Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Benchtop Nickel-Catalyzed Reductive Coupling of Aldehydes with Alkynes and Ynamides

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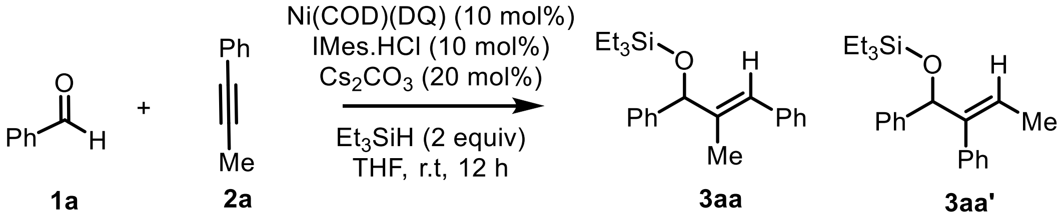
1. General experimental details

All air and water-sensitive reactions were carried out in flame-dried glassware under a nitrogen/argon atmosphere using the standard Schlenk manifold technique. Bulk solutions were evaporated under reduced pressure using a Büchi rotary evaporator. All solvents were commercially supplied, and dry solvents were prepared using the standard protocol.[1] THF was dried over sodium metal and benzophenone. Petroleum ether (hexanes) is the fraction collected between 40 – 60 °C. Unless noted, all other reagents were purchased from commercial sources and used as received. All reactions were followed by thin-layer chromatography (TLC) using Merck Kieselgel 60 F_{254} fluorescent-treated silica, visualized under UV light (254). Column chromatography was undertaken on silica gel (230-400 mesh). NMR spectra were recorded on BRUKER ULTRA SHIELD (400 MHz) instrument at 400 MHz for ^{1}H NMR, 101 MHz for ^{13}C NMR, or on a BRUKER ASCEND (500 MHz) spectrometer at 500 MHz for ^{1}H NMR, 126 MHz for ^{13}C NMR, 471 MHz for ^{19}F NMR. Chemical shifts were quoted in parts per million (ppm) referenced $CDCl_3$ at 7.26 ppm, CD_3OD at 4.87, and 3.31 ppm, DMSO-d_6 at 3.60 and 2.50 ppm, and 0.0 ppm for tetramethylsilane. The following abbreviations were used to describe peak splitting patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of a doublet, td = triplet of a doublet, ddd = doublet of a doublet of a doublet, tt=triplet of triplet, m = multiplet. Coupling constants, J, were reported in hertz (Hz). ^{13}C NMR spectra were fully decoupled by broadband proton decoupling. Chemical shifts were reported in ppm referenced to the center of the triplet at 77.2 ppm of $CDCl_3$, the center of septet at 49.0 ppm of Methanol-d_4, or the center of septet at 39.5 ppm of DMSO-d_6. Infrared (IR) spectra were recorded using Spectrum BX FT-IR instrument from Perkin Elmer. Frequencies are given in reciprocal centimeters (cm^{-1}), and only selected peaks are reported. High-resolution mass spectra (HRMS) were recorded in the ESI (+ve) method using a time-of-flight (TOF) mass analyzer (Agilent AdvanceBio 6545XT LC/Q-

TOF). The single crystal XRD was done with BRUKER D8 QUEST instrument. Materials obtained from commercial suppliers were purified using standard protocol[1] or prepared according to standard procedures unless otherwise noted. We acknowledge National Supercomputing Mission (NSM) for providing computing resources of 'PARAM Shakti' at IIT Kharagpur, which is implemented by C-DAC and supported by the Ministry of Electronics and Information Technology (MeitY) and Department of Science and Technology (DST), Government of India.

2. Investigation of reaction conditions

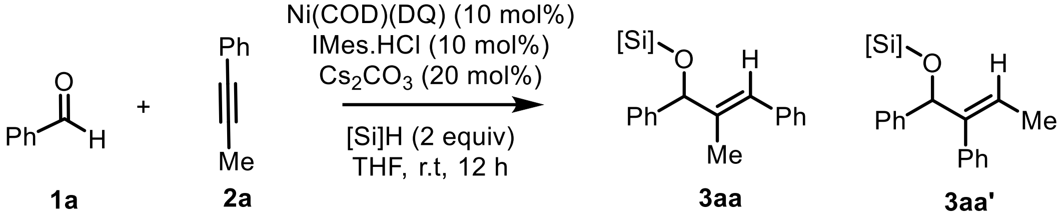
2A. Investigation of reaction conditions for reductive coupling of aldehydes and alkynes



entry	Deviation from standard conditions	yield%[f]	r.r (**3aa**:**3aa'**)
1	none	82 (79)	97:3
2[a,b]	PCy_3, P(*p*-anisyl)$_3$, dcpe	n.r.	-
3[a]	free IPr carbene	20	55:45
4[a]	sIPr.HCl, Icy.HBF_4, Ibn.HBF_4	n.r.	-
5[a]	*i*-Pr_3SiH, Et_2SiH_2, Ph_2SiH_2, $(OMe)_2MeSiH$ instead of Et_3SiH	n.r.	-
6[a]	*t*-Bu_2MeSiH instead of Et_3SiH	46	98:2
7[a,c]	*n*-BuLi instead of Cs_2CO_3	20	97:3
8[a,c]	KO*t*Bu instead of Cs_2CO_3	46	97:3
9[a,c]	LiO*t*Bu instead of Cs_2CO_3	63	97:3
10[a,d]	K_3PO_4 instead of Cs_2CO_3	47	97:3
11[a,c]	DBU instead of Cs_2CO_3	n.r.	-
12	Reaction performed at 70 °C	63	97:3
13[e]	Ni(COD)(DQ) (15 mol%), IMes.HCl (15 mol%), Cs_2CO_3 (30 mol%)	41	97:3
14	Ni(COD)(DQ) (2 mol%), IMes.HCl (2 mol%), Cs_2CO_3 (4 mol%)	13	97:3
15	**2a** in 1.7 equiv	52	97:3
16	in absence of IMes.HCl and base	n.r.	-

Reaction Conditions: [a]performed at 45 °C, 12 h; [b]monophosphines (20 mol%) and bisphosphines (10 mol%) in absence of base ; [c]base (10 mol%) ; [d]base (20 mol%); [e]in presence of 50 mg of 4 Å MS; [f]Yields were determined by analysis of ^1H NMR of the crude reaction mixture using 1,1,2,2-tetrachloroethane as an internal standard, isolated yields in paranthesis; n.r.: no reaction

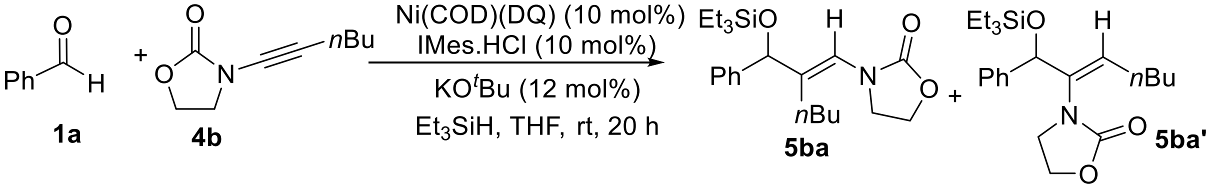
2B. Silane screening for the reductive coupling of aldehydes and alkynes



entry	Deviation from standard conditions	yield%[c]	r.r (**3aa**:**3aa'**)
1[a]	*t*-Bu_2MeSiH	46	98:2
2[a]	Et_2SiH_2, Ph_2SiH_2	n.r.[b]	-
3[a]	*i*-Pr_3SiH, $(OMe)_2MeSiH$	n.r.	-

Reaction Conditions: [a]performed at 45 °C, 12 h; [b]alkyne hydrosilylation was observed; [c]Yields were determined by analysis of ^1H NMR of the crude reaction mixture using 1,1,2,2-tetrachloroethane as an internal standard, isolated yields in paranthesis; n.r.: no reaction

2C. Investigation of reaction conditions for reductive coupling of aldehydes and ynamides

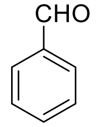


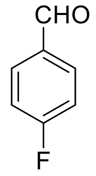
entry	Deviation from standard conditions	yield%[a]	r.r (**5ba:5ba'**)
1	none	91 (86)	>95:5
2	LiO^{t}Bu (12 mol%)	83	>95:5
3	Cs_2CO_3 (20 mol%)	74	>95:5
4	K_3PO_4 (12 mol%)	39	>95:5
5	DBU (20 mol%)	n.r.	-

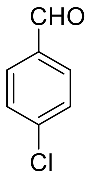
Reaction Conditions: [a]Yields were determined by analysis of ^1H NMR of the crude reaction mixture using 1,1,2,2-tetrachloroethane as an internal standard, isolated yields in paranthesis; n.r.: no reaction

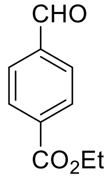
3. Literature procedures for preparation of catalyst, aldehydes, and alkynes

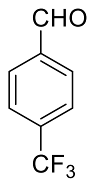
Ni(COD)(DQ) was prepared using the literature protocol. [2] Aldehydes **1a-c, 1e-n** were commercially obtained. Aldehyde **1d** was prepared from 4-formyl benzoic acid using the literature procedure. [3] Alkynes **2a**, **2g**, **2h**, and **2i** were commercially obtained. Alkyne **2b** and **2c** were prepared using literature procedures. [4] **2d**, **2e,** and **2f** were synthesized following literature reports from the corresponding terminal alkynes and iodobenzene via Sonogashira coupling. [5]

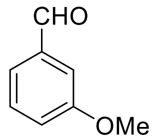

1a

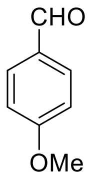

1b

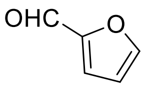

1c

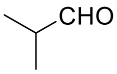

1d

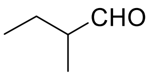

1e

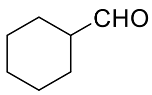

1f

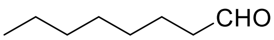

1g

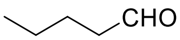

1h

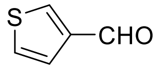

1i

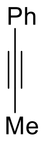

1j

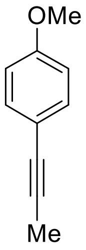

1k

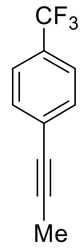

1l

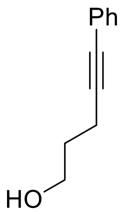

1m

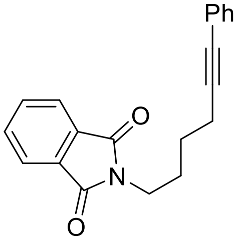

1n

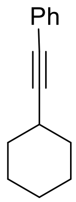

2a


2b


2c

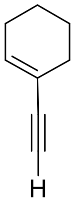

2d


2e


2f

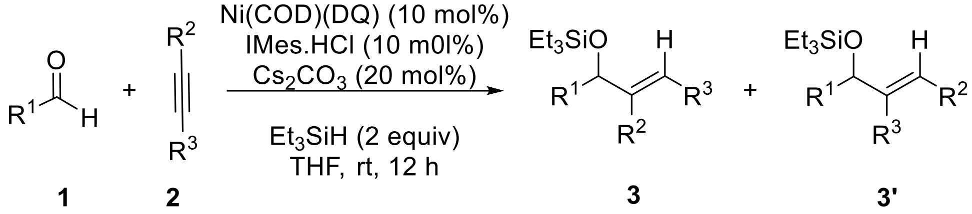

2g


2h


2i

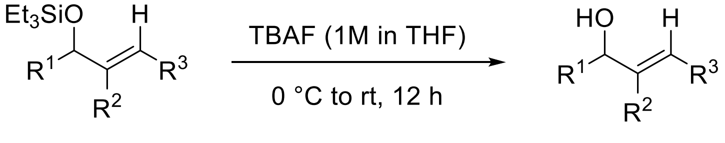
4. General procedure for reductive coupling of aldehydes 1 and alkynes 2

4A. General procedure (GP1): Reductive coupling of aldehydes and alkynes at room temperature.



To a flame-dried Schlenk tube was added Ni(COD)(DQ) (10 mol%), IMes.HCl (10 mol%), and Cs_2CO_3 (20 mol%) under nitrogen atmosphere. At 0 °C, dry THF (0.4 M) was added, and the reaction mixture was stirred vigorously for 1 h at the same temperature. After 1 h, the Schlenk tube was warmed to rt and Et_3SiH (2 equiv) was added, and the mixture was stirred for 15 min. Aldehyde **1** (1 equiv) was then added dropwise, followed by a solution of alkyne **2** (1.2 equiv) in dry THF (0.4 M) over 15 mins. When the addition was complete, the reaction mixture was allowed to stir at rt for 12 h. The reaction mixture was quenched with sat. aq. NH_4Cl. The crude reaction mixture was diluted with 25 mL of EtOAc and washed with distilled water (2 x 10 mL) and brine (10 mL). The organic layer was separated and dried over anhydrous Na_2SO_4. The crude reaction mixture was purified by flash column chromatography (EtOAc/*n*-hexane as eluents) over silica gel.

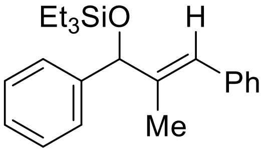
4B. General procedure (GP-D): Desilylation of silylated allylic alcohol



To a solution of the crude reaction mixture obtained from **GP1** in THF (0.15 M), TBAF (1 M in THF, 2 equiv) was added dropwise at 0 °C. The reaction mixture was left to stir at rt for an additional 12 h. The crude reaction mixture was diluted with 25 mL of EtOAc and washed with distilled water (2 x 10 mL) and brine (10 mL). The organic layer was separated and dried over anhydrous Na_2SO_4. The crude reaction mixture was purified by flash column chromatography (EtOAc/*n*-hexane as eluents) over silica gel.

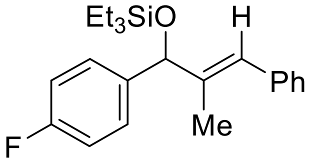
5. Characterization data of silylated allyl alcohols (3aa-3ai)

(E)-triethyl((2-methyl-1,3-diphenylallyl)oxy)silane (3aa)



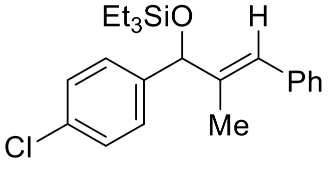
Following general procedure **GP1**, benzaldehyde **1a** (31.8 mg, 0.3 mmol), 1-phenyl-1-propyne **2a** (41.8 mg, 0.36 mmol) was converted to silylated allyl alcohol **3aa** in 79% yield in 97:3 regioisomeric ratio (80.2 mg, 0.237 mmol) as a colorless oil; R$_f$ (hexanes): 0.65; The spectral data matched those reported in the literature.[6] **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.48 (d, *J* = 7.6 Hz, 2H), 7.41-7.29 (m, 6H), 7.31–7.22 (m, 2H), 6.77 (s, 1H), 5.30 (s, 1H), 1.72 (s, 3H), 1.01 (t, *J* = 7.9 Hz, 9H), 0.70 (q, *J* = 7.9 Hz, 6H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 143.5, 141.0, 138.0, 129.1, 128.2, 128.1, 127.0, 126.5, 126.3, 125.7, 80.1, 13.3, 7.0, 5.0.

(E)-triethyl((1-(4-fluorophenyl)-2-methyl-3-phenylallyl)oxy)silane (3ba)



Following general procedure **GP1**, benzaldehyde **1b** (37.2 mg, 0.3 mmol), 1-phenyl-1-propyne **2a** (41.8 mg, 0.36 mmol) was converted to silylated allyl alcohol **3ba** in 79% yield in 97:3 regioisomeric ratio (85.0 mg, 0.238 mmol) as a colorless oil; R$_f$ (*n*-hexane): 0.65; The spectral data matched those reported in the literature.[7] **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.43–7.19 (m, 7H), 7.01 (t, *J* = 8.6 Hz, 2H), 6.70 (s, 1H), 5.22 (s, 1H), 1.66 (s, 3H), 0.95 (t, *J* = 7.9 Hz, 9H), 0.64 (q, *J* = 7.9 Hz, 6H).

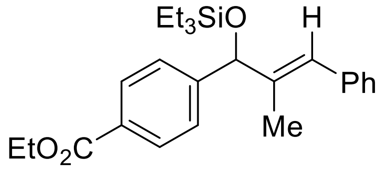
(E)-((1-(4-chlorophenyl)-2-methyl-3-phenylallyl)oxy)triethylsilane (3ca)



Following general procedure **GP1**, benzaldehyde **1c** (42 mg, 0.3 mmol), 1-phenyl-1-propyne **2a** (41.8 mg, 0.36 mmol) was converted to silylated allyl alcohol **3ca** in 72% yield in 97:3

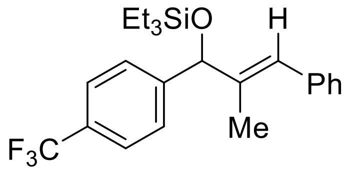
regioisomeric ratio (80.1 mg, 0.215 mmol) as a colorless oil; R_f (*n*-hexane): 0.65; **IR** (film) ν_{max}/cm^{-1}: 2955, 1652, 1488, 1077, 1238, 875; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38–7.25 (m, 8H), 7.23-7.17 (m, 1H), 6.68 (s, 1H), 5.20 (s, 1H), 1.64 (s, 3H), 0.94 (t, *J* = 7.9 Hz, 9H), 0.64 (q, *J* = 7.9 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.1, 140.5, 137.7, 132.7, 129.1, 128.3, 128.3, 127.6, 126.6, 126.1, 79.6, 13.2, 7.0, 5.0; **HRMS** (ESI) Calculated for $C_{22}H_{29}ClOSiK$ $[M+K]^+$: 411.1308, Found: 411.1299.

ethyl (E)-4-(2-methyl-3-phenyl-1-((triethylsilyl)oxy)allyl)benzoate (3da)



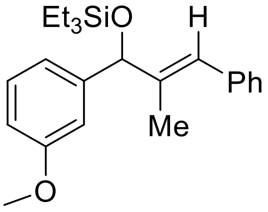
Following general procedure **GP1**, benzaldehyde **1d** (52.2 mg, 0.3 mmol), 1-phenyl-1-propyne **2a** (41.8 mg, 0.36 mmol) was converted to silylated allyl alcohol **3da** in 77% yield in 97:3 regioisomeric ratio (95.0 mg, 0.231 mmol) as a colorless oil; R_f (5% EtOAc in *n*-hexane): 0.3; **IR** (film) ν_{max}/cm^{-1}: 2956, 1718, 1611, 1410, 1173, 1103; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.2 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.42–7.25 (m, 5H), 6.78 (s, 1H), 5.35 (s, 1H), 4.43 (q, *J* = 7.1 Hz, 2H), 1.71 (s, 3H), 1.45 (t, *J* = 7.1 Hz, 3H), 1.02 (t, *J* = 8.0 Hz, 9H), 0.71 (q, *J* = 7.8 Hz, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.8, 148.7, 140.3, 137.7, 129.5, 129.4, 129.1, 128.3, 126.7, 126.4, 126.2, 80.0, 61.0, 14.5, 13.1, 7.0, 5.0; **HRMS** (ESI) Calculated for $C_{25}H_{35}O_3Si$ $[M+H]^+$: 411.2350, Found: 411.2367.

(E)-triethyl((2-methyl-3-phenyl-1-(4-(trifluoromethyl)phenyl)allyl)oxy)silane (3ea)



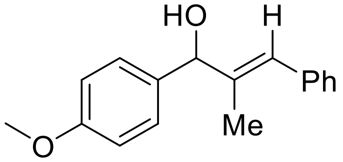
Following general procedure **GP1**, benzaldehyde **1e** (52.2 mg, 0.3 mmol), 1-phenyl-1-propyne **2a** (41.8 mg, 0.36 mmol) was converted to silylated allyl alcohol **3ea** in 75% yield in 97:3 regioisomeric ratio (92.0 mg, 0.226 mmol) as a colorless oil; R_f (*n*-hexane): 0.6; **IR** (film) ν_{max}/cm^{-1}: 2956, 1620, 1458, 1240, 1067; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66–7.57 (m, 4H), 7.43–7.31 (m, 4H), 7.31–7.23 (m, 1H), 6.77 (s, 1H), 5.34 (s, 1H), 1.70 (s, 3H), 1.01 (t, *J* = 7.9 Hz, 9H), 0.71 (q, *J* = 7.9 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.1, 139.8, 137.1, 128.6, 127.9, 126.3, 126.1, 126.0, 124.7, 124.7, 124.6, 124.6, 79.3, 12.5, 6.5, 4.5; **^{19}F NMR** (471 MHz, CDCl3) δ -62.4; **HRMS** (ESI) Calculated for $C_{17}H_{15}F_3OK$ $[M+K]^+$: 331.0707, Found: 331.0700 (Calculated for desilylated **3da)**.

(E)-triethyl((1-(3-methoxyphenyl)-2-methyl-3-phenylallyl)oxy)silane (3fa)



Following general procedure **GP1**, benzaldehyde **1f** (40.8 mg, 0.3 mmol), 1-phenyl-1-propyne **2a** (41.8 mg, 0.36 mmol) was converted to silylated allyl alcohol **3fa** in 71% yield in 97:3 regioisomeric ratio (78.6 mg, 0.213 mmol) as a colorless oil; R_f (5% EtOAc in *n*-hexane): 0.5; **IR** (film) ν_{max}/cm^{-1}: 2954, 1600, 1260, 1488, 1049, 876; **^{1}H NMR** (400 MHz, CDCl3) δ 7.28–7.18 (m, 3H), 7.19–7.09 (m, 3H), 6.97–6.88 (m, 2H), 6.70 (dd, *J* = 8.1, 2.7 Hz, 1H), 6.61 (s, 1H), 5.14 (s, 1H), 3.73 (s, 3H), 1.59 (s, 3H), 0.88 (t, *J* = 7.9 Hz, 9H), 0.57 (q, *J* = 7.9 Hz, 6H); **^{13}C NMR** (126 MHz, CDCl3) δ 159.5, 145.1, 140.8, 137.9, 129.0, 128.9, 128.1, 126.3, 125.7, 118.7, 112.2, 111.8, 79.8 55.2, 13.1, 6.9, 4.9; **HRMS** (ESI) Calculated for $C_{23}H_{32}O_2SiNa$ $[M+Na]^+$: 391.2064, Found: 391.2047.

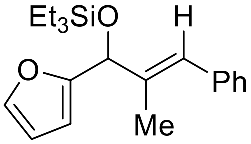
(E)-triethyl((1-(4-methoxyphenyl)-2-methyl-3-phenylallyl)oxy)silane (3ga)



To a flame-dried Schlenk tube was added Ni(COD)(DQ) (9.9 mg, 0.03 mmol, 10 mol%), IMes.HCl (10.2 mg, 0.03 mmol, 10 mol%), and Cs_2CO_3 (19.5 mg, 0.06 mmol, 20 mol%) under nitrogen atmosphere. At 0 °C, dry THF (0.7 mL, 0.4 M) was added, and the reaction mixture was stirred vigorously for 1 h at the same temperature. After 1 h, the Schlenk tube was warmed to 45 °C, Et_3SiH (96 μL, 0.6 mmol, 2 equiv) was added, and the mixture was stirred for 15 min. Benzaldehyde **1g** (40.8 mg, 0.3 mmol) was then added dropwise, followed by a solution of alkyne **2a** (41.8 mg, 0.36 mmol) in dry THF (0.6 mL, 0.4 M) over 15 min. When the addition was complete, the reaction mixture was allowed to stir at 45 °C for 24 h. The reaction mixture was quenched with sat. aq. NH_4Cl. The crude reaction mixture was diluted with 25 mL of EtOAc and washed with distilled water (2 x 10 mL), and brine (10 mL). The organic layer was separated and dried over anhydrous Na_2SO_4. The crude reaction mixture was purified by flash column chromatography (EtOAc/*n*-

hexane as eluents) over silica gel. Silylated allyl alcohol **3ga** was obtained in 54% yield in 97:3 regioisomeric ratio [NMR yield (int. std.: 1,1,2,2-tetrachloroethane)]. Duroquinone co-elutes with the desired product; therefore, following procedure **GP-D**, the corresponding desilylated allylic alcohol was obtained in 49% yield in 97:3 regioisomeric ratio (37.1 mg, 0.146 mmol) as a colorless oil; R_f (20% EtOAc in *n*-hexane): 0.3; The spectral data matched those reported in the literature.[8] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40–7.34 (m, 6H), 7.31–7.22 (m, 1H), 7.02–6.90 (m, 2H), 6.81 (s, 1H), 5.26 (s, 1H), 3.84 (s, 3H), 1.77 (s, 3H).

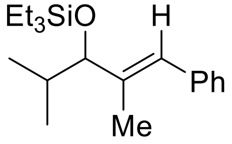
(E)-triethyl((1-(furan-2-yl)-2-methyl-3-phenylallyl)oxy)silane (3ha)



To a flame-dried Schlenk tube was added Ni(COD)(DQ) (9.9 mg, 0.03 mmol, 10 mol%), IMes.HCl (10.2 mg, 0.03 mmol, 10 mol%), and Cs_2CO_3 (19.5 mg, 0.06 mmol, 20 mol%) under nitrogen atmosphere. At 0 °C, dry THF (0.7 mL, 0.4 M) was added, and the reaction mixture was stirred vigorously for 1 h at the same temperature. After 1 h, the Schlenk tube was warmed to 45 °C, and Et_3SiH (96 μL, 0.6 mmol, 2 equiv) was added, and the mixture was stirred for 15 min. Benzaldehyde **1h** (28.8 mg, 0.3 mmol, 1 equiv) was then added dropwise, followed by a solution of alkyne **2a** (41.8 mg, 0.36 mmol, 1.2 equiv) in dry THF (0.6 mL, 0.4 M) over 15 min. When the addition was complete, the reaction mixture was allowed to stir at 45 °C for 24 h. The reaction mixture was quenched with sat. aq. NH_4Cl. The crude reaction mixture was diluted with 25 mL of EtOAc and washed with distilled water (2 x 10 mL), and brine (10 mL). The organic layer was separated and dried over anhydrous Na_2SO_4. The crude reaction mixture was purified by flash column chromatography (EtOAc/*n*-hexane as eluents) over silica gel. Silylated allyl alcohol **3ha** was obtained in 21% yield in >95:5 regioisomeric ratio (20.4 mg, 0.062 mmol) as a colorless oil; Low yield was probably due to undesired polymerization of furfural in the reaction medium; R_f (*n*-hexane): 0.5; **IR** (film) ν_{max}/cm^{-1}: 2923, 2371, 1726, 1620, 1260, 1096, 885; **^{1}H NMR** (400 MHz, $CDCl_3$) δ

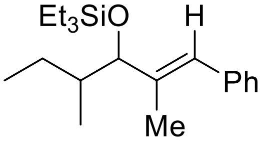
7.38-7.28 (m, 5H), 7.25-7.19 (m, 1H), 6.74 (s, 1H), 6.35-6.31 (m, 1H), 6.26 (d, *J* = 3.2 Hz, 1H), 5.24 (s, 1H), 1.83 (s, 3H), 0.98 (t, *J* = 7.9 Hz, 9H), 0.67 (q, *J* = 7.9 Hz, 6H); ^{13}**C NMR** (101 MHz, CDCl$_3$) δ 156.0, 141.8, 138.0, 137.7, 129.0, 128.1, 126.4, 126.0, 110.1, 106.6, 73.8, 14.2, 6.8, 4.7; **HRMS** (ESI) Calculated for $C_{20}H_{28}O_2SiNa$ [M+Na]$^+$: 351.1751, Found: 351.1722.

(E)-((2,4-dimethyl-1-phenylpent-1-en-3-yl)oxy)triethylsilane (3ia)



Following general procedure **GP1**, benzaldehyde **1i** (21.6 mg, 0.3 mmol), 1-phenyl-1-propyne **2a** (41.8 mg, 0.36 mmol) was converted to silylated allyl alcohol **3ia** in 80% yield in 97:3 regioisomeric ratio (73.7 mg, 0.241 mmol) as a colorless oil; R$_f$ (*n*-hexane): 0.6; The spectral data matched those reported in the literature.[9] ^{1}**H NMR** (400 MHz, CDCl$_3$) δ 7.35–7.29 (m, 2H), 7.27–7.23 (m, 2H), 7.22–7.17 (m, 1H), 6.36 (s, 1H), 3.68 (d, *J* = 7.9 Hz, 1H), 1.79 (s, 3H), 0.99–0.92 (m, 12H), 0.81 (d, *J* = 6.8 Hz, 3H), 0.60 (q, *J* = 7.9 Hz, 6H).

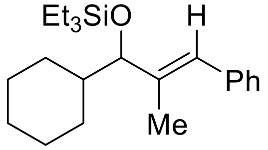
(E)-((2,4-dimethyl-1-phenylhex-1-en-3-yl)oxy)triethylsilane (3ja)



To a flame-dried Schlenk tube was added Ni(COD)(DQ) (9.9 mg, 0.03 mmol, 10 mol%) and taken inside the glovebox. To this, free IMes carbene, 1,3-Bis(2,4,6-trimethylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene (9.1 mg, 0.03 mmol, 10 mol%) was added, sealed with a rubber septum and taken outside the glovebox. The tube was placed at 0 °C before adding dry THF (0.7 mL, 0.4 M), and the reaction mixture was stirred vigorously for 1 h at the same temperature. Then, the mixture was warmed to rt, and Et$_3$SiH (96 μL, 0.6 mmol, 2 equiv) was added and stirred for 15 min. Benzaldehyde **1j** (26.0 mg, 0.3 mmol, 1 equiv) was then added dropwise, followed by a solution of alkyne **2a** (41.8 mg, 0.36 mmol, 1.2 equiv) in dry THF (0.6 mL, 0.4 M) over 15 min. After the addition, the reaction mixture was allowed to stir at rt for 12 h. The reaction mixture was quenched with sat. aq. NH$_4$Cl. The crude reaction mixture was diluted with 25 mL of EtOAc and washed with distilled water (2 x 10 mL), and brine (10 mL). The organic layer was separated and dried over anhydrous Na$_2$SO$_4$. The crude reaction mixture was purified by flash column chromatography

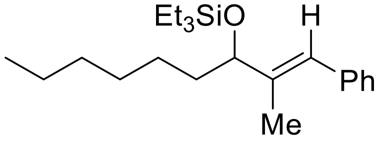
(EtOAc/*n*-hexane as eluents) over silica gel. The silylated allyl alcohol **3ja** was obtained in 71% yield in 97:3 regioisomeric ratio and as a mixture of 3:2 diastereomeric ratio (67.6 mg, 0.212 mmol) as a colorless oil; R$_f$ (*n*-hexane): 0.6; The spectral data matched those reported in the literature.[6] Major diastereomer: **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.44–7.22 (m, 5H), 6.42 (d, *J* = 13.9 Hz, 1H), 3.87 (d, *J* = 7.2 Hz, 0.6H), 1.85 (s, 3H), 1.70–1.53 (m, 1H), 1.50-1.36 (m, 1H), 1.18-1.06 (m, 1H), 1.06–0.92 (m, 14H), 0.82 (d, *J* = 6.8 Hz, 1H), 0.66 (q, *J* = 8.0 Hz, 6H); Minor diastereomer: **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.44–7.22 (m, 5H), 6.42 (d, *J* = 13.9 Hz, 1H), 3.81 (d, *J* = 8.2 Hz, 0.4H), 1.85 (s, 3H), 1.70–1.53 (m, 1H), 1.50-1.36 (m, 1H), 1.18-1.06 (m, 1H), 1.06–0.92 (m, 14H), 0.82 (d, *J* = 6.8 Hz, 1H), 0.66 (q, *J* = 8.0 Hz, 6H).

(E)-((1-cyclohexyl-2-methyl-3-phenylallyl)oxy)triethylsilane (3ka)



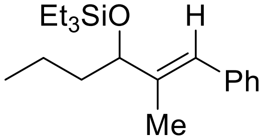
Following general procedure **GP1**, benzaldehyde **1k** (33.6 mg, 0.3 mmol), 1-phenyl-1-propyne **2a** (41.8 mg, 0.36 mmol) was converted to silylated allyl alcohol **3ka** in 68% yield in 97:3 regioisomeric ratio (70.3 mg, 0.204 mmol) as a colorless oil; R$_f$ (*n*-hexane): 0.6; The spectral data matched those reported in the literature.[9] **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.35–7.29 (m, 2H), 7.27–7.23 (m, 2H), 7.22–7.17 (m, 1H), 6.36 (s, 1H), 3.77 (d, *J* = 7.9 Hz, 1H), 2.09 (d, *J* = 12.9 Hz, 1H), 1.84 (s, 3H), 1.81–1.63 (m, 3H), 1.58-1.47 (m, 2H), 1.34–1.12 (m, 3H), 1.05-0.85 (m, 11H), 0.65 (q, *J* = 7.9 Hz, 6H).

(E)-triethyl((2-methyl-1-phenylnon-1-en-3-yl)oxy)silane (3la)



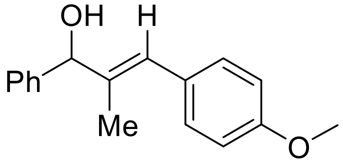
Following general procedure **GP1**, benzaldehyde **1l** (34.2 mg, 0.3 mmol), 1-phenyl-1-propyne **2a** (41.8 mg, 0.36 mmol) was converted to silylated allyl alcohol **3la** in 20% yield in 97:3 regioisomeric ratio (21 mg, 0.060 mmol) as a colorless oil; R$_f$ (*n*-hexane): 0.6; The spectral data matched those reported in the literature.[6] **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.39–7.18 (m, 5H), 6.42 (s, 1H), 4.12 (t, *J* = 6.5 Hz, 1H), 1.84 (s, 3H), 1.63–1.55 (m, 2H), 1.37-1.24 (m, 8H), 0.98 (t, *J* = 7.9 Hz, 9H), 0.92–0.88 (m, 3H), 0.63 (q, *J* = 7.9 Hz, 6H).

(E)-triethyl((2-methyl-1-phenylhex-1-en-3-yl)oxy)silane (3ma)



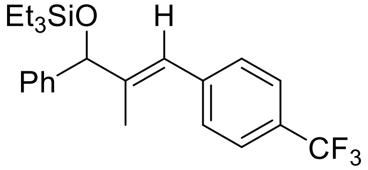
To a flame-dried Schlenk tube was added Ni(COD)(DQ) (9.9 mg, 0.03 mmol, 10 mol%) and taken inside the glovebox. To this, free IMes carbene, 1,3-Bis(2,4,6-trimethylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene (9.1 mg, 0.03 mmol, 10 mol%) was added, sealed with a rubber septum and taken outside the glovebox. The tube was placed at 0 °C before adding dry THF (0.7 mL, 0.4 M), and the reaction mixture was stirred vigorously for 1 h at the same temperature. Then, the mixture was warmed to rt, and Et_3SiH (96 μL, 0.6 mmol, 2 equiv) was added and stirred for 15 min. Benzaldehyde **1m** (21.6 mg, 0.3 mmol, 1 equiv) was then added dropwise, followed by a solution of alkyne **2a** (41.8 mg, 0.36 mmol, 1.2 equiv) in dry THF (0.6 mL, 0.4 M) over 15 min. After the addition, the reaction mixture was allowed to stir at rt for 12 h. The reaction mixture was quenched with sat. aq. NH_4Cl. The crude reaction mixture was diluted with 25 mL of EtOAc and washed with distilled water (2 x 10 mL), and brine (10 mL). The organic layer was separated and dried over anhydrous Na_2SO_4. The crude reaction mixture was purified by flash column chromatography (EtOAc/*n*-hexane as eluents) over silica gel. The silylated allyl alcohol **3ma** was obtained in 55% yield in 97:3 regioisomeric ratio (50.3 mg, 0.165 mmol) as a colorless oil; R_f (*n*-hexane): 0.6; **IR** (film) ν_{max}/cm^{-1}: 2917, 1640, 1379, 1173, 1092; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.4 Hz, 2H), 7.31–7.25 (m, 2H), 7.25–7.17 (m, 1H), 6.42 (s, 1H), 4.13 (t, *J* = 6.4 Hz, 1H), 1.84 (s, 3H), 1.63-1.51 (m, 2H), 1.48–1.38 (m, 1H), 1.36–1.25 (m, 1H), 1.03-0.91 (m, 12H), 0.63 (q, *J* = 7.8 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.3, 138.2, 129.0, 128.2, 126.3, 125.1, 78.7, 38.9, 19.2, 14.3, 13.2, 7.1, 5.0; **HRMS** (ESI) Calculated for $C_{19}H_{32}OSiK$ $[M+K]^+$: 343.1854, Found: 343.1849.

(E)-triethyl((3-(4-methoxyphenyl)-2-methyl-1-phenylallyl)oxy)silane (3ab)



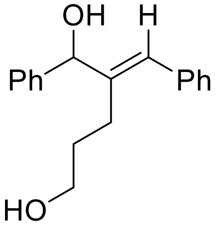
Following general procedure **GP1**, the corresponding benzaldehyde **1a** (31.8 mg, 0.3 mmol), 1-methoxy-4-(prop-1-yn-1-yl)benzene **2b** (52.6 mg, 0.36 mmol) was converted to silylated allyl alcohol **3ab** in 68% yield in 97:3 regioisomeric ratio (NMR yield (int. std.: 1,1,2,2-tetrachloroethane). Duroquinone co-elutes with the desired product; therefore, following procedure **GP-D**, the corresponding desilylated allylic alcohol was obtained in 62% yield in 97:3 regioisomeric ratio (47 mg, 0.186 mmol) as a colorless oil; R_f (2% EtOAc in *n*-hexane): 0.3; The spectral data matched those reported in the literature.[8] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53–7.44 (m, 2H), 7.44–7.33 (m, 3H), 7.32–7.26 (m, 2H), 6.98–6.89 (m, 2H), 6.74 (s, 1H), 5.30 (s, 1H), 3.84 (s, 2H), 1.78 (s, 3H).

(E)-triethyl((2-methyl-1-phenyl-3-(4-(trifluoromethyl)phenyl)allyl)oxy)silane (3ac)



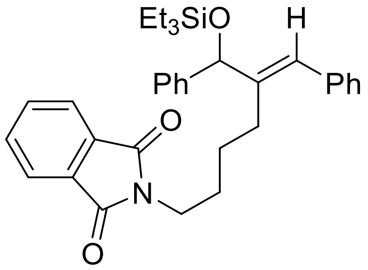
Following general procedure **GP1**, the reaction mixture was stirred at rt for 36 h. Benzaldehyde **1a** (31.8 mg, 0.3 mmol), 1-(prop-1-yn-1-yl)-4-(trifluoromethyl)benzene **2c** (66.3 mg, 0.36 mmol) was converted to silylated allyl alcohol **3ac** in 11% yield (13.3 mg, 0.033 mmol) as a colorless oil; R_f (*n*-hexane): 0.6; The low yield could be attributed to the low reactivity of the alkyne as majority of alkyne remained unreacted after 36 h; **IR** (film) ν_{max}/cm^{-1}: 3013, 2120, 1560, 1391, 1209; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.48–7.23 (m, 7H), 6.76 (s, 1H), 5.24 (s, 1H), 1.68 (s, 3H), 0.95 (t, *J* = 7.9 Hz, 9H), 0.64 (q, *J* = 7.9 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.4, 143.1, 141.6, 129.3, 128.2, 127.3, 126.4, 125.2, 125.1, 124.1, 79.8, 13.7, 7.0, 5.0; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -62.4; **HRMS** (ESI) Calculated for $C_{23}H_{29}F_3OSiK$ $[M+K]^+$: 445.1571, Found: 445.1552.

(E)-5-phenyl-4-(phenyl((triethylsilyl)oxy)methyl)pent-4-en-1-ol (3ad)



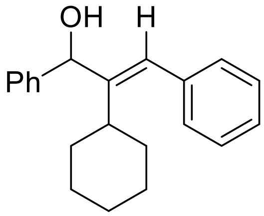
Following general procedure **GP1**, the corresponding benzaldehyde **1a** (33.3 mg, 0.3 mmol), 5-phenylpent-4-yn-1-ol **2d** (57.7 mg, 0.36 mmol) was converted to silylated allylic alcohol **3ad** in 58% yield in 97:3 regioisomeric ratio (66.5 mg, 0.174 mmol) as a colorless oil; R_f (20% EtOAc in *n*-hexane): 0.5. The product was prone to decomposition; therefore, the product was isolated as a free-diol after desilylation. Following general procedure **GP-D**, the corresponding desilylated allylic alcohol was obtained in 53% yield in 97:3 regioisomeric ratio (42.6 mg, 0.159 mmol) as a colorless oil; R_f (25% EtOAc in *n*-hexane): 0.2; **IR** (film) ν_{max}/cm^{-1}: 3592, 3015, 2927, 1449, 1215, 892; **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.49–7.39 (m, 4H), 7.42-7.32 (m, 3H), 7.29–7.20 (m, 3H), 6.07 (s, 1H), 5.19 (s, 1H), 4.13-4.03 (m, 1H), 3.93-3.83 (m, 1H), 2.87-2.74 (m, 1H), 2.63–2.51 (m, 1H), 1.91-1.81 (m, 2H); **^{13}C NMR** (126 MHz, CDCl$_3$) δ 140.0, 139.9, 137.3, 129.1, 128.4, 128.3, 127.7, 127.6, 126.8, 126.7, 82.9, 66.2, 28.1, 26.2; **HRMS** (ESI) Calculated for $C_{18}H_{20}O_2Na$ [M+Na]$^+$: 291.1356, Found: 291.1368.

(E)-2-(6-phenyl-5-(phenyl((triethylsilyl)oxy)methyl)hex-5-en-1-yl)isoindoline-1,3-dione (3ae)



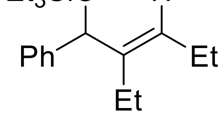
To a flame-dried Schlenk tube was added Ni(COD)(DQ) (9.9 mg, 0.03 mmol, 10 mol%), IMes.HCl (10.2 mg, 0.03 mmol, 10 mol%), and Cs_2CO_3 (19.5 mg, 0.06 mmol, 20 mol%) under nitrogen atmosphere. At 0 °C, dry THF (0.7 mL, 0.4 M) was added, and the reaction mixture was stirred vigorously for 1 h at the same temperature. After 1 h, the Schlenk tube was warmed to 45 °C, Et_3SiH (96 µL, 0.6 mmol, 2 equiv) was added, and the mixture was stirred for 15 min. Benzaldehyde **1a** (31.8 mg, 0.3 mmol) was then added dropwise, followed by a solution of 2-(6-phenylhex-5-yn-1-yl)isoindoline-1,3-dione **2e** (109.2 mg, 0.36 mmol) in dry THF (0.6 mL, 0.4 M) over 15 mins. When the addition was complete, the reaction mixture was allowed to stir at 45 °C for 24 h. The reaction mixture was quenched with sat. aq. NH_4Cl. The crude reaction mixture was diluted with 25 mL of EtOAc and washed with distilled water (2 x 10 mL) and brine (10 mL). The organic layer was separated and dried over anhydrous Na_2SO_4. The crude reaction mixture was purified by flash column chromatography (EtOAc/*n*-hexane as eluents) over silica gel. The silylated allyl alcohol **3ae** was obtained in 61% yield in 97:3 regioisomeric ratio (96.2 mg, 0.183 mmol) as a yellowish oil; R_f (10% EtOAc in *n*-hexane): 0.3; **IR** (film) ν_{max}/cm^{-1}: 2953, 1772, 1713, 1467, 1396, 1239; **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.78 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.66 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.37–7.32 (m, 2H), 7.29–7.17 (m, 6H), 7.11 (ddd, *J* = 11.3, 6.6, 1.6 Hz, 2H), 6.71 (s, 1H), 5.20 (s, 1H), 3.47 (t, *J* = 7.1 Hz, 2H), 2.20-2.09 (m, 1H), 2.06–1.96 (m, 1H), 1.52–1.43 (m, 2H), 1.33–1.08 (m, 2H), 0.88 (t, *J* = 8.0 Hz, 9H), 0.56 (q, *J* = 8.0 Hz, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.4, 144.6, 143.5, 138.0, 133.9, 132.4, 128.7, 128.3, 128.1, 127.1, 126.6, 126.5, 126.2, 123.2, 79.0, 37.9, 28.9, 27.5, 26.3, 7.0, 5.0; **HRMS** (ESI) Calculated for $C_{33}H_{39}NO_3SiNa$ $[M+Na]^+$: 548.2591, Found: 548.2604.

(E)-((2-cyclohexyl-1,3-diphenylallyl)oxy)triethylsilane (3af)



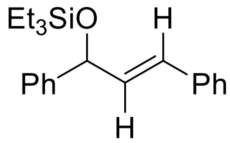
Following modified procedure **GP1**, the corresponding benzaldehyde **1a** (31.8 mg, 0.3 mmol), (cyclohexylethynyl)benzene **2f** (66.3 mg, 0.36 mmol) was converted to silylated allyl alcohol **3af** in 63% yield in 56:44 regioisomeric ratio (NMR yield (int. std.: 1,1,2,2-tetrachloroethane). Duroquinone co-elutes with the desired product, therefore, following general procedure **GP-D**, the corresponding desilylated allylic alcohol was obtained in 55% yield and isolated as 77:23 regioisomeric ratio (48.3 mg, 0.165 mmol) as a colorless oil; R_f (*n*-hexane): 0.5; **IR** (film) ν_{max}/cm^{-1}: 3592, 3015, 2927, 1449, 1215; Major regioisomer: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49–7.11 (m, 13H), 6.61 (s, 1H), 5.40 (s, 1H), 2.70 (tt, *J* = 11.7, 3.2 Hz, 1H), 1.84-0.98 (m, 15H); Minior regioisomer: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49–7.11 (m, 13H), 5.68 (s, 0.3H), 5.14 (s, 0.3H), 2.34 (tt, *J* = 12.3, 3.5 Hz, 0.3H), 1.84-0.98 (m, 15H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.5, 143.6, 138.0, 129.5, 128.9, 128.5, 128.4, 128.3, 127.9, 127.68, 127.3, 127.2, 126.9, 126.6, 106.4, 76.3, 73.8, 41.6, 40.0, 32.9, 32.4, 32.2, 30.9, 30.7, 27.1, 26.7, 26.2, 25.0; **HRMS** (ESI) Calculated for $C_{21}H_{24}ONa$ $[M+Na]^+$: 315.1719, Found: 315.1750.

(E)-triethyl((2-ethyl-1-phenylpent-2-en-1-yl)oxy)silane (3ag)



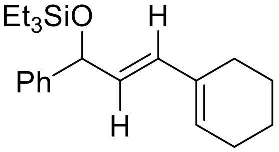
Following general procedure **GP1**, benzaldehyde **1a** (31.8 mg, 0.3 mmol), 3-hexyne **2g** (29.5 mg, 0.36 mmol) was converted to silylated allyl alcohol **3ag** in 72% yield in 97:3 regioisomeric ratio (66 mg, 0.216 mmol) as a colorless oil; R_f (*n*-hexane): 0.6; The spectral data matched those reported in the literature.[9] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48–7.39 (m, 2H), 7.38-7.22 (m, 3H), 5.58 (t, *J* = 7.3 Hz, 1H), 5.16 (s, 1H), 2.20-2.06 (m, 2H), 2.02-1.89 (m, 2H), 1.07 (t, *J* = 7.5 Hz, 3H), 0.98 (t, *J* = 7.9 Hz, 9H), 0.79 (t, *J* = 7.6 Hz, 3H), 0.65 (q, *J* = 7.9 Hz, 6H).

(E)-((1,3-diphenylallyl)oxy)triethylsilane (3ah)



To a flame-dried Schlenk tube was added Ni(COD)(DQ) (9.9 mg, 0.03 mmol, 10 mol%), IMes.HCl (10.2 mg, 0.03 mmol, 10 mol%), and Cs_2CO_3 (19.5 mg, 0.06 mmol, 20 mol%) under nitrogen atmosphere. At 0 °C, dry THF (0.7 mL, 0.4 M) was added, and the reaction mixture was stirred vigorously for 1 h at the same temperature. After 1 h, the Schlenk tube was warmed to rt, Et_3SiH (96 μL, 0.6 mmol, 2 equiv) was added and stirred for 15 min. Benzaldehyde **1a** (31.8 mg, 0.3 mmol, 1 equiv) was then added dropwise to the reaction mixture, followed by the addition of ethynylbenzene **2h** (29.5 mg, 0.36 mmol, 1.2 equiv) in dry THF (0.6 mL, 0.4 M) over 2 h using a syringe pump. When the addition was complete, the reaction mixture was allowed to stir at rt for 12 h. The reaction mixture was quenched with sat. aq. NH_4Cl. The crude reaction mixture was diluted with 25 mL of EtOAc and washed with distilled water (2 x 10 mL) and brine (10 mL). The organic layer was separated and dried over anhydrous Na_2SO_4. The crude reaction mixture was purified by flash column chromatography (EtOAc/*n*-hexane as eluents) over silica gel. Silylated allyl alcohol **3ah** was obtained in 74% yield in 97:3 regioisomeric ratio (72.0 mg, 0.221 mmol) as a colorless oil; R_f (*n*-hexane): 0.4; The spectral data matched those reported in the literature.[6] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46–7.17 (m, 10H), 6.63 (dd, *J* = 15.7, 1.3 Hz, 1H), 6.30 (dd, *J* = 15.7, 6.4 Hz, 1H), 5.35 (d, *J* = 6.4 Hz, 1H), 0.95 (t, *J* = 7.9 Hz, 9H), 0.64 (qd, *J* = 7.9, 3.1 Hz, 6H).

(E)-((3-(cyclohex-1-en-1-yl)-1-phenylallyl)oxy)triethylsilane (3ai)

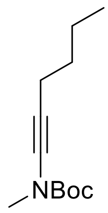


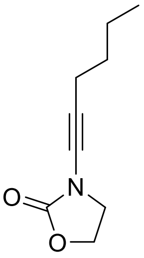
To a flame-dried Schlenk tube was added Ni(COD)(DQ) (9.9 mg, 0.03 mmol, 10 mol%), IMes.HCl (10.2 mg, 0.03 mmol, 10 mol%), and Cs_2CO_3 (19.5 mg, 0.06 mmol, 20 mol%) under nitrogen atmosphere. At 0 °C, dry THF (0.7 mL, 0.4 M) was added, and the reaction mixture was stirred vigorously for 1 h at the same temperature. After 1 h, the Schlenk tube was warmed to rt,

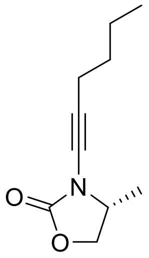
Et_3SiH (96 μL, 0.6 mmol, 2 equiv) was added and stirred for 15 min. Benzaldehyde **1a** (31.8 mg, 0.3 mmol, 1 equiv) was then added dropwise to the reaction mixture, followed by the addition of 1-ethynylcyclohex-1-ene **2i** (38.2 mg, 0.36 mmol 1.2 equiv) in dry THF (0.6 mL, 0.4 M) over 2 h using a syringe pump. When the addition was complete, the reaction mixture was allowed to stir at rt for 12 h. The reaction mixture was quenched with sat. aq. NH_4Cl. The crude reaction mixture was diluted with 25 mL of EtOAc and washed with distilled water (2 x 10 mL) and brine (10 mL). The organic layer was separated and dried over anhydrous Na_2SO_4. The crude reaction mixture was purified by flash column chromatography (EtOAc/*n*-hexane as eluents) over silica gel. The silylated allyl alcohol **3ai** was obtained in 55% yield in 98:2 regioisomeric ratio (54.2 mg, 0.165 mmol) as a colorless oil; R_f (*n*-hexane): 0.5; **IR** (film) ν_{max}/cm^{-1}: 2925, 1715, 1662, 1453, 1187, 1081; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40–7.22 (m, 5H), 6.24 (d, *J* = 15.6 Hz, 1H), 5.78 (t, *J* = 4.2 Hz, 1H), 5.65 (dd, *J* = 15.6, 6.9 Hz, 1H), 5.24 (d, *J* = 6.9 Hz, 1H), 2.18-2.06 (m, 4H), 1.71–1.60 (m, 4H), 0.96 (t, *J* = 7.9 Hz, 9H), 0.63 (q, *J* = 7.9 Hz, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.6, 135.3, 132.9, 129.5, 129.2, 128.1, 126.8, 126.0, 75.7, 25.9, 24.8, 22.5, 6.8, 5.8, 5.0; **HRMS** (ESI) Calculated for $C_{21}H_{32}OSiNa$ $[M+Na]^+$: 351.2115, Found: 351.2127.

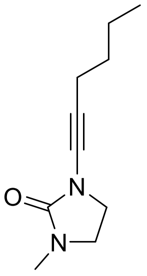
6. Procedure for preparation of ynamides (4a-4e)

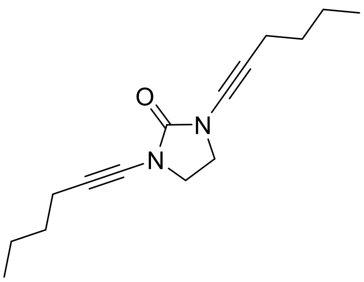
Ynamide **4b**[10], **4c**[11], **4d**[11b, 12],**4f-g**[11b] were synthesized using literature procedures. Ynamide **4a** and **4e** were prepared following the general procedure (**GP2**).[11b] 1-bromohex-1-yne was synthesized following the literature procedure.[13] (CAUTION: Exposure to 1-bromohex-1-yne may cause a severe burning sensation in the eye. Handling of the chemical must be strictly performed in fume hoods and with protective eye gears.)


4a

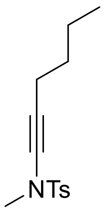

4b

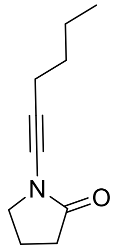

4c


4d

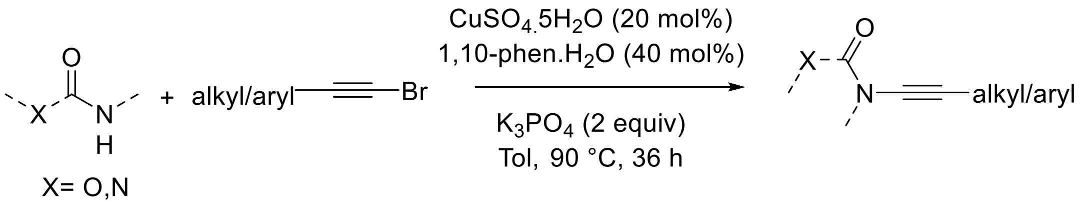

4e

Failed substrates


4f


4g

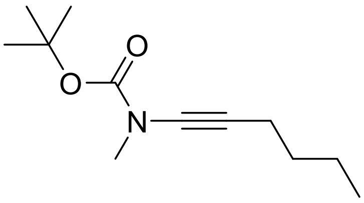
6A. General procedure for the synthesis of 4a and 4e GP2



To a solution of amide (1 equiv) in dry toluene (0.5 M) was added $CuSO_4.5H_2O$ (20 mol%), 1,10-phenanthroline monohydrate (40 mol%), and K_3PO_4 (2 equiv) under inert atmosphere. Next, alkynyl bromide (1.2 equiv) was added to the reaction mixture dropwise, and the resultant mixture was heated to 90 °C and stirred for 36 h. After completion of the reaction, the reaction mixture was cooled to rt and subjected to Celite pad filtration with CH_2Cl_2 as the solvent. Further purification was performed using flash column chromatography on silica gel using EtOAc/hexanes mixture as eluent.

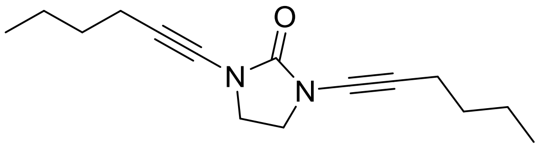
7. Characterization data of ynamides (4a, 4e)

tert-butyl hex-1-yn-1-yl(methyl)carbamate (4a)



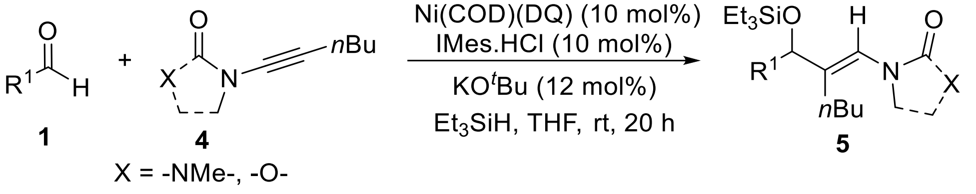
Following general procedure **GP2**, *tert*-butyl methylcarabamate (500 mg, 3.8 mmol) and 1-bromohex-1-yne (673 mg, 4.18 mmol) was converted to **4a** in 20% yield (156 mg, 0.738 mmol) as a yellow oil; R_f (5% EtOAc in *n*-hexane): 0.5; **IR** (film) ν_{max}/cm^{-1}: 2926, 2155, 1732, 1389, 1257; ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 3.04 (s, 3H), 2.26 (t, *J* = 6.8 Hz, 2H), 1.46 (s, 9H), 1.45–1.35 (m, 4H), 0.89 (t, *J* = 7.2 Hz, 3H); ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 155.0, 81.7, 75.8, 68.0, 37.1, 31.1, 28.0, 21.8, 18.1, 13.5; **HRMS** (ESI) Calculated for $C_{12}H_{22}NO_2$ $[M+H]^+$: 212.1645, Found: 212.1651.

1,3-di(hex-1-yn-1-yl)imidazolidin-2-one (4e)



Following general procedure **GP2**, imidazolidin-2-one (500 mg, 5.8 mmol) and 1-bromohex-1-yne (1.12 g, 6.96 mmol) was converted to **4e** in 32% yield (456 mg, 1.85 mmol) as a waxy white solid; m.p. 38-39 °C; R_f (20% EtOAc in *n*-hexane): 0.5; **IR** (film) ν_{max}/cm^{-1}: 2930, 2263, 1738, 1418; ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 3.69 (s, 4H), 2.28 (t, *J* = 7.0 Hz, 4H), 1.54–1.44 (m, 4H), 1.43–1.33 (m, 4H), 0.88 (t, *J* = 7.2 Hz, 6H); ^{13}**C NMR** (126 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3, 71.4, 70.4, 44.7, 31.0, 21.9, 18.2, 13.6; **HRMS** (ESI) Calculated for $C_{15}H_{23}N_2O$ $[M+H]^+$: 247.1805, Found: 247.1813.

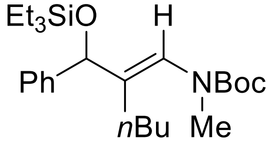
8. General procedure for reductive coupling of aldehydes (1) and ynamides (4): GP3



To a flame-dried Schlenk tube were added Ni(COD)(DQ) (10 mol%) and IMes.HCl (10 mol%) under nitrogen atmosphere. At 0 °C, dry THF (0.16 M) and KO^{t}Bu (1M solution in THF) (12 mol%) was added, and the reaction mixture was stirred for 30 min. Then, the reaction mixture was warmed to rt, and Et_3SiH (5 equiv) was added and stirred for 15 min. Next, aldehyde **1** (3 equiv) was added dropwise, followed by the addition of ynamide **4** (1 equiv) in dry THF (0.16 M) over 7 h using a syringe pump. The reaction mixture was allowed to stir at rt for an additional 13 h. The consumption of ynamide was confirmed by TLC, and the reaction mixture was subjected to Celite pad filtration. The crude reaction mixture was purified by flash column chromatography (EtOAc/*n*-hexane as eluents) over silica gel.

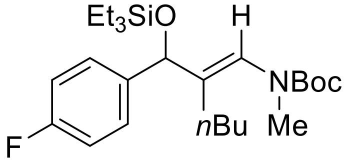
9. Characterization data of allyl ene-carbamates (5aa-5ea)

***tert*-butyl (E)-methyl(2-(phenyl((triethylsilyl)oxy)methyl)hex-1-en-1-yl)carbamate (5aa)**



Following procedure **GP3**, ynamide **4a** (32 mg, 0.15 mmol), benzaldehyde **1a** (47.7 mg, 0.45 mmol) was converted to allyl ene-carbamate **5aa** in 52% yield as a single regioisomer (33.8 mg, 0.078 mmol) as a colorless oil.; R$_f$ (5% EtOAc in *n*-hexane): 0.4; **IR** (film) ν_{max}/cm^{-1}: 2956, 1703, 1452, 1365, 1255, 1147; **^{1}H NMR** (400 MHz, Methanol-*d*$_4$) δ 7.42-7.34 (m, 2H), 7.34–7.26 (m, 2H), 7.26–7.20 (m, 1H), 6.38 (s, 1H), 5.22 (s, 1H), 3.31 (s, 3H), 1.98–1.89 (m, 1H), 1.83-1.71 (m, 1H), 1.44 (s, 9H), 1.32-1.15 (m, 4H), 0.94 (t, *J* = 7.9 Hz, 9H), 0.80 (t, *J* = 7.0 Hz, 3H), 0.62 (q, *J* = 7.4, 7.9 Hz, 6H); **^{13}C NMR** (126 MHz, Methanol-*d*$_4$) δ 153.5, 143.0, 135.8, 127.6, 126.9, 126.2, 126.0, 80.1, 76.3, 34.8, 29.9, 27.3, 26.0, 22.5, 12.7, 5.8, 4.4; **HRMS** (ESI) Calculated for $C_{25}H_{44}NO_3Si$ [M+H]$^+$: 434.3085, Found: 434.3097.

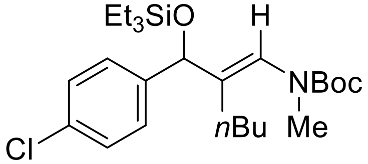
***tert*-butyl (E)-(2-((4-fluorophenyl)((triethylsilyl)oxy)methyl)hex-1-en-1-yl)(methyl) carbamate (5ab)**



Following procedure **GP3**, ynamide **4a** (32 mg, 0.15 mmol), 4-fluorobenzaldehyde **1b** (55.8 mg, 0.45 mmol) was converted to allyl ene-carbamate **5ab** in 59% yield as a single regioisomer (39.7 mg, 0.088 mmol) as a colorless oil.; R$_f$ (5% EtOAc in *n*-hexane): 0.4; **IR** (film) ν_{max}/cm^{-1}: 2957, 1703, 1507, 1458, 1366, 1221; **^{1}H NMR** (400 MHz, DMSO-*d*$_6$) δ 7.36 (td, *J* = 5.8, 2.1 Hz, 2H), 7.16–7.09 (m, 2H), 6.37 (s, 1H), 5.21 (s, 1H), 2.86 (s, 3H), 1.88–1.76 (m, 1H), 1.72-1.63 (m, 1H), 1.36 (s, 9H), 1.24–1.06 (m, 4H), 0.86 (t, *J* = 7.9 Hz, 9H), 0.74 (t, *J* = 7.0 Hz 3H), 0.56 (q, *J* = 7.9 Hz, 6H); **^{13}C NMR** (126 MHz, Methanol-*d*$_4$) δ 163.1, 161.1, 139.1, 135.1, 128.

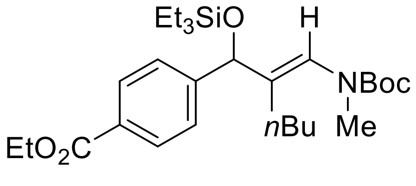
0, 125.8, 114.3, 80.2, 75.7, 35.7, 29.9, 27.3, 25.9, 22.5, 12.7, 5.8, 4.3; ^{19}F NMR (471 MHz, Methanol-*d₄*) δ -117.8; **HRMS** (ESI) Calculated for $C_{25}H_{43}FNO_3Si$ [M+H]$^+$: 452.2965, Found: 452.2991.

tert-butyl (E)-(2-((4-chlorophenyl)((triethylsilyl)oxy)methyl)hex-1-en-1-yl)(methyl) carbamate (5ac)



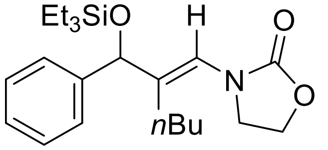
Following procedure **GP3**, ynamide **4a** (32 mg, 0.15 mmol), 4-chlorobenzaldehyde **1c** (64 mg, 0.45 mmol) was converted to allyl ene-carbamate **5ac** in 55% yield as a single regioisomer (38.6 mg, 0.082 mmol) as a colorless oil.; R$_f$ (5% EtOAc in *n*-hexane): 0.4; **IR** (film) ν_{max}/cm^{-1}: 2960, 1703, 1489, 1366, 1261; **^{1}H NMR** (500 MHz, Methanol-*d₄*) δ 7.37 (d, *J* = 8.2 Hz, 2H), 7.32–7.25 (m, 2H), 6.38 (s, 1H), 5.22 (s, 1H), 2.94 (s, 3H), 1.93 (ddd, *J* = 14.9, 9.3, 5.6 Hz, 1H), 1.84–1.75 (m, 1H), 1.44 (s, 9H), 1.31–1.24 (m, 1H), 1.24–1.16 (m, 3H), 0.94 (t, *J* = 7.9 Hz, 9H), 0.80 (t, *J* = 7.0 Hz, 3H), 0.63 (m, *J* = 7.9 Hz, 6H); **^{13}C NMR** (126 MHz, Methanol-*d₄*) δ 155.3, 142.0, 132.6, ,128.6, 128.5, 127.7, 127.2, 80.2, 75.8, 34.8, 30.0, 27.4, 25.9, 22.6, 12.8, 5.9, 4.4; **HRMS** (ESI) Calculated for $C_{25}H_{42}ClNO_3SiNa$ [M+Na]$^+$: 490.2515, Found: 490.2502.

ethyl (E)-4-(6-butyl-3,3-diethyl-8,11,11-trimethyl-9-oxo-4,10-dioxa-8-aza-3-siladodec-6-en-5-yl)benzoate (5ad)



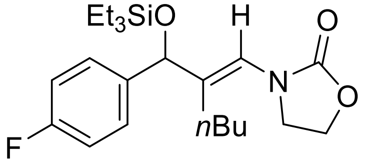
Following procedure **GP3**, ynamide **4a** (32 mg, 0.15 mmol), ethyl 4-formylbenzoate **1d** (80.2 mg, 0.45 mmol) was converted to allyl ene-carbamate **5ad** in 53% yield as a single regioisomer (40.3 mg, 0.079 mmol) as a colorless oil.; R$_f$ (5% EtOAc in *n*-hexane): 0.4; **IR** (film) ν_{max}/cm^{-1}: 2958, 1719, 1366, 1274, 1150, 1104; **^{1}H NMR** (500 MHz, Methanol-*d₄*) δ 7.97 (d, *J* = 8.2 Hz, 3H), 7.51 (d, *J* = 8.1 Hz, 2H), 6.42 (s, 1H), 5.30 (s, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 2.95 (s, 3H), 1.93 (ddd, *J* = 15.2, 9.6, 5.6 Hz, 1H), 1.86-1.76 (m, 1H), 1.44 (s, 9H), 1.39 (t, *J* = 7.1 Hz, 4H), 1.27–1.16 (m, 4H), 0.95 (t, *J* = 7.9 Hz, 9H), 0.79 (t, *J* = 7.0 Hz, 3H), 0.65 (q, *J* = 7.9 Hz, 6H); **^{13}C NMR** (126 MHz, Methanol-*d*$_4$) δ 166.6, 148.7, 129.2, 129.1, 128.9, 128.9, 126.2, 125.7, 80.2, 76.5, 60.7, 30.0, 27.3, 25.8, 22.5, 14.1, 13.2, 12.7, 5.8, 4.3; **HRMS** (ESI) Calculated for $C_{28}H_{48}NO_5Si$ [M+H]$^+$: 506.3296, Found: 506.3272.

(E)-3-(2-(phenyl((triethylsilyl)oxy)methyl)hex-1-en-1-yl)oxazolidin-2-one (5ba)



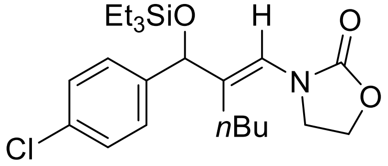
Following procedure **GP3**, ynamide **4b** (50.1 mg, 0.3 mmol), benzaldehyde **1a** (99.8 mg, 0.9 mmol) was converted to allyl ene-carbamate **5ba** in 8 h in 86% yield as a single regioisomer (100.4 mg, 0.258 mmol) as a colorless oil; R$_f$ (20% EtOAc in *n*-hexane): 0.3; The spectral data matched those reported in the literature.[14] **^{1}H NMR** (400 MHz, Methanol-*d*$_4$) δ 7.41–7.35 (m, 2H), 7.34–7.27 (m, 2H), 7.27–7.20 (m, 1H), 6.59 (s, 1H), 5.22 (s, 1H), 4.41 (t, *J* = 8.2 Hz, 2H), 3.90 (t, *J* = 8.2 Hz, 2H), 2.04 (ddd, *J* = 14.2, 10.6, 5.2 Hz, 1H), 1.90 (ddd, *J* = 14.1, 10.5, 5.1 Hz, 1H), 1.32–1.12 (m, 4H), 0.93 (t, *J* = 7.9 Hz, 9H), 0.81 (t, *J* = 7.0 Hz, 3H), 0.61 (qd, *J* = 8.3, 7.9 Hz, 6H).

(E)-3-(2-((4-fluorophenyl)((triethylsilyl)oxy)methyl)hex-1-en-1-yl)oxazolidin-2-one (5bb)



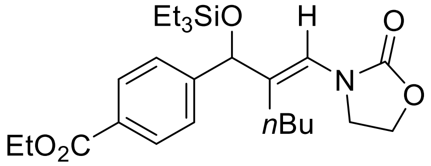
Following procedure **GP3**, ynamide **4b** (50.1 mg, 0.3 mmol), 4-fluorobenzaldehyde **1b** (111.7 mg, 0.9 mmol) was converted to allyl ene-carbamate **5bb** in 73% yield as a single regioisomer (89.4 mg, 0.219 mmol) as a colorless oil.; R$_f$ (20% EtOAc in *n*-hexane): 0.3; The spectral data matched those reported in the literature.[14] **^{1}H NMR** (400 MHz, Methanol-*d*$_4$) δ 7.44-7.36 (m, 2H), 7.11-7.01 (m, 2H), 6.62 (s, 1H), 5.25 (s, 1H), 4.44 (t, *J* = 7.7 Hz, 2H), 3.93 (t, *J* = 7.7 Hz, 2H), 2.13–1.96 (m, 1H), 1.95-1.84 (m, 1H), 1.38-1.19 (m, 4H), 0.95 (t, *J* = 6.8 Hz, 9H), 0.84 (t, *J* = 6.9 Hz, 3H), 0.64 (q, *J* = 6.8 Hz, 6H).

(E)-3-(2-((4-chlorophenyl)((triethylsilyl)oxy)methyl)hex-1-en-1-yl)oxazolidin-2-one (5bc)



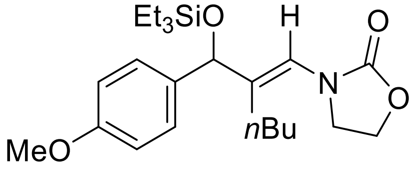
Following procedure **GP3**, ynamide **4b** (50.1 mg, 0.3 mmol), 4-chlorobenzaldehyde **1c** (126 mg, 0.9 mmol) was converted to allyl ene-carbamate **5bc** in 71% yield as a single regioisomer (90.3 mg, 0.213 mmol) as a colorless oil; R_f (20% EtOAc in *n*-hexane): 0.3; The spectral data matched those reported in the literature.[14] **^{1}H NMR** (400 MHz, CD_3OD) δ 7.49–7.25 (m, 4H), 6.62 (s, 1H), 5.25 (s, 1H), 4.44 (t, *J* = 8.1 Hz, 2H), 3.93 (td, *J* = 7.7, 1.7 Hz, 2H), 2.13–1.85 (m, 2H), 1.30-1.14 (m, 4H), 0.95 (t, *J* = 7.9 Hz, 9H), 0.85 (t, *J* = 7.0 Hz, 3H), 0.65 (q, *J* = 7.9 Hz, 6H).

ethyl (E)-4-(2-((2-oxooxazolidin-3-yl)methylene)-1-((triethylsilyl)oxy)hexyl)benzoate (5bd)



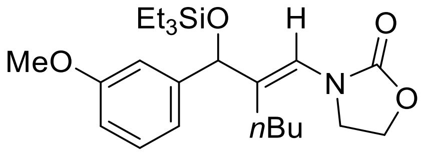
Following procedure **GP3**, ynamide **4b** (50.1 mg, 0.3 mmol), ethyl 4-formylbenzoate **1d** (160 mg, 0.9 mmol) was converted to allyl ene-carbamate **5bd** in 8 h in 86% yield as a single regioisomer (119 mg, 0.258 mmol) as a colorless oil; R_f (20% EtOAc in *n*-hexane): 0.25; **IR** (film) ν_{max}/cm^{-1}: 2983, 1732, 1375, 1244, 1026; **^{1}H NMR** (500 MHz, DMSO-*d_6*) δ 7.92 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 6.63 (s, 1H), 5.32 (s, 1H), 4.42–4.24 (m, 4H), 3.86 (q, *J* = 8.2 Hz, 2H), 2.01–1.76 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.23–0.99 (m, 4H), 0.86 (t, *J* = 7.9 Hz, 9H), 0.75 (t, *J* = 7.1 Hz, 3H), 0.56 (q, *J* = 7.9 Hz, 6H); **^{13}C NMR** (126 MHz, DMSO-*d_6*) δ 166.1, 157.2, 149.4, 129.4, 129.2, 128.4, 126.9, 122.2, 77.0, 62.8, 61.1, 45.3, 32.1, 25.7, 22.8, 14.6, 14.1, 7.1, 4.8; **HRMS** (ESI) Calculated for $C_{25}H_{40}NO_5Si$ $[M+H]^+$: 462.2670, Found: 462.2651.

(E)-3-(2-((4-methoxyphenyl)((triethylsilyl)oxy)methyl)hex-1-en-1-yl)oxazolidin-2-one (5bg)



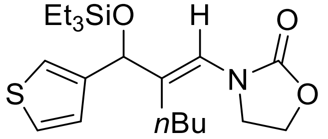
Following procedure **GP3**, ynamide **4b** (50.1 mg, 0.3 mmol), 4-methoxybenzaldehyde **1g** (122.5 mg, 0.9 mmol) was converted to allyl ene-carbamate **5bg** in 29% yield as a single regioisomer (40.3 mg, 0.087 mmol) as a colorless oil; R_f (20% EtOAc in *n*-hexane): 0.3; The spectral data matched those reported in the literature.[14] **^{1}H NMR** (400 MHz, DMSO-*d_6*) δ 7.27–7.21 (m, 2H), 6.91–6.84 (m, 2H), 6.55 (s, 1H), 5.15 (s, 1H), 4.34 (t, *J* = 8.0 Hz, 2H), 3.84 (t, *J* = 8.0 Hz, 2H), 3.73 (s, 3H), 2.03-1.90 (m, 1H), 1.84-1.72 (m, 1H), 1.28–1.12 (m, 4H), 0.86 (t, *J* = 7.9 Hz, 9H), 0.79 (t, *J* = 6.7 Hz 3H), 0.59–0.49 (m, 6H).

(E)-3-(2-((3-methoxyphenyl)((triethylsilyl)oxy)methyl)hex-1-en-1-yl)oxazolidin-2-one (5bf)



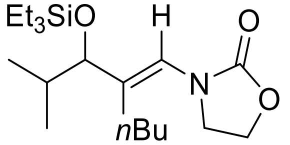
Following procedure **GP3**, ynamide **4b** (50.1 mg, 0.3 mmol), 3-methoxybenzaldehyde **1f** (122.5 mg, 0.9 mmol) was converted to allyl ene-carbamate **5bf** in 67% yield in 8 h as a single regioisomer (84.9 mg, 0.202 mmol) as a colorless oil; R_f (20% EtOAc in *n*-hexane): 0.3; **IR** (film) ν_{max}/cm^{-1}: 3018, 2957, 1754, 1669, 1600, 1484, 1254; **^{1}H NMR** (500 MHz, Methanol-*d_4*) δ 7.20 (t, *J* = 7.8 Hz, 1H), 6.99-6.92 (m, 2H), 6.79 (dd, *J* = 8.2, 2.6 Hz, 1H), 6.56 (s, 1H), 5.20 (s, 1H), 4.39 (t, *J* = 8.0 Hz, 2H), 3.89 (t, *J* = 8.0 Hz, 2H), 3.77 (s, 3H), 2.05 (ddt, *J* = 14.1, 10.3, 5.4 Hz, 1H), 1.93 (ddd, *J* = 14.2, 10.5, 4.7 Hz, 1H), 1.34–1.18 (m, 4H), 0.94 (t, *J* = 8.0 Hz, 9H), 0.82 (t, *J* = 7.0 Hz, 3H), 0.62 (qd, *J* = 7.9, 2.1 Hz, 6H); **^{13}C NMR** (126 MHz, Methanol-*d_4*) δ 159.7, 158.2, 144.9, 133.0, 128.7, 120.7, 118.7, 112.4, 111.9, 77.2, 62.7, 54.3, 45.7, 31.4, 25.8, 22.6, 12.8, 5.8, 4.4; **HRMS** (ESI) Calculated for $C_{23}H_{37}NO_4SiK$ [M+K]$^+$: 458.2123, Found: 458.2130.

(E)-3-(2-(thiophen-3-yl((triethylsilyl)oxy)methyl)hex-1-en-1-yl)oxazolidin-2-one (5bn)



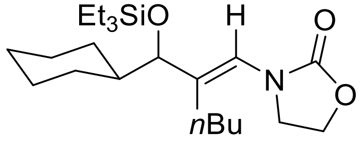
Following procedure **GP3**, ynamide **4b** (50.1 mg, 0.3 mmol), thiophene-3-carbaldehyde **1n** (100.9 mg, 0.9 mmol) was converted to allyl ene-carbamate **5bn** in 39% yield as a single regioisomer (46.3 mg, 0.117 mmol) as a colorless oil; A second round purification of the title compound was performed by flash column chromatography using 10% EtOAc/toluene mixture; R_f (20% EtOAc in *n*-hexane): 0.3; **IR** (film) ν_{max}/cm^{-1}: 3393, 1652, 1237, 993; ^{1}**H NMR** (400 MHz, DMSO-*d*$_6$) δ 7.58–7.29 (m, 2H), 7.06-6.85 (m, 1H), 6.54 (s, 1H), 5.27 (s, 1H), 4.46–4.27 (m, 2H), 3.97–3.77 (m, 2H), 1.99 (d, *J* = 11.6 Hz, 1H), 1.93–1.80 (m, 1H), 1.30-1.08 (m, 4H), 0.87 (t, *J* = 7.5 Hz, 9H), 0.79 (t, *J* = 4.7 Hz, 3H), 0.65–0.49 (m, 6H); ^{13}**C NMR** (126 MHz, DMSO-*d*$_6$) δ 156.6, 145.2, 128.6, 126.3, 125.9, 121.2, 120.8, 73.5, 62.2, 44.9, 31.4, 25.6, 22.3, 13.6, 6.6, 4.3; **HRMS** (ESI) Calculated for $C_{20}H_{33}NO_3SSiK$ [M+K]$^+$: 434.1582, Found: 434.1585.

(E)-3-(2-(2-methyl-1-((triethylsilyl)oxy)propyl)hex-1-en-1-yl)oxazolidin-2-one (5bi)



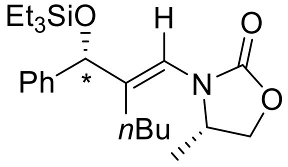
Following procedure **GP3**, ynamide **4b** (50.1 mg, 0.3 mmol), isobutyraldehyde **1i** (64.7 mg, 0.9 mmol) was converted to allyl ene-carbamate **5bi** in 67% yield as a single regioisomer (71.6 mg, 0.201 mmol) as a colorless oil; R_f (20% EtOAc in *n*-hexane): 0.3; **IR** (film) ν_{max}/cm^{-1}: 2957, 1755, 1667, 1467, 1242, 1063; ^{1}**H NMR** (400 MHz, Methanol-*d*$_4$) δ 6.05 (s, 1H), 4.32 (t, *J* = 8.3 Hz, 2H), 3.78 (t, *J* = 8.3 Hz, 2H), 3.71 (d, *J* = 6.2 Hz, 1H), 2.12–2.01 (m, 1H), 1.99–1.90 (m, 1H), 1.71–1.61 (m, 1H), 1.39–1.24 (m, 4H), 0.92–0.78 (m, 18H), 0.55 (t, *J* = 8.0 Hz, 6H); ^{13}**C NMR** (101 MHz, Methanol-*d*$_4$) δ 158.1, 133.3, 121.0, 80.9, 62.7, 45.8, 32.0, 31.4, 26.3, 22.9, 19.1, 16.7, 12.9, 6.0, 4.5; **HRMS** (ESI) Calculated for $C_{19}H_{37}NO_3SiK$ [M+K]$^+$: 394.2174, Found: 394.2153.

(E)-3-(2-(cyclohexyl((triethylsilyl)oxy)methyl)hex-1-en-1-yl)oxazolidin-2-one (5bk)



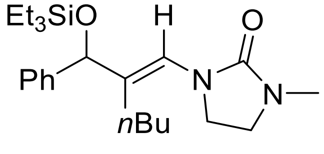
Following procedure **GP3**, ynamide **4b** (50.1 mg, 0.3 mmol), cyclohexane carboxaldehyde **1k** (100.9 mg, 0.9 mmol) was converted to allyl ene-carbamate **5bk** in 56% yield as a single regioisomer (66.3 mg, 0.168 mmol) as a colorless oil; R_f (20% EtOAc in *n*-hexane): 0.3; **IR** (film) ν_{max}/cm^{-1}: 2928, 1755, 1666, 1046, 1216, 1004; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 6.11 (s, 1H), 4.35 (t, *J* = 7.9 Hz, 2H), 3.82 (t, *J* = 7.9 Hz, 2H), 3.72 (d, *J* = 6.9 Hz, 1H), 2.10-1.90 (m, 2H), 1.93-1.79 (m, 1H), 1.88-1.44 (m, 4H), 1.39-1.27 (m, 6H), 1.21–1.05 (m, 4H), 0.93–0.86 (m, 12H), 0.55 (q, *J* = 7.9 Hz, 6H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 156.6, 128.7, 121.5, 80.4, 62.3, 45.1, 41.4, 31.5, 29.7, 28.0, 26.1, 25.8, 25.7, 25.6, 22.7, 13.7, 6.8, 4.5; **HRMS** (ESI) Calculated for $C_{22}H_{42}NO_3Si$ [M+H]$^+$: 396.2928, Found: 396.2928.

(4*S*)-4-methyl-3-((E)-2-(phenyl((triethylsilyl)oxy)methyl)hex-1-en-1-yl)oxazolidin-2-one (5ca)



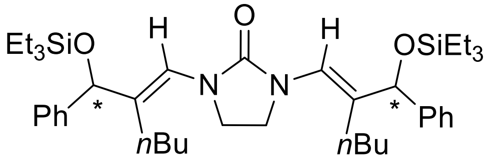
Following general procedure **GP3**, ynamide **4c** (27.18 mg, 0.15 mmol), benzaldehyde **1a** (39 mg, 0.45 mmol) was converted to allyl ene-carbamate **5ca** in 64% yield in 85:15 regioisomeric ratio (39 mg, 0.096 mmol) as a colorless oil; R_f (20% EtOAc in *n*-hexane): 0.3; The spectral data matched those reported in the literature.[15] Major diastereomer: **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.38–7.22 (m, 5H), 6.30 (s, 1H), 5.24 (s, 1H), 4.44 (t, *J* = 8.2 Hz, 1H), 4.18–4.05 (m, 1H), 3.94 (dd, *J* = 8.5, 5.0 Hz, 1H), 1.97-1.87 (m, 1H), 1.75-1.62 (m,1H), 1.30–1.17 (m, 4H), 1.14 (d, *J* = 6.0 Hz, 3H), 0.86 (t, *J* = 7.8 Hz, 9H), 0.74 (t, *J* = 7.0 Hz, 3H), 0.55 (q, *J* = 7.8 Hz, 6H).

(E)-1-methyl-3-(2-(phenyl((triethylsilyl)oxy)methyl)hex-1-en-1-yl)imidazolidin-2-one (5da)



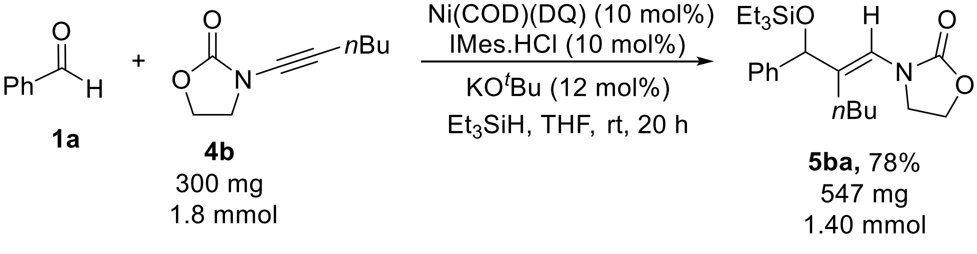
Following procedure **GP3**, ynamide **4d** (58.5 mg, 0.3 mmol), benzaldehyde **1a** (99.8 mg, 0.9 mmol) was converted to allyl ene-carbamate **5da** in 51% yield as a single regioisomer (61.5 mg, 0.153 mmol) as a colorless oil; R_f (20% EtOAc in *n*-hexane): 0.3; **IR** (film) ν_{max}/cm^{-1}: 2924, 1698, 1598, 1492, 1434,1261, 1062; ^{1}**H NMR** (400 MHz, DMSO-*d*$_6$) δ 7.51–7.02 (m, 5H), 6.71 (s, 1H), 5.17 (s, 1H), 3.82–3.55 (m, 2H), 3.44-3.35 (m, 2H), 2.71 (s, 3H), 2.14–1.73 (m, 2H), 1.30-1.12 (m, 4H), 0.87 (t, *J* = 7.9 Hz, 9H), 0.75 (t, *J* = 7.1 Hz, 3H), 0.55 (q, *J* = 7.9 Hz, 6H); ^{13}**C NMR** (126 MHz, DMSO-*d*$_6$) δ 158.9, 144.5, 128.3, 127.2, 126.4, 123.2, 122.8, 78.2, 44.7, 42.8, 32.6, 31.2, 25.8, 22.8, 14.1, 7.2, 4.9; **HRMS** (ESI) Calculated for $C_{23}H_{38}N_2O_2SiNa$ [M+Na]$^+$: 425.2595, Found: 425.2581.

1,3-bis((E)-2-(phenyl((triethylsilyl)oxy)methyl)hex-1-en-1-yl)imidazolidin-2-one (5ea)



Following procedure **GP3**, ynamide **4e** (78 mg, 0.3 mmol), benzaldehyde **1a** (99.8 mg, 0.9 mmol) was converted to bis-allyl ene-carbamate **5ea** in 33% yield as a single regioisomer (68.4 mg, 0.099 mmol) as a colorless oil; R$_f$ (20% EtOAc in *n*-hexane): 0.7; **IR** (film) ν_{max}/cm^{-1}: 2956, 1683, 1412, 1263, 1059, 1008; ^{1}**H NMR** (400 MHz, DMSO-*d*$_6$) δ 7.36–7.29 (m, 8H), 7.24 (dd, *J* = 6.6, 2.0 Hz, 2H), 6.76 (d, *J* = 2.5 Hz, 2H), 5.21 (s, 2H), 3.78 (s, 4H), 1.98–1.90 (m, 2H), 1.89-1.77 (m, 2H), 1.27–1.13 (m, 8H), 0.88 (t, *J* = 7.9 Hz, 18H), 0.76 (t, *J* = 7.0 Hz, 6H), 0.62-0.52 (m, 12H); ^{13}**C NMR** (126 MHz, DMSO-*d*$_6$) δ 156.3, 143.8, 129.5, 129.4, 127.8, 126.8, 126.0, 126.0, 121.8, 121.8, 77.4, 77.4, 42.5, 31.9, 25.5, 22.3, 13.6, 6.6, 4.4; **HRMS** (ESI) Calculated for $C_{41}H_{66}N_2O_3Si_2K$ [M+K]$^+$: 729.4244, Found: 729.4268.

10. Representative synthesis of 5ba in 1.8 mmol scale

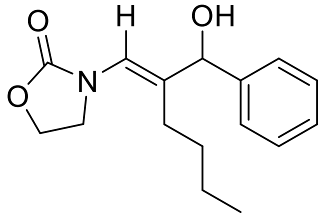


To a 100 mL flame-dried Schlenk round-bottomed flask was added Ni(COD)(DQ) (59.4 g, 0.18 mmol, 10 mol%) and IMes.HCl (61.2 g, 0.18 mmol, 10 mol%) under nitrogen atmosphere. At 0 °C, dry THF (10.2 mL, 0.17 M) and KO*^{t}*Bu (1 M in THF, 0.216 mL, 0.216

mmol, 12 mol%) were added, and the reaction mixture was stirred for 1 h at the same temperature. Then, the reaction mixture was warmed to rt, and Et_3SiH (1.44 mL, 10.8 mmol) was added. The reaction mixture was stirred for 30 min, followed by dropwise addition of benzaldehyde **1a** (0.576 mL, 5.4 mmol). A solution of ynamide **4b** (300 mg, 1.8 mmol) in dry THF (8 mL, 0.2 M) was added to the reaction mixture over 7 h using a syringe pump. The reaction mixture was allowed to stir at rt for an additional 13 h. The complete consumption of ynamide was confirmed by TLC, and the reaction mixture was subjected to Celite pad filtration with EtOAc as the solvent. The crude reaction mixture was purified by flash column chromatography (EtOAc/*n*-hexane as eluents) over silica gel to furnish **5ba** in 78% of isolated yield as a single regioisomer (547 mg, 1.40 mmol).

11. Characterization data of compounds from application studies (6-9)

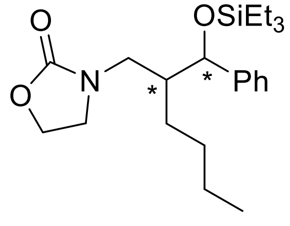
(E)-3-(2-(hydroxy(phenyl)methyl)hex-1-en-1-yl)oxazolidin-2-one (6)



To a solution of **5ba** (100 mg, 0.256 mmol) in dry THF (10 mL, 0.02 M) TBAF (1 M in THF, 0.78 mL, 0.78 mmol) was added dropwise at 0 °C, under a nitrogen atmosphere.[16] The resultant reaction mixture was allowed to stir at rt for an additional 12 h. The reaction mixture was concentrated under reduced pressure, diluted with 25 mL of EtOAc, and the organic layer was washed twice with distilled water (2 x 10 mL) and once with brine (10 mL). The organic layer was separated and dried over anhydrous Na_2SO_4. The crude reaction mixture was subjected to column chromatographic purification on silica (1:5 to 3:10 EtOAc/*n*-hexane as eluent). The desilylated product **6** was obtained in 88% yield (61.9 mg, 0.225 mmol) as colorless crystalline needles; m.p. 96 -97 °C; R_f (30% EtOAc in hexanes): 0.3; **IR** (film) ν_{max}/cm^{-1}: 3413, 2128, 1746, 1663, 1409, 1262; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.38–7.26 (m, 4H), 7.28–7.17 (m, 1H), 6.46 (s, 1H), 5.50 (d, *J* = 4.0 Hz, 1H), 5.06 (d, *J* = 4.0 Hz, 1H), 4.34 (t, *J* = 7.9 Hz, 2H), 3.86 (td, *J* = 8.0, 4.9 Hz, 2H), 2.05-1.90 (m, 1H), 1.91-1.78 (m, 1H), 1.35–1.06 (m, 4H), 0.77 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR** (101 MHz, DMSO-

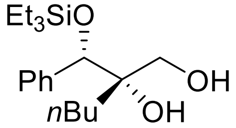
*d*6) δ 156.8, 143.9, 130.0, 127.9, 126.8, 126.5, 120.8, 75.1, 62.3, 45.1, 31.4, 26.0, 22.9, 13.7; **HRMS** (ESI) Calculated for $C_{16}H_{22}NO_3$ $[M+H]^+$: 276.1594, Found: 276.1598.

3-(2-(phenyl((triethylsilyl)oxy)methyl)hexyl)oxazolidin-2-one (7)



To a flame-dried round-bottomed flask, was added a solution of **5ba** (40 mg, 0.102 mmol) in dry MeOH (1 mL, 0.1 M) and 10% w/w basis Pd/C (10 mg, 10 mol%) under nitrogen atmosphere. Dry MeOH (1.5 mL, 0.07 M) was carefully added such that all the Pd/C was suspended at this point. The reaction mixture was stirred well before the flask was evacuated and backfilled with nitrogen gas. This process was repeated twice before the evacuated flask was opened to a H_2 balloon (> 1 atm) through a three-neck adapter. Next, the flask was evacuated and then refilled with H_2 twice. The reaction mixture was finally left to stir under the H_2 atmosphere for 3 h at rt.[17] After the complete consumption of **5ba**, the reaction mixture was subjected to Celite pad filtration using CH_2Cl_2 as the eluent. Further purification was performed by column chromatography on silica gel (1:5 EtOAc/*n*-hexane as eluent). The hydrogenated product **7** was obtained as a colorless liquid in 83% yield (33.1 mg, 0.0845 mmol) as a 1:1 mixture of inseparable diastereomers; R_f (20% EtOAc in hexanes): 0.3; **IR** (film) ν_{max}/cm^{-1}: 2956, 1754, 1454, 1261, 1066; ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.25–7.18 (m, 8H), 7.18-7.13 (m, 2H), 4.66 (d, *J* = 4.5 Hz, 1H), 4.58 (d, *J* = 5.9 Hz, 1H), 4.22–3.98 (m, 4H), 3.35 (td, *J* = 8.8, 6.6 Hz, 1H), 3.31–3.17 (m, 4H), 3.17–3.07 (m, 2H), 3.02 (dd, *J* = 13.9, 8.1 Hz, 1H), 1.90-1.82 (m, 1H), 1.80-1.72 (m, 1H), 1.42-1.08 (m, 12H), 0.79 (dt, *J* = 11.3, 7.9 Hz, 24H), 0.48–0.38 (m, 12H); ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 158.6, 158.5, 143.8, 143.0, 127.93, 127.89, 127.3, 127.0, 126.7, 126.3, 75.7, 75.1, 61.5, 61.4, 45.7, 45.0, 44.83, 44.80, 44.7, 44.6, 29.24, 29.18, 28.8, 28.0, 23.0, 22.9, 13.94, 13.94, 6.8, 6.7, 4.9, 4.8; **HRMS** (ESI) Calculated for $C_{22}H_{37}NO_3SiNa$ $[M+Na]^+$: 414.2435, Found: 414.2442.

2-(phenyl((triethylsilyl)oxy)methyl)hexane-1,2-diol (9)

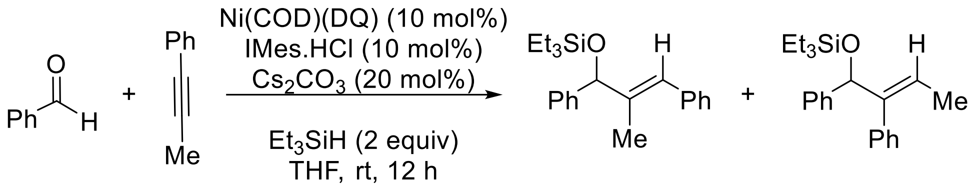


According to the literature procedure,[18] in a flame-dried Schlenk tube, a solution of **5ba** (50 mg, 0.128 mmol, 1.0 equiv) was taken in dry $CHCl_3$ (1.5 mL, 0.08 M) . To this solution, *m*CPBA (65% assay) (37.4 mg, 0.141 mmol, 1.1 equiv) was added under N_2 atmosphere. The resultant reaction mixture was stirred at rt for 22 h. After the complete consumption of **5ba**, 200 mg of K_2CO_3 was added to the reaction mixture and stirred for 30 min at rt. The reaction mixture was filtered, and the filtrate was washed with sat. aq. $NaHCO_3$ (2 x 20 mL), distilled water (2 x 20 mL), and brine (10 mL). The organic layer was separated and dried over anhydrous Na_2SO_4. The solvent was evaporated using a rotary evaporator, and the crude reaction mixture was concentrated in vacuo. To this crude reaction mixture dissolved in EtOH (1.5 mL, 0.08 M) was added $NaBH_4$ (4.8 mg, 0.128 mmol. 1.0 equiv). The resultant reaction mixture was stirred at rt for 24 h. The crude reaction mixture was diluted with 25 mL EtOAc, washed with distilled water (2 x 20 mL), and brine (20 mL). The collected organic layer was dried over anhydrous Na_2SO_4 and subjected to further purification by flash column chromatography. The title compound was obtained in 69% yield (29.8 mg, 0.088 mmol) as a mixture of 85:15 diastereomers as a sticky white solid. R_f (30% EtOAc in hexanes): 0.6; **IR** (film) ν_{max}/cm^{-1}: 3408, 3087, 2388, 1579, 1261; Major diastereomer: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.8 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 2H), 7.29 (d, *J* = 7.0 Hz, 1H), 4.72 (s, 1H), 3.92 (s, 1H), 3.72 (d, *J* = 9.9 Hz, 1H), 3.37 (d, *J* = 9.8 Hz, 1H), 3.01 (s, 1H), 1.46–1.25 (m, 7H), 0.98 (t, *J* = 8.0 Hz, 9H), 0.90 (t, *J* = 7.2 Hz, 3H), 0.64 (q, *J* = 7.9 Hz, 6H). Minor diastereomer: : **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.8 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 2H), 4.77 (s, 0.16 H), 3.63 (s, 0.32H), 3.35 (s, 0.16H), , 2.67 (s, 0.16H), 1.46–1.25 (m, 7H), 0.98 (t, *J* = 8.0 Hz, 9H), 0.90 (t, *J* = 7.2 Hz, 3H), 0.64 (q, *J* = 7.9 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.2, 128.0, 127.6, 127.2, 79.3, 74.9, 66.8, 33.4, 25.0, 23.3, 14.0, 6.6, 4.2; **HRMS** (ESI) Calculated for $C_{19}H_{34}O_3SiNa$ $[M+Na]^+$: 361.2169, Found: 361.2168.

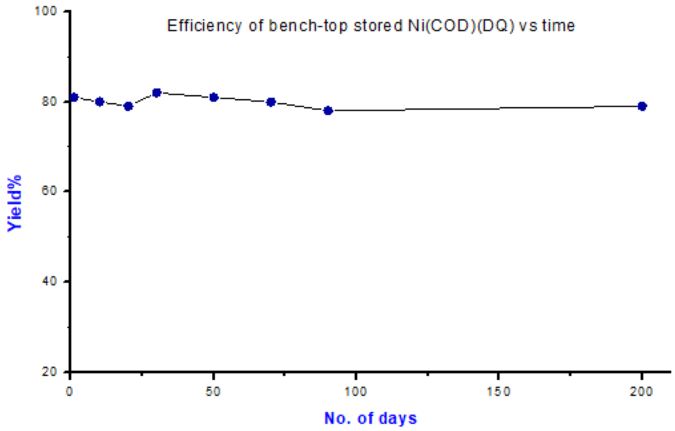
12. Control experiments and mechanistic studies

A. Sensitivity Study (time vs. efficiency of benchtop stored catalyst)

A batch of Ni(COD)(DQ) was stored on a benchtop under air and ambient temperature without special precautions. The standard reaction between **1a** and **2a** was performed at regular intervals, up to 200 days, from the same batch of Ni(COD)(DQ) stored on the benchtop.



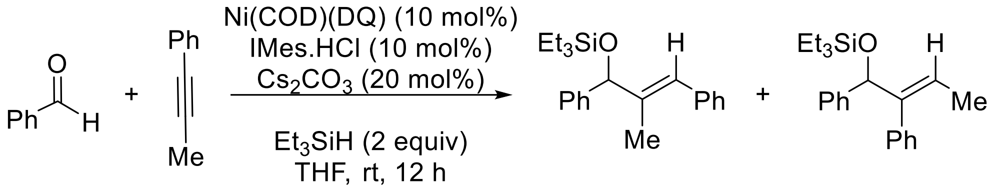
1a **2a** **3aa** **3aa'**



No. of days	Yield%^{a,b}
1	81
10	80
20	79
30	82
50	81
70	80
90	78
200	79

Reaction Conditions: ^{a}**1a** (0.3 mmol), **2a** (0.36 mmol, Et_3SiH (0.6 mmol), Ni(COD)(DQ) (10 mol%), IMes.HCl (10 mol%), Cs_2CO_3 (20 mol%), and THF (1.6 mL) at rt for 12 h. ^{b}Yields were determined by analysis of ^{1}H NMR of the crude reaction mixture using 1,1,2,2-tetrachloroethane as an internal standard.

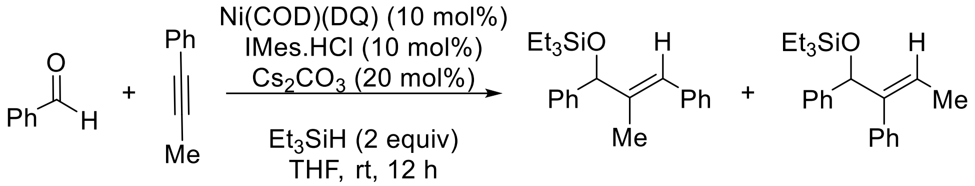
B. Sensitivity Study (under ambient conditions)



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

Under open air	No reaction
With moist THF (THF/H_2O = 4:1)	No reaction

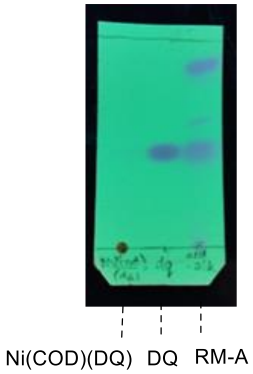
C. TLC and GC-MS analyses of the reaction mixture



1a **2a** **3a** **3a'**

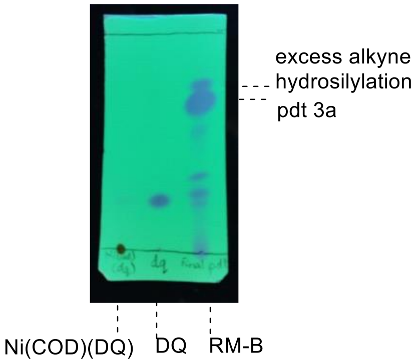
A standard reaction was performed according to **GP1**. After adding alkyne **2a**, 5 μL aliquot of reaction mixture, **RM-A** was taken for TLC analysis. After 12 h, a final TLC analysis of 5 μL of reaction mixture **RM-B** was performed. The results are shown below.

5% EtOAc in hexanes



RM-A: after 5 min of reaction time

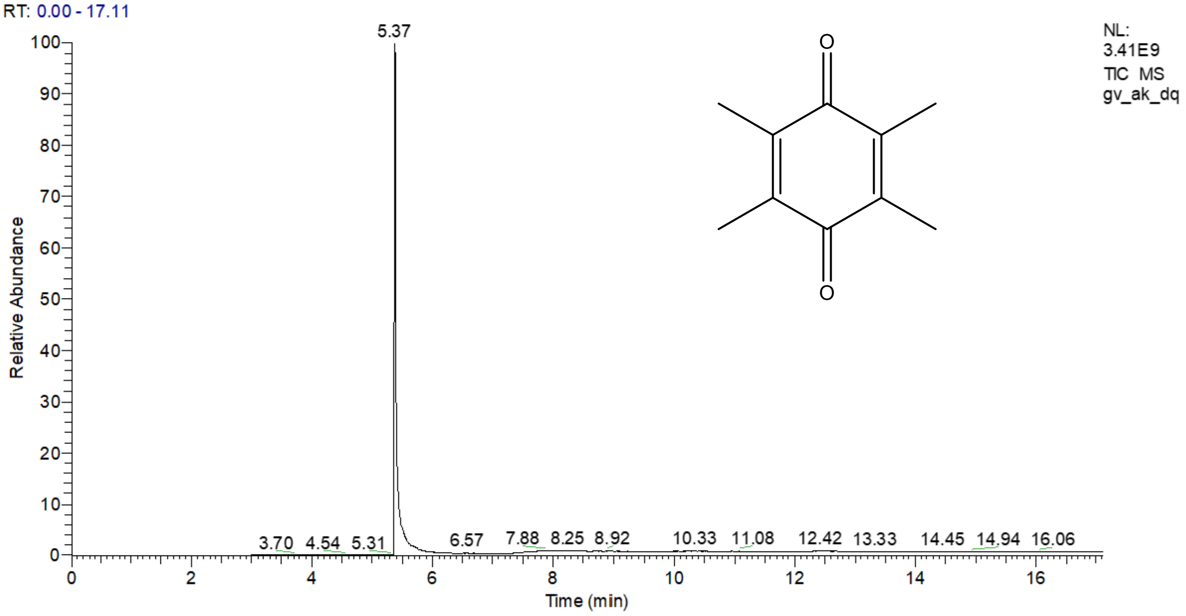
2% EtOAc in hexanes

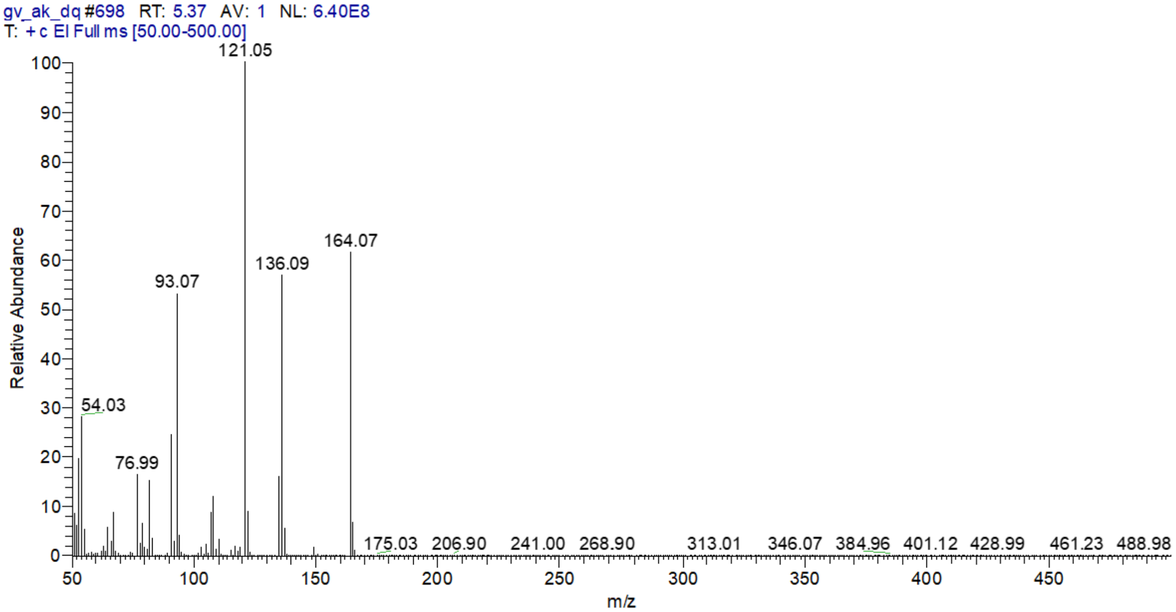


RM-B: After 12 h of reaction time

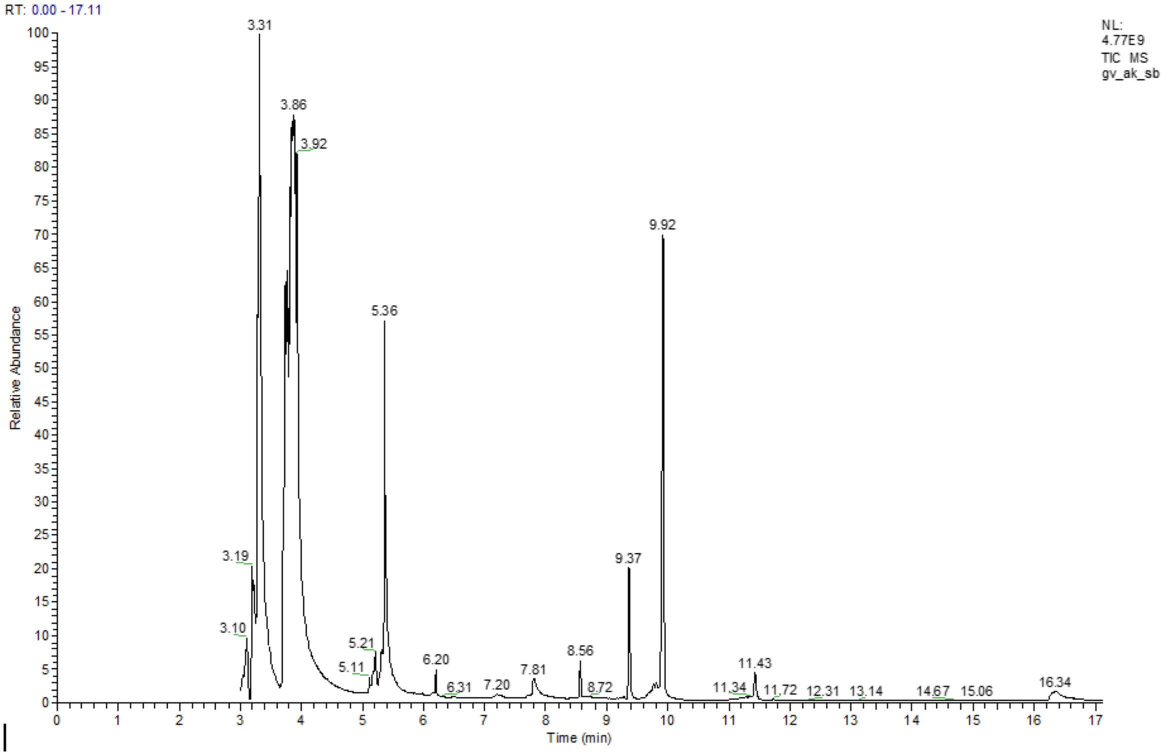
Another standard reaction was performed according to **GP1**. After 12 h, 0.5 mL of reaction mixture was passed through silica plug and analyzed by GC-MS. Duroquinone is observed and the fragmentation pattern matched with the standard one.

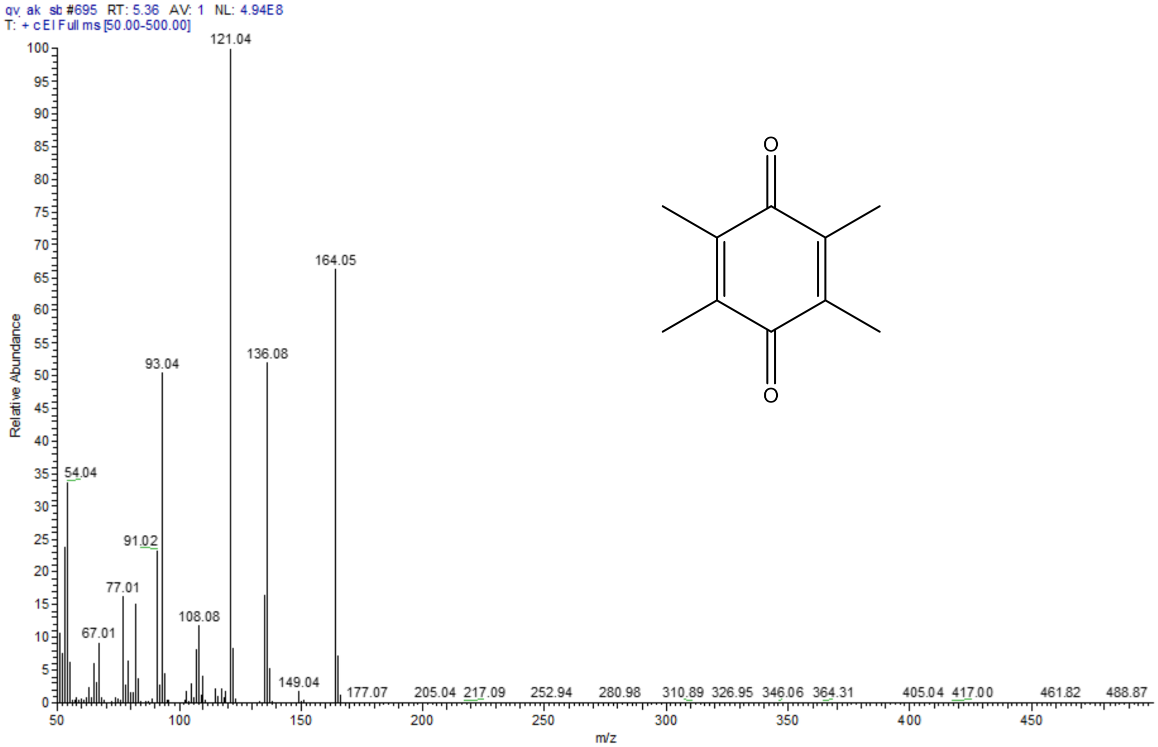
GC-MS trace for duroquinone (standard):

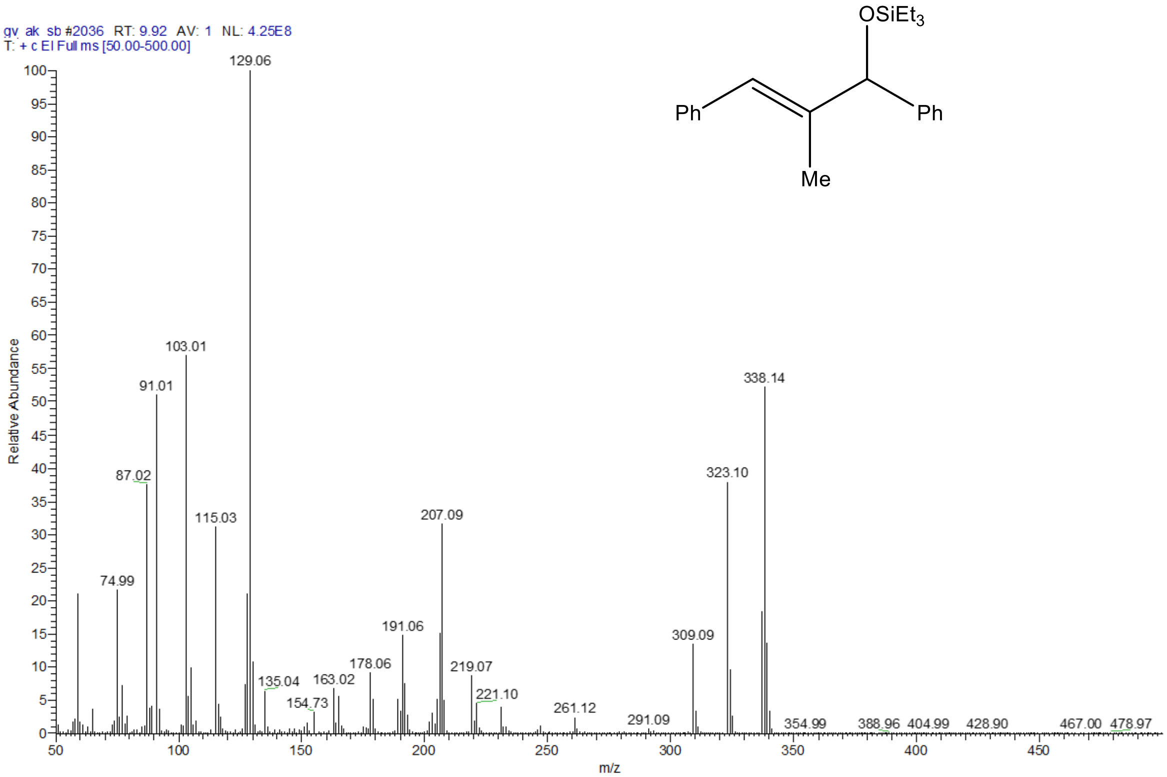




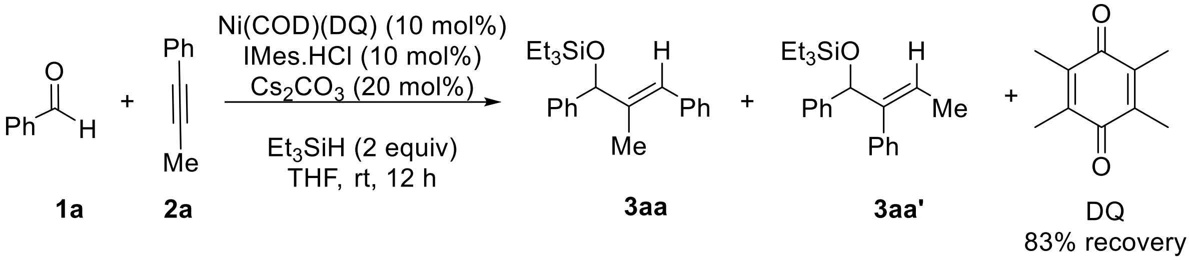
GC-MS trace of reaction mixture:







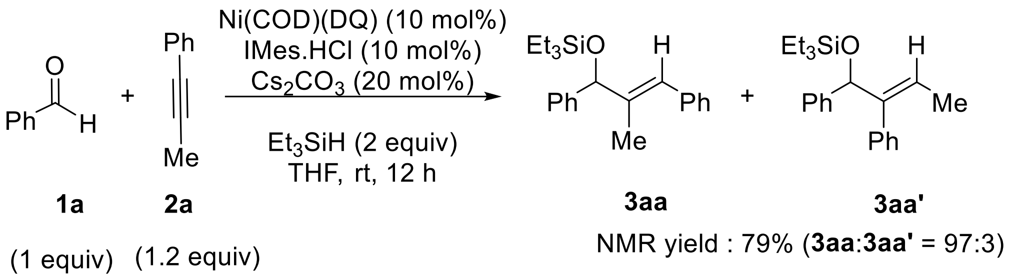
D. Duroquinone Recovery and Inhibition Studies

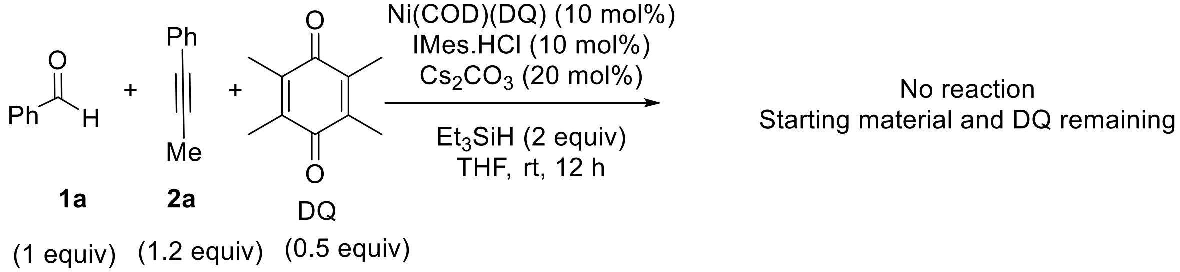


A standard reaction was performed according to **GP1**. After isolation of desired product **3aa** in 79% yield as 97:3 regioisomeric ratio (**3aa**:**3aa'**) via flash column chromatography on silica gel with hexanes as eluent, the eluent percentage was increased to 2% EtOAc/hexanes and DQ was isolated (4.1 mg. 0.025 mmol, 83% recovery).

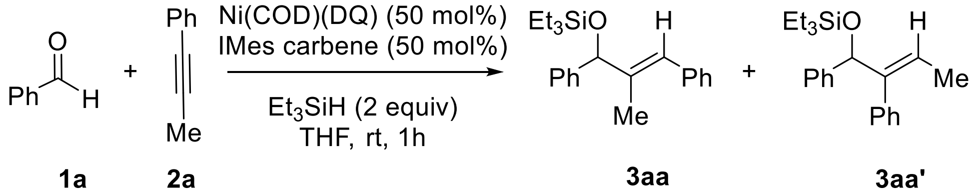
Two parallel reactions were set up: (A) One standard reaction between aldehyde and alkyne, and (b) standard reaction containing 0.5 equiv of duroquinone. Addition of excess

DQ completely shutdown the reaction leaving the starting materials intact, indicating the inhibition the catalytic activity altogether



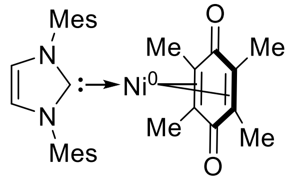


E. Preparation of samples for characterization of intermediates by mass spectrometry

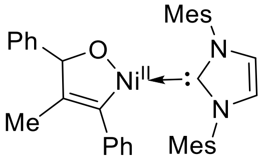


To a flame-dried Schlenk tube was added Ni(COD)(DQ) (25 mg, 0.075 mmol, 50 mol%) under nitrogen atmosphere. After weighing the catalyst, free IMes carbene, 1,3-Bis(2,4,6-trimethylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene (23 mg, 0.075 mmol, 50 mol%), was weighed inside the glovebox, instead of IMes.HCl. No external base was administered. Outside the glovebox, at 0 °C, 0.7 mL of dry THF was added and the reaction mixture was stirred vigorously for 1 h at the same temperature. After 1 h, 0.05 mL of the reaction mixture was transferred to an **HRMS vial A** under an inert atmosphere and the same vial was analyzed for mass spectrometry. The remaining reaction mixture was warmed to rt and Et_3SiH (96 μL, 0.6 mmol, 2 equiv) was added. The reaction mixture was stirred for 15 min followed by the addition of aldehyde **1a** (33.3 mg, 0.3 mmol, 1 equiv) was added to it. A solution of alkyne **2a** (41.8 mg, 0.36 mmol, 1.2 equiv) in 0.9 mL of THF was added next to the reaction mixture dropwise over 15 mins. A second aliquot of the reaction mixture (0.05 mL) was transferred to **HRMS vial B** under an inert atmosphere and analyzed for mass spectrometry. TLC analysis of the reaction mixture after 1 h showed the formation of desired product **3aa**.

HRMS vial A: HRMS (ESI) [M+Na]+ Calcd: 549.2022, Found: 549.2053



HRMS vial B: HRMS (ESI) [M+Na]+ Calcd: 607.2230, Found: 607.2227



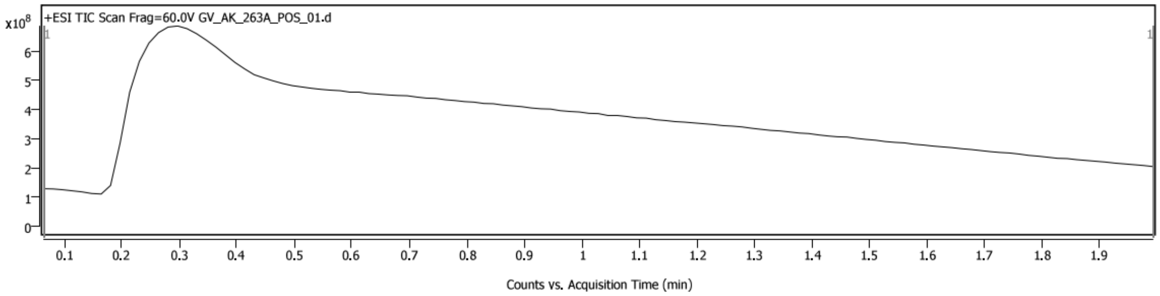
HRMS vial A

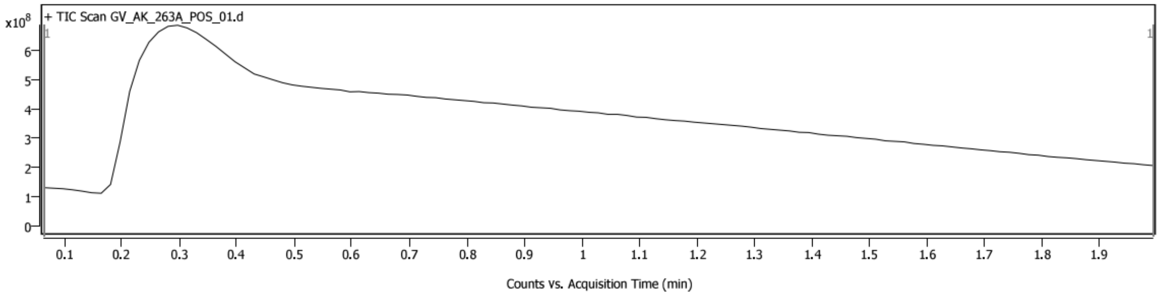
Target Screening Report

Sample Information

Name	GV_AK_263A	**Data File Path**	D:\MassHunter\Data\MARCH 2023\30-03-2023\GV_AK_263A_POS_01.d
Sample ID		**Acq. Time (Local)**	3/30/2023 11:59:40 AM (UTC+05:30)
Instrument	IITKGP	**Method Path (Acq)**	D:\MassHunter\Methods\TRAINING\MS SCAN POS_ORGANOMETALLICS_08 TEMP 250 FRG60.m
MS Type	QTOF	**Version (Acq SW)**	6200 series TOF/6500 series Q-TOF B.09.00 (B9044.1 SP1)
Inj. Vol. (ul)	2	**IRM Status**	Success
Position	P1-F4	**Method Path (DA)**	D:\MassHunter\Methods\TARGETED ANALYSIS ORGANOMETALLICS REPORTING_01.m
Plate Pos.		**Target Source Path**	
Operator		**Result Summary**	1 qualified (1 targets)

Sample Chromatograms





Compound Summary

Cpd	Name	Formula	CAS	RT	Mass	Mass (Tgt)	Diff (Tgt, ppm)	Score	Algorithm
1		C31 H36 N2 Ni O2		0.264	526.2098	526.2130	-6.21	33.69	FBF

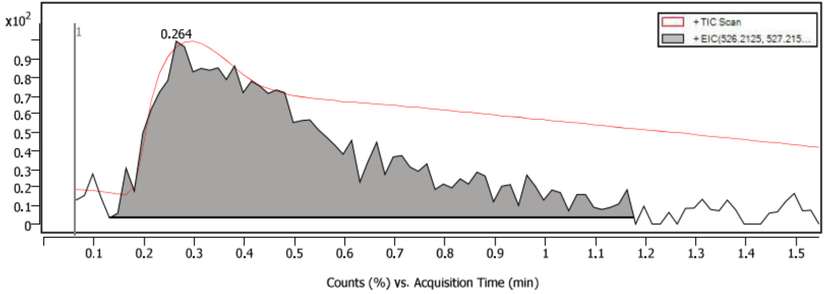
Compound Details

Cpd. 1: C31 H36 N2 Ni O2

Name	Formula	RT	RI	Mass	Diff (Tgt, ppm)	CAS	ID Source	Score	Algorithm
	C31 H36 N2 Ni O2	0.264		526.2098	-6.21		FBF	33.69	FBF

Species	m/z	Score (Tgt)	Score (Lib)	Score (DB)	Score (MFG)	Score (RT)
(M+NH4)+ (M+Na)+ (M+K)+	544.2436 549.2053 565.1564	33.69				

Compound Chromatograms (overlaid)



Structure

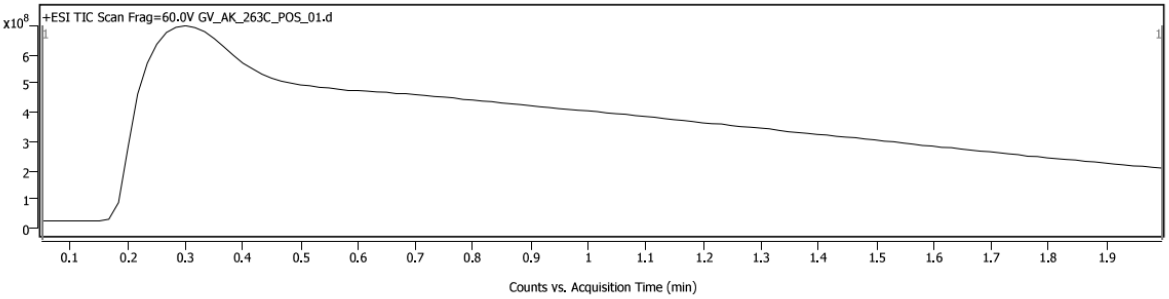
HRMS vial B

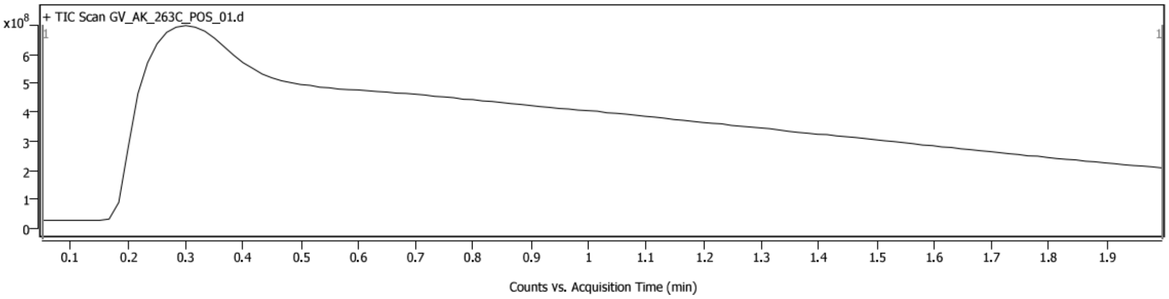
Target Screening Report

Sample Information

Name	GV_AK_263C	**Data File Path**	D:\MassHunter\Data\MARCH 2023\30-03-2023\GV_AK_263C_POS_01.d
Sample ID		**Acq. Time (Local)**	3/30/2023 3:55:15 PM (UTC+05:30)
Instrument	IITKGP	**Method Path (Acq)**	D:\MassHunter\Methods\TRAINING\MS SCAN POS_ORGANOMETALLICS_08 TEMP 250 FRG60.m
MS Type	QTOF	**Version (Acq SW)**	6200 series TOF/6500 series Q-TOF B.09.00 (B9044.1 SP1)
Inj. Vol. (ul)	2	**IRM Status**	Success
Position	P1-F9	**Method Path (DA)**	D:\MassHunter\Methods\TARGETED ANALYSIS ORGANOMETALLICS REPORTING_01.m
Plate Pos.		**Target Source Path**	
Operator		**Result Summary**	1 qualified (1 targets)

Sample Chromatograms





Compound Summary

Cpd	Name	Formula	CAS	RT	Mass	Mass (Tgt)	Diff (Tgt, ppm)	Score	Algorithm
1		C37 H38 N2 Ni O		0.333	584.2542	584.2338	35.06	47.52	FBF

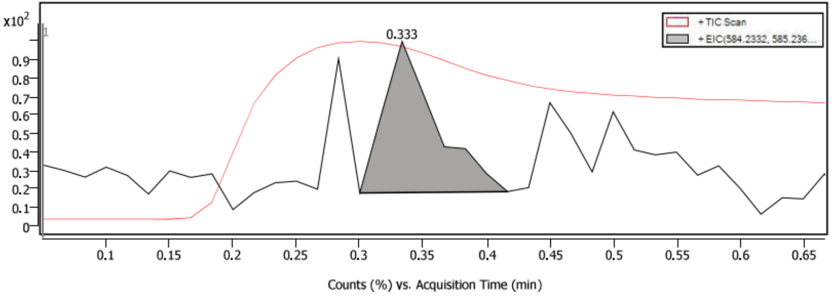
Compound Details

Cpd. 1: C37 H38 N2 Ni O

Name	Formula	RT	RI	Mass	Diff (Tgt, ppm)	CAS	ID Source	Score	Algorithm
	C37 H38 N2 Ni O	0.333		584.2542	35.06		FBF	47.52	FBF

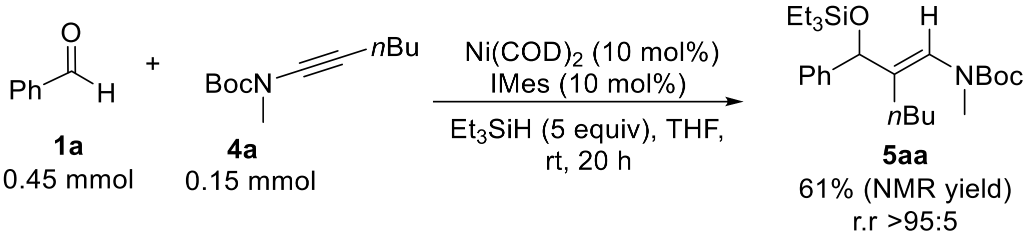
Species	m/z	Score (Tgt)	Score (Lib)	Score (DB)	Score (MFG)	Score (RT)
M+ (M+Na)+ (M+K)+	584.2293 607.2227 623.2196	47.52				

Compound Chromatograms (overlaid)



Structure

E. Reductive coupling of aldehyde and acyclic ynamide in the presence of Ni(COD)$_2$



1a 0.45 mmol

4a 0.15 mmol

5aa 61% (NMR yield) r.r >95:5

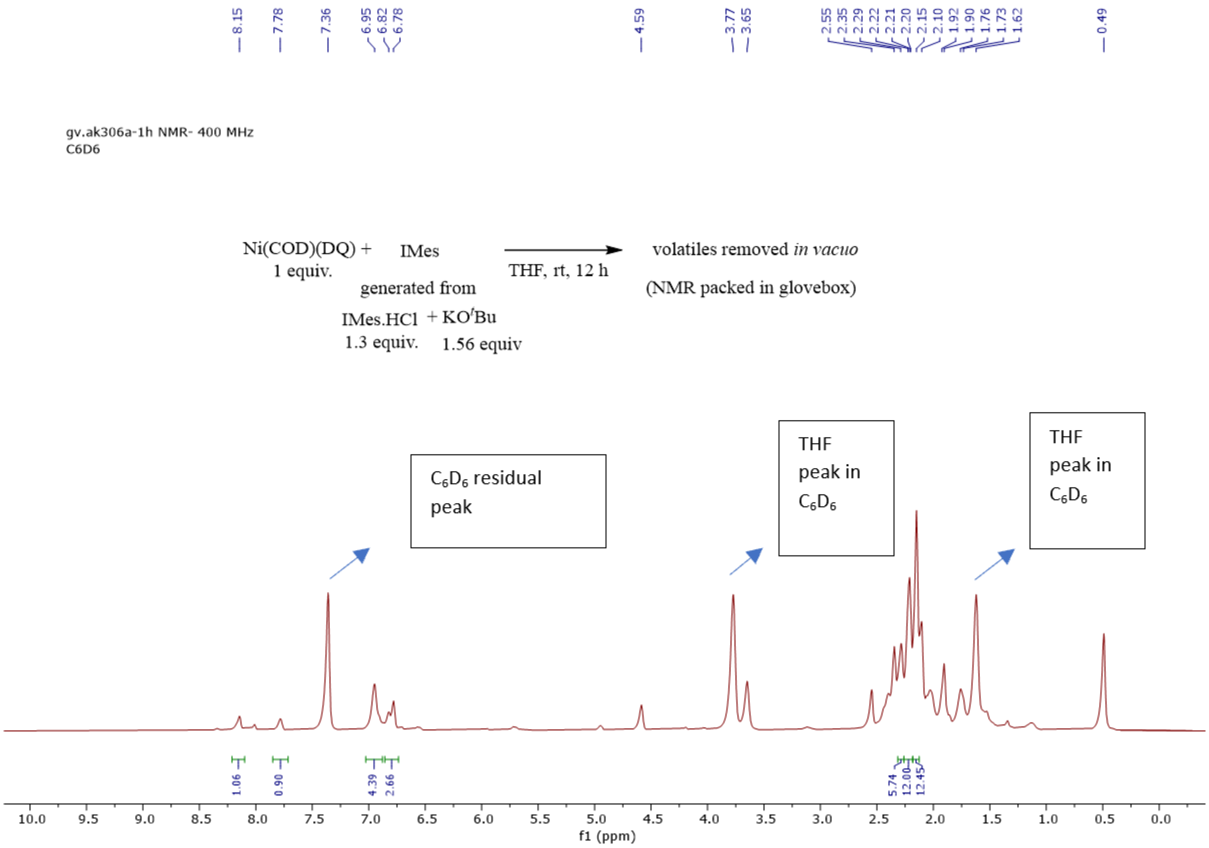
Reaction Conditions: 4a added over 7 h using a syringe pump, additional 13 h of stirring; NMR yield determined by using 1,1,2,2-tetrachloroethane as internal standard

F. Attempts at isolation of Ni(IMes)(DQ)

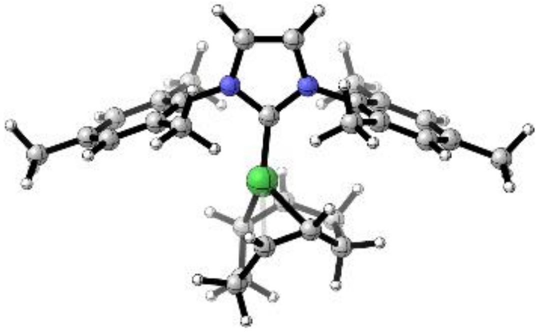
Our attempts to isolate and characterize Ni(IMes)(DQ) proved challenging even after applying stringent inert conditions. It was highly air-sensitive. The broad NMR spectra obtained in several attempts indicated the presence of paramagnetic species (probably through the comproportionation of Ni^0 and Ni^{II}) and hence we carried out experiment under stringent inert conditions.

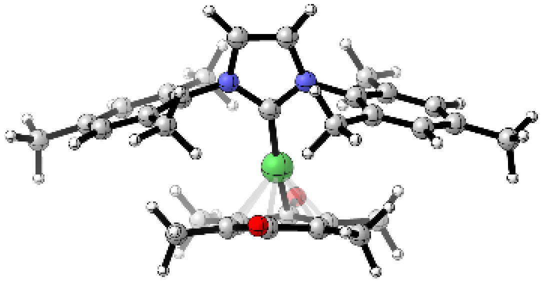
To a flame-dried Schlenk tube was added Ni(COD)(DQ) (19.8 mg, 0.06 mmol, 1 equiv) and dry THF (0.1 M). Dry THF was obtained by refluxing over sodium/benzophenone still followed by fresh distillation. The dry THF was further degassed using freeze-pump-thaw technique. Free carbene was generated in a separate Schlenk tube from the corresponding imidazolium salt (26.7 mg, 0.078 mmol, 1.3 equiv) and KO^{t}Bu (1 M in THF) (0.094 m L, 0.094 mmol, 1.56 equiv). The generated carbene solution was filtered using a syringe filter and subsequently added to a Schlenk tube containing Ni(COD)(DQ). After stirring for 12 h, the volatiles were removed *in vacuo*, the Schenk was taken inside the glovebox, and the NMR sample was packed with benzene-d_6.

The solid precipitated out from this experiment was added to a flame-dried Schlenk tube inside the glovebox (IMes)Ni(DQ), 11 mg, 0.02 mmol). The schlenk tube was taken outside and dry THF was added, followed by Et3SiH (0.064 mL, 0.04 mmol), benzaldehyde (21 mg, 0.02 mmol), and alkyne (27 mg, 0.024 mmol) as solution in dry THF (0.1 M) over 15 min. After stirring for 12 h at room temperature, the desired reductive coupled product **3aa** in 57% NMR yield.



13. Computational Details



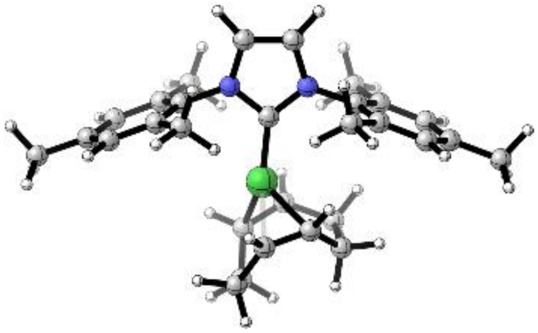


	(IMes)Ni(COD)	(IMes)Ni(DQ)
$\Delta G_{(THF)}{}^{a}$	0 kcal/mol	-26.4 kcal/mol
Charges	+0.05	+0.41

[a] Gibbs free energies were calculated at M062x(SMD)/def2-TZVP (THF). Natural Charges (NBO)at M062x/def2-TZVP.

The formation of (IMes)Ni(DQ) was thermodynamically more favorable compared to Ni(IMes)(COD) by 26.4 kcal/mol. Enhanced back-bonding into DQ in the complex was evident from the natural charges obtained from the NBO analysis.

(IMes)Ni(COD) intermediate



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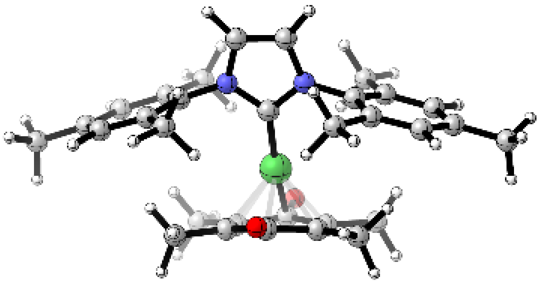
(IMes)Ni(DQ) intermediate



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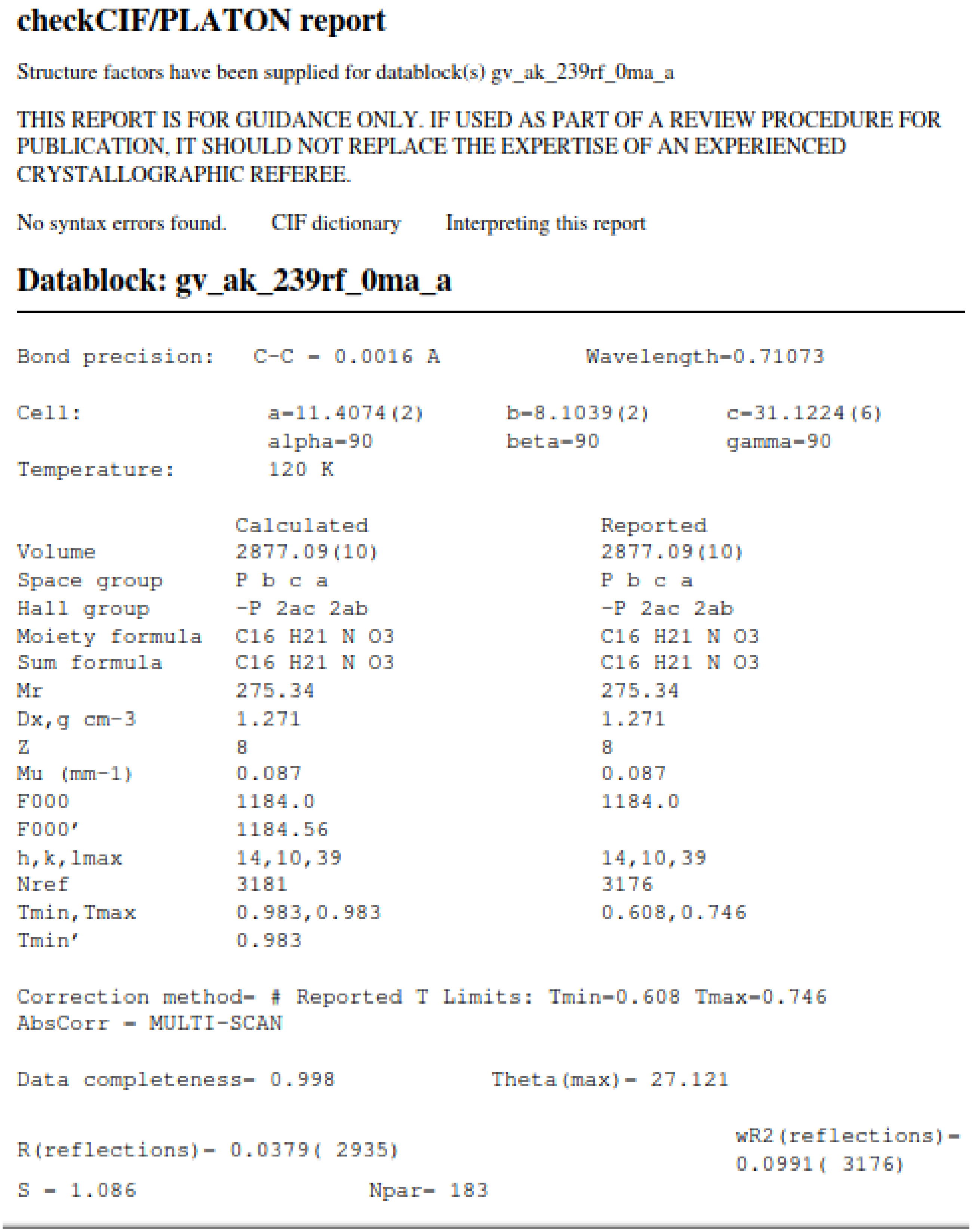
14. Single Crystal X-Ray Diffraction Data For Compound 6



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) gv_ak_239rf_0ma_a

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found.   CIF dictionary   Interpreting this report

Datablock: gv_ak_239rf_0ma_a

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Bond precision:   C-C = 0.0016 A          Wavelength=0.71073

Cell:              a=11.4074(2)      b=8.1039(2)      c=31.1224(6)
                   alpha=90          beta=90          gamma=90
Temperature:       120 K

                 Calculated                  Reported
Volume           2877.09(10)                 2877.09(10)
Space group      P b c a                     P b c a
Hall group       -P 2ac 2ab                  -P 2ac 2ab
Moiety formula   C16 H21 N O3                C16 H21 N O3
Sum formula      C16 H21 N O3                C16 H21 N O3
Mr               275.34                      275.34
Dx,g cm-3        1.271                       1.271
Z                8                           8
Mu (mm-1)        0.087                       0.087
F000             1184.0                      1184.0
F000'            1184.56
h,k,lmax         14,10,39                    14,10,39
Nref             3181                        3176
Tmin,Tmax        0.983,0.983                 0.608,0.746
Tmin'            0.983

Correction method= # Reported T Limits: Tmin=0.608 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.998          Theta(max)= 27.121

                                                     wR2(reflections)=
R(reflections)= 0.0379( 2935)                        0.0991( 3176)

S = 1.086                Npar= 183
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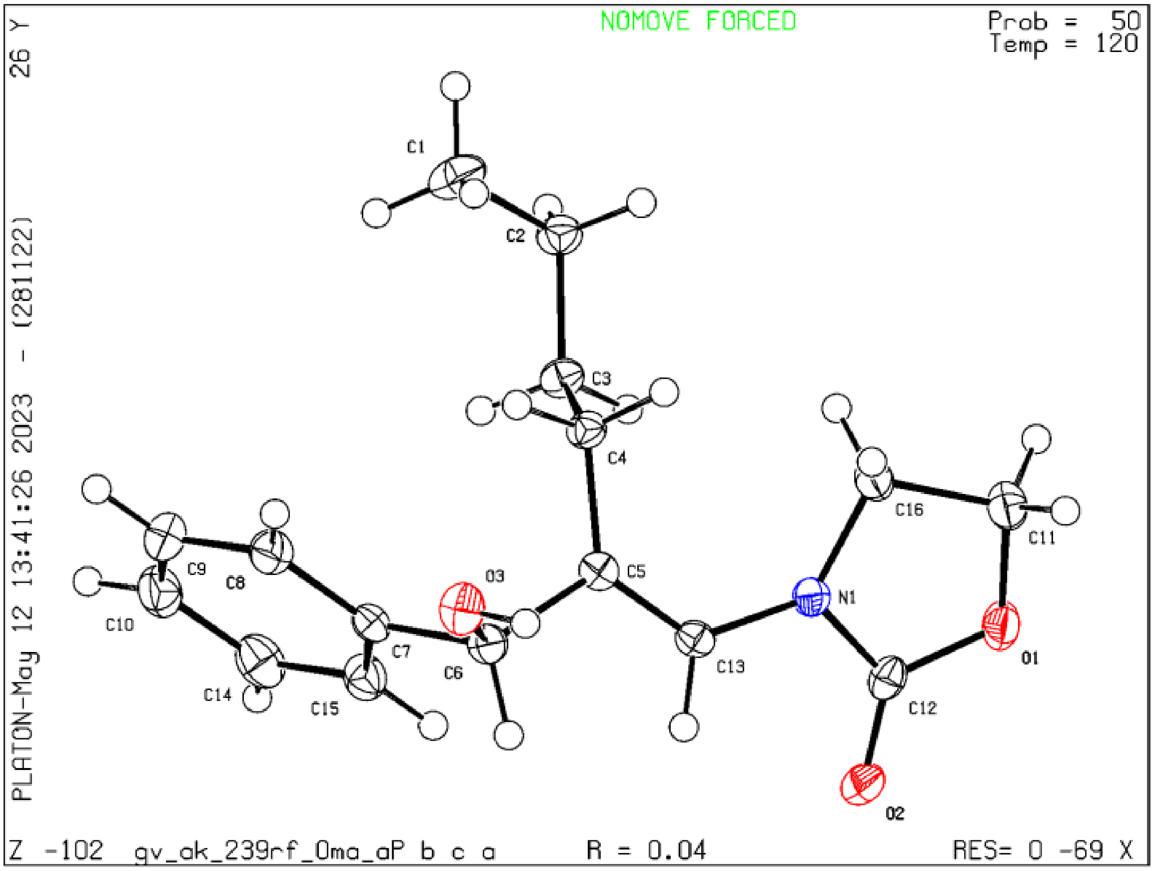
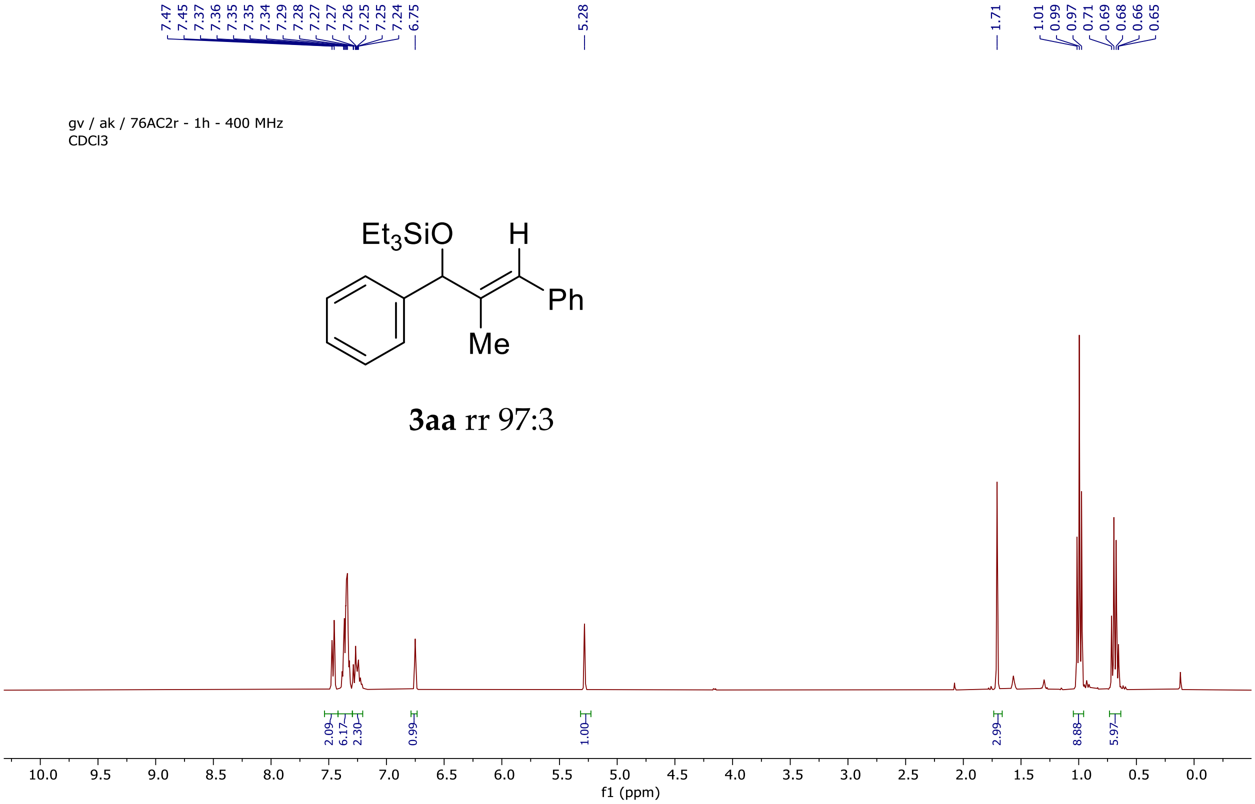
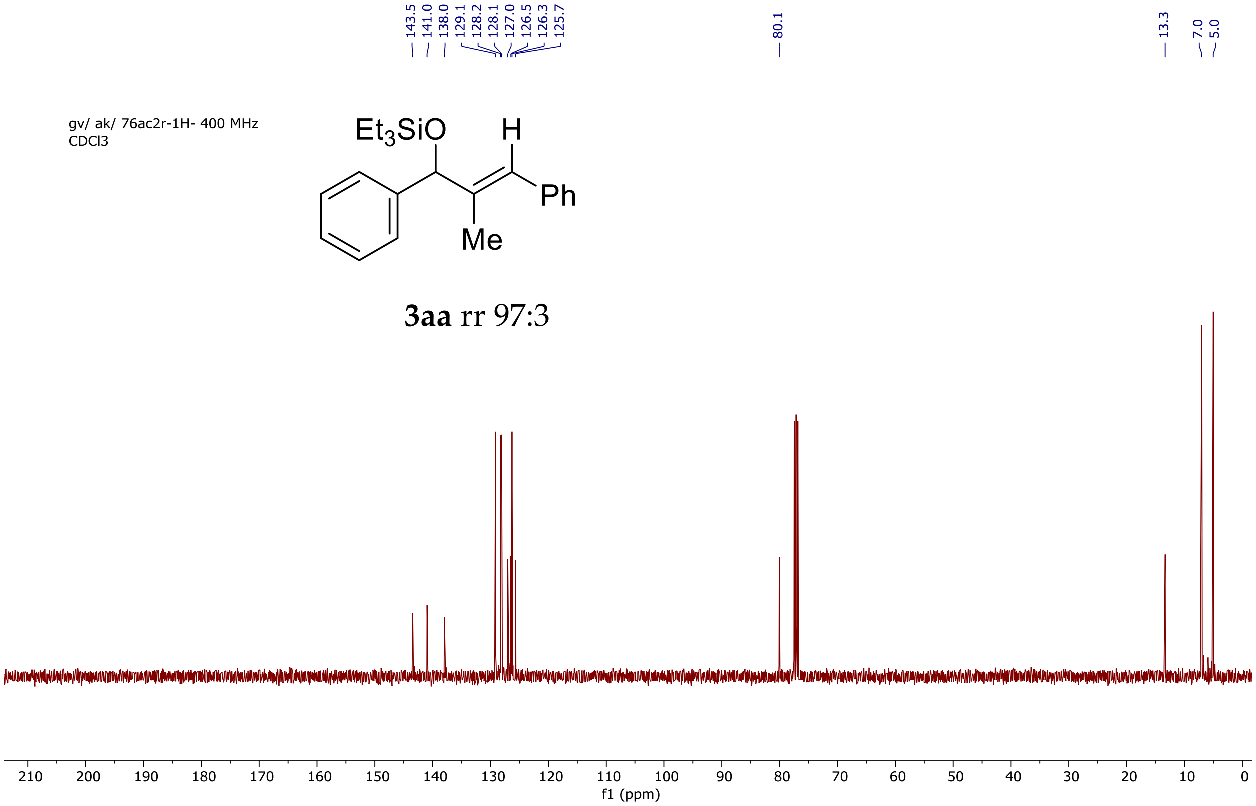
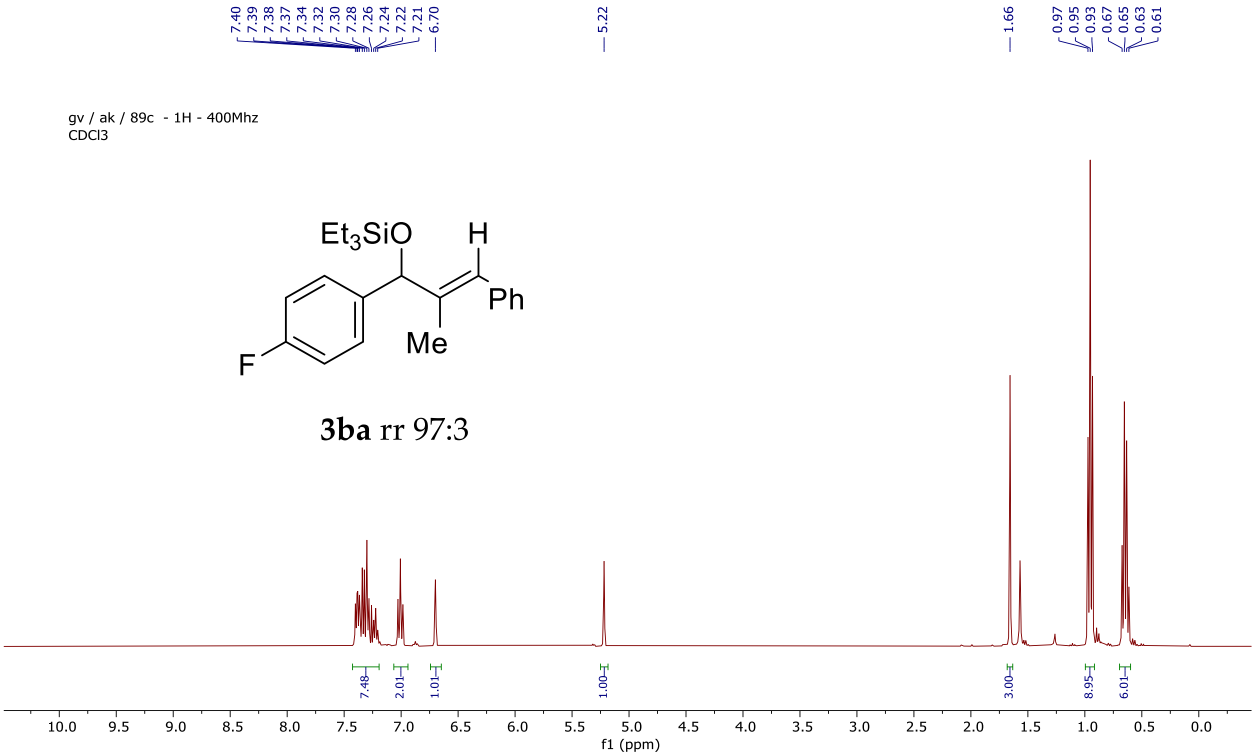
Datablock gv_ak_239rf_0ma_a - ellipsoid plot



15. Copies of ^{1}H, ^{13}C, ^{19}F, COSY, HSQC







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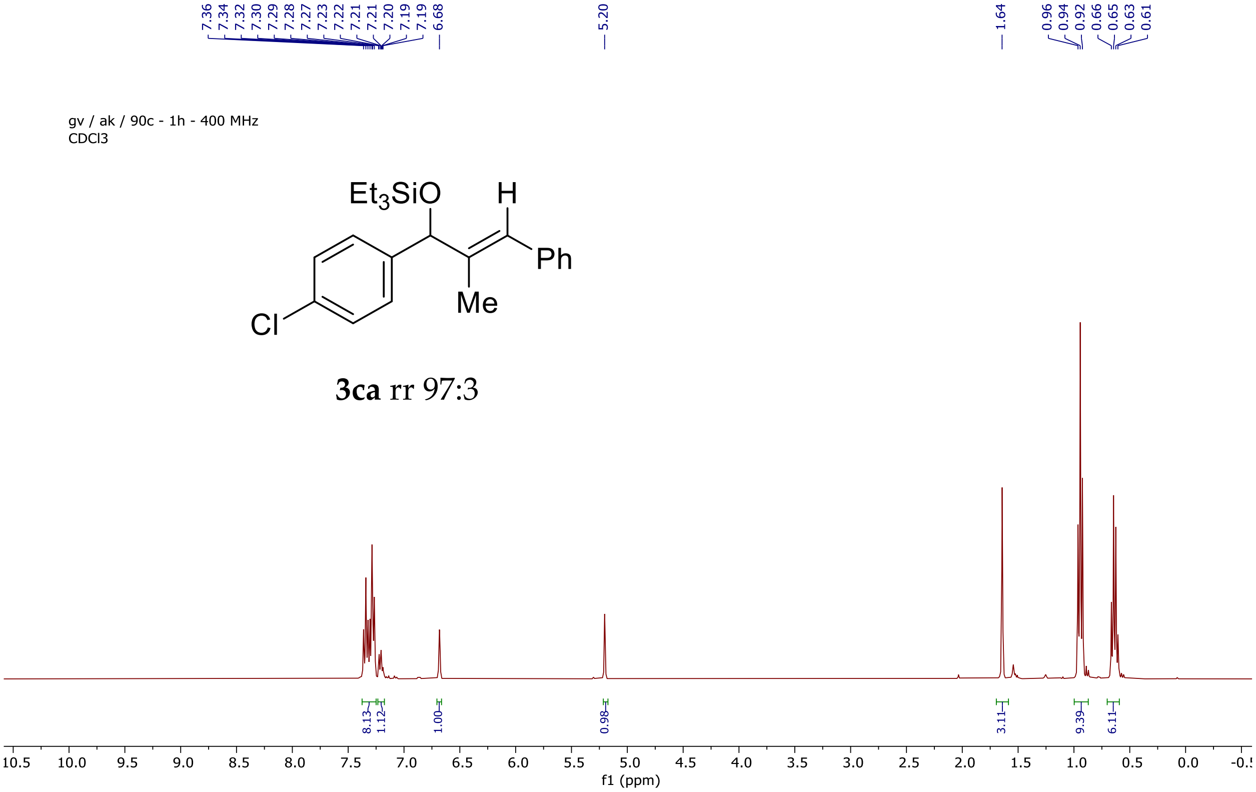

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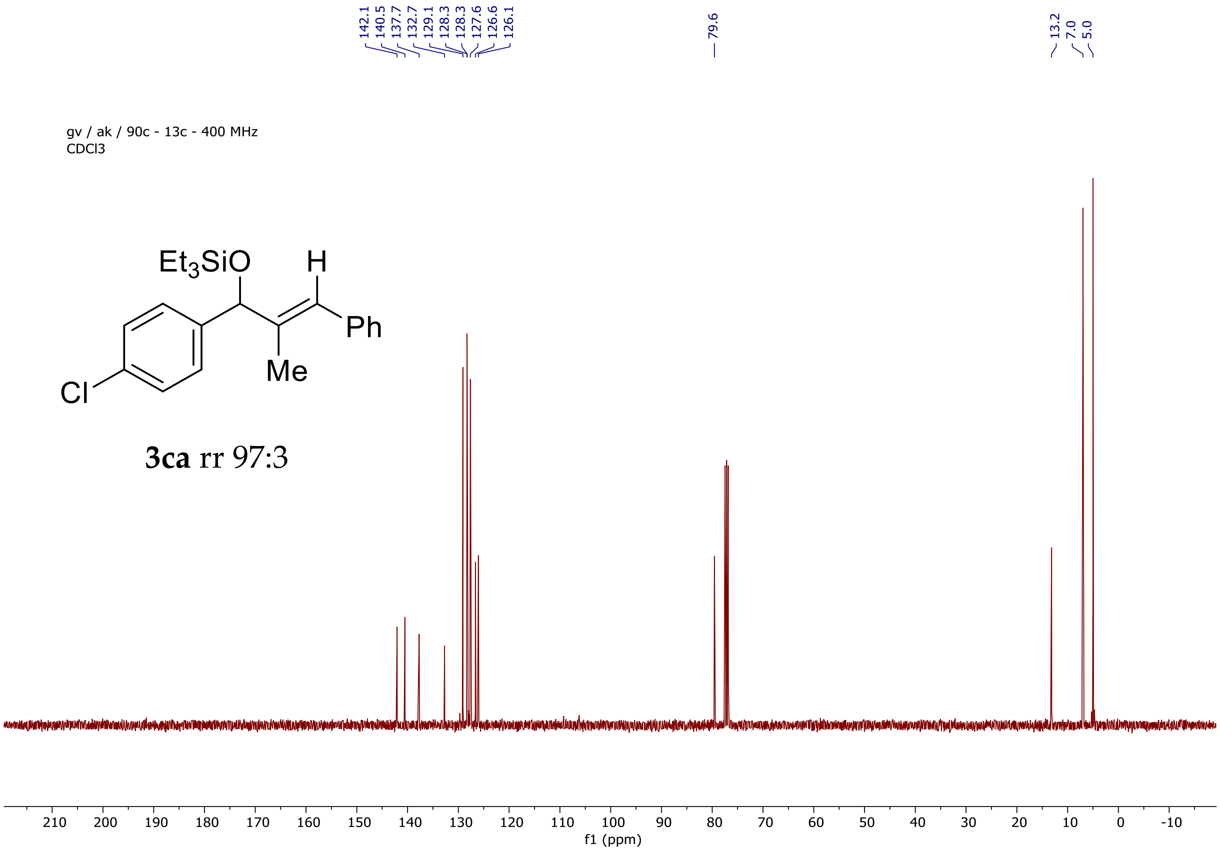

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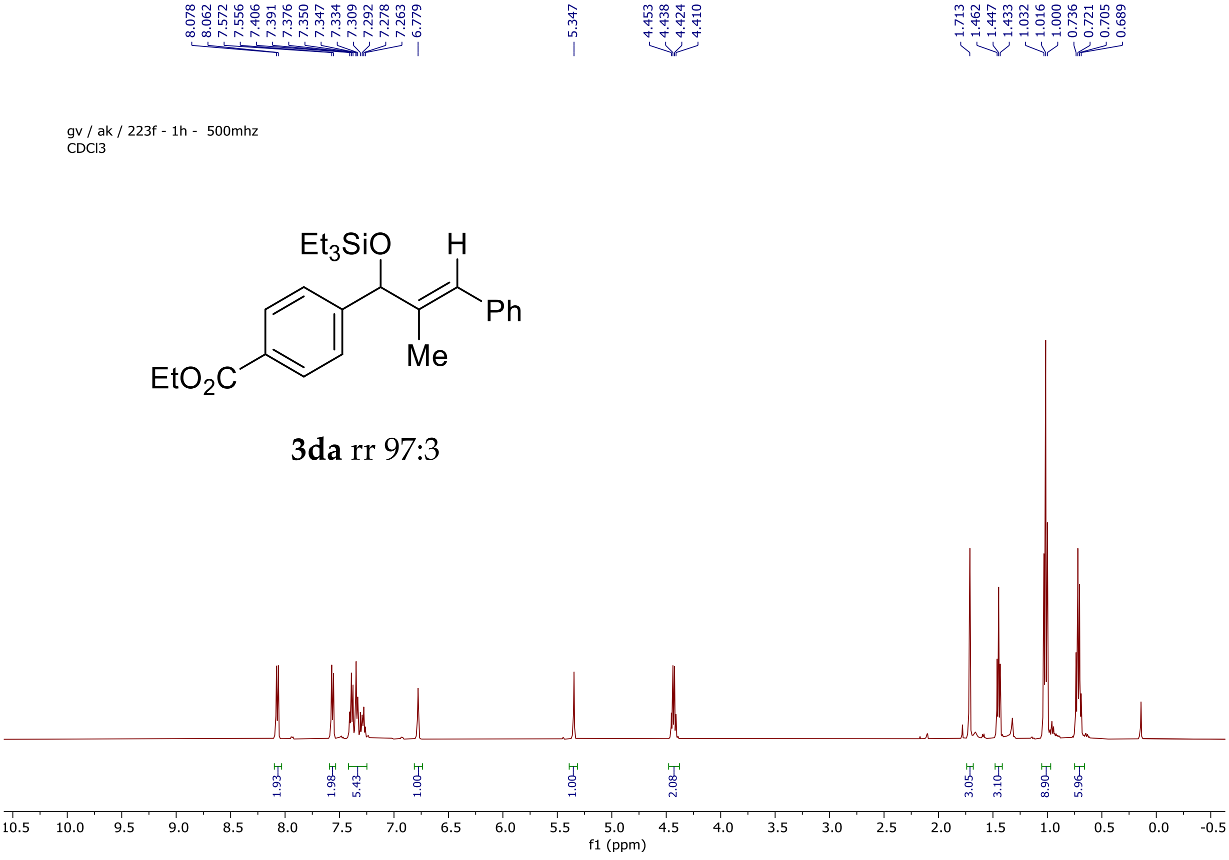

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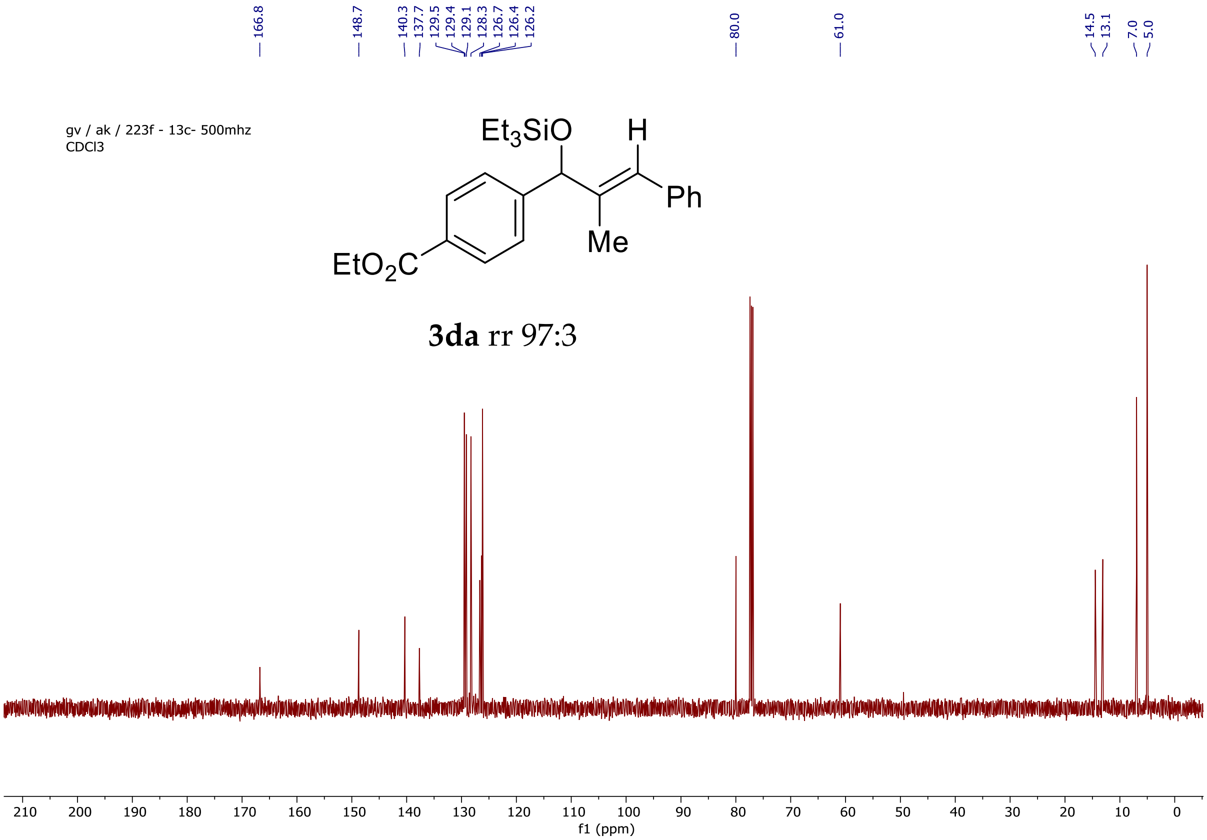

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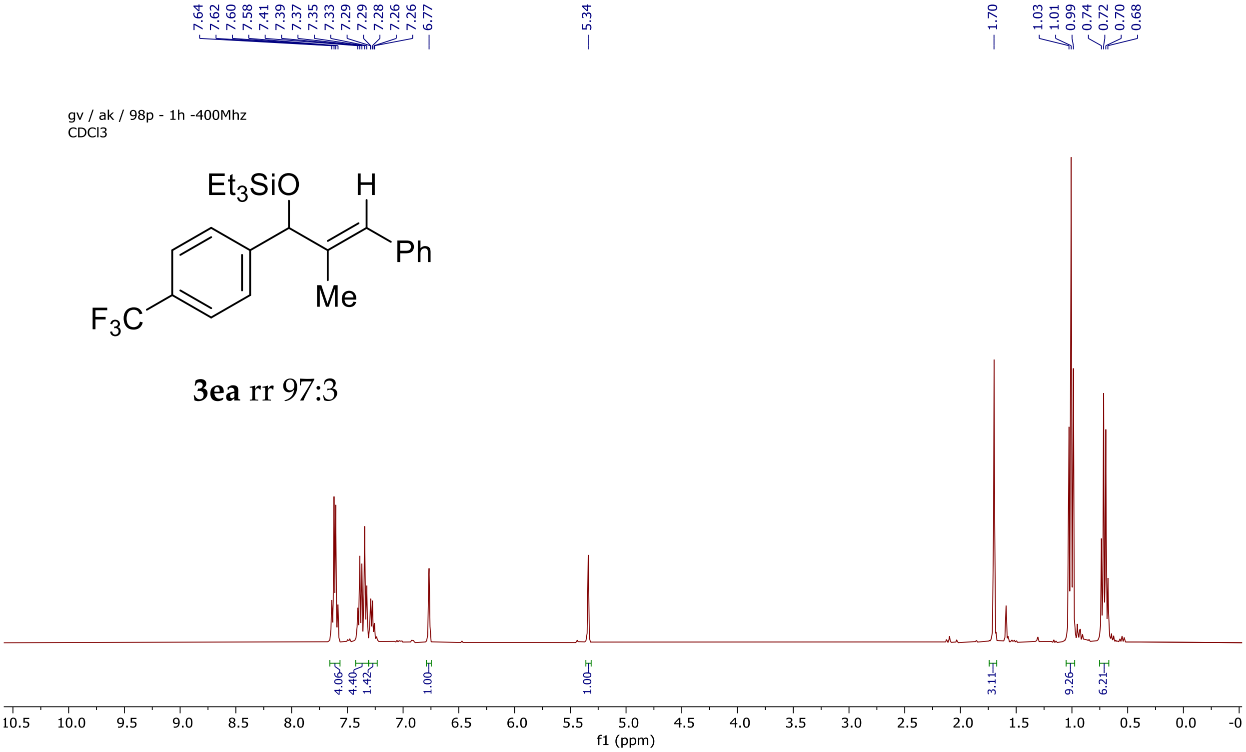

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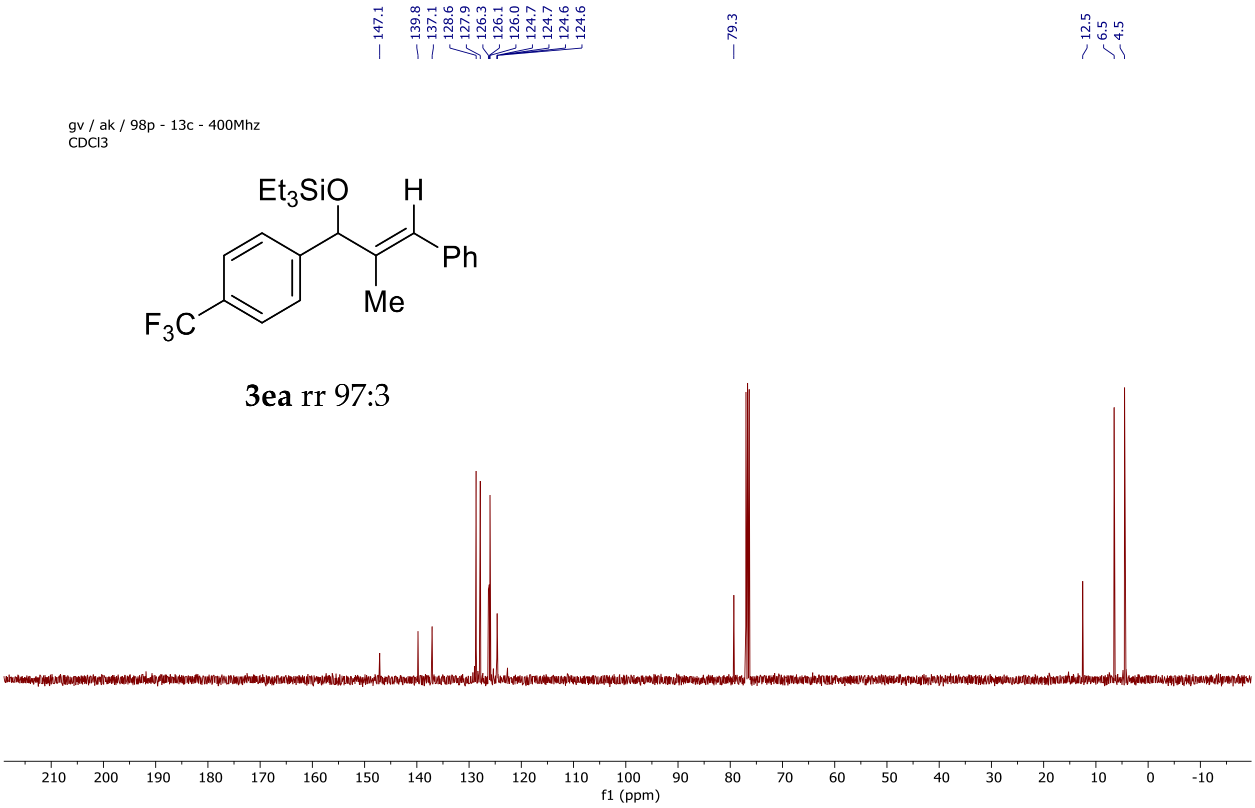

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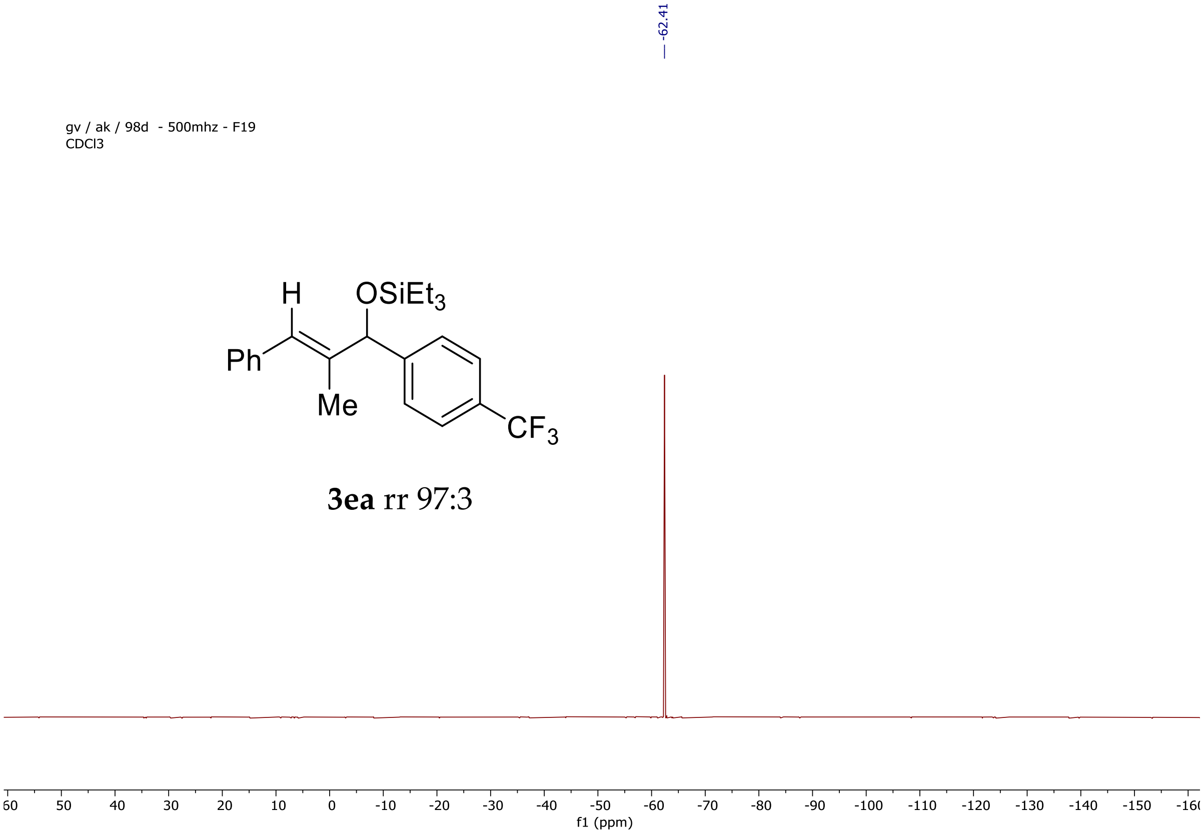

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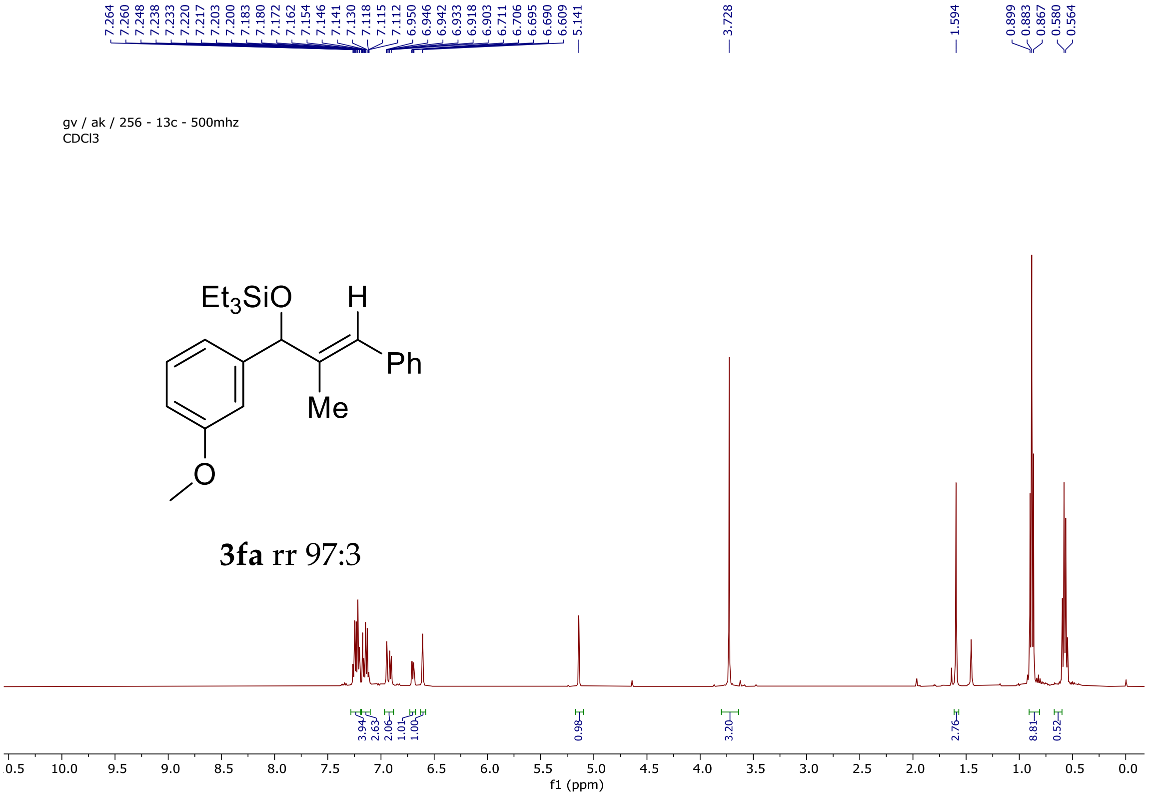
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6.933
6.918
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6.711
6.706
6.695
6.690
6.609
5.141
3.728
1.594
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0.883
0.867
0.580
0.564
gv / ak / 256 - 13c - 500mhz
CDCl3
Et3SiO
H
Ph
Me
O
3fa rr 97:3
3.94
2.63
2.06
1.01
1.00
0.98
3.20
2.76
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9.0
8.5
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7.5
7.0
6.5
6.0
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2.5
2.0
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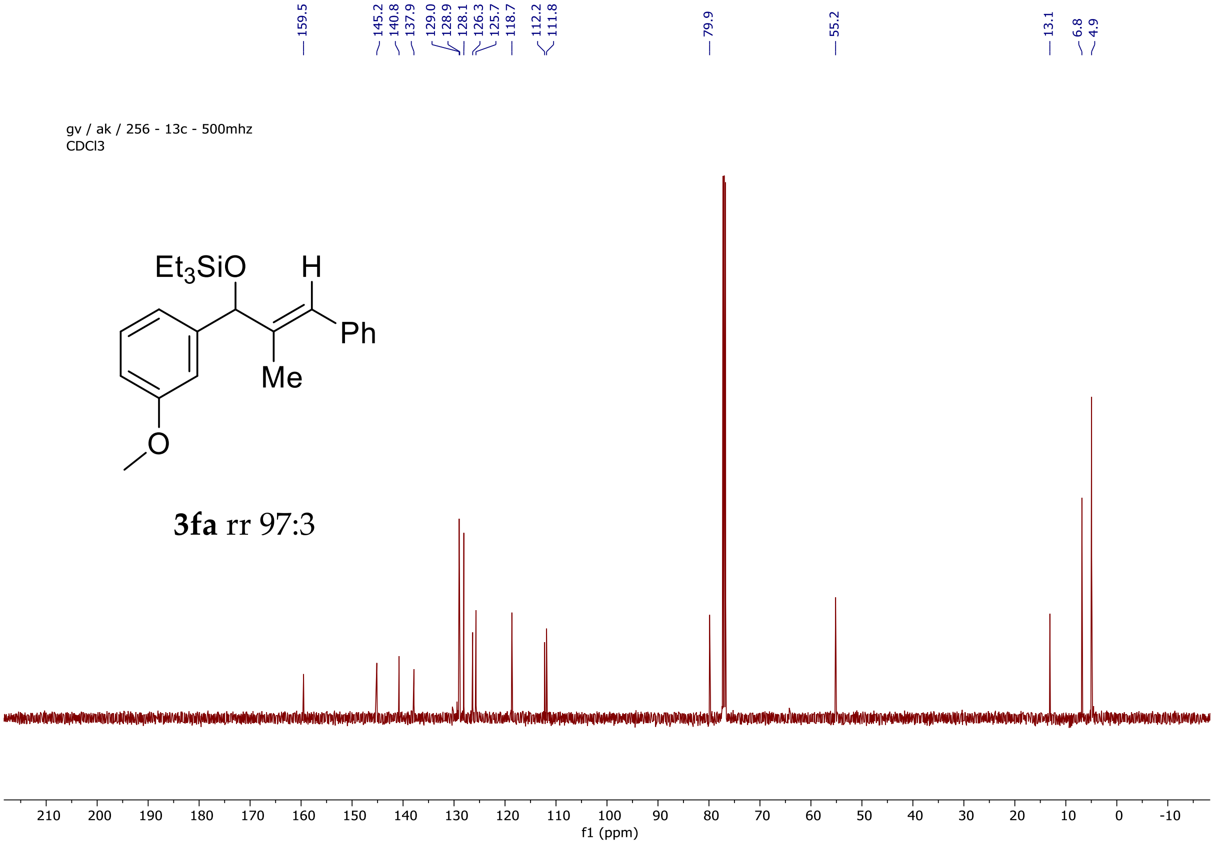
0.5
0.0
f1 (ppm)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137.9
129.0
128.9
128.1
126.3
125.7
118.7
112.2
111.8
79.9
55.2
13.1
6.8
4.9
gv / ak / 256 - 13c - 500mhz
CDCl3
Et3SiO
H
Ph
Me
O
3fa rr 97:3
210
200
190
180
170
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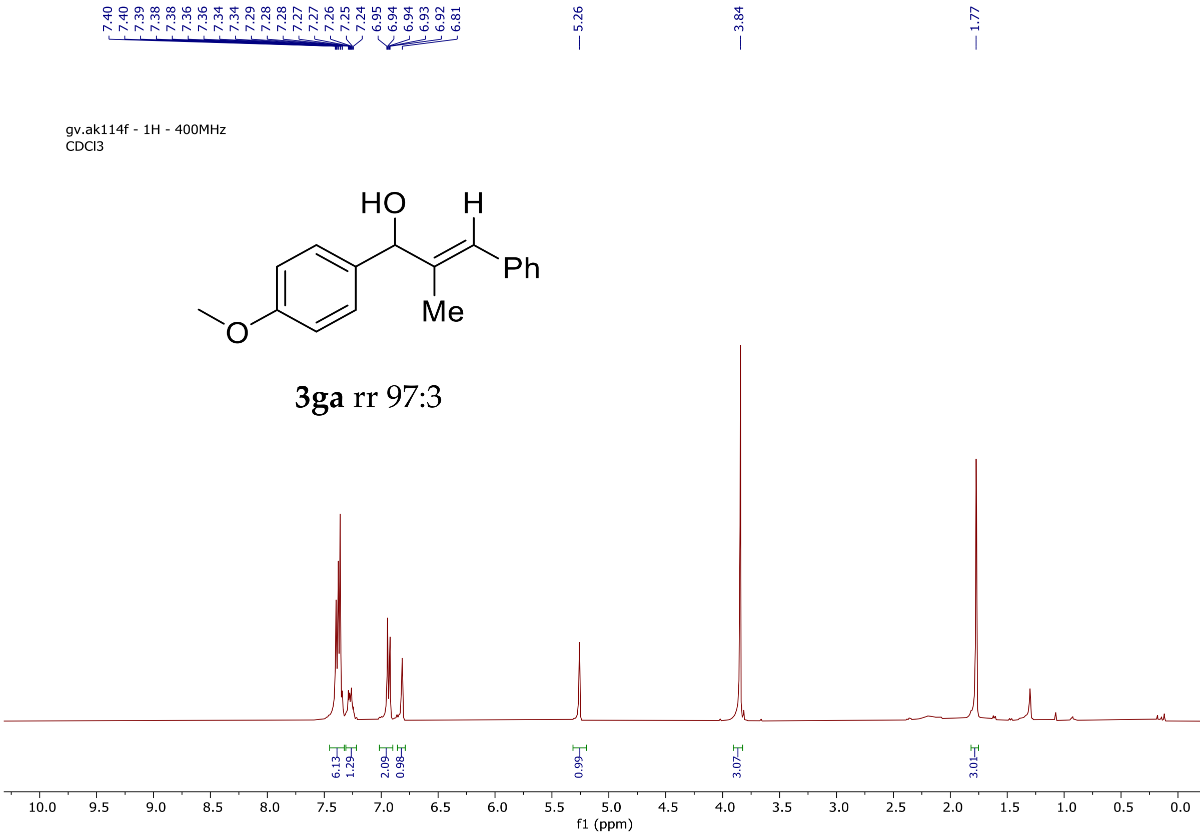
f1 (ppm)



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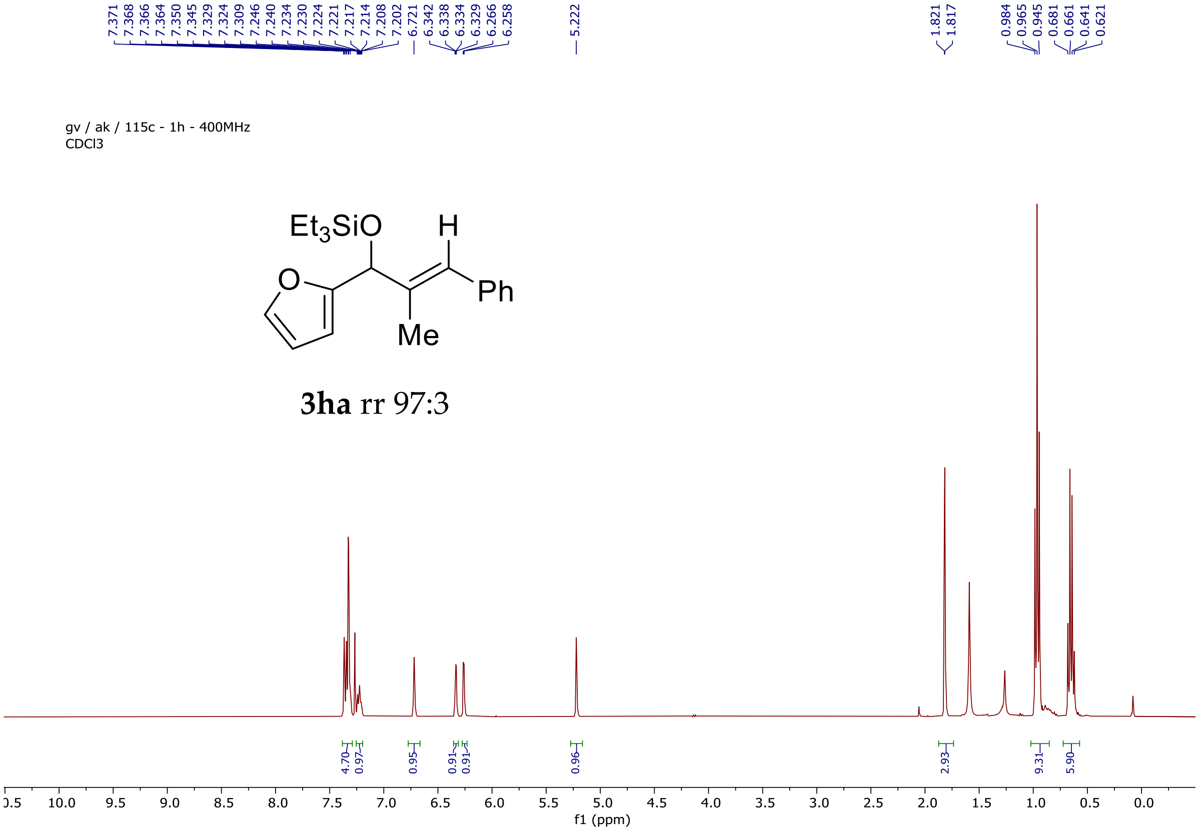
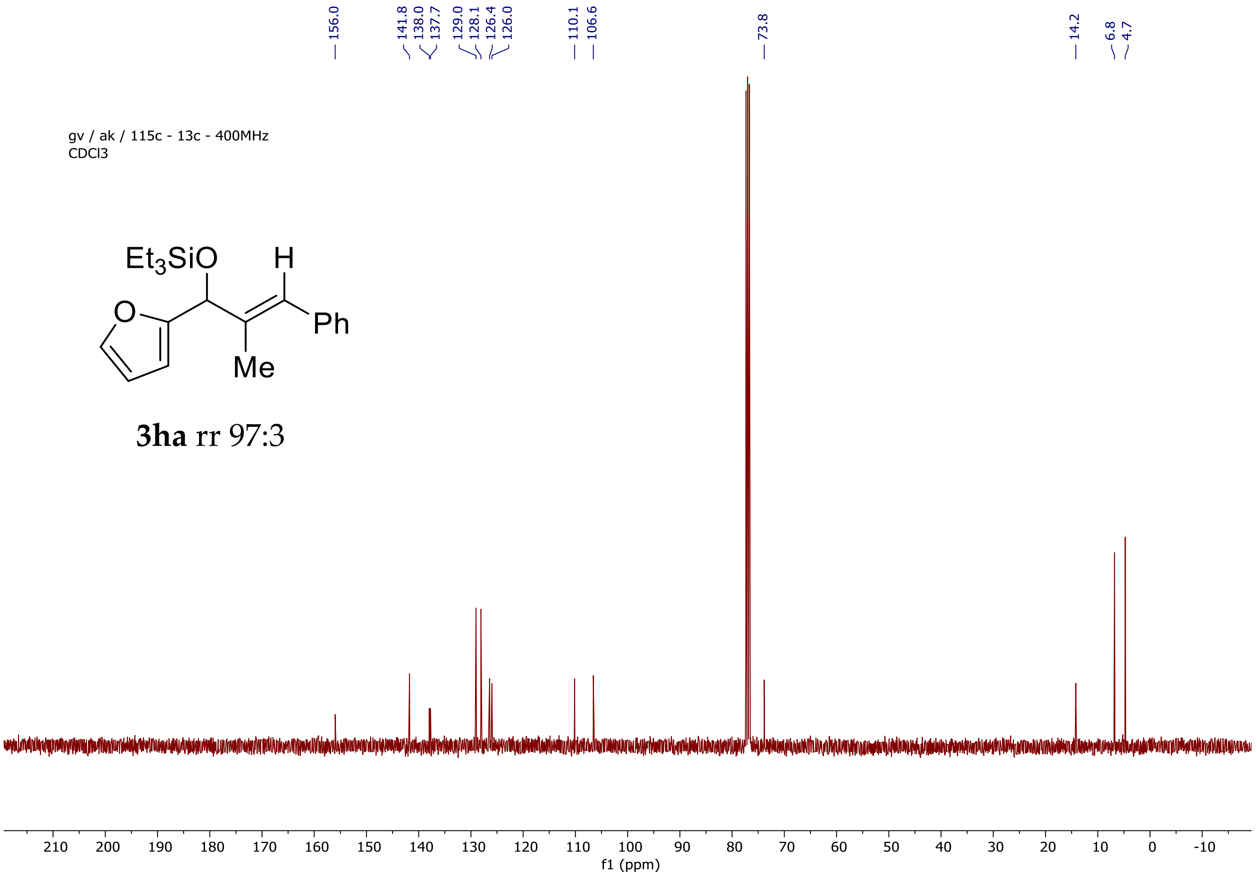
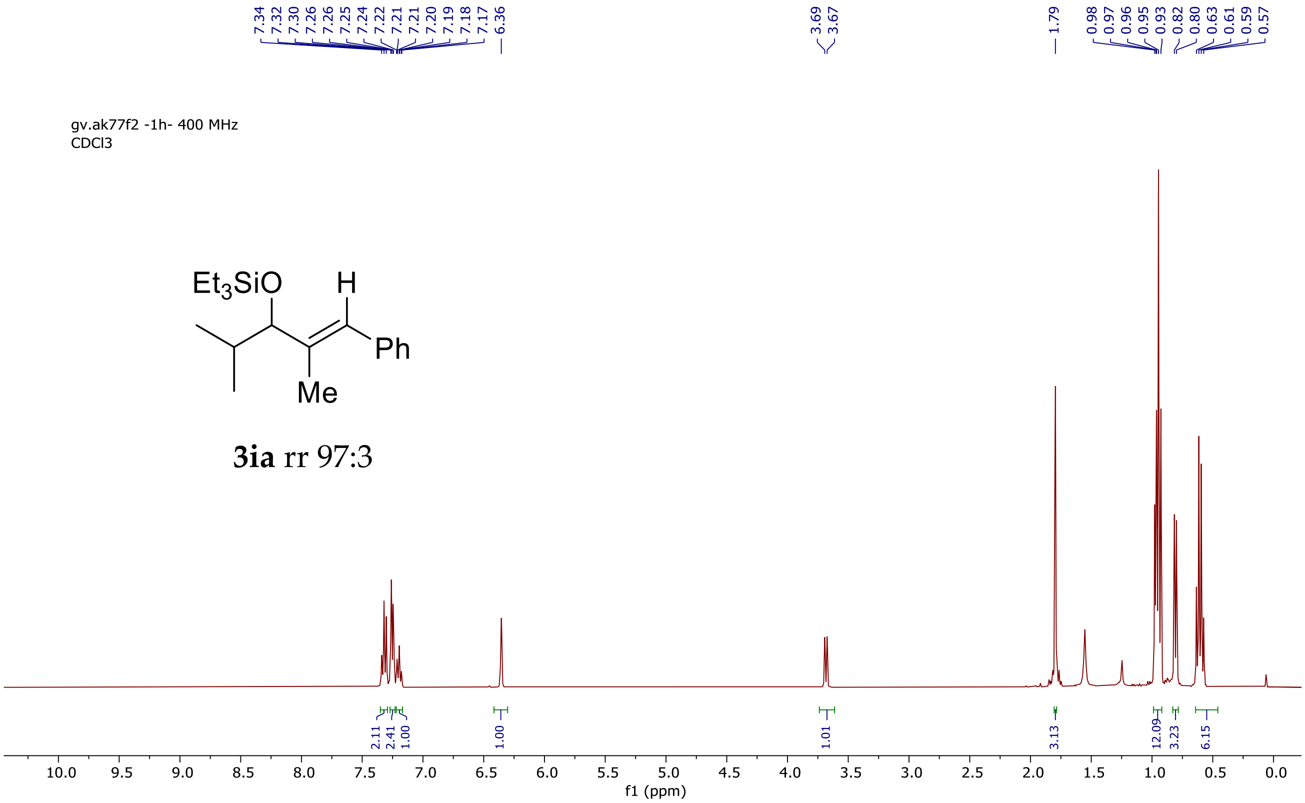


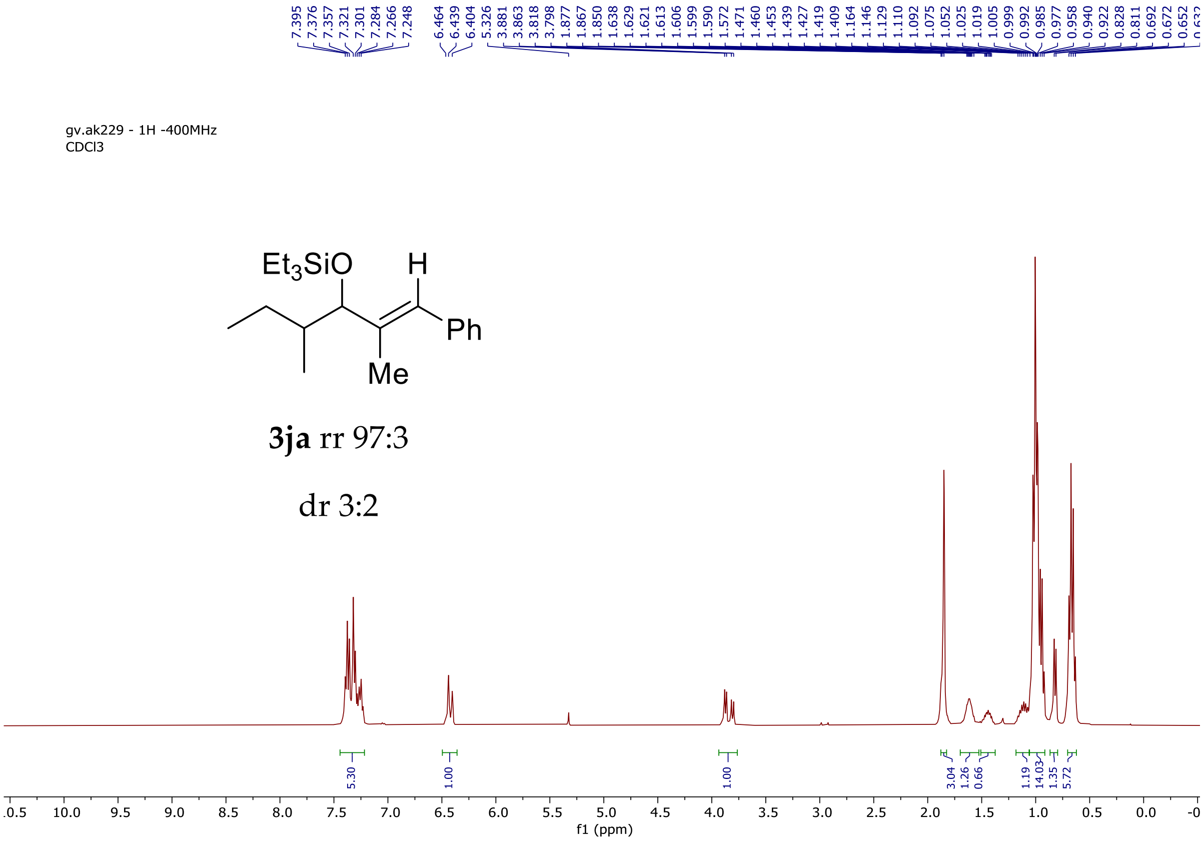
3ha rr 97:3



3ha rr 97:3

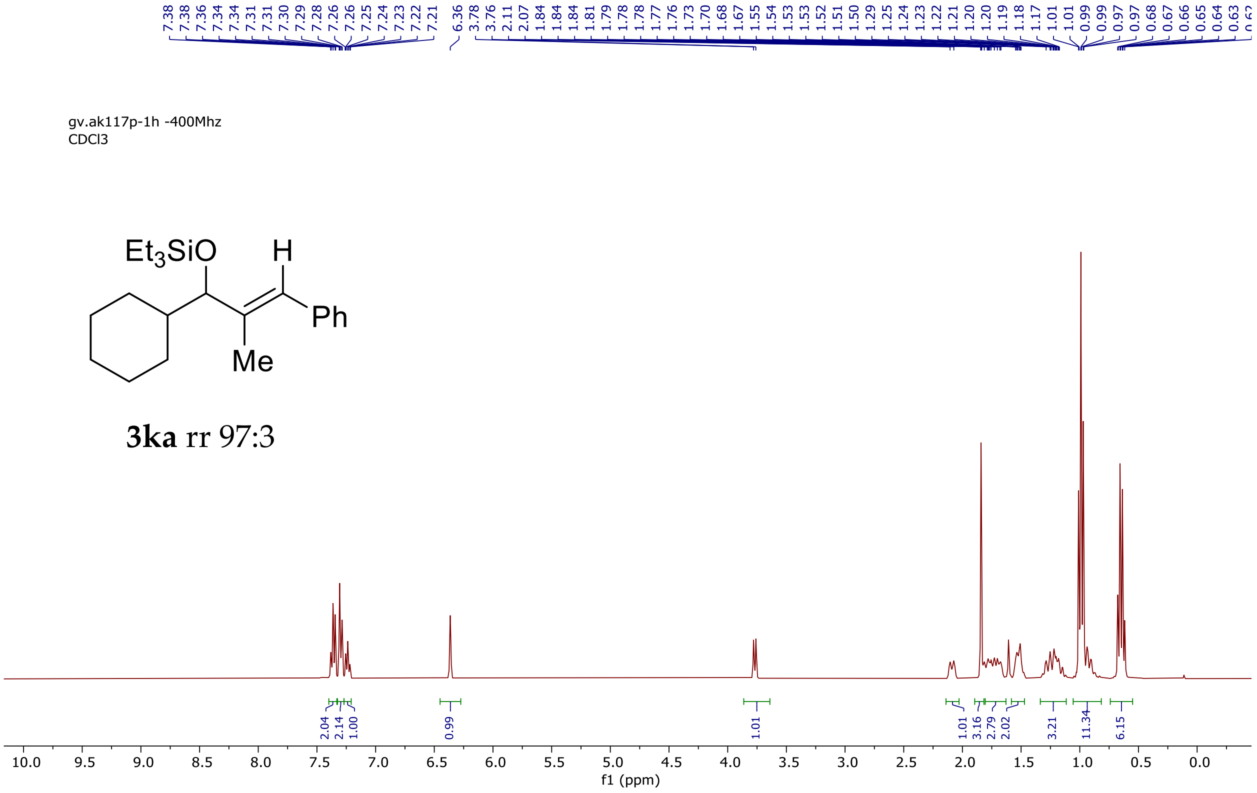


3ia rr 97:3

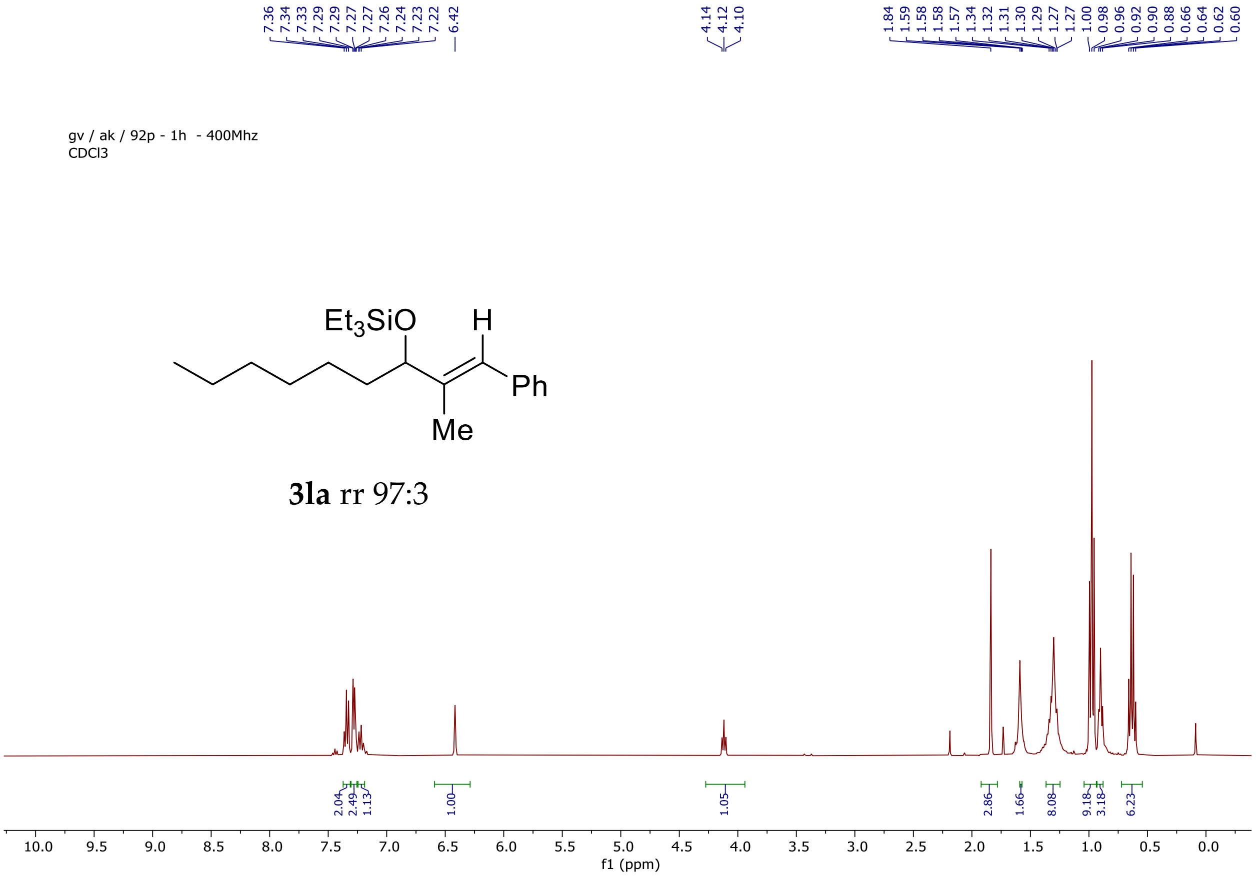


3ja rr 97:3

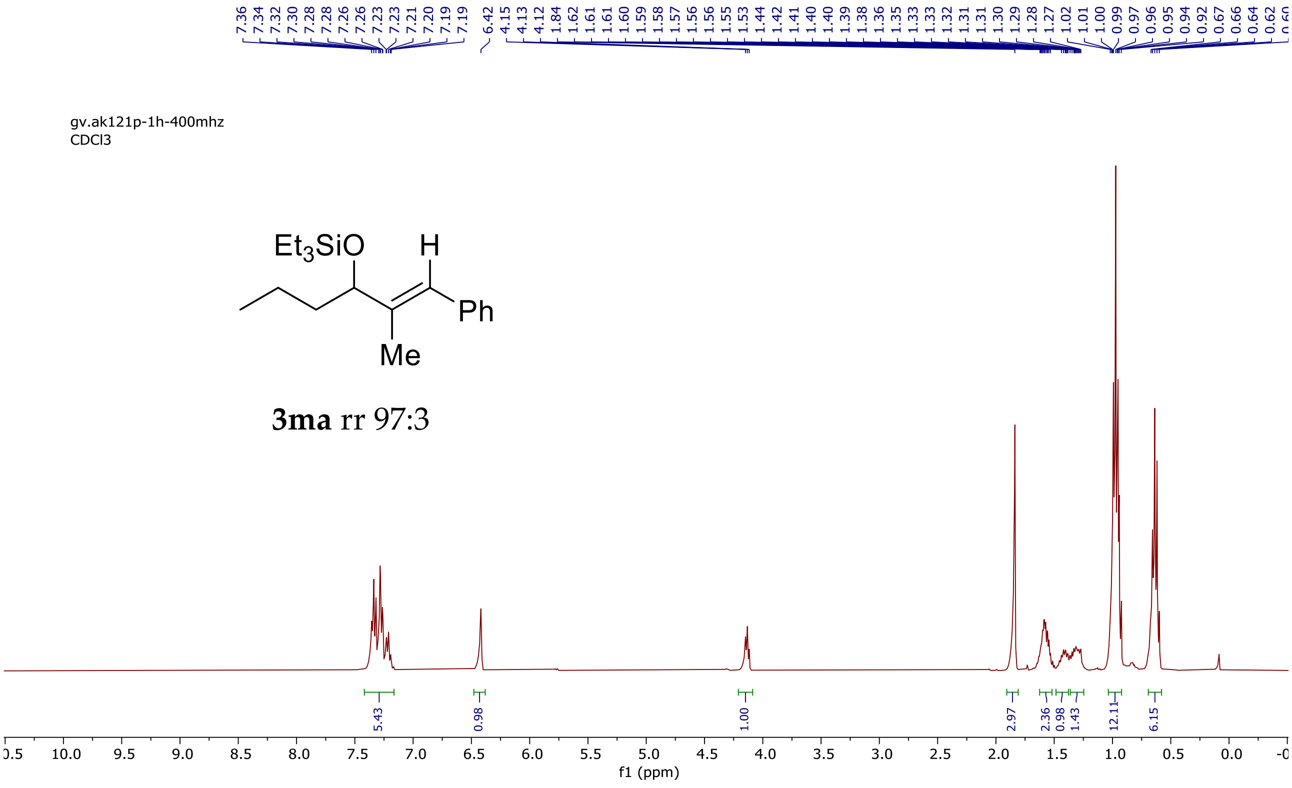
dr 3:2



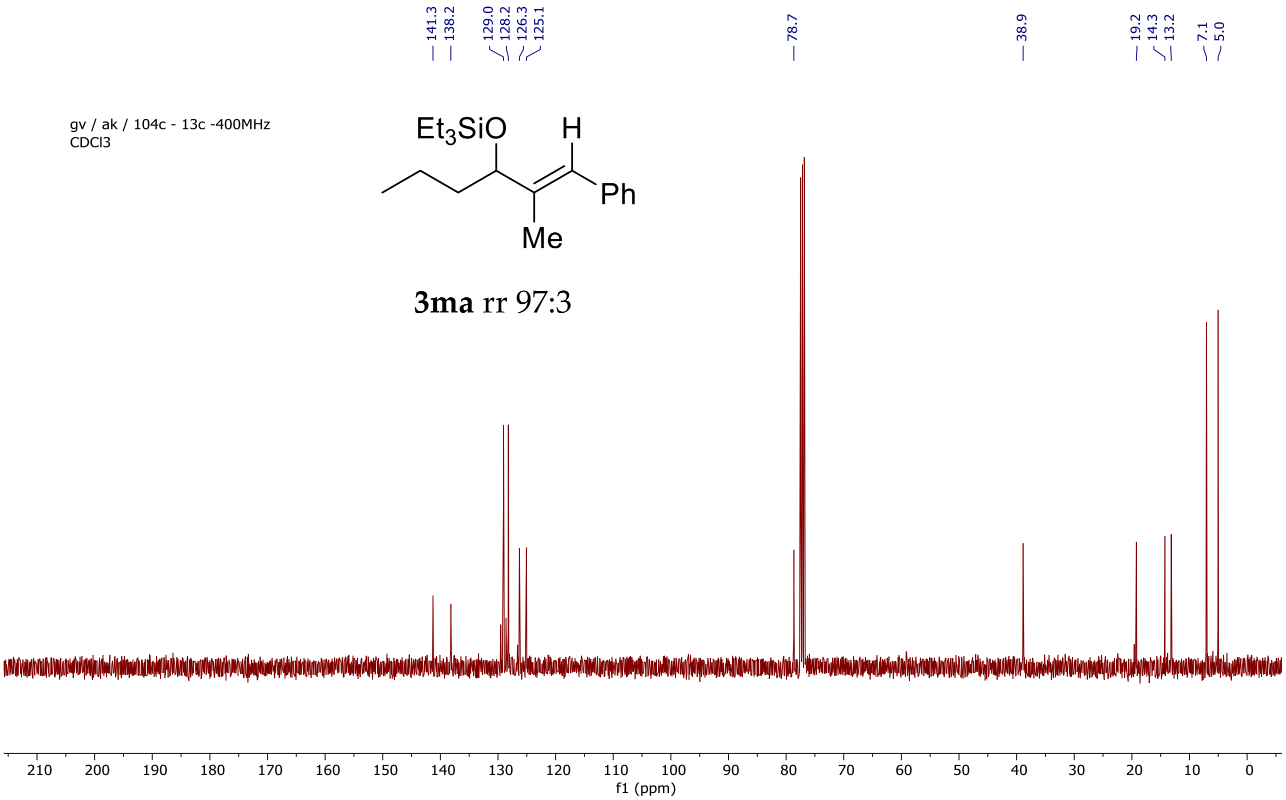
3ka rr 97:3



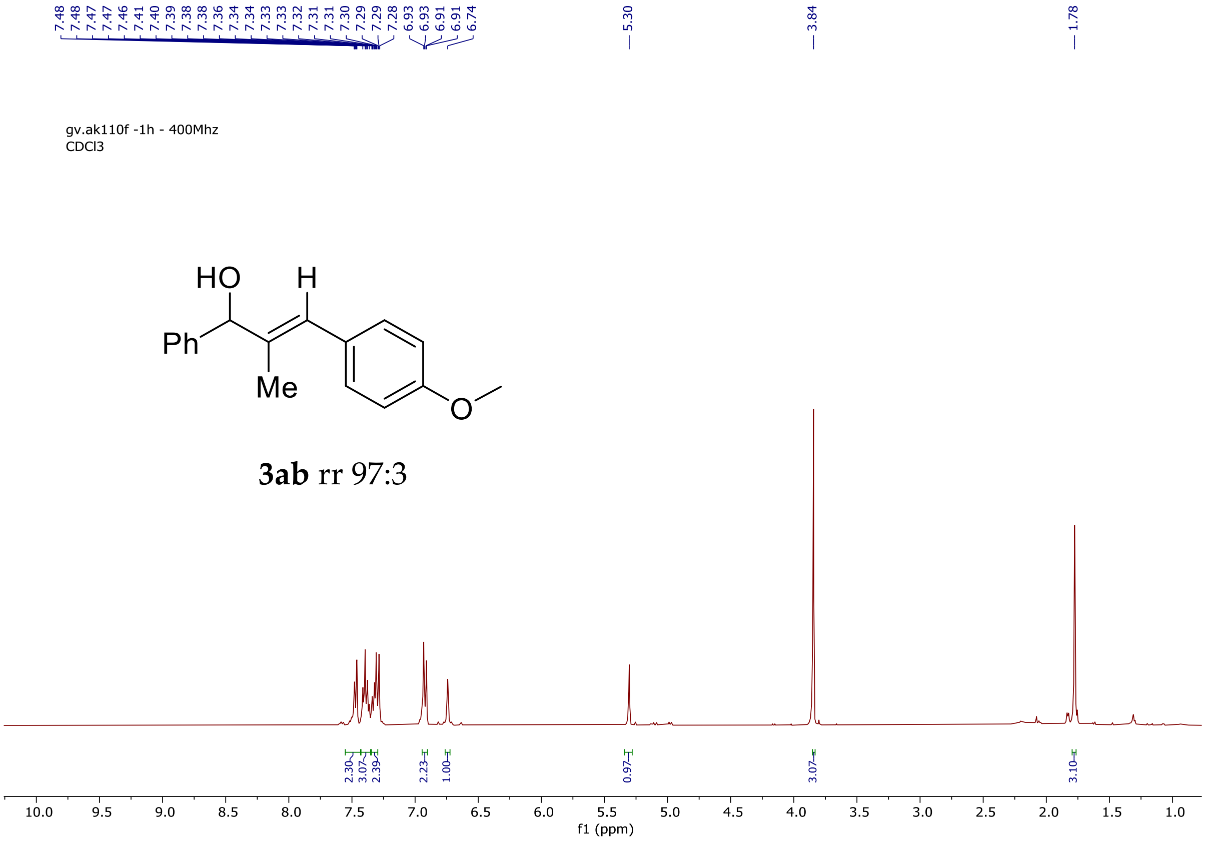
3la rr 97:3



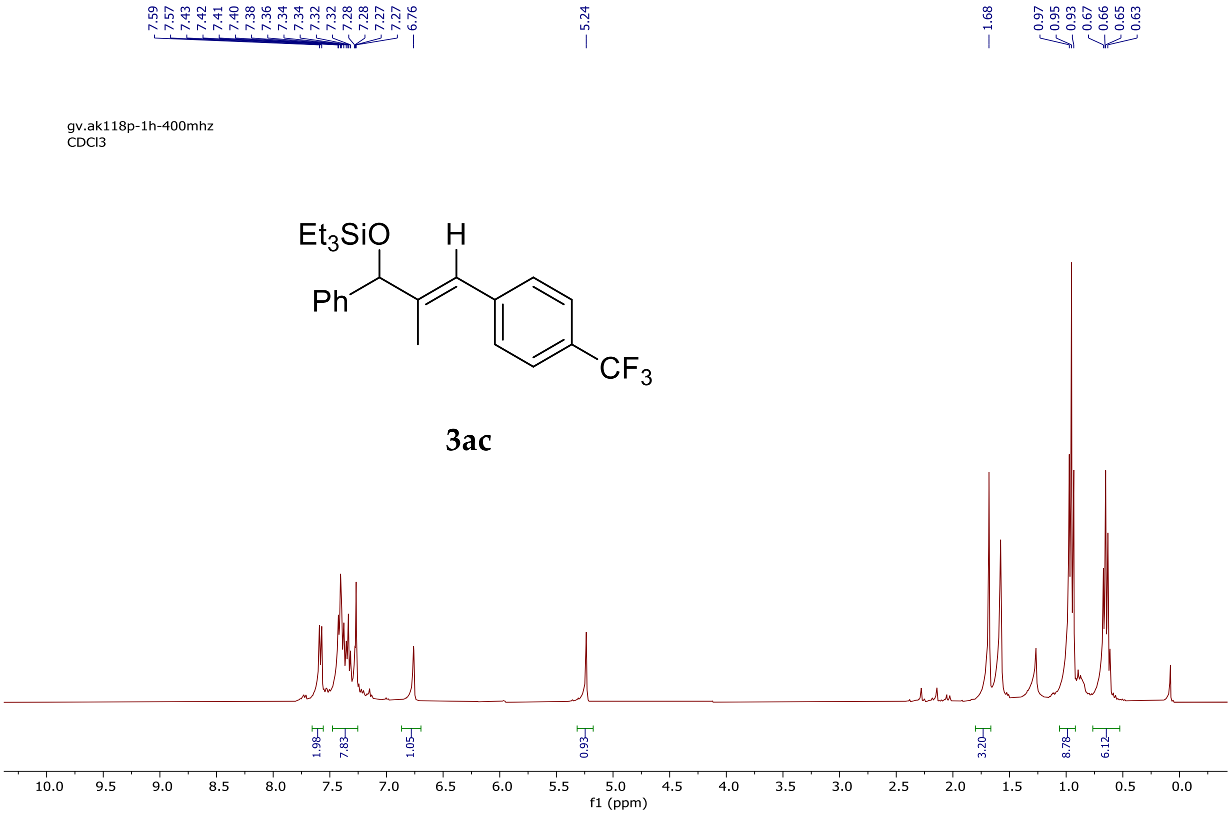
3ma rr 97:3

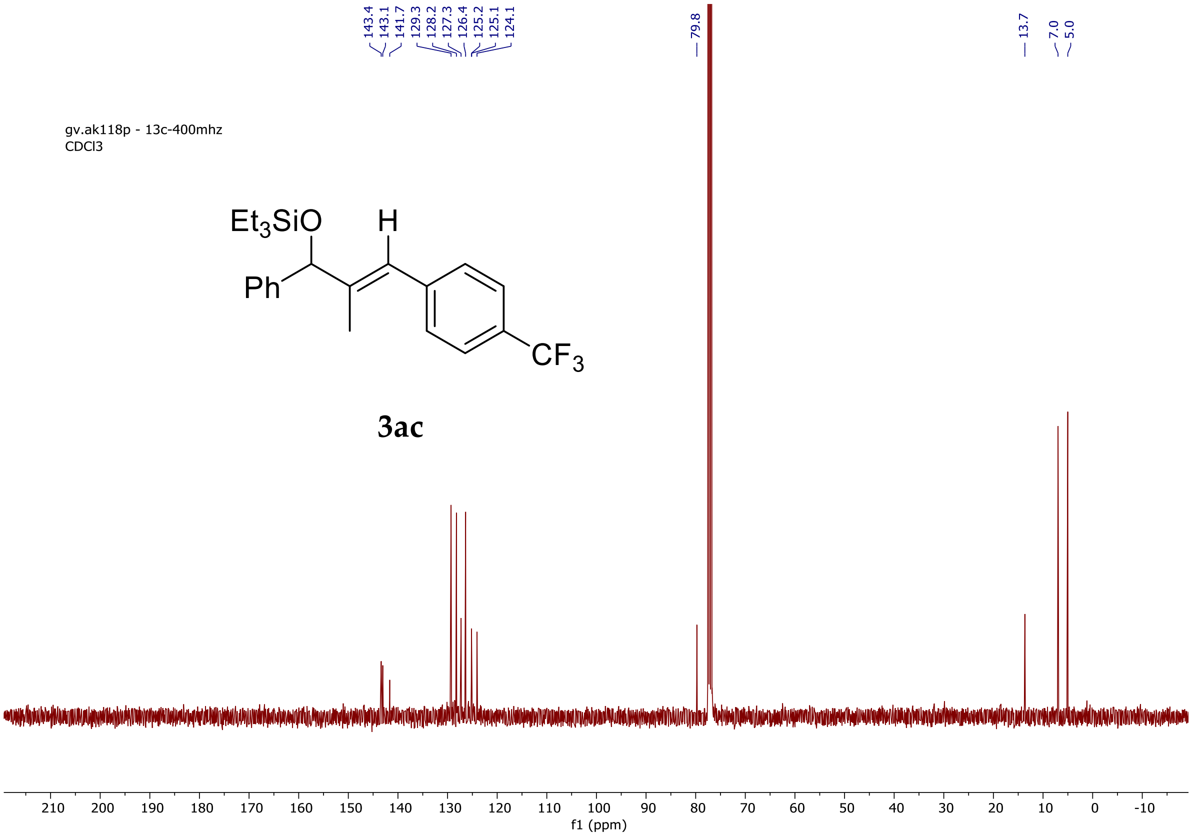


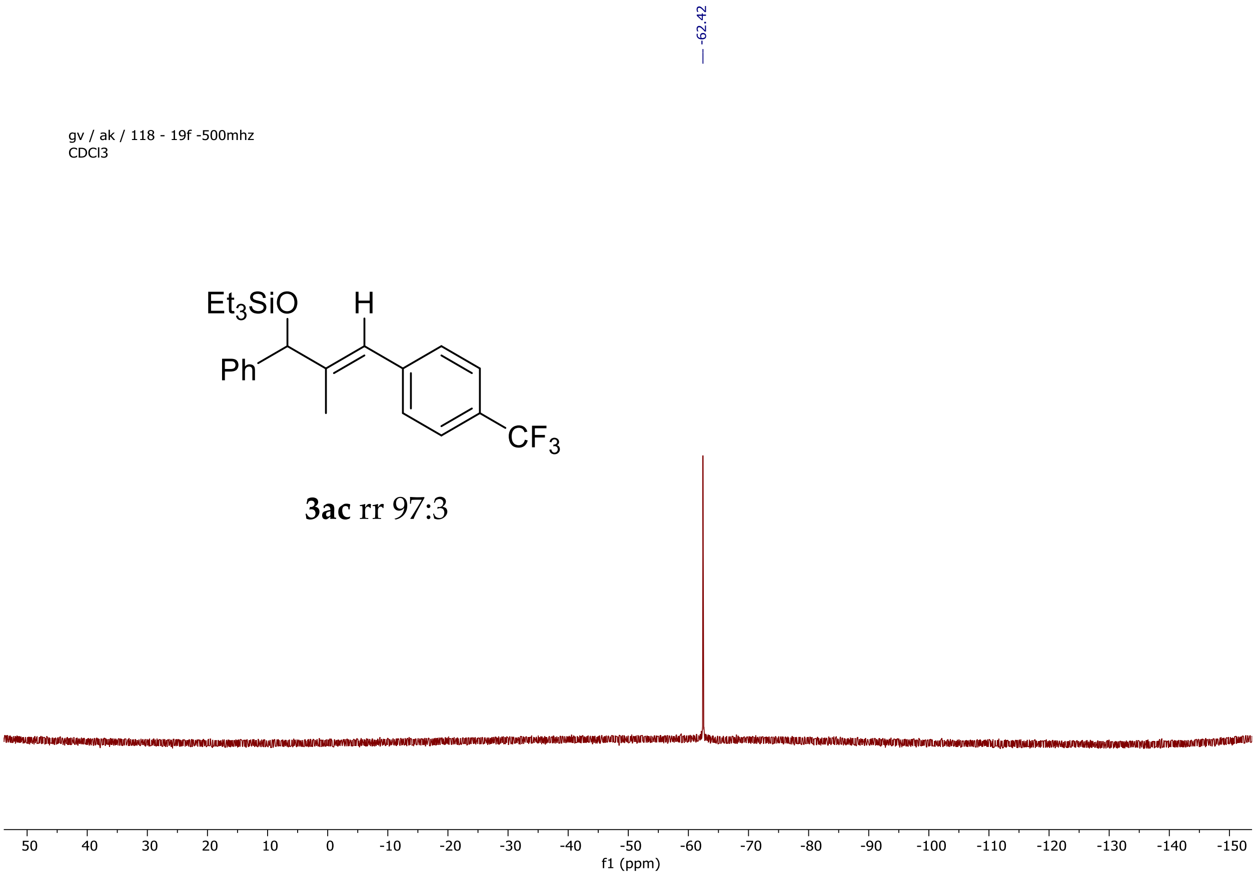
3ma rr 97:3



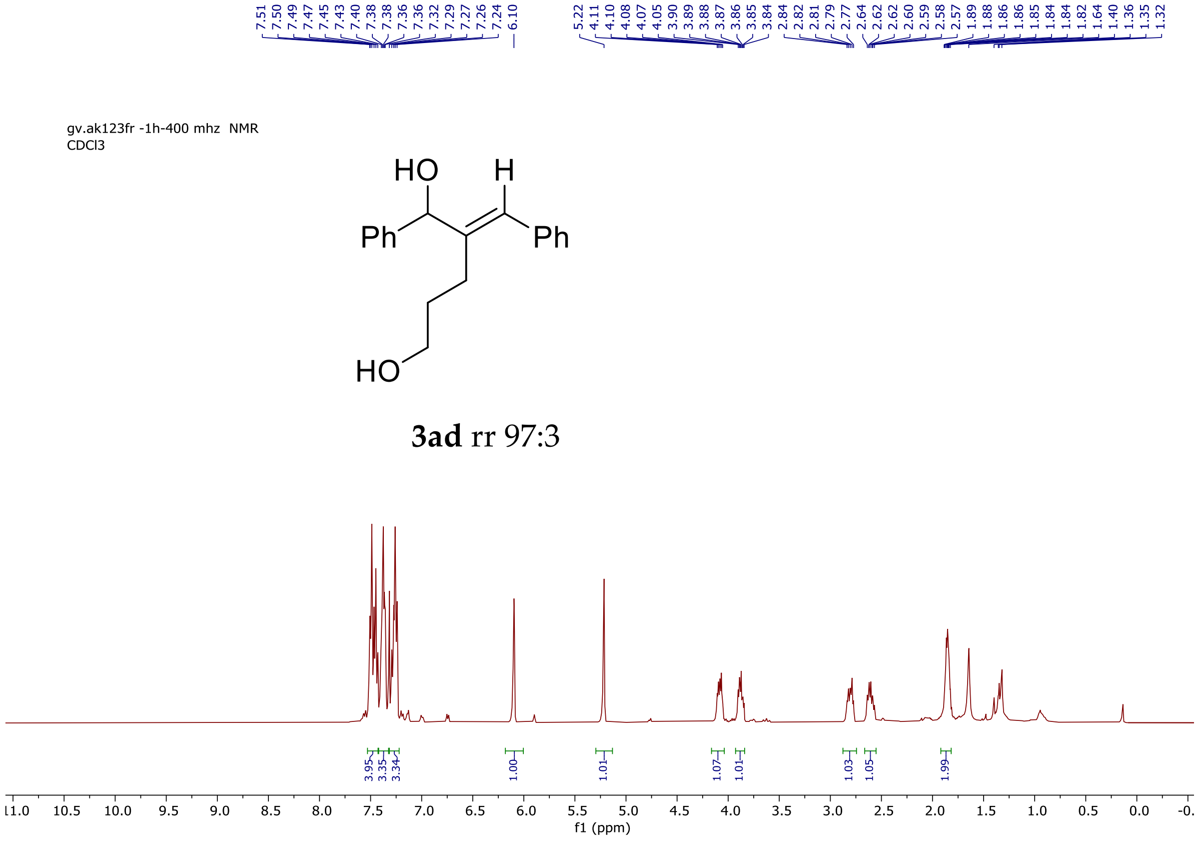
3ab rr 97:3


7.59
7.57
7.43
7.42
7.41
7.40
7.38
7.36
7.34
7.34
7.32
7.32
7.28
7.28
7.27
7.27
6.76
5.24
1.68
0.97
0.95
0.93
0.67
0.66
0.65
0.63
gv.ak118p-1h-400mhz
CDCl3
Et3SiO
H
Ph
CF3
3ac
1.98
7.83
1.05
0.93
3.20
8.78
6.12
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

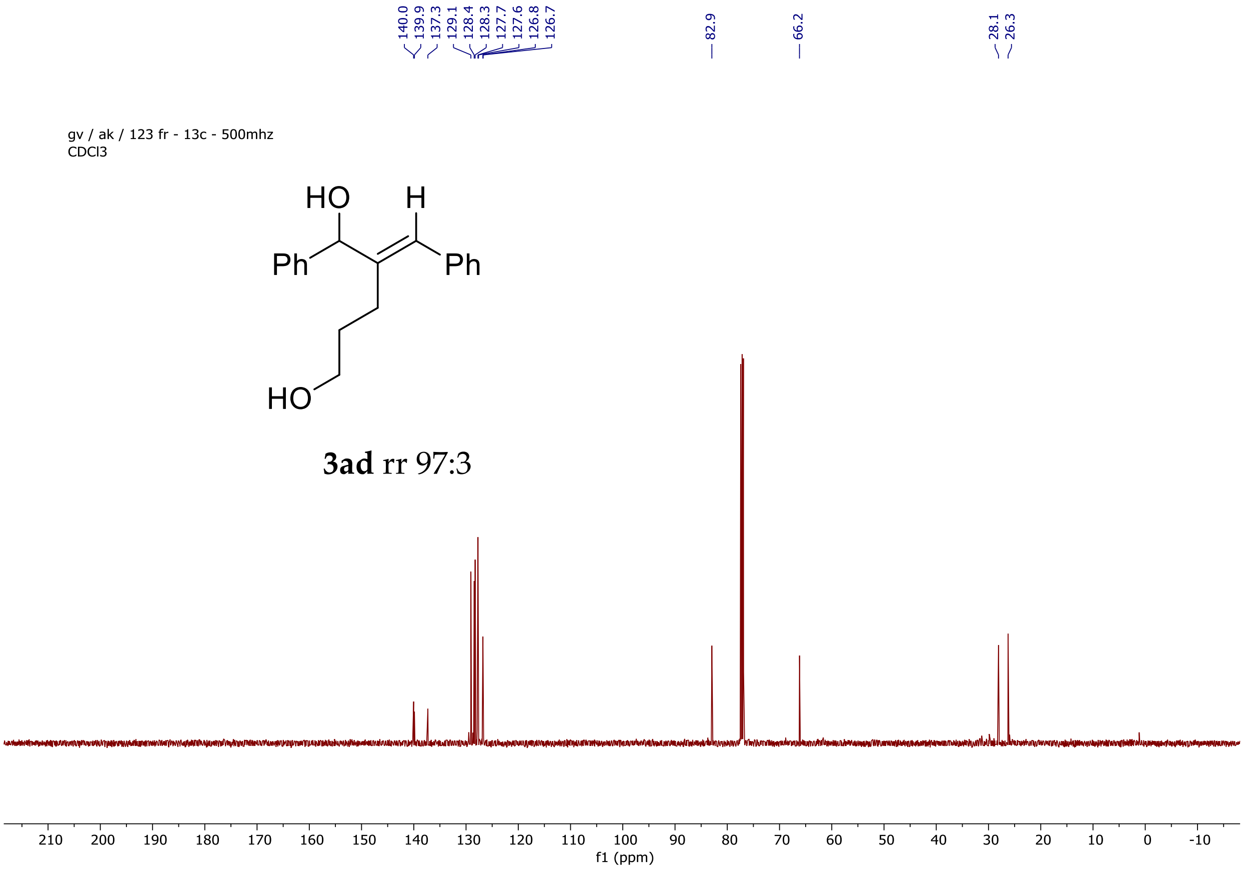

143.4
143.1
141.7
129.3
128.2
127.3
126.4
125.2
125.1
124.1
79.8
13.7
7.0
5.0
gv.ak118p - 13c-400mhz
CDCl3
Et3SiO
H
Ph
CF3
3ac
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



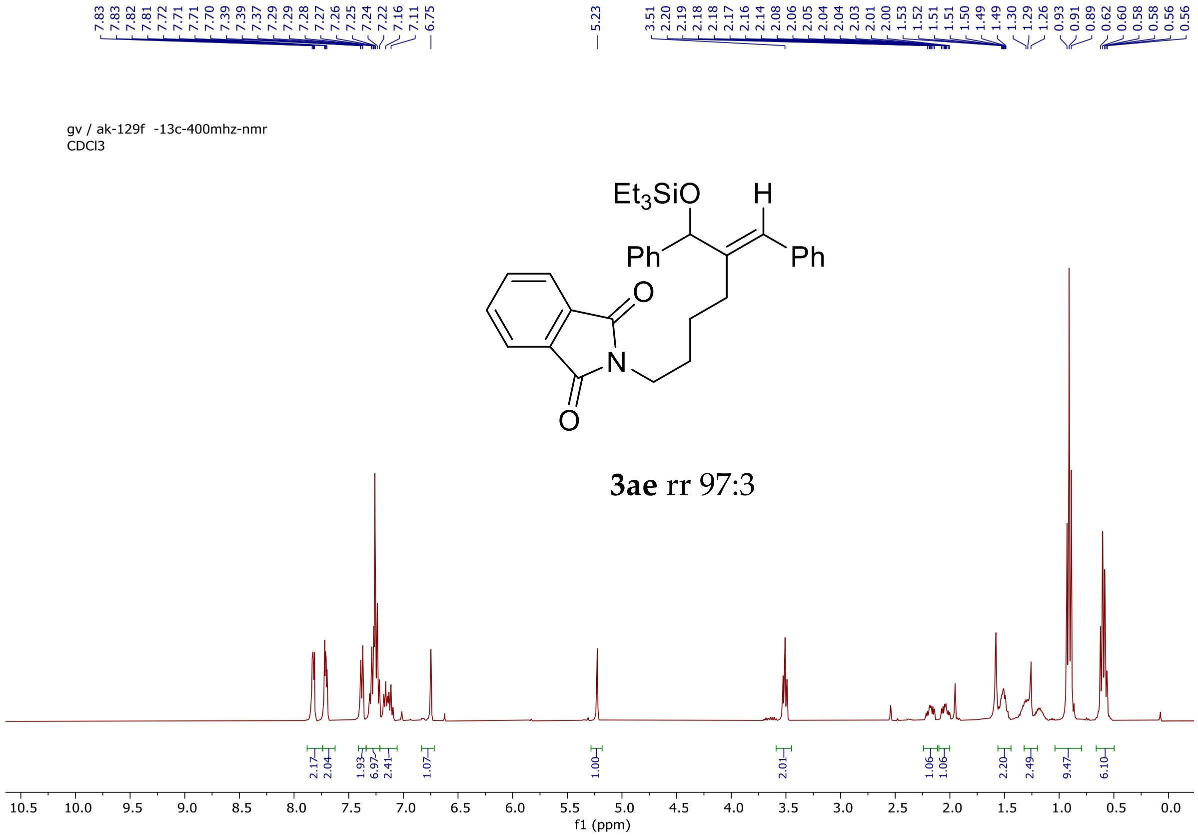
3ac rr 97:3



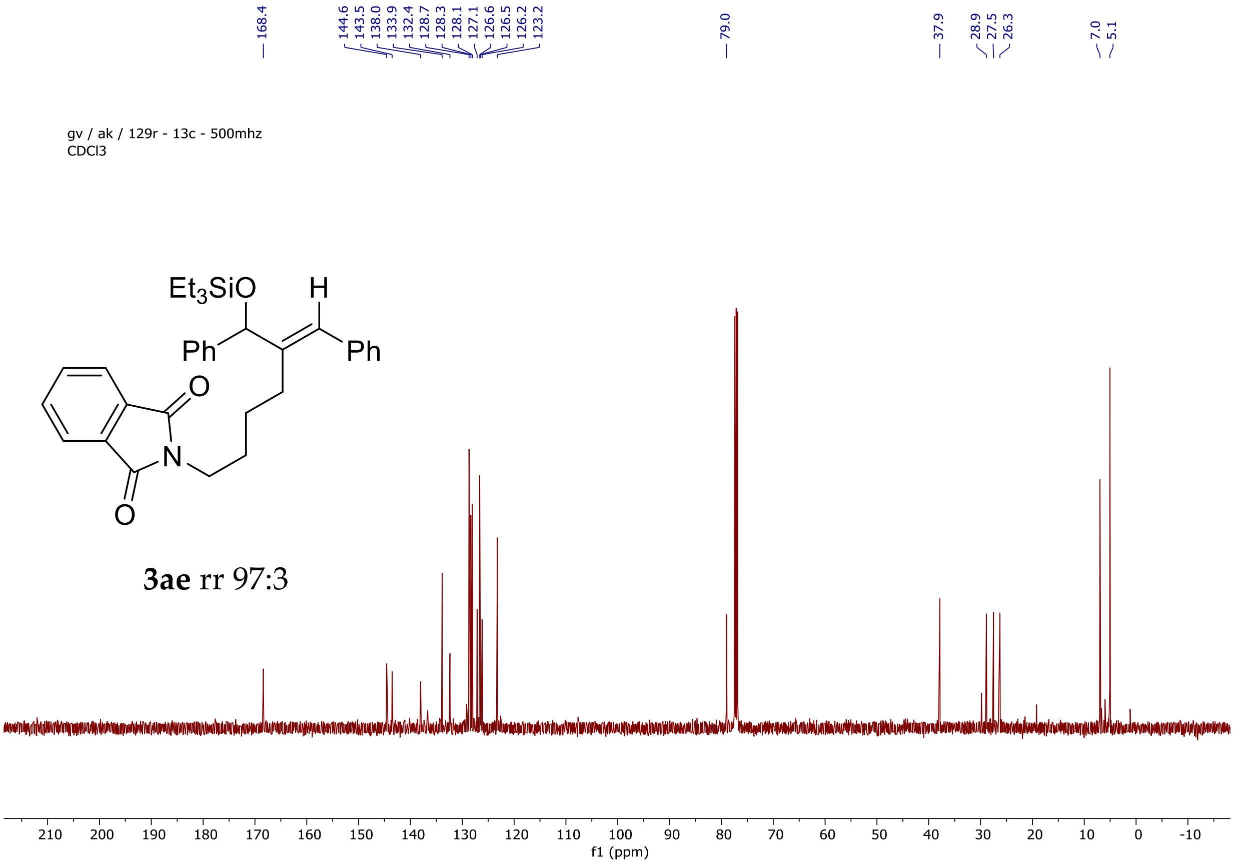
3ad rr 97:3



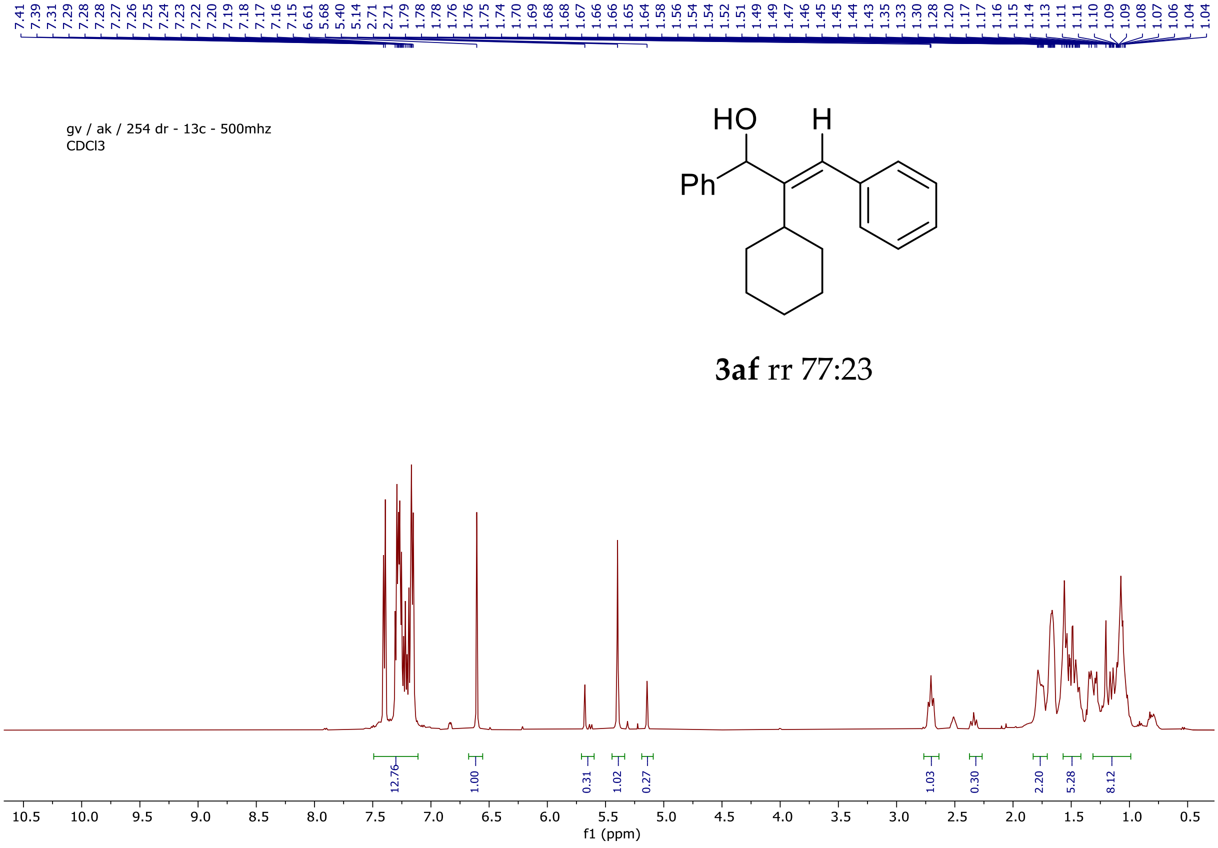
3ad rr 97:3



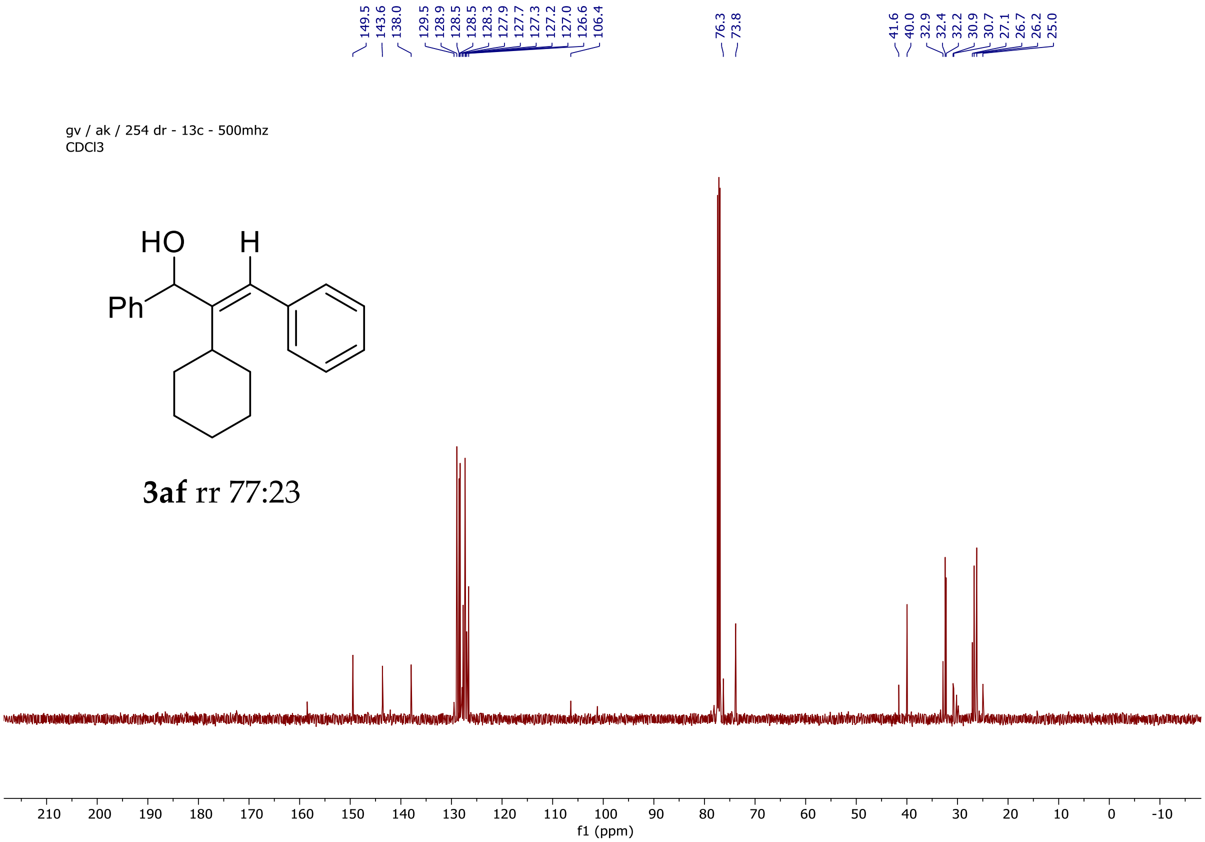
3ae rr 97:3



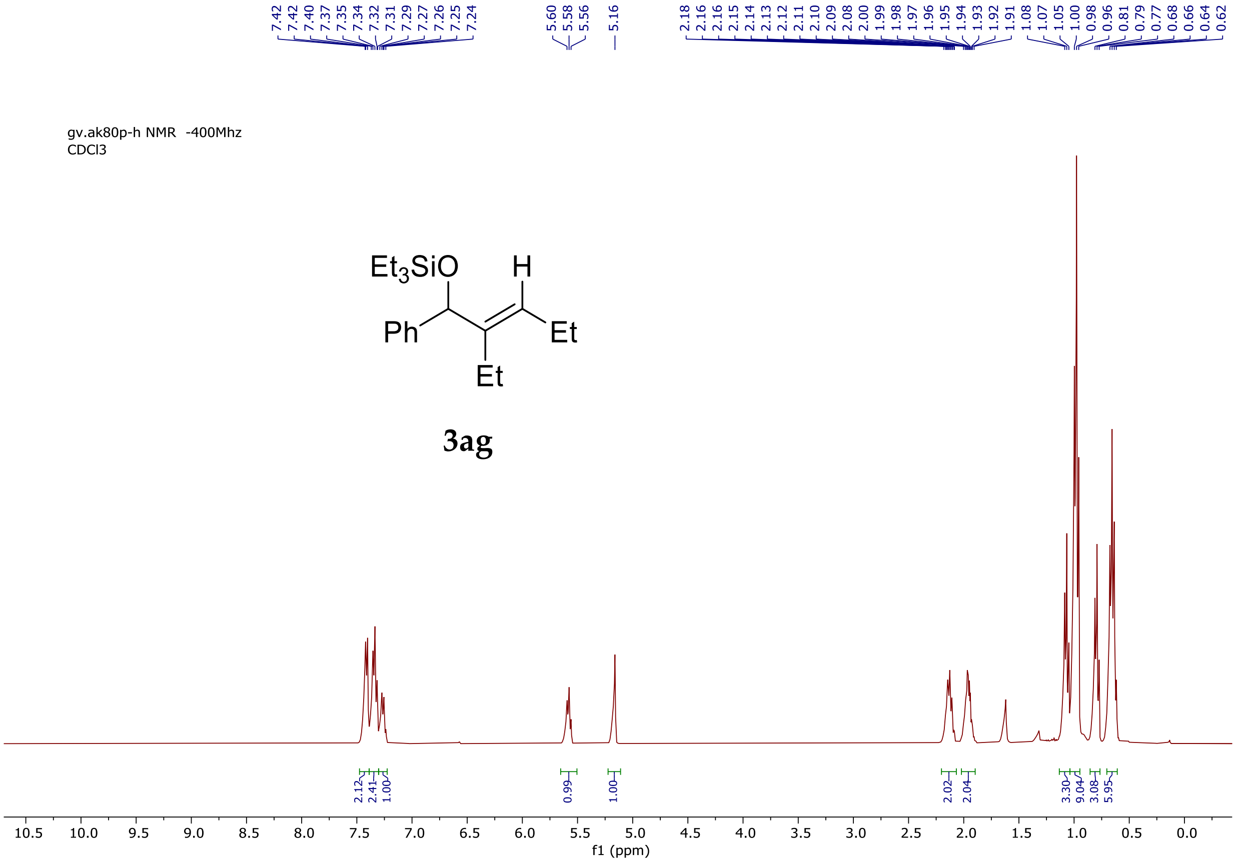
3ae rr 97:3



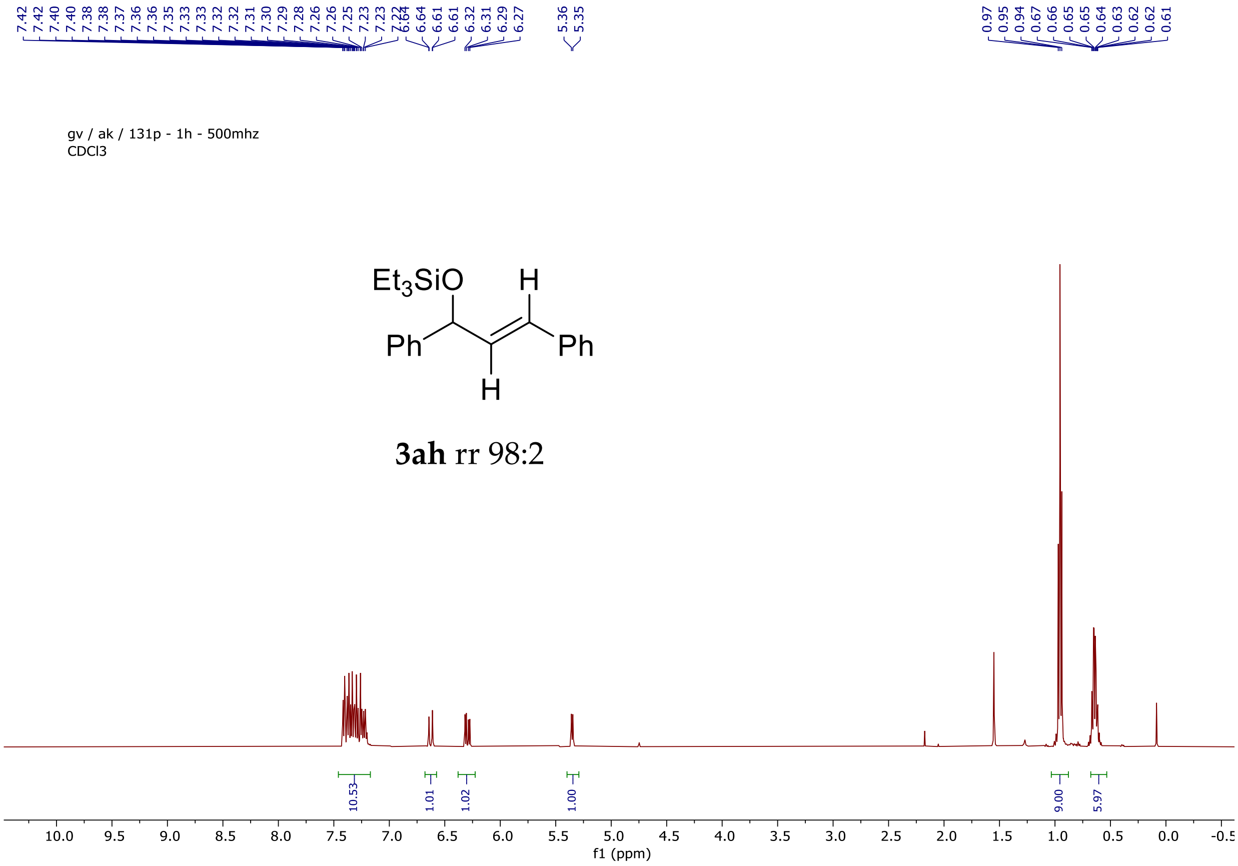
3af rr 77:23



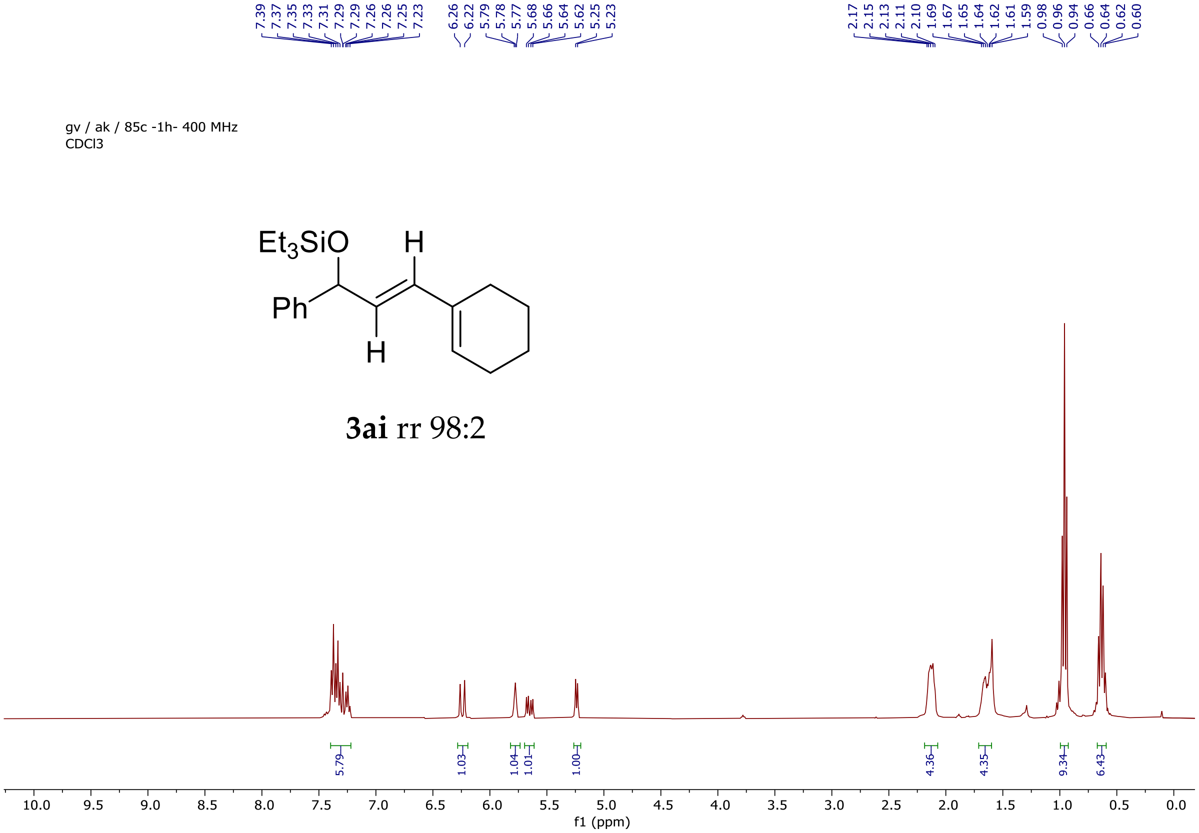
3af rr 77:23



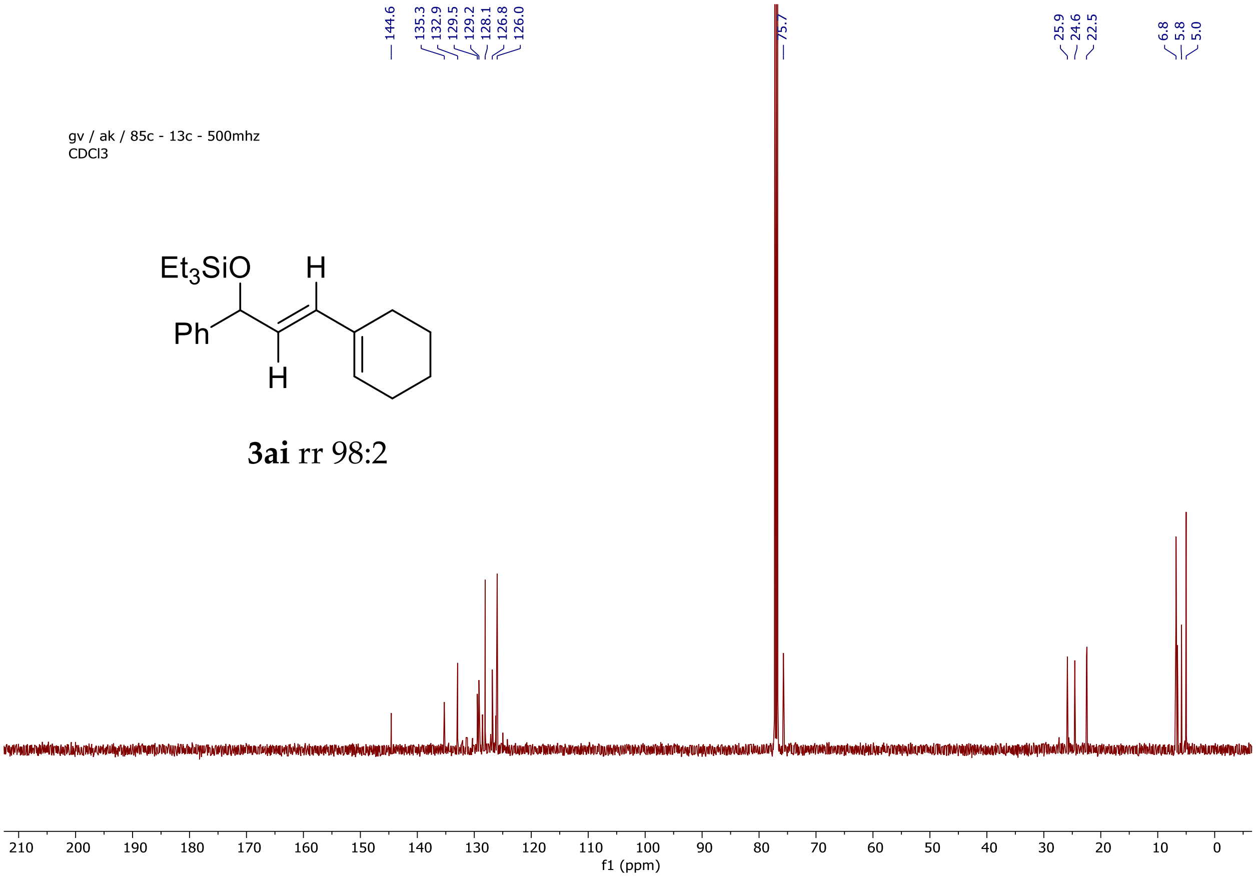
3ag



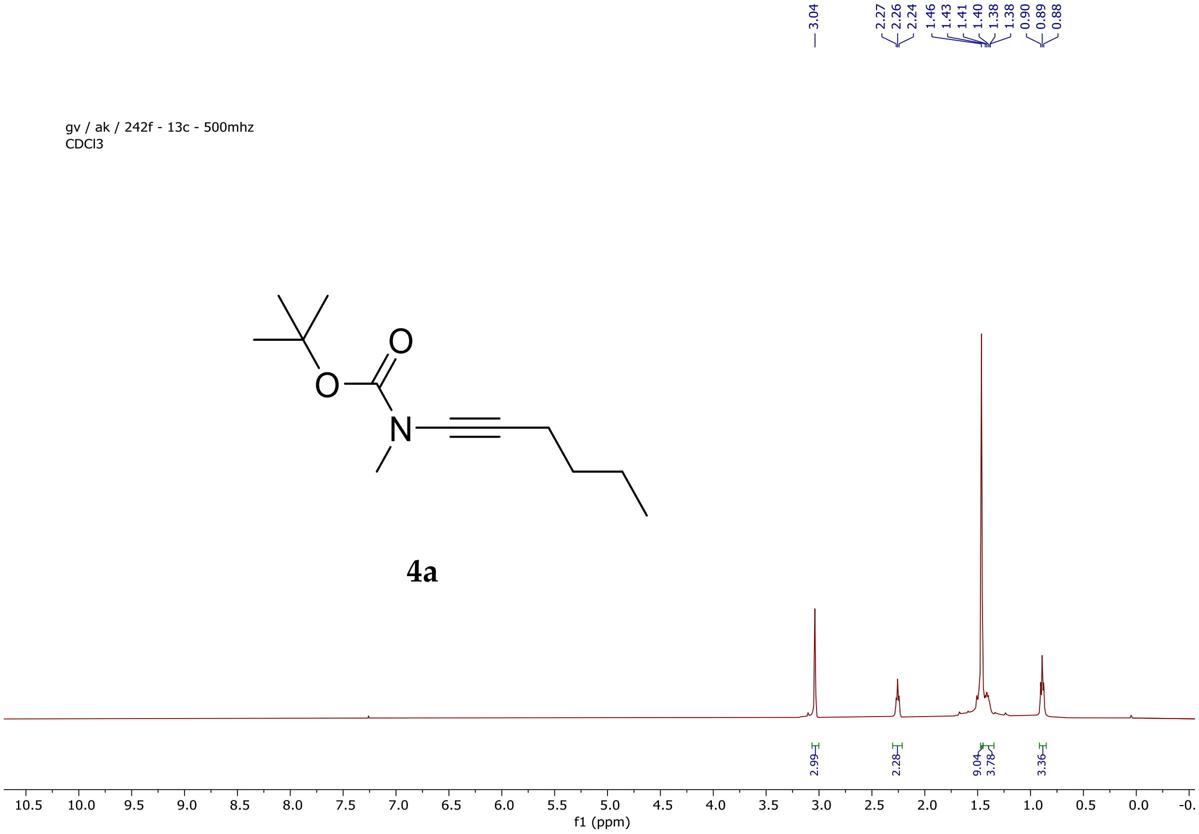
3ah rr 98:2



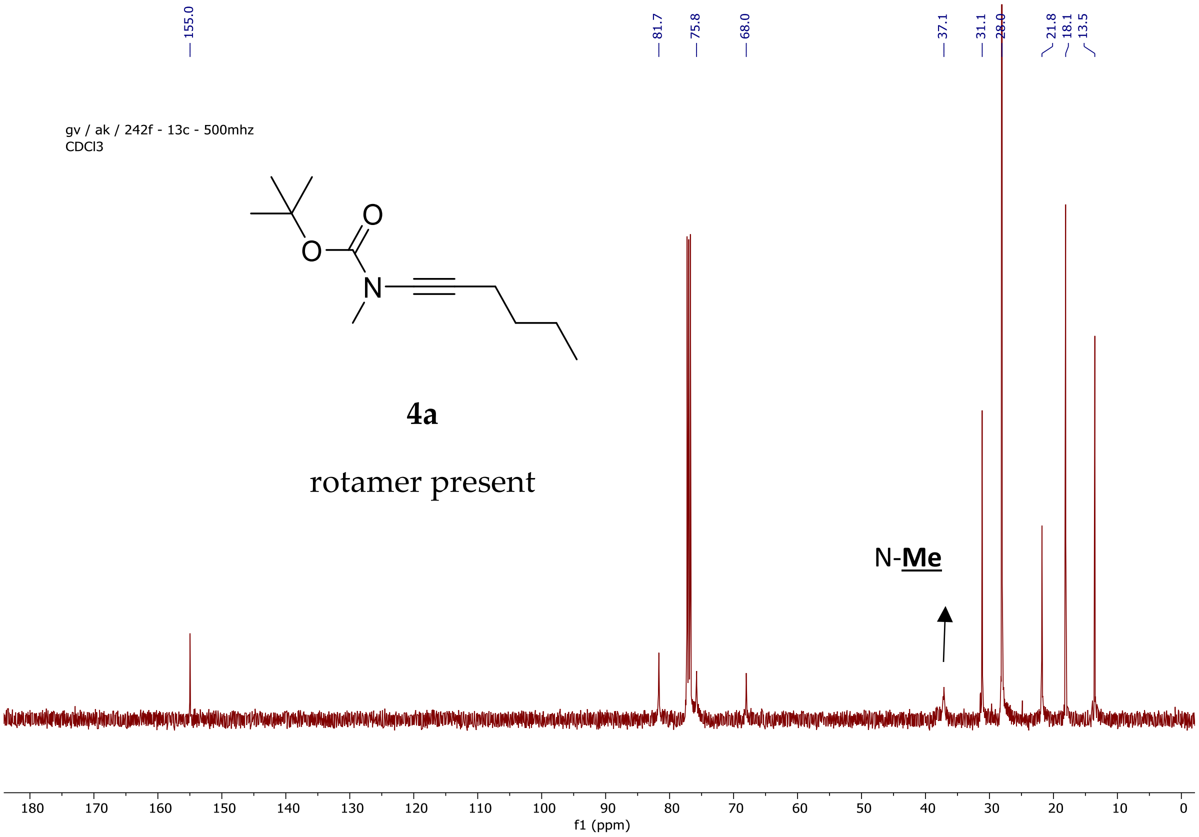
3ai rr 98:2


144.6
135.3
132.9
129.5
129.2
128.1
126.8
126.0
75.7
25.9
24.6
22.5
6.8
5.8
5.0
gv / ak / 85c - 13c - 500mhz
CDCl3
Et3SiO
H
Ph
H
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3ai rr 98:2

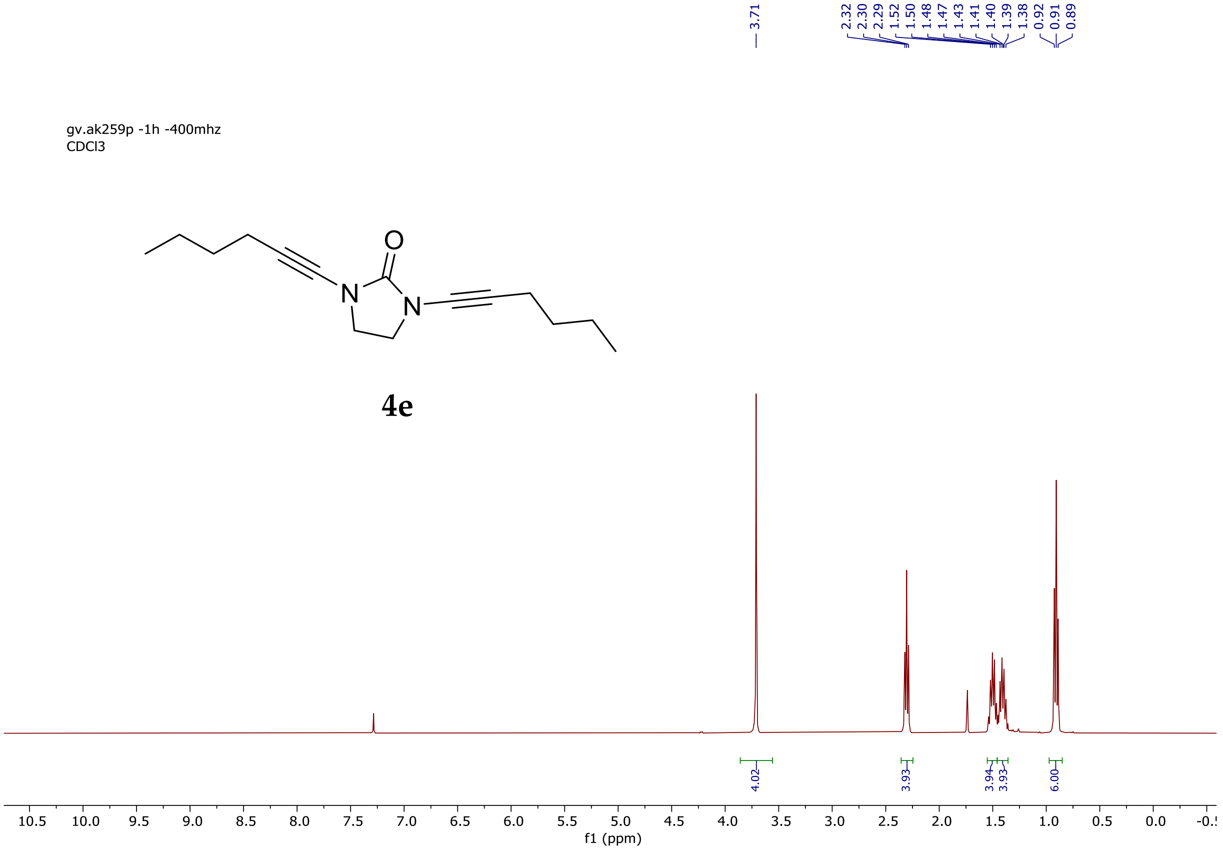

3.04
2.27
2.26
2.24
1.46
1.43
1.41
1.40
1.38
1.38
0.90
0.89
0.88
gv / ak / 242f - 13c - 500mhz
CDCl3
O
O
N
2.99
2.28
9.04
3.78
3.36
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

4a

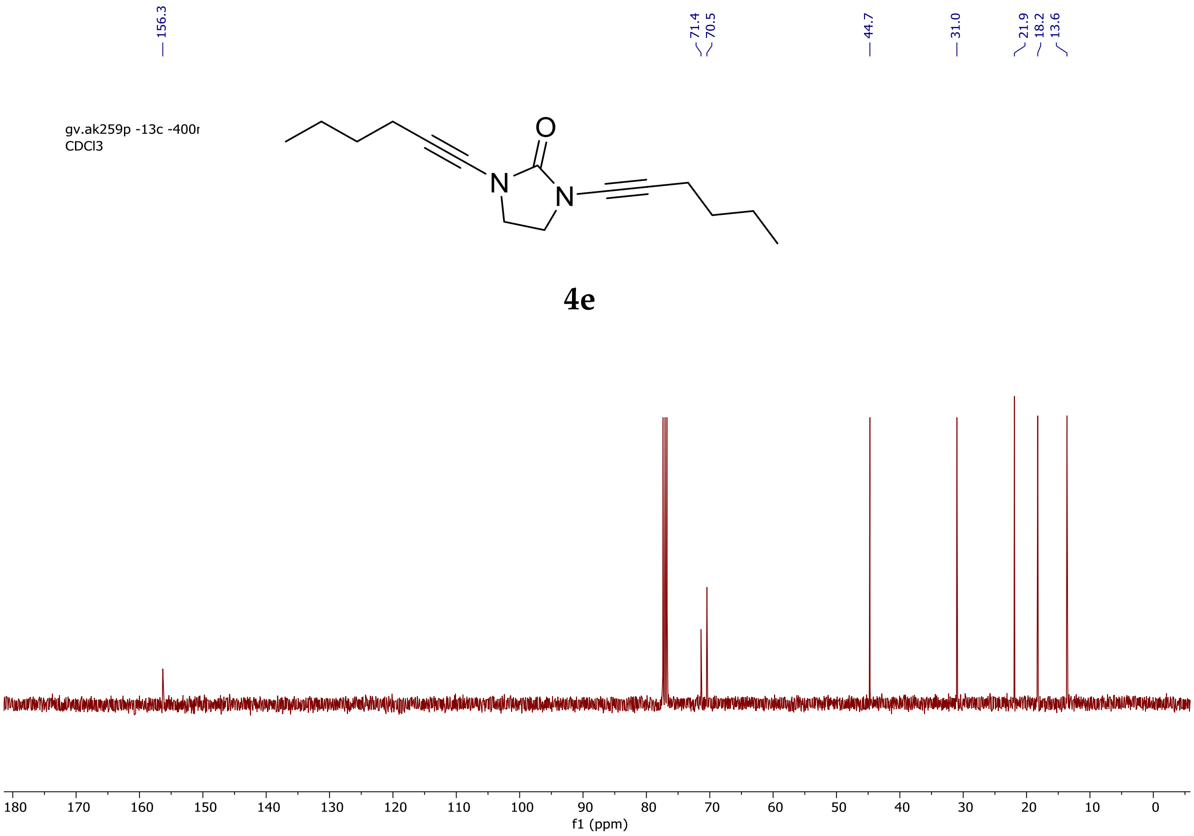


4a

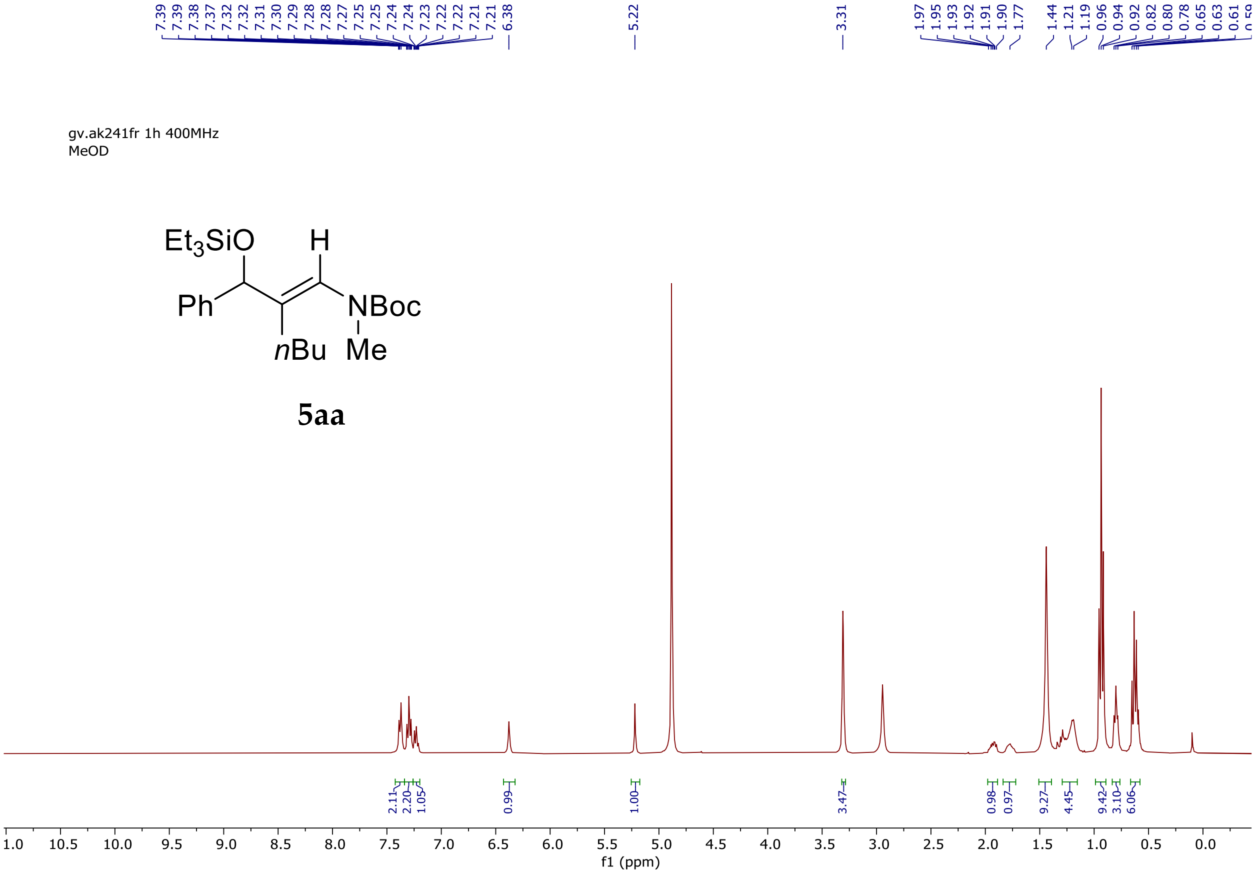
rotamer present



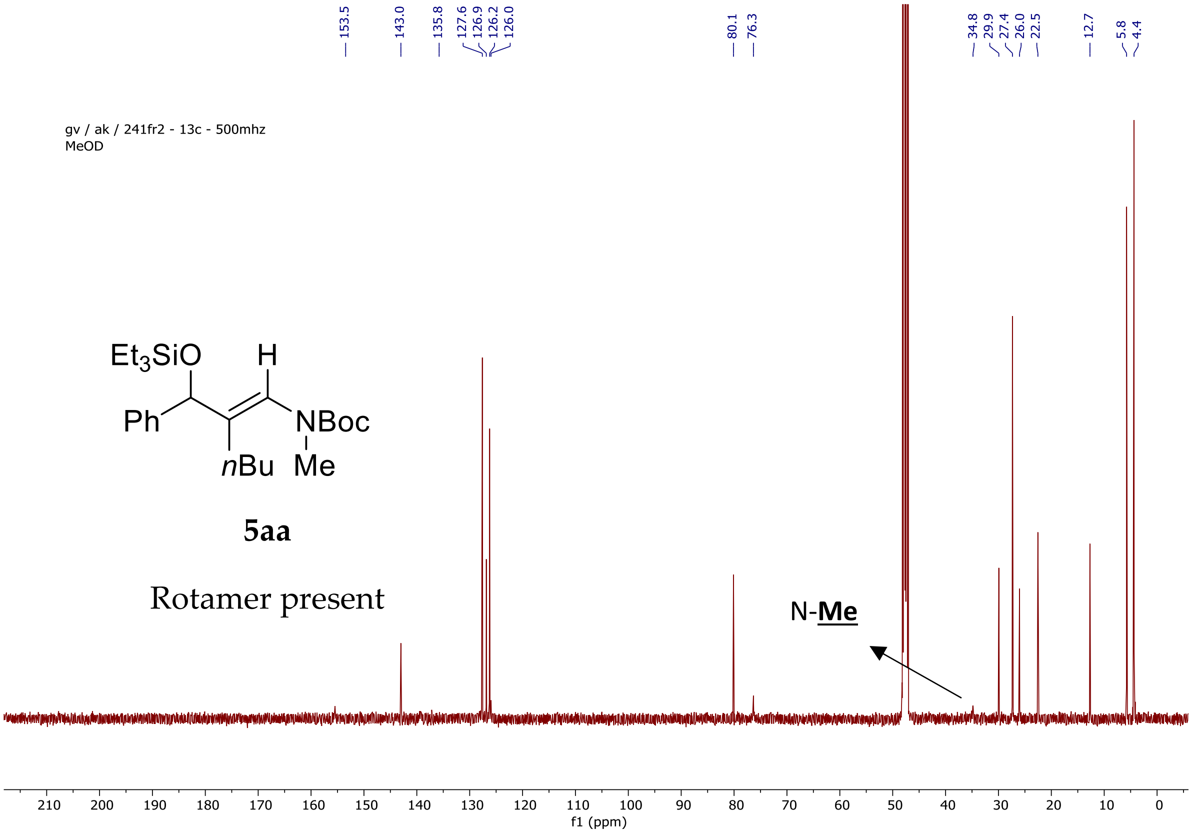
4e

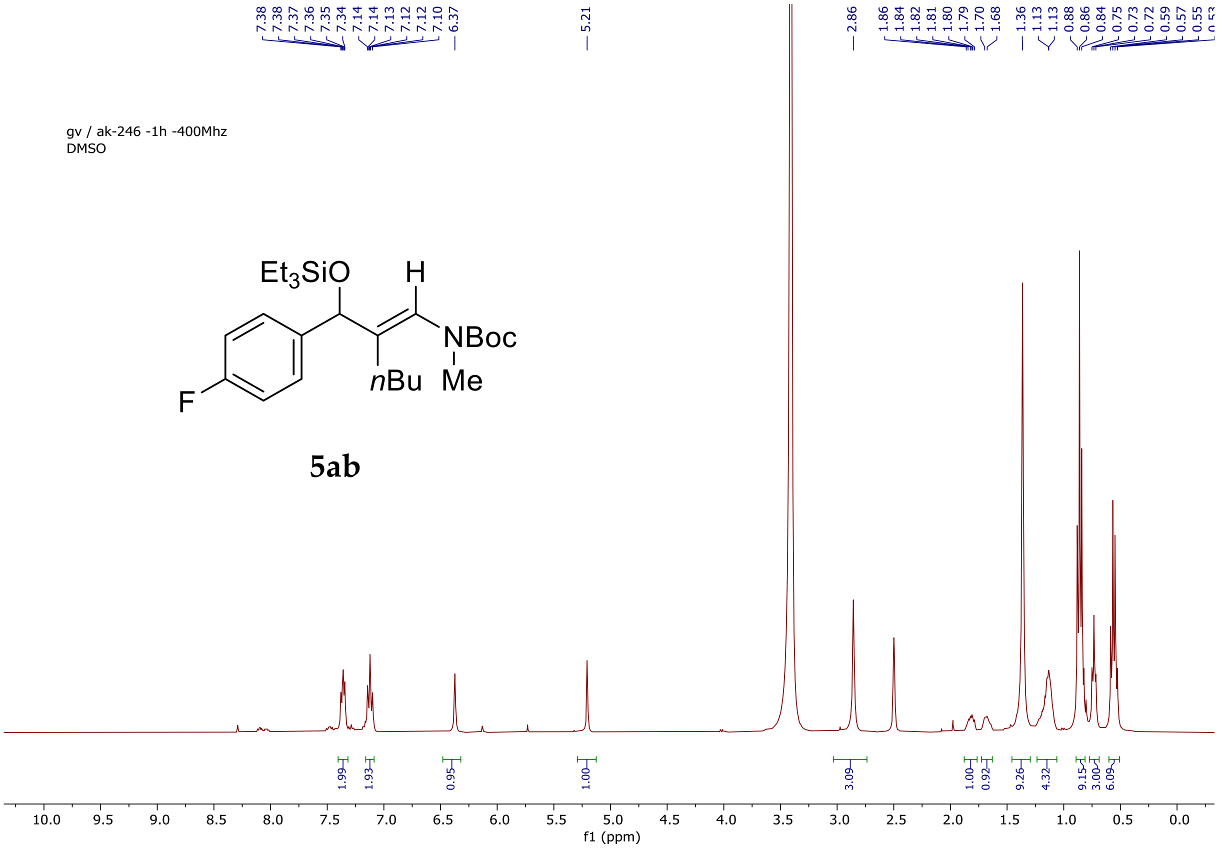

156.3
71.4
70.5
44.7
31.0
21.9
18.2
13.6
gv.ak259p -13c -400r
CDCl3
O
N
N
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

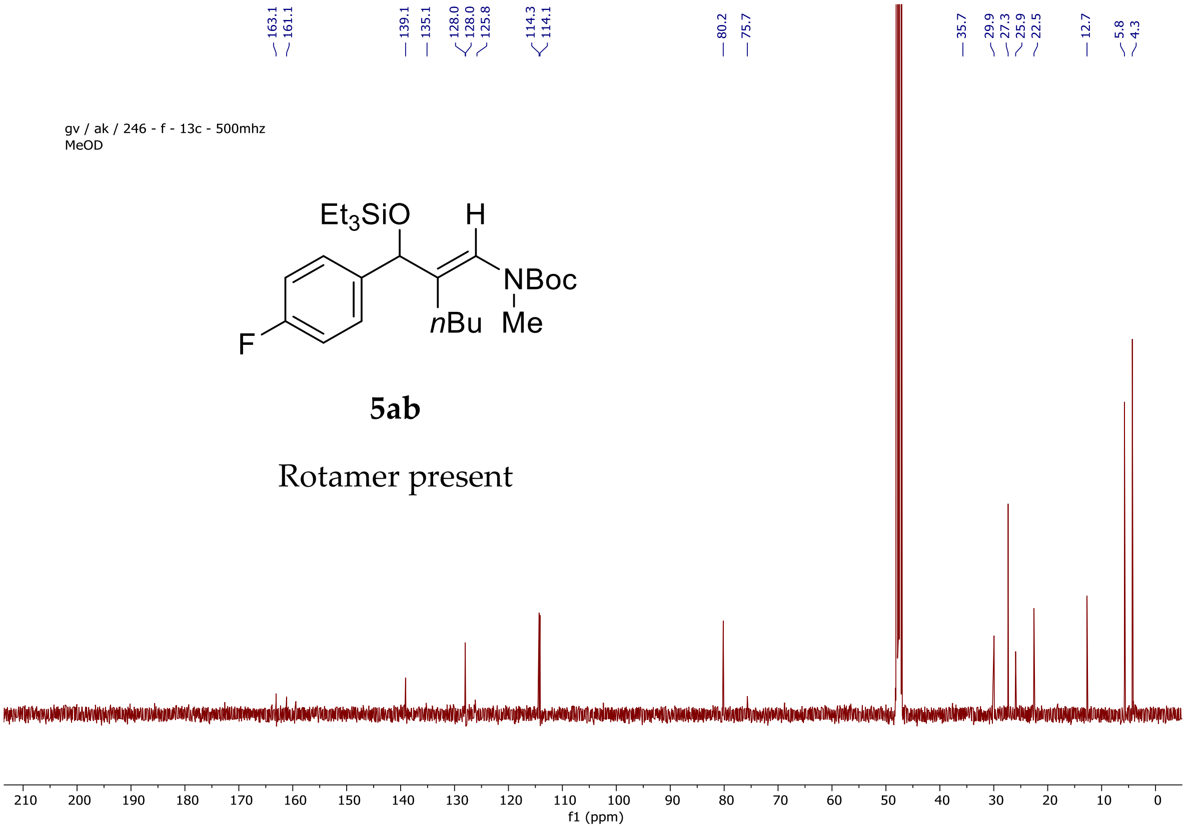
4e


7.39
7.39
7.38
7.37
7.32
7.32
7.31
7.30
7.29
7.28
7.28
7.27
7.25
7.24
7.24
7.23
7.22
7.22
7.21
7.21
6.38
5.22
3.31
1.97
1.95
1.93
1.92
1.91
1.90
1.77
1.44
1.21
1.19
0.96
0.94
0.92
0.82
0.80
0.78
0.65
0.63
0.61
gv.ak241fr 1h 400MHz
MeOD
Et3SiO
H
Ph
NBoc
nBu
Me
2.11
2.20
1.05
0.99
1.00
3.47
0.98
0.97
9.27
4.45
9.42
3.10
6.06
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

5aa

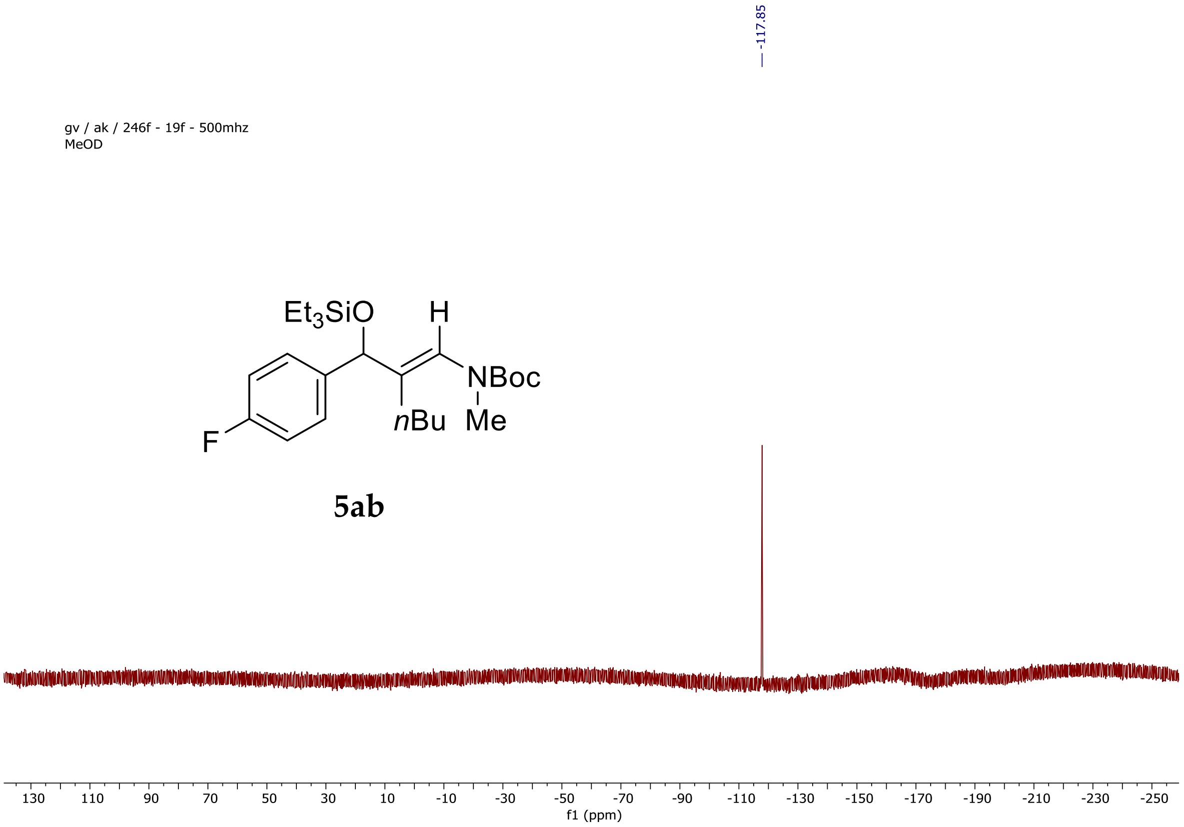

153.5
143.0
135.8
127.6
126.9
126.2
126.0
80.1
76.3
34.8
29.9
27.4
26.0
22.5
12.7
5.8
4.4
gv / ak / 241fr2 - 13c - 500mhz
MeOD
Et3SiO
H
Ph
NBoc
nBu
Me
5aa
Rotamer present
N-Me
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.38
7.38
7.37
7.36
7.35
7.34
7.14
7.14
7.13
7.12
7.12
7.10
6.37
5.21
2.86
1.86
1.84
1.82
1.81
1.80
1.79
1.70
1.68
1.36
1.13
1.13
0.88
0.86
0.84
0.75
0.73
0.72
0.59
0.57
0.55
gv / ak-246 -1h -400Mhz
DMSO
Et3SiO
H
NBoc
F
nBu
Me
5ab
1.99
1.93
0.95
1.00
3.09
1.00
0.92
9.26
4.32
9.15
3.00
6.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

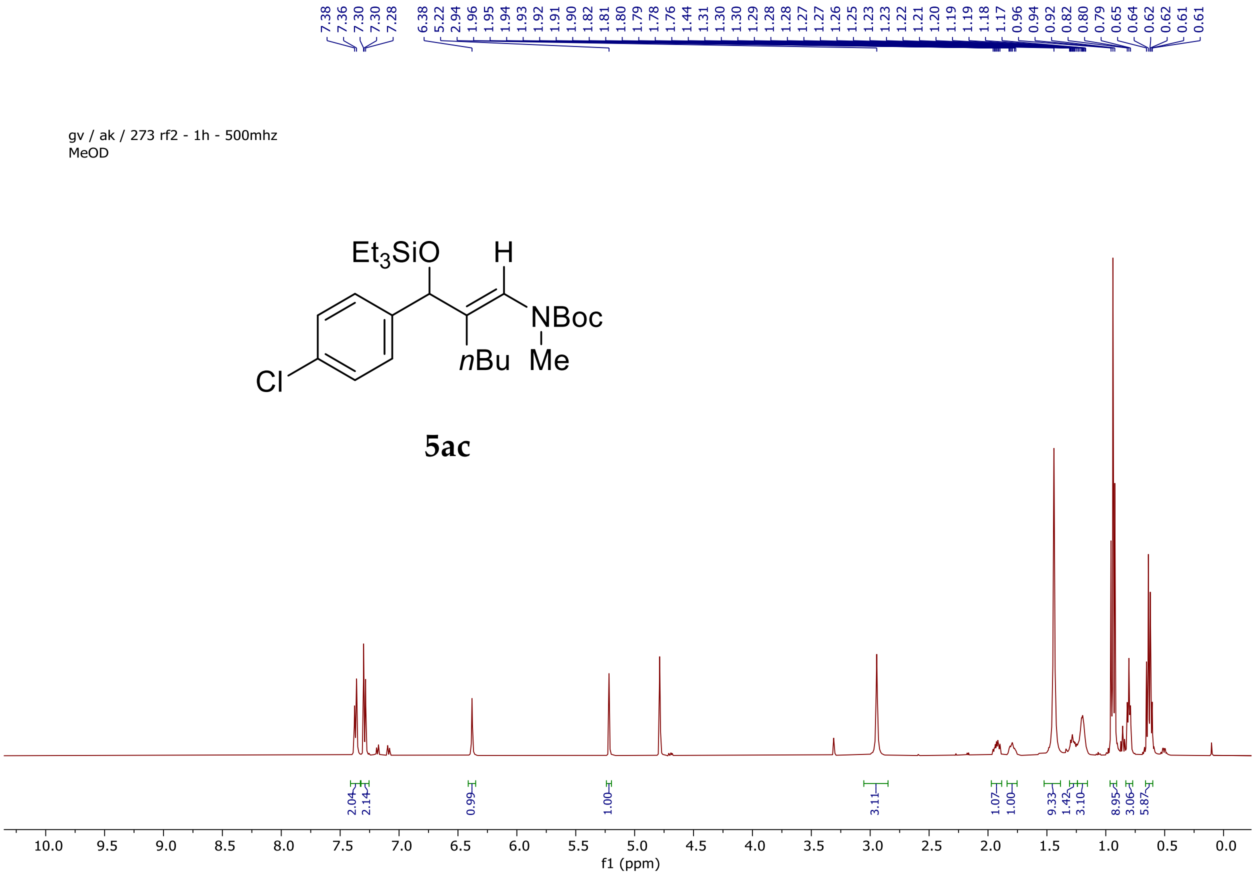


5ab

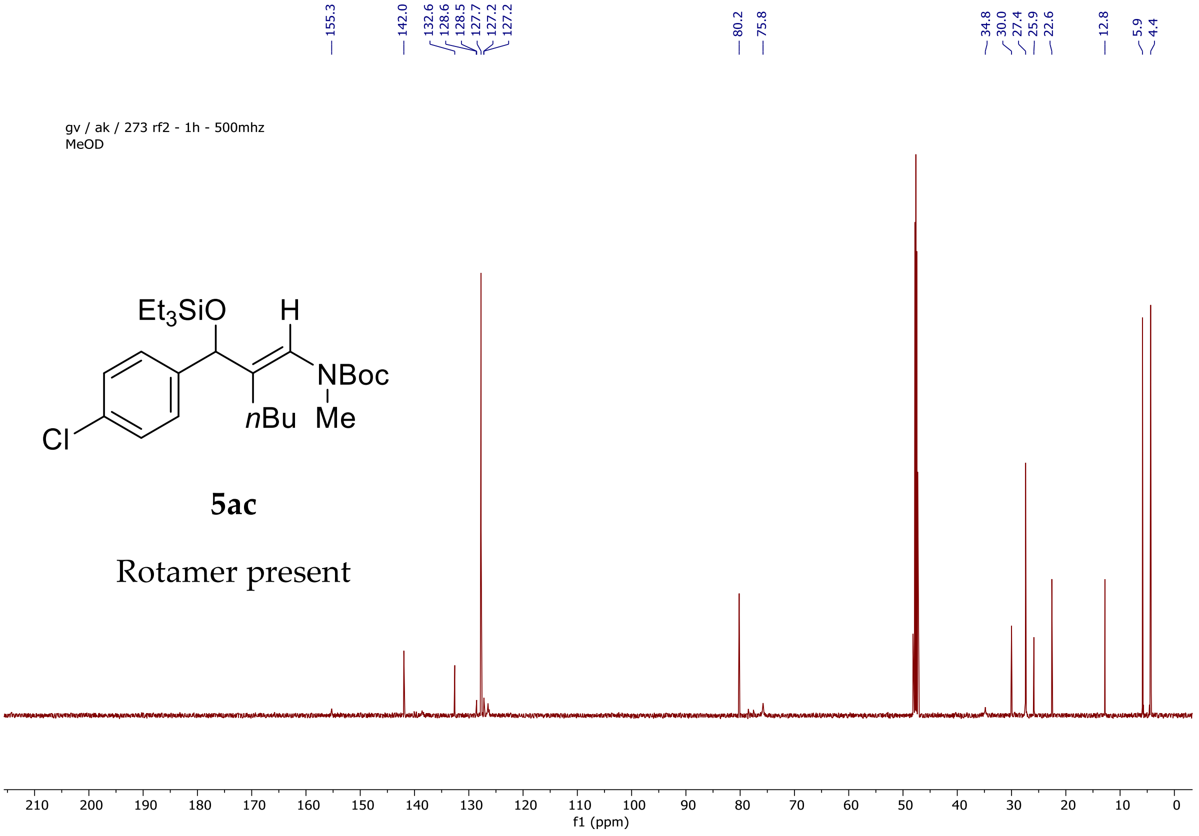
Rotamer present



5ab

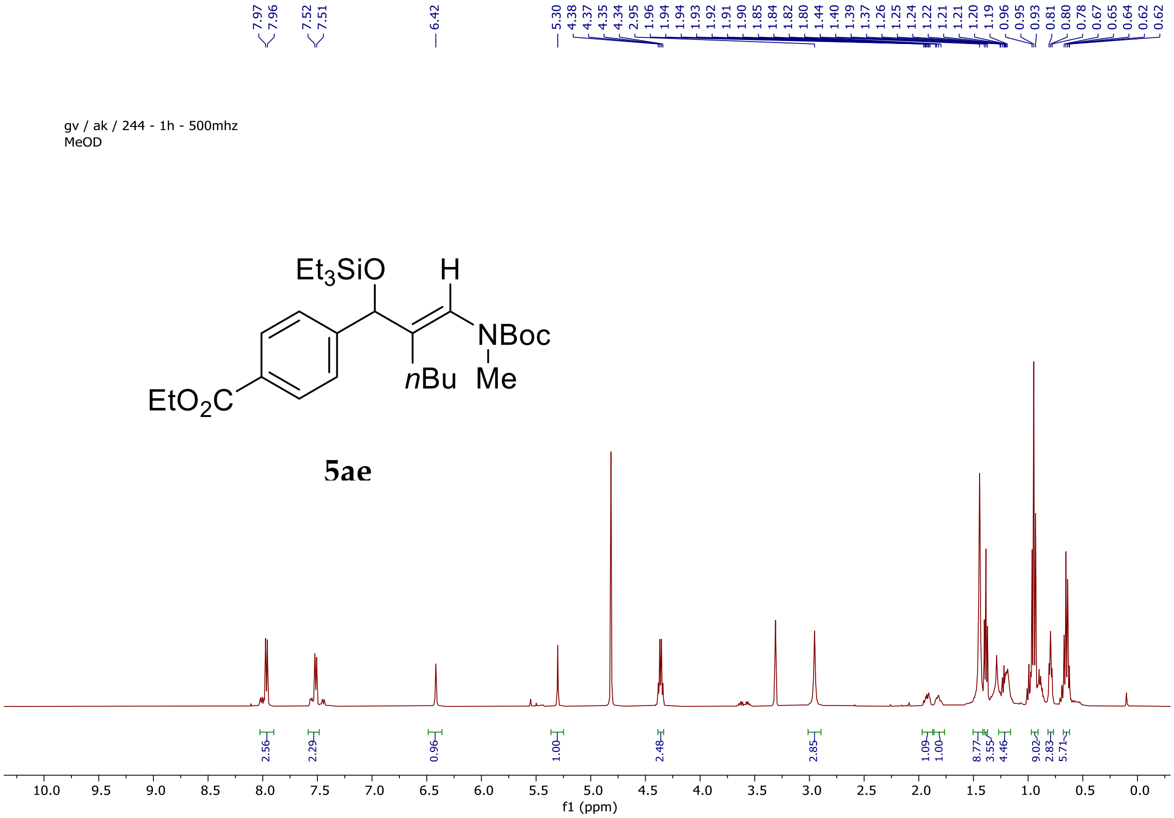


5ac

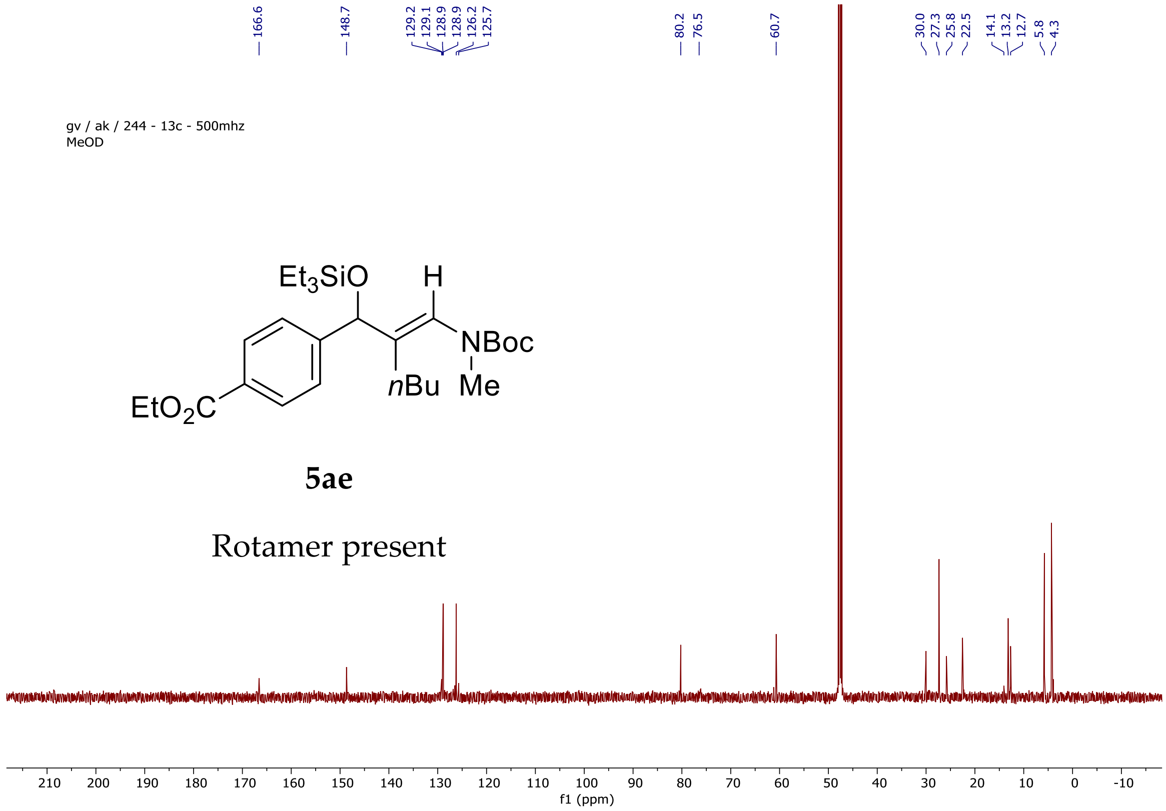


5ac

Rotamer present

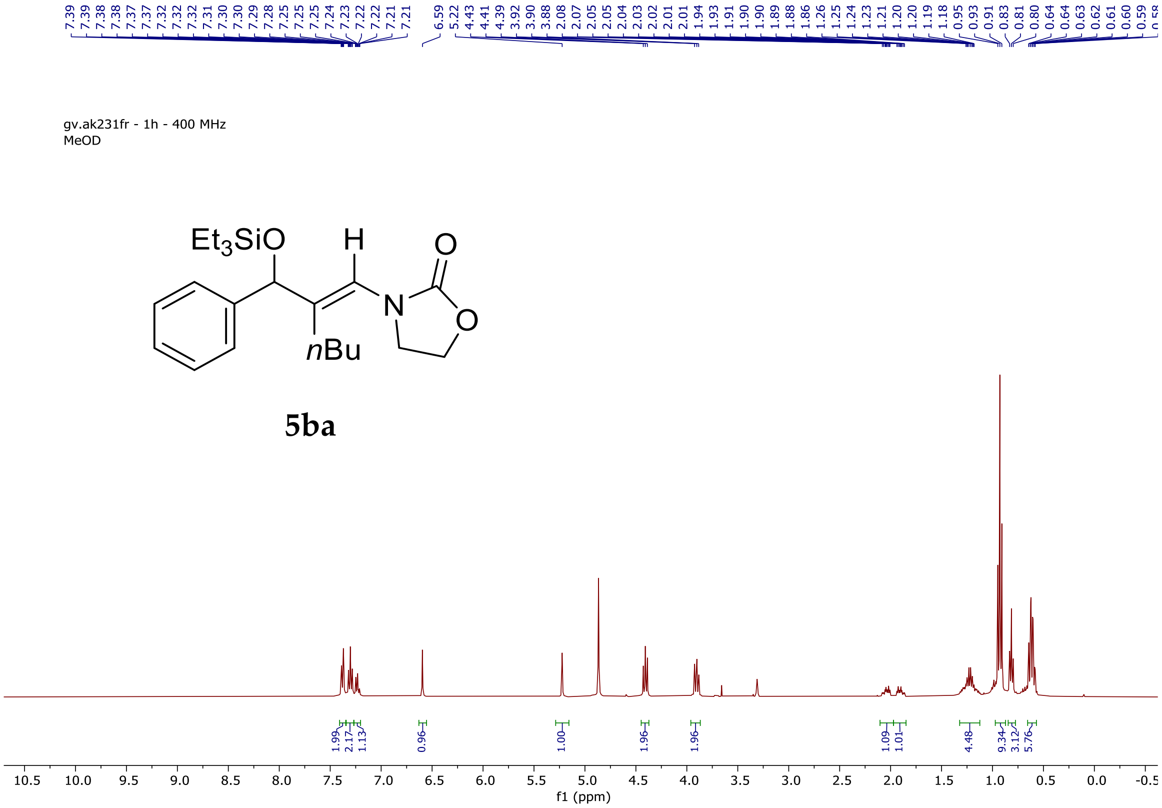


5ae

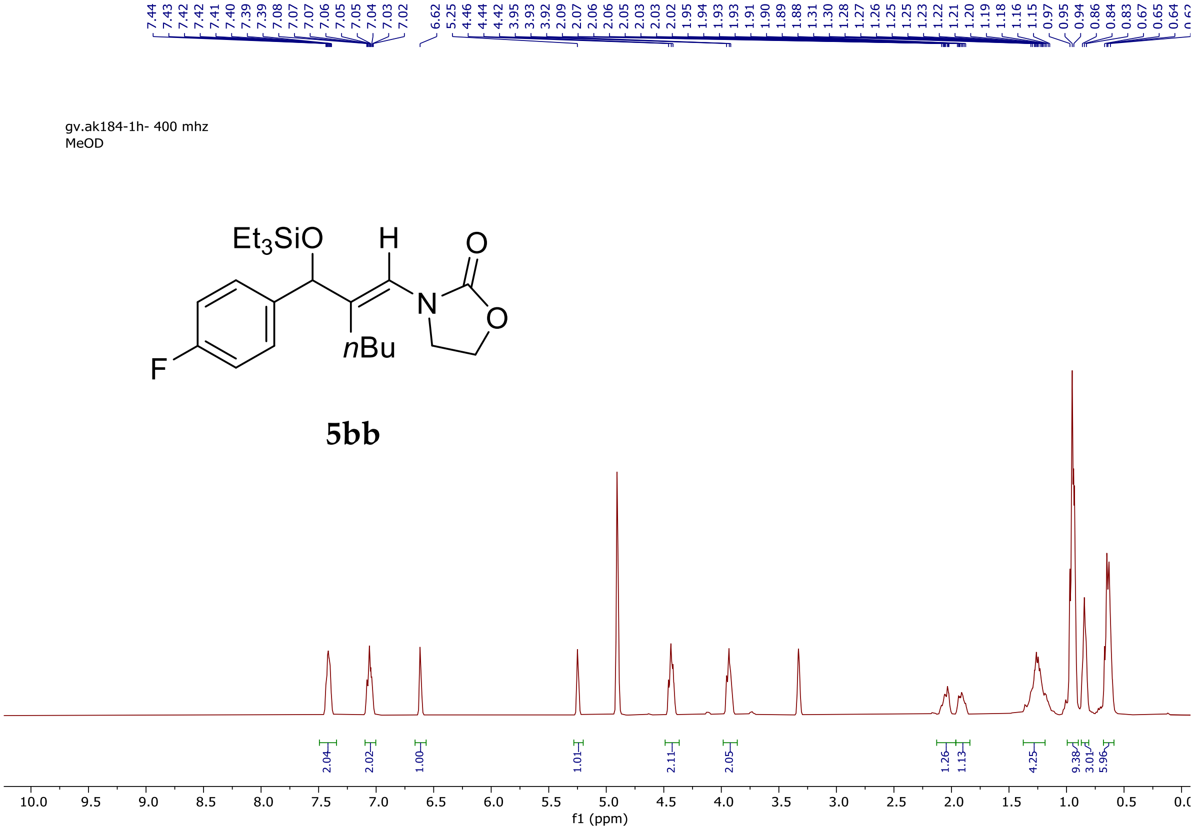


5ae

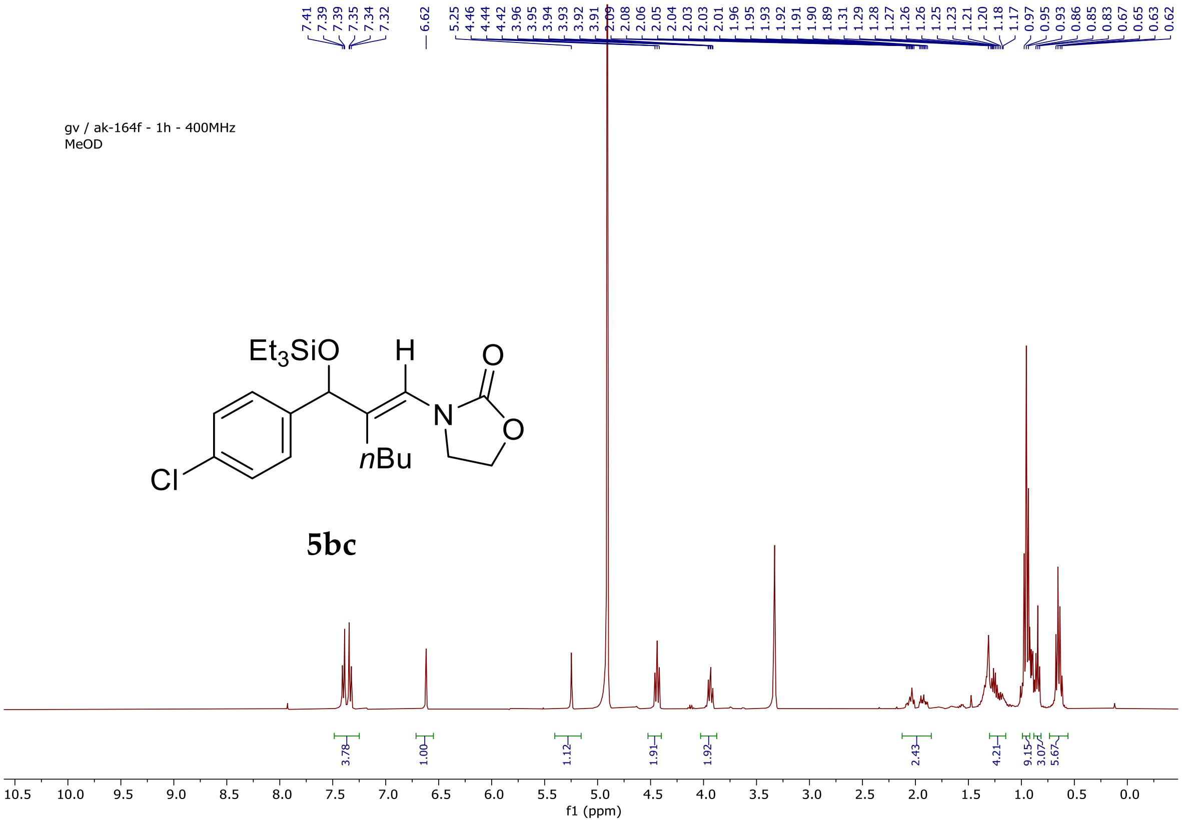
Rotamer present


7.39 7.39 7.38 7.38 7.37 7.37 7.32 7.32 7.32 7.31 7.30 7.30 7.29 7.28 7.25 7.25 7.25 7.24 7.23 7.22 7.22 7.21 7.21 6.59 5.22 4.43 4.41 4.39 3.92 3.90 3.88 2.08 2.07 2.05 2.04 2.03 2.02 2.01 2.01 1.94 1.93 1.91 1.90 1.90 1.89 1.88 1.86 1.26 1.25 1.24 1.23 1.21 1.20 1.20 1.19 1.18 0.95 0.93 0.91 0.83 0.81 0.80 0.64 0.64 0.63 0.62 0.61 0.60 0.59 0.5
gv.ak231fr - 1h - 400 MHz
MeOD
Et3SiO
H
O
N
O
nBu
1.99 2.17 1.13 0.96 1.00 1.96 1.96 1.09 1.01 4.48 9.34 3.12 5.76
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

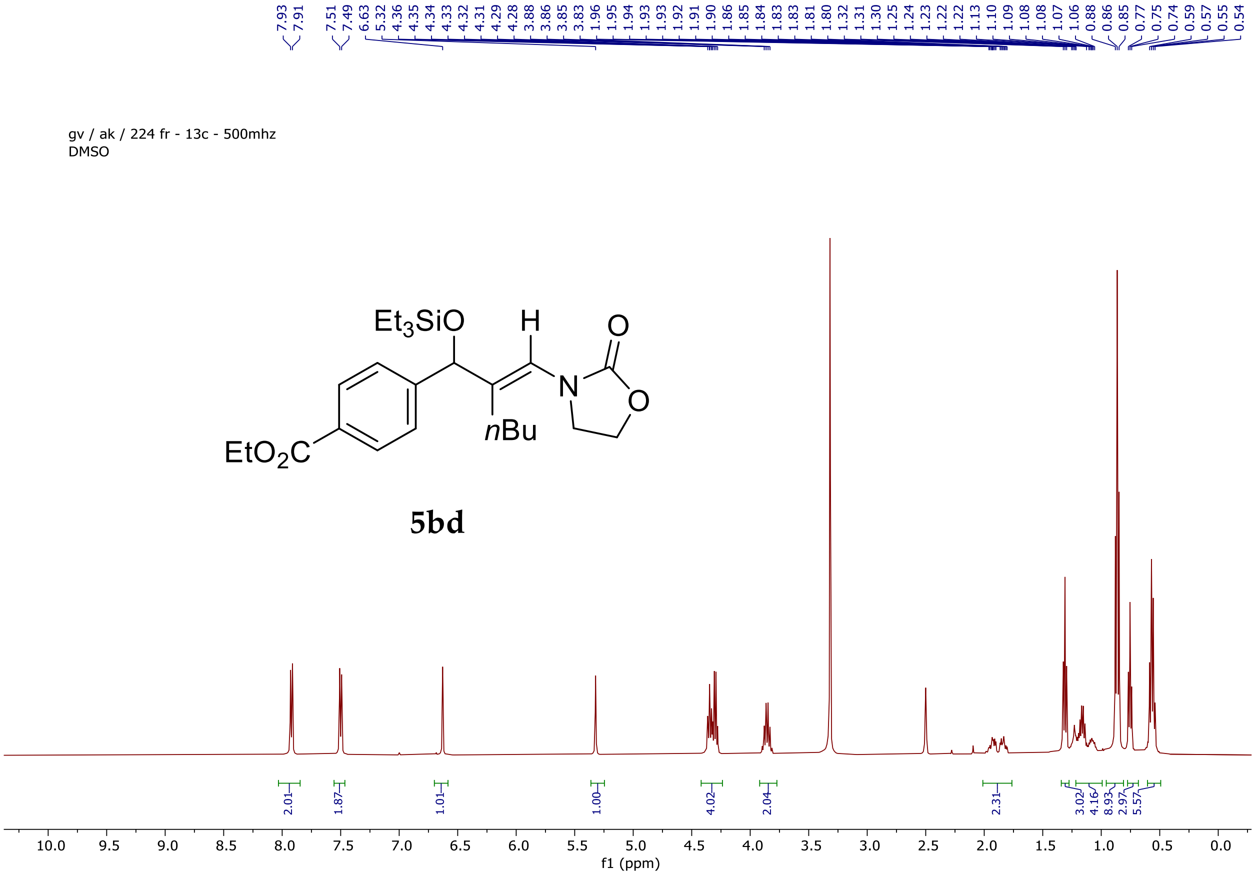
5ba


7.44 7.43 7.42 7.41 7.40 7.39 7.39 7.08 7.07 7.07 7.06 7.05 7.05 7.04 7.03 7.02 6.62 5.25 4.46 4.44 4.42 3.95 3.93 3.93 3.92 2.09 2.07 2.06 2.05 2.03 2.02 1.95 1.94 1.93 1.93 1.91 1.90 1.89 1.88 1.31 1.30 1.28 1.27 1.26 1.25 1.25 1.23 1.22 1.21 1.20 1.19 1.18 1.16 1.15 0.97 0.95 0.94 0.86 0.84 0.83 0.67 0.65 0.64
gv.ak184-1h- 400 mhz
MeOD
Et3SiO
H
O
N
O
F
nBu
2.04 2.02 1.00 1.01 2.11 2.05 1.26 1.13 4.25 9.38 3.01 5.96
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

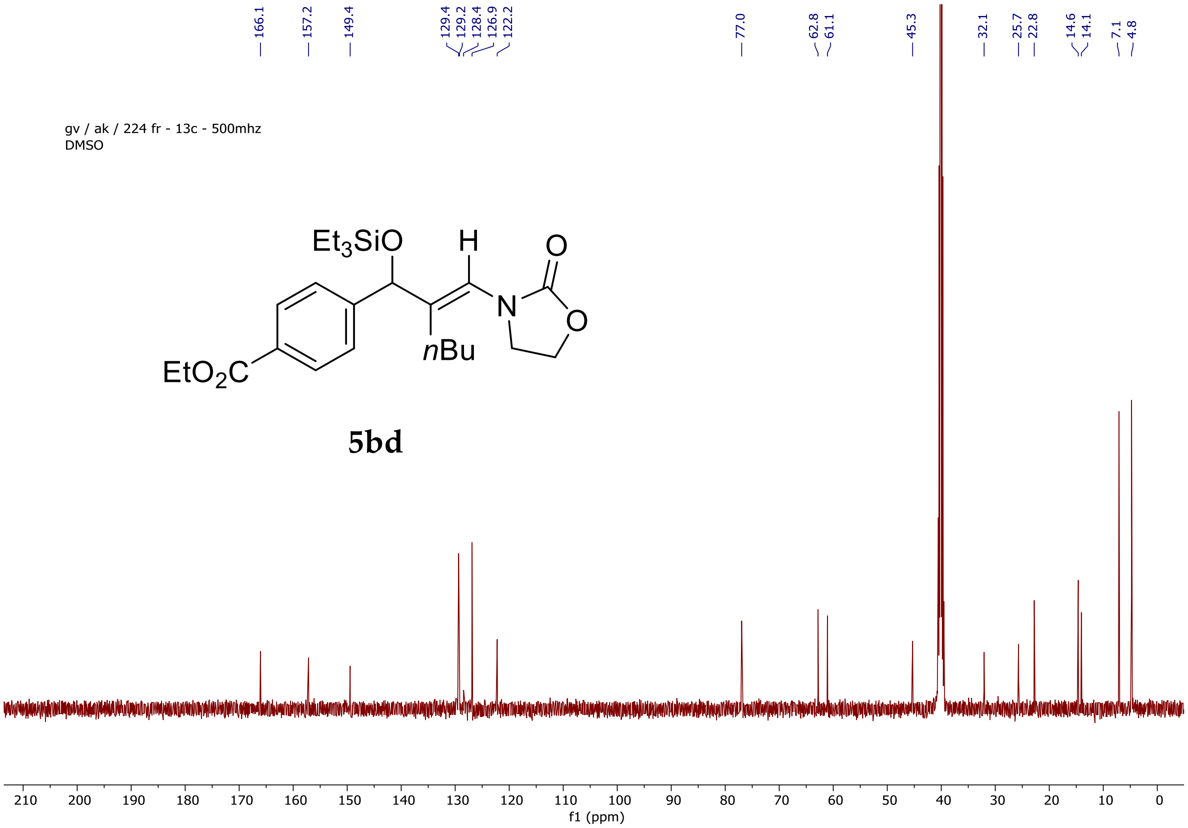
5bb


7.41
7.39
7.39
7.35
7.34
7.32
6.62
5.25
4.46
4.44
4.42
3.96
3.95
3.94
3.93
3.92
3.91
2.09
2.08
2.06
2.05
2.04
2.03
2.01
1.96
1.95
1.93
1.92
1.91
1.90
1.89
1.31
1.29
1.28
1.27
1.26
1.25
1.23
1.21
1.20
1.18
1.17
0.97
0.95
0.93
0.86
0.85
0.83
0.67
0.65
0.63
0.62
gv / ak-164f - 1h - 400MHz
MeOD
Et3SiO
H
O
N
O
nBu
Cl
3.78
1.00
1.12
1.91
1.92
2.43
4.21
9.15
3.07
5.67
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

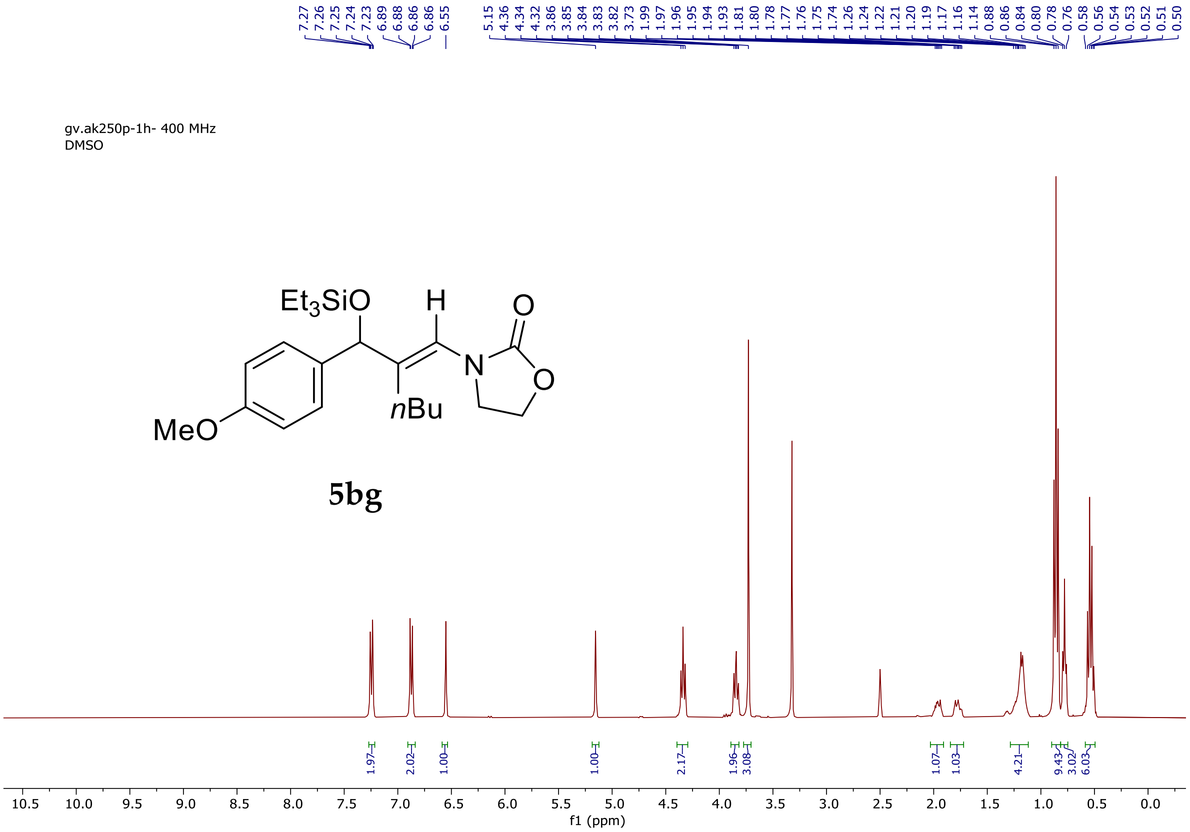
5bc


7.93
7.91
7.51
7.49
6.63
5.32
4.36
4.35
4.34
4.33
4.32
4.31
4.29
4.28
3.88
3.86
3.85
3.83
1.96
1.95
1.94
1.93
1.93
1.92
1.91
1.90
1.86
1.85
1.84
1.83
1.83
1.81
1.80
1.32
1.31
1.30
1.25
1.24
1.23
1.22
1.22
1.13
1.10
1.09
1.08
1.08
1.07
1.06
0.88
0.86
0.85
0.77
0.75
0.74
0.59
0.57
0.55
0.54
gv / ak / 224 fr - 13c - 500mhz
DMSO
Et3SiO
H
O
N
O
nBu
EtO2C
2.01
1.87
1.01
1.00
4.02
2.04
2.31
3.02
4.16
8.93
2.97
5.57
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

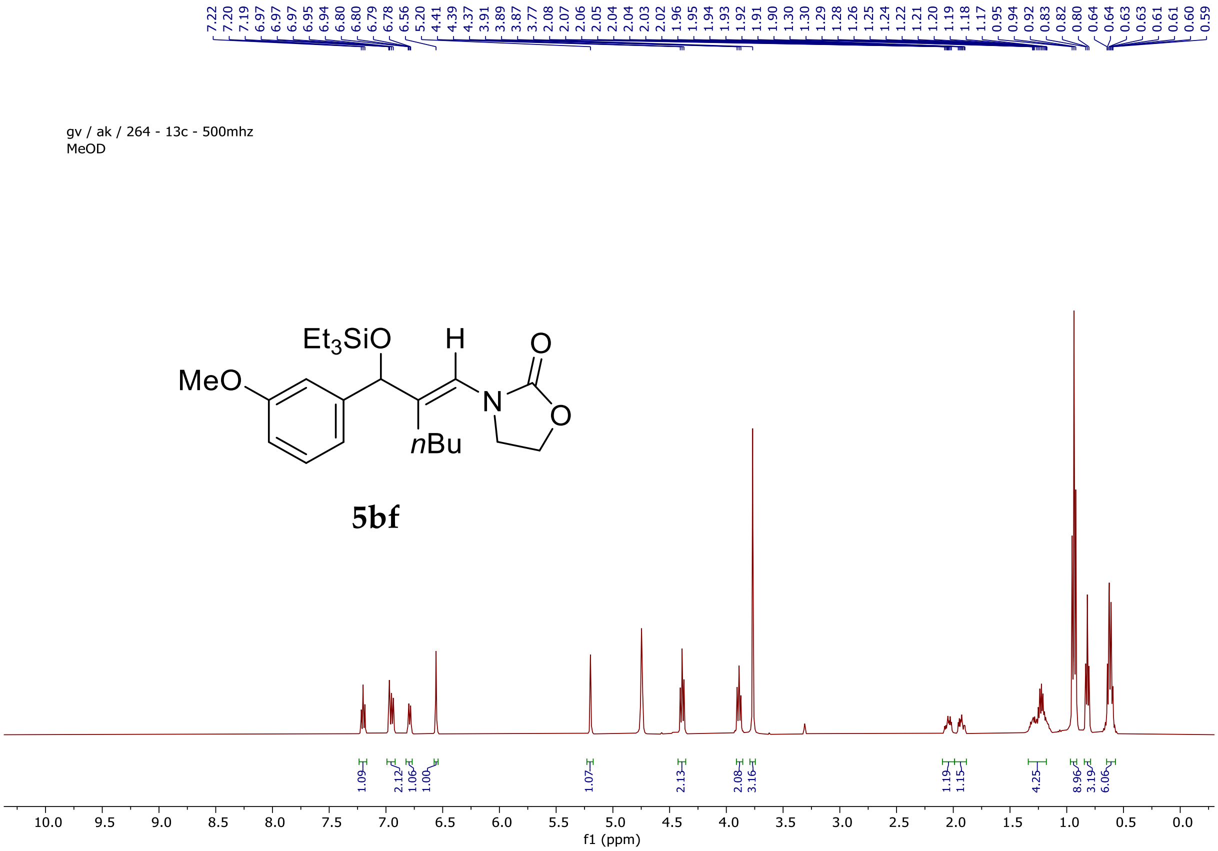
5bd

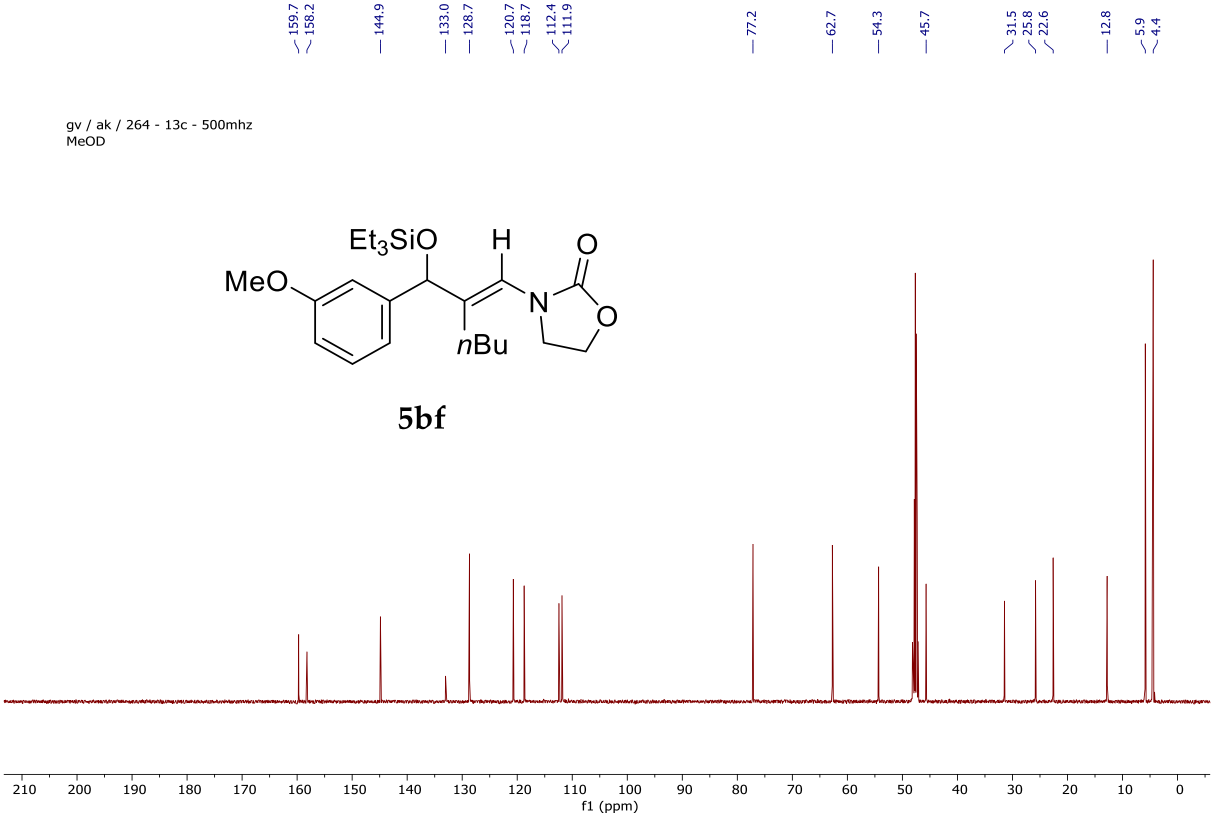

166.1
157.2
149.4
129.4
129.2
128.4
126.9
122.2
77.0
62.8
61.1
45.3
32.1
25.7
22.8
14.6
14.1
7.1
4.8
gv / ak / 224 fr - 13c - 500mhz
DMSO
Et$_3$SiO
H
O
N
O
EtO$_2$C
nBu
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

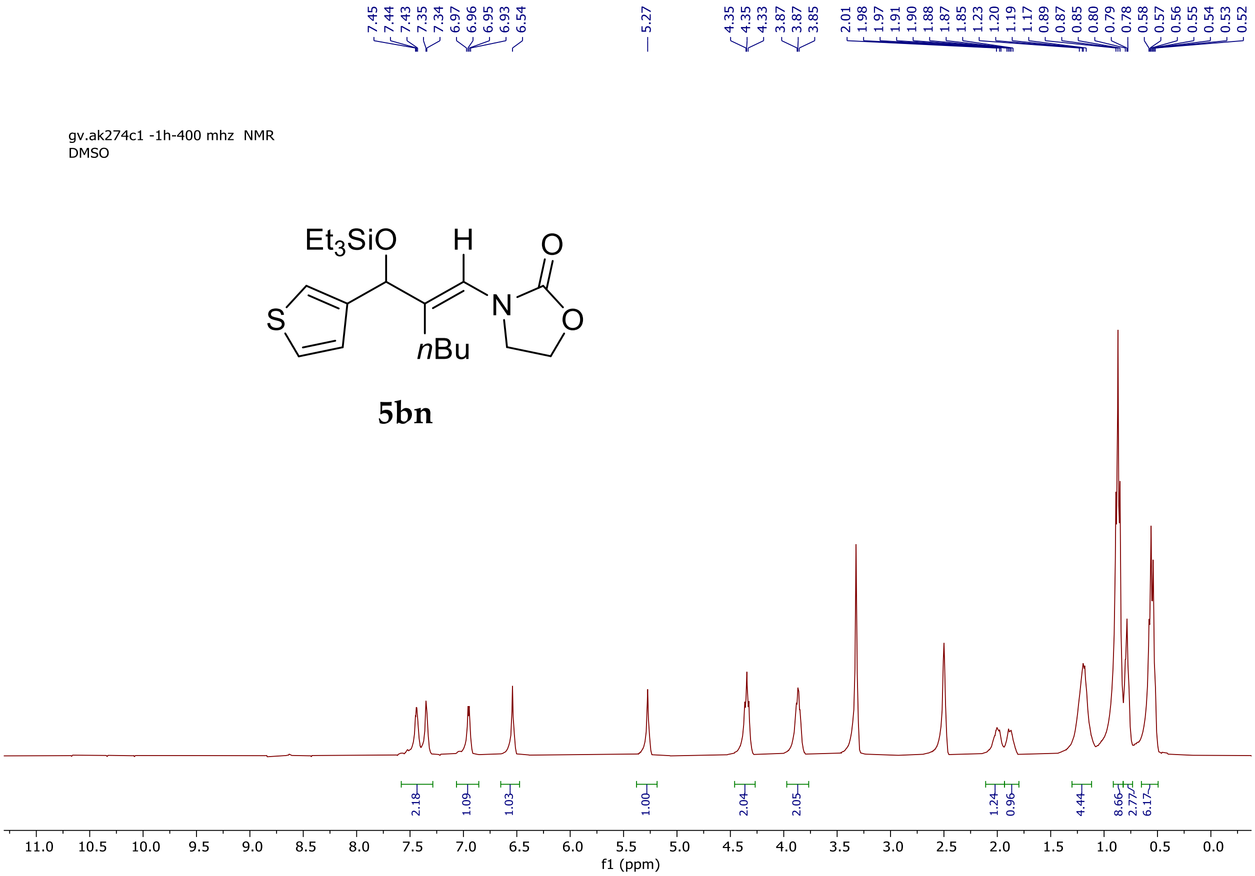
5bd

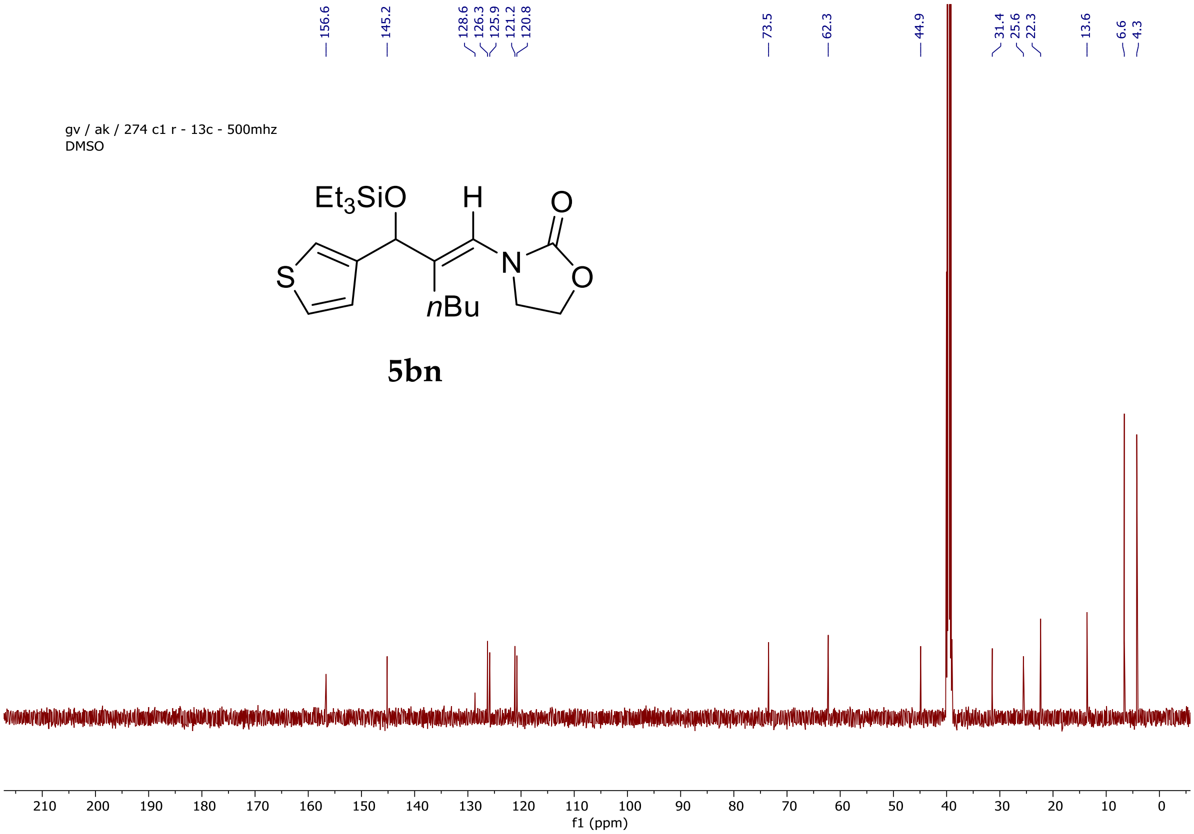

7.27
7.26
7.25
7.24
7.23
6.89
6.88
6.86
6.86
6.55
5.15
4.36
4.34
4.32
3.86
3.85
3.84
3.83
3.82
3.73
1.99
1.97
1.96
1.95
1.94
1.93
1.81
1.80
1.78
1.77
1.76
1.75
1.74
1.26
1.24
1.22
1.21
1.20
1.19
1.17
1.16
1.14
0.88
0.86
0.84
0.80
0.78
0.76
0.58
0.56
0.54
0.53
0.52
0.51
0.50
gv.ak250p-1h- 400 MHz
DMSO
Et$_3$SiO
H
O
N
O
MeO
nBu
1.97
2.02
1.00
1.00
2.17
1.96
3.08
1.07
1.03
4.21
9.43
3.02
6.03
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

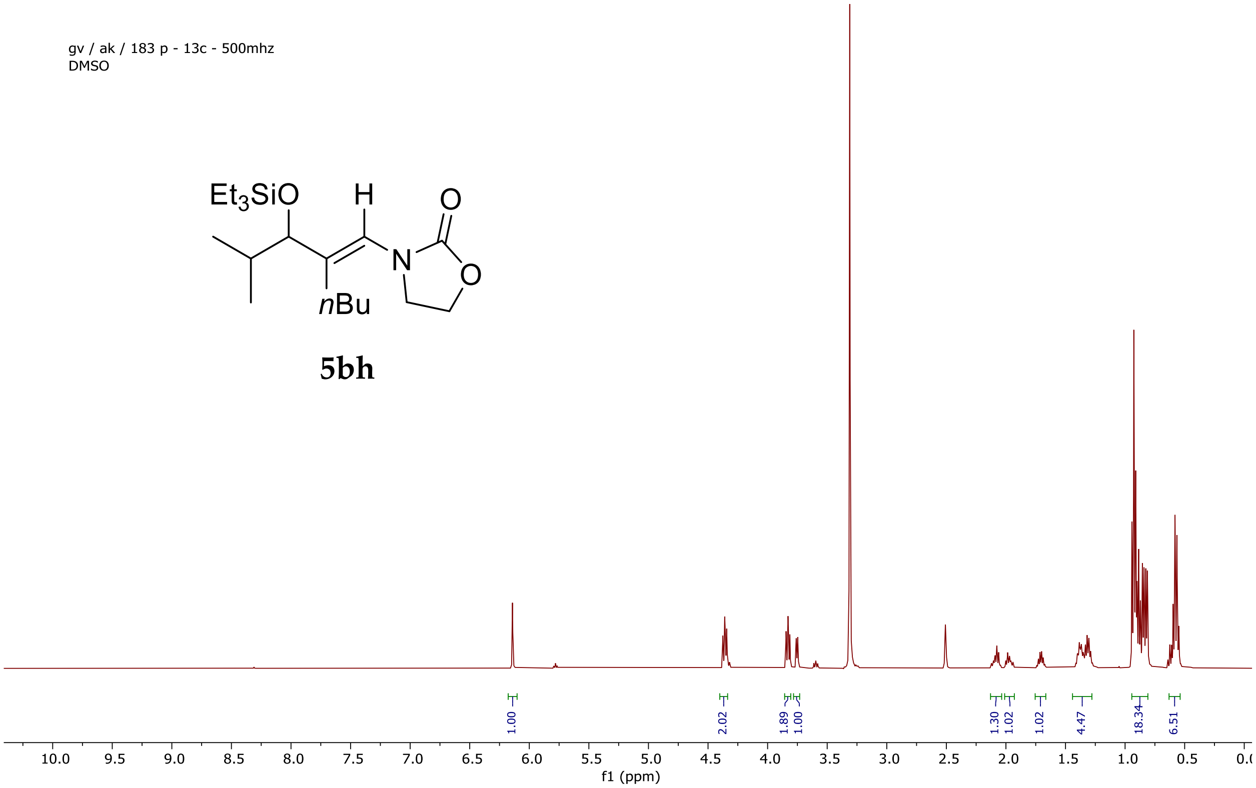
5bg

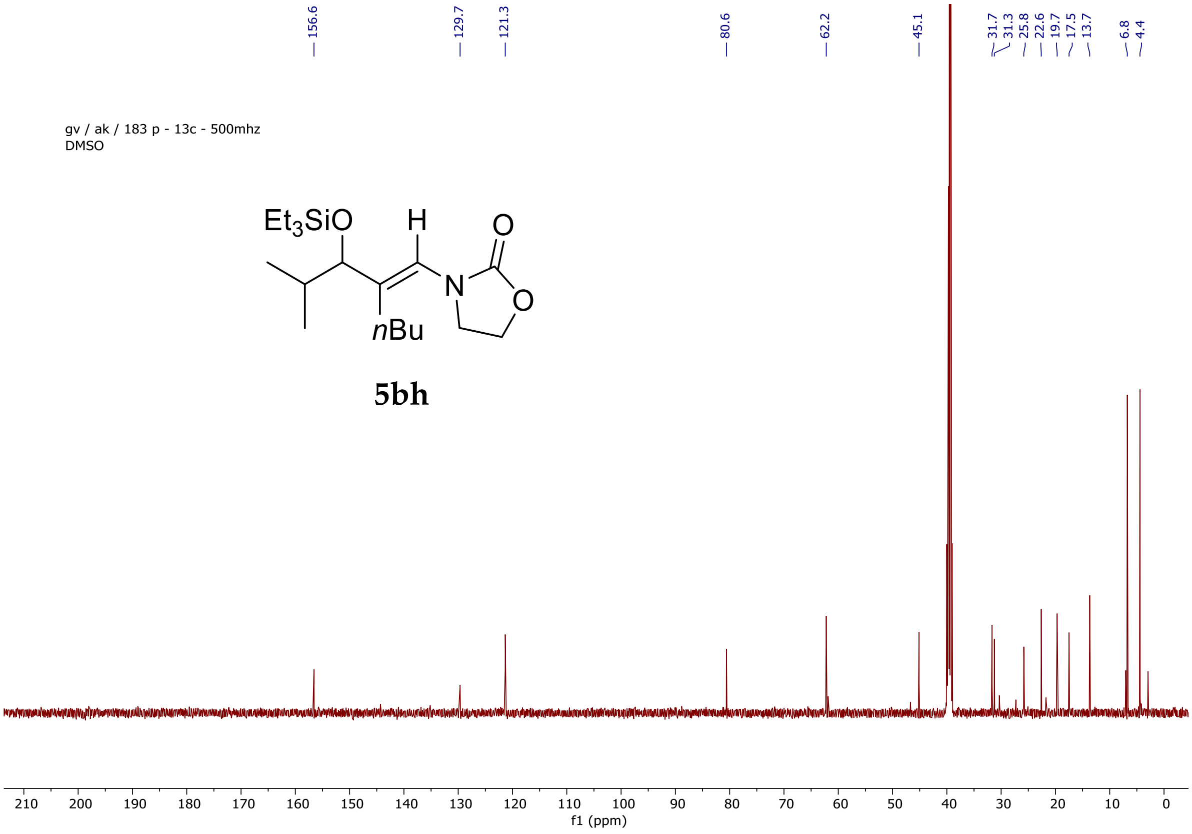

7.22 7.20 7.19 6.97 6.97 6.95 6.94 6.80 6.80 6.79 6.78 6.56 5.20 4.41 4.39 4.37 3.91 3.89 3.87 3.77 2.08 2.07 2.06 2.05 2.04 2.04 2.03 2.02 1.96 1.95 1.94 1.93 1.92 1.91 1.90 1.30 1.30 1.29 1.28 1.26 1.25 1.24 1.22 1.21 1.20 1.19 1.18 1.17 0.95 0.94 0.92 0.83 0.82 0.80 0.64 0.64 0.63 0.63 0.61 0.61 0.60 0.59
gv / ak / 264 - 13c - 500mhz
MeOD
Et3SiO
H
O
MeO
N
O
nBu
5bf
1.09 2.12 1.06 1.00 1.07 2.13 2.08 3.16 1.19 1.15 4.25 8.96 3.19 6.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

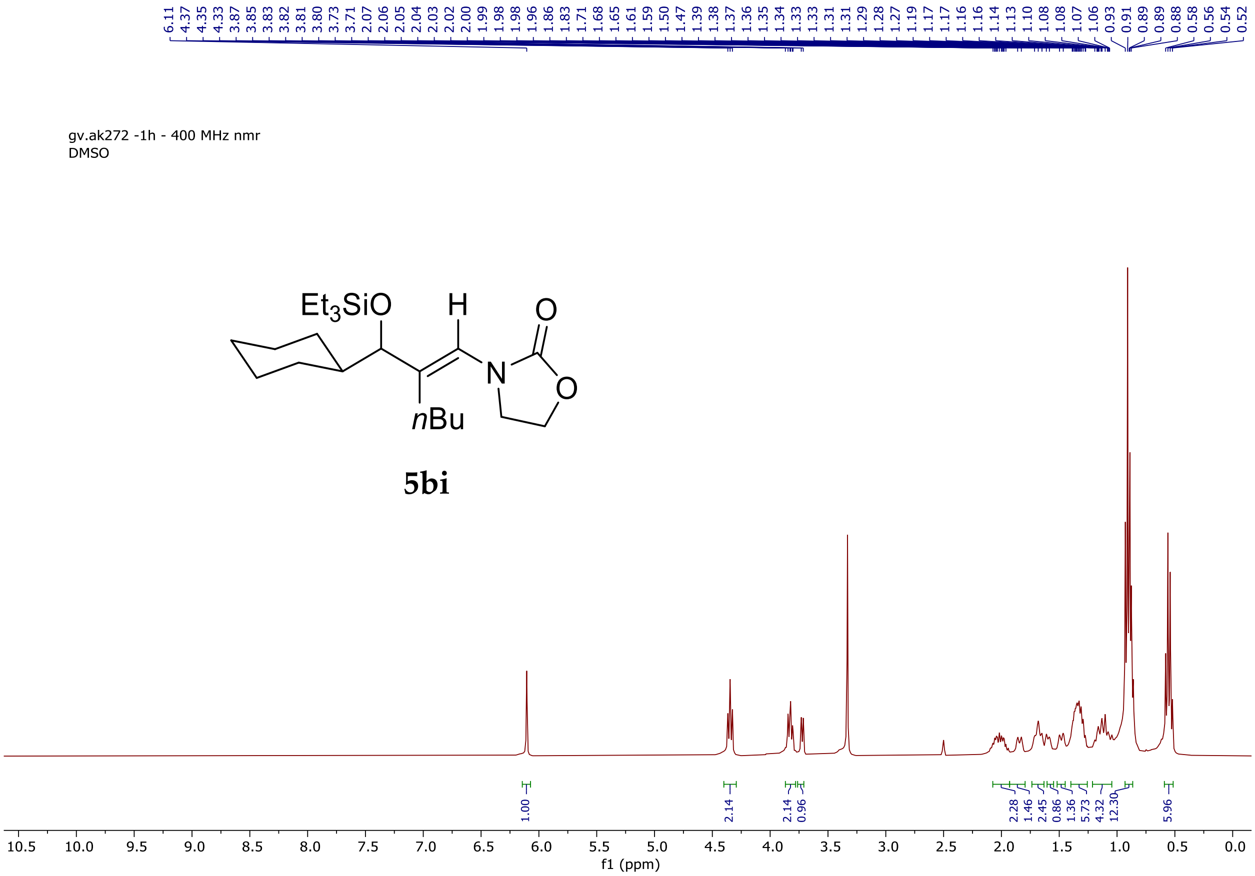

159.7 158.2 144.9 133.0 128.7 120.7 118.7 112.4 111.9 77.2 62.7 54.3 45.7 31.5 25.8 22.6 12.8 5.9 4.4
gv / ak / 264 - 13c - 500mhz
MeOD
Et3SiO
H
O
MeO
N
O
nBu
5bf
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

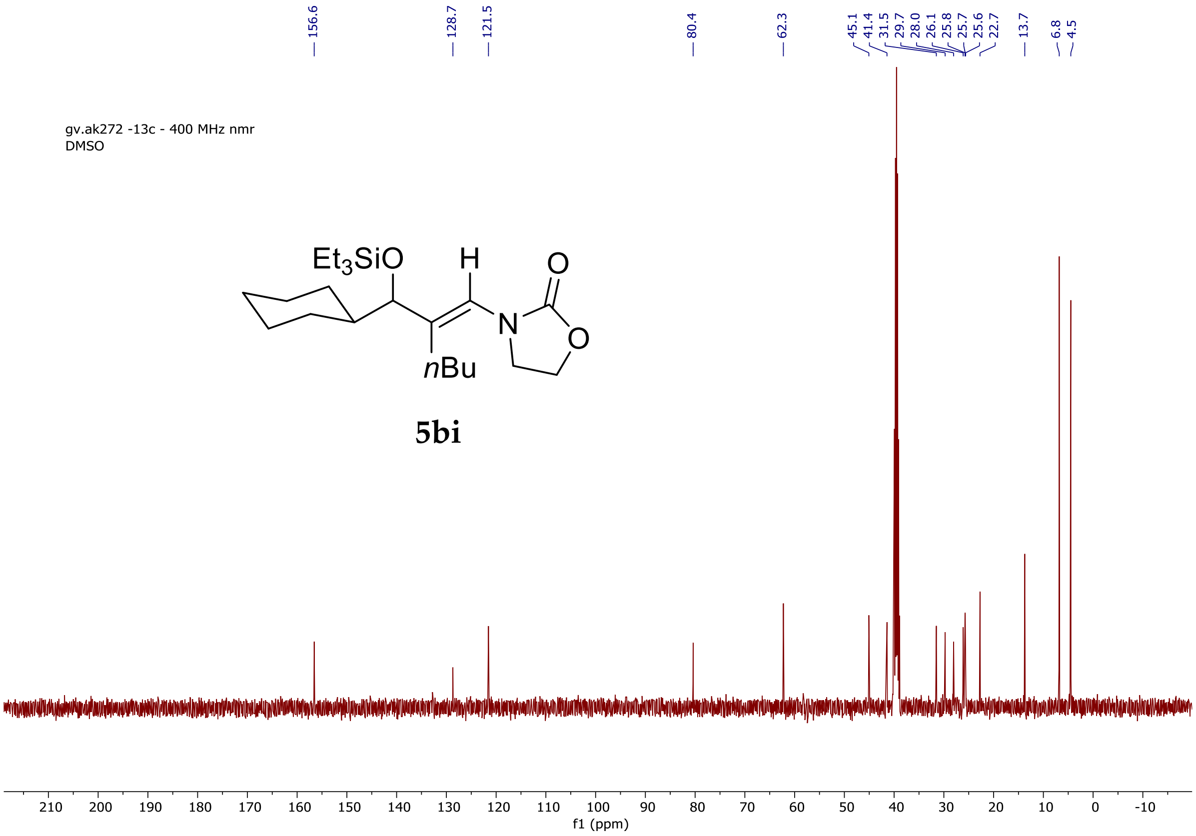

7.45
7.44
7.43
7.35
7.34
6.97
6.96
6.95
6.93
6.54
5.27
4.35
4.35
4.33
3.87
3.87
3.85
2.01
1.98
1.97
1.91
1.90
1.88
1.87
1.85
1.23
1.20
1.19
1.17
0.89
0.87
0.85
0.80
0.79
0.78
0.58
0.57
0.56
0.55
0.54
0.53
0.52
gv.ak274c1 -1h-400 mhz NMR
DMSO
Et3SiO
H
O
S
N
O
nBu
5bn
2.18
1.09
1.03
1.00
2.04
2.05
1.24
0.96
4.44
8.66
2.77
6.17
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

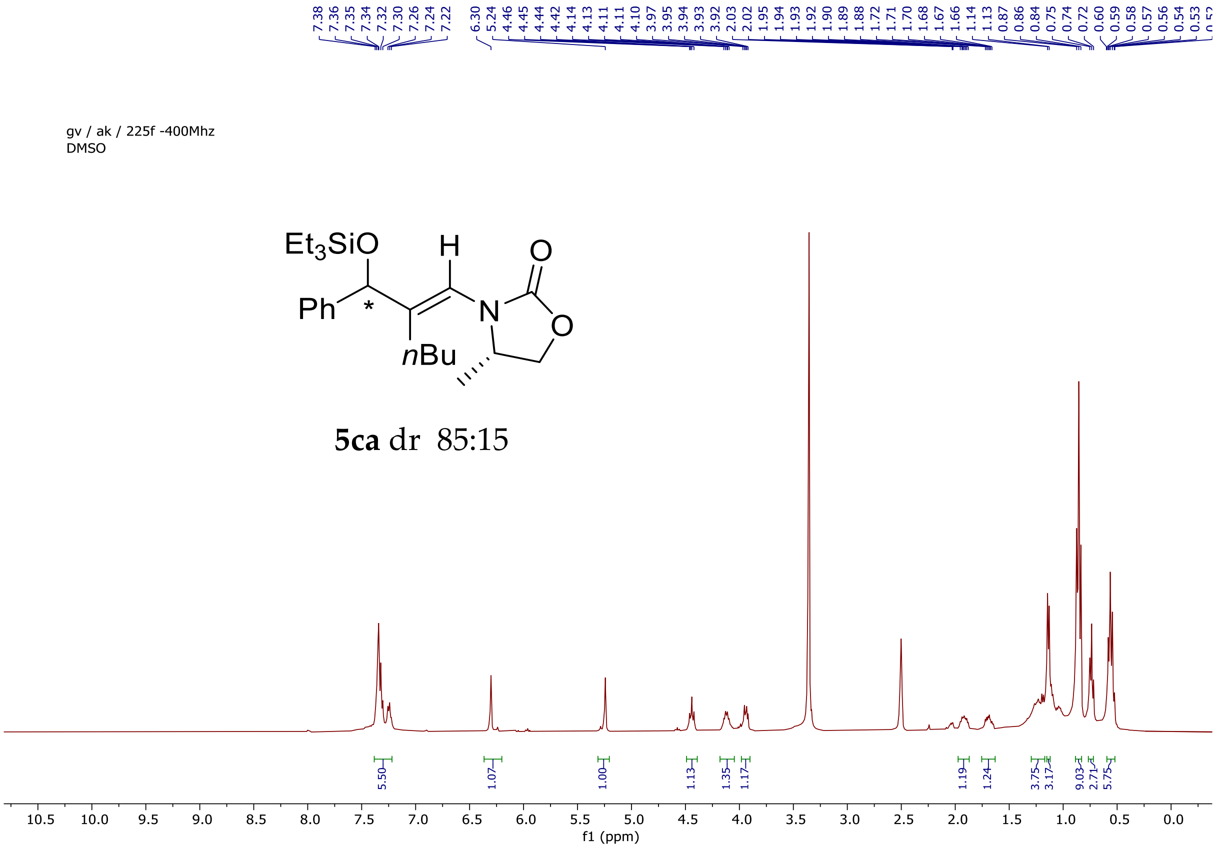

156.6
145.2
128.6
126.3
125.9
121.2
120.8
73.5
62.3
44.9
31.4
25.6
22.3
13.6
6.6
4.3
gv / ak / 274 c1 r - 13c - 500mhz
DMSO
Et3SiO
H
O
S
N
O
nBu
5bn
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


gv / ak / 183 p - 13c - 500mhz
DMSO
Et3SiO
H
O
N
O
nBu
5bh
1.00
2.02
1.89
1.00
1.30
1.02
1.02
4.47
18.34
6.51
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

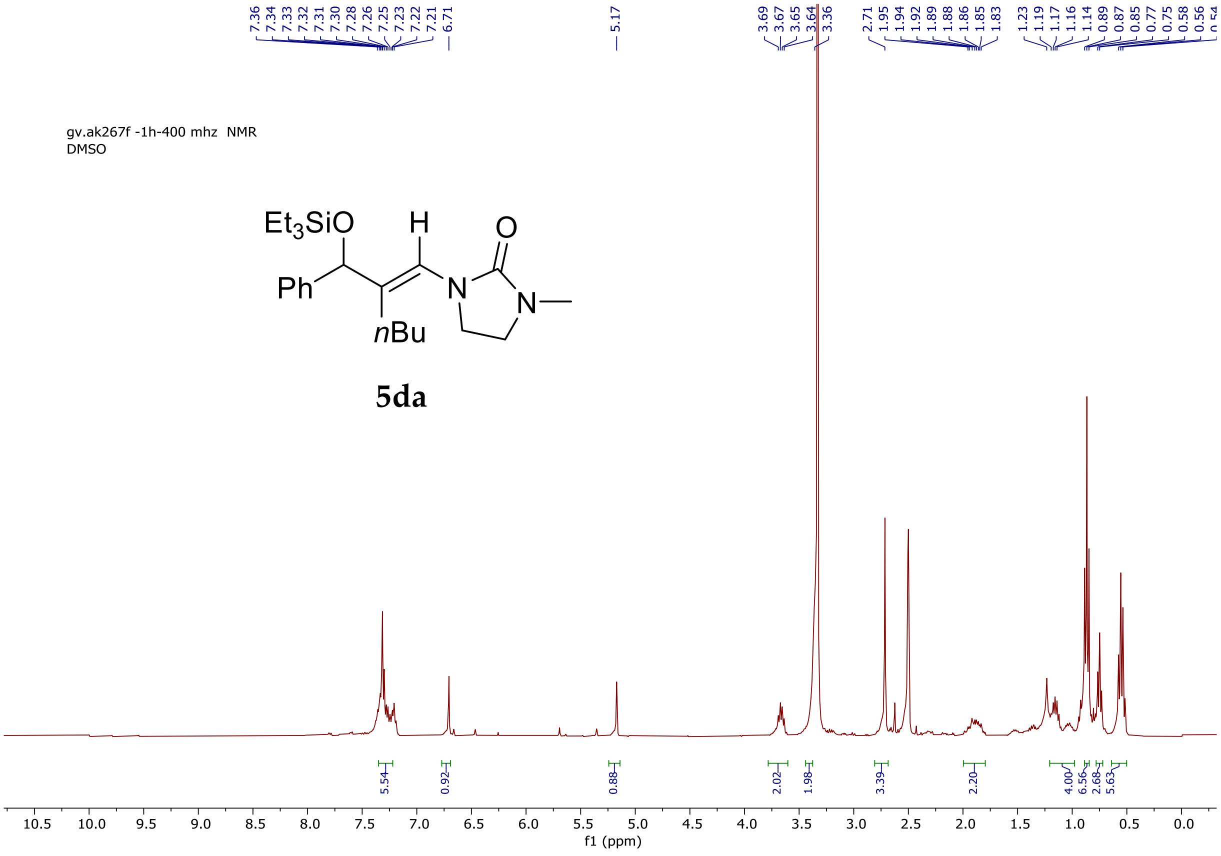

156.6
129.7
121.3
80.6
62.2
45.1
31.7
31.3
25.8
22.6
19.7
17.5
13.7
6.8
4.4
gv / ak / 183 p - 13c - 500mhz
DMSO
Et3SiO
H
O
N
O
nBu
5bh
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


6.11
4.37
4.35
4.33
3.87
3.85
3.83
3.82
3.81
3.80
3.73
3.71
2.07
2.06
2.05
2.04
2.03
2.02
2.00
1.99
1.98
1.98
1.96
1.86
1.83
1.71
1.68
1.65
1.61
1.59
1.50
1.47
1.39
1.38
1.37
1.36
1.35
1.34
1.33
1.33
1.31
1.31
1.29
1.28
1.27
1.19
1.17
1.17
1.16
1.16
1.14
1.13
1.10
1.08
1.08
1.07
1.06
0.93
0.91
0.89
0.89
0.88
0.58
0.56
0.54
0.52
gv.ak272 -1h - 400 MHz nmr
DMSO
Et3SiO
H
O
N
O
nBu
5bi
1.00
2.14
2.14
0.96
2.28
1.46
2.45
0.86
1.36
5.73
4.32
12.30
5.96
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

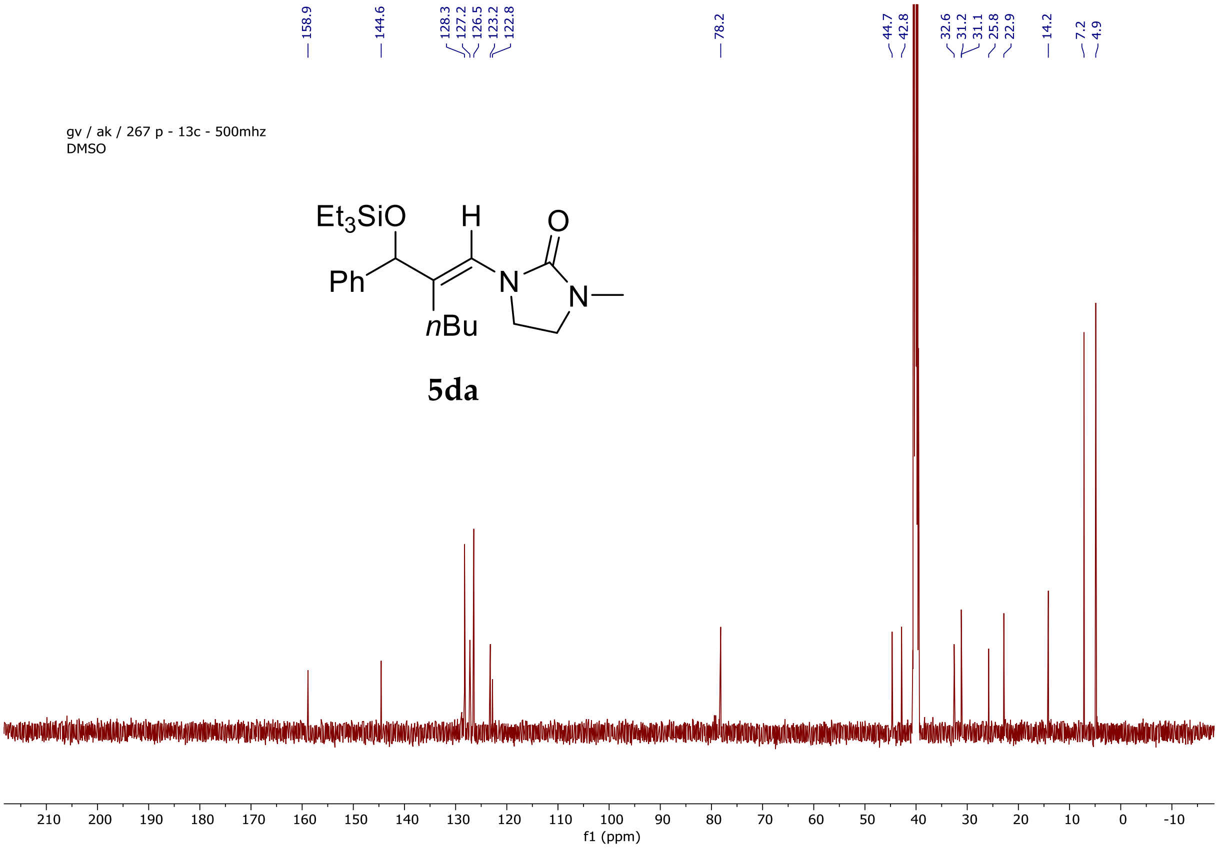

156.6
128.7
121.5
80.4
62.3
45.1
41.4
31.5
29.7
28.0
26.1
25.8
25.7
25.6
22.7
13.7
6.8
4.5
gv.ak272 -13c - 400 MHz nmr
DMSO
Et3SiO
H
O
N
O
nBu
5bi
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



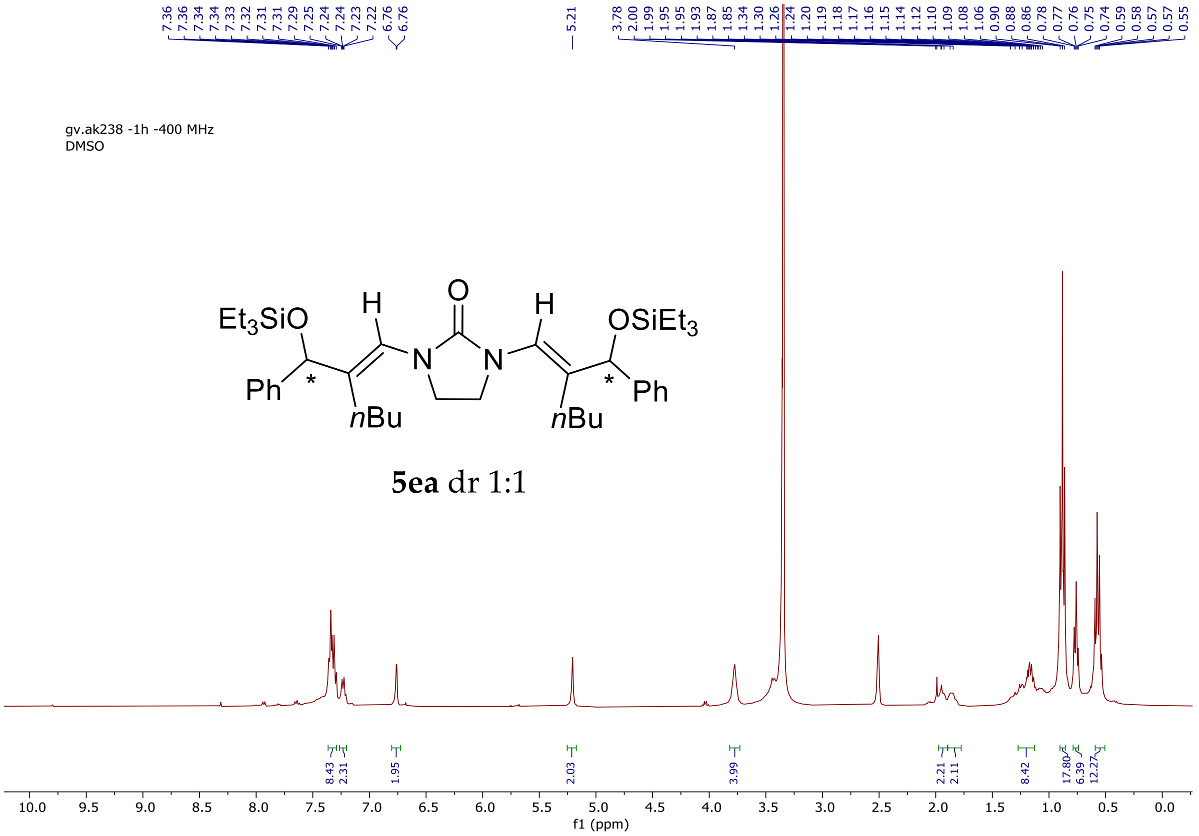
5ca dr 85:15



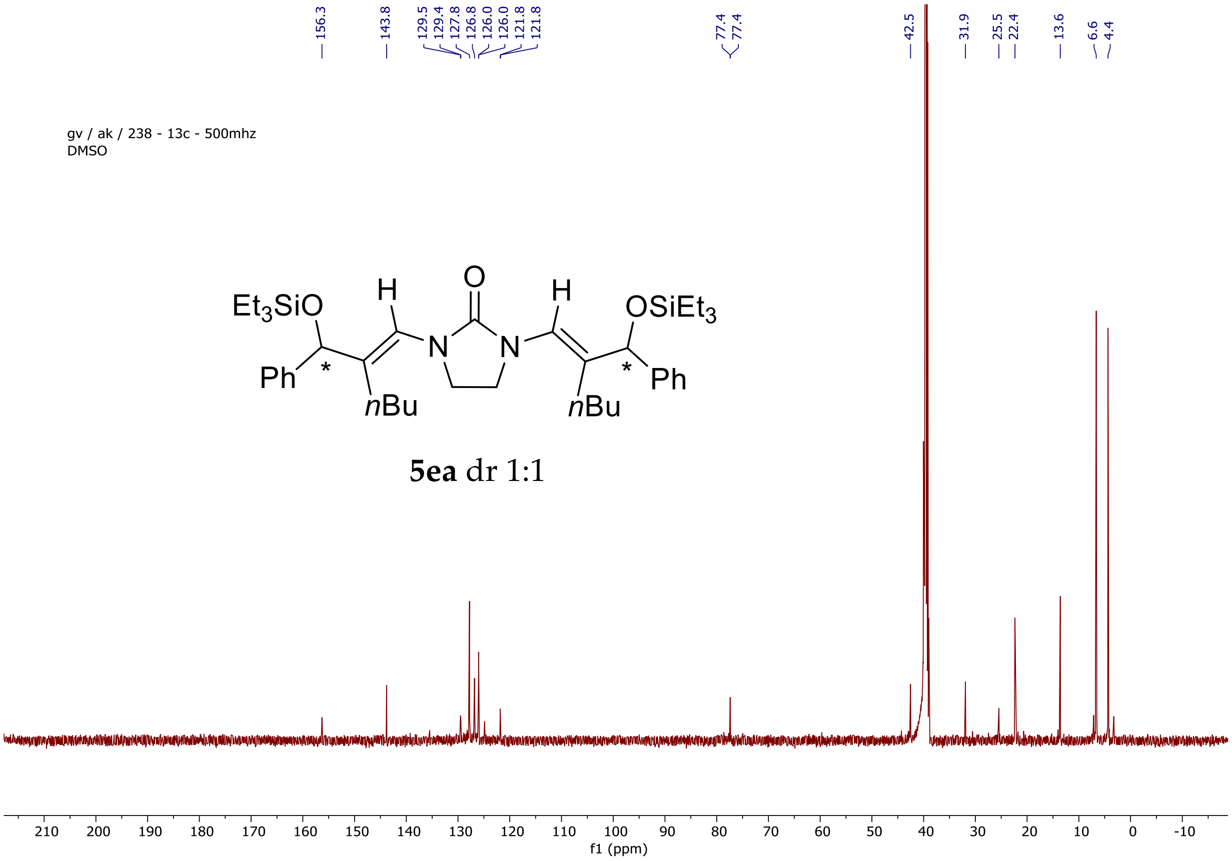
5da


158.9
144.6
128.3
127.2
126.5
123.2
122.8
78.2
44.7
42.8
32.6
31.2
31.1
25.8
22.9
14.2
7.2
4.9
gv / ak / 267 p - 13c - 500mhz
DMSO
Et3SiO
H
O
Ph
N
N
nBu
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

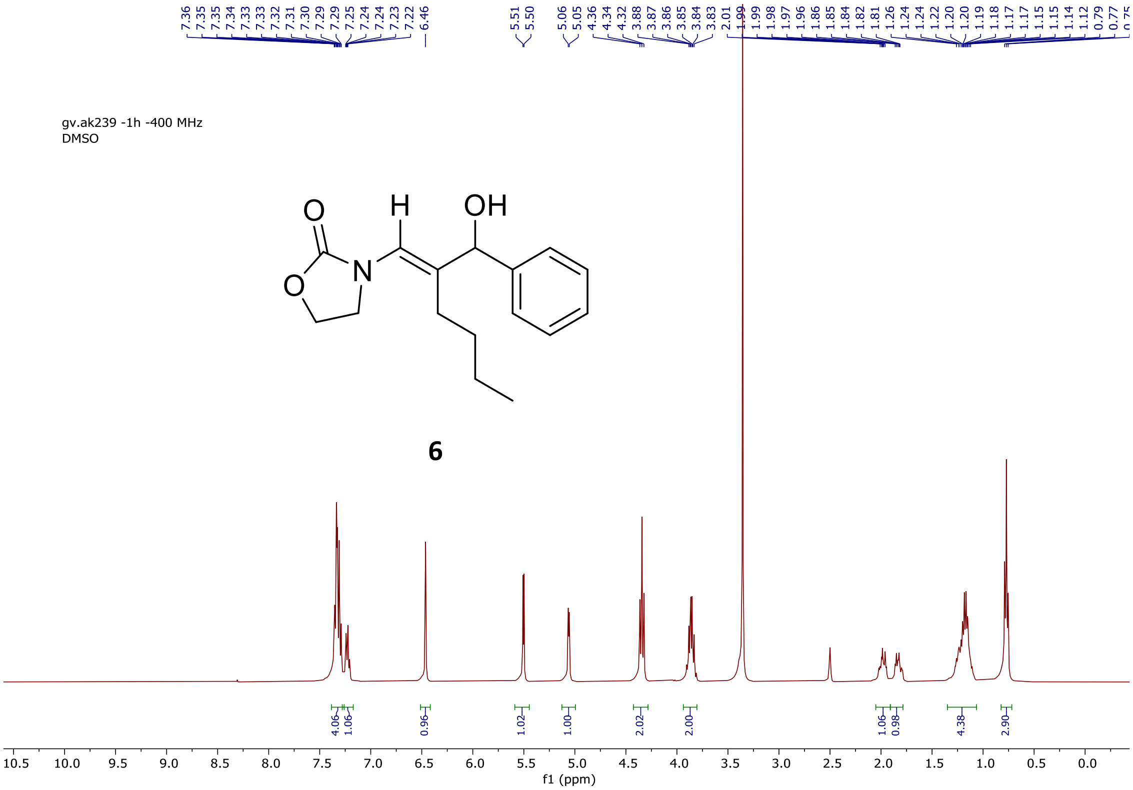
5da


7.36
7.36
7.34
7.34
7.33
7.32
7.31
7.29
7.25
7.24
7.24
7.23
7.22
6.76
6.76
5.21
3.78
2.00
1.99
1.95
1.93
1.87
1.85
1.34
1.30
1.26
1.24
1.20
1.19
1.18
1.17
1.16
1.15
1.14
1.12
1.10
1.09
1.08
1.06
0.90
0.88
0.86
0.78
0.77
0.76
0.75
0.74
0.59
0.58
0.57
0.57
0.55
gv.ak238 -1h -400 MHz
DMSO
Et3SiO
H
O
H
OSiEt3
Ph
*
N
N
*
Ph
nBu
nBu
8.43
2.31
1.95
2.03
3.99
2.21
2.11
8.42
17.80
6.39
12.27
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

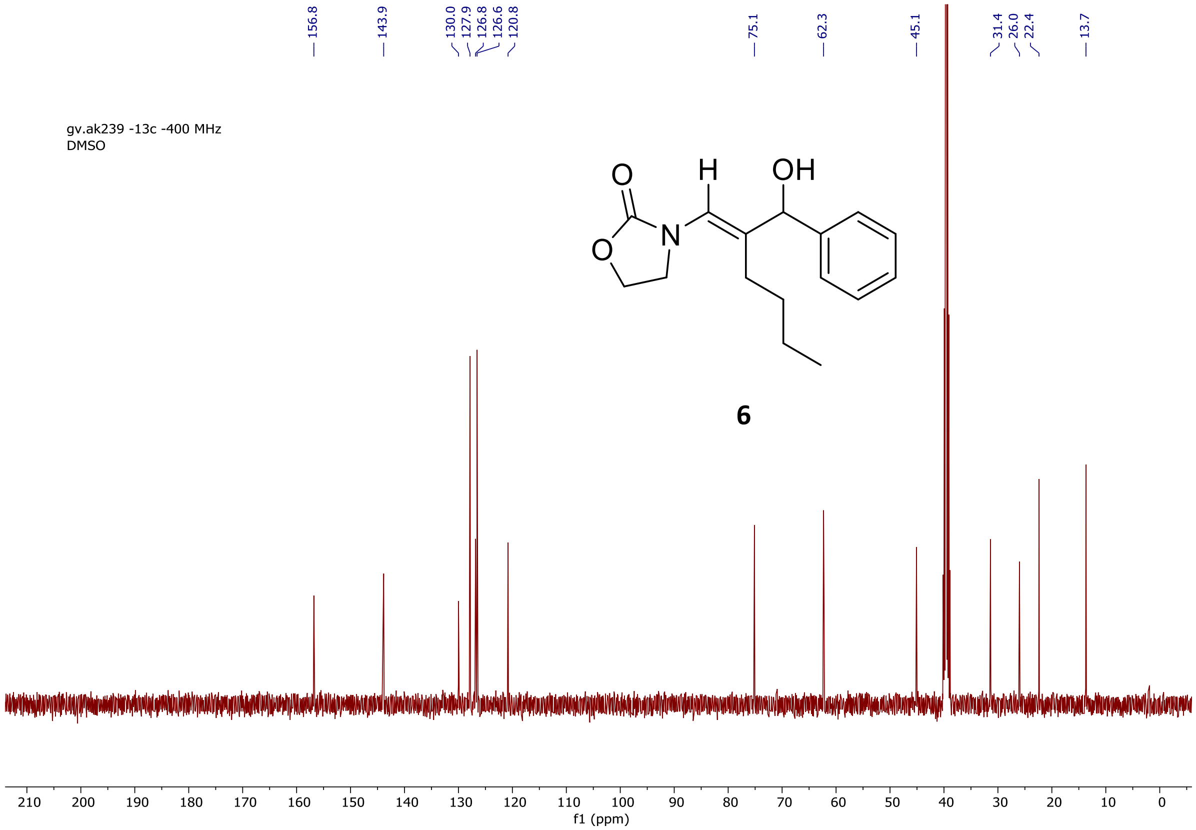
5ea dr 1:1


156.3
143.8
129.5
129.4
127.8
126.8
126.0
126.0
121.8
121.8
77.4
77.4
42.5
31.9
25.5
22.4
13.6
6.6
4.4
gv / ak / 238 - 13c - 500mhz
DMSO
Et3SiO
H
O
N
N
H
OSiEt3
Ph
*
nBu
nBu
*
Ph
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

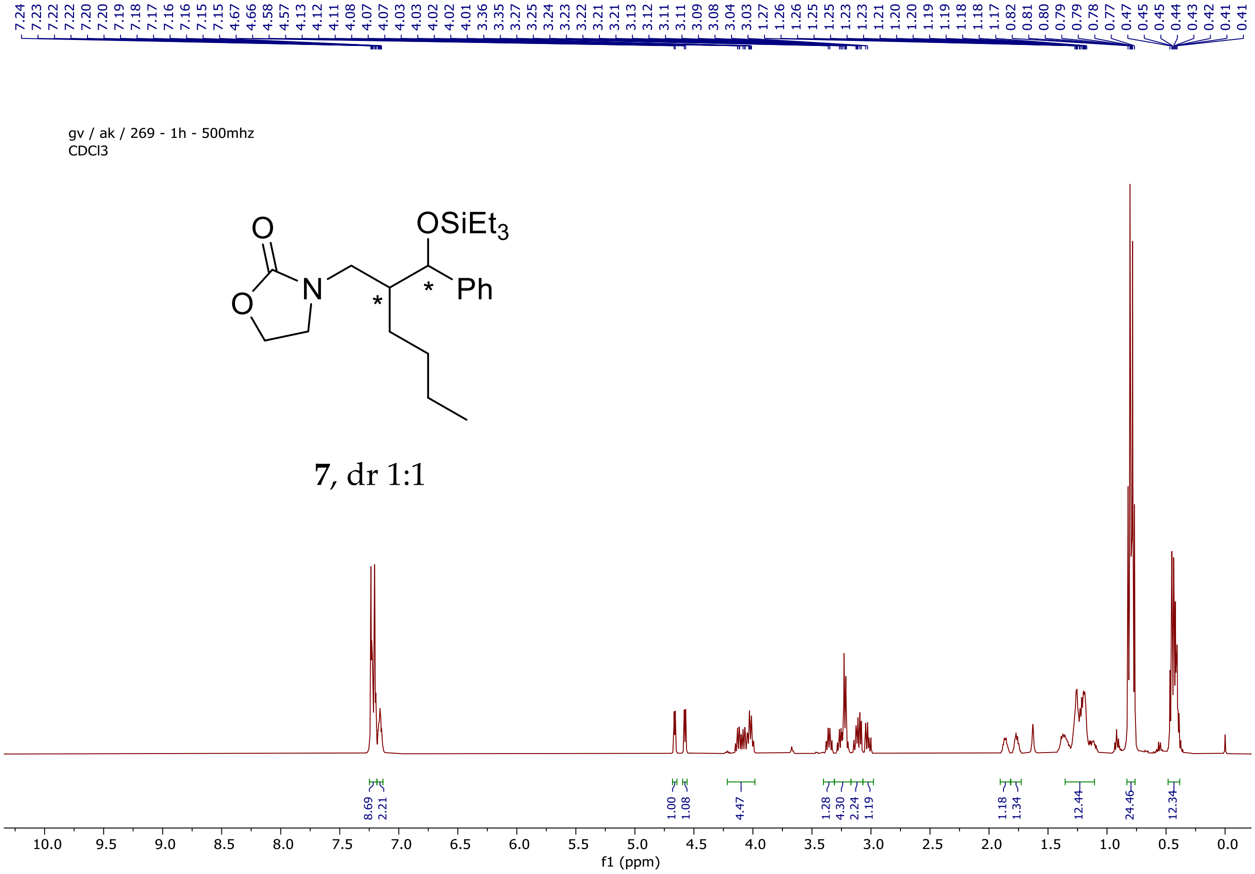
5ea dr 1:1


7.36
7.35
7.35
7.34
7.33
7.33
7.32
7.31
7.30
7.29
7.29
7.25
7.24
7.24
7.23
7.22
6.46
5.51
5.50
5.06
5.05
4.36
4.34
4.32
3.88
3.87
3.86
3.85
3.84
3.83
2.01
1.99
1.99
1.98
1.97
1.96
1.86
1.85
1.84
1.82
1.81
1.26
1.24
1.24
1.22
1.20
1.20
1.19
1.18
1.17
1.17
1.15
1.15
1.14
1.12
0.79
0.77
gv.ak239 -1h -400 MHz
DMSO
O
H
OH
O
N
4.06
1.06
0.96
1.02
1.00
2.02
2.00
1.06
0.98
4.38
2.90
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

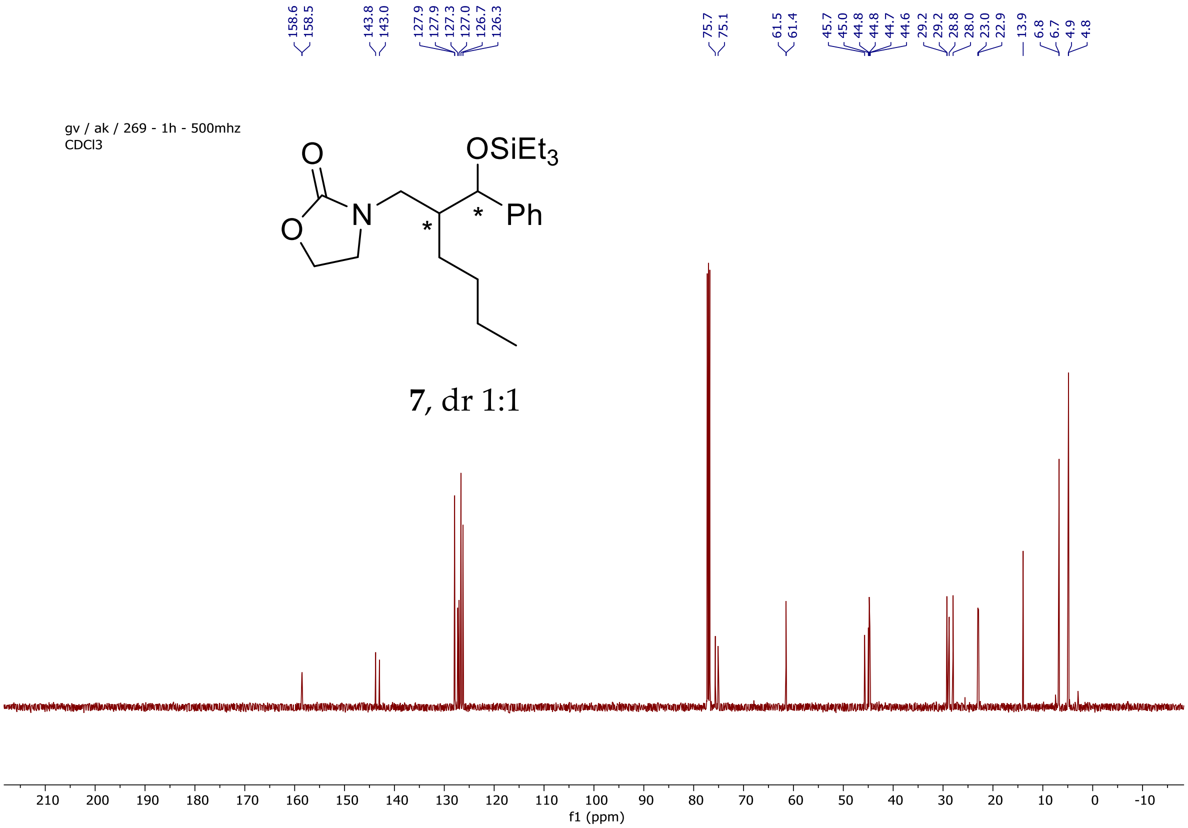
6


156.8
143.9
130.0
127.9
126.8
126.6
120.8
75.1
62.3
45.1
31.4
26.0
22.4
13.7
gv.ak239 -13c -400 MHz
DMSO
O
H
OH
N
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

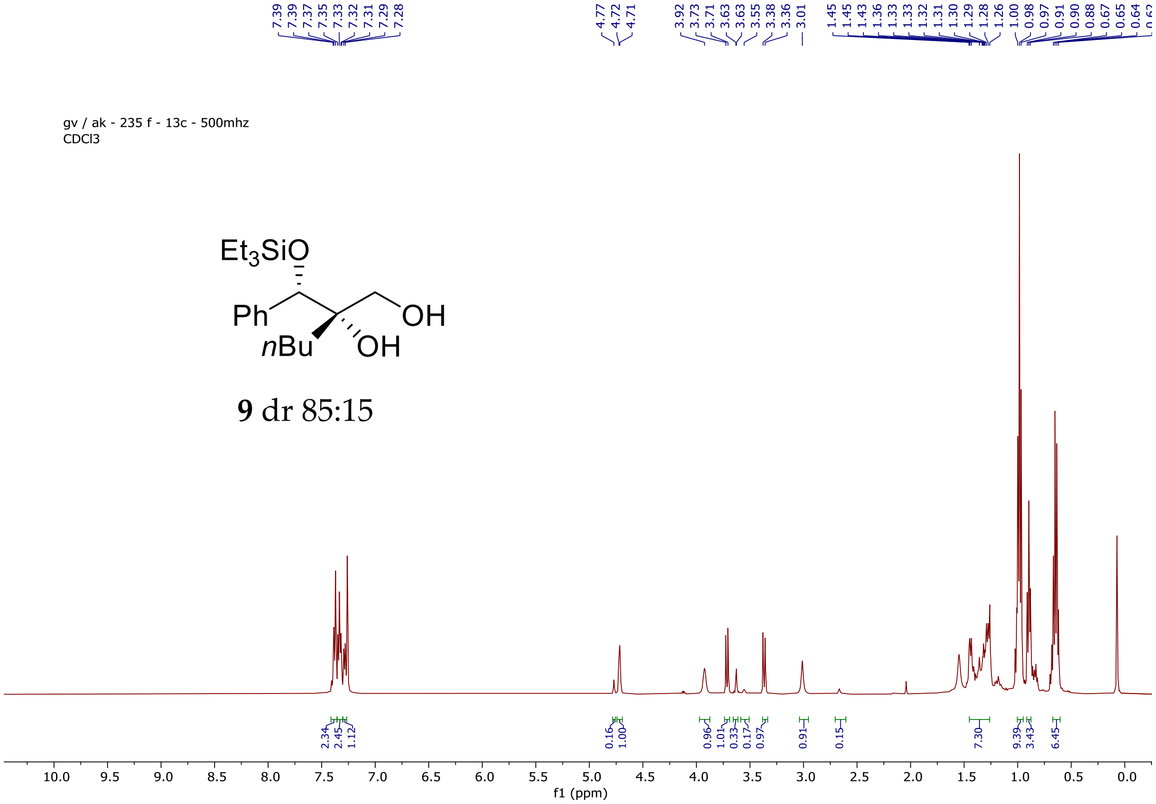
6


7.24
7.23
7.22
7.22
7.20
7.20
7.19
7.18
7.17
7.16
7.16
7.15
7.15
4.67
4.66
4.58
4.57
4.13
4.12
4.11
4.08
4.07
4.07
4.03
4.03
4.02
4.02
4.01
3.36
3.35
3.27
3.25
3.24
3.23
3.22
3.21
3.21
3.13
3.12
3.11
3.11
3.09
3.08
3.04
3.03
1.27
1.26
1.25
1.25
1.23
1.23
1.21
1.20
1.20
1.19
1.18
1.18
1.17
0.82
0.81
0.80
0.79
0.79
0.78
0.77
0.47
0.45
0.45
0.44
0.44
0.43
0.42
0.41
0.41
gv / ak / 269 - 1h - 500mhz
CDCl3
O
OSiEt3
N
O
*
*
Ph
8.69
2.21
1.00
1.08
4.47
1.28
4.30
2.24
1.19
1.18
1.34
12.44
24.46
12.34
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

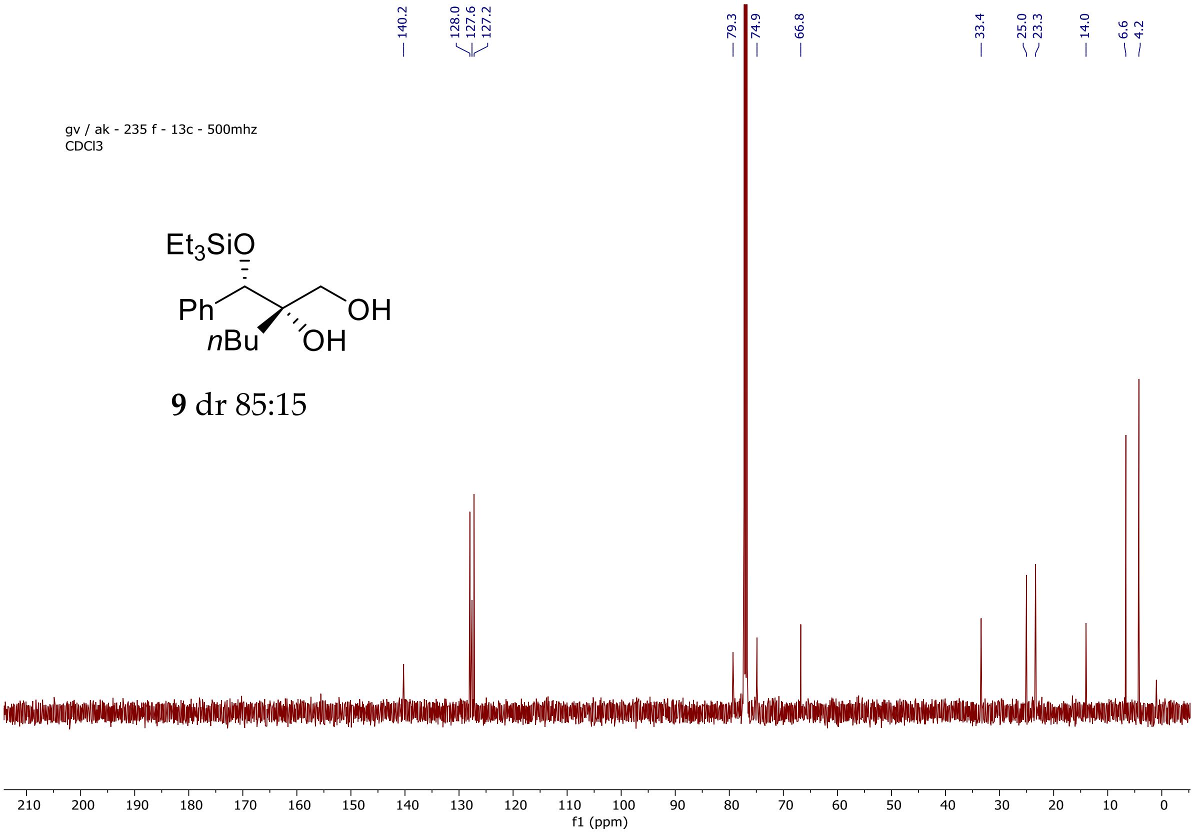
7, dr 1:1



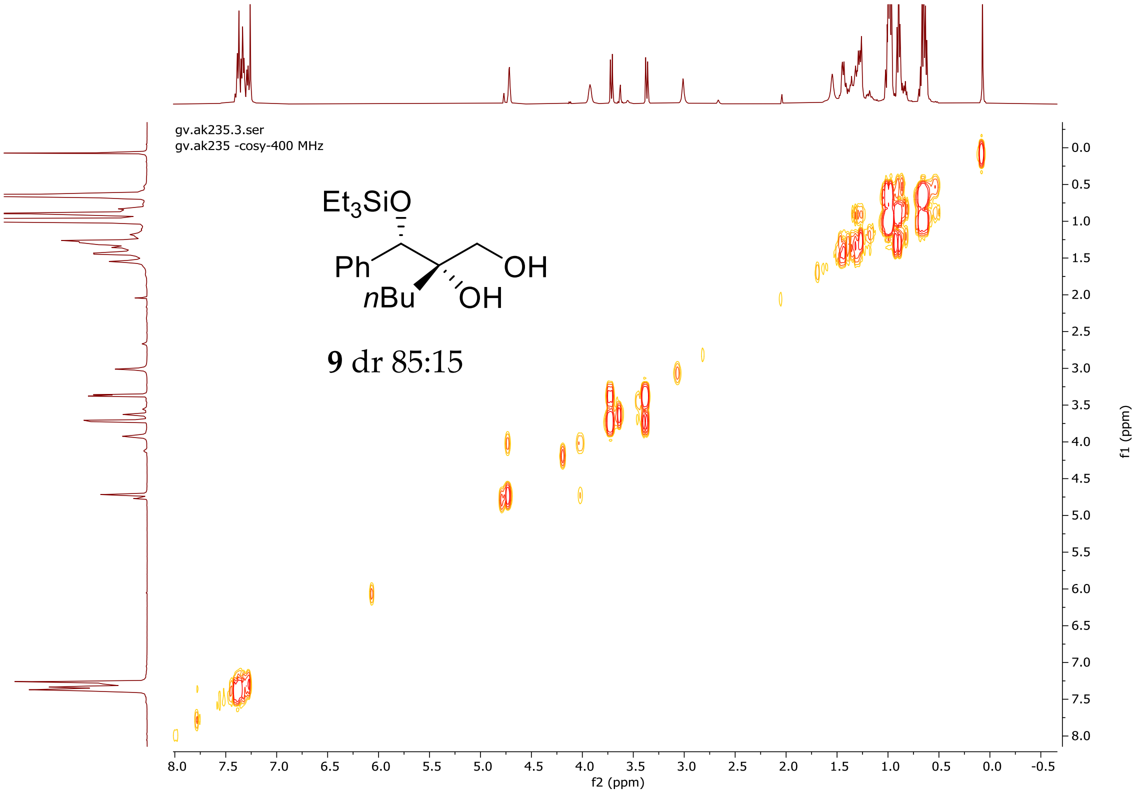
7, dr 1:1



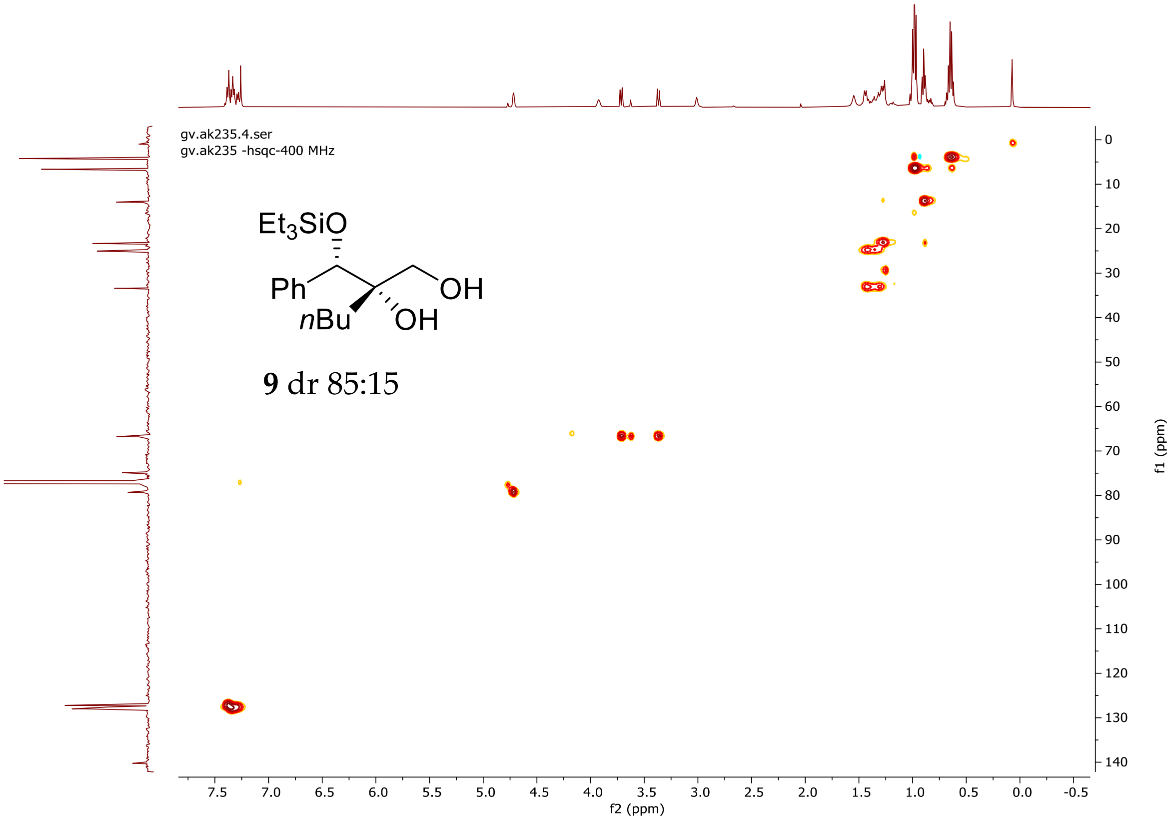
9 dr 85:15



9 dr 85:15



9 dr 85:15



9 dr 85:15

16. REFERENCES

1. (a) Armarego, W. L. F., *Purification of Laboratory Chemicals (Eighth Edition)*, Ed. Butterworth-Heinemann: 2017.
2. Tran, V. T.; Li, Z.-Q.; Apolinar, O.; Derosa, J.; Joannou, M. V.; Wisniewski, S. R.; Eastgate, M. D.; Engle, K. M., Ni(COD)(DQ): An Air-Stable 18-Electron Nickel(0)–Olefin Precatalyst. *Angew. Chem. Int. Ed.* **2020,** *59*, 7409-7413.
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