Supporting Information for:

Hydrohalogenative Aromatization of Multiynes Promoted by Ruthenium Alkylidene Complexes

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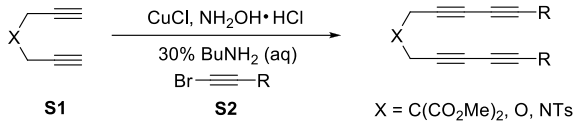
General Information

All reactions were run under an atmosphere of nitrogen, unless otherwise indicated. Flasks were oven-dried overnight and cooled under a stream of nitrogen. Compounds were purchased from Aldrich unless otherwise noted. CH_2Cl_2, THF, Et_2O were purified based on standard procedures. Flash chromatography was performed using silica gel 60 Å (32-63 mesh) purchased from Sorbent Technologies. Analytical thin layer chromatography (TLC) was performed on 0.25 mm E. Merck pre-coated silica gel 60 (particle size 0.040–0.063 mm). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV-500 spectrometer. ^{1}H and ^{13}C chemical shifts are referenced to internal solvent resonances and reported relative to $SiMe_4$; multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), qn (quintet), m (multiplet) and br (broad). Coupling constants, *J*, are reported in Hertz. Electrospray ionization (ESI) mass spectra were recorded on a Micromass LCT equipped with a time-of-flight analyzer.

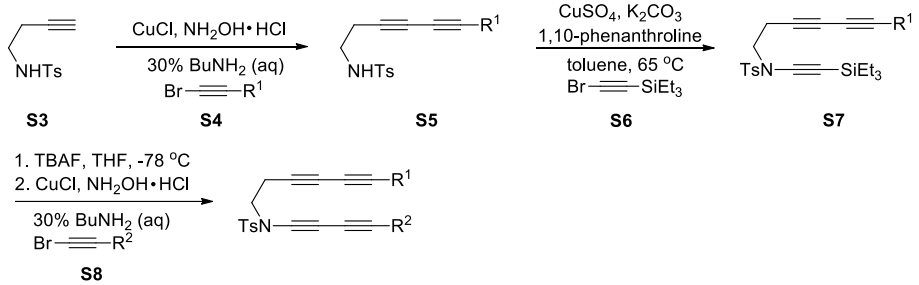
Experimental Details

General procedure for the synthesis of symmetric *bis*-1,3-diyne



Symmetrical *bis*-1,3-diynes was prepared in one step using Cadiot-Chodkiewicz coupling reaction. To an aqueous solution of *n*-$BuNH_2$ (30%, 3 mL/1 mmol of substrate) aqueous solution containing CuCl (0.6 equiv), and $NH_2OH{\cdot}HCl$ (0.1 equiv), was added diyne **S1** at 0 °C. Bromoalkyne **S2** (3–4 equiv) was then added dropwise over 5 min, and the reaction mixture was stirred at 0 °C for additional 5 min. After completion of the reaction (monitored by TLC) organic layer was separated, dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography (Hex/EtOAc 20:1 to 1:1) on silica gel to afford *bis*-1,3-diynes in moderate to good yields.

General procedure for the synthesis of unsymmetric *bis*-1,3-diyne

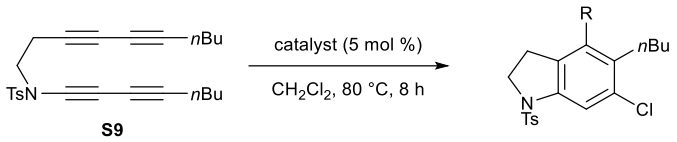


Unsymmetrical *bis*-1,3-diynes were synthesized in four steps involving Cadiot-Chodkiewicz coupling reaction, *N*-alkynalation of tosylamide, desilylation and Cadiot-Chodtiewicz coupling sequence. Tosylamide **S3** was coupled with bromoalkyne **S4** (1.5 equiv) under the typical Cadiot-Chodkiewicz

reaction conditions described above gave diyne **S5**. *N*-alkynylation of **S5** with bromoalkyne **S6** (1.1 equiv) in the presence of a catalytic amount of $CuSO_4 \cdot 5H_2O$ (0.1 equiv), 1,10-phenanthroline (0.2 equiv) and K_2CO_3 (2 equiv) in toluene at 65 °C for 8 h afforded triyne **S7**. Desilylaton of **S7** using TBAF (1.1 equiv) at –78 °C and a subsequent coupling reaction with bromoalkyne **S8** (1.5 equiv) generated unsymmetrical *bis*-1,3-diynes in moderate to good yields.

Catalyst screening for hydrohalogenation

To choose the best catalyst for hydrohalogenation reaction, several catalysts were screened. In a typical procedure, the unsymmetrical bis-1,3-diyne substrate **S9** heated at 80 °C in CH_2Cl_2 in presence of a catalyst (5 mol %) for 8 h. While in the absence of any catalyst the substrate decomposed over time without forming any trace of the hydrohalohenated product, the 2nd generation Grubbs catalyst was found to be the most effective catalyst for the transformation.



S9

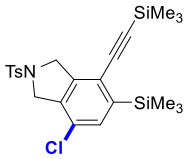
Entry	Catalyst	Yield (%)	Entry	Catalyst	Yield (%)
1	none	0	8	$[Ru(p\text{-cymene})Cl_2]_2$	0
2	G-I	43[a]	9	$(Ph_3P)_3RhCl$	15[b]
3	G-II	76[a]	10	$Rh_2(O_2CCH_3)_4$	<3[b]
4	HG-II	66[a]	11	$Rh(O_2C_5H_7)_3$	<3[b]
5	$Ru_3(CO)_{12}$	10[b]	12	$Pd(OAc)_2$	0
6	[Cp*Ru(COD)Cl]	0	13	$PtCl_2$	0
7	$[CpRu(CH_3CN)_3]PF_6$	0	14	$(Ph_3P)AuCl$	0

[a] Isolated yields. [b] ^1H NMR yield.

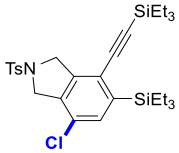
General procedure for hydrohalogenation

Grubbs second-generation catalyst (5 mol %) and *bis*-1,3-diyne (0.1 mmol) were dissolved in 2 mL of selected halogen-contained solvent (CH_2Cl_2, CH_2Br_2, or CH_2I_2) in a thick-walled 25 mL Schlenk tube equipped with a magnetic stirring bar. The reaction vessel was degased under vacuum and refilled with argon. The reaction vessel was stirred in an oil bath at 80 °C for 8 h. The solvent was removed under reduced pressure and the organic product was isolated by column chromatography on silica gel using Hex/EtOAc (1:20 to 1:1) as eluting solvents.

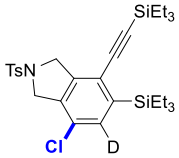
Characterization Data



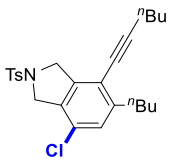
6a: Yield: 82%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 7.25 (s, 1H), 4.70 (s, 2H), 4.61 (s, 2H), 2.41 (s, 3H), 0.32 (s, 9H), 0.25 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 145.1, 143.8, 141.3, 135.3, 133.8, 133.2, 129.9, 128.6, 127.6, 121.5, 103.6, 102.0, 54.7, 53.9, 21.5, –0.3, –1.4; **HRMS** (ESI) calcd for $C_{23}H_{30}ClNO_2SSi_2$ $[M]^+$: 475.1224, found 475.1229.



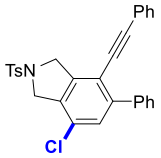
6b: Yield: 92%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.22 (s, 1H), 4.67 (s, 2H), 4.65 (s, 2H), 2.41 (s, 3H), 1.05 (t, *J* = 7.9 Hz, 6H), 0.91 (s, 15H), 0.70 (t, *J* = 7.9 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 143.8, 142.0 (2 peaks), 135.2, 134.2, 133.8, 129.9, 128.4, 127.5, 122.0, 103.0, 101.1, 54.9, 54.0, 21.5, 7.4, 7.3, 4.2, 3.0; **HRMS** (ESI) calcd for $C_{29}H_{42}ClNO_2SSi_2$ $[M]^+$: 559.2163, found 559.2164.



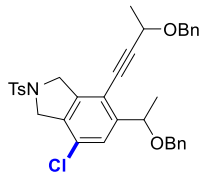
6b-*d*: This compound was formed when substrate **4b** was heated in CD_2Cl_2 in presence of 2nd generation Grubbs catalyst. **Yield**: 85%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 4.67 (s, 2H), 4.65 (s, 2H), 2.41 (s, 3H), 1.05 (t, *J* = 7.9 Hz, 9H) 0.92 (s, 15H), 0.69 (q, *J* = 7.9 Hz, 6H) ; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 143.8, 142.0, 141.9, 135.2, 133.8, 129.9, 128.4, 127.6, 122.0, 103.0, 101.1, 55.0, 54.0, 21.5, 7.44, 7.38, 4.3, 3.0; **HRMS** (ESI) calcd for $C_{29}H_{41}DClNO_2SSi_2$ $[M]^+$: 561.2304, found 561.2314.



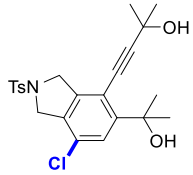
6c: Yield: 65%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.01 (s, 1H), 4.67 (s, 2H), 4.60 (s, 2H), 2.66 (m, 32), 2.45 (t, *J* = 7.0 Hz, 2H), 2.41 (s, 3H), 1.63–1.44 (m, 6H), 1.33 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H), 0.91 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 146.4, 143.8, 140.5, 133.8, 131.8, 129.9, 128.0, 127.6, 127.3, 117.1, 99.6, 75.4, 55.0, 53.8, 33.8, 32.7, 30.8, 22.4, 22.0, 21.5, 19.3, 13.9, 13.6; **HRMS** (ESI) calcd for $C_{25}H_{31}ClNO_2S$ $[M+H]^+$: 444.1764, found 444.1773.



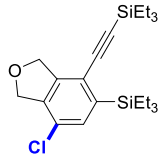
6d: Yield: 76%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.1 Hz, 2H), 7.57 (d, *J* = 7.0 Hz, 2H) 7.47–7.40 (m, 3H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.33)m, 5H), 7.30 (s, 1H), 4.87 (s, 2H), 4.72 (s, 2H), 2.43 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 145.2, 143.9, 141.0, 138.5, 133.7, 133.6, 131.5, 130.0, 129.1, 129.0, 128.8, 128.5, 128.4, 128.2, 128.1, 127.6, 122.5, 115.4, 97.5, 84.9, 55.0, 53.9, 21.5; **HRMS** (ESI) calcd for $C_{29}H_{23}ClNO_2S$ $[M+H]^+$: 484.1138, found 484.1129.



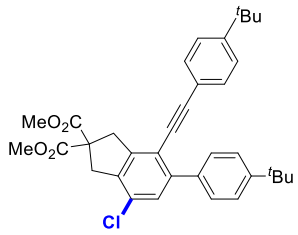
6f: Yield: 85%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.0 Hz, 2H), 7.45 (s, 1H), 7.42–7.22 (m, 12H), 4.91 (q, *J* = 6.3 Hz, 1H), 4.78–4.71 (m, 3H), 4.66 (s, 2H), 4.49 (dd, *J* = 2.1, 11.6 Hz, 2H), 4.47–4.42 (m, 2H), 4.30 (d, *J* = 8.0 Hz, 1H), 2.42 (s, 3H), 1.53 (t, *J* = 6.0 Hz, 3H), 1.43 (d, *J* = 6.3 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 147.9, 143.9, 140.7, 137.9, 137.6, 133.7, 129.9, 129.5, 128.5, 128.4, 127.9, 127.65, 127.55, 125.2, 114.4, 99.4, 78.6, 74.2, 70.8, 70.8, 64.9, 54.6, 53.7, 23.1, 22.1, 21.5; **HRMS** (ESI) calcd for $C_{35}H_{35}ClNO_4S$ $[M+H]^+$: 600.1975, found 600.1971.



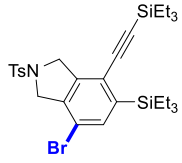
6g: Yield: 74%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.49 (s, 1H), 7.34 (d, *J* = 8.2 Hz, 2H), 4.68 (s, 2H), 4.60 (s, 2H), 2.69 (br, 1H), 2.42 (s, 3H), 2.36 (br, 1H), 1.67 (s, 6H), 1.63 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 152.0, 143.9, 142.3, 133.7, 133.1, 130.0, 128.8, 127.5, 125.0, 112.7, 105.5, 78.0, 72.9, 65.7, 54.9, 53.7, 31.1, 29.7, 21.5; **HRMS** (ESI) calcd for $C_{23}H_{27}ClNO_4S$ $[M+H]^+$: 448.1349, found 448.1349.



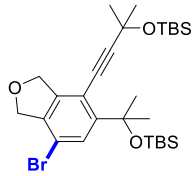
6h: Yield: 71%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.25 (s, 1H), 5.20 (s, 2H), 5.15 (s, 2H), 1.03 (t, *J* = 7.9 Hz, 9H), 0.95 (s, 15H), 0.68 (q, *J* = 7.9 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 145.2, 141.5, 138.0, 134.0, 127.5, 120.5, 103.6, 100.0, 75.2, 74.0, 7.4 (2 peaks), 4.3, 3.1; **HRMS** (ESI) calcd for $C_{22}H_{34}ClOSi_2$ $[M–H]^+$: 405.1837, found 405.1837.



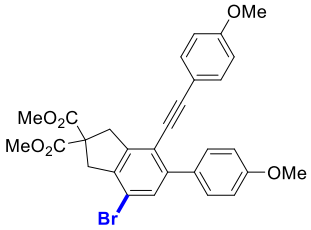
6j: Yield: 80%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.3 Hz, 2H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.34–7.25 (m, 5H), 3.87 (s, 2H), 3.81 (s, 6H), 3.74 (s, 2H), 1.39 (s, 9H), 1.31 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.8, 151.7, 150.7, 144.8, 144.2, 136.6, 136.3, 131.1, 129.8, 128.8, 128.3, 125.3, 124.9, 120.2, 116.8, 96.8, 86.0, 58.8, 53.2, 41.8, 40.3, 34.8, 34.6, 31.4, 31.1; **HRMS** (ESI) calcd for $C_{35}H_{37}ClO_4$ $[M]^+$: 556.2380, found 556.2381.



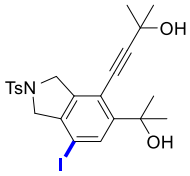
7b: Yield: 76%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.37 (s, 1H), 7.33 (d, *J* = 8.2 Hz, 2H), 4.70 (s, 2H), 4.61 (s, 2H), 2.41 (s, 3H), 1.65 (t, *J* = 7.9 Hz, 6H), 0.90 (s, 15H), 0.69 (t, *J* = 7.9 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 143.8, 142.1, 141.6, 137.3, 137.1, 133.6, 129.9, 127.6, 122.6, 117.2, 103.0, 101.3, 55.7, 55.1, 21.5, 7.2, 7.4, 4.2, 2.9; **HRMS** (ESI) calcd for $C_{29}H_{42}ClNO_2SSi_2$ $[M]^+$: 559.2163, found 559.2164.



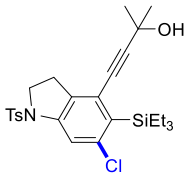
7i: Yield: 64%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.96 (s, 1H), 5.23 (s, 2H), 5.10 (s, 2H), 1.77 (s, 6H), 1.57 (s, 6H), 2.41 (s, 6H), 1.00 (s, 9H), 0.87 (s, 9H), 0.19 (s, 6H), 0.15 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 153.1, 145.4, 137.5, 128.4, 115.6, 111.4, 104.7, 79.0, 75.8, 75.6, 75.3, 67.1, 32.6, 30.1, 26.0, 25.6, 18.4, 17.9, –1.8, –2.8; **HRMS** (ESI) calcd for $C_{28}H_{46}BrO_3Si_2$ $[M–H]^+$: 525.2169, found 525.2181.



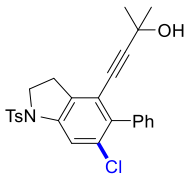
7k: Yield: 79%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.7 Hz, 2H), 7.41 (s, 1H), 7.31 (d, *J* = 8.8 Hz, 2H), 6.97 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 3.90 (s, 2H), 3.86 (s, 3H), 3.80 (s, 9H), 3.70 (s, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.8, 159.8, 159.4, 144.2, 143.7, 138.5, 132.9, 131.7, 131.1, 130.4, 118.6, 117.4, 115.3, 114.0, 113.4, 96.9, 85.4, 58.6, 55.3, 55.3, 53.2, 42.3, 42.0; **HRMS** (ESI) calcd for $C_{29}H_{25}BrO_6$ $[M]^+$: 548.0835, found 548.0843.



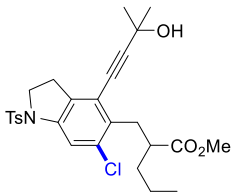
8g: Yield: 55%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.26 (s, 1H), 4.74 (s, 2H), 4.49 (s, 2H), 2.73(br, 1s), 2.51 (br, 1H), 2.41 (s, 3H), 1.67 (s, 6H), 1.63 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 151.3, 143.9, 140.8, 139.4, 133.8, 133.6, 130.0, 127.5, 114.2, 106.0, 89.8, 78.1, 72.7, 65.7, 58.6, 55.4, 31.1, 29.7, 21.5; **HRMS** (ESI) calcd for $C_{23}H_{27}INO_4S$ $[M+H]^+$: 540.0706, found 540.0701.



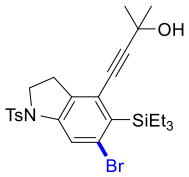
10a: Yield: 65%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.56 (s, 1H), 7.28 (d, *J* = 8.2 Hz, 2H), 3.89 (t, *J* = 8.6 Hz, 2H), 2.96 (t, *J* = 8.6 Hz, 2H), 2.40 (s, 3H), 1.92 (br, 1H), 1.56 (s, 6H); 1.04 (m, 6H), 0.94 (m, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 144.5, 143.0, 141.5, 134.3, 133.8, 130.7, 129.9, 127.3, 127.0, 115.5, 101.77, 80.9, 65.7, 49.5, 31.1, 28.2, 21.6, 7.8, 5.4; **HRMS** (ESI) calcd for $C_{26}H_{35}ClNO_3SSi$ $[M+H]^+$: 504.1795, found 504.1790.



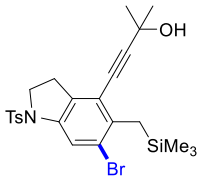
10d: Yield: 71%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.72 (s, 1H), 7.38 (m, 3H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 3.94 (t, *J* = 8.5 Hz, 2H), 2.98 (t, *J* = 8.5 Hz, 2H), 2.41 (s, 3H), 1.82 (br, 1H), 1.27 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 144.6, 141.7, 137.70, 137.67, 133.6, 132.9, 132.6, 129.99, 129.97, 127.8, 127.7, 127.3, 121.1, 115.1, 102.1, 78.3, 65.4, 49.9, 30.9, 27.8, 21.6; **HRMS** (ESI) calcd for $C_{26}H_{25}ClNO_3S$ $[M+H]^+$: 466.1244, found 466.1243.



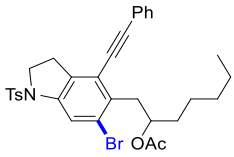
10g: Yield: 65%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.61 (s, 1H), 7.27 (d, *J* = 8.2 Hz, 2H), 3.93 (m, 2H), 3.60 (s, 3H), 3.18 (br, 1H), 3.13 (dd, *J* = 13.5, 7.7 Hz, 1H), 3.00 (dd, *J* = 13.5, 6.8 Hz, 1H), 2.91 (t, *J* = 8.5 Hz, 2H), 2.76 (m, 1H), 2.39 (s, 3H), 1.73 (m, 1H), 1.57 (s, 3H), 1.55 (s, 3H), 1.40 (m, 1H), 1.27 (m, 2H), 0.87 (t, *J* = 87.3 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 176.8, 144.4, 141.0, 134.0, 133.8, 133.6, 133.0, 129.8, 127.3, 121.2, 115.3, 103.1, 77.4, 65.2, 51.8, 49.8, 45.3, 34.5, 34.0, 31.4, 31.0, 27.7, 21.5, 20.7, 13.9; **HRMS** (ESI) calcd for $C_{27}H_{33}ClNO_5S$ $[M+H]^+$: 518.1768, found 518.1778.



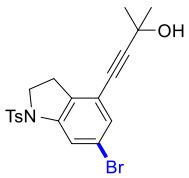
11a: Yield: 61%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.71 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 3.88 (t, *J* = 8.5 Hz, 2H), 2.93 (t, *J* = 8.5 Hz, 2H), 2.40 (s, 3H), 1.92 (br, 1H), 1.56 (s, 6H); 1.06 (m, 6H), 0.94 (m, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 144.5, 143.0, 135.0, 133.7, 132.9, 130.4, 129.9, 127.7, 127.3, 119.1, 102.0, 80.9, 65.7, 49.4, 31.1, 28.4, 21.6, 7.9, 5.7; **HRMS** (ESI) calcd for $C_{26}H_{35}BrNO_3SSi$ $[M+H]^+$: 540.1290, found 540.1294.



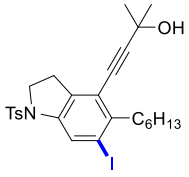
11c: Yield: 63%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.66–7.64 (m, 2H), 7.25–7.23 (m, 2H), 3.88 (t, 2H, *J* = 8.5 Hz), 2.84 (t, 2H, *J* = 8.5 Hz), 2.49 (s, 2H), 2.38 (s, 3H), 1.91 (brs, 1H), 1.57 (s, 6H), 0.05 (s, 9H); **^{13}C NMR** (125 MHz. $CDCl_3$): δ 144.3, 138.9, 138.5, 134.5, 133.6, 129.8, 127.3, 122.0, 119.2, 119.0, 102.1, 79.1, 65.7, 49.8, 31.6, 28.2, 25.3, 21.6, –0.2; **HRMS** (ESI) calcd for $C_{24}H_{31}NO_3SSiBr$ $[M+H]^+$ 520.0977, found 520.0978.



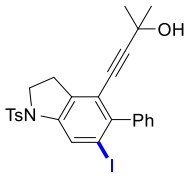
11f: Yield: 63%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.47 (m, 2H), 7.35 (m, 3H), 7.28 (d, *J* = 8.0 Hz, 2H), 5.29 (m, 1H), 3.93 (t, *J* = 8.5 Hz, 2H), 3.27 (dd, *J* = 13.5, 9.0 Hz, 1H), 3.16 (dd, *J* = 13.5, 4.0 Hz, 1H), 2.98 (m, 2H), 2.39 (s, 3H), 1.90 (s, 3H), 1.65 (m, 2H), 1.44–1.16 (m, 6H), 0.84 (t, *J* = 6.4 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.3, 144.5, 141.3, 134.4, 134.2, 133.7, 131.5, 129.9, 128.9, 128.5, 127.3, 124.2, 122.6, 122.0, 118.8, 97.8, 85.1, 73.8, 49.9, 38.9, 34.7, 31.7, 28.0, 25.1, 22.5, 21.6, 21.1, 14.0; **HRMS** (ESI) calcd for $C_{32}H_{35}BrNO_4S$ $[M+H]^+$: 608.1470, found 608.1468.



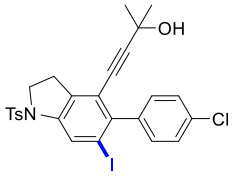
11h: Yield: 71%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.68 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 7.14 (s, 1H), 3.90 (t, *J* = 8.6 Hz, 2H), 2.90 (t, *J* = 8.6 Hz, 2H), 2.39 (s, 3H), 2.02 (br, 1H), 1.56 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 144.6, 143.2, 133.6, 133.2, 129.9, 128.8, 127.2, 121.2, 120.9, 117.6, 99.1, 78.1, 65.5, 49.8, 31.4, 27.2, 21.6; **HRMS** (ESI) calcd for $C_{20}H_{21}BrNO_3S$ $[M+H]^+$: 434.0426, found 434.0418.



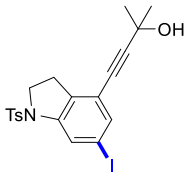
12b: Yield: 55%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 3.87 (t, *J* = 8.5 Hz, 2H), 2.89 (d, *J* = 8.5 Hz, 2H), 2.83 (m, 2H), 2.39 (s, 3H), 1.94 (br, 1H), 1.58 (s, 6H), 1.49 (m, 2H), 1.40 (m, 2H), 1.31 (m, 4H), 0.89 (m, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 144.4, 142.0, 140.5, 135.3, 133.6, 129.8, 127.3, 124.9, 119.2, 101.6, 97.9, 78.2, 65.7, 49.8, 39.2, 31.6, 31.5, 29.5, 29.3, 27.9, 22.6, 21.6, 14.1; **HRMS** (ESI) calcd for $C_{26}H_{33}INO_3S$ $[M+H]^+$: 566.1226, found 566.1229.



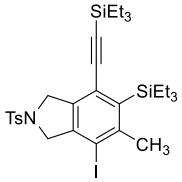
12d: Yield: 51%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.38 (m, 3H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 8.2 Hz, 2H), 3.94 (t, *J* = 8.5 Hz, 2H), 2.96 (t, *J* = 8.5 Hz, 2H), 2.43 (s, 3H), 1.59 (br, 1H), 1.23 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 144.6, 143.7, 143.2, 141.9, 134.4, 133.7, 129.9, 129.7, 127.8, 127.7, 127.4, 124.0, 119.9, 102.1, 97.3, 78.7, 65.4, 49.9, 30.9, 27.8, 21.6; **HRMS** (ESI) calcd for $C_{26}H_{25}INO_3S$ $[M+H]^+$: 558.0600, found 558.0589.



12e: Yield: 61%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.2 Hz, 2H), 3.93 (t, *J* = 8.5 Hz, 2H), 2.96 (t, *J* = 8.5 Hz, 2H), 2.42 (s, 3H), 1.67 (br, 1H), 1.27 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 144.6, 142.18, 142.15, 141.4, 134.7, 133.8, 133.6, 131.2, 130.0, 128.1, 127.3, 124.0, 119.9, 102.4, 97.2, 78.4, 65.4, 49.9, 31.0, 27.8, 21.6; **HRMS** (ESI) calcd for $C_{26}H_{24}ClINO_3S$ $[M+H]^+$: 592.0210, found 592.0209.

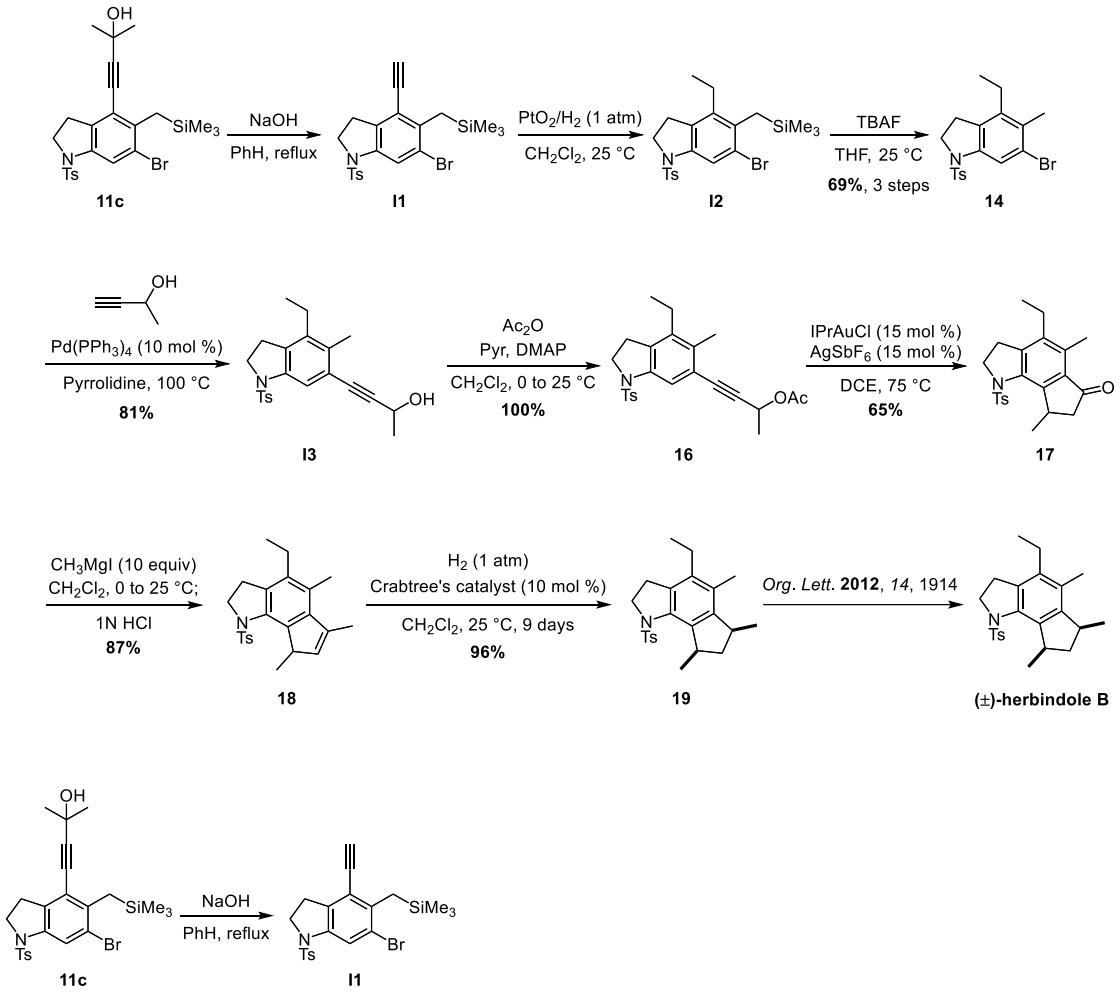


12h: Yield: 63%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.35 (s, 1H), 7.28 (d, *J* = 8.2 Hz, 2H), 3.89 (t, *J* = 8.6 Hz, 2H), 2.90 (d, *J* = 8.6 Hz, 2H), 2.40 (s, 3H), 1.98 (br, 1H), 1.55 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 144.6, 143.1, 134.8, 134.0, 133.6, 129.9, 127.2, 123.2, 121.6, 99.1, 91.6, 77.8, 65.6, 49.7, 31.4, 27.3, 21.6; **HRMS** (ESI) calcd for $C_{20}H_{21}INO_3S$ $[M+H]^+$: 482.0287, found 482.0287.

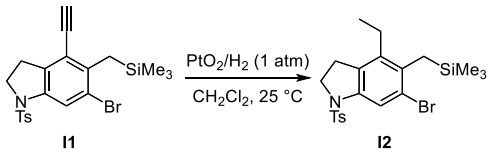


8b': This compound was produced in a reaction of substrate **4a** with CH_3I in presence of 2nd generation Grubbs catalyst. It was isolated as a mixture along with **8a** (**8a'**/**8a** ~3.5:1). **Total yield**: 68%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.78 – 7.76 (m, 2H), 7.33 – 7.31 (m, 2H), 4.72 (s, 2H), 4.58 (s, 2H), 2.52 (s, 3H), 2.41 (s, 3H), 1.07 – 0.99 (m, 15 H), 0.72 – 0.67 (m, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 146.4, 143.8, 143.7, 143.2, 142.2, 141.9, 141.4, 140.7, 138.7, 138.4, 133.8, 129.92, 129.87, 127.6, 124.7, 103.9, 103.1, 102.9, 101.7, 99.6, 61.0, 59.0, 56.3, 55.4, 29.4, 21.5, 7.9, 7.5, 7.4, 5.9, 4.2, 3.0.

Formal Synthesis of (±)-Herbindole B:

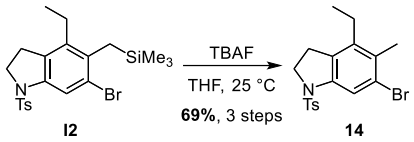


NaOH beads (97 mg, 2.42 mmol) were added to a solution of **11c** (630 mg, 1.21 mmol) in benzene and the mixture was stirred with refluxing for 20 h (progress was monitored by TLC). After completion of the reaction, the reaction mixture was concentrated under reduced pressure, diluted with EtOAc, washed with water (2×10 mL) and brine (1×10 mL). The organic layer was separated and dried over anhydrous $MgSO_4$, filtered through a small pad of silica gel, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (Hex/EtOAc 20:1 to 10:1) to get 453 mg of **I1** (81%). Otherwise, was used for the next reaction without further purification. HRMS (ESI) calcd for $C_{21}H_{25}NO_2SSiBr$ $[M+H]^+$ 462.0559, found 462.0557.



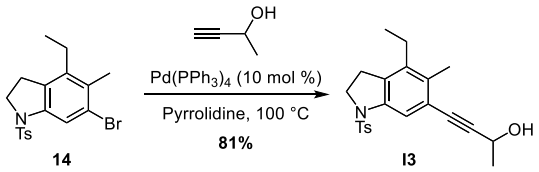
I1 **I2**

PtO_2 (45 mg, 10 wt%) was added to a solution of **I1** (453 mg, 0.98 mmol) in MeOH (10 mL) under N_2 balloon. The N_2 balloon was replaced with an H_2 balloon and the reaction mixture was stirred for 1 h at 25 °C. A small amount of the reaction mixture was used to take crude NMR for checking the progress of the reaction (completed within an hour). The crude product was passed through a celite/silica gel pad to filter off solid PtO_2 and the filtrate was concentrated under reduced pressure. The crude product **I2** was used for the next reaction.



I2 **14**

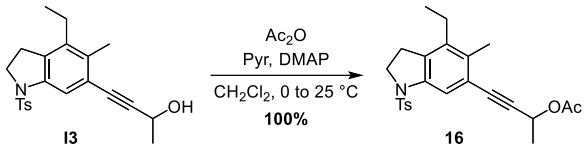
To a solution of crude materials of **I2** in dry THF was added 1.1 mL TBAF (1M in THF, 1.1 mmol) at 25 °C and the reaction mixture was stirred at the same temperature for 90 min (or until complete consumption of starting material, monitored by TLC). The reaction mixture was transferred to a separatory funnel, diluted with EtOAc, washed with water (2×10 mL) and brine (1×10 mL). The organic layer was separated, dried over anhydrous $MgSO_4$, filtered through a plug of cotton, and concentrated under reduced pressure. The crude product was then purified by flash column chromatography (Hex/EtOAc 20:1 to 10:1) to get 312 mg of **13** (81% over 2 steps). When the above reaction sequence was followed without column purification of **I1** and **I2**, 330 mg (69% over 3 steps) of **14** was isolated after purification by column chromatography as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72 (s, 1H), 7.68 (d, 2H, *J* = 10.0 Hz), 7.25 (d, 2H, *J* = 10.0 Hz), 3.88 (t, 2H, *J* = 10.0 Hz), 2.78 (t, 2H, *J* = 5.0 Hz), 2.50 (q, 2H, *J* = 7.5 Hz), 2.38 (s, 3H), 2.31 (s, 3H), 1.01 (t, 3H, *J* = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.1, 140.4, 140.3, 133.8, 130.4, 129.7, 129.5, 127.4, 124.8, 116.4, 49.8, 26.6, 24.6, 21.6, 18.3, 13.2; HRMS (ESI) calcd for$C_{18}H_{21}NO_2SBr$ $[M+H]^+$ 394.0476, found 394.0483.



14 **I3**

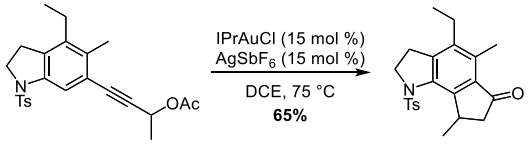
$Pd(PPh_3)_4$ (61 mg, 0.053 mmol) was added to a solution of **14** (209 mg, 0.53 mmol), 3-butyn-2-ol (186 mg, 2.65 mmol) and in pyrrolidine (10 mL) under N_2 balloon. The reaction mixture was stirred for 45 h at 100 °C. After the completion of the reaction (monitored by TLC), the reaction mixture was concentrated under reduced pressure and loaded on a silica gel column. After purification (Hex/EtOAc 5:1 to 3:1) 165 mg of pure **I3** was isolated (81%) as colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 (d, 2H, *J* = 8.0

Hz), 7.57 (s, 1H), 7.22 (d, 2H, *J* = 8.0 Hz), 4.82 (q, 1H, *J* = 6.5 Hz), 3.87 (t, 2H, *J* = 8.5 Hz), 2.79 (t, 2H, *J* = 8.5 Hz), 2.45 (q, 2H, *J* = 7.5 Hz), 2.36 (s, 3H), 2.33 (s, 3H), 1.59 (d, 3H, *J* = 6.5 Hz), 0.98 (t, 3H, *J* = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.0, 139.4, 139.3, 134.0, 133.6, 131.1, 129.7, 127.4, 122.4, 115.9, 94.4, 83.8, 59.0, 49.7, 26.8, 24.6, 23.8, 21.5, 16.2, 13.1; HRMS (ESI) calcd for $C_{22}H_{26}NO_3S$ $[M+H]^+$ 384.1633, found 384.1635.



I3 **16**

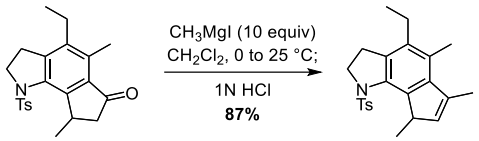
To a solution of **I3** (106 mg, 0.276 mmol) in CH_2Cl_2 (5 mL) was added Ac_2O (29 µL, 0.307 mmol), pyridine (26 µL, 0.321 mmol), and DMAP (3 mg, 0.025 mmol) at 0 °C. The reaction mixture was stirred at the same temperature for 5 minutes and then warmed up to 25 °C. After completion of the reaction (monitored by TLC) the reaction mixture was concentrated under reduced pressure and purified by flash column chromatography (Hex/EtOAc 10:1 to 5:1) which yielded 117 mg **16** (100%) as a colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 (d, 2H, *J* = 8.5 Hz), 7.58 (s, 1H), 7.23 (d, 2H, *J* = 8.5 Hz), 5.73 (q, 1H, *J* = 6.5 Hz), 3.86 (t, 2H, *J* = 8.3 Hz), 2.79 (t, 2H, *J* = 8.5 Hz), 2.45 (q, 2H, *J* = 7.5 Hz), 2.37 (s, 3H), 2.32 (s, 3H), 2.13 (s, 3H), 1.62 (d, 2H, *J* = 7.0 Hz), 0.98 (t, 3H, *J* = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.1, 144.0, 139.4, 139.3, 134.0, 133.8, 131.3, 129.7, 127.4, 122.0, 116.0, 90.8, 84.4, 61.0, 49.7, 26.8, 23.8, 21.6, 21.6, 21.2, 16.2, 13.1; HRMS (ESI) calcd for $C_{24}H_{28}NO_4S$ $[M+H]^+$ 426.1739, found 426.1738.



16 **17**

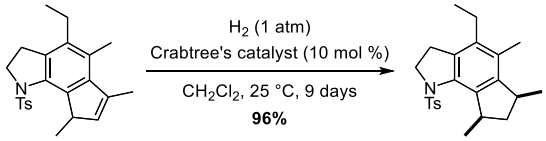
A solution of IPrAuCl (4.6 mg, 0.0074 mmol) and $AgSbF_6$ (2.6 mg, .0076 mmol) in anhydrous 1,2-dichloroethane (DCE, 2 mL) (a white solid appeared) was added to a solution of **16** (63 mg, 0.148 mmol) in 15 mL DCE at 25 °C under N_2 balloon. The reaction mixture was stirred at 75 °C for 1 day, and the same amount of IPrAuCl and $AgSbF_6$ (solution in DCE) was added in two additional portions which resulted in addition of total 15 mol % IPrAuCl and $AgSbF_6$ over 2 days for the complete conversion to **17** occurred. At this stage the reaction mixture was concentrated under reduced pressure and purified by flash column chromatography (Hex/EtOAc 20:1 to 10:1) to provide 37.1 mg of **17** (65%) as a colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 (d, 2H, *J* = 8.5 Hz), 7.13 (d, 2H, *J* = 8.0 Hz), 4.23–4.17 (m, 2H), 3.80 (dt, 1H, *J* = 12.5, 8.5 Hz), 2.99 (dd, 2H, *J* = 19.0, 5.0 Hz), 2.60 (s, 3H), 2.52–2.45 (m, 1H), 2.36 (s, 3H), 2.34–2.32 (m, 2H), 2.25 (dd, 1H, *J* = 18.5, 3.5 Hz), 1.89 (m, 1H), 1.44 (dd, 3H, *J* = 7.0 Hz), 0.82 (t, 3H, *J* = 8.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 207.8, 150.4, 144.2, 142.8, 138.9, 137.3, 135.5, 135.0, 134.0, 129.5, 127.6,

52.1, 46.2, 30.5, 28.0, 22.6, 21.5, 19.3, 13.1; HRMS (ESI) calcd for $C_{22}H_{26}NO_3S$ $[M+H]^+$ 384.1633, found 384.1632.



17 **18**

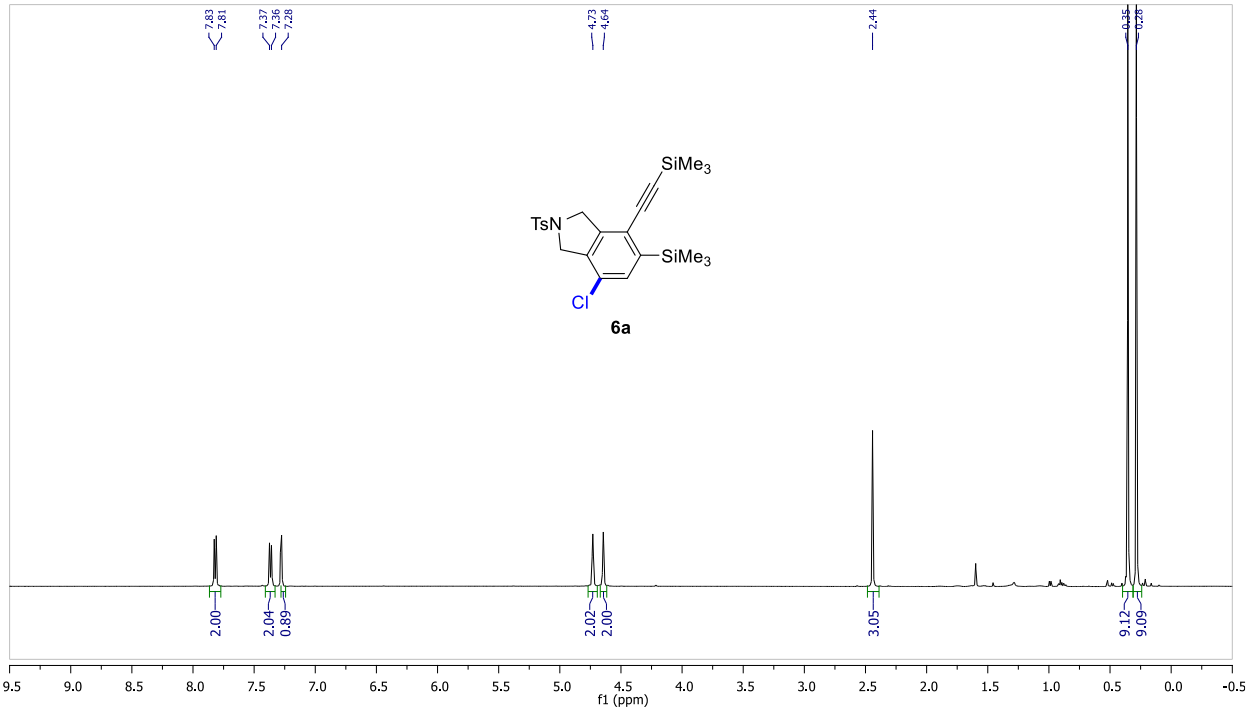
To a solution of **17** (36 mg, 0.094 mmol) in dry CH_2Cl_2 (5 mL) was added 0.3 mL CH_3MgI (3M in THF, 0.9 mmol) at 0 °C under N_2 atmosphere and warmed up to 25 °C and stirred overnight. After complete consumption of the starting material (monitored by TLC) 5 mL 1N HCl was added and the reaction mixture was stirred for 5 min at 25 °C. The biphasic mixture was transferred to a separatory funnel, diluted 5 mL with CH_2Cl_2 and washed with water (2×5 mL) and brine (1×5 mL). The organic layer was separated, dried over anhydrous $MgSO_4$, filtered through a cotton plug, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (Hex/EtOAc 40:1 to 20:1) to provide 31 mg of **18** (87%) as colorless liquid.^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 (d, 2H, *J* = 8.0 Hz), 7.10 (d, 2H, *J* = 8.0 Hz), 6.14 (s, 1H), 4.25 (m, 1H), 4.14 (dd, 2H, *J* = 13.0, 7.5 Hz), 3.75 (dt, 1H, *J* = 12.5, 8.5 Hz), 2.52–2.45 (m, 4H), 2.37–2.27 (m, 8H), 1.90–1.83 (m, 1H), 1.39 (d, 3H, *J* = 7.5 Hz), 0.83 (t, 3H, *J* = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.1, 143.6, 140.3, 139.5, 138.2, 137.4, 135.8, 134.5, 132.2, 129.2, 127.6, 52.3, 42.5, 27.5, 23.5, 21.5, 18.7, 14.4, 13.6, 13.5; HRMS (ESI) calcd for $C_{23}H_{28}NO_2S$ $[M+H]^+$ 382.1841, found 382.1837.



18 **19**

To a solution of **18** (14 mg, 0.037 mmol) in dry CH_2Cl_2 was added Crabtree's catalyst (3 mg, 0.0037 mmol) in glove box. After taking the flask out of glove box, an N_2 balloon was placed. The solution was cooled to –78 °C and degassed followed by filled with N_2. This process was repeated twice. Then the pressure was reduced and now an H_2 balloon was placed. Pressure was reduced again and refilled with H_2 by a balloon and the balloon was kept to maintain positive pressure of H_2. The reaction mixture was warmed up to 25 °C (color of the solution changed to yellow indicating generation of active catalyst) and stirred at this temperature and pressure for 9 days [TLC monitoring to check the progress of the reaction is tricky as the R_f of product is almost same as that of starting material (R_f of product is slightly higher though). However use of *p*-anisaldehyde stain was fruitful as they show different color]. After complete consumption of the starting material (as suggested by TLC) the reaction mixture was concentrated under reduced pressure and purified by flash column chromatography (Hex/EtOAc 20:1 to 10:1) to afford 13.5 mg **19** (96%) as a colorless oil. The characterization data matched with the reported data (N. Saito, T. Ichimaru, Y. Sato, *Org*.

Lett. **2012**, *14*, 1914). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 (d, 2H, *J* = 8.5 Hz), 7.10 (d, 2H, *J* = 8.0 Hz), 4.14–4.09 (m, 2H), 3.73 (dt, 1H, *J* = 12.5, 8.5 Hz), 3.37–3.30 (m, 1H), 2.67 (dt, 1H, *J* = 13.0, 9.3 Hz), 2.46 (m, 1H), 2.24 (m, 1H), 2.23 (s, 3H), 1.80 (m, 1H), 1.41 (dt, 1H, *J* = 13.0, 3.0 Hz), 1.39 (d, 3H, *J* = 7.0 Hz), 1.26 (d, 3H, *J* = 7.0 Hz), 0.80 (t, 3H, *J* = 7.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.4, 143.6, 138.5, 137.3, 136.3, 134.6, 130.1, 129.2, 129.1, 127.7, 127.6, 52.5, 41.3, 38.9, 37.6, 27.3, 23.3, 23.1, 21.5, 21.4, 15.1, 13.2; HRMS (ESI) calcd for $C_{23}H_{30}NO_2S$ $[M+H]^+$ 384.1997, found 384.2003.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7.36
7.28
4.73
4.64
2.44
0.35
0.28
SiMe3
TsN
SiMe3
Cl
6a
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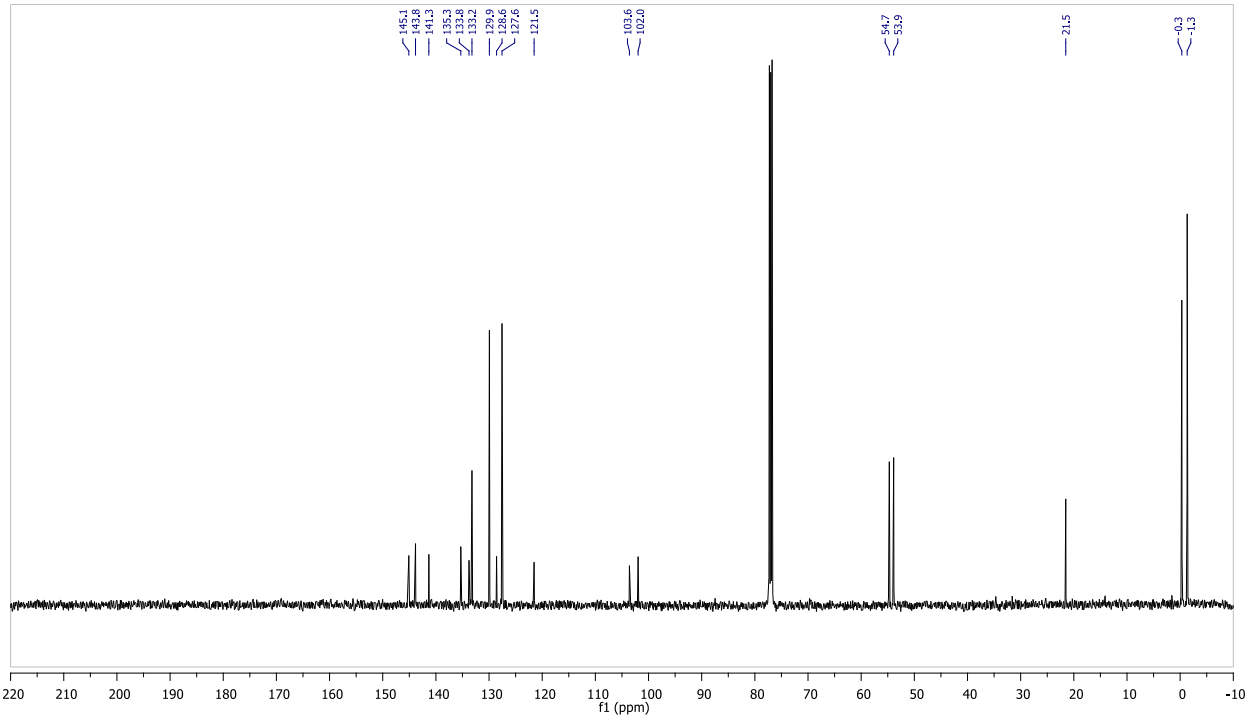
2.04
0.89
2.02
2.00
3.05
9.12
9.09
f1 (ppm)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133.2
129.9
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103.6
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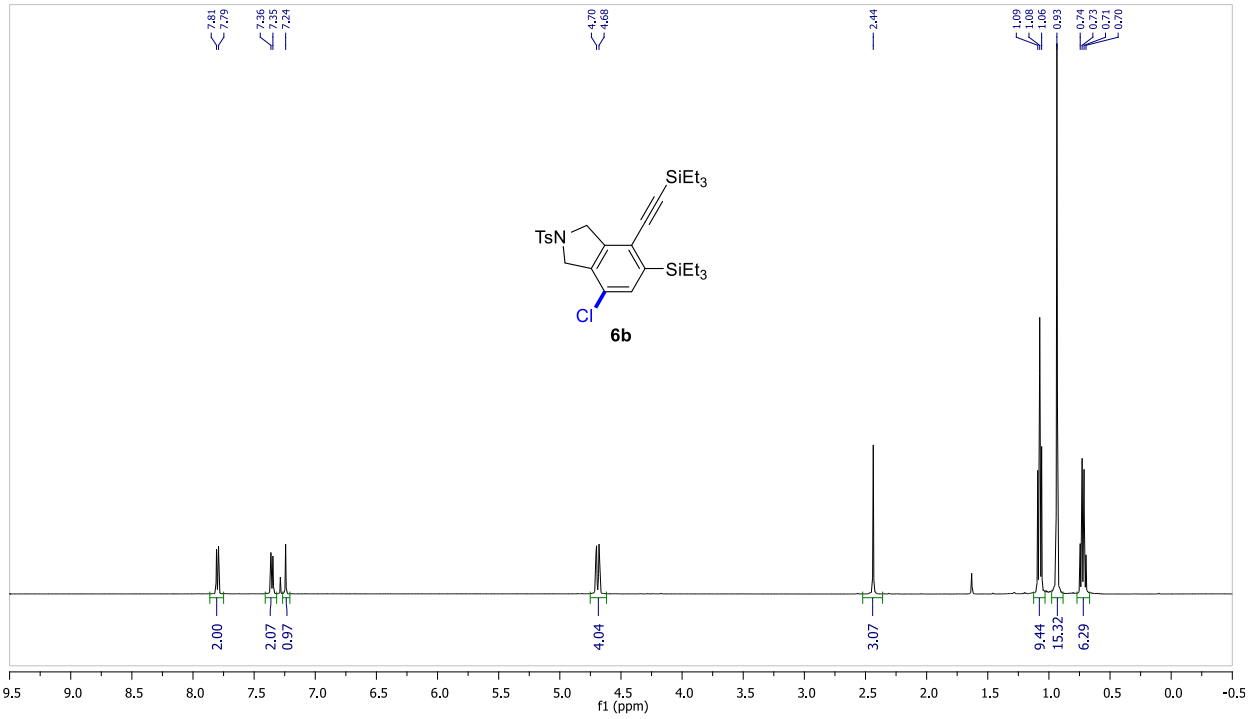
21.5
-0.3
-1.3
f1 (ppm)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7.35
7.24
4.70
4.68
2.44
1.09
1.08
1.06
0.93
0.74
0.73
0.71
0.70
SiEt3
TsN
SiEt3
Cl
6b
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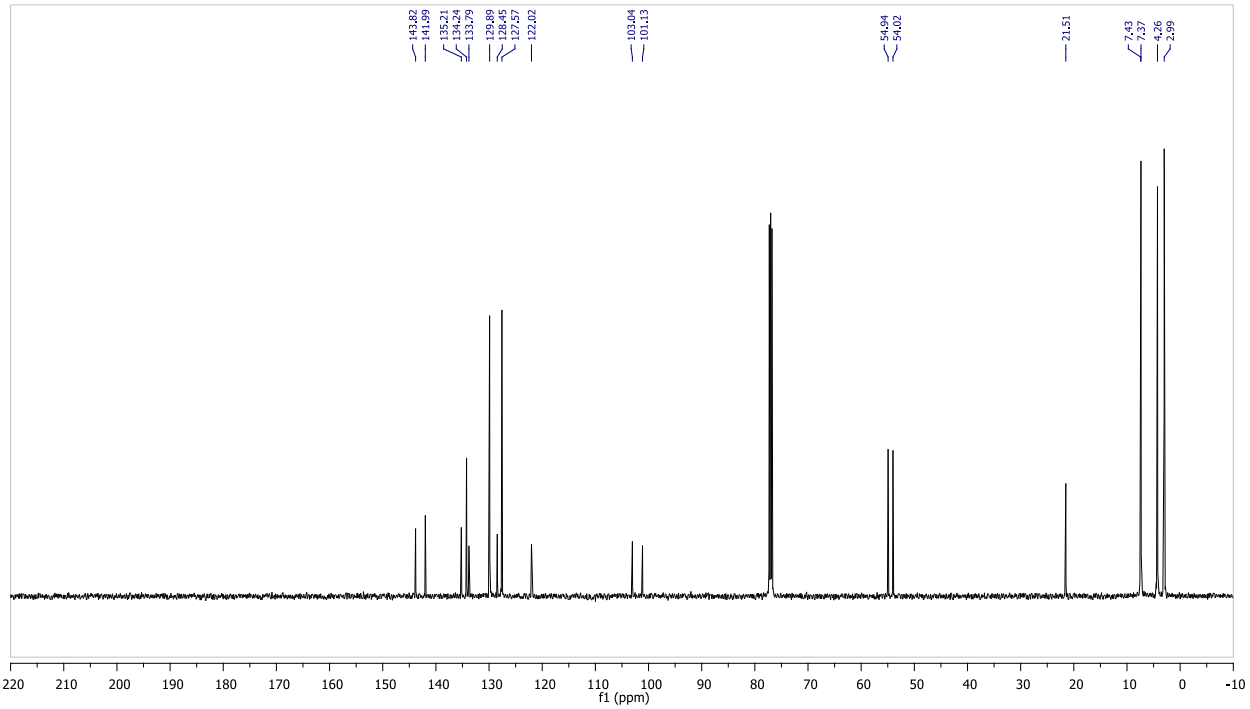
2.07
0.97
4.04
3.07
9.44
15.32
6.29
f1 (ppm)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129.89
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7.37
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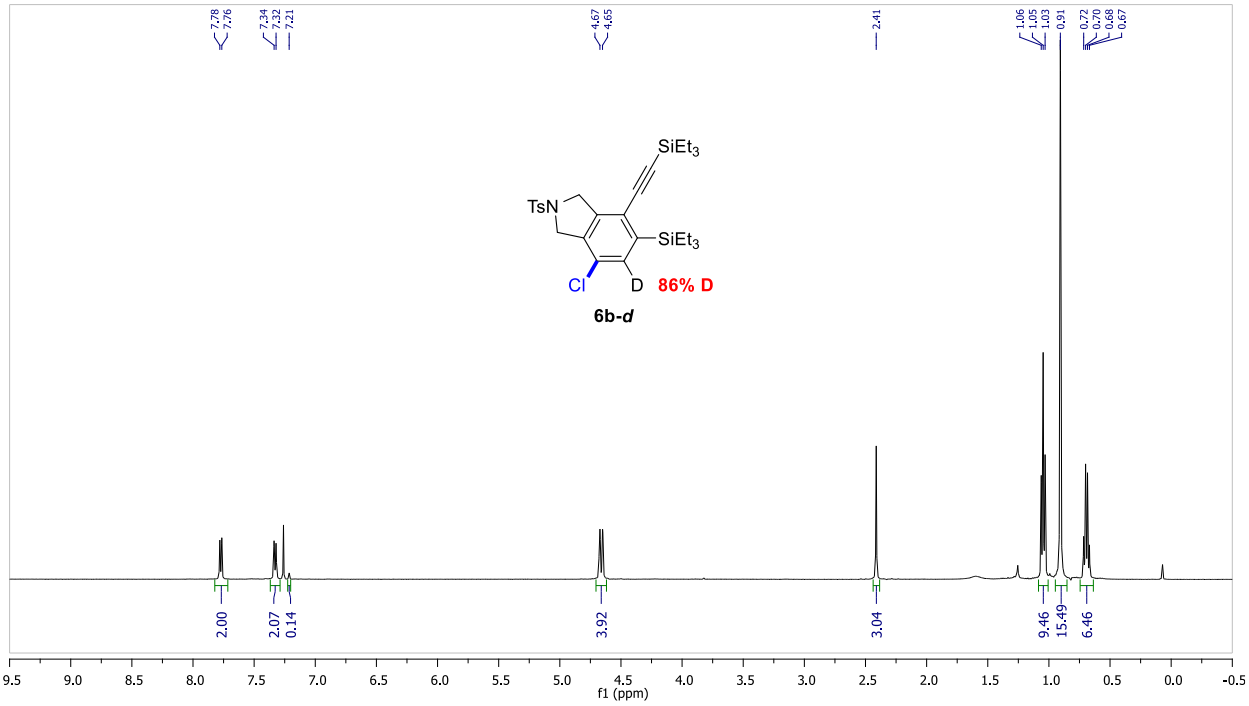
2.99
f1 (ppm)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7.34
7.32
7.21
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4.65
2.41
1.06
1.05
1.03
0.91
0.72
0.70
0.68
0.67
SiEt3
TsN
SiEt3
Cl
D
86% D
6b-d
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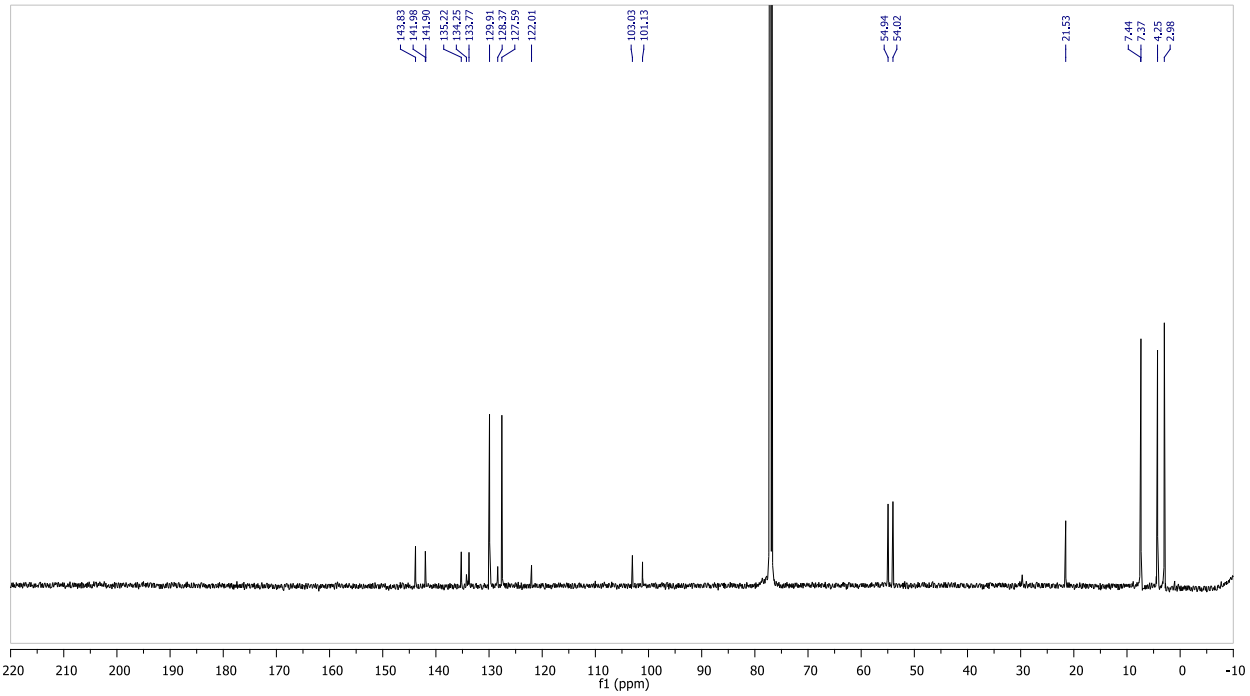
2.07
0.14
3.92
3.04
9.46
15.49
6.46
f1 (ppm)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129.91
128.37
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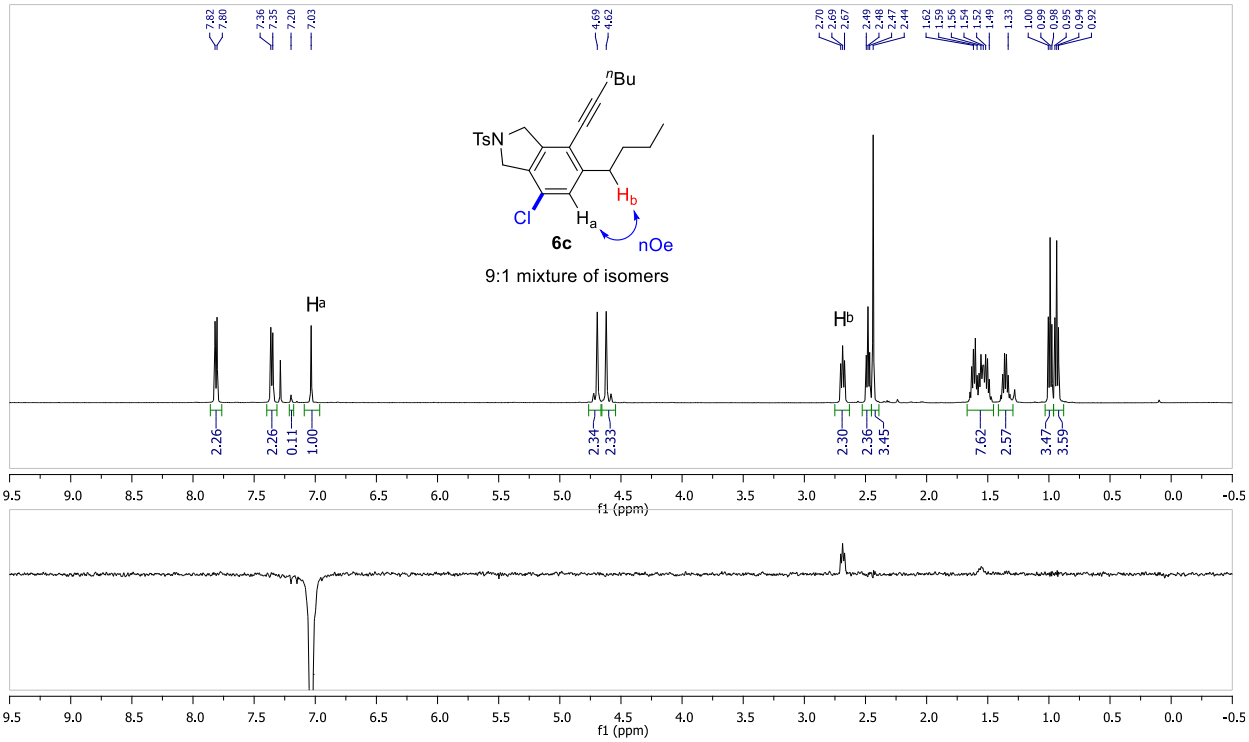
101.13
54.94
54.02
21.53
7.44
7.37
4.25
2.98
f1 (ppm)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7.20
7.03
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4.62
2.70
2.69
2.67
2.49
2.48
2.47
2.44
1.62
1.59
1.56
1.54
1.52
1.49
1.33
1.00
0.99
0.98
0.95
0.94
0.92
nBu
TsN
Hb
Cl
Ha
6c
nOe
9:1 mixture of isomers
Ha
Hb
2.26
2.26
0.11
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2.33
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2.36
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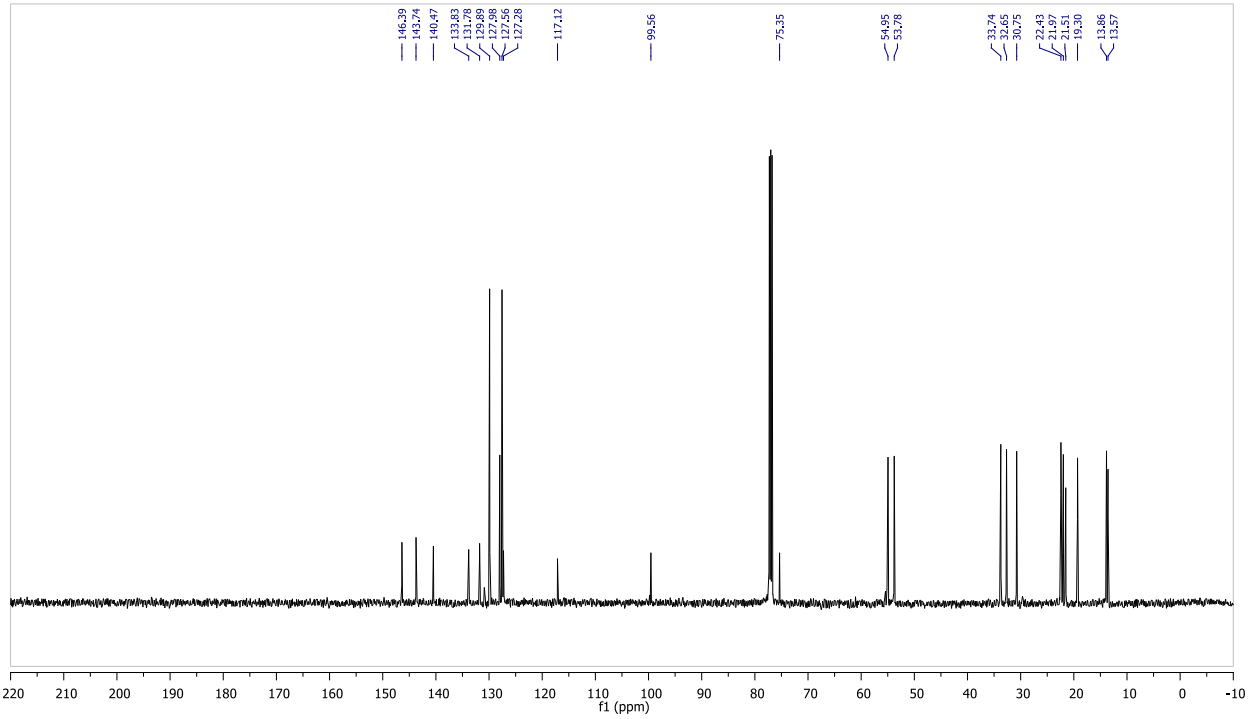
7.62
2.57
3.47
3.59
f1 (ppm)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19.30
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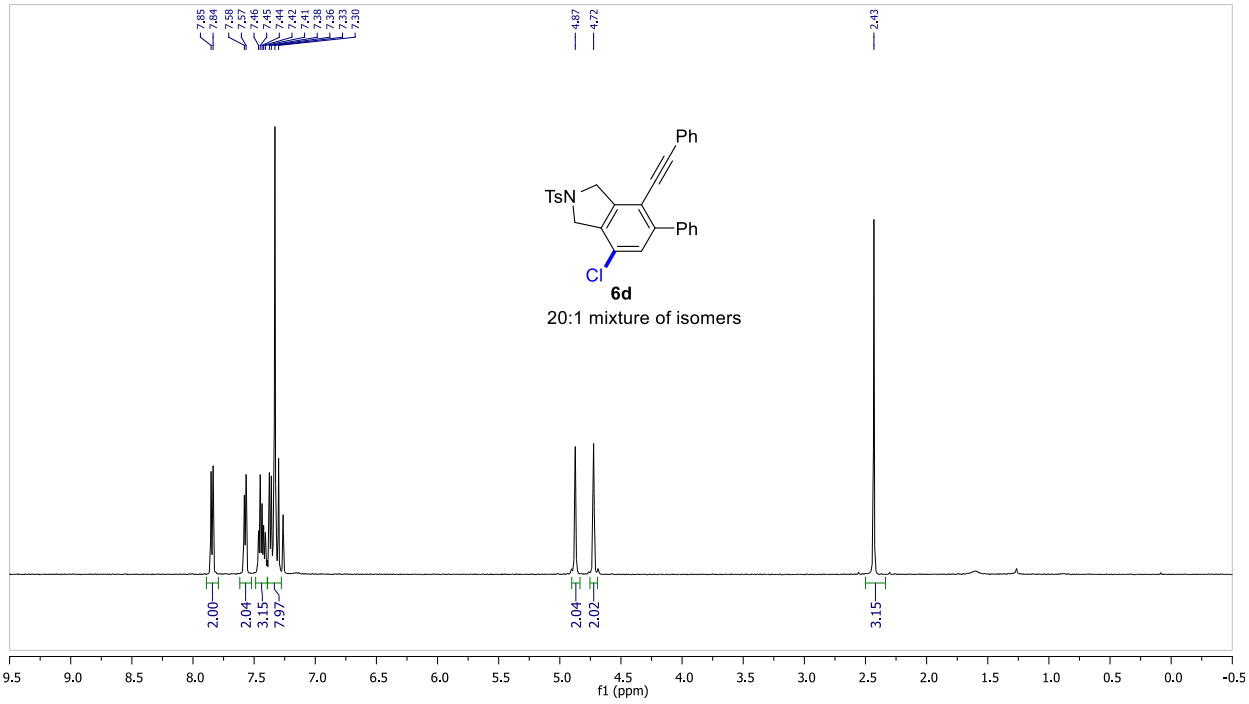
13.57
f1 (ppm)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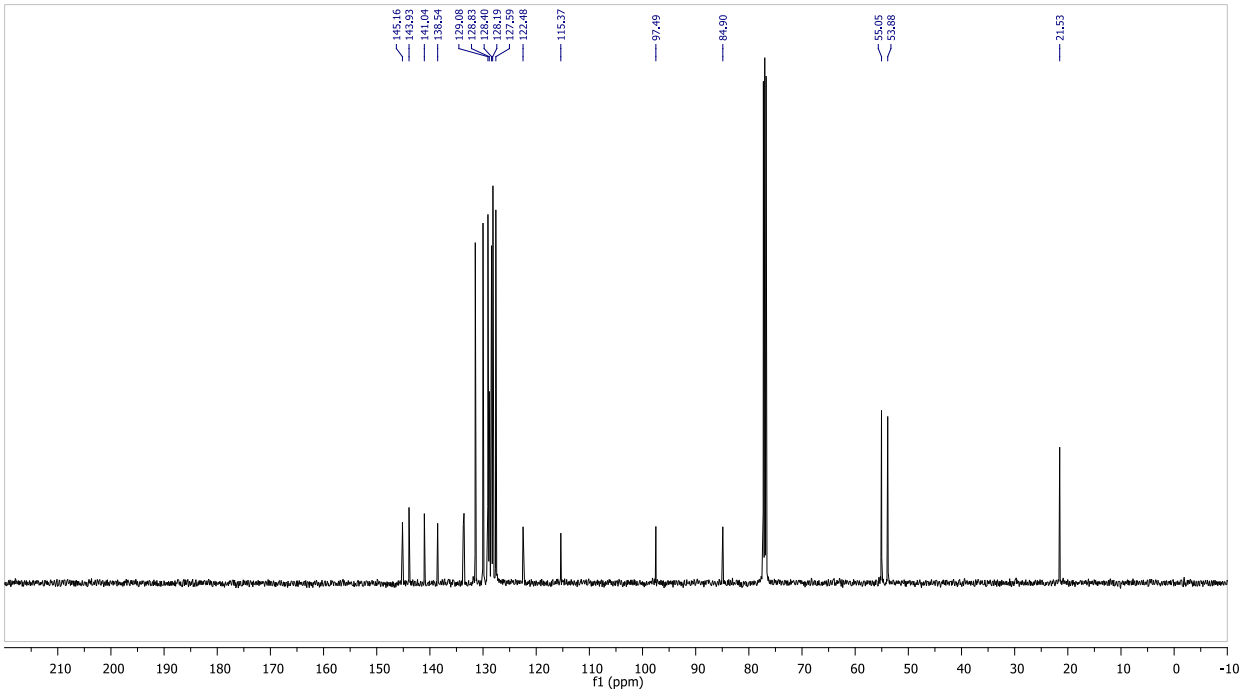
7.45
7.44
7.42
7.41
7.38
7.35
7.33
7.30
4.87
4.72
2.43
Ph
TsN
Ph
Cl
6d
20:1 mixture of isomers
2.00
2.04
3.15
7.97
2.04
2.02
3.15
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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141.04
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128.40
128.19
127.59
122.48
115.37
97.49
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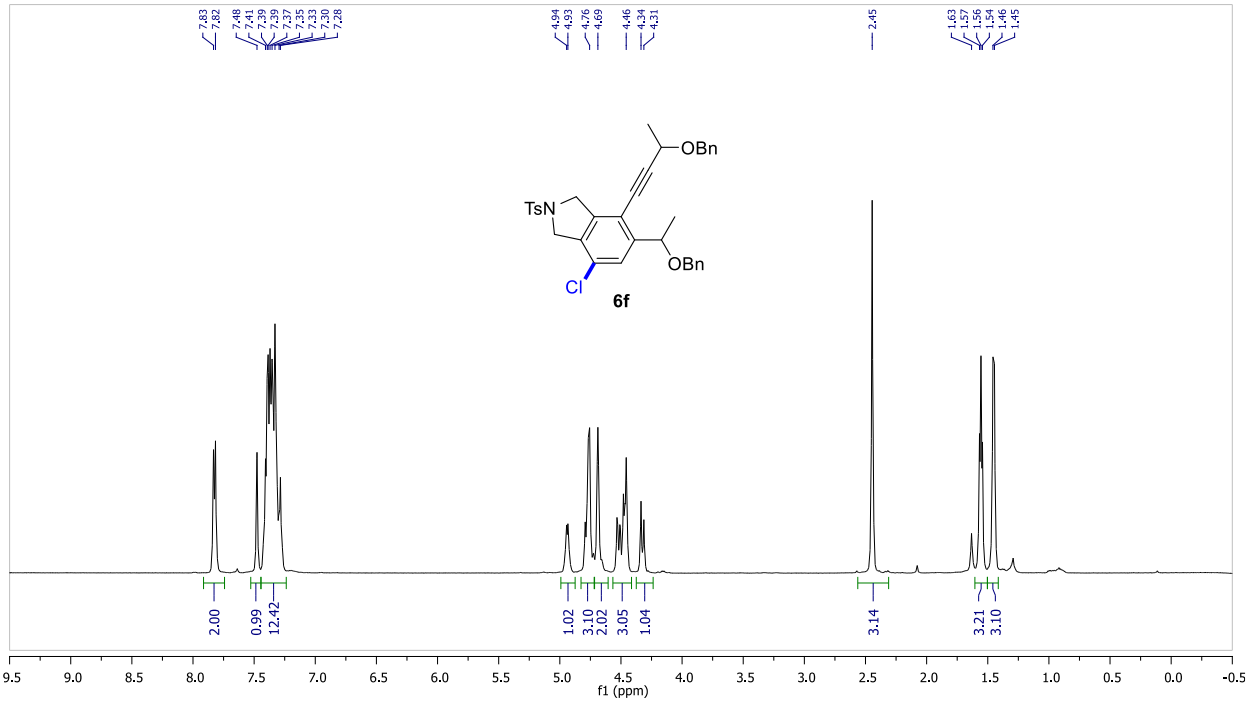
55.05
53.88
21.53
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.39
7.39
7.37
7.35
7.33
7.30
7.28
4.94
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4.76
4.69
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4.31
2.45
1.63
1.57
1.56
1.54
1.46
1.45
OBn
TsN
OBn
Cl
6f
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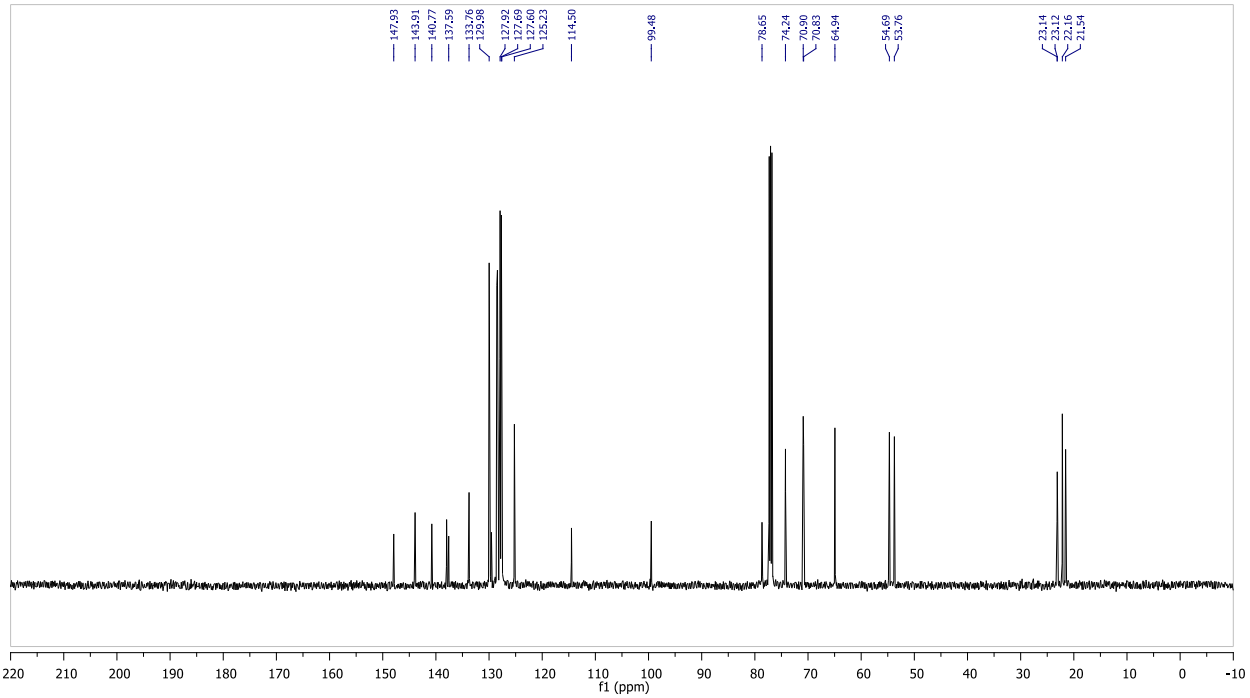
1.02
3.10
2.02
3.05
1.04
3.14
3.21
3.10
f1 (ppm)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127.60
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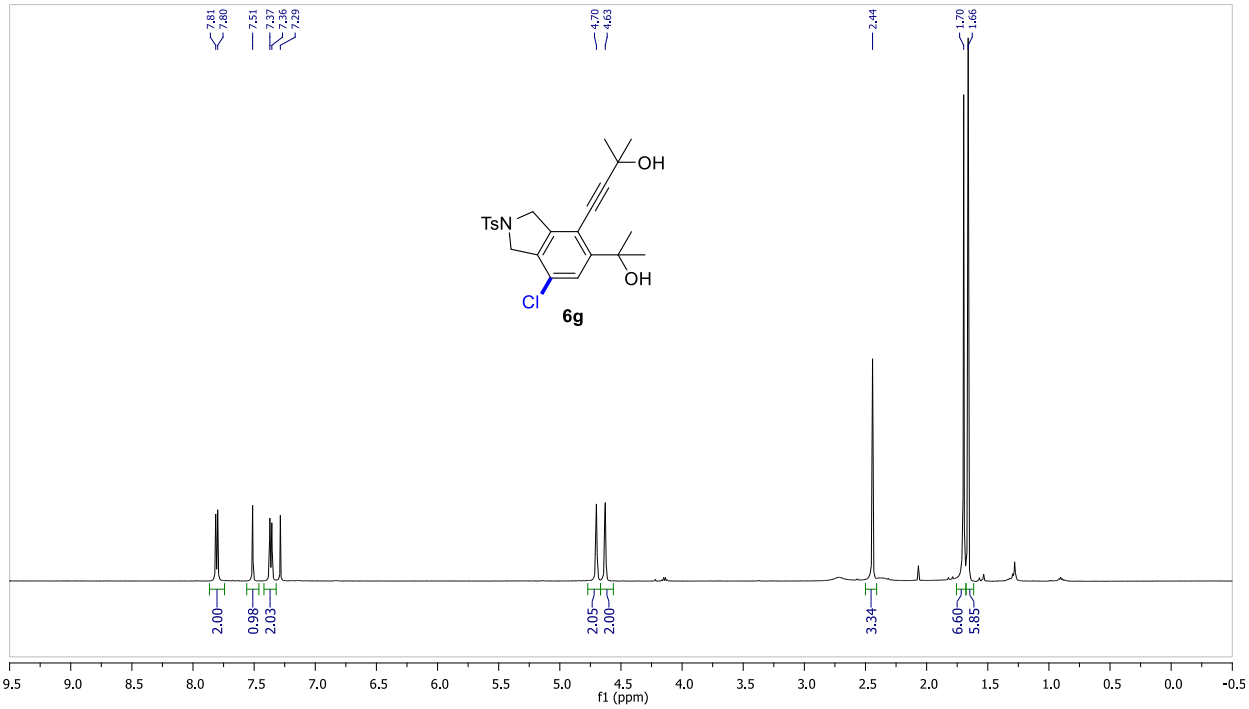
53.76
23.14
23.12
22.16
21.54
f1 (ppm)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1.66
OH
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OH
Cl
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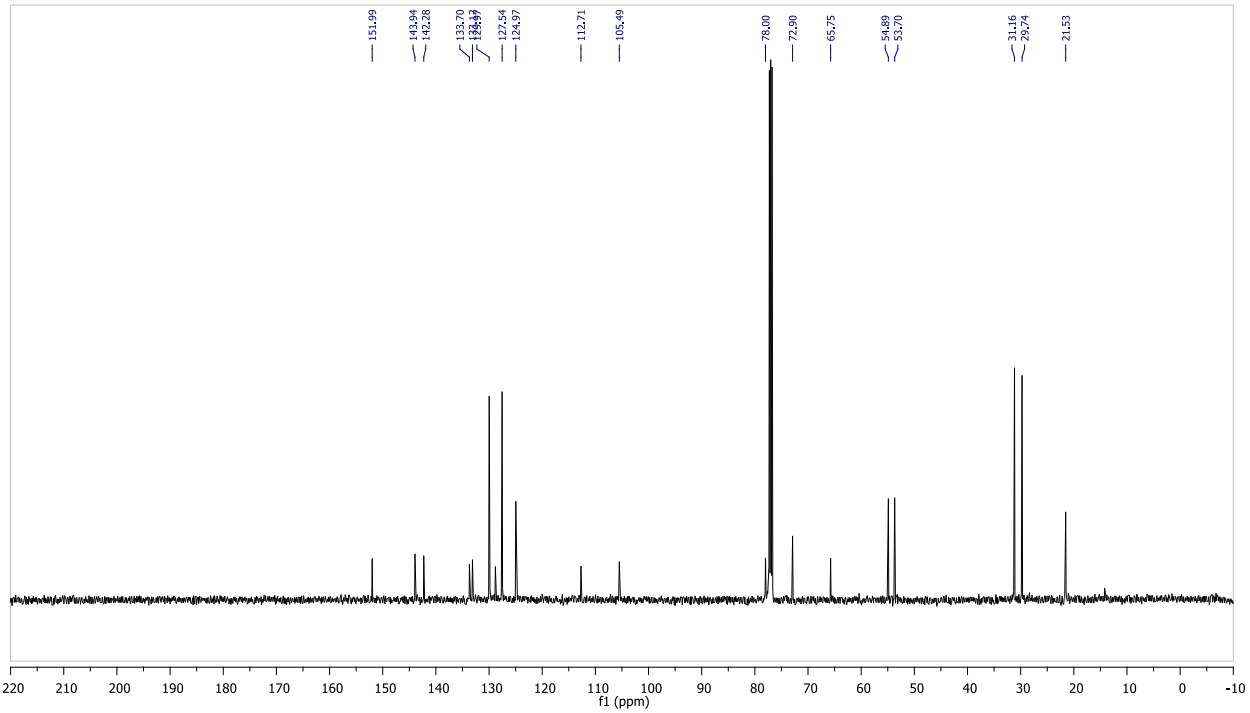
2.03
2.05
2.00
3.34
6.60
5.85
f1 (ppm)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31.16
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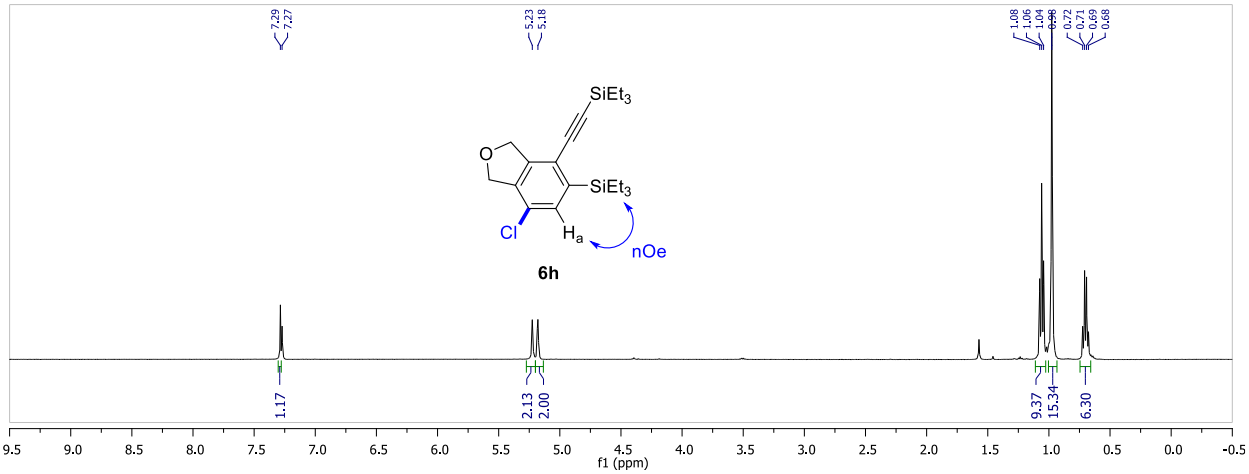
21.53
f1 (ppm)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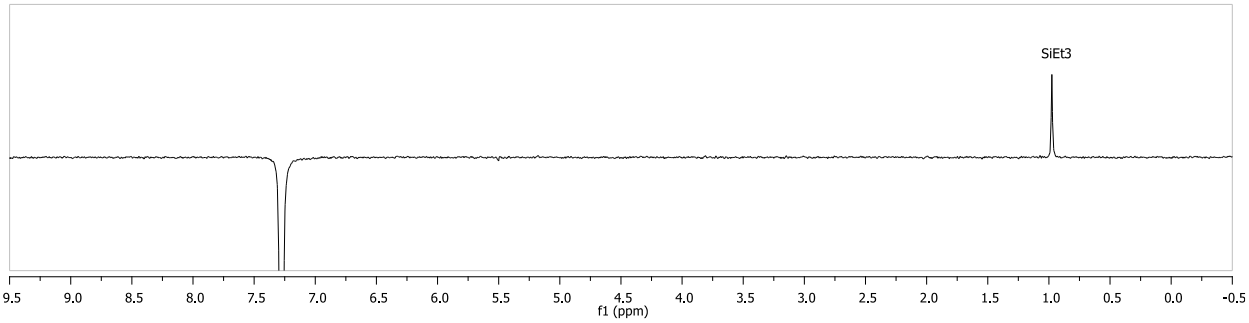
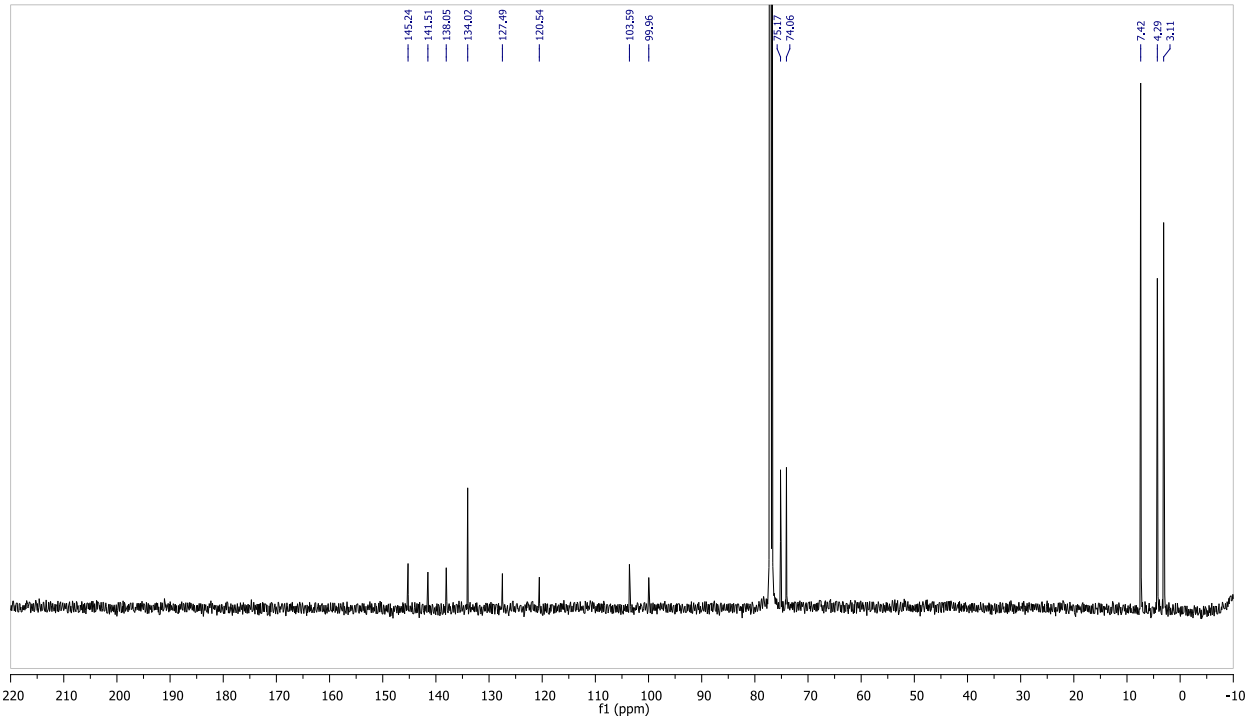
7.27
5.23
5.18
1.08
1.06
1.04
0.72
0.71
0.69
0.68
SiEt3
O
SiEt3
Cl
Ha
nOe
6h
1.17
2.13
2.00
9.37
15.34
6.30
f1 (ppm)


SiEt3
f1 (ppm)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74.06
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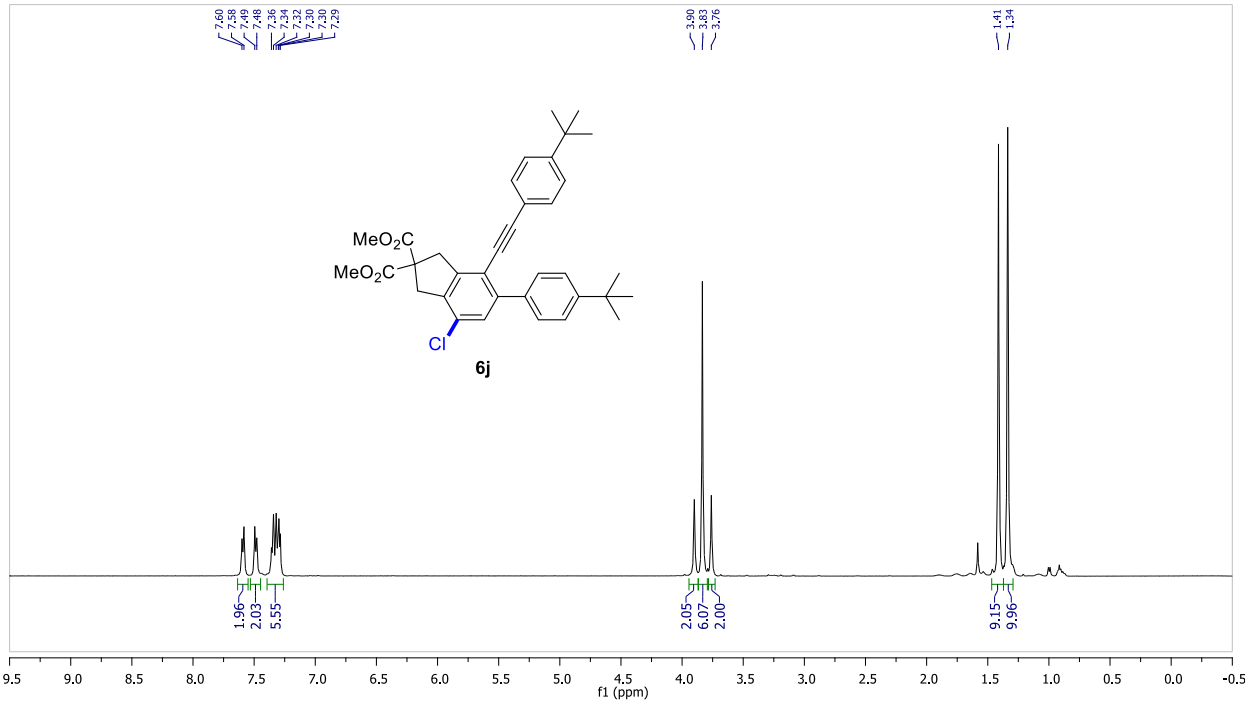
3.11
f1 (ppm)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7.34
7.32
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7.30
7.29
3.90
3.83
3.76
1.41
1.34
MeO2C
MeO2C
Cl
6j
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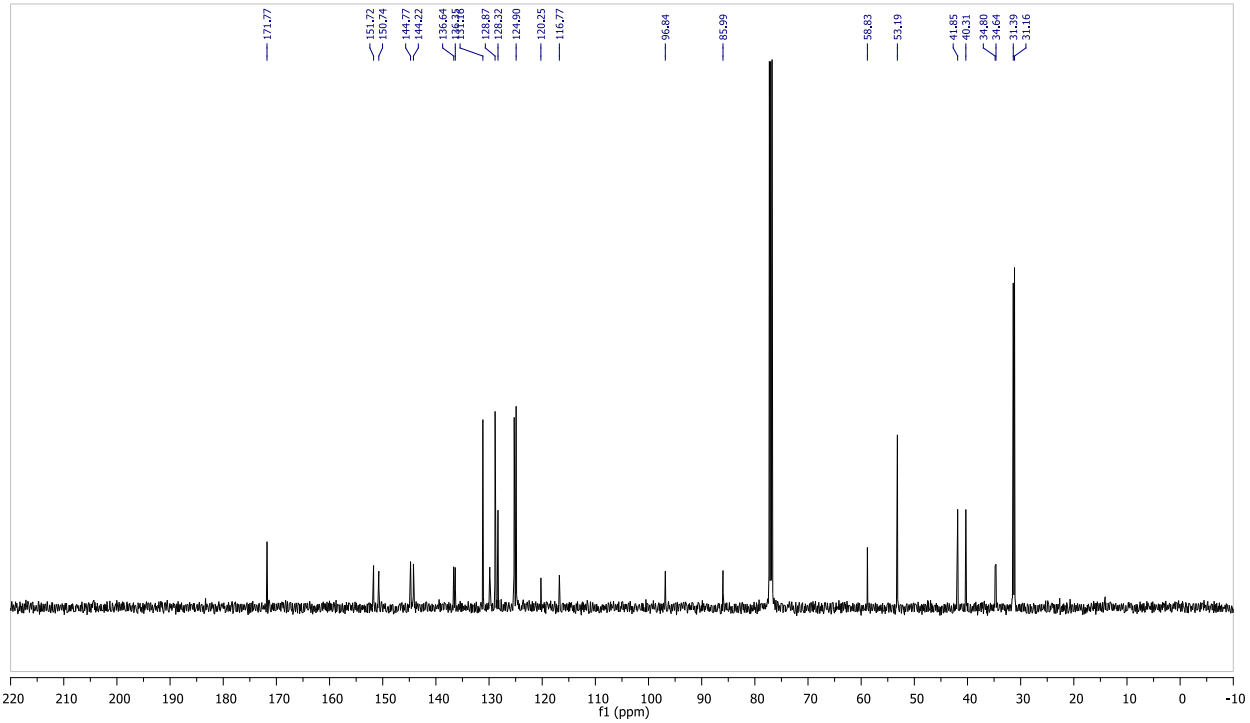
2.03
5.55
2.05
6.07
2.00
9.15
9.96
f1 (ppm)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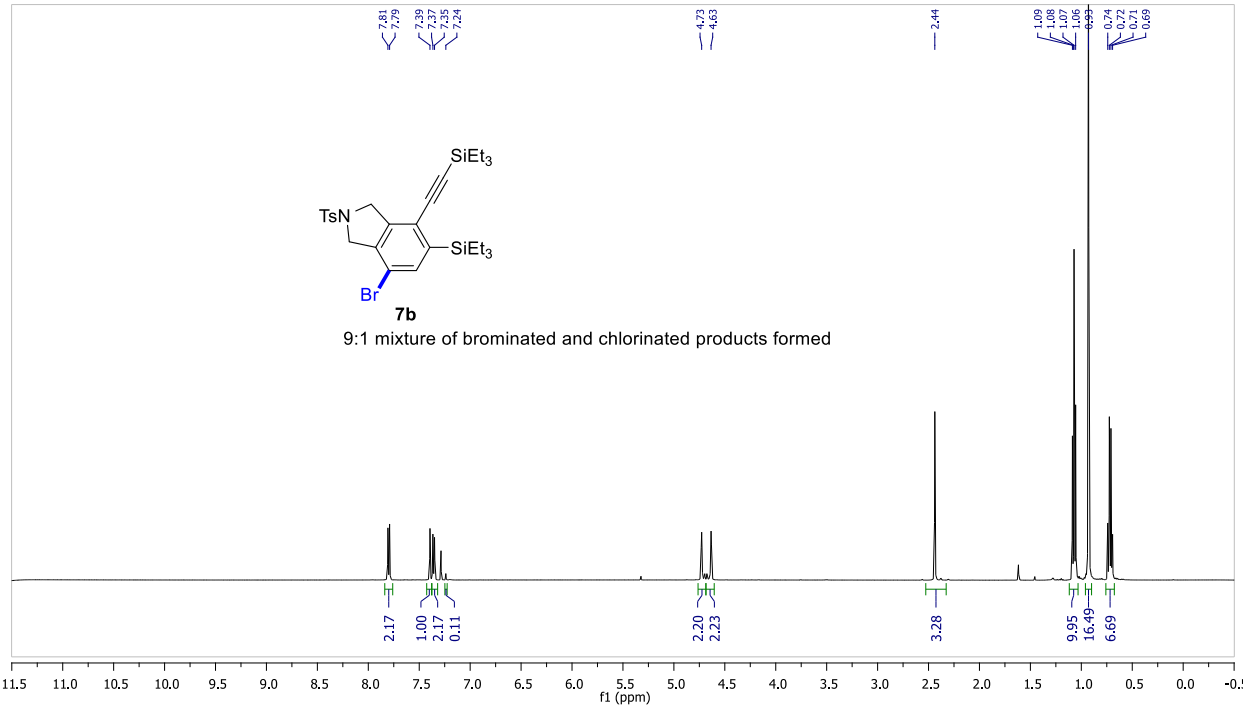
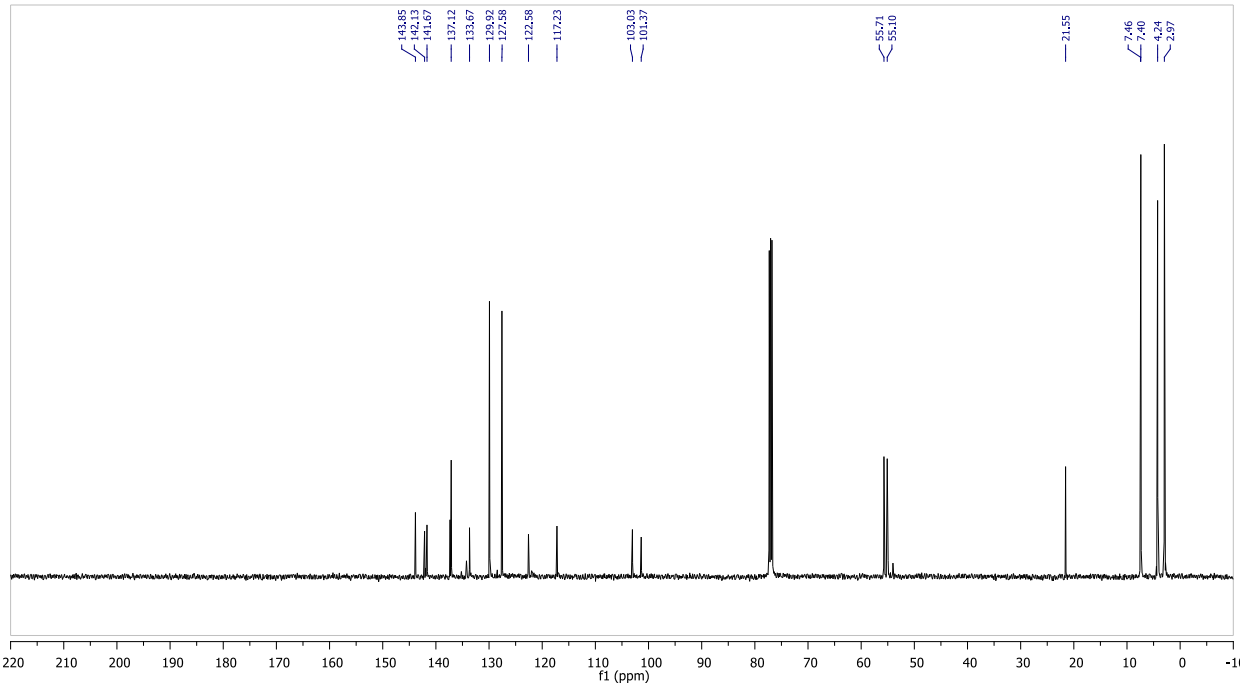
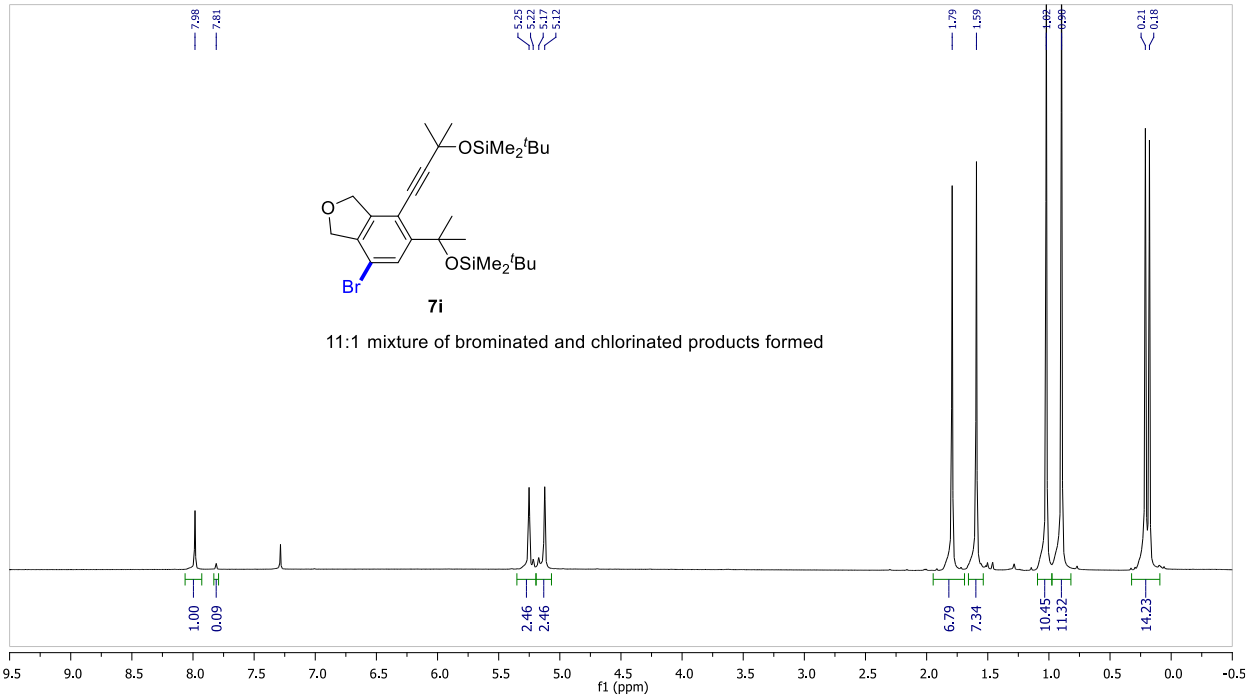
34.80
34.64
31.39
31.16
f1 (ppm)



7b

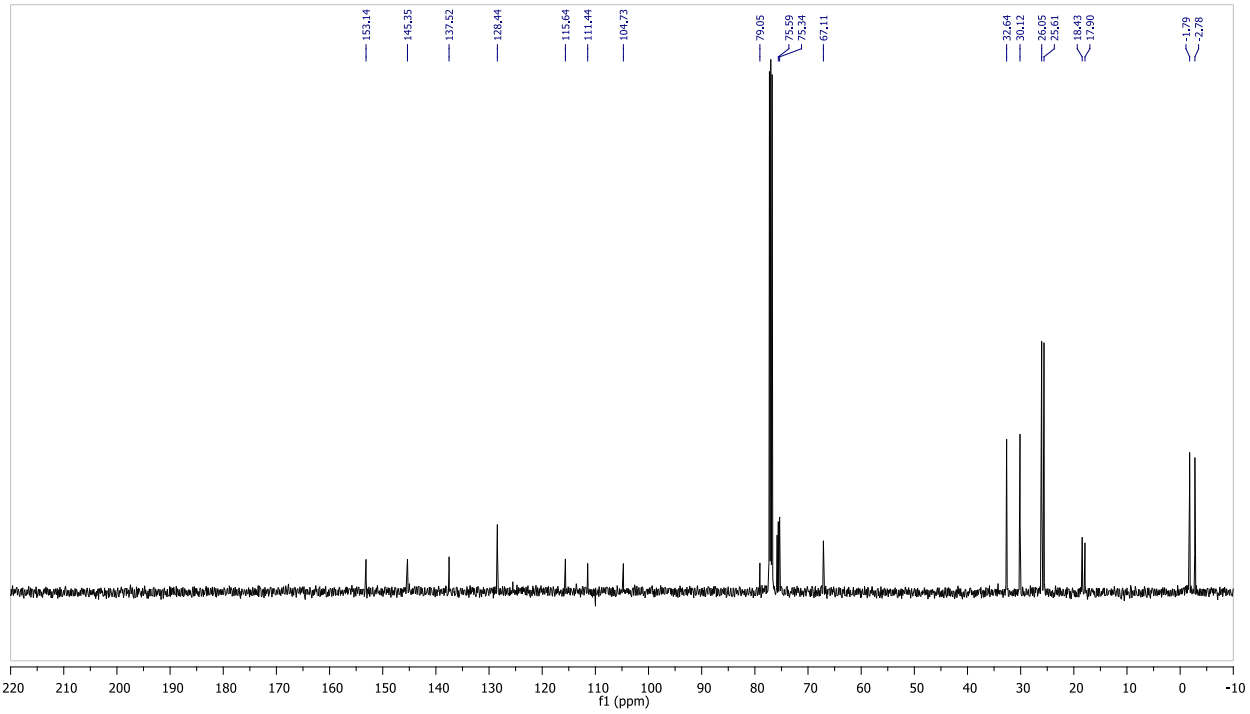
9:1 mixture of brominated and chlorinated products formed

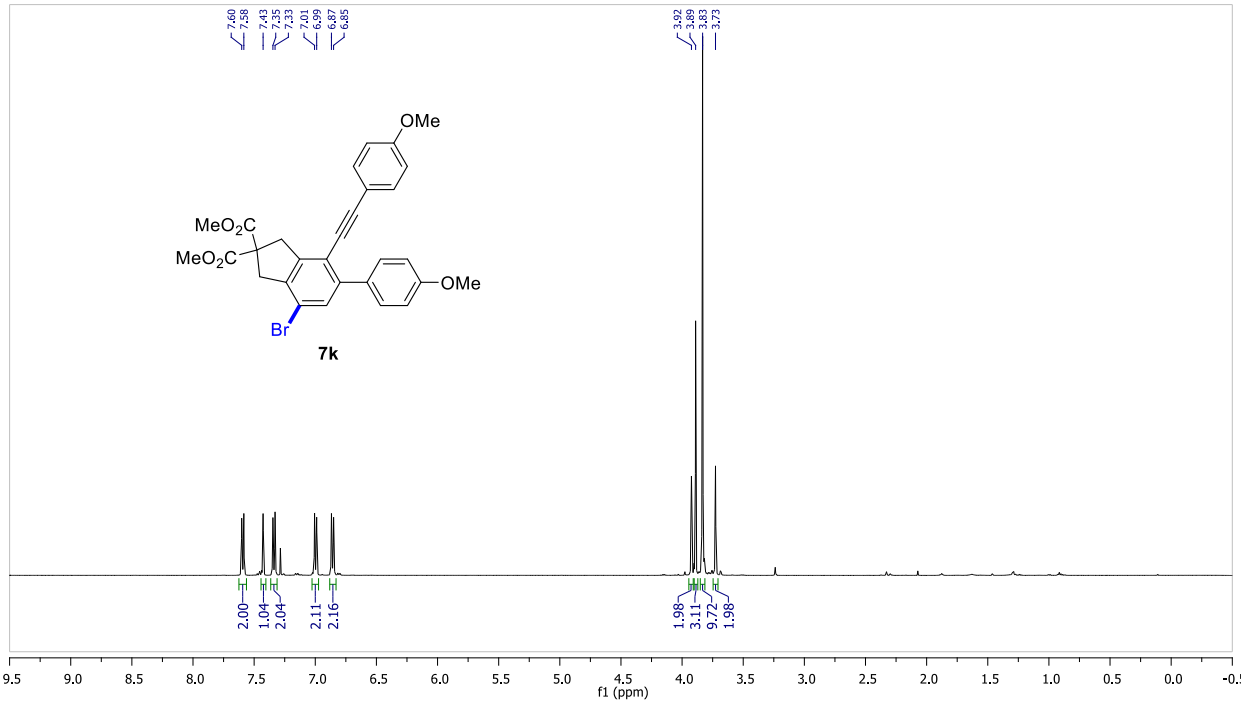




7i

11:1 mixture of brominated and chlorinated products formed

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7.35
7.33
7.01
6.99
6.87
6.85
3.92
3.89
3.83
3.73
OMe
MeO2C
MeO2C
OMe
Br
7k
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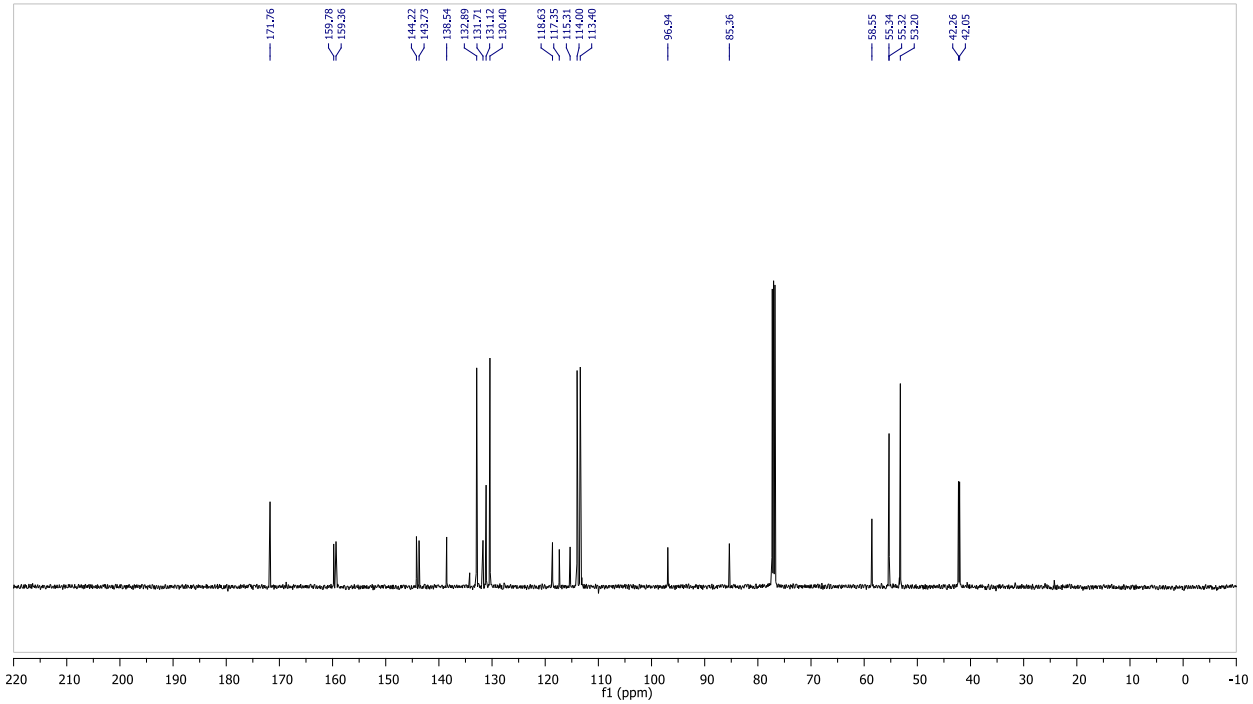
1.04
2.04
2.11
2.16
1.98
3.11
9.72
1.98
f1 (ppm)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144.22
143.73
138.54
132.89
131.71
131.12
130.40
118.63
117.35
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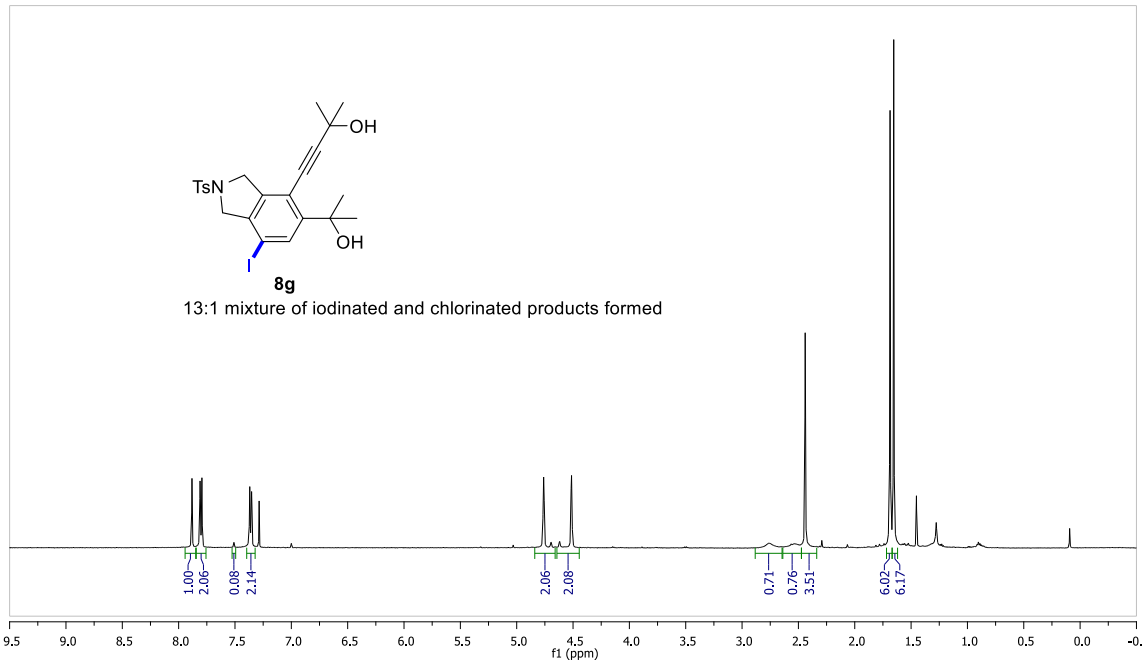
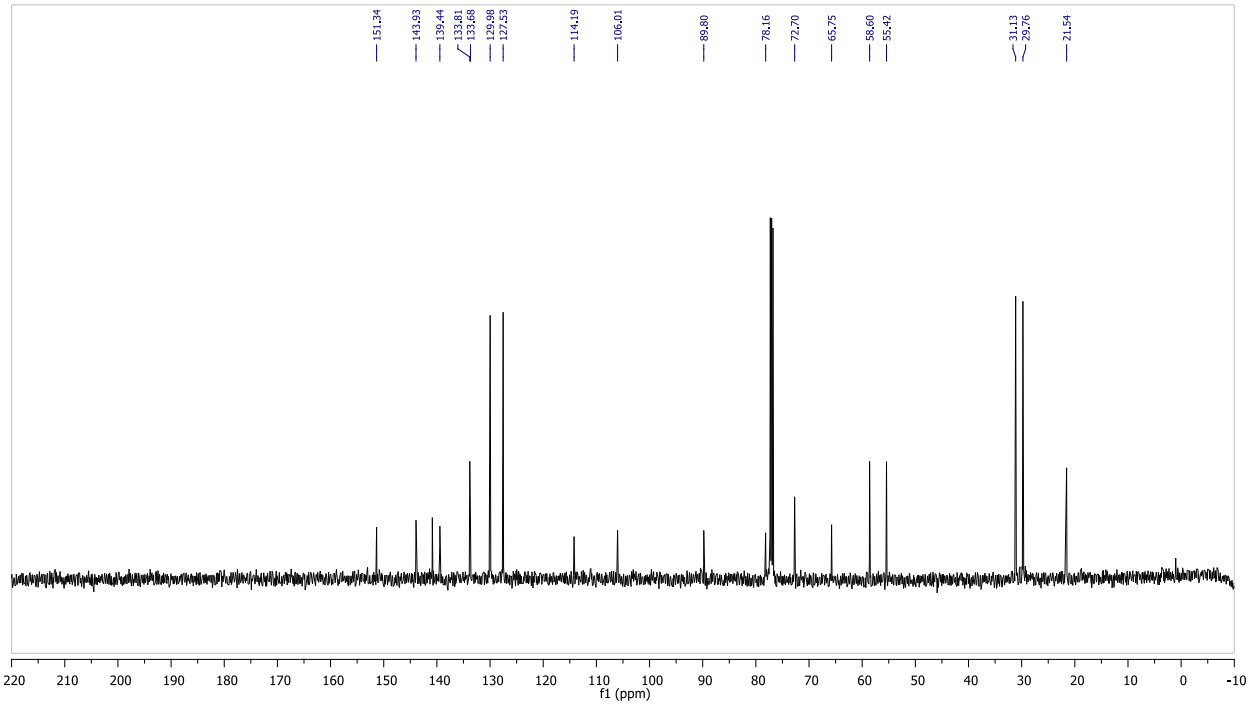
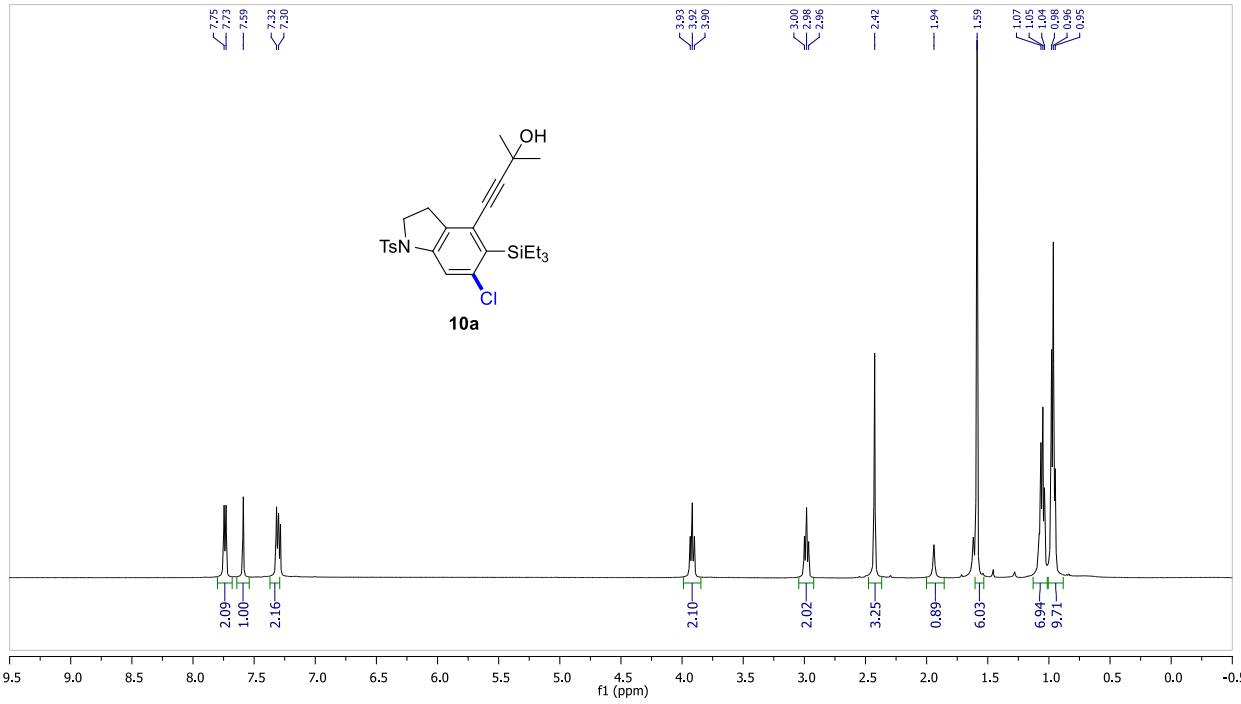
114.00
113.40
96.94
85.36
58.55
55.34
55.32
53.20
42.26
42.05
f1 (ppm)



8g

13:1 mixture of iodinated and chlorinated products formed

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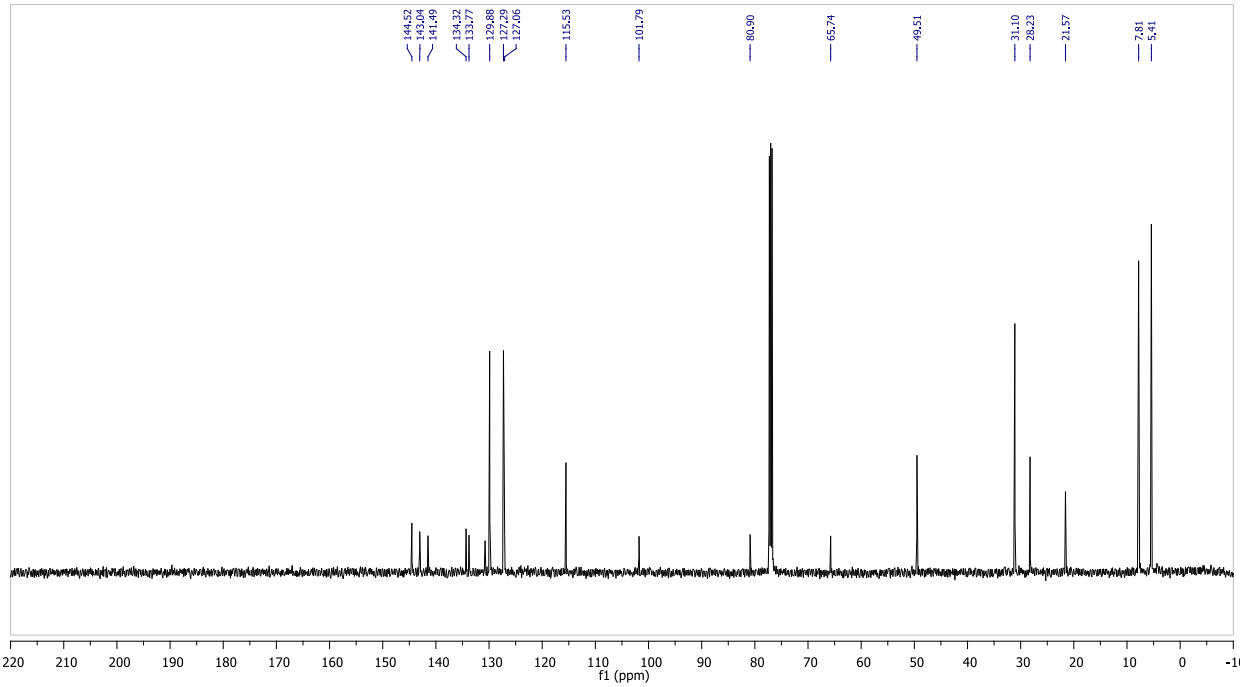
7.73
7.59
7.32
7.30
3.93
3.92
3.90
3.00
2.98
2.96
2.42
1.94
1.59
1.07
1.05
1.04
0.98
0.96
0.95
OH
TsN
SiEt3
Cl
10a
2.09
1.00
2.16
2.10
2.02
3.25
0.89
6.03
6.94
9.71
f1 (ppm)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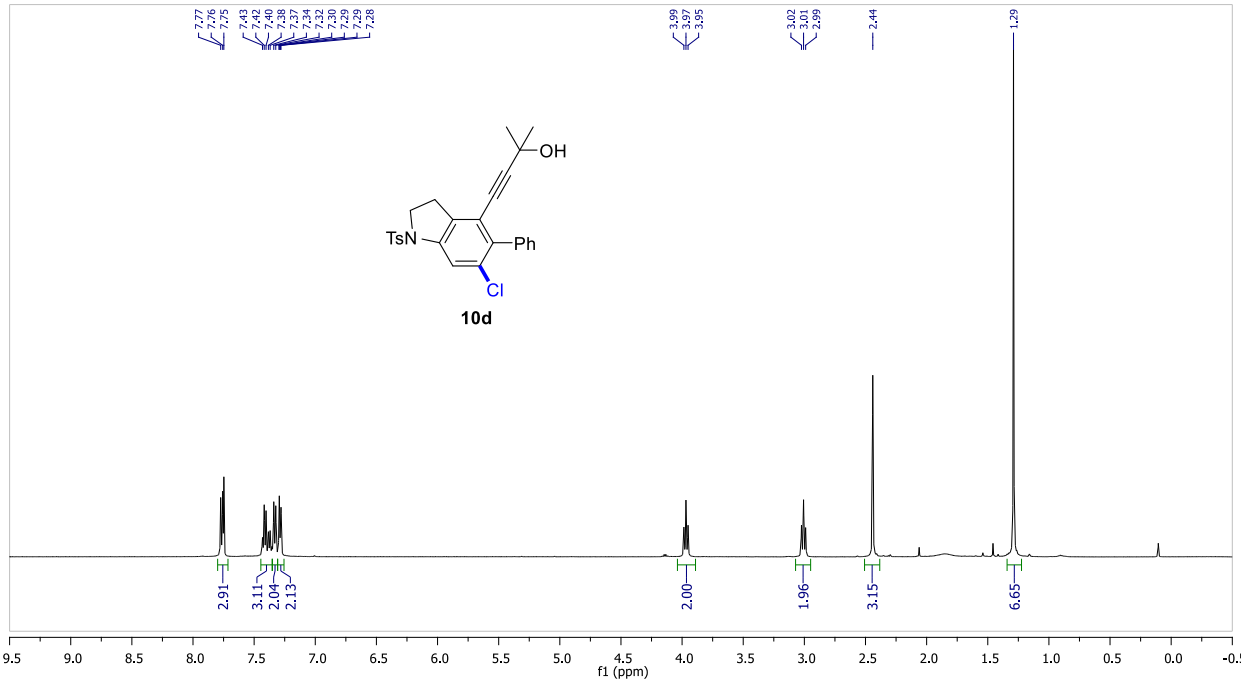
143.04
141.49
134.32
133.77
129.88
127.29
127.06
115.53
101.79
80.90
65.74
49.51
31.10
28.23
21.57
7.81
5.41
f1 (ppm)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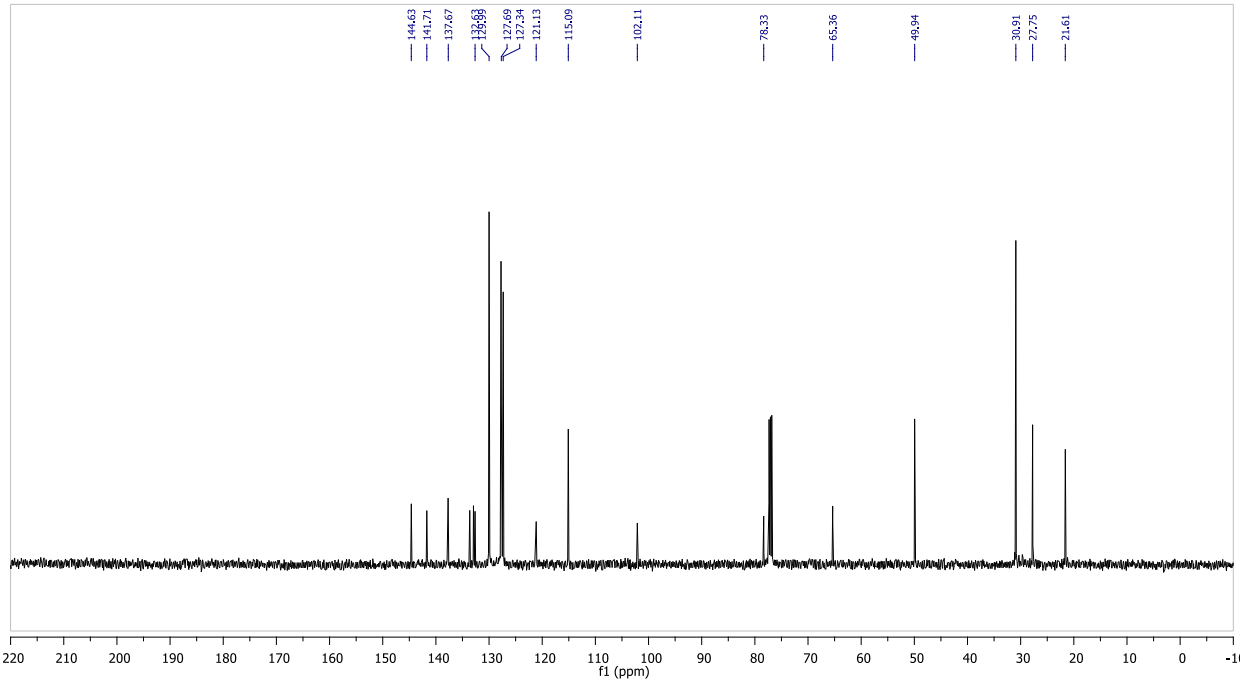
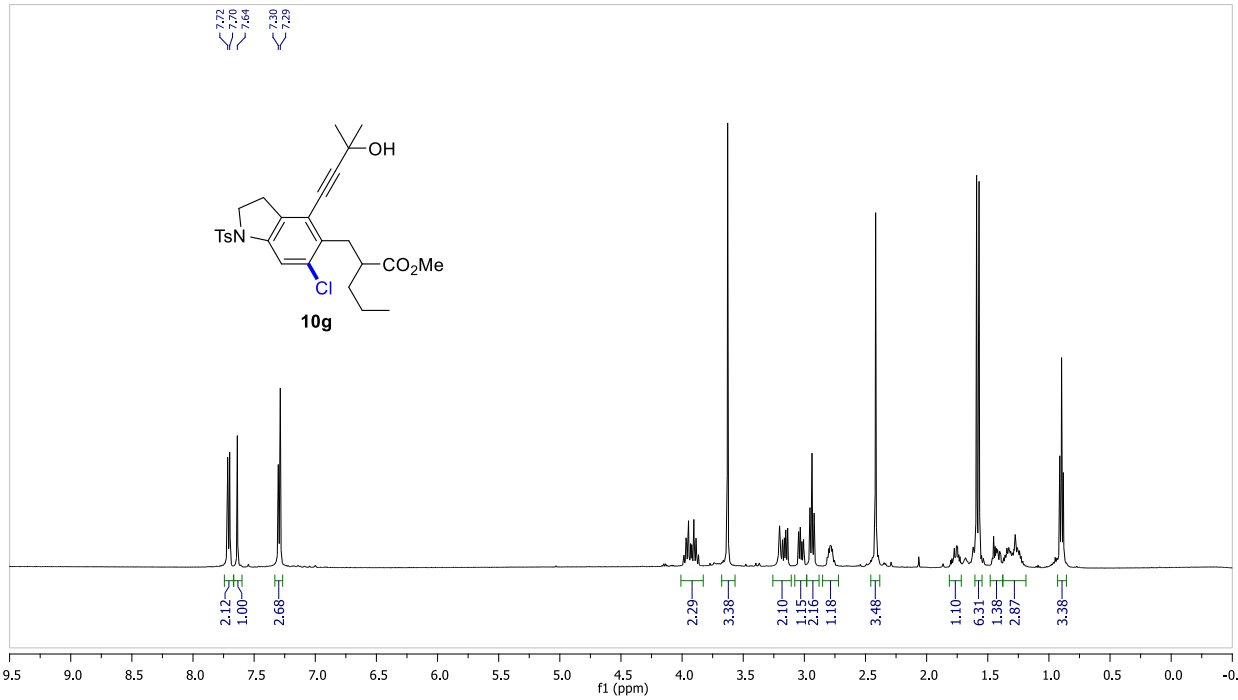
7.76
7.75
7.43
7.42
7.40
7.38
7.37
7.34
7.32
7.30
7.29
7.28
3.99
3.97
3.95
3.02
3.01
2.99
2.44
1.29
OH
TsN
Ph
Cl
10d
2.91
3.11
2.04
2.13
2.00
1.96
3.15
6.65
f1 (ppm)


144.63
141.71
137.67
132.68
132.58
132.49
127.69
127.34
121.13
115.09
102.11
78.33
65.36
49.94
30.91
27.75
21.61
f1 (ppm)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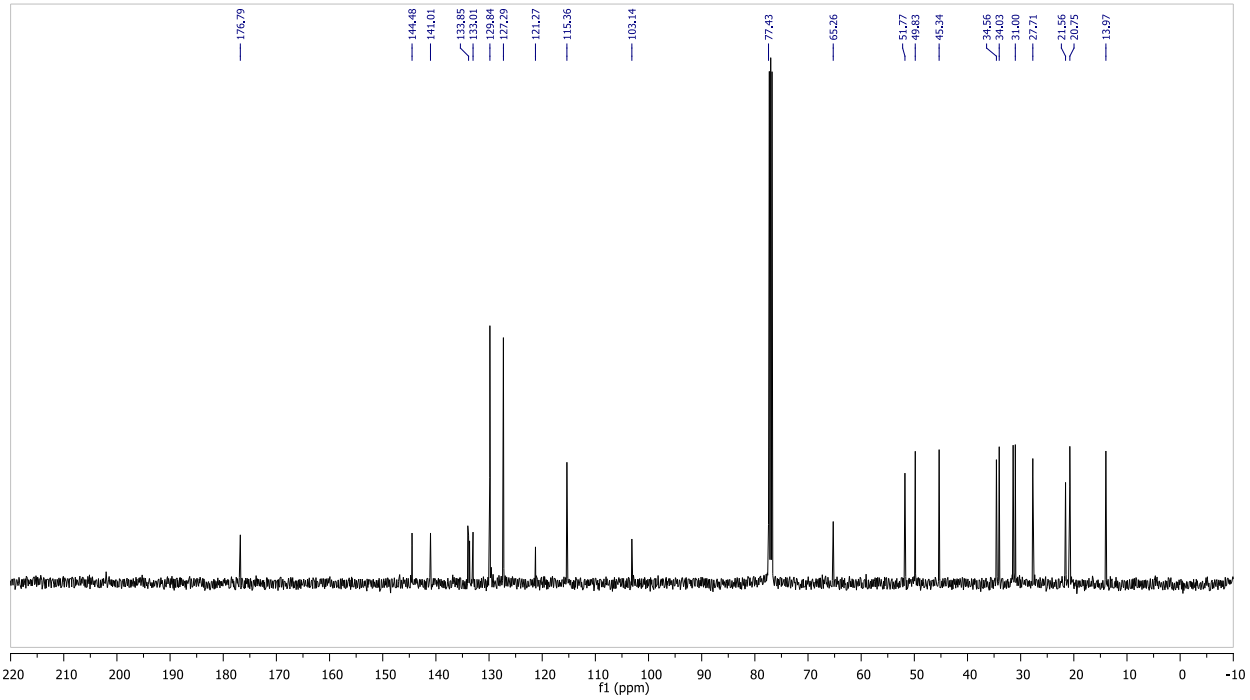
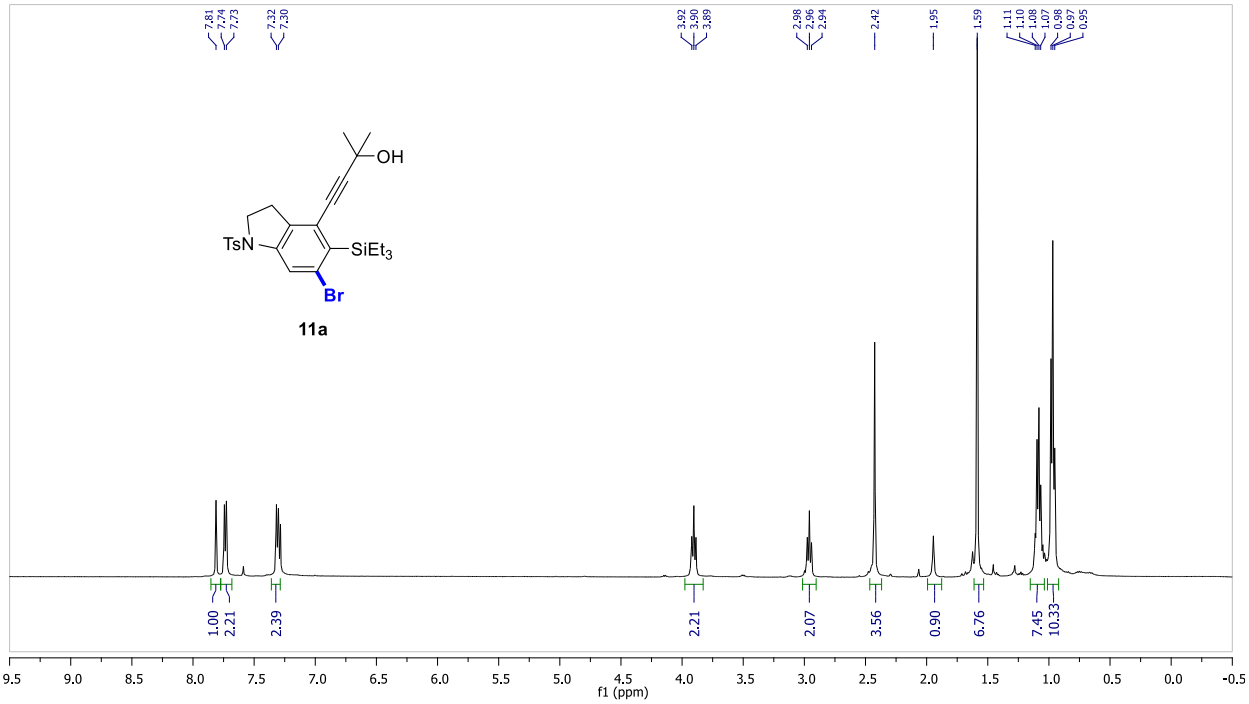
7.70
7.64
7.30
7.29
OH
TsN
CO2Me
Cl
10g
2.12
1.00
2.68
2.29
3.38
2.10
1.15
2.16
1.18
3.48
1.10
6.31
1.38
2.87
3.38
f1 (ppm)


176.79
144.48
141.01
133.85
133.01
129.84
127.29
121.27
115.36
103.14
77.43
65.26
51.77
49.83
45.34
34.56
34.03
31.00
27.71
21.56
20.75
13.97
f1 (ppm)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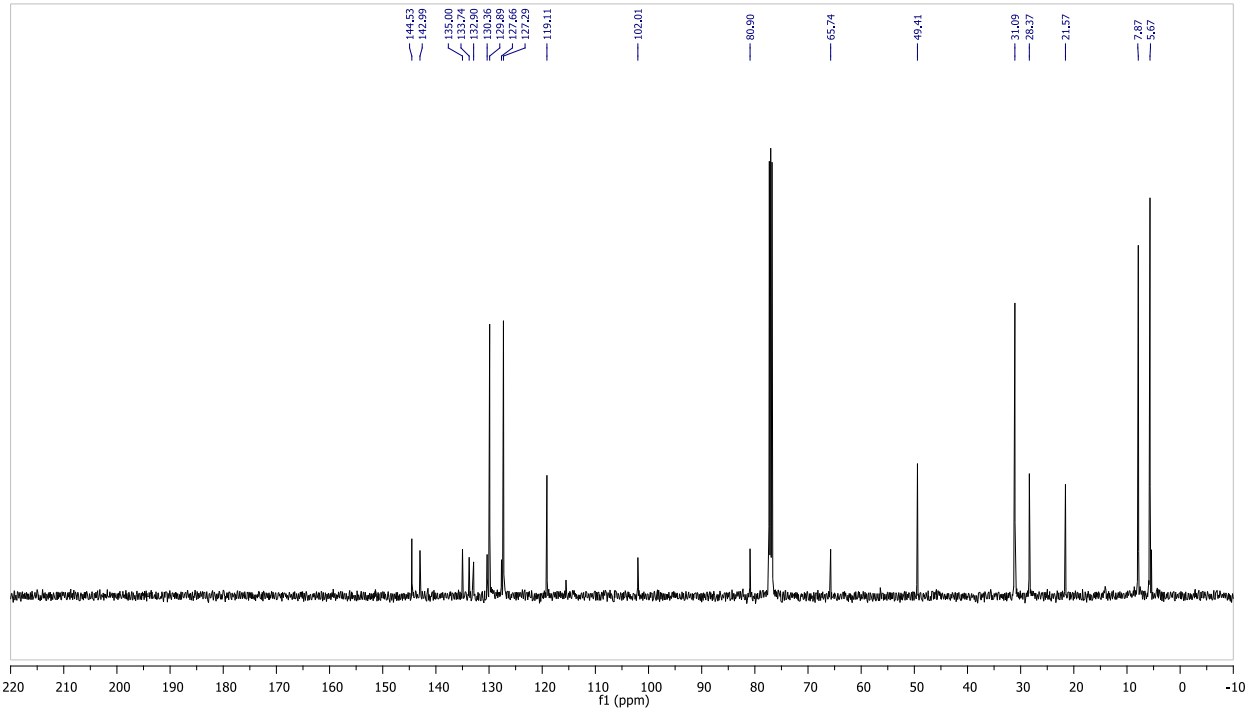
7.74
7.73
7.32
7.30
3.92
3.90
3.89
2.98
2.96
2.94
2.42
1.95
1.59
1.11
1.10
1.08
1.07
0.98
0.97
0.95
OH
TsN
SiEt3
Br
11a
1.00
2.21
2.39
2.21
2.07
3.56
0.90
6.76
7.45
10.33
f1 (ppm)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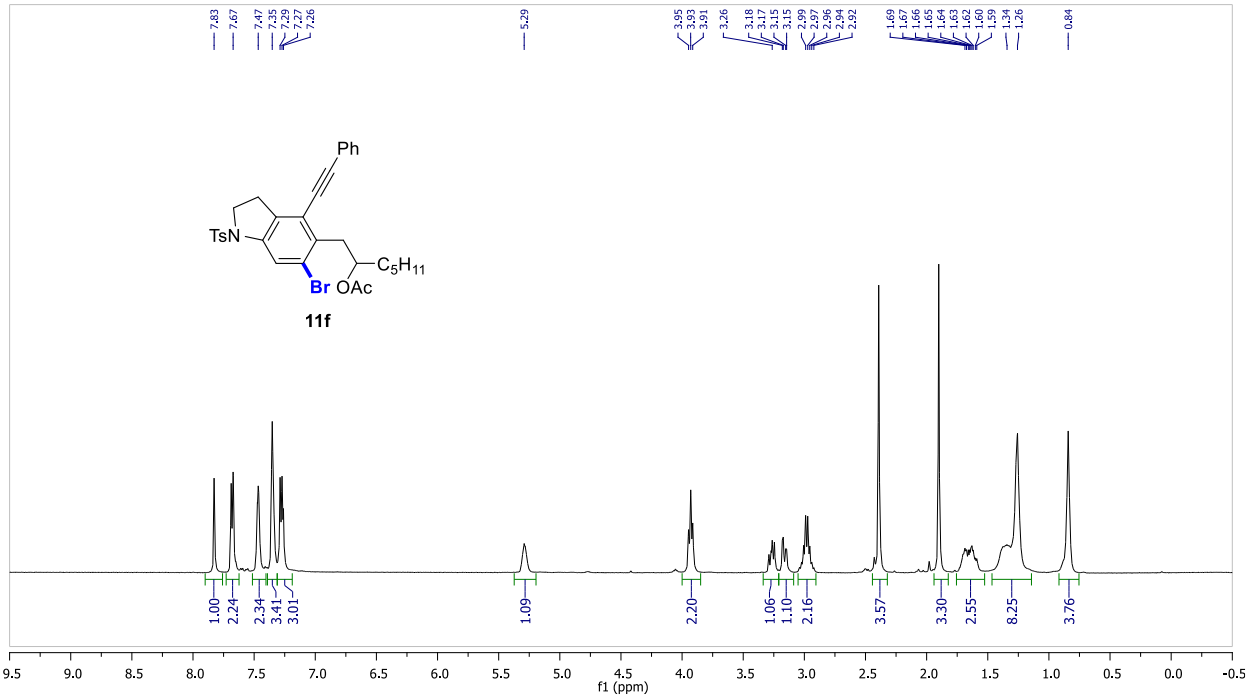
135.00
133.74
132.90
130.36
129.89
127.66
127.29
119.11
102.01
80.90
65.74
49.41
31.09
28.37
21.57
7.87
5.67
f1 (ppm)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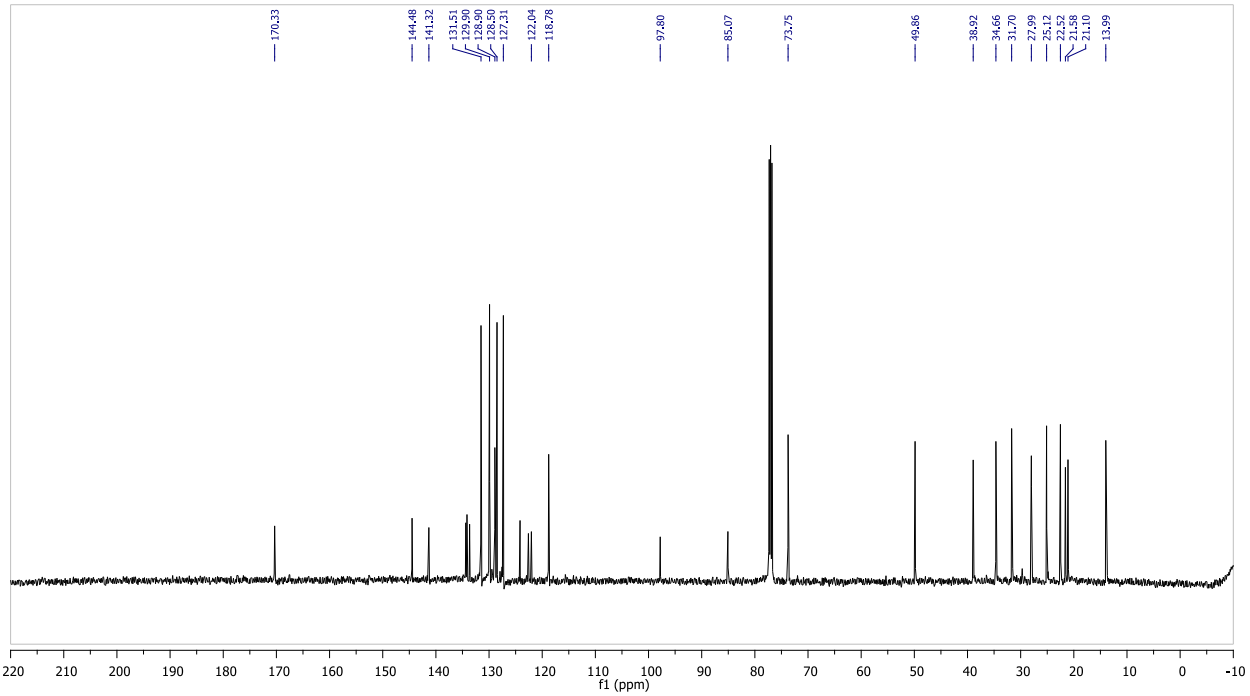
7.27
7.26
5.29
3.95
3.93
3.91
3.26
3.18
3.17
3.15
3.15
2.99
2.97
2.96
2.94
2.92
1.69
1.67
1.66
1.65
1.64
1.63
1.62
1.60
1.59
1.34
1.26
0.84
Ph
TsN
C5H11
Br OAc
11f
1.00
2.24
2.34
3.41
3.01
1.09
2.20
1.06
1.10
2.16
3.57
3.30
2.55
8.25
3.76
f1 (ppm)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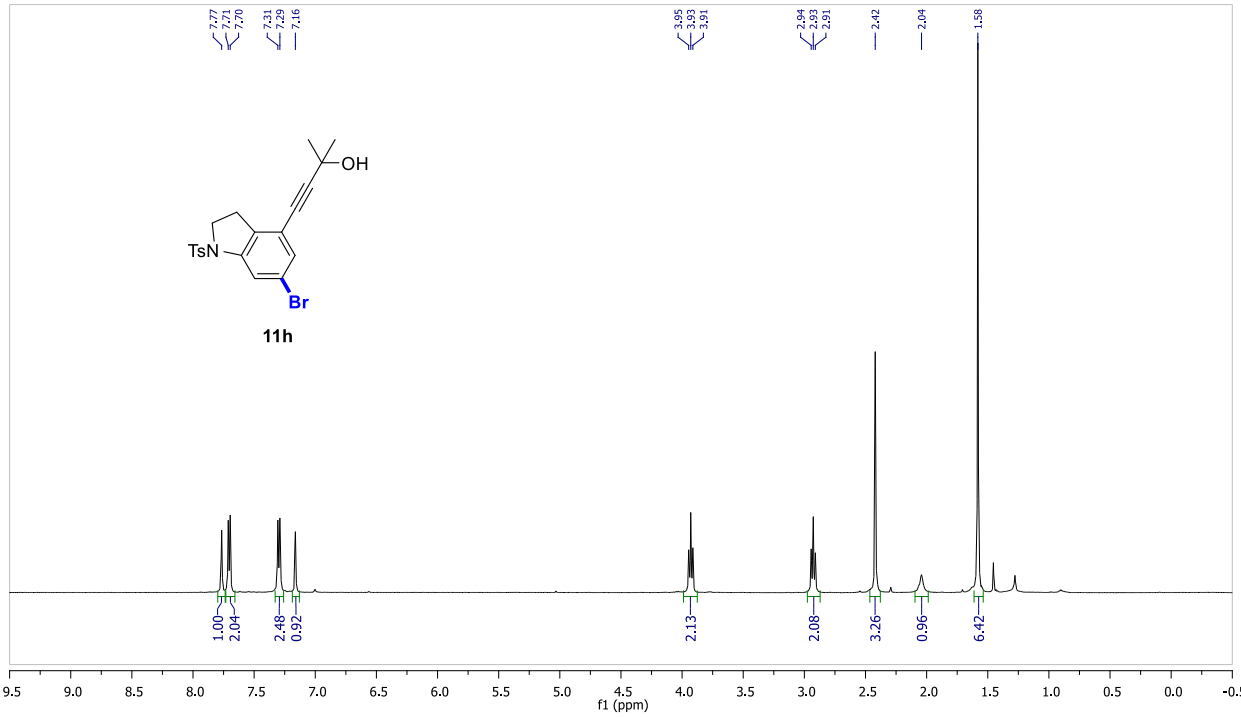
141.32
131.51
129.90
128.90
128.50
127.31
122.04
118.78
97.80
85.07
73.75
49.86
38.92
34.66
31.70
27.99
25.12
22.52
21.58
21.10
13.99
f1 (ppm)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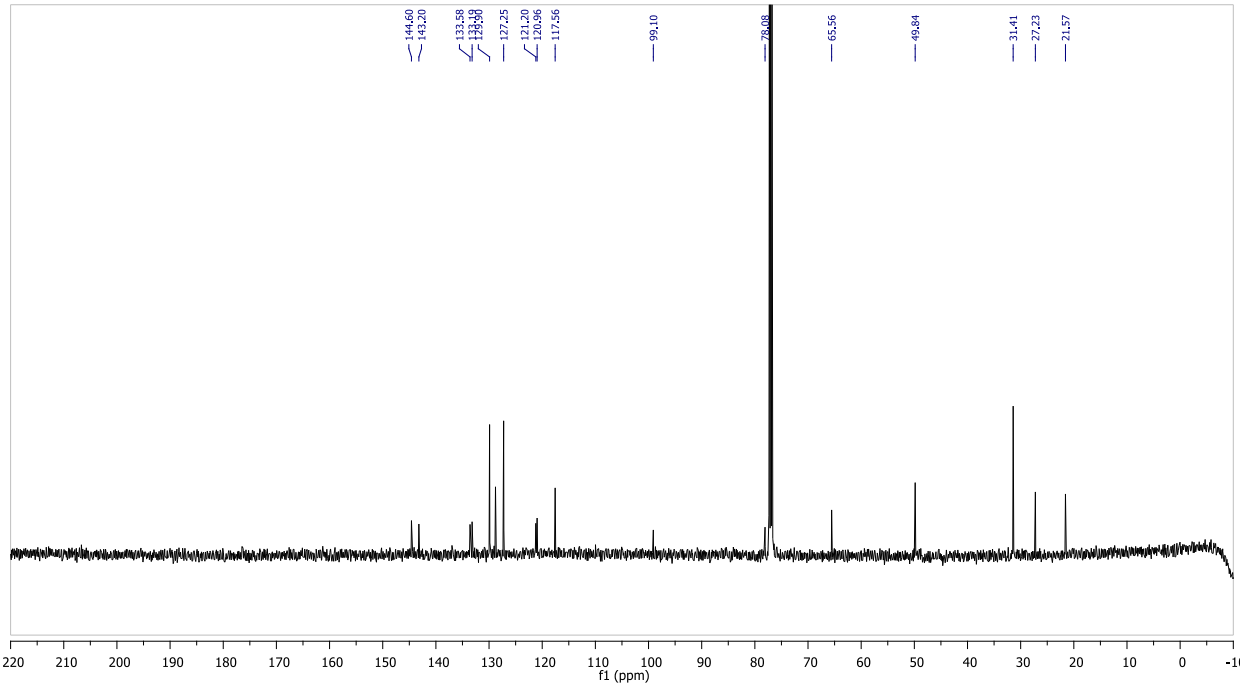
7.71
7.70
7.31
7.29
7.16
3.95
3.93
3.91
2.94
2.93
2.91
2.42
2.04
1.58
OH
TsN
Br
11h
1.00
2.04
2.48
0.92
2.13
2.08
3.26
0.96
6.42
f1 (ppm)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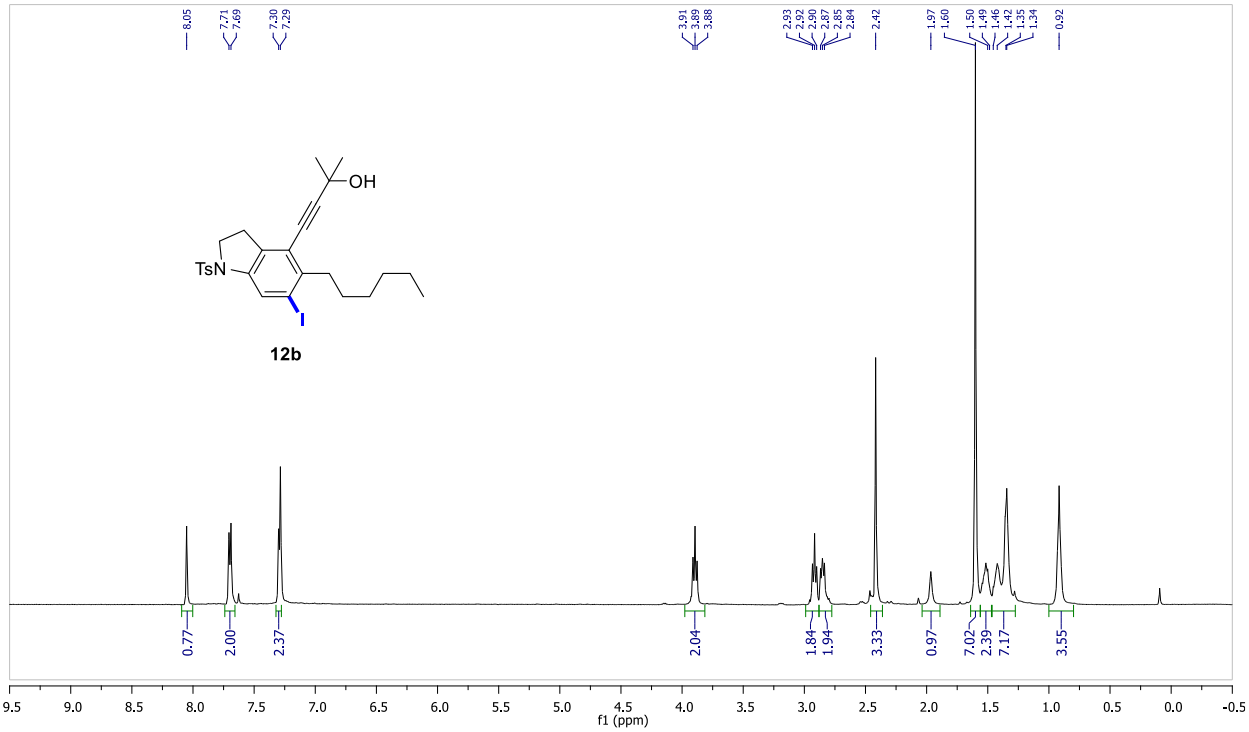
143.20
133.58
129.90
127.25
121.20
120.96
117.56
99.10
78.08
65.56
49.84
31.41
27.23
21.57
f1 (ppm)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3.91
3.89
3.88
2.93
2.92
2.90
2.87
2.85
2.84
2.42
1.97
1.60
1.50
1.49
1.46
1.42
1.35
1.34
0.92
OH
TsN
I
12b
0.77
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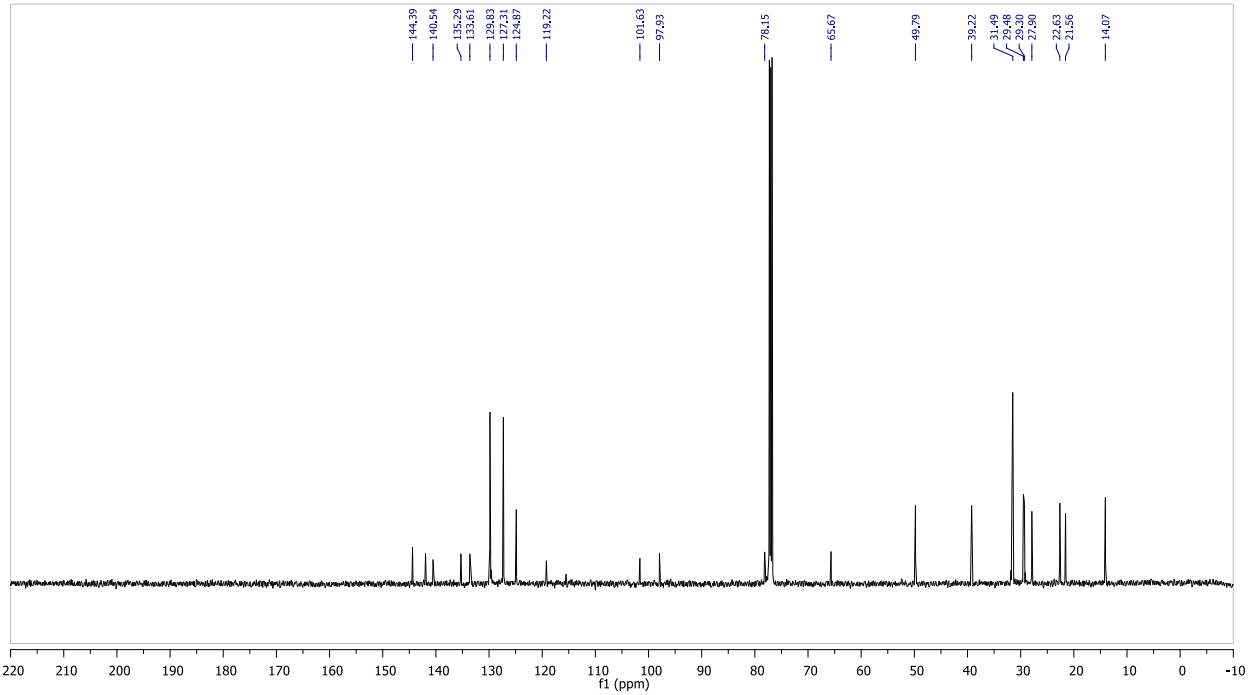
2.37
2.04
1.84
1.94
3.33
0.97
7.02
2.39
7.17
3.55
f1 (ppm)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127.31
124.87
119.22
101.63
97.93
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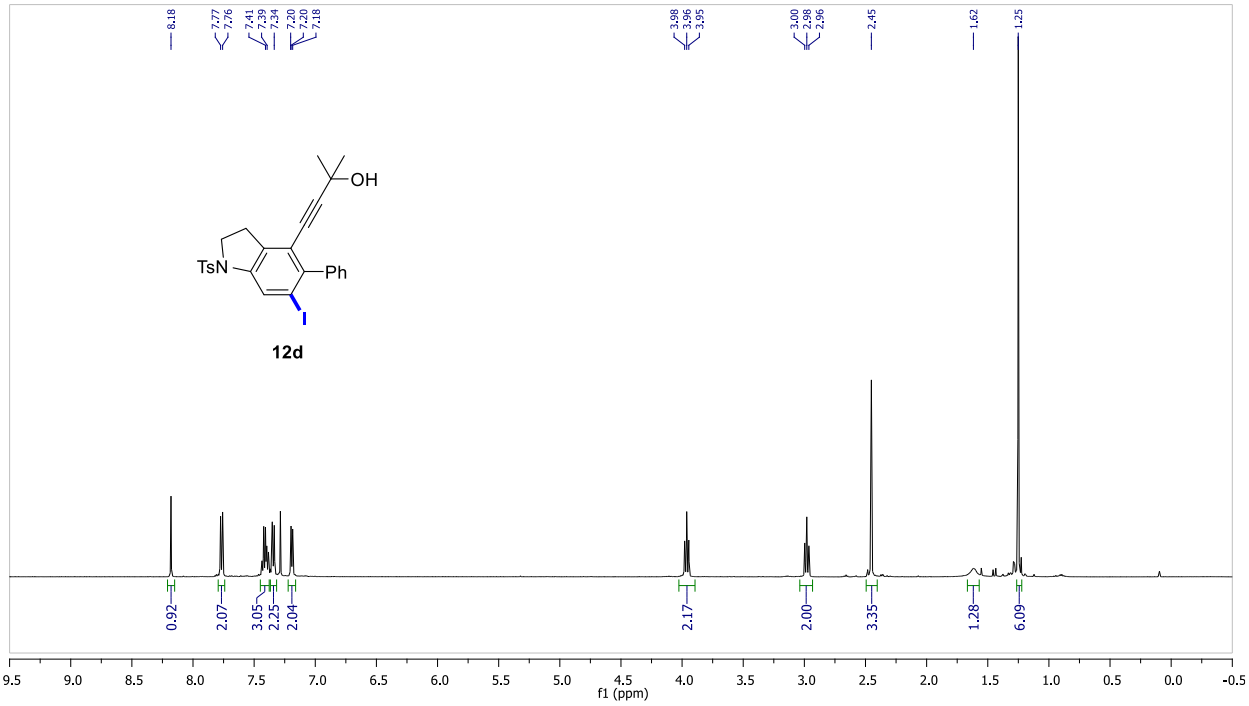
39.22
31.49
29.48
29.30
27.90
22.63
21.56
14.07
f1 (ppm)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7.76
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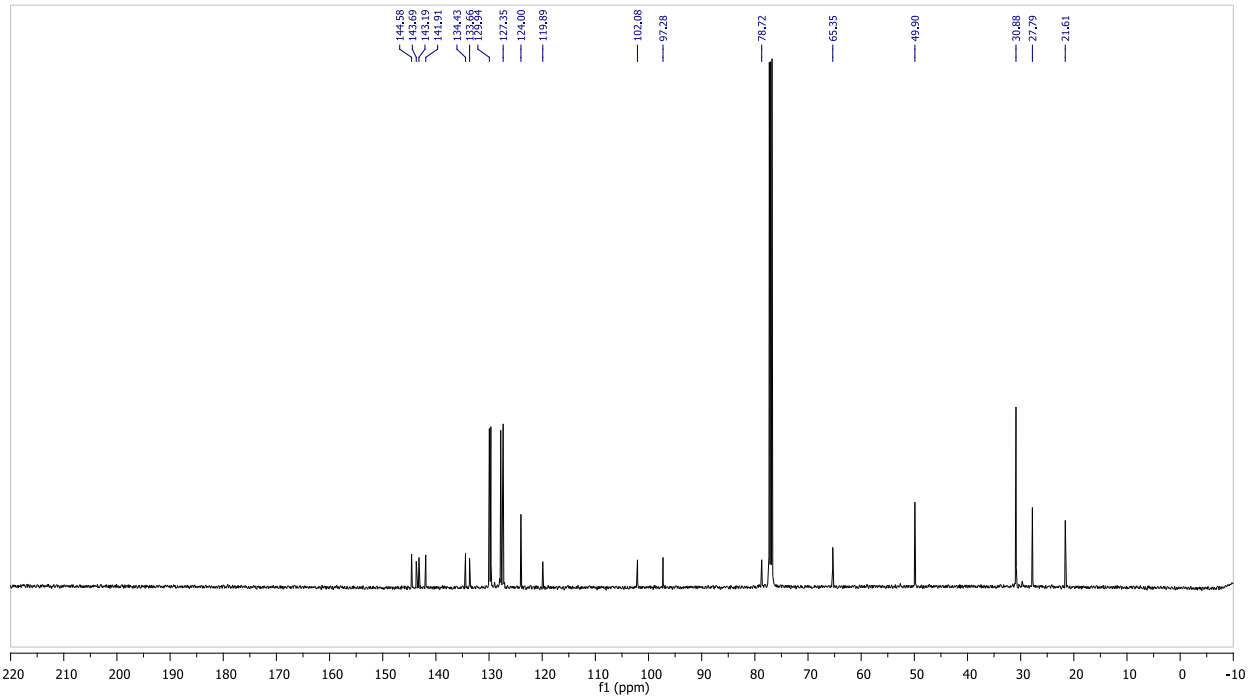
7.24
7.20
7.20
7.18
3.98
3.96
3.95
3.00
2.98
2.96
2.45
1.62
1.25
OH
TsN
Ph
I
12d
0.92
2.07
3.05
2.25
2.04
2.17
2.00
3.35
1.28
6.09
f1 (ppm)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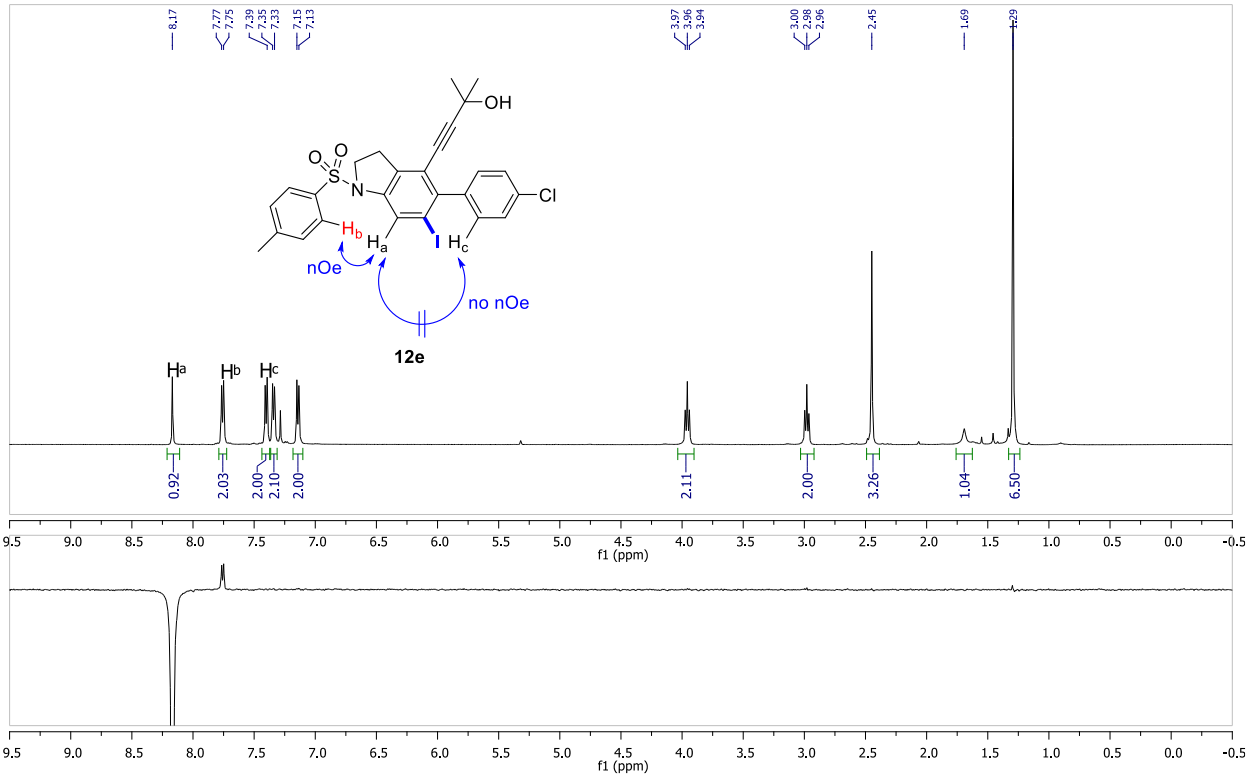
143.69
143.19
141.91
134.43
133.66
129.94
127.35
124.00
119.89
102.08
97.28
78.72
65.35
49.90
30.88
27.79
21.61
f1 (ppm)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7.13
3.97
3.96
3.94
3.00
2.98
2.96
2.45
1.69
1.00
OH
O
O
S
N
Cl
Hb
Ha
I
Hc
nOe
no nOe
12e
Ha
Hb
Hc
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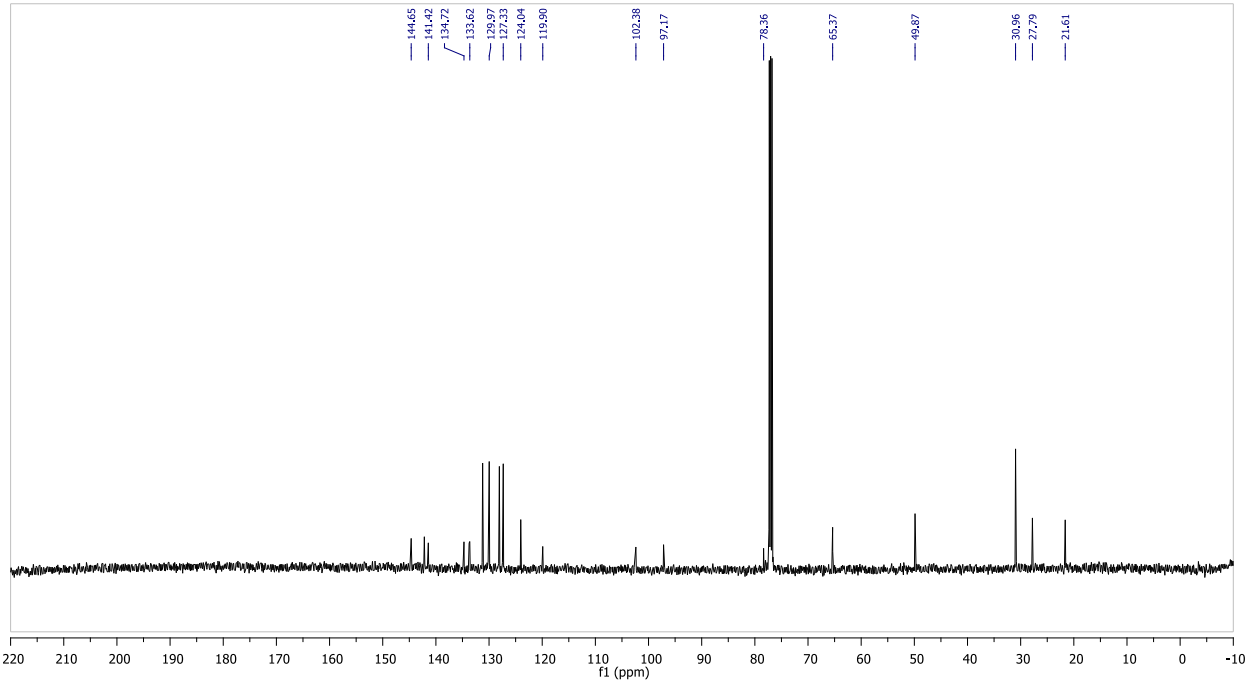
2.00
2.10
2.00
2.11
2.00
3.26
1.04
6.50
f1 (ppm)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129.97
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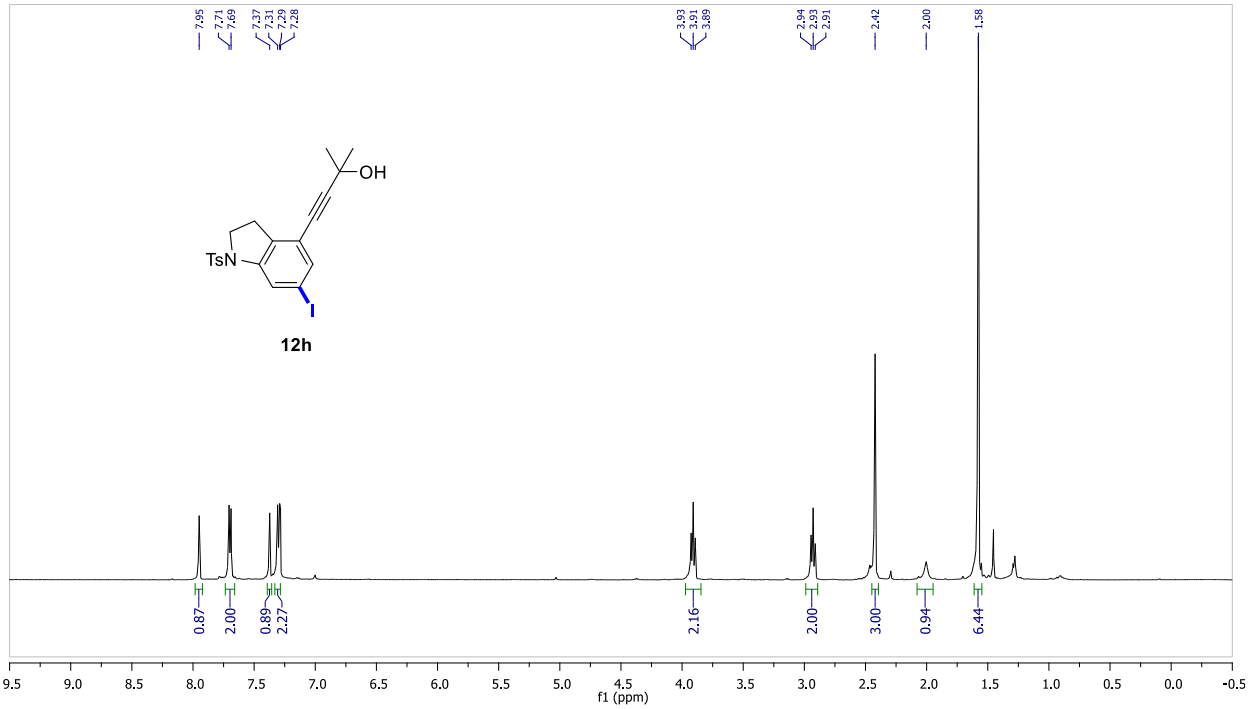
78.36
65.37
49.87
30.96
27.79
21.61
f1 (ppm)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3.93
3.91
3.89
2.94
2.93
2.91
2.42
2.00
1.58
OH
TsN
I
12h
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2.00
0.89
2.27
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2.00
3.00
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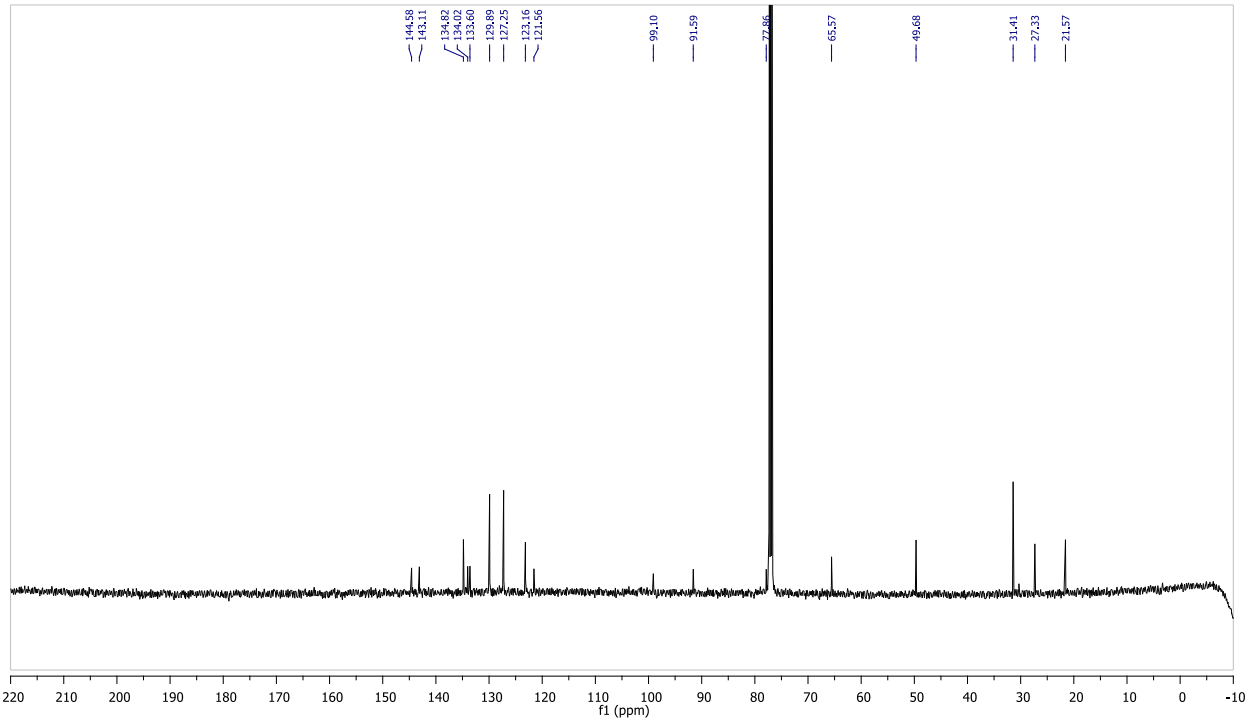
6.44
f1 (ppm)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134.82
134.22
133.60
129.89
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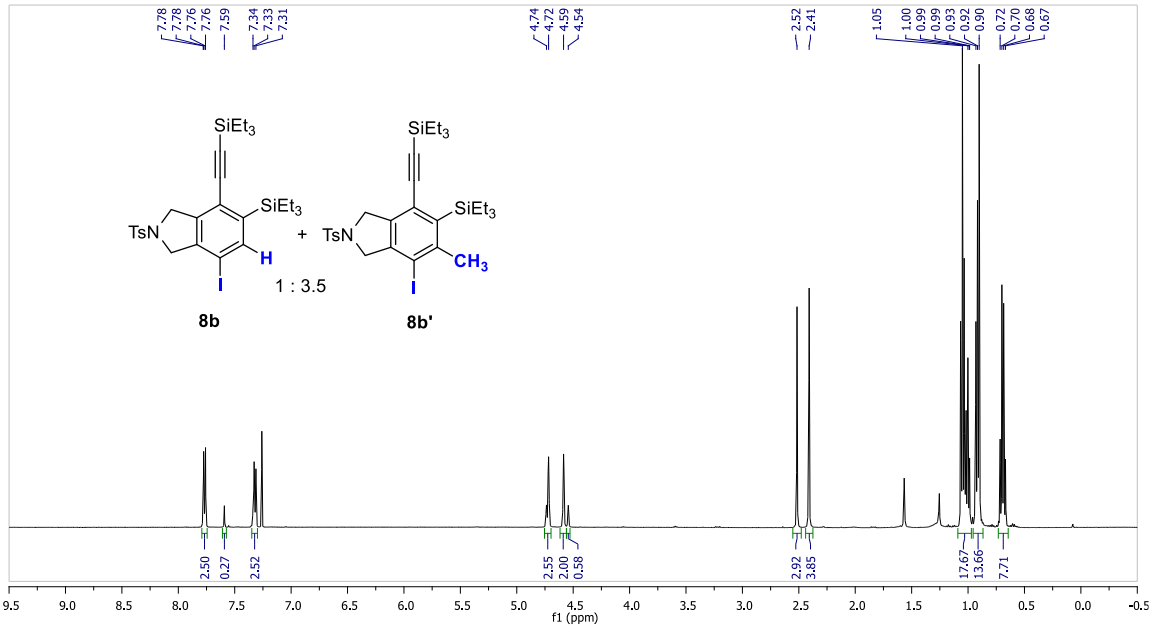
123.16
121.56
99.10
91.59
77.86
65.57
49.68
31.41
27.33
21.57
f1 (ppm)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7.76
7.76
7.59
7.34
7.33
7.31
4.74
4.72
4.59
4.54
2.52
2.41
1.05
1.00
0.99
0.99
0.93
0.92
0.90
0.72
0.70
0.68
0.67
SiEt3
SiEt3
TsN
H
I
+
SiEt3
SiEt3
TsN
CH3
I
1 : 3.5
8b
8b'
2.50
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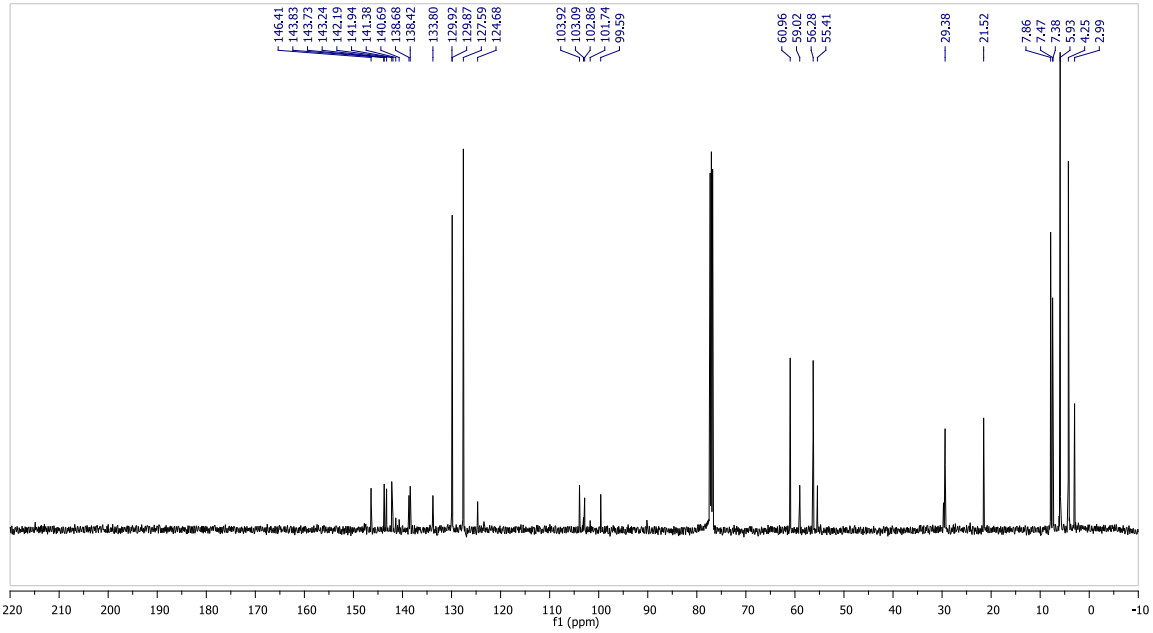
2.52
2.55
2.00
0.58
2.92
3.85
17.67
13.66
7.71
f1 (ppm)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140.69
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138.42
133.80
129.92
129.87
127.59
124.68
103.92
103.09
102.86
101.74
99.59
60.96
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29.38
21.52
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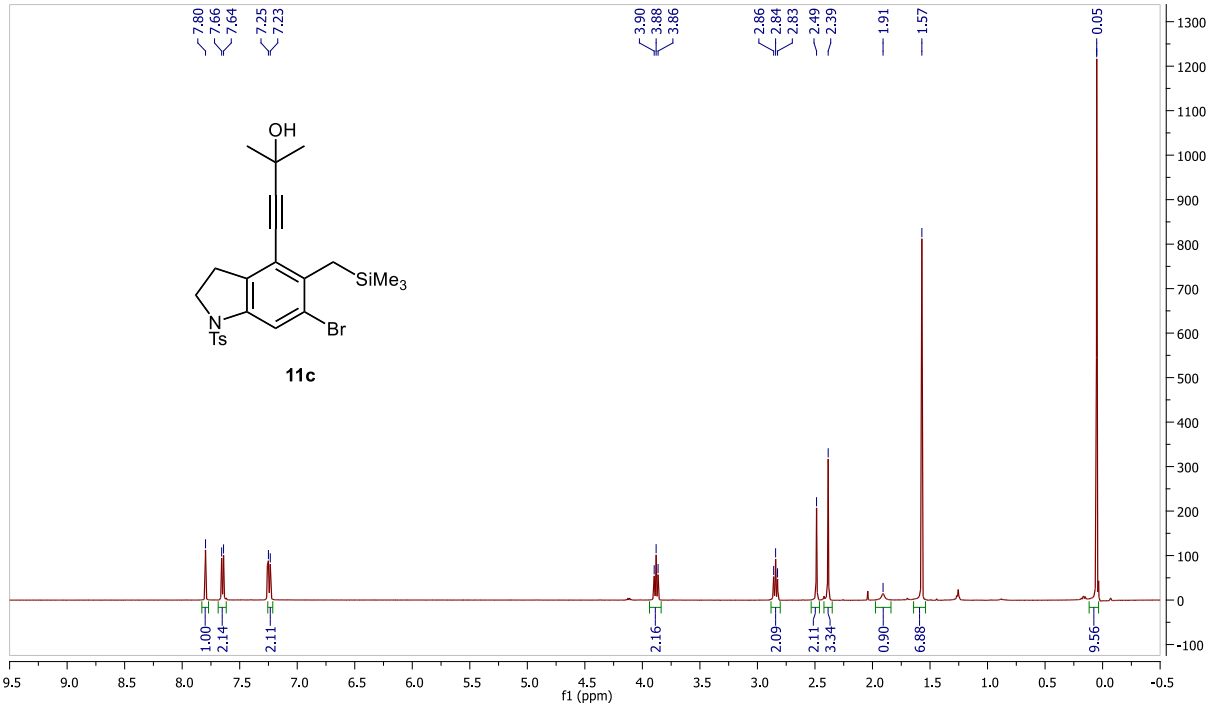
7.47
7.38
5.93
4.25
2.99
f1 (ppm)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3.88
3.86
2.86
2.84
2.83
2.49
2.39
1.91
1.57
0.05
OH
SiMe3
N
Ts
Br
11c
1.00
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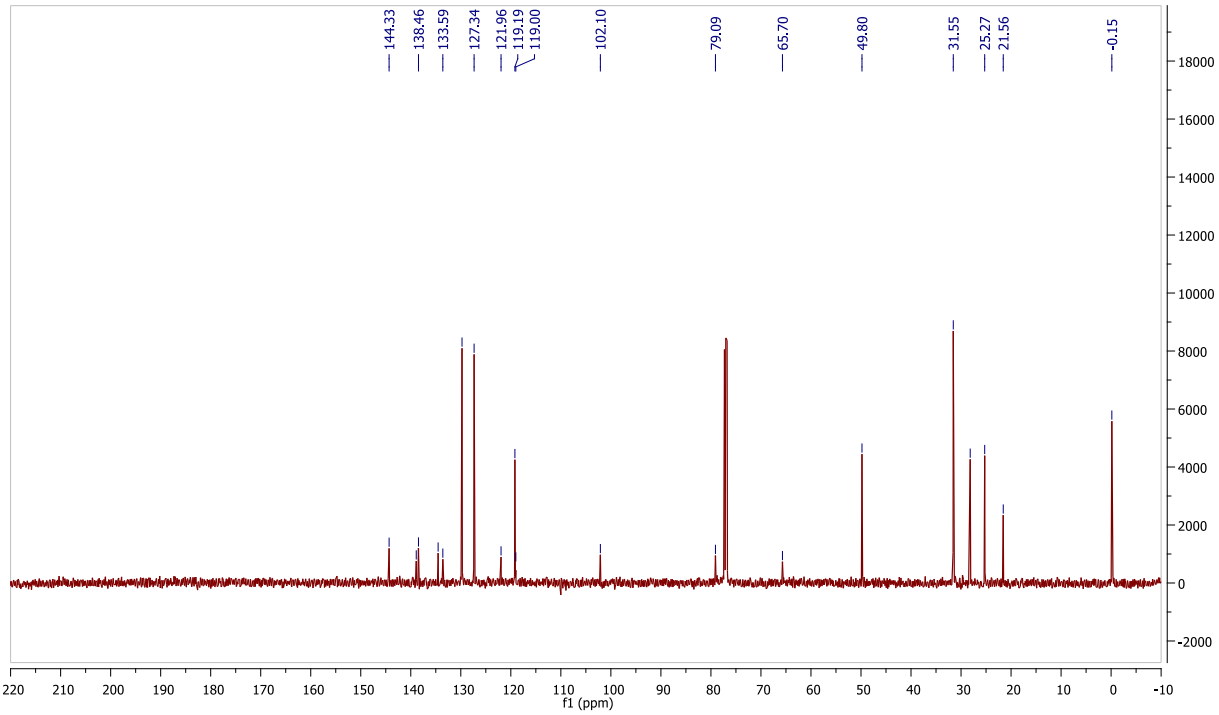
2.11
2.16
2.09
2.11
3.34
0.90
6.88
9.56
f1 (ppm)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102.10
79.09
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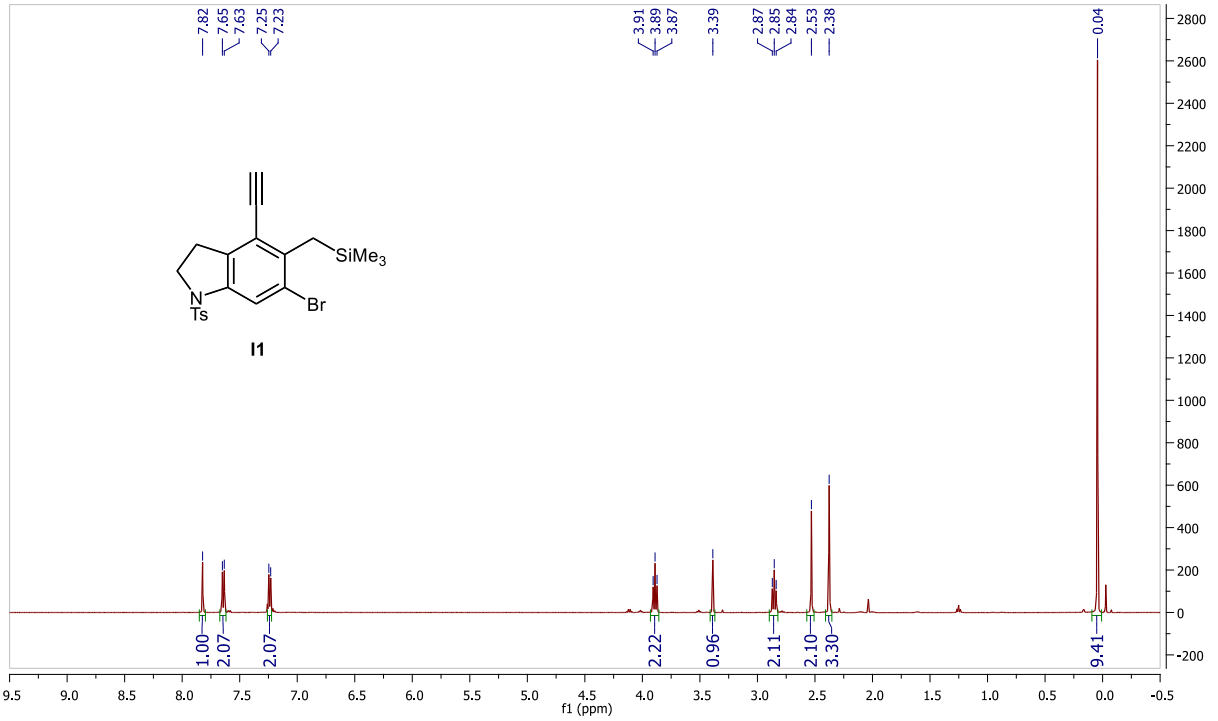
49.80
31.55
25.27
21.56
-0.15
f1 (ppm)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3.87
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2.84
2.53
2.38
0.04
SiMe3
N
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Br
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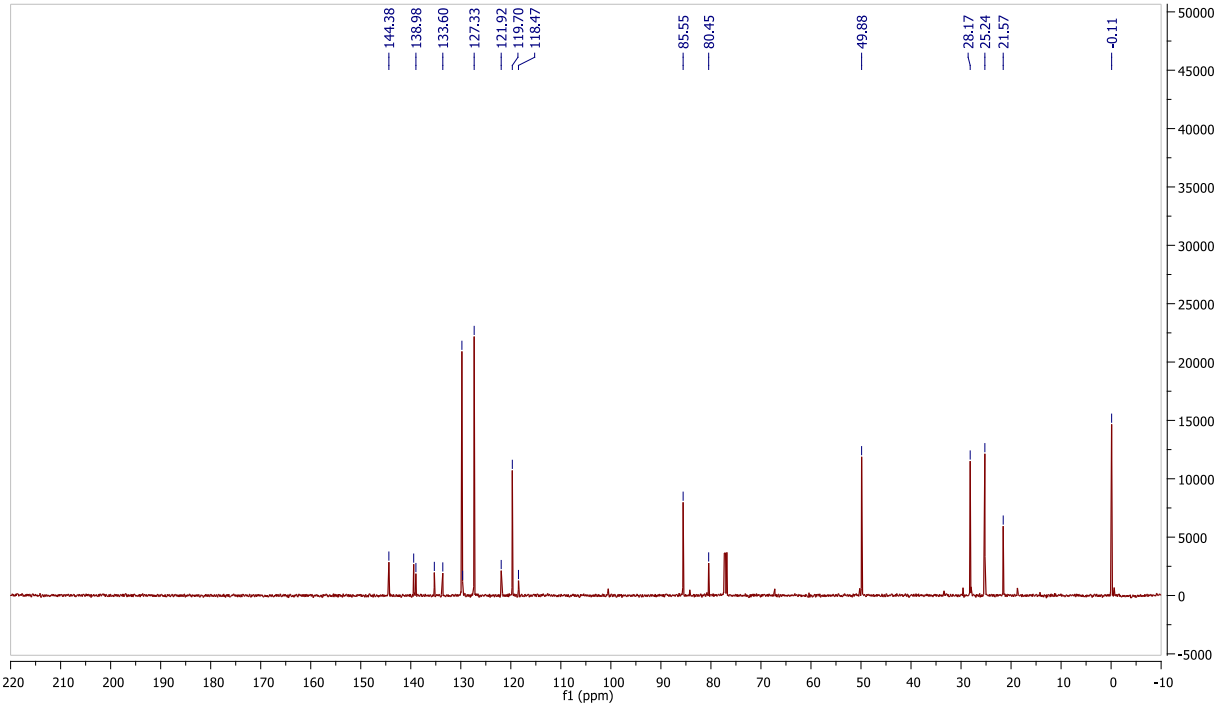
2.07
2.07
2.22
0.96
2.11
2.10
3.30
9.41
f1 (ppm)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85.55
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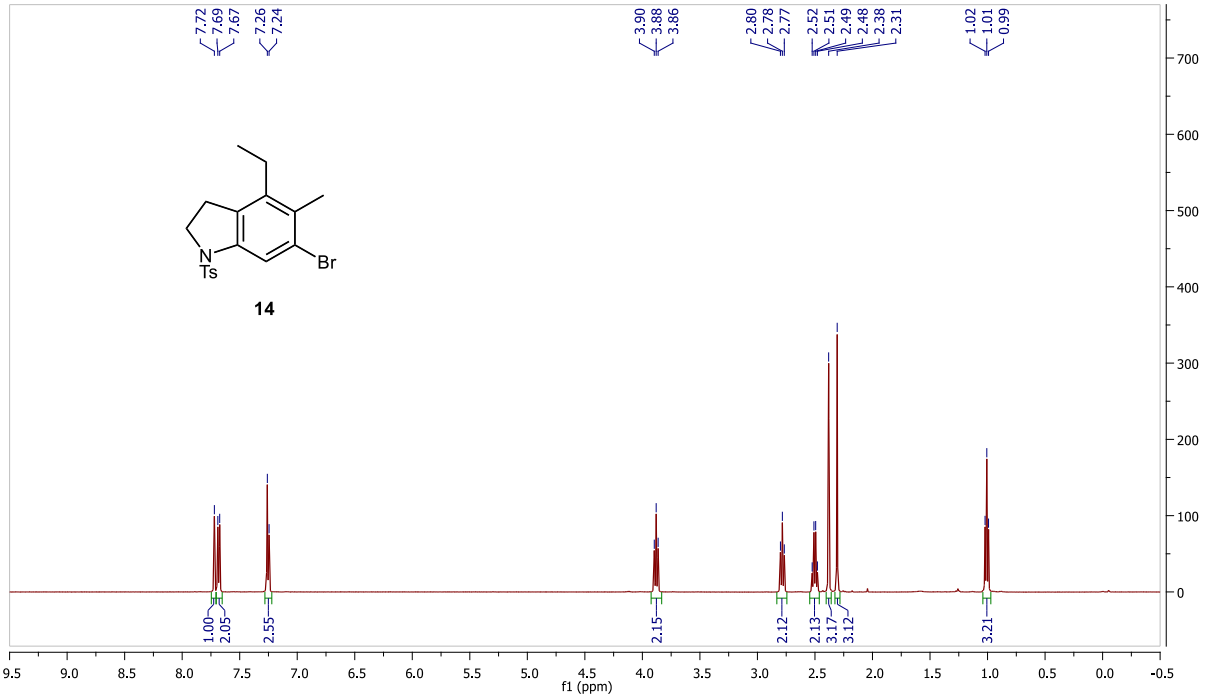
49.88
28.17
25.24
21.57
-0.11
f1 (ppm)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7.26
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3.90
3.88
3.86
2.80
2.78
2.77
2.52
2.51
2.49
2.48
2.38
2.31
1.02
1.01
0.99
N
Ts
Br
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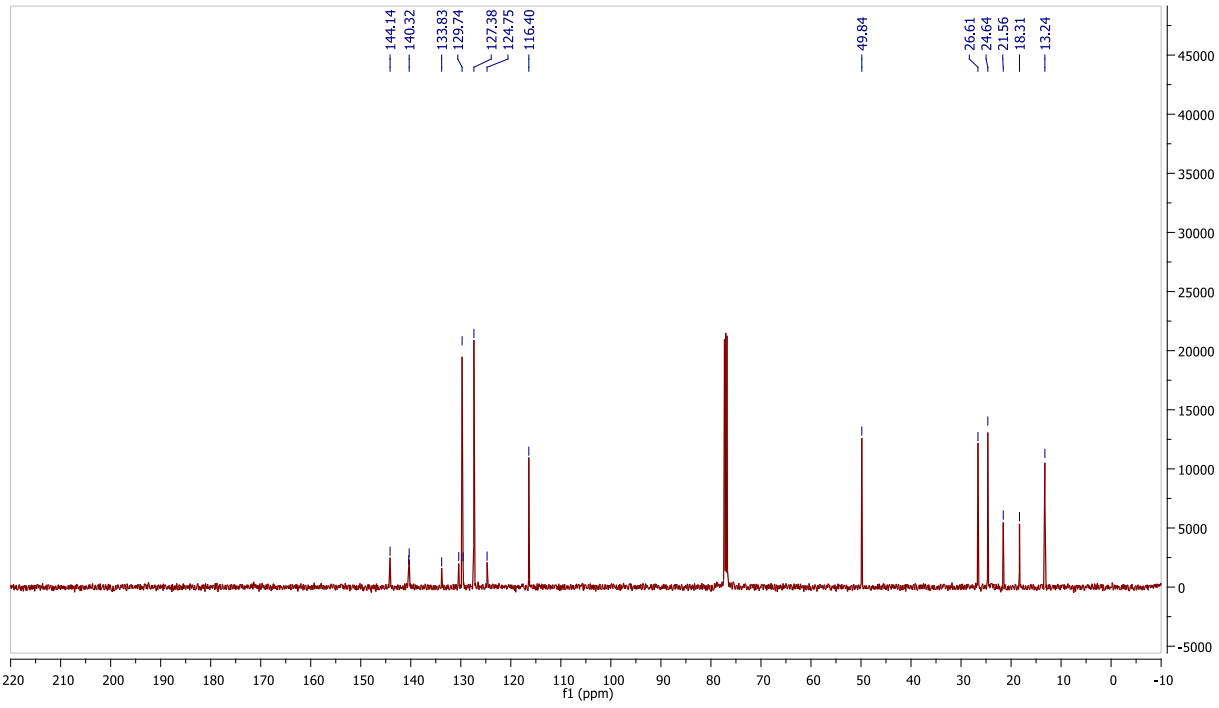
2.55
2.15
2.12
2.13
3.17
3.12
3.21
f1 (ppm)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124.75
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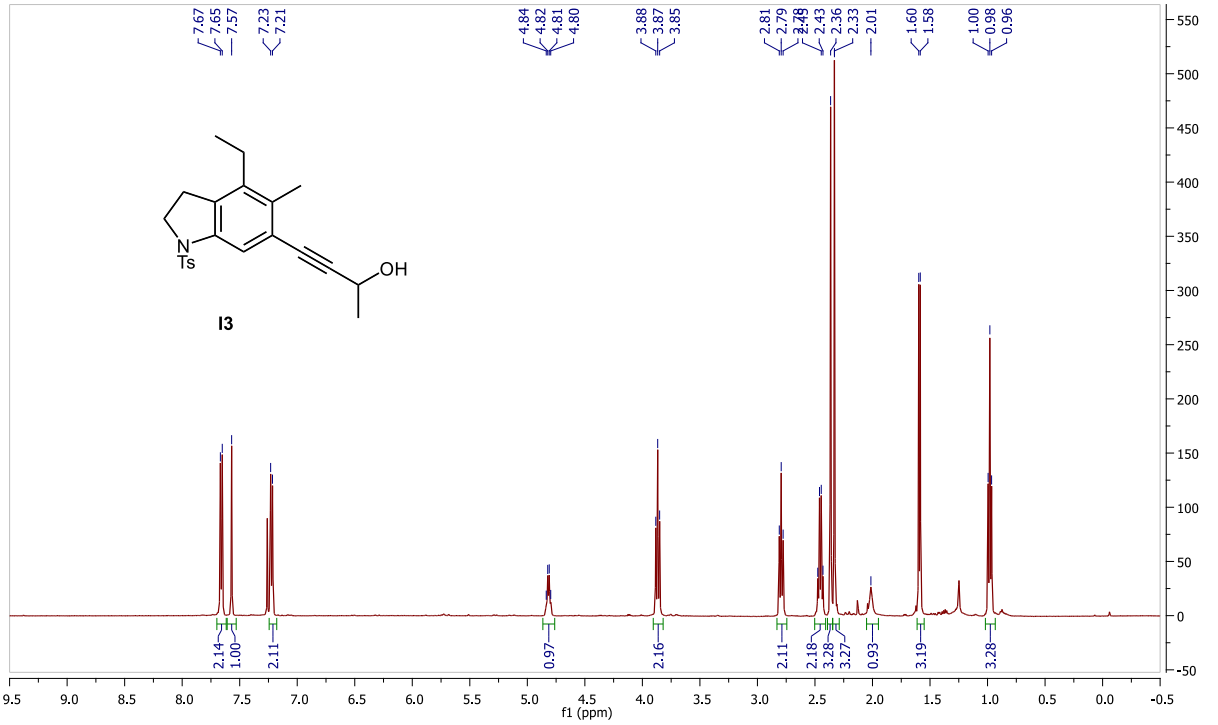
49.84
26.61
24.64
21.56
18.31
13.24
f1 (ppm)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7.65
7.57
7.23
7.21
4.84
4.82
4.81
4.80
3.88
3.87
3.85
2.81
2.79
2.43
2.36
2.33
2.01
1.60
1.58
1.00
0.98
0.96
N
Ts
OH
I3
2.14
1.00
2.11
0.97
2.16
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2.18
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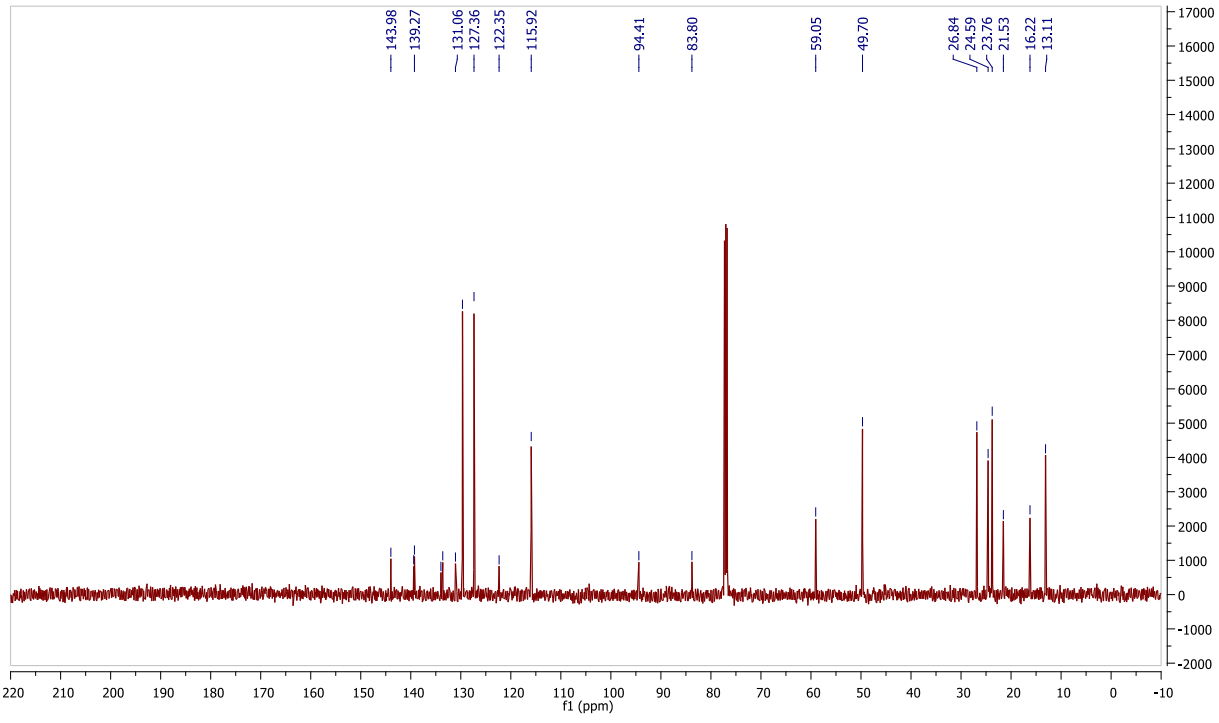
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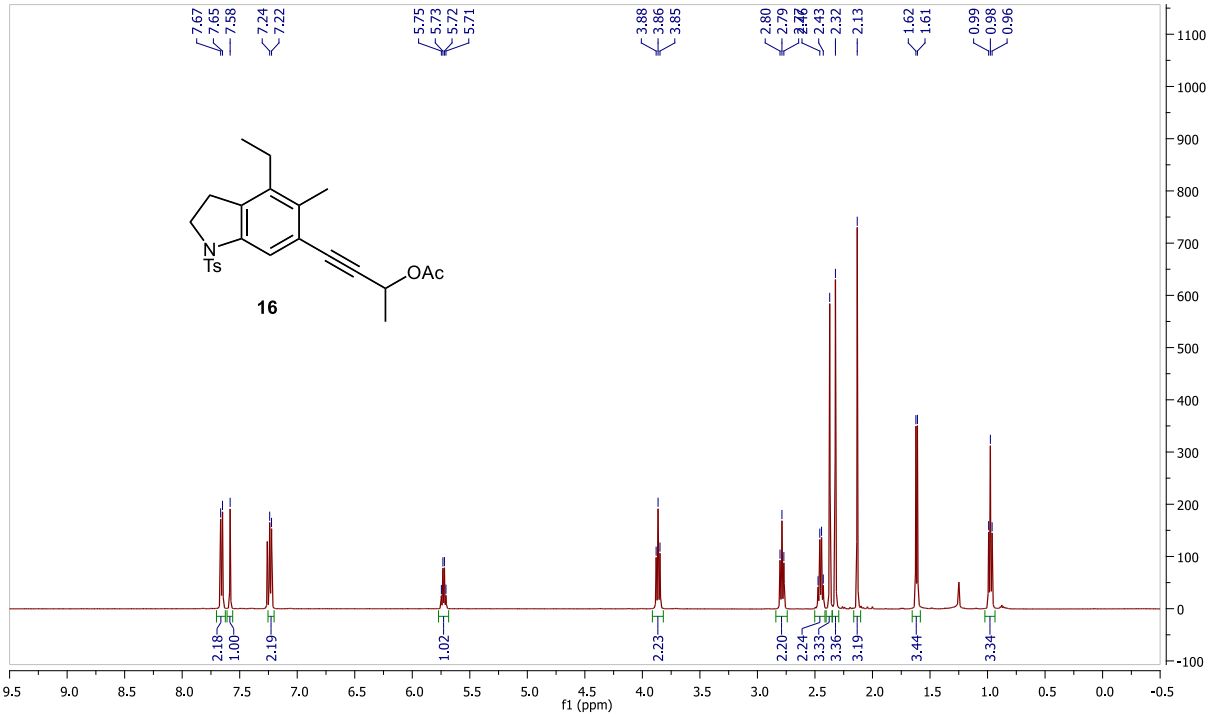
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1.61
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0.98
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N
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OAc
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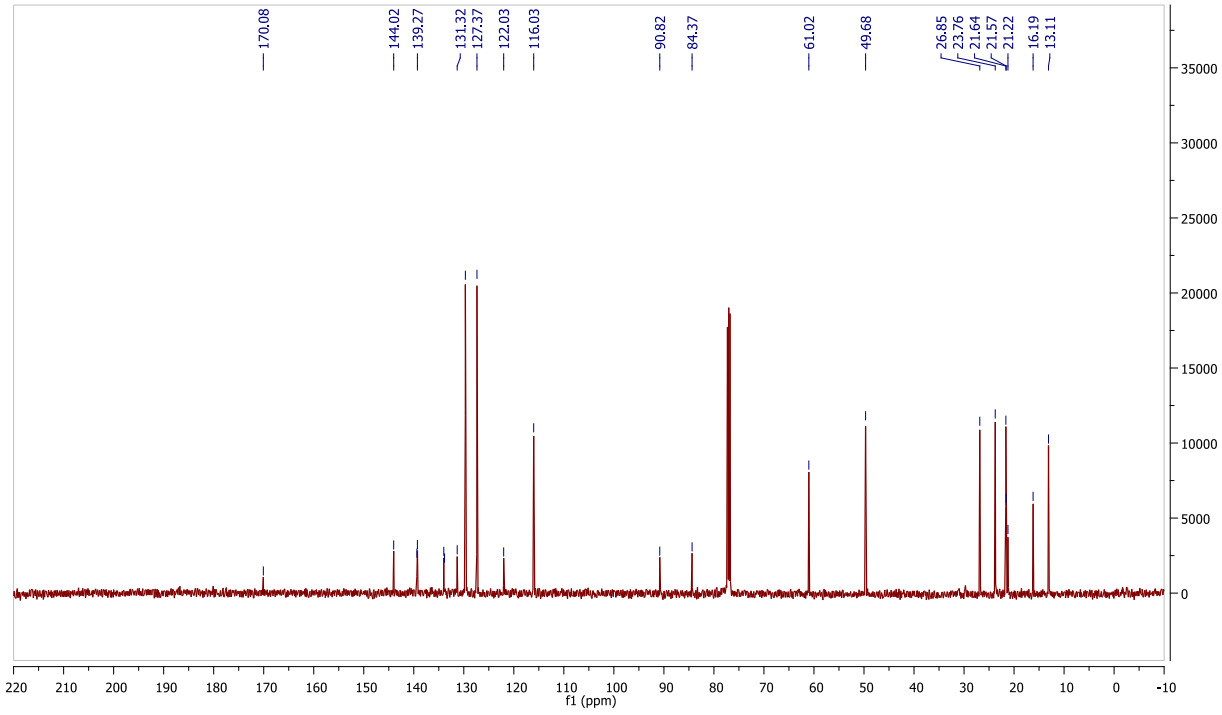
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21.22
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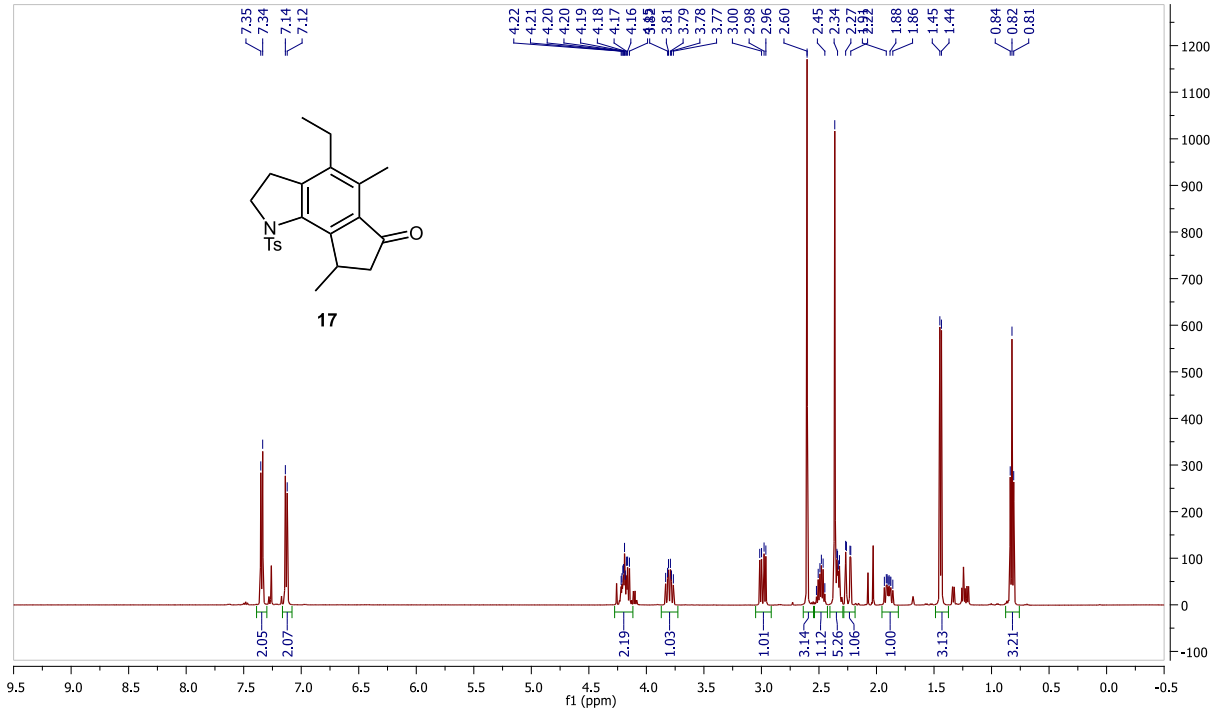
13.11
f1 (ppm)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3.00
2.98
2.96
2.60
2.45
2.34
2.27
1.88
1.86
1.45
1.44
0.84
0.82
0.81
N
Ts
O
17
2.05
2.07
2.19
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1.01
3.14
1.12
5.26
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1.00
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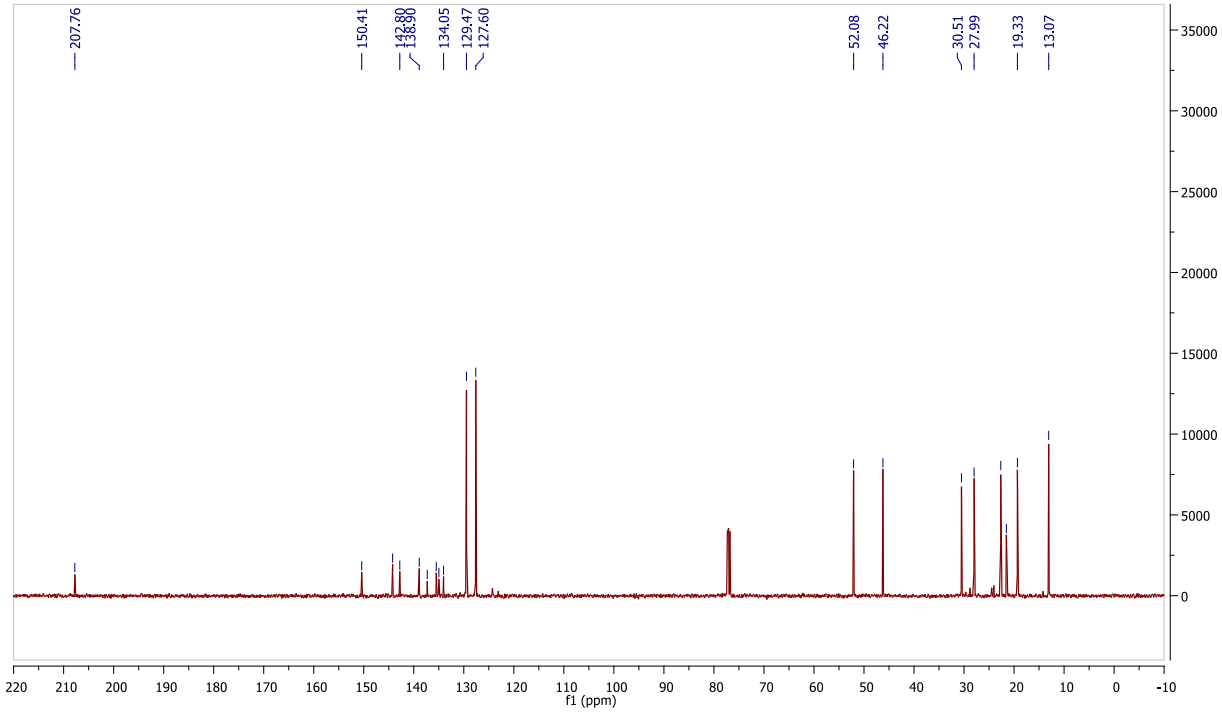
3.21
f1 (ppm)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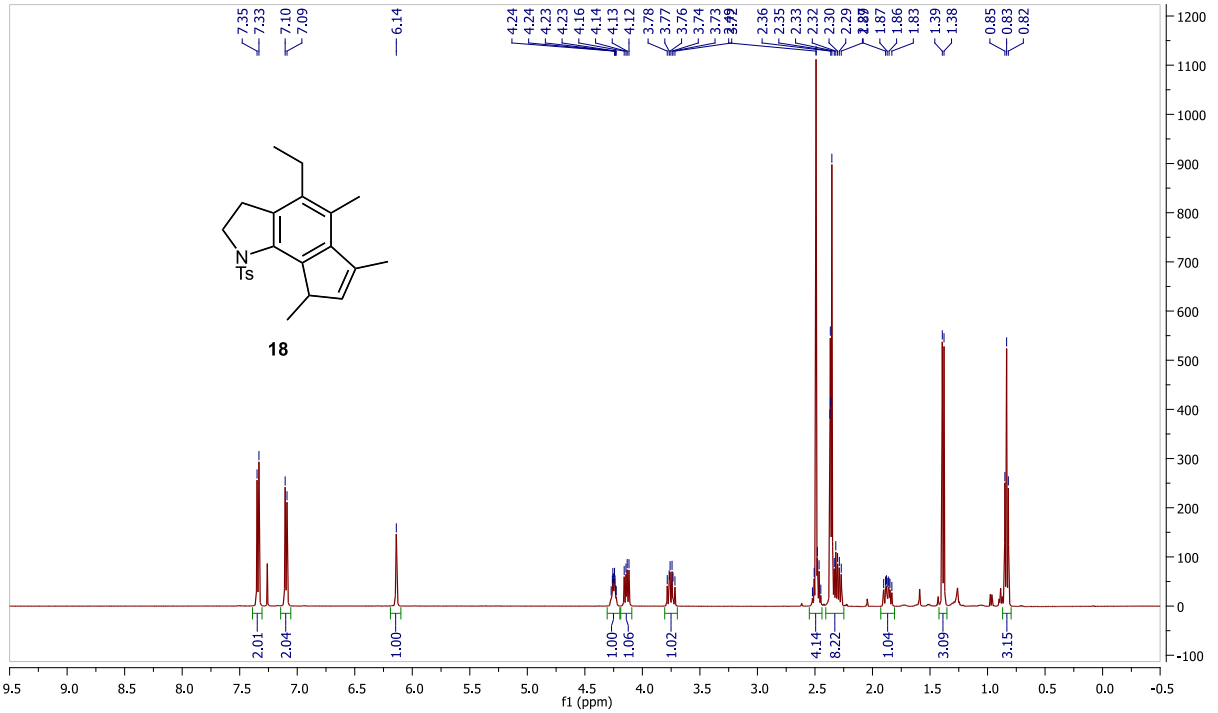
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2.33
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1.39
1.38
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0.83
0.82
N
Ts
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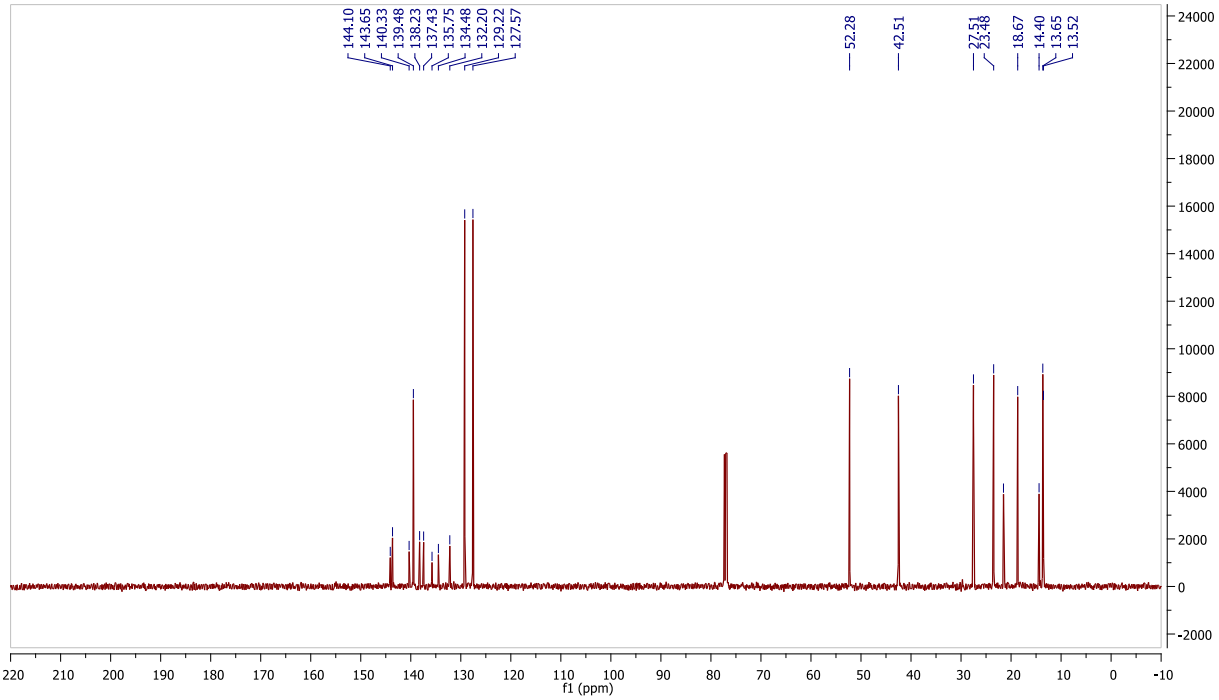
f1 (ppm)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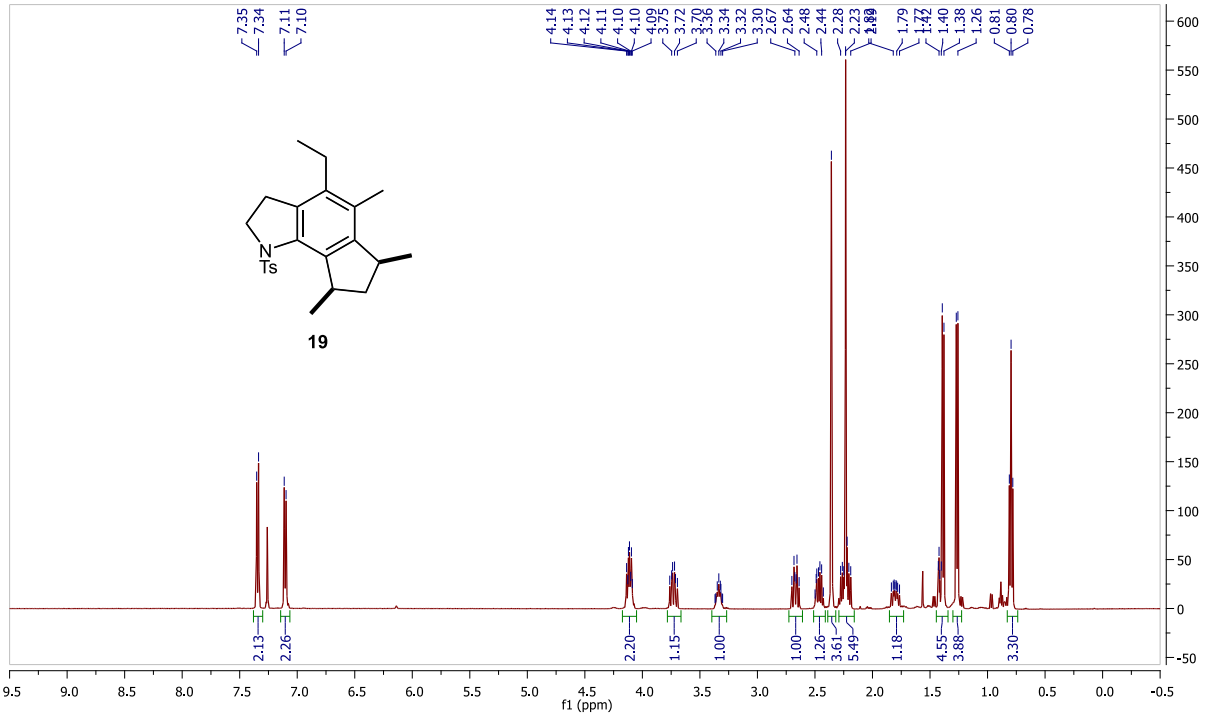
f1 (ppm)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4.11
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4.10
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3.75
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3.34
3.32
3.30
2.67
2.64
2.48
2.44
2.28
2.23
1.79
1.77
1.42
1.40
1.38
1.26
0.81
0.80
0.78
N
Ts
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2.13
2.26
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1.00
1.26
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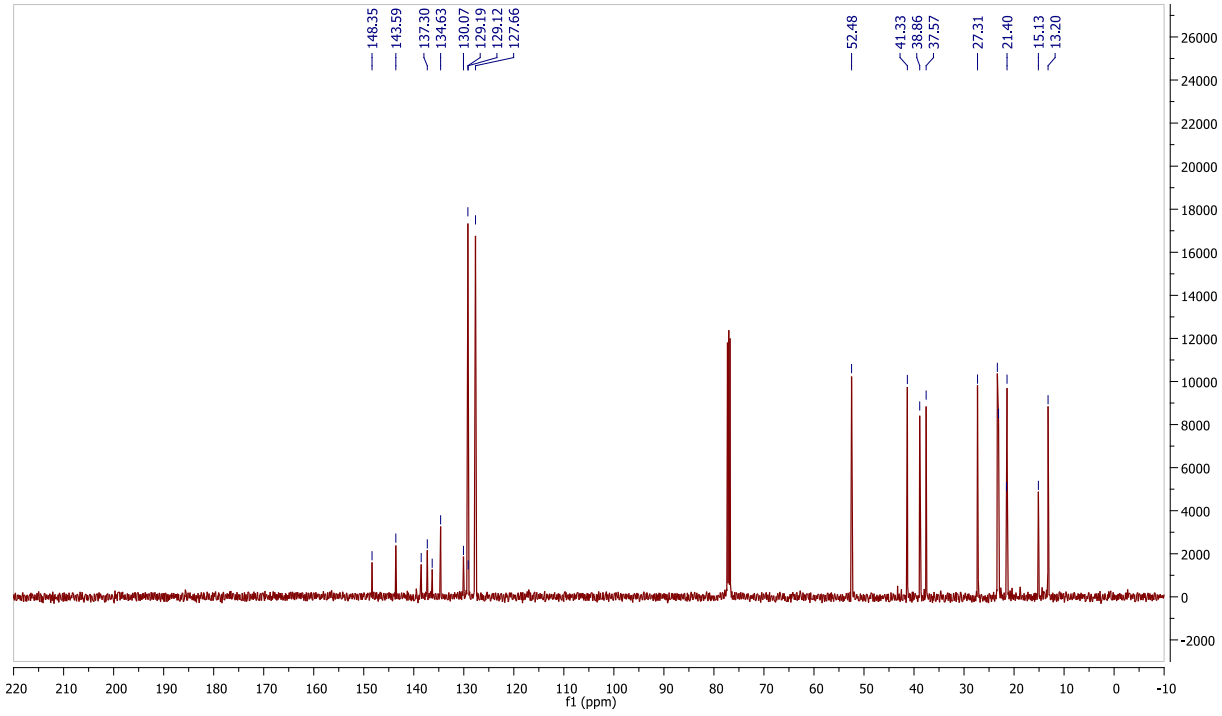
3.30
f1 (ppm)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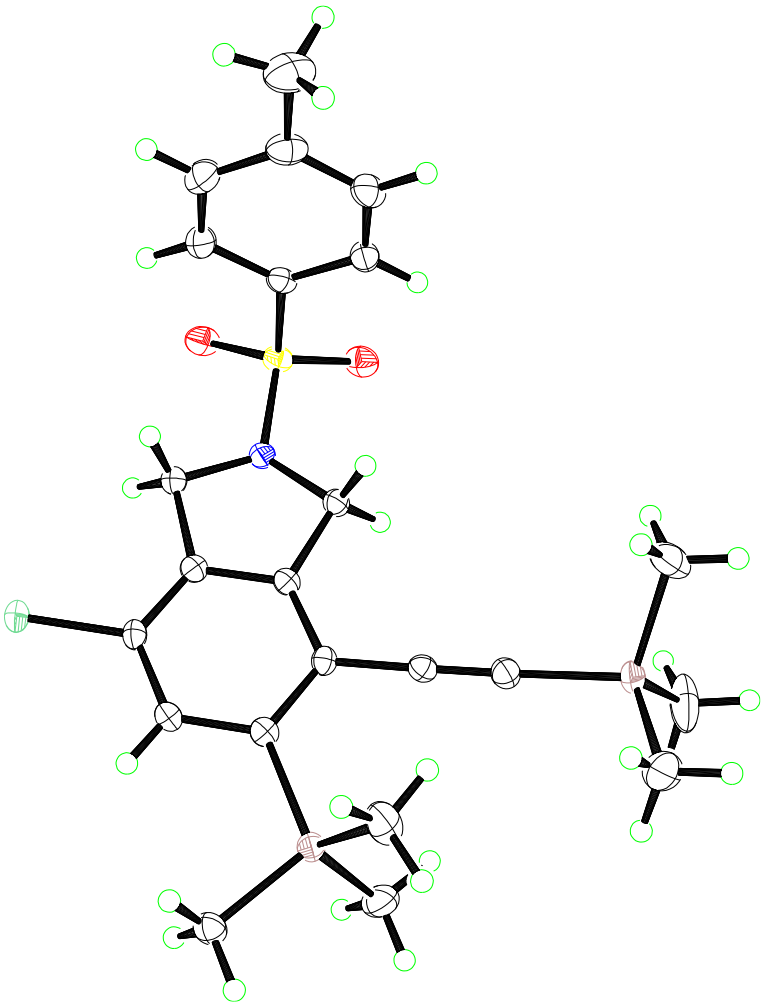
13.20
f1 (ppm)

ORTEP for **6a**



The structure of **6a** (CCDC 1039073) was confirmed by X-ray diffraction analysis. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Experimental

Data Collection

A colorless parallelapiped crystal of $C_{23}H_{30}Si_2O_2NS$ was mounted on a mitigen polymer mount. All measurements were made on a Bruker diffractometer equiped with an APEX2 CCD area detector with graphite monochromated MoKα radiation.

Cell constants and an orientation matrix for data collection corresponded to amonoclinic cell with dimensions:

a = 11.592(2) Å
b = 11.7363(13) Å
c = 11.7880(13) Å
α = 118.7280(10) Å
β = 104.041(2) Å
γ = 100.602(2) Å
V = 1276.3(3) Å^3

For Z = 2 and F.W. = 476.17, the calculated density is 1.239 g/cm^3. The space group was determine the to be:

P-1 (#2)

The data were collected in a stream of cold nitrogen gas to a maximum 2θ value of 55.02

Data Reduction

Of the 14633 reflections which were collected, 5746 were unique (R_{int} = 0.047); equivalent reflections were merged.

The linear absorption coefficient, μ, for MoKα radiation is 0.344 cm^{-1}. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods [1] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included

but not refined. The final cycle of full-matrix least-squares refinement was based on 5746 observed reflections ($I > 2.00\sigma(I)$) and 278 variable parameters and converged (largest parameter shift was 0.063 times its esd) with unweighted and weighted agreement factors of:

$$R = \Sigma \; ||Fo| - |Fc|| \; / \; \Sigma \; |Fo| = 0.0346$$

$$R_w = [(\Sigma \; w \; (|Fo| - |Fc|)^2 \; / \; \Sigma \; w \; Fo^2)]^{1/2} = 0.1314$$

The standard deviation of an observation of unit weight was 1.072. The weighting scheme was based on counting statistics. Plots of $\Sigma \; w \; (|Fo| - |Fc|)^2$ versus $|Fo|$, reflection order in data collection, $\sin \theta/\lambda$ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.377 and -0.573 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[2]. The values for the mass attenuation coefficients are those of Creagh and Hubbel[3].

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{23}H_{30}Si_2O_2NS$
Formula Weight	476.17
Crystal System	triclinic
Lattice Type	Primitive
Lattice Parameters	a = 11.592(2) Å b = 11.7363(13) Å c = 11.7880(13) Å α = 118.7280(10)° β = 104.041(2)° γ = 100.602(2)° V = 1276.3(3) Å^3
Space Group	P-1 (#2)
Z value	1
D_{calc}	1.239 g/cm^3
F_{000}	504.00
μ(MoKα)	0.344 cm^{-1}

B. Intensity Measurements

Diffractometer	Bruker APEX2 CCD
Radiation	MoKα (λ = 0.71069 Å) graphite monochromated
Crystal to Detector Distance	60.0 mm
Data Images	1464 exposures @ 30.0 seconds
Scan Type	ω
$2\theta_{max}$	55.02°
No. of Reflections Measured	Total: 14633 Unique: 5746 (R_{int}=0.0471)
Corrections	Lorentz-polarization

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SHELXS87)
Refinement	Full-matrix least-squares
Function Minimized	Σ w (|Fo| - |Fc|)^2

Least Squares Weights	$1/\sigma^2(Fo) = 4Fo^2/\sigma^2(Fo^2)$
No. Observations (I>2.00σ(I))	5746
No. Variables	278
Reflection/Parameter Ratio	20.7
Residuals: R; Rw	0.0346 ; 0.1314
Goodness of Fit Indicator	1.072
Max Shift/Error in Final Cycle	0.063
Maximum peak in Final Diff. Map	0.377 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.573 $e^-/Å^3$

Table 1 Atom Coordinates

Atom	x	y	z	Biso
Cl1	-0.21757(3)	0.22292(3)	0.35973(3)	0.02246(12)
S1	-0.13237(3)	0.81990(3)	0.68741(4)	0.01897(12)
Si1	0.33782(4)	0.80621(4)	1.25406(4)	0.02288(13)
Si2	0.17533(4)	0.30367(4)	0.80317(4)	0.01917(12)
O1	-0.19173(10)	0.78611(11)	0.54802(11)	0.0251(2)
O2	-0.02870(10)	0.94750(10)	0.79233(11)	0.0252(2)
N1	-0.07935(11)	0.69655(12)	0.67151(12)	0.0180(2)
C1	0.23966(18)	0.89981(18)	1.33569(19)	0.0358(4)
H1A	0.2181	0.9523	1.2970	0.054
H1B	0.2865	0.9616	1.4350	0.054
H1C	0.1633	0.8342	1.3175	0.054
C2	0.48587(18)	0.9297(2)	1.28560(19)	0.0503(6)
H2A	0.5372	0.8794	1.2457	0.076
H2B	0.5323	0.9947	1.3846	0.076
H2C	0.4648	0.9790	1.2428	0.076
C3	0.3736(2)	0.6942(2)	1.31759(19)	0.0471(5)
H3A	0.2955	0.6286	1.2961	0.071
H3B	0.4204	0.7509	1.4171	0.071
H3C	0.4233	0.6454	1.2724	0.071
C4	0.24252(14)	0.69229(14)	1.06403(15)	0.0208(3)
C5	0.17186(13)	0.61240(14)	0.94291(14)	0.0175(3)
C6	0.08401(12)	0.51657(13)	0.79983(13)	0.0159(3)
C7	0.07243(13)	0.37508(14)	0.72372(14)	0.0169(3)
C8	0.14340(19)	0.32652(17)	0.95899(16)	0.0328(4)
H8A	0.2071	0.3101	1.0123	0.049
H8B	0.0611	0.2617	0.9286	0.049
H8C	0.1455	0.4195	1.0163	0.049
C9	0.34442(15)	0.39573(17)	0.8480(2)	0.0351(4)
H9A	0.3977	0.3600	0.8878	0.053
H9B	0.3670	0.4933	0.9146	0.053
H9C	0.3558	0.3814	0.7647	0.053
C10	0.13448(15)	0.11539(14)	0.67367(16)	0.0234(3)
H10A	0.1479	0.1025	0.5917	0.035
H10B	0.0469	0.0664	0.6482	0.035
H10C	0.1875	0.0800	0.7143	0.035
C11	-0.01987(13)	0.28757(14)	0.58673(14)	0.0178(3)
H11	-0.0283	0.1946	0.5346	0.021
C12	-0.09900(13)	0.33658(14)	0.52708(14)	0.0170(3)
C13	-0.08481(13)	0.47550(14)	0.60050(14)	0.0165(3)
C14	-0.15732(13)	0.55114(14)	0.55788(14)	0.0192(3)
H14A	-0.1610	0.5327	0.4673	0.023
H14B	-0.2430	0.5270	0.5554	0.023
C15	0.00410(13)	0.70944(14)	0.79755(14)	0.0182(3)
H15A	-0.0319	0.7342	0.8686	0.022
H15B	0.0885	0.7771	0.8373	0.022
C16	0.00609(12)	0.56411(13)	0.73577(14)	0.0159(3)
C17	-0.25251(13)	0.81161(14)	0.75381(14)	0.0187(3)
C18	-0.37696(15)	0.72454(16)	0.66092(16)	0.0261(3)
H18	-0.3972	0.6731	0.5648	0.031
C19	-0.47024(15)	0.71597(17)	0.71432(17)	0.0304(4)
H19	-0.5534	0.6574	0.6529	0.036
C20	-0.44190(15)	0.79332(17)	0.85801(17)	0.0279(3)
C21	-0.31708(16)	0.88003(17)	0.94793(16)	0.0268(3)

H21	-0.2970	0.9327	1.0440	0.032
C22	-0.22183(14)	0.88983(15)	0.89759(15)	0.0226(3)
H22	-0.1386	0.9479	0.9591	0.027
C23	-0.54466(18)	0.7821(2)	0.9140(2)	0.0409(4)
H23A	-0.6227	0.7119	0.8381	0.061
H23B	-0.5566	0.8697	0.9589	0.061
H23C	-0.5200	0.7574	0.9806	0.061

Table 2 Atomic Displacement Parameters

Atom	U11	U22	U33	U23	U13	U12
Cl1	0.02102(19)	0.01980(19)	0.01565(19)	0.00561(15)	0.00108(14)	0.00531(14)
S1	0.0230(2)	0.0196(2)	0.0209(2)	0.01364(16)	0.01071(16)	0.01058(15)
Si1	0.0231(2)	0.0240(2)	0.0133(2)	0.00577(18)	0.00450(17)	0.00825(17)
Si2	0.0232(2)	0.0162(2)	0.0165(2)	0.00920(17)	0.00454(17)	0.00744(16)
O1	0.0340(6)	0.0312(6)	0.0235(6)	0.0200(5)	0.0151(5)	0.0191(5)
O2	0.0268(6)	0.0189(5)	0.0317(6)	0.0150(5)	0.0119(5)	0.0077(4)
N1	0.0206(6)	0.0177(6)	0.0159(6)	0.0093(5)	0.0055(5)	0.0089(5)
C1	0.0474(10)	0.0324(9)	0.0323(9)	0.0149(8)	0.0228(8)	0.0223(8)
C2	0.0327(10)	0.0538(12)	0.0224(9)	0.0027(8)	0.0048(7)	-0.0085(9)
C3	0.0651(13)	0.0567(12)	0.0261(9)	0.0231(9)	0.0133(9)	0.0396(11)
C4	0.0227(7)	0.0192(7)	0.0195(7)	0.0102(6)	0.0076(6)	0.0072(6)
C5	0.0200(7)	0.0168(6)	0.0183(7)	0.0107(5)	0.0085(6)	0.0076(5)
C6	0.0164(6)	0.0176(6)	0.0134(6)	0.0087(5)	0.0059(5)	0.0045(5)
C7	0.0192(6)	0.0176(6)	0.0167(6)	0.0105(5)	0.0088(5)	0.0063(5)
C8	0.0546(11)	0.0263(8)	0.0210(8)	0.0155(7)	0.0131(8)	0.0160(8)
C9	0.0220(8)	0.0253(8)	0.0446(10)	0.0150(8)	0.0023(7)	0.0077(6)
C10	0.0298(8)	0.0192(7)	0.0228(7)	0.0125(6)	0.0091(6)	0.0101(6)
C11	0.0205(7)	0.0154(6)	0.0164(6)	0.0077(5)	0.0078(6)	0.0061(5)
C12	0.0165(6)	0.0173(6)	0.0128(6)	0.0065(5)	0.0047(5)	0.0035(5)
C13	0.0173(6)	0.0188(6)	0.0157(6)	0.0102(5)	0.0081(5)	0.0067(5)
C14	0.0199(7)	0.0190(6)	0.0158(6)	0.0081(6)	0.0052(5)	0.0074(5)
C15	0.0225(7)	0.0179(7)	0.0150(6)	0.0092(6)	0.0065(5)	0.0089(5)
C16	0.0176(6)	0.0159(6)	0.0155(6)	0.0090(5)	0.0079(5)	0.0060(5)
C17	0.0226(7)	0.0193(7)	0.0193(7)	0.0119(6)	0.0104(6)	0.0112(5)
C18	0.0254(8)	0.0304(8)	0.0192(7)	0.0112(6)	0.0074(6)	0.0114(6)
C19	0.0208(7)	0.0355(9)	0.0299(8)	0.0157(7)	0.0080(6)	0.0093(6)
C20	0.0307(8)	0.0371(9)	0.0325(8)	0.0249(7)	0.0191(7)	0.0195(7)
C21	0.0348(8)	0.0331(8)	0.0197(7)	0.0159(7)	0.0140(7)	0.0181(7)
C22	0.0252(7)	0.0206(7)	0.0190(7)	0.0095(6)	0.0061(6)	0.0094(6)
C23	0.0388(10)	0.0607(12)	0.0466(11)	0.0376(10)	0.0282(9)	0.0256(9)

Table 3 Bond Lengths

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Cl1	C12	1.7437(14)	C8	H8C	0.9600
S1	O2	1.4327(11)	C9	H9A	0.9600
S1	O1	1.4337(11)	C9	H9B	0.9600
S1	N1	1.6220(12)	C9	H9C	0.9600
S1	C17	1.7646(14)	C10	H10A	0.9600
Si1	C1	1.8445(16)	C10	H10B	0.9600
Si1	C4	1.8446(15)	C10	H10C	0.9600
Si1	C2	1.855(2)	C11	C12	1.3917(19)
Si1	C3	1.859(2)	C11	H11	0.9300
Si2	C9	1.8595(17)	C12	C13	1.3821(19)
Si2	C10	1.8599(15)	C13	C16	1.3863(18)
Si2	C8	1.8643(16)	C13	C14	1.4984(18)
Si2	C7	1.8929(14)	C14	H14A	0.9700
N1	C14	1.4735(17)	C14	H14B	0.9700
N1	C15	1.4829(17)	C15	C16	1.5062(18)
C1	H1A	0.9600	C15	H15A	0.9700
C1	H1B	0.9600	C15	H15B	0.9700
C1	H1C	0.9600	C17	C22	1.3905(19)
C2	H2A	0.9600	C17	C18	1.393(2)
C2	H2B	0.9600	C18	C19	1.388(2)
C2	H2C	0.9600	C18	H18	0.9300
C3	H3A	0.9600	C19	C20	1.394(2)
C3	H3B	0.9600	C19	H19	0.9300
C3	H3C	0.9600	C20	C21	1.389(2)
C4	C5	1.205(2)	C20	C23	1.510(2)
C5	C6	1.4381(19)	C21	C22	1.386(2)
C6	C16	1.3989(18)	C21	H21	0.9300
C6	C7	1.4169(18)	C22	H22	0.9300
C7	C11	1.4036(19)	C23	H23A	0.9600
C8	H8A	0.9600	C23	H23B	0.9600
C8	H8B	0.9600	C23	H23C	0.9600

Table 4 Bond Angles

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
O2	S1	O1	121.45(7)	H9A	C9	H9C	109.5
O2	S1	N1	106.11(6)	H9B	C9	H9C	109.5
O1	S1	N1	106.09(6)	Si2	C10	H10A	109.5
O2	S1	C17	107.54(7)	Si2	C10	H10B	109.5
O1	S1	C17	107.37(7)	H10A	C10	H10B	109.5
N1	S1	C17	107.61(6)	Si2	C10	H10C	109.5
C1	Si1	C4	106.80(8)	H10A	C10	H10C	109.5
C1	Si1	C2	110.73(10)	H10B	C10	H10C	109.5
C4	Si1	C2	109.07(8)	C12	C11	C7	121.60(12)
C1	Si1	C3	111.04(9)	C12	C11	H11	119.2
C4	Si1	C3	107.85(8)	C7	C11	H11	119.2
C2	Si1	C3	111.20(11)	C13	C12	C11	120.24(13)
C9	Si2	C10	108.38(7)	C13	C12	Cl1	119.52(11)
C9	Si2	C8	112.68(9)	C11	C12	Cl1	120.24(10)
C10	Si2	C8	108.97(7)	C12	C13	C16	119.18(12)
C9	Si2	C7	108.57(7)	C12	C13	C14	129.62(13)
C10	Si2	C7	109.90(7)	C16	C13	C14	111.18(12)
C8	Si2	C7	108.33(7)	N1	C14	C13	101.03(11)
C14	N1	C15	112.54(10)	N1	C14	H14A	111.6
C14	N1	S1	119.90(9)	C13	C14	H14A	111.6
C15	N1	S1	120.13(9)	N1	C14	H14B	111.6
Si1	C1	H1A	109.5	C13	C14	H14B	111.6
Si1	C1	H1B	109.5	H14A	C14	H14B	109.4
H1A	C1	H1B	109.5	N1	C15	C16	100.81(10)
Si1	C1	H1C	109.5	N1	C15	H15A	111.6
H1A	C1	H1C	109.5	C16	C15	H15A	111.6
H1B	C1	H1C	109.5	N1	C15	H15B	111.6
Si1	C2	H2A	109.5	C16	C15	H15B	111.6
Si1	C2	H2B	109.5	H15A	C15	H15B	109.4
H2A	C2	H2B	109.5	C13	C16	C6	121.69(12)
Si1	C2	H2C	109.5	C13	C16	C15	110.64(12)
H2A	C2	H2C	109.5	C6	C16	C15	127.67(12)
H2B	C2	H2C	109.5	C22	C17	C18	120.85(13)
Si1	C3	H3A	109.5	C22	C17	S1	119.88(11)
Si1	C3	H3B	109.5	C18	C17	S1	119.26(11)
H3A	C3	H3B	109.5	C19	C18	C17	118.85(14)
Si1	C3	H3C	109.5	C19	C18	H18	120.6
H3A	C3	H3C	109.5	C17	C18	H18	120.6
H3B	C3	H3C	109.5	C18	C19	C20	121.39(15)
C5	C4	Si1	173.90(13)	C18	C19	H19	119.3
C4	C5	C6	178.07(15)	C20	C19	H19	119.3
C16	C6	C7	119.40(12)	C21	C20	C19	118.41(14)
C16	C6	C5	118.87(12)	C21	C20	C23	121.03(15)
C7	C6	C5	121.71(12)	C19	C20	C23	120.57(16)
C11	C7	C6	117.83(12)	C22	C21	C20	121.44(14)
C11	C7	Si2	120.42(10)	C22	C21	H21	119.3
C6	C7	Si2	121.74(10)	C20	C21	H21	119.3
Si2	C8	H8A	109.5	C21	C22	C17	119.06(14)
Si2	C8	H8B	109.5	C21	C22	H22	120.5
H8A	C8	H8B	109.5	C17	C22	H22	120.5
Si2	C8	H8C	109.5	C20	C23	H23A	109.5
H8A	C8	H8C	109.5	C20	C23	H23B	109.5
H8B	C8	H8C	109.5	H23A	C23	H23B	109.5

Si2	C9	H9A	109.5	C20	C23	H23C	109.5
Si2	C9	H9B	109.5	H23A	C23	H23C	109.5
H9A	C9	H9B	109.5	H23B	C23	H23C	109.5
Si2	C9	H9C	109.5	.	.	?	

Table 5. Torsion Angles

Atom 1	Atom 2	Atom 3	Atom 4	Angle	Atom 1	Atom 2	Atom 3	Atom 4	Angle
O2	S1	N1	C14	-171.71(10)	S1	N1	C14	C13	-169.40(9)
O1	S1	N1	C14	-41.28(12)	C12	C13	C14	N1	-169.99(14)
C17	S1	N1	C14	73.41(11)	C16	C13	C14	N1	11.67(14)
O2	S1	N1	C15	40.63(12)	C14	N1	C15	C16	19.25(14)
O1	S1	N1	C15	171.06(10)	S1	N1	C15	C16	169.11(9)
C17	S1	N1	C15	-74.26(12)	C12	C13	C16	C6	0.1(2)
C1	Si1	C4	C5	-57.7(12)	C14	C13	C16	C6	178.65(12)
C2	Si1	C4	C5	-177.4(12)	C12	C13	C16	C15	-178.89(12)
C3	Si1	C4	C5	61.7(12)	C14	C13	C16	C15	-0.35(15)
Si1	C4	C5	C6	21(5)	C7	C6	C16	C13	1.7(2)
C4	C5	C6	C16	78(4)	C5	C6	C16	C13	-176.82(12)
C4	C5	C6	C7	-101(4)	C7	C6	C16	C15	-179.51(12)
C16	C6	C7	C11	-1.32(19)	C5	C6	C16	C15	2.0(2)
C5	C6	C7	C11	177.12(12)	N1	C15	C16	C13	-11.05(14)
C16	C6	C7	Si2	179.61(9)	N1	C15	C16	C6	170.02(13)
C5	C6	C7	Si2	-1.94(18)	O2	S1	C17	C22	-21.72(13)
C9	Si2	C7	C11	119.53(12)	O1	S1	C17	C22	-153.96(11)
C10	Si2	C7	C11	1.14(13)	N1	S1	C17	C22	92.21(12)
C8	Si2	C7	C11	-117.81(12)	O2	S1	C17	C18	159.33(12)
C9	Si2	C7	C6	-61.43(13)	O1	S1	C17	C18	27.09(14)
C10	Si2	C7	C6	-179.82(11)	N1	S1	C17	C18	-86.74(13)
C8	Si2	C7	C6	61.23(13)	C22	C17	C18	C19	-0.6(2)
C6	C7	C11	C12	-0.8(2)	S1	C17	C18	C19	178.34(12)
Si2	C7	C11	C12	178.32(10)	C17	C18	C19	C20	0.6(2)
C7	C11	C12	C13	2.6(2)	C18	C19	C20	C21	-0.1(2)
C7	C11	C12	Cl1	-176.92(10)	C18	C19	C20	C23	-179.75(16)
C11	C12	C13	C16	-2.2(2)	C19	C20	C21	C22	-0.4(2)
Cl1	C12	C13	C16	177.28(10)	C23	C20	C21	C22	179.24(15)
C11	C12	C13	C14	179.55(13)	C20	C21	C22	C17	0.4(2)
Cl1	C12	C13	C14	-1.0(2)	C18	C17	C22	C21	0.1(2)
C15	N1	C14	C13	-19.45(14)	S1	C17	C22	C21	-178.83(11)

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