Organophosphorus-Catalyzed Deoxygenation of Sulfonyl Chlorides: Electrophilic (Fluoroalkyl)sulfenylation by $P^{III}/P^{V}=O$ Redox Cycling

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1. General methods

All reactions were carried out using dry glassware and standard Schlenk techniques (when applicable) unless otherwise noted. All reagents were purchased from commercial vendors (Sigma-Aldrich, Alfa Aesar, Acros, TCI, Combi-Blocks, A.K Scientific, or Oakwood Chemical) and used as received unless otherwise noted. All solvents were purified and collected under argon using a Glass Contour Solvent Purification System. Column chromatography was performed using 230-400 mesh silica gel (Silicycle) as the stationary phase unless otherwise noted. ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded with Bruker AVANCE-400 and AVANCE DRX 600 spectrometer and processed using MestReNova software. ^{1}H NMR chemical shifts are given in ppm with respect to the residual $CHCl_3$ peak (δ 7.26 ppm), CH_2Cl_2 peak (δ 5.32 ppm), residual DMSO (δ 2.50 ppm), $^{13}C\{^{1}H\}$ NMR chemical shifts are given in ppm with respect to $CDCl_3$ (δ 77.16 ppm), CD_2Cl_2 peak (δ 53.84 ppm), DMSO-d_6 (δ 39.52 ppm), and ^{31}P chemical shifts are given in ppm with respect to 85% H_3PO_4 (δ 0.0 ppm) as an external reference. Coupling constants are reported as *J*-values in Hz. ESI mass spectra were obtained from the Mass Spectrometry Laboratory at the School of Chemical Sciences, University of Illinois at Urbana-Champaign as well as at the MIT department of chemistry instrumentation on a JEOL AccuTOF-DART (JMS-T100LP, ionSense DART source).

2. Preparation of phosphorus catalysts

All phosphetanes were prepared according to: (a) S. E. Cremer, R. J. Chorvat, *J. Org. Chem*. **1967**, *32*, 4066. (b) T. V. Nykaza, T. S. Harrison, A. Ghosh, R. A. Putnik, A. T. Radosevich, *J. Am. Chem. Soc.* **2017**, *139*, 6839.

3. General procedures for catalytic (fluoroalkyl)sulfenylation reactions

General Procedure I: Trifluoromethylthiolation or perfluoroalkylthiolation of indoles

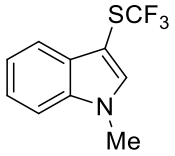
To a dry 40 mL vial equipped with Teflon cap and a stir bar was added 0.5 mmol of indole substrate, 15-25 mol% of phosphetane oxide precatalyst **2**·[O] and R_fSO_2Cl (1.8 equiv) if solid. The reaction vial was sealed and following evacuation and introduction of nitrogen on a Schlenk line, dry 1,4-dioxane (0.1 M or 0.25 M) was added *via* syringe from a SureSeal bottle. Phenylsilane (2 equiv) and RSO_2Cl (1.8 equiv) if liquid were added and the sealed reaction vial was placed in a heating block pre-heated to 40 °C. The reaction was stirred (~600 rpm) until completion as indicated by TLC. Following completion, the reaction mixture was cooled to RT, quenched with saturated aqueous NH_4F solution (25 mL) and stirred for 1 h. The aqueous layer was extracted with ethyl acetate (3x25 mL) and the combined organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. Column chromatography on silica gel subsequently afforded the desired sulfenylated products.

General Procedure II: Sulfenylation of indoles

To a dry 40 mL vial equipped with Teflon cap and a stir bar was added 0.5 mmol of indole substrate, 20 mol% of phosphetane oxide precatalyst **2**·[O] and RSO_2Cl (1.8 equiv) if solid. The reaction vial was sealed and following evacuation and introduction of nitrogen on a Schlenk line, dry 1,4-dioxane (0.25 M) was added *via* syringe from a SureSeal bottle. Phenylsilane (2 equiv) and RSO_2Cl (1.8 equiv) if liquid were added and the sealed reaction vial was placed in a heating block pre-heated to 40 °C. The reaction was stirred (~600 rpm) until completion as indicated by TLC. Following completion, the reaction mixture was cooled to RT, quenched with saturated aqueous NH_4F solution (25 mL) and stirred for 1 h. The aqueous layer was extracted with ethyl acetate (3x25 mL) and the combined organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. Column chromatography on silica gel subsequently afforded the desired sulfenylated products.

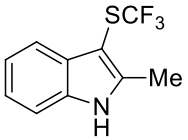
12

3-((Trifluoromethyl)thio)-1*H*-indole 12. Prepared according to general procedure I using 15 mol% of catalyst **2**·[O] in 1,4-dioxane (0.1 M). Yield: 98% (107 mg). Colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.46 (bs, 1H), 7.87–7.82 (m, 1H), 7.52 (d, *J* = 2.8 Hz, 1H), 7.44–7.41 (m, 1H), 7.35–7.30 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 136.1, 133.0, 129.6 (q, *J* = 310.0 Hz), 129.6, 123.6, 121.8, 119.5, 111.8, 95.7 (q, *J* = 2.3 Hz); ^{19}F NMR (565 MHz, $CDCl_3$): δ -44.52. HRMS calculated for $[C_9H_6F_3NS]^+$ 217.0173, found 217.0164.



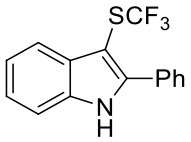
13

1-Methyl-3-((trifluoromethyl)thio)-1*H*-indole 13. Prepared according to general procedure I using 15 mol% of catalyst **2**·[O] in 1,4-dioxane (0.1 M). Yield: 85% (99 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.6 Hz, 1H), 7.41 – 7.36 (m, 2H), 7.36 – 7.27 (m, 2H), 3.84 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.4, 137.1, 130.4, 129.6 (q, *J* = 311.3 Hz), 123.1, 121.4, 119.5, 110.0, 93.2, 33.3; ^{19}F NMR (376 MHz, $CDCl_3$): δ -44.88. HRMS calculated for $[C_{10}H_8F_3NS]^+$ 231.0329, found 231.0329.



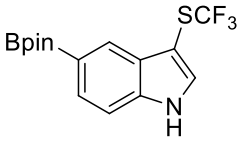
14

2-Methyl-3-((trifluoromethyl)thio)-1*H*-indole 14. Prepared according to general procedure I using 15 mol% of catalyst **2**·[O] in 1,4-dioxane (0.1 M). Yield: 70% (82 mg). Brown solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.29 (bs, 1H), 7.74–7.70 (m, 1H), 7.34–7.31 (m, 1H), 7.26–7.21 (m, 2H), 2.58 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 143.7, 135.2, 130.7, 129.9 (q, *J* = 310.6 Hz), 122.7, 121.5, 118.8, 110.9, 92.7 (q, *J* = 2.3 Hz), 12.2. ^{19}F NMR (565 MHz, $CDCl_3$): δ -44.43. HRMS calculated for $([C_{10}H_8F_3NS]+H)^+$ 232,0408, found 232.0410.



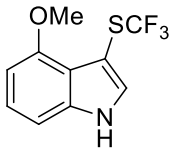
15

2-Phenyl-3-((trifluoromethyl)thio)-1*H*-indole 15. Prepared according to general procedure I using 15 mol% of catalyst **2**·[O] in 1,4-dioxane (0.1 M). Yield: 75% (110 mg). Brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.58 (s, 1H), 7.88 – 7.86 (m, 1H), 7.79 – 7.77 (m, 2H), 7.55 – 7.49 (m, 3H), 7.45 – 7.43 (m, 1H), 7.35 – 7.30 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.5, 135.4, 131.6, 130.8, 129.9 (d, *J* = 311 Hz), 129.4, 129.0, 128.9, 123.8, 121.9, 119.9, 111.4, 92.6; ^{19}F NMR (376 MHz, $CDCl_3$): *δ* -43.41. HRMS calculated for ($[C_{15}H_{10}F_3NS] + H)^+$ 294.0564, found 294.0563.



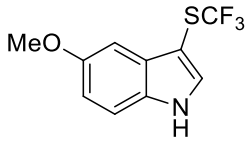
16

5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-3-((trifluoromethyl)thio)-1*H*-indole 16. Prepared according to general procedure I using 15 mol% of catalyst **2**·[O] in 1,4-dioxane (0.25 M). Yield: 96% (165 mg). White solid ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 8.33 (s, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.51 (d, *J* = 2.6 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 1H), 1.39 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.2, 133.4, 133.1, 129.6, 129.5 (d, *J* = 309.9 Hz), 129.2, 127.0, 111.3, 96.3, 83.9, 25.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -44.51. HRMS calculated for ($[C_{15}H_{17}BF_3NO_2S] - H)^-$ 342.0947, found 342.0943.



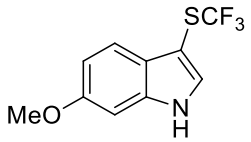
17

4-Methoxy-3-((trifluoromethyl)thio)-1*H*-indole 17. Prepared according to general procedure I using 15 mol% of catalyst **2**·[O] in 1,4-dioxane (0.1 M). Yield: 89% (111 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.47 (s, 1H), 7.40 (d, *J* = 2.7 Hz, 1H), 7.19 (app t, *J* = 8.0 Hz, 1H), 7.02 (d, *J* = 8.2 Hz, 1H), 6.65 (d, *J* = 7.9 Hz, 1H), 3.97 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): *δ* 154.7, 138.0, 132.4, 129.6 (q, *J* = 310.4 Hz), 124.5, 118.7, 104.9, 102.2, 94.8, 55.6; ^{19}F NMR (376 MHz, $CDCl_3$): *δ* -45.49. HRMS calculated for $[C_{10}H_8F_3NOS]^+$ 247.0279, found 247.0271.



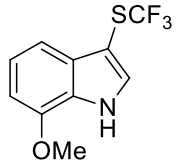
18

5-Methoxy-3-((trifluoromethyl)thio)-1*H*-indole 18. Prepared according to general procedure I using 15 mol% of catalyst **2**·[O] in 1,4-dioxane (0.1 M). Yield: 88% (109 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.51 (d, J = 2.8, 1H), 7.33 (d, J = 8.8, 1H), 7.30 – 7.28 (m, 1H), 6.99 (dd, J = 8.8, 2.4, 1H), 3.95 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 155.7, 133.4, 131.0, 130.4, 129.6 (q, J = 311.3 Hz), 114.1, 112.7, 100.7, 95.1 (q, J = 2.4 Hz), 56.0; ^{19}F NMR (376 MHz, $CDCl_3$): δ -44.61. HRMS calculated for $([C_{10}H_8F_3NOS] + H)^+$ 248.0357, found 248.0356.



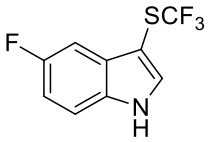
19

6-Methoxy-3-((trifluoromethyl)thio)-1H-indole 19. Prepared according to general procedure I using 15 mol% of catalyst **2**·[O] in 1,4-dioxane (0.1 M). Yield: 82% (102 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (s, 1H), 7.66 (d, J = 8.7 Hz, 1H), 7.43 (d, J = 2.7 Hz, 1H), 6.94 (dd, J = 8.7, 2.1 Hz, 1H), 6.90 (d, J = 1.8 Hz, 1H), 3.86 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.5, 137.0, 132.6 (q, J = 311.1 Hz), 131.7, 128.0, 123.7, 120.2, 111.8, 95.1, 55.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ -44.62. HRMS calculated for $([C_{10}H_8F_3NOS] + H)^+$ 248.0357, found 248.0357.



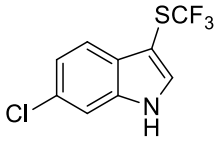
20

7-Methoxy-3-((trifluoromethyl)thio)-1*H*-indole 20. Prepared according to general procedure I using 15 mol% of catalyst **2**·[O] in 1,4-dioxane (0.1 M). Yield: 92% (114 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74 (s, 1H), 7.50 (d, J = 2.6 Hz, 1H), 7.40 (d, J = 8.1 Hz, 1H), 7.20 (app t, J = 7.9 Hz, 1H), 6.73 (d, J = 7.7 Hz, 1H), 3.98 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.4, 132.3, 131.0, 129.6 (q, J = 311.0 Hz), 126.8, 122.2, 111.9, 103.2, 96.0, 55.6; ^{19}F NMR (376 MHz, $CDCl_3$): δ -44.67. HRMS calculated for $[C_{10}H_8F_3NOS]^+$ 247.0279, found 247.0276.



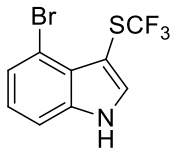
21

5-Fluoro-3-((trifluoromethyl)thio)-1*H*-indole 21. Prepared according to general procedure I using 20 mol% of catalyst **2**·[O] in 1,4-dioxane (0.25 M). Yield: 94% (111 mg). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.58 (d, *J* = 2.8 Hz, 1H), 7.45 (dd, *J* = 9.1, 2.4 Hz, 1H), 7.36 (dd, *J* = 8.8, 4.2 Hz, 1H), 7.05 (app td, *J* = 9.0, 2.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2 (d, *J* = 238.6 Hz, 1C), 134.5, 132.6, 130.5 (d, *J* = 10.5 Hz, 1C), 129.5 (q, *J* = 311.2 Hz, 1C), 112.8 (d, *J* = 9.6 Hz, 1C), 112.3 (d, *J* = 26.8 Hz, 1C), 104.7 (d, *J* = 24.7 Hz, 1H), 95.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -44.57 (3F), -121.64 (1F). HRMS calculated for $[C_9H_5F_4NS]^+$ 235.0079, found 235.0077.



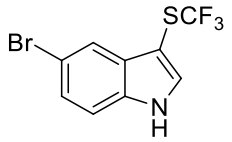
22

6-Chloro-3-((trifluoromethyl)thio)-1*H*-indole 22. Prepared according to general procedure I using 15 mol% of catalyst **2**·[O] in 1,4-dioxane (0.1 M). Yield: 99% (125 mg). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.61 (d, *J* = 8.5 Hz, 1H), 7.40 (d, *J* = 2.8 Hz, 1H), 7.29 (d, *J* = 1.8 Hz, 1H), 7.21 – 7.11 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.4, 133.5, 129.6, 129.4 (q, *J* = 311.2 Hz), 128.2, 122.6, 120.5, 111.8, 96.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -44.43. HRMS calculated for $[C_9H_5ClF_3NS]^+$ 250.9783, found 250.9788.



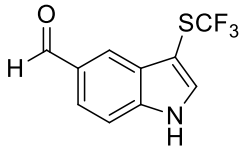
23

4-Bromo-3-((trifluoromethyl)thio)-1*H*-indole 23. Prepared according to general procedure I using 20 mol% of catalyst **2**·[O] in 1,4-dioxane (0.25 M). Yield: 98% (146 mg). White solid. ^{1}H NMR (600 MHz, $CDCl_3$): *δ* 8.62 (bs, 1H), 7.61 (d, *J* = 2.9 Hz, 1H), 7.43 (dd, *J* = 7.6, 0.9 Hz, 1H), 7.39 (dd, *J* = 8.2, 0.8 Hz, 1H), 7.12 (app t, *J* = 7.9 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.2, 135.4, 129.1 (q, *J* = 309.5 Hz), 126.9, 126.2, 124.4, 114.5, 111.4, 96.6 (q, *J* = 2.5 Hz); ^{19}F NMR (565 MHz, $CDCl_3$) δ -45.43. HRMS calculated for $[C_9H_5BrF_3NS]^+$ 294.9278, found 294.9283.



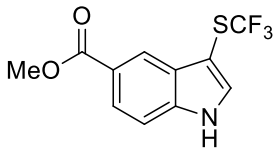
24

5-Bromo-3-((trifluoromethyl)thio)-1*H*-indole 24. Prepared according to general procedure I using 20 mol% of catalyst **2**·[O] in 1,4-dioxane (0.25 M). Yield: 95% (142 mg). Off-white solid. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.54 (bs, 1H), 7.93 (s, 1H), 7.53 (d, *J* = 2.8 Hz, 1H), 7.38 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.29 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): *δ* 134.8, 133.9, 131.3, 129.4 (q, *J* = 311.3 Hz), 126.7, 122.2, 115.4, 113.3, 95.5; ^{19}F NMR (376 MHz, $CDCl_3$): *δ* -44.46. HRMS calculated for $([C_9H_5NSBrF_3])^+$ 294.9278, found 294.9275.



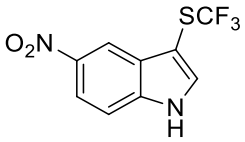
25

3-((Trifluoromethyl)thio)-1*H*-indole-5-carbaldehyde 25. Prepared according to general procedure I using 20 mol% of catalyst **2**·[O] in 1,4-dioxane (0.1 M). Yield: 64% (79 mg). White solid. ^{1}H NMR (600 MHz, acetone-d_6): *δ* 11.49 (bs, 1H), 10.14 (s, 1H), 8.33 (s, 1H), 8.04 (d, *J* = 2.8 Hz, 1H), 7.84 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.73 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR (151 MHz, acetone-d_6): *δ* 192.6, 141.1, 137.6, 132.3, 130.5 (q, *J* = 308.9 Hz), 30.4, 123.9, 123.6, 114.2, 96.0; ^{19}F NMR (565 MHz, acetone): *δ* -45.69. HRMS calculated for $([C_{10}H_6F_3NOS] + H)^+$ 246.0200, found 246.0200.



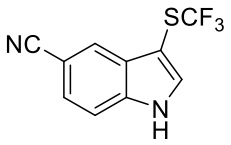
26

Methyl 3-((trifluoromethyl)thio)-1*H*-indole-5-carboxylate 26. Prepared according to general procedure I using 15 mol% of catalyst **2**·[O] in 1,4-dioxane (0.1 M). Yield: 99% (137 mg). White solid. ^{1}H NMR (600 MHz, acetone-d_6) δ 11.45 (bs, 1H), 8.46 (d, *J* = 1.7 Hz, 1H), 8.00 (d, *J* = 2.8 Hz, 1H), 7.94 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.65 (d, *J* = 8.6 Hz, 1H), 3.91 (s, 3H); ^{13}C NMR (151 MHz, acetone-d_6) δ 167.8, 140.3, 137.3, 130.5 (d, *J* = 309.1 Hz), 130.1, 124.8, 124.5, 121.8, 113.4, 95.3, 52.2; ^{19}F NMR (565 MHz, acetone-d_6) δ -45.77. HRMS calculated for $([C_{11}H_8F_3NO_2S] + H)^+$ 276.0306, found 276.0316.



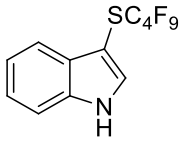
27

5-Nitro-3-((trifluoromethyl)thio)-1*H*-indole 27. Prepared according to general procedure I using 25 mol% of catalyst **2**·[O] in 1,4-dioxane (0.25 M). Yield: 58% (76 mg). Orange solid. ^{1}H NMR (600 MHz, acetone-d_6): δ 11.68 (bs, 1H), 8.64 (d, J = 2.2 Hz, 1H), 8.19 (dd, J = 9.0, 2.3 Hz, 1H), 8.16 (s, 1H), 7.79 (d, J = 9.0 Hz, 1H); ^{13}C NMR (151 MHz, acetone-d_6) δ 144.0, 140.8, 139.3, 130.4 (d, J = 308.9 Hz), 130.0, 119.1, 116.0, 114.2, 96.7; ^{19}F NMR (565 MHz, acetone-d_6) δ -45.64. HRMS calculated for ($[C_9H_5F_3N_2O_2S] + H)^+$ 263.0102, found 263.0110.



28

3-((Trifluoromethyl)thio)-1*H*-indole-5-carbonitrile 28. Prepared according to general procedure I using 25 mol% of catalyst **2**·[O] in 1,4-dioxane (0.25 M). Yield: 52% (63 mg). White solid. ^{1}H NMR (600 MHz, acetone-d_6): δ 11.55 (bs, 1H), 8.13 (s, 1H), 8.09 (d, J = 2.8 Hz, 1H), 7.77 (d, J = 8.4 Hz, 1H), 7.59 (dd, J = 8.5, 1.6 Hz, 1H); ^{13}C NMR (151 MHz, Acetone-d_6) δ 138.6, 137.2, 129.5 (d, J = 309.0 Hz), 129.5, 125.7, 123.8, 119.5, 113.9, 104.7, 94.3; ^{19}F NMR (565 MHz, acetone) δ -45.72. HRMS calculated for ($[C_{10}H_5F_3N_2S] + H)^+$ 243.0204, found 243.0200.



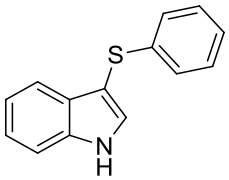
29

3-((Perfluorobutyl)thio)-1*H*-indole 29. Prepared according to general procedure I using 15 mol% of catalyst **2**·[O] in 1,4-dioxane (0.1 M). Yield: 79% (146 mg). Brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (bs, 1H), 7.87 – 7.78 (m, 1H), 7.53 (d, J = 2.8 Hz, 1H), 7.47 – 7.40 (m, 1H), 7.35 – 7.27 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.1, 133.7, 130.1, 123.6, 121.9, 119.6, 111.8, 93.8 (4 ^{13}C could not be observed due to C-F coupling); ^{19}F NMR (376 MHz, $CDCl_3$): δ -80.94 – -81.99 (m, 3F), -88.29 – -88.37

(m, 2F), -120.23 – -124.35 (m, 2F), -125.49 – -125.60 (m, 2F). HRMS calculated for $[C_{12}H_6F_9NS]^+$ 367.0077, found 367.0081.

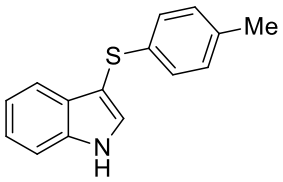
30

3-((Perfluorooctyl)thio)-1*H*-indole 30. Prepared according to general procedure I using 15 mol% of catalyst **2**·[O] in 1,4-dioxane (0.1 M). Yield: 61% (174 mg). Brown solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.56 (s, 1H), 7.82–7.78 (m, 1H), 7.55 (d, *J* = 2.8 Hz, 1H), 7.46 – 7.42 (m, 1H), 7.30 (ddd, *J* = 6.9, 4.7, 1.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.2, 133.7, 130.1, 123.6, 121.9, 119.6, 111.8, 93.9 (8 ^{13}C could not be observed due to C-F coupling); ^{19}F NMR (376 MHz, $CDCl_3$): δ -80.74 – -80.80 (m, 3F), -88.10 (tt, *J* = 14.1, 2.7 Hz, 2F), -119.29 – -119.40 (m, 2F), -121.21 – -121.24 (m, 2F), -121.87 – -122.93 (m, 4F), -122.73 – -122.75 (m, 2F), -126.08 – -126.23 (m, 2F). HRMS calculated for $[C_{16}H_6F_{17}NS]^+$ 566.9950, found 566.9954.



31

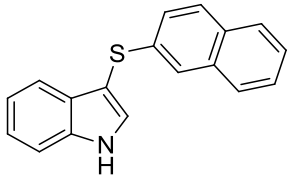
3-(Phenylthio)-1H-indole 31. Prepared according to general procedure II using 20 mol% of catalyst **2**·[O] in 1,4-dioxane (0.25 M). Yield: 75% (85 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (bs, 1H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.46 (d, *J* = 2.3 Hz, 1H), 7.41 (d, *J* = 8.2 Hz, 1H), 7.23 (m, 1H), 7.08 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 139.3, 136.6, 130.8, 129.2, 128.8, 126.0, 124.9, 123.2, 121.1, 119.8, 111.7, 103.0. HRMS calculated for $[C_{14}H_{11}NS]^+$ 225.0612, found 225.0607.



32

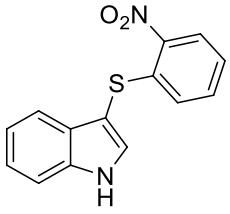
3-(p-Tolylthio)-1*H*-indole 32. Prepared according to general procedure II using 20 mol% of catalyst **2**·[O] in 1,4-dioxane (0.25 M). Yield: 61% (74 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (bs, 1H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.49 (d, *J* = 2.6 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 1H), 7.35 – 7.28 (m, 1H), 7.21

(app t, *J* = 7.5 Hz, 1H), 7.11 – 7.00 (m, 4H), 2.30 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): *δ* 136.6, 135.6, 134.8, 130.6, 129.6, 129.2, 126.3, 123.1, 121.0, 119.8, 111.7, 103.5, 21.0. HRMS calculated for $[C_{15}H_{13}NS]^+$ 239.0769, found 239.0760.



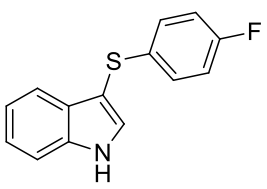
33

3-(Naphthalen-2-ylthio)-1*H*-indole 33. Prepared according to general procedure II using 20 mol% of catalyst **2**·[O] in 1,4-dioxane (0.25 M). Yield: 78% (108 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.45 (bs, 1H), 7.75 – 7.70 (m, 1H), 7.68 – 7.60 (m, 2H), 7.60 – 7.54 (m, 2H), 7.52 – 7.44 (m, 2H), 7.41 – 7.32 (m, 2H), 7.32 – 7.24 (m, 2H), 7.15 (app t, *J* = 7.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): *δ* 136.8, 136.7, 133.9, 131.5, 130.8, 129.2, 128.4, 127.8, 127.1, 126.5, 125.2, 124.9, 123.7, 123.2, 121.1, 119.9, 111.7, 103.0. HRMS calculated for $([C_{18}H_{13}NS] + H)^+$ 276.0847, found 276.0840.



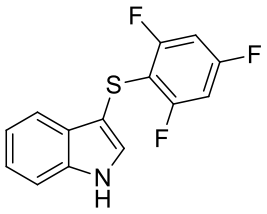
34

3-((2-Nitrophenyl)thio)-1*H*-indole 34. Prepared according to general procedure II using 20 mol% of catalyst **2**·[O] in 1,4-dioxane (0.25 M). Yield: 98% (133 mg). Bright-yellow solid. ^{1}H NMR (400 MHz, CD_2Cl_2): *δ* 8.77 (bs, 1H), 8.24 (d, *J* = 8.1 Hz, 1H), 7.60 (d, *J* = 2.5 Hz, 1H), 7.54 (d, *J* = 8.2 Hz, 1H), 7.47 (d, *J* = 7.9 Hz, 1H), 7.33 – 7.13 (m, 4H), 6.96 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (101 MHz, CD_2Cl_2): *δ* 145.5, 140.6, 137.4, 133.9, 132.6, 129.1, 128.4, 126.3, 125.2, 123.9, 121.8, 119.6, 112.6, 101.9. HRMS calculated for $[C_{14}H_{10}N_2O_2S]^+$ 270.0463, found 270.0456.



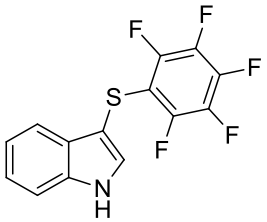
35

3-((4-Fluorophenyl)thio)-1*H*-indole 35. Prepared according to general procedure II using 20 mol% of catalyst **2**·[O] in 1,4-dioxane (0.25 M). Yield: 82% (100 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (bs, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.49 (d, J = 2.6 Hz, 1H), 7.45 – 7.43 (m, 1H), 7.30 – 7.28 (m, 1H), 7.20 – 7.16 (m, 1H), 7.12 – 7.08 (m, 2H), 6.90 – 6.85 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.0 (d, J = 244.9 Hz), 136.6, 134.1 (d, J = 3.1 Hz), 130.7, 128.9, 128.0 (d, J = 7.8 Hz), 123.3, 121.1, 119.6, 115.9 (d, J = 22.1 Hz), 111.8, 103.4; ^{19}F NMR (376 MHz, $CDCl_3$): δ -118.24. HRMS calculated for $[C_{14}H_{10}FNS]^+$ 243.0518, found 243.0517.



36

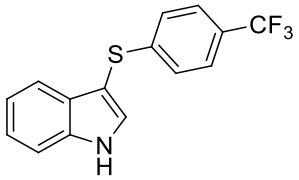
3-((2,4,6-Trifluorophenyl)thio)-1*H*-indole 36. Prepared according to general procedure II using 20 mol% of catalyst **2**·[O] in 1,4-dioxane (0.25 M). Yield: 95% (134 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (bs, 1H), 7.93 – 7.85 (m, 1H), 7.56 (d, J = 2.4 Hz, 1H), 7.44 – 7.33 (m, 1H), 7.32 – 7.22 (m, 2H), 6.67 (dd, J = 8.7, 6.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.6 (dd, J = 248.7, 6.9 Hz), 163.5 (dd, J = 248.6, 6.9 Hz), 162.8 (dt, J = 250.9, 15.4), 135.9, 130.9, 129.0, 123.0, 121.0, 119.4, 111.6, 109.2 (td, J = 22.8, 5.2 Hz), 104.0, 101.0 – 100.5 (m); ^{19}F NMR (376 MHz, $CDCl_3$): δ -101.82 (t, J = 7.0 Hz, 2F), -106.60 - -106.69 (m, 1F). HRMS calculated for $[C_{14}H_8F_3NS]^+$ 279.0330, found 279.0323.



37

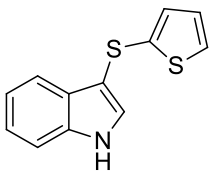
3-((Perfluorophenyl)thio)-1H-indole 37. Prepared according to general procedure II using 20 mol% of catalyst **2**·[O] in 1,4-dioxane (0.25 M). Yield: 94% (150 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (s, 1H), 7.79 – 7.63 (m, 1H), 7.48 (d, J = 2.7 Hz, 1H), 7.34 – 7.23 (m, 1H), 7.19 – 7.13 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.8 - 148.6 (m), 146.3 - 146.2 (m), 143.0 - 142.7 (m), 140.4 - 140.2 (m),

139.0 - 138.8 (m), 136.5 - 136.3 (m), 135.9, 131.5, 128.9, 123.3, 121.4, 119.2, 111.7, 102.3; ^{19}F NMR (376 MHz, $CDCl_3$): ^{19}F NMR (376 MHz, $CDCl_3$) δ -133.28 – -133.44 (m), -153.33 (tt, *J* = 20.9, 2.2 Hz), -161.10 – -161.29 (m). HRMS calculated for $[C_{14}H_6F_5NS]^+$ 315.0141, found 315.0128.



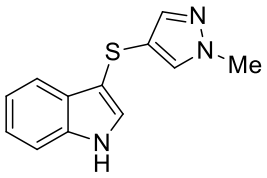
38

3-((4-(Trifluoromethyl)phenyl)thio)-1*H*-indole 38. Prepared according to general procedure II using 20 mol% of catalyst **2**·[O] in 1,4-dioxane (0.25 M). Yield: 89% (132 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.48 (s, 1H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.56 – 7.49 (m, 2H), 7.43 (d, *J* = 8.3 Hz, 2H), 7.36 (app t, *J* = 7.3 Hz, 1H), 7.29 - 7.23 (m, 1H), 7.19 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.8, 136.6, 131.2, 128.8, 126.8 (q, *J* = 32.3 Hz), 125.6 (q, *J* = 3.8 Hz), 125.4, 124.4 (q, *J* = 271.5 Hz), 123.5, 121.4, 119.5, 111.9, 101.3. ^{19}F NMR (376 MHz, $CDCl_3$): *δ* -62.13. HRMS calculated for $[C_{15}H_{10}F_3NS]^+$ 293.0486, found 293.0490.



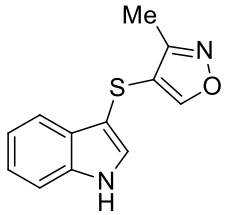
39

3-(Thiophen-2-ylthio)-1*H*-indole 39. Prepared according to general procedure II using 20 mol% of catalyst **2**·[O] in 1,4-dioxane (0.25 M). Yield: 88% (103 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.16 (s, 1H), 7.72 (d, *J* = 7.6 Hz, 1H), 7.37 (d, *J* = 2.5 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.18 – 7.10 (m, 2H), 7.10 – 7.06 (m, 1H), 7.03 (d, *J* = 2.8 Hz, 1H), 6.79 (dd, *J* = 5.1, 3.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): *δ* 138.0, 136.3, 130.0, 129.4, 128.6, 127.5, 127.4, 123.1, 121.0, 119.6, 111.7, 106.9. HRMS calculated for $[C_{12}H_9NS_2]^+$ 231.0176, found 231.0170.



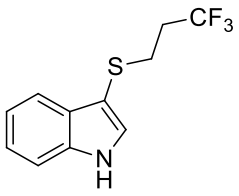
40

3-((1-Methyl-1*H*-pyrazol-4-yl)thio)-1*H*-indole 40. Prepared according to general procedure II using 20 mol% of catalyst **2**·[O] in 1,4-dioxane (0.25 M). Yield: 72% (83 mg). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (s, 1H), 7.77 (d, J = 7.2 Hz, 1H), 7.49 (s, 1H), 7.40 – 7.30 (m, 3H), 7.25 – 7.17 (m, 2H), 3.78 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.7, 136.3, 132.1, 128.7, 128.6, 122.9, 120.7, 119.4, 113.9, 111.7, 107.0, 39.2. HRMS calculated for ($[C_{12}H_{11}N_3S]$ + H)$^+$ 230.0752, found 230.0756.



41

4-((1*H*-Indol-3-yl)thio)-3-methylisoxazole 41. Prepared according to general procedure II using 20 mol% of catalyst **2**·[O] in 1,4-dioxane (0.25 M). Yield: 96% (111 mg). Pale-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (s, 1H), 8.14 (s, 1H), 7.72 (d, J = 7.6 Hz, 1H), 7.46 – 7.37 (m, 2H), 7.30 – 7.22 (m, 2H), 2.57 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.0, 153.3, 136.3, 129.1, 128.5, 123.2, 121.0, 119.0, 111.8, 109.0, 104.9, 11.2. HRMS calculated for ($[C_{12}H_{10}N_2OS]$ + H)$^+$ 231.0592, found 231.0588.



42

3-((3,3,3-Trifluoropropyl)thio)-1H-indole 42. Prepared according to general procedure II using 20 mol% of catalyst **2**·[O] in 1,4-dioxane (0.25 M). Yield: 45% (56 mg). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (s, 1H), 7.75 – 7.68 (m, 1H), 7.39 – 7.34 (m, 1H), 7.32 (d, J = 2.6 Hz, 1H), 7.27 – 7.16 (m, 2H), 2.85 – 2.74 (m, 2H), 2.38 – 2.18 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.5, 130.2, 129.4, 126.3 (q, J = 278.4 Hz), 123.2, 121.0, 119.2, 111.8, 104.2, 35.1 (q, J = 28.3 Hz), 28.3 (q, J = 3.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -65.95 (t, J = 10.4 Hz). HRMS calculated for ($[C_{11}H_{10}F_3NS]$ + H)$^+$ 246.0564, found 246.0574.

4. Mechanistic investigations

4.1. *In Situ* NMR Experiments

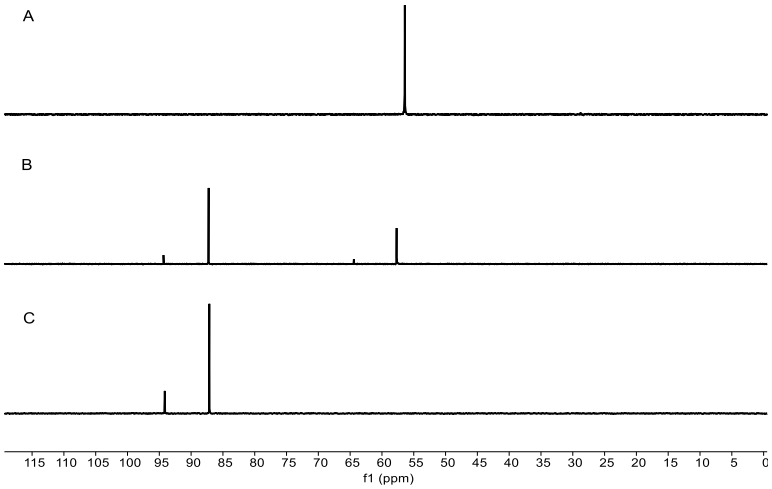


Figure S1. Time-stacked in situ ^{31}P NMR spectra during catalysis (*T* = 25 °C, 1,4-dioxane). (A) *t* = 0 min; (B) *t* = 60 min; (C) *t* = 90 min. Chemical shifts (δ): anti-**2**·[O], 56.4 ppm; unknown peaks at 87.3 and 94.4 ppm.

To a dry 4 mL vial equipped with Teflon cap was added indole **1** (29.4 mg, 0.25 mmol) and 20 mol% of phosphetane oxide precatalyst **2**·[O] (8.7 mg, 0.05 mmol). The reaction vial was sealed and following evacuation and introduction of nitrogen on a Schlenk line, dry 1,4-dioxane (1 mL, 0.25 M) followed by phenylsilane (61 μL, 0.50 mmol, 2 equiv) were added via syringe. The colorless solution was transferred to an oven-dried purged septum-sealed NMR tube. $PhSO_2Cl$ (59 μL, 0.46 mmol, 1.8 equiv) was added to the above reaction mixture in NMR tube and ^{1}H NMR spectra and ^{31}P NMR spectra were recorded subsequently at 10 minute intervals. Phosphetane oxide **2**·[O] (δ 57.7 *major*, 64.4 *minor* ppm) is converted to two new resonances (δ 87.3 *major*, 94.4 *minor* ppm) over the course of 90 min (In a separate experiment, it was determined that the ^{31}P NMR spectrum under these reaction conditions remained unchanged even after 48 h reaction time). Upon termination of the experiment after 16 h, an aliquot of the mixture was analyzed by GCMS, with the presence of phosphetane *P*-oxide **2**·[O], indole-3-sulfide **31** and diphenyl disulfide as the only observable products.

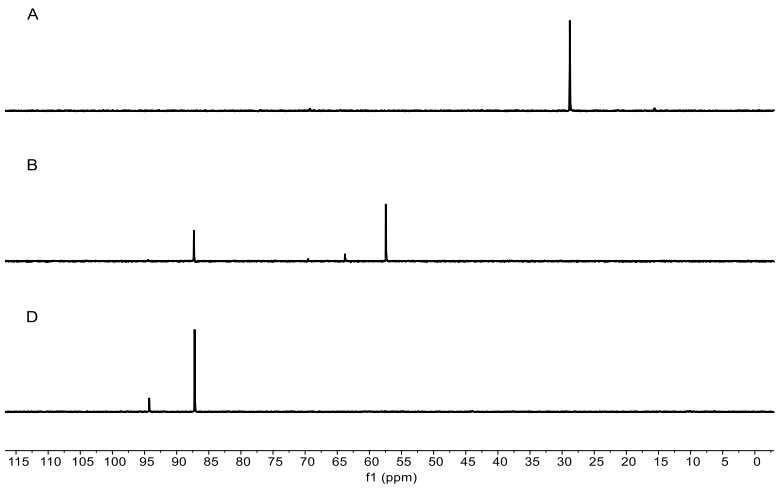


Figure S2. Time-stacked in situ ^{31}P NMR spectra during catalysis (*T* = 25 °C, 1,4-dioxane). (A) **2**·[O], $PhSiH_3$; *t* = 12 h; (B) $PhSiH_3$, $PhSO_2Cl$; *t* = 1 min; (C) *t* = 70 min. Chemical shifts (δ): *anti*-**2**·[O], 56.4 ppm; *anti*-2, 28.8 ppm; unknown peaks at 87.3 and 94.4 ppm.

To an oven-dried purged septum-sealed NMR tube, was added a solution of **2**·[O] (8.7 mg, 0.05 mmol) in dry 1,4-dioxane (1 mL, 0.25 M) followed by Phenylsilane (61 μL, 0.50 mmol, 2 equiv) and ^{31}P NMR spectra were recorded immediately. Phosphetane oxide **2**·[O] (δ 57.7 *major*, 64.4 *minor* ppm) is converted to two new resonances of phosphetane **2** (δ 28.8 *major*, 15.6 *minor* ppm) over the course of 12 h (Fig. 3B). $PhSO_2Cl$ (59 μL, 0.46 mmol, 1.8 equiv) was added to the above reaction mixture in NMR tube and ^{31}P NMR spectra, were recorded immediately and at 10 minute intervals. Phosphetane **2** is converted to mixture of **2**·[O] (δ 57.7 *major*, 64.4 *minor* ppm) and new resonance at 87.3 ppm within 1 min reaction time . After 70 min reaction time, **2**·[O] was completely converted to resonances at 87.3 ppm and 94.4 ppm which remained as the only observable phosphorus species in the reaction even after 48 h reaction time. Identical spectra were obtained when the experiment was conducted in presence of indole **1** (29.4 mg, 0.25 mmol).

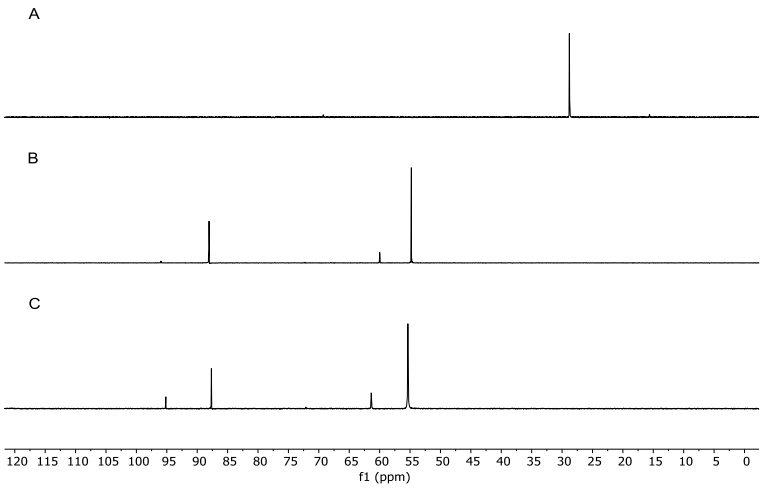
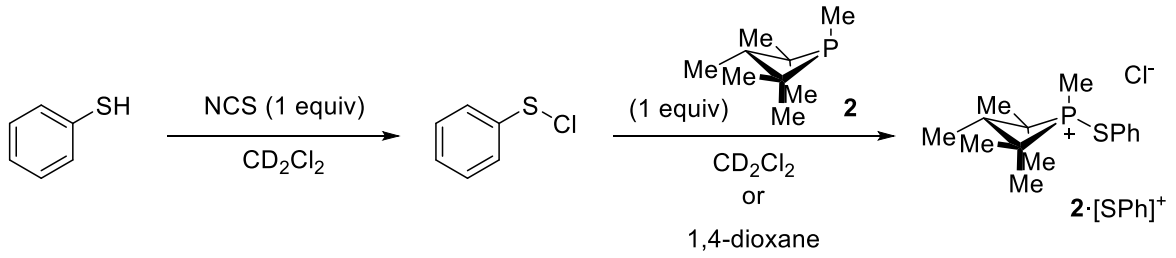


Figure S3. Time-stacked in situ ^{31}P NMR spectra during catalysis (*T* = 25 °C, 1,4-dioxane). (A) *anti*-3; (B) $PhSO_2Cl$; *t* = 1 min; (C) *t* = 12 h. Chemical shifts (δ): *anti*-**2**•[O], 57.7 ppm; *syn*-**2**•[O], 64.4 ppm; *anti*-3, 28.8 ppm; unknown peaks at 87.3 and 94.4 ppm (from text)

To an oven-dried purged septum-sealed NMR tube, was added a solution of **2** (8 mg, 0.05 mmol) in dry 1,4-dioxane (1 mL, 0.25 M) and ^{31}P NMR spectra, were recorded. $PhSO_2Cl$ (59 μL, 0.46 mmol, 1.8 equiv) was added to the above solution in NMR tube via syringe and ^{31}P NMR spectra, were recorded immediately and at 30 min intervals up to 6 h. Phosphetane **2** is converted to mixture of **2**·[O] (δ 57.7 *major*, 64.4 *minor* ppm) and new resonances at 87.3 ppm *major* and 94.4 ppm *minor* within 1 min reaction time. After 12 h reaction time, mixture of **2**·[O] (δ 57.7 *major*, 64.4 *minor* ppm) and new resonances at 87.3 ppm *major* and 94.4 ppm *minor* were still observed in the reaction via ^{31}P NMR spectra. Identical spectra were obtained when the experiment was conducted in presence of indole **1** (29.4 mg, 0.25 mmol).

4.2. Procedure for independent synthesis of intermediate 2·[SPh]$^+$



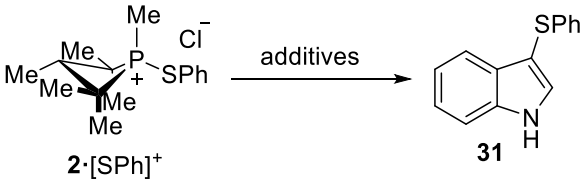
The following procedure was performed inside nitrogen-purged glove box. In a dry 1 dram vial, thiophenol (41 μL, 0.40 mmol, 1 equiv) followed by dry CD_2Cl_2 (0.4 mL, 1 M) was added. *N*-Chlorosuccinimide (NCS) (54.4 mg, 0.407 mmol, 1.02 equiv) was added to the above reaction mixture in three portions (*resulted in exothermic reaction*) over 5 min. The reaction mixture was stirred at RT for 0.5 h, during which time the pale-yellow solution turned to bright orange along with precipitation

of succinimide byproduct. The reaction mixture was filtered to remove the white solid and give a dichloromethane solution of PhSCl, which was used immediately due to the known risk of explosion (CAUTION!).[1] To this freshly prepared ca. 1 M solution of phenylsulfenyl chloride (PhSCl) in CD_2Cl_2, was added solution of **2** (63.3 mg, 0.4 mmol, 0.5 M, 1 equiv) in CD_2Cl_2 (0.8 mL) or 1,4-dioxane (0.8 mL) in dropwise fashion during which time the orange colored solution turned colorless. The resulting colorless solution of **2**·$[SPh]^+$ (0.4 mmol, 0.34 M, *dr 16:1*) was transferred to a screw-capped NMR tube equipped with septa, sealed and analyzed by ^1H, ^{13}C and ^{31}P NMR spectroscopy.

1,2,2,3,4,4-hexamethyl-1-(phenylthio)phosphetan-1-ium chloride (**2**·$[SPh]^+$): ^{31}P NMR (162 MHz, 1,4-dioxane) δ 87.3 *major*, 94.4 *minor* ppm. ^{31}P NMR (162 MHz, CD_2Cl_2) δ 85.8 *major*, 92.6 *minor* ppm. ^1H NMR (400 MHz, CD_2Cl_2) *Major* δ 7.61 – 7.46 (m, 5H), 3.23 (qd, J = 7.1, 2.5 Hz, 1H), 2.46 (d, J = 11.7 Hz, 3H), 1.58 – 1.47 (m, 12H), 1.05 (dd, J = 7.0, 1.3 Hz, 3H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 136.5 (d, J_{PC} = 3.0 Hz), 131.8 (d, J_{PC} = 2.5 Hz), 131.1 (d, J_{PC} = 2.2 Hz), 119.7 (d, J_{PC} = 7.3 Hz), 49.1 (d, J_{PC} = 5.2 Hz), 46.5 (d, J_{PC} = 37.5 Hz), 23.9 (d, J_{PC} = 4.0 Hz), 19.7 (d, J_{PC} = 3.7 Hz), 8.6 (d, J_{PC} = 23.4 Hz), 6.6 (d, J_{PC} = 20.5 Hz). HRMS calculated for $[C_{15}H_{24}PS]^+$ 267.1336, found 267.1336.

*N.B. The final solution of **2**·[SPh]⁺ contains some residual succinimide byproduct and NCS from the PhSCl synthesis step.*

4.3. Evaluation of the electrophilicity of 2·[SPh]⁺ against indole



a) none 0%
b) $PhSiH_3$ 0%
c) $PhSiH_3/PhSO_2Cl$ 99%

The following procedure was performed inside nitrogen-purged glove box.

Experiment (*a*): To a screw-capped NMR tube equipped with septa, was added solution of indole (22.1 mg, 0.19 mmol) in dry 1,4-dioxane (0.4 mL). Freshly prepared solution of **2**·$[SPh]^+$ (57.1 mg, 0.19 mmol, 1 equiv) in 1,4-dioxane (0.4 mL) was added to the above solution, sealed and the tube was inverted to facilitate mixing. The resulting reaction mixture was periodically analyzed by ^1H and ^{31}P NMR spectroscopy. No sulfenylated product **31** was observed even after 24 h at RT or 40 °C. GC-MS

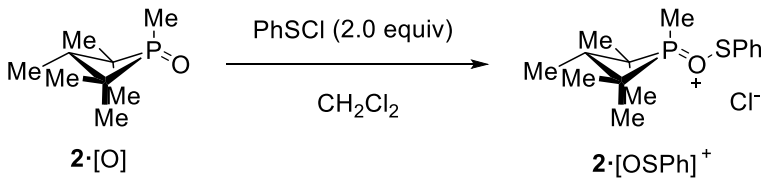
[1] D. G. Garratt, M. D. Ryan, A. Kabo, *Can. J. Chem.* **1980**, *58*, 2329–2339.

analysis of the reaction mixture further confirmed absence of **31**. **2**·[SPh]$^+$ was the only observable species in ^{31}P NMR spectra.

Experiment (*b*): To a screw-capped NMR tube equipped with septa, was added solution of indole (22.1 mg, 0.19 mmol) in dry 1,4-dioxane (0.4 mL) followed by $PhSiH_3$ (46.5 μL, 0.38 mmol, 2 equiv). Freshly prepared solution of **2**·[SPh]$^+$ (57.1 mg, 0.19 mmol, 1 equiv) in 1,4-dioxane (0.4 mL) was added to the above solution, sealed and the tube was inverted to facilitate mixing. The resulting reaction mixture was analyzed by ^{1}H and ^{31}P NMR spectroscopy and GC-MS analysis. No sulfenylated product **31** was observed even after 24 h at RT. ^{31}P NMR spectra showed presence of **2** and **2**·[SPh]$^+$ in 2.8:1 ratio.

Experiment (*c*): To a screw-capped NMR tube equipped with septa, was added solution of indole (22.1 mg, 0.19 mmol) in dry 1,4-dioxane (0.4 mL) followed by $PhSiH_3$ (46.5 μL, 0.38 mmol, 2 equiv) and $PhSO_2Cl$ (43.4 μL, 0.34 mmol, 1.8 equiv). Freshly prepared solution of **2**·[SPh]$^+$ (57.1 mg, 0.19 mmol, 1 equiv) in 1,4-dioxane (0.4 mL) was added to the above solution, sealed and the tube was inverted to facilitate mixing. The resulting reaction mixture was analyzed by ^{1}H and ^{31}P NMR spectroscopy and GC-MS analysis. Complete conversion of indole **1** to sulfenylated product **31** was observed. **2**·[SPh]$^+$ was the only observable species in ^{31}P NMR spectra.

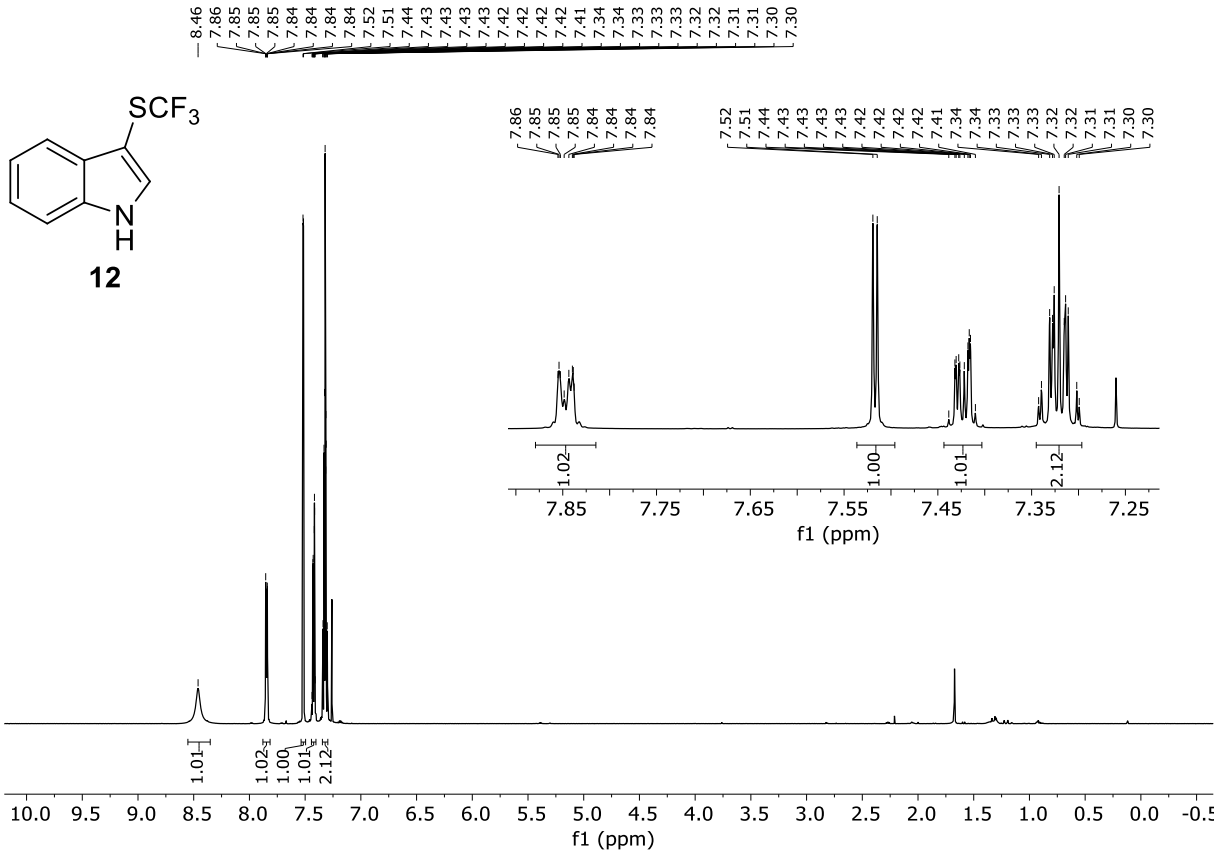
4.4. Detection of intermediate 2·[OSPh]$^+$ (*cf. Intermediate I in Fig. 4*)

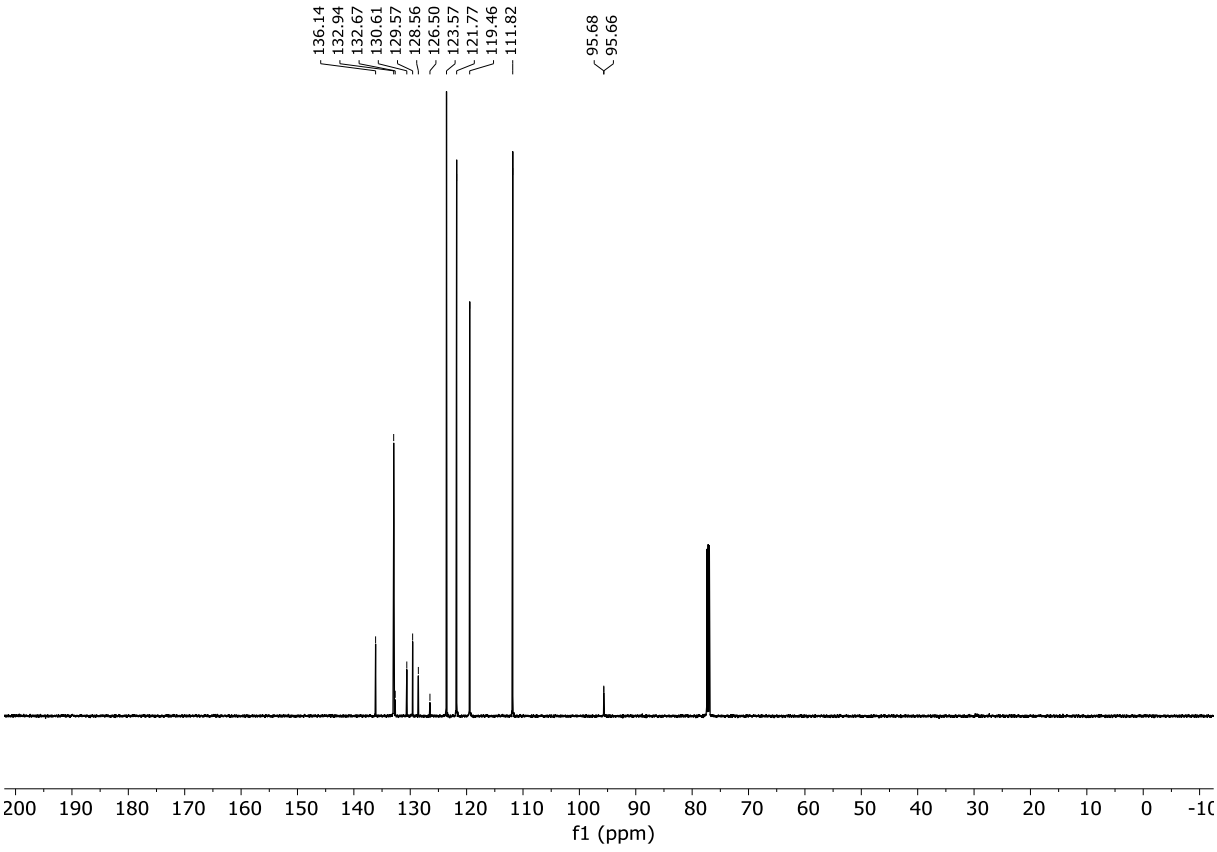


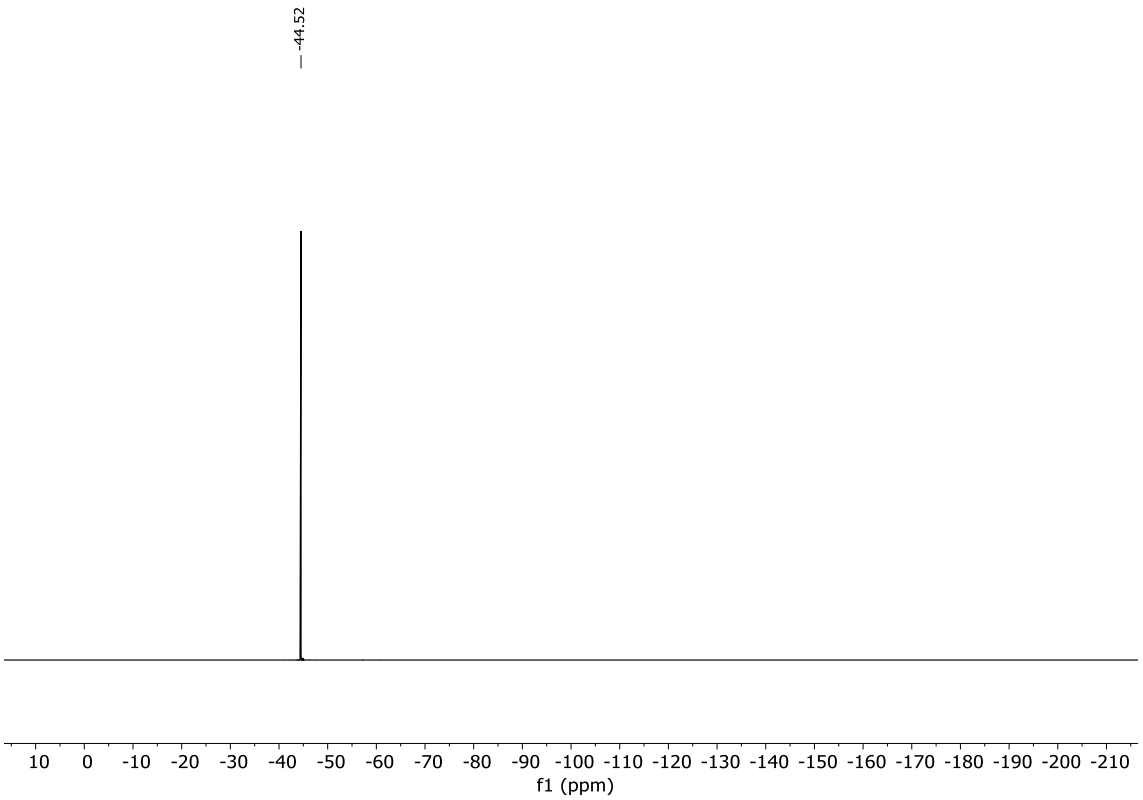
2·[O] **2**·[OSPh]$^+$

To a solution of **2**·[O] (17.4 mg, 100 μmol) in CH_2Cl_2 was added PhSCl (28.9 mg, 200 μmol) and then stirred for 5 min under N_2 atmosphere. Analysis of the crude by DART-MS revealed a mass peak of m/z = 281.13 amu consistent with the cationic species $[C_{15}H_{24}OPS]^+$.

5. Collection of NMR spectra



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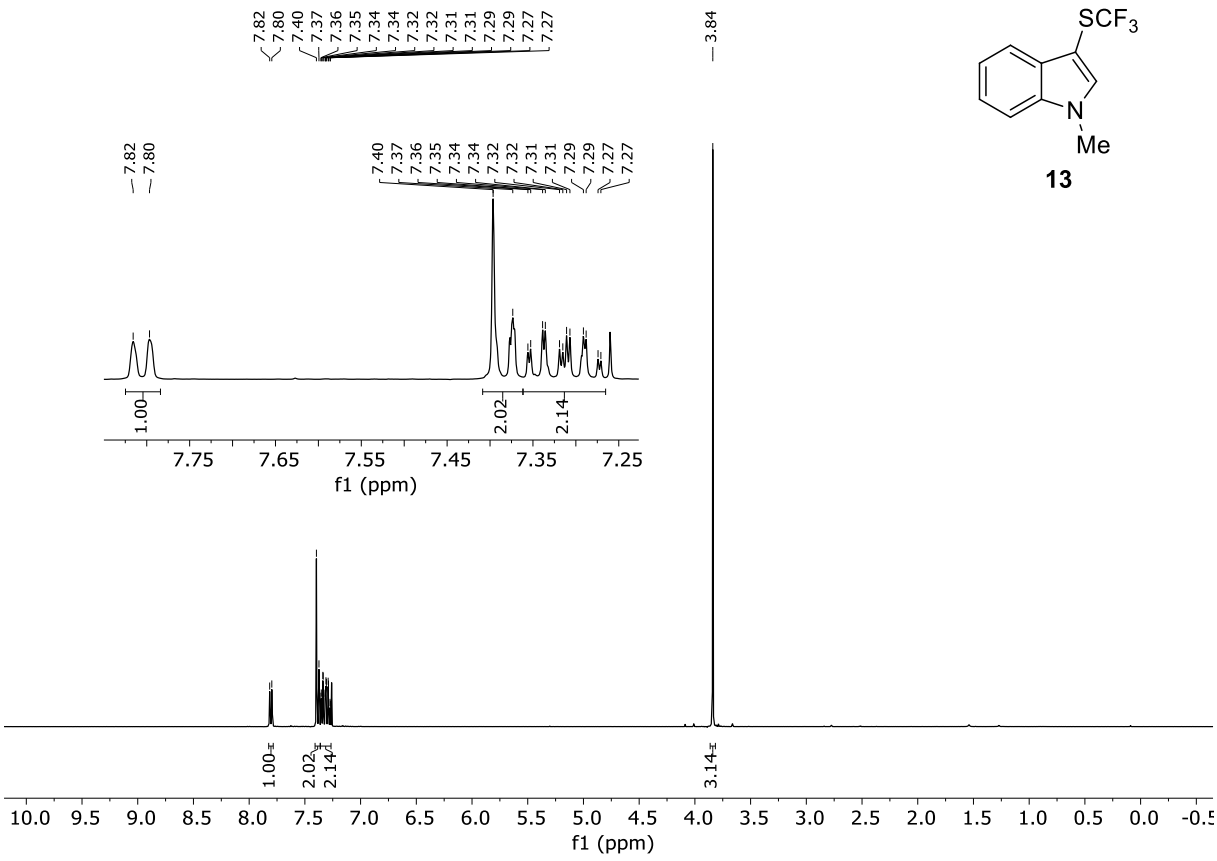
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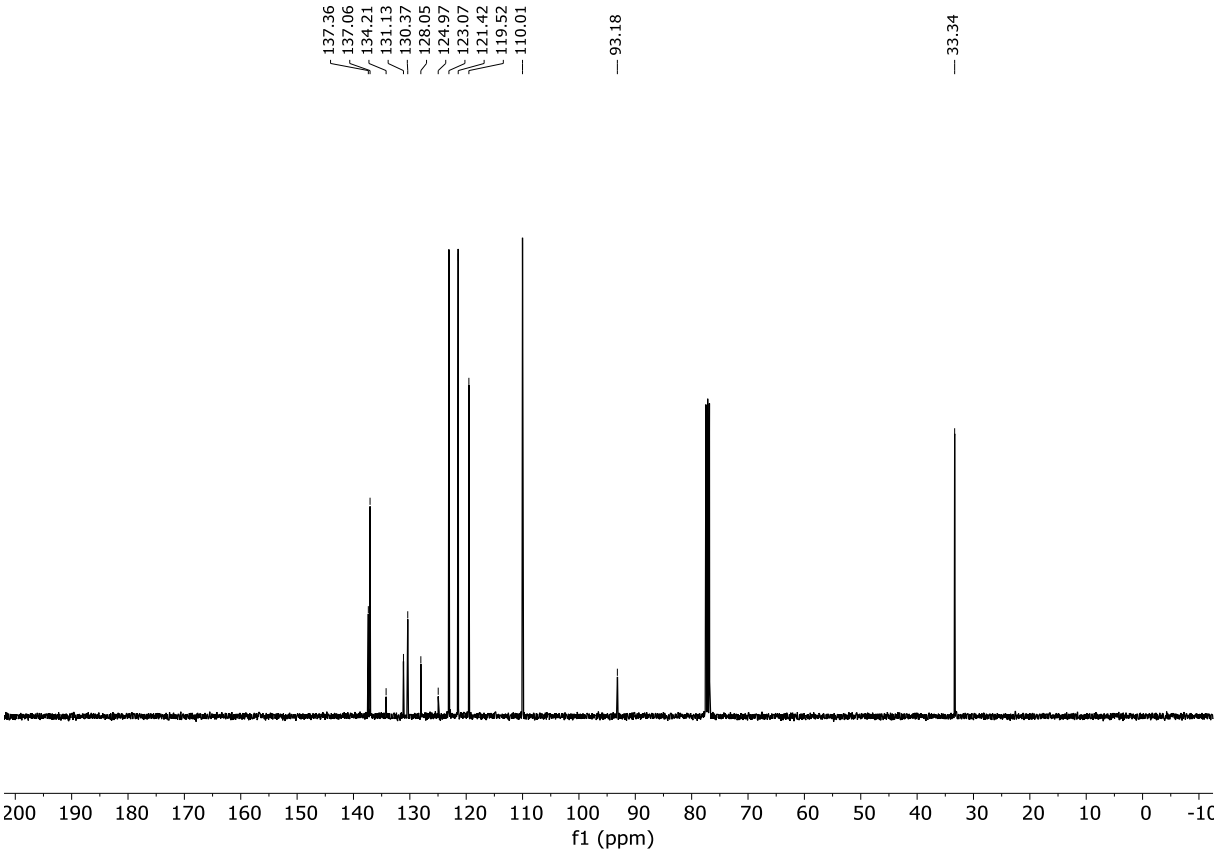
3.14
f1 (ppm)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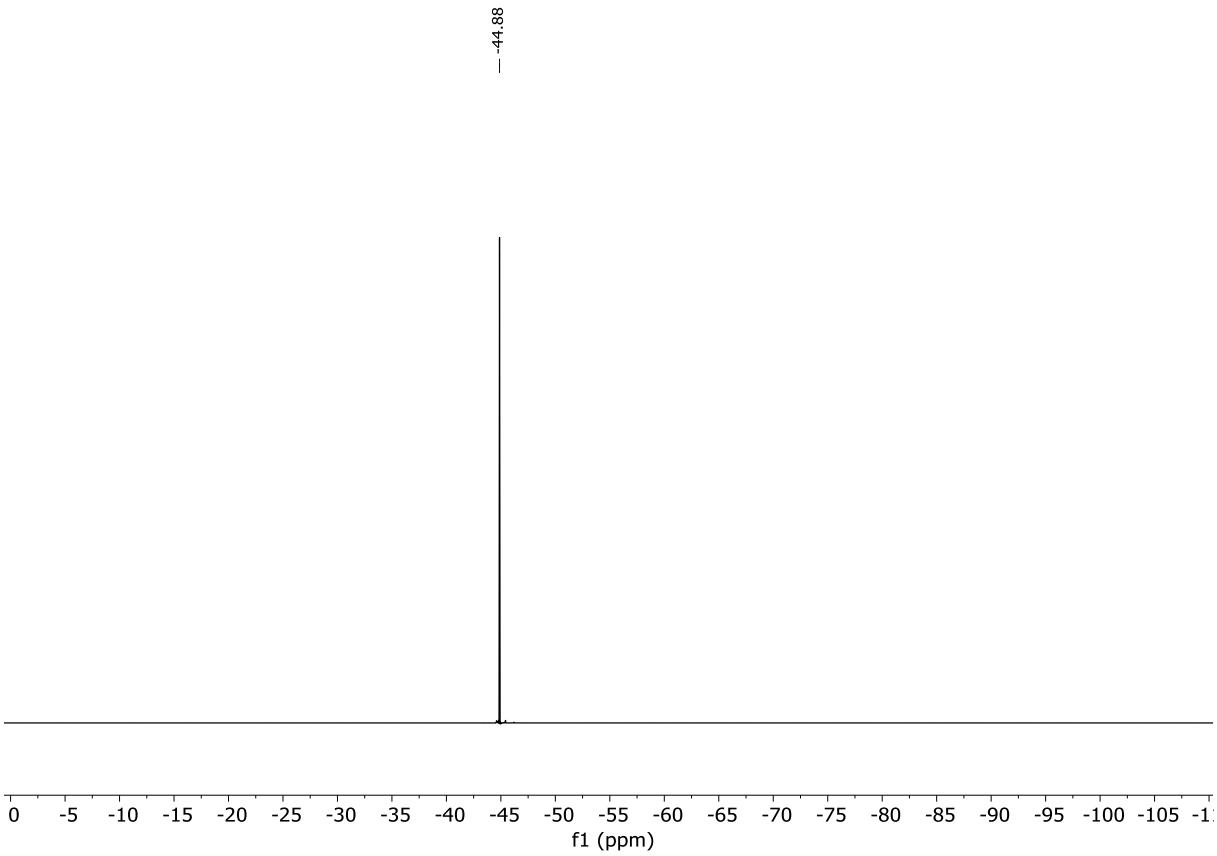
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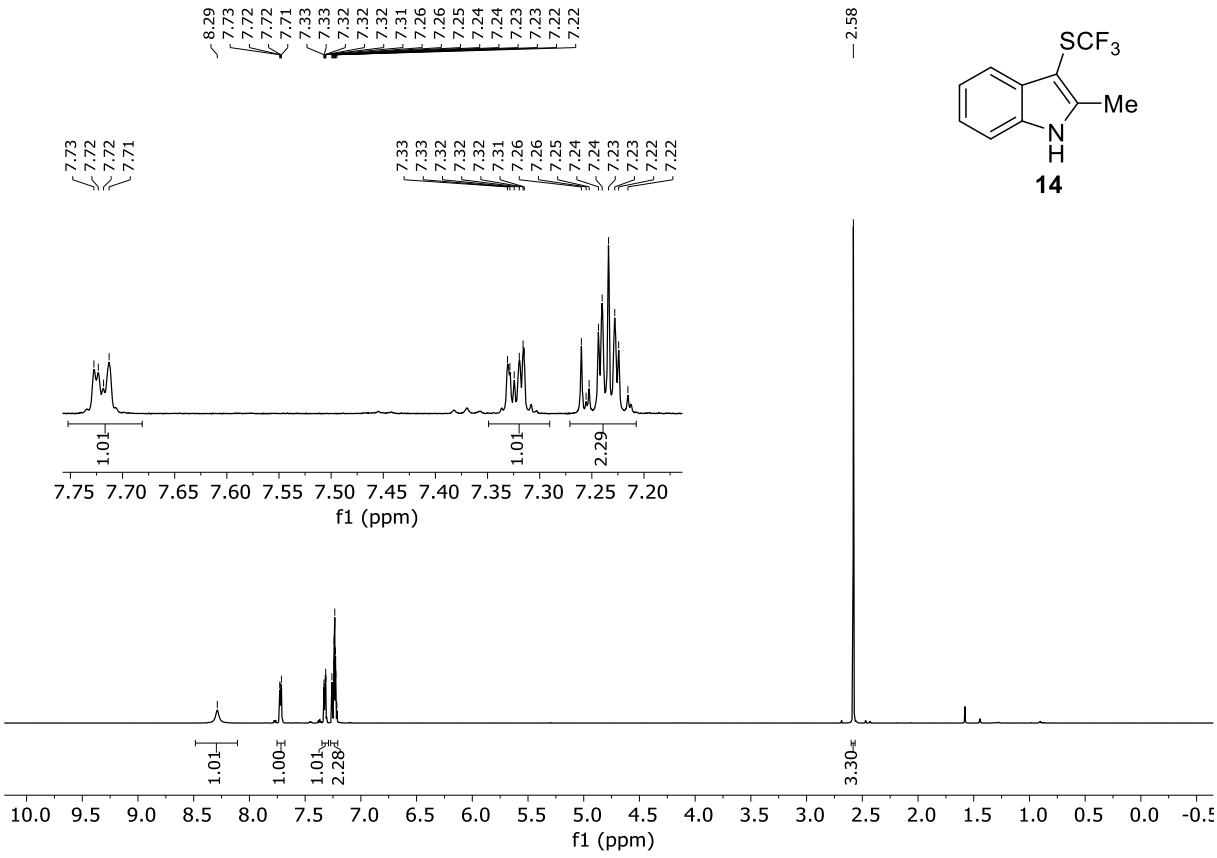
f1 (ppm)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Me
N
H
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1.01
2.29
7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20
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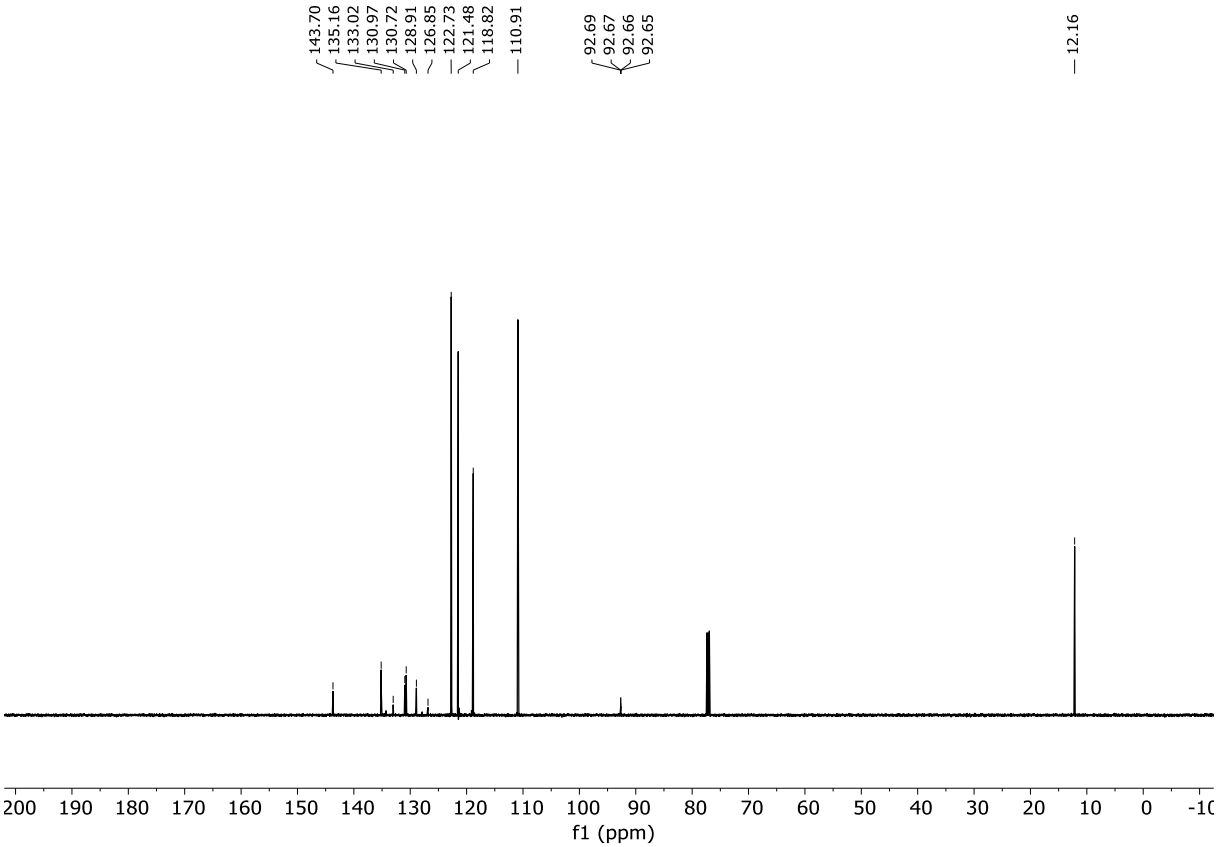
1.00
1.01
2.28
3.30
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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92.65
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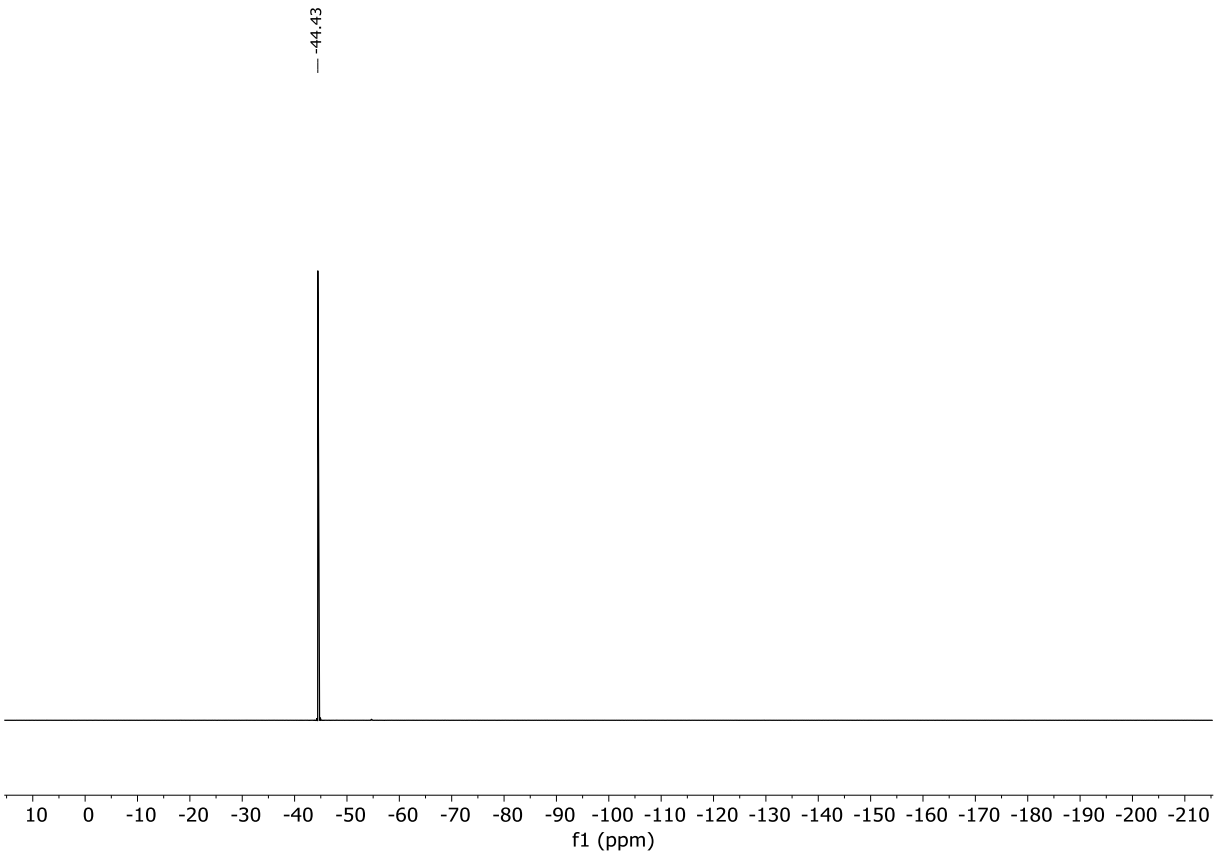
f1 (ppm)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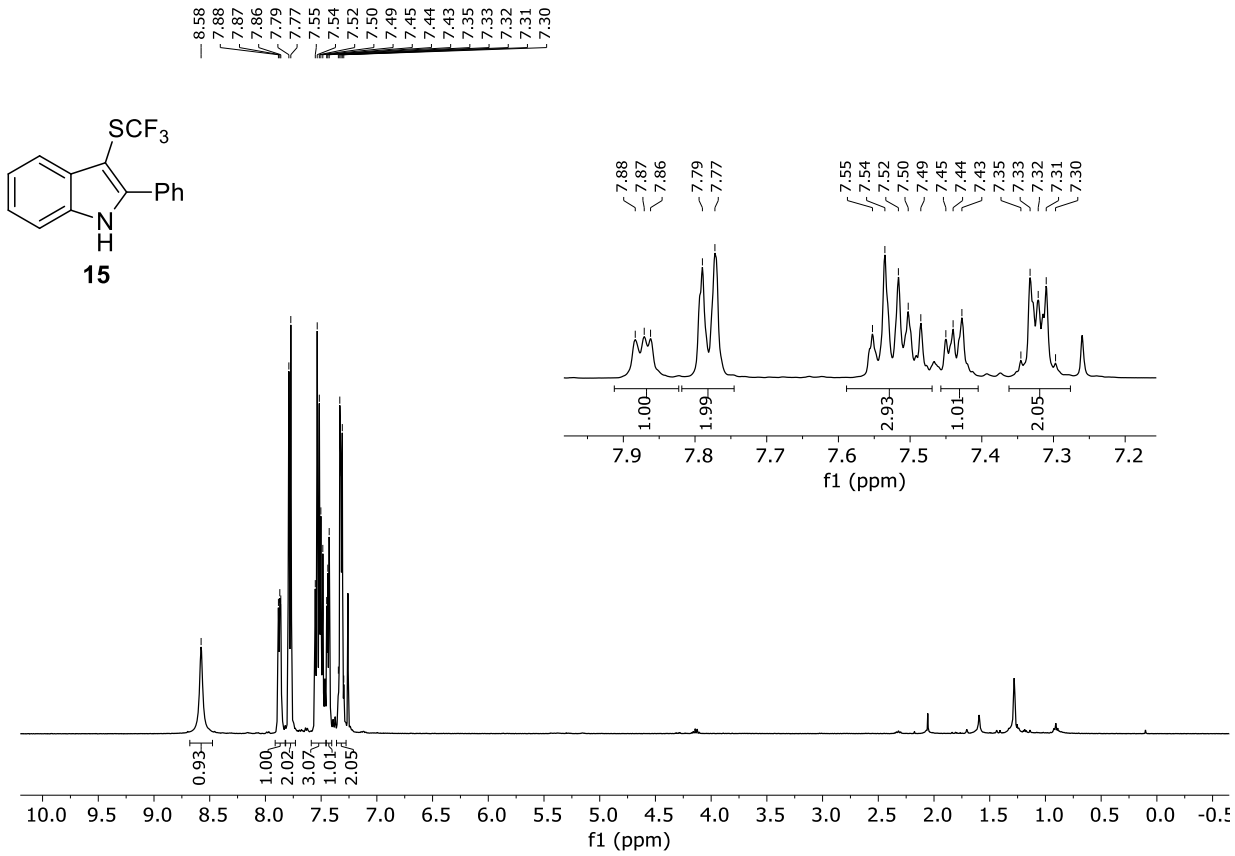
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7.31
7.30
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H
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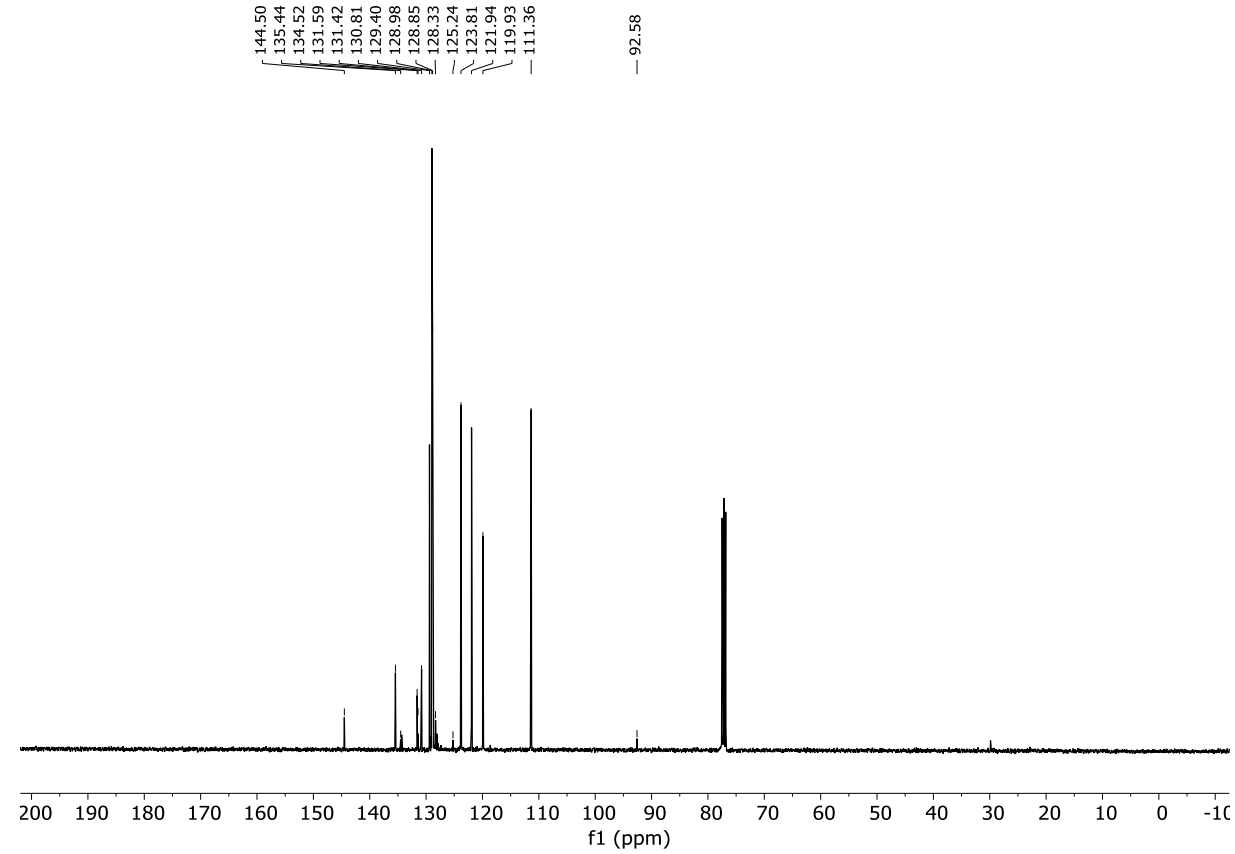
f1 (ppm)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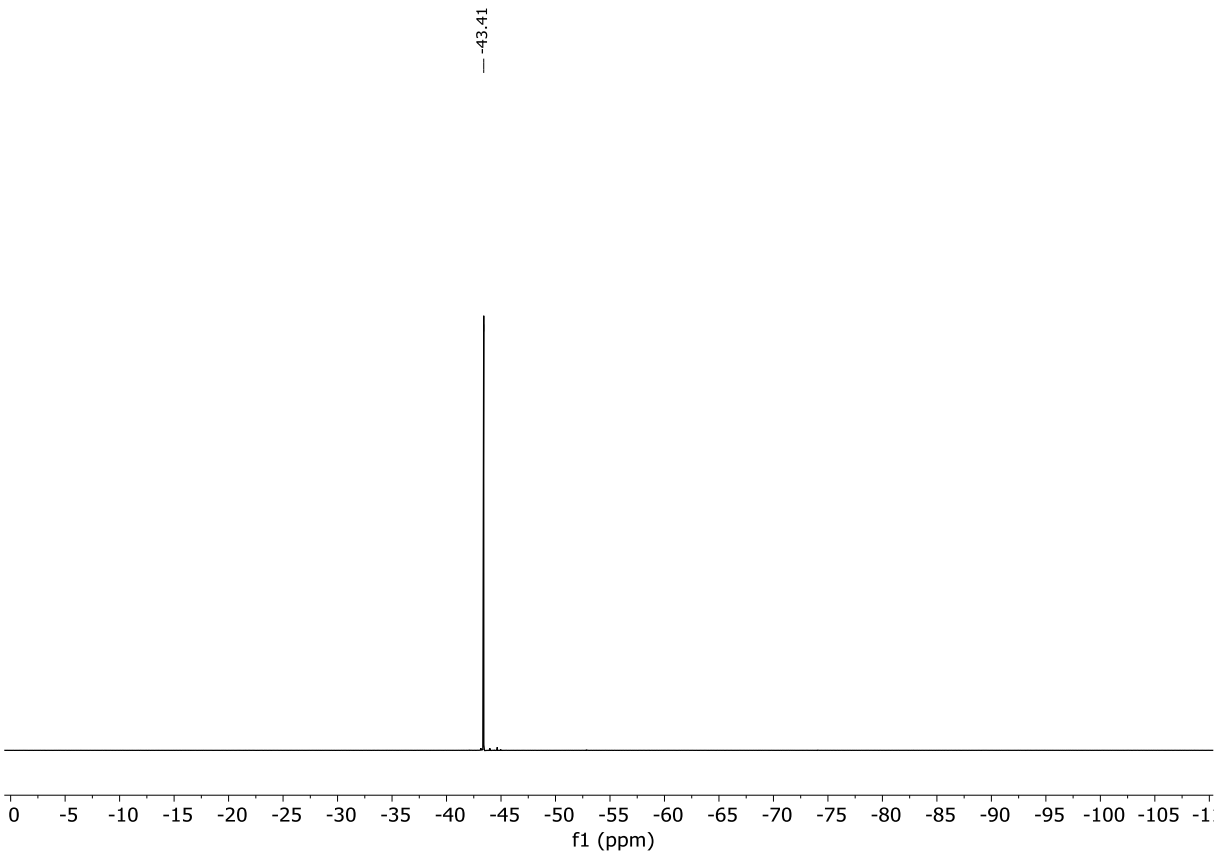
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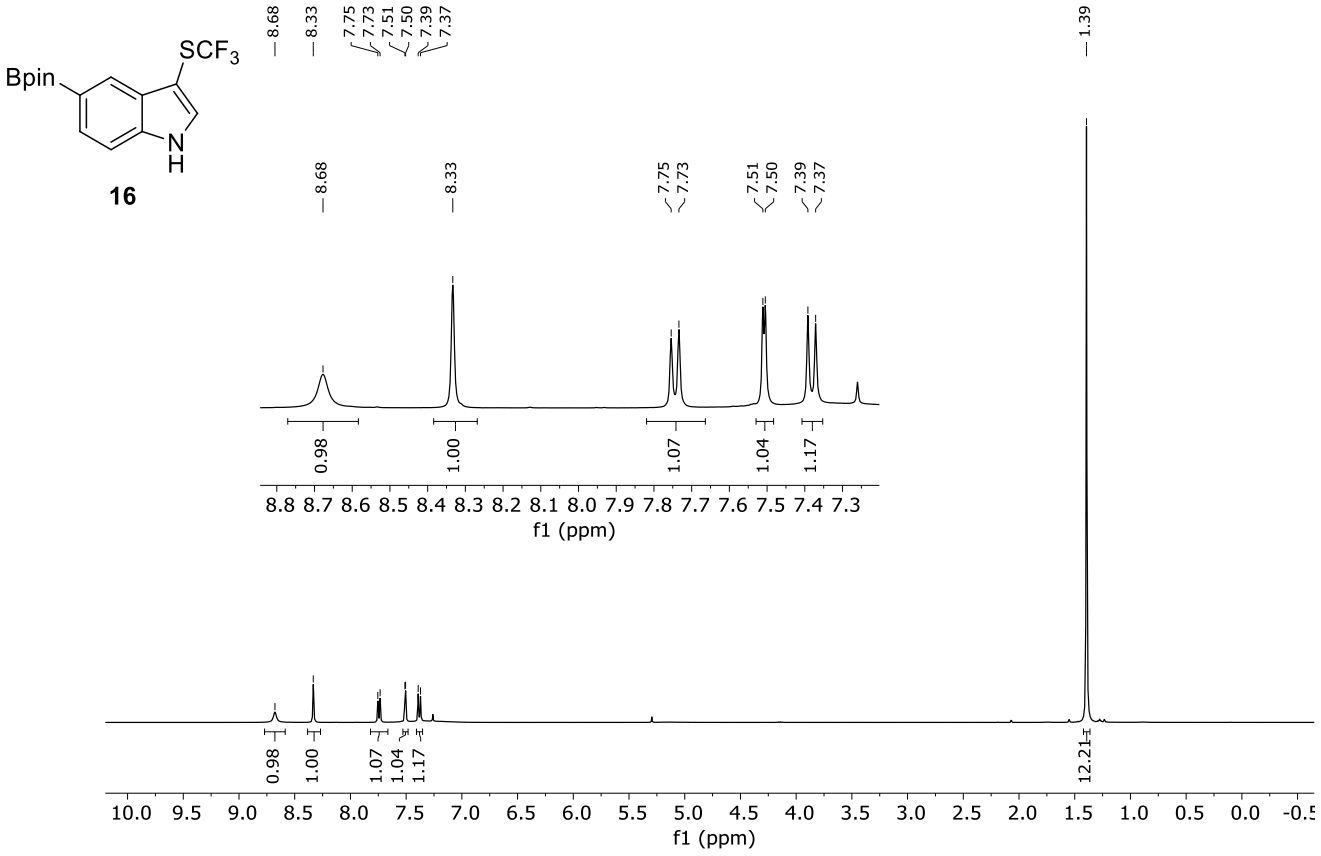
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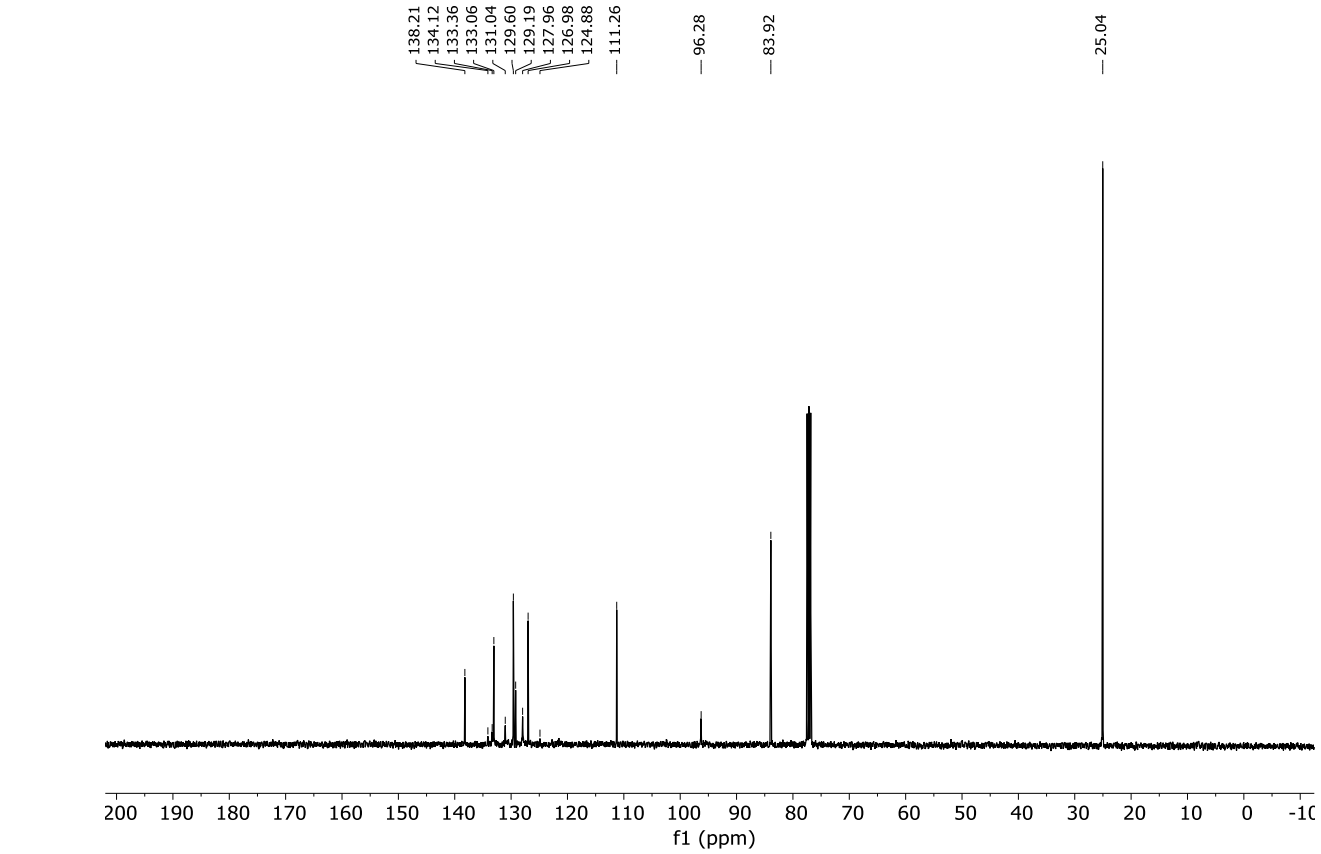
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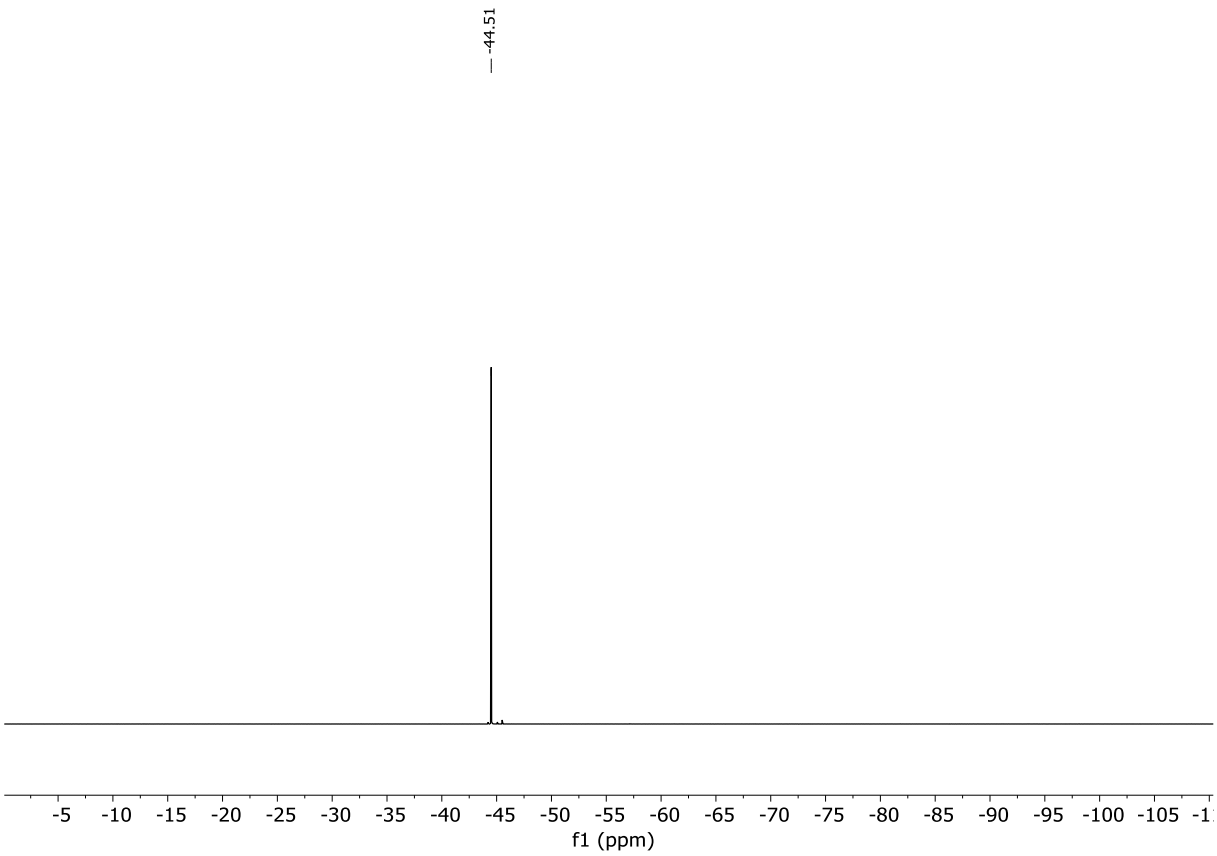
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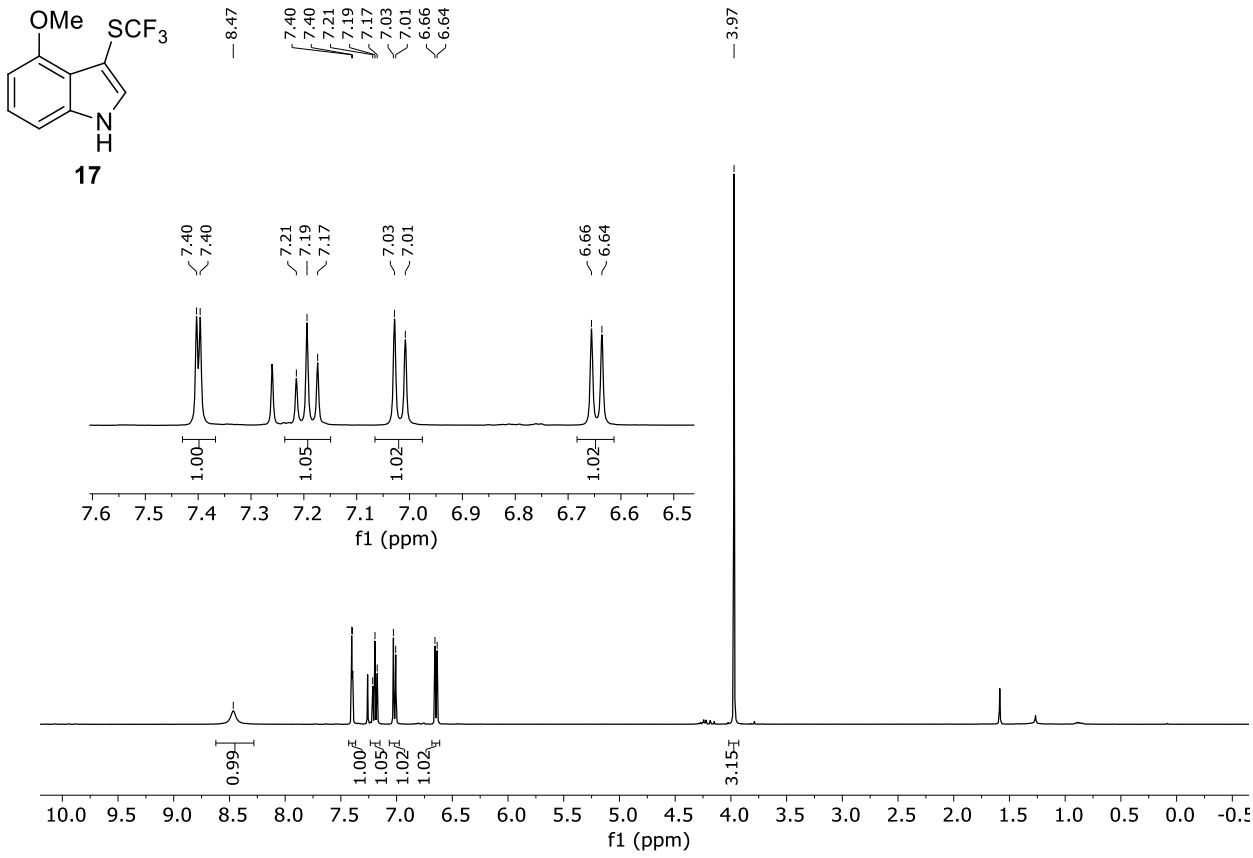
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6.64
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1.02
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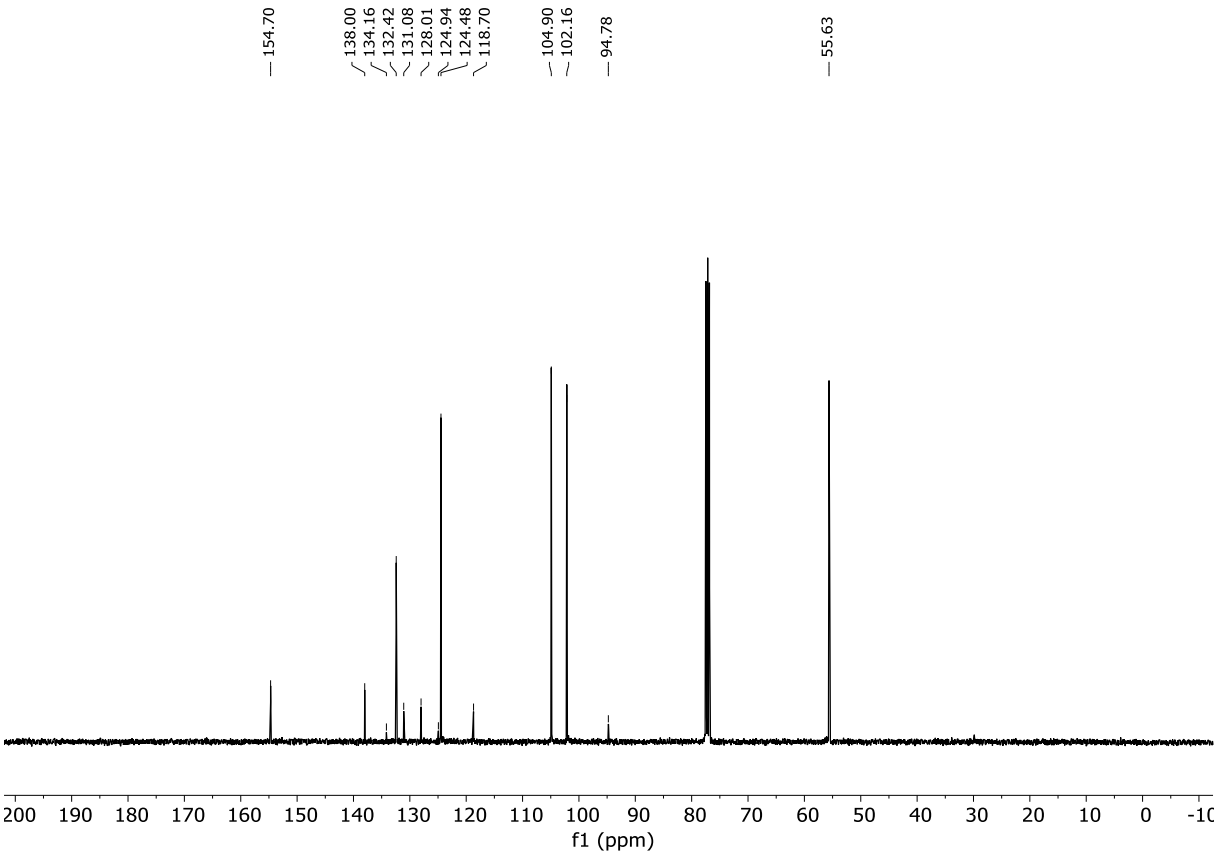
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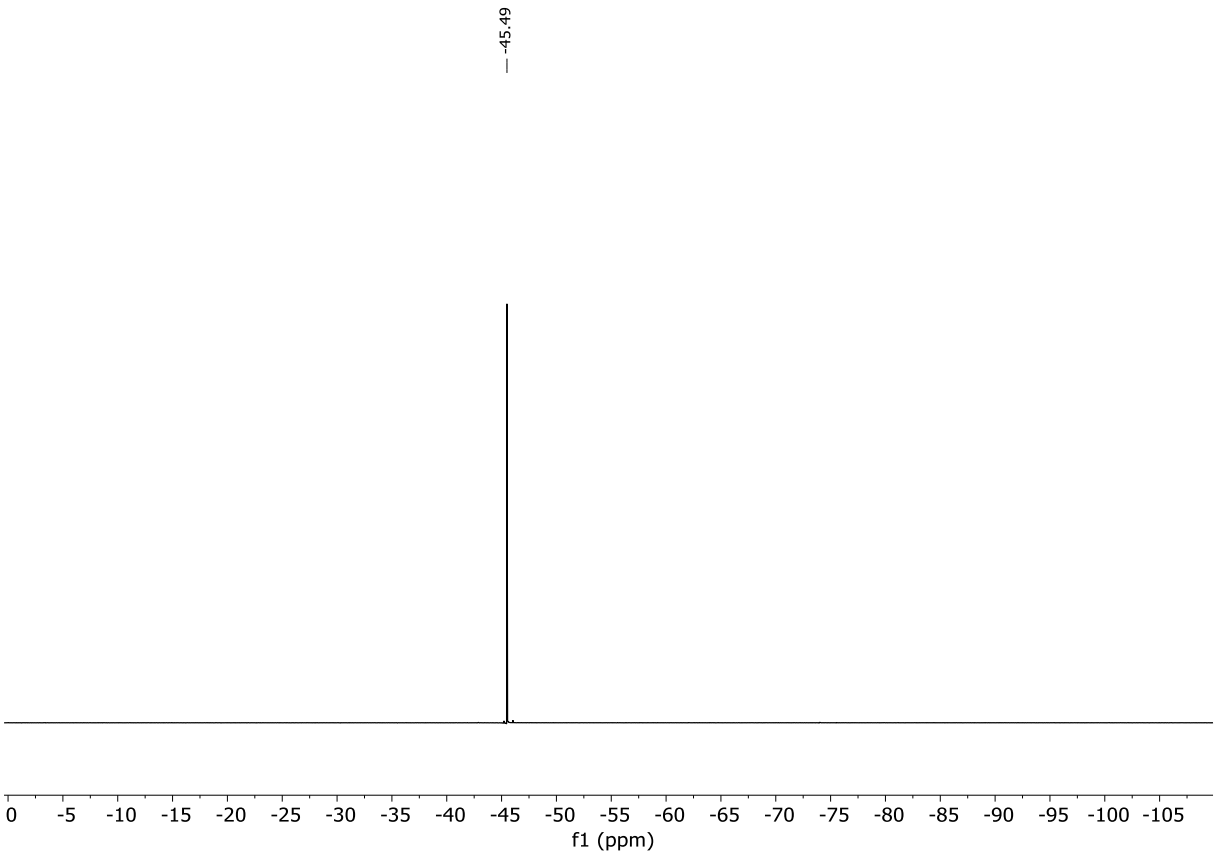
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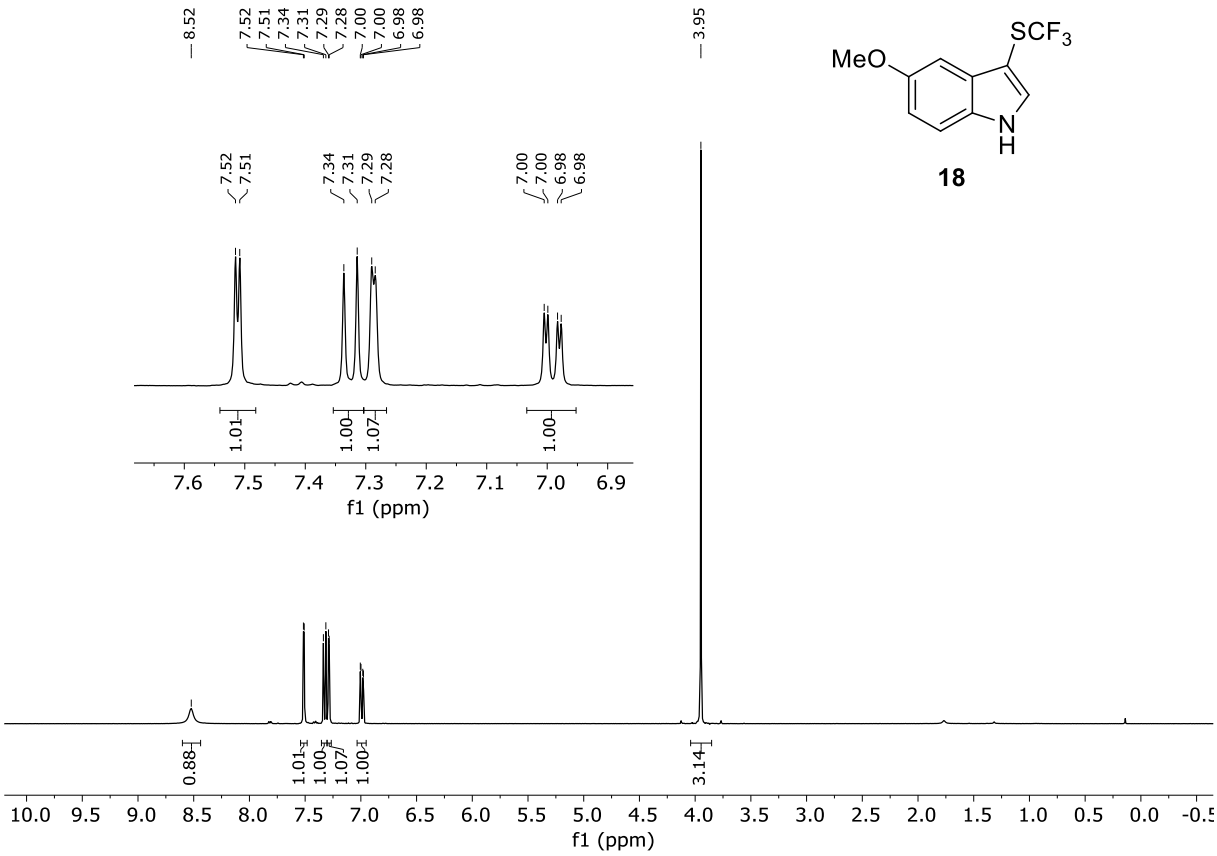
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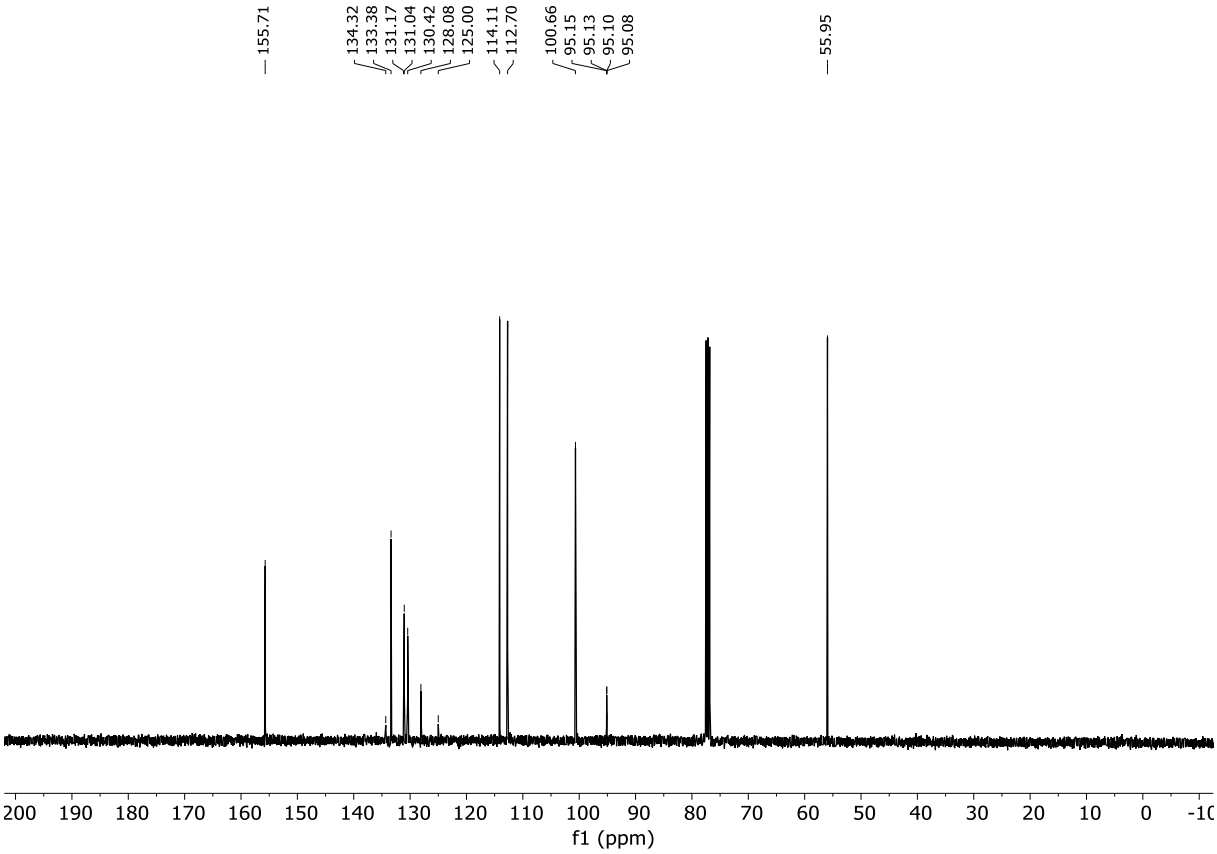
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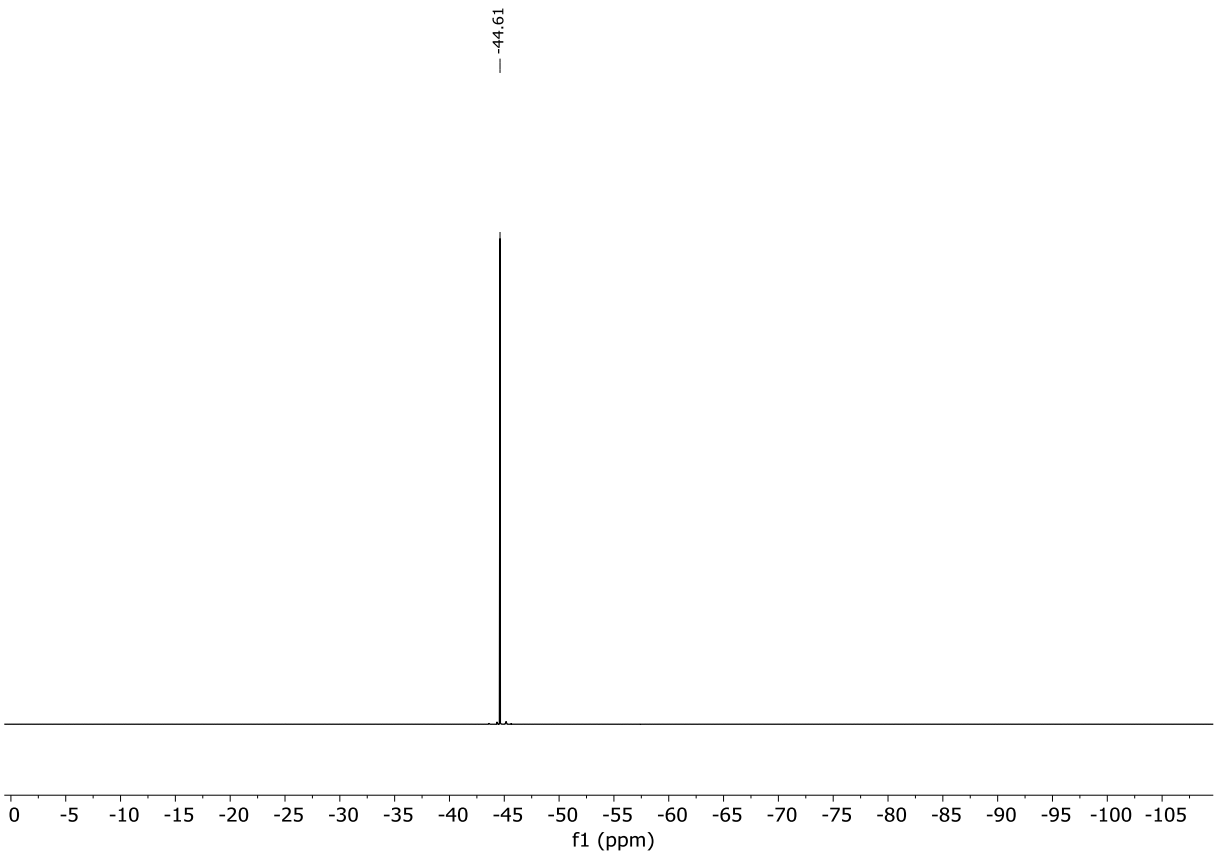
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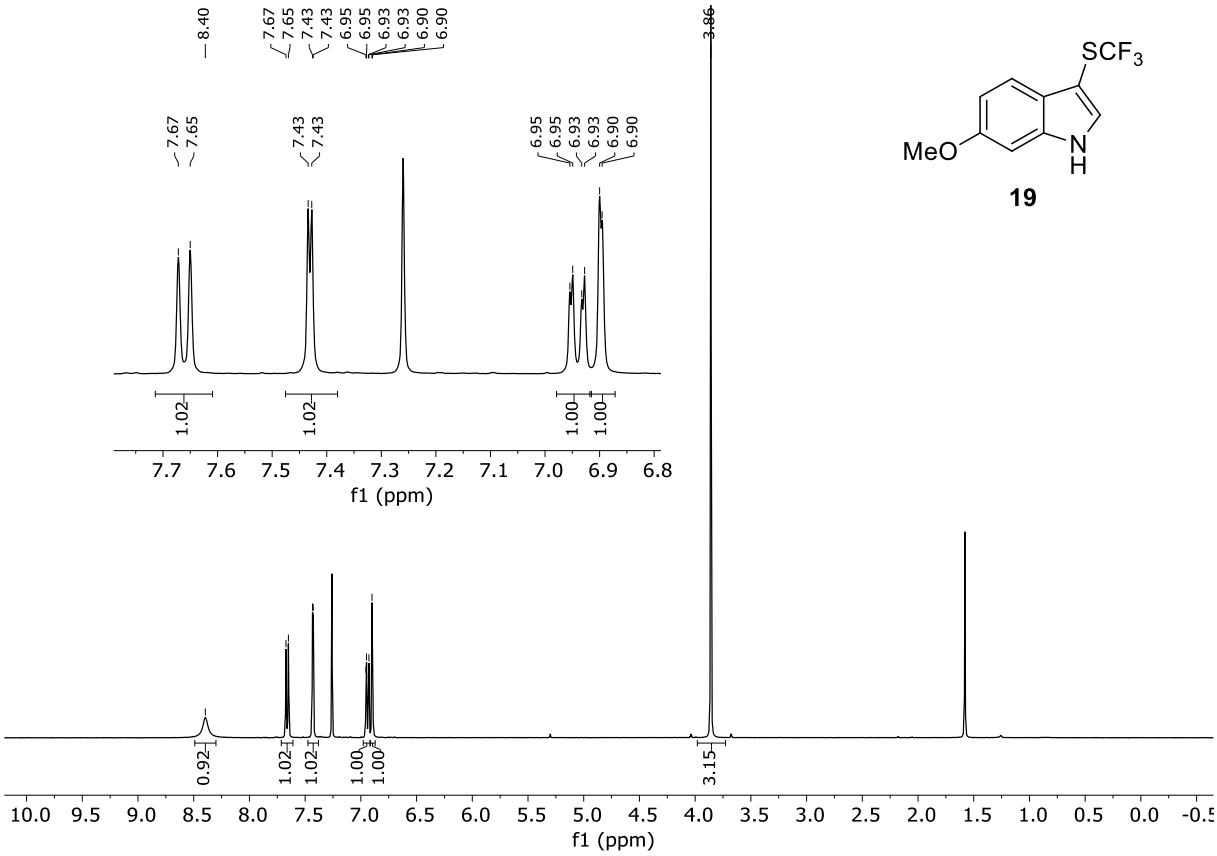
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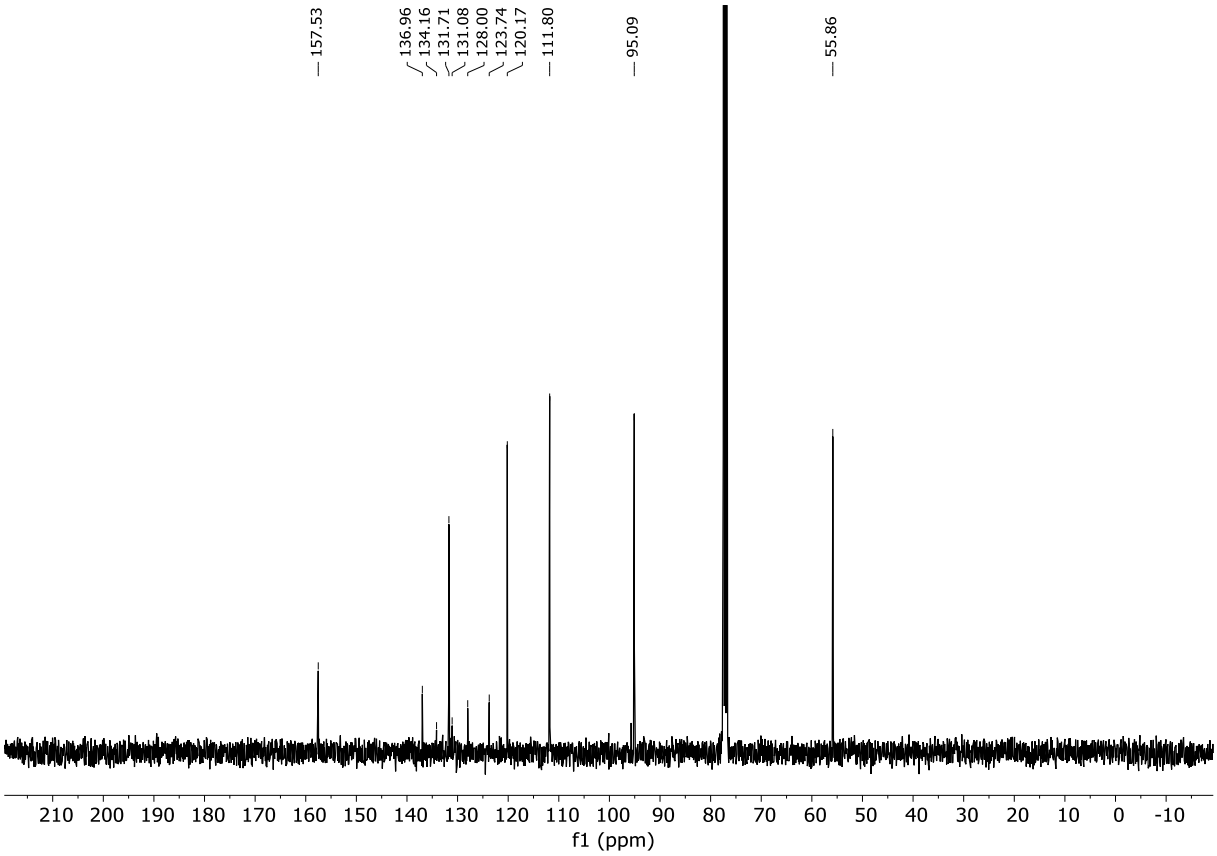
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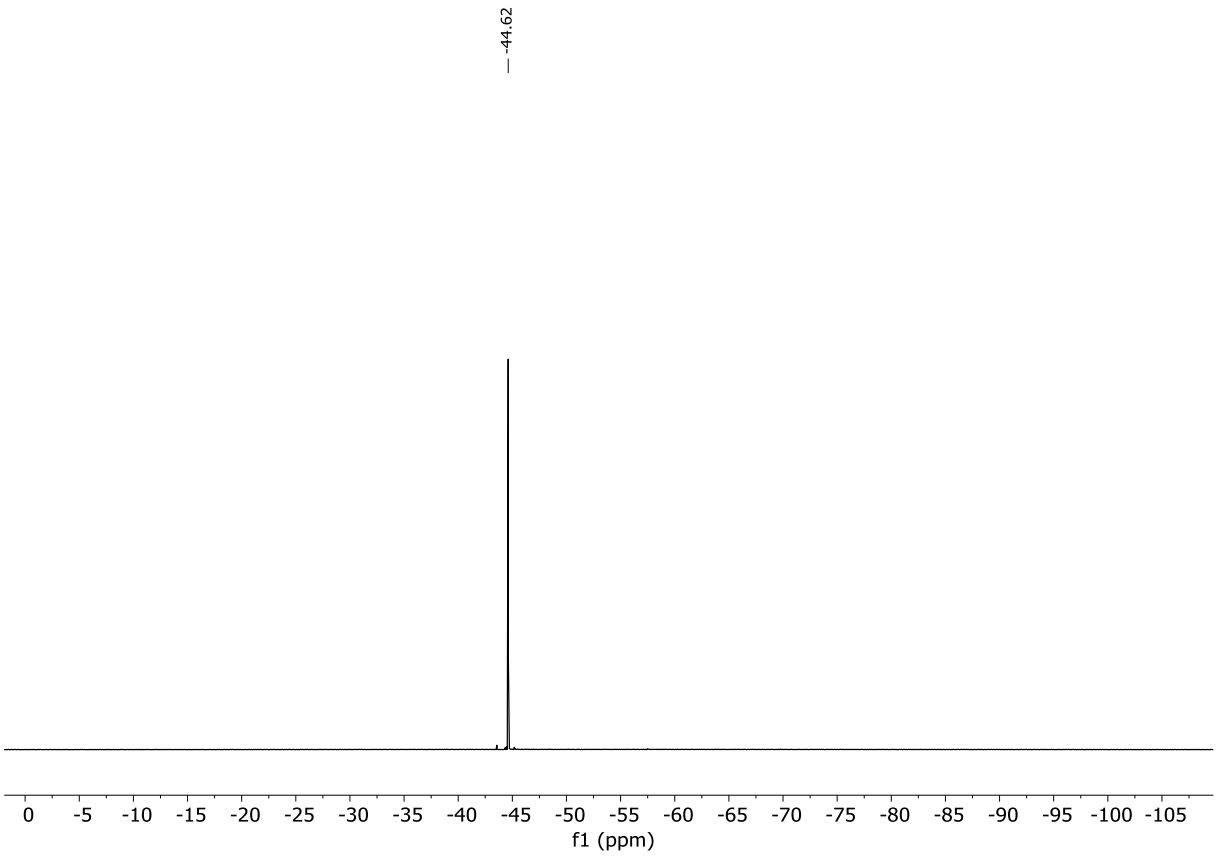
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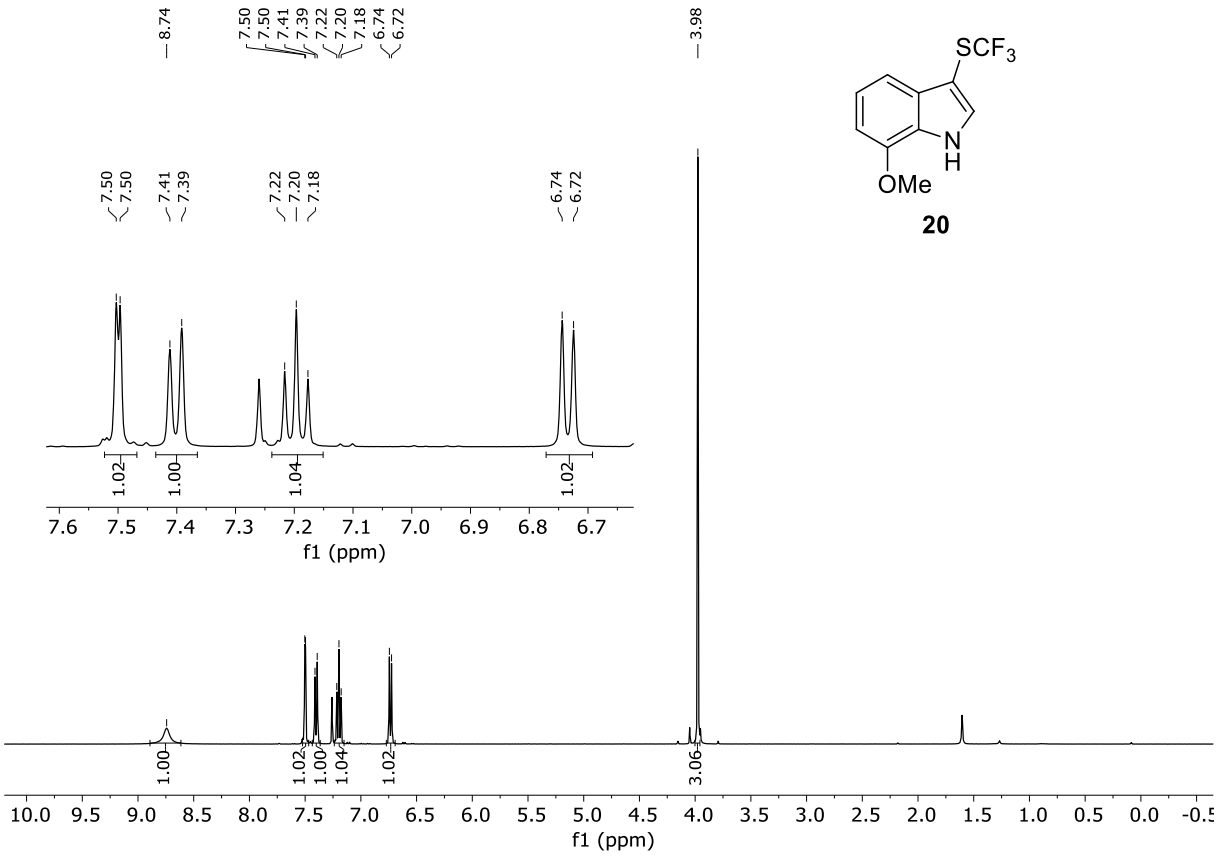
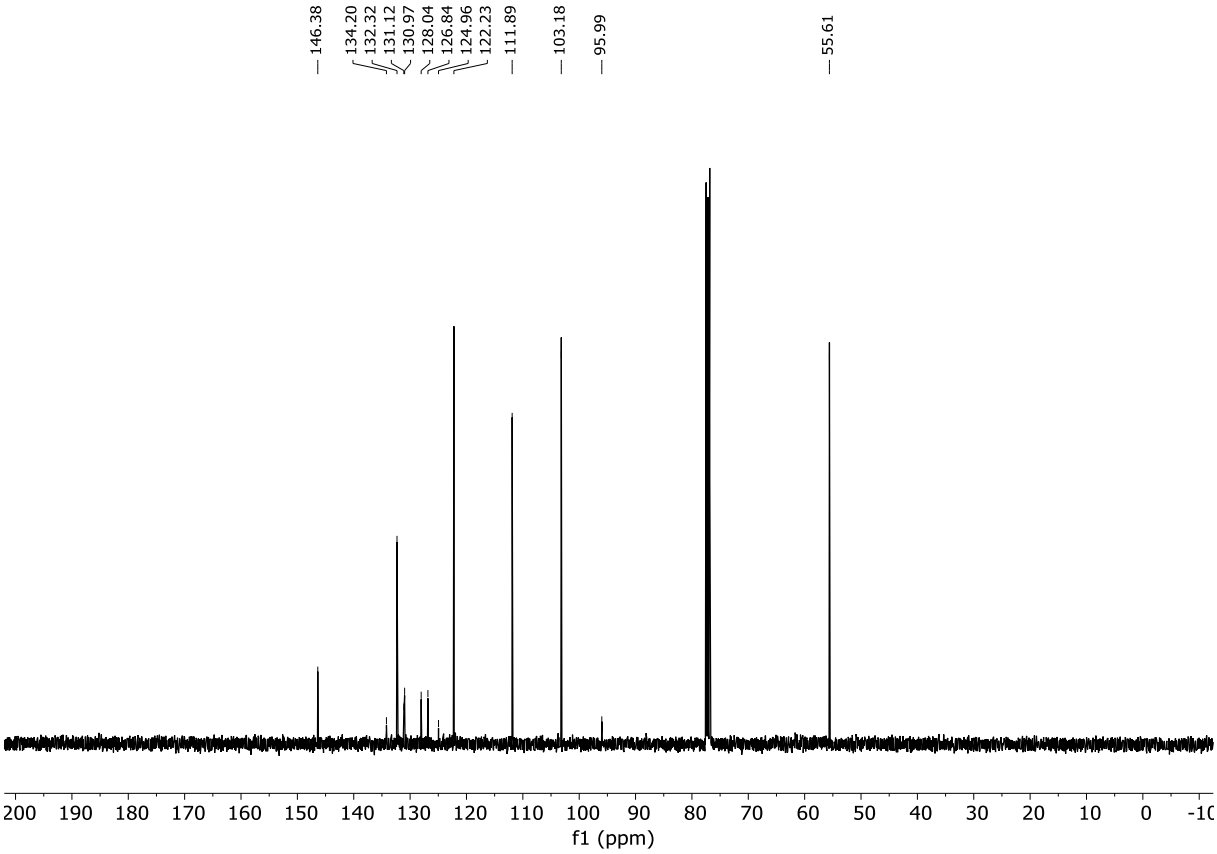
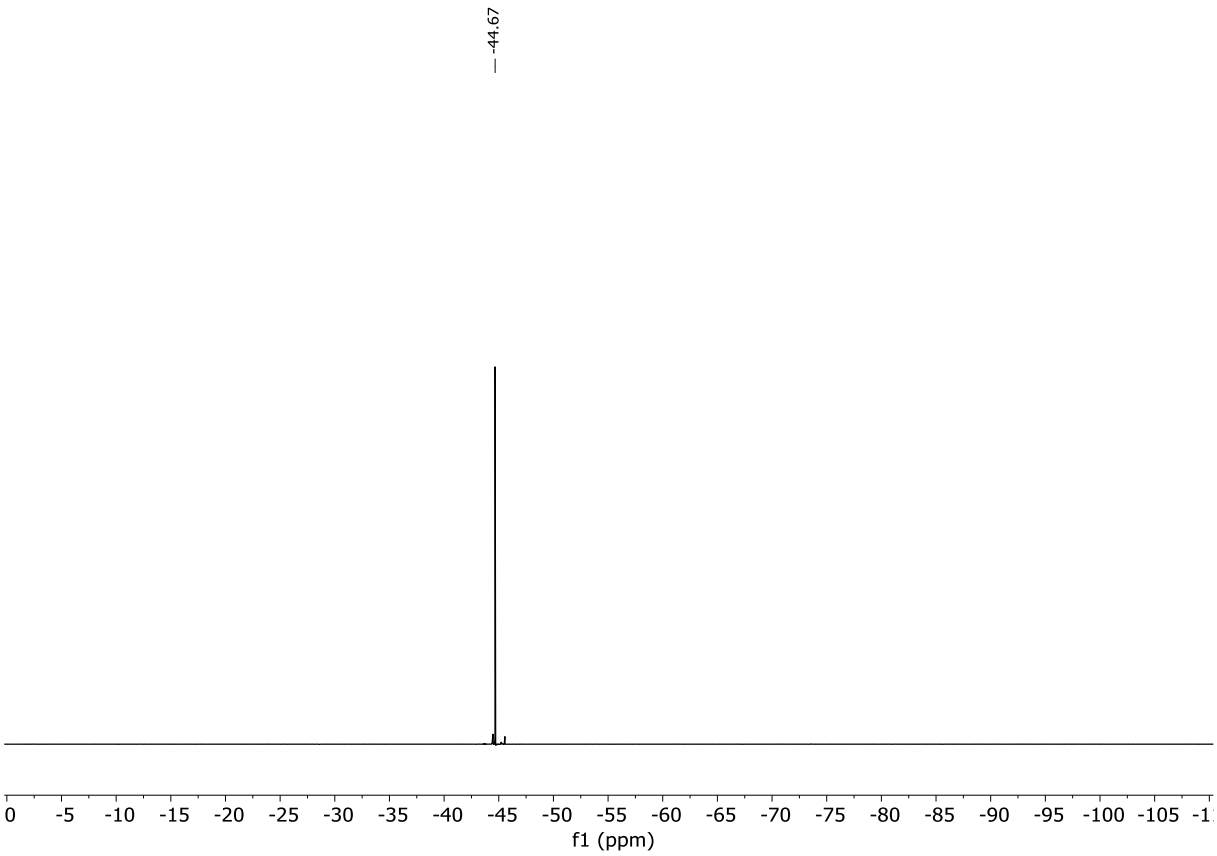
-105
f1 (ppm)


8.74
7.50
7.50
7.41
7.39
7.22
7.20
7.18
6.74
6.72
3.98
SCF3
N
H
OMe
20
1.00
1.02
1.00
1.04
1.02
3.06
f1 (ppm)


146.38
134.20
132.32
131.12
130.97
128.04
126.84
124.96
122.23
111.89
103.18
95.99
55.61
f1 (ppm)


-44.67
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
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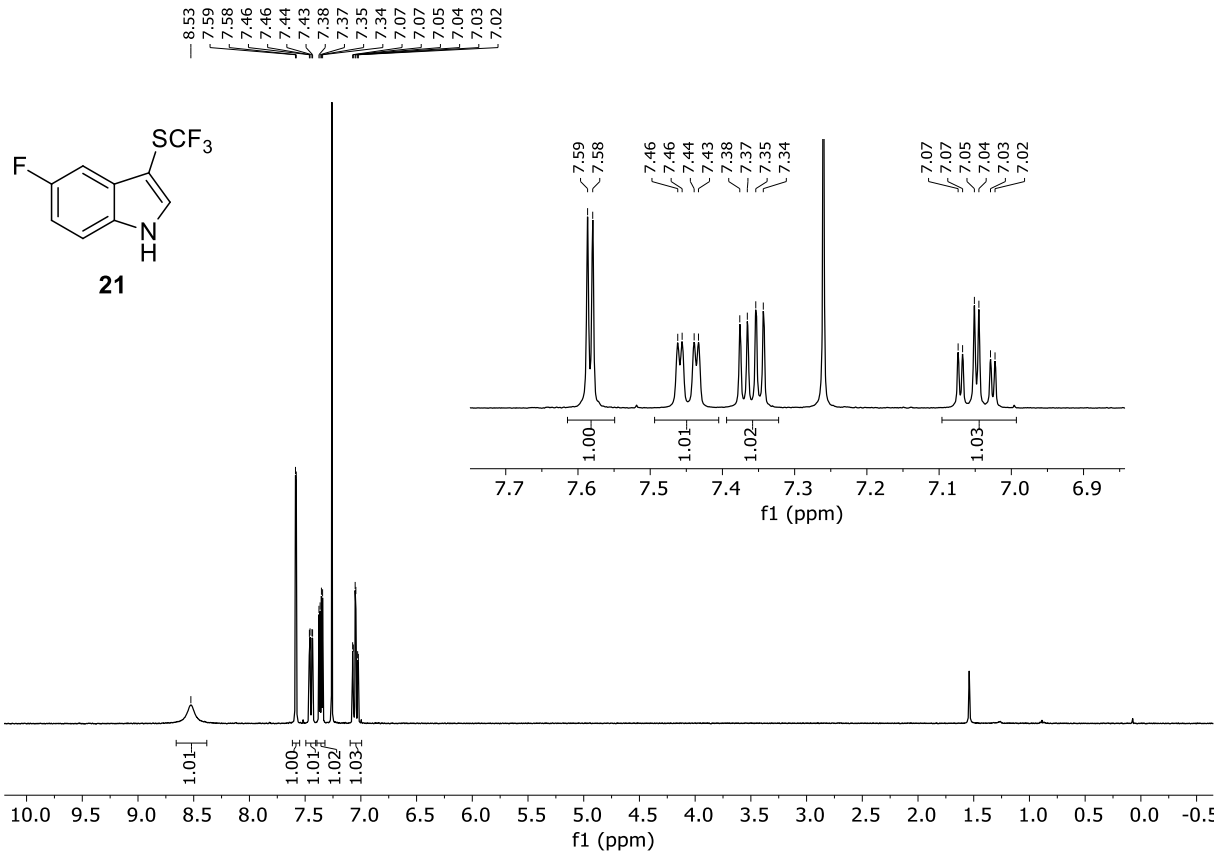
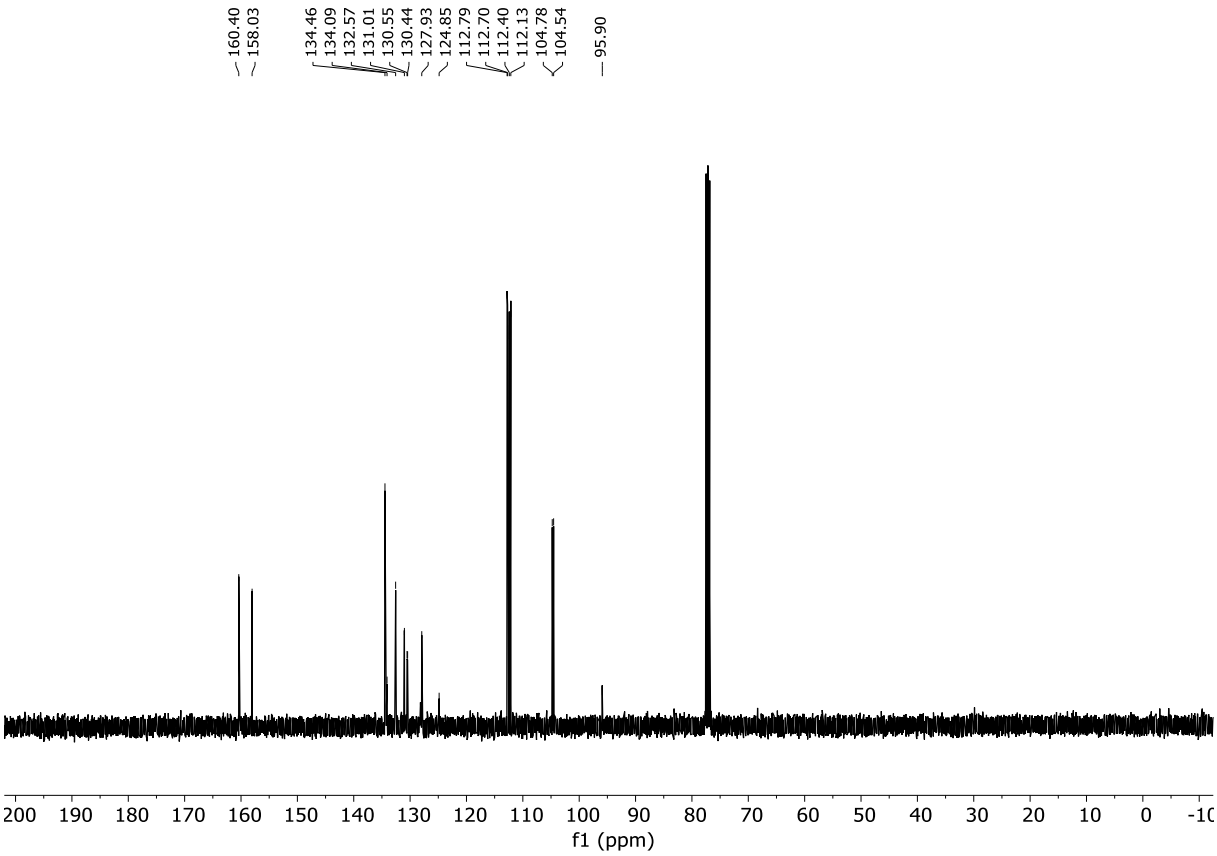
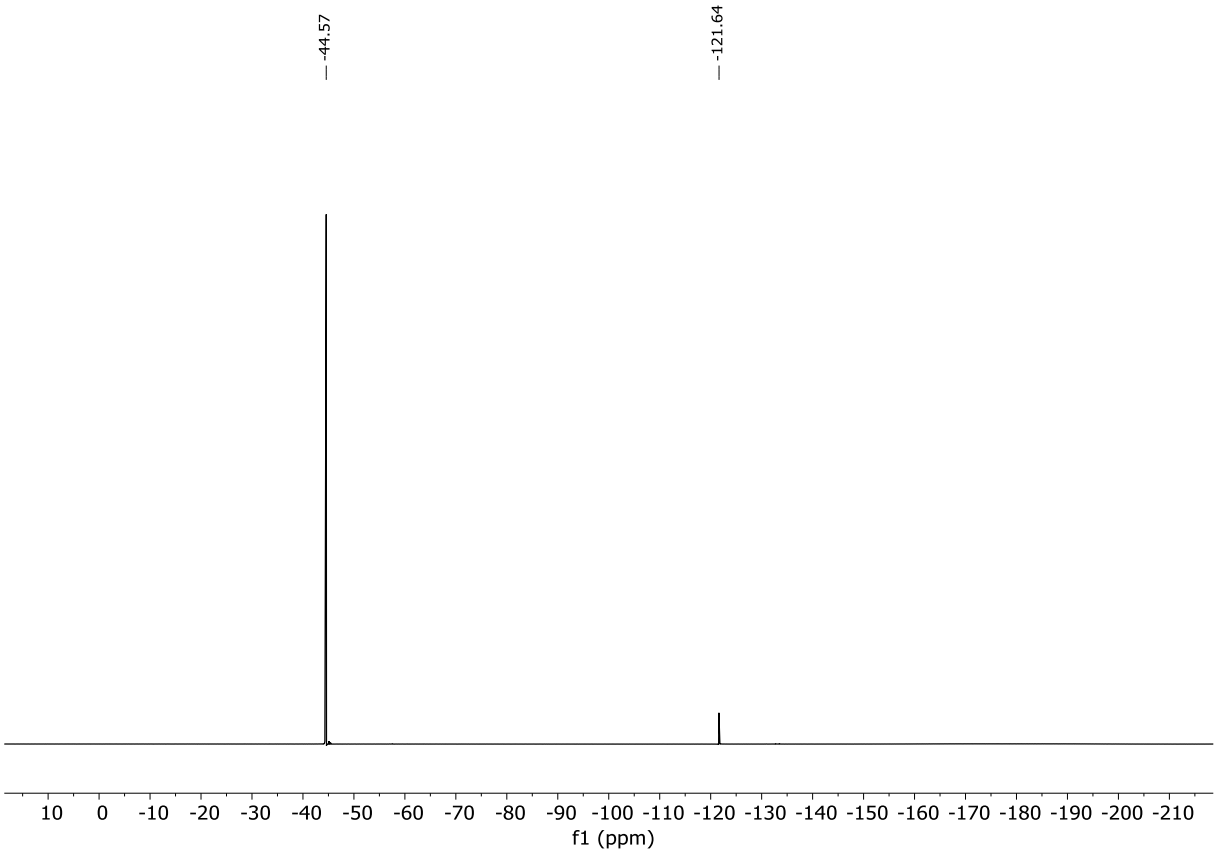
-70
-75
-80
-85
-90
-95
-100
-105
f1 (ppm)


8.53
7.59
7.58
7.46
7.46
7.44
7.43
7.38
7.37
7.35
7.34
7.07
7.07
7.05
7.04
7.03
7.02
SCF3
F
N
H
21
1.01
1.00
1.01
1.02
1.03
f1 (ppm)


160.40
158.03
134.46
134.09
132.57
131.01
130.55
130.44
127.93
124.85
112.79
112.70
112.40
112.13
104.78
104.54
95.90
f1 (ppm)


-44.57
-121.64
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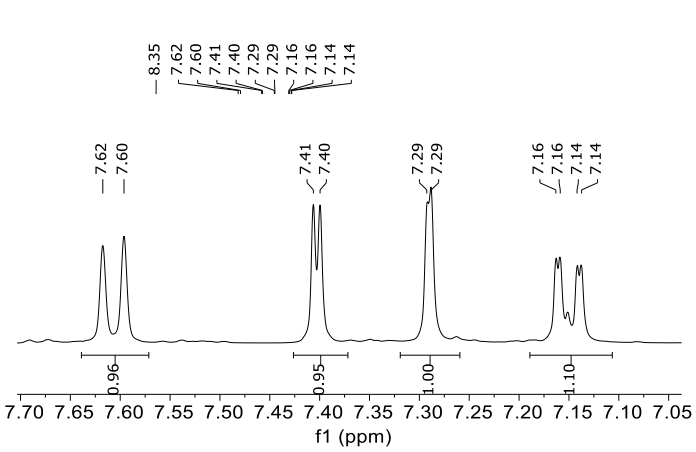
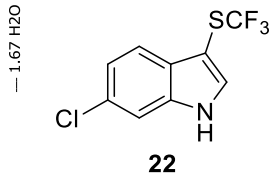
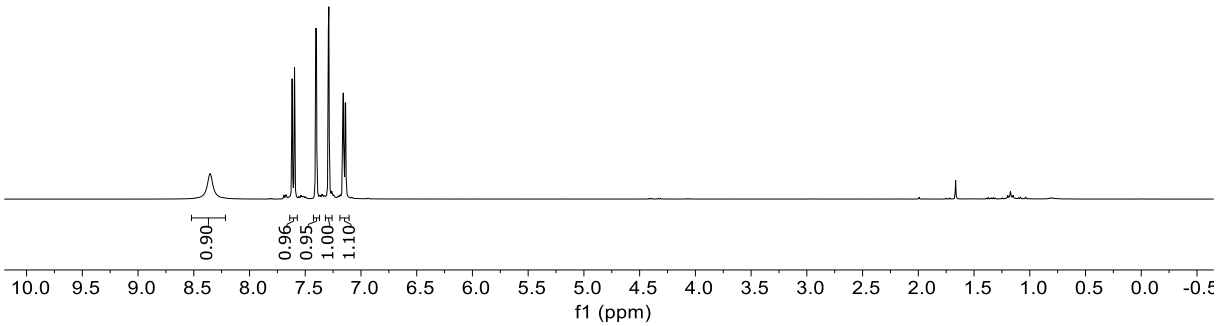
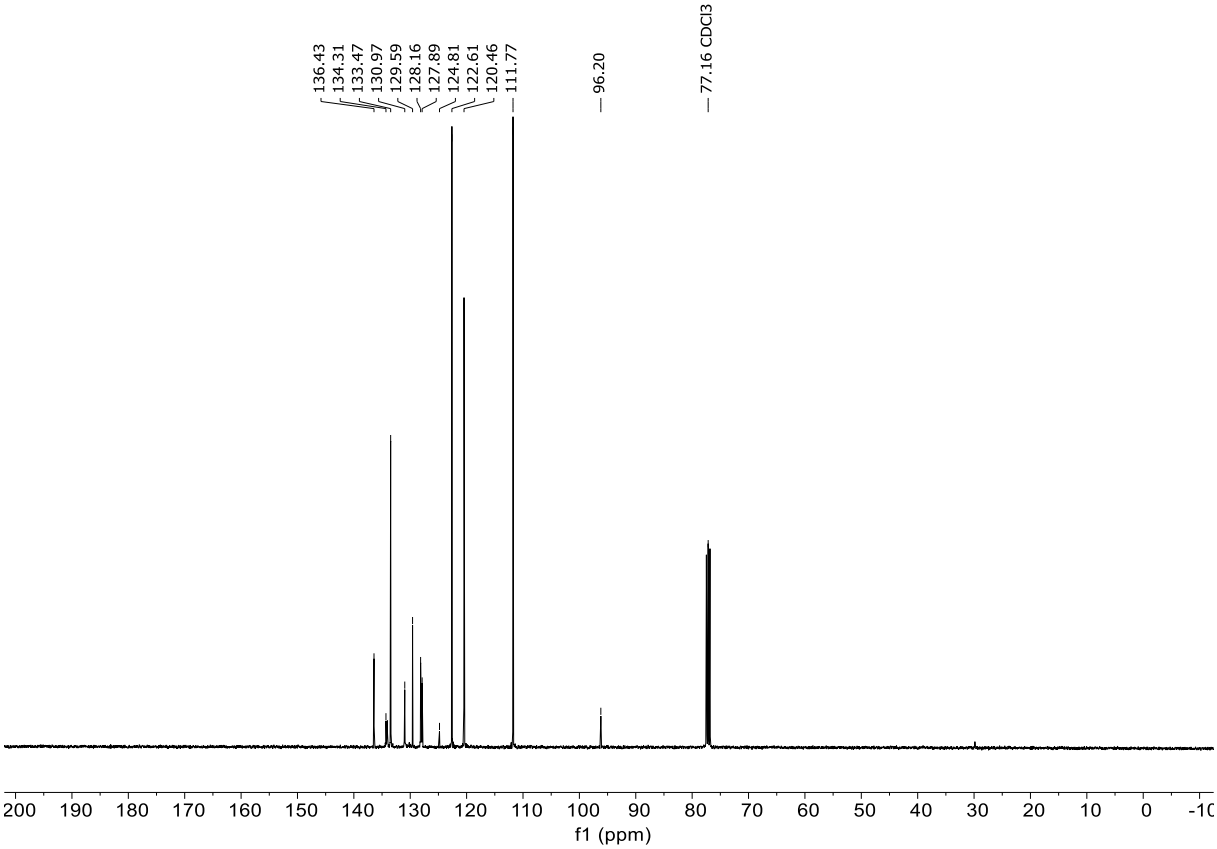
f1 (ppm)

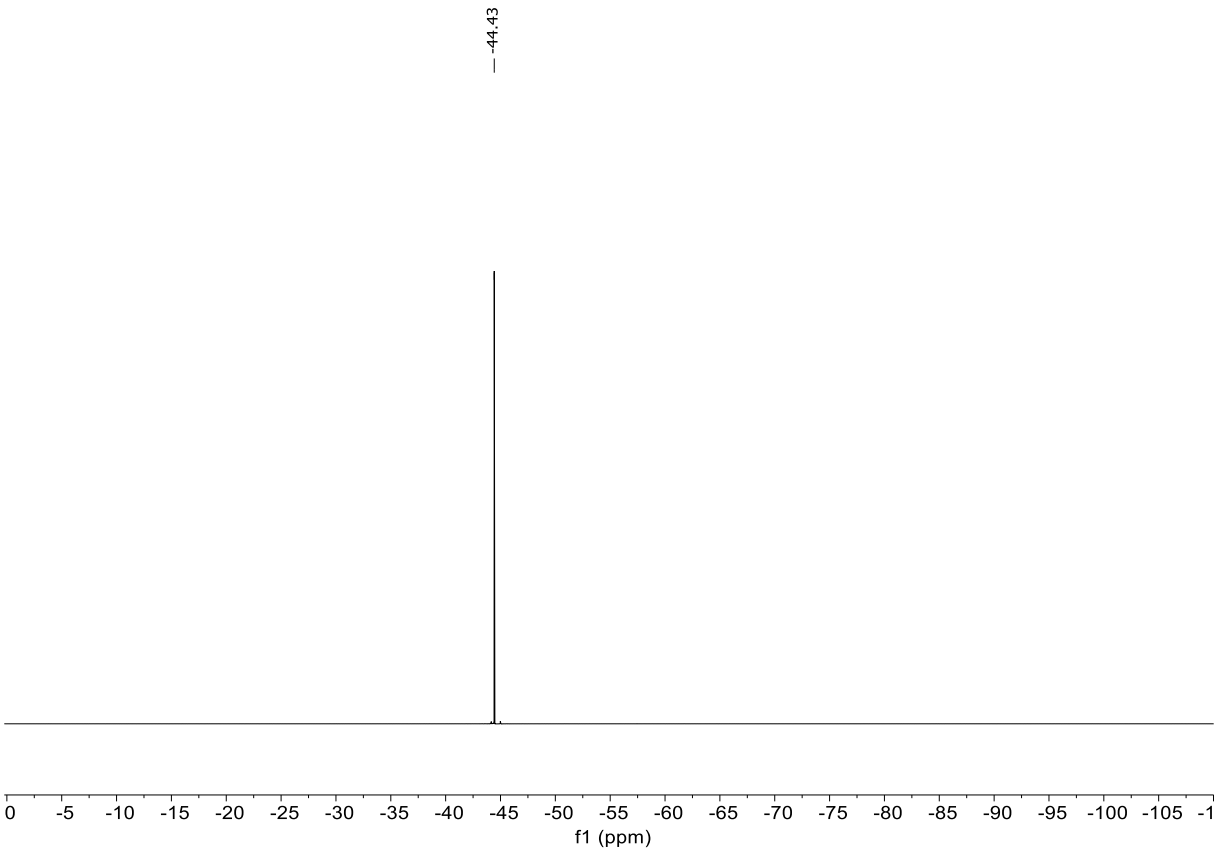

8.35
7.62
7.60
7.41
7.40
7.29
7.29
7.16
7.16
7.14
7.14
0.96
0.95
1.00
1.10
7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05
f1 (ppm)

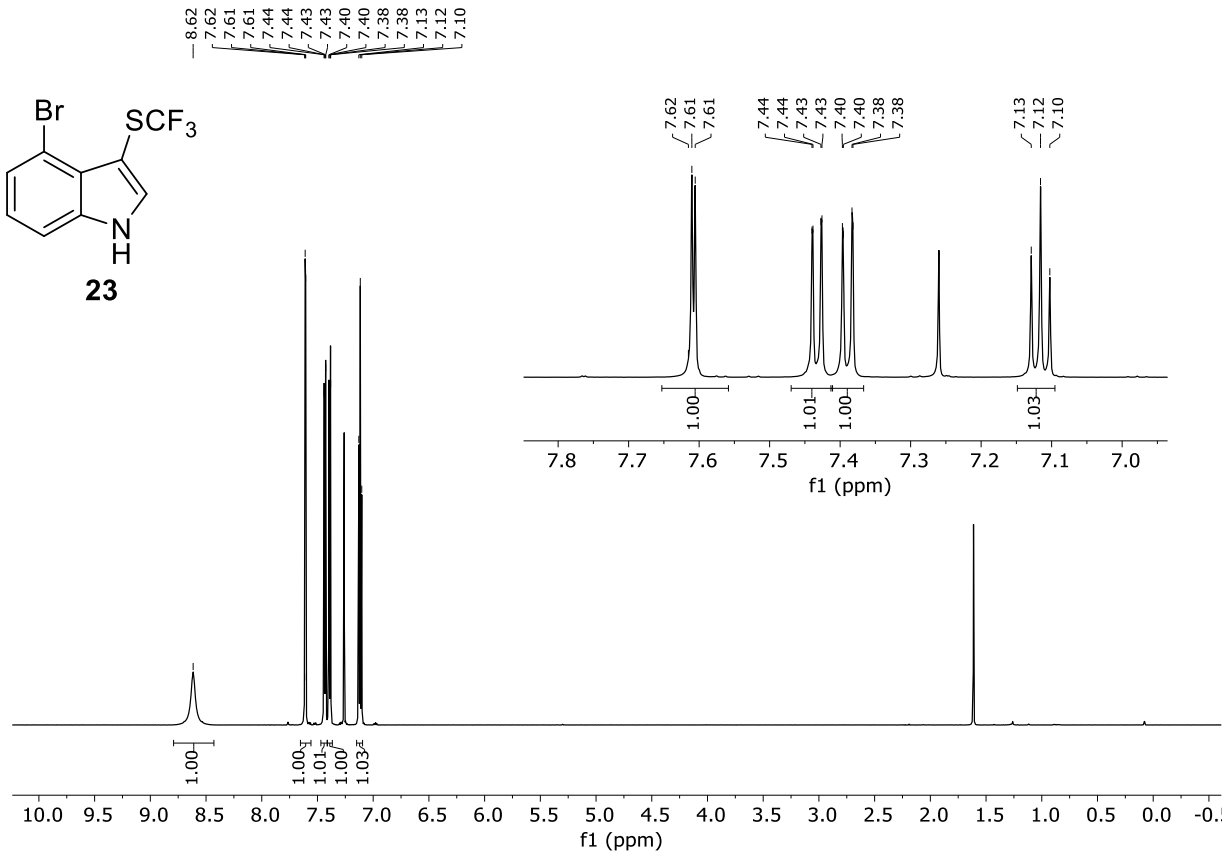

1.67 H2O
SCF3
Cl
N
H

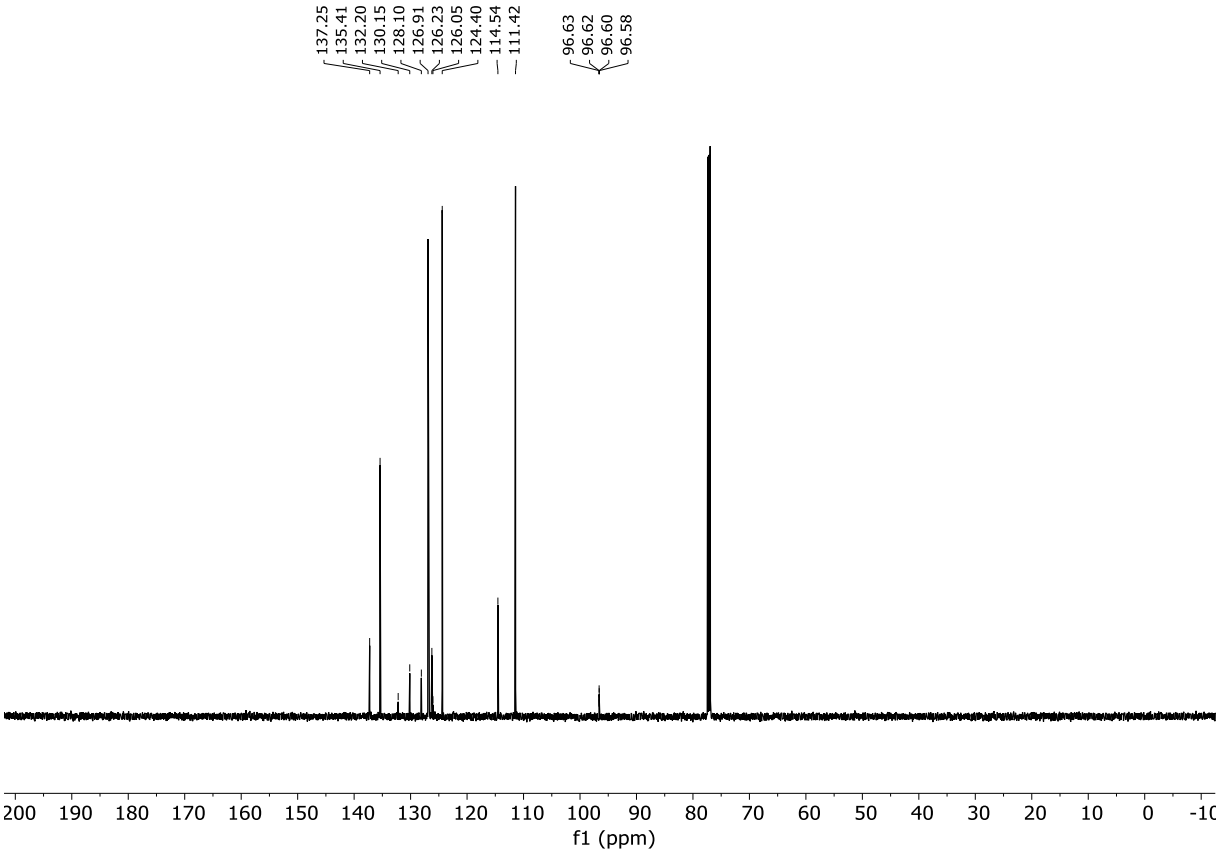
22

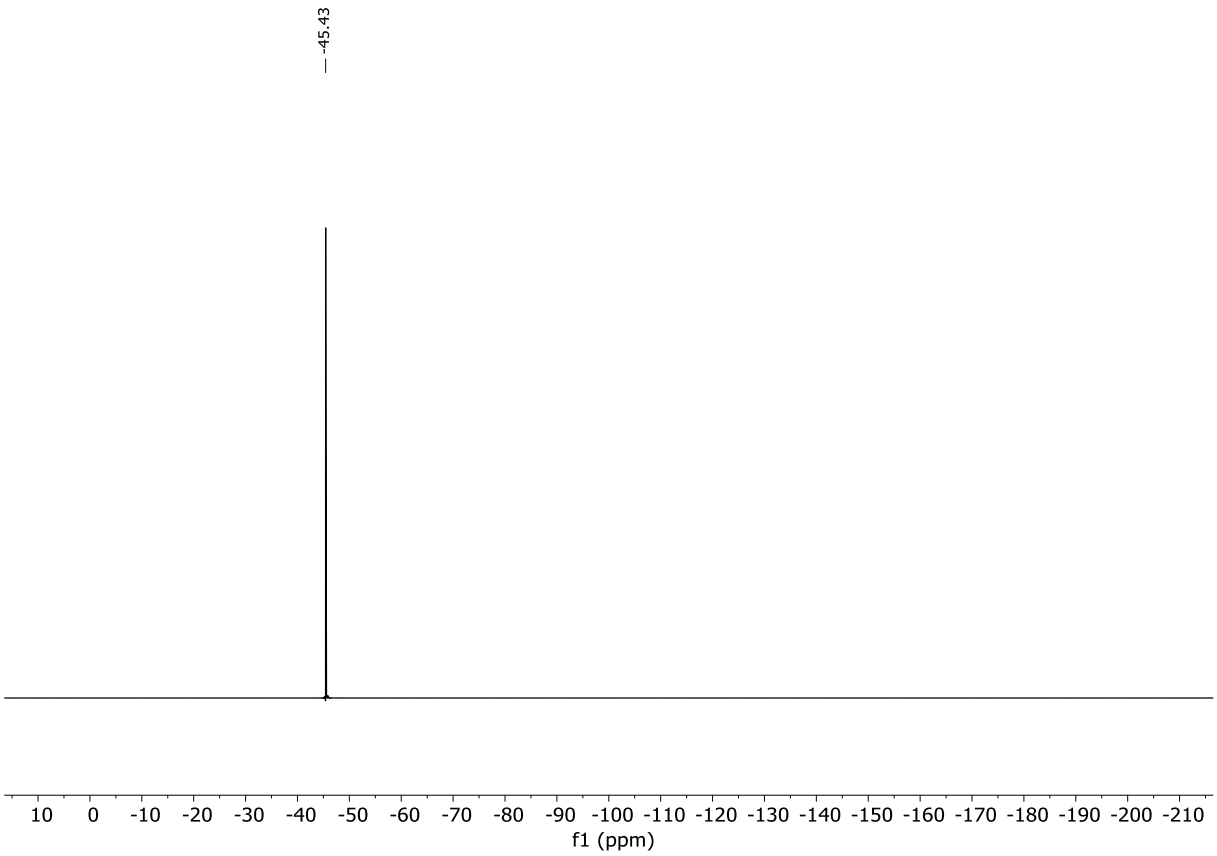

0.90
0.96
0.95
1.00
1.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

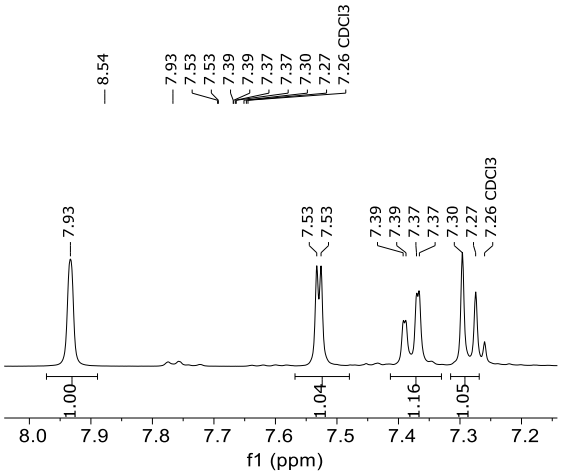

136.43
134.31
133.47
130.97
129.59
128.16
127.89
124.81
122.61
120.46
111.77
96.20
77.16 CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

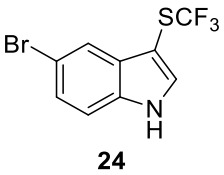

-44.43
0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -1
f1 (ppm)


8.62
7.62
7.61
7.61
7.44
7.44
7.43
7.43
7.40
7.40
7.38
7.38
7.13
7.12
7.10
Br
SCF3
N
H
23
1.00
1.00
1.01
1.00
1.03
f1 (ppm)

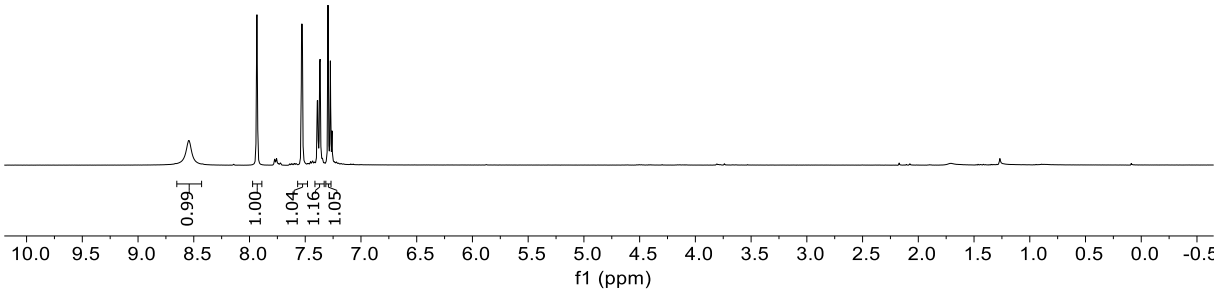

137.25
135.41
132.20
130.15
128.10
126.91
126.23
126.05
124.40
114.54
111.42
96.63
96.62
96.60
96.58
f1 (ppm)

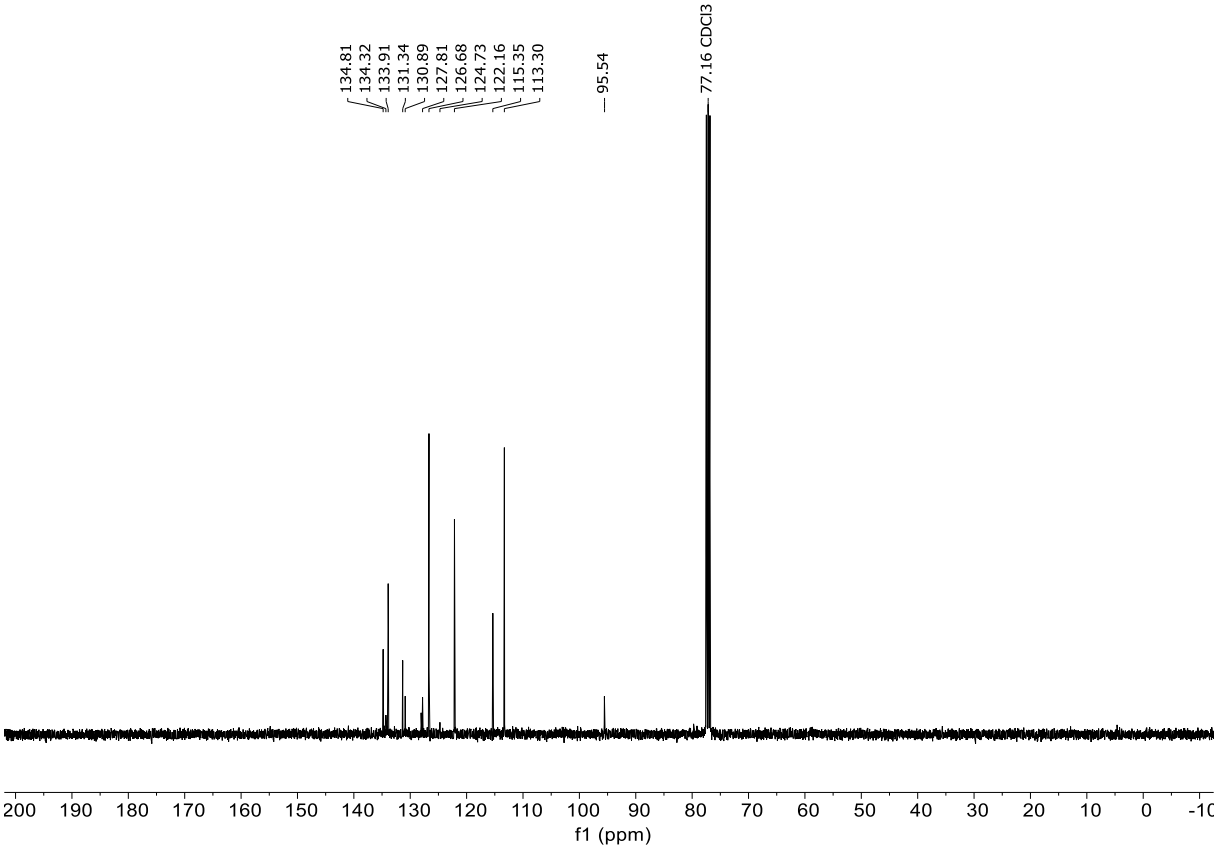

-45.43
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

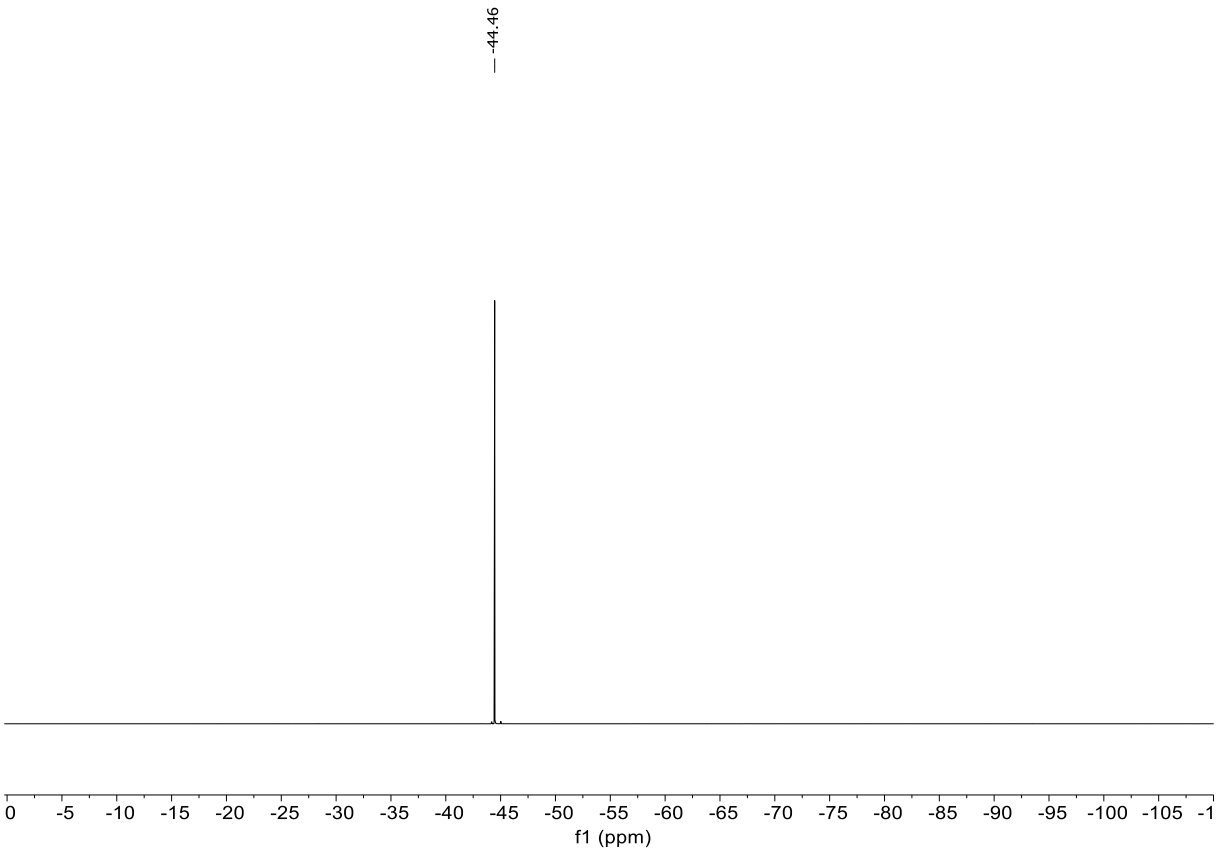

8.54
7.93
7.53
7.53
7.39
7.39
7.37
7.37
7.30
7.27
7.26 CDCl3
7.93
7.53
7.53
7.39
7.39
7.37
7.37
7.30
7.27
7.26 CDCl3
1.00
1.04
1.16
1.05
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2
f1 (ppm)


Br
SCF3
N
H

24


0.99
1.00
1.04
1.16
1.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


134.81
134.32
133.91
131.34
130.89
127.81
126.68
124.73
122.16
115.35
113.30
95.54
77.16 CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
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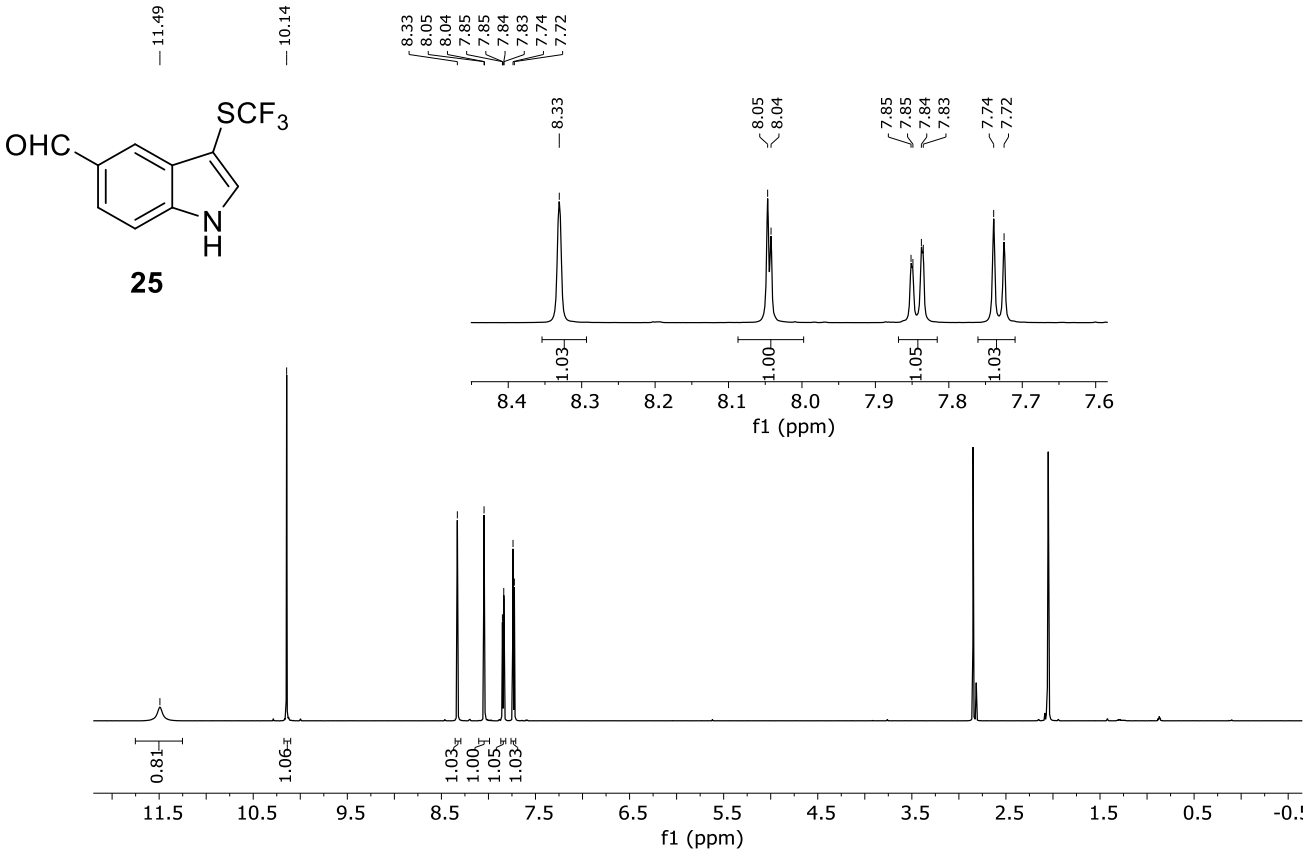
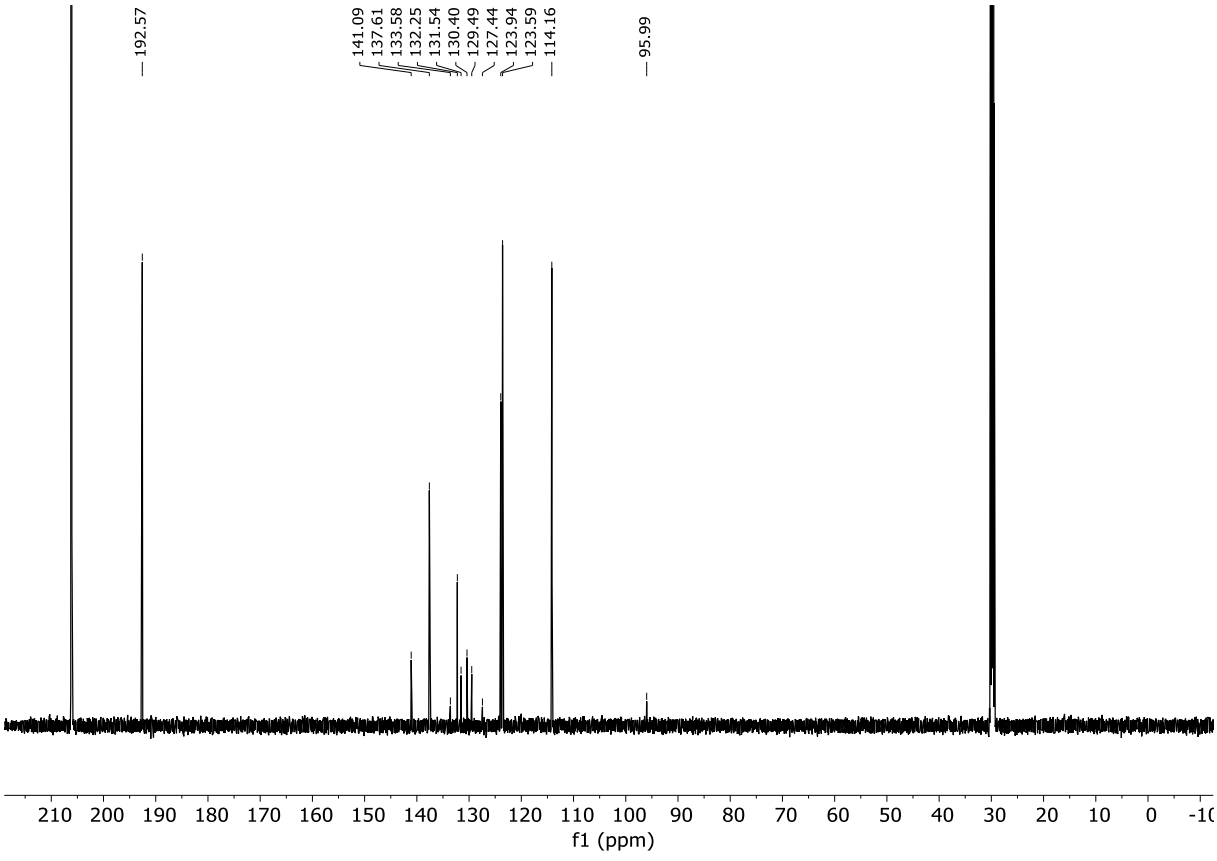
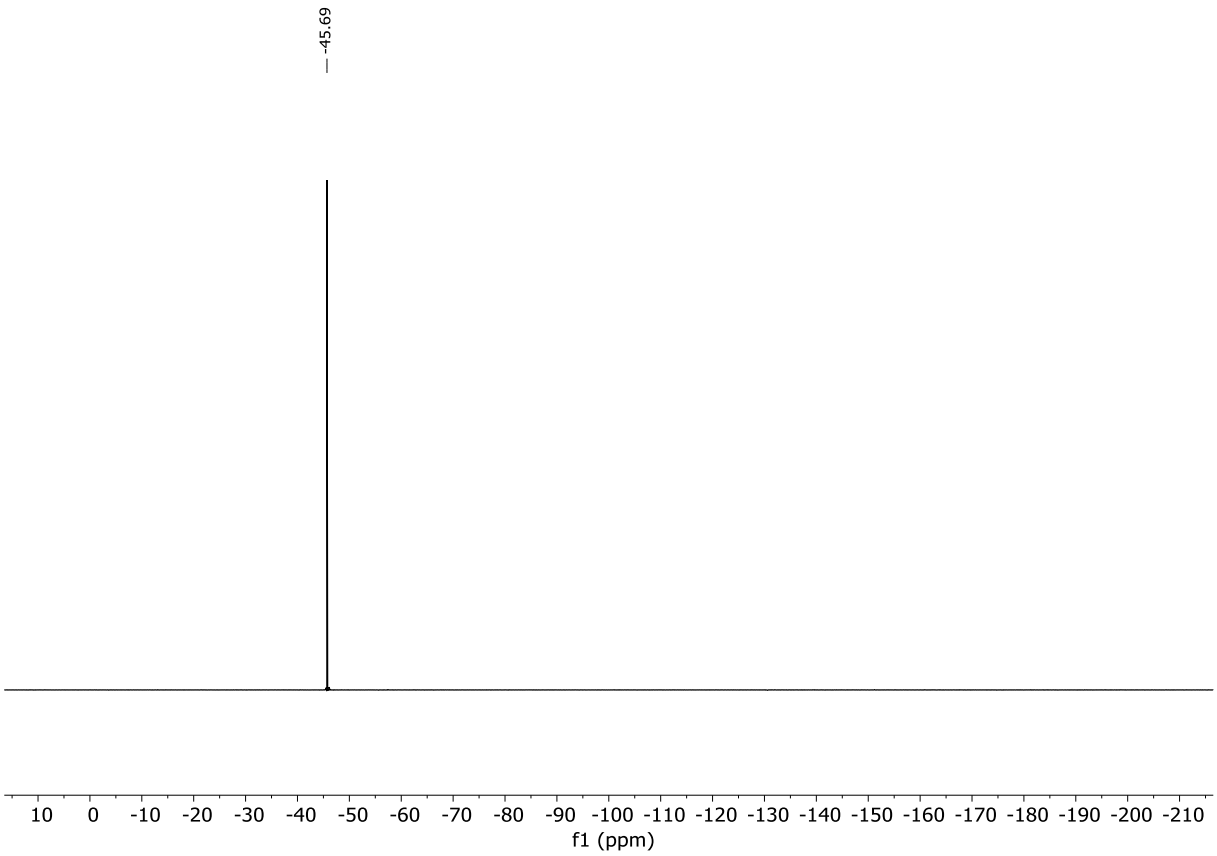
-85
-90
-95
-100
-105
-1
f1 (ppm)


11.49
10.14
8.33
8.05
8.04
7.85
7.85
7.84
7.83
7.74
7.72
OHC
SCF3
N
H
25
f1 (ppm)
f1 (ppm)


192.57
141.09
137.61
133.58
132.25
131.54
130.40
129.49
127.44
123.94
123.59
114.16
95.99
f1 (ppm)


-45.69
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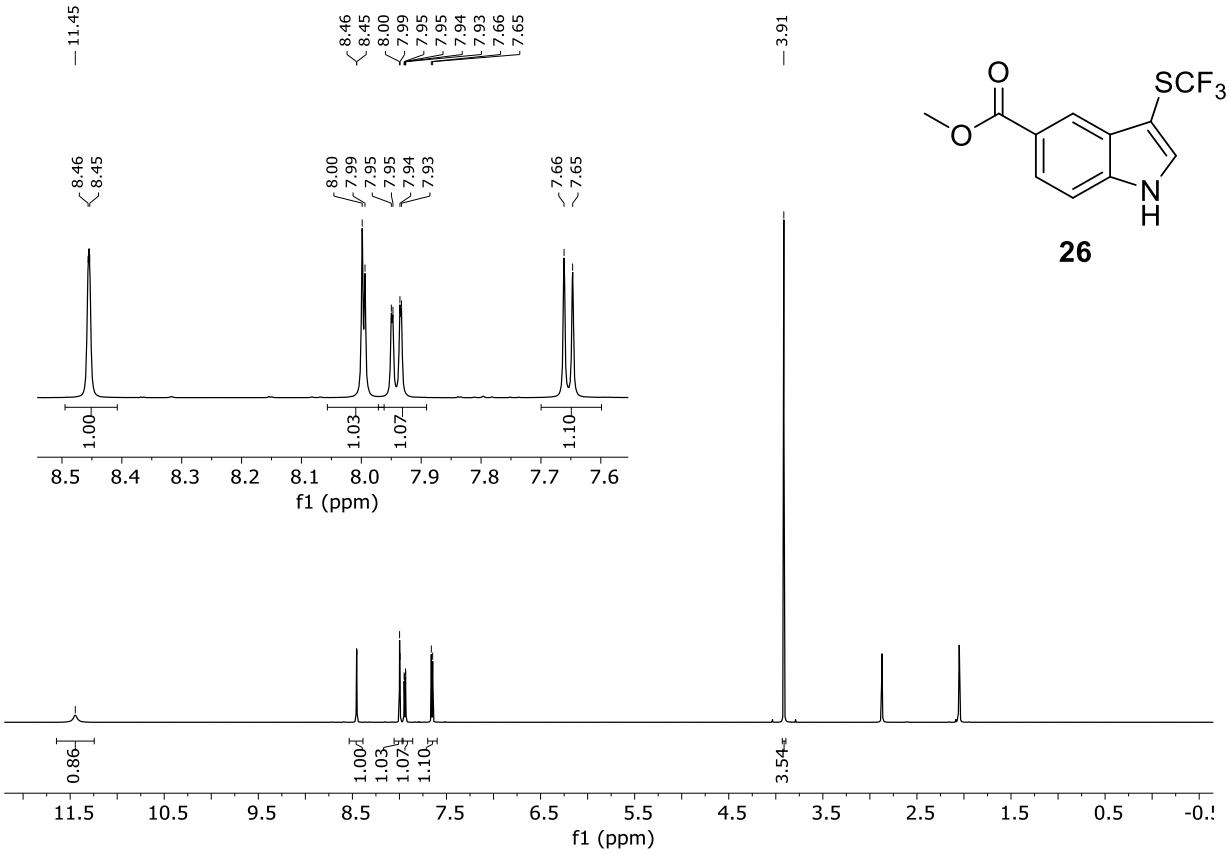
f1 (ppm)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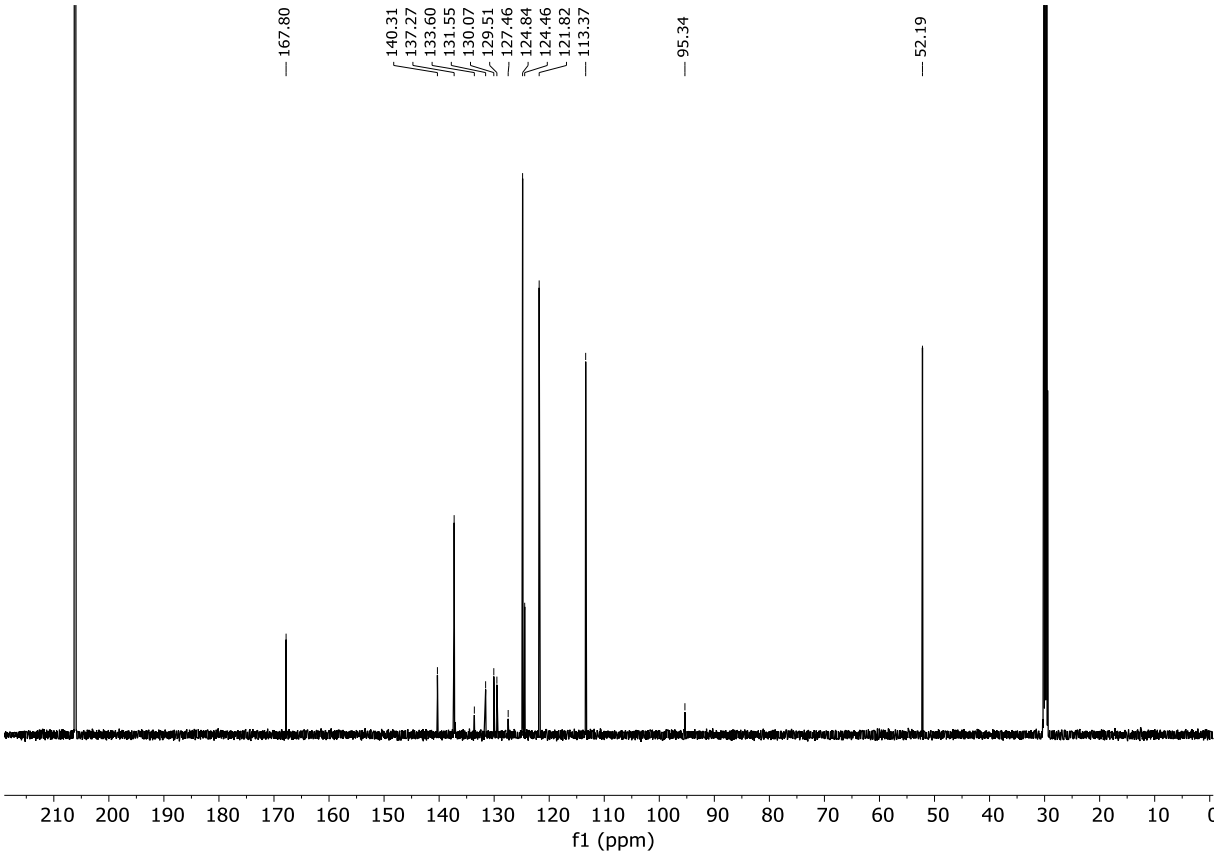
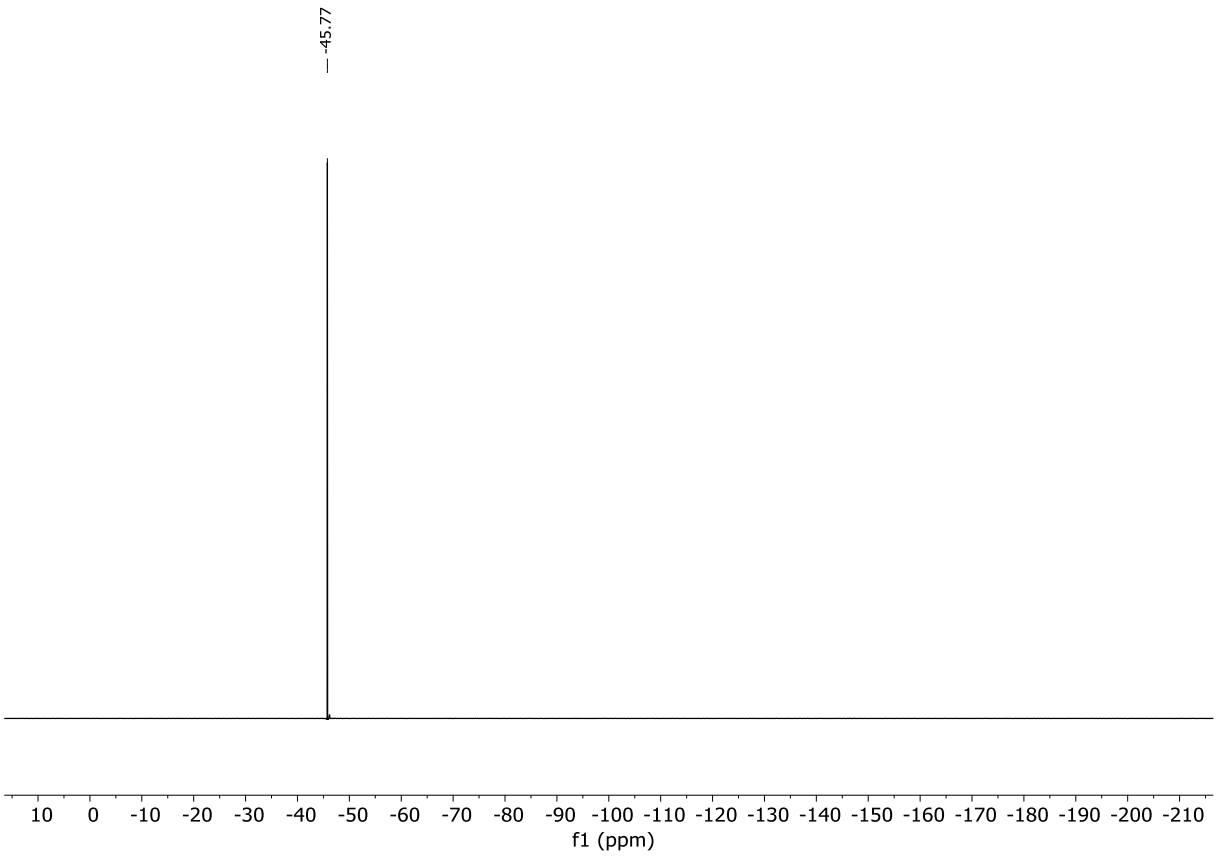
8.46
8.45
8.00
7.99
7.95
7.95
7.94
7.93
7.66
7.65
3.91
O
O
SCF3
N
H
26
1.00
1.03
1.07
1.10
0.86
3.54
f1 (ppm)


167.80
140.31
137.27
133.60
131.55
130.07
129.51
127.46
124.84
124.46
121.82
113.37
95.34
52.19
f1 (ppm)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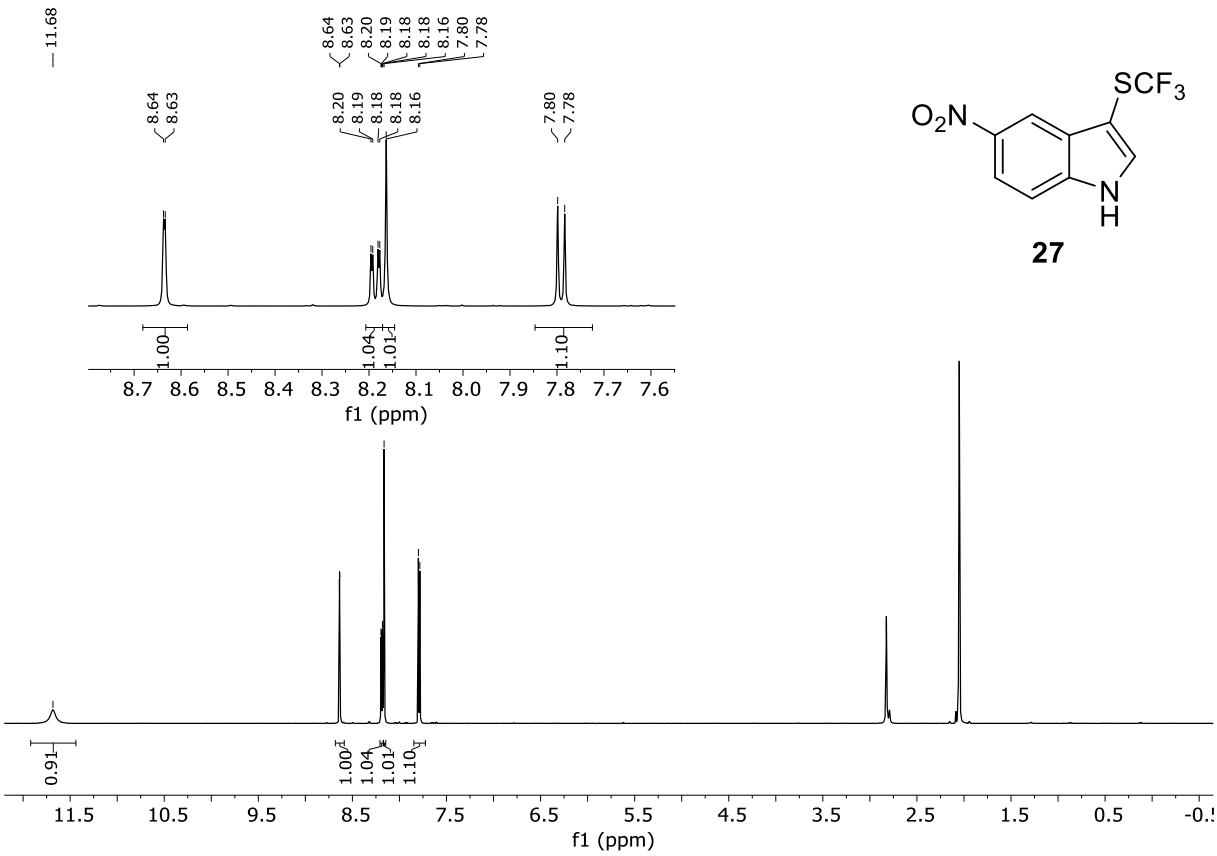
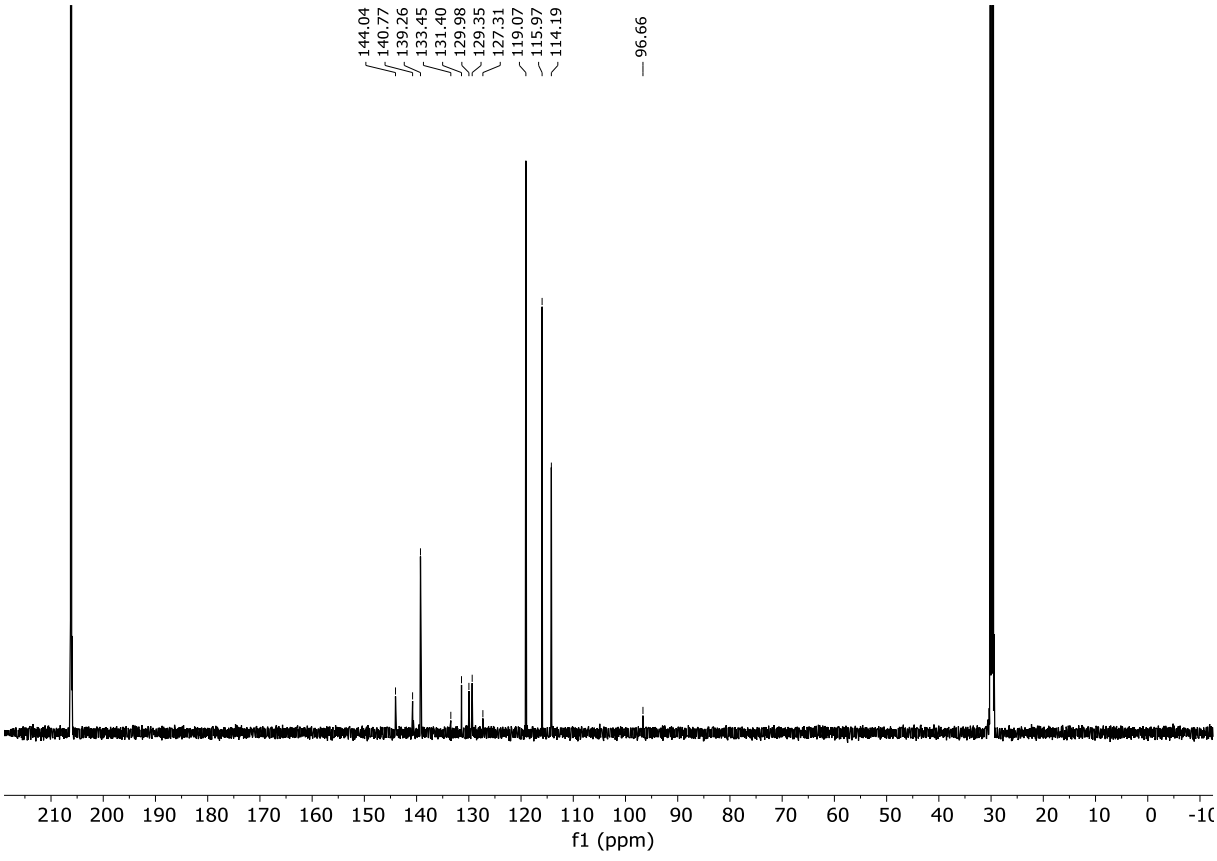
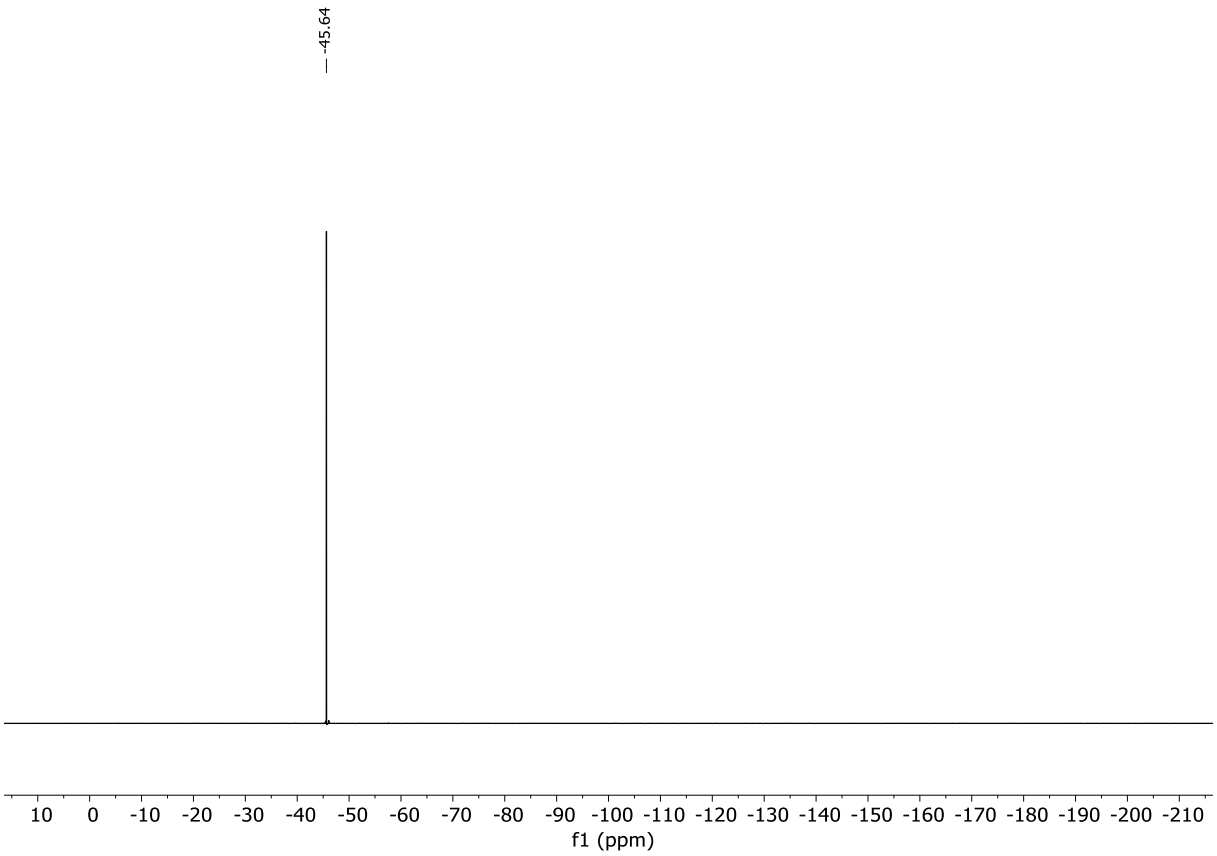
f1 (ppm)


11.68
8.64
8.63
8.20
8.19
8.18
8.18
8.16
7.80
7.78
1.00
1.04
1.01
1.10
f1 (ppm)
0.91
f1 (ppm)

SCF3
O2N
N
H

27


144.04
140.77
139.26
133.45
131.40
129.98
129.35
127.31
119.07
115.97
114.19
96.66
f1 (ppm)


-45.64
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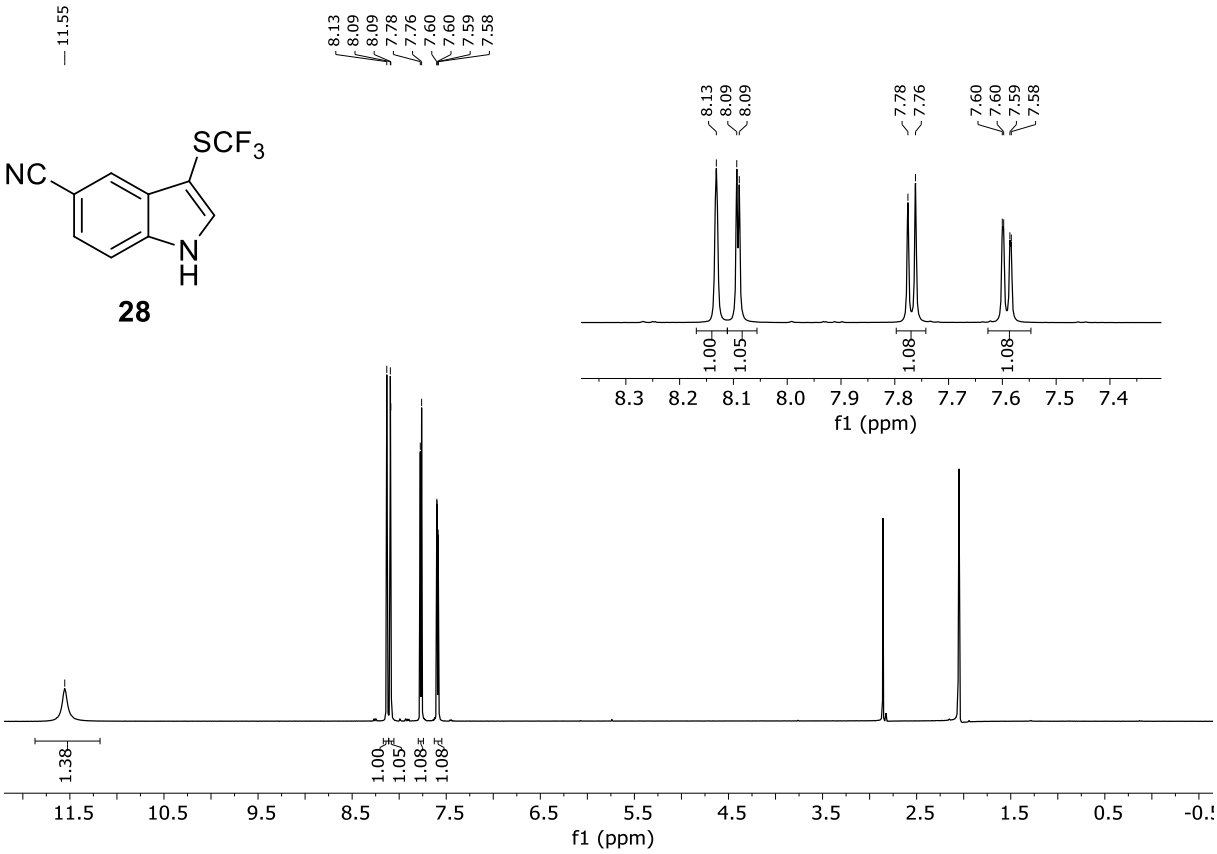
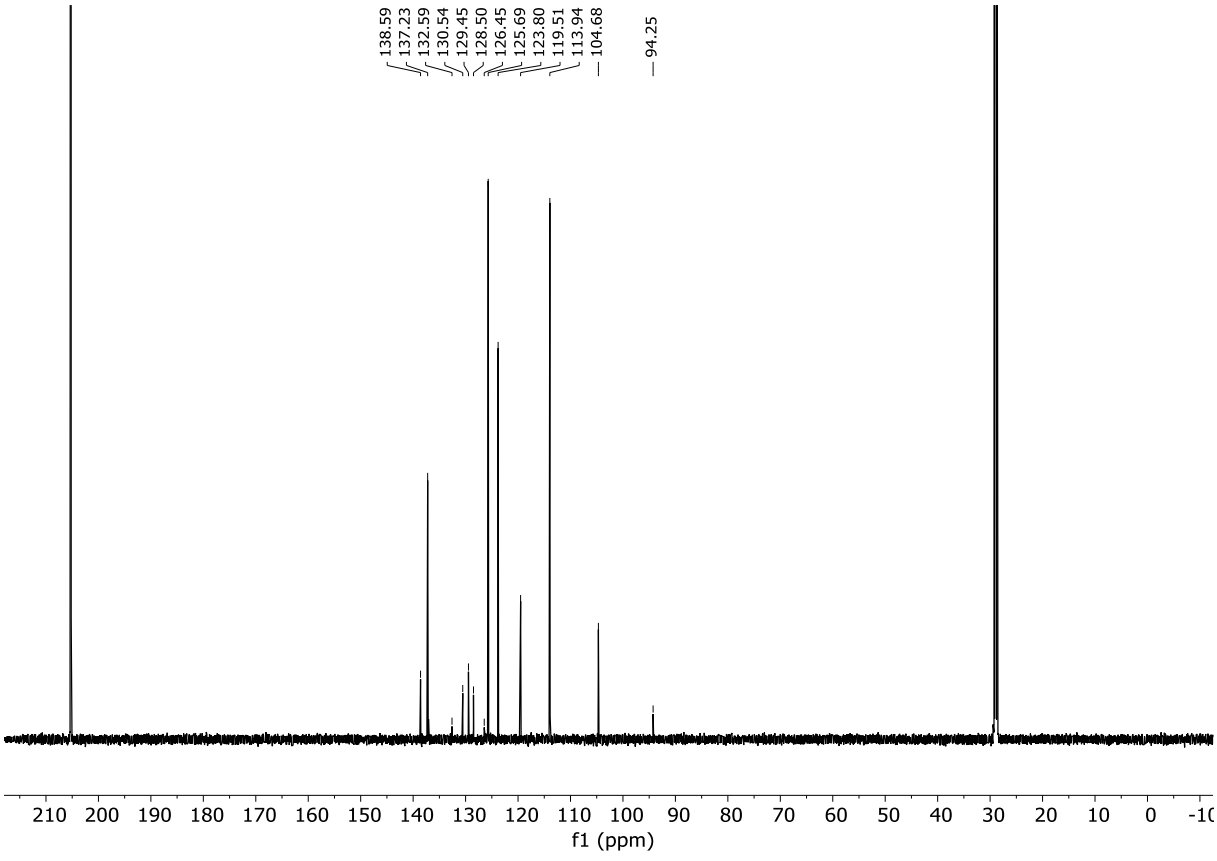
f1 (ppm)


11.55
8.13
8.09
8.09
7.78
7.76
7.60
7.60
7.59
7.58
NC
SCF3
N
H
28
1.38
1.00
1.05
1.08
1.08
f1 (ppm)


138.59
137.23
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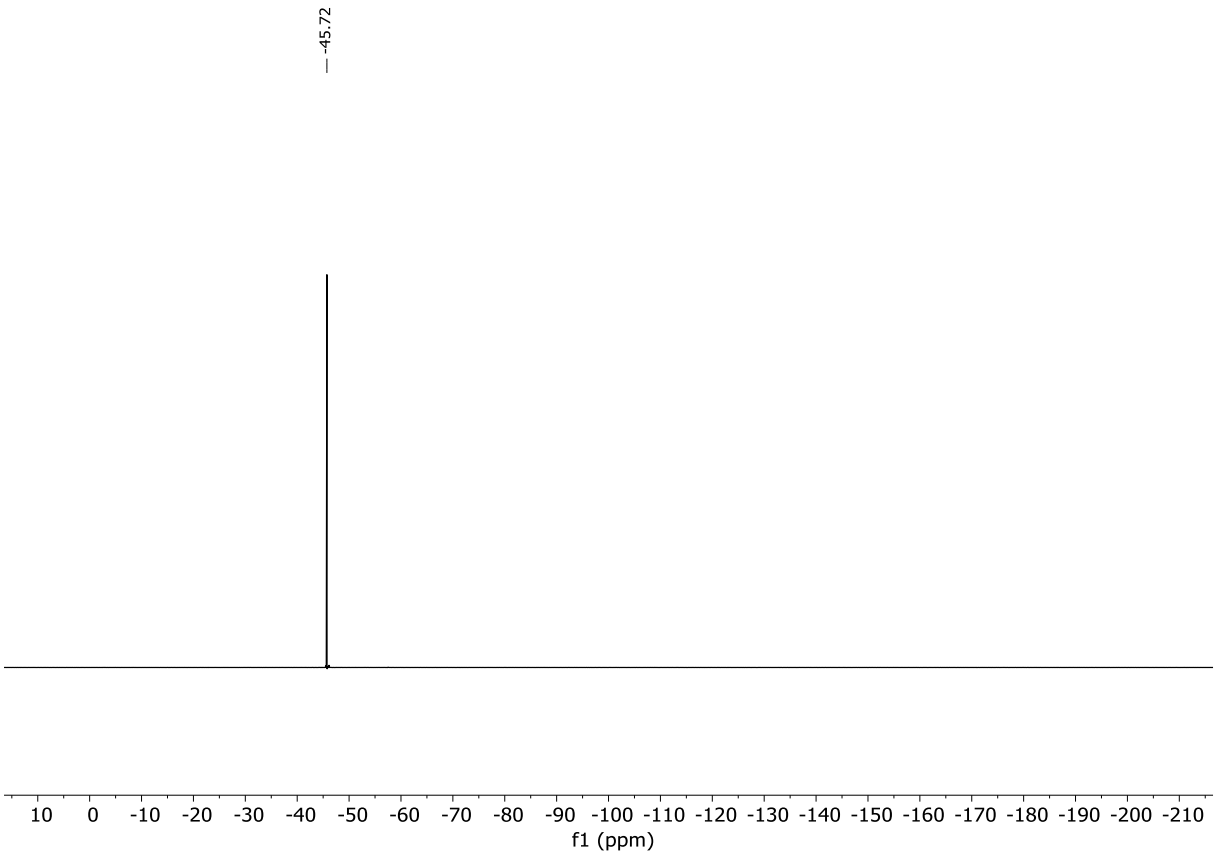
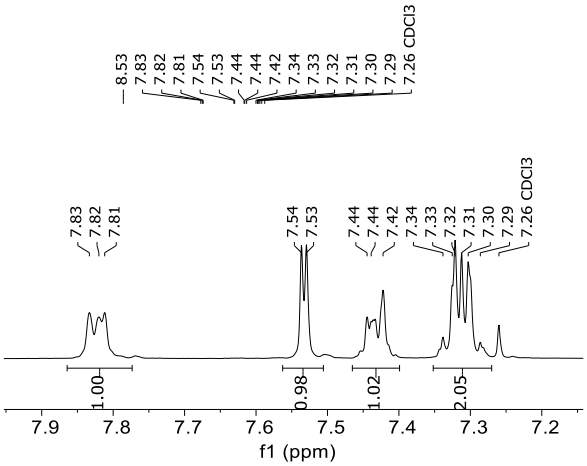
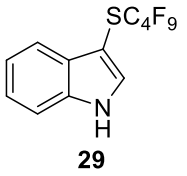
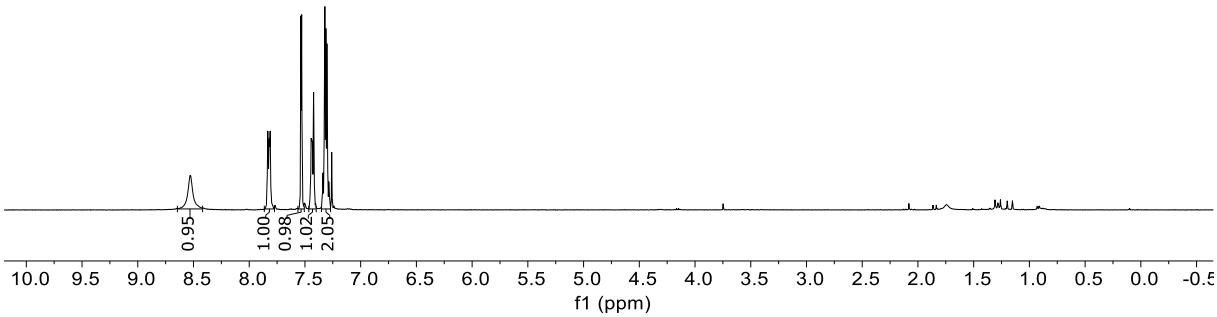
130.54
129.45
128.50
126.45
125.69
123.80
119.51
113.94
104.68
94.25
f1 (ppm)

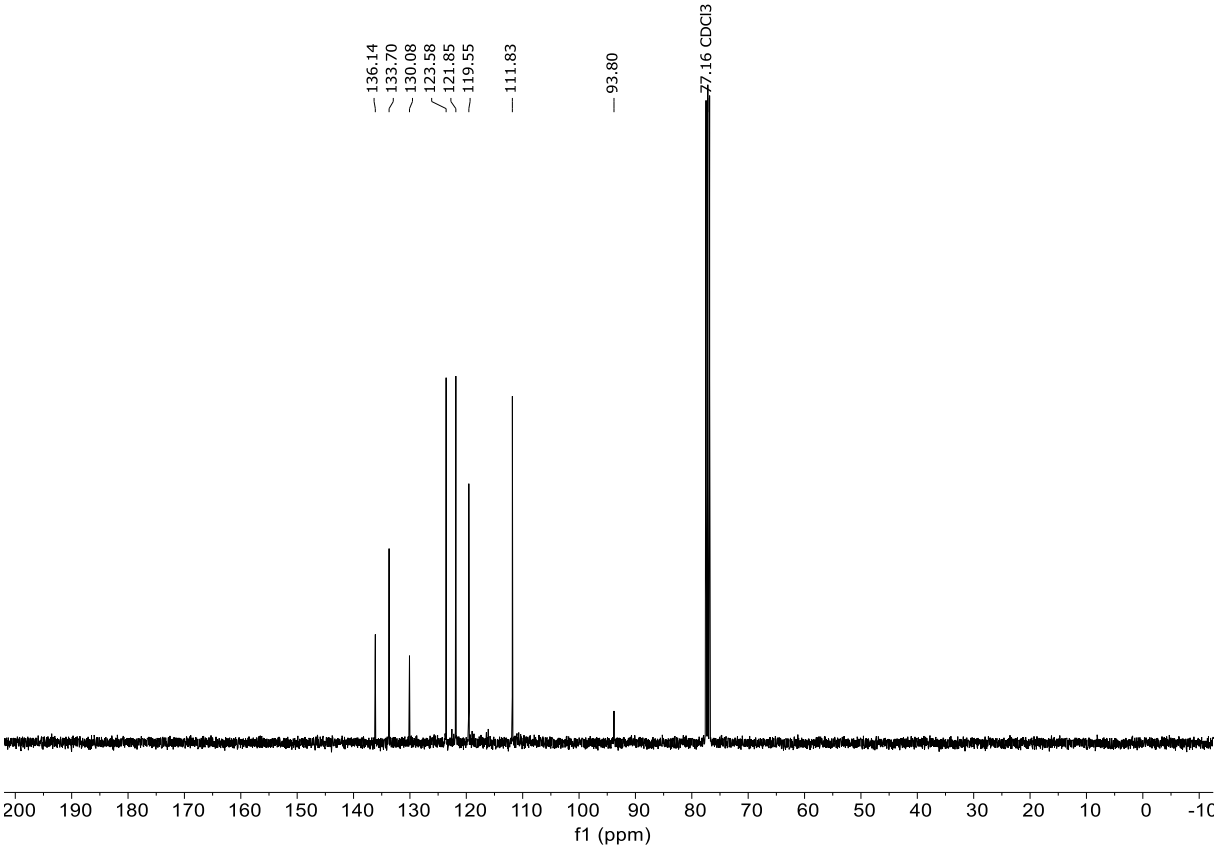

-45.72
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

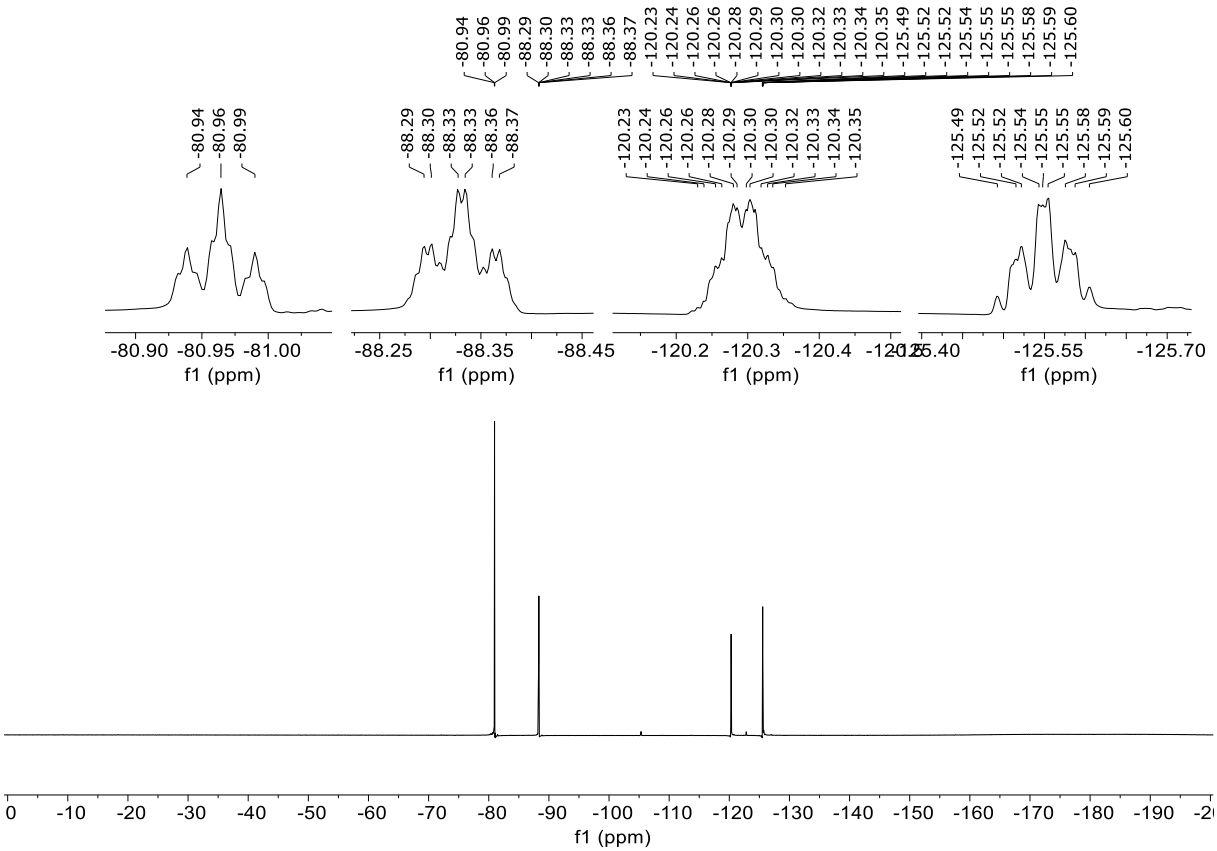

8.53
7.83
7.82
7.81
7.54
7.53
7.44
7.42
7.34
7.33
7.32
7.31
7.30
7.29
7.26 CDCl3
1.00
0.98
1.02
2.05
f1 (ppm)


SC4F9
N
H

29


0.95
1.00
0.98
1.02
2.05
f1 (ppm)


136.14
133.70
130.08
123.58
121.85
119.55
111.83
93.80
77.16 CDCl3
f1 (ppm)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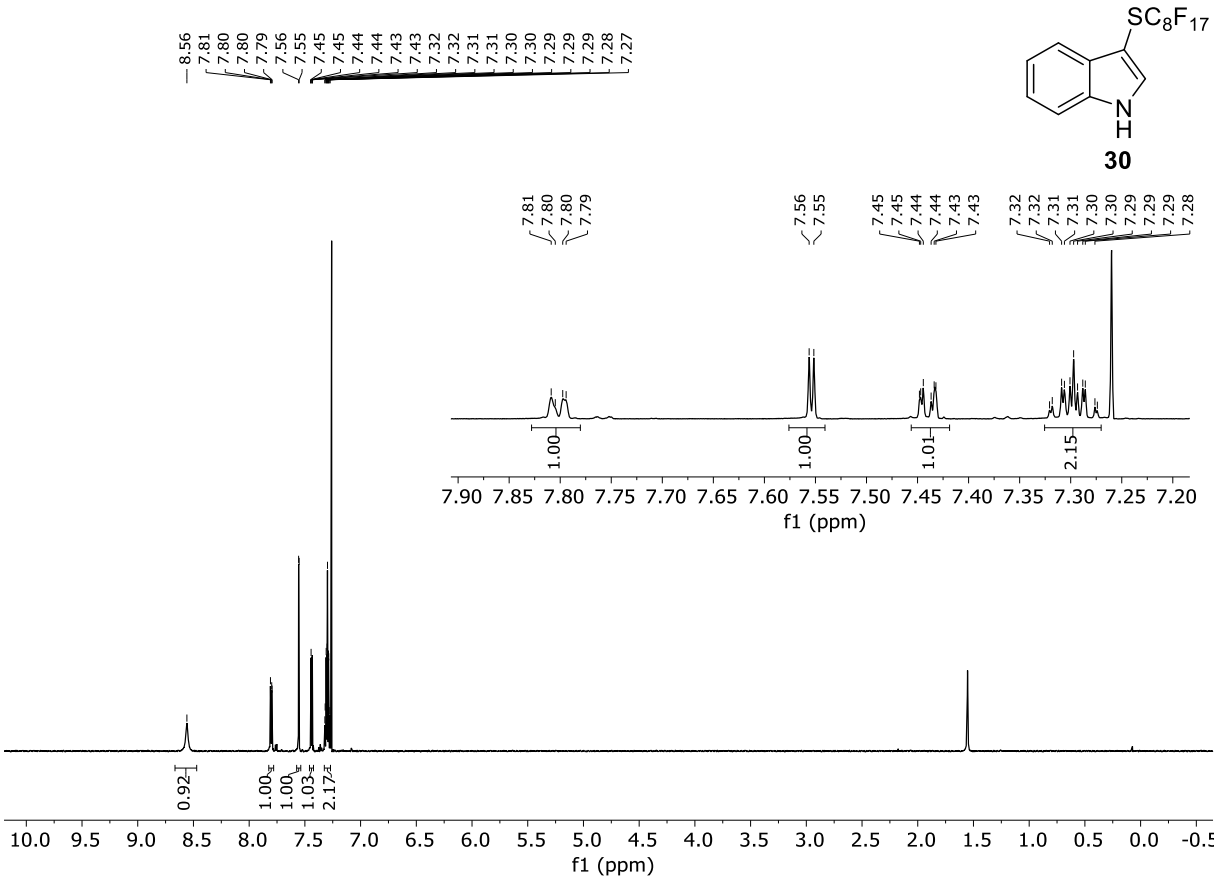
-80.96
-80.99
-88.29
-88.30
-88.33
-88.33
-88.36
-88.37
-120.23
-120.24
-120.26
-120.26
-120.28
-120.29
-120.30
-120.30
-120.32
-120.33
-120.34
-120.35
-125.49
-125.52
-125.52
-125.54
-125.55
-125.55
-125.58
-125.59
-125.60
-80.90 -80.95 -81.00
f1 (ppm)
-88.25 -88.35 -88.45
f1 (ppm)
-120.2 -120.3 -120.4
f1 (ppm)
-125.40 -125.55 -125.70
f1 (ppm)
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)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7.56
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7.32
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7.31
7.30
7.30
7.29
7.29
7.28
7.27
SC8F17
N
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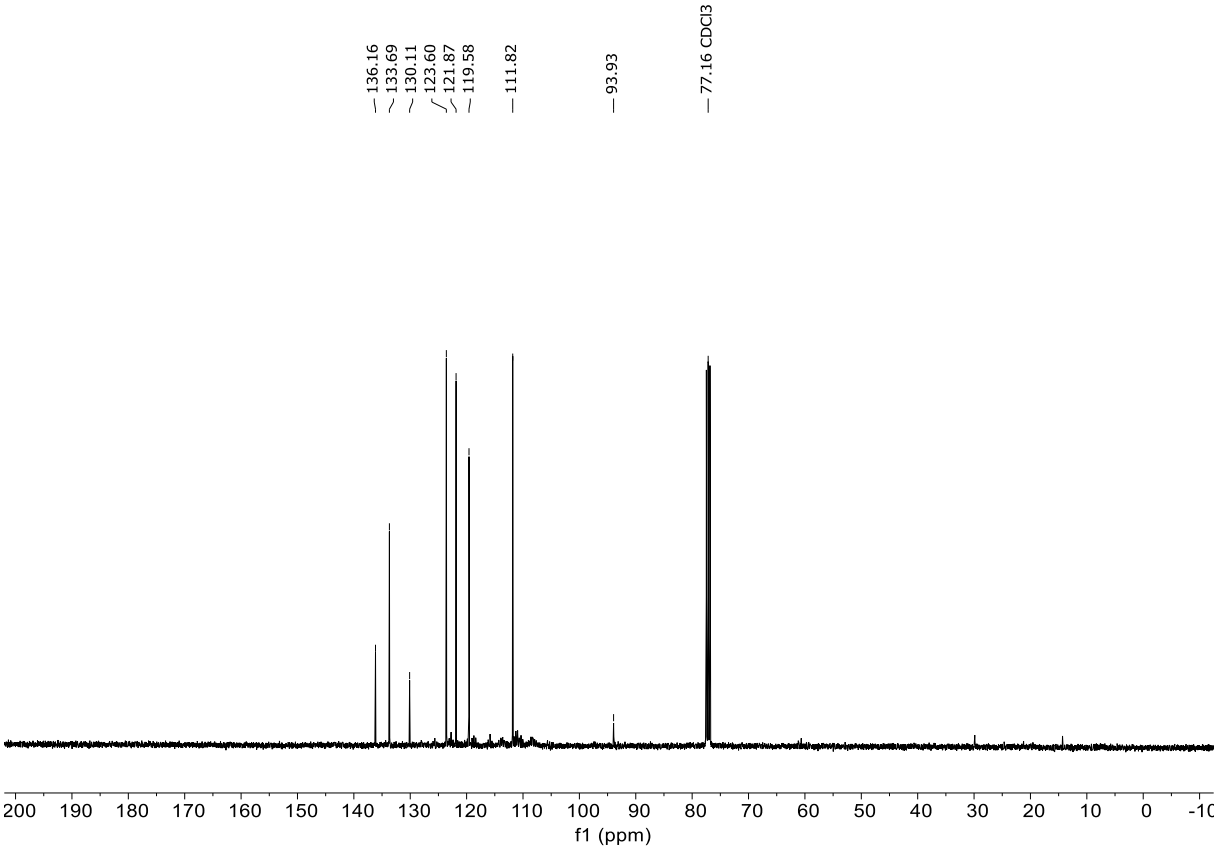
1.00
1.00
1.03
2.17
1.00
1.00
1.01
2.15
f1 (ppm)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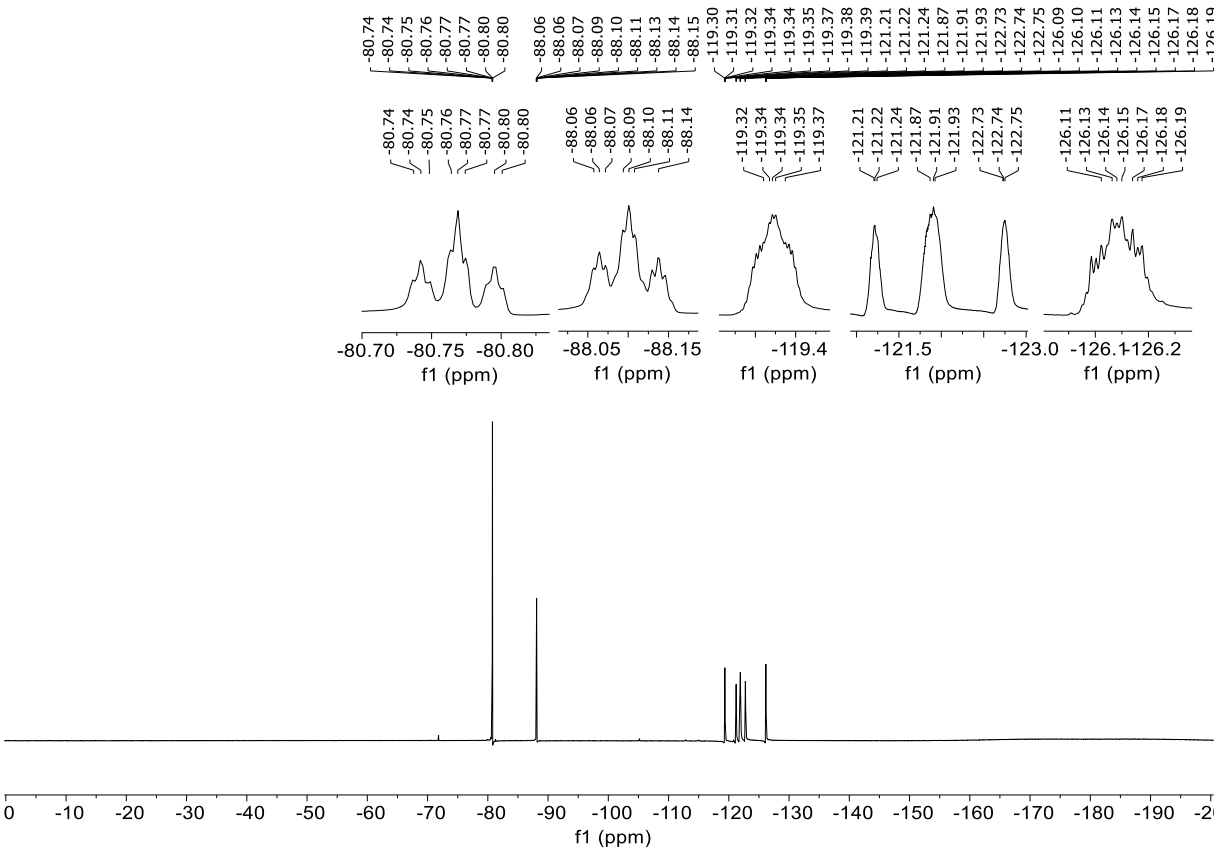
119.58
111.82
93.93
77.16 CDCl3
f1 (ppm)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-88.06
-88.07
-88.09
-88.10
-88.11
-88.13
-88.14
-88.15
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-119.32
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-119.34
-119.35
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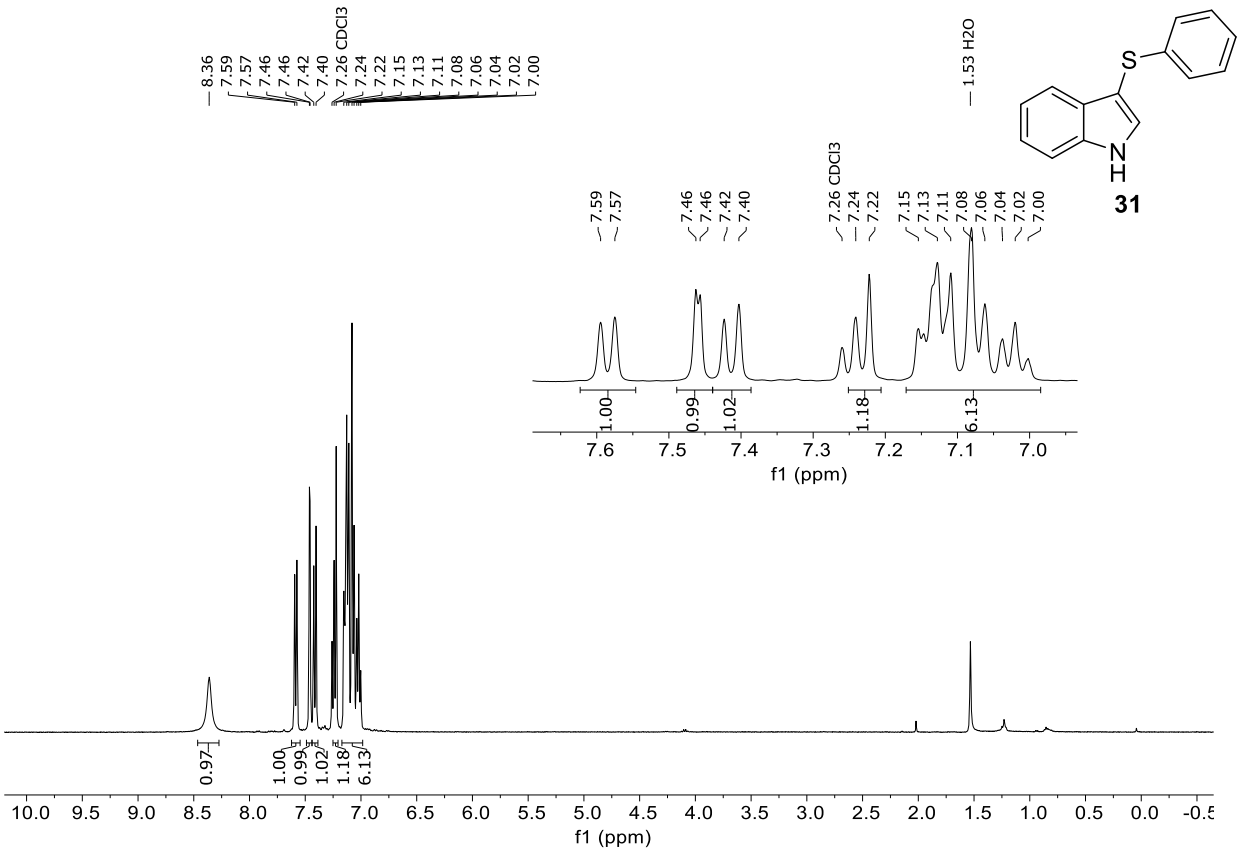
-121.87
-121.91
-121.93
-122.73
-122.74
-122.75
-126.09
-126.10
-126.11
-126.13
-126.14
-126.15
-126.17
-126.18
-126.19
-80.70 -80.75 -80.80
f1 (ppm)
-88.05 -88.15
f1 (ppm)
-119.4
f1 (ppm)
-121.5 -123.0
f1 (ppm)
-126.1 -126.2
f1 (ppm)
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)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7.46
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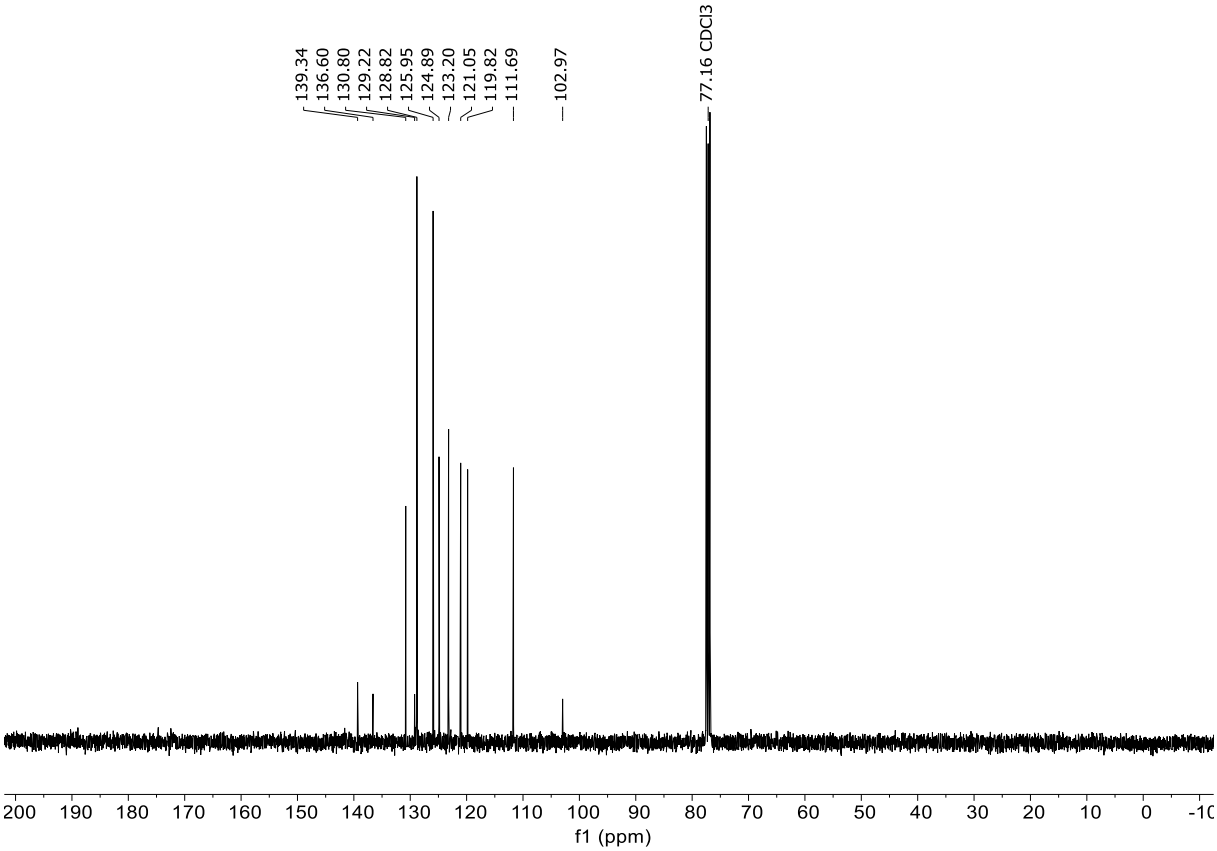
7.40
7.26 CDCl3
7.24
7.22
7.15
7.13
7.11
7.08
7.06
7.04
7.02
7.00
1.53 H2O
S
N
H
31
0.97
1.00
0.99
1.02
1.18
6.13
f1 (ppm)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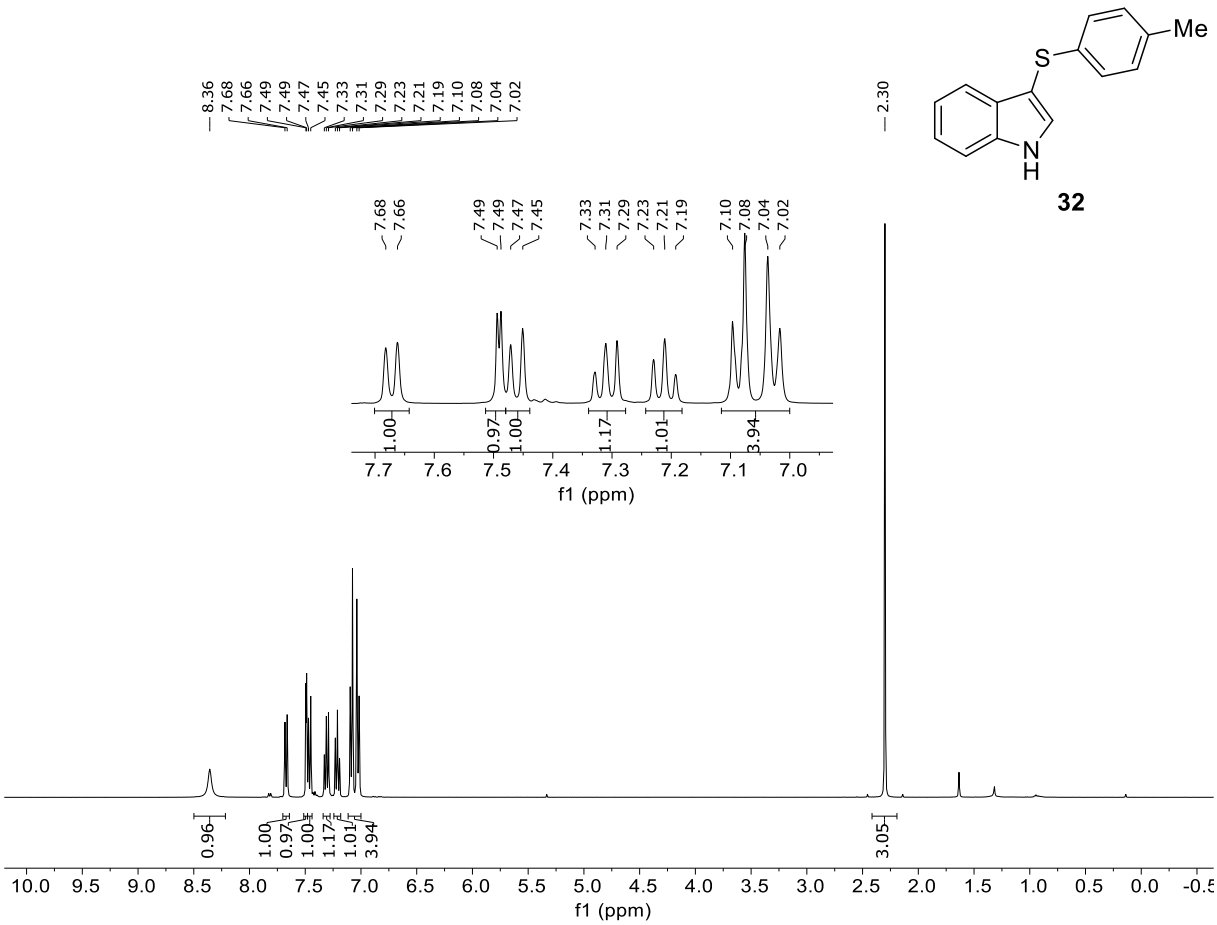
124.89
123.20
121.05
119.82
111.69
102.97
77.16 CDCl3
f1 (ppm)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7.66
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7.47
7.45
7.33
7.31
7.29
7.23
7.21
7.19
7.10
7.08
7.04
7.02
2.30
Me
S
N
H
32
f1 (ppm)
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1.00
0.97
1.00
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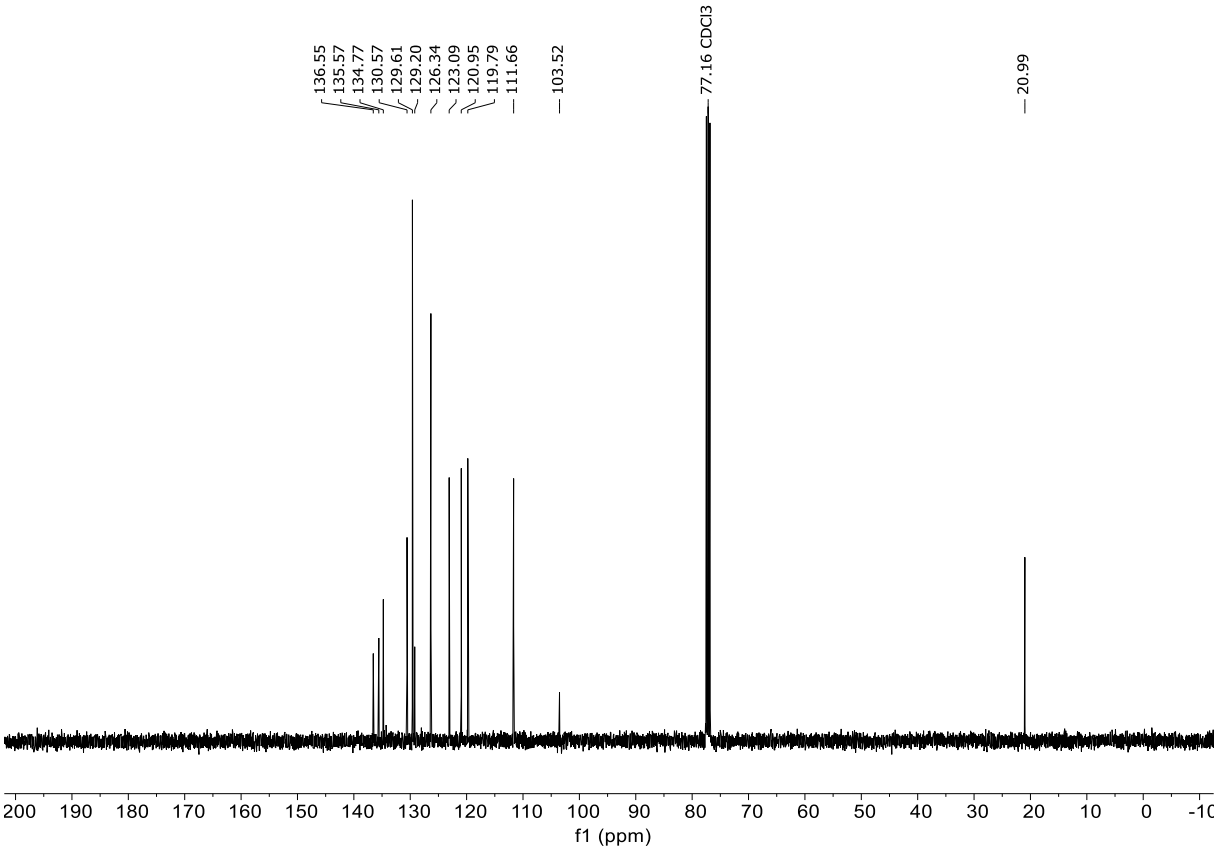
1.01
3.94
3.05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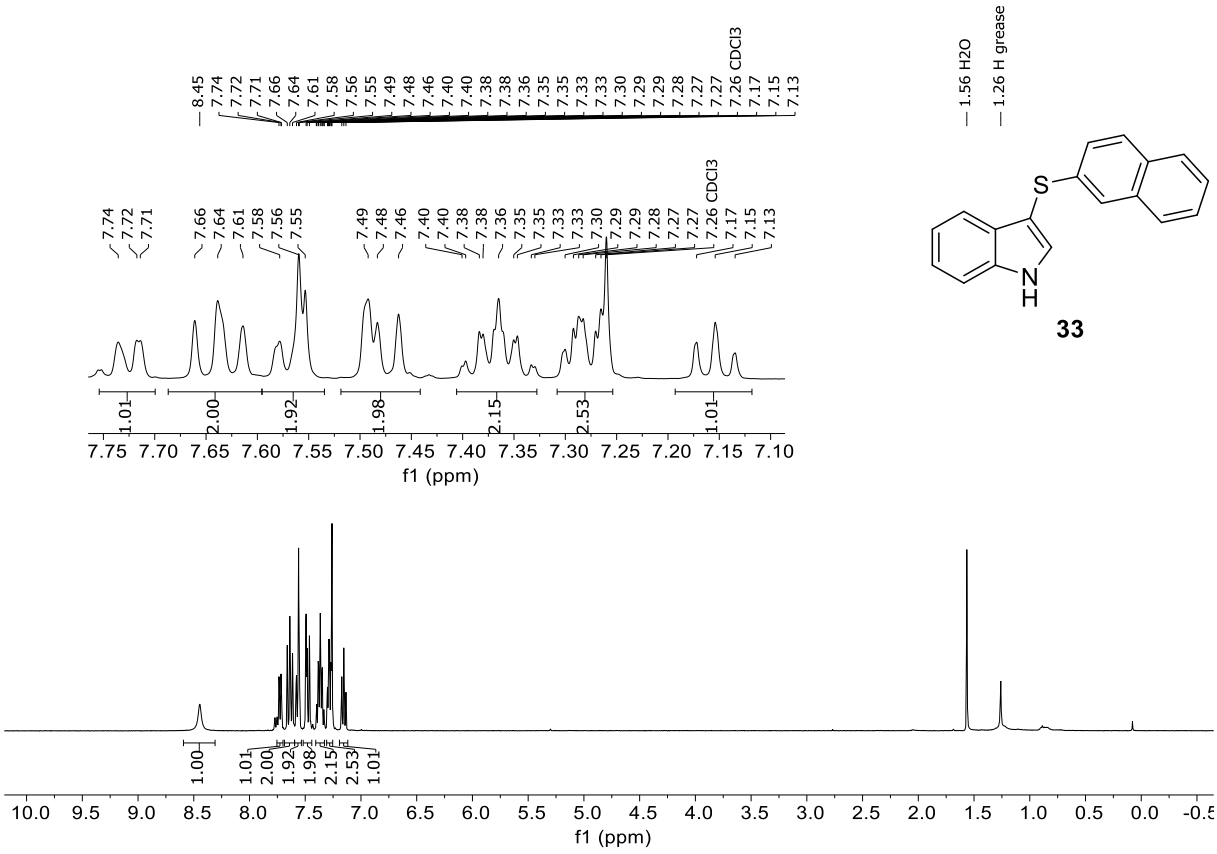
126.34
123.09
120.95
119.79
111.66
103.52
77.16 CDCl3
20.99
f1 (ppm)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7.48
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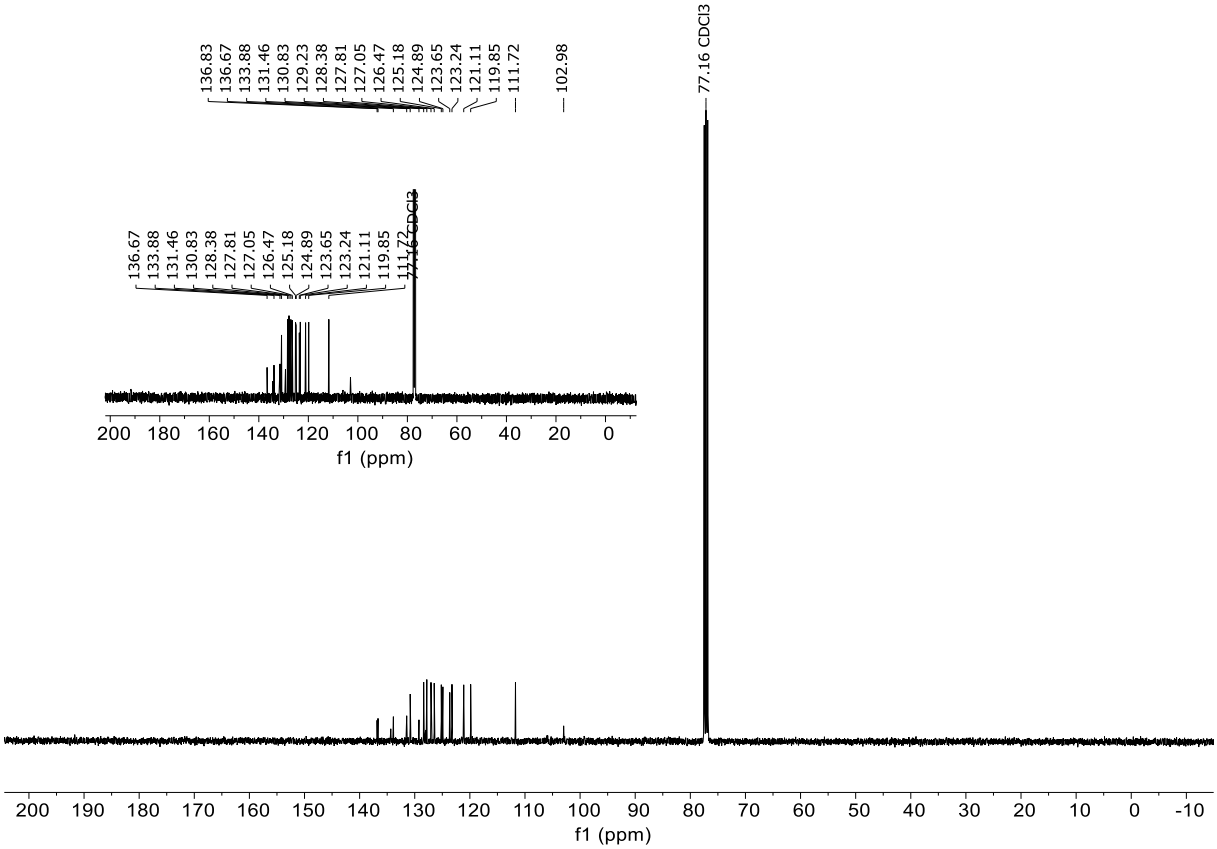
7.40
7.40
7.40
7.38
7.38
7.36
7.35
7.35
7.33
7.33
7.30
7.29
7.29
7.28
7.27
7.27
7.26 CDCl3
7.17
7.15
7.13
1.56 H2O
1.26 H grease
1.01
2.00
1.92
1.98
2.15
2.53
1.01
f1 (ppm)
33

1.00
1.01
2.00
1.92
1.98
2.15
2.53
1.01
f1 (ppm)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136.67
133.88
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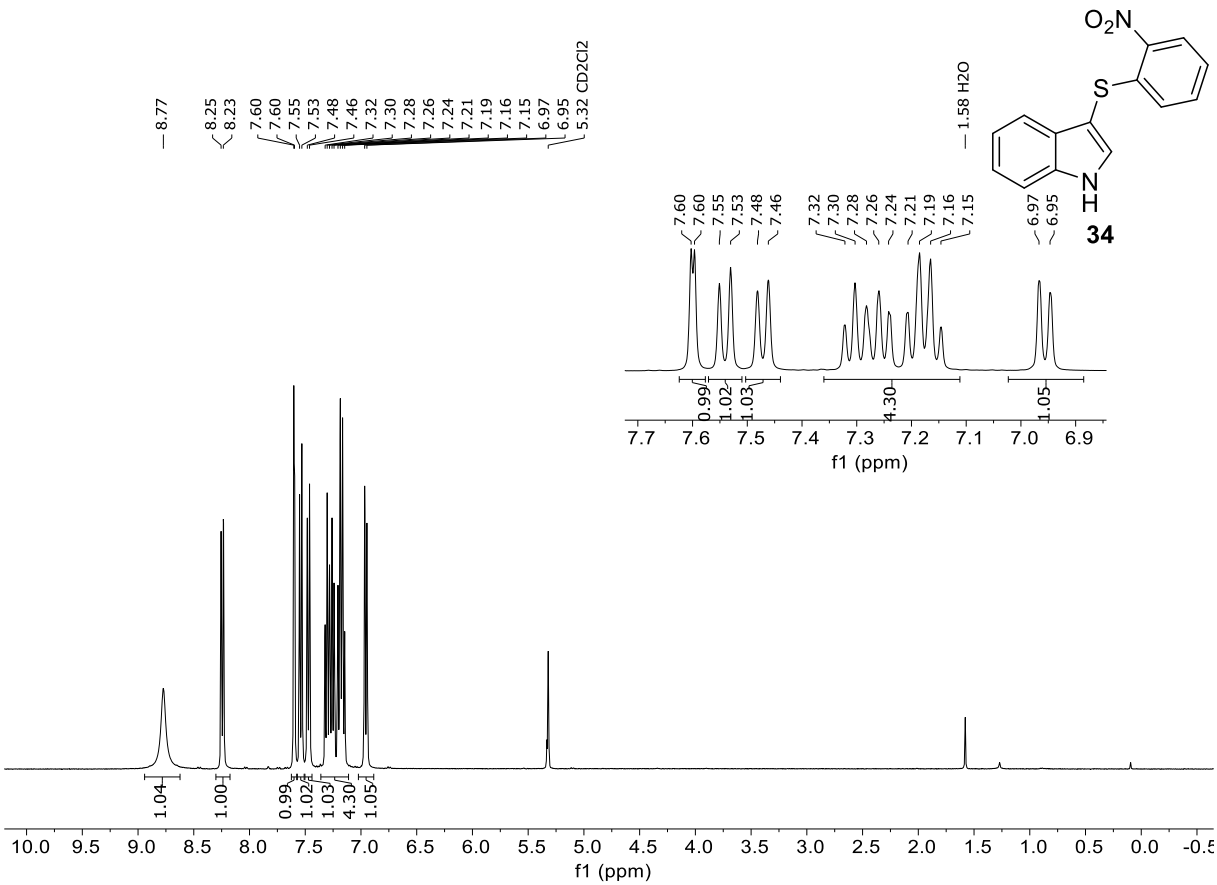
129.23
128.38
127.81
127.05
126.47
125.18
124.89
123.65
123.24
121.11
119.85
111.72
102.98
77.16 CDCl3
f1 (ppm)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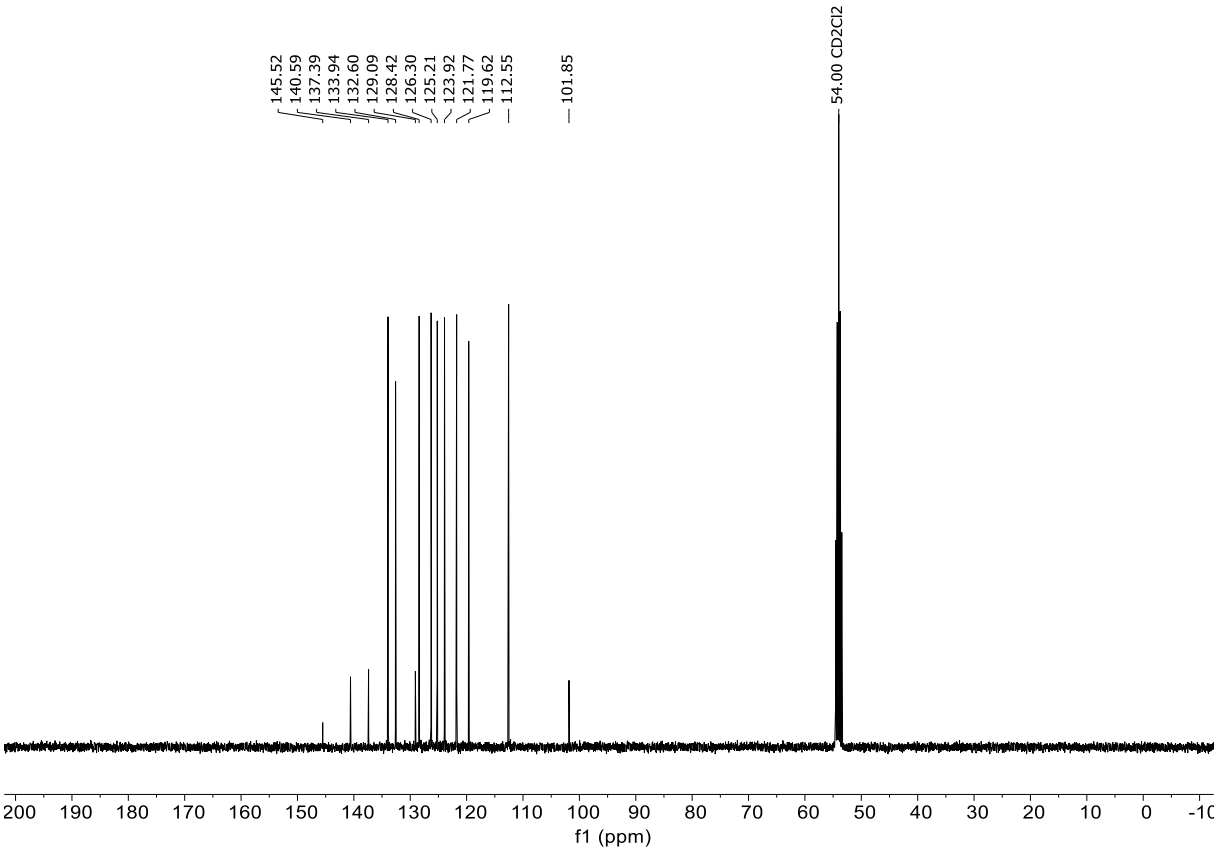
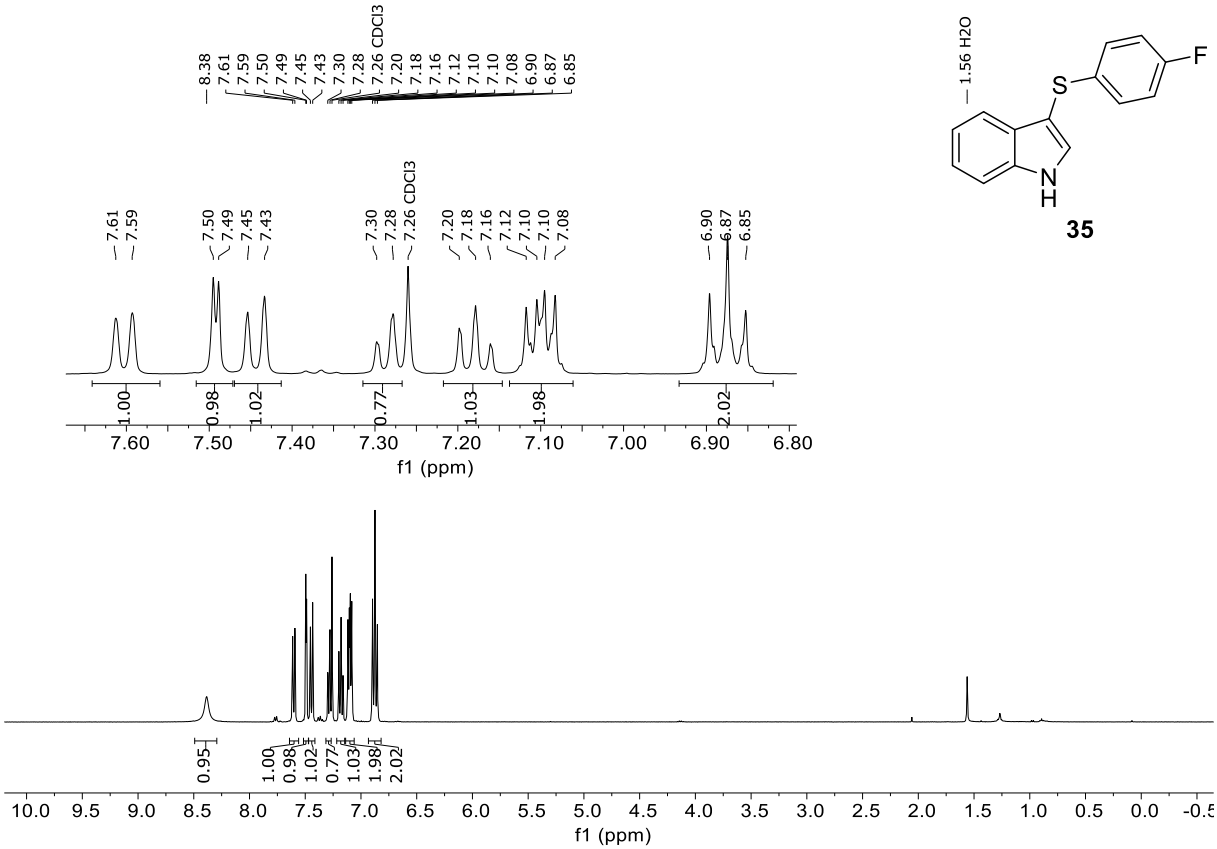
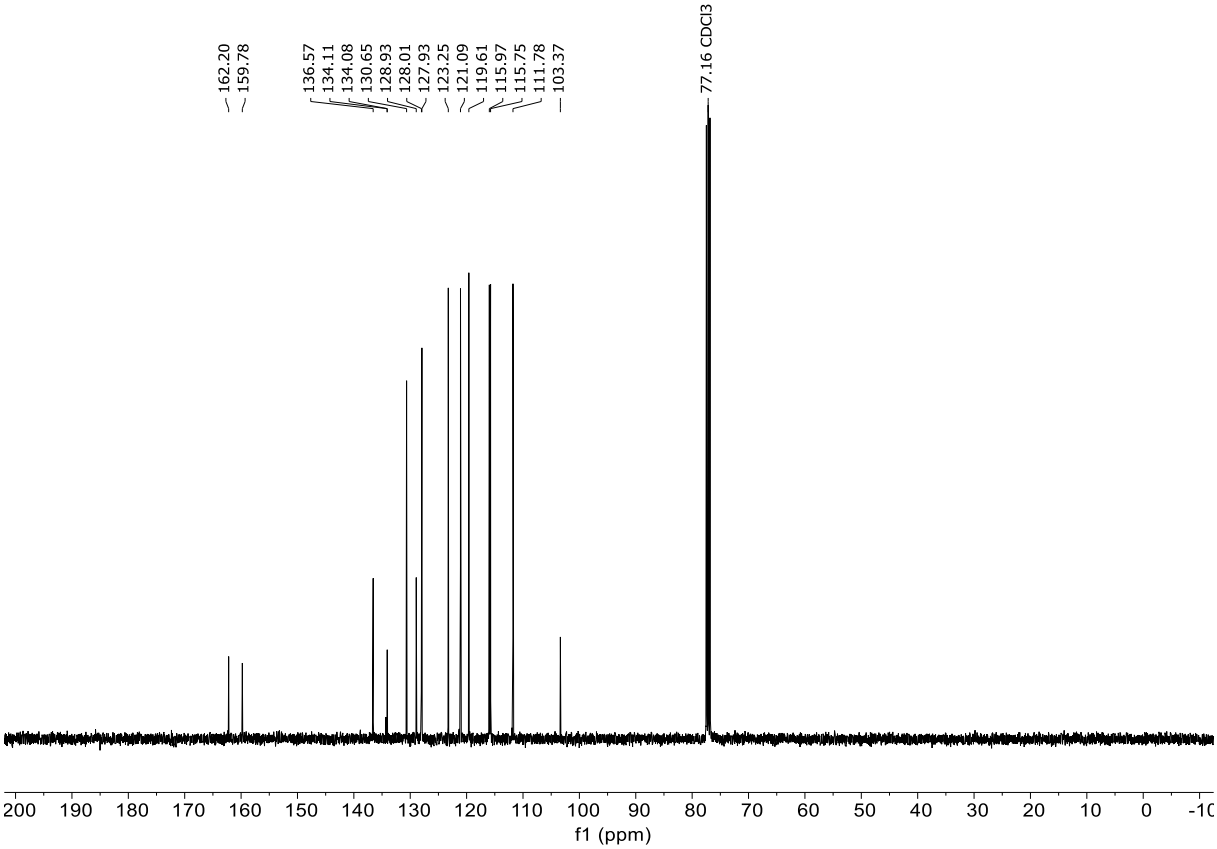
8.25
8.23
7.60
7.60
7.55
7.53
7.48
7.46
7.32
7.30
7.28
7.26
7.24
7.21
7.19
7.16
7.15
6.97
6.95
5.32 CD2Cl2
1.58 H2O
O2N
S
N
H
34
1.04
1.00
0.99
1.02
1.03
4.30
1.05
f1 (ppm)


145.52
140.59
137.39
133.94
132.60
129.09
128.42
126.30
125.21
123.92
121.77
119.62
112.55
101.85
54.00 CD2Cl2
f1 (ppm)


8.38
7.61
7.59
7.50
7.49
7.45
7.43
7.30
7.28
7.26 CDCl3
7.20
7.18
7.16
7.12
7.10
7.10
7.08
6.90
6.87
6.85
1.56 H2O
F
S
N
H
35
1.00
0.98
1.02
0.77
1.03
1.98
2.02
f1 (ppm)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134.08
130.65
128.93
128.01
127.93
123.25
121.09
119.61
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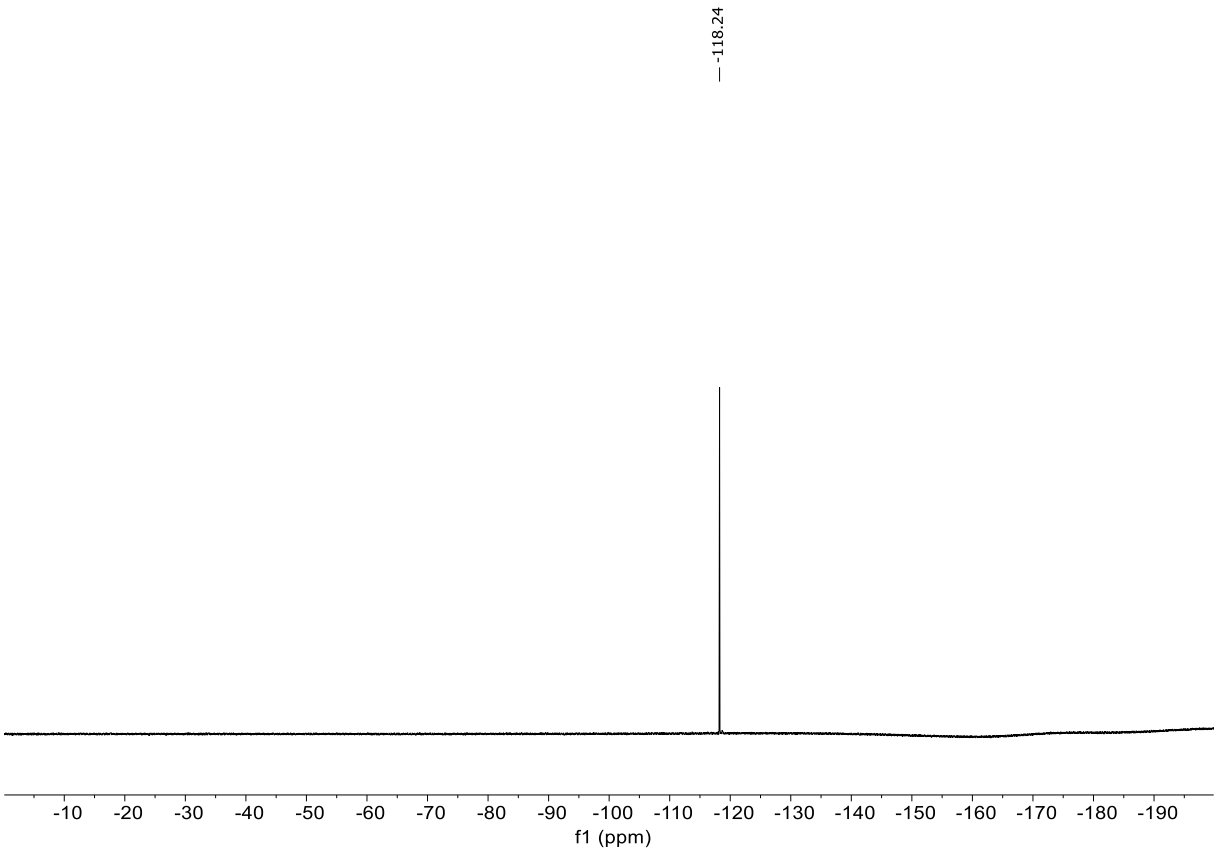
115.75
111.78
103.37
77.16 CDCl3
f1 (ppm)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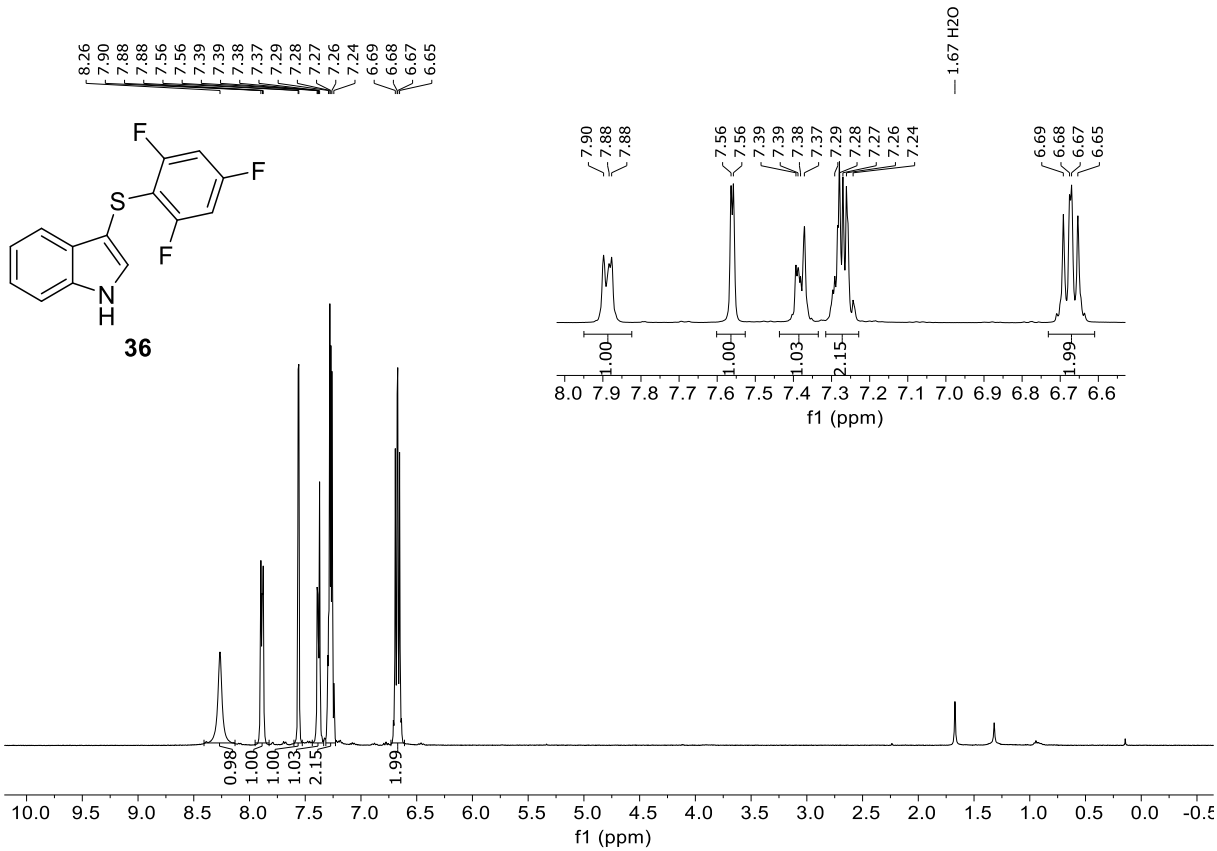
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)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7.90
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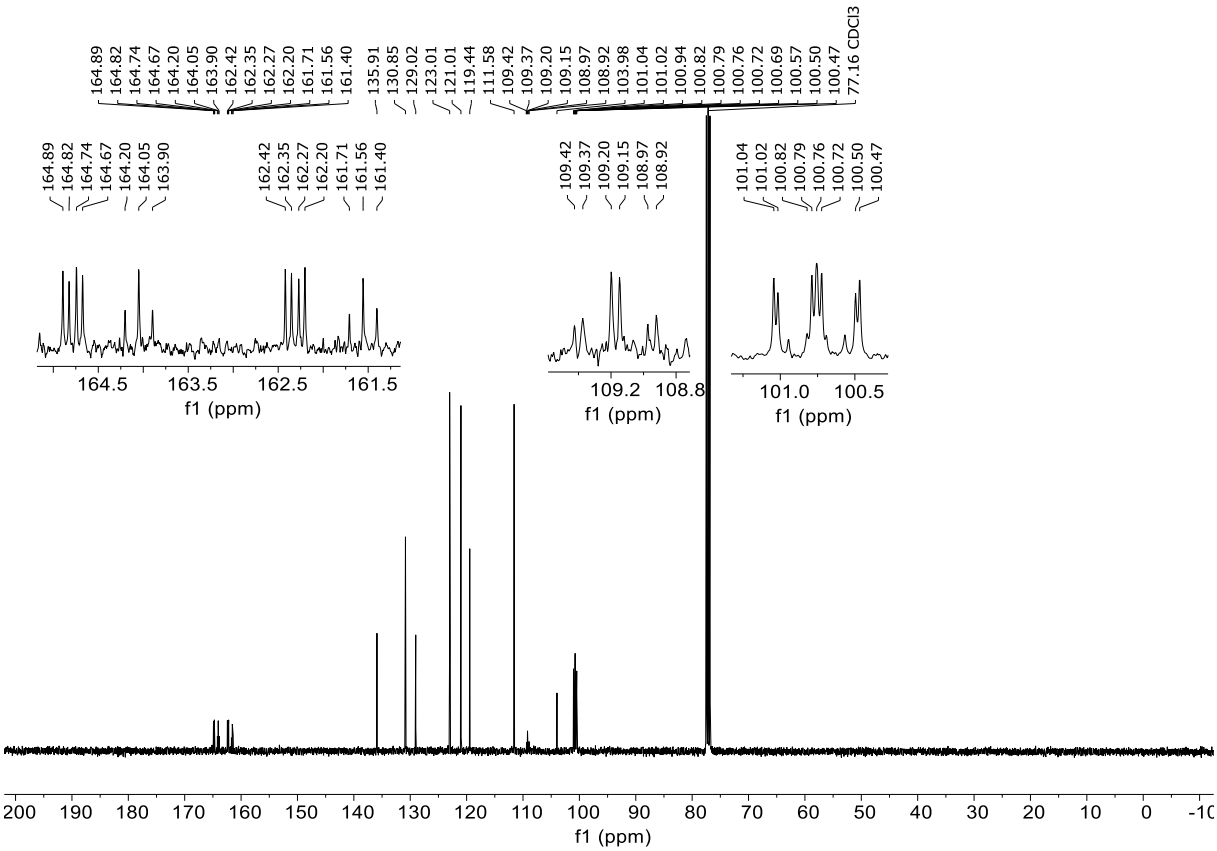
7.88
7.56
7.56
7.39
7.39
7.38
7.37
7.29
7.28
7.27
7.26
7.24
6.69
6.68
6.67
6.65
1.67 H2O
F
F
F
S
N
H
36
0.98
1.00
1.00
1.03
2.15
1.99
f1 (ppm)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162.27
162.20
161.71
161.56
161.40
135.91
130.85
129.02
123.01
121.01
119.44
111.58
109.42
109.37
109.20
109.15
108.97
108.92
103.98
101.04
101.02
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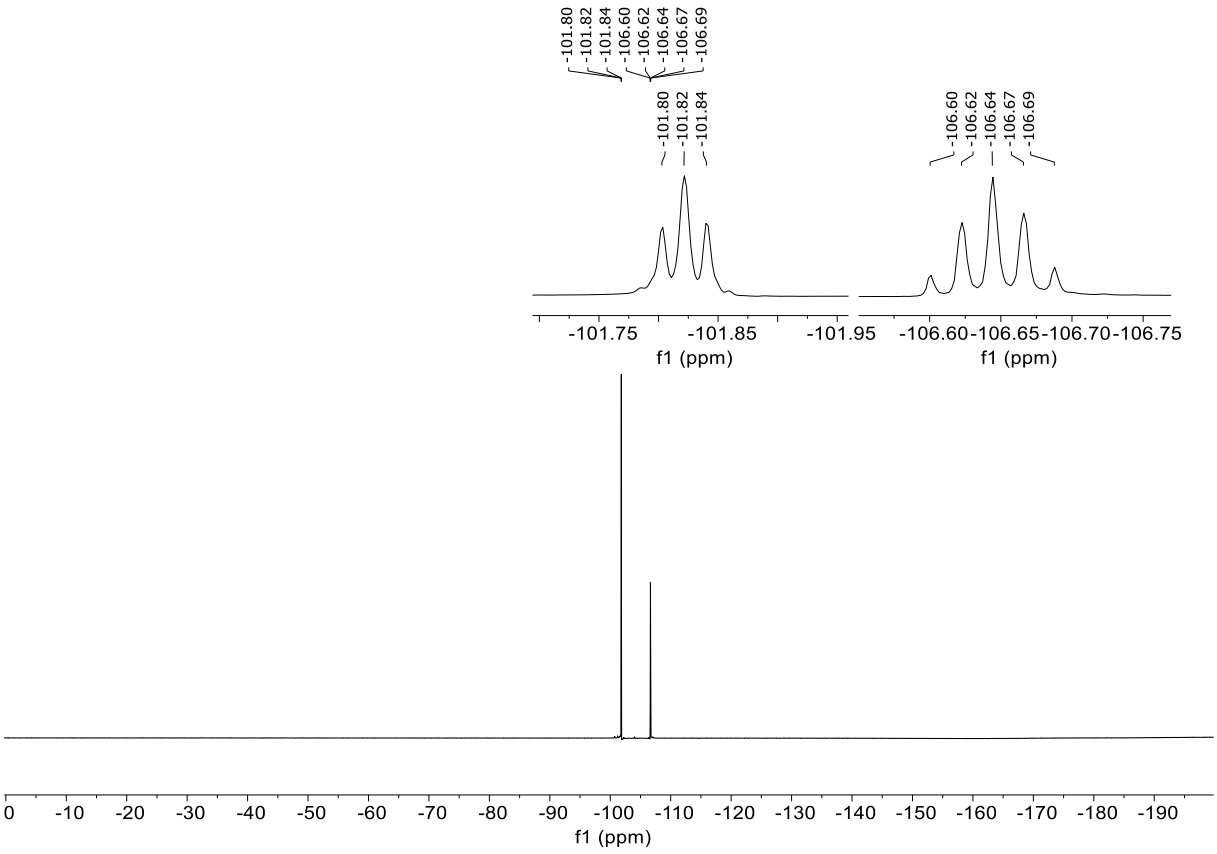
100.82
100.79
100.76
100.72
100.69
100.57
100.50
100.47
77.16 CDCl3
f1 (ppm)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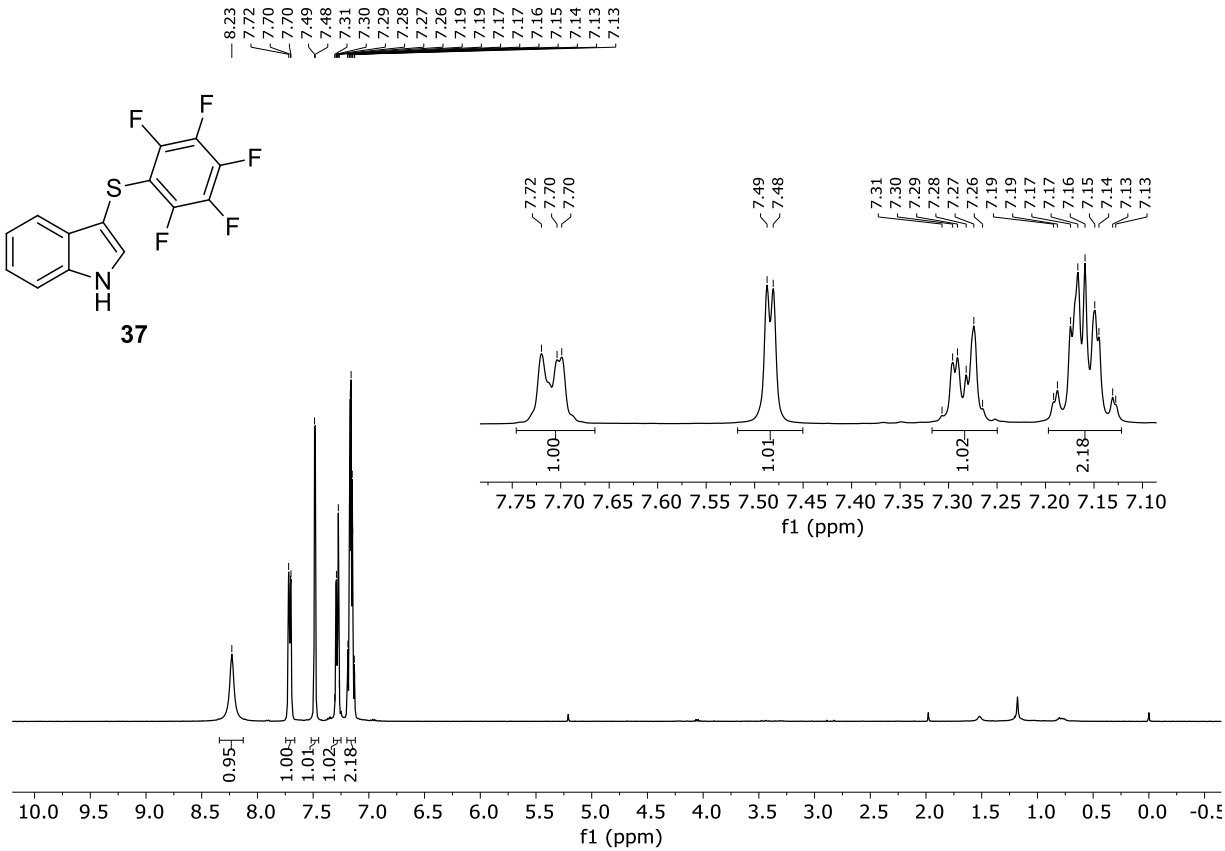
-101.82
-101.84
-106.60
-106.62
-106.64
-106.67
-106.69
-101.75
-101.85
-101.95
f1 (ppm)
-106.60-106.65-106.70-106.75
f1 (ppm)
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)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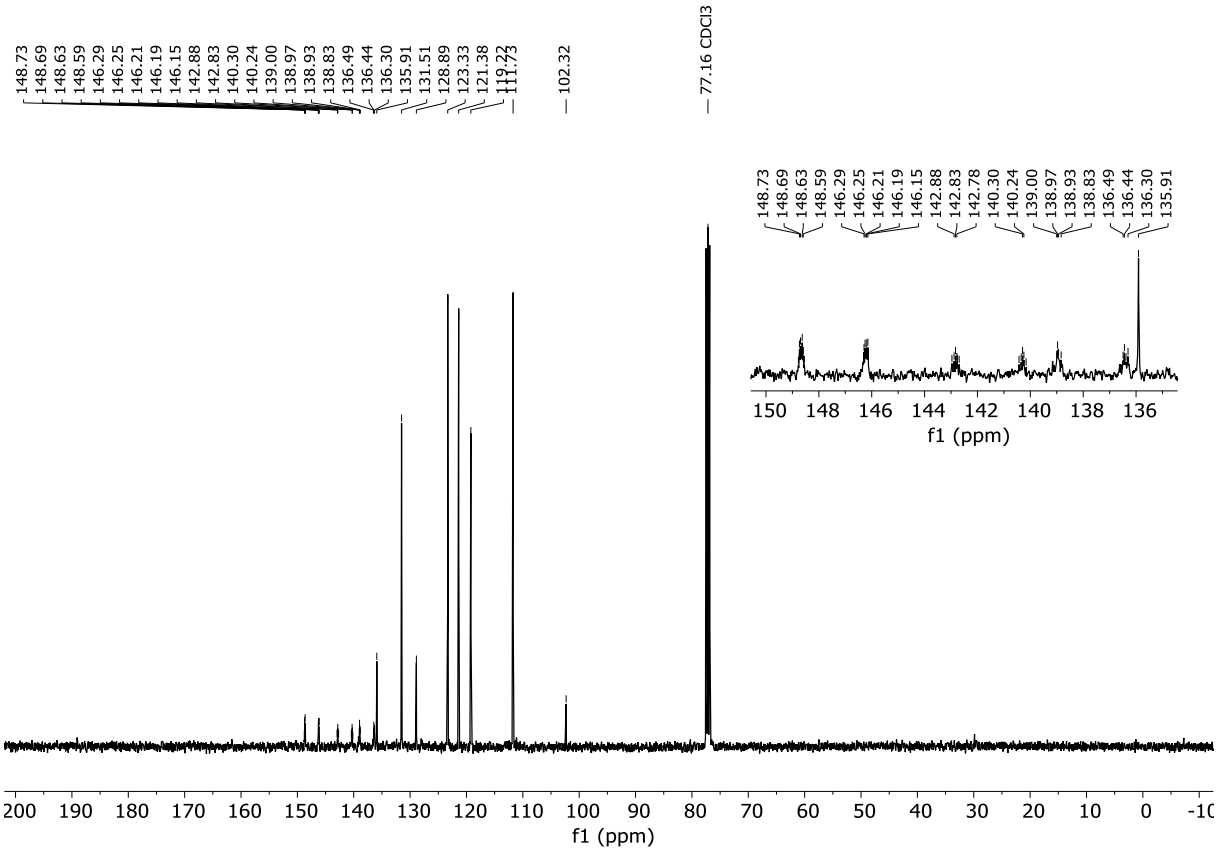
7.48
7.31
7.30
7.29
7.28
7.27
7.26
7.19
7.19
7.17
7.17
7.16
7.15
7.14
7.13
7.13
F
F
F
F
F
S
N
H
37
0.95
1.00
1.01
1.02
2.18
f1 (ppm)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148.63
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146.25
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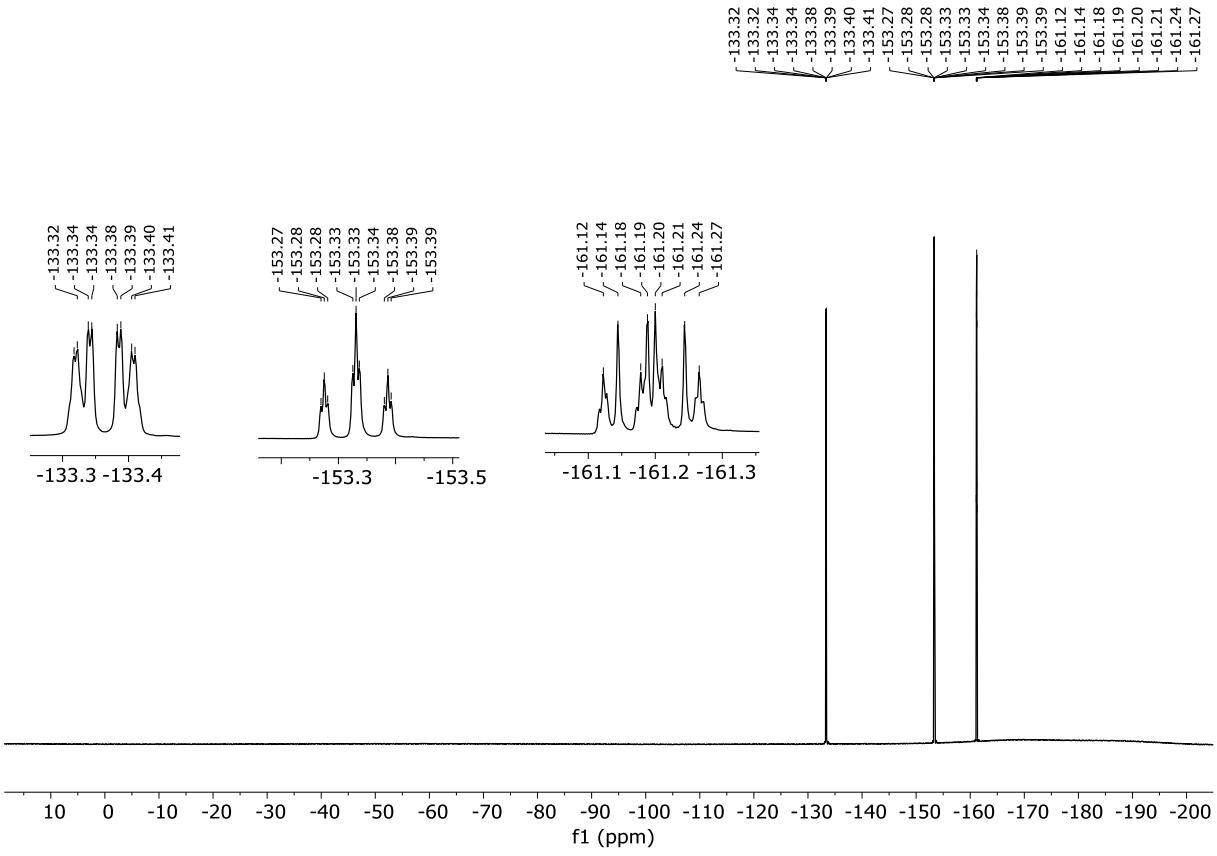
146.19
146.15
142.88
142.83
140.30
140.24
139.00
138.97
138.93
138.83
136.49
136.44
136.30
135.91
131.51
128.89
123.33
121.38
119.22
111.73
102.32
77.16 CDCl3
f1 (ppm)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-153.27
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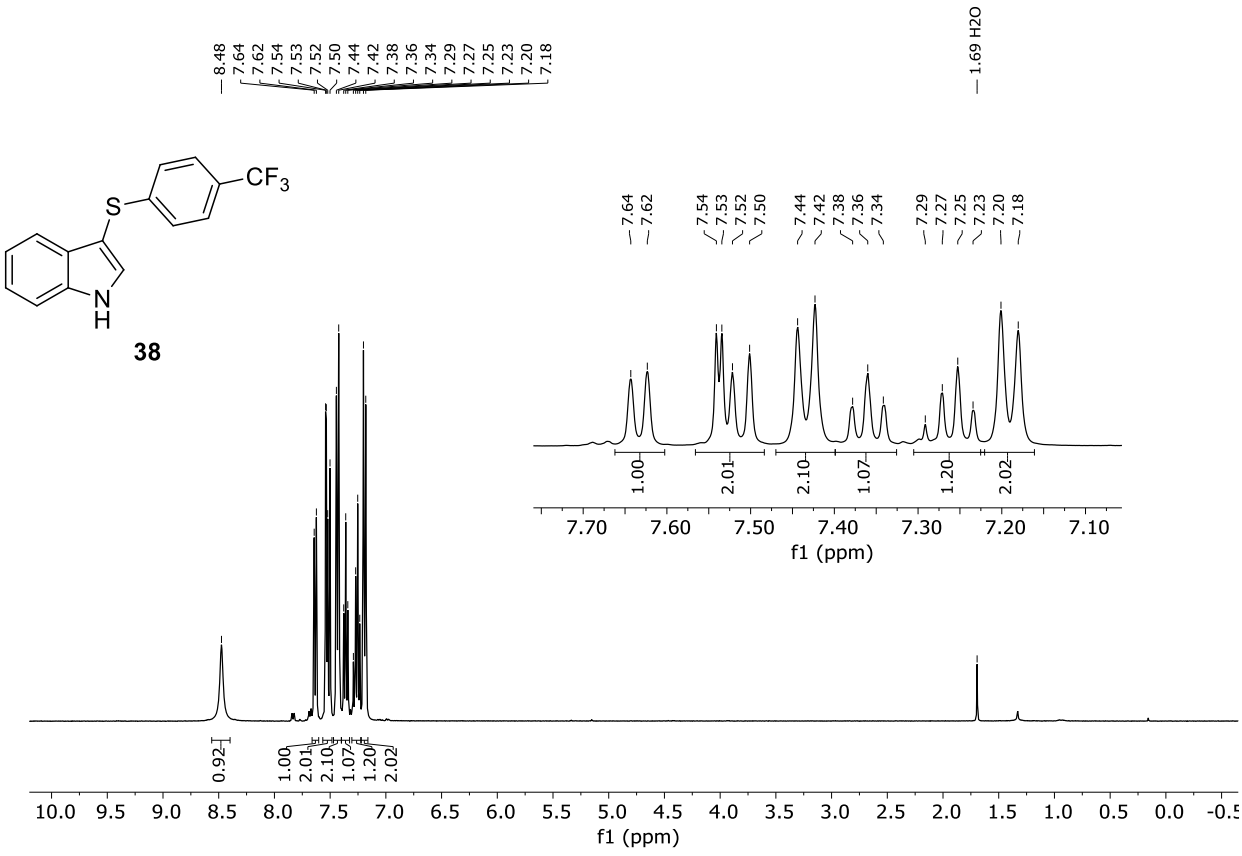
-153.33
-153.34
-153.38
-153.39
-161.12
-161.14
-161.18
-161.19
-161.20
-161.21
-161.24
-161.27
-133.3 -133.4
-153.3
-153.5
-161.1 -161.2 -161.3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)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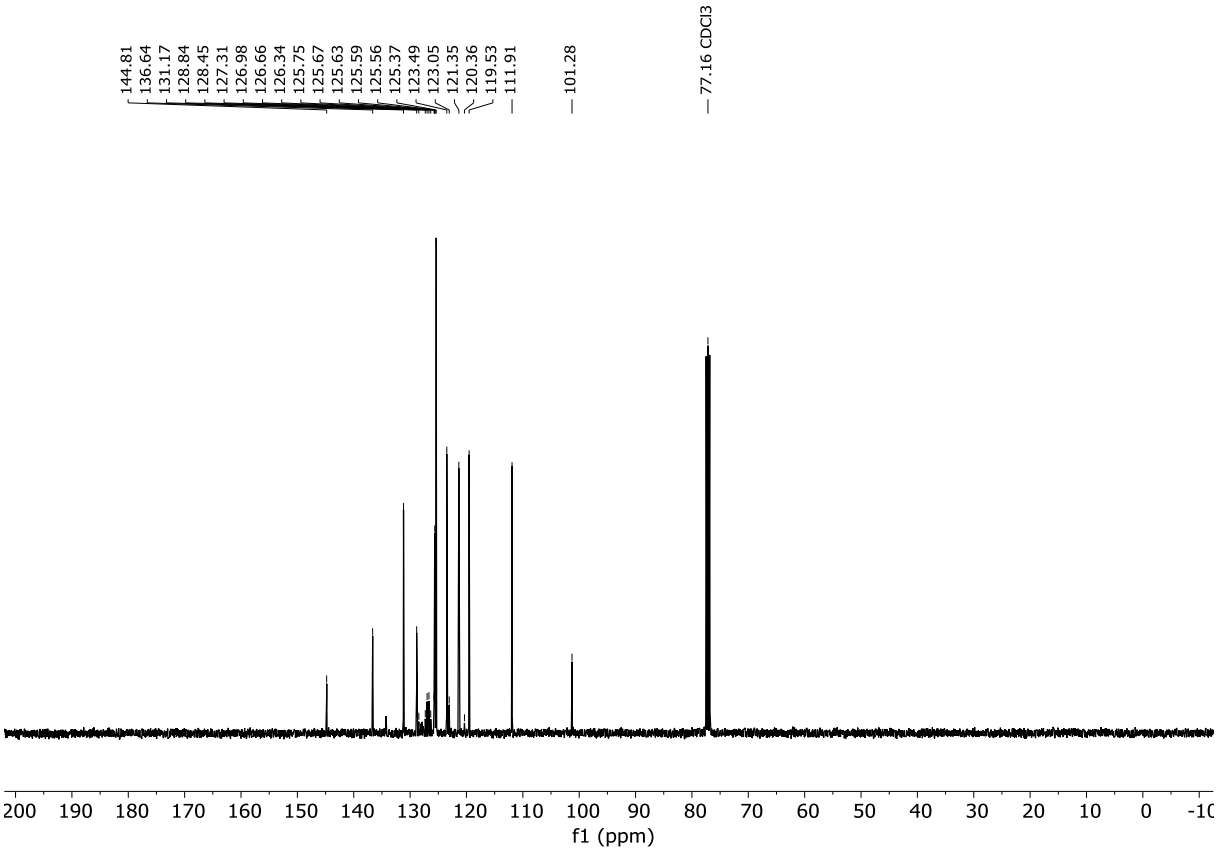
7.52
7.50
7.44
7.42
7.38
7.36
7.34
7.29
7.27
7.25
7.23
7.20
7.18
1.69 H2O
CF3
S
N
H
38
0.92
1.00
2.01
2.10
1.07
1.20
2.02
f1 (ppm)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128.45
127.31
126.98
126.66
126.34
125.75
125.67
125.63
125.59
125.56
125.37
123.49
123.05
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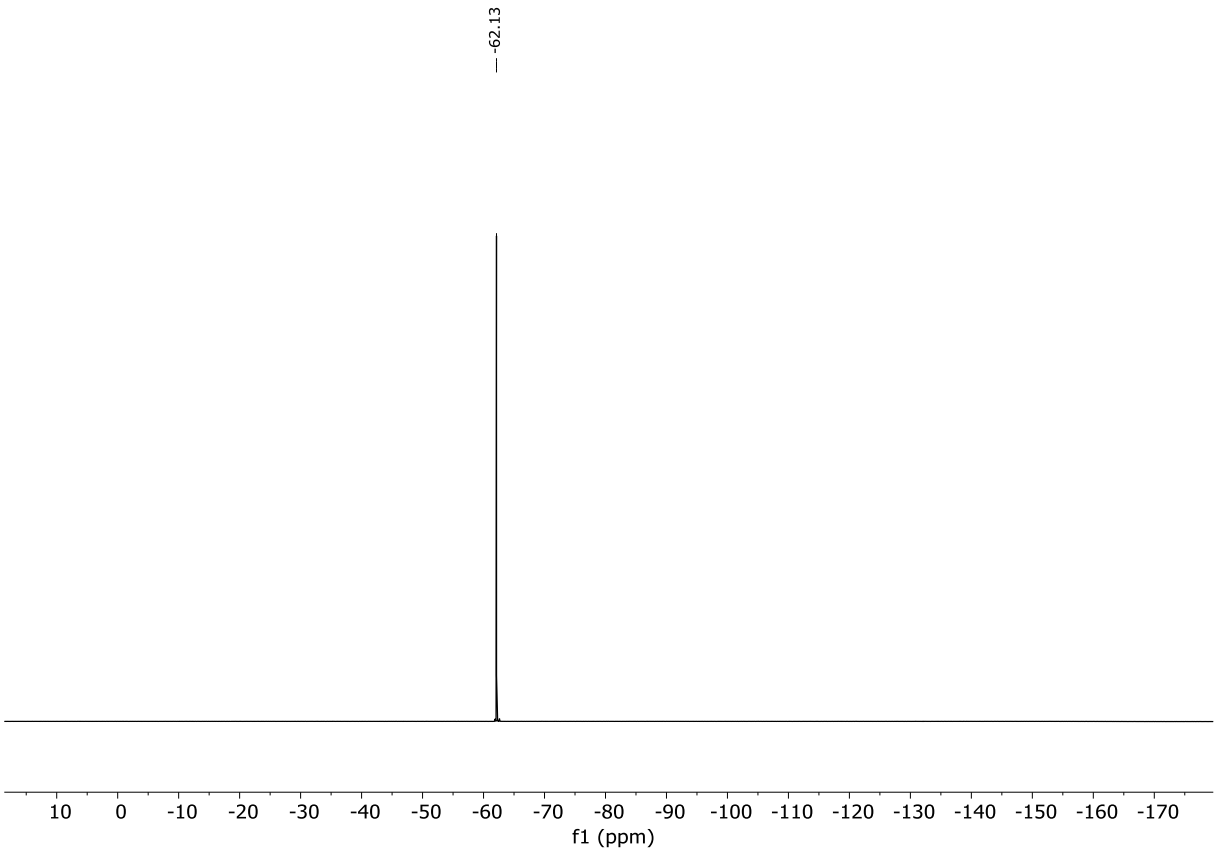
120.36
119.53
111.91
101.28
77.16 CDCl3
f1 (ppm)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10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
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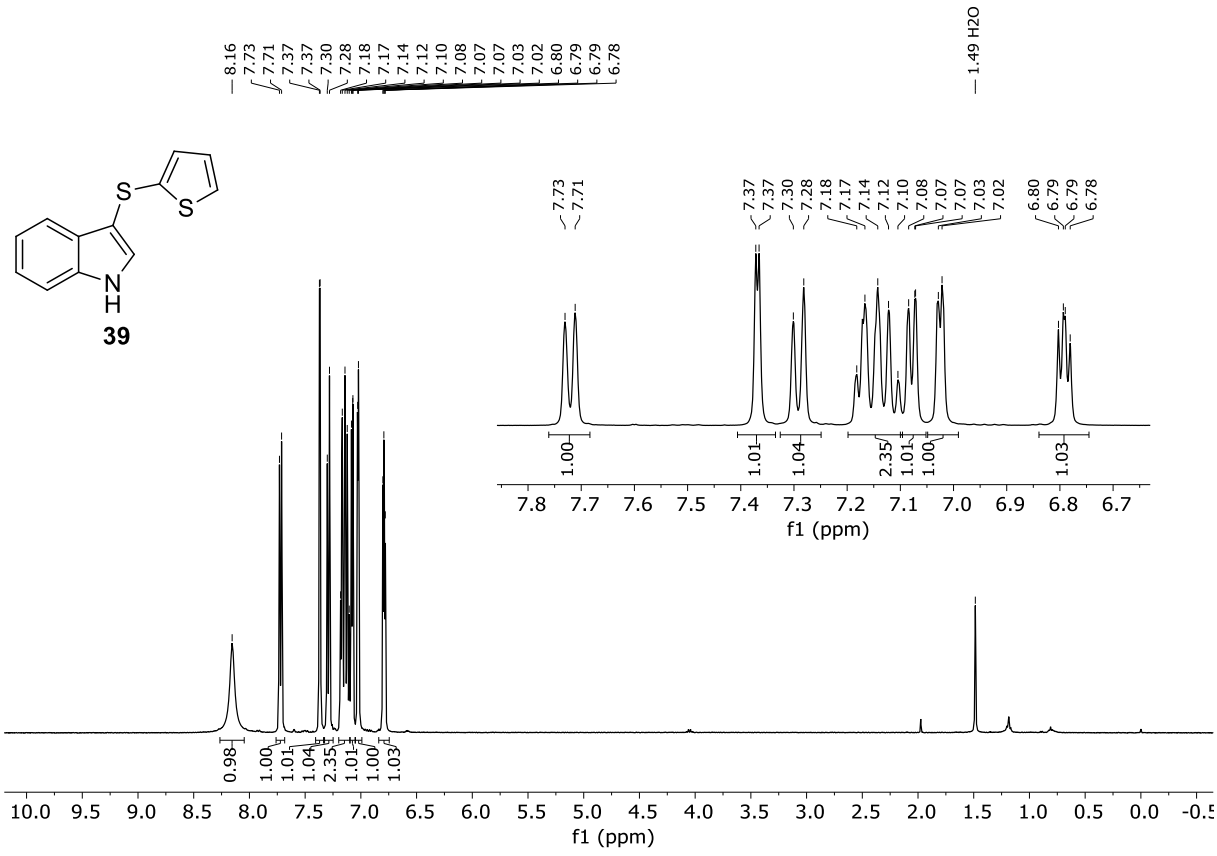
-130
-140
-150
-160
-170
f1 (ppm)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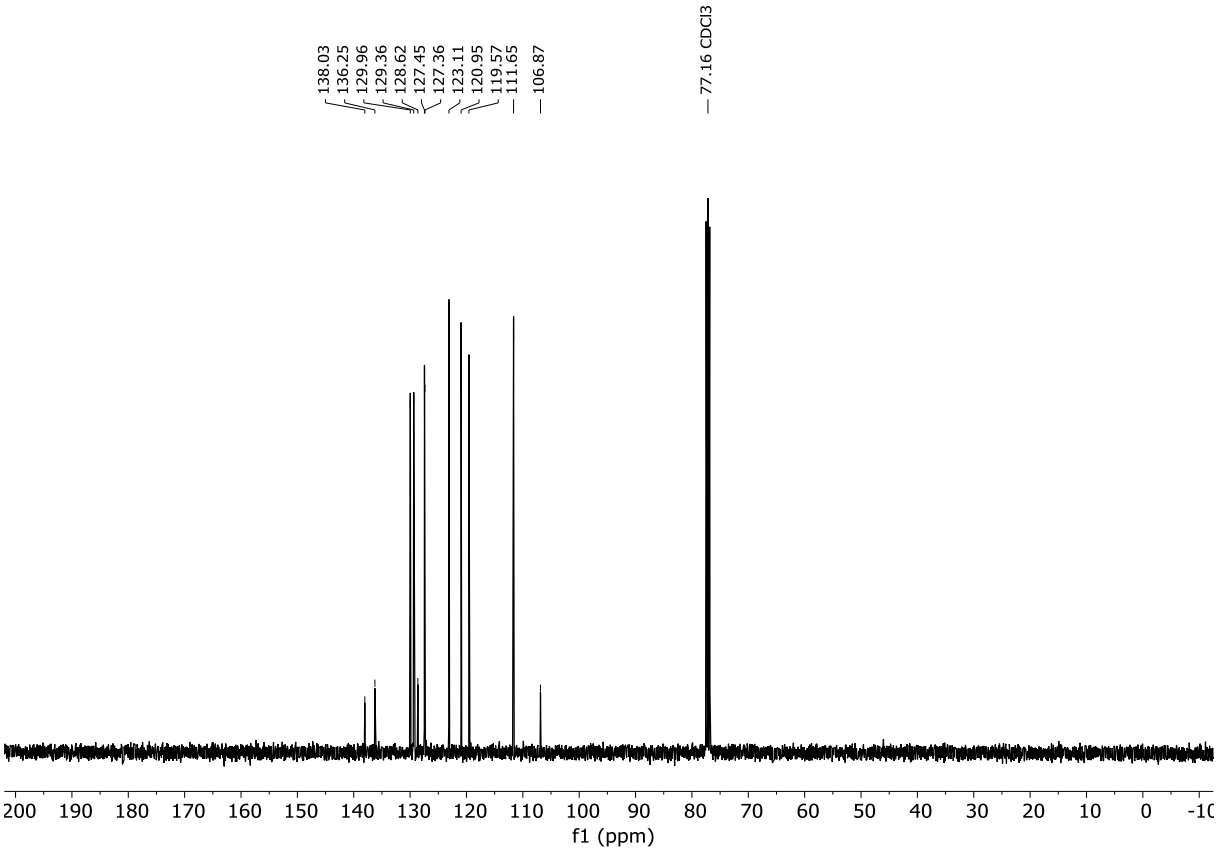
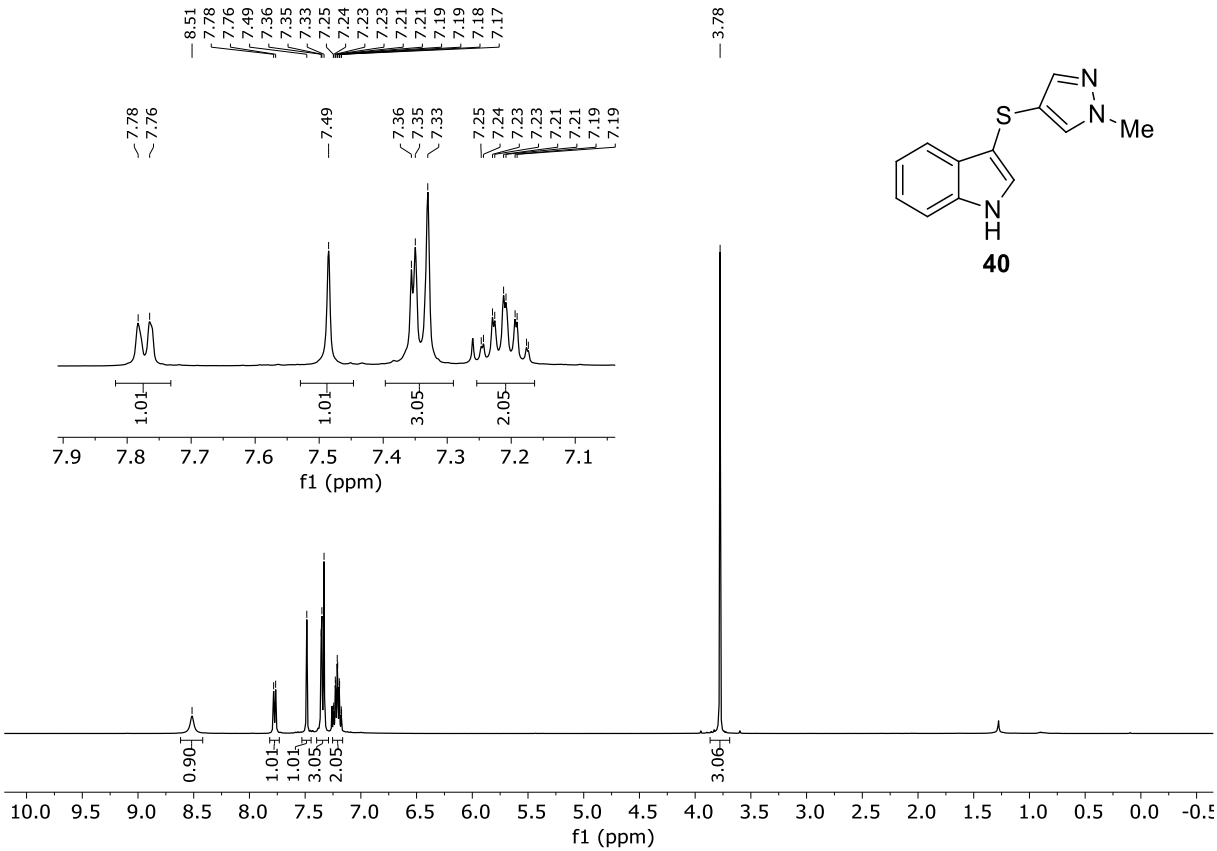
7.30
7.28
7.18
7.17
7.14
7.12
7.10
7.08
7.07
7.07
7.03
7.02
6.80
6.79
6.79
6.78
1.49 H2O
S
S
N
H
39
0.98
1.00
1.01
1.04
2.35
1.01
1.00
1.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
1.00
1.01
1.04
2.35
1.01
1.00
1.03
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7
f1 (ppm)


138.03
136.25
129.96
129.36
128.62
127.45
127.36
123.11
120.95
119.57
111.65
106.87
77.16 CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.76
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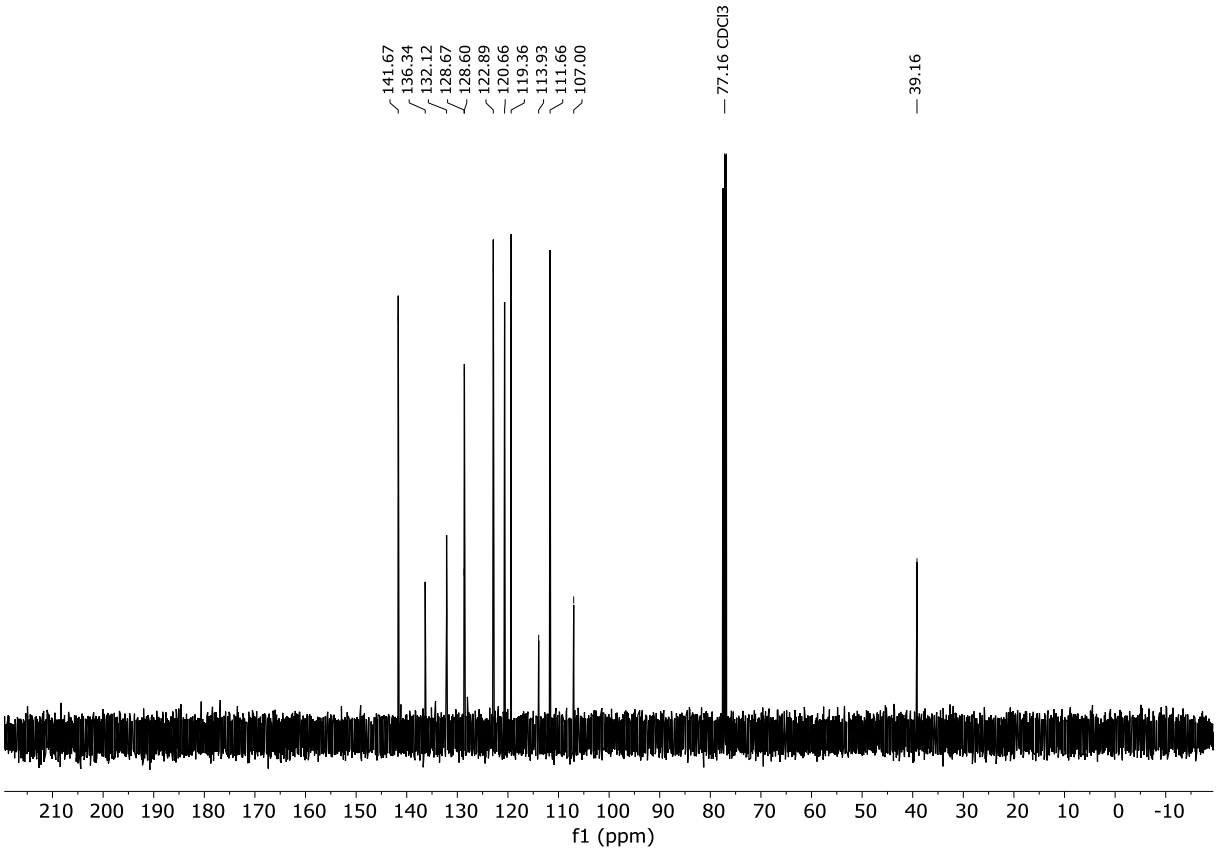
7.36
7.35
7.33
7.25
7.24
7.23
7.23
7.21
7.21
7.19
7.19
7.18
7.17
3.78
N
S
N
Me
N
H
40
1.01
1.01
3.05
2.05
f1 (ppm)
0.90
1.01
1.01
3.05
2.05
3.06
f1 (ppm)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136.34
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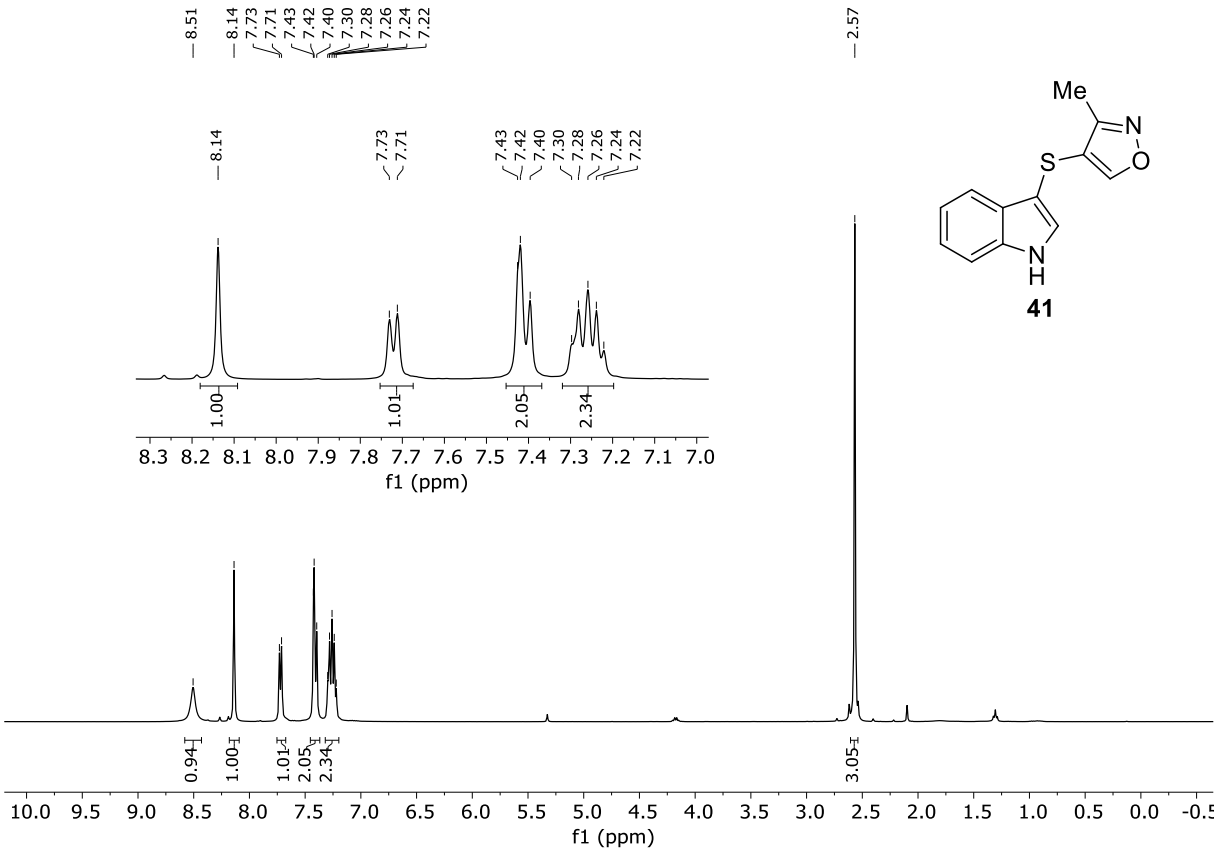
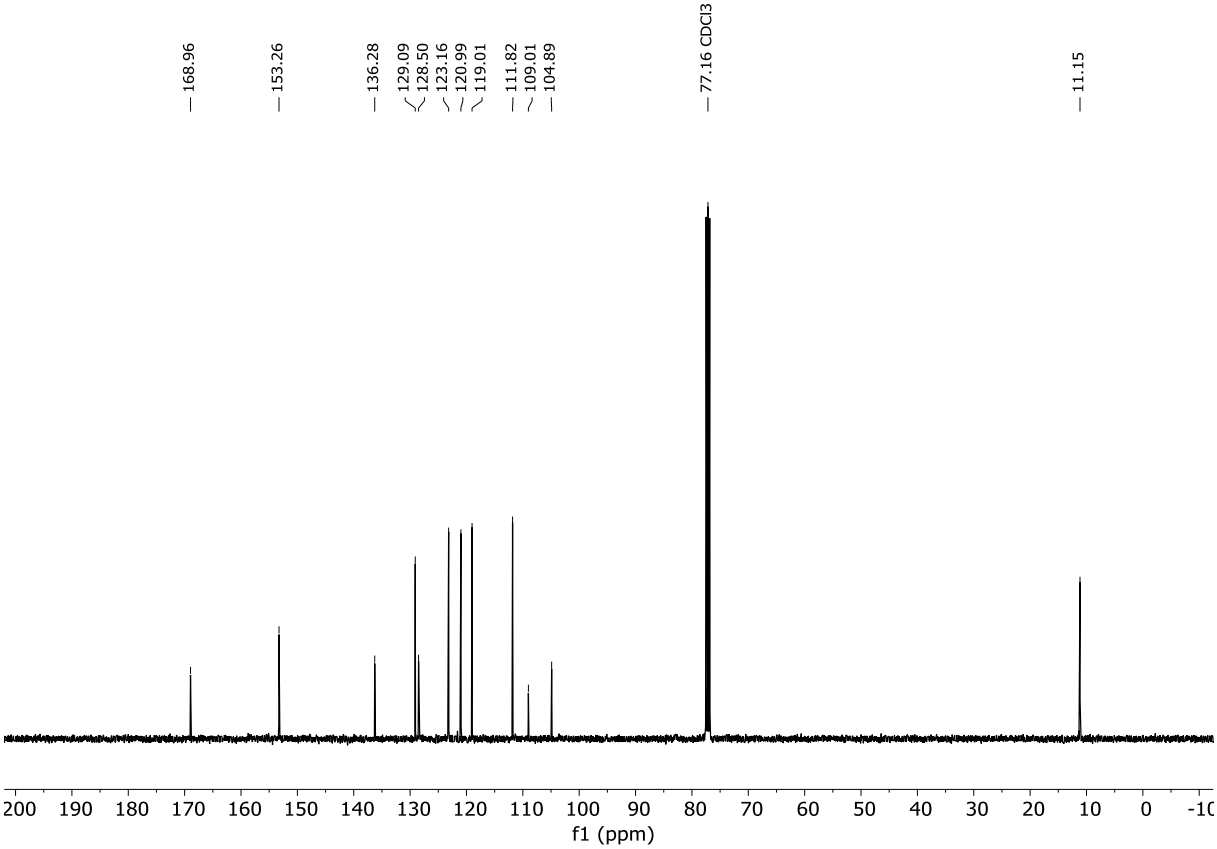
128.60
122.89
120.66
119.36
113.93
111.66
107.00
77.16 CDCl3
39.16
f1 (ppm)


8.51
8.14
7.73
7.71
7.43
7.42
7.40
7.30
7.28
7.26
7.24
7.22
2.57
Me
N
O
S
N
H
41
1.00
1.01
2.05
2.34
f1 (ppm)
0.94
1.00
1.01
2.05
2.34
3.05
f1 (ppm)


168.96
153.26
136.28
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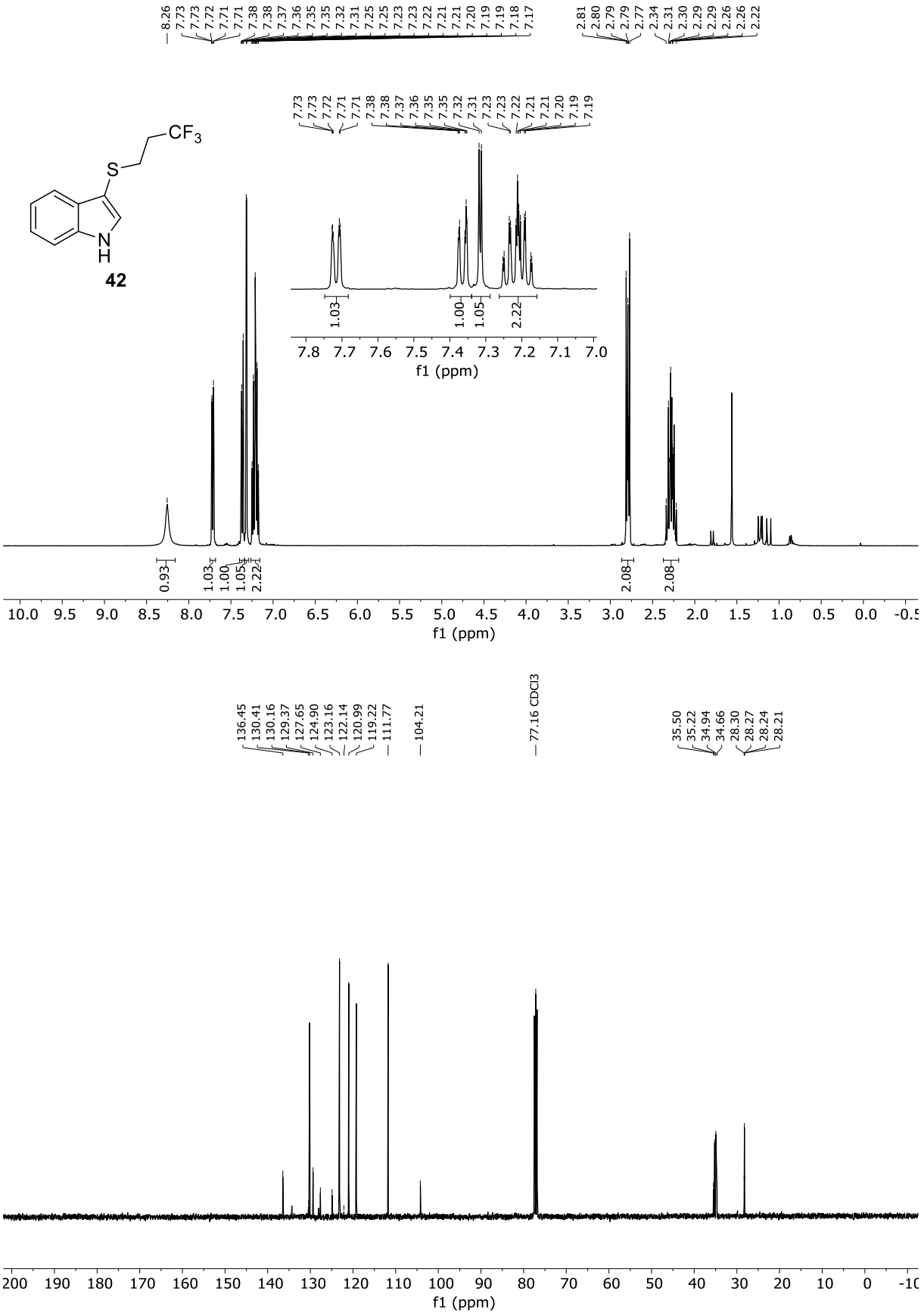
123.16
120.99
119.01
111.82
109.01
104.89
77.16 CDCl3
11.15
f1 (ppm)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7.38
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7.36
7.35
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7.32
7.31
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7.23
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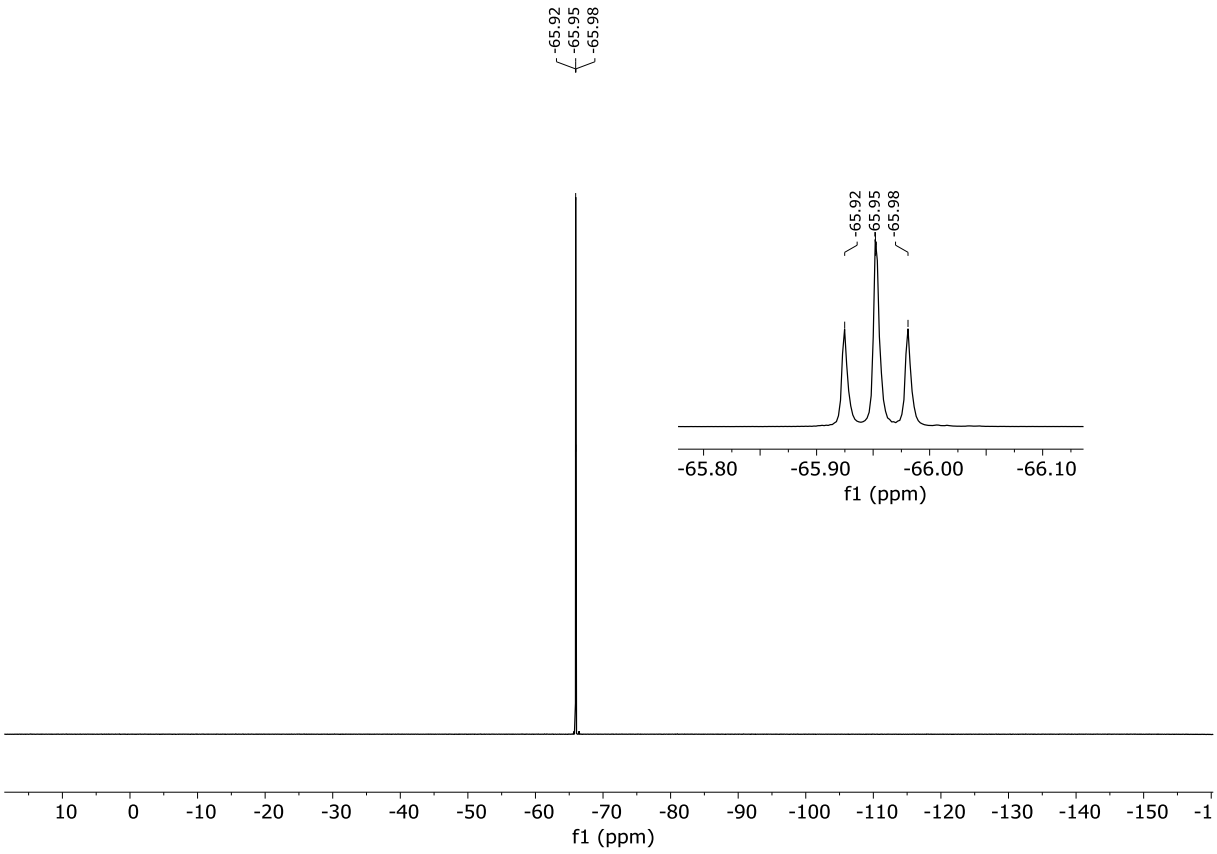
7.20
7.19
7.19
7.18
7.17
2.81
2.80
2.79
2.79
2.77
2.34
2.31
2.30
2.29
2.29
2.26
2.26
2.22
CF3
S
N
H
42
0.93
1.03
1.00
1.05
2.22
2.08
2.08
f1 (ppm)
1.03
1.00
1.05
2.22
f1 (ppm)
136.45
130.41
130.16
129.37
127.65
124.90
123.16
122.14
120.99
119.22
111.77
104.21
77.16 CDCl3
35.50
35.22
34.94
34.66
28.30
28.27
28.24
28.21
f1 (ppm)


-65.92
-65.95
-65.98
-65.92
-65.95
-65.98
-65.80
-65.90
-66.00
-66.10
f1 (ppm)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-1
f1 (ppm)