Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

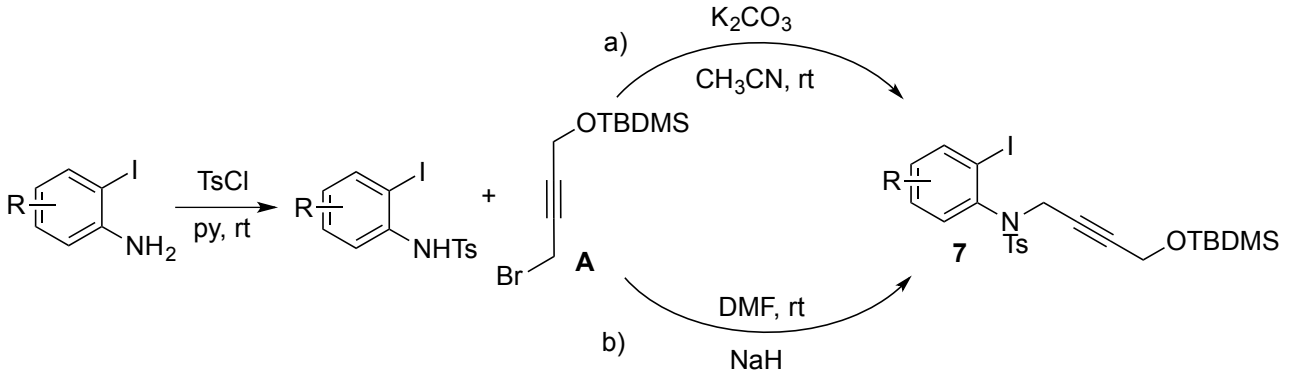
Supporting Information

Table of contents:

General Methods.

^{1}H-NMR spectra were recorded on Varian 400 (400 MHz) spectrometer. Chemical shifts are reported in ppm from TMS with the solvent resonance as the internal standard (deuterochloroform: 7.27 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = duplet, t = triplet, q = quartet, sext = sextet, sept = septet, p = pseudo, b = broad, m = multiplet), coupling constants (Hz). ^{13}C-NMR spectra were recorded on a Varian 400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from TMS with the solvent as the internal standard (deuterochloroform: 77.0 ppm). GC-MS spectra were taken by EI ionization at 70 eV on a Hewlett-Packard 5971 with GC injection. They are reported as: *m/z* (rel. intense). LC-electrospray ionization mass spectra were obtained with Agilent Technologies MSD1100 single-quadrupole mass spectrometer. Chromatographic purification was done with 240-400 mesh silica gel. Elemental analyses were carried out by using a EACE 1110 CHNOS analyzer. All anhydrous solvents were supplied by Sigma Aldrich in Sureseal® bottles and used without any further purification. Commercially available chemicals were purchased from Sigma Aldrich, Stream and TCI and used without any further purification. Melting points were measured using open glass capillaries in a Bibby Stuart Scientific Melting Point Apparatus SMP 3 and are calibrated by comparison with literature values (Aldrich).

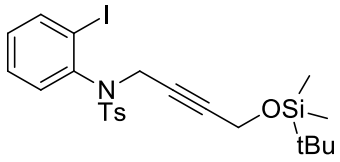
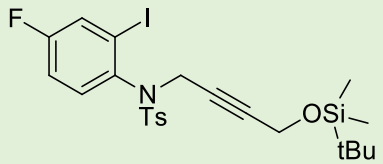
General procedure for the synthesis of 7:



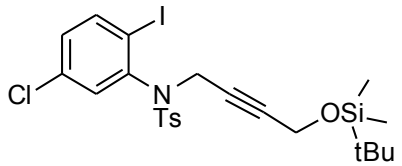
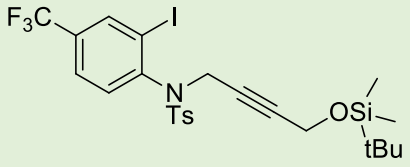
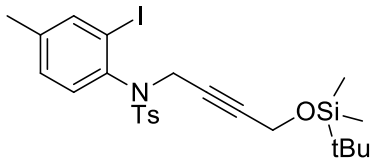
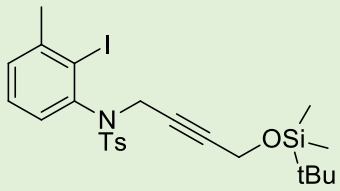
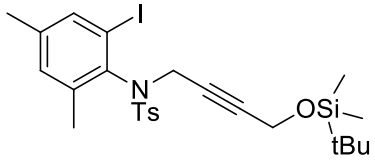
Substituted *N*-tosyl-2-iodoaniline and [(4-bromo-2-butyn-1-yl)oxy](tert-butyl)dimethylsilane (**A**) were prepared following reported procedures.[1]

Method a) for compounds 7a,e-g. To a solution of substituted *N*-tosyl-2-iodoaniline (1 mmol) in dry acetonitrile (5 mL) under nitrogen atmosphere, K_2CO_3 (2 eq) followed by the propargyl bromide **A** (1.2 eq) was added. The mixture was stirred at room temperature until TLC analysis indicates complete consumption of starting material. Subsequently, water (10 mL) was added and the aqueous layer was extracted with AcOEt (3 x 10 mL). The combined organic layers were dried with Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to give the desired product.

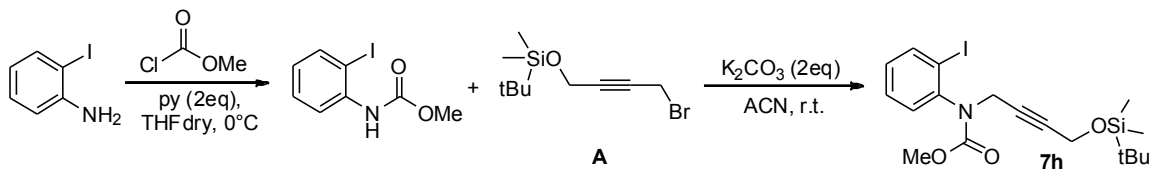
Method b) for compounds 7b and 7c. To a solution of substituted *N*-tosyl-2-iodoaniline (1 mmol) in dry DMF (5 mL) under nitrogen atmosphere, NaH (2.0 eq) and the solution was stirred at rt for 15. Then propargyl bromide **A** (1.2 eq) was added and the mixture stirred at room temperature until the TLC analysis indicates complete consumption of starting material. Subsequently, water (10 mL) was added and the aqueous layer was extracted with AcOEt (1 x 10 mL). The organic phase was washed with water (3 x 5 mL) in order to remove traces of DMF and subsequently dried over Na_2SO_4. The crude product was purified by column chromatography on silica gel to give the desired product.

	**7a.** Yellow oil. Yield = 62%, (*c*Hex:EtOAc = 9:1). ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 6.6 Hz, 1H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.31 – 7.25 (m, 3H), 7.11 (d, *J* = 7.9 Hz, 1H), 7.06 (t, *J* = 7.7 Hz, 1H), 4.76 (d, *J* = 16.7 Hz, 1H), 4.18 (d+s, *J* = 16.6 Hz, 3H), 2.45 (s, 3H), 0.86 (s, 9H), 0.02 (d, *J* = 4.2 Hz, 6H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$) 143.72, 140.74, 140.12, 136.62, 130.96, 130.26, 129.30, 128.61, 128.21, 102.68, 84.40, 78.32, 51.43, 41.02, 25.67, 21.53, 18.12, -5.36. ***GC-MS*****:** 498 (M-tBu).
	**7b.** Colorless oil. **Yield** = 76%, (*c*Hex:EtOAc = 95:5). ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.61 (dd, *J* = 7.8, 2.8 Hz, 1H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.06 (dd, *J* = 8.8, 5.5 Hz, 1H), 7.01 – 6.95 (m, 1H), 4.75 (d, *J* = 18.4 Hz, 1H), 4.14 (d+s, *J* = 13.2 Hz, 3H), 2.45 (s, 3H), 0.86 (d, *J* = 2.8 Hz, 9H), 0.03 (d, *J* = 4.4 Hz, 6H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$) δ 162.91, 160.39, 143.95, 137.10, 137.07, 136.40, 131.70, 131.61, 129.44, 128.25, 127.17, 126.92, 115.74, 115.52, 102.97, 102.89, 84.70, 78.18, 51.46, 41.09, 25.69, 21.59, 18.18, -5.33. ***LC-MS***: 574.2 (M^+), 591.2 (M+H_2O).

[1] a) A.K. Mailyan, I.M. Geraskin, V.N. Nemykin V.V. Zhdankin, *J. Org. Chem.*, 2009, **74**, 8444; b) G. Cera, P. Crispino, M. Monari, M. Bandini, *Chem. Commun.* 2011, **47**, 7803.

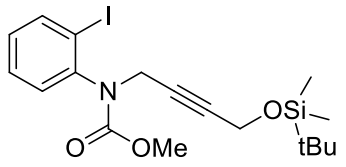
	**7c.** Pale yellow oil. **Yield** = 89%, (*c*Hex:EtOAc = 9:1). ***^{1}H-NMR*** (400 MHz, $CDCl_3$) 7.81 (d, *J* = 9.1 Hz, 1H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.08-7.05 (m, 2H), 4.70 (d, *J* = 18.3 Hz, 1H), 4.23 – 4.12 (m, 3H), 2.45 (s, 3H), 0.85 (s, 9H), -0.02 (s, 6H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$) δ144.16, 141.97, 140.64, 134.36, 131.27, 130.55, 129.49, 128.26, 100.12, 84.97, 77.83, 51.43, 40.99, 30.87, 25.72, 21.60, 18.19, -5.31. ***LC-MS***: 607.2 ($M+H_2O$), 612.2 ($M+Na^+$), 628.2 ($M+K^+$).
	**7d.** Yellow oil. **Yield** = 52% (not optimized), (*c*Hex:EtOAc = 9:1). ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.54 (d, *J* = 8.3, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 1H), 4.74 (d, *J* = 18.0 Hz, 1H), 4.21 (d, *J* = 18.0 Hz, 1H), 4.15 (s, 2H), 2.46 (s, 3H), 0.85 (s, 9H), 0.01 (s, 6H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$) δ 144.24, 137.16, 137.12, 136.22, 131.23, 129.58, 128.24, 125.73, 125.69, 102.88, 85.02, 77.78, 51.43, 40.92, 26.88, 25.66, 21.61, 18.16, -5.37. ***LC-MS*:** 646 ($M+Na^+$).
	**7e.** Yellow oil. **Yield** = 62% (not optimized), (*c*Hex:EtOAc = 95:5). ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 7.73 – 7.69 (m, 3H), 7.29 – 7.26 (m, 2H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 4.74 (d, *J* = 18.3 Hz, 1H), 4.17- 4.13 (m, 3H), 2.44 (s, 3H), 2.30 (s, 3H), 0.85 (s, 9H), 0.02 (d, *J* = 4.4 Hz, 6H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$) δ 143.65, 140.71, 140.60, 138.09, 136.79, 130.42, 129.45, 129.32, 128.27, 102.46, 84.31, 78.51, 65.81, 51.51, 41.11, 25.72, 21.58, 20.57, 18.19, 15.25, -5.31. ***LC-MS***: 570.0 ($M+H^+$) 587 (M^++H_2O).
	**7f.** Yellow oil. **Yield** = 55% (not optimized), (*c*Hex:EtOAc = 95:5). ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 6.6 Hz, 1H), 7.09 (t, *J* = 7.7 Hz, 1H), 6.81 (d, *J* = 6.7 Hz, 1H), 4.76 (dt, *J* = 17.9, 1.7 Hz, 1H), 4.19 – 4.07 (m, 3H), 2.48 (s, 3H), 2.42 (s, 3H), 0.83 (s, 9H), -0.01 (d, *J* = 4.6 Hz, 6H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$) δ 144.32, 143.65, 141.12, 136.85, 129.98, 129.29, 128.33, 127.92, 127.79, 110.05, 84.37, 78.47, 51.48, 41.09, 25.72, 21.59, 18.18, -5.31, -5.33. ***LC-MS***: 570.2 ($M+H^+$) 609.2 ($M+K^+$).
	**7g.** Yellow oil. **Yield** = 51% (not optimized), (*c*Hex:EtOAc = 95:5). ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.51 (s, 1H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.03 (s, 1H), 4.69 (dt, *J* = 17.7, 1.8 Hz, 1H), 4.36 (dt, *J* = 17.7, 1.8 Hz, 1H), 4.21 (t, *J* = 1.9 Hz, 2H), 2.43 (s, 3H), 2.36 (s, 3H), 2.25 (s, 3H), 0.86 (s, 9H), 0.03 (s, 6H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$) δ 143.51, 142.40, 140.23, 138.64, 138.43, 137.58, 132.29, 129.45, 128.03, 100.90, 83.99, 78.91, 51.61, 40.68, 25.74, 21.56, 20.65, 20.38, 18.21, -5.34. ***LC-MS***: 601.4 ($M+ H_2O$).

Procedure for the synthesis of 7h:



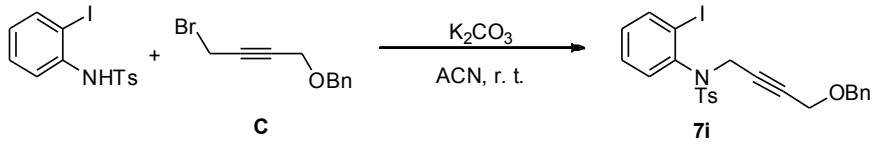
N-methyl 2-iodophenylcarbamate was prepared following reported procedures.[2] The product **7h** was synthetized following the procedure utilized for the synthesis of products **7a-g**.

[2] C. Guissart, A. Dolbois, C. Tresse, S. Saint-Auret, G. Evano, N. Blanchard, *Synlett*, 2016, **27**, 2575.



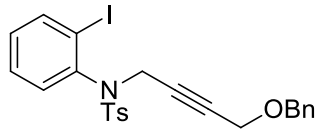
7h. Yellow oil. **Yield** = 56% (not optimized), (*c*Hex:EtOAc = 95:5). ***[1]H-NMR*** (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.8 Hz, 1H), 7.40 – 7.35 (m, 2H), 7.07 – 7.00 (m, 1H), 4.84 (d, *J* = 17.5 Hz, 1H), 4.29 (s, 2H), 4.00 (d, *J* = 17.6 Hz, 1H), 3.66 (s, 3H), 0.89 (s, 9H), 0.07 (d, *J* = 2.1 Hz, 6H). ***[13]C-NMR*** (100 MHz, $CDCl_3$) δ 155.06, 142.75, 139.47, 130.05, 129.48, 129.02, 100.03, 83.21, 79.61, 53.35, 51.70, 39.38, 25.77, 18.24, -5.21. ***GC-MS*:** 402 (M-tBu).

Procedure for the synthesis of 7i:



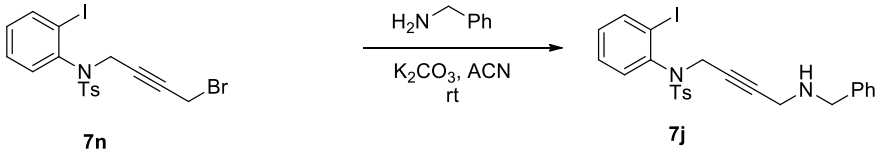
C **7i**

1-(Benzyloxy)-4-bromo-but-2-yne **C** was prepared following reported procedures.[3] The product **7i** was synthetized following the procedure utilized for the synthesis of products **7a-g**.



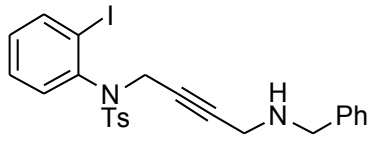
7i. Yellow oil. **Yield** = 94%, (*c*Hex:EtOAc = 9:1). ***[1]H-NMR*** (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.37 – 7.17 (m, 7H), 7.10 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.07 – 6.98 (m, 1H), 4.76 (d, *J* = 18.1 Hz, 1H), 4.38 (s, 2H), 4.21 (d, *J* = 18.1 Hz, 1H), 4.02 (t, *J* = 1.9 Hz, 2H), 2.38 (s, 3H). ***[13]C-NMR*** (100 MHz, $CDCl_3$) δ 143.88, 140.82, 140.25, 137.24, 136.59, 130.92, 130.35, 129.39, 128.67, 128.37, 128.27, 127.90, 127.83, 102.75, 81.87, 80.33, 71.29, 57.11, 41.05, 21.53. ***LC-MS*:** 531.8 (M) 549 (M+H_2O).

General procedure for the synthesis of 7j:



7n **7j**

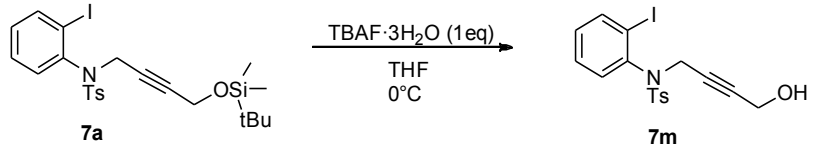
To a solution of **7n** (0.5 mmol) in dry acetonitrile (3 mL) under nitrogen atmosphere, K_2CO_3 (1.5 eq) was added, then the benzyl amine (1.2 eq) was added and the mixture was stirred at room temperature until TLC analysis indicates complete consumption of starting material. Subsequently, water (10 mL) was added and the aqueous layer was extracted with AcOEt (3 x 10 mL). The combined organic layers were dried with Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to give the desired product.



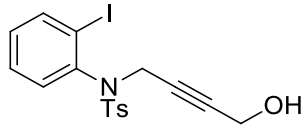
7j. Yellow oil. **Yield** = 73% (not optimized), (*c*Hex:EtOAc = 8:2). ***[1]H-NMR*** (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.9 Hz, 1H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.38-7.17 (m, 8H), 7.12 (d, *J* = 7.9 Hz, 1H), 7.03 (t, *J* = 7.6 Hz, 1H), 4.71 (d, *J* = 17.9 Hz, 1H), 4.19 (d, *J* = 17.9 Hz, 1H), 3.65 (s, 2H), 3.26 (s, 2H), 2.37 (s, 3H). ***[13]C-NMR*** (100 MHz, $CDCl_3$) δ 143.84, 140.96, 139.24, 136.66, 130.83, 130.29, 129.34, 128.61, 128.37, 128.31, 128.23, 127.12, 102.87, 84.12, 77.10, 52.15, 41.16, 37.40, 21.51. ***LC-MS*:** 531.2 (M).

[3] a) A.J. Cresswell, S.T.-C. Eey, S.E. Denmark, *Nat. Chem.*, 2015, **7**, 146; b) N. Kern, A. Blanc, J.M. Weibela, P. Pale, *Chem. Commun.* 2011, **47**, 6665.

Procedure for the synthesis of 7m:

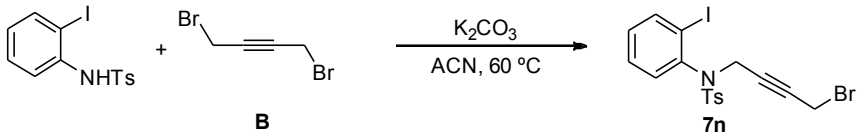


To a solution of compound **7a** (0.5 mmol, 278 mg) in THF (5 mL) at 0 °C, TBAF·$3H_2O$ (1eq, 0.5 mmol, 158 mg) was added then the mixture was stirred until TLC analysis indicates complete consumption of starting material. Subsequently, water (10 mL) was added and the aqueous layer was extracted with AcOEt (3 x 10 mL). The combined organic layers were dried with Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to give the desired product.

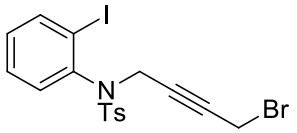


7m. Yellow oil. **Yield** = 67% (not optimized), (*c*Hex:EtOAc = 9:1). ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.31 (m, 3H), 7.15 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.07 (m, 1H), 4.74 (d, *J* = 18.0 Hz, 1H), 4.17 (d, *J* = 17.9 Hz, 1H), 4.12 (s, 2H), 2.46 (s, 3H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$) δ 143.99, 140.81, 140.21, 136.49, 130.97, 130.39, 129.36, 128.77, 128.34, 102.60, 84.08, 79.62, 50.82, 41.06, 21.57. ***LC-MS*****:** 441.8 ($M+H^+$), 459.0 ($M+H_2O$) 463.8 ($M+Na^+$).

Procedure for the synthesis of 7n:



1,4-Dibromo-2-butyne was prepared following reported procedure.[4] The product **7n** was synthetized following a reported procedure for a similar product.[5]

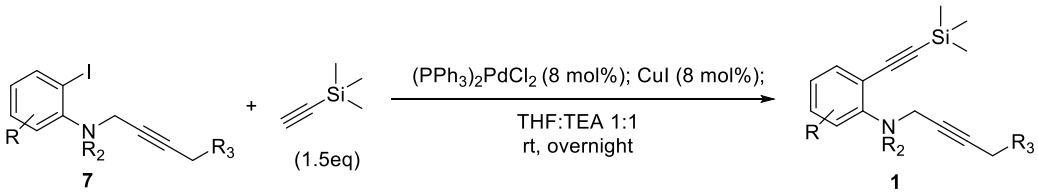


7n. Yellow oil. **Yield** = 75% (not optimized), (*c*Hex:EtOAc = 9:1). ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.9 Hz, 1H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.32-7.30 (m, 3H), 7.17 – 7.02 (m, 2H), 4.82 (d, *J* = 18.3 Hz, 1H), 4.14 (d, *J* = 18.3 Hz, 1H), 3.74 (t, *J* = 2.1 Hz, 2H), 2.46 (s, 3H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$) δ 143.99, 140.74, 140.24, 136.58, 131.00, 130.46, 129.48, 128.79, 128.27, 102.71, 80.88, 80.62, 41.05, 21.63, 13.88. ***LC-MS*****:** 505 ($M+H^+$) 543.8 ($M+K^+$).

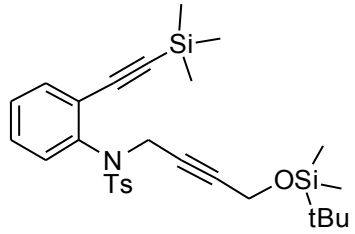
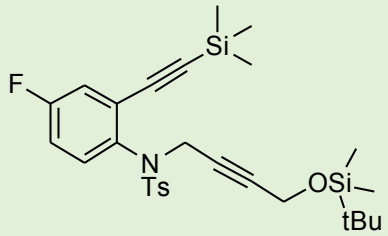
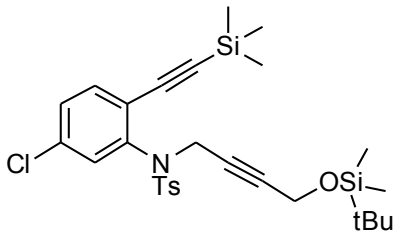
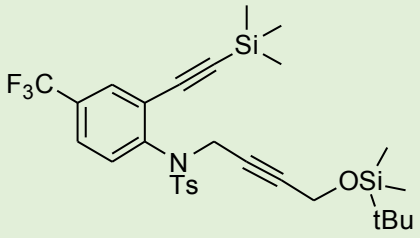
[4] G. Blond, C. Bour, B. Salem, J. Suffert, *Org. Lett.*, 2008**, 10**, 1075.

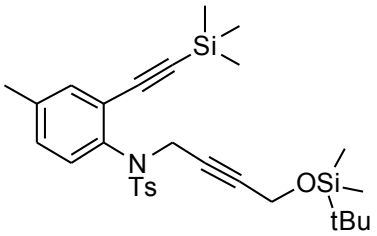
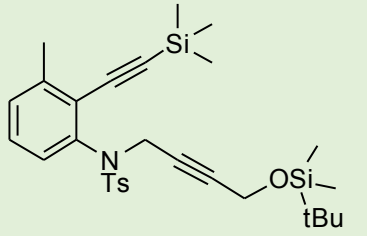
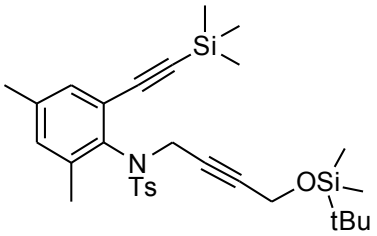
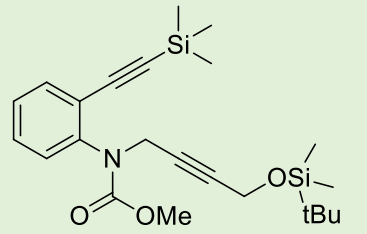
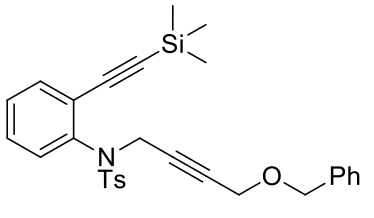
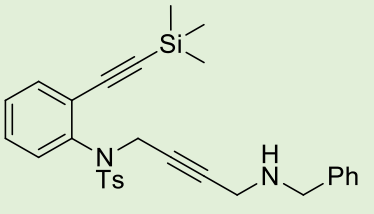
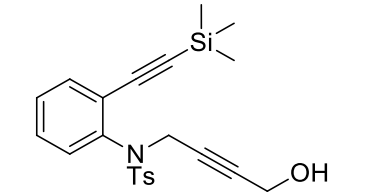
[5] R. Grigg, V. Loganathan, V. Sridharan, P. Stevenson, S. Sukirthalingam, T. Worakun, *Tetrahedron*, 1996, **52**, 11479.

General procedure for the synthesis of 1:

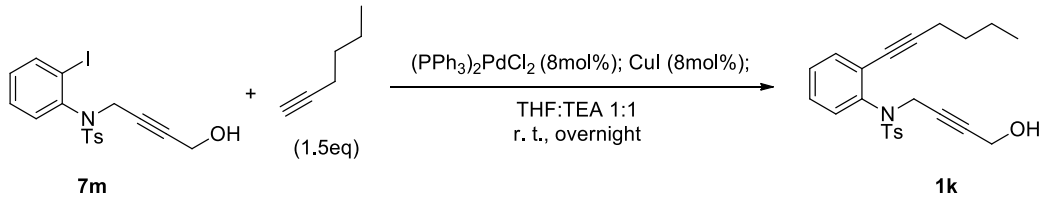


To a solution of **7** (0.5 mmol) in anhydrous THF (2 mL), freshly distilled TEA (2 mL), trimethylsilylacetylene (1.5 eq), $(PPh_3)_2PdCl_2$ (8 mol%) and CuI (8 mol%) were added. The mixture was stirring at room temperature and the reaction progress was monitored using TLC. After the consumption of starting material, the reaction mixture was extracted with ethyl acetate and water. The organic layers were combined and dried with Na_2SO_4. After filtration, the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel.

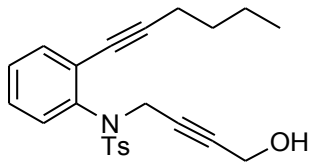
	**1a.** Pale yellow solid. **Yield** = 65% (*c*Hex:EtOAc = 95:5). **Mp =** 117-119 °C. ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 7.3 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.04 (t, *J* = 7.2 Hz, 1H), 4.67 (s, 2H), 4.23 (s, 2H), 2.37 (s, 3H), 0.94 (s, 9H), 0.26 (s, 9H), 0.12 (s, 6H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$) δ 145.26, 144.38, 139.60, 133.70, 130.68, 129.76, 129.00, 127.10, 124.70, 123.20, 114.25, 111.84, 103.19, 64.51, 53.99, 25.89, 21.48, 18.33, -0.22, -5.28. ***LC-MS*:** 548.0 ($M+Na^+$), 564.0 ($M+K^+$).
	**1b.** Pale yellow solid. **Yield** = 43% (not optimized), (*c*Hex:EtOAc = 95:5). **Mp** = 94-96 °C. ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 9.5, 2.7 Hz, 1H), 7.73 (dd, *J* = 8.9, 4.6 Hz, 1H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.2 Hz, 2H), 7.02 (t, *J* = 8.6, 1H), 4.67 (s, 2H), 4.21 (s, 2H), 2.38 (s, 3H), 0.93 (d, *J* = 2.9 Hz, 9H), 0.31 – 0.21 (m, 9H), 0.15 – 0.08 (m, 6H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$) δ 160.31, 157.92, 144.54, 141.30, 138.49, 138.46, 133.32, 130.80, 130.71, 129.81, 129.43, 127.85, 127.13, 117.42, 117.18, 115.29, 115.21, 113.36, 111.44, 111.18, 104.47, 103.31, 64.35, 54.46, 25.86, 25.71, 21.49, 18.32, -0.35, -5.32. ***LC-MS***: 545 ($M+H^+$), 562 ($M+H_2O$).
	**1c.** White solid. **Yield** = 58% (not optimized), (*c*Hex:EtOAc = 98:2). **Mp** = 135-136 °C. ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.5 Hz, 2H), 7.76 (d, *J* = 1.9 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 6.97 (dd, *J* = 8.5, 1.9 Hz, 1H), 4.65 (s, 2H), 4.18 (s, 2H), 2.36 (s, 3H), 0.90 (s, 9H), 0.21 (s, 9H), 0.08 (s, 6H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$) δ 146.10, 144.73, 138.24, 136.37, 133.53, 129.93, 127.61, 127.07, 125.28, 123.40, 114.31, 112.37, 103.90, 103.69, 64.47, 54.33, 25.86, 21.52, 18.32, -0.27, -5.32. ***LC-MS***: 559.0 (M), 597.4 ($M+K^+$).
	**1d.** Yellow wax. **Yield** = 44% (not optimized), (*c*Hex:EtOAc = 95:5). ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 8.70 (s, 1H), 7.83 (d, *J* = 8.6 Hz, 1H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.55 (d, *J* = 8.6 Hz, 1H), 7.26 (d, *J* = 7.6 Hz, 3H), 4.75 (s, 2H), 4.24 (s, 2H), 2.39 (s, 3H), 0.94 (s, 9H), 0.25 (s, 9H), 0.12 (s, 6H). ***^{13}C NMR*** (100 MHz, $CDCl_3$) δ 144.92, 137.51, 133.62, 130.08, 130.01, 129.41, 127.61, 127.12, 127.05, 125.50, 121.95, 113.96, 113.67, 105.09, 102.88, 64.60, 54.40, 25.89, 21.55, 18.34, -0.40, -5.30. ***LC-MS***: 593.2 (M).

	**1e.** Pale yellow solid. **Yield** = 40% (not optimized), (*c*Hex:EtOAc = 98:2). Mp = 118-120 °C. ***[1]H-NMR*** (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.67 (m, 3H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 7.1 Hz, 1H), 4.64 (s, 2H), 4.21 (s, 2H), 2.36 (s, 3H), 2.31 (s, 3H), 0.92 (s, 9H), 0.26 (s, 9H), 0.11 (s, 6H). ***[13]C-NMR*** (100 MHz, $CDCl_3$) δ 144.25, 143.19, 139.80, 133.57, 132.95, 131.53, 129.71, 129.07, 127.13, 124.96, 114.12, 111.47, 104.08, 102.96, 64.44, 54.15, 31.36, 25.88, 21.46, 20.99, 18.32, 0.98, -0.15, -5.28. ***LC-MS***: 539.0 (M^+), 557.0 ($M+H_2O$), 579.0 (M+K).
	**1f.** Pale yellow wax. **Yield** = 58% (not optimized), (*c*Hex:EtOAc = 9:1). ***[1]H-NMR*** (400 MHz, $CDCl_3$) 7.68 (d, *J* = 8.3 Hz, 2H), 7.59 (d, *J* = 8.1 Hz, 1H), 7.23- 7.19 (m, 3H), 6.85 (d, *J* = 7.6 Hz, 1H), 4.58 (s, 2H), 4.30 (s, 2H), 2.49 (s, 3H), 2.37 (s, 3H), 0.93 (s, 9H), 0.18 (s, 9H), 0.12 (s, 6H). ***[13]C-NMR*** (100 MHz, $CDCl_3$) 144.92, 144.01, 141.00, 135.84, 133.21, 130.04, 129.43, 127.96, 127.21, 126.45, 115.83, 111.28, 105.58, 102.49, 66.24, 55.09, 25.69, 23.98, 21.31, 18.07, -0.33, -5.45. ***LC-MS***: 539.4 (M^+), 578.4 (M+K).
	**1g.** Pale yellow solid. **Yield** = 44% (not optimized), (*c*Hex:EtOAc = 9:1). **Mp** = 132-134 °C. ***[1]H-NMR*** (400 MHz, $CDCl_3$) 7.84 (s, 1H), 7.22 (d, *J* = 8.3 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.04 (s, 1H), 4.50 (s, 2H), 3.99 (s, 2H), 2.57 (s, 3H), 2.35 (s, 3H), 2.32 (s, 3H), 0.92 (s, 9H), 0.24 (s, 9H), 0.09 (s, 6H). ***[13]C-NMR*** (100 MHz, $CDCl_3$) 144.03, 142.57, 141.40, 136.17, 134.80, 133.48, 131.87, 129.06, 128.03, 122.20, 112.71, 103.23, 101.53, 64.33, 56.58, 25.89, 21.45, 21.23, 19.55, 18.35, -0.09, -5.30. ***LC-MS***: 575.4 ($M+Na^+$), 625.8 ($M+CH_3OH+CH_3CN$).
	**1h.** Yellow oil. **Yield** = 46% (not optimized), (*c*Hex:EtOAc = 9:1). ***[1]H-NMR*** (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 7.5 Hz, 1H), 7.99 (d, *J* = 7.5 Hz, 1H), 7.36 – 7.28 (m, 1H), 7.03 (t, *J* = 7.6 Hz, 1H), 4.72 (s, 2H), 4.29 (s, 2H), 3.85 (s, 3H), 0.94 (s, 9H), 0.28 (s, 9H), 0.14 (s, 6H). ***[13]C-NMR*** (100 MHz, $CDCl_3$) δ 210.46, 130.63, 124.52, 124.28, 122.59, 122.37, 120.62, 114.96, 114.70, 104.42, 102.84, 93.21, 86.99, 64.82, 64.46, 53.62, 52.66, 52.37, 25.90, -0.14, -5.22. ***LC-MS***: 462.2 (M + MeOH + H^+).
	**1i.** Yellow wax. **Yield** = 48% (not optimized), (*c*Hex:EtOAc = 9:1). ***[1]H-NMR*** (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 7.9 Hz, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.44 – 7.30 (m, 6H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.06 (t, *J* = 7.7 Hz, 1H), 4.66 (s, 2H), 4.54 (s, 2H), 4.14 (s, 2H), 2.35 (s, 3H), 0.28 (s, 9H). ***[13]C-NMR*** (100 MHz, $CDCl_3$) δ 145.52, 144.40, 141.73, 137.74, 133.56, 131.01, 129.76, 128.75, 128.40, 127.85, 127.79, 127.09, 124.83, 123.27, 114.38, 109.03, 104.27, 103.06, 72.03, 70.77, 54.08, 21.49, -0.18. ***LC-MS***: 524.4 ($M+Na^+$).
	**1j.** Yellow oil. **Yield** = 59% (not optimized), (*c*Hex:EtOAc = 8:2). ***[1]H-NMR*** (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 7.8 Hz, 1H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.36 – 7.26 (m, 5H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.02 (t, *J* = 7.6 Hz, 1H), 4.53 (s, 2H), 3.74 (s, 2H), 3.29 (s, 2H), 2.33 (s, 3H), 0.25 (s, 9H).***[13]C-NMR*** (100 MHz, $CDCl_3$) δ 145.42, 144.48, 133.65, 130.68, 129.80, 128.70, 128.46, 128.23, 127.21, 127.10, 124.51, 123.28, 114.36, 103.61, 54.03, 21.51, -0.12. ***LC-MS*:** 501.4 (M).
	**1m.** White solid. **Yield** = 50% (not optimized), (*c*Hex:EtOAc = 9:1). ***[1]H-NMR*** (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 7.3 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.39 – 7.30 (m, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.11 – 6.98 (m, 1H), 4.64 (s, 2H), 4.17 (s, 2H), 2.37 (s, 3H), 0.27 (s, 8H). ***[13]C-NMR*** (100 MHz, $CDCl_3$) δ 145.57, 144.54, 139.61, 133.71, 131.03, 129.85, 128.52, 127.12, 124.61, 123.30, 114.33, 111.37, 104.37, 63.09, 53.70, 21.51, -0.19. ***LC-MS***: 412.0 (M^+), 434.0 ($M+Na^+$).

General procedure for the synthesis of 1k:

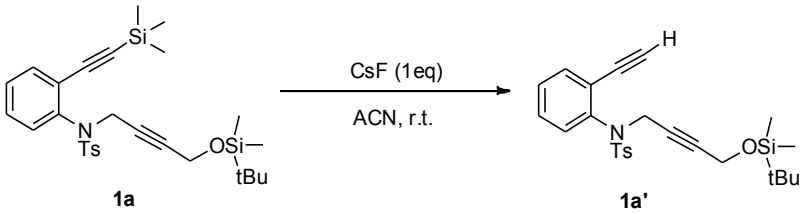


To a solution of **7m** (0.3 mmol) in anhydrous THF (2 mL) under nitrogen anhydrous TEA (2 mL), 1-hexyne (1.5 eq), $(PPh_3)_2PdCl_2$ (0.08 eq) and CuI (0.08 eq) were added. The mixture was stirring at room temperature and the reaction progress was monitored using TLC. After the consumption of starting material, the reaction mixture was extracted with ethyl acetate and water. The organic layers were combined and dried with Na_2SO_4. After filtration, the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel.

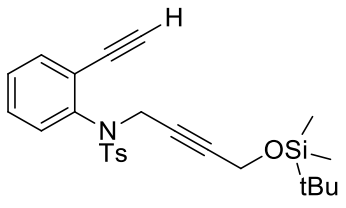


1k. Yellow oil. **Yield** = 44% (not optimized), (*c*Hex:EtOAc = 9:1). ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 7.7 Hz, 1H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.35 – 7.27 (m, 1H), 7.23 (d, *J* = 8.3 Hz, 2H), 7.03 (t, *J* = 7.7, 1H), 4.61 (s, 2H), 4.13 (s, 2H), 2.51 (t, *J* = 7.1 Hz, 2H), 2.37 (s, 3H), 1.66 – 1.57 (m, 2H), 1.53 – 1.44 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$) δ 145.09, 144.38, 136.42, 133.71, 130.40, 129.76, 128.82, 127.06, 123.96, 123.26, 114.16, 112.19, 100.07, 78.15, 63.32, 53.52, 30.61, 26.73, 22.01, 21.45, 19.53, 13.49. ***LC-MS*:** 396.2 (M+ H^+). **Anal. Calc.** for ($C_{23}H_{25}NO_3S$: 395.16): C, 69.85; H, 6.37; N, 3,54; found: C, 69.71, H, 6.49; N, 3.65.

General procedure for the synthesis of 1a':



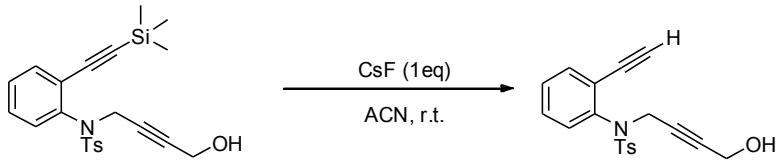
To a solution of compound **1a** (0.1 mmol, 53 mg) in ACN (3 mL) at room temperature, CsF (1 eq, 0.1 mmol, 15 mg) was added then the mixture was stirred until TLC analysis indicates complete consumption of starting material. Subsequently, water (10 mL) was added and the aqueous layer was extracted with AcOEt (3 x 10 mL). The combined organic layers were dried with Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to give the desired product.



1a'. Brown oil. **Yield** = 85% (not optimized), (*c*Hex:EtOAc = 9:1). ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 7.8 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.04 (t, *J* = 7.7 Hz, 1H), 4.69 (s, 2H), 4.26 (s, 2H), 3.50 (s, 1H), 2.37 (s, 3H), 0.93 (s, 9H), 0.11 (s, 6H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$) δ 145.28, 144.42, 140.35, 133.81, 130.87, 129.80, 128.77, 127.15, 124.67, 123.40, 114.32, 110.70, 85.34, 82.62, 64.73, 54.02, 25.90, 21.51, 18.34, -5.30. ***LC-MS*:** 454.4

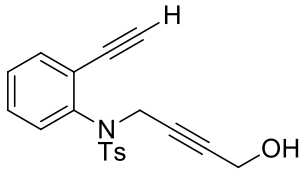
(M+H$^+$), 476.4 (M+Na$^+$).

General procedure for the synthesis of 1a'':



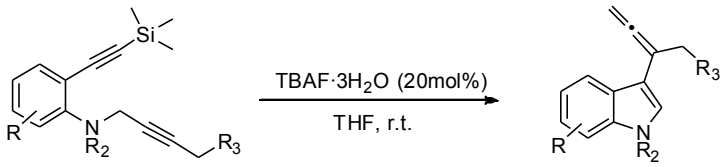
1m **1a"**

To a solution of compound **1m** (0.1 mmol, 41 mg) in ACN (3 mL) at room temperature, CsF (1eq, 0.1 mmol, 15 mg) was added then the mixture was stirred until TLC analysis indicates complete consumption of starting material. Subsequently, water (10 mL) was added and the aqueous layer was extracted with AcOEt (3 x 10 mL). The combined organic layers were dried with Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to give the desired product.



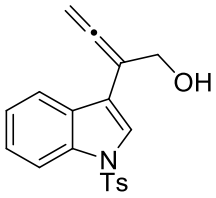
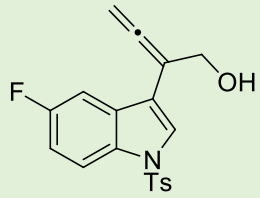
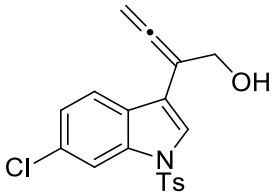
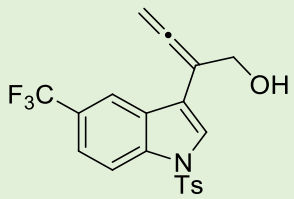
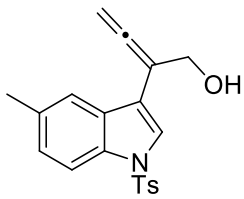
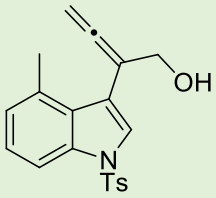
1a''. Brown waxy solid. **Yield** = 71%, (*c*Hex:EtOAc = 9:1). ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 7.4 Hz, 1H), 7.77 (d, *J* = 8.3 Hz, 1H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.39 – 7.31 (m, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.10 – 7.02 (m, 1H), 4.65 (s, 2H), 4.20 (s, 2H), 3.56 (s, 1H), 2.38 (s, 3H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$) δ 145.46, 144.52, 140.25, 133.64, 131.16, 129.82, 128.14, 127.07, 124.58, 123.43, 114.29, 110.08, 85.98, 81.51, 63.26, 53.61, 21.47. ***LC-MS***: 340.2 (M+H$^+$), 362.2 (M+Na$^+$). **Anal. Calc.** for ($C_{19}H_{17}NO_3S$: 339.09): C, 67.24; H, 5.05; N, 4,13; found: C, 67.16, H, 5.11; N, 4.09.

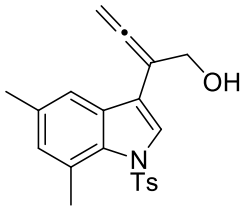
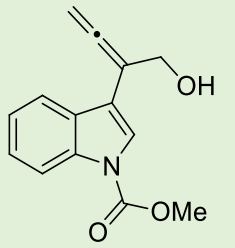
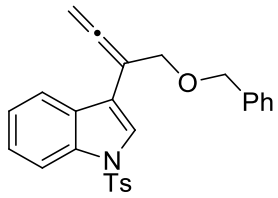
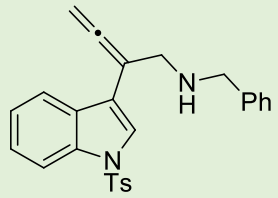
General procedure for the one-pot synthesis of allenyl-indoles 2:



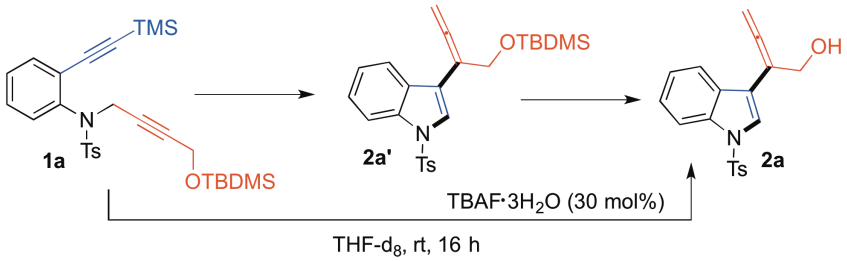
1 **2**

To a solution of **1** (0.05 mmol) in THF (800 µL), a solution of TBAF·3H_2O in THF (0.05 M, 0.2 eq) was added. The mixture was stirred at room temperature and the reaction progress was monitored using TLC. After the consumption of starting material, the reaction mixture was extracted with ethyl acetate and NH_4Cl (sat.). The organic layers were combined and dried with Na_2SO_4. After filtration, the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel.

	**2a.** Yellow waxy solid. (*c*Hex:EtOAc = 8:2). ***[1]H-NMR*** (400 MHz, $CDCl_3$) δ 7.99 (t, *J* = 7.3 Hz, 2H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.65 (s, 1H), 7.37 – 7.31 (m, 1H), 7.26 – 7.17 (m, 3H), 5.35 (td, *J* = 2.5, 0.9 Hz, 2H), 4.53 (t, *J* = 2.5 Hz, 2H), 2.33 (s, 3H), 1.81 (s, 1H). ***[13]C-NMR*** (100 MHz, $CDCl_3$) δ 208.41, 144.99, 135.34, 135.17, 130.01, 129.89, 127.81, 126.85, 125.02, 123.29, 122.69, 120.89, 113.59, 99.32, 80.59, 63.03, 21.54. ***LC-MS*****:** 340.0 ($M+H^+$), 357.0 ($M + H_2O$), 362.0 ($M+Na^+$). **Anal. Calc.** for ($C_{19}H_{17}NO_3S$: 339.09): C, 67.24; H, 5.05; N, 4,13; found: C, 67.01, H, 5.00; N, 4.01.
	**2b.** Pale yellow solid. **Yield** = 84%, (*c*Hex:EtOAc = 8:2). **Mp** = 132-134 ºC. ***[1]H-NMR*** (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 9.0, 4.5 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.69 (s, 1H), 7.64 (dd, *J* = 9.4, 2.4 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.06 (td, *J* = 9.0, 2.6 Hz, 1H), 5.36 (s, 2H), 4.52 (s, 2H), 2.35 (s, 3H). ***[13]C-NMR*** (100 MHz, $CDCl_3$) δ 208.19, 160.67, 158.29, 145.24, 145.19, 134.80, 129.97, 129.93, 126.79, 126.77, 124.27, 114.60, 114.50, 113.14, 113.07, 112.88, 112.82, 106.81, 106.56, 99.00, 80.84, 63.06, 21.54.***LC-MS***: 358.0 ($M + H^+$), 375.0 ($M + H_2O$), 380.0 ($M + K^+$). **Anal**. **Calc**. for ($C_{19}H_{16}FNO_3S$: 357.09): C, 63.85; H, 4.51; N, 3,92; found: C, 63.75, H, 4.66; N, 3.86.
	**2c.** White solid. **Yield** = 93%, (*c*Hex:EtOAc = 8:2). **Mp** = 108-110 ºC. ***[1]H-NMR*** (400 MHz, $CDCl_3$) δ 7.98 (t, *J* = 2.4 Hz, 1H), 7.86 (d, *J* = 8.6 Hz, 1H), 7.75 (dd, *J* = 8.4, 3.6 Hz, 2H), 7.61 (s, 1H), 7.23 (d, *J* = 7.9 Hz, 3H), 7.20 – 7.14 (m, 1H), 5.32 (t, *J* = 2.4 Hz, 2H), 4.49 (t, *J* = 2.4 Hz, 2H), 2.34 (s, 3H). ***[13]C-NMR*** (100 MHz, $CDCl_3$) δ 208.40, 145.35, 135.74, 134.85, 131.10, 130.07, 127.60, 126.86, 123.95, 123.13, 121.72, 115.04, 113.71, 99.00, 80.70, 63.09, 21.60. ***LC-MS***: 374.2 ($M + H^+$), 391.2 ($M + H_2O$), 412.2 ($M + K^+$). **Anal**. **Calc.** for ($C_{19}H_{16}ClNO_3S$: 373.05): C, 61.04; H, 4.31; N, 3,75; found: C, 61.20, H, 4.38; N, 3.66.
	**2d.** Yellow solid. **Yield** = 38%, (*c*Hex:EtOAc = 8:2). **Mp** = 137-139 ºC ***[1]H-NMR*** (400 MHz, $CDCl_3$) δ 8.38 – 8.20 (m, 1H), 8.09 (d, *J* = 8.7 Hz, 1H), 7.78 (d, *J* = 8.6 Hz, 3H), 7.57 (d, *J* = 8.8 Hz, 1H), 7.27 – 7.24 (m, 2H), 5.40 (td, *J* = 2.4, 1.0 Hz, 2H), 4.54 (t, *J* = 2.3 Hz, 2H), 2.36 (s, 3H). ***[13]C-NMR*** (100 MHz, $CDCl_3$) δ 208.49, 145.53, 136.67, 134.73, 130.08, 128.87, 126.86, 124.21, 123.12, 121.72, 118.51, 118.47, 115.32, 113.81, 98.71, 80.79, 63.22, 21.57. ***LC-MS***: 408.0 ($M + H^+$), 425.0 ($M + H_2O$). **Anal**. **Calc.** for ($C_{20}H_{16}F_3NO_3S$: 407.08): C, 58.96; H, 3.96; N, 3.44; found: C, 58.81, H, 3.85; N, 3.29.
	**2e.** Yellow solid. **Yield** = 86%, (*c*Hex:EtOAc = 85:15). **Mp** = 95-97 ºC. ***[1]H-NMR*** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.5 Hz, 1H), 7.75 (d, *J* = 8.2 Hz, 3H), 7.59 (s, 1H), 7.21 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 8.5 Hz, 1H), 5.36 (t, *J* = 2.3 Hz, 2H), 4.52 (t, *J* = 2.3 Hz, 2H), 2.41 (s, 3H), 2.34 (s, 3H). ***[13]CNMR*** (100 MHz, $CDCl_3$) δ 208.24, 144.88, 135.09, 133.55, 132.99, 129.84, 126.80, 126.40, 124.68, 122.77, 120.69, 119.39, 113.27, 99.36, 80.69, 62.97, 21.54, 21.50. ***LC-MS***: 371.4 ($M + H_2O$). **Anal**. **Calc.** for ($C_{20}H_{19}NO_3S$: 353.11): C, 67.97; H, 5.42; N, 3.96; found: C, 67.81, H, 5.31; N, 3.80.
	**2f.** Pale yellow solid. **Yield** = 68%. (*c*Hex:EtOAc = 85:15). **Mp** = 99-101 °C. ***[1]H-NMR*** (400 MHz, $CDCl_3$) δ 7.86 – 7.81 (m, 1H), 7.78 (t, *J* = 8.5 Hz, 2H), 7.54 (s, 1H), 7.26 – 7.16 (m, 3H), 7.02 – 6.96 (m, 1H), 5.05 (t, *J* = 3.1 Hz, 2H), 4.33 (t, *J* = 3.1 Hz, 2H), 2.58 (s, 2H), 2.35 (s, 3H). ***[13]C-NMR*** (100 MHz, $CDCl_3$) δ 207.00, 144.96, 135.12, 131.63, 129.90, 129.87, 126.93, 126.86, 125.54, 125.27, 124.77, 124.44, 111.62, 111.23, 78.17, 64.41, 21.56, 20.09. ***LC-MS***: 371.2 ($M + H_2O$). **Anal**. **Calc.** for ($C_{20}H_{19}NO_3S$: 353.11): C, 67.97; H, 5.42; N, 3.96; found: C, 67.90, H, 5.32; N, 3.66.

	**2g.** Brown solid. **Yield** = 85%. (*c*Hex:EtOAc = 85:15). **Mp** = 98-100 ºC ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ. 7.78 (s, 1H), 7.64 (s, 1H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.24 – 7.16 (m, 2H), 6.88 (s, 1H), 5.38 (t, *J* = 2.4 Hz, 2H), 4.54 (t, *J* = 2.4 Hz, 2H), 2.51 (s, 3H), 2.37 (s, 3H), 2.35 (s, 3H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$) δ 208.10, 144.53, 136.63, 133.38, 130.13, 129.82, 128.37, 126.54, 126.43, 124.65, 118.40, 116.97, 114.43, 99.18, 80.77, 62.91, 21.66, 21.56, 21.12. ***LC-MS***: 385.2 (M + H_2O). **Anal**. **Calc.** for ($C_{21}H_{21}NO_3S$: 367.12): C, 68.64; H, 5.76; N, 3.81; found: C, 68.51, H, 5.64; N, 3.64.
	**2h.** Brown waxy solid. **Yield** = 45% (51% deprotected product **2h''**), (*c*Hex:EtOAc = 85:15). ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.1 Hz, 1H), 8.04 (d, *J* = 8.1 Hz, 1H), 7.68 (s, 1H), 7.41 – 7.33 (m, 1H), 7.29 – 7.24 (m, 1H), 5.38 (td, *J* = 2.5, 1.0 Hz, 2H), 4.55 (s, 2H), 4.05 (s, 3H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$) δ 208.46, 128.71, 125.03, 123.04, 121.92, 120.49, 115.05, 114.10, 99.48, 80.54, 63.05, 53.82. ***LC-MS***: 244.2 (M + H^+), 261.2 (M + H_2O). **Anal**. **Calc.** for ($C_{14}H_{13}NO_3$: 243.09): C, 69.12; H, 5.39; N, 5.76; found: C, 69.30, H, 5.41; N, 5.85.
	**2i.** Yellow oil. **Yield** = 70%. (*c*Hex:EtOAc = 9:1). ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.4 Hz, 2H), 7.78 (s, 1H), 7.71 (d, *J* = 8.1 Hz, 2H), 7.46 – 7.28 (m, 6H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 8.3 Hz, 2H), 5.27 (s, 2H), 4.59 (s, 2H), 4.49 (s, 2H), 2.31 (s, 3H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$) δ 210.29, 144.79, 137.98, 135.27, 135.08, 129.78, 129.25, 128.42, 127.86, 127.68, 126.80, 124.82, 123.65, 123.20, 120.87, 115.47, 113.59, 95.70, 78.51, 77.20, 71.43, 29.67, 21.52. ***LC-MS***: 447.4 (M^+ + H_2O). **Anal**. **Calc.** for ($C_{26}H_{23}NO_3S$: 429.14): C, 72.70; H, 5.40; N, 3.26; found: C, 72.65, H, 5.28; N, 3.15.
	**2j.** Yellow oil. **Yield** = 45%, (*c*Hex:EtOAc = 8:2). ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 8.04 – 7.93 (t, 1H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.60 (s, 1H), 7.40 – 7.28 (m, 6H), 7.25 – 7.16 (m, 3H), 5.31 (s, 2H), 3.90 (s, 2H), 3.69 (s, 2H), 2.33 (s, 3H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$) δ 208.91, 144.91, 135.37, 135.08, 129.84, 128.43, 128.27, 128.00, 127.05, 126.80, 124.93, 123.23, 122.56, 121.00, 119.72, 116.51, 113.57, 97.33, 79.87, 71.57, 53.07, 49.93, 21.54. ***LC-MS***: 429.4 (M + H^+). **Anal**. **Calc.** for ($C_{26}H_{24}N_2O_2S$: 428.16): C, 72.87; H, 5.65; N, 6.54; found: C, 72.75, H, 5.51; N, 6.38.

^{1}H-NMR experiment



To a solution of **1a** (0.05 mmol, 26 mg) in THF-d_8 (500 µL), a solution of TBAF·$3H_2O$ (30 mol%, 4.7 mg, 0.3 eq) in THF-d_8 (200 µL) was added. The reaction was monitored by ^{1}H-NMR.

Table S1. Calculation of the relative conversions of product 2a, intermediate 2a' and unknown compound and starting material 1a, at different reaction times by ^{1}H-NMR spectroscopy.

Reaction time *(min)*	**Conversion *(%)***			
	2a	**2a'**	**Unknown**	**1a**
2	49.5	17.3	18.8	14.3
4	54.5	17.4	19.3	8.7
6	60.0	15.6	16.5	7.8
8	64.9	17.2	17.8	n.d.
10	67.1	16.1	16.8	n.d.
20	73.8	12.1	14.0	n.d.
30	78.4	11.0	10.6	n.d.
3 hours	>98%	n.d.	n.d.	n.d.

n.d. = not determined

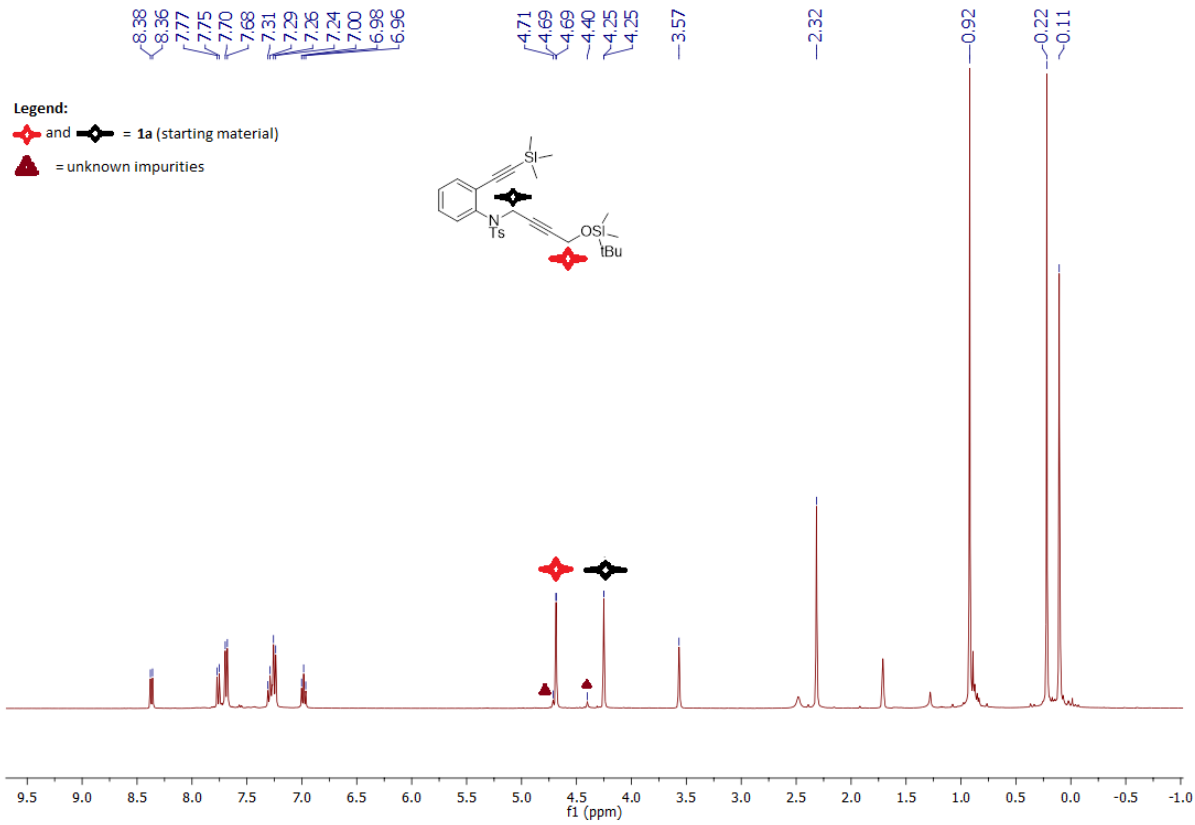


Figure S1: *^{1}H-NMR of compound **1a**.*

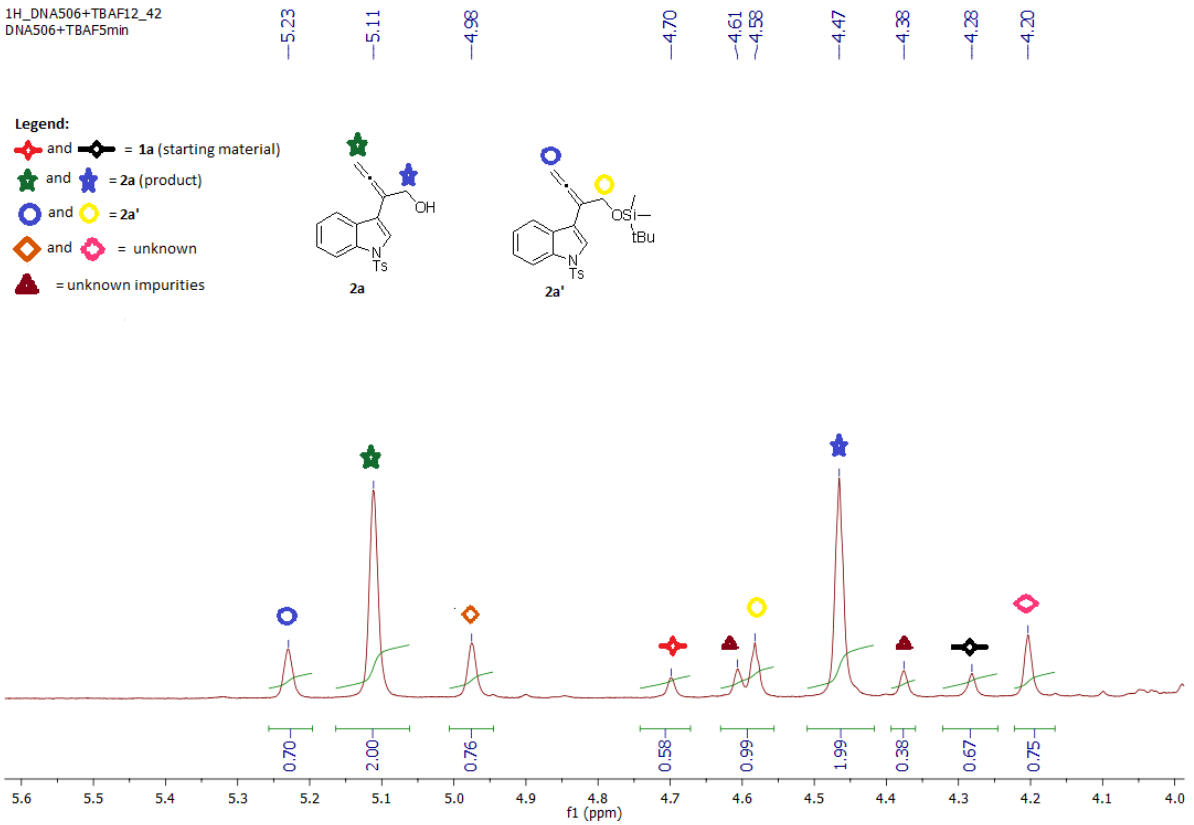


Figure S2: *^{1}H-NMR 2 minutes after the addition of TBAF solution.*

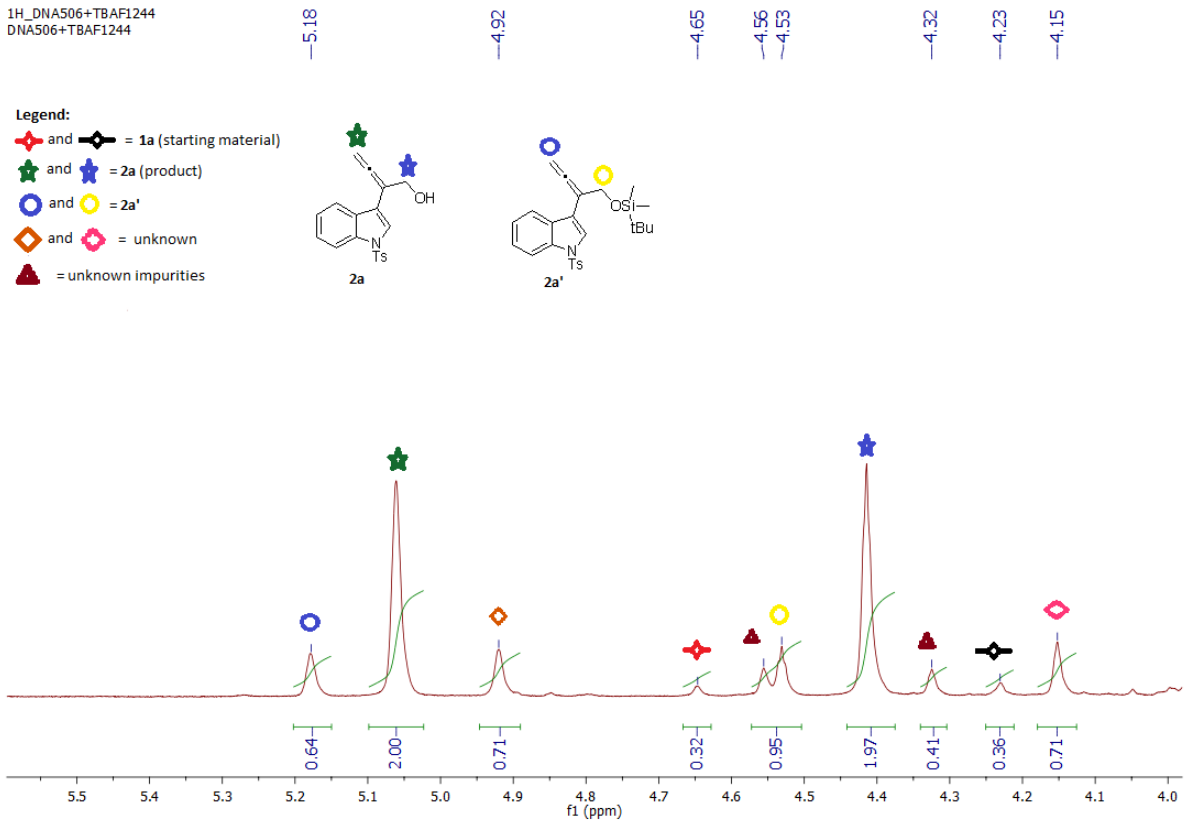


Figure S3: *[1]H-NMR 4 minutes after the addition of TBAF solution.*

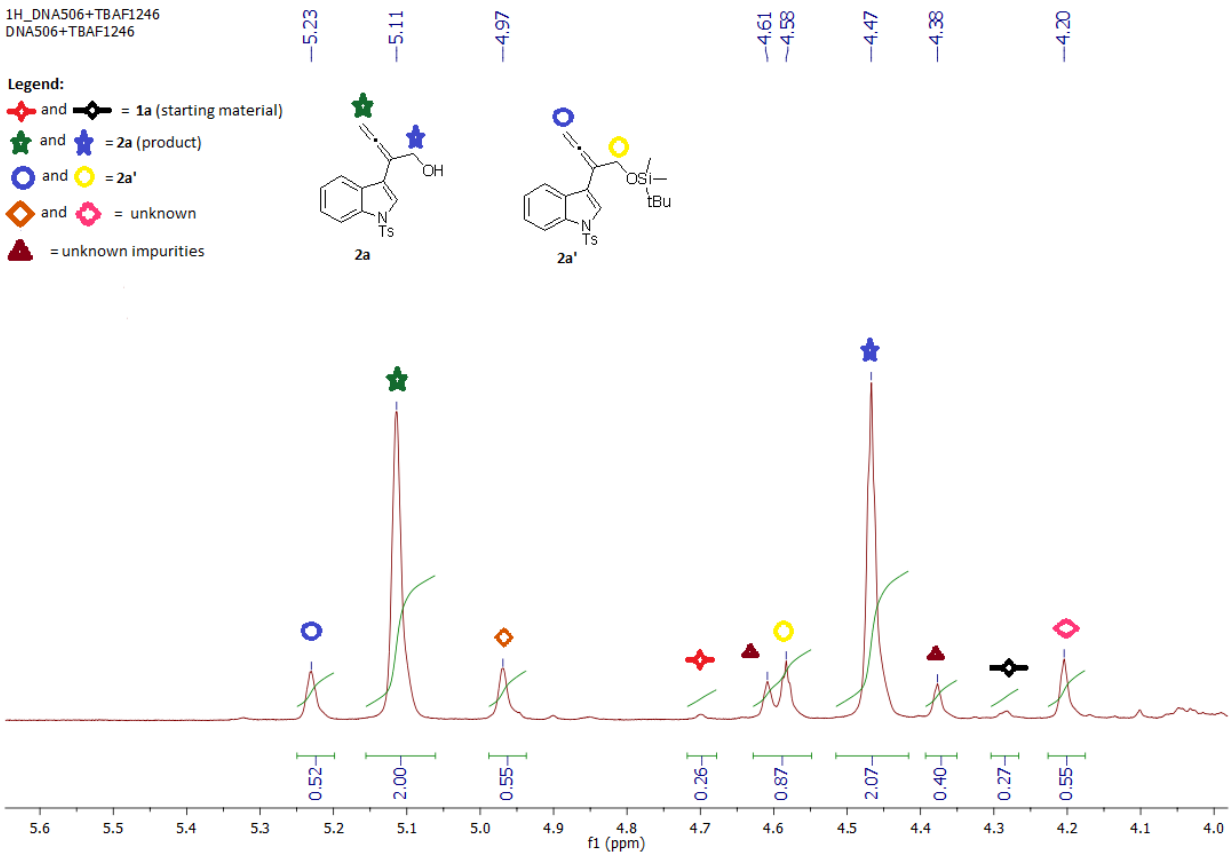


Figure S4: *[1]H-NMR 6 minutes after the addition of TBAF solution.*

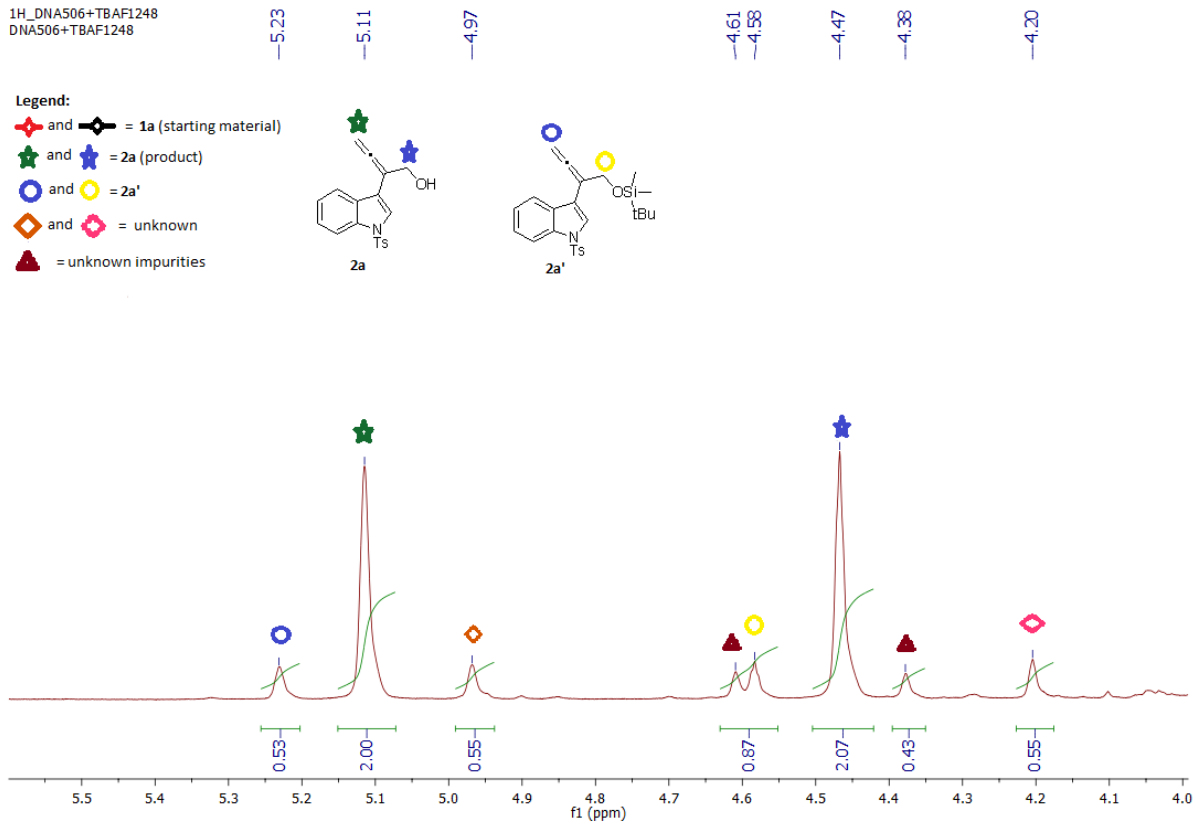


Figure S5: *[1]H-NMR 8 minutes after the addition of TBAF solution.*

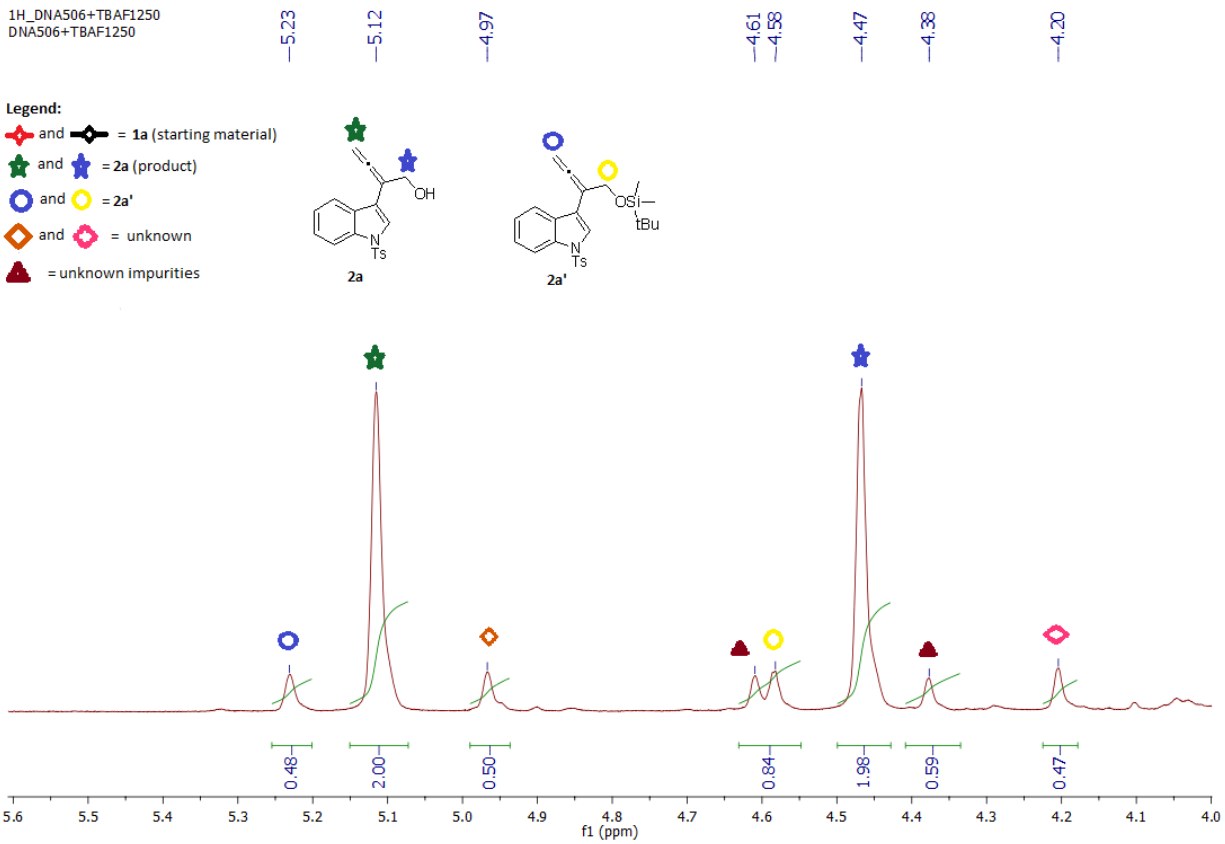


Figure S6: *[1]H-NMR 10 minutes after the addition of TBAF solution.*

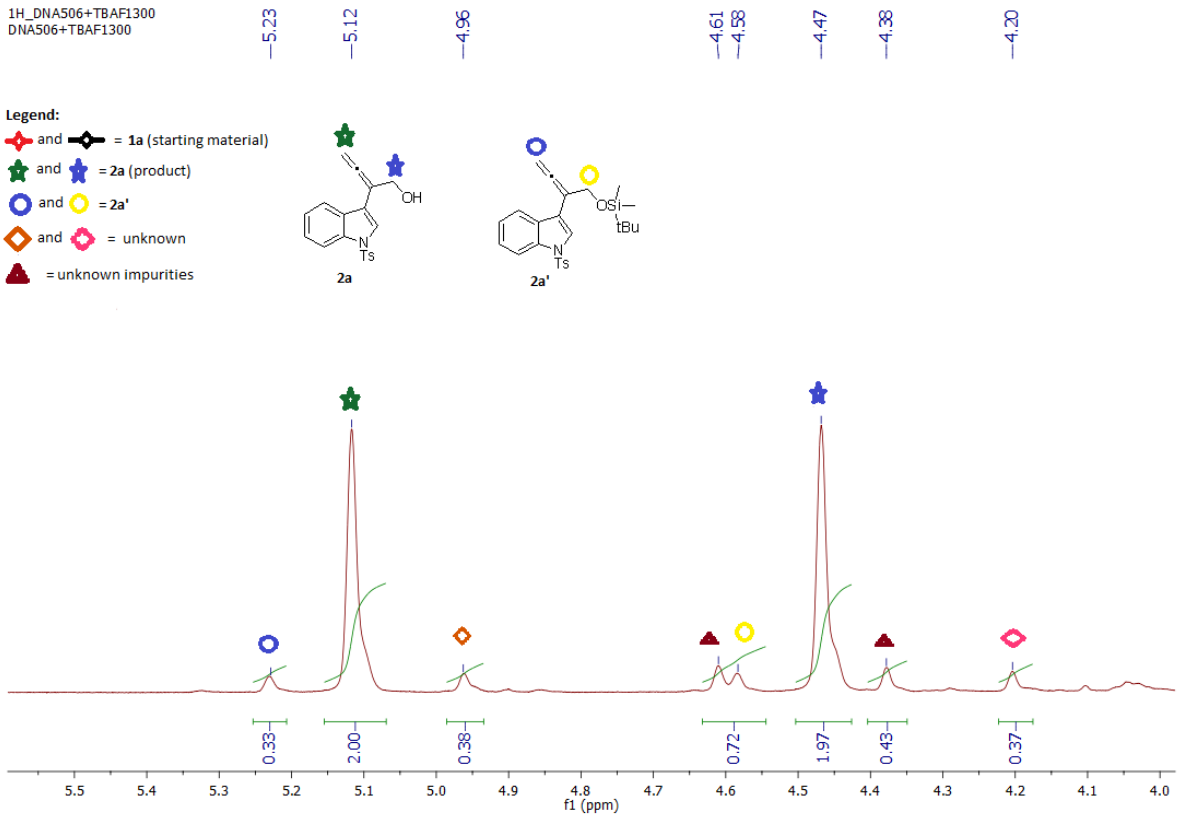


Figure S7: *[1]H-NMR 20 minutes after the addition of TBAF solution.*

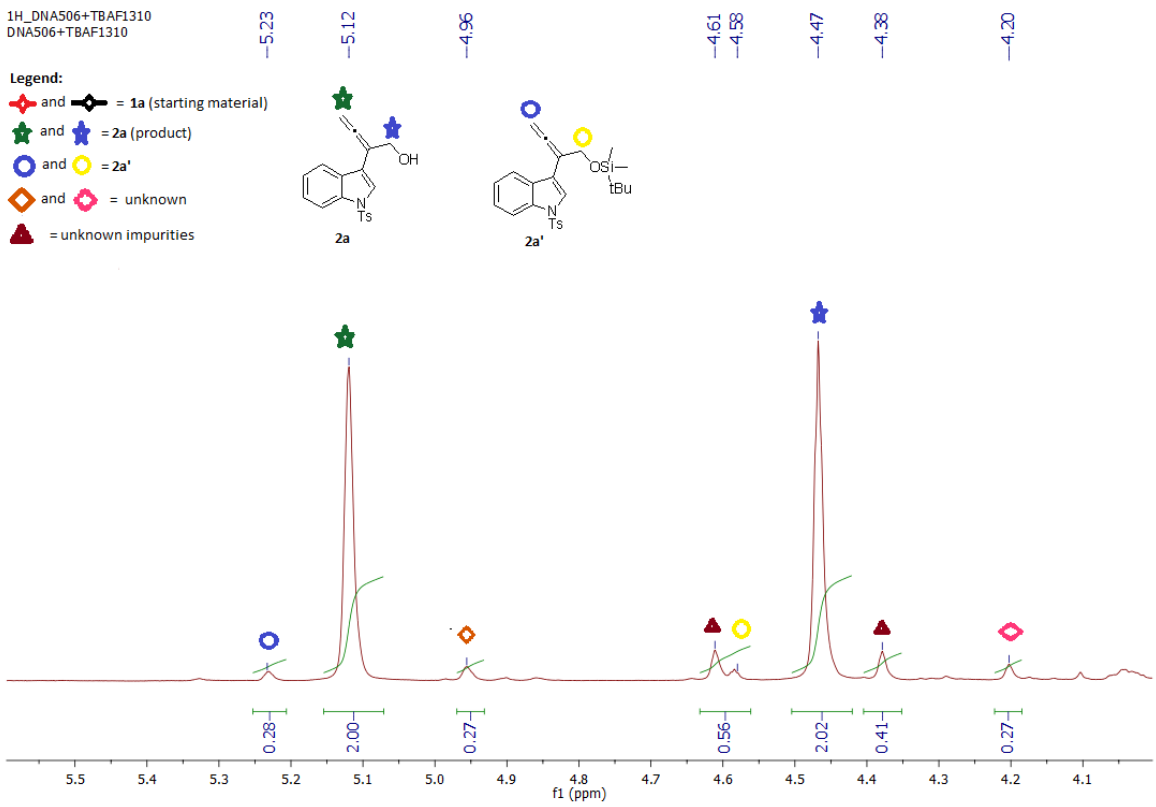


Figure S8: *[1]H-NMR 30 minutes after the addition of TBAF solution.*

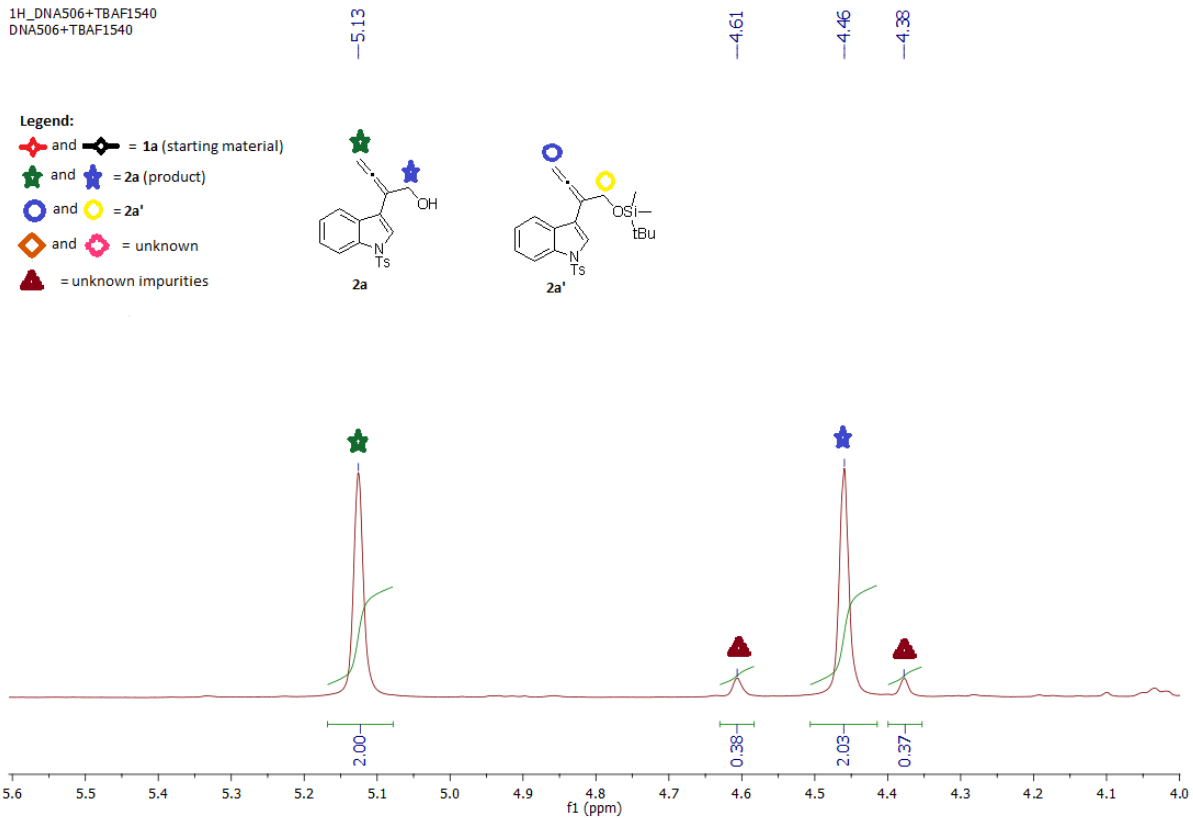
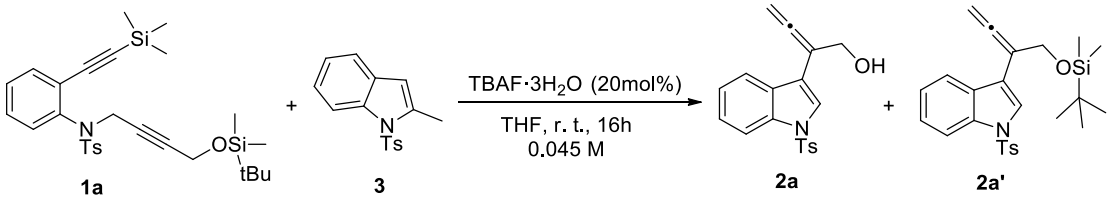


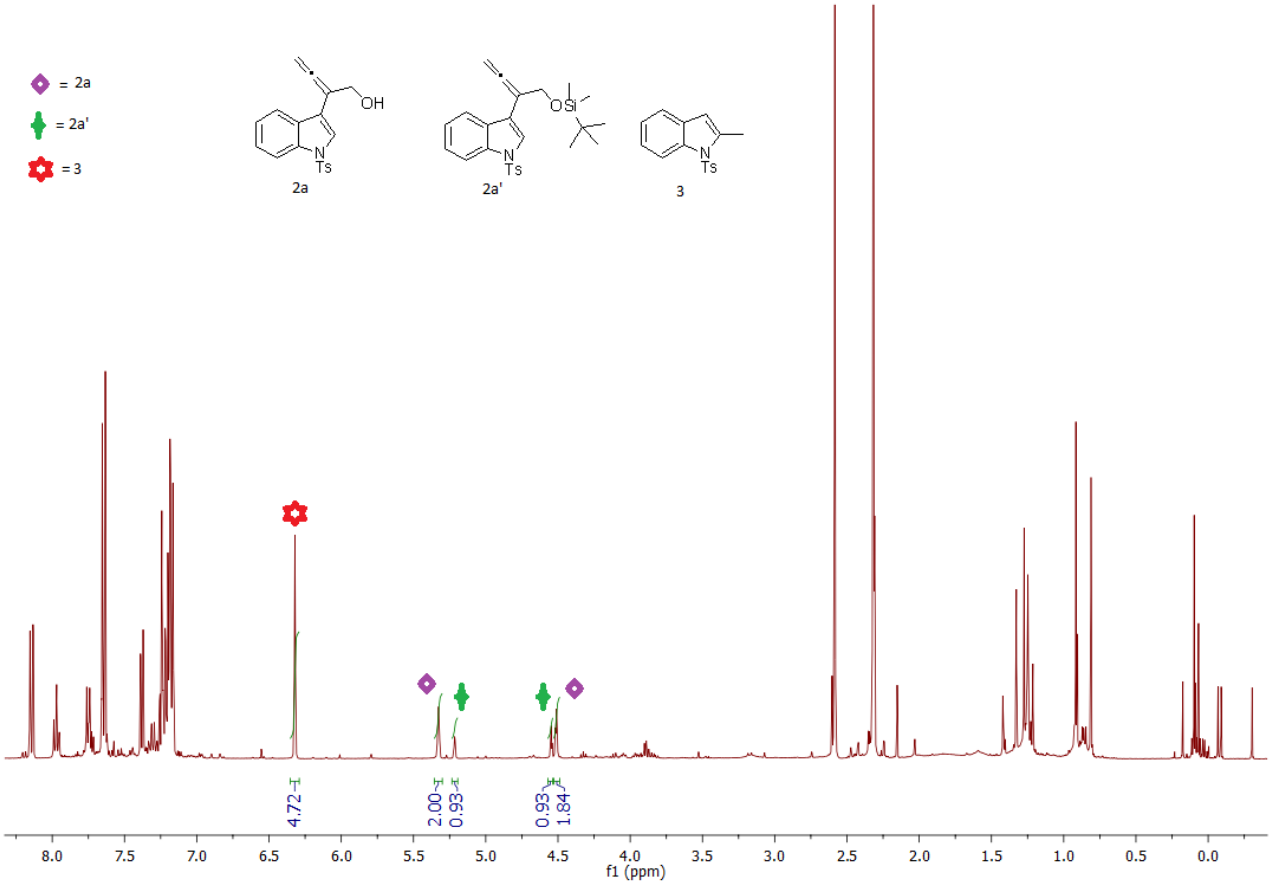
Figure S9: *^{1}H-NMR 3 hours after the addition of TBAF solution.*

Procedure for the scrambling reaction:



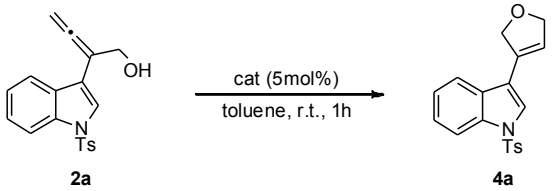
2-Methyl-*N*-tosylindole **3** was prepared following a reported procedure.[6]

A screw vial was charged with 800 µL of reagent grade THF, **1a** (34 mg, 0.065 mmol), indole **3** (28 mg, 0.098 mmol) and a solution of TBAF in THF (10 mg/mL, 330 µL, 20 mol%). The mixture was stirred at room temperature and the reaction progress was monitored using TLC. After the consumption of starting material, the reaction mixture was extracted with ethyl acetate and NH_4Cl (sat.). The organic layers were combined and dried with Na_2SO_4. ^{1}H-NMR of the reaction crude (see below) revealed a complete conversion of **1a** forming a mixture of **2a** and **2a'** in 2:1 ratio. Flash chromatographic purification allowed the quantitative recovering of unreacted **3**.

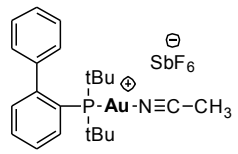


[6] R. Kuwano, M. Kashiwabara, K. Sato, T. Ito, K. Kaneda and Y. Ito *Tetrahedron: Asymmetry*, 2006, **17,** 521.

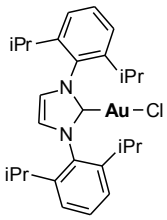
Optimization of the catalytic cyclization of 2a to dihydrofuran 4a:



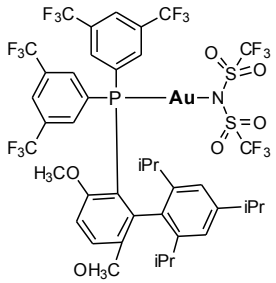
2a **4a**



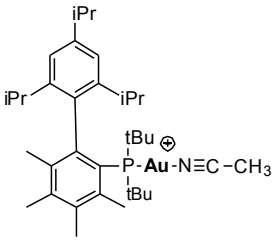
JhonPhosAu(CH_3CN)SbF_6



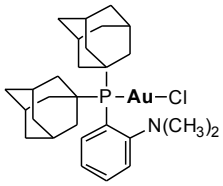
iPrAuCl



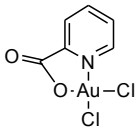
JackiePhosAuNTf_2



Me-4-tBuXphosAu(CH_3CN)SbF_6



MeDalPhosAuCl



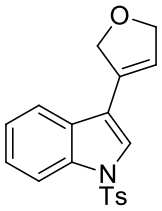
(2-pyridinecarboxylato)$AuCl_2$

Table S2. Optimization of the reaction conditions.

Entry	Catalyst	Yield 4a (%)
1	JhonPhos**Au**(CH_3CN)SbF_6	80%
2	IPr**Au**Cl / $AgNTf_2$	59%
3	IPr**Au**Cl / AgOTf	83%
4	IPr**Au**Cl / $AgSbF_6$	91%
5	$AgSbF_6$	20%
6	**Au**Cl·DMS	28%
7	PPh_3**Au**Cl/$AgSbF_6$	63%
8	JackiePhos**Au**NTf_2	40%

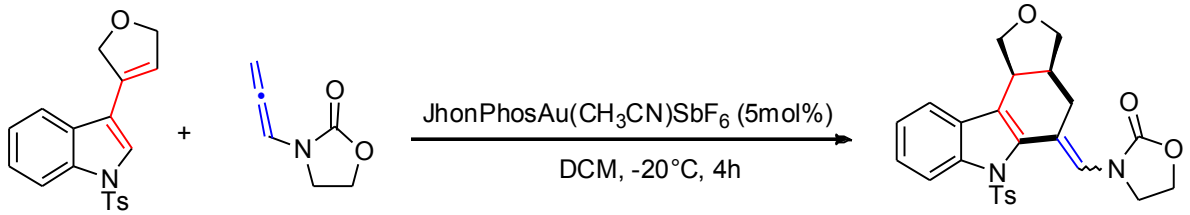
9	Me-*4*-tBuXphos**Au**(CH_3CN)SbF_6	75%
10	MeDalPhos**Au**Cl/$AgSbF_6$	53%
11	(2-Pyridinecarboxylato)**Au**Cl_2/2$AgSbF_6$	70%

To a solution of LAuCl (5 mol%) in anhydrous toluene (1 mL), 5 mol% of AgX (X = OTf, SbF_6, NTf_2) was added and the reaction mixture stirred for 15 min in the dark. Then **2a** (0.075 mmol, 25 mg) was added. The reaction was allowed to stir for 1 h, then directly charged into a column for the flash chromatography purification (*c*Hex:EtOAc = 9:1).



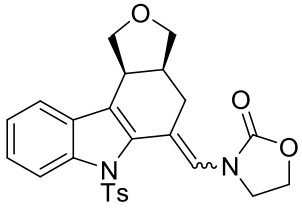
4a. White waxy solid. ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 8.03 – 7.99 (m, 1H), 7.79 – 7.75 (m, 3H), 7.44 (s, 1H), 7.41 – 7.35 (m, 1H), 7.34 – 7.29 (m, 1H), 7.24 (d, J = 8.0 Hz, 2H), 6.35 (s, 1H), 5.00 (td, J = 4.6, 2.0 Hz, 2H), 4.89 (td, J = 4.8, 1.7 Hz, 2H), 2.35 (s, 3H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$) δ 145.16, 135.33, 134.98, 130.80, 129.93, 128.66, 126.81, 125.13, 123.71, 123.44, 121.23, 120.75, 115.18, 113.78, 76.86, 75.84, 21.52. ***LC-MS***: 340.2 ($M + H^+$), 362.0 ($M + Na^+$), 378.2 ($M + K^+$). **Anal. Calc.** for ($C_{19}H_{17}NO_3S$: 339.09): C, 67.24; H, 5.05; N, 4.13; found: C, 67.21, H, 5.00; N, 4.25.

Gold-catalyzed synthesis of the tetrahydrocarbazole 6aa through intermolecular cycloaddition of allenyl indoles and *N*-allenyl amides.



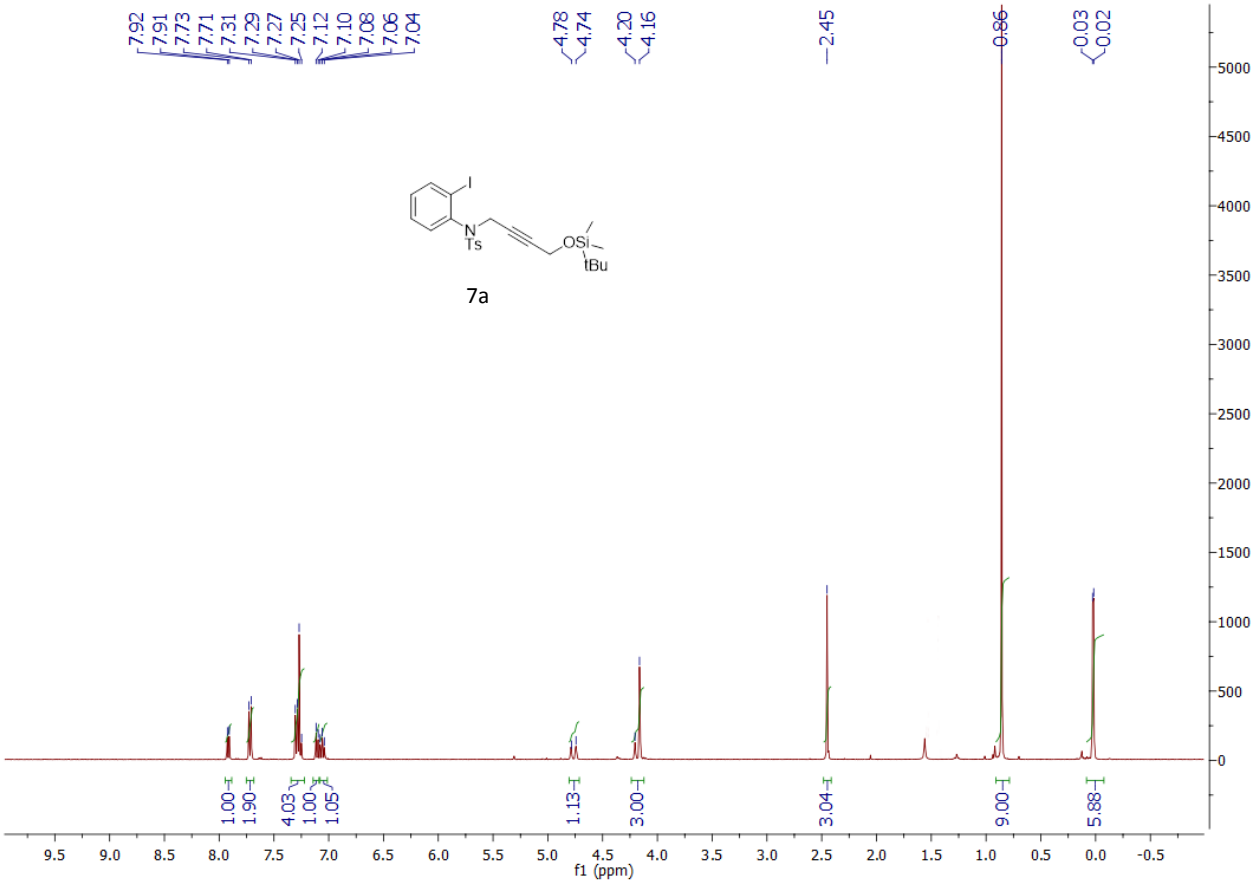
4a **5a** **6aa**

To a solution of **4a** (0.12 mmol, 40 mg) and allenamide **5a** (0.11 mmol, 13 mg) in dry DCM (1.5 mL) at -20 ºC, [JhonPhosAu(CH_3CN)SbF_6] (5 mol%) was added. The resulting mixture was stirred at this temperature until disappearance of the starting reagents was confirmed by TLC analysis. The solvent was removed under reduced pressure and the resulting residue purified by column chromatography (*c*Hex:EtOAc = 6:4).

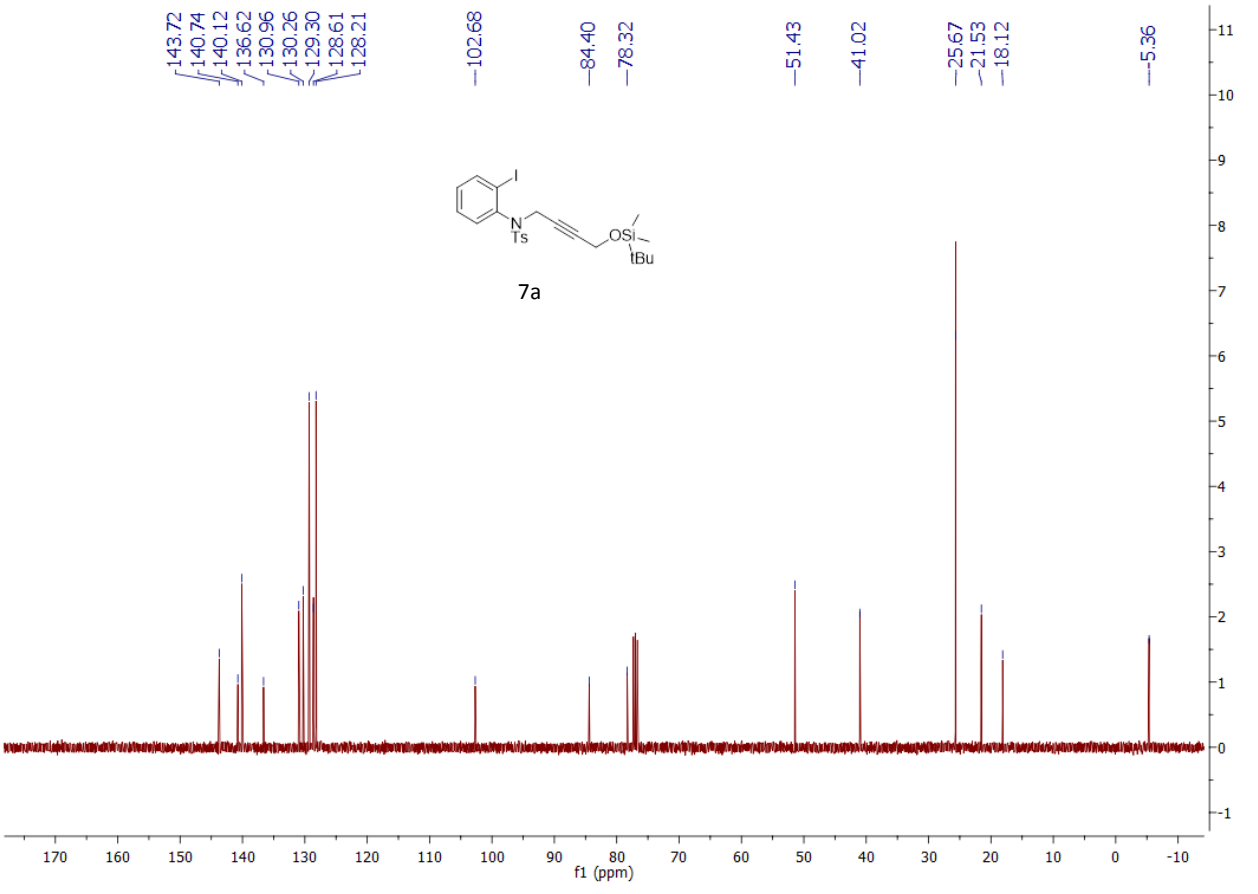


6aa. White waxy solid. **Yield** = 55%. ***^{1}H-NMR*** (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.2 Hz, 1H), 7.47 (d, *J* = 8.3 Hz, 2H), 7.28 (t, *J* = 7.3 Hz, 1H), 7.11 (dd, *J* = 16.0, 7.9 Hz, 3H), 6.97 (d, *J* = 7.4 Hz, 1H), 6.26 (s, 1H), 5.14 (d, *J* = 2.3 Hz, 1H), 4.60 (ddd, *J* = 14.1, 3.6, 1.8 Hz, 1H), 4.49 (dd, *J* = 17.0, 8.3 Hz, 1H), 4.44 – 4.32 (m, 2H), 4.26 (td, *J* = 8.6, 5.2 Hz, 1H), 4.18 (t, *J* = 8.0 Hz, 1H), 3.79 (dd, *J* = 16.9, 8.3 Hz, 1H), 3.46 (q, *J* = 7.0 Hz, 1H), 3.01 (dd, *J* = 10.1, 8.2 Hz, 1H), 2.83 (s, 1H), 2.50 (dd, *J* = 14.4, 7.6 Hz, 1H), 2.31 (s, 3H), 1.40 – 1.29 (m, 2H). ***^{13}C-NMR*** (100 MHz, $CDCl_3$) δ 157.19, 144.15, 144.02, 135.31, 134.86, 129.52, 129.18, 128.83, 127.34, 126.32, 124.89, 122.78, 122.16, 117.32, 72.63, 68.46, 63.55, 62.45, 46.07, 41.42, 31.04, 29.65, 21.45, 17.85. ***LC-MS***: 465.2 ($M+H^+$), 503.2 ($M+K^+$).

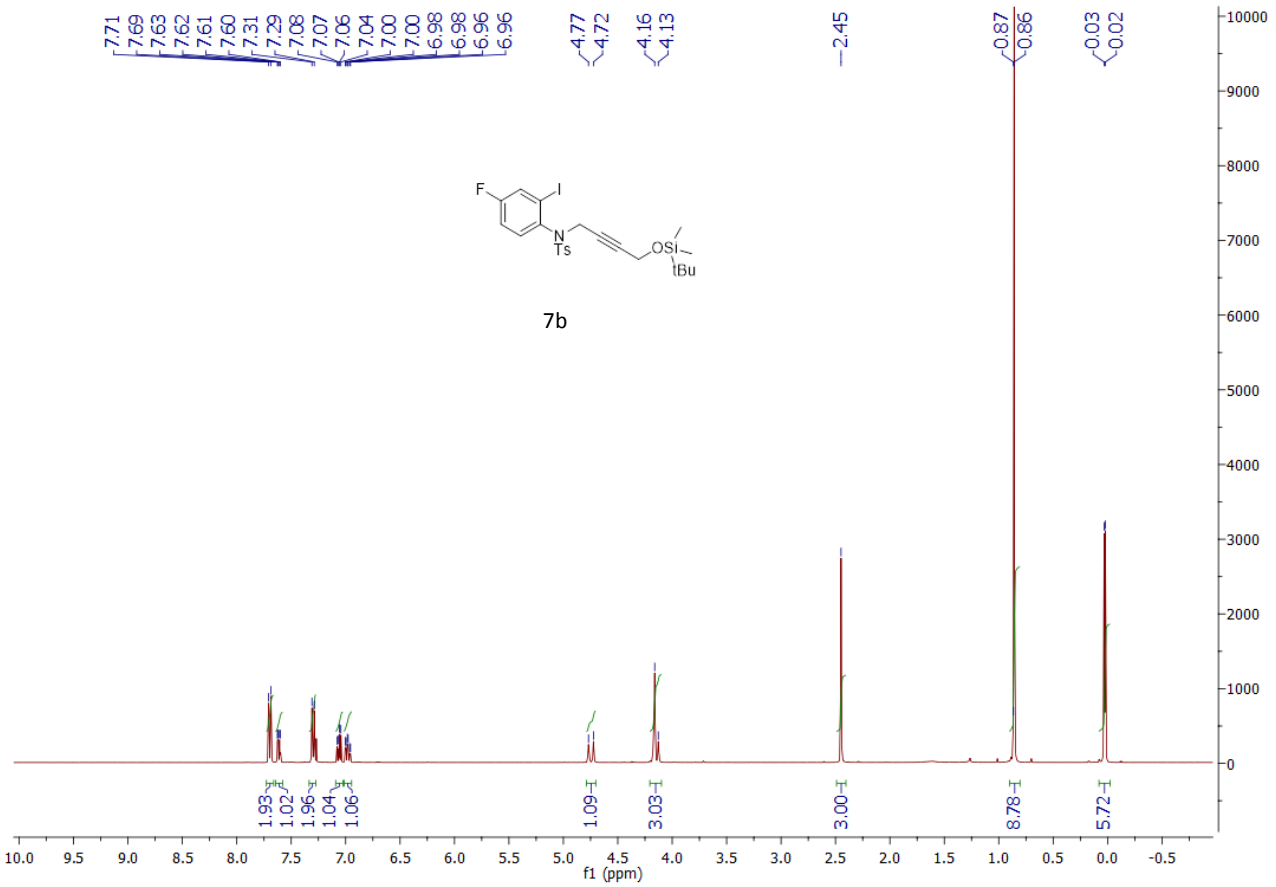
NMR spectra



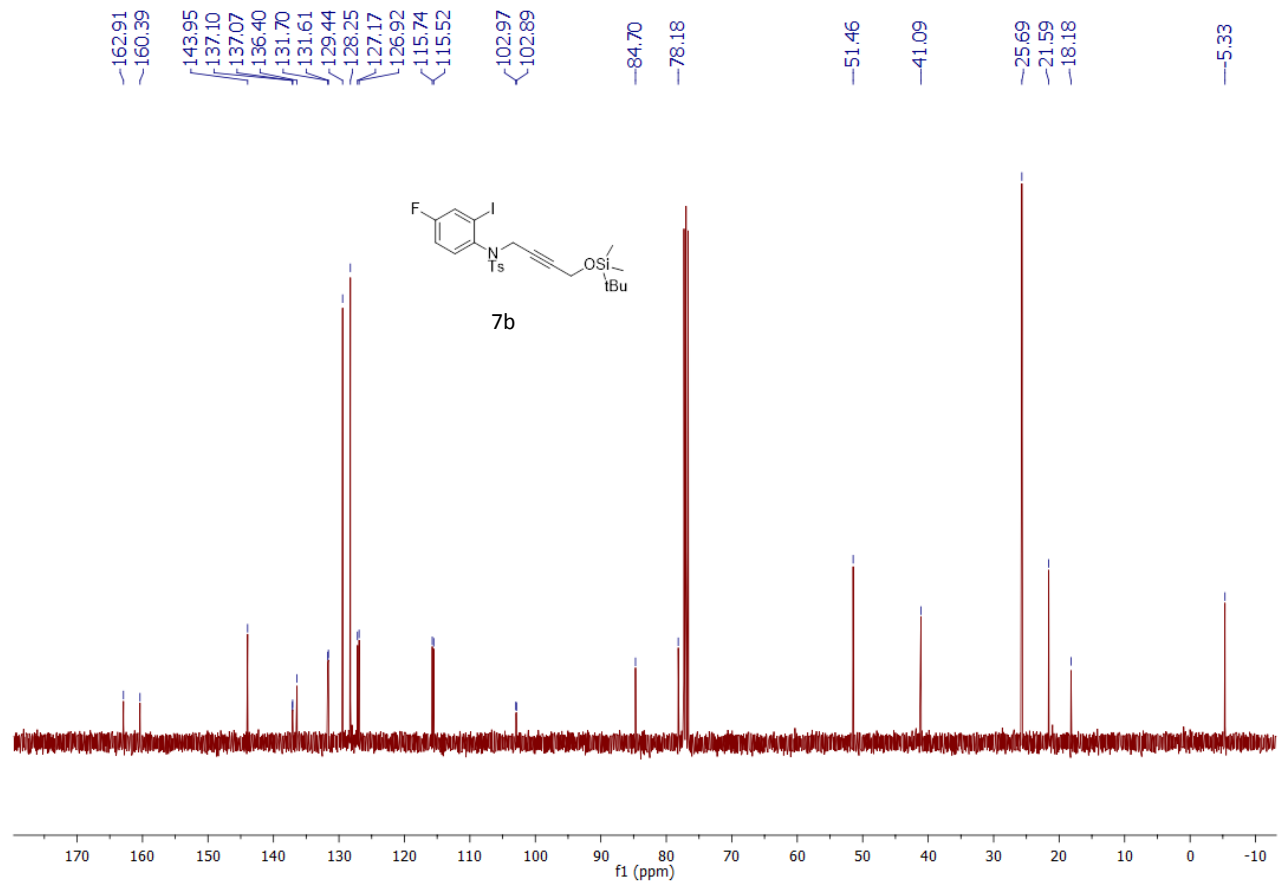
7a



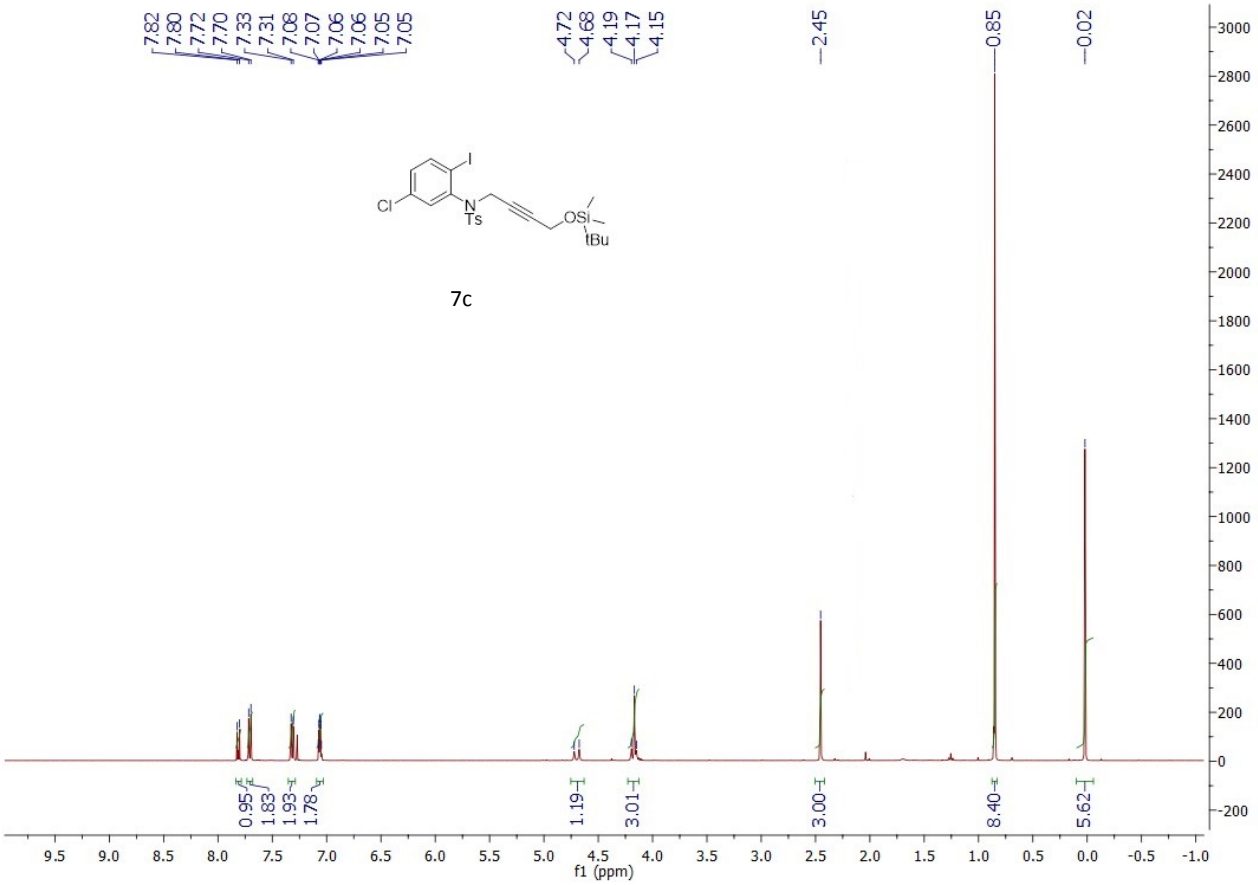
7a


7.71
7.69
7.63
7.62
7.61
7.60
7.31
7.29
7.08
7.07
7.06
7.04
7.00
7.00
6.98
6.98
6.96
6.96
4.77
4.72
4.16
4.13
2.45
0.87
0.86
0.03
0.02
F
I
N
Ts
OSi
tBu
1.93
1.02
1.96
1.04
1.06
1.09
3.03
3.00
8.78
5.72
f1 (ppm)

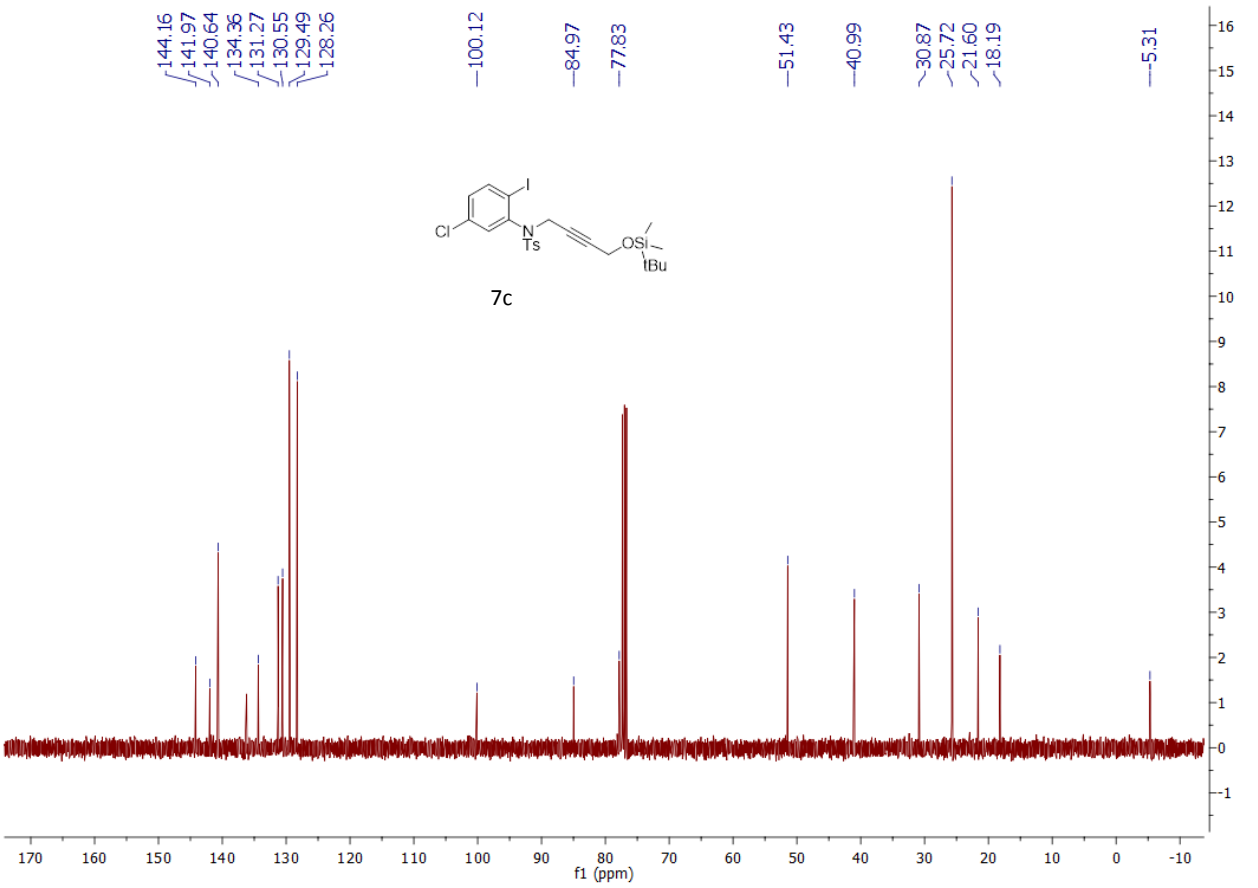
7b


162.91
160.39
143.95
137.10
137.07
136.40
131.70
131.61
129.44
128.25
127.17
126.92
115.74
115.52
102.97
102.89
84.70
78.18
51.46
41.09
25.69
21.59
18.18
5.33
F
I
N
Ts
OSi
tBu
f1 (ppm)

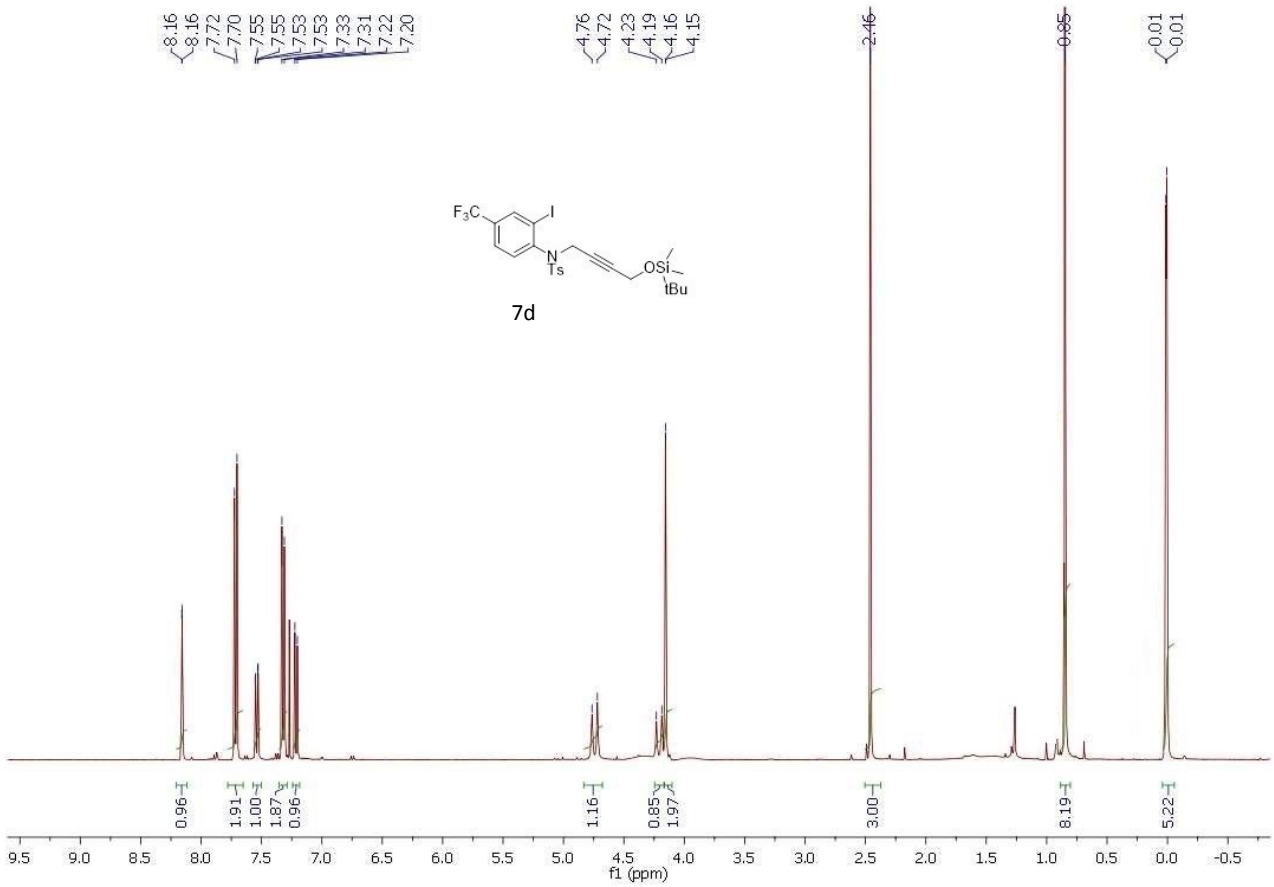
7b

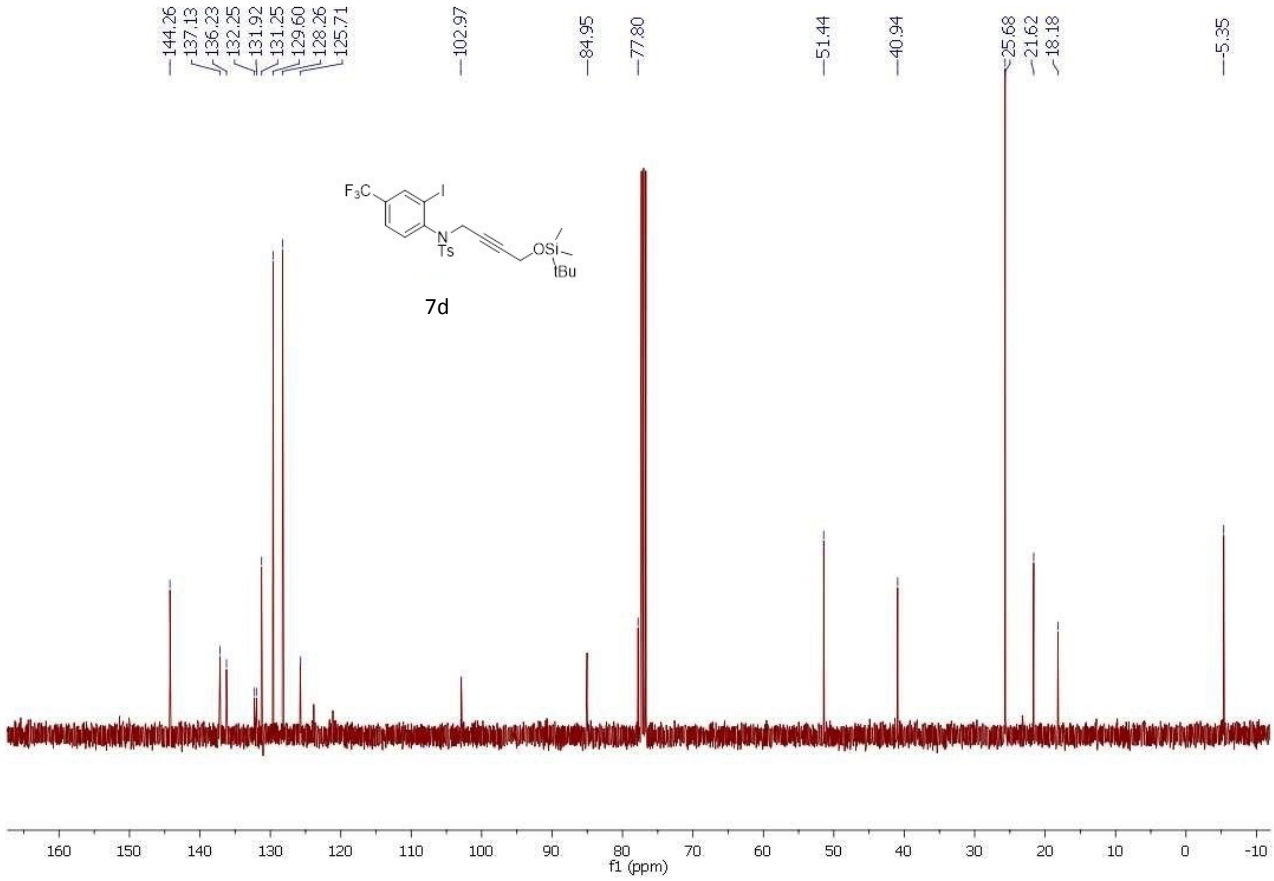

7.82
7.80
7.72
7.70
7.33
7.31
7.08
7.07
7.06
7.06
7.05
7.05
4.72
4.68
4.19
4.17
4.15
2.45
0.85
0.02
I
Cl
N
Ts
OSi
tBu
0.95
1.83
1.93
1.78
1.19
3.01
3.00
8.40
5.62
f1 (ppm)

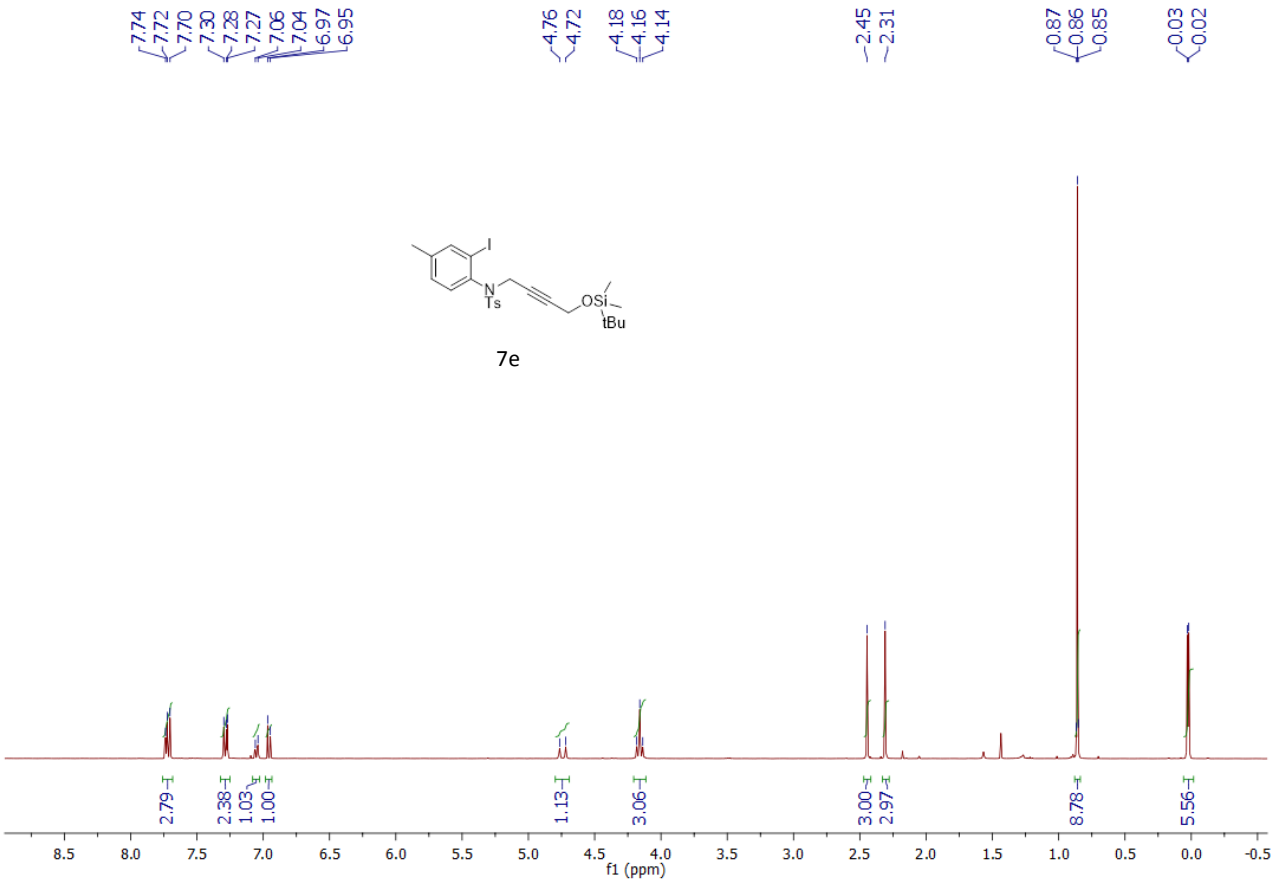
7c


144.16
141.97
140.64
134.36
131.27
130.55
129.49
128.26
100.12
84.97
77.83
51.43
40.99
30.87
25.72
21.60
18.19
5.31
I
Cl
N
Ts
OSi
tBu
f1 (ppm)

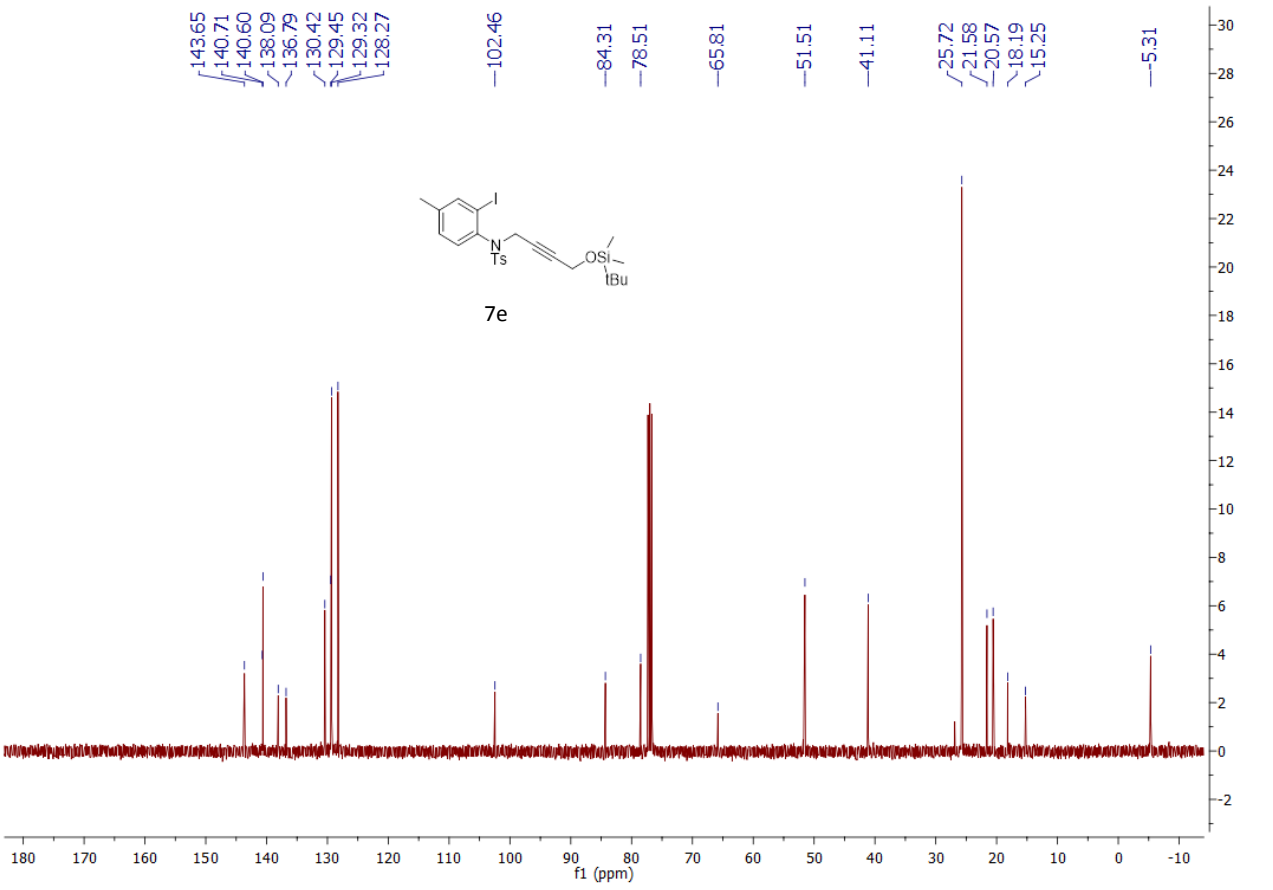
7c


8.16
8.16
7.72
7.70
7.55
7.55
7.53
7.53
7.33
7.31
7.22
7.20
4.76
4.72
4.23
4.19
4.16
4.15
2.46
0.95
0.01
0.01
F3C
I
N
Ts
OSi
tBu
7d
0.96
1.91
1.00
1.87
0.96
1.16
0.85
1.97
3.00
8.19
5.22
f1 (ppm)

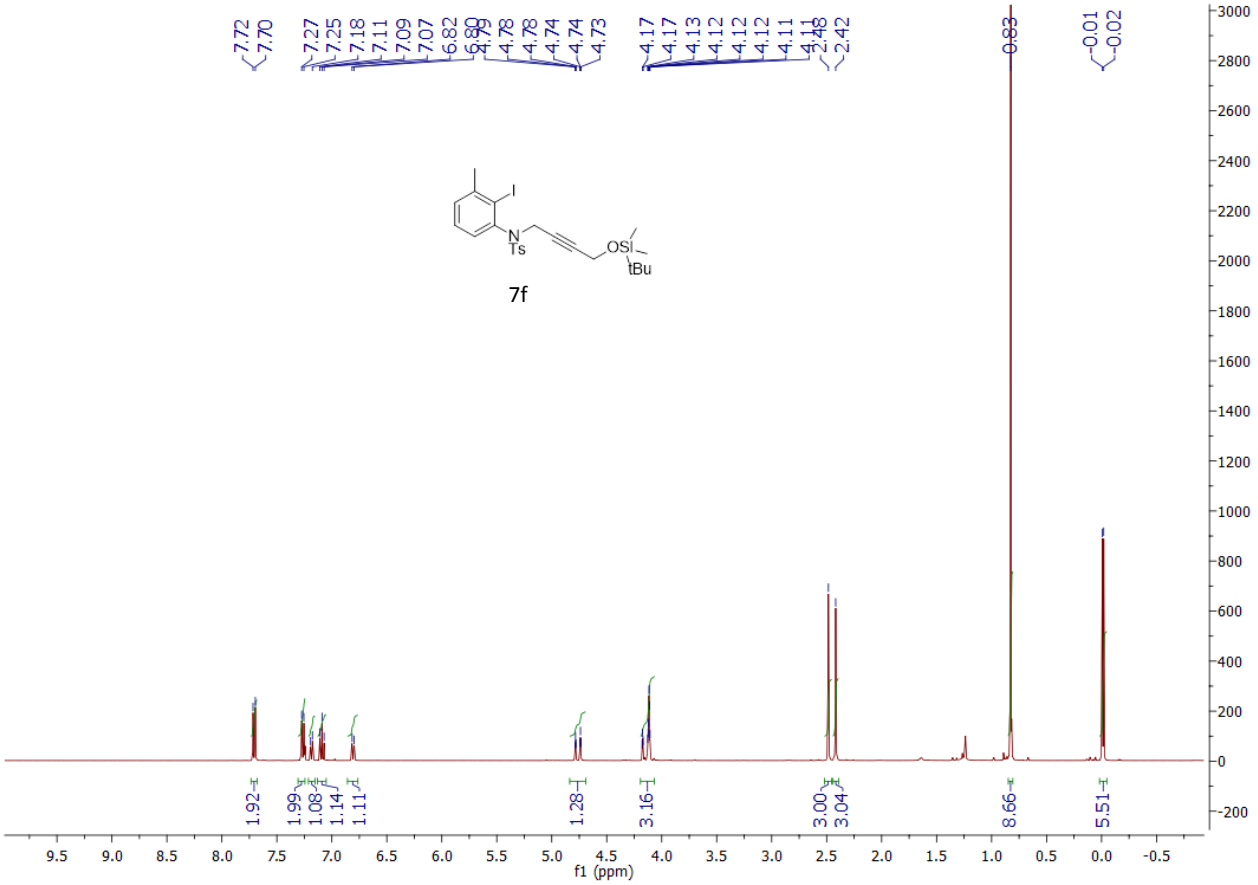

144.26
137.13
136.23
132.25
131.92
131.25
129.60
128.26
125.71
102.97
84.95
77.80
51.44
40.94
25.68
21.62
18.18
5.35
F3C
I
N
Ts
OSi
tBu
7d
f1 (ppm)


7.74
7.72
7.70
7.30
7.28
7.27
7.06
7.04
6.97
6.95
4.76
4.72
4.18
4.16
4.14
2.45
2.31
0.87
0.86
0.85
0.03
0.02
I
N
Ts
OSi
tBu
2.79
2.38
1.03
1.00
1.13
3.06
3.00
2.97
8.78
5.56
f1 (ppm)

7e

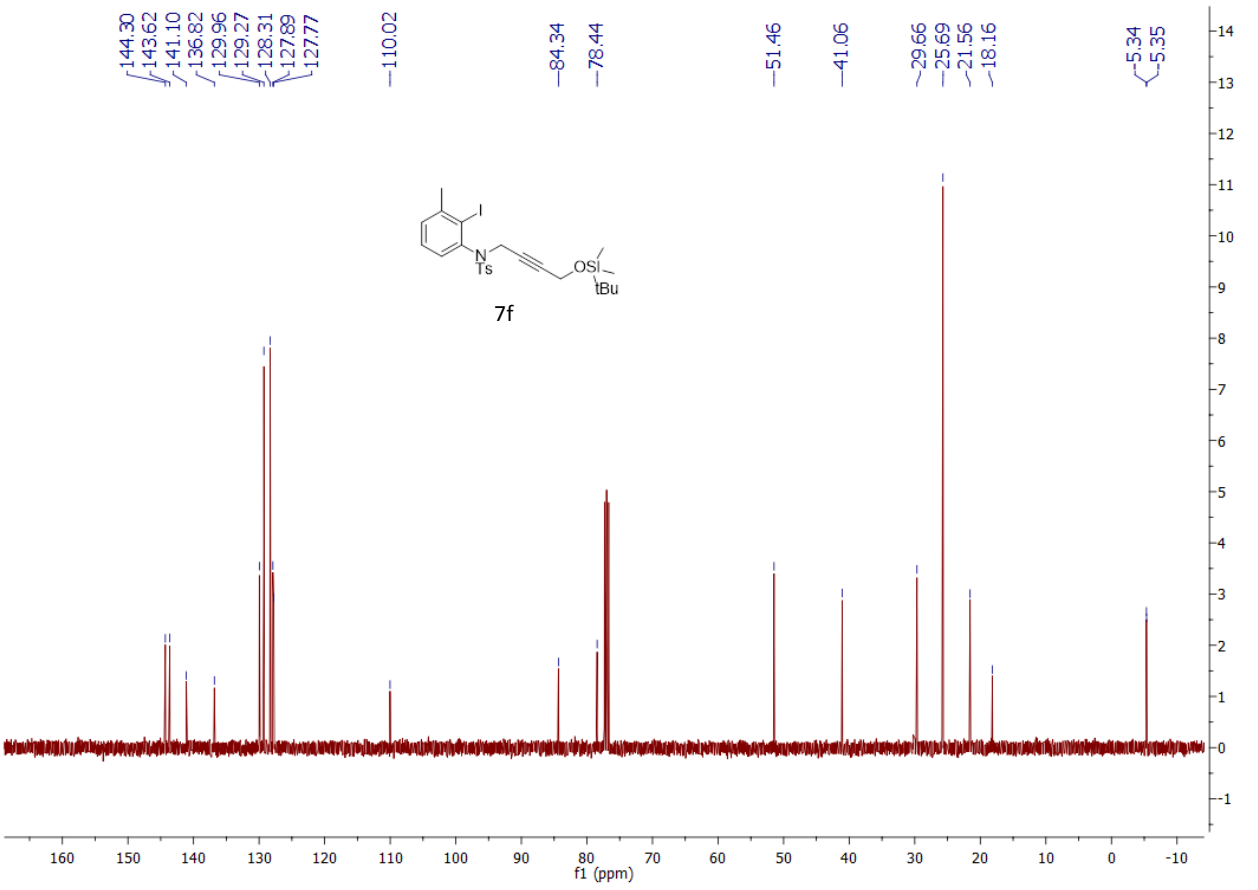

143.65
140.71
140.60
138.09
136.79
130.42
129.45
129.32
128.27
102.46
84.31
78.51
65.81
51.51
41.11
25.72
21.58
20.57
18.19
15.25
5.31
I
N
Ts
OSi
tBu
f1 (ppm)

7e


7.72
7.70
7.27
7.25
7.18
7.11
7.09
7.07
6.82
6.80
4.78
4.78
4.74
4.74
4.73
4.17
4.17
4.13
4.12
4.12
4.12
4.11
2.48
2.42
0.83
0.01
0.02
1.92
1.99
1.08
1.14
1.11
1.28
3.16
3.00
3.04
8.66
5.51
f1 (ppm)

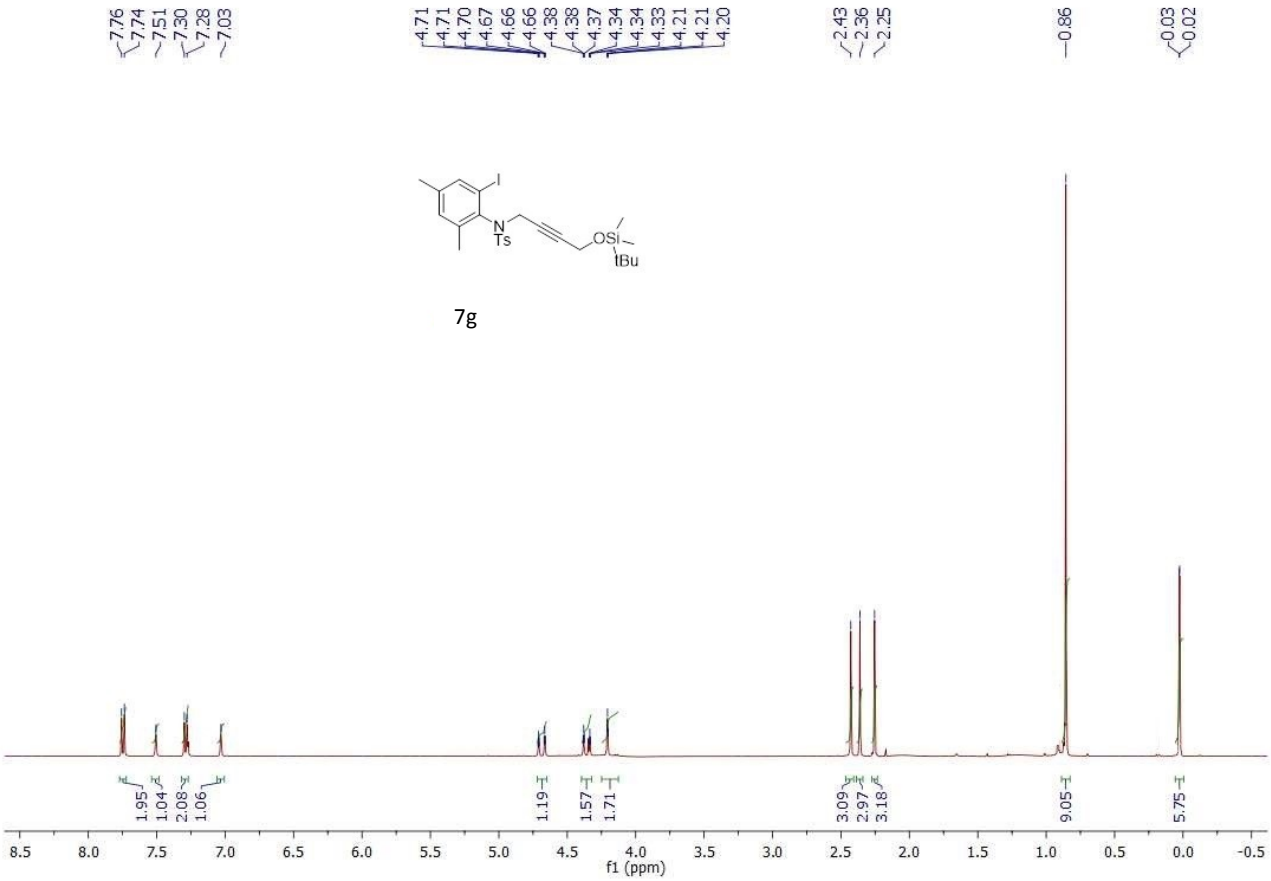
I
N
Ts
OSi
tBu

7f

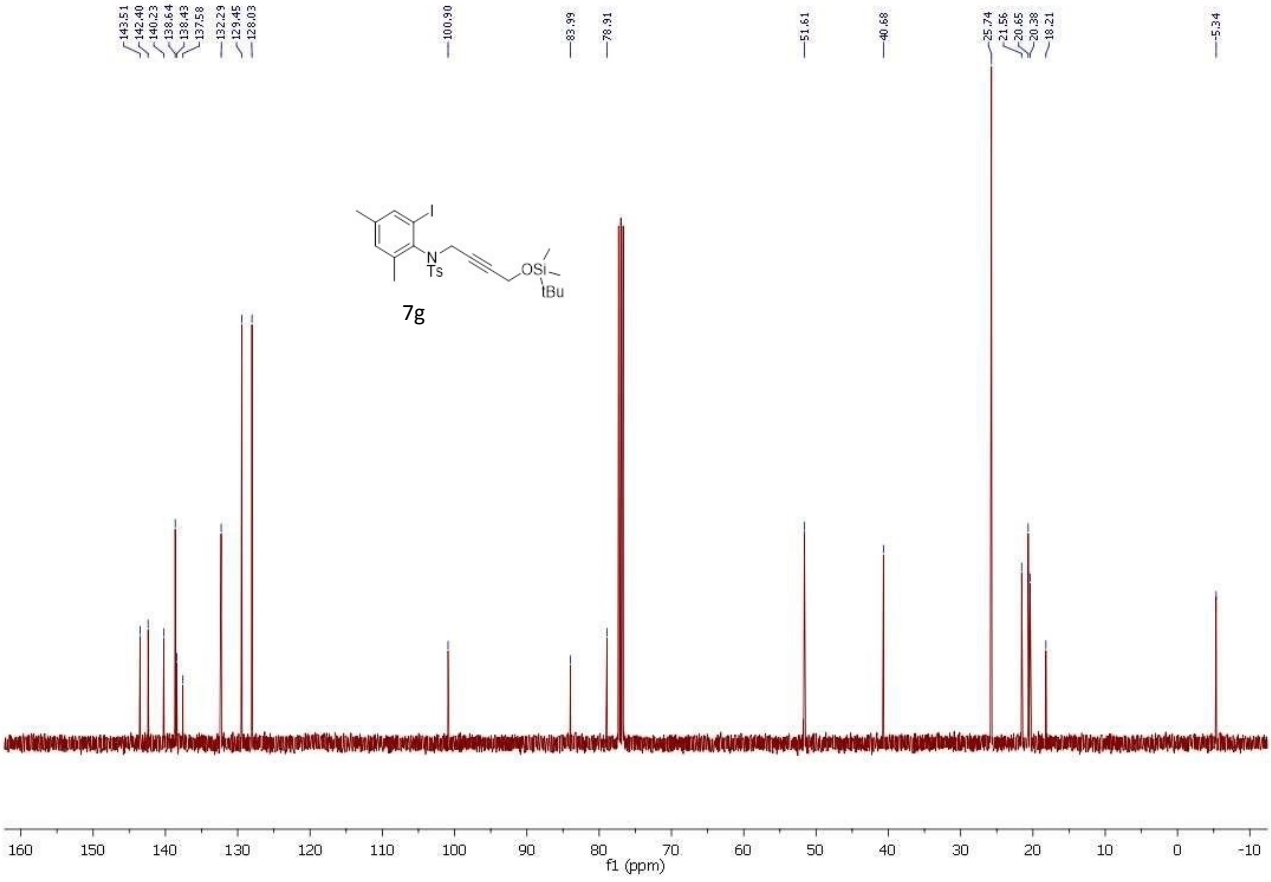

144.30
143.62
141.10
136.82
129.96
129.27
128.31
127.89
127.77
110.02
84.34
78.44
51.46
41.06
29.66
25.69
21.56
18.16
5.34
5.35
f1 (ppm)

I
N
Ts
OSi
tBu

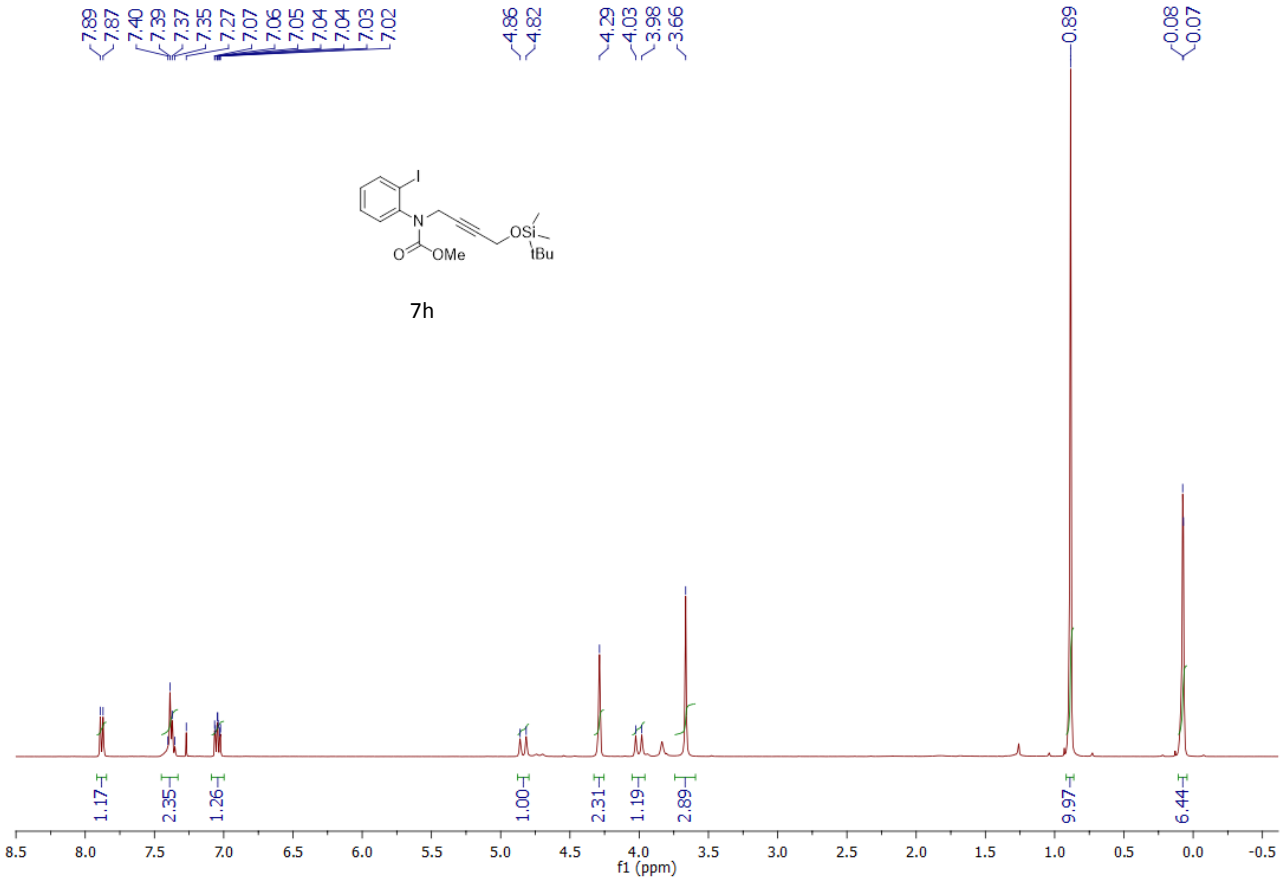
7f


7.76
7.74
7.51
7.30
7.28
7.03
4.71
4.71
4.70
4.67
4.66
4.66
4.38
4.38
4.37
4.34
4.34
4.33
4.21
4.21
4.20
2.43
2.36
2.25
0.86
0.03
0.02
I
N
Ts
OSi
tBu
1.95
1.04
2.08
1.06
1.19
1.57
1.71
3.09
2.97
3.18
9.05
5.75
f1 (ppm)

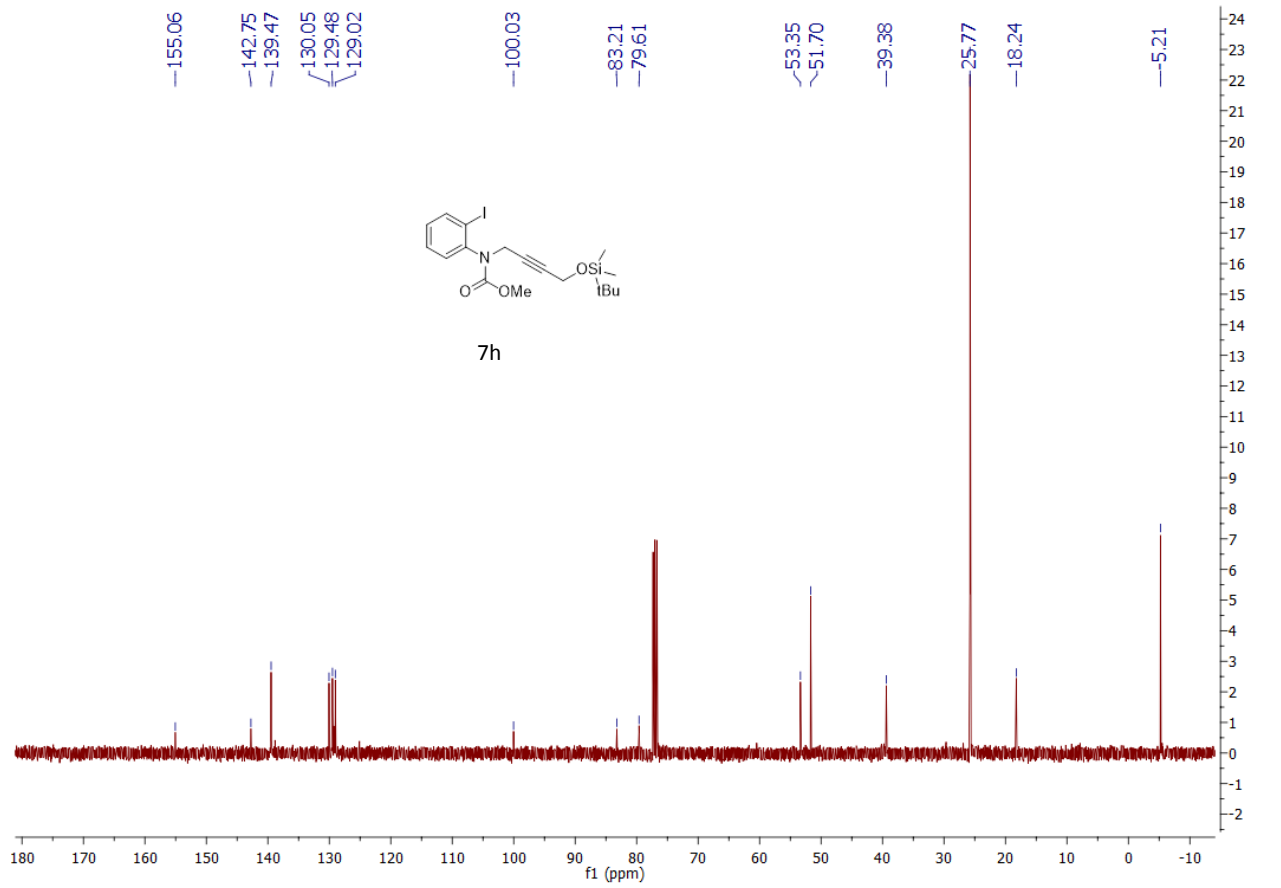
7g


143.51
142.40
140.23
138.64
138.43
137.58
132.29
129.45
128.03
100.90
83.99
78.91
51.61
40.68
25.74
21.56
20.65
20.38
18.21
-5.34
I
N
Ts
OSi
tBu
f1 (ppm)

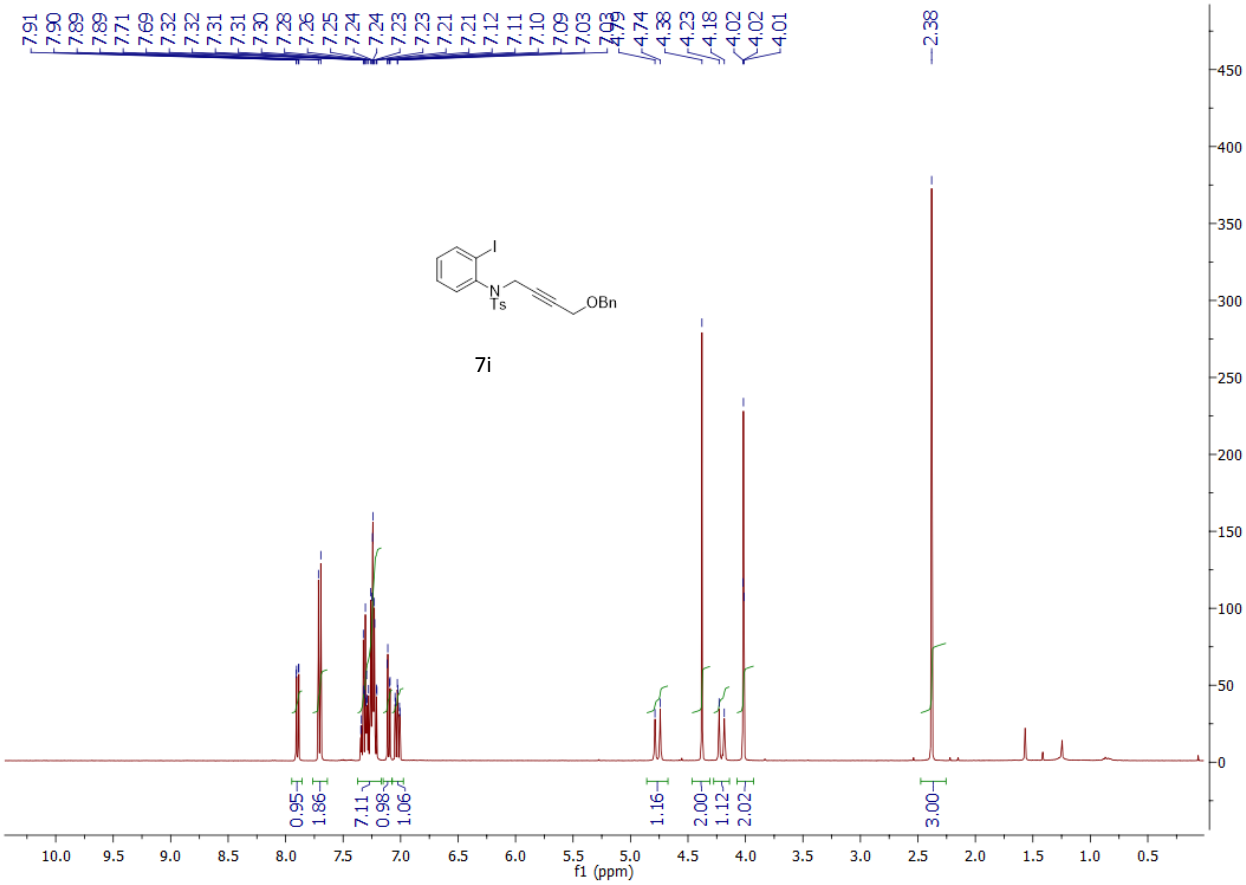
7g

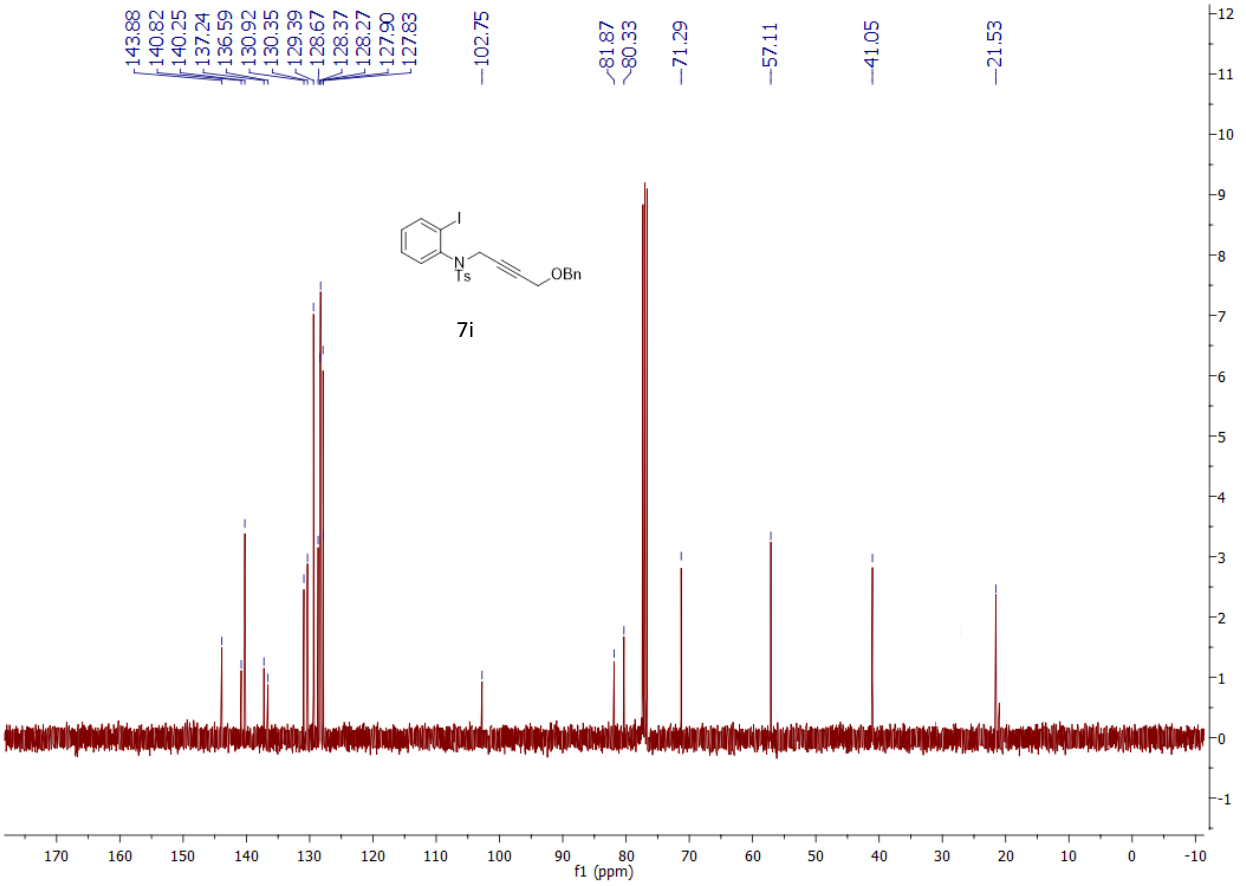

7.89
7.87
7.40
7.39
7.37
7.35
7.27
7.07
7.06
7.05
7.04
7.04
7.03
7.02
4.86
4.82
4.29
4.03
3.98
3.66
0.89
0.08
0.07
I
N
O
OMe
OSi
tBu
1.17
2.35
1.26
1.00
2.31
1.19
2.89
9.97
6.44
f1 (ppm)

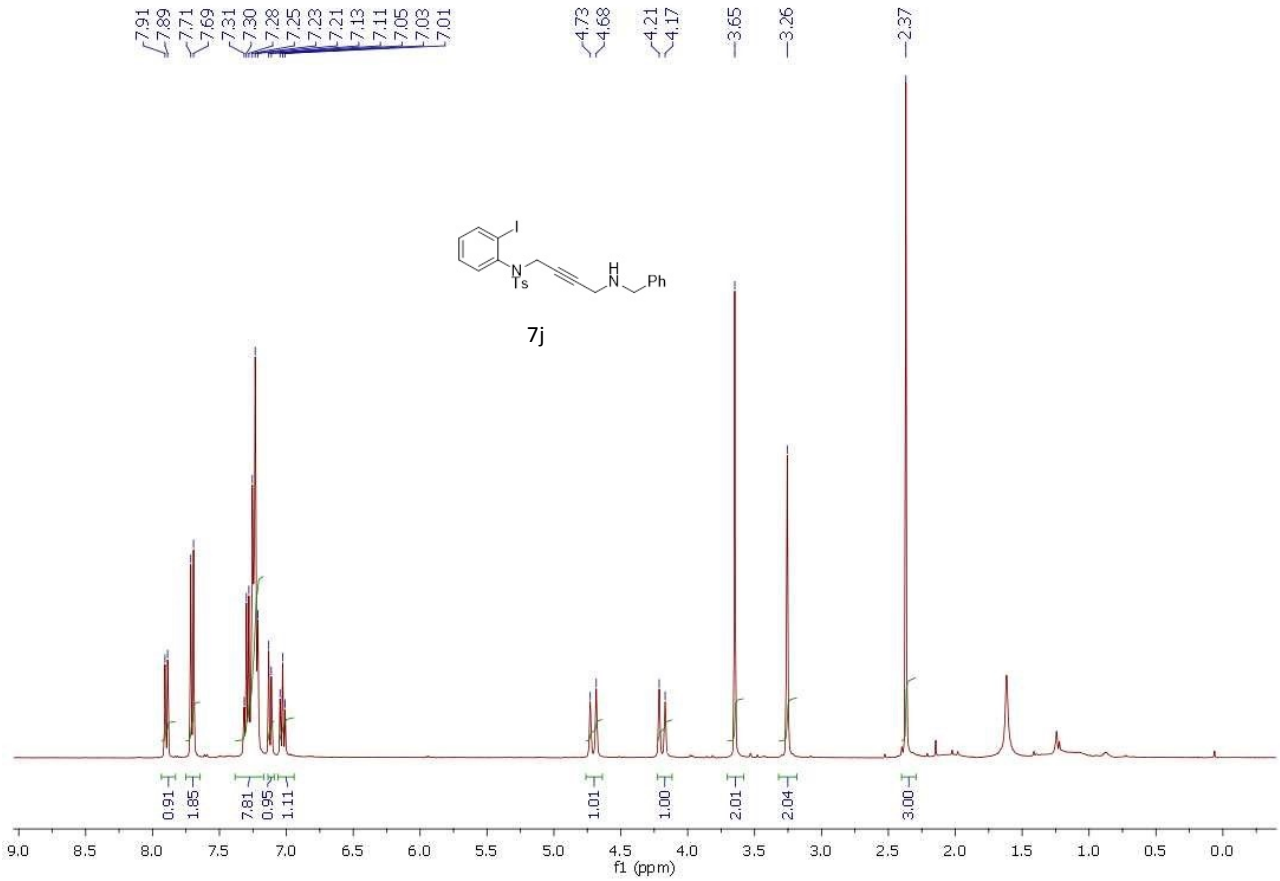
7h


155.06
142.75
139.47
130.05
129.48
129.02
100.03
83.21
79.61
53.35
51.70
39.38
25.77
18.24
5.21
I
N
O
OMe
OSi
tBu
f1 (ppm)

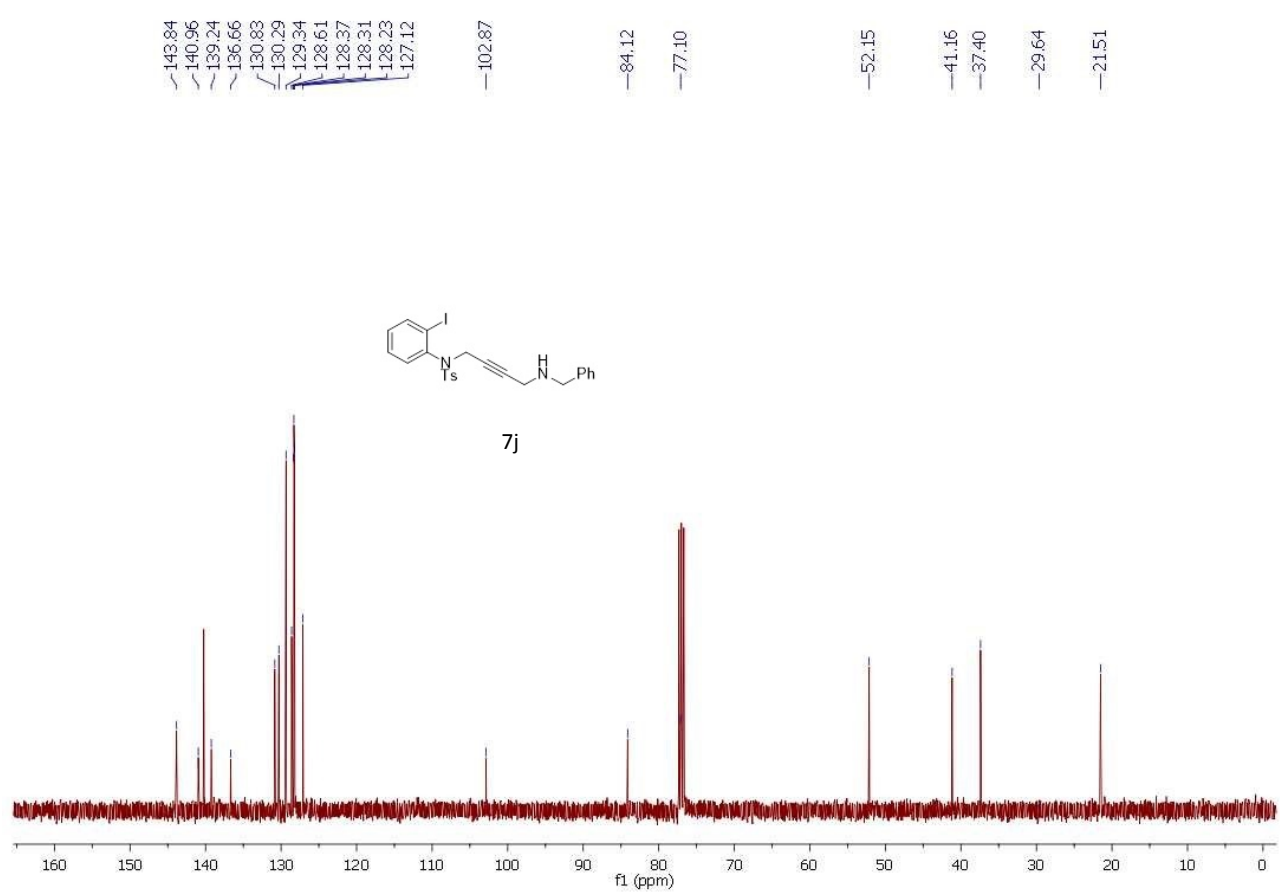
7h


7.91
7.90
7.89
7.89
7.71
7.69
7.32
7.32
7.31
7.31
7.30
7.28
7.26
7.25
7.24
7.24
7.23
7.23
7.21
7.21
7.12
7.11
7.10
7.09
7.03
4.74
4.38
4.23
4.18
4.02
4.02
4.01
2.38
I
N
Ts
OBn
7i
0.95
1.86
7.11
0.98
1.06
1.16
2.00
1.12
2.02
3.00
f1 (ppm)

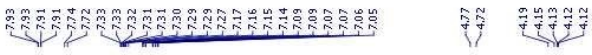

143.88
140.82
140.25
137.24
136.59
130.92
130.35
129.39
128.67
128.37
128.27
127.90
127.83
102.75
81.87
80.33
71.29
57.11
41.05
21.53
I
N
Ts
OBn
7i
f1 (ppm)

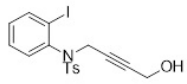

7.91
7.89
7.71
7.69
7.31
7.30
7.28
7.25
7.23
7.21
7.13
7.11
7.05
7.03
7.01
4.73
4.68
4.21
4.17
3.65
3.26
2.37
I
N
Ts
H
N
Ph
0.91
1.85
7.81
0.95
1.11
1.01
1.00
2.01
2.04
3.00
f1 (ppm)

7j

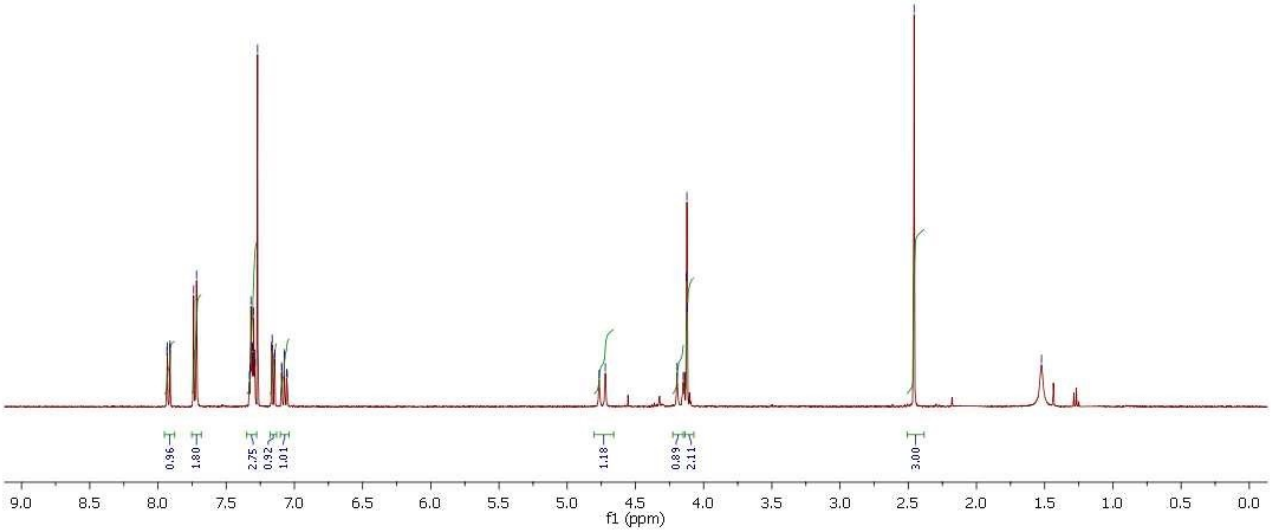

143.84
140.96
139.24
136.66
130.83
130.29
129.34
128.61
128.37
128.31
128.23
127.12
102.87
84.12
77.10
52.15
41.16
37.40
29.64
21.51
I
N
Ts
H
N
Ph
f1 (ppm)

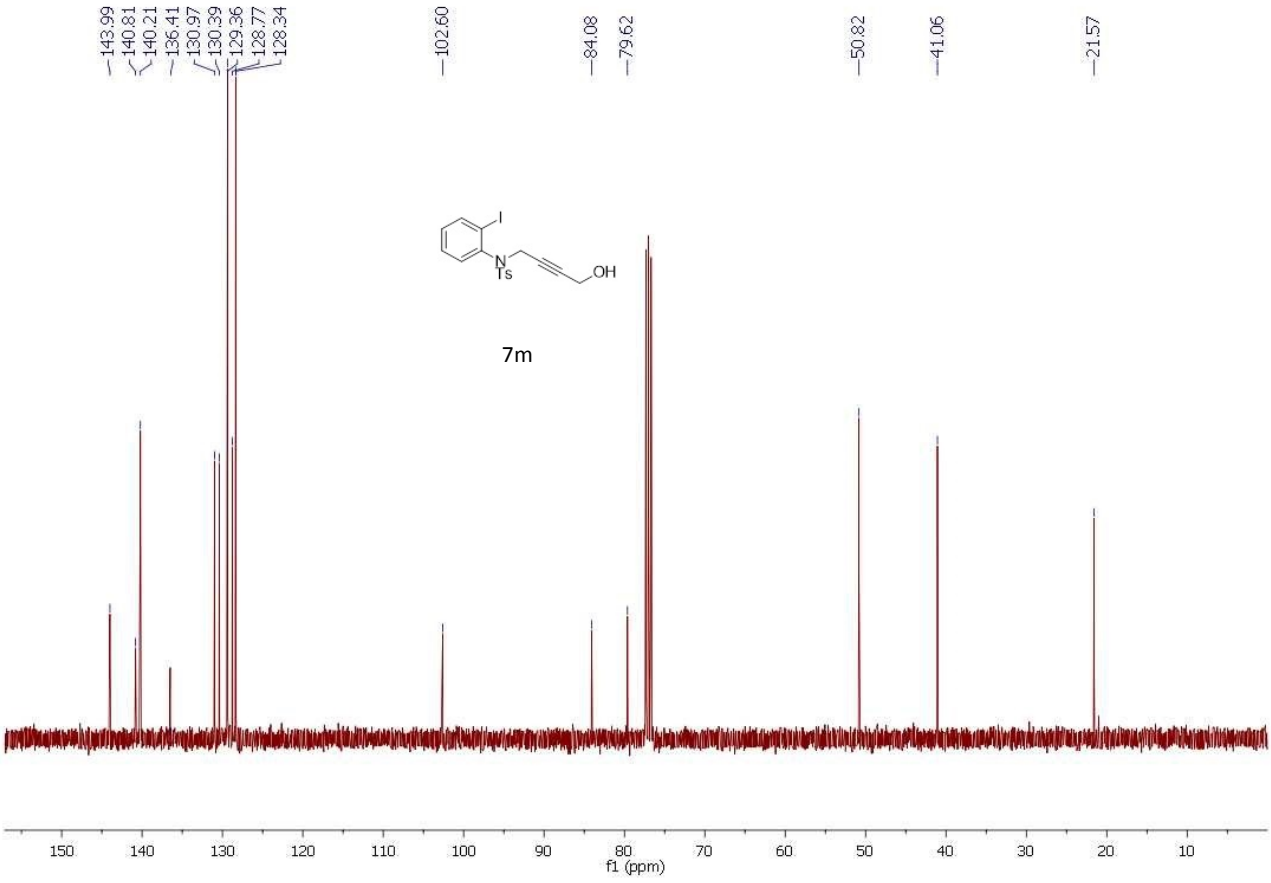
7j


7.93
7.93
7.91
7.91
7.74
7.72
7.33
7.32
7.31
7.31
7.30
7.29
7.29
7.27
7.17
7.16
7.15
7.14
7.09
7.09
7.07
7.07
7.06
7.05
4.77
4.72
4.19
4.15
4.13
4.12
4.12
2.46
1.52

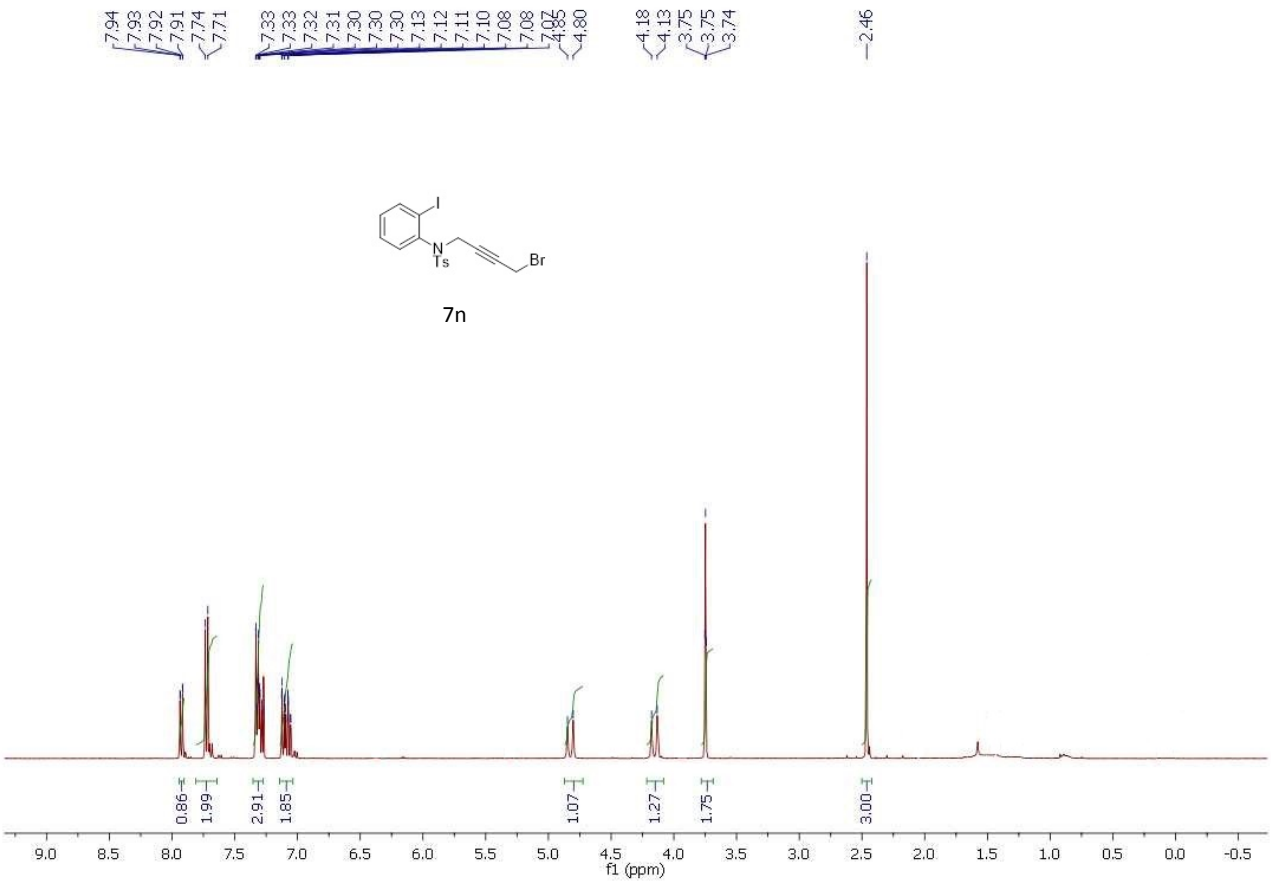

I
N
Ts
OH

7m

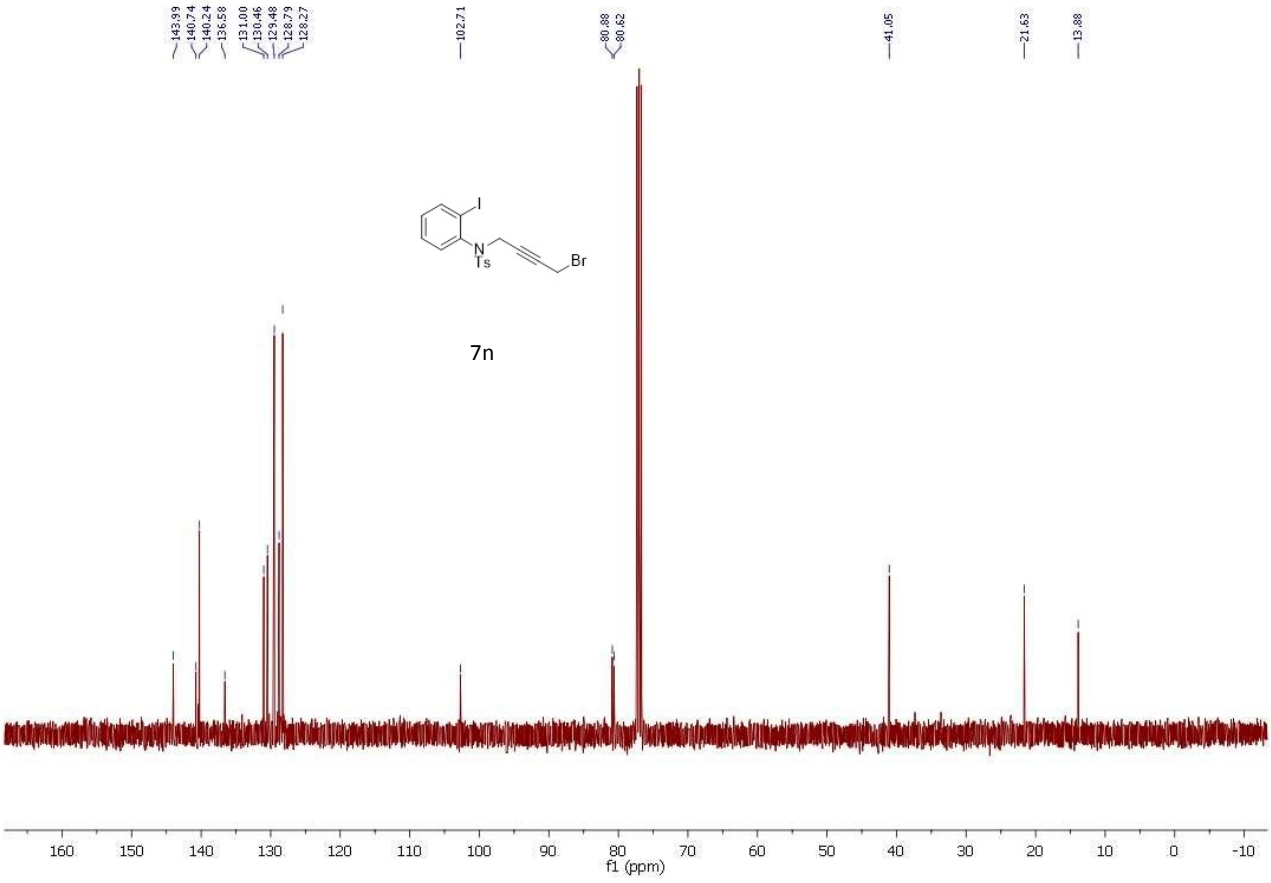

0.96
1.80
2.75
0.92
1.01
1.18
0.89
2.11
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


143.99
140.81
140.21
136.41
130.97
130.39
129.36
128.77
128.34
102.60
84.08
79.62
50.82
41.06
21.57
I
N
Ts
OH
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

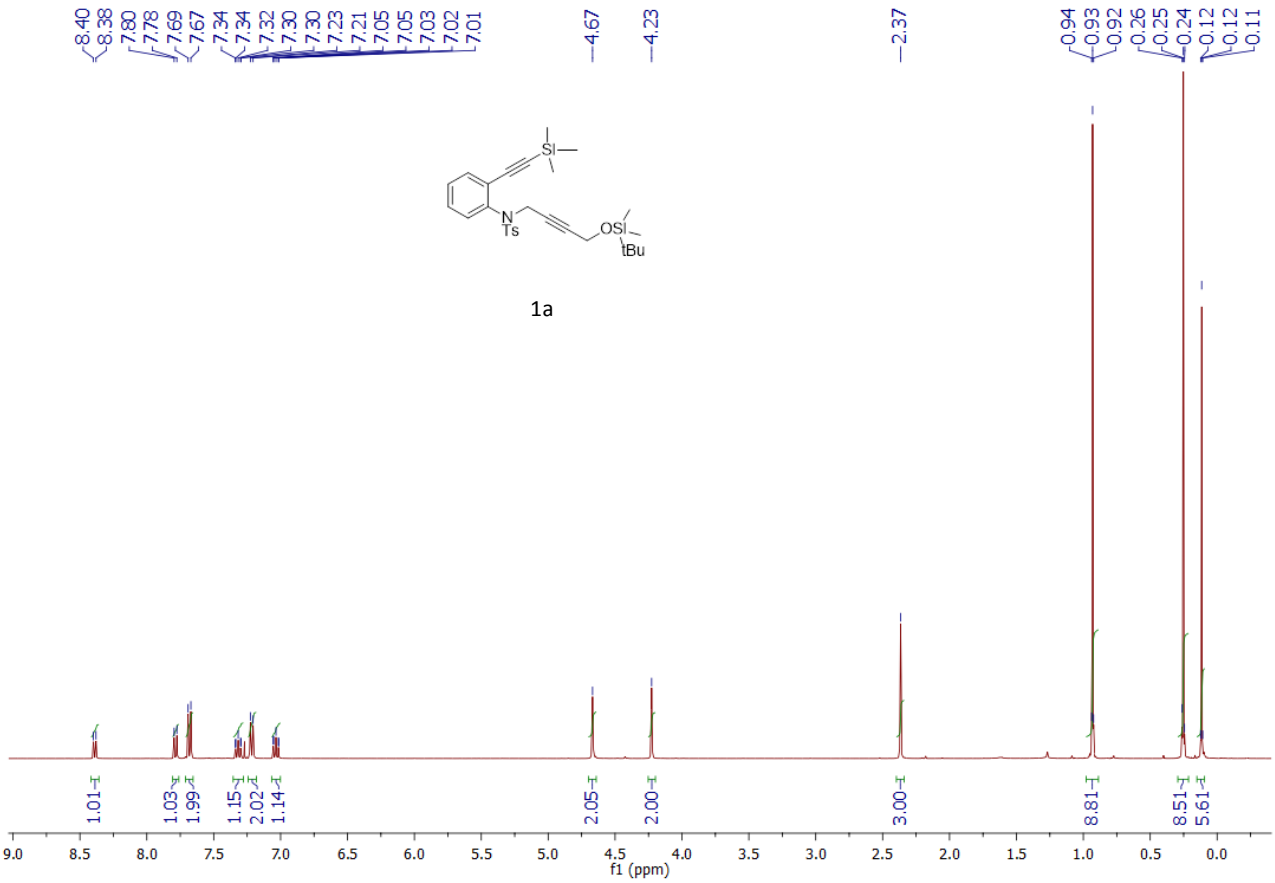
7m


7.94
7.93
7.92
7.91
7.74
7.71
7.33
7.33
7.32
7.31
7.30
7.30
7.30
7.13
7.12
7.11
7.10
7.08
7.08
7.07
4.85
4.80
4.18
4.13
3.75
3.75
3.74
2.46
I
N
Ts
Br
0.86
1.99
2.91
1.85
1.07
1.27
1.75
3.00
f1 (ppm)

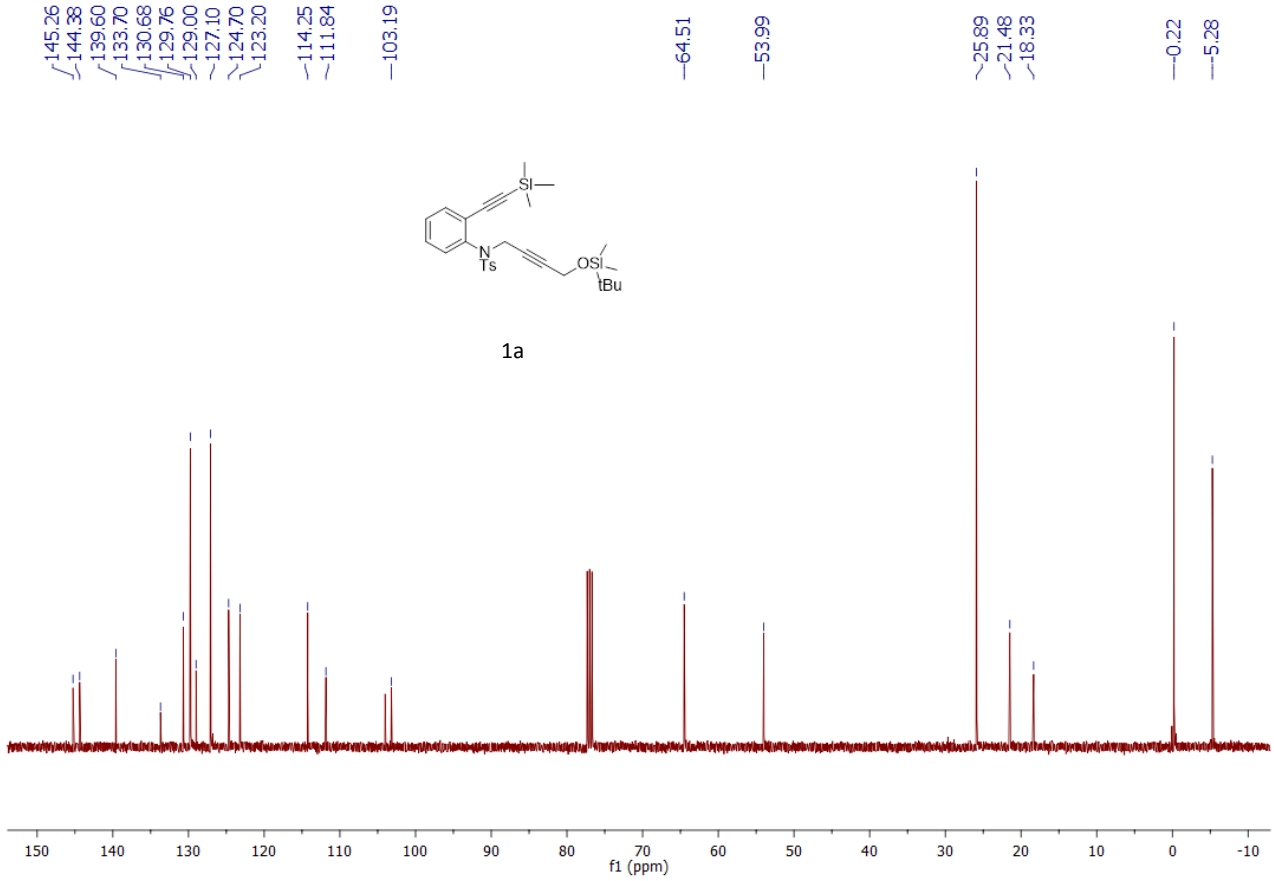
7n


143.99
140.74
140.24
136.58
131.00
130.46
129.48
128.79
128.27
102.71
80.88
80.62
41.05
21.63
13.88
I
N
Ts
Br
f1 (ppm)

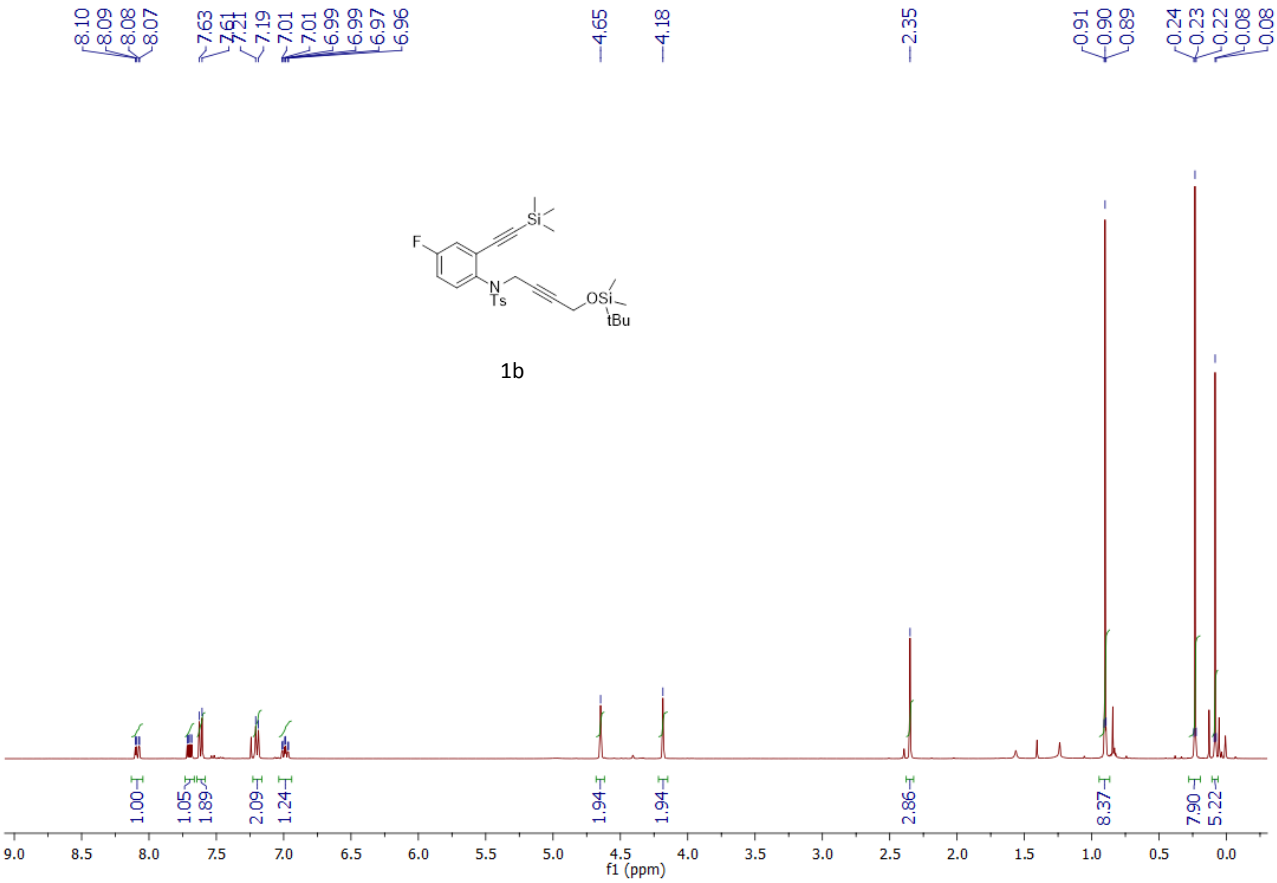
7n


8.40
8.38
7.80
7.78
7.69
7.67
7.34
7.34
7.32
7.30
7.30
7.23
7.21
7.05
7.05
7.03
7.02
7.01
4.67
4.23
2.37
0.94
0.93
0.92
0.26
0.25
0.24
0.12
0.12
0.11
Si
N
Ts
OSi
tBu
1.01
1.03
1.99
1.15
2.02
1.14
2.05
2.00
3.00
8.81
8.51
5.61
f1 (ppm)

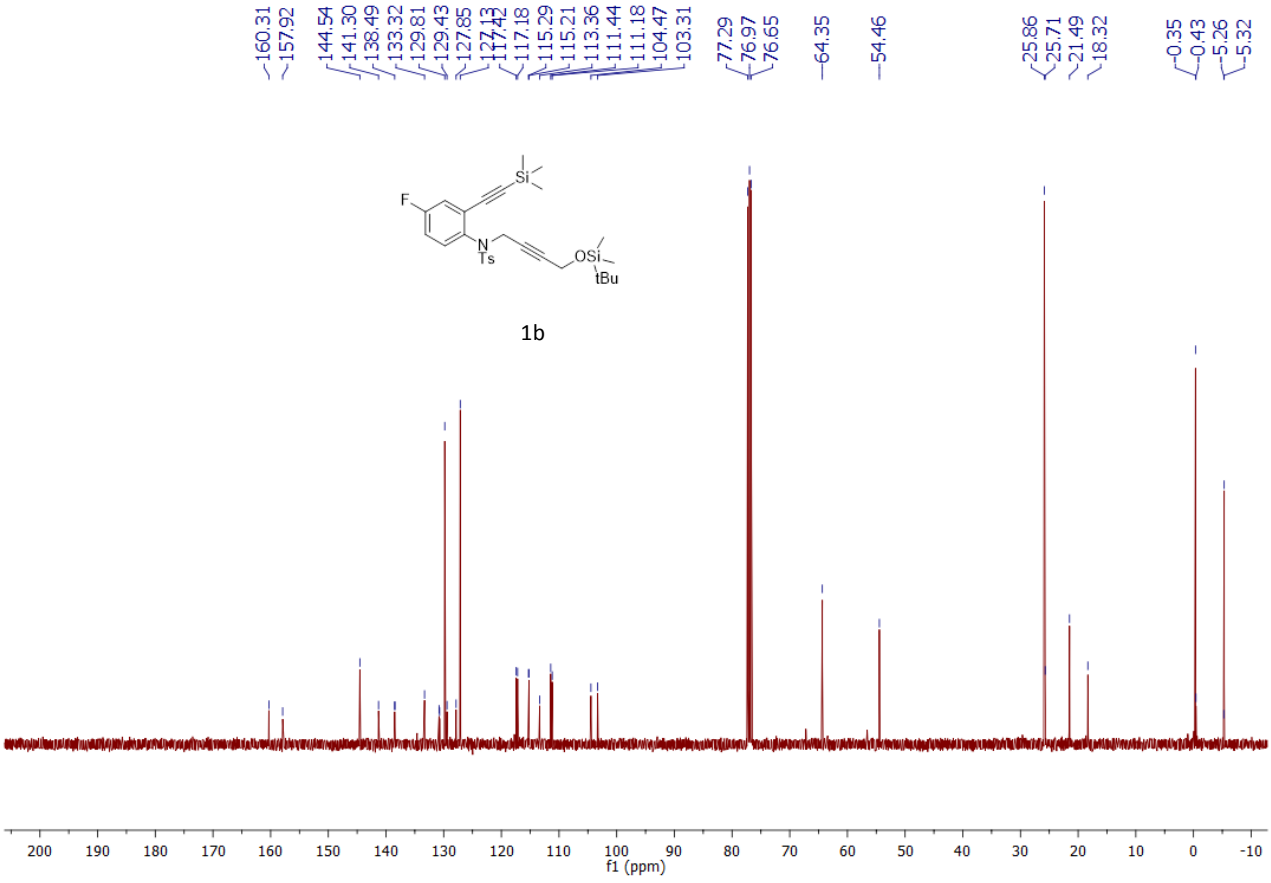
1a


145.26
144.38
139.60
133.70
130.68
129.76
129.00
127.10
124.70
123.20
114.25
111.84
103.19
64.51
53.99
25.89
21.48
18.33
0.22
5.28
Si
N
Ts
OSi
tBu
f1 (ppm)

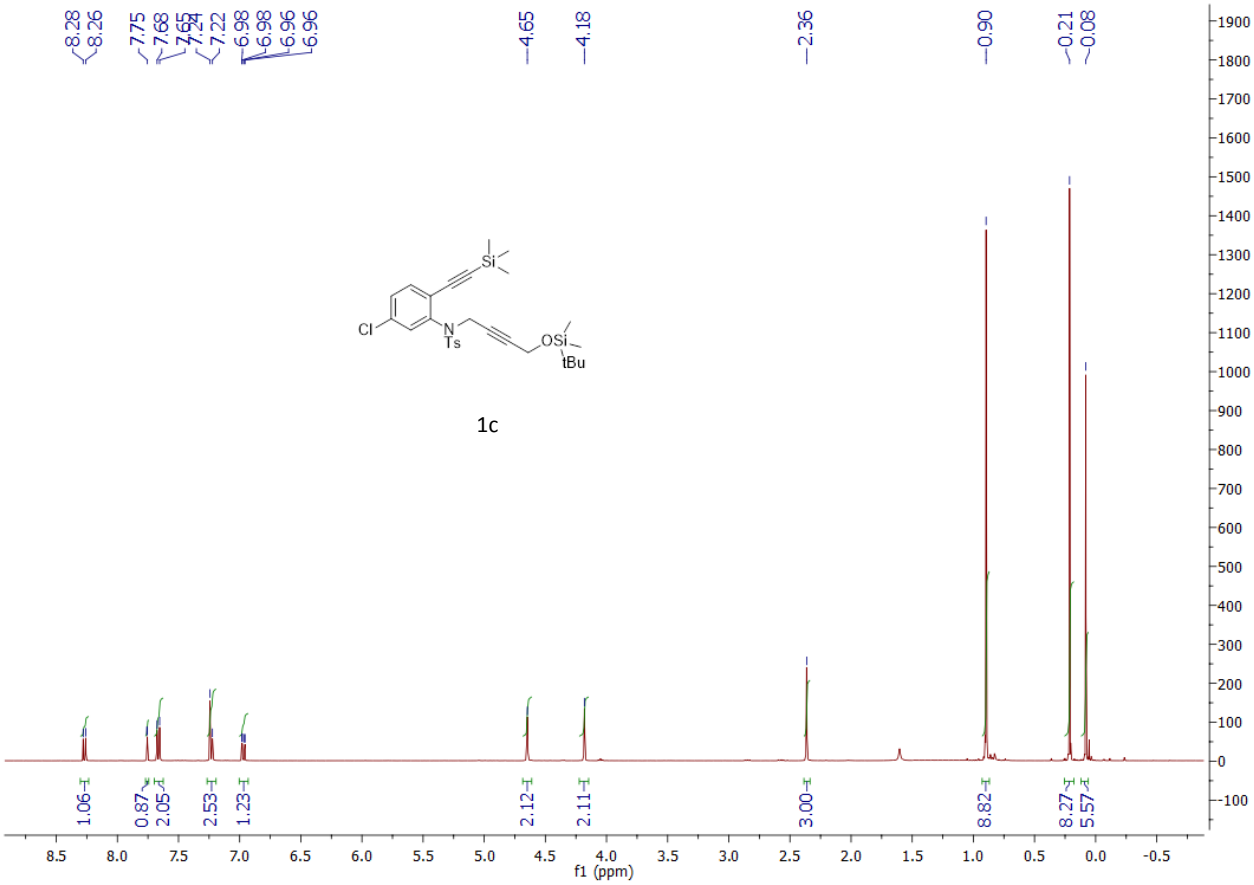
1a


8.10
8.09
8.08
8.07
7.63
7.61
7.21
7.19
7.01
7.01
6.99
6.99
6.97
6.96
4.65
4.18
2.35
0.91
0.90
0.89
0.24
0.23
0.22
0.08
0.08
F
Si
N
Ts
OSi
tBu
1.00
1.05
1.89
2.09
1.24
1.94
1.94
2.86
8.37
7.90
5.22
f1 (ppm)

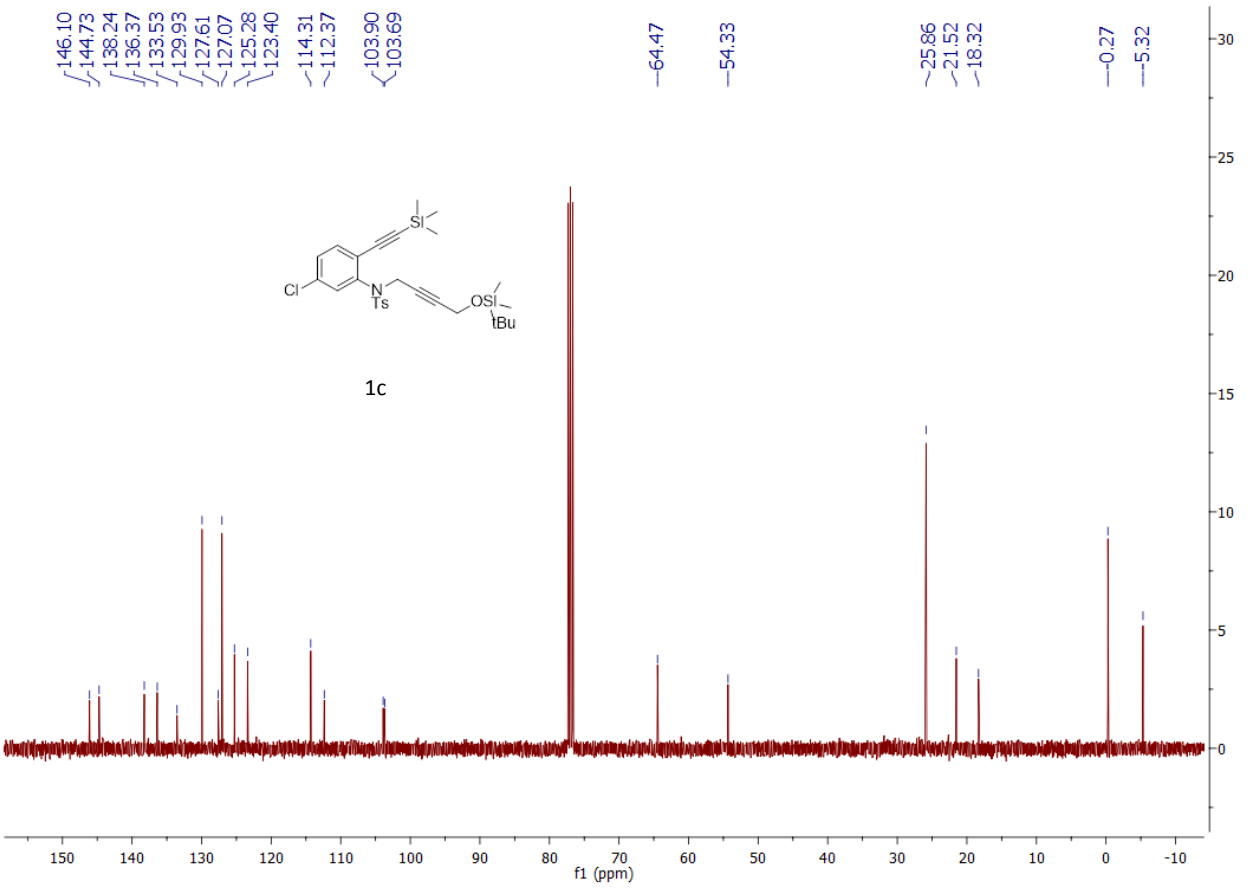
1b


160.31
157.92
144.54
141.30
138.49
133.32
129.81
129.43
127.85
117.18
115.29
115.21
113.36
111.44
111.18
104.47
103.31
77.29
76.97
76.65
64.35
54.46
25.86
25.71
21.49
18.32
0.35
0.43
5.26
5.32
F
Si
N
Ts
OSi
tBu
f1 (ppm)

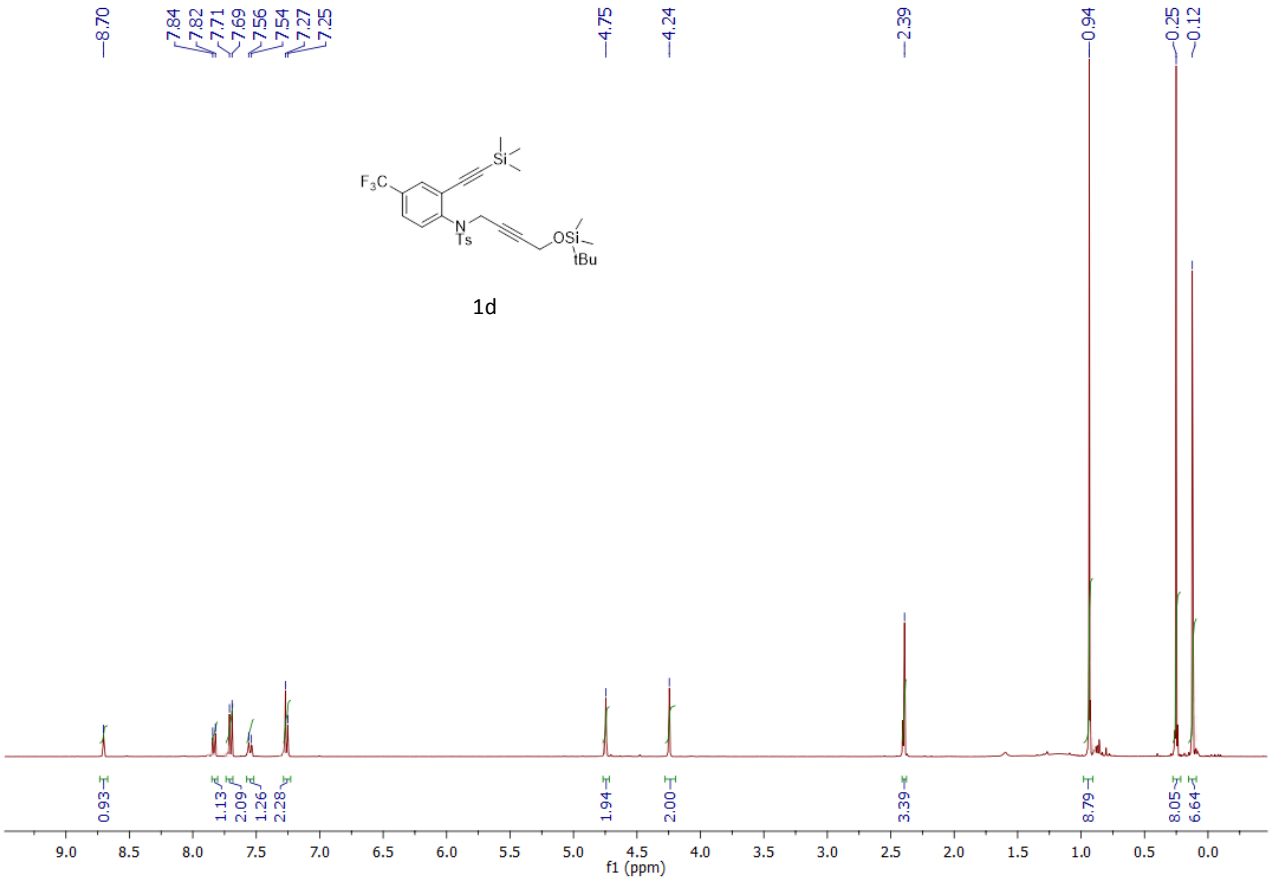
1b


8.28
8.26
7.75
7.68
7.65
7.24
7.22
6.98
6.98
6.96
6.96
4.65
4.18
2.36
0.90
0.21
0.08
Si
Cl
N
Ts
OSi
tBu
1.06
0.87
2.05
2.53
1.23
2.12
2.11
3.00
8.82
8.27
5.57
f1 (ppm)

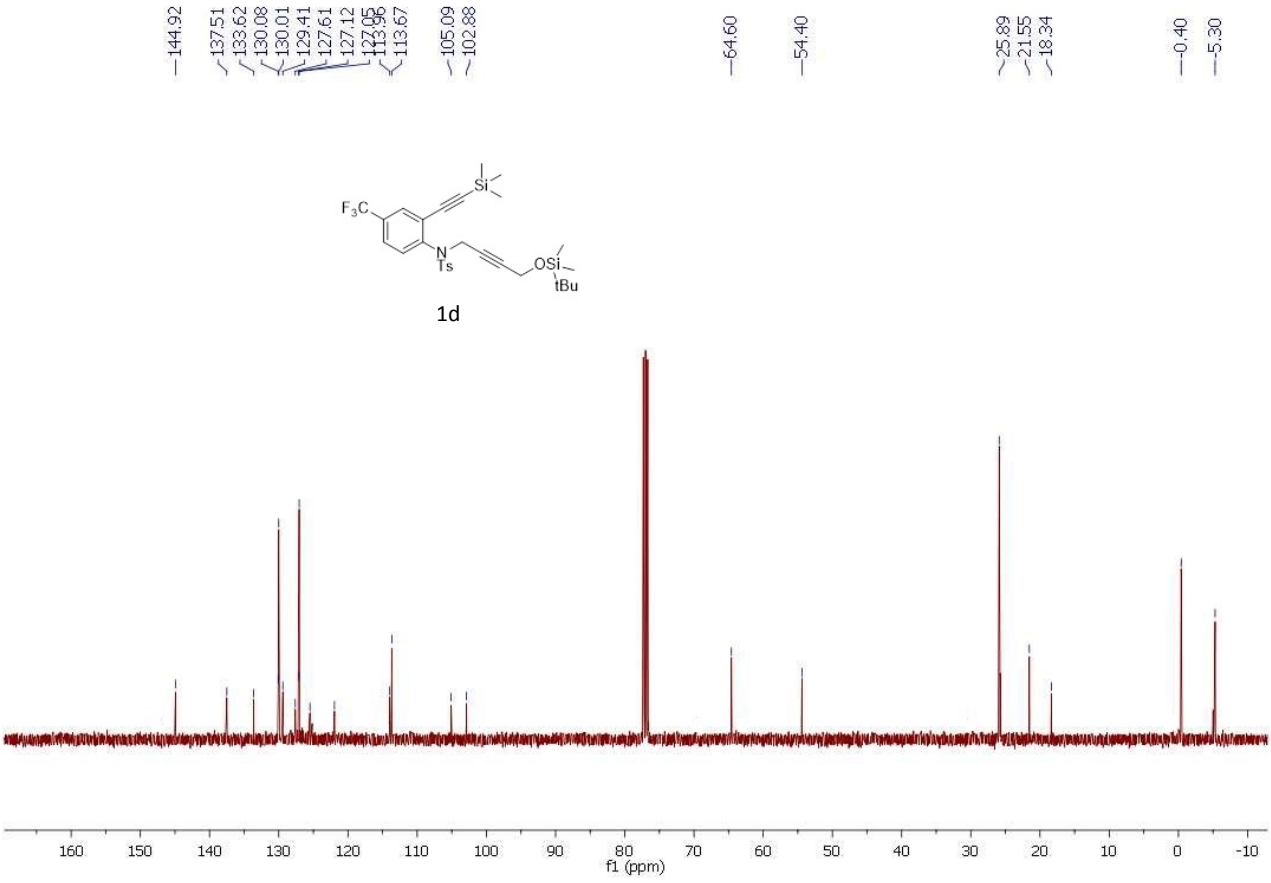
1c


146.10
144.73
138.24
136.37
133.53
129.93
127.61
127.07
125.28
123.40
114.31
112.37
103.90
103.69
64.47
54.33
25.86
21.52
18.32
0.27
5.32
Si
Cl
N
Ts
OSi
tBu
f1 (ppm)

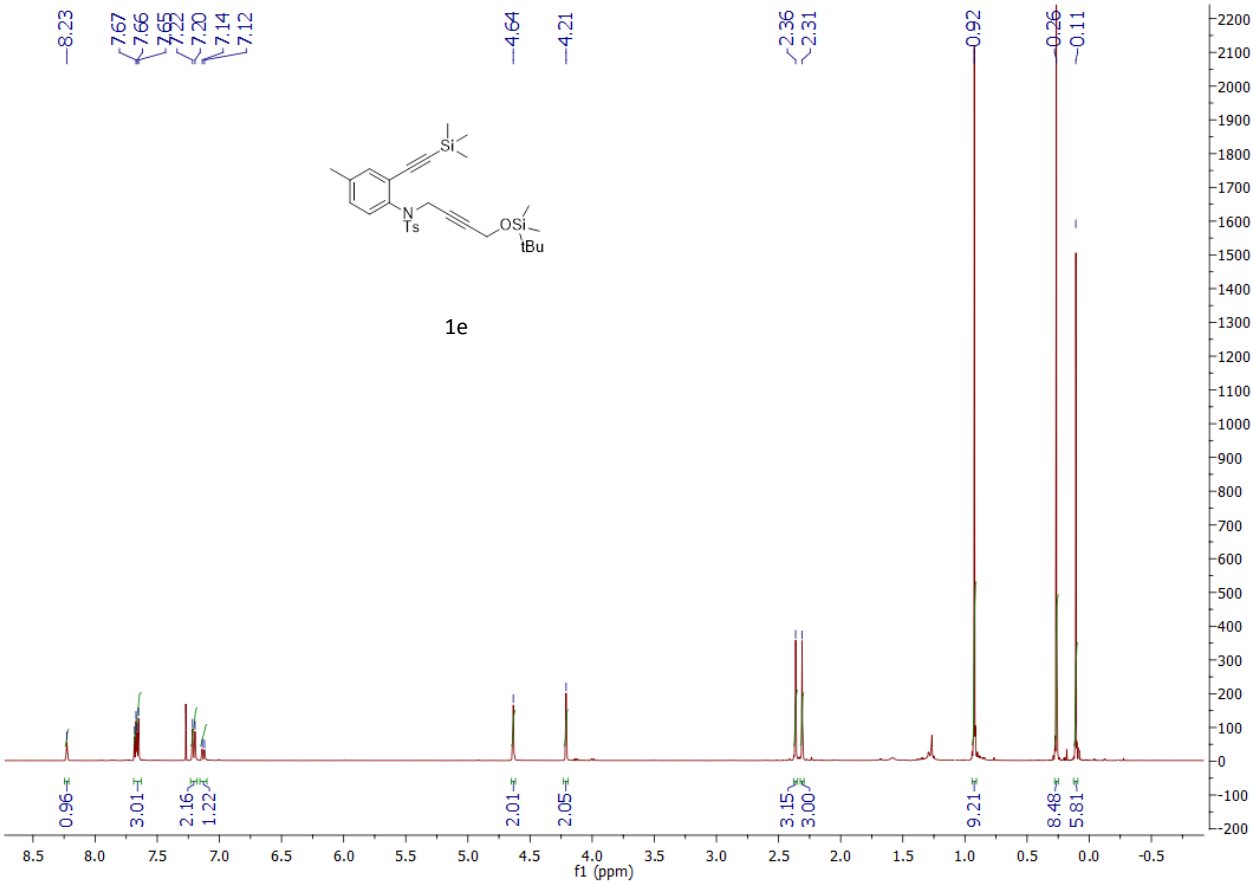
1c


8.70
7.84
7.82
7.71
7.69
7.56
7.54
7.27
7.25
4.75
4.24
2.39
0.94
0.25
0.12
0.93
1.13
2.09
1.26
2.28
1.94
2.00
3.39
8.79
8.05
6.64
f1 (ppm)

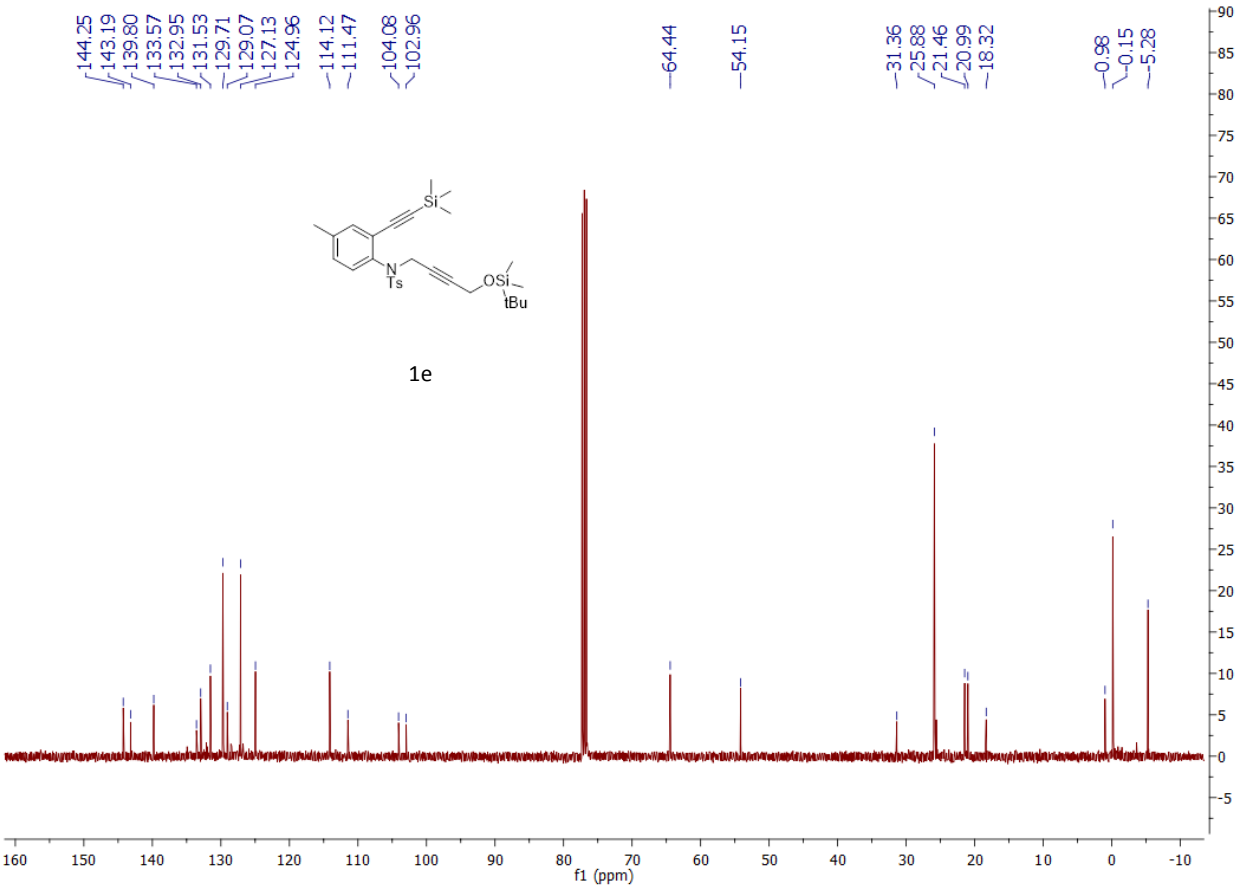
1d


144.92
137.51
133.62
130.08
130.01
129.41
127.61
127.12
113.67
105.09
102.88
64.60
54.40
25.89
21.55
18.34
-0.40
-5.30
f1 (ppm)

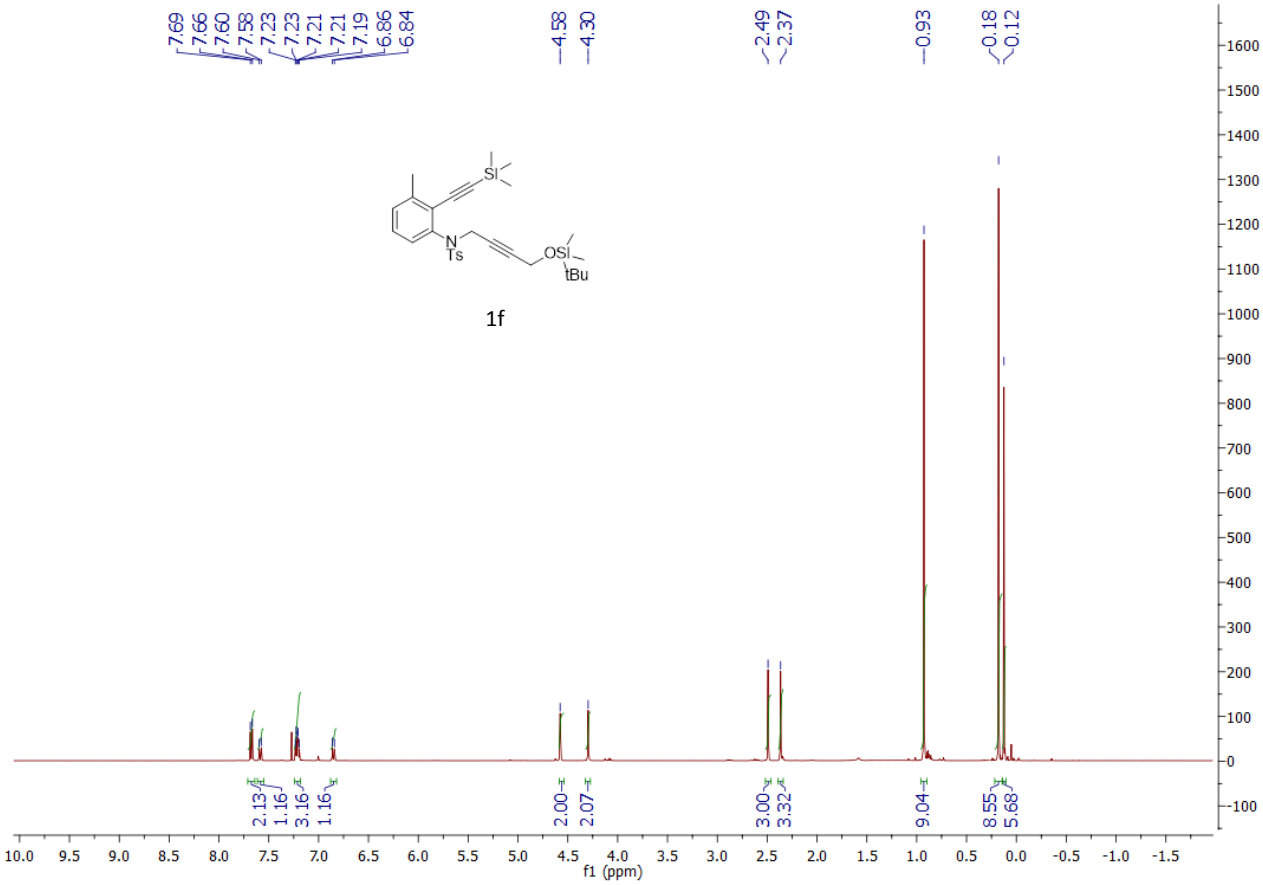
1d


8.23
7.67
7.66
7.65
7.22
7.20
7.14
7.12
4.64
4.21
2.36
2.31
0.92
0.26
0.11
Si
N
Ts
OSi
tBu
0.96
3.01
2.16
1.22
2.01
2.05
3.15
3.00
9.21
8.48
5.81
f1 (ppm)

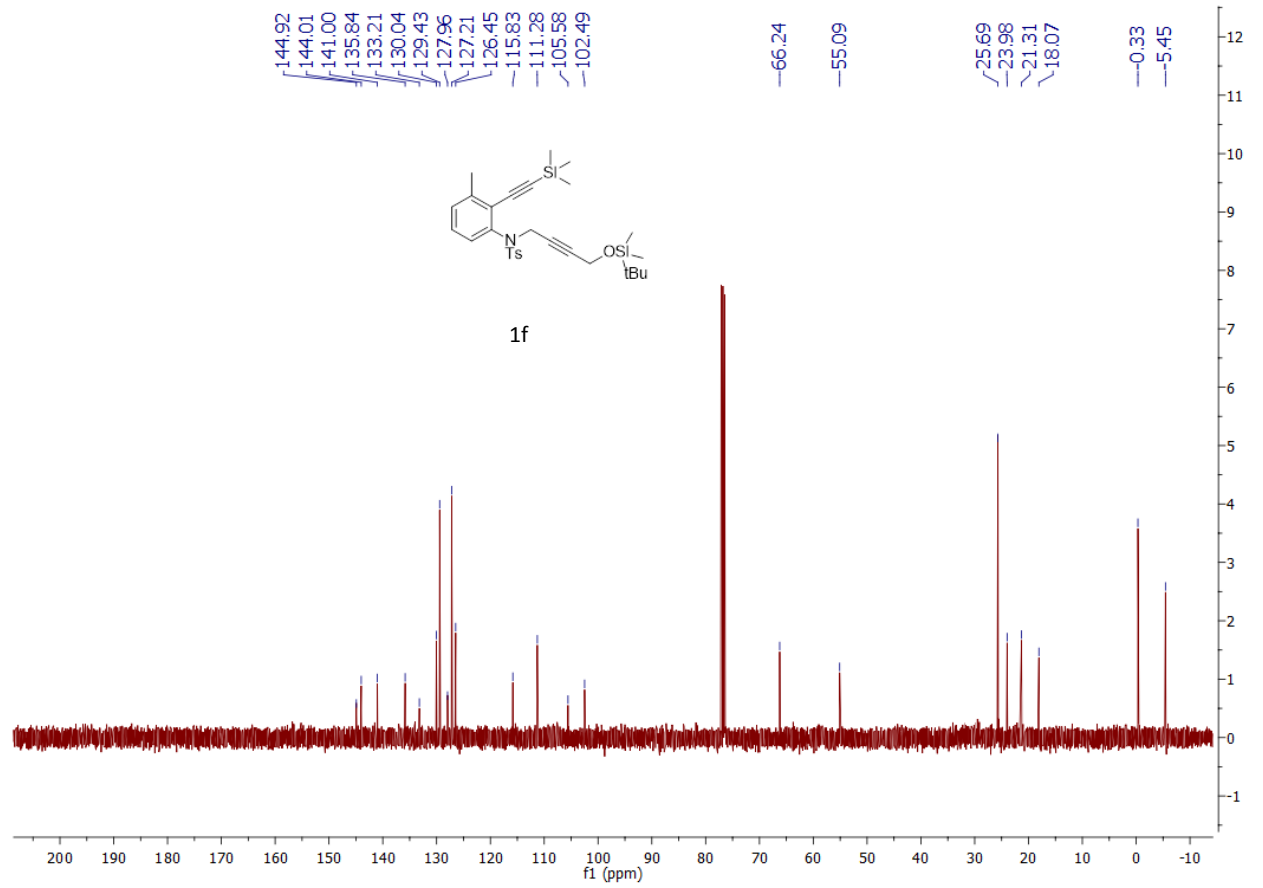
1e


144.25
143.19
139.80
133.57
132.95
131.53
129.71
129.07
127.13
124.96
114.12
111.47
104.08
102.96
64.44
54.15
31.36
25.88
21.46
20.99
18.32
0.98
0.15
-5.28
Si
N
Ts
OSi
tBu
f1 (ppm)

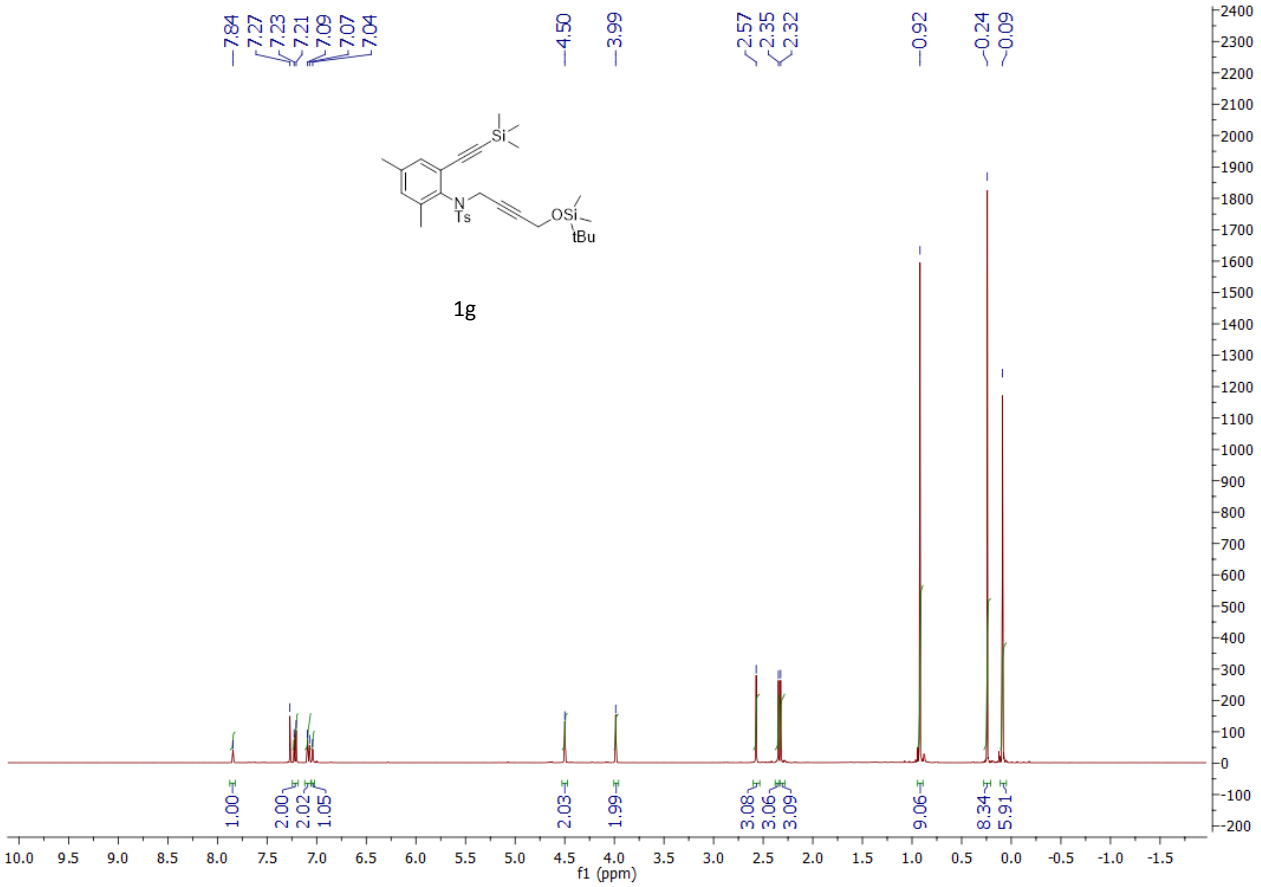
1e


7.69
7.66
7.60
7.58
7.23
7.23
7.21
7.21
7.19
6.86
6.84
4.58
4.30
2.49
2.37
0.93
0.18
0.12
Si
N
Ts
OSi
tBu
2.13
1.16
3.16
1.16
2.00
2.07
3.00
3.32
9.04
8.55
5.68
f1 (ppm)

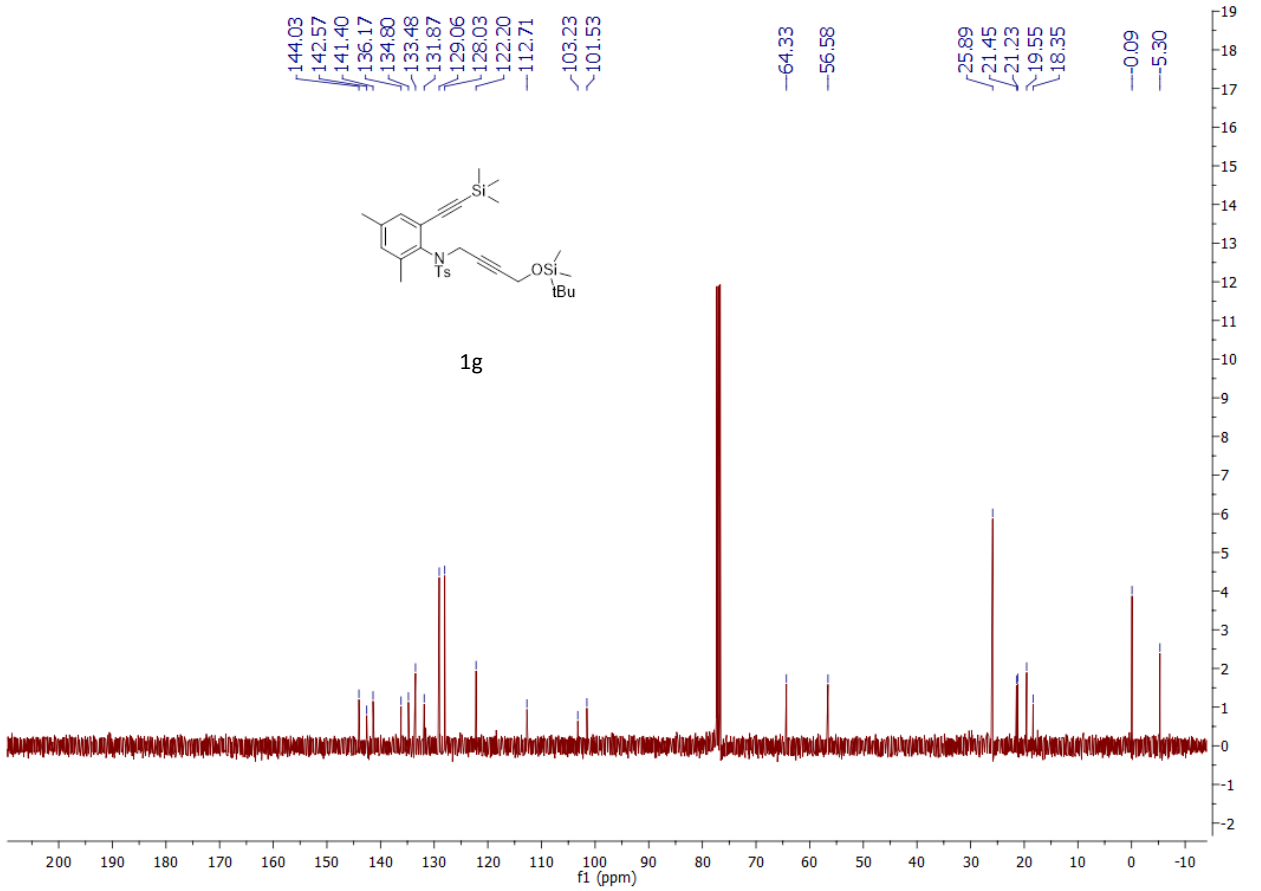
1f


144.92
144.01
141.00
135.84
133.21
130.04
129.43
127.96
127.21
126.45
115.83
111.28
105.58
102.49
66.24
55.09
25.69
23.98
21.31
18.07
0.33
5.45
Si
N
Ts
OSi
tBu
f1 (ppm)

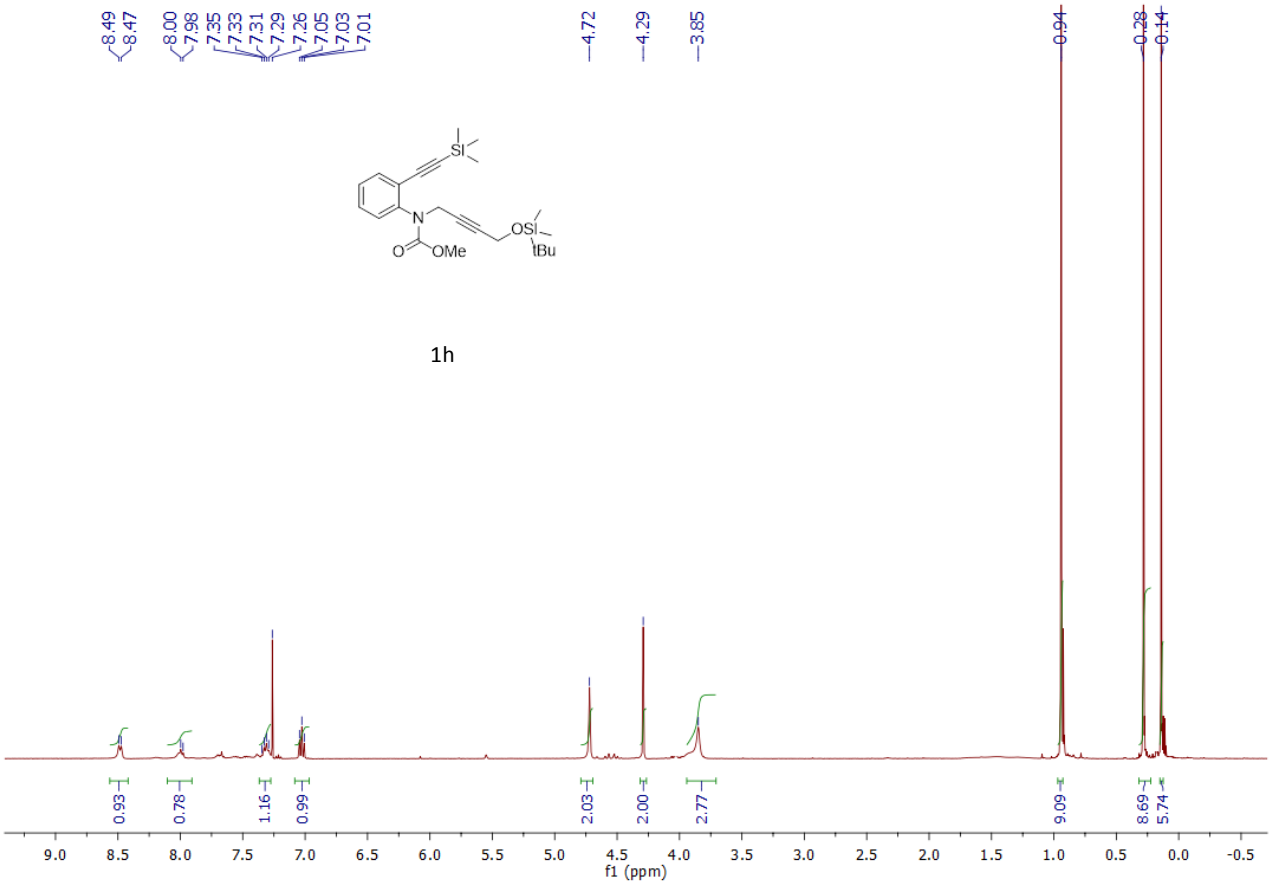
1f


7.84
7.27
7.23
7.21
7.09
7.07
7.04
4.50
3.99
2.57
2.35
2.32
0.92
0.24
0.09
Si
N
Ts
OSi
tBu
1.00
2.00
2.02
1.05
2.03
1.99
3.08
3.06
3.09
9.06
8.34
5.91
f1 (ppm)

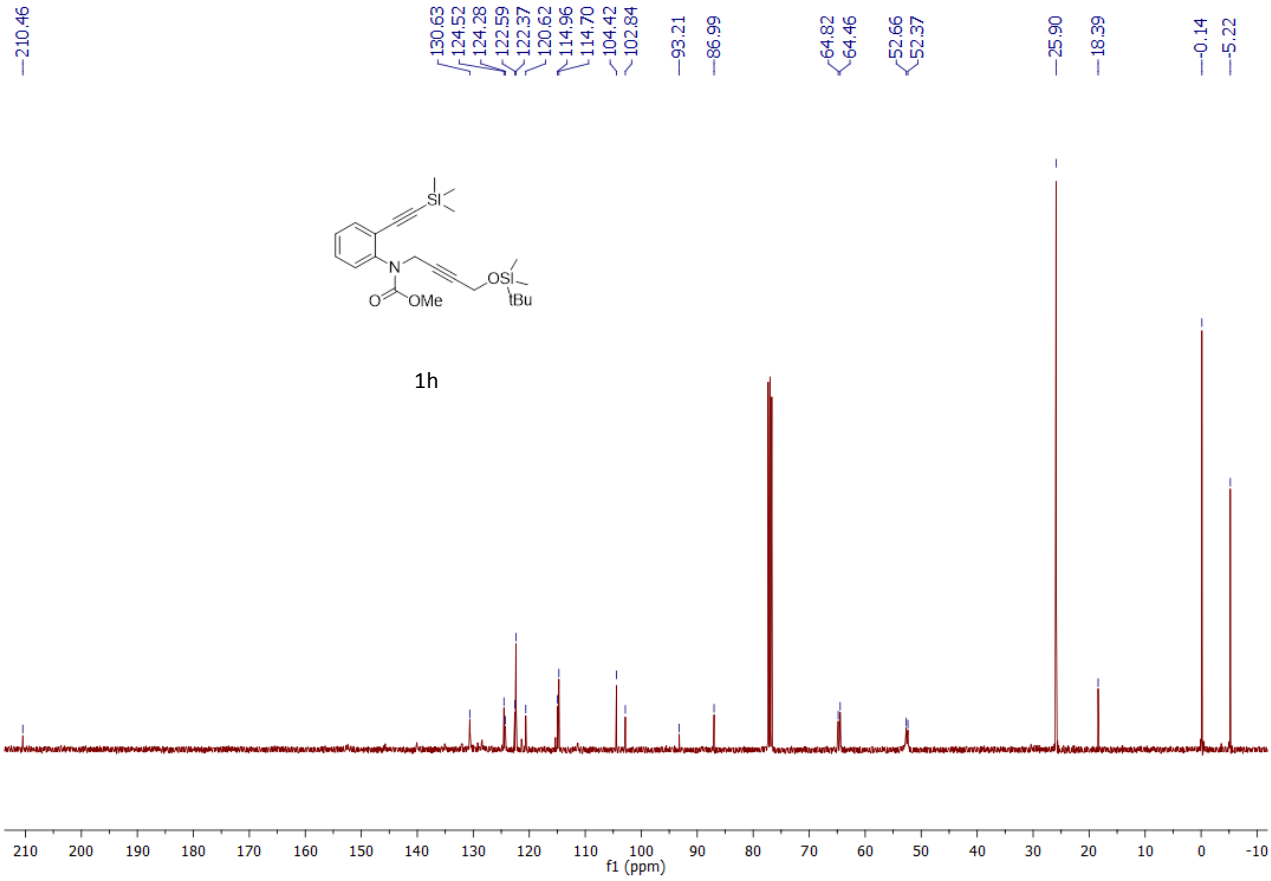
1g


144.03
142.57
141.40
136.17
134.80
133.48
131.87
129.06
128.03
122.20
112.71
103.23
101.53
64.33
56.58
25.89
21.45
21.23
19.55
18.35
0.09
5.30
Si
N
Ts
OSi
tBu
f1 (ppm)

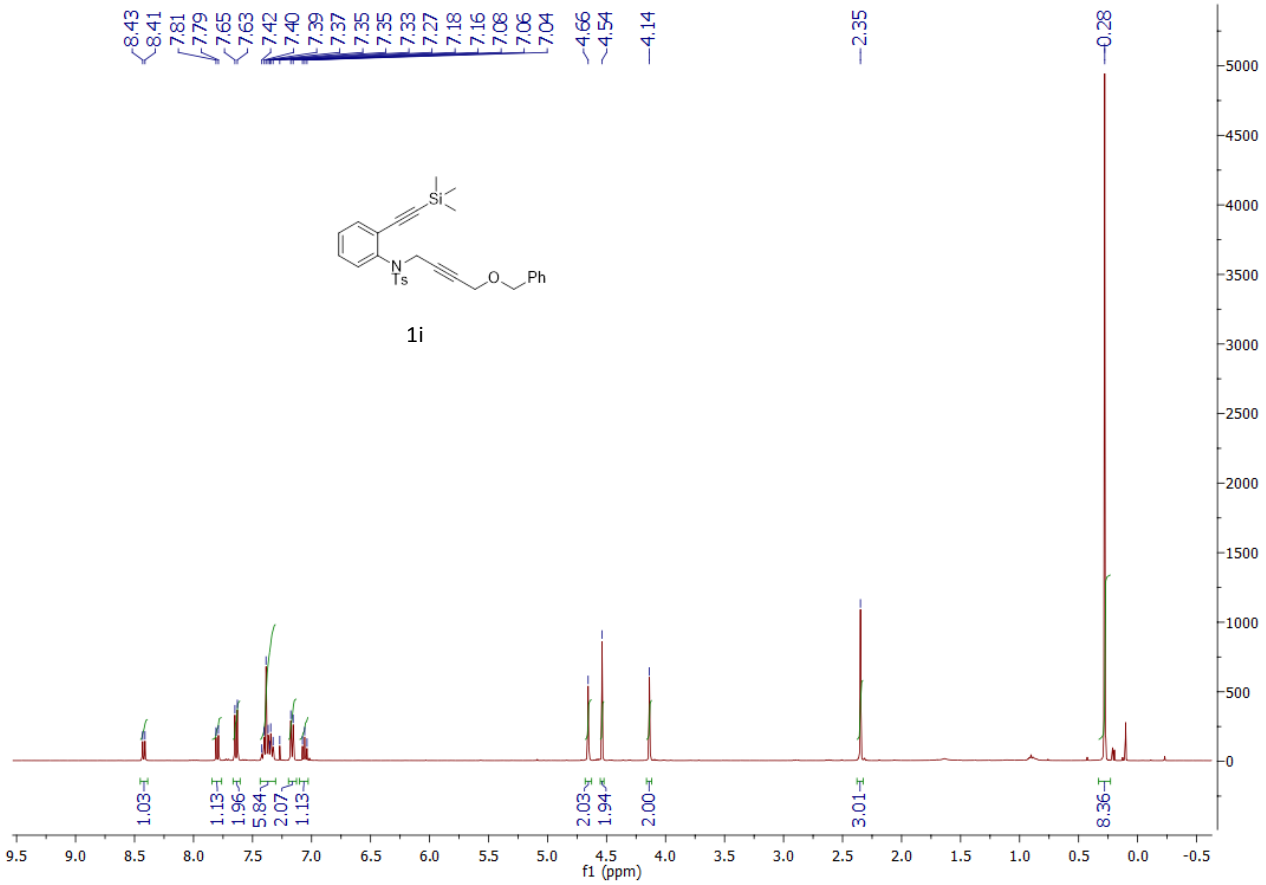
1g


8.49
8.47
8.00
7.98
7.35
7.33
7.31
7.29
7.26
7.05
7.03
7.01
4.72
4.29
3.85
0.94
0.28
0.14
Si
N
O
OMe
OSi
tBu
0.93
0.78
1.16
0.99
2.03
2.00
2.77
9.09
8.69
5.74
f1 (ppm)

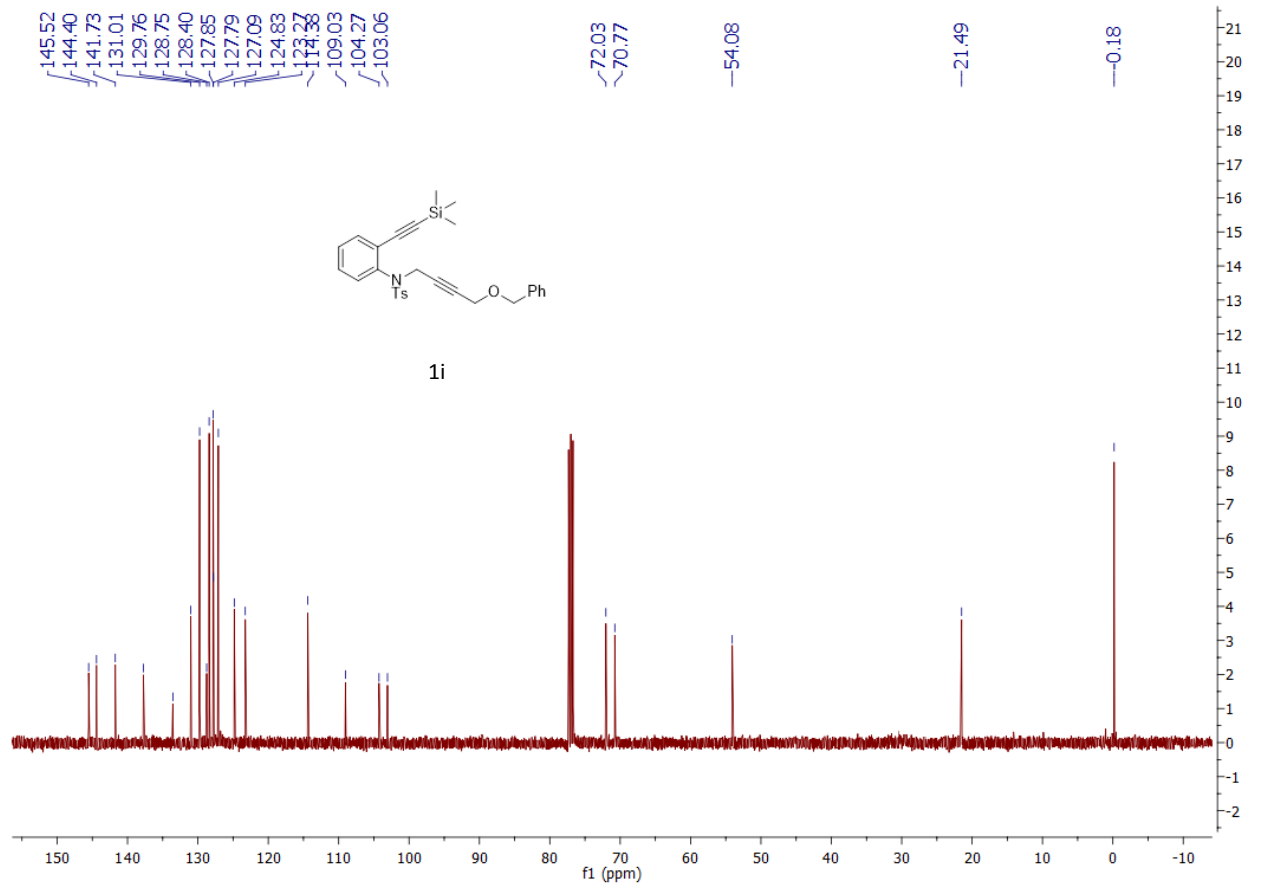
1h


210.46
130.63
124.52
124.28
122.59
122.37
120.62
114.96
114.70
104.42
102.84
93.21
86.99
64.82
64.46
52.66
52.37
25.90
18.39
0.14
5.22
Si
N
O
OMe
OSi
tBu
f1 (ppm)

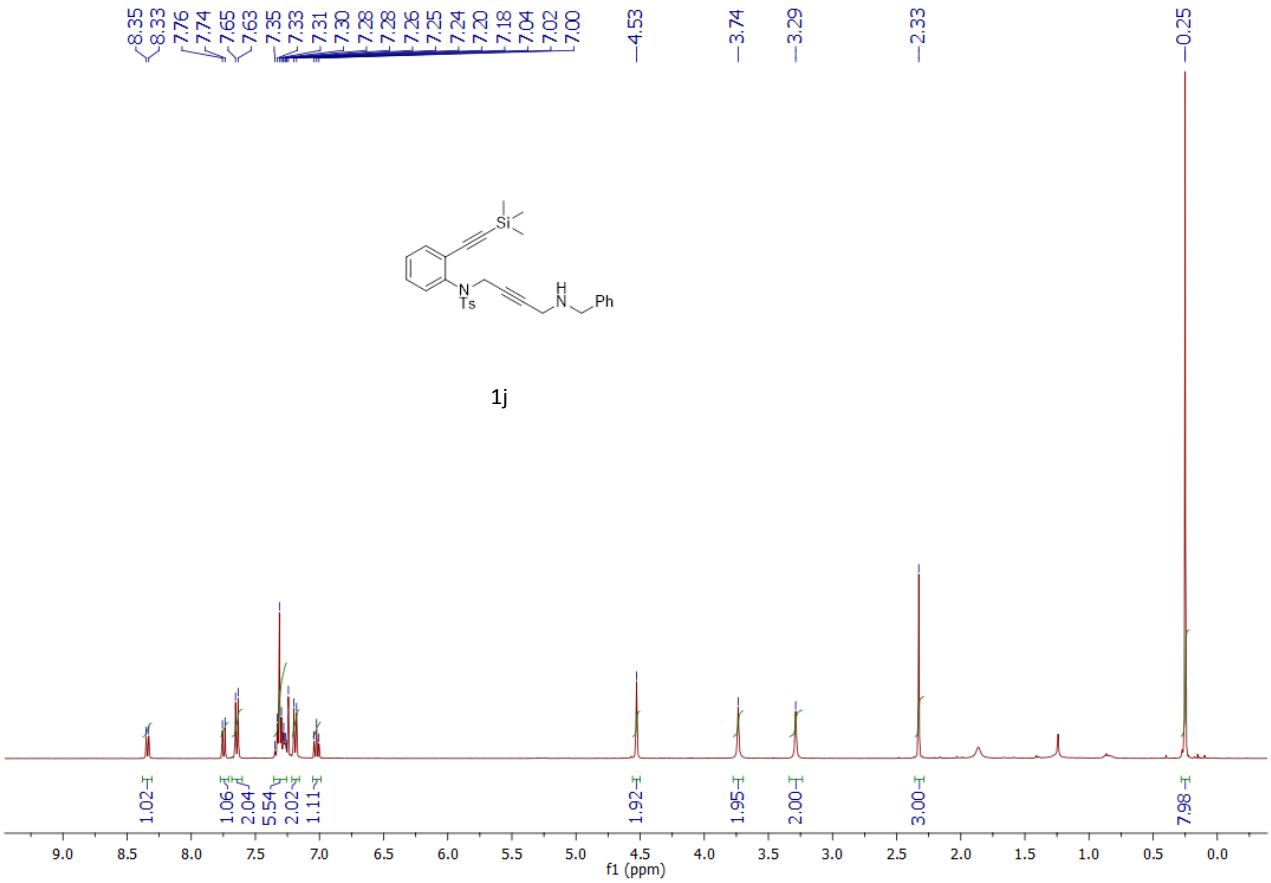
1h


8.43
8.41
7.81
7.79
7.65
7.63
7.42
7.40
7.39
7.37
7.35
7.35
7.33
7.27
7.18
7.16
7.08
7.06
7.04
4.66
4.54
4.14
2.35
0.28
Si
N
Ts
O
Ph
1.03
1.13
1.96
5.84
2.07
1.13
2.03
1.94
2.00
3.01
8.36
f1 (ppm)

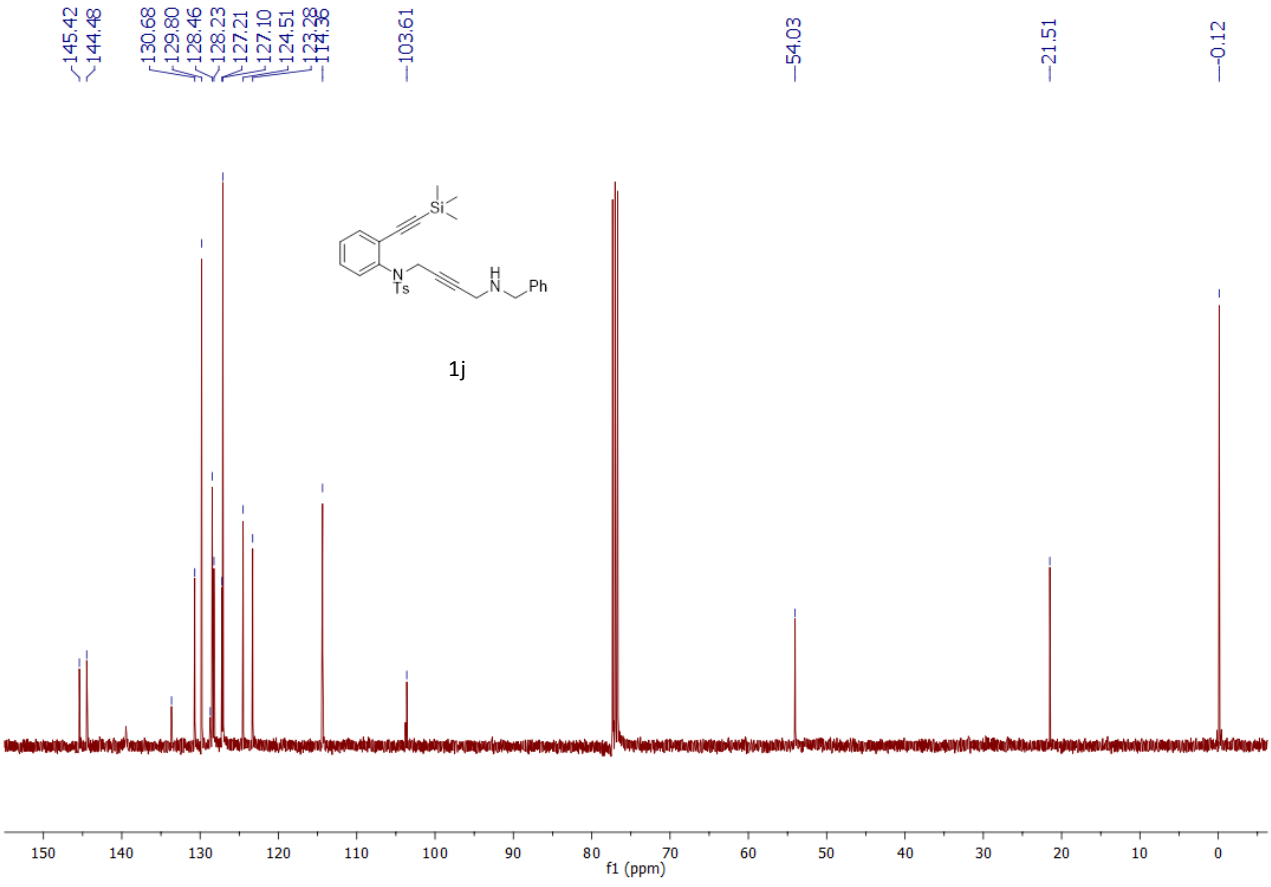
1i


145.52
144.40
141.73
131.01
129.76
128.75
128.40
127.85
127.79
127.09
124.83
109.03
104.27
103.06
72.03
70.77
54.08
21.49
0.18
Si
N
Ts
O
Ph
f1 (ppm)

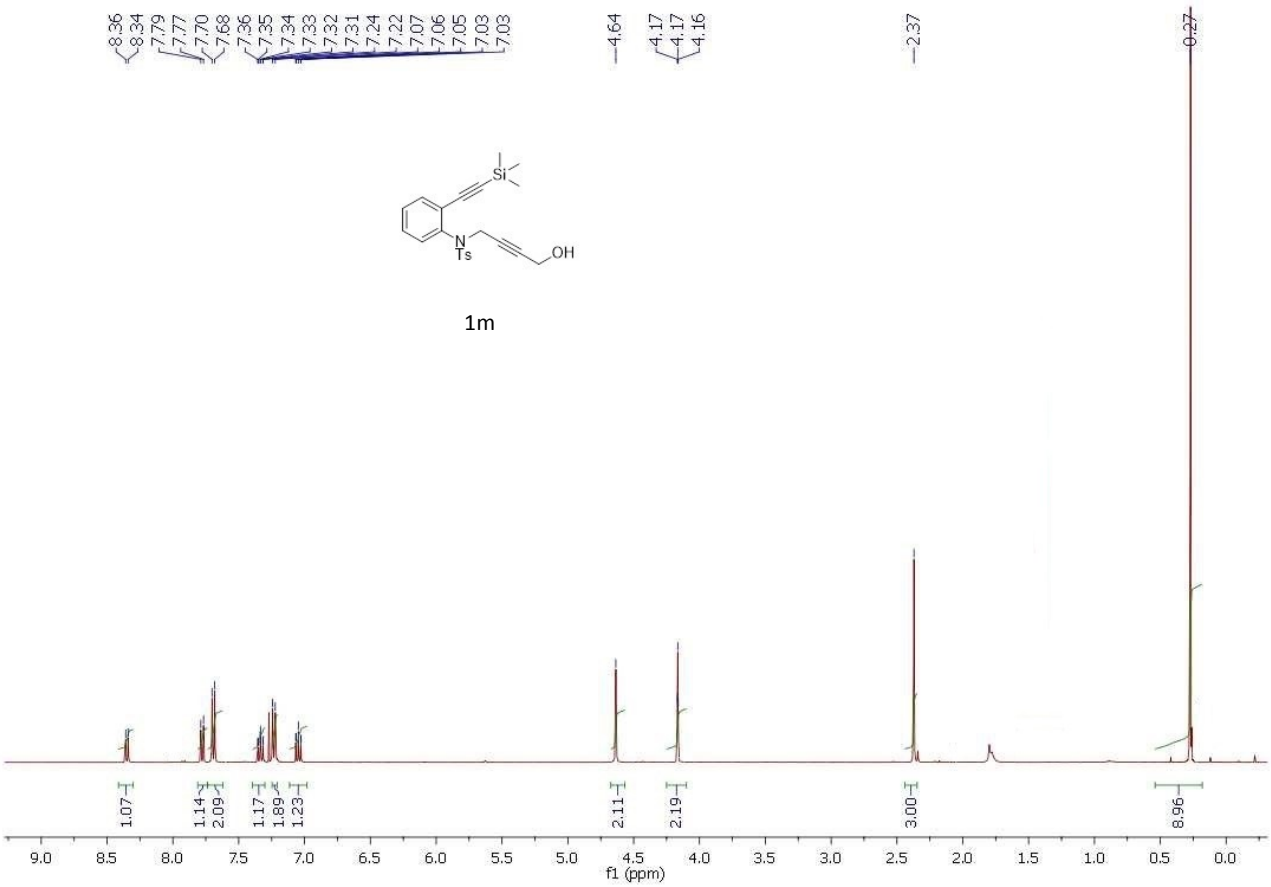
1i


8.35
8.33
7.76
7.74
7.65
7.63
7.35
7.33
7.31
7.30
7.28
7.28
7.26
7.25
7.24
7.20
7.18
7.04
7.02
7.00
4.53
3.74
3.29
2.33
0.25
Si
N
Ts
H
N
Ph
1.02
1.06
2.04
5.54
2.02
1.11
1.92
1.95
2.00
3.00
7.98
f1 (ppm)

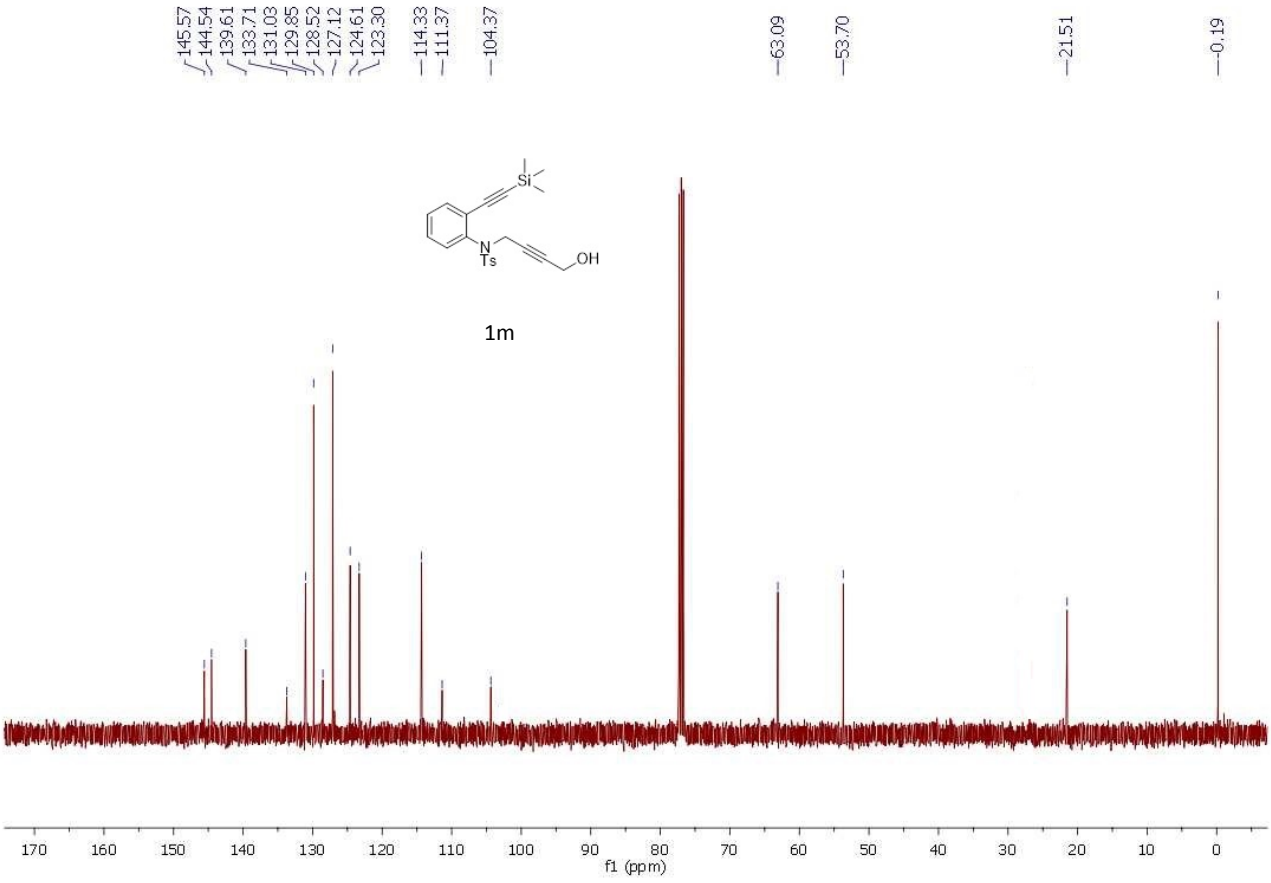
1j


145.42
144.48
130.68
129.80
128.46
128.23
127.21
127.10
124.51
103.61
54.03
21.51
0.12
Si
N
Ts
H
N
Ph
f1 (ppm)

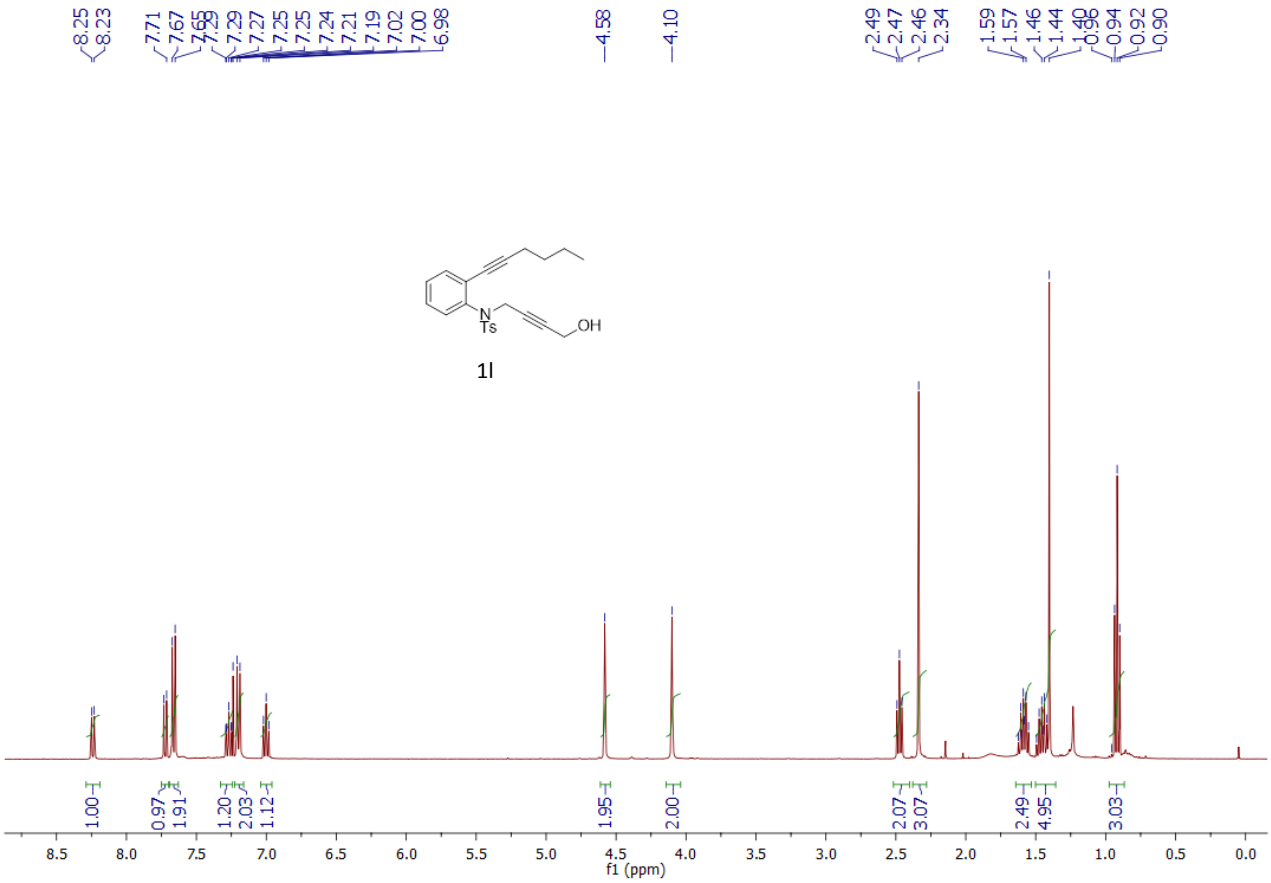
1j


8.36
8.34
7.79
7.77
7.70
7.68
7.36
7.35
7.34
7.33
7.32
7.31
7.24
7.22
7.07
7.06
7.05
7.03
7.03
4.64
4.17
4.17
4.16
2.37
0.27
Si
N
Ts
OH
1.07
1.14
2.09
1.17
1.89
1.23
2.11
2.19
3.00
8.96
f1 (ppm)

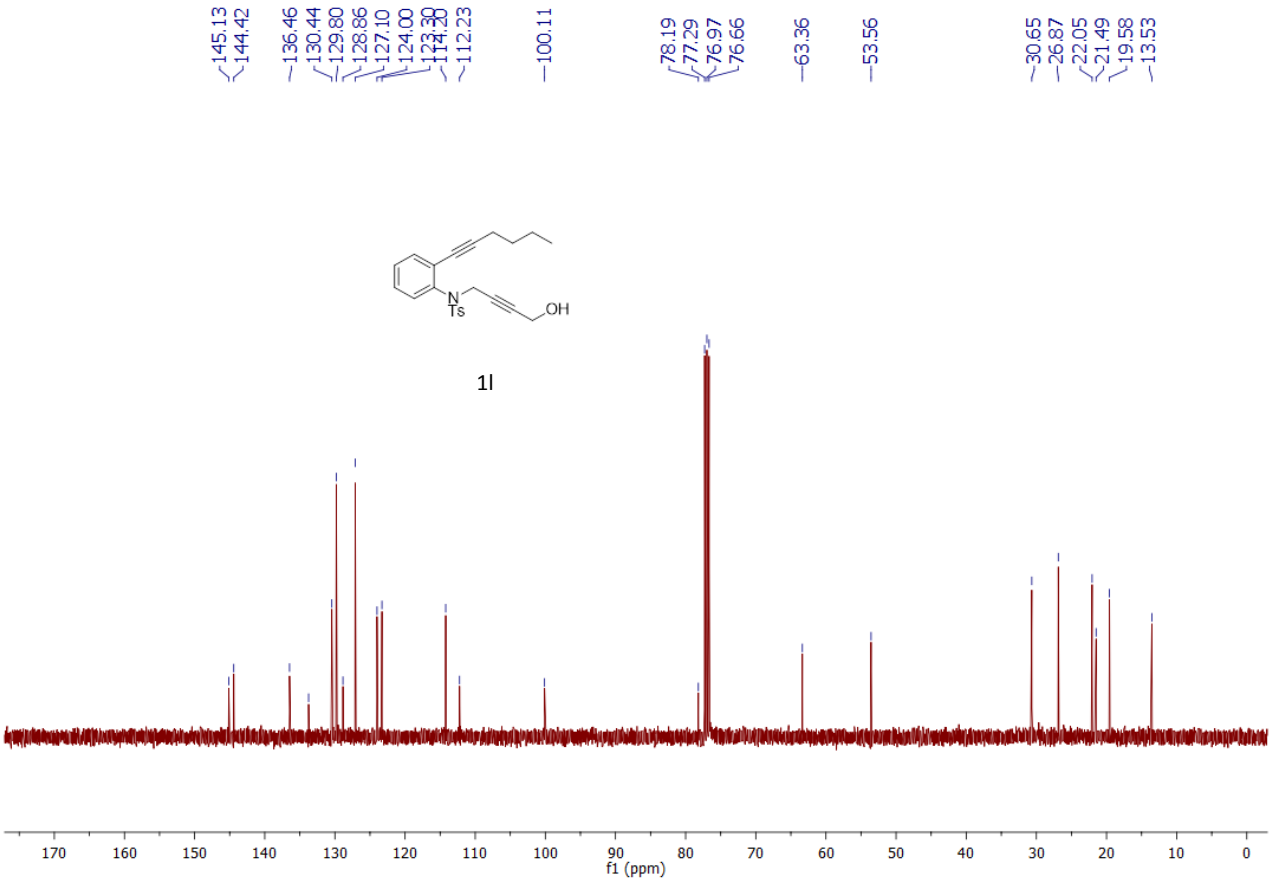
1m


145.57
144.54
139.61
133.71
131.03
129.85
128.52
127.12
124.61
123.30
114.33
111.37
104.37
63.09
53.70
21.51
0.19
Si
N
Ts
OH
f1 (ppm)

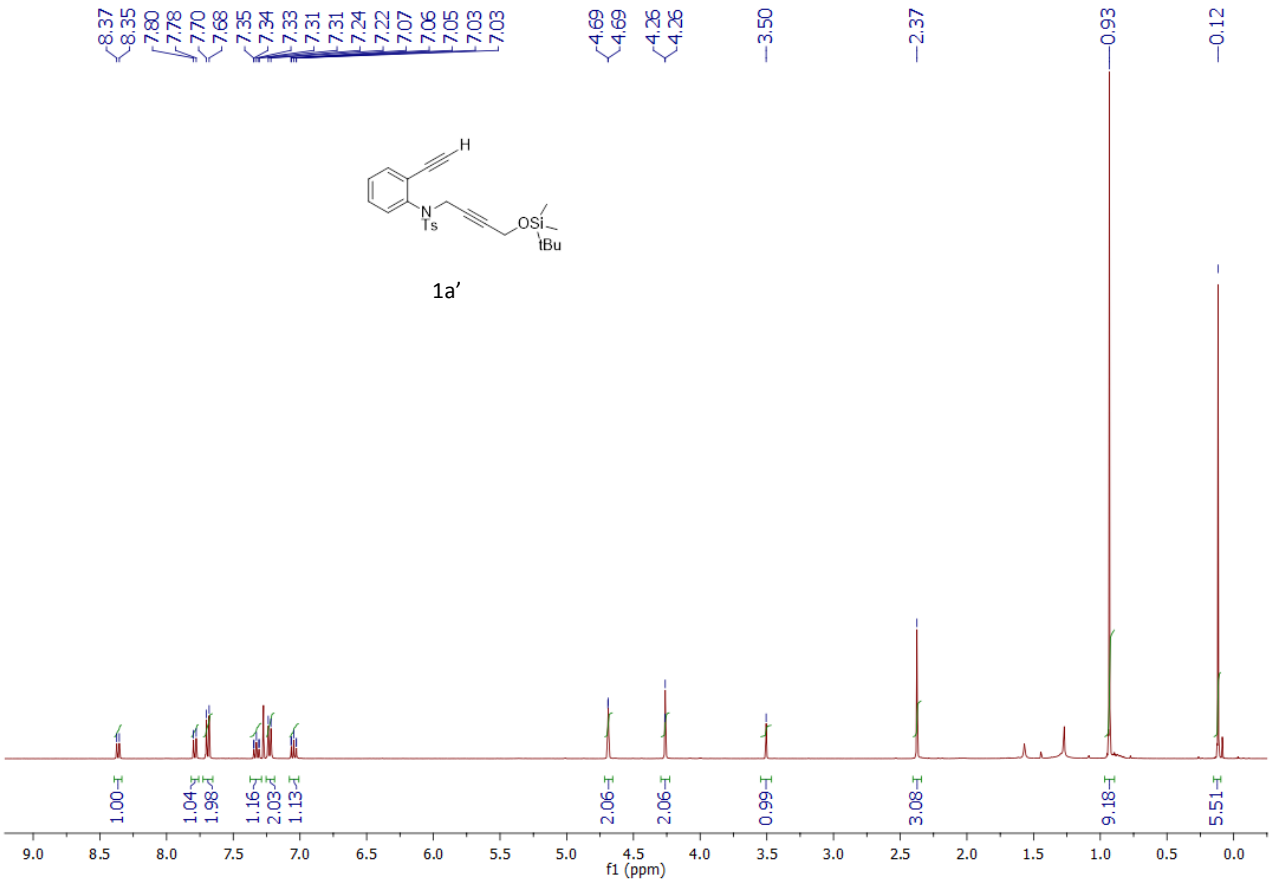
1m


8.25
8.23
7.71
7.67
7.65
7.29
7.27
7.25
7.25
7.24
7.21
7.19
7.02
7.00
6.98
4.58
4.10
2.49
2.47
2.46
2.34
1.59
1.57
1.46
1.44
1.40
0.96
0.94
0.92
0.90
N
Ts
OH
1.00
0.97
1.91
1.20
2.03
1.12
1.95
2.00
2.07
3.07
2.49
4.95
3.03
f1 (ppm)

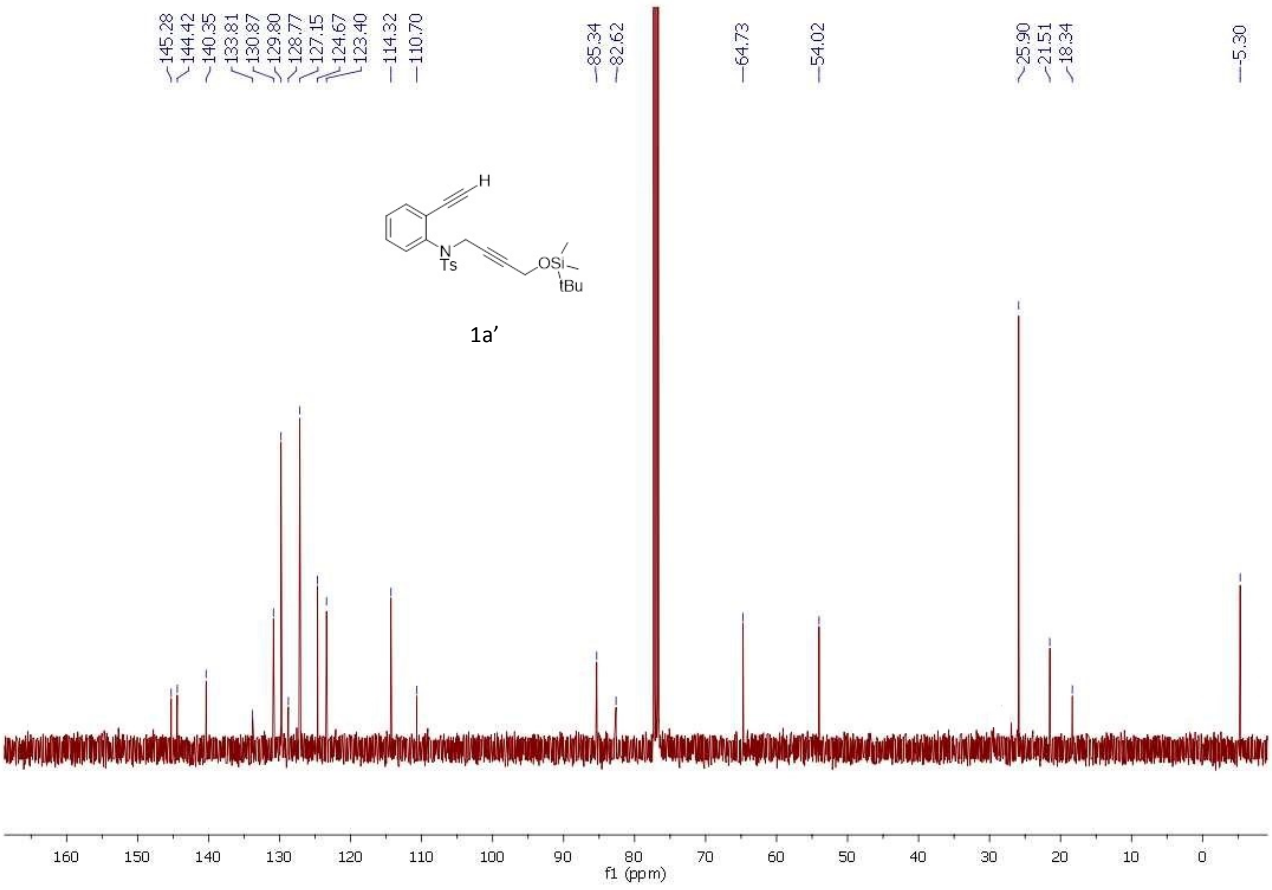
1l


145.13
144.42
136.46
130.44
129.80
128.86
127.10
124.00
112.23
100.11
78.19
77.29
76.97
76.66
63.36
53.56
30.65
26.87
22.05
21.49
19.58
13.53
N
Ts
OH
f1 (ppm)

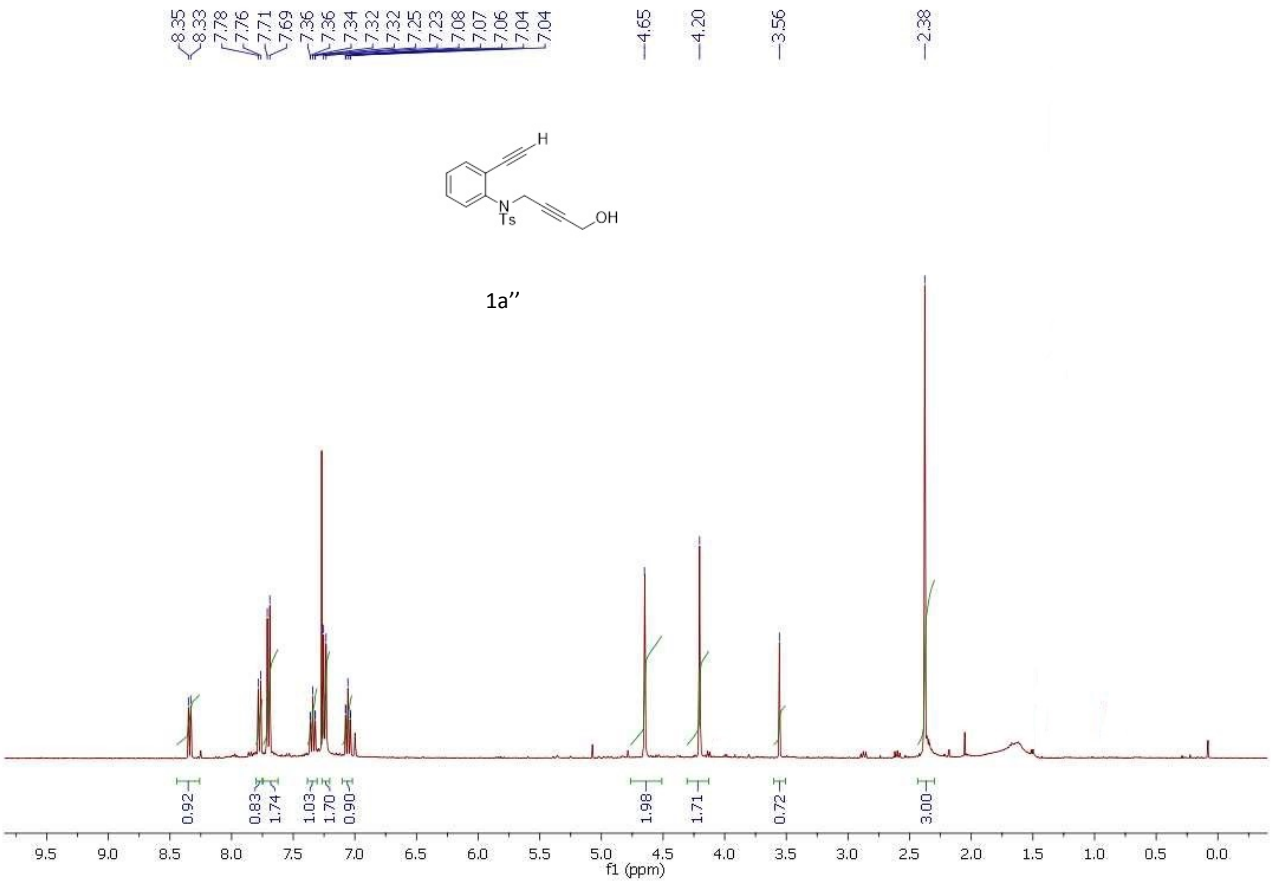
1l


8.37
8.35
7.80
7.78
7.70
7.68
7.35
7.34
7.33
7.31
7.31
7.24
7.22
7.07
7.06
7.05
7.03
7.03
4.69
4.69
4.26
4.26
3.50
2.37
0.93
0.12
H
N
Ts
OSi
tBu
1.00
1.04
1.98
1.16
2.03
1.13
2.06
2.06
0.99
3.08
9.18
5.51
f1 (ppm)

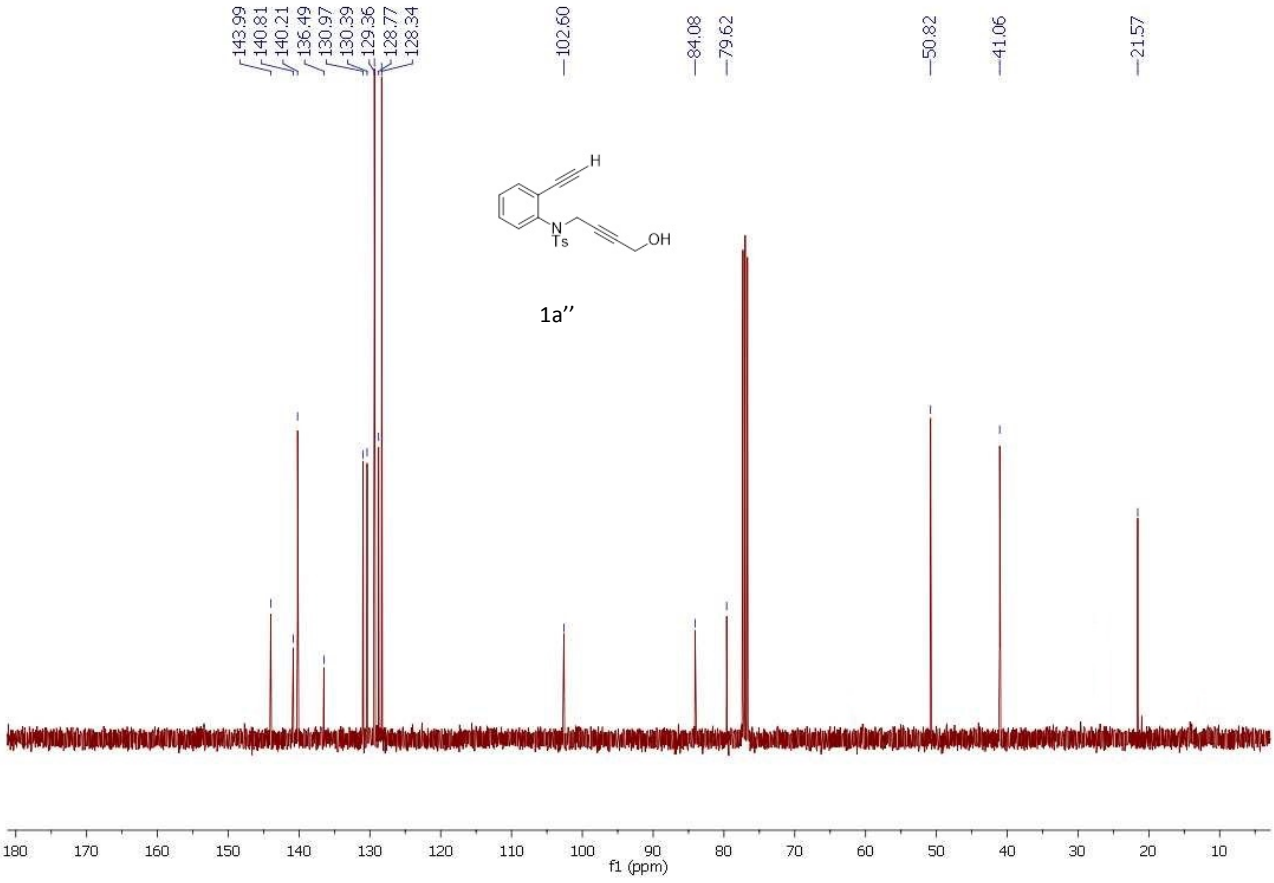
1a'


145.28
144.42
140.35
133.81
130.87
129.80
128.77
127.15
124.67
123.40
114.32
110.70
85.34
82.62
64.73
54.02
25.90
21.51
18.34
5.30
H
N
Ts
OSi
tBu
f1 (ppm)

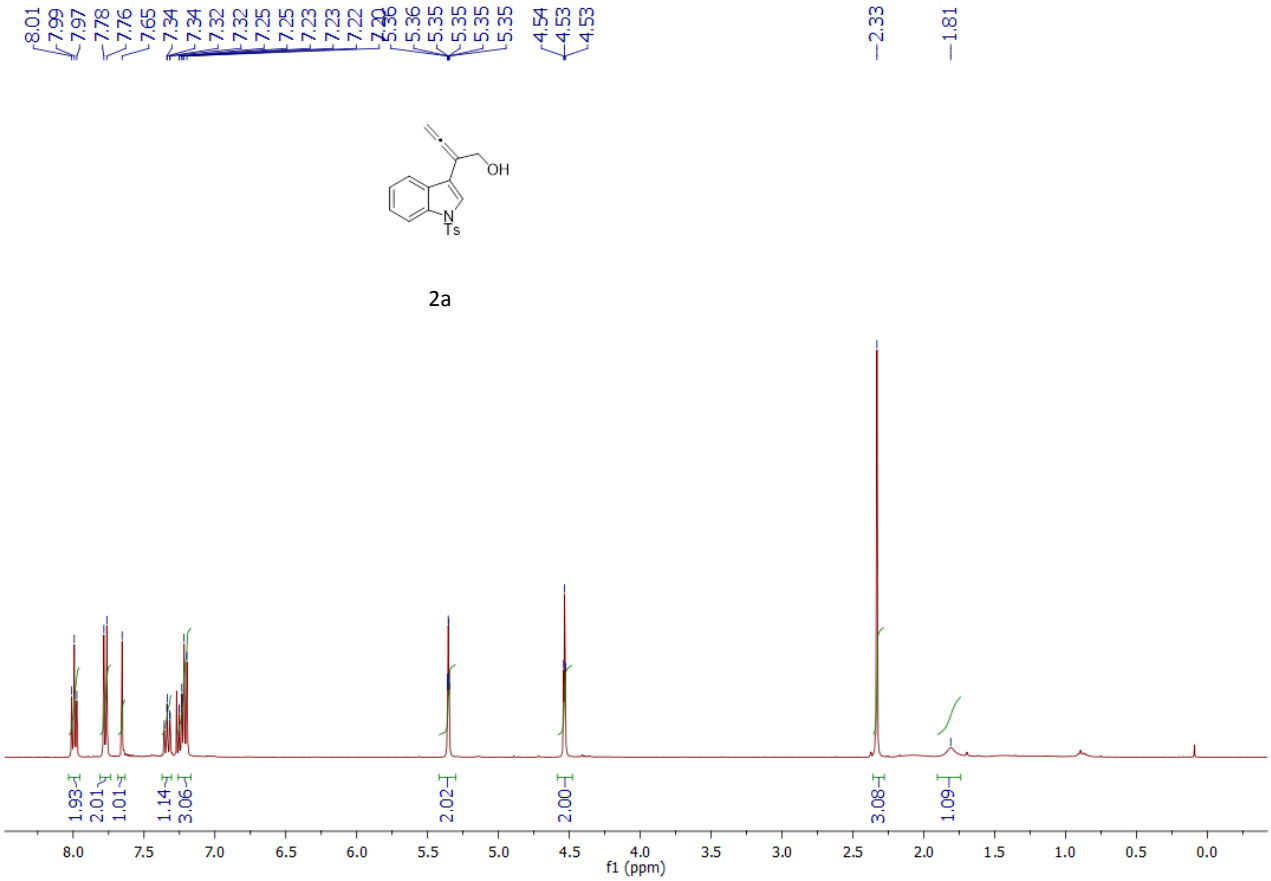
1a'


8.35
8.33
7.78
7.76
7.71
7.69
7.36
7.36
7.34
7.32
7.32
7.25
7.23
7.08
7.07
7.06
7.04
7.04
4.65
4.20
3.56
2.38
H
N
Ts
OH
0.92
0.83
1.74
1.03
1.70
0.90
1.98
1.71
0.72
3.00
f1 (ppm)

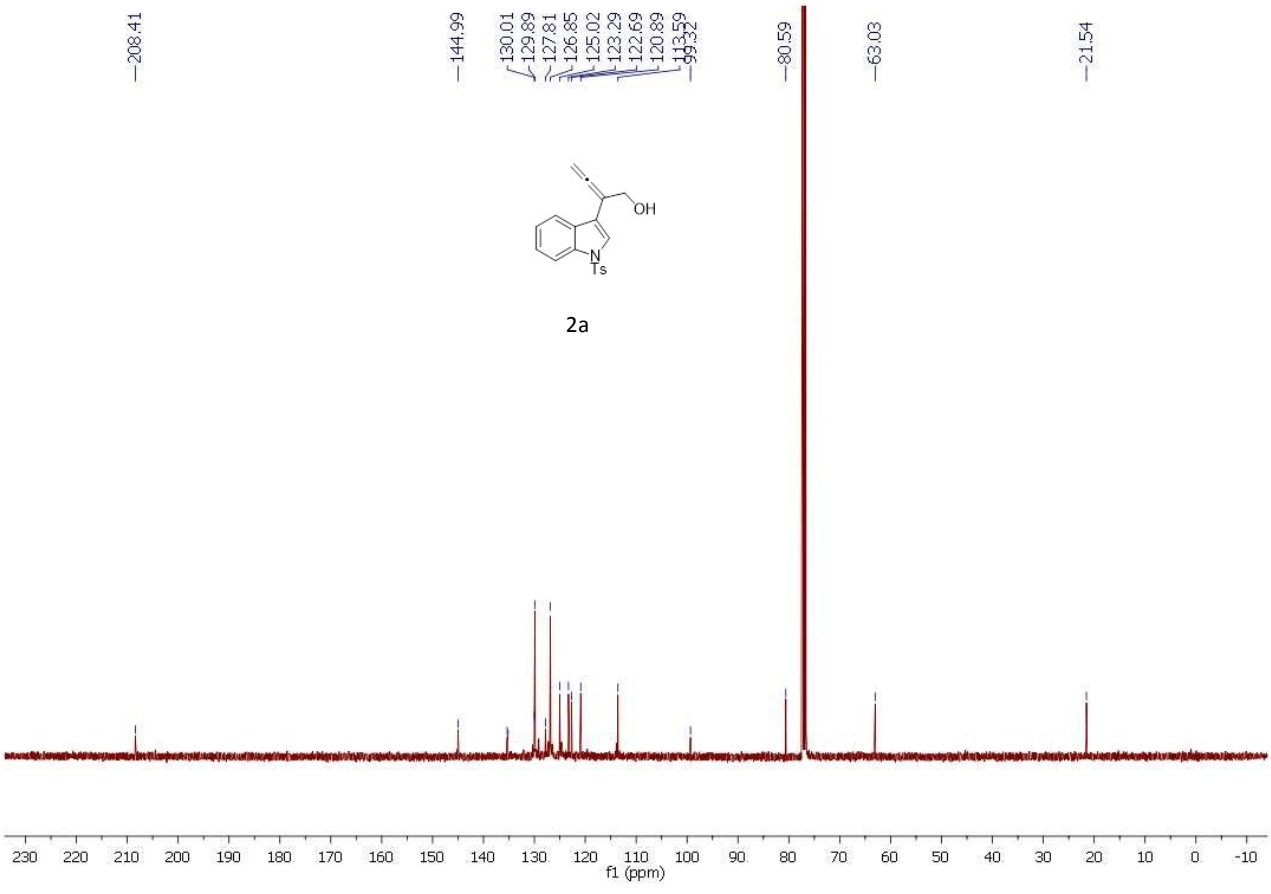
1a''


143.99
140.81
140.21
136.49
130.97
130.39
129.36
128.77
128.34
102.60
84.08
79.62
50.82
41.06
21.57
H
N
Ts
OH
f1 (ppm)

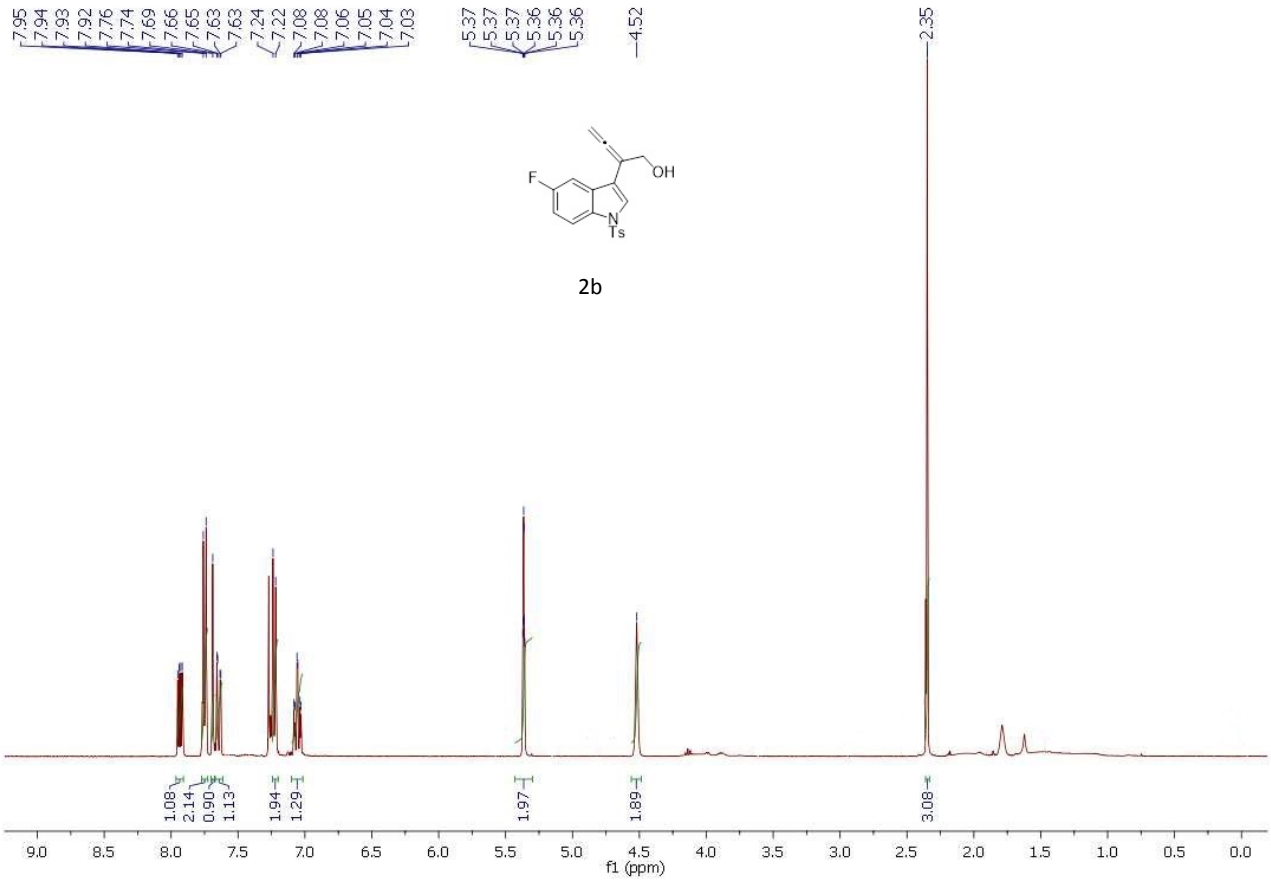
1a''


8.01
7.99
7.97
7.78
7.76
7.65
7.34
7.34
7.32
7.32
7.25
7.25
7.23
7.23
7.22
7.20
5.36
5.36
5.35
5.35
5.35
5.35
4.54
4.53
4.53
2.33
1.81
OH
N
Ts
1.93
2.01
1.01
1.14
3.06
2.02
2.00
3.08
1.09
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

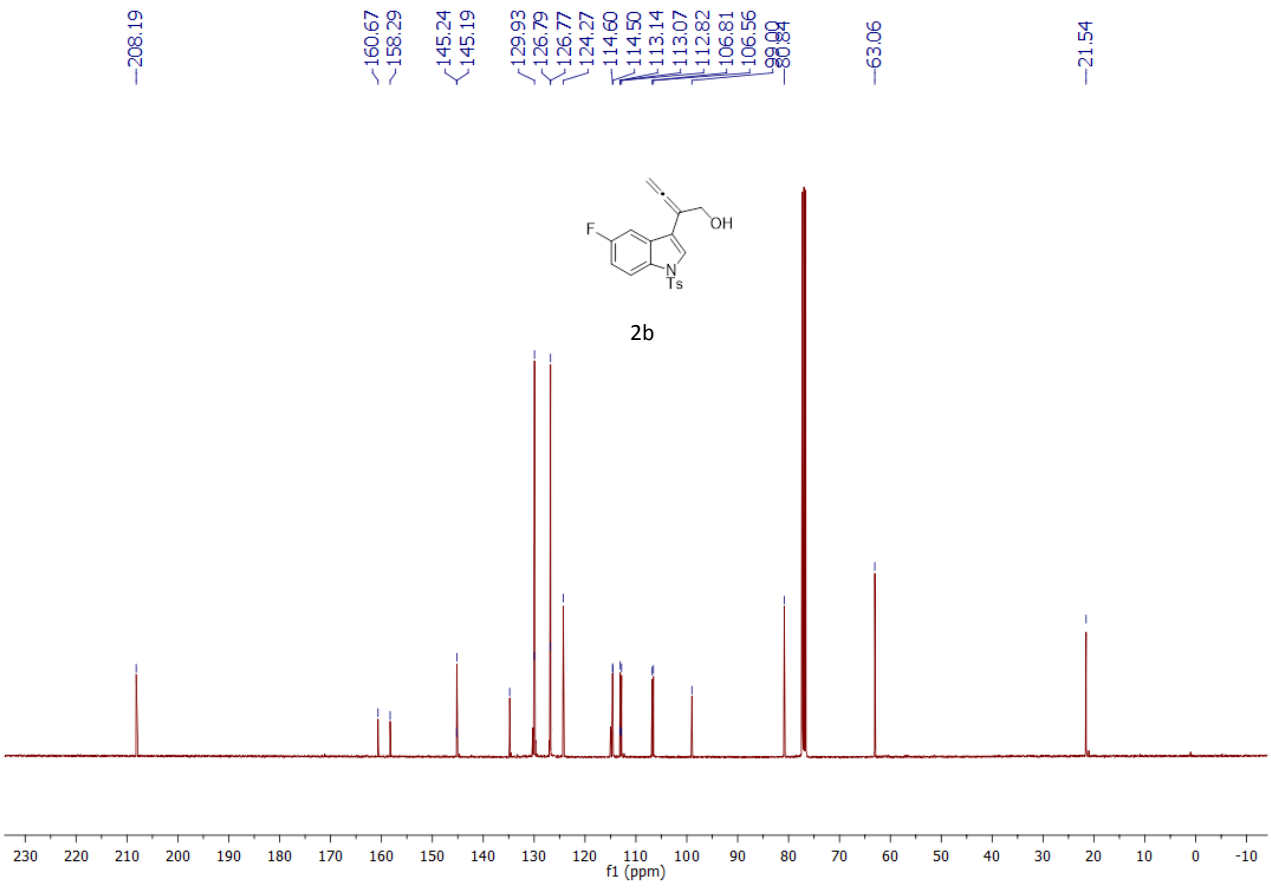
2a


208.41
144.99
130.01
129.89
127.81
126.85
125.02
123.29
122.69
120.89
113.59
99.32
80.59
63.03
21.54
OH
N
Ts
230
220
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)

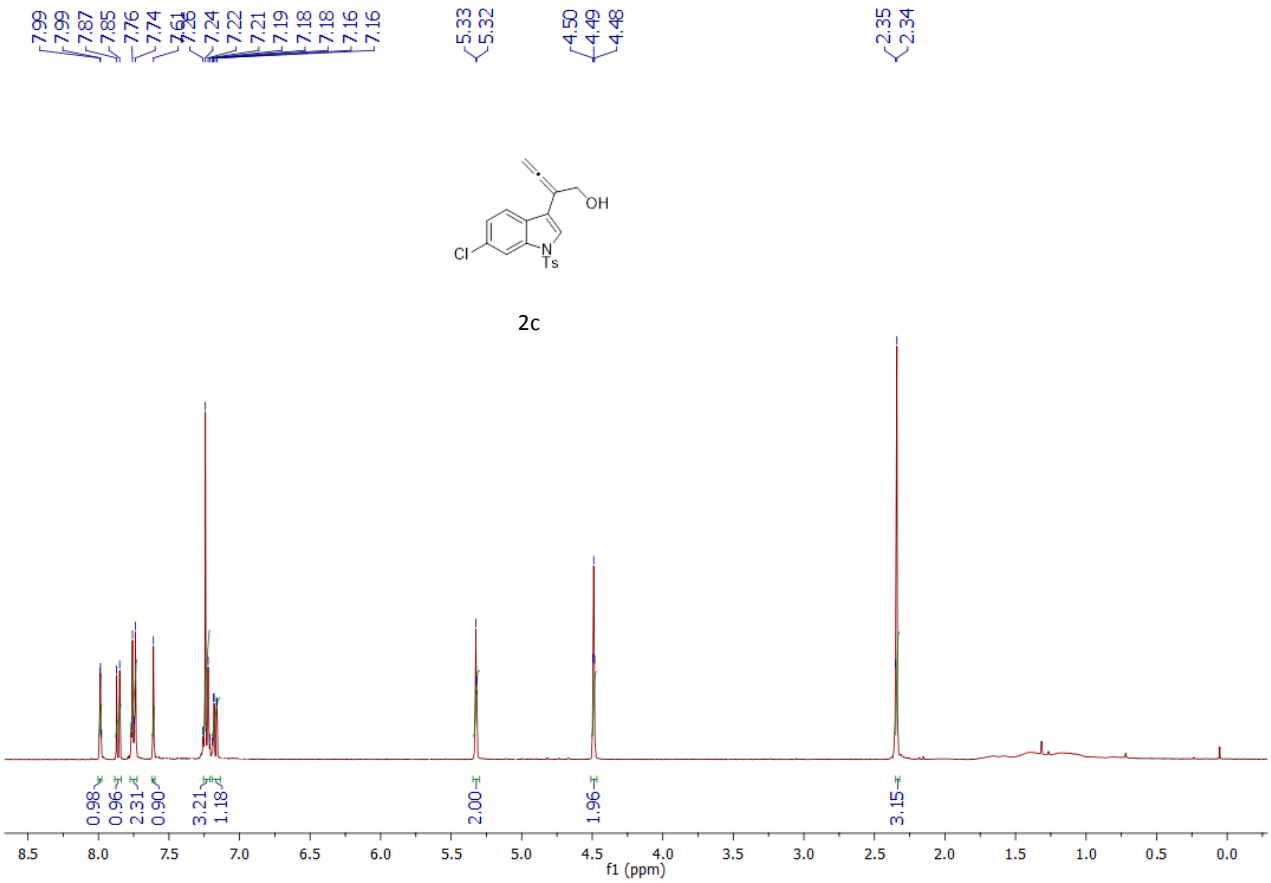
2a


7.95
7.94
7.93
7.92
7.76
7.74
7.69
7.66
7.65
7.63
7.63
7.24
7.22
7.08
7.08
7.06
7.05
7.04
7.03
5.37
5.37
5.37
5.36
5.36
5.36
4.52
2.35
F
OH
N
Ts
1.08
2.14
0.90
1.13
1.94
1.29
1.97
1.89
3.08
f1 (ppm)

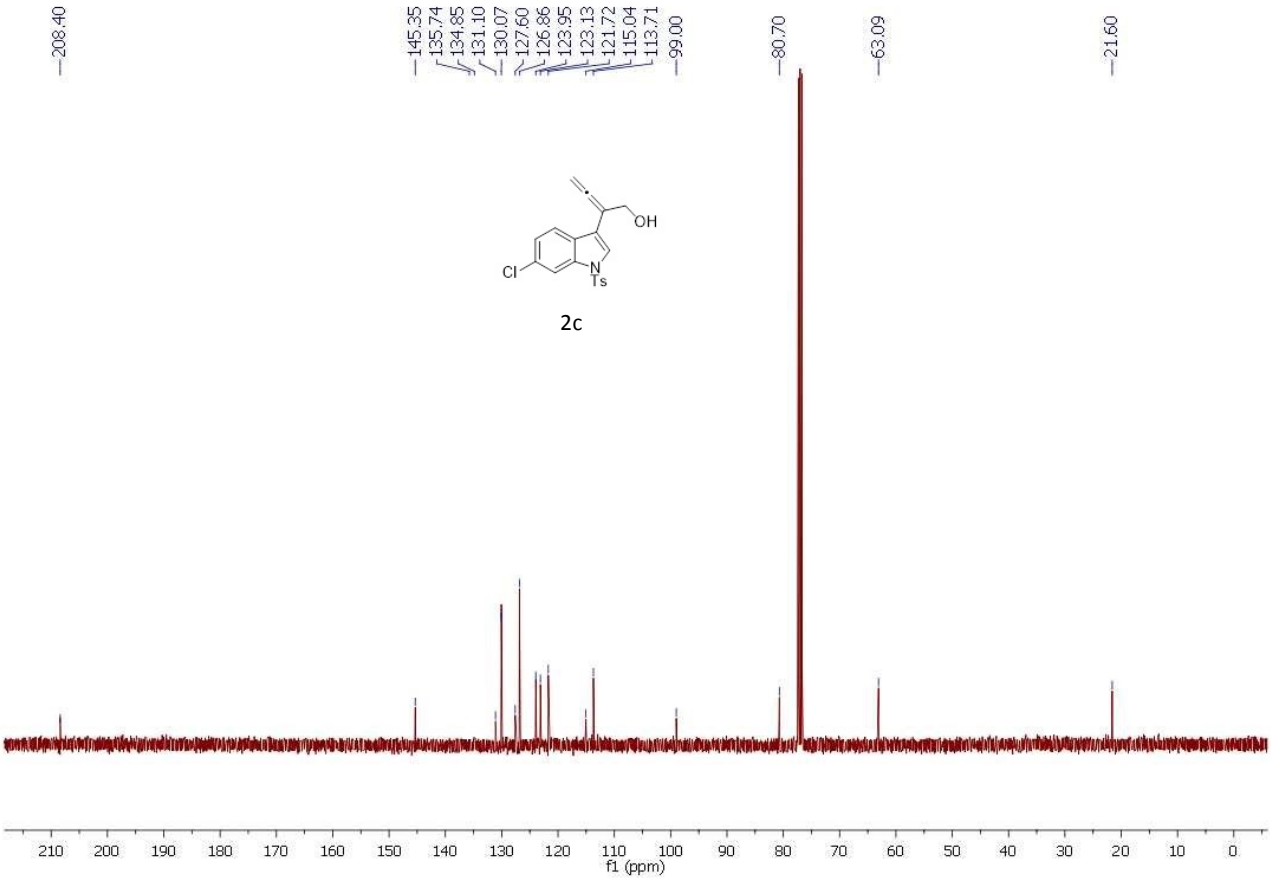
2b


208.19
160.67
158.29
145.24
145.19
129.93
126.79
126.77
124.27
114.60
114.50
113.14
113.07
112.82
106.81
106.56
63.06
21.54
F
OH
N
Ts
f1 (ppm)

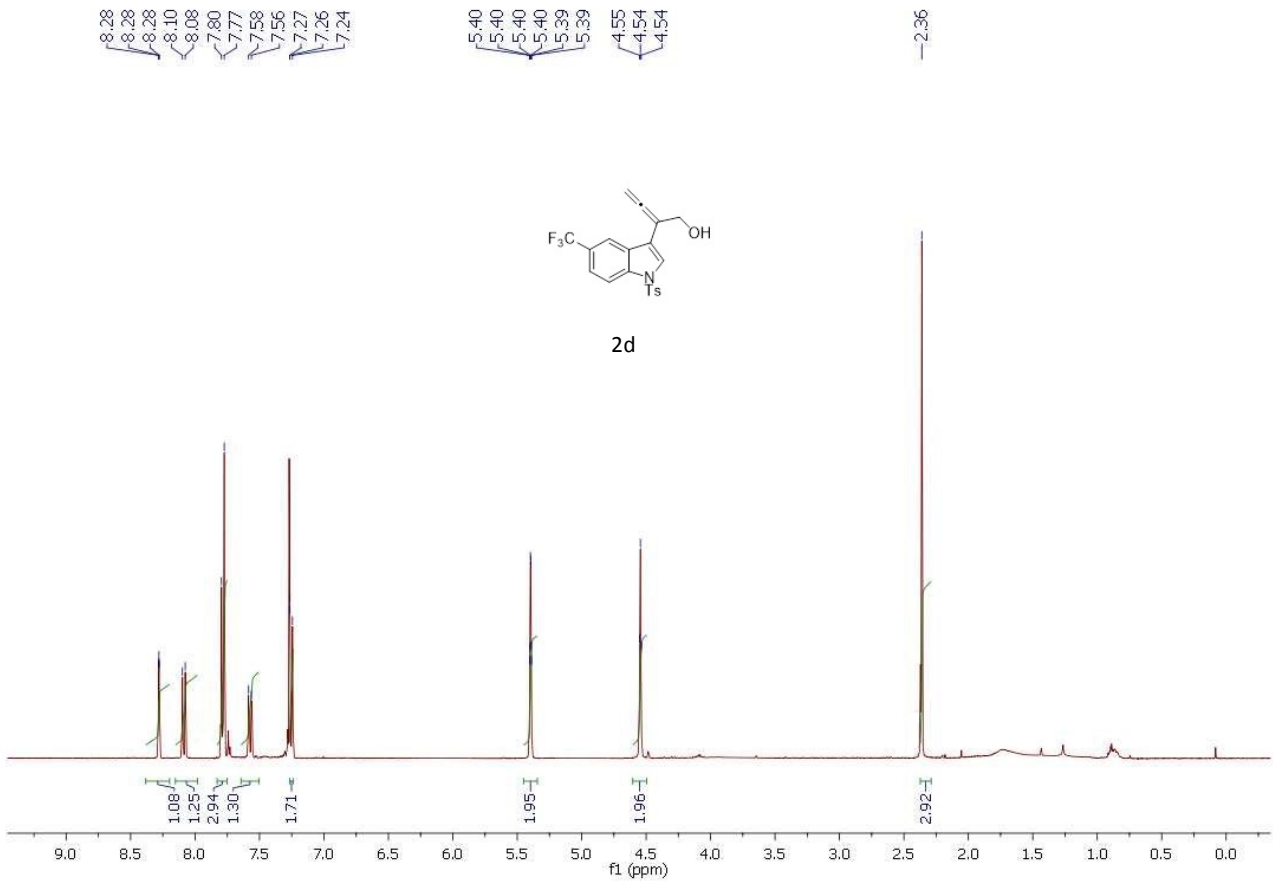
2b


7.99
7.99
7.87
7.85
7.76
7.74
7.24
7.22
7.21
7.19
7.18
7.16
7.16
5.33
5.32
4.50
4.49
4.48
2.35
2.34
OH
Cl
N
Ts
0.98
0.96
2.31
0.90
3.21
1.18
2.00
1.96
3.15
f1 (ppm)

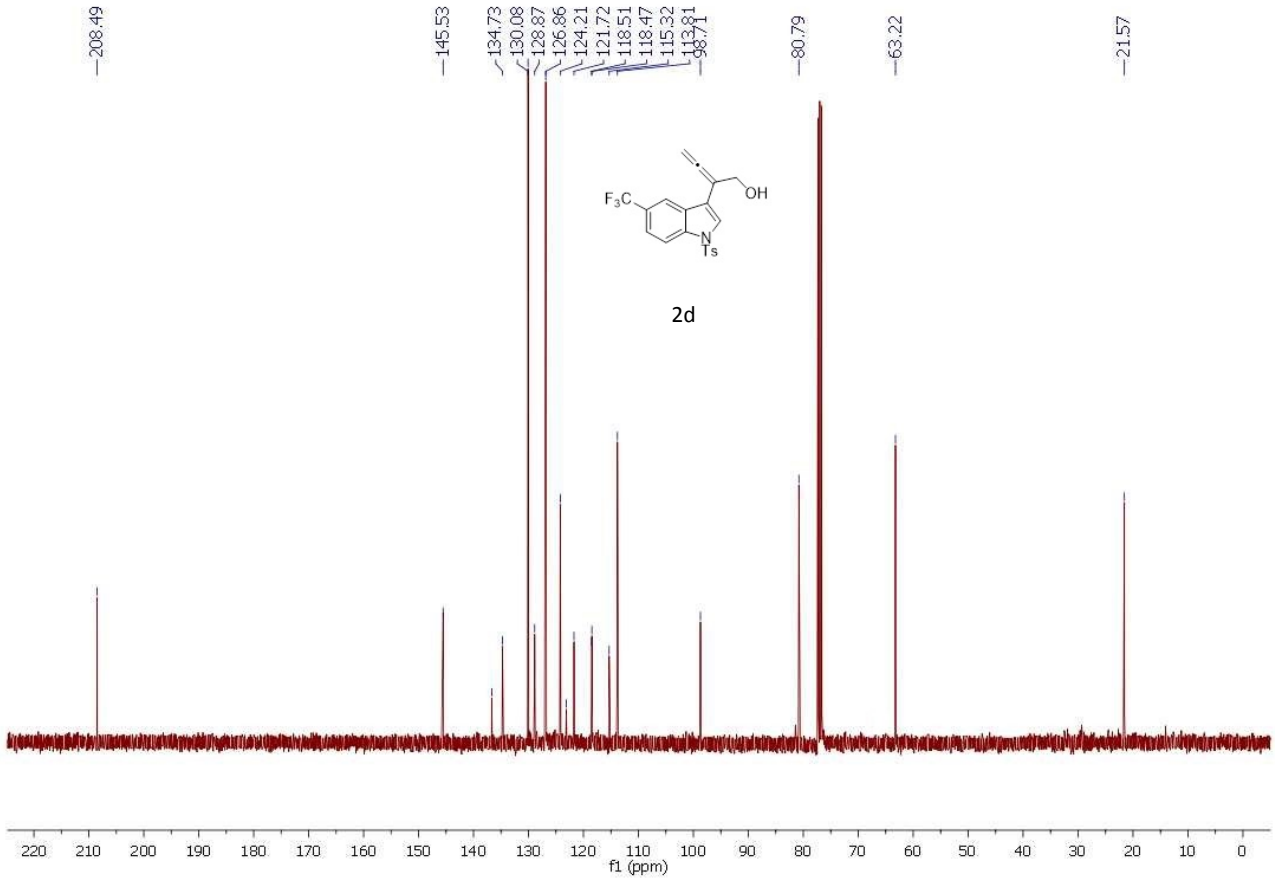
2c


208.40
145.35
135.74
134.85
131.10
130.07
127.60
126.86
123.95
123.13
121.72
115.04
113.71
99.00
80.70
63.09
21.60
OH
Cl
N
Ts
f1 (ppm)

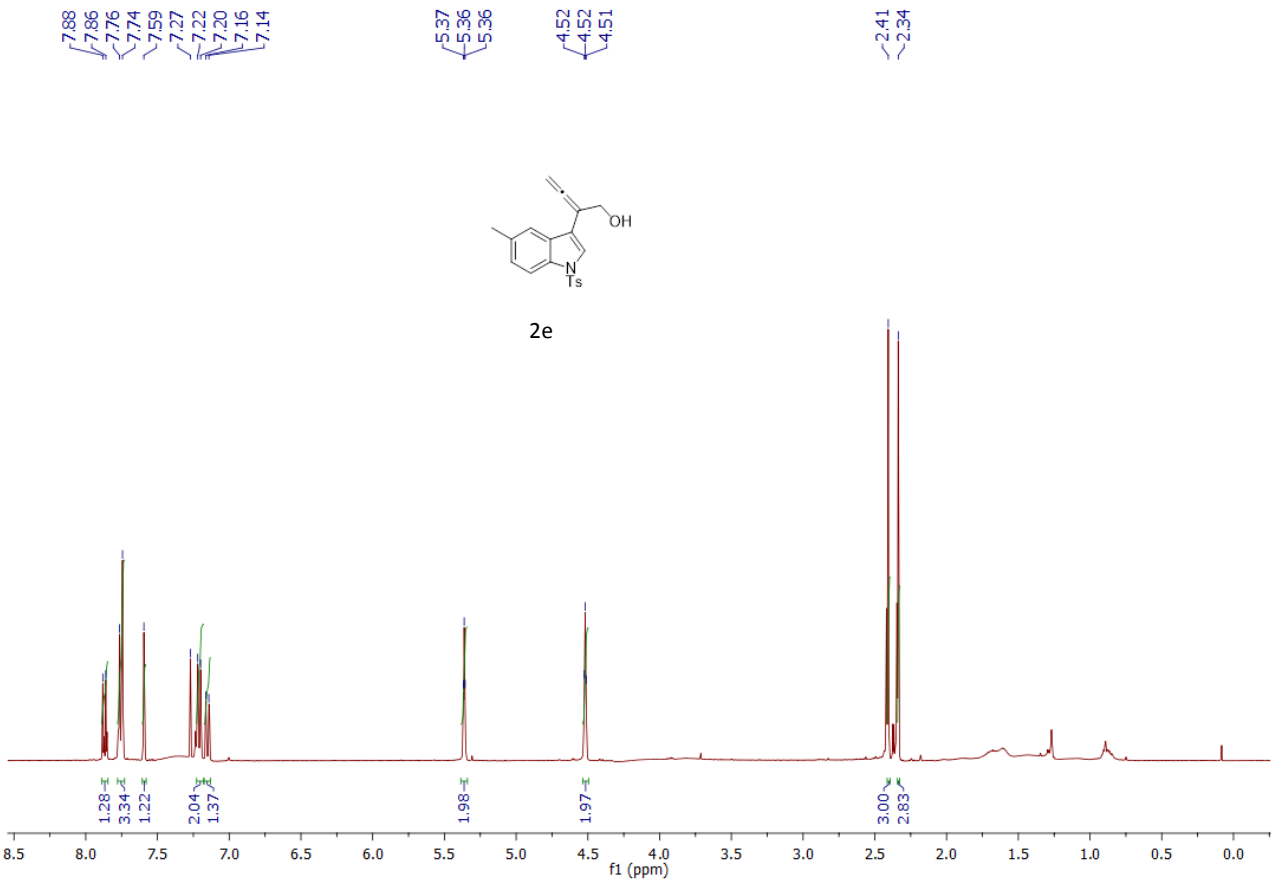
2c


8.28
8.28
8.28
8.10
8.08
7.80
7.77
7.58
7.56
7.27
7.26
7.24
5.40
5.40
5.40
5.40
5.39
5.39
4.55
4.54
4.54
2.36
F3C
OH
N
Ts
1.08
1.25
2.94
1.30
1.71
1.95
1.96
2.92
f1 (ppm)

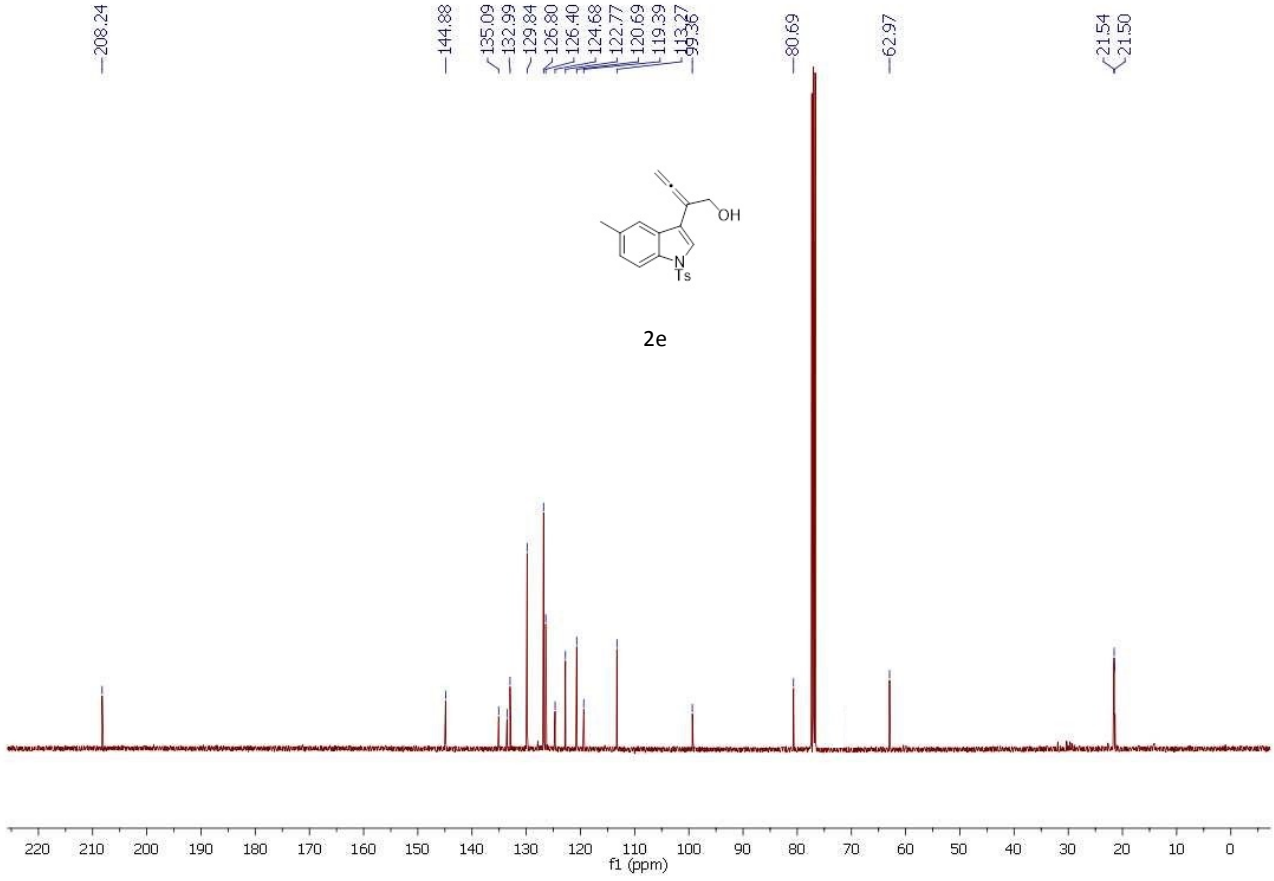
2d


208.49
145.53
134.73
130.08
128.87
126.86
124.21
121.72
118.51
118.47
115.32
113.81
98.71
80.79
63.22
21.57
F3C
OH
N
Ts
f1 (ppm)

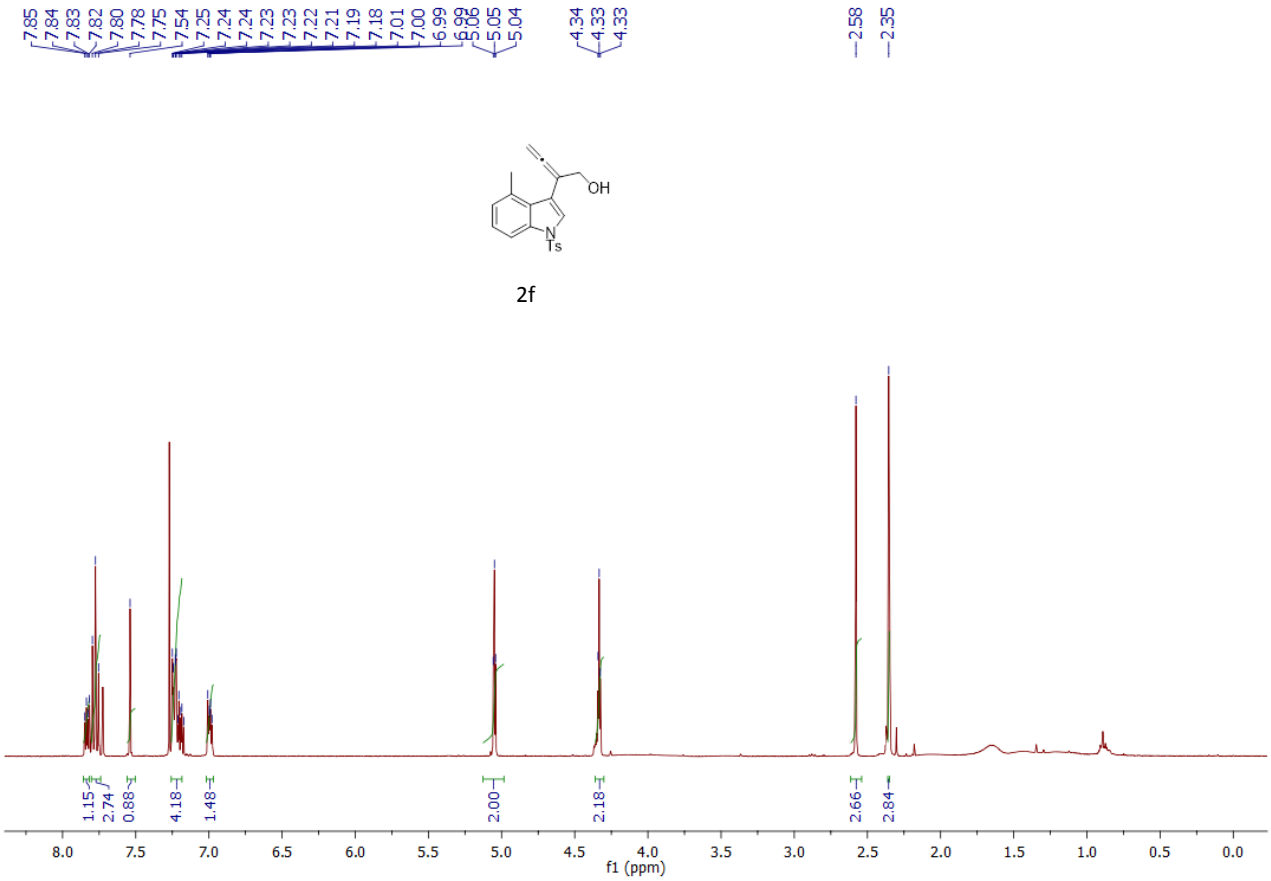
2d


7.88
7.86
7.76
7.74
7.59
7.27
7.22
7.20
7.16
7.14
5.37
5.36
5.36
4.52
4.52
4.51
2.41
2.34
OH
N
Ts
1.28
3.34
1.22
2.04
1.37
1.98
1.97
3.00
2.83
f1 (ppm)

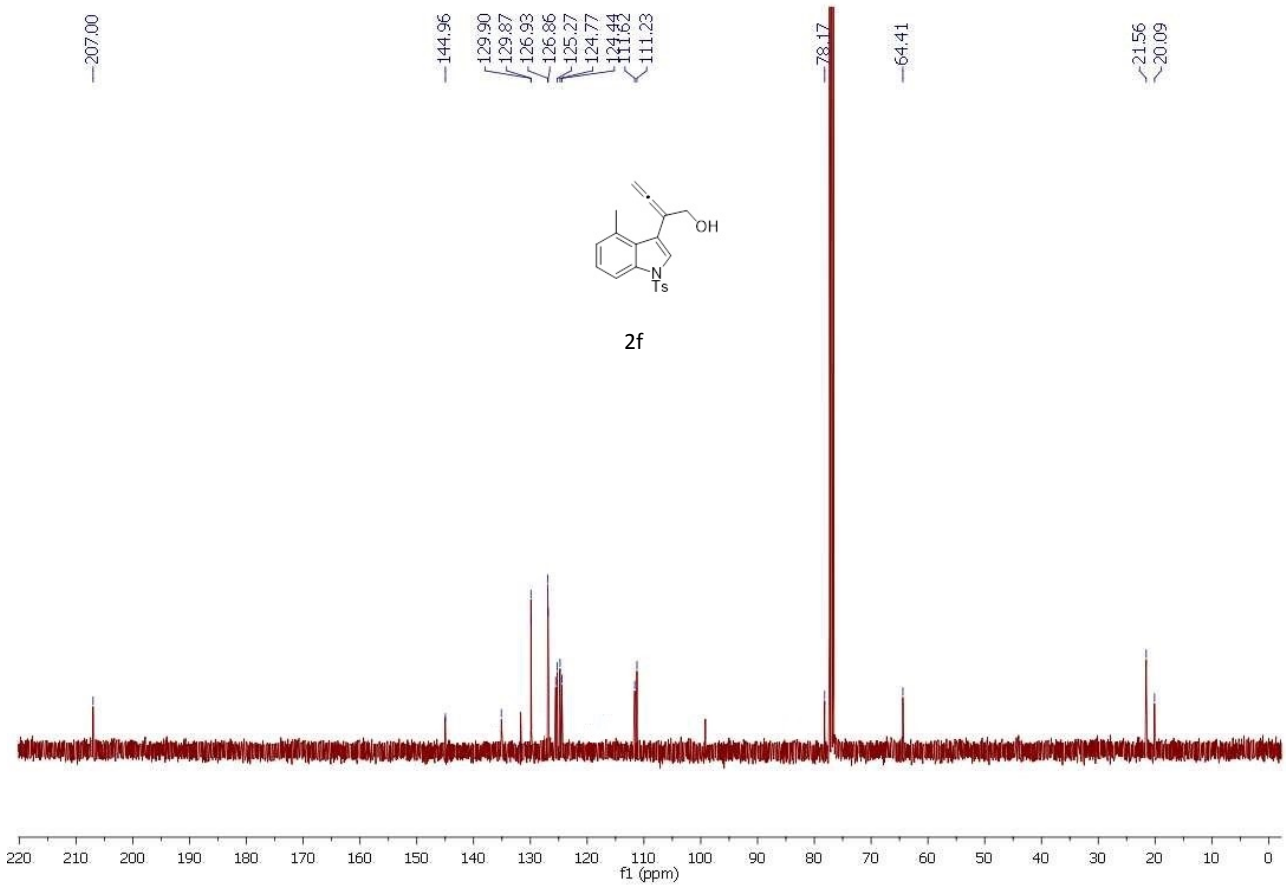
2e


208.24
144.88
135.09
132.99
129.84
126.80
126.40
124.68
122.77
120.69
119.39
113.27
99.36
80.69
62.97
21.54
21.50
OH
N
Ts
f1 (ppm)

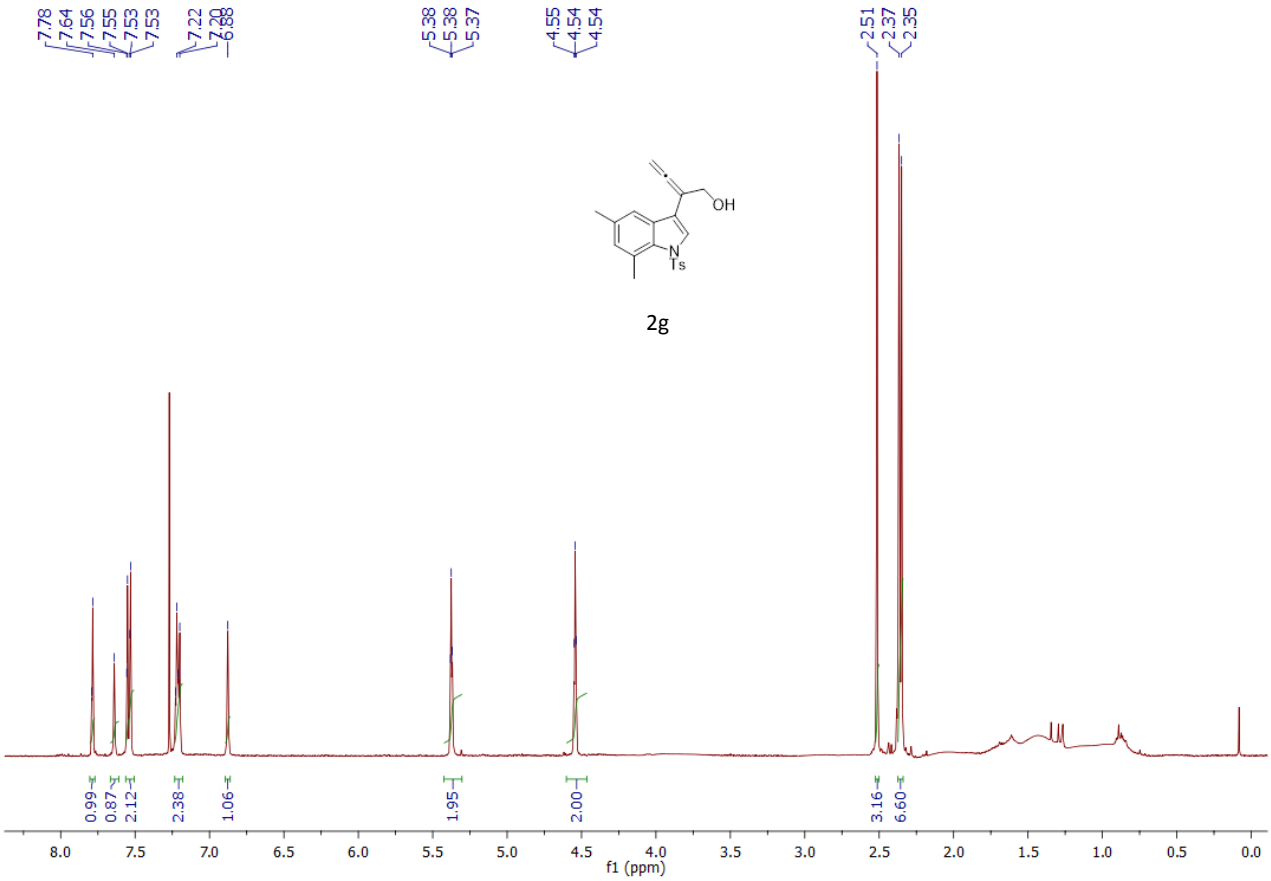
2e


7.85
7.84
7.83
7.82
7.80
7.78
7.75
7.54
7.25
7.24
7.24
7.23
7.23
7.22
7.21
7.19
7.18
7.01
7.00
6.99
6.89
5.06
5.05
5.04
4.34
4.33
4.33
2.58
2.35
OH
N
Ts
1.15
2.74
0.88
4.18
1.48
2.00
2.18
2.66
2.84
f1 (ppm)

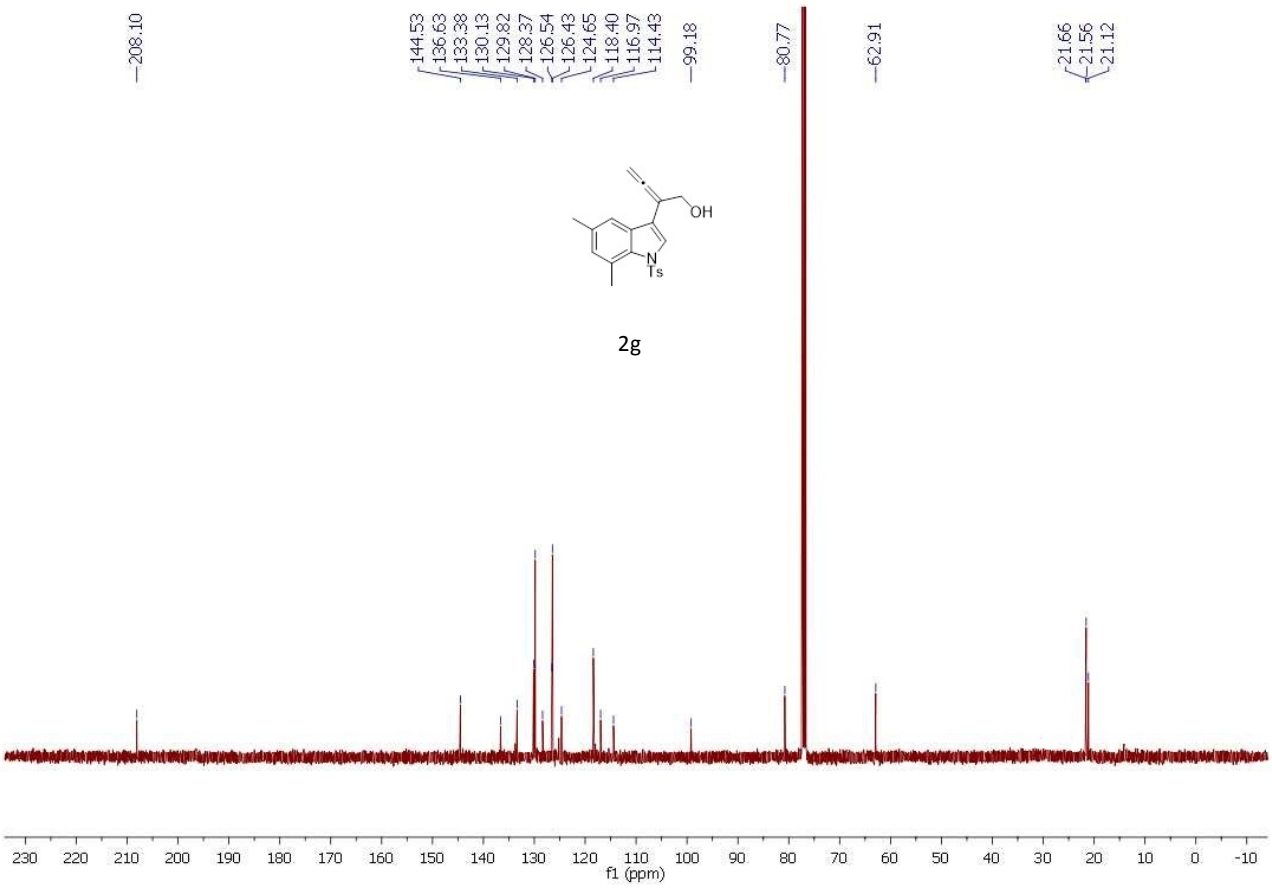
2f


207.00
144.96
129.90
129.87
126.93
126.86
125.27
124.77
124.44
111.62
111.23
78.17
64.41
21.56
20.09
OH
N
Ts
f1 (ppm)

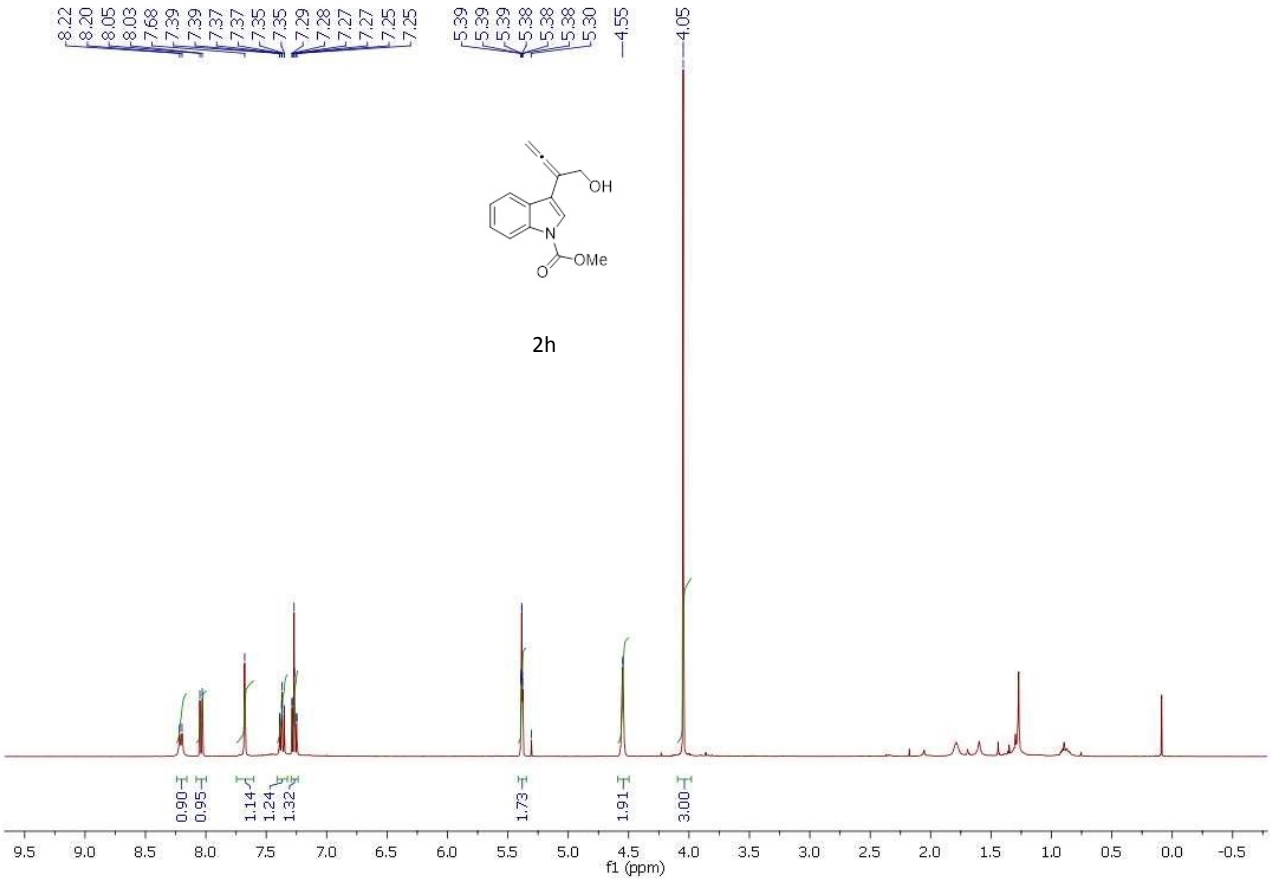
2f


7.78
7.64
7.56
7.55
7.53
7.53
7.22
7.20
6.88
5.38
5.38
5.37
4.55
4.54
4.54
2.51
2.37
2.35
OH
N
Ts
0.99
0.87
2.12
2.38
1.06
1.95
2.00
3.16
6.60
f1 (ppm)

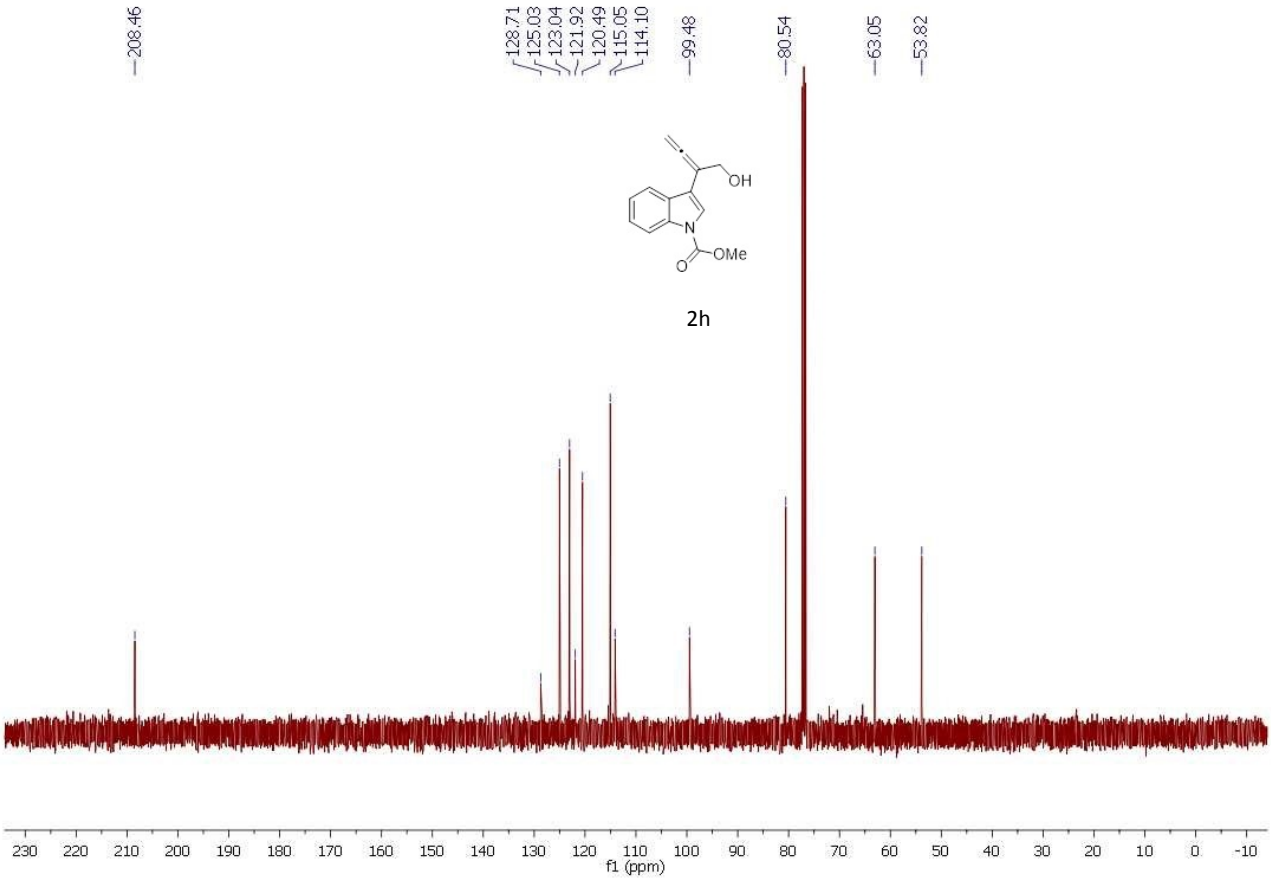
2g


208.10
144.53
136.63
133.38
130.13
129.82
128.37
126.54
126.43
124.65
118.40
116.97
114.43
99.18
80.77
62.91
21.66
21.56
21.12
OH
N
Ts
f1 (ppm)

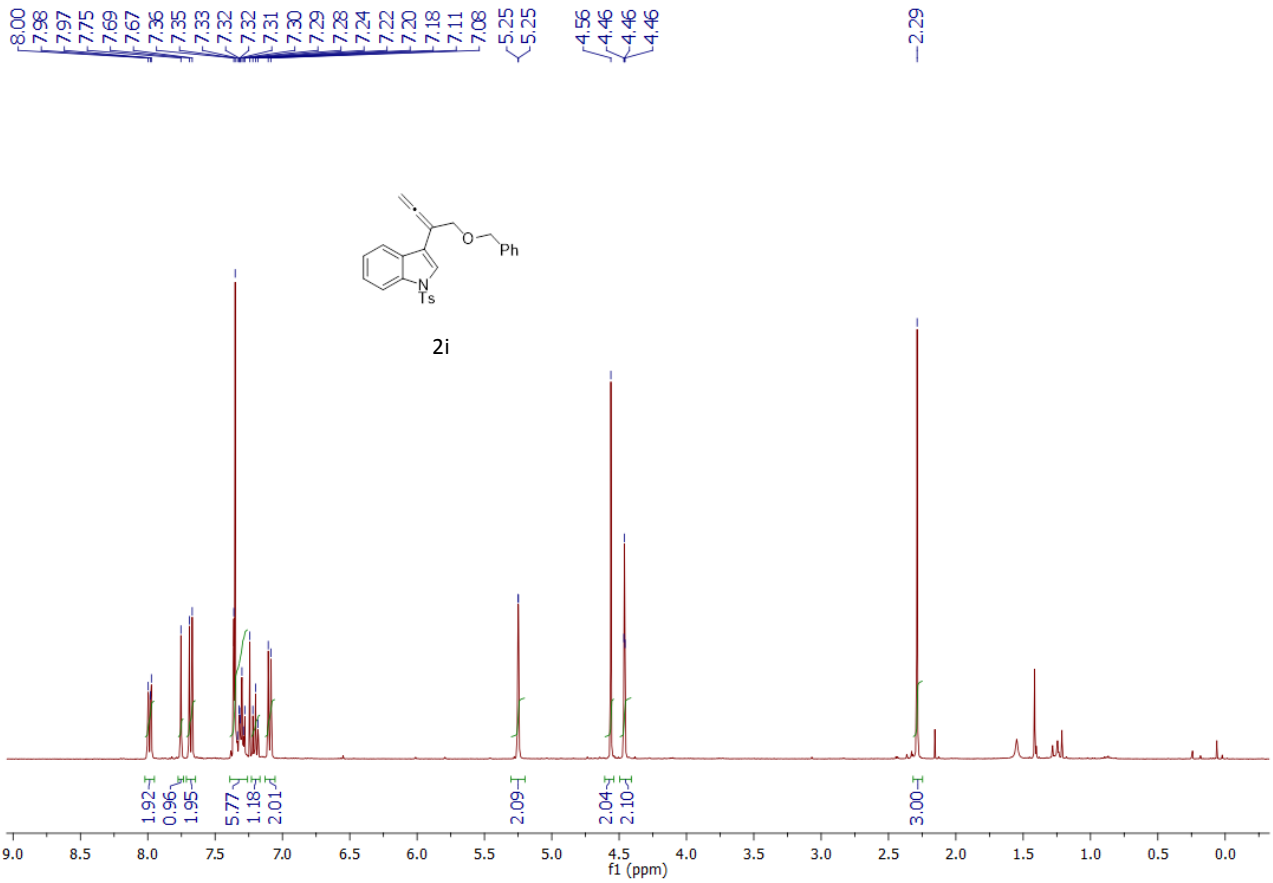
2g


8.22
8.20
8.05
8.03
7.68
7.39
7.39
7.37
7.37
7.35
7.35
7.29
7.28
7.27
7.27
7.25
7.25
5.39
5.39
5.39
5.38
5.38
5.38
5.30
4.55
4.05
OH
N
OMe
O
0.90
0.95
1.14
1.24
1.32
1.73
1.91
3.00
f1 (ppm)

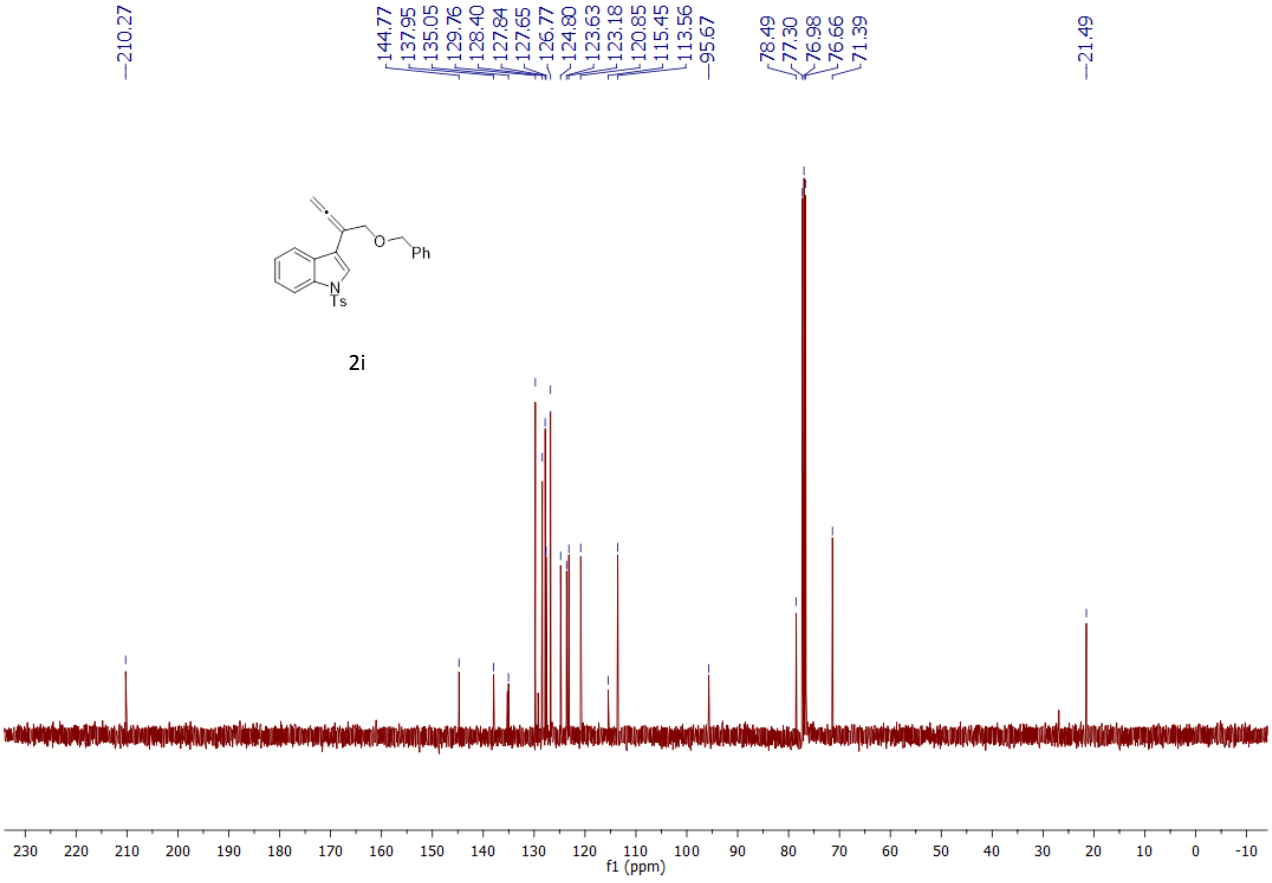
2h


208.46
128.71
125.03
123.04
121.92
120.49
115.05
114.10
99.48
80.54
63.05
53.82
OH
N
OMe
O
f1 (ppm)

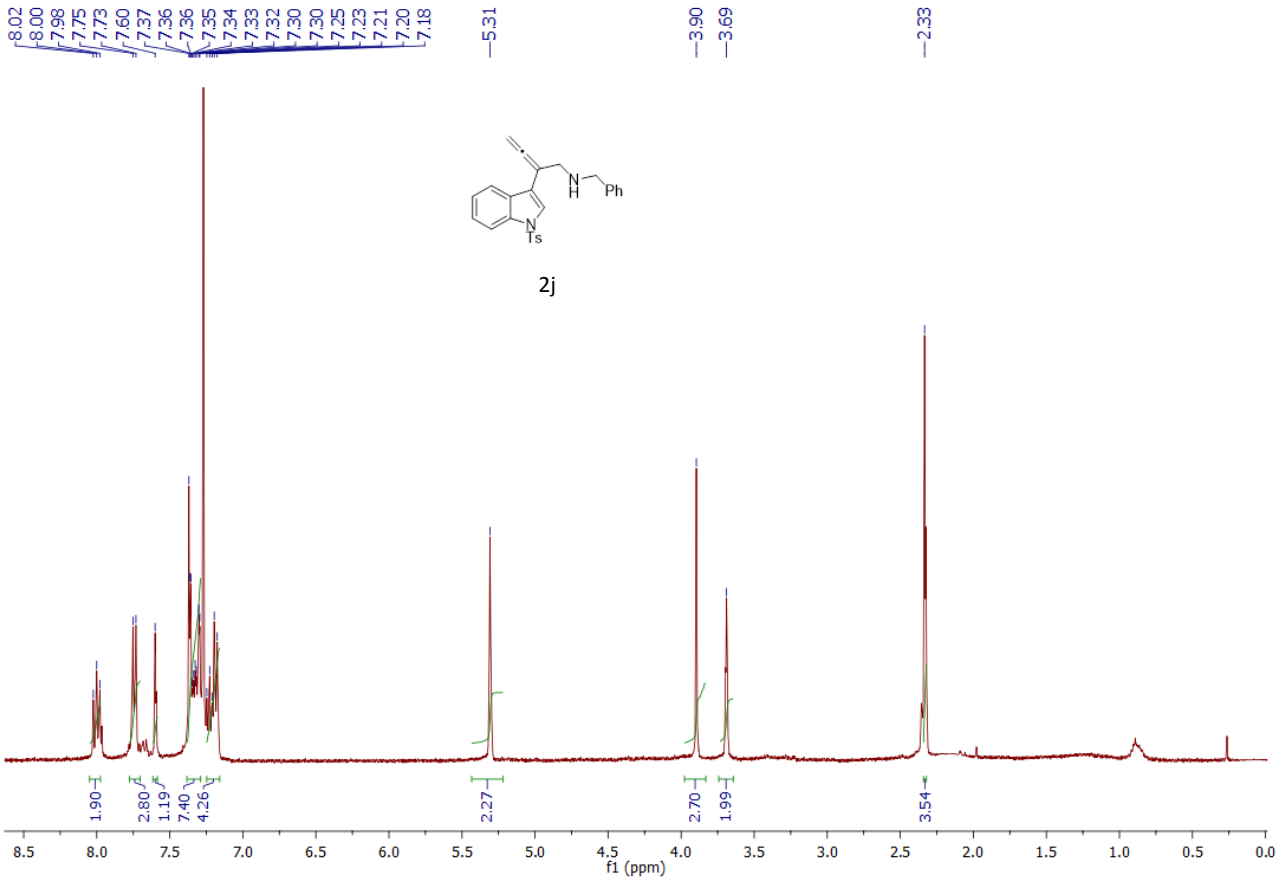
2h


8.00
7.98
7.97
7.75
7.69
7.67
7.36
7.35
7.33
7.32
7.32
7.31
7.30
7.29
7.28
7.24
7.22
7.20
7.18
7.11
7.08
5.25
5.25
4.56
4.46
4.46
4.46
2.29
O
Ph
N
Ts
1.92
0.96
1.95
5.77
1.18
2.01
2.09
2.04
2.10
3.00
f1 (ppm)

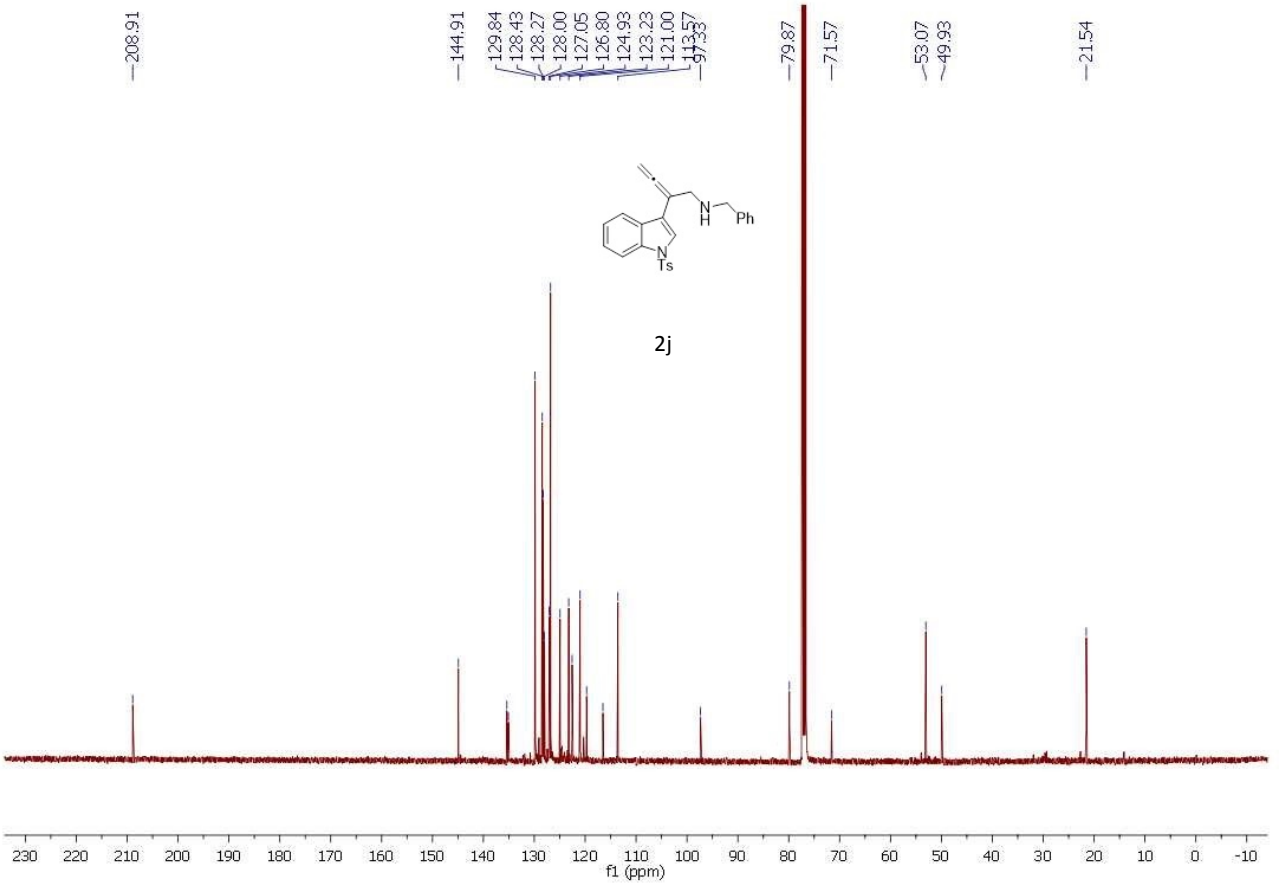
2i


210.27
144.77
137.95
135.05
129.76
128.40
127.84
127.65
126.77
124.80
123.63
123.18
120.85
115.45
113.56
95.67
78.49
77.30
76.98
76.66
71.39
21.49
O
Ph
N
Ts
f1 (ppm)

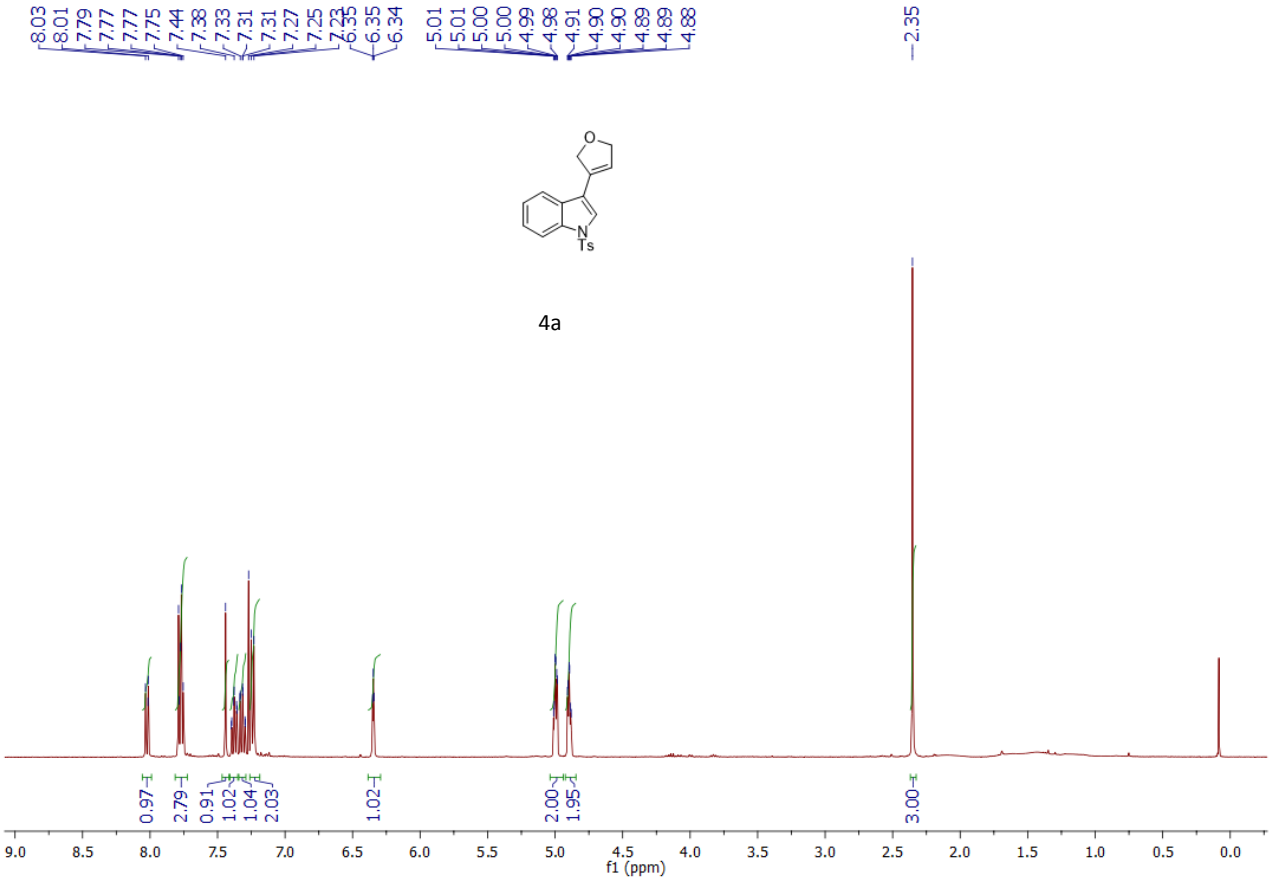
2i


8.02
8.00
7.98
7.75
7.73
7.60
7.37
7.36
7.36
7.35
7.34
7.33
7.32
7.30
7.30
7.25
7.23
7.21
7.20
7.18
5.31
3.90
3.69
2.33
Ph
N
H
N
Ts
1.90
2.80
1.19
7.40
4.26
2.27
2.70
1.99
3.54
f1 (ppm)

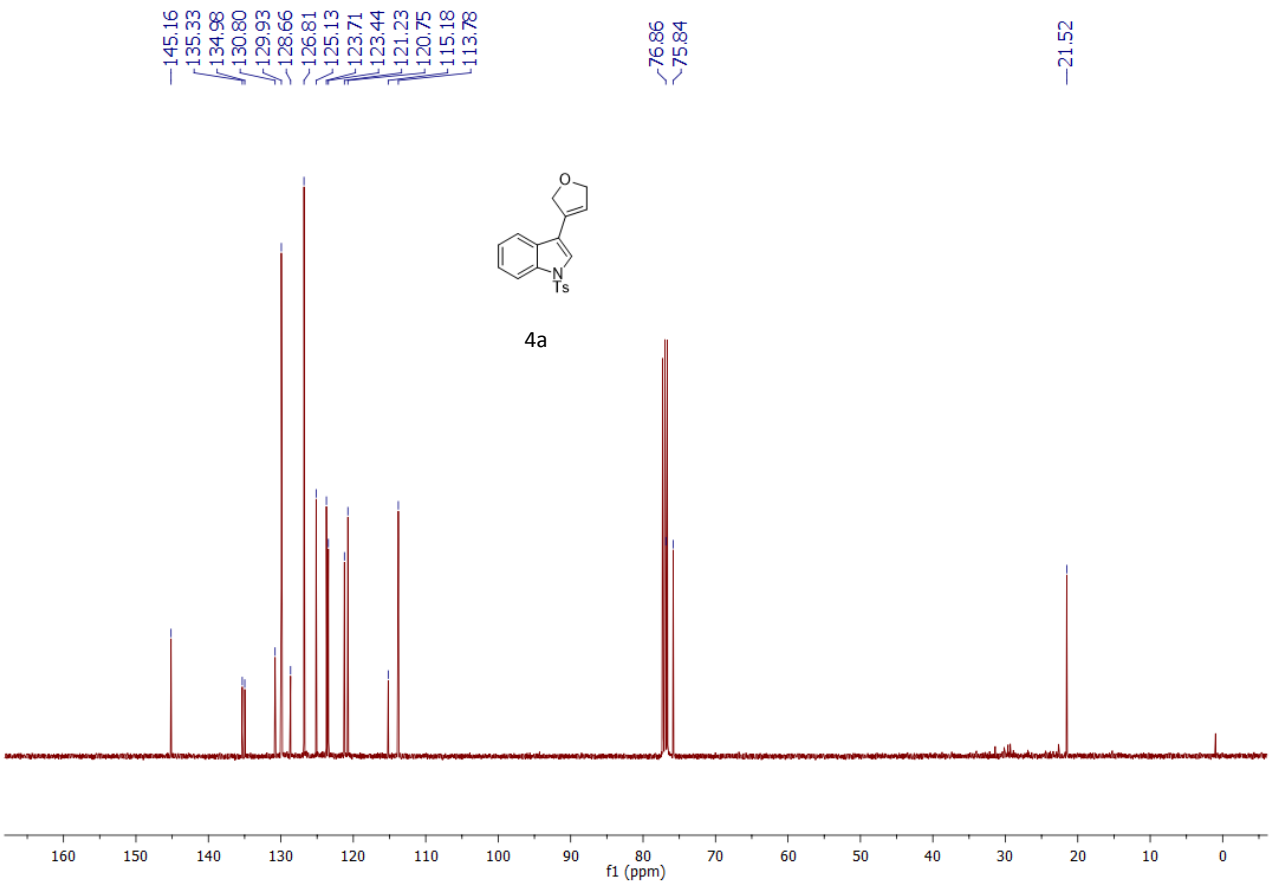
2j


208.91
144.91
129.84
128.43
128.27
128.00
127.05
126.80
124.93
123.23
121.00
113.57
97.33
79.87
71.57
53.07
49.93
21.54
Ph
N
H
N
Ts
f1 (ppm)

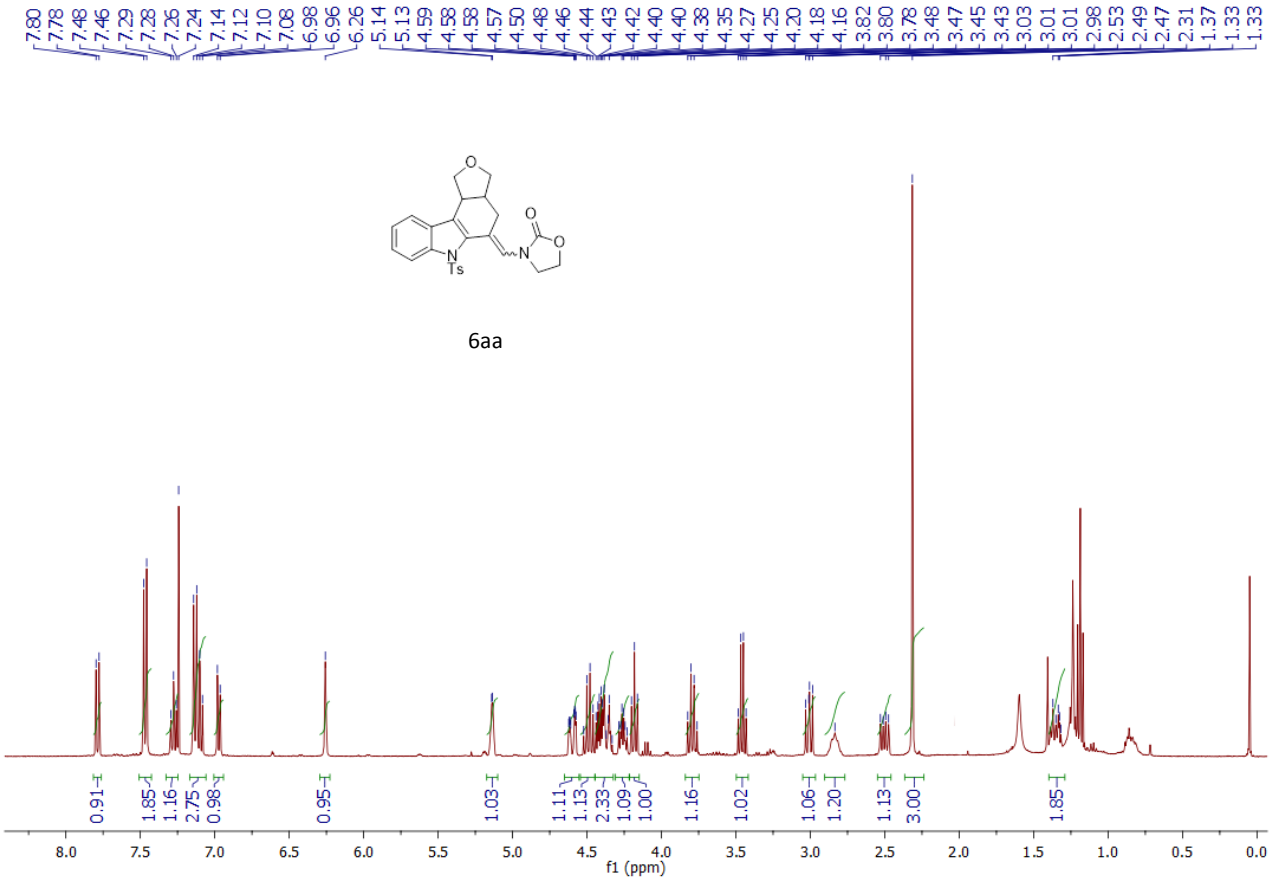
2j

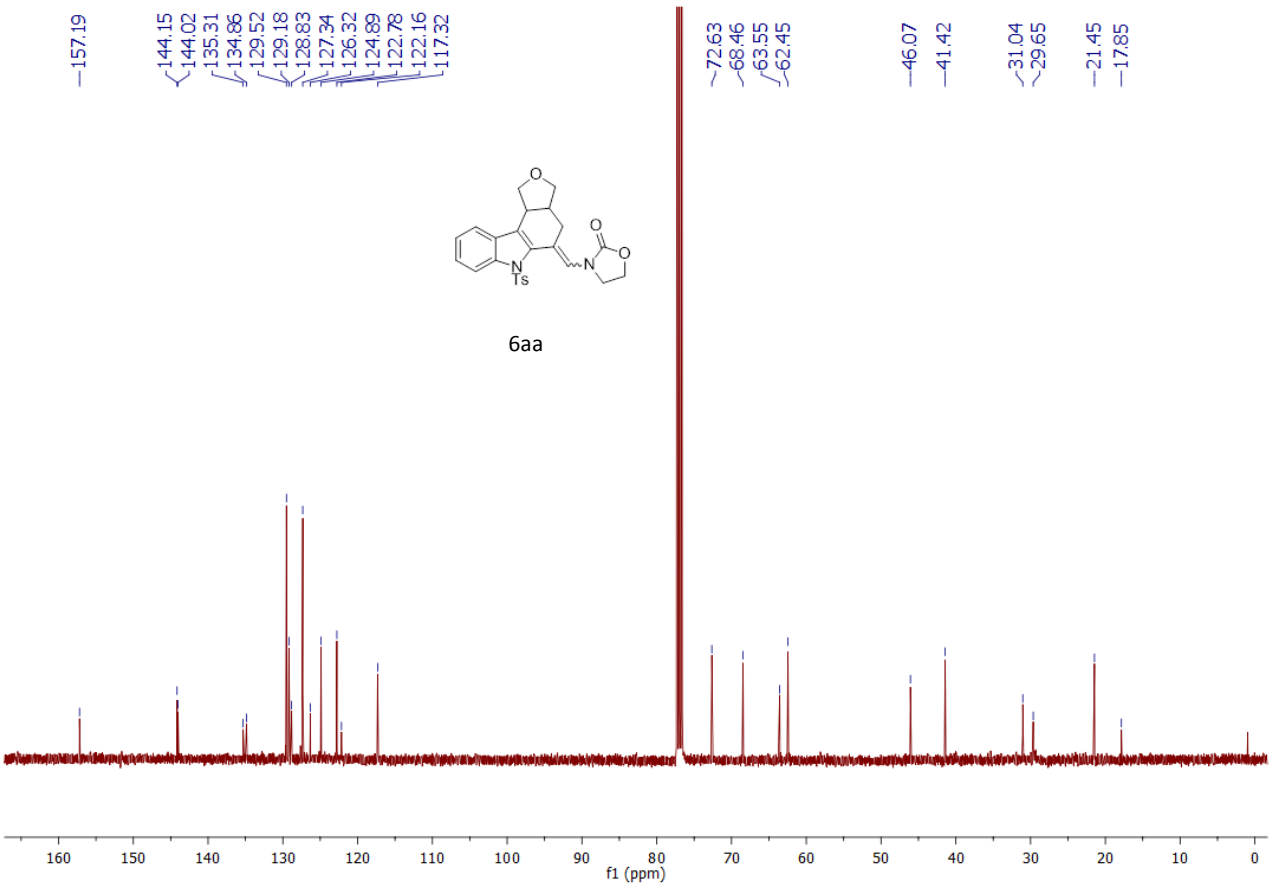

8.03
8.01
7.79
7.77
7.77
7.75
7.44
7.38
7.33
7.31
7.31
7.27
7.25
7.23
6.35
6.34
5.01
5.01
5.00
5.00
4.99
4.98
4.91
4.90
4.90
4.89
4.89
4.88
2.35
O
N
Ts
0.97
2.79
0.91
1.02
1.04
2.03
1.02
2.00
1.95
3.00
f1 (ppm)

4a


145.16
135.33
134.98
130.80
129.93
128.66
126.81
125.13
123.71
123.44
121.23
120.75
115.18
113.78
76.86
75.84
21.52
O
N
Ts
f1 (ppm)

4a


7.80
7.78
7.48
7.46
7.29
7.28
7.26
7.24
7.14
7.12
7.10
7.08
6.98
6.96
6.26
5.14
5.13
4.59
4.58
4.58
4.57
4.50
4.48
4.46
4.44
4.43
4.42
4.40
4.40
4.38
4.35
4.27
4.25
4.20
4.18
4.16
3.82
3.80
3.78
3.48
3.47
3.45
3.43
3.03
3.01
3.01
2.98
2.53
2.49
2.47
2.31
1.37
1.33
1.33
O
O
O
N
Ts
N
6aa
0.91
1.85
1.16
2.75
0.98
0.95
1.03
1.11
1.13
2.33
1.09
1.00
1.16
1.02
1.06
1.20
1.13
3.00
1.85
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


157.19
144.15
144.02
135.31
134.86
129.52
129.18
128.83
127.34
126.32
124.89
122.78
122.16
117.32
72.63
68.46
63.55
62.45
46.07
41.42
31.04
29.65
21.45
17.85
O
O
O
N
Ts
N
6aa
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

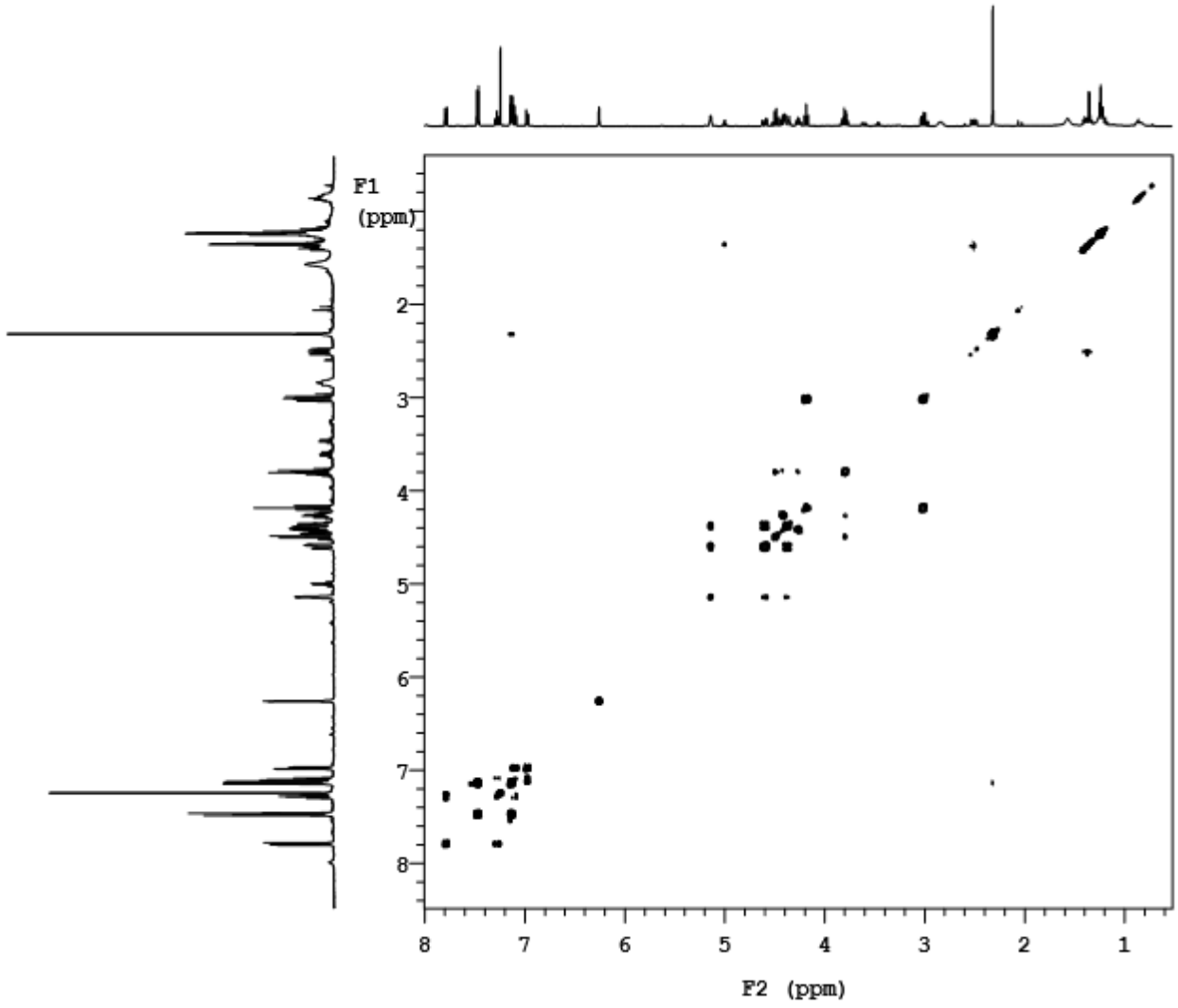


Figura S10: gCosy of product **6aa.**

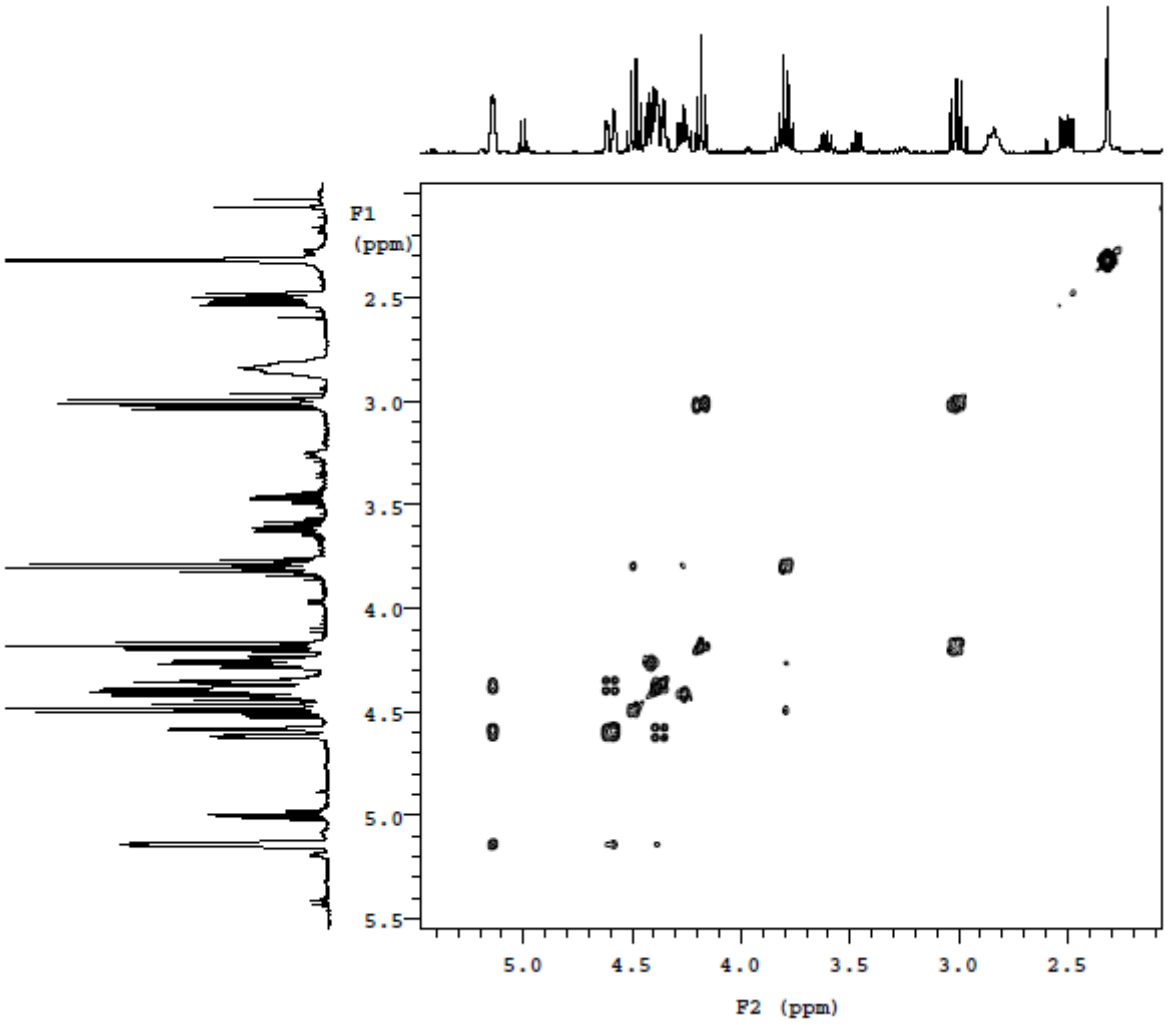


Figura S11: gCosy of product **6aa** from 6.0 to 2.0 ppm.

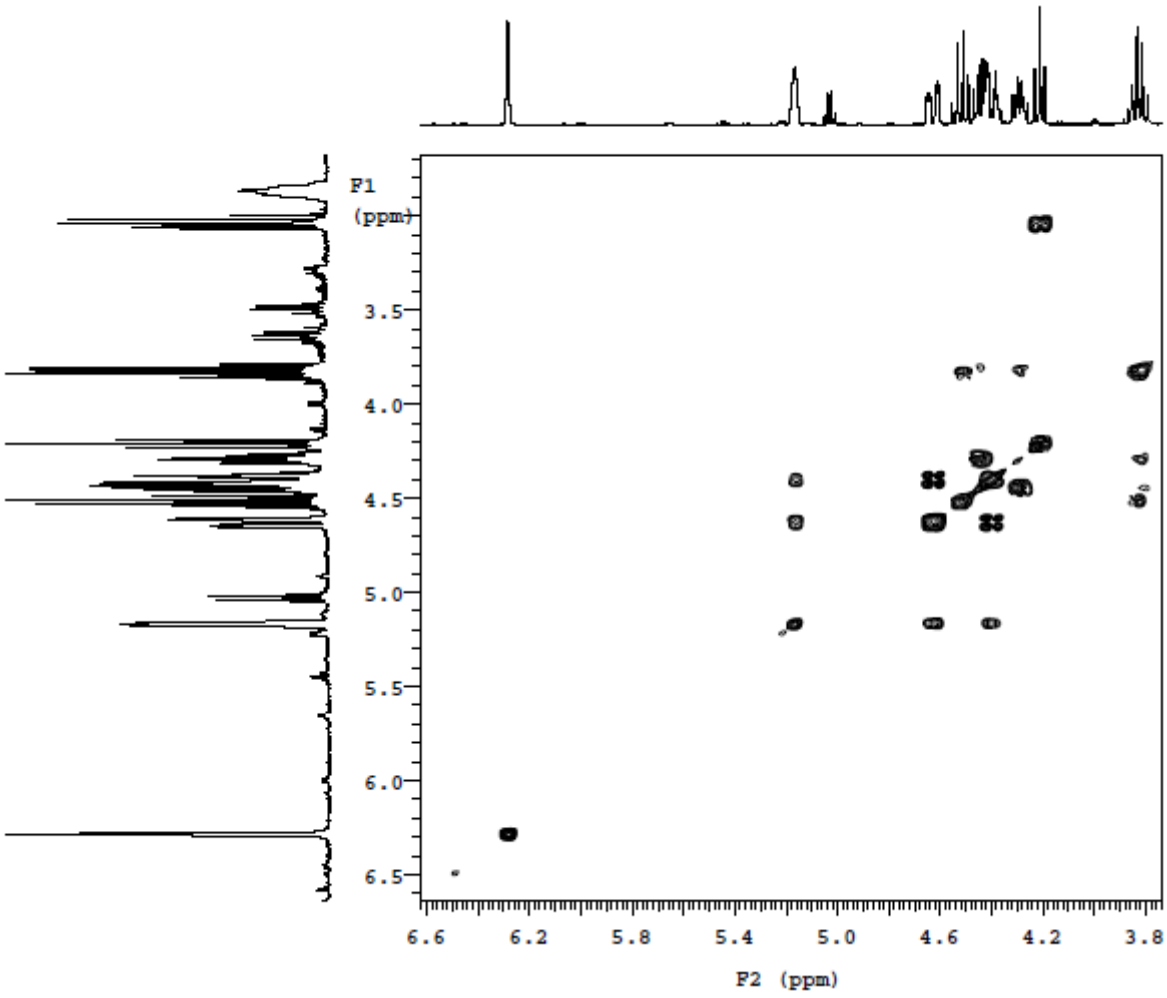


Figura S12: gCosy of product **6aa** from 6.6 to 3.8 ppm.

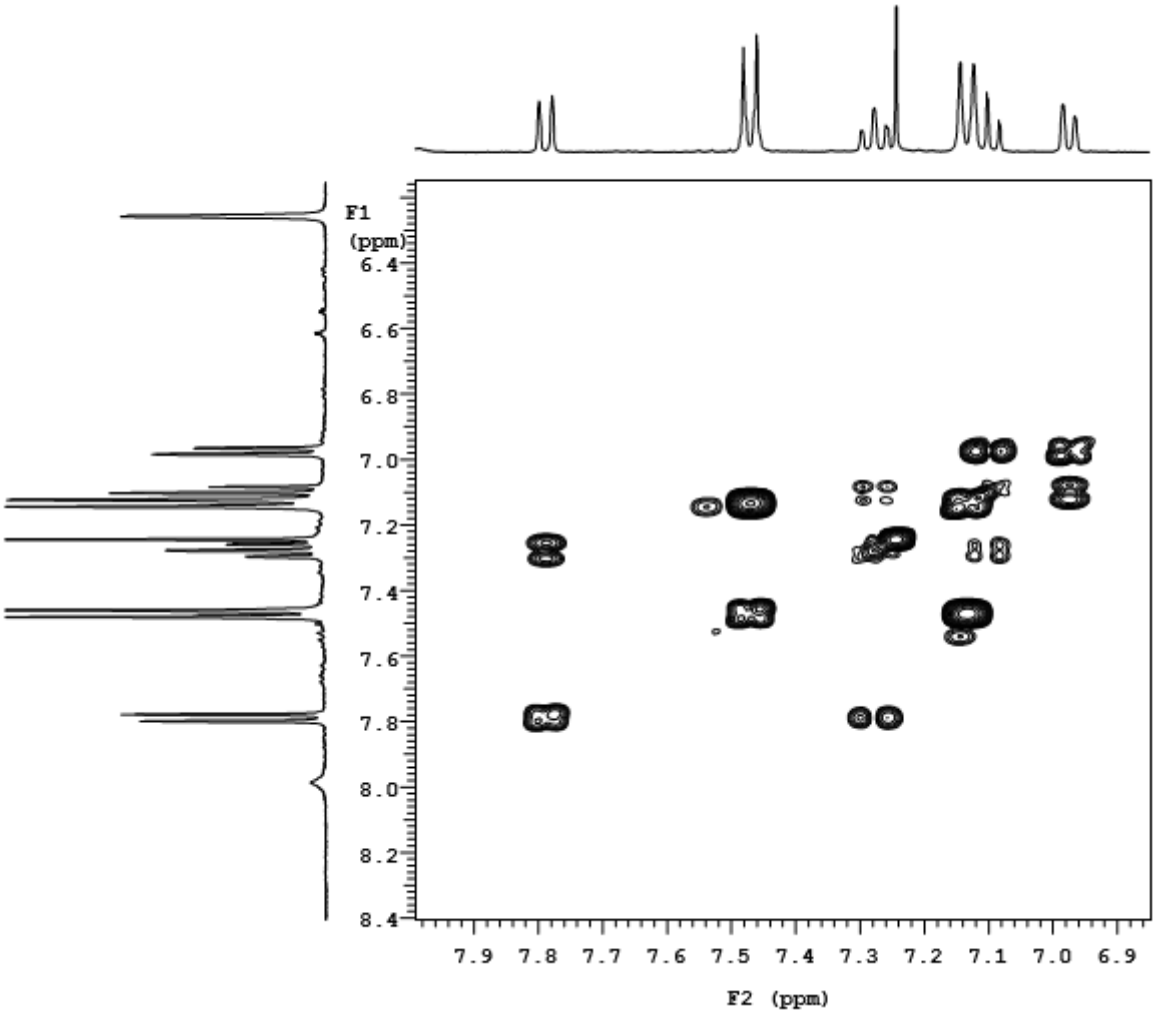


Figura S13: gCosy of product **6aa** from 8.0 to 6.9 ppm.

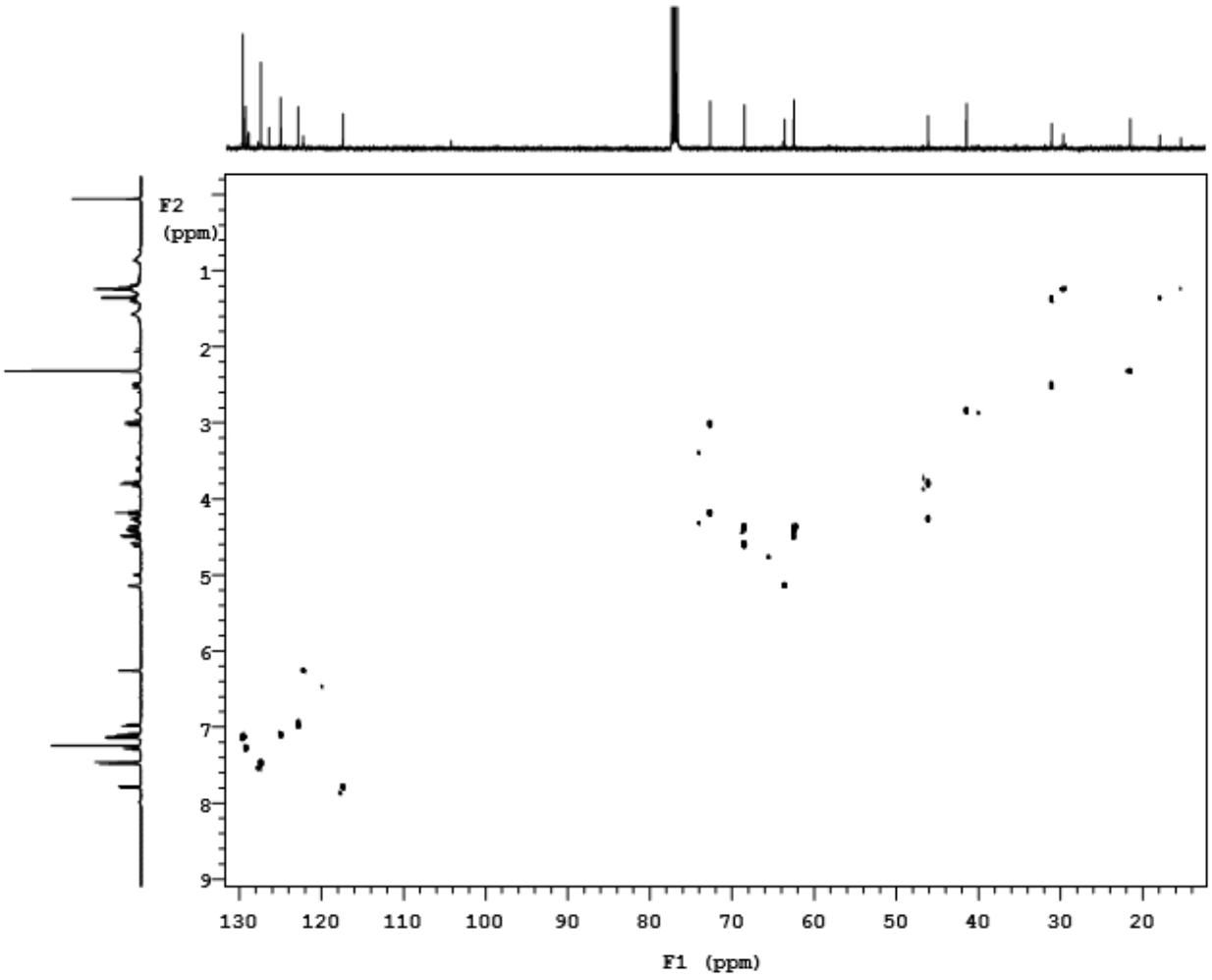


Figura S14: gHSQC of product **6aa**.

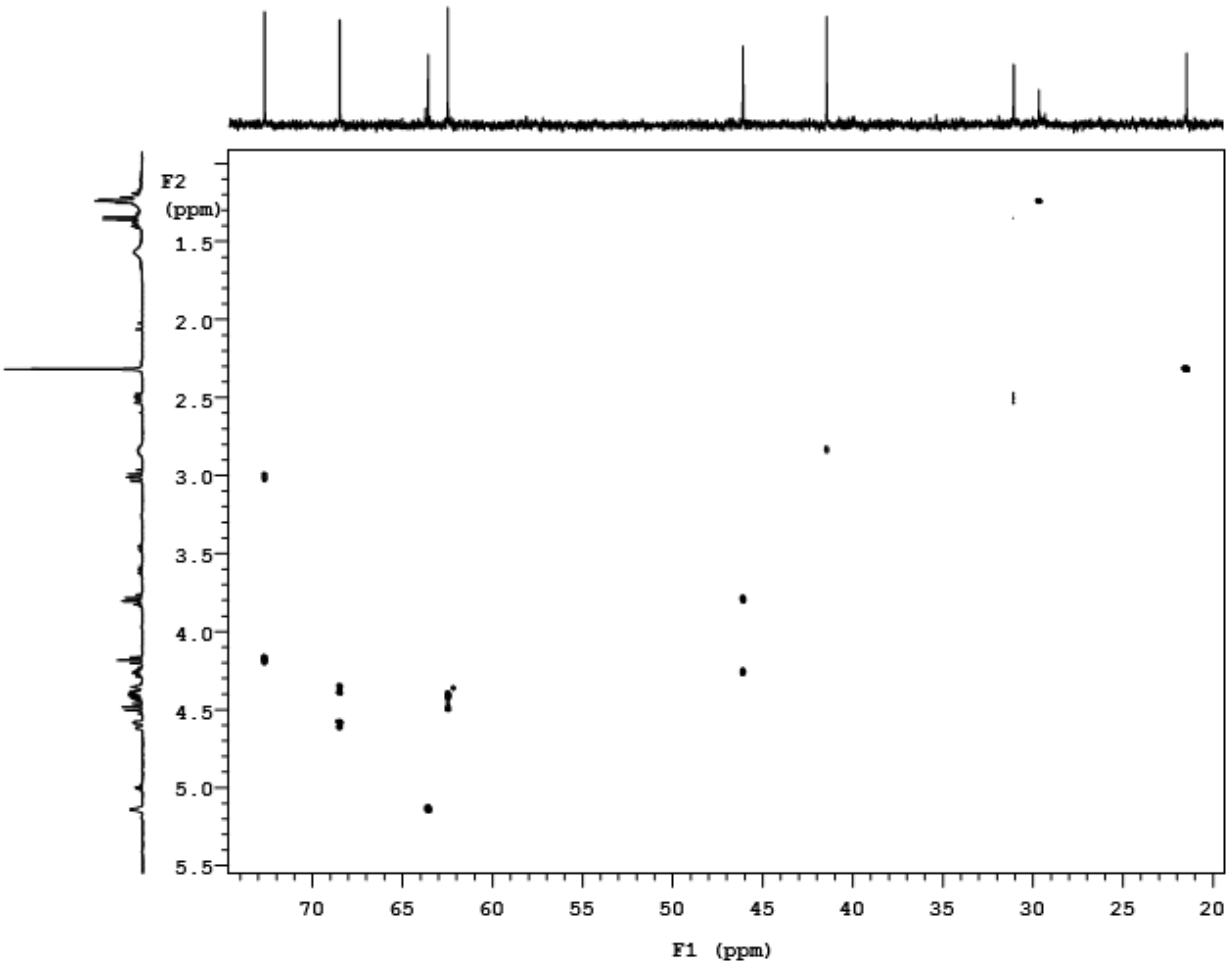


Figura S15: gCosy of product **6aa** from 1.0 to 5.5 ppm and from 20 to 75 ppm.

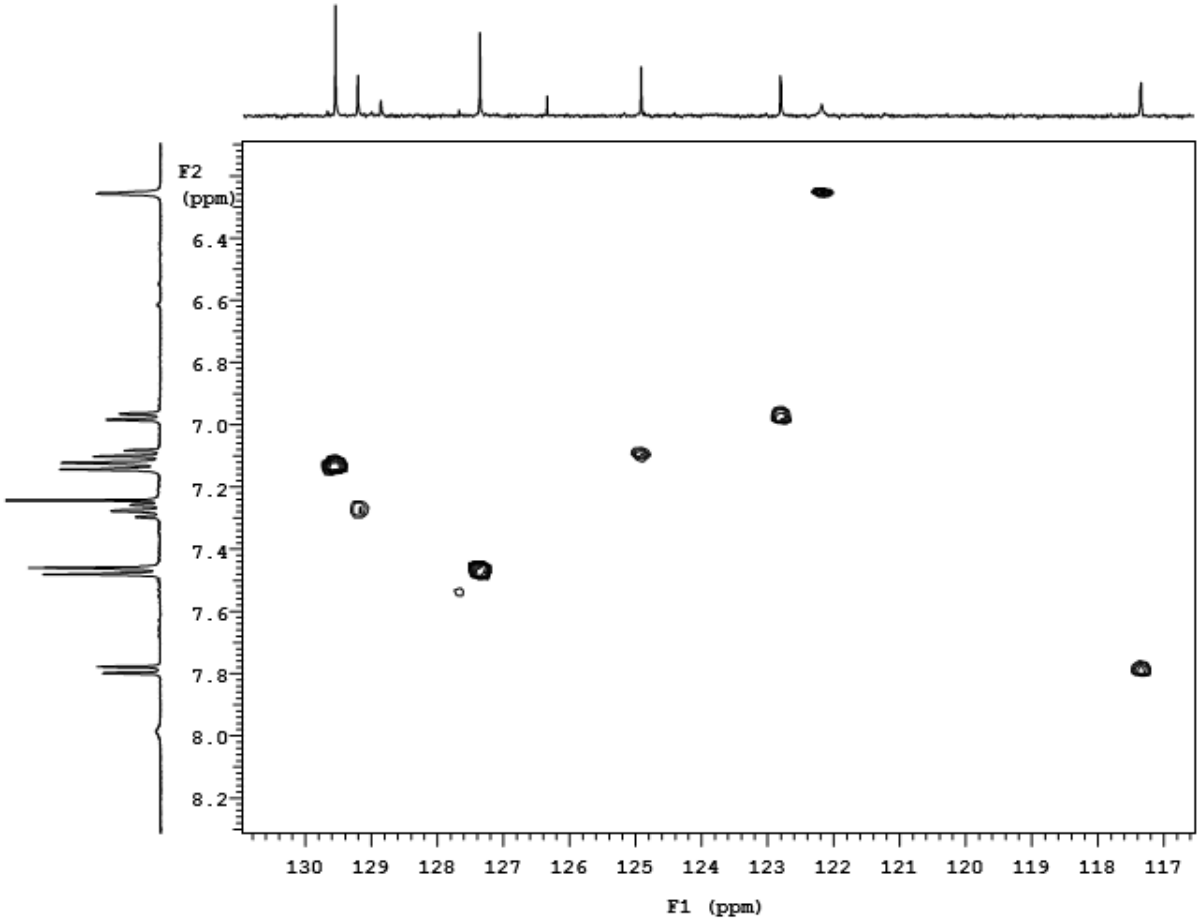


Figura S16: gCosy of product **6aa** from 6.0 to 8.3 ppm and from 117 to 131 ppm.

Single Crystal X-ray crystallography

A suitable crystal of **4a** was mounted on a goniometer head and cooled to 100 K in a stream of cold N_2 using Bruker Kryoflex low temperature device whereas the **2d** was mounted on a goniometer head and kept at room temperature. The X-ray intensity data for both structures were measured on a Bruker SMART Apex II CCD area detector diffractometer. Cell dimensions and the orientation matrix were initially determined from a least-squares refinement on reflections measured in three sets of 20 exposures, collected in three different ω regions, and eventually refined against all data. A full sphere of reciprocal space was scanned by 0.3° ω steps. The software SMART[7] was used for collecting frames of data, indexing reflections, and determination of lattice parameters. The collected frames were then processed for integration by the SAINT program[6] and an empirical absorption correction was applied using SADABS.[8] The structures were solved by direct methods (SIR 2004)[9] and subsequent Fourier syntheses and refined by full-matrix least-squares on F^2 (SHELXTL),[10] using anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms were added in calculated positions, included in the final stage of refinement with isotropic thermal parameters, U(H) = 1.2 U_{eq}(C) [U(H) = 1.5 U_{eq}(C-Me)], and allowed to ride on their carrier carbons.

Crystal data and details of the data collection for **2d** and **4a** are reported in Table **S2**.

Table S3. Crystal data and structure refinement for **2d** and **4a**.

	2d	**4a**
Empirical formula	$C_{20}H_{16}F_3NO_3S$	$C_{19}H_{17}NO_3S$
Formula weight	407.40	339.39
Temperature/K	293(2)	100(2)
Crystal system	Triclinic	*Monoclinic*
Space group	P1	*P 2$_1$/n*
a, Å	8.5679(12)	7.8333(1)
b, Å	12.3701(14)	8.7742(2)
c, Å	18.181(3)	23.1441(4)
α, °	83.843(7)	90
β, °	89.595(12)	95.475(1)
γ, °	80.871(9)	90

[7] *SMART & SAINT Software Reference Manuals*, version 5.051 (Windows NT Version), Bruker Analytical X-ray Instruments Inc.: Madison, WI, **1998**.

[8] G. M. Sheldrick, *SADABS, program for empirical absorption correction*, University of Göttingen, Germany, **1996**.

[9] M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, Cascarano, G. L. De Caro, C. Giacovazzo, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **2005**, *38*, 381-388.

[10] G. M. Sheldrick, SHELXTL*plus (Windows NT Version) Structure Determination Package,* Version 5.1. Bruker Analytical X-ray Instruments Inc.: Madison, WI, USA, **1998**.

Cell volume, $Å^3$	1891.4(5)	1583.46(5)
Z	4	4
ρ_c, Mg m^{-3}	1.431	1.424
μ(Mo-K_α), mm^{-1}	0.221	0.222
F(000)	840	712
Crystal size, mm	0.20 x 0.10 x 0.05	0.30 x 0.20 x 0.10
θ limits, °	1.677 to 28.604	1.768 to 23.351
Refl. collected, unique	31491 / 17775 [R(int) = 0.1039]	19332 / 2296 [R(int) =0.0528]
Goodness-of-fit-on F^2	0.892	1.235
$R_1(F)^a$, $wR_2(F^2)$ $[I > 2\sigma(I)]^b$	0.0738, 0.1707	0.0328, 0.0849
Largest diff. peak and hole, e. $Å^{-3}$	0.489, -0.278	0.185, -0.307
CCDC deposition number	1531577	1531578

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + F_c^2)/3$.

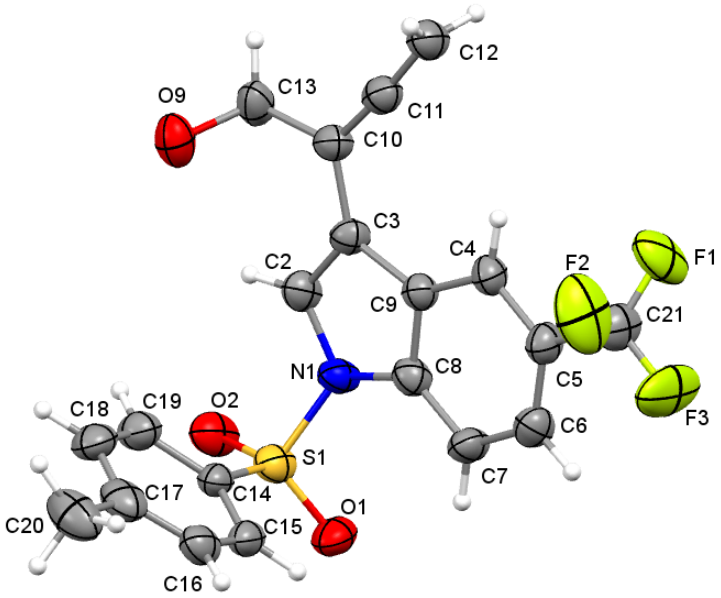


Figure S17. ORTEP drawing of one of the conformers of **2d** (thermal ellipsoids at the 30% of the probability level). The alcoholic H atom was not located.

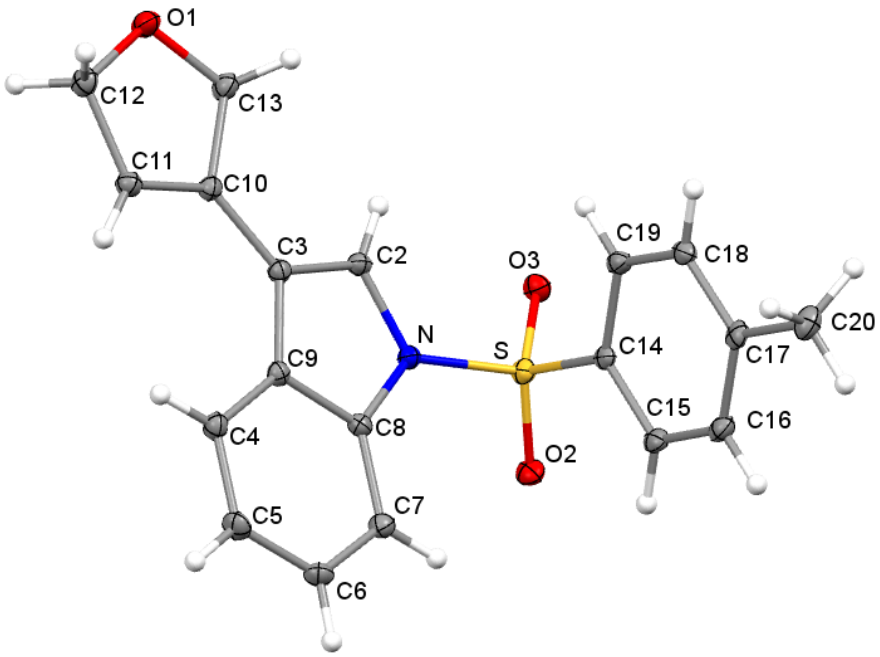


Figure S18. ORTEP drawing of **4a** (thermal ellipsoids are at 50% of the probability level).