

Supporting Information

Asymmetric Synthesis of CF₃- and Indole-Containing Thiochromanes via a Squaramide-Catalyzed Michael-Aldol Reaction

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1. General Information

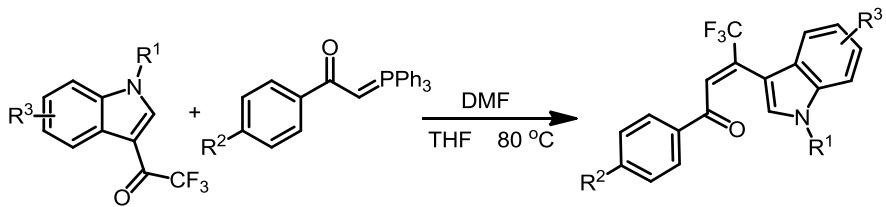
Reactions were monitored by thin layer chromatography (TLC), and compounds were visualized with a UV light at 254 nm. Column chromatography purifications were carried out using silica gel. ^1H , ^{13}C and ^{19}F NMR spectra were recorded on a Bruker (300 MHz) spectrometer in CDCl_3 using tetramethylsilane (TMS) as internal standard. Data are presented as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet) and coupling constant in Hertz (Hz). Mass peaks are identified by the corresponding m/z values. The ee values determination was carried out using chiral high-performance liquid chromatography (HPLC) with Chiracel IA column, Chiracel IC column and Chiracel OD column. Optical rotations were measured on a digital polarimeter and are reported as follows: $[\alpha]_D^T$ (1 g/100 mL, CHCl_3).

All solvents were obtained from commercial sources and were purified according to standard procedures. The starting materials 2,2,2-trifluoro-1-(1H-indol-3-yl)ethan-1-ones were prepared according to literature procedure,^[1, 2] 1-phenyl-2-(triphenyl-15-phosphanylidene)ethan-1-ones were synthesized by literature method.^[3]

Reference:

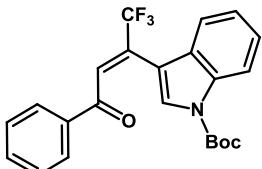
- [1] a) Martinelli, E.; Vicini, A. C.; Mancinelli, M.; Mazzanti, A.; Zani, P.; Bernardi, L.; Fochi, M. *Chem. Commun.* **2015**, 51(4), 658-660. b) Raimer, B.; Wartmann, T.; Jones, P. G.; Lindel, T. *Eur. J. Org. Chem.* **2014**, 2014(25), 5509-5520. c) Kumar, P. D.; Arun, V.; Kumar, N. M.; Acosta, G.; Noel, B.; Shah, P. K. *ChemMedChem.* **2012**, 7(11), 1915-1920.
- [2] a) Yan, Z. L.; Chen, W. L.; Gao, Y. R.; Mao, S.; Zhang, Y. L.; Wang, Y. Q. *Advanced Synthesis & Catalysis.* **2014**, 356(5), 1085-1092. b) Fraile, J. M.; Jeune, K. L.; Mayoral, J. A.; Ravasio, N.; Zaccheria, F. *Org. Biomol. Chem.* **2013**, 11(26), 4327-4332. c) Chen, M.; Huang, Z. T.; Zheng, Q. Y. *Chem. Commun.* **2012**, 48(95), 11686-11688.
- [3] a) Chen, S. j.; Lu, G. p.; Cai, C. *RSC Adv.* **2015**, 5(17), 13208-13211. b) An, X. L.; Chen, J. R.; Li, C. F.; Zhang, F. G.; Zou, Y. Q.; Guo, Y. C.; Xiao, W. J. *Chemistry - An Asian Journal.* **2010**, 5(10), 2258-2265. c) Balema, V. P.; Wiench, J. W.; Pruski, M.; Pecharsky, V. K. *J. Am. Chem. Soc.* **2002**, 124 (22), 6244-6245.

2. General procedure for the syntheses of β -indole- β -CF₃ enones and their Analytical Data



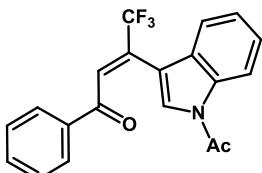
A solution of 2,2,2-trifluoro-1-(1H-indol-3-yl)ethan-1-one (1.0 equiv) in DMF was added into the solution of 1-phenyl-2-(triphenylphosphoranylidene)ethan-1-one (1.4 equiv) in dry THF under nitrogen atmosphere at 0 °C, then the mixture was stirred at 80 °C until complete disappearance of the starting materials, after which it was cooled to room temperature, then saturated solution of ammonium chloride was added to quench the reaction, then the mixture was extracted with ethyl acetate, washed with saturated brine solution and dried by Na₂SO₄, after an evaporation of the organic solvent, the crude residue was purified by silica gel column chromatography (hexane/ethyl acetate) and afforded the resulting β -indole- β -CF₃ enones as described below.

tert-butyl-(E)-3-(1,1,1-trifluoro-4-oxo-4-phenylbut-2-en-2-yl)-1H-indole-1-carboxylate (2a)



From 0.63 g (2 mmol) *tert*-butyl 3-(2,2,2-trifluoroacetyl)-1H-indole-1-carboxylate and 1.06 g (2.8 mmol, 1.4 equiv) 1-phenyl-2-(triphenylphosphoranylidene)ethanone, β -indole- β -CF₃ enone **2a** was obtained as a yellow solid (0.58 g, 70% yield), mp = 79 - 80 °C. ¹H NMR (300 MHz, CDCl₃) δ 8.07 (d, *J* = 8.4 Hz, 1H), 7.85 (s, 1H), 7.82 (d, *J* = 1.5 Hz, 1H), 7.66 (s, 1H), 7.52 (d, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 1.4 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.32 - 7.25 (m, 2H), 7.17 - 7.12 (m, 1H), 1.65 (s, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 191.2, 149.1, 136.2, 134.9, 133.8, 132.4 (q, *J*_{C-F} = 31.8 Hz), 131.1 (q, *J*_{C-F} = 4.8 Hz), 128.7, 128.7, 128.6, 126.7, 124.9, 123.1, 122.8 (q, *J*_{C-F} = 273.3 Hz), 119.9, 115.3, 111.1, 84.5, 28.1. ¹⁹F NMR (282 MHz, CDCl₃) δ -66.9. HRMS (ESI) *m/z* calcd for C₂₃H₂₁F₃NO₃ [M+H]⁺: 416.1468, found 416.1474.

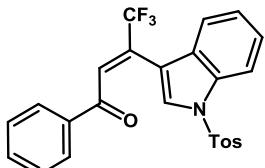
(E)-3-(1-acetyl-1H-indol-3-yl)-4,4,4-trifluoro-1-phenylbut-2-en-1-one (2b)



From 0.52 g (2 mmol) 1-(1-acetyl-1H-indol-3-yl)-2,2,2-trifluoroethanone and 1.06 g (2.8 mmol, 1.4 equiv) 1-phenyl-2-(triphenylphosphoranylidene)ethanone, β -indole- β -

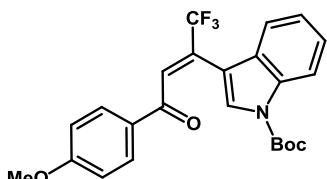
CF_3 enone **2b** was obtained as a yellow solid (0.49 g, 69% yield), mp = 92 - 93 °C. ^1H NMR (300 MHz, CDCl_3) δ 8.35 (d, J = 8.4 Hz, 1H), 7.81 (d, J = 7.5 Hz, 2H), 7.51 (s, 2H), 7.45 (d, J = 7.2 Hz, 1H), 7.36 - 7.26 (m, 4H), 7.17 (t, J = 7.5 Hz, 1H), 2.53 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 191.1, 168.4, 136.0, 135.3, 134.0, 131.9 (q, $J_{\text{C}-\text{F}}$ = 5.0 Hz), 131.8 (q, $J_{\text{C}-\text{F}}$ = 32.3 Hz), 128.7, 128.7, 128.5, 126.4, 125.8, 124.1, 122.8 (q, $J_{\text{C}-\text{F}}$ = 273.3 Hz), 119.8, 116.7, 112.6, 23.8. ^{19}F NMR (282 MHz, CDCl_3) δ -66.4. HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{15}\text{F}_3\text{NO}_2$ [M+H] $^+$: 358.1049, found 358.1058.

(E)-4,4,4-trifluoro-1-phenyl-3-(1-tosyl-1H-indol-3-yl)but-2-en-1-one (2c)



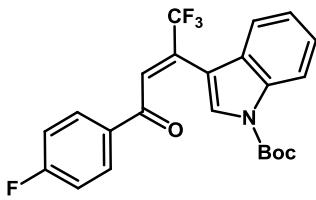
From 0.73 g (2 mmol) 2,2,2-trifluoro-1-(1-tosyl-1H-indol-3-yl)ethanone and 1.06 g (2.8 mmol, 1.4 equiv) 1-phenyl-2-(triphenylphosphoranylidene)ethanone, β -indole- β - CF_3 enone **2c** was obtained as a yellow solid (0.55 g, 59% yield), mp = 76 - 77 °C. ^1H NMR (300 MHz, CDCl_3) δ 7.73 (d, J = 8.1 Hz, 1H), 7.62 (d, J = 7.2 Hz, 2H), 7.57 (s, 1H), 7.52 (d, J = 7.8 Hz, 2H), 7.33 (s, 1H), 7.25 (t, J = 9.2 Hz, 2H), 7.14 (t, J = 7.4 Hz, 3H), 7.02 (d, J = 7.2 Hz, 3H), 2.14 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 191.3, 145.4, 135.8, 134.7, 134.4, 133.9, 132.4 (q, $J_{\text{C}-\text{F}}$ = 4.8 Hz), 131.2 (q, $J_{\text{C}-\text{F}}$ = 32.3 Hz), 130.0, 129.0, 128.7, 128.6, 127.3, 126.9, 125.2, 123.7, 122.8 (q, $J_{\text{C}-\text{F}}$ = 273.0 Hz), 120.6, 113.5, 112.5, 21.5. ^{19}F NMR (282 MHz, CDCl_3) δ -66.5. HRMS (ESI) m/z calcd for $\text{C}_{25}\text{H}_{19}\text{F}_3\text{NO}_3\text{S}$ [M+H] $^+$: 470.1032, found 470.1041.

tert-butyl-(E)-3-(1,1,1-trifluoro-4-(4-methoxyphenyl)-4-oxobut-2-en-2-yl)-1H-indole-1-carboxylate (2d)



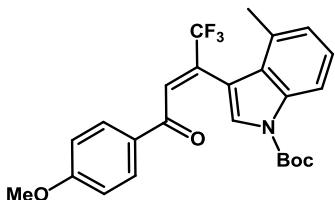
From 0.63 g (2 mmol) *tert*-butyl 3-(2,2,2-trifluoroacetyl)-1H-indole-1-carboxylate and 1.15 g (2.8 mmol, 1.4 equiv) 1-(4-methoxyphenyl)-2-(triphenylphosphoranylidene)-ethanone, β -indole- β - CF_3 enone **2d** was obtained as a yellow solid (0.66 g, 74% yield), mp = 123 - 124 °C. ^1H NMR (300 MHz, CDCl_3) δ 8.09 (d, J = 8.1 Hz, 1H), 7.77 (d, J = 8.7 Hz, 2H), 7.73 (s, 1H), 7.46 (s, 1H), 7.36 (d, J = 7.8 Hz, 1H), 7.22 (t, J = 7.5 Hz, 1H), 7.11 (t, J = 7.4 Hz, 1H), 6.73 (d, J = 9.0 Hz, 2H), 3.63 (s, 3H), 1.58 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3) δ 189.4, 164.2, 149.1, 135.0, 132.0 (q, $J_{\text{C}-\text{F}}$ = 5.0 Hz), 131.2, 131.1 (q, $J_{\text{C}-\text{F}}$ = 31.8 Hz), 129.2, 128.8, 126.6, 124.9, 123.1 (q, $J_{\text{C}-\text{F}}$ = 272.8 Hz), 121.3, 120.0, 115.4, 113.9, 111.3, 84.4, 55.3, 27.9. ^{19}F NMR (282 MHz, CDCl_3) δ -66.6. HRMS (ESI) m/z calcd for $\text{C}_{24}\text{H}_{23}\text{F}_3\text{NO}_4$ [M+H] $^+$: 446.1574, found 446.1583.

tert-butyl-(E)-3-(1,1,1-trifluoro-4-(4-fluorophenyl)-4-oxobut-2-en-2-yl)-1H-indole-1-carboxylate (2e)



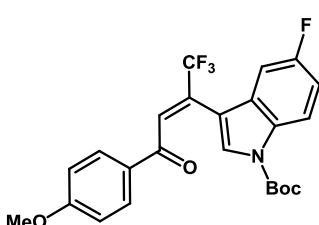
From 0.63 g (2 mmol) *tert*-butyl 3-(2,2,2-trifluoroacetyl)-1H-indole-1-carboxylate and 1.11 g (2.8 mmol, 1.4 equiv) 1-(4-fluorophenyl)-2-(triphenylphosphoranylidene)-ethanone, β -indole- β -CF₃ enone **2e** was obtained as a yellow oil (0.61 g, 70% yield). ¹H NMR (300 MHz, CDCl₃) δ 8.08 (d, *J* = 8.4 Hz, 1H), 7.87 - 7.83 (m, 2H), 7.67 (s, 1H), 7.42 (d, *J* = 1.5 Hz, 1H), 7.31 - 7.25 (m, 2H), 7.18 - 7.13 (m, 1H), 7.07 - 7.00 (m, 2H), 1.65 (s, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 189.8, 166.0 (d, *J*_{C-F} = 255.0 Hz), 149.1, 134.9, 132.7 (d, *J*_{C-F} = 5.3 Hz), 132.5 (q, *J*_{C-F} = 32.0 Hz), 131.5 (d, *J*_{C-F} = 9.0 Hz), 130.7 (q, *J*_{C-F} = 4.8 Hz), 128.5, 126.7, 125.0, 123.1, 122.8 (q, *J*_{C-F} = 273.0 Hz), 119.8, 115.9 (d, *J*_{C-F} = 21.8 Hz), 115.4, 110.9, 84.6, 28.1. ¹⁹F NMR (282 MHz, CDCl₃) δ -66.9, -103.2. HRMS (ESI) *m/z* calcd for C₂₃H₂₀F₄NO₃ [M+H]⁺: 434.1374, found 434.1378.

***tert*-butyl-(E)-4-methyl-3-(1,1,1-trifluoro-4-(4-methoxyphenyl)-4-oxobut-2-yl)-1H-indole-1-carboxylate (2f)**



From 0.65 g (2 mmol) *tert*-butyl 4-methyl-3-(2,2,2-trifluoroacetyl)-1H-indole-1-carboxylate and 1.15 g (2.8 mmol, 1.4 equiv) 1-(4-methoxyphenyl)-2-(triphenylphosphoranylidene)ethanone, β -indole- β -CF₃ enone **2f** was obtained as a yellow oil (0.56 g, 70% yield). ¹H NMR (300 MHz, CDCl₃) δ 8.00 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 9.0 Hz, 2H), 7.62 (d, *J* = 1.5 Hz, 1H), 7.47 (s, 1H), 7.20 (t, *J* = 7.8 Hz, 1H), 6.98 (d, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 9.0 Hz, 2H), 3.82 (s, 3H), 2.47 (s, 3H), 1.62 (s, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 188.0, 164.2, 149.3, 135.1, 134.6 (q, *J*_{C-F} = 31.8 Hz), 131.9 (q, *J*_{C-F} = 4.3 Hz), 131.1, 129.7, 128.7, 125.3, 124.9, 124.8, 124.5, 122.6 (q, *J*_{C-F} = 272.8 Hz), 114.0, 113.1, 110.8, 84.1, 55.5, 28.1, 19.1. ¹⁹F NMR (282 MHz, CDCl₃) δ -67.8. HRMS (ESI) *m/z* calcd for C₂₅H₂₅F₃NO₄ [M+H]⁺: 460.1730, found 460.1740.

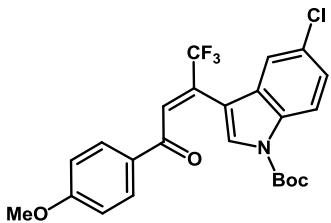
***tert*-butyl-(E)-5-fluoro-3-(1,1,1-trifluoro-4-(4-methoxyphenyl)-4-oxobut-2-yl)-1H-indole-1-carboxylate (2g)**



From 0.66 g (2 mmol) *tert*-butyl 5-fluoro-3-(2,2,2-trifluoroacetyl)-1H-indole-1

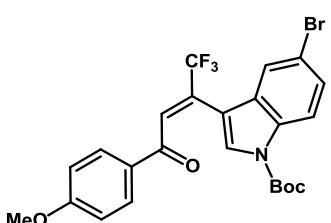
-carboxylate and 1.15 g (2.8 mmol, 1.4 equiv) 1-(4-methoxyphenyl)-2-(triphenylphosphoranylidene)ethanone, β -indole- β -CF₃ enone **2g** was obtained as a yellow solid (0.70 g, 76% yield), mp = 101 - 102 °C. ¹H NMR (300 MHz, CDCl₃) δ 8.04 (dd, J = 9.0, 3.9 Hz, 1H), 7.84 (d, J = 8.7 Hz, 2H), 7.69 (s, 1H), 7.49 (d, J = 1.5 Hz, 1H), 7.00 (s, 1H), 6.97 (d, J = 2.1 Hz, 1H), 6.87 (d, J = 9.0 Hz, 2H), 3.82 (s, 3H), 1.64 (s, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 189.3, 164.3, 159.3 (d, J_{C-F} = 238.5 Hz), 148.9, 131.8 (q, J_{C-F} = 4.8 Hz), 131.3, 131.2, 131.0 (q, J_{C-F} = 32.0 Hz), 129.7 (d, J_{C-F} = 9.8 Hz), 129.2, 128.0, 122.8 (q, J_{C-F} = 273.0 Hz), 116.4 (d, J_{C-F} = 9.0 Hz), 114.0, 113.0, 112.6, 110.9 (d, J_{C-F} = 4.5 Hz), 105.6 (d, J_{C-F} = 24.0 Hz), 84.7, 55.5. ¹⁹F NMR (282 MHz, CDCl₃) δ -66.8, -119.8. HRMS (ESI) *m/z* calcd for C₂₄H₂₂F₄NO₄ [M+H]⁺: 464.1479, found 464.1489.

tert-butyl-(E)-5-chloro-3-(1,1,1-trifluoro-4-(4-methoxyphenyl)-4-oxobut-2-en-2-yl)-1H-indole-1-carboxylate (2h)



From 0.68 g (2 mmol) *tert*-butyl 5-chloro-3-(2,2,2-trifluoroacetyl)-1*H*-indole-1-carboxylate and 1.15 g (2.8 mmol, 1.4 equiv) 1-(4-methoxyphenyl)-2-(triphenylphosphoranylidene)ethanone, β -indole- β -CF₃ enone **2h** was obtained as a yellow solid (0.70 g, 84% yield), mp = 109 - 110 °C. ¹H NMR (300 MHz, CDCl₃) δ 7.87 (d, J = 9.0 Hz, 1H), 7.68 (d, J = 9.0 Hz, 2H), 7.56 (s, 1H), 7.37 (d, J = 1.2 Hz, 1H), 7.18 (d, J = 1.8 Hz, 1H), 7.05 (dd, J = 8.7, 1.8 Hz, 1H), 6.69 (d, J = 9.0 Hz, 2H), 3.60 (s, 3H), 1.47 (s, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 189.1, 164.3, 148.7, 133.4, 132.3 (q, J_{C-F} = 4.3 Hz), 131.2, 130.6 (q, J_{C-F} = 32.3 Hz), 130.0, 129.1, 128.8, 127.7, 125.0, 122.9 (q, J_{C-F} = 273 Hz), 119.7, 116.4, 114.0, 110.5, 84.9, 55.4, 27.9. ¹⁹F NMR (282 MHz, CDCl₃) δ -66.8. HRMS (ESI) *m/z* calcd for C₂₄H₂₂ClF₃NO₄ [M+H]⁺: 480.1184, found 480.1195.

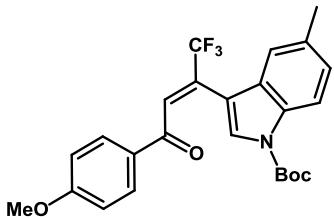
tert-butyl-(E)-5-bromo-3-(1,1,1-trifluoro-4-(4-methoxyphenyl)-4-oxobut-2-en-2-yl)-1H-indole-1-carboxylate (2i)



From 0.78 g (2 mmol) *tert*-butyl 5-bromo-3-(2,2,2-trifluoroacetyl)-1*H*-indole-1-carboxylate and 1.15 g (2.8 mmol, 1.4 equiv) 1-(4-methoxyphenyl)-2-(triphenylphosphoranylidene)ethanone, β -indole- β -CF₃ enone **2i** was obtained as a yellow solid (0.79 g, 75% yield), mp = 114 - 115 °C. ¹H NMR (300 MHz, CDCl₃) δ 7.97 (d, J = 8.7 Hz, 1H), 7.84 (d, J = 8.7 Hz, 2H), 7.65 (s, 1H), 7.51 (d, J = 1.2 Hz, 1H),

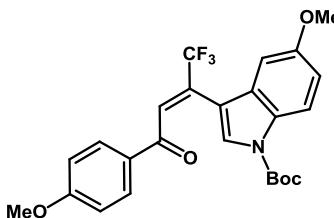
7.43 (d, $J = 1.5$ Hz, 1H), 7.35 (dd, $J = 8.7, 1.8$ Hz, 1H), 6.89 (d, $J = 9.0$ Hz, 2H), 3.83 (s, 3H), 1.64 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3) δ 189.3, 164.3, 148.7, 133.7, 132.2 (q, $J_{\text{C}-\text{F}} = 4.5$ Hz), 131.2, 130.7 (q, $J_{\text{C}-\text{F}} = 32.3$ Hz), 130.4, 129.2, 127.7, 127.5, 122.7, 122.7 (q, $J_{\text{C}-\text{F}} = 272.8$ Hz), 116.8, 116.5, 114.1, 110.3, 84.9, 55.6, 28.1. ^{19}F NMR (282 MHz, CDCl_3) δ -66.8. HRMS (ESI) m/z calcd for $\text{C}_{24}\text{H}_{22}\text{BrF}_3\text{NO}_4$ [$\text{M}+\text{H}]^+$: 524.0679, found 524.0690.

tert-butyl-(E)-5-methyl-3-(1,1,1-trifluoro-4-(4-methoxyphenyl)-4-oxobut-2-en-2-yl)-1H-indole-1-carboxylate (2j)



From 1.00 g (3.06 mmol) *tert*-butyl 5-methyl-3-(2,2,2-trifluoroacetyl)-1H-indole-1-carboxylate and 1.76 g (4.28 mmol, 1.4 equiv) 1-(4-methoxyphenyl)-2-(triphenylphosphoranylidene)ethanone, β -indole- β -CF₃ enone **2j** was obtained as a yellow solid (0.99 g, 70% yield), mp = 98 - 99 °C. ^1H NMR (300 MHz, CDCl_3) δ 7.94 (d, $J = 8.7$ Hz, 1H), 7.84 (d, $J = 9.0$ Hz, 2H), 7.63 (s, 1H), 7.46 (d, $J = 1.2$ Hz, 1H), 7.08 - 7.06 (m, 2H), 6.85 (d, $J = 8.7$ Hz, 2H), 3.79 (s, 3H), 2.27 (s, 3H), 1.62 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3) δ 189.7, 164.1, 149.2, 133.1, 132.5, 131.5 (q, $J_{\text{C}-\text{F}} = 5.0$ Hz), 131.4 (q, $J_{\text{C}-\text{F}} = 32.0$ Hz), 131.2, 129.4, 128.8, 126.5, 126.2, 123.0 (q, $J_{\text{C}-\text{F}} = 273.0$ Hz), 119.9, 114.9, 113.9, 110.9, 84.2, 55.5, 28.1, 21.3. ^{19}F NMR (282 MHz, CDCl_3) δ -66.8. HRMS (ESI) m/z calcd for $\text{C}_{25}\text{H}_{25}\text{F}_3\text{NO}_4$ [$\text{M}+\text{H}]^+$: 460.1730, found 460.1740.

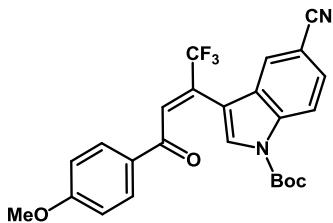
tert-butyl-(E)-5-methoxy-3-(1,1,1-trifluoro-4-(4-methoxyphenyl)-4-oxobut-2-en-2-yl)-1H-indole-1-carboxylate (2k)



From 0.69 g (2 mmol) *tert*-butyl 5-methoxy-3-(2,2,2-trifluoroacetyl)-1H-indole-1-carboxylate and 1.15 g (2.8 mmol, 1.4 equiv) 1-(4-methoxyphenyl)-2-(triphenylphosphoranylidene)ethanone, β -indole- β -CF₃ enone **2k** was obtained as a yellow oil (0.71 g, 75% yield). ^1H NMR (300 MHz, CDCl_3) δ 7.94 (d, $J = 9.0$ Hz, 1H), 7.87 (d, $J = 8.7$ Hz, 2H), 7.68 (s, 1H), 7.46 (d, $J = 1.5$ Hz, 1H), 6.90 - 6.84 (m, 3H), 6.66 (d, $J = 2.4$ Hz, 1H), 3.82 (s, 3H), 3.52 (s, 3H), 1.64 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3) δ 189.7, 164.2, 156.0, 149.1, 131.3 (q, $J_{\text{C}-\text{F}} = 6.0$ Hz), 131.3 (q, $J_{\text{C}-\text{F}} = 31.8$ Hz), 131.2, 129.5, 129.3, 129.3, 126.8, 123.0 (q, $J_{\text{C}-\text{F}} = 273.0$ Hz), 116.2, 114.3, 114.0, 111.0, 101.8, 84.3, 55.5, 55.1, 28.1. ^{19}F NMR (282 MHz, CDCl_3) δ -66.9. HRMS (ESI) m/z calcd for $\text{C}_{25}\text{H}_{25}\text{F}_3\text{NO}_5$ [$\text{M}+\text{H}]^+$: 476.1679, found 476.1691.

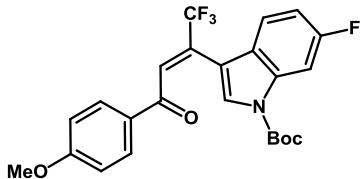
tert-butyl-(E)-5-cyano-3-(1,1,1-trifluoro-4-(4-methoxyphenyl)-4-oxobut-2-en-2-yl)

-1H-indole-1-carboxylate (2l)



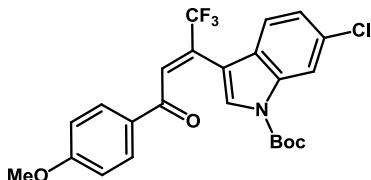
From 1.08 g (3.2 mmol) *tert*-butyl 5-cyano-3-(2,2,2-trifluoroacetyl)-1H-indole-1-carboxylate and 1.84 g (4.48 mmol, 1.4 equiv) 1-(4-methoxyphenyl)-2-(triphenylphosphoranylidene)ethanone, β -indole- β -CF₃ enone **2l** was obtained as a yellow oil (1.01 g, 67% yield). ¹H NMR (300 MHz, CDCl₃) δ 8.09 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.65 (s, 1H), 7.55 (s, 1H), 7.49 (s, 1H), 7.39 (d, *J* = 8.4 Hz, 1H), 6.77 (d, *J* = 8.4 Hz, 2H), 3.69 (s, 3H), 1.53 (s, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 188.7, 164.5, 148.4, 136.8, 132.8 (q, *J*_{C-F} = 4.5 Hz), 131.2, 130.2 (q, *J*_{C-F} = 32.0 Hz), 129.0, 128.9, 128.4, 127.8, 124.9, 122.7 (q, *J*_{C-F} = 275.0 Hz), 119.4, 116.3, 114.2, 110.8, 106.5, 85.7, 55.5, 27.9. ¹⁹F NMR (282 MHz, CDCl₃) δ -67.0. HRMS (ESI) *m/z* calcd for C₂₅H₂₂F₃N₂O₄ [M+H]⁺: 471.1526, found 471.1534.

***tert*-butyl-(E)-6-fluoro-3-(1,1,1-trifluoro-4-(4-methoxyphenyl)-4-oxobut-2-en-2-yl)-1H-indole-1-carboxylate (2m)**



From 0.66 g (2 mmol) *tert*-butyl 6-fluoro-3-(2,2,2-trifluoroacetyl)-1H-indole-1-carboxylate and 1.15 g (2.8 mmol, 1.4 equiv) 1-(4-methoxyphenyl)-2-(triphenylphosphoranylidene)ethanone, β -indole- β -CF₃ enone **2m** was obtained as a yellow solid (0.72 g, 77% yield), mp = 100 - 101 °C. ¹H NMR (300 MHz, CDCl₃) δ 7.72 (d, *J* = 8.7 Hz, 3H), 7.54 (s, 1H), 7.37 (s, 1H), 7.14 (dd, *J* = 8.4, 5.4 Hz, 1H), 6.81 (d, *J* = 8.4 Hz, 1H), 6.74 (d, *J* = 8.7 Hz, 2H), 3.70 (s, 3H), 1.53 (s, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 189.4, 164.3, 161.0 (d, *J*_{C-F} = 240.0 Hz), 148.8, 135.2 (d, *J*_{C-F} = 13.5 Hz), 131.8 (q, *J*_{C-F} = 4.8 Hz), 131.2, 131.0 (q, *J*_{C-F} = 32.0 Hz), 129.2, 126.7, 125.0, 122.9 (q, *J*_{C-F} = 273.0 Hz), 120.7 (d, *J*_{C-F} = 9.8 Hz), 114.0, 111.6, 111.1 (d, *J*_{C-F} = 16.5 Hz), 102.7 (d, *J*_{C-F} = 28.5 Hz), 84.9, 55.5, 28.0. ¹⁹F NMR (282 MHz, CDCl₃) δ -66.8, -116.7. HRMS (ESI) *m/z* calcd for C₂₄H₂₂F₄NO₄ [M+H]⁺: 464.1479, found 464.1489.

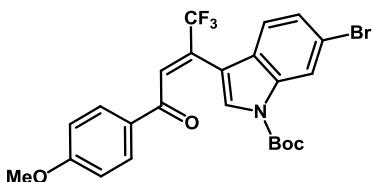
***tert*-butyl-(E)-6-chloro-3-(1,1,1-trifluoro-4-(4-methoxyphenyl)-4-oxobut-2-en-2-yl)-1H-indole-1-carboxylate (2n)**



From 0.69 g (2 mmol) *tert*-butyl 6-chloro-3-(2,2,2-trifluoroacetyl)-1H-indole-1-

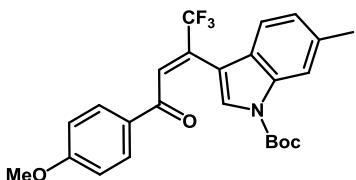
carboxylate and 1.15 g (2.8 mmol, 1.4 equiv) 1-(4-methoxyphenyl)-2-(triphenylphosphoranylidene)ethanone, β -indole- β -CF₃ enone **2n** was obtained as a yellow solid (0.79 g, 82% yield), mp = 99 - 100 °C. ¹H NMR (300 MHz, CDCl₃) δ 8.01 (s, 1H), 7.68 (d, J = 8.7 Hz, 2H), 7.53 (s, 1H), 7.36 (d, J = 1.2 Hz, 1H), 7.09 (d, J = 8.4 Hz, 1H), 6.97 (dd, J = 8.6, 2.0 Hz, 1H), 6.69 (d, J = 8.7 Hz, 2H), 3.63 (s, 3H), 1.49 (s, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 189.3, 164.3, 148.8, 133.7, 132.2 (q, J_{C-F} = 5.0 Hz), 131.2, 130.8 (q, J_{C-F} = 32.3 Hz), 130.3, 129.2, 127.7, 127.5, 122.7, 122.7 (q, J_{C-F} = 272.3 Hz), 116.8, 116.5, 114.1, 110.3, 84.9, 55.6, 28.1. ¹⁹F NMR (282 MHz, CDCl₃) δ -66.8. HRMS (ESI) m/z calcd for C₂₄H₂₂ClF₃NO₄ [M+H]⁺: 480.1184, found 480.1195.

tert-butyl-(E)-6-bromo-3-(1,1,1-trifluoro-4-(4-methoxyphenyl)-4-oxobut-2-en-2-yl)-1H-indole-1-carboxylate (2o)



From 0.78 g (2 mmol) *tert*-butyl 6-bromo-3-(2,2,2-trifluoroacetyl)-1H-indole-1-carboxylate and 1.15 g (2.8 mmol, 1.4 equiv) 1-(4-methoxyphenyl)-2-(triphenylphosphoranylidene)ethanone, β -indole- β -CF₃ enone **2o** was obtained as a yellow solid (0.80 g, 76% yield), mp = 112 - 113 °C. ¹H NMR (300 MHz, CDCl₃) δ 7.97 (d, J = 8.7 Hz, 1H), 7.85 (d, J = 9.0 Hz, 2H), 7.64 (s, 1H), 7.51 (d, J = 1.5 Hz, 1H), 7.43 (d, J = 1.5 Hz, 1H), 7.36 (dd, J = 8.7, 1.8 Hz, 1H), 6.90 (d, J = 9.0 Hz, 2H), 3.85 (s, 3H), 1.64 (s, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 189.3, 164.3, 148.8, 133.7, 132.2 (q, J_{C-F} = 4.8 Hz), 131.2, 130.8 (q, J_{C-F} = 32.3 Hz), 130.3, 129.2, 127.7, 127.5, 122.7, 122.7 (q, J_{C-F} = 272.8 Hz), 116.8, 116.5, 114.1, 110.3, 84.9, 55.6, 28.1. ¹⁹F NMR (282 MHz, CDCl₃) δ -66.9. HRMS (ESI) m/z calcd for C₂₄H₂₂BrF₃NO₄ [M+H]⁺: 524.0679, found 524.0689.

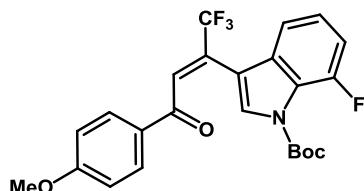
tert-butyl-(E)-6-methyl-3-(1,1,1-trifluoro-4-(4-methoxyphenyl)-4-oxobut-2-en-2-yl)-1H-indole-1-carboxylate (2p)



From 1.06 g (3.2 mmol) *tert*-butyl 6-methyl-3-(2,2,2-trifluoroacetyl)-1H-indole-1-carboxylate and 1.84 g (4.48 mmol, 1.4 equiv) 1-(4-methoxyphenyl)-2-(triphenylphosphoranylidene)ethanone, β -indole- β -CF₃ enone **2p** was obtained as a yellow solid (1.07 g, 73% yield), mp = 108 - 109 °C. ¹H NMR (300 MHz, CDCl₃) δ 7.84 (s, 1H), 7.73 (d, J = 8.7 Hz, 2H), 7.49 (s, 1H), 7.32 (d, J = 1.2 Hz, 1H), 7.08 (d, J = 8.1 Hz, 1H), 6.86 (dd, J = 8.6, 2.0 Hz, 1H), 6.73 (d, J = 9.0 Hz, 2H), 3.68 (s, 3H), 2.31 (s, 3H), 1.53 (s, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 189.7, 164.1, 149.2, 135.4, 134.9, 131.5 (q, J_{C-F} = 31.8 Hz), 131.3 (q, J_{C-F} = 4.0 Hz), 129.3, 126.4, 126.0, 124.5, 123.0 (q,

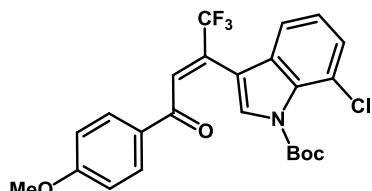
$J_{C-F} = 273.0$ Hz), 119.5, 115.6, 114.1, 113.9, 111.2, 84.2, 55.5, 28.1, 21.9. ^{19}F NMR (282 MHz, $CDCl_3$) δ -66.7. HRMS (ESI) m/z calcd for $C_{25}H_{25}F_3NO_4$ [M+H] $^+$: 460.1730, found 460.1742.

***tert*-butyl-(*E*)-7-fluoro-3-(1,1,1-trifluoro-4-(4-methoxyphenyl)-4-oxobut-2-en-2-yl)-1H-indole-1-carboxylate (2q)**



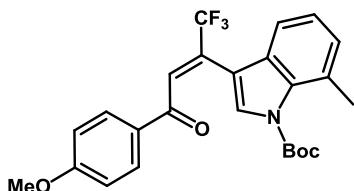
From 1.06 g (3 mmol) *tert*-butyl 7-fluoro-3-(2,2,2-trifluoroacetyl)-1H-indole-1-carboxylate and 1.72 g (4.2 mmol, 1.4 equiv) 1-(4-methoxyphenyl)-2-(triphenylphosphoranylidene)ethanone, β -indole- β -CF₃ enone **2q** was obtained as a yellow oil (1.05 g, 76% yield). 1H NMR (300 MHz, $CDCl_3$) δ 7.81 (d, $J = 9.0$ Hz, 2H), 7.73 (s, 1H), 7.51 (d, $J = 1.2$ Hz, 1H), 7.12 - 7.03 (m, 2H), 7.00 - 6.93 (m, 1H), 6.83 (d, $J = 8.4$ Hz, 2H), 3.77 (s, 3H), 1.61 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.1, 164.3, 151.6, 148.2 (d, $J_{C-F} = 3.0$ Hz), 132.9 (d, $J_{C-F} = 3.8$ Hz), 132.1 (q, $J_{C-F} = 4.8$ Hz), 131.1, 130.8 (q, $J_{C-F} = 32.0$ Hz), 129.1, 128.7, 123.9 (d, $J_{C-F} = 6.8$ Hz), 122.9 (q, $J_{C-F} = 273.0$ Hz), 121.9 (d, $J_{C-F} = 10.5$ Hz), 115.8 (d, $J_{C-F} = 3.0$ Hz), 113.9, 112.1 (d, $J_{C-F} = 21.8$ Hz), 111.2, 84.9, 55.4, 27.7. ^{19}F NMR (282 MHz, $CDCl_3$) δ -66.9, -115.8. HRMS (ESI) m/z calcd for $C_{24}H_{22}F_4NO_4$ [M+H] $^+$: 464.1479, found 464.1492.

***tert*-butyl-(*E*)-7-chloro-3-(1,1,1-trifluoro-4-(4-methoxyphenyl)-4-oxobut-2-en-2-yl)-1H-indole-1-carboxylate (2r)**



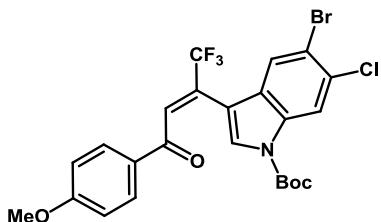
From 1.08 g (3.1 mmol) *tert*-butyl 7-chloro-3-(2,2,2-trifluoroacetyl)-1H-indole-1-carboxylate and 1.78 g (4.34 mmol, 1.4 equiv) 1-(4-methoxyphenyl)-2-(triphenylphosphoranylidene)ethanone, β -indole- β -CF₃ enone **2r** was obtained as a yellow solid (1.24 g, 84% yield), mp = 108 - 109 °C. 1H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, $J = 9.0$ Hz, 2H), 7.51 (s, 1H), 7.41 (d, $J = 1.2$ Hz, 1H), 7.15 - 7.11 (m, 2H), 6.95 (t, $J = 7.8$ Hz, 1H), 6.74 (d, $J = 9.0$ Hz, 2H), 3.70 (s, 3H), 1.50 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.1, 164.3, 148.7, 133.4, 132.3 (q, $J_{C-F} = 4.5$ Hz), 131.2, 130.6 (q, $J_{C-F} = 31.8$ Hz), 130.0, 129.1, 128.8, 127.7, 125.1, 122.9 (q, $J_{C-F} = 272.5$ Hz), 119.7, 116.4, 114.0, 110.5, 84.9, 55.5, 28.0. ^{19}F NMR (282 MHz, $CDCl_3$) δ -66.8. HRMS (ESI) m/z calcd for $C_{24}H_{22}ClF_3NO_4$ [M+H] $^+$: 480.1184, found 480.1193.

***tert*-butyl-(*E*)-7-methyl-3-(1,1,1-trifluoro-4-(4-methoxyphenyl)-4-oxobut-2-en-2-yl)-1H-indole-1-carboxylate (2s)**



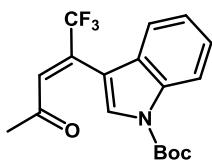
From 0.66 g (2 mmol) *tert*-butyl 7-methyl-3-(2,2,2-trifluoroacetyl)-1H-indole-1-carboxylate and 1.15 g (2.8 mmol, 1.4 equiv) 1-(4-methoxyphenyl)-2-(triphenylphosphoranylidene)ethanone, β -indole- β -CF₃ enone **2s** was obtained as a yellow solid (0.67 g, 73% yield), mp = 113 - 114 °C. ¹H NMR (300 MHz, CDCl₃) δ 7.66 (d, *J* = 8.7 Hz, 2H), 7.47 (s, 1H), 7.31 (d, *J* = 1.5 Hz, 1H), 7.04 (q, *J* = 3.0 Hz, 1H), 6.92 (s, 1H), 6.90 (d, *J* = 3.3 Hz, 1H), 6.64 (d, *J* = 8.7 Hz, 2H), 3.57 (s, 3H), 2.41 (s, 3H), 1.45 (s, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 189.6, 164.2, 148.9, 134.5, 131.8 (q, *J*_{C-F} = 4.8 Hz), 131.4 (q, *J*_{C-F} = 31.8 Hz), 131.2, 130.0, 129.3, 128.8, 128.3, 125.5, 123.5, 123.0 (q, *J*_{C-F} = 272.8 Hz), 117.6, 113.9, 111.1, 84.1, 55.4, 27.9, 22.2. ¹⁹F NMR (282 MHz, CDCl₃) δ -66.6. HRMS (ESI) *m/z* calcd for C₂₅H₂₅F₃NO₄ [M+H]⁺: 460.1730, found 460.1739.

tert-butyl-(E)-5-bromo-6-chloro-3-(1,1,1-trifluoro-4-(4-methoxyphenyl)-4-oxobut-2-en-2-yl)-1H-indole-1-carboxylate (2t)



From 0.88 g (2.1 mmol) *tert*-butyl 5-bromo-6-chloro-3-(2,2,2-trifluoroacetyl)-1H-indole-1-carboxylate and 1.21 g (2.94 mmol, 1.4 equiv) 1-(4-methoxyphenyl)-2-(triphenylphosphoranylidene)ethanone, β -indole- β -CF₃ enone **2t** was obtained as a yellow oil (0.84 g, 71% yield). ¹H NMR (300 MHz, CDCl₃) δ 8.11 (s, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.53 (s, 1H), 7.41 (s, 2H), 6.69 (d, *J* = 8.4 Hz, 2H), 3.62 (s, 3H), 1.48 (s, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 188.9, 164.4, 148.4, 134.3, 132.6 (q, *J*_{C-F} = 4.8 Hz), 131.1, 130.6, 130.2 (q, *J*_{C-F} = 32.0 Hz), 129.0, 128.7, 127.9, 124.4, 122.7 (q, *J*_{C-F} = 273.0 Hz), 117.0, 116.7, 114.1, 110.1, 85.4, 55.5, 27.9. ¹⁹F NMR (282 MHz, CDCl₃) δ -66.9. HRMS (ESI) *m/z* calcd for C₂₄H₂₁BrClF₃NO₄ [M+H]⁺: 558.0289, found 558.0299.

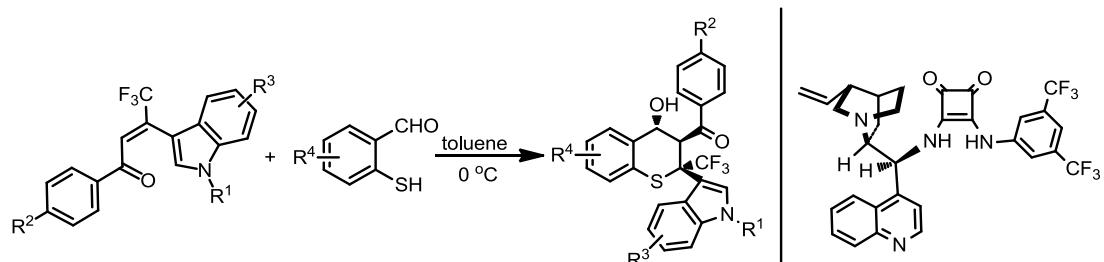
(E)-tert-butyl-3-(1,1,1-trifluoro-4-oxopent-2-en-2-yl)-1H-indole-1-carboxylate (2u)



From 0.63 g (2 mmol) *tert*-butyl 3-(2,2,2-trifluoroacetyl)-1H-indole-1-carboxylate and 0.89 g (2.8 mmol, 1.4 equiv) 1-(triphenylphosphoranylidene)propan-2-one, β -indole- β -CF₃ enone **2u** was obtained as a yellow solid (0.56 g, 79% yield), mp = 91

- 92 °C. ^1H NMR (300 MHz, CDCl_3) δ 8.10 (d, $J = 8.4$ Hz, 1H), 7.63 (s, 1H), 7.33 - 7.26 (m, 2H), 7.23 - 7.16 (m, 1H), 6.80 (d, $J = 1.5$ Hz, 1H), 1.93 (s, 3H), 1.61 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3) δ 198.8, 149.1, 135.0, 133.6 (q, $J_{\text{C}-\text{F}} = 4.5$ Hz), 131.6 (q, $J_{\text{C}-\text{F}} = 32.0$ Hz), 129.0, 126.3, 125.3, 123.5, 122.8 (q, $J_{\text{C}-\text{F}} = 273.2$ Hz), 119.5, 115.5, 110.7, 84.8, 30.2, 28.1. ^{19}F NMR (282 MHz, CDCl_3) δ -67.6. HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{19}\text{F}_3\text{NO}_3$ [M+H] $^+$: 354.1267, found 354.1277.

3. Representative Procedure

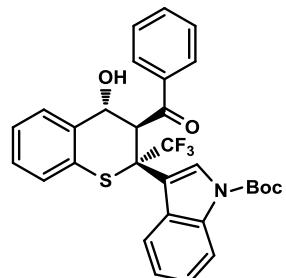


To a solution of cinchonidine derived squaramide organocatalyst **C6** (12 mg, 0.02 mmol) and 2-mercaptopbenzaldehyde (0.2 mmol) in toluene (2.0 mL) was added β -indole- β -CF₃ enones (0.22 mmol) in toluene (1.0 mL) under nitrogen atmosphere with protecting from light conditions at 0 °C. The reaction mixture was monitored by TLC inspection. The solvent was evaporated under reduced pressure and the crude residue was purified on silica gel flash column chromatography using ethyl acetate/hexanes (1/7) eluent to give the corresponding CF₃- and indole-containing thiochromanes **3a-w**.

Racemates were prepared following the general procedure by combination of 7.5 mol % quinidine and 2.5 mol % quinine.

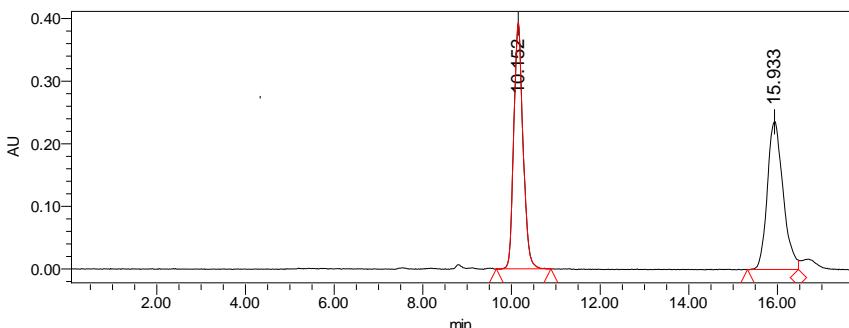
4. Analytical Data and HPLC Chromatogram of the Addition Products

tert-butyl-3-((2*S*,3*S*,4*R*)-3-benzoyl-4-hydroxy-2-(trifluoromethyl)thiochroman-2-yl)-1*H*-indole-1-carboxylate (**3a**)

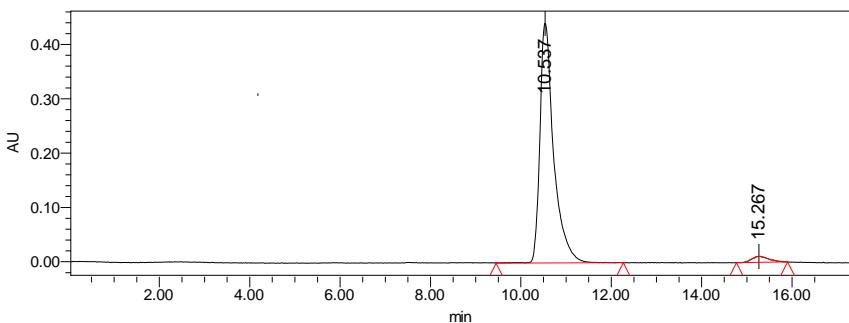


From 27.6 mg (0.2 mmol) 2-mercaptopbenzaldehyde and 91.3 mg (0.22 mmol, 1.1 equiv) β -indole- β -CF₃ enones **2a**, 88.6 mg (80.0% yield) compound **3a** was obtained as a white solid, mp = 174 - 175 °C. $[\alpha]_D^{20} = +35$ (c = 1.0, CHCl_3). Dr (>20:1) determined by ^1H and ^{19}F NMR analysis. 94% ee was determined by HPLC analysis (Daicel Chiralcel IA-H column, hexane/2-propanol 3:1, 1.0 mL/min). Retention time: $t_{\text{major}} = 10.5$ and $t_{\text{minor}} = 15.3$ min. ^1H NMR (300 MHz, CDCl_3) δ 8.14 (d, $J = 7.8$ Hz, 1H), 7.99 (d, $J = 8.1$ Hz, 1H), 7.63 (d, $J = 7.5$ Hz, 1H), 7.34 - 7.21 (m, 4H), 7.14 - 7.04 (m, 7H), 5.65 (dd, $J = 9.5, 5.6$ Hz, 1H), 4.18 (d, $J = 9.9$ Hz, 1H), 3.55 (d, $J = 5.7$ Hz, 1H), 1.48 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3) δ 198.9, 148.9, 139.5, 139.0, 135.2, 132.7,

131.0, 128.4, 128.0, 128.0, 127.8, 127.7, 127.4, 126.9 (q, $J_{C-F} = 290.0$ Hz), 126.2, 125.0, 124.8, 123.9, 122.1, 114.9, 112.1, 84.3, 70.2, 57.1, 56.8 (q, $J_{C-F} = 27.0$ Hz), 28.1. ^{19}F NMR (282 MHz, CDCl₃) δ -69.0. HRMS (ESI) m/z calcd for C₃₀H₂₇F₃NO₄S [M+H]⁺: 554.1607, found 554.1626.

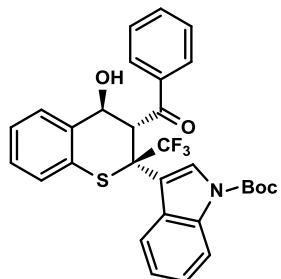


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	10.152	5657133	49.27	393197	bb	Unknown
2	15.933	5824788	50.73	236491	bv	Unknown



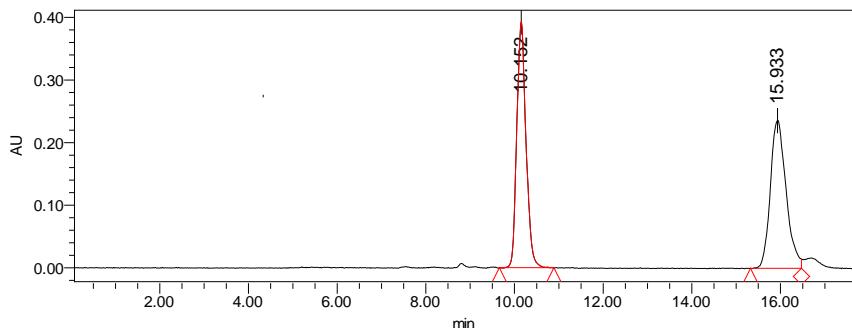
	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	10.537	9333784	97.00	441572	bb	Unknown
2	15.267	288645	3.00	11008	bb	Unknown

tert-butyl-3-((2*R*,3*R*,4*S*)-3-benzoyl-4-hydroxy-2-(trifluoromethyl)thiochroman-2-yl)-1*H*-indole-1-carboxylate (3a')

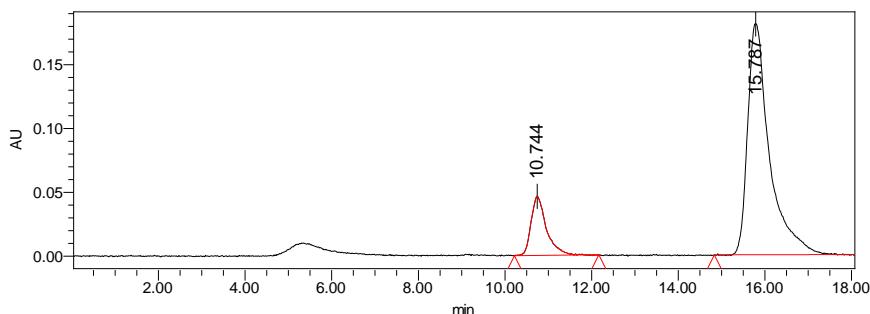


From 27.6 mg (0.2 mmol) 2-mercaptopbenzaldehyde and 91.3 mg (0.22 mmol, 1.1 equiv) β -indole- β -CF₃ enones **2a**, with **C7** (12 mg, 10 mol %) as catalyst, 91.9 mg (83.0% yield) compound **3a'** was obtained as a white solid, mp = 91 - 92 °C. $[\alpha]_D^{20} = -25$ (c = 1.0, CHCl₃). Dr (>20:1) determined by ¹H and ¹⁹F NMR analysis. -69% ee was determined by HPLC analysis (Daicel Chiralcel IA-H column, hexane/2-propanol 3:1, 1.0 mL/min). Retention time: $t_{\text{major}} = 15.8$ and $t_{\text{minor}} = 10.7$ min. ¹H NMR (300

MHz, CDCl₃) δ 8.21 (t, *J* = 8.0 Hz, 1H), 8.11 (t, *J* = 8.4 Hz, 1H), 7.73 (d, *J* = 7.2 Hz, 1H), 7.43 - 7.32 (m, 4H), 7.30 - 7.14 (m, 7H), 5.76 (dd, *J* = 9.3, 4.8 Hz, 1H), 4.28 (d, *J* = 9.9 Hz, 1H), 3.53 (d, *J* = 5.4 Hz, 1H), 1.58 (s, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 198.9, 148.9, 139.6, 139.0, 135.2, 132.7, 131.1, 128.4, 128.0, 128.0, 127.8, 127.7, 127.4, 126.9 (q, *J*_{C-F} = 290.5 Hz), 126.2, 125.0, 124.8, 123.9, 122.1, 114.9, 112.1, 84.3, 70.2, 57.1, 57.1 (q, *J*_{C-F} = 12.3 Hz), 28.1. ¹⁹F NMR (282 MHz, CDCl₃) δ -69.0. HRMS (ESI) *m/z* calcd for C₃₀H₂₇F₃NO₄S [M+H]⁺: 554.1607, found 554.1610.

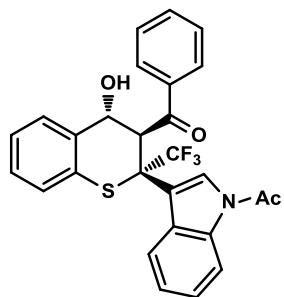


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	10.152	5657133	49.27	393197	bb	Unknown
2	15.933	5824788	50.73	236491	bv	Unknown



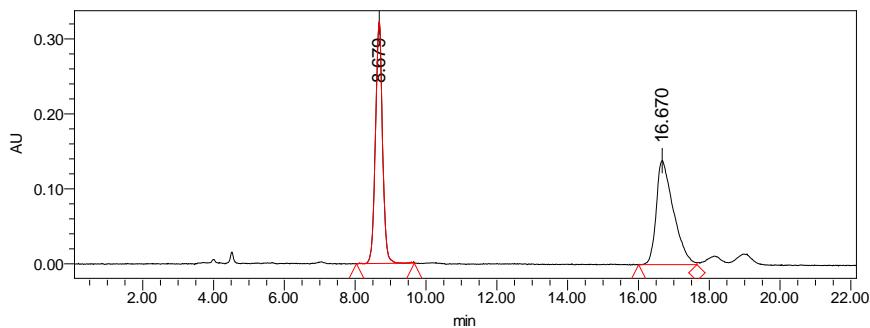
	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	10.744	1147083	15.32	46491	bb	Unknown
2	15.787	6342574	84.68	181399	bb	Unknown

1-(3-((2*S*,3*S*,4*R*)-3-benzoyl-4-hydroxy-2-(trifluoromethyl)thiochroman-2-yl)-1*H*-indol-1-yl)ethanone (**3b**)

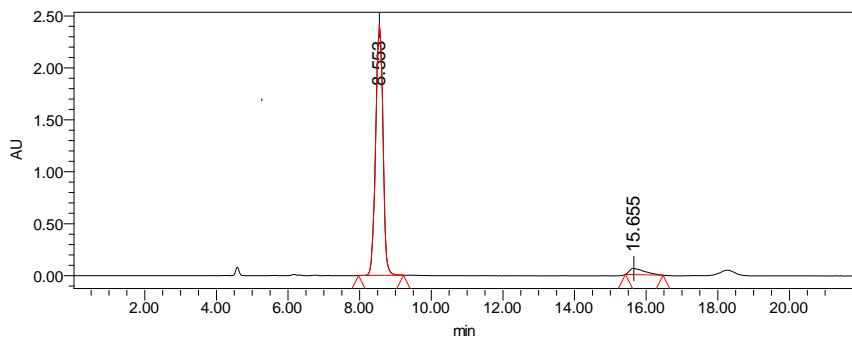


From 27.6 mg (0.2 mmol) 2-mercaptopbenzaldehyde and 78.6 mg (0.22 mmol, 1.1 equiv) β -indole- β -CF₃ enones **2b**, 80.2 mg (81.0% yield) compound **3b** was obtained

as a colorless oil. $[\alpha]_D^{20} = +45$ ($c = 1.0$, CHCl_3). Dr (>20:1) determined by ^1H and ^{19}F NMR analysis. 90% ee was determined by HPLC analysis (Daicel Chiralcel IA-H column, hexane/2-propanol 3:1, 1.0 mL/min). Retention time: $t_{\text{major}} = 8.6$ and $t_{\text{minor}} = 15.7$ min. ^1H NMR (300 MHz, CDCl_3) δ 8.28 (d, $J = 7.8$ Hz, 1H), 8.13 (d, $J = 8.1$ Hz, 1H), 7.63 (d, $J = 7.2$ Hz, 1H), 7.33 - 7.23 (m, 4H), 7.21 - 7.06 (m, 6H), 6.87 (s, 1H), 5.65 (dd, $J = 9.3, 5.1$ Hz, 1H), 4.20 (d, $J = 9.9$ Hz, 1H), 3.71 (d, $J = 5.4$ Hz, 1H), 2.17 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 198.7, 168.3, 139.5, 138.9, 135.6, 132.8, 130.7, 128.3, 128.1, 128.0, 127.9, 127.7, 127.6, 126.9 (q, $J_{\text{C}-\text{F}} = 283.0$ Hz), 125.7, 125.4 (d, $J_{\text{C}-\text{F}} = 3.8$ Hz), 125.2, 123.8, 123.1, 116.2, 113.9, 70.1, 57.0, 56.8 (q, $J_{\text{C}-\text{F}} = 26.8$ Hz), 23.8. ^{19}F NMR (282 MHz, CDCl_3) δ -68.8. HRMS (ESI) m/z calcd for $\text{C}_{27}\text{H}_{21}\text{F}_3\text{NO}_3\text{S}$ [$\text{M}+\text{H}]^+$: 496.1189, found 496.1186.

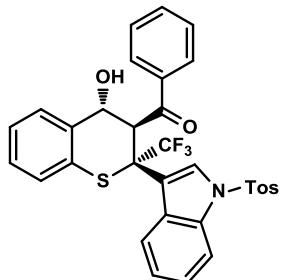


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	8.679	4439631	48.79	323987	bb	Unknown
2	16.670	4659881	51.21	138823	bv	Unknown

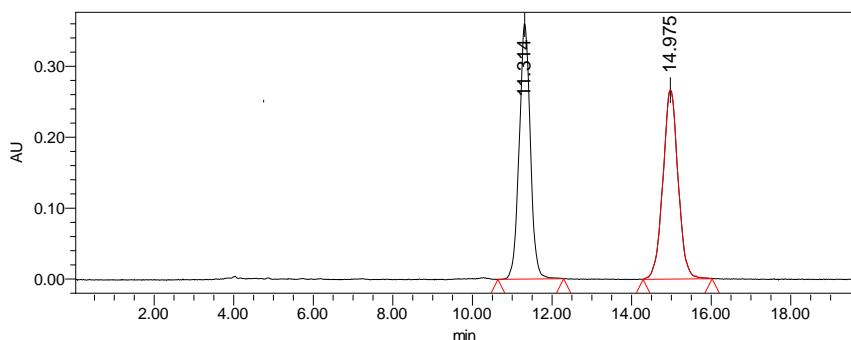


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	8.553	34157565	95.06	2387393	bb	Unknown
2	15.655	1773621	4.94	60257	bb	Unknown

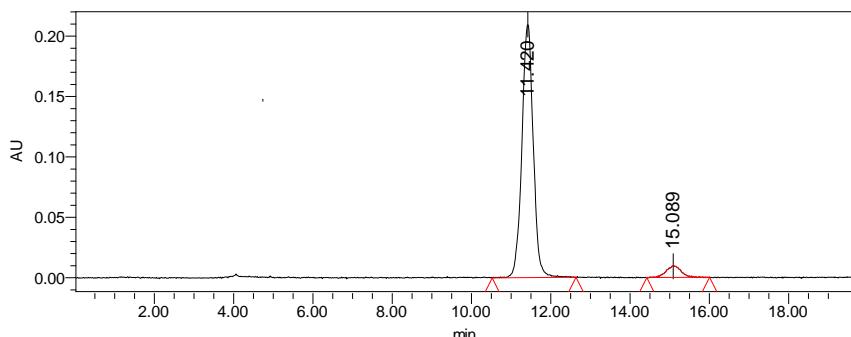
((2*S*,3*S*,4*R*)-4-hydroxy-2-(1-tosyl-1*H*-indol-3-yl)-2-(trifluoromethyl)thiochroman-3-yl)(phenyl)methanone (3c)



From 27.6 mg (0.2 mmol) 2-mercaptopbenzaldehyde and 103.2 mg (0.22 mmol, 1.1 equiv) β -indole- β -CF₃ enones **2c**, 106.9 mg (88.0% yield) compound **3c** was obtained as a white solid, mp = 77 - 78 °C. $[\alpha]_D^{20} = +82$ (c = 1.0, CHCl₃). Dr (>20:1) determined by ¹H and ¹⁹F NMR analysis. 89% ee was determined by HPLC analysis (Daicel Chiralcel IA-H column, hexane/2-propanol 3:1, 1.0 mL/min). Retention time: $t_{\text{major}} = 11.4$ and $t_{\text{minor}} = 15.1$ min. ¹H NMR (300 MHz, CDCl₃) δ 8.24 - 8.21 (m, 1H), 7.89 - 7.85 (m, 1H), 7.68 - 7.63 (m, 3H), 7.46 - 7.31 (m, 4H), 7.29 (s, 1H), 7.24 - 7.13 (m, 8H), 5.65 (dd, $J = 9.8, 5.9$ Hz, 1H), 4.28 (d, $J = 9.9$ Hz, 1H), 3.46 (d, $J = 5.1$ Hz, 1H), 2.33 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 198.6, 145.3, 139.5, 138.4, 134.7, 134.5, 133.1, 130.6, 130.0, 130.0, 128.9, 128.3, 127.8, 127.8, 127.4, 126.9, 126.8 (q, $J_{\text{C-F}} = 282.3$ Hz), 125.9, 125.8, 125.0, 124.9, 124.3, 122.4, 113.9, 113.1, 70.4, 56.8 (q, $J_{\text{C-F}} = 26.8$ Hz), 56.4, 21.6. ¹⁹F NMR (282 MHz, CDCl₃) δ -69.1. HRMS (ESI) *m/z* calcd for C₃₂H₂₅F₃NO₄S₂ [M+H]⁺: 608.1172, found 608.1173.



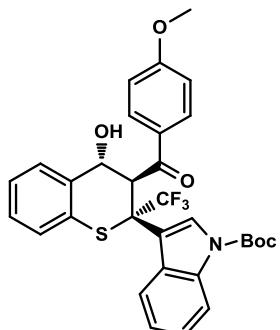
	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	11.314	7042202	50.00	360469	bb	Unknown
2	14.975	7042762	50.00	266442	bb	Unknown



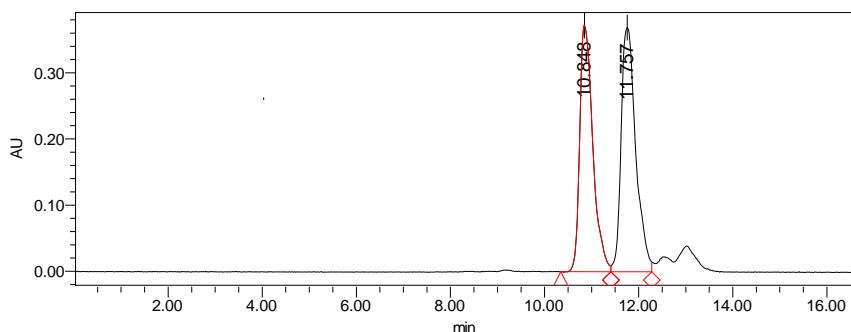
	Retention Time	Area	% Area	Height	Int Type	Peak Type

1	11.420	4165490	94.25	209800	bb	Unknown
2	15.089	254246	5.75	9439	bb	Unknown

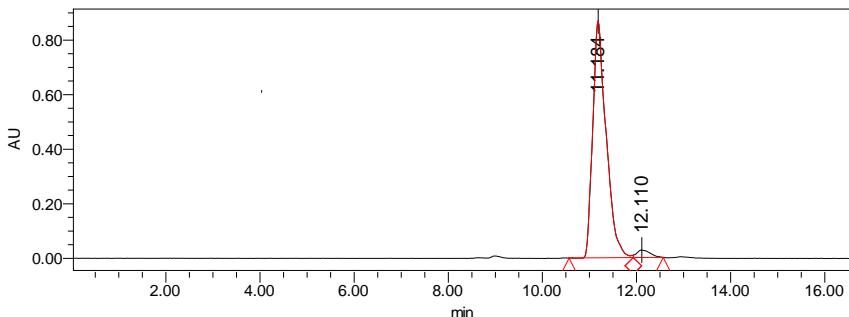
tert-butyl-3-((2*S*,3*S*,4*R*)-4-hydroxy-3-(4-methoxybenzoyl)-2-(trifluoromethyl)thiochroman-2-yl)-1*H*-indole-1-carboxylate (3d**)**



From 27.6 mg (0.2 mmol) 2-mercaptopbenzaldehyde and 97.9 mg (0.22 mmol, 1.1 equiv) β -indole- β -CF₃ enones **2d**, 99.2 mg (85.0% yield) compound **3d** was obtained as a white solid, mp = 81 - 82 °C. $[\alpha]_D^{20} = +75$ (c = 1.0, CHCl₃). Dr (>20:1) determined by ¹H and ¹⁹F NMR analysis. 94% ee was determined by HPLC analysis (Daicel Chiralcel IC-H column, hexane/2-propanol 4:1, 0.7 mL/min). Retention time: *t*_{major} = 11.2 and *t*_{minor} = 12.1 min. ¹H NMR (300 MHz, CDCl₃) δ 8.12 (d, *J* = 7.5 Hz, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.61 (d, *J* = 7.5 Hz, 1H), 7.35 - 7.21 (m, 6H), 7.13 - 7.02 (m, 2H), 6.60 (d, *J* = 9.0 Hz, 2H), 5.58 (dd, *J* = 9.5, 5.6 Hz, 1H), 4.15 (d, *J* = 9.6 Hz, 1H), 3.68 (s, 3H), 3.59 (d, *J* = 5.7 Hz, 1H), 1.50 (s, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 196.8, 163.5, 149.0, 139.9, 135.2, 131.6, 131.0, 130.5, 128.8, 127.8, 127.7, 127.2, 127.1 (q, *J*_{C-F} = 281.0 Hz), 126.0, 125.2, 124.6, 123.9, 122.0, 114.9, 113.3, 112.6, 84.3, 70.4, 57.1 (q, *J*_{C-F} = 26.8 Hz), 56.2, 55.4, 28.1. ¹⁹F NMR (282 MHz, CDCl₃) δ -68.8. HRMS (ESI) *m/z* calcd for C₃₁H₂₉F₃NO₅S [M+H]⁺: 584.1713, found 584.1729.

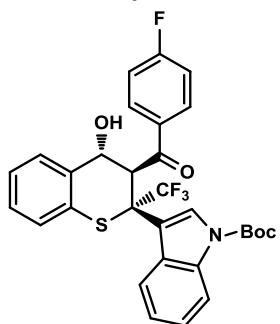


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	10.848	7210855	47.52	372801	bv	Unknown
2	11.757	7961978	52.48	369035	vv	Unknown

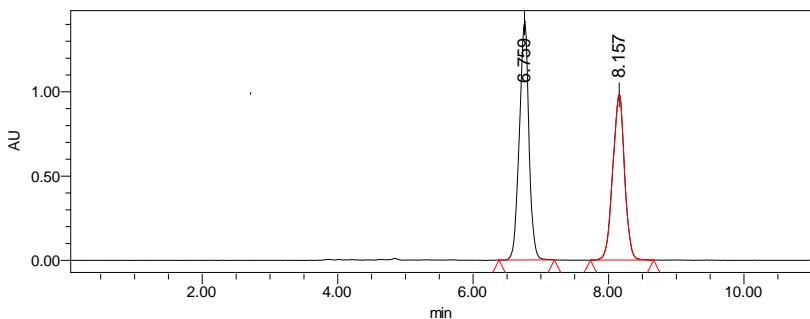


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	11.184	17218354	96.93	867704	bv	Unknown
2	12.110	546258	3.07	27747	vb	Unknown

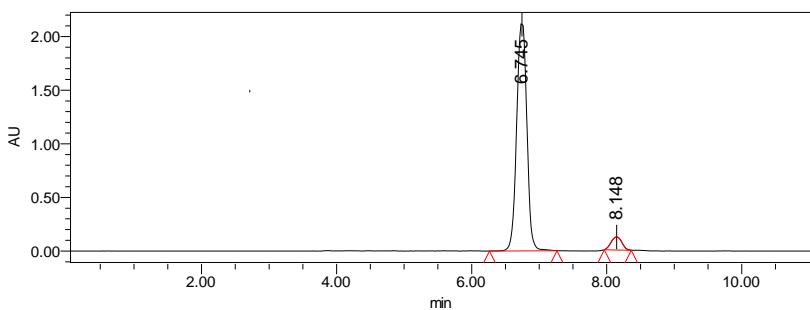
tert-butyl-3-((2*S*,3*S*,4*R*)-3-(4-fluorobenzoyl)-4-hydroxy-2-(trifluoromethyl)thiochroman-2-yl)-1*H*-indole-1-carboxylate (3e**)**



From 27.6 mg (0.2 mmol) 2-mercaptopbenzaldehyde and 95.3 mg (0.22 mmol, 1.1 equiv) β -indole- β -CF₃ enones **2e**, 89.2 mg (78.0% yield) compound **3e** was obtained as a white solid, mp = 59 - 60 °C. $[\alpha]_D^{20} = +35$ (c = 1.0, CHCl₃). Dr (>20:1) determined by ¹H and ¹⁹F NMR analysis. 89% ee was determined by HPLC analysis (Daicel Chiralcel IA-H column, hexane/2-propanol 3:1, 1.0 mL/min). Retention time: *t*_{major} = 6.7 and *t*_{minor} = 8.1 min. ¹H NMR (300 MHz, CDCl₃) δ 8.12 (d, *J* = 8.1 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 7.2 Hz, 1H), 7.35 - 7.25 (m, 3H), 7.22 - 7.06 (m, 5H), 6.80 (t, *J* = 8.6 Hz, 2H), 5.66 (dd, *J* = 9.3, 5.1 Hz, 1H), 4.13 (d, *J* = 9.9 Hz, 1H), 3.41 (d, *J* = 5.4 Hz, 1H), 1.51 (s, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 197.2, 165.5 (d, *J*_{C-F} = 253.5 Hz), 148.8, 139.4, 135.3 (d, *J*_{C-F} = 3.0 Hz), 135.2, 131.0, 130.4 (d, *J*_{C-F} = 9.0 Hz), 128.3, 128.0, 127.8, 127.5, 126.9 (q, *J*_{C-F} = 282.3 Hz), 126.0 (d, *J*_{C-F} = 3.8 Hz), 124.9, 124.8, 123.8, 122.1, 115.3, 114.9 (d, *J*_{C-F} = 6.8 Hz), 112.0, 84.5, 70.2, 57.1, 56.8 (q, *J*_{C-F} = 27.0 Hz), 28.0. ¹⁹F NMR (282 MHz, CDCl₃) δ -68.9, -105.2. HRMS (ESI) *m/z* calcd for C₃₀H₂₆F₄NO₄S [M+H]⁺: 572.1513, found 572.1523.

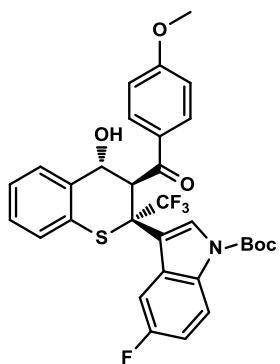


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	6.759	13847411	53.78	1419487	bb	Unknown
2	8.157	11902144	46.22	989275	bb	Unknown



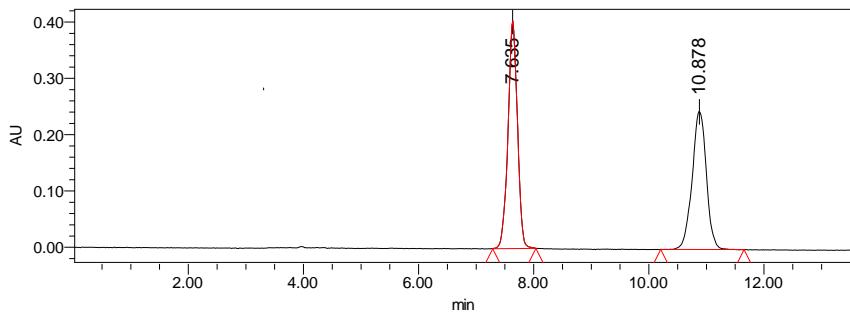
	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	6.745	22318128	94.34	2135912	bb	Unknown
2	8.148	1339276	5.66	121812	bb	Unknown

***tert*-butyl-5-fluoro-3-((2*S*,3*S*,4*R*)-4-hydroxy-3-(4-methoxybenzoyl)-2-(trifluoromethyl)thiochroman-2-yl)-1*H*-indole-1-carboxylate (**3f**)**

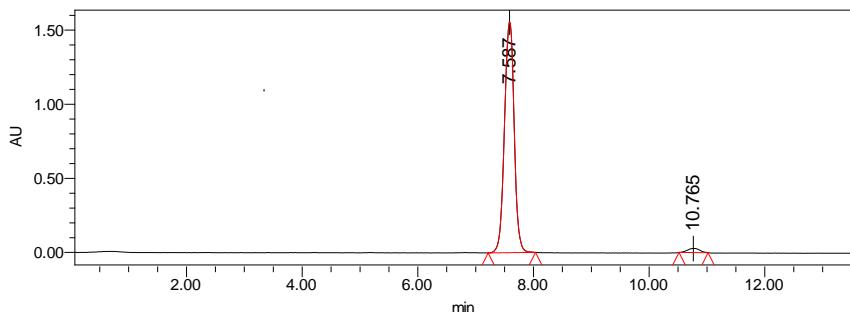


From 27.6 mg (0.2 mmol) 2-mercaptopbenzaldehyde and 101.9 mg (0.22 mmol, 1.1 equiv) β -indole- β -CF₃ enones **2g**, 99.9 mg (83.0% yield) compound **3f** was obtained as a white solid, mp = 59 - 60 °C. [α]_D²⁰ = +90 (c = 1.0, CHCl₃). Dr (>20:1) determined by ¹H and ¹⁹F NMR analysis. 96% ee was determined by HPLC analysis (Daicel Chiralcel IA-H column, hexane/2-propanol 3:1, 1.0 mL/min). Retention time: *t*_{major} = 7.6 and *t*_{minor} = 10.8 min. ¹H NMR (300 MHz, CDCl₃) δ 8.03 (dd, *J* = 9.0, 4.8 Hz, 1H), 7.90 (dd, *J* = 10.4, 2.6 Hz, 1H), 7.71 (d, *J* = 7.5 Hz, 1H), 7.44 - 7.31 (m, 6H), 6.92 (td, *J* = 8.9, 2.6 Hz, 1H), 6.72 (d, *J* = 9.0 Hz, 2H), 5.63 (dd, *J* = 9.6, 5.4 Hz, 1H),

4.23 (d, $J = 9.9$ Hz, 1H), 3.79 (s, 3H), 3.51 (d, $J = 5.7$ Hz, 1H), 1.59 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3) δ 196.8, 163.6, 158.2 (d, $J_{\text{C}-\text{F}} = 237.0$ Hz), 148.8, 139.8, 131.6, 131.4, 130.7, 130.6, 129.9 (d, $J_{\text{C}-\text{F}} = 9.8$ Hz), 127.8 (d, $J_{\text{C}-\text{F}} = 6.0$ Hz), 127.5, 127.3, 126.9 (q, $J_{\text{C}-\text{F}} = 284.8$ Hz), 125.1, 115.7 (d, $J_{\text{C}-\text{F}} = 9.8$ Hz), 113.4, 112.8, 112.6, 112.5 (d, $J_{\text{C}-\text{F}} = 3.8$ Hz), 109.6 (d, $J_{\text{C}-\text{F}} = 26.3$ Hz), 84.6, 70.5, 57.0 (q, $J_{\text{C}-\text{F}} = 27.0$ Hz), 56.0, 55.4, 28.0. ^{19}F NMR (282 MHz, CDCl_3) δ -68.7, -119.3. HRMS (ESI) m/z calcd for $\text{C}_{31}\text{H}_{28}\text{F}_4\text{NO}_5\text{S} [\text{M}+\text{H}]^+$: 602.1619, found 602.1633.

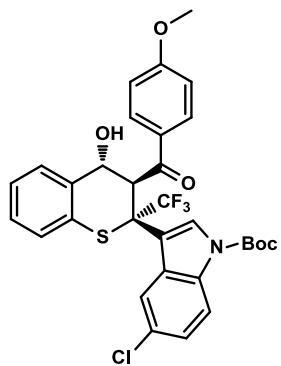


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	7.635	4596333	52.16	403745	bb	Unknown
2	10.878	4216210	47.84	245396	bb	Unknown



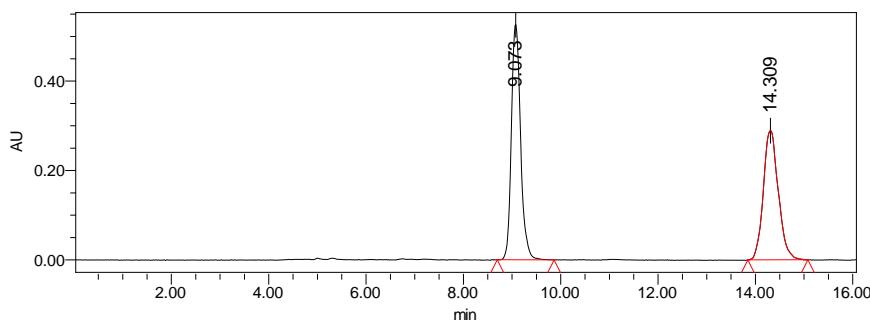
	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	7.587	18094193	97.78	1559765	bb	Unknown
2	10.765	410452	2.22	28179	bb	Unknown

tert-butyl-5-chloro-3-((2*S*,3*S*,4*R*)-4-hydroxy-3-(4-methoxybenzoyl)-2-(trifluoromethyl)thiochroman-2-yl)-1*H*-indole-1-carboxylate (3g)

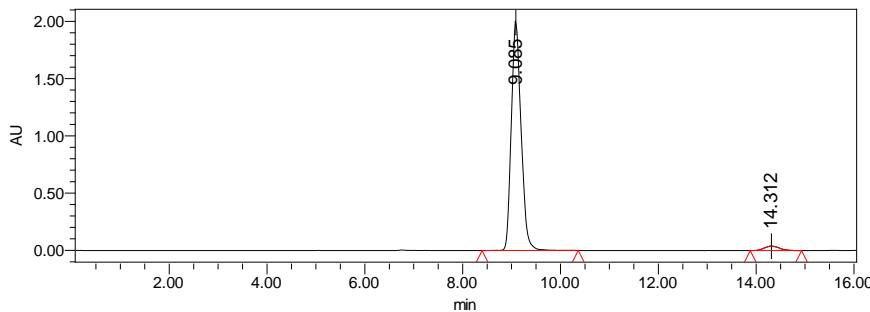


From 27.6 mg (0.2 mmol) 2-mercaptopbenzaldehyde and 105.4 mg (0.22 mmol, 1.1

equiv) β -indole- β -CF₃ enones **2h**, 102.6 mg (83.0% yield) compound **3g** was obtained as a white solid, mp = 75 - 76 °C. $[\alpha]_D^{20} = +112$ ($c = 1.0$, CHCl₃). Dr (>20:1) determined by ¹H and ¹⁹F NMR analysis. 94% ee was determined by HPLC analysis (Daicel Chiralcel IA-H column, hexane/2-propanol 3:1, 1.0 mL/min). Retention time: $t_{\text{major}} = 9.1$ and $t_{\text{minor}} = 14.3$ min. ¹H NMR (300 MHz, CDCl₃) δ 8.25 (d, $J = 1.8$ Hz, 1H), 8.04 (d, $J = 9.0$ Hz, 1H), 7.71 (d, $J = 7.5$ Hz, 1H), 7.45 - 7.32 (m, 6H), 7.15 (dd, $J = 9.0$, 1.8 Hz, 1H), 6.70 (d, $J = 8.7$ Hz, 2H), 5.67 (dd, $J = 9.6$, 5.1 Hz, 1H), 4.24 (d, $J = 9.6$ Hz, 1H), 3.79 (s, 3H), 3.58 (d, $J = 5.7$ Hz, 1H), 1.59 (s, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 196.8, 163.6, 148.7, 139.9, 133.6, 131.3, 130.7, 130.6, 130.1, 128.0, 127.9, 127.8, 127.4, 127.2, 127.0 (q, $J_{\text{C}-\text{F}} = 282.0$ Hz), 125.1, 125.0, 123.4, 115.8, 113.4, 112.3, 84.8, 70.8, 57.0 (q, $J_{\text{C}-\text{F}} = 27.0$ Hz), 56.1, 55.4, 28.0. ¹⁹F NMR (282 MHz, CDCl₃) δ -68.9. HRMS (ESI) m/z calcd for C₃₁H₂₈ClF₃NO₅S [M+H]⁺: 618.1323, found 618.1346.

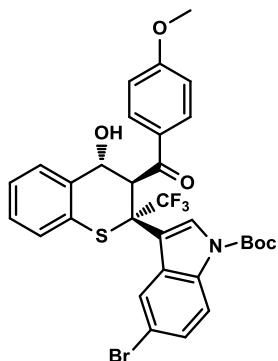


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	9.073	6927091	52.92	526822	bb	Unknown
2	14.309	6162936	47.08	289555	bb	Unknown

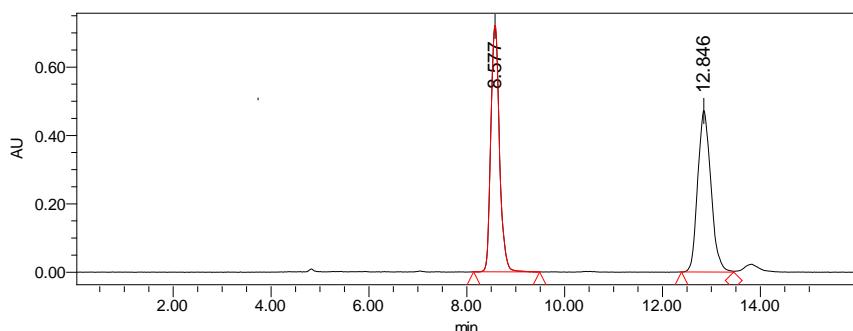


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	9.085	27799832	97.08	2001356	bb	Unknown
2	14.312	837466	2.92	39543	bb	Unknown

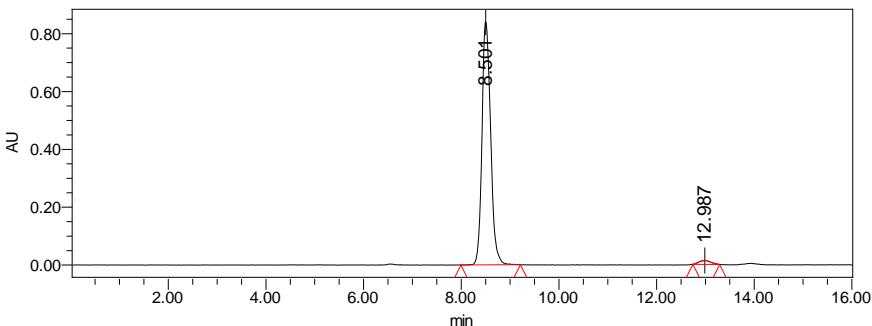
tert-butyl-5-bromo-3-((2S,3S,4R)-4-hydroxy-3-(4-methoxybenzoyl)-2-(trifluoromethyl)thiochroman-2-yl)-1H-indole-1-carboxylate (3h)



From 27.6 mg (0.2 mmol) 2-mercaptopbenzaldehyde and 115.1 mg (0.22 mmol, 1.1 equiv) β -indole- β -CF₃ enones **2i**, 110.0 mg (83.0% yield) compound **3h** was obtained as a white solid, mp = 66 - 67 °C. $[\alpha]_D^{20} = +82$ (c = 1.0, CHCl₃). Dr (>20:1) determined by ¹H and ¹⁹F NMR analysis. 96% ee was determined by HPLC analysis (Daicel Chiralcel IA-H column, hexane/2-propanol 3:1, 1.0 mL/min). Retention time: $t_{\text{major}} = 8.5$ and $t_{\text{minor}} = 13.0$ min. ¹H NMR (300 MHz, CDCl₃) δ 8.34 (d, $J = 1.5$ Hz, 1H), 7.90 (d, $J = 8.7$ Hz, 1H), 7.61 (d, $J = 7.5$ Hz, 1H), 7.35 - 7.30 (m, 3H), 7.26 (d, $J = 8.7$ Hz, 3H), 7.19 (dd, $J = 8.9, 1.7$ Hz, 1H), 6.59 (d, $J = 8.7$ Hz, 2H), 5.58 (dd, $J = 9.6, 5.7$ Hz, 1H), 4.16 (d, $J = 9.6$ Hz, 1H), 3.69 (s, 3H), 1.49 (s, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 196.8, 163.6, 148.7, 139.9, 134.0, 131.3, 130.7, 130.6, 130.5, 128.0, 127.8, 127.7, 127.4, 127.1, 127.0 (q, $J_{\text{C-F}} = 282.3$ Hz), 126.4, 125.1, 116.2, 115.8, 113.4, 112.3, 84.8, 70.8, 57.0 (q, $J_{\text{C-F}} = 26.8$ Hz), 56.1, 55.4, 28.0. ¹⁹F NMR (282 MHz, CDCl₃) δ -68.9. HRMS (ESI) m/z calcd for C₃₁H₂₈BrF₃NO₅S [M+H]⁺: 662.0818, found 662.0832.

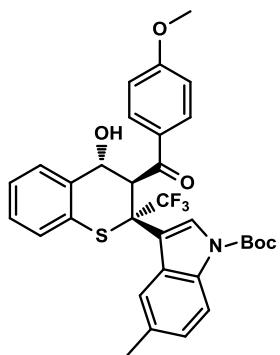


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	8.577	8837034	50.00	721100	bb	Unknown
2	12.846	8837125	50.00	472536	bv	Unknown

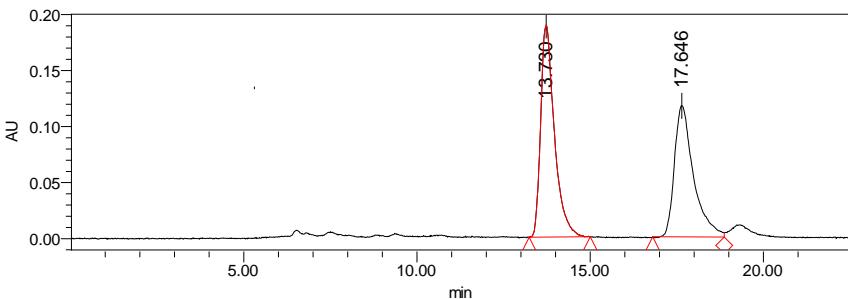


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	8.501	10351174	97.81	846108	bb	Unknown
2	12.987	231376	2.19	13565	bb	Unknown

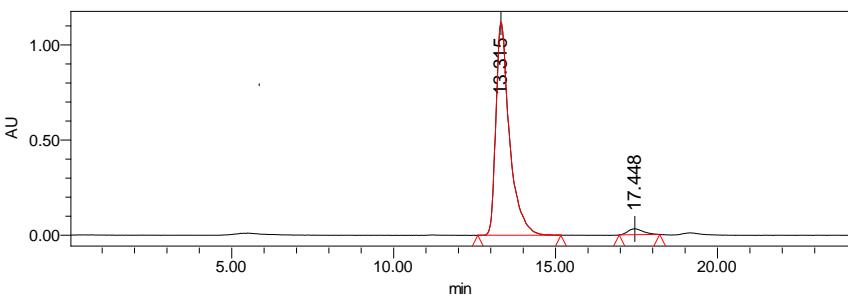
tert-butyl-3-((2*S*,3*S*,4*R*)-4-hydroxy-3-(4-methoxybenzoyl)-2-(trifluoromethyl)thiochroman-2-yl)-5-methyl-1*H*-indole-1-carboxylate (3i)



From 27.6 mg (0.2 mmol) 2-mercaptopbenzaldehyde and 101.0 mg (0.22 mmol, 1.1 equiv) β -indole- β -CF₃ enones **2j**, 99.2 mg (83.0% yield) compound **3i** was obtained as a white solid, mp = 89 - 90 °C. $[\alpha]_D^{20} = +97$ (c = 1.0, CHCl₃). Dr (>20:1) determined by ¹H and ¹⁹F NMR analysis. 94% ee was determined by HPLC analysis (Daicel Chiralcel IA-H column, hexane/2-propanol 3:1, 1.0 mL/min). Retention time: *t*_{major} = 13.3 and *t*_{minor} = 17.4 min. ¹H NMR (300 MHz, CDCl₃) δ 7.91 (s, 1H), 7.87 (d, *J* = 5.1 Hz, 1H), 7.64 (d, *J* = 7.5 Hz, 1H), 7.35 - 7.22 (m, 6H), 6.98 (d, *J* = 8.7 Hz, 1H), 6.61 (d, *J* = 8.7 Hz, 2H), 5.64 (dd, *J* = 9.3, 5.7 Hz, 1H), 4.15 (d, *J* = 9.9 Hz, 1H), 3.69 (s, 3H), 3.35 (t, *J* = 4.4 Hz, 1H), 2.24 (s, 3H), 1.50 (s, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 195.7, 162.3, 147.9, 138.7, 132.4, 130.6, 130.2, 130.1, 129.3, 129.3, 127.8, 126.9, 126.7, 126.2, 126.0 (*q*, *J*_{C-F} = 282.5 Hz), 125.1, 123.9, 122.7, 113.4, 112.2, 111.1, 83.0, 69.5, 56.0 (*q*, *J*_{C-F} = 26.5 Hz), 55.3, 54.3, 27.0, 20.6. ¹⁹F NMR (282 MHz, CDCl₃) δ -68.7. HRMS (ESI) *m/z* calcd for C₃₂H₃₁F₃NO₅S [M+H]⁺: 598.1870, found 598.1870.

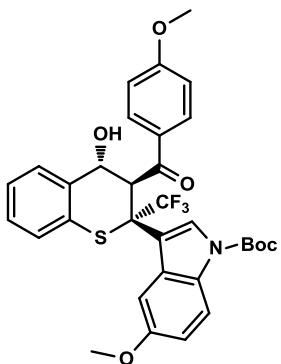


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	13.730	5197231	53.67	188983	bb	Unknown
2	17.646	4486983	46.33	117212	bv	Unknown



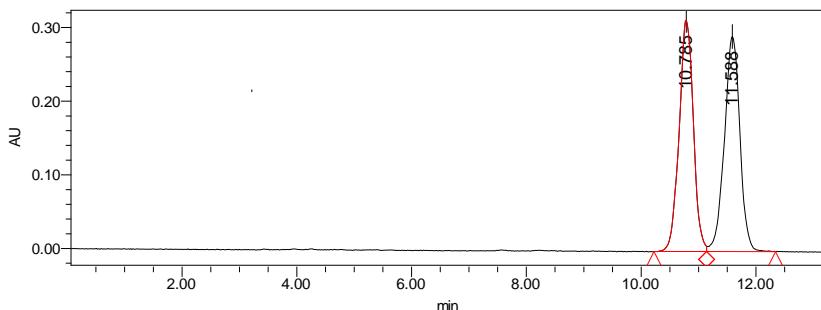
	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	13.315	32515647	96.95	1118160	bb	Unknown
2	17.448	1021600	3.05	30967	bb	Unknown

tert-butyl-3-((2*S*,3*S*,4*R*)-4-hydroxy-3-(4-methoxybenzoyl)-2-(trifluoromethyl)thiochroman-2-yl)-5-methoxy-1*H*-indole-1-carboxylate (3j**)**

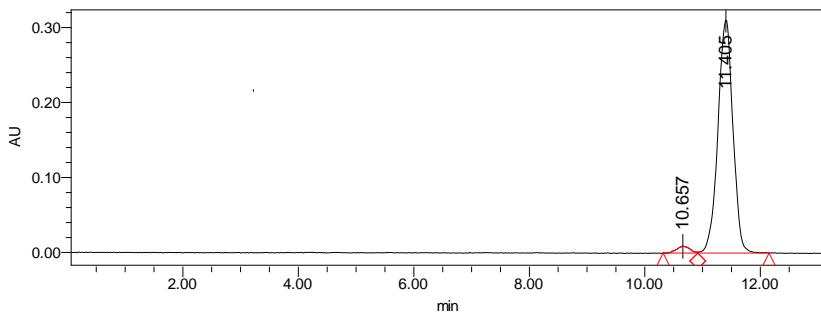


From 27.6 mg (0.2 mmol) 2-mercaptopbenzaldehyde and 104.5 mg (0.22 mmol, 1.1 equiv) β -indole- β -CF₃ enones **2k**, 101.9 mg (83.0% yield) compound **3j** was obtained as a white solid, mp = 92 - 93 °C. [α]_D²⁰ = +90 (c = 1.0, CHCl₃). Dr (>20:1) determined by ¹H and ¹⁹F NMR analysis. 95% ee was determined by HPLC analysis (Daicel Chiralcel IA-H column, hexane/2-propanol 3:1, 1.0 mL/min). Retention time: *t*_{major} = 11.4 and *t*_{minor} = 10.7 min. ¹H NMR (300 MHz, CDCl₃) δ 7.98 (d, *J* = 9.0 Hz, 1H), 7.72 (d, *J* = 7.5 Hz, 1H), 7.59 (d, *J* = 2.1 Hz, 1H), 7.43 - 7.28 (m, 6H), 6.87 (dd, *J* = 9.3, 2.4 Hz, 1H), 6.70 (d, *J* = 8.7 Hz, 2H), 5.72 (dd, *J* = 9.5, 5.6 Hz, 1H), 4.25 (d, *J* = 9.6

Hz, 1H), 3.77 (s, 3H), 3.63 (s, 3H), 3.49 (d, $J = 5.7$ Hz, 1H), 1.58 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3) δ 196.8, 163.4, 154.8, 148.9, 139.6, 131.7, 131.1, 130.4, 130.0, 129.5, 127.8, 127.3, 127.0 (q, $J_{\text{C}-\text{F}} = 282.8$ Hz), 126.9, 125.1, 115.4, 113.3, 113.1, 112.2, 106.9, 84.1, 70.4, 57.1 (q, $J_{\text{C}-\text{F}} = 26.8$ Hz), 56.2, 55.4, 55.4, 28.0. ^{19}F NMR (282 MHz, CDCl_3) δ -68.5. HRMS (ESI) m/z calcd for $\text{C}_{32}\text{H}_{31}\text{F}_3\text{NO}_6\text{S} [\text{M}+\text{H}]^+$: 614.1819, found 614.1844.

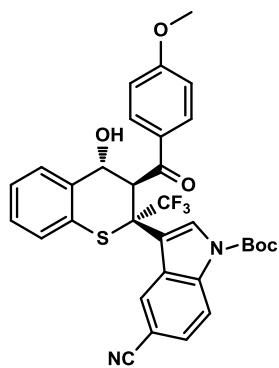


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	10.785	5407460	49.56	313826	bv	Unknown
2	11.588	5503812	50.44	292373	vb	Unknown



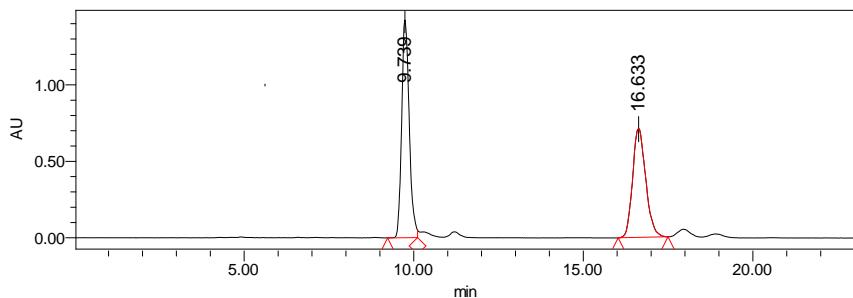
	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	10.657	144436	2.51	9110	bv	Unknown
2	11.405	5606495	97.49	310574	vb	Unknown

tert-butyl-5-cyano-3-((2*S*,3*S*,4*R*)-4-hydroxy-3-(4-methoxybenzoyl)-2-(trifluoromethyl)thiochroman-2-yl)-1*H*-indole-1-carboxylate (3k)

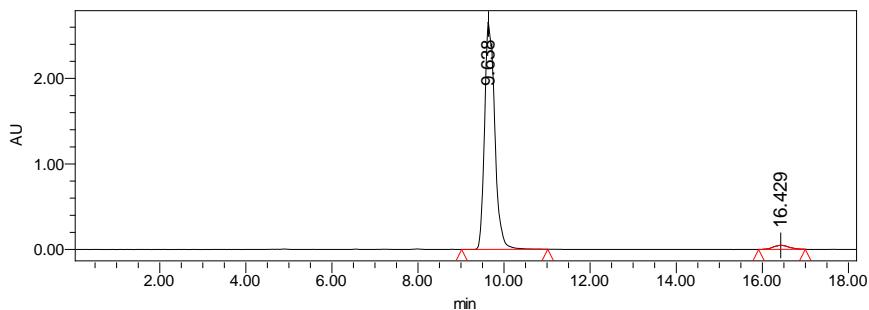


From 27.6 mg (0.2 mmol) 2-mercaptopbenzaldehyde and 103.4 mg (0.22 mmol, 1.1 equiv) β -indole- β -CF₃ enones **2l**, 101.1 mg (83.0% yield) compound **3k** was obtained

as a white solid, mp = 112 - 113 °C. $[\alpha]_D^{20} = +118$ (c = 1.0, CHCl₃). Dr (>20:1) determined by ¹H and ¹⁹F NMR analysis. 95% ee was determined by HPLC analysis (Daicel Chiralcel IA-H column, hexane/2-propanol 3:1, 1.0 mL/min). Retention time: $t_{\text{major}} = 9.6$ and $t_{\text{minor}} = 16.4$ min. ¹H NMR (300 MHz, CDCl₃) δ 8.47 (s, 1H), 8.13 (d, *J* = 8.7 Hz, 1H), 7.63 (d, *J* = 7.2 Hz, 1H), 7.48 (s, 1H), 7.42 - 7.23 (m, 6H), 6.66 (d, *J* = 8.7 Hz, 2H), 5.54 (dd, *J* = 9.6, 5.4 Hz, 1H), 4.20 (d, *J* = 10.2 Hz, 1H), 3.72 (s, 3H), 3.43 (d, *J* = 5.7 Hz, 1H), 1.52 (s, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 196.7, 163.8, 148.3, 139.6, 137.1, 131.2, 130.7, 130.2, 128.9, 128.3, 128.1, 128.0, 127.6, 127.5, 126.9 (q, *J*_{C-F} = 283.5 Hz), 125.0, 125.0, 119.7, 115.9, 113.6, 113.0, 105.6, 85.6, 70.7, 56.9 (q, *J*_{C-F} = 27.0 Hz), 55.8, 55.5, 28.0. ¹⁹F NMR (282 MHz, CDCl₃) δ -68.9. HRMS (ESI) *m/z* calcd for C₃₂H₂₈F₃N₂O₅S [M+H]⁺: 609.1666, found 609.1666.

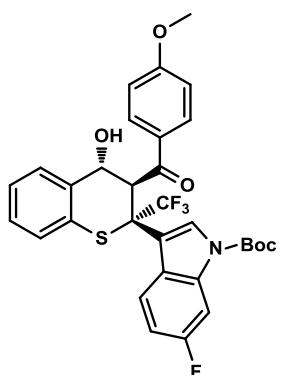


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	9.739	22034430	53.47	1423069	bv	Unknown
2	16.633	19171403	46.53	710867	bb	Unknown

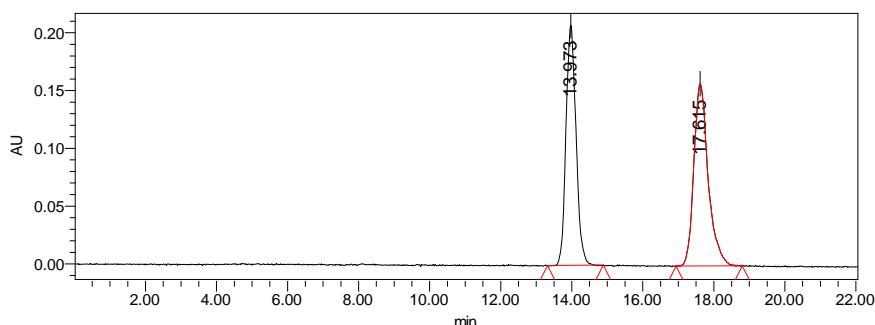


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	9.638	43646281	97.28	2642916	bb	Unknown
2	16.429	1221242	2.72	47459	bb	Unknown

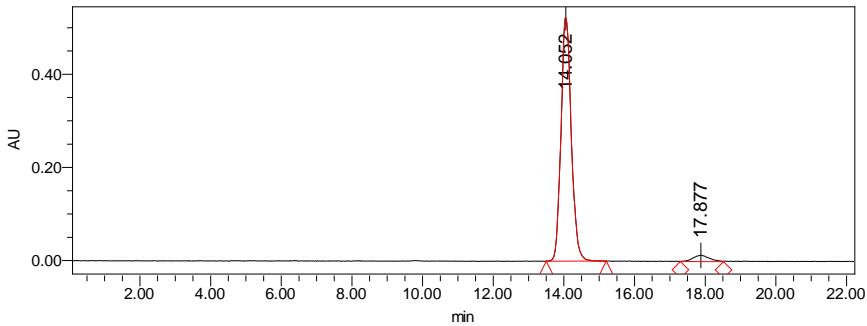
tert-butyl-6-fluoro-3-((2*S*,3*S*,4*R*)-4-hydroxy-3-(4-methoxybenzoyl)-2-(trifluoromethyl)thiochroman-2-yl)-1*H*-indole-1-carboxylate (3l)



From 27.6 mg (0.2 mmol) 2-mercaptopbenzaldehyde and 101.9 mg (0.22 mmol, 1.1 equiv) β -indole- β -CF₃ enones **2m**, 95.1 mg (79.0% yield) compound **3l** was obtained as a white solid, mp = 72 - 73 °C. $[\alpha]_D^{20} = +66$ (c = 1.0, CHCl₃). Dr (>20:1) determined by ¹H and ¹⁹F NMR analysis. 92% ee was determined by HPLC analysis (Daicel Chiralcel IA-H column, hexane/2-propanol 3:1, 1.0 mL/min). Retention time: $t_{\text{major}} = 14.1$ and $t_{\text{minor}} = 17.9$ min. ¹H NMR (300 MHz, CDCl₃) δ 8.09 (dd, $J = 9.0, 5.4$ Hz, 1H), 7.79 (d, $J = 10.2$ Hz, 1H), 7.71 (d, $J = 7.2$ Hz, 1H), 7.44 - 7.31 (m, 6H), 6.90 (td, $J = 8.9, 2.5$ Hz, 1H), 6.72 (d, $J = 9.0$ Hz, 2H), 5.64 (dd, $J = 9.6, 5.4$ Hz, 1H), 4.23 (d, $J = 9.9$ Hz, 1H), 3.79 (s, 3H), 3.46 (d, $J = 5.4$ Hz, 1H), 1.59 (s, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 196.8, 163.6, 162.2, 159.0, 148.7, 139.6, 135.5 (d, $J_{\text{C-F}} = 12.8$ Hz), 131.5, 130.7, 130.5, 127.9, 127.8, 127.5, 127.0 (q, $J_{\text{C-F}} = 279.8$ Hz), 126.3, 125.0, 124.7 (d, $J_{\text{C-F}} = 9.8$ Hz), 113.4, 112.5, 110.4 (d, $J_{\text{C-F}} = 24.0$ Hz), 102.0 (d, $J_{\text{C-F}} = 27.8$ Hz), 84.7, 70.4, 57.0 (q, $J_{\text{C-F}} = 26.8$ Hz), 56.1, 55.4, 28.0. ¹⁹F NMR (282 MHz, CDCl₃) δ -68.8, -116.6. HRMS (ESI) m/z calcd for C₃₁H₂₈F₄NO₅S [M+H]⁺: 602.1619, found 602.1649.

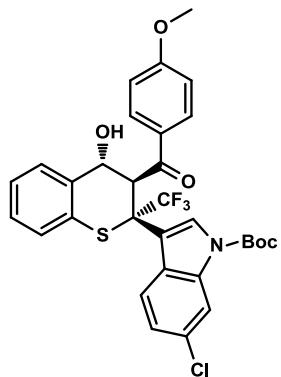


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	13.973	4089352	48.03	208032	bb	Unknown
2	17.615	4424794	51.97	157514	bb	Unknown

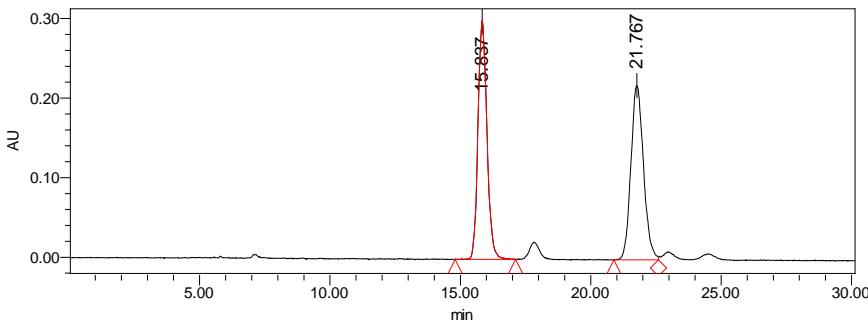


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	14.052	10593952	96.02	523459	bb	Unknown
2	17.877	439656	3.98	13585	VV	Unknown

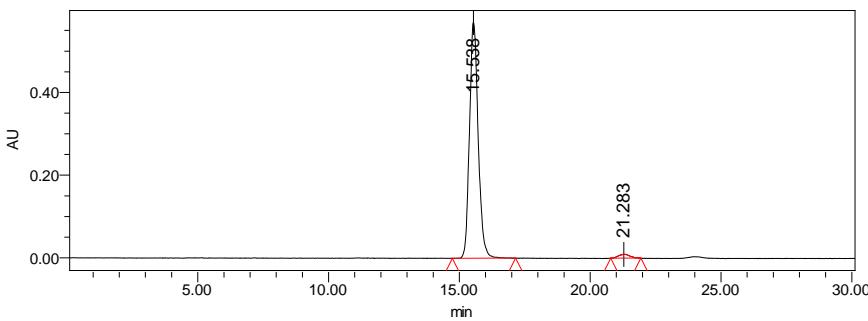
tert-butyl-6-chloro-3-((2*S*,3*S*,4*R*)-4-hydroxy-3-(4-methoxybenzoyl)-2-(trifluoromethyl)thiochroman-2-yl)-1*H*-indole-1-carboxylate (3m)



From 27.6 mg (0.2 mmol) 2-mercaptopbenzaldehyde and 105.4 mg (0.22 mmol, 1.1 equiv) β -indole- β -CF₃ enones **2n**, 102.6 mg (83.0% yield) compound **3m** was obtained as a white solid, mp = 74 - 75 °C. $[\alpha]_D^{20} = +131$ (c = 1.0, CHCl₃). Dr (>20:1) determined by ¹H and ¹⁹F NMR analysis. 96% ee was determined by HPLC analysis (Daicel Chiralcel IA-H column, hexane/2-propanol 3:1, 1.0 mL/min). Retention time: *t*_{major} = 15.5 and *t*_{minor} = 21.3 min. ¹H NMR (300 MHz, CDCl₃) δ 8.08 (d, *J* = 6.6 Hz, 1H), 8.04 (s, 1H), 7.70 (d, *J* = 7.2 Hz, 1H), 7.42 - 7.31 (m, 6H), 7.11 (dd, *J* = 8.9, 2.0 Hz, 1H), 6.68 (d, *J* = 8.7 Hz, 2H), 5.57 (dd, *J* = 9.5, 5.6 Hz, 1H), 4.22 (d, *J* = 9.9 Hz, 1H), 3.88 (d, *J* = 5.4 Hz, 1H), 3.77 (s, 3H), 1.59 (s, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 196.8, 163.6, 148.6, 139.7, 135.6, 131.4, 130.7, 130.6, 130.5, 127.9, 127.8, 127.5, 127.3, 126.9 (q, *J*_{C-F} = 284.8 Hz), 126.5, 125.0, 124.6, 122.6, 115.1, 113.4, 112.6, 84.9, 70.3, 56.9 (q, *J*_{C-F} = 26.5 Hz), 56.0, 55.4, 28.0. ¹⁹F NMR (282 MHz, CDCl₃) δ -68.8. HRMS (ESI) *m/z* calcd for C₃₁H₂₈ClF₃NO₅S [M+H]⁺: 618.1323, found 618.1352.

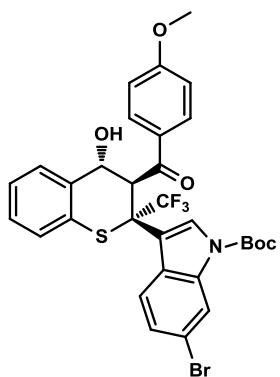


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	15.837	7210826	49.48	299556	bb	Unknown
2	21.767	7362641	50.52	219042	bv	Unknown



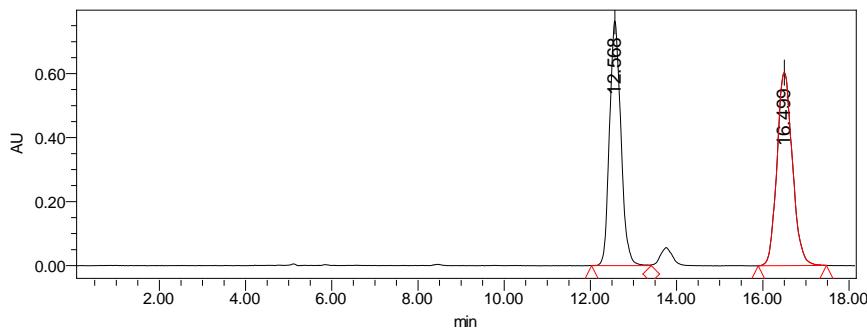
	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	15.538	13208290	98.01	570746	bb	Unknown
2	21.283	268329	1.99	9026	bb	Unknown

***tert*-butyl-6-bromo-3-((2*S*,3*S*,4*R*)-4-hydroxy-3-(4-methoxybenzoyl)-2-(trifluoromethyl)thiochroman-2-yl)-1*H*-indole-1-carboxylate (**3n**)**

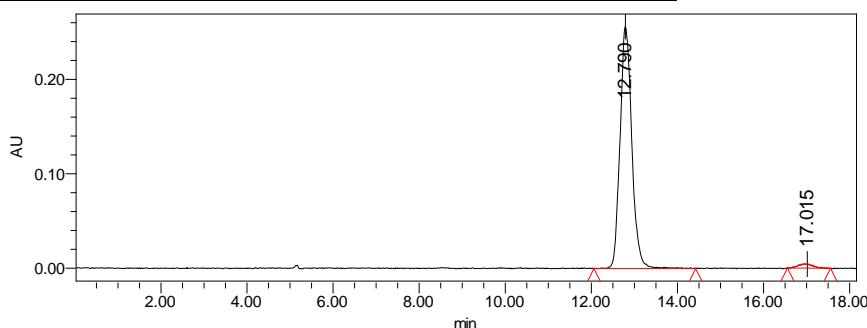


From 27.6 mg (0.2 mmol) 2-mercaptopbenzaldehyde and 115.1 mg (0.22 mmol, 1.1 equiv) β -indole- β -CF₃ enones **2o**, 107.3 mg (81.0% yield) compound **3n** was obtained as a white solid, mp = 77 - 78 °C. $[\alpha]_D^{20} = +115$ (c = 1.0, CHCl₃). Dr (>20:1) determined by ¹H and ¹⁹F NMR analysis. 96% ee was determined by HPLC analysis (Daicel Chiralcel IA-H column, hexane/2-propanol 3:1, 1.0 mL/min). Retention time: *t*_{major} = 12.8 and *t*_{minor} = 17.0 min. ¹H NMR (300 MHz, CDCl₃) δ 8.18 (s, 1H), 7.91 (d,

J = 8.7 Hz, 1H), 7.62 (d, *J* = 7.5 Hz, 1H), 7.32 (t, *J* = 6.8 Hz, 2H), 7.25 (d, *J* = 8.7 Hz, 3H), 7.21 - 7.16 (m, 2H), 6.61 (d, *J* = 8.7 Hz, 2H), 5.49 (dd, *J* = 9.2, 5.9 Hz, 1H), 4.13 (d, *J* = 9.9 Hz, 1H), 3.69 (s, 3H), 3.62 (d, *J* = 5.7 Hz, 1H), 1.50 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3) δ 196.8, 163.6, 148.5, 139.6, 135.9, 131.4, 130.6, 130.5, 127.9, 127.8, 127.7, 127.6, 126.9 (q, $J_{\text{C}-\text{F}} = 284.3$ Hz), 126.4, 125.3, 125.0, 124.9, 118.6, 118.1, 113.4, 112.6, 84.9, 70.3, 56.9 (q, $J_{\text{C}-\text{F}} = 26.8$ Hz), 56.0, 55.4, 28.0. ^{19}F NMR (282 MHz, CDCl_3) δ -68.8. HRMS (ESI) *m/z* calcd for $\text{C}_{31}\text{H}_{28}\text{BrF}_3\text{NO}_5\text{S} [\text{M}+\text{H}]^+$: 662.0818, found 662.0850.

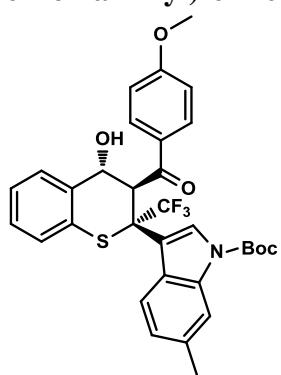


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	12.568	13960268	48.21	765791	bv	Unknown
2	16.499	14994547	51.79	603113	bb	Unknown

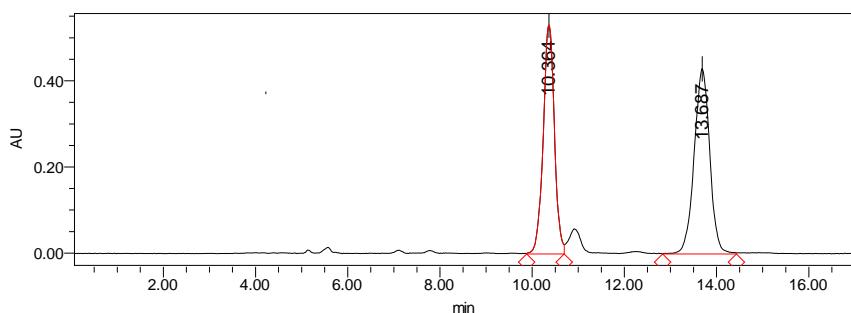


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	12.790	4877894	97.89	256341	bb	Unknown
2	17.015	105284	2.11	4366	bb	Unknown

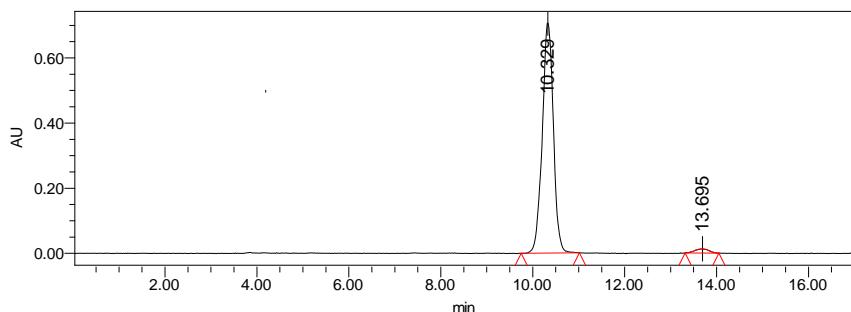
***tert*-butyl-3-((2*S*,3*S*,4*R*)-4-hydroxy-3-(4-methoxybenzoyl)-2-(trifluoromethyl)thiochroman-2-yl)-6-methyl-1*H*-indole-1-carboxylate (3o)**



From 27.6 mg (0.2 mmol) 2-mercaptobenzaldehyde and 101.0 mg (0.22 mmol, 1.1 equiv) β -indole- β -CF₃ enones **2p**, 95.6 mg (80.0% yield) compound **3o** was obtained as a white solid, mp = 74 - 75 °C. $[\alpha]_D^{20} = +109$ (c = 1.0, CHCl₃). Dr (>20:1) determined by ¹H and ¹⁹F NMR analysis. 96% ee was determined by HPLC analysis (Daicel Chiralcel IA-H column, hexane/2-propanol 3:1, 1.0 mL/min). Retention time: *t*_{major} = 10.3 and *t*_{minor} = 13.7 min. ¹H NMR (300 MHz, CDCl₃) δ 7.99 (d, *J* = 8.4 Hz, 1H), 7.81 (s, 1H), 7.61 (d, *J* = 7.2 Hz, 1H), 7.35 - 7.21 (m, 5H), 7.13 (d, *J* = 9.6 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.60 (d, *J* = 9.0 Hz, 2H), 5.55 (dd, *J* = 9.3, 5.1 Hz, 1H), 4.11 (d, *J* = 9.6 Hz, 1H), 3.75 (d, *J* = 5.7 Hz, 1H), 3.68 (s, 3H), 2.23 (s, 3H), 1.49 (s, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 196.7, 163.4, 149.1, 140.3, 135.7, 134.7, 131.6, 131.0, 130.5, 129.5, 127.8, 127.7, 127.3, 127.1 (q, *J*_{C-F} = 282.0 Hz), 126.6, 125.3, 125.1, 123.5, 115.1, 113.3, 112.6, 84.0, 70.4, 57.2 (q, *J*_{C-F} = 26.3 Hz), 56.1, 55.4, 28.0, 21.8. ¹⁹F NMR (282 MHz, CDCl₃) δ -68.8. HRMS (ESI) *m/z* calcd for C₃₂H₃₁F₃NO₅S [M+H]⁺: 598.1870, found 598.1897.

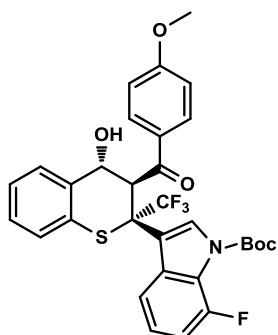


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	10.364	8971766	46.99	531616	VV	Unknown
2	13.687	10120130	53.01	430036	VV	Unknown

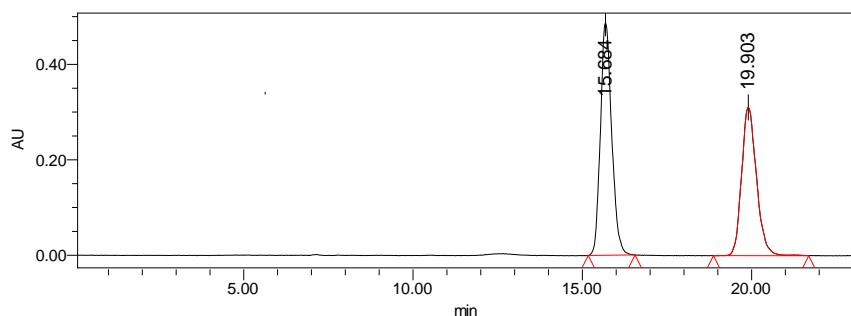


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	10.329	11844520	97.75	706484	bb	Unknown
2	13.695	272789	2.25	12920	bb	Unknown

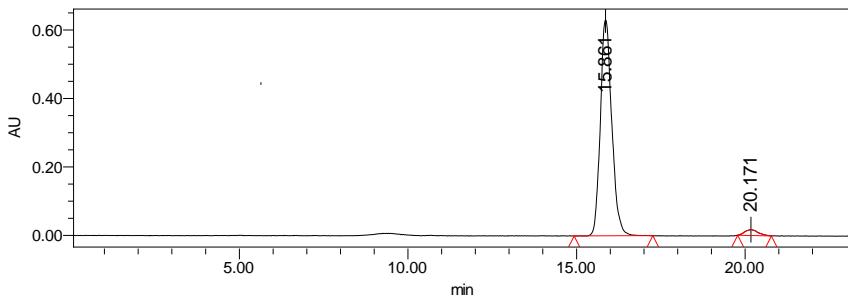
tert-butyl-7-fluoro-3-((2S,3S,4R)-4-hydroxy-3-(4-methoxybenzoyl)-2-(trifluoromethyl)thiochroman-2-yl)-1H-indole-1-carboxylate (3p)



From 27.6 mg (0.2 mmol) 2-mercaptopbenzaldehyde and 101.9 mg (0.22 mmol, 1.1 equiv) β -indole- β -CF₃ enones **2q**, 96.3 mg (80.0% yield) compound **3p** was obtained as a white solid, mp = 98 - 99 °C. $[\alpha]_D^{20} = +74$ (c = 1.0, CHCl₃). Dr (>20:1) determined by ¹H and ¹⁹F NMR analysis. 94% ee was determined by HPLC analysis (Daicel Chiralcel IA-H column, hexane/2-propanol 3:1, 1.0 mL/min). Retention time: *t*_{major} = 15.9 and *t*_{minor} = 20.2 min. ¹H NMR (300 MHz, CDCl₃) δ 8.10 (d, *J* = 8.1 Hz, 1H), 7.71 (d, *J* = 7.2 Hz, 1H), 7.44 - 7.31 (m, 6H), 7.11 - 7.04 (m, 1H), 6.88 (dd, *J* = 12.5, 8.0 Hz, 1H), 6.71 (d, *J* = 9.0 Hz, 2H), 5.70 (dd, *J* = 9.8, 4.1 Hz, 1H), 4.22 (d, *J* = 9.9 Hz, 1H), 3.78 (s, 3H), 3.65 (d, *J* = 6.0 Hz, 1H), 1.57 (s, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 196.8, 163.5, 149.6 (d, *J*_{C-F} = 250.5 Hz), 148.1, 139.7, 132.8 (d, *J*_{C-F} = 3.0 Hz), 131.5, 130.8, 130.4, 128.4 (d, *J*_{C-F} = 4.5 Hz), 127.8 (d, *J*_{C-F} = 9.8 Hz), 127.4, 127.0 (q, *J*_{C-F} = 282.5 Hz), 125.0, 122.6, 122.5, 122.3, 119.9 (d, *J*_{C-F} = 3.8 Hz), 113.4, 112.3 (d, *J*_{C-F} = 1.5 Hz), 111.6 (d, *J*_{C-F} = 21.0 Hz), 84.8, 70.4, 56.9 (q, *J*_{C-F} = 27.0 Hz), 56.2, 55.4, 27.8. ¹⁹F NMR (282 MHz, CDCl₃) δ -68.9, -116.5. HRMS (ESI) *m/z* calcd for C₃₁H₂₈F₄NO₅S [M+H]⁺: 602.1619, found 602.1639.

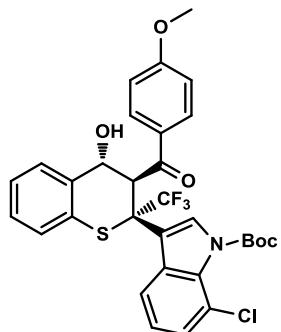


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	15.684	11262614	54.19	486270	bb	Unknown
2	19.903	9519617	45.81	311017	bb	Unknown

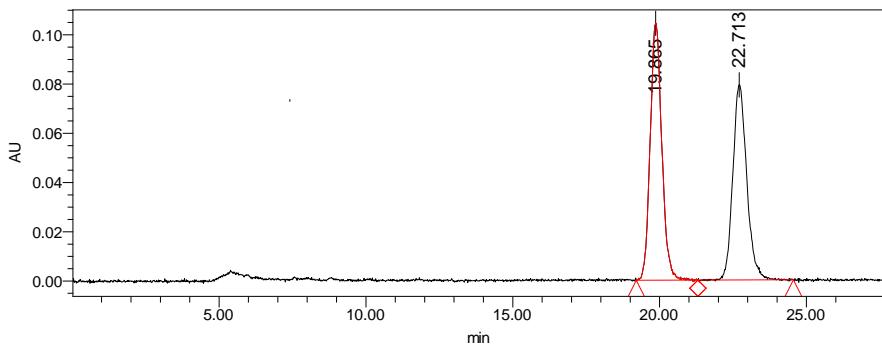


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	15.861	14877547	96.92	631115	bb	Unknown
2	20.171	472777	3.08	17048	bb	Unknown

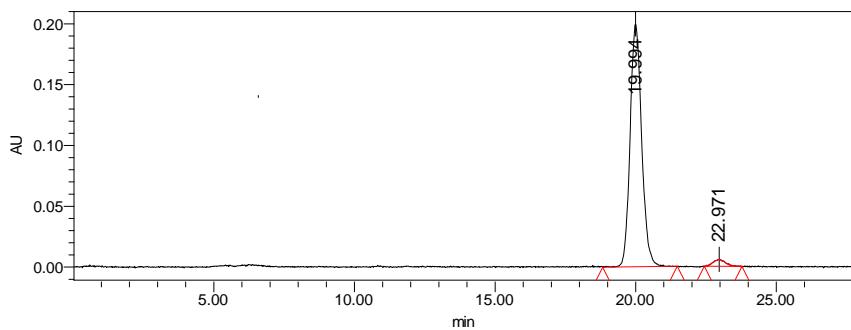
***tert*-butyl-7-chloro-3-((2*S*,3*S*,4*R*)-4-hydroxy-3-(4-methoxybenzoyl)-2-(trifluoromethyl)thiochroman-2-yl)-1*H*-indole-1-carboxylate (3q)**



From 27.6 mg (0.2 mmol) 2-mercaptopbenzaldehyde and 105.4 mg (0.22 mmol, 1.1 equiv) β -indole- β -CF₃ enones **2r**, 100.1 mg (81.0% yield) compound **3q** was obtained as a white solid, mp = 79 - 80 °C. $[\alpha]_D^{20} = +49$ (c = 1.0, CHCl₃). Dr (>20:1) determined by ¹H and ¹⁹F NMR analysis. 94% ee was determined by HPLC analysis (Daicel Chiralcel IA-H column, hexane/2-propanol 3:1, 1.0 mL/min). Retention time: $t_{\text{major}} = 20.0$ and $t_{\text{minor}} = 23.0$ min. ¹H NMR (300 MHz, CDCl₃) δ 8.27 (d, $J = 7.8$ Hz, 1H), 7.70 (d, $J = 7.5$ Hz, 1H), 7.44 - 7.33 (m, 3H), 7.27 (d, $J = 8.7$ Hz, 2H), 7.13 (d, $J = 8.4$ Hz, 2H), 7.05 (t, $J = 7.8$ Hz, 1H), 6.67 (d, $J = 9.0$ Hz, 2H), 5.72 (dd, $J = 9.6, 5.4$ Hz, 1H), 4.20 (d, $J = 9.9$ Hz, 1H), 3.88 (d, $J = 5.7$ Hz, 1H), 3.74 (s, 3H), 1.54 (s, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 196.8, 163.4, 148.0, 139.9, 132.1, 132.0, 131.5, 130.8, 130.3, 129.2, 128.0, 127.7, 127.6, 127.0 (q , $J_{\text{C-F}} = 282.5$ Hz), 126.5, 125.1, 122.9, 122.7, 119.9, 113.4, 111.8, 85.0, 70.4, 56.9 (q , $J_{\text{C-F}} = 26.8$ Hz), 56.4, 55.4, 27.8. ¹⁹F NMR (282 MHz, CDCl₃) δ -69.0. HRMS (ESI) m/z calcd for C₃₁H₂₈ClF₃NO₅S [M+H]⁺: 618.1323, found 618.1348.

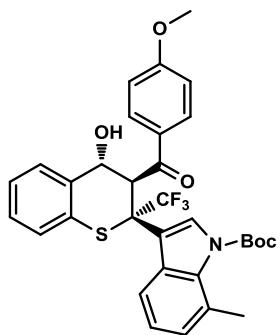


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	19.865	2884324	52.40	104473	bv	Unknown
2	22.713	2620286	47.60	79360	vb	Unknown



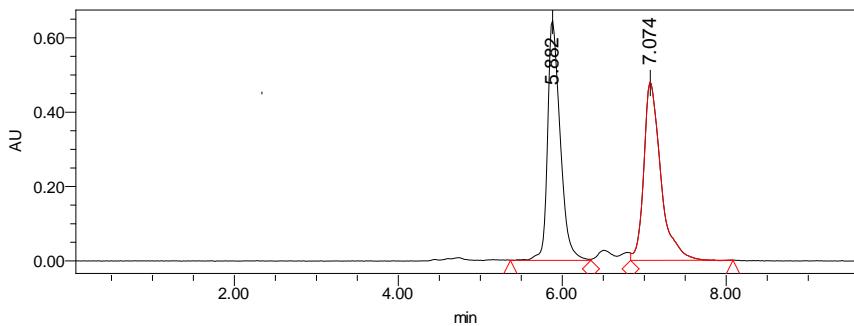
	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	19.994	5692452	96.96	199720	bb	Unknown
2	22.971	178334	3.04	5796	bb	Unknown

tert-butyl-3-((2S,3S,4R)-4-hydroxy-3-(4-methoxybenzoyl)-2-(trifluoromethyl)thiochroman-2-yl)-7-methyl-1H-indole-1-carboxylate (3r)

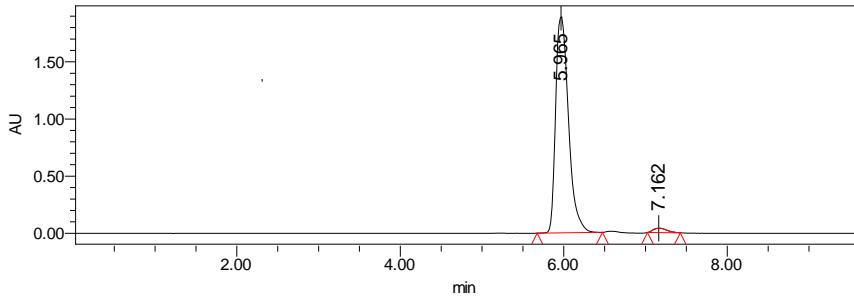


From 27.6 mg (0.2 mmol) 2-mercaptopbenzaldehyde and 101.0 mg (0.22 mmol, 1.1 equiv) β -indole- β -CF₃ enones **2s**, 94.4 mg (79.0% yield) compound **3r** was obtained as a white solid, mp = 70 - 71 °C. [α]_D²⁰ = +37 (c = 1.0, CHCl₃). Dr (>20:1) determined by ¹H and ¹⁹F NMR analysis. 96% ee was determined by HPLC analysis (Daicel Chiralcel IC-H column, hexane/2-propanol 3:1, 1.0 mL/min). Retention time: *t*_{major} = 6.0 and *t*_{minor} = 7.2 min. ¹H NMR (300 MHz, CDCl₃) δ 8.14 (d, *J* = 8.1 Hz, 1H), 7.71 (d, *J* = 7.5 Hz, 1H), 7.43 - 7.29 (m, 3H), 7.25 (d, *J* = 8.7 Hz, 2H), 7.12 - 7.07 (m, 2H), 6.98 (d, *J* = 7.2 Hz, 1H), 6.67 (d, *J* = 8.7 Hz, 2H), 5.76 (d, *J* = 9.6 Hz, 1H), 4.21 (d,

J = 9.6 Hz, 1H), 3.75 (s, 3H), 3.60 (s, 1H), 2.51 (s, 3H), 1.50 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3) δ 196.8, 163.2, 148.7, 139.9, 134.8, 131.9, 131.2, 130.2, 129.8, 128.2, 127.9, 127.8, 127.7, 127.3, 127.2 (q, $J_{\text{C}-\text{F}} = 282.8$ Hz), 125.1, 124.7, 122.2, 121.7, 113.3, 111.8, 83.8, 70.4, 57.0 (q, $J_{\text{C}-\text{F}} = 26.3$ Hz), 56.6, 55.3, 27.9, 22.0. ^{19}F NMR (282 MHz, CDCl_3) δ -68.7. HRMS (ESI) m/z calcd for $\text{C}_{32}\text{H}_{31}\text{F}_3\text{NO}_5\text{S} [\text{M}+\text{H}]^+$: 598.1870, found 598.1893.

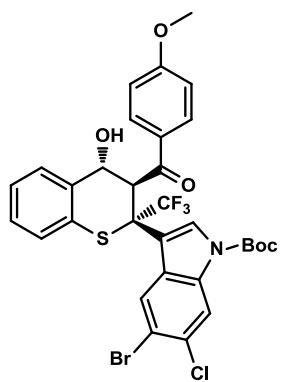


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	5.882	6836547	49.79	644040	bv	Unknown
2	7.074	6894603	50.21	480813	vb	Unknown



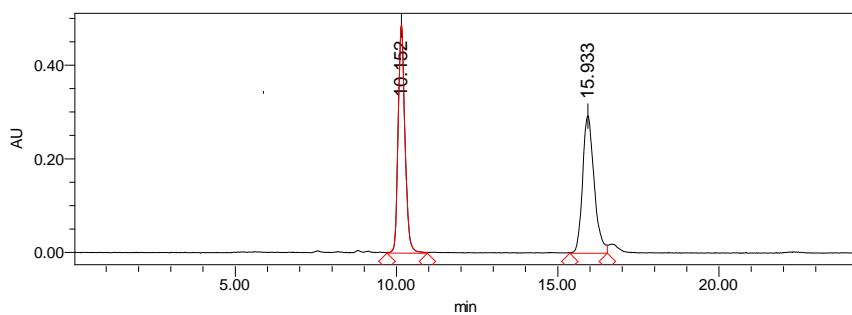
	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	5.965	20717524	97.90	1893092	bb	Unknown
2	7.162	443627	2.10	37933	bb	Unknown

tert-butyl-5-bromo-6-chloro-3-((2*S*,3*S*,4*R*)-4-hydroxy-3-(4-methoxybenzoyl)-2-(trifluoromethyl)thiochroman-2-yl)-1*H*-indole-1-carboxylate (3s)

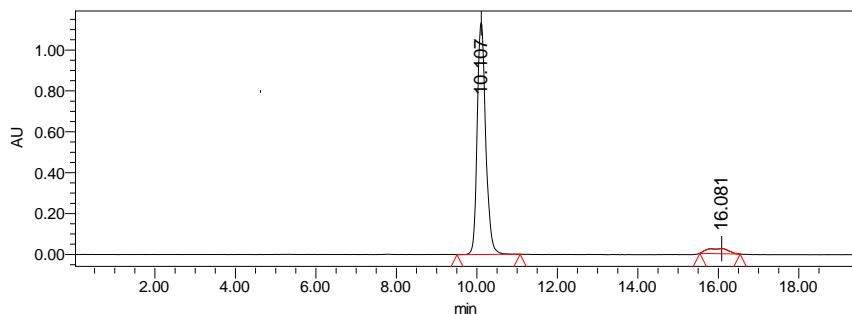


From 27.6 mg (0.2 mmol) 2-mercaptopbenzaldehyde and 122.5 mg (0.22 mmol, 1.1

equiv) β -indole- β -CF₃ enones **2t**, 114.3 mg (82.0% yield) compound **3s** was obtained as a white solid, mp = 84 - 85 °C. $[\alpha]_D^{20} = +111$ ($c = 1.0$, CHCl₃). Dr (>20:1) determined by ¹H and ¹⁹F NMR analysis. 90% ee was determined by HPLC analysis (Daicel Chiralcel IA-H column, hexane/2-propanol 3:1, 1.0 mL/min). Retention time: $t_{\text{major}} = 10.1$ and $t_{\text{minor}} = 16.1$ min. ¹H NMR (300 MHz, CDCl₃) δ 8.49 (s, 1H), 8.29 (s, 1H), 7.70 (d, $J = 7.5$ Hz, 1H), 7.43 - 7.31 (m, 6H), 6.67 (d, $J = 9.0$ Hz, 2H), 5.65 (dd, $J = 9.5, 5.6$ Hz, 1H), 4.24 (d, $J = 9.9$ Hz, 1H), 4.00 (d, $J = 5.7$ Hz, 1H), 3.77 (s, 3H), 1.58 (s, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 197.0, 163.7, 148.4, 139.8, 134.6, 131.0, 130.7, 130.7, 130.5, 130.3, 128.9, 128.0, 128.0, 127.8, 127.5, 126.9 (q, $J_{\text{C-F}} = 281.3$ Hz), 125.1, 116.4, 116.0, 113.5, 112.2, 85.3, 70.9, 56.9 (q, $J_{\text{C-F}} = 26.8$ Hz), 55.9, 55.5, 28.0. ¹⁹F NMR (282 MHz, CDCl₃) δ -68.9. HRMS (ESI) m/z calcd for C₃₁H₂₇BrClF₃NO₅S [M+H]⁺: 696.0428, found 696.0428.

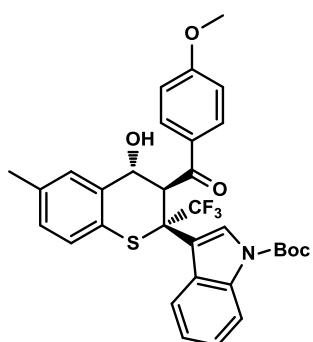


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	10.152	7140471	49.37	488761	VV	Unknown
2	15.933	7321920	50.63	293701	VV	Unknown

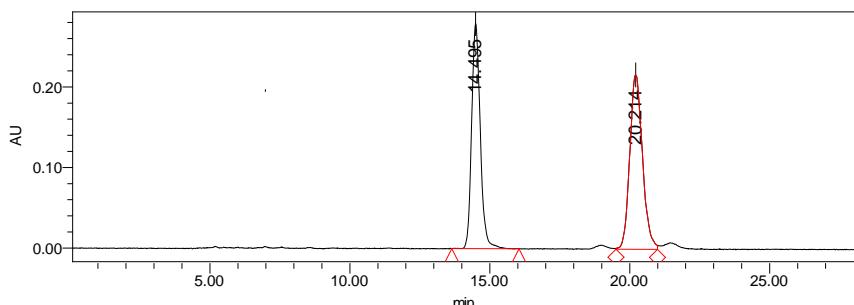


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	10.107	16625039	94.77	1136657	bb	Unknown
2	16.081	918314	5.23	25247	bb	Unknown

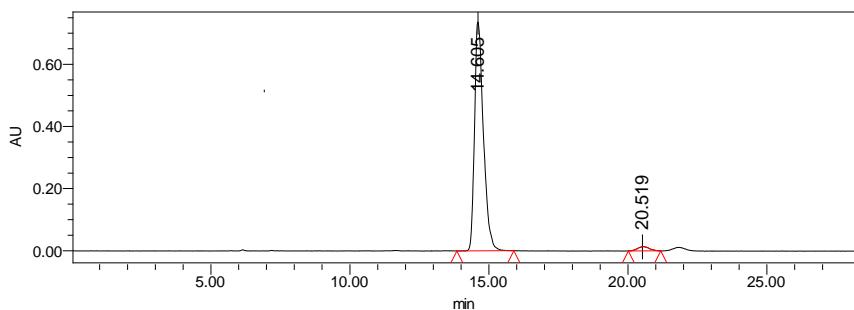
tert-butyl-3-((2S,3S,4R)-4-hydroxy-3-(4-methoxybenzoyl)-6-methyl-2-(trifluoromethyl)thiochroman-2-yl)-1H-indole-1-carboxylate (3t)



From 30.4 mg (0.2 mmol) 2-mercaptop-5-methylbenzaldehyde and 97.9 mg (0.22 mmol, 1.1 equiv) β -indole- β -CF₃ enones **2d**, 94.4 mg (79.0% yield) compound **3t** was obtained as a white solid, mp = 109 - 110 °C. $[\alpha]_D^{20} = +50$ (c = 1.0, CHCl₃). Dr (>20:1) determined by ¹H and ¹⁹F NMR analysis. 95% ee was determined by HPLC analysis (Daicel Chiralcel IA-H column, hexane/2-propanol 3:1, 1.0 mL/min). Retention time: *t*_{major} = 14.6 and *t*_{minor} = 20.5 min. ¹H NMR (300 MHz, CDCl₃) δ 8.22 (d, *J* = 7.2 Hz, 1H), 8.07 (d, *J* = 8.1 Hz, 1H), 7.53 (s, 1H), 7.31 (d, *J* = 7.8 Hz, 4H), 7.22 - 7.11 (m, 3H), 6.69 (d, *J* = 8.7 Hz, 2H), 5.67 (dd, *J* = 9.6, 5.7 Hz, 1H), 4.21 (d, *J* = 9.9 Hz, 1H), 3.77 (s, 3H), 3.62 (d, *J* = 5.7 Hz, 1H), 2.43 (s, 3H), 1.59 (s, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 196.9, 163.4, 149.0, 139.5, 137.3, 135.2, 131.7, 130.4, 128.8, 128.5, 127.8, 127.5, 127.1 (q, *J*_{C-F} = 282.5 Hz), 126.0, 125.8, 124.6, 123.9, 122.0, 114.8, 113.3, 112.6, 84.2, 70.5, 57.0 (q, *J*_{C-F} = 26.8 Hz), 56.3, 55.4, 28.0, 21.6. ¹⁹F NMR (282 MHz, CDCl₃) δ -68.8. HRMS (ESI) *m/z* calcd for C₃₂H₃₁F₃NO₅S [M+H]⁺: 598.1870, found 598.1892.

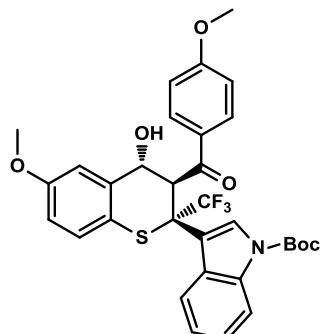


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	14.495	5995863	46.82	279572	bb	Unknown
2	20.214	6810957	53.18	216288	vv	Unknown

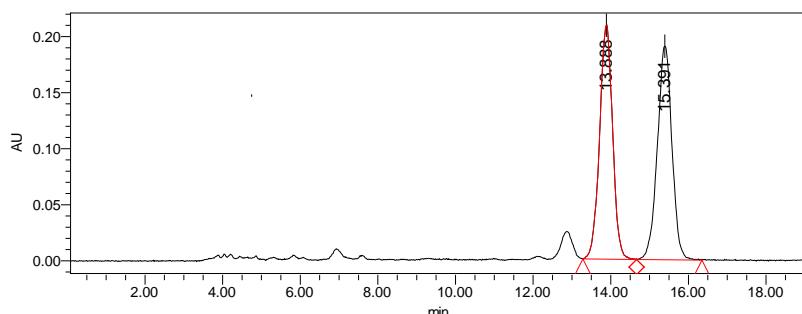


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	14.605	16329298	97.64	737571	bb	Unknown
2	20.519	395434	2.36	13388	bb	Unknown

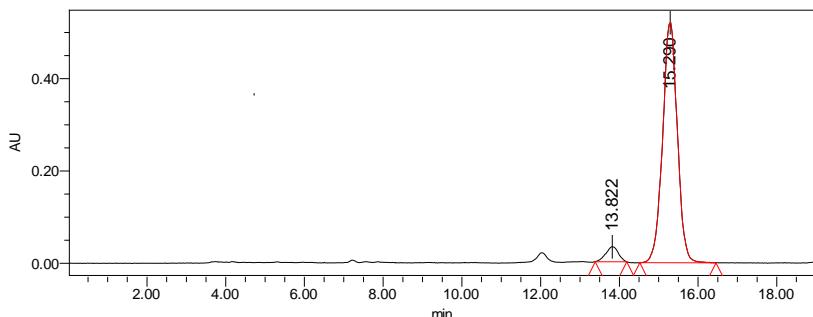
tert-butyl-3-((2*S*,3*S*,4*R*)-4-hydroxy-6-methoxy-3-(4-methoxybenzoyl)-2-(trifluoromethyl)thiochroman-2-yl)-1*H*-indole-1-carboxylate (3u**)**



From 33.6 mg (0.2 mmol) 2-mercaptop-5-methoxybenzaldehyde and 97.9 mg (0.22 mmol, 1.1 equiv) β -indole- β -CF₃ enones **2d**, 98.2 mg (80.0% yield) compound **3u** was obtained as a colorless oil. $[\alpha]_D^{20} = +16$ (c = 1.0, CHCl₃). Dr (>20:1) determined by ¹H and ¹⁹F NMR analysis. 90% ee was determined by HPLC analysis (Daicel Chiralcel IA-H column, hexane/2-propanol 3:1, 1.0 mL/min). Retention time: *t*_{major} = 15.3 and *t*_{minor} = 13.8 min. ¹H NMR (300 MHz, CDCl₃) δ 8.21 (d, *J* = 7.8 Hz, 1H), 8.10 (d, *J* = 8.1 Hz, 1H), 7.56 (s, 1H), 7.35 (s, 1H), 7.33 - 7.30 (m, 3H), 7.26 (t, *J* = 3.8 Hz, 1H), 7.17 (q, *J* = 7.5 Hz, 2H), 6.73 (d, *J* = 8.7 Hz, 2H), 5.74 (dd, *J* = 9.6, 5.4 Hz, 1H), 4.21 (d, *J* = 9.9 Hz, 1H), 3.81 (s, 3H), 3.11 (d, *J* = 5.4 Hz, 1H), 2.44 (s, 3H), 1.60 (s, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 195.8, 162.4, 148.0, 138.8, 132.5, 130.6, 130.2, 130.1, 129.4, 129.4, 127.7, 126.9, 126.7, 126.3, 126.0 (q, *J*_{C-F} = 281.5 Hz), 125.1, 124.0, 122.7, 113.3, 112.2, 111.1, 83.0, 69.5, 56.1 (q, *J*_{C-F} = 27.0 Hz), 55.3, 54.3, 27.0, 20.6. ¹⁹F NMR (282 MHz, CDCl₃) δ -68.7. HRMS (ESI) *m/z* calcd for C₃₂H₃₁F₃NO₆S [M+H]⁺: 614.1819, found 614.1845.

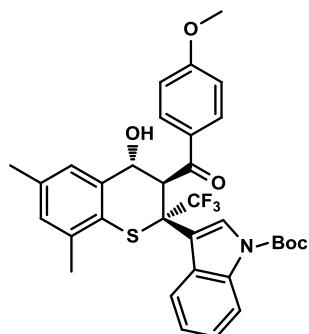


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	13.888	4860537	49.38	209062	bv	Unknown
2	15.391	4983259	50.62	190530	vb	Unknown

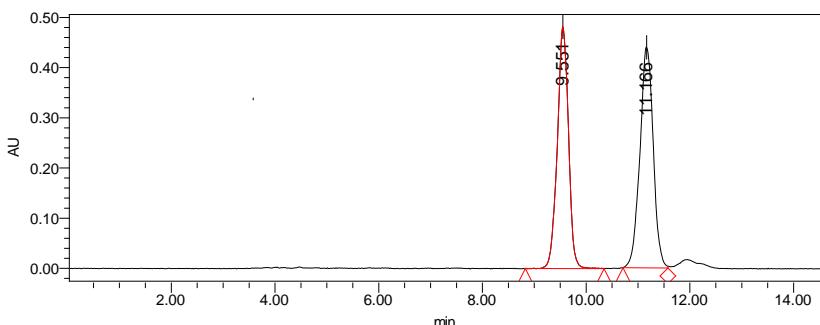


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	13.822	727504	5.11	32615	bb	Unknown
2	15.290	13508722	94.89	520721	bb	Unknown

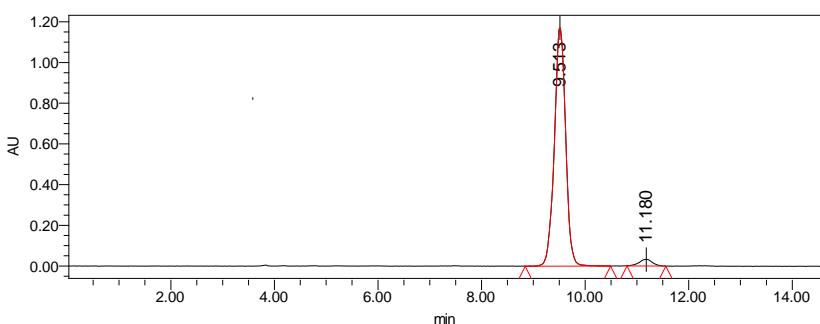
tert-butyl-3-((2*S*,3*S*,4*R*)-4-hydroxy-3-(4-methoxybenzoyl)-6,8-dimethyl-2-(trifluoromethyl)thiochroman-2-yl)-1*H*-indole-1-carboxylate (3v**)**



From 33.2 mg (0.2 mmol) 2-mercaptop-3,5-dimethylbenzaldehyde and 97.9 mg (0.22 mmol, 1.1 equiv) β -indole- β -CF₃ enones **2d**, 101.5 mg (83.0% yield) compound **3v** was obtained as a white solid, mp = 109 - 110 °C. $[\alpha]_D^{20} = +78$ (c = 1.0, CHCl₃). Dr (>20:1) determined by ¹H and ¹⁹F NMR analysis. 94% ee was determined by HPLC analysis (Daicel Chiralcel IA-H column, hexane/2-propanol 3:1, 1.0 mL/min). Retention time: $t_{\text{major}} = 9.5$ and $t_{\text{minor}} = 11.2$ min. ¹H NMR (300 MHz, CDCl₃) δ 8.23 (d, *J* = 7.8 Hz, 1H), 8.08 (d, *J* = 8.1 Hz, 1H), 7.40 (s, 1H), 7.30 (d, *J* = 8.7 Hz, 3H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.15 (t, *J* = 7.2 Hz, 1H), 7.06 (s, 1H), 6.69 (d, *J* = 9.0 Hz, 2H), 5.70 (dd, *J* = 9.3, 5.4 Hz, 1H), 4.16 (d, *J* = 9.6 Hz, 1H), 3.77 (s, 3H), 3.49 (d, *J* = 5.4 Hz, 1H), 2.39 (s, 6H), 1.59 (s, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 197.1, 163.4, 149.0, 139.7, 136.7, 136.3, 135.2, 131.8, 130.3, 129.8, 128.6, 127.0 (q, *J*_{C-F} = 283.0 Hz), 126.8, 126.1 (d, *J*_{C-F} = 3.8 Hz), 124.6, 124.0, 123.0, 122.0, 114.8, 113.2, 112.6, 84.2, 70.8, 56.9 (q, *J*_{C-F} = 27.0 Hz), 56.4, 55.4, 28.0, 21.4, 19.9. ¹⁹F NMR (282 MHz, CDCl₃) δ -69.1. HRMS (ESI) *m/z* calcd for C₃₃H₃₃F₃NO₅S [M+H]⁺: 612.2026, found 612.2033.

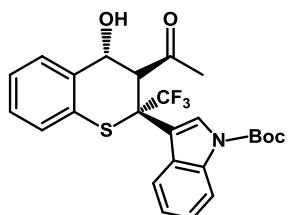


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	9.551	7209078	47.91	482737	bb	Unknown
2	11.166	7836983	52.09	441049	bv	Unknown



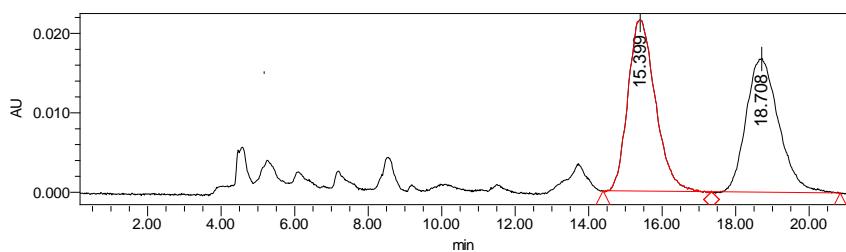
	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	9.513	17754561	96.88	1176409	bb	Unknown
2	11.180	571684	3.12	31983	bb	Unknown

tert-butyl-3-((2*S*,3*R*,4*R*)-3-acetyl-4-hydroxy-2-(trifluoromethyl)thiochroman-2-yl)-1*H*-indole-1-carboxylate (3w)

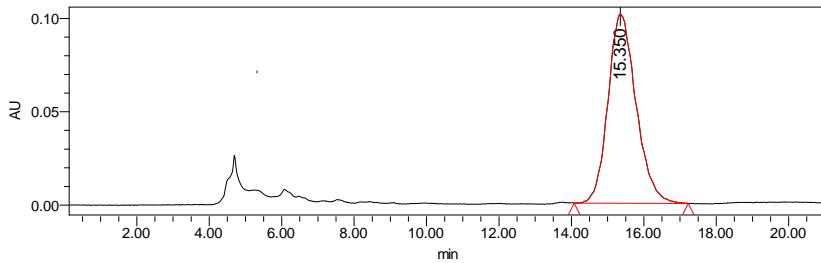


From 27.6 mg (0.2 mmol) 2-mercaptopbenzaldehyde and 77.7 mg (0.22 mmol, 1.1 equiv) β -indole- β -CF₃ enones **2u**, 78.6 mg (80.0% yield) compound **3w** was obtained as a white solid, mp = 88 - 89 °C. $[\alpha]_D^{20} = +66$ (c = 1.0, CHCl₃). Dr (>20:1) determined by ¹H and ¹⁹F NMR analysis. >99% ee was determined by HPLC analysis (Daicel Chiralcel OD-H column, hexane/2-propanol 20:1, 1.0 mL/min). Retention time: *t*_{major} = 15.4 min. ¹H NMR (300 MHz, CDCl₃) δ 8.22 (d, *J* = 8.1 Hz, 1H), 7.93 (d, *J* = 6.0 Hz, 2H), 7.64 - 7.61 (m, 1H), 7.36 - 7.30 (m, 2H), 7.28 - 7.21 (m, 3H), 5.31 (t, *J* = 6.5 Hz, 1H), 4.59 (d, *J* = 5.4 Hz, 1H), 2.88 (d, *J* = 8.1 Hz, 1H), 1.69 (s, 12H). ¹³C NMR (75 MHz, CDCl₃) δ 205.3, 149.0, 136.0, 134.0, 130.9, 127.9, 127.4, 126.6 (q,

$J_{C-F} = 283.7$ Hz), 126.2, 126.1, 125.4, 125.1, 123.1, 121.8, 121.7, 115.7, 114.3, 84.9, 68.0 (q, $J_{C-F} = 3.5$ Hz), 54.6, 54.3, 32.7, 28.1. ^{19}F NMR (282 MHz, $CDCl_3$) δ -69.0. HRMS (ESI) m/z calcd for $C_{25}H_{25}F_3NO_4S$ [M+H] $^+$: 492.1378, found 492.1370.

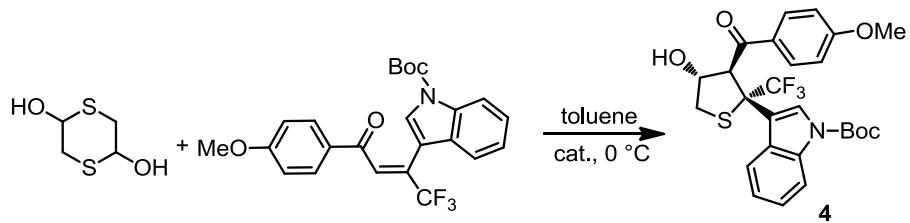


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	15.399	1113021	51.83	21521	bv	Unknown
2	18.708	1034321	48.17	16776	vb	Unknown



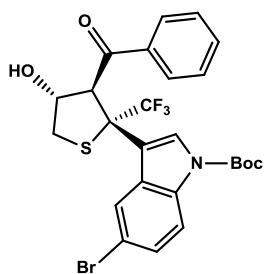
	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	15.350	5449605	100.00	101333	bb	Unknown

5. Screening of Catalysts for the synthesis of Compound 4.

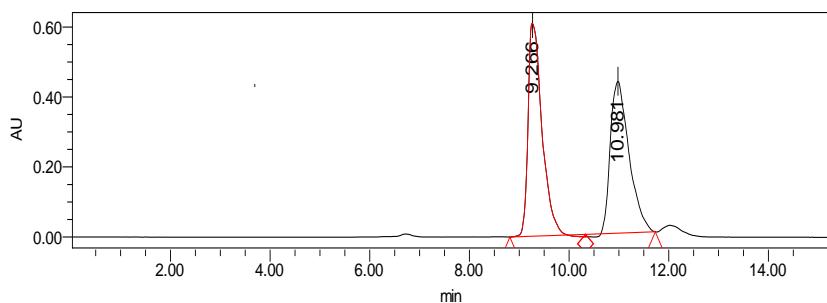


catalyst	time (h)	yield (%)	ee (%)
C1	48	61	64
C2	48	63	53
C3	48	81	14
C4	48	81	13
C5	48	85	84
C6	48	85	77
C7	48	84	73

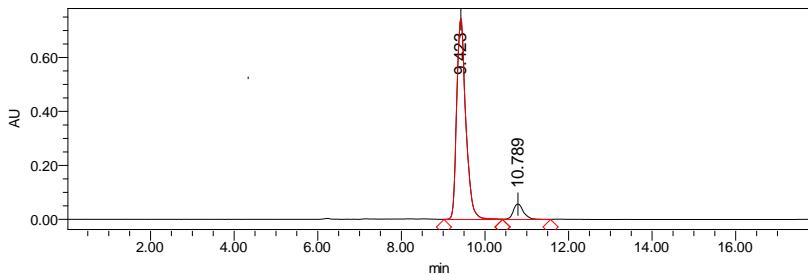
tert-butyl-3-((2*S*,3*S*,4*R*)-3-benzoyl-4-hydroxy-2-(trifluoromethyl)tetrahydrothiophen-2-yl)-5-bromo-1*H*-indole-1-carboxylate (4)



From 30.4 mg (0.2 mmol) 1,4-dithiane-2,5-diol and 115.1 mg (0.22 mmol, 1.1 equiv) β -indole- β -CF₃ enones **2i**, with **C5** (12 mg, 10 mol %) as catalyst, 102.1 mg (85.0% yield) compound **4** was obtained as a white solid, mp = 109 - 110 °C. $[\alpha]_D^{20} = +82$ (c = 1.0, CHCl₃). Dr (>20:1) determined by ¹H and ¹⁹F NMR analysis. 84% ee was determined by HPLC analysis (Daicel Chiralcel IA-H column, hexane/2-propanol 2:1, 1.0 mL/min). Retention time: $t_{\text{major}} = 9.4$ and $t_{\text{minor}} = 10.8$ min. ¹H NMR (300 MHz, CDCl₃) δ 7.93 (d, $J = 8.7$ Hz, 1H), 7.84 (s, 1H), 7.60 (d, $J = 8.7$ Hz, 2H), 7.30 (s, 1H), 7.19 (dd, $J = 8.9, 1.7$ Hz, 1H), 6.83 (d, $J = 9.0$ Hz, 2H), 5.05 (t, $J = 6.8$ Hz, 2H), 3.84 (s, 3H), 3.38 (t, $J = 9.2$ Hz, 1H), 3.21 (dd, $J = 9.8, 5.9$ Hz, 1H), 3.14 (d, $J = 5.1$ Hz, 1H), 1.63 (s, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 196.0, 163.8, 148.8, 134.6, 131.4, 130.5, 129.4, 129.2, 127.1, 127.1 (q, $J_{\text{C-F}} = 279.5$ Hz), 124.8, 116.4, 115.7, 115.5, 114.0, 84.8, 77.0, 61.1 (q, $J_{\text{C-F}} = 28.3$ Hz), 55.6, 52.8, 36.2, 28.0. ¹⁹F NMR (282 MHz, CDCl₃) δ -70.3. HRMS (ESI) m/z calcd for C₂₆H₂₆BrF₃NO₅S [M+H]⁺: 600.0662, found 600.0673.

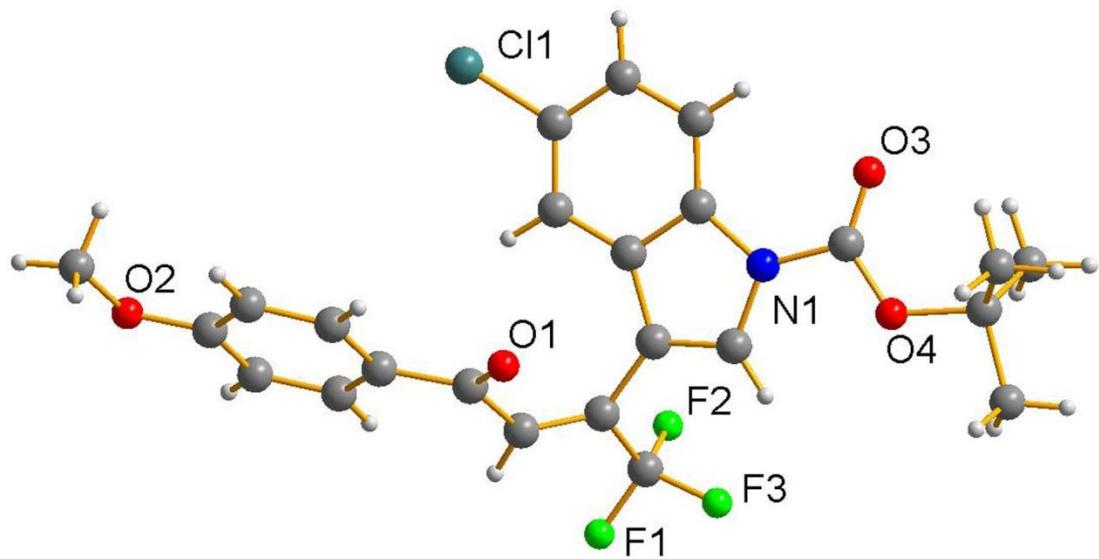


	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	9.266	11937296	51.00	609367	bv	Unknown
2	10.981	11468887	49.00	434077	vb	Unknown

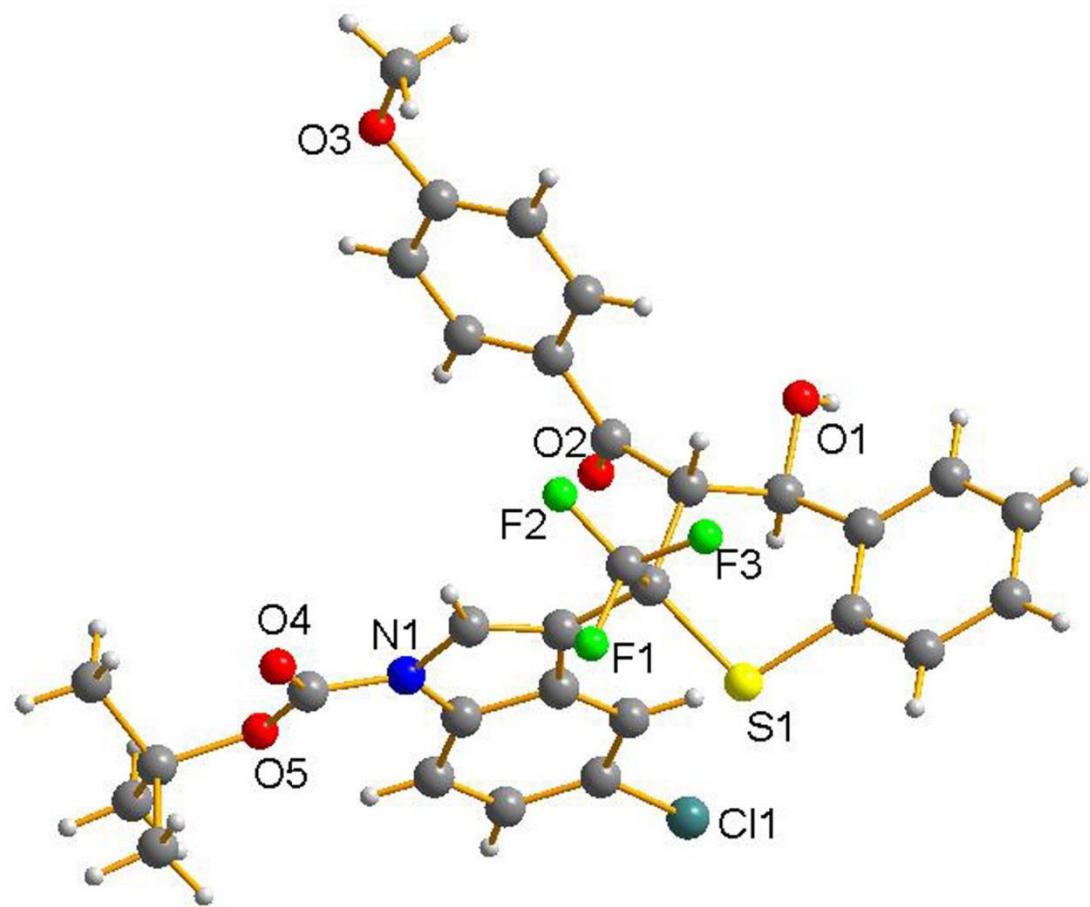


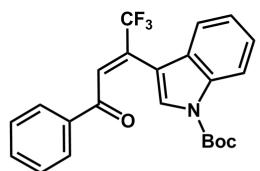
	Retention Time	Area	% Area	Height	Int Type	Peak Type
1	9.423	11241780	91.87	745034	VV	Unknown
2	10.789	995424	8.13	57293	VV	Unknown

5. X-ray Structure of Compound 2h

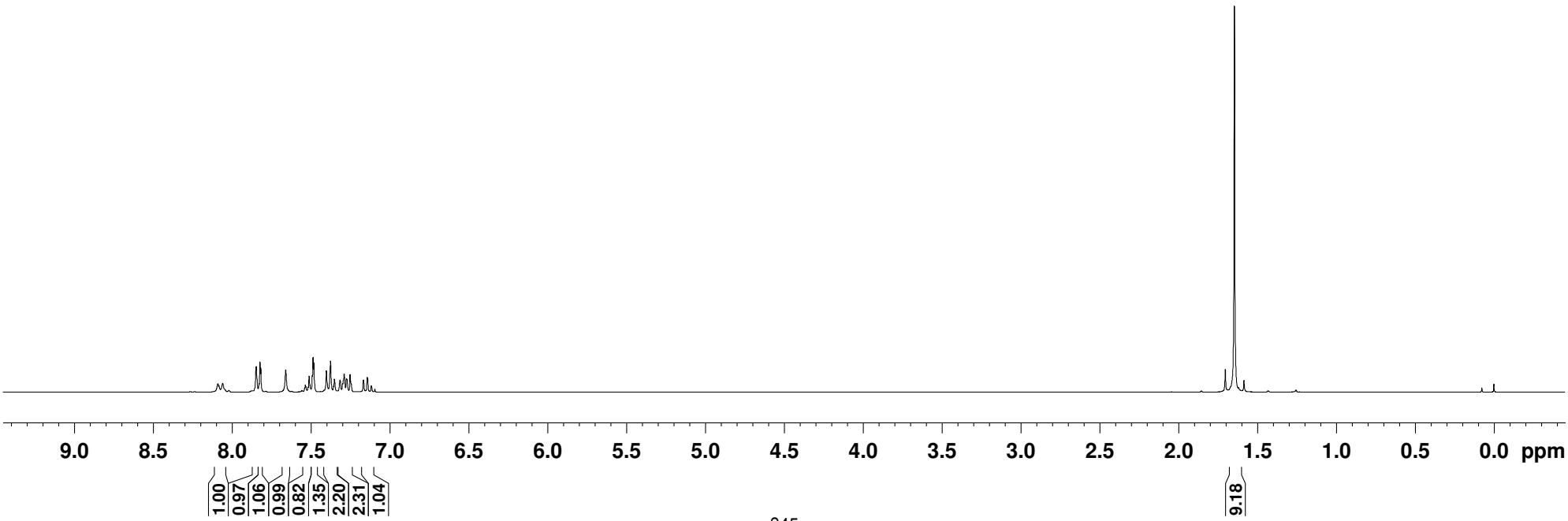


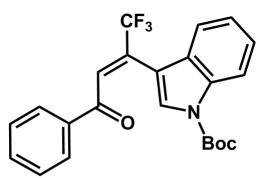
6. X-ray Structure of Compound 3g



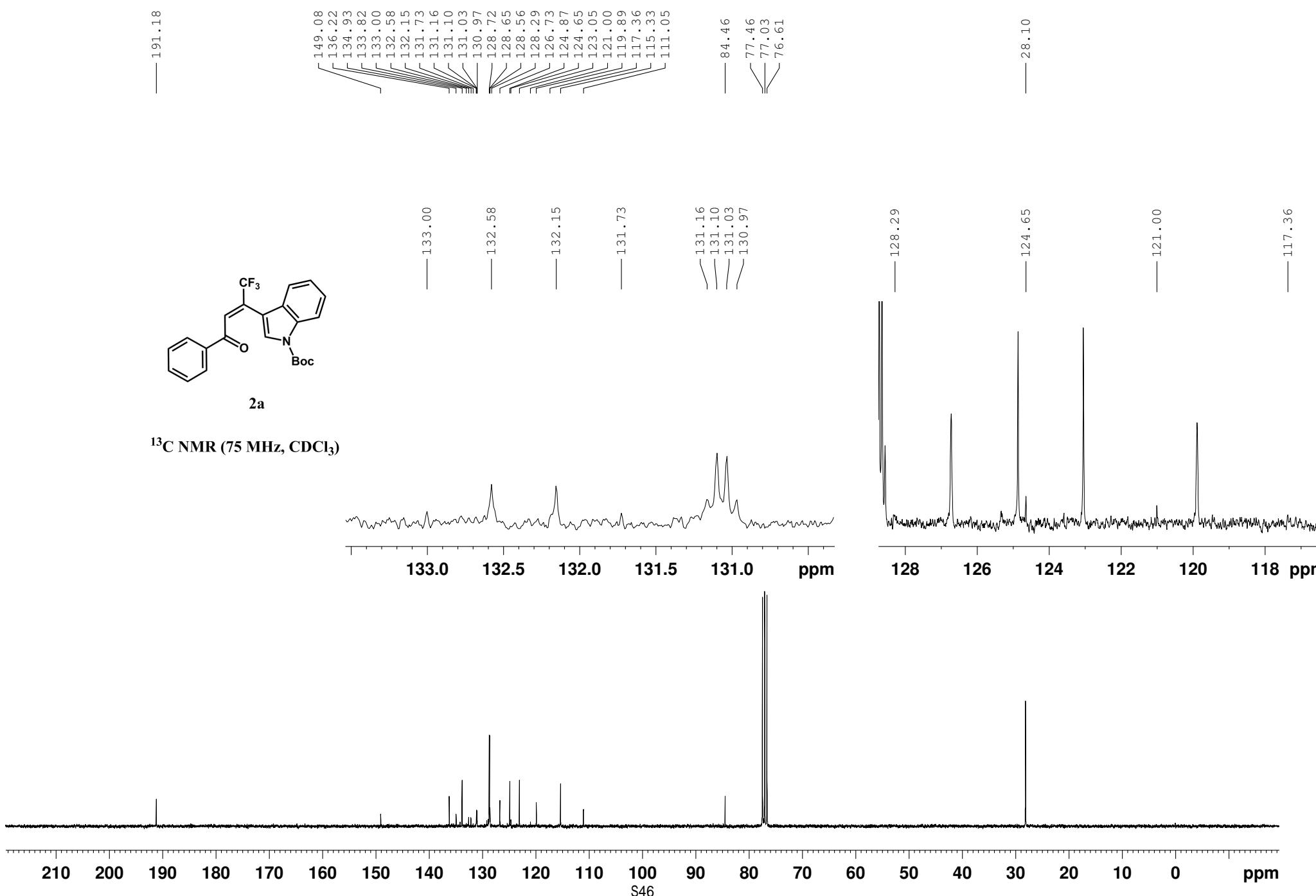


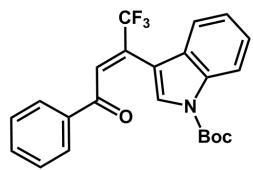
¹H NMR (300 MHz, CDCl₃)





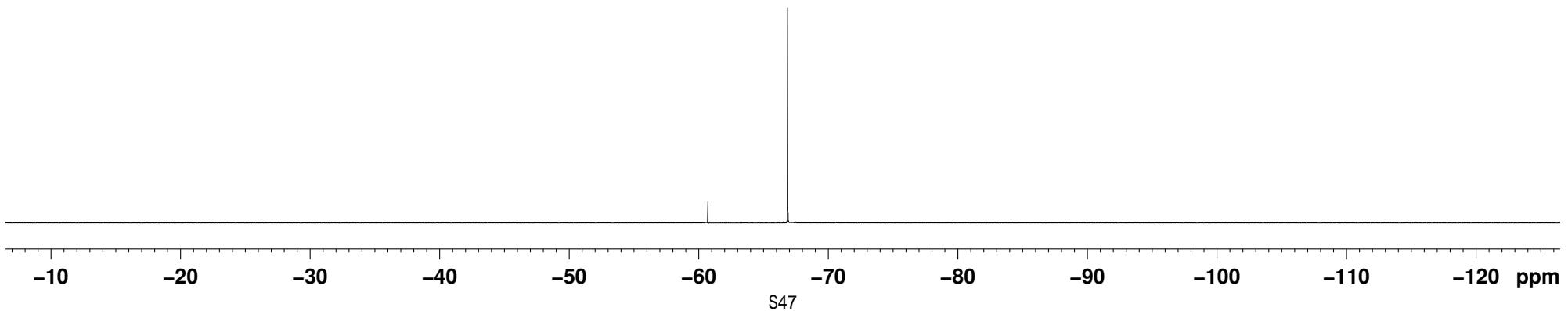
¹³C NMR (75 MHz, CDCl₃)





2a

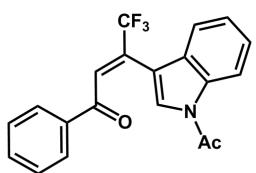
^{19}F NMR (282 MHz, CDCl_3)



8.363
8.335
7.821
7.796
7.506
7.466
7.442
7.355
7.329
7.308
7.286
7.260
7.199
7.173
7.149

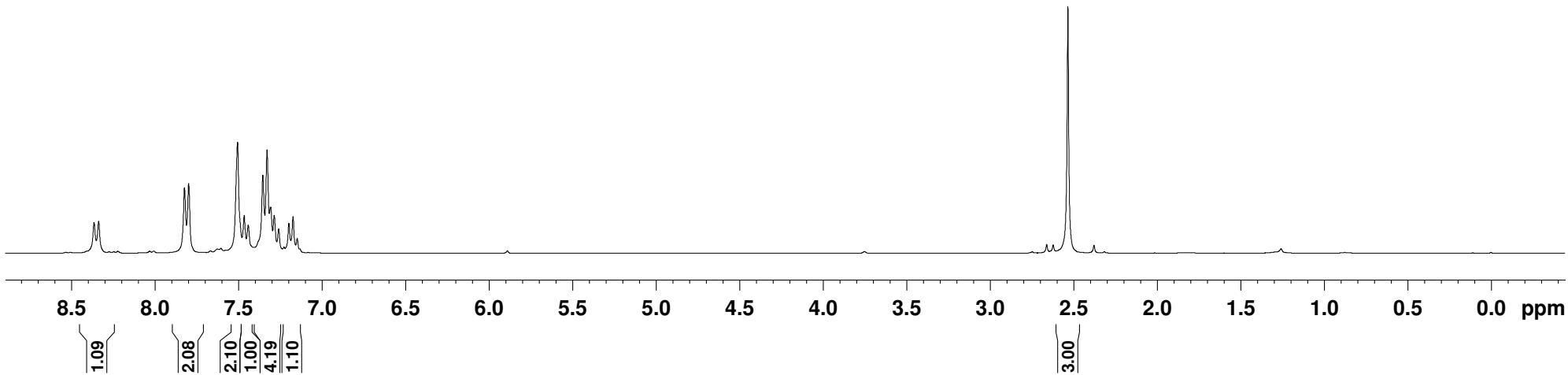
— 2.533

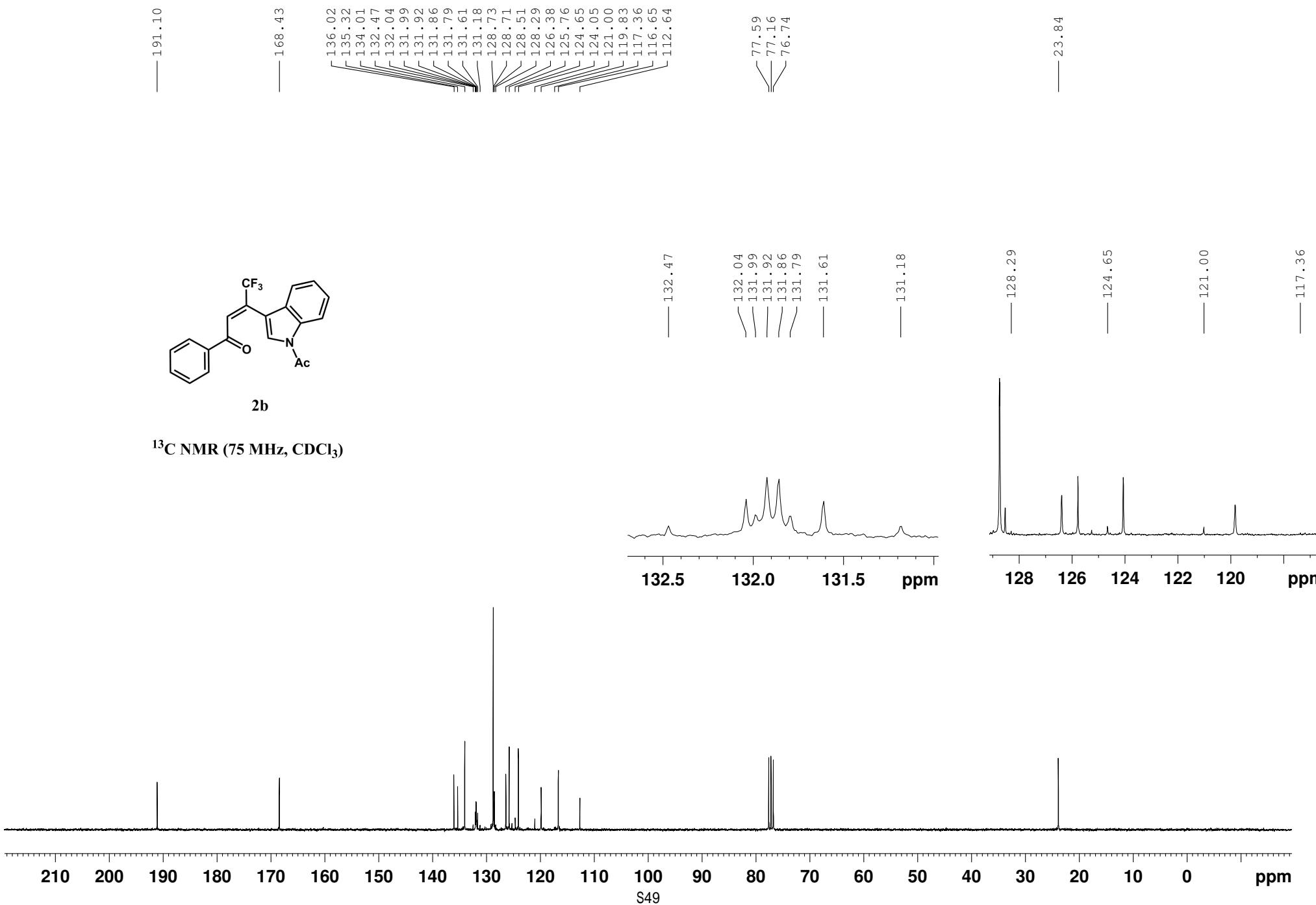
— -0.000

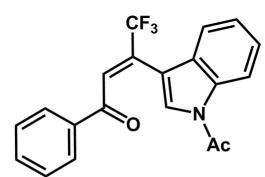


2b

¹H NMR (300 MHz, CDCl₃)

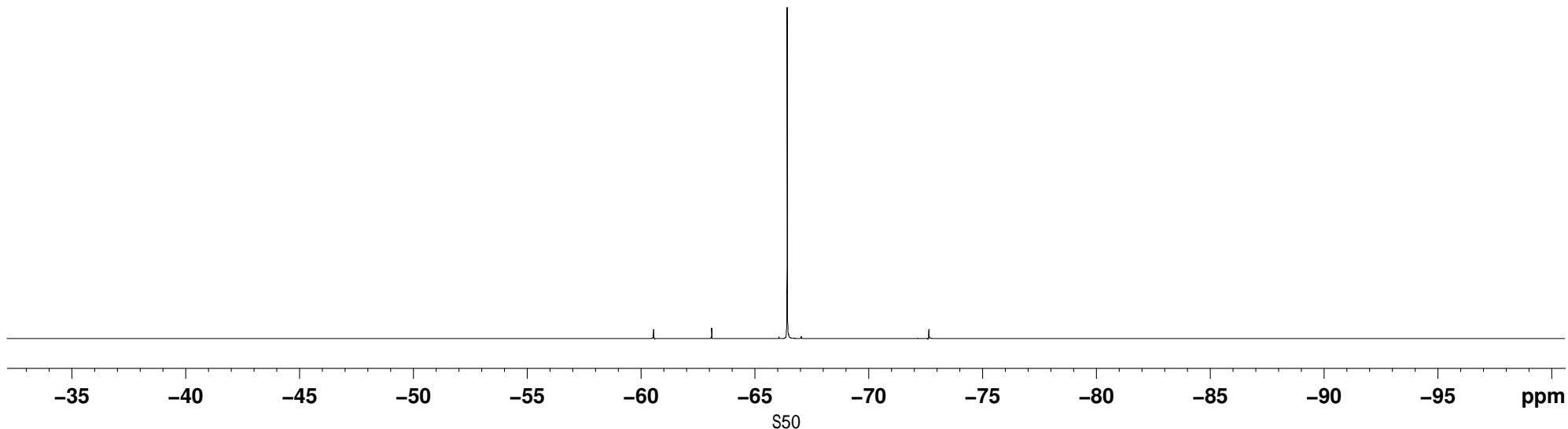






2b

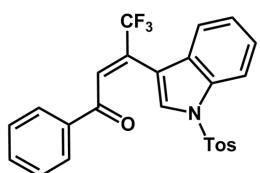
^{19}F NMR (282 MHz, CDCl_3)



7.740
7.713
7.633
7.609
7.568
7.533
7.507
7.333
7.278
7.247
7.217
7.163
7.139
7.114
7.029
7.005

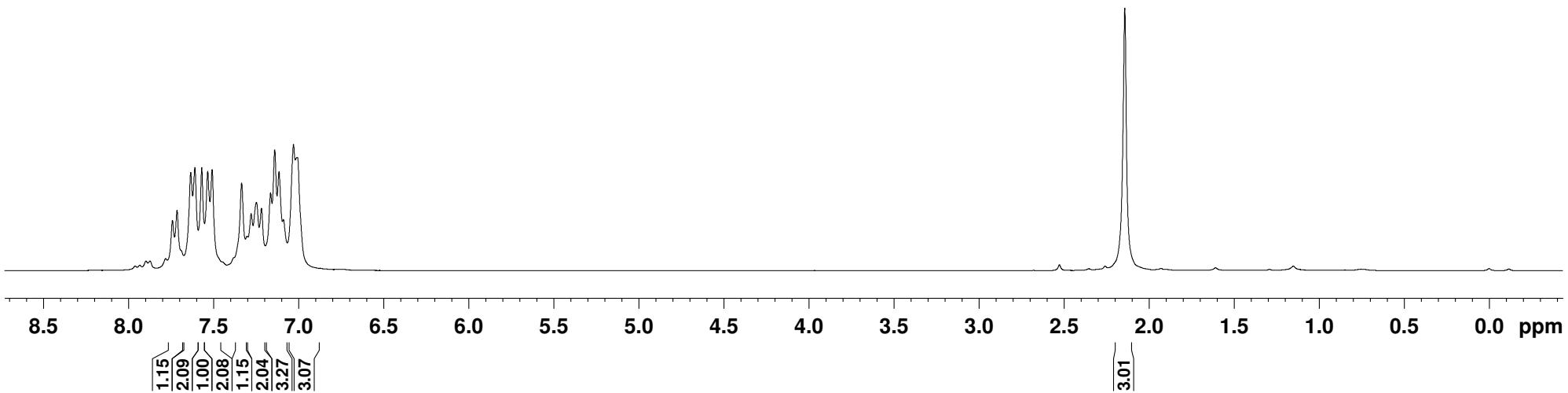
2.142

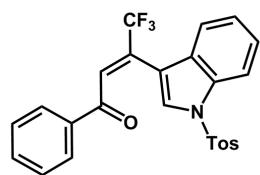
-0.000



2c

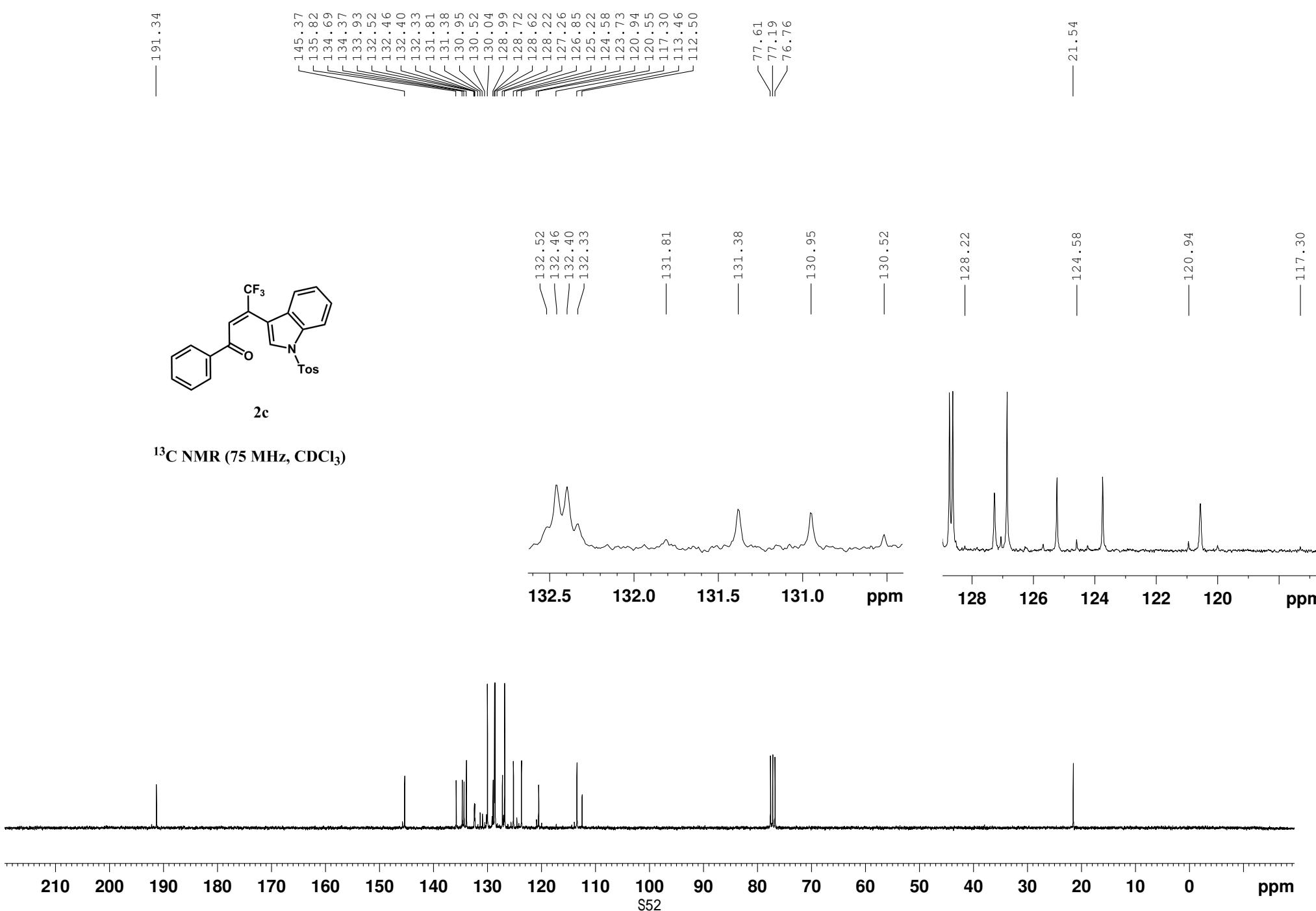
¹H NMR (300 MHz, CDCl₃)

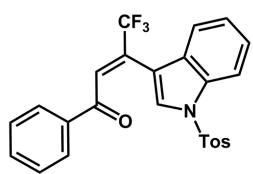




2c

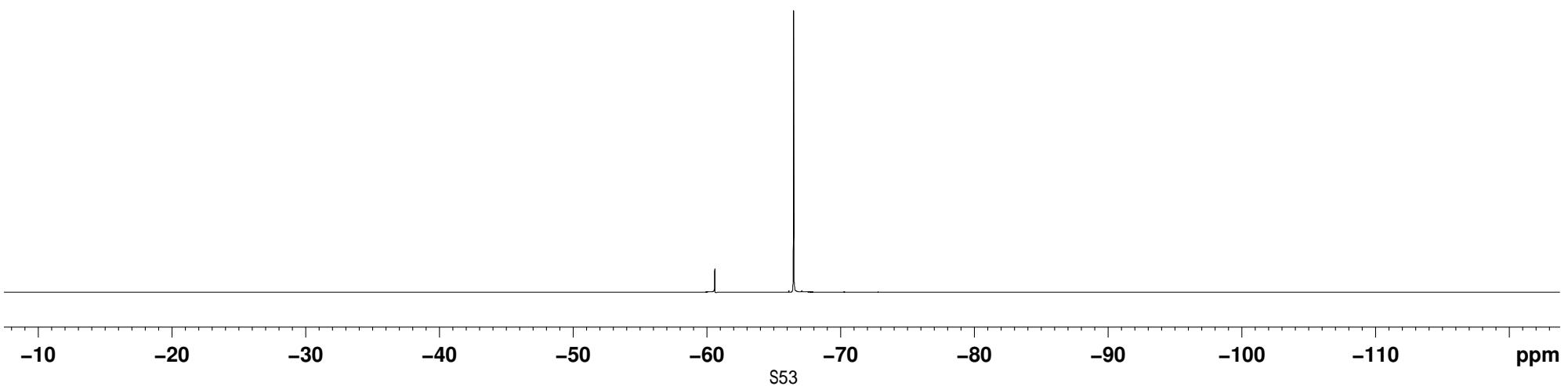
¹³C NMR (75 MHz, CDCl₃)





2c

¹⁹F NMR (282 MHz, CDCl₃)

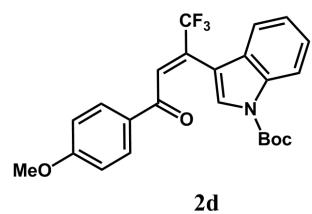


8.106
8.079
7.785
7.756
7.727
7.459
7.372
7.346
7.247
7.222
7.197
7.133
7.108
7.084
6.745
6.715

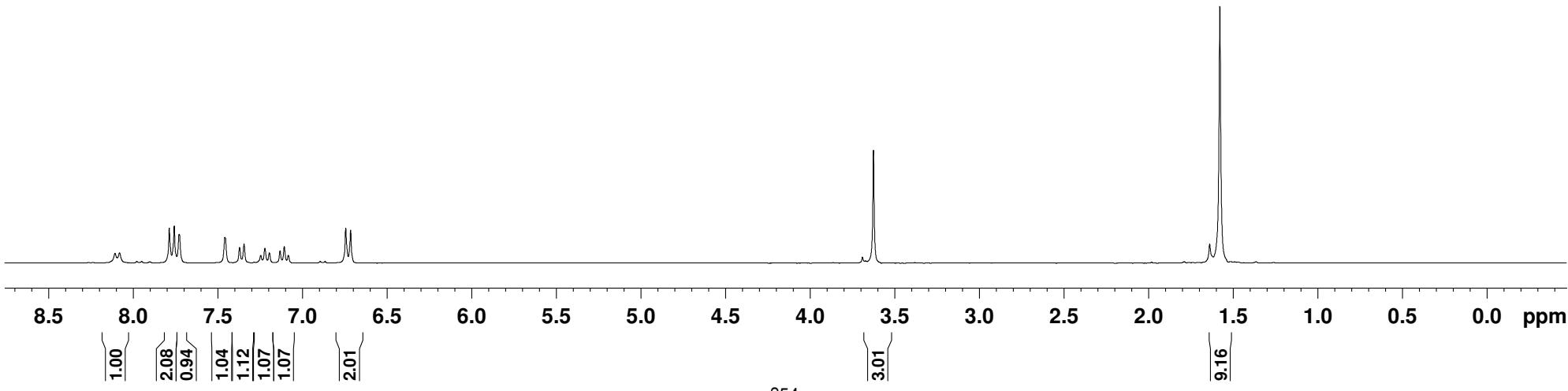
3.626

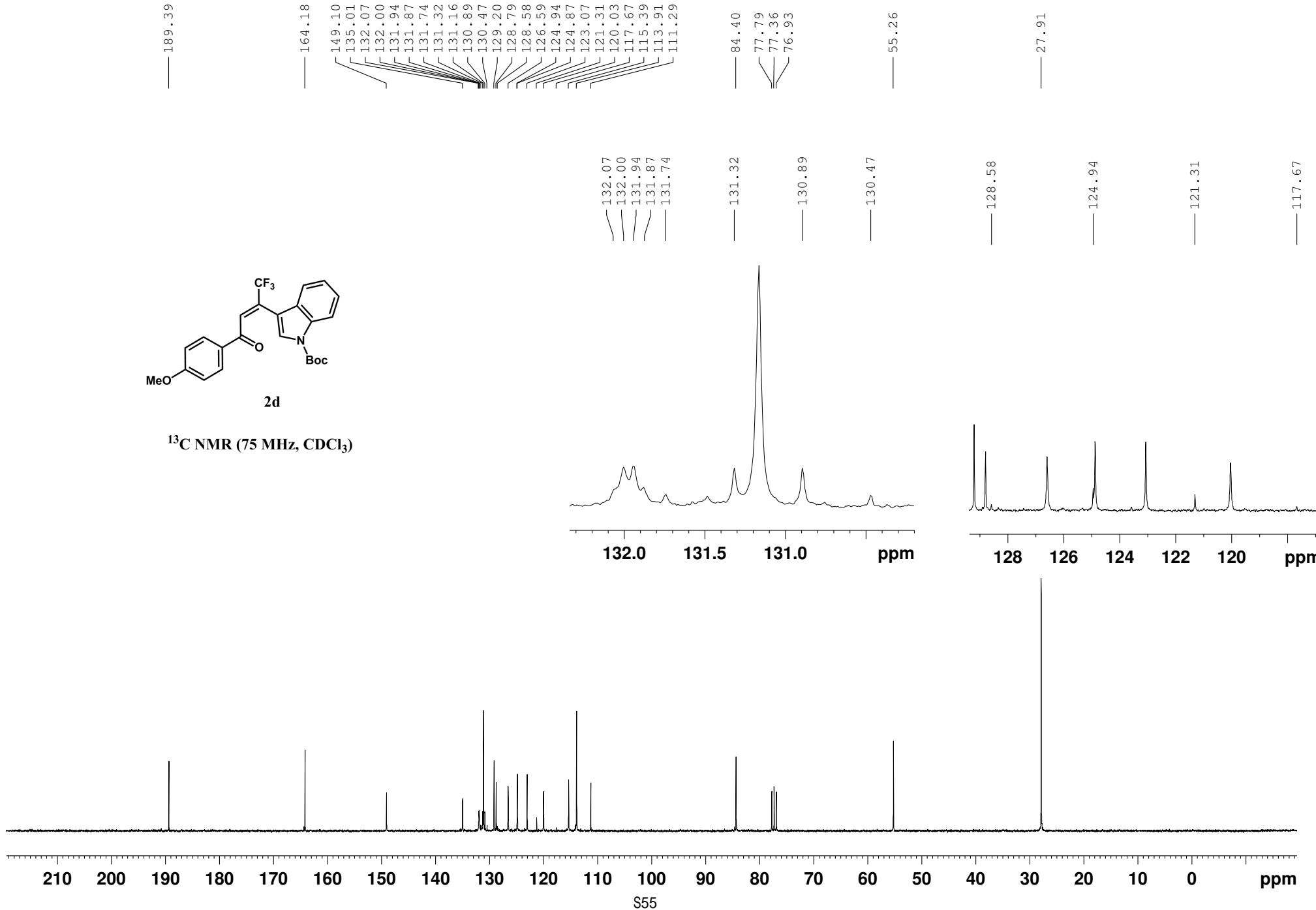
1.578

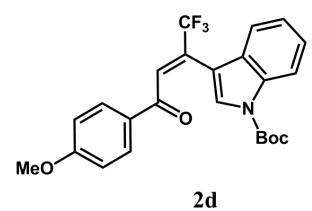
-0.000



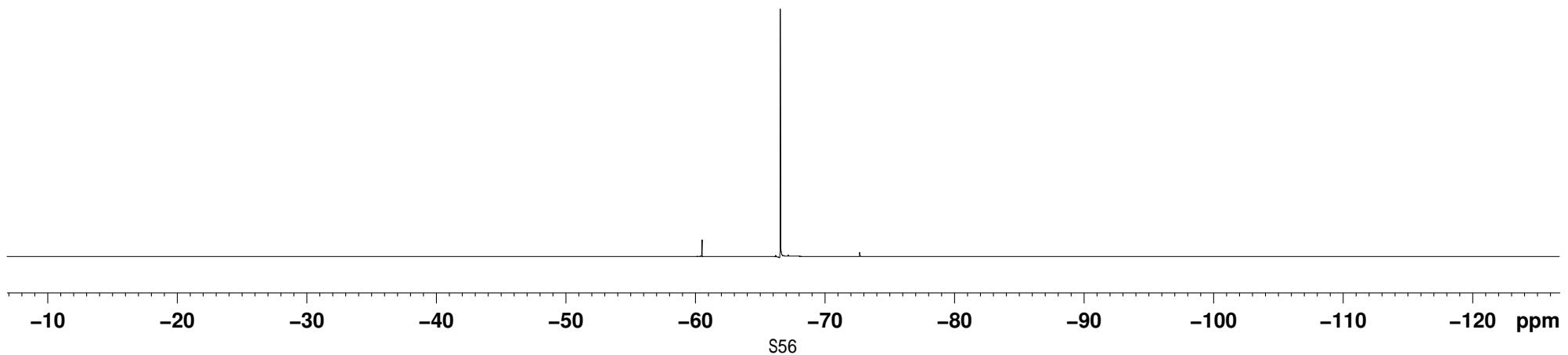
¹H NMR (300 MHz, CDCl₃)

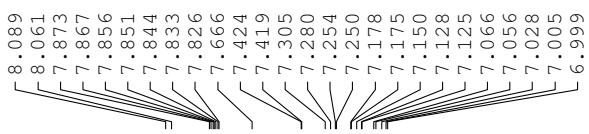






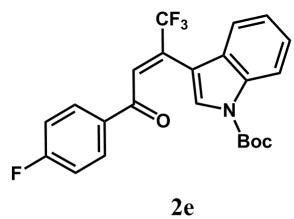
¹⁹F NMR (282 MHz, CDCl₃)





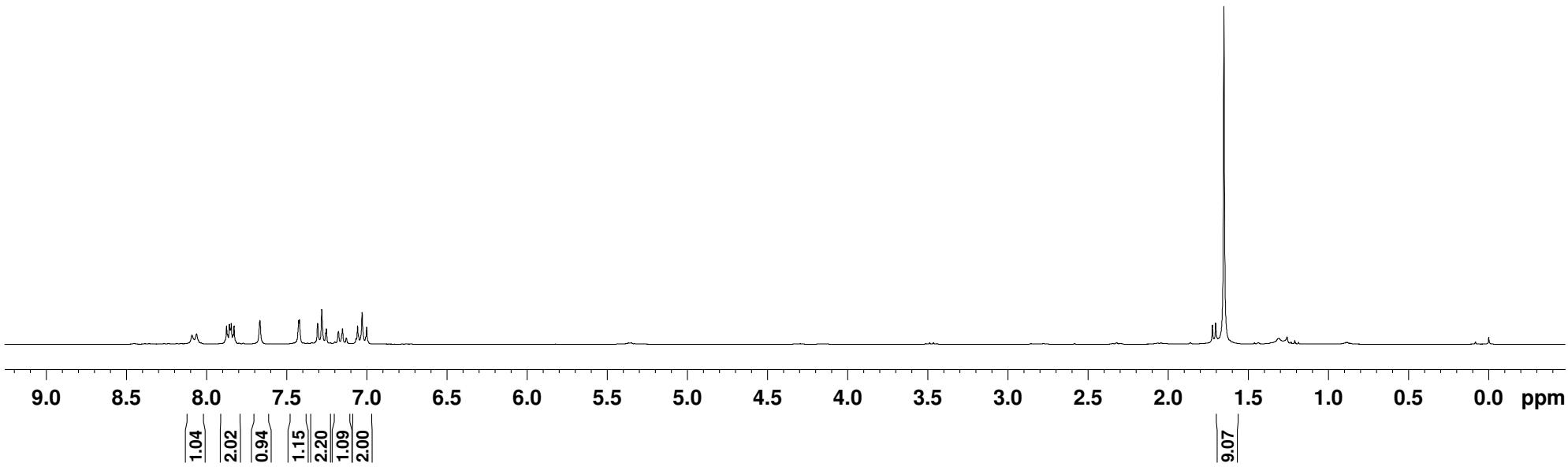
1 650

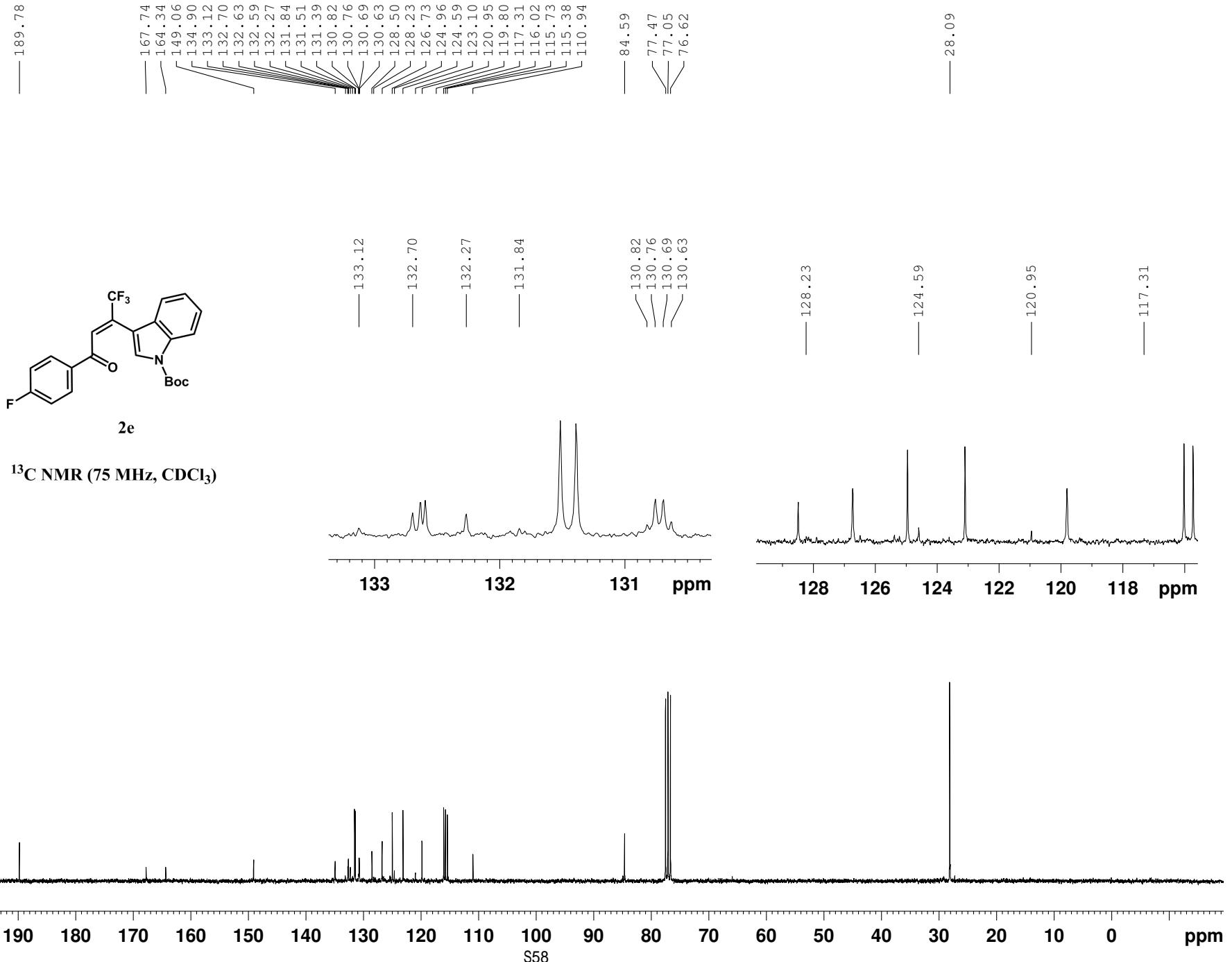
=0 000

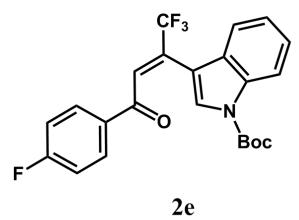


2e

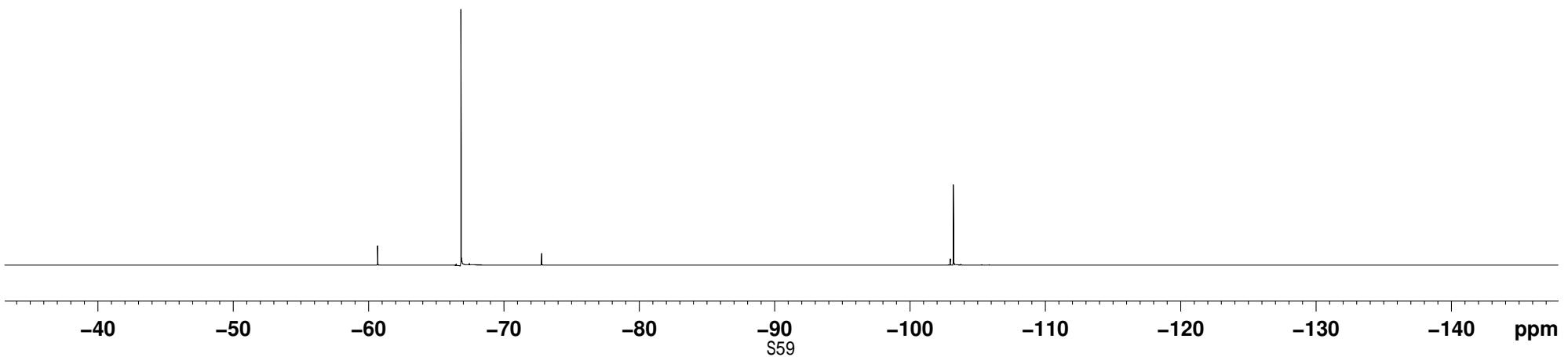
^1H NMR (300 MHz, CDCl_3)







^{19}F NMR (282 MHz, CDCl_3)



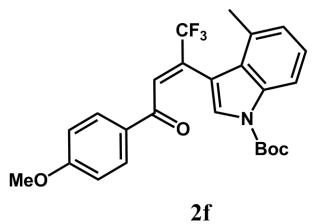
8.012
7.984
7.855
7.825
7.627
7.622
7.465
7.224
7.199
7.172
6.994
6.969
6.906
6.876

— 3.817

— 2.474

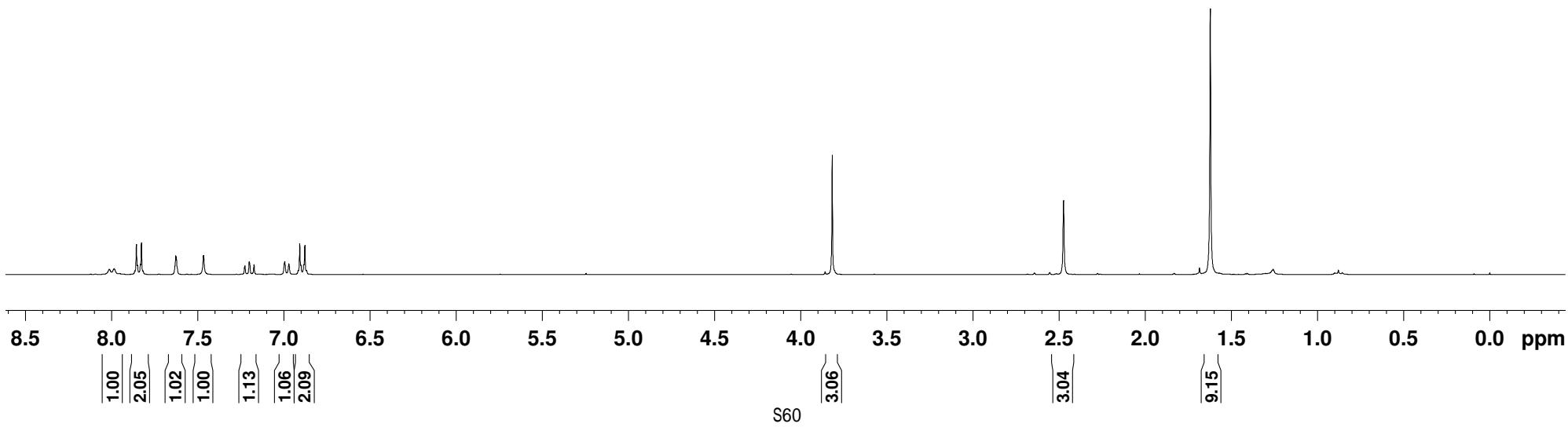
— 1.622

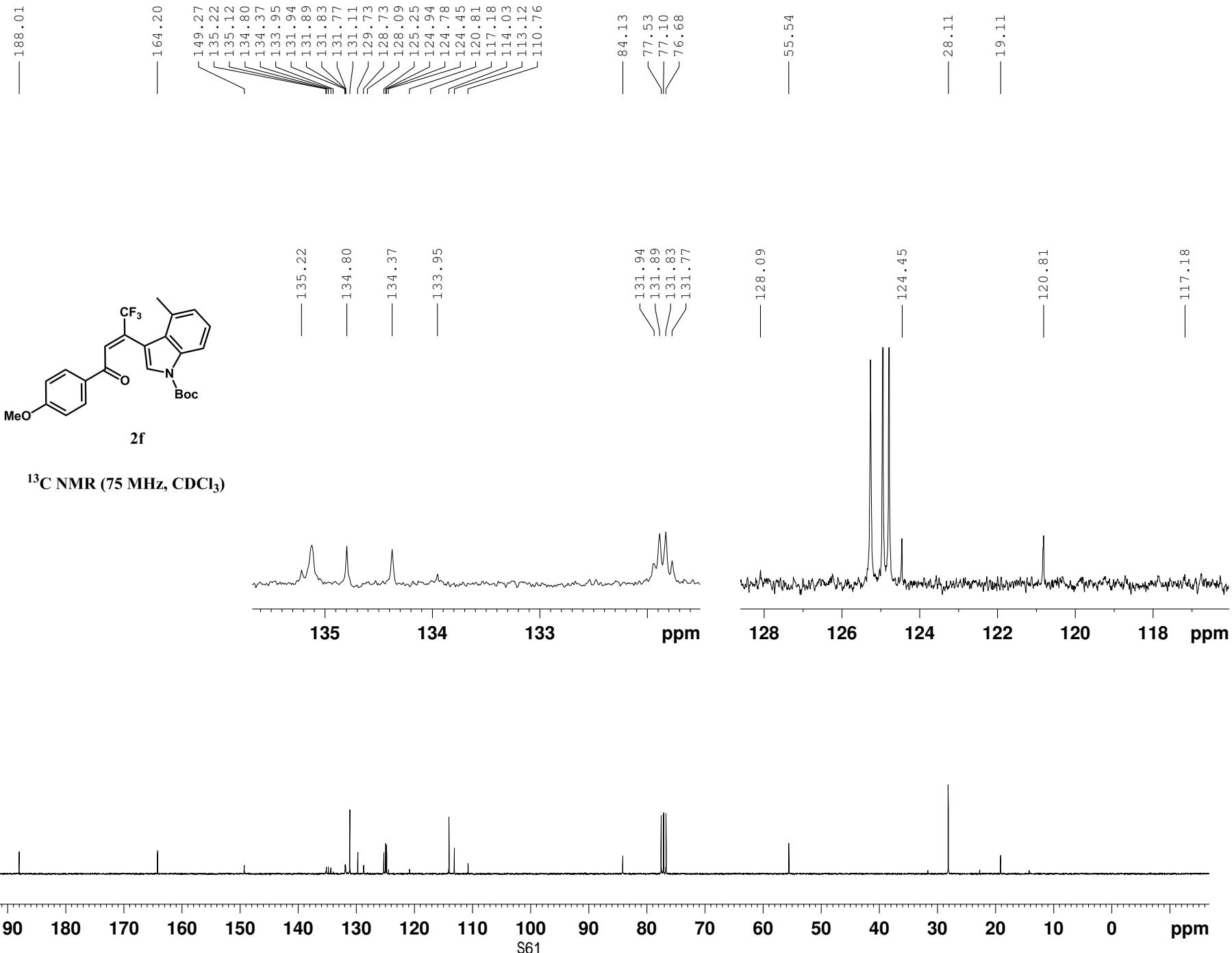
— -0.000

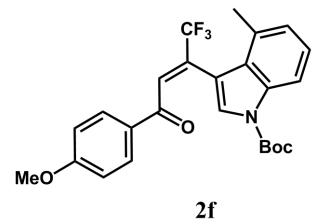


2f

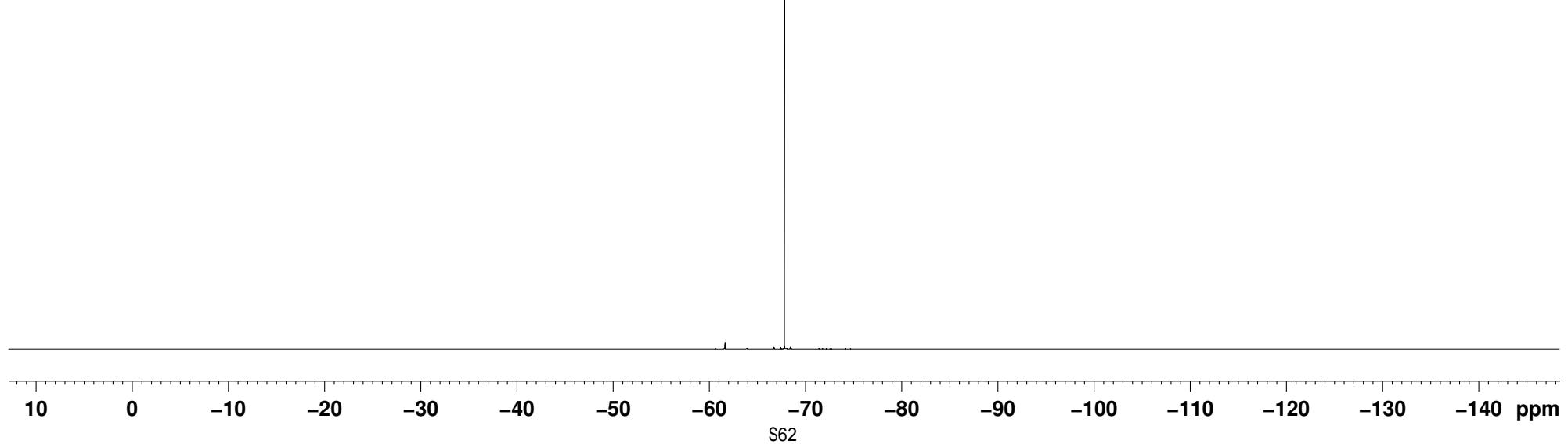
¹H NMR (300 MHz, CDCl₃)

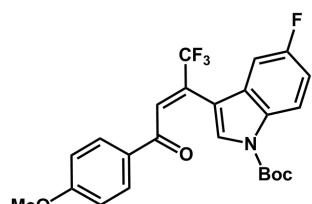




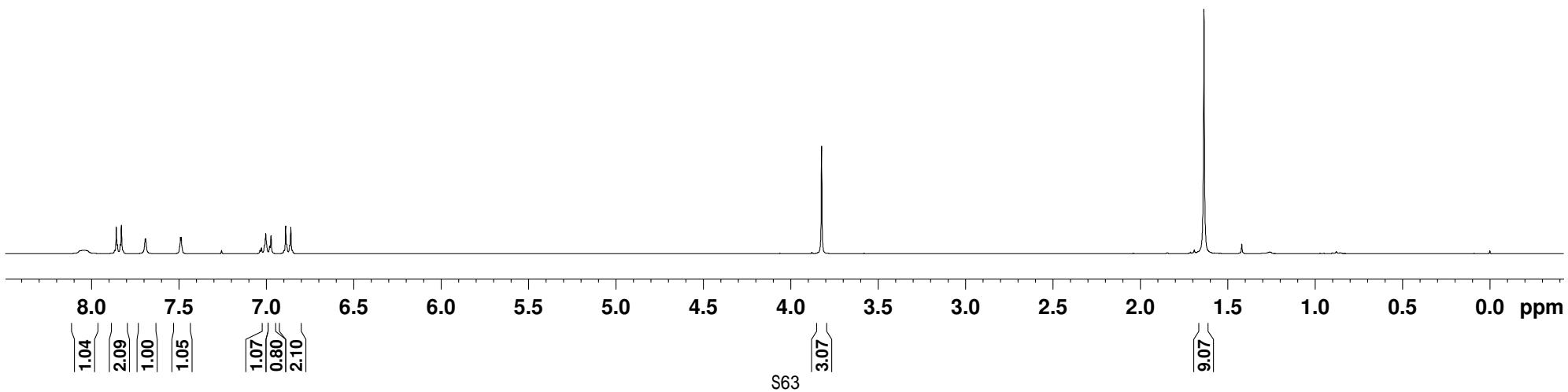


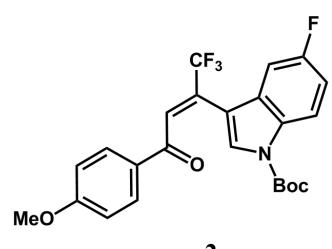
¹⁹F NMR (282 MHz, CDCl₃)





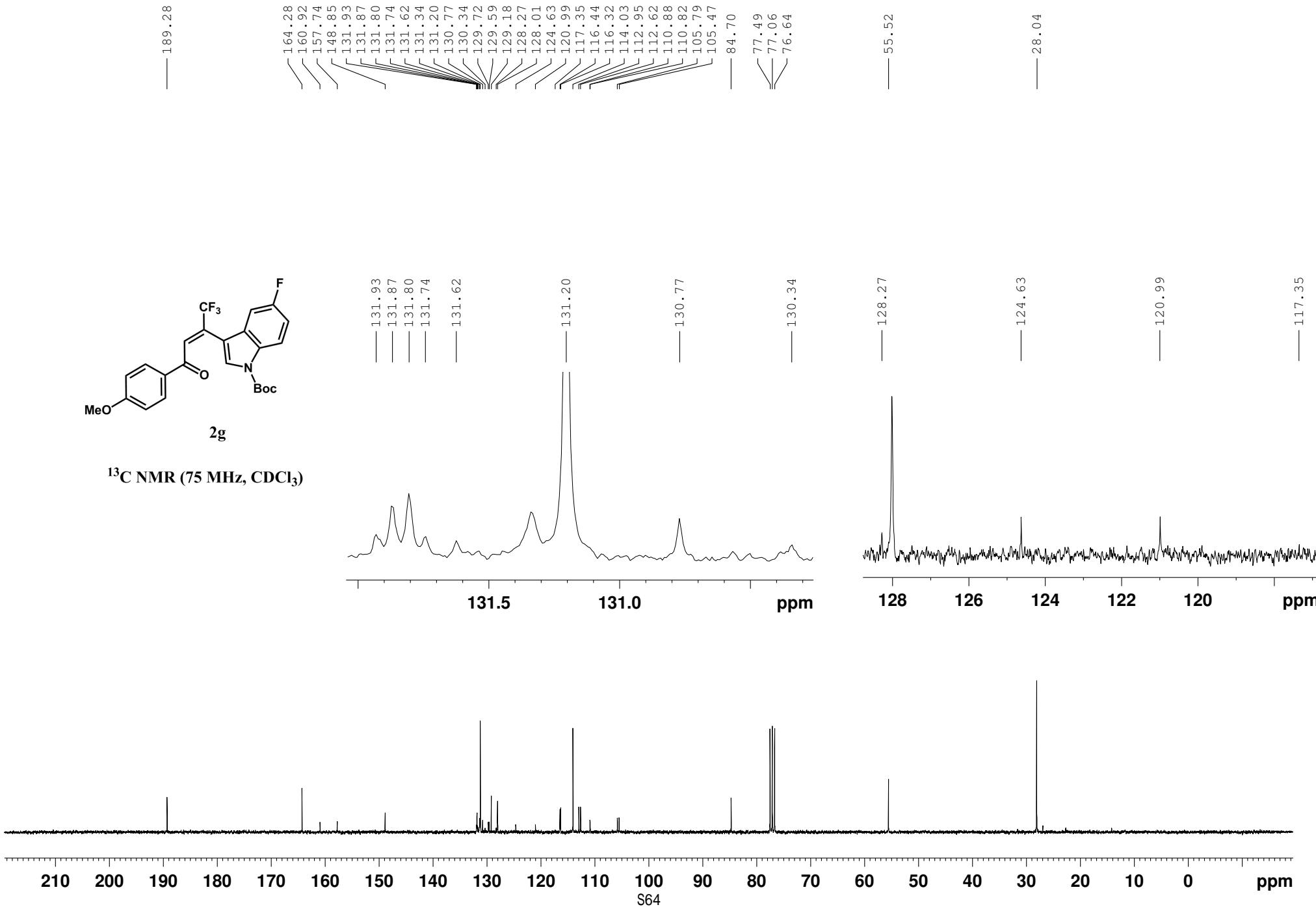
^1H NMR (300 MHz, CDCl_3)

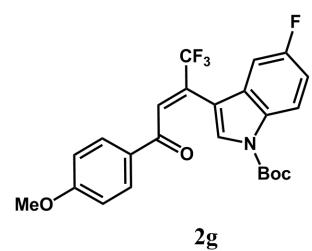




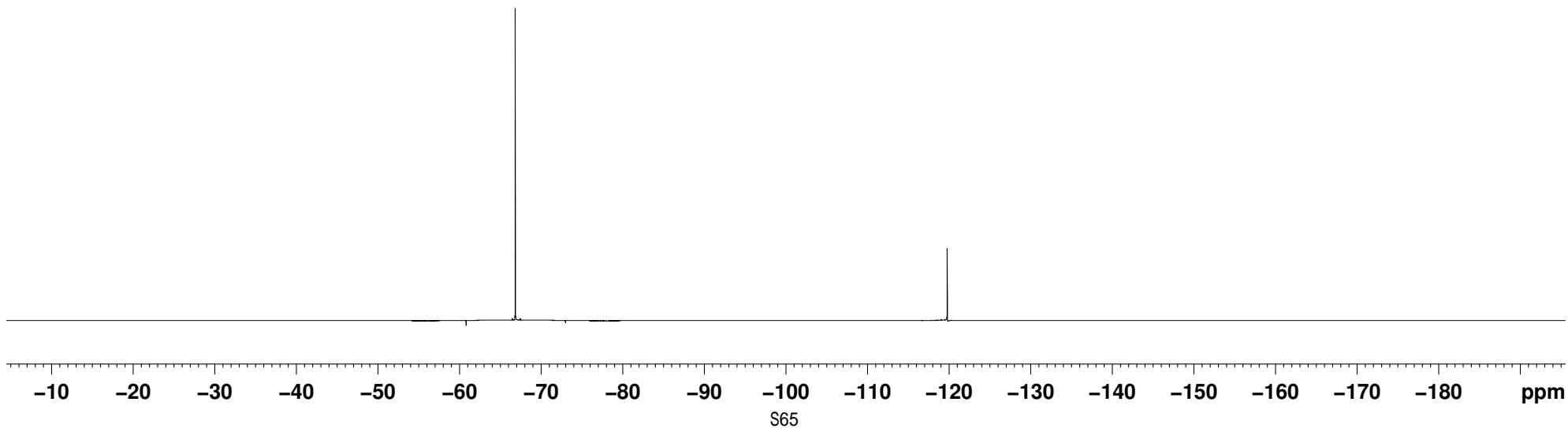
2g

^{13}C NMR (75 MHz, CDCl_3)





^{19}F NMR (282 MHz, CDCl_3)

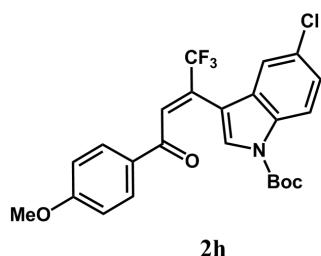


7.882
7.852
7.691
7.661
7.559
7.374
7.370
7.180
7.174
7.068
7.061
7.039
7.032
6.700
6.670

3.601

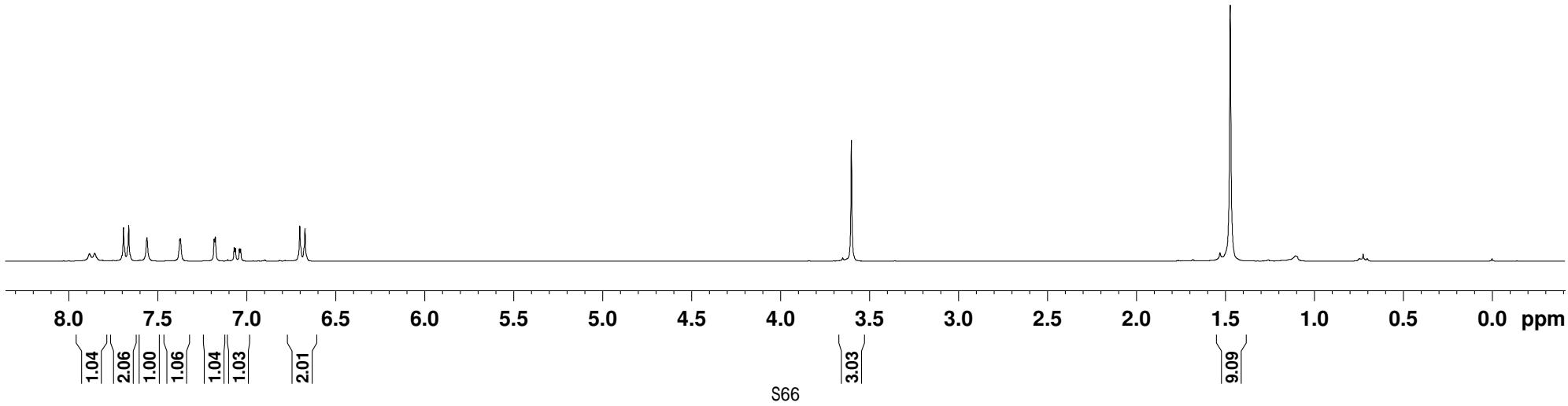
1.471

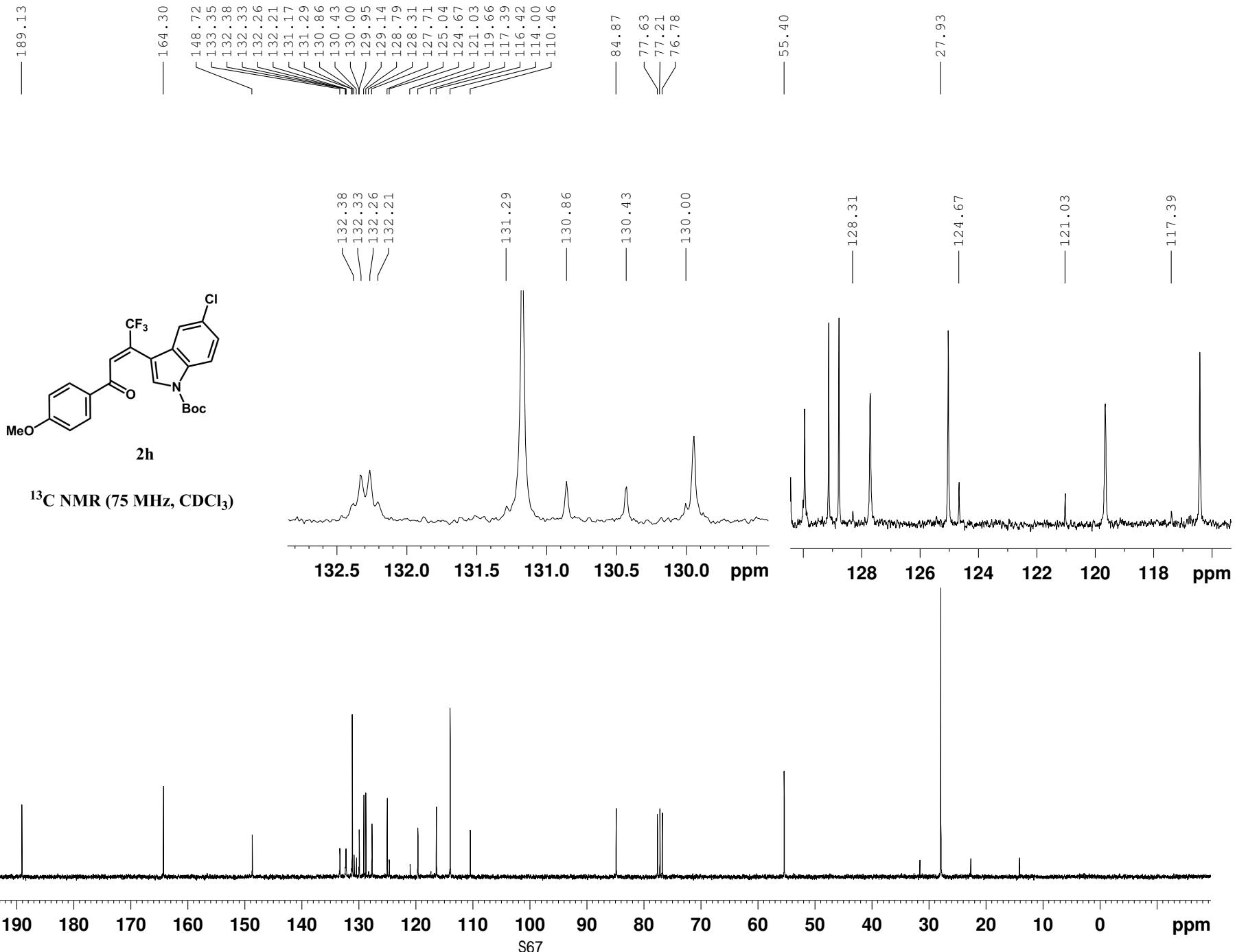
-0.000

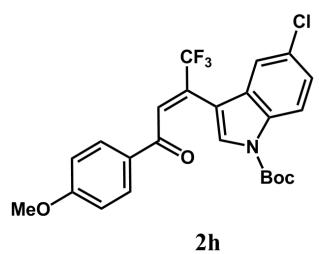


2h

¹H NMR (300 MHz, CDCl₃)

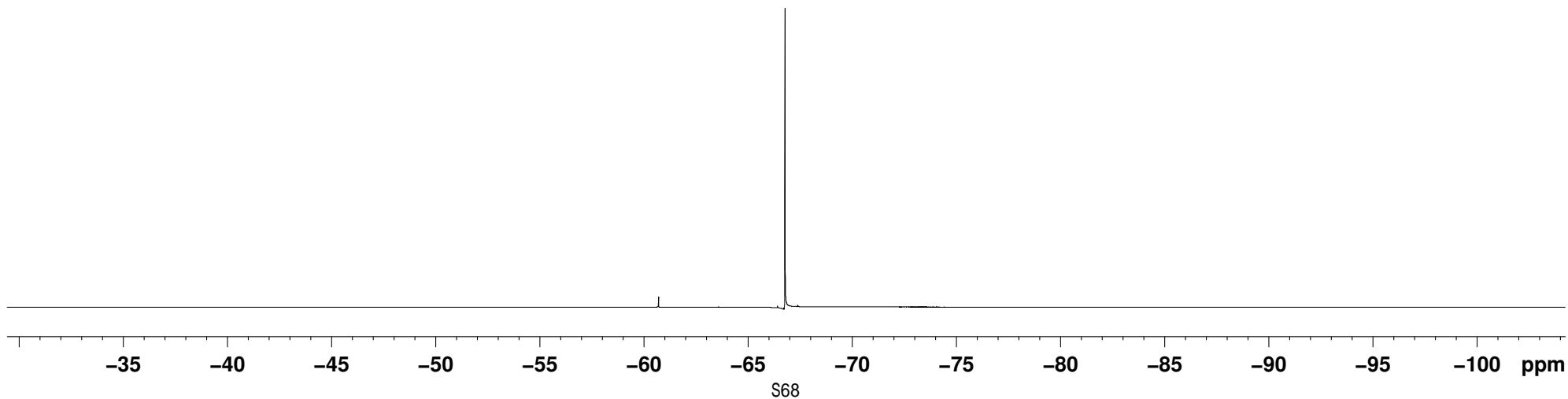






2h

¹⁹F NMR (282 MHz, CDCl₃)

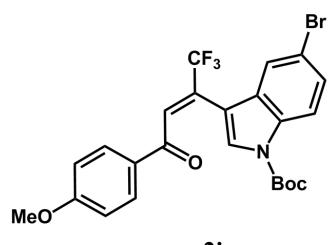


7.981
7.952
7.857
7.828
7.648
7.516
7.512
7.436
7.431
7.372
7.366
7.343
7.337
6.900
6.870

3.829

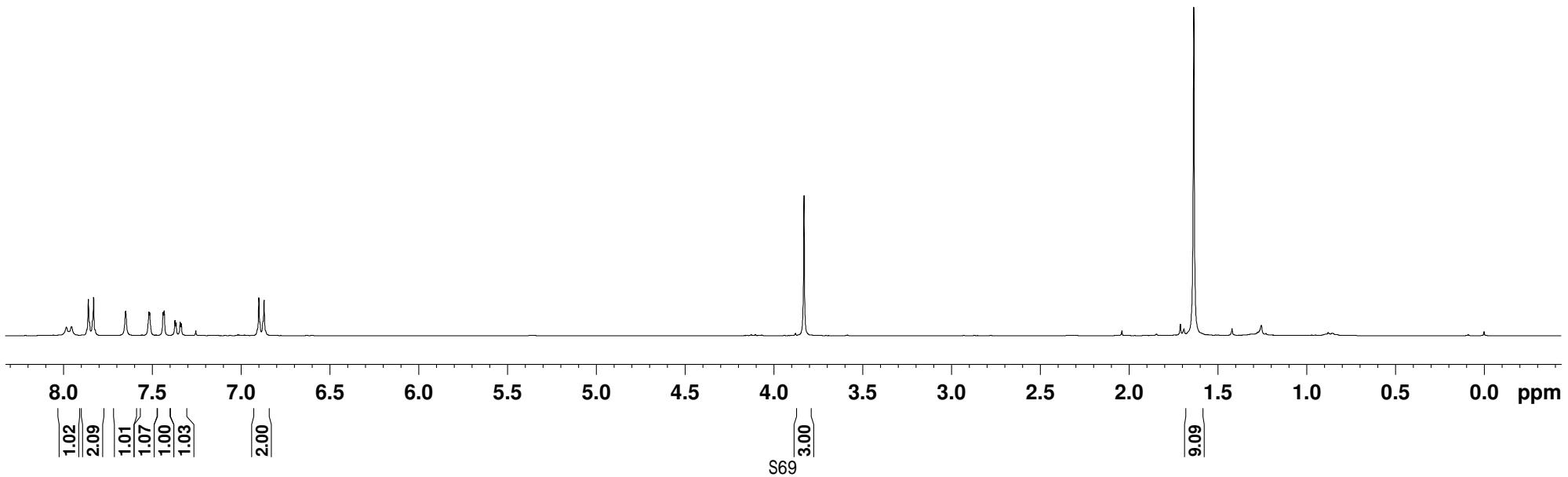
1.635

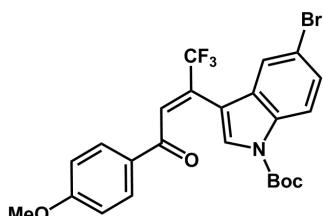
-0.000



2i

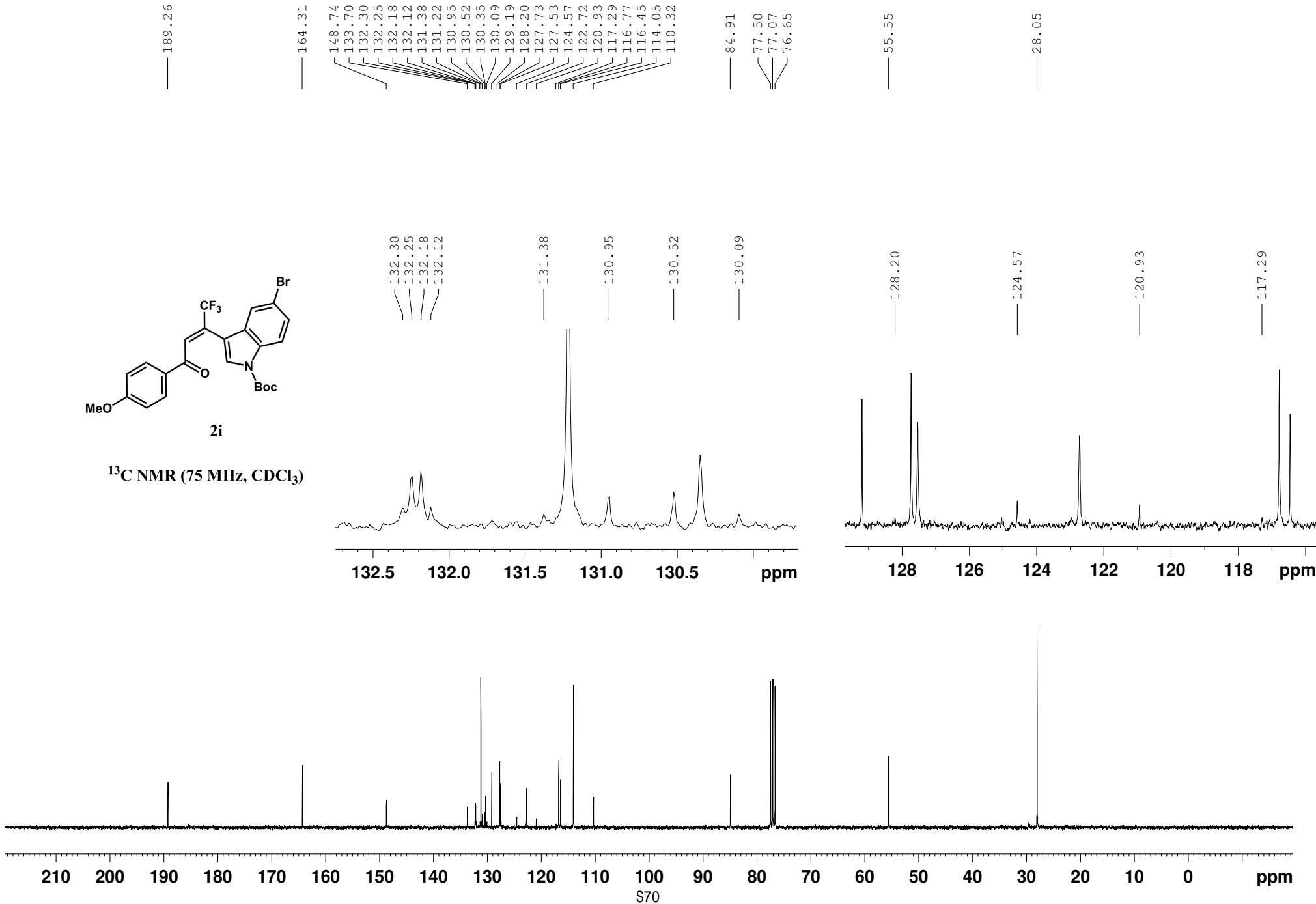
¹H NMR (300 MHz, CDCl₃)

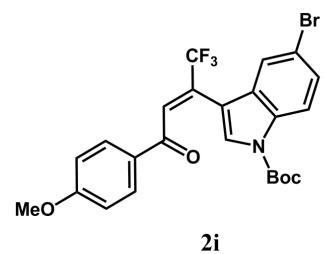




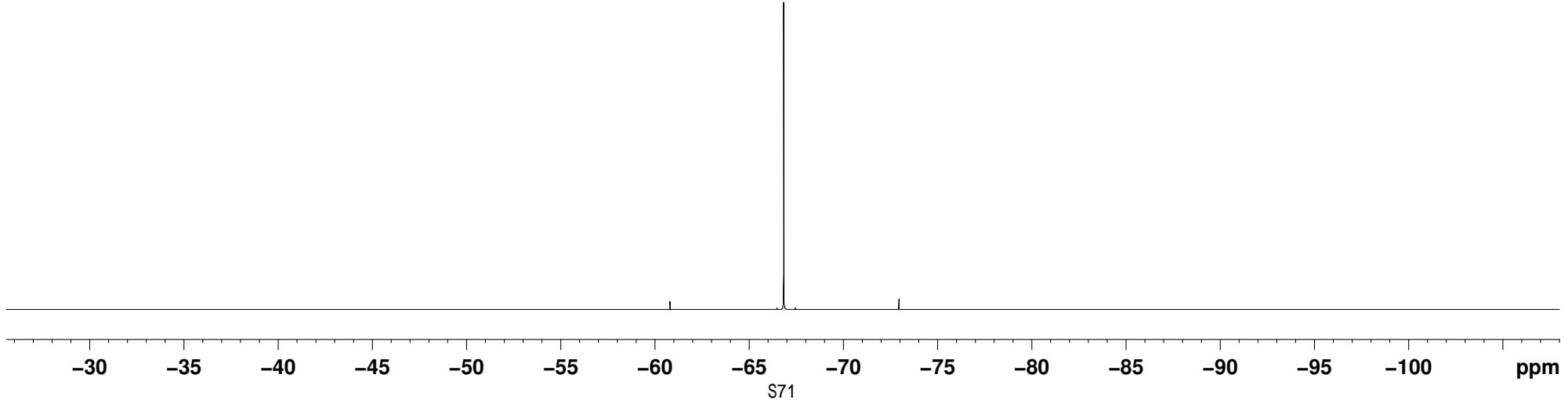
2i

¹³C NMR (75 MHz, CDCl₃)





^{19}F NMR (282 MHz, CDCl_3)



7.953
7.924
7.853
7.823
7.633
7.458
7.454

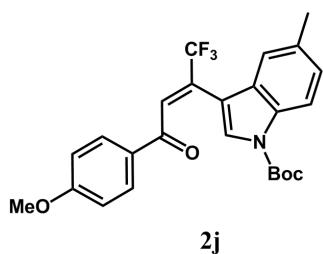
7.079
7.071
7.056
6.861
6.832

3.788

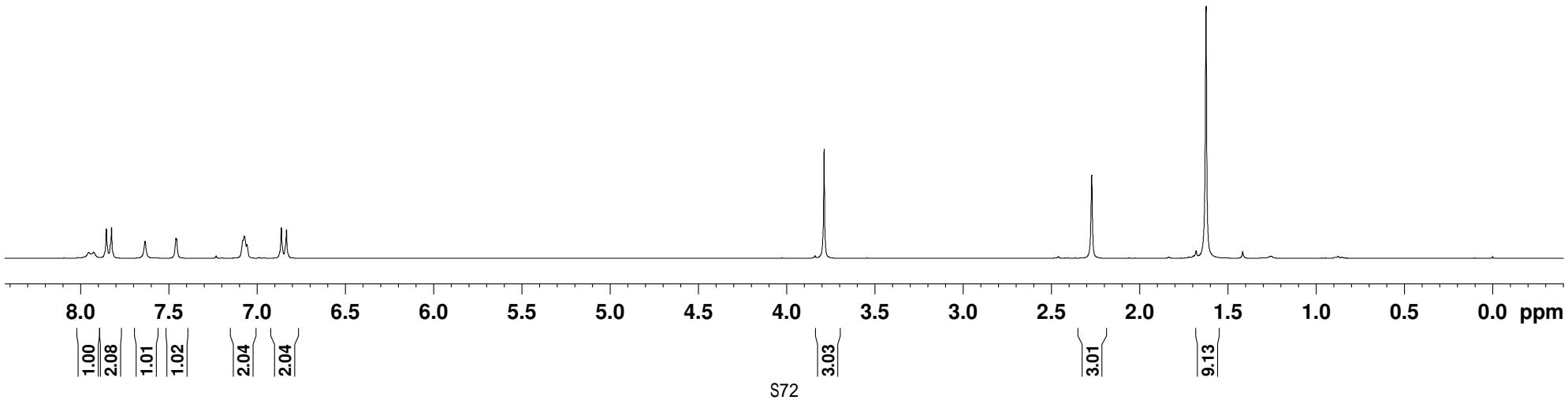
2.271

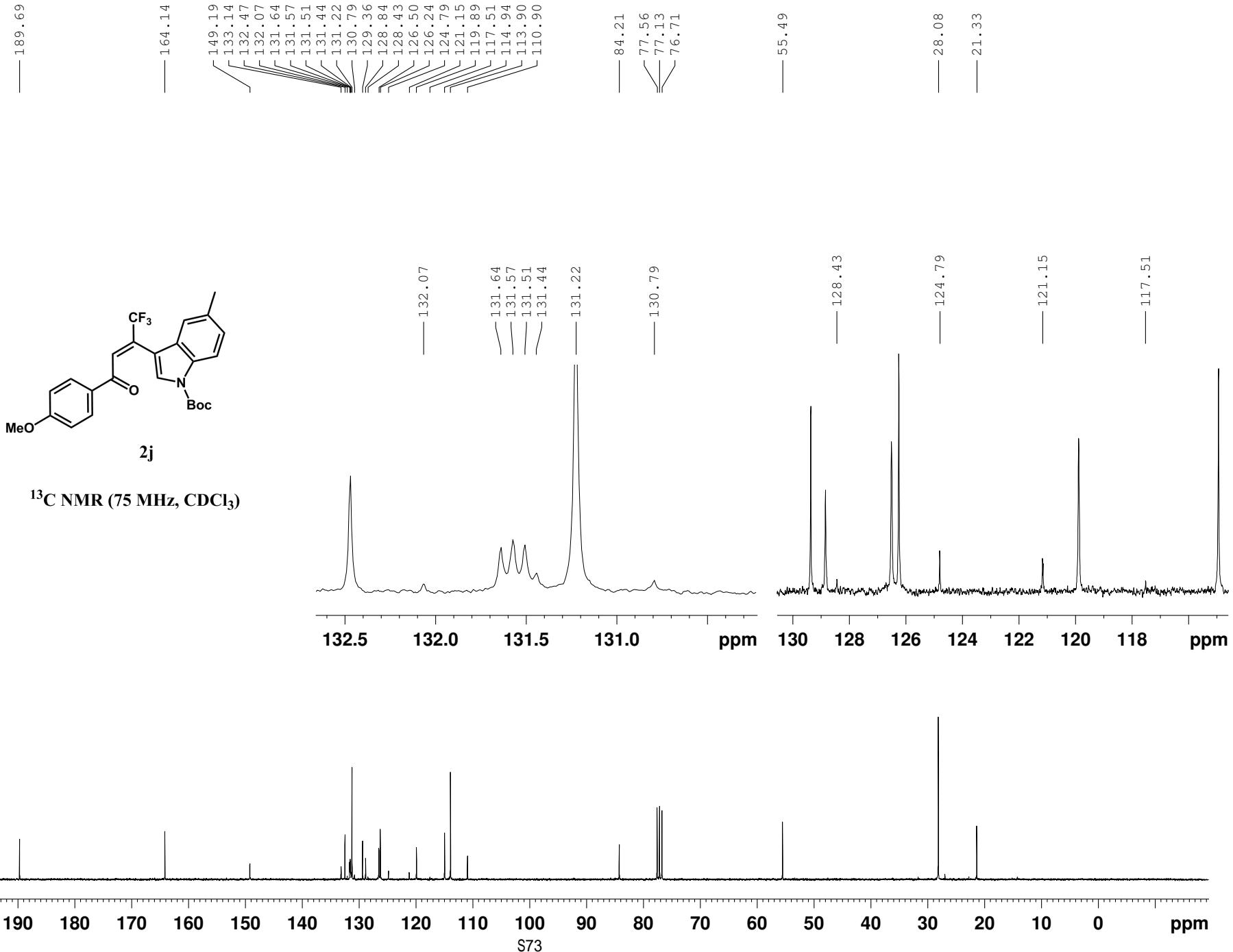
1.624

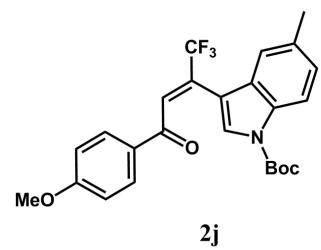
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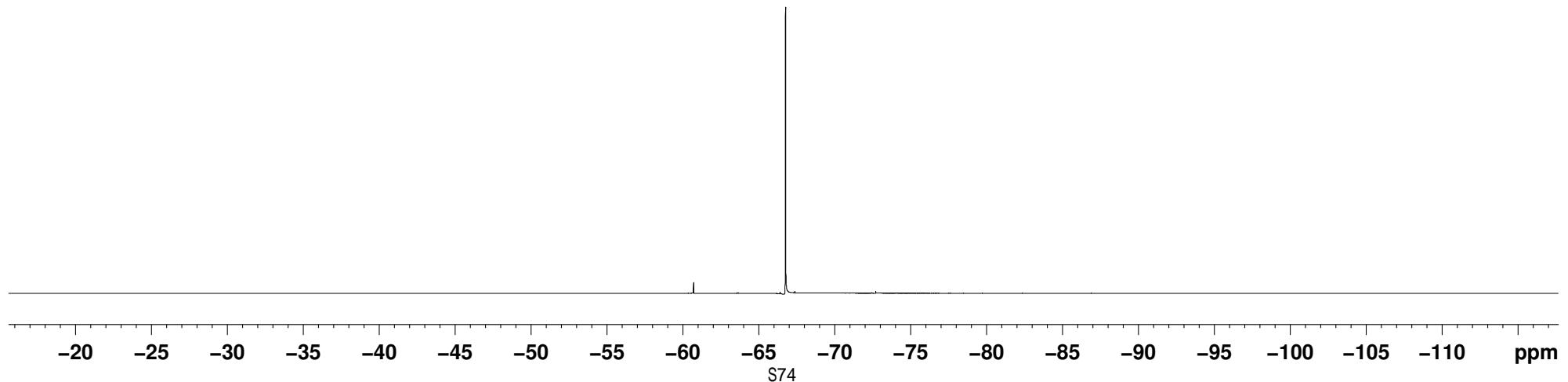
¹H NMR (300 MHz, CDCl₃)

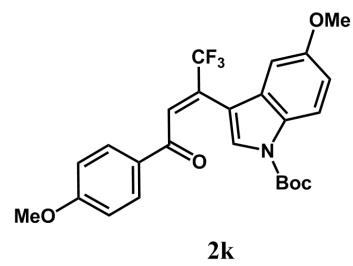




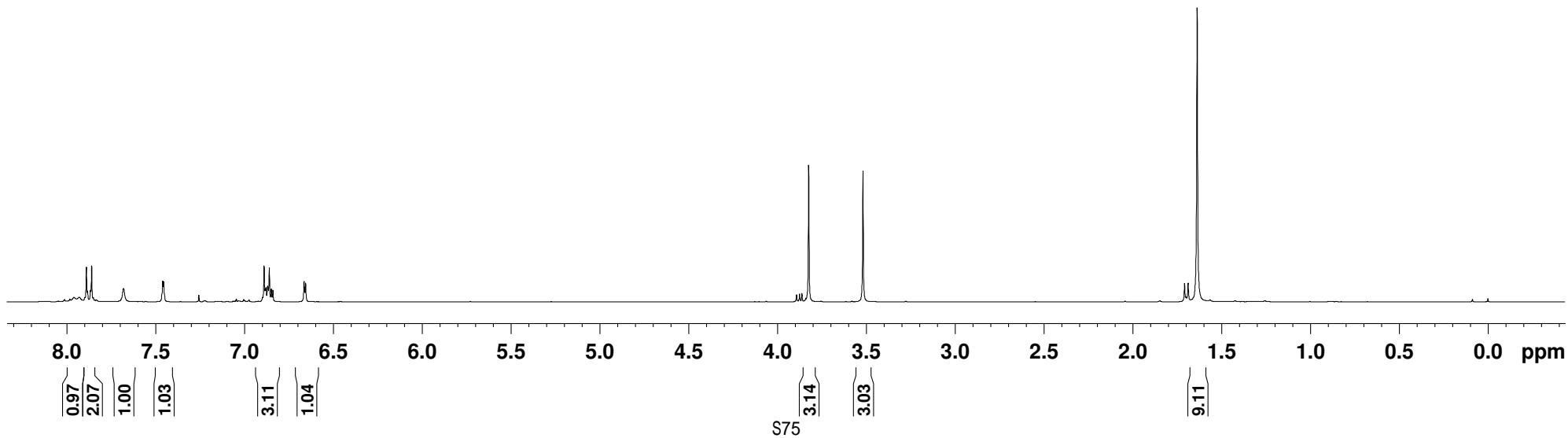


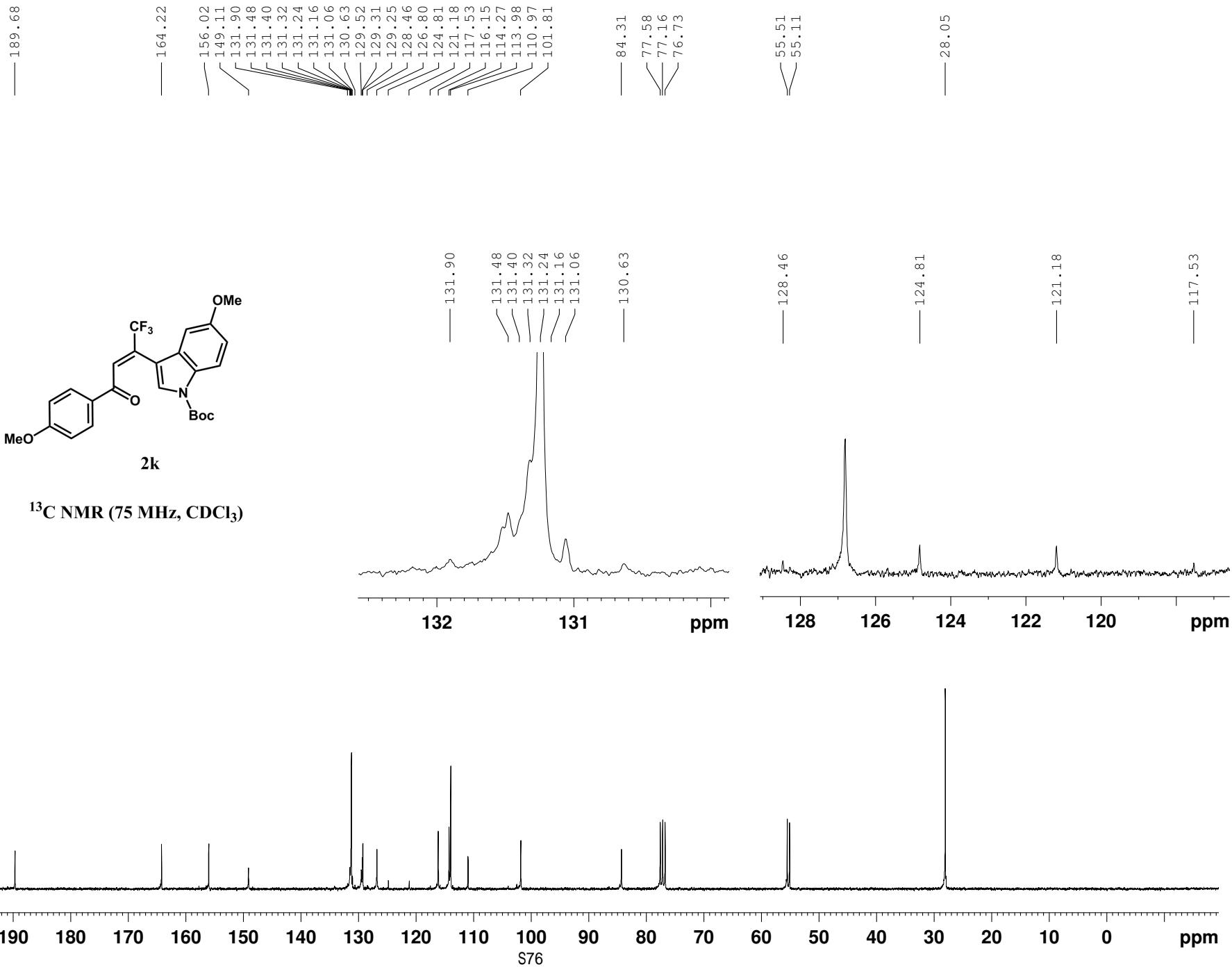
^{19}F NMR (282 MHz, CDCl_3)

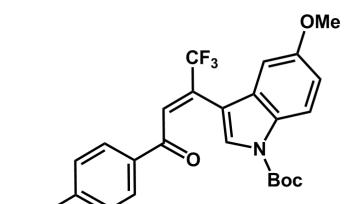




^1H NMR (300 MHz, CDCl_3)

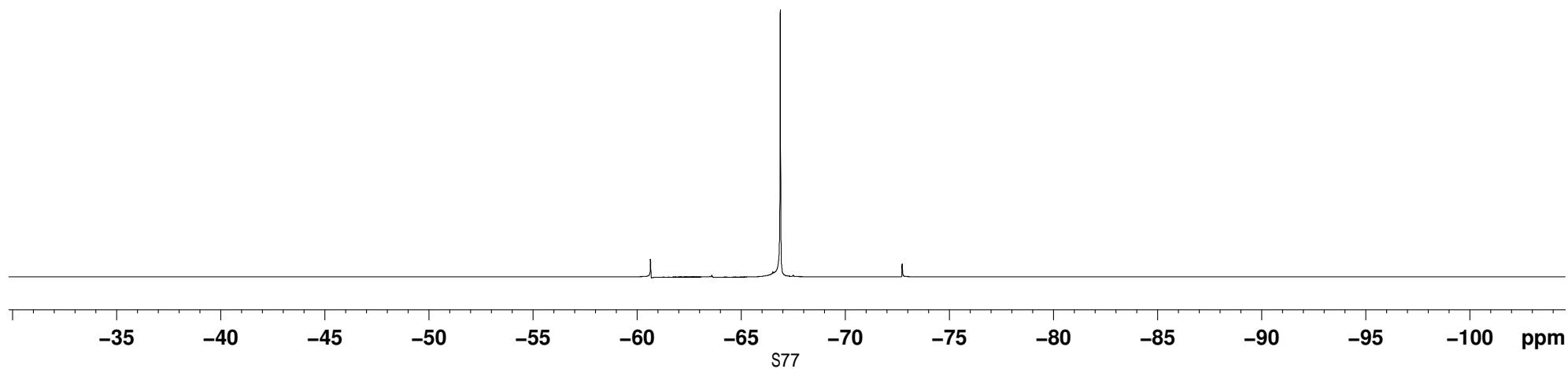






2k

^{19}F NMR (282 MHz, CDCl_3)



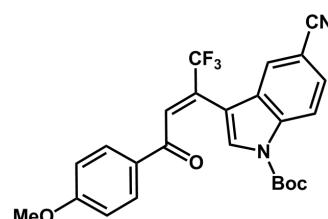
8.104
 8.076
 7.732
 7.704
 7.654
 7.547
 7.488
 7.399
 7.371

6.784
 6.756

3.694

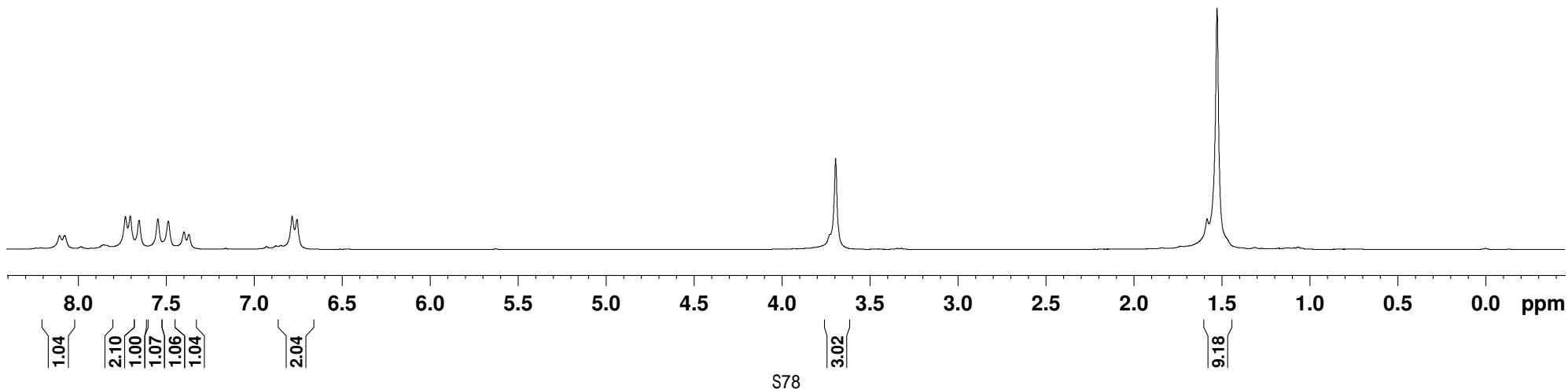
1.526

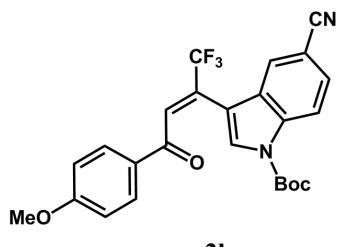
-0.000



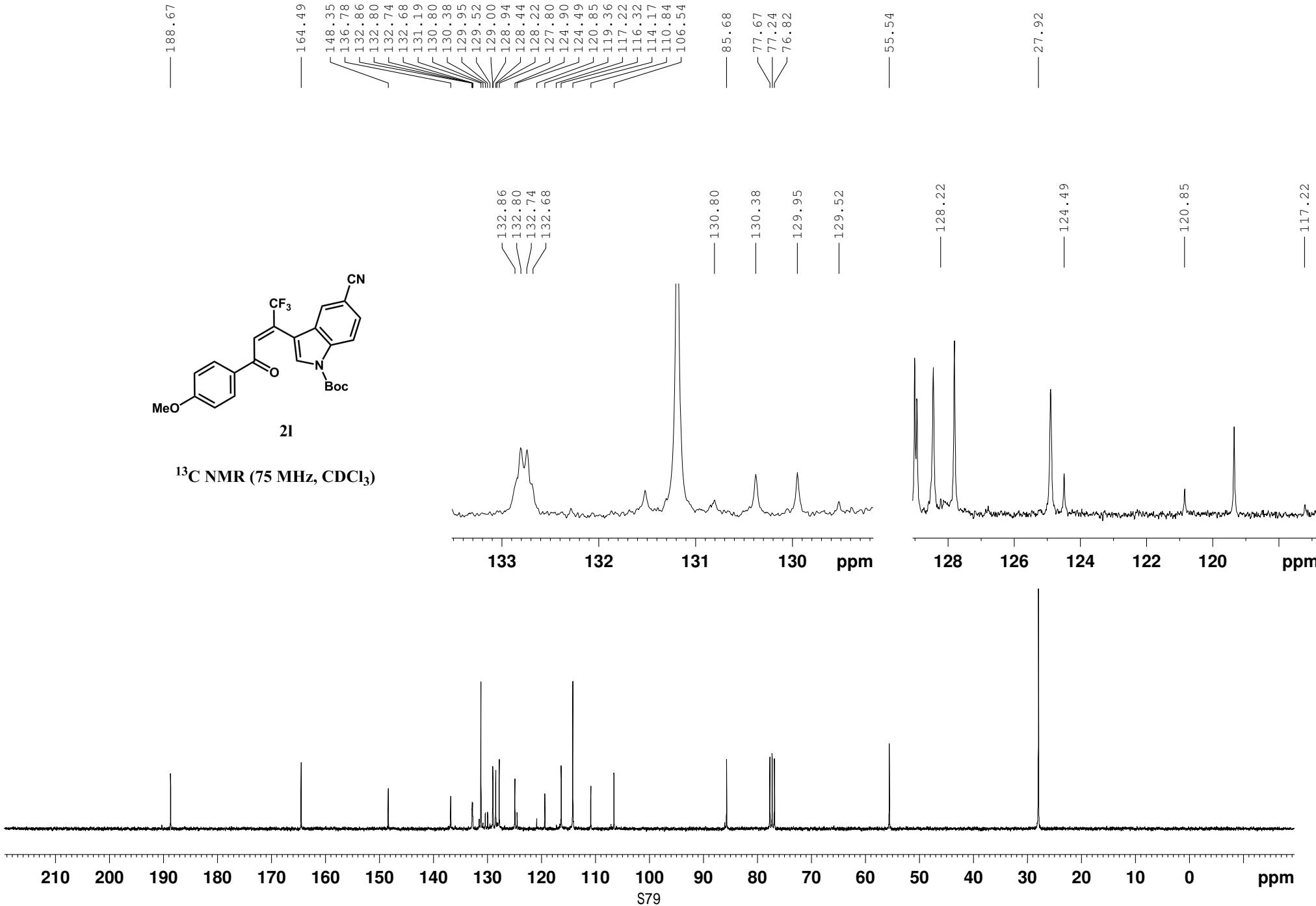
2l

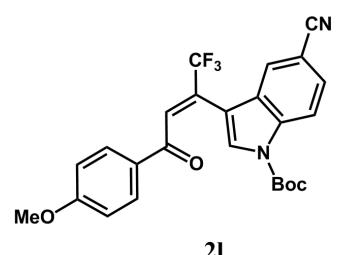
¹H NMR (300 MHz, CDCl₃)



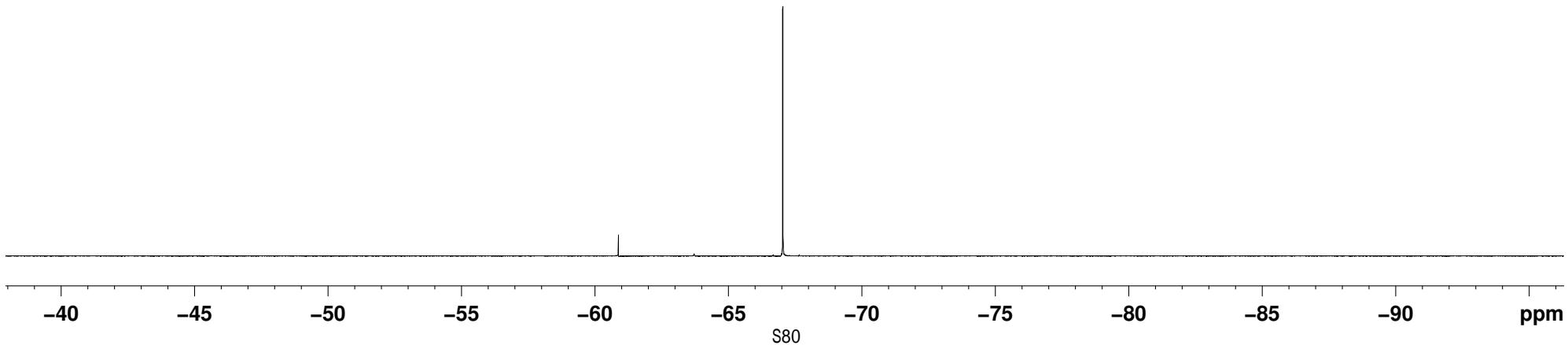


¹³C NMR (75 MHz, CDCl₃)





^{19}F NMR (282 MHz, CDCl_3)

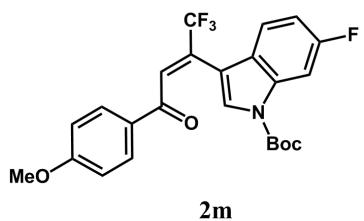


7.732
7.703
7.537
7.366
7.161
7.143
7.133
7.115
6.822
6.794
6.759
6.730

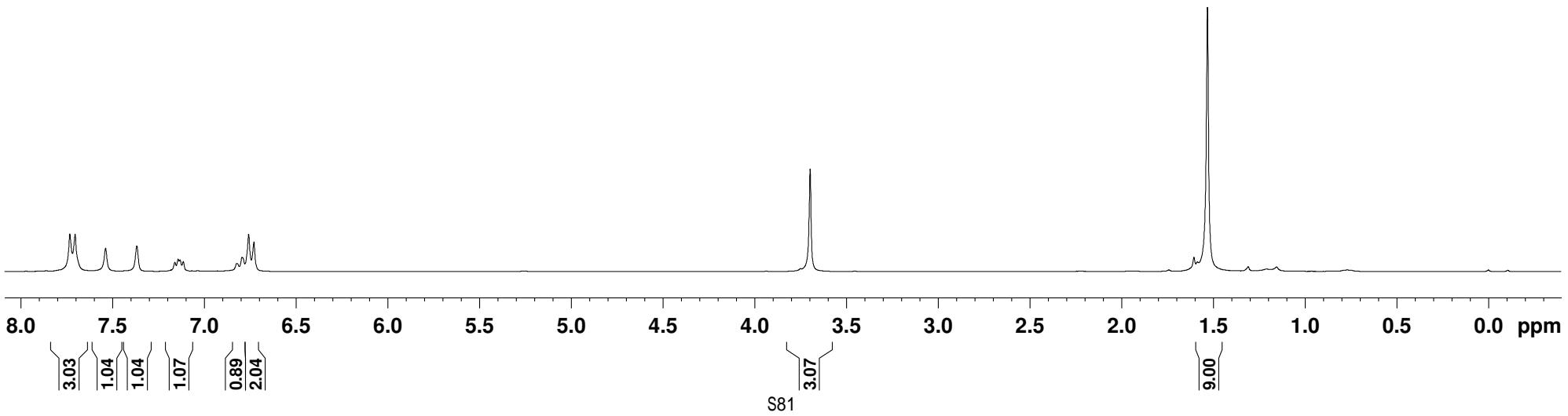
3.698

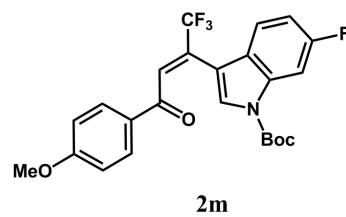
1.531

-0.000

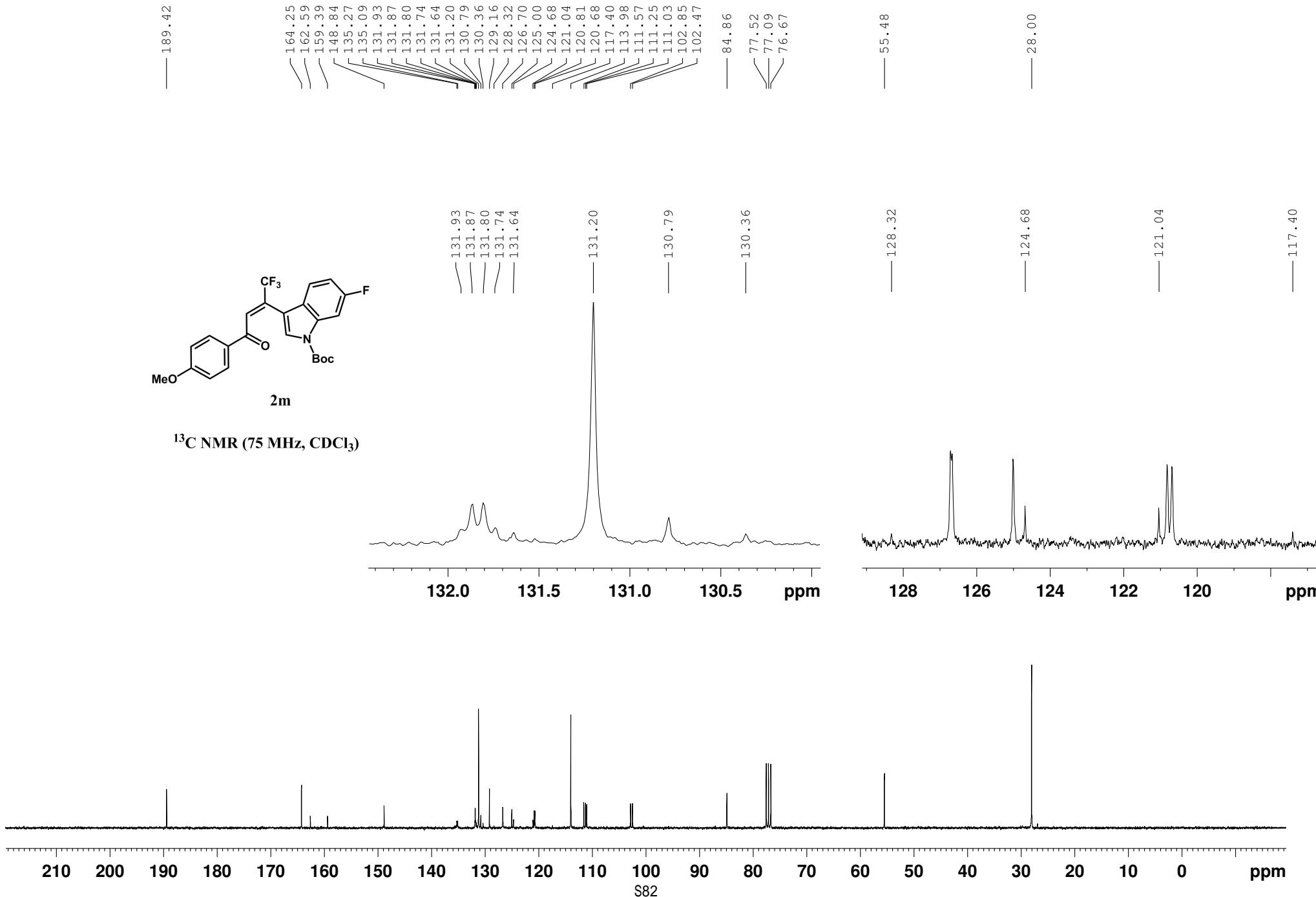


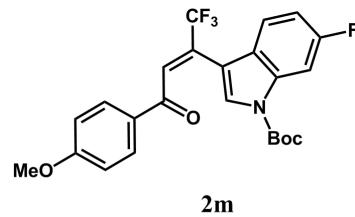
¹H NMR (300 MHz, CDCl₃)



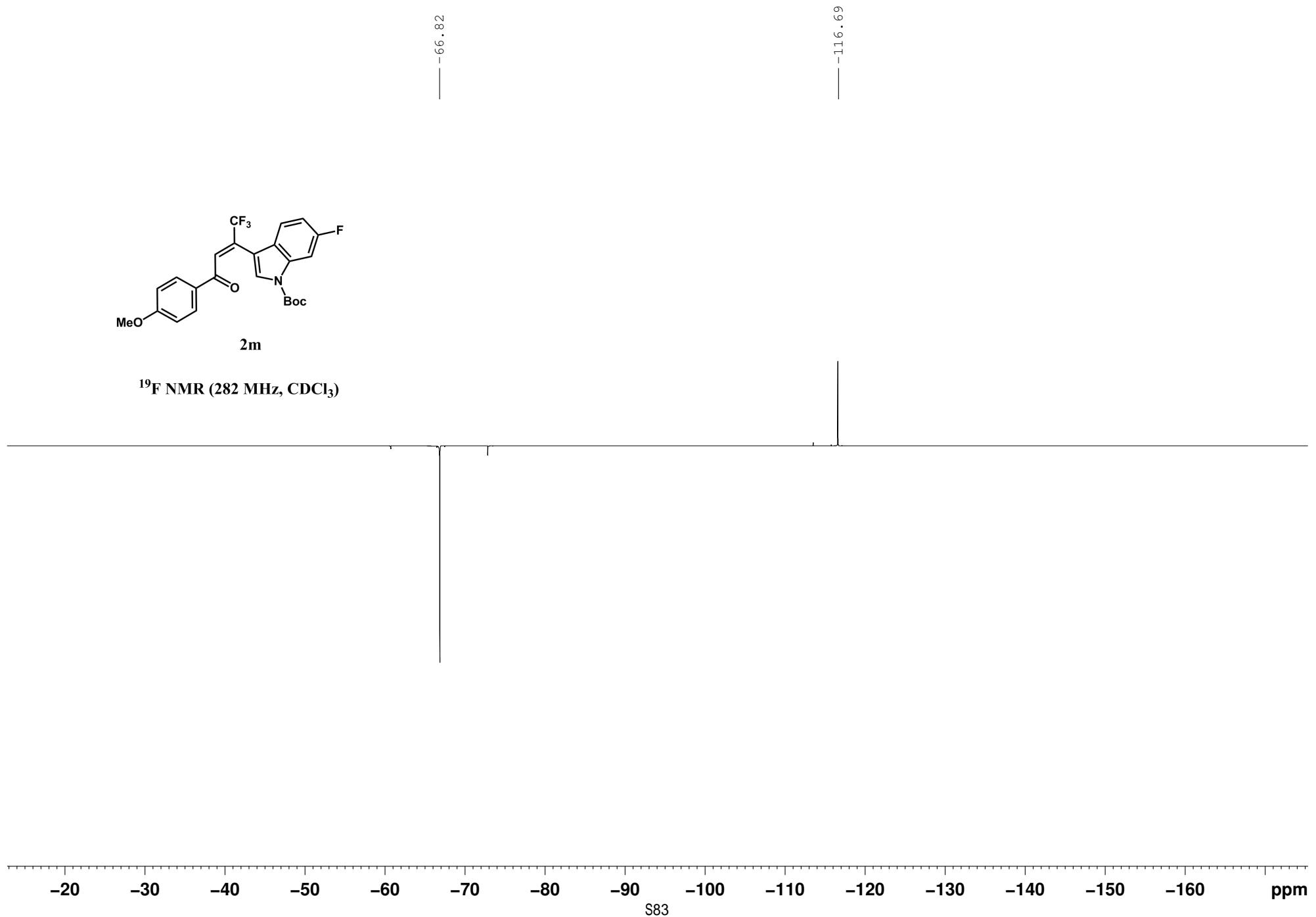


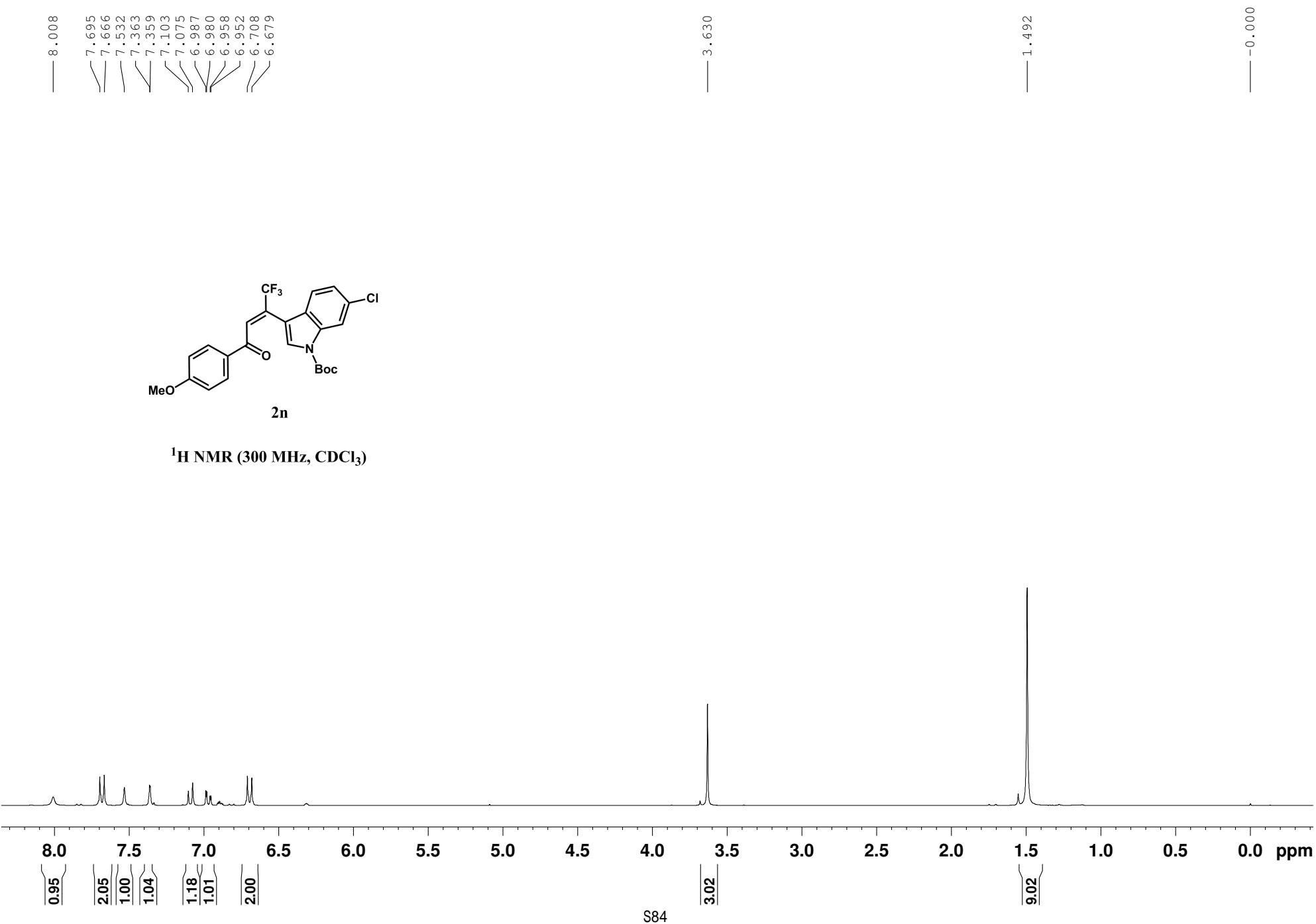
¹³C NMR (75 MHz, CDCl₃)

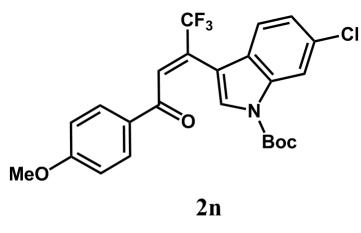




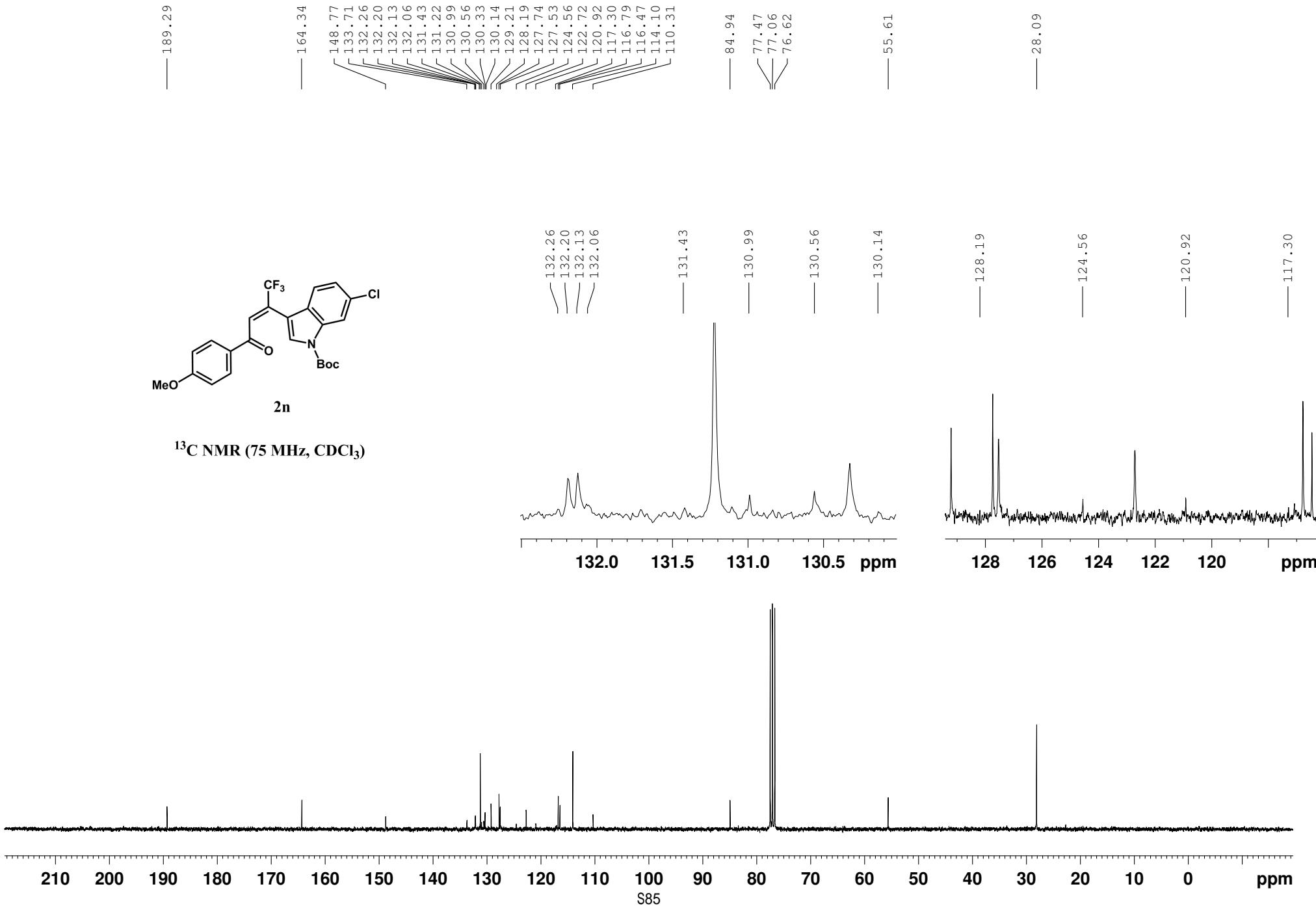
^{19}F NMR (282 MHz, CDCl_3)

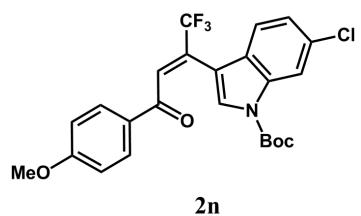




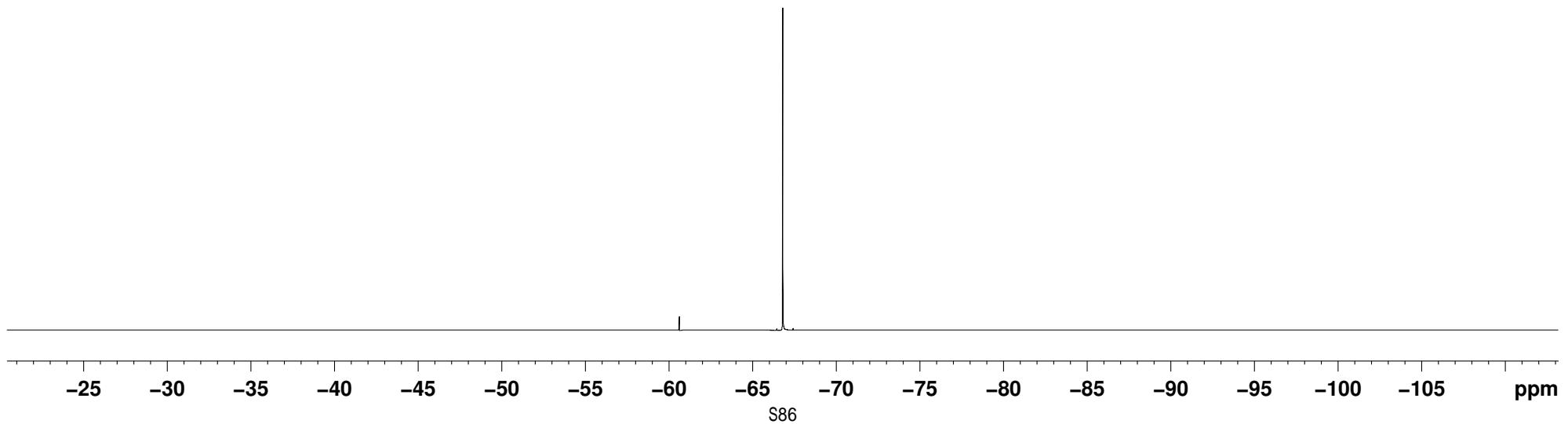


¹³C NMR (75 MHz, CDCl₃)





¹⁹F NMR (282 MHz, CDCl₃)

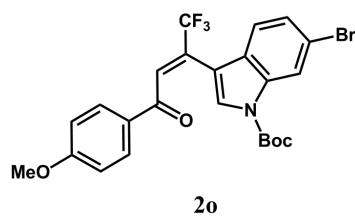


7.982
7.953
7.864
7.834
7.640
7.516
7.511
7.428
7.423
7.378
7.372
7.349
7.343
6.913
6.883

3.851

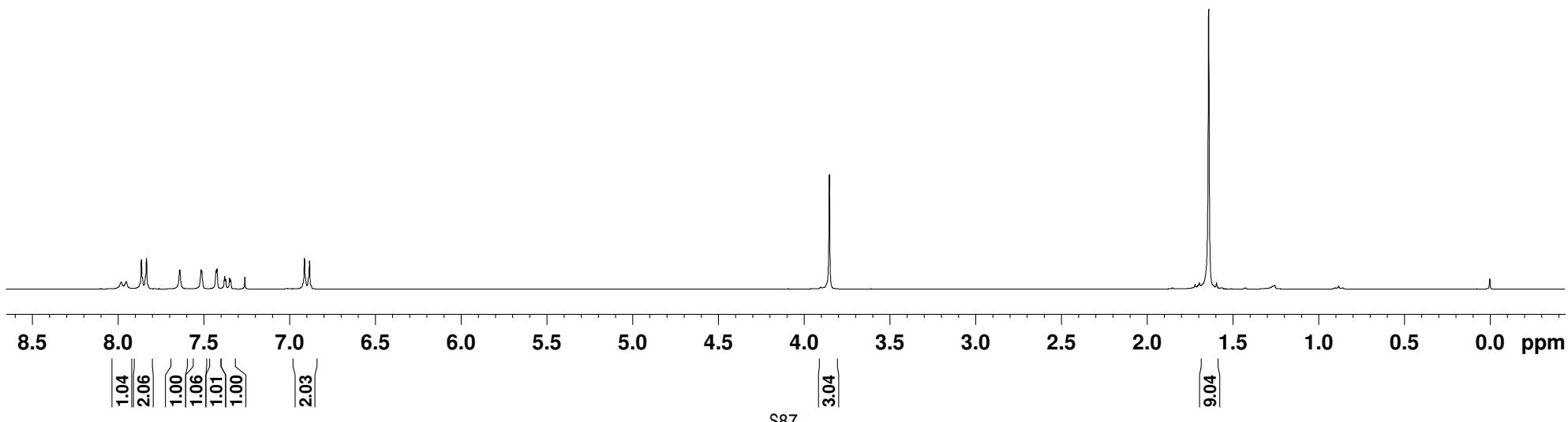
1.639

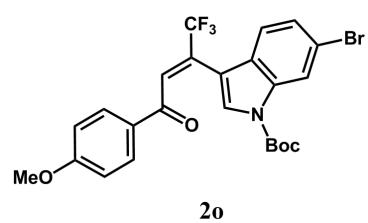
-0.000



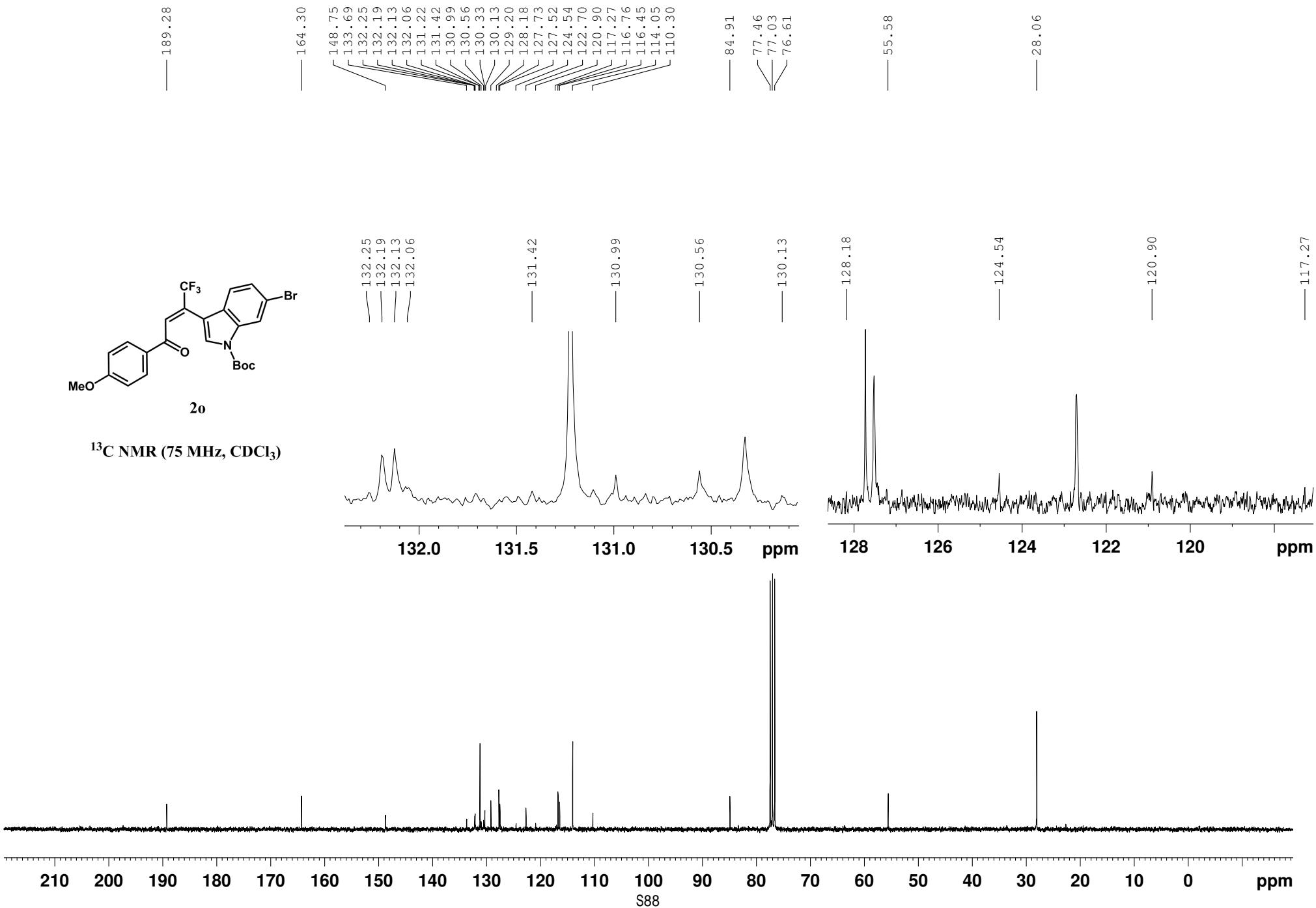
2o

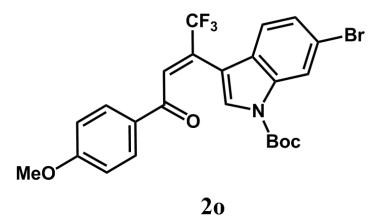
^1H NMR (300 MHz, CDCl_3)





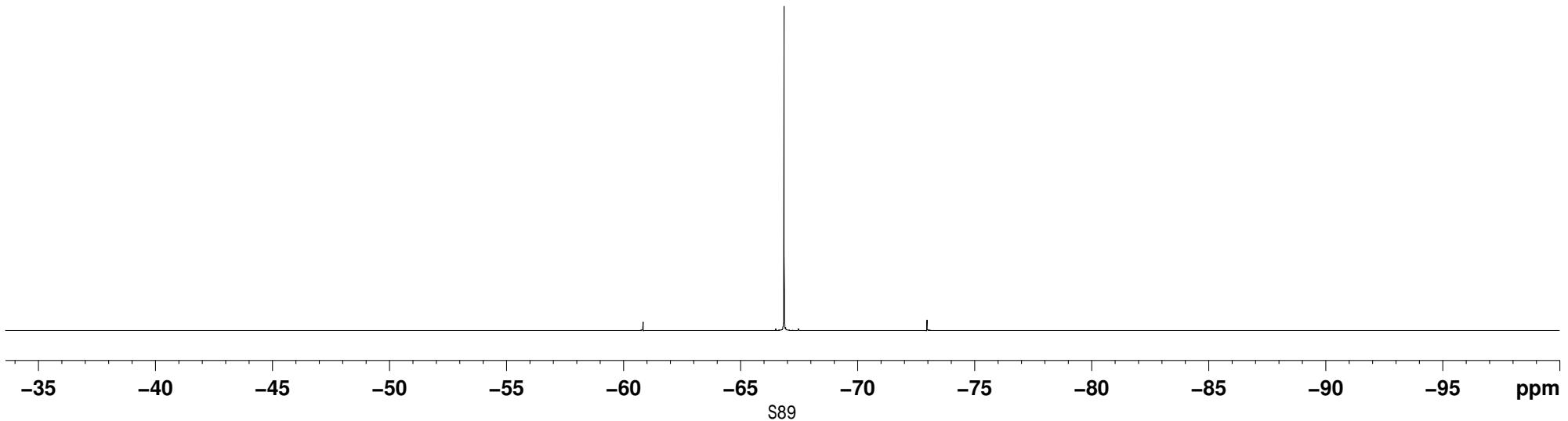
¹³C NMR (75 MHz, CDCl₃)





2o

¹⁹F NMR (282 MHz, CDCl₃)



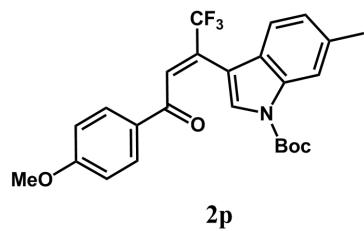
7.842
7.740
7.711
7.488
7.326
7.322
7.097
7.070
6.878
6.875
6.850
6.846
6.743
6.713

3.677

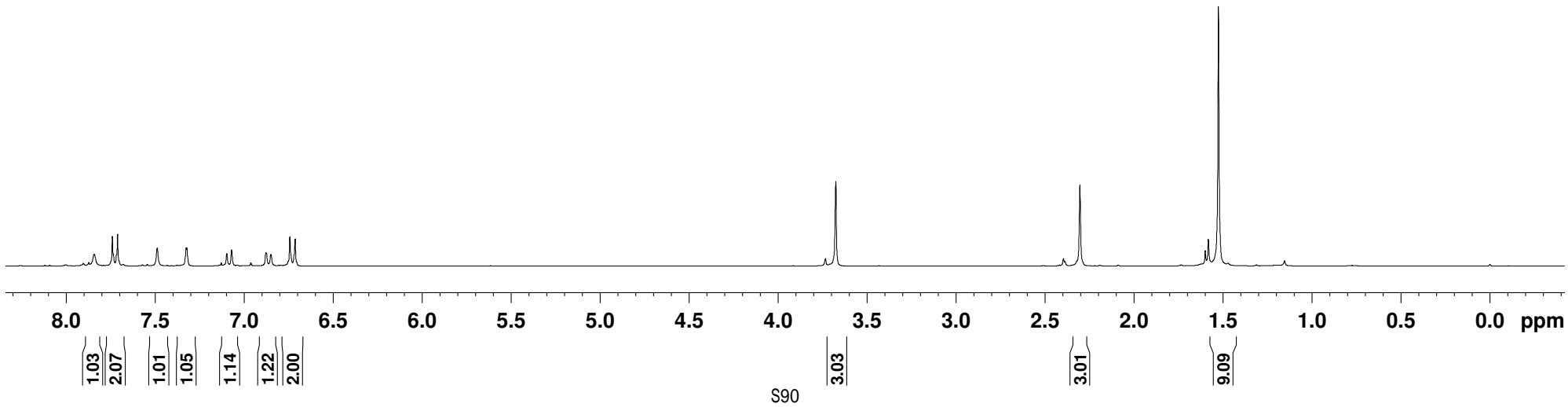
2.305

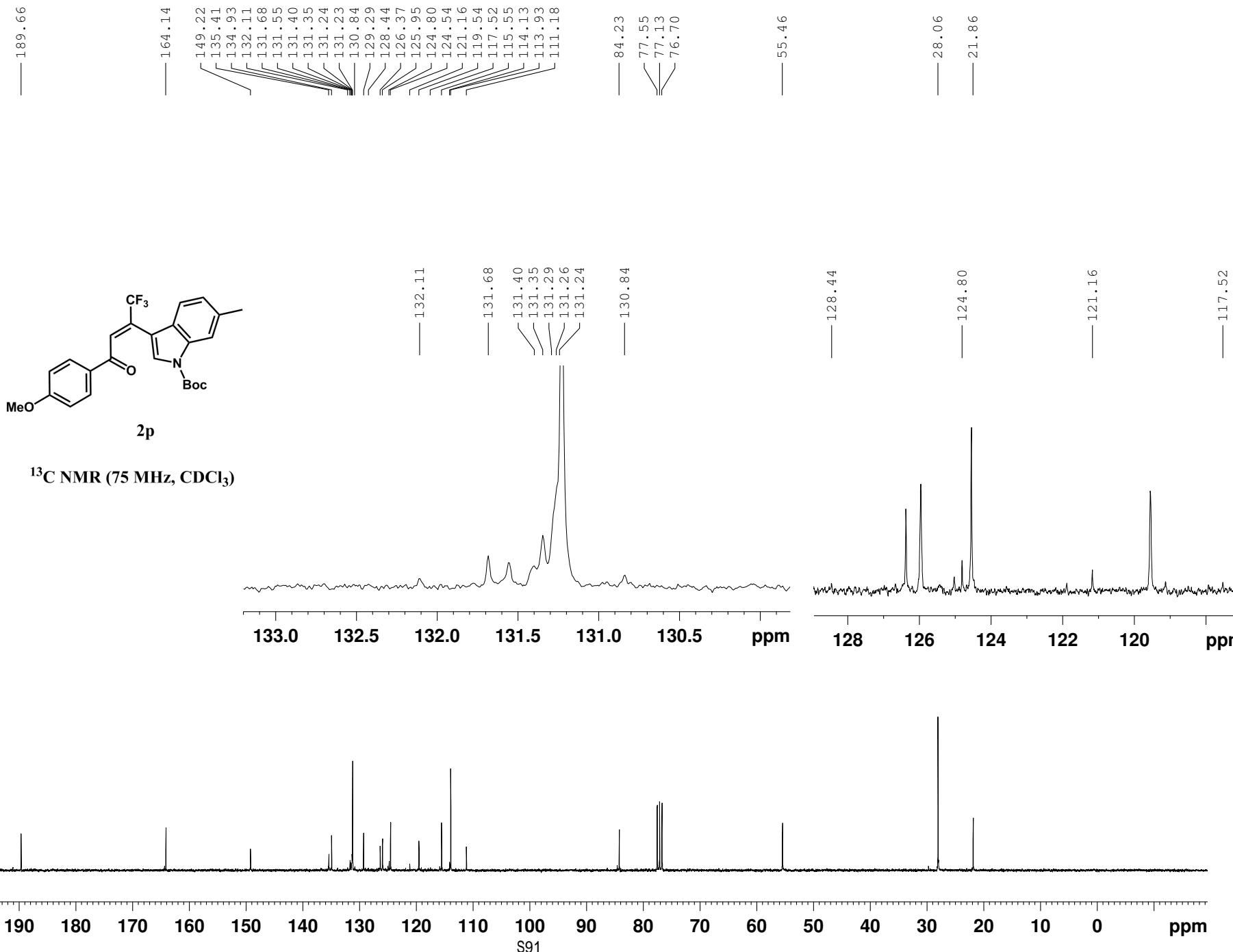
1.527

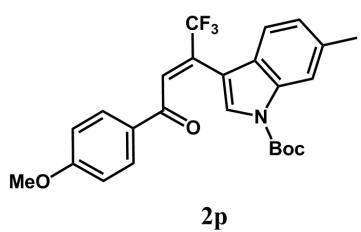
0.000



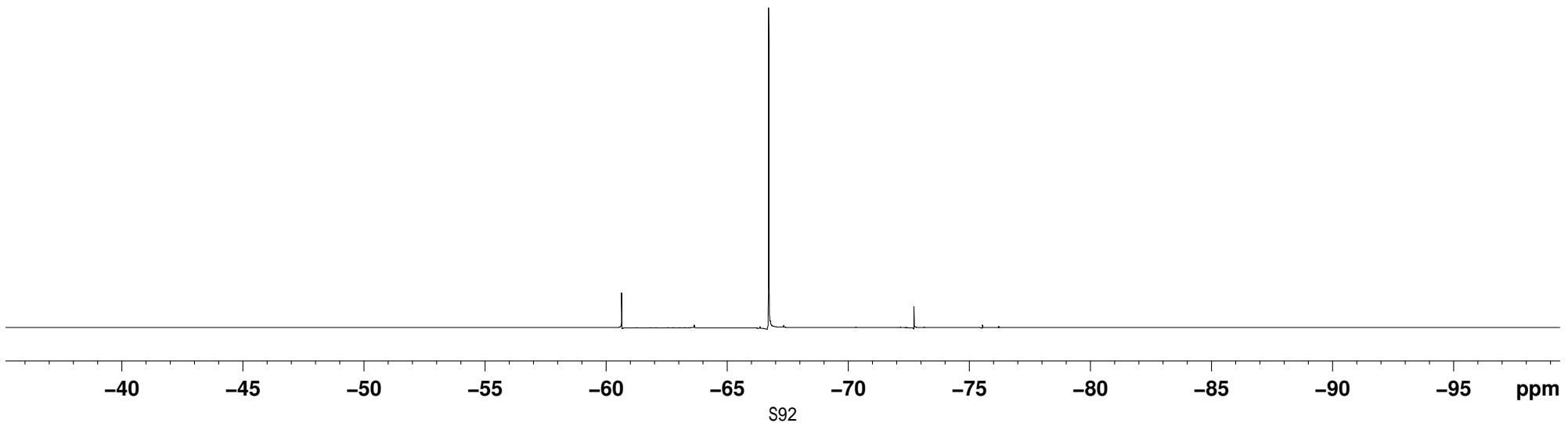
¹H NMR (300 MHz, CDCl₃)







^{19}F NMR (282 MHz, CDCl_3)

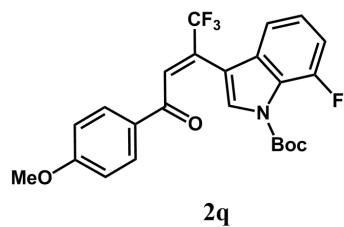


7.822
7.792
7.729
7.507
7.503
7.120
7.094
7.081
7.069
7.056
7.042
7.029
6.999
6.995
6.972
6.956
6.931
6.839
6.811

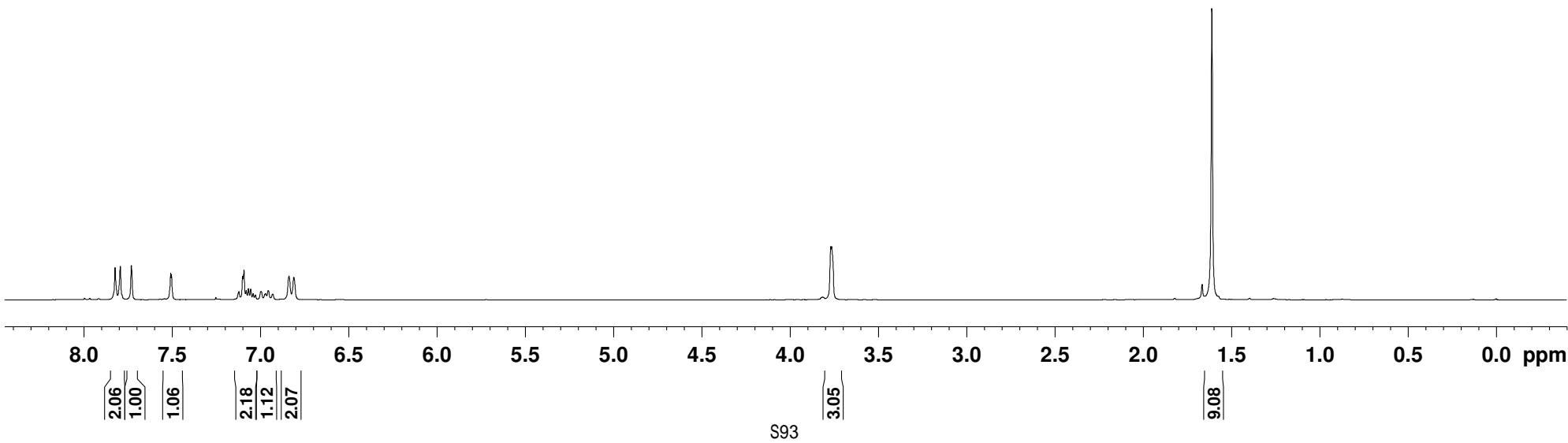
3.769

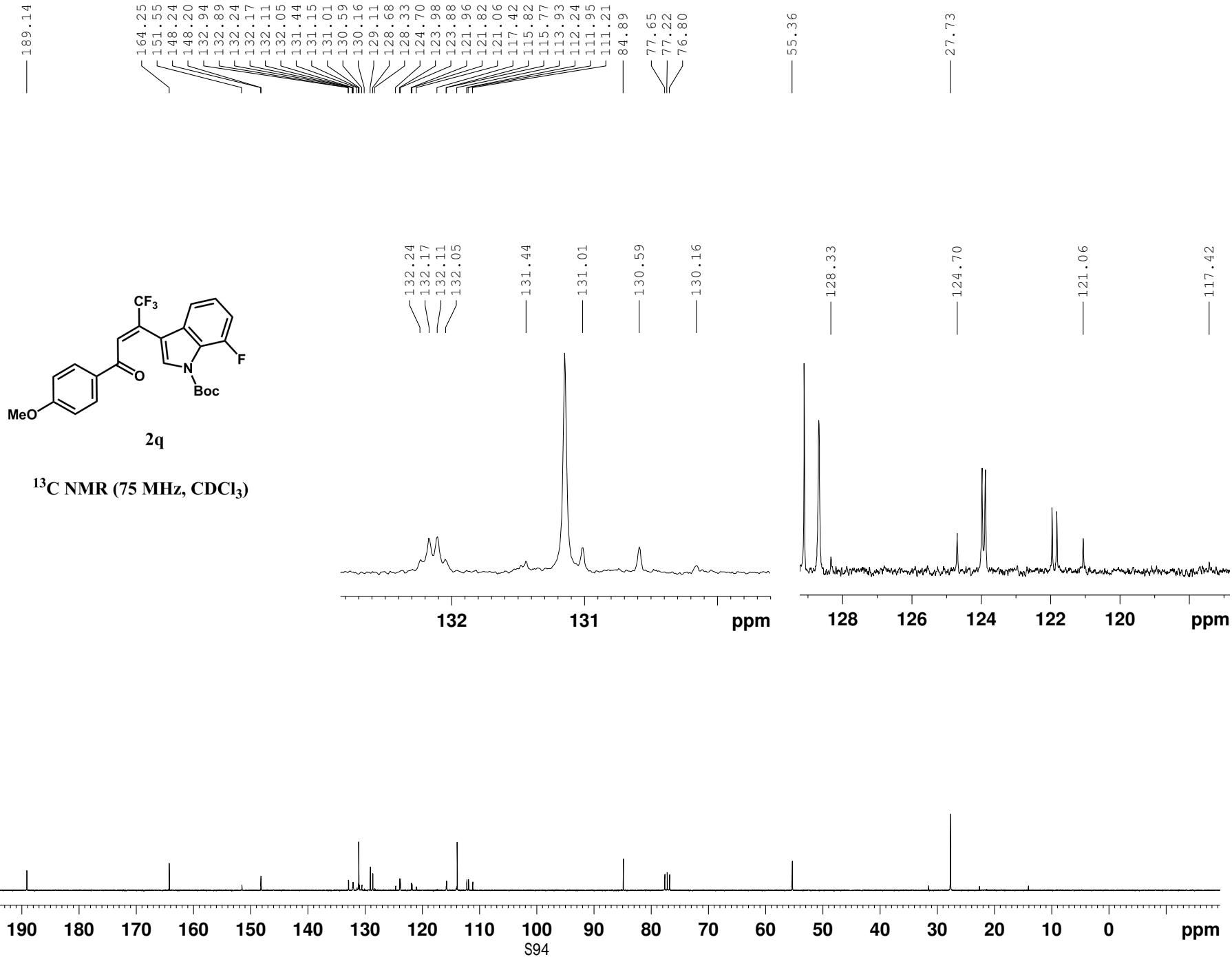
-1.610

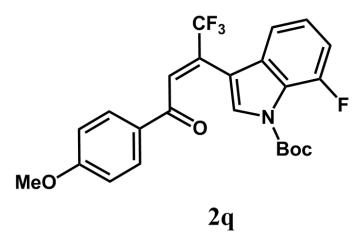
-0.000



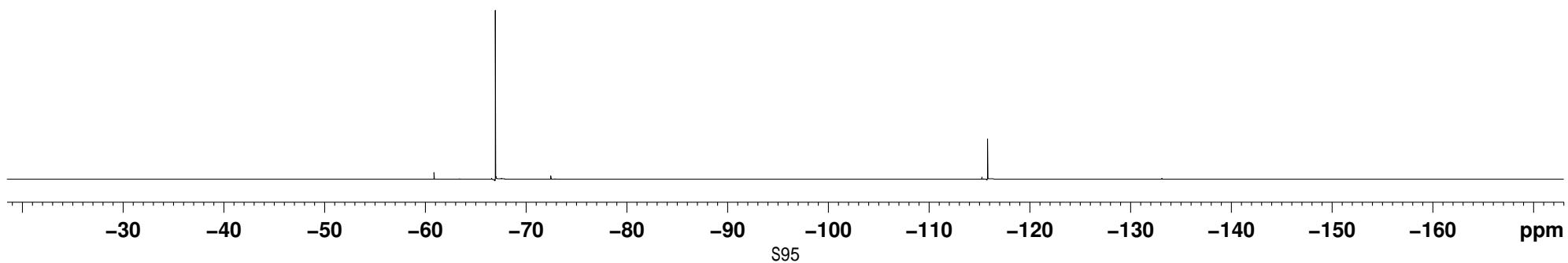
¹H NMR (300 MHz, CDCl₃)

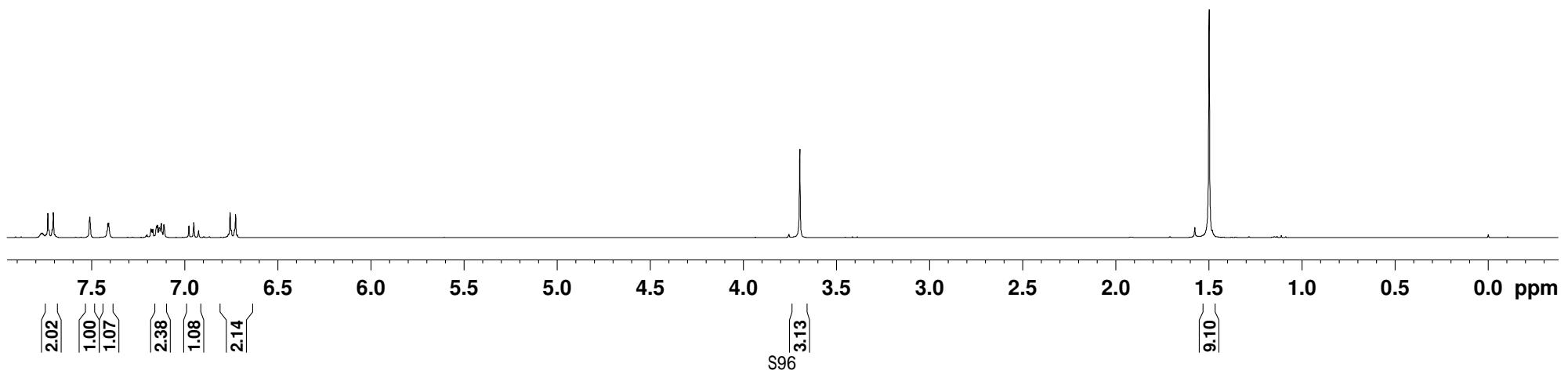
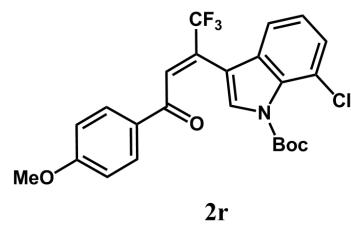


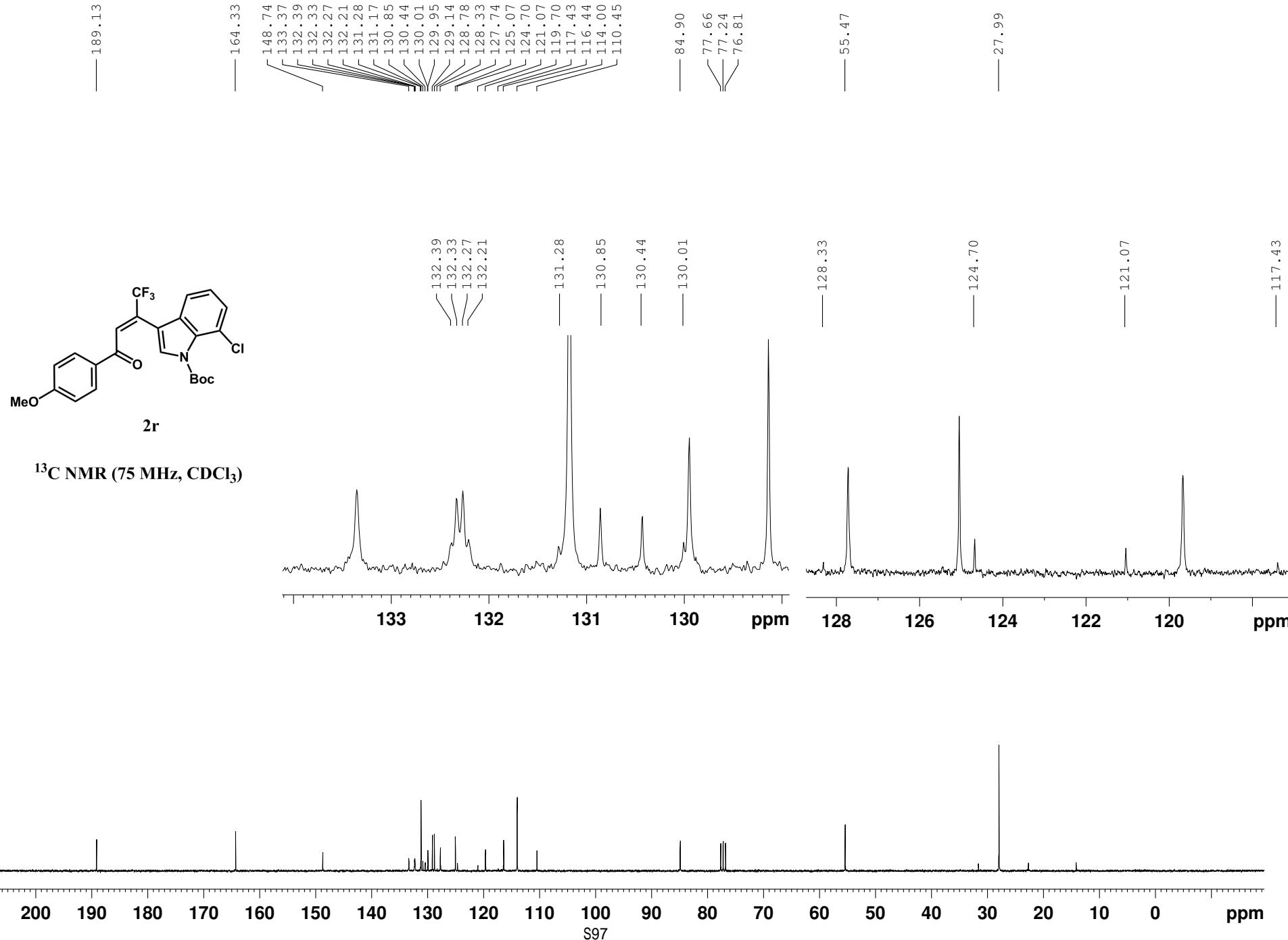


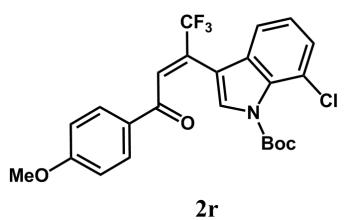


^{19}F NMR (282 MHz, CDCl_3)



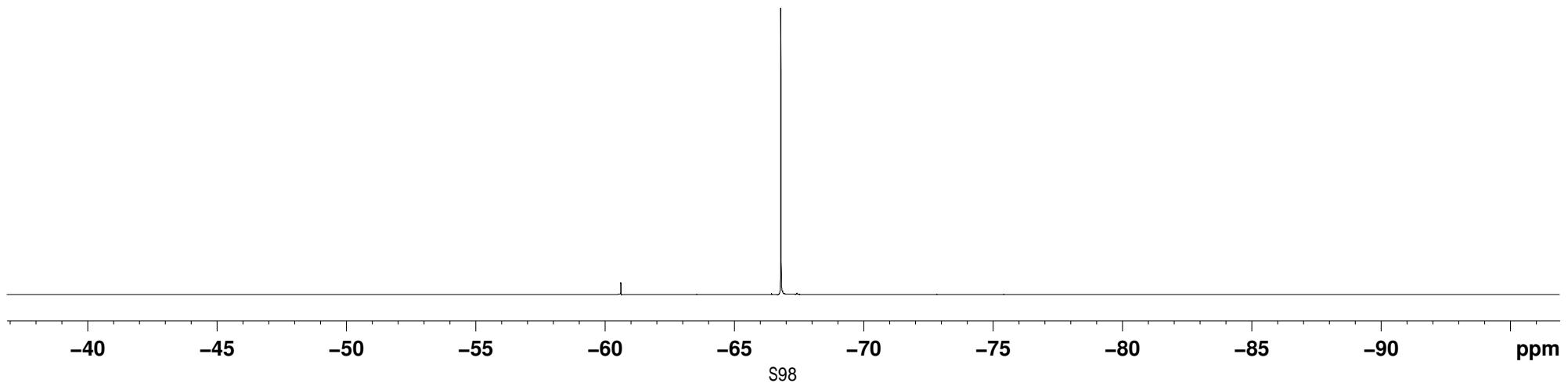


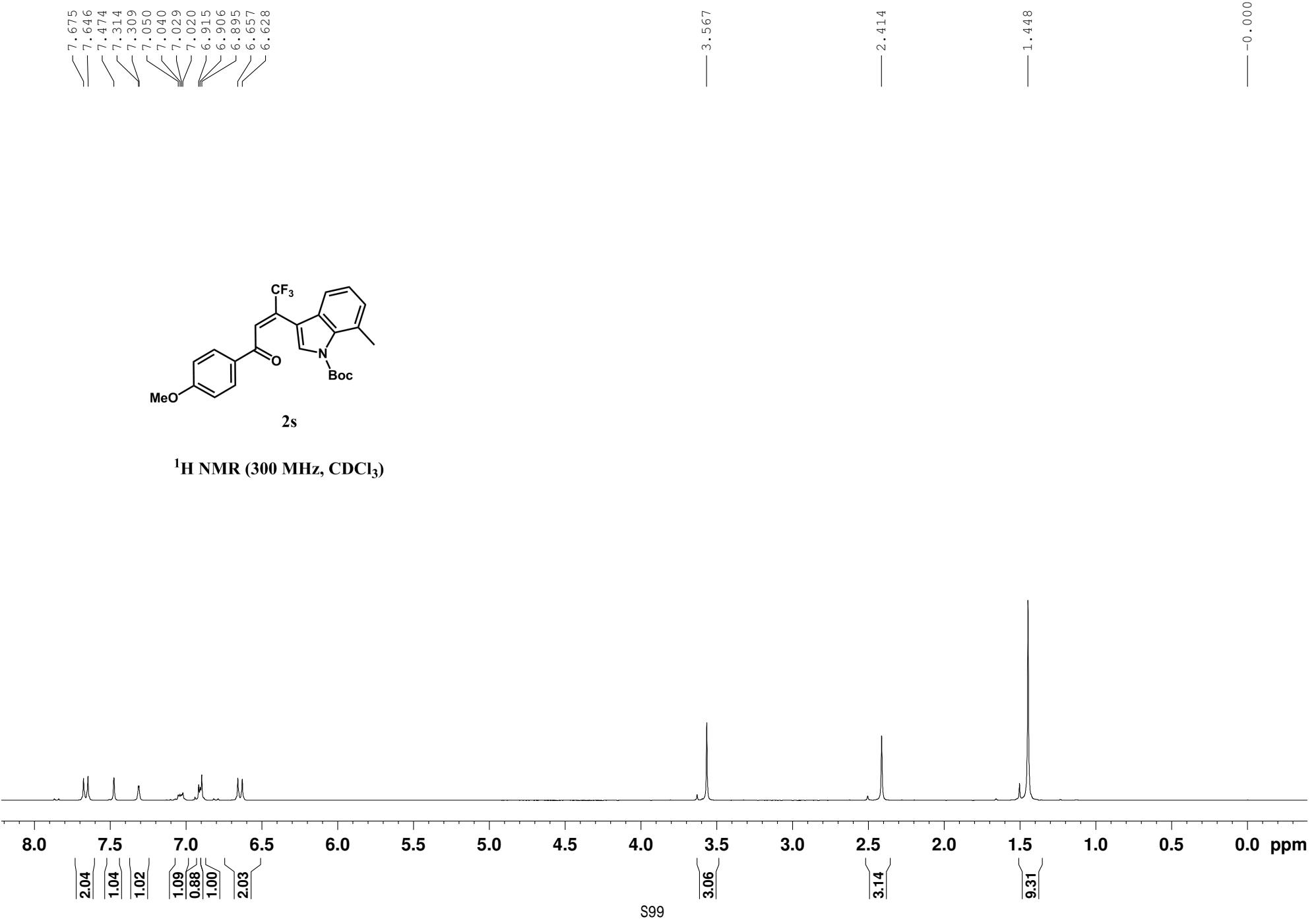


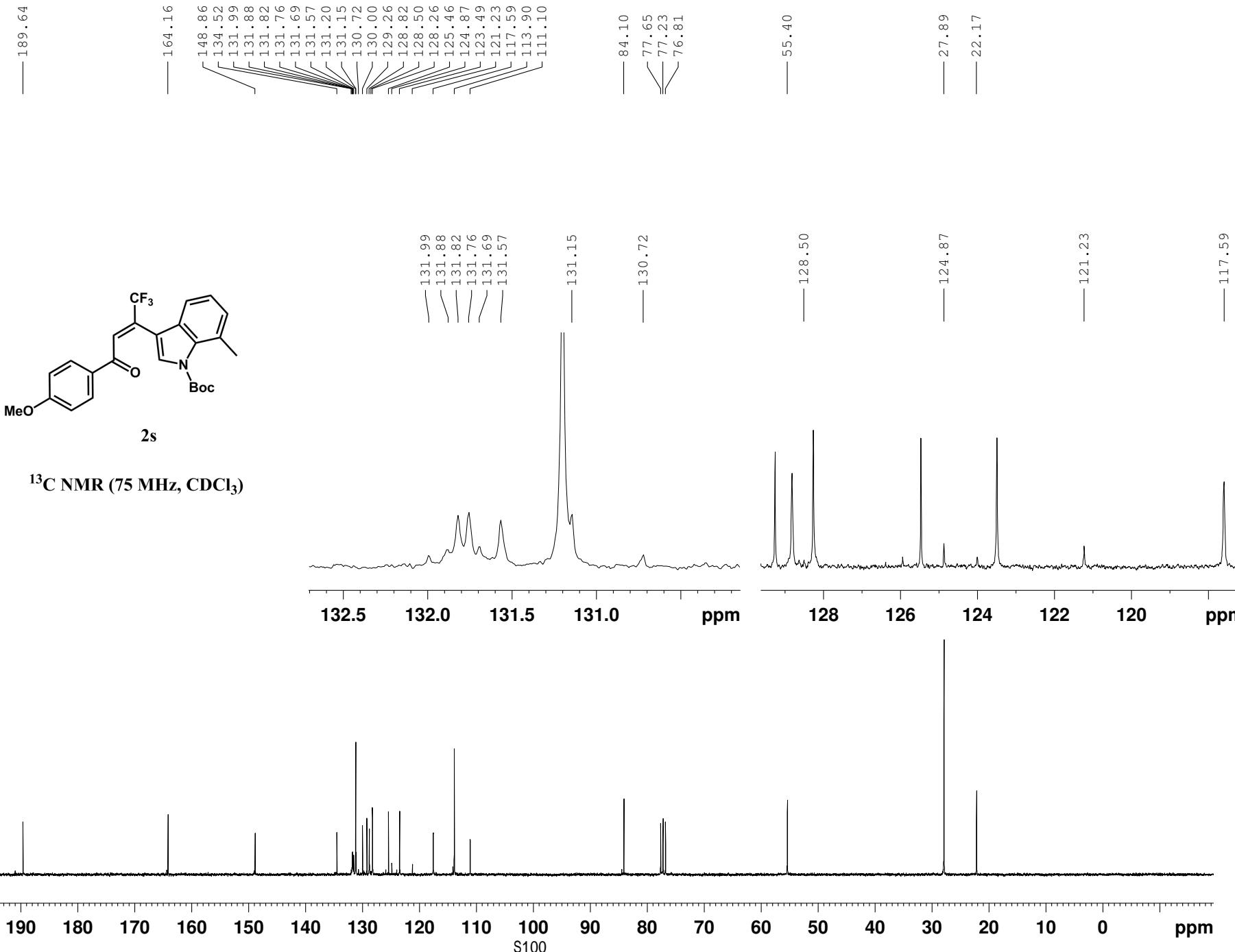


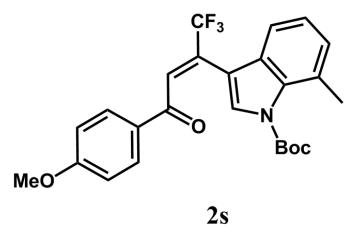
2r

¹⁹F NMR (282 MHz, CDCl₃)



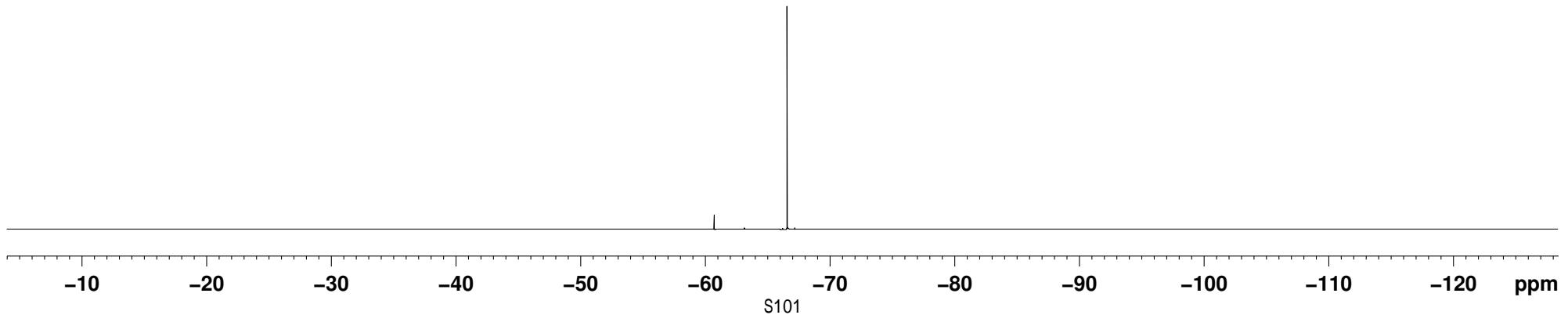


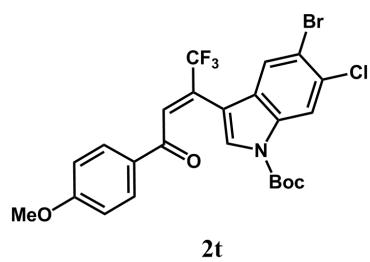




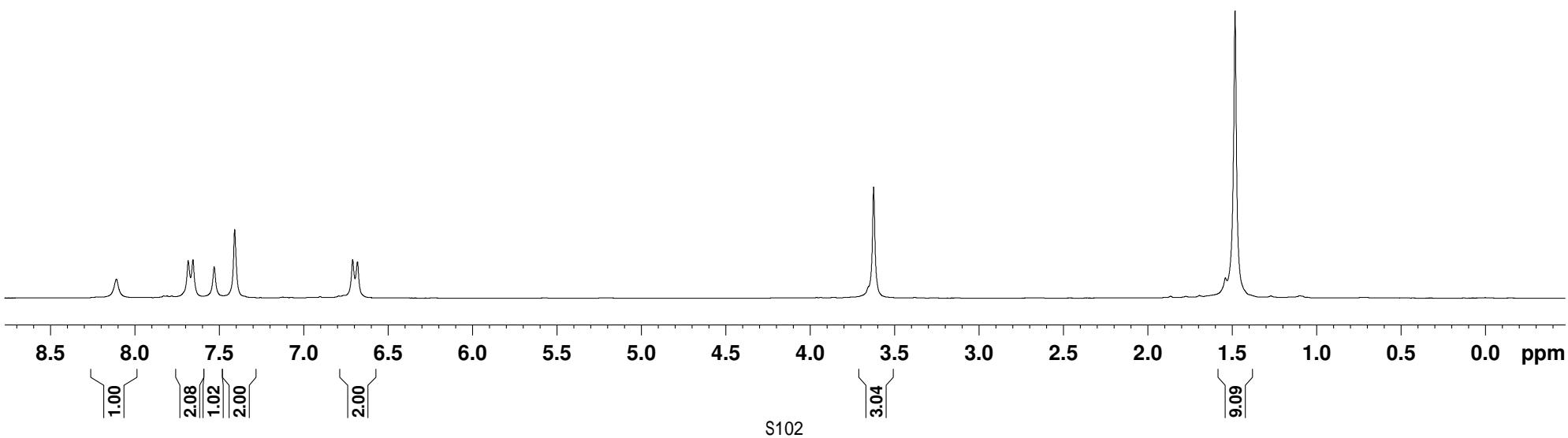
2s

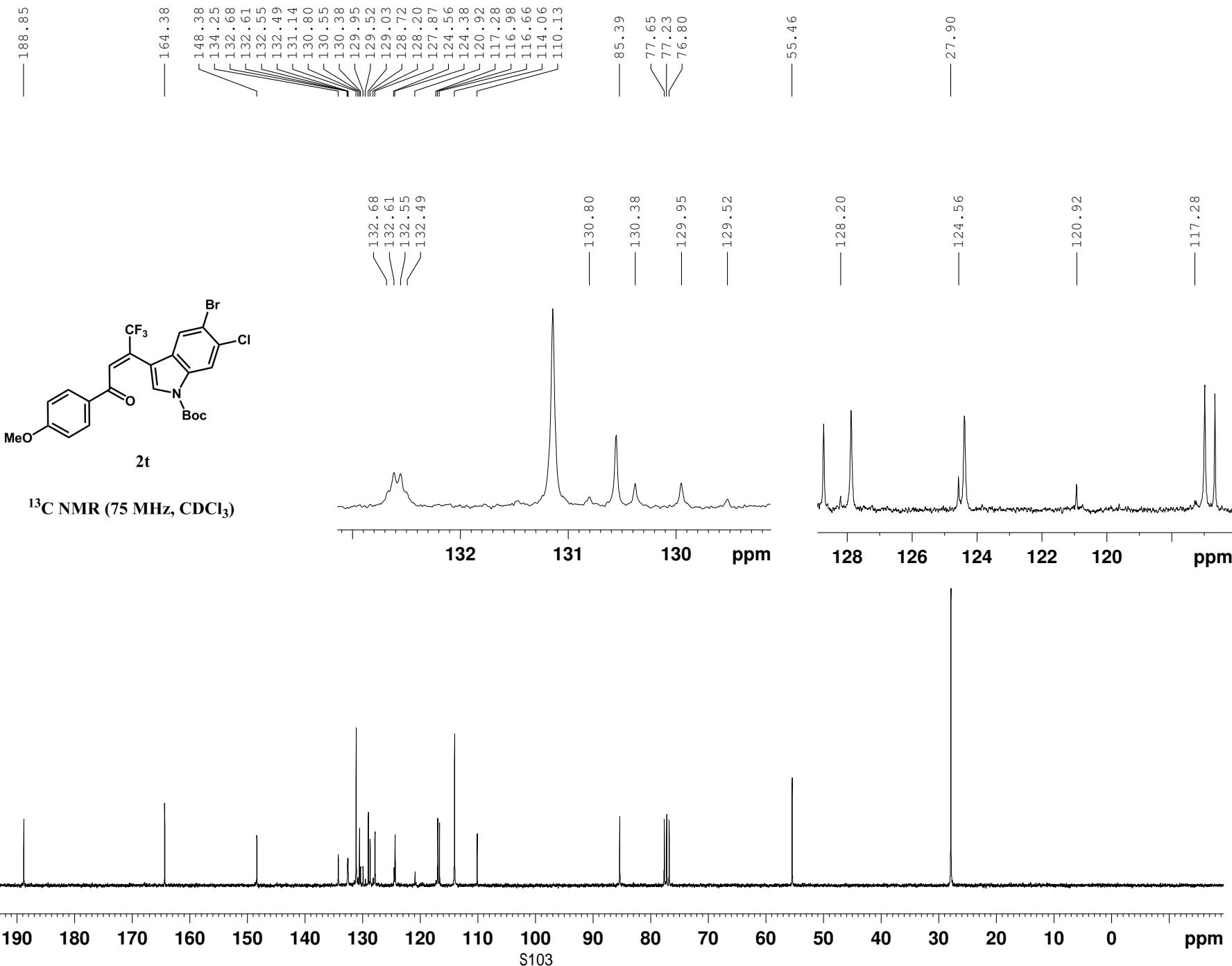
^{19}F NMR (282 MHz, CDCl_3)

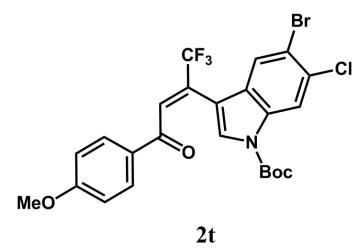




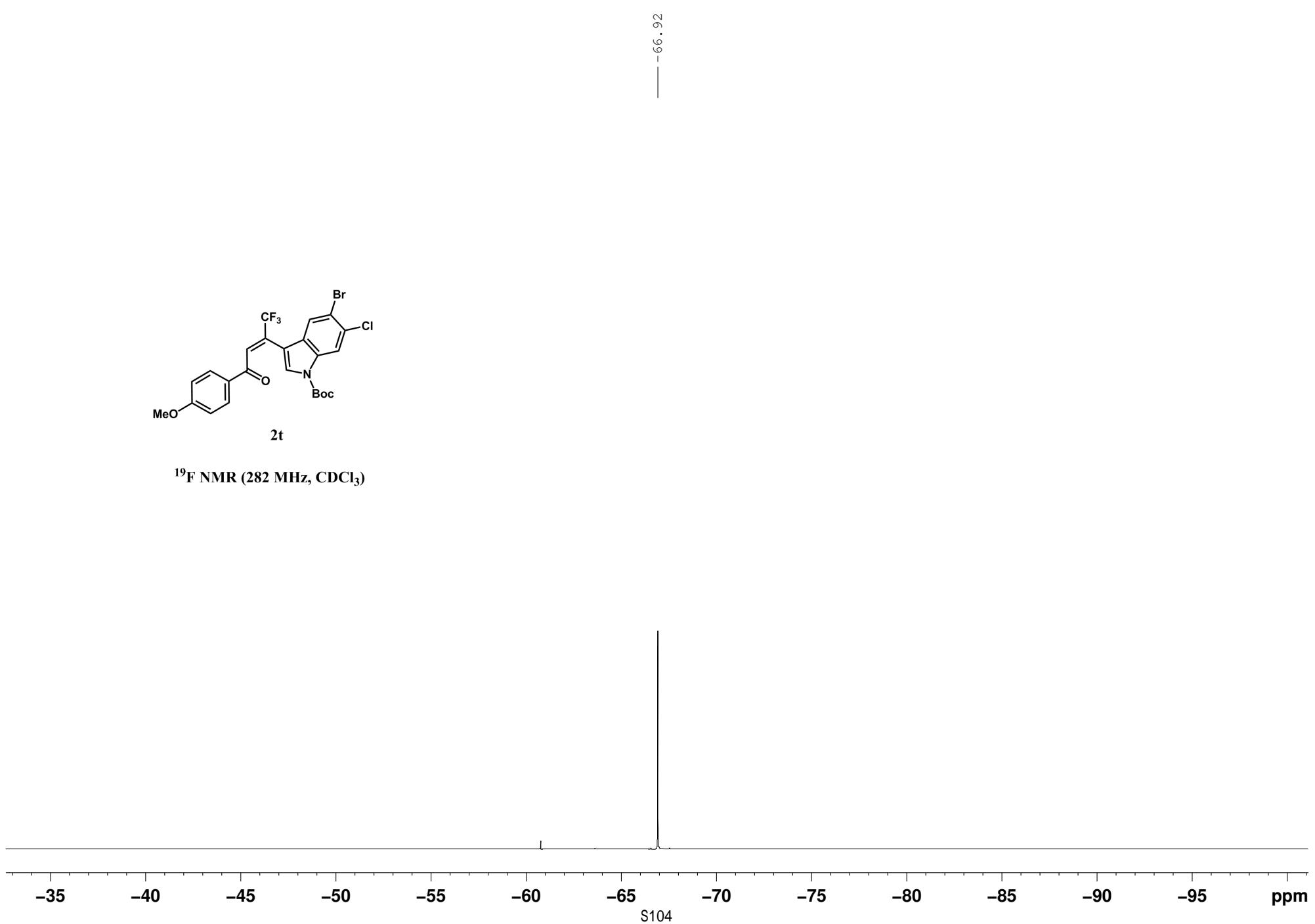
¹H NMR (300 MHz, CDCl₃)





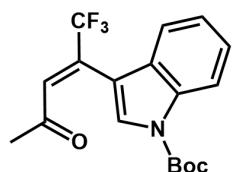


¹⁹F NMR (282 MHz, CDCl₃)



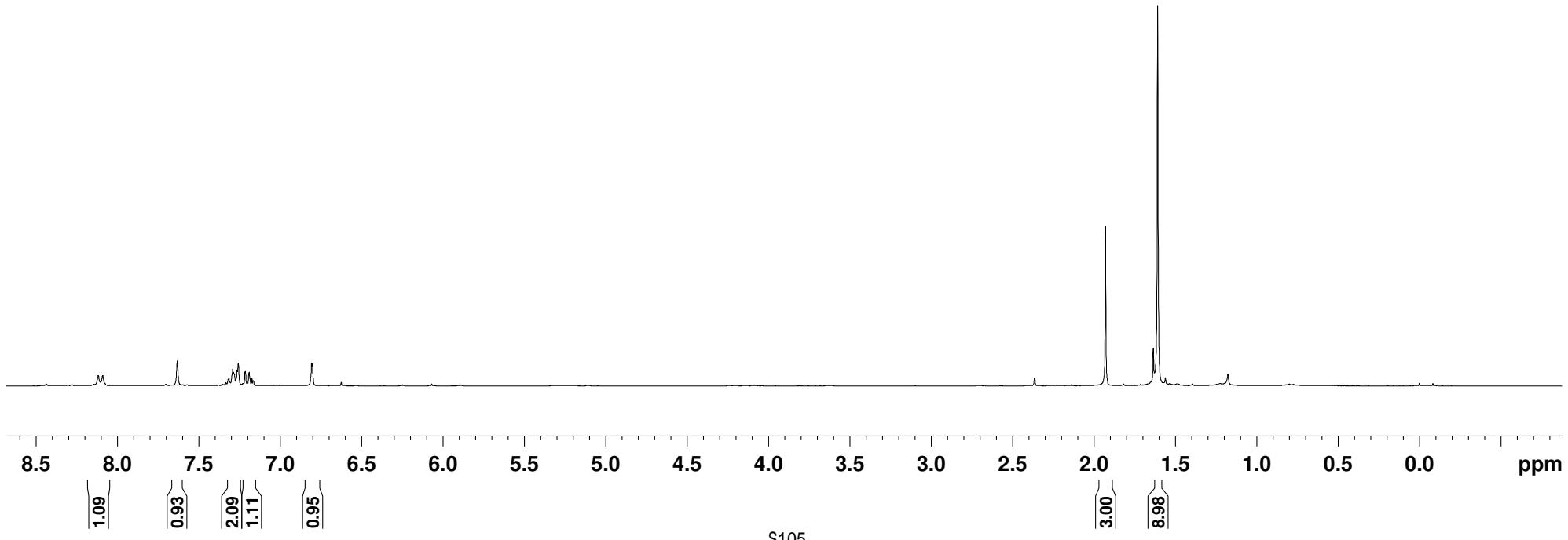
8.117
 8.089
 7.631
 7.332
 7.319
 7.314
 7.291
 7.263
 7.256
 7.226
 7.215
 7.212
 7.189
 7.173
 7.165
 7.162
 6.806
 6.801

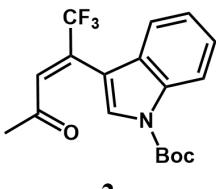
1.928
 1.608
 -0.000



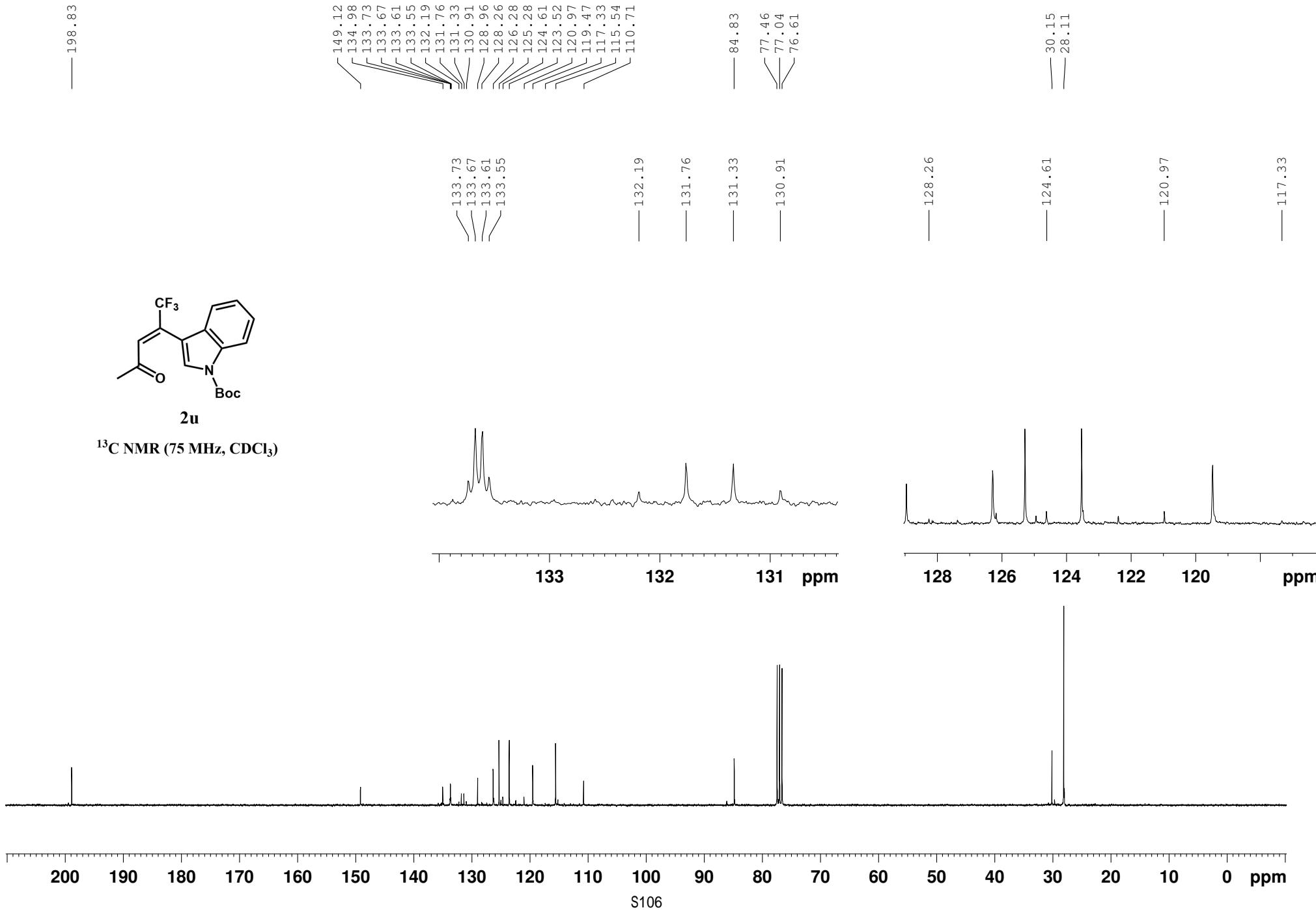
2u

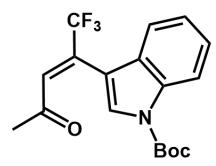
¹H NMR (300 MHz, CDCl₃)





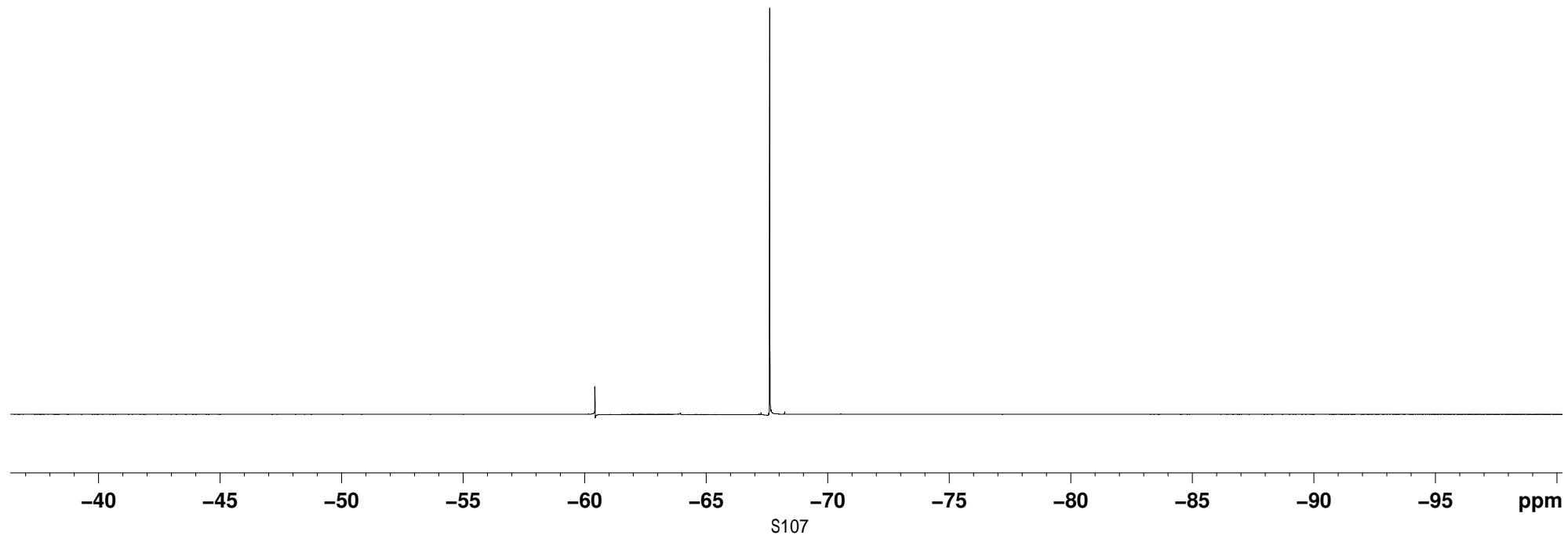
¹³C NMR (75 MHz, CDCl₃)

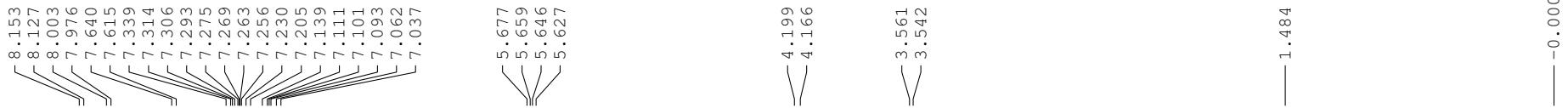




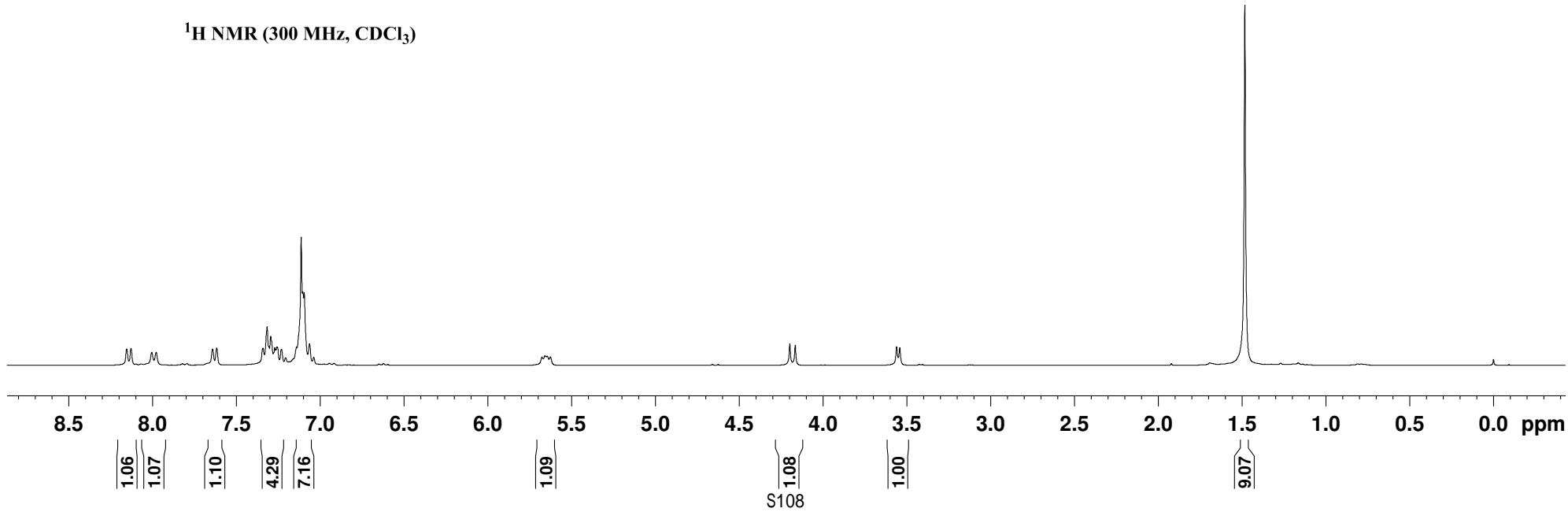
2u

^{19}F NMR (282 MHz, CDCl_3)

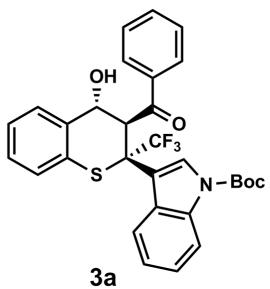




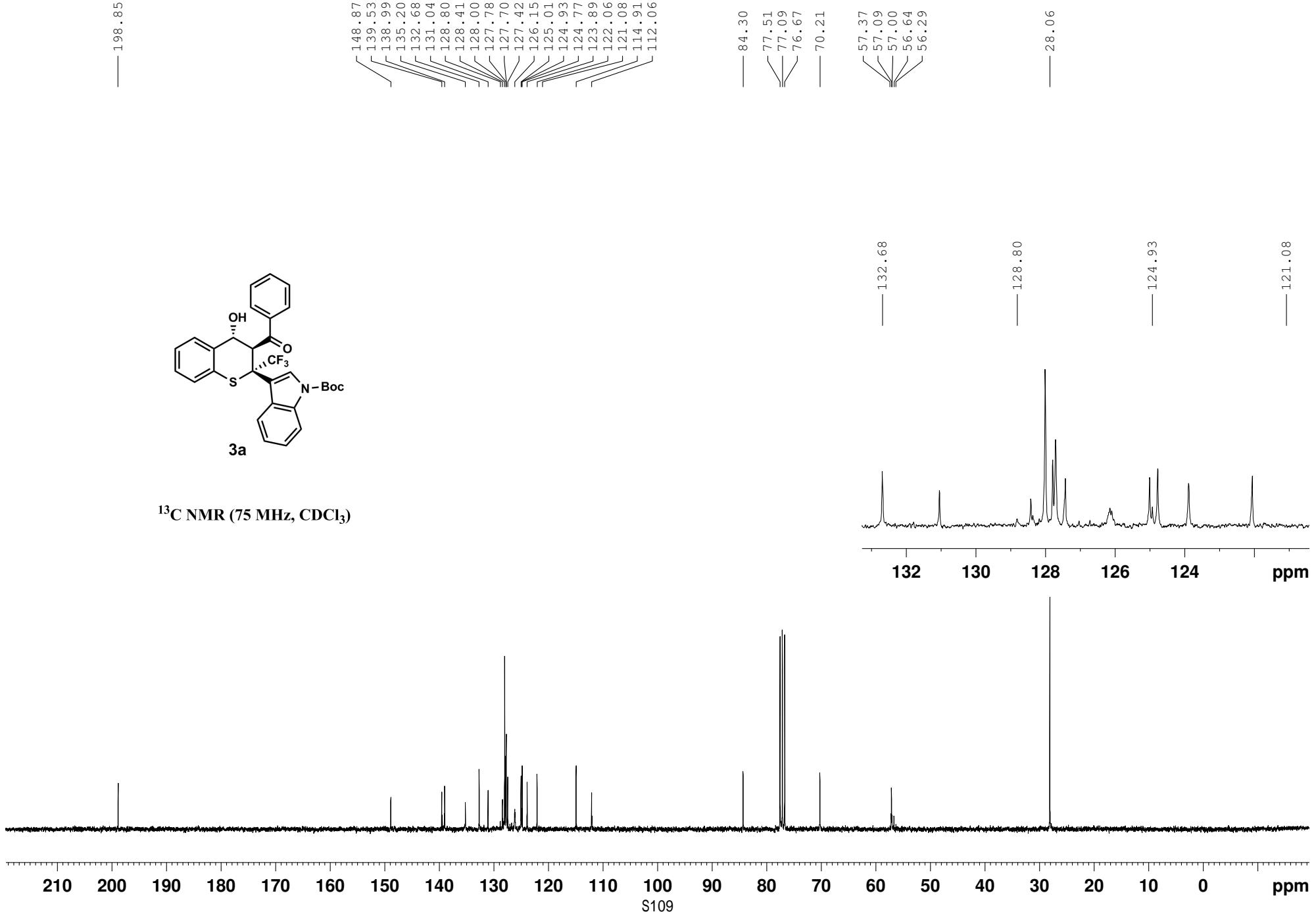
^1H NMR (300 MHz, CDCl_3)

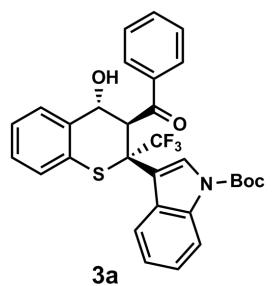


S108

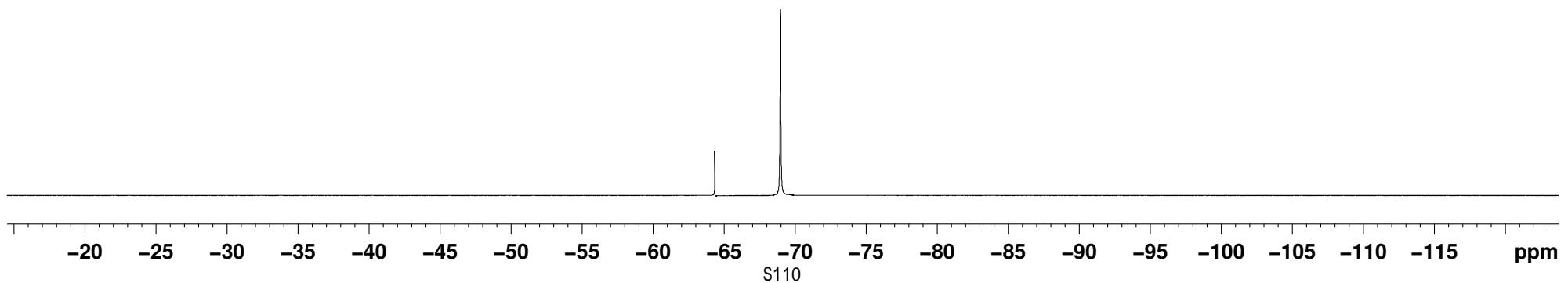


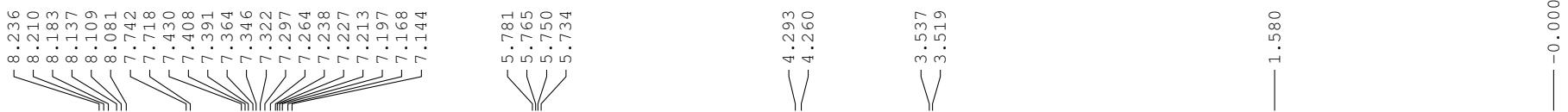
¹³C NMR (75 MHz, CDCl₃)



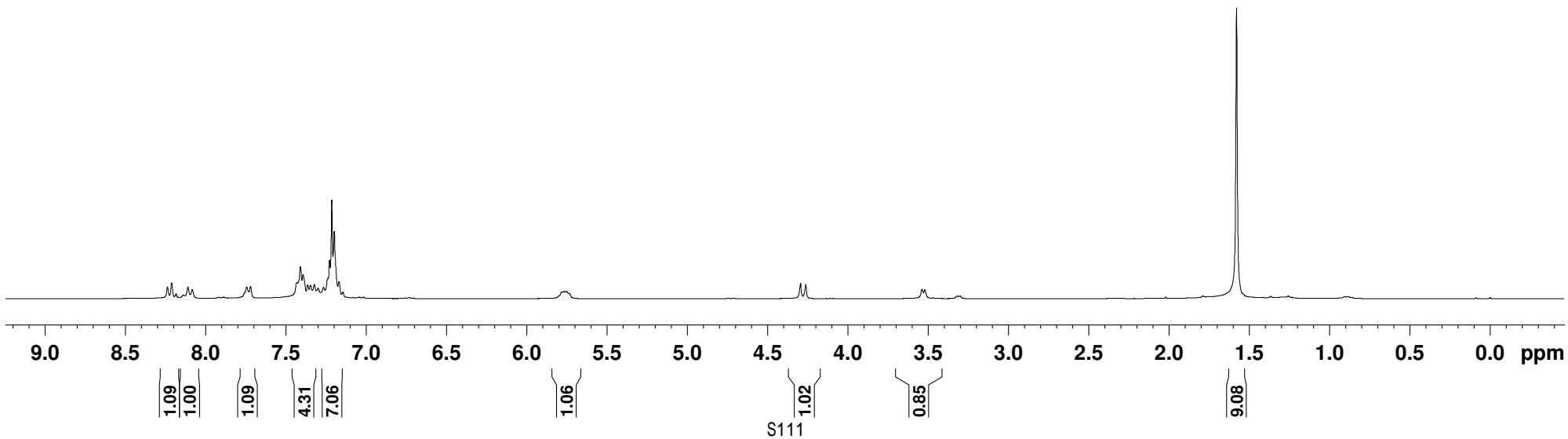


^{19}F NMR (282 MHz, CDCl_3)

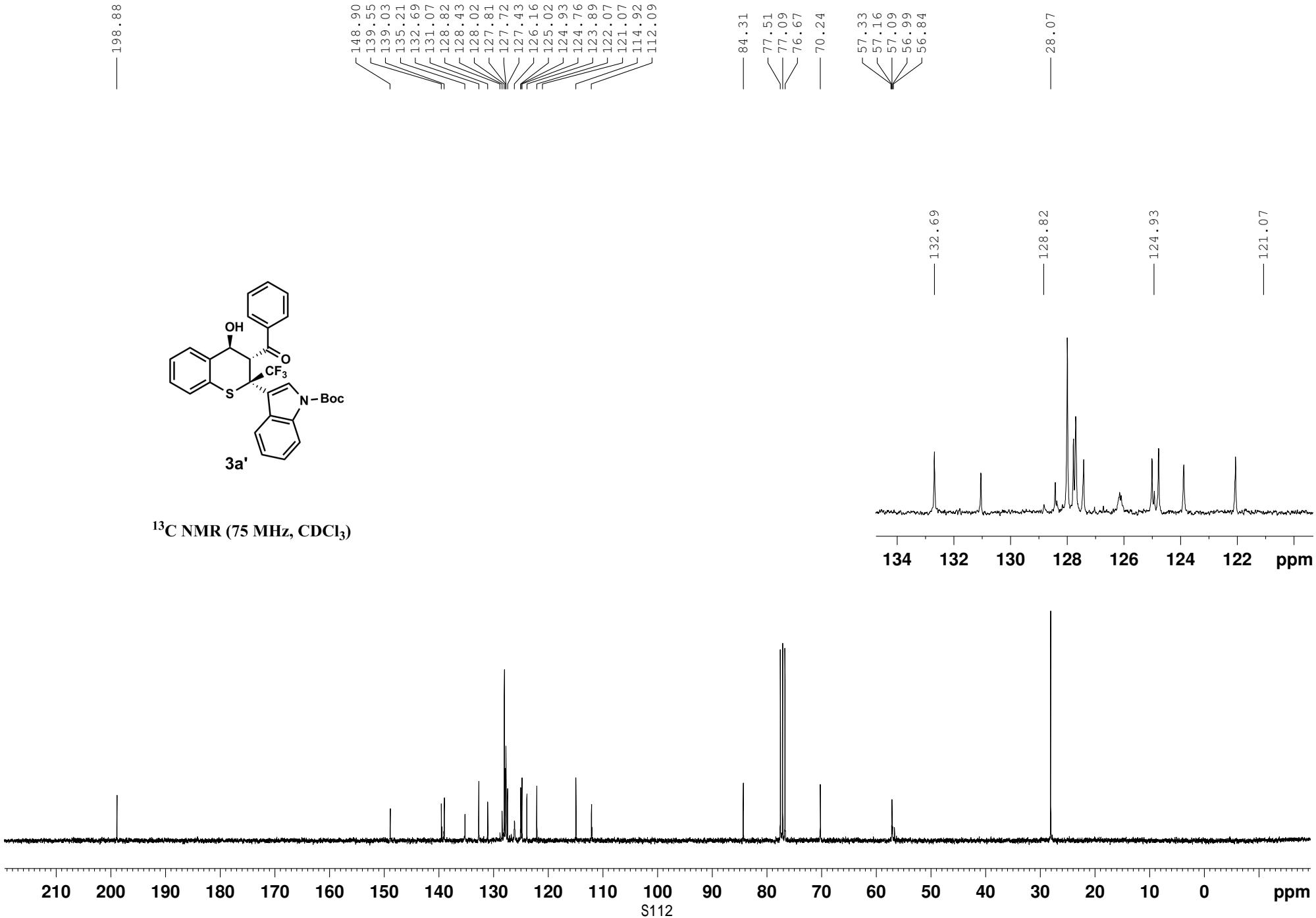


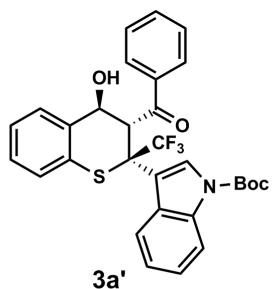


¹H NMR (300 MHz, CDCl₃)

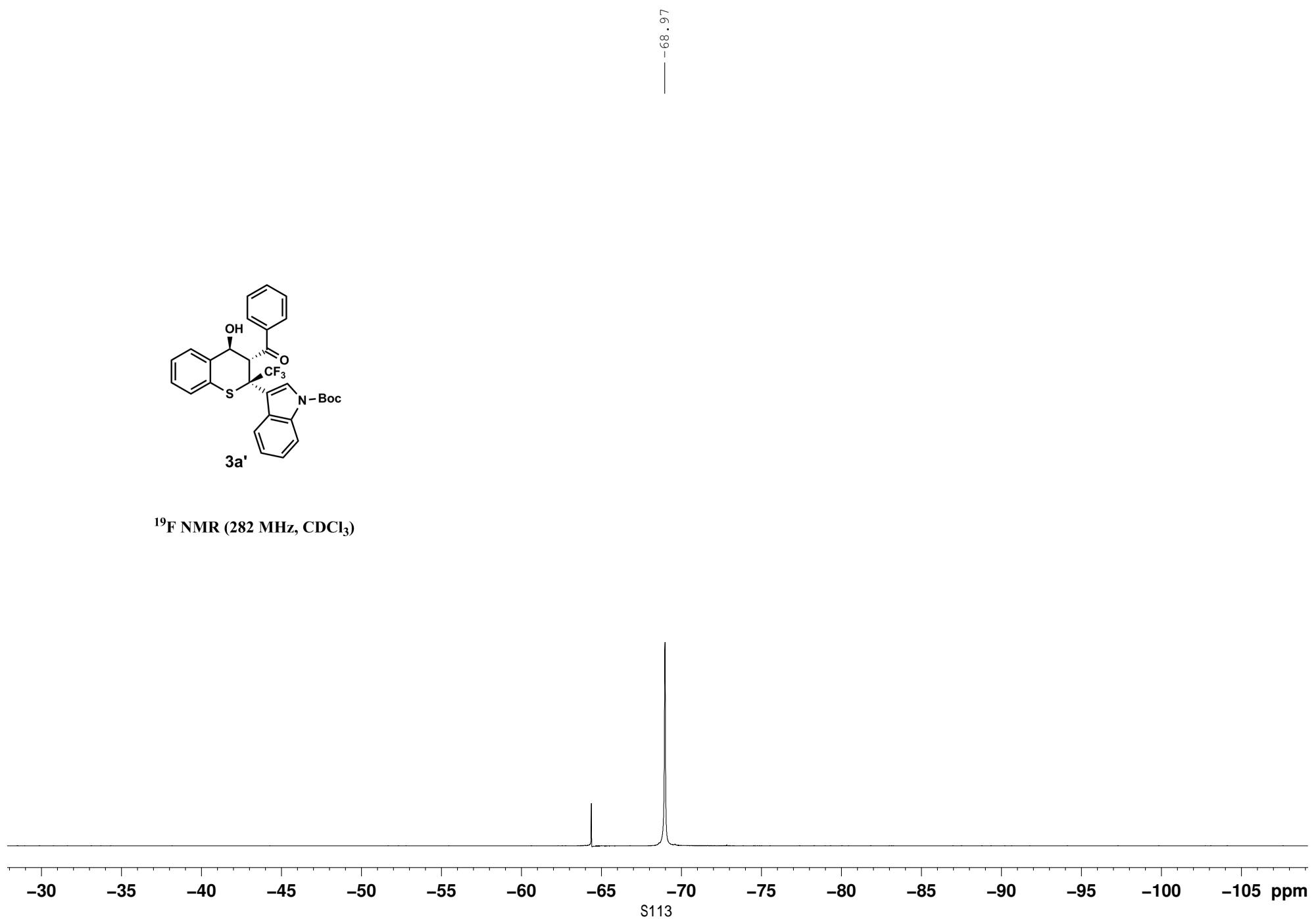


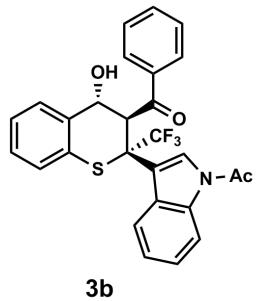
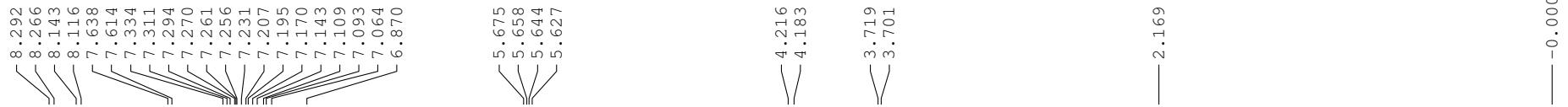
S111



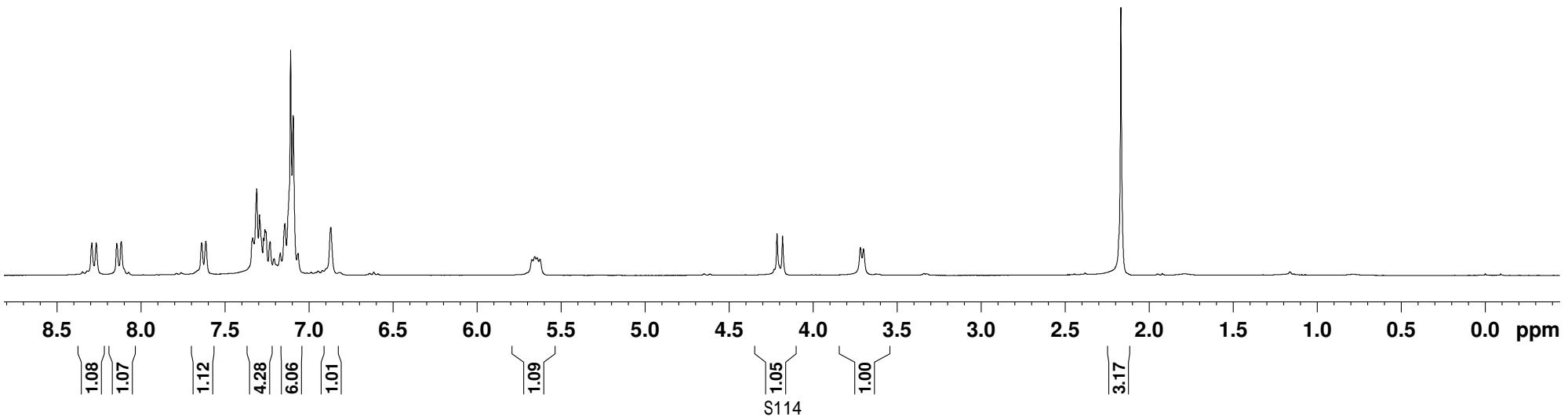


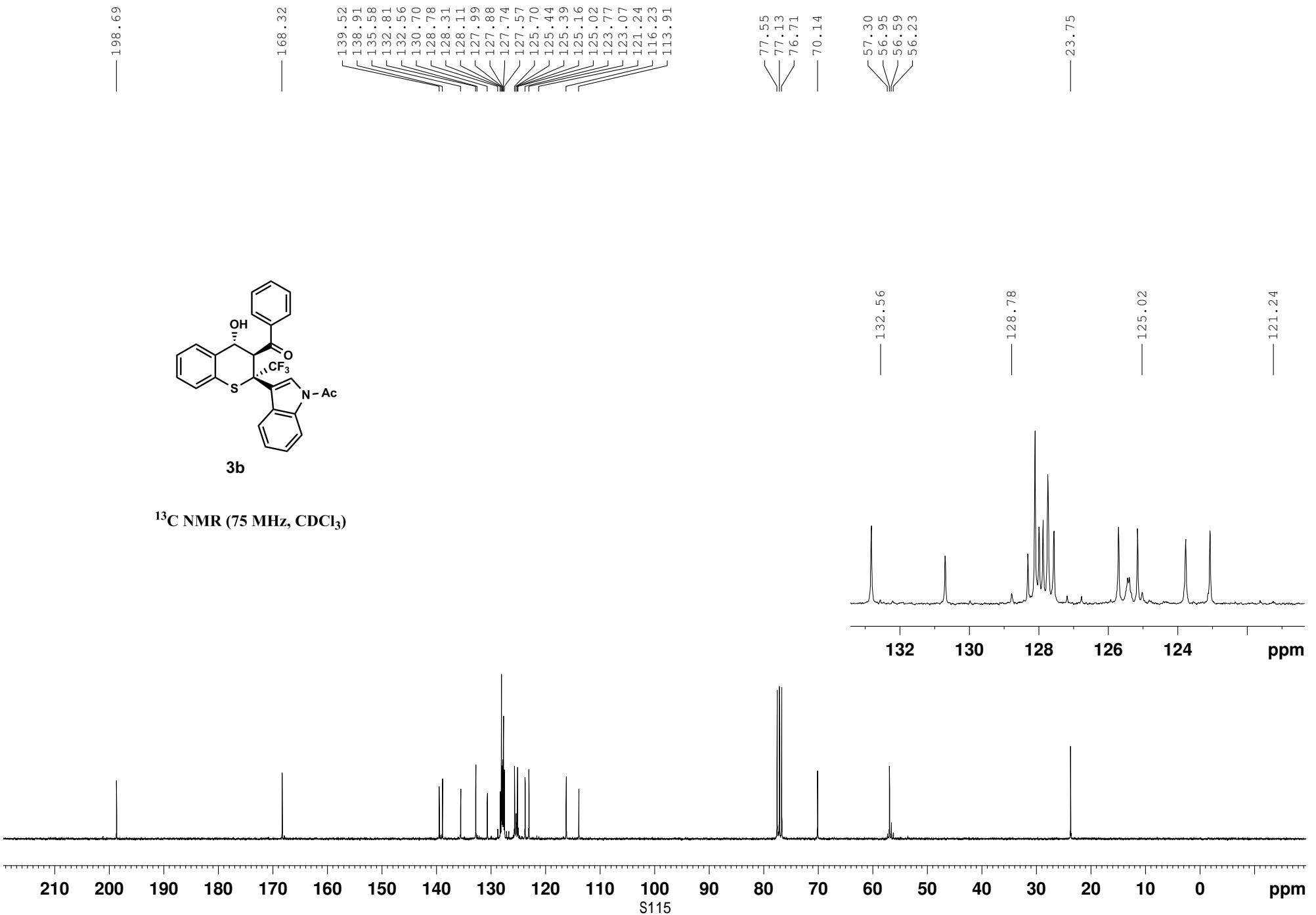
^{19}F NMR (282 MHz, CDCl_3)

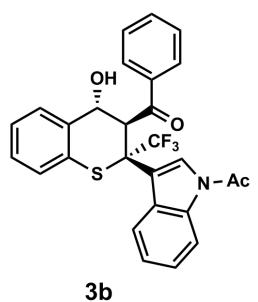




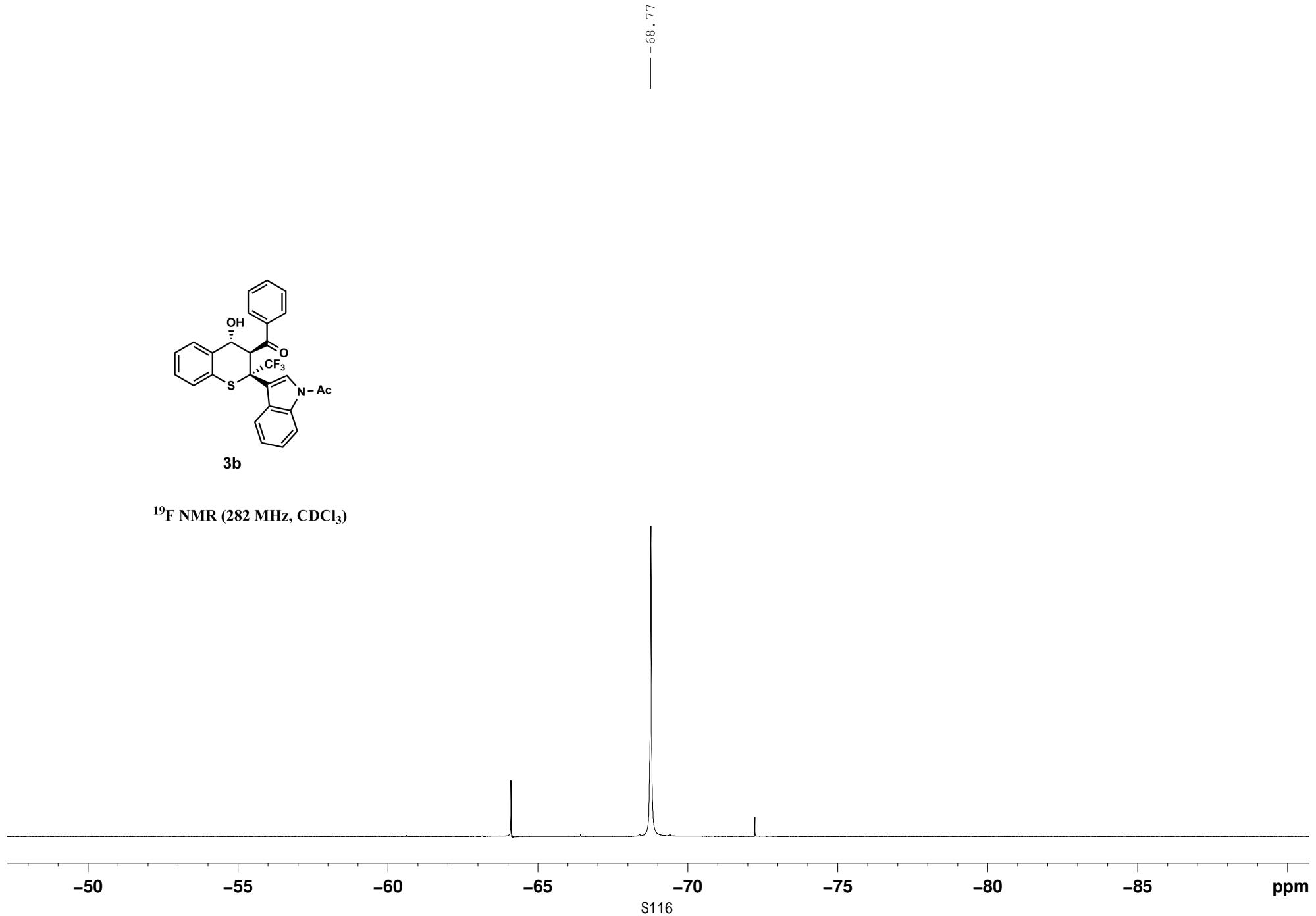
¹H NMR (300 MHz, CDCl₃)





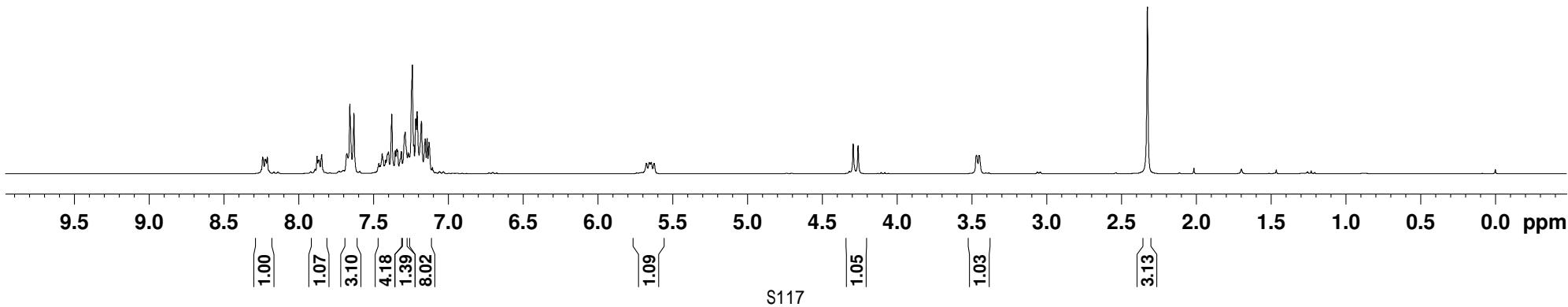


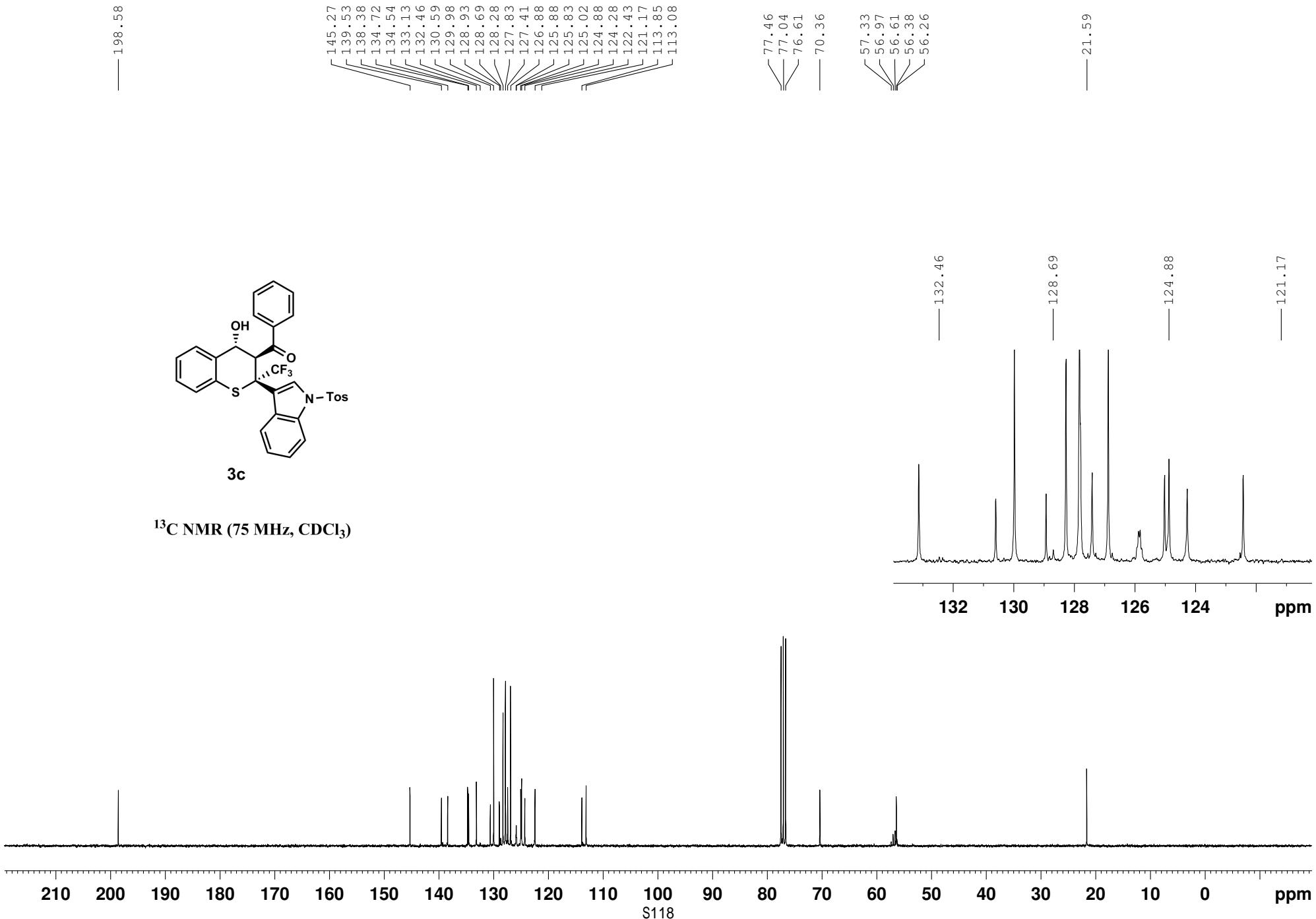
¹⁹F NMR (282 MHz, CDCl₃)

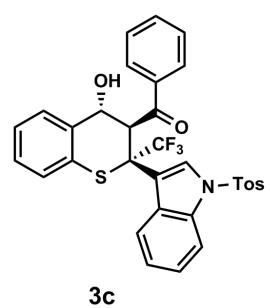




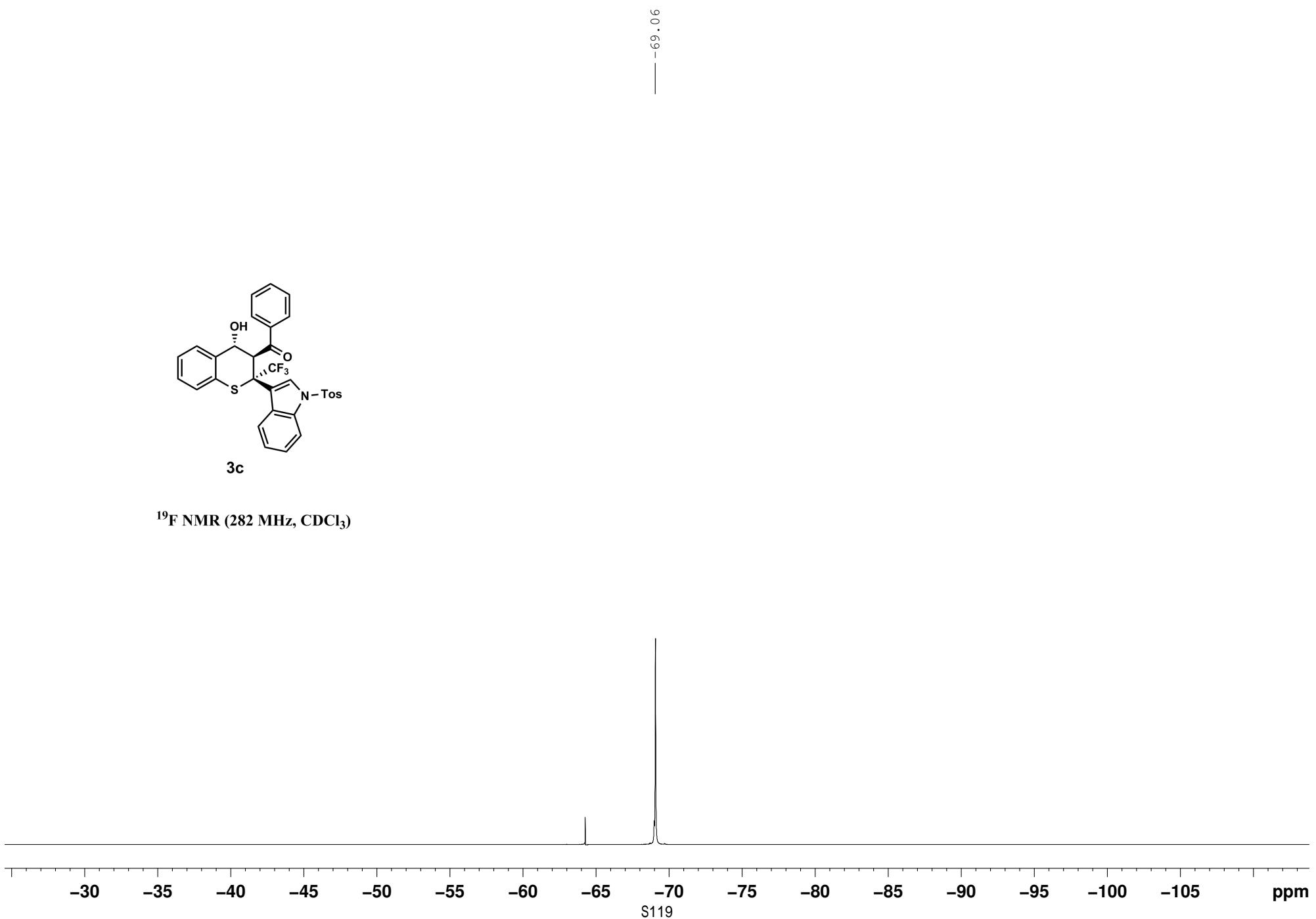
^1H NMR (300 MHz, CDCl_3)

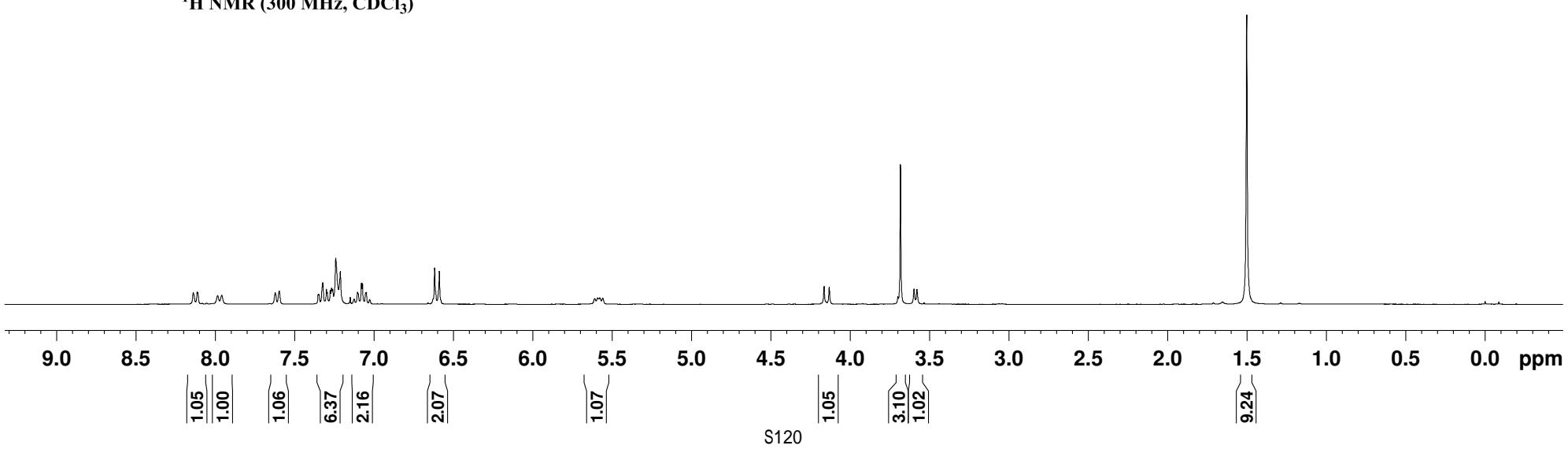
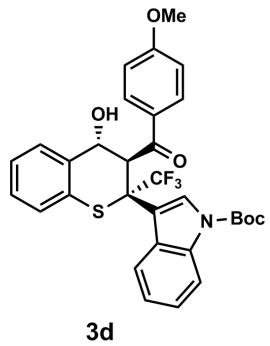
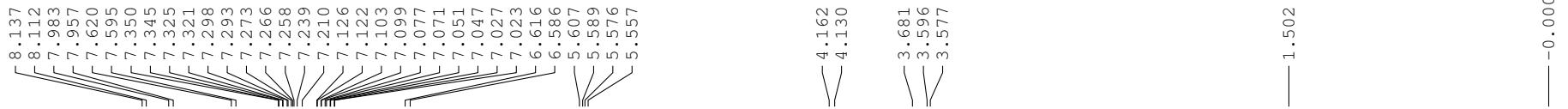


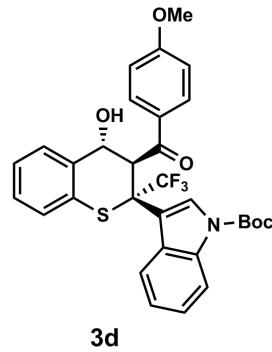




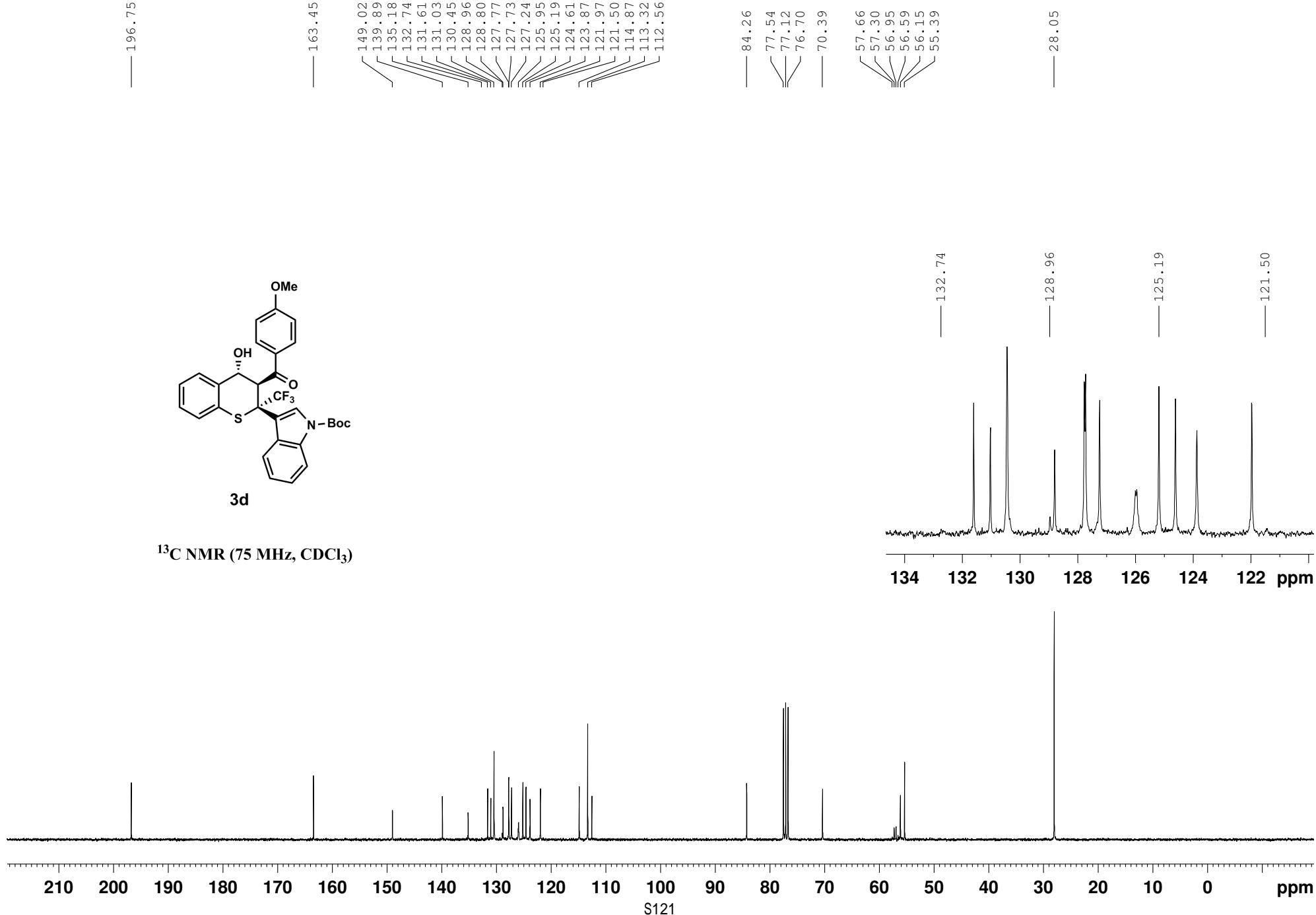
¹⁹F NMR (282 MHz, CDCl₃)

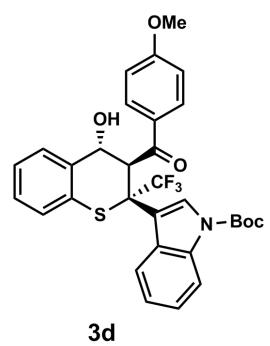




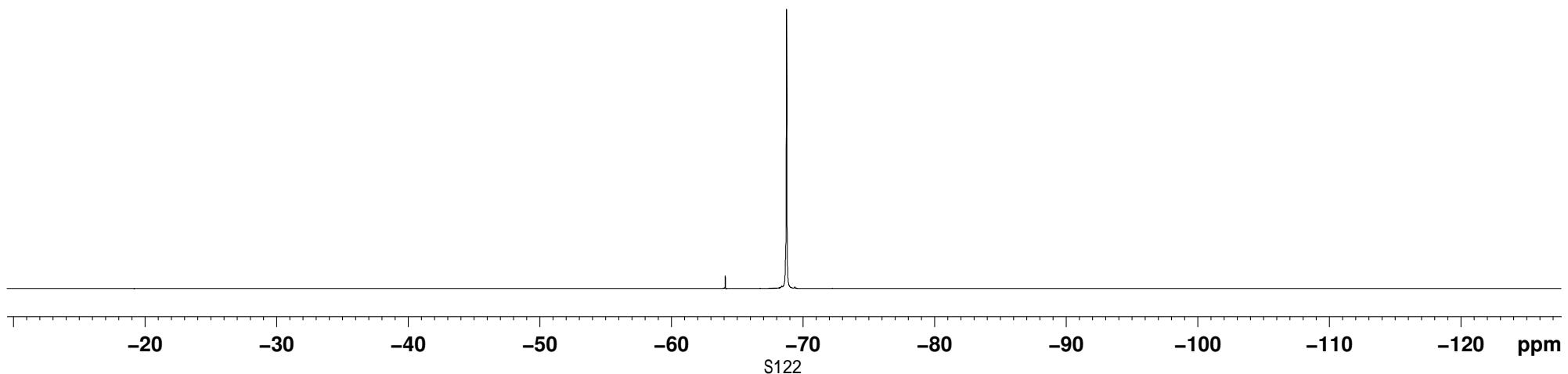


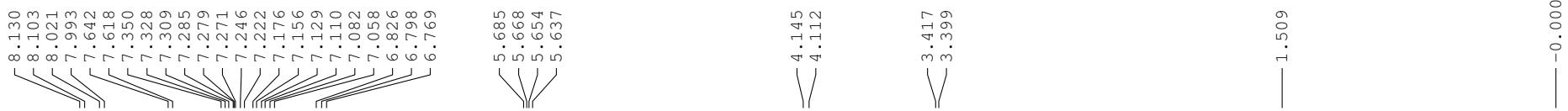
¹³C NMR (75 MHz, CDCl₃)



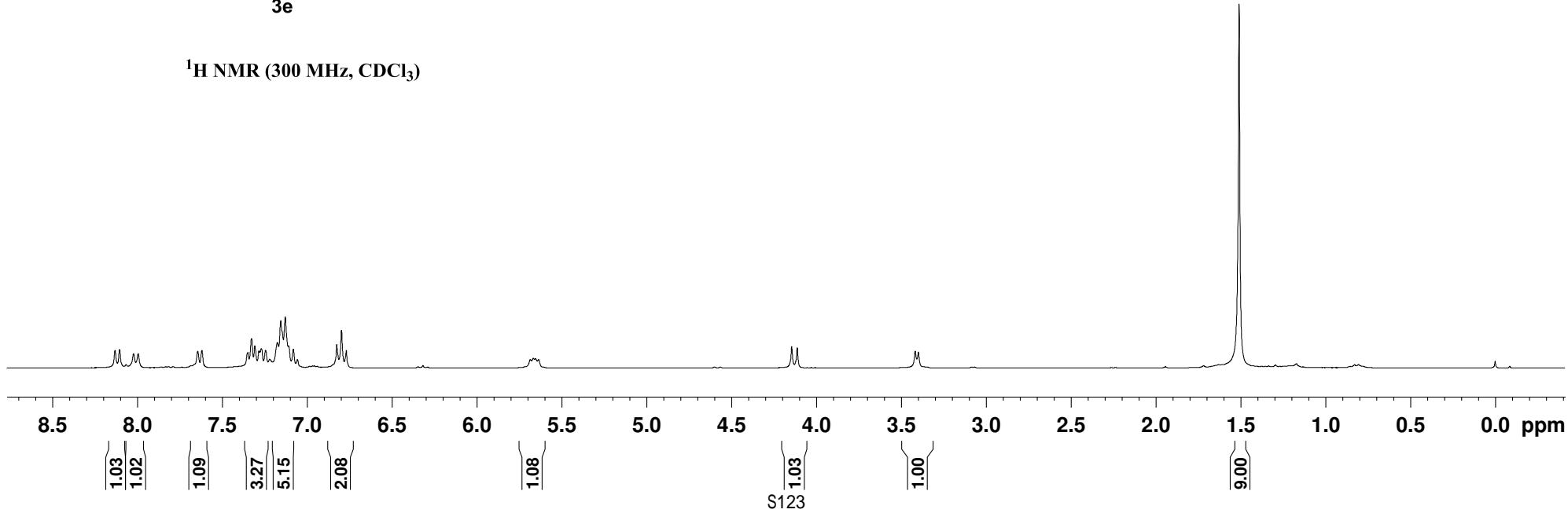


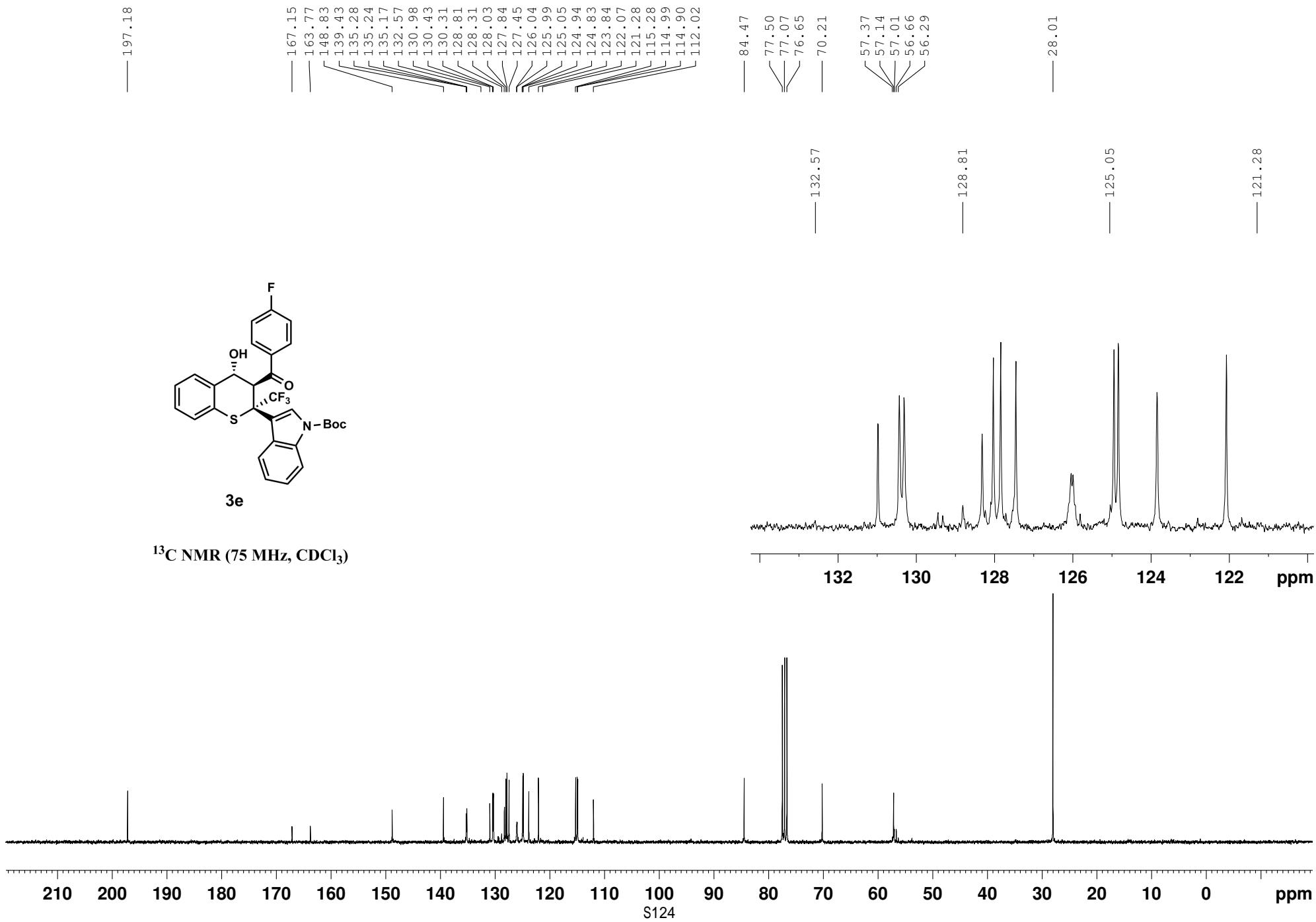
¹⁹F NMR (282 MHz, CDCl₃)

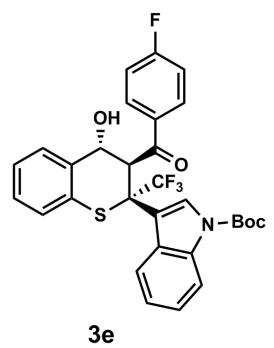




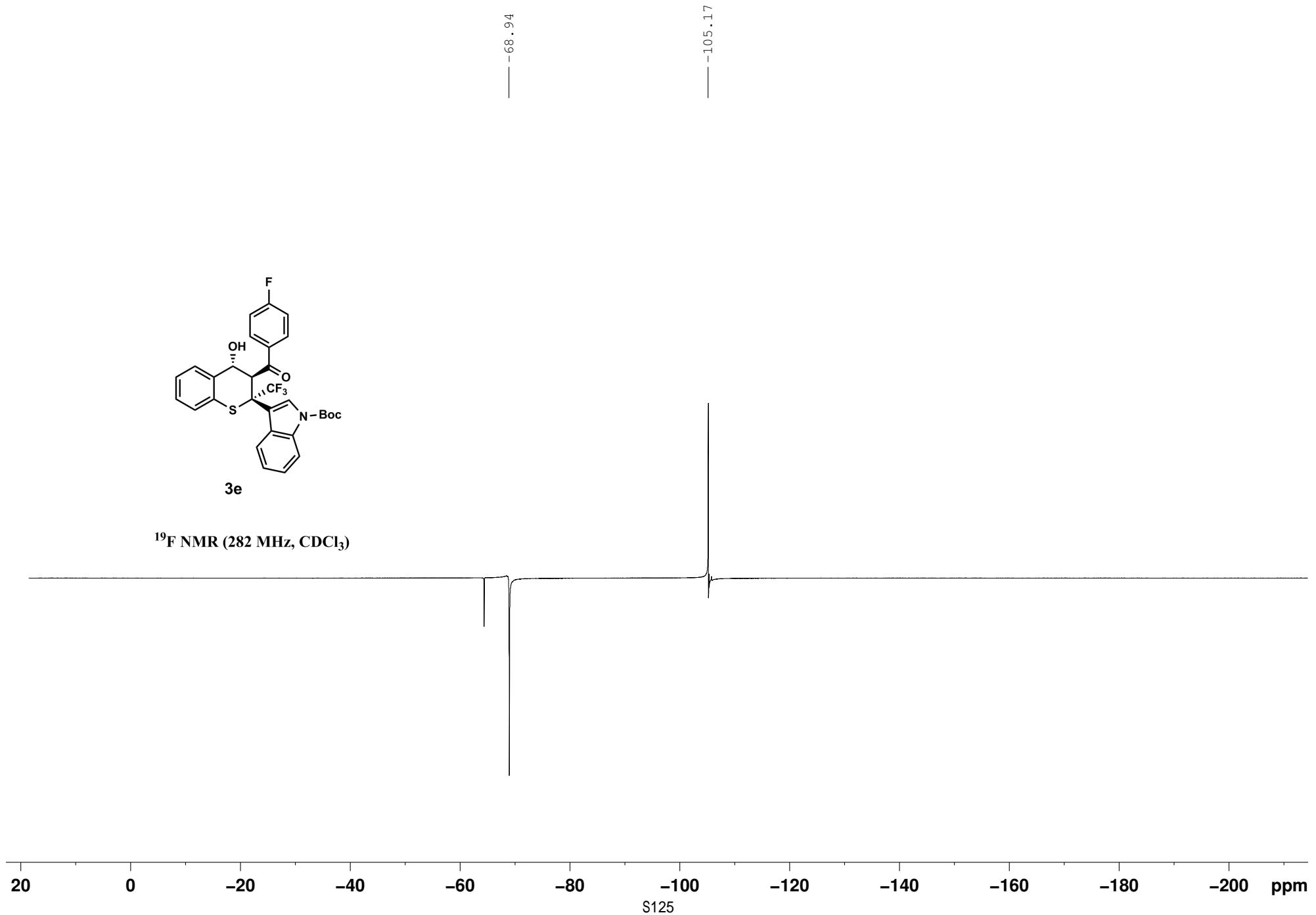
¹H NMR (300 MHz, CDCl₃)

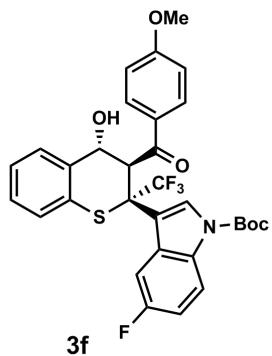




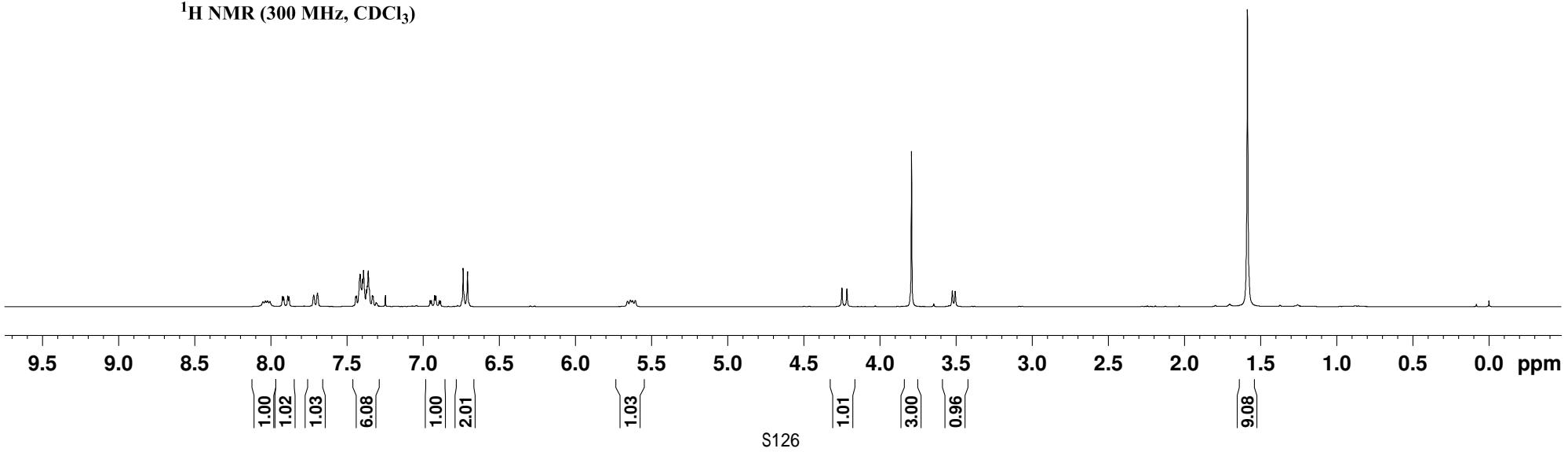


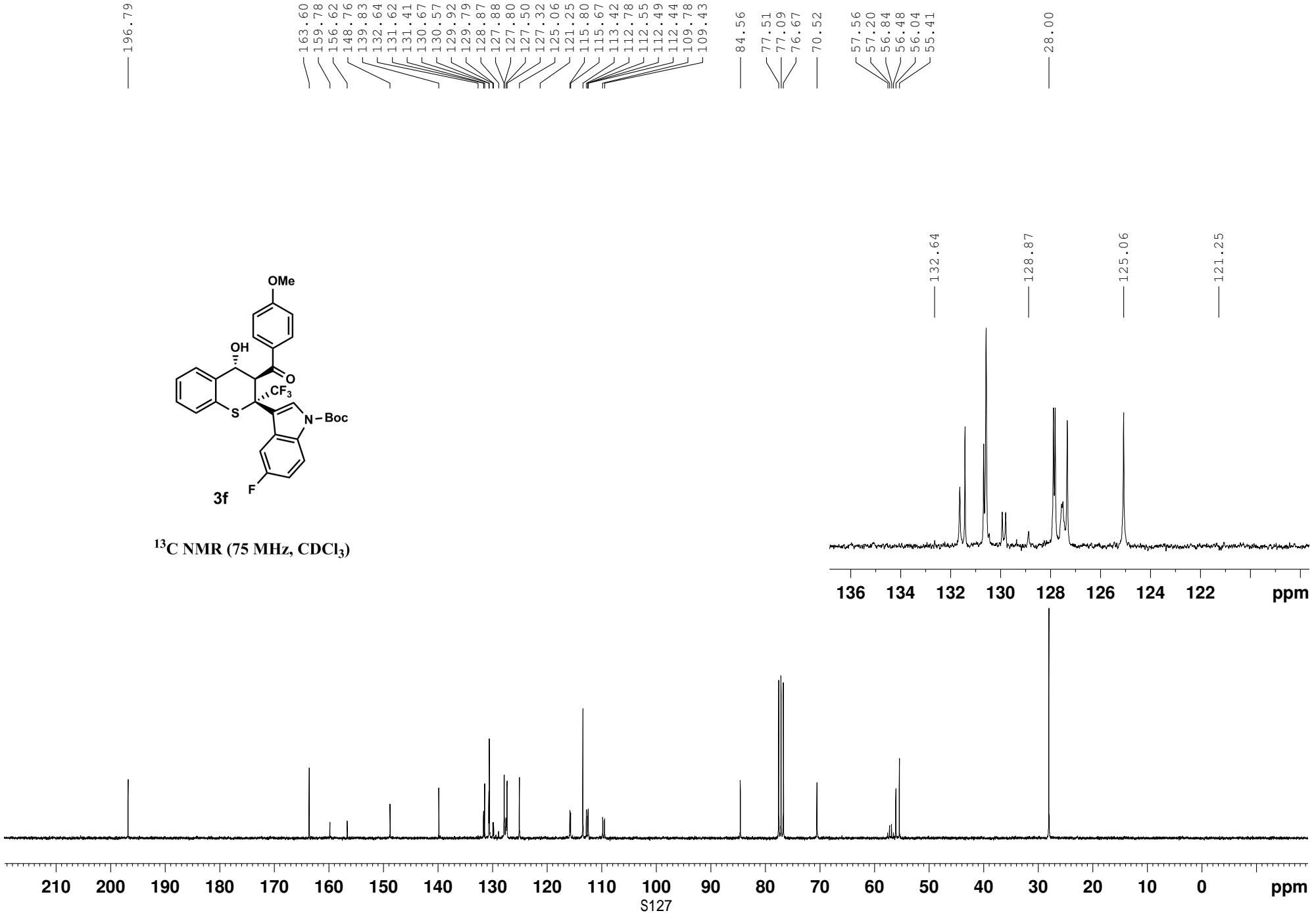
¹⁹F NMR (282 MHz, CDCl₃)

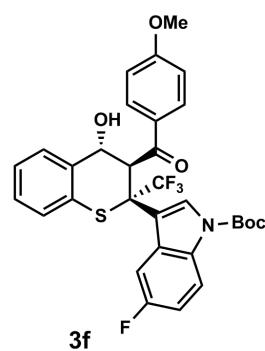




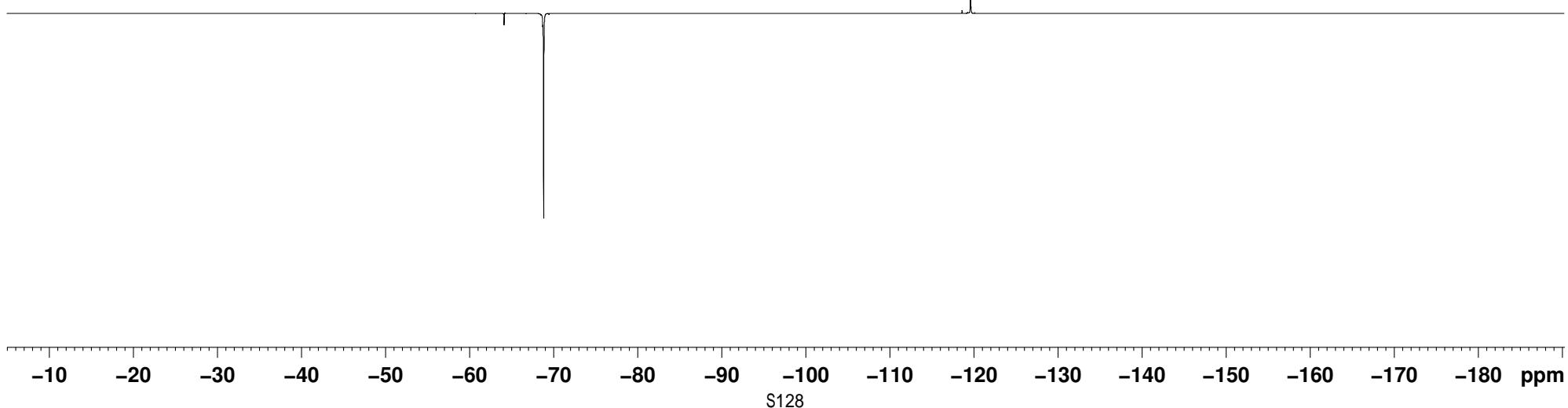
¹H NMR (300 MHz, CDCl₃)

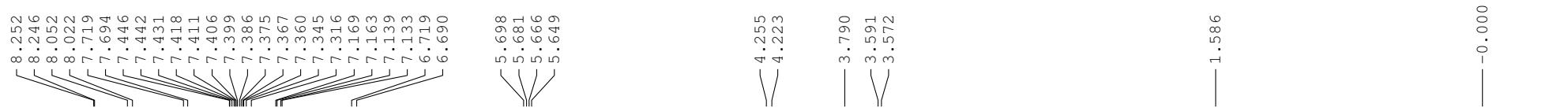


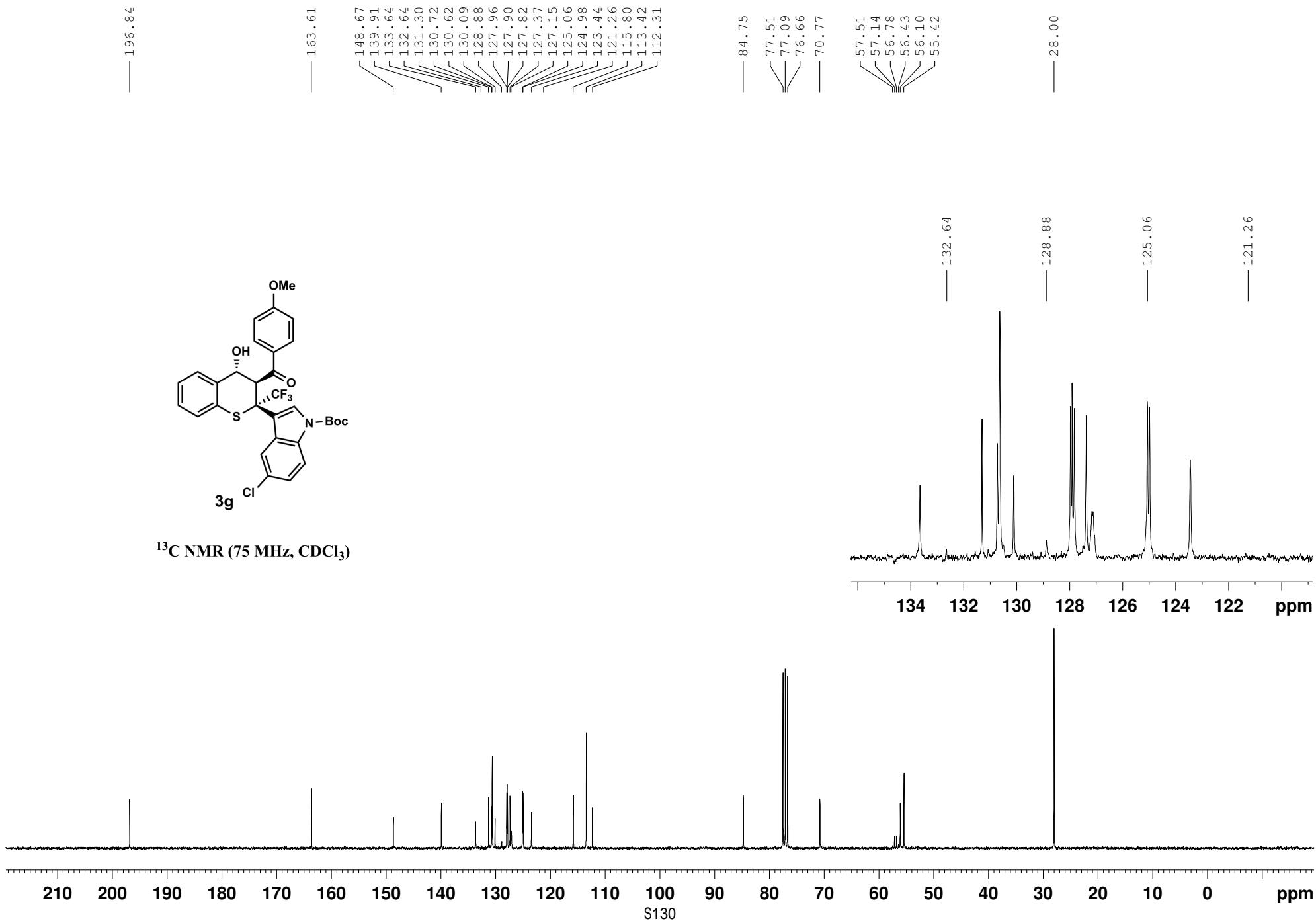


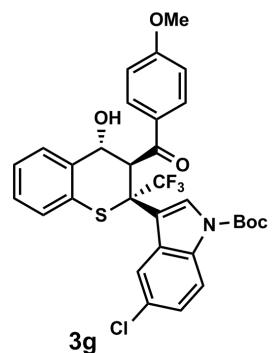


¹⁹F NMR (282 MHz, CDCl₃)

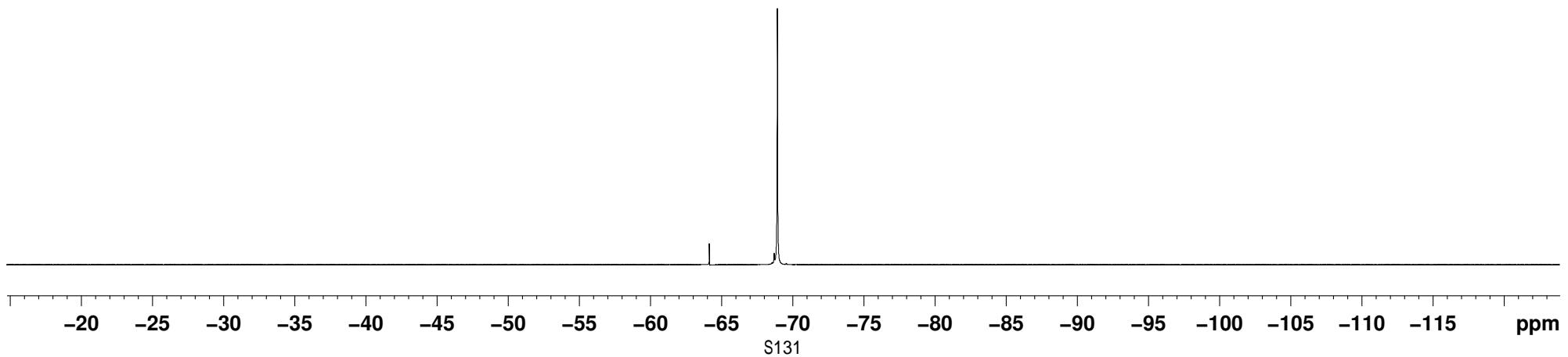








¹⁹F NMR (282 MHz, CDCl₃)



8.341
8.336
7.919
7.890
7.623
7.598
7.351
7.344
7.324
7.310
7.299
7.272
7.243
7.212
7.207
7.183
7.177
6.607
6.578

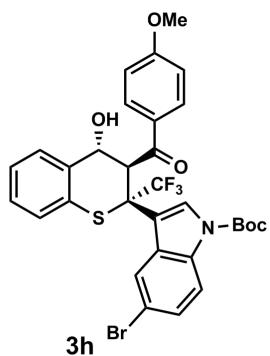
5.609
5.590
5.577
5.558

4.173
4.141

3.690

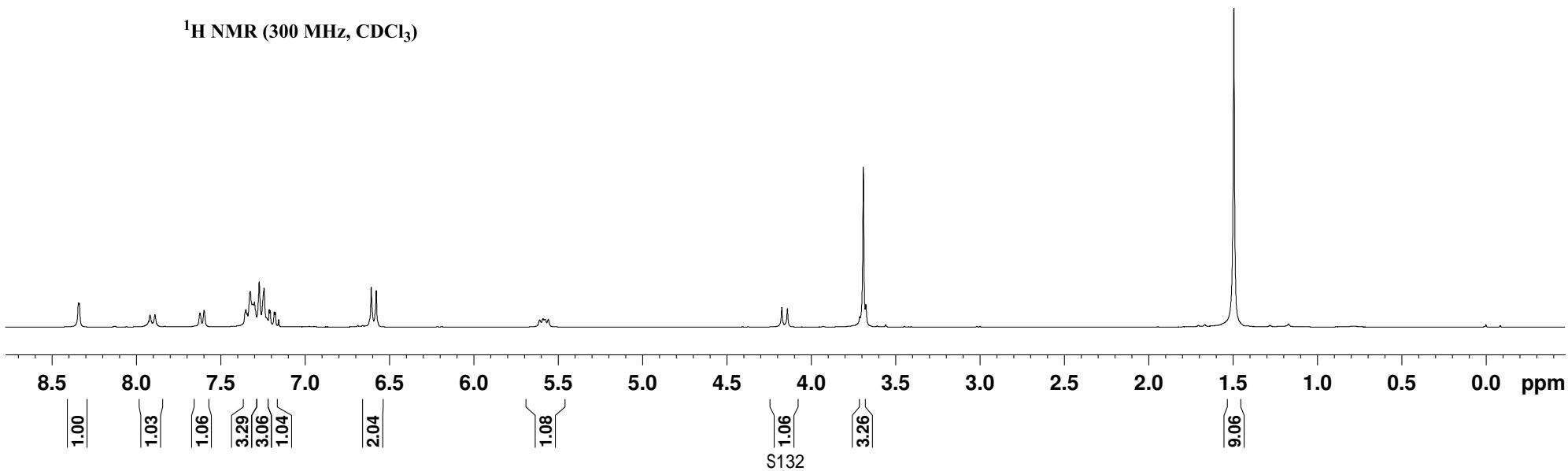
1.493

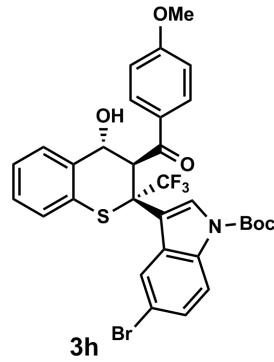
-0.000



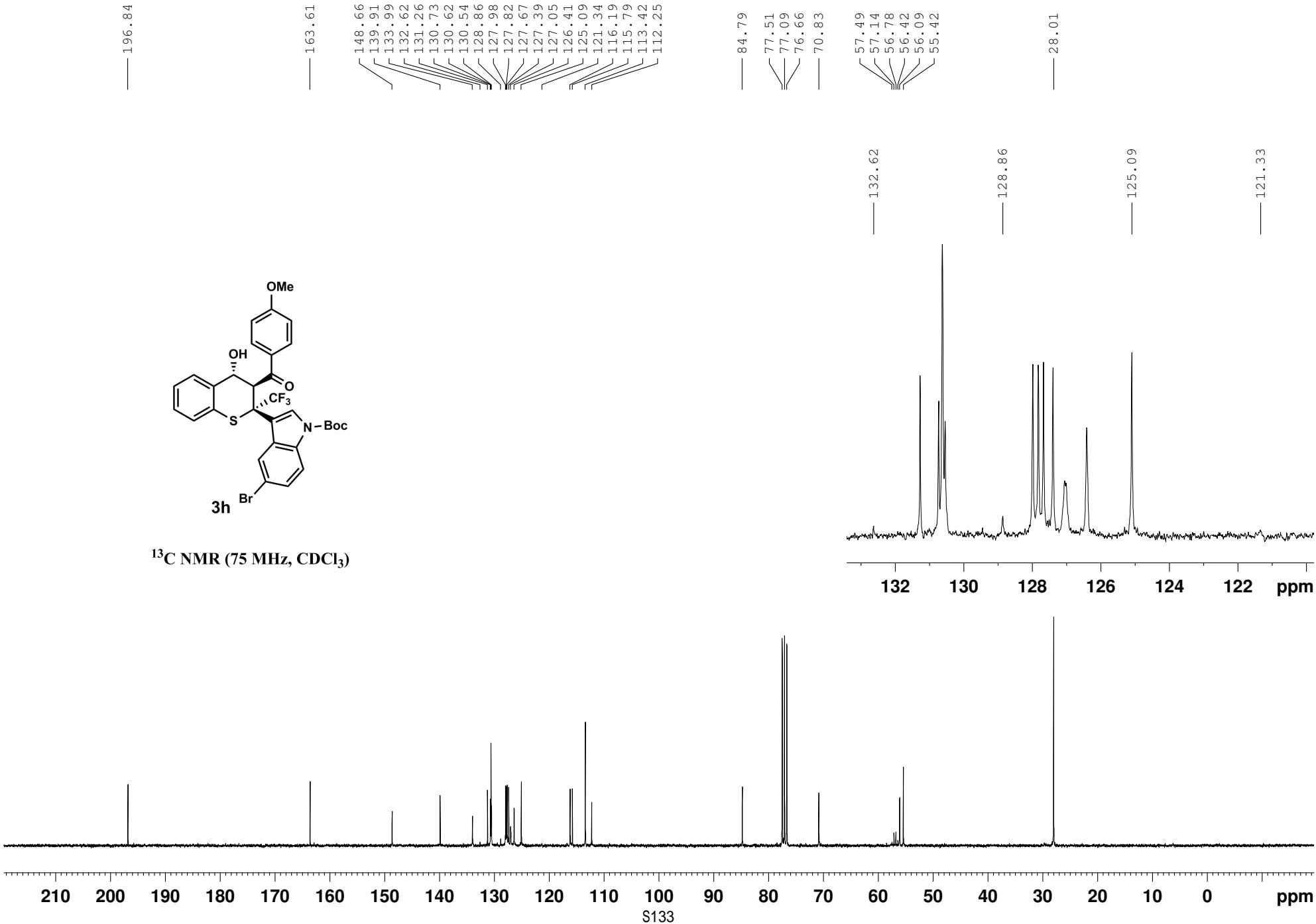
3h

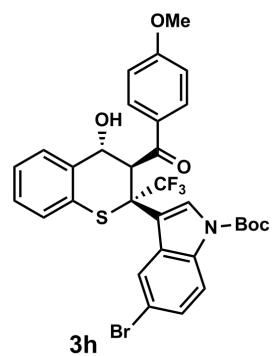
¹H NMR (300 MHz, CDCl₃)



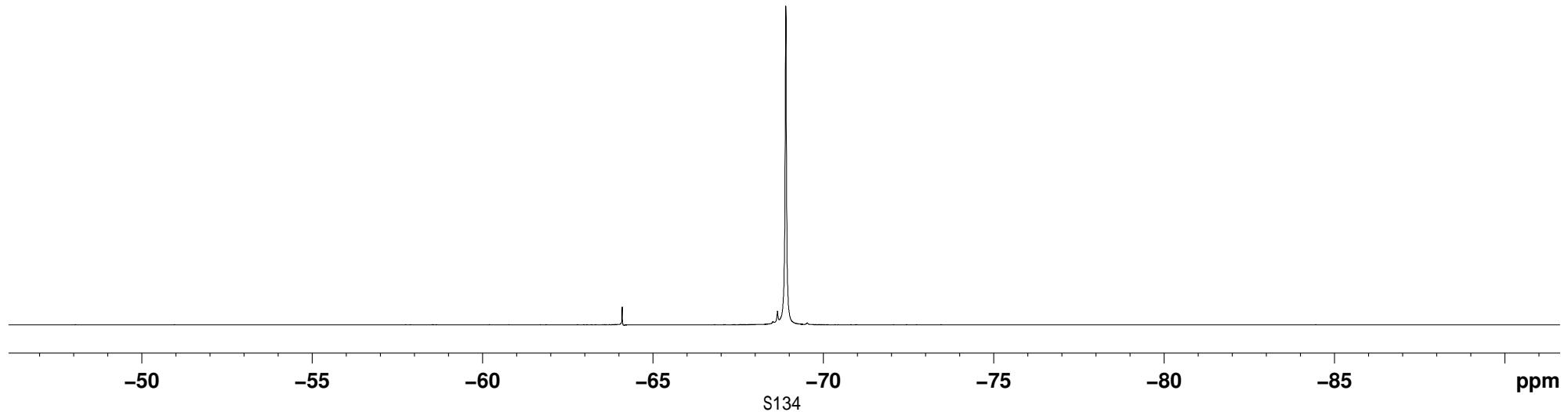


¹³C NMR (75 MHz, CDCl₃)





¹⁹F NMR (282 MHz, CDCl₃)

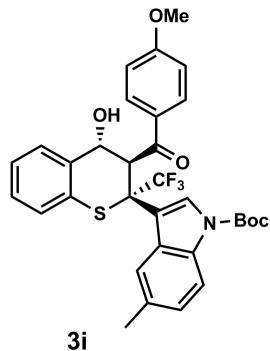


7.906
7.877
7.860
7.649
7.624
7.353
7.329
7.309
7.285
7.260
7.244
7.216
6.994
6.965
6.623
6.594

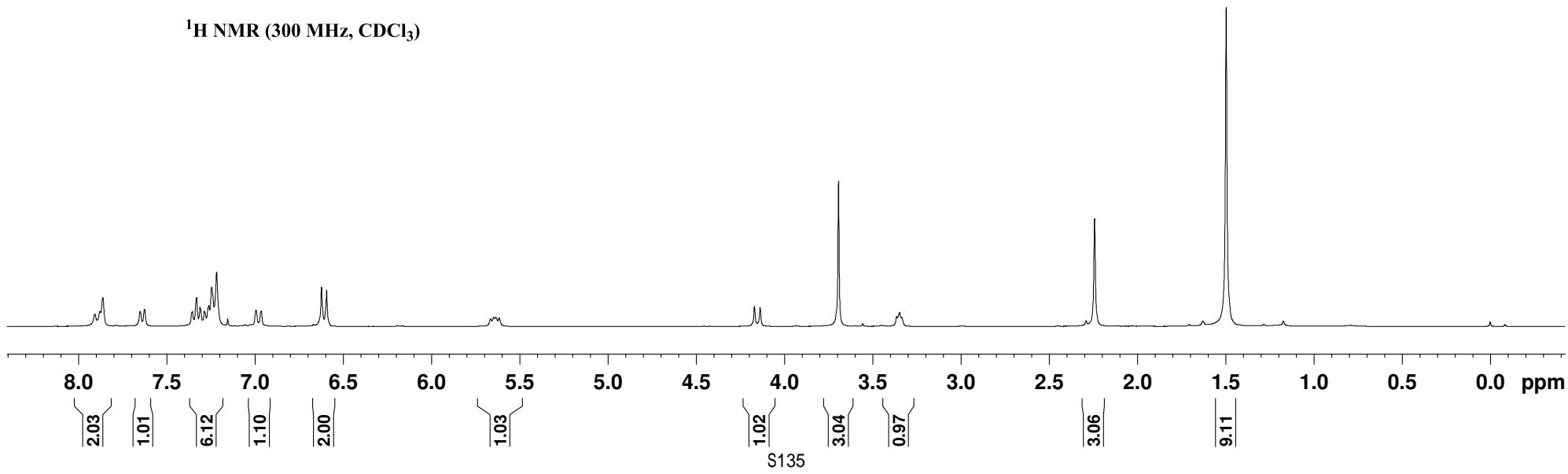
5.666
5.647
5.635
5.616

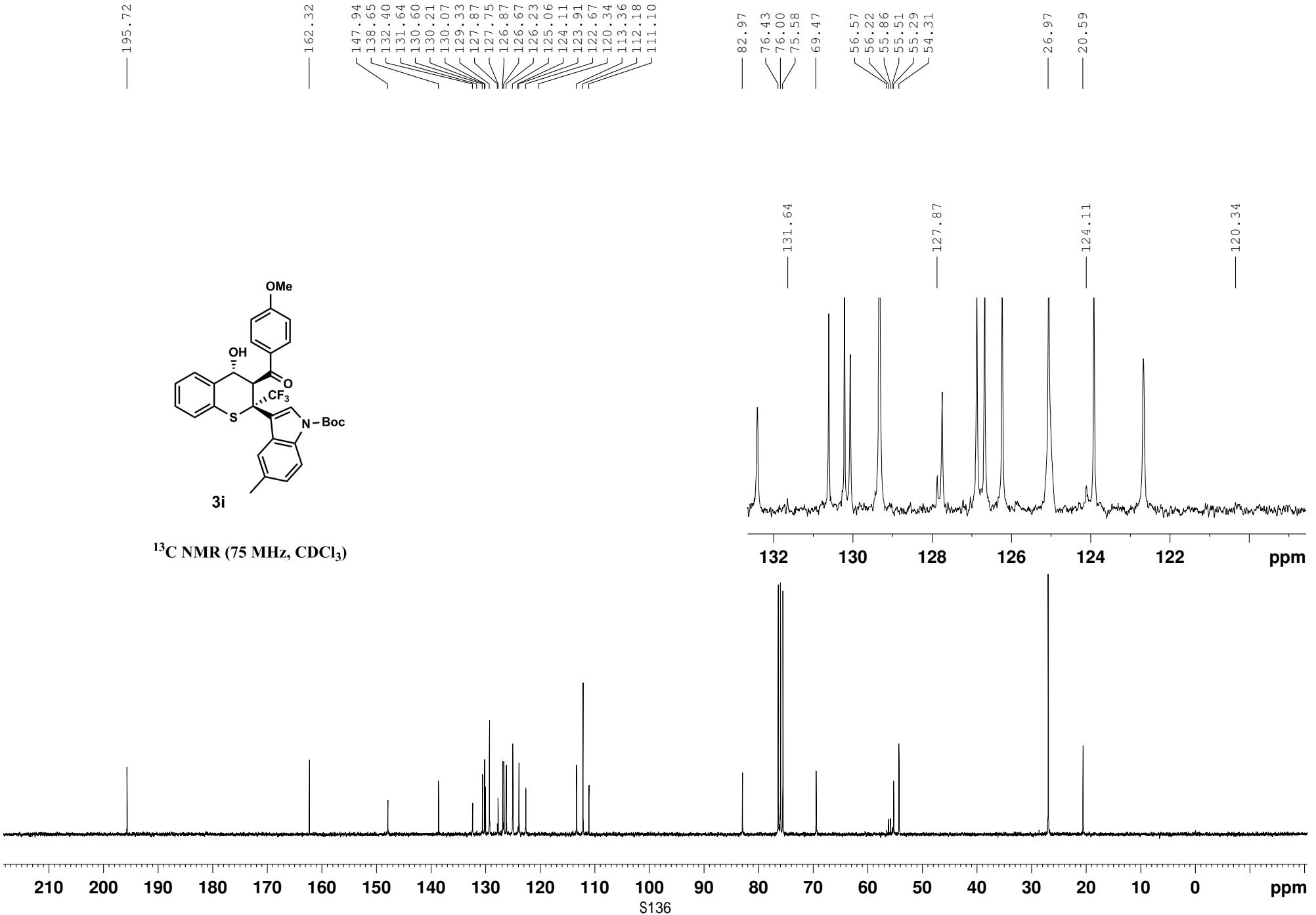
4.170
4.137
3.693
3.364
3.347
3.335

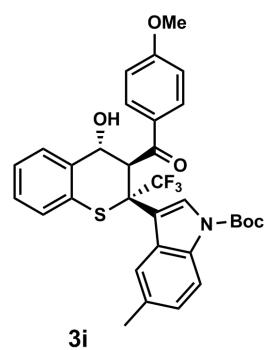
2.242
1.496
-0.000



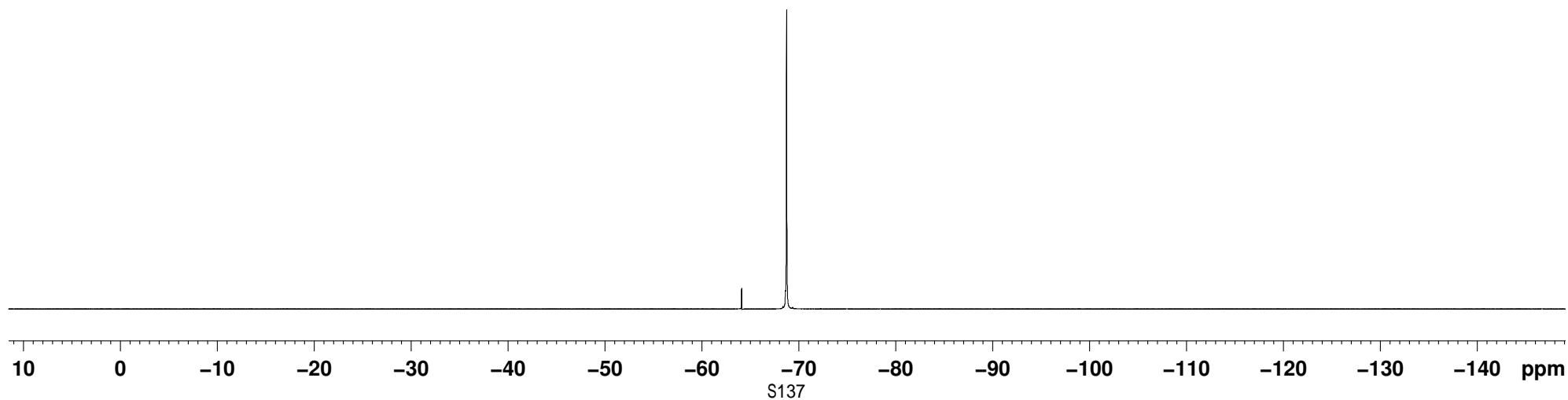
¹H NMR (300 MHz, CDCl₃)







¹⁹F NMR (282 MHz, CDCl₃)



-0.000

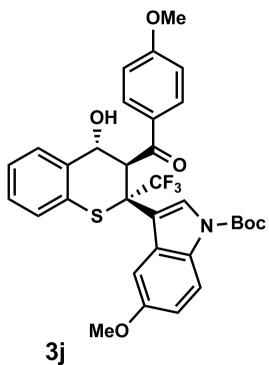
— 1.575

— 3.770
— 3.633
— 3.502
— 3.483

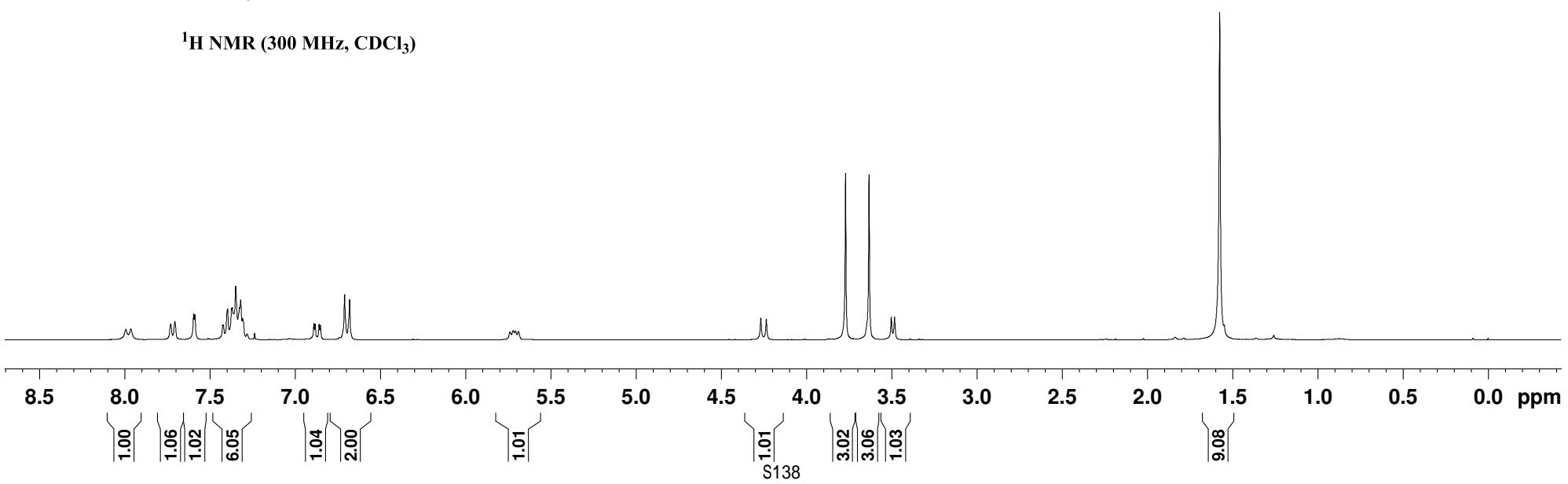
— 4.268
— 4.236

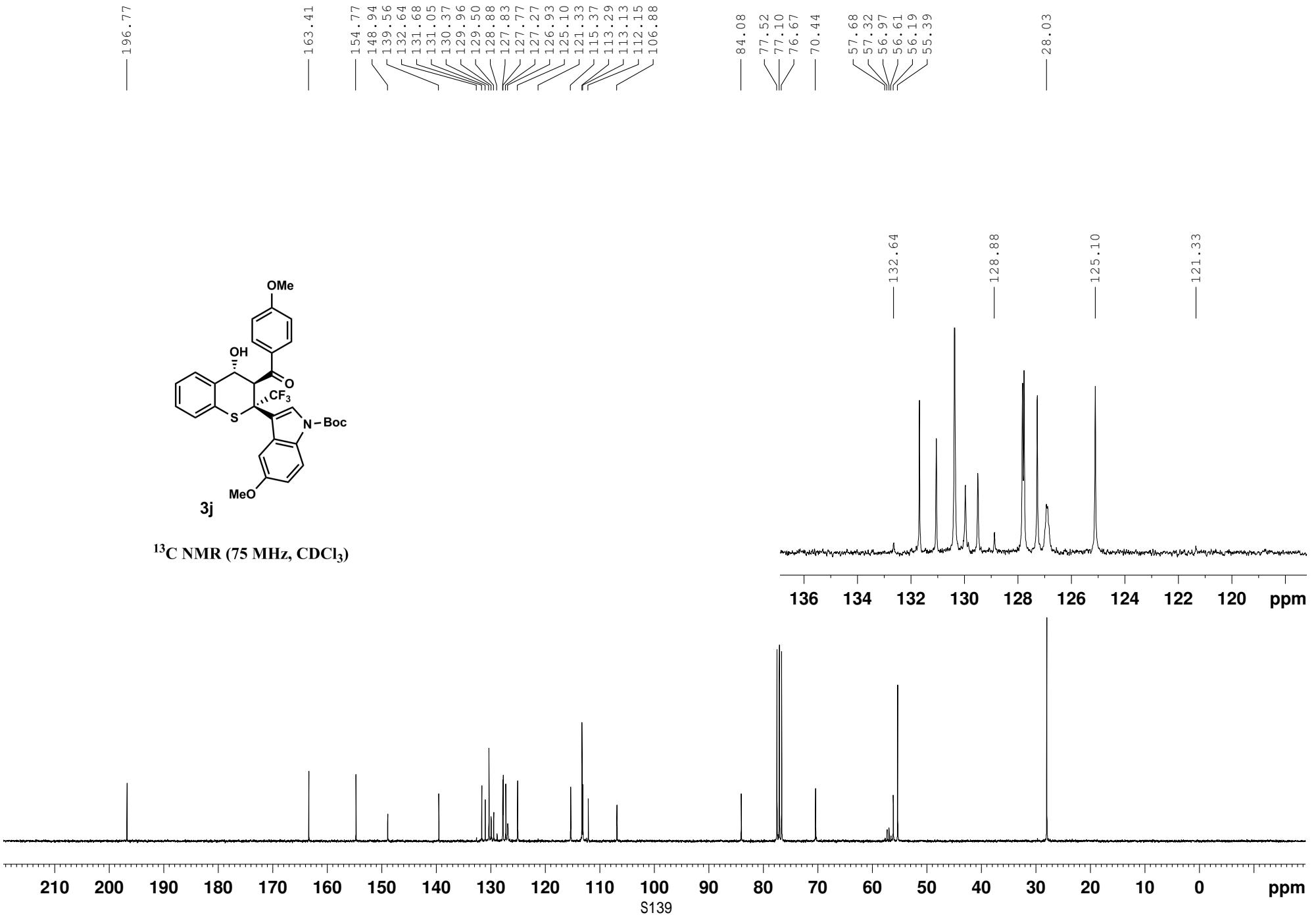
— 5.740
— 5.721
— 5.708
— 5.690

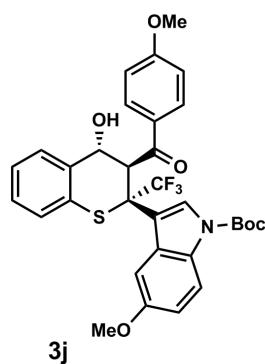
— 7.994
— 7.964
— 7.731
— 7.706
— 7.596
— 7.589
— 7.426
— 7.422
— 7.397
— 7.374
— 7.369
— 7.350
— 7.327
— 7.320
— 7.309
— 7.283
— 6.891
— 6.883
— 6.860
— 6.852
— 6.710
— 6.681



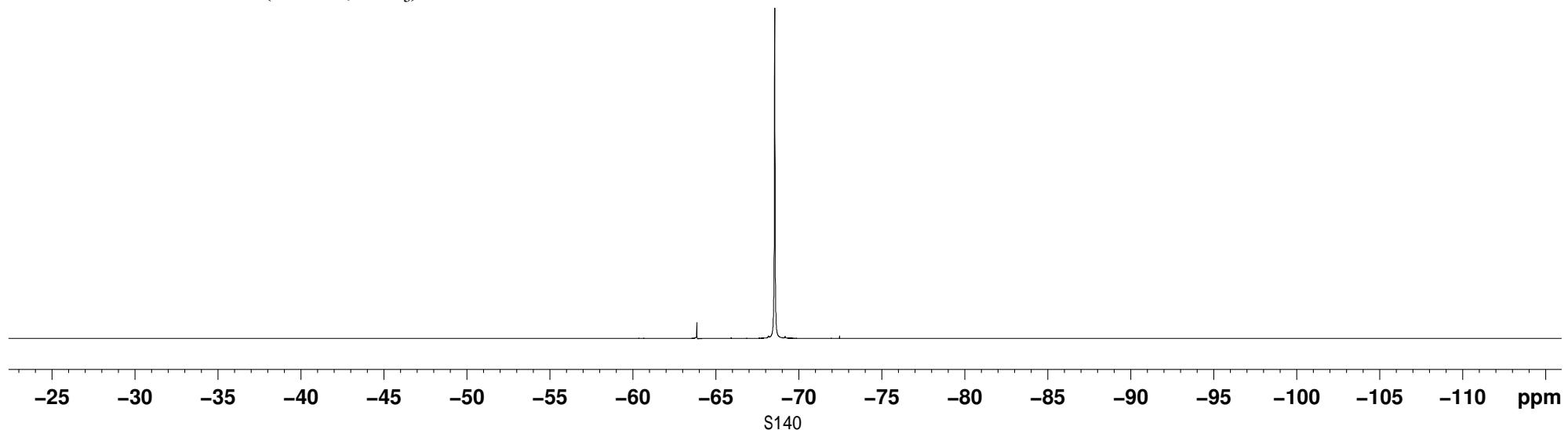
¹H NMR (300 MHz, CDCl₃)







¹⁹F NMR (282 MHz, CDCl₃)



8.465
8.145
8.116
7.644
7.620
7.484
7.417
7.397
7.367
7.363
7.354
7.346
7.331
7.317
7.298
7.274
7.250
7.228
6.672
6.643

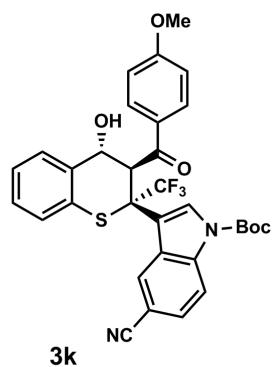
5.564
5.546
5.532
5.514

4.220
4.186

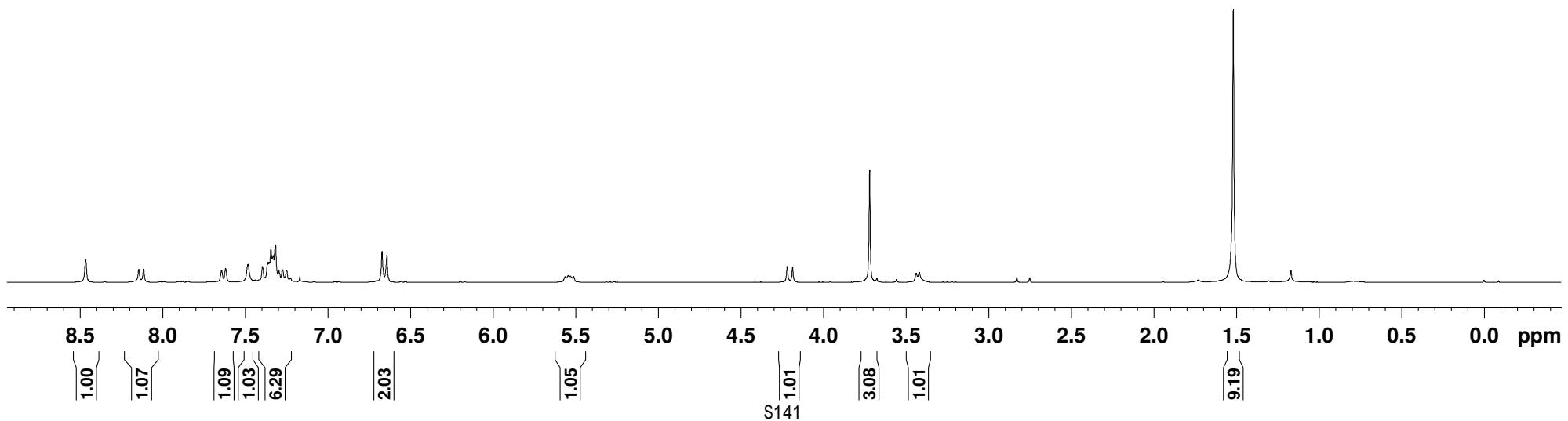
3.720
3.438
3.419

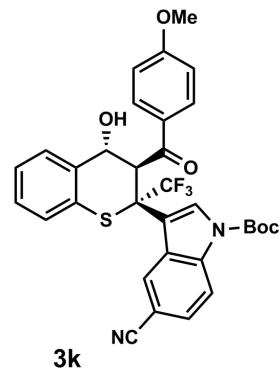
1.518

-0.000

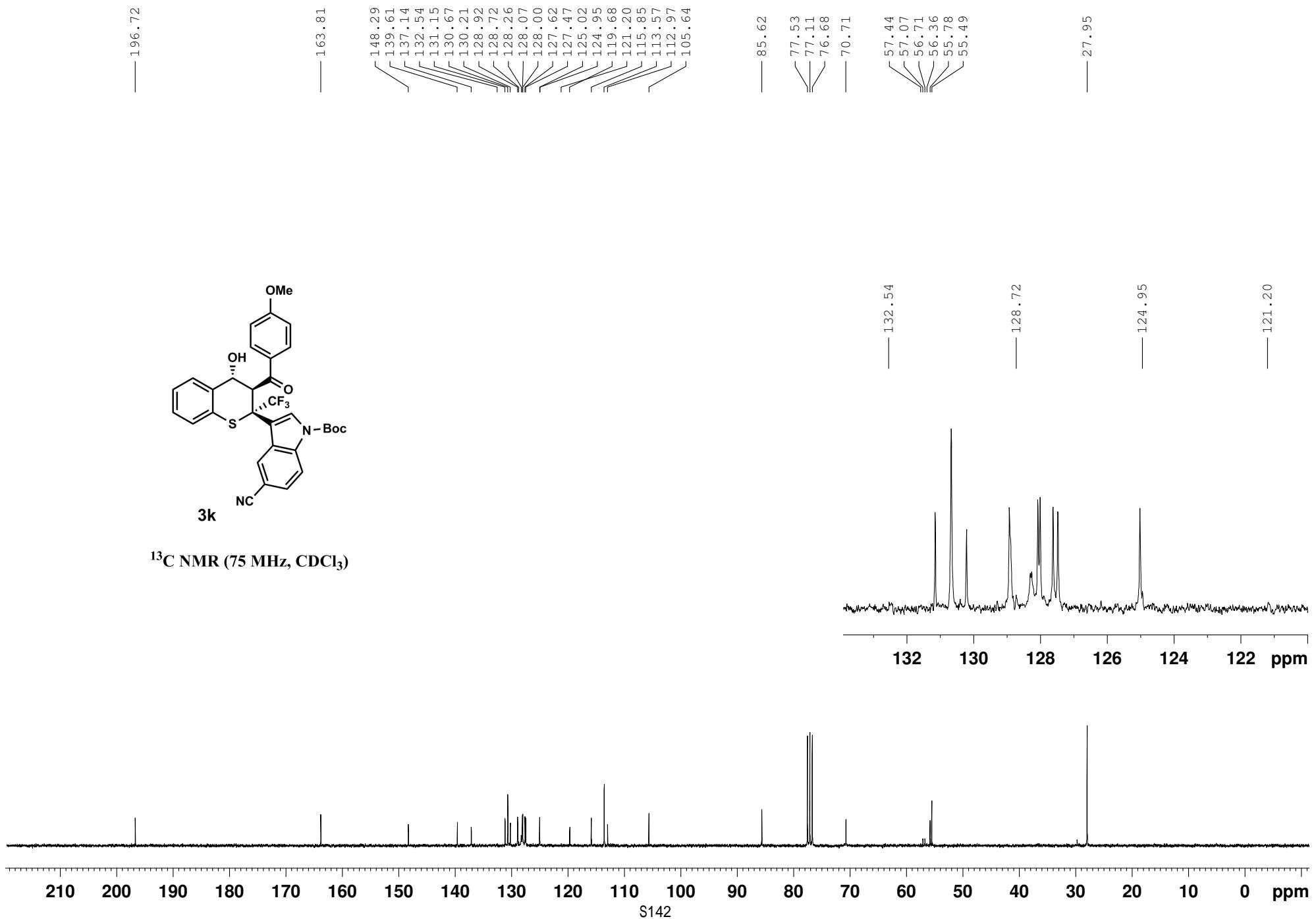


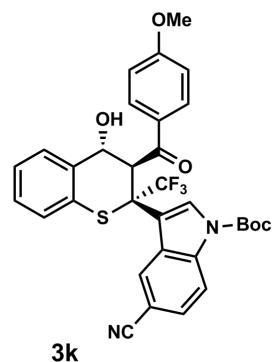
¹H NMR (300 MHz, CDCl₃)



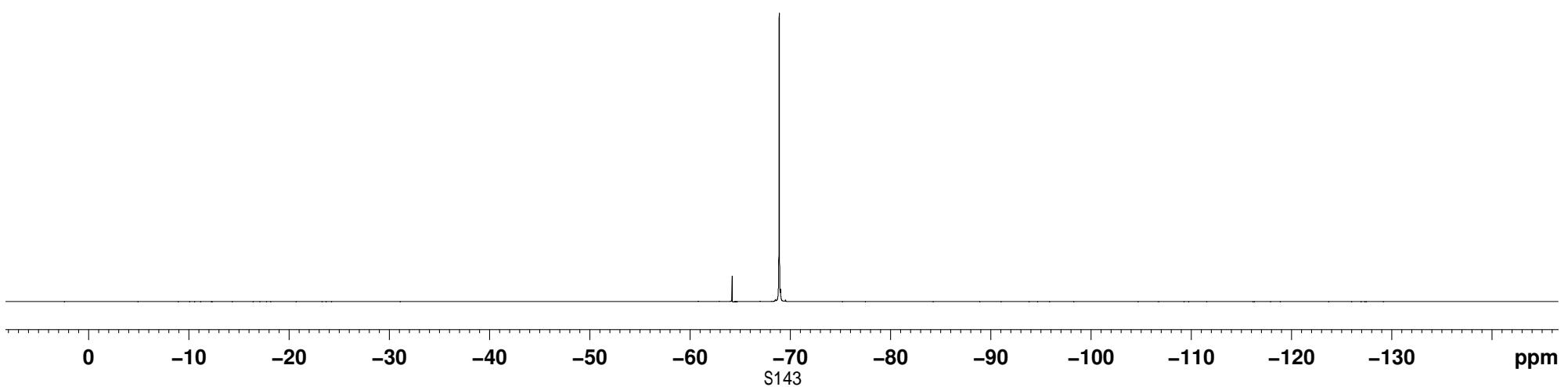


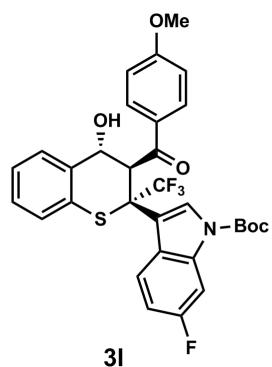
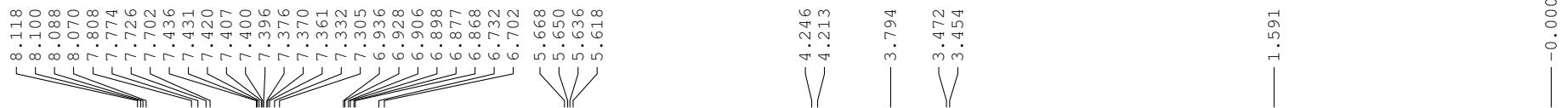
¹³C NMR (75 MHz, CDCl₃)



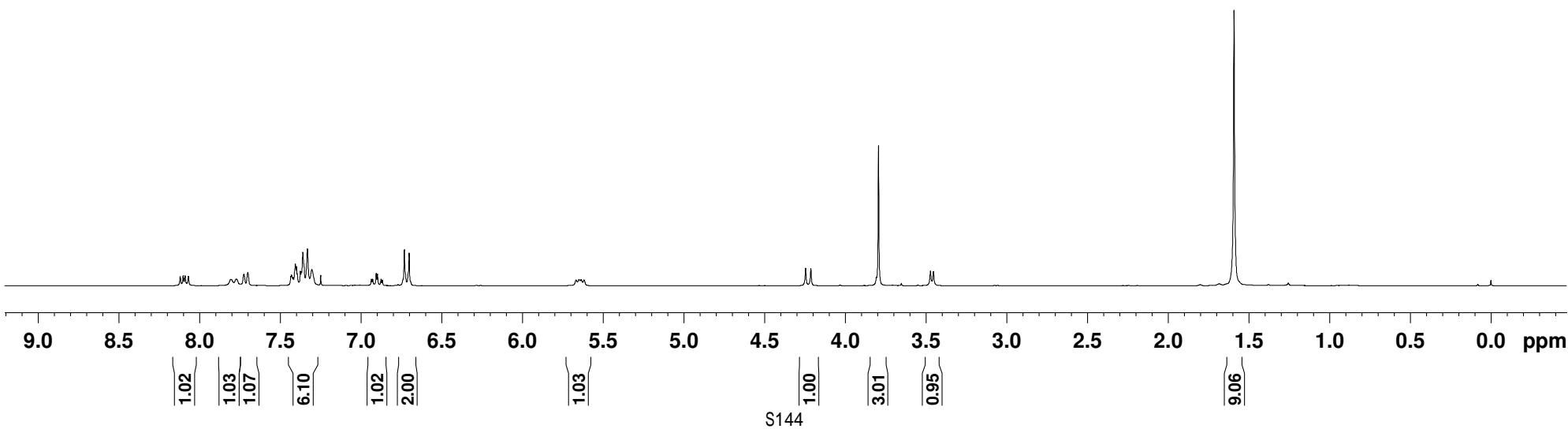


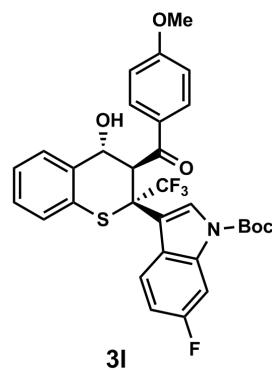
^{19}F NMR (282 MHz, CDCl_3)



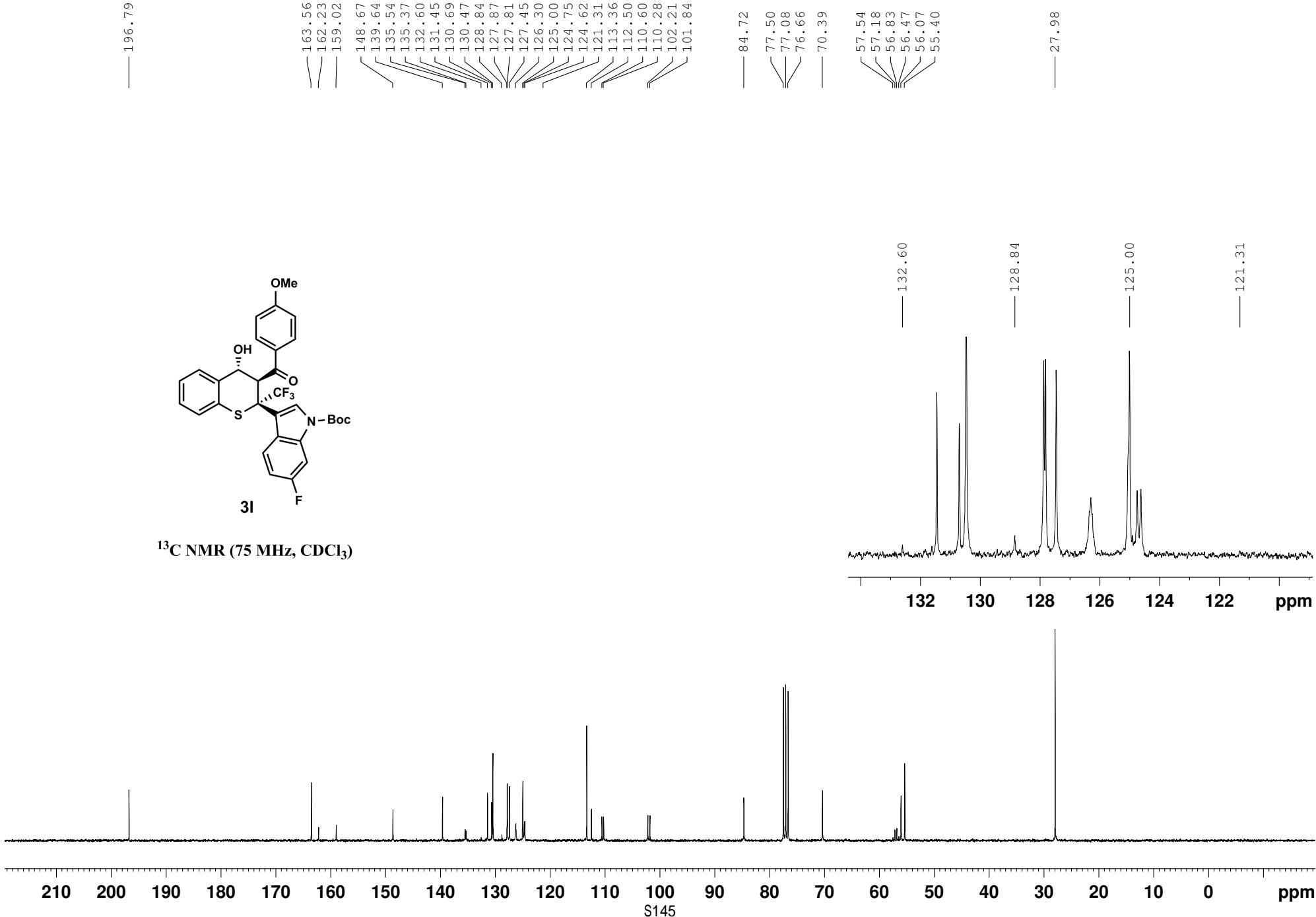


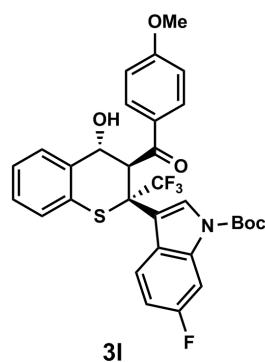
¹H NMR (300 MHz, CDCl₃)



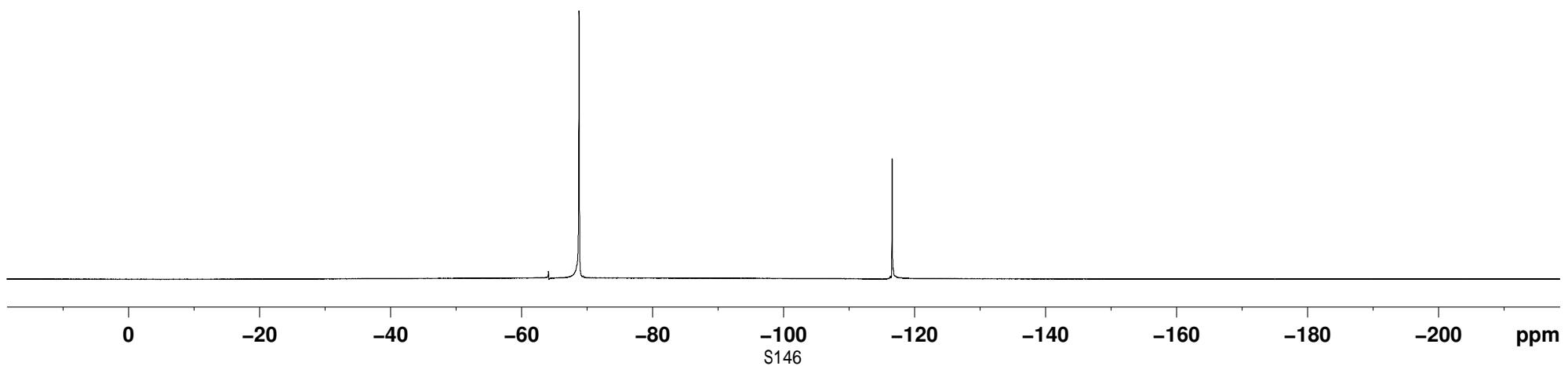


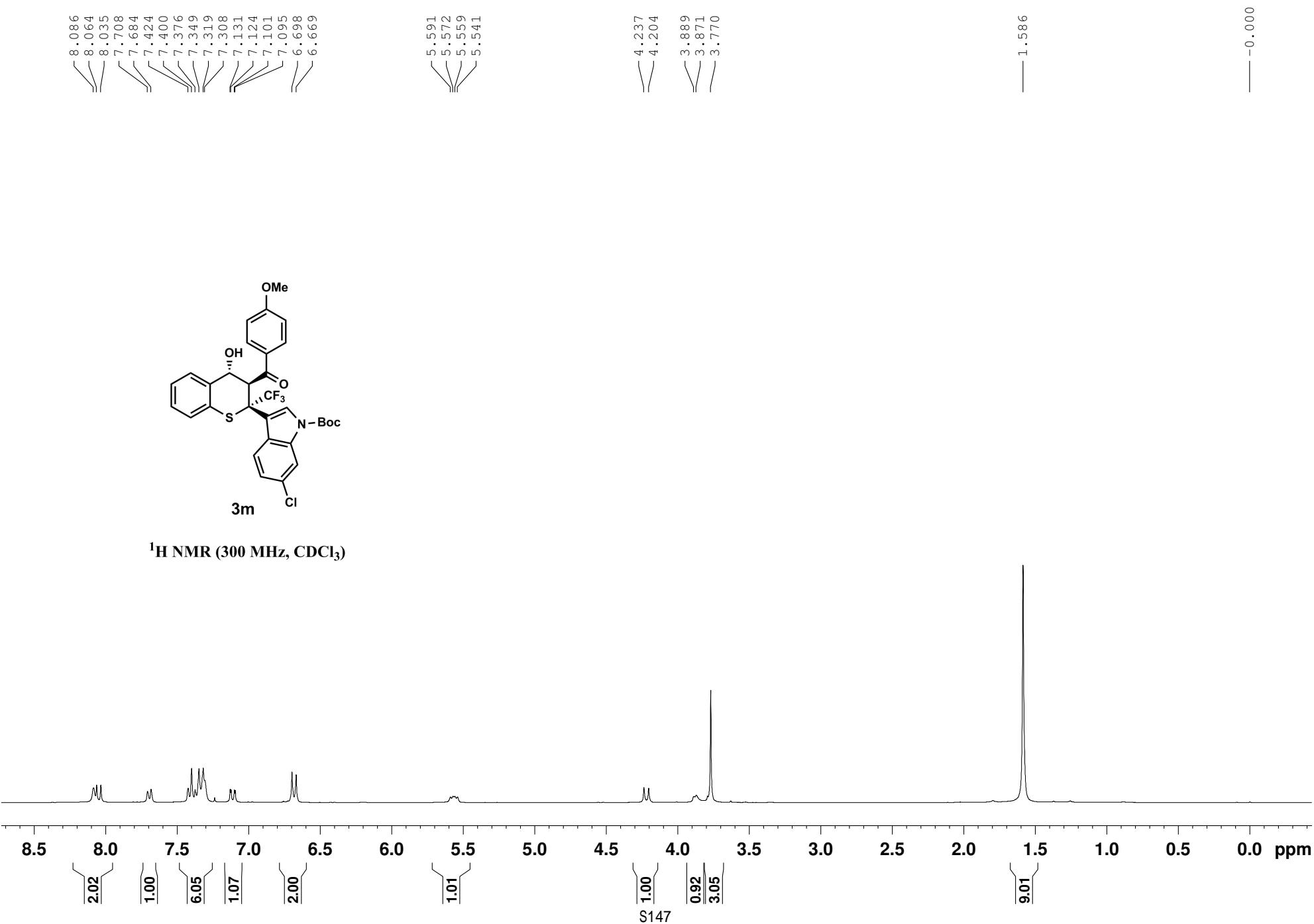
^{13}C NMR (75 MHz, CDCl_3)

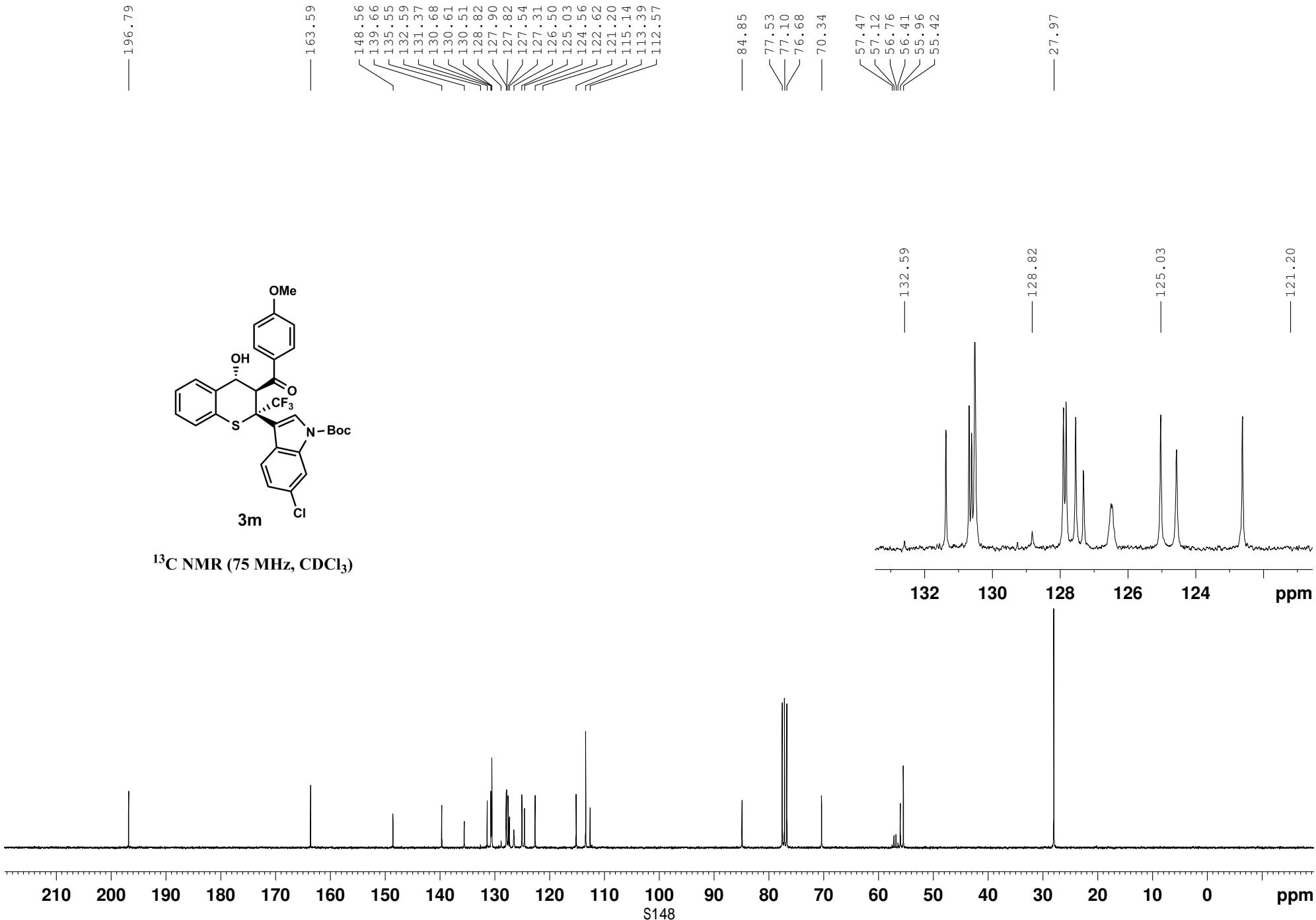


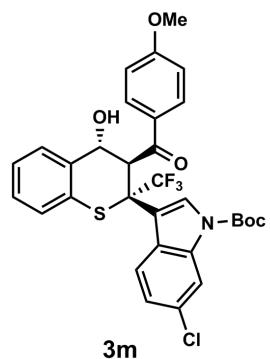


¹⁹F NMR (282 MHz, CDCl₃)

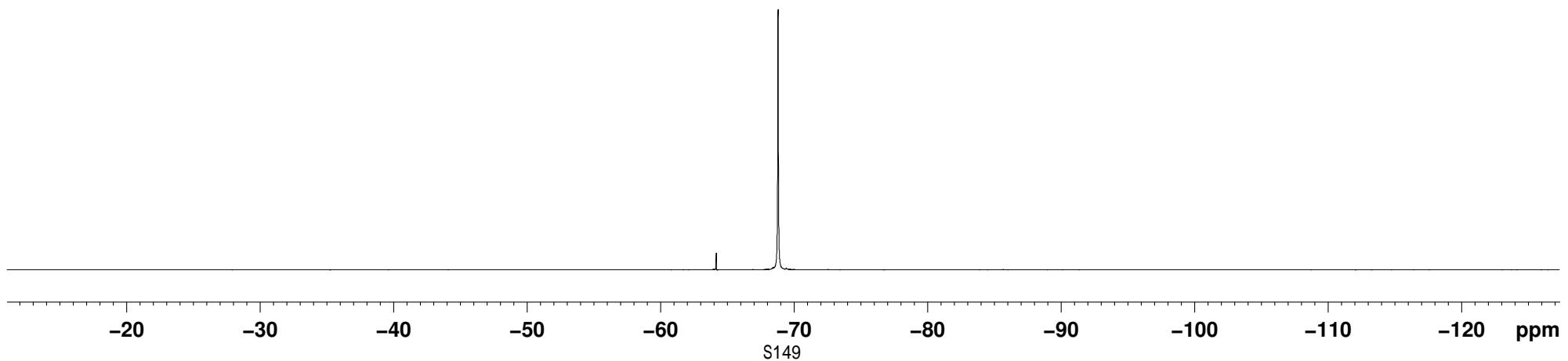








¹⁹F NMR (282 MHz, CDCl₃)



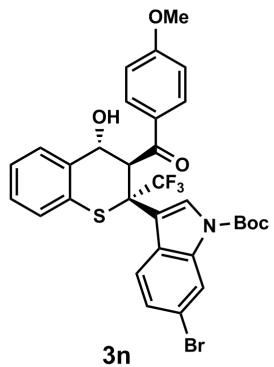
— 8.181
— 7.926
— 7.897
— 7.631
— 7.606
— 7.338
— 7.315
— 7.293
— 7.266
— 7.237
— 7.210
— 7.198
— 7.167
— 7.163
— 6.621
— 6.592

— 5.519
— 5.499
— 5.488
— 5.469

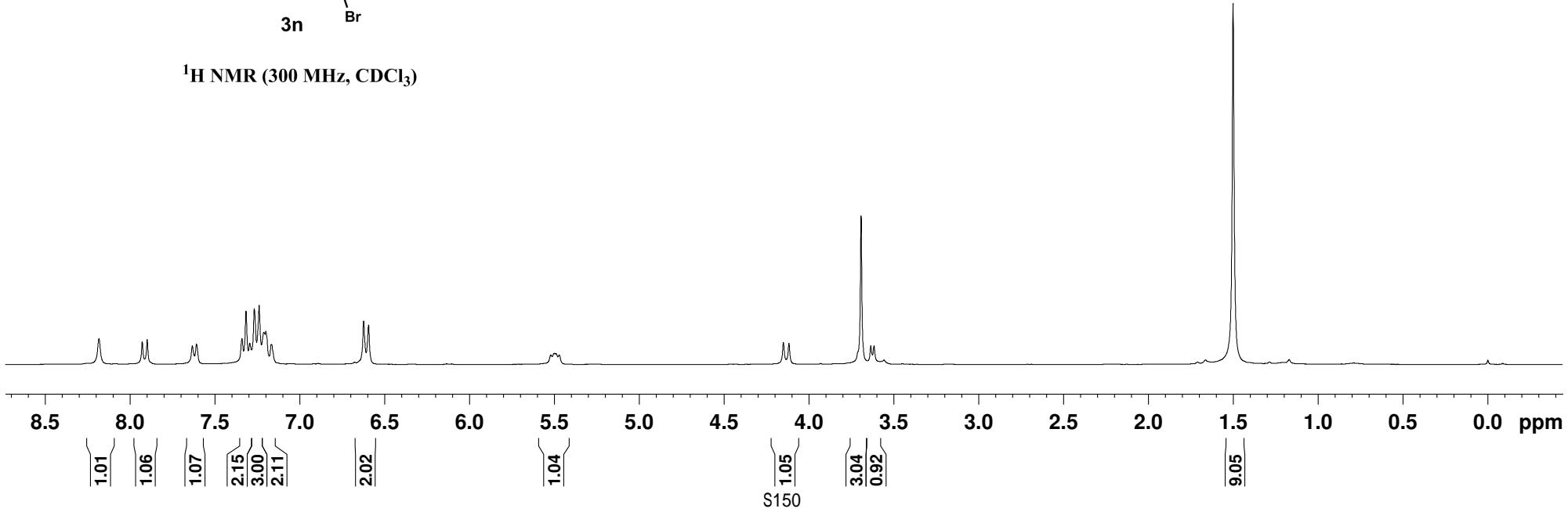
— 4.148
— 4.115
— 3.690
— 3.633
— 3.614

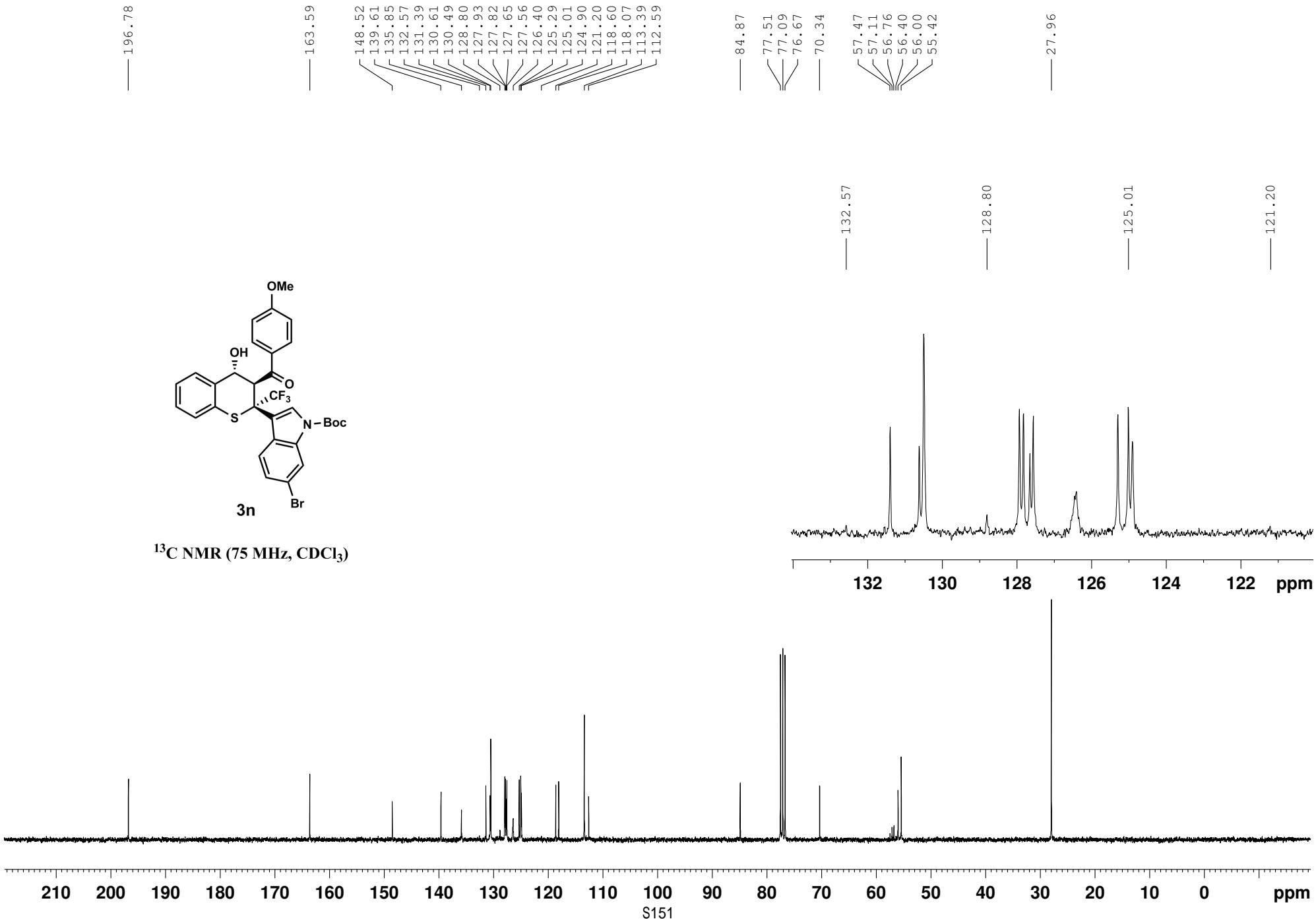
— 1.498

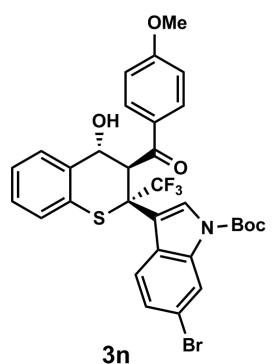
— -0.000



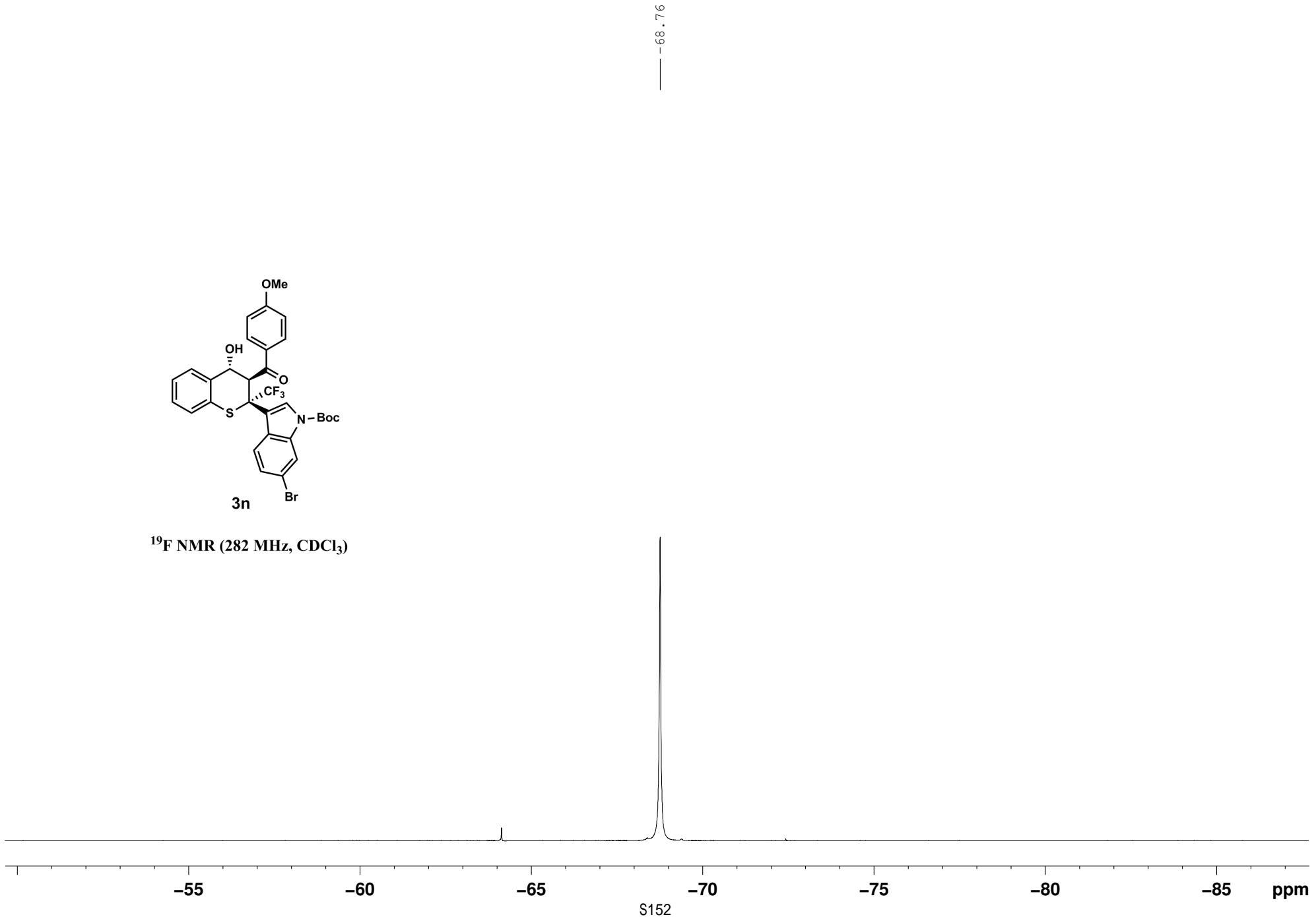
¹H NMR (300 MHz, CDCl₃)

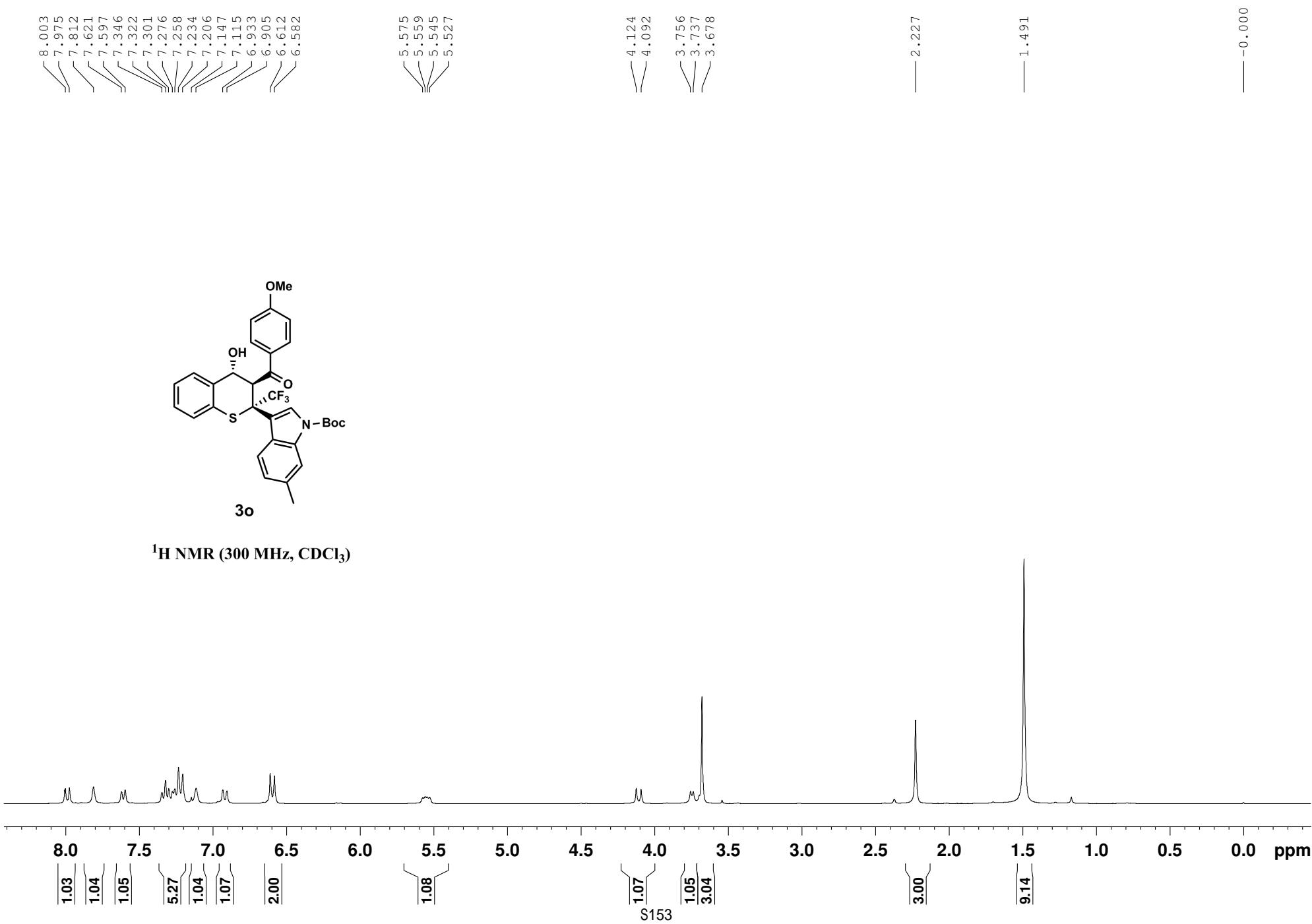


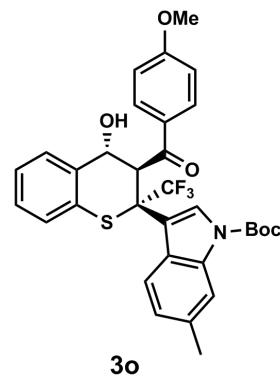




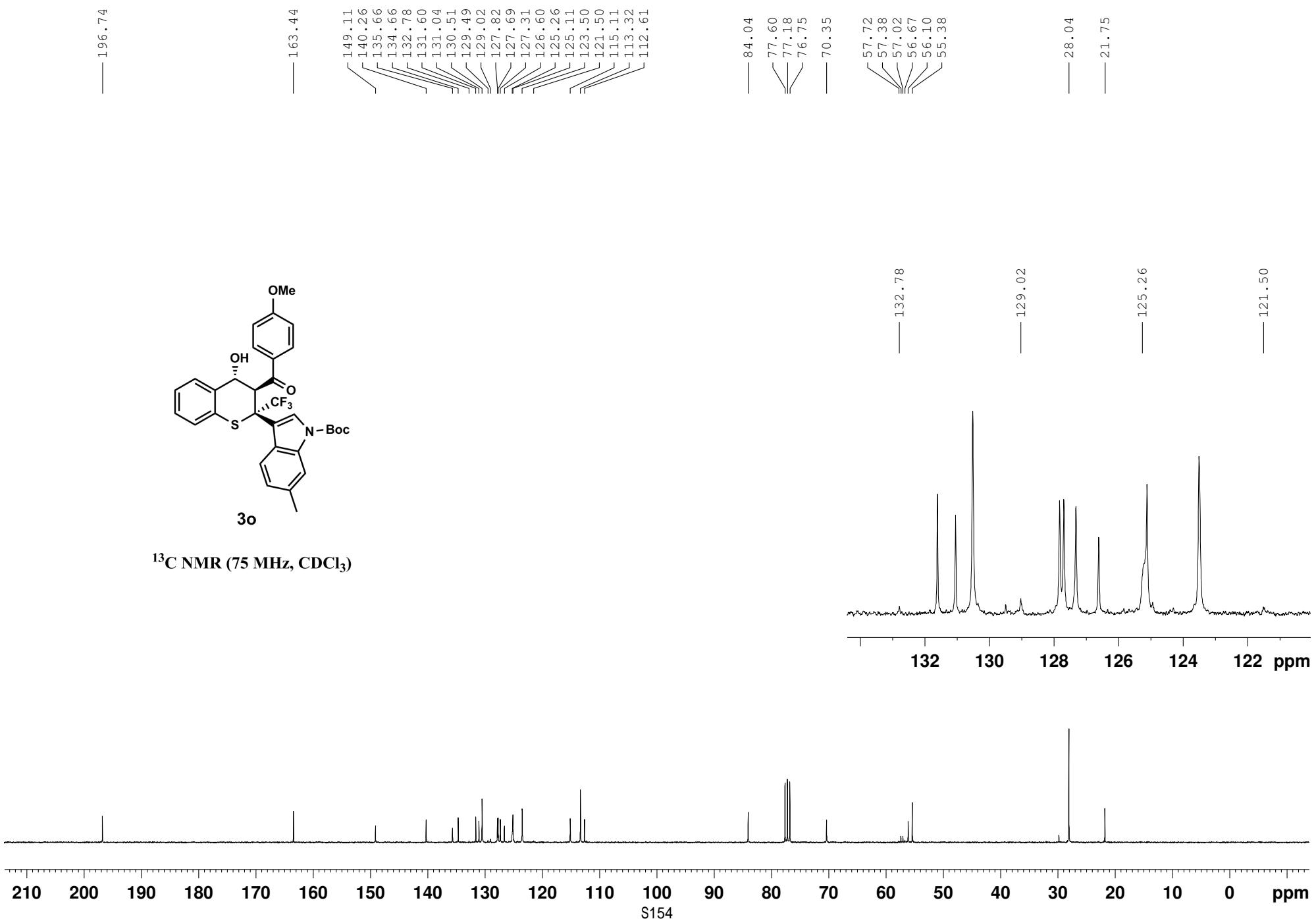
^{19}F NMR (282 MHz, CDCl_3)

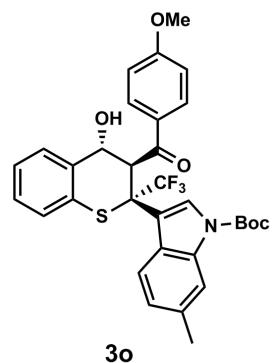




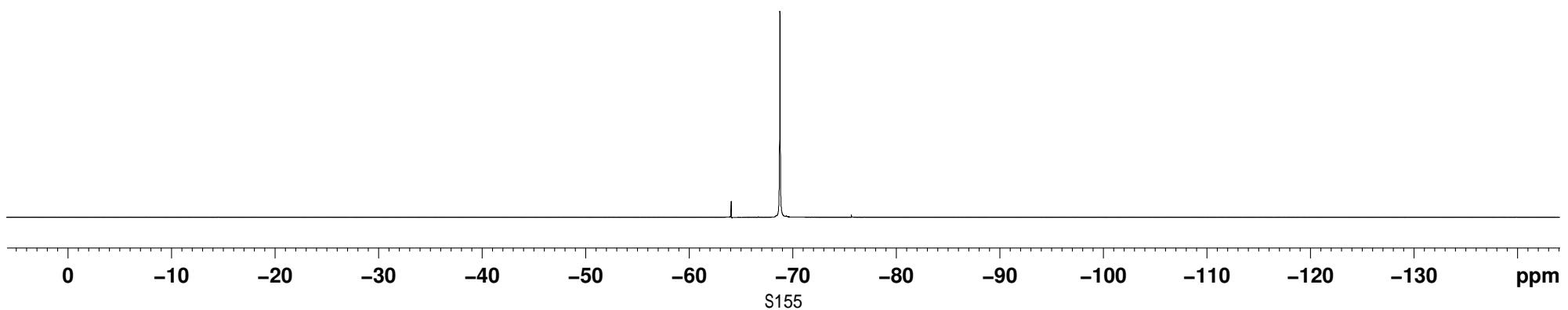


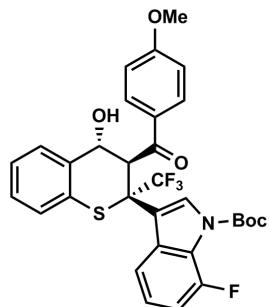
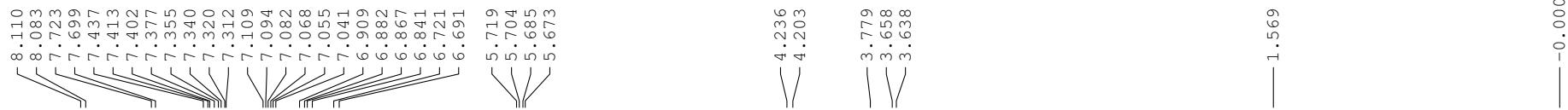
¹³C NMR (75 MHz, CDCl₃)



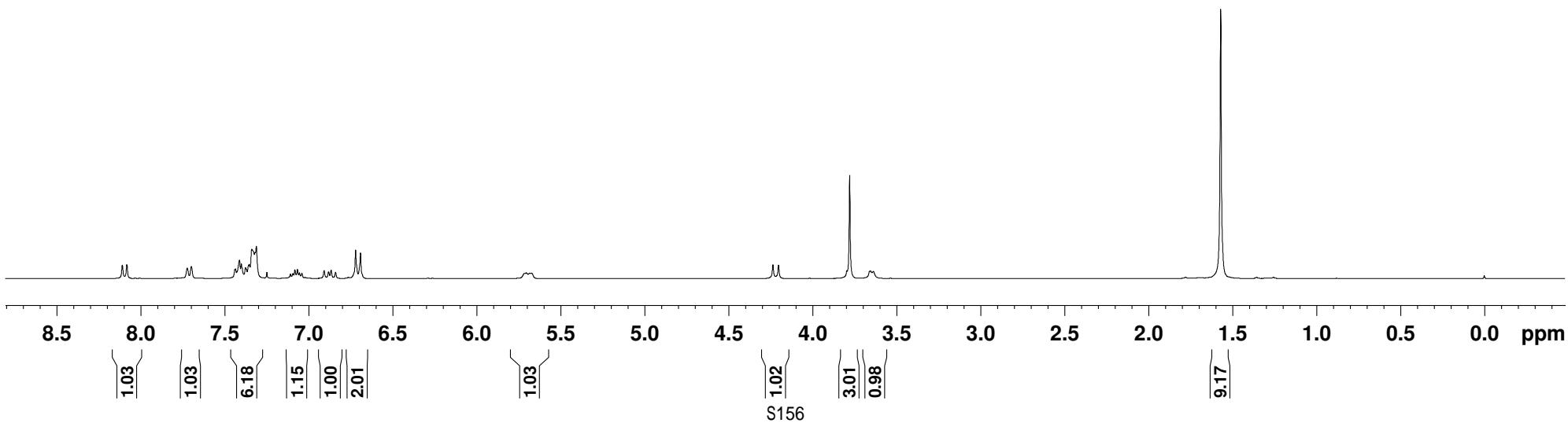


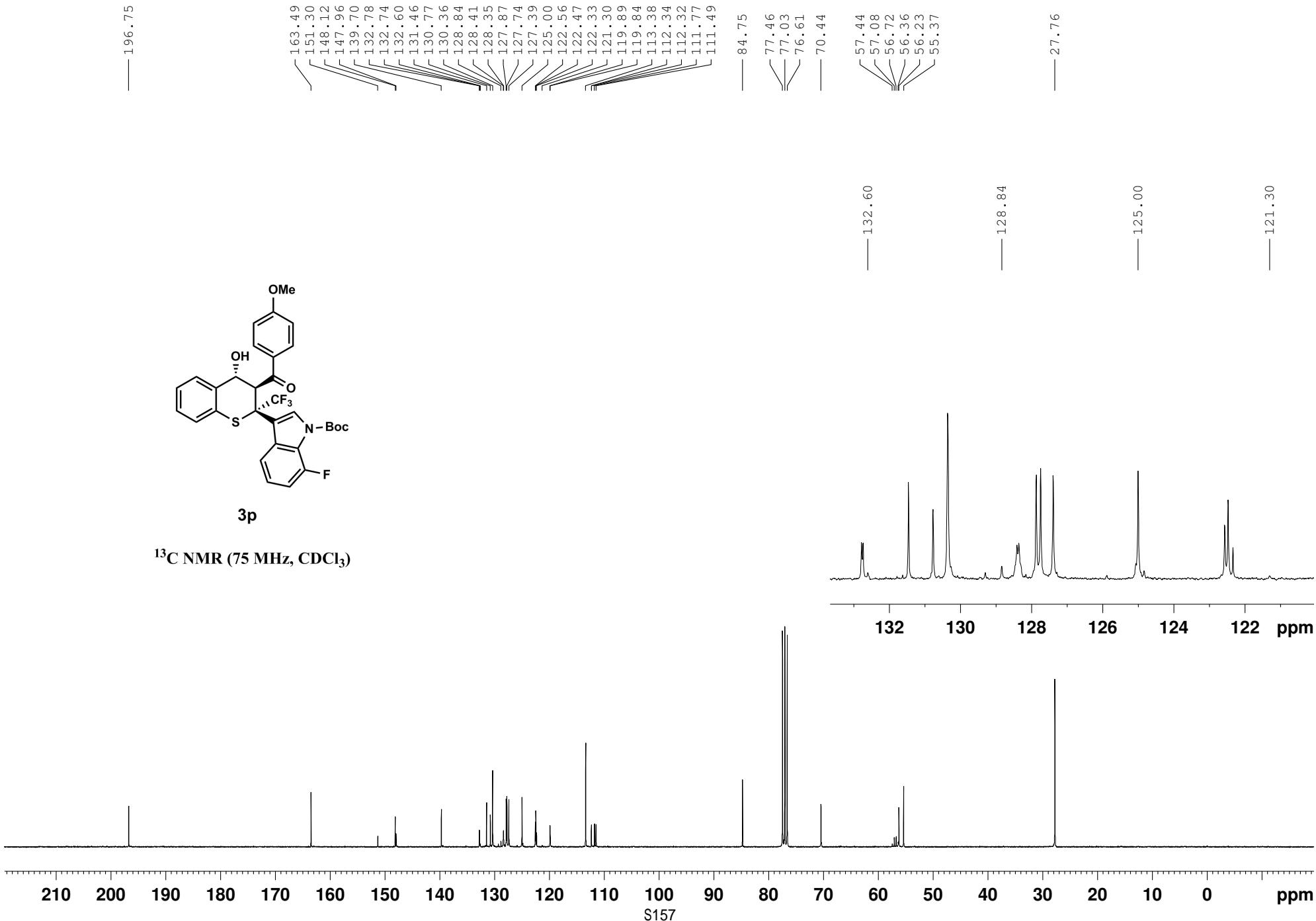
¹⁹F NMR (282 MHz, CDCl₃)

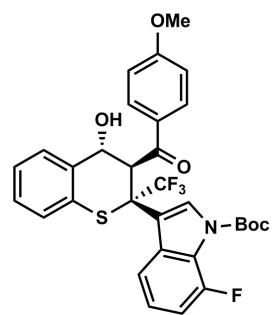




¹H NMR (300 MHz, CDCl₃)

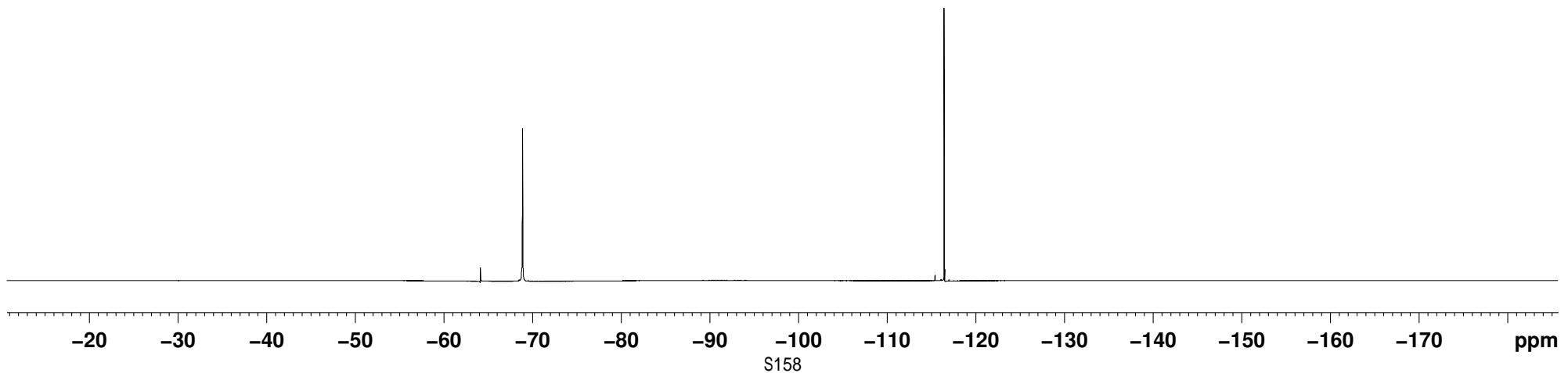


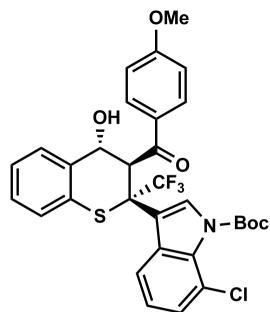
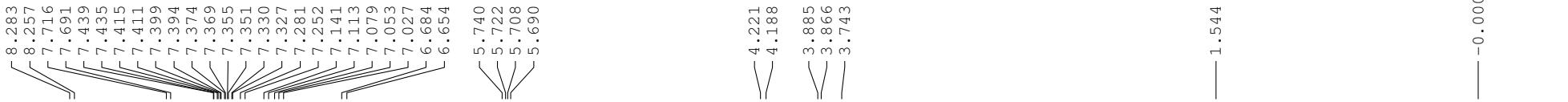




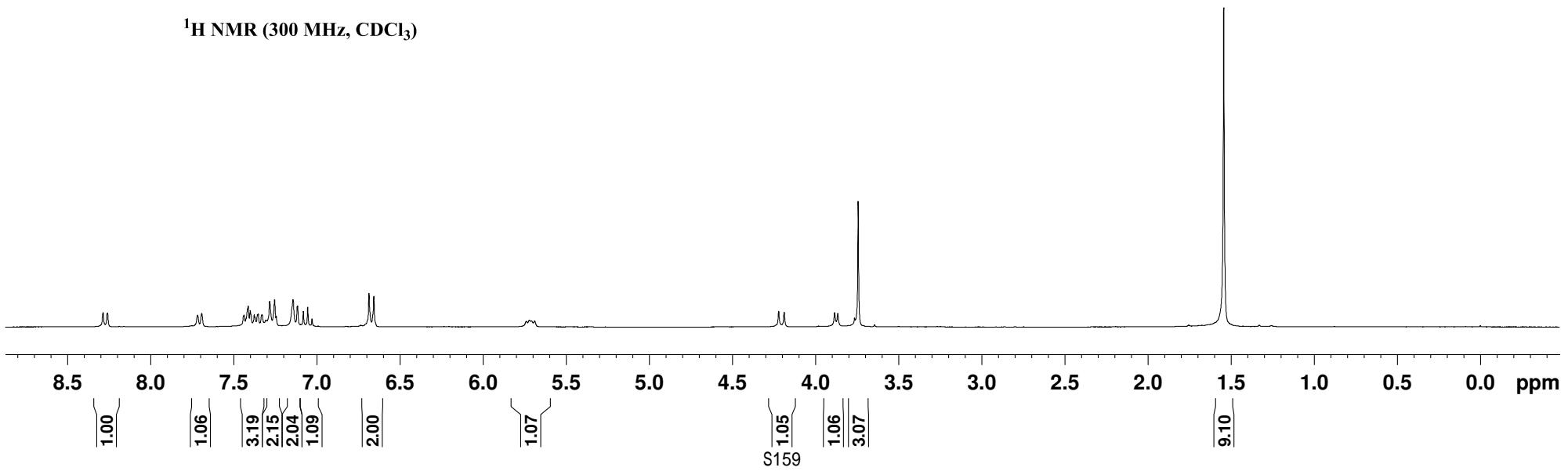
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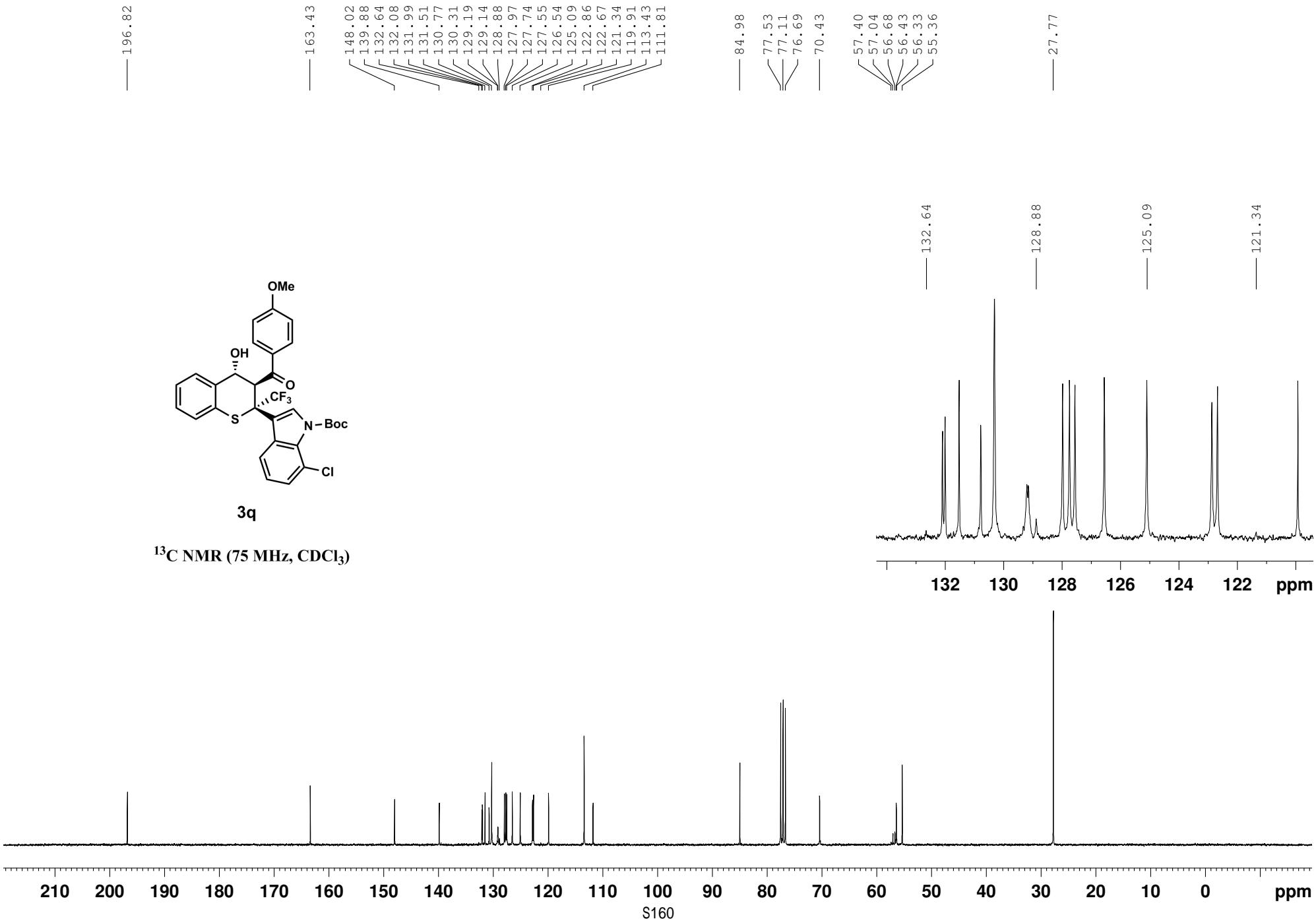
¹⁹F NMR (282 MHz, CDCl₃)

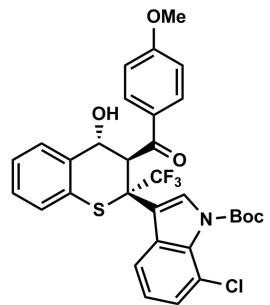




¹H NMR (300 MHz, CDCl₃)

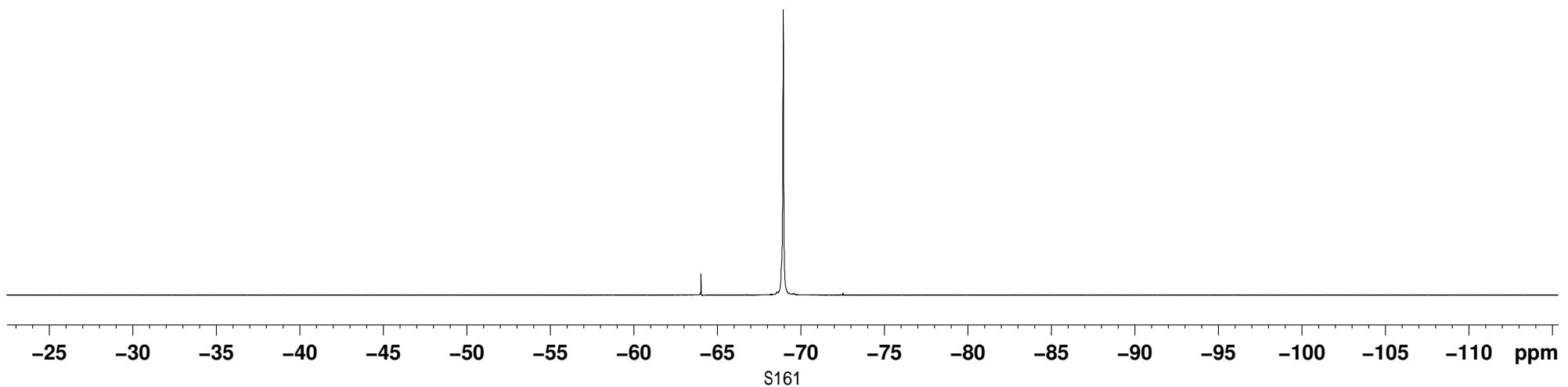


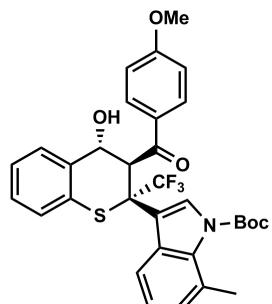
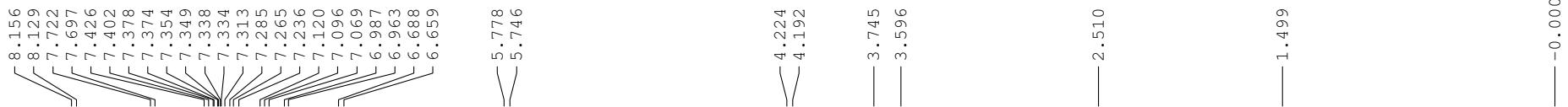




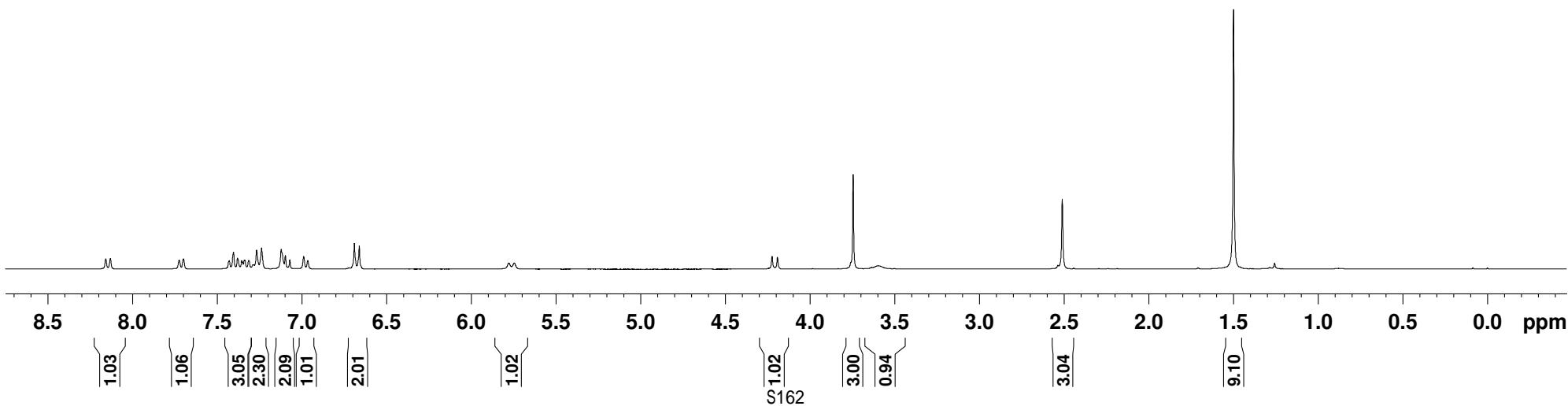
3q

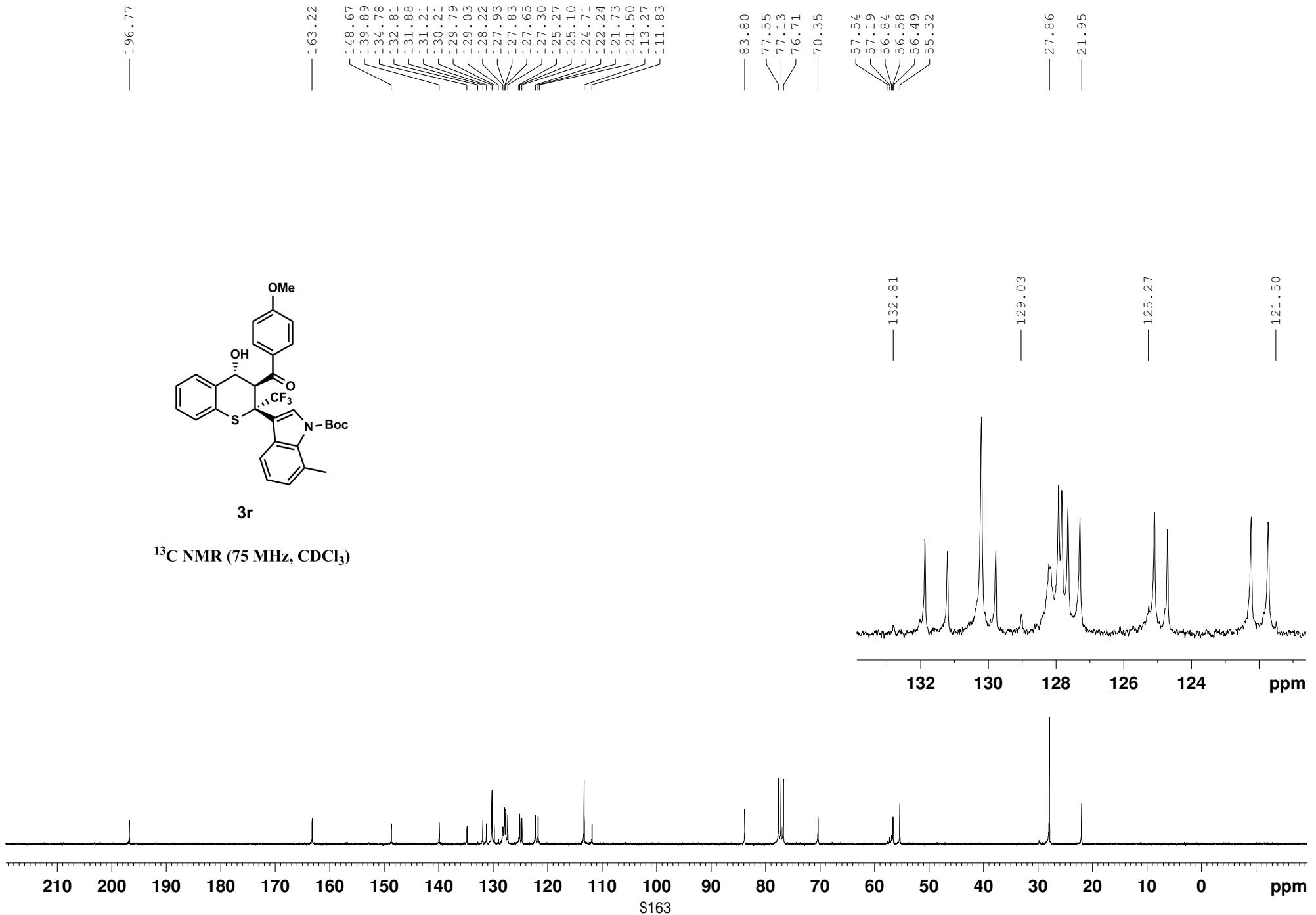
¹⁹F NMR (282 MHz, CDCl₃)

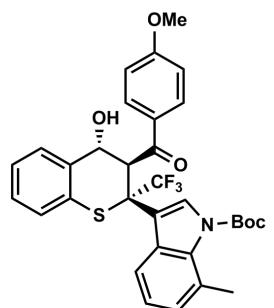




¹H NMR (300 MHz, CDCl₃)

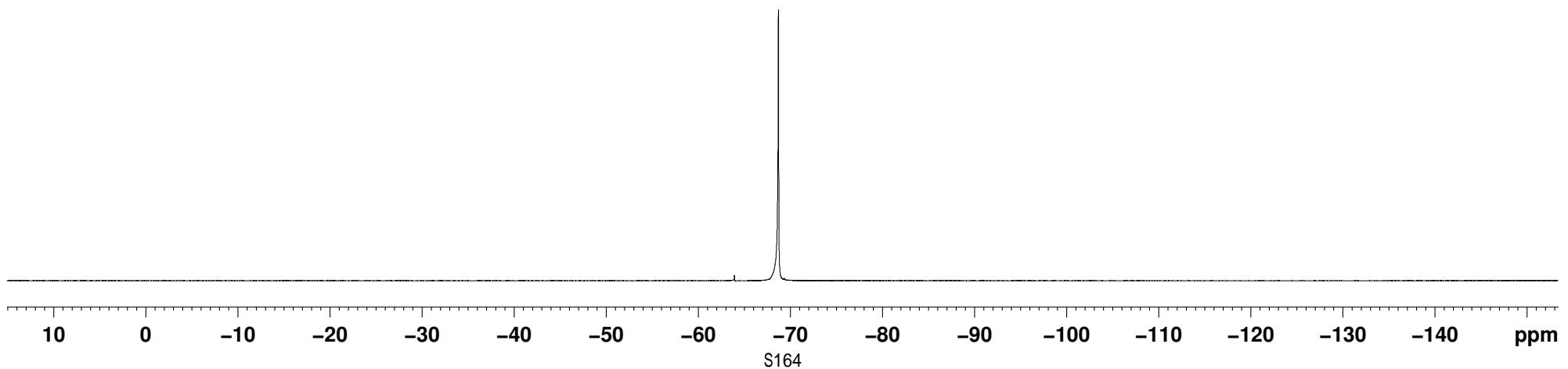


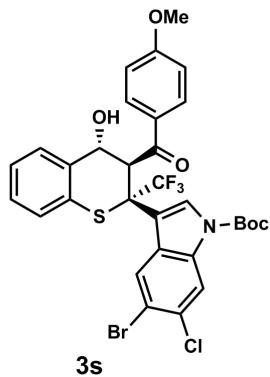
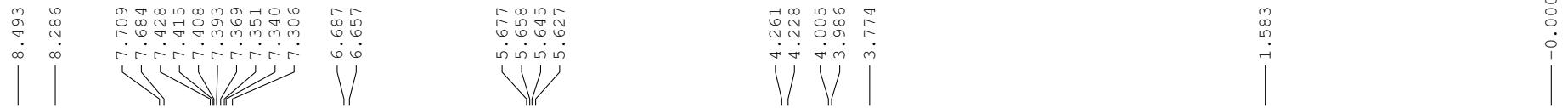




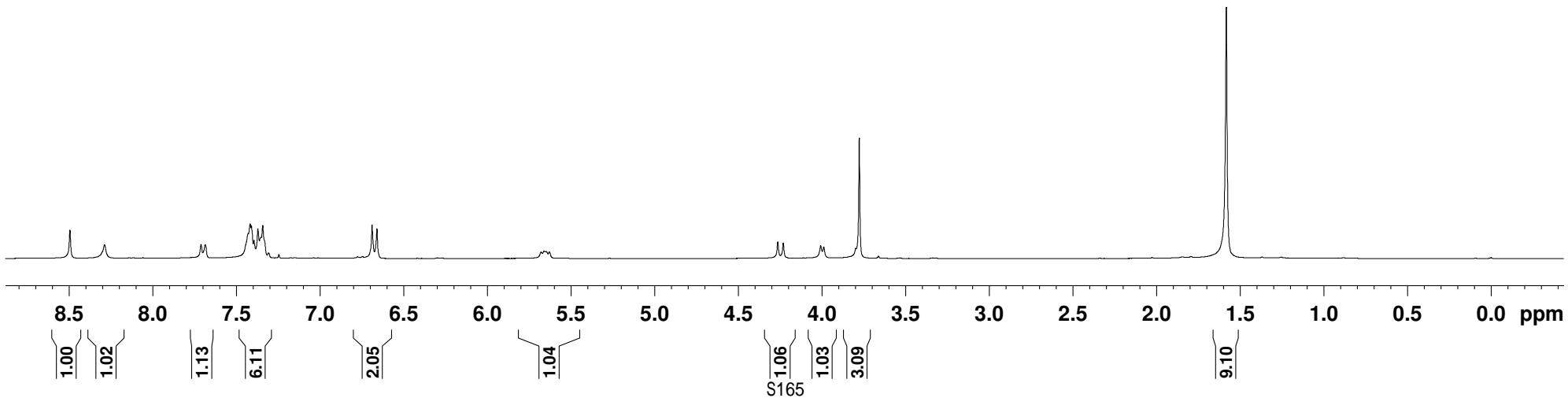
3r

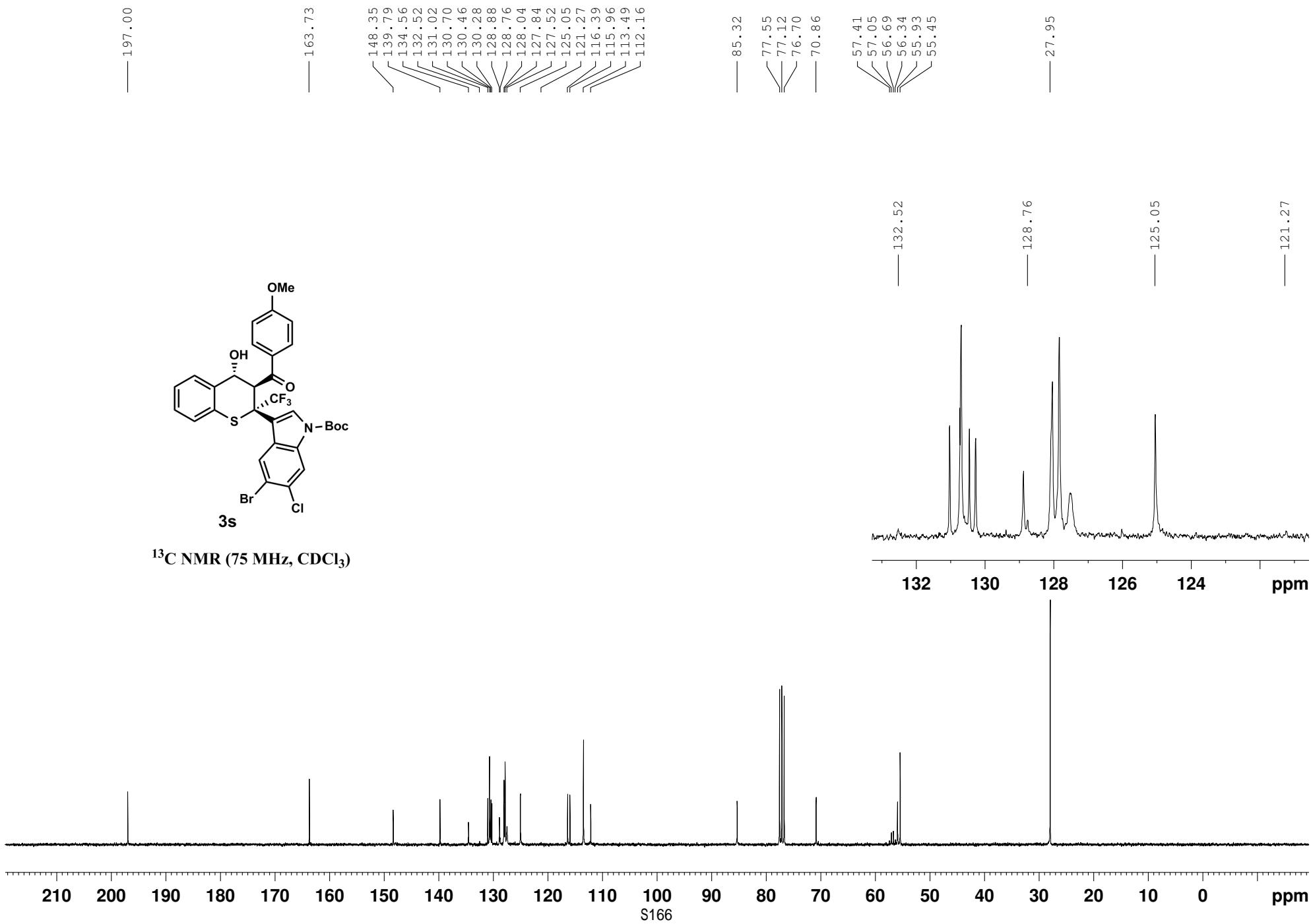
¹⁹F NMR (282 MHz, CDCl₃)

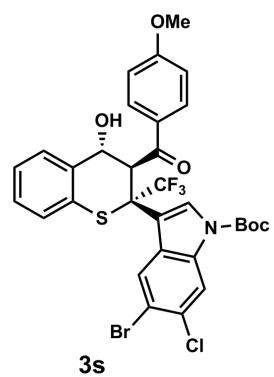




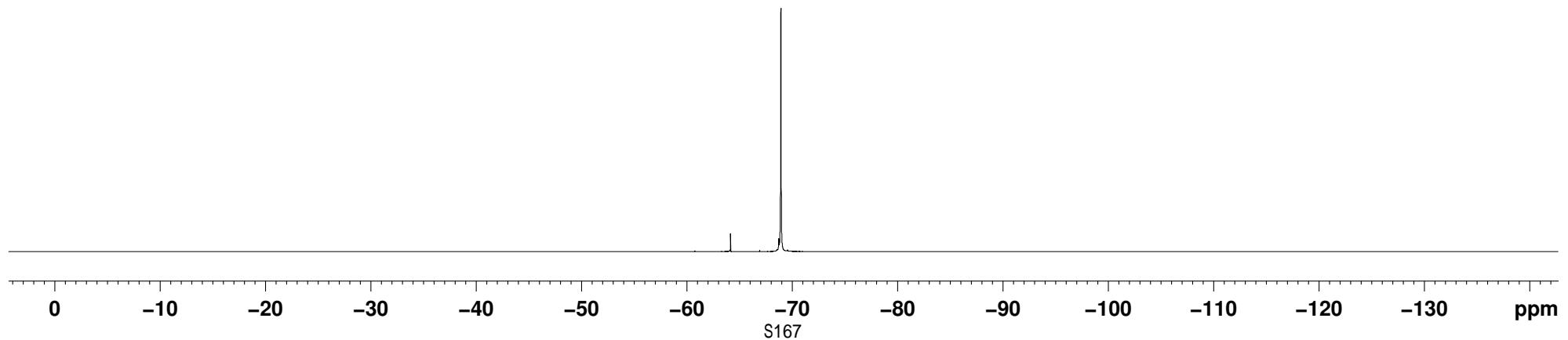
¹H NMR (300 MHz, CDCl₃)







¹⁹F NMR (282 MHz, CDCl₃)



8.233
8.209
8.086
8.059
7.526
7.322
7.296
7.219
7.215
7.194
7.191
7.168
7.162
7.157
7.132
7.112
7.108
6.702
6.673

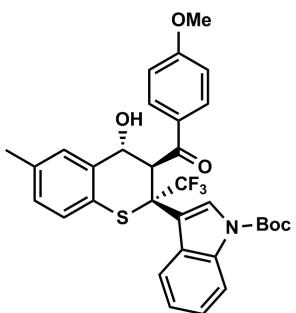
5.693
5.674
5.661
5.642

4.222
4.189
3.772
3.632
3.613

2.431

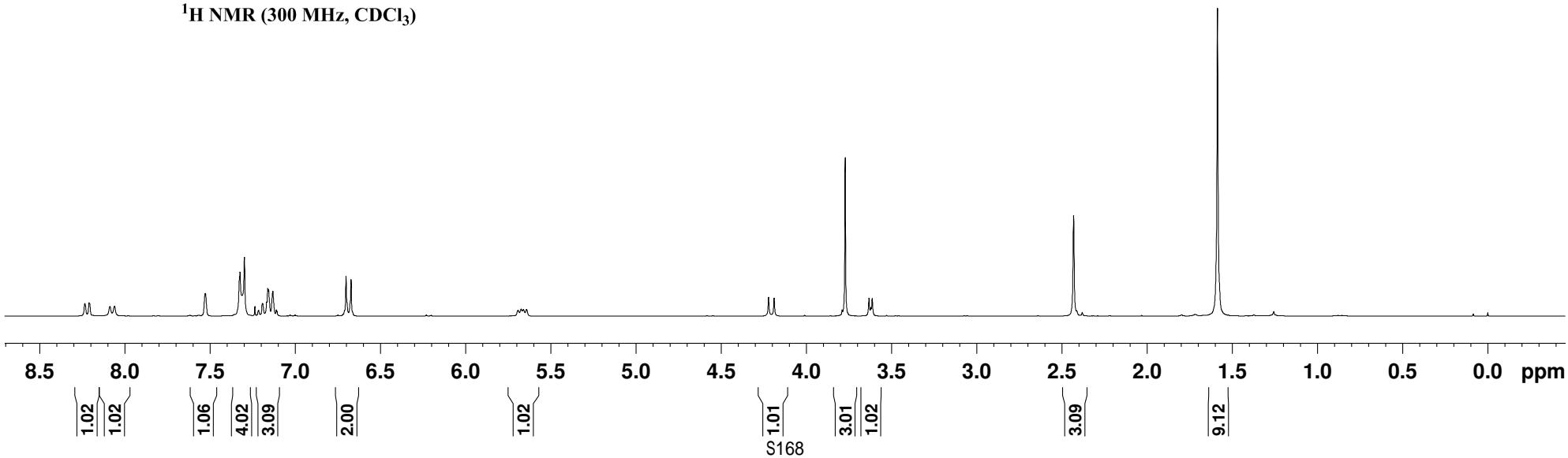
1.587

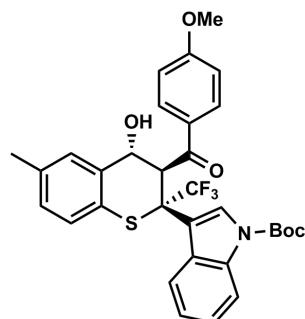
-0.000



3t

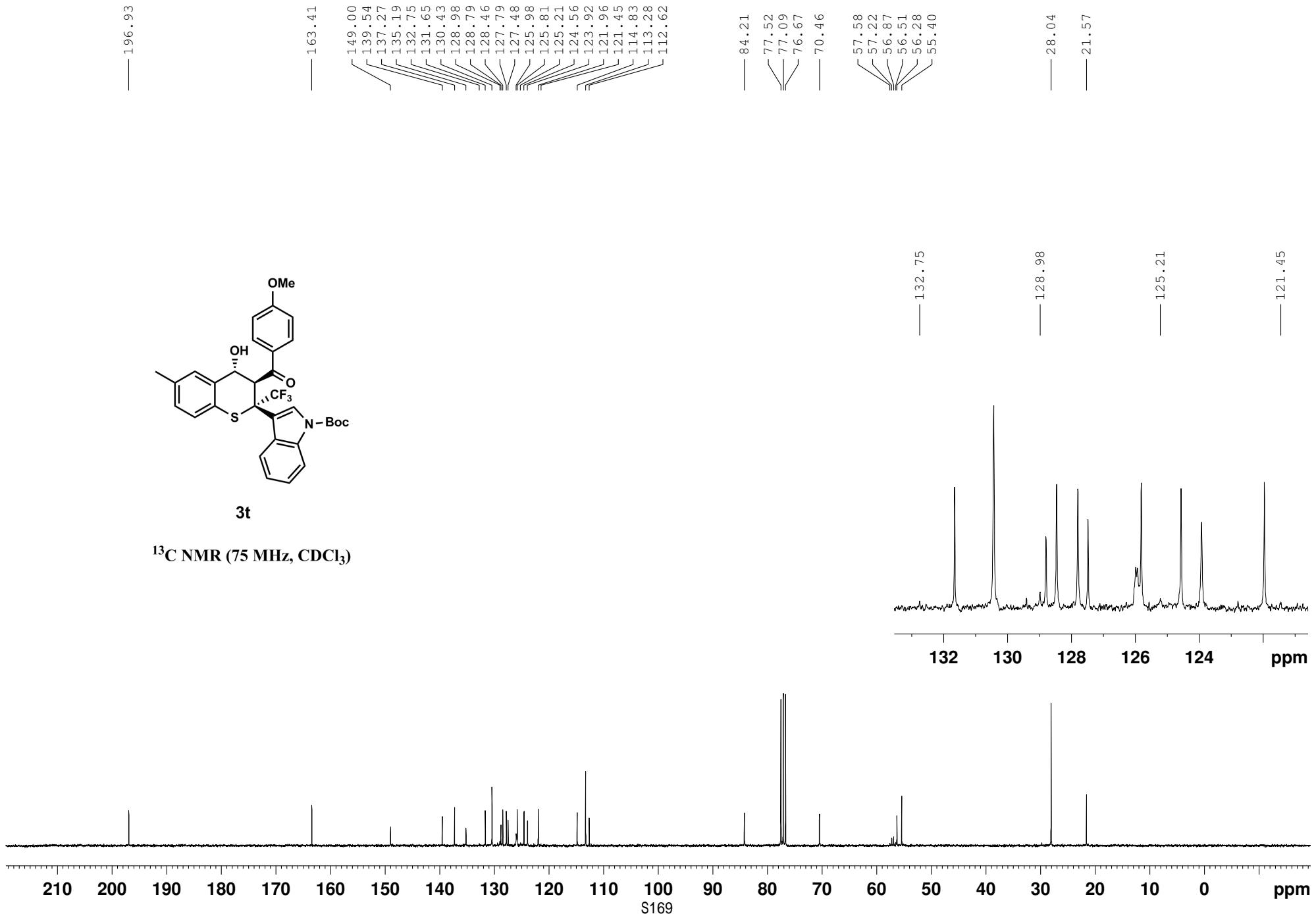
¹H NMR (300 MHz, CDCl₃)

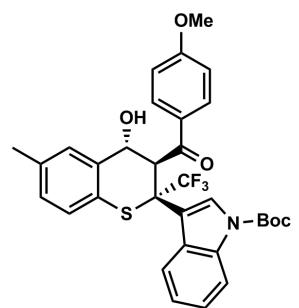




3t

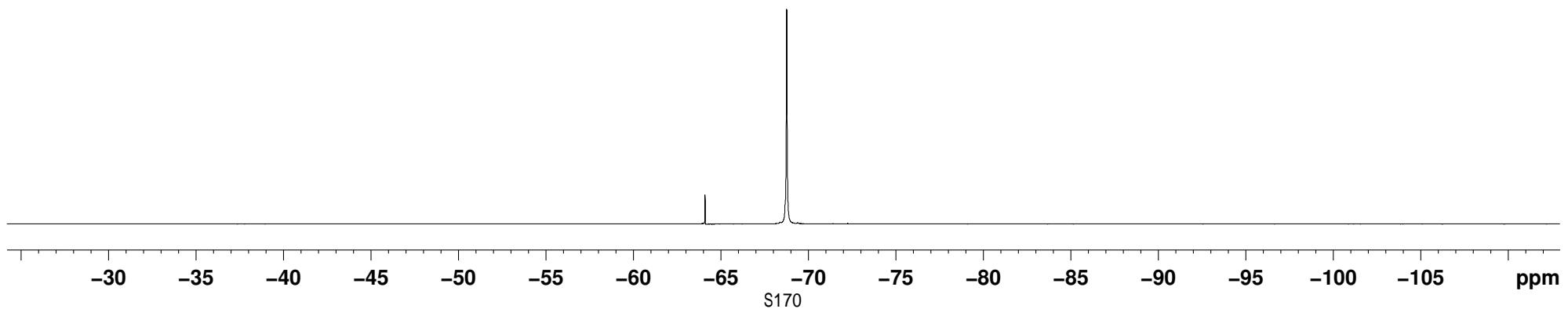
¹³C NMR (75 MHz, CDCl₃)





3t

¹⁹F NMR (282 MHz, CDCl₃)



8.225
 8.199
 8.115
 8.088
 7.561
 7.347
 7.326
 7.317
 7.301
 7.270
 7.256
 7.245
 7.210
 7.186
 7.160
 7.135
 6.748
 6.719

5.763
 5.745
 5.731
 5.713

4.227
 4.194

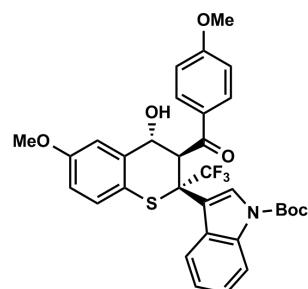
3.806

3.115
 3.097

2.435

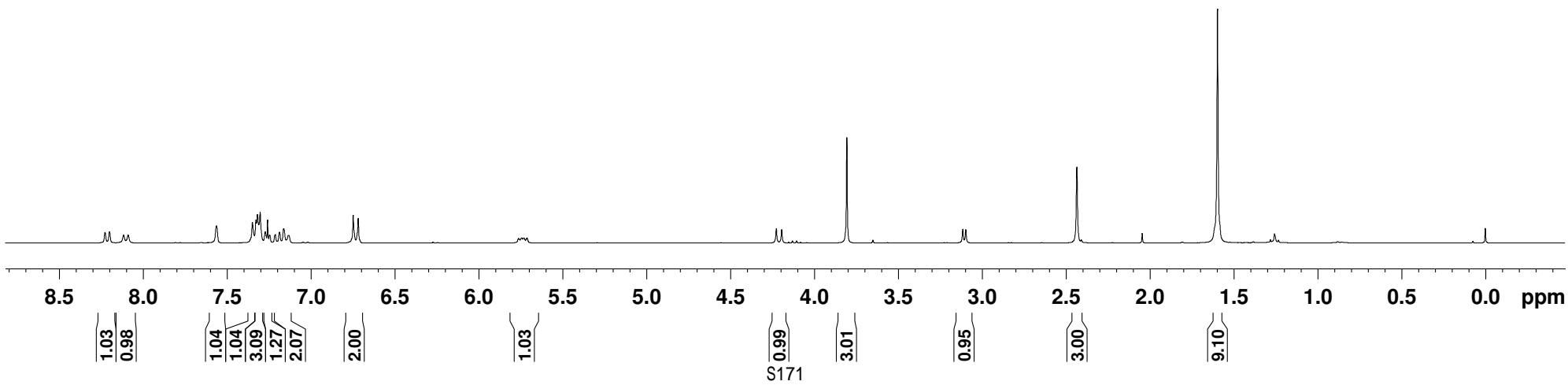
1.597

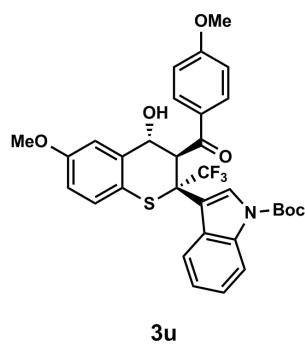
-0.000



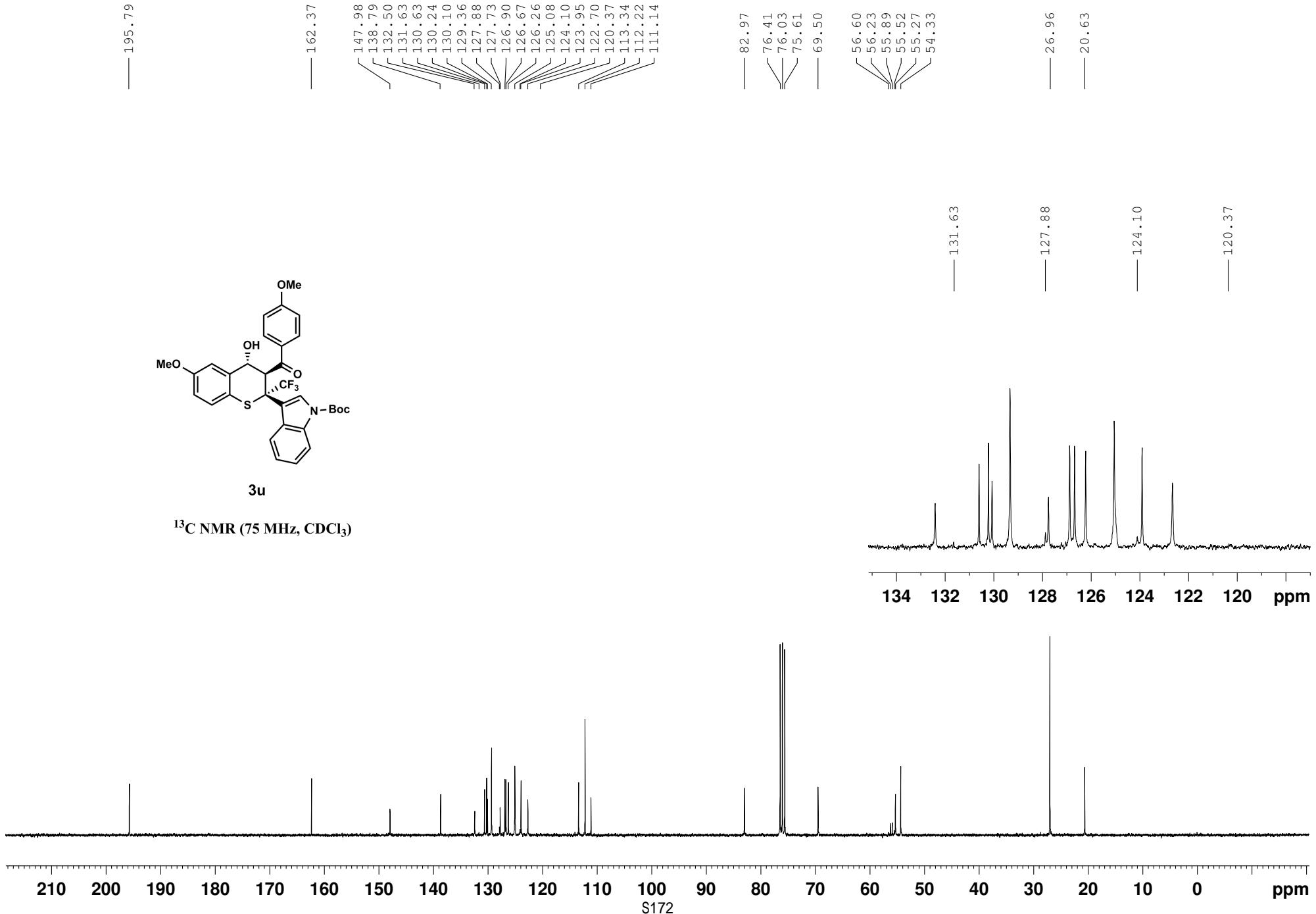
3u

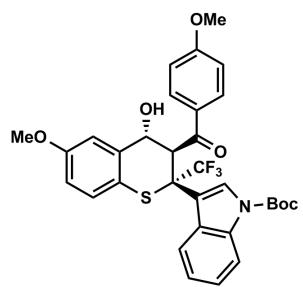
¹H NMR (300 MHz, CDCl₃)





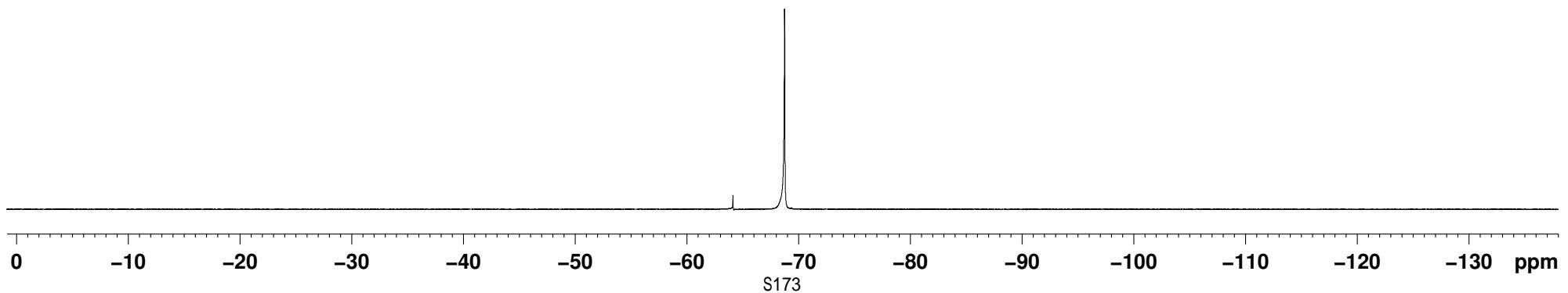
¹³C NMR (75 MHz, CDCl₃)





3u

¹⁹F NMR (282 MHz, CDCl_3)



8.245
8.219
8.098
8.071

7.402
7.311
7.282
7.256
7.232
7.206
7.171
7.147
7.123
7.059
6.701
6.671

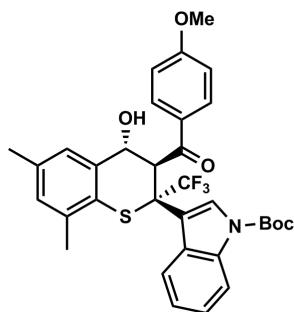
5.728
5.710
5.697
5.679

4.172
4.140
3.768
3.499
3.481

2.389

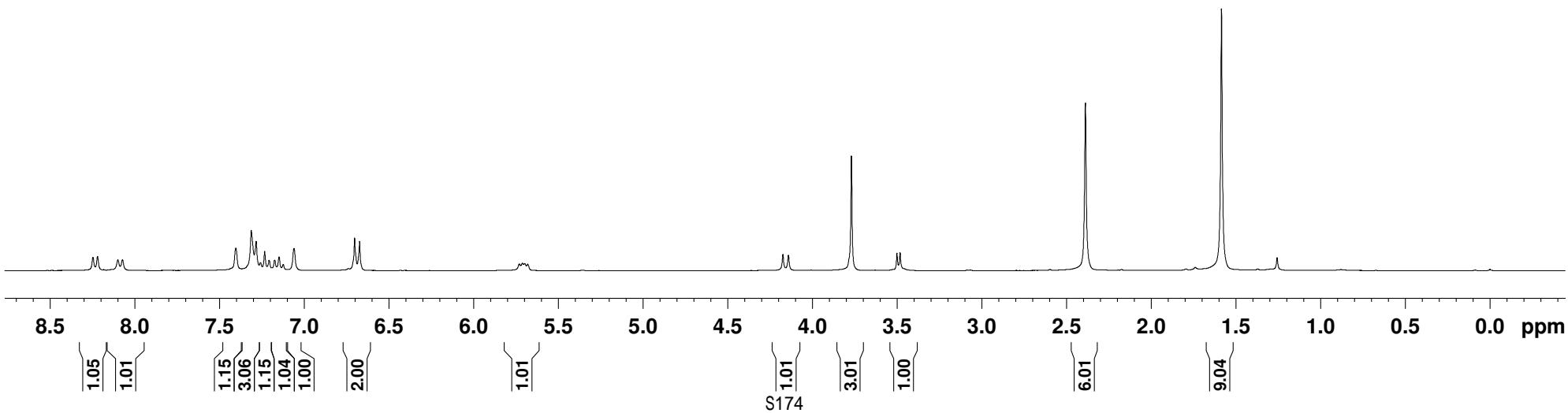
1.585

-0.000

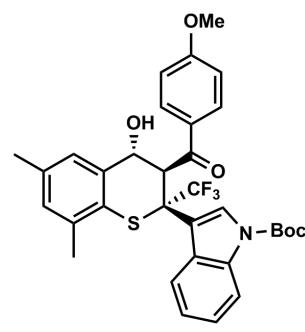


3v

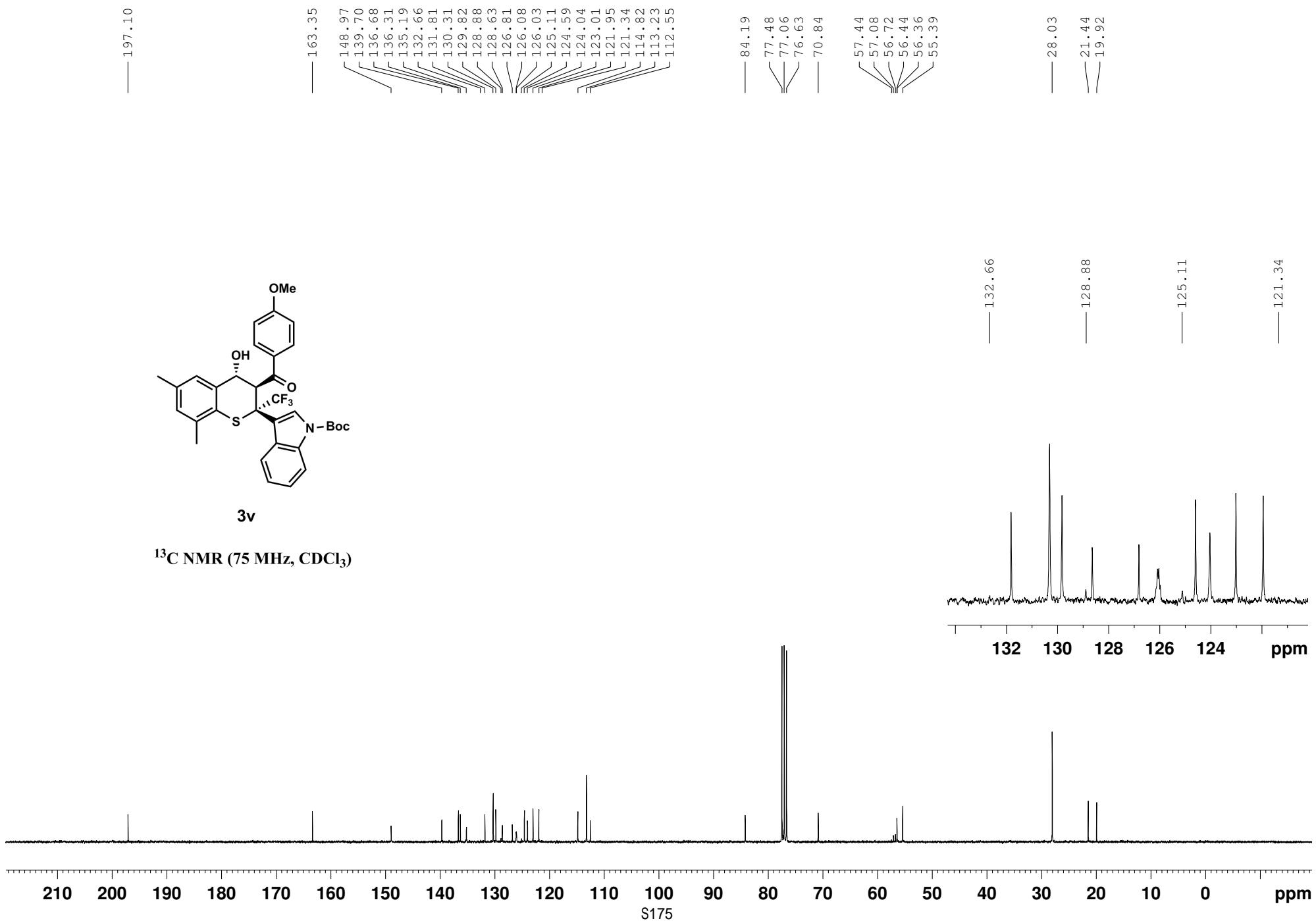
¹H NMR (300 MHz, CDCl₃)

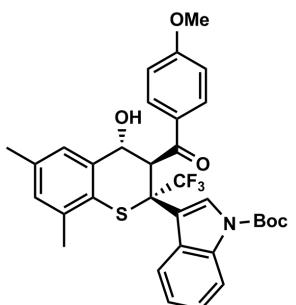


S174



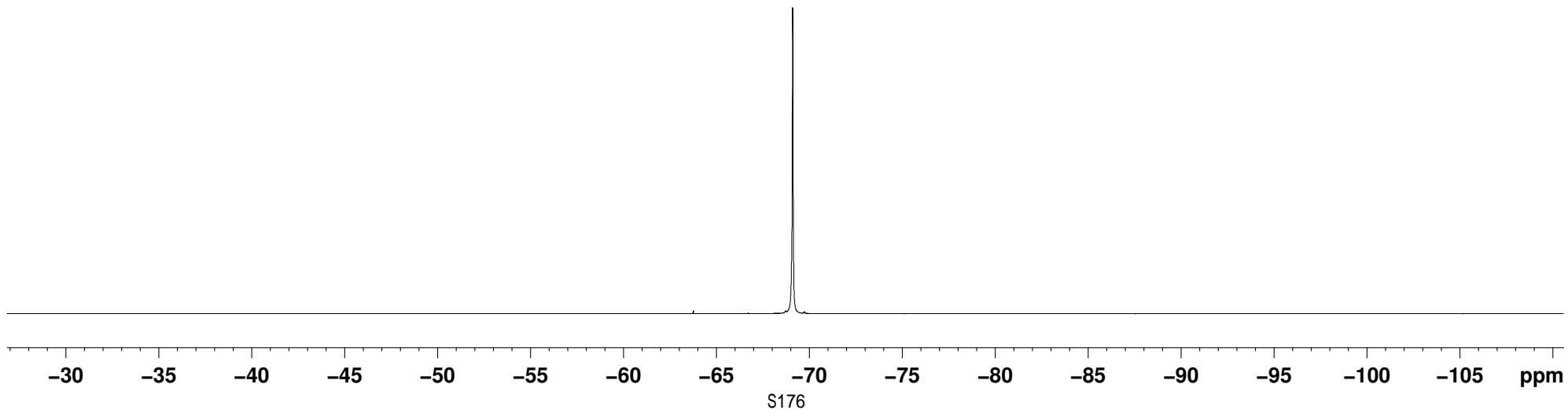
¹³C NMR (75 MHz, CDCl₃)



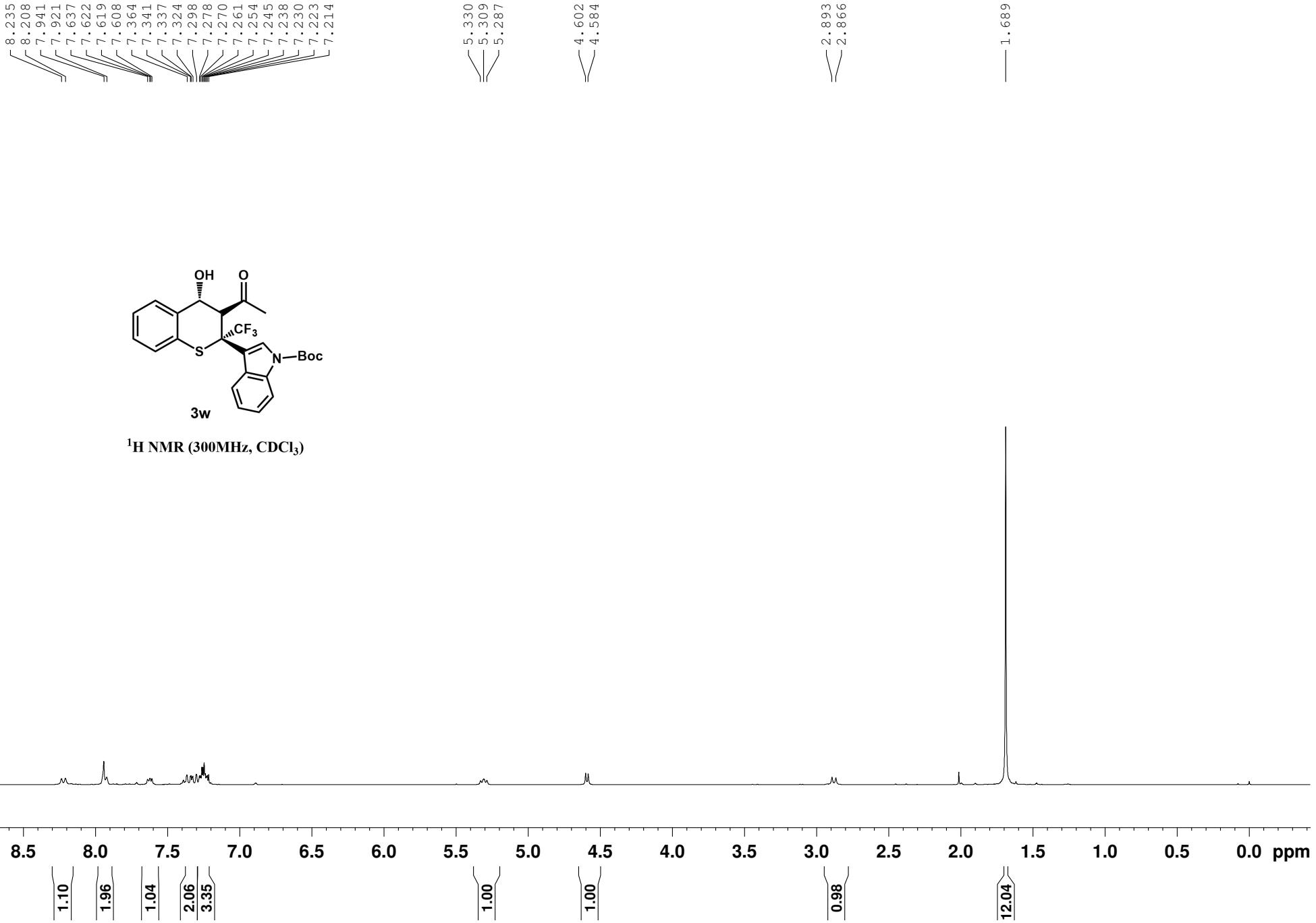


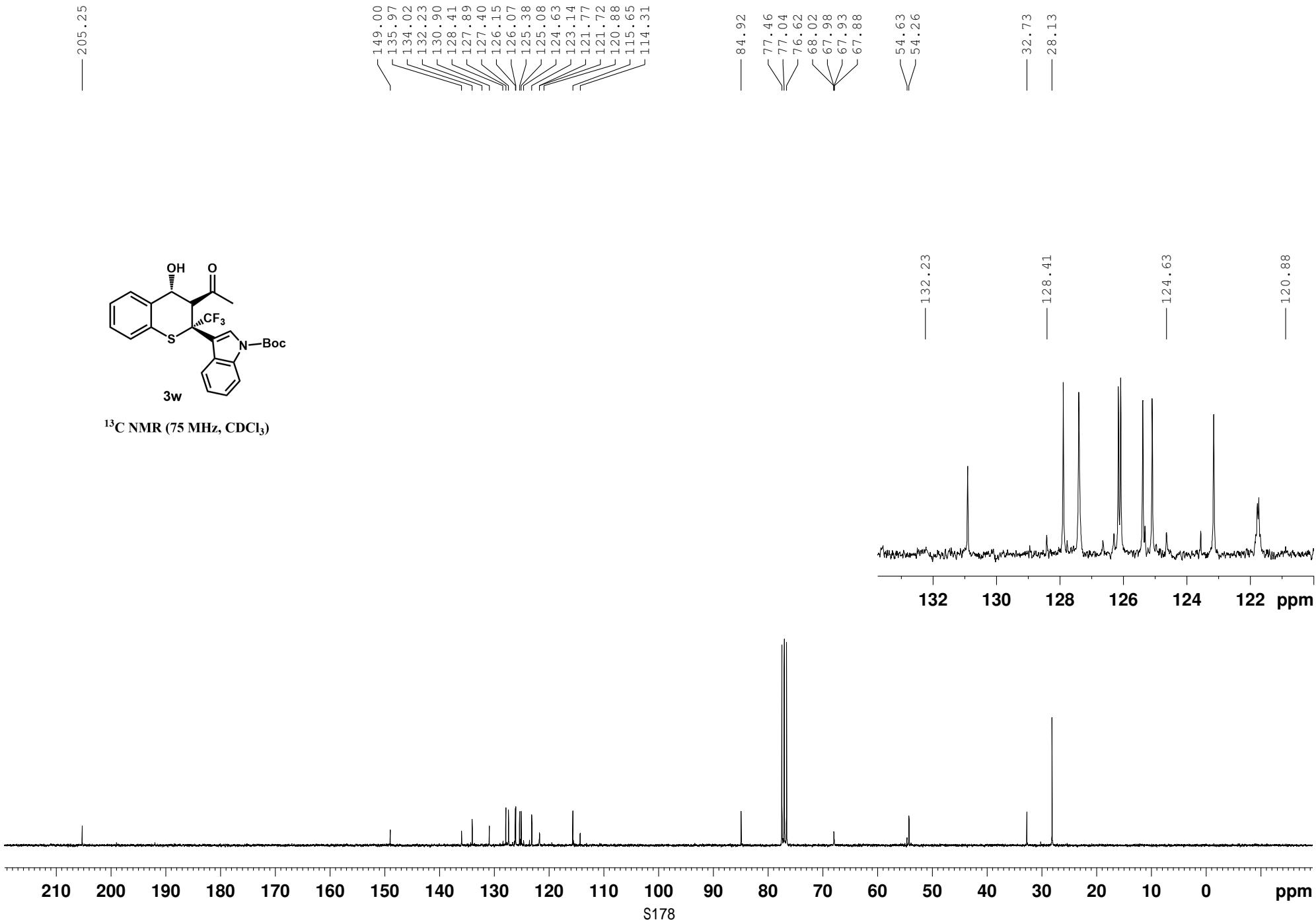
3v

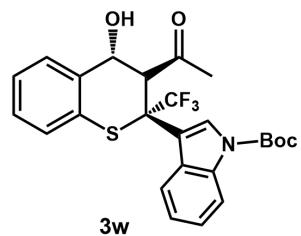
¹⁹F NMR (282 MHz, CDCl₃)



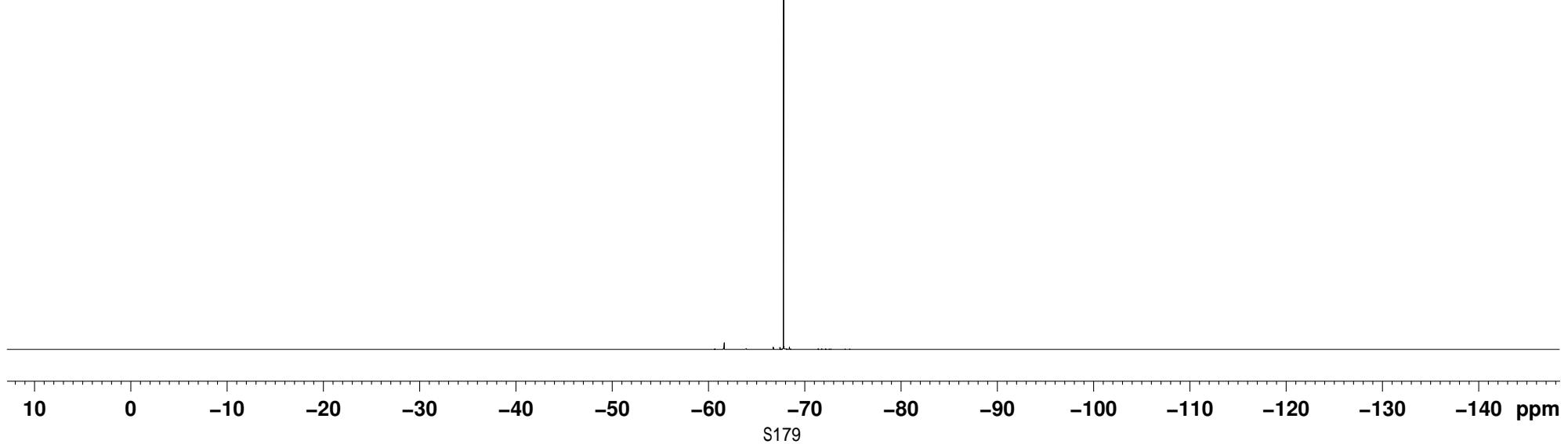
— -69.13







¹⁹F NMR (282 MHz, CDCl₃)



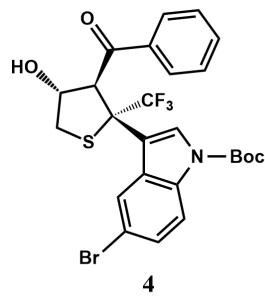
7.943
7.914
7.837
7.618
7.589
7.299
7.208
7.203
7.179
7.173
6.847
6.817

5.069
5.045
5.024

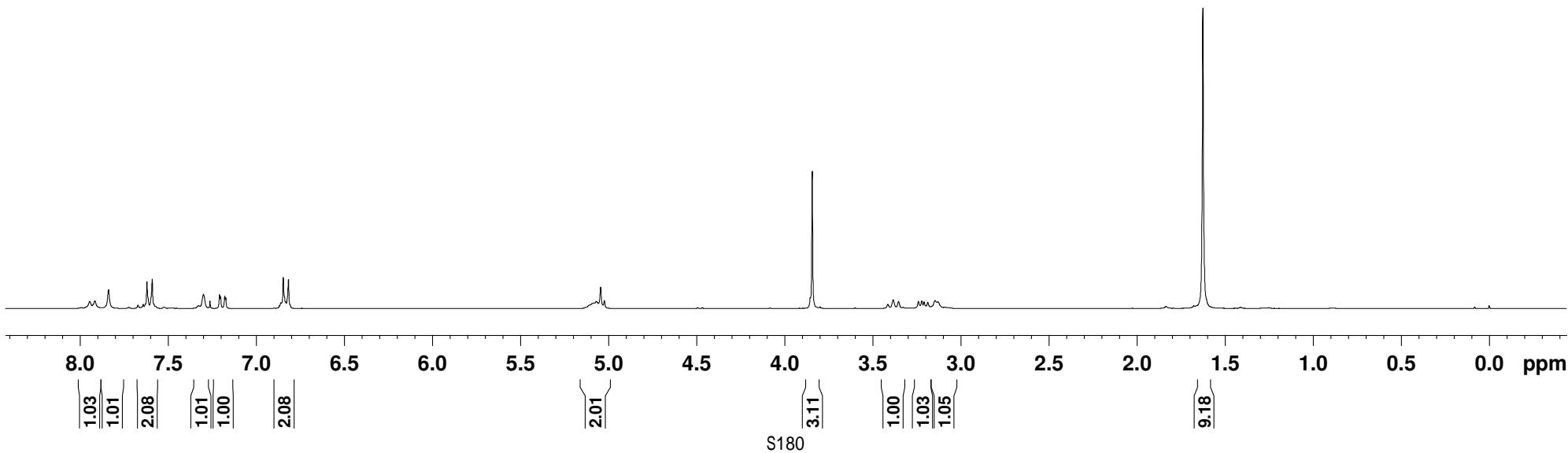
3.843
3.414
3.383
3.353
3.240
3.221
3.208
3.188
3.146
3.129

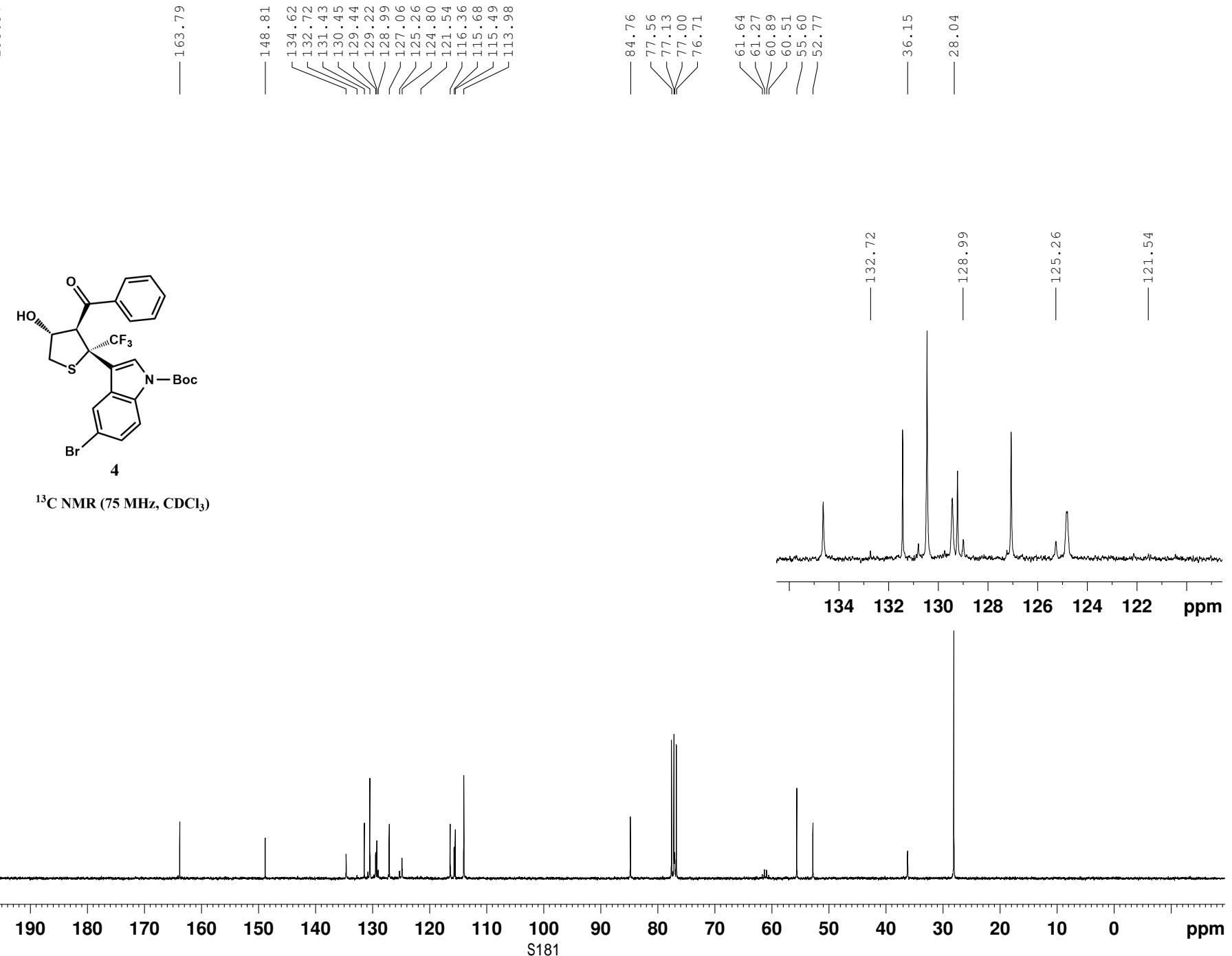
1.625

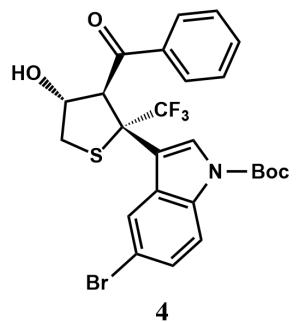
-0.000



¹H NMR (300 MHz, CDCl₃)







¹⁹F NMR (282 MHz, CDCl₃)

