Electronic Supplementary Material (ESI) for Chemical Science

Silver-Mediated Fluorination, Trifluoromethylation, and Trifluoromethylthiolation of Arynes

Kung-Pern Wang,[‡] Sang Young Yun,[‡] Phani Mamidipalli and Daesung Lee

Department of Chemistry, University of Illinois at Chicago
845 W. Taylor Street, Chicago, Illinois, 60607-7061

E-mail: dsunglee@uic.edu

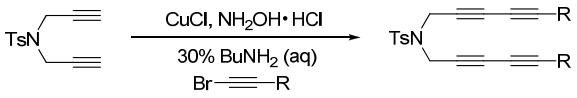
Table of Contents **Page**

Materials and Methods

All reactions were run under an atmosphere of nitrogen, unless otherwise indicated. Flasks were oven-dried overnight and cooled under a stream of nitrogen. Compounds were purchased from Aldrich unless otherwise noted. CH_2Cl_2, THF, Et_2O, MeCN and toluene were purified based on standard procedures. AgF was purchased from Oakwood Product Inc, and $TMSCF_3$ was purchased from Matrix Scientific. $AgSCF_3$ was made followed the literature procedure[1] and stored at -20 °C in the glove box. Flash chromatography was performed using silica gel 60 Å (32-63 mesh) purchased from Silicycle. Analytical thin layer chromatography (TLC) was performed on 0.25 mm E. Merck pre-coated silica gel 60 (particle size 0.040-0.063 mm). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV-500 spectrometer at 501 MHz and 126 MHz respectively, ^{19}F NMR spectra was recorded on Bruker Avance 400 MHz (at 375 MHz) or Varian Mercury 300 MHz (at 283 MHz) spectrometer using CF_3COOH (-76.6 ppm) as a reference standard; multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), qn (quintet), m (multiplet) and br (broad). Coupling constants, *J*, are reported in Hertz. Electrospray ionization (ESI) mass spectra were recorded on a Micromass LCT equipped with a time-of-flight analyzer at the Mass Spectrometry Laboratory at the University of Illinois at Urbana-Champaign.

Experimental Details

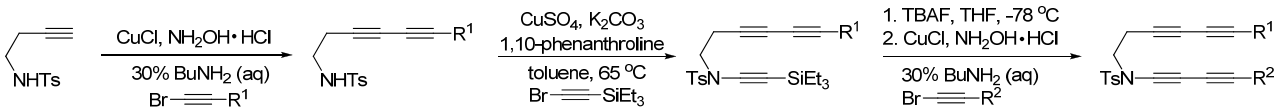
General procedure for symmetric *bis*-1,3-diyne synthesis.



S1 **S2**

Symmetrical *bis*-1,3-diyne substrates can be prepared in one step using Cadiot-Chodkiewicz coupling reaction. To a 30% *n*-$BuNH_2$ (3 mL/1 mmol of substrate) aqueous solution containing CuCl (2 equiv), and $NH_2OH{\cdot}HCl$ (0.1 equiv) was added diyne **S1** at 0 °C. Bromoalkyne **S2** (3 – 4 equiv) was then added dropwise over 5 min and the reaction mixture was stirred at 0 °C for additional 5 min. After aqueous work up, the crude product was purified by column chromatography on silica gel to afford *bis*-1,3-diynes in moderate to good yields

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



S3 **S4** **S5** **S6** **S7** **S8**

Unsymmetrical *bis*-1,3-diyne substrates can be synthesized in four steps involving Cadiot-Chodkiewicz coupling reaction, N-alkynalation of tosylamide, desilylation and Cadiot-Chodtiewicz coupling reaction sequence.

[1] J. H. Clark, C. W. Jones, A. P. Kybett, M. A. Mcclinton, J. M. Miller, D. Bishop and R. J. Blade, *J. Fluorine Chem.* 1990, **48**, 249.

Tosylamide **S3** was coupled with bromoalkyne **S4** (1.5 equiv) under the typical Cadiot-Chodkiewicz reaction condition described above gave diyne **S5**. N-alkynylation of **S5** with bromoalkyne **S6** (1.1 equiv) in the presence of catalytic amount of $CuSO_4 \cdot 5H_2O$ (0.1 equiv), 1,10-phenanthroline (0.2 equiv) and K_2CO_3 (2 equiv) in toluene at 65 ^oC for 8 h afforded triyne **S7**. Desilylaton of **S7** using TBAF (1.1 equiv) at -78 ^oC and a subsequent coupling reaction with bromoalkyne **S8** (1.5 equiv) generated unsymmetrical *bis*-1,3-diynes in moderate to good yields.

General procedure for stoichiometric fluorination reaction: In a glove box, *bis*-1,3-diyne (0.1 mmol) and $AgBF_4$ (0.15 mmol) were dissolved in 5 mL of toluene in a thick-walled 25 mL Schlenk tube equipped with a magnetic stirring bar. The reaction tube was brought out of the box, and was stirred in an oil bath at 90 °C for 2 h. The tube was opened to air at room temperature and the crude reaction mixture was filtered through a small pipet column packed with silica gel. The solvent was removed from a rotary aspirator and the organic product was isolated by column chromatography on silica gel.

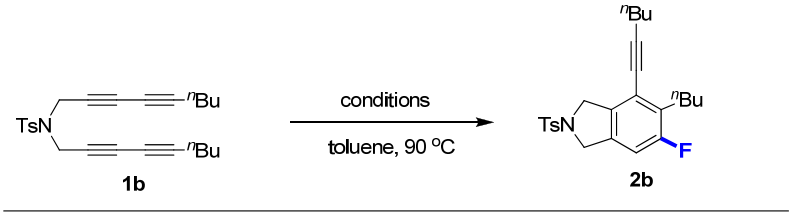
General procedure for catalytic fluorination reaction: In a glove box, *bis*-1,3-diyne (0.1 mmol), pyridinium salt (0.15 mmol, generated in situ by mixing 1:1 ratio of selected base and $HBF_4 \cdot OEt_2$) and $AgBF_4$ (0.01 mmol) were dissolved in 5 mL of toluene in a thick-walled 25 mL Schlenk tube equipped with a magnetic stirring bar. The reaction tube was brought out of the box, and was stirred in an oil bath at 90 °C for 4 h. The tube was opened to air at room temperature and the crude reaction mixture was filtered through a small pipet column packed with silica gel. The solvent was removed from a rotary aspirator and the organic product was isolated by column chromatography on silica gel.

General procedure for trapping of a putative organosilver intermediate by using halosuccinimide: In a glove box, *bis*-1,3-diyne (0.1 mmol), $AgBF_4$ (0.15 mmol) and halosuccinimide (0.2 mmol) were dissolved in 5 mL of toluene in a thick-walled 25 mL Schlenk tube equipped with a magnetic stirring bar. The reaction tube was brought out of the box and stirred in an oil bath at 90 ^oC for 4 h. The tube was opened to air at room temperature and the crude reaction mixture was filtered through a small pipet column packed with silica gel. The solvent was removed from a rotary aspirator and desired 1,2-halofluoroarenes were isolated by column chromatography on silica gel.

General procedure for trifluoromethylation: In a glove box, AgF (0.15 mmol) was added into a solution of $TMSCF_3$ (0.2 mmol) in 3 mL of MeCN in a thick-walled 25 mL Schlenk tube equipped with a magnetic stirring bar. The reaction tube was stirred at room temperature for 30 min, then the *bis*-1,3-diyne (0.1mmol) in 2 mL of MeCN was added. The reaction tube was brought out of the box, and was stirred in an oil bath at 90 °C for 4 h. The tube was opened to air at room temperature and solvent was removed from a rotary aspirator. The organic product was isolated by column chromatography on silica gel.

General procedure for trifluoromethylthiolation: In a glove box, *bis*-1,3-diyne (0.1 mmol), and $AgSCF_3$ (0.15 mmol) were dissolved in 5 mL of toluene in a thick-walled 25 mL Schlenk tube equipped with a magnetic stirring

bar. The reaction tube was brought out of the box, and was stirred in an oil bath at 90 °C for 4 h. The tube was opened to air at room temperature and solvent was removed from a rotary aspirator. The organic product was isolated by column chromatography on silica gel.



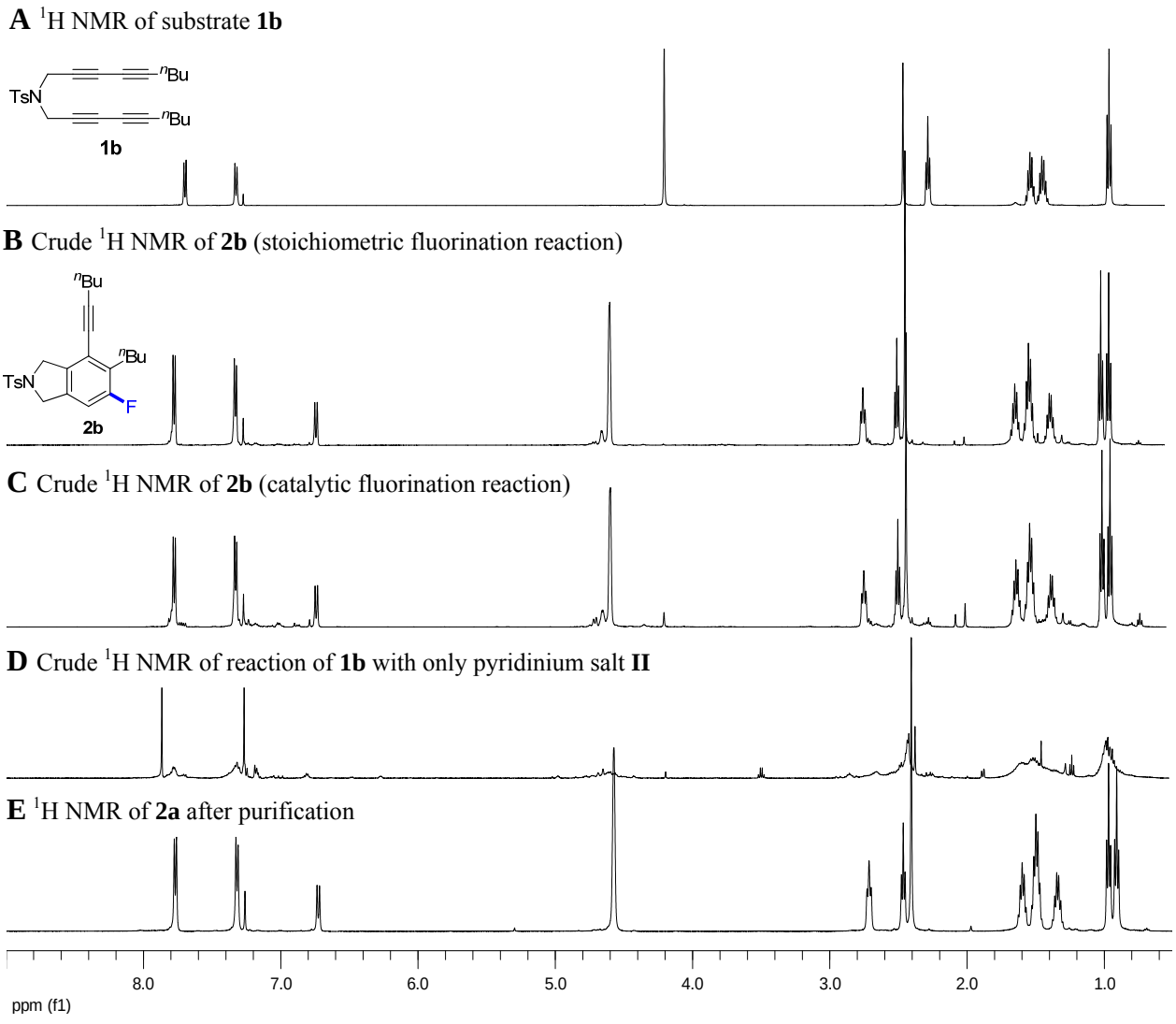
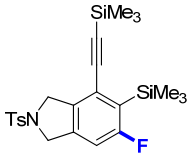
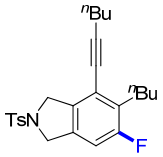


Figure S1. Efficiency of fluorination reaction under specified conditions

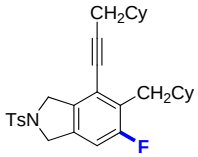
Characterization Data



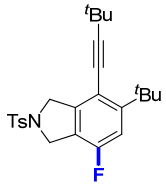
2a: **^{1}H NMR** (501 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.74 (d, *J* = 8.5 Hz, 1H), 4.5 (s, 4H), 2.40 (s, 3H), 0.37 (s, 9H), 0.25 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.7 (d, *J* = 238.7 Hz), 143.7, 138.8 (d, *J* = 10 Hz), 136.0, 133.7, 129.9, 127.5, 127.1 (d, *J* = 31.2 Hz), 124.5 (d, *J* = 13.7 Hz), 110.1 (d, *J* = 30 Hz), 104.0, 102.1, 54.1, 53.6, 21.5, 0.4, -0.3; **^{19}F NMR** (375 MHz, $CDCl_3$) δ -99.4; **HRMS** (ESI) calcd for $C_{24}H_{31}FNO_2SSi_2$ $[M+H]^+$: 460.1598, found 460.1596.



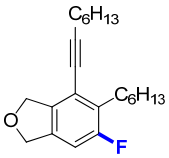
2b: **^{1}H NMR** (501 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.5 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 2H), 6.73 (d, *J* = 9.0 Hz, 1H), 4.57 (s, 4H), 2.72 (t, *J* = 7.0 Hz, 2H), 2.47 (t, *J* = 7.0 Hz, 2H), 2.40 (s, 3H), 1.61 (qn, *J* = 7.0 Hz, 2H), 1.52 (m, 4H), 1.36 (m, 2H), 0.98 (t, *J* = 7.0 Hz, 3H), 0.92 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.7 (d, *J* = 242.1 Hz), 143.7, 134.3, 134.2, 133.9, 131.2 (d, *J* = 17.5 Hz), 129.9, 127.6, 120.3 (d, *J* = 6.3 Hz), 108.9 (d, *J* = 26.2 Hz), 99.5, 75.5 (d, *J* = 2.9 Hz), 54.1, 53.8, 31.8, 30.7, 27.0, 22.6, 22.0, 21.5, 19.3, 13.9, 13.6; **^{19}F NMR** (375 MHz, $CDCl_3$) δ -118.5 (d, *J* = 8.3 Hz); **HRMS** (ESI) calcd for $C_{25}H_{31}FNO_2S$ $[M+H]^+$: 428.2060, found 428.2068.



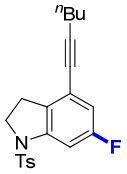
2c: **^{1}H NMR** (501 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.5 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 2H), 6.73 (d, *J* = 9 Hz, 1H), 4.57 (s, 4H), 2.61 (d, *J* = 5.5 Hz, 2H), 2.43 (s, 3H), 2.37 (d, *J* = 5.5 Hz, 2H), 1.86 (d, *J* = 12 Hz, 2H), 1.78 (d, *J* = 12 Hz, 2H), 1.75 – 1.54 (m, 8H), 1.39 – 1.03 (m, 10H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.9 (d, *J* = 241.9 Hz), 143.6, 134.3, 134.2, 133.8, 129.9, 129.8, 129.7, 127.5, 120.9 (d, *J* = 13.7 Hz), 108.7 (d, *J* = 26.2 Hz), 98.6, 76.7, 54.2, 53.8, 38.5, 37.5, 34.8, 33.1, 32.7, 32.6, 27.4, 26.4, 26.39, 26.30, 26.2, 26.1, 21.5; **^{19}F NMR** (375 MHz, $CDCl_3$) δ -116.7 (d, *J* = 8.0 Hz); **HRMS** (ESI) calcd for $C_{31}H_{39}FNO_2S$ $[M+H]^+$: 508.2686, found 508.2687.



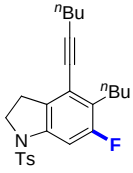
2d′: ^{1}**H NMR** (501 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 11 Hz, 1H), 4.64 (s, 2H), 4.63 (s, 2H), 2.41(s, 3H), 1.46 (s, 9H), 1.36 (s, 9H); ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 163.0 (d, *J* = 240 Hz), 154.2 (d, *J* = 5.3 Hz), 143.8 (d, *J* = 12.5 Hz), 133.8, 129.8, 127.5, 119.6 (d, *J* = 17.5 Hz), 113.4, 112.5 (d, *J* = 21 Hz), 108.9, 76.3, 54.7, 51.4, 35.9, 30.6, 29.6, 28.5, 21.5; ^{19}**F NMR** (375 MHz, $CDCl_3$) δ -117.4 (d, *J* = 11.4 Hz); **HRMS** (ESI) calcd for $C_{25}H_{31}FNO_2S$ $[M+H]^+$: 428.2060, found 428.2050.



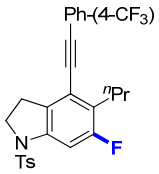
2e: ^{1}**H NMR** (501 MHz, $CDCl_3$) δ 6.80 (d, *J* = 9.0 Hz, 2H), 2.78 (t, *J* = 8.5 Hz, 2H), 2.46 (t, *J* = 8.5 Hz, 2H), 1.63 (m, 4H), 1.48 (m, 2H), 1.37 (m, 10H), 0.92 (m, 6H); ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 161.7 (d, *J* = 241.2 Hz), 137.4 (d, *J* = 8.7 Hz), 137.0, 130.6 (d, *J* = 18.7 Hz), 118.6 (d, *J* = 7.5 Hz), 107.5 (d, *J* = 25 Hz), 98.4, 75.9, 74.0, 73.8, 31.6, 31.3, 29.7, 29.2, 28.5, 27.2, 22.5, 19.5, 14.08, 14.06; ^{19}**F NMR** (375 MHz, $CDCl_3$) δ -119.9 (d, *J* = 8.4 Hz); **HRMS** (ESI) calcd for $C_{22}H_{32}FO$ $[M+H]^+$: 331.2437, found 331.2452.



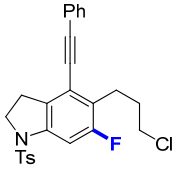
2f: ^{1}**H NMR** (501 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 10.0 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 2H), 6.68 (d, *J* = 10.0 Hz, 1H), 3.94 (t, *J* = 8.5 Hz, 2H), 2.93 (t, *J* = 8.5 Hz, 2H), 2.39 (s, 3H), 2.37 (t, *J* = 7.0 Hz, 2H), 1.54 (qn, *J* = 7.5 Hz, 2H), 1.45 (qn, *J* = 7.5 Hz, 2H), 0.93 (t, *J* = 7.5 Hz, 3H); ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 163.3 (d, *J* = 240 Hz), 144.5, 143.1 (d, *J* = 12.5 Hz), 133.7, 129.7, 127.3, 121.8 (d, *J* = 11.2 Hz), 112.6 (d, *J* = 23.7 Hz), 102.5 (d, *J* = 28.7 Hz), 95.6, 76.7, 50.2, 30.6, 27.0, 21.9, 21.5, 19.0, 13.5; ^{19}**F NMR** (375 MHz, $CDCl_3$) δ -114.2 (t, *J* = 9.4 Hz) **HRMS** (ESI) calcd for $C_{21}H_{23}FNO_2S$ $[M+H]^+$: 372.1434, found 372.1442.



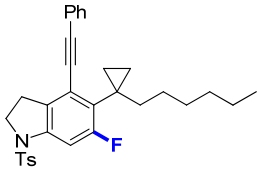
2g: **^{1}H NMR** (501 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 10.5 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 3.90 (d, *J* = 8.5 Hz, 2H), 2.91 (d, *J* = 8.0 Hz, 2H), 2.68 (d, *J* = 7.5 Hz, 2H), 2.42 (d, *J* = 7.5 Hz, 2H), 2.38 (s, 3H), 1.53 – 1.44 (m, 6H), 1.36 (m, 2H), 0.93 (d, *J* = 7.5 Hz, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.5 (d, *J* = 238.7 Hz), 144.2, 140.2 (d, *J* = 13.7 Hz), 133.7, 129.7, 129.4, 127.3, 126.3 (d, *J* = 18.7 Hz), 121.8 (d, *J* = 7.5 Hz), 102.4 (d, *J* = 31.2 Hz), 98.6, 76.0, 50.0, 31.9, 30.7, 27.6, 26.8, 22.5, 21.9, 21.5, 19.1, 13.9, 13.5; **^{19}F NMR** (375 MHz, $CDCl_3$) δ -117.6 (d, *J* = 10.1 Hz); **HRMS** (ESI) calcd for $C_{25}H_{31}FNO_2S$ $[M+H]^+$: 428.2060, found 428.2065.



2h: **^{1}H NMR** (501 MHz, $CDCl_3$) δ 7.72 (d, *J* = 10 Hz, 2H), 7.61 (d, *J* = 10 Hz, 2H), 7.55 (d, *J* = 10 Hz, 2H), 7.39 (d, *J* = 10.5 Hz, 2H), 7.28 (d, *J* = 10 Hz, 2H), 3.97 (t, *J* = 8.5 Hz, 2H), 3.04 (t, *J* = 8.5 Hz, 2H), 2.77 (t, *J* = 8 Hz, 2H), 2.39 (s, 3H), 1.66 (m, 2H), 0.98 (t, *J* = 8 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.5 (d, *J* = 237.5 Hz), 144.4, 140.6 (d, *J* = 12.5 Hz), 133.6, 131.7, 130.4 (q, *J* = 32.5), 129.8, 127.3 126.6, 126.4, 123.8 (q, *J* = 271.2), 120.2 (d, *J* = 7.5 Hz), 103.6 (d, *J* = 31.5), 95.3, 87.0, 50.0, 29.1, 27.6, 23.1, 21.5, 13.9; **^{19}F NMR** (375 MHz, $CDCl_3$) δ -63.3, -116.8 (d, *J* = 9.9 Hz); **HRMS** (ESI) calcd for $C_{27}H_{24}FNO_2S$ $[M+H]^+$: 502.1464, found 502.1454.

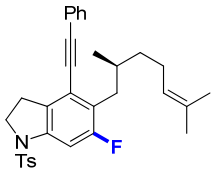


2i: **^{1}H NMR** (501 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.5 Hz, 2H), 7.52 (m, 2H), 7.41 (d, *J* = 10.5 Hz, 1H), 7.39 (m, 3H), 7.33 (d, *J* = 8.5 Hz, 2H), 4.01 (t, *J* = 7.5 Hz, 2H), 3.63 (t, *J* = 7.5 Hz, 2H), 3.09 (t, *J* = 8.5 Hz, 2H),3.00 (t, *J* = 8.5 Hz, 2H), 2.43 (s, 3H), 2.15 (qn, *J* = 8.5 Hz, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.6 (d, *J* = 240 Hz), 144.5, 141.1 (d, *J* = 12.5), 133.6, 131.6, 129.9, 128.9, 128.5, 127.3, 124.2 (d, *J* = 18.7), 122.5, 121.2 (d, *J* = 7.5), 103.1 (d, *J* = 31.2), 97.7, 84.2, 50.1, 44.6, 32.6, 27.6, 24.8, 21.6; **^{19}F NMR** (375 MHz, $CDCl_3$) δ -116.8 (d, *J* = 10.1 Hz); **HRMS** (ESI) calcd for $C_{26}H_{24}ClFNO_2S$ $[M+H]^+$: 468.1200, found 468.1194.

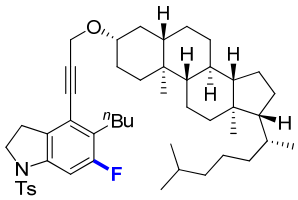


2j: **^{1}H NMR** (501 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.5 Hz, 2H), 7.47 (m, 2H), 7.35 (m, 3H), 7.32 (d, *J* = 10.5 Hz, 1H), 7.28 (d, *J* = 7.5 Hz, 2H), 3.96 (t, *J* = 8.5 Hz, 2H), 3.05 (t, *J* = 8.5 Hz, 2H), 2.39 (s, 3H), 1.32 (t, *J* = 4.6 Hz, 2H), 1.23 (m, 7H), 0.84 – 0.88 (m, 8H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.4 (d, *J* = 242 Hz), 144.4, 140.9 (d, *J* = 13 Hz),

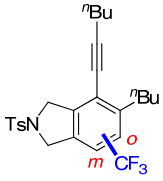
133.7, 131.3, 125.9, 129.8, 129.6, 128.6, 128.4, 128.3 (d, J = 17.5 Hz), 127.3, 123.1, 122.7(d, J = 7.5 Hz),102.9 (d, J = 31.3 Hz), 98.1, 85.6, 50.0, 39.9, 29.5, 27.6, 27.1, 22.6, 21.5, 19.4, 14.0, 13.7; **^{19}F NMR** (375 MHz, $CDCl_3$) δ -113.2 (d, J = 10.6 Hz); **HRMS** (ESI) calcd for $C_{32}H_{35}FNO_2S$ $[M+H]^+$: 516.2373, found 516.2377.



2k: ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.71 (d, J = 8.5 Hz, 2H), 7.45 (m, 2H), 7.37 (d, obscured by Ph resonance, 1H), 7.35 (m, 3H), 7.27 (d, J = 8.5 Hz, 2H), 5.09 (t, J = 7 Hz, 1H), 3.96 (t, J = 9 Hz, 2H), 3.03 (t, J = 9 Hz, 2H), 2.80 (ABX, J = 13, 5.5 Hz, 1H), 2.61 (ABX, J = 12, 8.5 Hz, 1H), 2.36 (s, 3H), 2.06 (m, 1H), 2.00 (m, 1H), 1.88 (m, 1H), 1.64 (s, 3H), 1.56 (s, 3H), 1.43 (m, 1H), 1.29 (m, 1H), 0.89 (d, J = 8.5 Hz, 6.5H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.7 (d, J = 238.7 Hz), 144.4, 140.6 (d, J = 12.5 Hz), 133.7, 131.4, 131.1, 129.8, 129.7, 128.7, 128.4, 127.3, 125.5 (d, J = 18.7 Hz), 124.7, 122.7, 121.4 (d, J = 7.5 Hz), 103.1(d, J = 31.2 Hz), 97.3, 85.0, 50.1, 37.2, 34.6, 33.7, 27.6, 25.7, 25.6, 21.5, 19.2, 17.6; **^{19}F NMR** (375 MHz, $CDCl_3$) δ -115.6 (d, J = 9.9 Hz); **HRMS** (ESI) calcd for $C_{32}H_{35}FNO_2S$ $[M+H]^+$: 516.2373, found 516.2372.

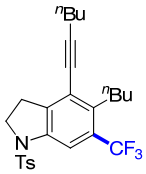


2l: ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.67 (d, J = 8.0 Hz, 2H), 7.32(d, J = 10 Hz, 1H), 7.26 (d, J = 8 Hz, 2H), 4.40 (s, 2H), 3.90 (t, J = 8.4 Hz, 2H), 3.50 (m, 1H), 2.91 (t, J = 8.4 Hz, 2H), 2.69 (t, J = 7.2 Hz, 2H), 2.39 (s, 3H), 1.96 (d, J = 13 Hz, 1H), 1.86 (d, J = 14 Hz, 1H), 1.81 (m, 1H), 1.73 (d, J = 13 Hz, 1H), 1.64 (m, 2H), 1.51 (m, 4H), 1.33 (m, 8H), 1.25 (m, 6H), 1.09 (m, 8H), 0.98 (m, 2H), 0.91 (m, 6H), 0.86 (d, J = 1.4 Hz, 3H), 0.85 (d, J = 1.4 Hz, 3H), 0.79 (s, 3H), 0.64 (s, 3H), 0.60 (t, J = 9.1 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.5 (d, J = 240.2 Hz), 144.4, 140.4 (d, J = 13.0 Hz), 133.7, 129.9, 129.8, 127.4, 126.6 (d, J = 19.2 Hz), 120.5 (d, J = 8.10 Hz), 103.2 (d, J = 30.6 Hz), 93.9, 80.8 (d, J = 3.40 Hz), 77.5, 56.3, 55.5, 54.4, 50.1, 44.9, 42.6, 40.1, 39.5, 37.0, 36.2, 35.8, 35.7, 35.5, 34.5, 32.1, 32.0, 28.9, 28.3, 28.0, 27.6, 26.9, 24.2, 23.8, 22.8, 22.6, 21.6, 21.3, 18.7, 14.0, 12.3, 12.1; **^{19}F NMR** (283 MHz, $CDCl_3$) δ -117.1 (d, J = 10.2 Hz); **HRMS** (ESI) calcd for $C_{49}H_{70}FNO_3S$ $[M+H]^+$: 772.5139, found 772.5145.

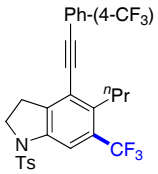


3b: *Ortho*-CF_3 isoindoline: ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.30 (s, 1H), 4.65 (s, 2H), 4.62 (s, 2H), 2.84 (m, 2H), 2.49 (t, *J* = 7.0 Hz, 2H), 2.41 (s, 3H), 1.61 (m, 2H), 1.51 (m, 4H), 1.43 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H), 0.94 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.9, 143.6, 142.8, 133.7, 133.4, 129.9, 128.6 (d, *J* = 30.0 Hz), 127.6, 124.2 (q, *J* = 274.7 Hz), 121.3, 119.0 (dd, *J* = 11.3, 5.5 Hz), 100.7, 75.3, 54.3, 54.1, 32.8, 31.2, 30.7, 23.3, 22.0, 21.5, 19.3, 13.8, 13.7, 13.6; **^{19}F NMR** (283 MHz, $CDCl_3$) δ -60.0; **HRMS** (ESI) calcd for $C_{26}H_{31}F_3NO_2S$ $[M+H]^+$: 478.2028, found 478.2029;

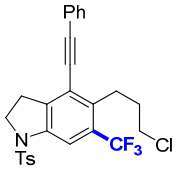
3b′: *Meta*-CF_3 isoindoline: ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.27 (s, 1H), 4.72 (s, 2H), 4.64 (s, 2H), 2.72 (m, 2H), 2.49 (t, *J* = 6.9 Hz, 2H), 2.41 (s, 3H), 1.61 (m, 2H), 1.52 (m, 4H), 1.34 (m, 2H), 0.98 (t, *J* = 7.3 Hz, 3H), 0.92 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.1, 143.8, 140.7, 133.7, 130.9, 129.9, 127.6, 125.01 (d, *J* = 4.1 Hz), 123.7 (q, *J* = 272.7 Hz), 123.5 (d, *J* = 32.6 Hz), 122.3, 101.6, 75.4, 53.8, 53.3, 33.8, 32.6, 30.7, 22.47, 22.0, 21.5, 19.4, 13.8, 13.6; **^{19}F NMR** (283 MHz, $CDCl_3$) δ -62.6.



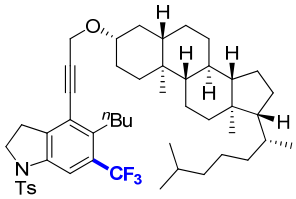
3g: ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 3.93 (t, *J* = 8.6 Hz, 2H), 2.98 (t, *J* = 8.5 Hz, 2H), 2.80 (m, 2H), 2.43 (t, *J* = 6.9 Hz, 2H), 2.39 (s, 3H), 1.59 – 1.39 (m, 8H), 0.94 (t, *J* = 7.3 Hz, 3H), 0.93 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.4, 139.6, 139.1, 138.7, 133.7, 128.2 (d, *J* = 29.9 Hz), 127.3, 124.3 (q, *J* = 274.2 Hz), 123.2, 110.9 (d, *J* = 6.3 Hz), 99.6, 75.8, 49.7, 32.9, 30.9, 30.7, 28.3, 23.2, 21.9, 21.5, 19.2, 13.7, 13.5; **^{19}F NMR** (283 MHz, $CDCl_3$) δ -59.7; **HRMS** (ESI) calcd for $C_{26}H_{31}F_3NO_2S$ $[M+H]^+$: 478.2028, found 478.2024.



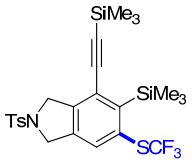
3h: ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.70 (d, *J* = 8.3 Hz, 2H) 7.62 (d, *J* = 8.2 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 3.99 (t, *J* = 8.5 Hz, 2H), 3.11 (t, *J* = 8.5 Hz, 2H), 2.88 (m, 2H), 2.40 (s, 3H), 1.05 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.6, 140.1, 139.3, 138.4, 133.6, 131.7, 130.6 (d, *J* = 33.0 Hz), 129.9, 128.7 (d, *J* = 29.9 Hz), 127.8, 126.3, 125.54, 125.52, 124.2 (q, *J* = 274.4 Hz), 123.8 (q, *J* = 272.9 Hz), 121.8, 112.1 (d, *J* = 6.2 Hz), 96.3, 86.6, 49.7, 33.4, 28.3, 24.4, 21.6, 14.7; **^{19}F NMR** (283 MHz, $CDCl_3$) δ -59.8, -63.3; **HRMS** (ESI) calcd for $C_{28}H_{24}F_6NO_2S$ $[M+H]^+$: 552.1432, found 552.1432.



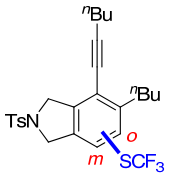
3i: **^{1}H NMR** (501 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.49 (m, 2H), 7.36 (m, 3H), 7.29 (d, *J* = 8.2 Hz, 2H), 3.99 (t, *J* = 8.6 Hz, 2H), 3.66 (t, *J* = 6.4 Hz, 2H), 3.12 (t, *J* = 8.6 Hz, 2H), 3.08 (m, 2H), 2.40 (s, 3H), 2.11 (m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.7, 140.4, 138.4, 136.9, 131.6, 130.0, 129.1, 128.8 (d, *J* = 30.6 Hz), 128.6, 128.3, 124.2 (q, *J* = 275.0 Hz), 122.7, 122.3, 111.6 (dd, *J* = 12.0, 5.8 Hz), 98.7, 83.9, 49.8, 45.1, 33.4, 29.0, 28.3, 21.6; **^{19}F NMR** (283 MHz, $CDCl_3$) δ -59.7; **HRMS** (ESI) calcd for $C_{27}H_{24}ClF_3NO_2S$ $[M+H]^+$: 518.1168, found 518.1174.



3l: **^{1}H NMR** (501 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 4.41 (s, 2H), 3.94 (t, *J* = 8.5 Hz, 2H), 3.49 (m, 1H), 3.00 (t, *J* = 8.5 Hz, 2H), 2.81 (m, 2H), 2.39 (s, 3H), 1.96 (d, *J* = 12.6 Hz, 1H), 1.89 –1.77 (m, 2H), 1.73 (d, *J* = 13.3 Hz, 1H), 1.64 (t, *J* = 11.8 Hz, 2H), 1.58 – 1.47 (m, 4H), 1.47 – 1.39 (m, 4H), 1.39 – 1.21 (m, 11H), 1.19 – 0.97 (m, 10H), 0.94 (t, *J* = 7.2 Hz, 3H), 0.90 (d, *J* = 6.3 Hz, 3H), 0.86 (d, *J* = 6.4 Hz, 6H), 0.79 (s, 3H), 0.64 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.5, 139.8, 139.5, 138.6, 133.6, 129.9, 128.4 (d, *J* = 29.8 Hz), 127.3, 124.2 (q, *J* = 247.4 Hz), 122.1, 111.8 (d, *J* = 6.1 Hz), 94.9, 80.5, 77.6, 56.5, 56.3, 55.4, 54.4, 49.7, 44.9, 42.6, 40.1, 39.5, 37.0, 36.2, 35.8, 35.5, 34.5, 33.0, 32.1, 30.9, 28.9, 28.3, 28.0, 24.2, 23.8, 23.2, 22.8, 22.6, 21.6, 21.3, 18.7, 13.8, 12.3, 12.1; **^{19}F NMR** (283 MHz, $CDCl_3$) δ -59.7; **HRMS** (ESI) calcd for $C_{50}H_{71}F_3NO_3S$ $[M+H]^+$: 822.5107, found 822.5115.

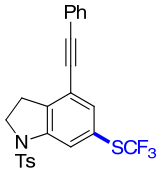


4a: **^{1}H NMR** (501 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.6 Hz, 2H), 7.42 (s, 1H), 7.33 (d, *J* = 8.6 Hz, 2H), 4.64 (s, 4H), 2.41 (s, 3H), 0.48 (s, 9H), 0.27 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.2, 143.9, 143.6, 137.6, 133.7, 132.3, 130.5, 129.9, 129.5 (q, *J* = 308.3 Hz), 127.6, 125.9, 106.4, 102.2, 54.3, 54.0, 21.5, 2.90, -0.41; **^{19}F NMR** (283 MHz, $CDCl_3$) δ -43.1; **HRMS** (ESI) calcd for $C_{24}H_{31}F_3NO_2S_2Si_2$ $[M+H]^+$: 542.1287, found 542.1281.

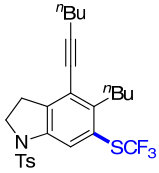


4b: *Ortho*-SCF_3 isoindoline: ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.1 Hz, 2H) 7.36 (s, 1H), 7.32 (d, *J* = 8.1 Hz, 2H), 4.64 (s, 2H), 4.61 (s, 2H), 3.02 (m, 2H), 2.48 (t, *J* = 6.9 Hz, 2H), 2.40 (s, 3H), 1.61 (m, 2H), 1.48 (m, 4H), 1.41 (m, 2H) 0.97 (t, *J* = 7.3 Hz, 3H), 0.94 (t, *J* = 7.3 Hz, 3H);**^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.6, 143.9, 142.6, 134.4, 133.7, 130.7, 129.9, 129.3 (q, *J* = 309.5 Hz), 127.6, 123.4, 120.6, 75.7, 54.2, 53.8, 32.7, 32.6, 30.7, 22.9, 22.0, 21.5, 19.3, 13.6, 13.5; **^{19}F NMR** (283 MHz, $CDCl_3$) δ -42.8; **HRMS** (ESI) calcd for $C_{26}H_{31}F_3NO_2S_2$ $[M+H]^+$: 510.1748, found 510.1749.

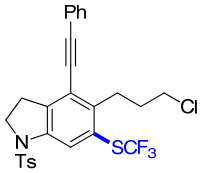
4b′: *Meta*-SCF_3 isoindoline: ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.2 Hz, 2H) 7.33 (d, *J* = 8.2 Hz, 2H), 7.31 (s, 1H), 4.73 (s, 2H), 4.69 (s, 2H), 2.71 (m, 2H), 2.49 (t, *J* = 7.0 Hz, 2H), 2.41 (s, 3H), 1.55 (m, 6H), 1.32 (td, *J* = 14.7, 7.4 Hz, 2H), 0.97 (t, *J* = 7.3 Hz, 2H), 0.92 (t, *J* = 7.3 Hz, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.8, 143.8, 140.3, 139.5, 136.8, 133.7, 129.9, 129.3 (q, *J* = 310.0 Hz), 127.6, 122.0. 116.7, 101.9, 75.5, 54.9, 54.5, 33.6, 32.6, 30.7, 29.7, 22.4, 22.0, 21.5, 19.4, 13.8, 13.6; **^{19}F NMR** (283 MHz, $CDCl_3$) δ -42.3.



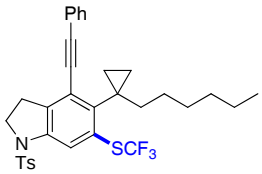
4f: ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.47 (m, 2H), 7.41 (s, 1H), 7.35 (m, 2H), 7.27 (d, *J* = 8.3 Hz, 2H), 4.00 (t, *J* = 8.6 Hz, 2H), 3.11 (t, *J* = 8.6 Hz, 2H), 2.39 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.8, 143.1, 137.3, 134.0, 133.2, 131.7, 129.9, 129.6 (q, *J* = 309.0 Hz), 129.0, 128.4, 127.4, 124.0, 122.3, 121.6, 121.5, 94.8, 85.1, 49.9, 27.7.; **^{19}F NMR** (283 MHz, $CDCl_3$) δ -43.1; **HRMS** (ESI) calcd for $C_{24}H_{19}F_3NO_2S_2$ $[M+H]^+$: 474.0809, found 474.0807.



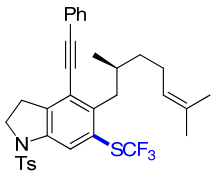
4g: ^{1}H NMR (501 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.69 (d, *J* = 8.2 Hz, 2H) 7.24 (d, *J* = 8.3 Hz, 2H), 3.91 (t, *J* = 8.5 Hz, 2H), 2.97 (m, 4H), 2.42 (t, *J* = 6.9 Hz, 2H), 2.38 (s, 3H), 1.54 (m, 2H), 1.46 (m, 4H), 1.38 (m, 2H), 0.93 (m, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.4, 144.5, 140.0, 138.2, 133.2, 129.78, 129.73 (q, *J* = 309.1 Hz), 127.4, 122.8, 122.4, 122.1, 99.2, 76.3, 49.7, 32.8, 32.4, 30.8, 28.3, 22.9, 22.0, 21.6, 19.2, 13.9, 13.6; **^{19}F NMR** (283 MHz, $CDCl_3$) δ -42.8; **HRMS** (ESI) calcd for $C_{26}H_{31}F_3NO_2S_2$ $[M+H]^+$: 510.1748, found 510.1746.



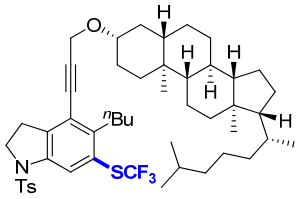
4i: **^{1}H NMR** (501 MHz, $CDCl_3$) δ 7.94, (s, 1H), 7.72 (d, *J* = 8.2 Hz, 2H) 7.48 (m, 2H), 7.36 (m, 3H), 7.27 (d, *J* = 8.2 Hz, 2H), 3.98 (t, *J* = 8.5 Hz, 2H), 3.63 (t, *J* = 6.4 Hz, 2H), 3.24 (m, 2H), 3.12 (t, *J* = 8.5 Hz, 2H), 2.39 (s, 3H), 2.06 (m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.7, 143.3, 140.8, 138.5, 133.2, 131.6, 129.9, 129.6 (q, *J* = 309.3 Hz), 129.1, 128.6, 127.4, 123.4, 122.9, 122.4, 121.9, 98.2, 84.3, 49.7, 44.8, 33.2, 30.4, 28.3, 21.6; **^{19}F NMR** (283 MHz, $CDCl_3$) δ -42.7; **HRMS** (ESI) calcd for $C_{27}H_{24}ClF_3NO_2S_2$ $[M+H]^+$: 550.0889, found 550.0884.



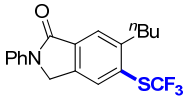
4j: **^{1}H NMR** (501 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.47 (m, 2H), 4.36 (m, 3H), 7.27 (d, *J* = 8.2 Hz, 2H), 3.98 (m, 2H), 3.10 (m, 2H), 2.39 (s, 3H), 1.82 (td, *J* = 12.6 Hz, 4.1 1H), 1.39 (m, 2H), 1.23 (m, 7H), 1.07 (m, 1H), 0.94 (m, 2H), 0.81 (t, *J* = 6.8 Hz, 3H) 0.78 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.5, 144.3, 140.7, 137.0, 133.4, 131.3, 129.82, 129.80 (q, *J* = 309.2 Hz), 129.7, 128.8, 128.52, 128.45, 127.4, 123.8, 123.1, 119.5, 99.0, 85.7, 49.8, 40.3, 31.8, 29.6, 28.2, 26.9, 23.8, 22.6, 21.6, 16.6, 14.8, 14.0; **^{19}F NMR** (283 MHz, $CDCl_3$) δ -40.6; **HRMS** (ESI) calcd for $C_{33}H_{35}F_3NO_2S_2$ $[M+H]^+$: 598.2061, found 598.2067.



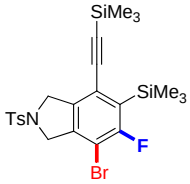
4k: **^{1}H NMR** (501 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.45 (m, 2H), 7.35 (m, 3H), 7.26 (d, *J* = 8.2 Hz, 2H), 5.05 (t, *J* = 6.9 Hz, 1H), 3.98 (t, *J* = 8.6 Hz, 2H), 3.11 (t, *J* = 8.6 Hz, 2H), 3.09 (dd, *J* = 13.2, 8.8 Hz, 1H), 2.96 (dd, *J* = 13.2, 8.8 Hz, 1H), 2.39 (s, 3H), 2.06 (m, 1H), 1.98 (m, 1H), 1.89 (m, 1H), 1.64 (s, 3H), 1.56 (s, 3H), 1.41 (m, 1H), 1.31 (m, 1H), 0.87 (d, *J* = 7.4 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.6, 144.1, 140.3, 138.2, 133.4, 131.4, 131.3, 131.0, 129.8, 129.7 (q, *J* = 309.8 Hz), 129.6, 128.9, 128.5, 127.4, 124.6, 124.1, 122.7, 122.6, 122.3, 98.0, 85.3, 49.8, 39.6, 37.2, 34.9, 28.4; ; **^{19}F NMR** (283 MHz, $CDCl_3$) δ -42.7; **HRMS** (ESI) calcd for $C_{33}H_{35}F_3NO_2S_2$ $[M+H]^+$: 598.2061, found 598.2046.



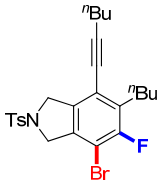
4l: **^{1}H NMR** (501 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.69 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 8.1 Hz, 2H), 4.41 (s, 2H), 3.92 (t, *J* = 8.5 Hz, 2H), 3.49 (m, 1H), 2.99 (m, 4H), 2.39 (s, 3H), 1.93 (d, *J* = 12.5 Hz, 1H), 1.89 –1.77 (m, 2H), 1.73 (d, *J* = 13.3 Hz, 1H), 1.64 (t, *J* = 13.9 Hz, 2H), 1.59 – 1.43 (m, 6H), 1.42 – 1.19 (m, 12H), 1.18 – 0.97 (m, 10H), 0.93 (t, *J* = 7.2 Hz, 3H), 0.90 (d, *J* = 6.4 Hz, 3H), 0.864 (d, *J* = 6.6 Hz, 3H), 0.860 (d, *J* = 6.6 Hz, 3H), 0.79 (s, 3H), 0.65 (s, 3H), 0.60 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.6, 144.5, 140.2, 138.6, 133.2, 129.8, 129.7 (q, *J* = 309.2 Hz), 127.4, 123.0, 122.9, 121.2, 94.5, 80.9, 77.5, 56.5, 56.3, 55.4, 54.4, 49.7, 44.9, 42.6, 40.1, 39.5, 37.0, 36.2, 35.8, 35.5, 34.5, 32.9, 32.4, 32.1, 28.9, 28.3, 28.0, 24.2, 23.8, 22.8, 22.6, 21.6, 21.3, 18.7, 14.0, 12.3, 12.1; **^{19}F NMR** (283 MHz, $CDCl_3$) δ -42.7; **HRMS** (ESI) calcd for $C_{50}H_{71}F_3NO_3S_2$ $[M+H]^+$: 854.4827, found 854.4810.



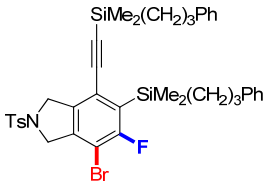
4o: **^{1}H NMR** (501 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.84 (d, *J* = 7.7 Hz, 2H), 7.83 (s, 1H), 7.42 (t, *J* = 7.9 Hz, 2H), 7.19 (t, *J* = 7.3 Hz, 1H), 4.85 (s, 2H), 3.00 (m, 2H), 1.63 (m, 2H), 1.42 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.4, 148.6, 139.2, 138.0, 135.8, 131.7, 129.4 (d, *J* = 308.9 Hz), 129.2, 128.0, 125.4, 124.9, 119.6, 50.2, 34.1, 33.4, 22.5, 13.9; **^{19}F NMR** (283 MHz, $CDCl_3$) δ -42.1.



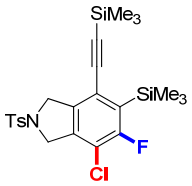
5a: **^{1}H NMR** (501 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 4.68 (s, 2H), 4.59 (s, 2H), 2.42 (s, 3H), 0.39 (s, 9H), 0.25 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.8 (d, *J* = 239.8 Hz), 143.9, 139.7, 136.8, 133.6, 130.0 128.7 (d, *J* = 33.2 Hz), 127.5, 123.1 (d, *J* = 13.0 Hz), 105.0 (d, *J* = 33.7 Hz), 101.4, 77.0, 55.7, 54.8, 21.5, 0.4, -0.3; **^{19}F NMR** (375 MHz, $CDCl_3$) δ -96.0; **HRMS** (ESI) calcd for $C_{23}H_{30}BrFNO_2S$ $[M+H]^+$: 538.0703, found 538.0709.



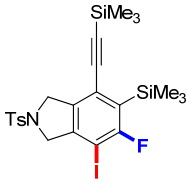
5b: **^{1}H NMR** (501 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8 Hz, 2H), 7.34 (d, *J* = 8 Hz, 2H), 4.67 (s, 2H), 4.56 (s, 2H), 2.75 (t, *J* = 7 Hz, 2H), 2.46 (t, *J* = 7 Hz, 2H), 2.44 (s, 3H), 1.62 (m, 2H), 1.50 (m, 2H), 1.35 (m, 2H), 0.98 (t, *J* = 7 Hz, 3H), 0.92 (t, *J* = 7 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.7 (d, *J* = 242.5 Hz), 143.8, 135.3, 134.7, 133.7, 132.6 (d, *J* = 20 Hz), 129.9, 127.6, 127.5, 119.2 (d, *J* = 6.2Hz), 103.4 (d, *J* = 26.2 Hz), 100.3, 74.9, 55.4, 54.8, 31.6, 30.6, 27.6, 21.9, 21.5, 19.3, 13.8, 13.7, 13.5; **^{19}F NMR** (375 MHz, $CDCl_3$) δ -113.9; **HRMS** (ESI) calcd for $C_{25}H_{30}BrFNO_2S$ $[M+H]^+$: 506.1165, found 506.1164.



5m: **^{1}H NMR** (501 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.32 – 7.14 (m, 10H), 7.12 (d, *J* = 8.0 Hz, 2H), 4.67 (s, 2H), 4.60 (s, 2H), 2.73 (t, *J* = 8.5 Hz, 2H), 2.61 (t, *J* = 8.5 Hz, 2H), 2.41 (s, 3H), 1.78 (m, 2H), 1.61 (m, 2H), 0.98 (m, 2H), 0.78 (m, 2H), 0.39 (s, 3H), 0.38 (s, 3H), 0.24 (s, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.0 (d, *J* = 240 Hz), 143.9, 142.3 (d, *J* = 18.7 Hz), 139.8, 137.1, 133.7, 130.0, 128.5, 128.4, 128.3, 128.2, 127.5, 125.8 (d, *J* = 12.5 Hz), 105.2 (d, *J* = 30 Hz), 104.4, 102, 55.7, 54.8, 39.7, 39.5, 25.94, 25.91, 21.5, 15.9, 15.6, -1.1, -2.0; **^{19}F NMR** (375 MHz, $CDCl_3$) δ -99.2; **HRMS** (ESI) calcd for $C_{39}H_{46}BrFNO_2SSi_2$ $[M+H]^+$: 746.1955, found 746.1950.

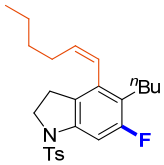


6a: **^{1}H NMR** (501 MHz, $CDCl_3$) δ 7.79 (d, *J* = 10 Hz, 2H), 7.35 (d, *J* = 10 Hz, 2H), 4.64 (s, 2H), 4.62 (s, 2H), 2.42 (s, 3H), 0.39 (s, 9H), 0.25 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.0 (d, *J* = 255 Hz), 143.9, 137.5, 137.0, 133.7, 129.9, 129.0 (d, *J* = 31.2), 127.5, 22.2 (d, *J* = 12.5), 116.6 (d, *J* = 26.2), 104.8, 101.4, 54.6, 53.9, 21.5, 0.3, -0.3; **^{19}F NMR** (375 MHz, $CDCl_3$) δ -104.1; **HRMS** (ESI) calcd for $C_{23}H_{30}ClFNO_2SSi_2$ $[M+H]^+$: 494.1208, found 494.1204.

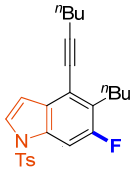


7a: **^{1}H NMR** (501 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8 Hz, 2H), 7.35 (d, *J* = 8 Hz, 2H), 4.71 (s, 2H), 4.53 (s, 2H), 2.41 (s, 3H), 0.38 (s, 9H), 0.25 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.4 (d, *J* = 237.5 Hz), 143.9, 143.8 (d, *J* = 12.5 Hz), 136.1, 133.7, 129.9, 127.6, 127.5, 127.3, 124.3 (d, *J* = 12.5 Hz), 105.3, 101.4, 78.4 (d, *J* = 36.2 Hz), 59.0, 55.0,

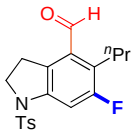
21.5, 0.40, -0.38; **^{19}F NMR** (375 MHz, $CDCl_3$) δ -82.2; **HRMS** (ESI) calcd for $C_{23}H_{30}FINO_2SSi_2$ $[M+H]^+$ 586.0565, found 586.0570.



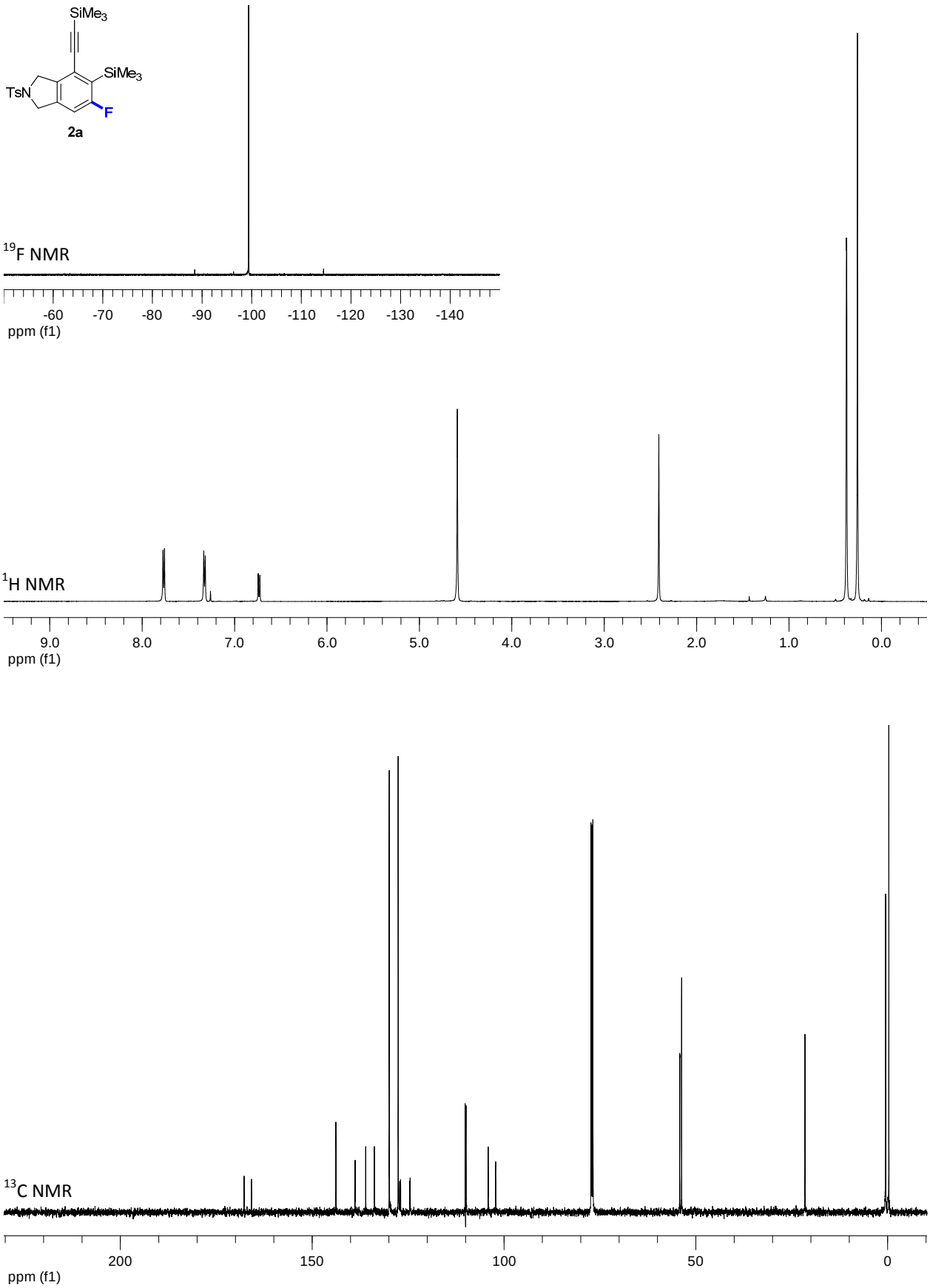
8g: **^{1}H NMR** (501 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8 Hz, 2H), 7.27 (d, *J* = 10 Hz, 1H), 7.24 (d, *J* = 8 Hz, 2H), 6.13 (d, *J* = 11Hz, 1H), 5.69 (dt, *J* = 10, 7.5 Hz, 1H), 3.88 (d, *J* = 8.5 Hz, 2H), 2.58 (d, *J* = 8 Hz, 2H), 2.47 (d, *J* = 7 Hz, 2H), 2.37 (s, 3H), 1.62 (q, *J* = 7.5 Hz, 2H), 1.38 – 1.18 (m, 6H), 0.89 (t, *J* = 8 Hz, 3H), 0.79 (t, *J* = 8 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.6 (d, *J* = 240 Hz), 144.0, 140.0 (d, *J* = 13 Hz), 135.5 (d, *J* = 6 Hz), 134.8, 134.0, 129.6, 127.3, 125.9, 124.4, 123.4 (d, *J* = 16.7 Hz), 102.0 (d, *J* = 30.2 Hz), 50.3, 31.9, 31.1, 28.5, 27.3, 25.8, 22.6, 22.3, 21.5, 13.9, 13.8; **^{19}F NMR** (375 MHz, $CDCl_3$) δ -117.9 (d, *J* = 10.1 Hz); **HRMS** (ESI) calcd for $C_{25}H_{33}FNO_2S$ $[M+H]^+$ 430.2216, found 430.2212.

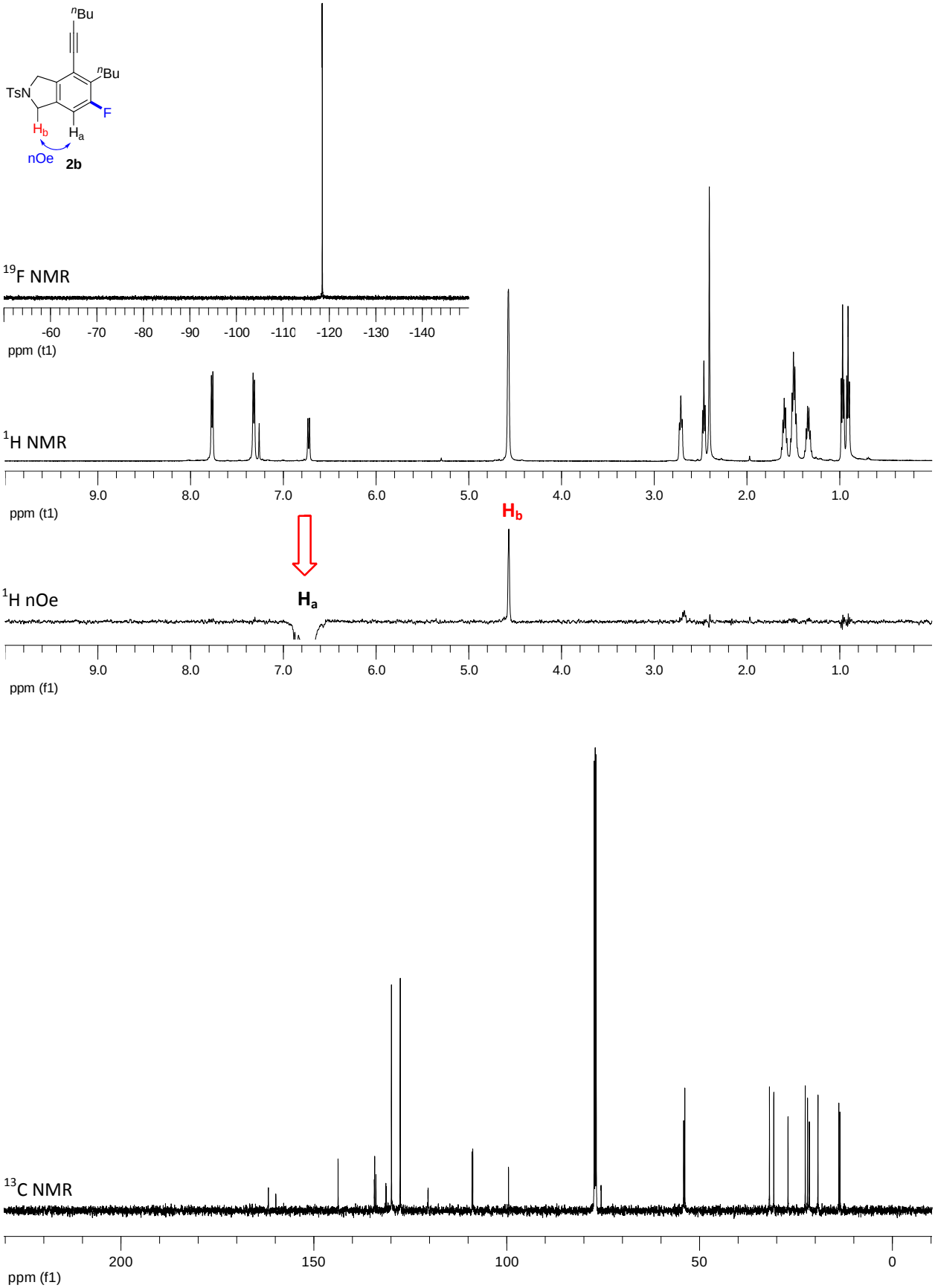


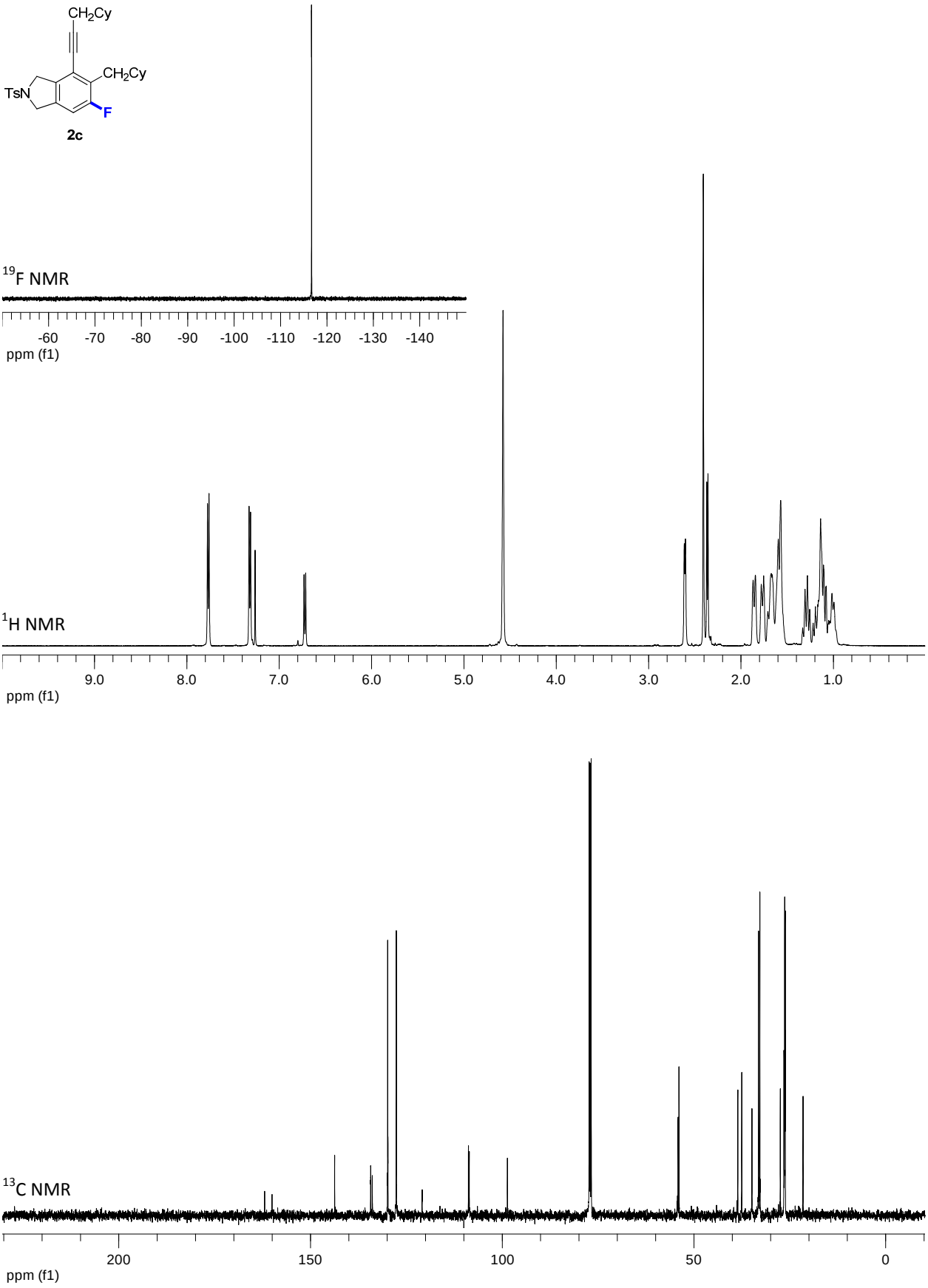
9g: **^{1}H NMR** (501 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8 Hz, 2H), 7.61(d, *J* = 10 Hz, 1H), 7.49 (d, *J* = 3.5 Hz, 1H), 7.23 (d, *J* = 8 Hz, 2H), 6.73 (d, *J* = 3.5 Hz, 1H), 2.84 (t, *J* = 8 Hz, 2H), 2.52 (t, *J* = 7 Hz, 2H), 2.34 (s, 3H), 1.63 (qn, *J* = 8 Hz, 2H), 1.55 (m, 4H), 1.39 (qn, *J* = 8 Hz, 2H), 0.97 (t, *J* = 8 Hz, 3H), 0.94 (t, *J* = 8 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.3 (d, *J* = 238.8 Hz), 145.1, 135.1, 132.5 (d, *J* = 14.6 Hz), 130.0, 129.0, 128.3 (d, *J* = 19.3 Hz), 126.8, 126.2 (d, *J* = 2.5 Hz), 117.1, 108.7, 100.6 (d, *J* = 30.4 Hz), 98.2, 76.1 (d, *J* = 3.2 Hz), 32.2, 30.9, 27.3, 22.6, 22.0, 21.6, 19.3, 13.9, 13.6; **^{19}F NMR** (375 MHz, $CDCl_3$) δ -120.0 (d, *J* = 9.7 Hz); **HRMS** (ESI) calcd for $C_{25}H_{29}FNO_2S$ $[M+H]^+$ 426.1903, found 426.1902.

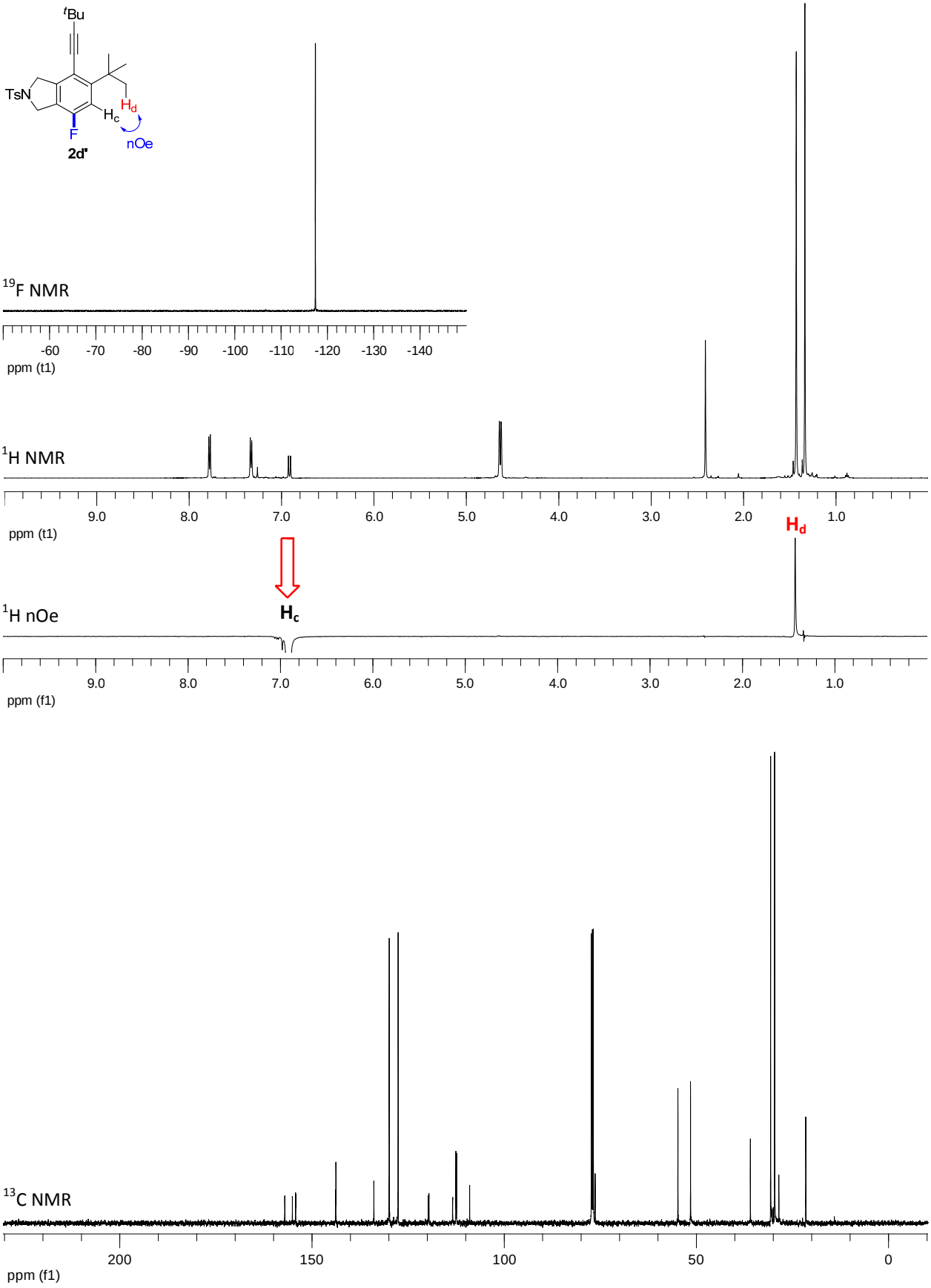


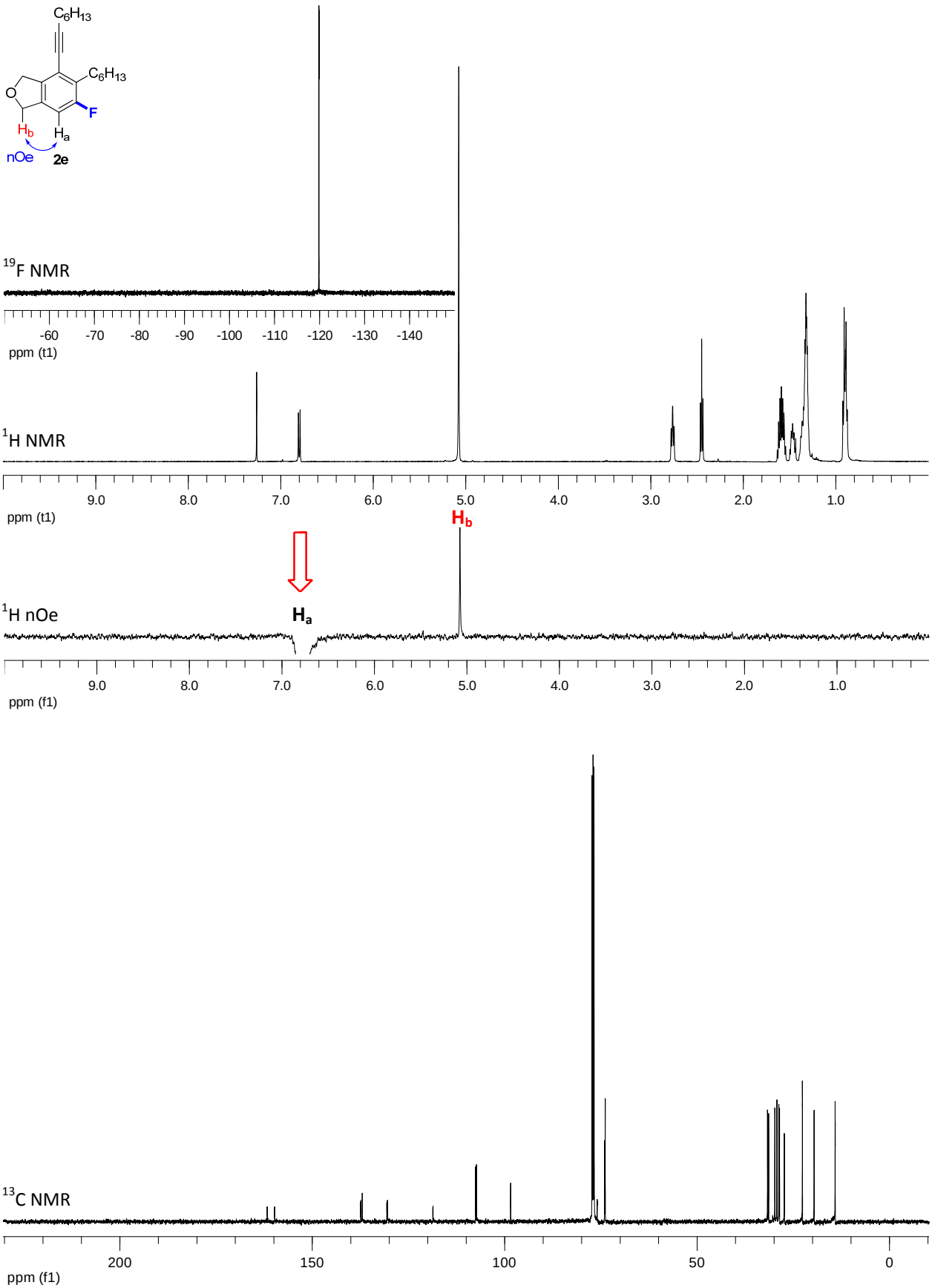
10n: **^{1}H NMR** (501 MHz, $CDCl_3$) δ 10.4 (s, 1H), 7.77(d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.09 (d, *J* = 8.8 Hz, 1H), 4.84 (s, 2H), 4.56 (s, 2H), 2.96 (t, *J* = 7.3 Hz, 2H), 2.39 (s, 3H), 1.61 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 190.0 (d, *J* = 2 Hz), 160.9 (d, *J* = 245 Hz), 143.8, 136.8 (d, *J* = 8.9 Hz), 133.7 (d, *J* = 19.7 Hz), 132.7 (d, *J* = 16.9 Hz), 129.9, 129.7, 127.6, 127.5, 115.0 (d, *J* = 25.9 Hz), 54.5, 52.3, 25.5, 25.4, 25.3, 21.5, 13.7; **^{19}F NMR** (375 MHz, $CDCl_3$) δ -117.8 (d, *J* = 8.7 Hz); **GC-Ms** $[M]^+$ = 361.1.

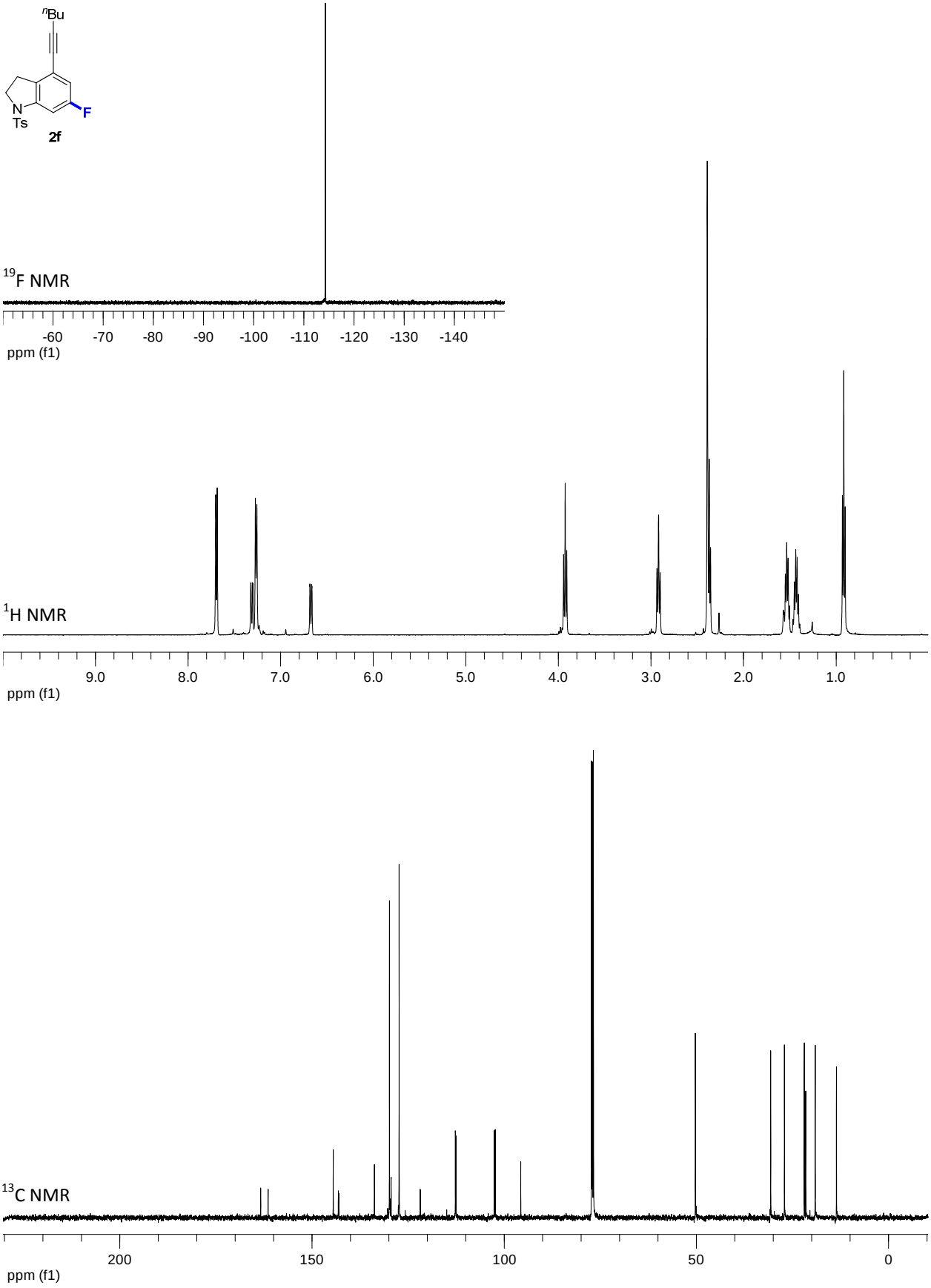


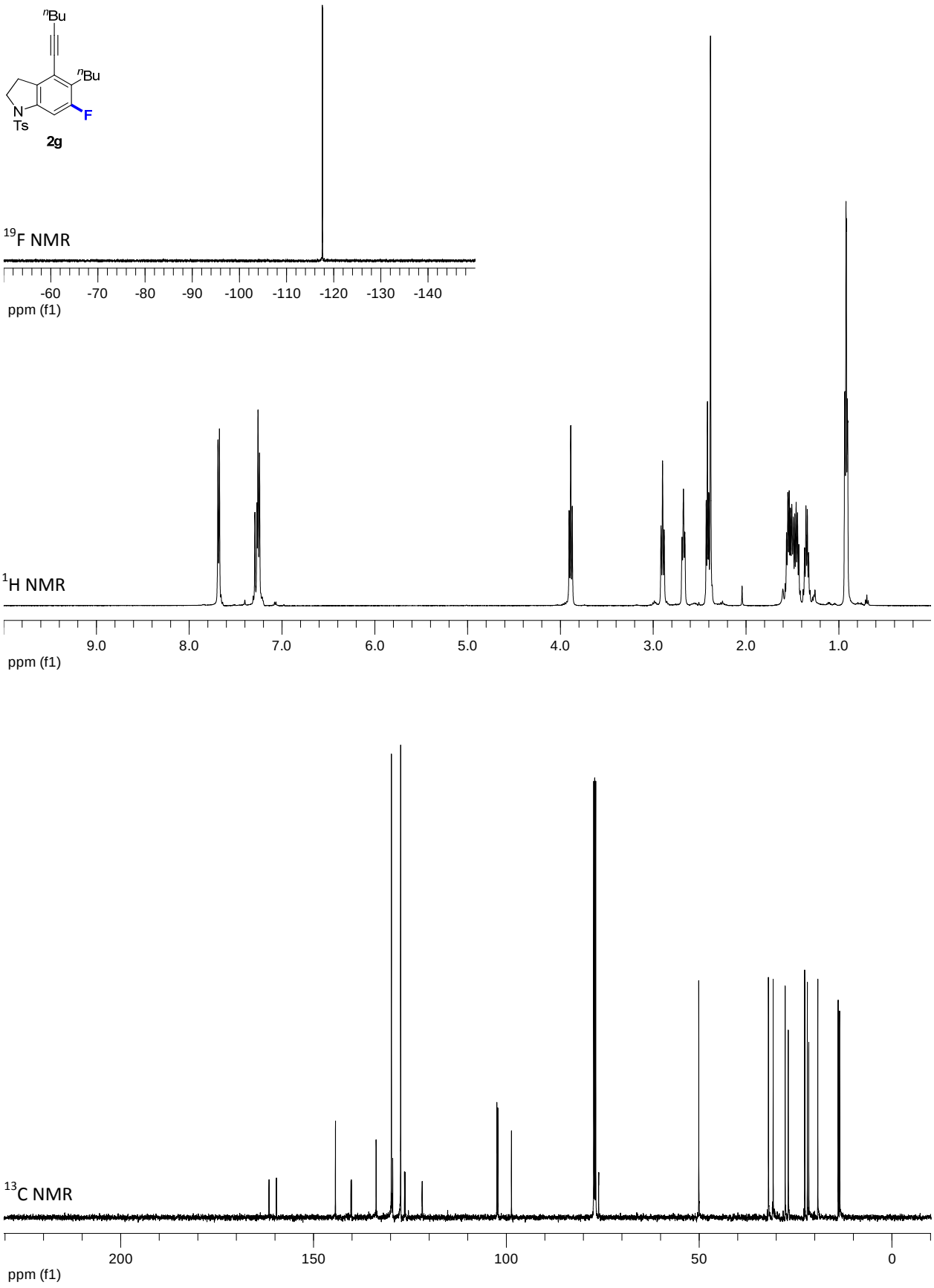


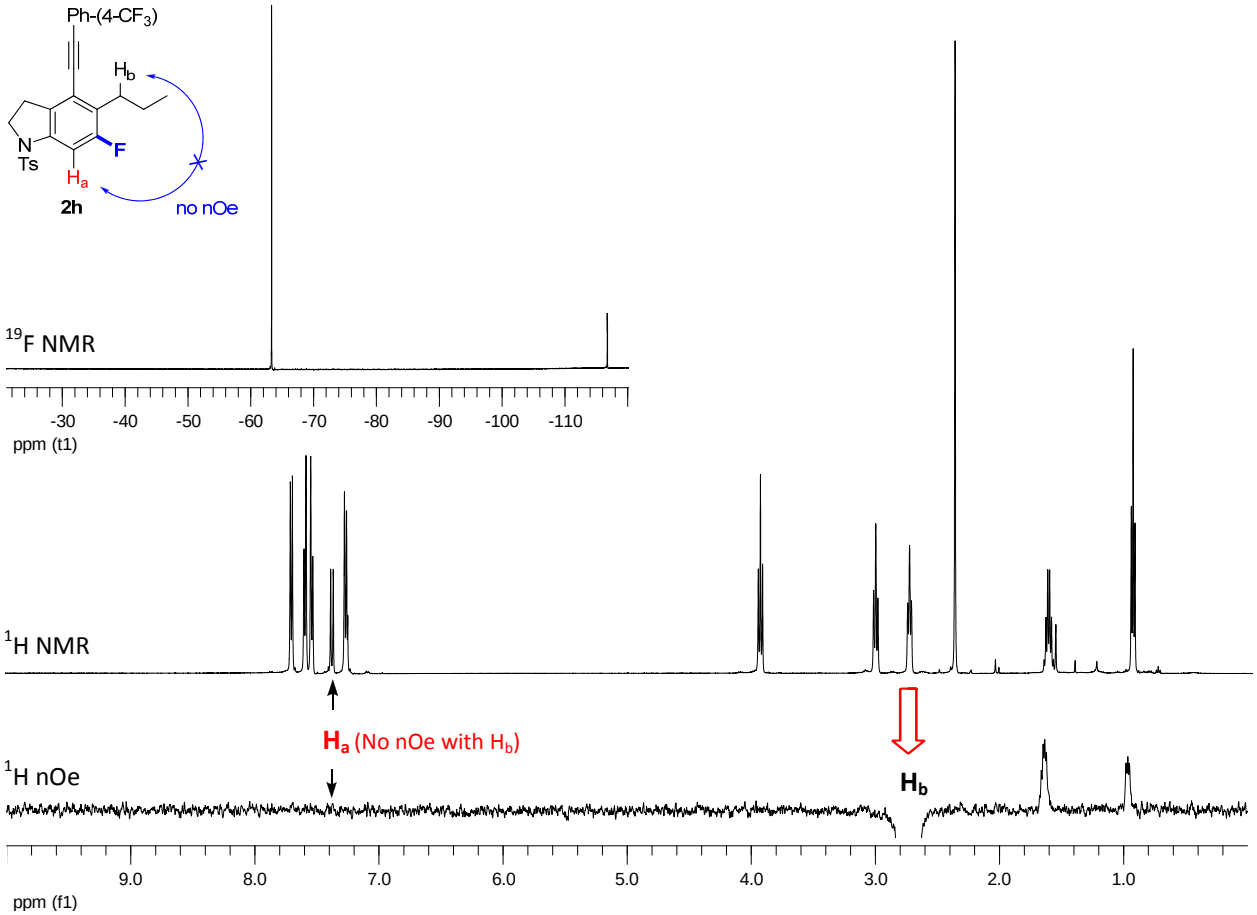


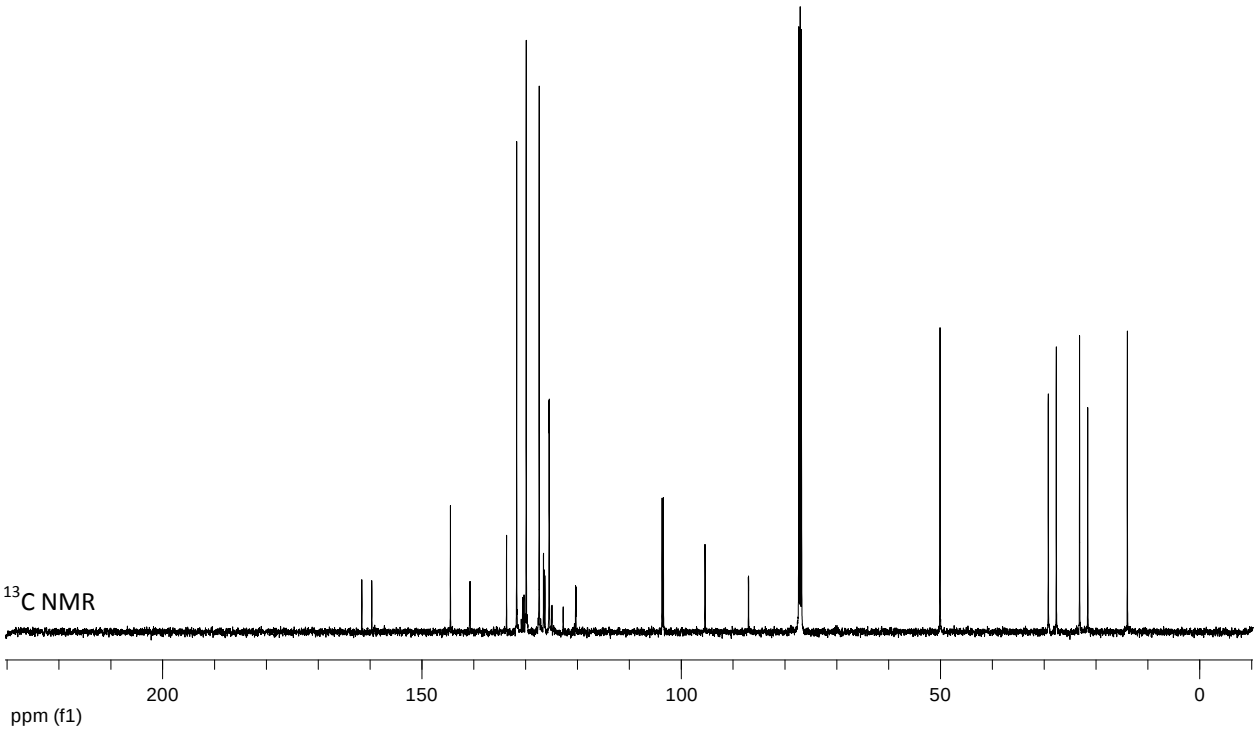


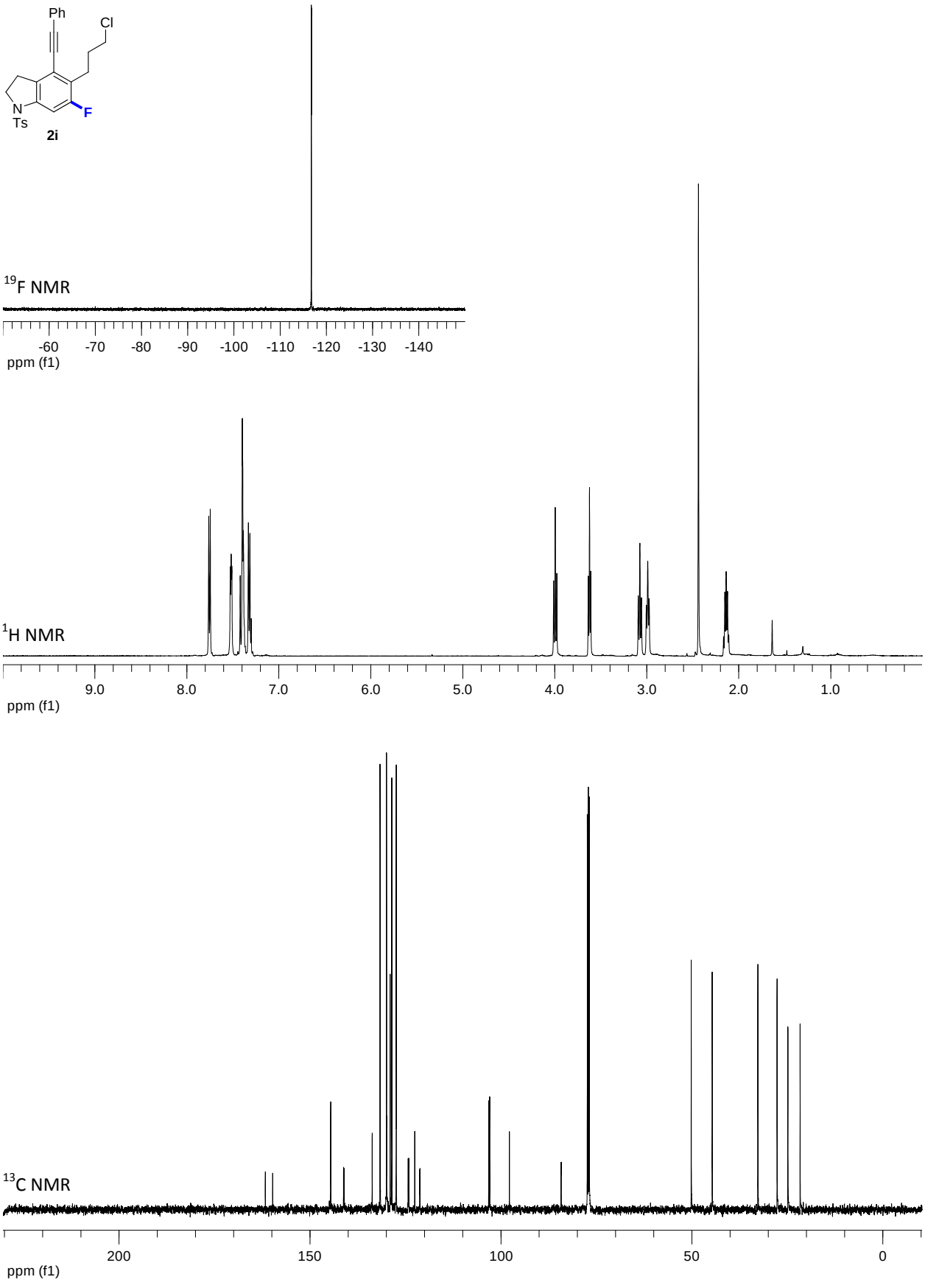


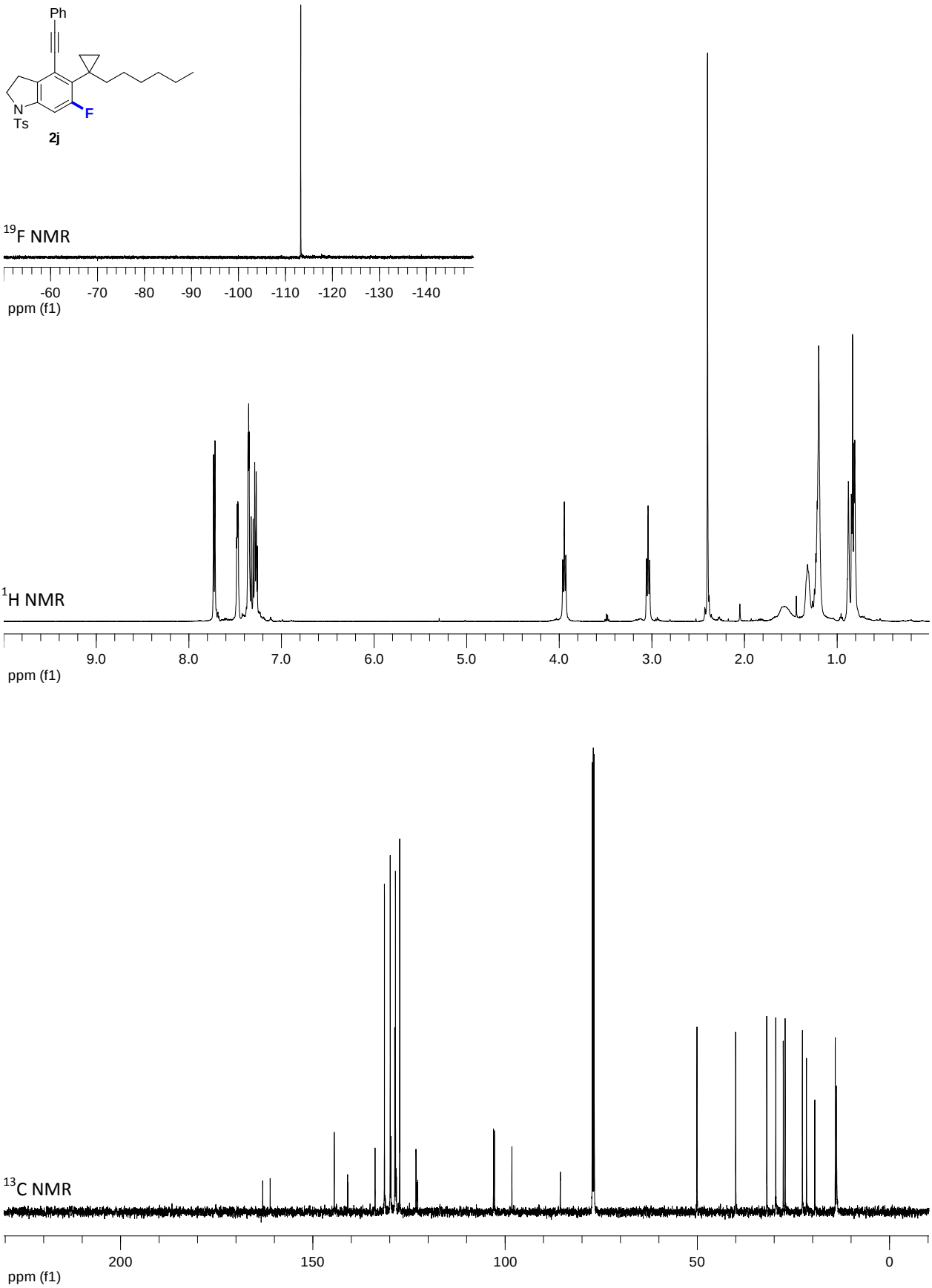


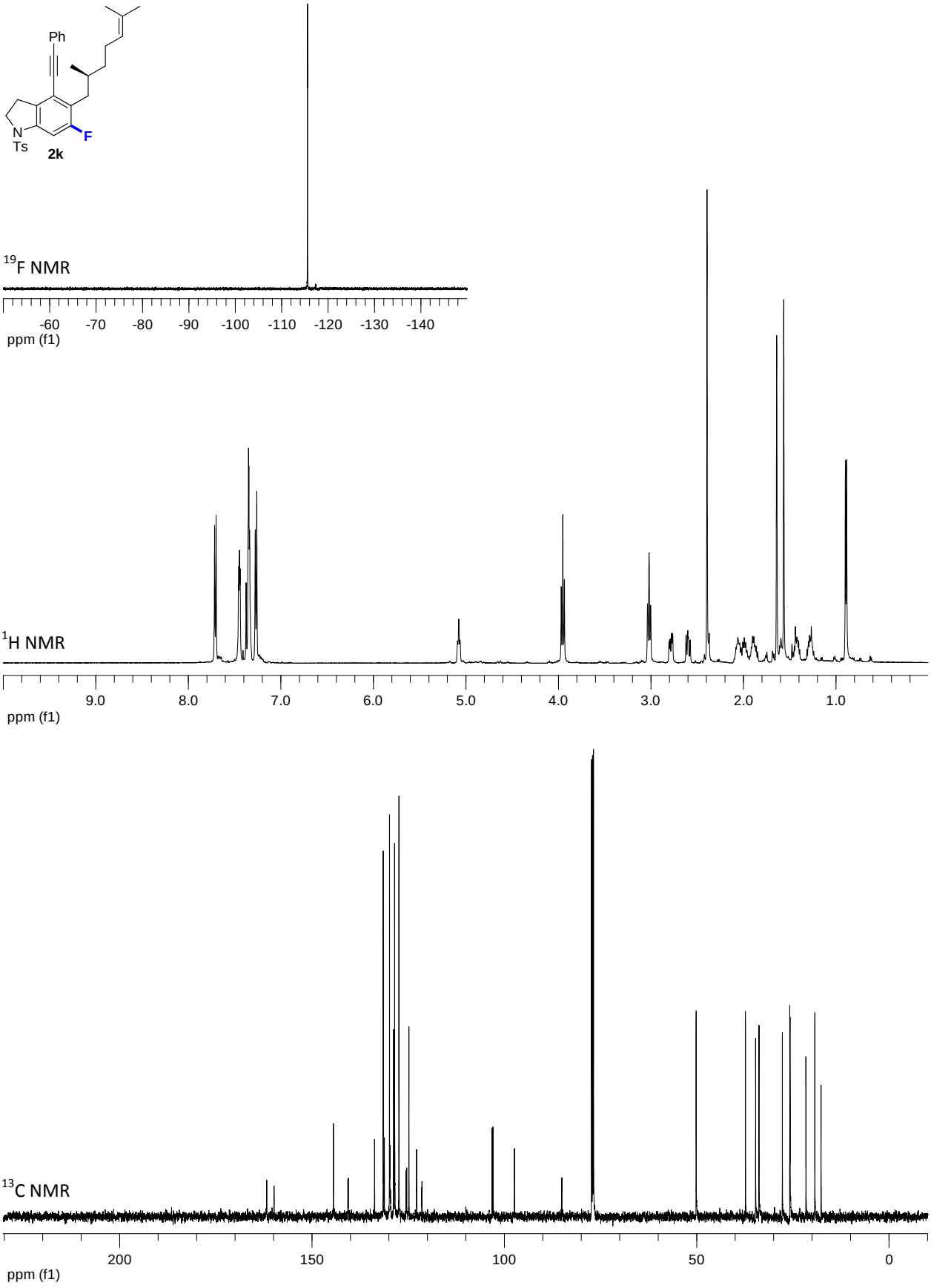




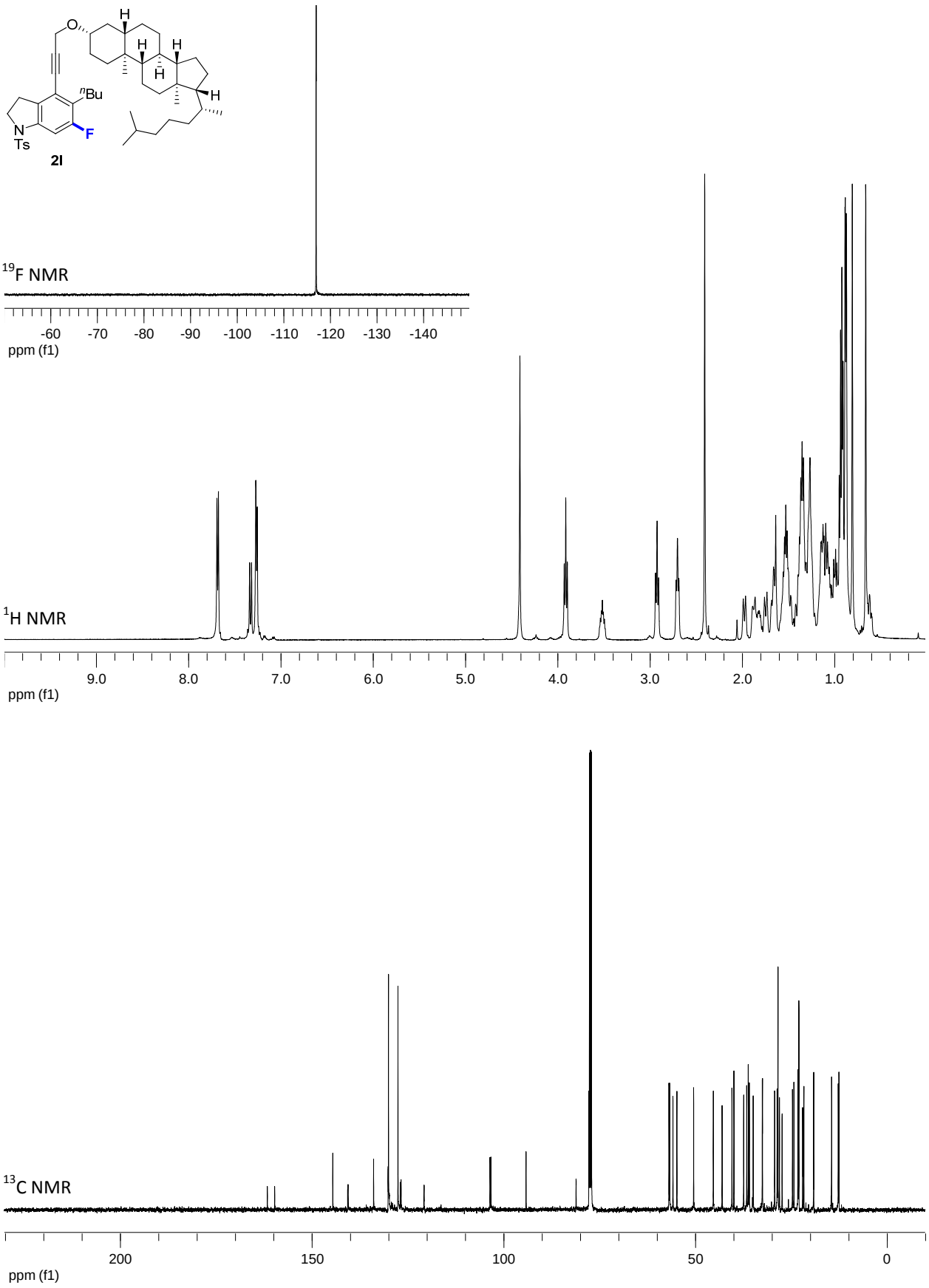


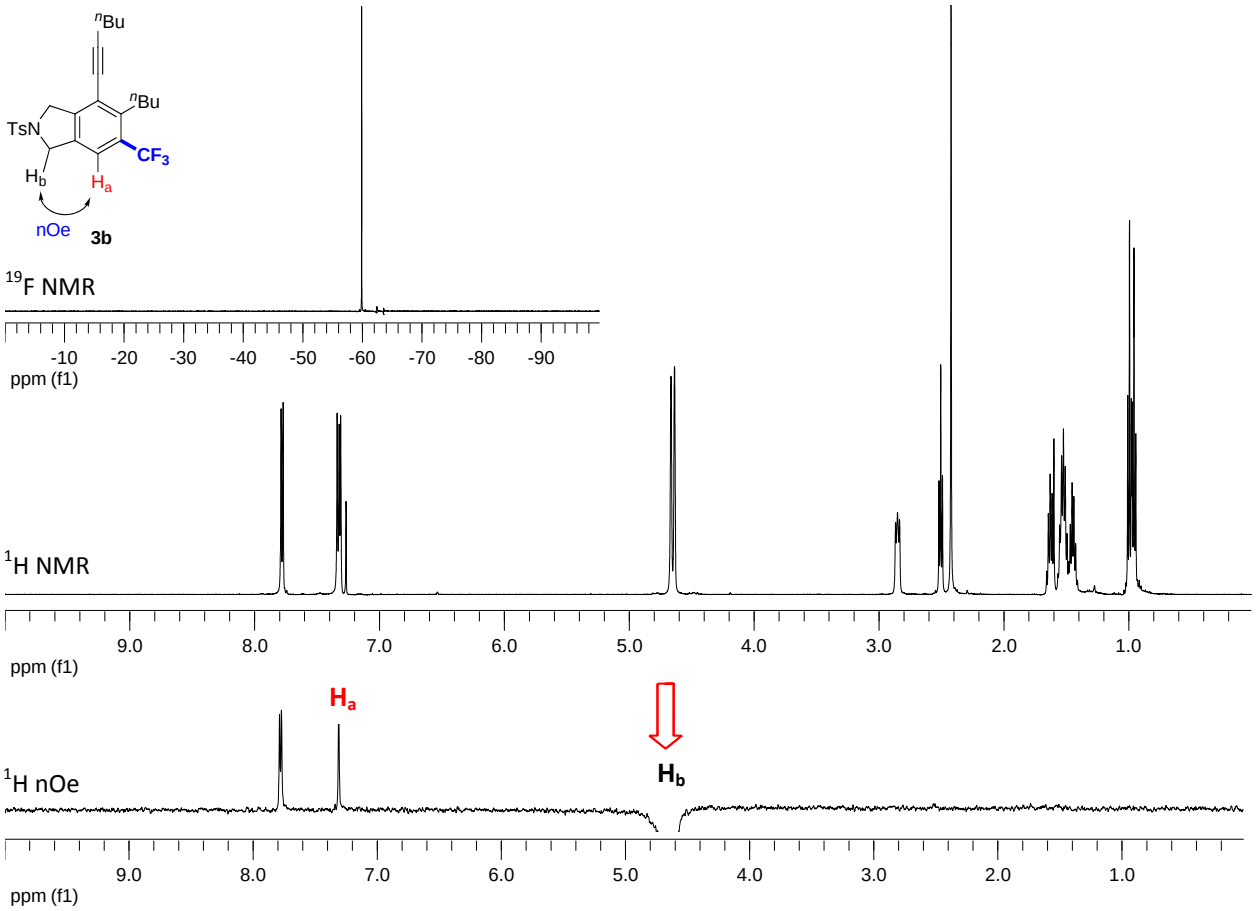


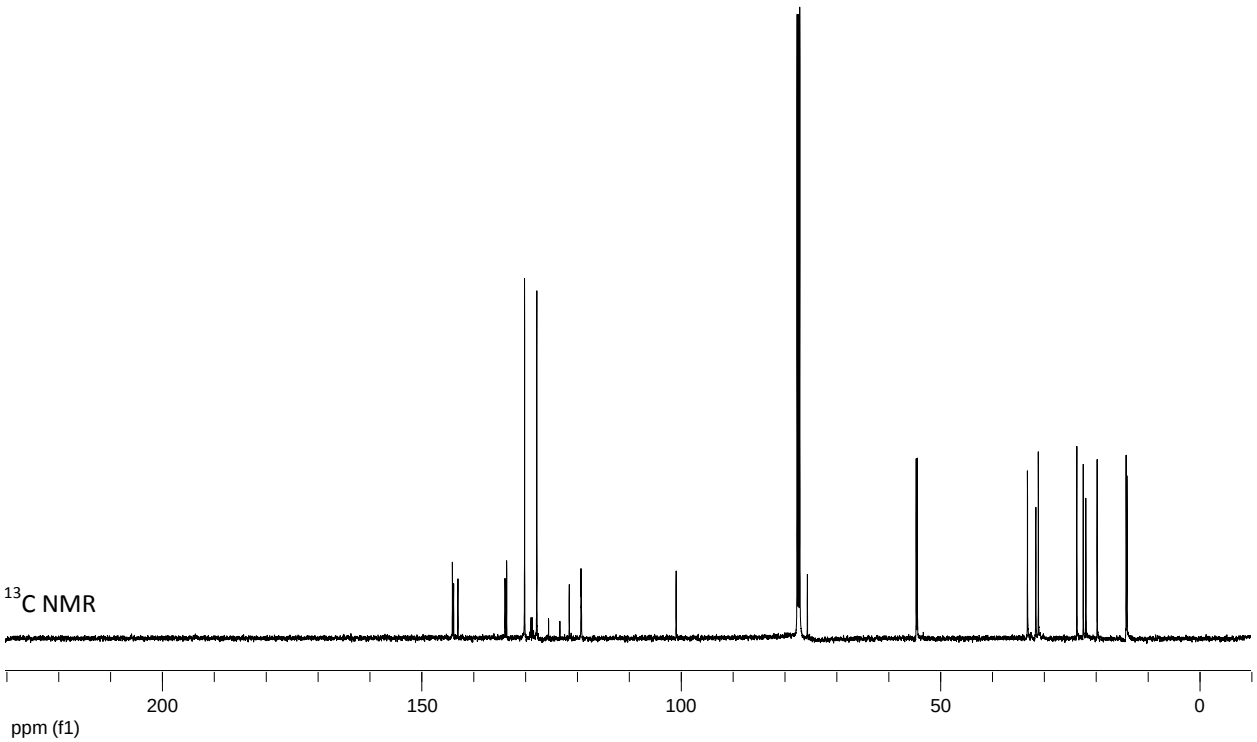


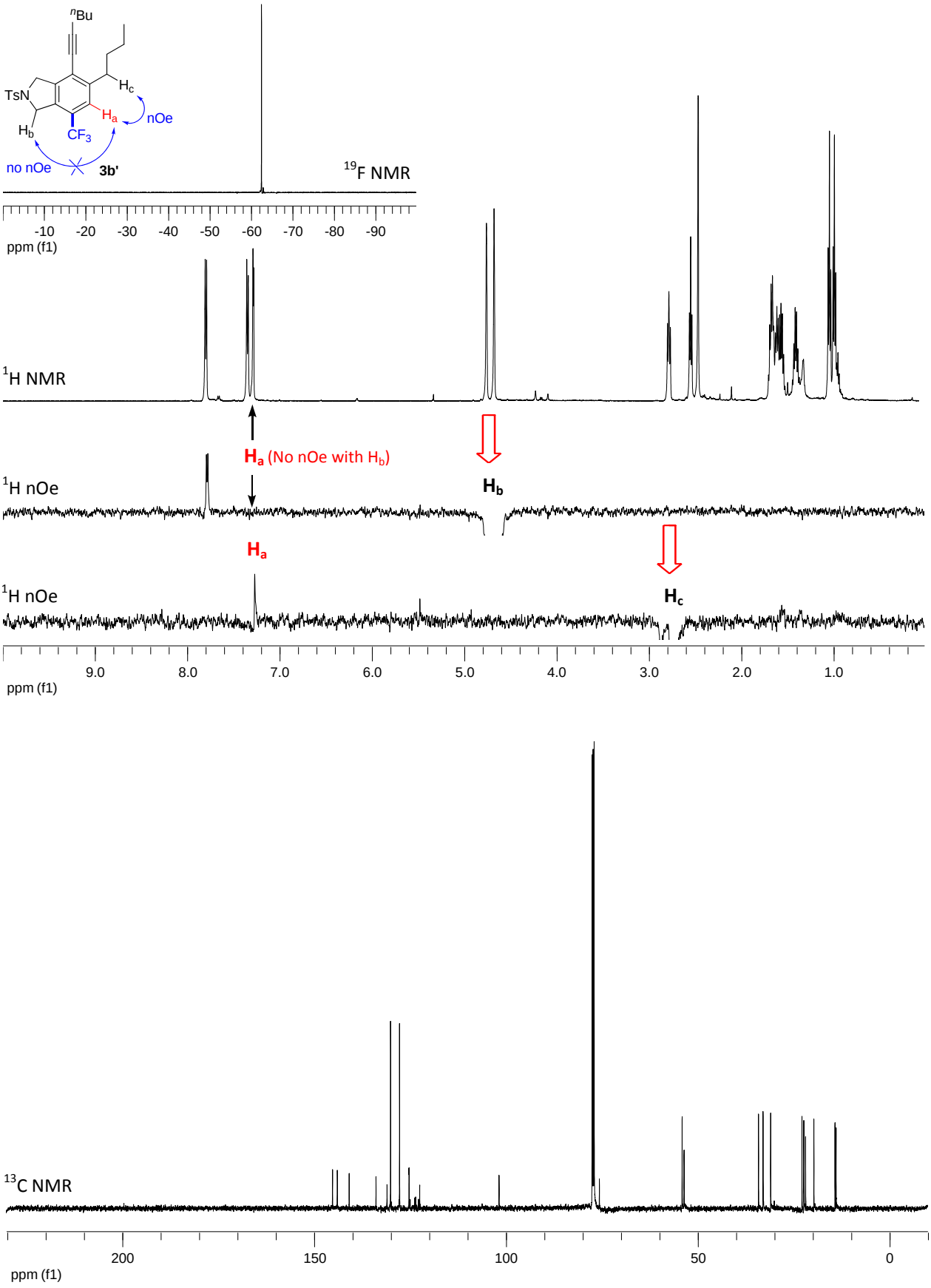


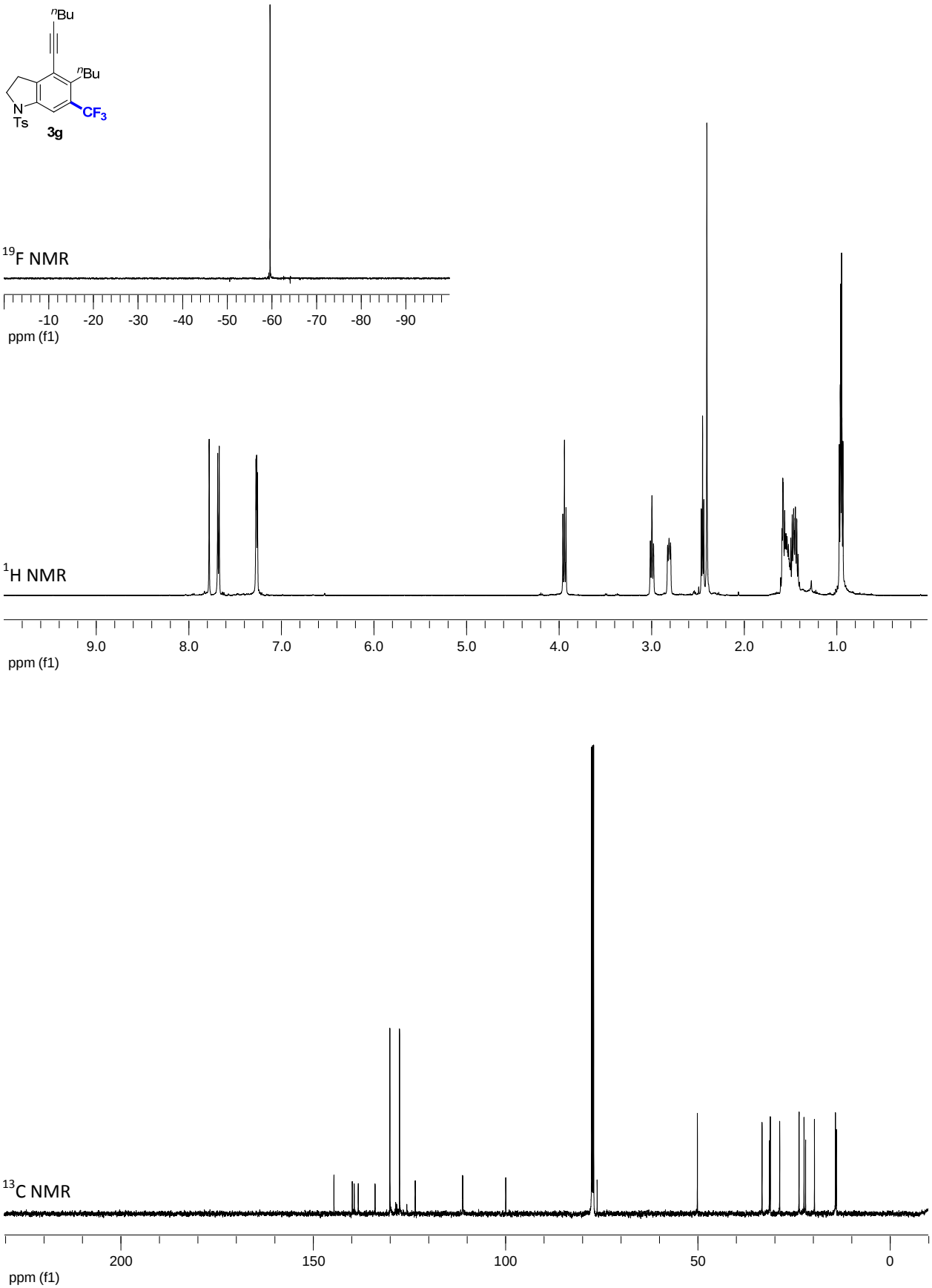
2l

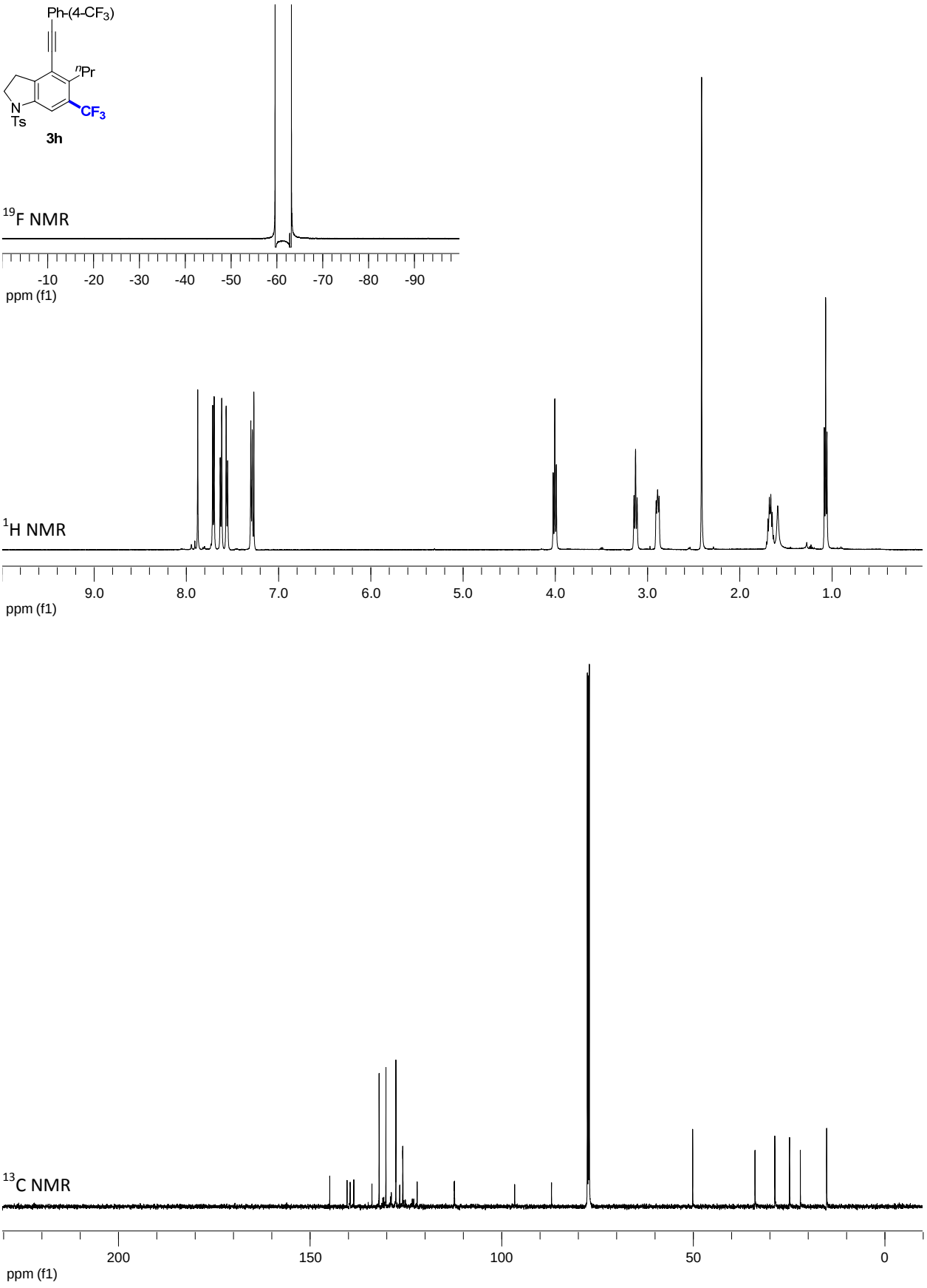


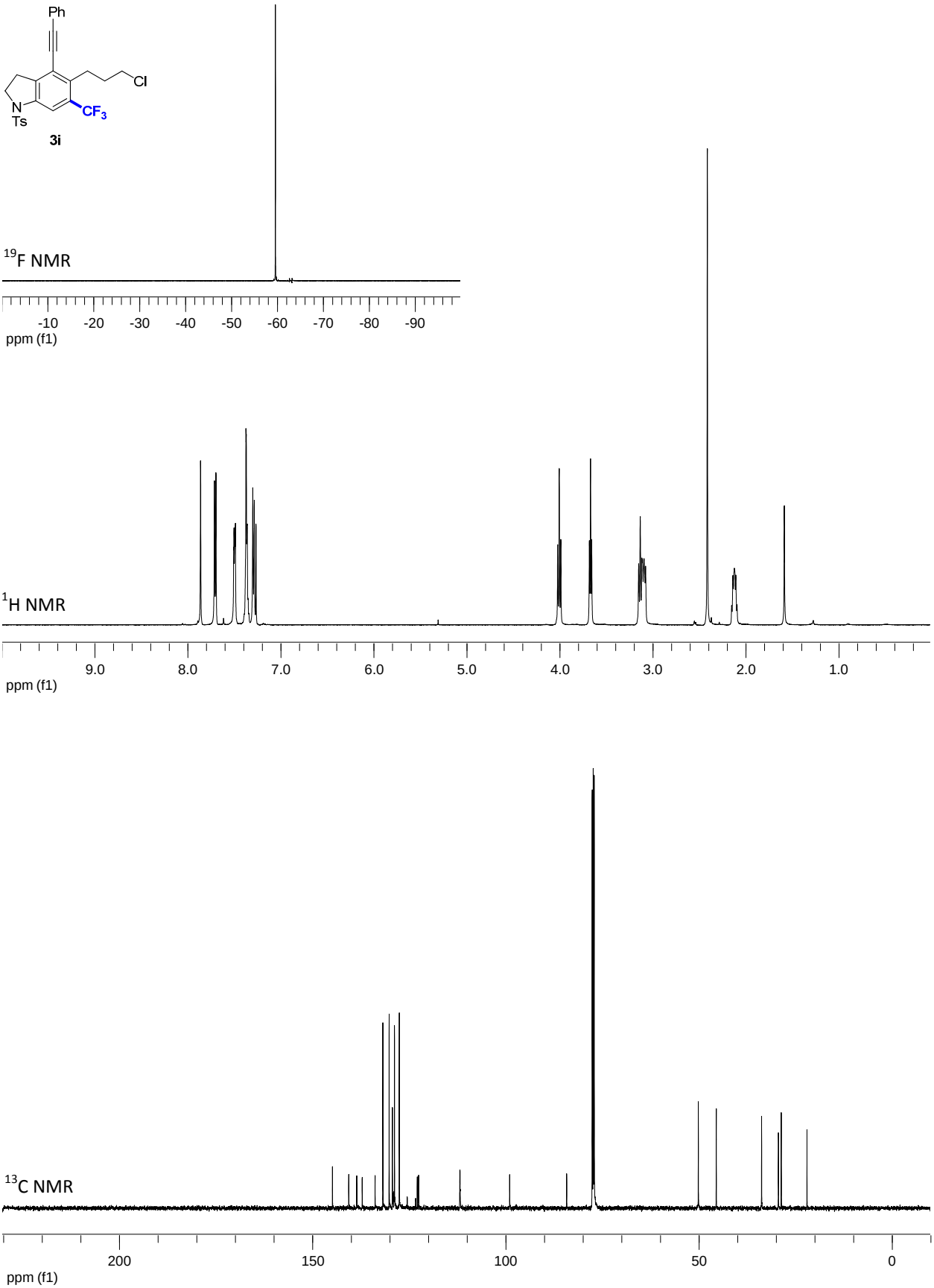




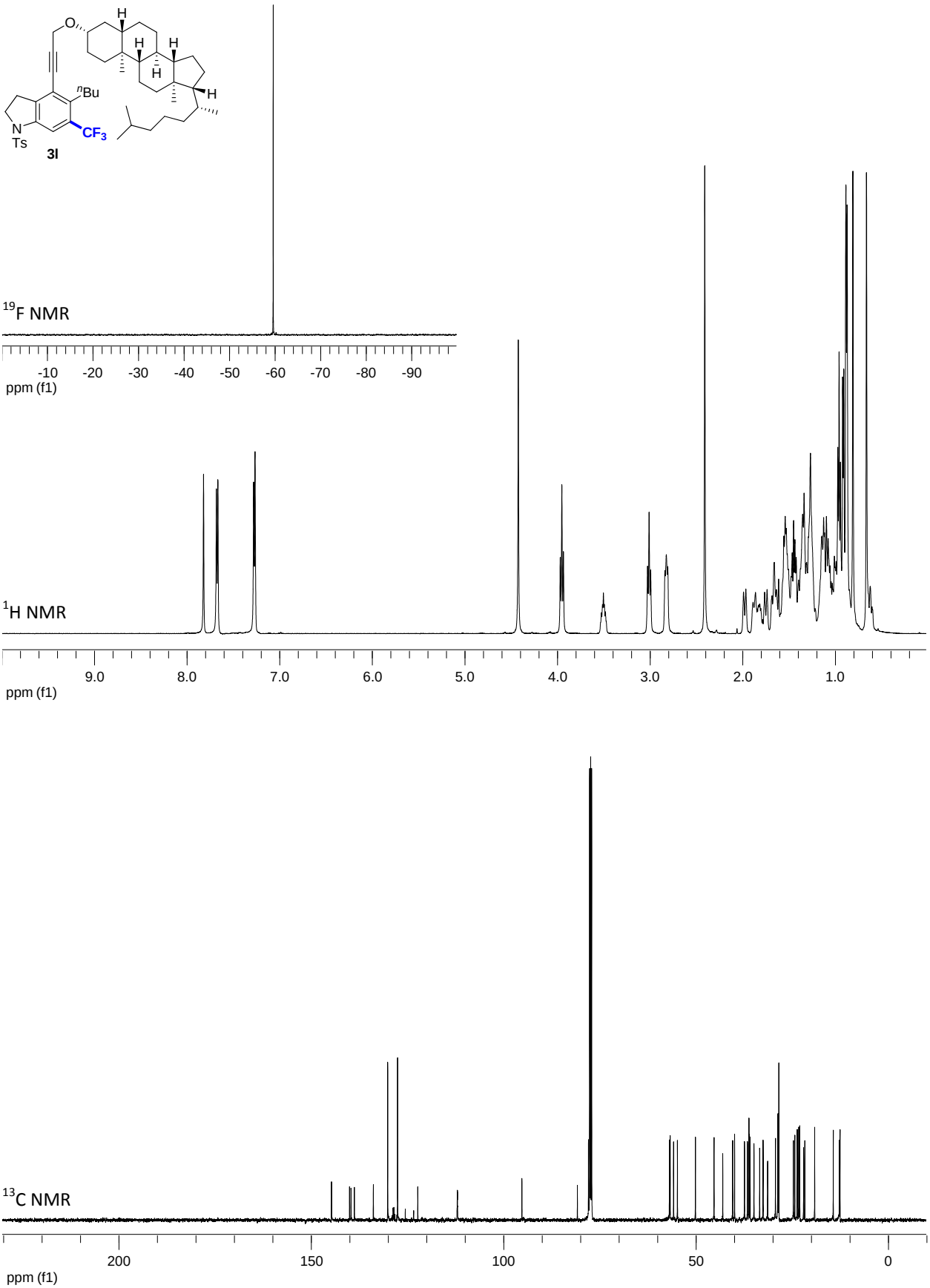


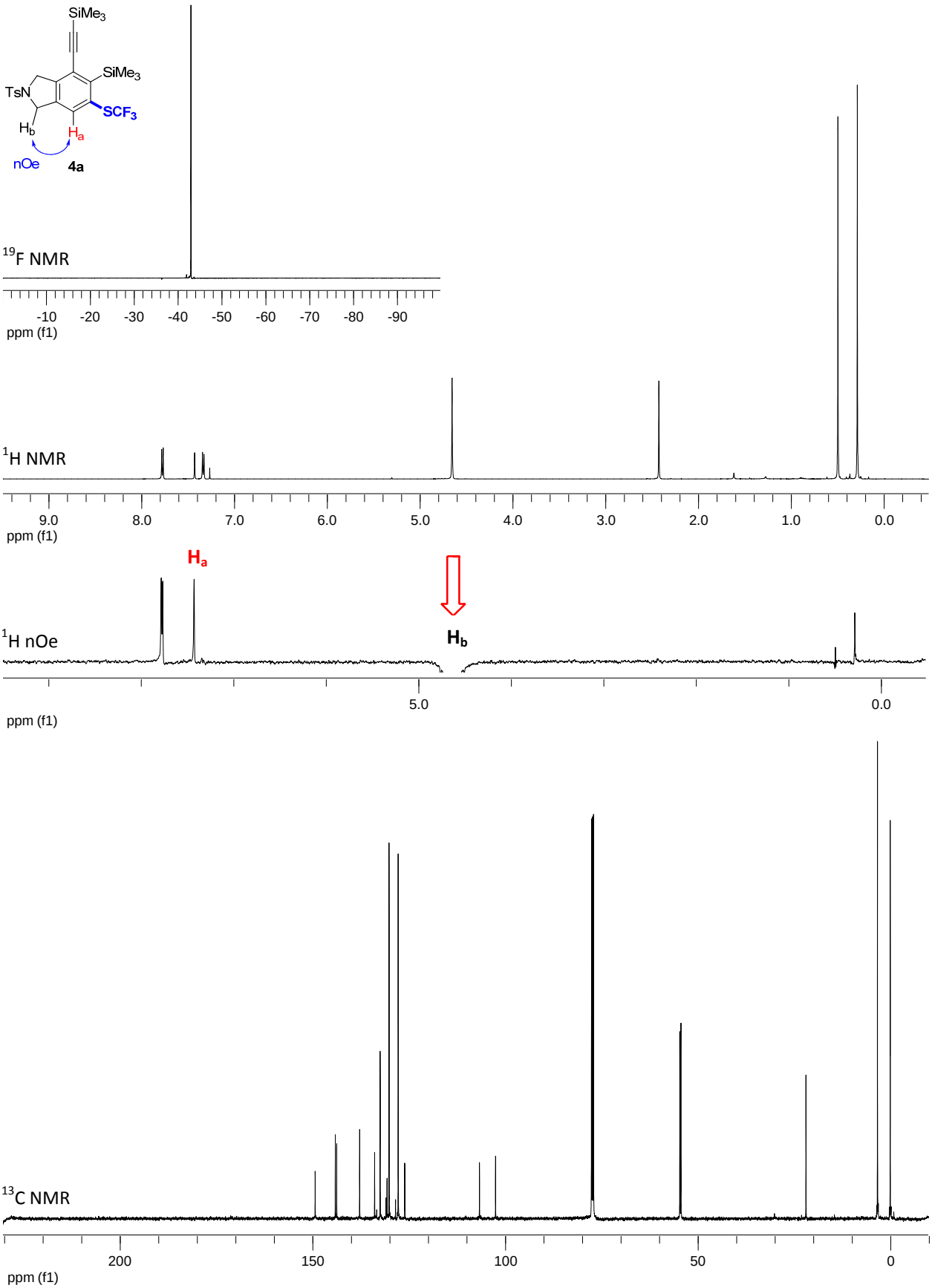


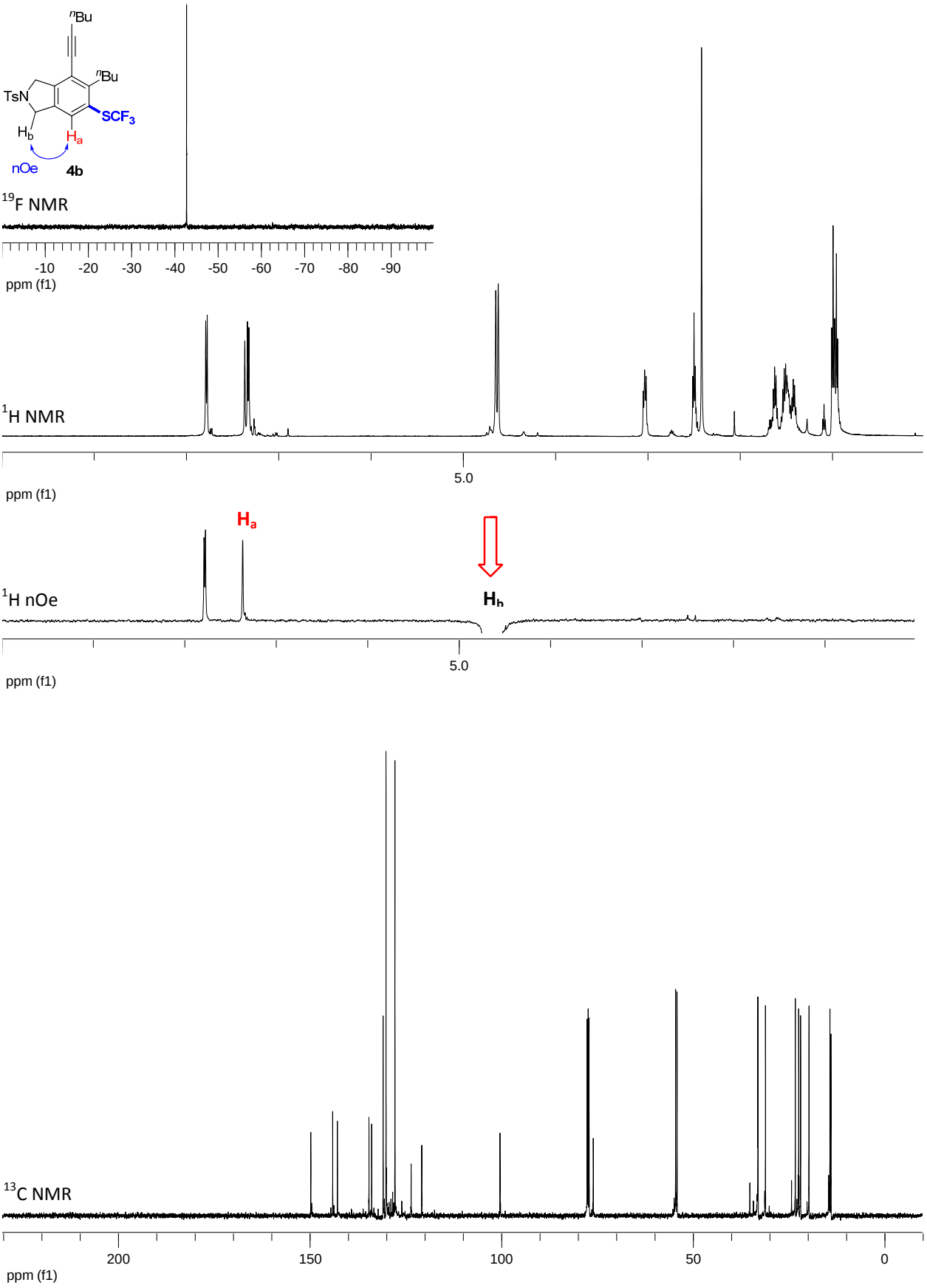


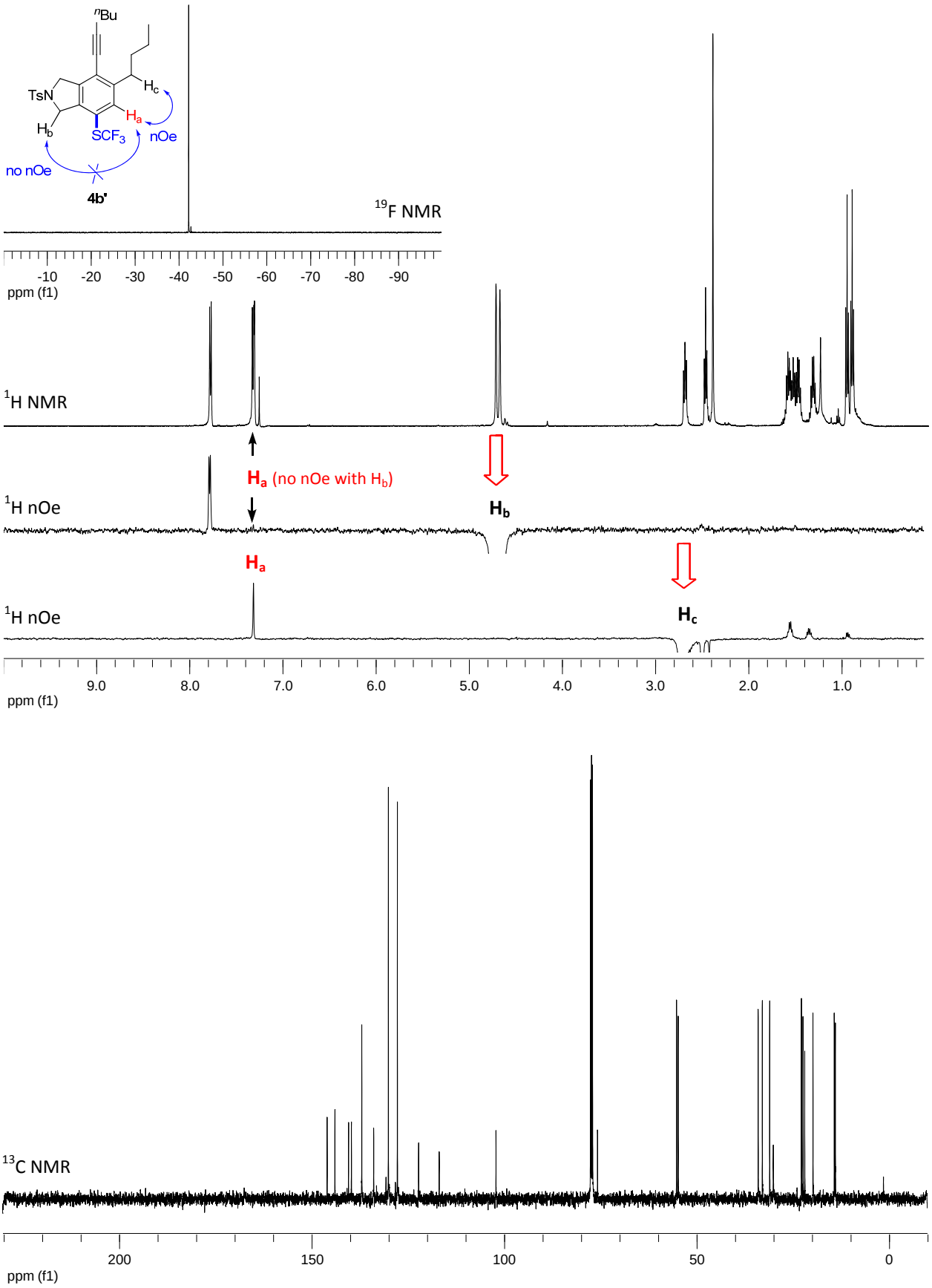


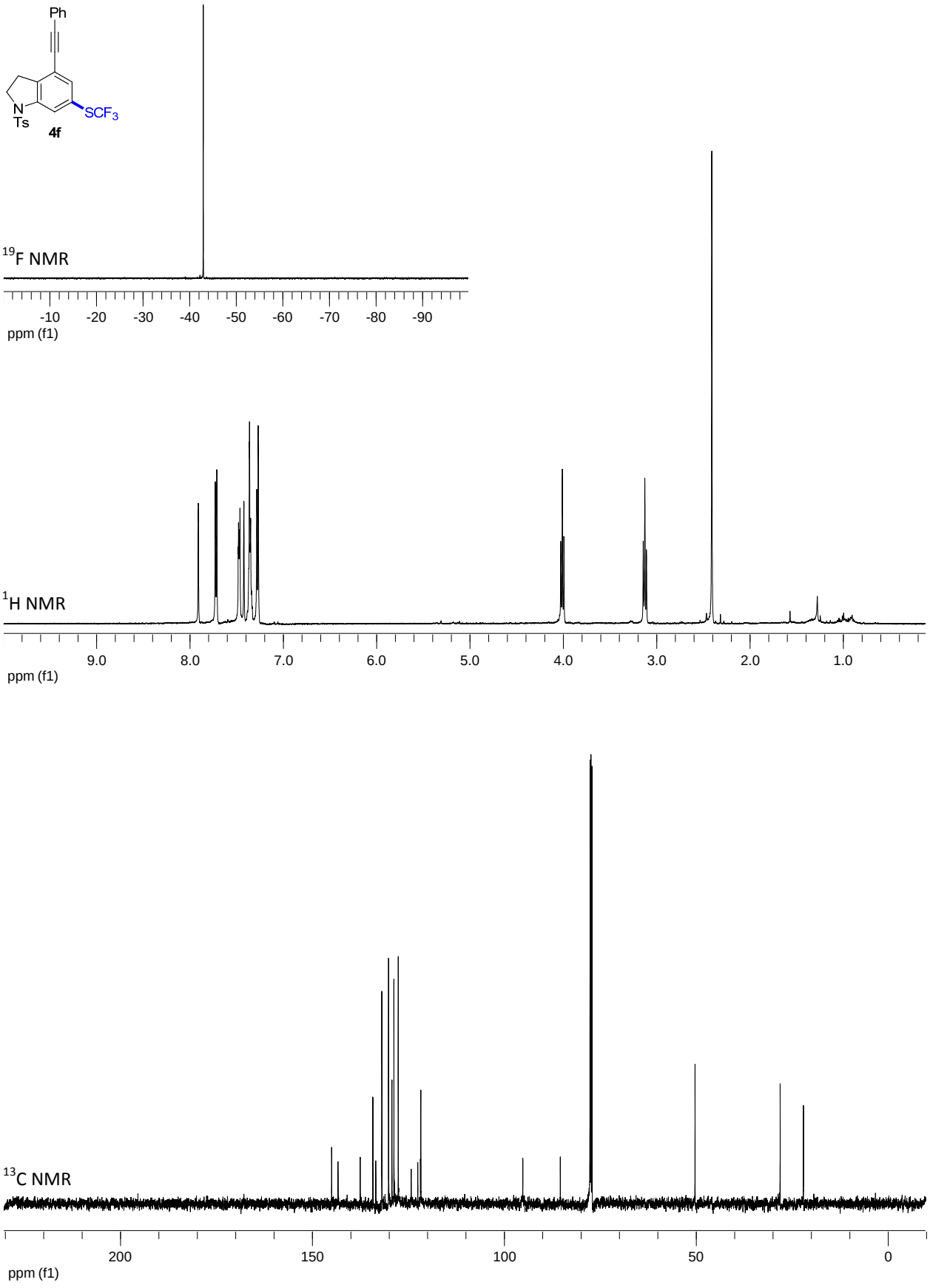
3l

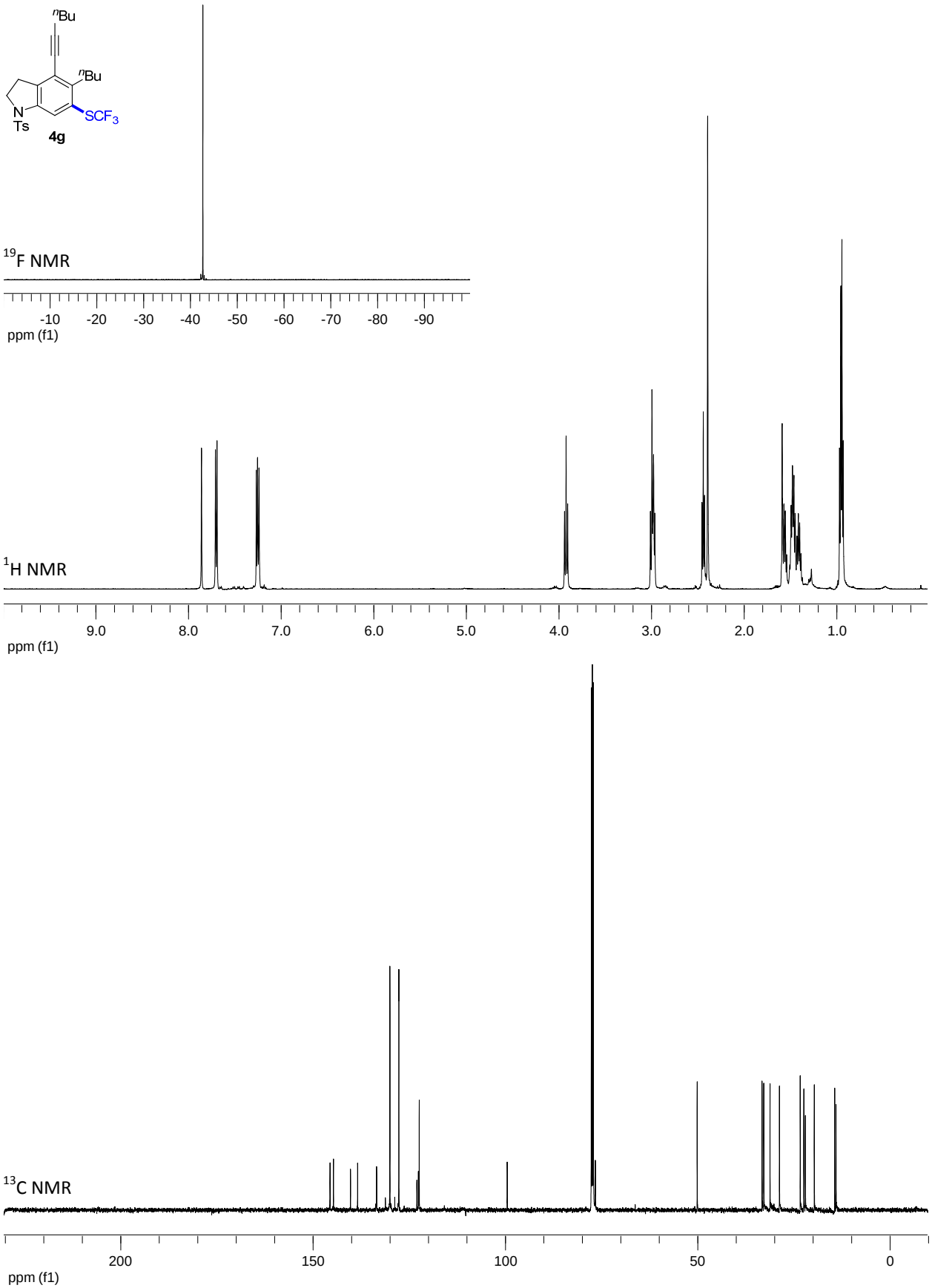


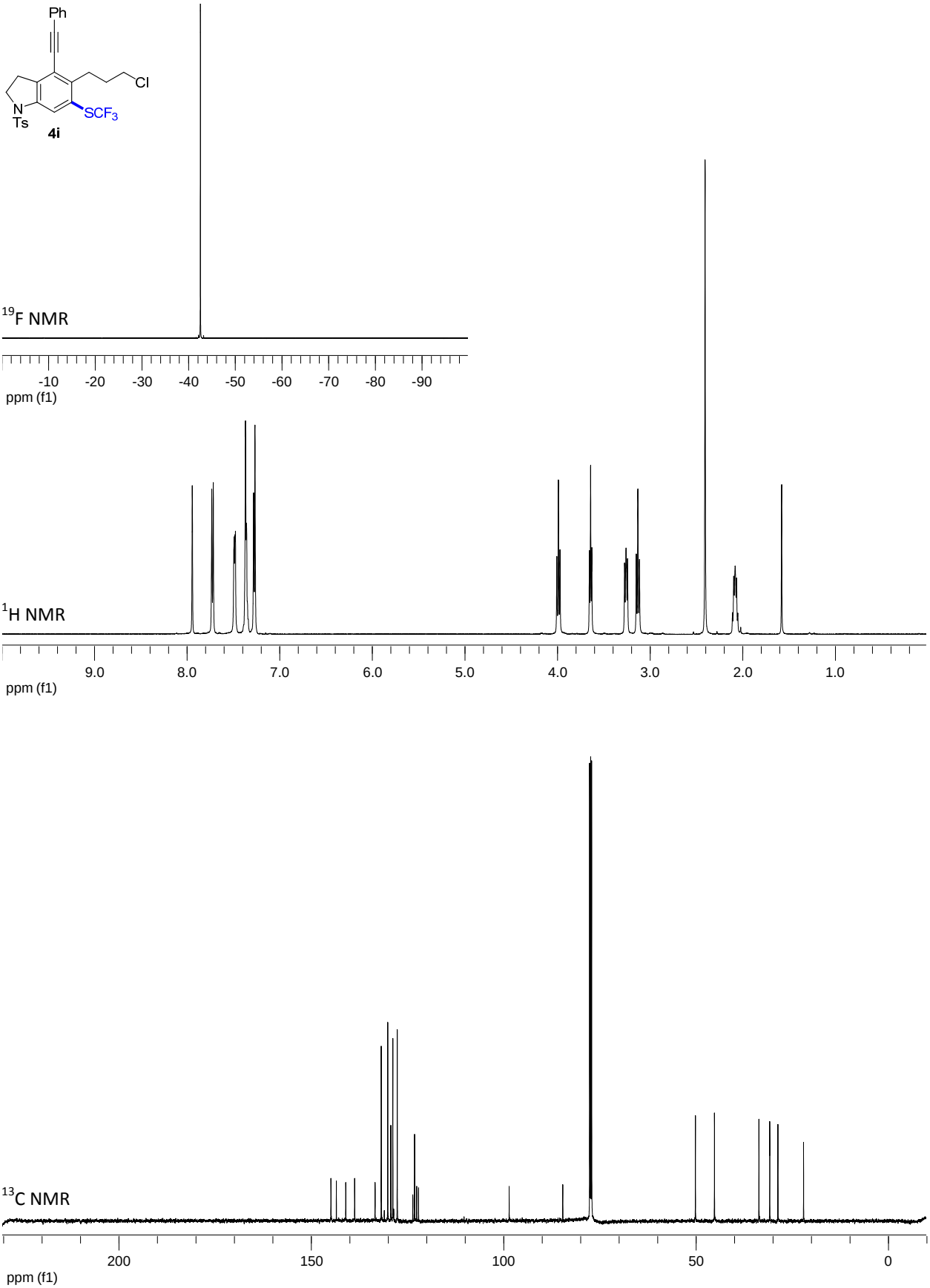


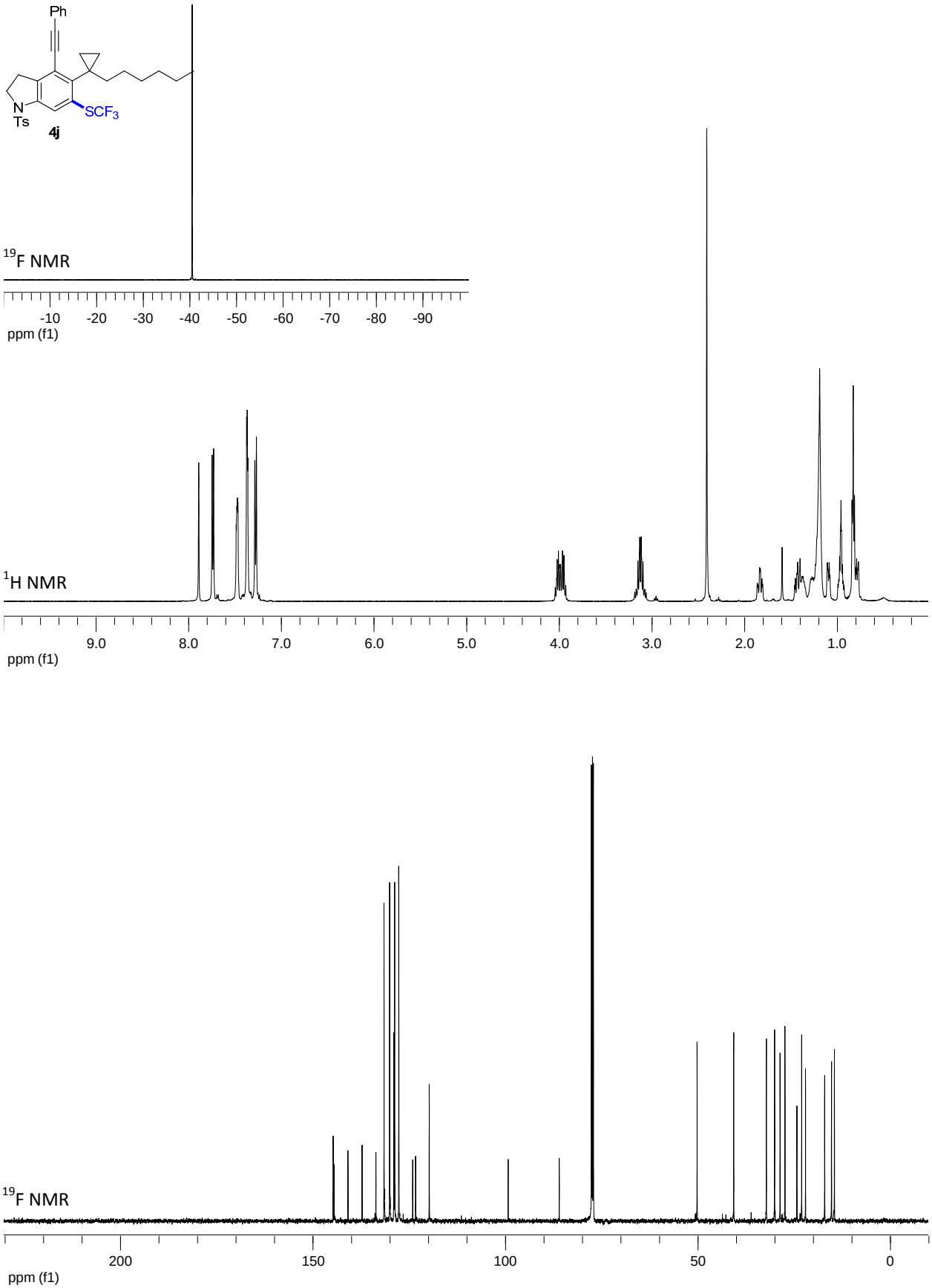


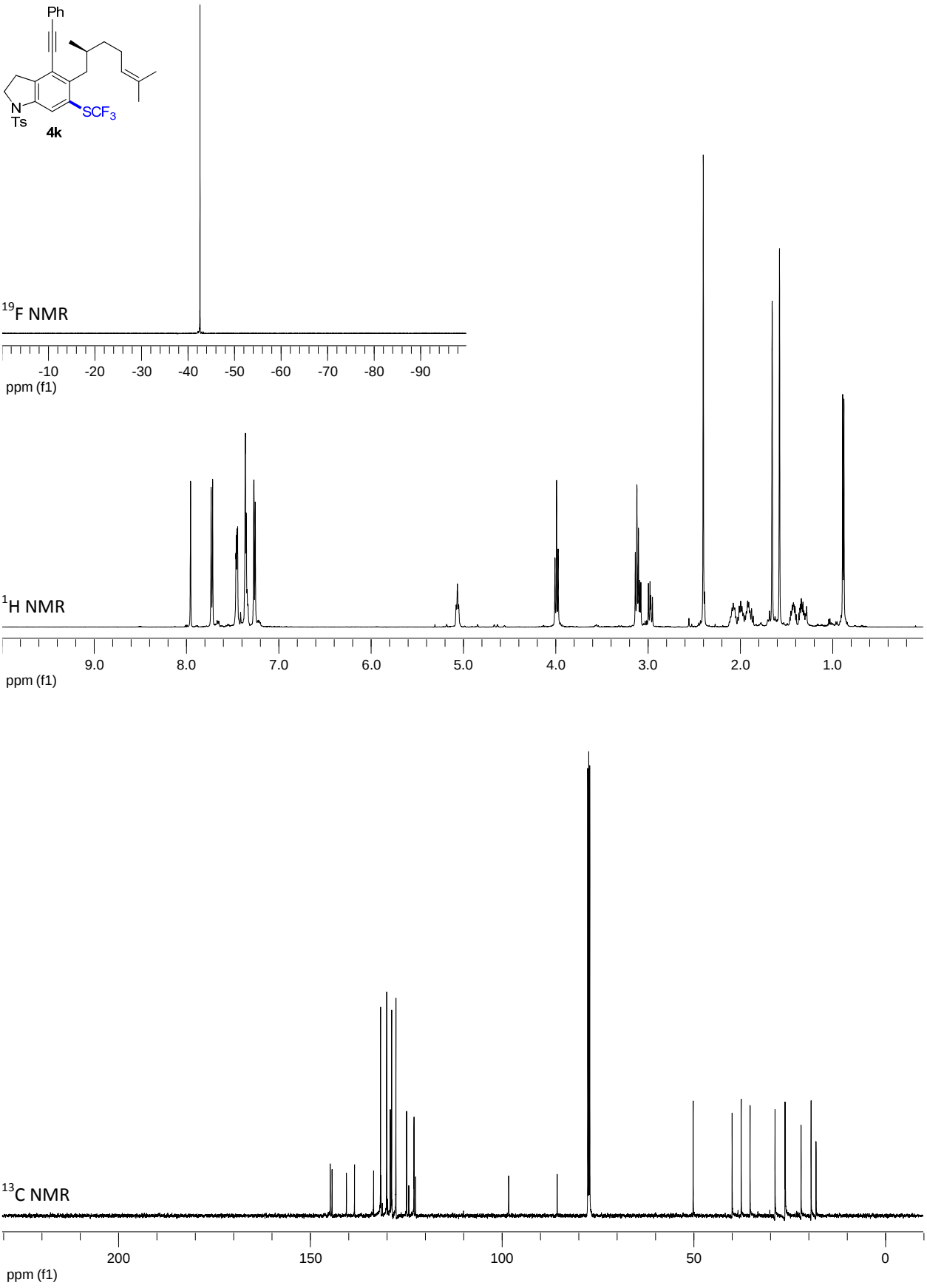


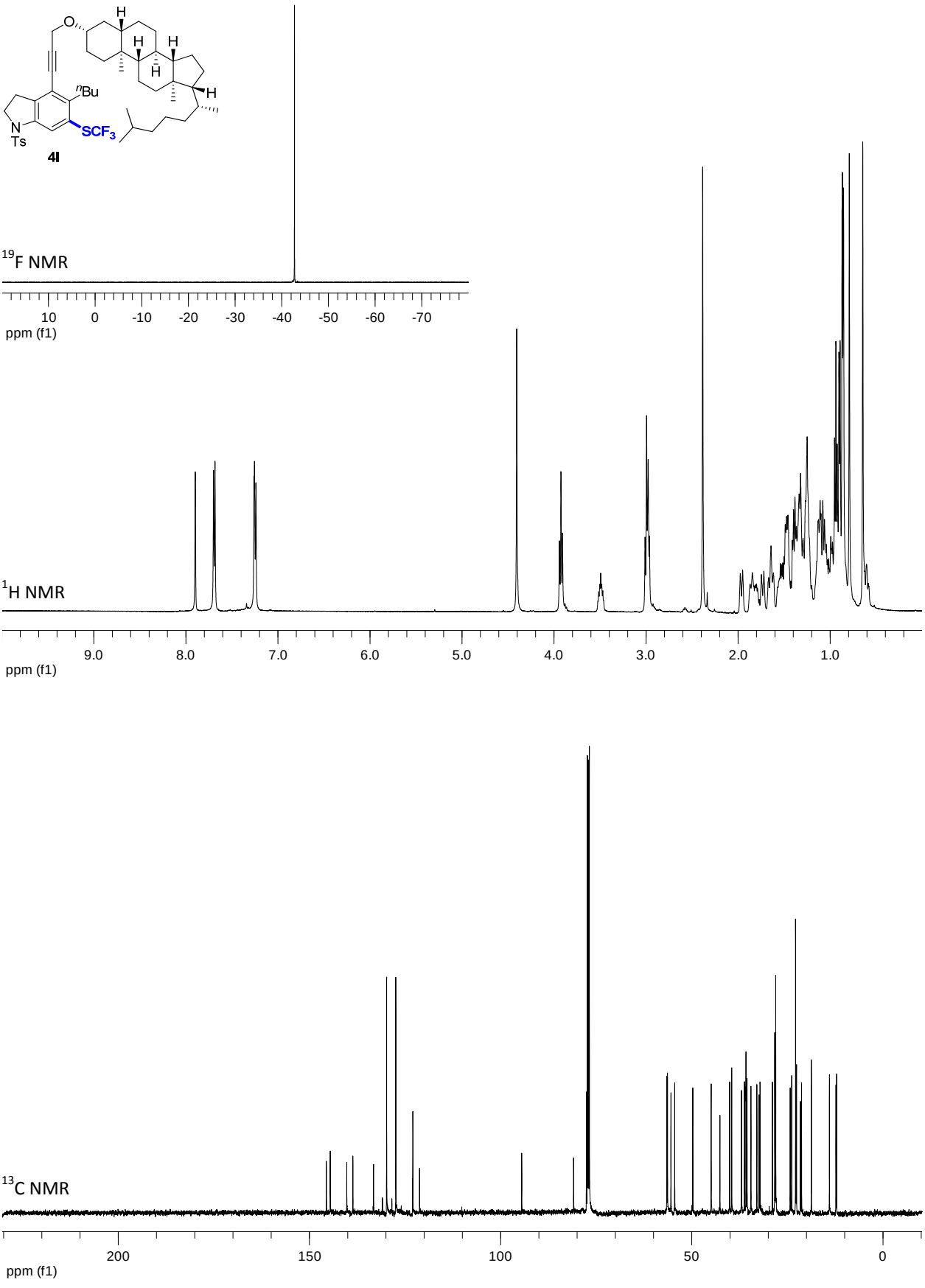


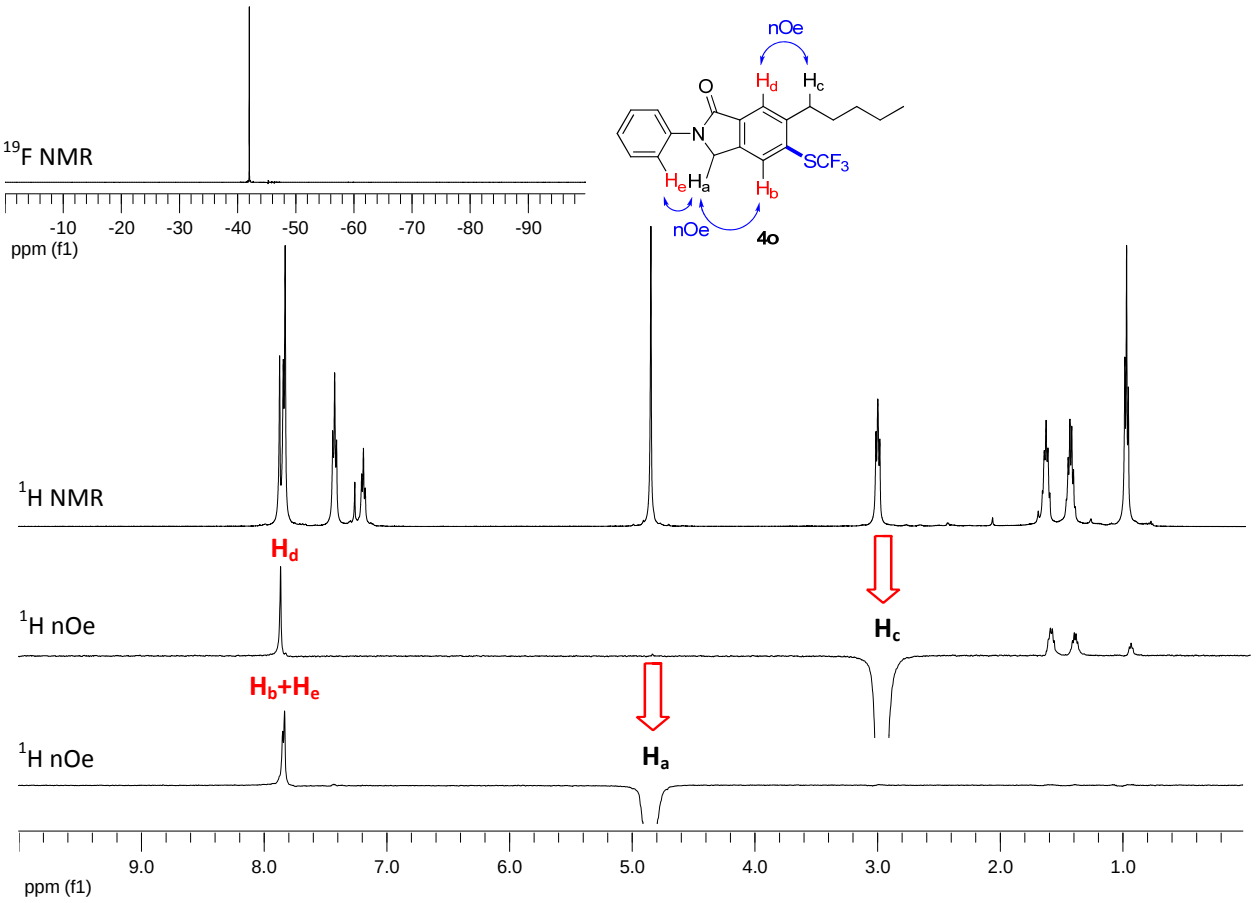

nBu
nBu
N
Ts
SCF3
4g
19F NMR
-10 -20 -30 -40 -50 -60 -70 -80 -90
ppm (f1)
1H NMR
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0
ppm (f1)
13C NMR
200 150 100 50 0
ppm (f1)

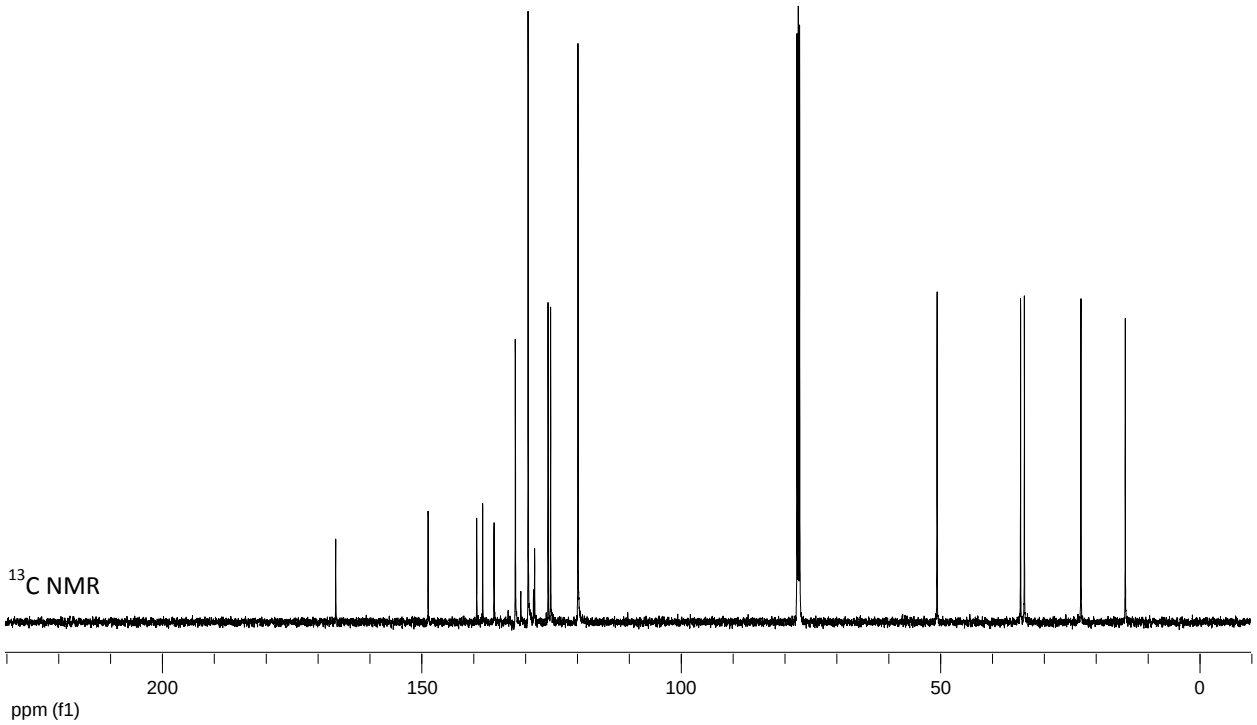


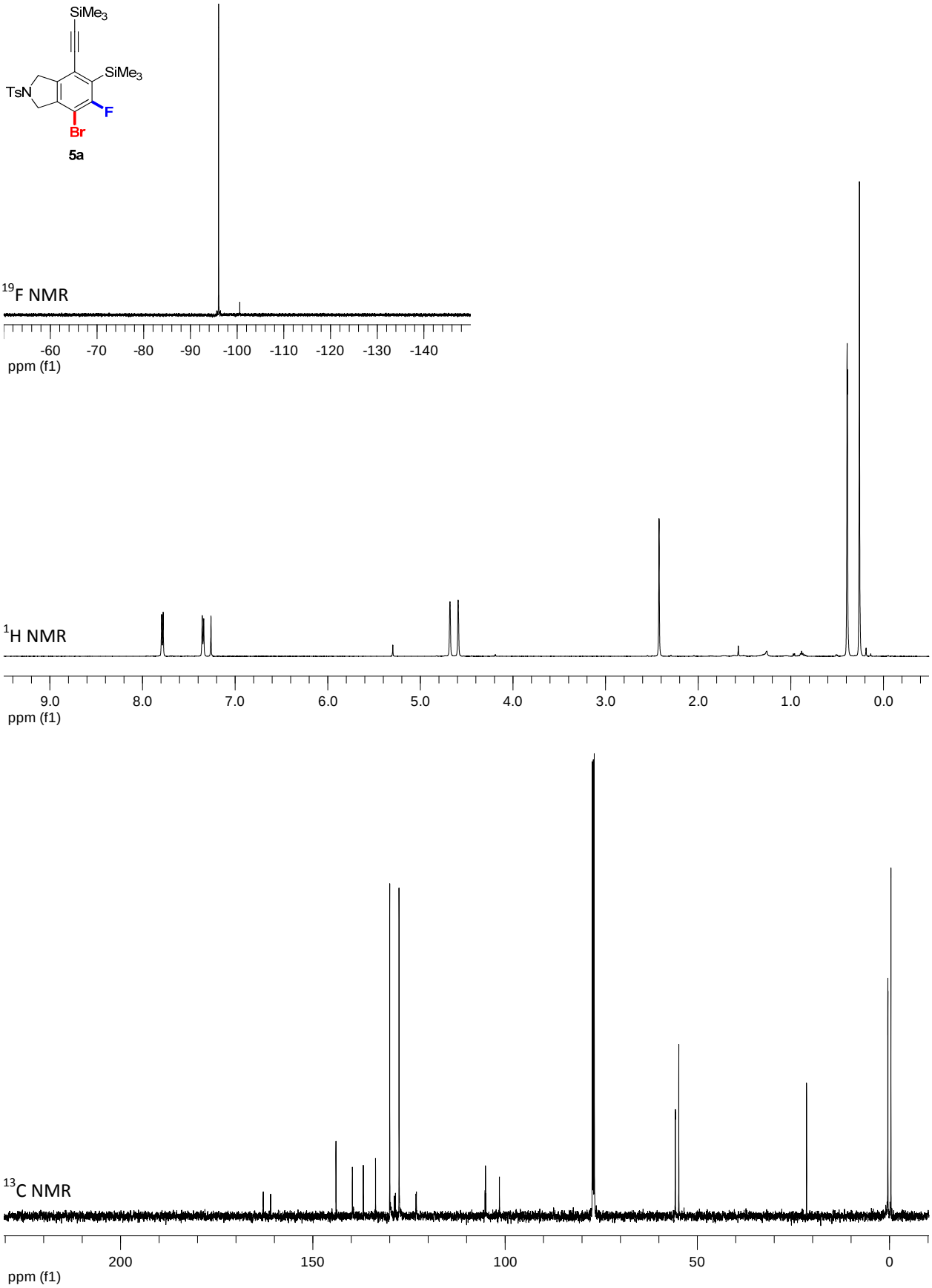


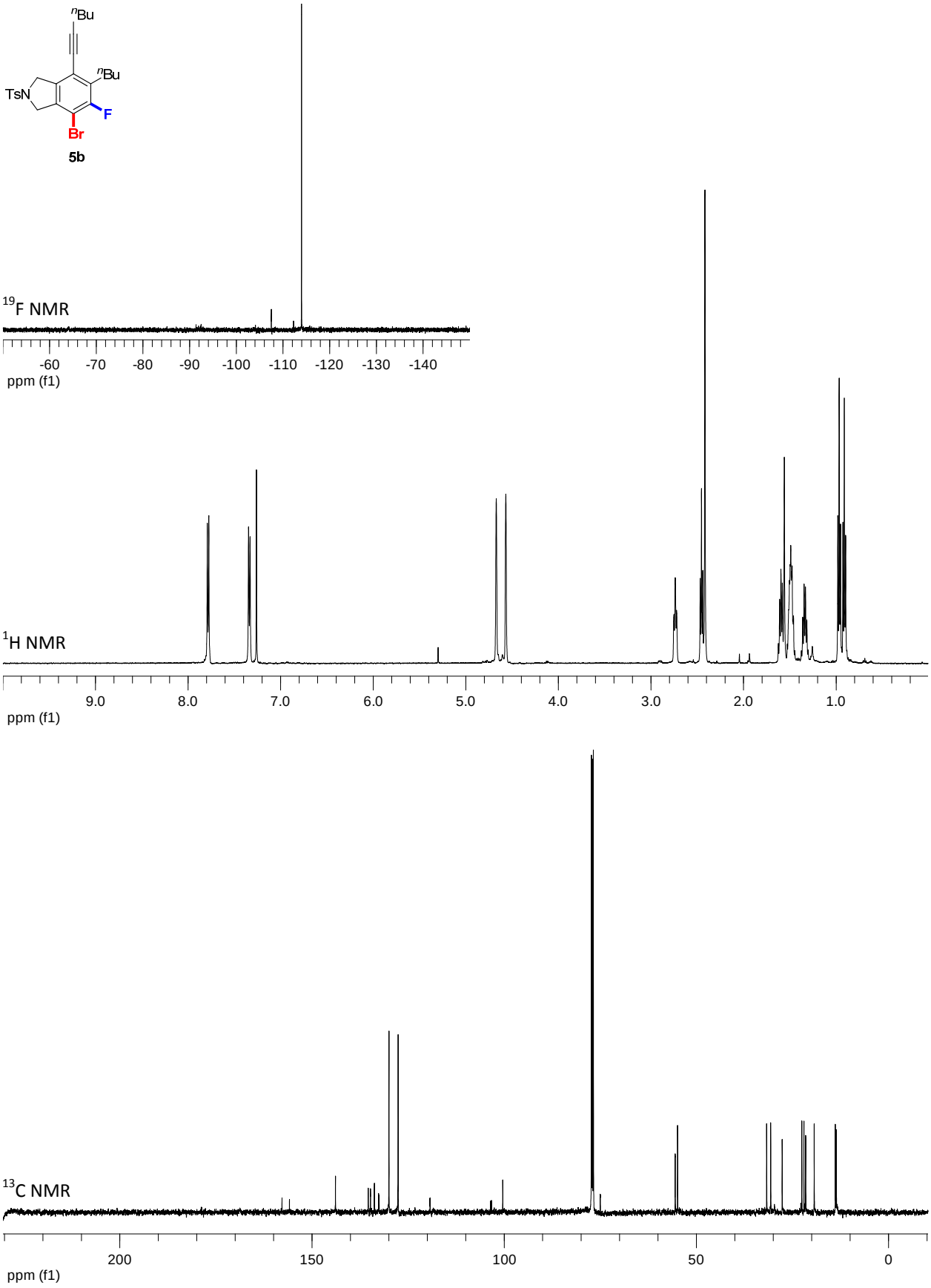


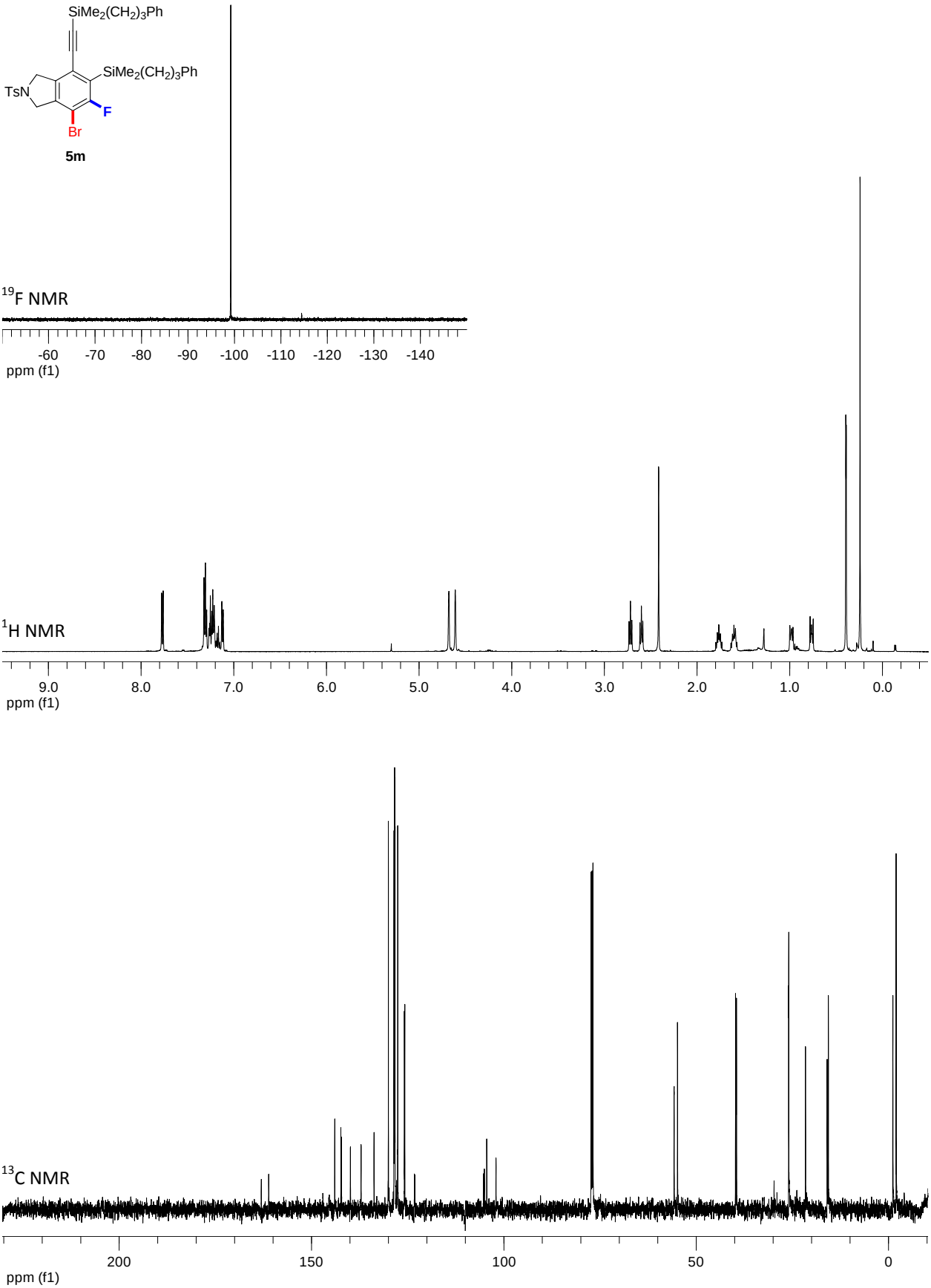




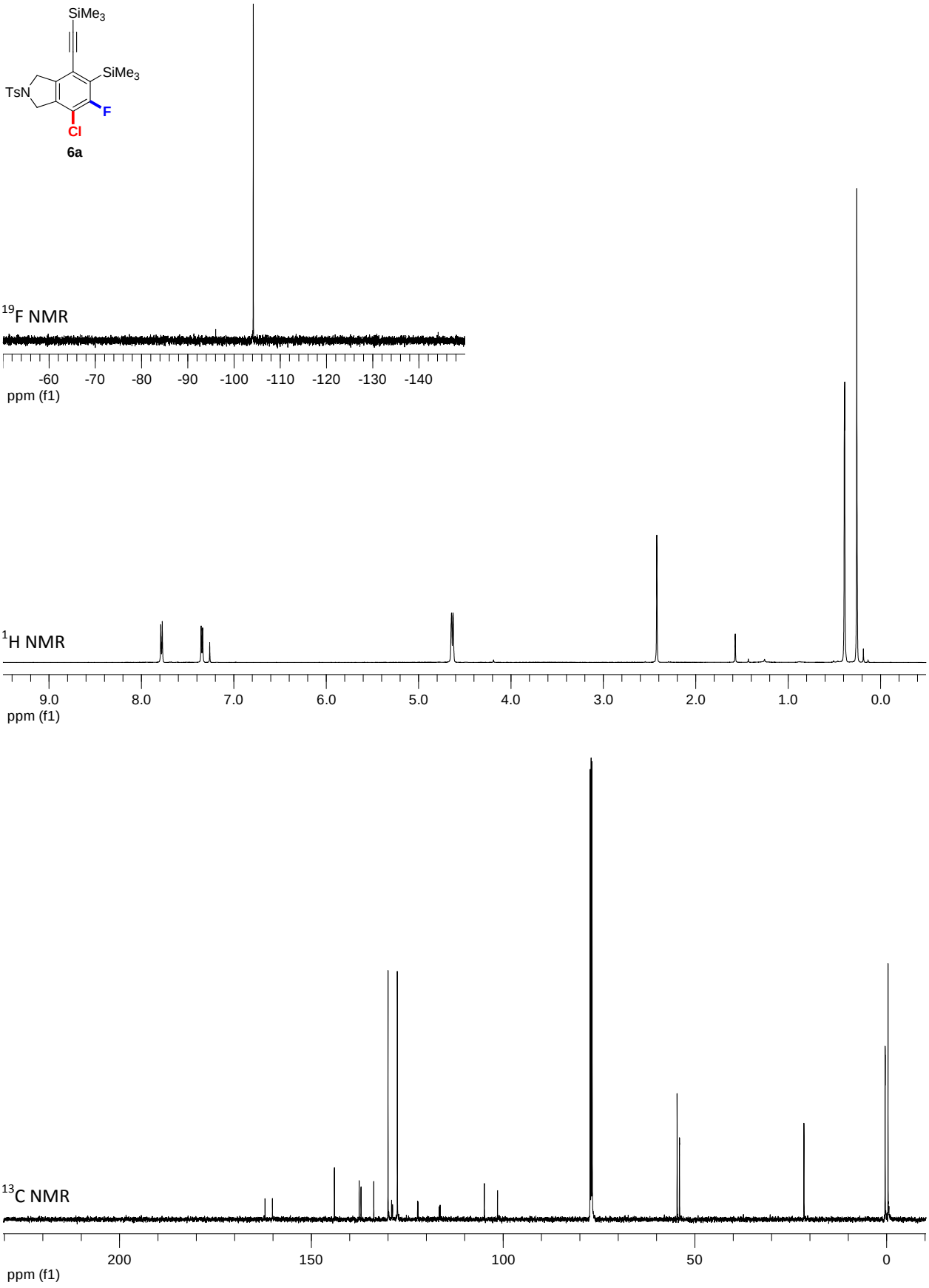


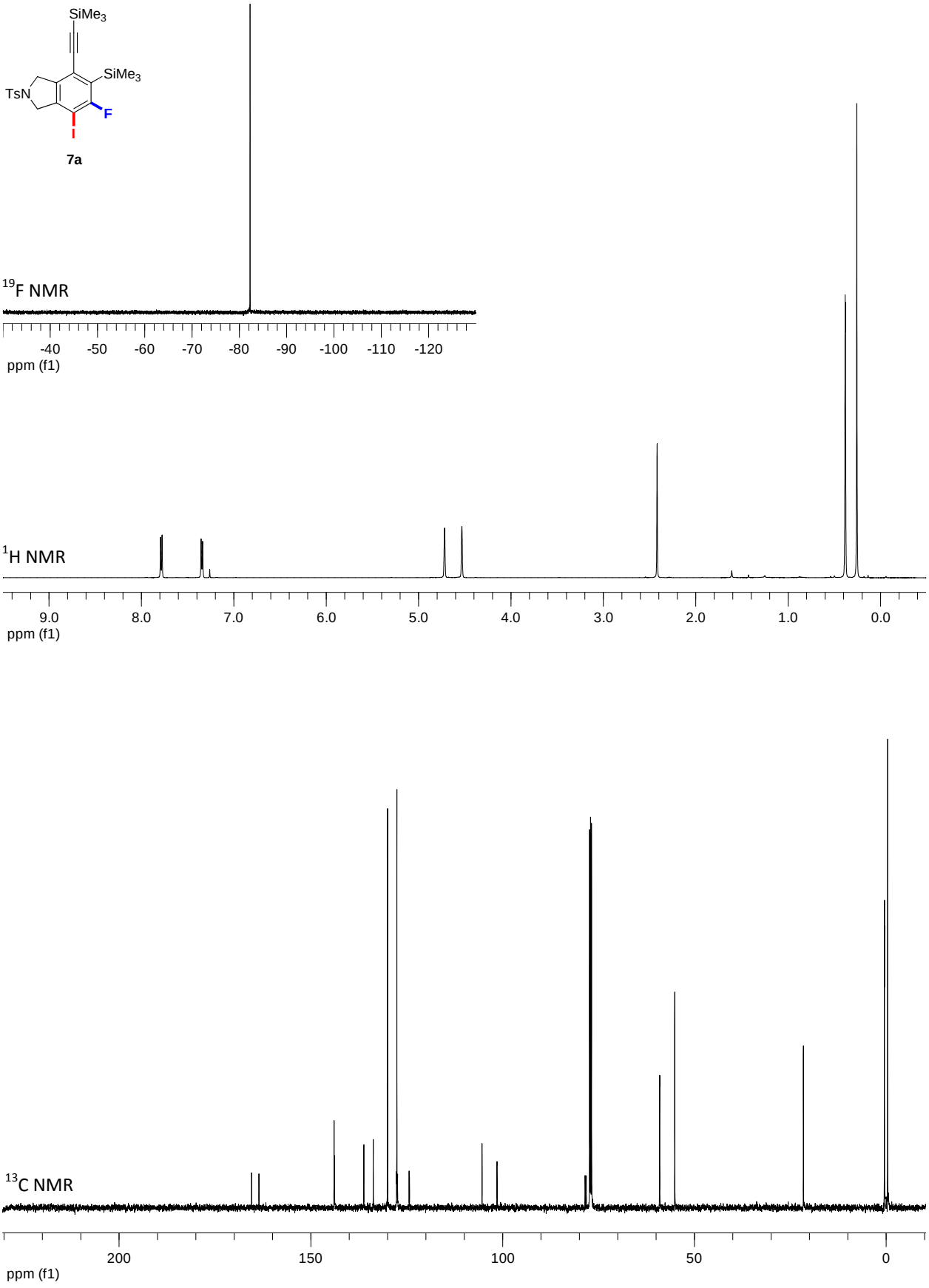




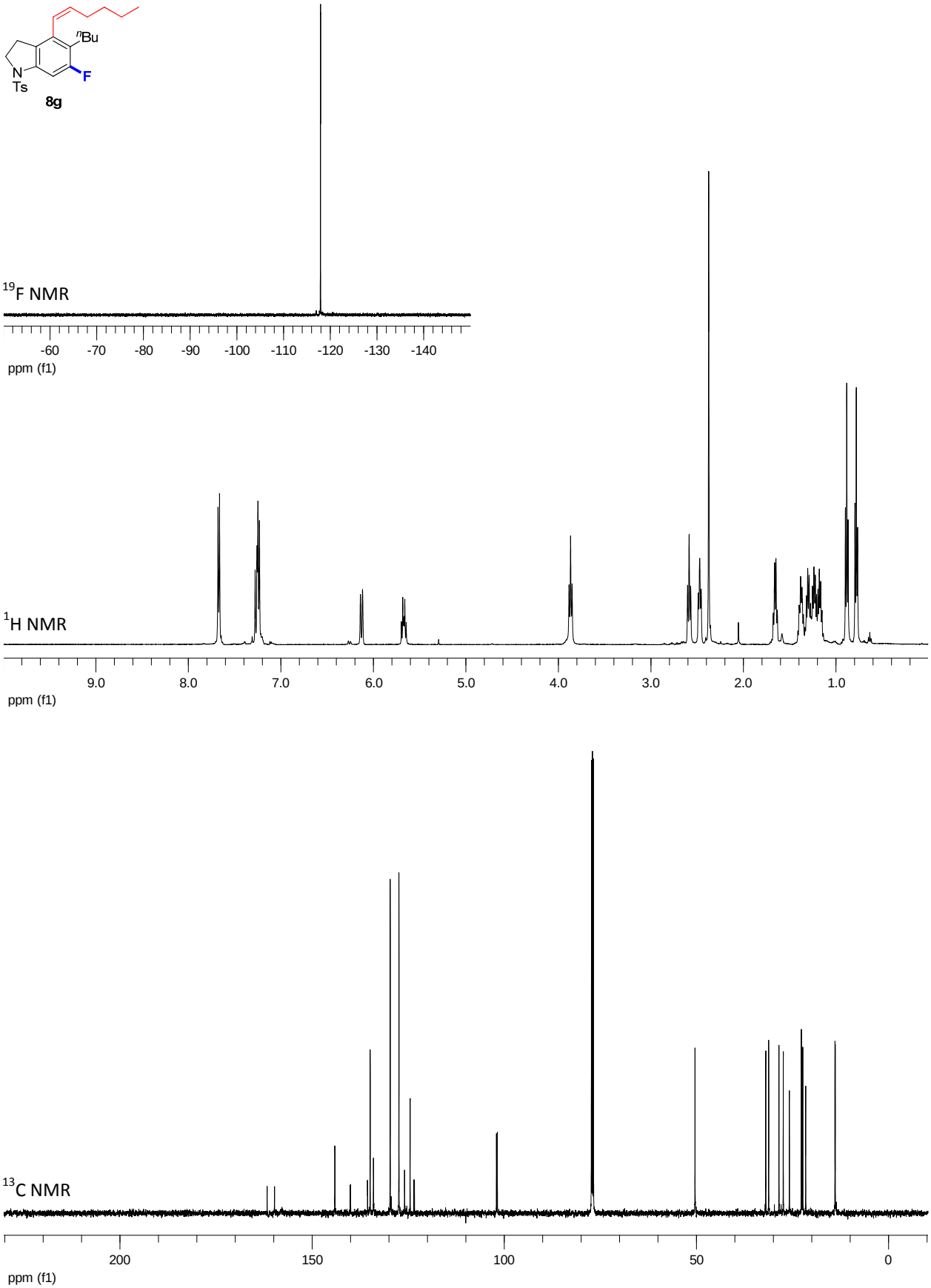


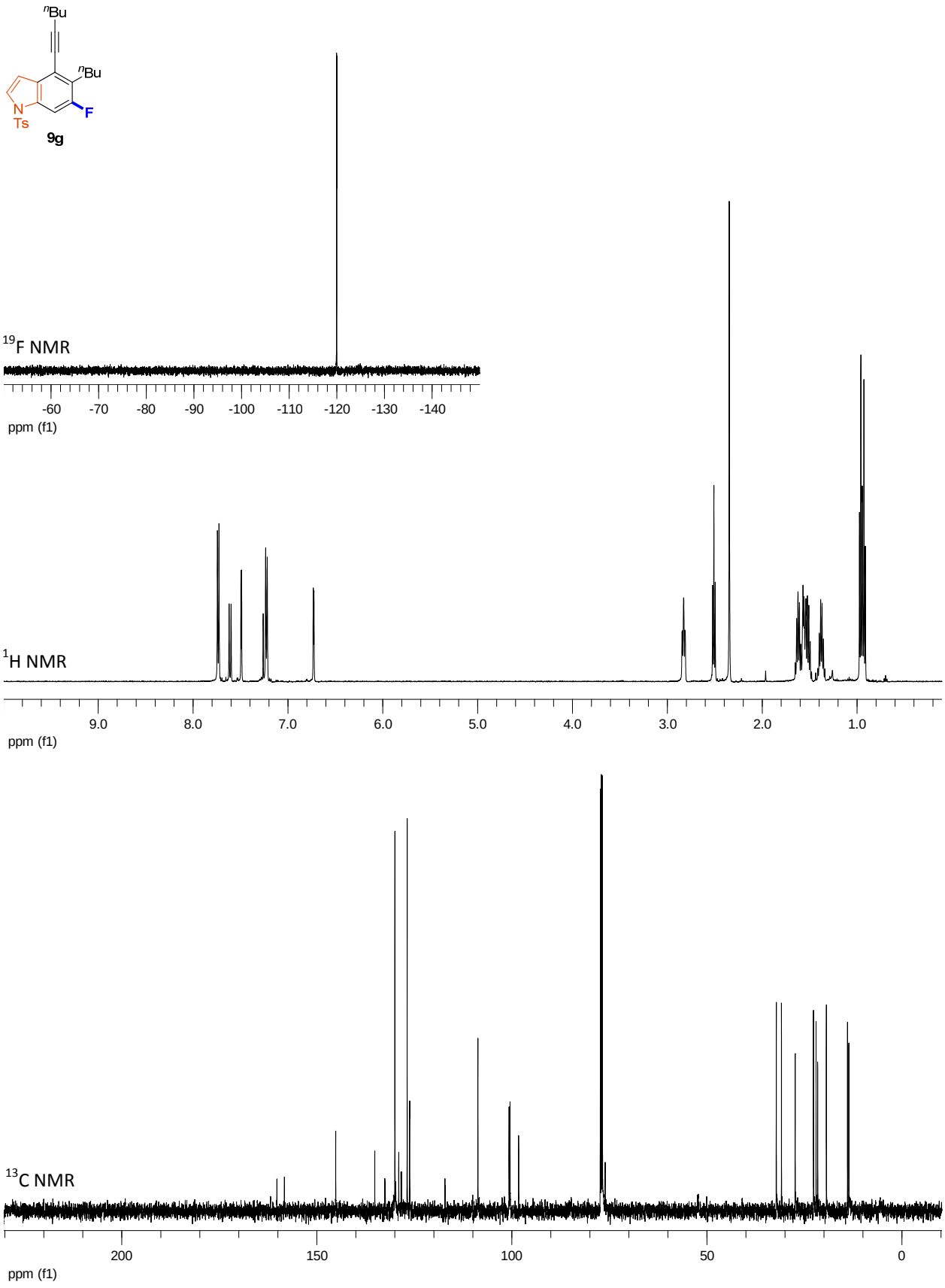
6a

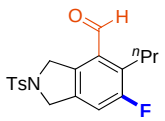




8g

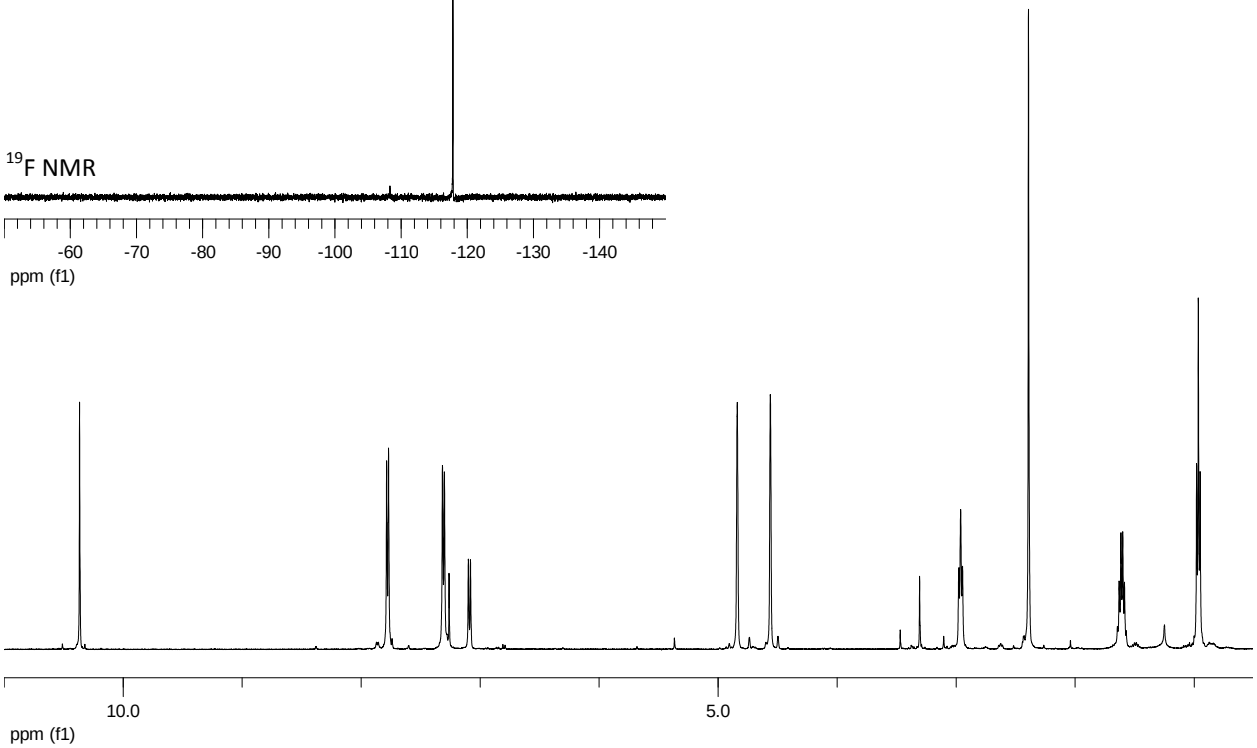






10n

^{19}F NMR



^{13}C NMR