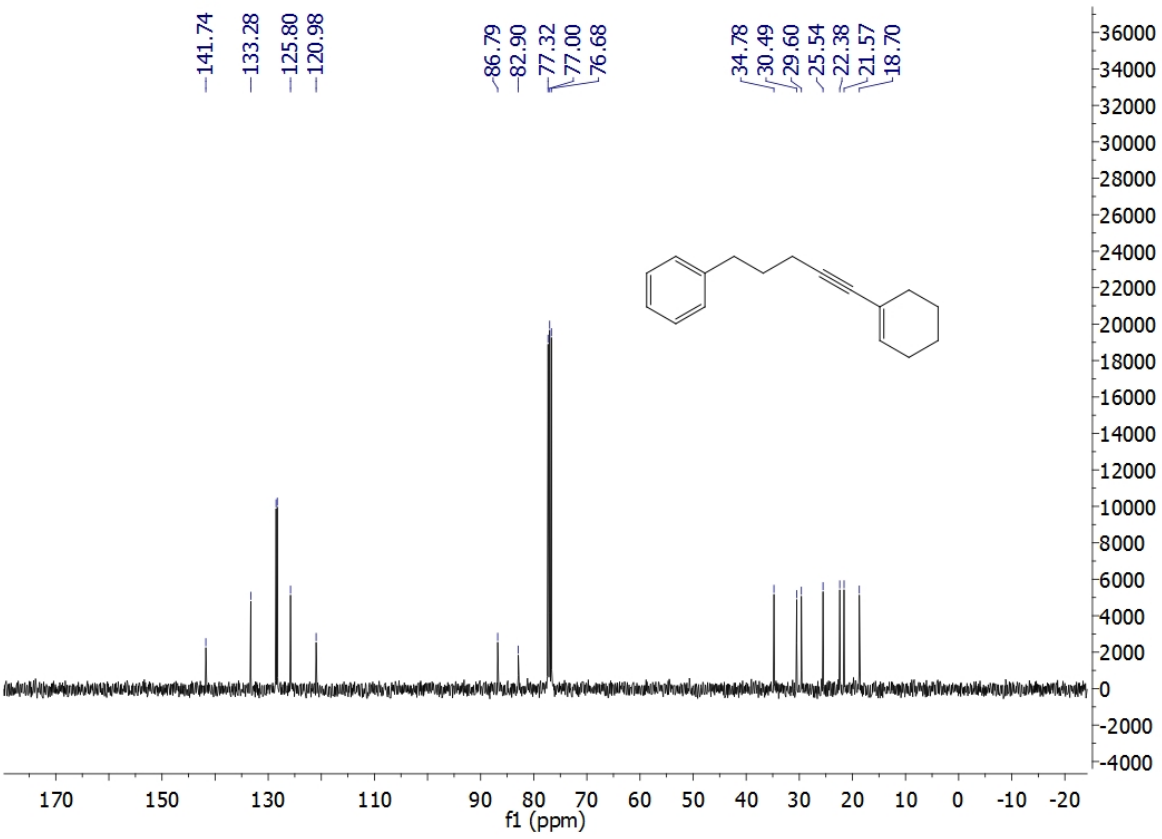
3t


7.092
7.084
7.081
7.072
6.944
6.936
6.933
6.924
6.546
6.527
6.509
6.439
6.420
3.075
3.058
3.040
1.936
1.917
1.898
1.519
1.177
1.160
1.143
1.125
1.002
0.984
0.965
0.947
0.929
O
N
O
1.99
2.00
2.02
2.93
2.08
2.00
2.10
2.08
2.15
1.97
f1 (ppm)

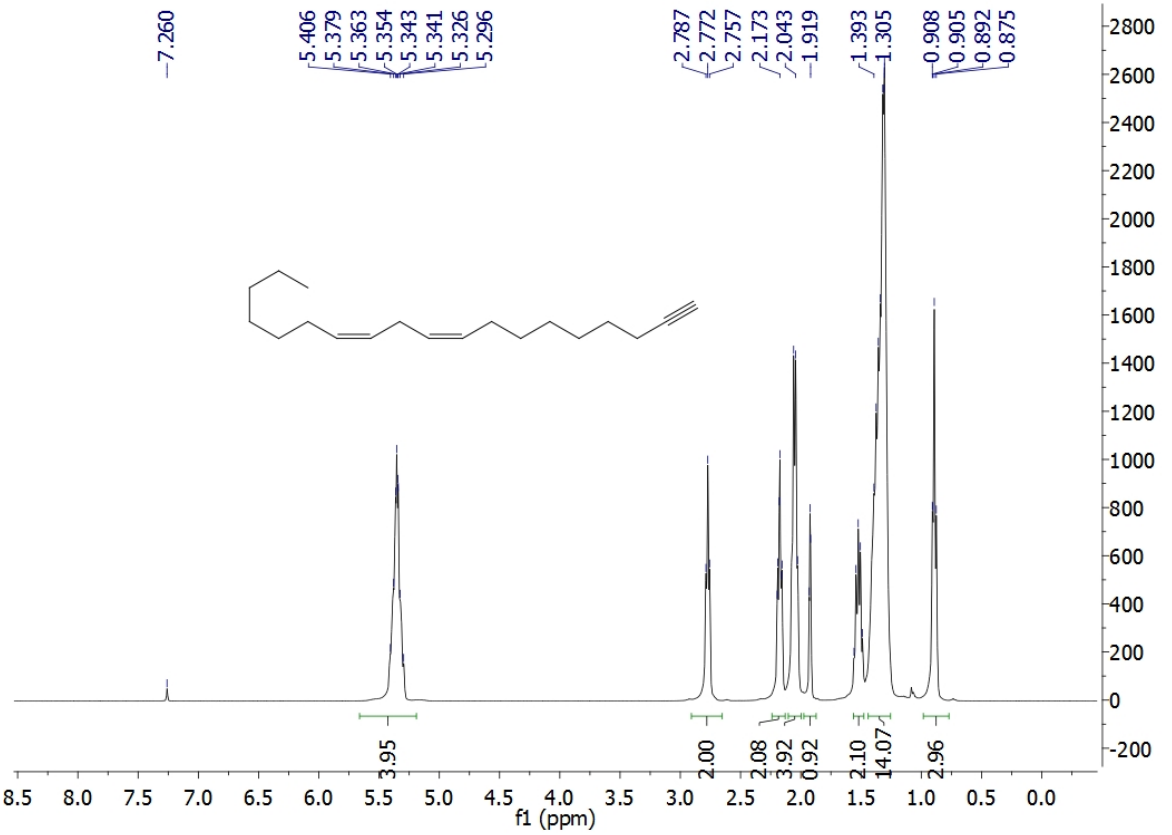

168.27
141.71
133.75
132.11
128.45
128.19
125.68
123.07
80.45
79.15
77.32
77.00
76.68
37.34
34.70
30.44
27.65
18.02
16.60
O
N
O
f1 (ppm)

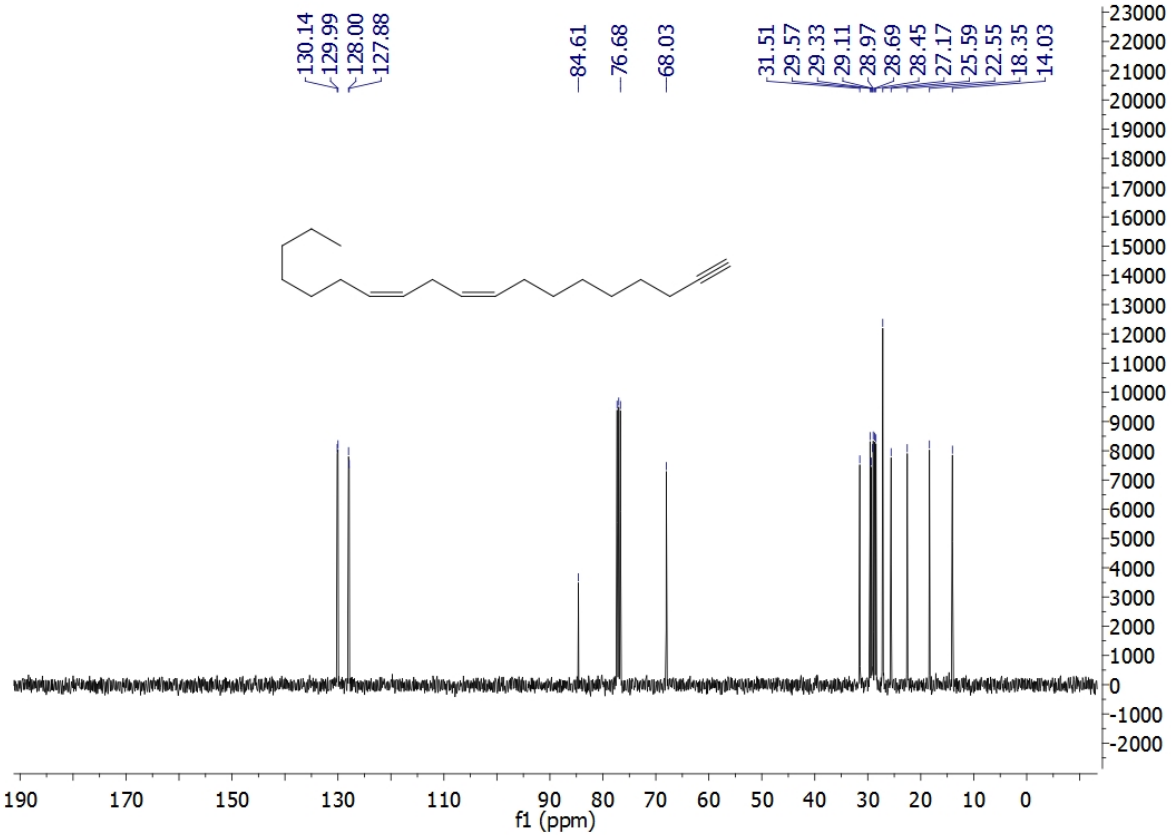
3u


7.395
7.376
7.357
7.346
7.302
7.283
7.260
6.128
2.846
2.827
2.808
2.405
1.974
1.957
1.938
1.919
1.901
1.744
1.731
1.716
1.700
1.683
1.669
1.656
1.639
2.05
2.85
0.96
2.00
2.08
4.05
2.07
4.19
f1 (ppm)

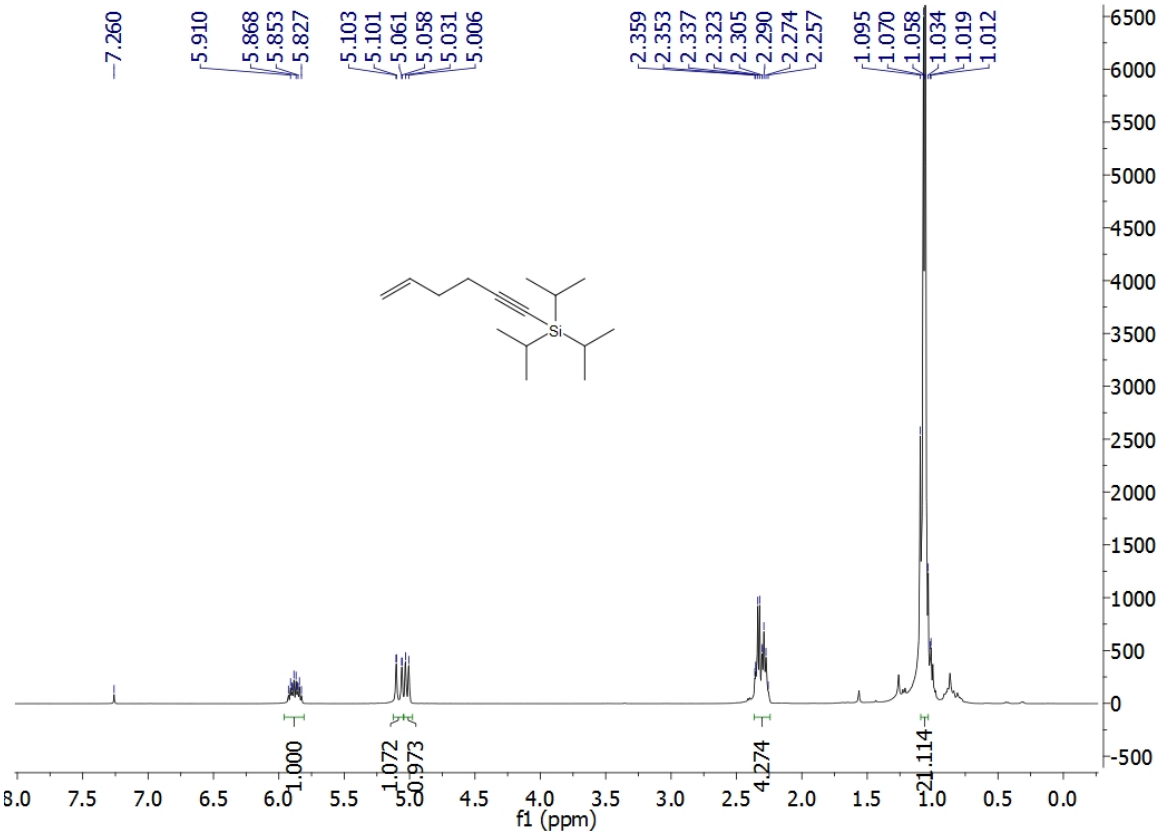

141.74
133.28
125.80
120.98
86.79
82.90
77.32
77.00
76.68
34.78
30.49
29.60
25.54
22.38
21.57
18.70
f1 (ppm)

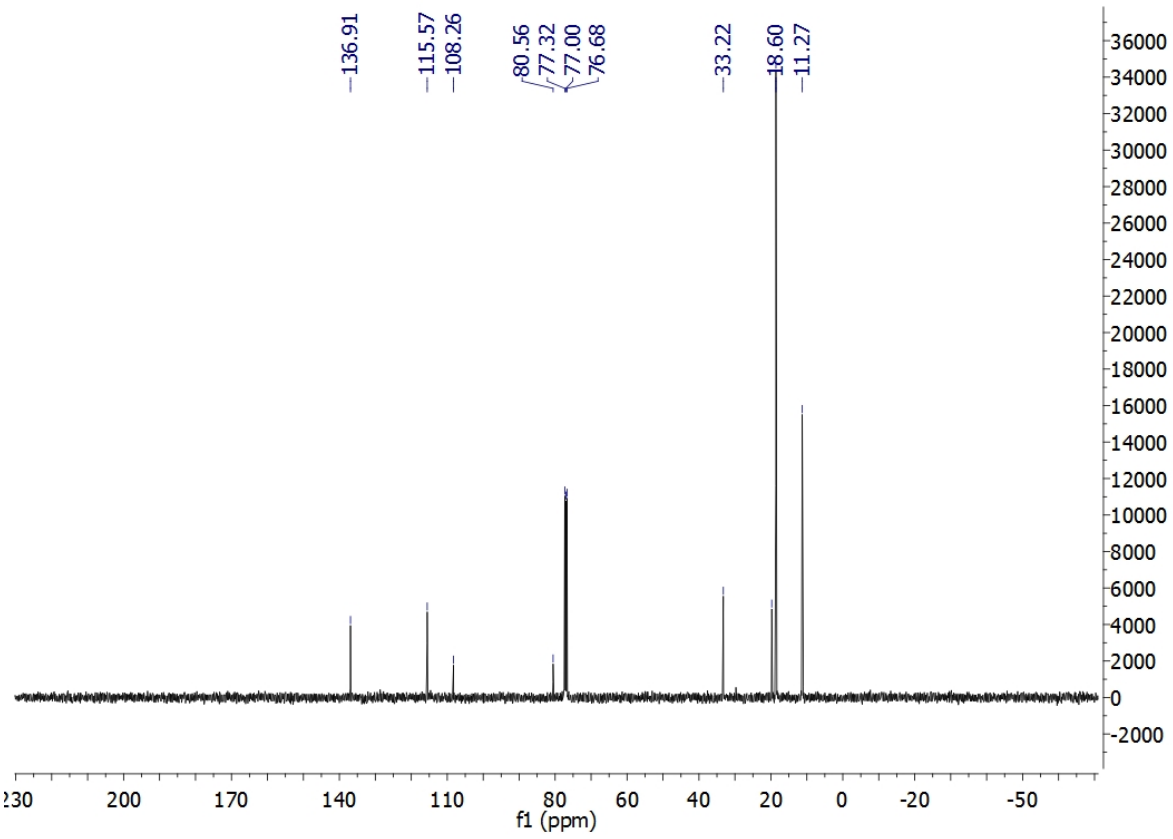
4i


7.260
5.406
5.379
5.363
5.354
5.343
5.341
5.326
5.296
2.787
2.772
2.757
2.173
2.043
1.919
1.393
1.305
0.908
0.905
0.892
0.875
3.95
2.00
2.08
3.92
0.92
2.10
14.07
2.96
f1 (ppm)

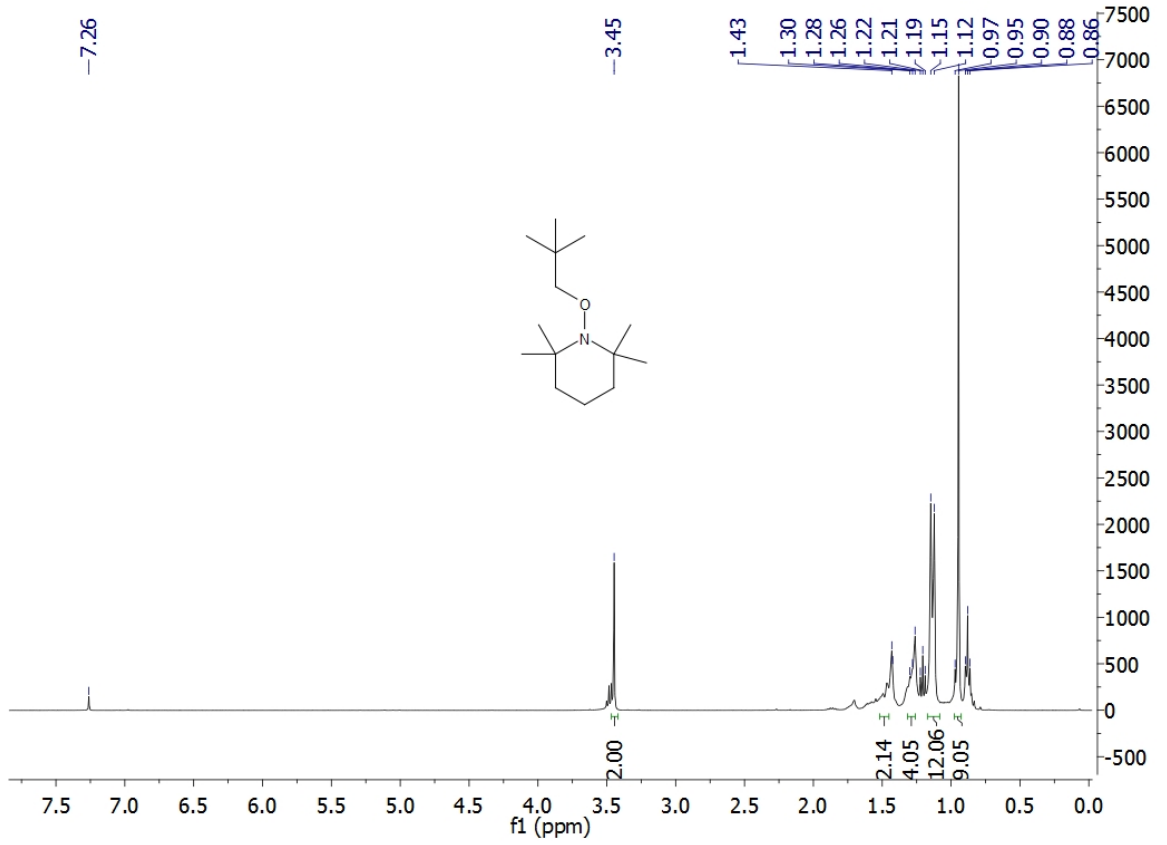

130.14
129.99
128.00
127.88
84.61
76.68
68.03
31.51
29.57
29.33
29.11
28.97
28.69
28.45
27.17
25.59
22.55
18.35
14.03
f1 (ppm)

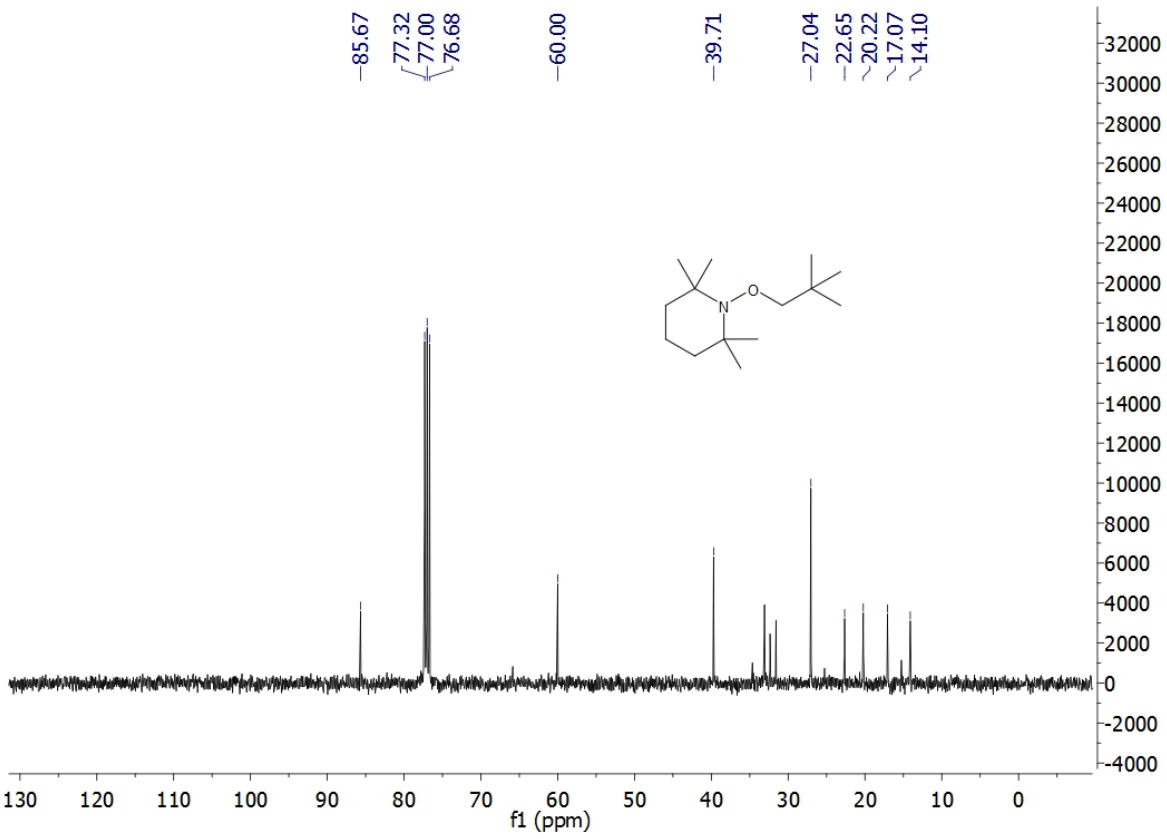
3v


7.260
5.910
5.868
5.853
5.827
5.103
5.101
5.061
5.058
5.031
5.006
2.359
2.353
2.337
2.323
2.305
2.290
2.274
2.257
1.095
1.070
1.058
1.034
1.019
1.012
Si
1.000
1.072
0.973
4.274
21.114
f1 (ppm)


136.91
115.57
108.26
80.56
77.32
77.00
76.68
33.22
18.60
11.27
f1 (ppm)

7a


7.26
3.45
1.43
1.30
1.28
1.26
1.22
1.21
1.19
1.15
1.12
0.97
0.95
0.90
0.88
0.86
2.00
2.14
4.05
12.06
9.05
f1 (ppm)


85.67
77.32
77.00
76.68
60.00
39.71
27.04
22.65
20.22
17.07
14.10
f1 (ppm)