

Supporting Information

Photoredox Catalyzed C—H Trifluoroethylamination of Heteroarenes

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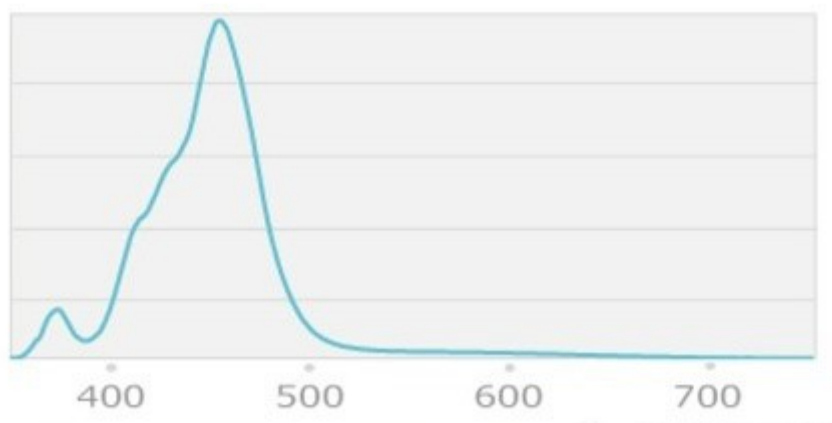
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1. General Information

^1H NMR (TMS as the internal standard) were recorded on a Bruker AM 400 or 600 spectrometer, ^{13}C NMR and ^{19}F NMR (CFCl_3 as outside standard and low field is positive) spectra were recorded on a Bruker AM 400 or 600 spectrometer. For the determination of ^{19}F NMR yield, PhCF_3 was used as an internal standard and the relaxation delay (d1) was set to 5 s. Chemical shifts (δ) were reported in per million (ppm), and coupling constants (J) were in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet. High resolution mass spectra (HRMS) were obtained on a GC-TOF mass spectrometer.

Materials: Unless otherwise noted, all reagents were obtained commercially and used without further purification. Substrates were purchased from commercial sources or prepared according to literature procedures. Reactions were performed using glassware that was flame-dried under vacuum.

All photochemical reactions were performed in 10 mL screw cap scintillation vials (unless noted otherwise) under a nitrogen atmosphere at room temperature and irradiated with a 40 W White LED (Kessil A160WE, America) from a distance of 10 cm.



Emission spectra of the used light sources

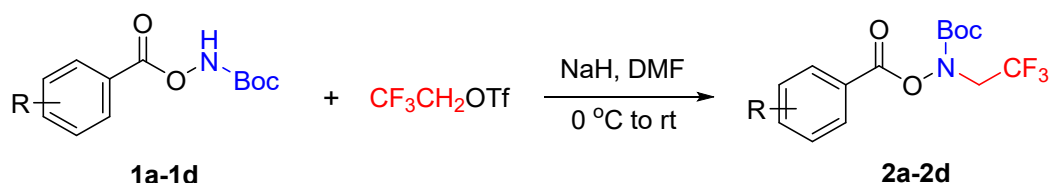
(picture originated from <https://www.instrument.com.cn/netshow/C327600.htm>)

2. Preparation of Substrates

Substrates **3a** (603-76-9), **3q** (10075-52-2), **3t** (21535-97-7), **5a** (271-89-6), **5b** (21535-97-7), **5c** (59214-70-9), **5d** (23145-07-5), **5e** (1455-18-1) were obtained commercially and used without further purification.

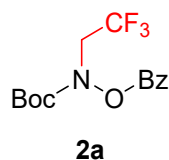
Substrates **1a-1d**¹, **1e**², **1f**², **3b**³, **3c**⁴, **3d**⁵, **3e**⁶, **3f-3k**⁷, **3l**⁸⁻¹⁰, **3m-3p**⁷, **3r**⁷, **3s**³, **5f**⁷ and **5h**⁷ were prepared according to the reported literatures.

General procedure for synthesis of **2a-2d**



To a solution of *tert*-butyl (benzoyloxy)carbamate (**1a-1d**) (10 mmol, 1.0 equiv.) in dry DMF (80 mL) was added portion wise NaH (15 mmol, 1.6 equiv., 60% dispersion in mineral oil) at 0 °C. The reaction mixture was stirred at 0 °C for 30 minutes and 2,2,2-trifluoroethyl trifluoromethanesulfonate (12 mmol, 1.5 equiv.) was added dropwise at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 30 minutes. After completion of the reaction monitored by TLC, the reaction mixture was quenched by H₂O, extracted with CH₂Cl₂. The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica-gel eluting with a mixture of pentane and EtOAc to give the desired product **2a-2d**.

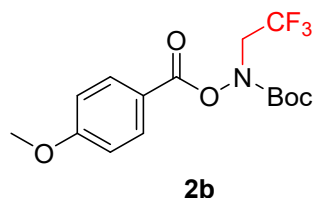
tert-Butyl (benzoyloxy)(2,2,2-trifluoroethyl)carbamate (**2a**)



The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 100:1) to afford **2a** (2.39 g, 75%) as a white solid. Mp. 48-50 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.00 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.60 – 7.55 (m, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 4.21 (s, 2H), 1.40 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 164.3, 153.5, 134.3, 123.0, 128.7, 126.8, 123.5 (q, *J* = 279.7 Hz), 84.0, 51.2 (q, *J* = 33.9 Hz), 27.9; ¹⁹F NMR (377 MHz, CDCl₃) δ -70.87 (t, *J* = 8.4 Hz); IR (thin film) ν 3013, 1768, 1719, 1607, 1599,

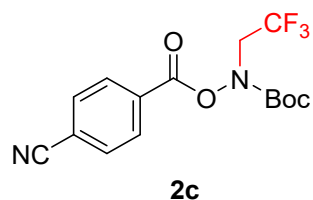
1451, 1266, 1143, 1013, 939, 708, 624 cm^{-1} ; **MS** (ESI): m/z 342.1 $[\text{M}+\text{Na}]^+$; **HRMS** (ESI-TOF): m/z Calculated for $\text{C}_{14}\text{H}_{16}\text{F}_3\text{NNaO}_4$ $[\text{M}+\text{Na}]^+$: 342.0924; Found: 342.0922.

***tert*-Butyl ((4-methoxybenzoyl)oxy)(2,2,2-trifluoroethyl)carbamate (2b)**



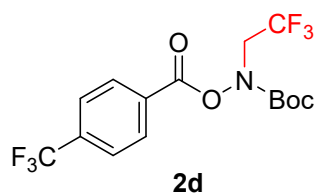
The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 50:1) to afford **2b** (2.41 g, 69%) as a white solid. Mp. 72-74 °C. **^1H NMR** (400 MHz, CDCl_3) δ 8.03 (d, J = 8.7 Hz, 2H), 6.96 (d, J = 8.7 Hz, 2H), 4.27 (s, 2H), 3.88 (s, 3H), 1.47 (s, 9H); **^{13}C NMR** (101 MHz, CDCl_3) δ 164.4, 164.0, 153.6, 132.2, 123.6 (q, J = 279.6 Hz), 118.9, 114.1, 83.8, 55.5, 51.3 (q, J = 32.8 Hz), 27.9; **^{19}F NMR** (377 MHz, CDCl_3) δ -70.88 (t, J = 8.5 Hz); **IR** (thin film) ν 3018, 1762, 1723, 1607, 1509, 1372, 1250, 1143, 1045, 1027, 852, 762, 584 cm^{-1} ; **MS** (ESI): m/z 372.1 $[\text{M}+\text{Na}]^+$; **HRMS** (ESI-TOF): m/z Calculated for $\text{C}_{15}\text{H}_{18}\text{F}_3\text{NNaO}_5$ $[\text{M}+\text{Na}]^+$: 372.1029; Found: 372.1025.

***tert*-Butyl ((4-cyanobenzoyl)oxy)(2,2,2-trifluoroethyl)carbamate (2c)**



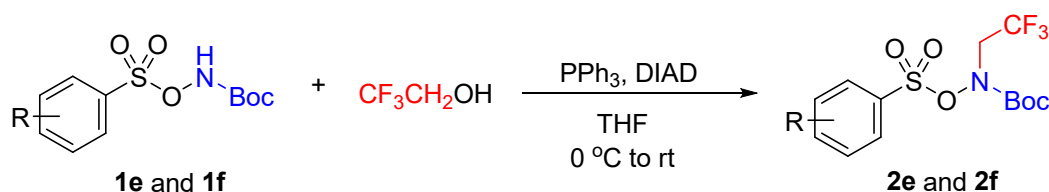
The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 100:1) to afford **2c** (2.79 g, 81%) as a white solid. Mp. 98-100 °C. **^1H NMR** (400 MHz, CDCl_3) δ 8.20 (d, J = 8.0 Hz, 2H), 7.82 (d, J = 8.1 Hz, 2H), 4.31 (q, J = 8.5 Hz, 2H), 1.50 (s, 9H); **^{13}C NMR** (101 MHz, CDCl_3) δ 162.8, 153.1, 132.5, 130.7, 130.4, 123.4 (q, J = 279.7 Hz), 117.7, 117.5, 84.6, 51.3 (q, J = 35.3 Hz), 27.9; **^{19}F NMR** (377 MHz, CDCl_3) δ -70.74 (t, J = 8.4 Hz); **IR** (thin film) ν 2946, 1771, 1727, 1370, 1355, 1299, 1271, 1137, 1064, 1042, 846, 755, 543 cm^{-1} ; **MS** (ESI): m/z 367.1 $[\text{M}+\text{Na}]^+$; **HRMS** (ESI-TOF): m/z Calculated for $\text{C}_{15}\text{H}_{15}\text{F}_3\text{N}_2\text{NaO}_4$ $[\text{M}+\text{Na}]^+$: 367.0876; Found: 367.0880.

***tert*-Butyl (2,2,2-trifluoroethyl)((4-(trifluoromethyl)benzoyl)oxy)carbamate (2d)**



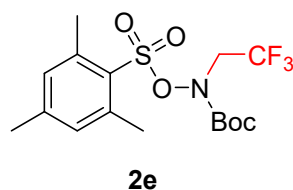
The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 100:1) to afford **2d** (3.06 g, 79%) as a white solid. Mp. 80-82 °C. **¹H NMR** (400 MHz, CDCl₃) δ 8.12 (d, *J* = 8.1 Hz, 2H), 7.70 (d, *J* = 8.2 Hz, 2H), 4.23 (q, *J* = 8.7 Hz, 2H), 1.41 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) δ 163.2, 153.2, 135.6 (q, *J* = 32.9 Hz), 130.4, 130.2, 125.8 (q, *J* = 3.7 Hz), 123.4 (q, *J* = 279.7 Hz), 123.3 (q, *J* = 272.9 Hz), 84.4, 51.2 (q, *J* = 35.1 Hz), 27.9; **¹⁹F NMR** (377 MHz, CDCl₃) δ -63.35 (s, 3F), -70.79 (t, *J* = 8.5 Hz, 3F); **IR** (thin film) ν 3013, 1772, 1733, 1376, 1354, 1269, 1141, 1069, 1016, 861, 591 cm⁻¹; **MS** (ESI): *m/z* 410.1 [M+Na]⁺; **HRMS** (ESI-TOF): *m/z* Calculated for C₁₅H₁₅F₆NNaO₄ [M+Na]⁺: 410.0797; Found: 410.0794.

General procedure for synthesis of **2e** and **2f**.



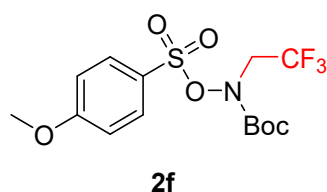
Under a nitrogen atmosphere, to a solution of PPh₃ (6 mmol, 1.2 equiv.) in anhydrous THF (2 M) was added drop wise diisopropyl azodicarboxylate (6 mmol, 1.2 equiv.) at 0 °C. The mixture was stirred at this temperature for 30 minutes, a solution of *tert*-butyl ((phenylsulfonyl)oxy)carbamate (6 mmol, 1.2 equiv.) and 2,2,2-trifluoroethanol (5 mmol, 1.0 equiv.) in anhydrous THF (10 mL) were added. The reaction mixture was stirred at 0 °C for 1 hour, after which it was stirred at room temperature and monitored by TLC. Upon completion, the reaction mixture was concentrated in vacuo and purification by column chromatography on silica gel eluting with a mixture of pentane and EtOAc gave **2e** and **2f**.

tert-Butyl ((mesitylsulfonyl)oxy)(2,2,2-trifluoroethyl)carbamate (**2e**)



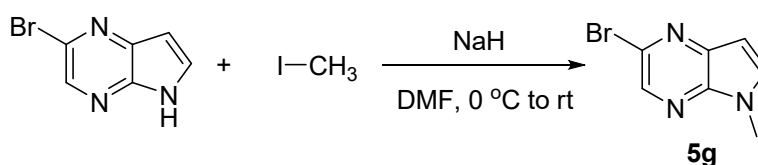
The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 50:1) to afford **2e** (1.11 g, 56%) as a white solid. Mp. 102-104 °C. **¹H NMR** (400 MHz, CDCl₃) δ 6.94 (s, 2H), 4.20 (s, 2H), 2.58 (s, 6H), 2.26 (s, 3H), 1.23 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) δ 153.6, 144.8, 142.0, 131.8, 128.7, 123.4 (q, *J* = 282.8 Hz), 84.8, 52.1 (q, *J* = 33.8 Hz), 27.5, 23.3, 21.1; **¹⁹F NMR** (377 MHz, CDCl₃) δ -68.02 (t, *J* = 8.2 Hz); **IR** (thin film) ν 2982, 1732, 1601, 1369, 1304, 1259, 1194, 1146, 1033, 855, 745, 670, 575 cm⁻¹; **MS** (ESI): *m/z* 420.1 [M+Na]⁺; **HRMS** (ESI-TOF): *m/z* Calculated for C₁₆H₂₂F₃NNaO₅S [M+Na]⁺: 420.1063; Found: 420.1054.

***tert*-Butyl (((4-methoxyphenyl)sulfonyl)oxy)(2,2,2-trifluoroethyl)carbamate (**2f**)**



The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 100:1) to afford **2f** (1.50 g, 78%) as a white solid. Mp. 82-84 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.84 (d, *J* = 9.0 Hz, 2H), 6.96 (d, *J* = 9.0 Hz, 2H), 4.22 (s, 2H), 3.83 (s, 3H), 1.20 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) δ 164.9, 153.5, 132.0, 124.6, 123.3 (q, *J* = 282.6 Hz), 114.4, 84.7, 55.9, 52.2 (q, *J* = 33.9 Hz), 27.5; **¹⁹F NMR** (376 MHz, CDCl₃) δ -67.89 (t, *J* = 8.0 Hz); **IR** (thin film) ν 2988, 1756, 1594, 1576, 1496, 1375, 1197, 1090, 855, 868, 769, 633 cm⁻¹; **MS** (ESI): *m/z* 408.1 [M+Na]⁺; **HRMS** (ESI-TOF): *m/z* Calculated for C₁₄H₁₈F₃NNaO₆S [M+Na]⁺: 408.0699; Found: 408.0692.

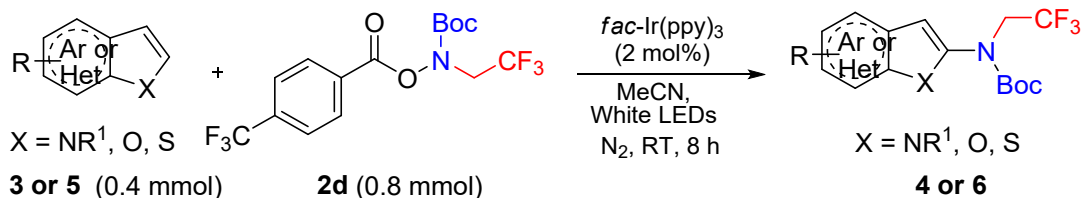
Preparation of 2-Bromo-5-methyl-5*H*-pyrrolo[2,3-*b*]pyrazine (5g**)**



To a solution of 2-bromo-5*H*-pyrrolo[2,3-*b*]pyrazine (8 mmol, 1.0 equiv.) in dry DMF (20 mL) was added portion wise NaH (12.8 mmol, 1.6 equiv., 60% dispersion in mineral oil) at 0 °C. The reaction mixture was stirred at 0 °C for 30 minutes and methyl iodide (9.6 mmol, 1.2 equiv.) was added drop wise at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for overnight. After completion of the reaction monitored by TLC, the reaction mixture was quenched by H₂O, extracted with CH₂Cl₂ (10 × 3 mL). The combined organic layers were washed with brine, dried over

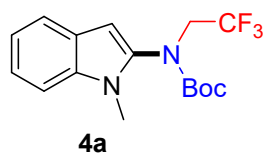
anhydrous Na₂SO₄, and concentrated under reduced pressure. The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 8:1) to afford **5g**. (0.911 g, 59%) as a yellow solid. Mp. 102-104 °C. **¹H NMR** (400 MHz, CDCl₃) δ 8.31 (s, 1H), 7.47 (d, *J* = 2.7 Hz, 1H), 6.63 (s, 1H), 3.90 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 139.8, 139.6, 138.1, 134.4, 133.0, 100.4, 31.7; IR (thin film) ν 2968, 1718, 1459, 1367, 1248, 1152, 1057, 923, 864, 760 cm⁻¹; MS (ESI): *m/z* 212.0 [M+H]⁺; **HRMS** (ESI-TOF): *m/z* Calculated for C₇H₇BrN₃ [M+H]⁺: 211.9818; Found: 211.9821.

3. General Procedures for C-H Trifluoroethylation of Heteroarenes



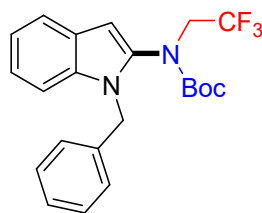
A 15 mL screw-cap vial was charged with a magnetic stir bar, *N*-trifluoroethylhydroxylamine **2d** (309.7 mg, 0.8 mmol, 2.0 equiv.), *fac*-Ir(ppy)₃ (5.2 mg, 0.008 mmol), and heteroarene **3** or **5** (0.4 mmol, 1 equiv., if it is a solid). The vial was evacuated and backfilled nitrogen three times. Then, MeCN (4 mL) was added via a syringe (If the heteroarene **3** or **5** is a liquid, it is dissolved in MeCN). The reaction mixture was irradiated by a 40 W white LED and stirred at room temperature for 8 h. The mixture was diluted with saturated NaHCO₃ aqueous solution and extracted by ethyl acetate. The combined organic phase was dried over anhydrous Na₂SO₄, filtered, and concentrated in vacuum to give a residue. The residue was purified by silica-gel column chromatography to give the desired product **4** or **6**.

tert-Butyl (1-methyl-1*H*-indol-2-yl)(2,2,2-trifluoroethyl)carbamate (**4a**)



The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 50:1) to afford **4a** (116.8 mg, 89%) as a light yellow solid. Mp. 64-66 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.51 (s, 1H), 7.23 – 7.21 (m, 1H), 7.19 – 7.15 (m, 1H), 7.04 (t, *J* = 7.4 Hz, 1H), 6.24 (s, 1H), 4.53 (s, 1H), 3.92 (s, 1H), 3.49 (s, 3H), 1.31 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 153.3, 135.9, 133.9, 125.2, 123.2 (q, *J* = 280.4 Hz), 121.0, 119.8, 118.8, 108.5, 94.9, 81.6, 50.9, 27.7, 27.0; ¹⁹F NMR (376 MHz, CDCl₃) δ -71.25 (t, *J* = 8.6 Hz); IR (thin film) ν 2976, 1712, 1557, 1471, 1372, 1265, 1146, 1018, 858, 748, 655 cm⁻¹; MS (ESI): *m/z* 351.1 [M+Na]⁺; HRMS (ESI-TOF): *m/z* Calculated for C₁₆H₁₉F₃N₂NaO₂ [M+Na]⁺: 351.1291; Found: 351.1290.

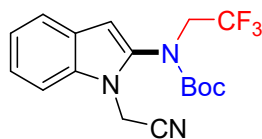
tert-Butyl (1-benzyl-1*H*-indol-2-yl)(2,2,2-trifluoroethyl)carbamate (**4b**)



4b

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 50:1) to afford **4b** (98.6 mg, 61%) as a yellow solid. Mp. 128-130 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.54 (d, *J* = 7.7 Hz, 1H), 7.23 – 7.17 (m, 3H), 7.11 – 7.08 (m, 2H), 7.07 – 7.03 (m, 1H), 7.00 (d, *J* = 6.7 Hz, 2H), 6.41 (s, 1H), 5.23 – 4.97 (m, 2H), 4.06 (s, 1H), 3.46 (s, 1H), 1.28 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) δ 153.2, 136.1, 135.0, 133.9, 127.7, 126.5, 125.6, 125.3, 123.1 (q, *J* = 280.7 Hz), 121.5, 120.1, 119.0, 109.3, 98.3, 81.7, 49.9, 45.2, 26.9; **¹⁹F NMR** (377 MHz, CDCl₃) δ -70.08 (t, *J* = 8.8 Hz); **IR** (thin film) ν 2982, 1706, 1558, 1456, 1360, 1271, 1155, 1057, 727, 697, 661 cm⁻¹; **MS** (ESI): *m/z* 427.2 [M+Na]⁺; **HRMS** (ESI-TOF): *m/z* Calculated for C₂₂H₂₃F₃N₂NaO₂ [M+Na]⁺: 427.1604; Found: 427.1599.

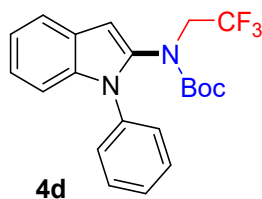
***tert*-Butyl (1-(cyanomethyl)-1*H*-indol-2-yl)(2,2,2-trifluoroethyl)carbamate (4c)**



4c

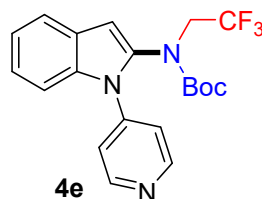
The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 10:1) to afford **4c** (125.7 mg, 89%) as a white solid. Mp. 99-101 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.51 (d, *J* = 7.9 Hz, 1H), 7.30 – 7.23 (m, 2H), 7.12 (t, *J* = 7.4 Hz, 1H), 6.32 (s, 1H), 4.70 (d, *J* = 5.4 Hz, 2H), 4.55 (s, 1H), 3.82 (s, 1H), 1.35 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) δ 154.0, 136.0, 134.0, 126.6, 123.7, 124.2 (q, *J* = 280.2 Hz), 121.6, 121.5, 114.3, 109.5, 98.8, 84.2, 52.1 (d, *J* = 35.3 Hz), 30.3, 27.9; **¹⁹F NMR** (377 MHz, CDCl₃) δ -70.97 (s); **IR** (thin film) ν 2971, 1718, 1584, 1566, 1462, 1364, 1152, 1054, 858, 757, 655 cm⁻¹; **MS** (ESI): *m/z* 376.1 [M+Na]⁺; **HRMS** (ESI-TOF): *m/z* Calculated for C₁₇H₁₈F₃N₃NaO₂ [M+Na]⁺: 376.1243; Found: 376.1241.

***tert*-Butyl (1-phenyl-1*H*-indol-2-yl)(2,2,2-trifluoroethyl)carbamate (4d)**



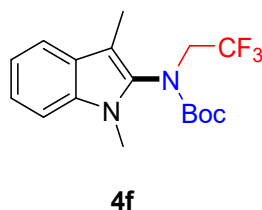
The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 50:1) to afford **4d** (117.0 mg, 75%) as a white solid. Mp. 116-118 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.56 (d, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.27 (d, *J* = 7.5 Hz, 2H), 7.13 – 7.07 (m, 3H), 6.51 (s, 1H), 4.03 (d, *J* = 246.8 Hz, 2H), 1.18 (s, 9H); **¹³C NMR** (151 MHz, CDCl₃) δ 154.1, 136.5, 135.6, 129.6, 128.0, 127.6, 127.1, 126.5, 124.1 (q, *J* = 281.2 Hz), 122.9, 121.1, 120.7, 110.6, 100.9, 82.5, 51.0, 27.9; **¹⁹F NMR** (377 MHz, CDCl₃) δ -69.85 (s, 2F), -70.41 (s, 1F); **IR** (thin film) ν 2985, 1714, 1498, 1455, 1392, 1141, 1011, 930, 736, 660 cm⁻¹; **MS** (ESI): *m/z* 413.1 [M+Na]⁺; **HRMS** (ESI-TOF): *m/z* Calculated for C₂₁H₂₁F₃N₂NaO₂ [M+Na]⁺: 413.1447; Found: 413.1450.

***tert*-Butyl (1-(pyridin-4-yl)-1*H*-indol-2-yl)(2,2,2-trifluoroethyl)carbamate (**4e**)**



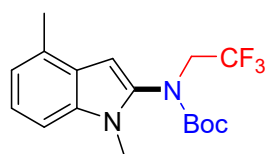
The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 15:1) to afford **4e** (109.5 mg, 70%) as a white solid. Mp. 115-117 °C. **¹H NMR** (400 MHz, CDCl₃) δ 8.80 (d, *J* = 5.2 Hz, 2H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.38 (s, 3H), 7.31-7.23 (m, 2H), 6.67 (s, 1H), 4.45 (s, 1H), 3.88 (s, 1H), 1.25 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) δ 157.0, 153.7, 151.3, 144.5, 135.6, 127.0, 123.9 (q, *J* = 279.8 Hz), 123.7, 121.6, 121.5, 120.7, 110.5, 102.2, 83.1, 51.7, 27.8; **¹⁹F NMR** (377 MHz, CDCl₃) δ -69.99 (s, 2F), -70.24 (s, 1F); **IR** (thin film) ν 2997, 1709, 1593, 1566, 1459, 1358, 1143, 929, 771, 587 cm⁻¹; **MS** (ESI): *m/z* 392.2 [M+H]⁺; **HRMS** (ESI-TOF): *m/z* Calculated for C₂₀H₂₁F₃N₃O₂ [M+H]⁺: 392.1580; Found: 392.1583.

***tert*-Butyl (1,3-dimethyl-1*H*-indol-2-yl)(2,2,2-trifluoroethyl)carbamate (**4f**)**



The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 100:1) to afford **4f** (98.6 mg, 72%) as a yellow oil. **¹H NMR** (400 MHz, CDCl₃) δ 7.45 (d, *J* = 7.8 Hz, 1H), 7.16 (d, *J* = 5.6 Hz, 2H), 7.03 (d, *J* = 6.3 Hz, 1H), 4.48 (s, 1H), 3.82-3.76 (m, 1H), 3.44 (s, 3H), 2.10 (s, 3H), 1.26 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) δ 154.9, 134.7, 133.2, 126.7, 124.4 (q, *J* = 280.3 Hz), 122.2, 119.2, 119.1, 109.3, 104.0, 82.3, 50.3 (d, *J* = 35.2 Hz), 28.7, 28.1, 8.1; **¹⁹F NMR** (376 MHz, CDCl₃) δ -71.10 (t, *J* = 9.1 Hz); **IR** (thin film) ν 2979, 1717, 1470, 1437, 1355, 1138, 1016, 932, 880, 772 cm⁻¹; **MS** (ESI): *m/z* 343.2 [M+H]⁺; **HRMS** (ESI-TOF): *m/z* Calculated for C₁₇H₂₂F₃N₂O₂ [M+H]⁺: 343.1628; Found: 343.1626.

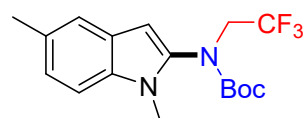
***tert*-Butyl (1,4-dimethyl-1*H*-indol-2-yl)(2,2,2-trifluoroethyl)carbamate (**4g**)**



4g

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 100:1) to afford **4g** (111.8 mg, 81%) as a light yellow solid. Mp. 92-94 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.18 (d, *J* = 6.3 Hz, 2H), 6.95 (d, *J* = 6.1 Hz, 1H), 6.35 (s, 1H), 4.65 (s, 1H), 4.04 (s, 1H), 3.59 (s, 3H), 2.55 (s, 3H), 1.43 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) δ 154.4, 136.5, 134.7, 130.4, 126.2, 124.2 (q, *J* = 280.5 Hz), 122.2, 120.1, 107.1, 94.6, 82.6, 52.3, 28.9, 28.1, 18.6; **¹⁹F NMR** (376 MHz, CDCl₃) δ -71.24 (t, *J* = 8.7 Hz); **IR** (thin film) ν 2983, 1706, 1569, 1471, 1358, 1263, 1144, 1016, 864, 774, 664 cm⁻¹; **MS** (ESI): *m/z* 343.2 [M+H]⁺; **HRMS** (ESI-TOF): *m/z* Calculated for C₁₇H₂₂F₃N₂O₂ [M+H]⁺: 343.1628; Found: 343.1628.

***tert*-Butyl (1,5-dimethyl-1*H*-indol-2-yl)(2,2,2-trifluoroethyl)carbamate (**4h**)**

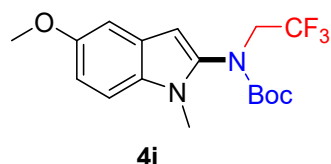


4h

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 50:1) to afford **4h** (97.2 mg, 71%) as a white solid. Mp. 114-116 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.41 (s, 1H), 7.24 (dd, *J* = 8.4, 2.6 Hz, 1H), 7.12 (d, *J* = 7.9 Hz, 1H), 6.27 (s, 1H), 4.64 (s, 1H), 4.03 (s, 1H), 3.59 (s, 3H), 2.48 (s, 3H), 1.43 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) δ 154.1, 136.9, 133.3, 129.1, 126.4, 124.2 (q, *J* = 280.9 Hz),

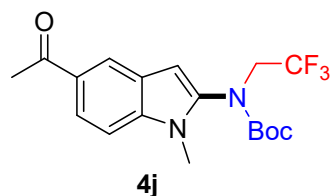
123.6, 120.5, 109.2, 95.4, 82.5, 51.9, 28.8, 28.1, 21.5; ^{19}F NMR (376MHz, CDCl_3) δ -71.27 (t, J = 8.6 Hz); **IR** (thin film) ν 2973, 1714, 1552, 1490, 1439, 1404, 1146, 1012, 800, 771, 655 cm^{-1} ; **MS** (ESI): m/z 343.2 $[\text{M}+\text{H}]^+$; **HRMS** (ESI-TOF): m/z Calculated for $\text{C}_{17}\text{H}_{22}\text{F}_3\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 343.1628; Found: 343.1628.

***tert*-Butyl (5-methoxy-1-methyl-1*H*-indol-2-yl)(2,2,2-trifluoroethyl)carbamate (4i)**



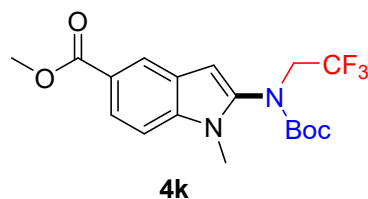
The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 50:1) to afford **4i** (101.7 mg, 71%) as a light yellow solid. Mp. 101-103 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.22 (d, J = 8.9 Hz, 1H), 7.07 (d, J = 2.4 Hz, 1H), 6.93 (dd, J = 8.9, 2.4 Hz, 1H), 6.27 (s, 1H), 4.62 (s, 1H), 4.03 (d, J = 13.7 Hz, 1H), 3.87 (s, 3H), 3.57 (s, 3H), 1.41 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 154.3, 153.4, 137.2, 130.2, 126.5, 124.2 (q, J = 280.3 Hz), 112.4, 110.3, 102.6, 95.6, 82.5, 55.9, 51.7, 28.8, 28.1; ^{19}F NMR (377 MHz, CDCl_3) δ -71.27 (t, J = 8.7 Hz); **IR** (thin film) ν 2928, 1704, 1558, 1488, 1464, 1455, 1148, 1077, 723, 577 cm^{-1} ; **MS** (ESI): m/z 359.2 $[\text{M}+\text{H}]^+$; **HRMS** (ESI-TOF): m/z Calculated for $\text{C}_{17}\text{H}_{22}\text{F}_3\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$: 359.1577; Found: 359.1576.

***tert*-Butyl (5-acetyl-1-methyl-1*H*-indol-2-yl)(2,2,2-trifluoroethyl)carbamate (4j)**



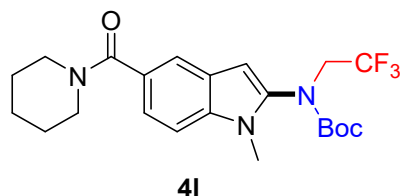
The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 20:1) to afford **4j** (87.3 mg, 59%) as a white solid. Mp. 121-123 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.18 (s, 1H), 7.86 (d, J = 8.7 Hz, 1H), 7.26 (d, J = 8.7 Hz, 1H), 6.38 (s, 1H), 4.57 (s, 1H), 3.93 (s, 1H), 3.54 (s, 3H), 2.59 (s, 3H), 1.32 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 198.1, 153.8, 138.4, 137.5, 130.0, 125.6, 124.1 (q, J = 280.3 Hz), 123.1, 122.4, 109.4, 97.9, 83.0, 52.0, 29.0, 28.0, 26.6; ^{19}F NMR (377 MHz, CDCl_3) δ -71.32 (t, J = 9.2 Hz); **IR** (thin film) ν 2994, 1723, 1667, 1560, 1366, 1298, 1143, 813, 667 cm^{-1} ; **MS** (ESI): m/z 371.2 $[\text{M}+\text{H}]^+$; **HRMS** (ESI-TOF): m/z Calculated for $\text{C}_{18}\text{H}_{22}\text{F}_3\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$: 371.1577; Found: 371.1577.

Methyl 2-((tert-Butoxycarbonyl)(2,2,2-trifluoroethyl)amino)-1-methyl-1H-indole-5-carboxylate (4k)



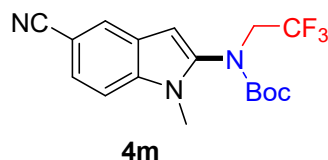
The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 30:1) to afford **4k** (123.5 mg, 80%) as a white solid. Mp. 138-140 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.26 (d, *J* = 1.5 Hz, 1H), 7.87 (dd, *J* = 8.7, 1.6 Hz, 1H), 7.22 (d, *J* = 8.7 Hz, 1H), 6.34 (s, 1H), 4.54 (s, 1H), 3.93 (s, 1H), 3.83 (s, 3H), 3.51 (s, 3H), 1.30 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 168.0, 153.9, 138.3, 137.4, 125.6, 124.1 (q, *J* = 279.6 Hz), 123.9, 123.5, 122.0, 109.2, 97.6, 82.9, 52.0, 51.9, 29.0, 28.0; ¹⁹F NMR (377 MHz, CDCl₃) δ -71.33 (d, *J* = 9.2 Hz); IR (thin film) ν 2994, 1732, 1706, 1566, 1435, 1313, 1143, 1012, 774, 664 cm⁻¹; MS (ESI): *m/z* 387.2 [M+H]⁺; HRMS (ESI-TOF): *m/z* Calculated for C₁₈H₂₂F₃N₂O₄ [M+H]⁺: 387.1526; Found: 387.1525.

tert-Butyl(1-methyl-5-(piperidine-1-carbonyl)-1H-indol-2-yl)(2,2,2-trifluoroethyl)carbamate (4l)



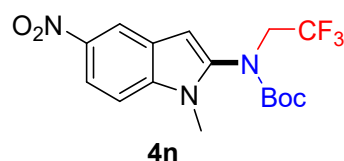
The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 20:1) to afford **4l** (145.0 mg, 82%) as a yellow solid. Mp. 159-161 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.57 (s, 1H), 7.23 (s, 2H), 6.28 (s, 1H), 4.56 (s, 1H), 3.92 (s, 1H), 3.51 (brs, 7H), 1.62 – 1.54 (m, 6H), 1.31 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 171.6, 154.0, 137.9, 135.4, 128.1, 125.7, 124.1 (q, *J* = 279.7 Hz), 121.4, 120.1, 109.4, 96.7, 82.8, 51.8, 31.6, 28.9, 28.0, 26.2, 24.7, 22.7, 14.1; ¹⁹F NMR (377 MHz, CDCl₃) δ -71.31 (t, *J* = 8.7 Hz); IR (thin film) ν 2920, 1712, 1614, 1557, 1464, 1452, 1147, 1006, 855, 763, 654 cm⁻¹; MS (ESI): *m/z* 440.2 [M+H]⁺; HRMS (ESI-TOF): *m/z* Calculated for C₂₂H₂₉F₃N₃O₃ [M+H]⁺: 440.2156; Found: 440.2156.

tert-Butyl (5-cyano-1-methyl-1H-indol-2-yl)(2,2,2-trifluoroethyl)carbamate (4m)



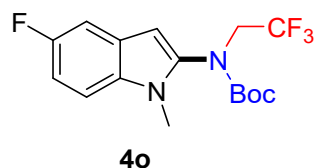
The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 50:1) to afford **4m** (113.0 mg, 80%) as a yellow oil. **¹H NMR** (400 MHz, CDCl₃) δ 7.81 (d, *J* = 1.5 Hz, 1H), 7.37 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.27 (d, *J* = 8.6 Hz, 1H), 6.35 (s, 1H), 4.55 (s, 1H), 3.93 (s, 1H), 3.53 (s, 3H), 1.31 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) δ 152.5, 138.2, 135.4, 125.3, 124.9, 124.0, 123.1 (q, *J* = 280.2 Hz), 119.5, 109.4, 102.0, 96.1, 82.3, 50.8, 28.0, 27.0; **¹⁹F NMR** (376 MHz, CDCl₃) δ -71.33 (t, *J* = 8.8 Hz); **IR** (thin film) ν 2979, 1720, 1615, 1560, 1484, 1434, 1144, 1096, 852, 700, 656 cm⁻¹; **MS** (ESI): *m/z* 354.1 [M+H]⁺; **HRMS** (ESI-TOF): *m/z* Calculated for C₁₇H₁₉F₃N₃O₂ [M+H]⁺: 354.1424; Found: 354.1425.

***tert*-Butyl (1-methyl-5-nitro-1*H*-indol-2-yl)(2,2,2-trifluoroethyl)carbamate (**4n**)**



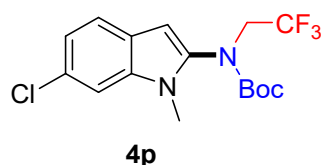
The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 20:1) to afford **4n** (87.0 mg, 58%) as a yellow solid. Mp. 120-122 °C. **¹H NMR** (400 MHz, CDCl₃) δ 8.45 (d, *J* = 2.1 Hz, 1H), 8.06 (dd, *J* = 9.1, 2.2 Hz, 1H), 7.26 (d, *J* = 9.1 Hz, 1H), 6.46 (s, 1H), 4.58 (s, 1H), 3.92 (s, 1H), 3.56 (s, 3H), 1.32 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) δ 153.4, 141.9, 139.9, 137.8, 125.2, 124.1 (q, *J* = 280.0 Hz), 118.1, 117.8, 109.6, 98.7, 83.2, 51.7, 29.3, 28.0; **¹⁹F NMR** (377 MHz, CDCl₃) δ -71.35; **IR** (thin film) ν 2979, 1728, 1562, 1515, 1480, 1434, 1140, 1067, 853, 748, 663 cm⁻¹; **MS** (ESI): *m/z* 374.1 [M+H]⁺; **HRMS** (ESI-TOF): *m/z* Calculated for C₁₆H₁₉F₃N₃O₄ [M+H]⁺: 374.1322; Found: 374.1321.

***tert*-Butyl (5-fluoro-1-methyl-1*H*-indol-2-yl)(2,2,2-trifluoroethyl)carbamate (**4o**)**



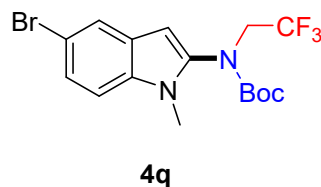
The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 100:1) to afford **4o** (112.1 mg, 81%) as a white solid. Mp. 86-88 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.20 – 7.08 (m, 2H), 6.91 (td, *J* = 9.2, 2.5 Hz, 1H), 6.20 (s, 1H), 4.54 (s, 1H), 3.90 (s, 1H), 3.48 (s, 3H), 1.31 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) δ 158.0 (d, *J* = 234.5 Hz), 154.2, 138.2, 131.5, 126.3 (q, *J* = 10.4 Hz), 124.2 (q, *J* = 280.2 Hz), 110.5 (d, *J* = 26.1 Hz), 110.2 (d, *J* = 9.5 Hz), 105.7 (d, *J* = 23.7 Hz), 96.1, 82.8, 52.0, 29.0, 28.0; **¹⁹F NMR** (377 MHz, CDCl₃) δ -71.31 (t, *J* = 8.7 Hz, 3F), -124.35 – -124.53 (m, 1F); **IR** (thin film) ν 2988, 1718, 1491, 1411, 1369, 1259, 1111, 1024, 959, 768, 658 cm⁻¹; **MS** (ESI): *m/z* 347.1 [M+H]⁺; **HRMS** (ESI-TOF): *m/z* Calculated for C₁₆H₁₉F₄N₂O₂ [M+H]⁺: 347.1377; Found: 347.1377.

***tert*-Butyl (6-chloro-1-methyl-1*H*-indol-2-yl)(2,2,2-trifluoroethyl)carbamate (**4p**)**



The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 50:1) to afford **4p** (125.6 mg, 86%) as a yellow oil. **¹H NMR** (400 MHz, CDCl₃) δ 7.37 (d, *J* = 8.4 Hz, 1H), 7.20 (d, *J* = 1.9 Hz, 1H), 6.98 (dd, *J* = 8.4, 1.9 Hz, 1H), 6.21 (s, 1H), 4.50 (s, 1H), 3.89 (s, 1H), 3.43 (s, 3H), 1.29 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) δ 152.8, 136.5, 134.3, 127.0, 123.7, 123.1 (q, *J* = 280.3 Hz), 120.8, 119.6, 108.5, 95.3, 81.8, 50.8, 27.8, 27.0; **¹⁹F NMR** (376 MHz, CDCl₃) δ -71.29 (t, *J* = 8.7 Hz); **IR** (thin film) ν 2982, 1720, 1552, 1473, 1426, 1394, 1144, 1117, 810, 769 cm⁻¹; **MS** (ESI): *m/z* 363.1 [M+H]⁺; **HRMS** (ESI-TOF): *m/z* Calculated for C₁₆H₁₉ClF₃N₂O₂ [M+H]⁺: 363.1082; Found: 363.1082.

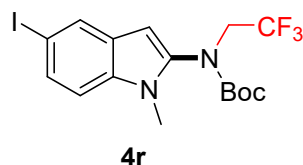
***tert*-Butyl (5-bromo-1-methyl-1*H*-indol-2-yl)(2,2,2-trifluoroethyl)carbamate (**4q**)**



The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 50:1) to afford **4q** (140.0 mg, 86%) as a yellow oil. **¹H NMR** (400 MHz, CDCl₃) δ 7.60 (d, *J* = 1.9 Hz, 1H), 7.22 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.07 (d, *J* = 8.7 Hz, 1H), 6.18 (s, 1H), 4.51 (s, 1H), 3.89 (s, 1H), 3.45 (s, 3H), 1.29 (s, 9H); **¹³C NMR** (101 MHz,

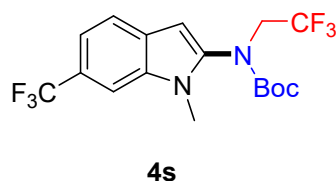
CDCl₃) δ 152.8, 136.9, 132.5, 126.8, 123.9, 123.1 (q, J = 280.4 Hz), 122.3, 112.1, 110.0, 94.7, 81.8, 50.7, 27.8, 27.0; **¹⁹F NMR** (376 MHz, CDCl₃) δ -71.28 (t, J = 8.8 Hz); **IR** (thin film) ν 2980, 1729, 1595, 1444, 1392, 1370, 1140, 1049, 900, 797, 671 cm⁻¹; **MS** (ESI): m/z 407.1 [M+H]⁺; **HRMS** (ESI-TOF): m/z Calculated for C₁₆H₁₉BrF₃N₂O₂ [M+H]⁺: 407.0577; Found: 407.0577.

***tert*-Butyl (5-iodo-1-methyl-1*H*-indol-2-yl)(2,2,2-trifluoroethyl)carbamate (4r)**



The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 50:1) to afford **4r** (125.3 mg, 69%) as a white solid. Mp. 103-105 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.84 (d, J = 1.5 Hz, 1H), 7.42 (d, J = 8.6 Hz, 1H), 7.01 (d, J = 8.6 Hz, 1H), 6.18 (s, 1H), 4.53 (s, 1H), 3.90 (s, 1H), 3.47 (d, J = 1.2 Hz, 3H), 1.32 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) δ 153.3, 137.5, 134.0, 130.4, 129.6, 128.6, 124.1 (q, J = 280.6 Hz), 111.5, 95.2, 83.3, 82.8, 51.7, 28.8, 28.0; **¹⁹F NMR** (376 MHz, CDCl₃) δ -71.31 – -71.33 (m); **IR** (thin film) ν 2977, 1703, 1569, 1471, 1403, 1355, 1141, 1010, 864, 774, 664 cm⁻¹; **MS** (ESI): m/z 455.0 [M+H]⁺; **HRMS** (ESI-TOF): m/z Calculated for C₁₆H₁₉F₃IN₂O₂ [M+H]⁺: 455.0438; Found: 455.0437.

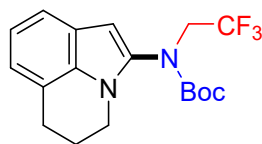
***tert*-Butyl(1-methyl-6-(trifluoromethyl)-1*H*-indol-2-yl)(2,2,2-trifluoroethyl)carbamate (4s)**



The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 50:1) to afford **4s** (115.3 mg, 73%) as a yellow oil. **¹H NMR** (400 MHz, CDCl₃) δ 7.55 (d, J = 8.3 Hz, 1H), 7.50 (s, 1H), 7.26 (dd, J = 8.4, 1.5 Hz, 1H), 6.30 (s, 1H), 4.55 (s, 1H), 3.90 (s, 1H), 3.53 (s, 3H), 1.31 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) δ 153.8, 139.4, 133.9, 128.6, 125.2 (q, J = 270.0 Hz), 124.2 (q, J = 31.7 Hz), 124.1 (q, J = 278.3 Hz), 121.3, 116.5, 107.1 (q, J = 3.9 Hz), 96.4, 83.1, 51.6, 28.9, 28.0; **¹⁹F NMR** (376 MHz, CDCl₃) δ -60.65 (s, 3F), -71.37 (t, J = 8.7 Hz, 3F); **IR** (thin film) ν 2982, 1721, 1552, 1473, 1431, 1342, 1146, 1054, 859, 771, 656 cm⁻¹; **MS** (ESI): m/z 397.1 [M+H]⁺;

HRMS (ESI-TOF): m/z Calculated for $C_{17}H_{19}F_6N_2O_2$ $[M+H]^+$: 397.1345; Found: 397.1343.

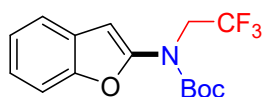
***tert*-Butyl (5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinolin-2-yl)(2,2,2-trifluoroethyl)carbamate (4t)**



4t

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 50:1) to afford **4t** (72.4 mg, 51%) as a white solid. Mp. 108-110 °C. **¹H NMR** (400 MHz, $CDCl_3$) δ 7.30 (d, J = 7.9 Hz, 1H), 6.93 (t, J = 7.5 Hz, 1H), 6.85 (d, J = 7.0 Hz, 1H), 6.14 (s, 1H), 4.57 (s, 1H), 3.85 (s, 3H), 2.89 (t, J = 5.9 Hz, 2H), 2.14 – 2.09 (m, 2H), 1.30 (s, 9H); **¹³C NMR** (101 MHz, $CDCl_3$) δ 154.3, 135.8, 132.3, 124.4, 124.3 (q, J = 280.6 Hz), 121.8, 119.9, 119.0, 118.1, 95.1, 82.6, 52.0, 41.4, 28.1, 24.9, 22.8; **¹⁹F NMR** (377 MHz, $CDCl_3$) δ -71.45 (t, J = 8.6 Hz); **IR** (thin film) ν 2943, 1709, 1552, 1401, 1367, 1258, 1139, 1025, 855, 775, 656 cm^{-1} ; **MS** (ESI): m/z 355.2 $[M+H]^+$; **HRMS** (ESI-TOF): m/z Calculated for $C_{18}H_{22}F_3N_2O_2$ $[M+H]^+$: 355.1628; Found: 355.1627.

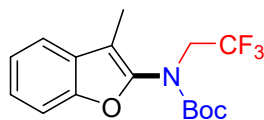
***tert*-Butyl benzofuran-2-yl(2,2,2-trifluoroethyl)carbamate (6a)**



6a

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 50:1) to afford **6a** (56.7 mg, 45%) as a yellow oil. **¹H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.41 (m, 1H), 7.34 – 7.31 (m, 1H), 7.20 – 7.12 (m, 2H), 6.47 (s, 1H), 4.31 (q, J = 8.5 Hz, 2H), 1.43 (s, 9H); **¹³C NMR** (101 MHz, $CDCl_3$) δ 150.2, 148.2, 127.5, 122.9 (q, J = 280.6 Hz), 122.9, 122.1, 119.8, 109.8, 103.3, 96.7, 82.4, 47.3 (q, J = 34.8 Hz), 27.0; **¹⁹F NMR** (376 MHz, $CDCl_3$) δ -70.90 (t, J = 8.6 Hz); **IR** (thin film) ν 2980, 1727, 1596, 1455, 1393, 1370, 1141, 1103, 886, 745, 657 cm^{-1} ; **MS** (ESI): m/z 338.1 $[M+Na]^+$; **HRMS** (ESI-TOF): m/z Calculated for $C_{15}H_{16}F_3NNaO_3$ $[M+Na]^+$: 338.0975; Found: 338.0979.

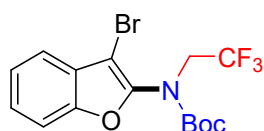
***tert*-Butyl (3-methylbenzofuran-2-yl)(2,2,2-trifluoroethyl)carbamate (6b)**



6b

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 50:1) to afford **6b** (107.9 mg, 82%) as a white solid. Mp. 60-62 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.40 (d, *J* = 7.4 Hz, 1H), 7.29 (d, *J* = 8.1 Hz, 1H), 7.23 – 7.13 (m, 2H), 4.17 (q, *J* = 8.6 Hz, 2H), 2.04 (s, 3H), 1.33 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) δ 152.3, 150.5, 143.7, 128.4, 123.6, 123.1 (q, *J* = 280.4 Hz), 121.5, 118.6, 110.0, 108.4, 81.7, 47.3, 26.9, 6.5; **¹⁹F NMR** (376 MHz, CDCl₃) δ -71.30 (t, *J* = 8.8 Hz); **IR** (thin film) ν 2985, 1728, 1658, 1455, 1392, 1370, 1129, 1105, 858, 745, 655 cm⁻¹; **MS** (ESI): *m/z* 352.1 [M+Na]⁺; **HRMS** (ESI-TOF): *m/z* Calculated for C₁₆H₁₈F₃NNaO₃ [M+Na]⁺: 352.1131; Found: 352.1130.

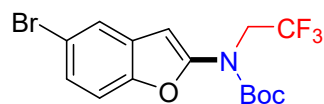
***tert*-Butyl (3-bromobenzofuran-2-yl)(2,2,2-trifluoroethyl)carbamate (6c)**



6c

The product mixture was purified by silica gel column chromatography (hexane/EtOAc =50:1) to afford **6c** (103.3 mg, 66%) as a yellow oil. **¹H NMR** (400 MHz, CDCl₃) δ 7.43 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.31 – 7.26 (m, 1H), 7.23 (t, *J* = 7.5 Hz, 1H), 4.19 (q, *J* = 8.6 Hz, 2H), 1.35 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) δ 152.5, 151.2, 146.2, 127.6, 126.0, 123.8 (d, *J* = 280.1 Hz), 123.6, 112.0, 111.6, 93.1, 83.5, 48.3, 27.9; **¹⁹F NMR** (376 MHz, CDCl₃) δ -71.29 (t, *J* = 8.6 Hz); **IR** (thin film) ν 2981, 1731, 1624, 1450, 1370, 1320, 1130, 1104, 995, 744, 658 cm⁻¹; **MS** (ESI): *m/z* 416.0 [M+Na]⁺; **HRMS** (ESI-TOF): *m/z* Calculated for C₁₅H₁₅BrF₃NNaO₃ [M+Na]⁺: 416.0080; Found: 416.0081.

***tert*-Butyl (5-bromobenzofuran-2-yl)(2,2,2-trifluoroethyl)carbamate (6d)**

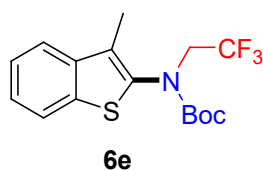


6d

The product mixture was purified by silica gel column chromatography (hexane/EtOAc =50:1) to afford **6d** (117.9 mg, 75%) as a yellow oil. **¹H NMR** (400 MHz, CDCl₃) δ

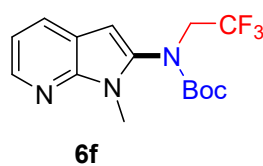
7.55 (s, 1H), 7.27 (d, $J = 8.7$ Hz, 1H), 7.19 (d, $J = 7.2$ Hz, 1H), 6.44 (s, 1H), 4.33 (q, $J = 8.4$ Hz, 2H), 1.44 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 151.9, 150.3, 149.8, 130.6, 126.7, 123.8 (q, $J = 280.7$ Hz), 123.3, 116.2, 112.3, 96.3, 83.8, 45.0 (q, $J = 35.0$ Hz), 28.0; ^{19}F NMR (377 MHz, CDCl_3) δ -70.92 (t, $J = 8.4$ Hz); IR (thin film) ν 2980, 1729, 1595, 1444, 1392, 1370, 1140, 1002, 900, 797, 671 cm^{-1} ; MS (ESI): m/z 416.0 [M+Na] $^{+}$; HRMS (ESI-TOF): m/z Calculated for $\text{C}_{15}\text{H}_{15}\text{BrF}_3\text{NNaO}_3$ [M+Na] $^{+}$: 416.0080; Found: 416.0076

***tert*-Butyl (3-methylbenzo[b]thiophen-2-yl)(2,2,2-trifluoroethyl)carbamate (6e)**



The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 100:1) to afford **6e** (70.4 mg, 51%) as a yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.65 (d, $J = 7.1$ Hz, 1H), 7.58 (d, $J = 7.6$ Hz, 1H), 7.32 – 7.25 (m, 2H), 4.17 (s, 2H), 2.16 (s, 3H), 1.32 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 154.1, 147.1, 138.4, 137.3, 137.0, 125.2, 124.3, 124.2 (q, $J = 280.8$ Hz), 122.5, 122.4, 82.4, 50.7, 28.0, 11.1; ^{19}F NMR (377 MHz, CDCl_3) δ -70.57 (t, $J = 8.7$ Hz); IR (thin film) ν 2979, 1716, 1437, 1368, 1305, 1138, 1021, 859, 753, 583 cm^{-1} ; MS (ESI): m/z 368.1 [M+Na] $^{+}$; HRMS (ESI-TOF): m/z Calculated for $\text{C}_{16}\text{H}_{18}\text{F}_3\text{NNaO}_2\text{S}$ [M+Na] $^{+}$: 368.0903; Found: 368.0905.

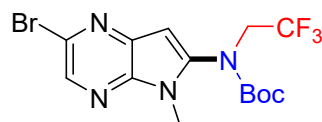
***tert*-Butyl (1-methyl-1*H*-pyrrolo[2,3-*b*]pyridin-2-yl)(2,2,2-trifluoroethyl)carbamate (6f)**



The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 30:1) to afford **6f** (94.0 mg, 70%) as a yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 8.27 (d, $J = 4.7$ Hz, 1H), 7.78 (d, $J = 7.8$ Hz, 1H), 7.01 – 6.98 (m, 1H), 6.21 (s, 1H), 4.49 (s, 1H), 3.97 (s, 1H), 3.62 (s, 3H), 1.31 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 153.8, 146.0, 143.4, 137.6, 128.8, 124.1 (q, $J = 280.4$ Hz), 119.2, 116.3, 94.5, 83.0, 51.7, 28.0, 27.5; ^{19}F NMR (377 MHz, CDCl_3) δ -71.29 (t, $J = 8.6$ Hz); IR (thin film) ν 2979, 1720, 1598, 1551, 1488, 1463, 1144, 1115, 908, 727, 535 cm^{-1} ; MS (ESI): m/z 330.1 [M+H] $^{+}$;

HRMS (ESI-TOF): m/z Calculated for $C_{15}H_{19}F_3N_3O_2$ $[M+H]^+$: 330.1424; Found: 330.1427.

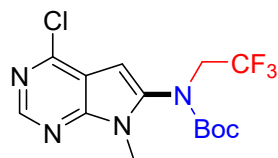
***tert*-Butyl (2-bromo-5-methyl-5*H*-pyrrolo[2,3-*b*]pyrazin-6-yl)(2,2,2-trifluoroethyl)carbamate (6g)**



6g

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 40:1) to afford **6g** (81.6 mg, 50%) as a white solid. Mp. 162-164 °C. **¹H NMR** (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 6.48 (s, 1H), 4.30 (s, 2H), 3.71 (s, 3H), 1.46 (s, 9H); **¹³C NMR** (101 MHz, $CDCl_3$) δ 152.8, 142.7, 139.1, 138.3, 133.6, 123.9 (q, J = 280.3 Hz), 95.3, 83.9, 51.6, 28.0, 27.7; **¹⁹F NMR** (376 MHz, $CDCl_3$) δ -71.49 (s); **IR** (thin film) ν 2970, 1728, 1537, 1419, 1409, 1394, 1135, 1009, 931, 867, 762 cm^{-1} ; **MS** (ESI): m/z 431.0 $[M+Na]^+$; **HRMS** (ESI-TOF): m/z Calculated for $C_{14}H_{16}BrF_3N_4NaO_2$ $[M+Na]^+$: 431.0301; Found: 431.0292.

***tert*-Butyl (4-chloro-7-methyl-4*a*,7*a*-dihydro-7*H*-pyrrolo[2,3-*d*]pyrimidin-6-yl)(2,2,2-trifluoroethyl)carbamate (6h)**

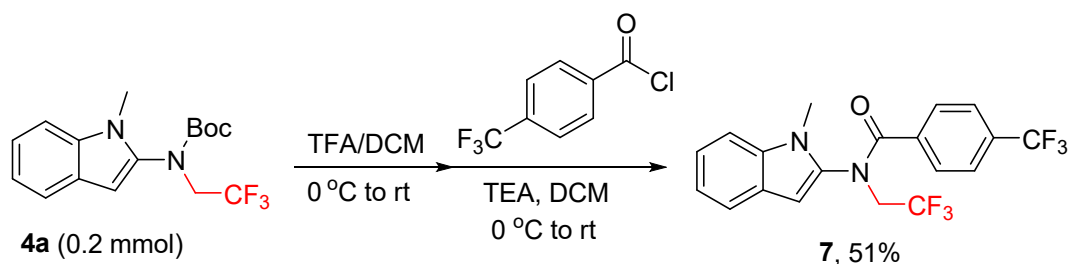


6h

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 20:1) to afford **6h** (69.9 mg, 48%) as a white solid. Mp. 107-109 °C. **¹H NMR** (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 6.38 (s, 1H), 4.03 (s, 2H), 3.62 (s, 3H), 1.38 (s, 9H); **¹³C NMR** (101 MHz, $CDCl_3$) δ 153.0, 151.9, 151.2, 149.7, 139.0, 123.9 (q, J = 280.1 Hz), 116.3, 94.2, 83.9, 51.8, 28.1, 28.0; **¹⁹F NMR** (376 MHz, $CDCl_3$) δ -71.47 (s); **IR** (thin film) ν 2973, 1724, 1595, 1538, 1487, 1150, 1110, 1012, 863, 784, 564 cm^{-1} ; **MS** (ESI): m/z 365.1 $[M+H]^+$; **HRMS** (ESI-TOF): m/z Calculated for $C_{14}H_{17}ClF_3N_4O_2$ $[M+H]^+$: 365.0987; Found: 365.0989.

4. Transformation of Trifluoroethylaminated Product

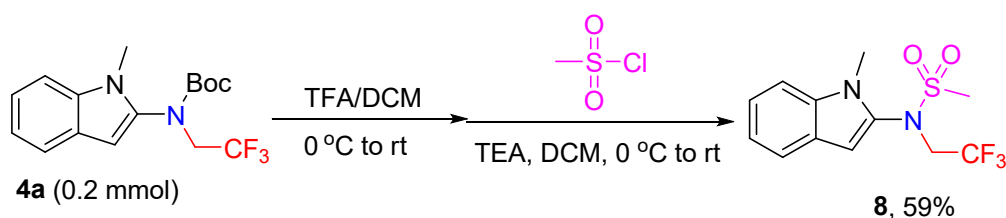
N-(1-methyl-1*H*-indol-2-yl)-*N*-(2,2,2-trifluoroethyl)-4-(trifluoromethyl)benzamide (**7**)



To a solution of **4a** (65.0 mg, 0.2 mmol) in DCM (2 mL) was added TFA (0.4 mL). The reaction mixture was stirred at room temperature for 4 h, the reaction mixture was concentrated to a residue in vacuo. To the intermediate solution in dichloromethane (2 mL) at 0 °C was added triethylamine (101.0 mg, 1.0 mmol) followed by a slow addition of methanesulfonyl chloride (23.0 mg, 0.2 mmol) under nitrogen atmosphere in a round bottomed flask. The reaction mixture was stirred at room temperature. Until completion of the reaction monitored by TLC, the reaction mixture was quenched with water, extracted with dichloromethane. Combined organic layers were dried over MgSO_4 , filtered and evaporated under reduced pressure to afford the crude product, which was further purified by flash chromatography on silica gel with *n*-hexane/EtOAc (15:1) to

give the desired product **7** as a yellow solid (40.8 mg, 51%). Mp. 138-140 °C. **¹H NMR** (400 MHz, CDCl₃) δ 8.78 (s, 1H), 7.71 – 7.65 (m, 4H), 7.14 (d, *J* = 7.9 Hz, 1H), 7.10 – 7.05 (m, 1H), 6.93 – 6.89 (m, 1H), 6.65 (d, *J* = 7.9 Hz, 1H), 3.93 (q, *J* = 8.4 Hz, 2H), 3.68 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 190.0, 154.8, 144.5, 135.3, 132.3 (q, *J* = 32.5 Hz), 128.3, 125.4 (q, *J* = 3.8 Hz), 125.1, 124.1 (q, *J* = 279.8 Hz), 123.9 (q, *J* = 272.4 Hz), 122.3, 122.0, 119.2, 109.0, 101.1, 47.8 (q, *J* = 33.7 Hz), 31.1; **¹⁹F NMR** (376 MHz, CDCl₃) δ -62.68 (s, 3F), -72.43 (t, *J* = 8.6 Hz, 3F); **IR** (thin film) ν 2979, 1587, 1560, 1254, 1154, 1095, 1066, 840, 780, 557 cm⁻¹; **MS** (ESI): *m/z* 401.1 [M+H]⁺; **HRMS** (ESI-TOF): *m/z* Calculated for C₁₉H₁₅F₆N₂O [M+H]⁺: 401.1083; Found: 401.1087.

***N*-(1-methyl-1*H*-indol-2-yl)-*N*-(2,2,2-trifluoroethyl)methanesulfonamide (**8**)**



To a solution of **4a** (65.0 mg, 0.2 mmol) in DCM (2 mL) was added TFA (0.4 mL). The reaction mixture was stirred at room temperature for 4 h, the reaction mixture was concentrated to a residue in vacuo. To the intermediate solution in dichloromethane (2 mL) at 0 °C was added triethylamine (101.0 mg, 1.0 mmol) followed by a slow addition of methanesulfonyl chloride (23.0 mg, 0.2 mmol) under nitrogen atmosphere in a round bottomed flask. The reaction mixture was stirred at room temperature. Until completion of the reaction monitored by TLC, the reaction mixture was quenched with water, extracted with dichloromethane. Combined organic layers were dried over MgSO₄, filtered and evaporated under reduced pressure to afford the crude product, which was further purified by flash chromatography on silica gel with *n*-hexane/EtOAc (2:1) to give the desired product **8** as a white solid (36.1 mg, 59%). Mp. 135-137 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.78 – 7.74 (m, 1H), 7.28 – 7.26 (m, 3H), 6.12 (t, *J* = 7.8 Hz, 1H), 3.83 – 3.74 (m, 2H), 3.69 (s, 3H), 3.12 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 147.4, 134.5, 124.3 (q, *J* = 280.5 Hz), 124.0, 122.8, 122.6, 118.2, 109.5, 98.1, 49.2 (q, *J* = 32.8 Hz), 45.2, 30.6; **¹⁹F NMR** (377 MHz, CDCl₃) δ -72.13 (t, *J* = 8.8 Hz); **IR** (thin film) ν 3342, 1614, 1267, 1538, 1146, 1126, 1019, 955, 619, 544, 459 cm⁻¹; **MS** (ESI): *m/z* 307.1 [M+H]⁺; **HRMS** (ESI-TOF): *m/z* Calculated for C₁₂H₁₄F₃N₂O₂S [M+H]⁺: 307.0723; Found: 307.0722.

5. Stern-Volmer Experiments

Stern-Volmer quenching experiments were carried by Edinburgh Fluorescence Spectrometer FS5, using a 10 μ M solution of photocatalyst *fac*-Ir(ppy)₃ and variable concentrations (0.5, 1.0, 1.5, 2.0, 2.5 mM) of **2d**, *N*-methyl indole (**3a**) in MeCN. The samples were prepared in 4 mL quartz cuvettes, equipped with PTFE stoppers, and sealed with parafilm inside nitrogen filled glove-box. The intensity of the emission peak at 532 nm (λ_{ex} = 375 nm) expressed as the ratio I_0/I , where I_0 is the emission intensity of photocatalyst at 532 nm in the absence of a quencher and I is the observed intensity, as a function of the quencher concentration was measured. Stern-Volmer plots for each component are given in the Supplementary Figures below.

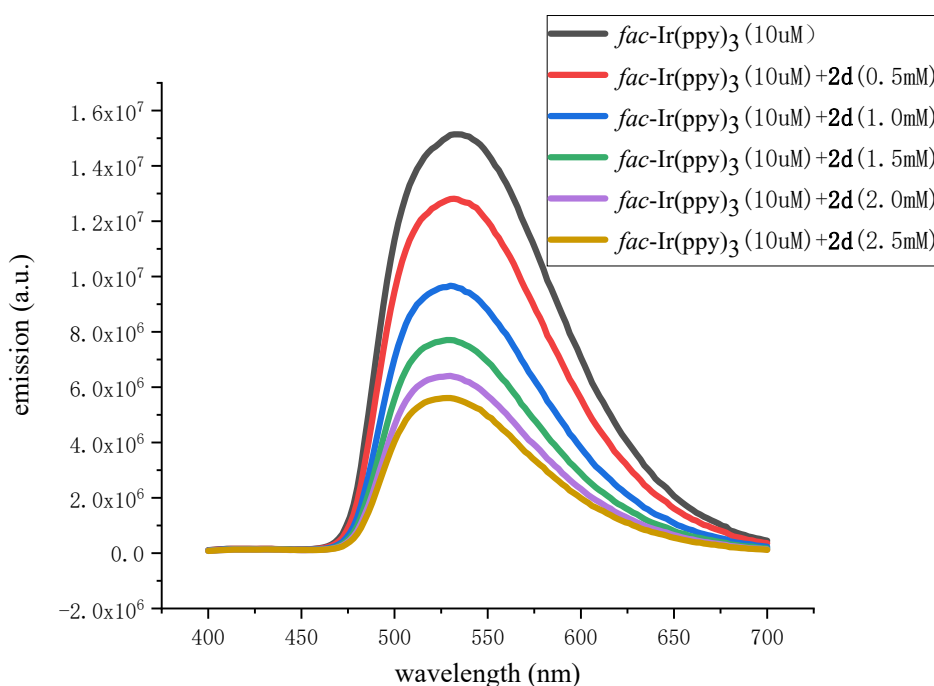


Fig. S1 Emission profile of *fac*-Ir(ppy)₃ with **2d** in CH₃CN

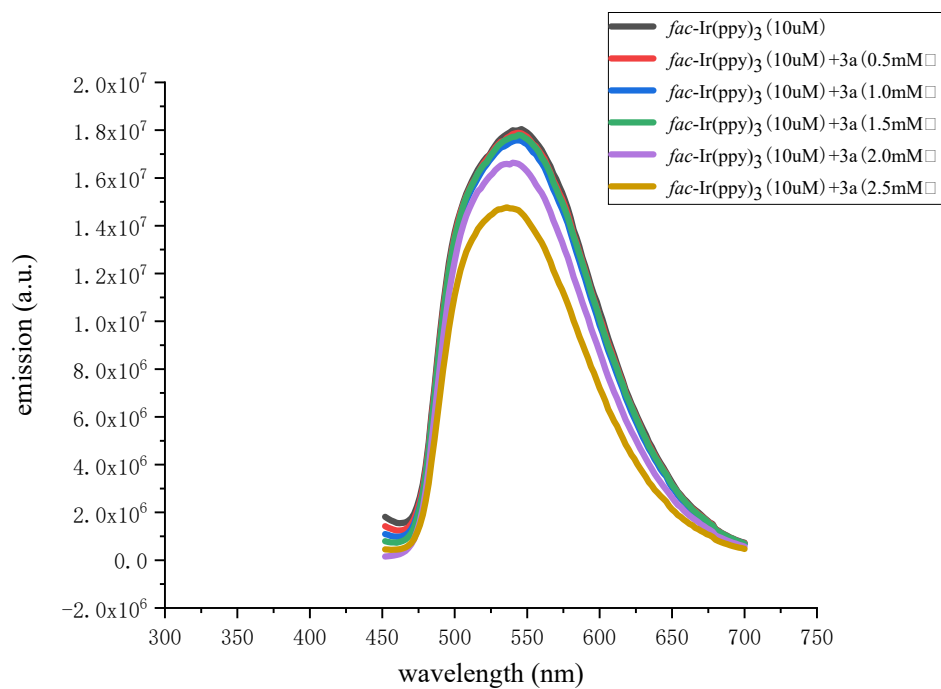


Fig. S2 Emission profile of *fac*-Ir(ppy)₃ with *N*-methyl indole (**3a**) in CH₃CN

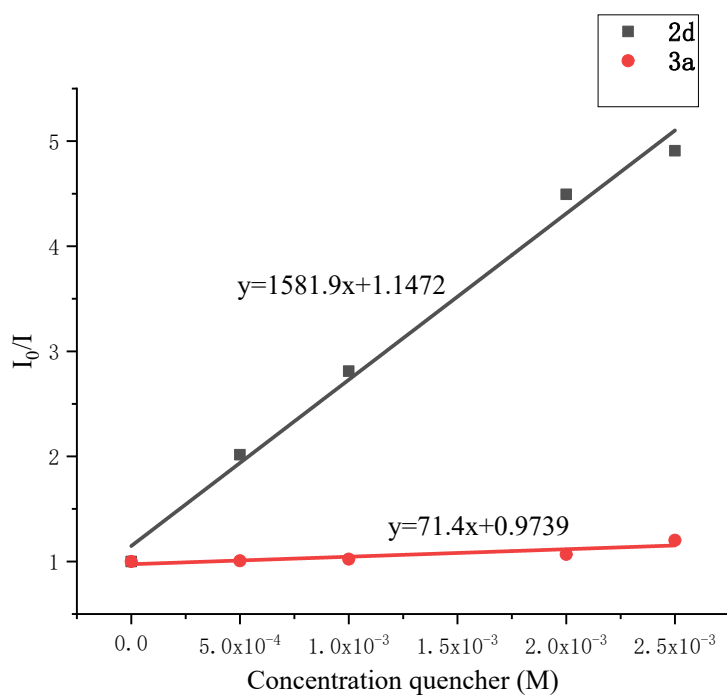
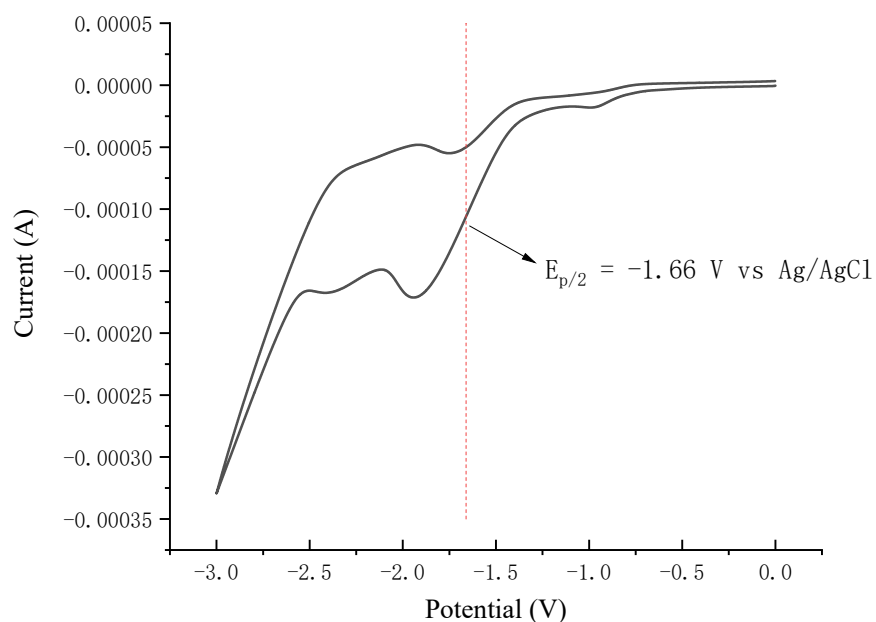


Fig. S3 Stern-Volmer plots. I_0 and I are respective luminescence intensities in the absence and presence of the indicated concentrations of the corresponding quencher.

6. Cyclic Voltammetry Analysis

Electrochemical measurements were performed on a CHI730E electrochemical analyzer, using a standard three-electrode setup with a glassy carbon working electrode (2 mm diameter), a platinum wire counter electrode, and a non-aqueous Ag/Ag⁺ reference electrode (degassed THF containing 0.1 M ⁿBu₄NPF₆). Samples were prepared with 0.01 mmol of substrate in 10 mL of 0.1 M ⁿBu₄NPF₆ in dry, degassed THF, with a scan rate of 0.05 V/s. Solutions were kept under positive pressure of nitrogen during the measurements. Data was analyzed using Origin. The obtained value was referenced to Ag/Ag⁺ and converted to SCE by subtracting 0.03 V.¹¹

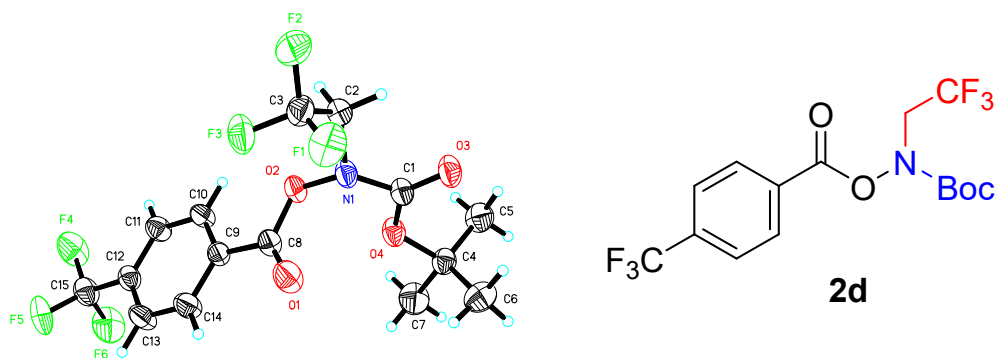


$$E_{p/2} = -1.69 \text{ V vs (SCE)}$$

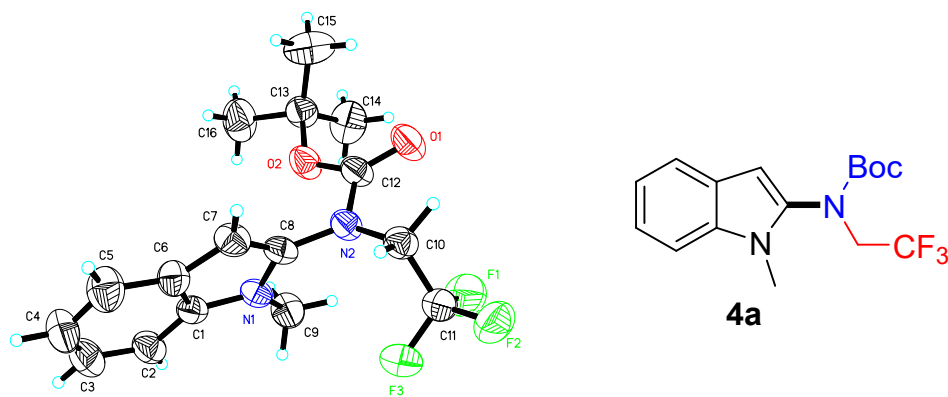
Figure S4 Cyclic voltammetry of **2d** in THF from 0 V to -3.0 V.

7. ORTEP Drawing of the X-Ray Crystallographic Structure of Compounds 2d and 4a

The crystals were obtained from a solution of hexane upon slow volatilization. The X-ray intensity data were measured at 293(2) K, on a Rigaku AFC7R diffractometer.



The crystal structure has been deposited at the Cambridge Crystallographic Data Center and allocated the deposition number CCDC 2123735. The thermal ellipsoids are shown at the 30% probability level. This data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif



The crystal structure has been deposited at the Cambridge Crystallographic Data Center and allocated the deposition number CCDC 2123736. The thermal ellipsoids are shown at the 30% probability level. This data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif

Talbe S1. Crystal data and structure refinement for 2d

Identification code	2d	
Empirical formula	C15 H15 F6 N O4	
Formula weight	387.28	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 16.8153(11) Å	a = 90°.
	b = 8.7366(5) Å	b = 102.655(2)°.
	c = 12.2243(7) Å	g = 90°.
Volume	1752.23(18) Å ³	
Z	4	
Density (calculated)	1.468 Mg/m ³	
Absorption coefficient	0.146 mm ⁻¹	
F(000)	792	
Crystal size	0.200 x 0.150 x 0.100 mm ³	
Theta range for data collection	2.483 to 26.000°.	
Index ranges	-20<=h<=16, -10<=k<=10, -15<=l<=15	
Reflections collected	19678	
Independent reflections	3424 [R(int) = 0.0307]	
Completeness to theta = 25.242°	99.2 %	
Absorption correction	Semi-empirical from equiv.alents	
Max. and min. transmission	0.7456 and 0.6622	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3424 / 36 / 266	
Goodness-of-fit on F ²	1.032	
Final R indices [I>2sigma(I)]	R1 = 0.0430, wR2 = 0.1058	
R indices (all data)	R1 = 0.0584, wR2 = 0.1192	
Extinction coefficient	0.026(5)	
Largest diff. peak and hole	0.335 and -0.154 e.Å ⁻³	

Talbe S2. Crystal data and structure refinement for 4a

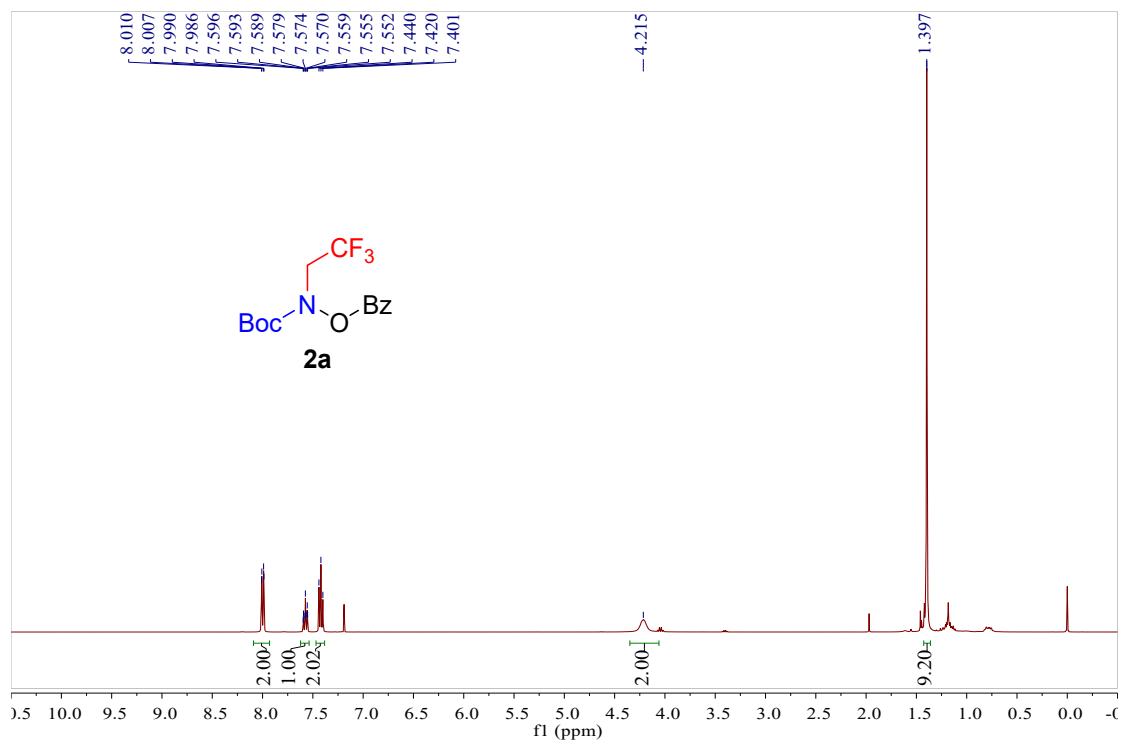
Identification code	4a	
Empirical formula	C ₁₆ H ₁₉ F ₃ N ₂ O ₂	
Formula weight	328.33	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2 ₁ /c	
Unit cell dimensions	a = 10.5525(15) Å	a = 90°.
	b = 38.111(5) Å	b = 105.355(4)°.
	c = 9.0256(12) Å	g = 90°.
Volume	3500.2(8) Å ³	
Z	8	
Density (calculated)	1.246 Mg/m ³	
Absorption coefficient	0.104 mm ⁻¹	
F(000)	1376	
Crystal size	0.150 x 0.120 x 0.080 mm ³	
Theta range for data collection	2.269 to 24.998°.	
Index ranges	-12 ≤ h ≤ 12, -45 ≤ k ≤ 45, -10 ≤ l ≤ 10	
Reflections collected	51834	
Independent reflections	6155 [R(int) = 0.0781]	
Completeness to theta = 25.242°	97.1 %	
Absorption correction	Semi-empirical from equiv.alents	
Max. and min. transmission	0.7456 and 0.5390	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6155 / 1 / 424	
Goodness-of-fit on F ²	1.414	
Final R indices [I > 2sigma(I)]	R1 = 0.1180, wR2 = 0.3480	
R indices (all data)	R1 = 0.1664, wR2 = 0.3998	
Extinction coefficient	0.019(6)	
Largest diff. peak and hole	1.041 and -0.434 e.Å ⁻³	

8. References

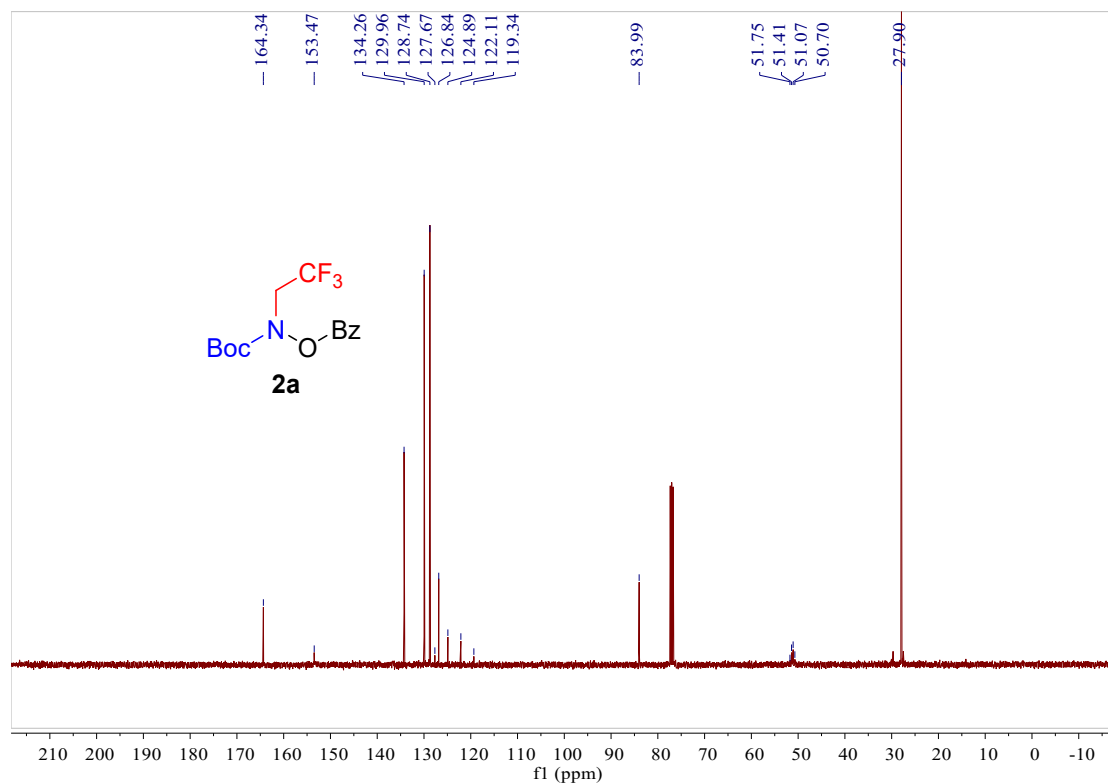
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9. Copies of NMR Spectra for the Products

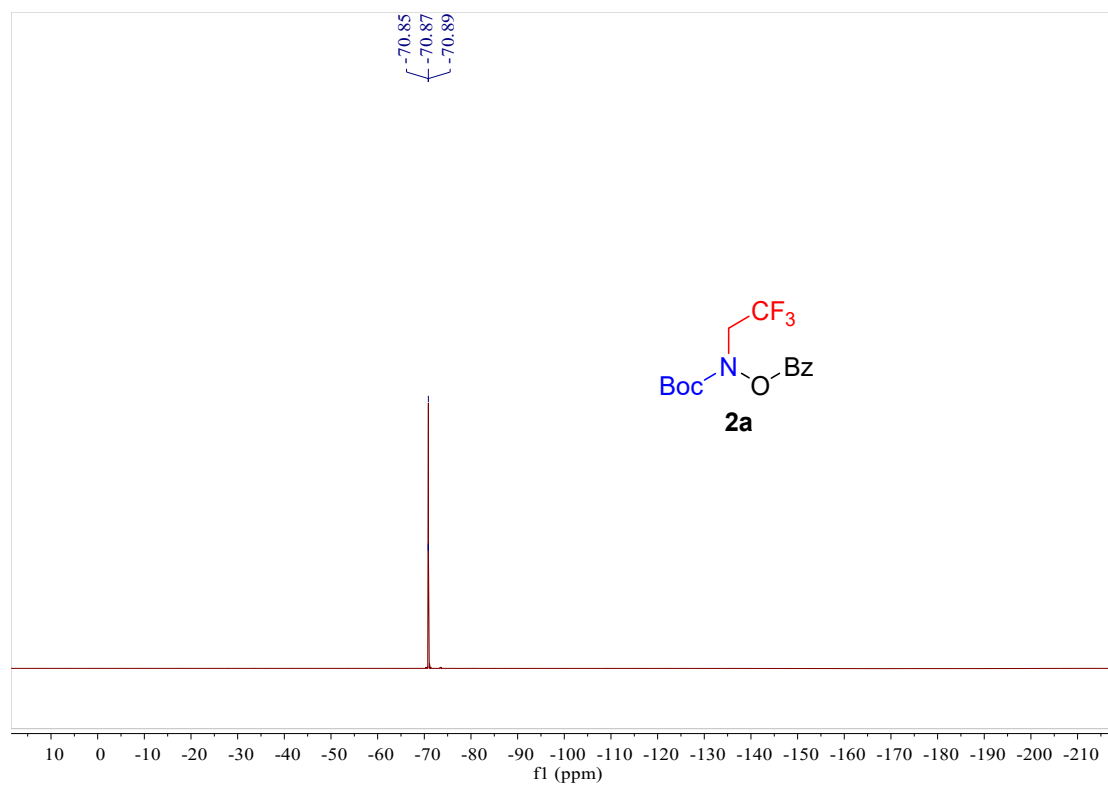
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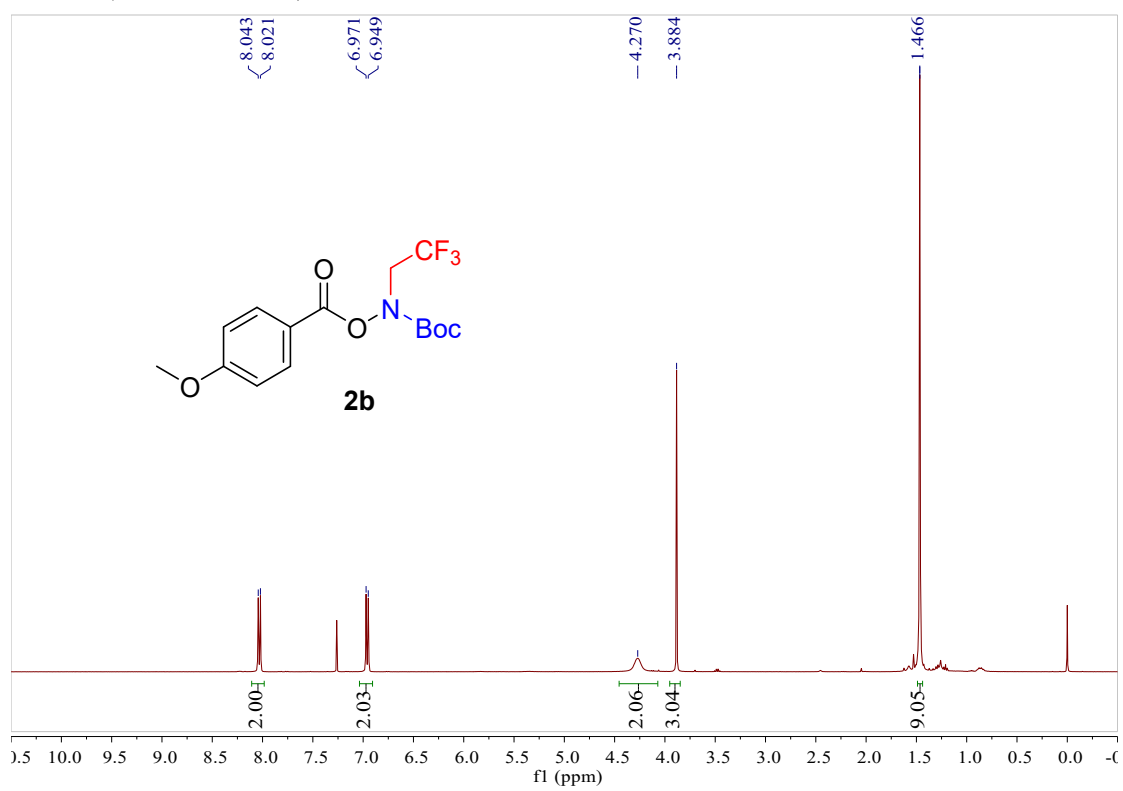
^{13}C NMR (101 MHz, CDCl_3)



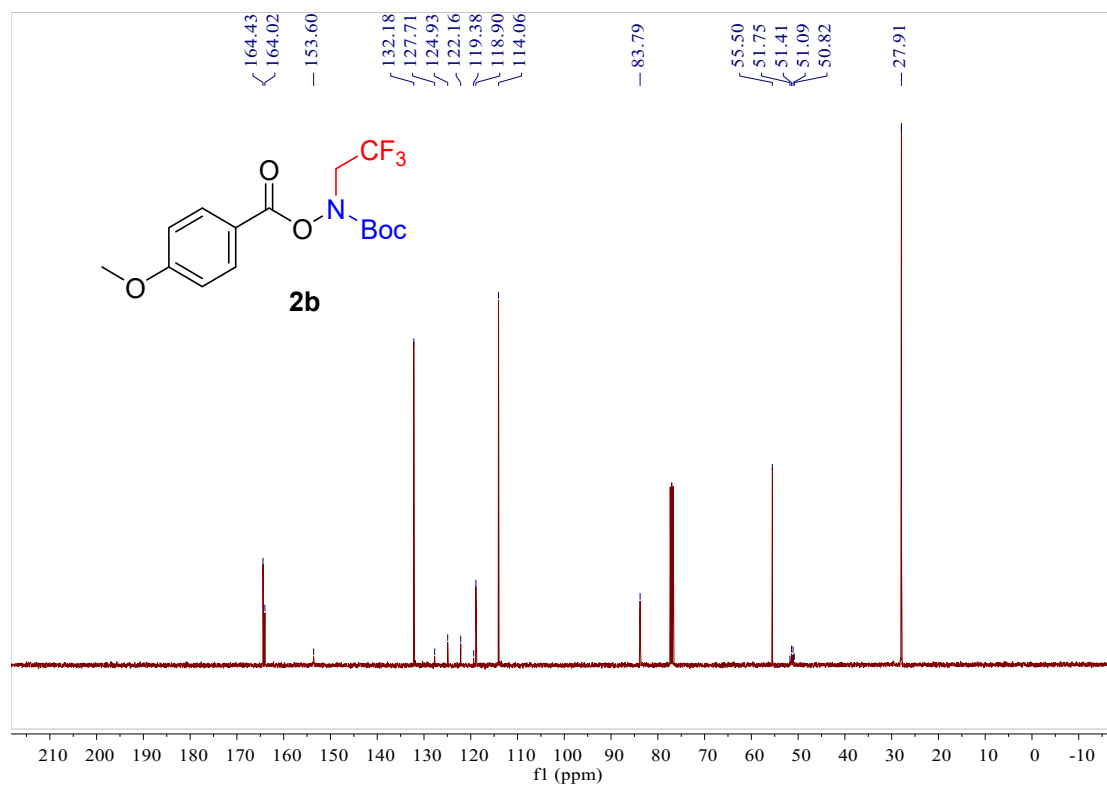
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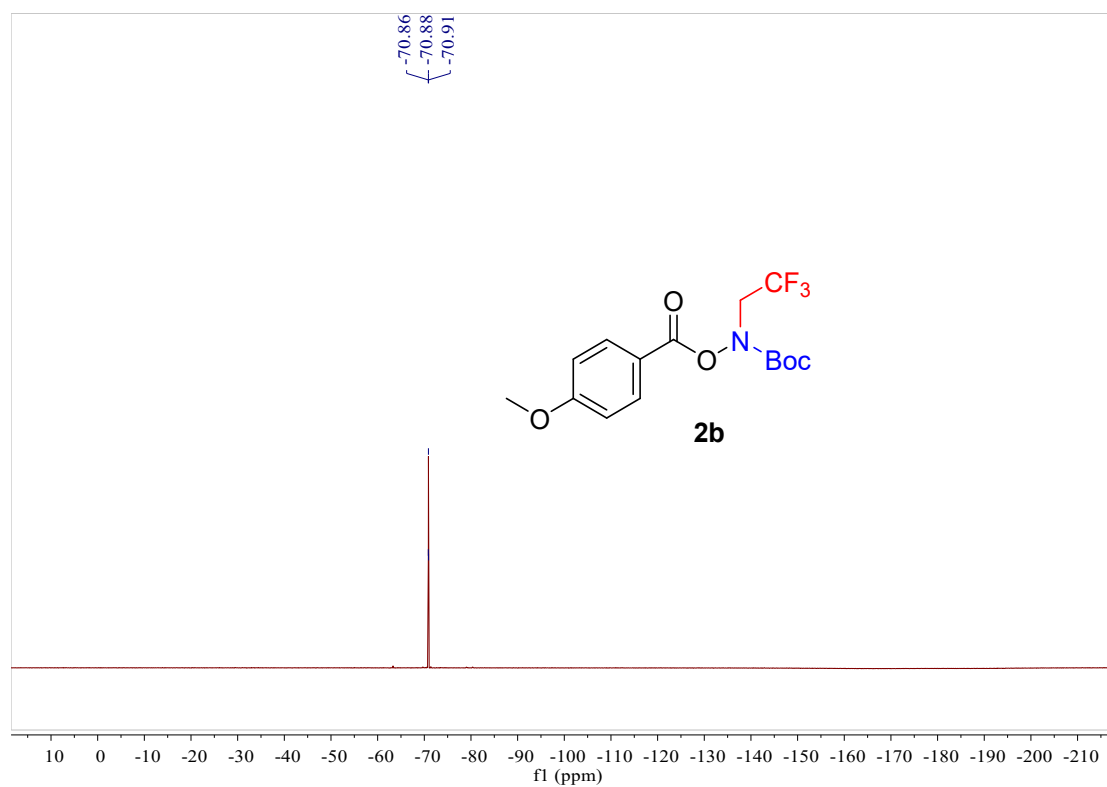
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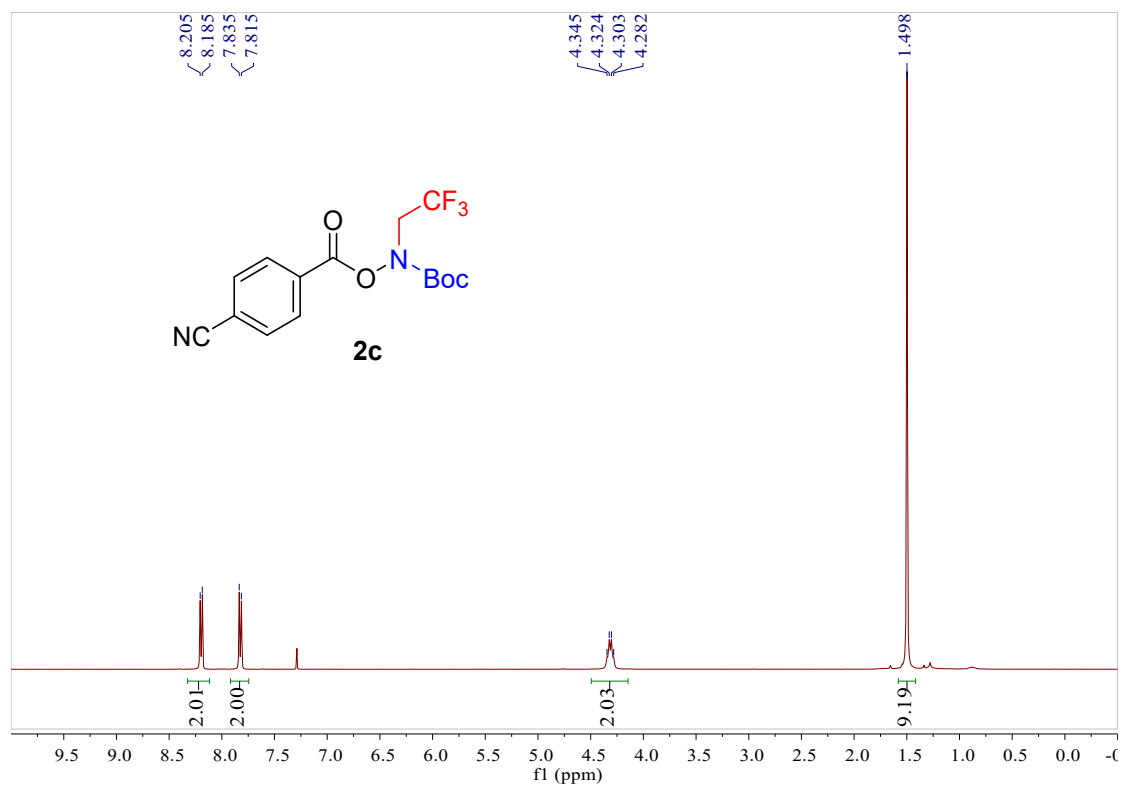
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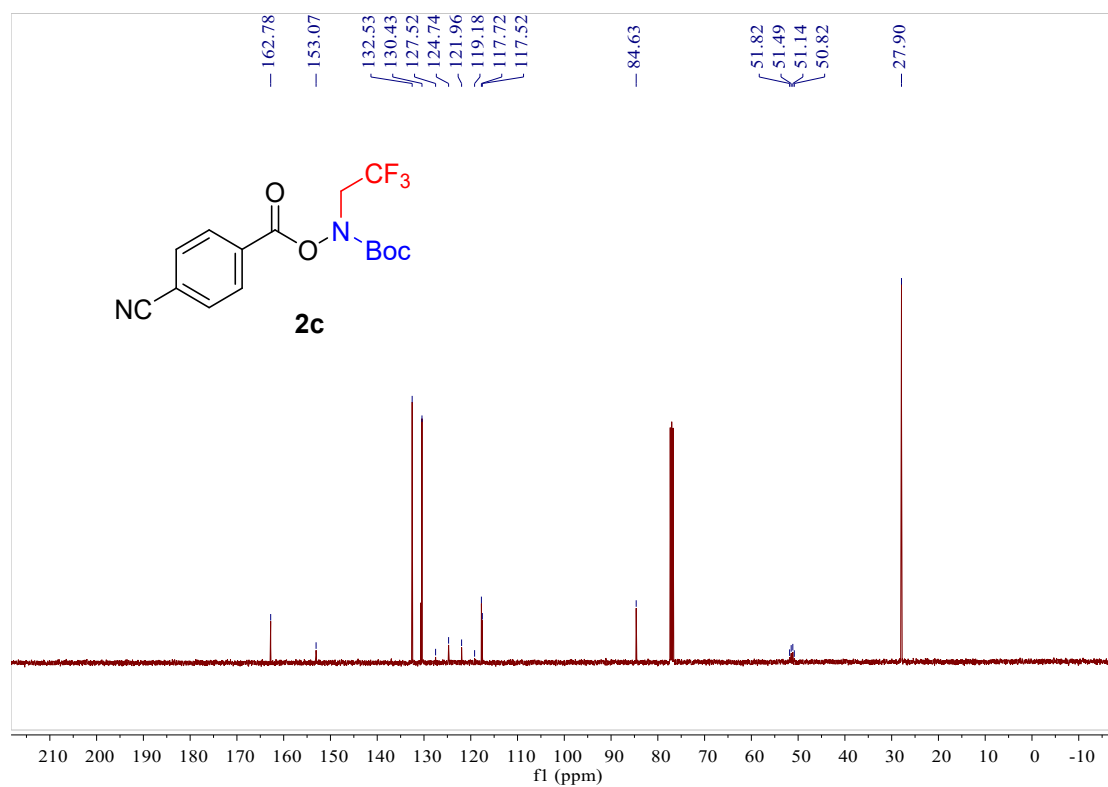
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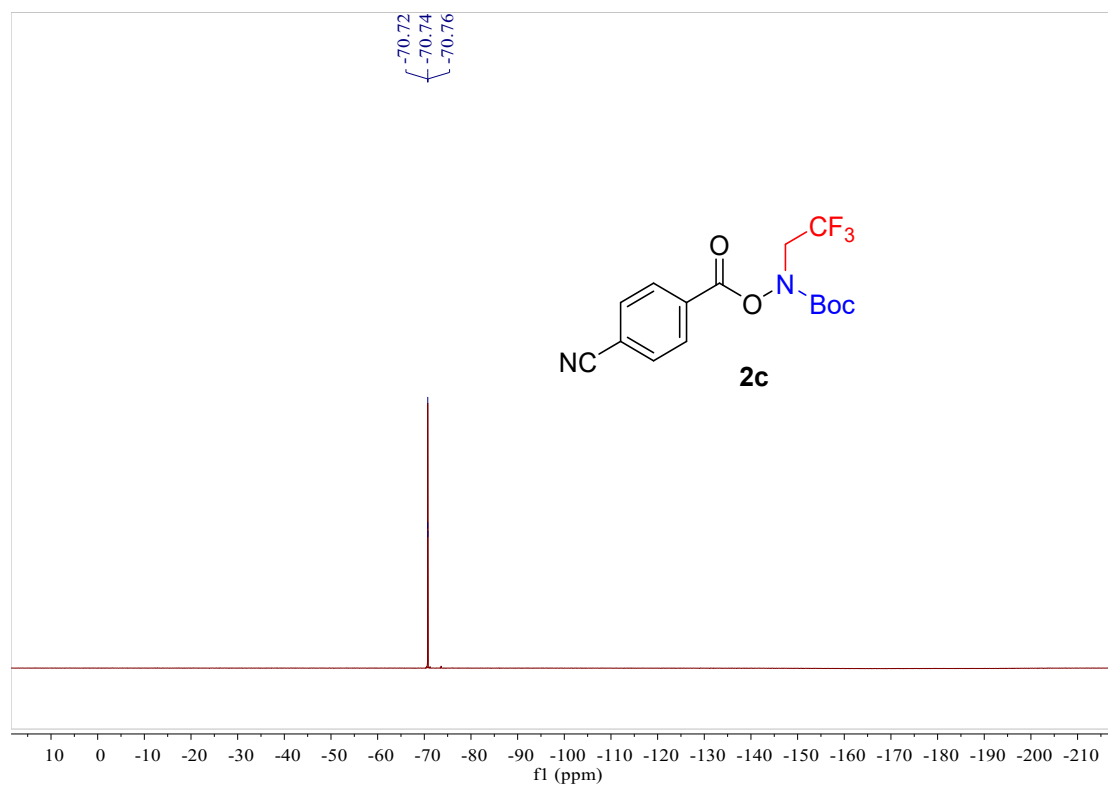
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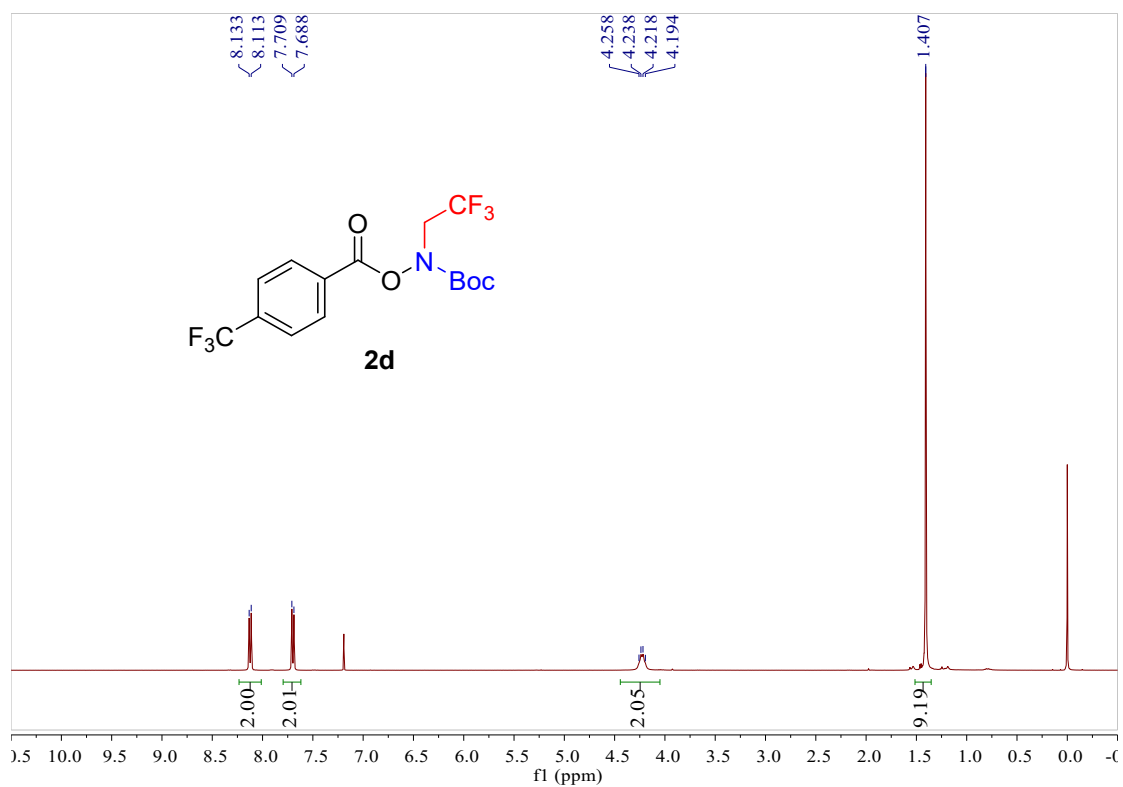
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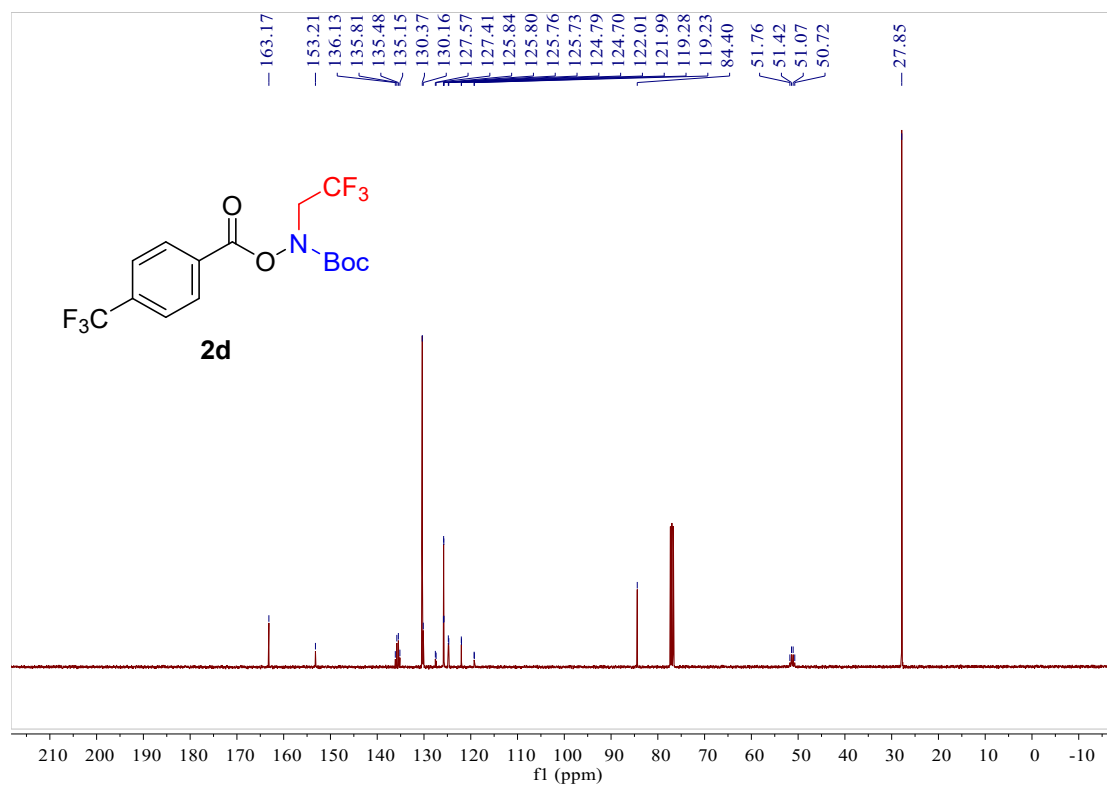
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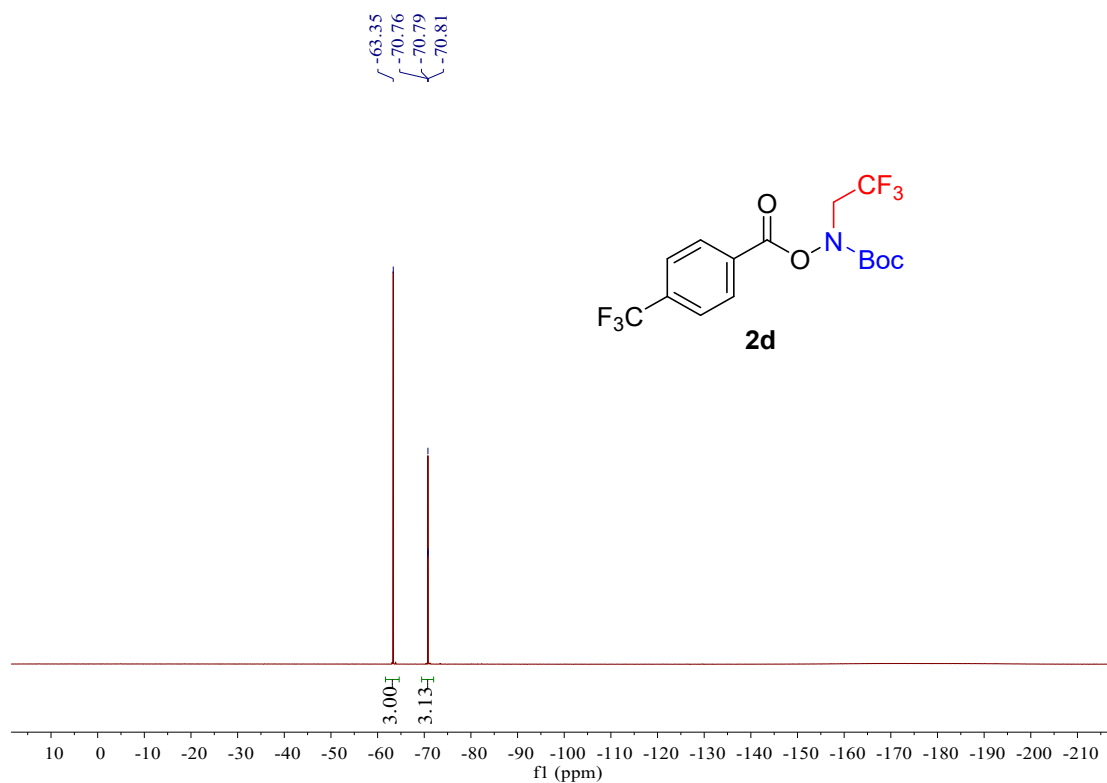
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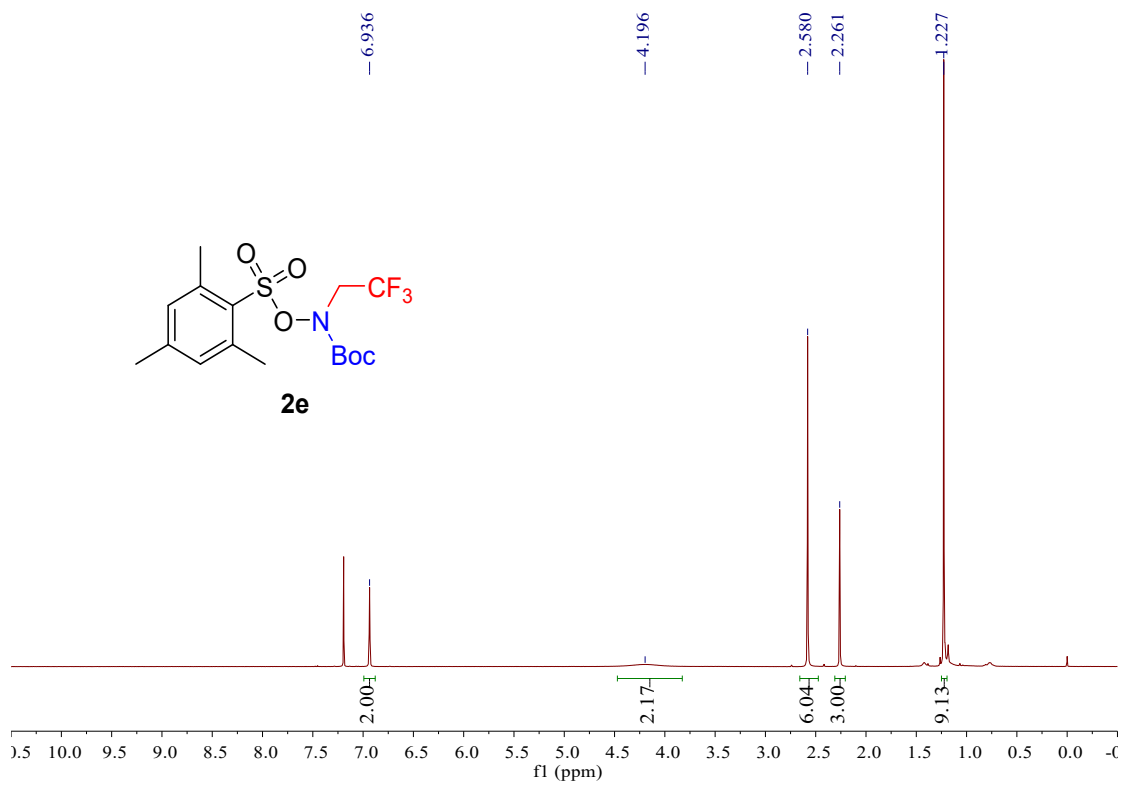
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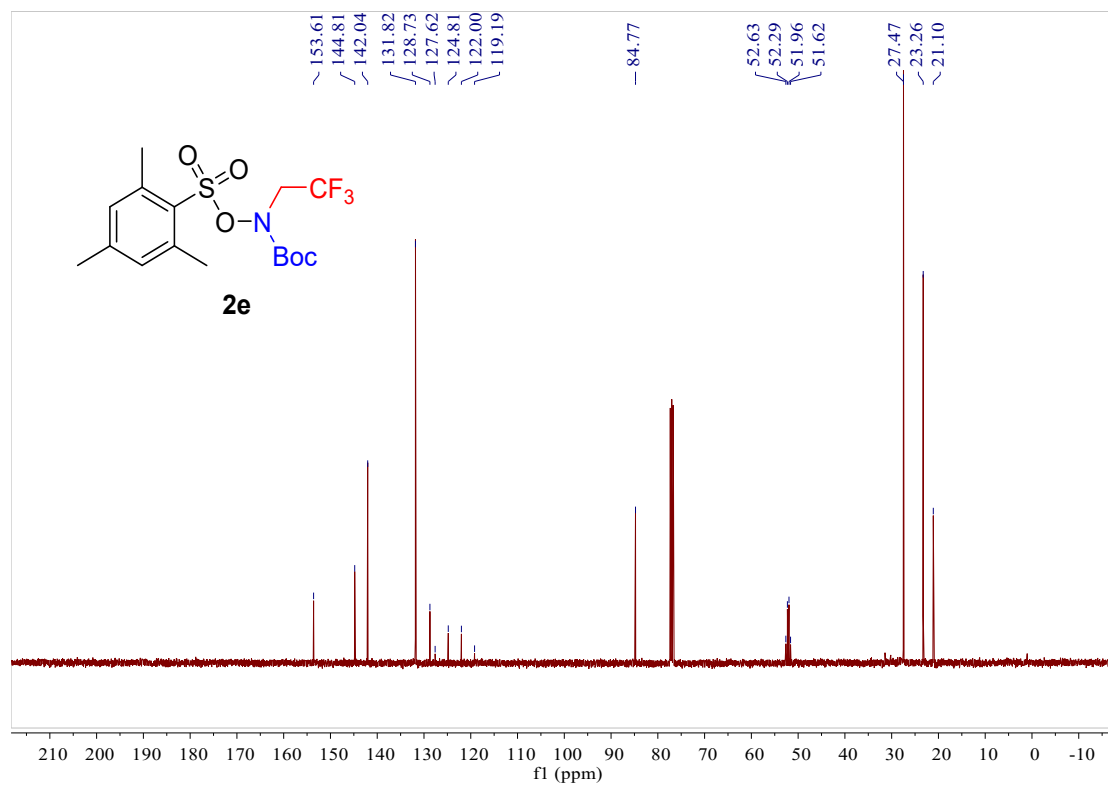
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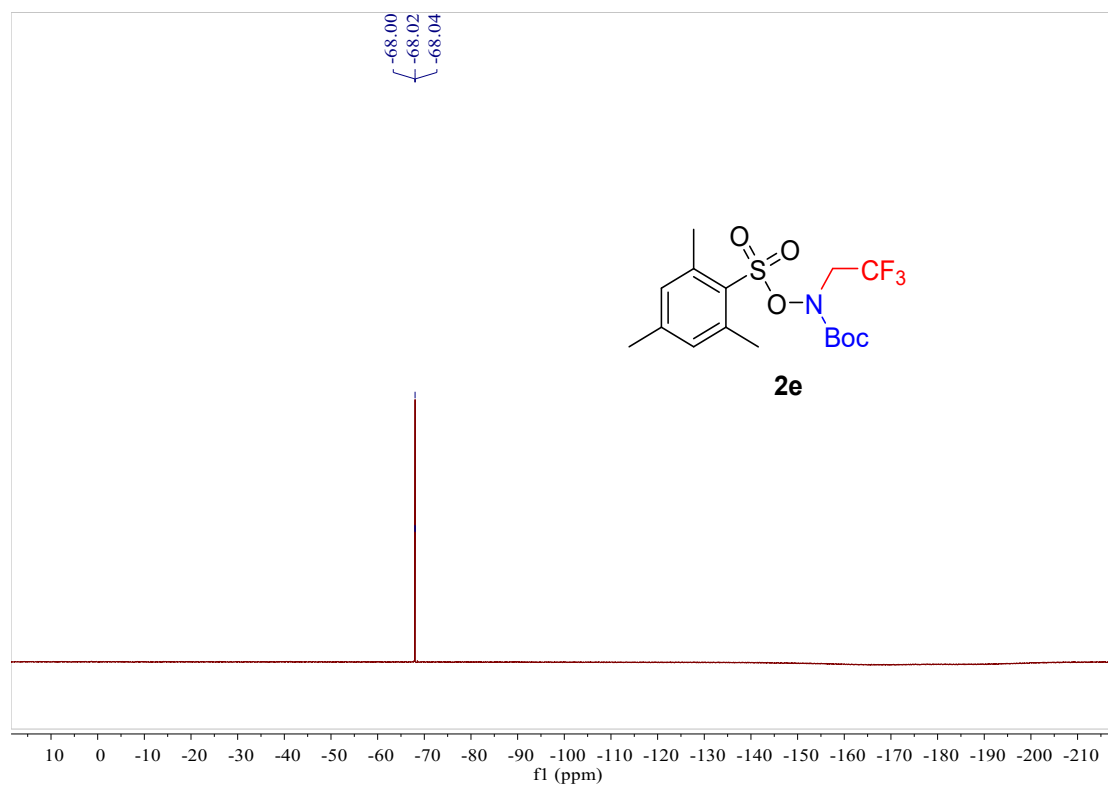
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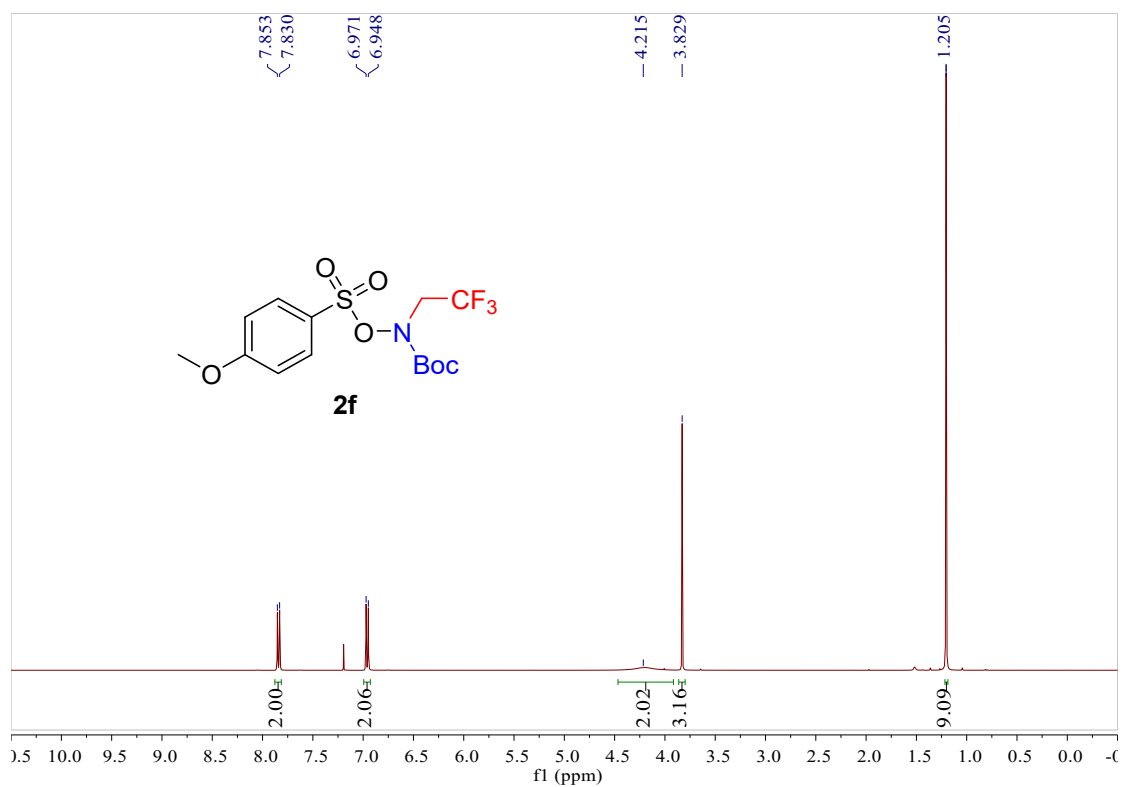
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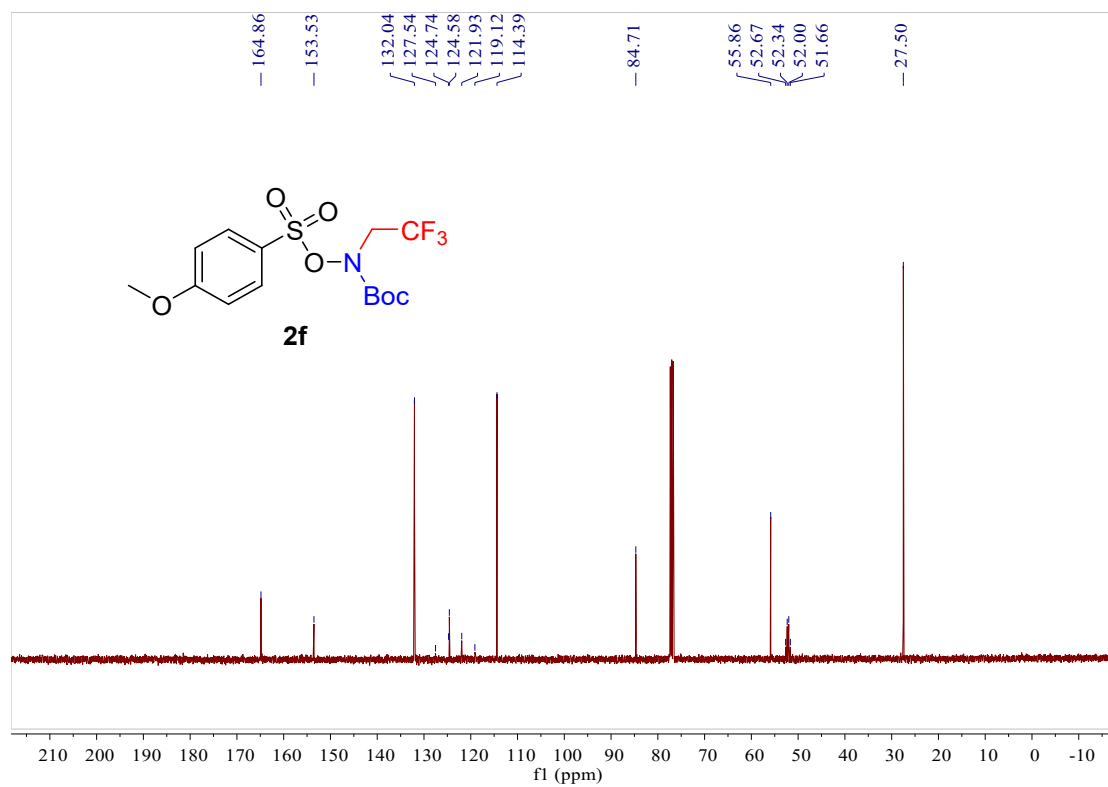
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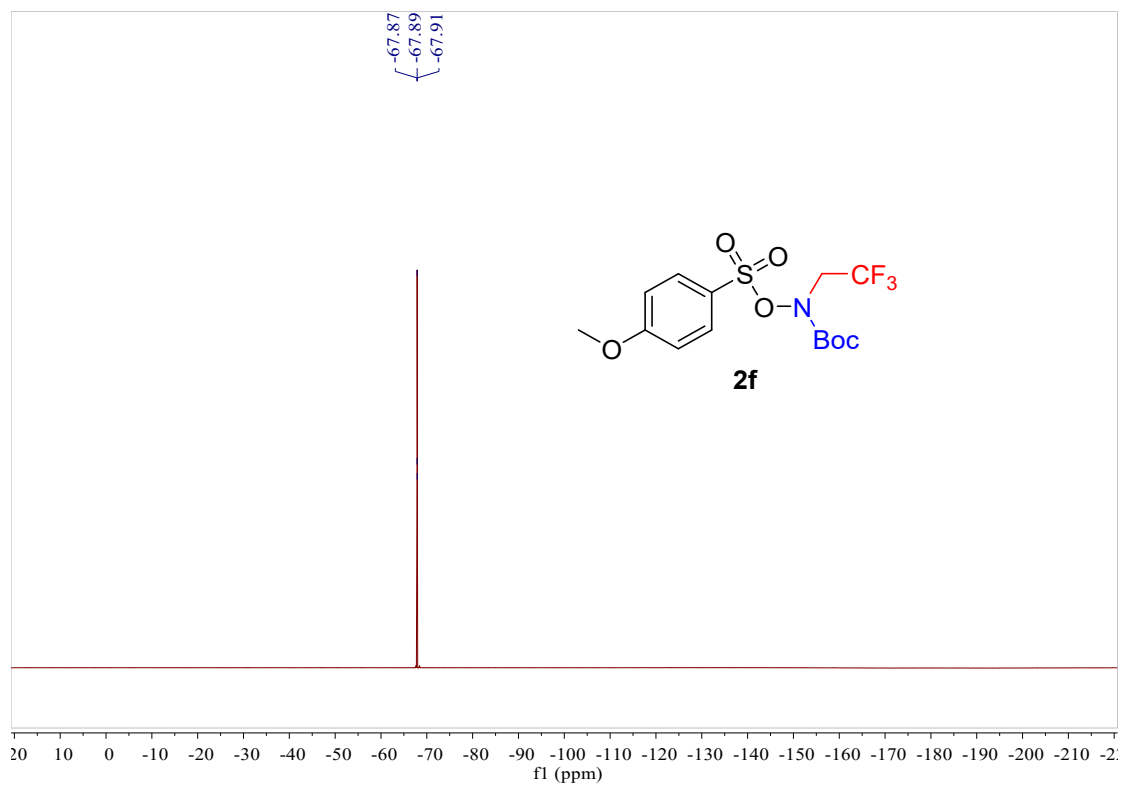
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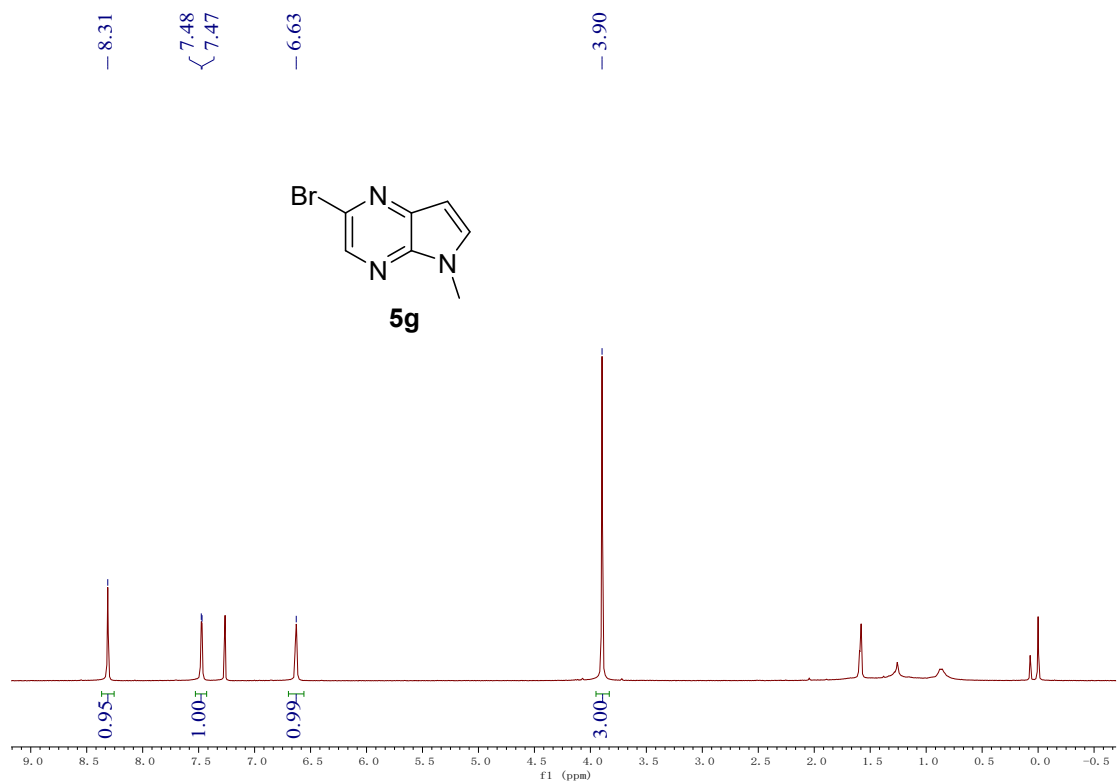
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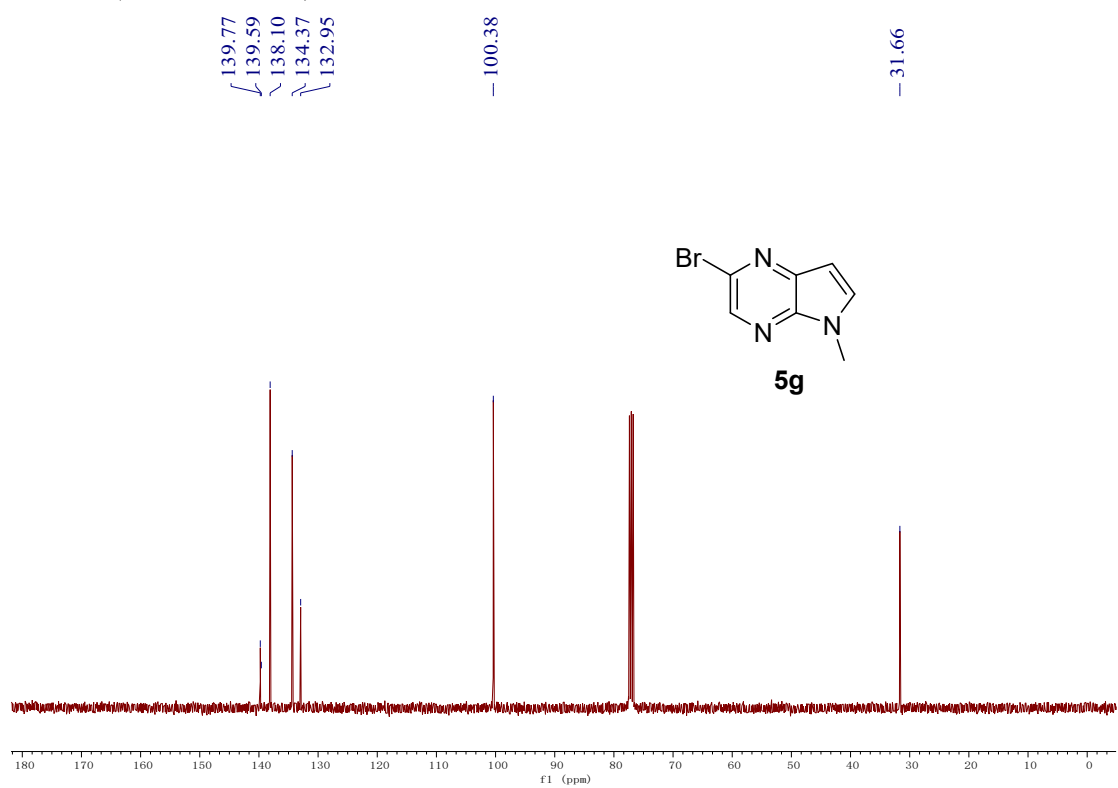
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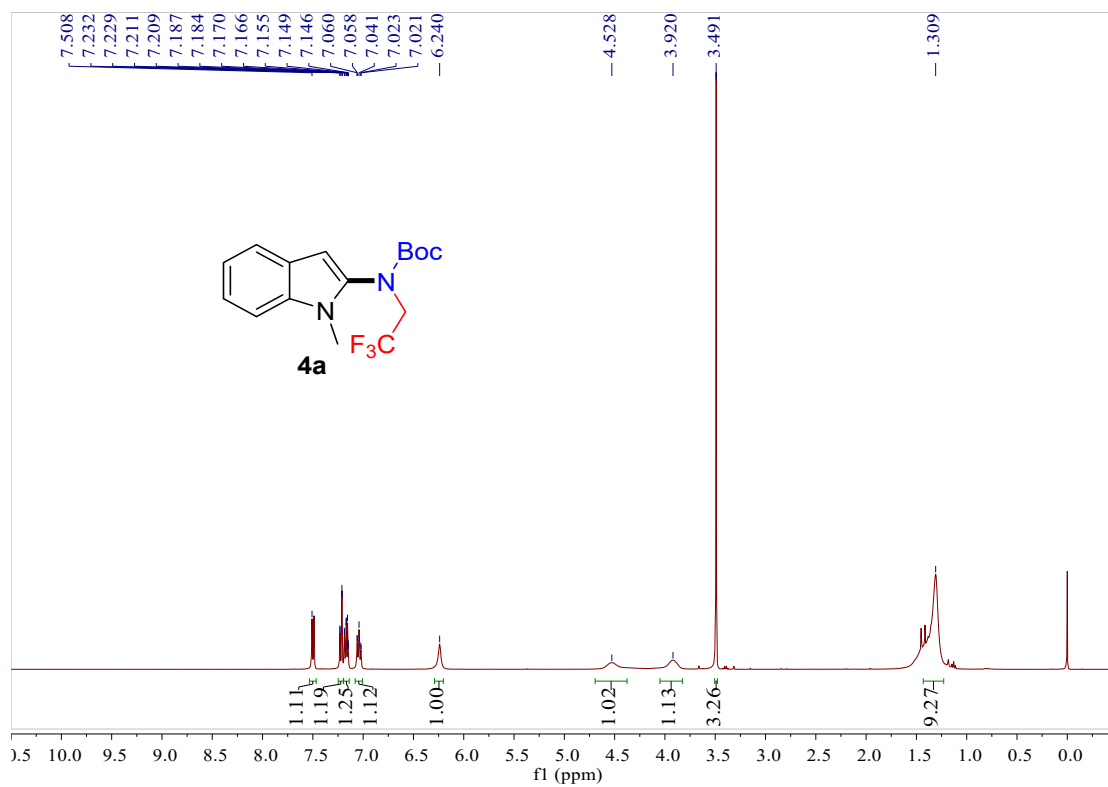
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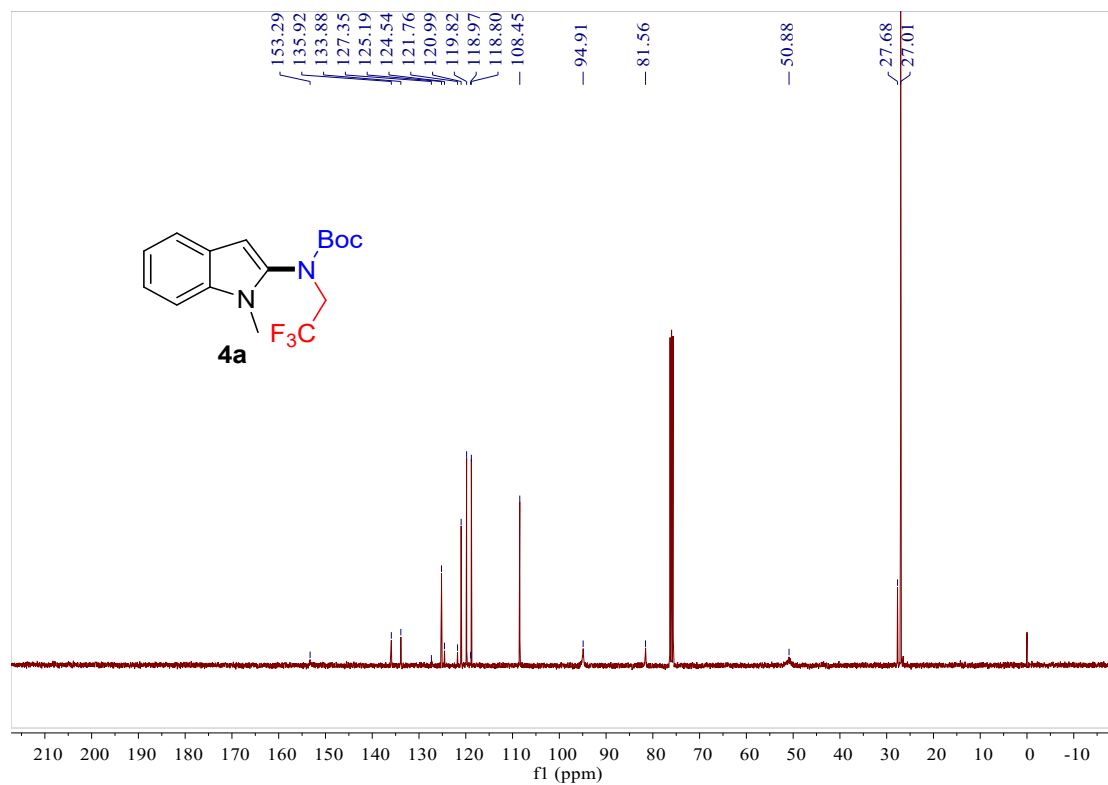
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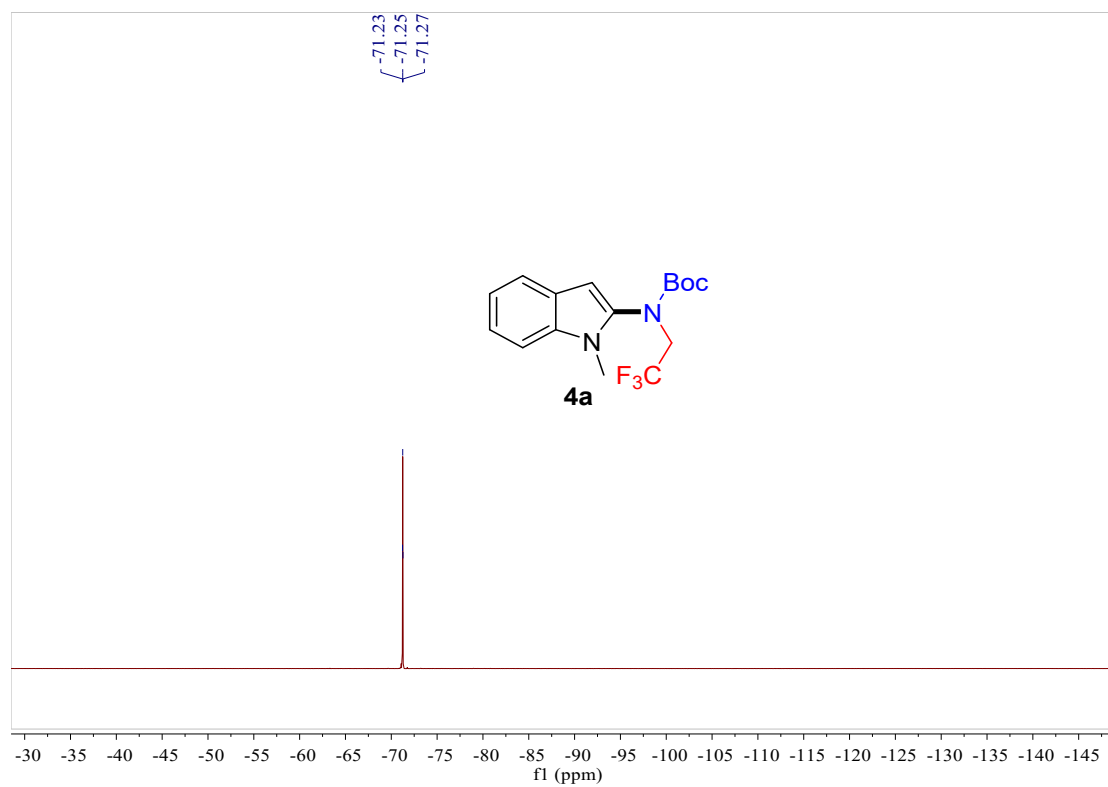
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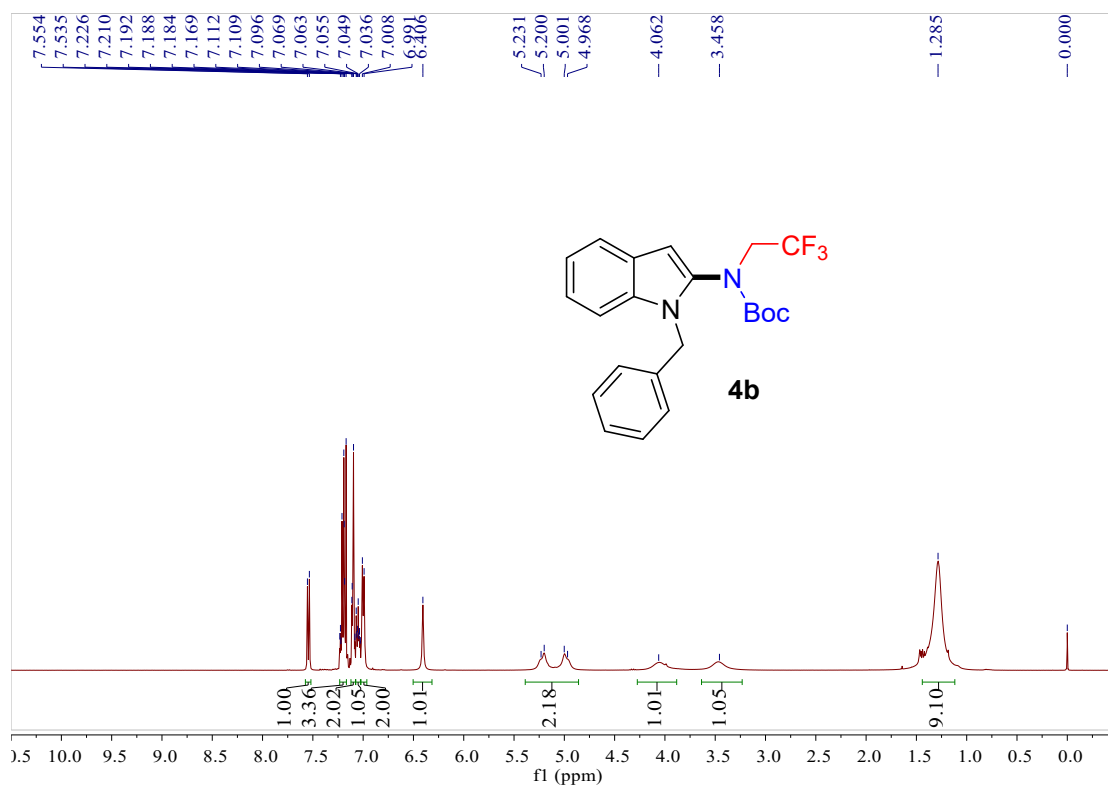
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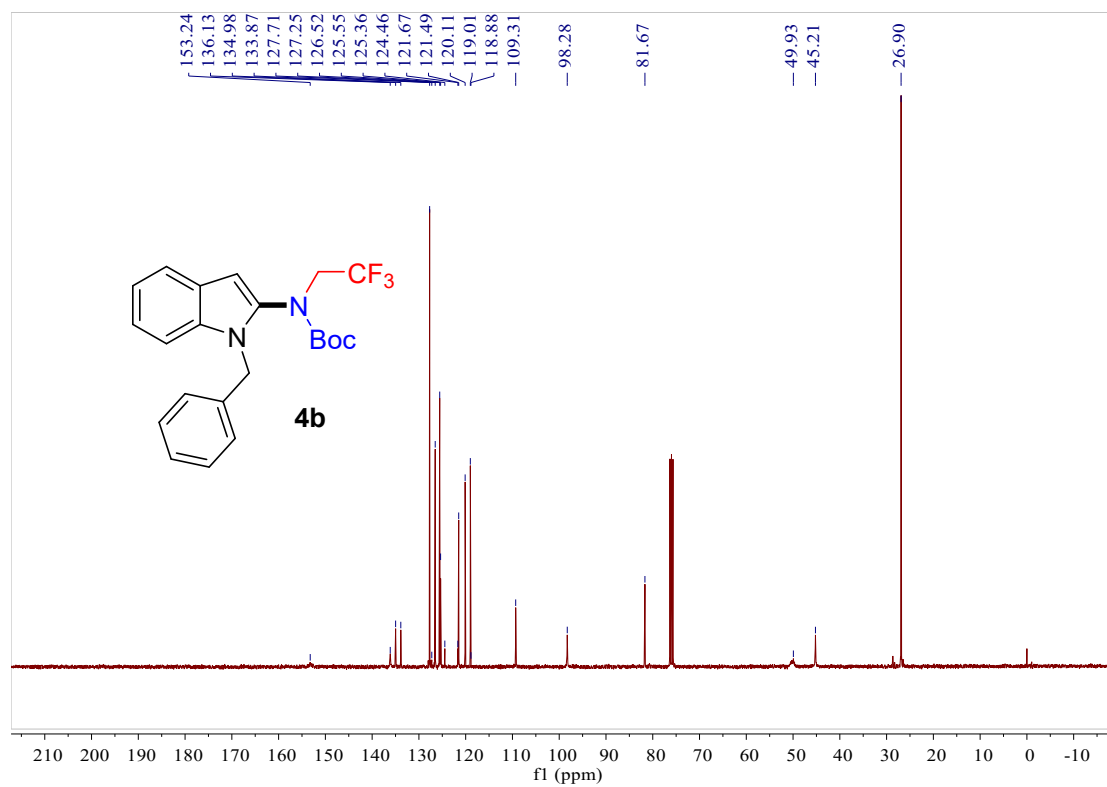
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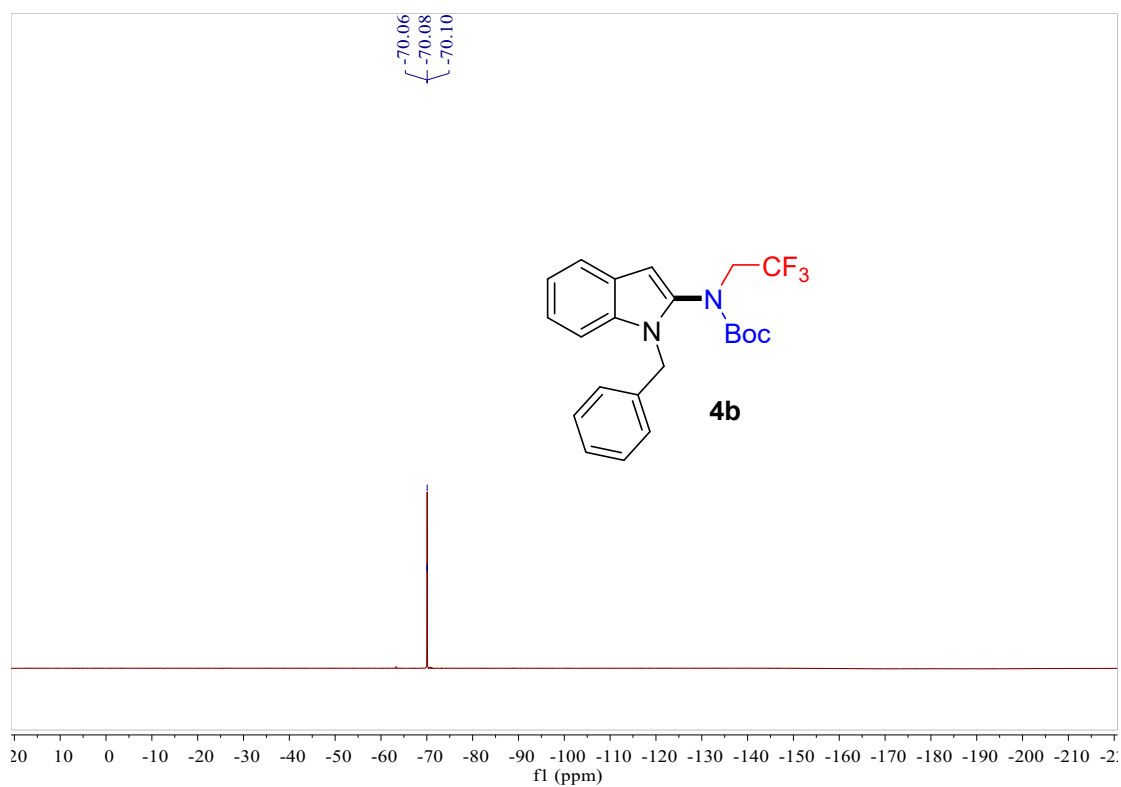
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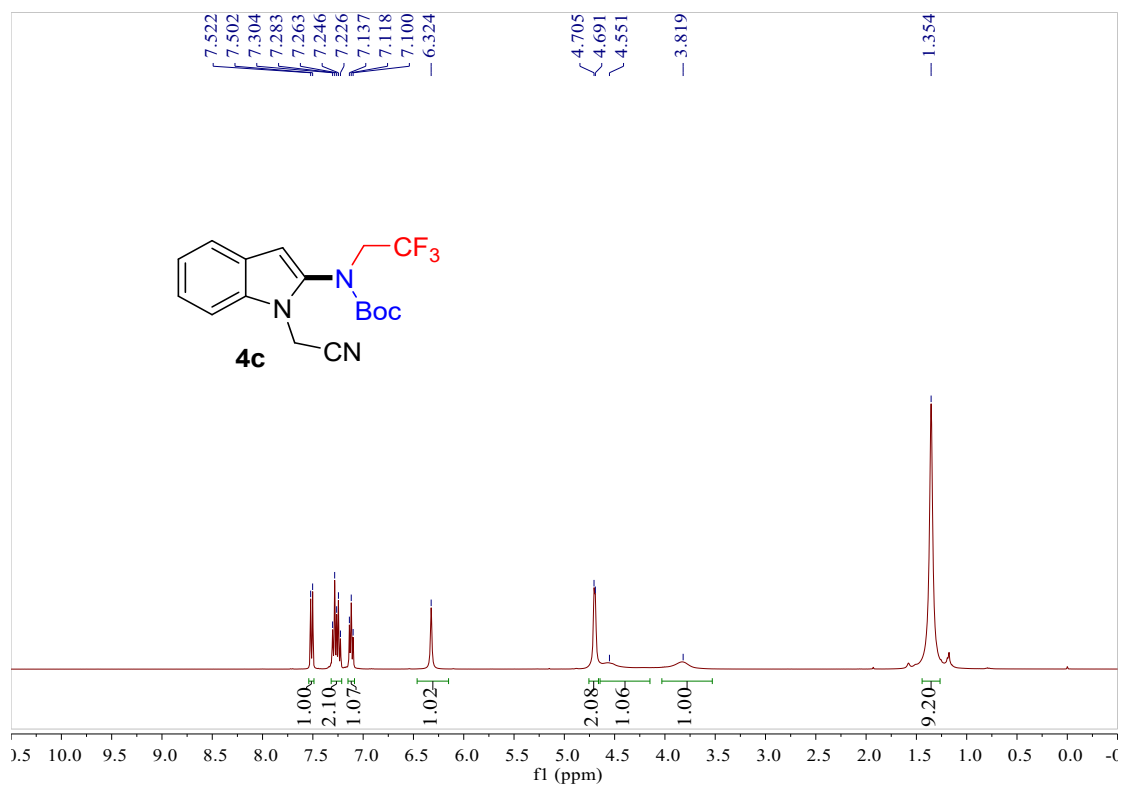
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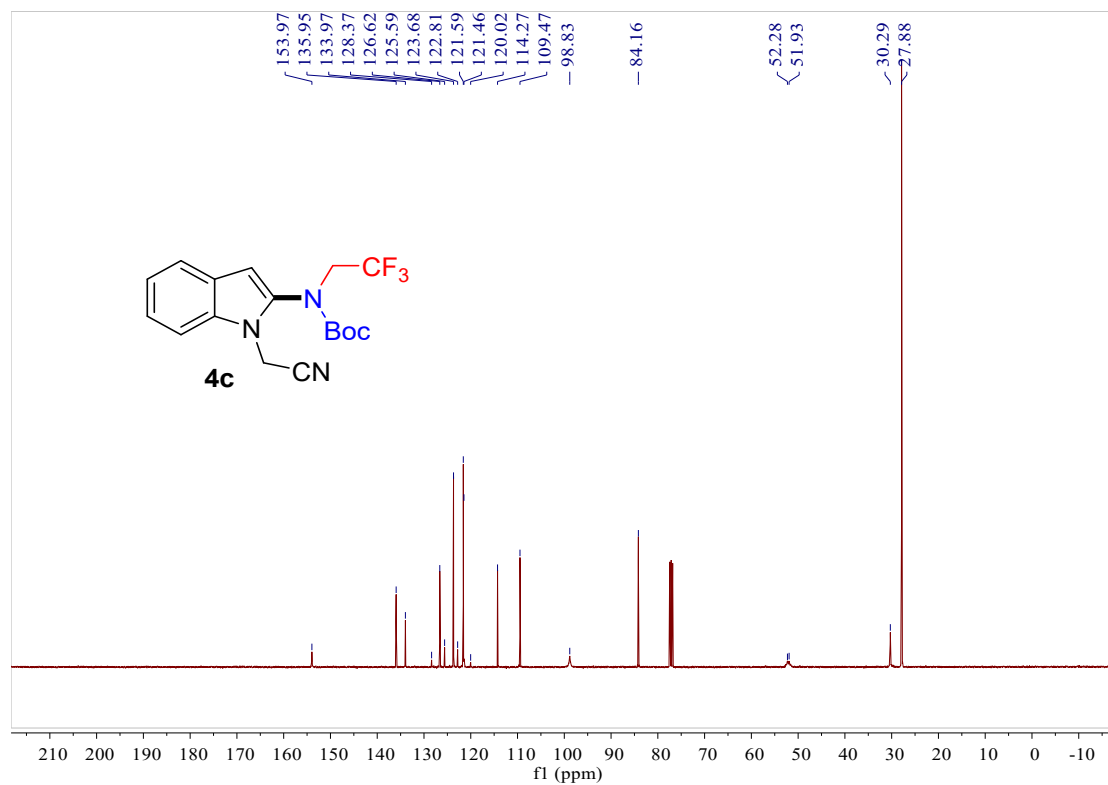
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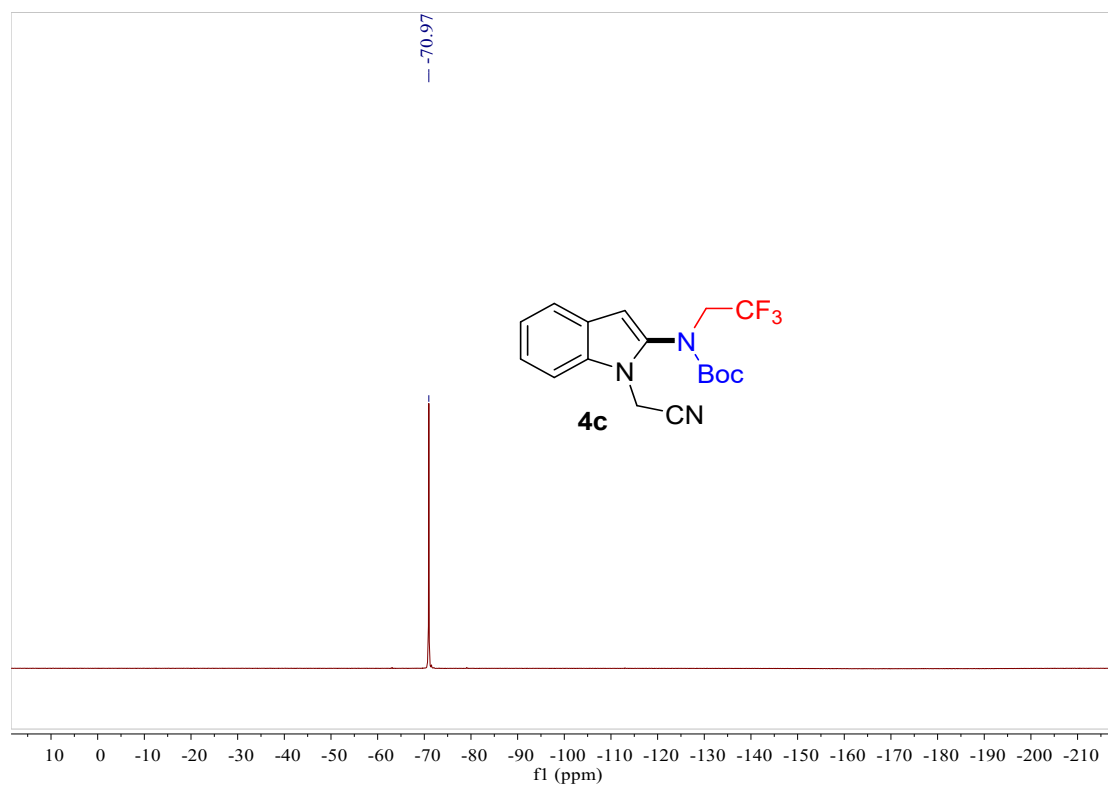
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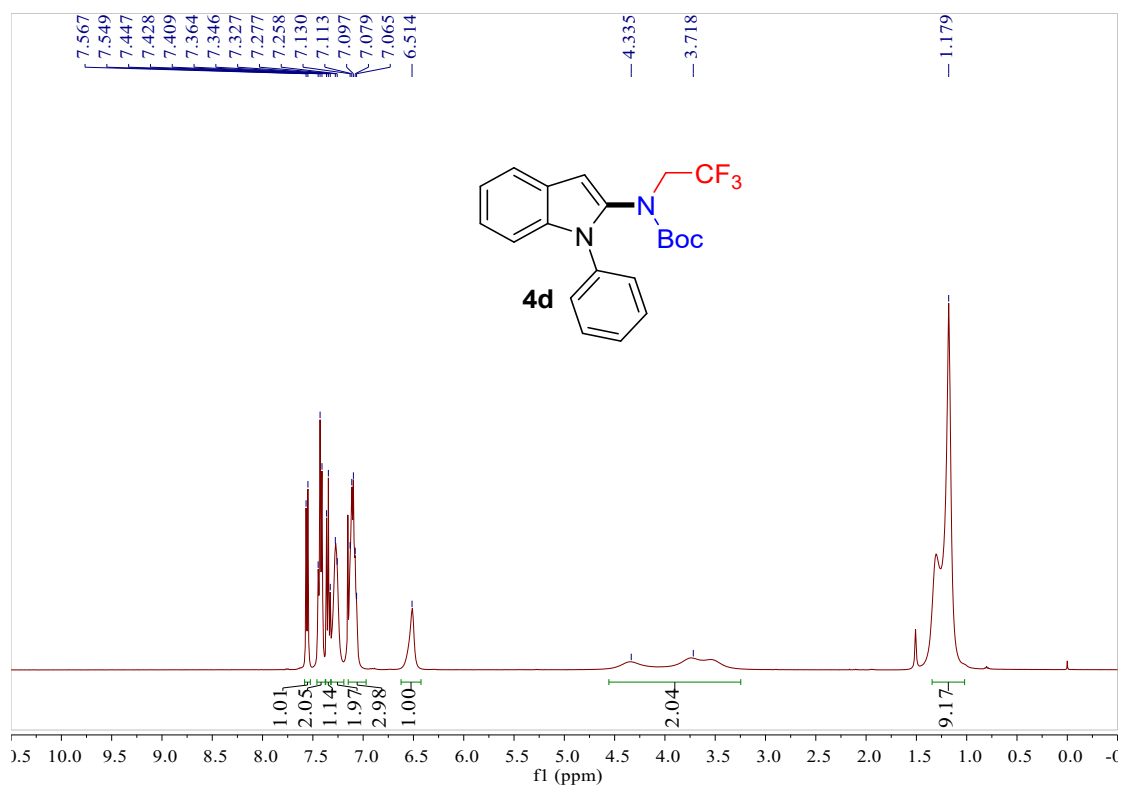
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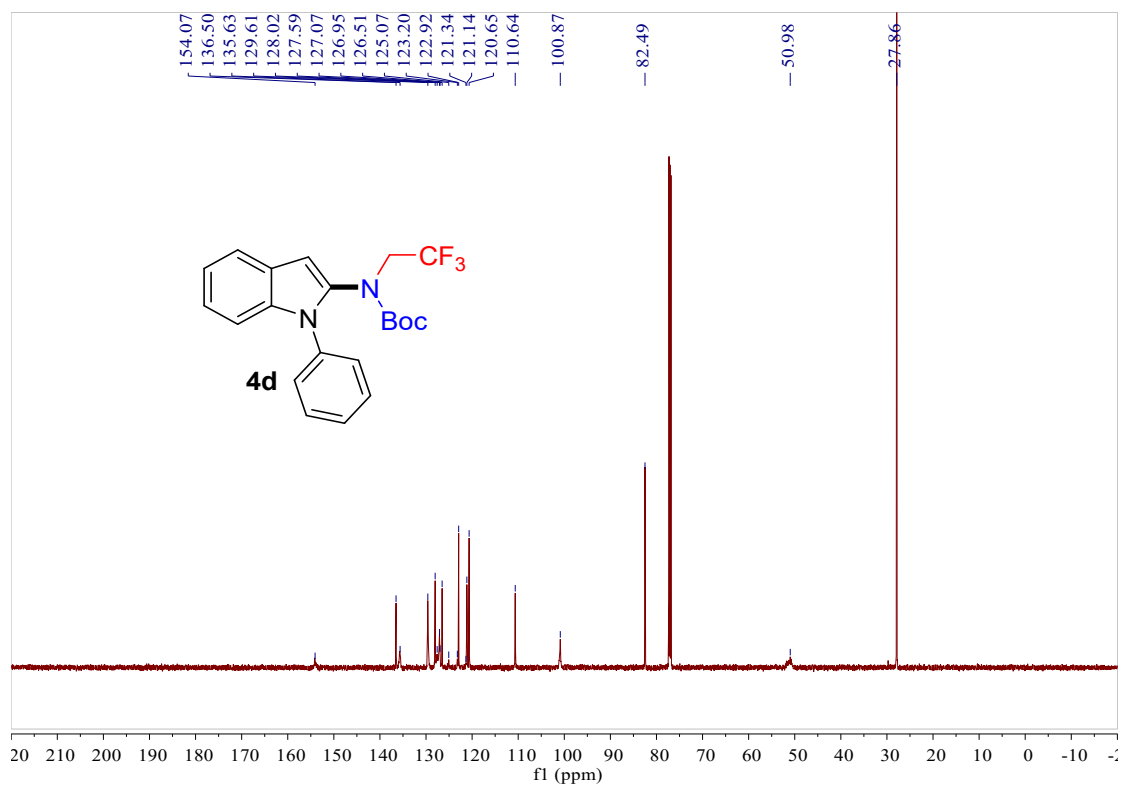
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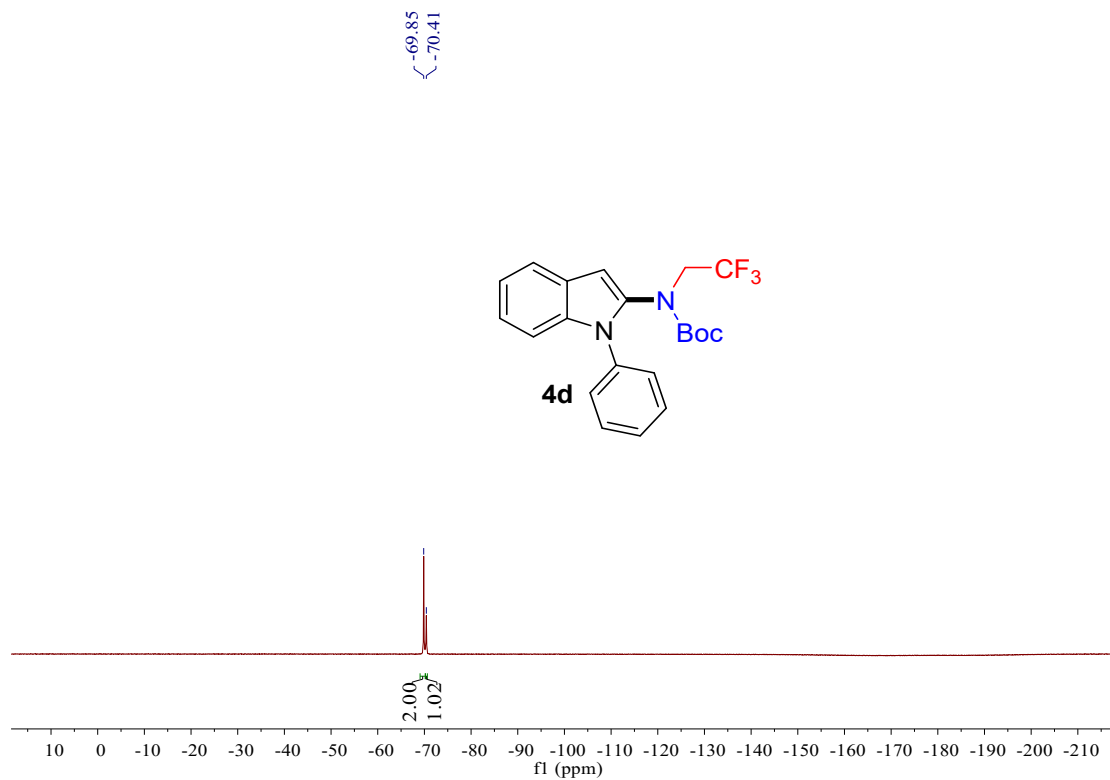
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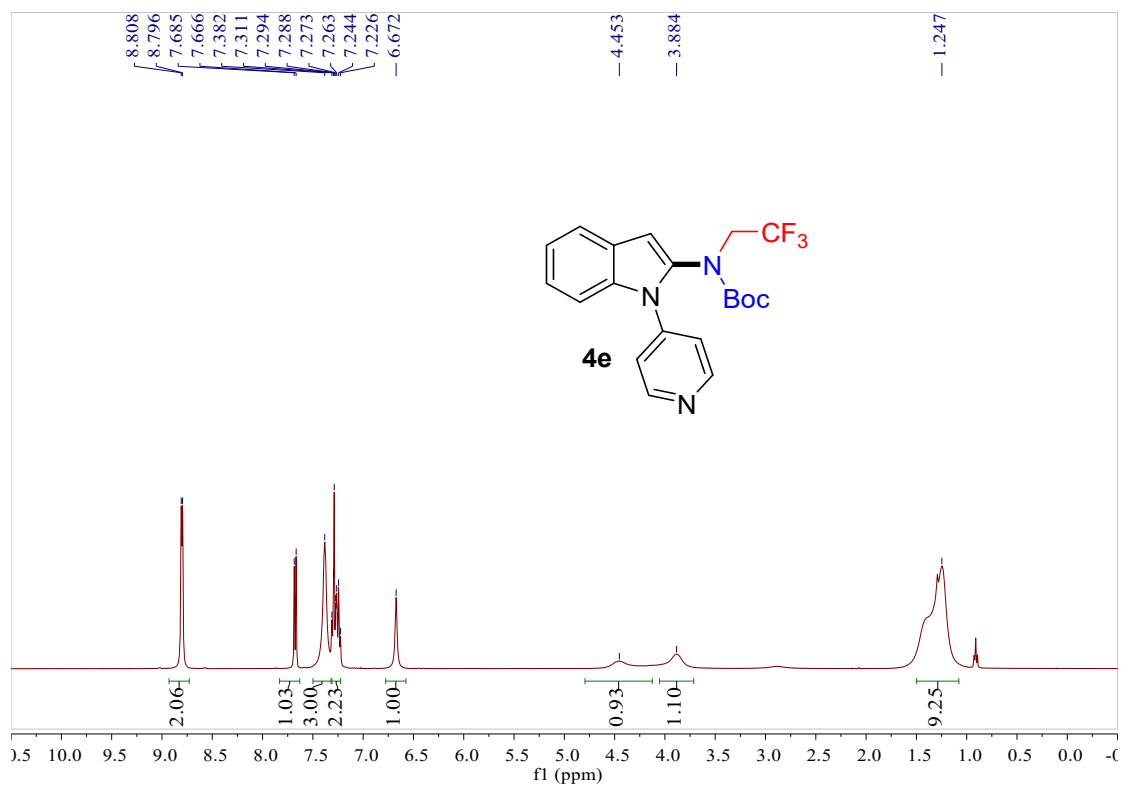
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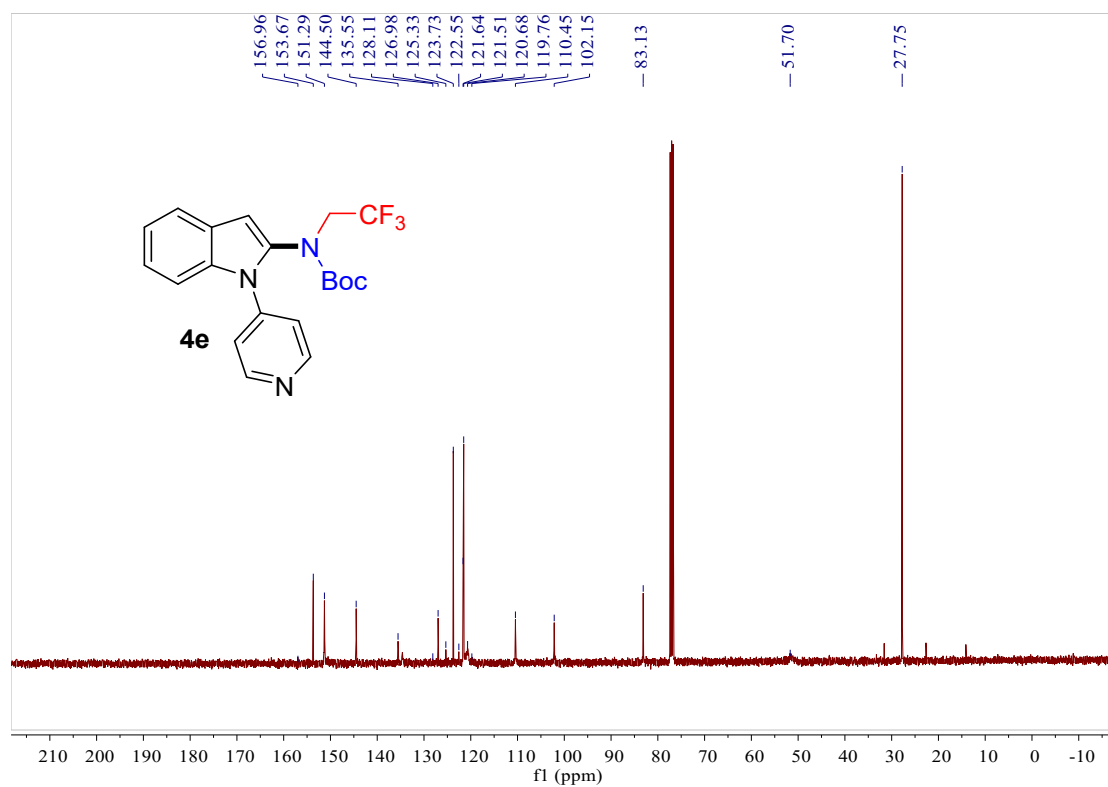
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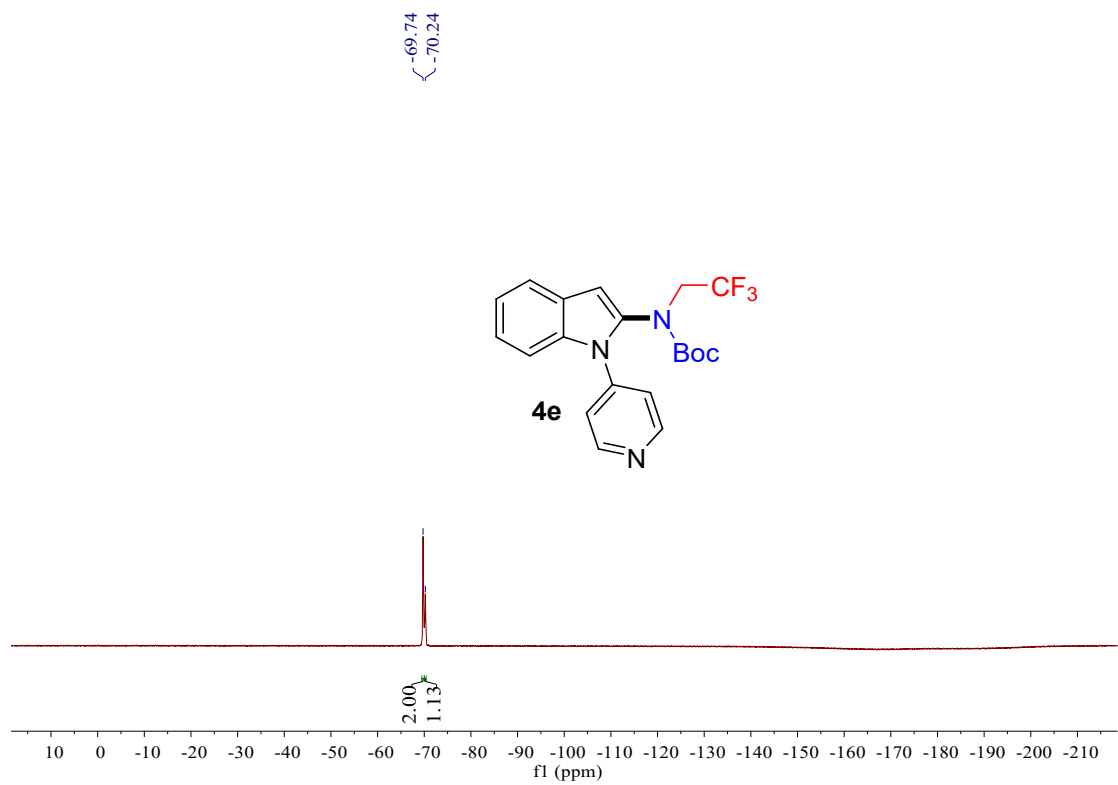
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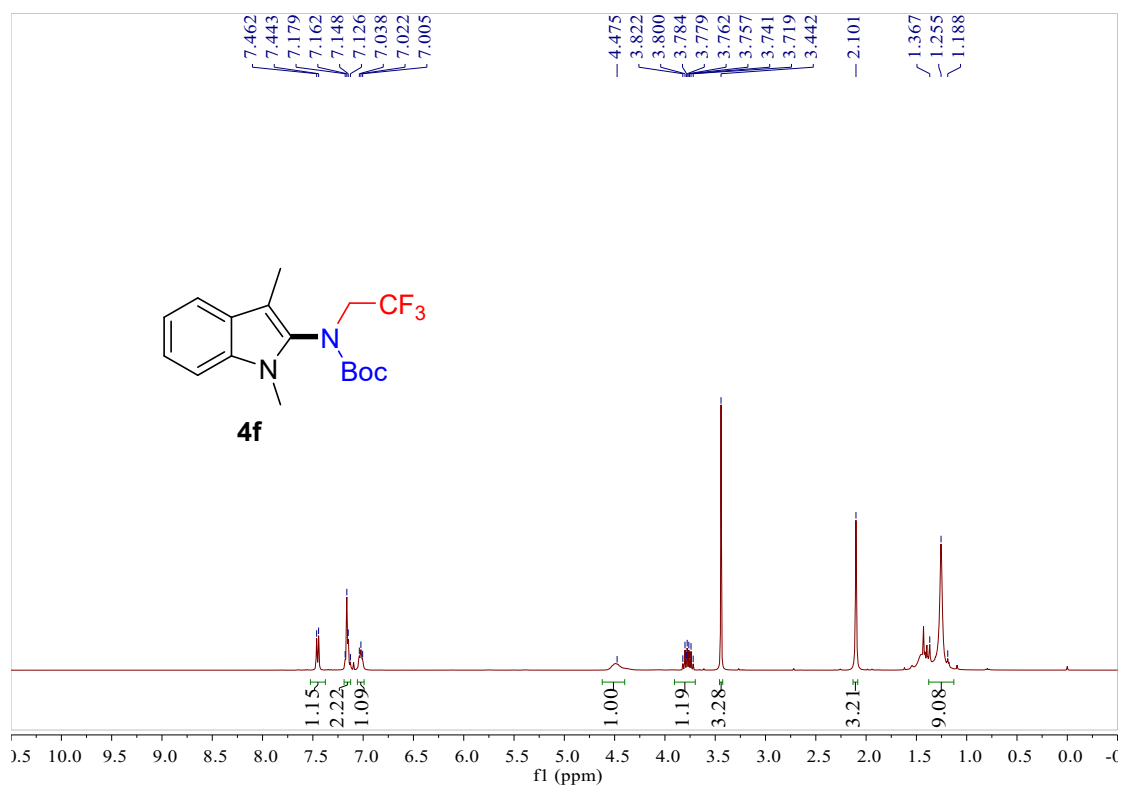
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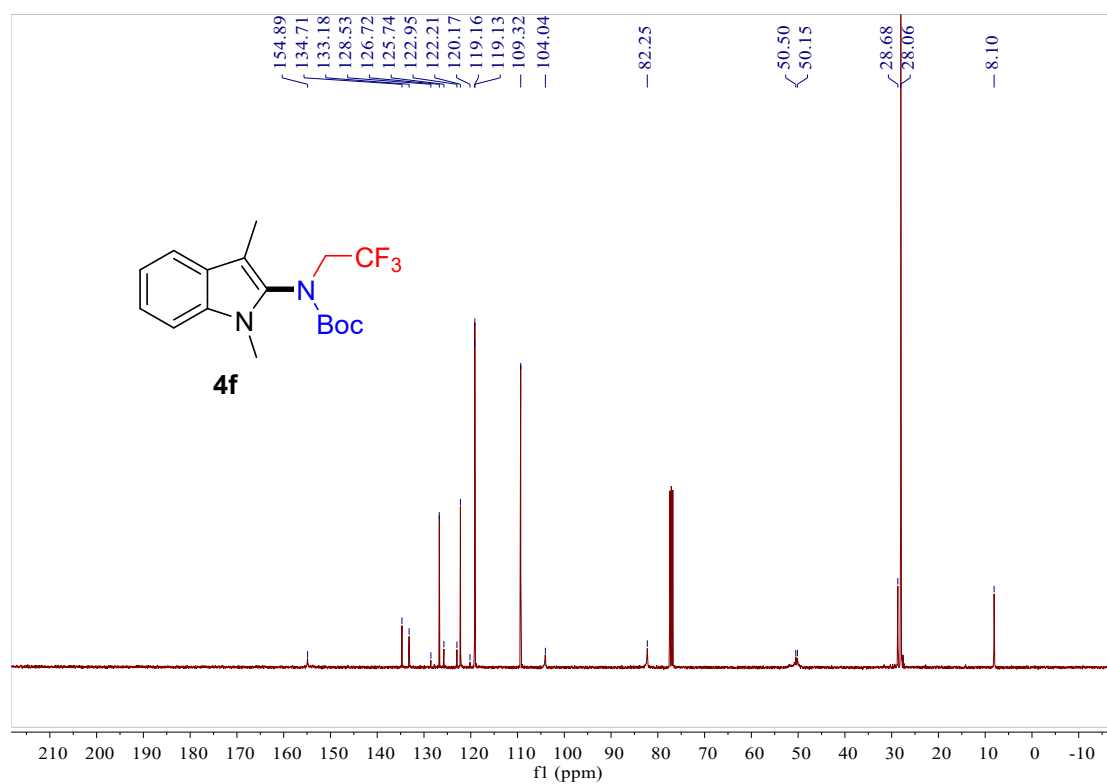
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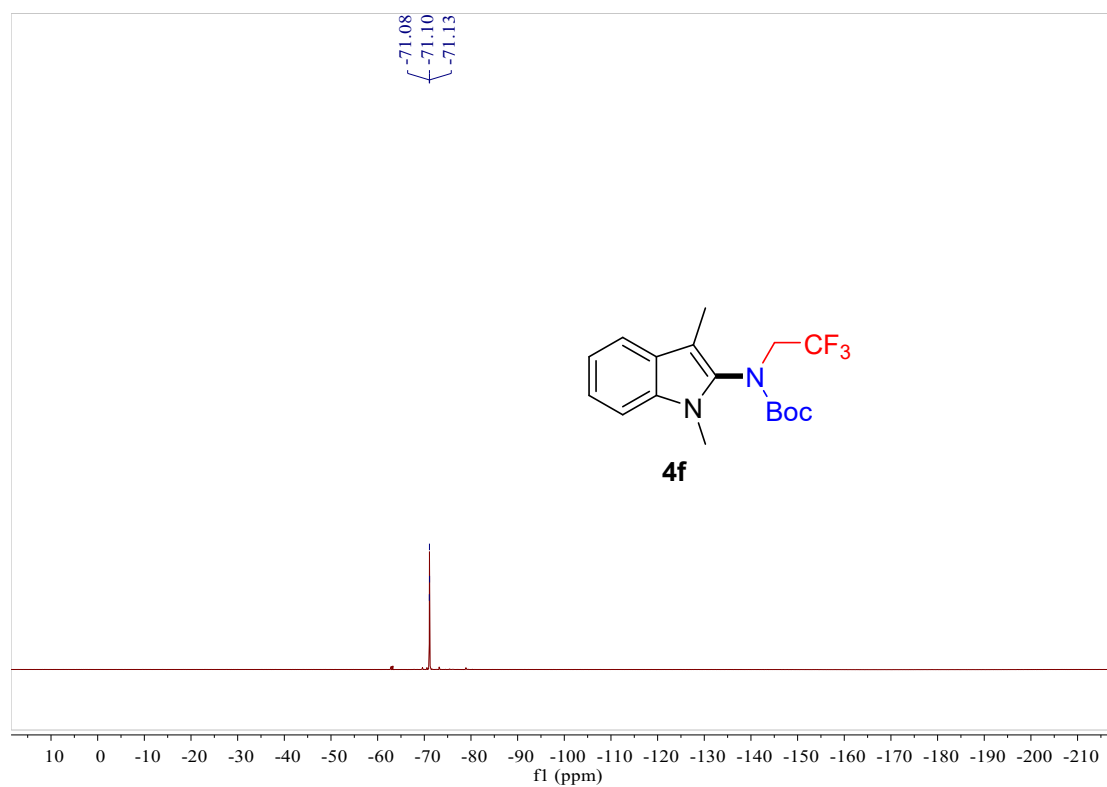
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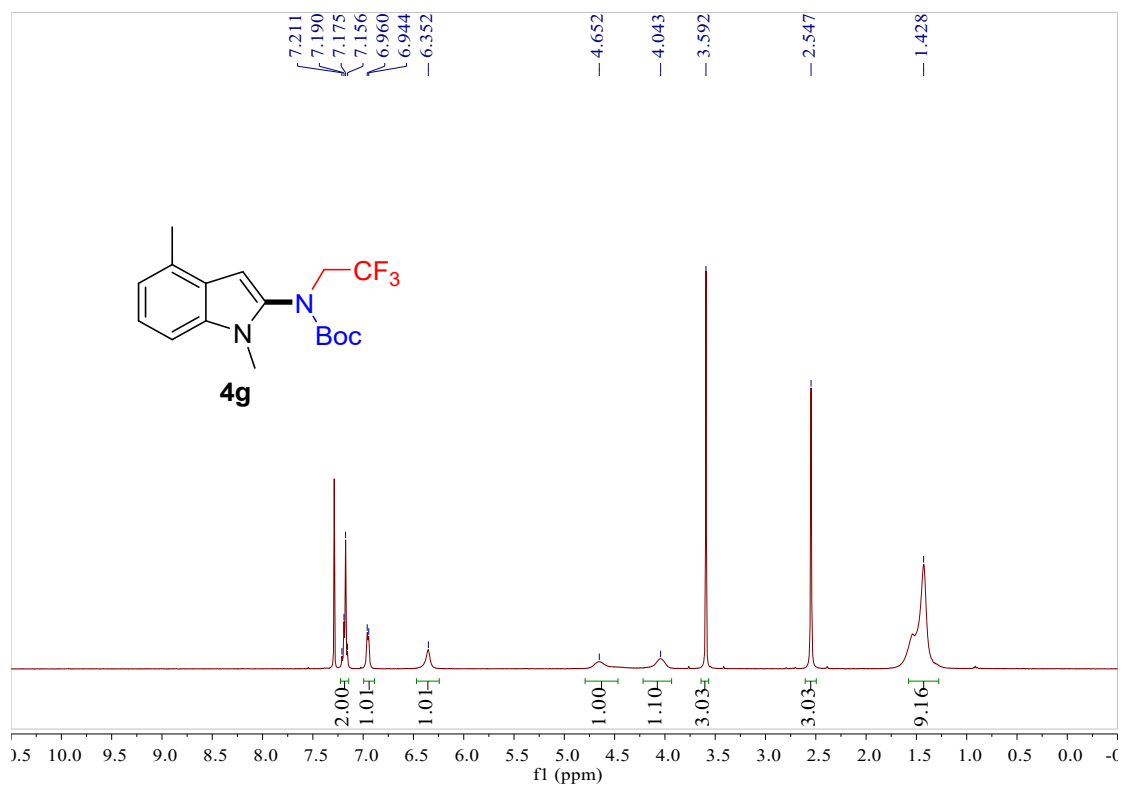
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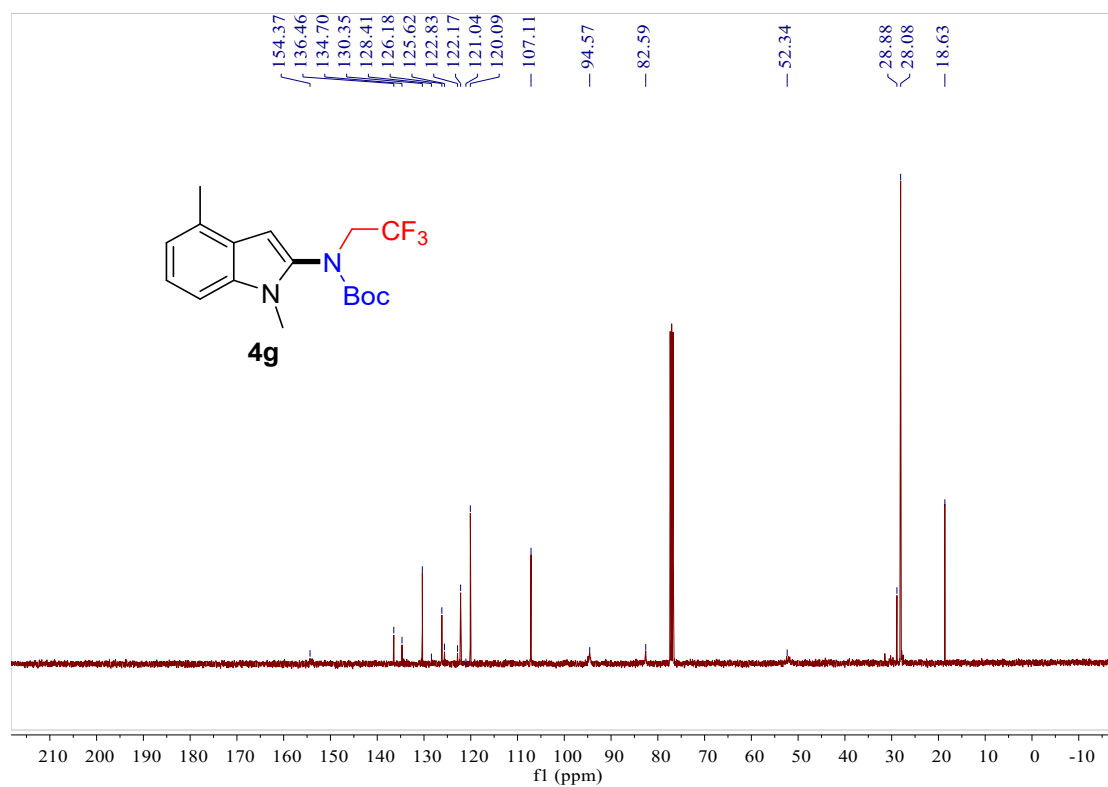
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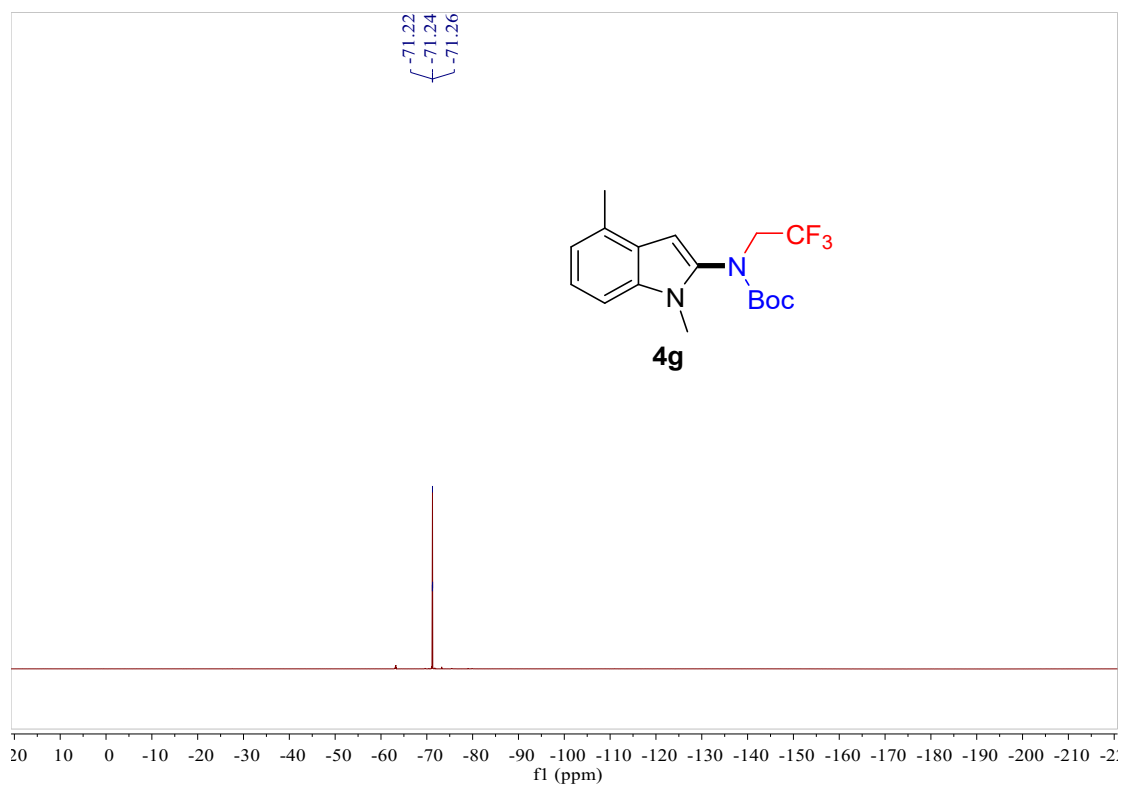
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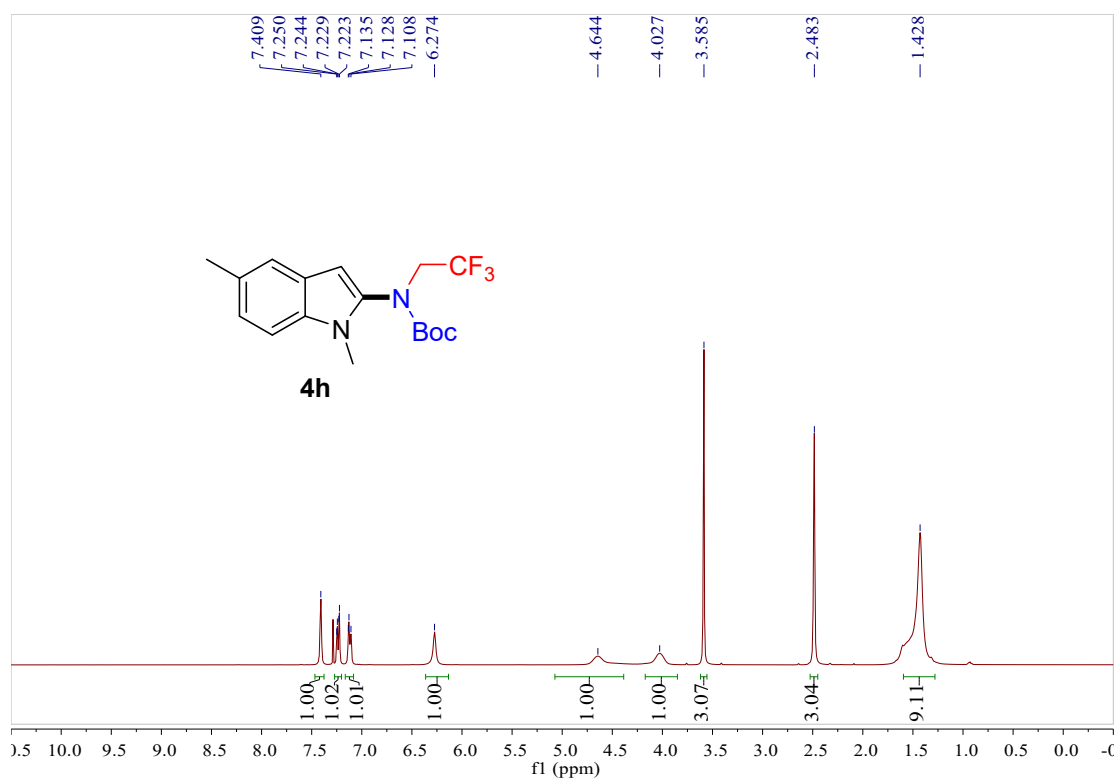
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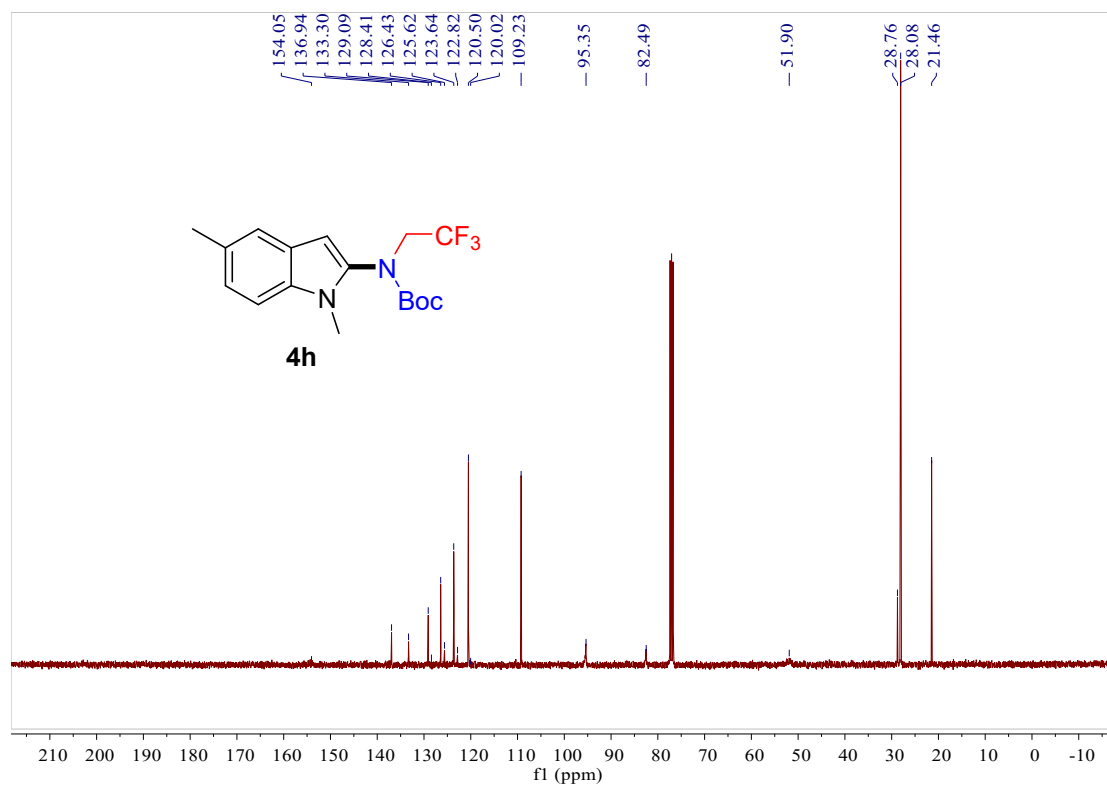
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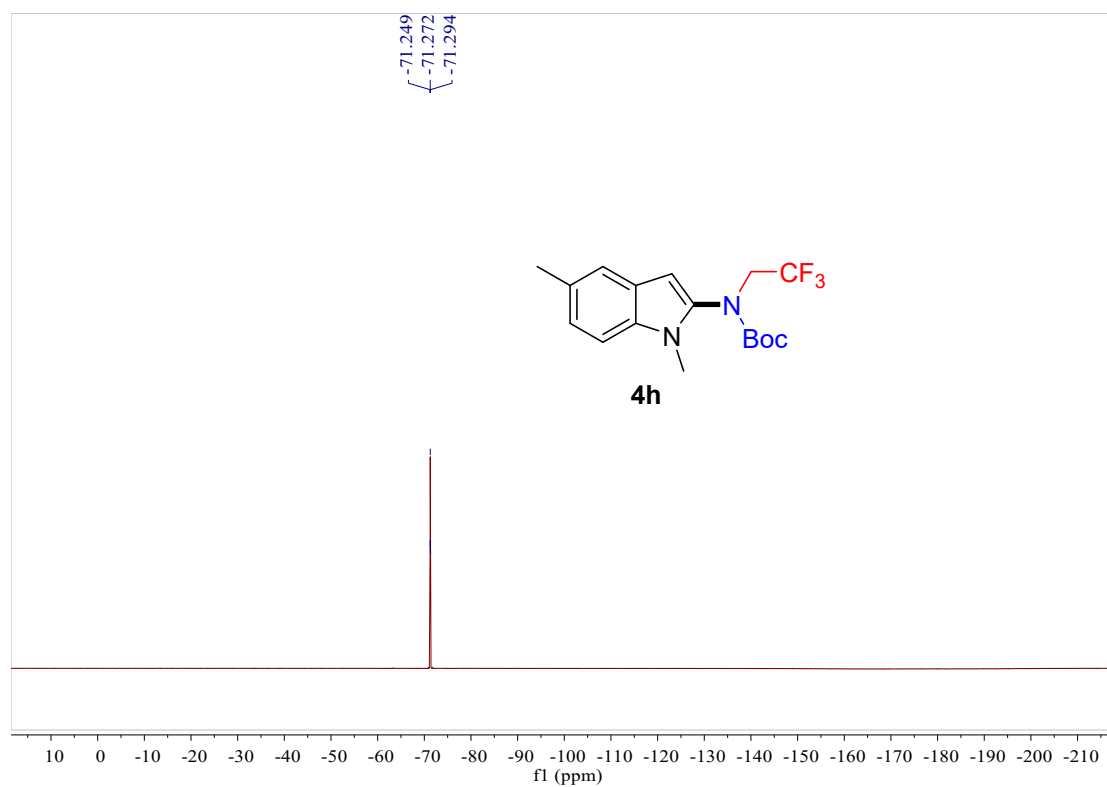
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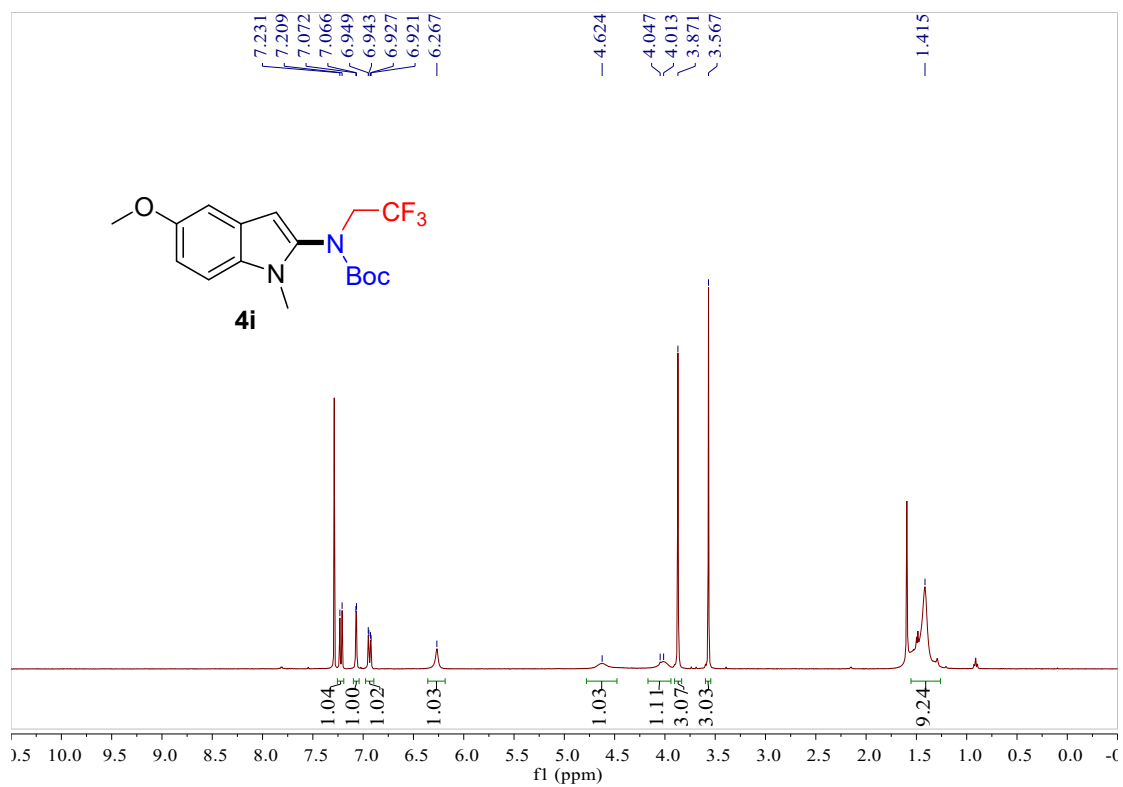
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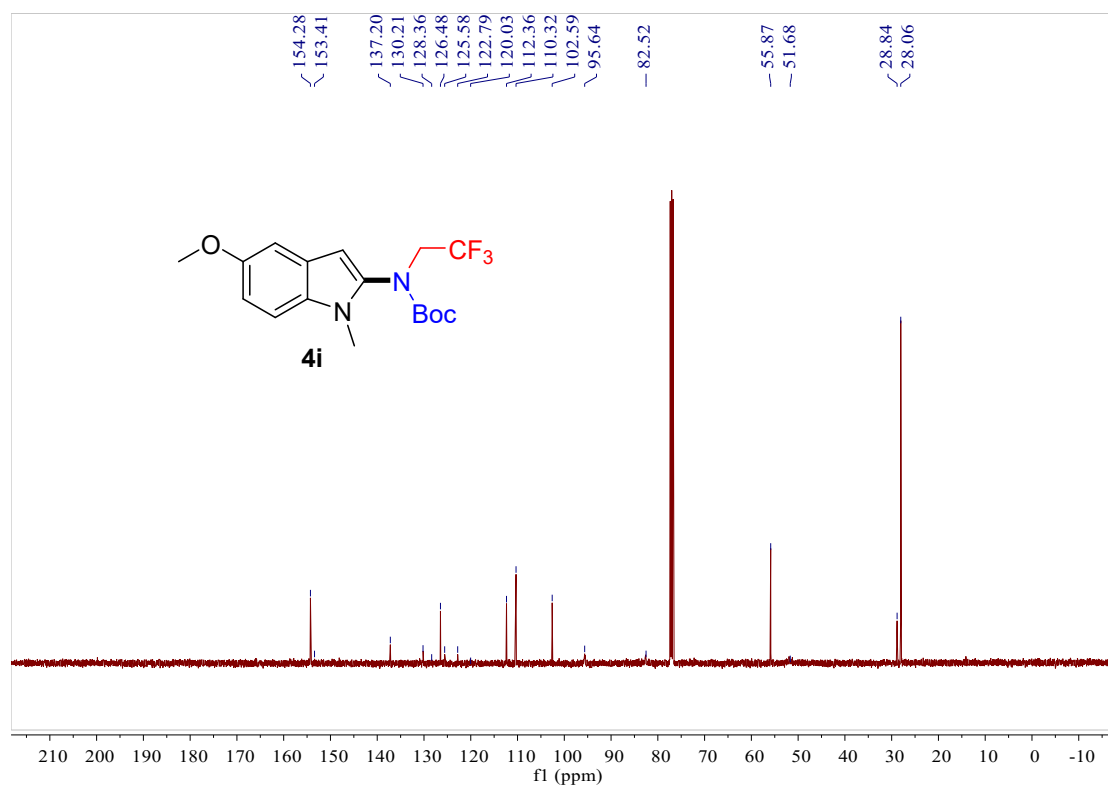
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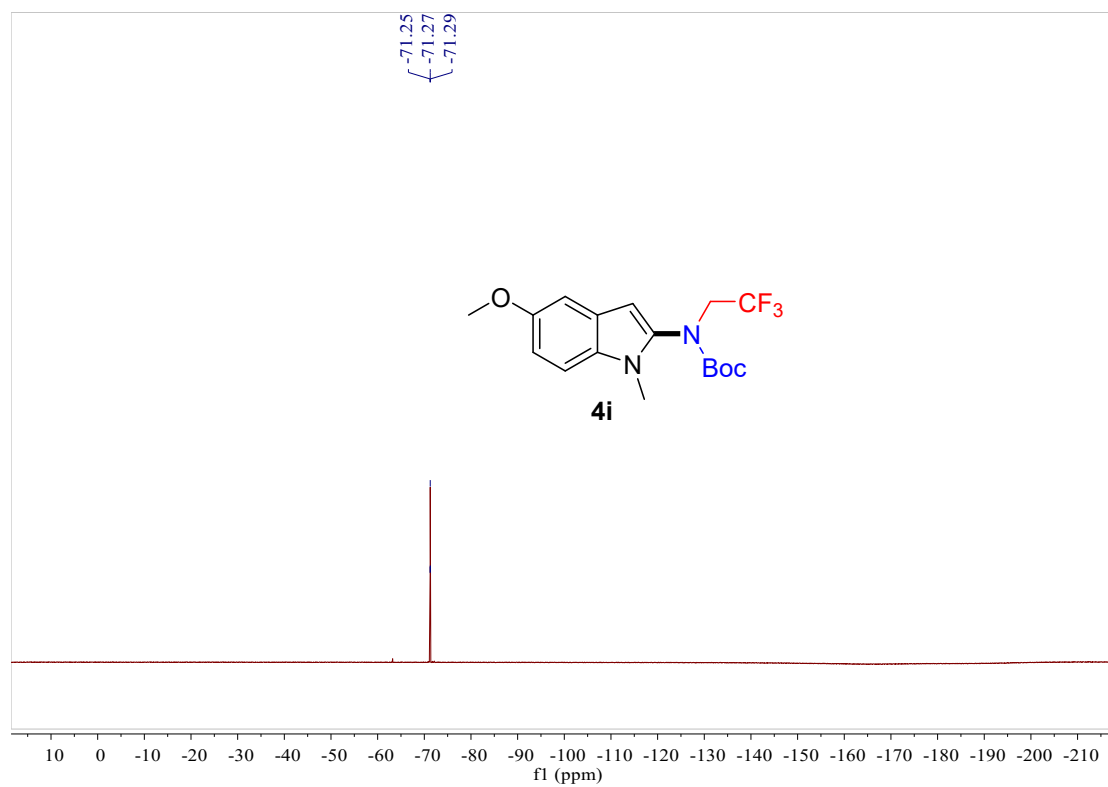
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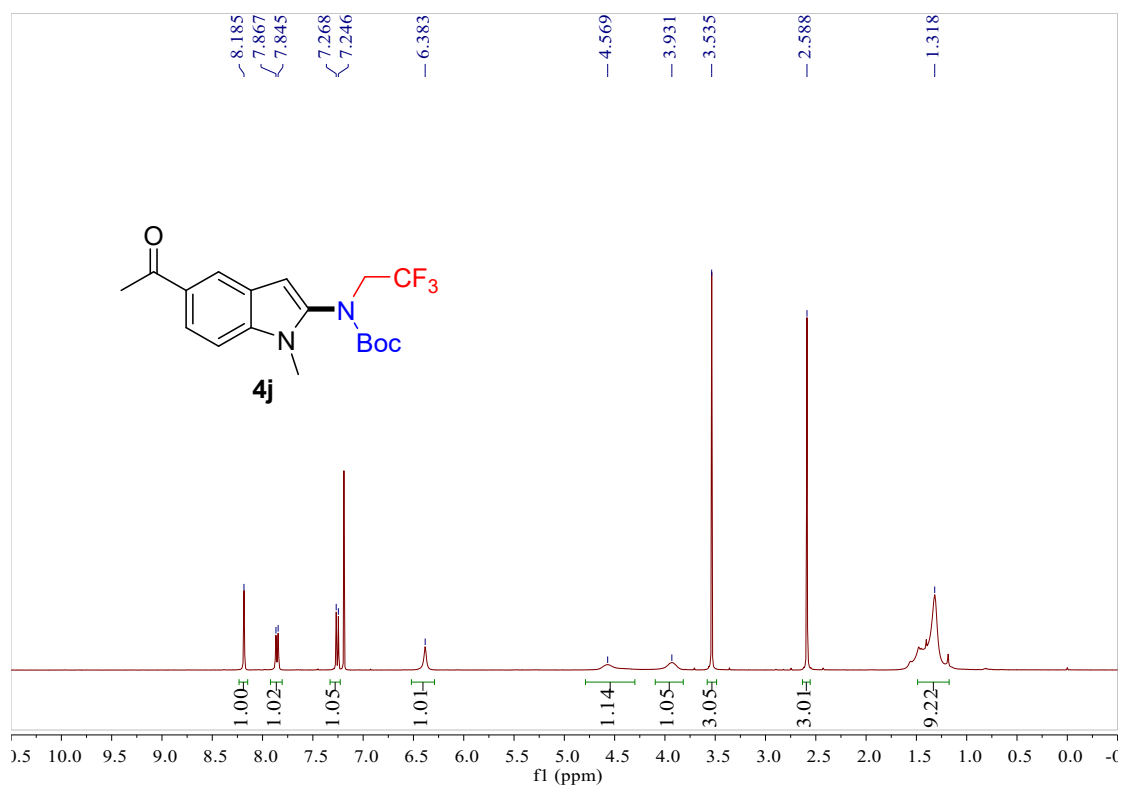
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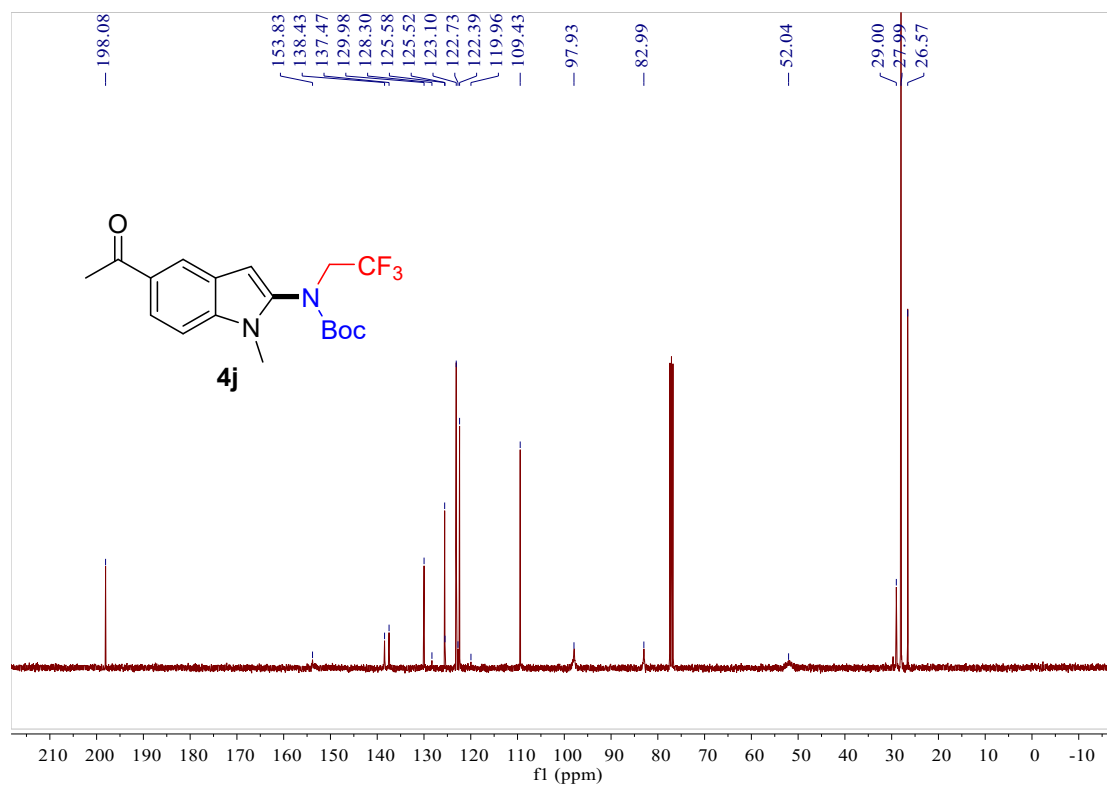
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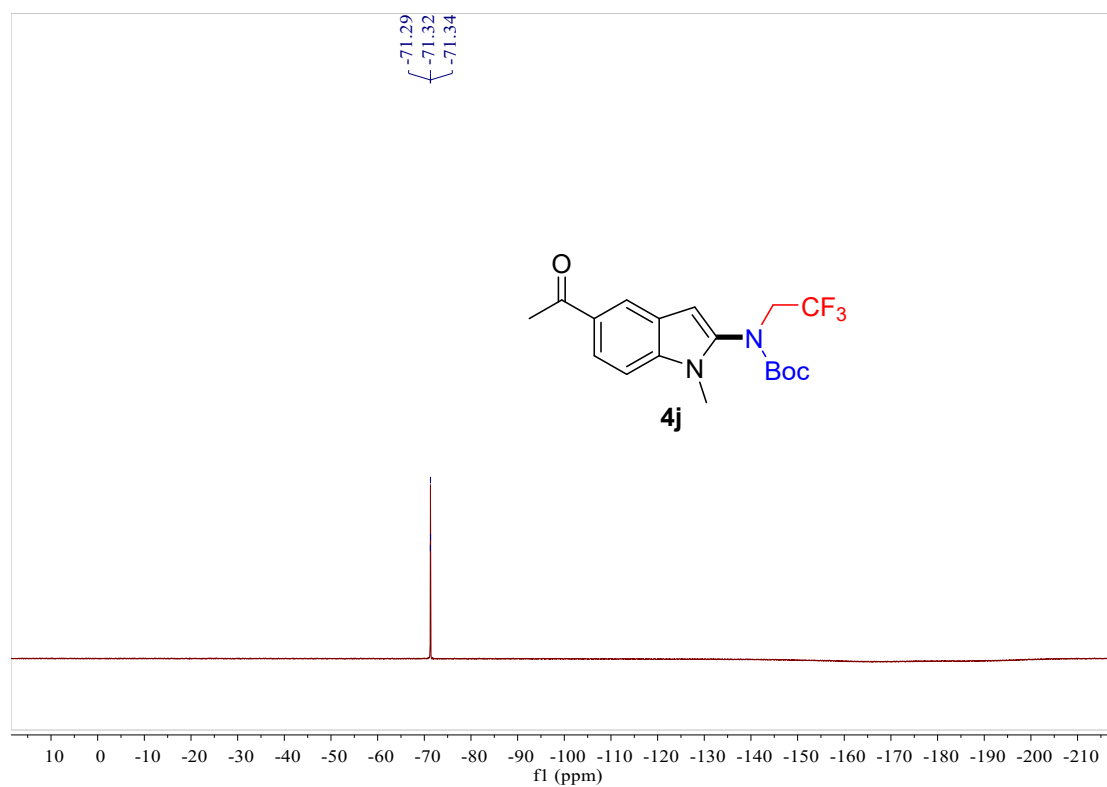
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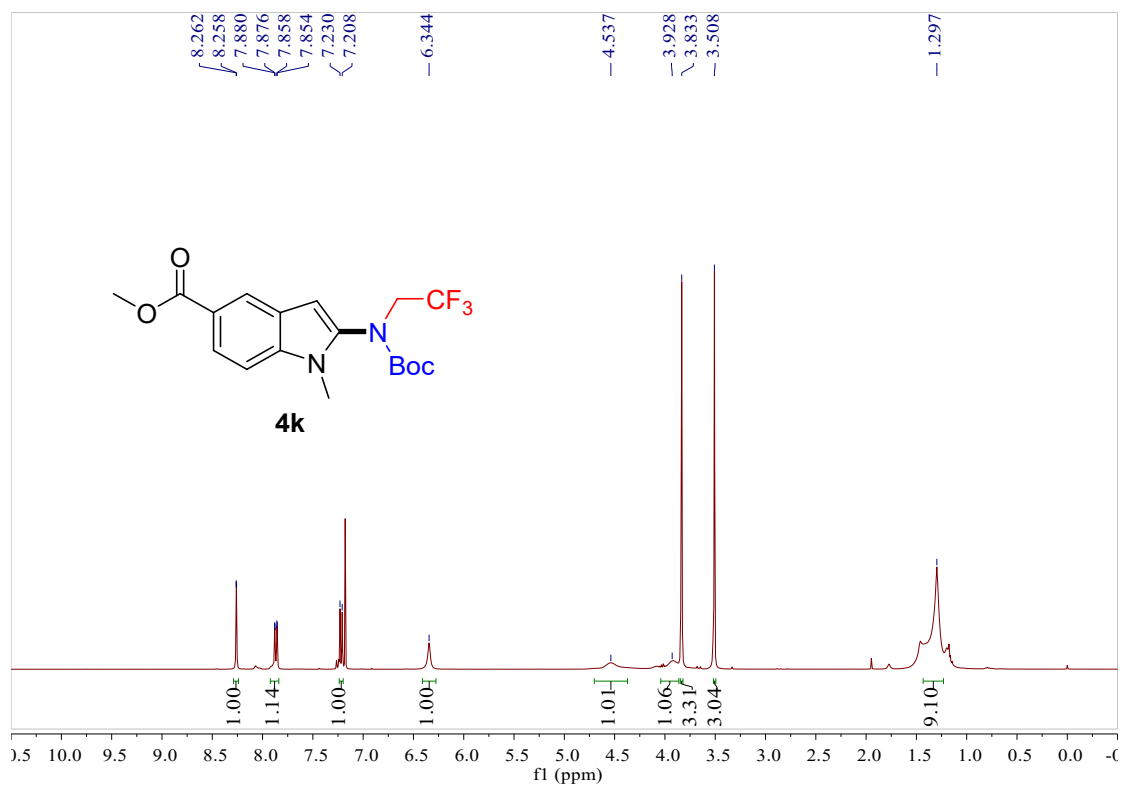
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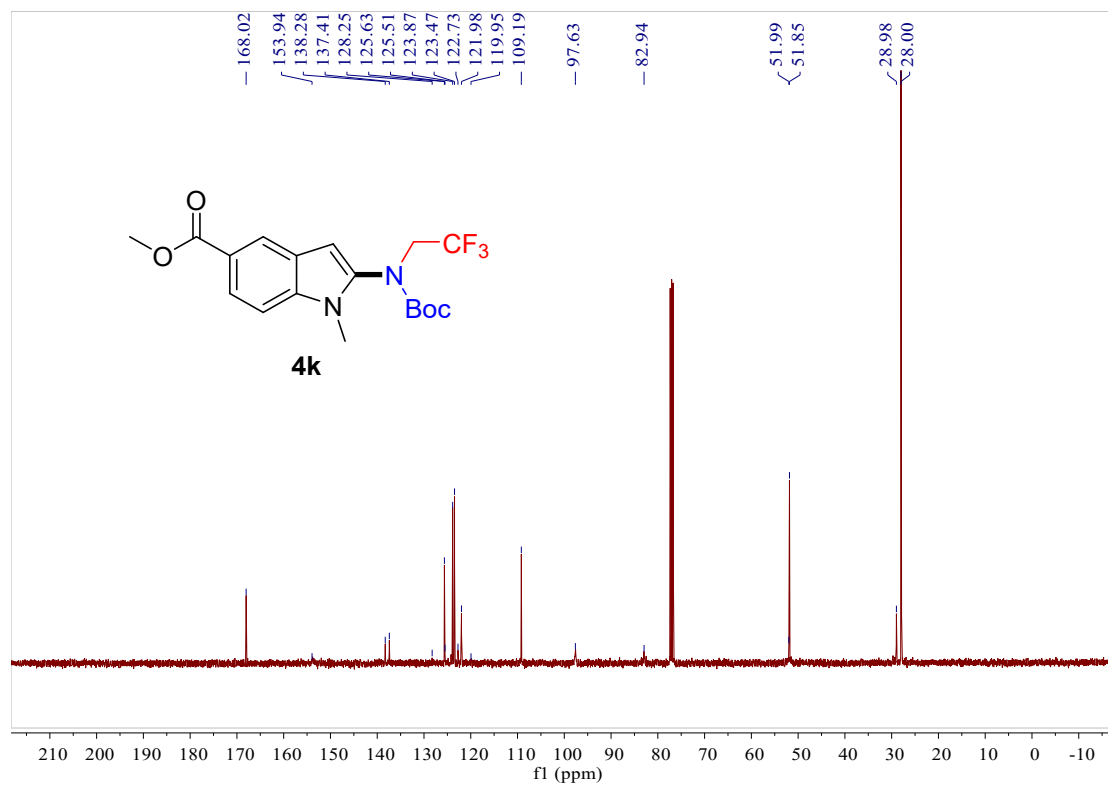
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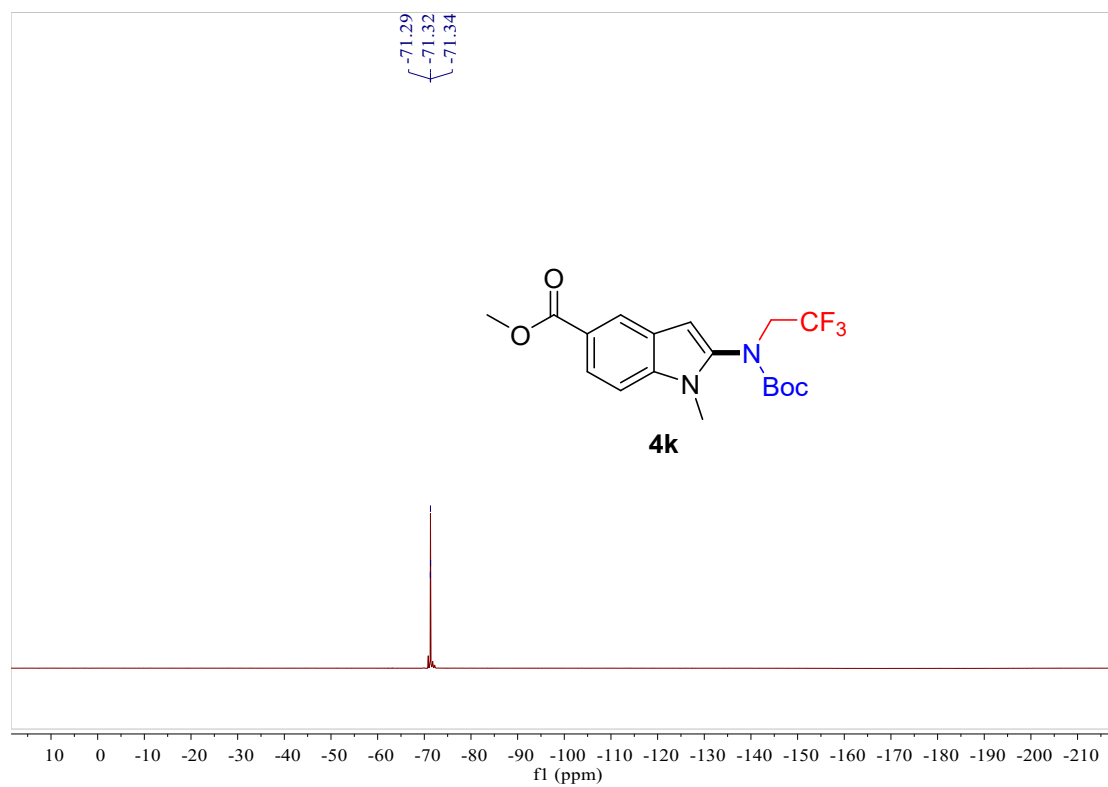
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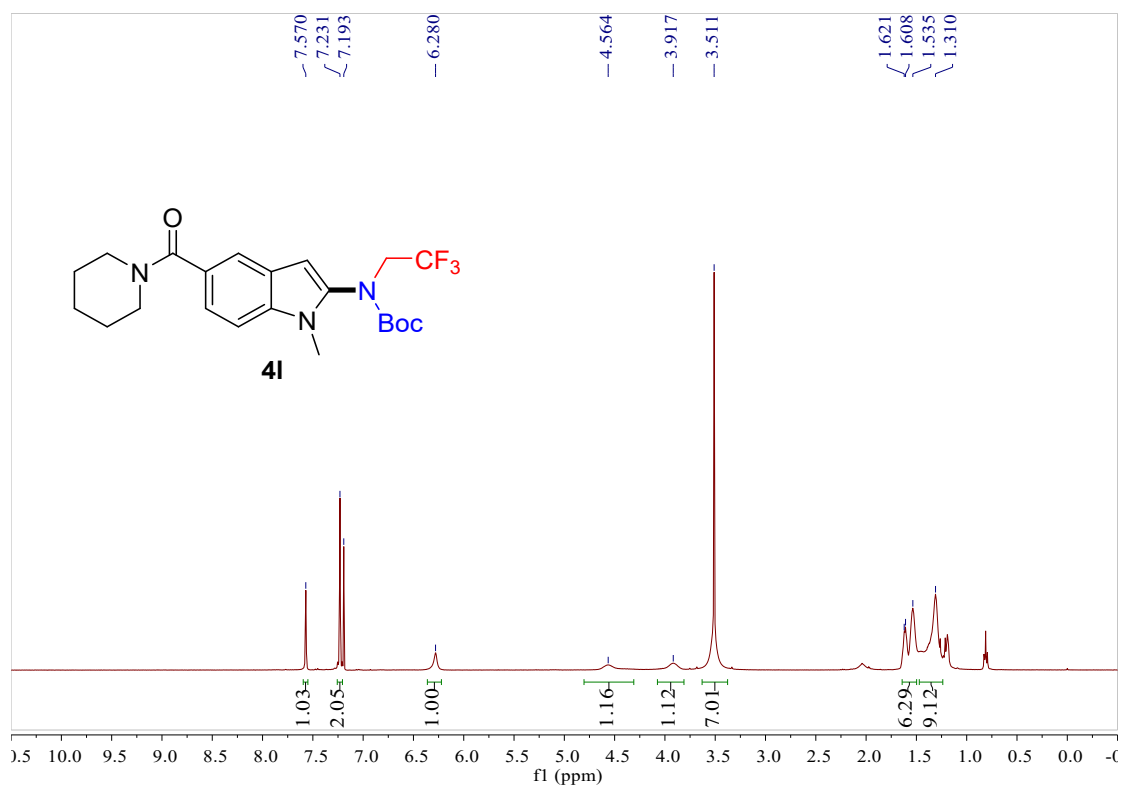
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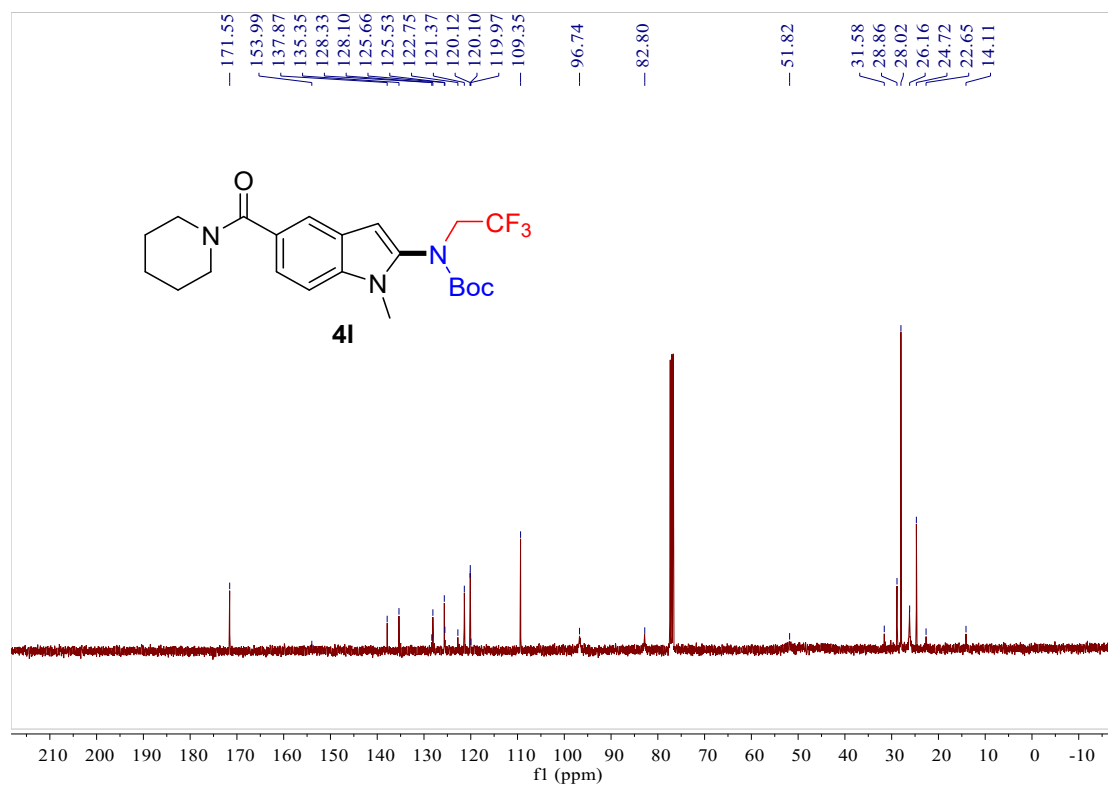
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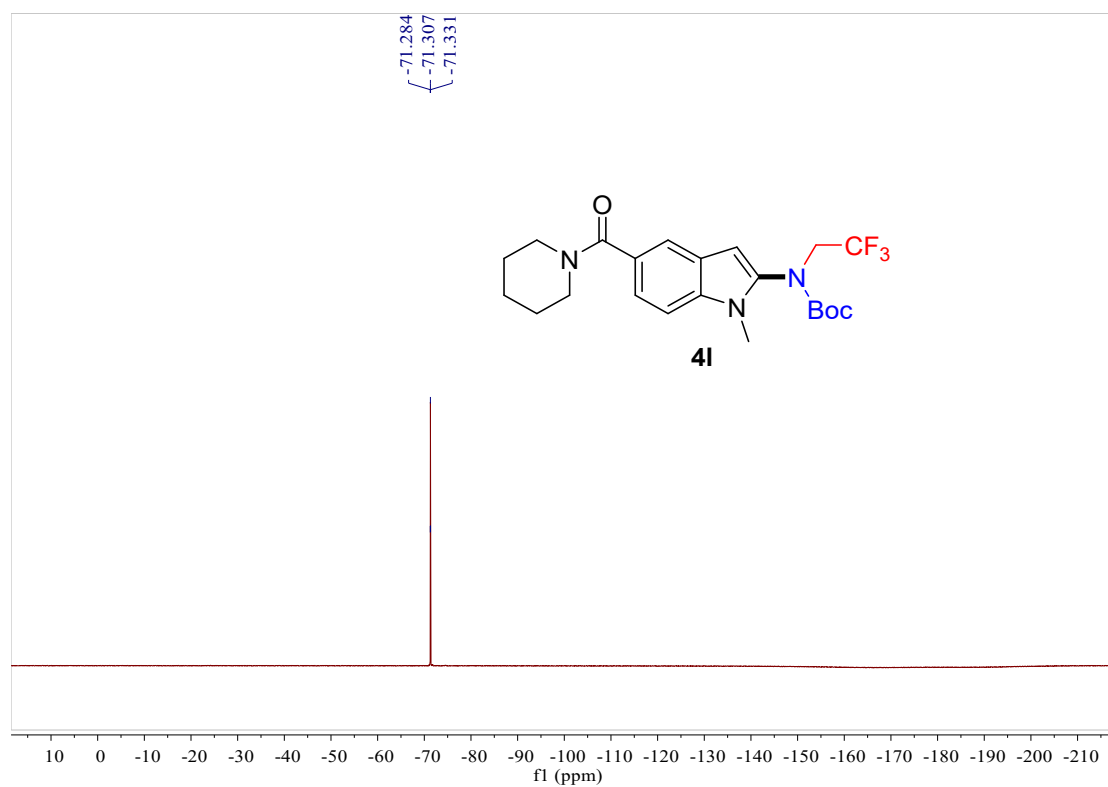
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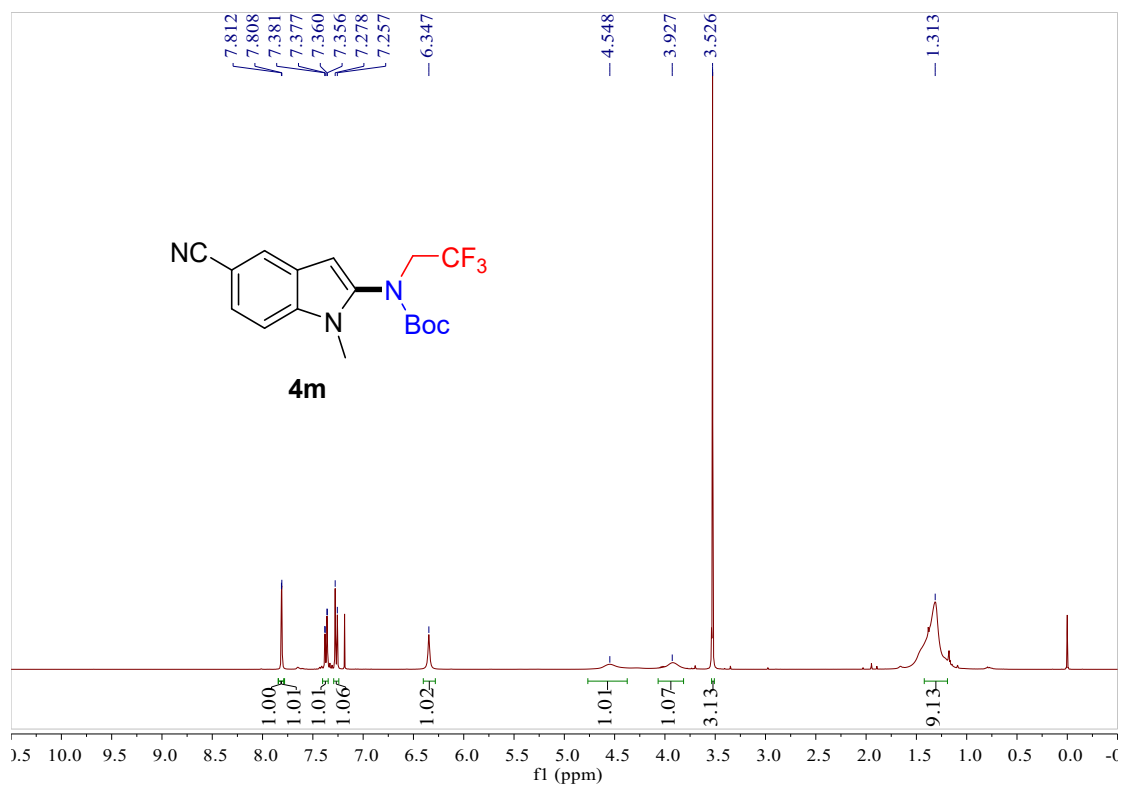
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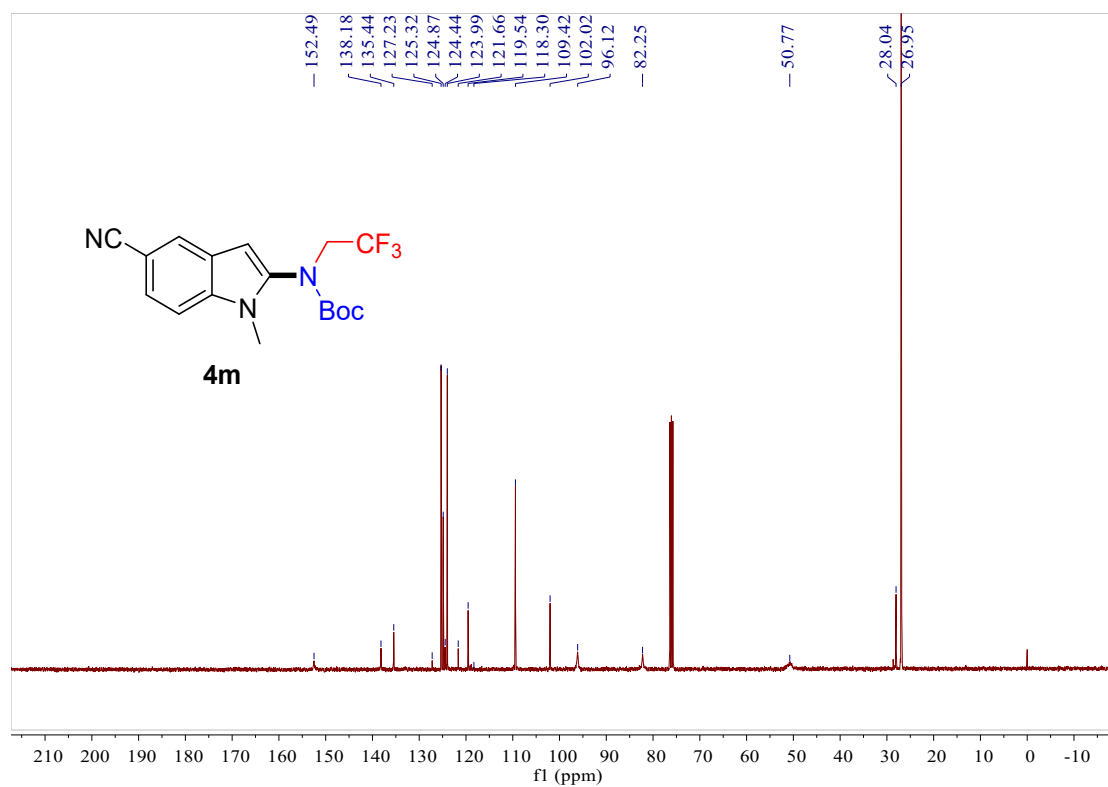
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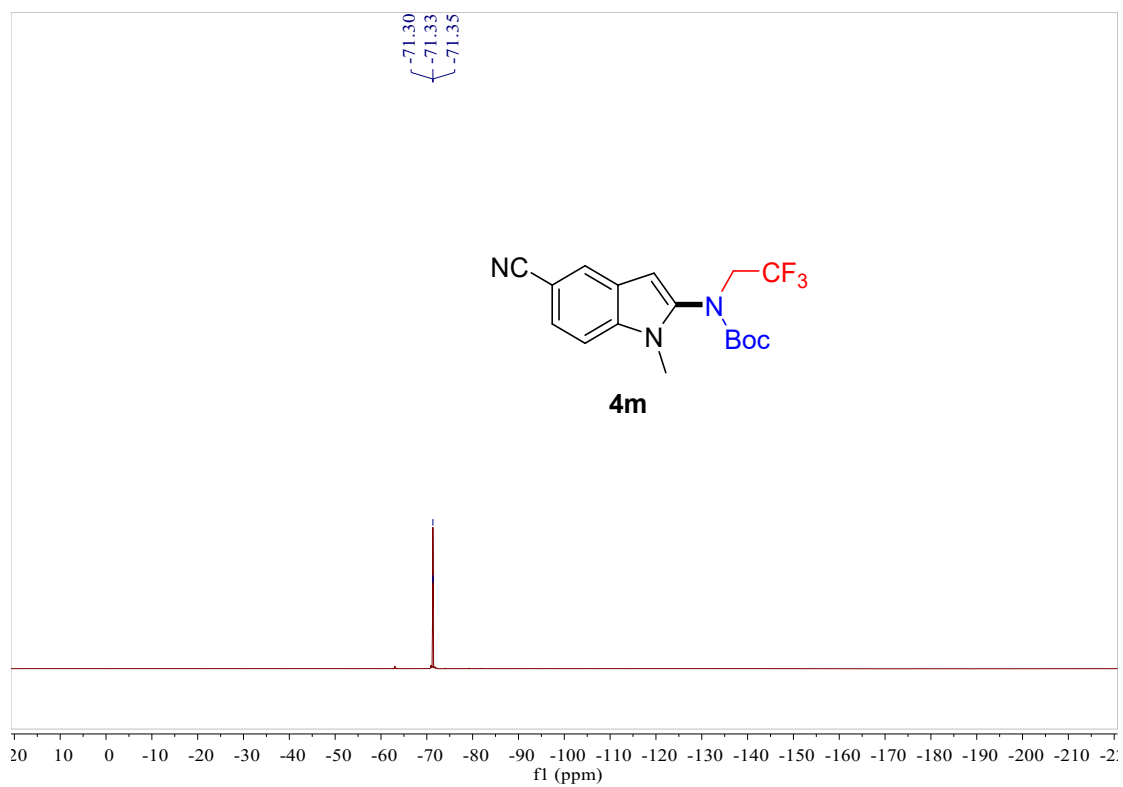
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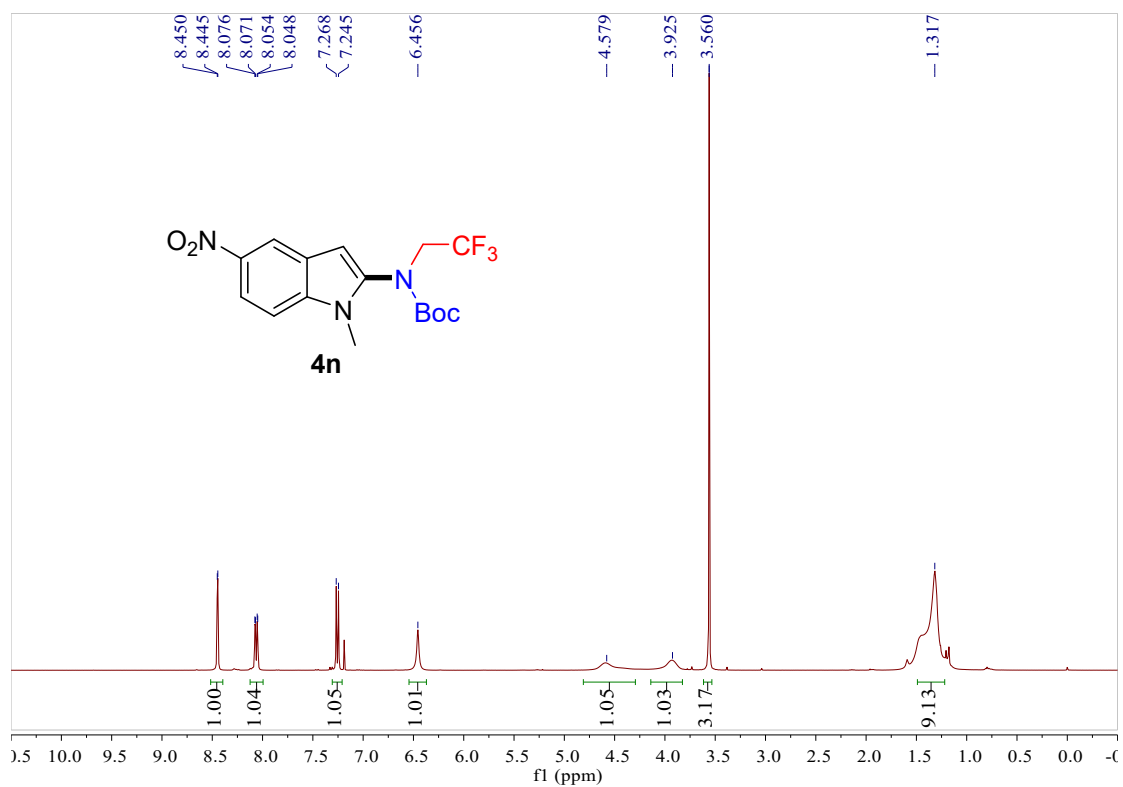
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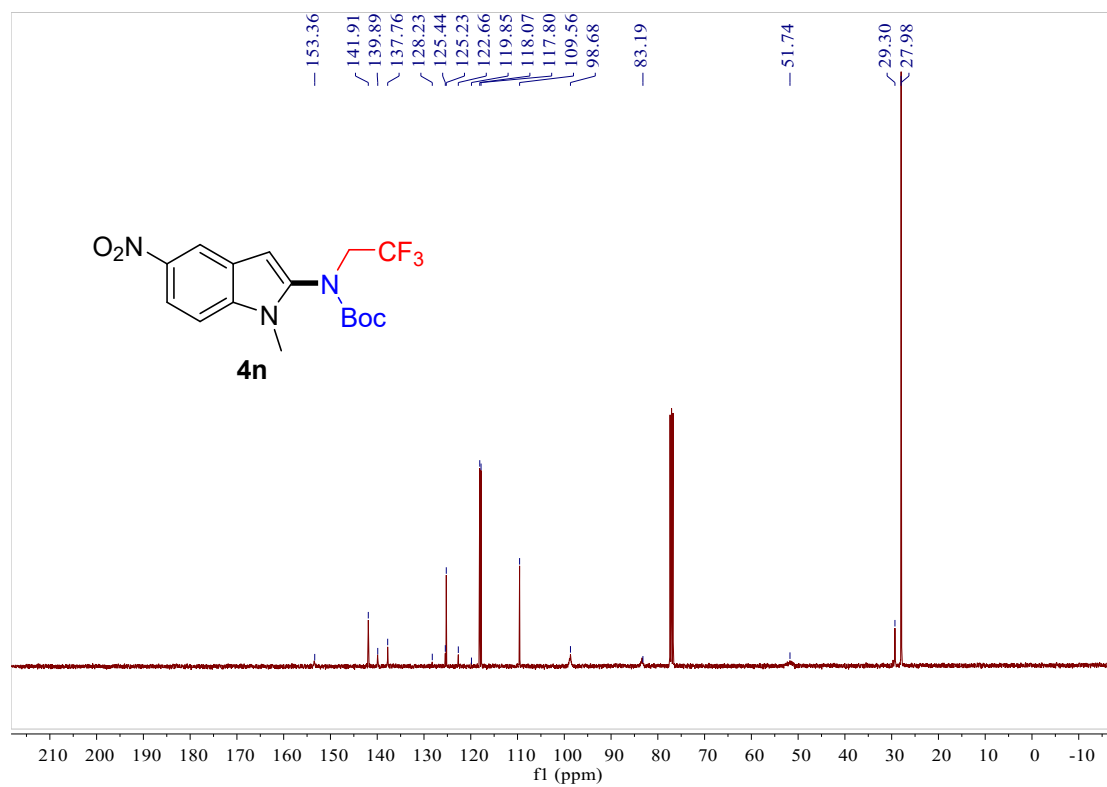
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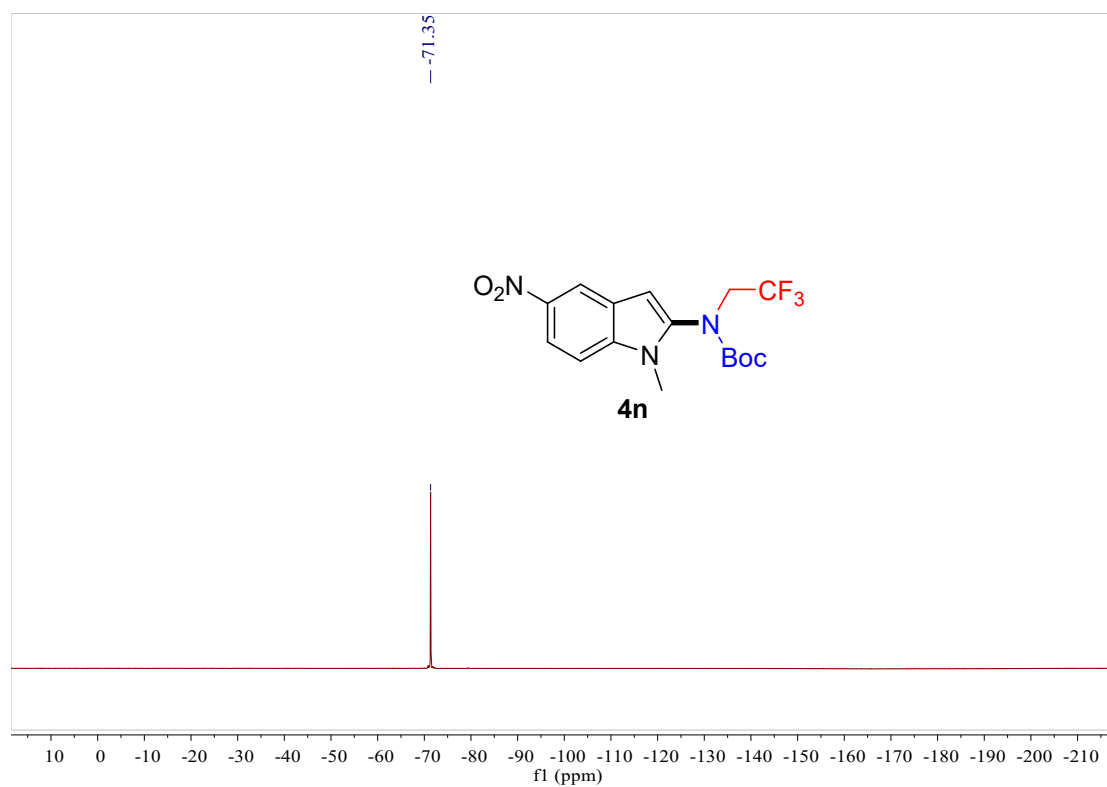
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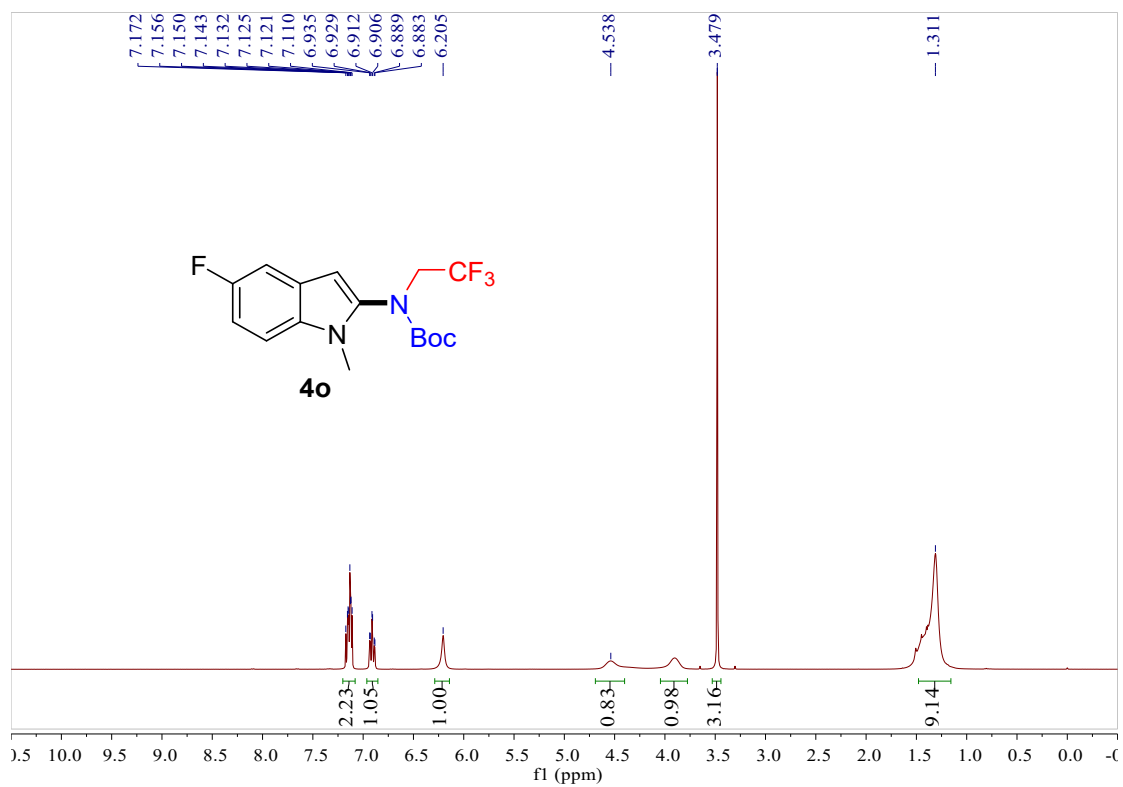
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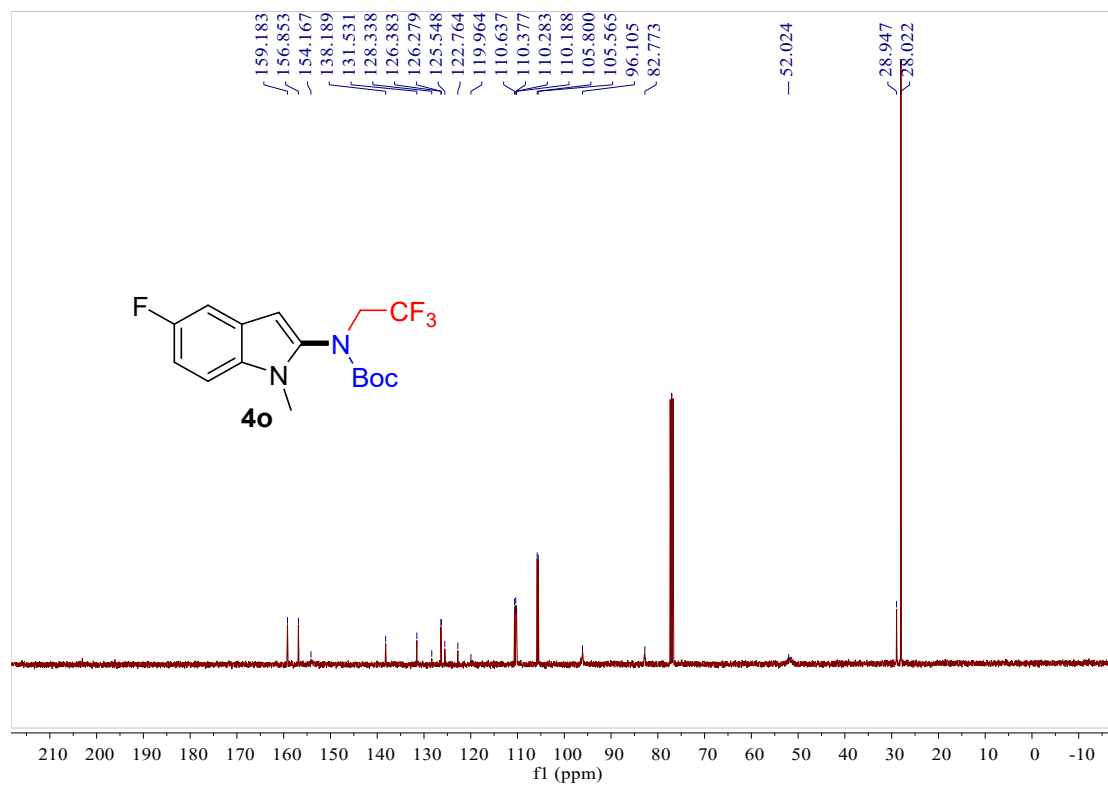
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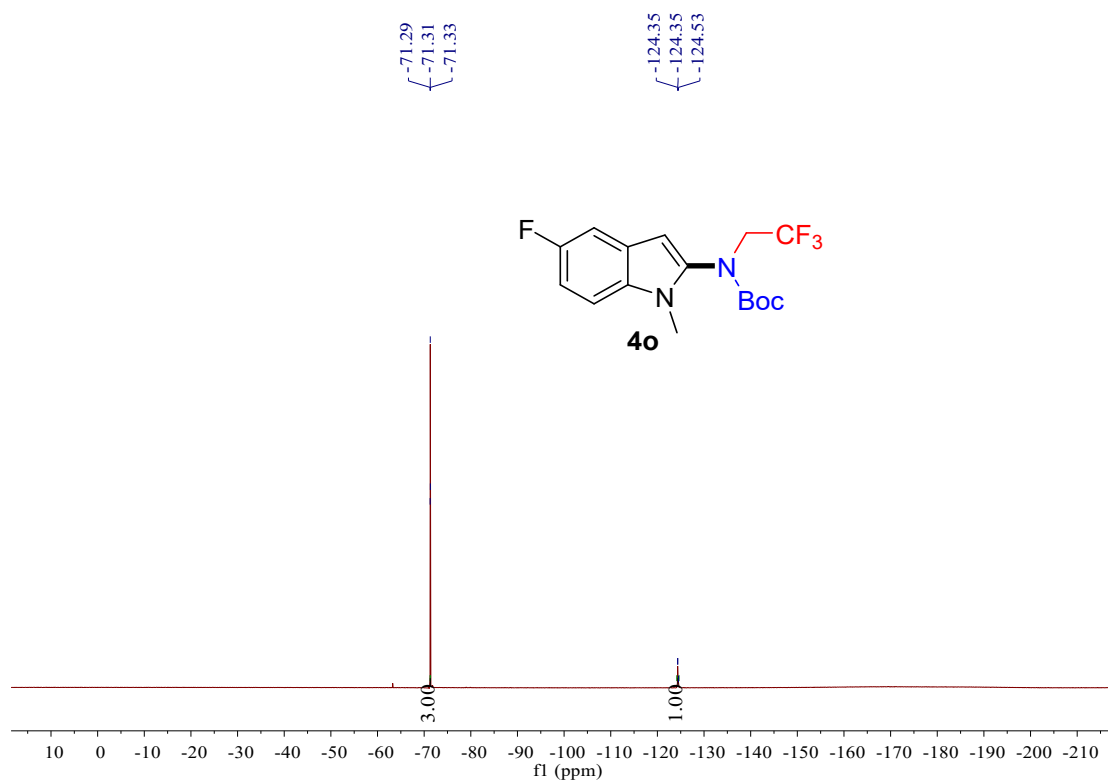
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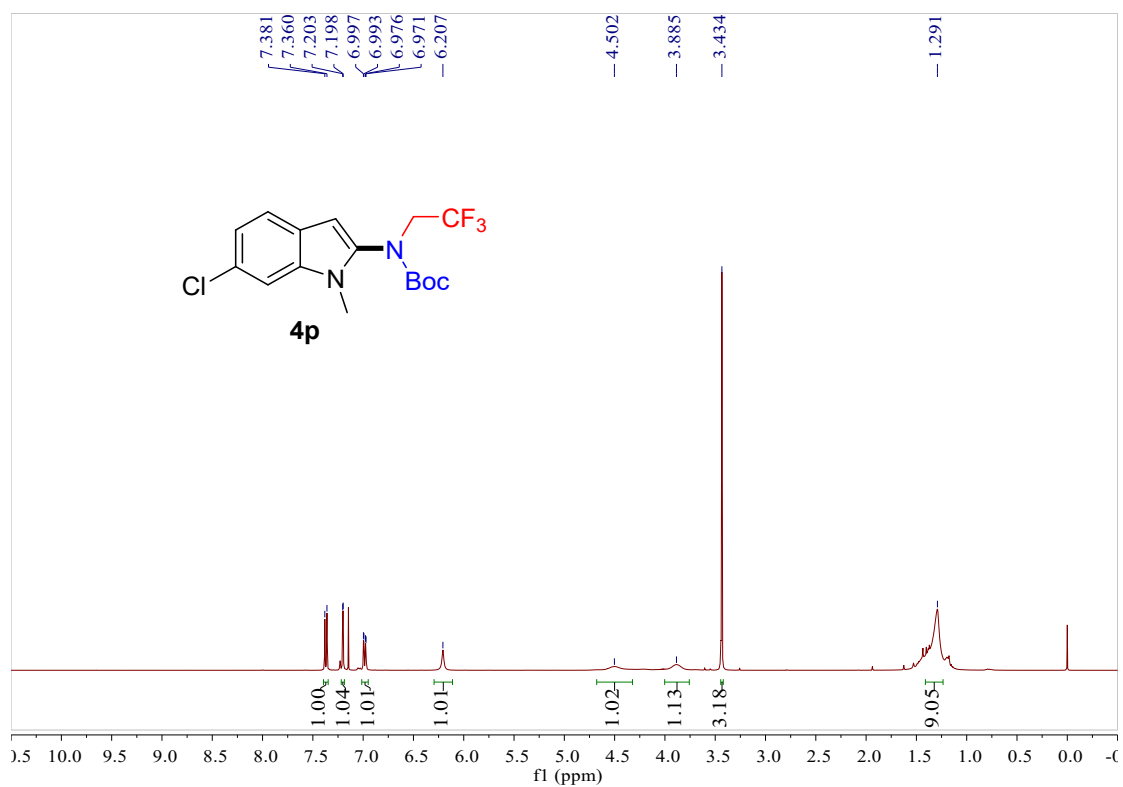
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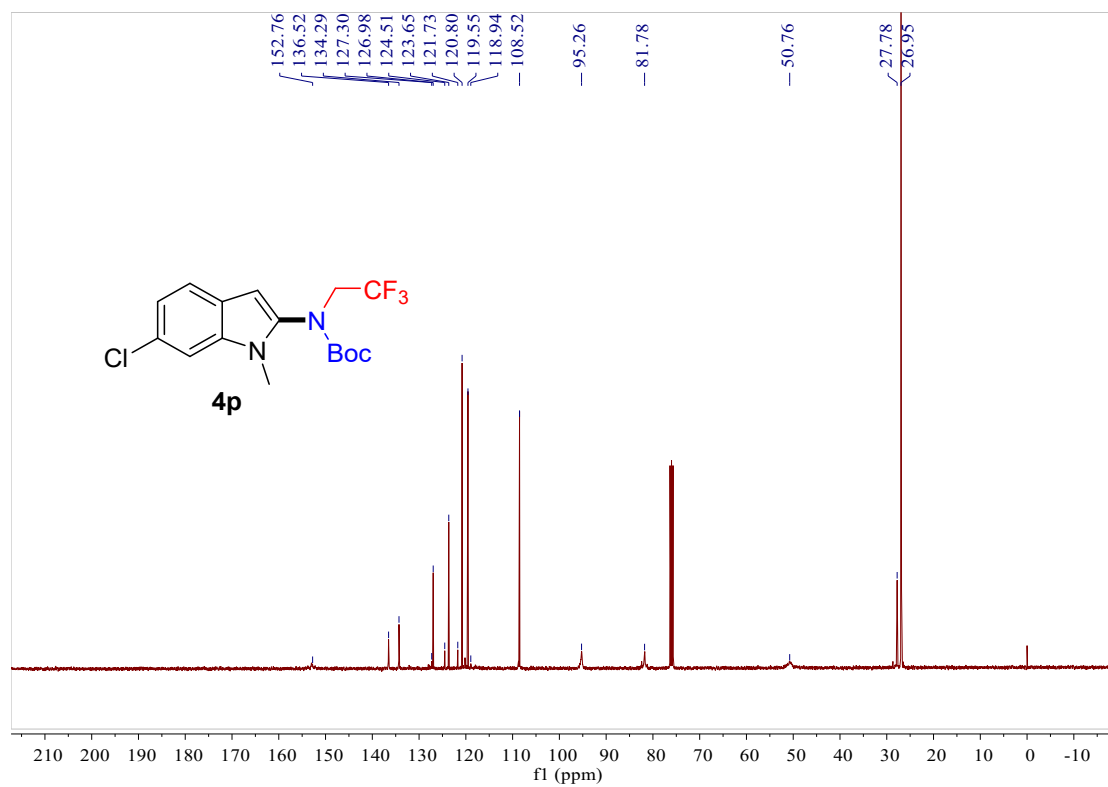
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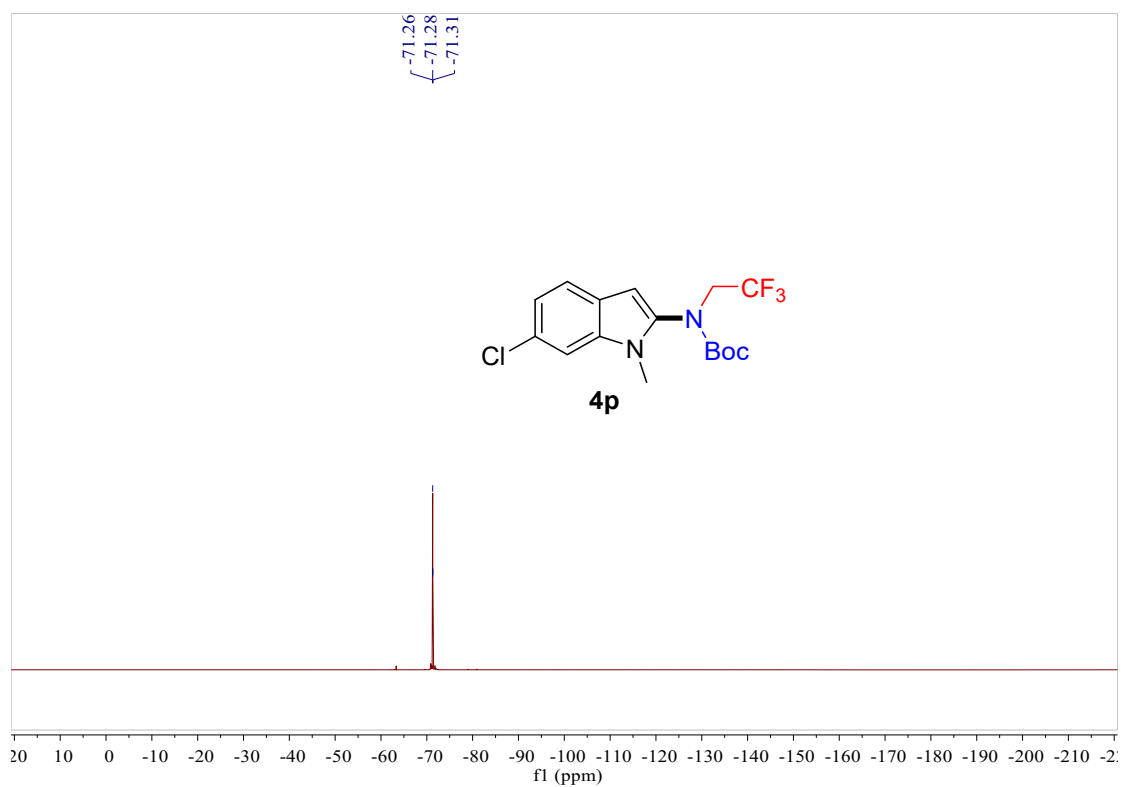
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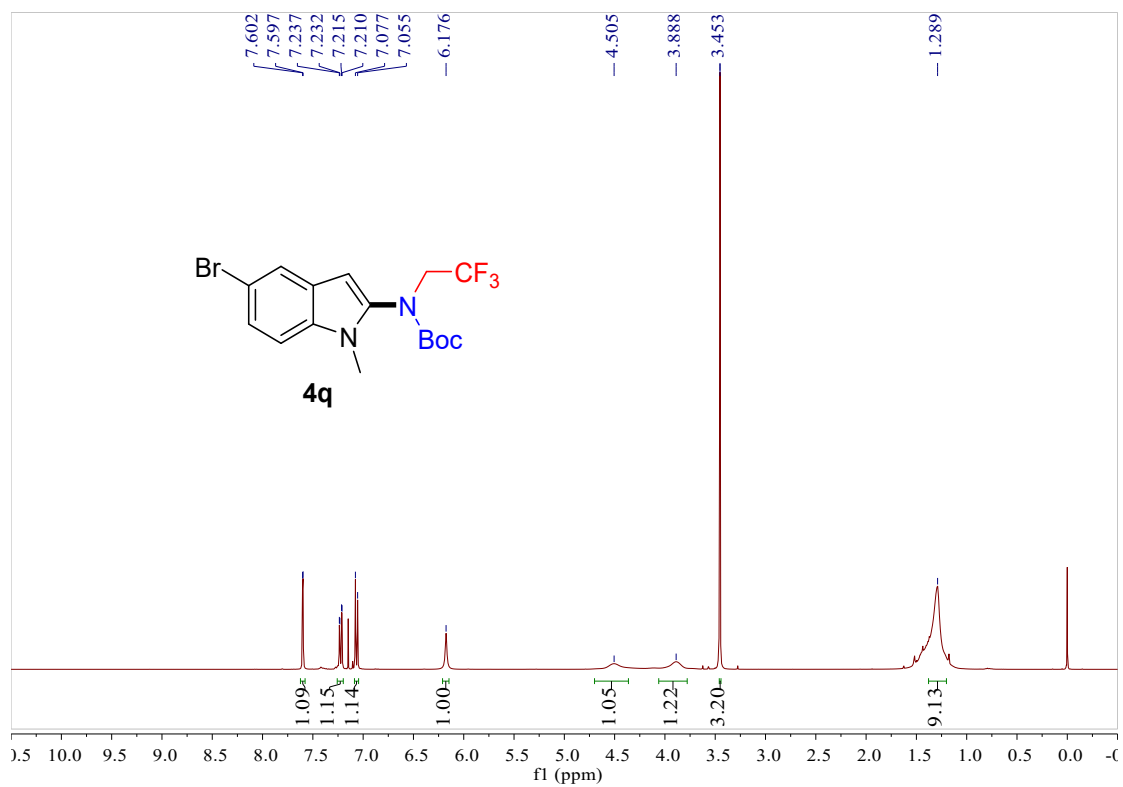
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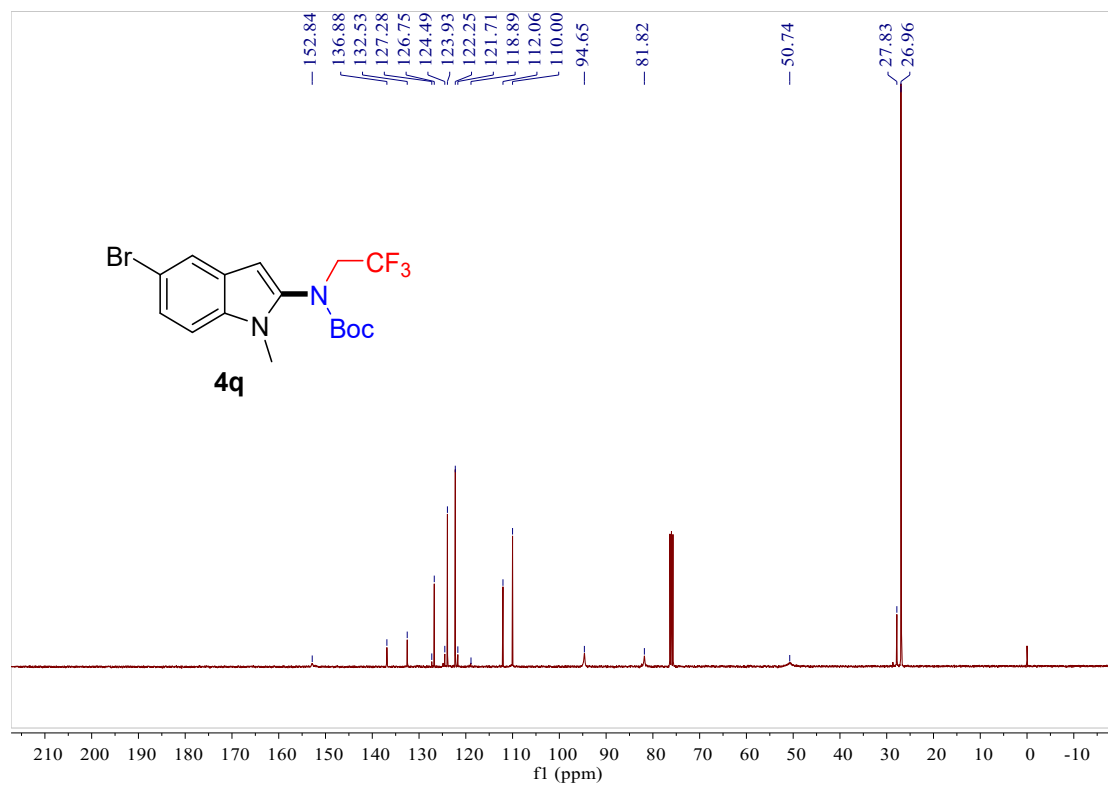
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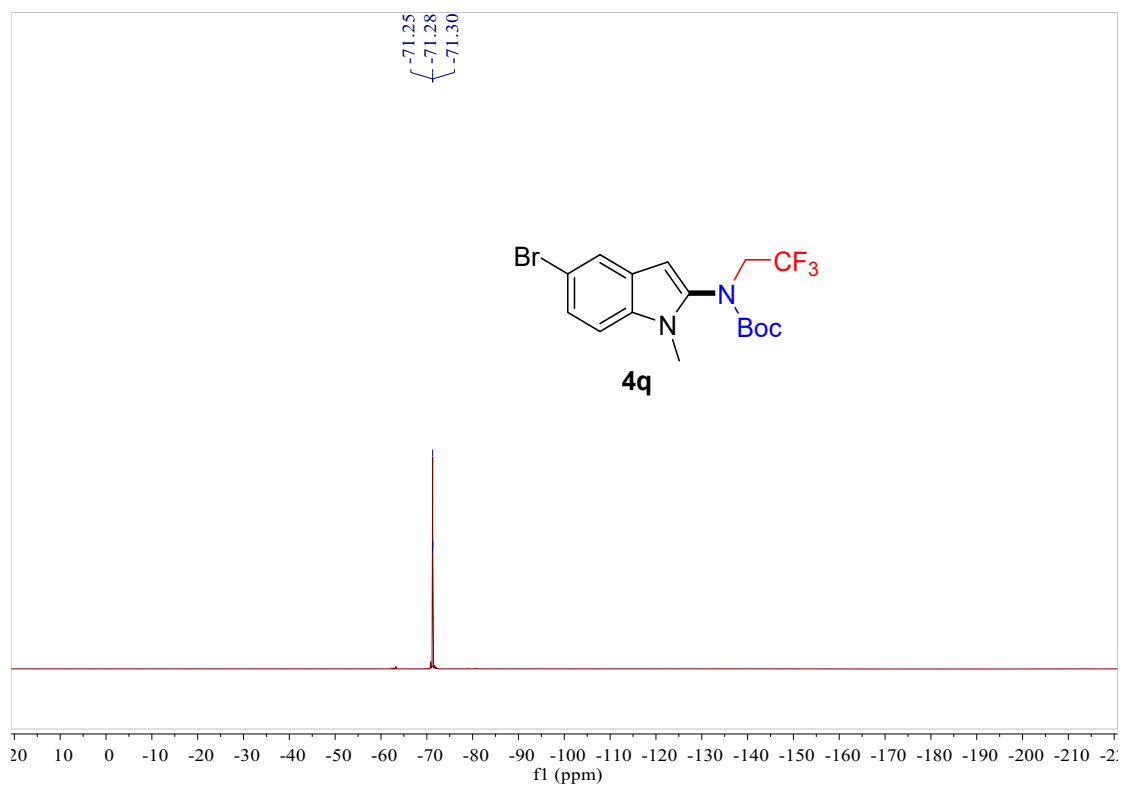
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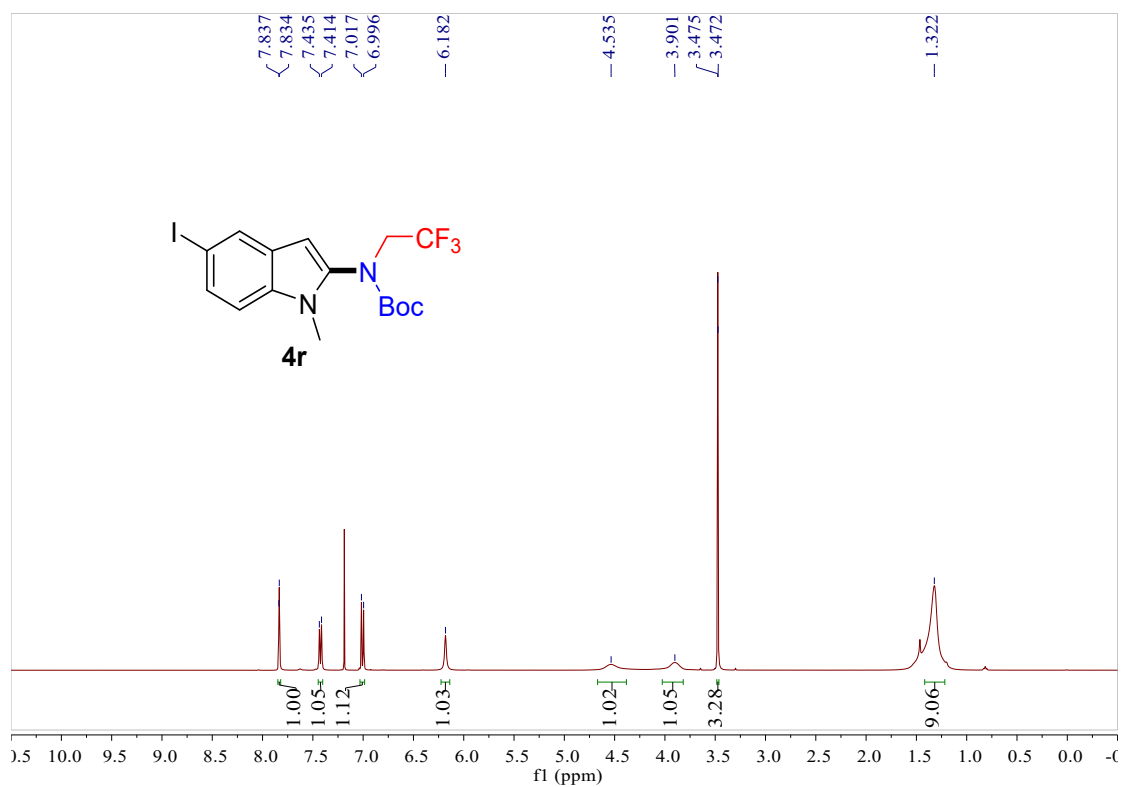
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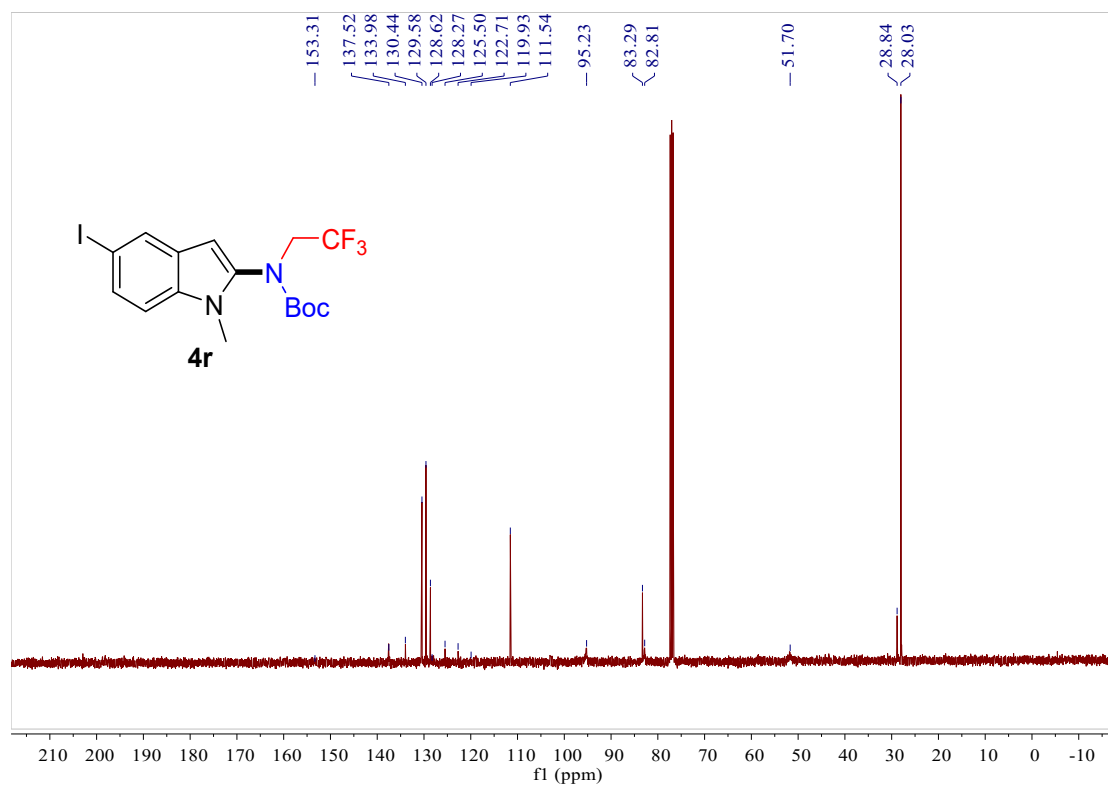
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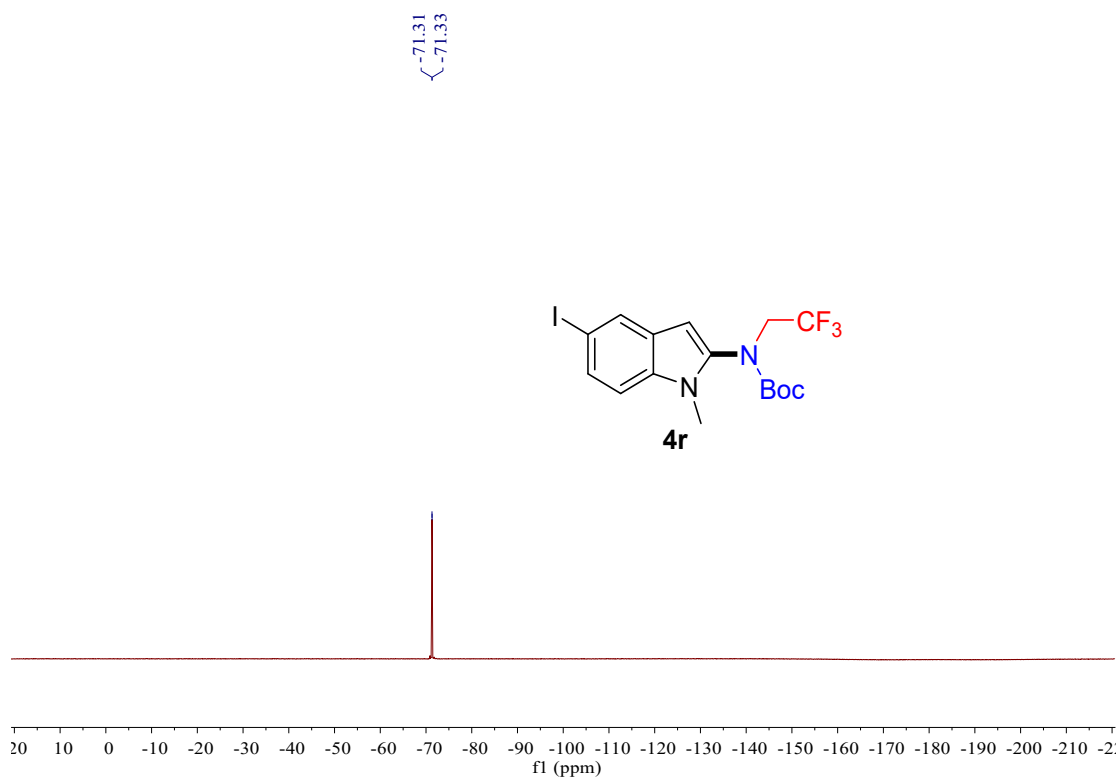
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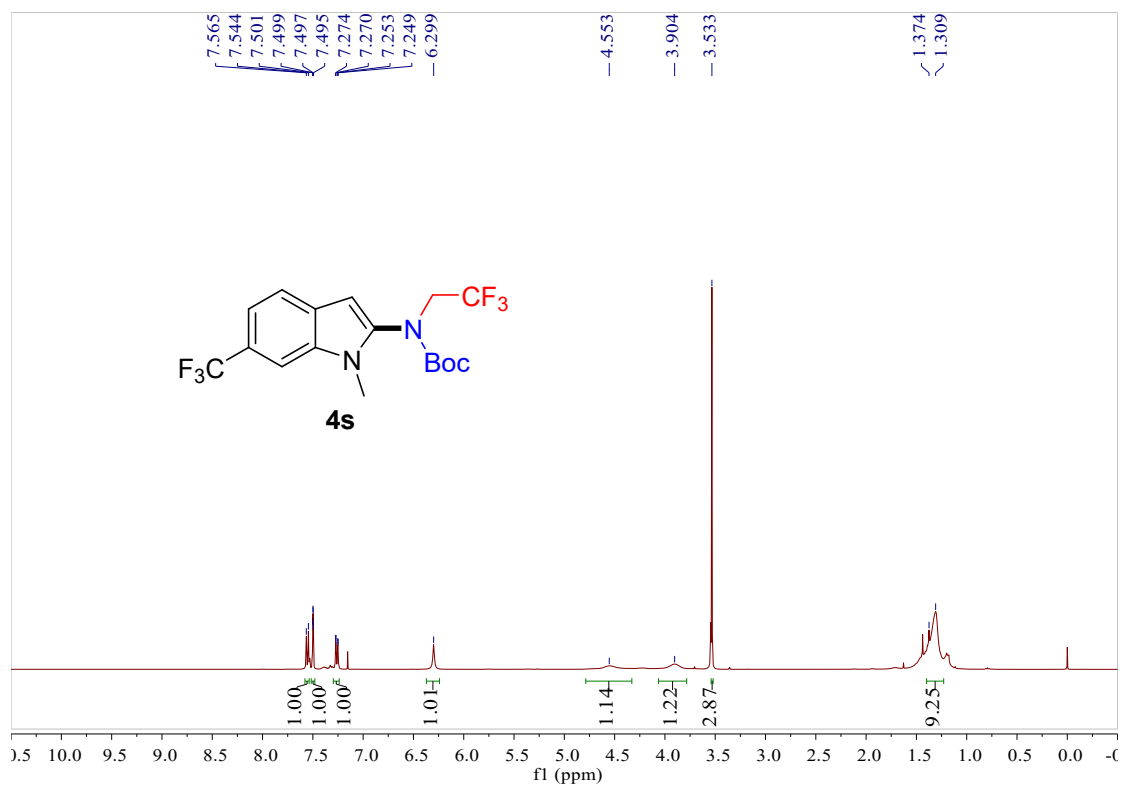
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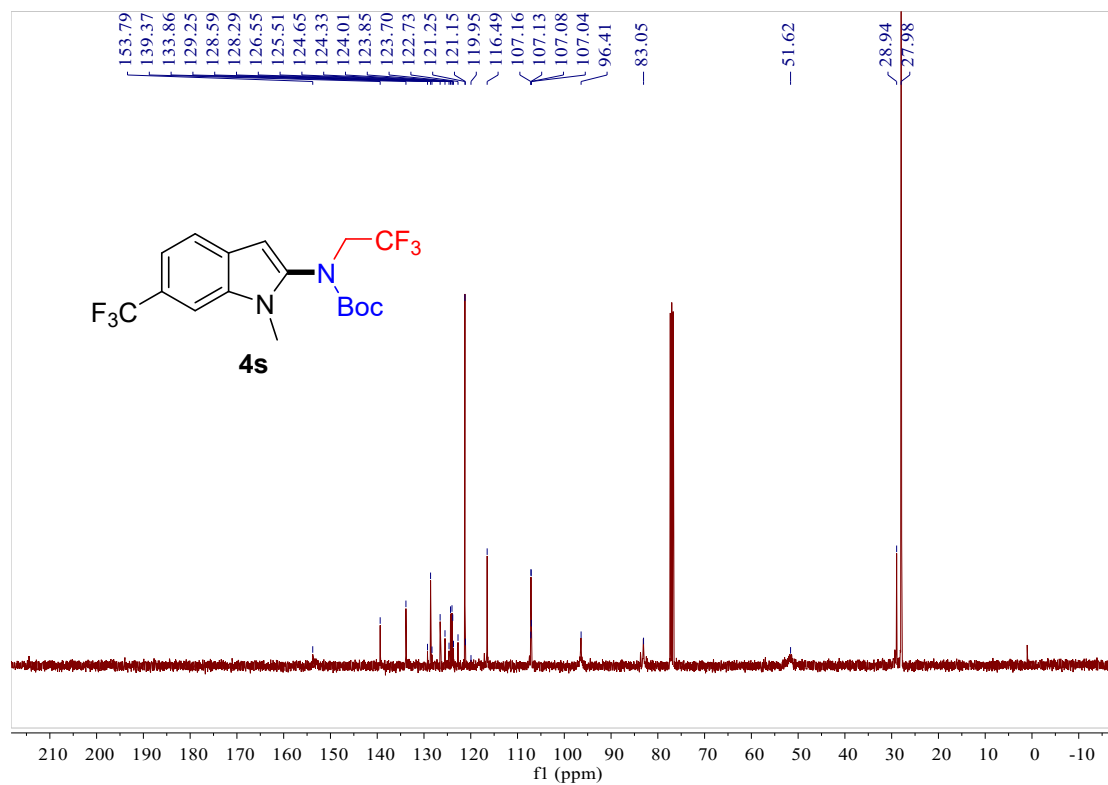
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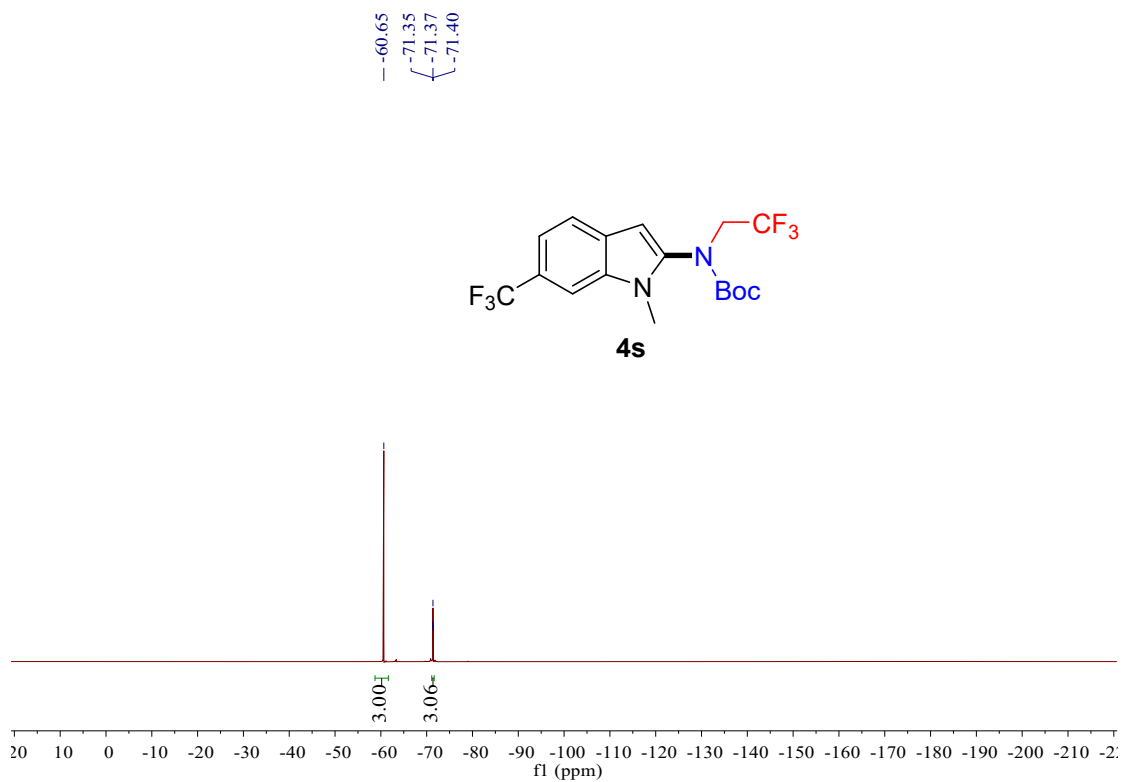
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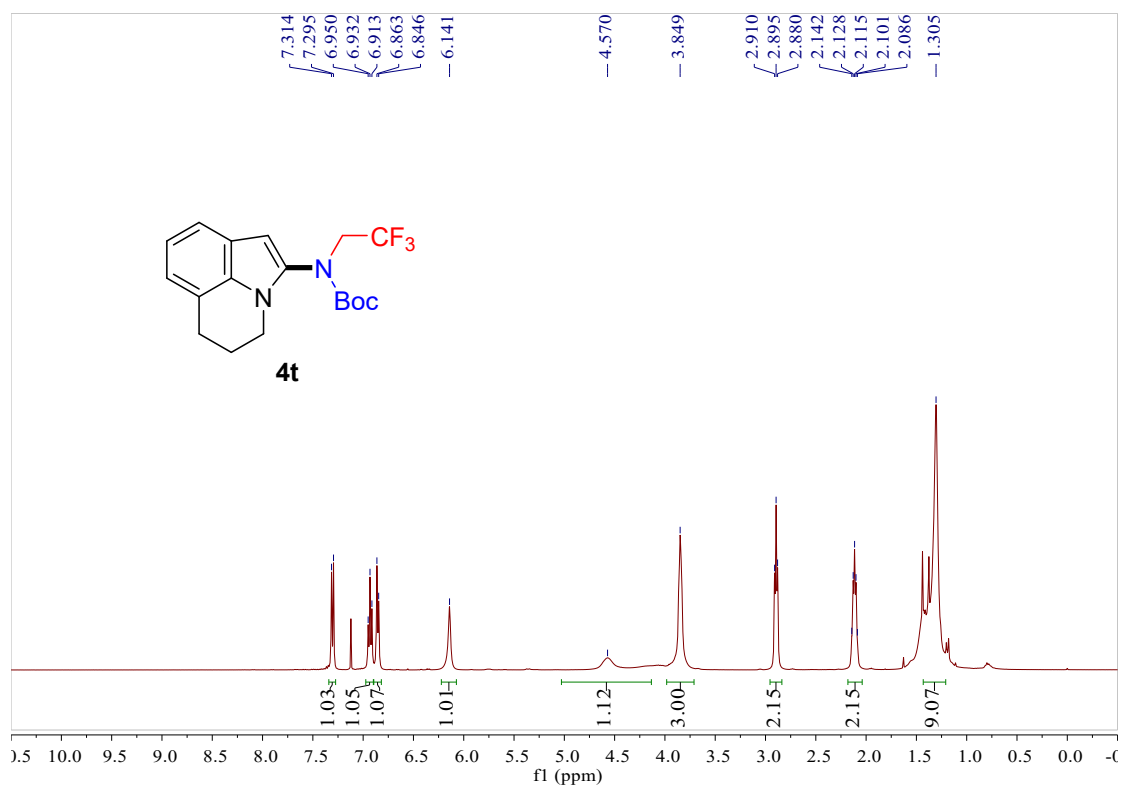
¹³C NMR (101 MHz, CDCl₃)



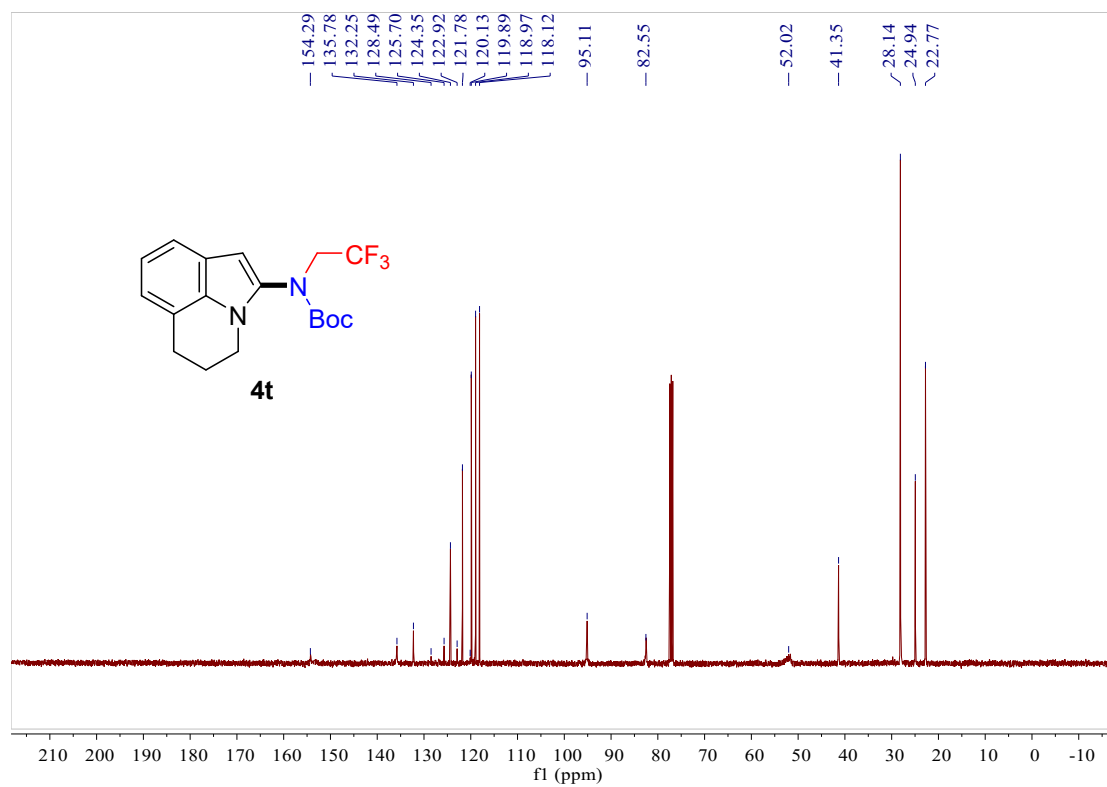
¹⁹F NMR (376 MHz, CDCl₃)



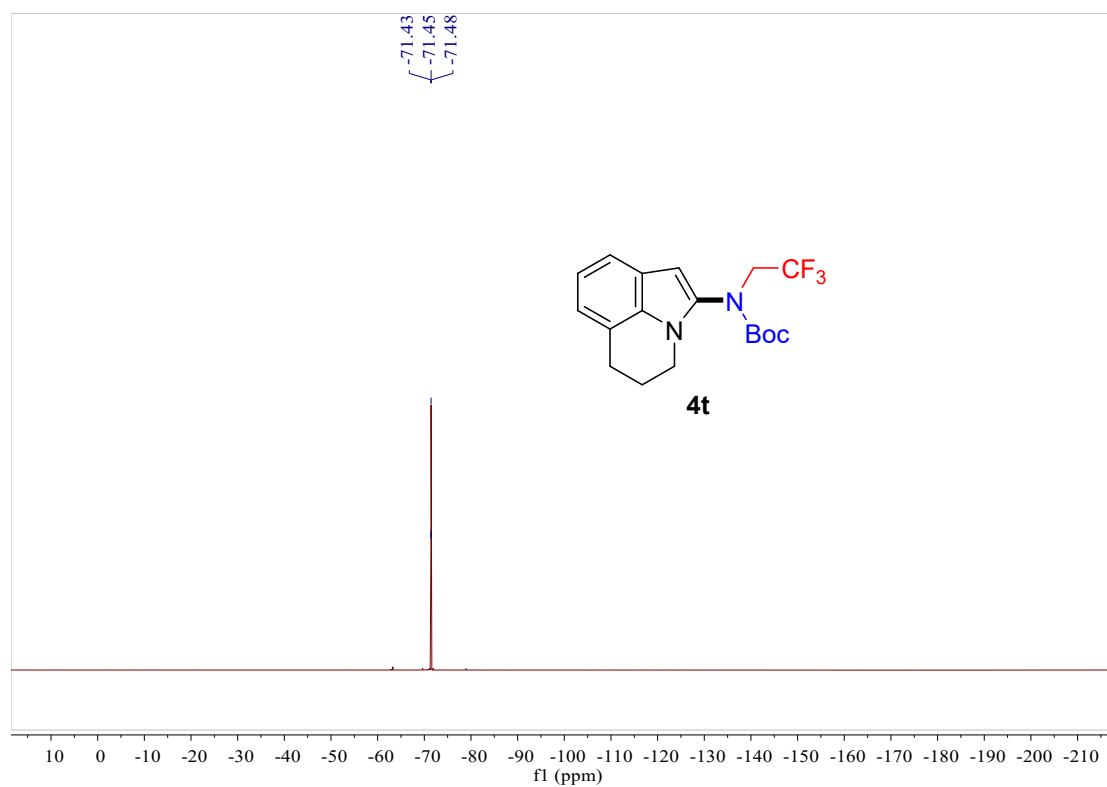
^1H NMR (400 MHz, CDCl_3)



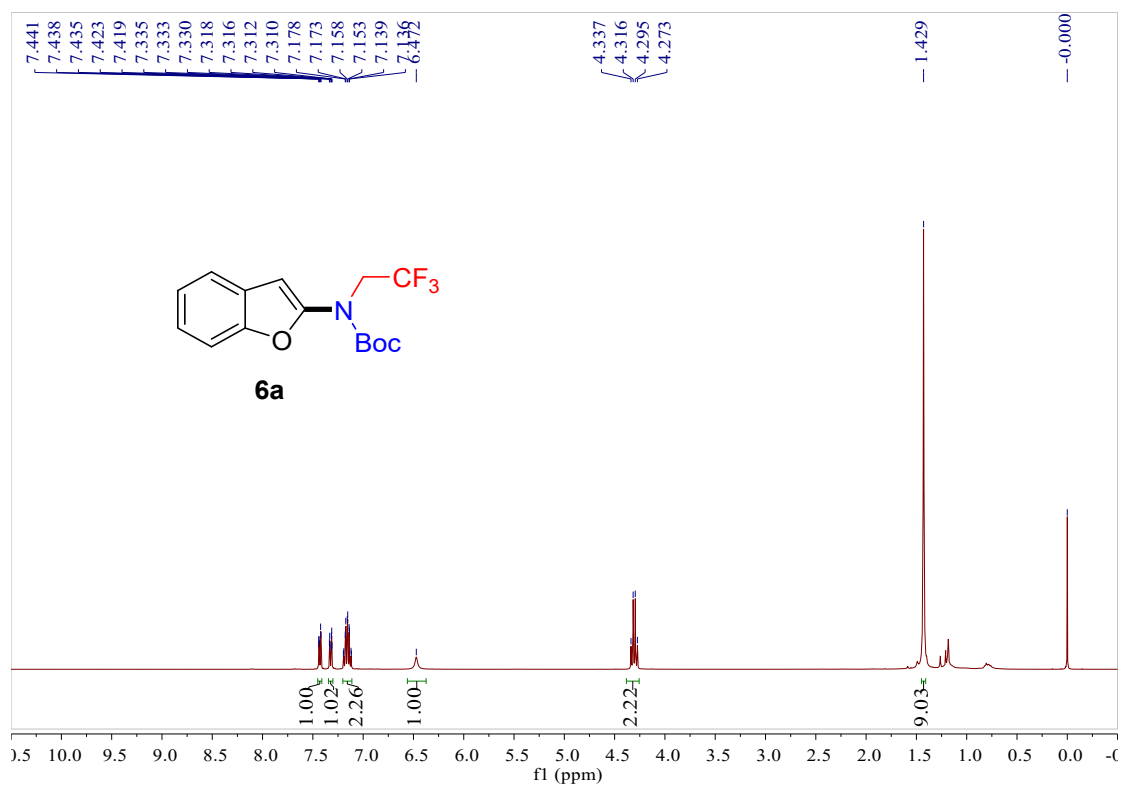
^{13}C NMR (101 MHz, CDCl_3)



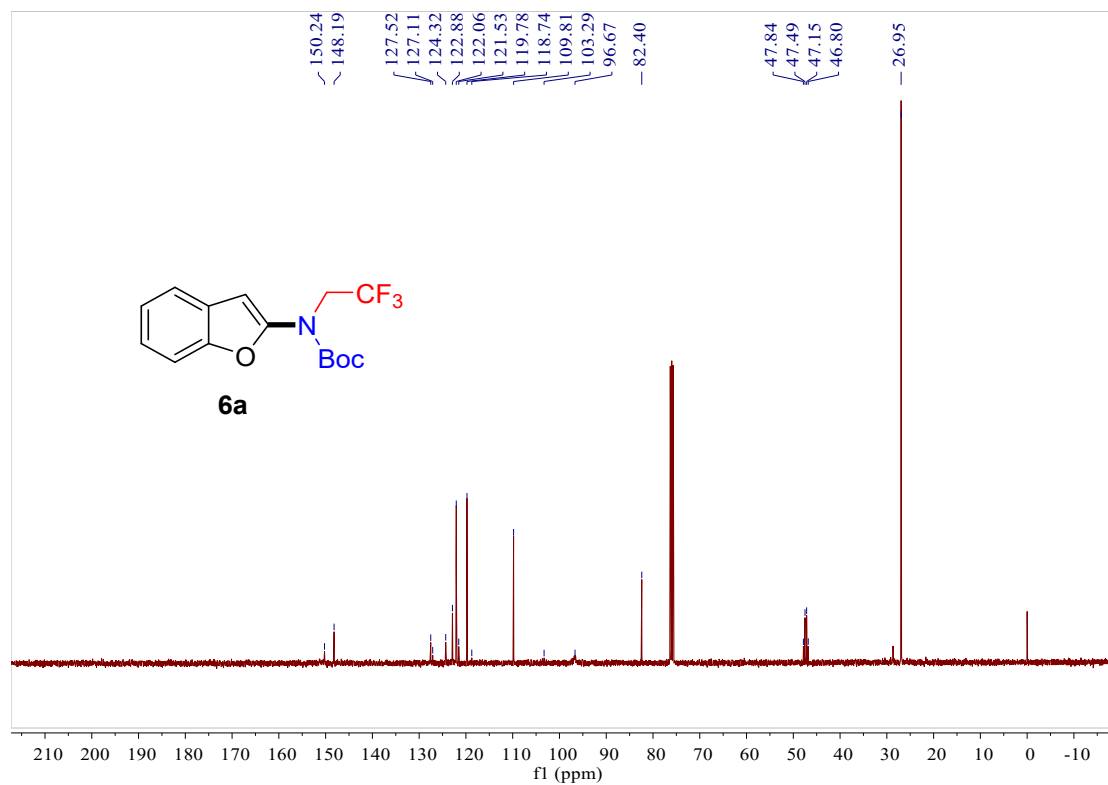
¹⁹F NMR (377 MHz, CDCl₃)



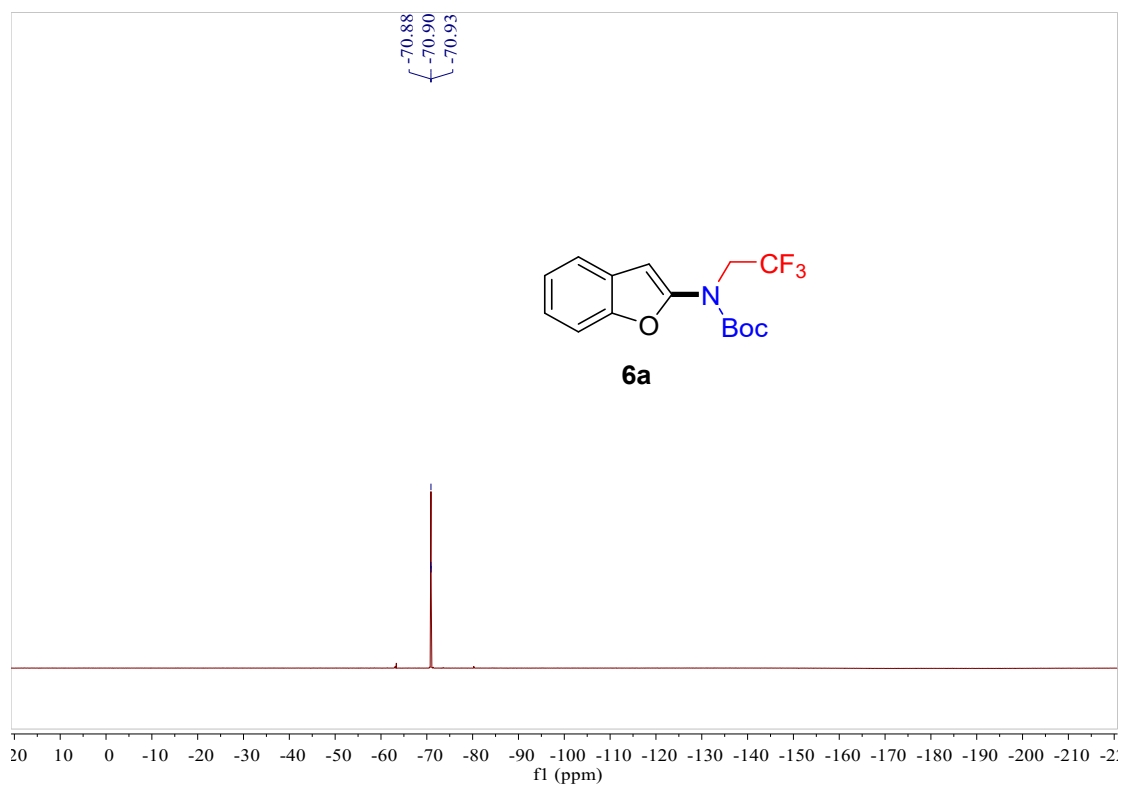
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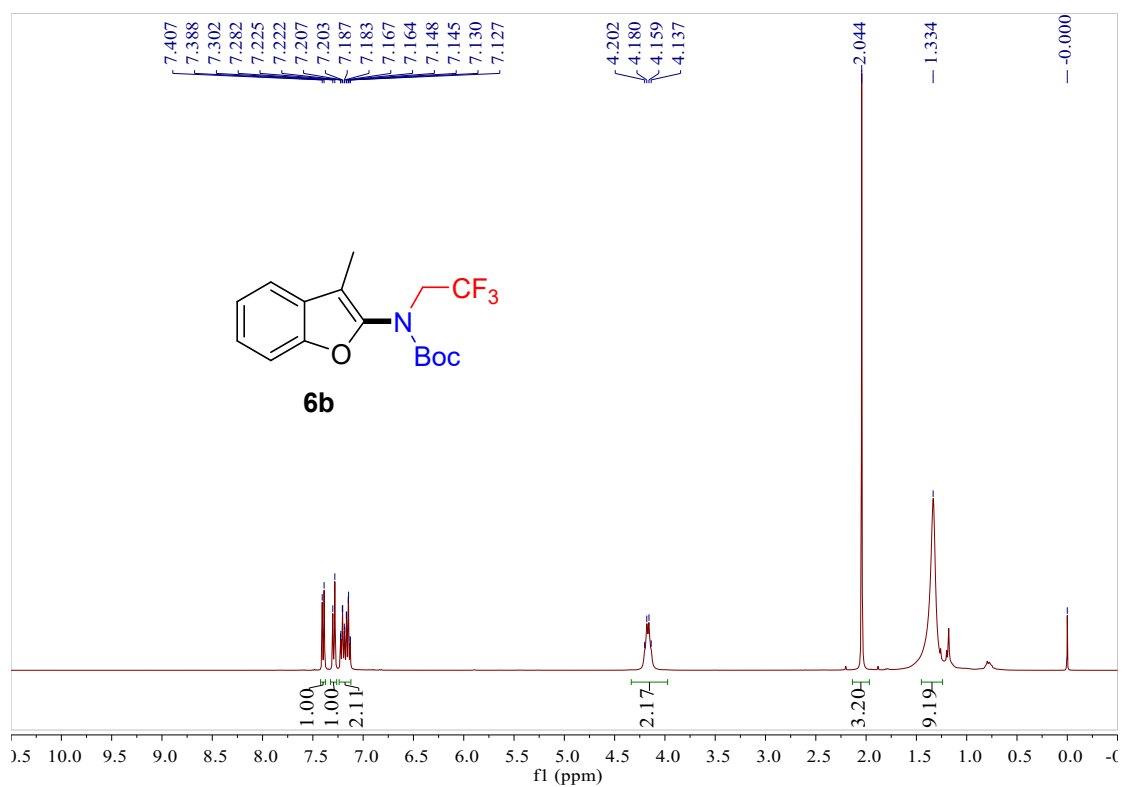
¹³C NMR (101 MHz, CDCl₃)



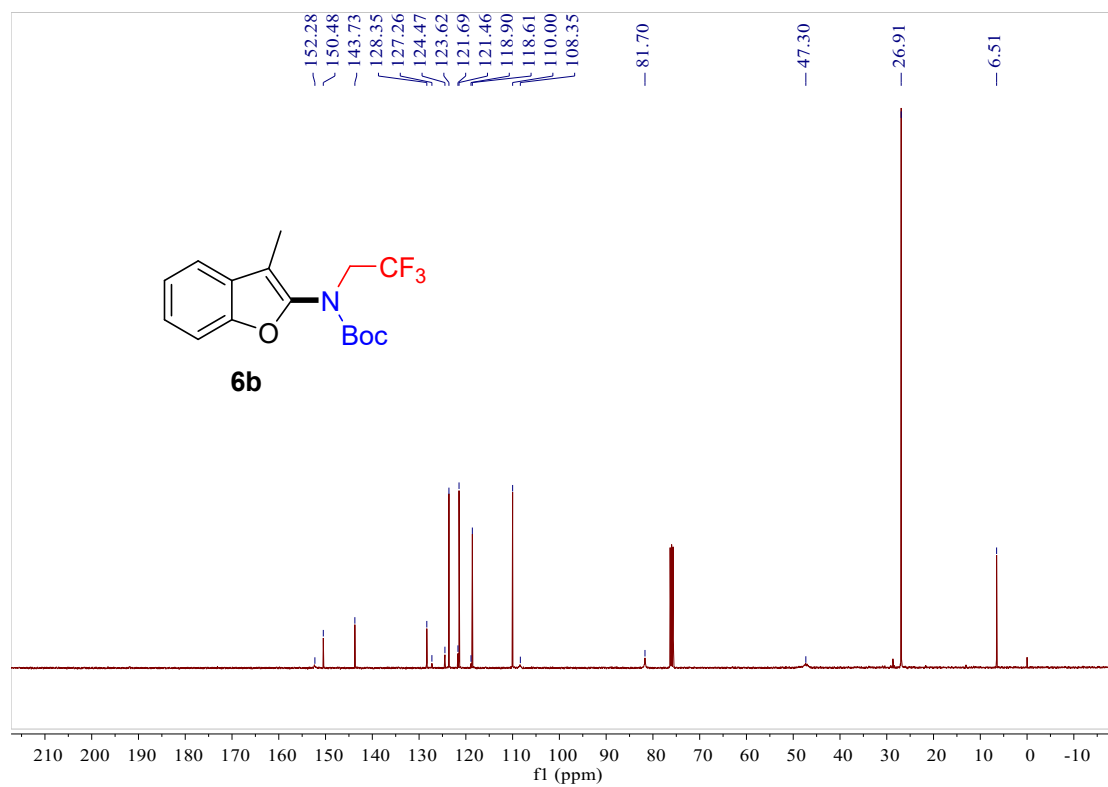
¹⁹F NMR (376 MHz, CDCl₃)



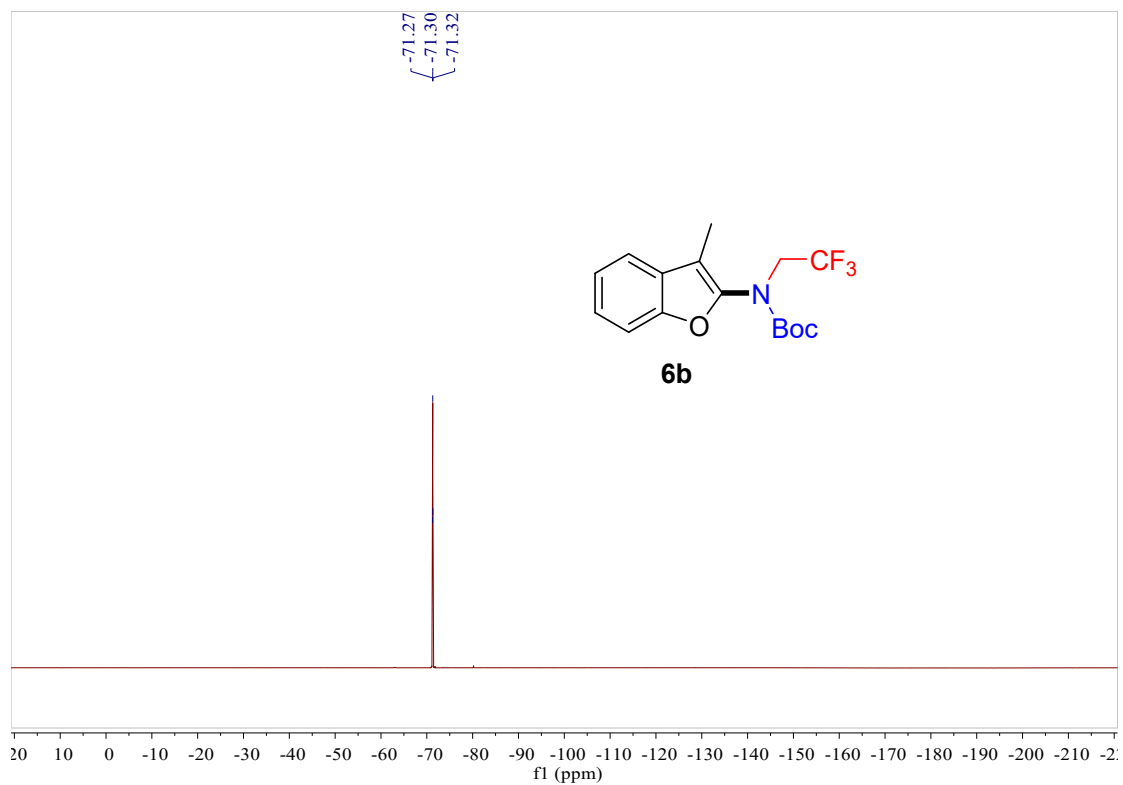
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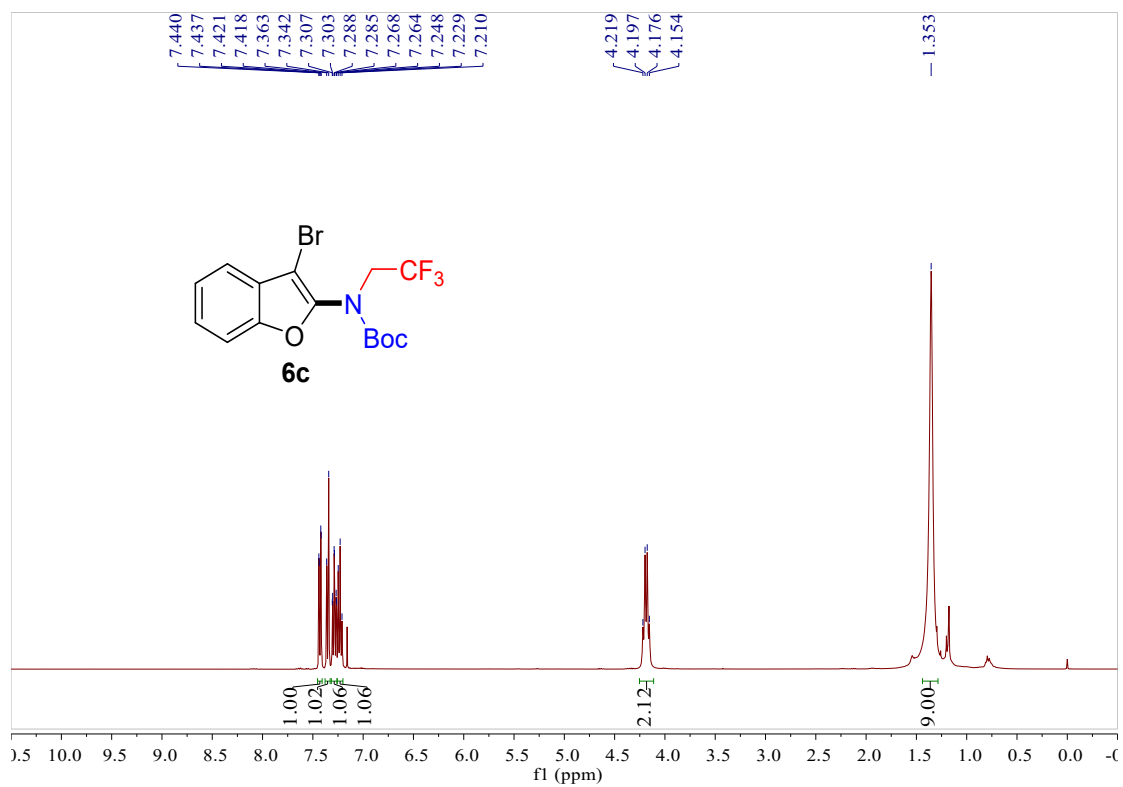
^{13}C NMR (101 MHz, CDCl_3)



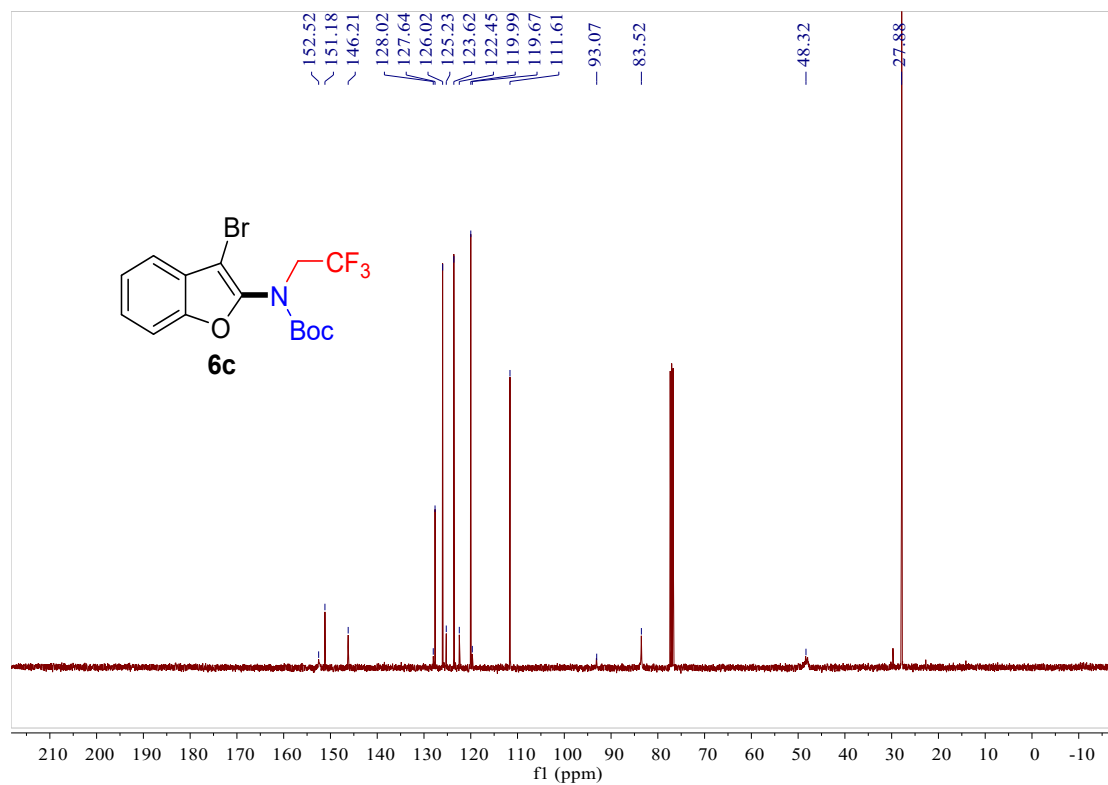
¹⁹F NMR (376 MHz, CDCl₃)



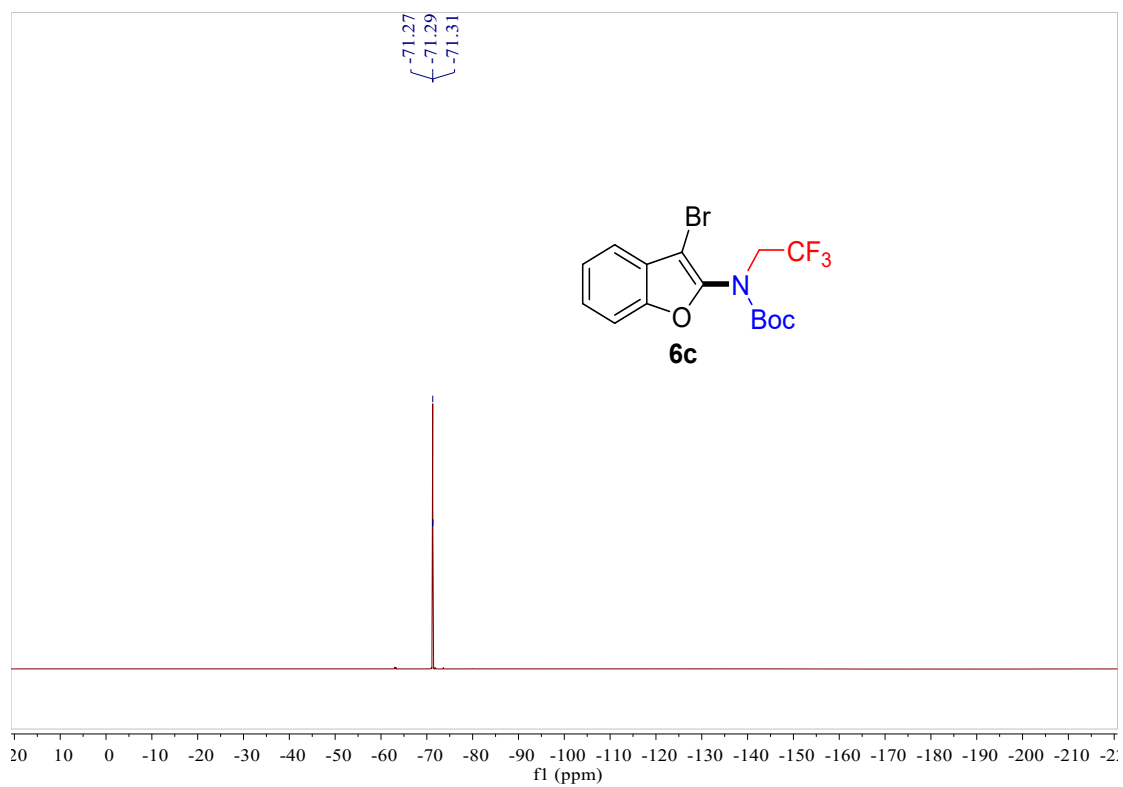
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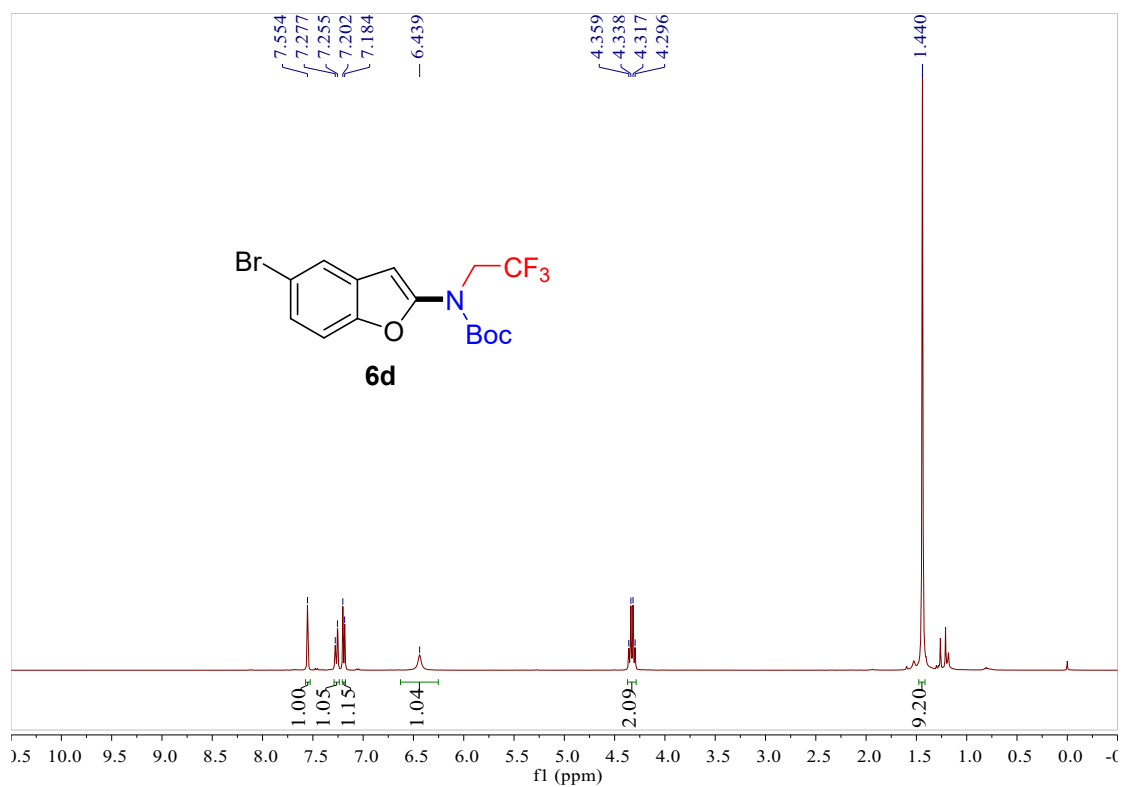
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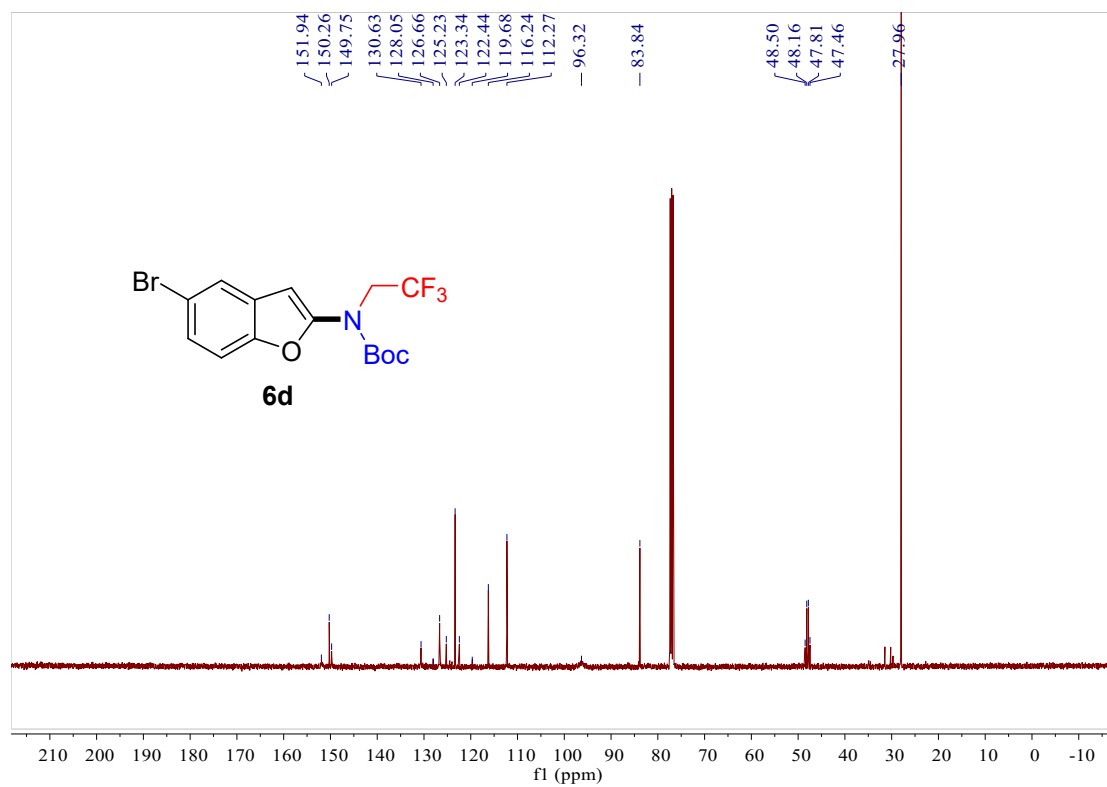
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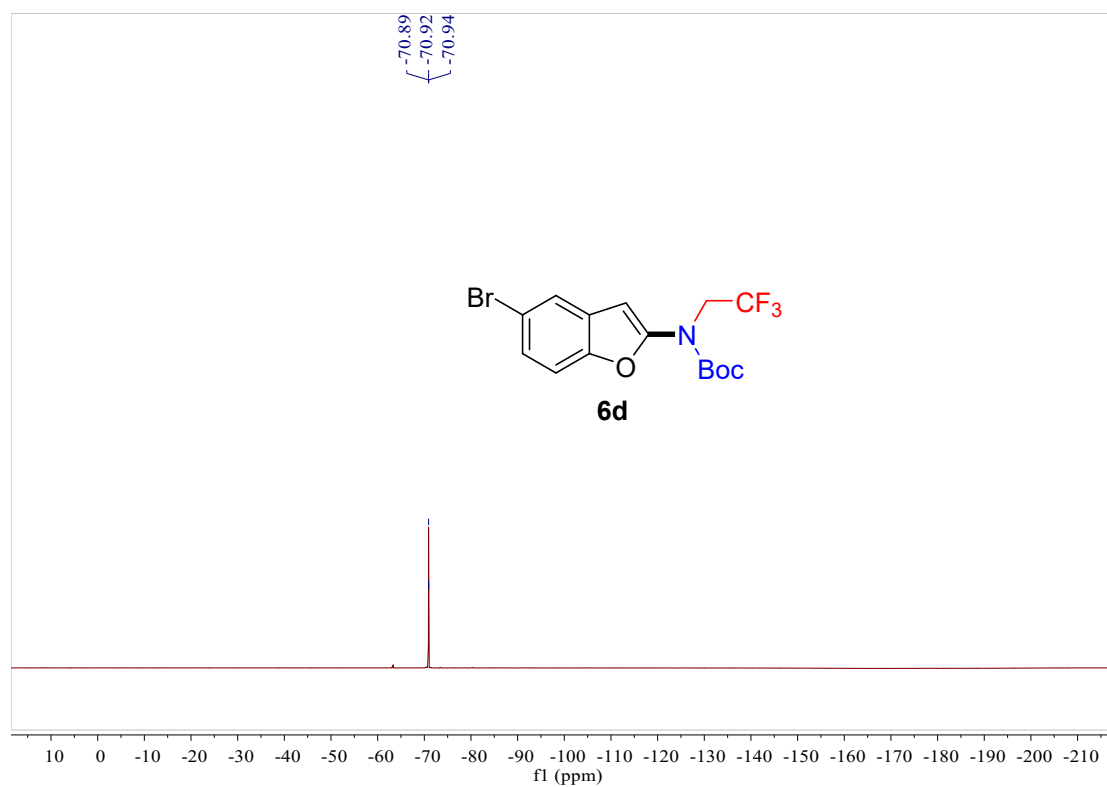
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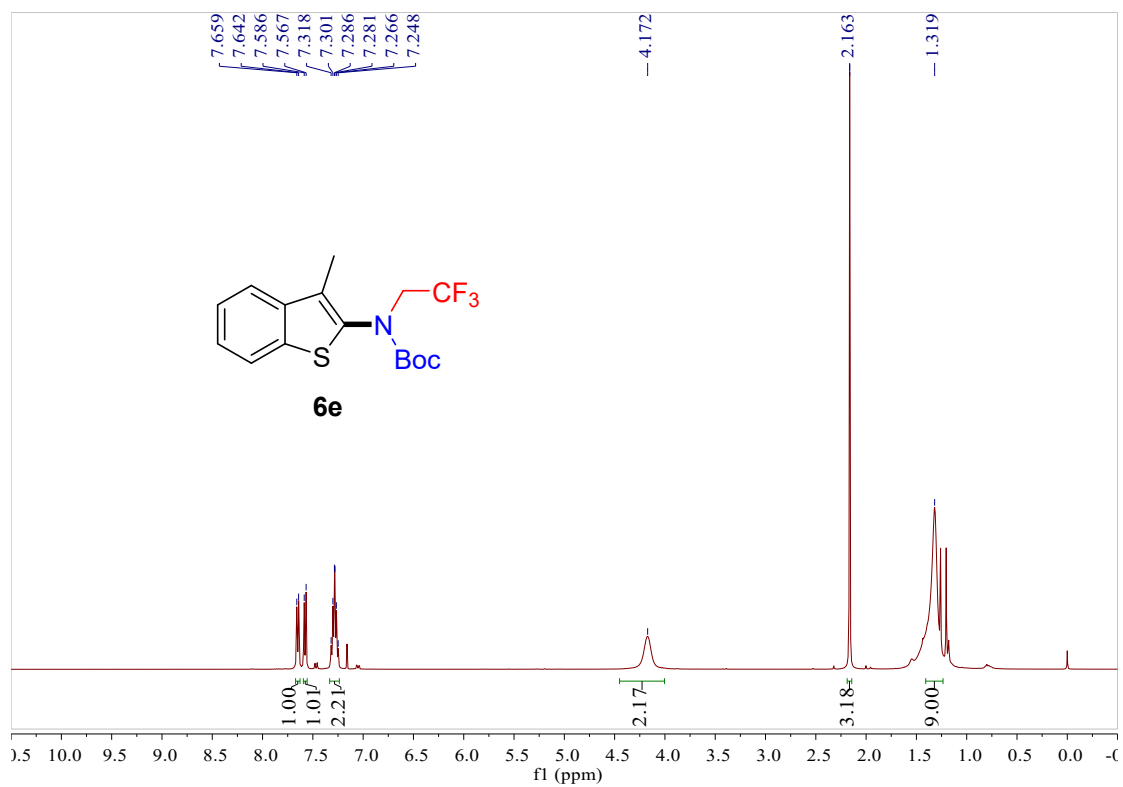
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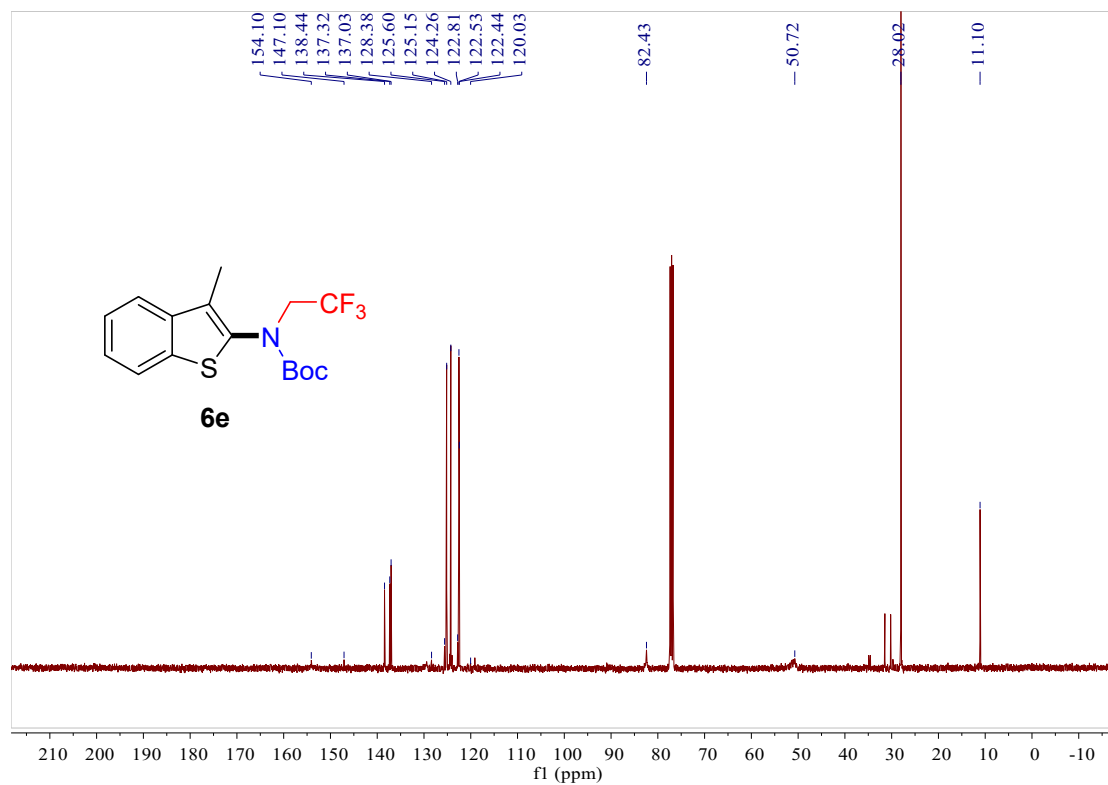
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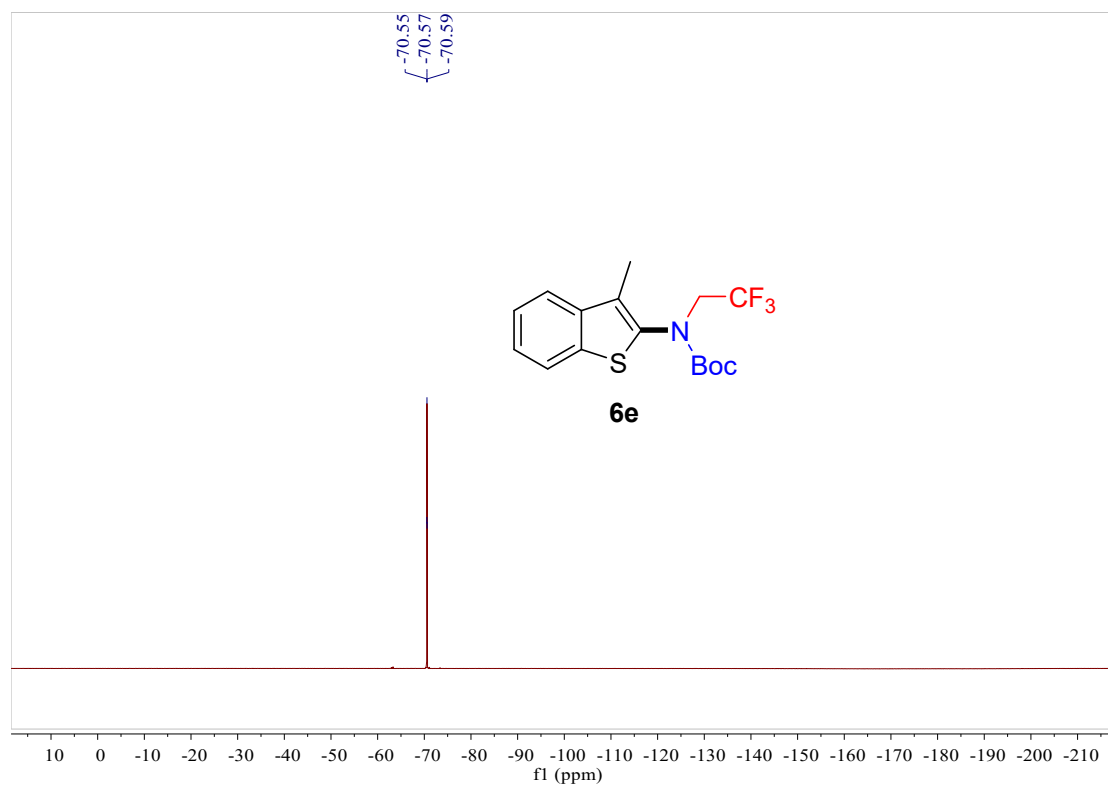
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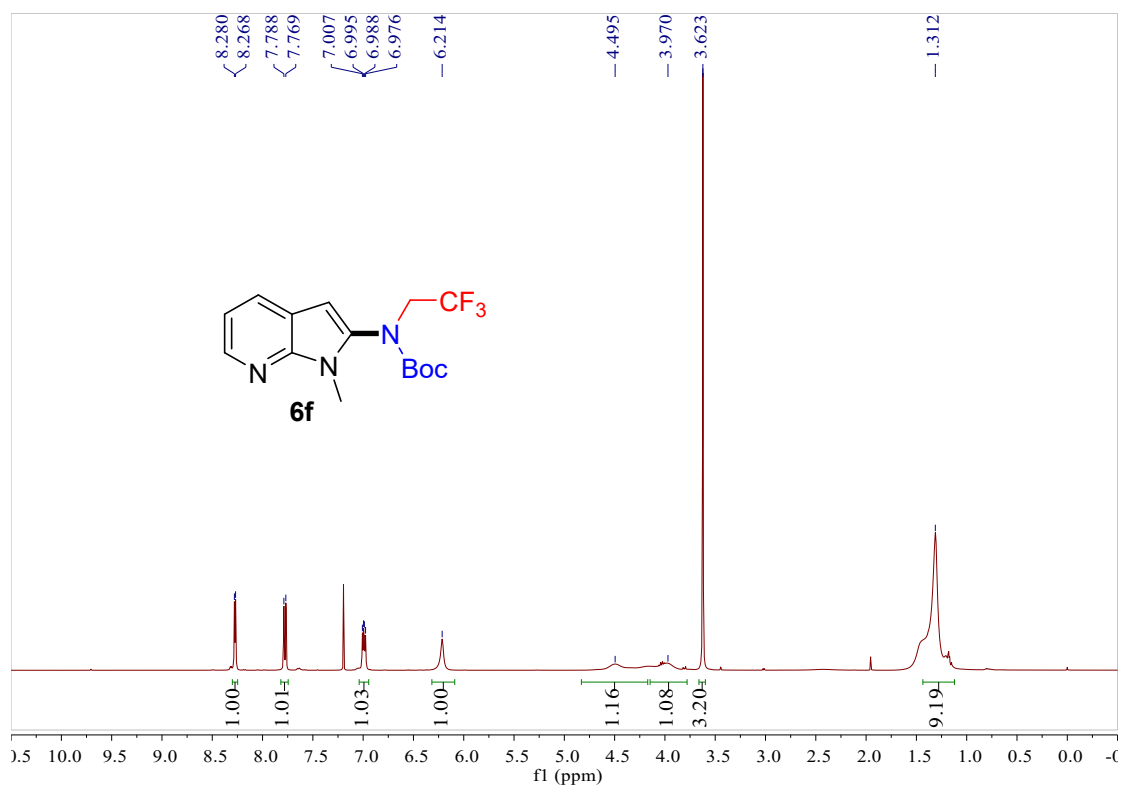
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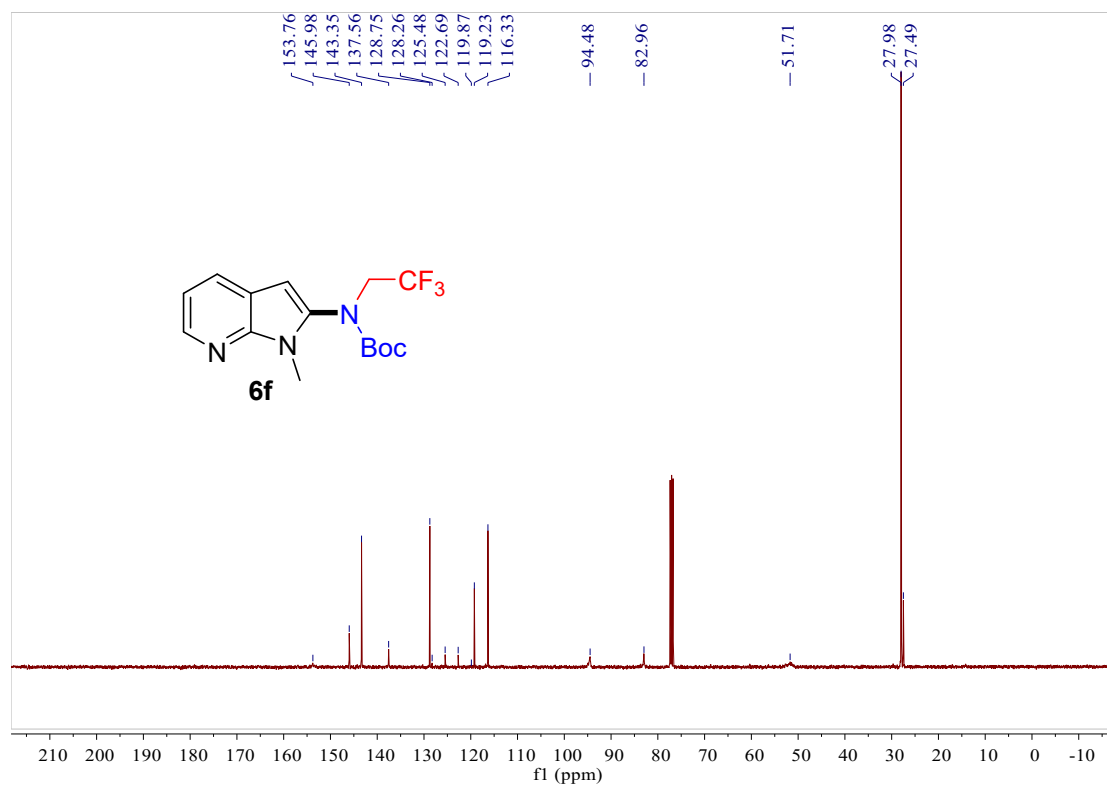
¹⁹F NMR (377 MHz, CDCl₃)



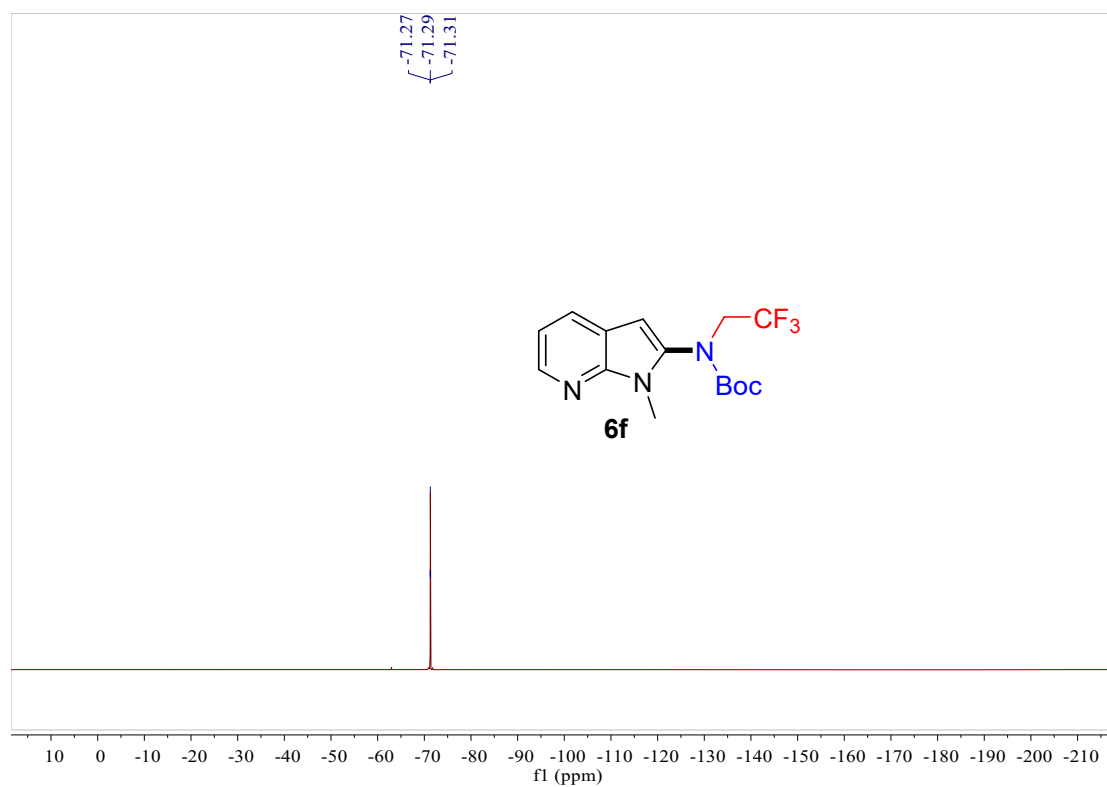
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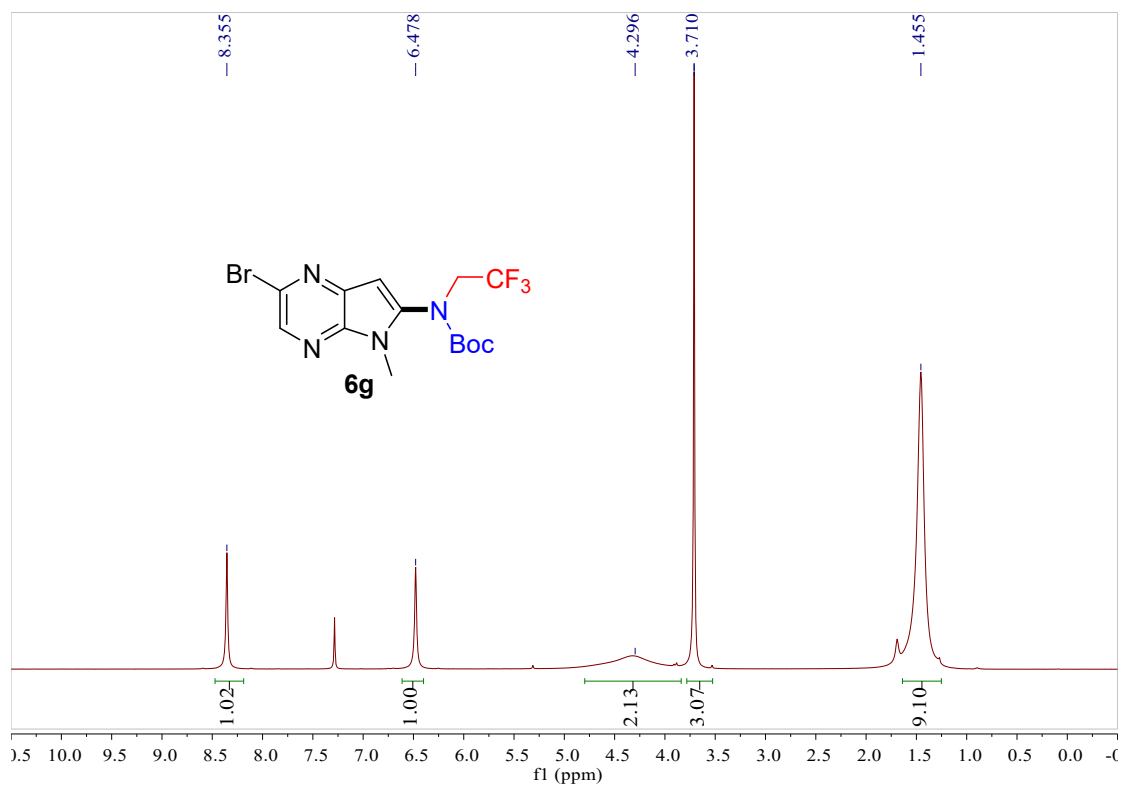
^{13}C NMR (101 MHz, CDCl_3)



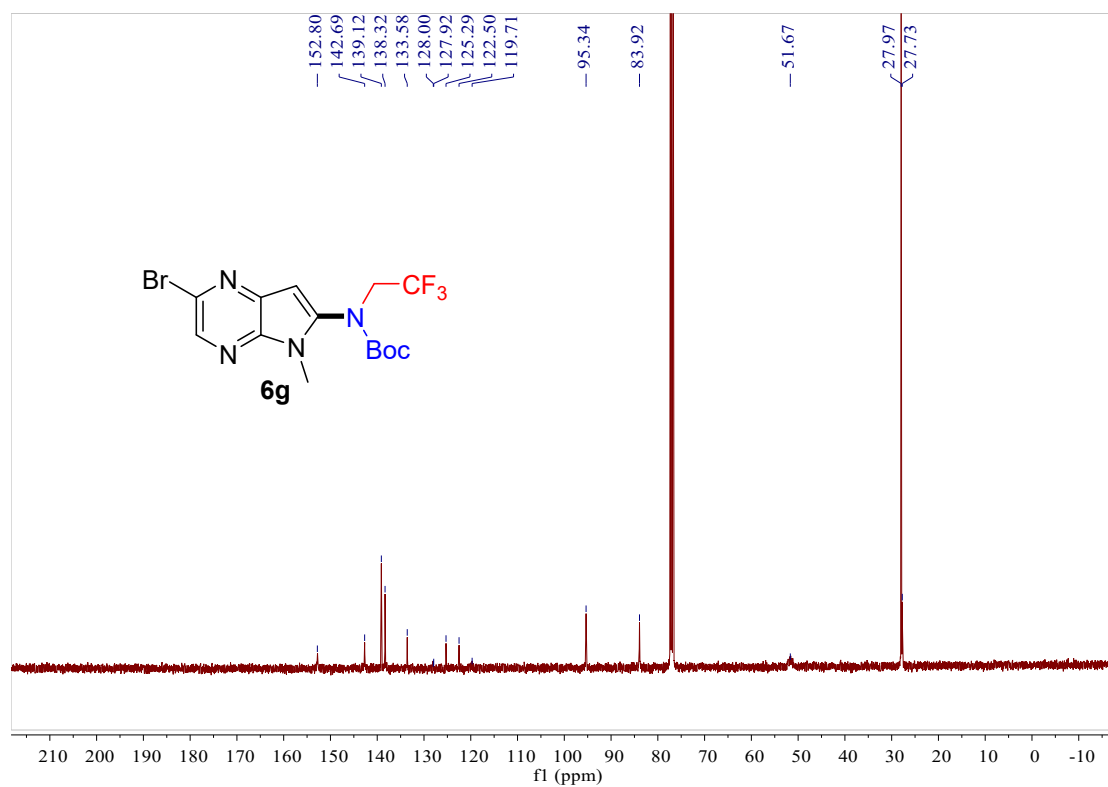
¹⁹F NMR (377 MHz, CDCl₃)



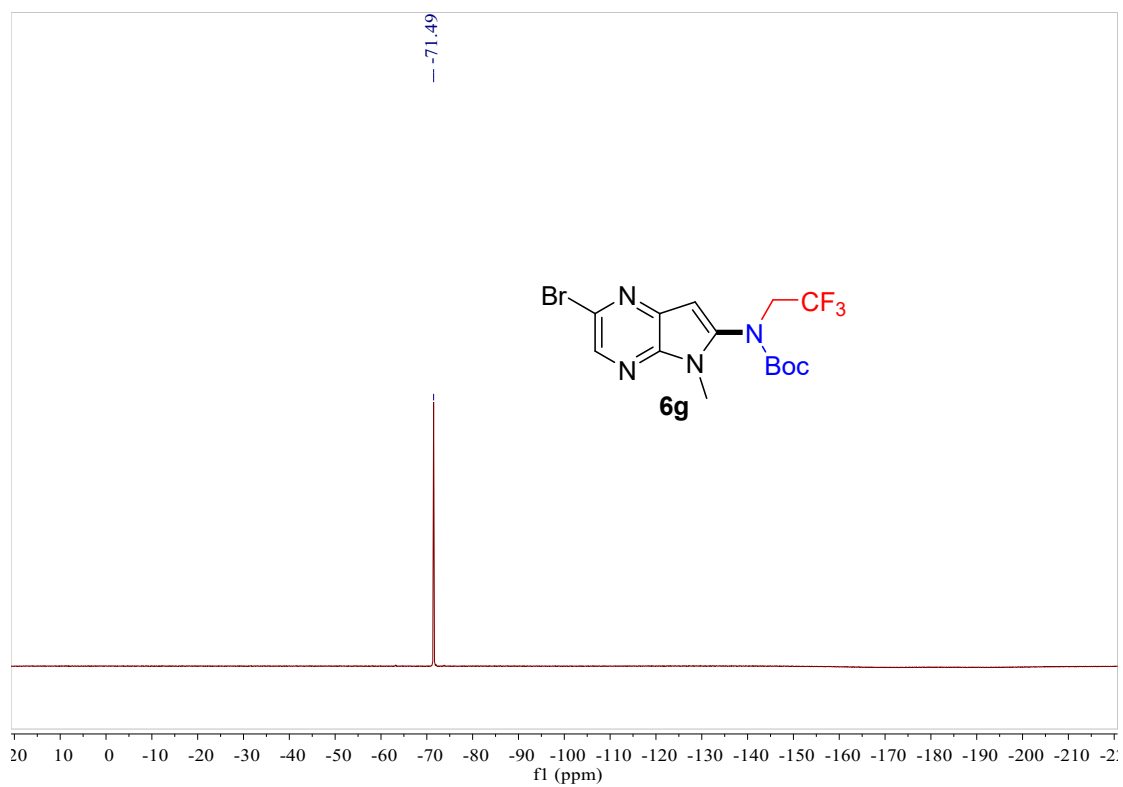
¹H NMR (400 MHz, CDCl₃)



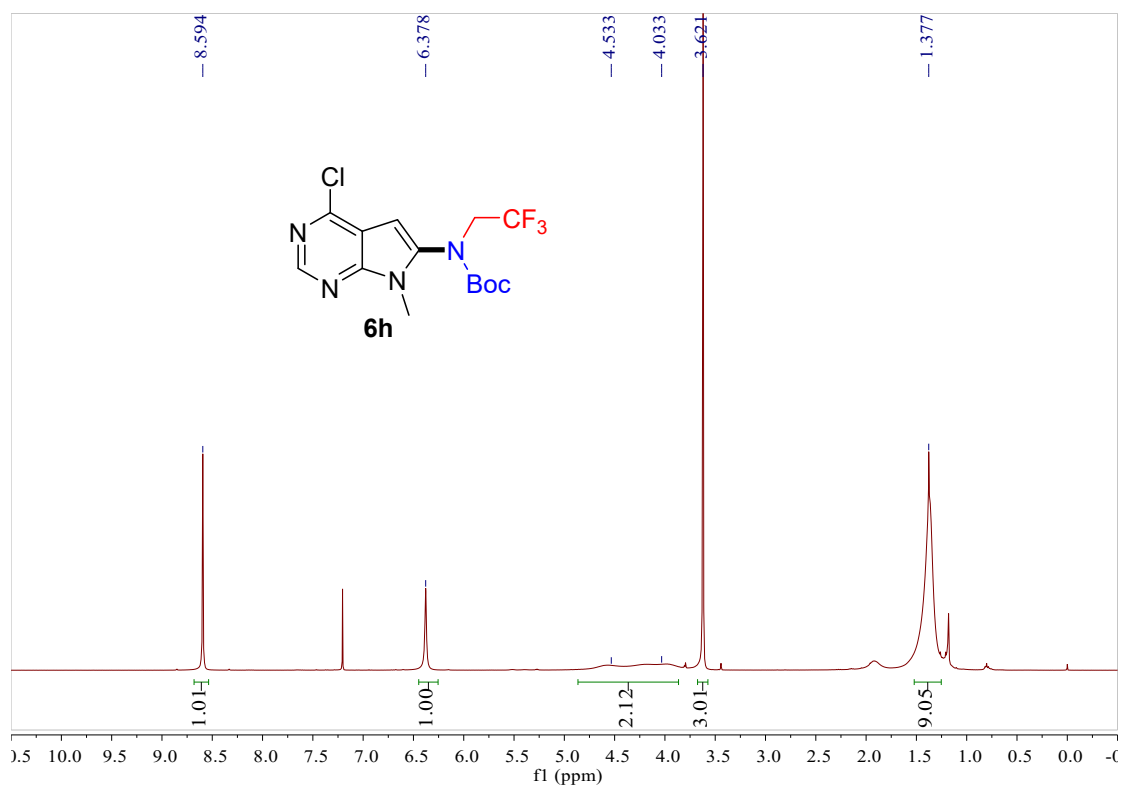
¹³C NMR (101 MHz, CDCl₃)



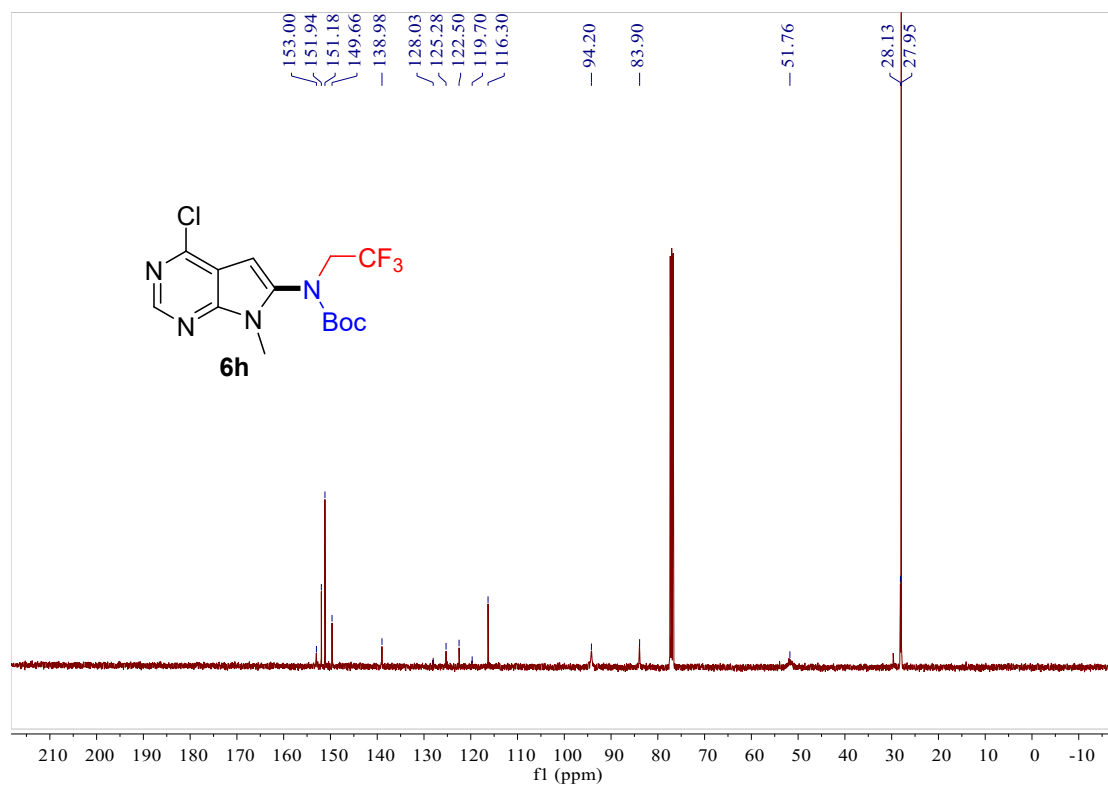
¹⁹F NMR (376 MHz, CDCl₃)



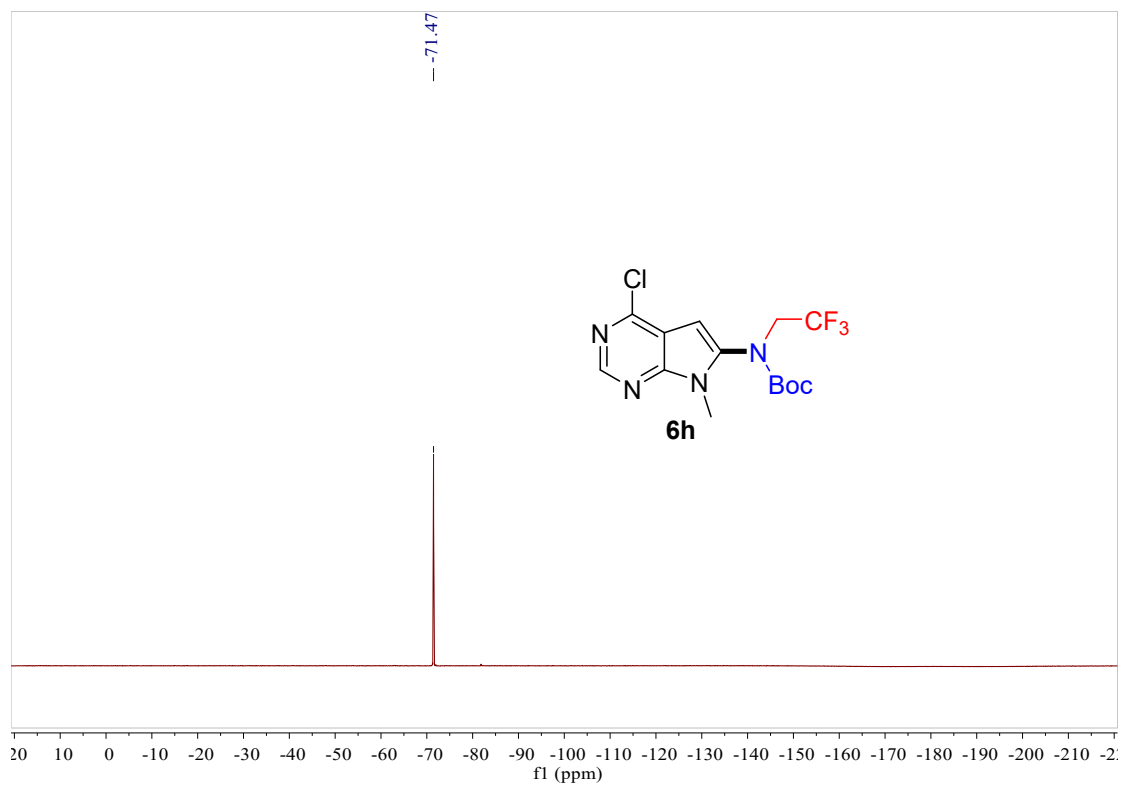
^1H NMR (400 MHz, CDCl_3)



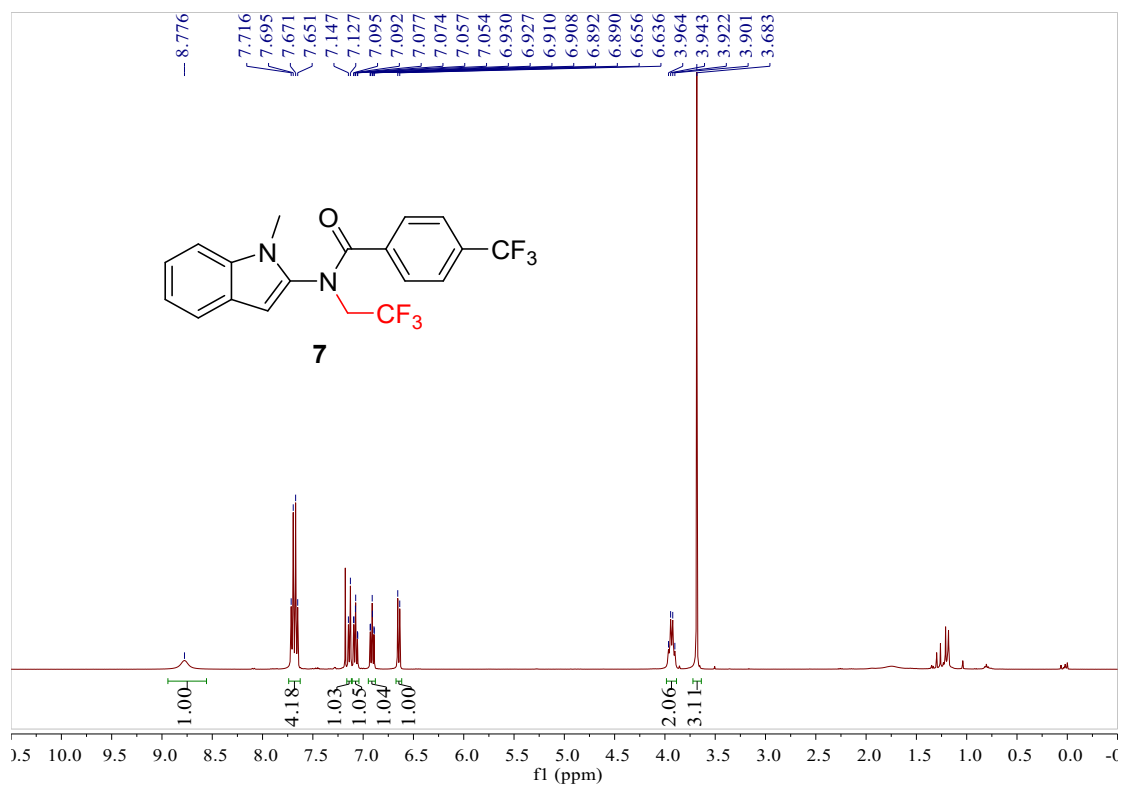
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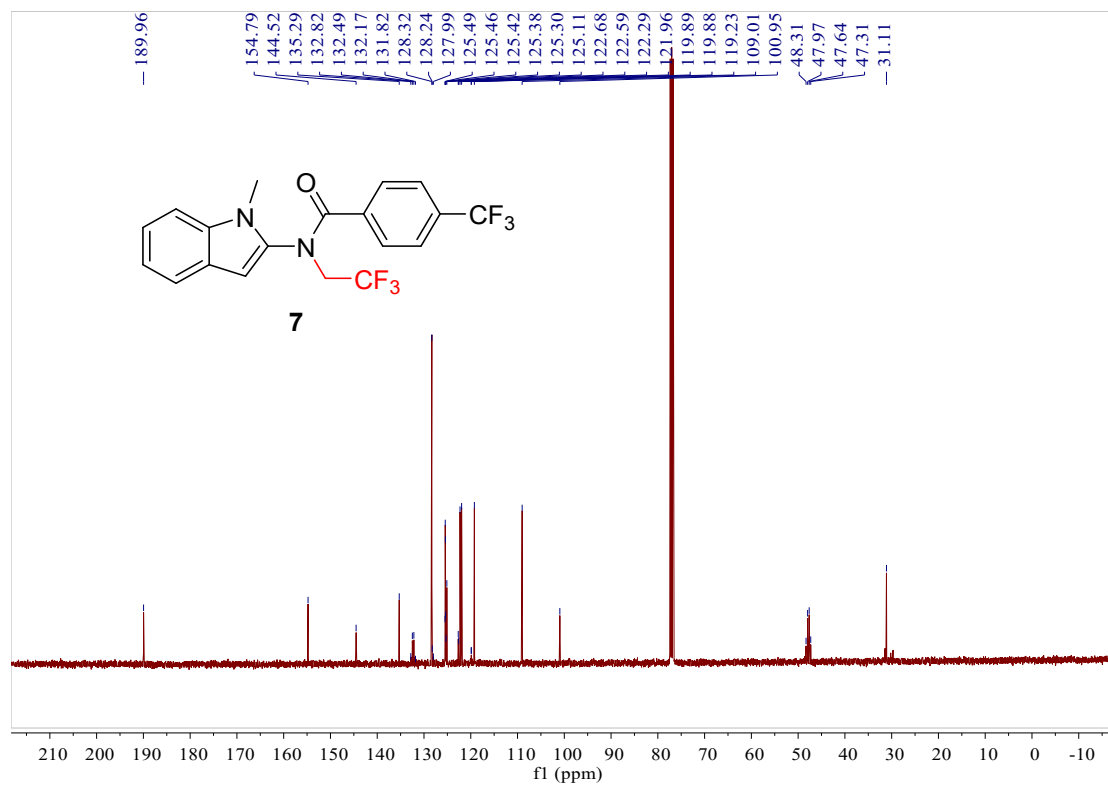
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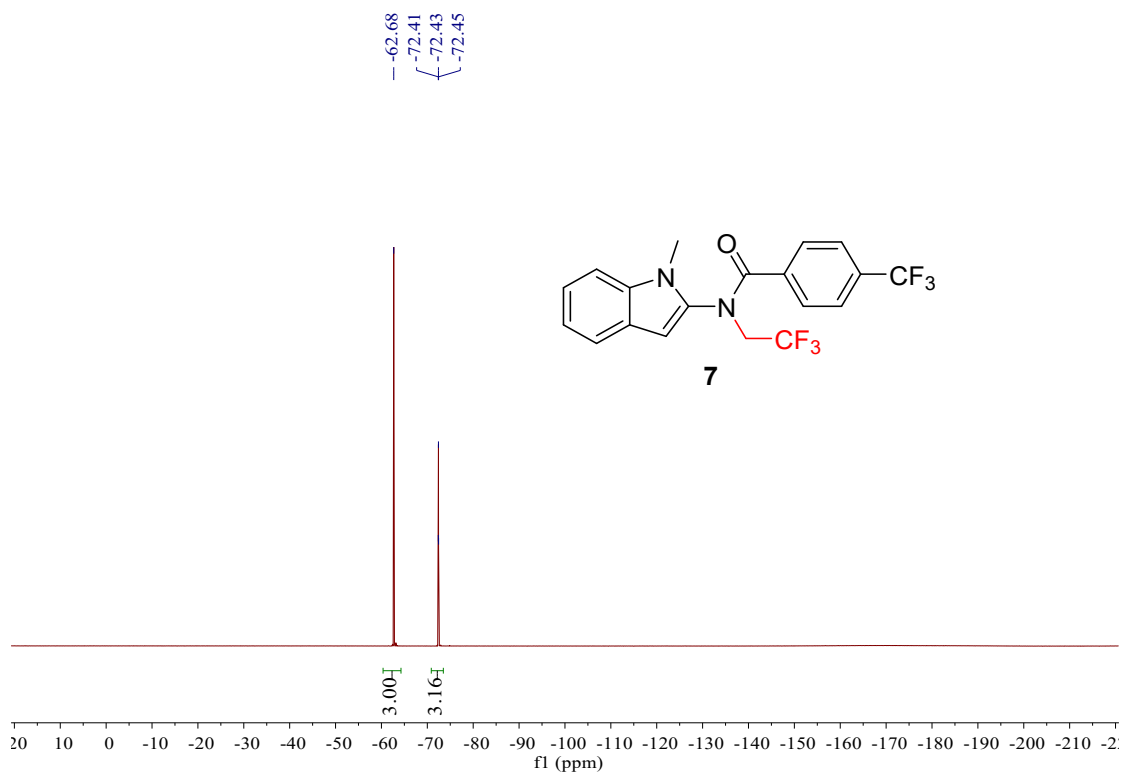
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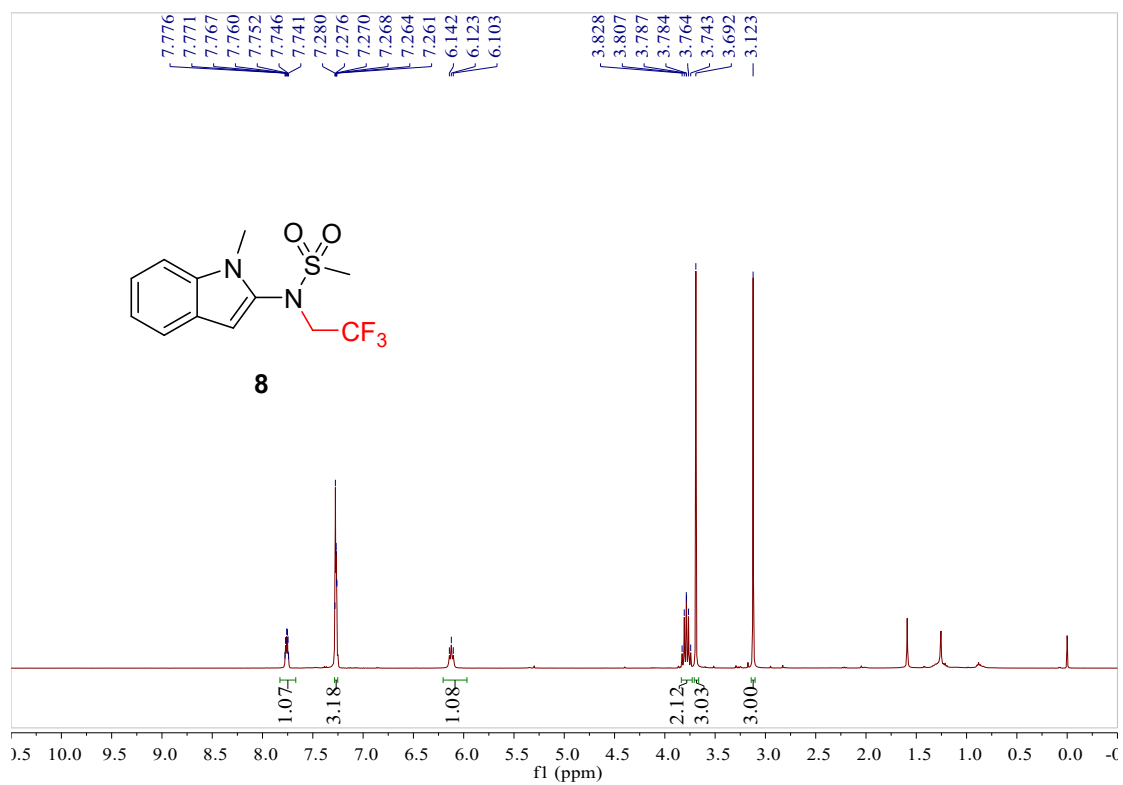
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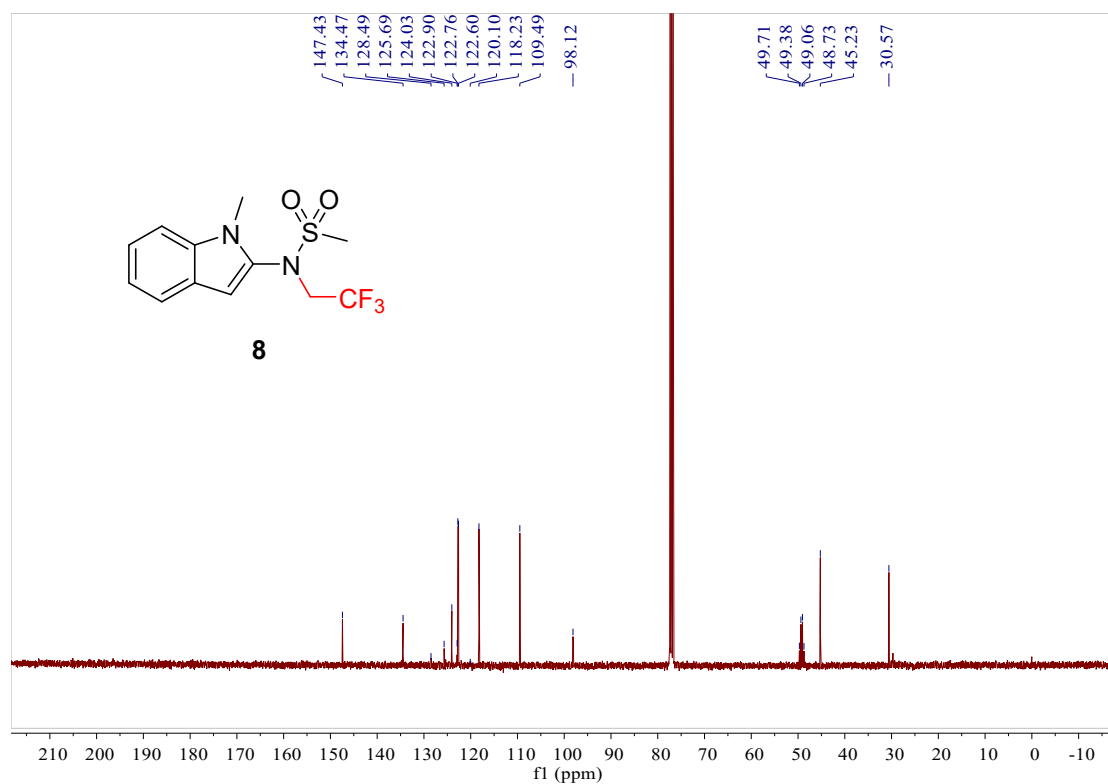
^{19}F NMR (376 MHz, CDCl_3)



¹H NMR (400 MHz, CDCl₃)



¹³C NMR (101 MHz, CDCl₃)



^{19}F NMR (377 MHz, CDCl_3)

