SUPPORTING INFORMATION

Ruthenium-Catalyzed *trans*-Hydroalkynylation and *trans*-Chloroalkynylation of Internal Alkynes

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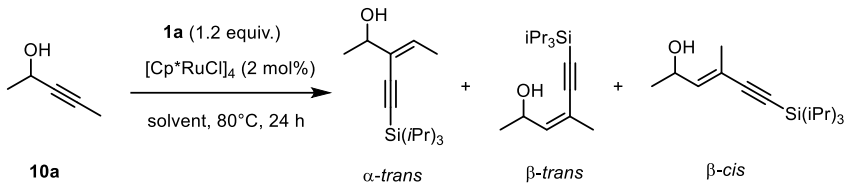
Additional Screening Results

Table S-1. Solvent-dependence of the Product Distribution[a]



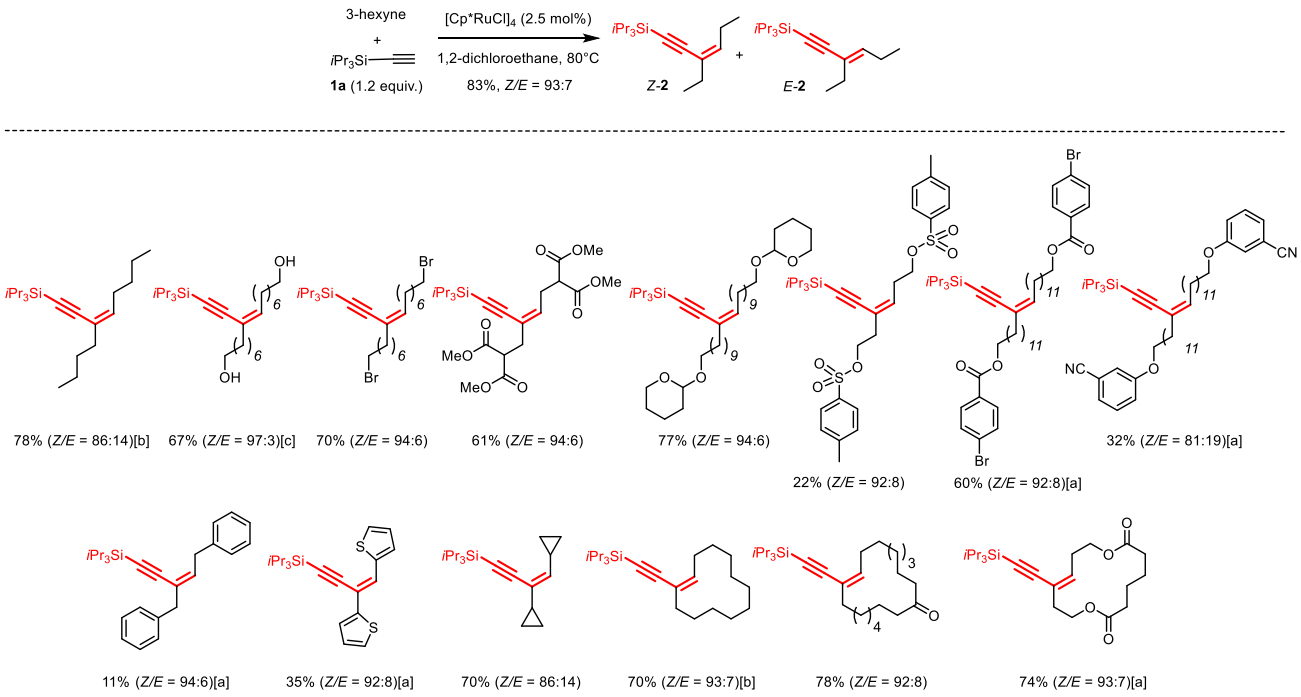
Entry	Solvent	α-*trans*	β-*trans*	β-*cis*
1	1,2-DCE	74	10	16
2	$CHCl_3$	73	20	7
3	CH_2Cl_2 [b]	75	9	16
4	C_6H_5Cl	74	10	16
5	MeCN	64	10	26
6	THF	62	15	23
7	acetone	64	11	25
8	toluene	64	7	29
9	1,4-dioxane	55	22	23
10	EtOAc	66	13	21

[a] the isomer ratios as determined by ^{1}H NMR of the crude reaction mixtures; the fourth possible isomer (α-*cis*) was below the limited of detection in all cases investigated; [b] incomplete conversion

Table S-2. Screening of Other Alkynes RC≡CX in the Reaction with Propargyl Alcohol 10a (R^1 = R^2 = Me)

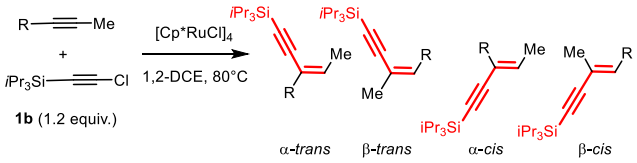
R	X	Outcome (NMR)
Ph_2MeSi-	H	< 5% conversion
Ph_2MeSi-	Cl	< 5% conversion; partial homo-coupling of chloro-alkyne (see Scheme 6)
$PhMe_2Si$-	H	< 5% conversion
Me_3Si-	H	homodimerization of RC≡CH (see Scheme 6)
^{t}BuMe$_2$Si-	H	homodimerization of RC≡CH (see Scheme 6)
Ph-	H	homodimerization of RC≡CH (see Scheme 6)
Ph-	Cl	no product formation; partial homo-coupling of chloro-alkyne (see Scheme 6)
cyclohexyl-	H	17% conversion to product (GC) after 24 h
cyclohexyl-	Cl	< 5% conversion; partial homo-coupling of chloro-alkyne (see Scheme 6)
n-octyl	H	8% conversion to product (GC) after 24 h

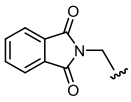
Table S-3. Scope and Limitations of the *trans*-Hydroalkynylation: Symmetrical Alkynes



[a] using 5 mol% of catalyst; [b] NMR yield [c] the product also contains traces of the aldehyde

Table S-4. Scope and Limitations of the *trans*-Hydroalkynylation: Unsymmetrical Substrates Containing Aromatic Rings



Entry	R	α-*trans*	β-*trans*	α-*cis*	β-*cis*
1		63	27	5	5
2	Ph	25	28	n. d.	47
3	*p*-$F_3CC_6H_4$	34	34	n. d.	32
4	*o*-$MeOC_6H_4$	21	18	n. d.	61

n. d. = not detected

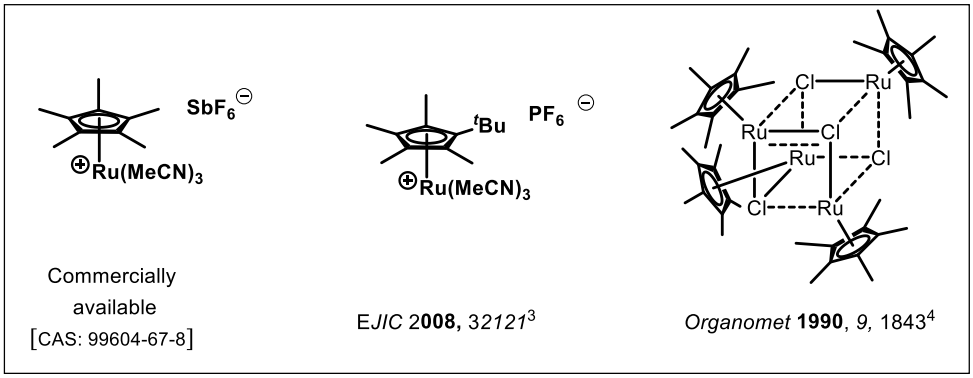
General. Unless stated otherwise, all reactions were carried out under argon atmosphere in flame dried Schlenk glassware. The solvents were purified by distillation over the indicated drying agents under argon: THF, THP, Et_2O (Mg/anthracene), hexanes (Na/K), EtOH, MeOH (Mg), 1,2-dichloroethane, CD_2Cl_2, CH_2Cl_2 (CaH_2). DMF, MeCN and Et_3N, dioxane were dried by an absorption solvent purification system based on molecular sieves. 1,2-Dichloroethane (1,2-DCE), CD_2Cl_2 and CH_2Cl_2 were degassed via freeze-pump-thaw procedure (3 x) and stored over molecular sieves. Column chromatography: Merck Geduran silica gel 60 (40 – 63 µm). NMR spectra were recorded on Bruker AvanceIII 300, 400, 500 MHz and an Avance Neo 600 MHz NMR spectrometers in the solvents indicated; chemical shifts are given in ppm relative to TMS, coupling constants (*J*) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δ_C = 77.16 ppm; residual $CHCl_3$: δ_H = 7.26 ppm; CD_2Cl_2: δ_C = 54.00 ppm; residual CD_2Cl_2: δ_H = 5.32 ppm). Signal assignments were established using HSQC, HMBC and NOESY experiments. IR: Alpha Platinum ATR (Bruker), wavenumbers ($\tilde{\nu}$) in cm^{-1}. MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: ESQ 3000 (Bruker), Thermo Scientific LTQ-FT or Thermo Scientific Exactive. HRMS: Bruker APEX III FT-MS (7 T magnet), MAT 95 (Finnigan), Thermo Scientific LTQ-FT or Thermo Scientific Exactive. GC-MS: Shimadzu GCMS-QP2010 Ultra instrument.

The molecular sieves used in this investigation were dried for 24 h at 150°C (sand bath) under vacuum prior to use and were stored and transferred under argon atmosphere.

Unless stated otherwise, all commercially available compounds (Strem, Fluka, Lancaster, Acros, TCI, Aldrich, Alfa Aesar) were used as received.

(Chloroethynyl)triisopropylsilane[1] and the alkyne substrates[2] were prepared according to literature procedures.

All ruthenium complexes were prepared according to literature procedures,[3,4] or were purchased from commercial suppliers:

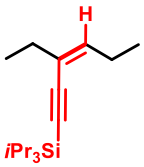


Commercially available [CAS: 99604-67-8]

E*JIC* 2**008,** 3*2121*[3]

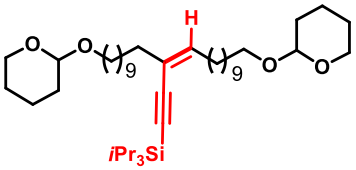
Organomet **1990**, *9,* 1843[4]

***trans*-Hydroalkynylation**

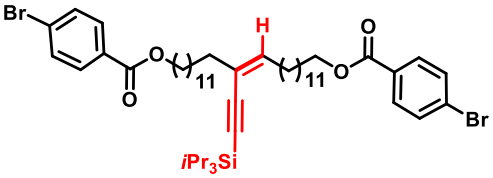
Representative Procedure for the *trans*-Hydroalkynylation of Symmetrical Alkynes. (*Z*)-(3-Ethylhex-3-en-1-yn-1-yl)triisopropylsilane (2). 

A flame-dried 10 mL pressure Schlenk tube was charged under Ar with $[Cp^*RuCl]_4$ (5.43 mg, 5 µmol, 2.5 mol%), 3-hexyne (16.4 mg, 0.2 mmol), ethynyltriisopropylsilane (**1a**) (43.7 mg, 0.24 mmol) and 1,2-dichloroethane (0.2 M, 1.0 mL). The Schlenk tube was closed and the mixture stirred at 80 °C for 42 h. For work up, the solvent was evaporated and the residue purified by flash chromatography (EtOAc/hexanes) on silica gel to give the title compound as a colorless oil (83%, *Z:E* = 93:7 (NMR)). ^{1}H NMR (500 MHz, CD_2Cl_2) δ = 5.69 (tt, *J* = 7.3, 2.4 Hz, 1H), 2.33-2.25 (m, 2H), 2.17-2.09 (m, 2H), 1.09 (m, 24H), 0.99 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 139.1, 124.6, 105.7, 94.4, 30.3, 24.0, 18.8, 13.8, 11.4, 10.9; IR (film, cm^{-1}): $\tilde{\nu}$ = 2962, 2942, 2865, 2138, 1461, 1382, 1198, 995, 882, 848, 674, 602, 459; HRMS (ESI): *m/z* calcd for $C_{17}H_{32}Si$ [M]: 264.2273; found: 264.2264.

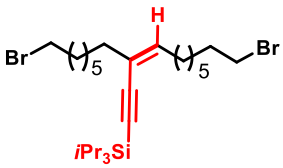
The following compounds were prepared analogously:

(*Z*)-Triisopropyl(14-((tetrahydro-2*H*-pyran-2-yl)oxy)-3-(10-((tetrahydro-2*H*-pyran-2-yl)oxy)decyl)-tetradec-3-en-1-yn-1-yl)silane (3a): 

Colorless oil (0.2 mmol scale; 106 mg, 77%, *Z:E* = 94:6 (NMR)); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.67 (t, *J* = 7.5 Hz, 1H), 4.56 (m, 2H), 3.75-3.69 (m, 2H), 3.75-3.69 (m, 2H), 3.52-3.46 (m, 2H), 3.40-3.34 (m, 2H), 2.26 (q, *J* = 7.1 Hz, 2H), 2.09 (t, *J* = 7.6 Hz, 2H), 1.89-1.79 (m, 2H), 1.74-1.67 (m, 2H), 1.60-1.49 (m, 16H), 1.30-1.26 (m, 24H), 1.08 (s, 21H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.6, 123.7, 106.1, 98.9, 94.1, 80.3, 67.8, 62.4, 37.0, 30.9, 30.8, 29.9, 29.76, 29.73, 29.68, 29.66, 29.63, 29.5, 29.4, 29.35, 29.32, 29.30, 29.0, 28.9, 28.4, 26.4, 25.6, 19.8, 18.8, 11.4; IR (film, cm^{-1}): $\tilde{\nu}$ = 2924, 2854, 1741, 1683, 1463, 1352, 1200, 1120, 1077, 1032, 992, 882, 814, 676, 460; HRMS (ESI+): *m/z* calcd for $C_{43}H_{80}SiO_4Na$ [M+Na]: 711.5724; found: 711.5716.

(*Z*)-13-((Triisopropylsilyl)ethynyl)hexacos-13-ene-1,26-diyl bis(4-bromobenzoate) (3b): 

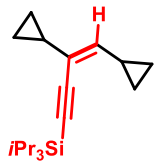
Prepared analogously with 5 mol% of $[Cp^*RuCl]_4$ (5.43 mg, 5 µmol). Colorless oil (0.1 mmol scale; 56 mg, 60%, *Z:E* = 92:8 (NMR)); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99-7.95 (m, 2H), 7.91-7.88 (m, 2H), 7.59-7.88 (m, 2H), 7.41-7.39 (m, 2H), 5.68 (t, *J* = 7.4 Hz, 1H), 4.30 (t, *J* = 6.5 Hz, 4H), 2.27 (q, *J* = 7.0 Hz, 2H), 2.09 (t, *J* = 7.2 Hz, 2H), 1.75 (p, *J* = 6.7 Hz, 4H), 1.55-1.50 (m, 2H), 1.44-1.34 (m, 10H), 1.31-1.26 (m, 24H), 1.08 (s, 21H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.0, 165.9, 139.3, 138.6, 131.8, 131.2, 131.0, 129.5, 129.1, 128.8, 128.0, 123.7, 106.1, 94.1, 65.5, 37.1, 30.8, 29.79, 29.77, 29.74, 29.72, 29.69, 29.65, 29.61, 29.4, 29.3, 28.9, 28.8, 28.4, 26.1, 18.8, 11.4; IR (film, cm^{-1}): $\tilde{\nu}$ = 2923, 2853, 2139, 1721, 1592, 1463, 1268, 1172, 1102, 1013, 883, 848, 757, 678; HRMS (ESI+): *m/z* calcd for $C_{51}H_{78}SiClBr_2O_4Na$ [M+Na]: 963.3934; found: 963.3934.

(*Z*)-(11-Bromo-3-(7-bromoheptyl)undec-3-en-1-yn-1-yl)triisopropylsilane (3c): 

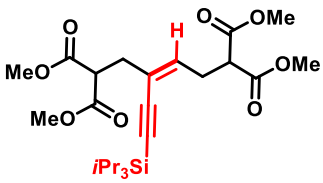
Colorless oil (0.2 mmol scale; 78 mg, 70%, *Z:E* = 94:6 (NMR)); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.68 (tt, *J* = 7.4, 1.0 Hz, 1H), 3.55-3.50 (m, 3H), 2.28 (q, *J* = 7.2 Hz, 2H), 2.10 (t, *J* = 7.3 Hz, 2H), 1.88-1.82 (m, 1H), 1.79-1.72 (m, 3H), 1.56-1.49 (m, 2H), 1.45-1.37 (m, 6H), 1.34-1.28 (m, 9H), 1.09 (s, 21H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.5, 123.7, 105.9, 94.3, 45.2, 37.0, 34.1, 32.9, 32.79, 30.77, 29.2, 29.1, 28.87, 28.85, 28.7, 28.3,

27.0, 26.9, 18.8, 11.4; IR (film, cm^{-1}): $\tilde{\nu}$ = 2929, 2859, 2138, 1462, 1264, 995, 907, 882, 728, 655, 604,453; HRMS (ESI+): *m/z* calcd for $C_{27}H_{50}SiBr_2Na$ [M+Na]: 583.1946; found: 583.1943.

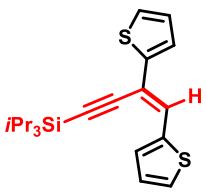
(*Z*)-(3,4-Ddicyclopropylbut-3-en-1-yn-1-yl)triisopropylsilane (4): Colorless oil (0.2 mmol scale; 40 mg, 70%, *Z:E* = 86:14 (NMR)); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.22 (d, *J* = 9.8 Hz, 1H), 2.00-1.91 (m, 1H), 1.45-1.39 (m, 1H), 1.08 (s, 21H), 0.84-0.79 (m, 2H), 0.74-0.70 (m, 2H), 0.62-0.57 (m, 2H), 0.45-0.42 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 141.01, 123.2, 102.5, 94.4, 18.6, 15.7, 13.2, 11.3, 7.3, 5.0; IR (film, cm^{-1}): $\tilde{\nu}$ = 2942, 2865, 2139, 1727, 1462, 1384, 1242, 966, 918, 882, 812, 675, 594, 461; HRMS (ESI): *m/z* calcd for $C_{19}H_{32}Si$ [M]: 288.2273; found: 288.2264.



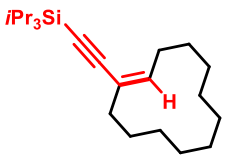
Tetramethyl (*Z*)-3-((triisopropylsilyl)ethynyl)hex-3-ene-1,1,6,6-tetracarboxylate (5): Colorless oil (0.2 mmol scale; 60 mg, 61%, *Z:E* = 96:4 (NMR)); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.79 (t, *J* = 7.3 Hz, 1H), 3.77 (t, *J* = 7.7 Hz, 1H), 3.71 (d, *J* = 2.3 Hz, 12H), 3.43 (t, *J* = 7.6 Hz, 1H), 2.83 (t, *J* = 7.3 Hz, 2H), 2.69 (d, *J* = 7.6 Hz, 2H), 1.07 (s, 21H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.1, 135.7, 122.5, 102.9, 98.0, 52.6, 51.1, 50.6, 36.1, 29.8, 18.6, 11.2; IR (film, cm^{-1}): $\tilde{\nu}$ = 2924, 2855, 2136, 1742, 1603, 1463, 1200, 1121, 1077, 1032, 993, 882, 815, 734, 676, 460; HRMS (ESI+): *m/z* calcd for $C_{25}H_{40}SiO_8Na$ [M+Na]: 519.2390; found: 519.2383.



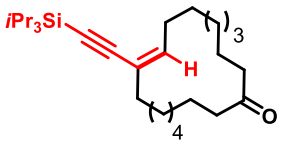
(*E*)-(3,4-Di(thiophen-2-yl)but-3-en-1-yn-1-yl)triisopropylsilane (6): Prepared analogously with 5 mol% of [Cp*RuCl]$_4$ (10.86 mg, 10 µmol) as a bright yellow oil (0.2 mmol scale; 26 mg, 35%, *Z:E* = 92:8 (NMR)); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40-7.31 (m, 2H), 7.21-7.16 (m, 2H), 7.05-7.00 (m, 2H), 6.91 (dd, *J* = 5.1, 3.7 Hz, 1H), 1.08 (s, 21H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 139.0, 131.5, 130.2, 128.1, 127.7, 127.2, 127.1, 126.7, 124.8, 115.3, 108.7, 92.1, 18.8, 11.5; IR (film, cm^{-1}): $\tilde{\nu}$ = 2941, 2863, 2132, 1461, 1246, 1051, 996, 881, 768, 693, 660, 603, 460; HRMS (ESI+): *m/z* calcd for $C_{21}H_{29}S_2Si$ [M+H]: 373.1480; found: 373.1474.



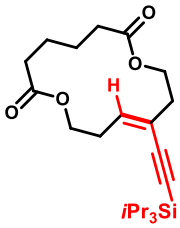
(*Z*)-(Cyclododec-1-en-1-ylethynyl)triisopropylsilane (7): Colorless oil (0.2 mmol scale; 49 mg, 70%, *Z:E* = 93:7 (NMR)); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.81 (tt, *J* = 7.8, 1.7 Hz, 1H), 2.39-2.34 (m, 2H), 2.20-2.17 (m, 2H), 1.60-1.53 (m, 4H), 1.31-1.26 (m, 12H), 1.10 (s, 21H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 141.1, 122.8, 106.0, 94.6, 36.5, 30.4, 27.2, 26.2, 26.1, 25.3, 24.9, 24.9, 24.8, 24.5, 18.8, 11.5; IR (film, cm^{-1}): $\tilde{\nu}$ = 2925, 2863, 2139, 1462, 1383, 1239, 1071, 995, 918, 882, 659, 604, 457; HRMS (ESI): *m/z* calcd for $C_{23}H_{42}Si$ [M]: 346.3056; found: 346.3044.



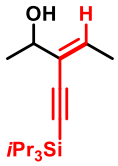
(*Z*)-9-((Triisopropylsilyl)ethynyl)cycloheptadec-9-en-1-one (8): Colorless oil (0.2 mmol scale; 67 mg, 78%, *Z:E* = 92:8 (NMR)); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.53 (tt, *J* = 7.7, 1.8 Hz, 1H), 2.37-2.30 (m, 6H), 2.14-2.11 (m, 2H), 1.61-1.50 (m, 6H), 1.44-1.37 (m, 2H), 1.29-1.23 (m, 10H), 1.08 (s, 21H), 0.88-0.82 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 213.2, 139.3, 123.8, 105.8, 94.2, 42.7, 42.3, 36.7, 30.2, 29.1, 29.0, 28.9, 28.7, 28.6, 28.1, 27.4, 27.3, 24.3, 24.0, 18.8, 11.4; IR (film, cm^{-1}): $\tilde{\nu}$ = 2927, 2861, 2139, 1711, 1460, 1365, 1242, 995, 675, 660, 614, 459; HRMS (ESI+): *m/z* calcd for $C_{28}H_{51}OSi$ [M+H]: 431.3709; found: 431.3707.



(*Z*)-11-((Triisopropylsilyl)ethynyl)-1,8-dioxacyclotetradec-11-ene-2,7-dione (9): Prepared analogously with 5 mol% of $[Cp^*RuCl]_4$ (10.86 mg, 10 µmol) as a colorless oil (0.2 mmol scale; 60 mg, 74%, *Z:E* = 93:7 (NMR)); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.74 (tt, *J* = 7.3, 1.2 Hz, 1H), 4.28-4.26 (m, 2H), 4.16-4.14 (m, 2H), 2.69-2.66 (m, 2H), 2.47-2.45 (m, 2H), 2.34-2.29 (m, 4H), 1.62-1.57 (m, 4H), 1.07 (s, 21H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.3, 172.9, 136.4, 122.8, 103.7, 96.2, 63.3, 61.6, 36.2, 35.2, 35.1, 30.2, 24.79, 24.74, 18.7, 11.3; IR (film, cm^{-1}): $\tilde{\nu}$ = 2940, 2863, 2143, 1728, 1462, 1380, 1268, 1238, 1141, 1065, 1017, 998, 881, 862, 796, 660, 601, 574, 446; HRMS (ESI+): *m/z* calcd for $C_{23}H_{38}O_4SiNa$ [M+Na]: 429.2437; found: 429.2434.



***trans*-Hydroalkynylation of a Propargyl Alcohol.** A flame-dried 10 mL pressure Schlenk tube was charged under Ar with $[Cp^*RuCl]_4$ (5.43 mg, 5 µmol, 2.5 mol%), pent-3-yn-2-ol (**10**) (16.8 mg, 0.2 mmol), ethynyltriisopropylsilane (**1a**) (43.7 mg, 0.24 mmol) and 1,2-dichloroethane (0.2 M, 1.0 mL). The Schlenk tube was closed and the mixture stirred at 80 °C for 24 h. After evaporation of the solvent, the residue was purified by flash chromatography (4% EtOAc/hexanes) on silica gel to give the *trans*-hydroalkynylated product as colorless oil (45 mg, 84%, α-*trans*:β-*trans*:α-*cis*:β-*cis* = 74:10:0:16 (NMR)).



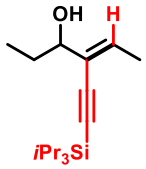
Spectral data of the major isomer (*E*)-3-((triisopropylsilyl)ethynyl)pent-3-en-2-ol (**11aa**) (α-*trans*): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.02 (qd, *J* = 6.8, 0.9 Hz, 1H), 4.25 (qt, *J* = 6.8, 0.78 Hz, 1H), 1.89 (dd, *J* = 6.8, 0.5 Hz, 3H), 1.78 (bs, 1H), 1.37 (d, *J* = 6.8 Hz, 3H), 1.10 (s, 21H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 132.6, 129.2, 102.5, 97.8, 70.8, 22.8, 18.8, 16.1, 11.3.

Spectral characteristic data of the minor isomer (*Z*)-4-methyl-6-(triisopropylsilyl)hex-3-en-5-yn-2-ol (**11ab**) (β-*trans*)**:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.72 (dq, *J* = 7.9, 1.5 Hz, 1H), 4.83-4.77 (m, 1H), 1.86 (d, *J* = 1.4 Hz, 3H), 1.78 (bs, 1H), 1.27 (d, *J* = 6.4 Hz, 3H), 1.78 (s, 21H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 141.9, 119.4, 105.2, 96.0, 67.1, 23.2, 18.7, 15.8, 11.3; IR (film, cm^{-1}): $\tilde{\nu}$ = 3426, 2943, 2893, 2866, 2144, 1715, 1462, 1368, 1227, 1071, 995, 881, 675, 660, 577, 459; HRMS (ESI+): *m/z* calcd for $C_{16}H_{30}SiONa$ [M+Na]: 289.1964; found: 289.1957.

Spectral data of the minor isomer (*E*)-4-methyl-6-(triisopropylsilyl)hex-3-en-5-yn-2-ol (**11ac**) (β-*cis*)**:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.88 (dq, *J* = 8.4, 1.4 Hz, 1H), 4.63-4.56 (m, 1H), 1.86 (d, *J* = 1.5 Hz, 3H), 1.52 (s, 1H), 1.27 (d, *J* = 6.3 Hz, 3H), 1.07 (s, 21H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 140.9, 119.8, 109.5, 88.5, 64.7, 23.1, 18.7, 17.8, 11.4; IR (film, cm^{-1}): $\tilde{\nu}$ = 3426, 2943, 2893, 2866, 2144, 1715, 1462, 1368, 1227, 1071, 995, 881, 675, 660, 577, 459; HRMS (ESI+): *m/z* calcd for $C_{16}H_{30}SiONa$ [M+Na]: 289.1964; found: 289.1957.

The following compounds were prepared analogously:

(*E*)-4-((triisopropylsilyl)ethynyl)hex-4-en-3-ol (11ba): Colorless oil (0.2 mmol scale; 46 mg, 82%, α-*trans*:β-*trans*:α-*cis*:β-*cis* = 72:10:0:16).

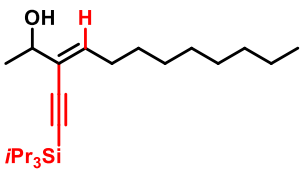


Spectral data of the major isomer (*E*)-4-((triisopropylsilyl)ethynyl)hex-4-en-3-ol (**11ba**) (α-*trans*): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.00 (qd, *J* = 6.8, 0.8 Hz, 1H), 3.94 (t, *J* = 6.6 Hz, 1H), 1.90 (dd, *J* = 6.8, 0.4 Hz, 3H), 1.74-1.65 (m, 3H), 1.09 (s, 21H), 0.89 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 134.0, 127.9, 102.4, 97.6, 76.5, 29.3, 18.8, 16.1, 11.3, 10.0.

Spectral characteristic data of the minor isomer (*E*)-5-methyl-7-(triisopropylsilyl)hept-4-en-6-yn-3-ol (**11bc**) (β-*cis*)**:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.84 (dq, *J* = 8.8, 1.5 Hz, 1H), 4.34-4.29 (m, 1H), 1.86 (d, *J* = 1.5 Hz, 3H), 1.67-1.60 (m, 1H), 1.53-1.48 (m, 1H), 1.44 (bs, 1H), 1.08 (s, 21H), 0.93 (t, *J* = 7.5 Hz, 3H).

Spectral characteristic data of the minor isomer (*Z*)-5-methyl-7-(triisopropylsilyl)hept-4-en-6-yn-3-ol (**11bb**) (β-*trans*)**:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.68 (dq, *J* = 8.2, 1.4 Hz, 1H); IR (film, cm^{-1}): $\tilde{\nu}$ = 2942, 2864, 2136, 1767, 1713, 1466, 1430, 1392, 1321, 1188, 1114, 996, 951, 882, 728, 659, 529; HRMS (ESI+): *m/z* calcd for $C_{17}H_{33}OSi$ [M+H]: 281.2301; found: 281.2291.

(*E*)-3-((triisopropylsilyl)ethynyl)dodec-3-en-2-ol (11ca): Colorless oil (0.2 mmol scale; 45 mg, 62%, α-*trans*:β-*trans*:α-*cis*:β-*cis* = 83:11:0:6).

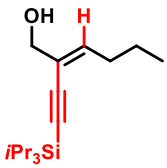


Spectral data of the major isomer (*E*)-3-((triisopropylsilyl)ethynyl)dodec-3-en-2-ol (**11ca**) (α-*trans*): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.96 (td, *J* = 7.5, 0.5 Hz, 1H), 4.25 (qd, *J* = 6.2, 0.5 Hz, 1H), 2.31 (q, *J* = 7.2 Hz, 2H), 1.72 (s, 1H), 1.37 (d, *J* = 6.4 Hz, 3H), 1.31-1.25 (m, 12H), 1.10 (s, 21H), 0.87 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.2, 128.3, 102.7, 97.3, 70.8, 32.0, 30.5, 29.5, 29.47, 29.42, 29.0, 22.9, 22.8, 18.8, 14.2, 11.4.

Spectral characteristic data of the minor isomer (*Z*)-4-((triisopropylsilyl)ethynyl)dodec-3-en-2-ol (**11cb**) (β-*trans*)**:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.84 (dq, *J* = 8.0, 1.4 Hz, 1H).

Spectral characteristic data of the minor isomer (*E*)-4-((triisopropylsilyl)ethynyl)dodec-3-en-2-ol (**11cc**) (β-*cis*)**:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.87 (dt, *J* = 8.7, 1.0 Hz, 1H).; IR (film, cm^{-1}): $\tilde{\nu}$ = 2941, 2863, 2135, 1762, 1714, 1468, 1432, 1390, 1321, 1182, 1112, 998, 952, 880, 724, 652, 520; HRMS (ESI+): *m/z* calcd for $C_{23}H_{45}OSi$ [M+H]: 365.3240; found: 365.3231.

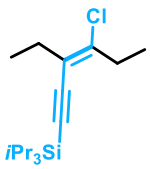
(*E*)-2-((triisopropylsilyl)ethynyl)hex-2-en-1-ol (11da): Colorless oil (0.2 mmol scale; 36 mg, 65%, ratio of α-*trans*:β-*trans*:α-*cis*:β-*cis* isomers = 65:6:0:29). Spectral data of the major isomer (α-*trans*) **(11da)**; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.98 (tt, *J* = 7.6, 1.3 Hz, 1H), 4.11 (q, *J* = 1.0 Hz, 2H), 2.31 (q, *J* = 7.4 Hz, 2H), 1.71 (s, 1H), 1.44 (h, *J* = 7.4 Hz, 2H), 1.09 (s, 21H), 0.92 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 139.2, 123.8, 103.4, 96.4, 66.0, 32.6, 22.3, 18.7, 13.9, 11.3.



Spectral data of the minor isomer (*Z*)-2-((triisopropylsilyl)ethynyl)hex-2-en-1-ol **(11d)** (α-*cis*)**:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.03 (tt, *J* = 7.7, 0.8 Hz, 1H), 4.17 (d, *J* = 5.7 Hz, 2H), 2.12 (q, *J* = 7.4 Hz, 2H), 1.75 (t, *J* = 6.1 Hz, 1H), 1.43 (h, *J* = 7.3 Hz, 2H), 1.08 (s, 21H), 0.92 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 139.2, 123.8, 103.4, 96.4, 66.0, 32.6, 22.3, 18.7, 13.9, 11.3; IR (film, cm^{-1}): $\tilde{\nu}$ = 3313, 2942, 2892, 2865, 2141, 1462, 1382, 1366, 1240, 1107, 1047, 995, 882, 817, 675, 588, 469; HRMS (ESI+): *m/z* calcd for $C_{17}H_{32}SiONa$ [M+Na]: 303.2120; found: 303.2113.

trans-Chloroalkynylation

Representative Procedure for the *trans*-Chloroalkynylation. (*E*)-(4-Chloro-3-ethylhex-3-en-1-yn-1-yl)triisopropylsilane (13). A flame-dried 10 mL pressure Schlenk tube was charged under Ar with $[Cp^*RuCl]_4$ (5.43 mg, 5 µmol, 2.5 mol%), 3-hexyne (16.4 mg, 0.2 mmol), (chloroethynyl)triisopropylsilane (**1b**) (51.8 mg, 0.24 mmol), and 1,2-dichloroethane (0.2 M, 1.0 mL). The Schlenk tube was closed and the resulting mixture stirred at 80 °C for 42 h. After completion of the reaction, the solvent was evaporated and the residue purified by flash chromatography (pentane) on silica gel to give the title compound as a colorless oil (54 mg, 90%, *E:Z* = 93:7 (NMR)). Spectral data of the major isomer**:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.70 (q, *J* = 7.3 Hz, 2H),

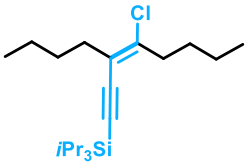


2.33 (q, J = 7.6 Hz, 2H), 1.16-1.11 (m, 6H), 1.09 (s, 21H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 144.3, 121.2, 104.4, 95.9, 31.7, 26.6, 18.7, 18.6, 12.3, 11.4; IR (film, cm^{-1}): $\tilde{\nu}$ = 2942, 2892, 2865, 2138, 1605, 1461, 1383, 1242, 1113, 995, 926, 875, 775, 660, 458; HRMS (ESI+): m/z calcd for $C_{17}H_{32}ClSi$ [M+H]: 299.1962; found: 299.1956.

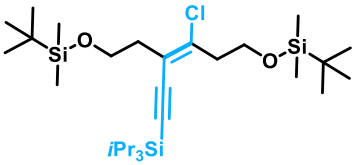
Larger Scale Reaction with Reduced Catalyst Loading. (*E*)-(4-Chloro-3-ethylhex-3-en-1-yn-1-yl)triisopropylsilane (13). A flame-dried 100 mL pressure Schlenk flask was charged under Ar with $[Cp^*RuCl]_4$ (165.7 mg, 0.152 mmol, 1.25 mol%), 3-hexyne (1.00 g, 12.19 mmol, 1 equiv), (chloroethynyl)triisopropylsilane (3.16 mg, 14.62 mmol, 1.2 equiv) and 1,2-dichloroethane (60 mL). The Schlenk tube was closed and the resulting mixture stirred at 80 °C for 42 h. After reaching ambient temperature, the solvent was evaporated and the residue was purified by flash chromatography (pentane) on silica gel to afford the title compound as a colorless oil (3.36 g, 92%, $E:Z \geq$ 95:5 (NMR)); spectral data as compiled above.

The following compounds were prepared in analogy to the representative procedure:

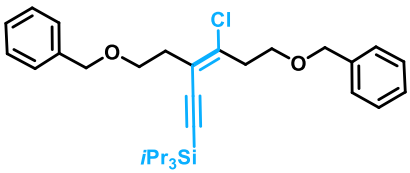
(*E*)-(3-Butyl-4-chlorooct-3-en-1-yn-1-yl)triisopropylsilane (14): Colorless oil (0.2 mmol scale; 65 mg, 92%, $E:Z$ = 93:7 (NMR)); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.70 (t, J = 7.5 Hz, 2H), 2.33 (t, J = 7.4 Hz, 2H), 1.61-1.51 (m, 4H), 1.40-1.29 (m, 4H), 1.09 (s, 21H), 0.92 (td, J = 7.4, 2.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 143.5, 120.7, 104.9, 95.7, 37.9, 32.9, 29.98, 29.90, 22.2, 22.0, 18.78, 18.72, 14.0, 11.4; IR (film, cm^{-1}): $\tilde{\nu}$ = 2957, 2925, 2863, 2148, 1608, 1462, 1380, 1242, 1070, 1016, 996, 882, 747, 675, 607, 456; HRMS (ESI+): m/z calcd for $C_{21}H_{40}SiCl$ [M+H]: 355.2588; found: 355.2577.

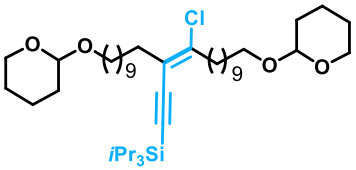


(*E*)-7-Chloro-2,2,3,3,12,12,13,13-octamethyl-8-((triisopropylsilyl)ethynyl)-4,11-dioxa-3,12-disilatetradec-7-ene (15a): Colorless oil (0.11 mmol scale; 60 mg, 98%, $E:Z$ = 95:5 (NMR)); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.81-3.77 (m, 4H), 2.92 (t, J = 6.8 Hz, 2H), 2.59 (t, J = 7.5 Hz, 2H), 1.08 (s, 21H), 0.89 (s, 9H), 0.88 (s, 9H), 0.06 (s, 6H), 0.04 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 141.4, 118.8, 104.3, 96.2, 61.2, 60.7, 41.5, 37.1, 26.1, 25.9, 18.8, 18.4, 18.3, 11.4, -5.15, -5.28; IR (film, cm^{-1}): $\tilde{\nu}$ = 3322, 2942, 2864, 2144, 1606, 1462, 1253, 1045, 881, 835, 776, 661, 458; HRMS (ESI+): m/z calcd for $C_{29}H_{59}ClSi_3O_2Na$ [M+Na]: 581.3409; found: 581.3403.

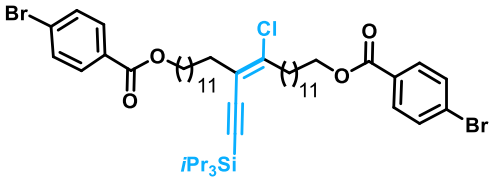


(*E*)-(6-(Benzyloxy)-3-(2-(benzyloxy)ethyl)-4-chlorohex-3-en-1-yn-1-yl)triisopropylsilane (15b): Prepared analogously with 5 mol% of $[Cp^*RuCl]_4$ (6.52 mg, 6 µmol); colorless oil (0.12 mmol scale; 28 mg, 45%, $E:Z$ = 93:7 (NMR)); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32-7.23 (m, 10H), 4.51 (d, J = 4.4 Hz, 4H), 3.71-3.65 (m, 4H), 3.04 (t, J = 6.8 Hz, 2H), 2.68 (t, J = 7.2 Hz, 2H), 1.06 (s, 21H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 141.0, 138.5, 138.4, 130.8, 128.47, 128.45, 127.7, 127.69, 127.6, 119.1, 103.8, 97.0, 73.0, 72.8, 68.0, 67.6, 38.6, 33.8, 18.8, 11.3; IR (film, cm^{-1}): $\tilde{\nu}$ = 2941, 2863, 2137, 1726, 1605, 1455, 1362, 1094, 995, 882, 733, 696, 676, 662, 458; HRMS (ESI+): m/z calcd for $C_{31}H_{43}ClSiO_2Na$ [M+Na]: 533.2619; found: 533.2619.

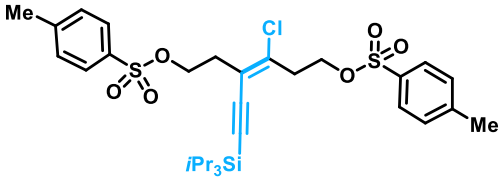


(*E*)-(4-Chloro-14-((tetrahydro-2*H*-pyran-2-yl)oxy)-3-(10-((tetrahydro-2*H*-pyran-2-yl)oxy)decyl)tetradec-3-en-1-yn-1-yl)triisopropylsilane (15c): 

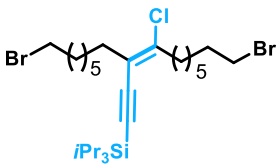
Colorless oil (0.2 mmol scale; 108 mg, 75%, *E:Z* = 91:9 (NMR)); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.57-4.55 (m, 2H), 3.89-3.83 (m, 2H), 3.74-3.69 (m, 2H), 3.51-3.46 (m, 2H), 3.39-3.34 (m, 2H), 2.67 (t, *J* = 7.2 Hz, 2H), 2.29 (t, *J* = 7.3 Hz, 2H), 1.86-1.78 (m, 2H), 1.73-1.67 (m, 2H), 1.60-1.52 (m, 16H), 1.34-1.26 (m, 24H), 1.07 (s, 21H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 143.5, 120.6, 104.9, 98.9, 95.6, 67.8, 62.4, 38.2, 33.2, 30.9, 29.9, 29.7, 29.67, 29.64, 29.5, 29.0, 28.8, 27.7, 26.3, 25.6, 19.8, 18.7, 11.4; IR (film, cm^{-1}): $\tilde{\nu}$ = 2924, 2855, 2139, 1741, 1603, 1463, 1352, 1200, 1121, 1077, 1032, 993, 882, 815, 676, 458; HRMS (ESI+): *m/z* calcd for $C_{43}H_{79}SiClO_4Na$ [M+Na]: 745.5334; found: 745.5334.

(*E*)-13-Chloro-14-((triisopropylsilyl)ethynyl)hexacos-13-ene-1,26-diyl bis(4-bromobenzoate) (15d): 

Prepared analogously with 5 mol% of $[Cp^*RuCl]_4$ (5.43 mg, 5 µmol); colorless oil (0.1 mmol scale; 85 mg, 87%, *E:Z* = 95:5 (NMR)); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91-7.88 (m, 4H), 7.58-7.55 (m, 4H), 4.30 (t, *J* = 6.8 Hz, 4H), 2.68 (t, *J* = 7.3 Hz, 2H), 2.31 (t, *J* = 7.3 Hz, 2H), 1.74 (p, *J* = 6.7 Hz, 4H), 1.59-1.53 (m, 4H), 1.46-1.40 (m, 4H), 1.34-1.24 (m, 28H), 1.08 (s, 21H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.0, 143.5, 131.7, 131.2, 129.5, 128.7, 128.0, 120.7, 105.0, 95.6, 65.5, 38.2, 33.2, 29.77, 29.73, 29.70, 29.68, 29.60, 29.4, 29.1, 29.0, 28.89, 28.82, 27.75, 27.74, 26.16, 22.7, 18.8, 11.4; IR (film, cm^{-1}): $\tilde{\nu}$ = 2923, 2854, 2137, 1721, 1591, 1463, 1397, 1268, 1172, 1101, 1069, 1012, 882, 847, 756, 678, 468; HRMS (ESI+): *m/z* calcd for $C_{51}H_{77}SiClBr_2O_4Na$ [M+Na]: 997.3544; found: 997.3551.

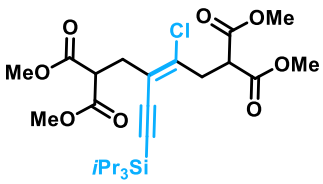
(*E*)-3-Chloro-4-((triisopropylsilyl)ethynyl)hex-3-ene-1,6-diyl bis(4-methylbenzenesulfonate) (15e): 

Colorless oil (0.2 mmol scale; 63 mg, 50%, *E:Z* = 89:11 (NMR)); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (dd, *J* = 7.6, 5.6 Hz, 4H), 7.33 (d, *J* = 7.8 Hz, 4H), 4.15 (q, *J* = 6.3 Hz, 4H), 3.00 (t, *J* = 6.6 Hz, 2H), 2.62 (t, *J* = 7.0 Hz, 2H), 2.43 (s, 6H), 1.01 (s, 21H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 144.9, 144.8, 139.2, 133.1, 132.9, 129.97, 129.94, 128.05, 128.00, 118.5, 101.9, 99.4, 67.4, 66.6, 37.4, 32.9, 21.7, 18.6, 11.1; IR (film, cm^{-1}): $\tilde{\nu}$ = 2943, 2864, 2145, 1598, 1462, 1361, 1174, 1096, 973, 882, 813, 766, 660, 552, 491; HRMS (ESI+): *m/z* calcd for $C_{31}H_{43}SiClS_2O_6Na$ [M+Na]: 661.1857; found: 661.1854.

(*E*)-(11-Bromo-3-(7-bromoheptyl)-4-chloroundec-3-en-1-yn-1-yl)triisopropylsilane (15f): 

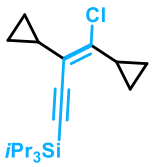
Colorless oil (0.2 mmol scale; 110 mg, 92%, *E:Z* = 95:5 (NMR)); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.52 (t, *J* = 6.7 Hz, 2H), 3.39 (t, *J* = 6.8 Hz, 2H), 2.69 (t, *J* = 7.2 Hz, 2H), 2.32 (t, *J* = 7.2 Hz, 2H), 1.88-1.81 (m, 2H), 1.79-1.72 (m, 2H), 1.62-1.52 (m, 4H), 1.46-1.39 (m, 4H), 1.36-1.30 (m, 8H), 1.08 (s, 21H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 143.4, 120.7, 104.8, 95.9, 45.2, 38.1, 34.07, 33.1, 32.97, 32.90, 32.71, 28.85, 28.7, 28.64, 28.27, 27.6, 26.98, 26.94, 18.8, 11.4; IR (film, cm^{-1}): $\tilde{\nu}$ = 2929, 2861, 2138, 1603, 1462, 1252, 1072, 995, 882, 726, 659, 460; HRMS (ESI+): *m/z* calcd for $C_{27}H_{50}ClBr_2Si$ [M+H]: 595.1737; found: 595.1743.

tetramethyl (*E*)-3-chloro-4-((triisopropylsilyl)ethynyl)hex-3-ene-1,1,6,6-tetracarboxylate (16): Colorless



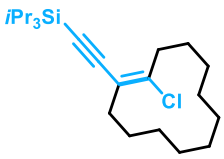
oil (0.2 mmol scale; 99 mg, 93%, *E:Z* = 93:7 (NMR)); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.81 (t, *J* = 7.7 Hz, 1H), 3.75 (t, *J* = 7.8 Hz, 1H), 3.71 (d, *J* = 3.7 Hz, 12H), 3.30 (d, *J* = 7.8 Hz, 2H), 2.92 (d, *J* = 7.5 Hz, 2H), 1.07 (s, 21H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.9, 168.5, 140.3, 119.5, 101.8, 99.9, 52.77, 52.73, 49.96, 49.93, 36.9, 32.1, 18.6, 11.2; IR (film, cm^{-1}): $\tilde{\nu}$ = 2952, 2866, 2138, 1737, 1435, 1341, 1236, 1151, 1036, 882, 677, 625, 458; HRMS (ESI+): *m/z* calcd for $C_{25}H_{39}SiClO_8Na$ [M+Na]: 553.2000; found: 553.1994.

(*E*)-(4-Chloro-3,4-dicyclopropylbut-3-en-1-yn-1-yl)triisopropylsilane (17): Colorless oil (0.2 mmol scale;



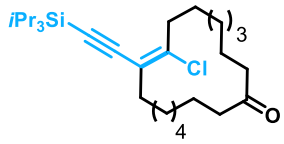
46 mg, 72%, *E:Z* = 80:20 (NMR)); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.53-2.47 (m, 1H), 2.05-1.99 (m, 1H), 1.07 (s, 21H), 0.93-0.89 (m, 2H), 0.83-0.78 (m, 2H), 0.77-0.70 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 143.1, 121.6, 101.6, 96.4, 18.4, 17.4, 12.8, 11.4, 6.2, 5.9; IR (film, cm^{-1}): $\tilde{\nu}$ = 2942, 2865, 2138, 1585, 1462, 1153, 1050, 1022, 995, 927, 887, 814, 673, 596, 461; HRMS (ESI+): *m/z* calcd for $C_{19}H_{32}ClSi$ [M+H]: 323.1962; found: 323.1954.

(*E*)-((2-chlorocyclododec-1-en-1-yl)ethynyl)triisopropylsilane (18): Colorless oil (0.2 mmol scale; 75 mg,



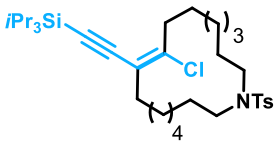
98%, *E:Z* = 93:7 (NMR)); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.34-3.27 (m, 1H), 2.84-2.77 (m, 1H), 2.33-2.27 (m, 1H), 2.12-2.05 (m, 1H), 1.75-1.67 (m, 4H), 1.61-1.45 (m, 3H), 1.49-1.21 (m, 9H), 1.10 (s, 21H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 144.4, 122.0, 105.6, 96.2, 37.0, 32.9, 26.0, 25.83, 25.81, 25.4, 25.2, 25.0, 24.8, 24.7, 18.7, 11.5; IR (film, cm^{-1}): $\tilde{\nu}$ = 2925, 2863, 2140, 1597, 1462, 1383, 1241, 1197, 995, 919, 881, 675, 660, 611, 459; HRMS (ESI+): *m/z* calcd for $C_{23}H_{42}ClSi$ [M+H]: 381.2744; found: 381.2736.

(*E*)-9-Chloro-10-((triisopropylsilyl)ethynyl)cycloheptadec-9-en-1-one (19): Colorless oil (0.2 mmol scale;



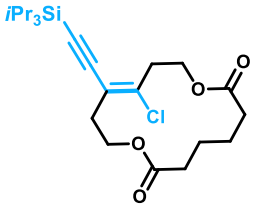
77 mg, 83%, *E:Z* = 98:2 (NMR)); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.74 (s, 2H), 2.34 (t, *J* = 7.0 Hz, 6H), 1.63-1.54 (m, 8H), 1.29-1.25 (m, 12H), 1.08 (s, 21H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 213.1, 143.7, 121.3, 105.0, 95.9, 42.8, 42.3, 37.5, 32.9, 29.0, 28.84, 28.81. 28.7, 27.7, 27.6, 27.4, 27.3, 24.2, 24.1, 18.8, 11.4; IR (film, cm^{-1}): $\tilde{\nu}$ = 2927, 2861, 2139, 1711, 1460, 1365, 1242, 1073, 995, 919, 882, 675, 614, 459; HRMS (ESI+): *m/z* calcd for $C_{28}H_{49}ClSiONa$ [M+Na]: 487.3139; found: 487.3131.

(*E*)-9-Chloro-1-tosyl-10-((triisopropylsilyl)ethynyl)azacycloheptadec-9-ene (20): Colorless oil (0.11 mmol



scale; 59 mg, 87%, *E:Z* = 99:1 (NMR)); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66 (m, 2H), 7.28 (m, 2H), 2.97 (t, *J* = 7.2 Hz, 4H), 2.41 (s, 3H), 1.70-1.52 (m, 10H), 1.39-1.21 (m, 14H), 1.07 (s, 21H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 143.6, 142.9, 136.3, 129.6, 127.2, 121.2, 104.8, 96.0, 50.5, 50.4, 37.5, 32.8, 28.9, 28.7, 27.5, 27.2, 27.1, 26.9, 26.5, 26.3, 21.5, 18.8, 11.4; IR (film, cm^{-1}): $\tilde{\nu}$ = 2928, 2861, 2141, 1721, 1599, 1461, 1342, 1160, 1091, 883, 814, 654, 550; HRMS (ESI+): *m/z* calcd for $C_{34}H_{57}ClNO_2SSi$ [M+H]: 606.3568; found: 606.3562.

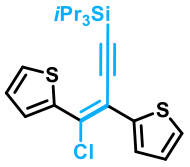
(*E*)-11-Chloro-12-((triisopropylsilyl)ethynyl)-1,8-dioxacyclotetradec-11-ene-2,7-dione (21): Prepared



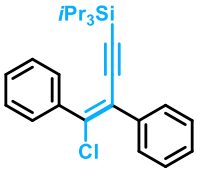
analogously with 5 mol% of $[Cp^*RuCl]_4$ (10.86 mg, 10 µmol); colorless oil (0.2 mmol scale; 76 mg, 86%, *E:Z* = 93:7 (NMR)); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.53-4.47 (m, 2 H), 4.17-4.12 (m, 2H), 3.76 (ddd, *J* = 15.5, 11.5, 4.2 Hz, 1H), 3.27 (ddd, *J* = 15.5, 11.6, 4.0 Hz, 1H), 2.51-2.39 (m, 3H), 2.25-2.17 (m, 3H), 1.85-1.68 (m, 2H), 1.46-1.38 (m, 2H), 1.08 (s, 21H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.9(one carbon

is overlapped), 140.7, 120.2, 102.7, 97.9, 61.9, 60.8, 36.9, 35.33, 35.30, 32.1, 24.6, 24.5, 18.7, 11.3; IR (film, cm^{-1}): $\tilde{\nu}$ = 2939, 2863, 2145, 1731, 1613, 1465, 1275, 1265, 1239, 1138, 1099, 1069, 1010, 993, 939, 879, 820, 672, 658, 615, 500, 481; HRMS (ESI+): *m/z* calcd for $C_{23}H_{38}O_4ClSi$ [M+Na]: 463.2047; found: 463.2048.

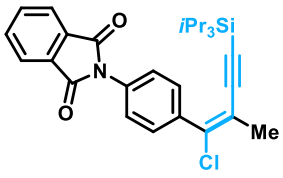
(*Z*)-(4-Chloro-3,4-di(thiophen-2-yl)but-3-en-1-yn-1-yl)triisopropylsilane (22): Prepared analogously with 5 mol% of $[Cp^*RuCl]_4$ (8.15 mg, 7 µmol) as a bright yellow oil (0.15 mmol scale; 35 mg, 57%, *E:Z* = 90:10 (NMR)); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (dd, *J* = 3.8, 1.2 Hz, 1H), 7.75 (dd, *J* = 3.8, 1.2 Hz, 1H), 7.41-7.39 (m, 2H), 7.08 (dd, *J* = 5.2, 3.7 Hz, 1H), 7.04 (dd, *J* = 5.2, 3.7 Hz, 1H), 1.14 (s, 21H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 141.2, 140.4, 130.7, 130.6, 130.3, 128.1, 127.5, 126.7, 126.5, 113.6, 104.8, 102.7, 18.8, 11.5; IR (film, cm^{-1}): $\tilde{\nu}$ = 2941, 2863, 2134, 1461, 1422, 1355, 1237, 1062, 998, 881, 829, 696, 674, 459; HRMS (ESI+): *m/z* calcd for $C_{21}H_{28}ClS_2Si$ [M+H]: 407.1090; found: 407.1091.



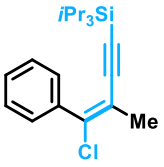
(*E*)-(4-Chloro-3,4-diphenylbut-3-en-1-yn-1-yl)triisopropylsilane (23): Colorless oil (0.2 mmol scale; 70 mg, 88%, *E:Z* = 45:55 (NMR)); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33-7.81 (m, 2H), 7.65-7.31 (m, 2H), 7.43-7.36 (m, 6H), 0.96 (s, 21H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 139.4, 138.8, 138.3, 129.4, 129.3, 129.1, 128.14, 128.11, 128.0, 122.0, 105.9, 97.5, 18.6, 11.3; major isomer (*cis*) (NMR)); NMR (400 MHz, $CDCl_3$): δ = 7.25-7.14 (m, 10H), 1.15 (s, 21H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.6, 137.8, 137.3, 129.9, 129.7, 128.8, 128.14, 128.10, 127.6, 123.2, 105.9, 99.7, 18.85, 11.50; IR (film, cm^{-1}): $\tilde{\nu}$ = 2942, 2864, 2134, 1462, 1444, 1261, 1219, 1219, 1068, 907, 882, 757, 732, 691, 461; HRMS (ESI+): *m/z* calcd for $C_{25}H_{32}ClSi$ [M+H]: 395.1962; found: 395.1954.



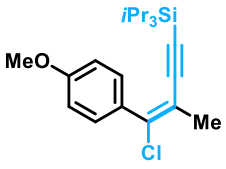
(*E*)-2-(4-(1-Chloro-2-methyl-4-(triisopropylsilyl)but-1-en-3-yn-1-yl)phenyl)isoindoline-1,3-dione (24): Prepared analogously on 3.83 mmol scale as a colorless solid (1.67 g, 92%, β-*trans*:α-*trans*:α-*cis*:β-*cis* = 96:1:1:2 (crude product); isomer ratio after recrystallization from CH_2Cl_2/MeOH (β-*trans*:α-*trans*:α-*cis*:β-*cis* = 98:0:1:1 (NMR)); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 5.5, 3.0 Hz, 2H), 7.89-7.85 (m, 2H), 7.79 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.46-7.42 (m, 2H), 2.20 (s, 3H), 1.01 (s, 21H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.1, 138.1, 137.7, 134.5, 131.8, 129.9, 125.6, 123.9, 117.7, 106.1, 96.8, 22.5, 18.6, 11.3; IR (film, cm^{-1}): $\tilde{\nu}$ = 2941, 2864, 2133, 1736, 1711, 1603, 1510, 1368, 1075, 920, 882, 830, 716, 666, 530, 461; HRMS (ESI+): *m/z* calcd for $C_{28}H_{32}SiO_2ClNNa$ [M+Na]: 500.1789; found: 500.1781.



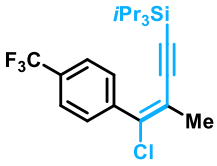
(*E*)-(4-Chloro-3-methyl-4-phenylbut-3-en-1-yn-1-yl)triisopropylsilane (25a): Colorless oil (0.2 mmol scale; 62 mg, 92%, β-*trans*:α-*trans*:α-*cis*:β-*cis* = 92:1:2:5 (NMR)); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72-7.69 (m, 2H), 7.34-7.28 (m, 3H), 2.18 (s, 3H), 0.99 (s, 21H)**;** ^{13}C NMR (101 MHz, $CDCl_3$): δ = 139.3, 138.4, 129.2, 128.7, 127.8, 117.0, 106.4, 95.9, 22.4, 18.6, 11.3; IR (film, cm^{-1}): $\tilde{\nu}$ = 2942, 2864, 2133, 1593, 1462, 1383, 1201, 1073, 995, 930, 906, 882, 758, 677, 659, 632, 565, 458; HRMS (ESI): *m/z* calcd for $C_{20}H_{29}SiCl$ [M]: 332.1719; found: 332.1719.



(*E*)-(4-Chloro-4-(4-methoxyphenyl)-3-methylbut-3-en-1-yn-1-yl)triisopropylsilane (25b): Colorless oil (0.2 mmol scale; 65 mg, 90%, β-*trans*:α-*trans*:α-*cis*:β-*cis* = 92:1:1:6 (NMR)); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70-7.67 (m, 2H), 6.85-6.81 (m, 2H), 3.81 (s, 3H), 2.16 (s, 3H), 1.01 (s, 21H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 159.8, 139.2, 130.9, 130.6, 115.7, 113.1, 106.8, 95.5, 55.4, 22.5, 18.7, 11.3; IR (film, cm^{-1}): $\tilde{\nu}$ = 2941, 2864, 2133, 1606, 1508, 1462, 1298, 1248, 1176, 1037, 916, 882, 828, 665, 609, 457; HRMS (ESI): *m/z* calcd for $C_{21}H_{31}SiClO$ [M]: 362.1833; found: 362.1826.

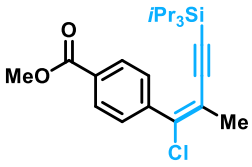


(*E*)-(4-Chloro-3-methyl-4-(4-(trifluoromethyl)phenyl)but-3-en-1-yn-1-yl)triisopropylsilane (25c):

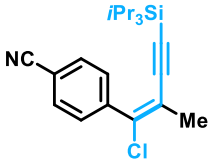


Colorless oil (0.2 mmol scale; 75 mg, 94%, β-*trans*:α-*trans*:α-*cis*:β-*cis* = 95:2:1:2 (NMR)); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (d, J = 8.2 Hz, 2H), 7.58 (d, J = 8.2 Hz, 2H), 2.19 (s, 3H), 0.97 (s, 21H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 141.9 (q, J = 1.2 Hz), 137.7, 130.6 (q, J = 32 Hz), 129.6, 123.1 (q, J = 271 Hz), 124.9 (q, J = 3.7 Hz), 119.0, 105.7, 97.2, 22.2, 18.6, 11.2; ^{19}F NMR (565 MHz, $CDCl_3$): δ = -62.9; IR (film, cm^{-1}): $\tilde{\nu}$ = 2944, 2866, 2137, 1617, 1463, 1408, 1322, 1167, 1129, 1068, 926, 882, 837, 676, 662, 460; HRMS (ESI): *m/z* calcd for $C_{21}H_{28}SiClF_3$ [M]: 400.1601; found: 400.1595.

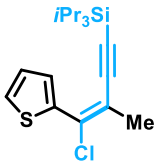
Methyl (*E*)-4-(1-chloro-2-methyl-4-(triisopropylsilyl)but-1-en-3-yn-1-yl)benzoate (25d): Colorless oil (0.2 mmol scale; 70 mg, 90%, β-*trans*:α-*trans*:α-*cis*:β-*cis* = 95:2:1:2 (NMR)); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99-7.97 (m, 2H), 7.81-7.78 (m, 2H), 3.92 (s, 3H), 2.19 (s, 3H), 0.98 (s, 21H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.7, 142.6, 137.8, 130.0, 129.2, 129.1, 118.6, 105.9, 97.4, 52.2, 22.6, 18.6, 11.2; IR (film, cm^{-1}): $\tilde{\nu}$ = 2943, 2865, 2137, 1727, 1608, 1462, 1435, 1273, 1191, 1107, 1019, 996, 925, 854, 770, 662, 459; HRMS (ESI): *m/z* calcd for $C_{22}H_{31}SiClO_2$ [M]: 390.1782; found: 390.1780.



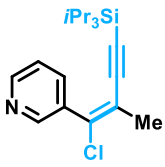
(*E*)-4-(1-Chloro-2-methyl-4-(triisopropylsilyl)but-1-en-3-yn-1-yl)benzonitrile (25e): Colorless oil (0.2 mmol scale; 69 mg, 96%, β-*trans*:α-*trans*:α-*cis*:β-*cis* = 94:3:1:2 (NMR)); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84-7.81 (m, 2H), 7.62-7.59 (m, 2H), 2.19 (s, 3H), 0.98 (s, 21H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 142.6, 136.6, 131.6, 129.9, 119.7, 118.6, 112.1, 105.4, 98.2, 22.6, 18.6, 11.2; IR (film, cm^{-1}): $\tilde{\nu}$ = 2942, 2864, 2227, 2140, 1605, 1502, 1462, 1462, 1203, 1183, 996, 926, 882, 836, 665, 553, 459; HRMS (ESI+): *m/z* calcd for $C_{21}H_{28}SiClNNa$ [M+Na]: 380.1577; found: 380.1572.



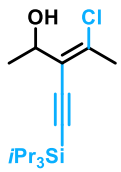
(*E*)-(4-Chloro-3-methyl-4-(thiophen-2-yl)but-3-en-1-yn-1-yl)triisopropylsilane (26): Colorless oil (0.2 mmol scale; 65 mg, 96%, β-*trans*:α-*trans*:α-*cis*:β-*cis* = 95:0:1:4 (NMR)); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (d, J = 3.7 Hz, 1H), 7.31 (dd, J = 5.0, 1.2 Hz, 1H), 7.00-6.98 (m, 1H), 2.22 (s, 3H), 1.13 (s, 21H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 140.6, 132.8, 129.2, 126.9, 126.5, 114.3, 106.8, 102.3, 23.4, 18.8, 11.4; IR (film, cm^{-1}): $\tilde{\nu}$ = 2942, 2864, 2134, 1462, 1383, 1231, 996, 881, 824, 669, 676, 459; HRMS (ESI): *m/z* calcd for $C_{18}H_{27}SiSCl$ [M]: 388.1286; found: 388.1286.



(*E*)-3-(1-Chloro-2-methyl-4-(triisopropylsilyl)but-1-en-3-yn-1-yl)pyridine (27): Colorless oil (0.2 mmol scale; 5 mol% of the catalyst were used for the reaction and reaction time was 72 h, 35 mg, 53%, β-*trans*:α-*trans*:α-*cis*:β-*trans* = 97:0:1:2 (NMR)); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.91 (d, J = 1.5 Hz, 1H), 8.52-8.50 (m, 1H), 7.98 (dt, J = 8.0, 1.8 Hz, 1H), 7.25-7.23 (m, 1H), 2.10 (s, 3H), 0.97 (s, 21H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 150.0, 149.3, 136.4, 135.5, 134.5, 122.6, 119.2, 105.5, 97.1, 22.2, 18.6, 11.2; IR (film, cm^{-1}): $\tilde{\nu}$ = 2942, 2865, 2143, 1582, 1463, 1463, 1411, 1211, 1072, 1019, 996, 918, 882, 804, 707, 663, 460; HRMS (ESI+): *m/z* calcd for $C_{19}H_{29}ClNSi$ [M+H]: 334.1758; found: 334.1754.



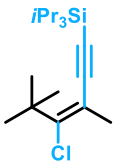
(*Z*)-4-chloro-3-((triisopropylsilyl)ethynyl)pent-3-en-2-ol (28); Colorless oil (0.2 mmol scale; 45 mg, 75%, ratio of α-*trans*:β-*trans*:α-*cis*:β-*cis* isomers = 52:45:2:1).



Spectral data of the major isomer (α-*trans*); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.83 (q, J = 6.3 Hz, 1H), 2.36 (s, 3H), 1.91 (s, 1H), 1.34 (d, J = 4.1 Hz, 3H), 1.09 (s, 21H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.4, 125.1, 99.6, 25.2, 21.8, 18.6, 11.1.

Spectral data of the minor isomer (*E*)-3-chloro-4-methyl-6-(triisopropylsilyl)hex-3-en-5-yn-2-ol (β -*trans*)**:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.27 (q, *J* = 6.2 Hz, 1H), 1.97 (s, 3H), 1.91 (s, 1H), 1.35 (d, *J* = 4.0 Hz, 3H), 1.08 (s, 21H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 145.6, 115.9, 103.9, 68.5, 21.1, 20.1, 18.59, 18.58, 11.1; IR (film, cm^{-1}): $\tilde{\nu}$ = 3417, 2942, 2892, 2865, 2140, 1724, 158, 1606, 1462, 1368, 1243, 1139, 1073, 997, 905, 881, 830, 663, 612, 459; HRMS (ESI+): *m/z* calcd for $C_{16}H_{29}SiONa$ [M+Na]: 323.1574; found: 323.1567.

(*E*)-(4-chloro-3,5,5-trimethylhex-3-en-1-yn-1-yl)triisopropylsilane (29): Colorless oil (0.2 mmol scale; 37 mg, 59%, ratio of α-*trans*:β-*trans*:α-*cis*:β-*cis* isomers = 70:10:10:10).



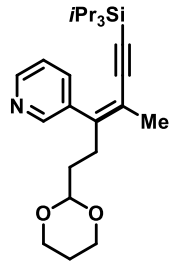
Spectral data of the major isomer (β-*trans*); ^{1}H NMR (400 MHz, $CDCl_3$): 1.97 (s, 3H), 1.33 (s, 9H), 1.02 (s, 21H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.0, 113.9, 106.7, 99.0, 30.4, 18.7, 11.5; IR (film, cm^{-1}): $\tilde{\nu}$ = 2943, 2865, 2137, 2063, 1462, 1365, 1072, 1365, 1072, 995, 904, 882, 664, 458; HRMS (ESI): *m/z* calcd for $C_{18}H_{33}SiCl$ [M]: 312.2040; found: 312.2031.

Spectral characteristic data of the minor isomer (*E*)-(3-(tert-butyl)-4-chloropent-3-en-1-yn-1-yl)triisopropylsilane (α-*trans*)**:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.36 (s, 1H).

Spectral data of the minor isomer (*Z*)-(4-chloro-3,5,5-trimethylhex-3-en-1-yn-1-yl)triisopropylsilane (β-*cis*); ^{1}H NMR (400 MHz, $CDCl_3$): 2.09 (s, 3H), 1.31 (s, 9H), 1.10 (s, 21H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 148.1, 115.8, 109.1, 94.0, 30.7, 18.8, 11.4; HRMS (ESI): *m/z* calcd for $C_{18}H_{33}SiCl$ [M]: 312.2040; found: 312.2031.

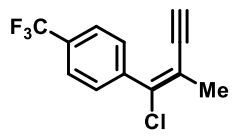
Downstream Functionalization

(*Z*)-3-(1-(1,3-Dioxan-2-yl)-4-methyl-6-(triisopropylsilyl)hex-3-en-5-yn-3-yl)pyridine (30). A flame dried



Schlenk tube was charged with (*E*)-3-(1-chloro-2-methyl-4-(triisopropylsilyl)but-1-en-3-yn-1-yl)pyridine (**27**) (44.6 mg, 0.134 mmol) in THF (1.5 mL) and $Fe(acac)_3$ (3.02 mg, 6 µmol 5 mol%). The resulting solution was cooled to −78 °C before a solution of (2-(1,3-dioxan-2-yl)ethyl)magnesium bromide (0.5 M in THF, 0.5 mL) was slowly added, causing an immediate color change from red to dark brown/black. Stirring was continued at this temperature for 3 h and for another 20 h at room temperature. The reaction was quenched with water (3 mL), the aqueous layer was extracted with ethyl acetate (3 x 5 mL), the combined organic layers were dried over Na_2SO_4 and evaporated, and the residue purified by flash chromatography (10% EtOAc/hexanes) to give the title compound as a colorless oil (30 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.56 (s, 1H), 8.44 (d, *J* = 3.7 Hz, 1H), 7.64 (dt, *J* = 7.7, 1.6 Hz, 1H), 7.20 (dd, *J* = 8.1, 4.9 Hz, 1H), 4.43 (t, *J* = 5.0 Hz, 1H), 4.07-4.02 (m, 2H), 3.68 (td, *J* = 12.1, 2.1 Hz, 2H), 2.57 (t, *J* = 7.7 Hz, 2H), 2.03 (s, 3H), 1.60-1.54 (m, 2H), 1.32-1.25 (m, 2H), 0.91 (s, 21H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 148.6, 146.8, 142.9, 135.1, 121.7, 116.6, 107.5, 100.2, 91.5, 65.8, 32.0, 26.8, 24.6, 18.5, 17.6, 17.4, 10.1; IR (film, cm^{-1}): $\tilde{\nu}$ = 2941, 2863, 2137, 1564, 1462, 1407, 1379, 1241, 1134, 1087, 996, 882, 713, 660, 466; HRMS (ESI+): *m/z* calcd for $C_{25}H_{40}NO_2Si$ [M+H]: 414.2828; found: 414.2820.

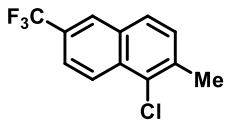
(*E*)-1-(1-Chloro-2-methylbut-1-en-3-yn-1-yl)-4-(trifluoromethyl)benzene (31). A flame-dried 10 mL



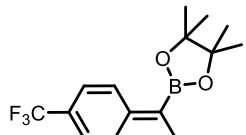
Schlenk flask equipped with a magnetic stirring bar was charged with (*E*)-(4-chloro-3-methyl-4-(4-(trifluoromethyl)phenyl)but-3-en-1-yn-1-yl)triisopropylsilane (**25c**) (160 mg, 0.4 mmol) and THF (2 mL). TBAF (208 mg, 0.8 mmol, 1.0 M in THF) was added dropwise, causing an immediate color change. Stirring was continued for 30 min before the solvent was evaporated under reduced pressure. The residue was purified by flash chromatography (pentane) to give the title compound as a colorless oil (90 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80-7.77 (m, 2H), 7.64-7.60 (m, 2H), 3.09 (s, 1H), 2.20 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ =

141.4 (*J* = 1.5 Hz), 138.3, 130.6 (*J* = 32.4 Hz), 129.5, 125.0 (*J* = 4.0 Hz), 122.6 (*J* = 272.4 Hz), 117.6, 82.7, 82.6, 22.5, 22.1; ^{19}F NMR (282 MHz, $CDCl_3$): δ = −62.3; IR (film, cm^{-1}): $\tilde{\nu}$ = 3304, 1618, 1408, 1322, 1167, 1126, 1068, 1020, 916, 832, 612, 451; HRMS (ESI): *m*/*z* calcd for $C_{12}H_8ClF_3$ [M]: 244.0267; found: 244.0261.

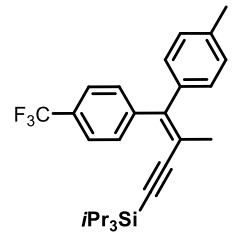
1-Chloro-2-methyl-6-(trifluoromethyl)naphthalene (32): A flame dried Schlenk tube was charged with (*E*)-1-(1-chloro-2-methylbut-1-en-3-yn-1-yl)-4-(trifluoromethyl)benzene (**31**) (48.9 mg, 0.2 mmol, 1 equiv), $PtCl_2$ (2.65 mg, 0.01 mmol, 5 mol%) and toluene (1.5 mL). The mixture was stirred at 100 °C for 24 h before the solvent was evaporated under reduced pressure. The residue was purified by flash chromatography (pentane) to give the title compound as a colorless liquid (34 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.39 (dq, *J* = 9.0, 0.5 Hz, 1H), 8.10 (s, 1H), 7.75-7.71 (m, 2H), 7.45 (d, *J* = 8.4 Hz, 1H), 2.61 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 136.2, 132.5, 131.9, 130.2, 129.2, 127.3 (*J* = 32.4 Hz), 125.8 (*J* = 4.2 Hz), 125.5 (*J* = 272.2 Hz), 122.7 (*J* = 2.8 Hz), 118.0, 21.1, 19.8; ^{19}F NMR (282 MHz, $CDCl_3$): δ = −62.7; IR (film, cm^{-1}): $\tilde{\nu}$ = 1633, 1483, 1334, 1307, 1263, 1195, 1120, 1070, 1032, 984, 900, 825, 719, 671, 542; HRMS (ESI): *m*/*z* calcd for $C_{12}H_8ClF_3$ [M]: 244.0267; found: 244.0261.



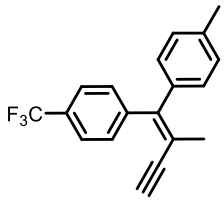
4,4,5,5-tetramethyl-2-(2-methyl-6-(trifluoromethyl)naphthalen-1-yl)-1,3,2-dioxaborolane (33). A flame-dried 10 mL Schlenk flask equipped with a magnetic stirring bar was charged with 1-chloro-2-methyl-6-(trifluoromethyl)naphthalene (**32**) (48 mg, 0.2 mmol, 1 equiv), $Fe(acac)_3$ (3.53 mg, 5 mol%), potassium *tert*-butoxide (47 mg, 2.1 equiv), bis(pinacolato)diboron (101 mg, 0.4 mmol) and toluene (1 mL). The resulting mixture was stirred at 130 °C for 18 h. After cooling to room temperature, saturated ammonium chloride aqueous solution (2.0 mL) was added. The organic phase was extracted with ethyl acetate (3×5 ml), and the organic layer was passed over a pad of Florisil. The volatiles were removed in *vacuo* to obtain an oily residue. The crude mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98:2) to give the title compound as a colorless oil (36 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.26 (dq, *J* = 8.8, 0.5 Hz, 1H), 8.06 (s, 1H), 7.83 (d, *J* = 8.5 Hz, 1H), 7.61 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.38 (d, *J* = 8.3 Hz, 1H), 2.66 (s, 3H), 1.49 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 144.3, 138.0, 130.5, 130.3, 129.9, 128.7, 126.7 (q, *J* = 32 Hz), 126.0, 125.9 (q, *J* = 4 Hz), 123.3 (q, *J* = 272 Hz), 121.7 (q, *J* = 3 Hz), 84.4, 25.2, 22.9; ^{19}F NMR (282 MHz, $CDCl_3$): δ = -62:24; IR (film, cm^{-1}): $\tilde{\nu}$ = 2979, 1632, 1411, 1311, 1257, 1119, 1069, 1033, 900, 853, 738, 714, 671; HRMS (ESI+): *m*/*z* calcd for $C_{18}H_{21}BF_3O_2$ [M+H]: 337.1587; found: 337.1578.



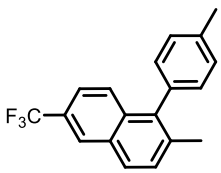
(*Z*)-1-methyl-4-(2-methyl-1-(4-(trifluoromethyl)phenyl)but-1-en-3-yn-1-yl)benzene. A flame-dried 10 mL Schlenk flask equipped with a magnetic stirring bar was charged with $Pd_2(dba)_3$ (10.3 mg, 5 mol %), Xphos (10.7 mg, 10 mol %), K_3PO_4 (93 mg, 0.675 mmol), (*E*)-(4-chloro-3-methyl-4-(4-(trifluoromethyl)phenyl)but-3-en-1-yn-1-yl)triisopropylsilane (**25c**) (90 mg, 0.22 mmol) and *p*-tolylboronic acid (61 mg, 0.2 mmol) were suspended under argon in toluene (2 mL). The mixture was stirred at 90 °C for 18 h before the solvent was evaporated under reduced pressure. The residue was purified by flash chromatography (hexane) to give the title compound as a colorless oil (97 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51 (d, *J* = 1.6 Hz, 4H), 7.15 (d, *J* = 7.8 Hz, 2H), 7.05-7.02 (m, 2H), 2.36 (s, 3H), 2.04 (s, 3H), 0.99 (s, 21H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 146.6, 146.3, 137.5, 137.4, 130.3, 129.7, 129.3 (q, *J* = 32 Hz), 129.0, 125.7 (q, *J* = 272 Hz), 124.7 (q, *J* = 3 Hz), 118.0, 108.8, 95.2, 18.6, 11.2; ^{19}F NMR (282 MHz, $CDCl_3$): δ = -62:61; IR (film, cm^{-1}): $\tilde{\nu}$ = 2943, 2865, 2132, 1616, 1509, 1462, 1322, 1164, 1125, 1067, 1018, 838, 817, 662, 490; HRMS (ESI+): *m*/*z* calcd for $C_{28}H_{36}F_3Si$ [M+H]: 457.2538; found: 457.2538.



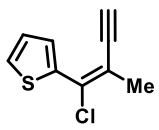
(*Z*)-1-methyl-4-(2-methyl-1-(4-(trifluoromethyl)phenyl)but-1-en-3-yn-1-yl)benzene (34). Prepared analogously using (*Z*)-triisopropyl(3-methyl-4-(*p*-tolyl)-4-(4-(trifluoromethyl)phenyl)but-3-en-1-yn-1-yl)silane. Colorless oil (0.2 mmol scale, 60 mg, 95%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55-7.45 (m, 4H), 7.16 (d, *J* = 7.8 Hz, 2H), 7.01 (d, *J* = 7.0 Hz, 2H), 3.00 (s, 1H), 2.36 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.6, 145.7, 137.6, 137.4, 130.2, 129.6, 129.5 (q, *J* = 32 Hz), 129.1, 124.8 (q, *J* = 3 Hz), 122.5 (q, *J* = 272 Hz), 116.6, 85.5, 81.0, 22.1, 21.3; ^{19}F NMR (282 MHz, $CDCl_3$): δ = -62:49; IR (film, cm^{-1}): $\tilde{\nu}$ = 3298, 2922, 1617, 1509, 1408, 1321, 1163, 1122, 1066, 1017, 836, 814, 604, 528; HRMS (ESI): *m*/*z* calcd for $C_{19}H_{15}F_3$ [M]: 300.1126; found: 300.1122.



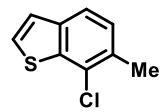
2-methyl-1-(*p*-tolyl)-6-(trifluoromethyl)naphthalene (35). Prepared analogously using (*Z*)-1-methyl-4-(2-methyl-1-(4-(trifluoromethyl)phenyl)but-1-en-3-yn-1-yl)benzene (**34**). Colorless liquid (0.19 mmol scale, 35 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 (s, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.56-7.46 (m, 3H), 7.33 (d, *J* = 7.6 Hz, 2H), 7.16-7.13 (m, 2H), 2.48 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.5, 137.1, 136.0, 135.9, 134.4, 130.8, 130.08, 130.01, 129.4, 127.9, 127.4, 126.8 (q, *J* = 32 Hz), 125.6 (q, *J* = 4 Hz), 123.3 (q, *J* = 272 Hz), 121.3 (q, *J* = 3 Hz), 21.45, 21.1; ^{19}F NMR (282 MHz, $CDCl_3$): δ = -62:16; IR (film, cm^{-1}): $\tilde{\nu}$ = 2923, 1632, 1483, 1348, 1309, 1168, 1154, 1122, 1068, 901, 809, 717; HRMS (ESI): *m*/*z* calcd for $C_{19}H_{15}F_3$ [M]: 300.1126; found: 300.1123.



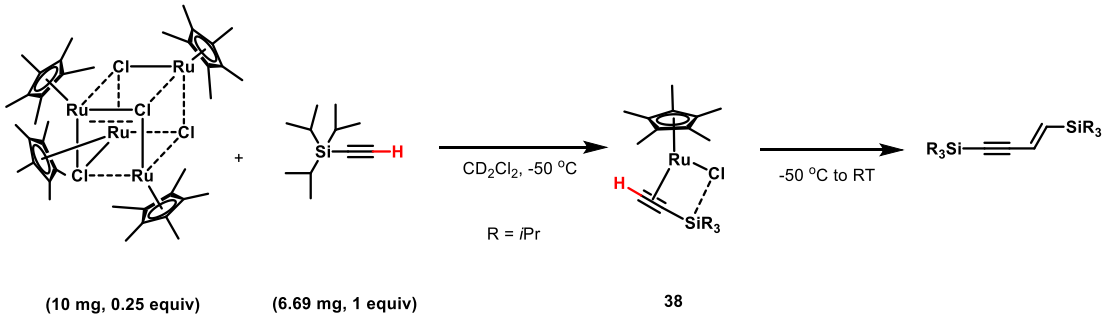
(*E*)-2-(1-chloro-2-methylbut-1-en-3-yn-1-yl)thiophene (36). Prepared analogously using (*E*)-(4-chloro-3-methyl-4-(thiophen-2-yl)but-3-en-1-yn-1-yl)triisopropylsilane (**26**). Brown color oil (0.75 mmol scale, 107 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (dd, *J* = 3.8, 1.1 Hz, 1H), 7.33 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.02 (dd, *J* = 3.7, 1.2 Hz, 1H), 3.55 (s, 1H), 2.20 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 140.2, 133.9, 129.4, 127.2, 126.6, 113.0, 86.6, 83.9, 22.7; IR (film, cm^{-1}): $\tilde{\nu}$ = 3288, 3105, 2920, 2087, 1574, 1420, 1355, 1255, 1230, 1015, 812, 699, 645, 604, 558, 496; HRMS (ESI): *m*/*z* calcd for C_9H_7ClS [M]: 181.9957; found: 181.9953.



7-chloro-6-methylbenzo[*b*]thiophene (**37**). Prepared analogously from **36** using 10 mol% of $PtCl_2$. Yellow color oil containing the 5-*exo*-*dig* cyclization product as a trace impurity (0.55 mmol scale, 65 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 7.9 Hz, 1H), 7.41 (d, *J* = 5.2 Hz, 1H), 7.33 (d, *J* = 5.4 Hz, 1H), 7.26 (d, *J* = 7.9 Hz, 1H), 2.54 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 139.9, 139.0, 131.5, 127.6, 126.4, 124.4, 121.5, 117.2, 19.5; IR (film, cm^{-1}): $\tilde{\nu}$ = 2915, 1552, 1460, 1369, 1339, 1307, 1213, 1116, 1009, 936, 807, 722, 690, 589, 500; HRMS (ESI): *m*/*z* calcd for C_9H_7ClS [M]: 181.9957; found: 181.9952.



Reactive Intermediates



(10 mg, 0.25 equiv) (6.69 mg, 1 equiv) **38**

Preparation and Characterization of Complex 38. Compound **38** was prepared by mixing $[Cp^*RuCl]_4$ (10 mg, 9.1 µmol) and ethynyltriisopropylsilane (**1a**) (6.69 mg, 36.7 µmol) under Ar in an J-Young NMR tube. CD_2Cl_2 (0.5 mL) was introduced at -78 °C and the NMR tube was tightly closed. The sample was quickly shaken to make sure that all components were dissolved and a cherry-red solution was formed. The probehead of the NMR spectrometer was precooled to –50 °C. The tube was inserted and spectra were recorded at -50°C before the temperature was raised in 10 °C increments until RT was reached.

At –50 °C, complex **38** was detected along with unreacted ethynyltriisopropylsilane (**1a**). Upon warming, slow homodimerization of the terminal alkyne with formation of (*E*)-but-1-en-3-yne-1,4-diylbis(triisopropylsilane)[5] was observed. Characterization data of complex **38**: ^{1}H NMR (500 MHz, CD_2Cl_2, 223K) δ = 8.64 (s, 1H), 1.64 (s, 15H), 1.24 (h, J = 7.5 Hz, 3H), 0.87 (d, J = 7.5 Hz, 18H); ^{13}C NMR (126 MHz, CD_2Cl_2, 223K): δ = 137.5, 135.7, 85.5, 18.7, 12.2, 10.2.

Single crystals suitable for X-ray crystallography were obtained by preparing complex **38** analogously in a Schlenk flask. The CH_2Cl_2 phase was layered with pentane, the Schlenk flask was placed in a Cryostat and the temperature was gradually lowered from 0 °C to -55 °C over the course of 36 h.

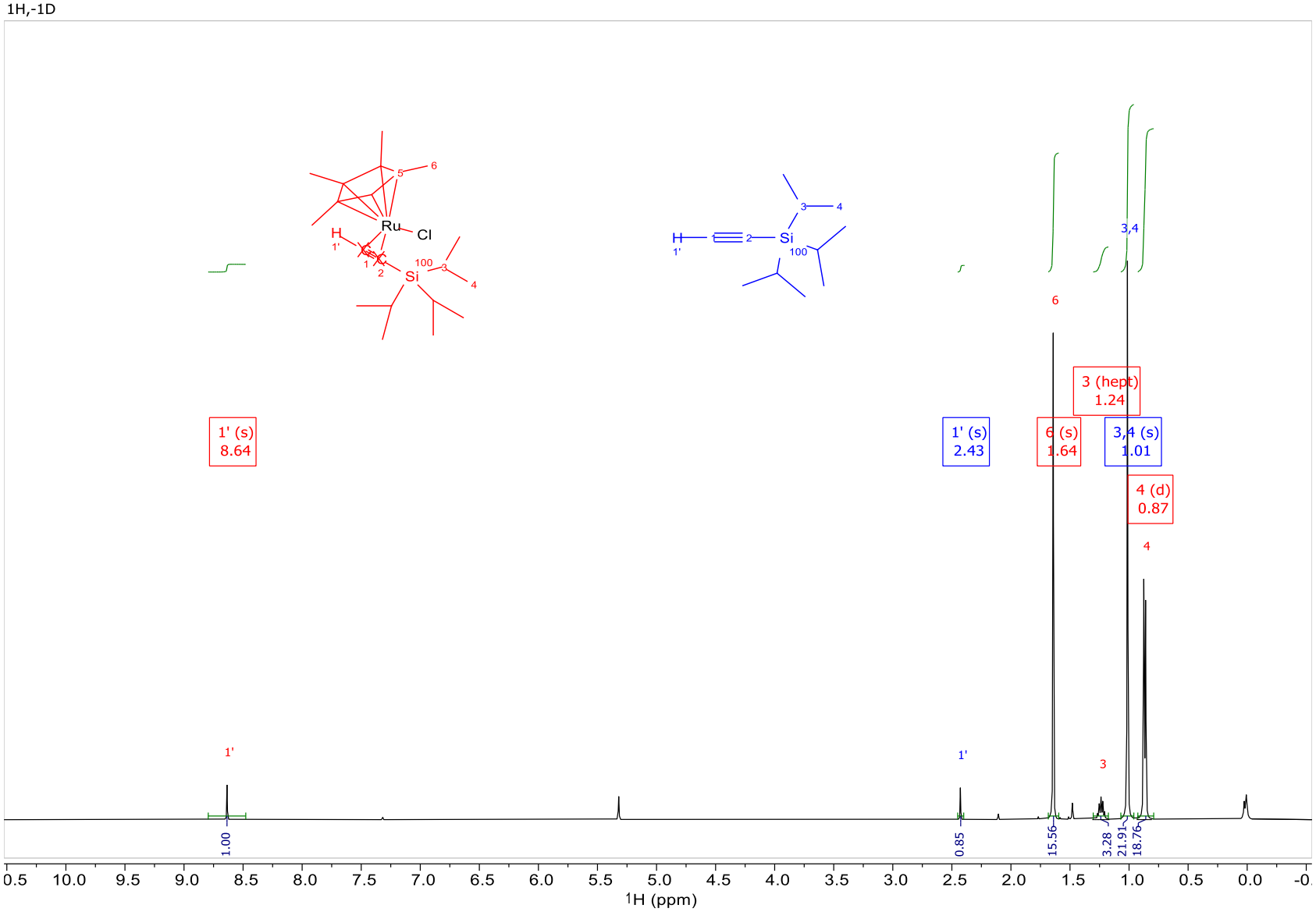


Figure S-1. ^{1}H NMR of complex **38**, 500 MHz, CD_2Cl_2, at -50 °C.

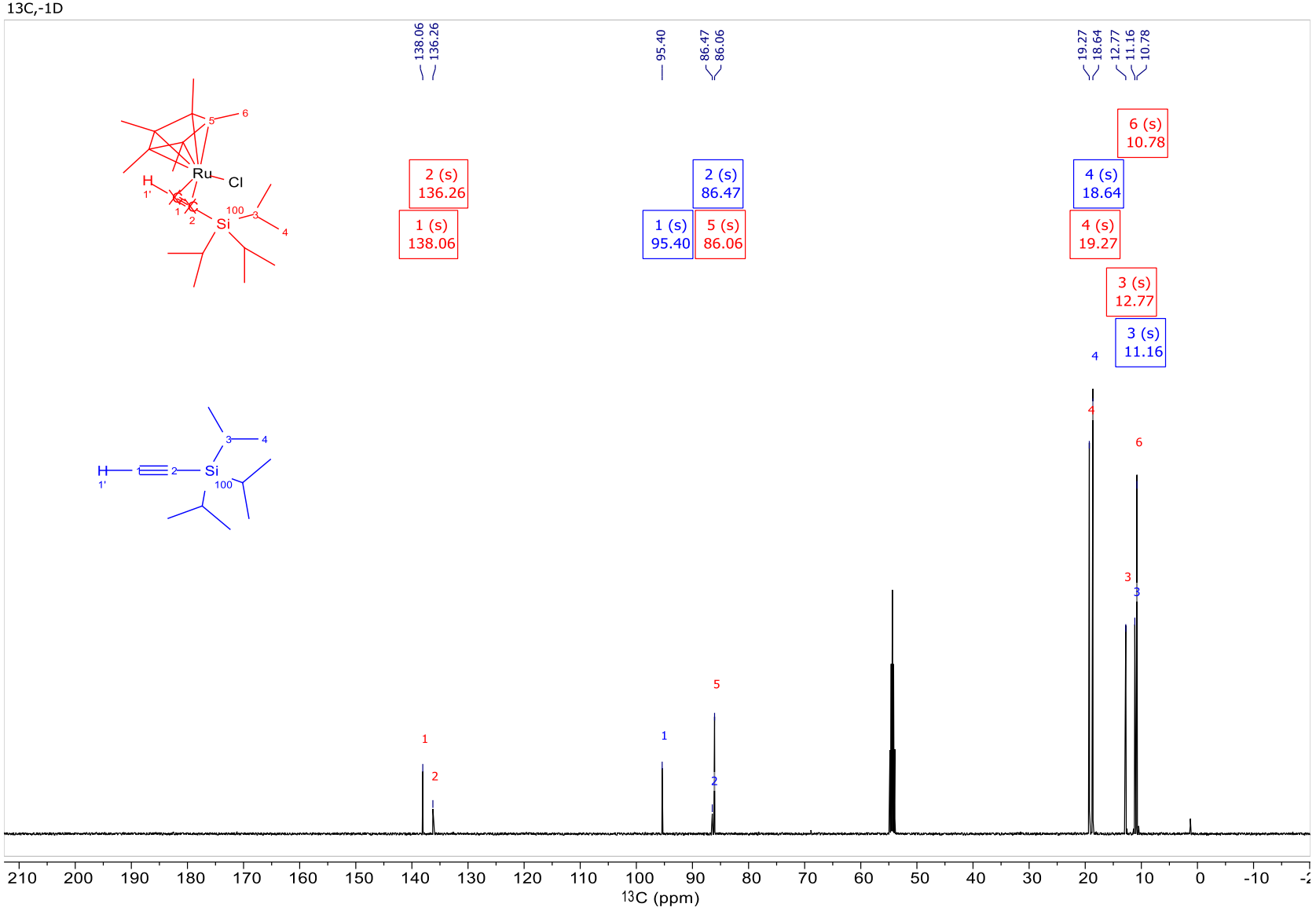


Figure S-2. ^{13}C NMR of complex **38**, 500 MHz, CD_2Cl_2, at -50 °C.

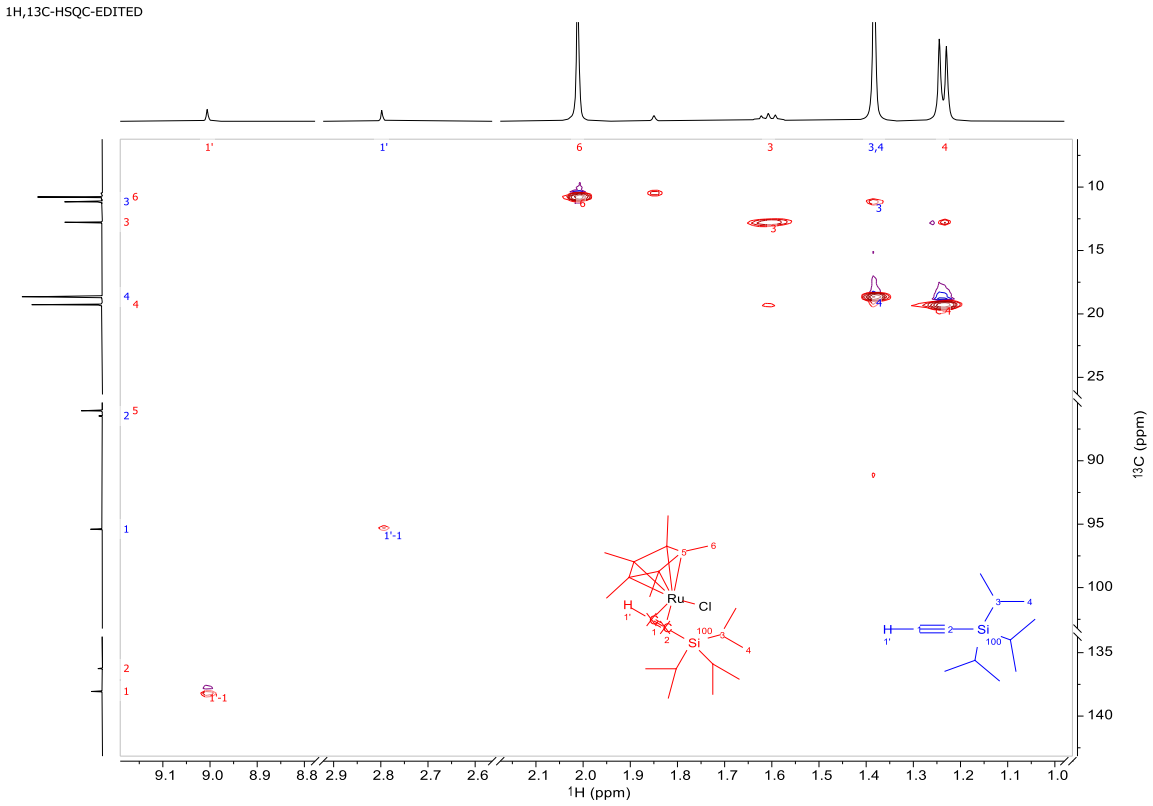


Figure S-3. HSQC NMR of complex **38**, 500 MHz, CD_2Cl_2, at -50 °C.

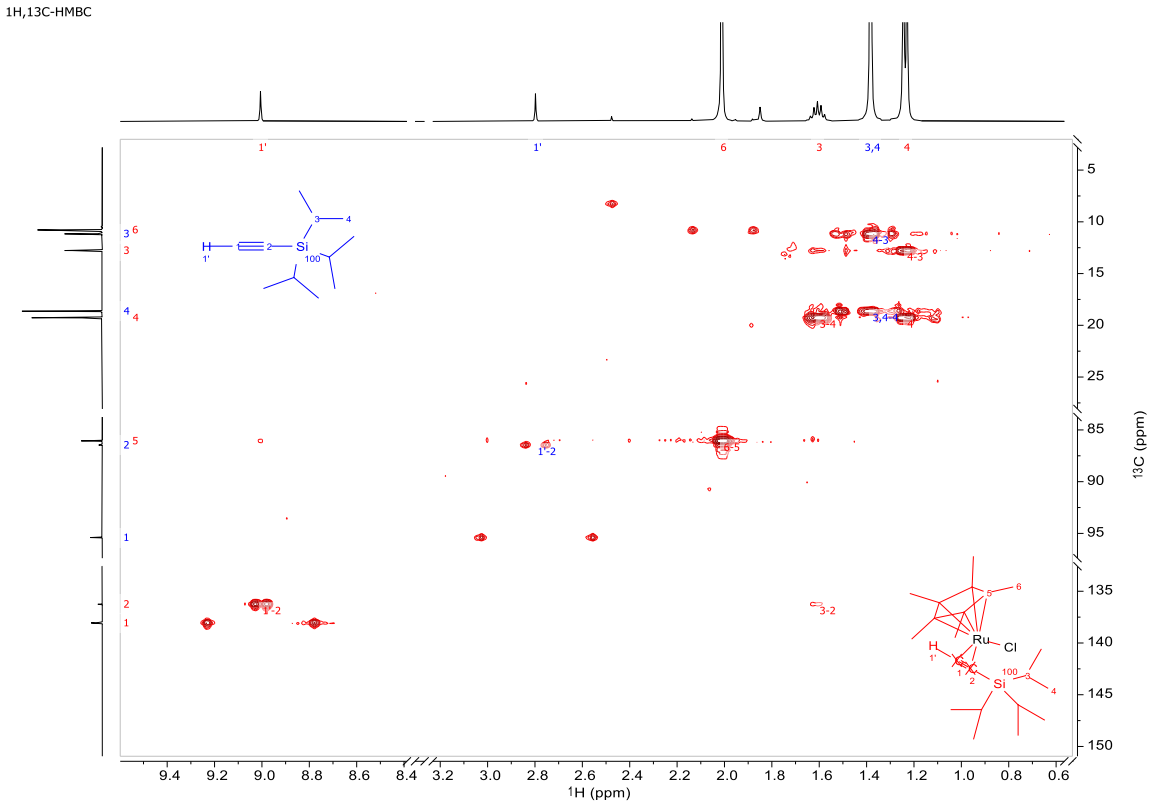


Figure S-4. HMBC NMR of complex **38**, 500 MHz, CD_2Cl_2, at -50 °C.

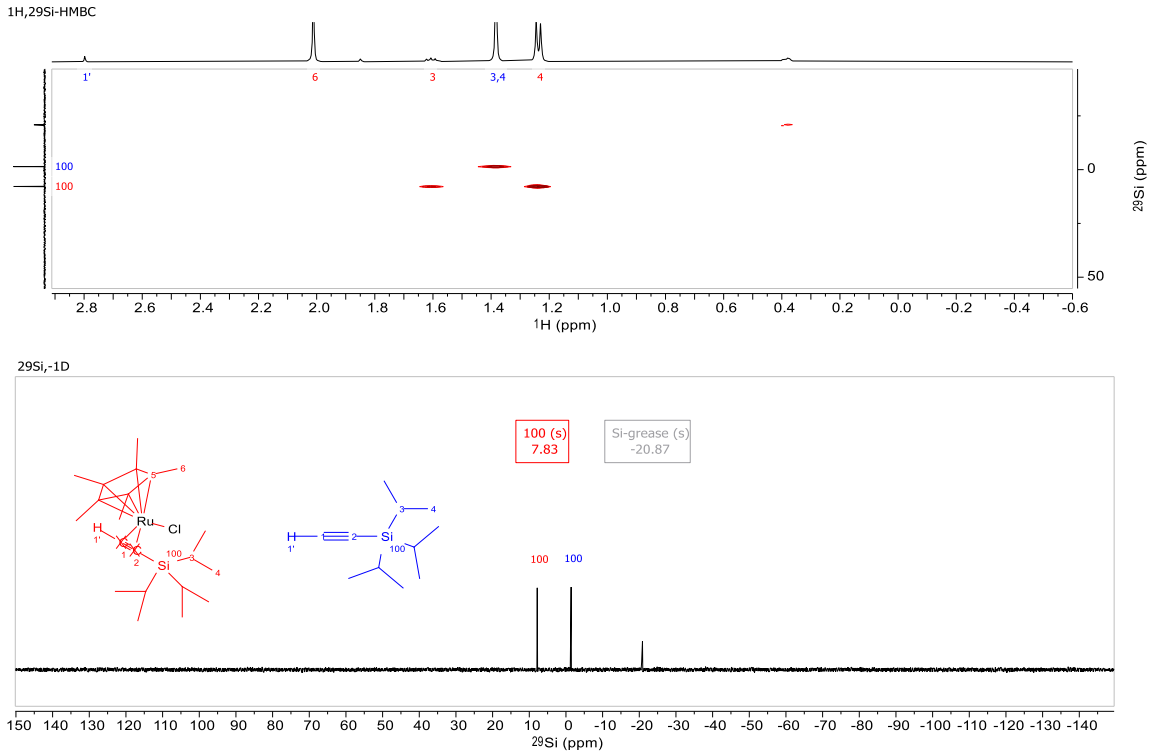


Figure S-5. $^{1}H,^{29}Si$ HMBC and 1D-Si NMR of complex **38**, 500 MHz, CD_2Cl_2, at -50 °C.

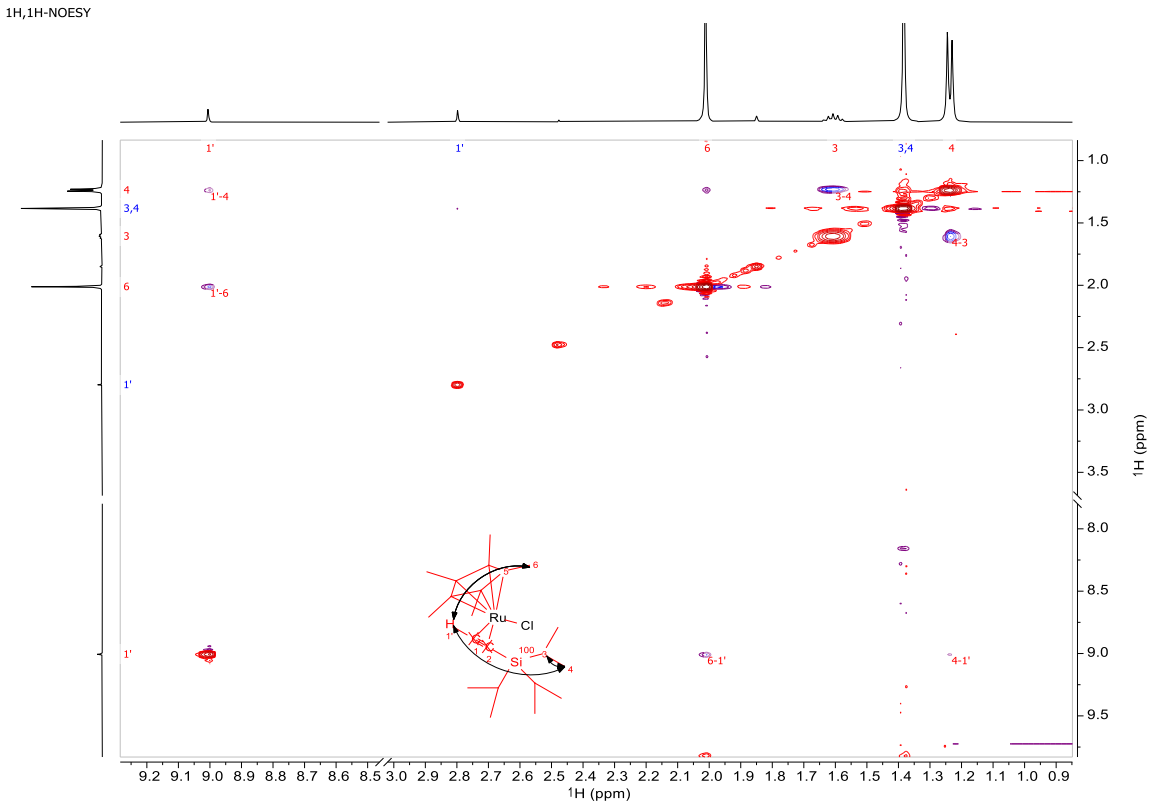


Figure S-6. NOESY NMR of complex **38**, 500 MHz, CD_2Cl_2, at -50 °C.

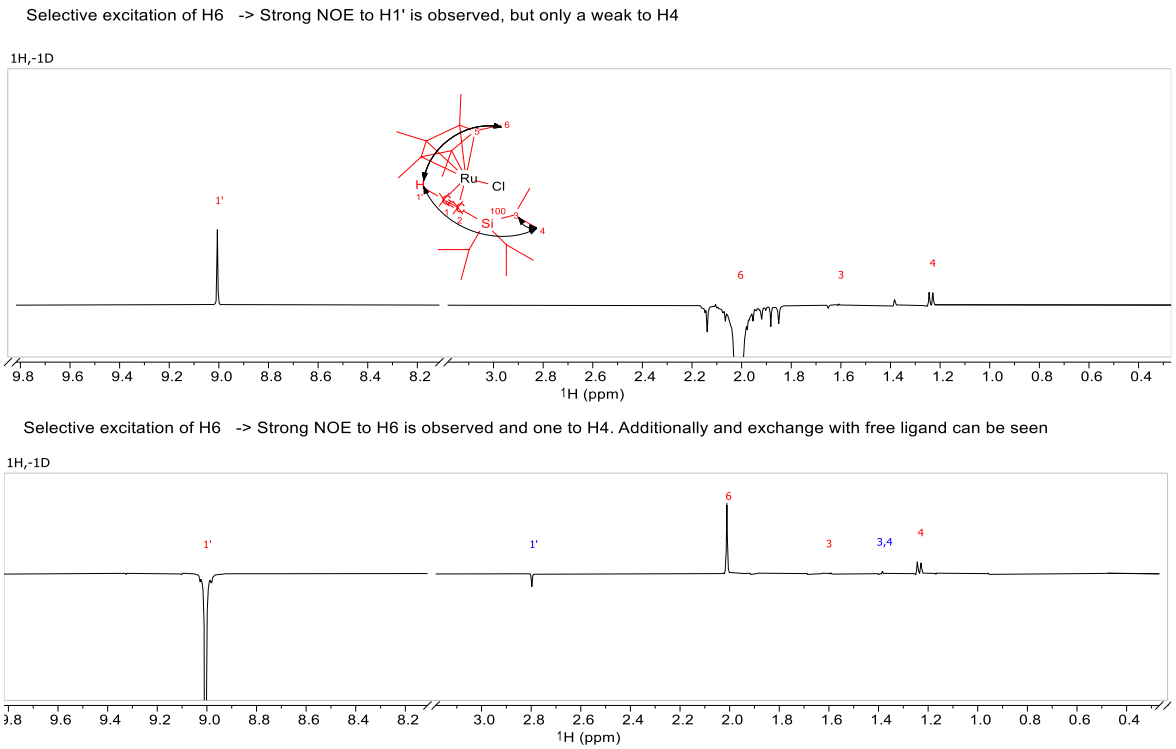


Figure S-7. NOESY selective excitation NMR of complex **38**, 500 MHz, CD_2Cl_2, at -50 °C.

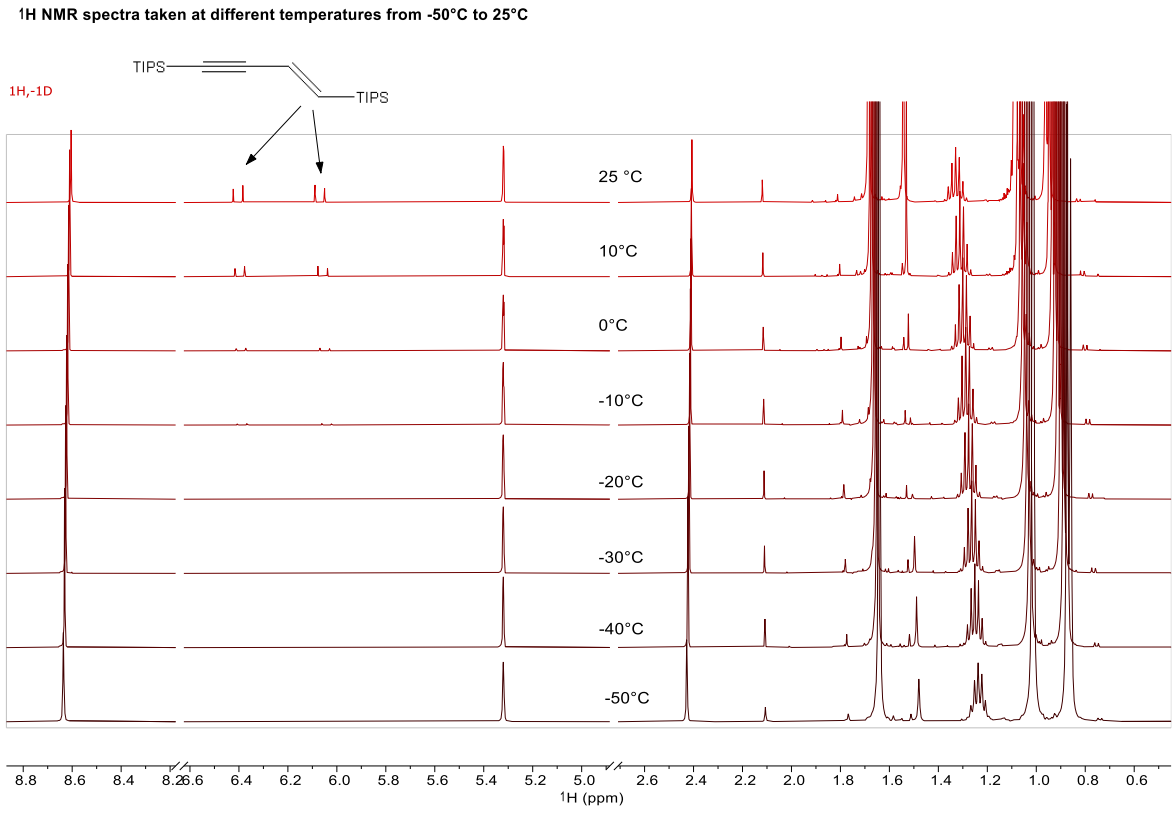
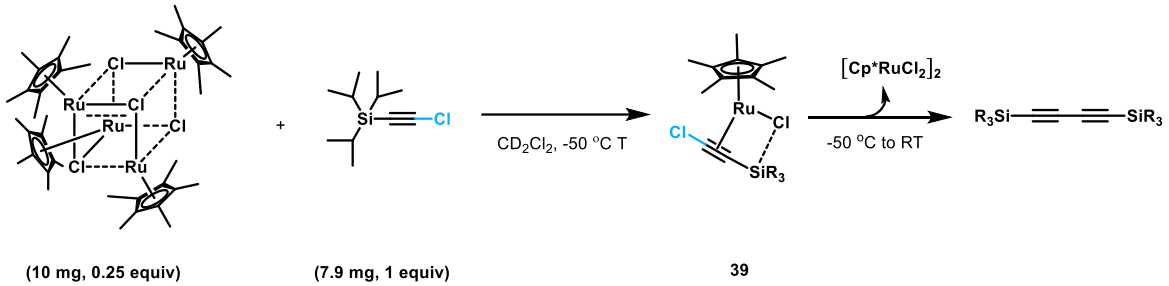


Figure S-8. ^1H NMR (500 MHz, CD_2Cl_2) of complex **38** at different temperatures and slow formation of the shown enyne



(10 mg, 0.25 equiv) (7.9 mg, 1 equiv) 39

Preparation and Characterization of Complex 39. Compound **39** was generated by mixing $[Cp^*RuCl]_4$ (10 mg, 9.1 µmol) and (chloroethynyl)triisopropylsilane **1b** (7.9 mg, 36.7 µmol) under Ar in an J-Young NMR tube. CD_2Cl_2 (0.5 mL) was introduced at −78 °C and the NMR tube was tightly closed. The sample was quickly shaken to make sure all the components were dissolved, giving rise to the formation of a cherry-red solution. The tube was inserted into the NMR probe-head that had been precooled to −50 °C. The temperature was then raised in 10 °C increments and spectra were recorded at each step until RT was reached.

At −50 °C, complex **39** was detected along with unreacted (chloroethynyl)triisopropylsilane (**1b**). Upon raising the temperature, slow formation of 1,4-bis(triisopropylsilyl)buta-1,3-diyne[6] was observed. Characterization data for **39**. ^{1}H NMR (500 MHz, CD_2Cl_2, 223K) δ = 1.71 (s, 15H), 1.29 (h, J = 7.5 Hz, 3H), 0.89 (d, J = 7.5 Hz, 18H); ^{13}C NMR (126 MHz, CD_2Cl_2, 223K): δ = 150.5, 141.1, 91.2, 18.6, 12.6, 9.8.

Single crystals suitable for X-ray crystallography were obtained when complex **39** was prepared analogously. The solution in CH_2Cl_2 was carefully layered with pentane, the Schlenk flask was placed in a Cryostat and the temperature gradually lowered from 0 °C to −55 °C over the course of 36 h.

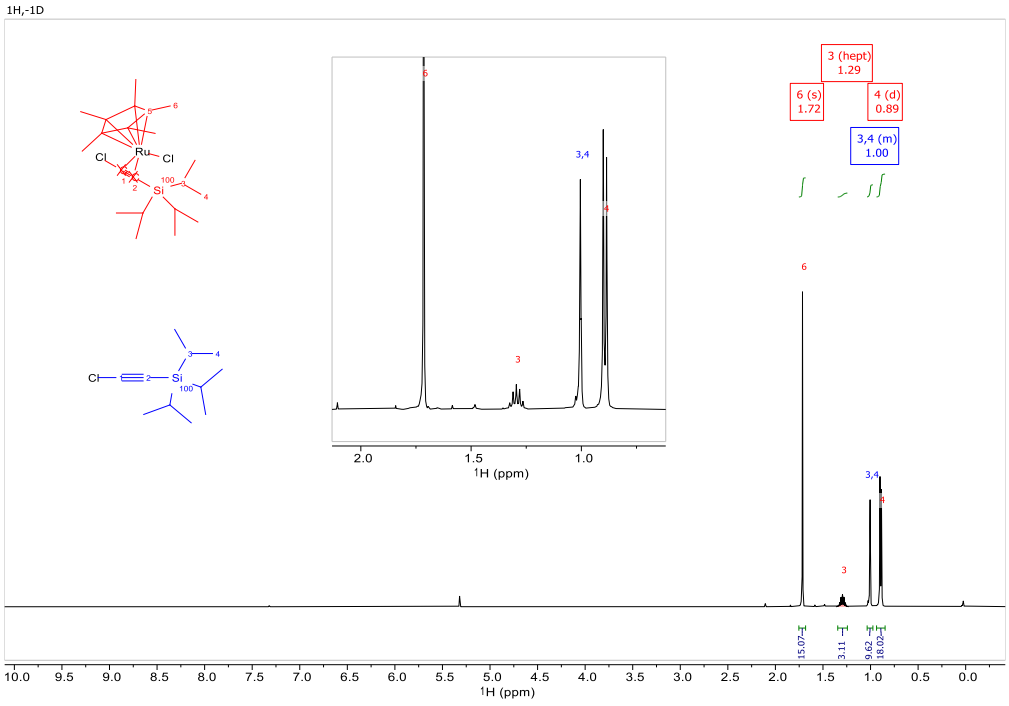


Figure S-9. ^{1}H NMR of complex **39**, 500 MHz, CD_2Cl_2, at -50 °C.

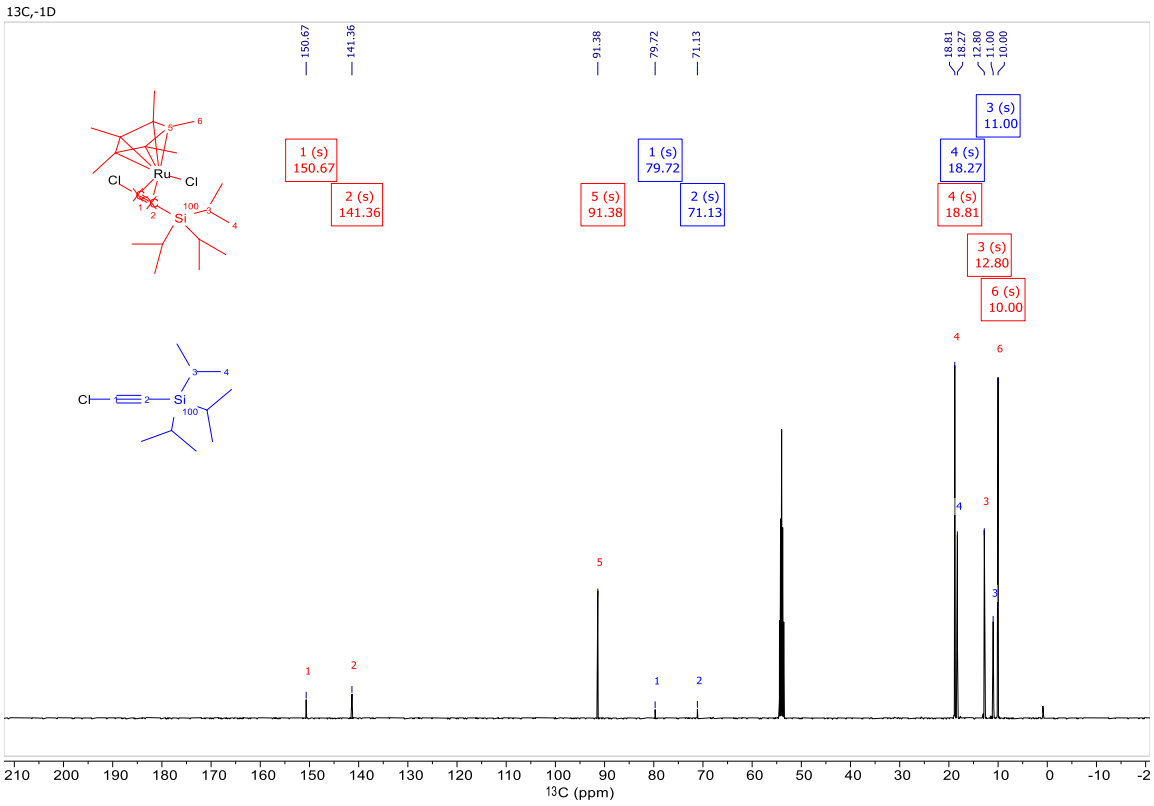


Figure S-10. ^{13}C NMR of complex **39**, 500 MHz, CD_2Cl_2, at -50 °C.

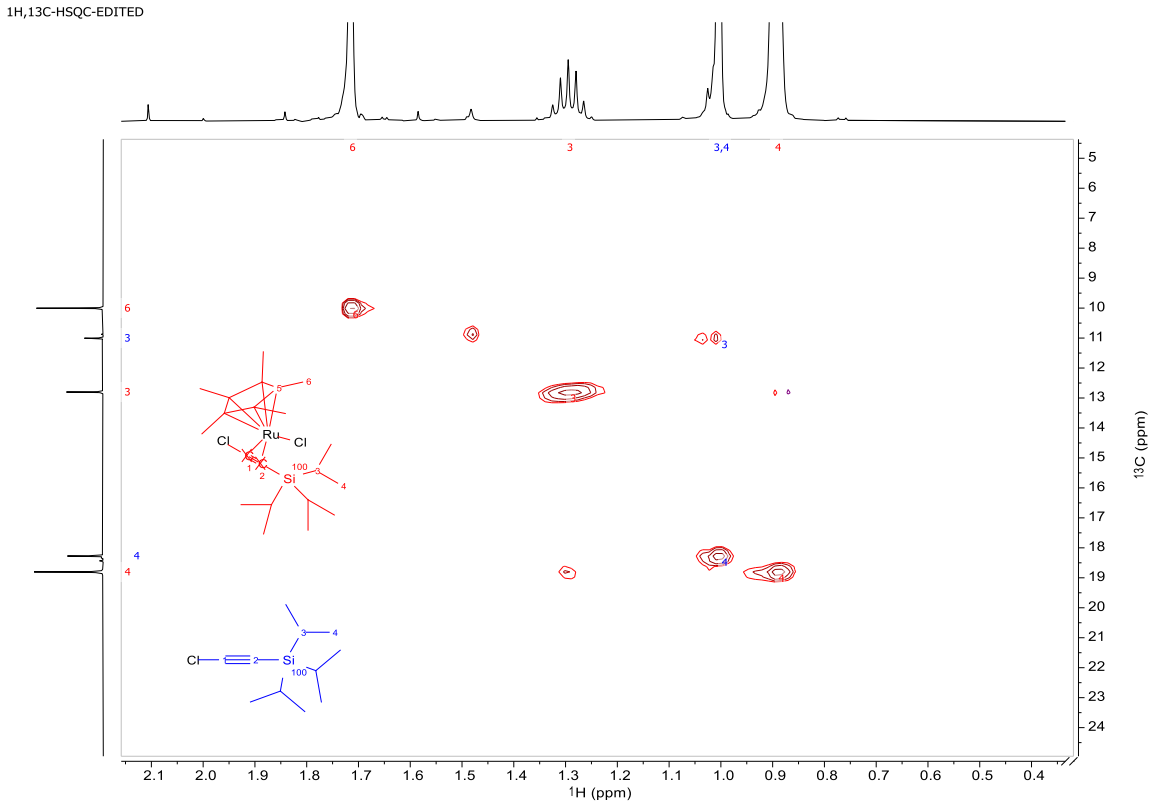


Figure S-11. HSQC NMR of complex **39**, 500 MHz, CD_2Cl_2, at -50 °C.

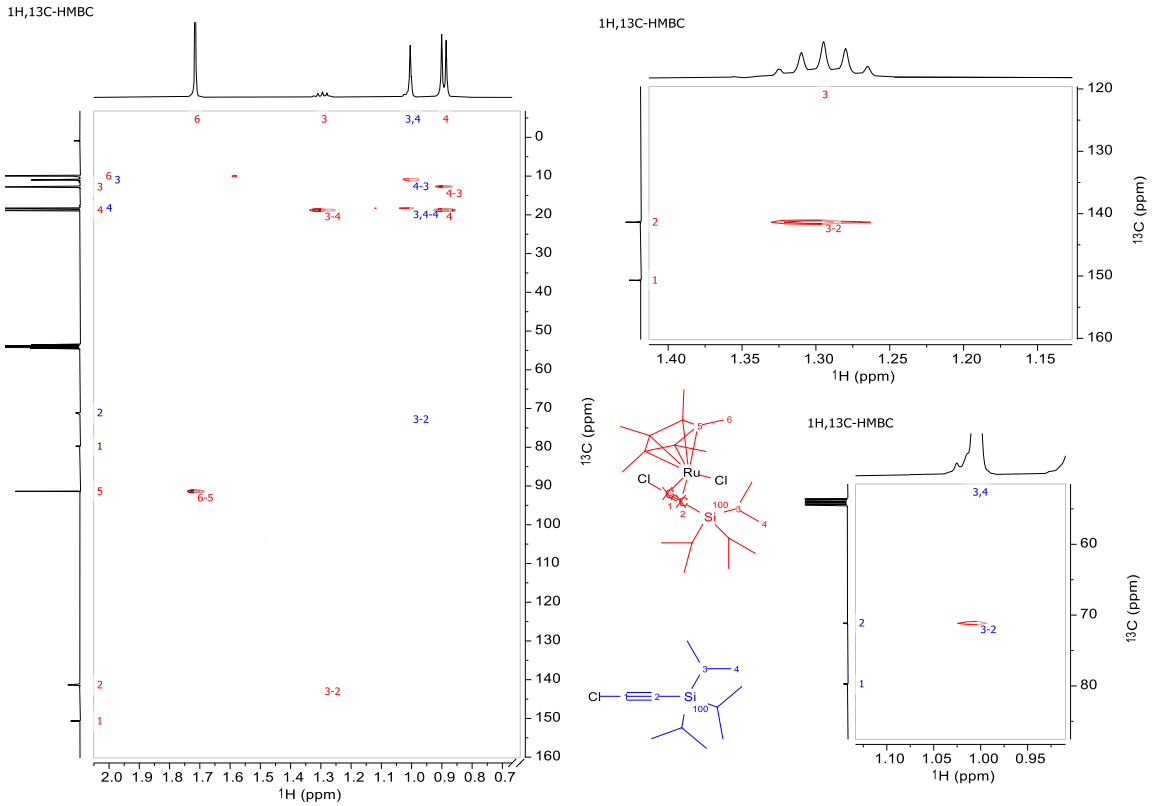


Figure S-12. HMBC NMR of complex **39**, 500 MHz, CD_2Cl_2, at -50 °C.

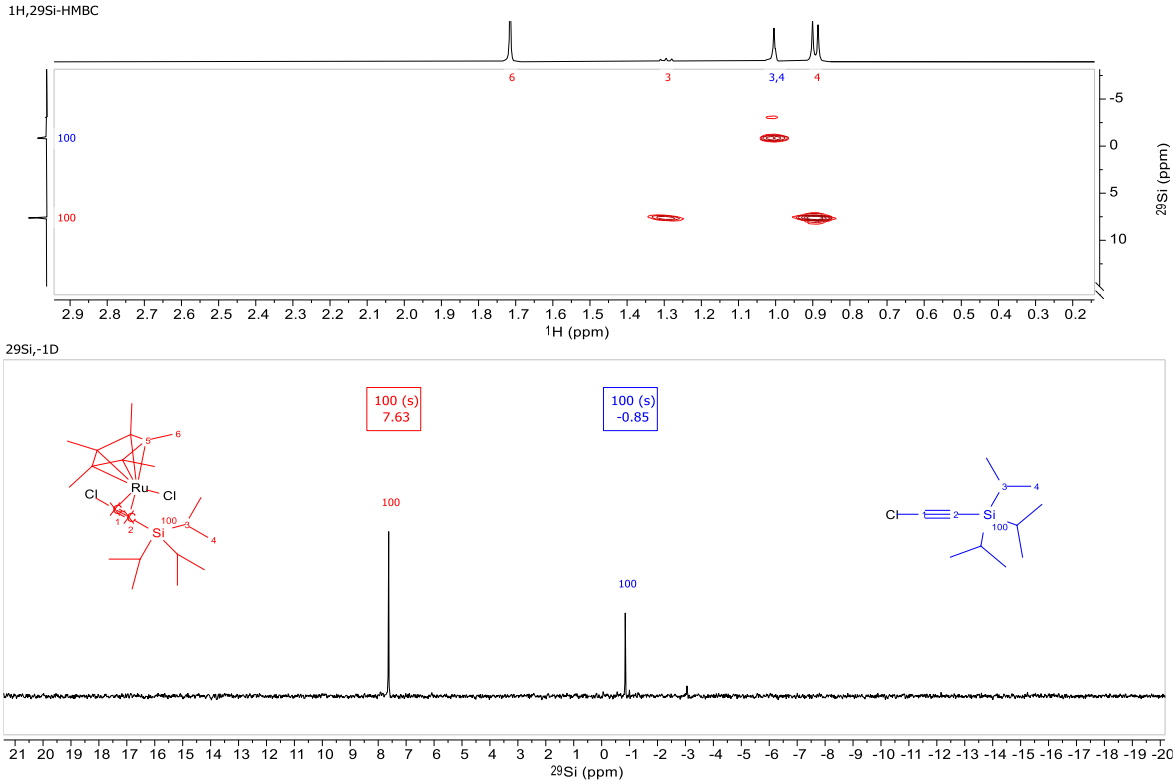


Figure S-13. $^{1}H,^{29}Si$ HMBC and 1D-Si NMR of complex **39**, 500 MHz, CD_2Cl_2, at -50 °C.

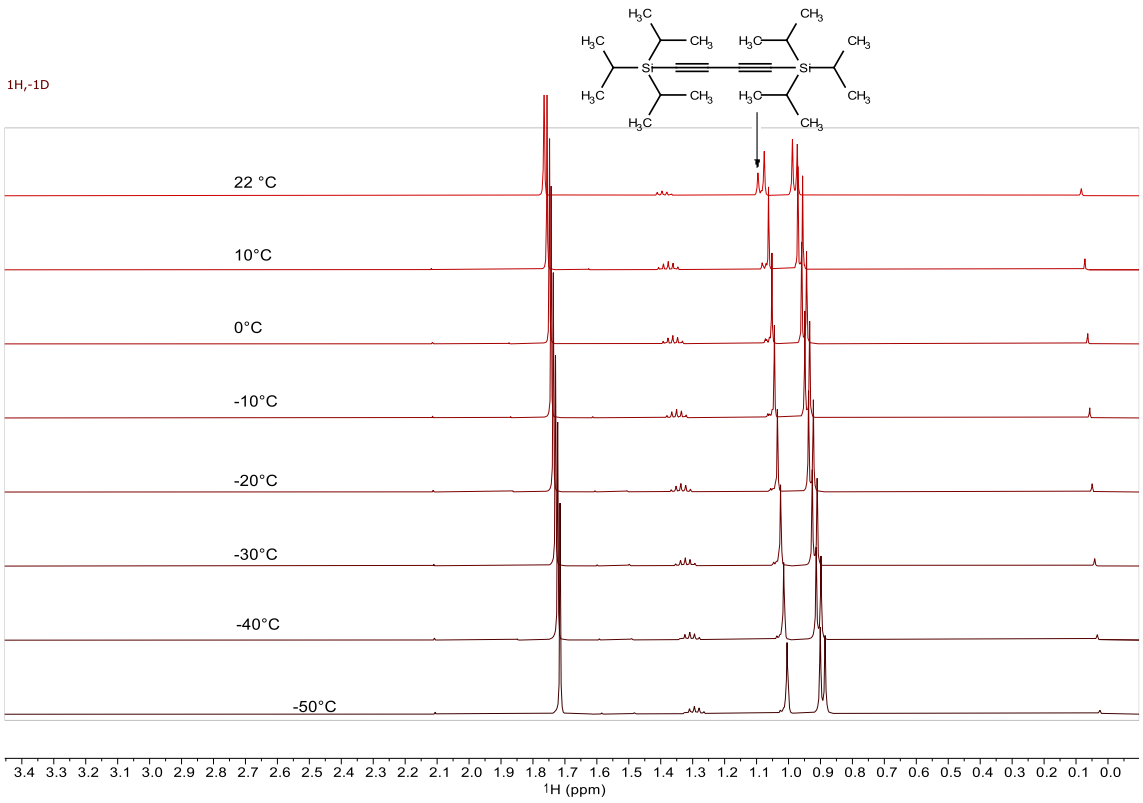


Figure S-14. ^{1}H NMR (500 MHz, CD_2Cl_2) of complex **39** at different temperatures, showing the slow formation of the diyne

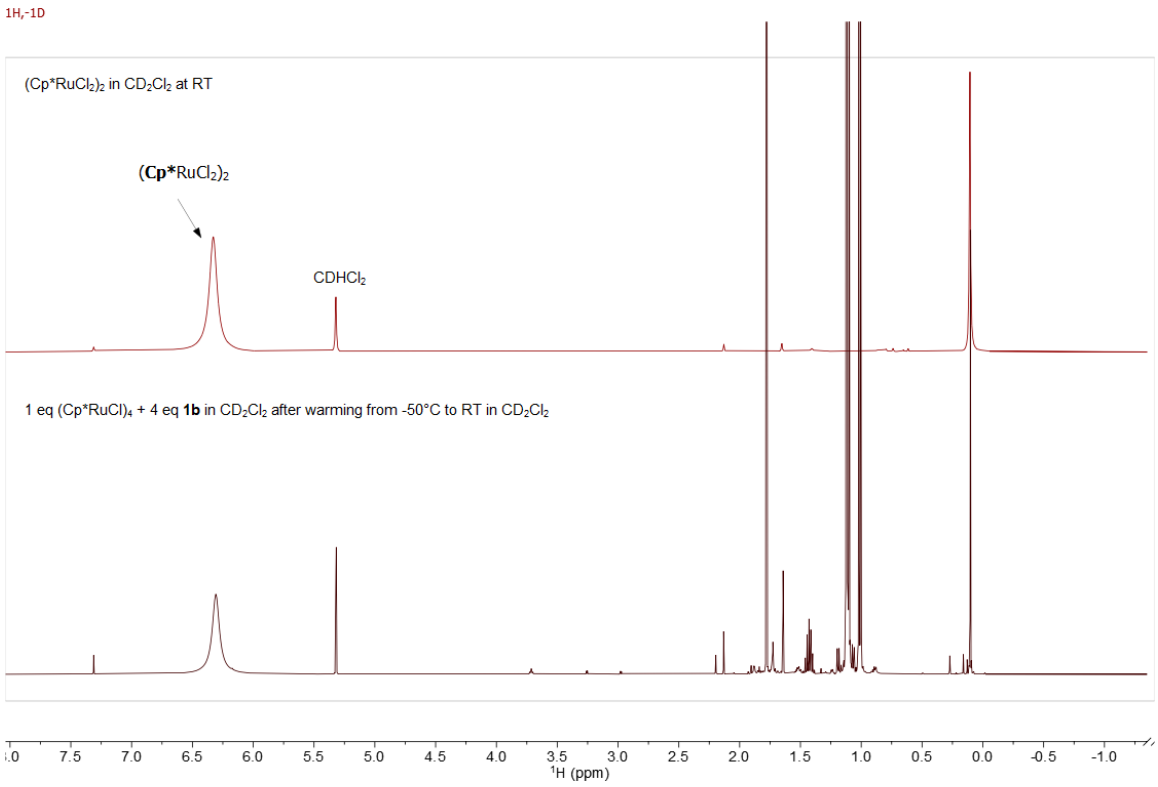
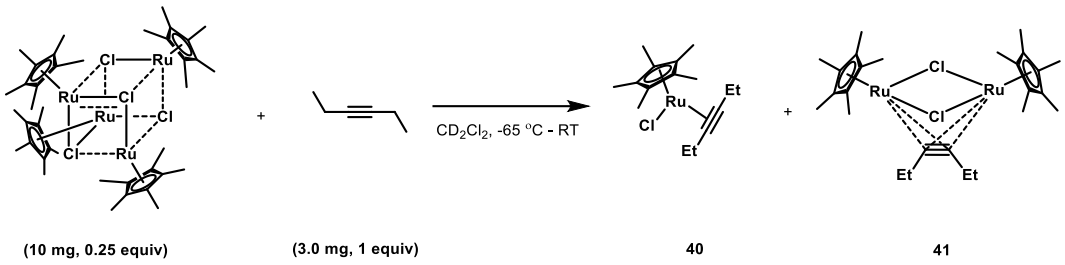


Figure S-15. ^{1}H NMR of authentic $[Cp^*RuCl_2]_2$ (500 MHz, CD_2Cl_2) and its comparison with the NMR spectrum when the solution of complex **39** had been warmed to room temperature.



Preparation and Characterization of Complexes 40 and 41. An J-Young NMR tube was charged with $[Cp^*RuCl]_4$ (10 mg, 9.1 µmol) and 3-hexyne (3.01 mg, 36.7 µmol) under Ar. CD_2Cl_2 (0.5 mL) was introduced at −78 °C. The NMR tube was tightly closed and the sample quickly shaken to make sure all the components are dissolved, leading to the formation of a brown solution. The tube was inserted into the probe-head of the NMR spectrometer, which had been precooled to −65 °C. The temperature was then raised in 10 °C increments until RT was reached and spectra were recorded at each step.

At −65 °C, the formation of mono-nuclear complex **40** and the dinuclear ruthenium π-complex **41** was observed along with unreacted 3-hexyne. At 0 °C, rapid exchange between these two complexes was observed; the exchange process was clearly visible between H2-H5 and H1-H6.

Spectral data of the mono-nuclear complex **40**: ^{1}H NMR (500 MHz, CD_2Cl_2, 208K) δ = 2.90 (q, J = 7.2 Hz, 2H), 2.53 (q, J = 7.1 Hz, 2H), 1.66 (s, 15H), 1.48 (t, J = 7.2 Hz, 3H), 1.03 (d, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, CD_2Cl_2, 223K): δ = 149.4, 132.5, 87.6, 23.1, 19.5, 15.7, 14.7, 10.16.

Spectral data of the di-nuclear complex **41**: ^{1}H NMR (500 MHz, CD_2Cl_2, 223K) δ = 3.54 (dq, J = 14.3, 7.1 Hz, 2H), 2.59 (dq, J = 14.3, 7.1 Hz, 2H), 1.55 (s, 30H), 0.89 (t, J = 7.5 Hz, 6H); ^{13}C NMR (126 MHz, CD_2Cl_2, 223K): δ = 125.7, 88.1, 23.2, 15.1, 10.2.

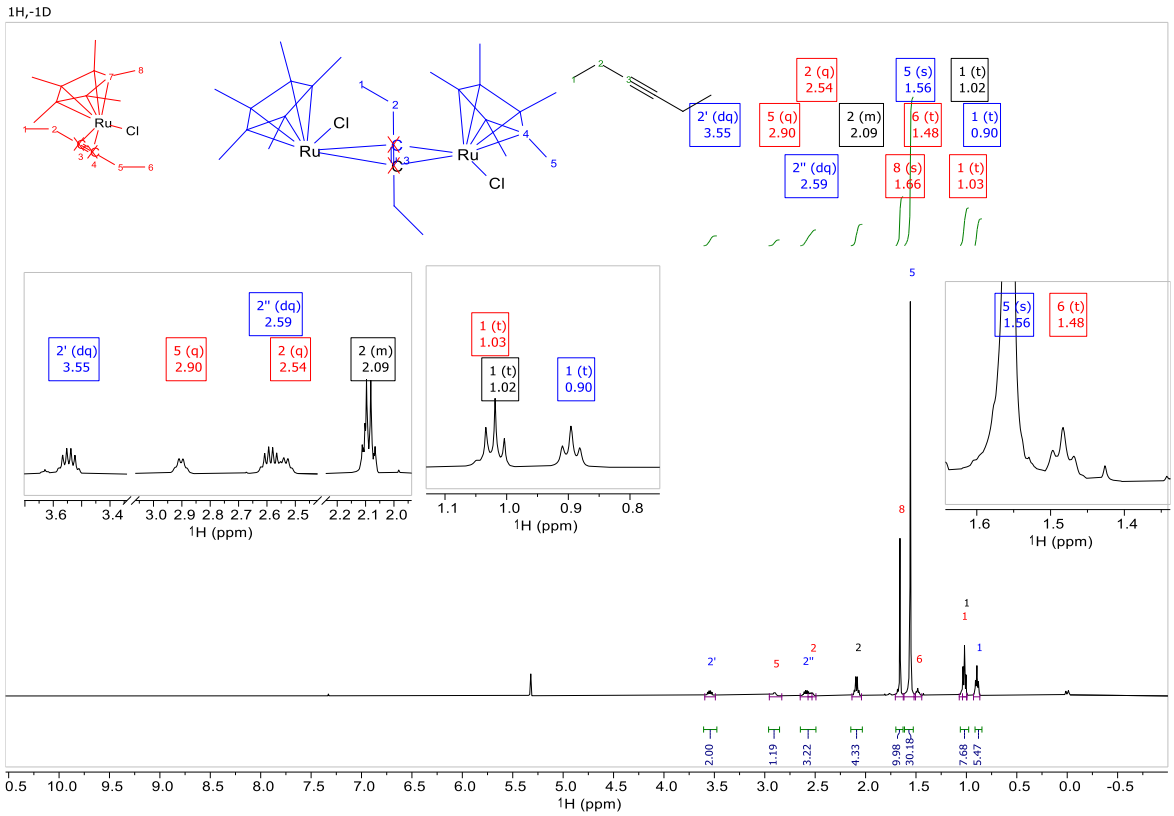


Figure S-16. ^{1}H NMR of complexes **40** and **41**, 500 MHz, CD_2Cl_2, at -65 °C.

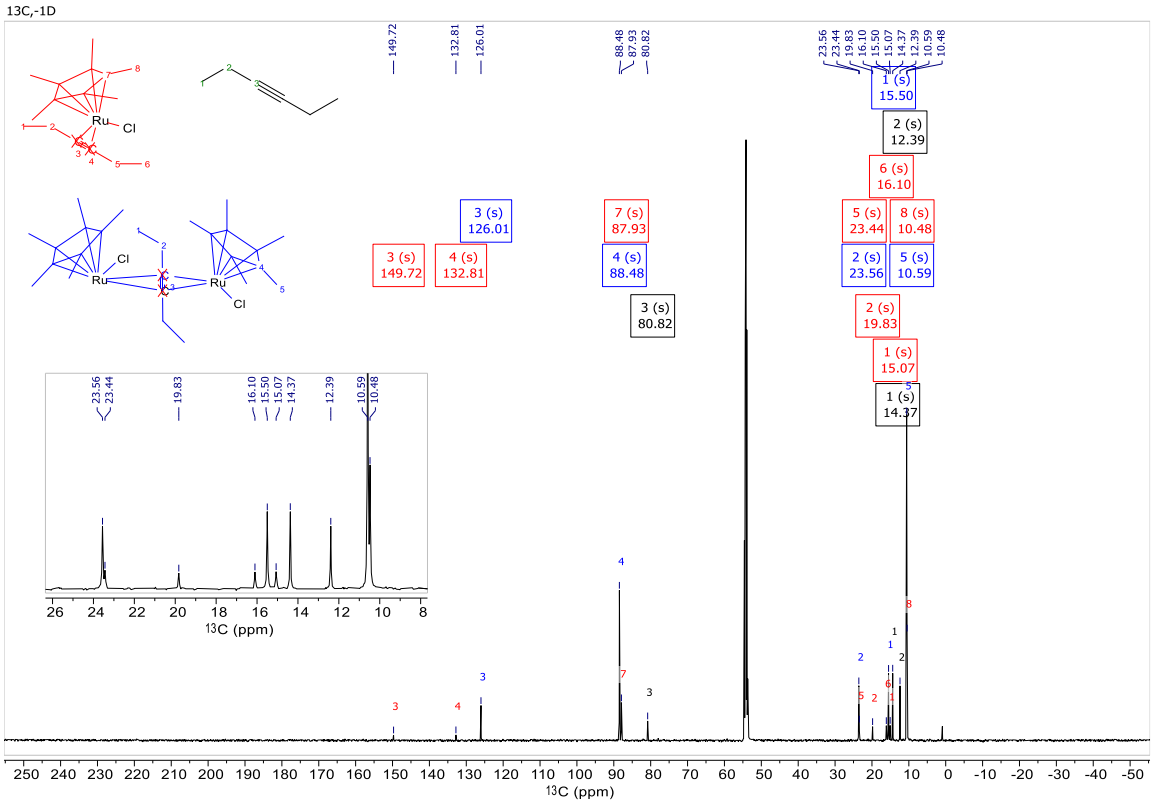


Figure S-17. ^{13}C NMR of complexes **40** and **41**, 500 MHz, CD_2Cl_2, at -65 °C.

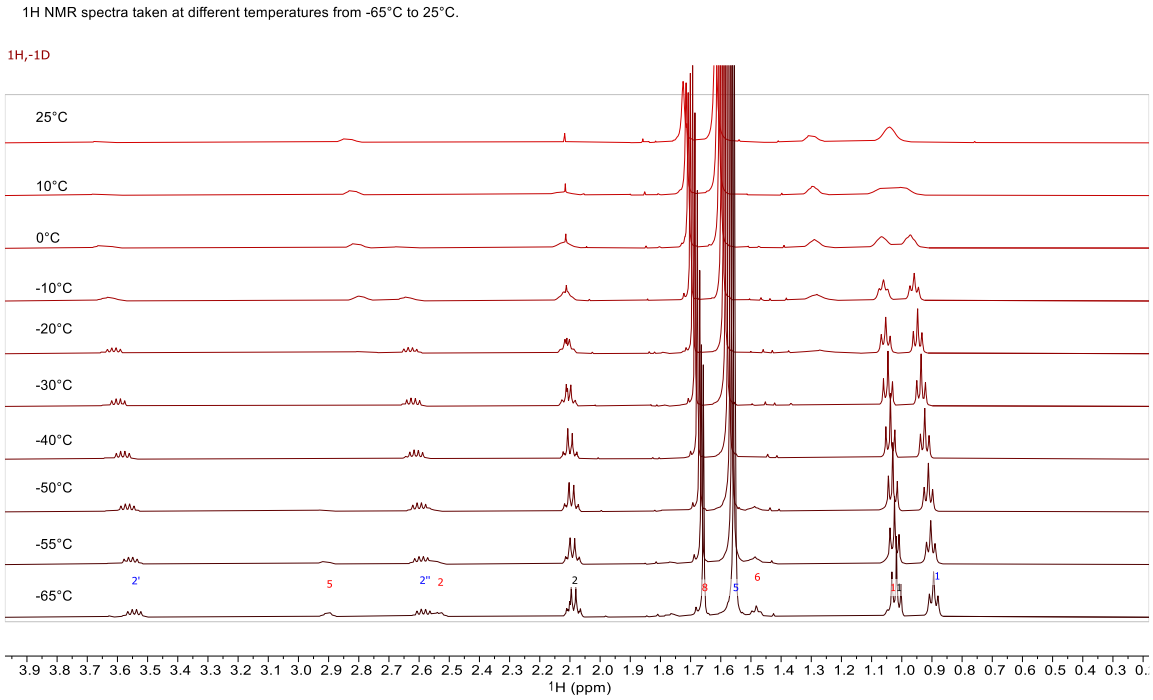


Figure S-18. ^{1}H NMR of complexes **40** and **41**, 500 MHz, CD_2Cl_2, at different temperatures.

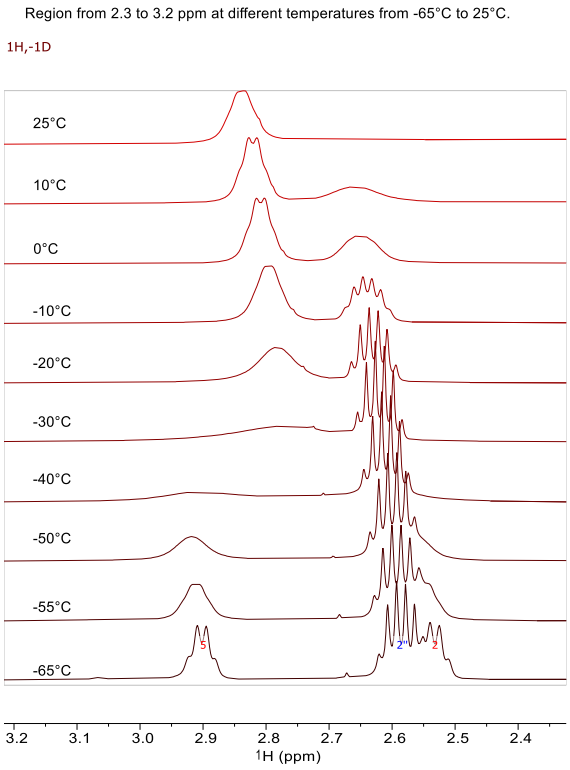


Figure S-19. ^{1}H NMR of complexes **40** and **41**, 500 MHz, CD_2Cl_2, at different temperatures.

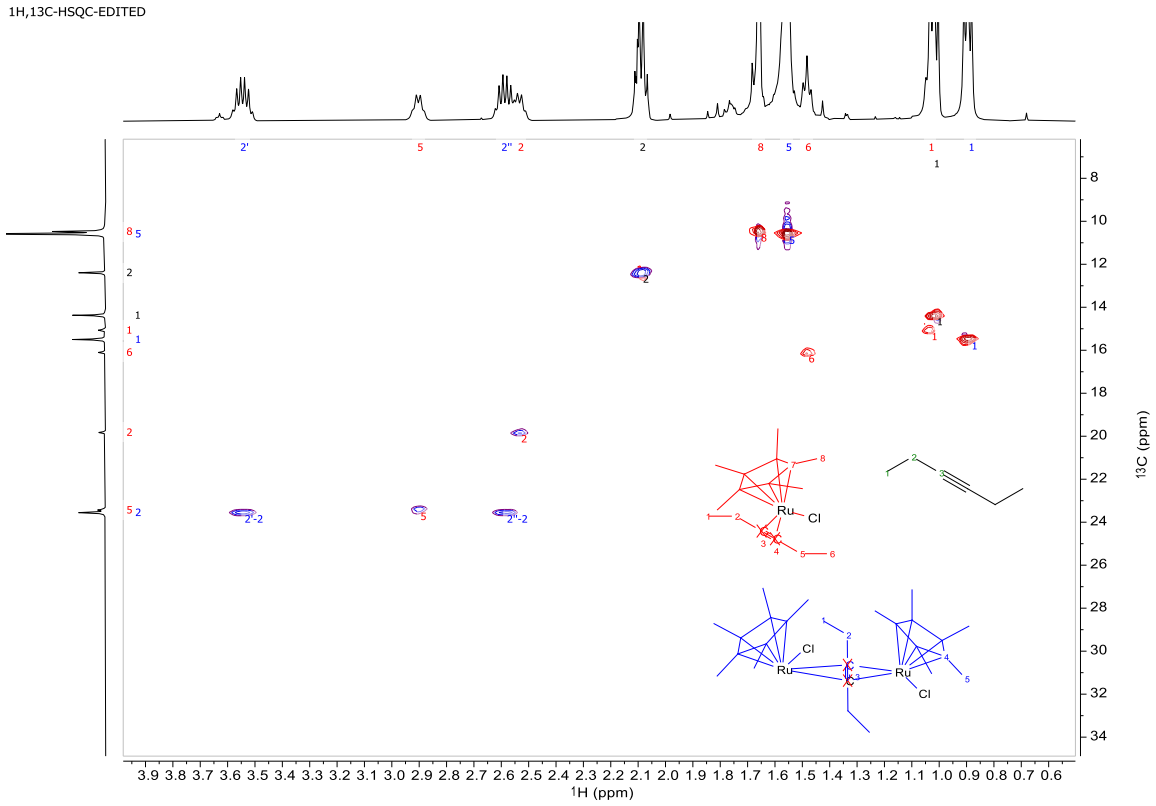


Figure S-20. HSQC NMR of complexes **40** and **41**, 500 MHz, CD_2Cl_2, at -65 °C.

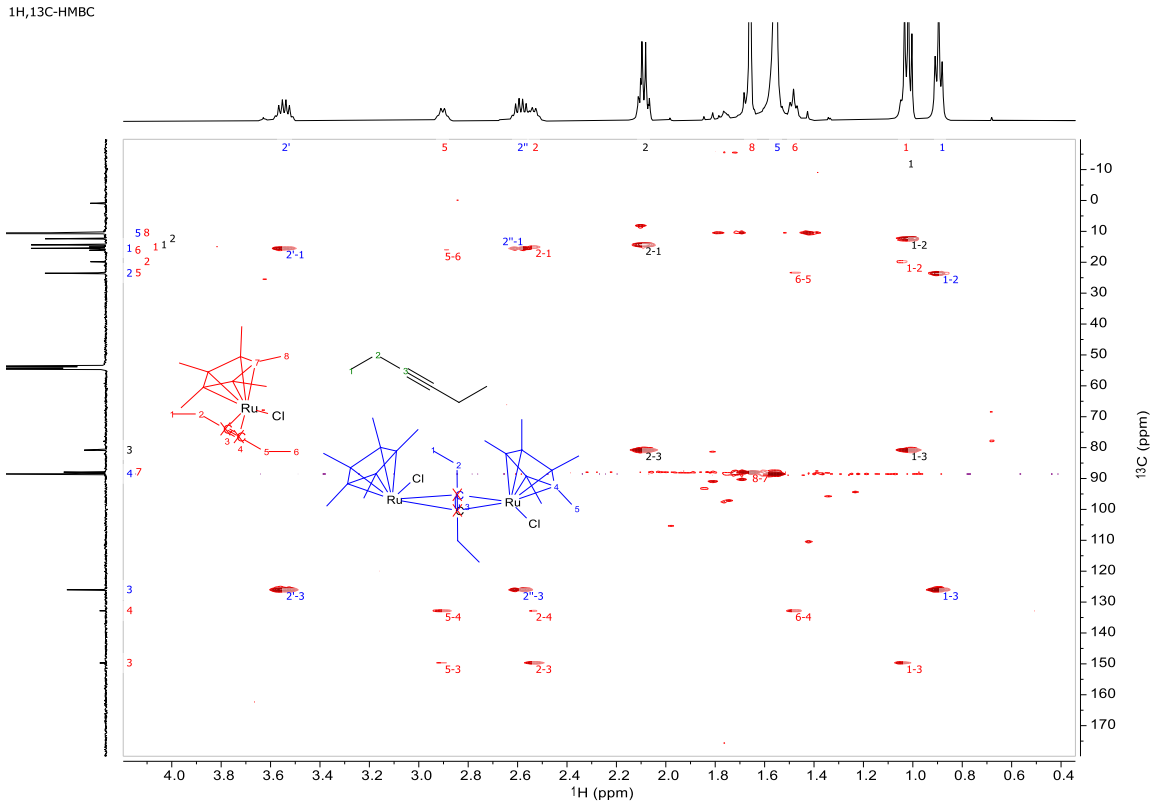


Figure S-21. HMBC NMR of complexes **40** and **41**, 500 MHz, CD_2Cl_2, at -65 °C.

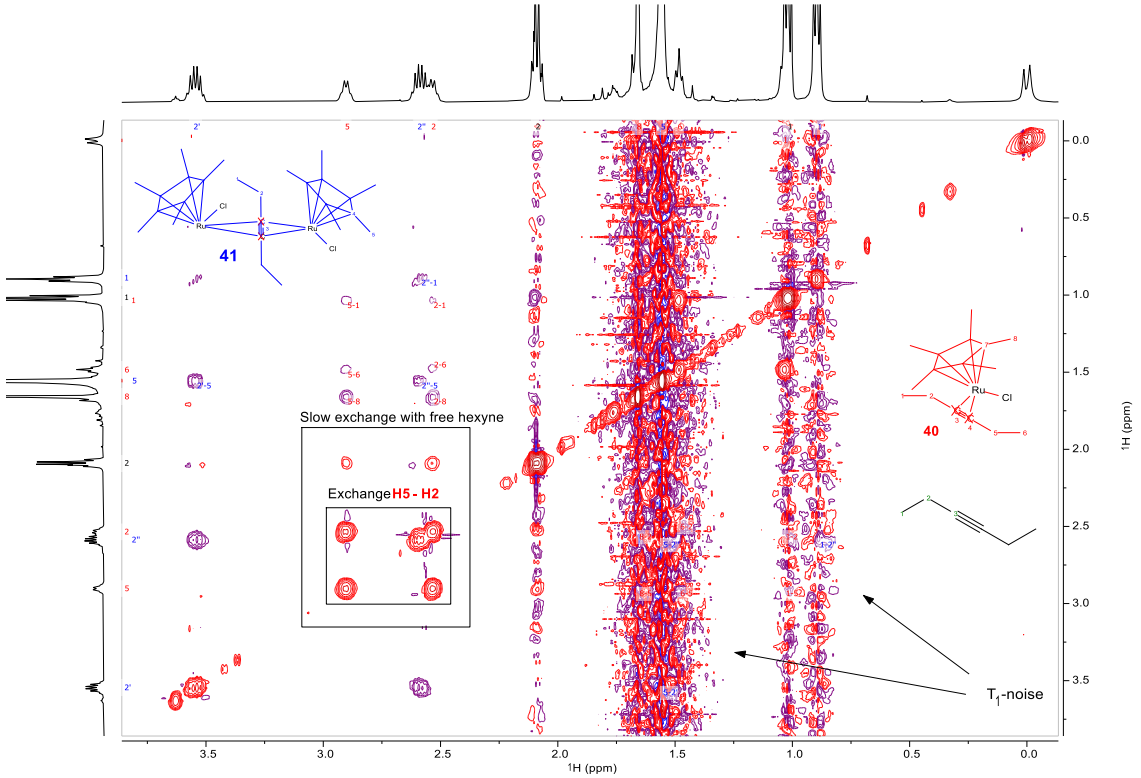


Figure S-22. NOESY NMR of complexes **40** and **41**, 500 MHz, CD_2Cl_2, at -65 °C.

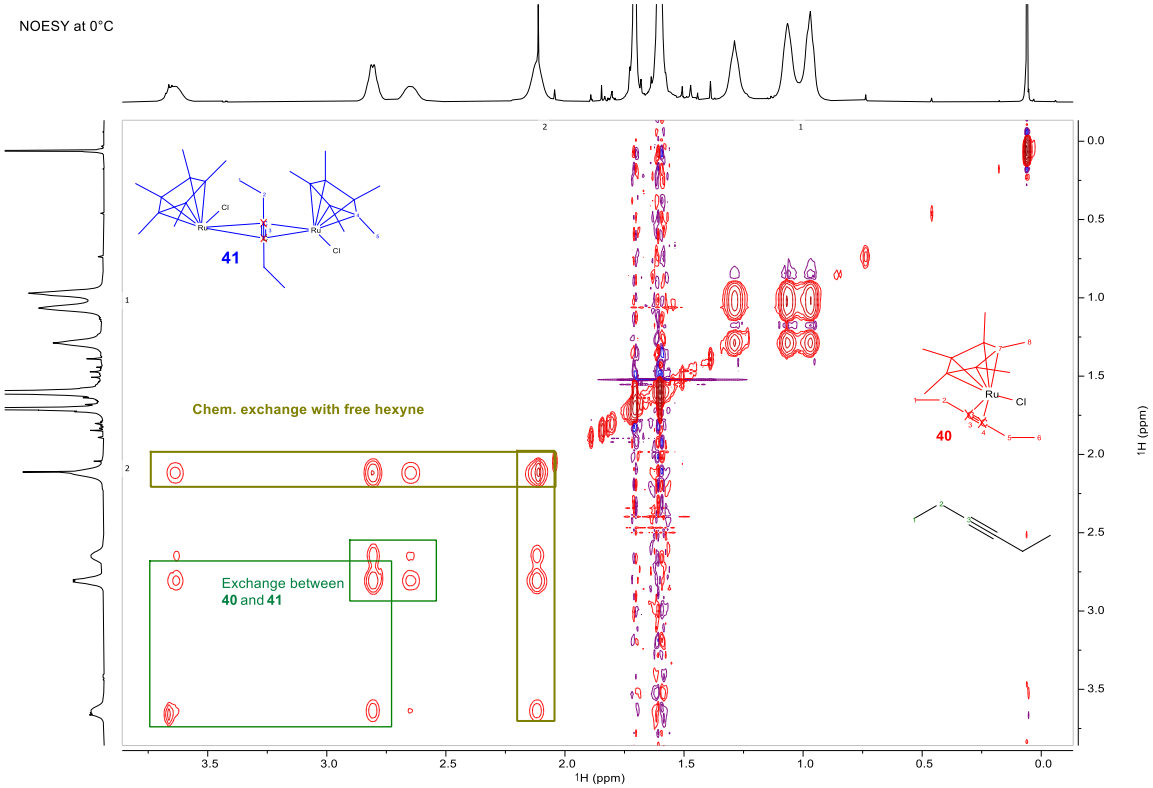
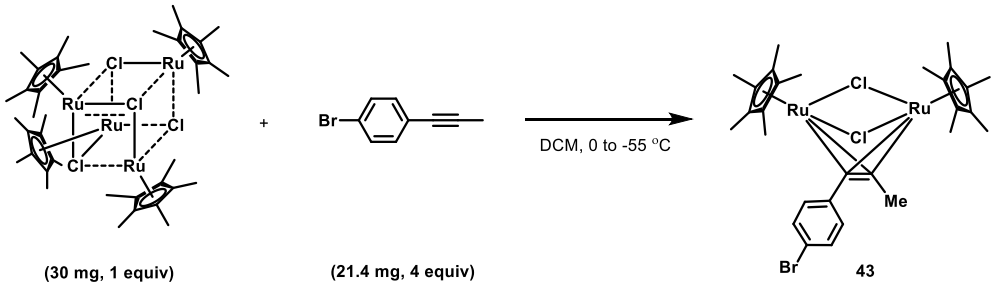
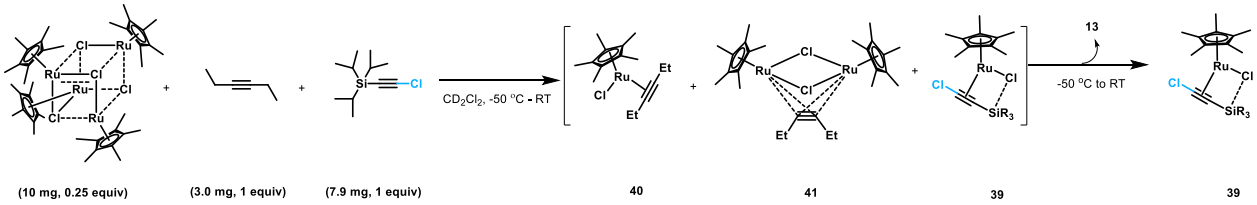


Figure S-23. NOESY NMR of complexes **40** and **41**, 500 MHz, CD_2Cl_2, at 0 °C.



Preparation of Complex 43. Compound **43** was generated by carefully layering a solution of $[Cp^*RuCl]_4$ (30 mg, 27.5 µmol) and 1-bromo-4-(prop-1-yn-1-yl)benzene (21.4 mg, 27.5 µmol) in dichloromethane with pentane. The Schlenk flask was placed in a cryostat and the temperature was gradually lowered from 0 °C to −55 °C over the course of 36 h.



Competition Experiment. A flame-dried J-Young NMR tube was charged with $[Cp^*RuCl]_4$ (10 mg, 9.1 µmol), 3-hexyne (3.01 mg, 36.7 µmol) and (chloroethynyl)triisopropylsilane (**1b**) (7.9 mg, 36.7 µmol) under Ar. CD_2Cl_2 (0.5 mL) was added at −78 °C and the NMR tube was tightly closed. The sample was quickly shaken to make sure all the components were dissolved, leading to the formation of a cherry red-solution. The tube was introduced into the probe-head of a NMR spectrometer, which had been precooled to −50 °C. The temperature was then raised in 10 °C increments until RT was reached and spectra were recorded at each step.

At −50 °C, complexes **40** and **41** were the major species in solution, which gradually disappeared to give rise to complex **39**, which was the only observable species at RT. When the sample was re-cooled to −50 °C, complex **39** remained the only detectable species, whereas complexes **40** and **41** were not re-generated.

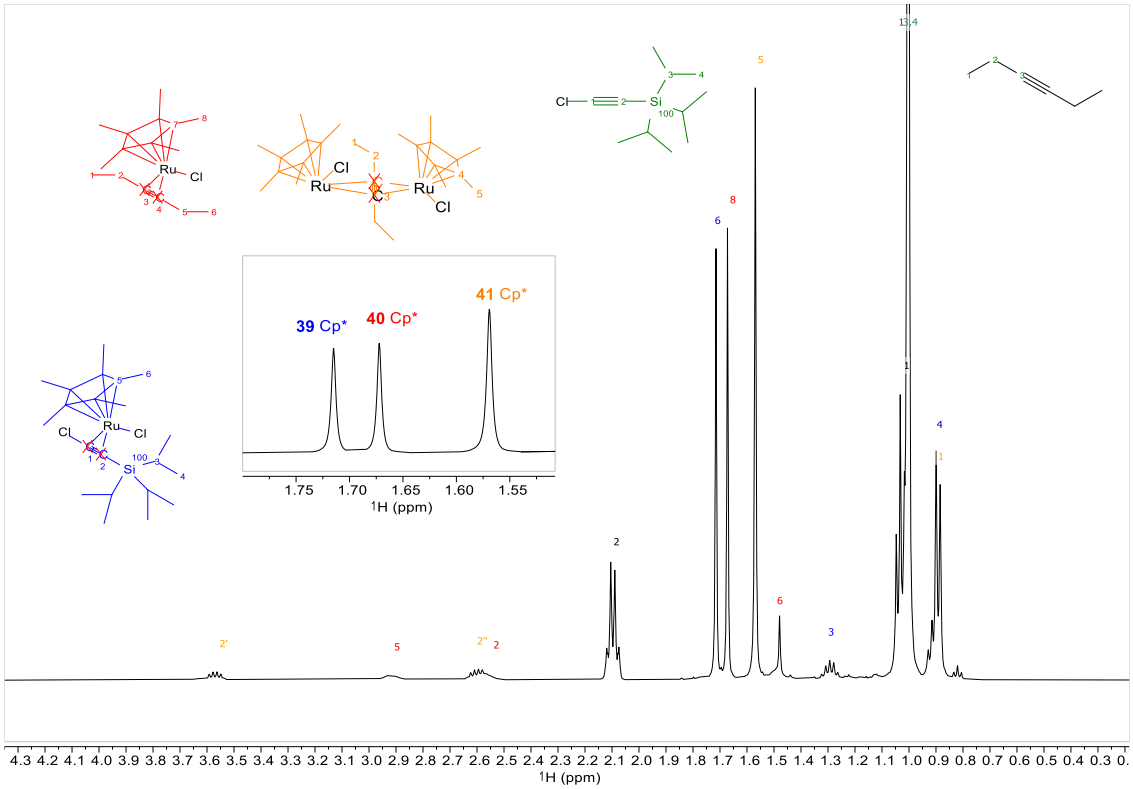


Figure S-24. ^{1}H NMR of complexes **39**, **40** and **41**, 500 MHz, CD_2Cl_2, at -50 °C.

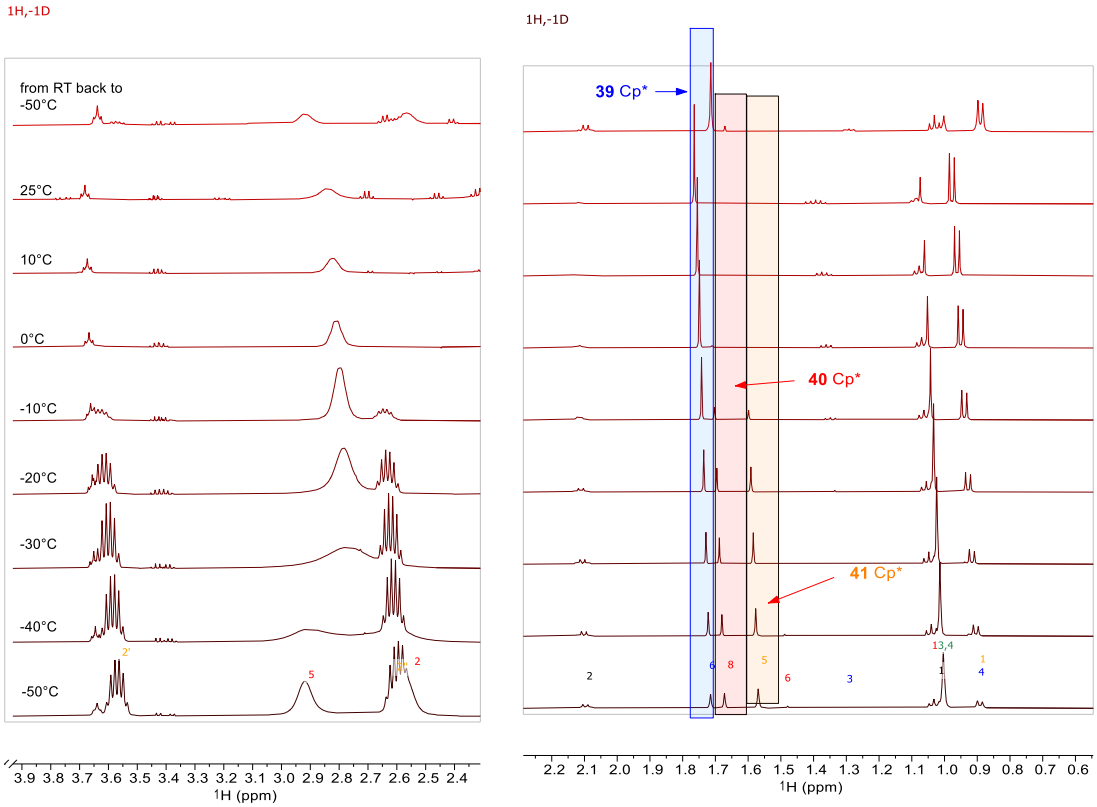


Figure S-25. ^{1}H NMR of complexes **39**, **40** and **41**, 500 MHz, CD_2Cl_2, at different temperatures.

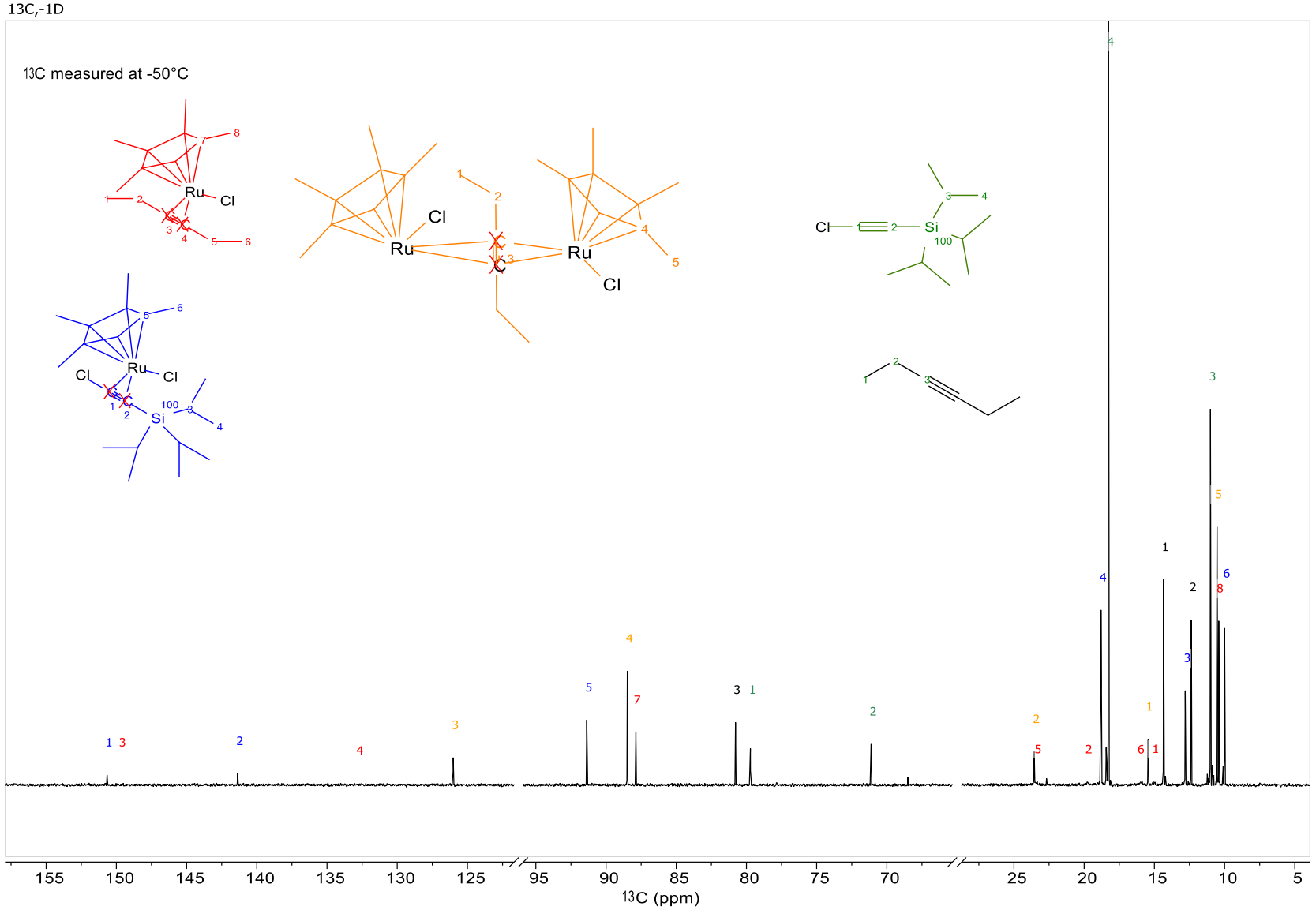


Figure S-26. ^{13}C NMR of complexes **39**, **40** and **41**, 500 MHz, CD_2Cl_2, at -50 °C.

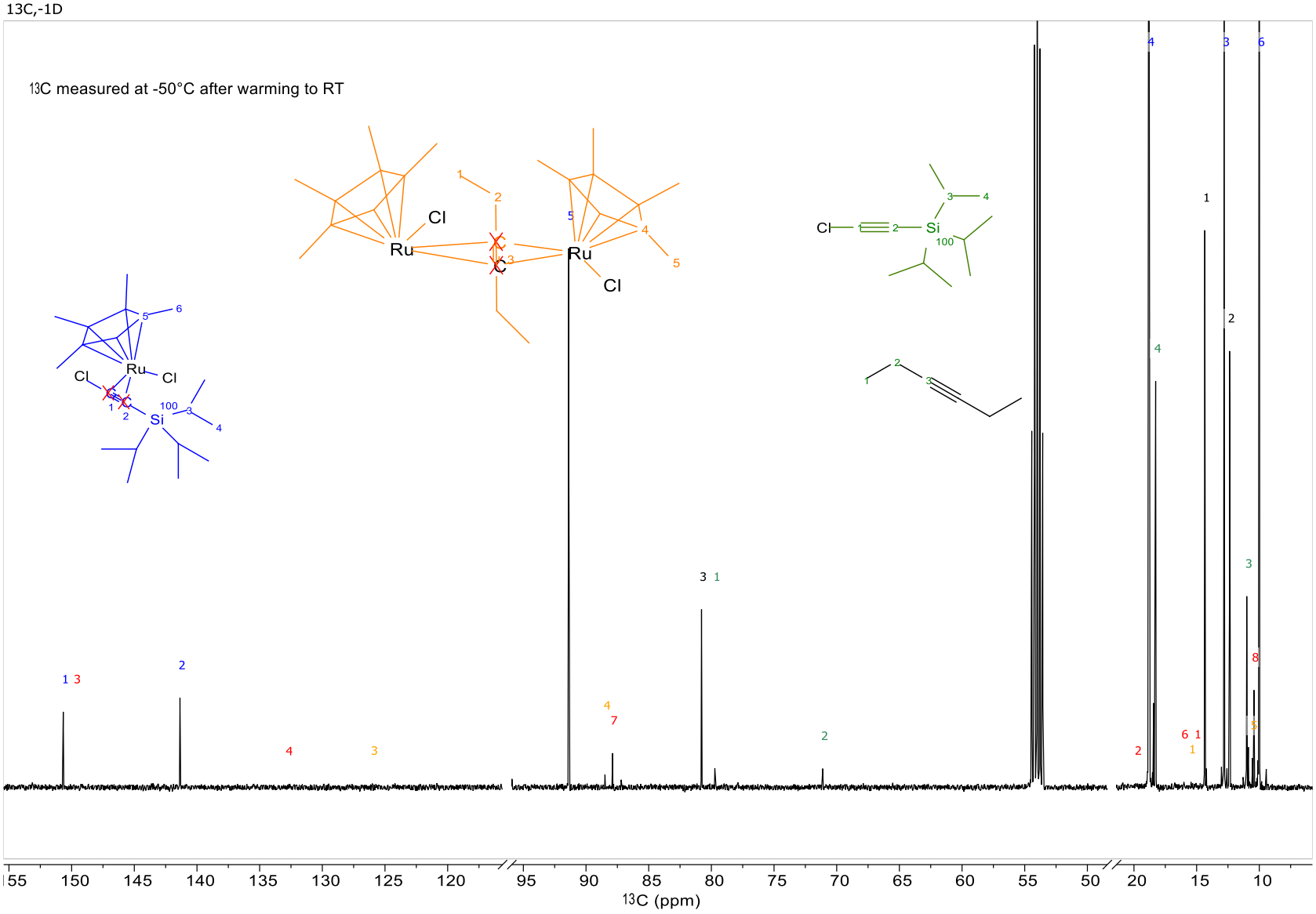
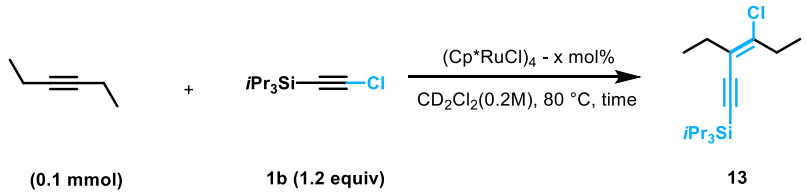


Figure S-27. ^{13}C NMR of complexes **39**, **40** and **41**, 500 MHz, CD_2Cl_2, at room temperature.

Kinetic NMR Studies



(0.1 mmol) 1b (1.2 equiv) 13

Representative Procedure. An oven-dried heavy wall precision pressure NMR tube was charged under Ar with $[Cp^*RuCl]_4$ (2.71 mg, 2 µmol, 2.5 mol%), 3-hexyne (8.2 mg, 0.1 mmol, 1 equiv), (chloroethynyl)triisopropylsilane **1b** (25.9 mg, 0.12 mmol, 1.2 equiv) and CD_2Cl_2 (0.2 M, 0.5 mL). The NMR tube was tightly closed under Ar and placed in the probe-head of an NMR spectrometer, which had been pre-heated to +80 °C. Spectra were recorded until full conversion of hexyne was reached.

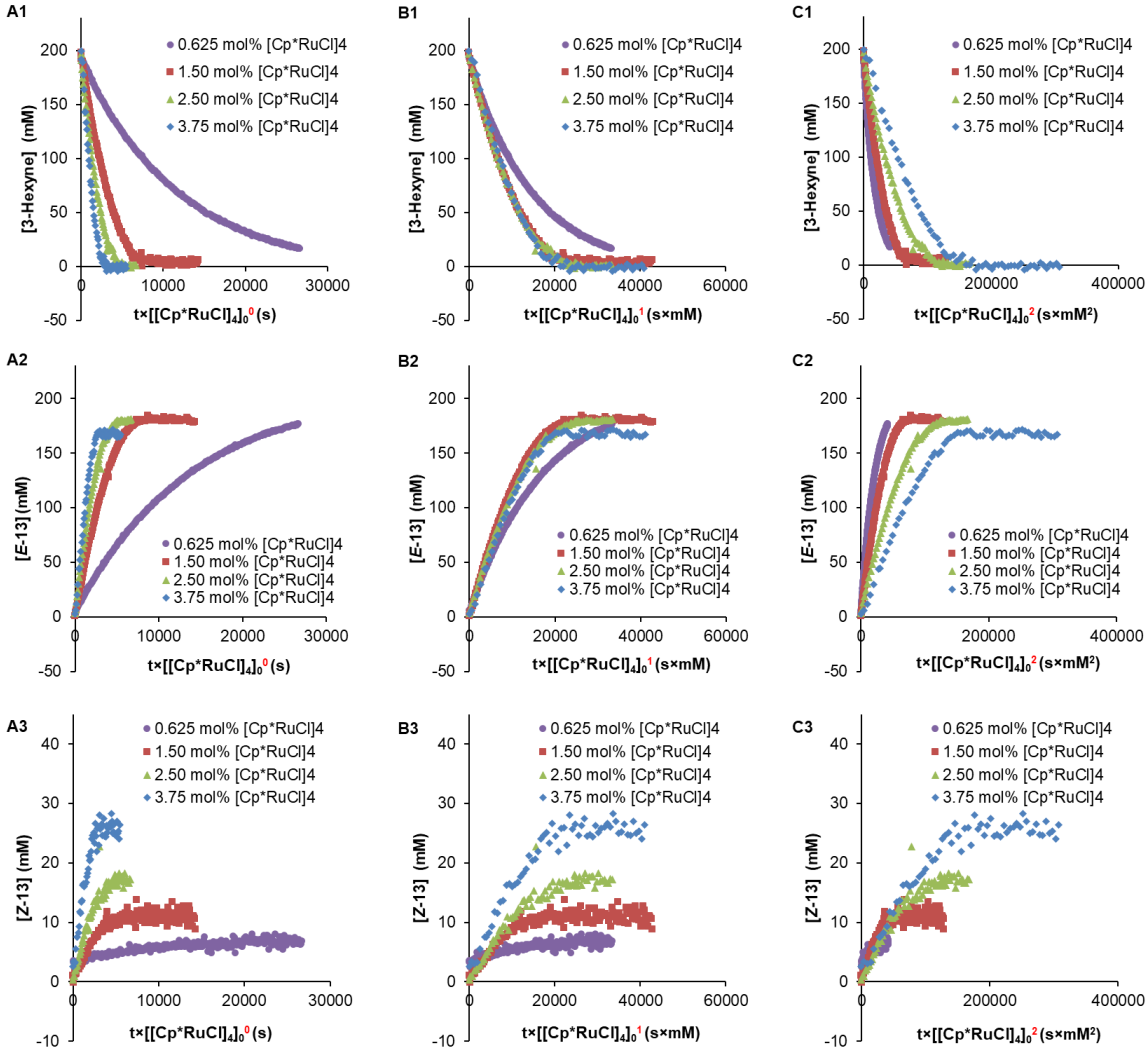


Figure S-28: Concentration plots obtained by NMR showing the concentration profiles of 3-hexyne (first row, 1), the *trans*-addition product (***E*-13**, second row, 2) and the *cis*-addition product (***Z*-13**, third row, 3) with time scales normalized to a zeroth- (A), first- (B) and second-(C) order dependence of the initial catalyst concentration.

The reaction order of the catalyst [Cp*RuCl]$_4$ was determined by variable time normalization analysis (VTNA).[7] The best fit of the time course for the consumption of the starting material conversion and the formation of the *trans*-chloroalkynylation product was obtained by assuming a first order dependence in catalyst (Figure S-28). At the lowest tested loading of 0.625 mol%, however, a deviation was observed that is thought to indicate competing catalyst degradation during the reaction.[8]

The observed first-order dependence of substrate consumption and *trans*-addition product formation suggests that the di-nuclear complex **41** has no major influence on the rate-determining step of the reaction. However, the *cis*/*trans* ratio was found to change upon changing the catalyst concentration, suggesting that **41** might be involved in the competing *cis*-addition process.

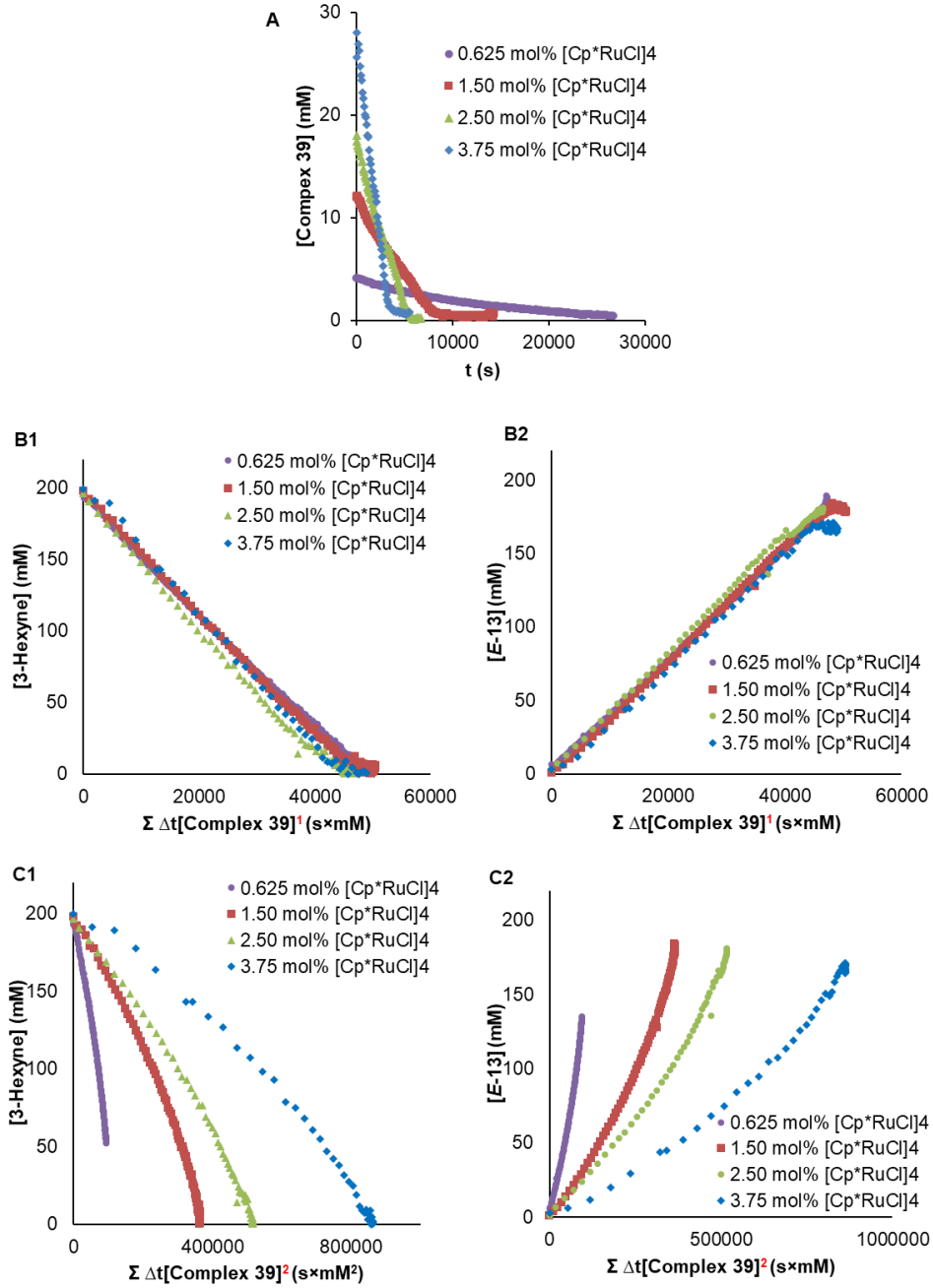


Figure S-29. Top row: Concentration profiles of complex [**39**] obtained from NMR spectra at different time points of the reaction. Middle row: Concentration profiles of 3-hexyne (SM) and the *trans*-addition product (*E*-**13**) with a time scale normalized to a first-order dependence on the concentration of complex **39** ([complex **39**]). Third row: Concentration profiles of 3-hexyne (SM) and the *trans*-addition product (*E*-**13**) with a time scale normalized to a second-order dependence on the concentration of complex **39** ([complex **39**]).

During the reaction complex **39** was found to be the major species in solution (Figure S-30); its concentration, however, significantly decreases over the course of the reaction (Figure S-29, A) and no new signals appears in the diamagnetic region of the NMR spectrum to compensate that. The concentration of the complex **39** could be extracted from the NMR data: the data was used to obtain a time-normalized concentration profile of the starting material and the *trans*-addition product. The concentration profiles are best fitted by assuming a first-order dependence on the concentration of complex **39**. This finding supports the hypothesis that complex **39** is a resting state (Figure S-31) of the reaction before the turnover-limiting step of the reaction.

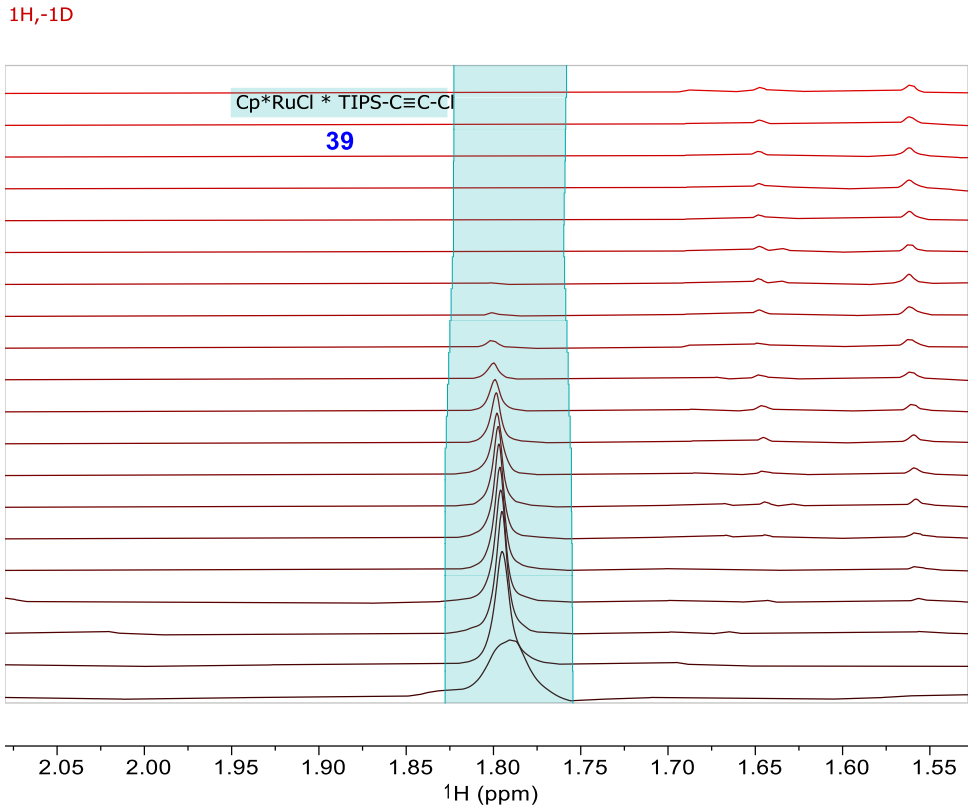


Figure S-30. ^{1}H NMR spectra showing the signal of complex **39** at different time points during the reaction of 3-hexyne with TIPS-C≡C-Cl (**1b**) in the presence of 1.5 mol% $[Cp^*RuCl]_4$.

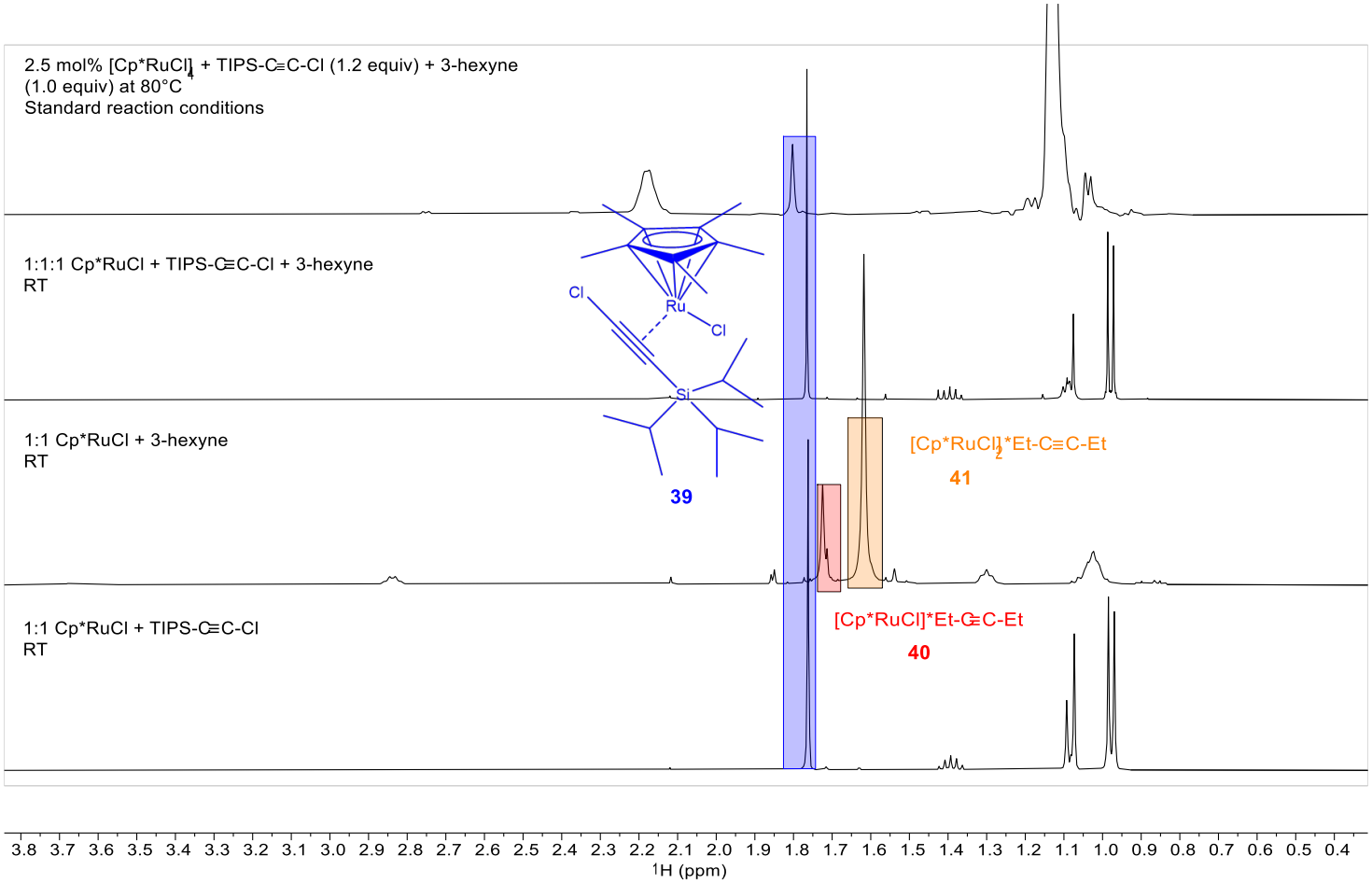


Figure S-31. ^{1}H NMR spectra of **39**. The data under reaction conditions agree with the results from the stoichiometric data at RT, suggesting that **39** is the resting state; the observed slight shift differences arise from the different temperatures at which the spectra were recorded.

SUPPORTING CRYSTALLOGRAPHIC DATA

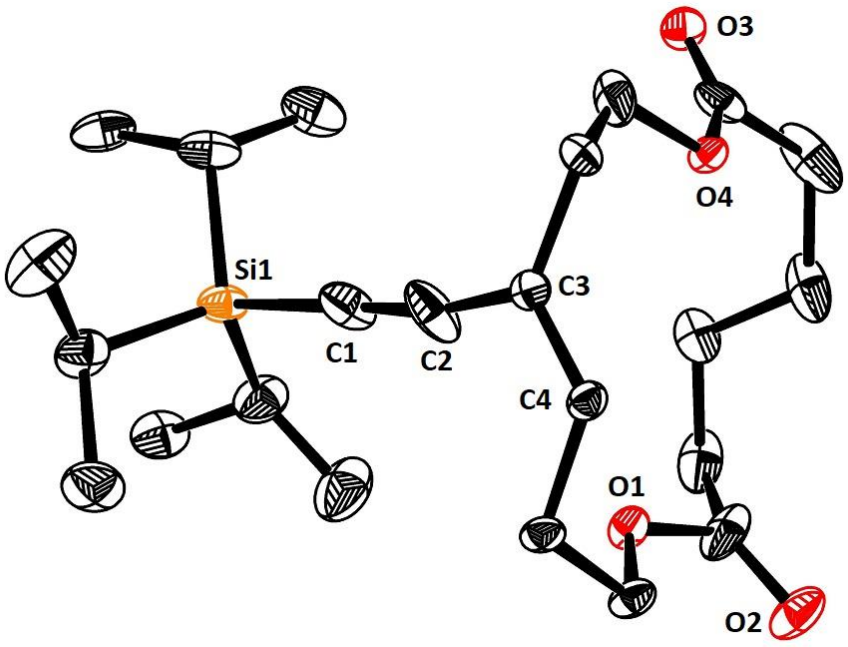


Figure S-32. Structure of the *trans*-hydroalkynylation product **9** in the solid state; H-atoms omitted and partial disorder not shown for clarity

X-ray Crystal Structure Analysis of Compound 9: C_{23} H_{37} O_4 Si, M_r = 405.61 g · mol^{-1}, colorless plate, crystal size 0.100 x 0.062 x 0.031 mm^3, triclinic, space group *P1̄* [2], a = 8.4426(5) Å, b = 8.9968(5) Å, c = 17.9958(10) Å, α = 90.508(3)°, β = 94.566(3), γ = 116.440(3)°, V = 1218.53(12) Å^3, T = 100(2) K, Z = 2, D_{calc} = 1.105 g · cm^3, λ = 0.71073 Å, μ(*Mo-K*$_\alpha$) = 0.119 mm^{-1}, analytical absorption correction (T_{min} = 0.99, T_{max} = 1.00), Bruker-AXS Kappa Mach3 diffractometer with APEX-II detector and IμS micro focus X-ray source, 1.137 < θ < 28.901°, 32056 measured reflections, 6334 independent reflections, 3754 reflections with I > 2σ(I), R_{int} = 0.0525, 331 parameters, S = 1.028, residual electron density +0.6 (1.06 Å from C16) / -0.4 (0.36 Å from C16) e · Å^{-3}. The structure was solved by *SHELXT* and refined by full-matrix least-squares (*SHELXL*) against F^2 to R_1 = 0.062 [I > 2σ(I)], wR_2 = 0.171. **CCDC-2021251.**

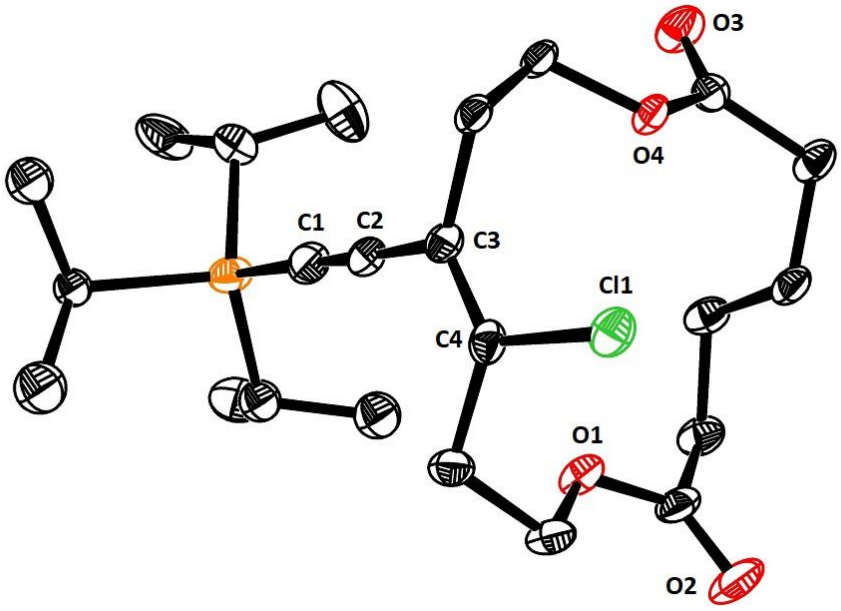


Figure S-33. Structure of the *trans*-chloroalkynylation product **21** in the solid state; H-atoms omitted for clarity

X-ray Crystal Structure Analysis of Compound 21: $C_{46}H_{74}BrClO_8Si_2$, M_r = 926.59 g · mol^{-1}, green prism, crystal size 0.09 x 0.09 x 0.06 mm^3, monoclinic, space group $P2_1/c$ [14], a = 20.230(8) Å, b = 14.151(4) Å, c = 9.106(2) Å, β = 98.35(3)°, V = 2579.3(14) Å^3, T = 100(2) K, Z = 2, D_{calc} = 1.193 g · cm^3, λ = 0.71073 Å, μ(*Mo-K*$_\alpha$) = 0.941 mm^{-1}, analytical absorption correction (T_{min} = 0.98, T_{max} = 0.99), Bruker AXS Enraf-Nonius KappaCCD diffractometer with a FR591 rotating Mo-anode X-ray source, 2.680 < θ < 28.985°, 41373 measured reflections, 6822 independent reflections, 4372 reflections with $I > 2\sigma(I)$, R_{int} = 0.1047, 296 parameters, S = 1.087, residual electron density +0.9 (0.96 Å from C4) / -0.7 (0.78 Å from Cl1) e · Å^{-3}. The structure was solved by *SHELXT* and refined by full-matrix least-squares (*SHELXL*) against F^2 to R_1 = 0.079 [$I > 2\sigma(I)$], wR_2 = 0.203. **CCDC-2021252**.

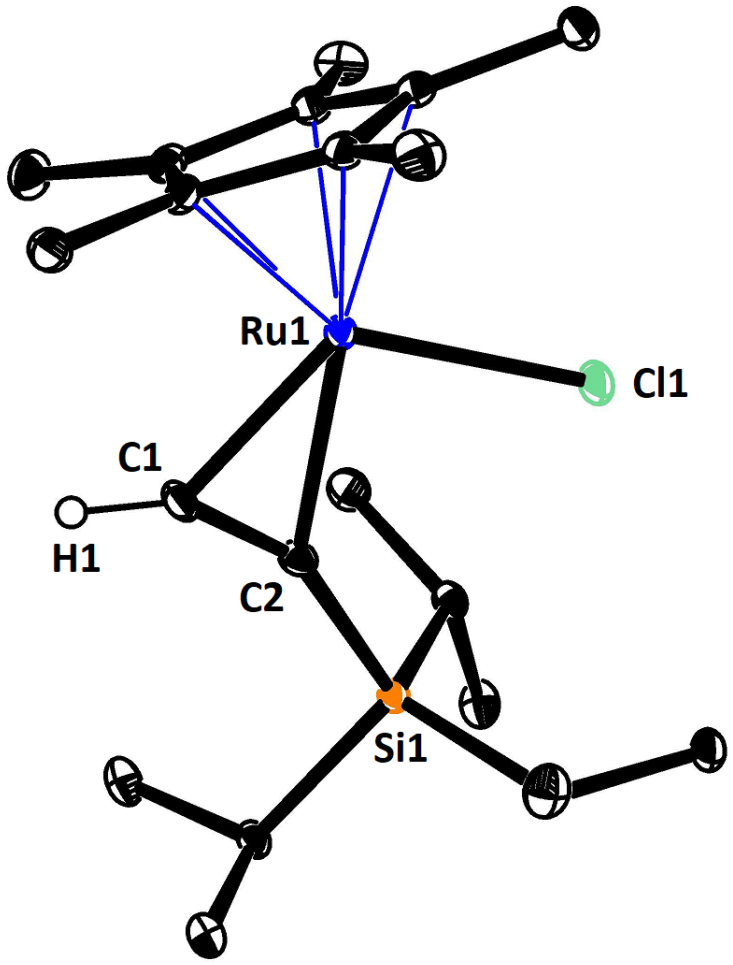


Figure S-34. Structure of complex **38** in the solid state; H-atoms except for the H-atopm at the alkyne terminus omitted for clarity

X-ray Crystal Structure Analysis of Complex 38: $C_{21}H_{37}ClRuSi$, M_r = 454.11 g · mol^{-1}, red plate, crystal size 0.14 x 0.06 x 0.01 mm^3, triclinic, space group *P1̄* [2], a = 8.0846(17) Å, b = 10.414(4) Å, c = 14.273(6) Å, α = 68.73(2)°, β = 85.88(3)°, γ = 83.49(3)°, V = 1112.1(7) Å^3, T = 100(2) K, Z = 2, D_{calc} = 1.356 g · cm^3, λ = 0.71073 Å, μ(*Mo-K*$_\alpha$) = 0.880 mm^{-1}, analytical absorption correction (T_{min} = 0.91, T_{max} = 0.98), Bruker AXS Enraf-Nonius KappaCCD diffractometer with a FR591 rotating Mo-anode X-ray source, 2.920 < θ < 33.117°, 33456 measured reflections, 8431 independent reflections, 6048 reflections with $I > 2\sigma(I)$, R_{int} = 0.1019, 232 parameters, S = 1.007, residual electron density +1.0 (0.86 Å from Ru1) / -1.3 (0.82 Å from Ru1) e · Å^{-3}. The structure was solved by *SHELXT* and refined by full-matrix least-squares (*SHELXL*) against F^2 to R_1 = 0.048 [$I > 2\sigma(I)$], wR_2 = 0.103. **CCDC-2021253**

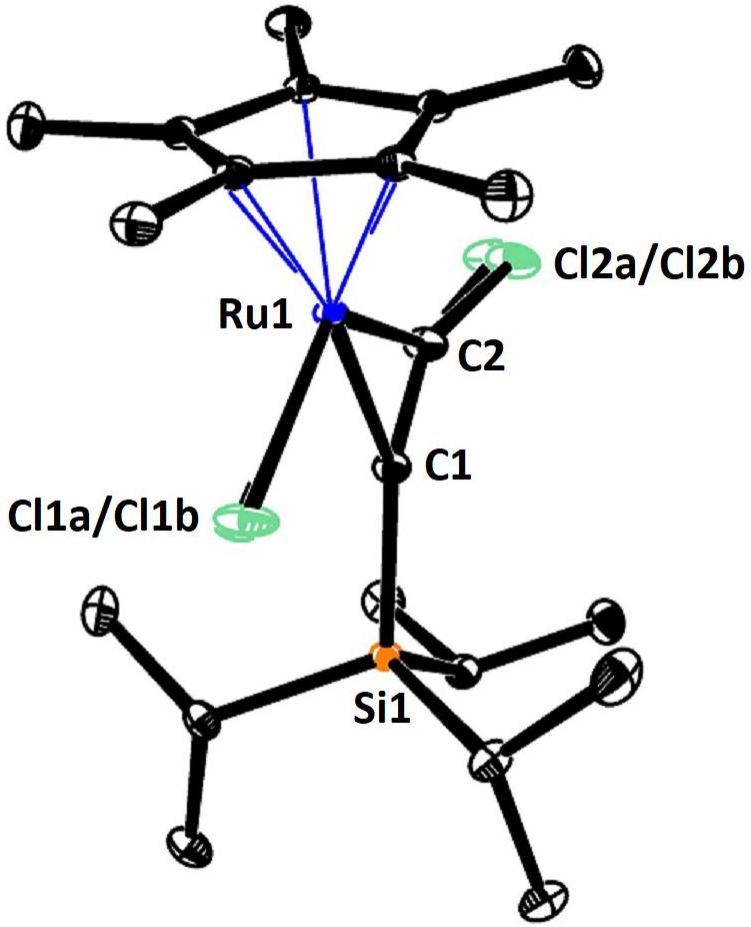


Figure S-35. Structure of complex **39** in the solid state showing the disorder of both chlorine atoms over two positions each; H-atoms omitted for clarity

X-ray Crystal Structure Analysis of Complex 39: C_{21} H_{36} Cl_2 Ru Si, M_r = 488.56 g · mol^{-1}, red plate, crystal size 0.11 x 0.10 x 0.06 mm^3, monoclinic, space group $P2_1/n$ [14], a = 11.4233(17) Å, b = 14.4169(18) Å, c = 14.874(2) Å, β = 108.354(12)°, V = 2324.9(6) Å^3, T = 100(2) K, Z = 4, D_{calc} = 1.396 g · cm^3, λ = 0.71073 Å, μ(*Mo*-K_α) = 0.958 mm^{-1}, analytical absorption correction (T_{min} = 0.91, T_{max} = 0.95), Bruker AXS Enraf-Nonius KappaCCD diffractometer with a FR591 rotating Mo-anode X-ray source, 2.705 < θ < 33.160°, 51888 measured reflections, 8846 independent reflections, 7467 reflections with $I > 2\sigma(I)$, R_{int} = 0.0379, 257 parameters, S = 1.083, residual electron density +0.5 (0.68 Å from C20) / -0.7 (0.67 Å from Ru1) e · Å^{-3}. The structure was solved by *SHELXT* and refined by full-matrix least-squares (*SHELXL*) against F^2 to R_1 = 0.025 [$I > 2\sigma(I)$], wR_2 = 0.055. **CCDC-2021254.**

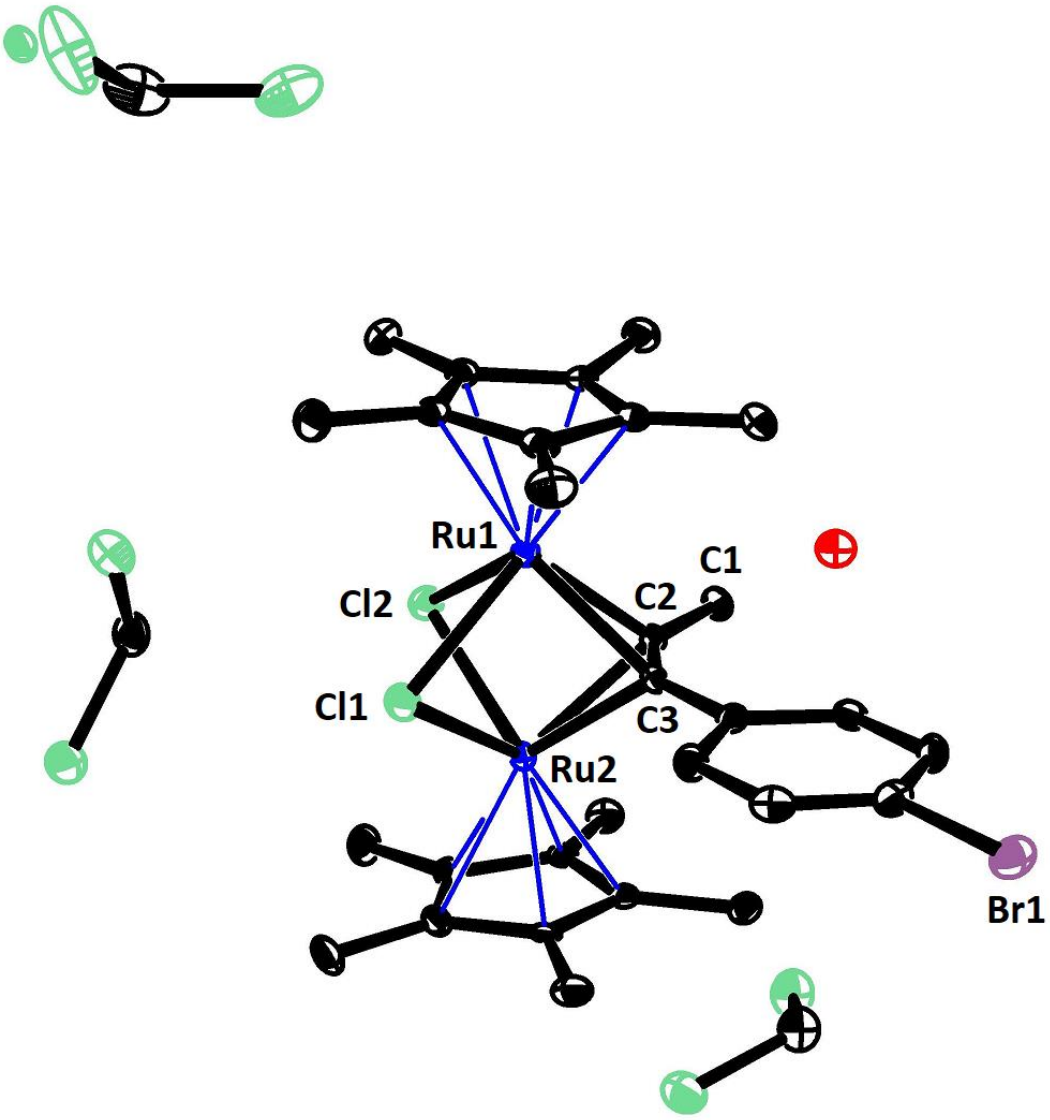
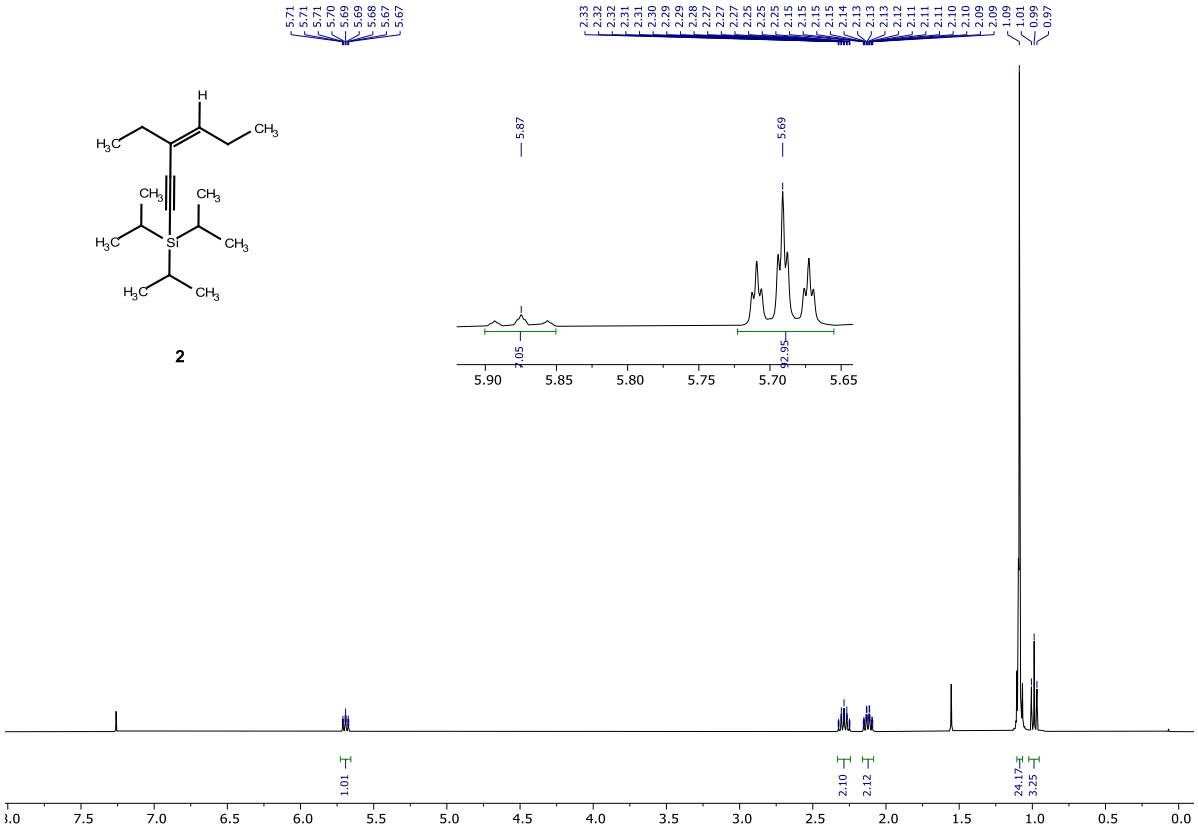


Figure S-36. Structure of complex **43** in the solid state with co-crystallized solutes in the unit cell; H-atoms omitted for clarity

X-ray Crystal Structure Analysis of Complex 43: $C_{32}H_{45}BrCl_9ORu_2$, M_r = 1046.78 g · mol^{-1}, red prism, crystal size 0.047 x 0.023 x 0.013 mm^3, triclinic, space group *P*$\bar{1}$ [2], a = 12.1055(7) Å, b = 13.6064(7) Å, c = 14.5860(9) Å, α = 110.798(3)°, β = 94.118(3)°, γ = 111.416(3)°, V = 2034.1(2) Å^3, T = 100(2) K, Z = 2, D_{calc} = 1.709 g · cm^3, λ = 0.71073 Å, μ(*Mo-K*$_\alpha$) = 2.341 mm^{-1}, analytical absorption correction (T_{min} = 0.93, T_{max} = 0.98), Bruker-AXS Kappa Mach3 diffractometer with APEX-II detector and IμS micro focus X-ray source, 1.535 < θ < 27.496°, 55147 measured reflections, 9253 independent reflections, 6309 reflections with I > 2σ(I), R_{int} = 0.1042, 420 parameters, S = 0.996, residual electron density +1.6 (1.18 Å from Br1) / -0.9 (0.79 Å from Ru2) e · Å^{-3}. The structure was solved by *SHELXT* and refined by full-matrix least-squares (*SHELXL*) against F^2 to R_1 = 0.041 [I > 2σ(I)], wR_2 = 0.088. **CCDC-2021255**.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2.14
2.13
2.13
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2.11
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2.09
2.09
1.09
1.01
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0.97
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CH3
CH3
H3C
Si
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H3C
CH3
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5.85
5.80
5.75
5.70
5.65
1.01
2.10
2.12
24.17
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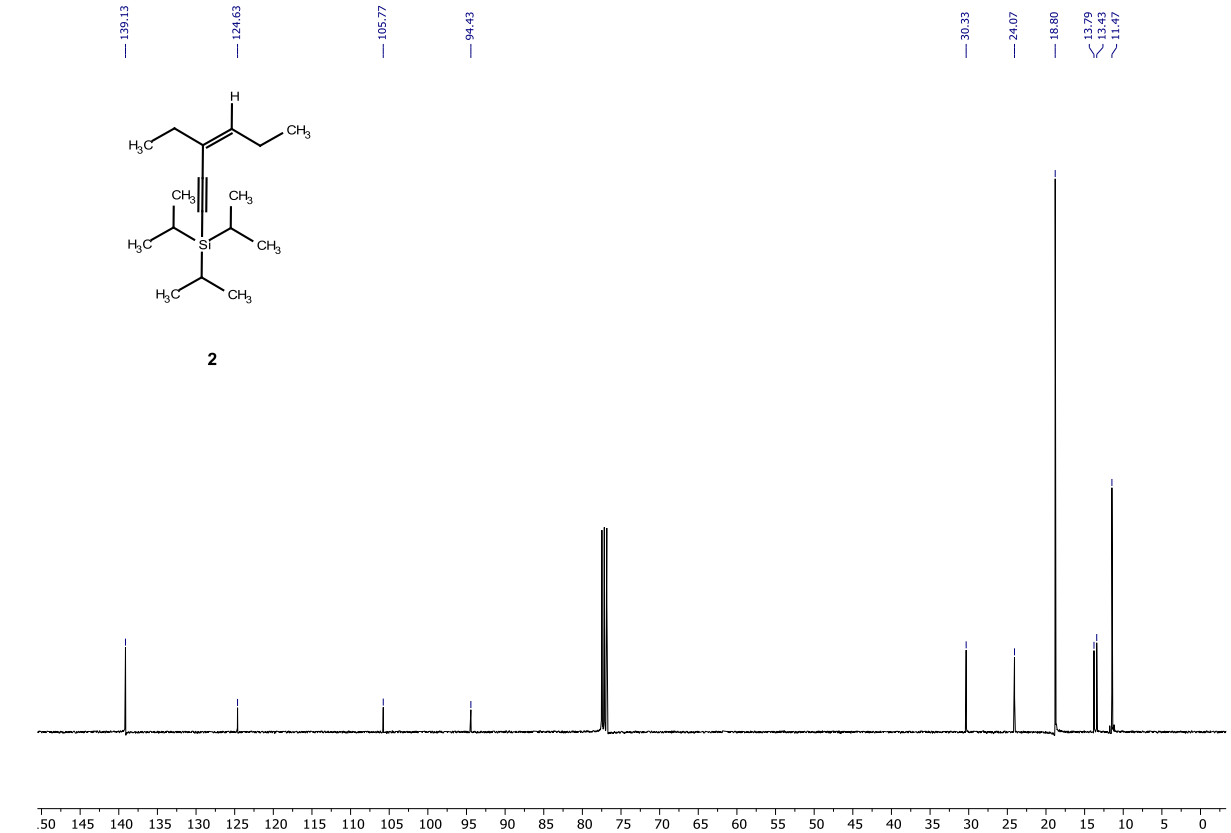
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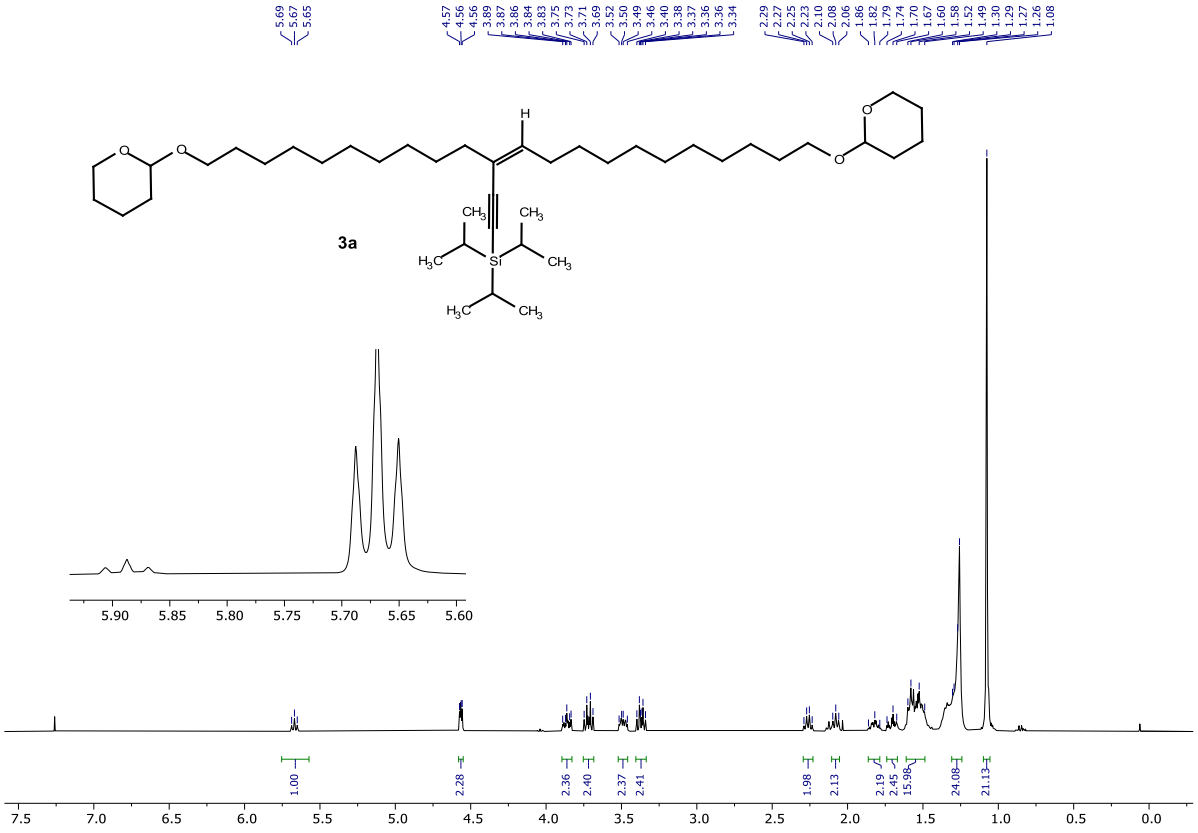
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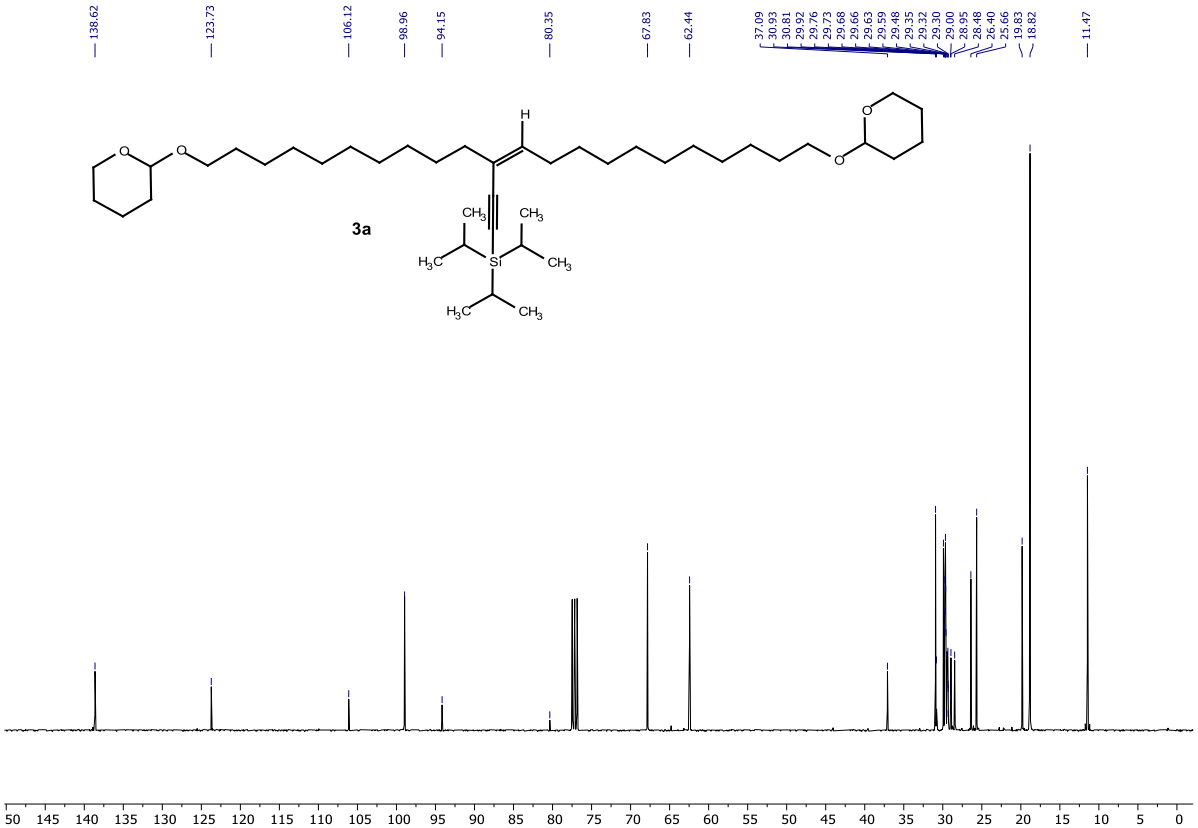
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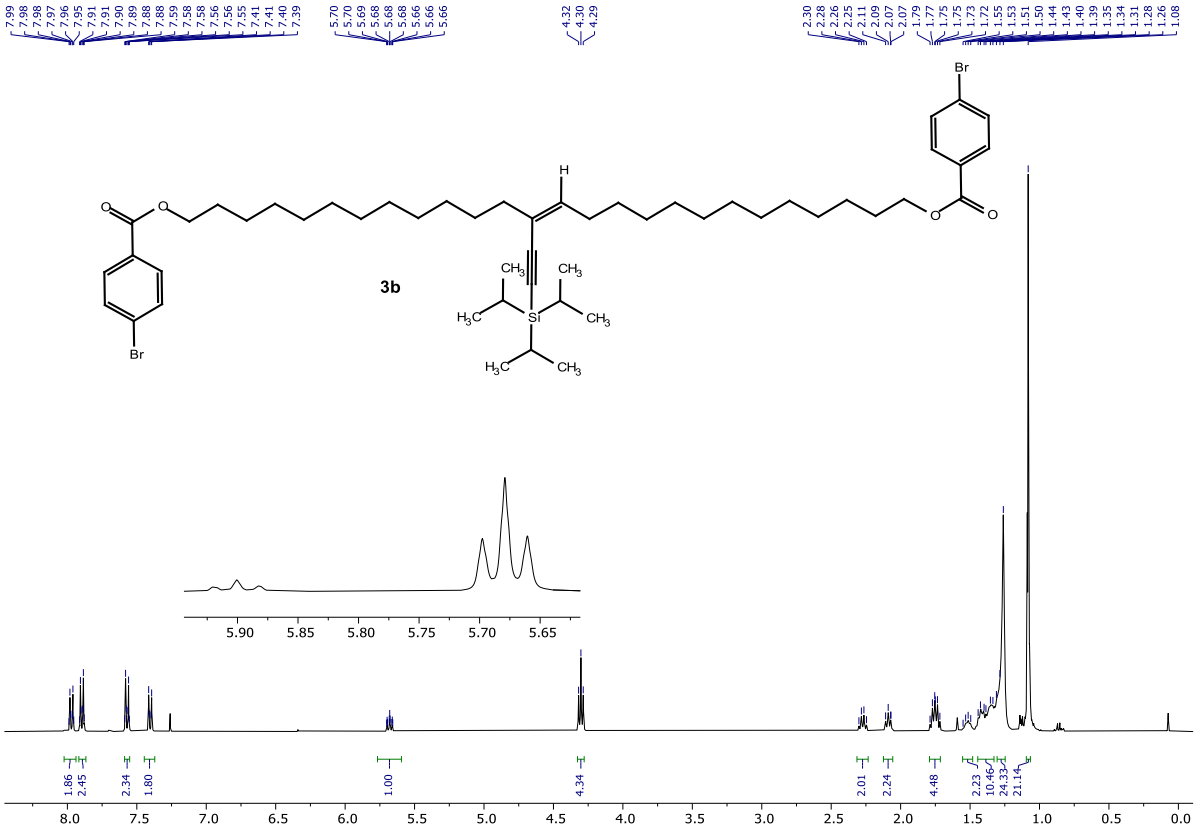
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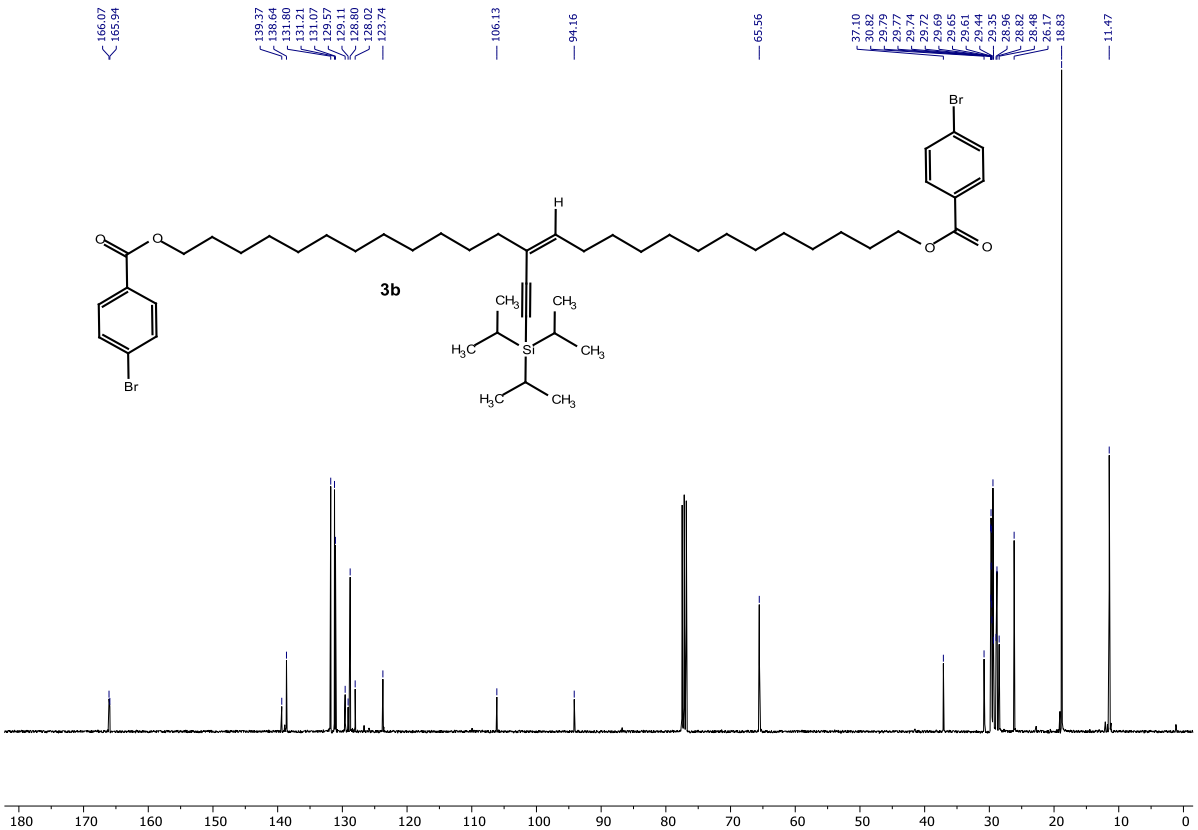
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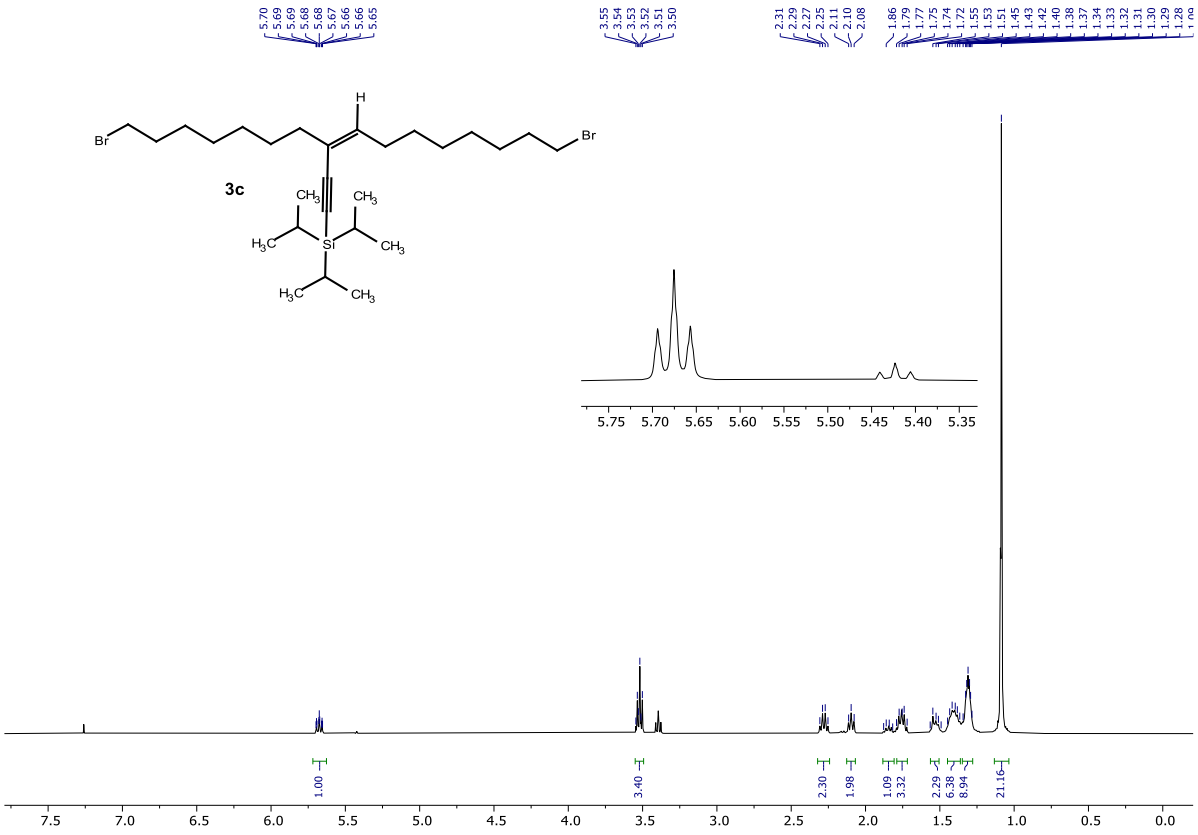
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CH3
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3.55 3.54 3.53 3.52 3.51 3.50
2.31 2.29 2.27 2.25 2.11 2.10 2.08
1.86 1.79 1.77 1.75 1.74 1.72 1.55 1.53 1.51 1.45 1.43 1.42 1.40 1.38 1.37 1.34 1.33 1.32 1.31 1.30 1.29 1.28
1.00 3.40 2.30 1.98 1.09 3.32 2.29 6.38 8.94 21.16
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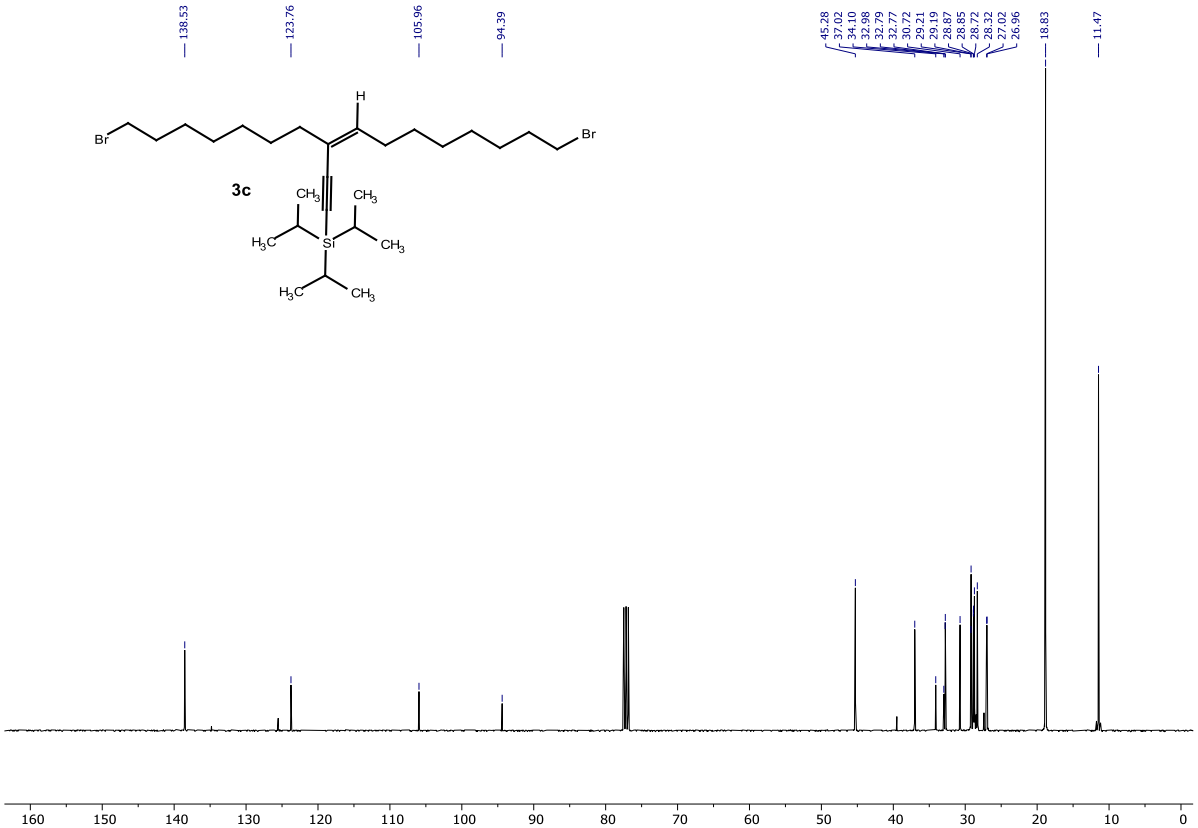
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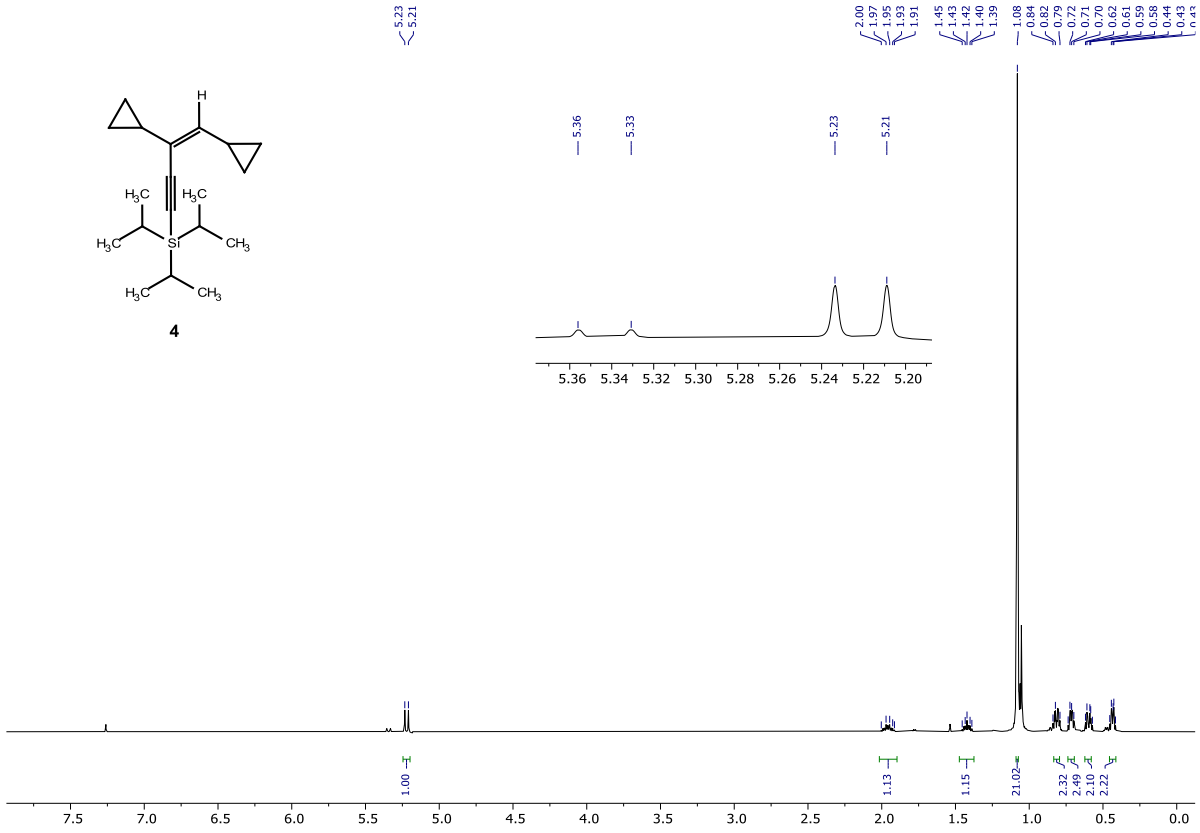
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0.71
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2.49
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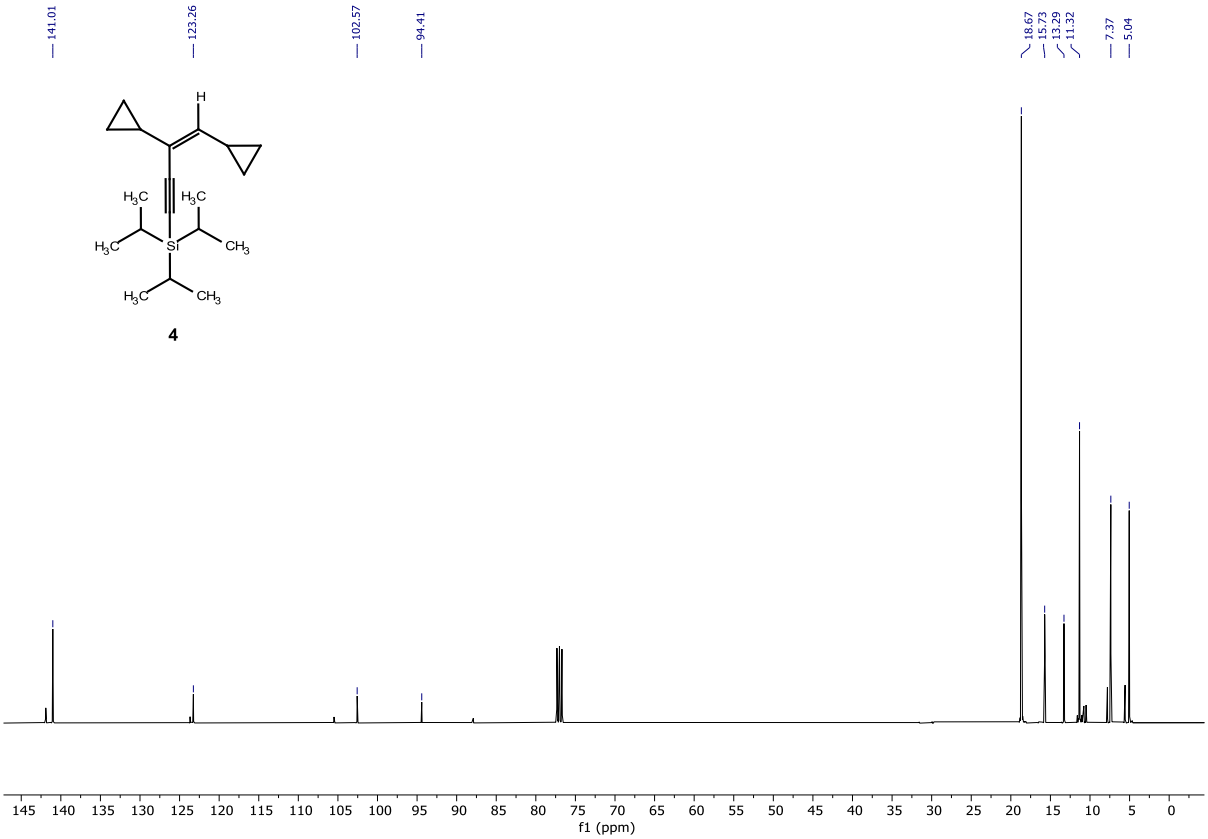
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4
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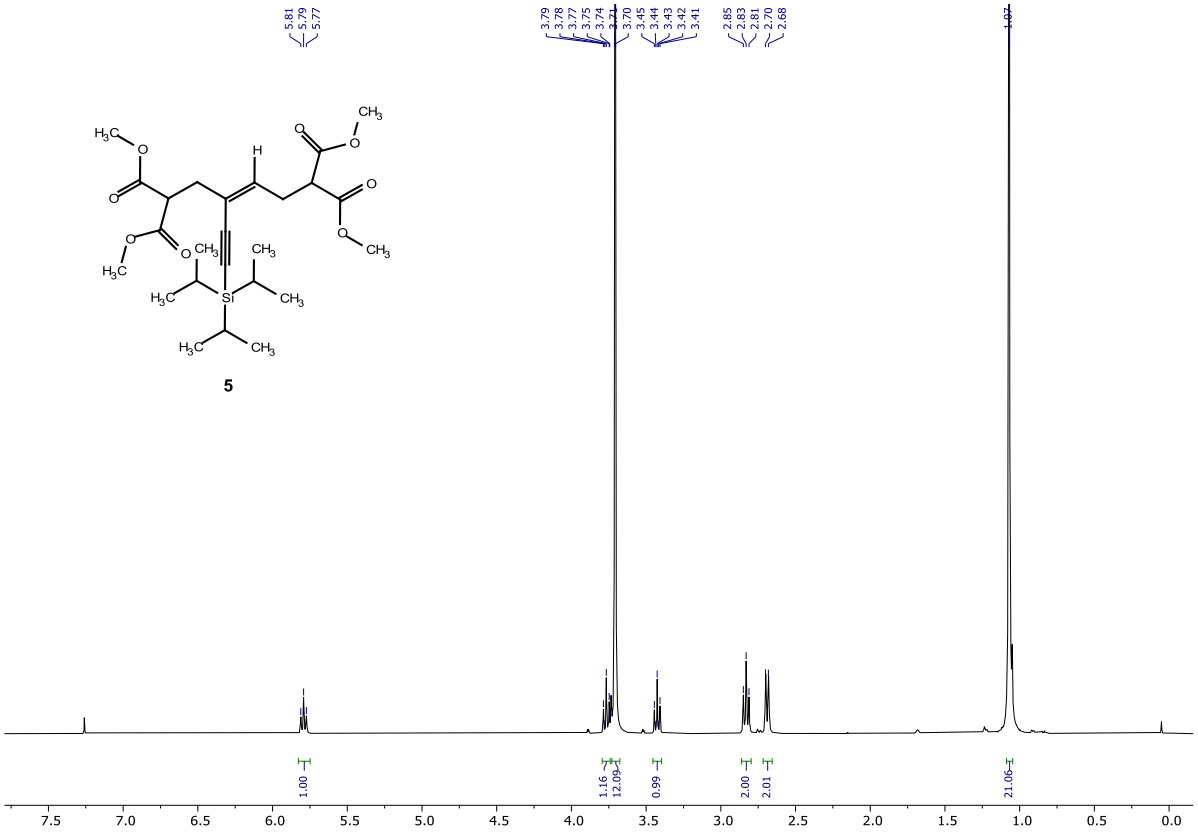
f1 (ppm)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3.70
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3.44
3.43
3.42
3.41
2.85
2.83
2.81
2.70
2.68
1.07
1.00
1.16
12.09
0.99
2.00
2.01
21.06
7.5
7.0
6.5
6.0
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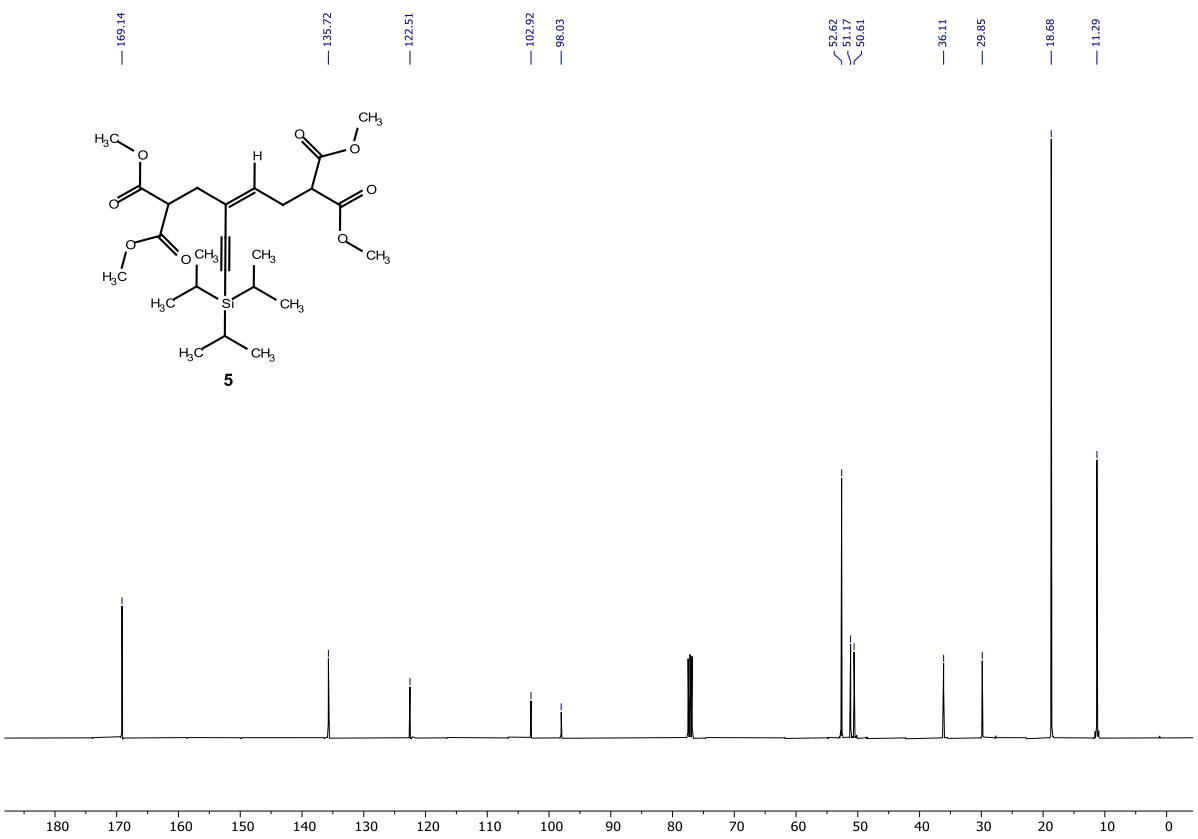
0.0

5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50.61
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18.68
11.29
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140
130
120
110
100
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80
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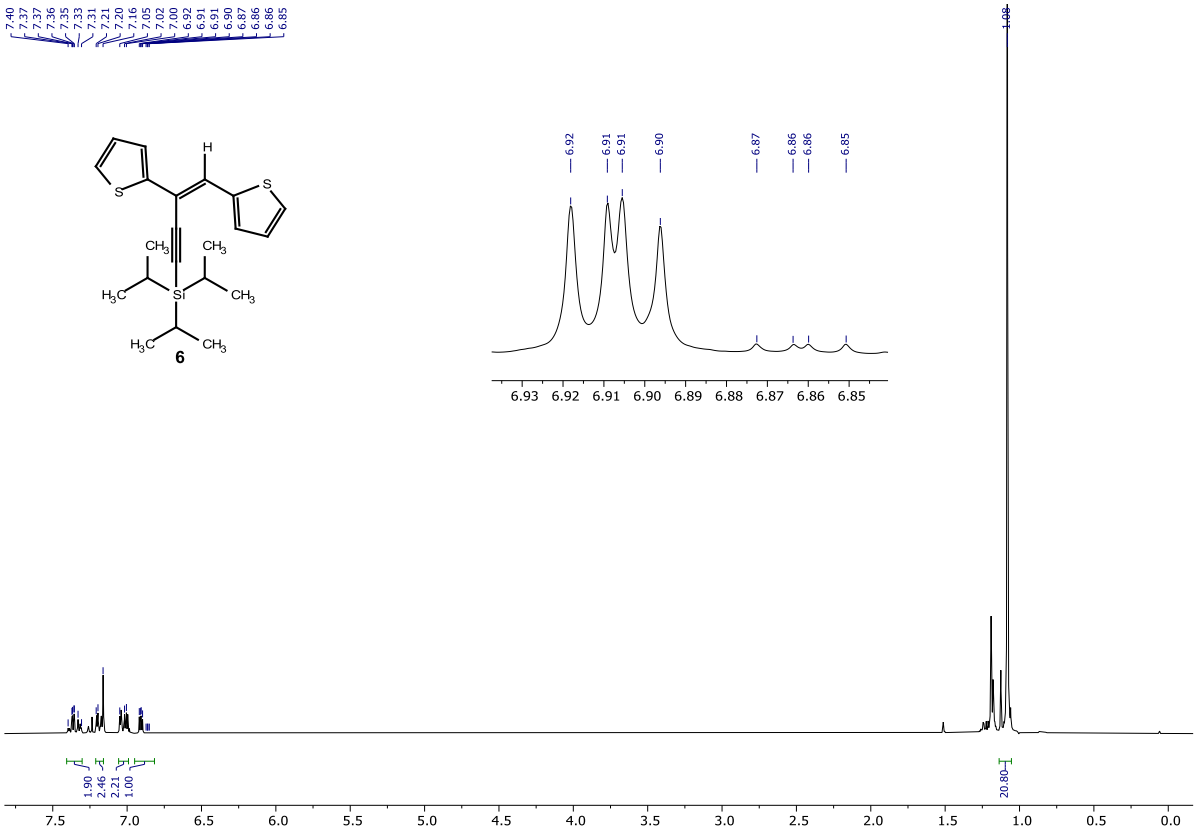
60
50
40
30
20
10
0

5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1.08
6.92 6.91 6.91 6.90 6.87 6.86 6.86 6.85
6.93 6.92 6.91 6.90 6.89 6.88 6.87 6.86 6.85
1.90 2.46 2.21 1.00 20.80
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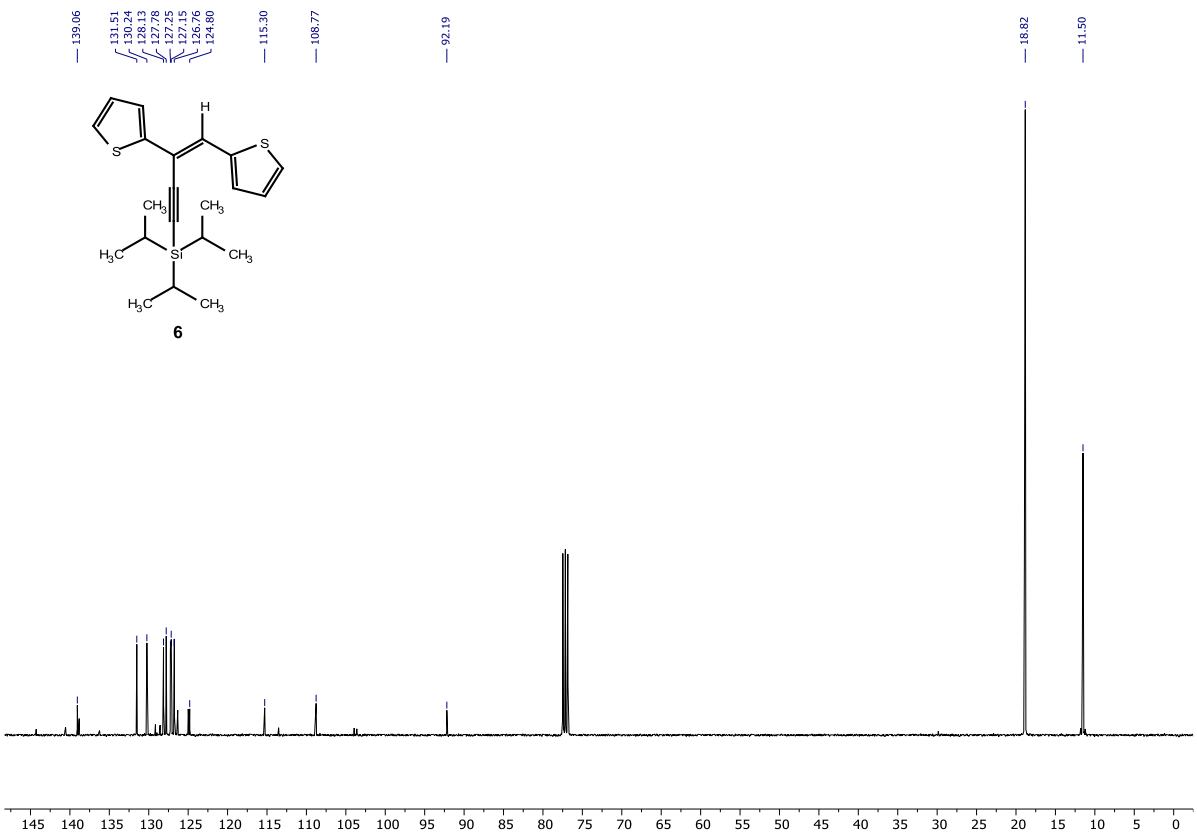
6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145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
6


5.83
5.83
5.83
5.81
5.81
5.81
5.79
5.79
5.79
2.39
2.37
2.35
2.34
2.20
2.18
2.17
1.60
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1.55
1.53
1.40
1.38
1.37
1.29
1.29
1.27
1.09
H3C
CH3
Si
CH3
H3C
CH3
CH3
H
0.94
1.94
1.94
4.41
12.00
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7.5
7.0
6.5
6.0
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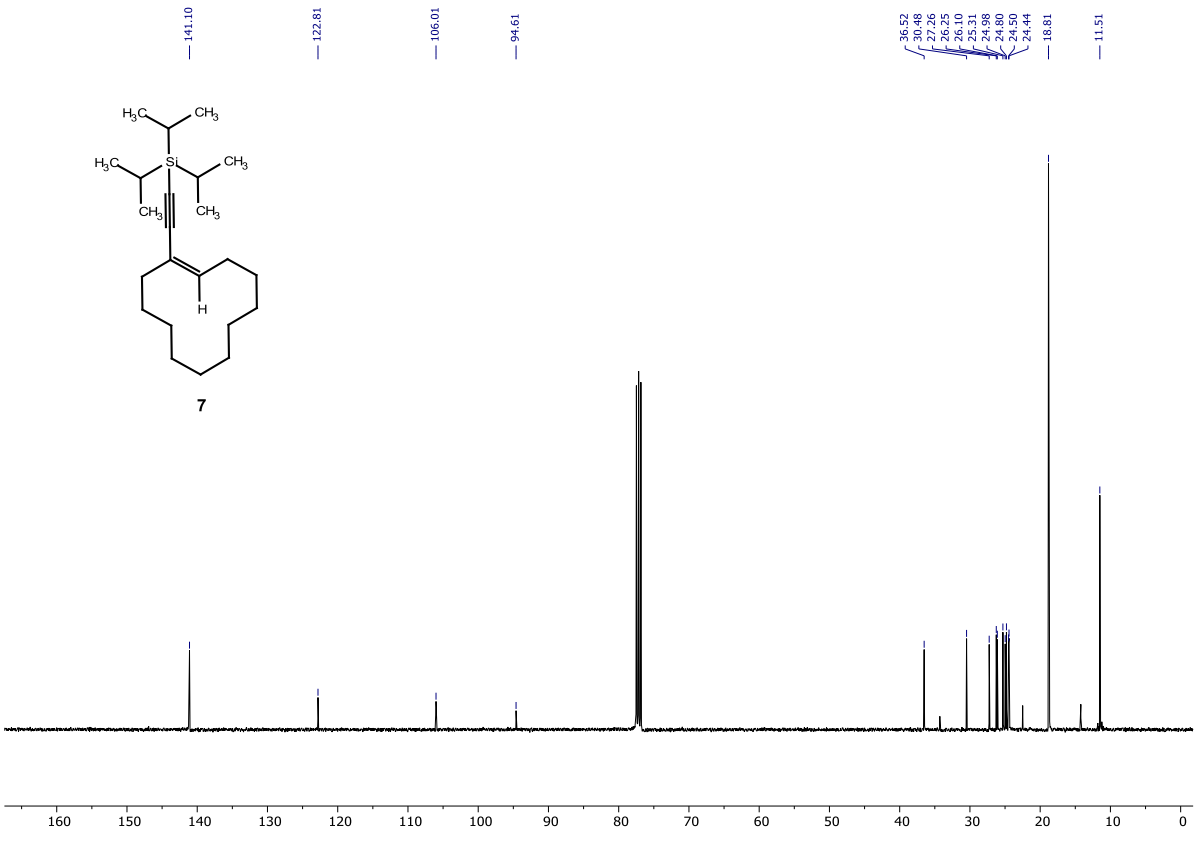
0.0

7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24.80
24.50
24.44
18.81
11.51
H3C
CH3
Si
CH3
H3C
CH3
CH3
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60
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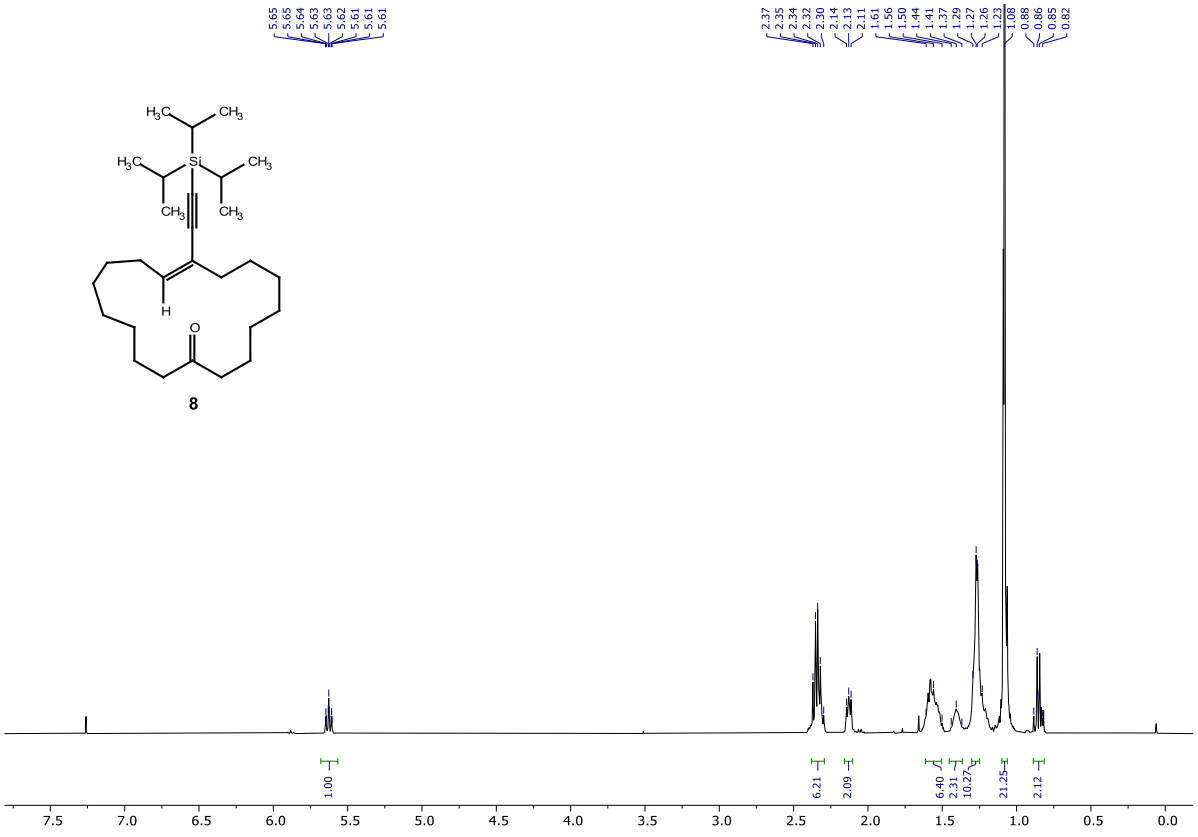
20
10
0

7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5.61
5.61
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2.34
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2.30
2.14
2.13
2.11
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1.56
1.50
1.44
1.41
1.37
1.29
1.27
1.26
1.23
1.08
0.88
0.86
0.85
0.82
H3C
CH3
Si
CH3
CH3
CH3
H
O
1.00
6.21
2.09
6.40
2.31
10.27
21.25
2.12
7.5
7.0
6.5
6.0
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4.0
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3.0
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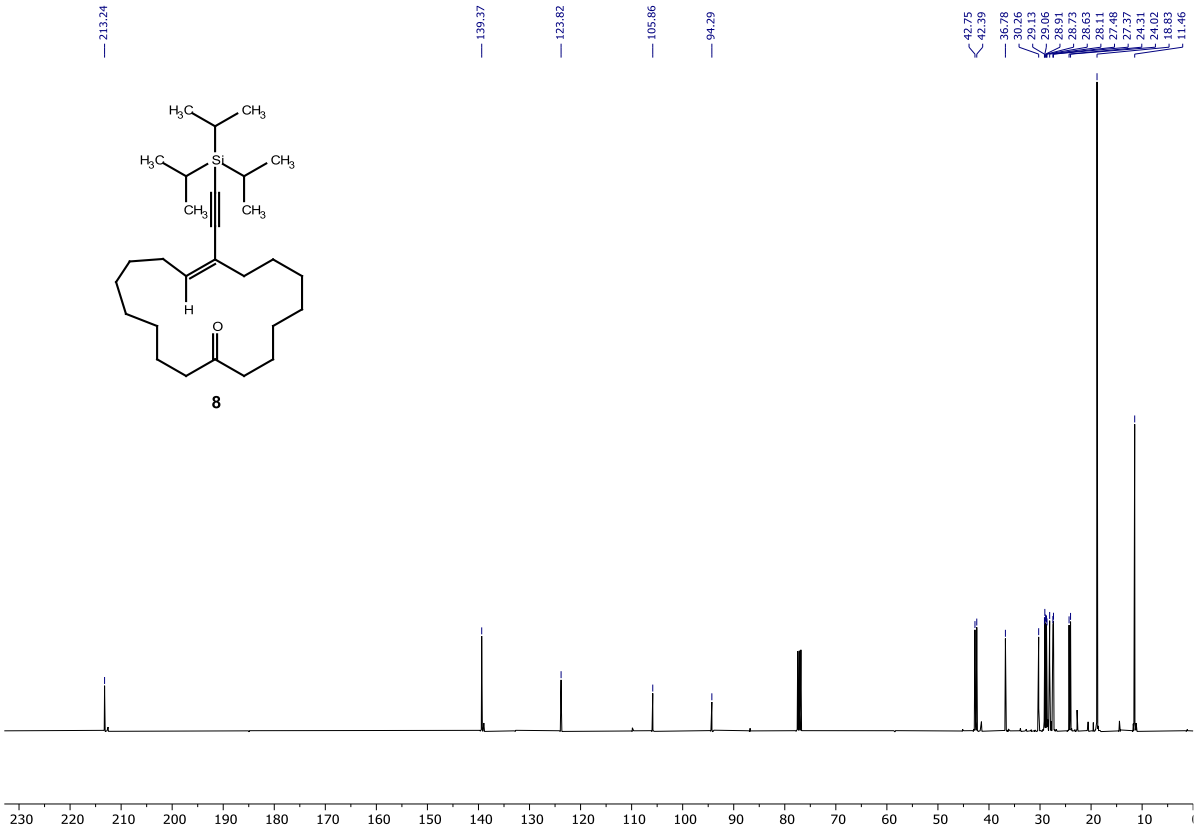
2.0
1.5
1.0
0.5
0.0

8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123.82
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94.29
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28.73
28.63
28.11
27.48
27.37
24.31
24.02
18.83
11.46
H3C
CH3
Si
CH3
CH3
CH3
H
O
230
220
210
200
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70
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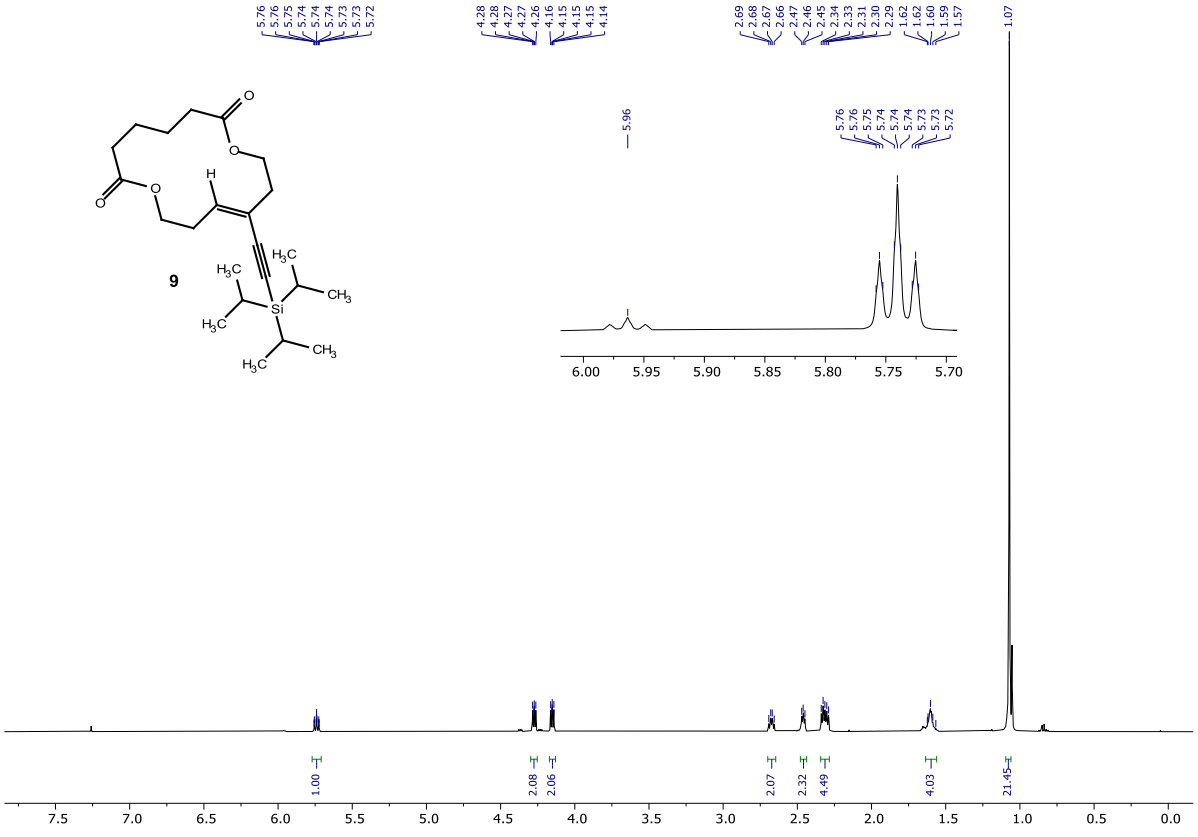
30
20
10

8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5.96
6.00
5.95
5.90
5.85
5.80
5.75
5.70
1.00
2.08
2.06
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2.32
4.49
4.03
21.45
7.5
7.0
6.5
6.0
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4.5
4.0
3.5
3.0
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2.0
1.5
1.0
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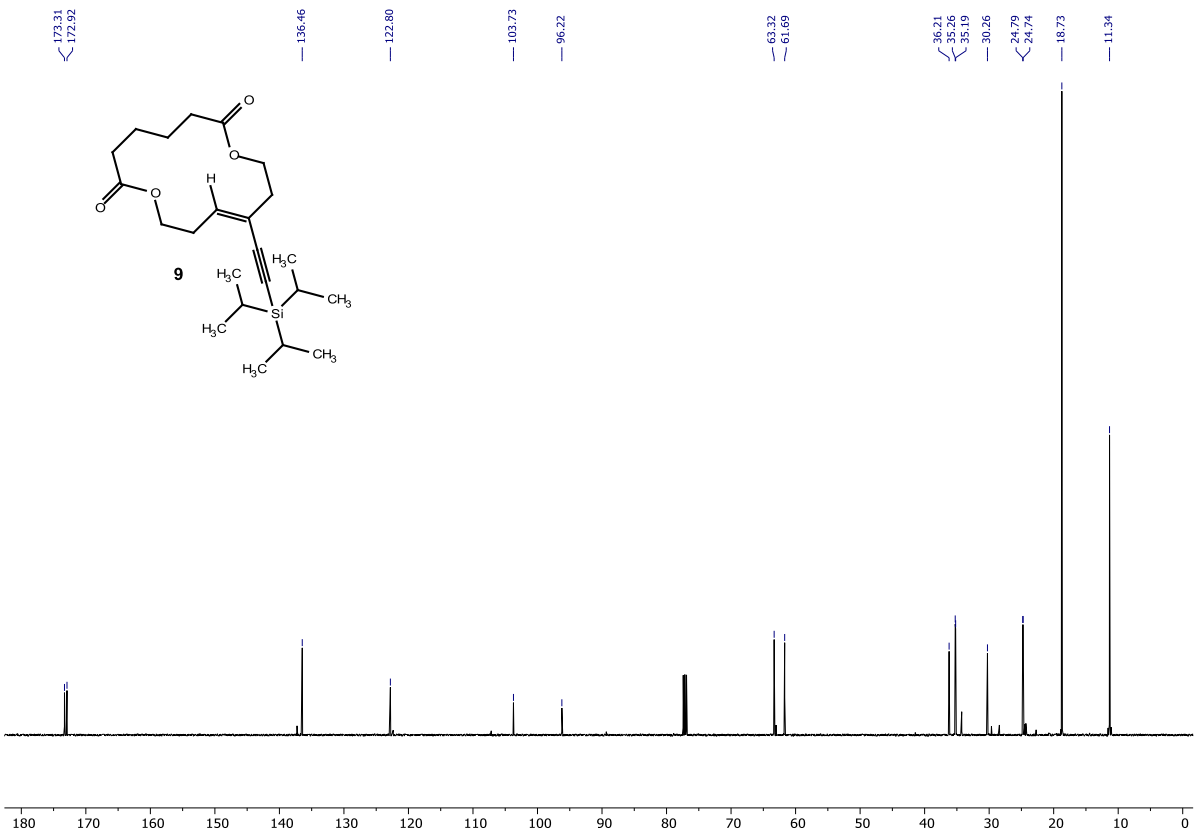
9
173.31
172.92
136.46
122.80
103.73
96.22
63.32
61.69
36.21
35.26
35.19
30.26
24.79
24.74
18.73
11.34
180
170
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150
140
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70
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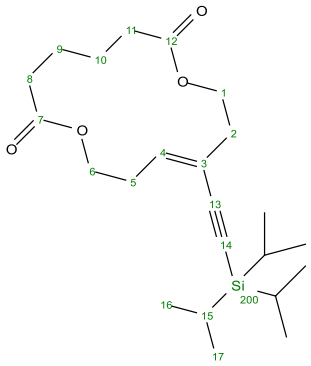
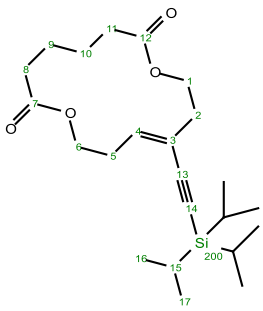
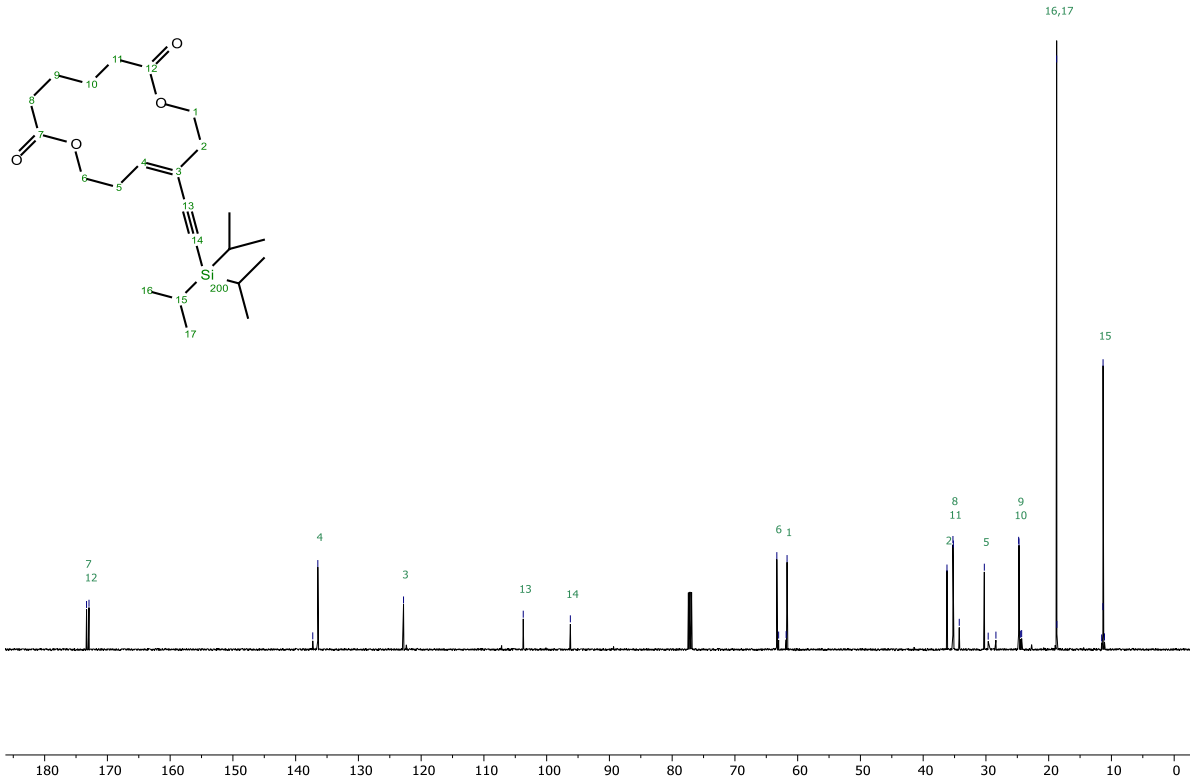
0



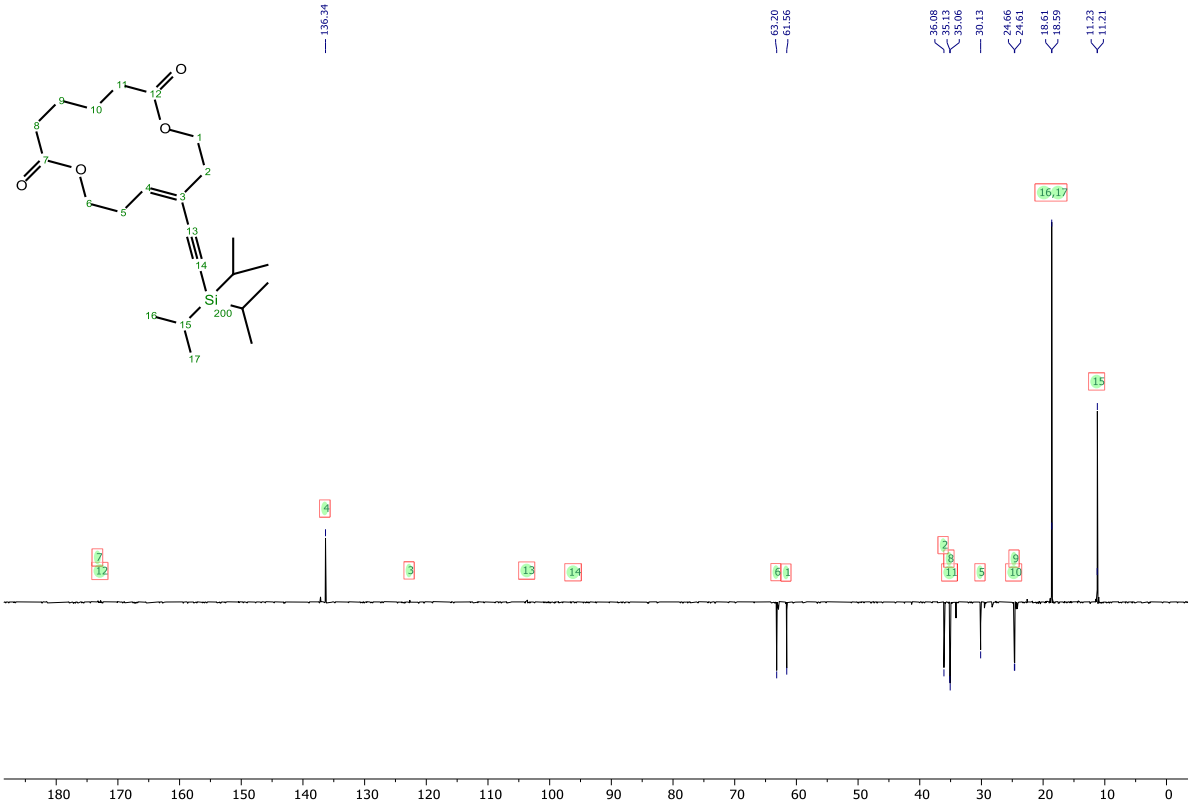
Mol Formula: $C_{23}H_{38}O_4Si$
Av Mass: 406.631
Mono Mass: 406.254

Assignments						
Atom	Chemical Shift	J	COSY	HSQC	HMBC	NOESY
1 C	61.56			1	2	
H2	4.27		2	1	2, 3, 12	2, 15, 16, 17
2 C	36.08			2	1, 4	
H2	2.46		1	2	1, 3, 4, 13	1, 4
3 C	122.68				1, 2, 5	
4 C	136.34			4	2, 5, 6	
H	5.74	7.35(?), 7.35(?), 1.35(?), 1.35(?)	5	4	2, 5, 6, 13	2, 5, 6
5 C	30.13			5	4, 6	
H2	2.67	6.88(?), 6.73(?), 4.87(?)	4, 6	5	3, 4, 6, 13	4, 6, 15, 16, 17
6 C	63.20			6	4, 5	
H2	4.15		5	6	4, 5, 7	4, 5
7 C	173.20				6, 8, 9	
8 C	35.13			8	9	
H2	2.30		9	8	7, 10	10, 15, 16, 17
9 C	24.61			9	10, 11	
H2	1.62		8	9	7, 8, 10	11, 15, 16, 17
10 C	24.66			10	8, 9	
H2	1.58		11	10	9, 11, 12	8, 15, 16, 17
11 C	35.06			11	10	
H2	2.33		10	11	9, 12	9
12 C	172.81				1, 10, 11	
13 C	103.60				2, 4, 5	
14 C	96.10				15	
15 C	11.21			15	16, 17	
H	1.07			15	14, 16, 17	1, 5, 8, 9, 10
16 C	18.60			16	15, 17	
H3	1.07			16	15, 17	1, 5, 8, 9, 10
17 C	18.60			17	15, 16	
H3	1.07			17	15, 16	1, 5, 8, 9, 10
200 Si	-1.88					

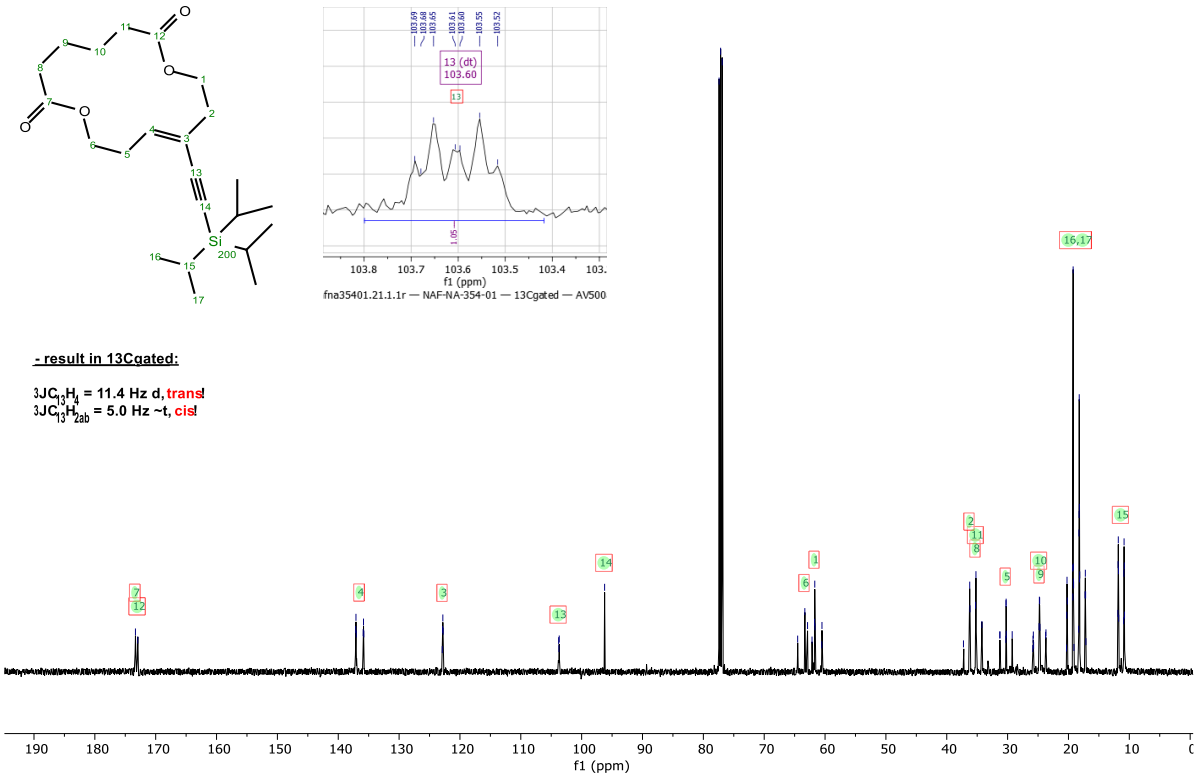




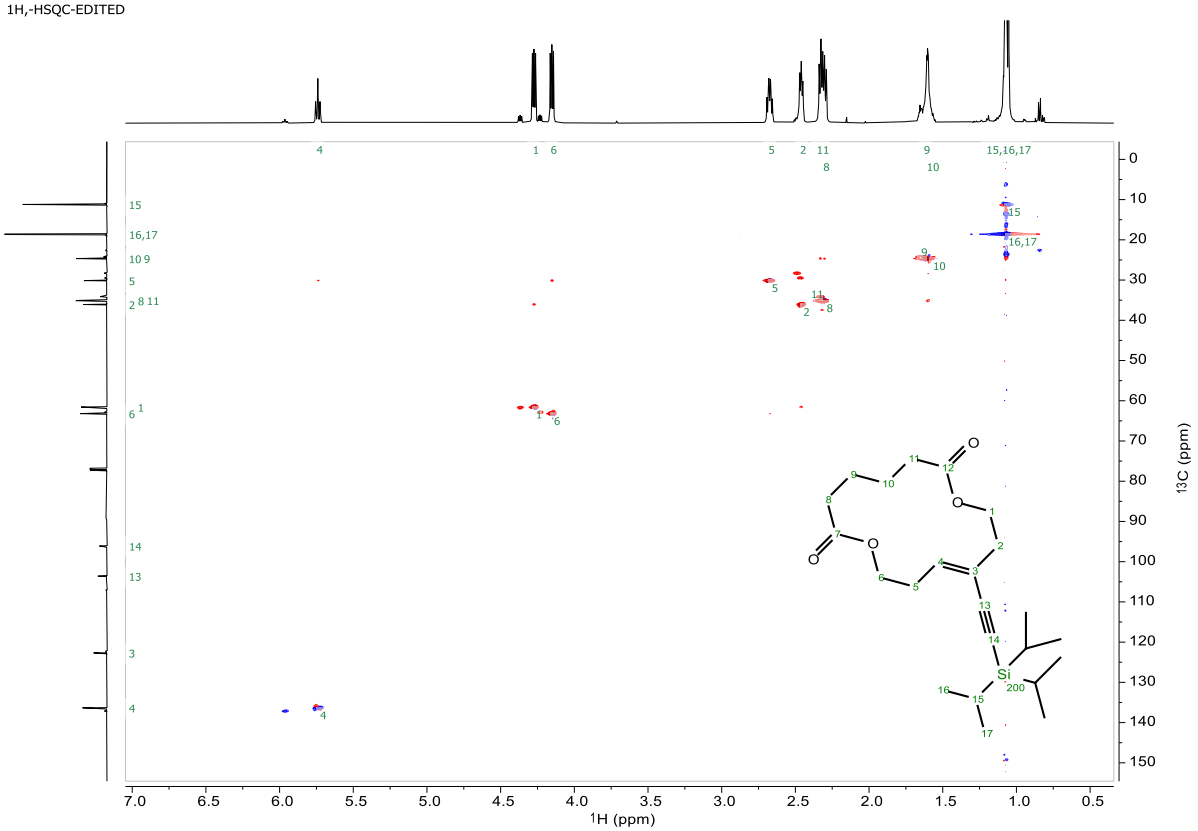
13C{1H}DEPT135

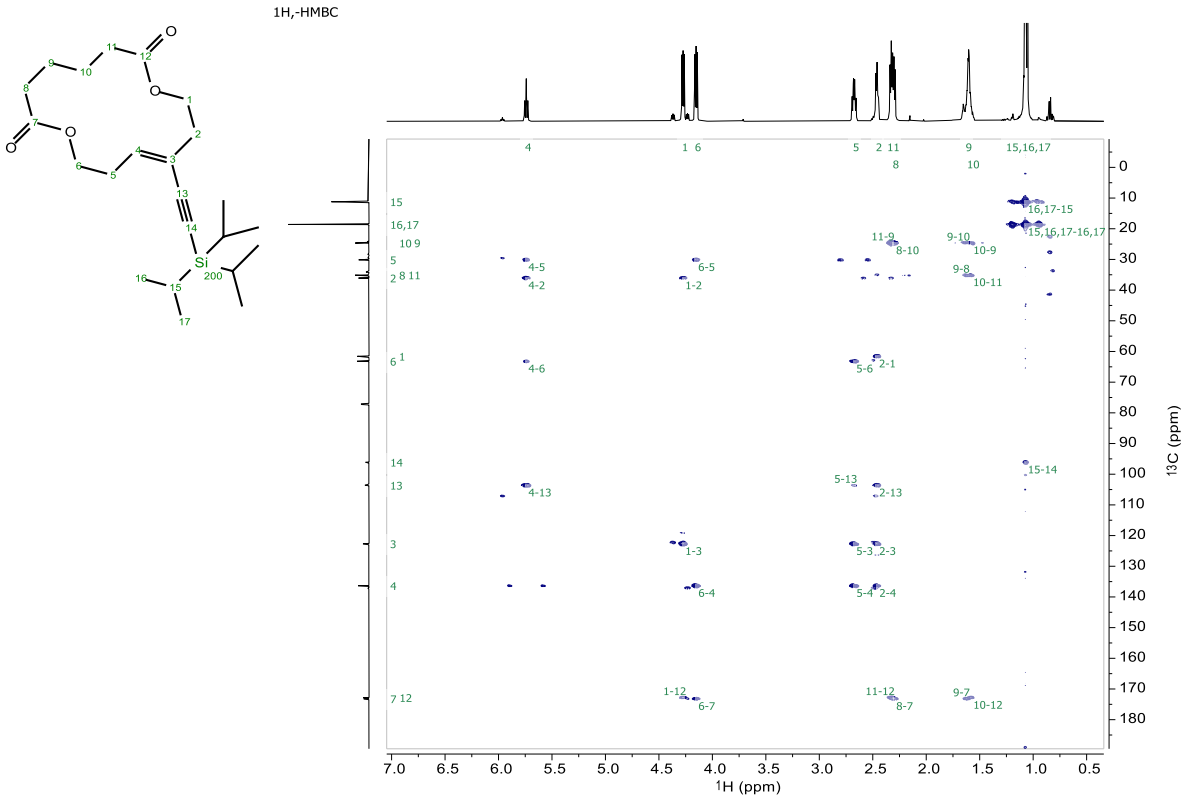


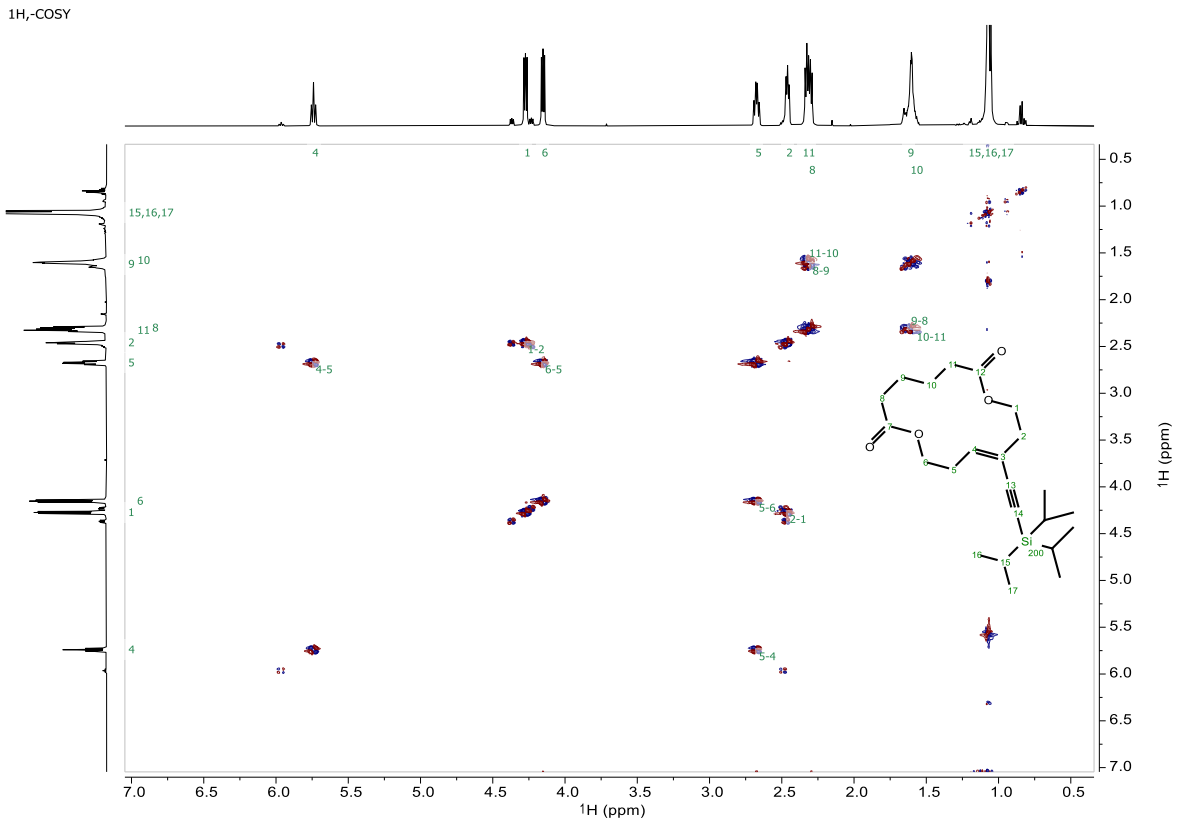
13C gated

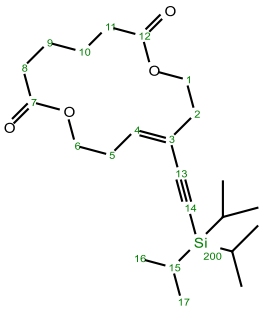


1H,-HSQC-EDITED

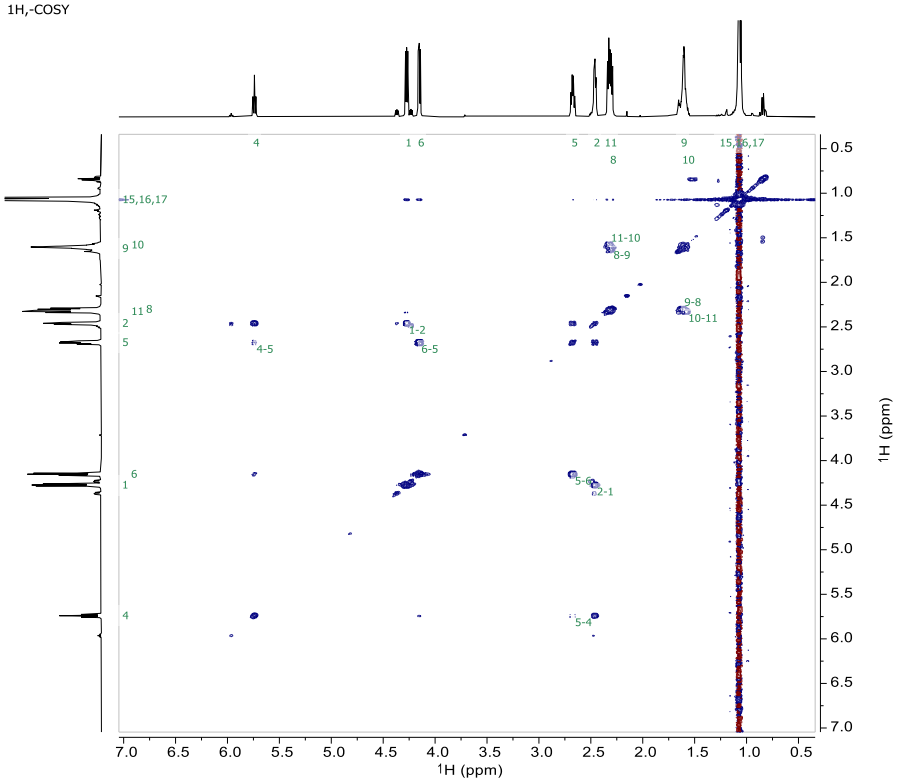



1H,-HMBC
13C (ppm)
1H (ppm)


1H,-COSY
1H (ppm)
1H (ppm)



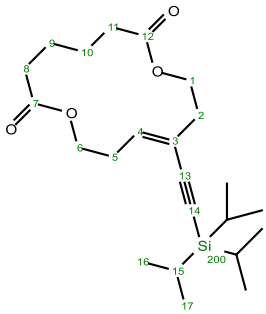
1H,-COSY

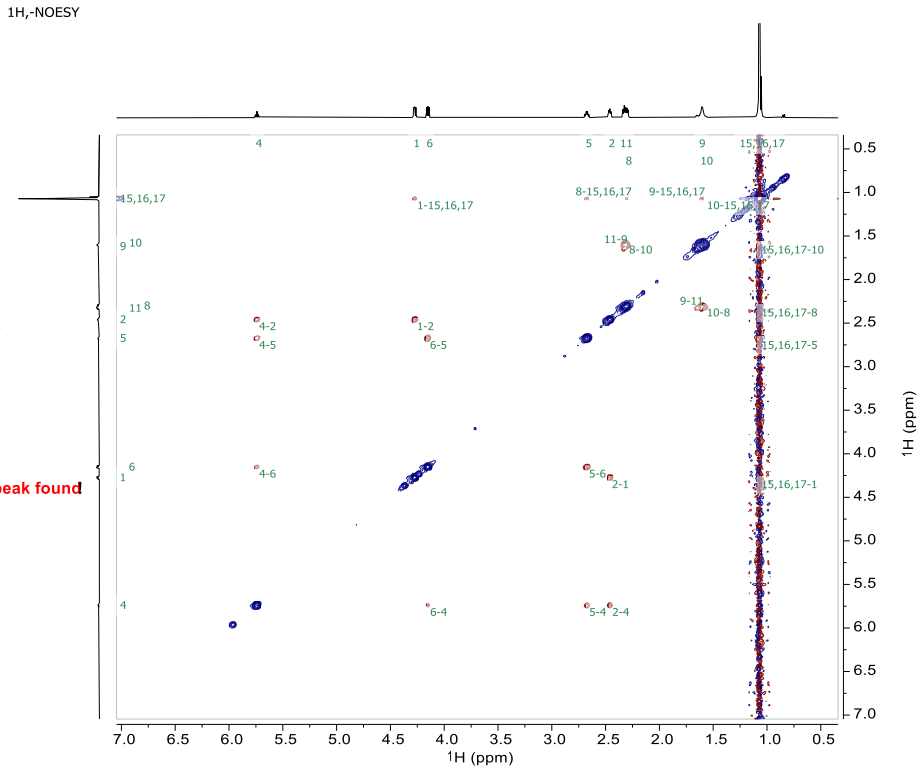


- additional crosspeaks in COSYLR:

4 - (6ab),2ab
1ab - (((11ab)))
6ab - (((8ab)))
2ab - 5ab

1H,-NOESY

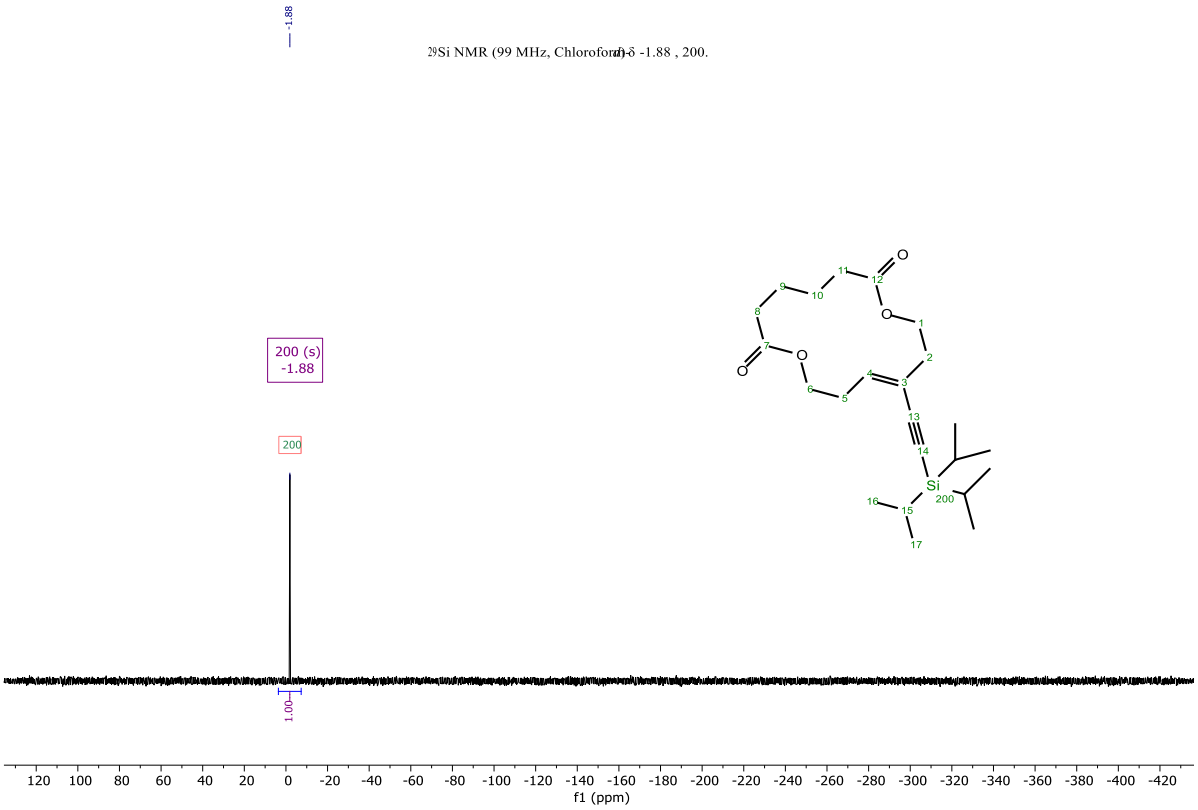




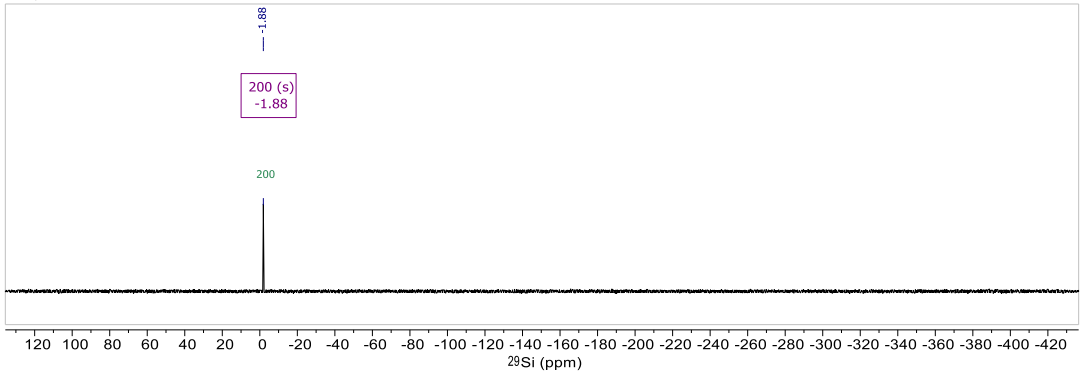
- in NOESY:

~~15,16,17~~ - 4 no crosspeak found

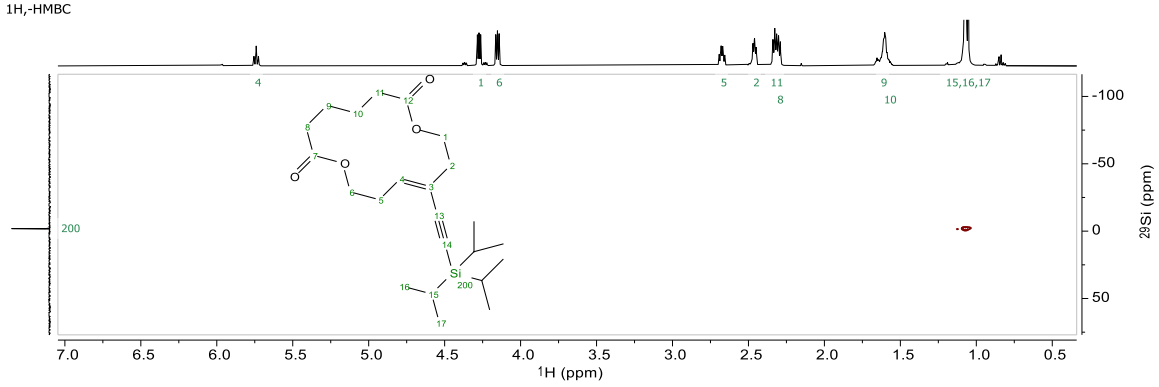
29Si{1H}DEPT45

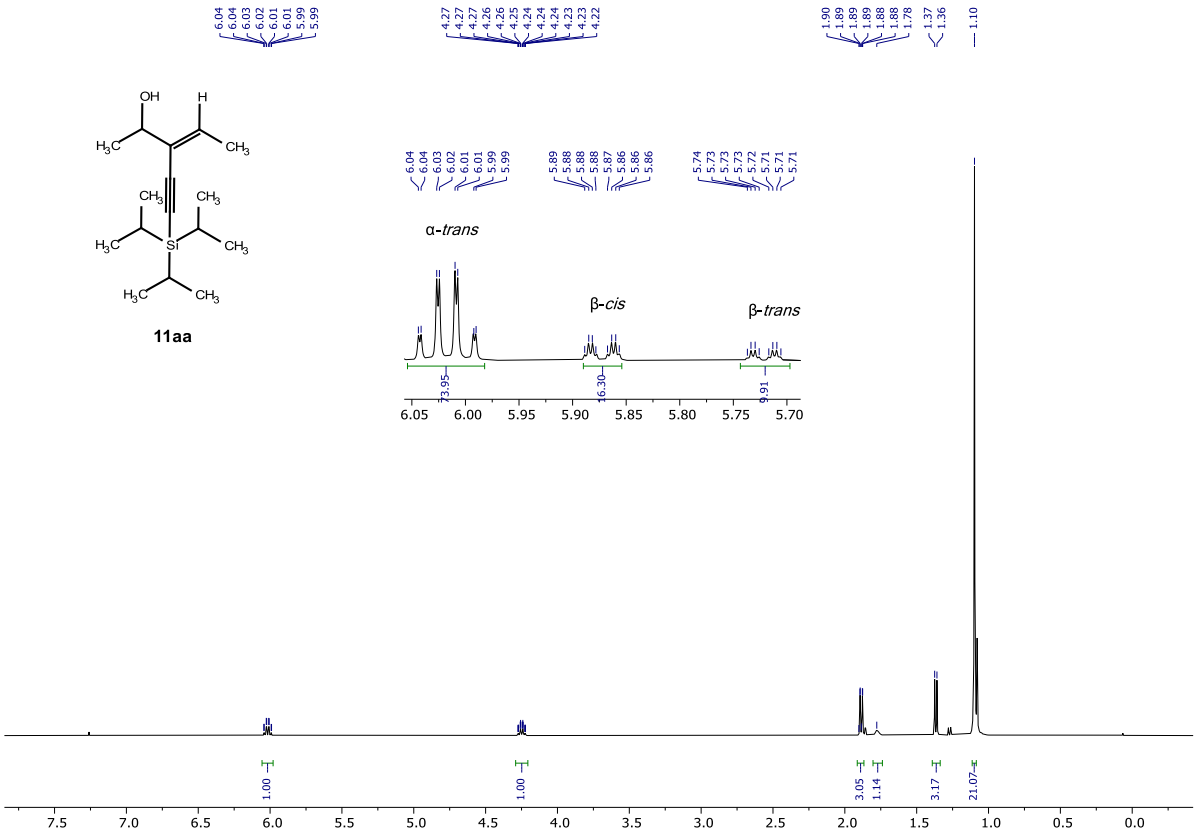


29Si,-DEPT-45



1H,-HMBC

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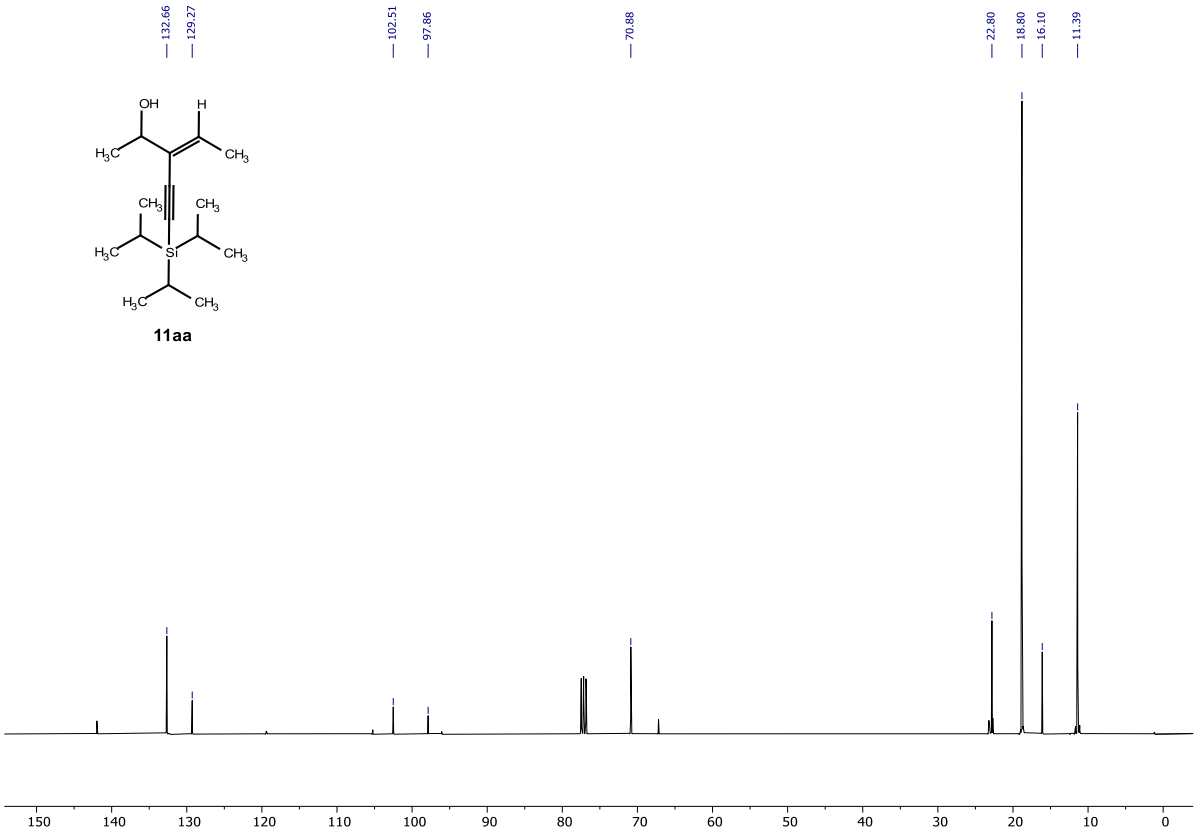
α-trans
β-cis
β-trans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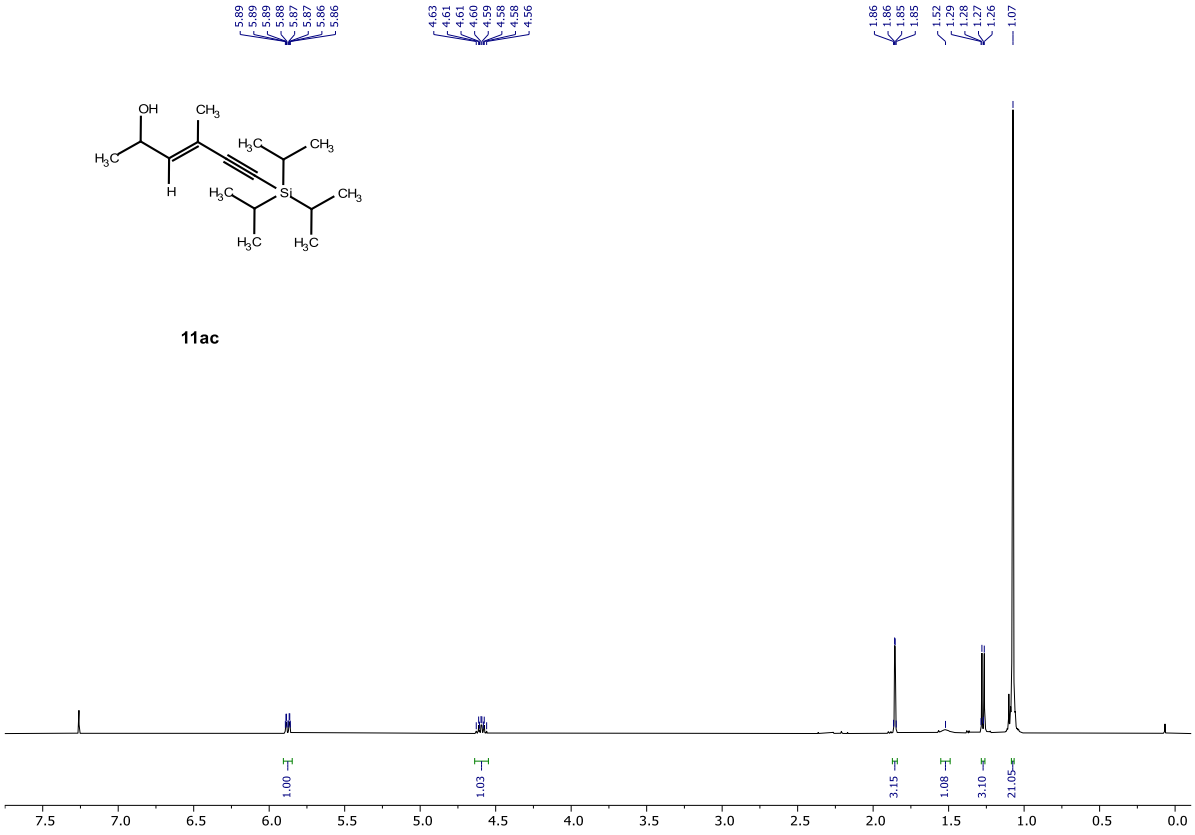
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1.85
1.52
1.29
1.28
1.27
1.26
1.07
OH
CH3
H3C
H
H3C
CH3
Si
H3C
CH3
H3C
H3C
1.00
1.03
3.15
1.08
3.10
21.05
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7.0
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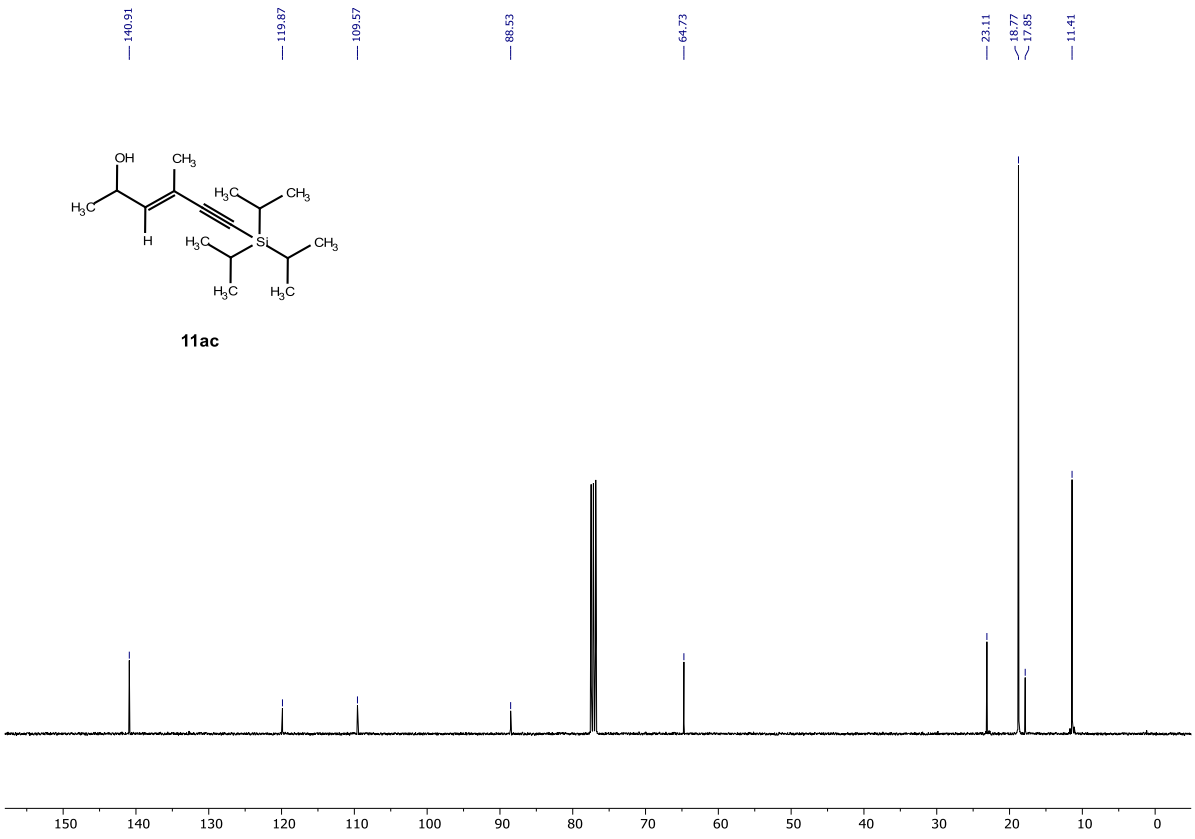
11ac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18.77
17.65
11.41
OH
CH3
H3C
H
H3C
CH3
Si
H3C
CH3
H3C
H3C
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40
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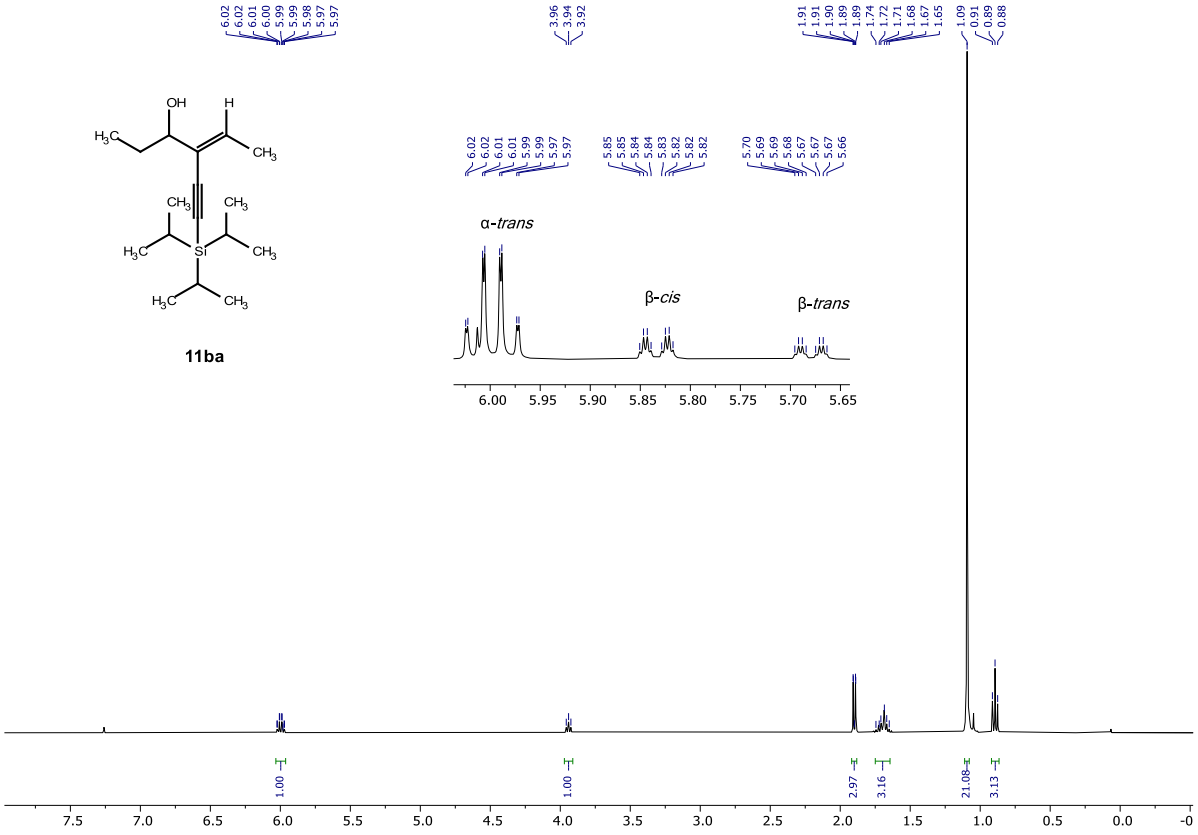
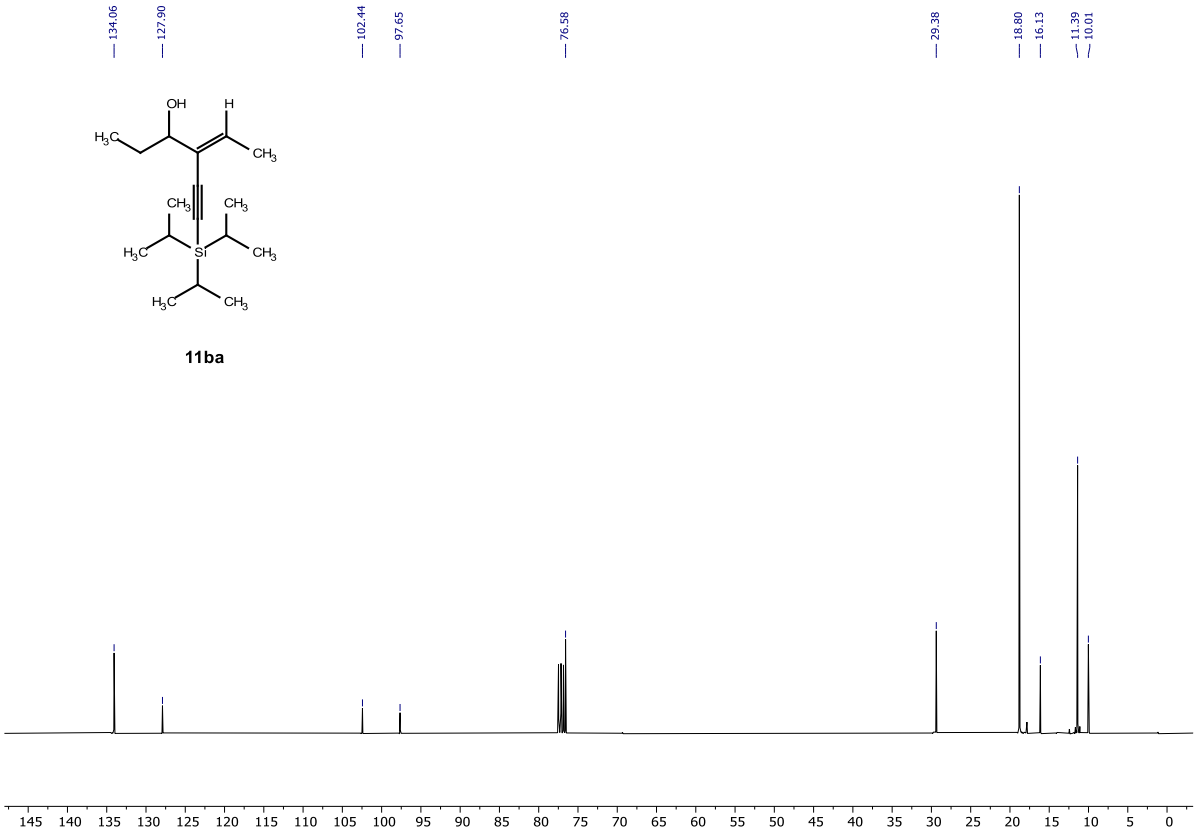
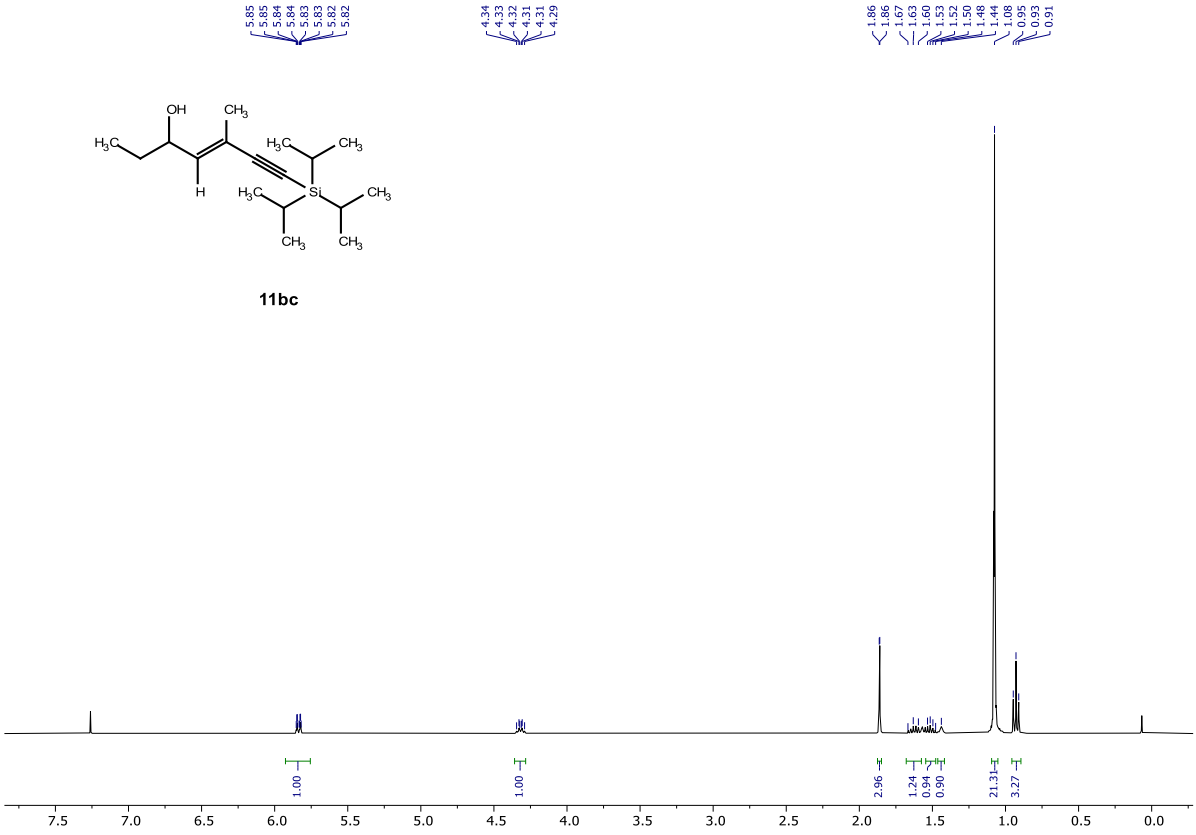
0

11ac


11ba
α-trans
β-cis
β-trans


11ba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5.82
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4.31
4.29
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1.86
1.67
1.63
1.60
1.53
1.52
1.50
1.48
1.44
1.08
0.95
0.93
0.91
OH
CH3
H3C
H
H3C
Si
CH3
CH3
CH3
CH3
1.00
1.00
2.96
1.24
0.94
0.90
21.31
3.27
7.5
7.0
6.5
6.0
5.5
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1.5
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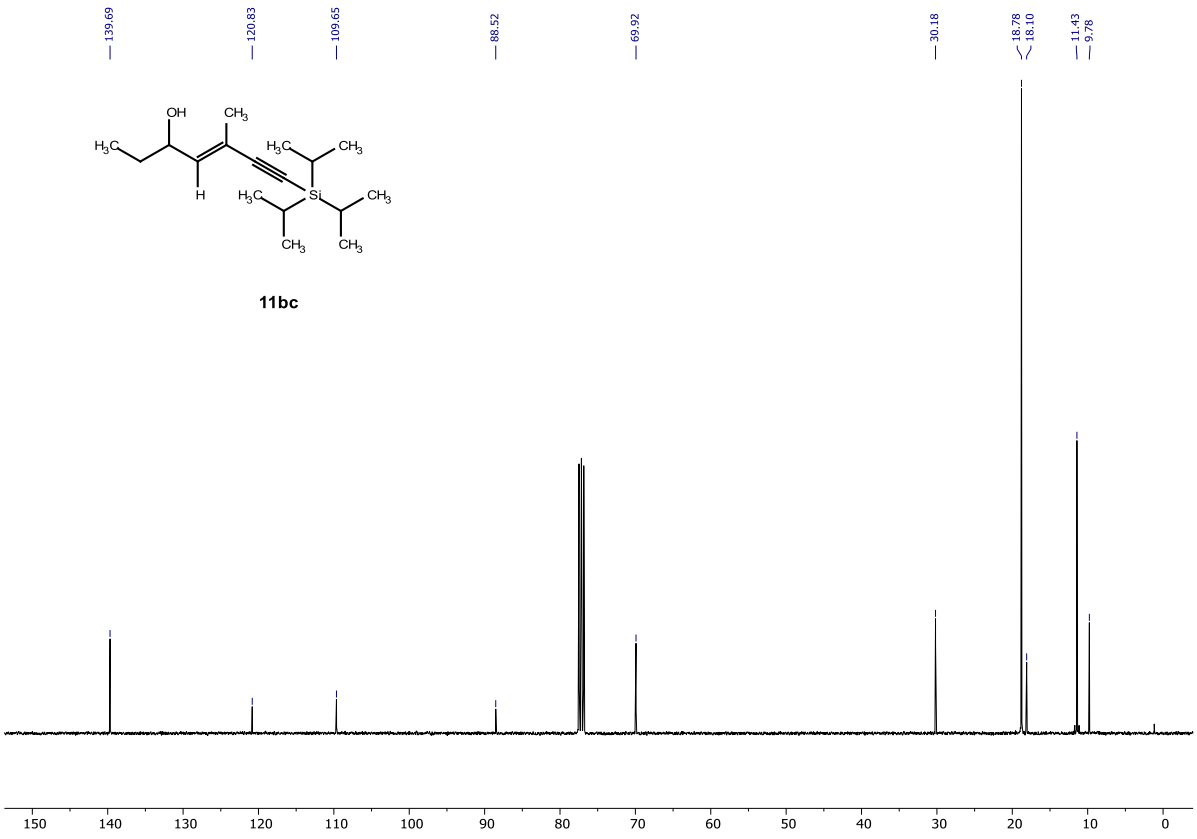
11bc


139.69
120.83
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88.52
69.92
30.18
18.78
18.10
11.43
9.78
OH
CH3
H3C
H
H3C
Si
CH3
CH3
CH3
CH3
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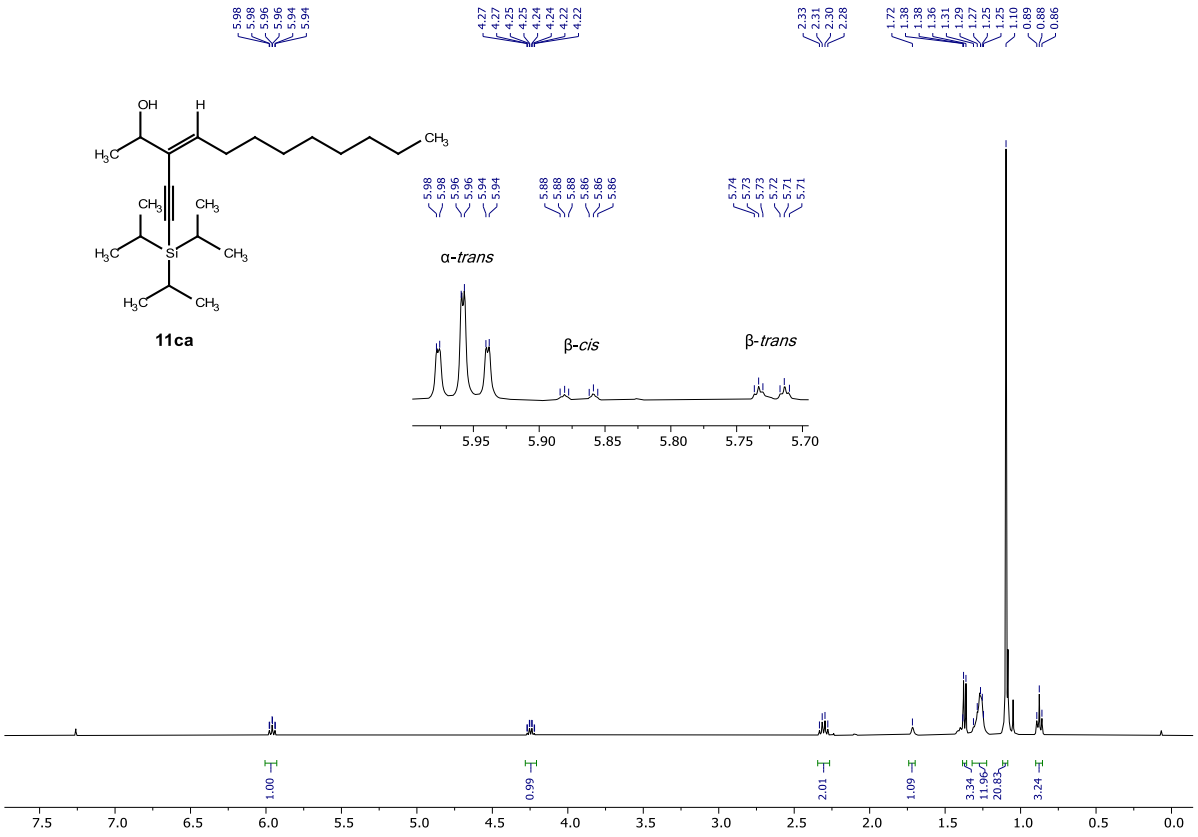
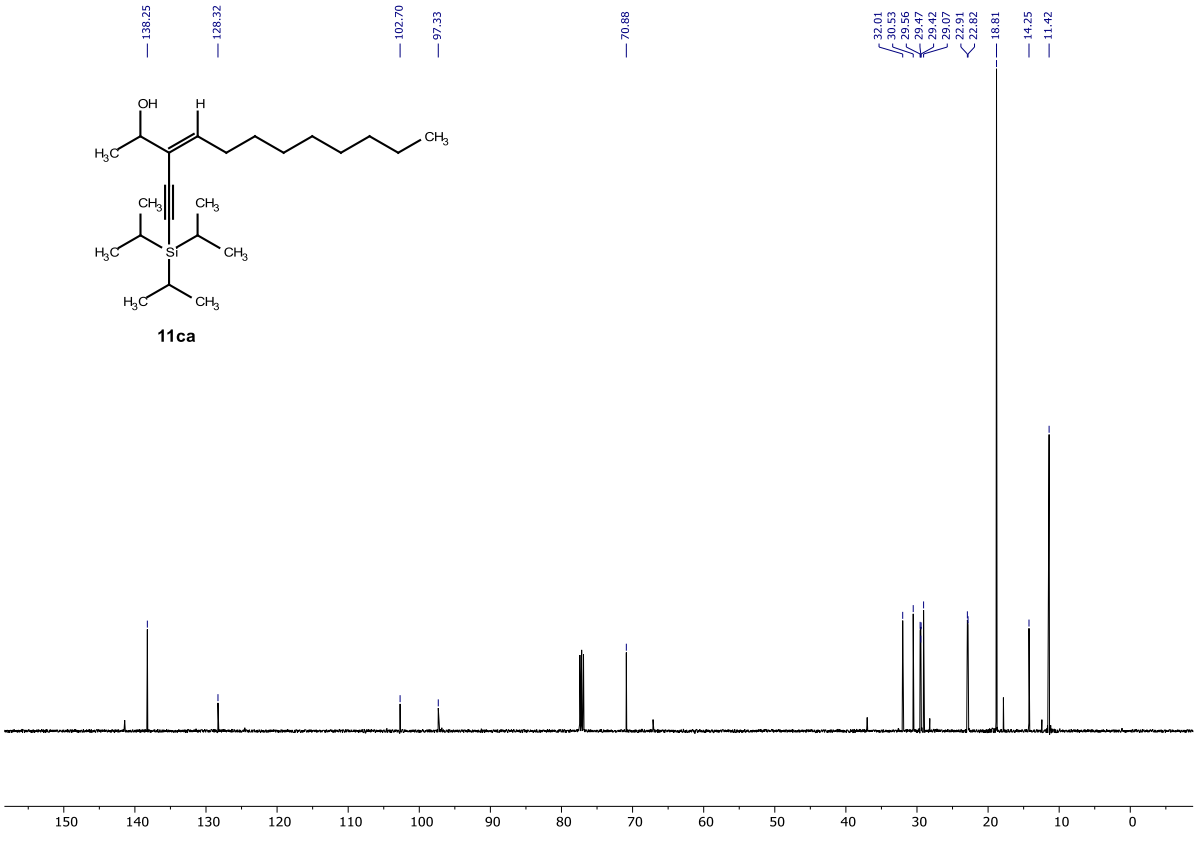
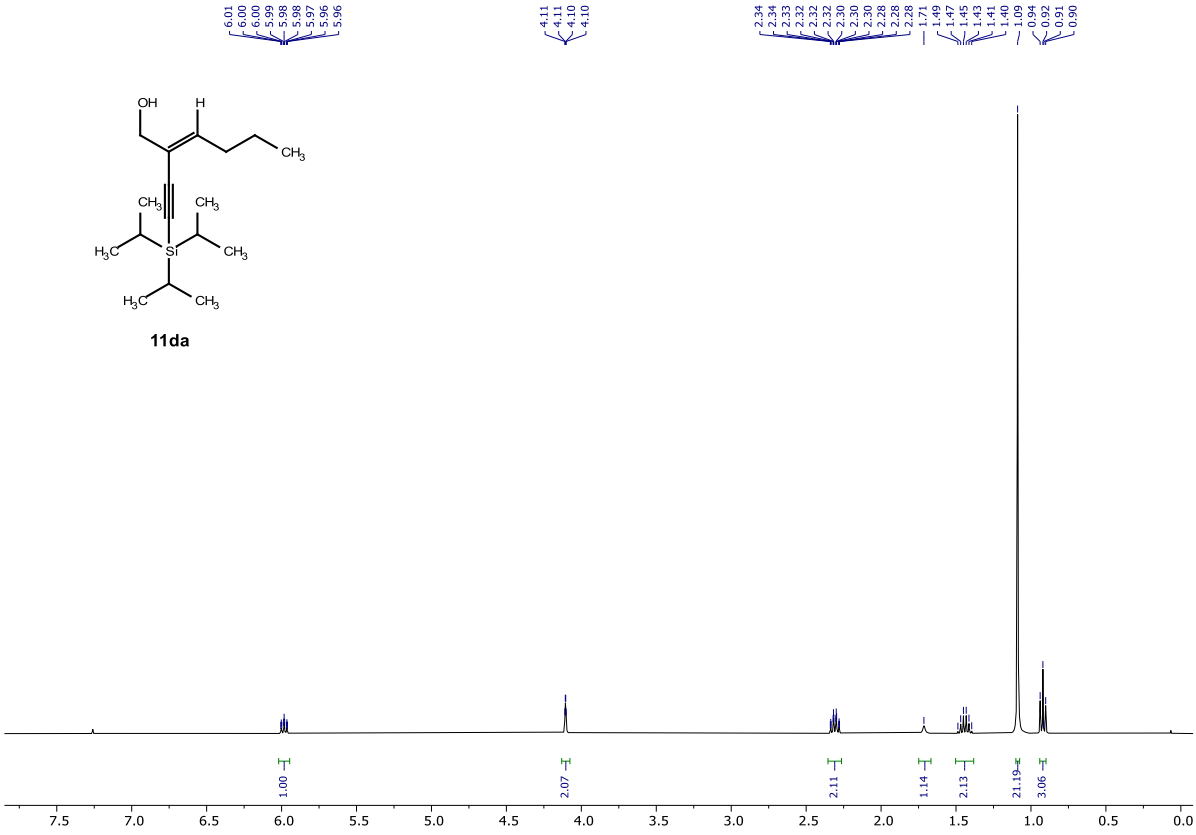
10
0

11bc


11ca
α-trans
β-cis
β-trans


11ca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2.34
2.33
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2.28
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1.49
1.47
1.45
1.43
1.41
1.40
1.09
0.94
0.92
0.91
0.90
OH
H
CH3
CH3
CH3
H3C
Si
CH3
H3C
CH3
1.00
2.07
2.11
1.14
2.13
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6.0
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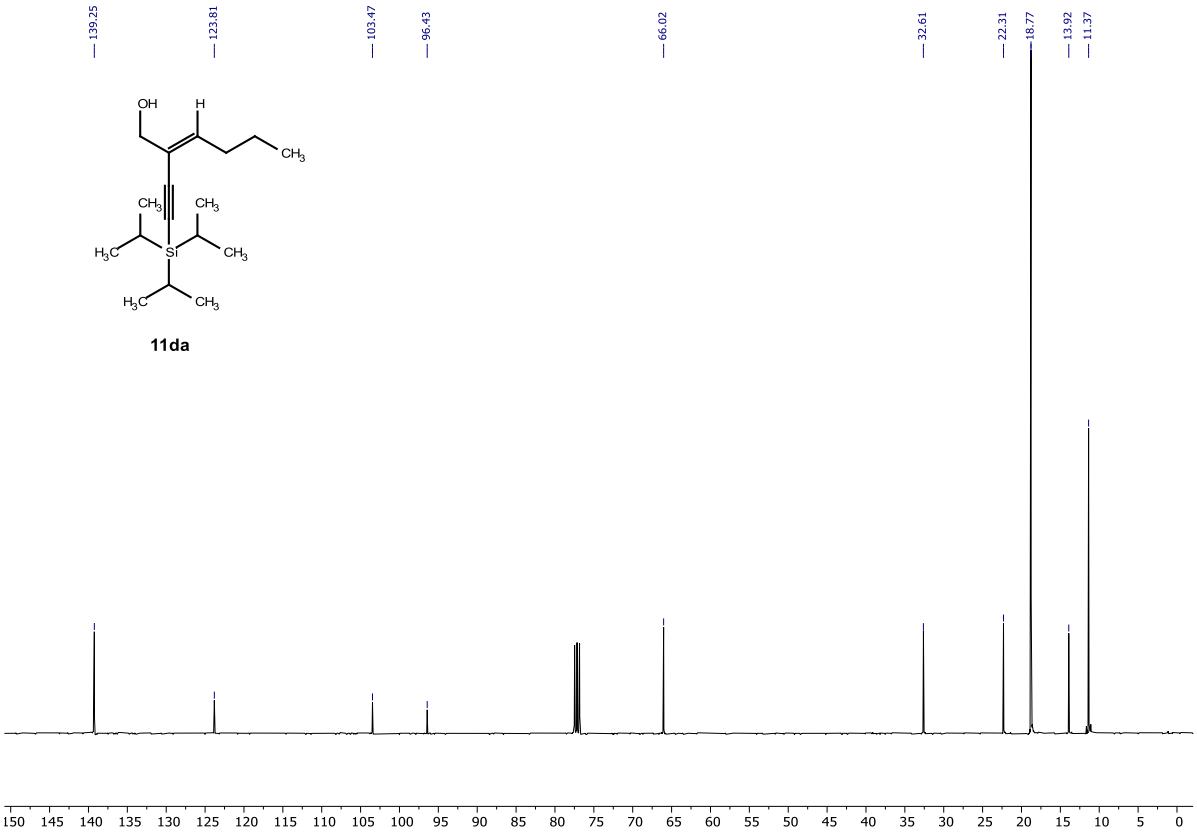
11da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18.77
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11.37
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CH3
CH3
H3C
Si
CH3
H3C
CH3
150
145
140
135
130
125
120
115
110
105
100
95
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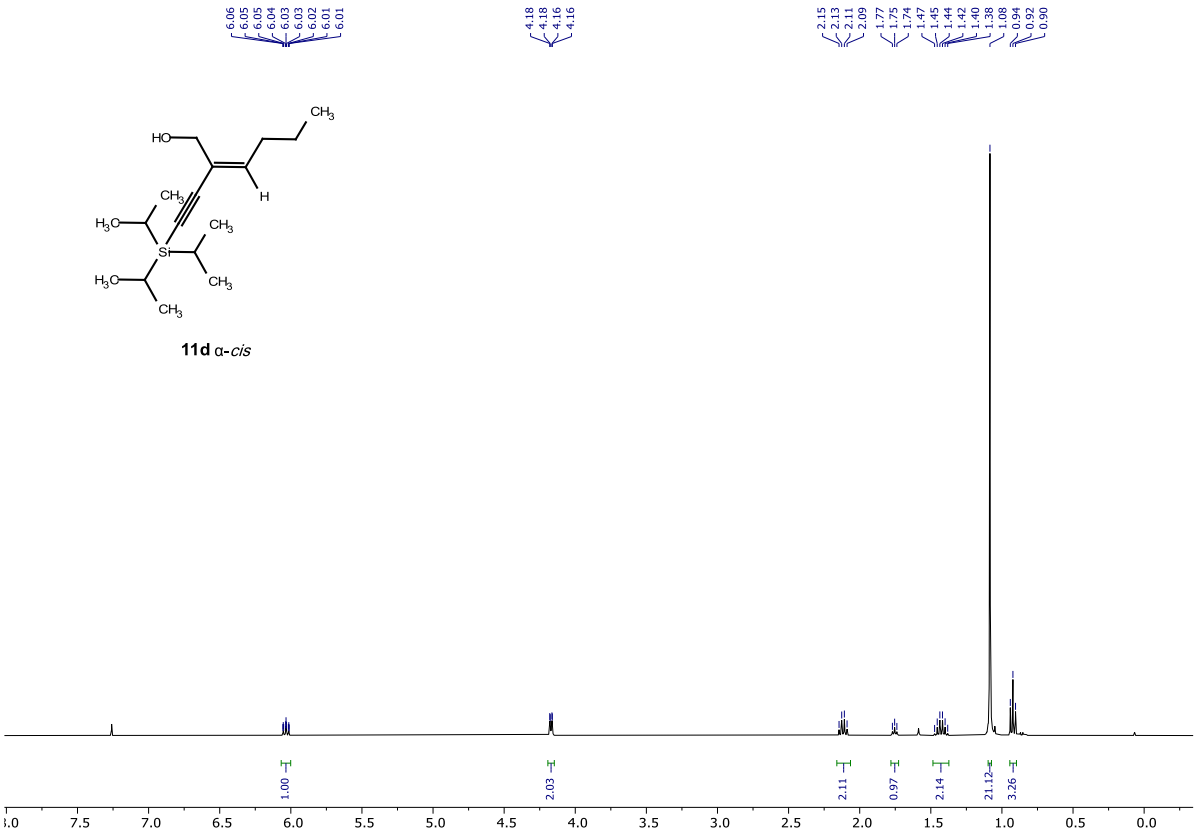
11da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4.16
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2.09
1.77
1.75
1.74
1.47
1.45
1.44
1.42
1.40
1.38
1.08
0.94
0.92
0.90
HO
CH3
H
CH3
H3O
Si
CH3
H3O
CH3
CH3
11d α-cis
1.00
2.03
2.11
0.97
2.14
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3.26
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7.0
6.5
6.0
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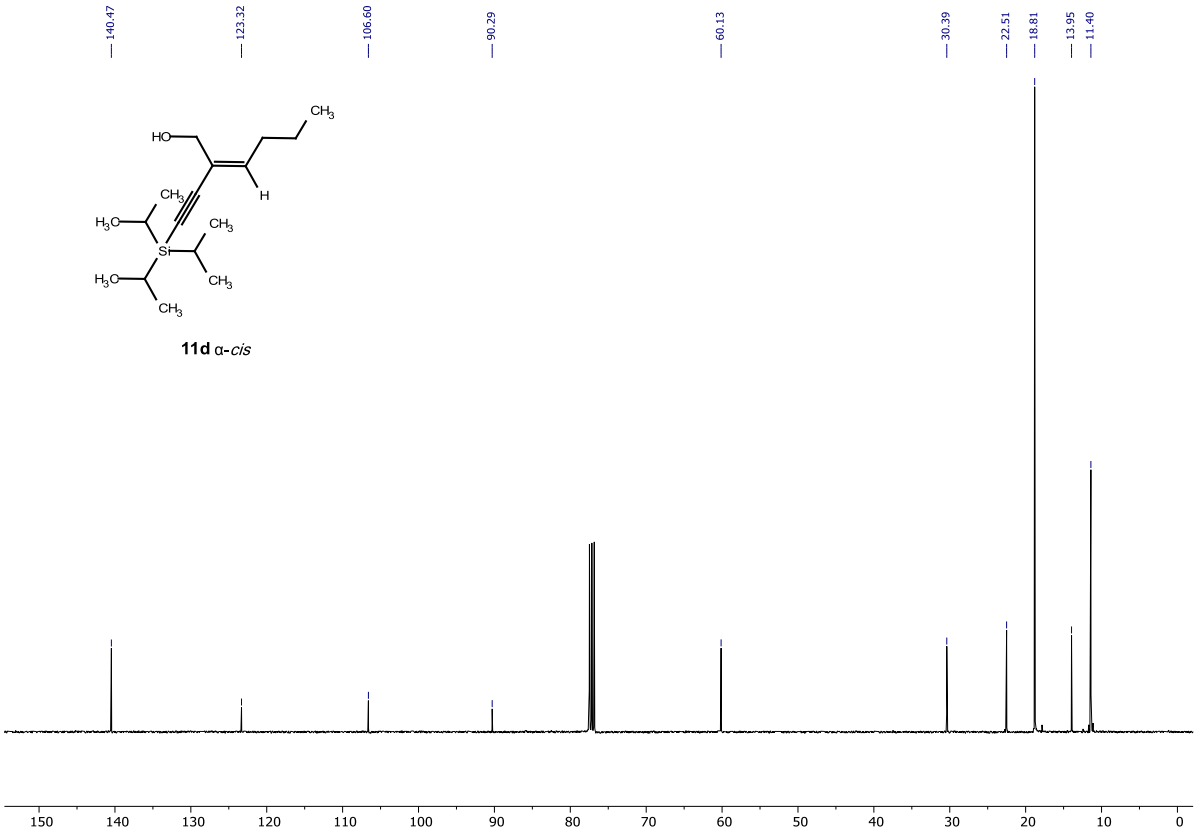
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106.60
90.29
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30.39
22.51
18.81
13.95
11.40
HO
CH3
H
CH3
H3O
Si
CH3
H3O
CH3
CH3
11d α-cis
150
140
130
120
110
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70
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50
40
30
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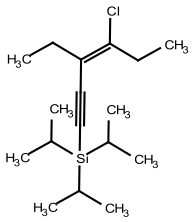
0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CH3
CH3
Si
H3C
CH3
H3C
CH3

13

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2.36
2.34
2.32
2.30
1.16
1.14
1.12
1.11
1.09
2.63
2.61
2.59
2.57
trans
2.38
2.36
2.34
2.33
cis
5.53
4.47
2.6
2.5
2.4
2.3
2.2
2.1
2.00
1.98
6.56
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6.0
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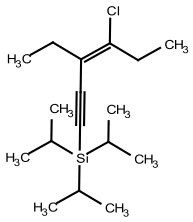
Cl
H3C
CH3
CH3
CH3
Si
H3C
CH3
H3C
CH3

13

144.32
121.23
104.44
95.93
31.78
26.67
18.78
18.64
12.37
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140
130
120
110
100
90
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70
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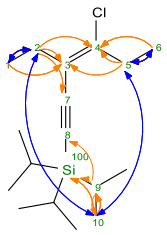
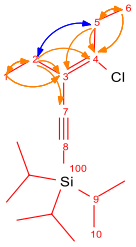
10
0



HMBC cross peak
NOESY cross peak



major

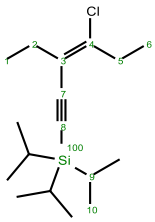
Atom	δ (ppm)	J	COSY	HSQC	HMBC	NOESY
1 C	12.181			1	2	
H3	1.104	7.50(2)	2	1	2, 3	2
2 C	26.499			2	1	
H2	2.324	7.50(1)	1	2	1, 3, 4, 7	1, 10
3 C	121.067				1, 2, 5	
4 C	144.148				2, 5, 6	
5 C	31.604			5	6	
H2	2.700	7.40(6)	6	5	3, 4, 6	6, 10
6 C	12.205			6	5	
H3	1.137	7.40(5)	5	6	4, 5	5
7 C	104.260				2	
8 C	95.773				9	
9 C	11.285			9	10	
H	1.088			9	8, 10, 100	
10 C	18.617			10	9	
H3	1.088			10	9, 100	2, 5
100 Si	-1.983				9, 10	

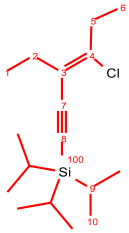
minor

Atom	δ (ppm)	J	COSY	HSQC	HMBC	NOESY
1 C	13.426			1	2	
H3*	1.142	7.50(2)	2	1	2, 3	
2 C	26.044			2	1	
H2	2.235	7.50(1)	1	2	1, 3, 4, 7	5
3 C	121.710				1, 2, 5	
4 C	141.022				2, 5, 6	
5 C	28.581			5	6	
H2	2.454	7.40(6)	6	5	3, 4, 6	2
6 C	12.588			6	5	
H3*	1.135	7.40(5)	5	6	4, 5	
7 C	105.028				2	
8 C	95.845					
9 C						
H						
10 C						
H3						
100 Si						

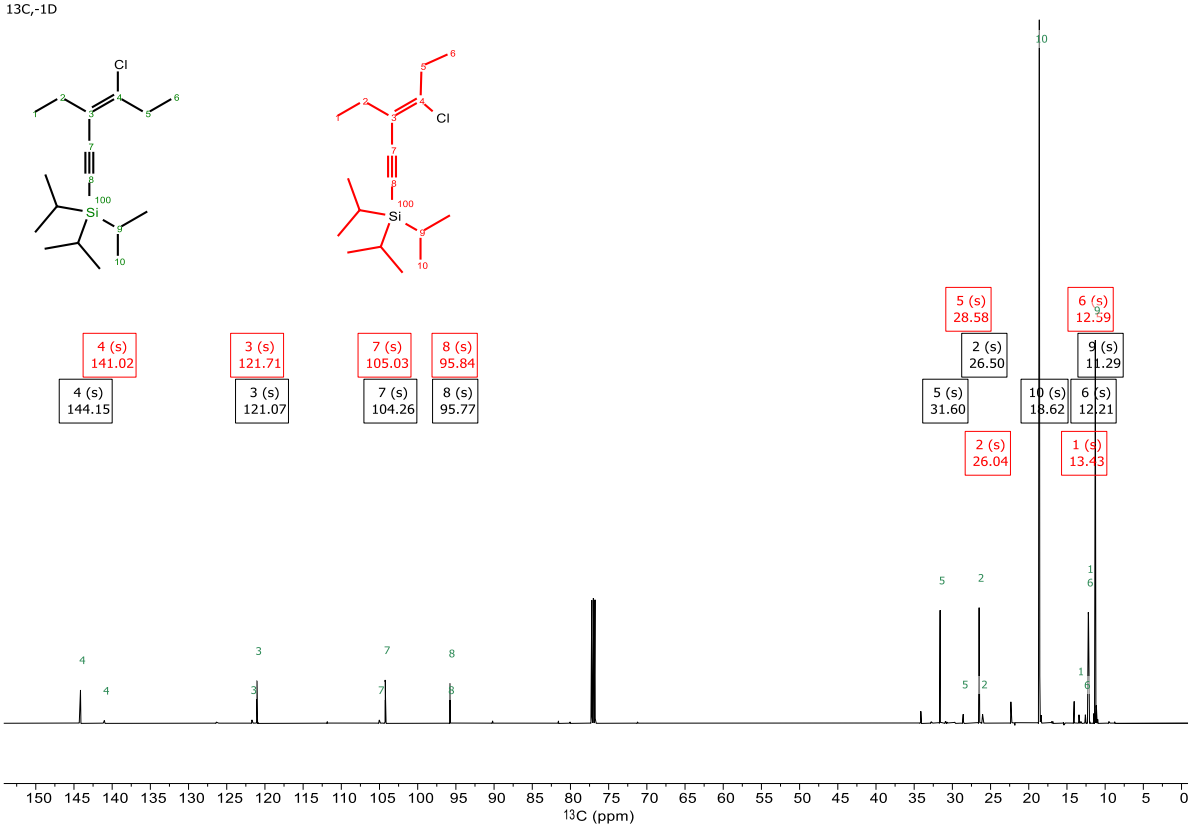
Due to overlapps, the shifts of the TIPS froups with other signals couldn't be assigned. Shifts with a * were extracted from the 2D cross peaks

1H,-1D

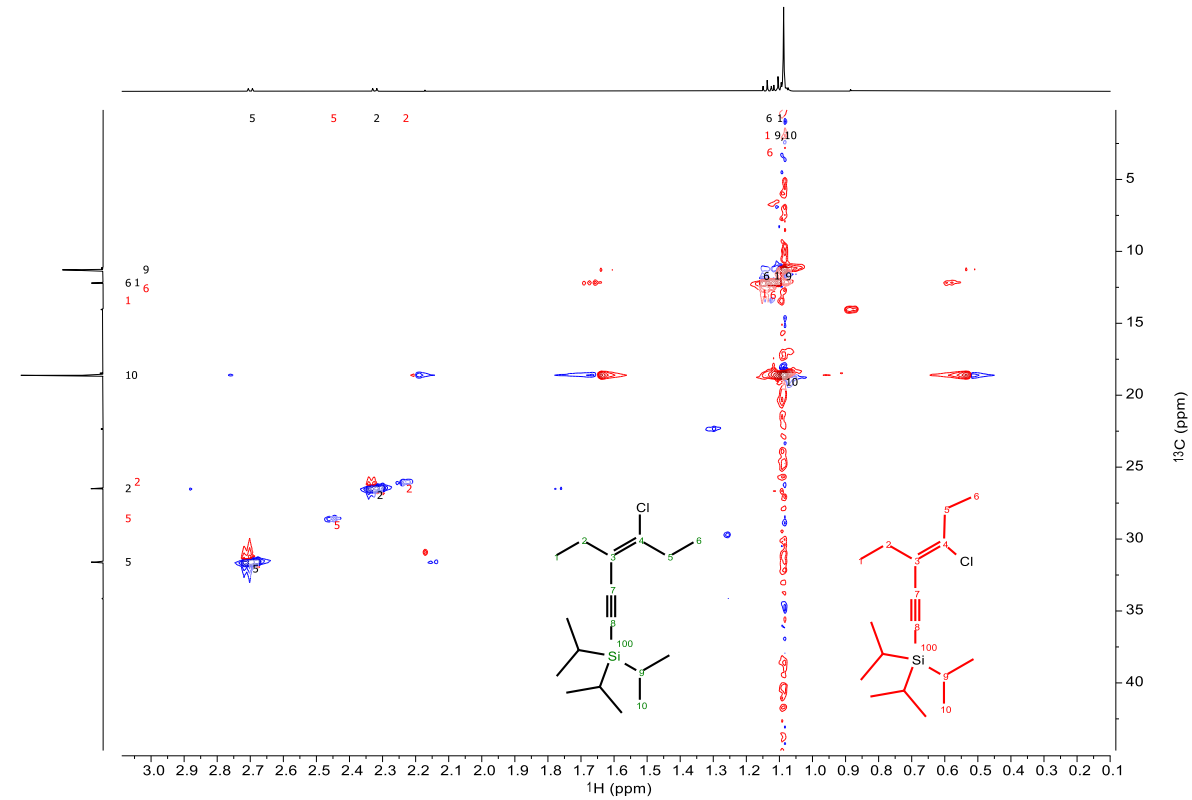




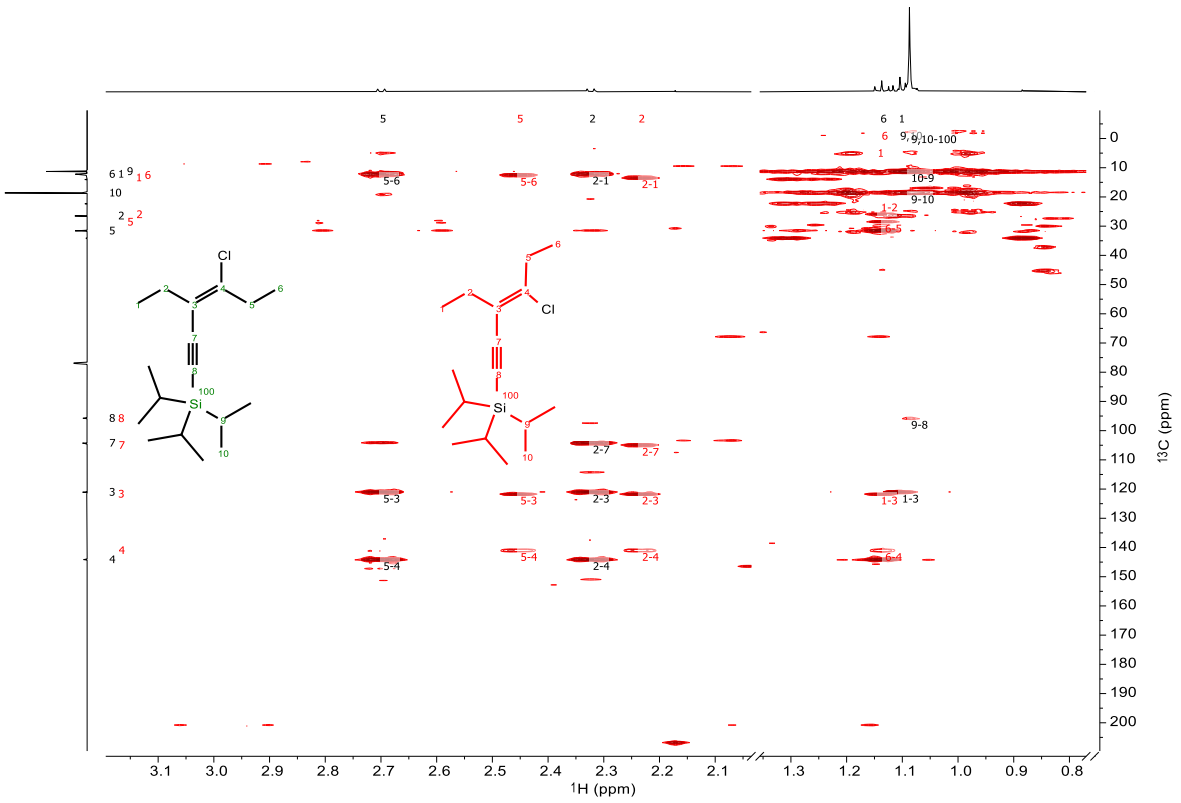
13C,-1D



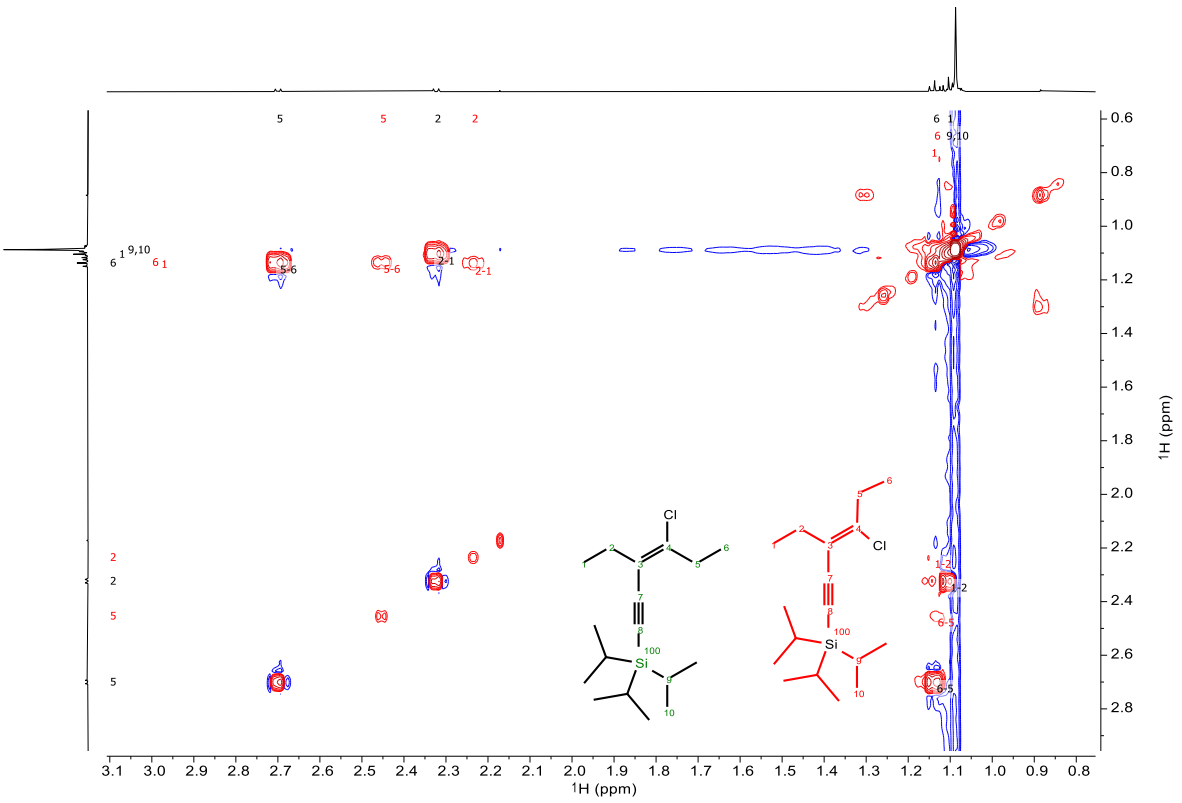
1H,13C-HSQC-EDITED



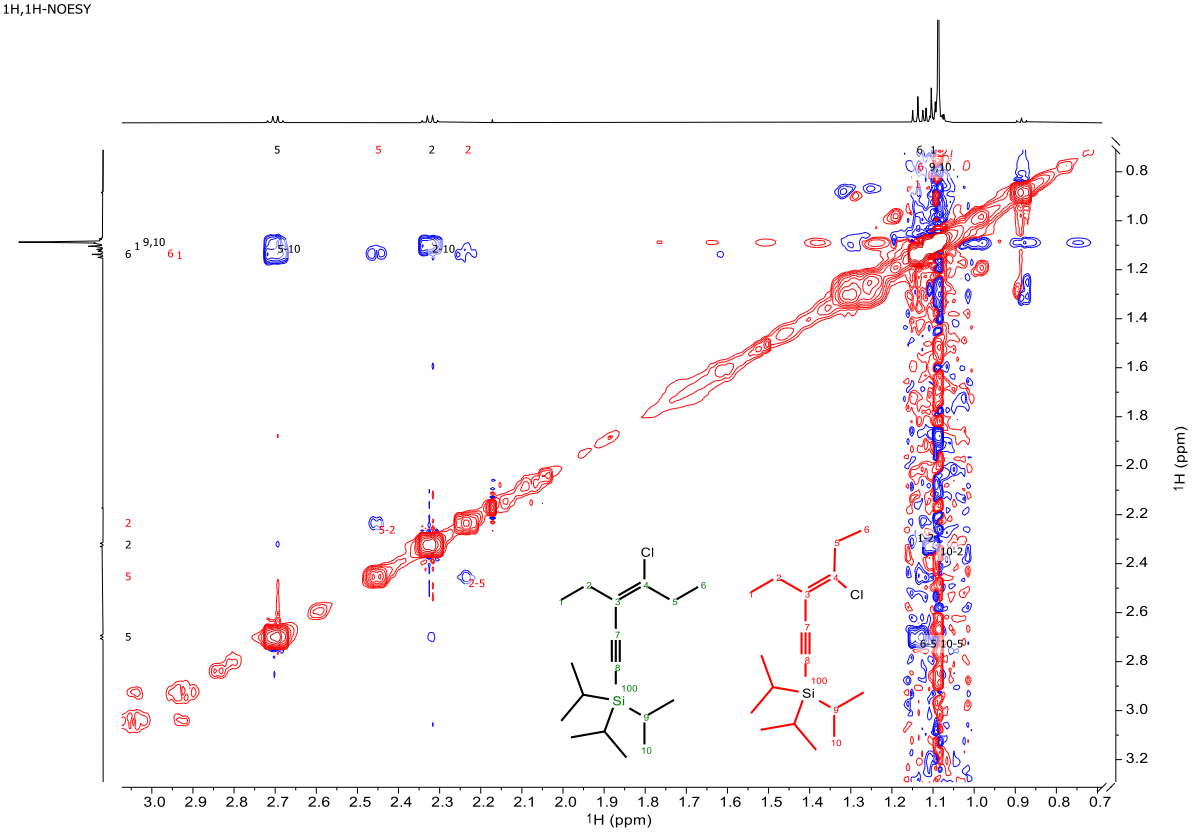
1H,13C-HMBC



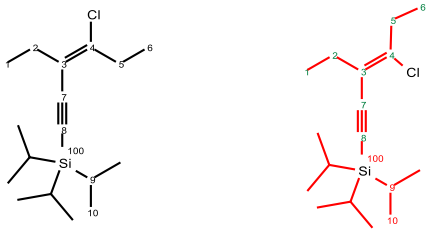
1H,1H-COSY

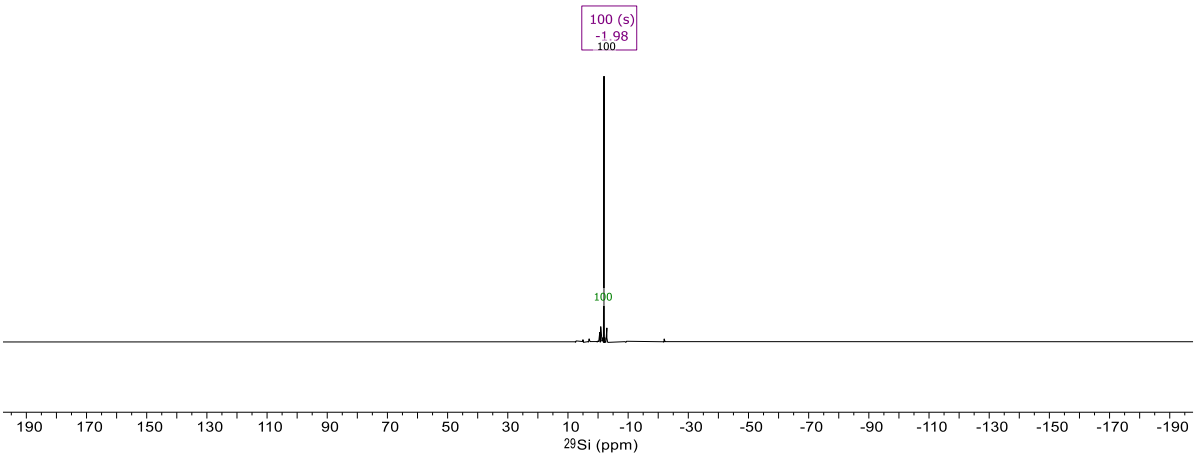


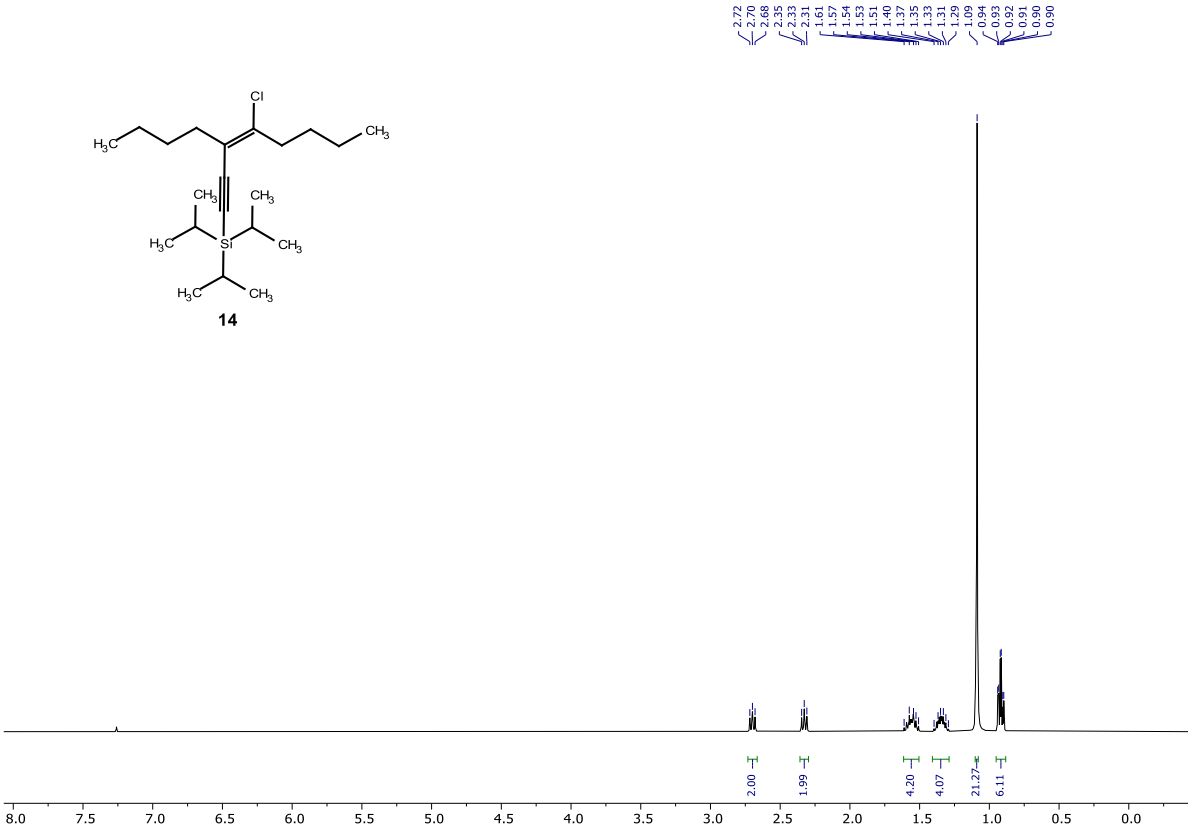
1H,1H-NOESY



29Si,-1D



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1.35
1.33
1.31
1.29
1.09
0.94
0.93
0.92
0.91
0.90
0.90
Cl
CH3
H3C
CH3
CH3
H3C
Si
CH3
H3C
CH3
14
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4.07
21.27
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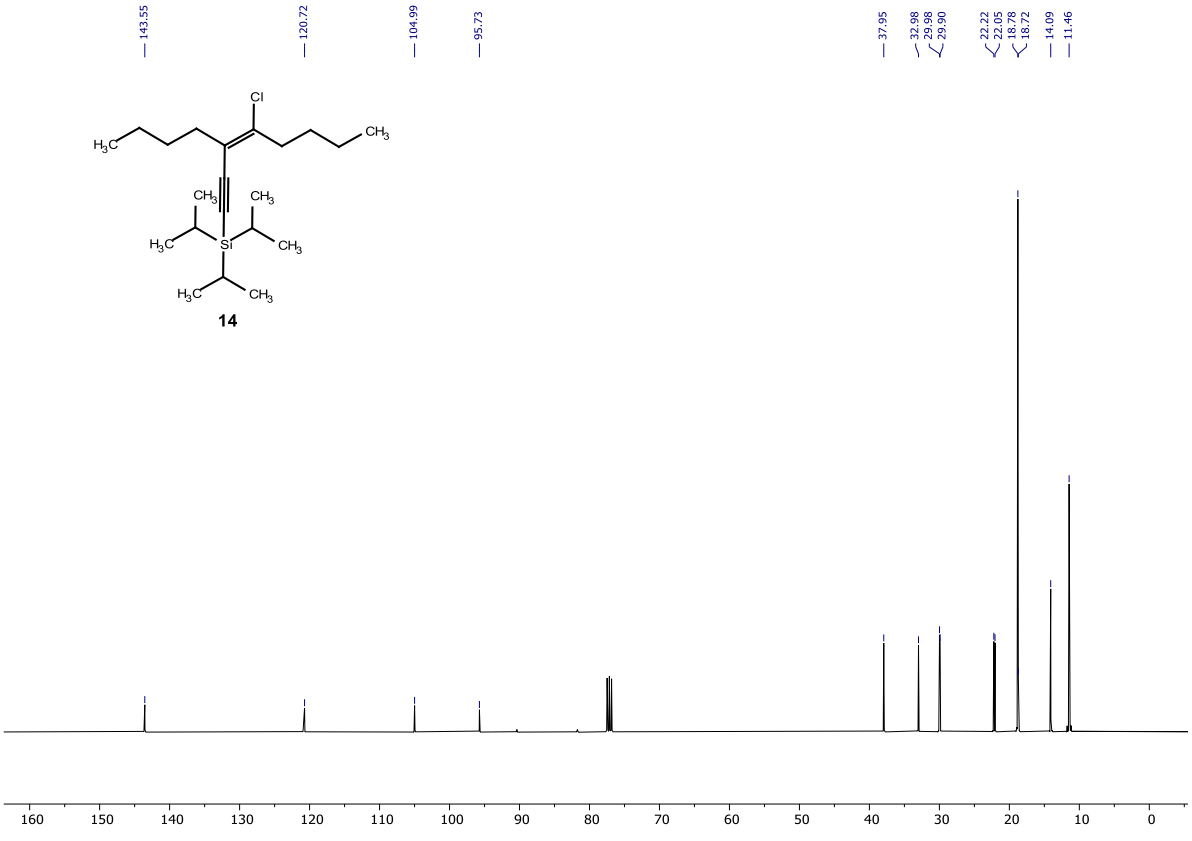
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Cl
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CH3
CH3
H3C
Si
CH3
H3C
CH3
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120
110
100
90
80
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50
40
30
20
10
0


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3.78
3.77
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2.91
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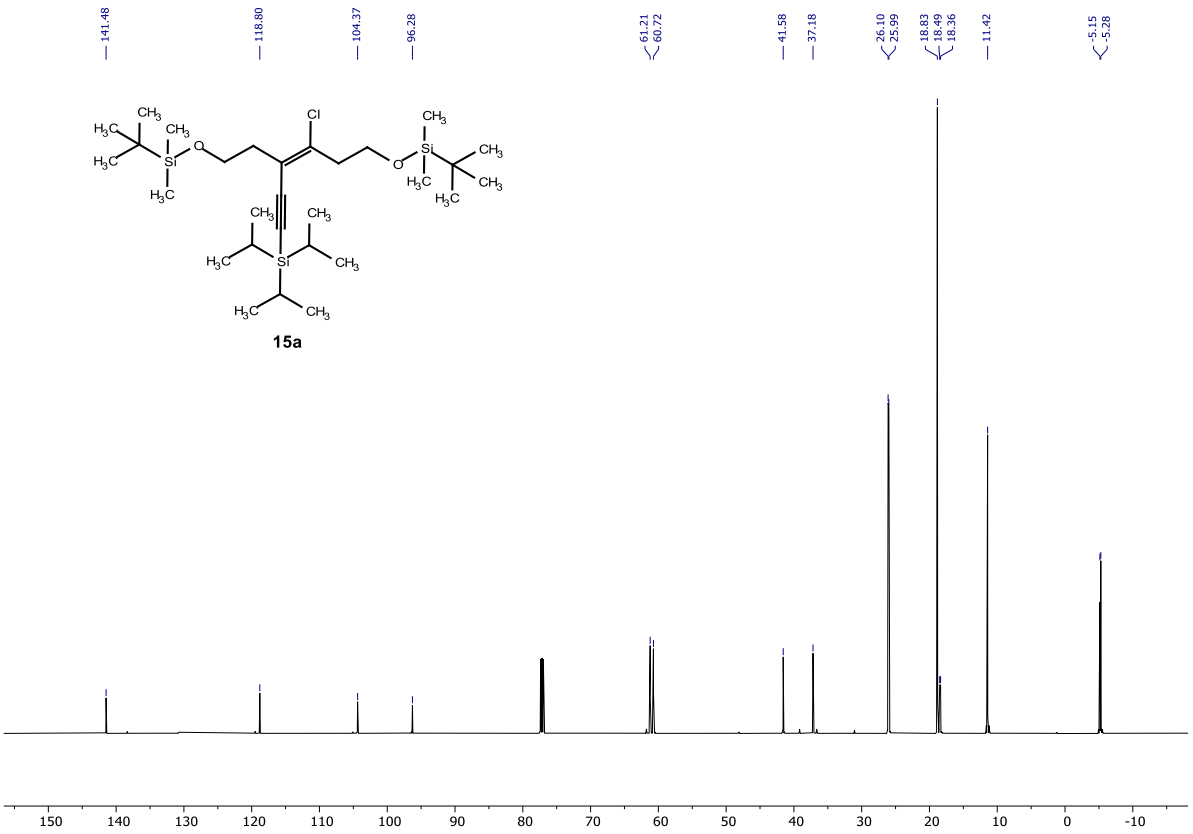
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18.83
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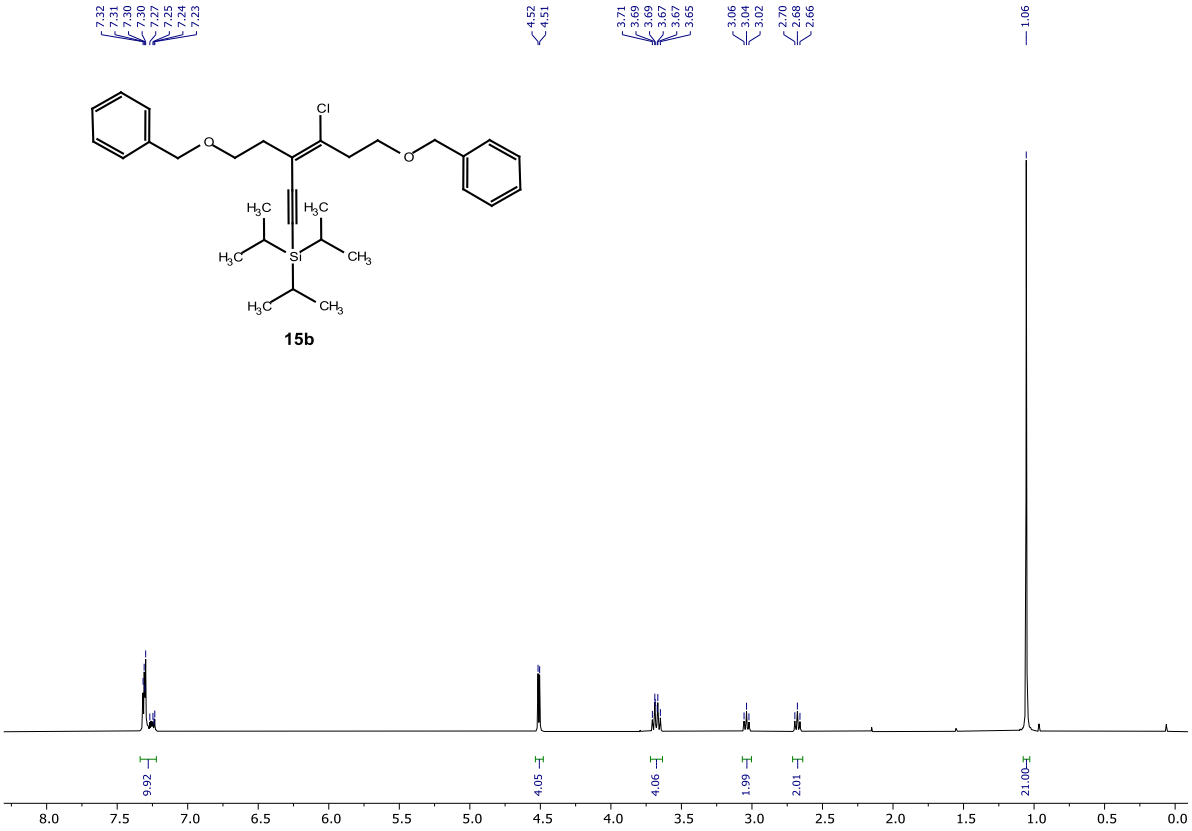
15a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3.67
3.65
3.06
3.04
3.02
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2.66
1.06
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H3C
H3C
H3C
Si
CH3
H3C
CH3
15b
9.92
4.05
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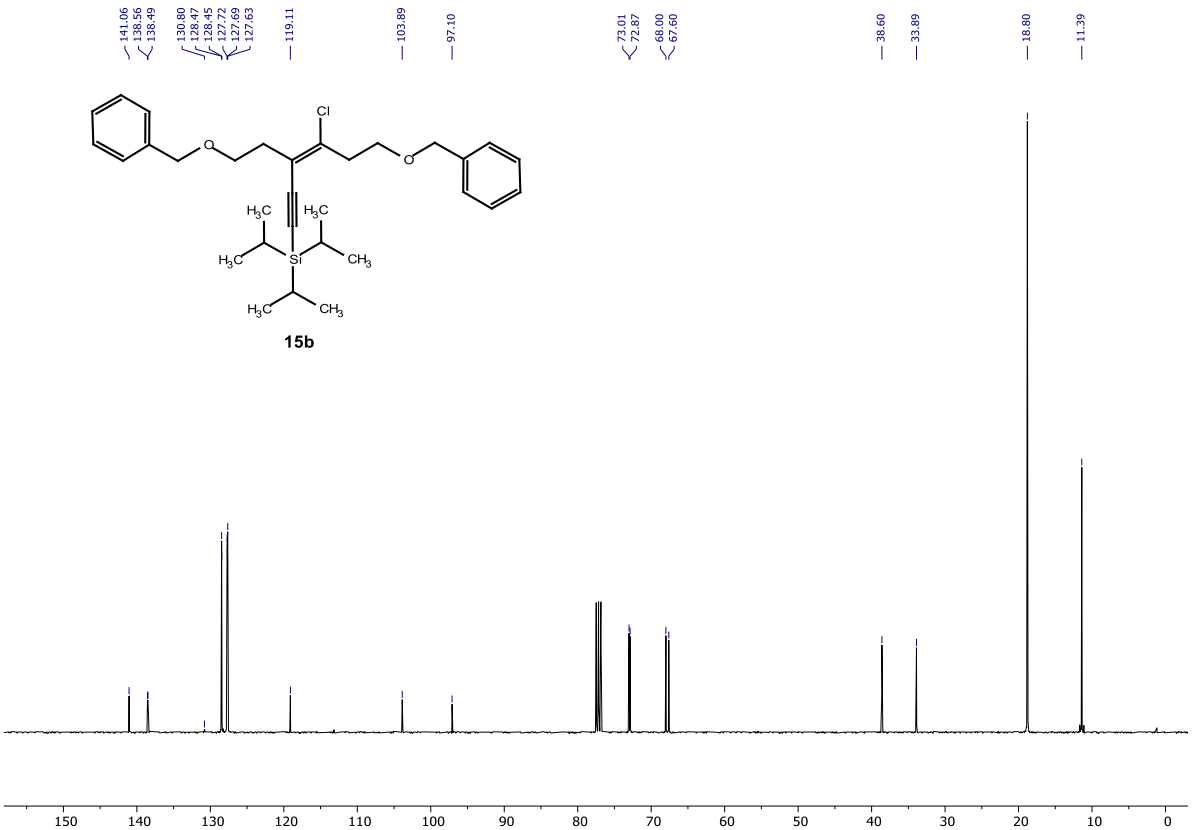
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H3C
H3C
Si
CH3
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10
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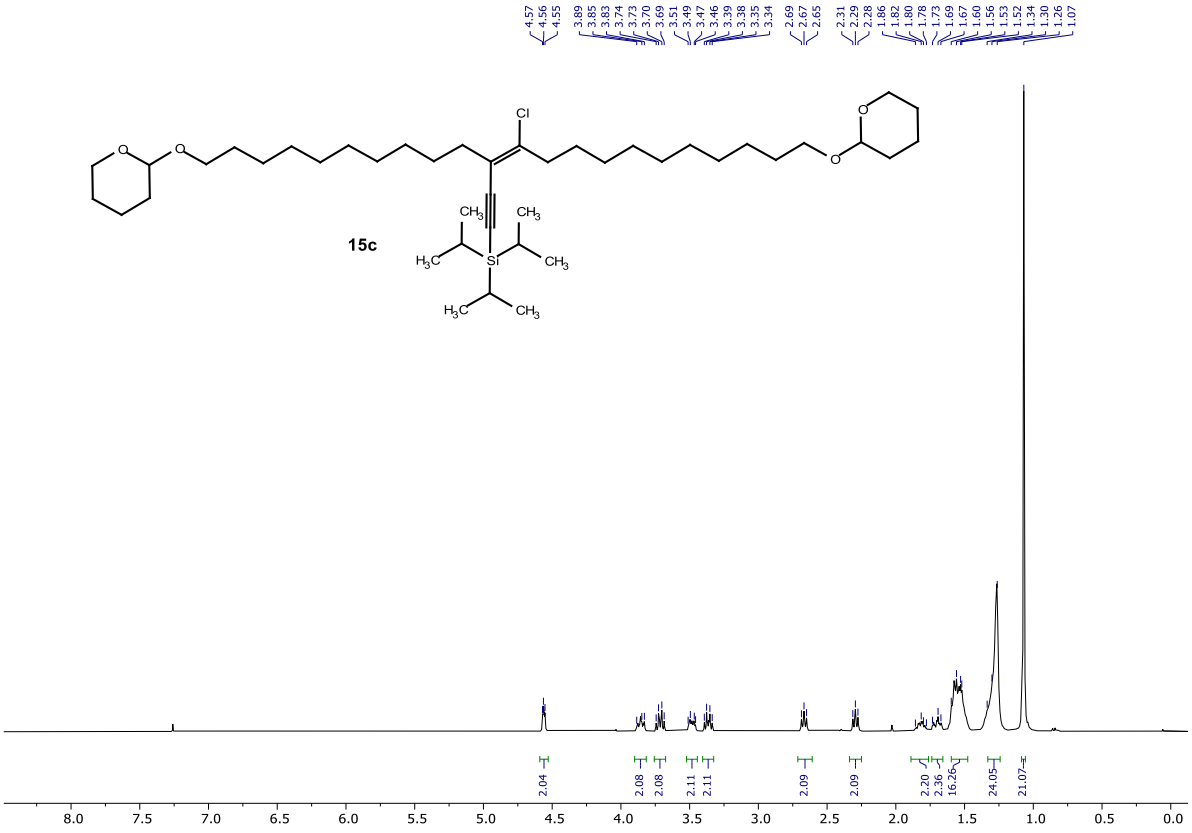
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Cl
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Si
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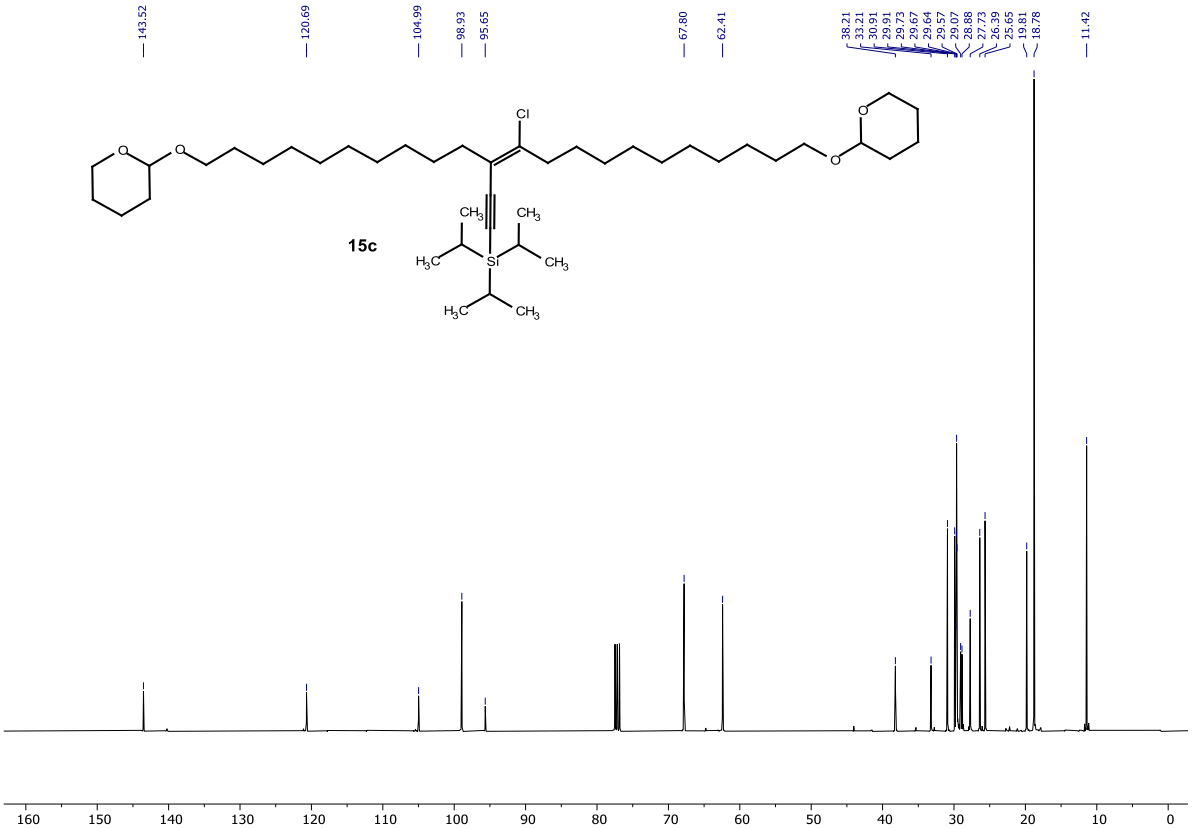
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H3C
Si
CH3
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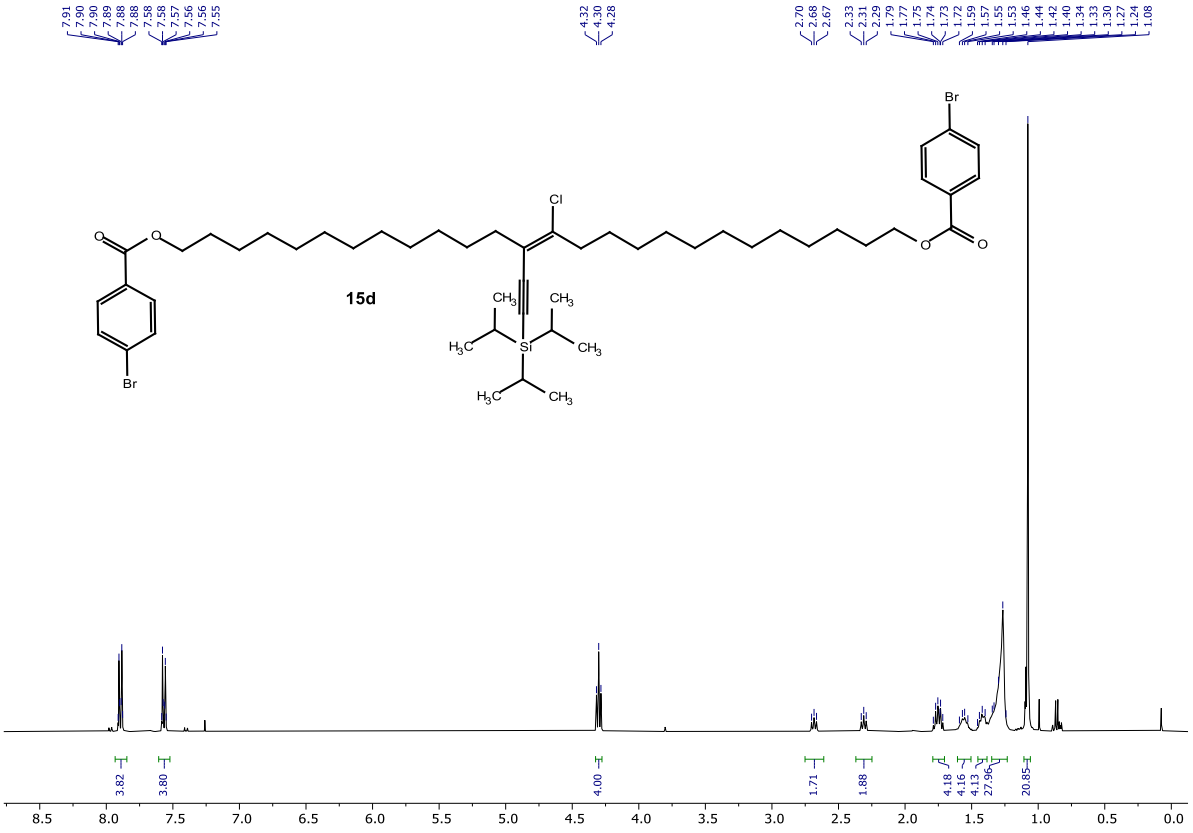
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1.55
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Br
Cl
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O
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Br
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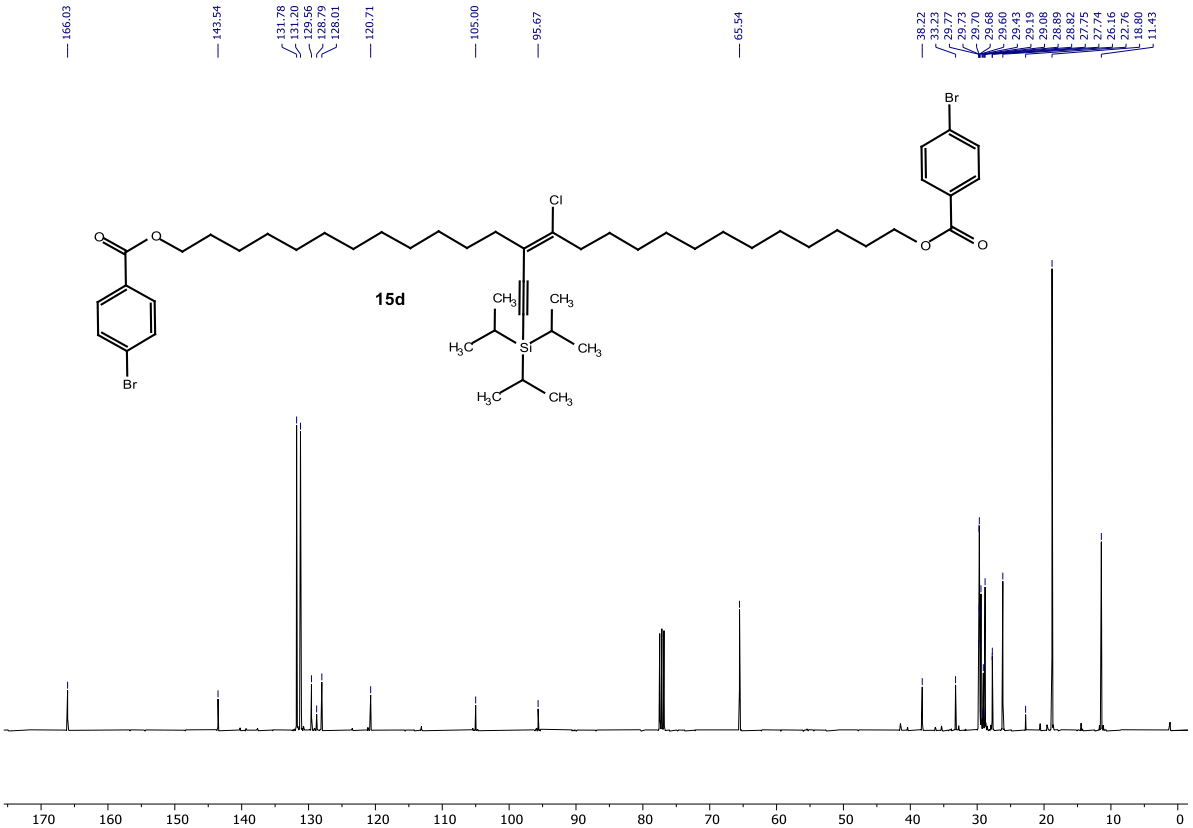
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11.43
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O
O
O
O
15d
CH3
CH3
H3C
Si
CH3
H3C
CH3
Br
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140
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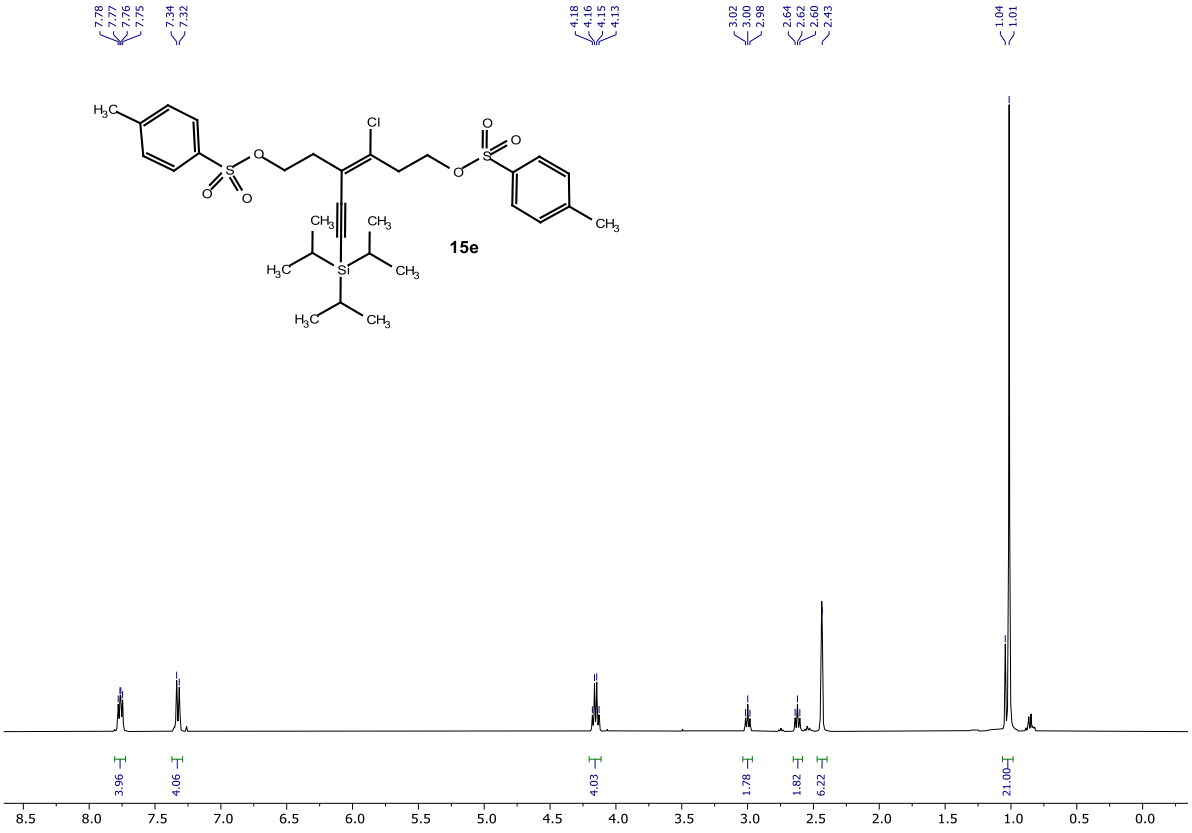
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4.16
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4.13
3.02
3.00
2.98
2.64
2.62
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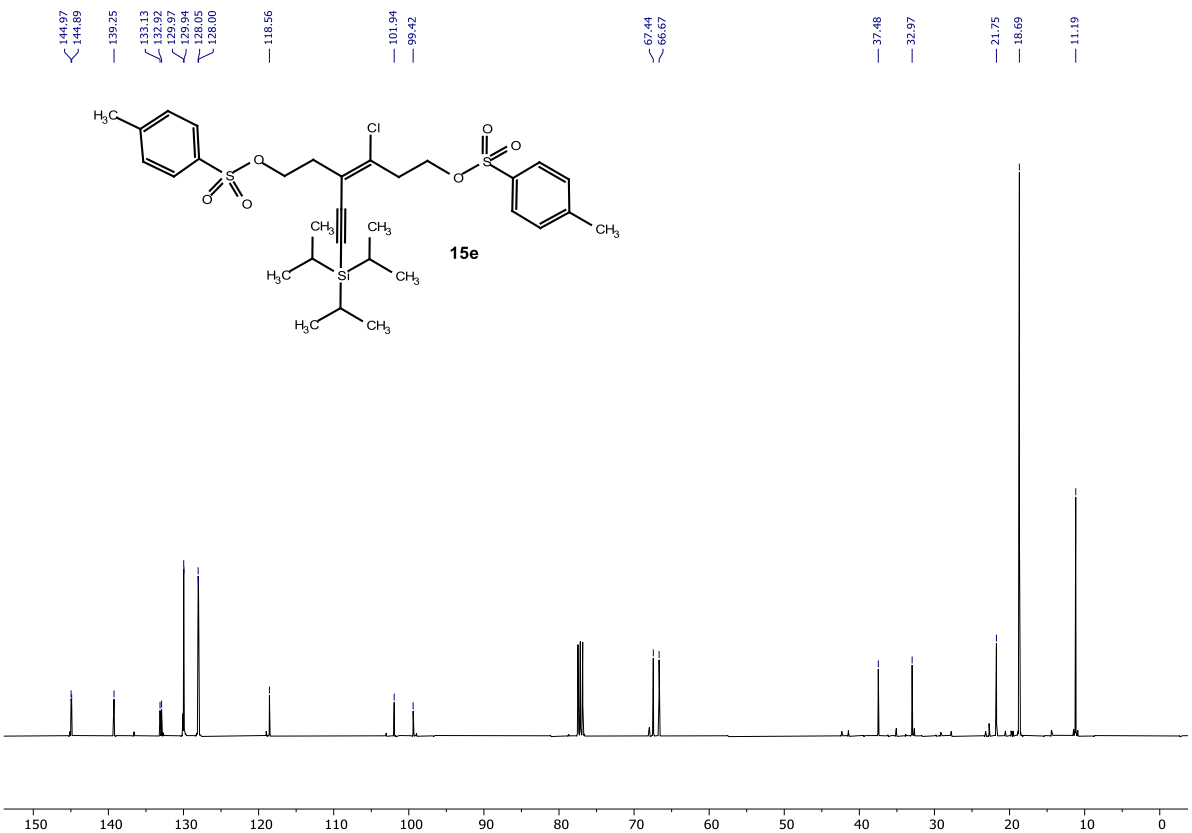
1.04
1.01
15e
3.96
4.06
4.03
1.78
1.82
6.22
21.00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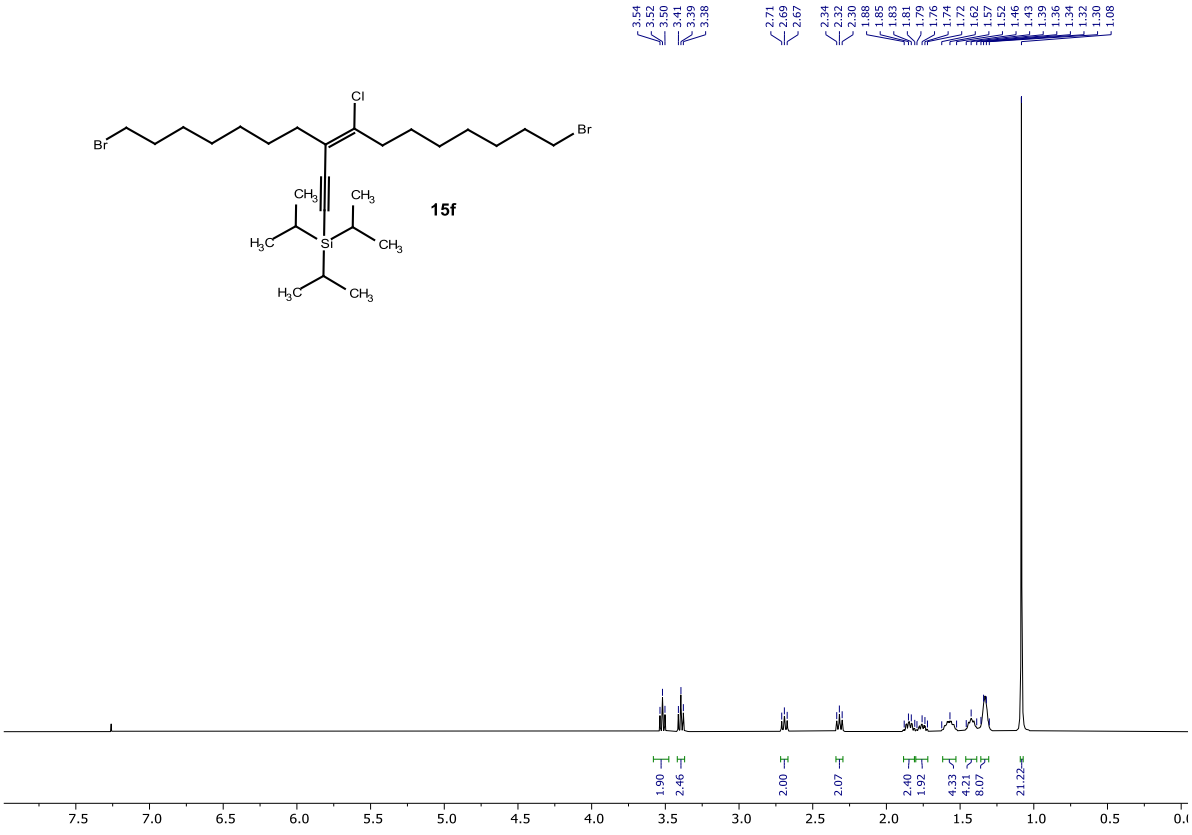
15e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3.50
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3.38
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2.69
2.67
2.34
2.32
2.30
1.88
1.85
1.83
1.81
1.79
1.76
1.74
1.72
1.62
1.57
1.52
1.46
1.43
1.39
1.36
1.34
1.32
1.30
1.08
Cl
Br
Br
CH3
CH3
H3C
Si
CH3
H3C
CH3
15f
1.90
2.46
2.00
2.07
2.40
1.92
4.33
4.21
8.07
21.22
7.5
7.0
6.5
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4.5
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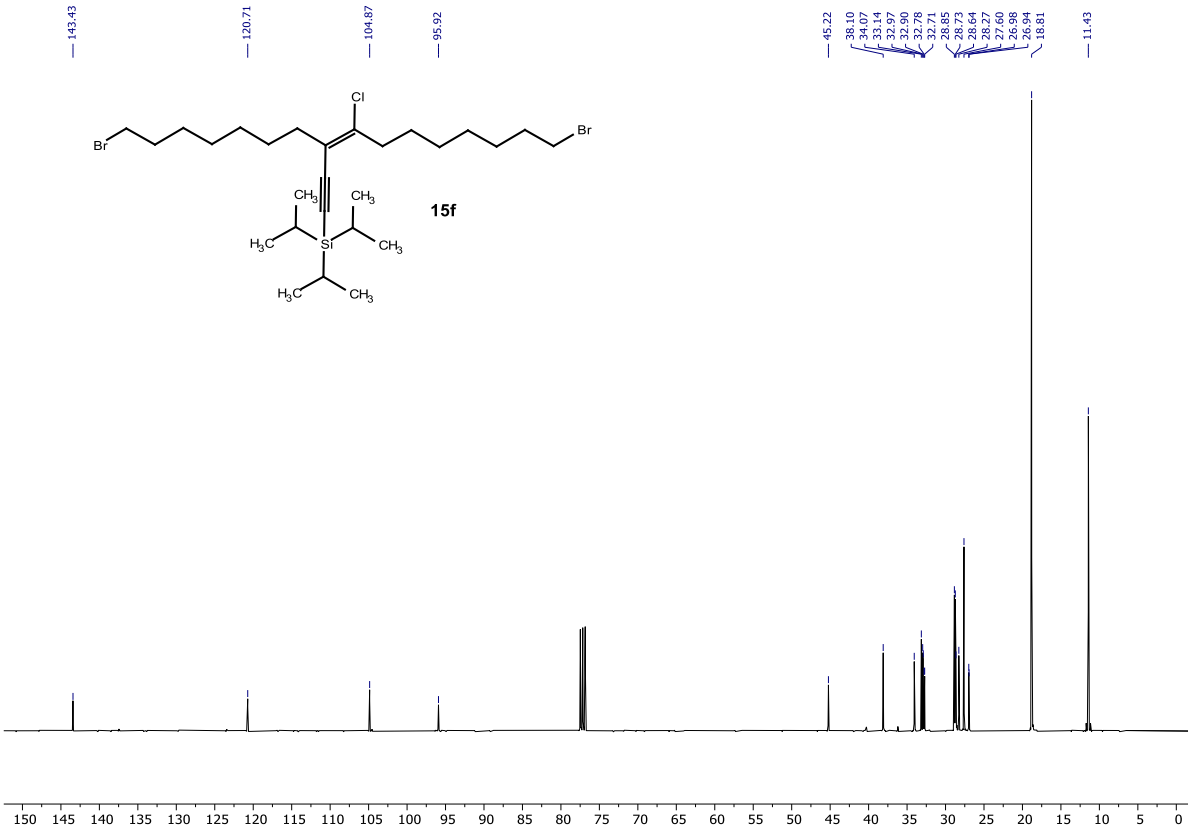
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120.71
104.87
95.92
45.22
38.10
34.07
33.14
32.97
32.90
32.78
32.71
28.85
28.73
28.64
28.27
27.60
26.98
26.94
18.81
11.43
Cl
Br
Br
CH3
CH3
H3C
Si
CH3
H3C
CH3
15f
150
145
140
135
130
125
120
115
110
105
100
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75
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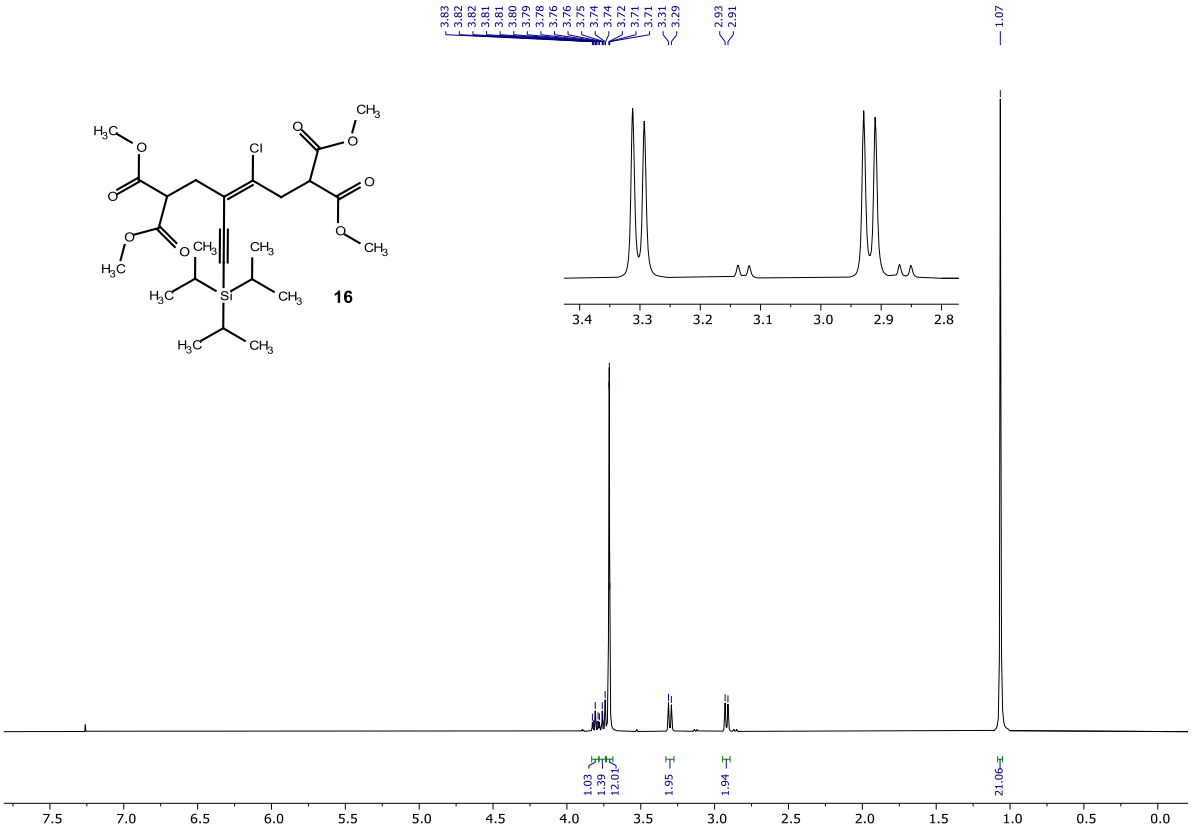
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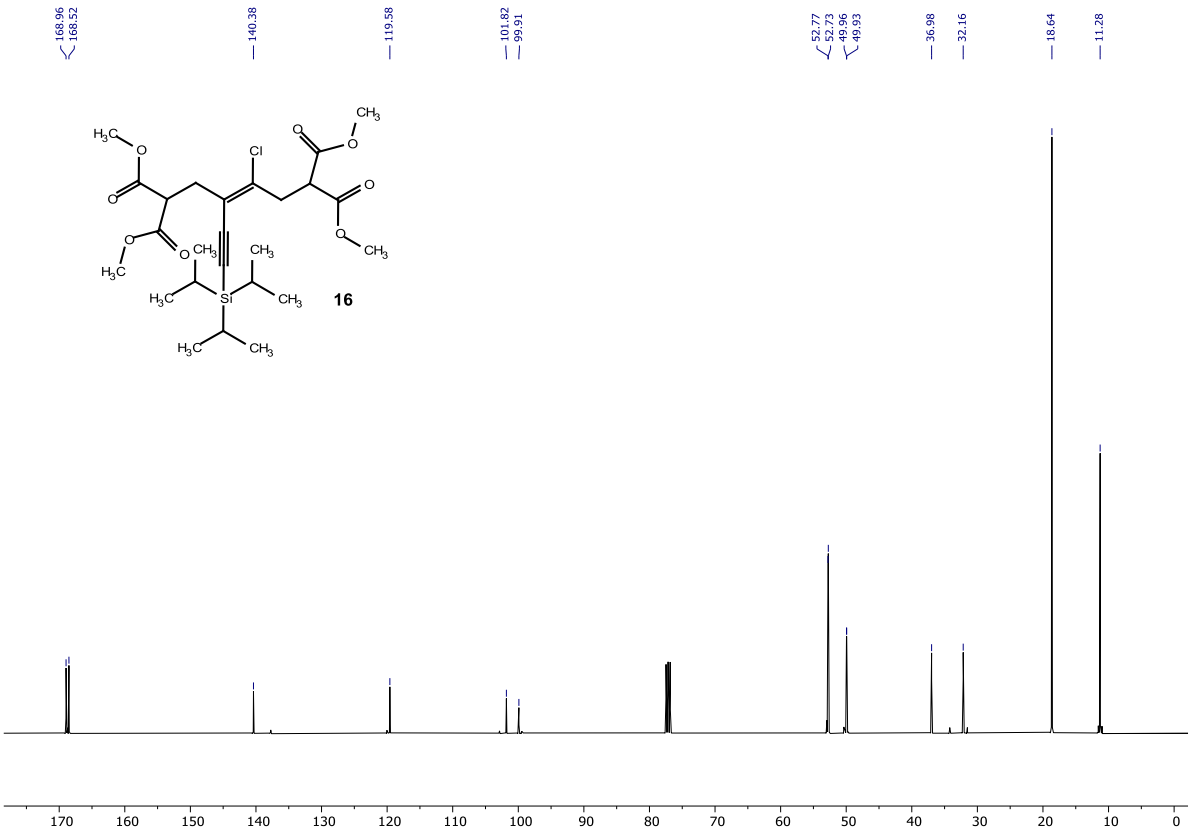
3.82
3.82
3.81
3.81
3.80
3.79
3.78
3.76
3.76
3.75
3.74
3.74
3.72
3.71
3.71
3.31
3.29
2.93
2.91
1.07
16
1.03
1.39
12.01
1.95
1.94
21.06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168.52
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99.91
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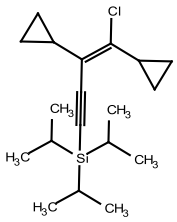
52.73
49.96
49.93
36.98
32.16
18.64
11.28
16


Cl
CH3
CH3
H3C
Si
CH3
H3C
CH3

17

2.53
2.52
2.50
2.48
2.47
2.05
2.03
2.02
2.01
1.99
1.07
0.93
0.91
0.90
0.89
0.83
0.82
0.80
0.79
0.78
0.77
0.75
0.73
0.70
1.00
0.99
21.11
2.12
2.34
4.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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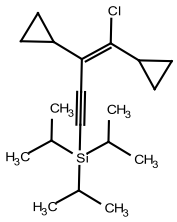
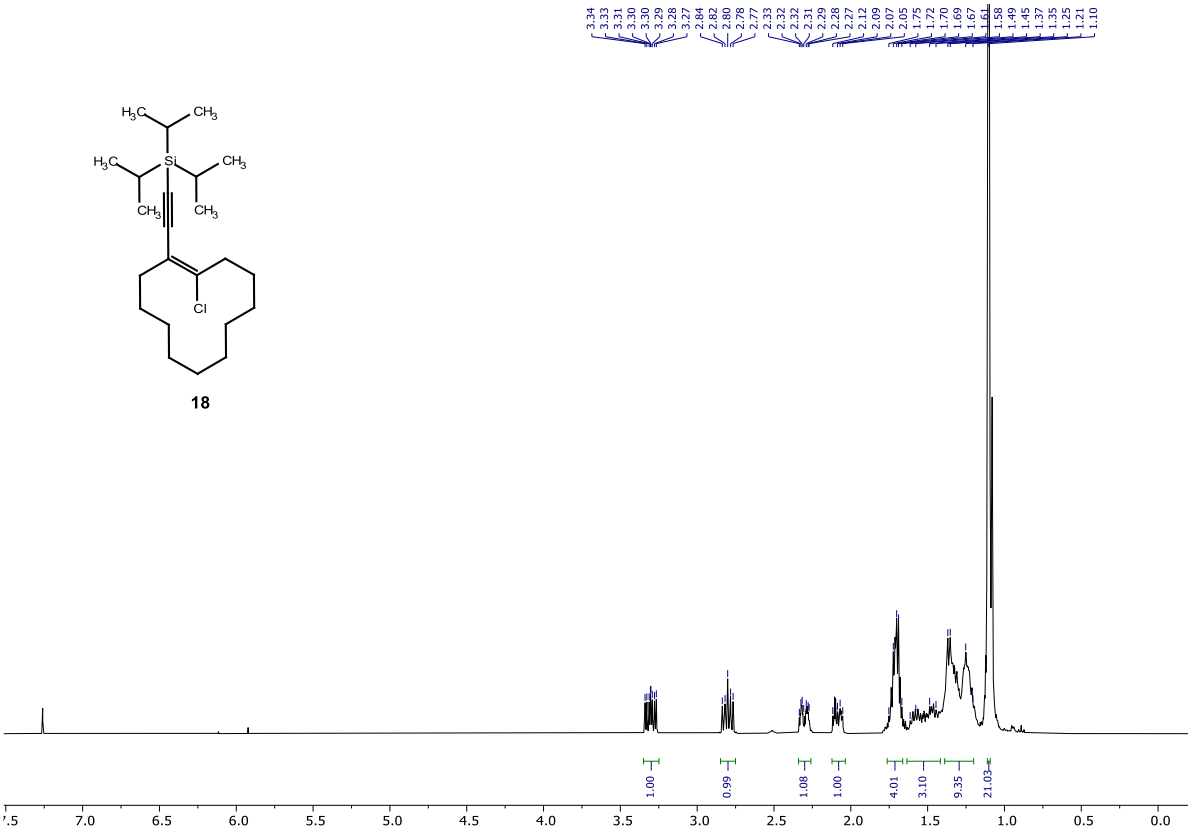
2.0
1.5
1.0
0.5
0.0


Cl
CH3
CH3
H3C
Si
CH3
H3C
CH3

17

143.16
121.69
101.64
96.48
18.78
17.45
12.89
11.43
6.20
5.91
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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3.33
3.31
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3.30
3.29
3.28
3.27
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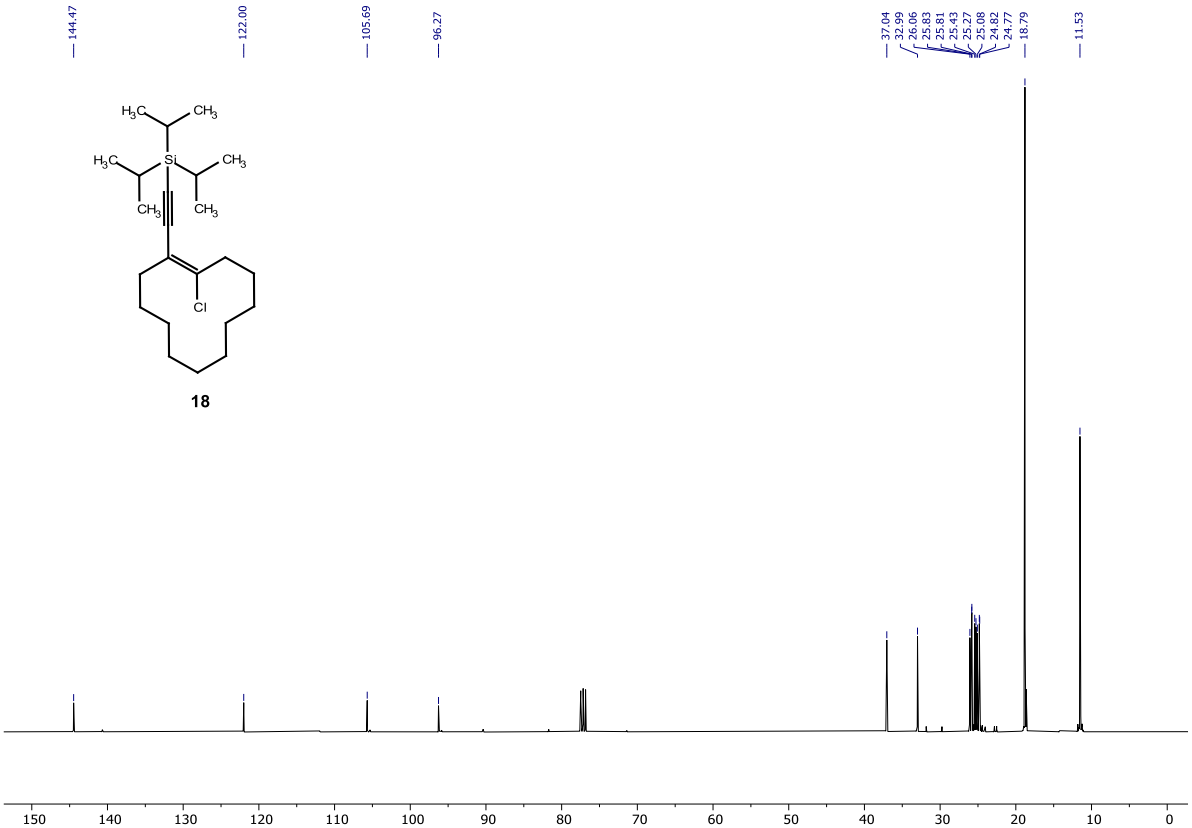
2.82
2.80
2.78
2.77
2.33
2.32
2.31
2.29
2.28
2.27
2.12
2.09
2.07
2.05
1.75
1.72
1.70
1.69
1.67
1.58
1.49
1.45
1.37
1.35
1.25
1.21
1.10
1.00
0.99
1.08
1.00
4.01
3.10
9.35
21.03
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

H3C
CH3
H3C
Si
CH3
CH3
CH3
Cl

18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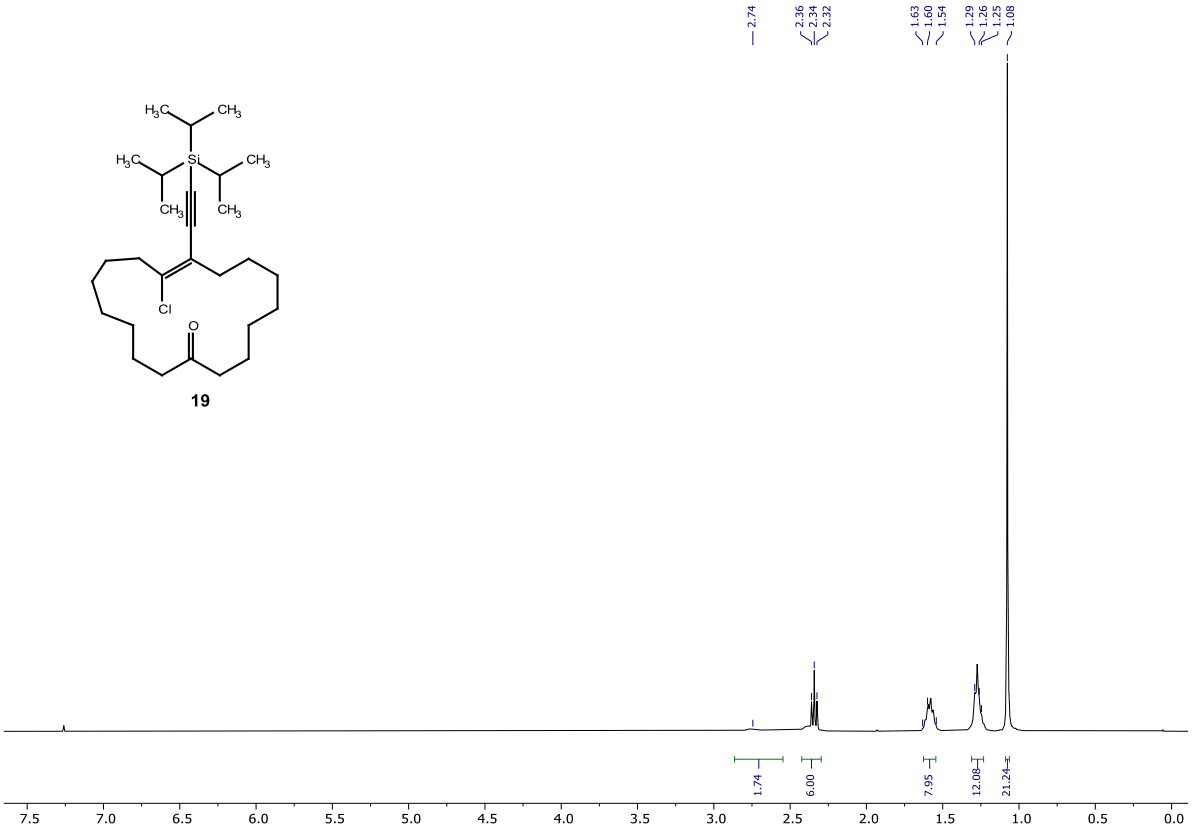
96.27
37.04
32.99
26.06
25.83
25.81
25.43
25.27
25.08
24.82
24.77
18.79
11.53
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

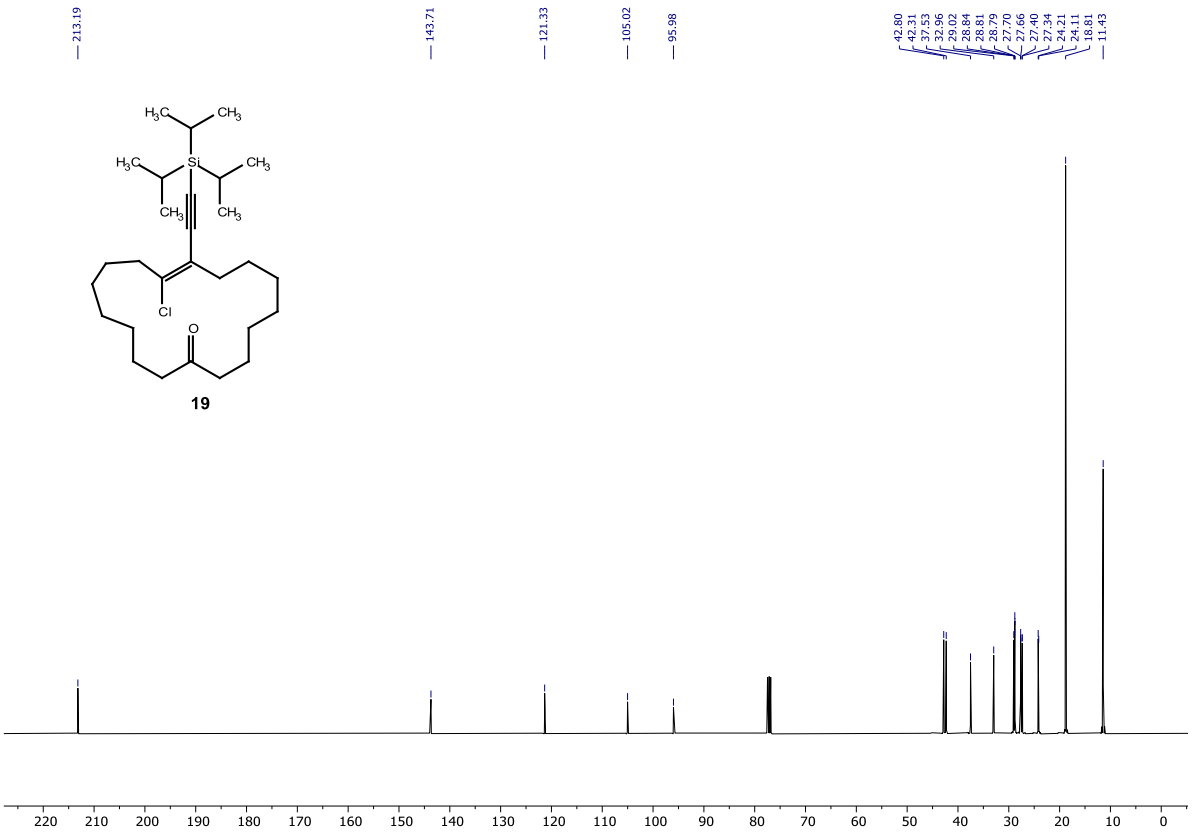
H3C
CH3
H3C
Si
CH3
CH3
CH3
Cl

18


2.74
2.36
2.34
2.32
1.63
1.60
1.54
1.29
1.26
1.25
1.08
1.74
6.00
7.95
12.08
21.24
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

H3C
CH3
Si
CH3
CH3
CH3
Cl
O

19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121.33
105.02
95.98
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42.31
37.53
32.96
29.02
28.84
28.81
28.79
27.70
27.66
27.40
27.34
24.21
24.11
18.81
11.43
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
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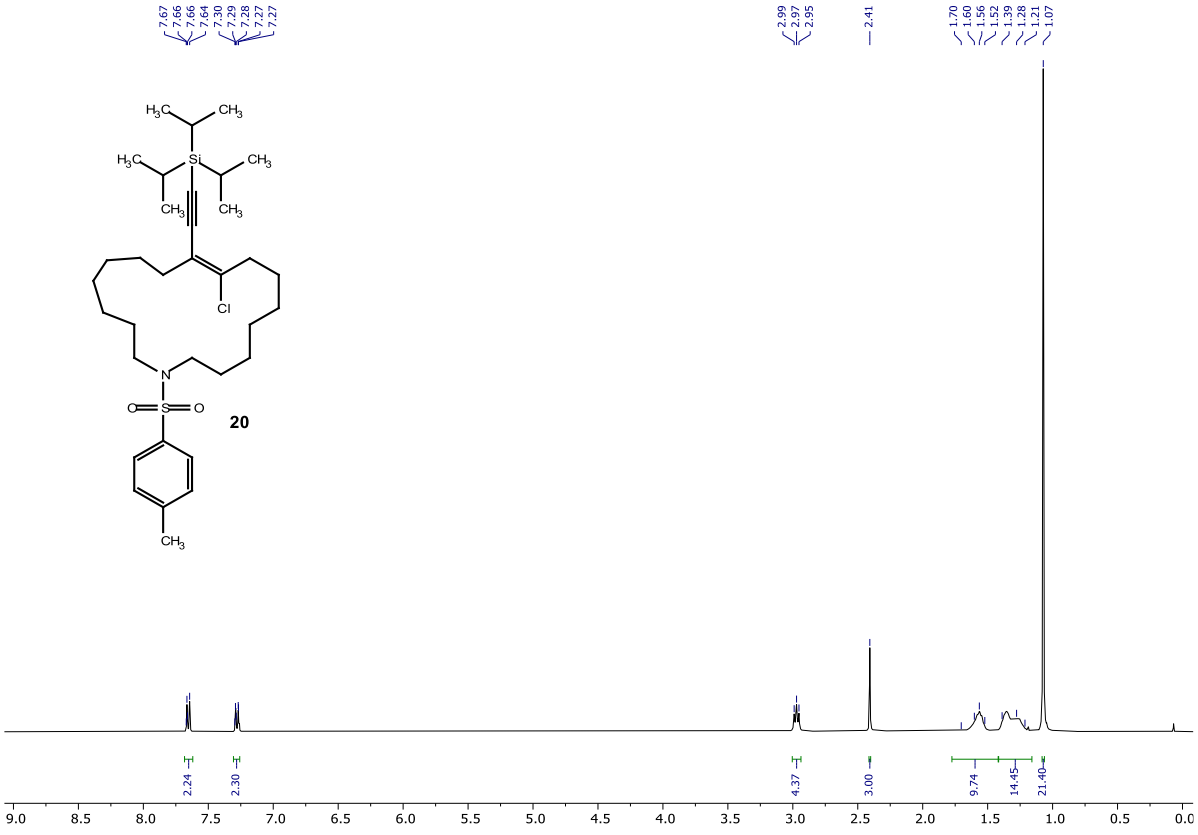
40
30
20
10
0

H3C
CH3
Si
CH3
CH3
CH3
Cl
O

19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7.66
7.66
7.64
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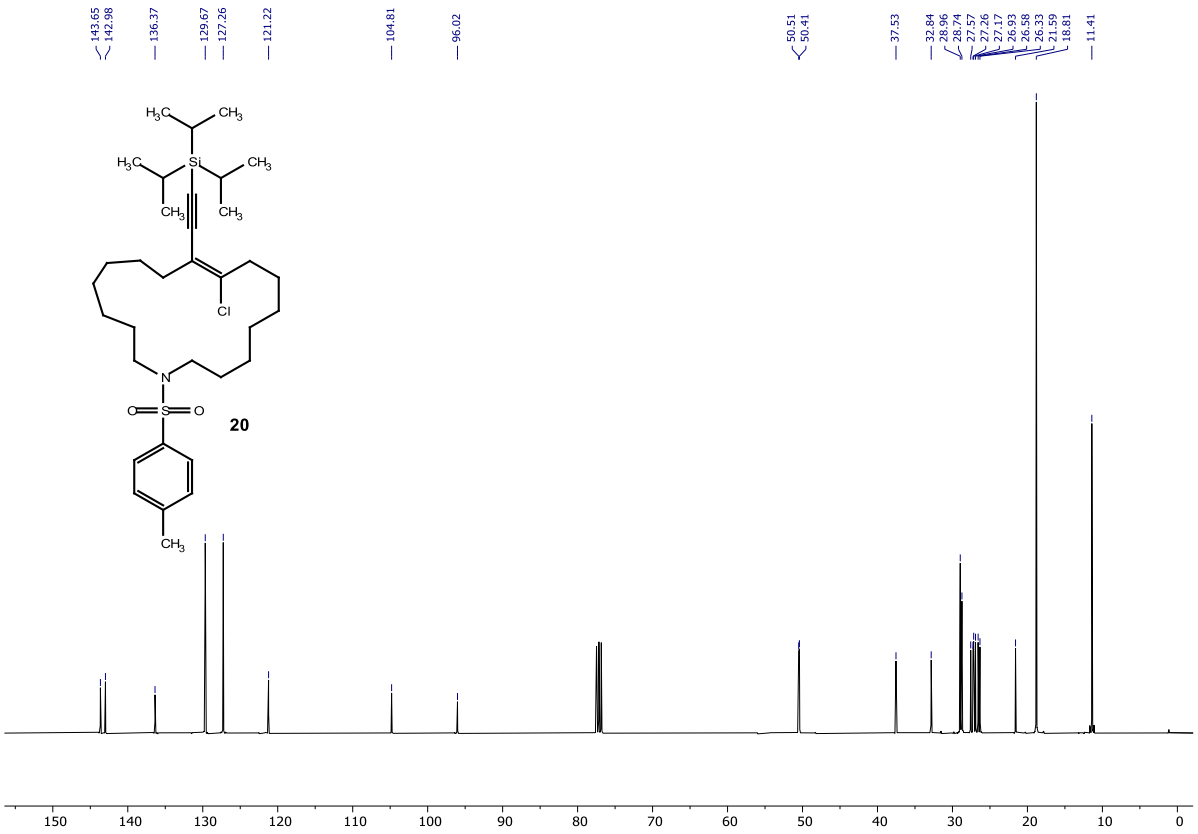
7.28
7.27
7.27
2.99
2.97
2.95
2.41
1.70
1.60
1.56
1.52
1.39
1.28
1.21
1.07
20
2.24
2.30
4.37
3.00
9.74
14.45
21.40


143.65
142.98
136.37
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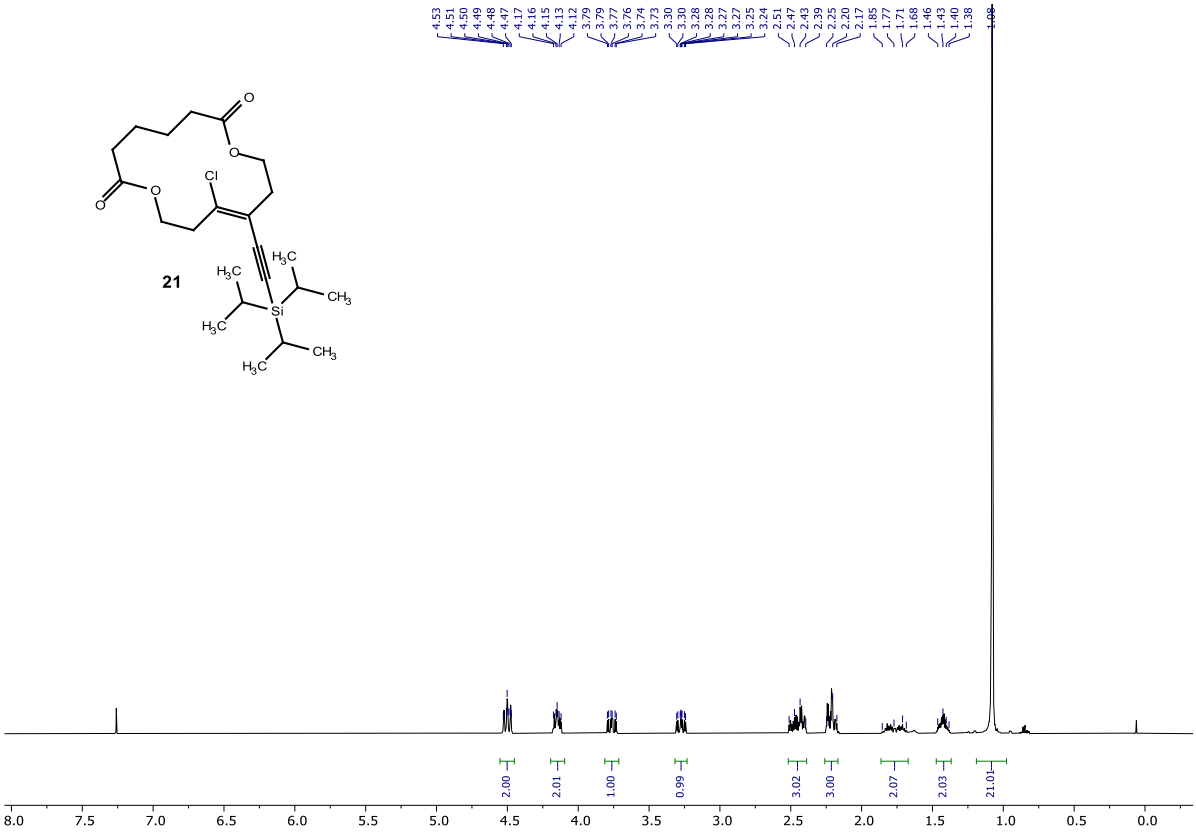
127.26
121.22
104.81
96.02
50.51
50.41
37.53
32.84
28.96
28.74
27.57
27.26
27.17
26.93
26.58
26.33
21.59
18.81
11.41
20


4.53
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4.50
4.49
4.48
4.47
4.17
4.16
4.15
4.13
4.12
3.79
3.79
3.77
3.76
3.74
3.73
3.30
3.30
3.28
3.28
3.27
3.27
3.25
3.24
2.51
2.47
2.43
2.39
2.25
2.20
2.17
1.85
1.77
1.71
1.68
1.46
1.43
1.40
1.38
1.08
21
Cl
O
O
O
O
H3C
CH3
Si
2.00
2.01
1.00
0.99
3.02
3.00
2.07
2.03
21.01
8.0
7.5
7.0
6.5
6.0
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4.0
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2.0
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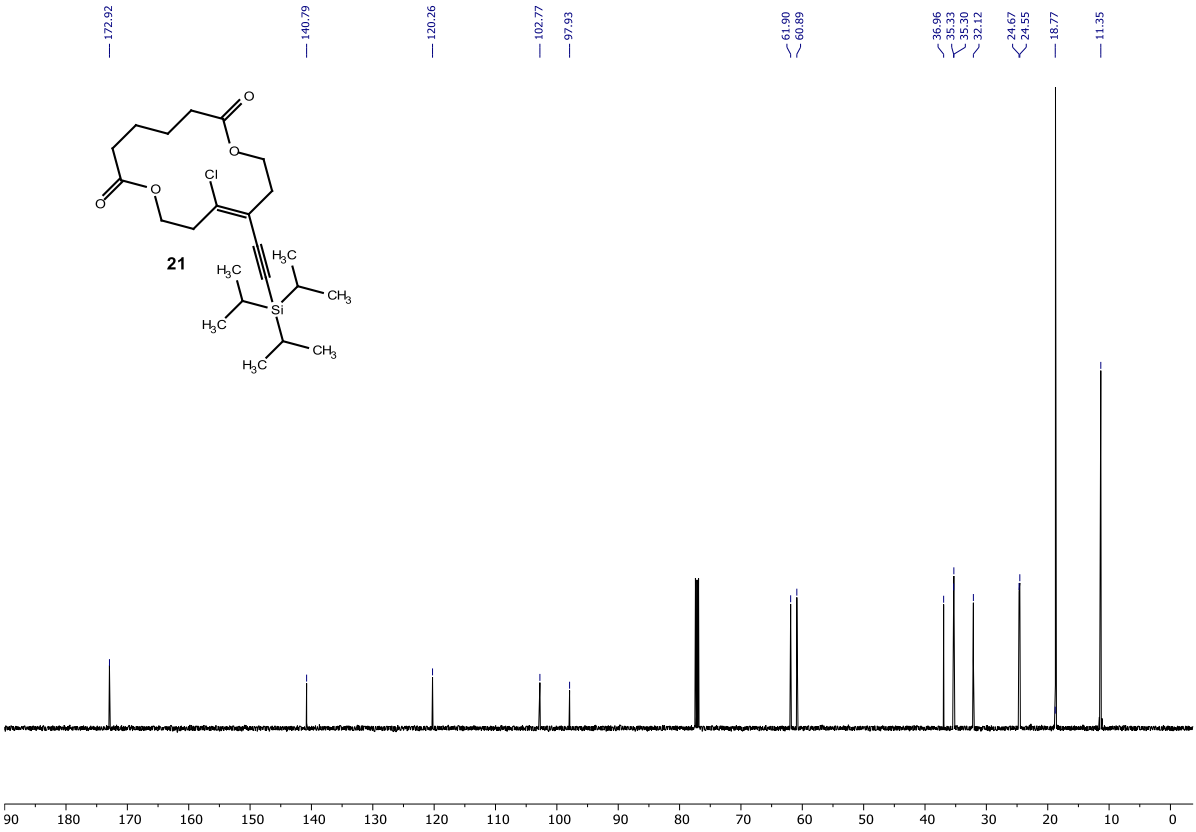
0.0


172.92
140.79
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102.77
97.93
61.90
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36.96
35.33
35.30
32.12
24.67
24.55
18.77
11.35
21
Cl
O
O
O
O
H3C
CH3
Si
90
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120
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70
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30
20
10
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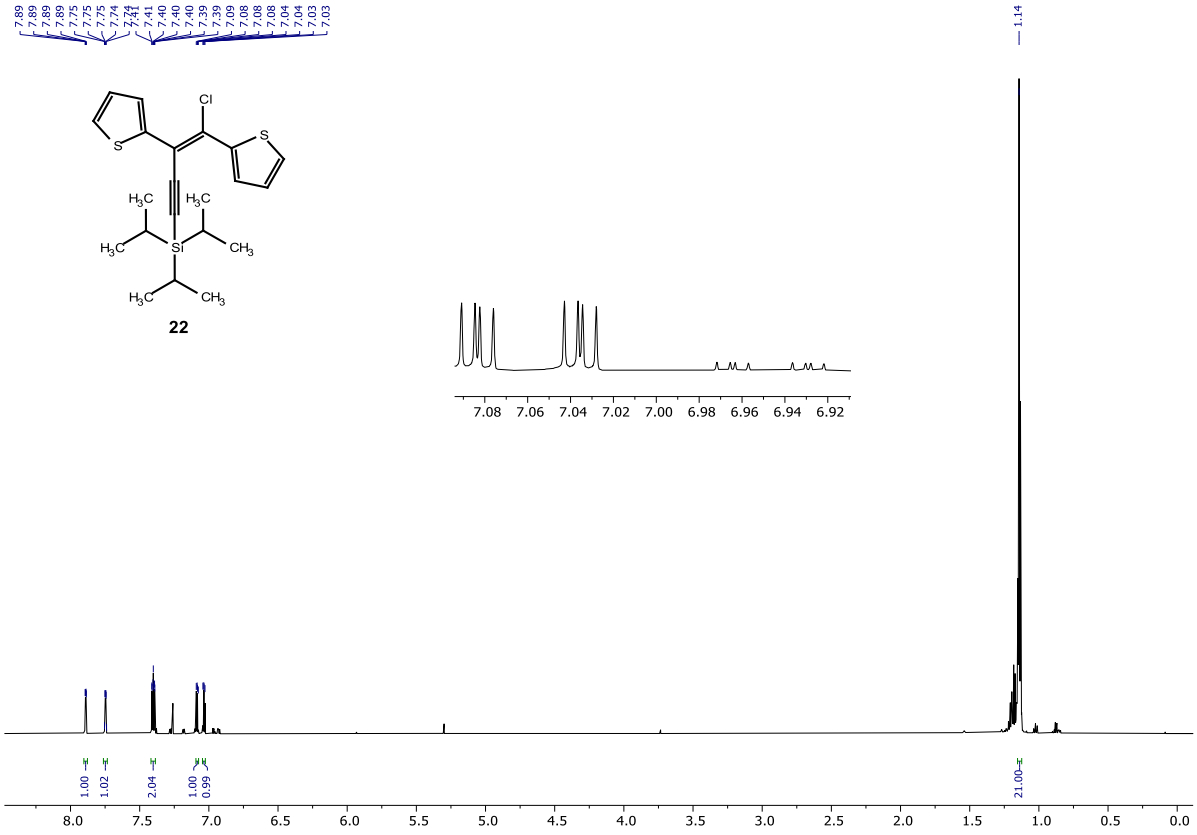
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7.89
7.89
7.89
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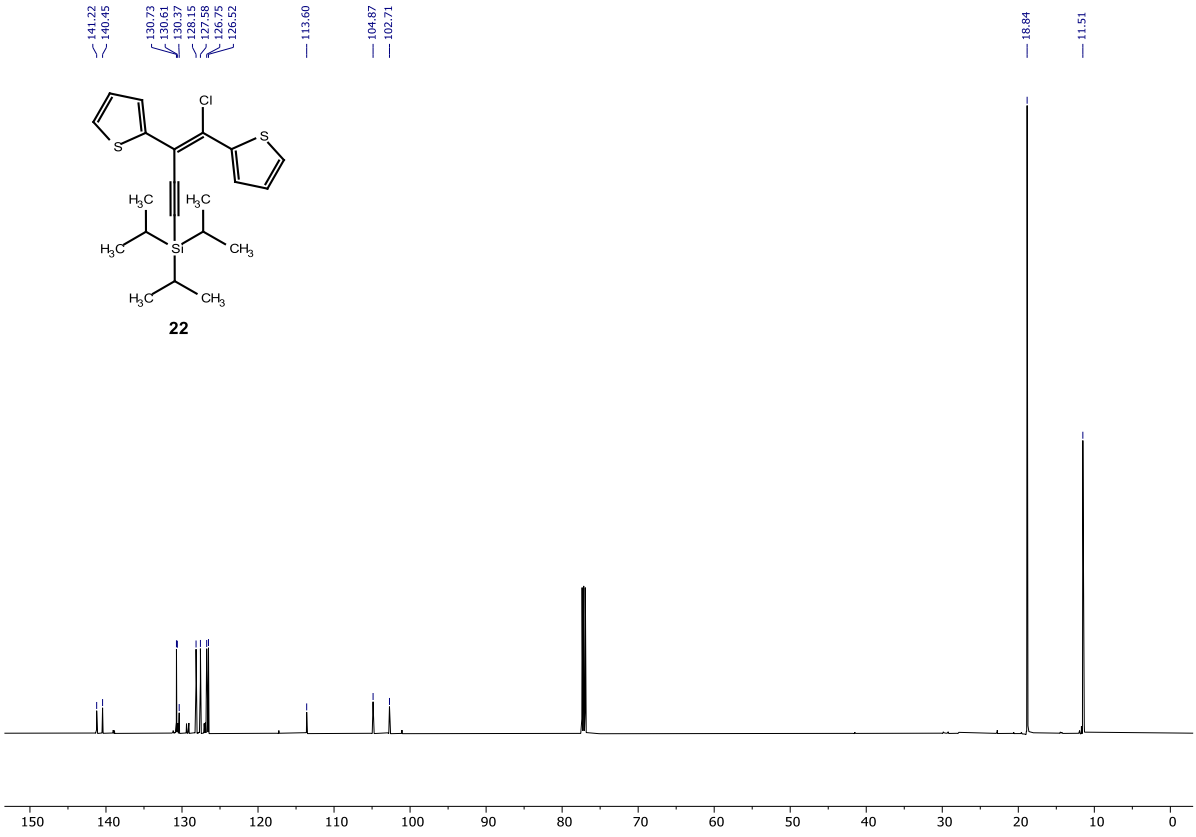
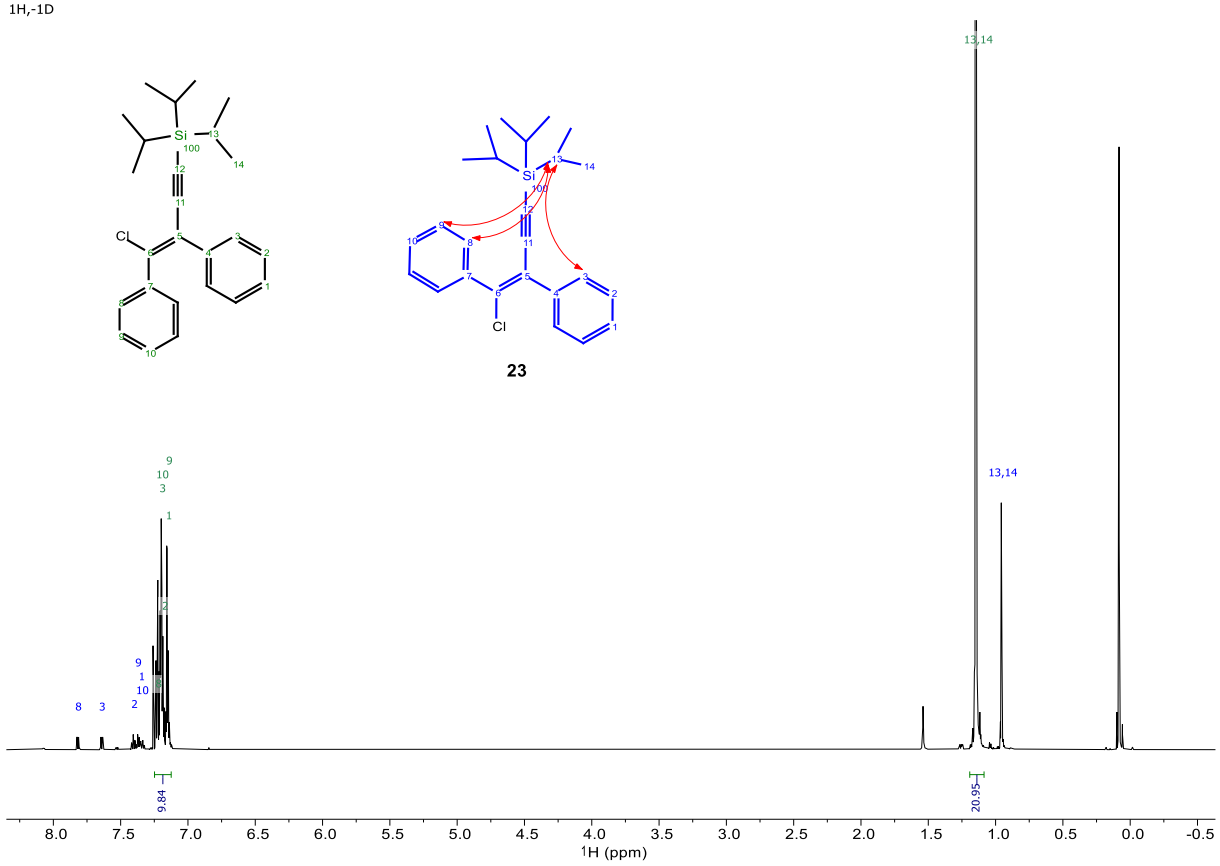
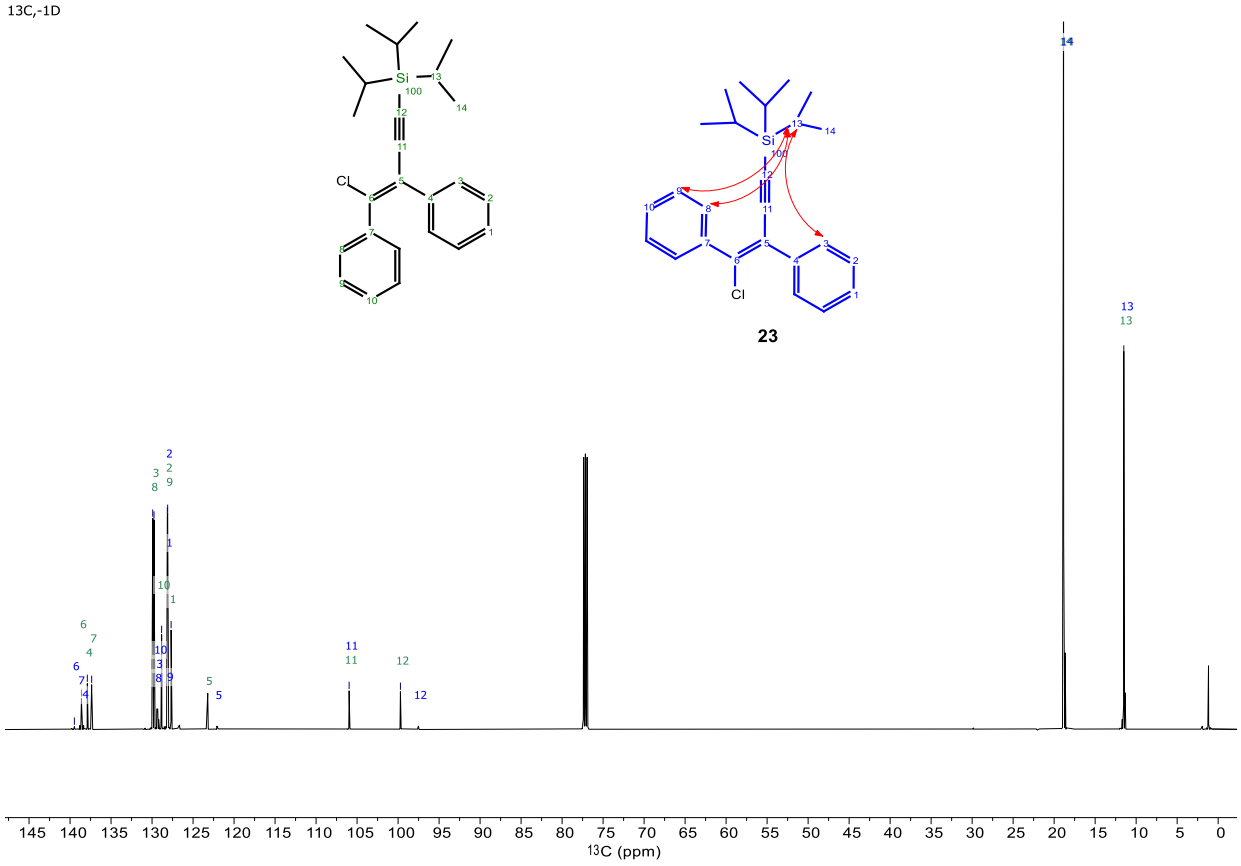
7.75
7.74
7.74
7.41
7.41
7.40
7.40
7.40
7.40
7.39
7.39
7.08
7.08
7.08
7.04
7.04
7.03
7.03
1.14
Cl
S
S
H3C
H3C
H3C
Si
CH3
H3C
CH3
22
7.08
7.06
7.04
7.02
7.00
6.98
6.96
6.94
6.92
1.00
1.02
2.04
1.00
0.99
21.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

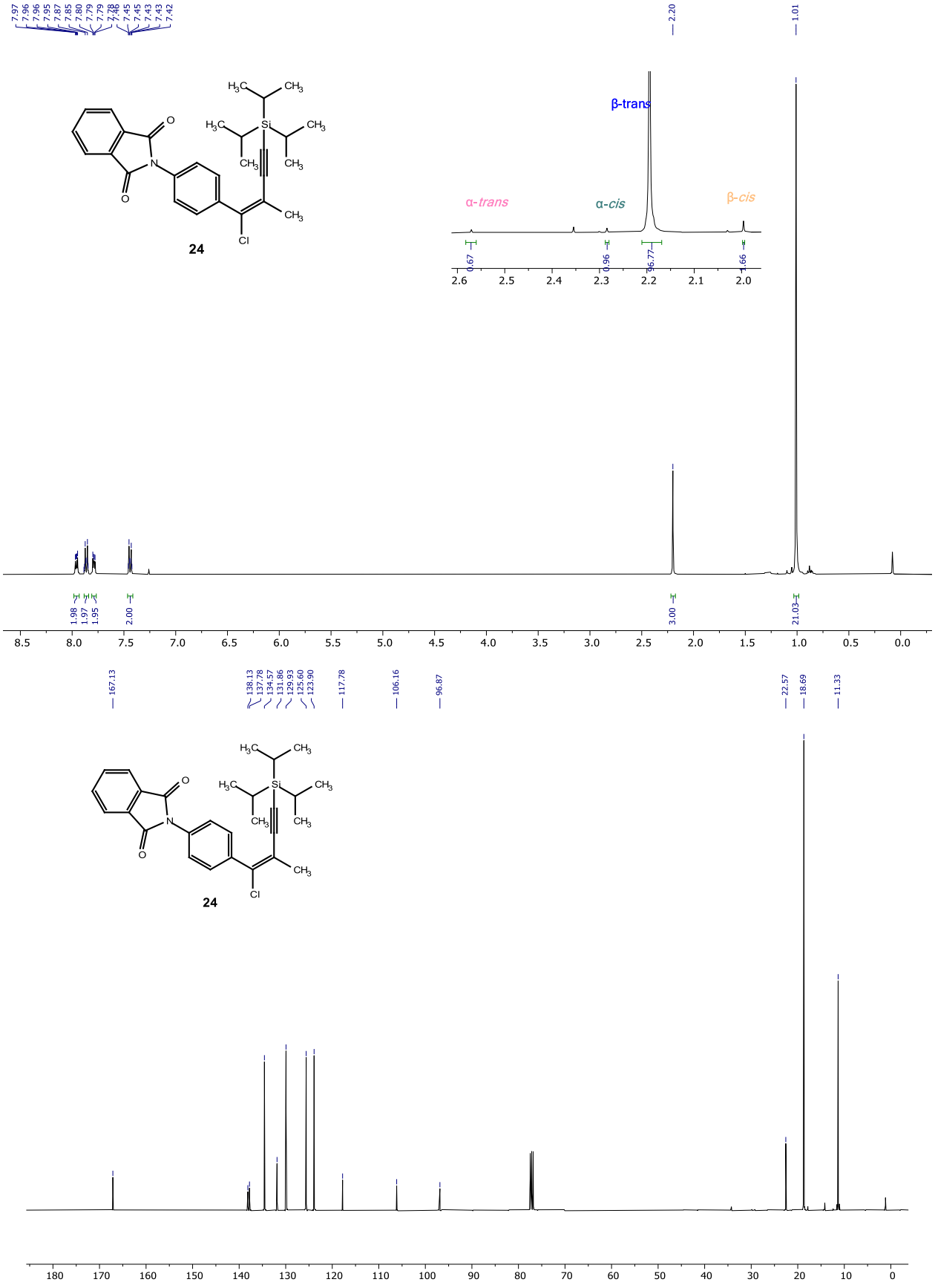

141.22
140.45
130.73
130.61
130.37
128.15
127.58
126.75
126.52
113.60
104.87
102.71
18.84
11.51
Cl
S
S
H3C
H3C
H3C
Si
CH3
H3C
CH3
22
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

1H,-1D


Si
100
13
14
12
11
Cl
5
6
4
3
2
1
7
8
9
10
23
13,14
9.84
20.95
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
1H (ppm)

13C,-1D


Si
100
13
14
12
11
Cl
5
6
4
3
2
1
7
8
9
10
23
14
13
13
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
13C (ppm)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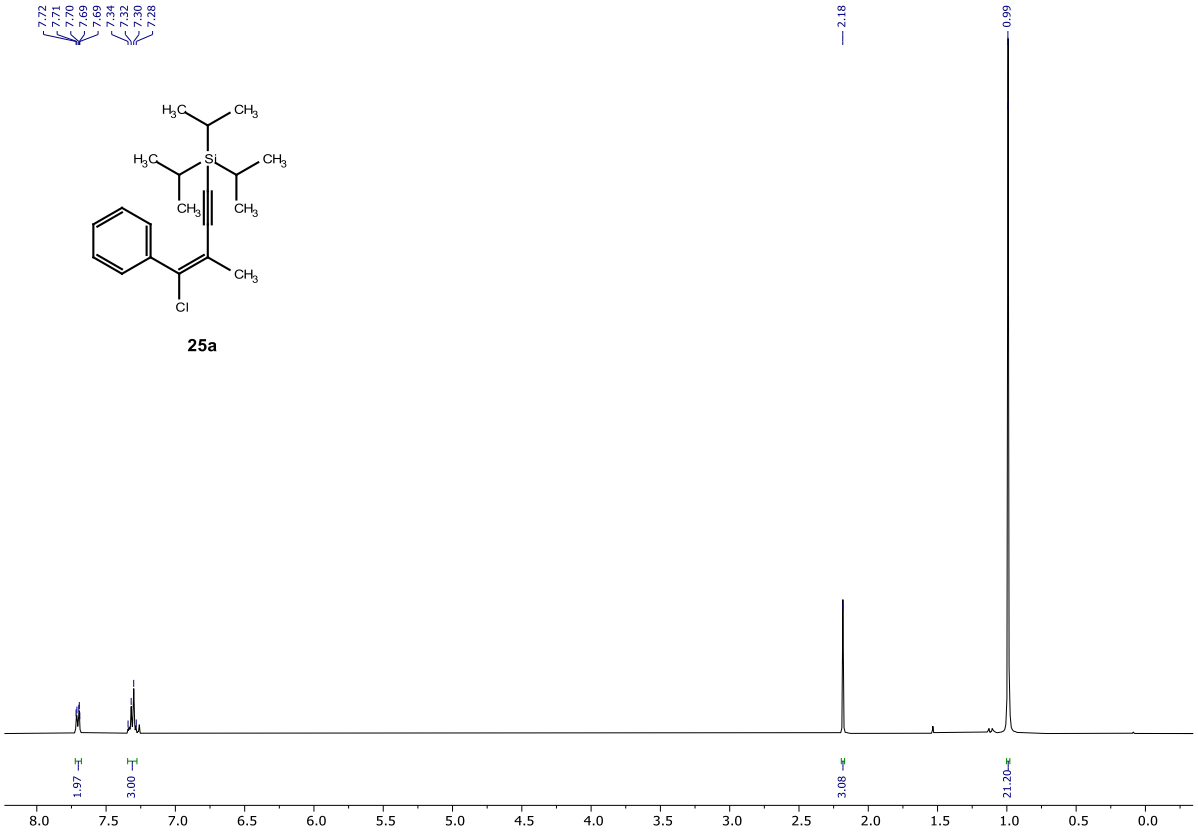
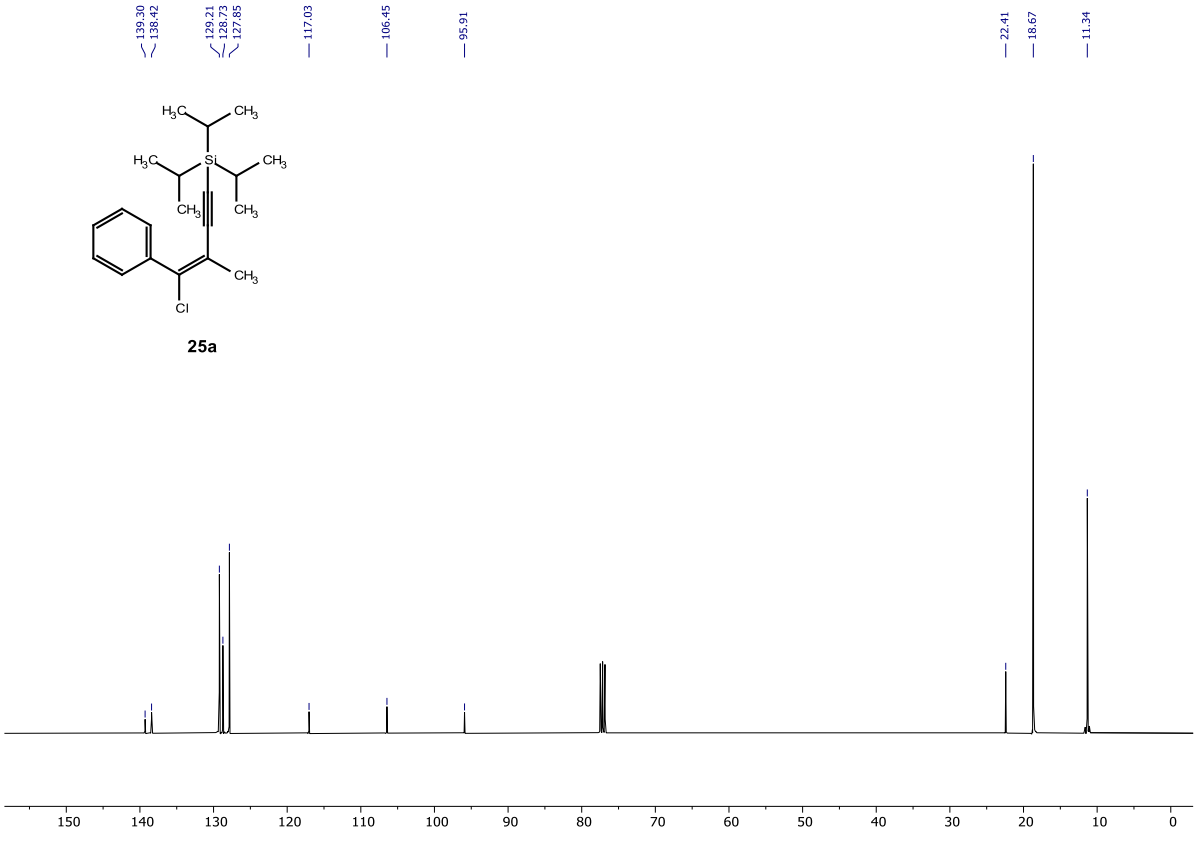
7.95
7.87
7.85
7.80
7.79
7.79
7.78
7.45
7.45
7.43
7.42
2.20
1.01
24
β-trans
α-trans
α-cis
β-cis
0.67
0.96
36.77
1.66
1.98
1.97
1.95
2.00
3.00
21.03
167.13
138.13
137.78
134.57
131.86
129.93
125.60
123.90
117.78
106.16
96.87
22.57
18.69
11.33
24


7.72
7.71
7.70
7.69
7.69
7.34
7.32
7.30
7.28
2.18
0.99
H3C
CH3
Si
CH3
CH3
CH3
CH3
CH3
Cl
1.97
3.00
3.08
21.20
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

25a


139.30
138.42
129.21
128.73
127.85
117.03
106.45
95.91
22.41
18.67
11.34
H3C
CH3
Si
CH3
CH3
CH3
CH3
CH3
Cl
150
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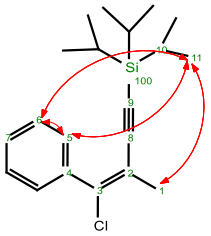
130
120
110
100
90
80
70
60
50
40
30
20
10
0

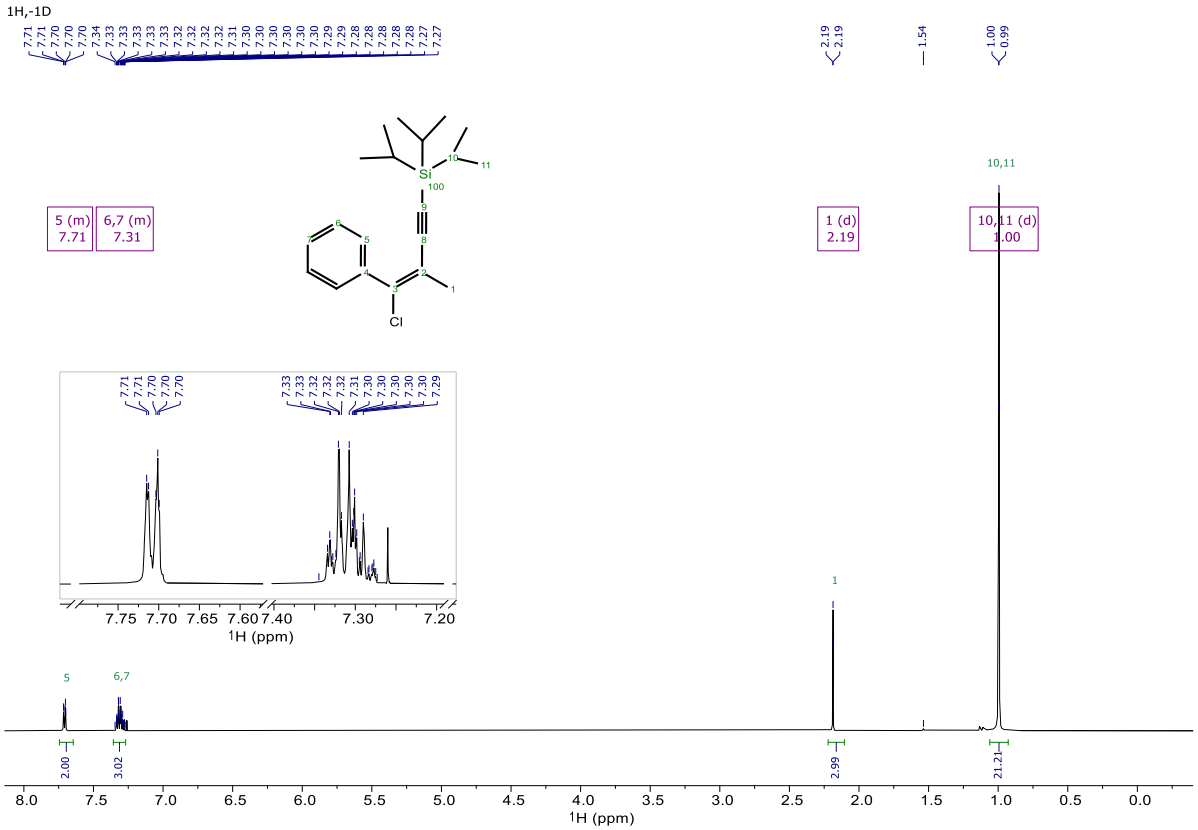
25a

NMR data supports the following structure:

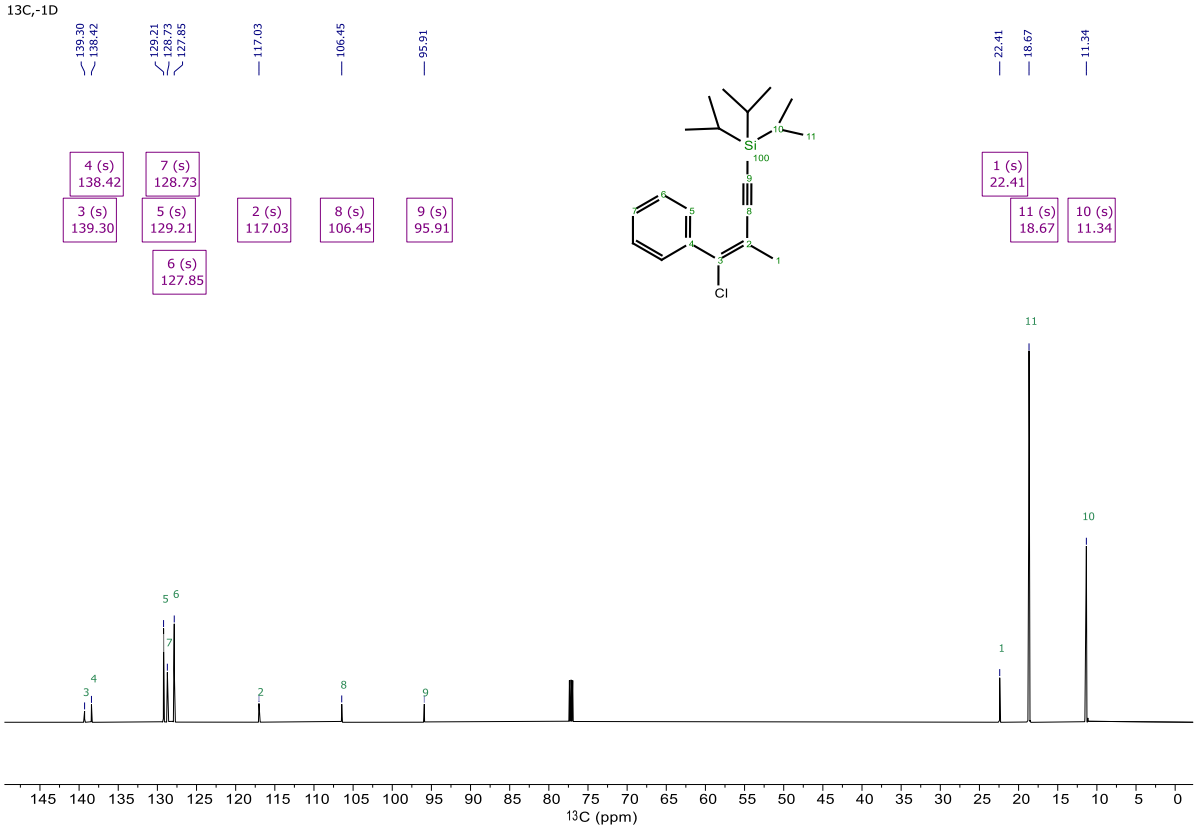


NOESY cross peaks

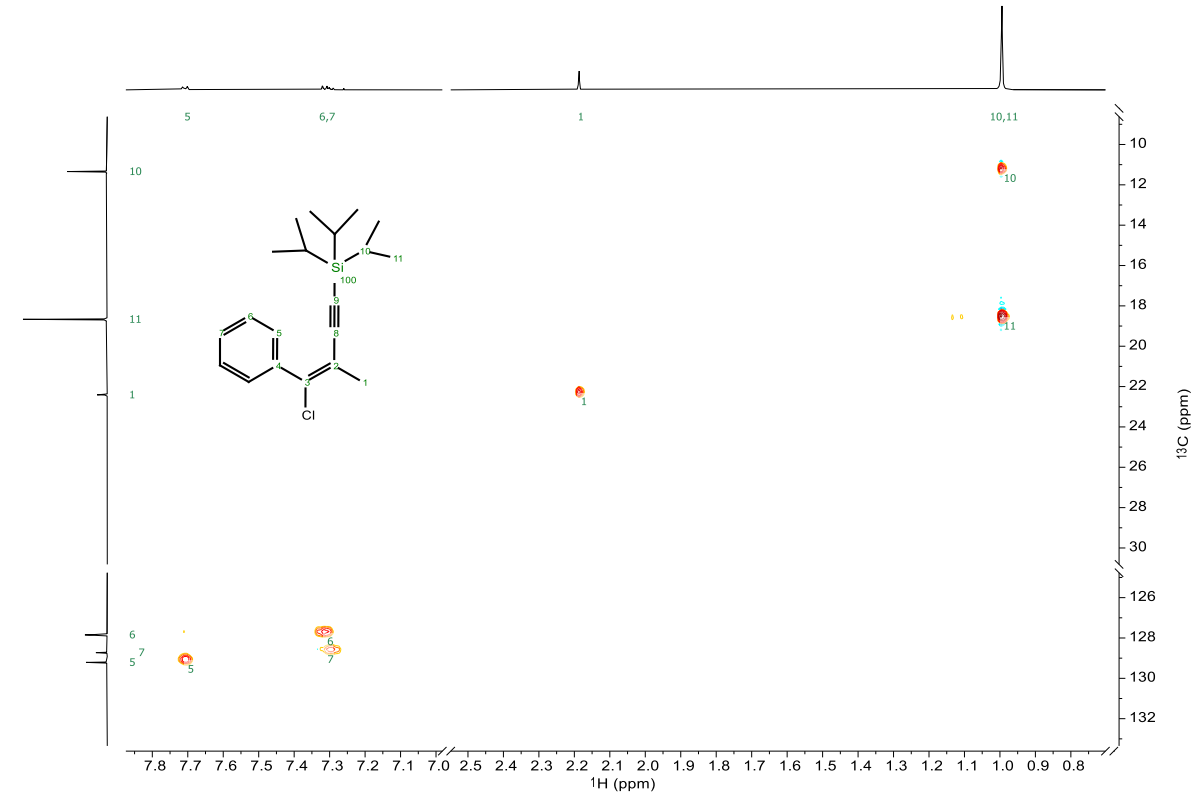
Atom	δ (ppm)	COSY	HSQC	HMBC	NOESY
1 C	22.410		1		
H3	2.187		1	2, 3, 8	11
2 C	117.053			1	
3 C	139.336			1, 5	
4 C	138.372			6	
5 C	129.210		5	5	
H	7.706	6	5	3, 5	6, 11
6 C	127.845		6	6	
H	7.313	5	6	4, 6	5, 11
7 C	128.726		7	7	
H	7.313		7	7	
8 C	106.447			1	
9 C	95.997			10	
10 C	11.341		10	10	
H	0.995		10	9, 10, 11, 100	
11 C	18.666		11	10, 11	
H3	0.995		11	11, 100	1, 5, 6
100 Si	-2.171			10, 11	



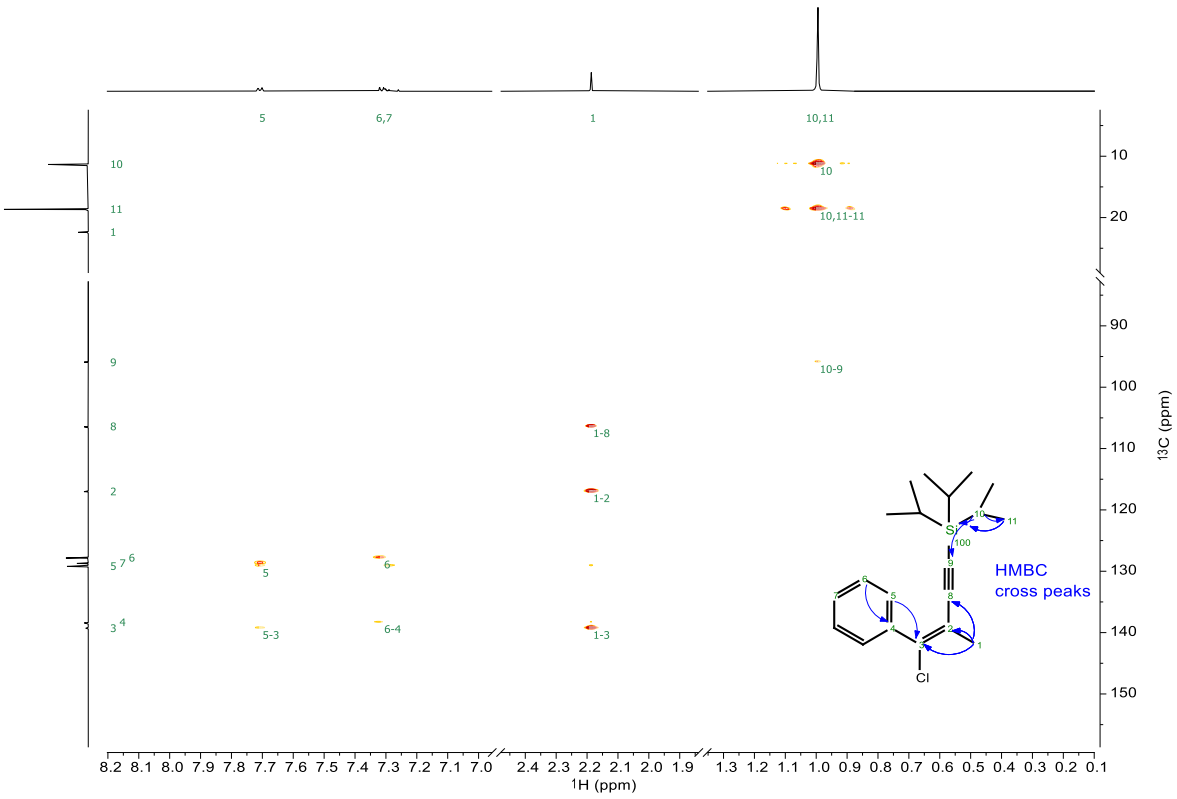
13C,-1D



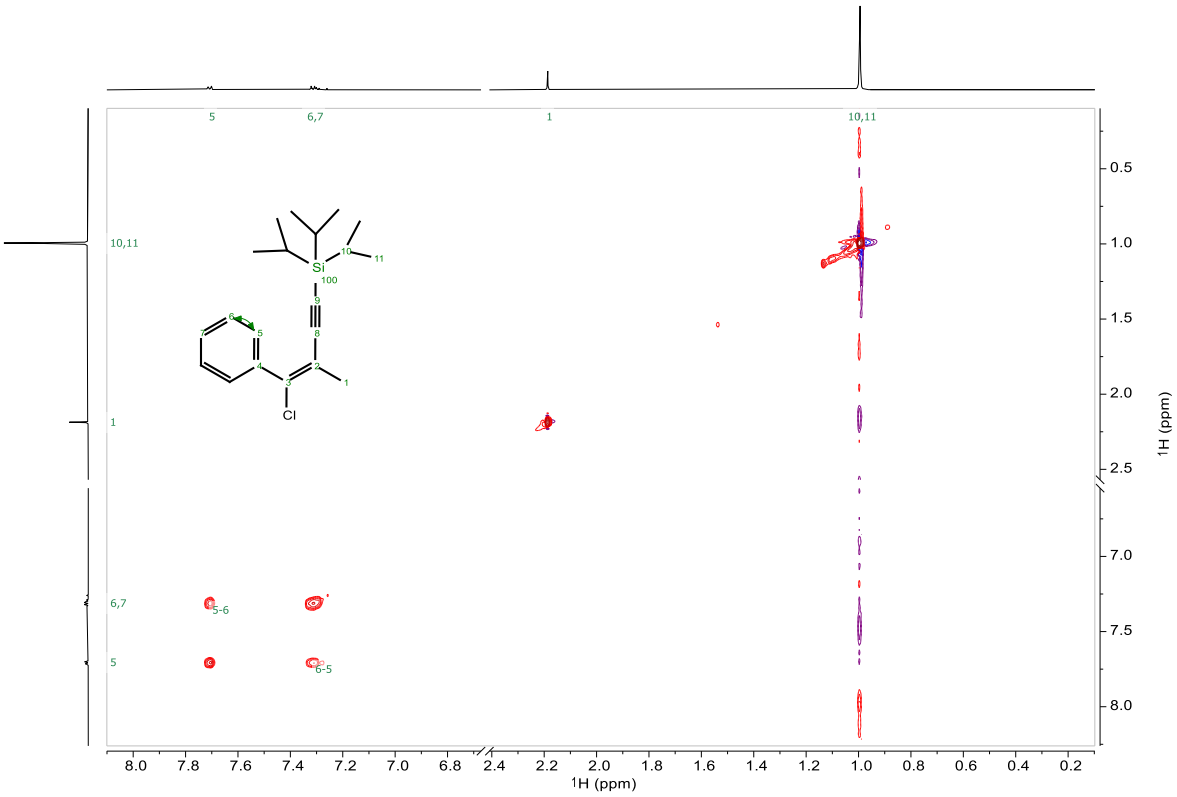
1H,13C-HSQC-EDITED



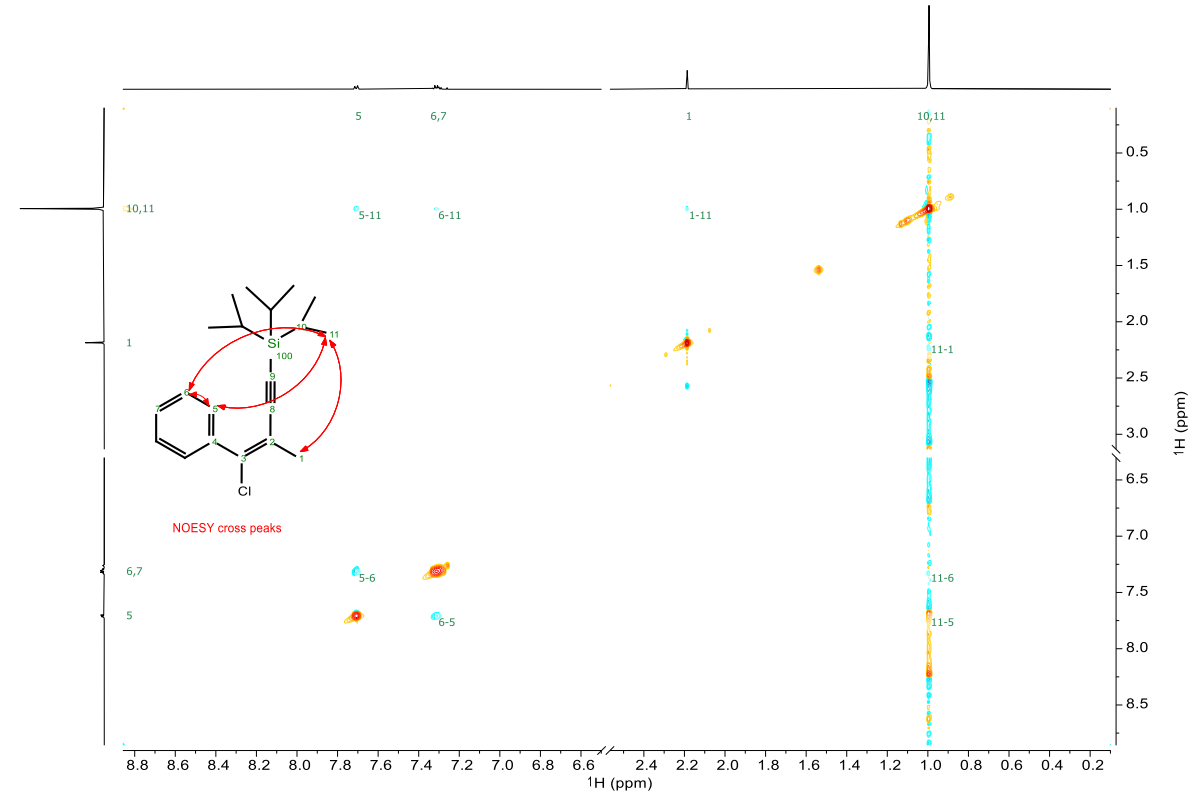
1H,13C-HMBC



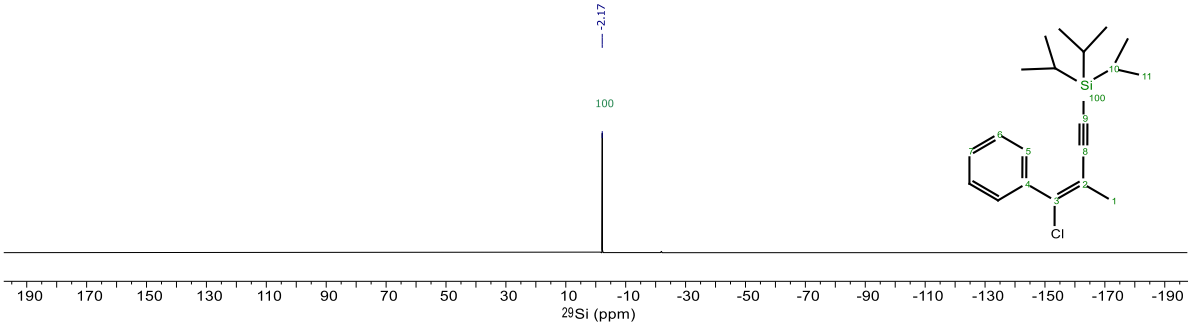
1H,1H-COSY



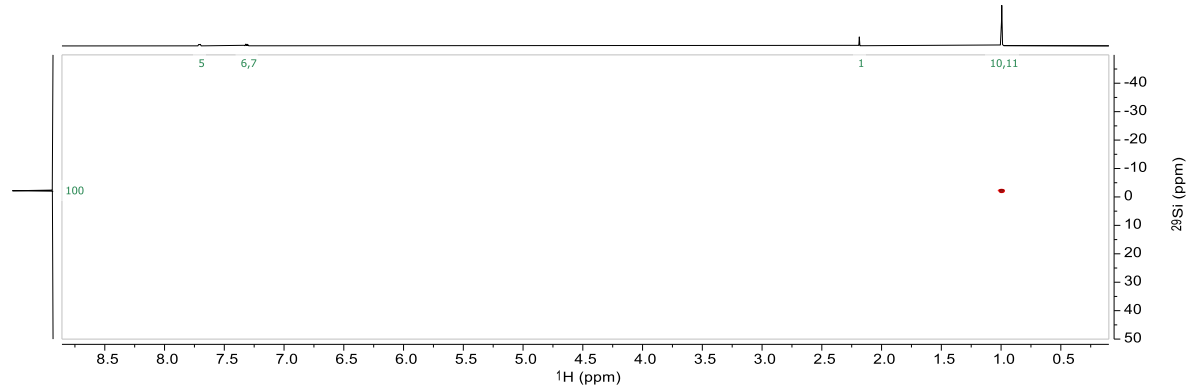
1H,1H-NOESY

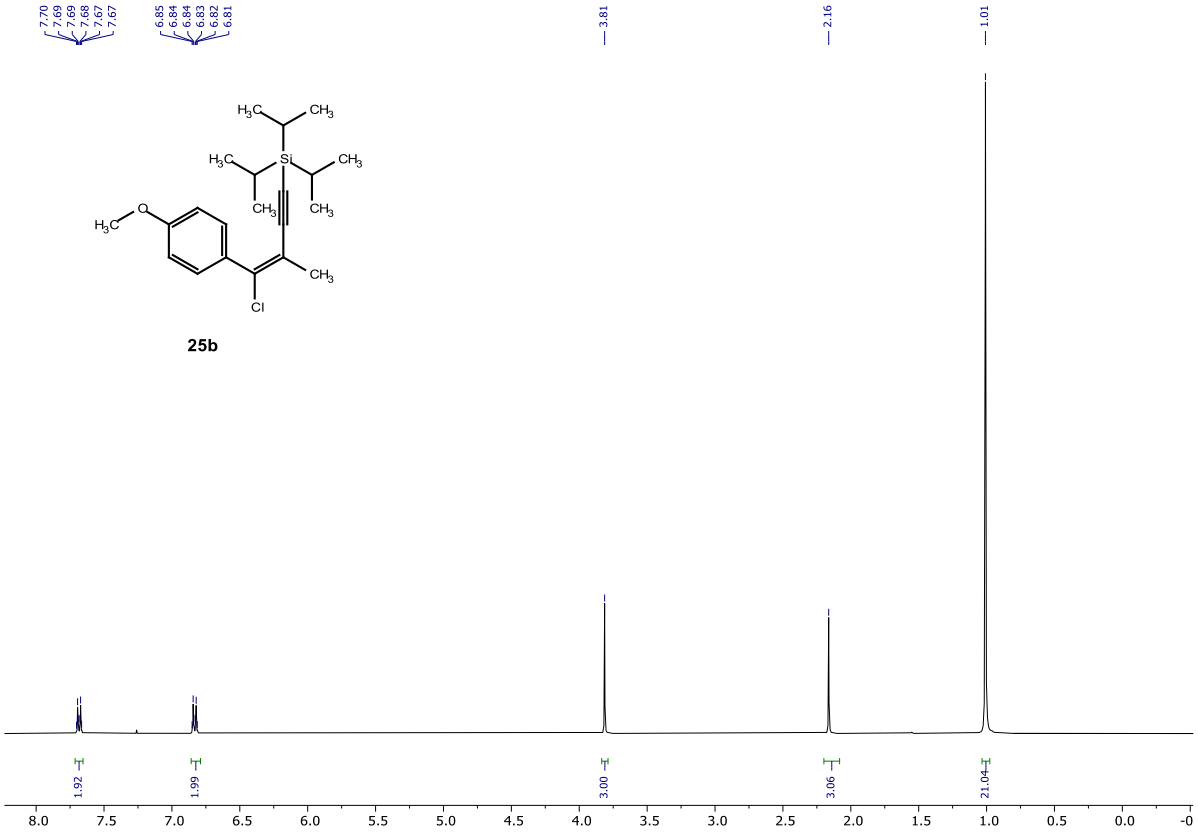


29Si,-1D

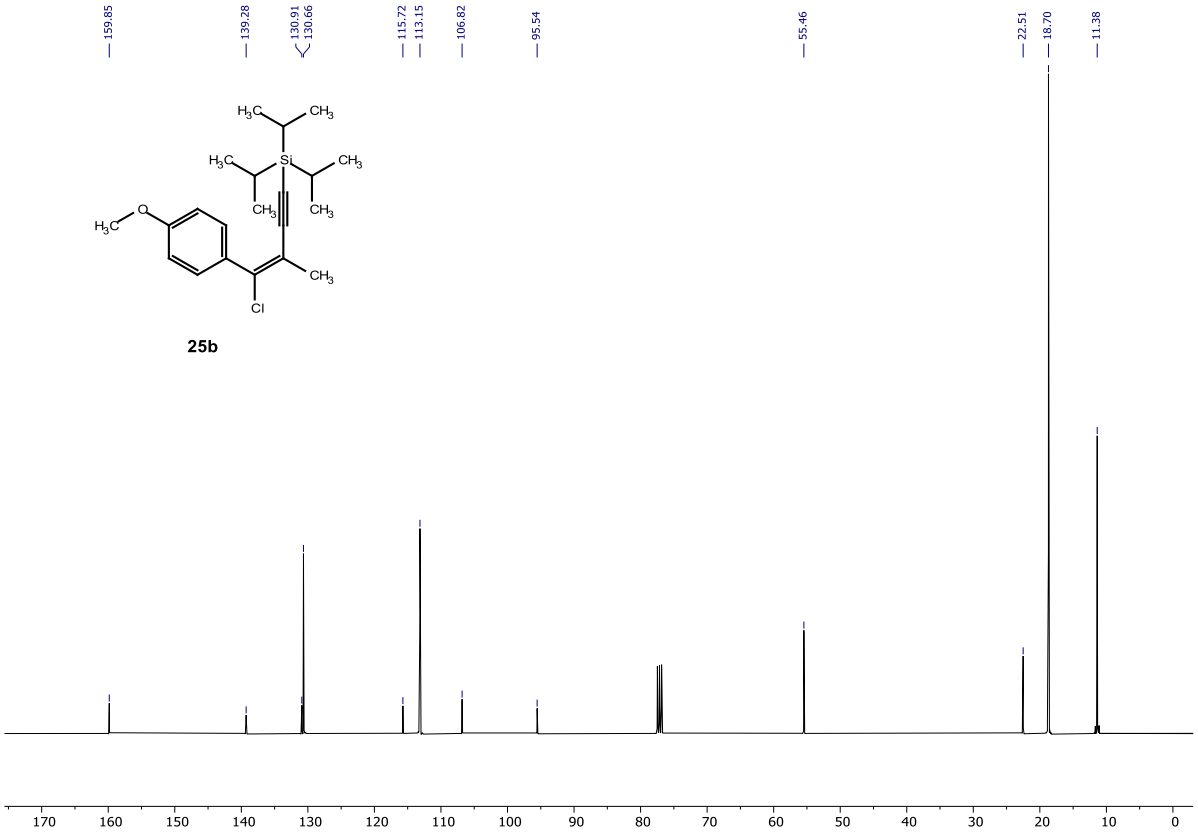


1H,29Si-HMBC



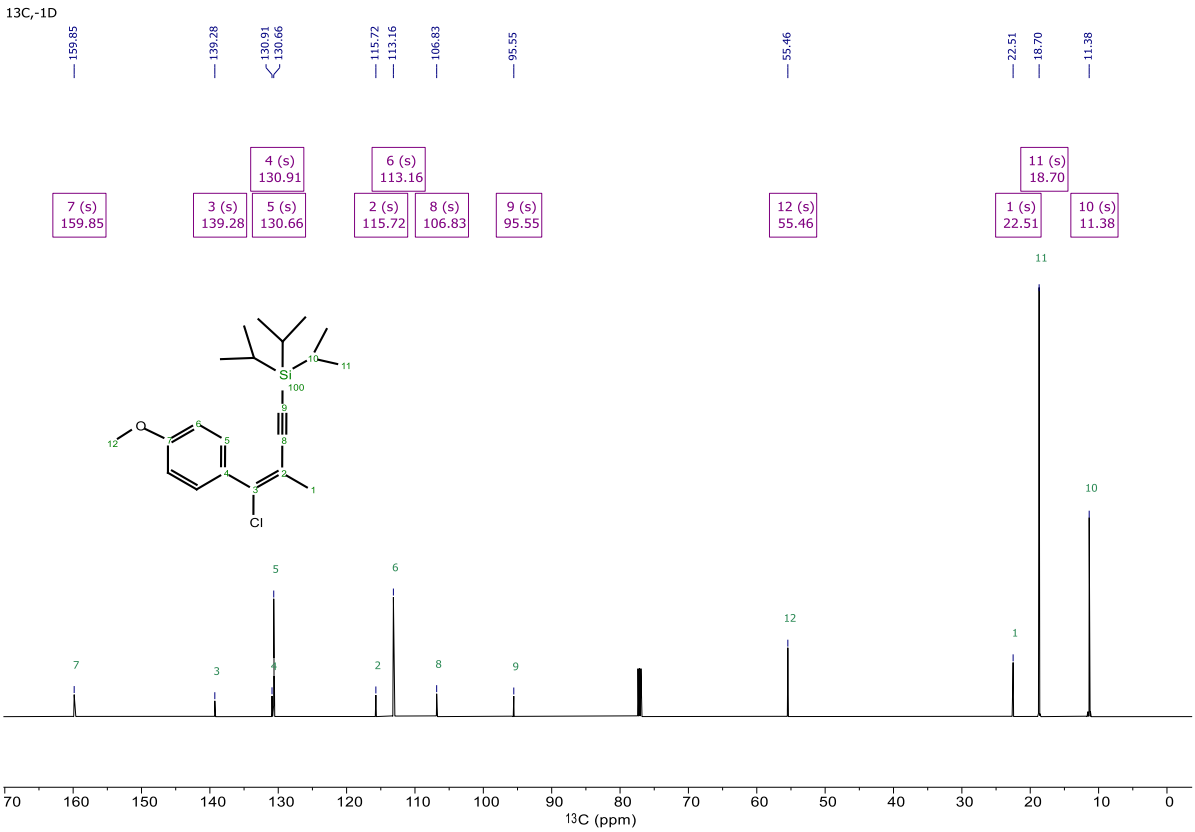

7.70
7.69
7.69
7.68
7.67
7.67
6.85
6.84
6.84
6.83
6.82
6.81
3.81
2.16
1.01
1.92
1.99
3.00
3.06
21.04
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0

25b

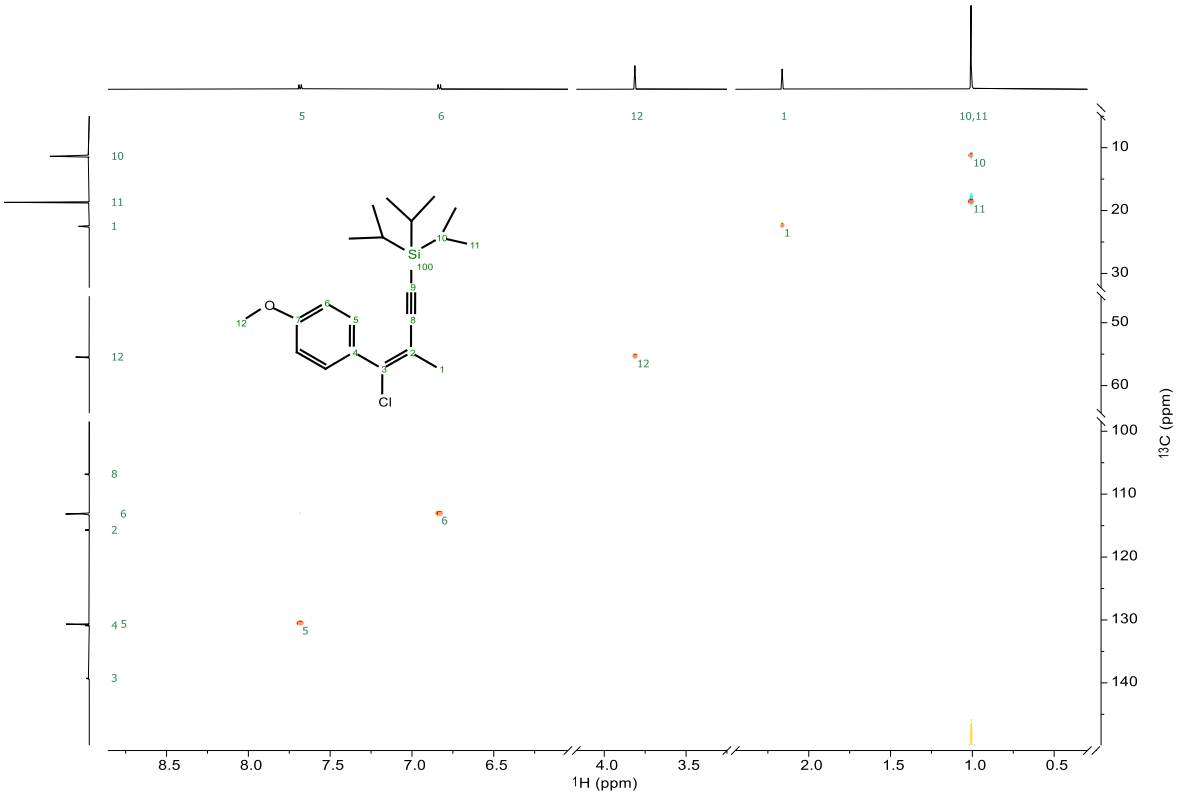

159.85
139.28
130.91
130.66
115.72
113.15
106.82
95.54
55.46
22.51
18.70
11.38
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

25b

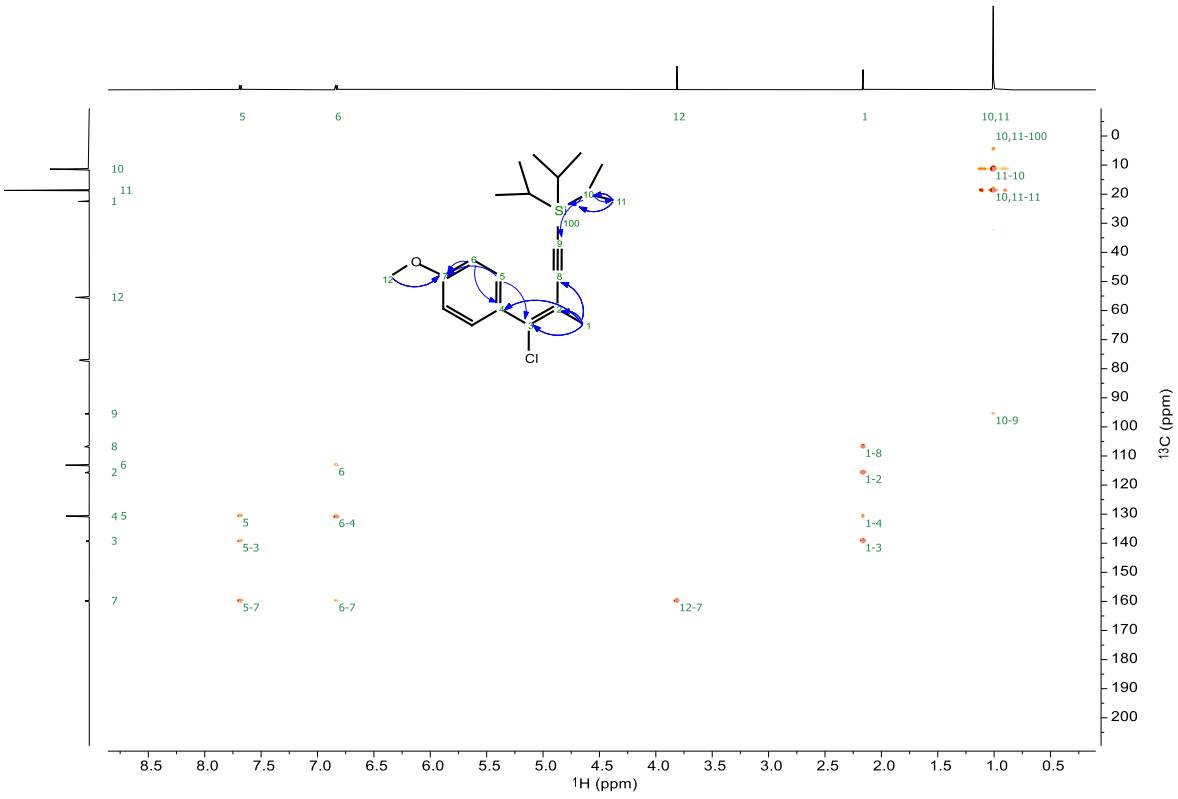
For pure compound NMR analysis



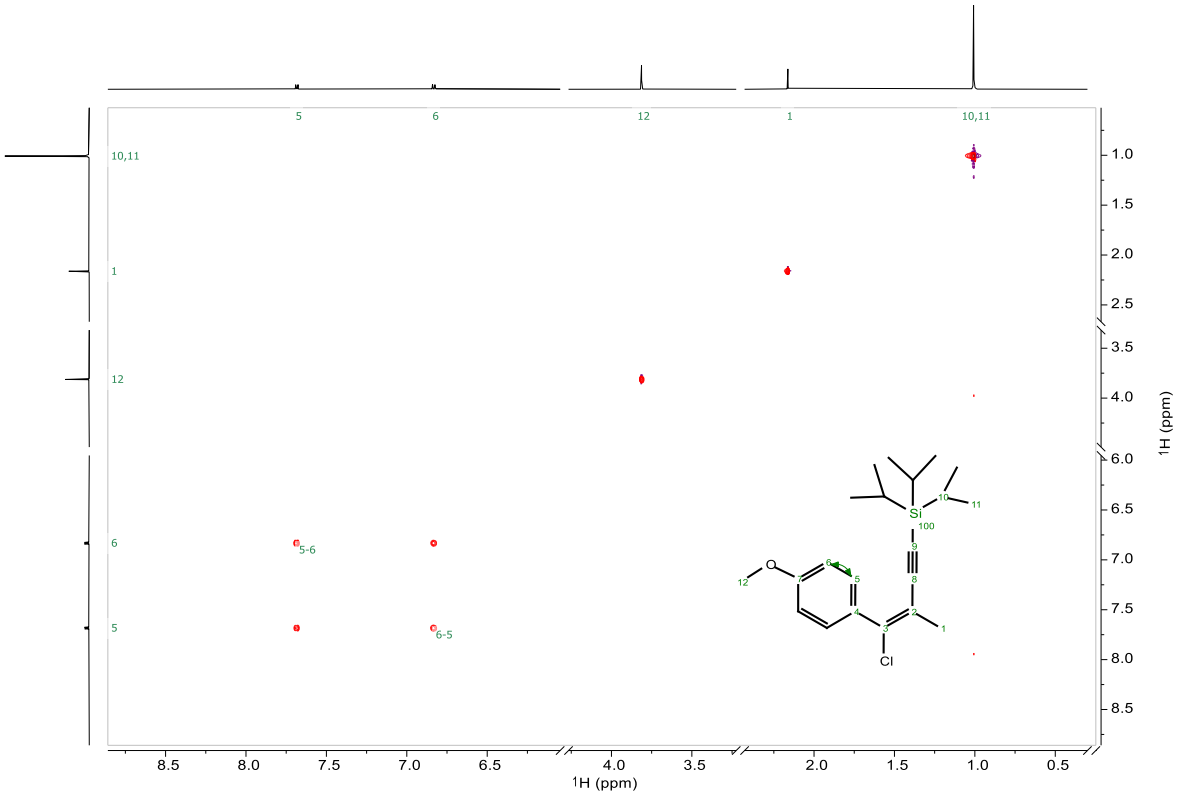
1H,13C-HSQC-EDITED



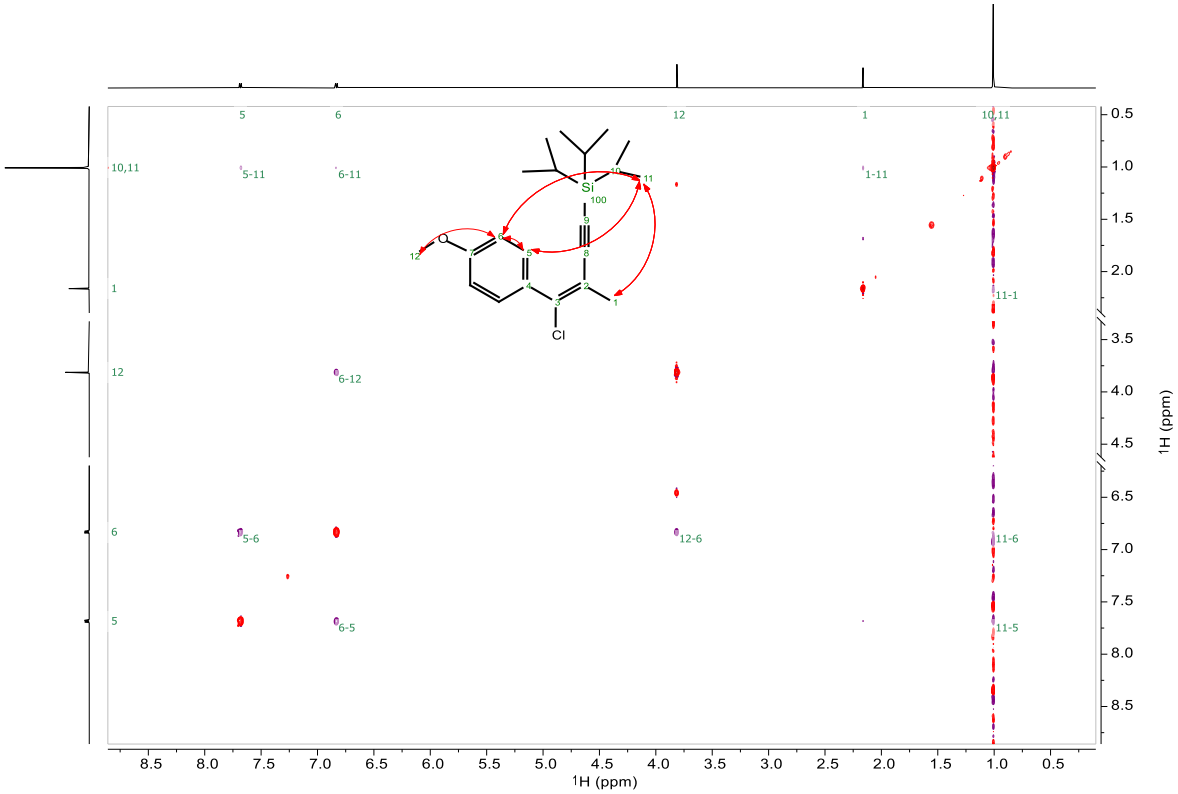
1H,13C-HMBC



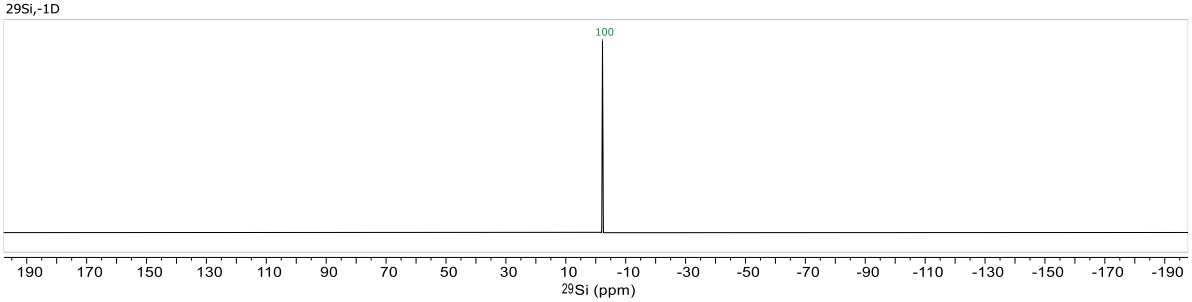
1H,1H-COSY



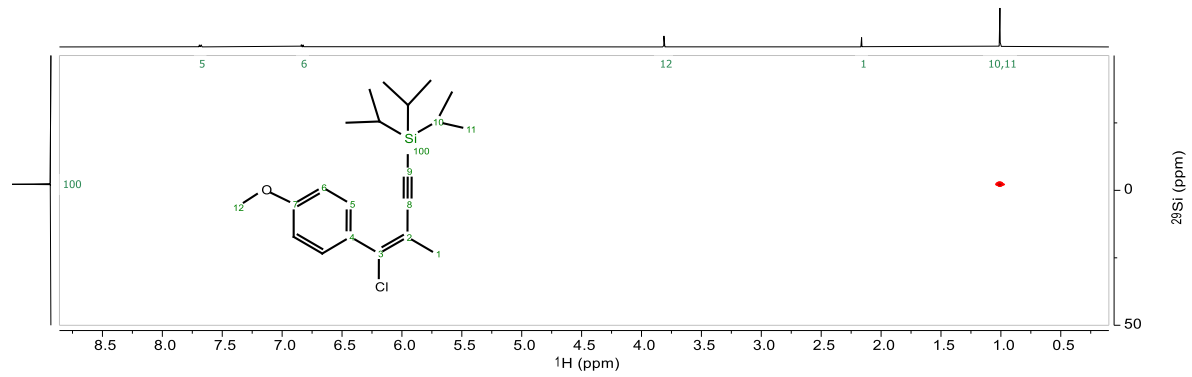
1H,1H-NOESY



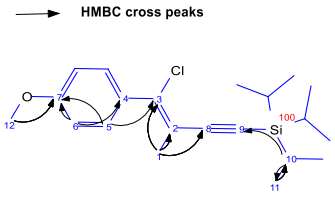
29Si,-1D



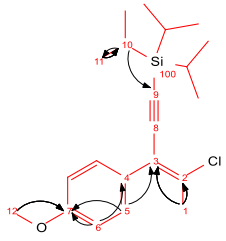
1H,29Si-HMBC



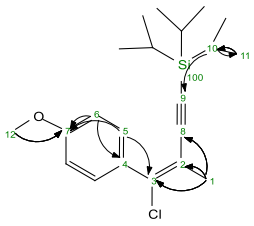
All possible isomers in the reaction and their NMR analysis



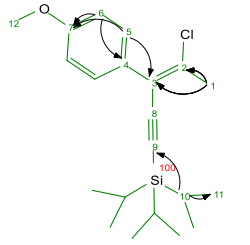
Atom	δ (ppm)	COSY	HSQC	HMBC	NOESY
1 C	21.189		1		
H3	1.943		1	2, 3, 8	5, 11
2 C	117.021			1	
3 C	135.954			1, 5	
4 C	130.122			6	
5 C	130.524		5	5	
H	7.311	6	5	3, 5, 7	1
6 C	113.654		6	6	
H	6.889	5	6	4, 6, 7	
7 C	159.861			5, 6, 12	
8 C	106.593			1	
9 C	97.560			10	
10 C	11.455		10	11	
H	1.131		10	9, 11	
11 C	18.820		11	10, 11	
H3	1.131		11	10, 11	1
12 C	55.470		12		
H3	3.825		12	7	
100 Si					



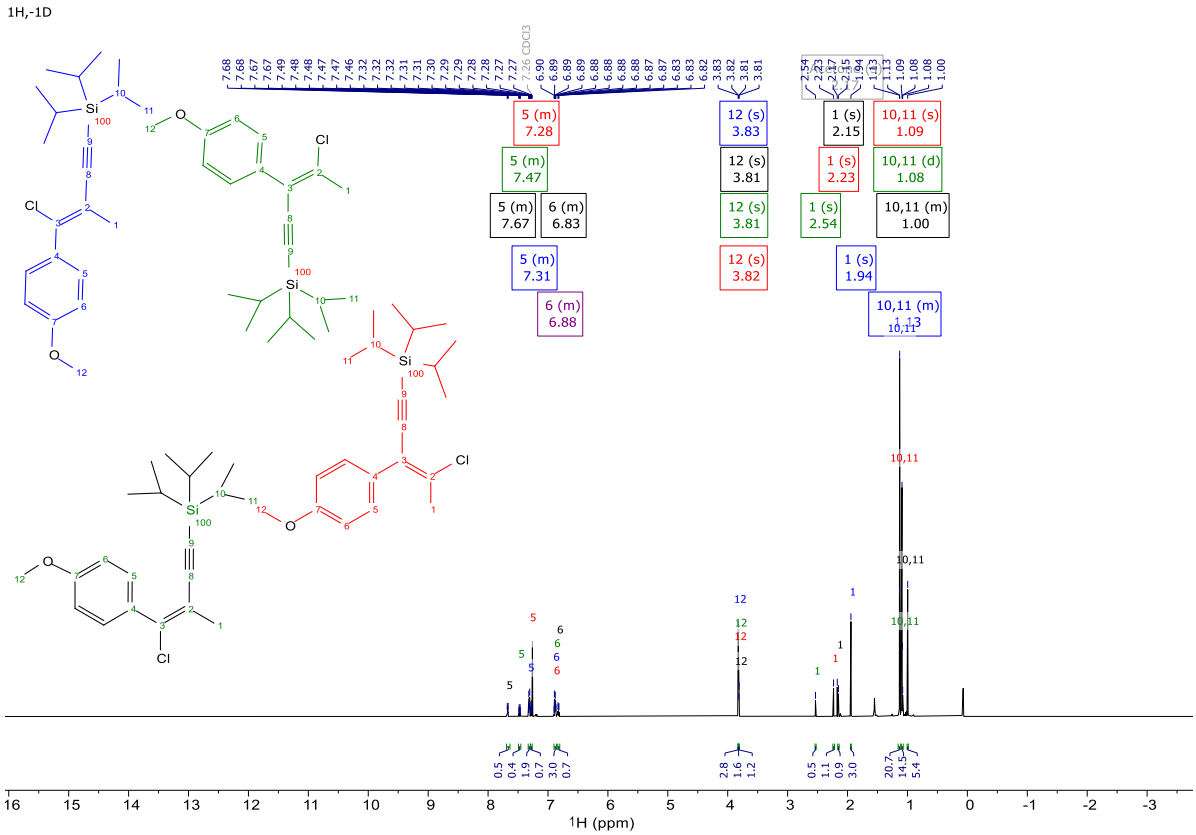
Atom	δ (ppm)	COSY	HSQC	HMBC	NOESY
1 C	24.105		1		
H3	2.234		1	2, 3	5
2 C	137.784			1	
3 C	122.056			1, 5	
4 C	129.811			6	
5 C	130.291		5	5	
H	7.280	6	5	3, 5, 7	1, 11
6 C	113.728		6	6	
H	6.880	5	6	4, 6, 7	
7 C	159.155			5, 6, 12	
8 C	105.450				
9 C	96.806			10	
10 C	11.455		10	11	
H	1.091		10	9, 11	
11 C	18.820		11	10, 11	
H3	1.091		11	10, 11	5
12 C	55.411		12		
H3	3.821		12	7	
100 Si					

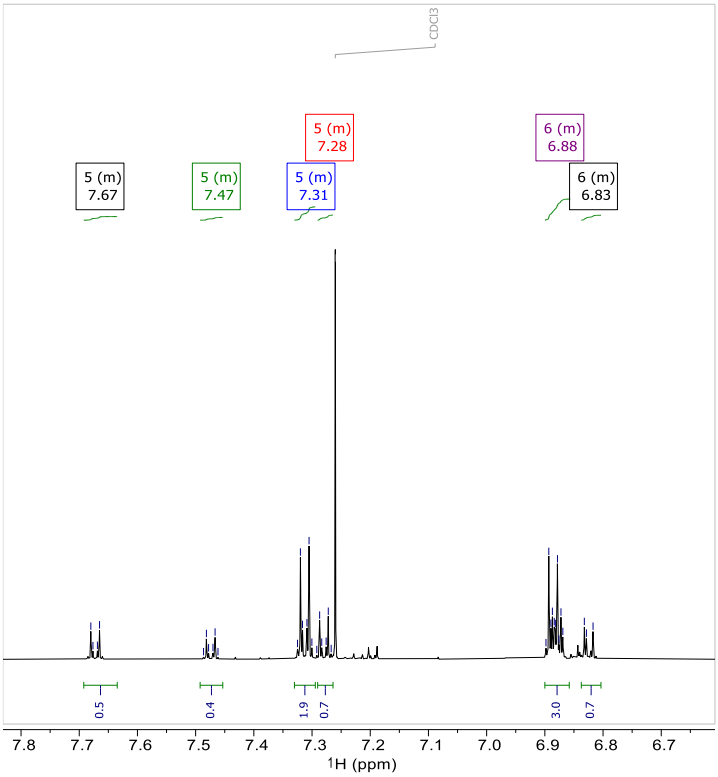


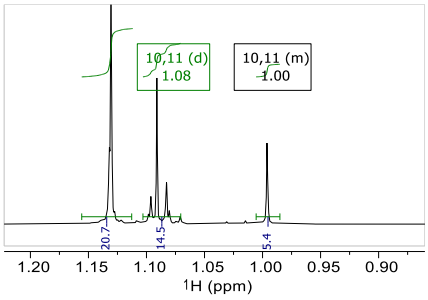
Atom	δ (ppm)	COSY	HSQC	HMBC	NOESY
1 C	22.513		1		
H3	2.152		1	2, 3, 8	11
2 C	115.741			1	
3 C	139.258			1, 5	
4 C	130.920			6	
5 C	130.663		5	5	
H	7.671	6	5	3, 5, 7	11
6 C	113.163		6	6	
H	6.828	5	6	4, 6, 7	11
7 C	159.842			5, 6, 12	
8 C	106.813			1	
9 C	95.562			10	
10 C	11.373		10	11	
H	0.996		10	9, 11	
11 C	18.701		11	10, 11	
H3	0.996		11	10, 11	1, 5, 6
12 C	55.486		12		
H3	3.811		12	7	
100 Si	-2.256				

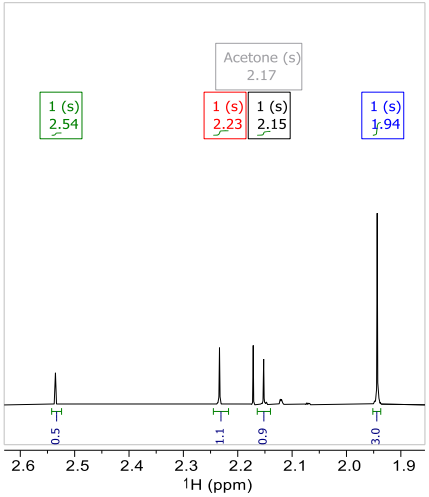


Atom	δ (ppm)	COSY	HSQC	HMBC	NOESY
1 C	26.377		1		
H3	2.535		1	2, 3	11
2 C	138.386			1	
3 C	120.696			1, 5	
4 C	129.606			6	
5 C	130.510		5		
H	7.474	6	5	3, 7	11
6 C	113.335		6	6	
H	6.874	5	6	4, 6, 7	
7 C	159.065			5, 6	
8 C	105.340				
9 C	96.673			10	
10 C	11.434		10		
H	1.082		10	9, 11	
11 C	18.795		11	10	
H3	1.082		11		1, 5
12 C	55.360		12		
H3	3.813		12		
100 Si					

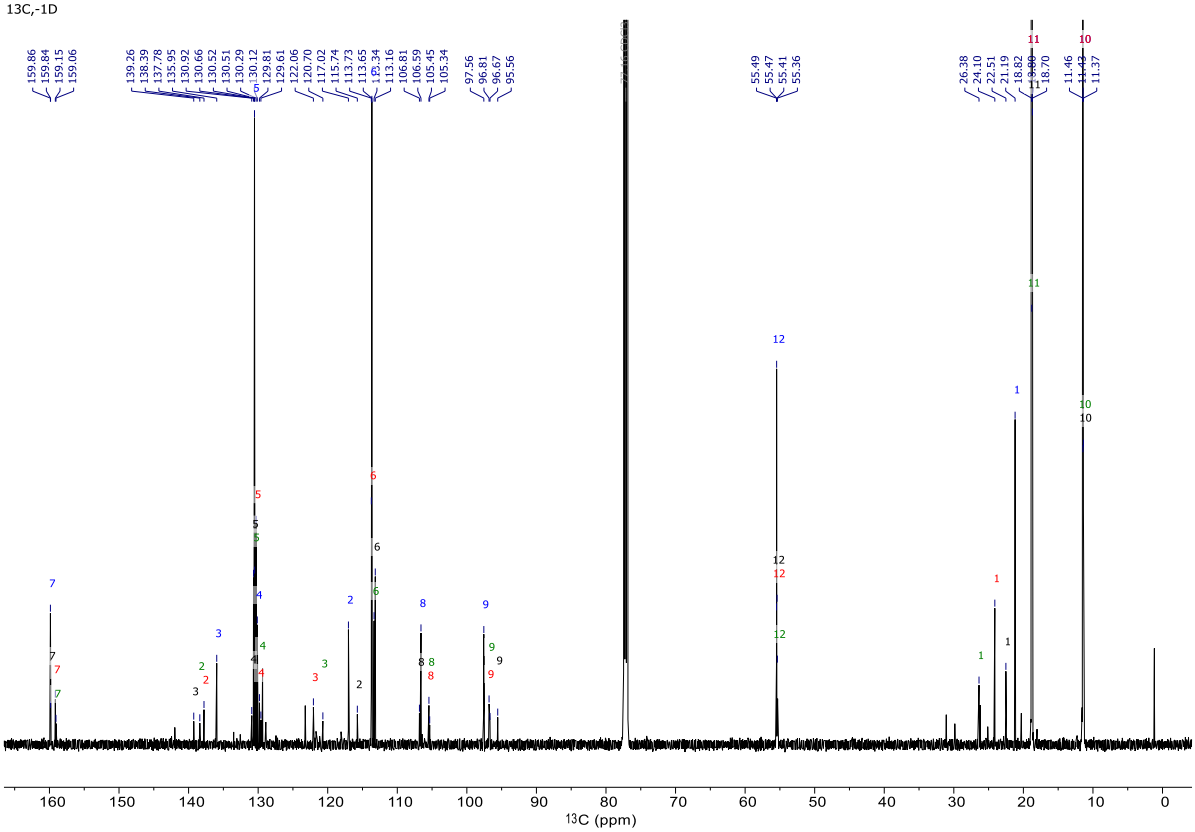

1H,-1D
CDCl3
5 (m) 7.28
5 (m) 7.47
5 (m) 7.67
6 (m) 6.83
5 (m) 7.31
6 (m) 6.88
12 (s) 3.83
12 (s) 3.81
12 (s) 3.81
12 (s) 3.82
1 (s) 2.15
1 (s) 2.23
1 (s) 2.54
1 (s) 1.94
10,11 (s) 1.09
10,11 (d) 1.08
10,11 (m) 1.00
10,11 (m) 1.13
1H (ppm)


CDCl3
5 (m) 7.67
5 (m) 7.47
5 (m) 7.28
5 (m) 7.31
6 (m) 6.88
6 (m) 6.83
1H (ppm)

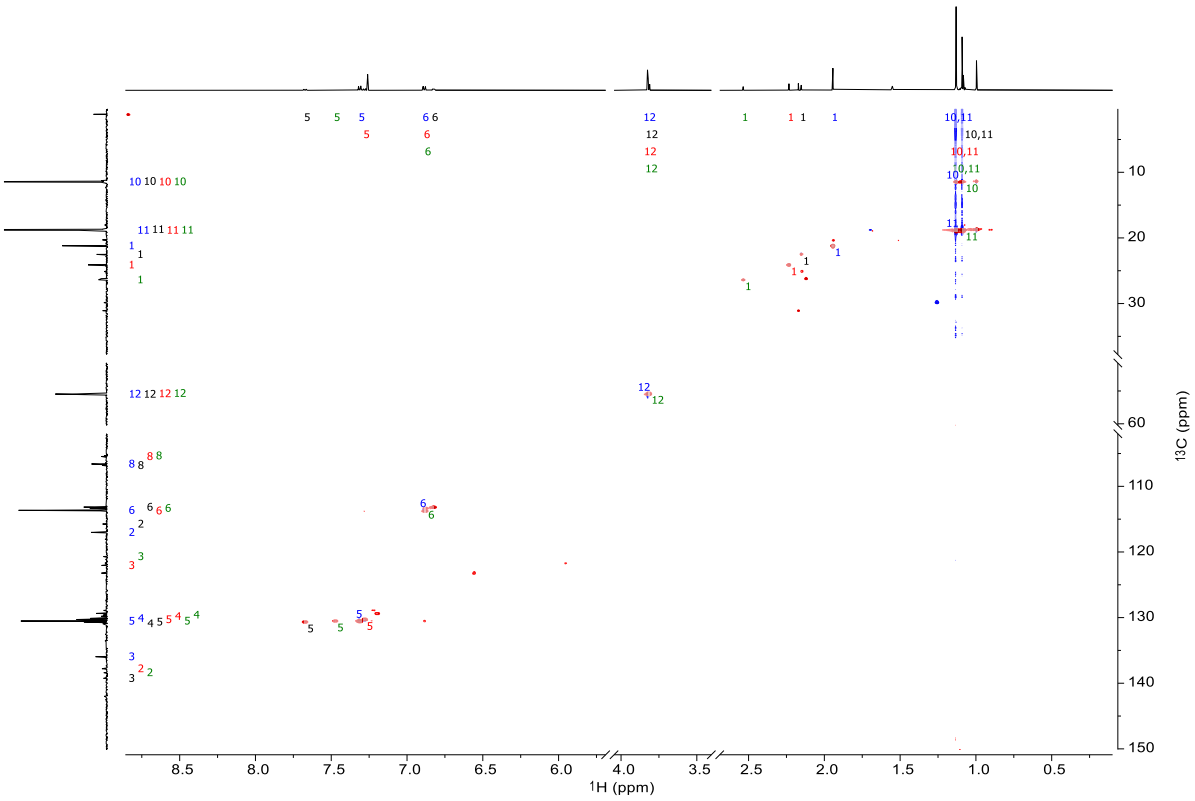

10,11 (d) 1.08
10,11 (m) 1.00
1H (ppm)


Acetone (s) 2.17
1 (s) 2.54
1 (s) 2.23
1 (s) 2.15
1 (s) 1.94
1H (ppm)

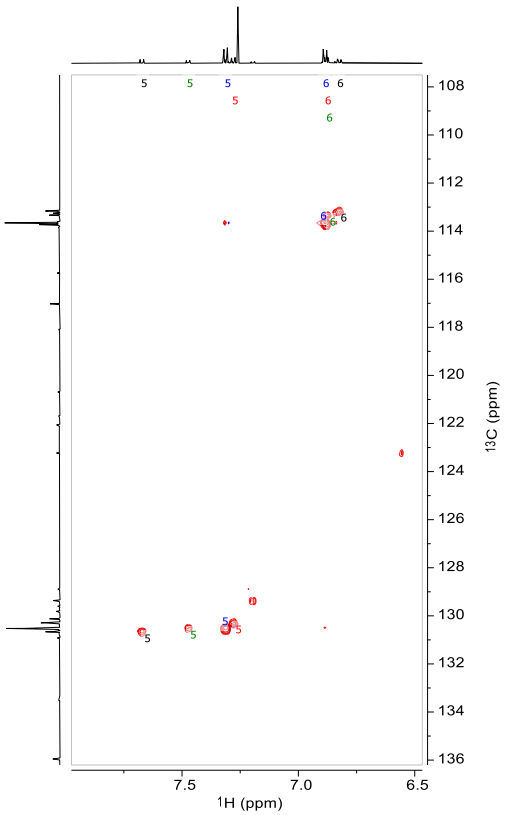
13C,-1D



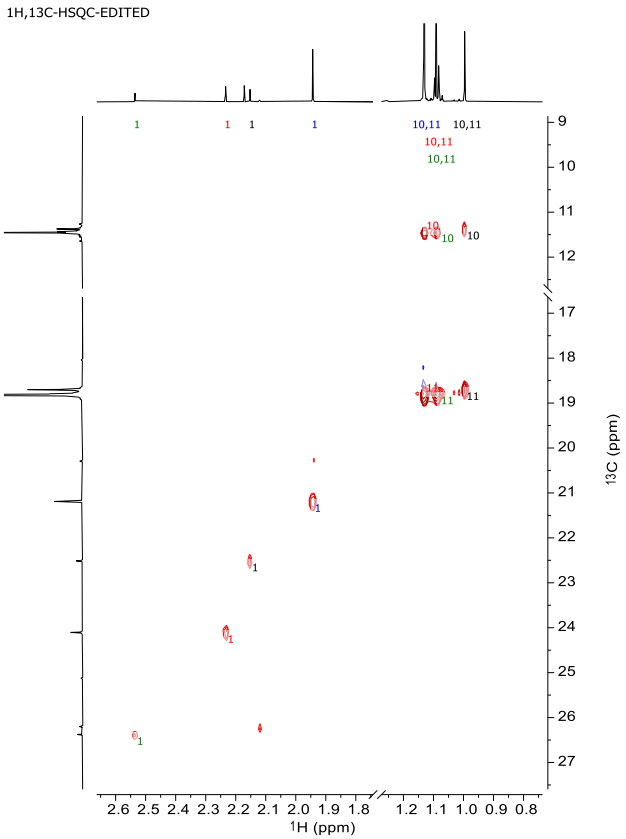
1H,13C-HSQC-EDITED



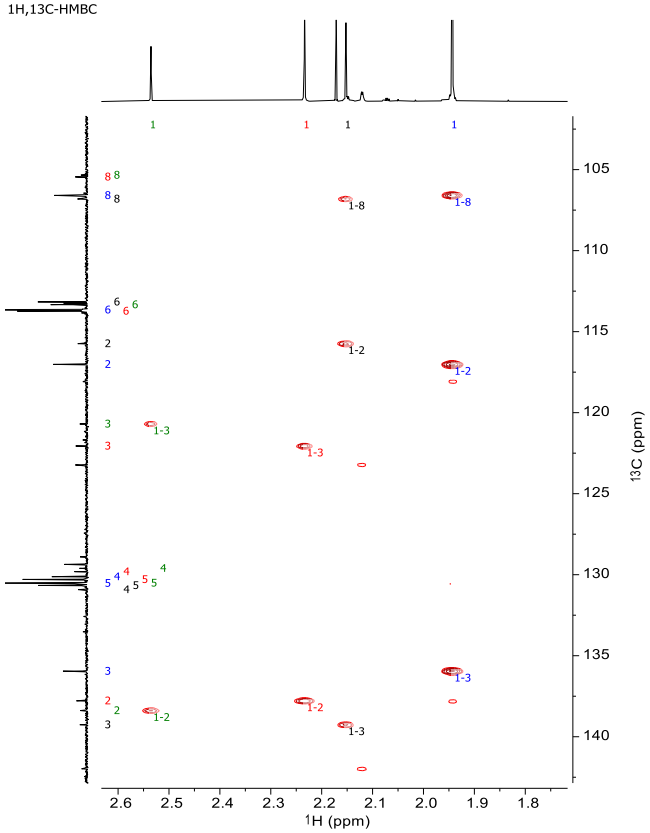
1H,13C-HSQC-EDITED

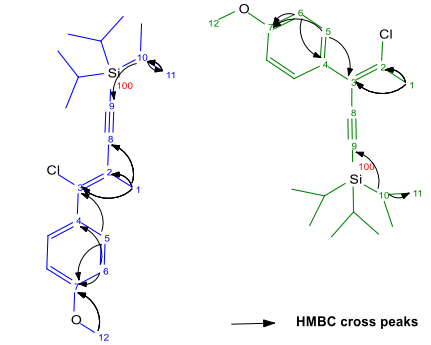


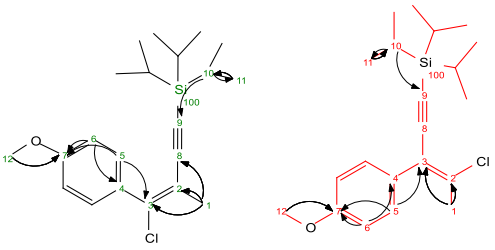
1H,13C-HSQC-EDITED



1H,13C-HMBC

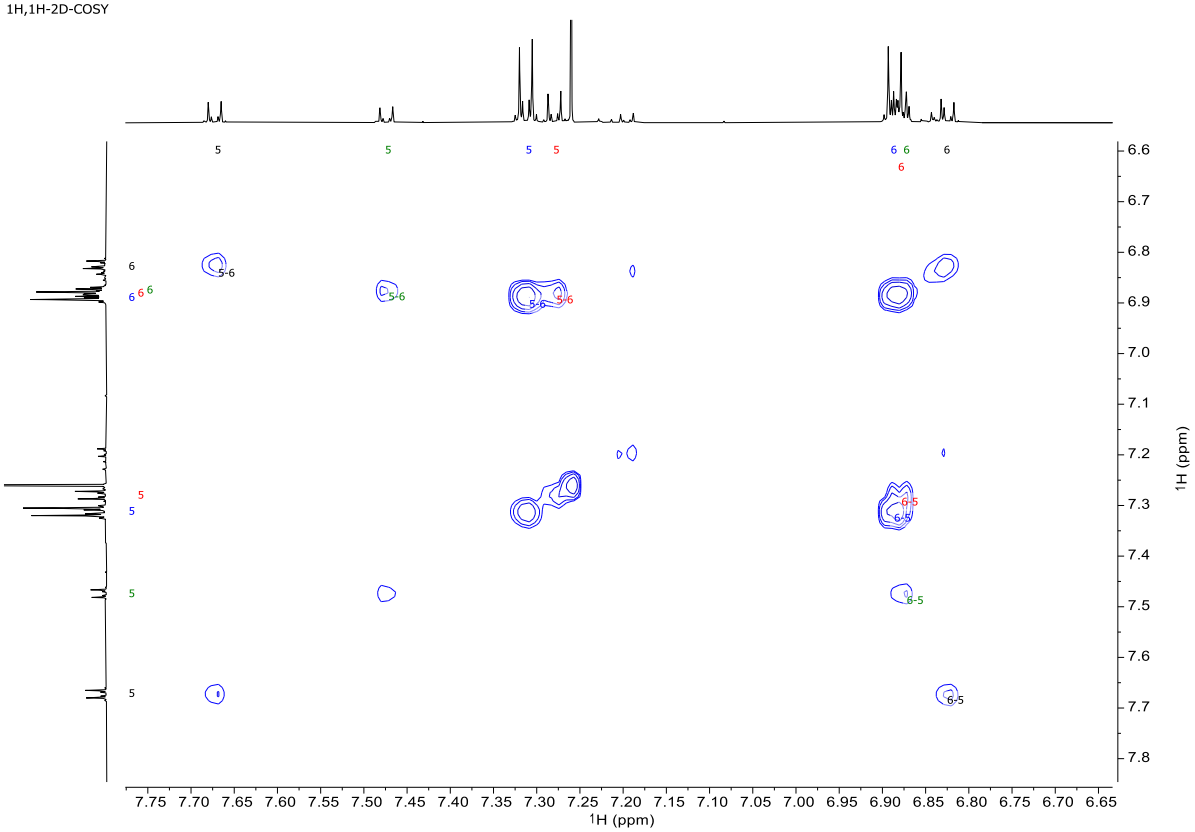




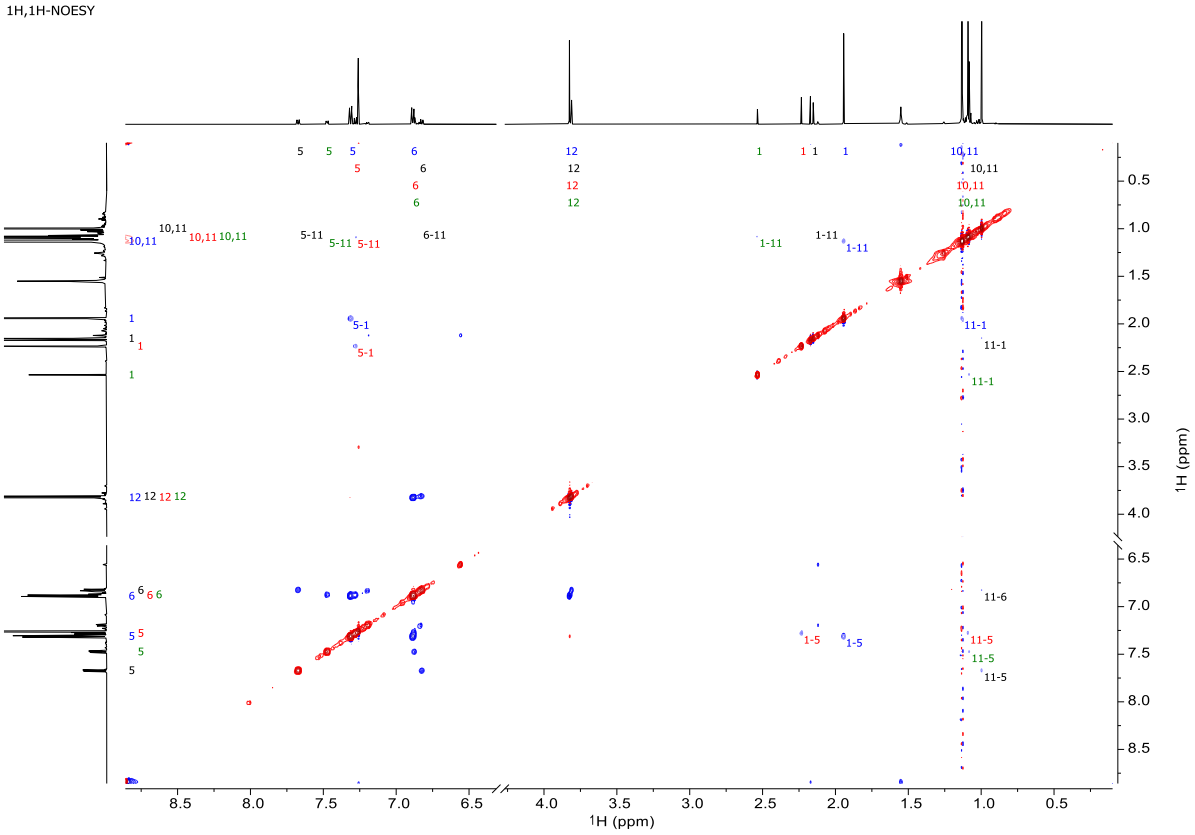


The most relevant HMBC cross peaks are seen between H1 and the carbons 2,3,8. If H1 has 3 strong cross peaks then the alkynyl group is on position 2, otherwise o position 3.

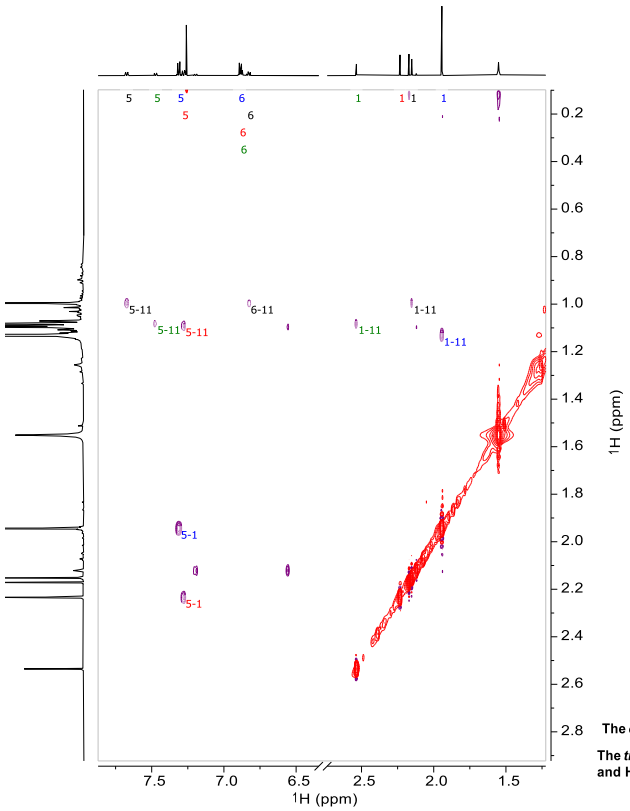
1H,1H-2D-COSY

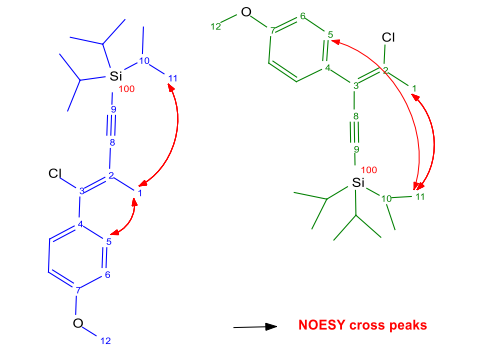


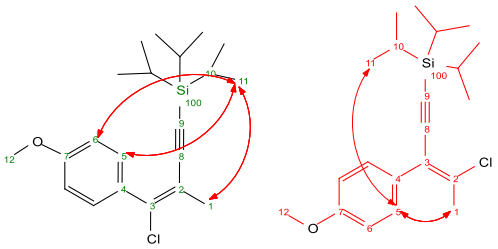
1H,1H-NOESY



1H,1H-NOESY



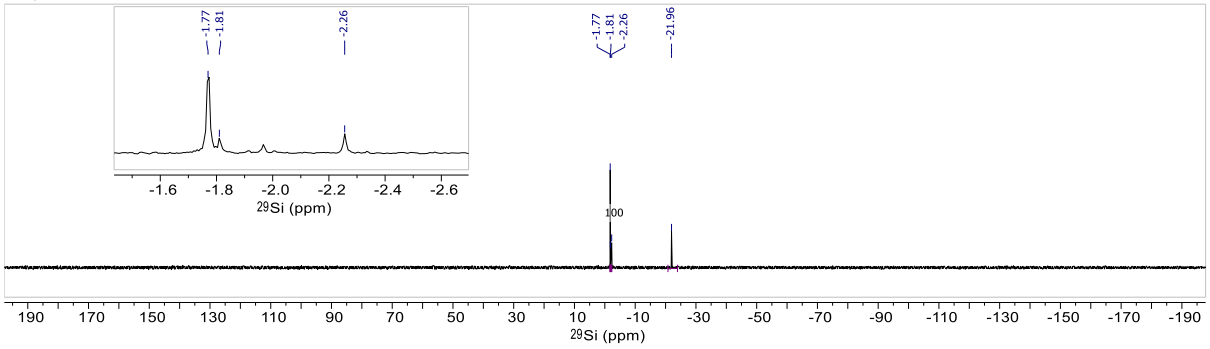




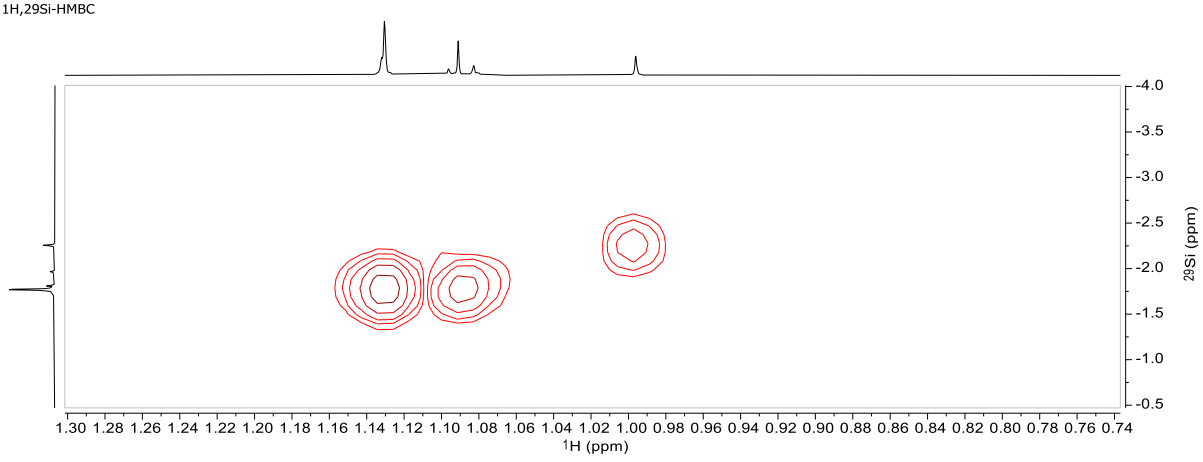
The *cis* addition products can be identified by a cross peaks between H5 and H1.

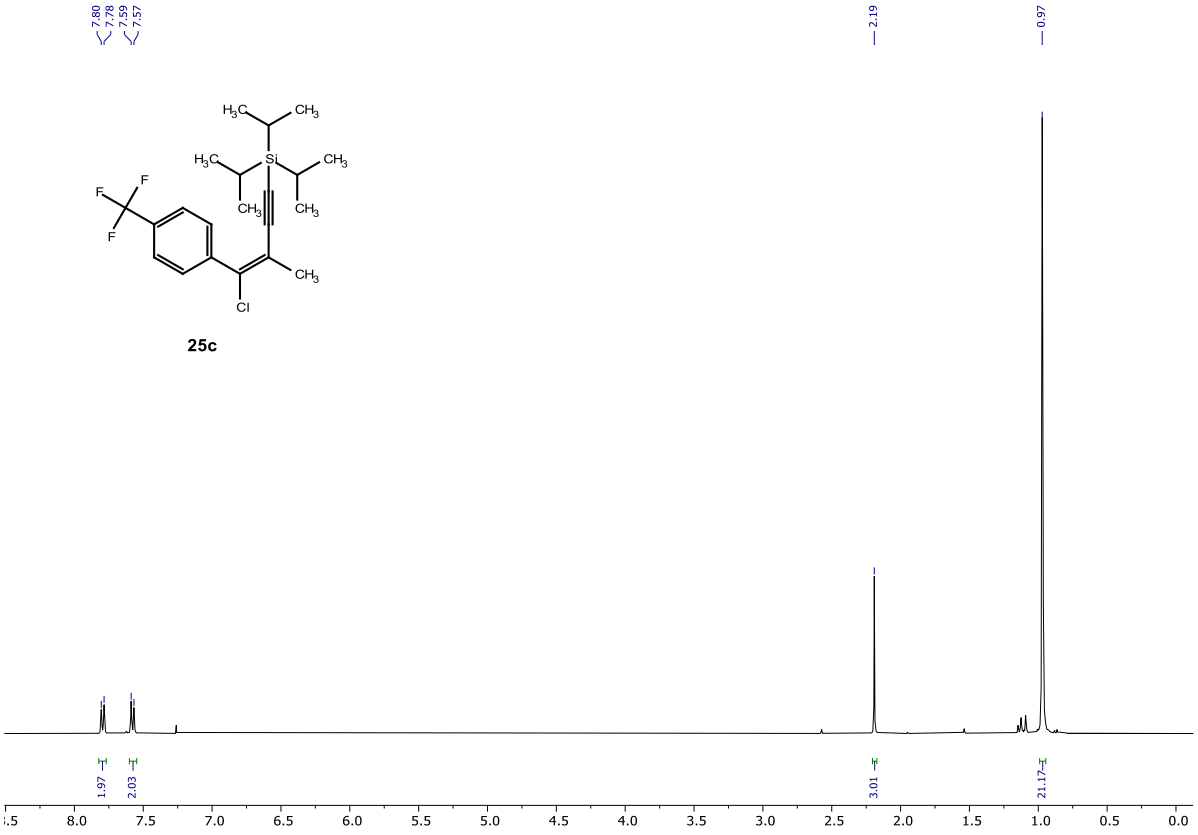
The *trans* addition products can be identified by presence of 2 cross peaks: One between H5 and H11/10 and one between H1 and H11/10

29Si,-1D

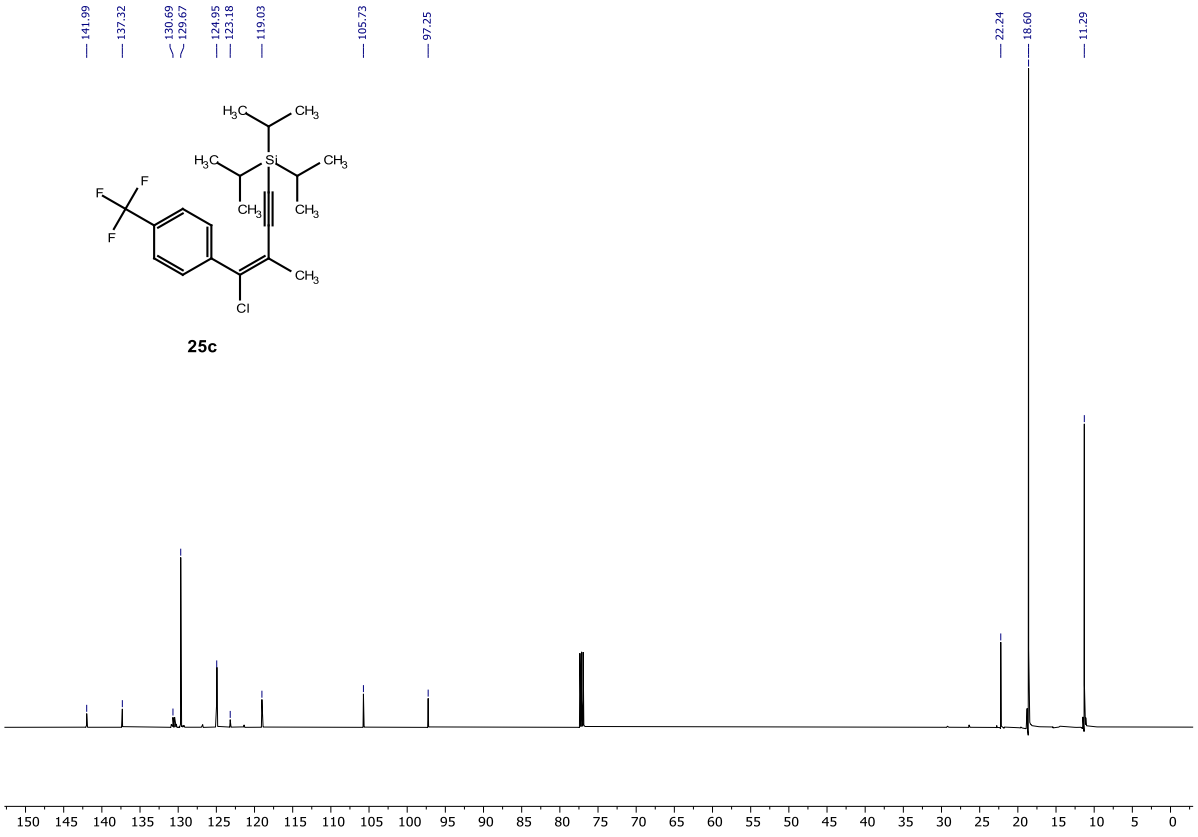


1H,29Si-HMBC

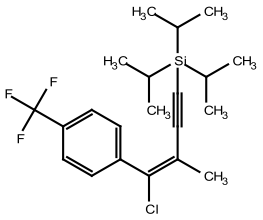



7.80
7.78
7.59
7.57
2.19
0.97
1.97
2.03
3.01
21.17

25c

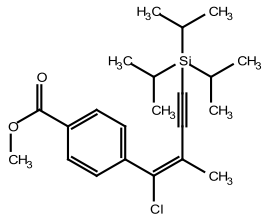

141.99
137.32
130.69
129.67
124.95
123.18
119.03
105.73
97.25
22.24
18.60
11.29

25c



25c

-62.91
50 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230



25d

7.99
7.99
7.99
7.98
7.97
7.97
7.81
7.80
7.78
7.78
3.92
2.19
0.98
2.00
1.98
3.10
2.99
21.09
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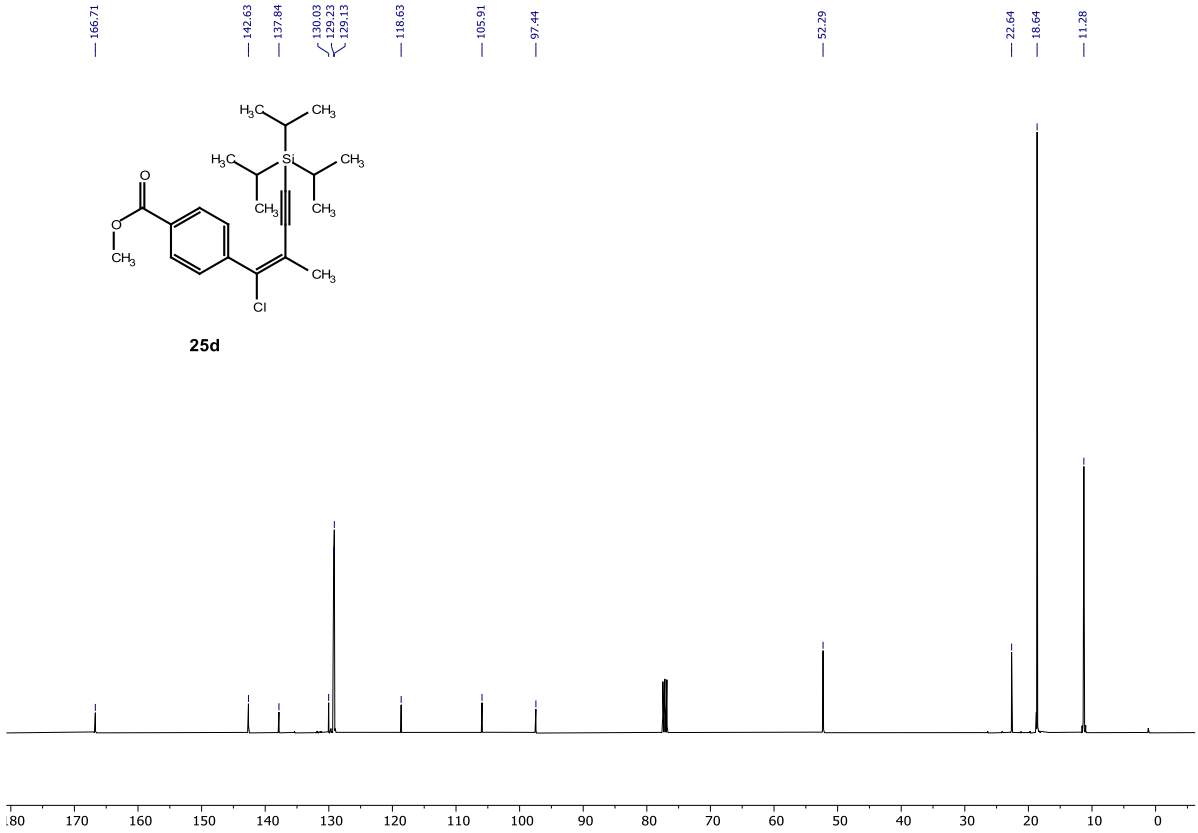
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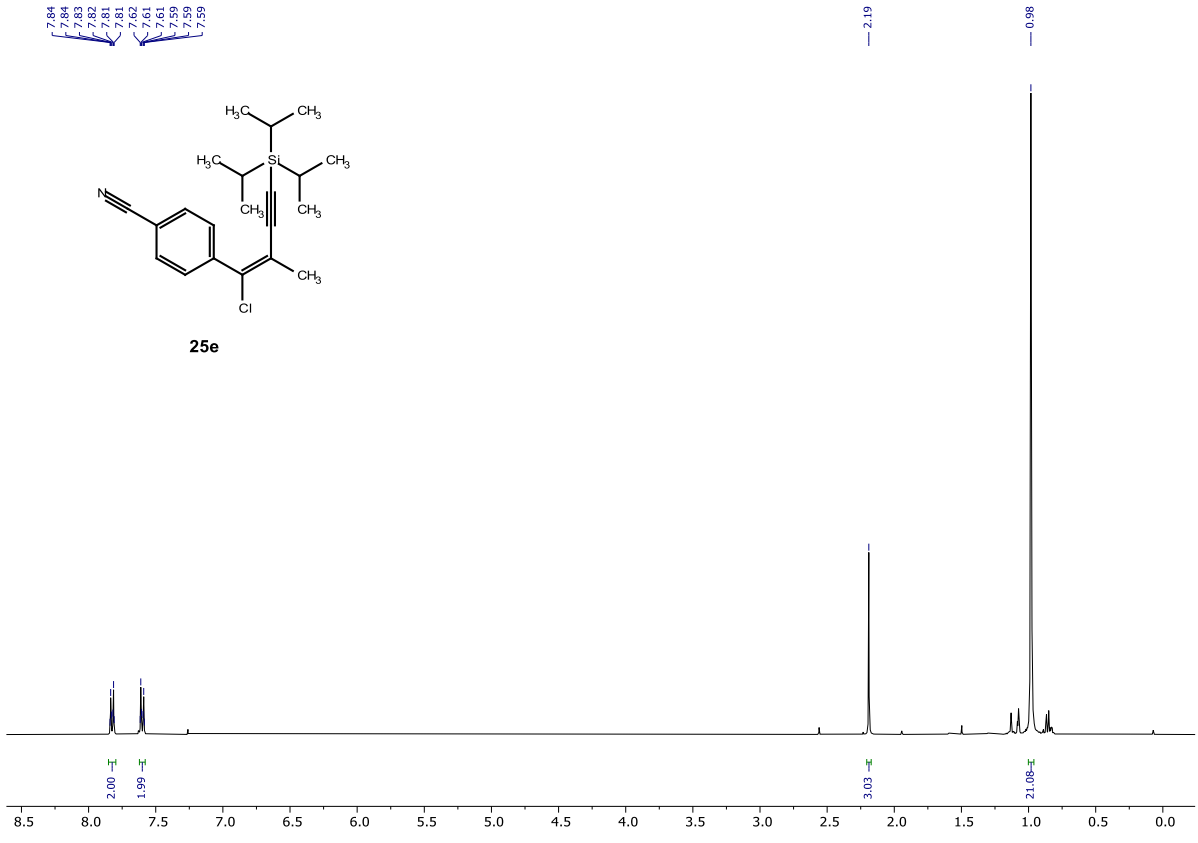
118.63
105.91
97.44
52.29
22.64
18.64
11.28
O
O
CH3
H3C
CH3
Si
CH3
CH3
CH3
CH3
Cl
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

25d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7.62
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7.59
7.59
7.59
2.19
0.98
N
H3C
CH3
Si
CH3
CH3
CH3
CH3
CH3
Cl
2.00
1.99
3.03
21.08
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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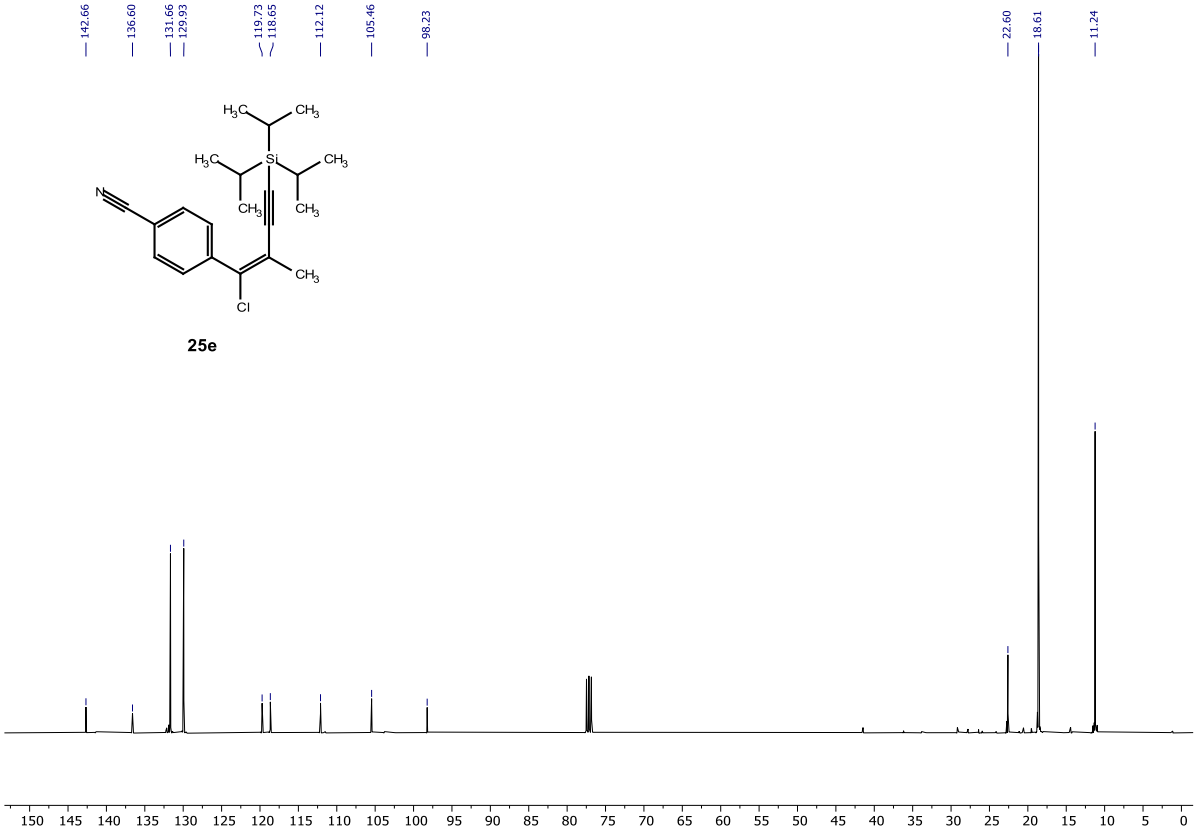
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

25e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136.60
131.66
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118.65
112.12
105.46
98.23
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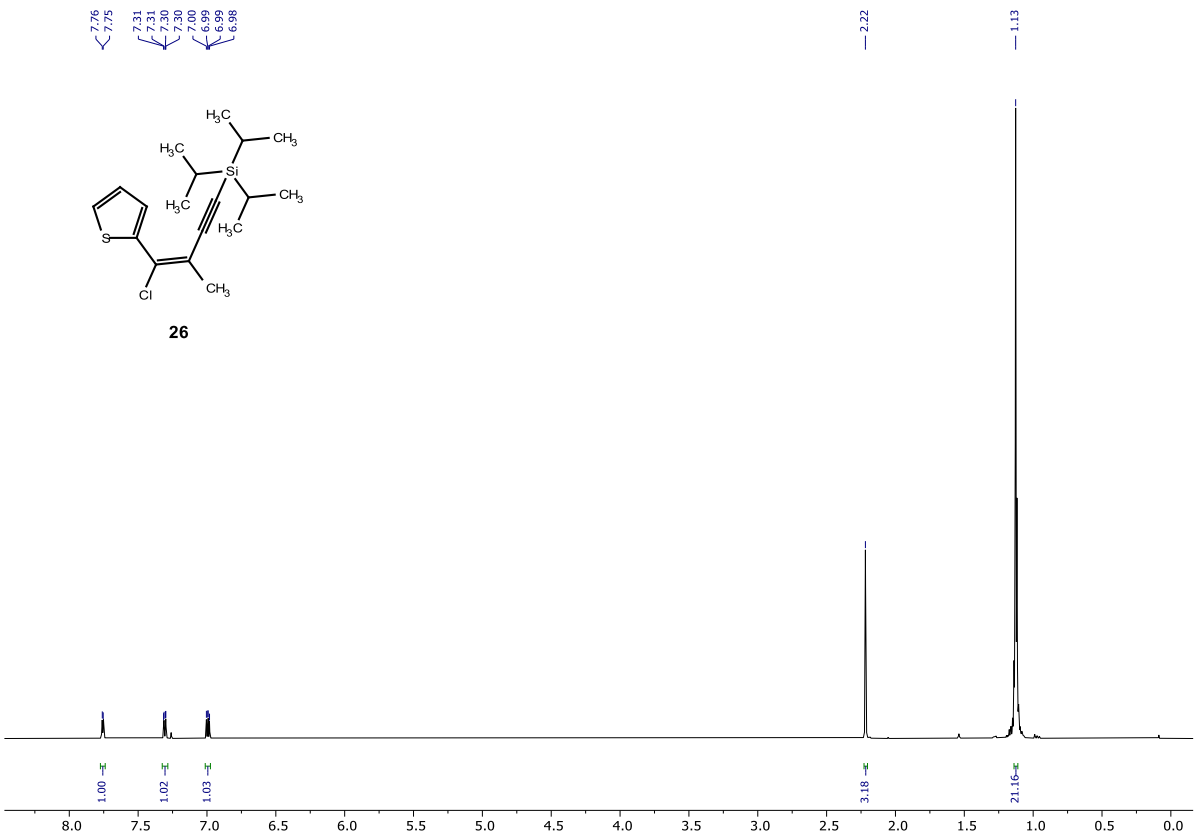
18.61
11.24
N
Cl
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0

25e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7.30
7.00
6.99
6.99
6.98
2.22
1.13
S
Cl
1.00
1.02
1.03
3.18
21.16
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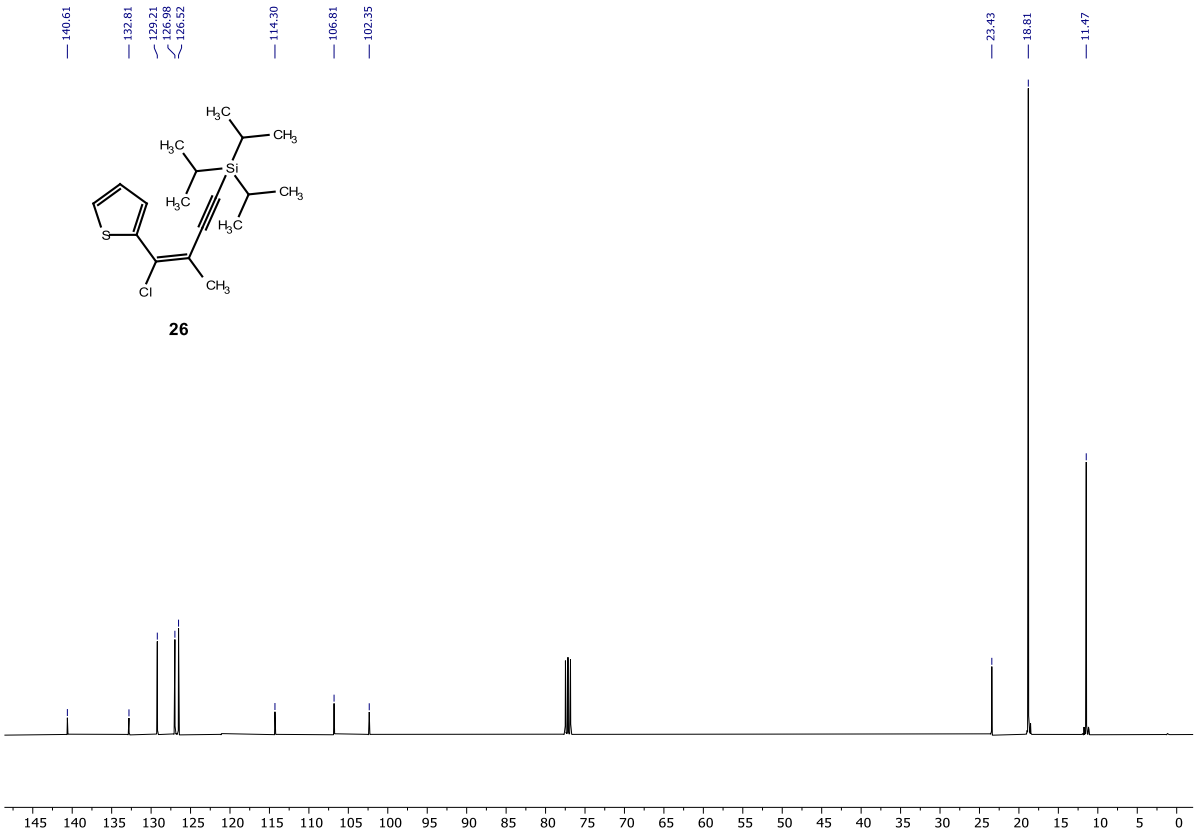
26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129.21
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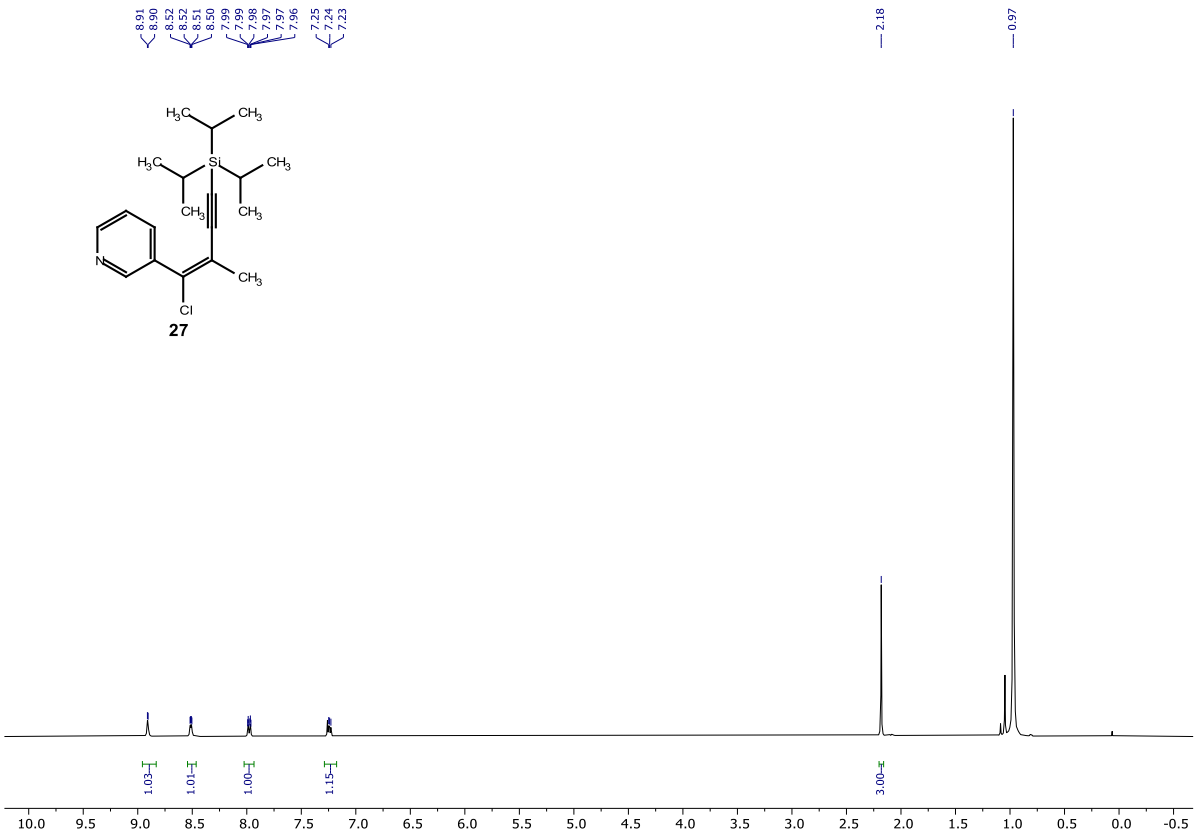
126.52
114.30
106.81
102.35
23.43
18.81
11.47
S
Cl
Si
CH3
H3C

26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8.52
8.52
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8.50
7.99
7.99
7.98
7.97
7.97
7.96
7.25
7.24
7.23
2.18
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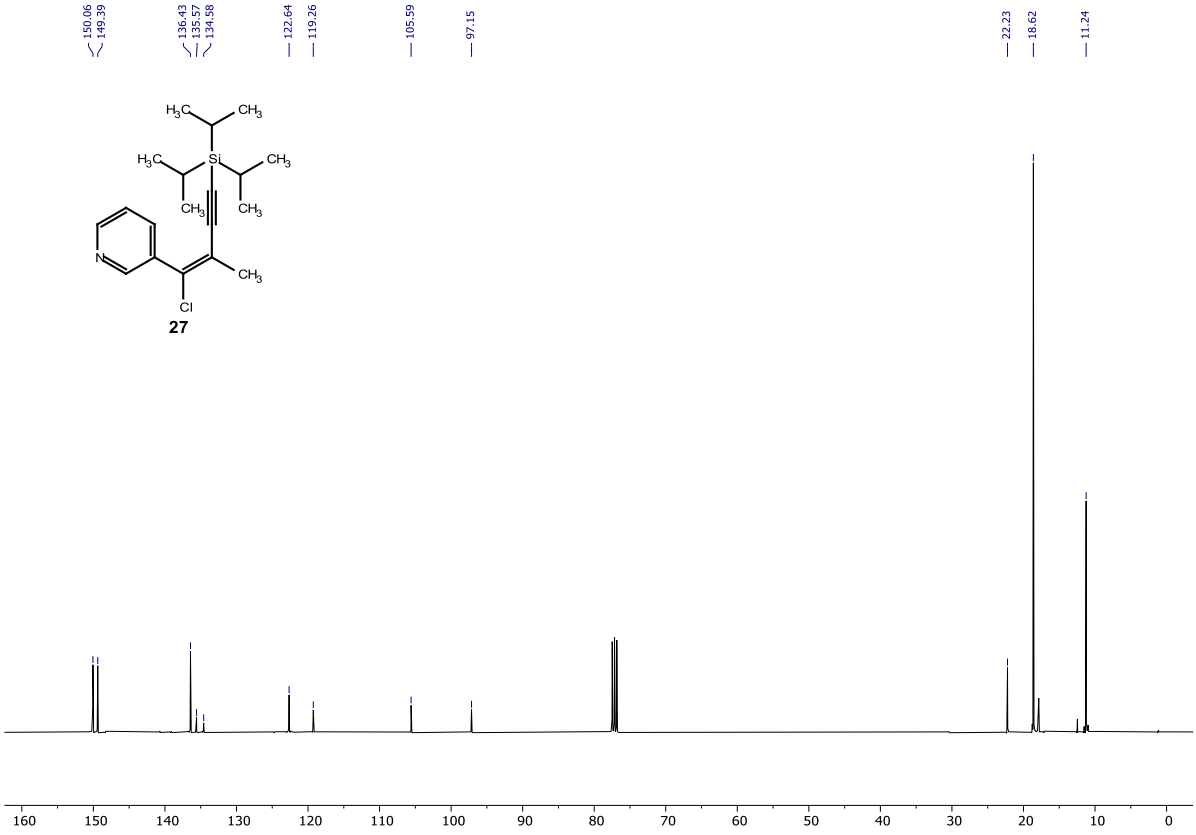
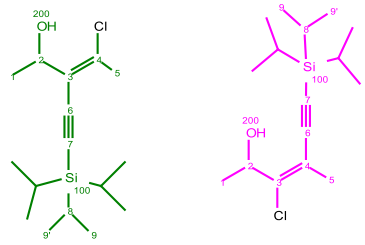
1.03
1.01
1.00
1.15
3.00
N
Cl
Si
CH3
H3C

27



27

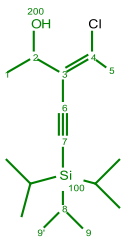
1H,-1D



28 α-*trans*

28 β-*trans*

13C,-1D



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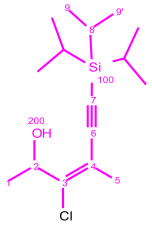

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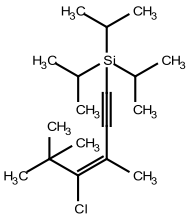
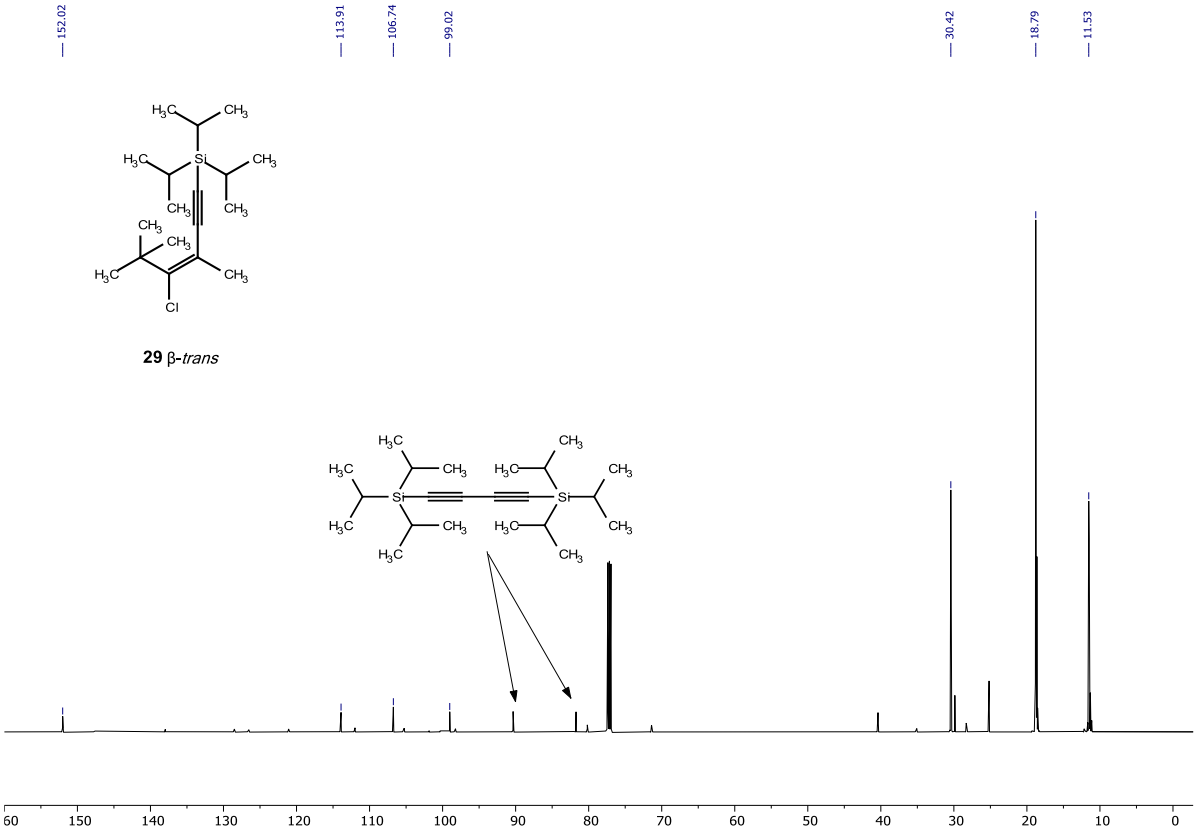
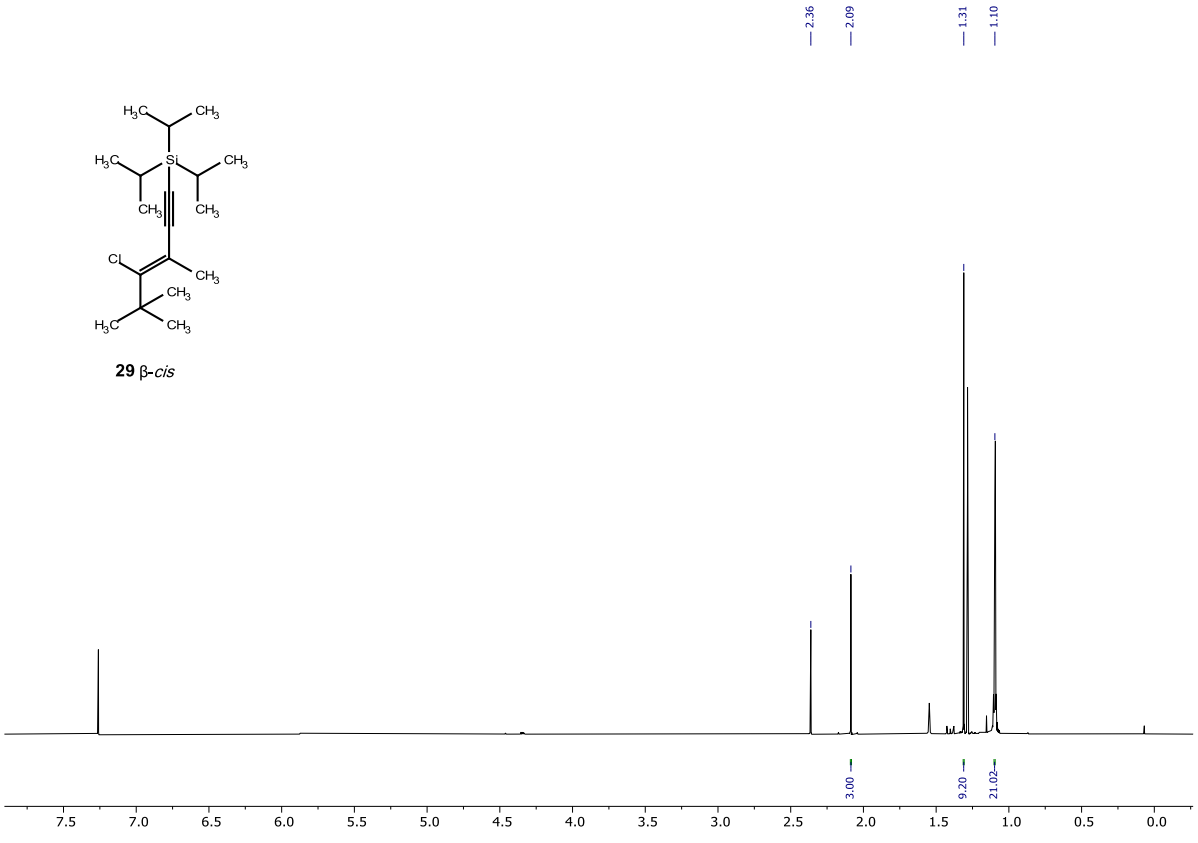


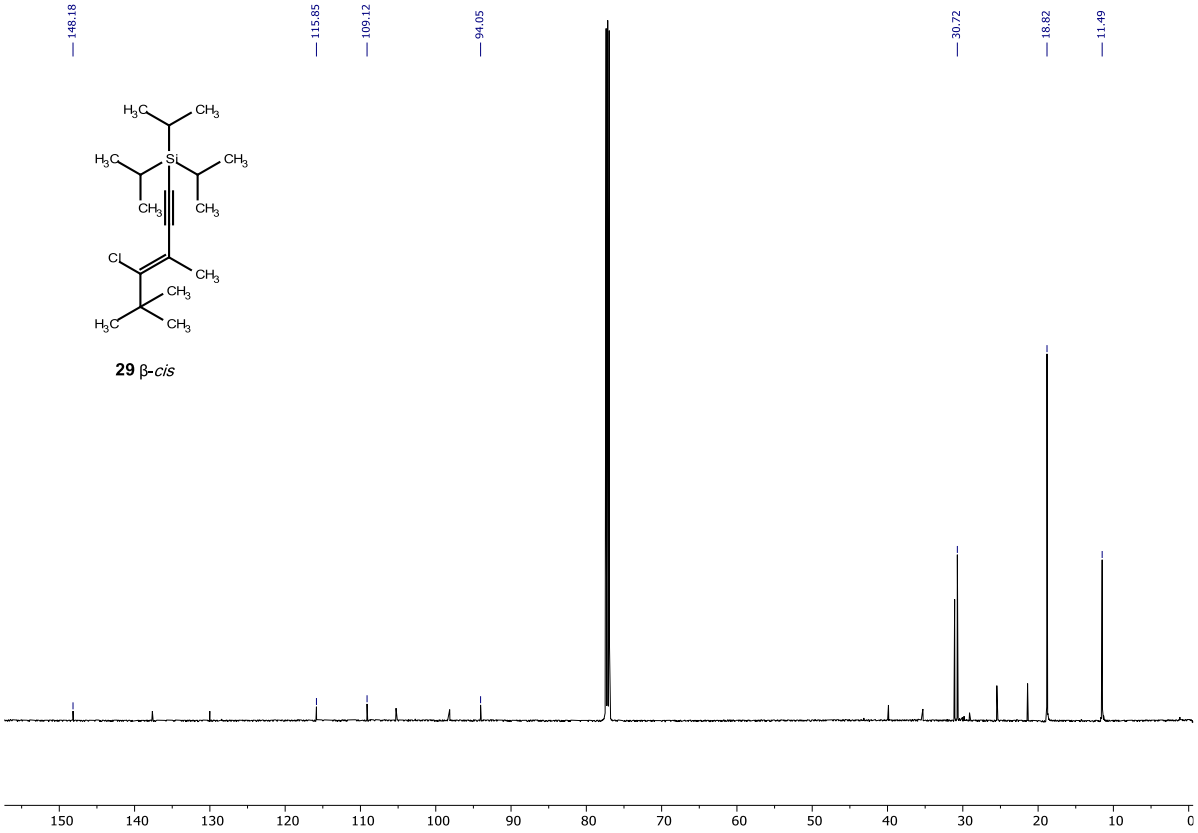
29 β-*trans*



29 β-*trans*



29 β-*cis*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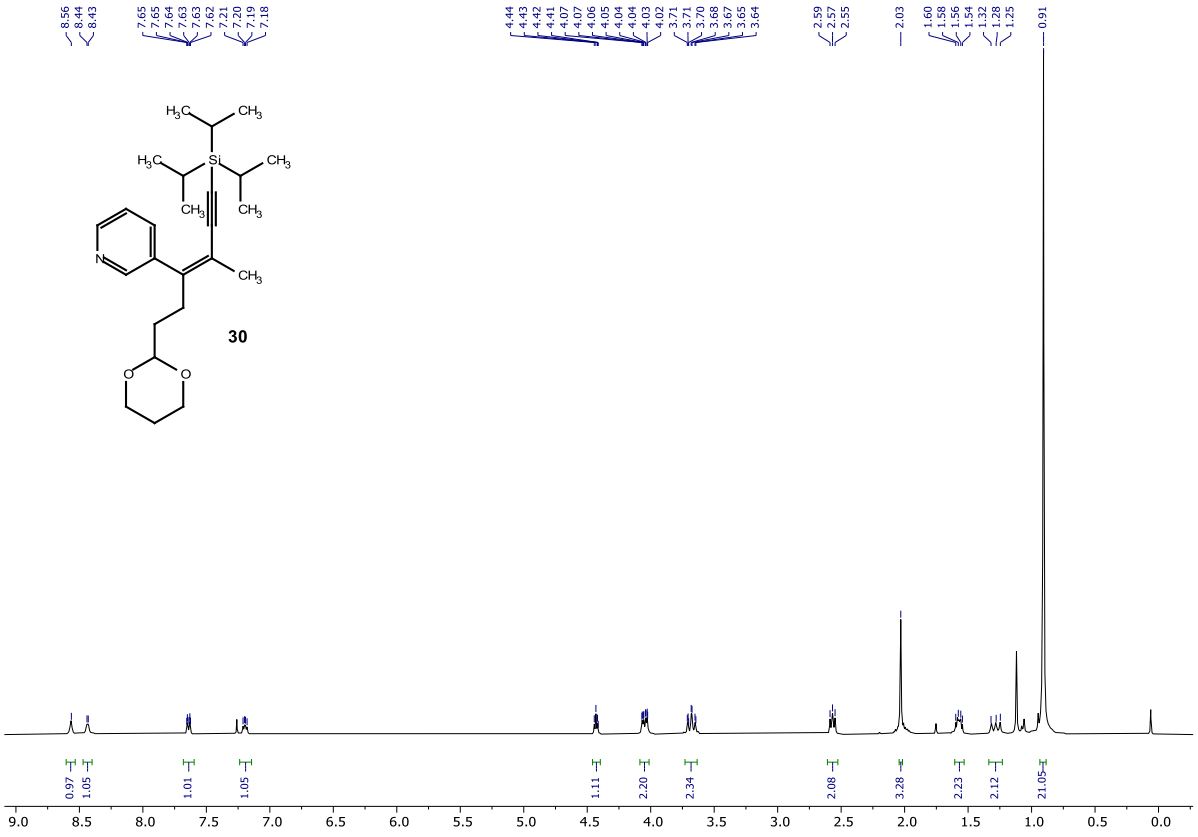
115.85
109.12
94.05
30.72
18.82
11.49
29 β-cis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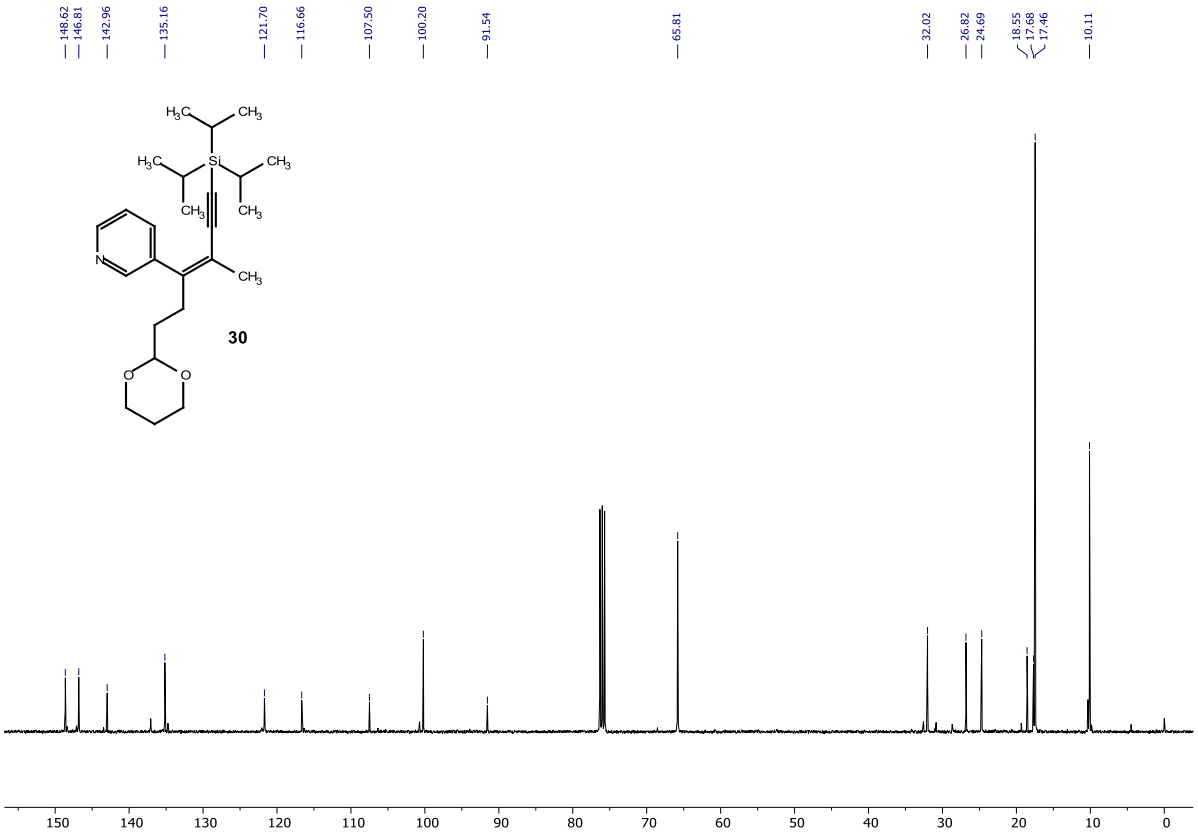
7.63
7.62
7.21
7.20
7.19
7.18
4.44
4.43
4.42
4.41
4.07
4.07
4.06
4.05
4.04
4.04
4.03
4.02
3.71
3.71
3.70
3.68
3.67
3.65
3.64
2.59
2.57
2.55
2.03
1.60
1.58
1.56
1.54
1.32
1.28
1.25
0.91
30
0.97
1.05
1.01
1.05
1.11
2.20
2.34
2.08
3.28
2.23
2.12
21.05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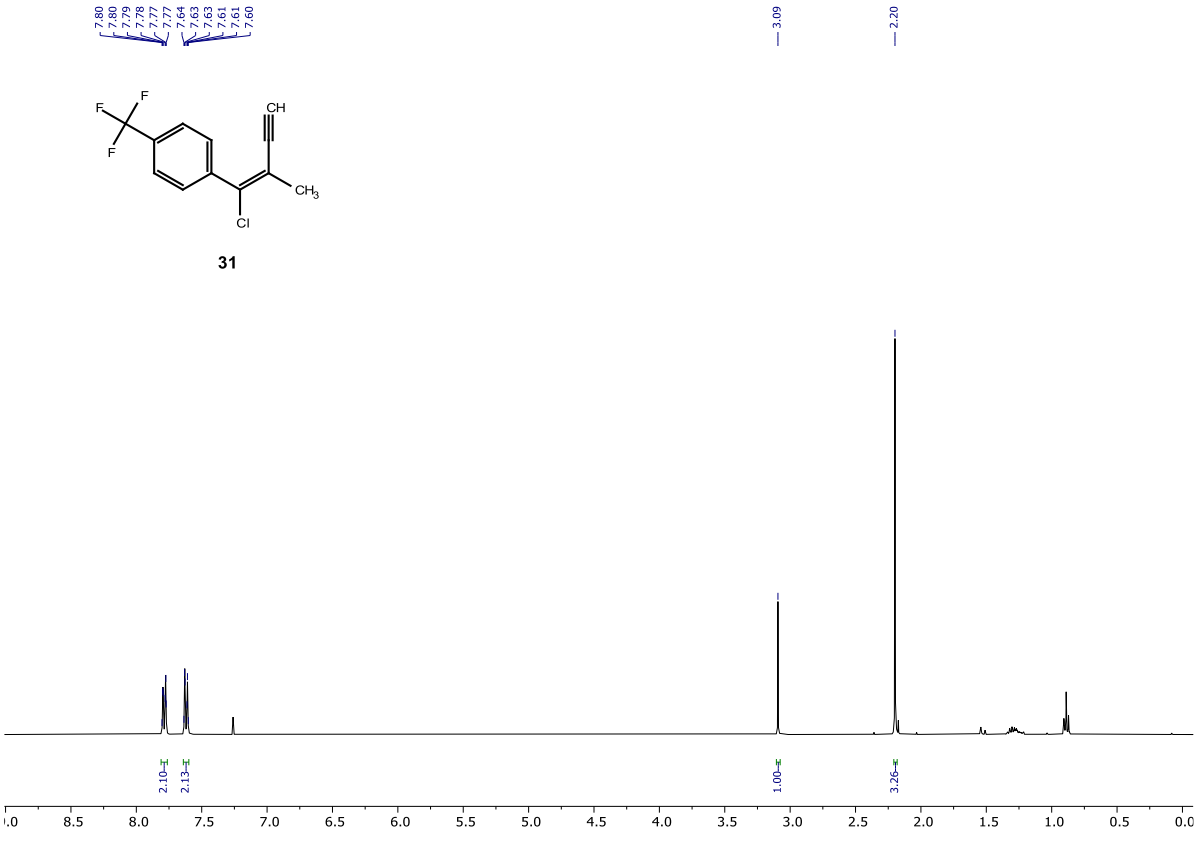
142.96
135.16
121.70
116.66
107.50
100.20
91.54
65.81
32.02
26.82
24.69
18.55
17.68
17.46
10.11
30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7.79
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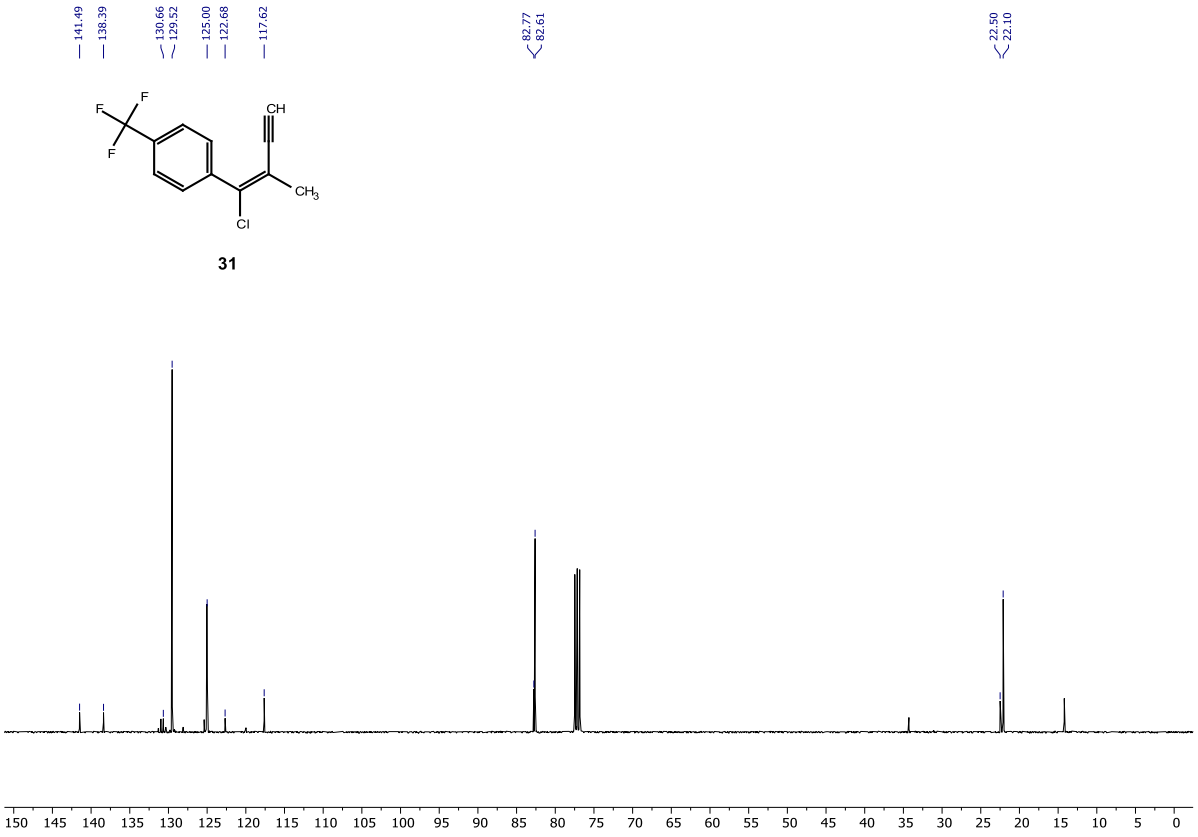
7.77
7.77
7.64
7.63
7.63
7.61
7.61
7.60
3.09
2.20
31
2.10
2.13
1.00
3.26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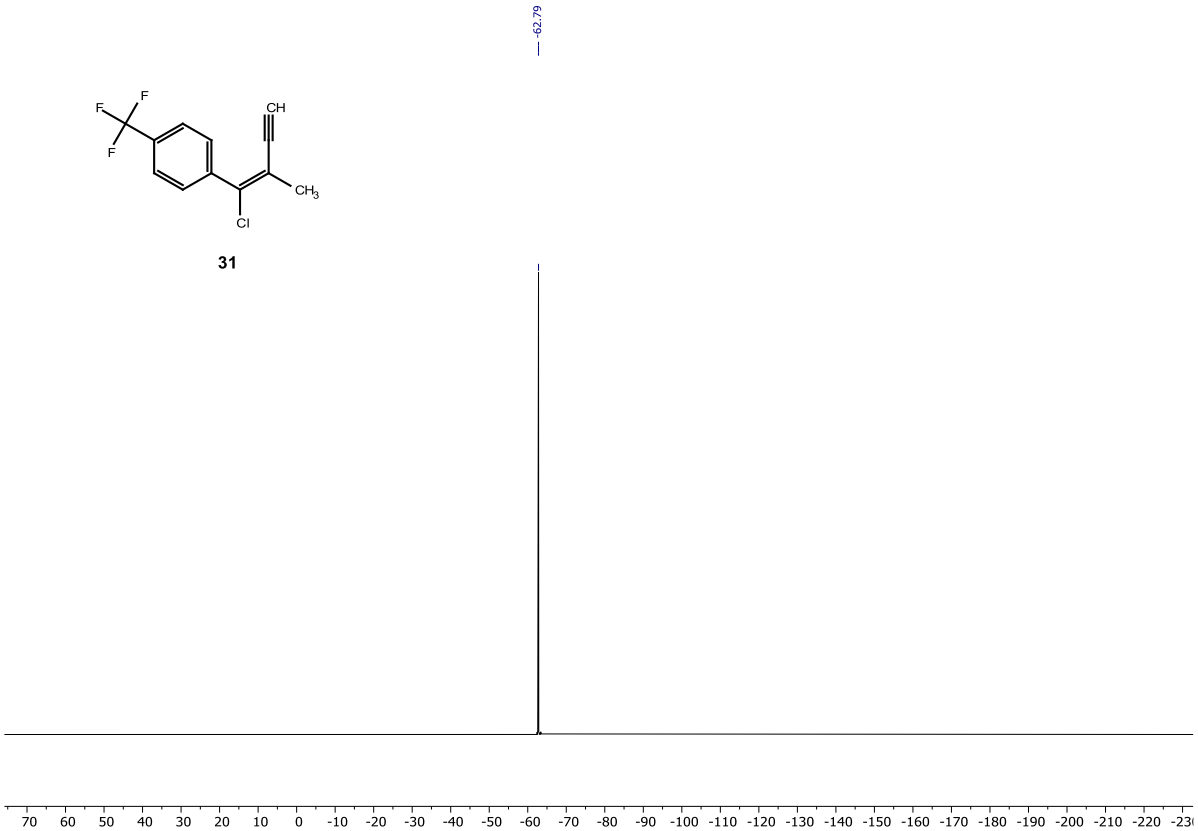
138.39
130.66
129.52
125.00
122.68
117.62
82.77
82.61
22.50
22.10
F
F
F
CH
CH3
Cl
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0

31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F
F
CH
CH3
Cl
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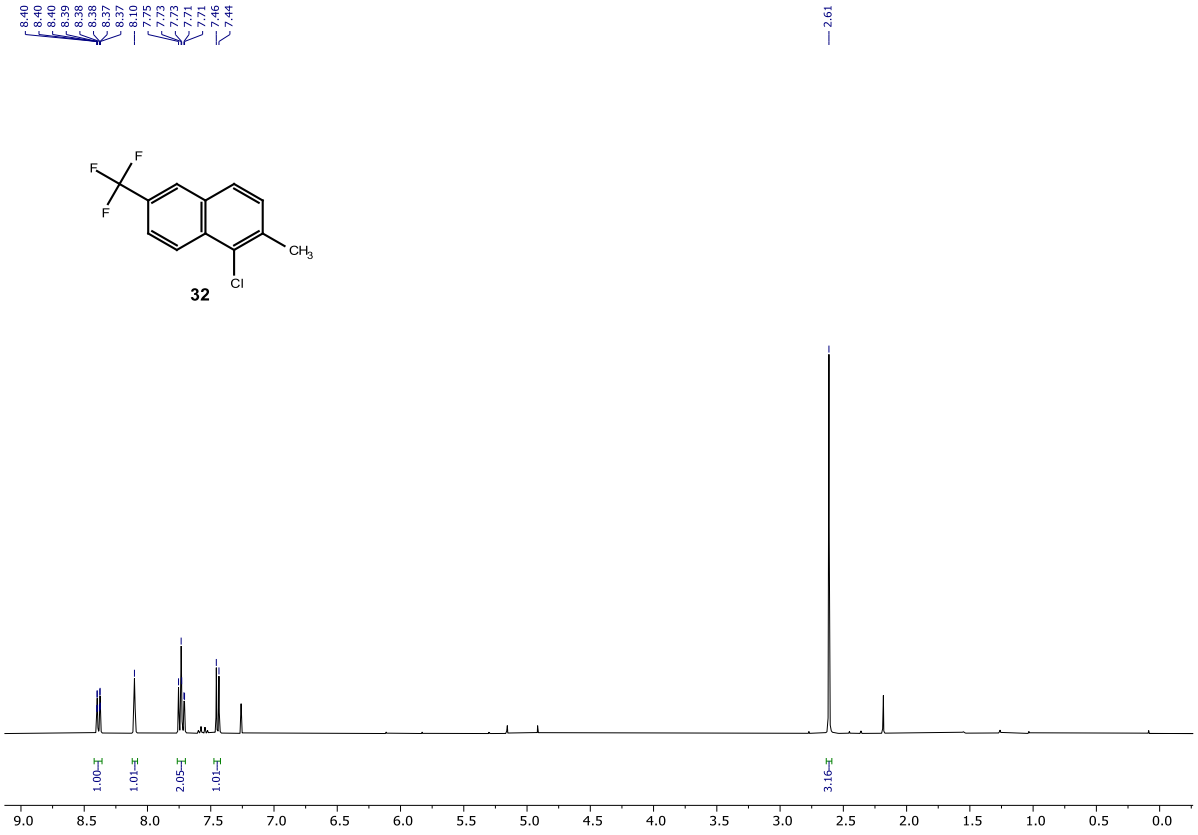
31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8.37
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7.73
7.71
7.71
7.46
7.44
2.61
F
F
F
CH3
Cl
1.00
1.01
2.05
1.01
3.16
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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3.0
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1.5
1.0
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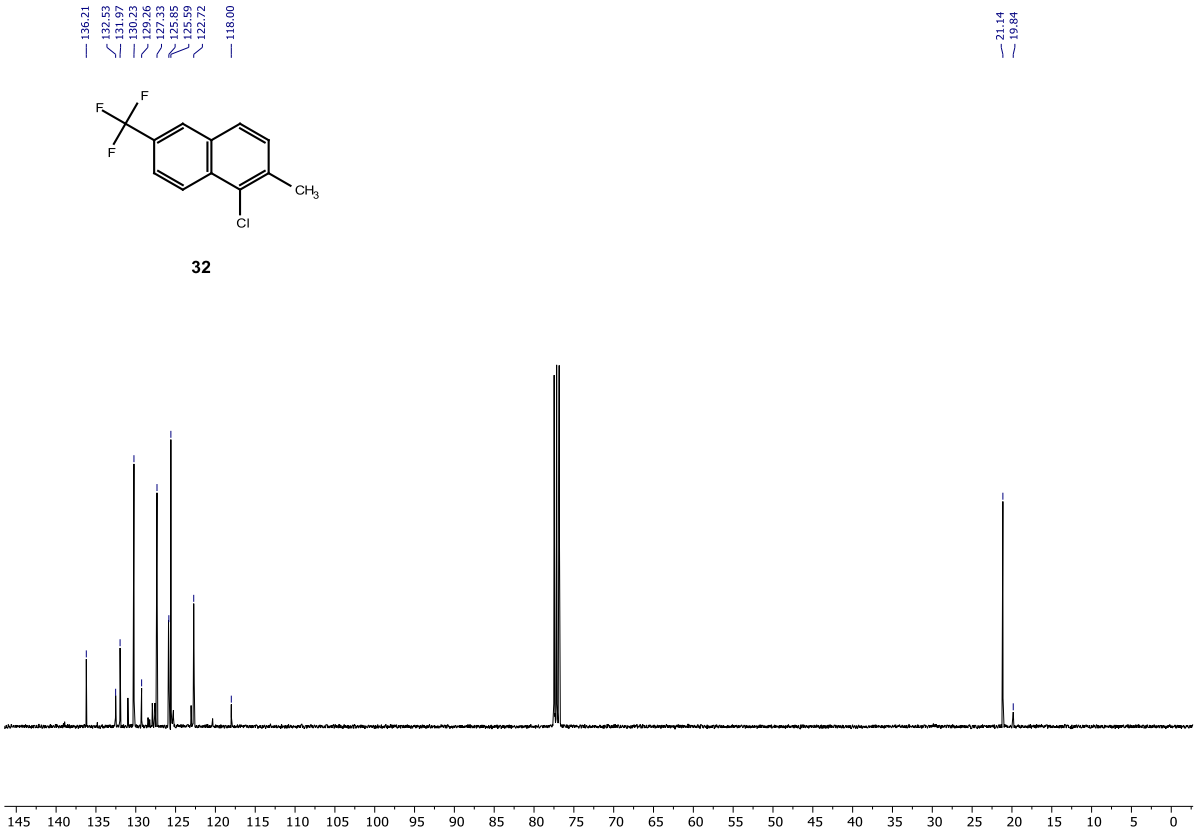
0.0

32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127.33
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125.59
122.72
118.00
21.14
19.84
F
F
F
CH3
Cl
145
140
135
130
125
120
115
110
105
100
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30
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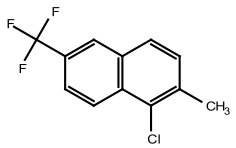
10
5
0

32


F
F
F
CH3
Cl

32

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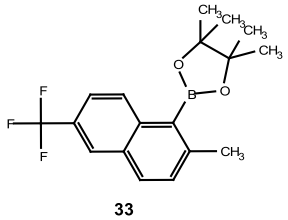
CH3
CH3
CH3
CH3
O
B
O
F
F
F
CH3

33

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8.27
8.27
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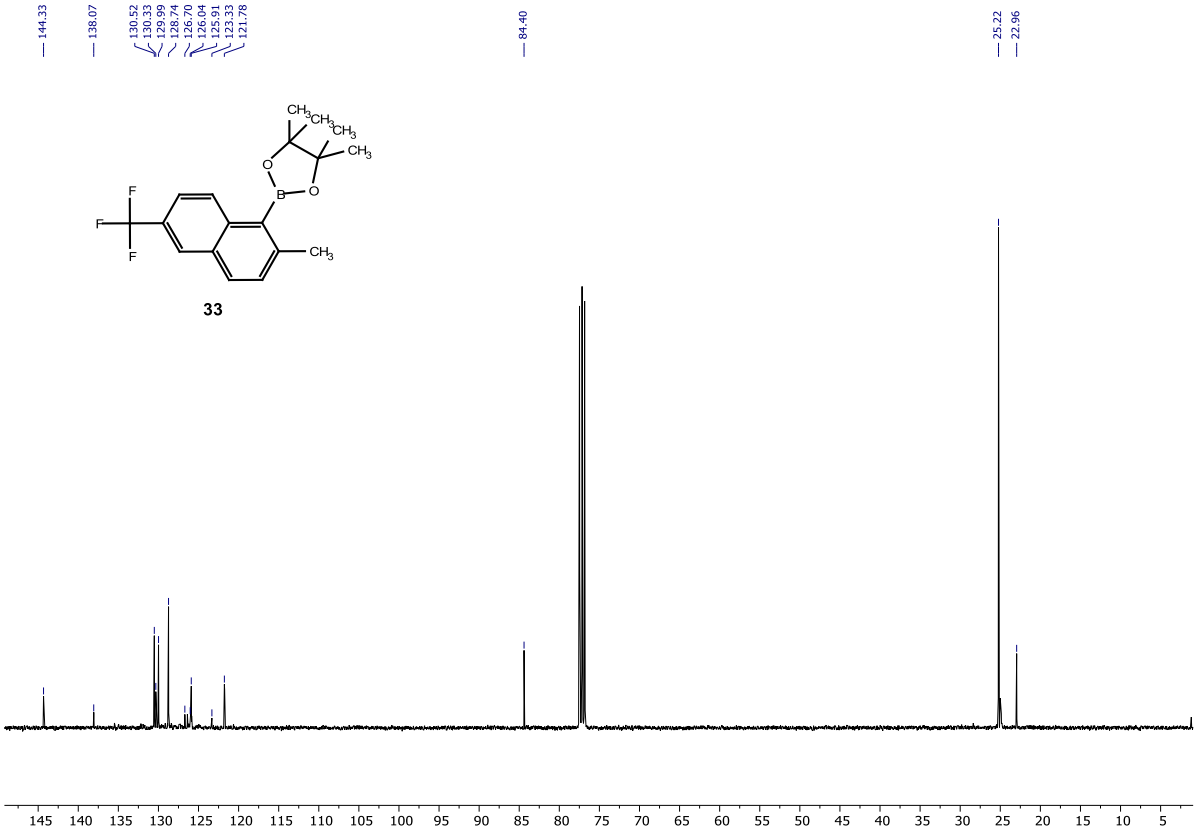
8.25
8.25
8.24
8.06
8.04
7.82
7.65
7.62
7.61
7.60
7.39
7.37
2.66
1.49
1.00
0.99
1.00
0.99
0.95
3.07
12.09
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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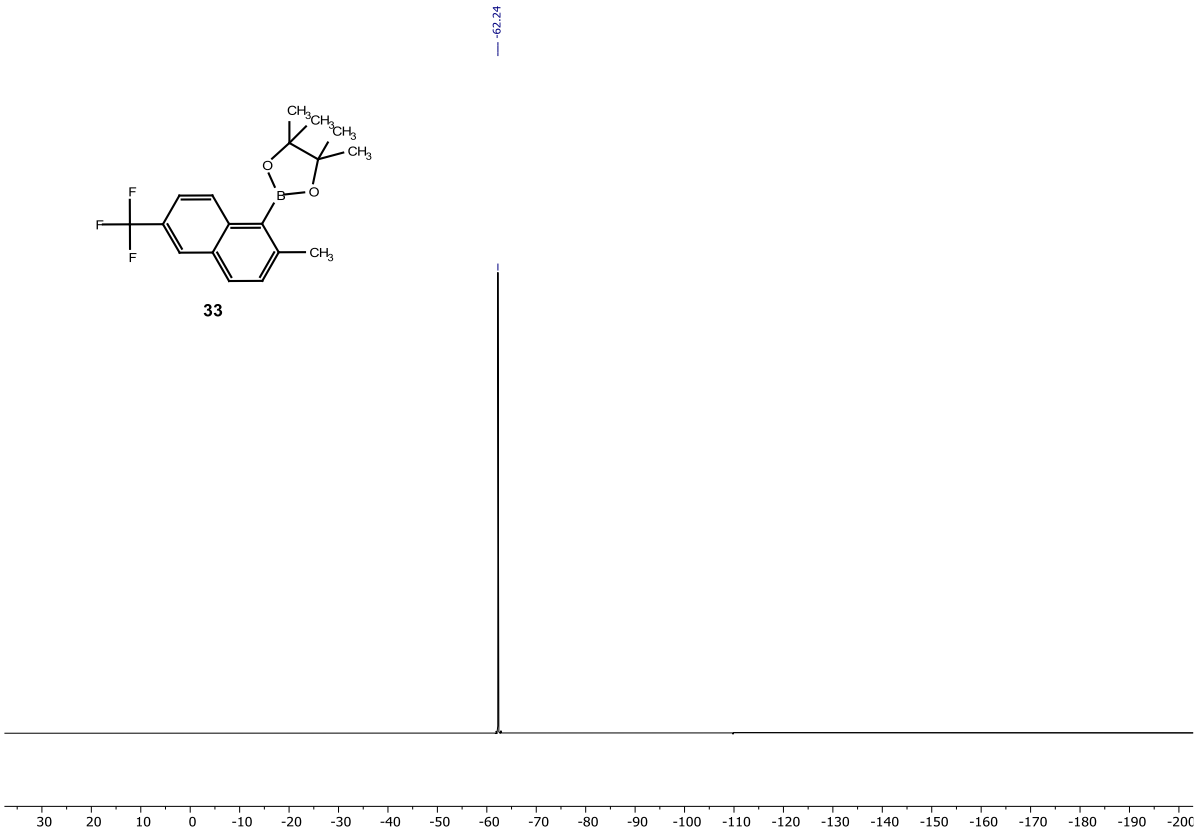
123.33
121.78
84.40
25.22
22.96
33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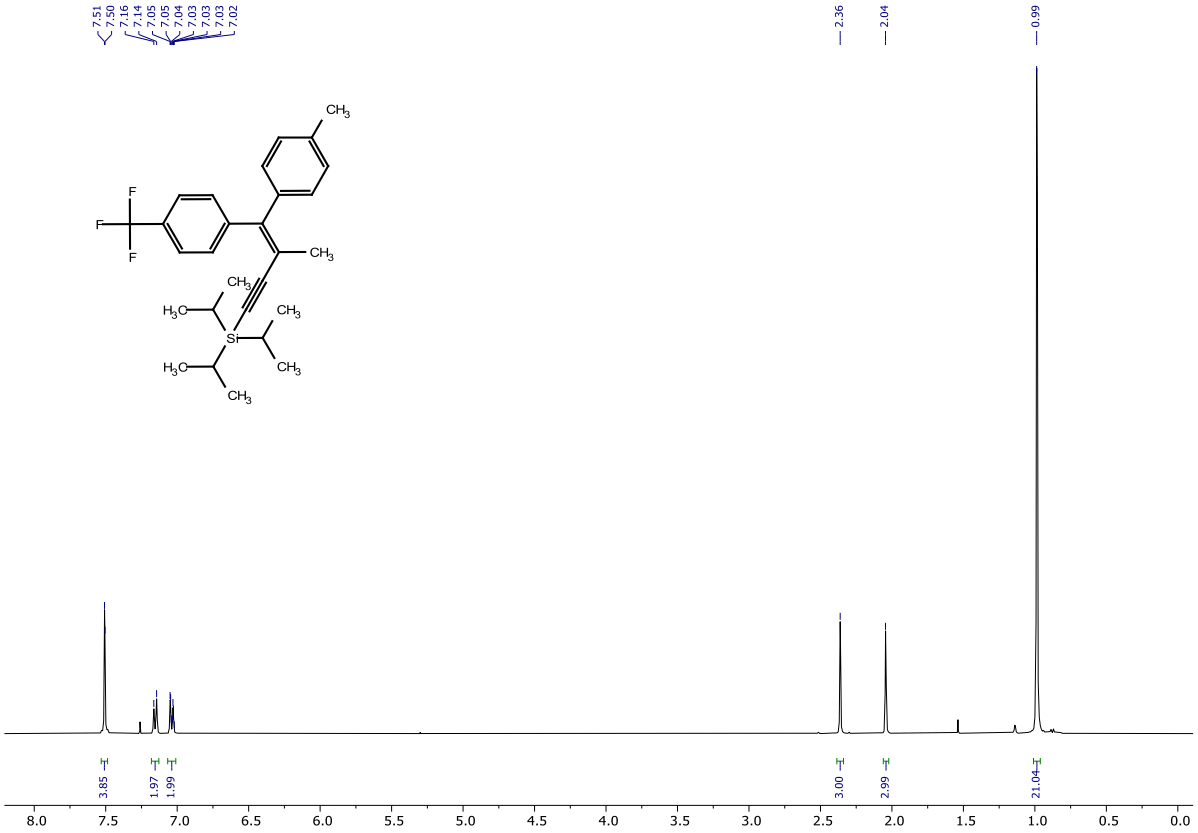
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7.05
7.05
7.04
7.03
7.03
7.03
7.02
2.36
2.04
0.99
CH3
F
F
F
CH3
CH3
H3C
Si
CH3
H3C
CH3
CH3
3.85
1.97
1.99
3.00
2.99
21.04
8.0
7.5
7.0
6.5
6.0
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4.0
3.5
3.0
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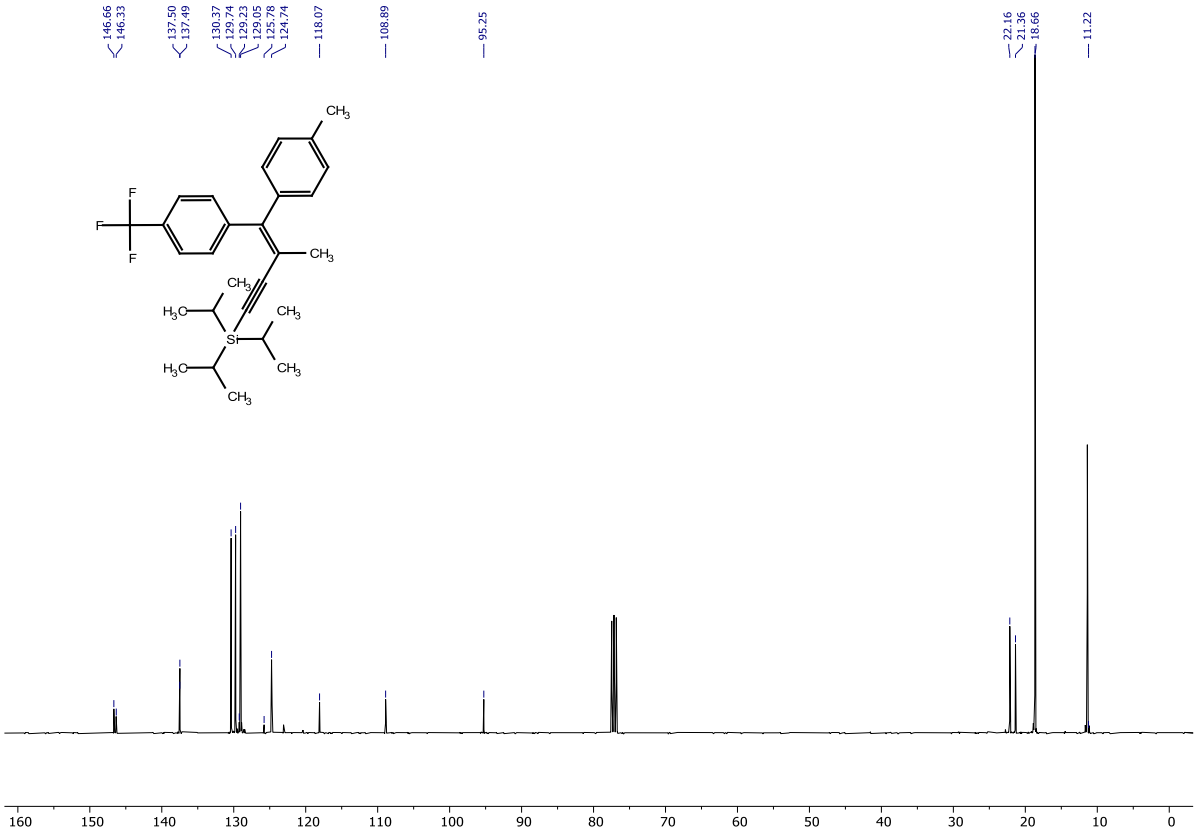
2.0
1.5
1.0
0.5
0.0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129.05
125.78
124.74
118.07
108.89
95.25
22.16
21.36
18.66
11.22
CH3
F
F
F
CH3
CH3
H3C
Si
CH3
H3C
CH3
CH3
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150
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70
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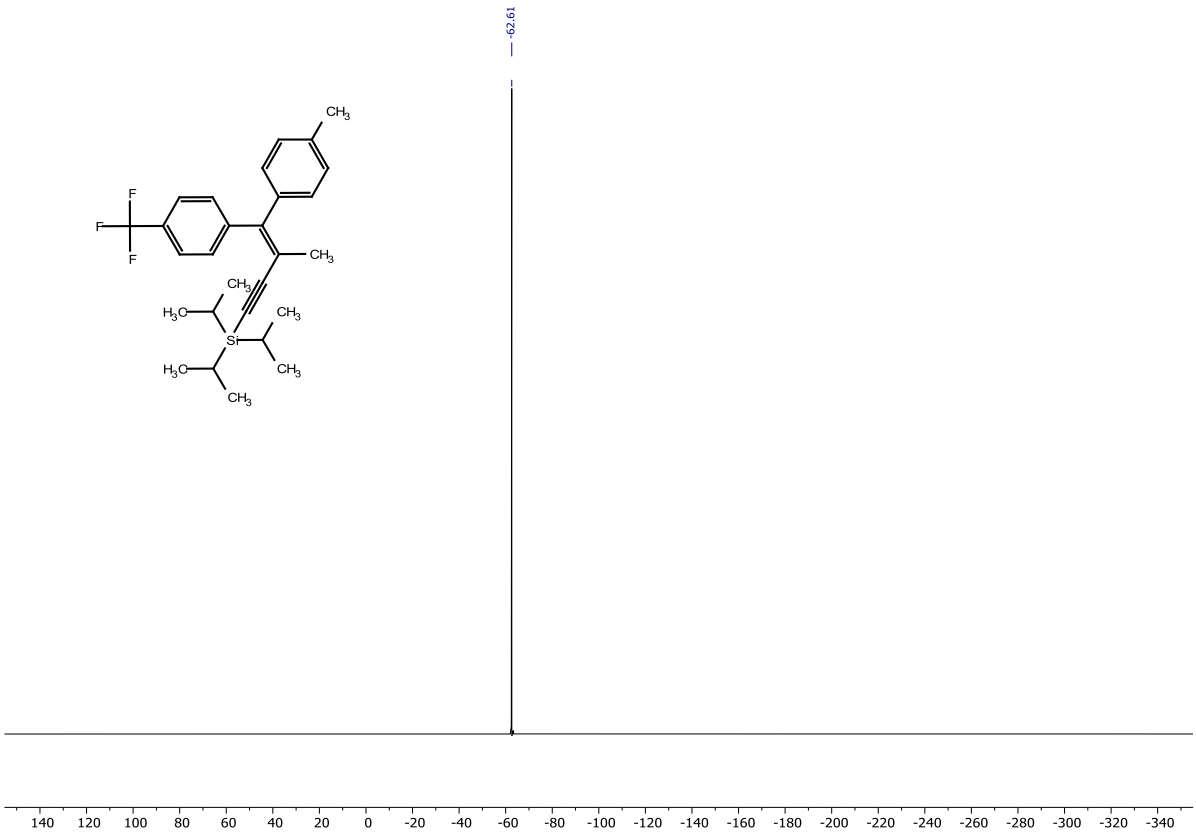
30
20
10
0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F
F
F
CH3
CH3
H3C
Si
CH3
H3C
CH3
CH3
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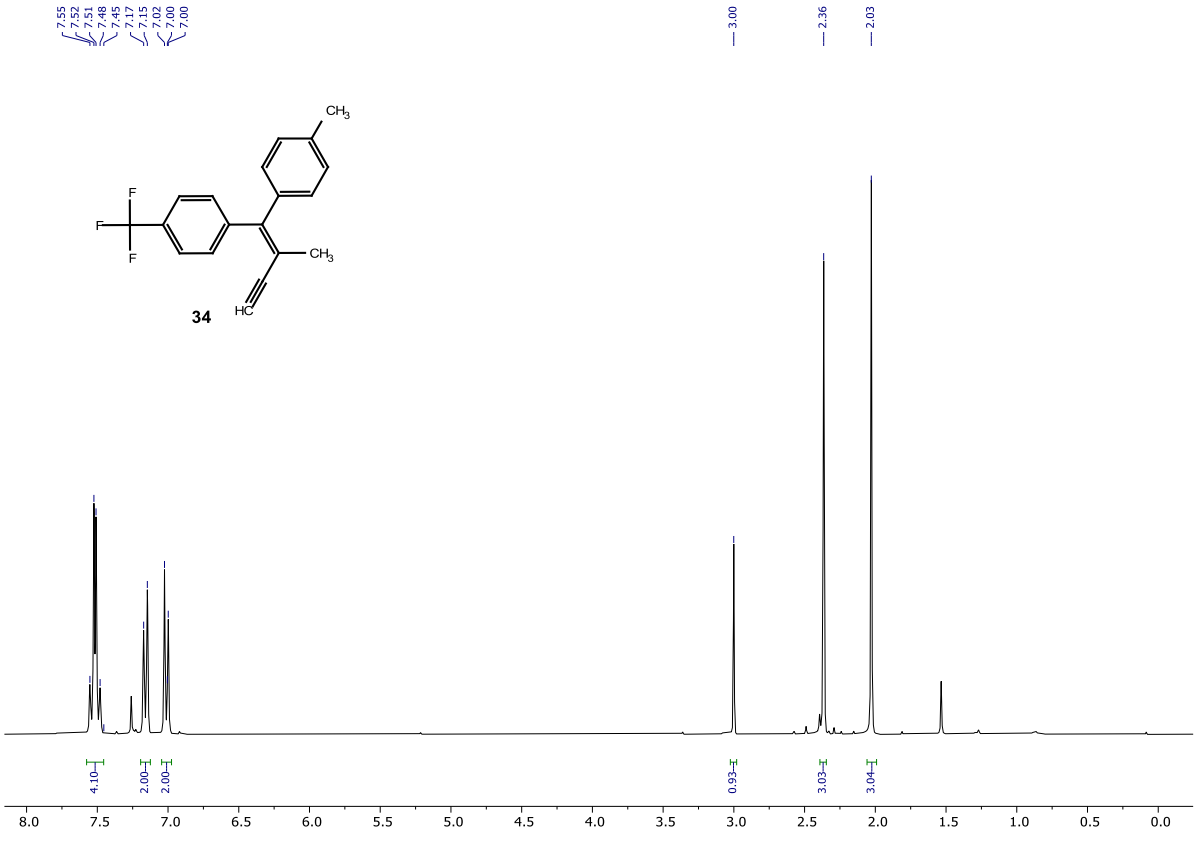
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7.15
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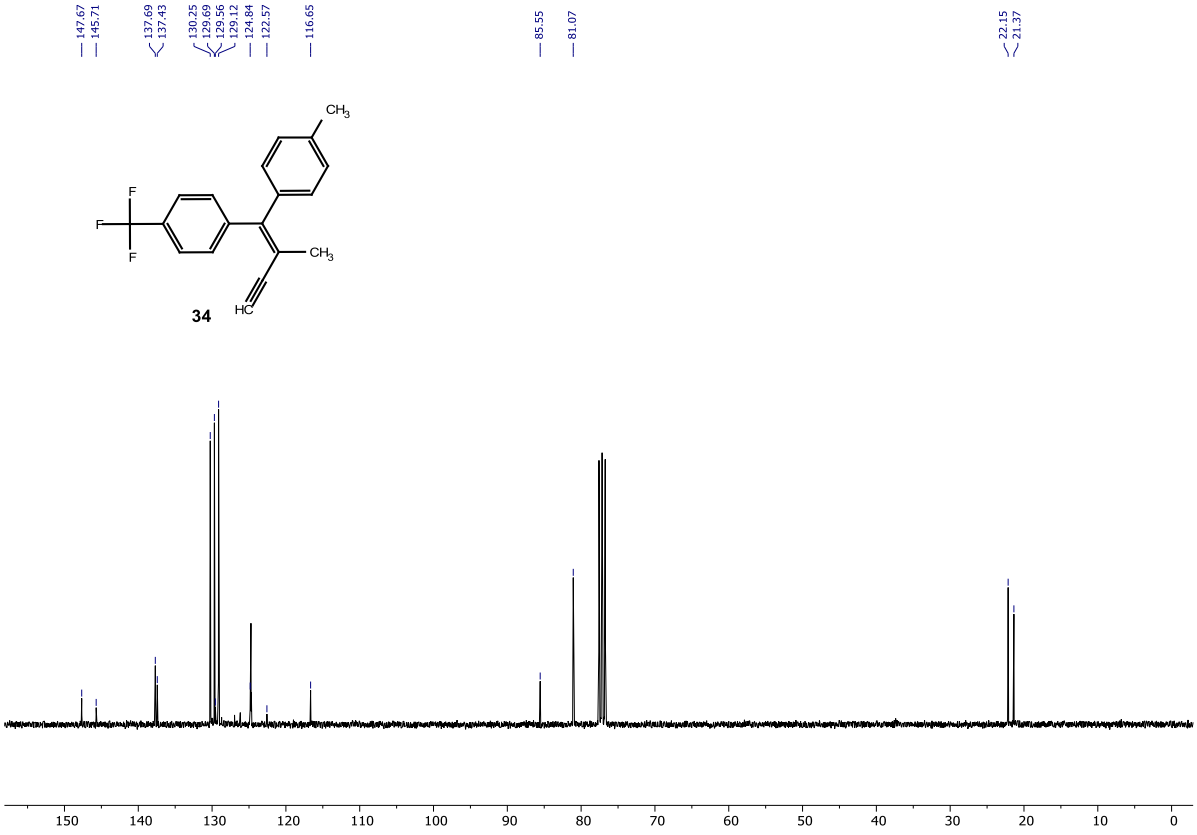
7.00
7.00
3.00
2.36
2.03
CH3
F
F
F
CH3
HC
4.10
2.00
2.00
0.93
3.03
3.04
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

34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122.57
116.65
85.55
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21.37
CH3
F
F
F
CH3
HC
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150
140
130
120
110
100
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70
60
50
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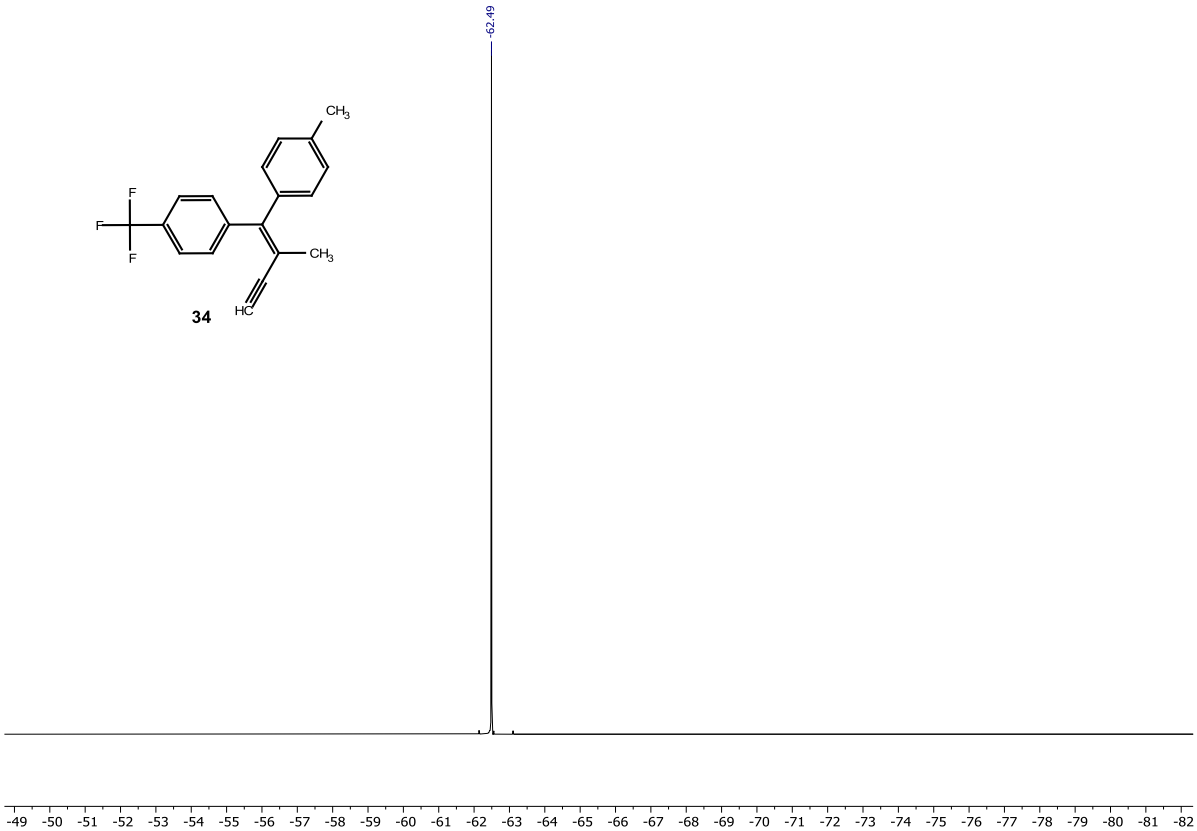
30
20
10
0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CH3
F
F
F
CH3
HC
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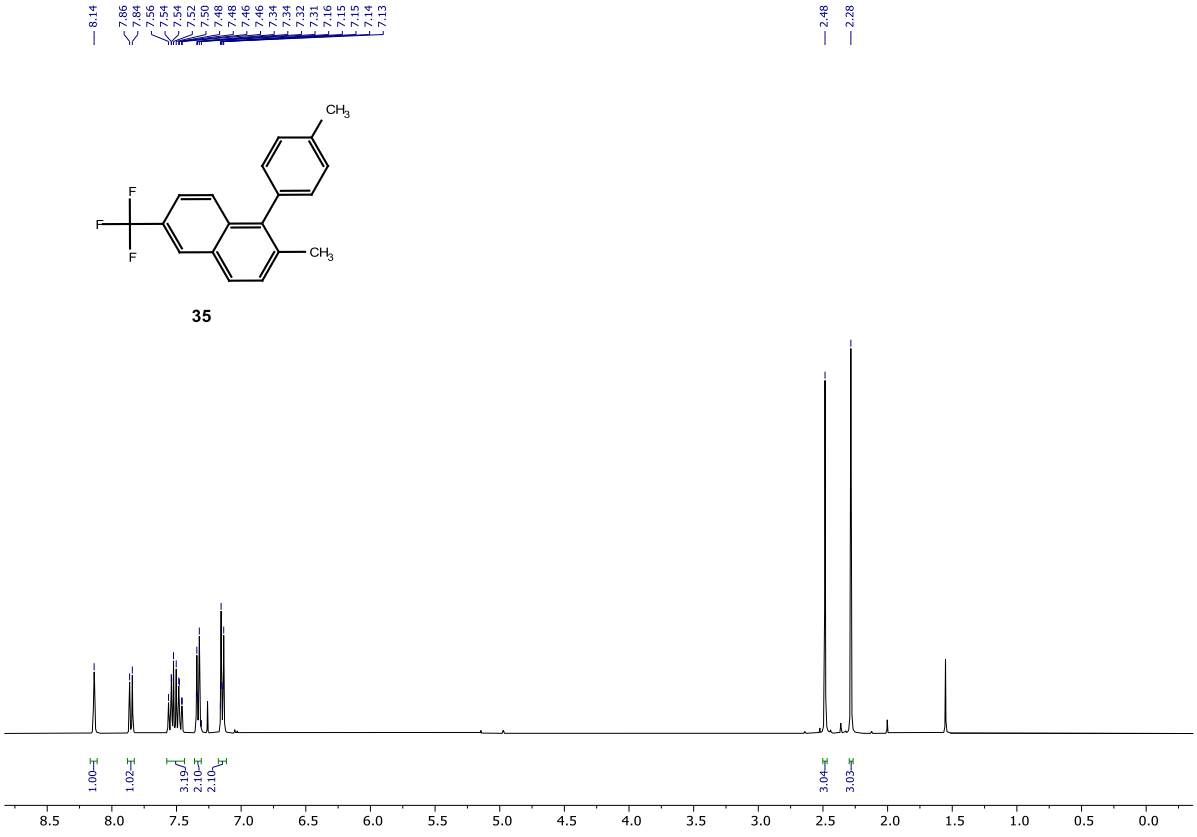
-82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7.48
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7.46
7.34
7.34
7.32
7.31
7.16
7.15
7.15
7.14
7.13
2.48
2.28
CH3
F
F
F
CH3
1.00
1.02
3.19
2.10
2.10
3.04
3.03
8.5
8.0
7.5
7.0
6.5
6.0
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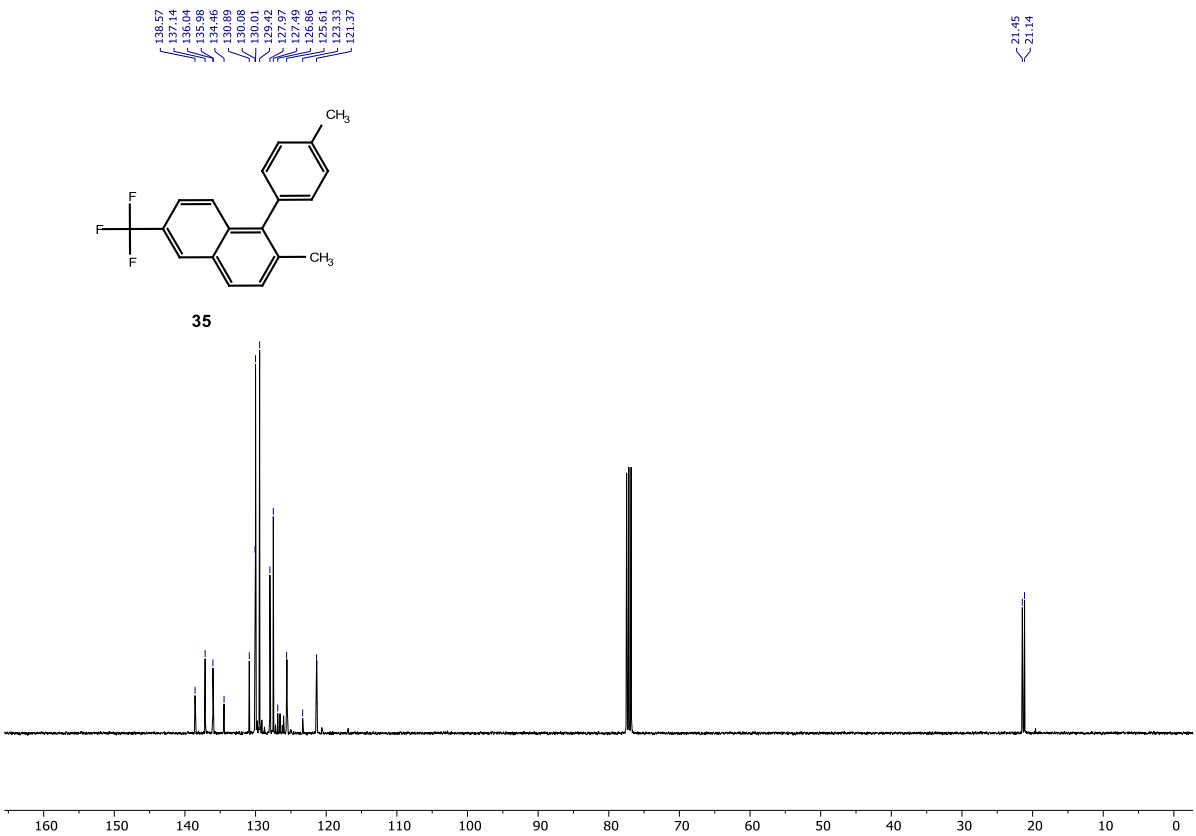
0.0

35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127.49
126.86
125.61
123.33
121.37
21.45
21.14
CH3
F
F
F
CH3
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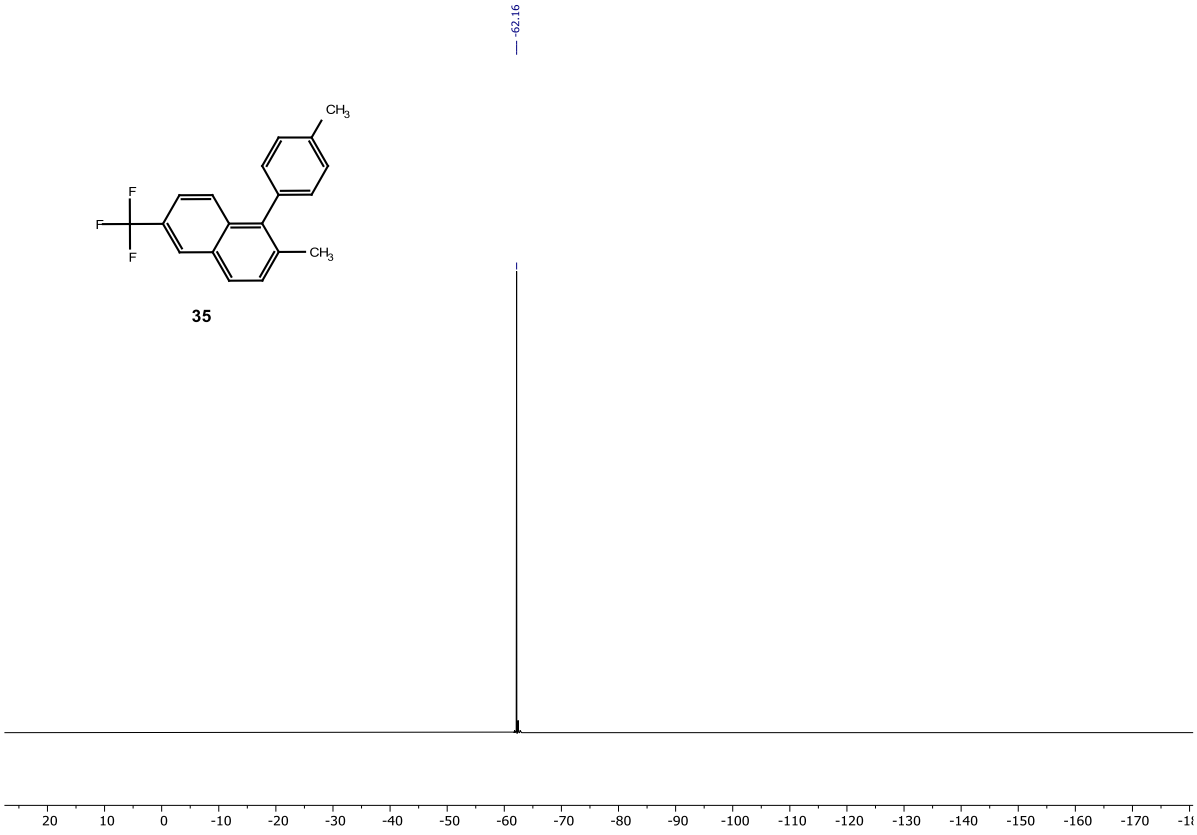
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

35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CH3
F
F
F
CH3
20
10
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-10
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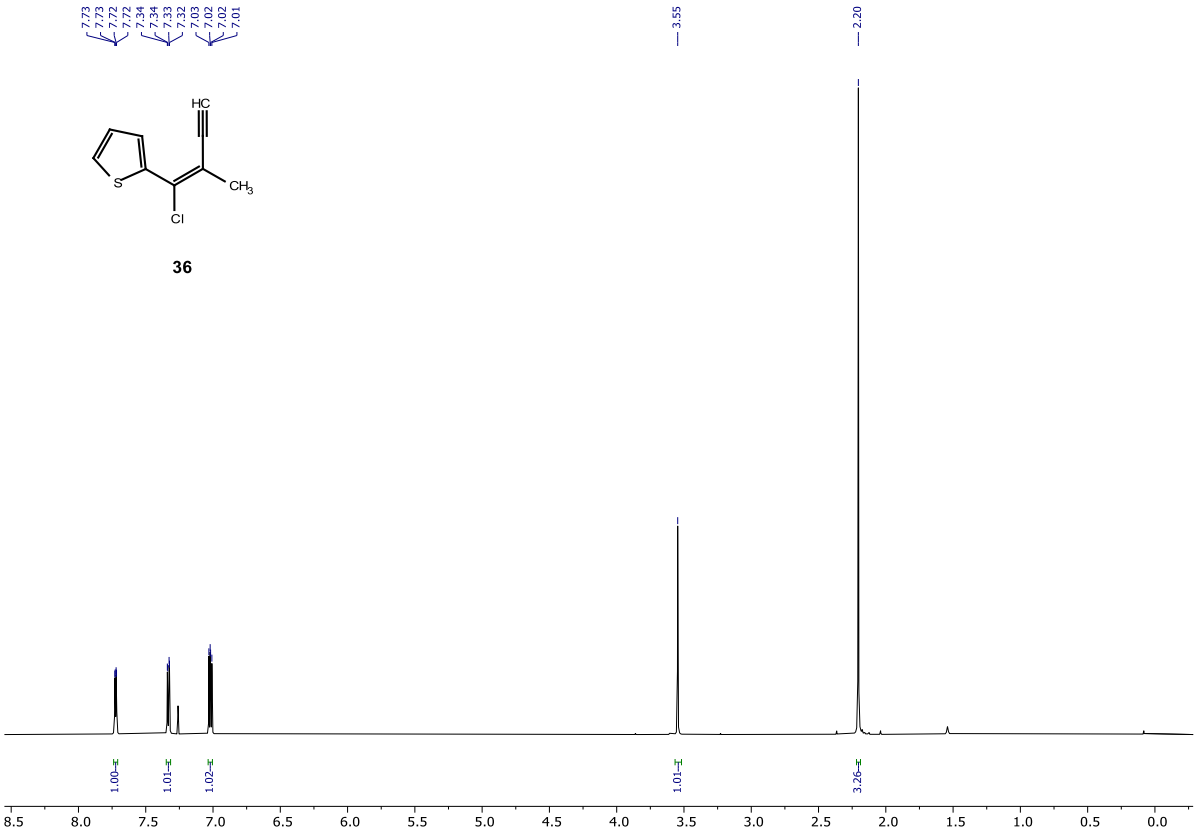
-90
-100
-110
-120
-130
-140
-150
-160
-170

35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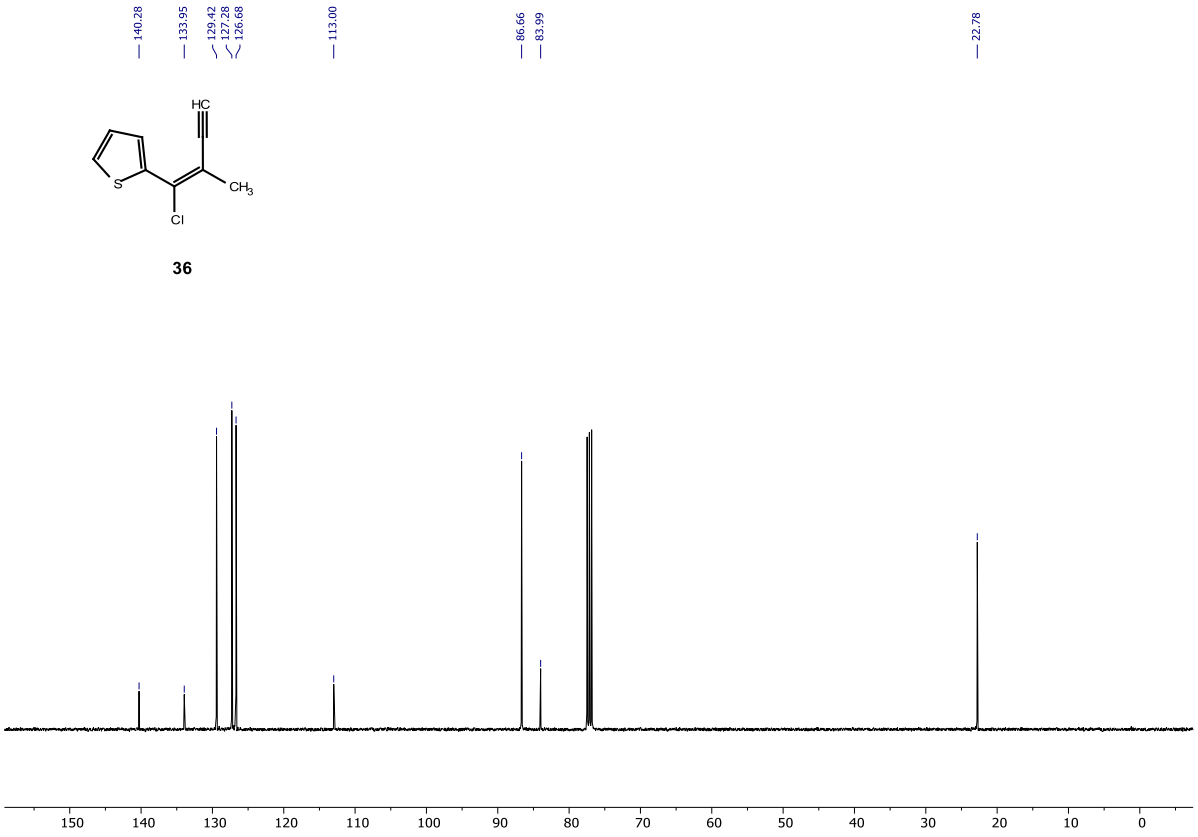
7.73
7.72
7.72
7.34
7.34
7.33
7.32
7.03
7.02
7.02
7.01
3.55
2.20
HC
S
CH3
Cl
1.00
1.01
1.02
1.01
3.26
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

36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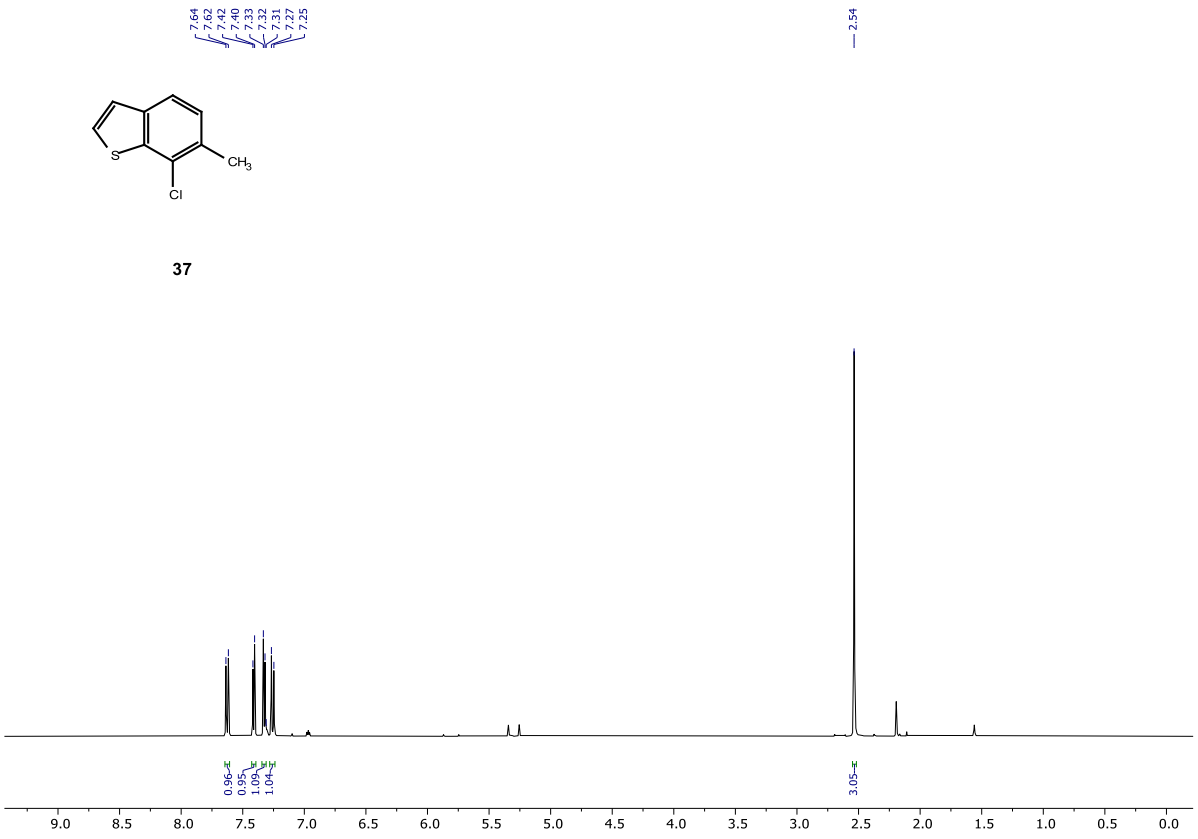
133.95
129.42
127.28
126.68
113.00
86.66
83.99
22.78
HC
S
CH3
Cl
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

36


7.64
7.62
7.42
7.40
7.33
7.32
7.31
7.27
7.25
2.54
S
CH3
Cl
0.96
0.95
1.09
1.04
3.05
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.5
3.0
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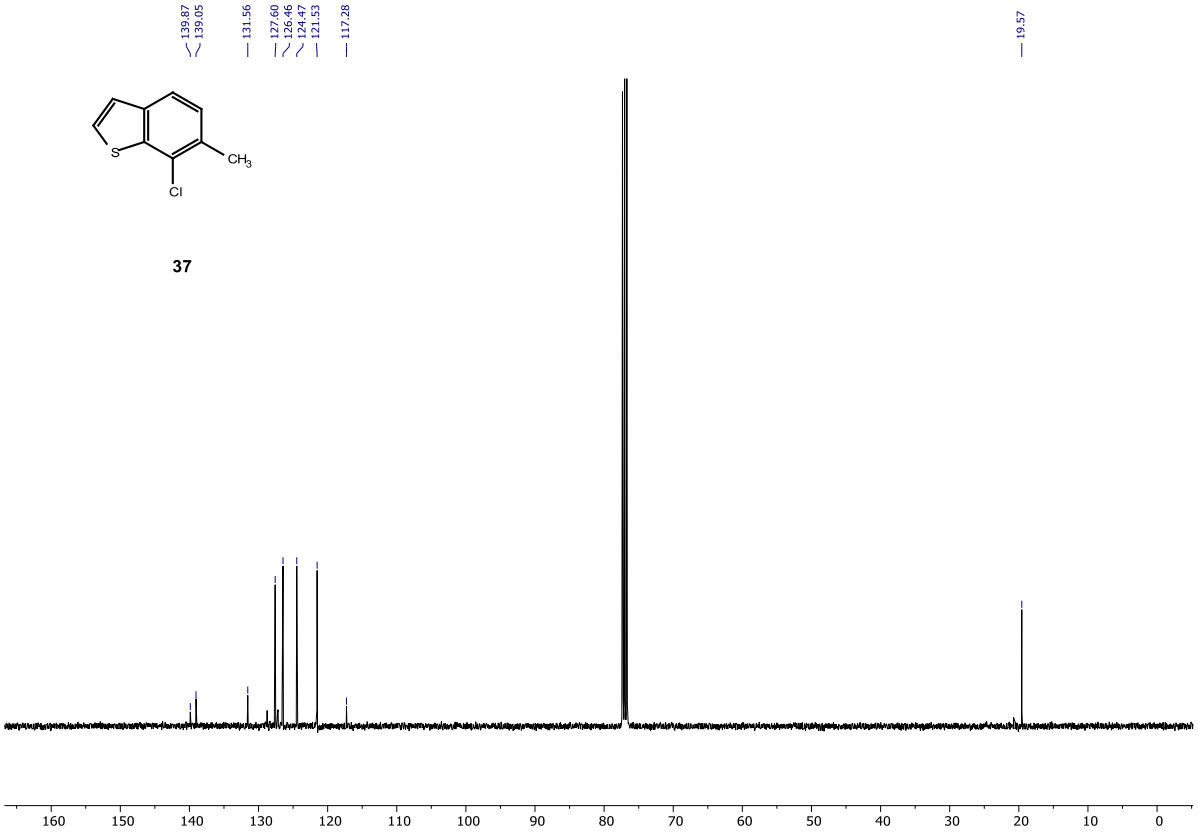
1.5
1.0
0.5
0.0

37



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