Supporting Information

Photoinduced metal-free trifluoro/perfluoroalkylation of heteroarenes

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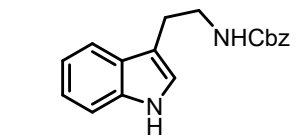
Table of Content

1. General Information.

Nuclear magnetic resonance (NMR) spectra were recorded in deuterated solvents with residual protonated solvent signal as internal reference on Bruker-Ava-500. Chemical shifts are reported in parts per million using the solvent resonance internal standard (chloroform, 7.26 and 77.0 ppm). Data is reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant, and integration. Electrospray and electron impact high resolution mass spectrometry was performed by Bruker mass spectrometer. The data is recorded as the ionization method followed by the calculated and measured masses. The Fluorescence emission intensities were measured on Agilent Cary Eclipse Fluorescence Spectrometer. Solvents for starting material preparation and coupling reactions were dried before use. Green LEDs (2.50 W, λ = 535 nm) Rebel LED, mounted on a 25 mm cool base was purchased from commercial supplier Luxeon Star LEDs Quadica Developments Inc.10-3447 30 Ave N. Lethbridge, Alberta T1H 7B5 Canada.

2. Experimental Section

2.1. Scope of Heteroarenes



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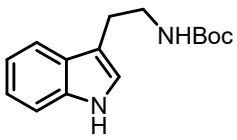

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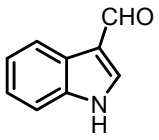

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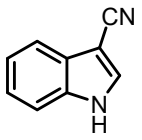

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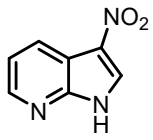

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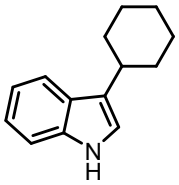

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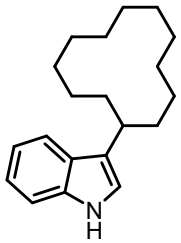

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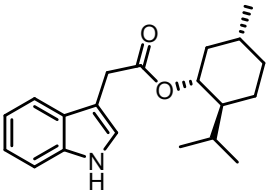

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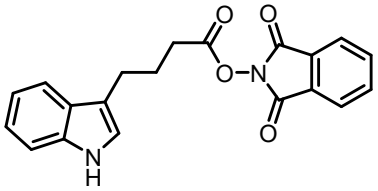

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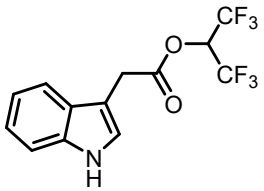

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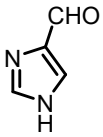

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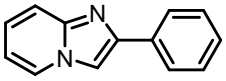

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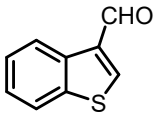

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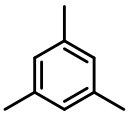

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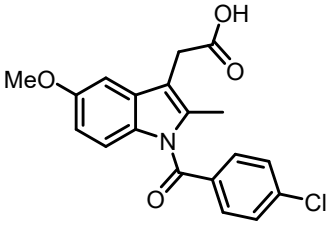

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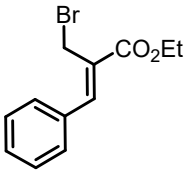

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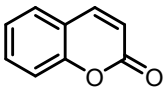

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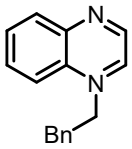


1r

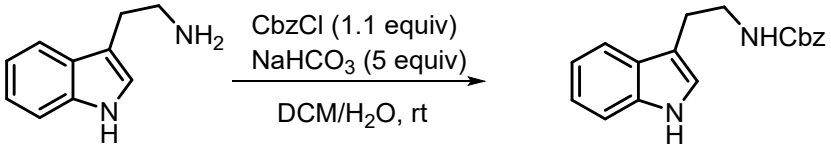
2.2: Preparation of Substrate

Materials: 1a-c, 1f, 1g, 1h, 1i, 1j were all prepared according to the previous reports.[1]

1l[2], **1m**[3], **1o**[4], **1p**[5], **1s**[6] were all prepared according to the previous reports.

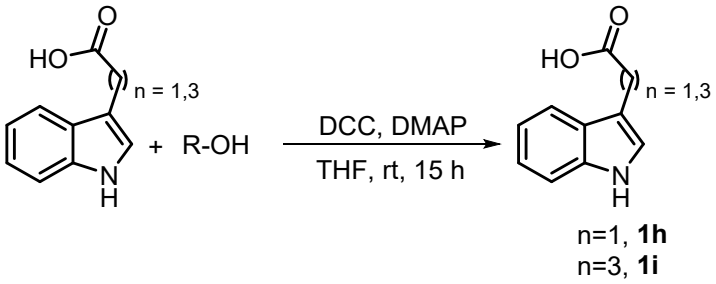
1d, 1e, 1k, 1n,1o, 1q were purchased from commercial sources and used without further purification and transformation.

2.2.1. General procedure for the Cbz protection of tryptamines



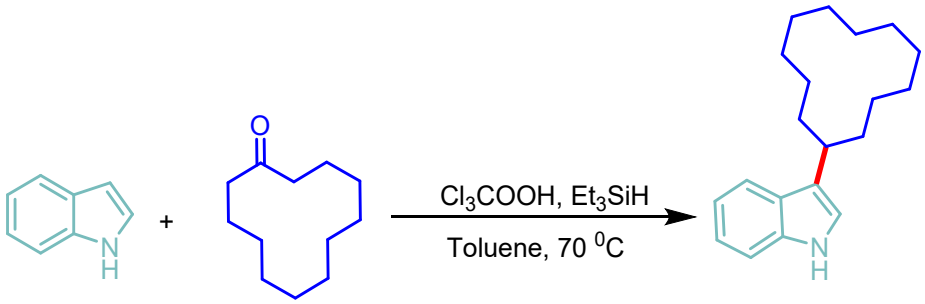
To a solution of tryptamine (1 equiv) in dichloromethane (0.1 M) was added a saturated aqueous solution of $NaHCO_3$ (5 equiv). The suspension was vigorously stirred and freshly distilled benzyl chloroformate (1.1 equiv) was added. The mixture was allowed to stir at rt for 2 h then the phases were separated and the aqueous phase extracted with dichloromethane. The combined organic extracts were washed with brine, dried over anhydrous sodium sulfate and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel using ethyl acetate and hexanes.

2.2.2 General procedure of synthesis of 3-substituted indole:



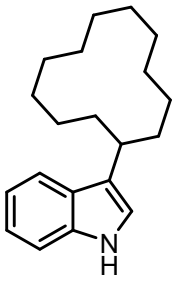
Indole-3-butyric acid for **1k** and Indole acetic acid for **1l** (1.0 equiv), respective alcohol (4.40 mmol, 1.1 equiv), *N*,*N*′-dicyclohexylcarbodiimide (1.2 equiv), and 4-dimethylaminopyridine (0.1 equiv) in a round-bottom flask. Dry THF was added, and the reaction mixture was stirred for 15 h at room temperature. After completion of reaction, the white precipitate was filtered off and the solution was concentrated by evaporation of the solvent. Purification by column chromatography on silica gel (EtOAc:hexane = 3:7) gave a solid **1h** and **1i**.

2.2.3 General procedure of synthesis of 3-substituted indole:



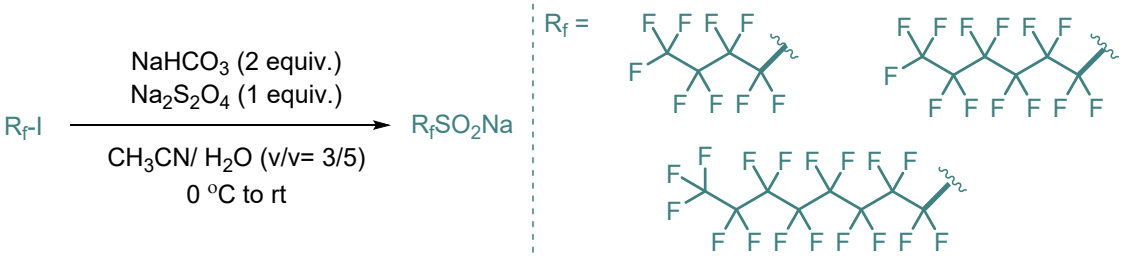
Into a 100 mL three-neck flask equipped with a magnetic stir bar, glass stopper and dropping funnel, dry toluene (3 mL), Et_3SiH (1.39 g, 12 mmol) and Cl_3CCOOH (1.23 g, 7.5 mmol) were added under N_2 atmosphere. The mixture was heated to 70 ºC and treated with a solution of cyclododecanone (1.0 g, 5.5 mmol) and indole (586 mg, 5 mmol) in toluene (2 mL) dropwise. The reaction mixture was then stirred for 2 h at this temperature. After cooling to room temperature, the mixture was quenched with saturated Na_2CO_3, extracted with Et_2O. The combined organic layer was dried over anhydrous MgSO, filtrated, concentrated under vacuum, and the residue was purified by flash column chromatography (petroleum ether/EtOAc = 30:1) to give a white solid (740 mg, 52 %).

3-cyclododecyl-1H-indole



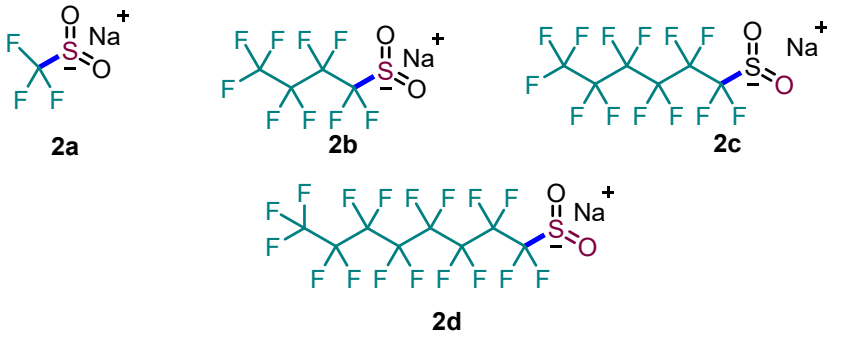
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 – 7.83 (m, 1H), 7.66 (d, J = 7.9 Hz, 1H), 7.35 (d, J = 8.1 Hz, 1H), 7.18 (t, J = 7.5 Hz, 1H), 7.11 (t, J = 7.5 Hz, 1H), 6.97 (s, 1H), 3.13 (p, J = 6.4 Hz, 1H), 1.92 – 1.82 (m, 2H), 1.66 (ddt, J = 13.2, 7.4, 5.5 Hz, 2H), 1.56 (ddd, J = 17.9, 7.7, 3.3 Hz, 3H), 1.50 – 1.43 (m, 6H), 1.42 – 1.31 (m, 10H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 136.6, 127.4, 122.3, 121.9, 120.4, 119.5, 119.0, 111.2, 77.4, 77.2, 76.9, 31.1, 30.7, 24.0, 24.0, 23.9, 23.7, 22.9. **HRMS (ESI/QTOF), m/z:** $[M-H]^-$ Calcd. $C_{20}H_{28}N$ 282.2222; Found 282.2224.

2.3 Preparation of perfluoroalkanesulfinates.



Perfluoroiodine compounds ($R_f = C_4F_9$, C_6F_{13}, C_8F_{17}) (10 mmol) was bubbled into CH_3CN (6 mL) in a round bottom flask at 0°C. $NaHCO_3$ (1.68 g, 20 mmol, 2 equiv.), $Na_2S_2O_4$ (1.58 g, 10 mmol, 2 equiv), and H_2O (10 mL) were added. The reaction mixture was stirred at room temperature overnight and then extracted with ethyl acetate (3 × 50 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated to dryness. The residue was washed with diethyl ether (3 × 20 mL) and dried in vacuum to give 1c/1d as a white solid. The spectral data matched with those reported in the literature.[9]

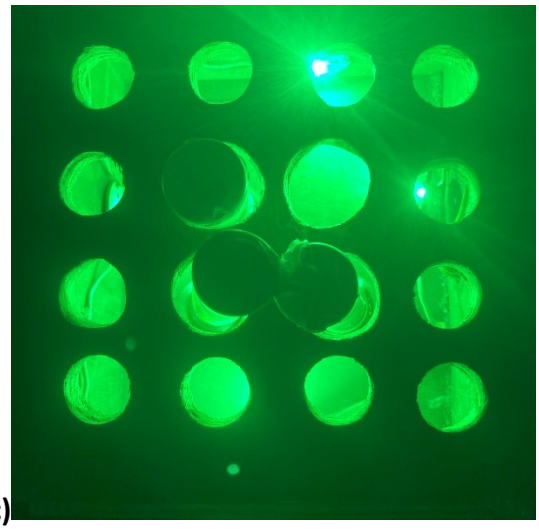
Trifluoro/Perfluoro alkyl sulfinates

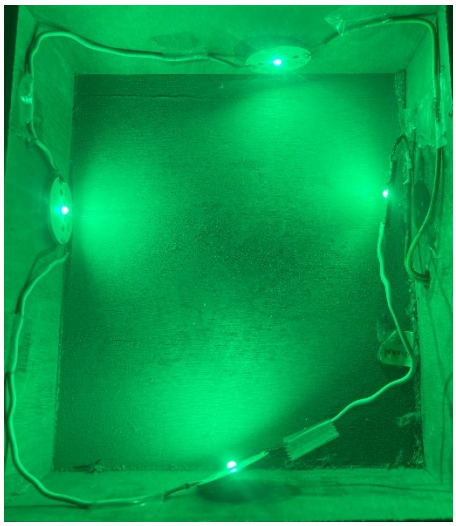


3: Photo Reaction Setup

(a) 

(b) 

(c) 

(d) 

(a) Whole Setup Setup

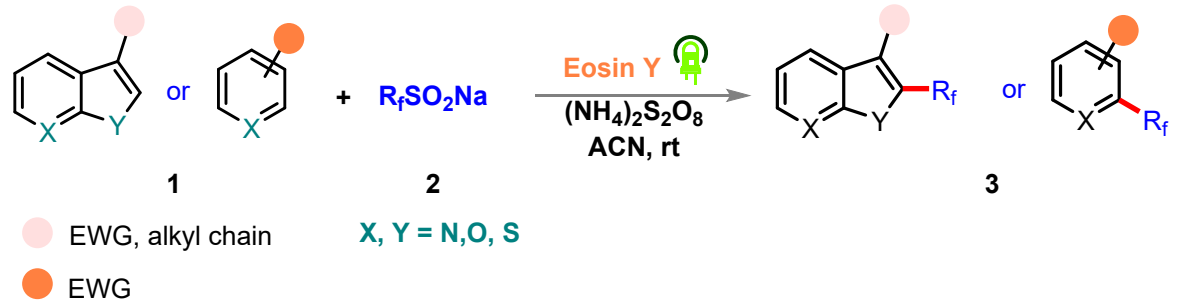
(b) DC Regulator controlling Current and voltage

(c) Box- cover with holes for RB and RB illuminated by Green LEDs

(d) Uncovered box (6' * 6') with 4 LEDs

Each RB was at 5cm distance from LEDs.

4: General procedures for the synthesis of 3 and spectral data

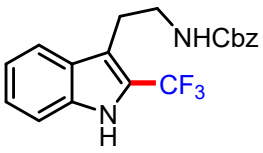


Scheme 1: Preparation of trifluoromethylated/perfluoroalkylated heteroarenes

0.2 mmol of **1** (1.0 equiv.), trifluoro/perfluoro alkyl sulfinates (0.6 mmol, 3 equiv.) were taken in a long neck round bottom flask and 2.5 mol % of Eosin Y was added into it followed by ammonium peroxodisulfate (3.0 equiv), and the RB was capped with septum. The mixture was degassed and filled with N_2 (three times). Subsequently 0.1M MeCN solution was added into the reaction mixture via syringe. The reaction mixture was then irradiated with green LED for 24 h. After completion (monitored through TLC), reaction was quenched with saturated $NaHCO_3$ solution and extracted with ethyl-acetate (3 x 10 mL), washed with brine solution. After removal of solvent in vacuo, the product was purified by silica gel chromatography using EtOAc-hexane (3:7 to 5:5) as eluent to provide the desired product.

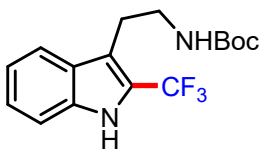
Analytical Data for Products

benzyl (2-(2-(trifluoromethyl)-1H-indol-3-yl)ethyl)carbamate (3a): Physical state: White



liquid; **Yield:** 52 mg (72 %). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.46 (s, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.41 – 7.31 (m, 7H), 7.17 (t, J = 7.5 Hz, 1H), 5.11 (s, 2H), 4.84 (d, J = 7.4 Hz, 1H), 3.51 (q, J = 6.7 Hz, 2H), 3.14 (t, J = 7.4 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 156.54, 136.71, 135.40, 134.17, 128.64, 128.22, 127.56, 125.14, 122.54(C-F, $1J_{C\text{-}F}$ = 268.38 Hz), 121.02, 120.66, 120.41 (C-F, $1J_{C\text{-}F}$ = 268.38 Hz), 111.94, 111.49, 66.80, 41.74, 24.59. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -58.06. **HRMS (ESI/QTOF), m/z:** $[M\text{-}H]^-$ Calcd. $C_{19}H_{16}N_2O_2F_3$ 361.1164; Found 361.1172.

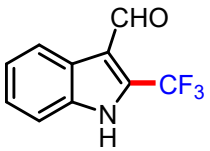
tert-butyl (2-(2-(trifluoromethyl)-1H-indol-3-yl)ethyl)carbamate (3b): Physical state:



White liquid; **Yield:** 44 mg (67 %). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.59 (s, 1H), 7.69 (d, J = 8.3 Hz, 1H), 7.41 (dd, J = 8.3, 1.0 Hz, 1H), 7.34 –

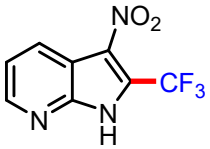
7.30 (m, 1H), 7.20 – 7.16 (m, 1H), 4.63 (s, 1H), 3.41 (s, 2H), 3.10 (t, J = 6.9 Hz, 2H), 1.44 (s, 9H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 155.95, 135.29, 127.49, 125.17 (C-F, 1$J_{C\text{-}F}$ = 269.6 Hz), 124.93, 123.04 (C-F, 1$J_{C\text{-}F}$ = 269.6 Hz), 122.39, 122.10, 120.90 (C-F, 1$J_{C\text{-}F}$ = 269.6 Hz), 120.75, 120.73, 120.35, 118.76 (C-F, 1$J_{C\text{-}F}$ = 269.6 Hz), 115.36, 111.78, 41.15, 28.38, 28.27, 24.53. **^{19}F NMR (376 MHz, CDCl$_3$)** δ -57.91. **HRMS (ESI/QTOF), m/z:** [M-H]$^-$ Calcd. $C_{16}H_{18}N_2O_2F_3$ 327.1321; Found 327.1329.

2-(trifluoromethyl)-1H-indole-3-carbaldehyde (3c): Physical state: White solid; **Yield:** 21

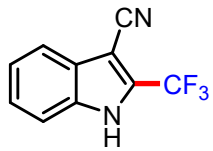


mg (50 %)**. ^{1}H NMR (500 MHz, DMSO-d_6)** δ 13.41 (s, 1H), 10.23 (s, 1H), 8.24 (d, J = 8.0 Hz, 1H), 7.61 – 7.59 (m, 1H), 7.43 – 7.41 (m, 1H), 7.37 – 7.34 (m, 1H). **^{13}C NMR (126 MHz, DMSO-d_6)** δ 184.24, 135.36, 131.35 (C-F, 2$J_{C\text{-}F}$ = 39.0 Hz), 131.04 (C-F, 2$J_{C\text{-}F}$ = 39.0 Hz), 130.72 (C-F, 2$J_{C\text{-}F}$ = 39.0 Hz), 130.41 (C-F, 2$J_{C\text{-}F}$ = 39.0 Hz), 125.82, 124.33, 124.02 (C-F, 1$J_{C\text{-}F}$ = 270.9 Hz), 123.84, 121.99, 121.87 (C-F, 1$J_{C\text{-}F}$ = 270.9 Hz), 119.71 (C-F, 1$J_{C\text{-}F}$ = 270.9 Hz), 115.45, 113.19. **^{19}F NMR (471 MHz, CDCl$_3$)** δ -56.65. **HRMS (ESI/QTOF), m/z:** [M-H]$^-$ Calcd. $C_{10}H_5NO_2F_3$ 212.0323; Found 212.0333.

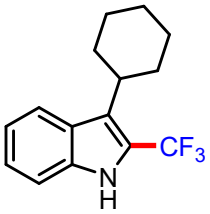
3-nitro-2-(trifluoromethyl)-1H-pyrrolo[2,3-β]pyridine (3d): Physical state: White solid;



Yield: 21 mg (45 %). **^{1}H NMR (500 MHz, DMSO-d_6)** δ 8.69 (dd, J = 8.0, 1.6 Hz, 1H), 8.63 (dd, J = 5.0, 1.6 Hz, 1H), 7.59 (dd, J = 8.1, 5.0 Hz, 1H), 4.01 (s, 1H). **^{13}C NMR (126 MHz, DMSO)** δ 144.01, 143.98, 132.56, 124.15, 123.24 (C-F, 1$J_{C\text{-}F}$ = 270.9 Hz), 121.09 (C-F, 1$J_{C\text{-}F}$ = 270.9 Hz), 120.04, 118.94 (C-F, 1$J_{C\text{-}F}$ = 270.9 Hz), 116.78 (C-F, 1$J_{C\text{-}F}$ = 270.9 Hz), 116.36. **^{19}F NMR (471 MHz, CDCl$_3$)** δ -60.37. **HRMS (ESI/QTOF), m/z:** [M-H]$^-$ Calcd. $C_{11}H_2N_3OF_2$ 230.0166; Found 230.0166.

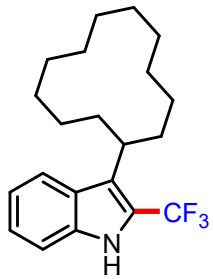


2-(trifluoromethyl)-1H-indole-3-carbonitrile (3e): Physical state: White liquid; **Yield:** 22 mg (52 %). **^{1}H NMR (500 MHz, CDCl$_3$)** δ 9.40 (s, 1H), 7.84 (d, J = 8.1 Hz, 1H), 7.55 (d, J = 8.3 Hz, 1H), 7.48 (t, J = 7.7 Hz, 1H), 7.40 (t, J = 7.5 Hz, 1H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 134.54, 126.98, 126.95, 123.89, 120.83 (C-F, 1$J_{C\text{-}F}$ = 270.9 Hz), 120.75, 118.68 (C-F, 1$J_{C\text{-}F}$ = 270.9 Hz), 112.88, 112.69. **^{19}F NMR (471 MHz, CDCl$_3$)** δ -60.31. **HRMS (ESI/QTOF), m/z:** [M-H]$^-$ Calcd.$C_{10}H_4N_2F_3$ 209.0327; Found 209.0334.



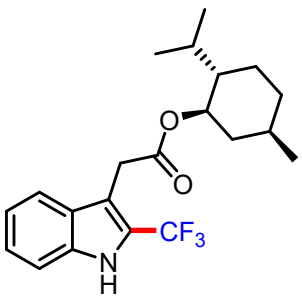
3-cyclohexyl-2-(trifluoromethyl)-1H-indole (3f): Physical state: White liquid; **Yield:** 37 mg (69 %). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.20 (s, 1H), 7.88 (d, J = 8.2 Hz, 1H), 7.39 (d, J = 8.3 Hz, 1H), 7.29 (t, J = 7.4 Hz, 1H), 7.17 – 7.13 (m, 1H), 3.06 – 3.00 (m, 1H), 1.98 – 1.80 (m, 7H), 1.48 – 1.36 (m, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 135.61, 126.51, 124.43, 124.06, 124.03, 123.37 (C-F, $1J_{C\text{-}F}$ = 269.64 Hz), 122.39, 121.23 (C-F, $1J_{C\text{-}F}$ = 269.64 Hz), 120.13, 36.39, 32.99, 27.13, 26.35. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -57.47. **HRMS (ESI/QTOF), m/z:** $[M\text{-}H]^-$ Calcd. $C_{15}H_{15}NF_3$ 266.1157; Found 266.1162.

3-cyclododecyl-2-(trifluoromethyl)-1H-indole (3g): Physical state: White liquid; **Yield:** 45

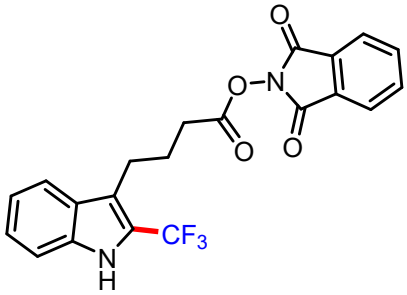


mg (64%). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.19 (s, 1H), 7.80 (d, J = 8.2 Hz, 1H), 7.40 (d, J = 8.3 Hz, 1H), 7.29 (t, J = 7.7 Hz, 1H), 7.14 (t, J = 7.6 Hz, 1H), 3.30 (t, J = 6.9 Hz, 1H), 2.10 – 2.05 (m, 2H), 1.71 – 1.66 (m, 2H), 1.63 (d, J = 6.2 Hz, 1H), 1.46 (q, J = 6.7 Hz, 6H), 1.44 – 1.26 (m, 11H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 135.86, 126.49, 124.42, 123.74, 123.42 (C-F, $1J_{C\text{-}F}$ = 269.64 Hz), 122.57, 121.26 (C-F, $1J_{C\text{-}F}$ = 269.64 Hz), 120.05, 119.03, 112.08, 30.71, 30.26, 24.44, 23.77, 22.45. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -57.38. **HRMS (ESI/QTOF), m/z:** $[M\text{-}H]^-$ Calcd. $C_{21}H_{27}NF_3$ 350.2096; Found 350.2105.

(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 2-(2-(trifluoromethyl)-1H-indol-3-yl)acetate



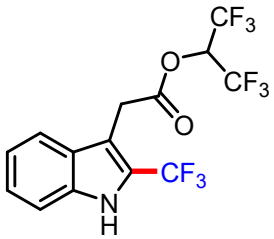
(3h): Physical state: White liquid; **Yield:** 65 mg (85 %). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.43 (s, 1H), 7.66 (d, J = 8.1 Hz, 1H), 7.38 (dd, J = 8.3, 1.4 Hz, 1H), 7.32 (dd, J = 8.2, 7.0 Hz, 1H), 7.22 – 7.18 (m, 1H), 4.70 – 3.90 (m, 1H), 3.90 (s, 2H), 1.99 – 1.95 (m, 1H), 1.68 – 1.60 (m, 4H), 1.44 – 143 (m, 1H), 1.33 – 1.27 (m, 1H), 1.02 – 0.90 (m, 1H), 0.87 (d, J = 6.6 Hz, 3H), 0.84 – 0.81 (m, 1H), 0.78 (d, J = 7.0 Hz, 3H), 0.64 (d, J = 7.0 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 170.29, 135.27, 127.49, 125.12, 122.93 (C-F, $2J_{C\text{-}F}$ = 35.3 Hz), 122.65 (C-F, $2J_{C\text{-}F}$ = 35.3 Hz), 121.06, 120.79 (C-F, $1J_{C\text{-}F}$ = 269.64 Hz), 120.41, 118.65 (C-F, $1J_{C\text{-}F}$ = 269.64 Hz), 111.82, 75.16, 47.11, 40.77, 34.33, 31.48, 30.33, 26.22, 23.50, 22.12, 20.75, 16.27. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -58.49. **HRMS (ESI/QTOF), m/z:** $[M\text{-}H]^-$ Calcd. $C_{21}H_{25}NO_2F_3$ 380.1837; Found 380.1841.



1,3-dioxoisoindolin-2-yl 4-(2-(trifluoromethyl)-1H-indol-3-yl)butanoate (3i) : Physical state: White liquid;

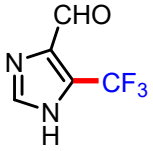
Yield: 46 mg (55 %). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.36 (s, 1H), 7.90 – 7.88 (m, 2H), 7.80 – 7.78 (m, 2H), 7.72 (d, J = 8.0 Hz, 1H), 7.41 (d, J = 8.3 Hz, 1H), 7.33 (t, J = 7.6 Hz, 1H), 7.21 (t, J = 7.5 Hz, 1H), 3.06 (t, J = 8.2 Hz, 2H), 2.73 (t, J = 7.5 Hz, 2H), 2.17 (p, J = 7.6 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 169.55, 162.11, 135.40, 135.01, 134.94, 134.90, 129.07, 127.41, 125.90 (C-F, $1J_{C\text{-}F}$ = 262.1 Hz), 125.09, 124.20, 124.16, 124.13, 123.83 (C-F, $1J_{C\text{-}F}$ = 262.1 Hz), 121.75 (C-F, $1J_{C\text{-}F}$ = 262.1 Hz), 120.95, 120.37, 119.65 (C-F, $1J_{C\text{-}F}$ = 262.1 Hz), 111.90, 30.59, 25.69, 22.94. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -58.03. **HRMS (ESI/QTOF), m/z:** $[M\text{-}H]^-$ Calcd. $C_{21}H_{14}N_2O_4F_3$ 415.0906; Found 415.0899.

1,1,1,3,3,3-hexafluoropropan-2-yl 2-(2-(trifluoromethyl)-1H-indol-3-yl)acetate (3j):



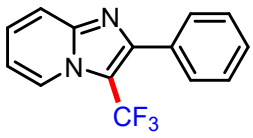
Physical state: White liquid; **Yield:** 47 mg (60 %). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.53 (s, 1H), 7.64 (d, J = 8.1 Hz, 1H), 7.45 (d, J = 8.3 Hz, 1H), 7.40 (t, J = 7.6 Hz, 1H), 7.29 – 7.26 (m, 1H), 5.78 (hept, J = 6.0 Hz, 1H), 4.15 (d, J = 1.3 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 167.69, 135.23, 126.98, 125.56, 124.79 (C-F, $1J_{C\text{-}F}$ = 269.64 Hz), 123.91 (C-F, $2J_{C\text{-}F}$ = 37.3 Hz), 123.61 (C-F, $2J_{C\text{-}F}$ = 37.3 Hz), 123.32 (C-F, $2J_{C\text{-}F}$ = 37.3 Hz), 123.02 (C-F, $2J_{C\text{-}F}$ = 37.3 Hz), 122.66 (C-F, $1J_{C\text{-}F}$ = 269.64 Hz), 121.62, 120.52 (C-F, $1J_{C\text{-}F}$ = 269.64 Hz), 119.76, 112.11, 108.25 (C-F, $3J_{C\text{-}F}$ = 3.7 Hz), 108.23 (C-F, $3J_{C\text{-}F}$ = 3.7 Hz), 108.20 (C-F, $3J_{C\text{-}F}$ = 3.7 Hz), 108.18 (C-F, $3J_{C\text{-}F}$ = 3.7 Hz), 67.66 (C-F, q, J=34.9), 67.39 (C-F, q, J=34.9), 67.11 (C-F, q, J=34.9), 66.83 (C-F, q, J=34.9), 66.56 (C-F, q, J=34.9), 28.86. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -58.82 (3F), -73.39 (6F). **HRMS (ESI/QTOF), m/z:** $[M\text{-}H]^-$ Calcd. $C_{14}H_7NO_2F_9$ 392.0333; Found 392.0341.

5-(trifluoromethyl)-1H-imidazole-4-carbaldehyde (3k): Physical state: White solid; **Yield:**



30 mg (90 %). **^{1}H NMR (500 MHz, DMSO-d_6)** δ 14.00 (s, 1H), 9.88 (s, 1H), 8.18 (s, 1H). **^{13}C NMR (126 MHz, DMSO- d_6)** δ 179.30, 140.65, 136.11 (C-F, $2J_{C\text{-}F}$ = 39.06 Hz), 135.82 (C-F, $2J_{C\text{-}F}$ = 39.06 Hz), 135.50 (C-F, $2J_{C\text{-}F}$ = 39.06 Hz), 135.18 (C-F, $2J_{C\text{-}F}$ = 39.06 Hz), 129.61, 124.56 (C-F, $1J_{C\text{-}F}$ = 268.38 Hz), 122.43 (C-F, $1J_{C\text{-}F}$ = 268.38 Hz), 120.30 (C-F, $1J_{C\text{-}F}$ = 268.38 Hz), 118.17 (C-F, $1J_{C\text{-}F}$ = 268.38 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -55.88. **HRMS (ESI/QTOF), m/z:** $[M\text{-}H]^-$ Calcd. $C_5H_2N_2OF_3$ 163.0119; Found 163.0112.

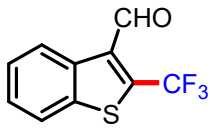
2-phenyl-3-(trifluoromethyl)imidazo[1,2-α]pyridine (3l): Physical



state: white solid; **Yield:** 46 mg (88 %). **^{1}H NMR (400 MHz, $CDCl_3$)**

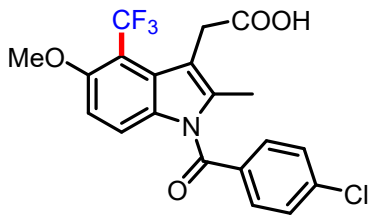
δ 8.31 (d, J = 7.0 Hz, 1H), 7.75 – 7.69 (m, 3H), 7.49 – 7.36 (m, 4H), 7.01 – 6.97 (m, 1H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 148.07, 146.16, 132.90, 129.71 (C-F, $J_{C\text{-}F}$ = 1.5 Hz), 129.69 (C-F, $J_{C\text{-}F}$ = 1.5 Hz), 129.68 (C-F, $J_{C\text{-}F}$ = 1.5 Hz), 129.66 (C-F, $J_{C\text{-}F}$ = 1.5 Hz), 129.08, 128.48, 128.30, 128.29, 127.14, 125.66 (C-F, $J_{C\text{-}F}$ = 3.3 Hz), 125.63 (C-F, $J_{C\text{-}F}$ = 3.3 Hz), 125.59 (C-F, $J_{C\text{-}F}$ = 3.3 Hz), 125.56 (C-F, $J_{C\text{-}F}$ = 3.3 Hz), 118.14, 114.09. **^{19}F NMR (376 MHz, CDCl$_3$)** δ -57.56. **HRMS (ESI/QTOF), m/z:** [M-H]$^-$ Calcd. $C_{14}H_8N_2F_3$ 261.0640; Found 261.0645.

2-(trifluoromethyl)benzo[β]thiophene-3-carbaldehyde (3m): **Physical state:** White liquid;



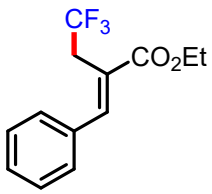
Yield: 36 mg (79 %). **^{1}H NMR (500 MHz, CDCl$_3$)** δ 10.43 (s, 1H), 8.11 (d, J = 8.3 Hz, 1H), 7.93 (d, J = 8.1 Hz, 1H), 7.60 – 7.53 (m, 2H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 183.83 (C-F, $J_{C\text{-}F}$ = 4.4 Hz), 183.79 (C-F, $J_{C\text{-}F}$ = 4.4 Hz), 183.76 (C-F, $J_{C\text{-}F}$ = 4.4 Hz), 183.72 (C-F, $J_{C\text{-}F}$ = 4.4 Hz), 144.35, 141.43, 135.86, 128.78, 126.48, 125.84 (C-F, 1$J_{C\text{-}F}$ = 273.4 Hz), 125.24 (C-F, $J_{C\text{-}F}$ = 2.4 Hz), 125.22 (C-F, $J_{C\text{-}F}$ = 2.4 Hz), 125.20 (C-F, $J_{C\text{-}F}$ = 2.4 Hz), 125.17 (C-F, $J_{C\text{-}F}$ = 2.4 Hz), 123.67 (C-F, 1$J_{C\text{-}F}$ = 273.4 Hz), 123.30, 121.50 (C-F, 1$J_{C\text{-}F}$ = 273.4 Hz), 119.32 (C-F, 1$J_{C\text{-}F}$ = 273.4 Hz). **^{19}F NMR (376 MHz, CDCl$_3$)** δ -53.82. **HRMS (ESI/QTOF), m/z:** [M-H]$^-$ Calcd. $C_{10}H_4OSF_3$ 228.9935; Found 228.9941.

2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-4-(trifluoromethyl)-1H-indol-3-yl)acetic

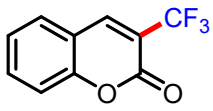


acid (3o): **Physical state:** Yellow Solid; **Yield:** 38 mg (45 %). **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.59 (d, J = 8.5 Hz, 2H), 7.41 (d, J = 8.5 Hz, 2H), 7.30 (d, J = 9.2 Hz, 1H), 6.77 (d, J = 9.2 Hz, 1H), 3.80 (s, 3H), 3.77 (q, J = 2.5 Hz, 2H), 2.20 (s, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 177.24, 168.14, 154.91, 154.89, 140.21, 139.30, 133.29, 132.03, 131.58, 131.48, 129.40, 128.88, 127.87 (C-F, 1$J_{C\text{-}F}$ = 273.42 Hz), 127.71, 127.23 (C-F, $J_{C\text{-}F}$ = 2.52 Hz), 127.21 (C-F, $J_{C\text{-}F}$ = 2.52 Hz), 127.20 (C-F, $J_{C\text{-}F}$ = 2.52 Hz), 125.69 (C-F, 1$J_{C\text{-}F}$ = 273.42 Hz), 123.52 (C-F, 1$J_{C\text{-}F}$ = 273.42 Hz), 121.35 (C-F, 1$J_{C\text{-}F}$ = 273.42 Hz), 57.74, 29.71, 13.72. **^{19}F NMR (376 MHz, CDCl$_3$)** δ -51.59. **HRMS (ESI/QTOF), m/z:** [M-H]$^-$ Calcd. $C_{20}H_{14}NO_4F_3Cl$ 424.0563; Found 424.0560.

ethyl (E)-2-benzylidene-4,4,4-trifluorobutanoate (3p): Physical state: White solid; **Yield:**

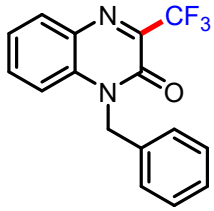


46 mg (90 %). **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.23 (s, 1H), 7.51 (d, J = 5.8 Hz, 2H), 7.46 (d, J = 6.6 Hz, 3H), 4.59 (s, 2H), 4.37 (q, J = 7.2 Hz, 2H), 1.38 (t, J = 7.2 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 165.60, 148.75, 133.25, 130.32, 129.10 (J = 13.86), 128.99 (J = 13.86), 120.89, 118.28, 117.51, 62.21, 49.46. **^{19}F NMR (376 MHz, CDCl$_3$)** δ -77.98.



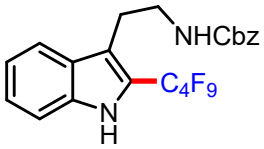
3-(trifluoromethyl)-2H-chromen-2-one (3q): Physical state: White solid; **Yield:** 32 mg (75 %). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.16 (s, 1H), 7.70 – 7.62 (m, 2H), 7.40 – 7.37 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 155.92, 154.65, 143.46 (C-F, $3J_{C\text{-}F}$ = 4.9 Hz), 143.42 (C-F, $3J_{C\text{-}F}$ = 4.9 Hz), 143.38 (C-F, $3J_{C\text{-}F}$ = 4.9 Hz), 143.34 (C-F, $3J_{C\text{-}F}$ = 4.9 Hz), 134.48, 133.76, 129.53, 125.32, 124.62 (C-F, $1J_{C\text{-}F}$ = 273.42 Hz), 122.46 (C-F, $1J_{C\text{-}F}$ = 273.42 Hz), 121.32, 120.29 (C-F, $1J_{C\text{-}F}$ = 273.42 Hz), 118.13 (C-F, $1J_{C\text{-}F}$ = 273.42 Hz), 118.09 (C-F, $2J_{C\text{-}F}$ = 34.02 Hz), 117.82 (C-F, $2J_{C\text{-}F}$ = 34.02 Hz), 117.56 (C-F, $2J_{C\text{-}F}$ = 34.02 Hz), 117.29 (C-F, $2J_{C\text{-}F}$ = 34.02 Hz), 117.00, 116.80, 116.42. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -66.08. **HRMS (ESI/QTOF), m/z:** $[M+H]^-$ Calcd. $C_{10}H_6O_2F_3$ 215.0321; Found 215.0320.

1-benzyl-3-(trifluoromethyl)quinoxaline-2(1H)-one (3r): Physical state: White solid;



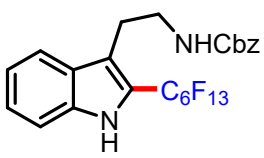
Yield: 49 mg (80 %). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.96 (dd, J = 8.1, 1.5 Hz, 1H), 7.58 – 7.55 (m, 1H), 7.38 – 7.22 (m, 7H), 5.50 (s, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 151.90, 144.60 (C-F, $2J_{C\text{-}F}$ = 34.02 Hz), 144.33 (C-F, $2J_{C\text{-}F}$ = 34.02 Hz), 144.06 (C-F, $2J_{C\text{-}F}$ = 34.02 Hz), 143.79 (C-F, $2J_{C\text{-}F}$ = 34.02 Hz), 134.58, 134.14, 133.63, 132.02, 131.33, 129.23, 128.21, 127.19, 124.68, 123.36 (C-F, $1J_{C\text{-}F}$ = 277.2 Hz), 121.16 (C-F, $1J_{C\text{-}F}$ = 277.2 Hz), 118.96 (C-F, $1J_{C\text{-}F}$ = 277.2 Hz), 116.77 (C-F, $1J_{C\text{-}F}$ = 277.2 Hz), 114.95, 46.18. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -69.80. **HRMS (ESI/QTOF), m/z:** $[M+H]^-$ Calcd. $C_{16}H_{12}N_2OF_3$ 305.0902; Found 305.0904.

benzyl (2-(2-(nonafluoro-4l12-buta-1,3-diyn-1-yl)-1H-indol-3-yl)ethyl)carbamate (3s):



Physical state: White liquid; **Yield:** 68 mg (66 %). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.62 - 8.57 (m, 1H), 7.75 (d, J = 8.1 Hz, 1H), 7.42 - 7.32 (m, 7H), 7.17 (t, J = 7.6 Hz, 1H), 5.13 (s, 2H), 4.93 (t, J = 6.2 Hz, 1H), 3.53 (q, J = 6.8 Hz, 2H), 3.13 (t, J = 7.3 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 156.50, 136.55, 136.19, 128.53, 128.12 (J = 3.78), 128.09 (J = 3.78), 127.62, 125.17, 120.83, 120.34, 119.99 (J = 28.96), 119.76 (J = 28.96), 117.64, 111.81, 66.70, 41.81, 24.79. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -80.80 – -80.85 (m, 3F), -107.52 (s, 2F), -122.66 (s, 2F), -125.67 – -125.75 (m, 2F). **HRMS (ESI/QTOF), m/z:** $[M-H]^-$ Calcd. $C_{22}H_{16}N_2O_2F_9$ 511.1068; Found 511.1059.

benzyl (2-(2-(tridecafluoro-6l16-hexa-1,3,5-triyn-1-yl)-1H-indol-3-yl)ethyl)carbamate

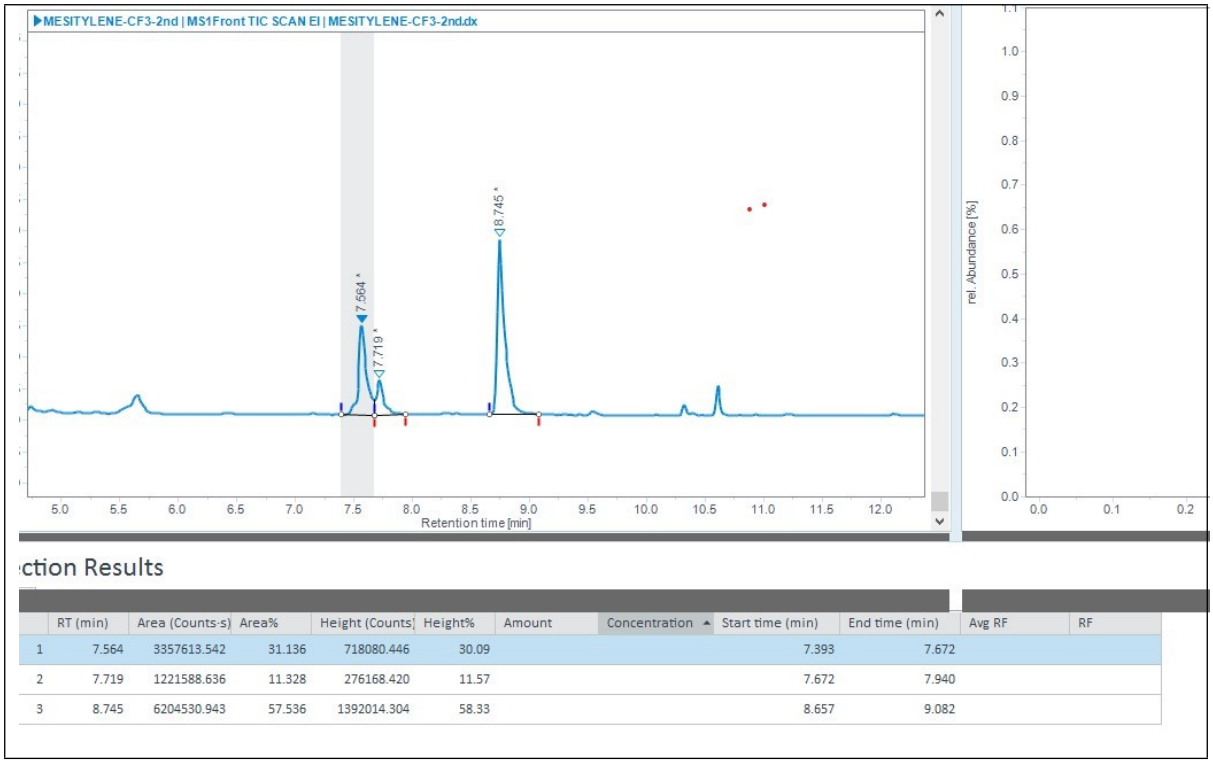


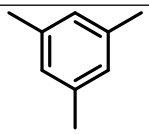
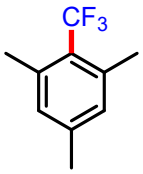
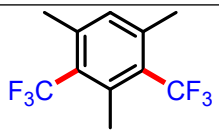
(3t): Physical state: White liquid; **Yield:** 73 mg (60 %). **^{1}H NMR (500**

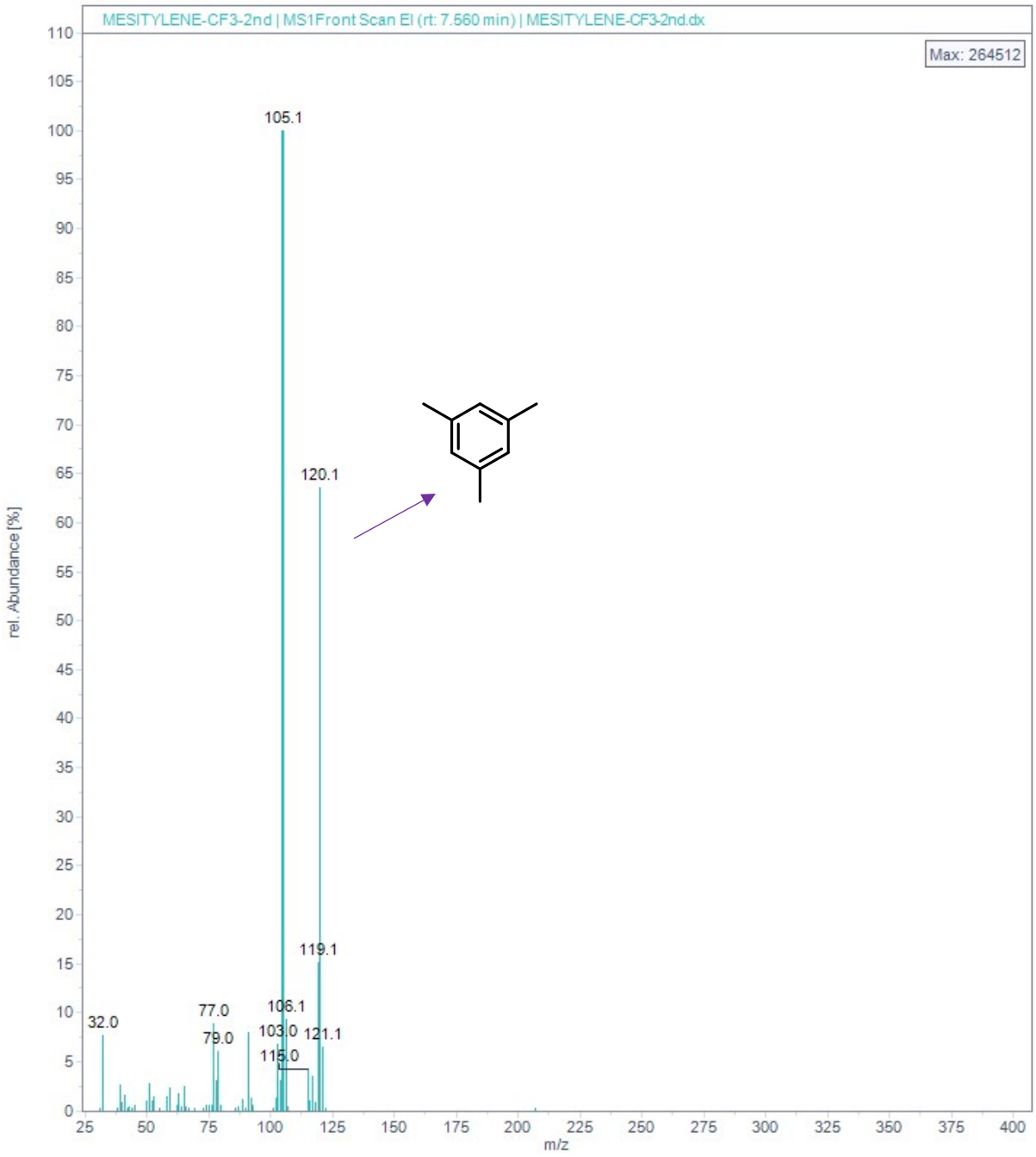
MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.42 - 7.31 (m, 7H), 7.18 (t, *J* = 7.6 Hz, 1H), 5.12 (s, 2H), 4.90 (s, 1H), 3.52 (q, *J* = 6.8 Hz, 2H), 3.13 (t, *J* = 7.3 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 156.46, 136.56, 136.14, 128.52, 128.11 (*J* = 2.52), 128.09 (*J* = 2.52), 127.63, 125.21, 120.87, 120.37, 120.04 (*J* = 28.98), 119.81(*J* = 28.98), 117.71, 111.76, 66.69, 41.80, 24.79. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -80.66 (t, *J* = 9.8 Hz, 3F), -107.32 – -107.51 (m, 2F), -121.57 – -121.84 (m, 4F), -122.60 – - 122.67 (m ,2H), -125.94 – -126.03 (m, 2H). **HRMS (ESI/QTOF), m/z:** $[M-H]^-$ Calcd. $C_{24}H_{16}N_2O_2F_{13}$ 611.1004; Found 611.1016.

benzyl (2-(2-(heptadecafluoro-8-octa-1,3,5,7-tetrayn-1-yl)-1H-indol-3-yl)ethyl)carbamate (3u): Physical state: White liquid; **Yield:** 75 mg (53 %). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.43 (s, 1H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.42 - 7.32 (m, 7H), 7.19 (d, *J* = 7.7 Hz, 1H), 5.12 (s, 2H), 4.88 (d, *J* = 6.4 Hz, 1H), 3.51 (t, *J* = 6.9 Hz, 2H), 3.12 (d, *J* = 7.5 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 155.41, 135.53, 135.09, 127.49, 127.08 (*J* = 3.78), 127.05 (*J* = 3.78), 126.60, 124.19, 119.85, 119.35, 119.02 (*J* = 28.98), 118.79 (*J* = 28.98), 116.70, 110.71, 65.65, 40.77, 23.76. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -80.68 (t, *J* = 10.0 Hz, 3F), -107.37 (t, *J* = 14.2 Hz, 2F), -121.74 (s, 7F), -122.59(s, 3F), -125.95 – -126.04 (m, 2F). **HRMS (ESI/QTOF), m/z:** $[M-H]^-$ Calcd. $C_{26}H_{16}N_2O_2F_{17}$ 711.0940; Found 711.0958.

GC- Analysis Data for 3n



Compound	Retention Time	Yield (Starting material) %	Yield (Conversion) %
 **1n**	7.564	31 (Unreacted); [M] = 120.1	
 **3n**	8.745		57.5; [M] = 188.1
 **3n'**	7.719		12; [M] = 256.1


MESITYLENE-CF3-2nd | MS1Front Scan EI (rt: 7.560 min) | MESITYLENE-CF3-2nd.dx
Max: 264512
rel. Abundance [%]
m/z
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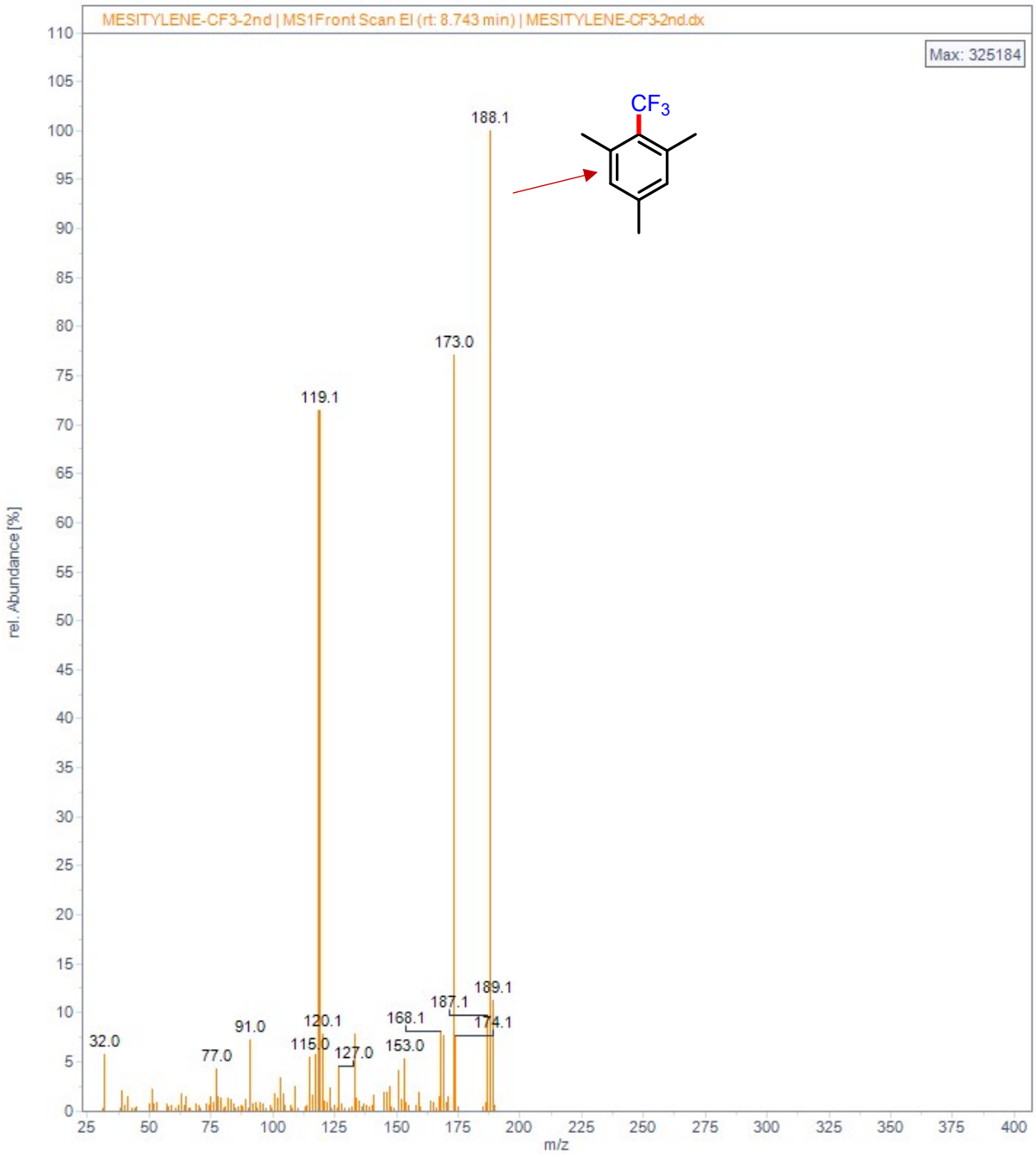
120.1
119.1
106.1
77.0
79.0
103.0
121.1
115.0
32.0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Max: 325184
CF3
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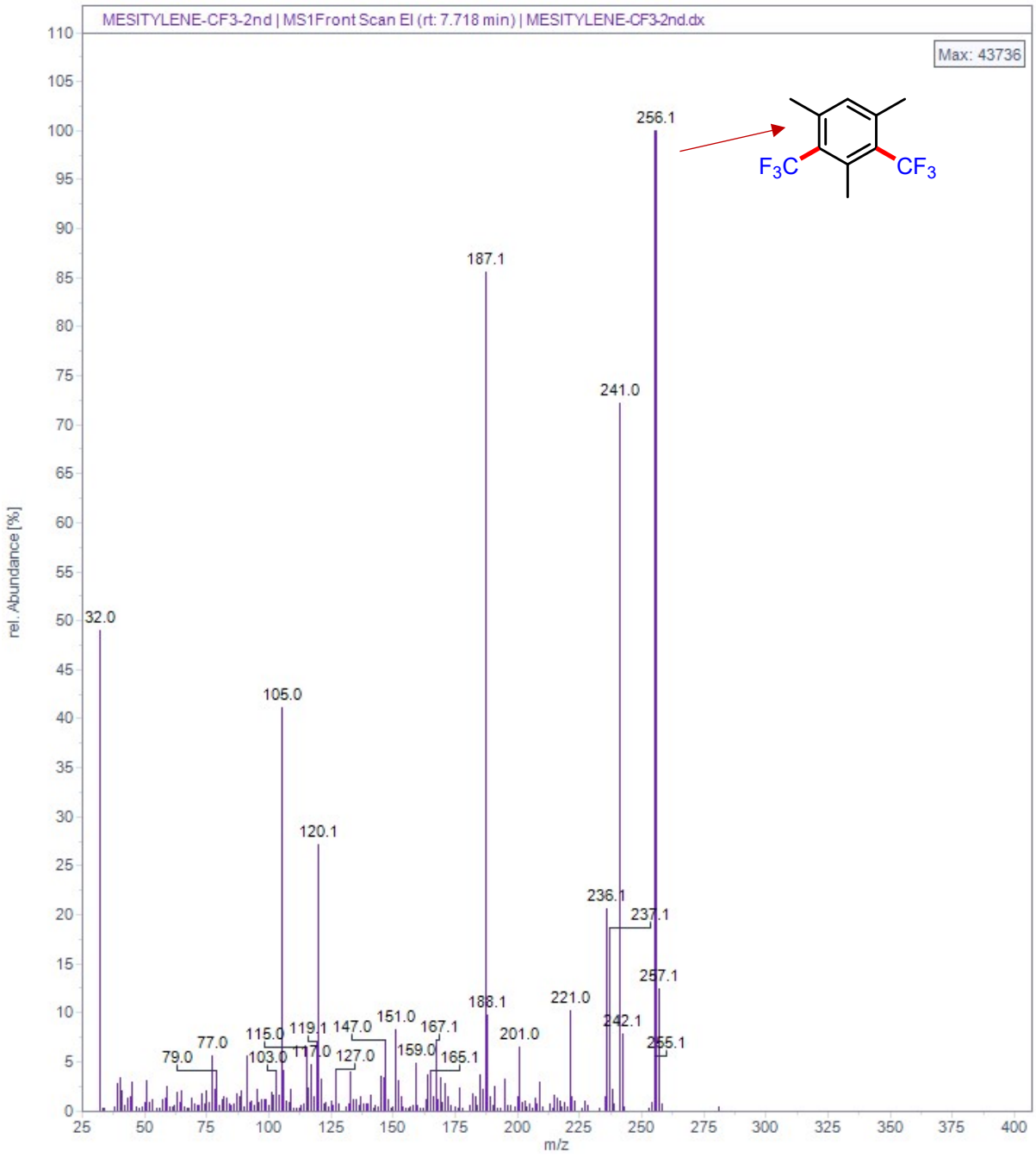
173.0
119.1
189.1
187.1
174.1
168.1
120.1
91.0
115.0
127.0
153.0
77.0
32.0
rel. Abundance [%]
m/z


MESITYLENE-CF3-2nd | MS1Front Scan EI (rt: 7.718 min) | MESITYLENE-CF3-2nd.dx
Max: 43736
rel. Abundance [%]
m/z
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187.1
241.0
32.0
105.0
120.1
236.1
237.1
257.1
188.1
221.0
242.1
255.1
201.0
77.0
79.0
115.0
103.0
119.1
117.0
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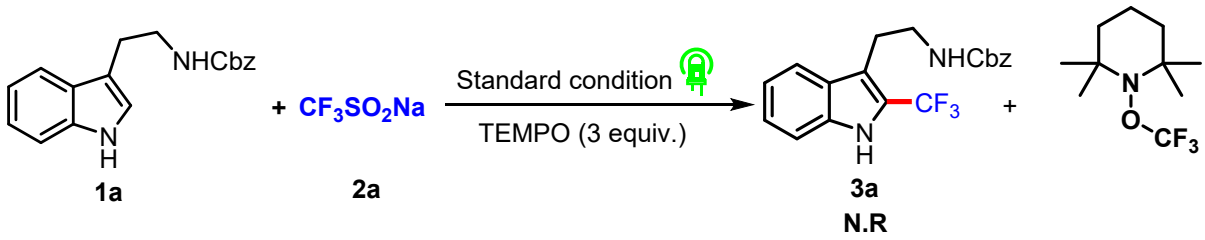
159.0
167.1
165.1
F3C
CF3

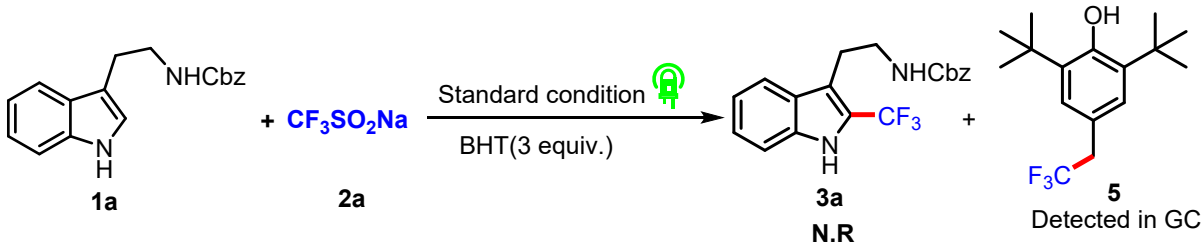
5: Mechanistic Investigation

5.1: Radical trapping experiments

Effect of TEMPO



Effect of BHT



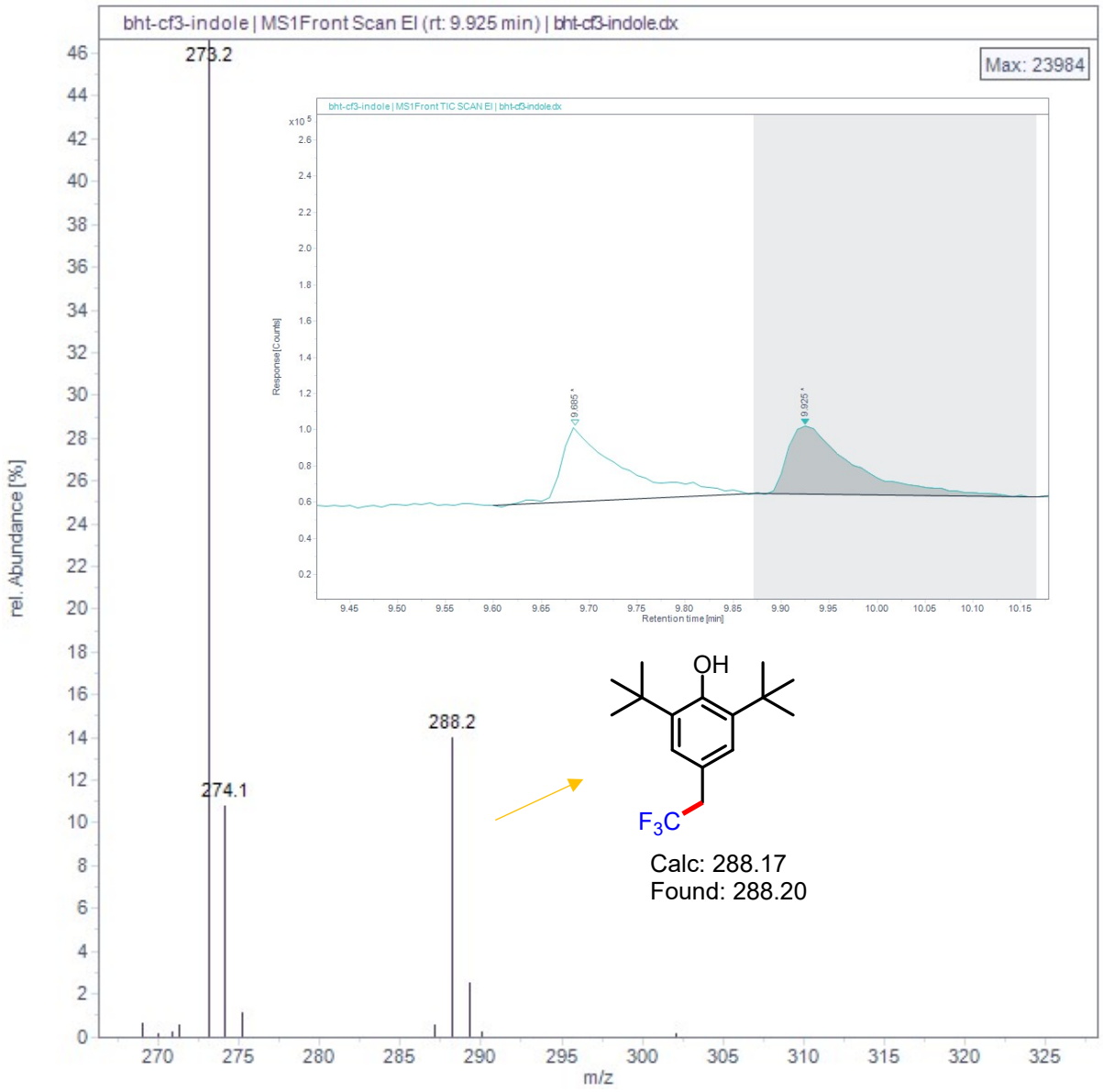


Figure 1: GC-MS Spectra for **5**

5.2. UV- Visible Studies

UV-Visible spectra were taken on a Agilent Cary 60 UV-Vis Spectrophotometer of catalyst (Eosin -Y) solutions as well solutions of **1a**, oxidant and **2a** ($1* 10^{-3}$ M). To investigate the possibility of a donor-acceptor complex between **1a**, **2a**, oxidant and Eosin Y along with other combination were studied and respective spectra are shown in Figure 2.

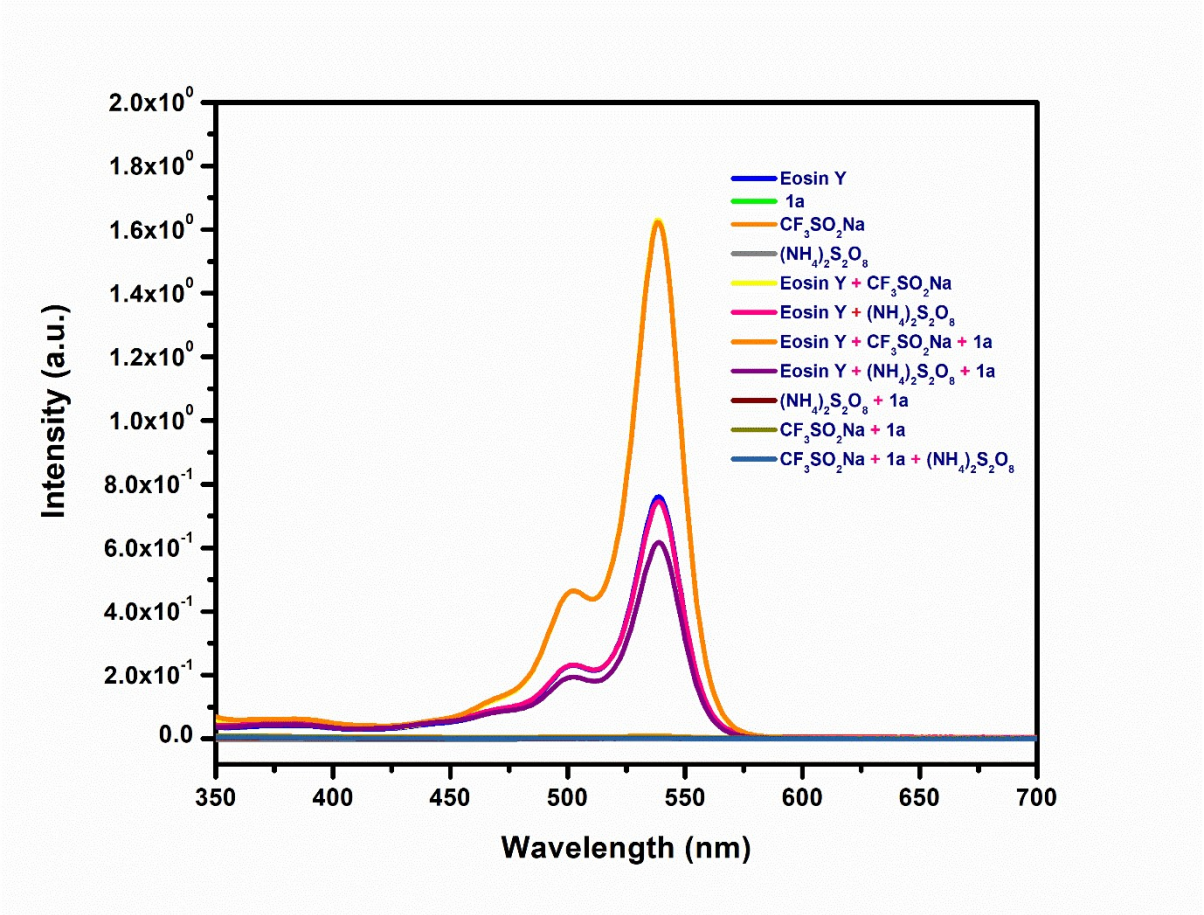


Figure 2: UV-Visible Spectra

Conclusion

*The aforementioned studies clearly show that the addition of the **1a**, **2a**, oxidant doesn't affect the stability of Eosin Y - as well as no evidence of EDA is concluding from above all spectral graphs, indicating that no possibility of EDA complex in the reaction medium.*

5.3. Fluorescence titration of photocatalyst

Fluorescence Quenching Experiments Test conditions for quenching reaction (I_0 and I are respective fluorescence intensities in the absence and presence of the indicated concentrations of the quenchers).

Eosin Y: 1.3 mg dissolved in 25 mL ACN (0.00008 M)

Quencher:

9.12 mg of $(NH_4)_2S_2O_8$ dissolved in 10 mL ACN (0.004 M)

15.6 mg of CF_3SO_2Na dissolved in 10 mL ACN (0.004 M)

11.8 mg **1a** dissolved in 10 mL ACN (0.004 M)

General procedure: 1 mL of prepared solution containing Eosin Y was added to a cuvette, keep the total volume at 3 mL, Quenchers and ACN were adjusted according to the table shown in Florescence Graphs.

Table 1: Preparation of Solution

Entry	Eosin Y	Quenchers	ACN	Total Volume
1	1 mL	0 mL	2 mL	3 mL
2	1 mL	20 μL	1.98 mL	3 mL
3	1 mL	25 μL	1.75 mL	3 mL
4	1 mL	30 μL	1.70 mL	3 mL
5	1 mL	40 μL	1.60 mL	3 mL
6	1 mL	45 μL	1.55 mL	3 mL

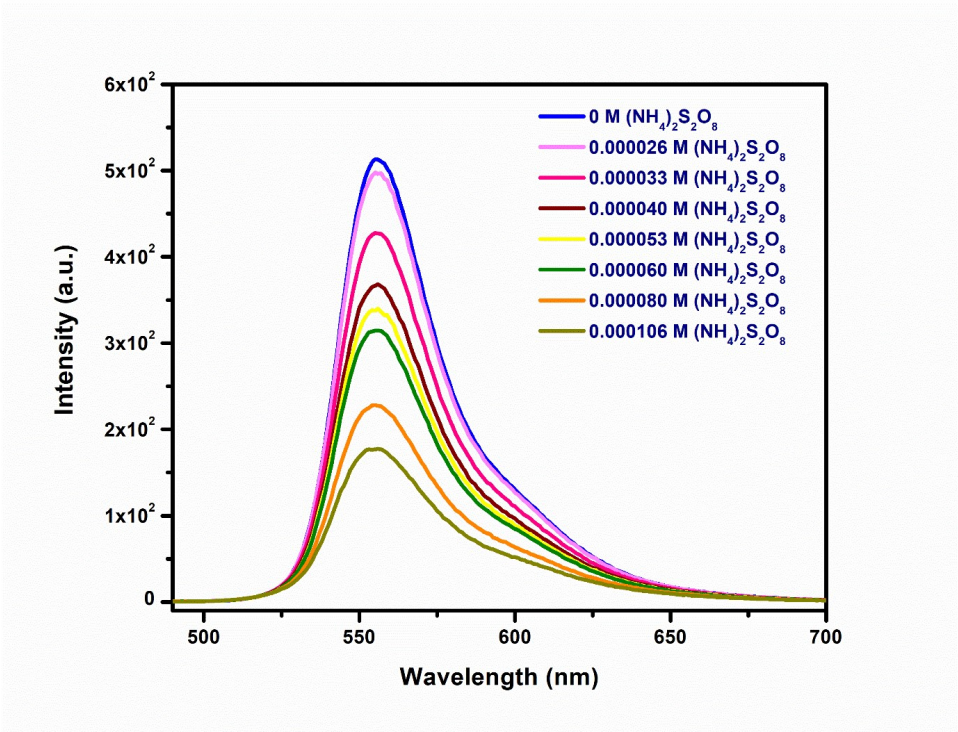


Figure 3: Fluorescence quenching experiments with $(NH_4)_2S_2O_8$

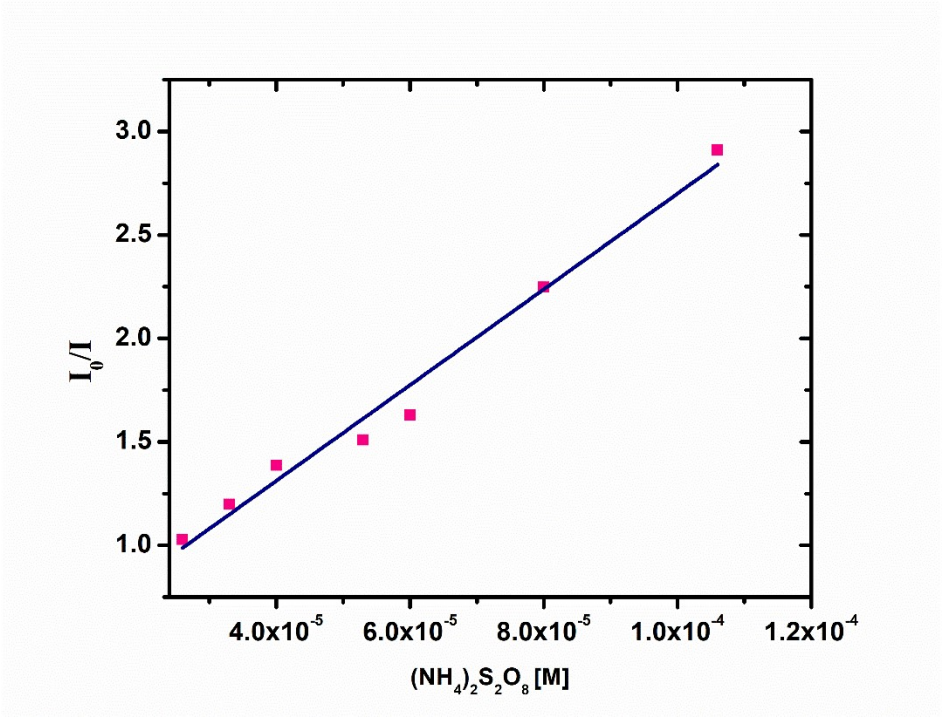


Figure 4: Stern-Volmer plots of $(NH_4)_2S_2O_8$

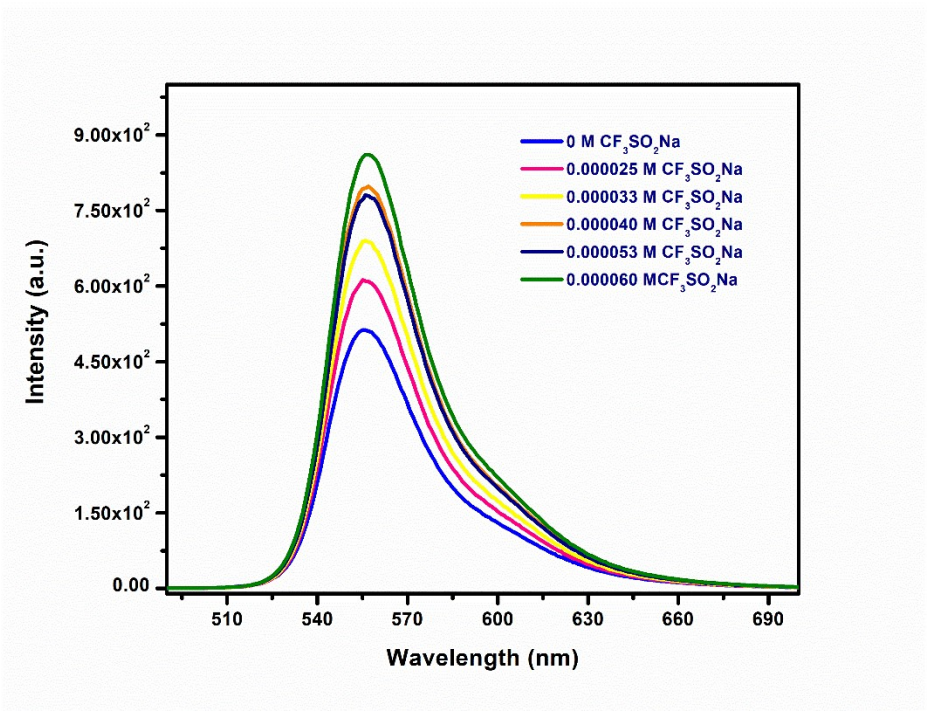


Figure 5: Fluorescence quenching experiments with CF_3SO_2Na

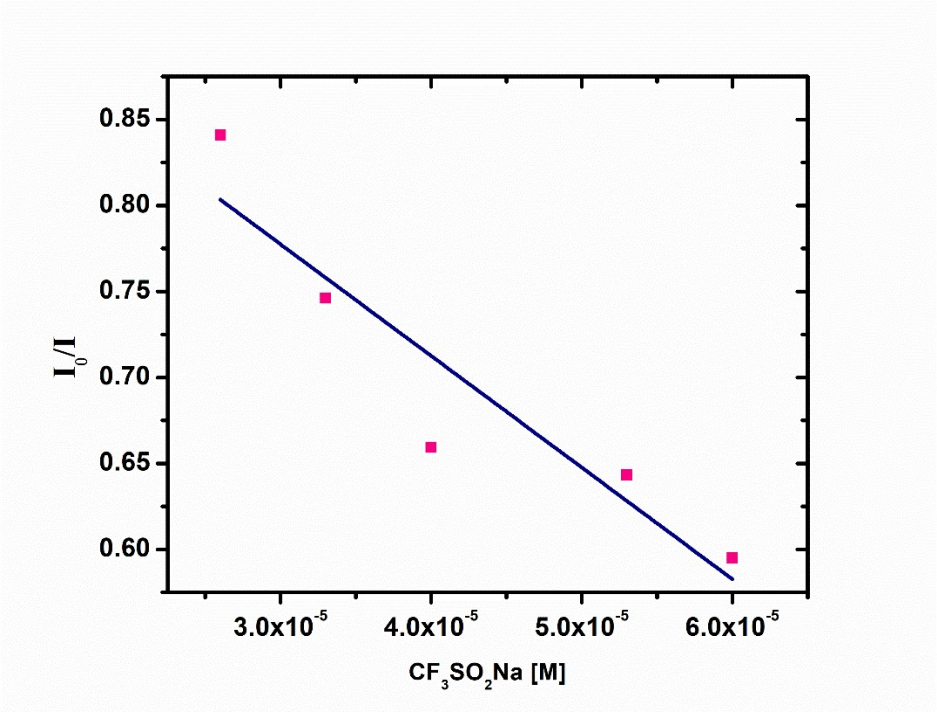


Figure 6: Stern-Volmer plots of CF_3SO_2Na

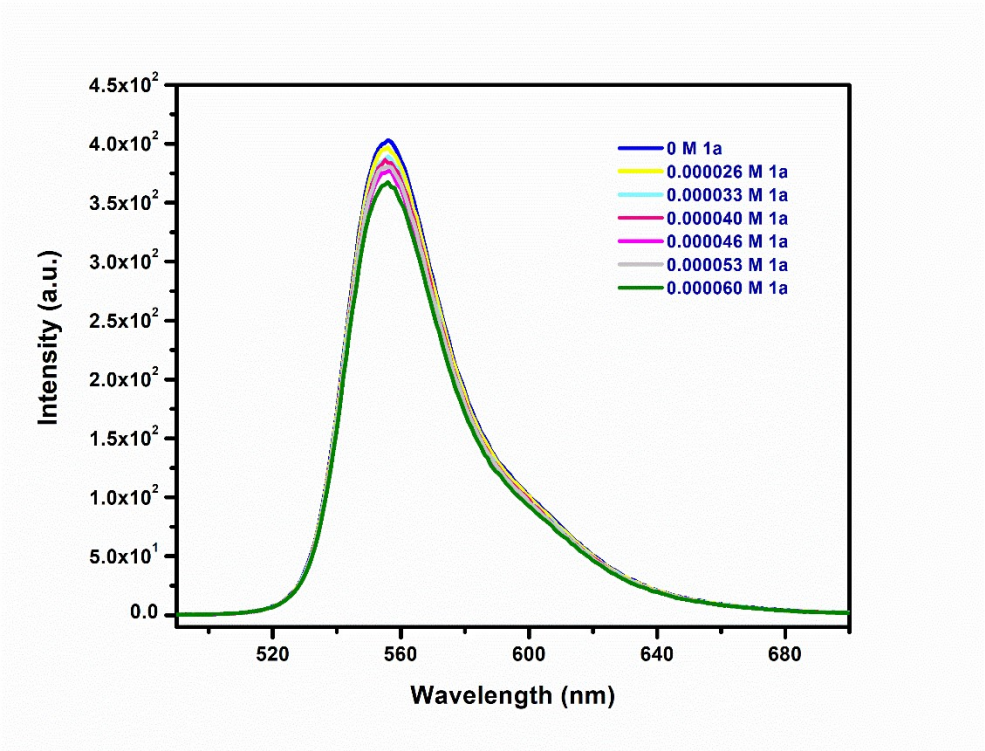


Figure 7: Fluorescence quenching experiments with **1a**

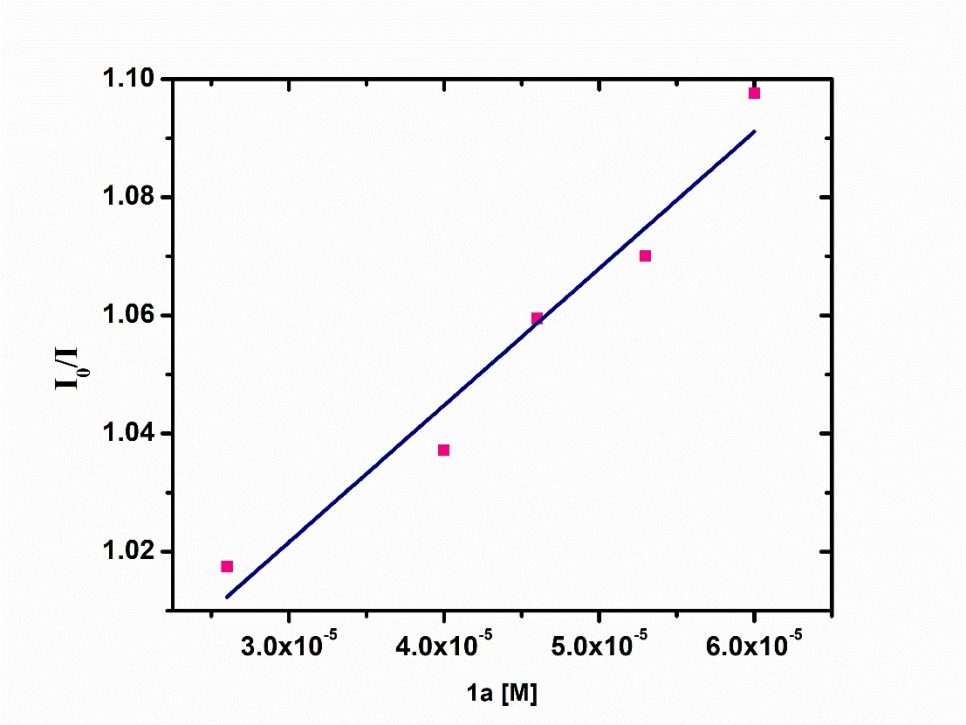


Figure 8: Stern-Volmer plots of **1a**

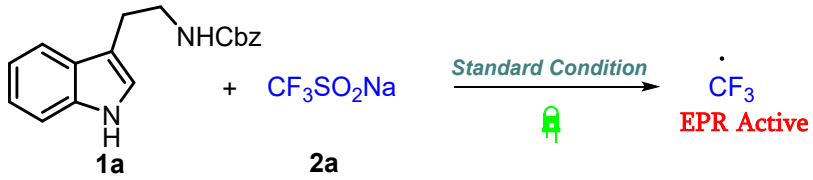
Conclusion

The aforementioned studies clearly show that the strongest quenching of Eosin Y occurs in the presence of oxidant as compared to substrate ***1a*** *i.e.,* $(NH_4)_2S_2O_8$*, No quenching was observed with* CF_3SO_2Na *indicating that quenching of the catalytic cycle is with* $(NH_4)_2S_2O_8$ *favouring Oxidative quenching cycle initiated by single electron reduction of Eosin Y on irradiation with green light.*

5.3: Electron Paramagnetic Resonance (EPR) Analysis

Continuous wave (CW) EPR spectra were obtained using a Bruker A300-9.5/12/S/W instrument with X-band of 8.75-9.65 GHz. The spectral data was collected at 77 K with the following spectrometer settings: microwave power = 0.48 mW, center field = 3350 G, sweep width = 100 G, sweep time = 30 s, modulation frequency = 9.6 GHz, modulation amplitude = 10 G, time constant = 0.01 ms.

For all the EPR measurements, the corresponding sample solution was transferred into the EPR tube and then placed in liquid Nitrogen to freeze the sample solution prior to recording of the spectra. After that, the sample tube was inserted in the EPR cavity which was kept frozen with continuous supply of liquid nitrogen for the recording of the spectra. For experiments in which the sample was irradiated, the sample tube was kept at 6 cm distance from the 535 nm Kessil lamp.



Scheme 4: General procedure for EPR study

Procedure: (Standard Condition) An oven dried 7 mL glass vial equipped with magnetic stirring bar was charged with 0.2 mmol of **1** (1.0 equiv.), trifluoro alkyl sulfinates (0.6 mmol, 3 equiv.) were taken in a long neck round bottom flask and 2.5 mol % of Eosin Y was added into it followed by ammonium peroxodisulfate (3.0 equiv. A screw cap equipped with a septum was then fitted tightly to the reaction vial. Next, the vial was placed into a magnetic stirrer and standard sample without irradiation with green light was recorded immediately by transferring into EPR tube and EPR spectra was recorded after freezing the solution by using liquid nitrogen (Figure 9).

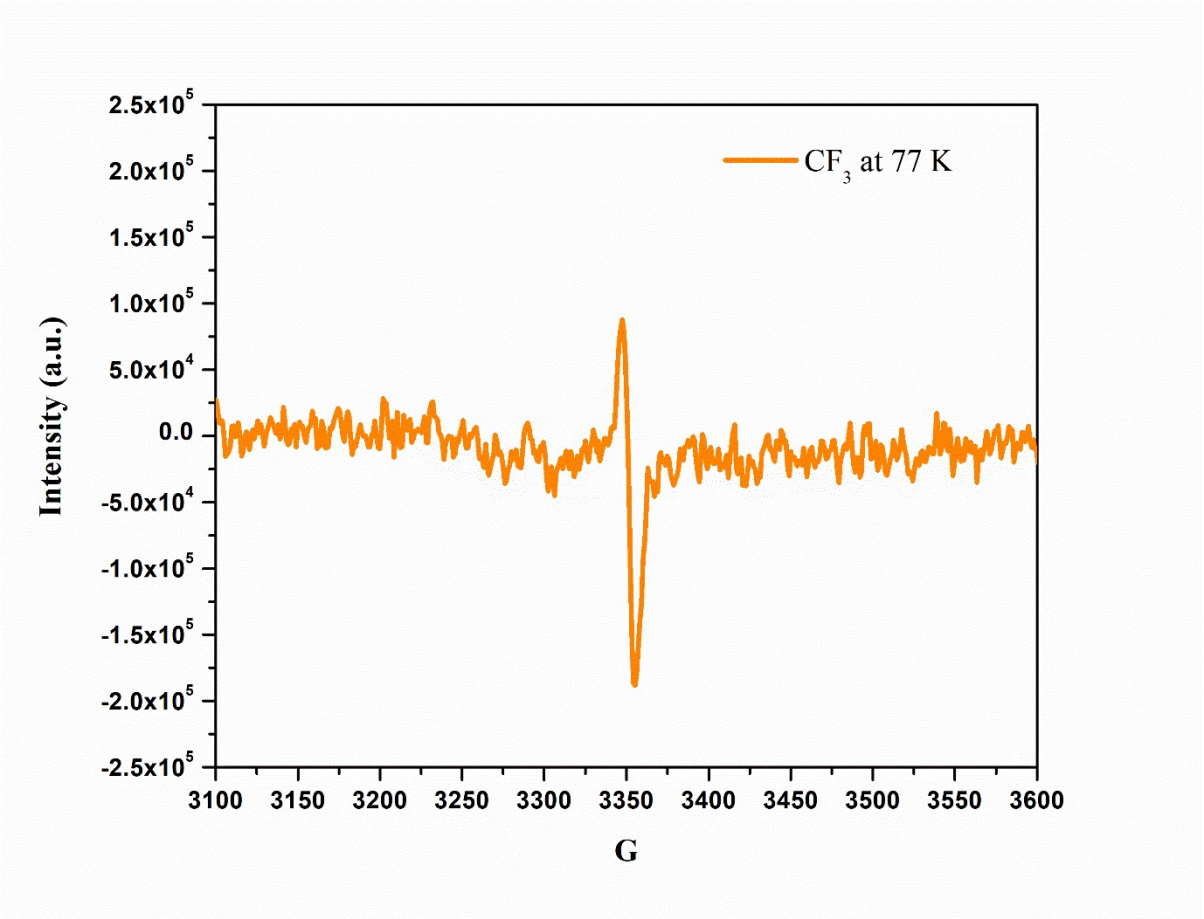


Figure 9: EPR analysis of standard solution at 77 K

6: References

1: S. Singh, K. S. Naskar, A. Kundu and R. P. Singh, *Synthesis*, 2023, **55**, 3685–3692.

2: X. Liu, L. Hao, Y. Wang and Y. Ji, *Chem. Asian J*, 2024, **19**, e202300901.

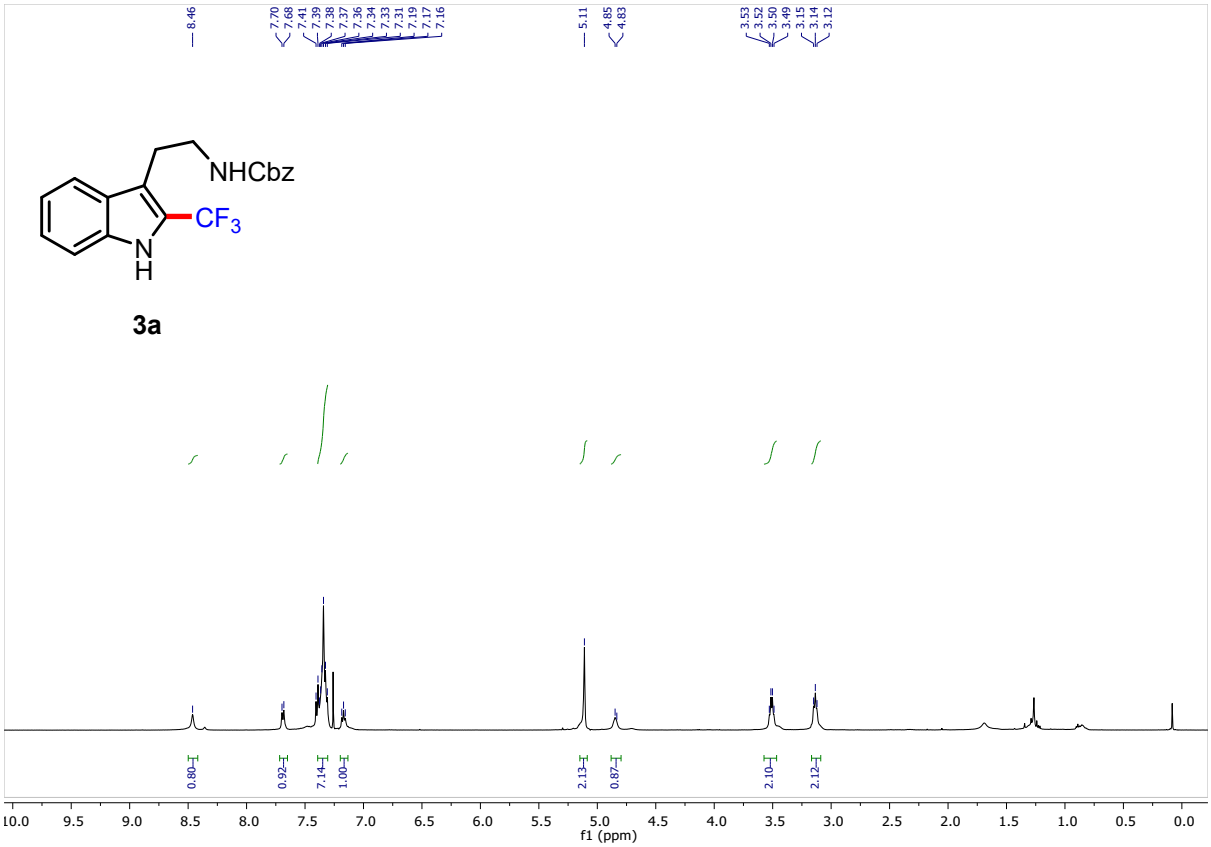
3: W. Gong, Y. Liu, J. Zhang, Y. Jiao, J. Xue and Y. Li, *Chem. Asian J*, 2013, **8**, 546–551.

4: H. Zhi, S. P.-M. Ung, Y. Liu, L. Zhao and C.-J. Li, *Adv. Synth. Catal*, 2016, **358**, 2553–2557.

5: V. U. B. Rao, S. Singh; K. N. Tripathi and R. P. Singh, *Synthesis*, 2020, **52**, 2551–2562.

6: A. Carrër, J.-D. Brion, S. Messaoudi and M. Alami, *Org. Lett.*, 2013, **15**, 5606–5609.

7: NMR Spectral Data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4.83
3.53
3.52
3.50
3.49
3.15
3.14
3.12
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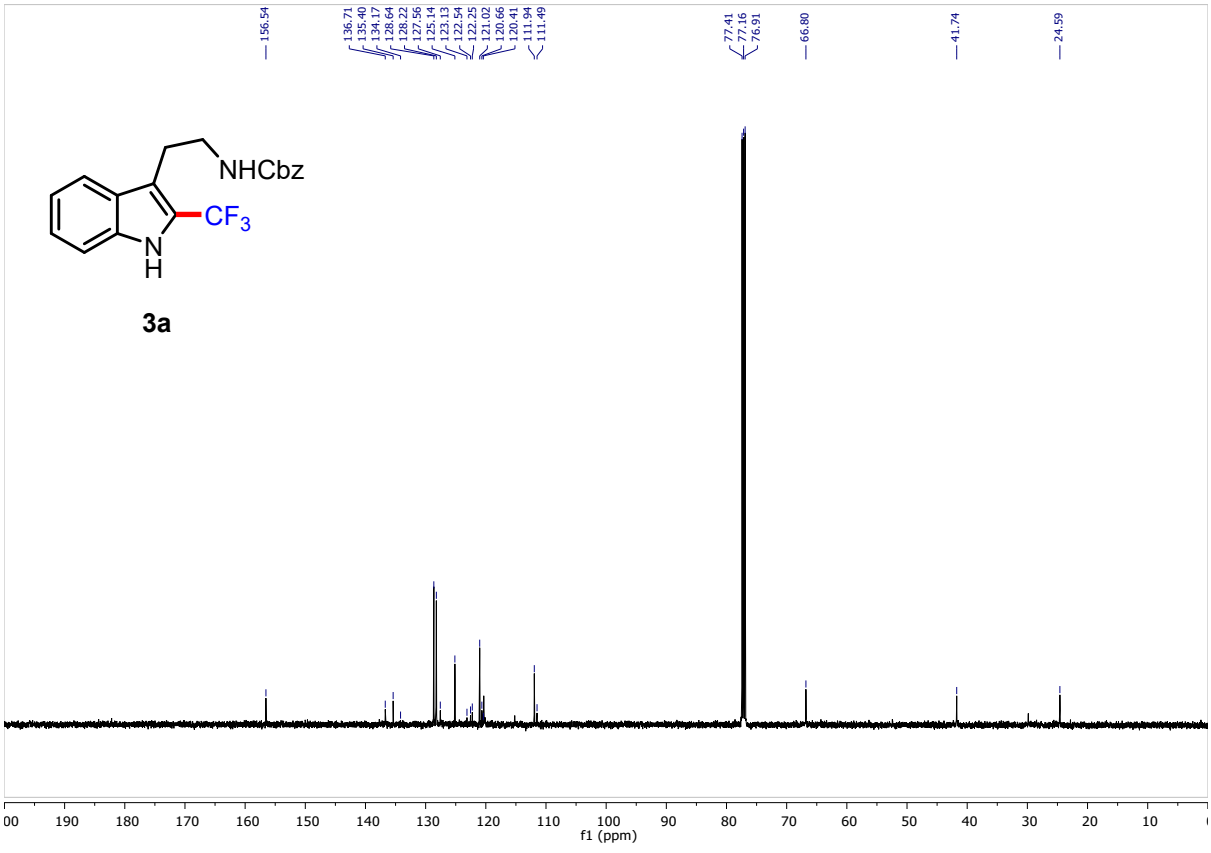
f1 (ppm)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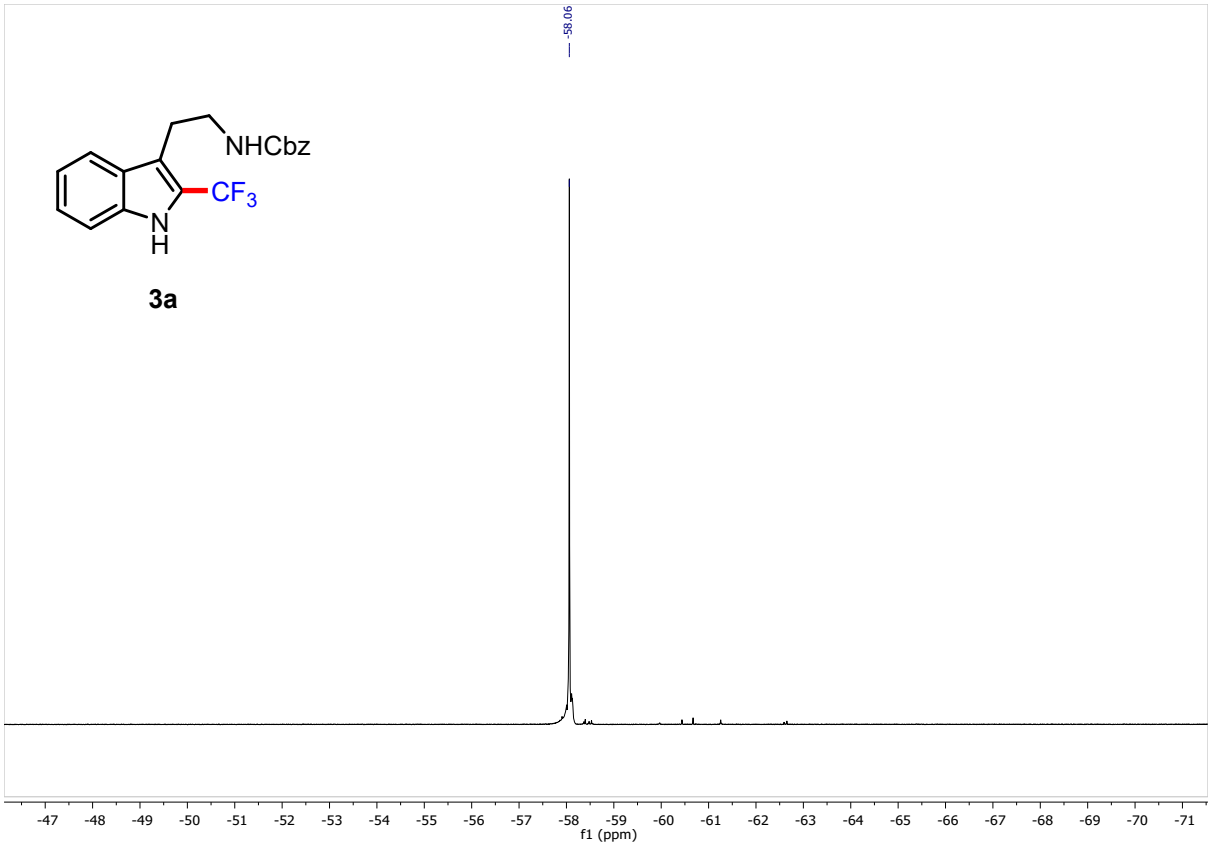
CF3
N
H
3a
f1 (ppm)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H
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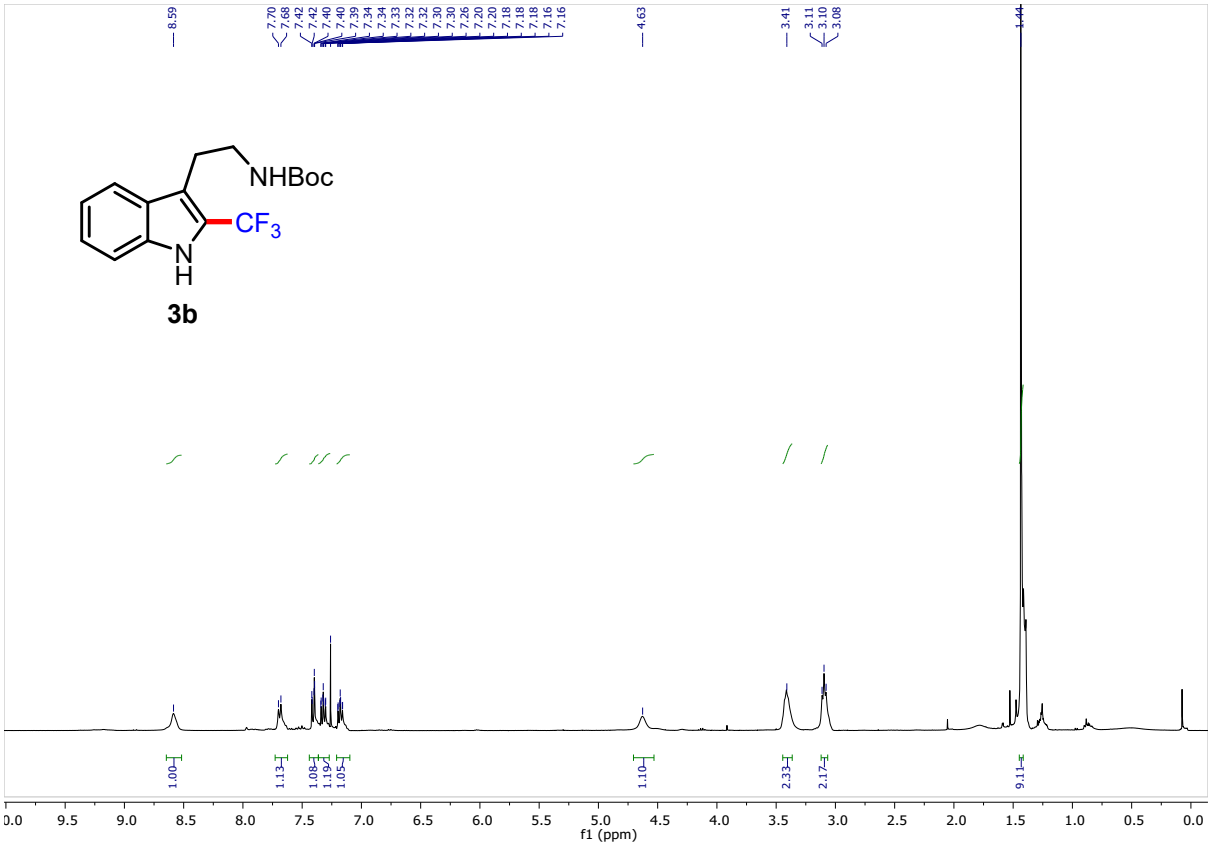
f1 (ppm)

3a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3.10
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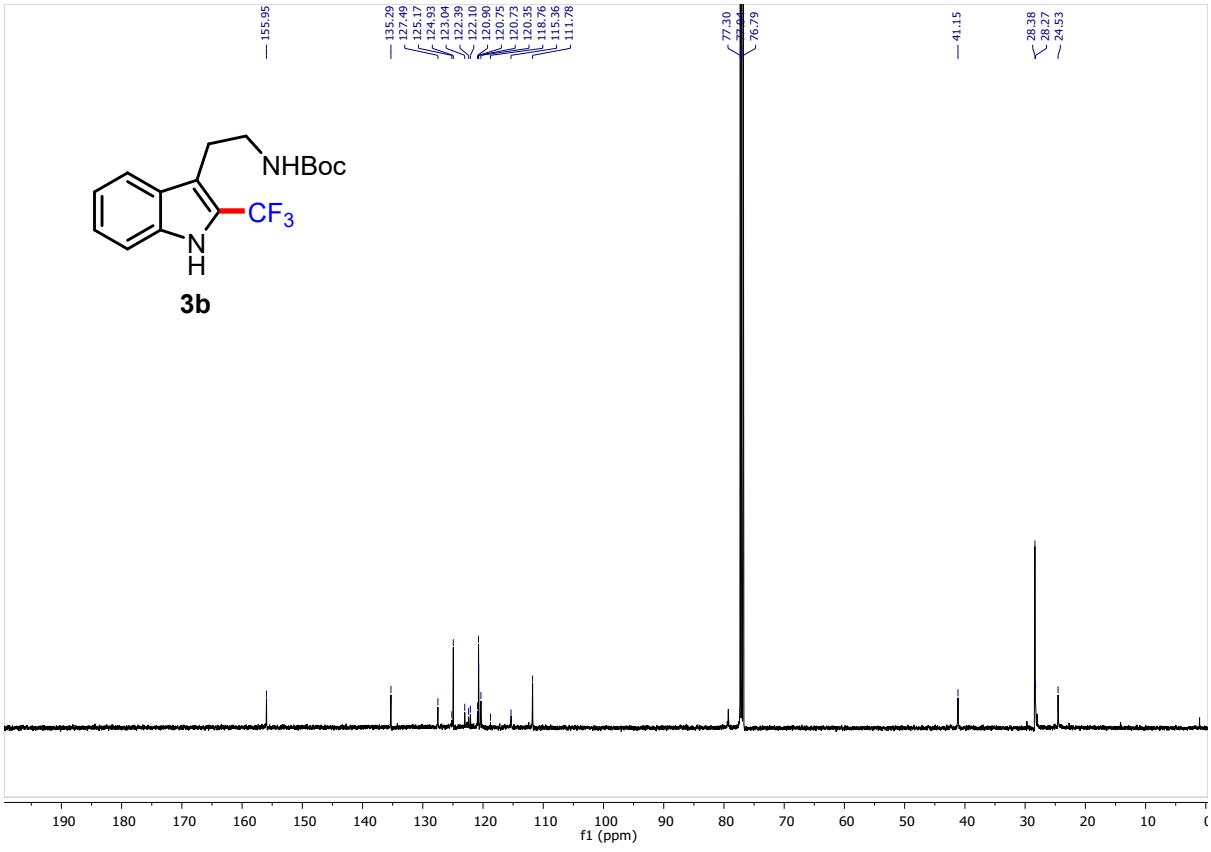
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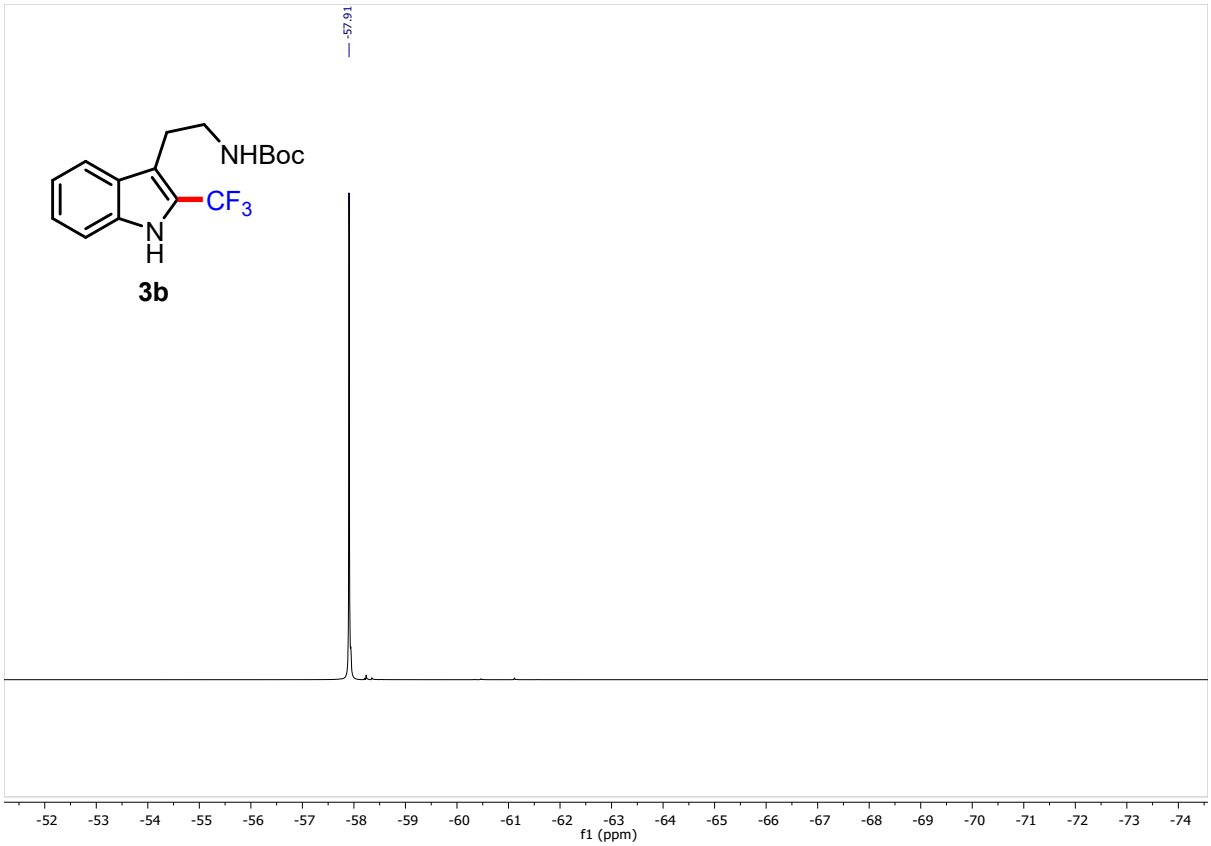
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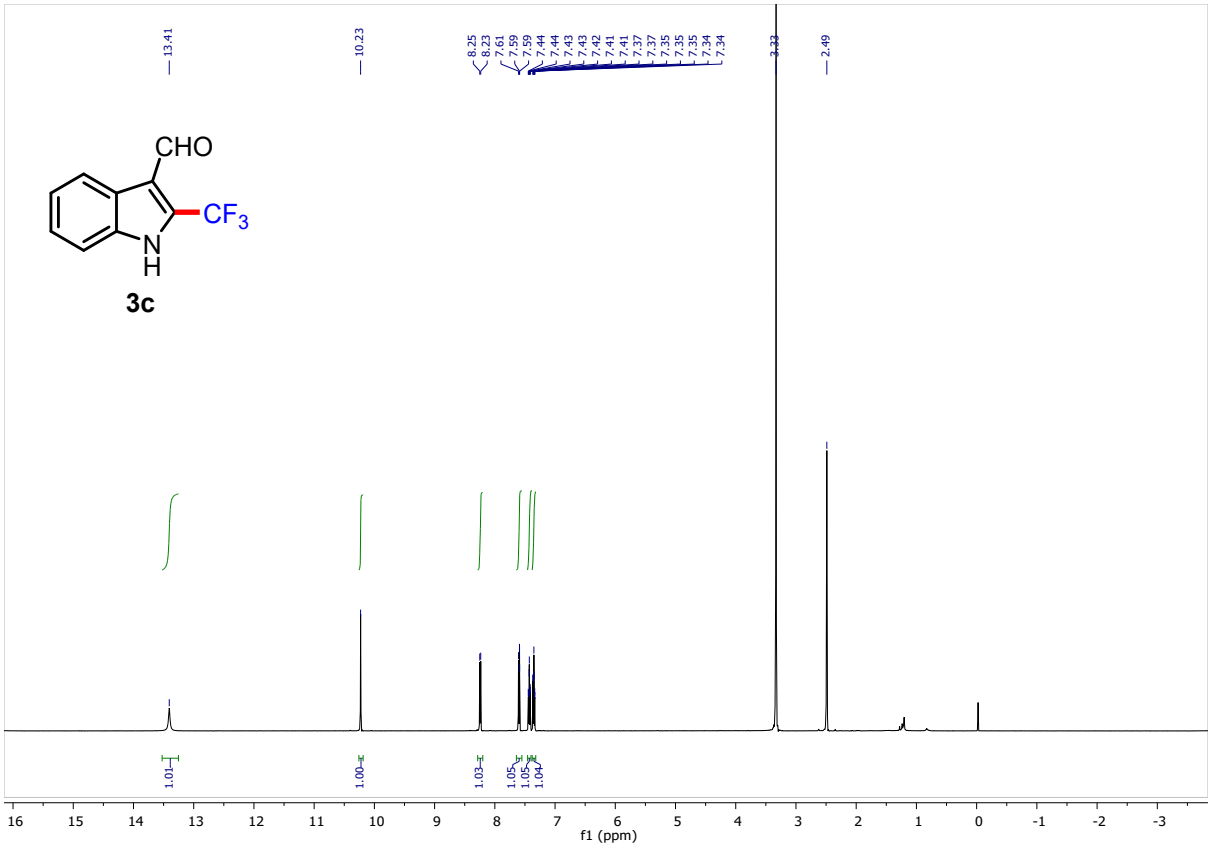
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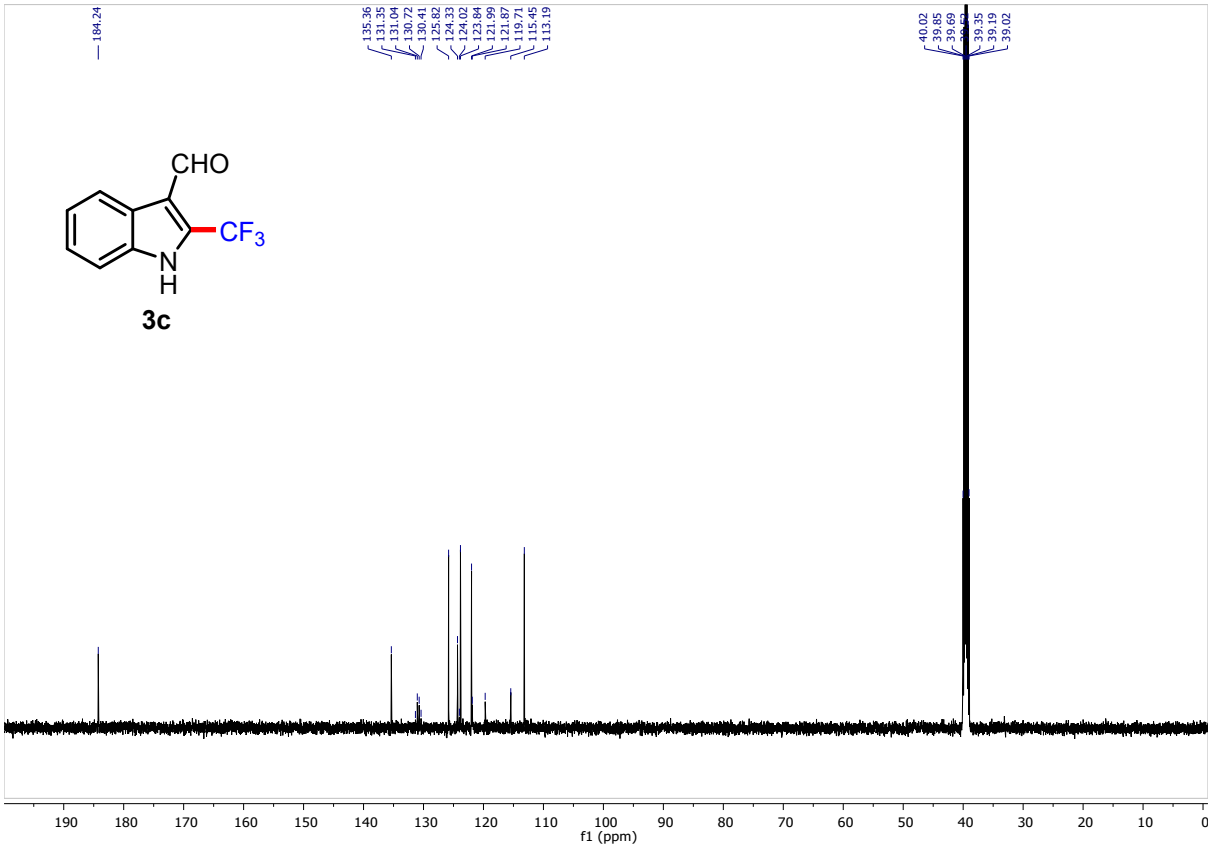
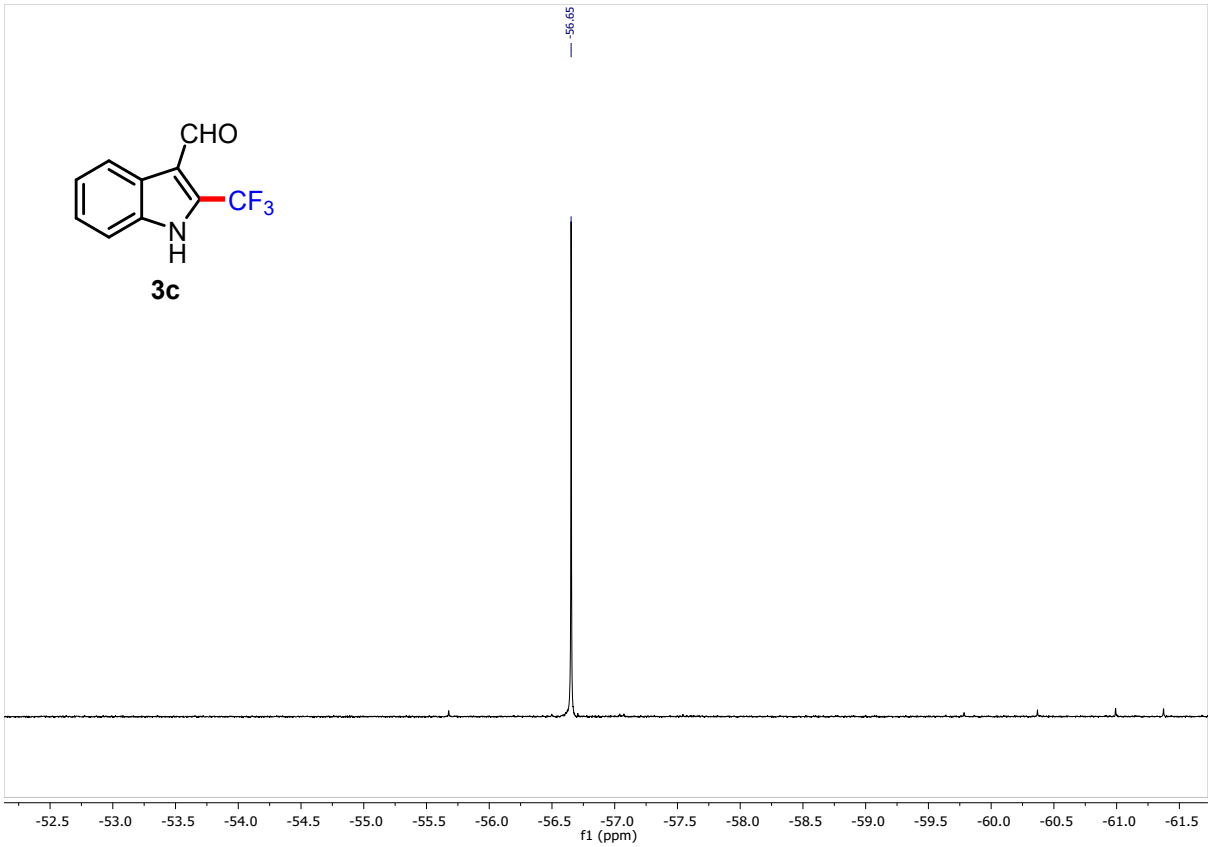
f1 (ppm)


184.24
135.36
131.35
131.04
130.72
130.41
125.82
124.33
124.02
123.84
121.99
121.87
119.71
115.45
113.19
40.02
39.85
39.69
39.35
39.19
39.02
CHO
CF3
N
H
3c
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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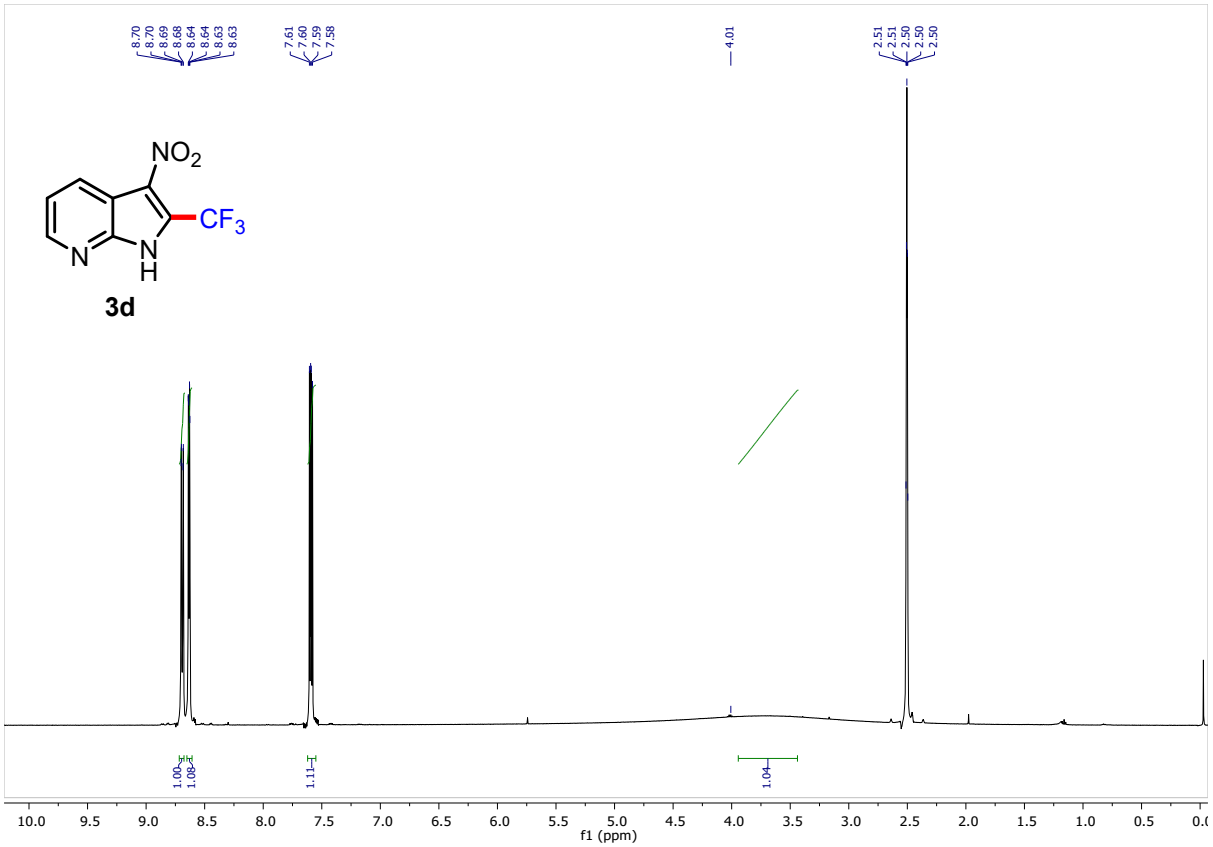
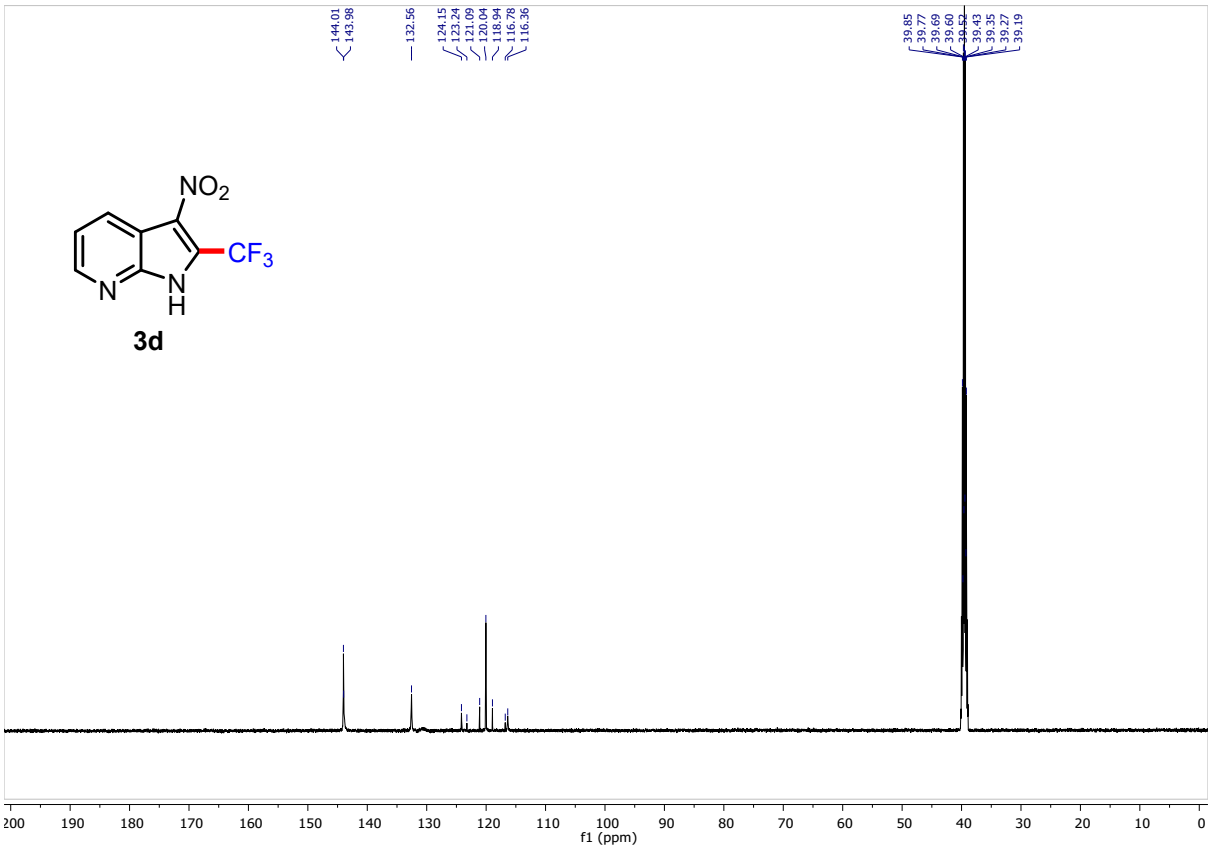
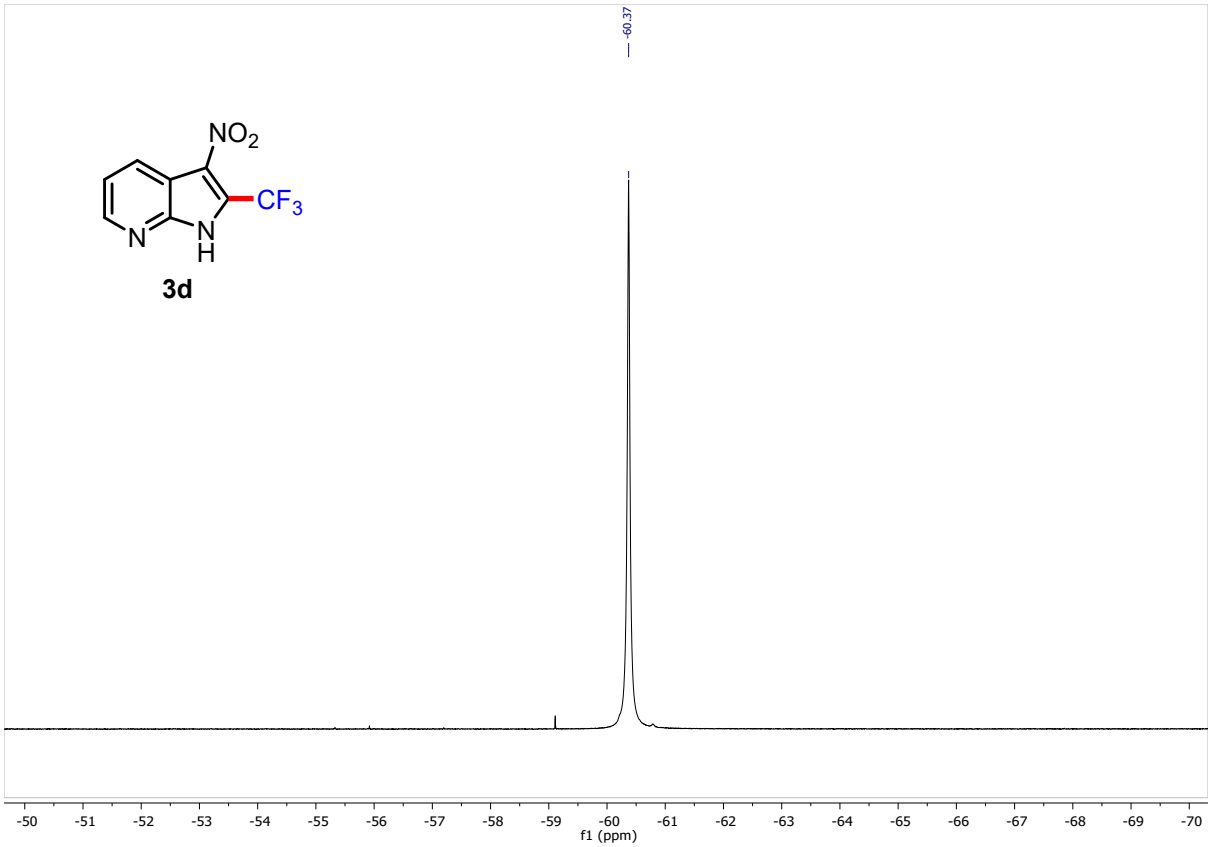
CHO
CF3
N
H
-52.5
-53.0
-53.5
-54.0
-54.5
-55.0
-55.5
-56.0
-56.5
-57.0
-57.5
-58.0
-58.5
-59.0
-59.5
-60.0
-60.5
-61.0
-61.5
f1 (ppm)

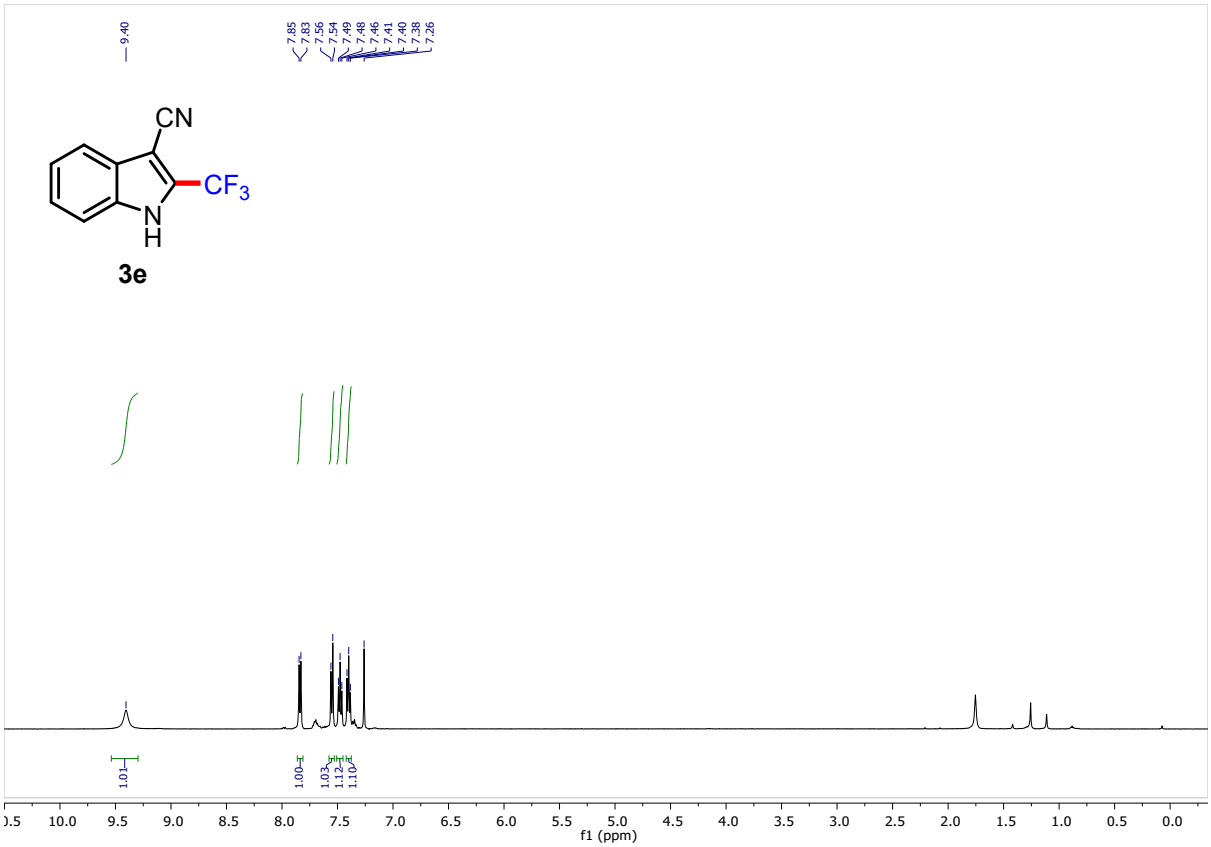
3c

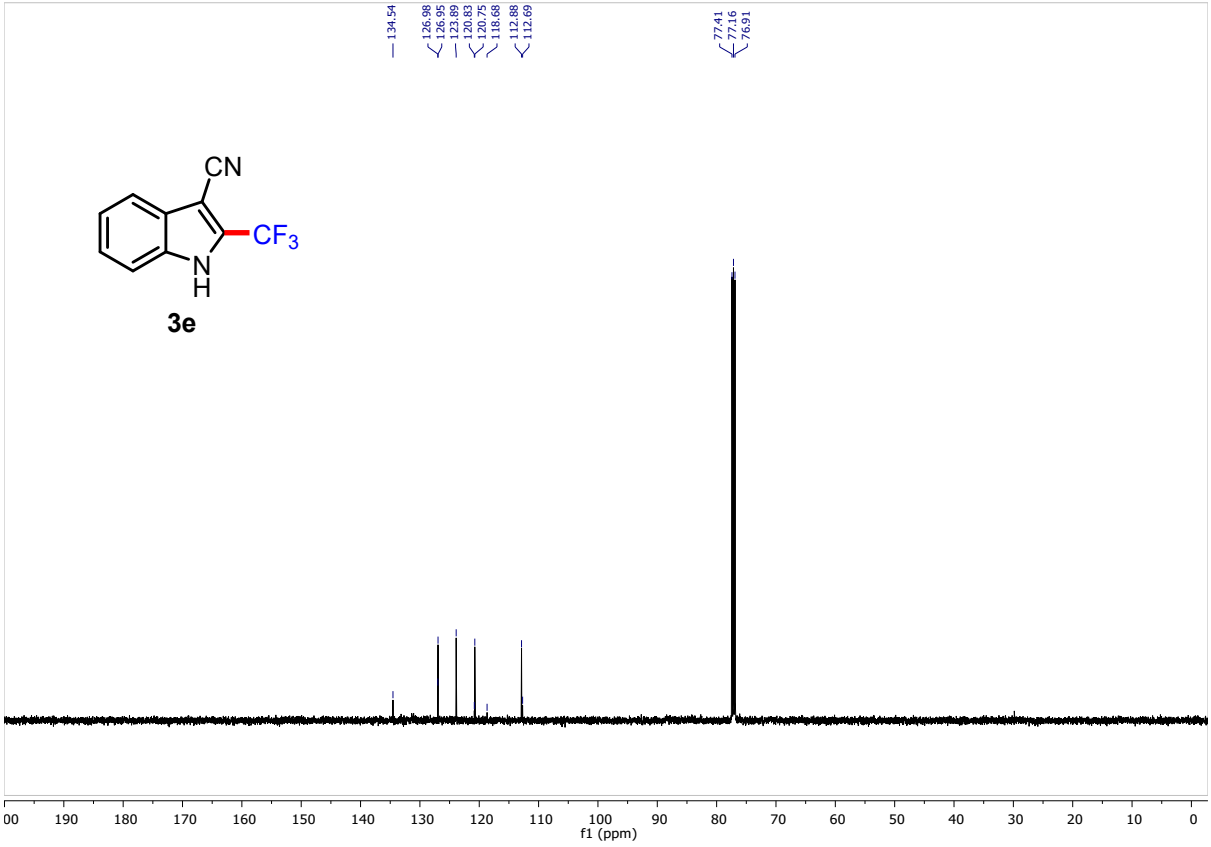

8.70
8.70
8.69
8.68
8.64
8.64
8.63
8.63
7.61
7.60
7.59
7.58
4.01
2.51
2.51
2.50
2.50
2.50
NO2
CF3
N
N
H
3d
1.00
1.08
1.11
1.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

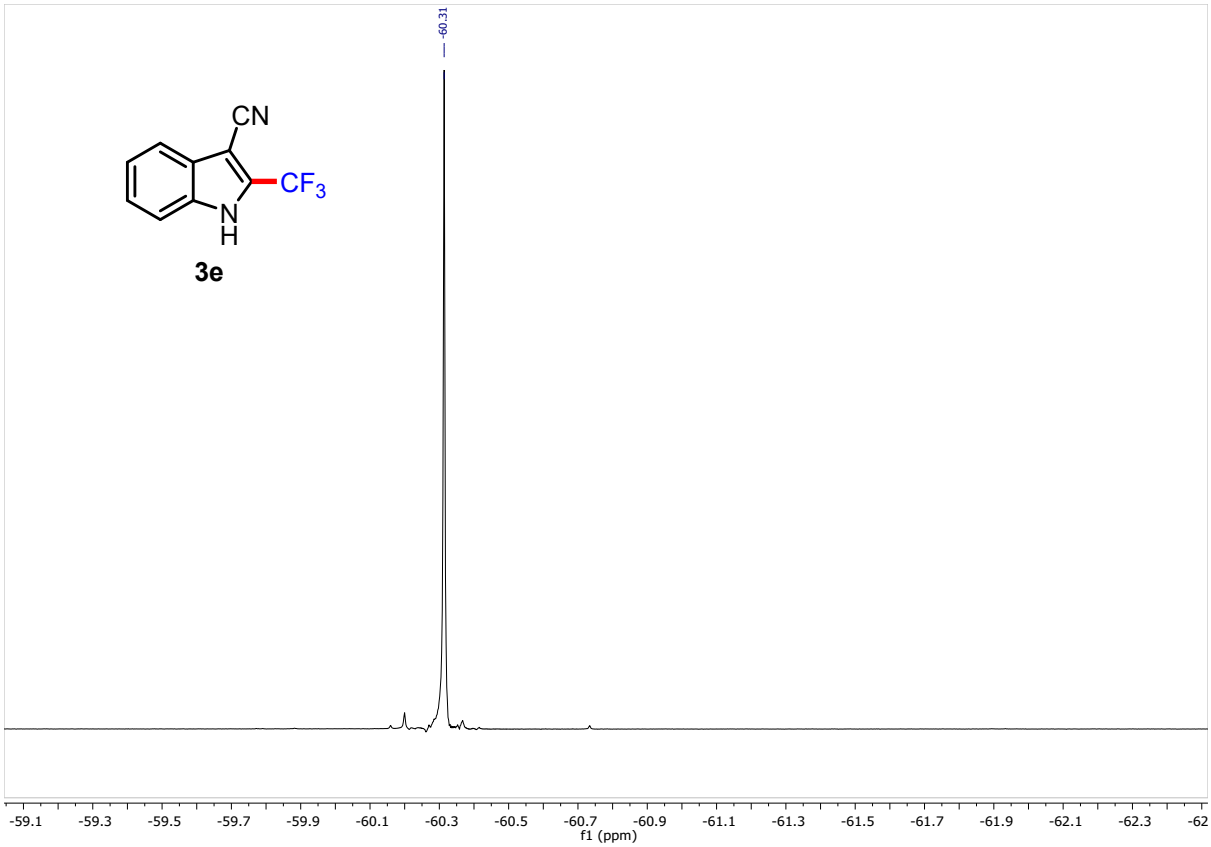

144.01
143.98
132.56
124.15
123.24
121.09
120.04
118.94
116.78
116.36
39.85
39.77
39.69
39.60
39.52
39.43
39.35
39.27
39.19
NO2
CF3
N
N
H
3d
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-60.37
NO2
CF3
N
N
H
-50
-51
-52
-53
-54
-55
-56
-57
-58
-59
-60
-61
-62
-63
-64
-65
-66
-67
-68
-69
-70
f1 (ppm)

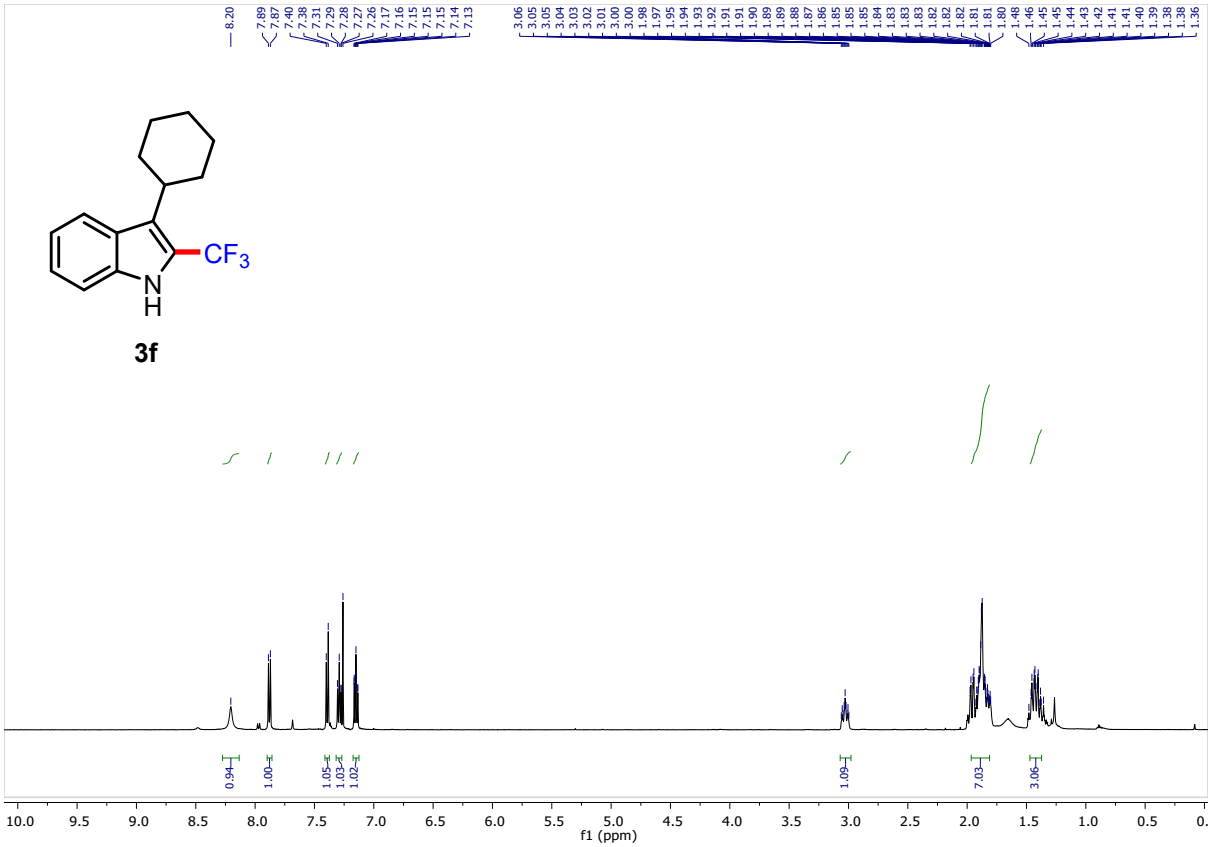
3d

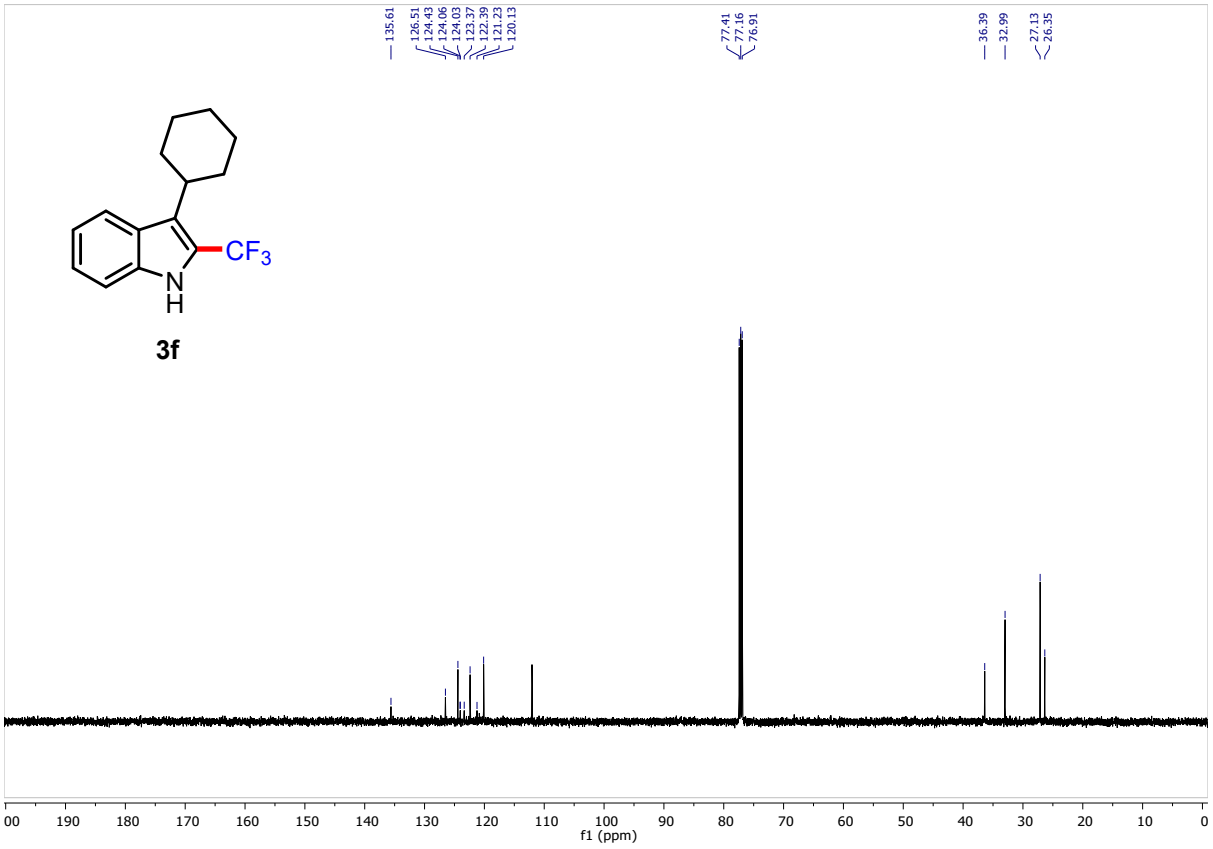

9.40
7.85
7.83
7.56
7.54
7.49
7.48
7.46
7.41
7.40
7.38
7.26
CN
CF3
N
H
3e
1.01
1.00
1.03
1.12
1.10
f1 (ppm)

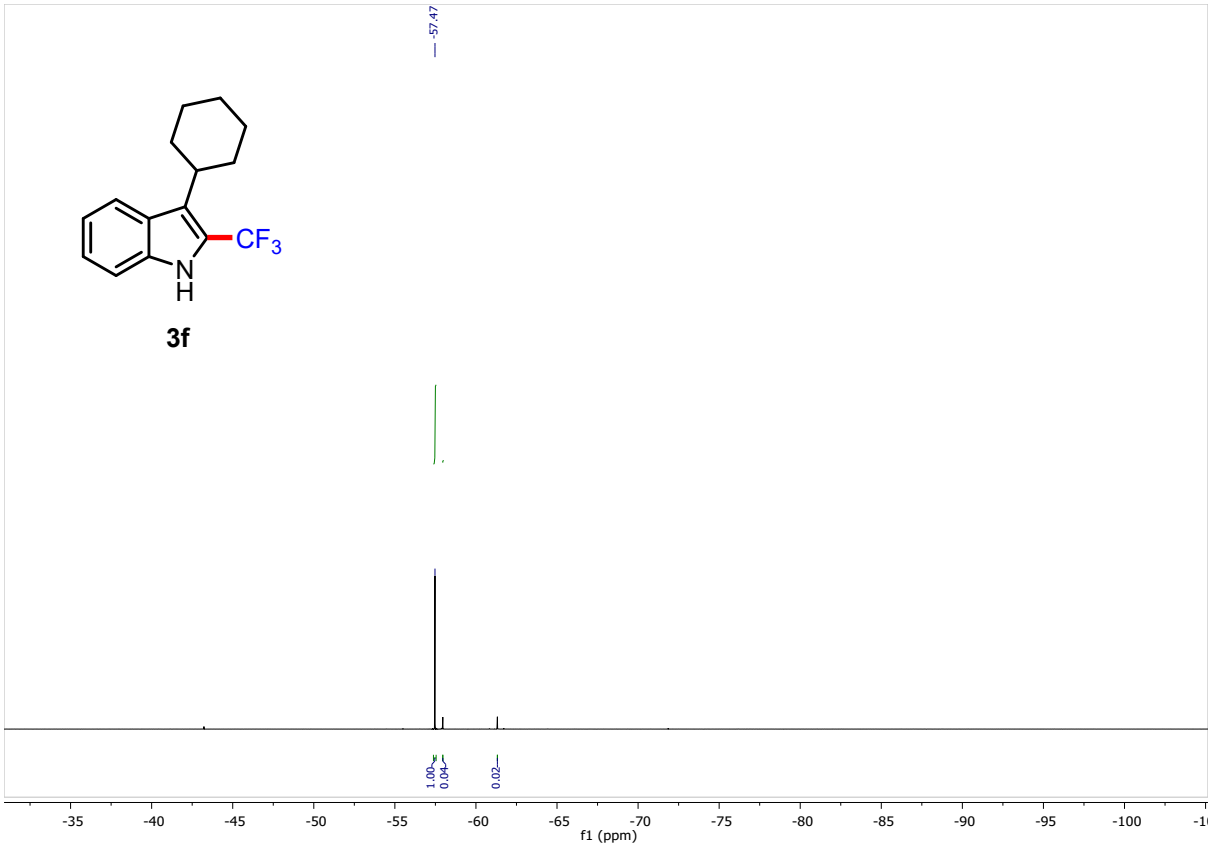

134.54
126.98
126.95
123.89
120.83
120.75
118.68
112.88
112.69
77.41
77.16
76.91
CN
CF3
N
H
3e
f1 (ppm)


-60.31
CN
CF3
N
H
-59.1
-59.3
-59.5
-59.7
-59.9
-60.1
-60.3
-60.5
-60.7
-60.9
-61.1
-61.3
-61.5
-61.7
-61.9
-62.1
-62.3
-62
f1 (ppm)

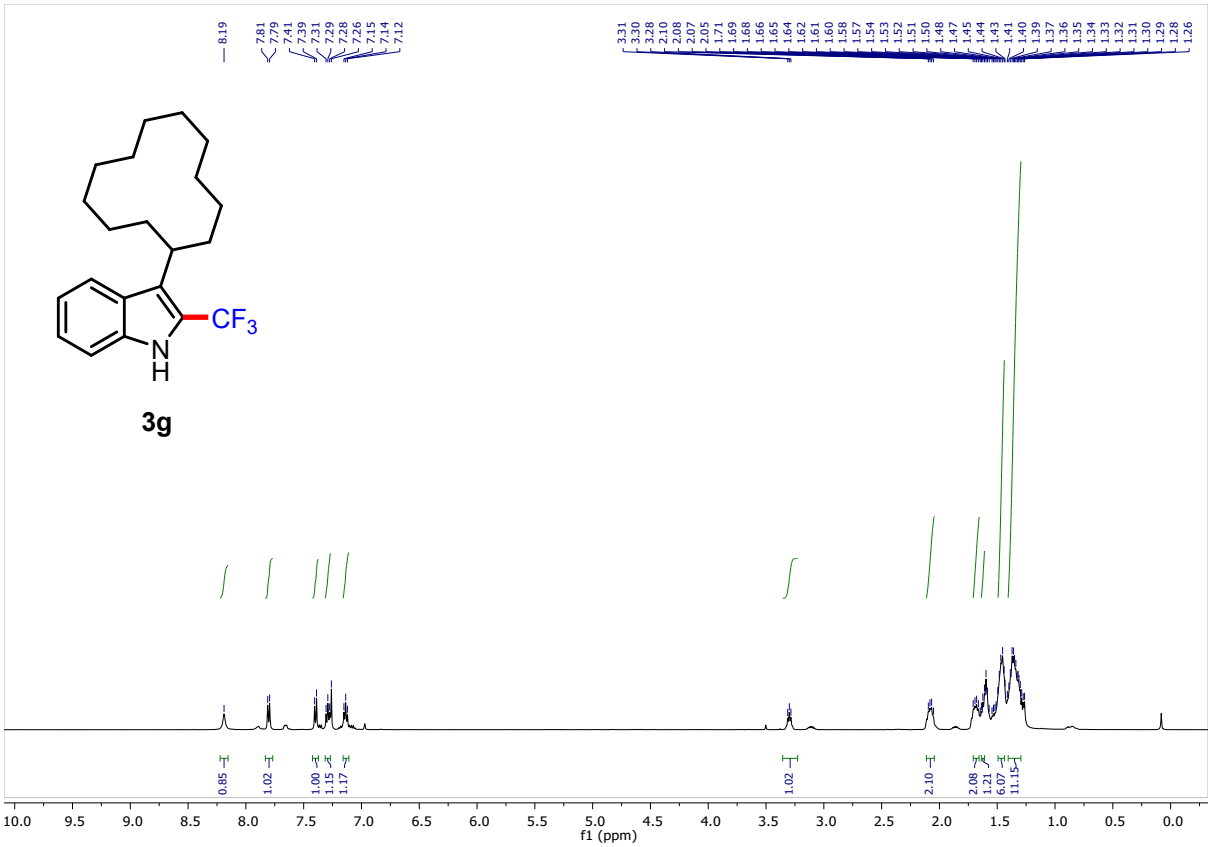
3e

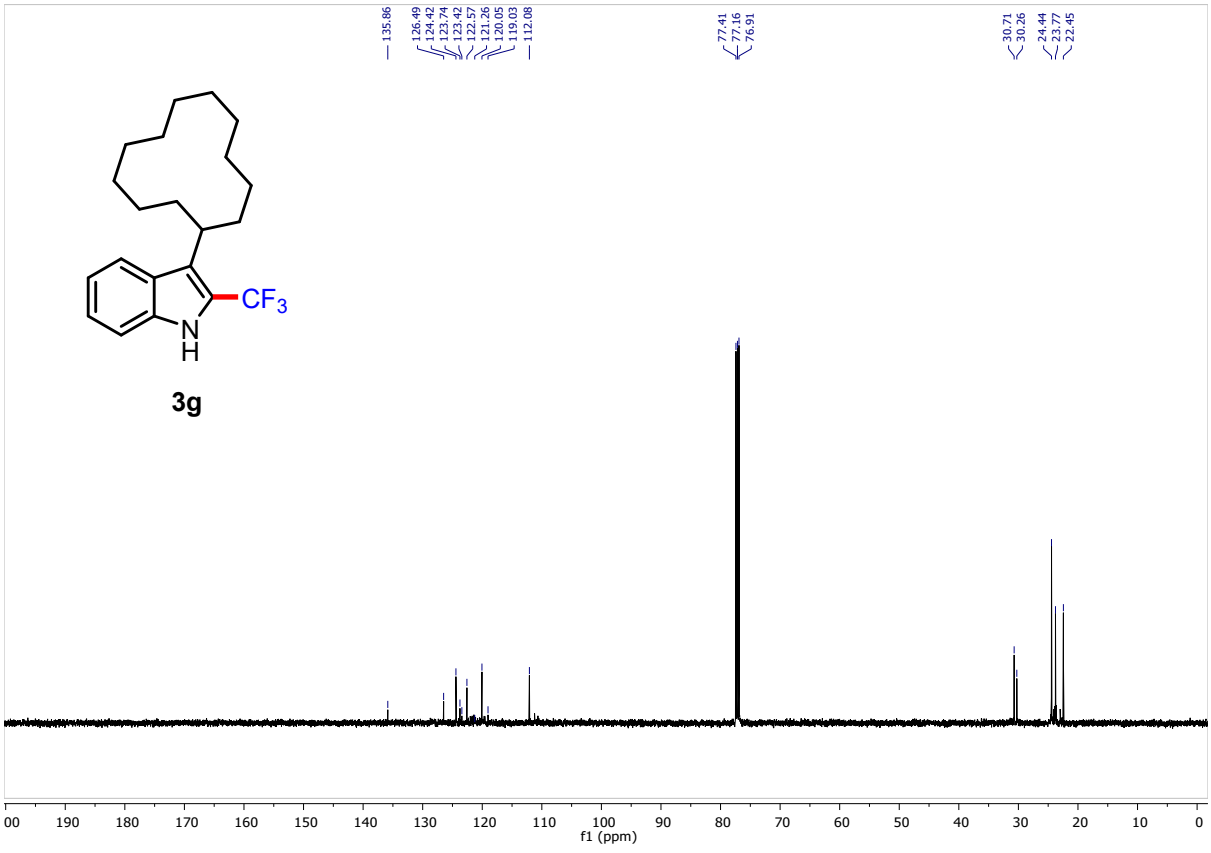

CF3
N
H
3f
f1 (ppm)

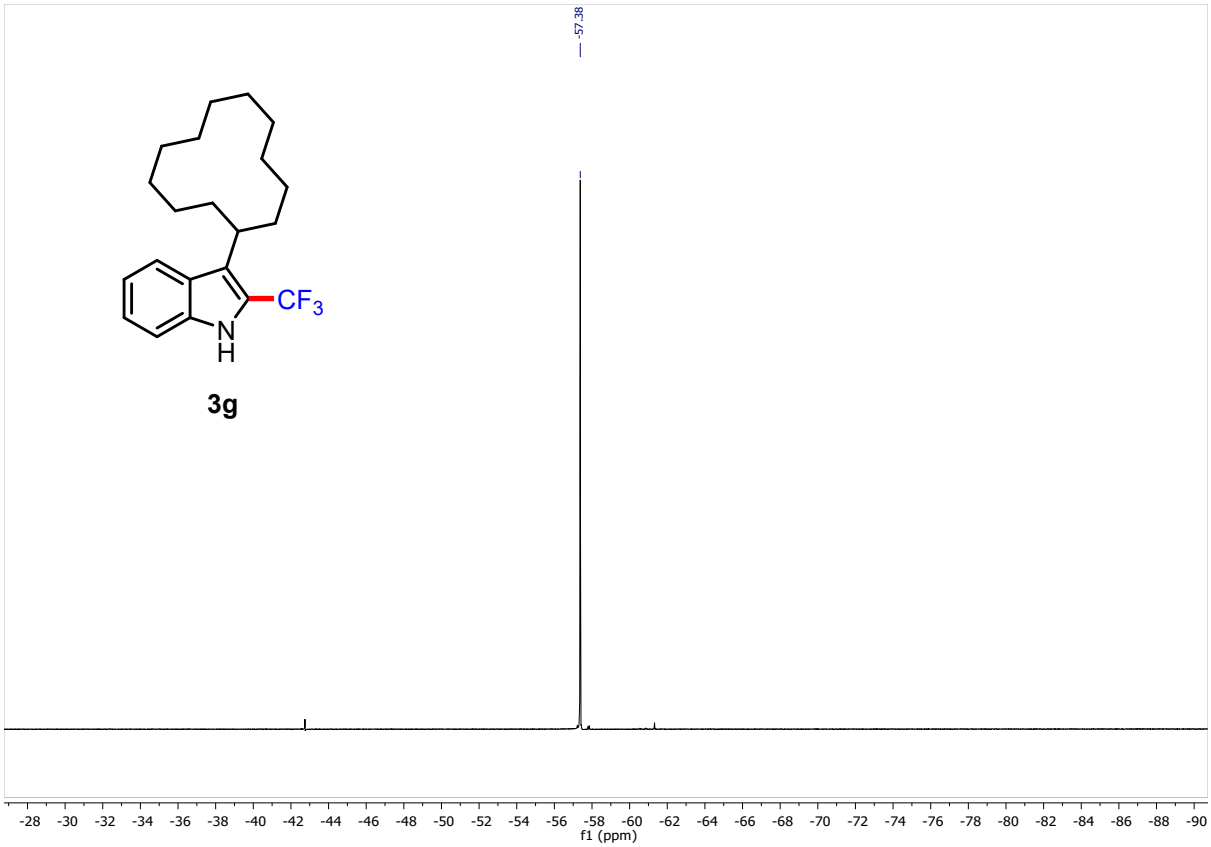

CF3
N
H
3f
f1 (ppm)


-57.47
CF3
N
H
1.00
0.04
0.02
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
f1 (ppm)

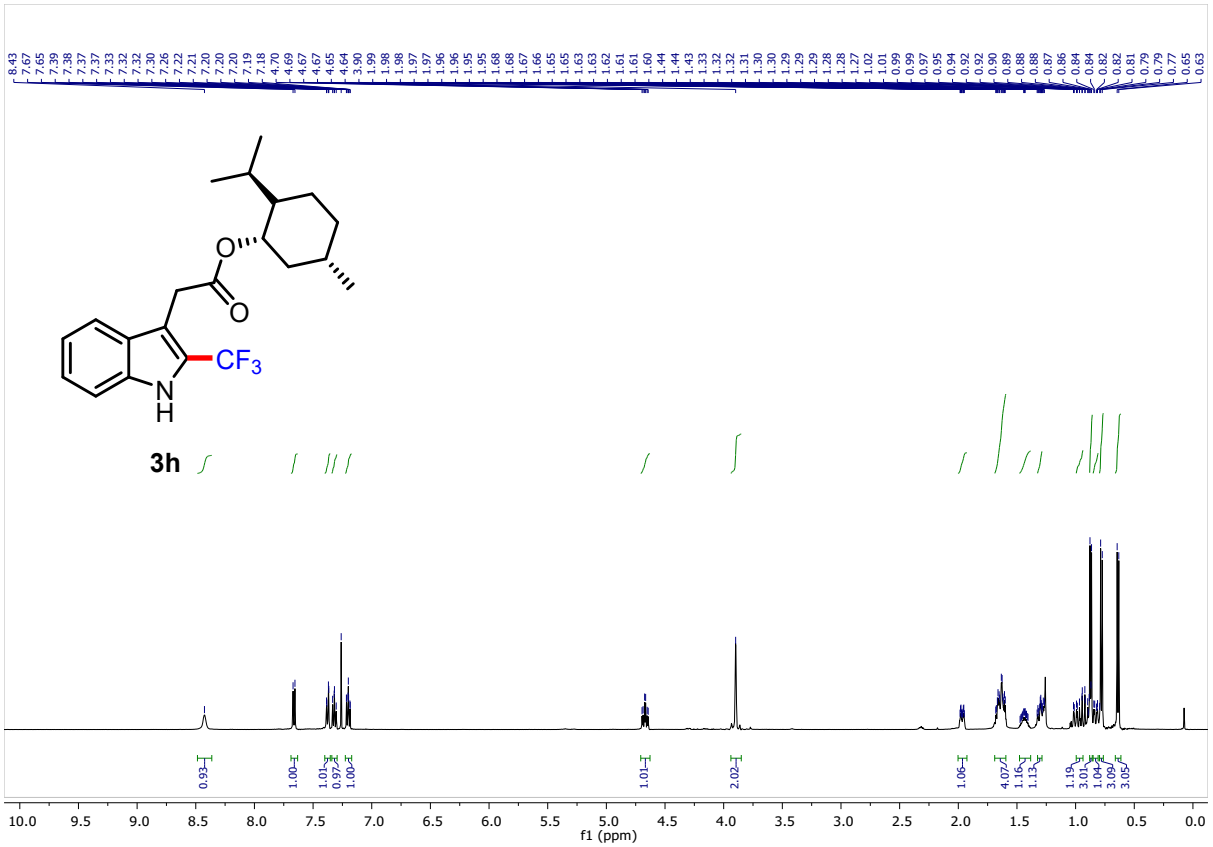
3f

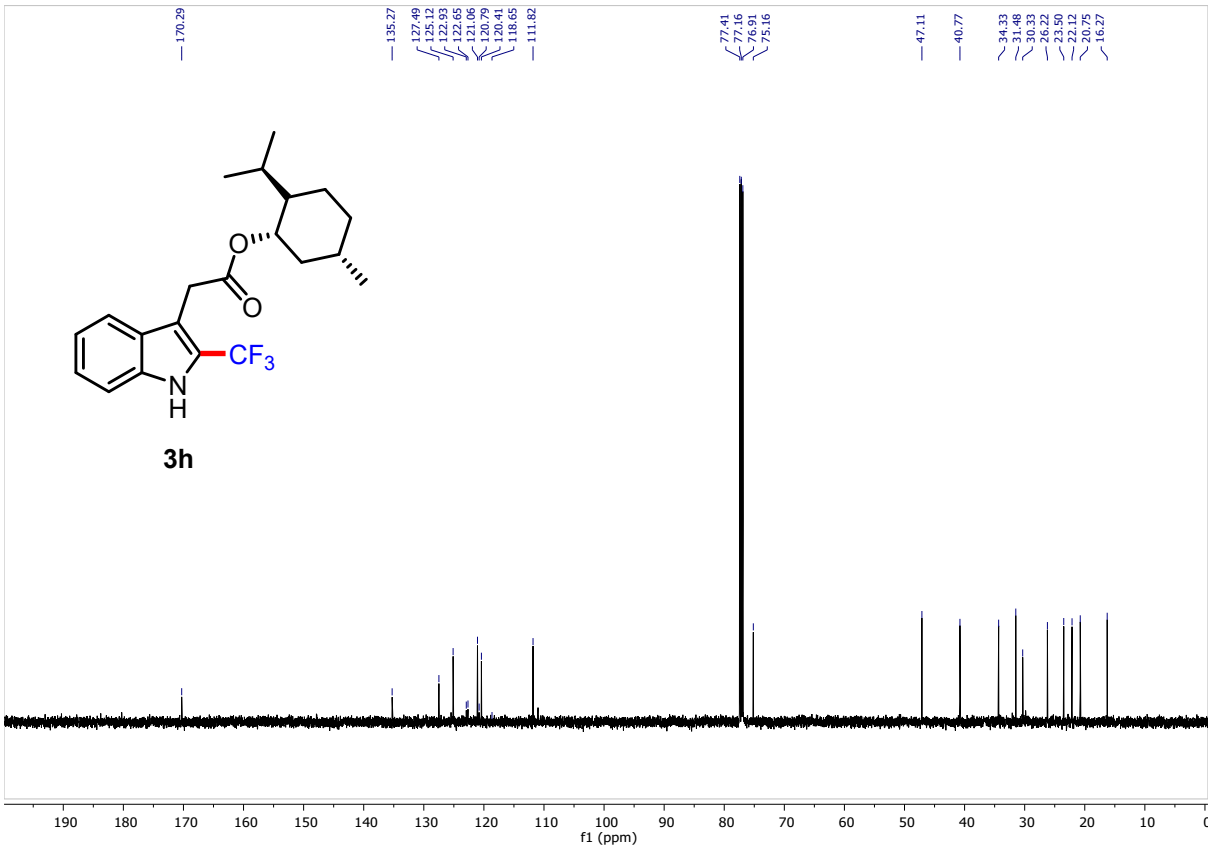

8.19
7.81
7.79
7.44
7.39
7.31
7.29
7.28
7.26
7.15
7.14
7.12
3.31
3.30
3.28
2.10
2.08
2.07
2.05
1.71
1.69
1.68
1.66
1.65
1.64
1.62
1.61
1.60
1.58
1.57
1.54
1.53
1.52
1.51
1.50
1.48
1.47
1.45
1.44
1.43
1.41
1.40
1.39
1.37
1.36
1.35
1.34
1.33
1.32
1.31
1.30
1.29
1.28
1.26
CF3
N
H
3g
0.85
1.02
1.00
1.15
1.17
1.02
2.10
2.08
1.21
6.07
11.15
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)

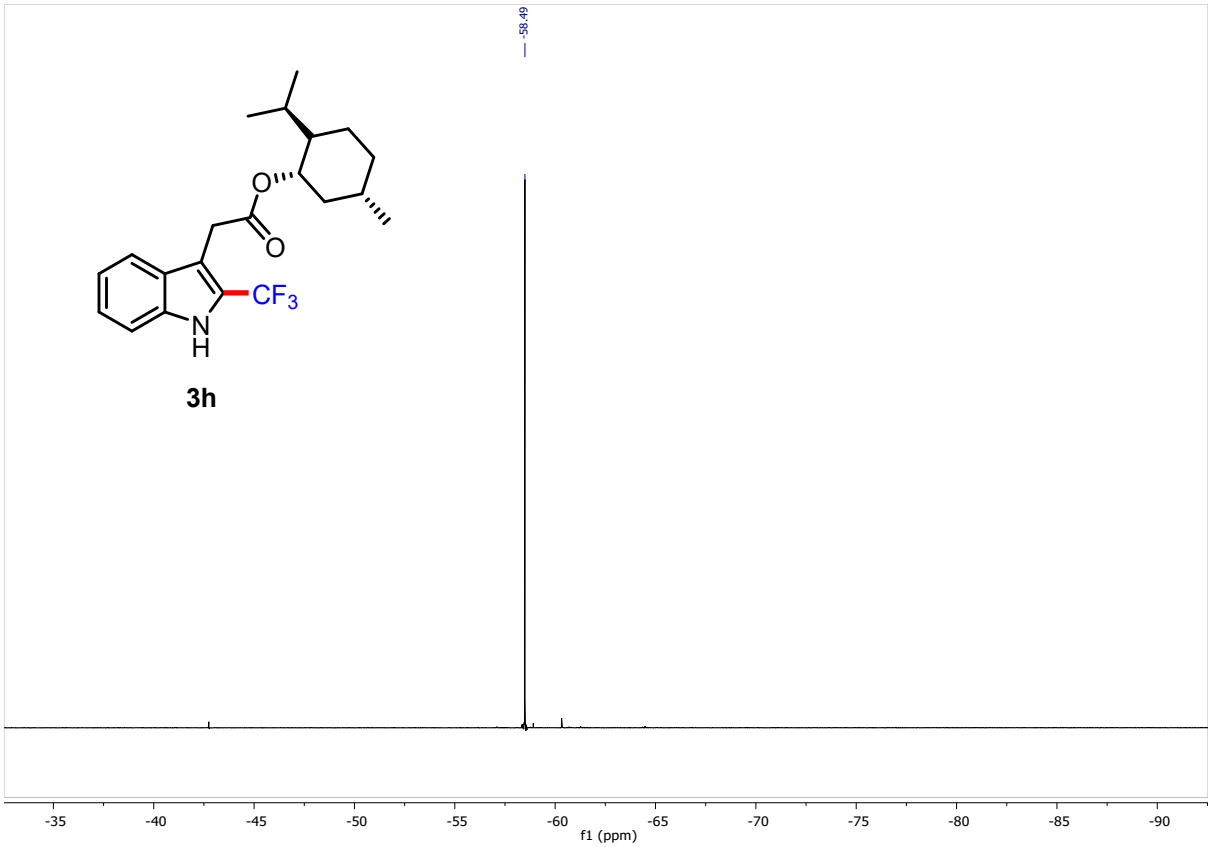

135.86
126.49
124.42
123.74
123.42
122.57
121.26
120.05
119.03
112.08
77.41
77.16
76.91
30.71
30.26
24.44
23.77
22.45
CF3
N
H
3g
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-57.38
CF3
N
H
-28 -30 -32 -34 -36 -38 -40 -42 -44 -46 -48 -50 -52 -54 -56 -58 -60 -62 -64 -66 -68 -70 -72 -74 -76 -78 -80 -82 -84 -86 -88 -90
f1 (ppm)

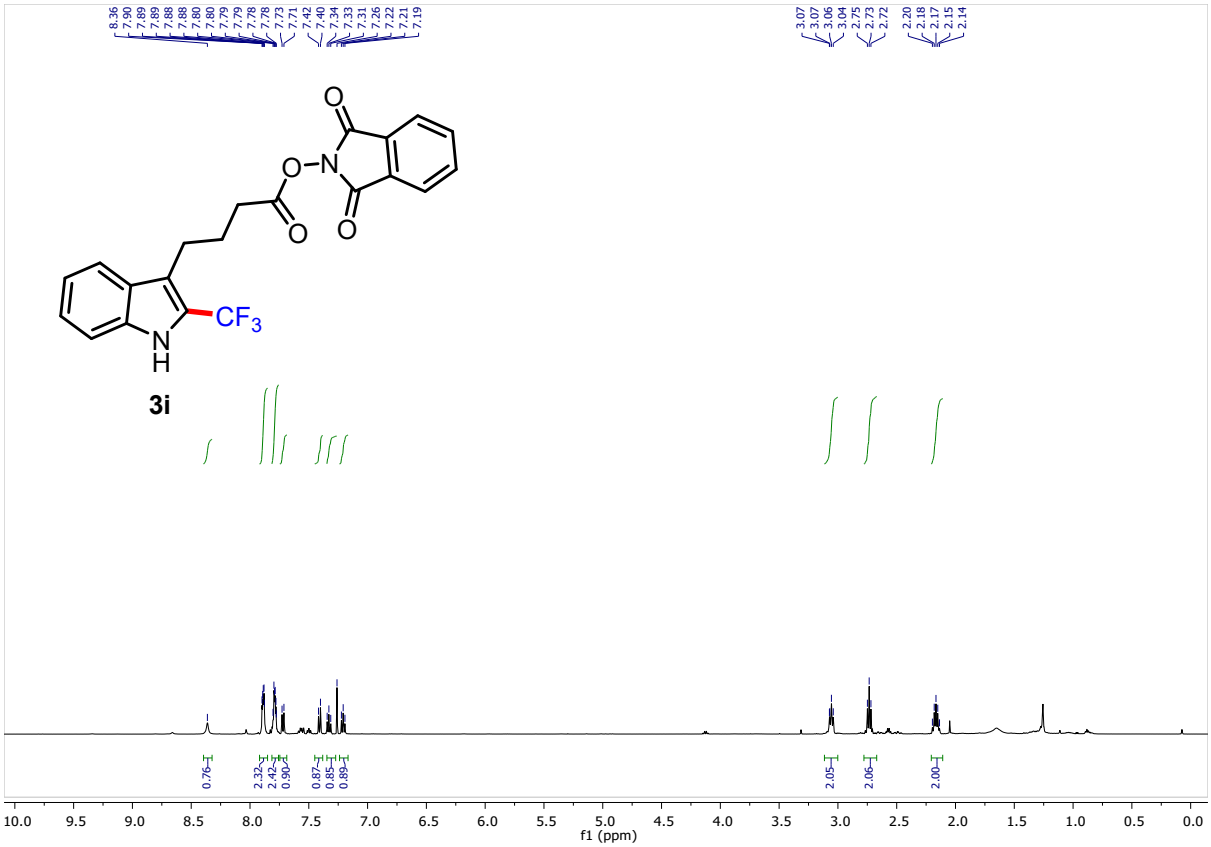
3g


O
O
CF3
N
H
3h
f1 (ppm)

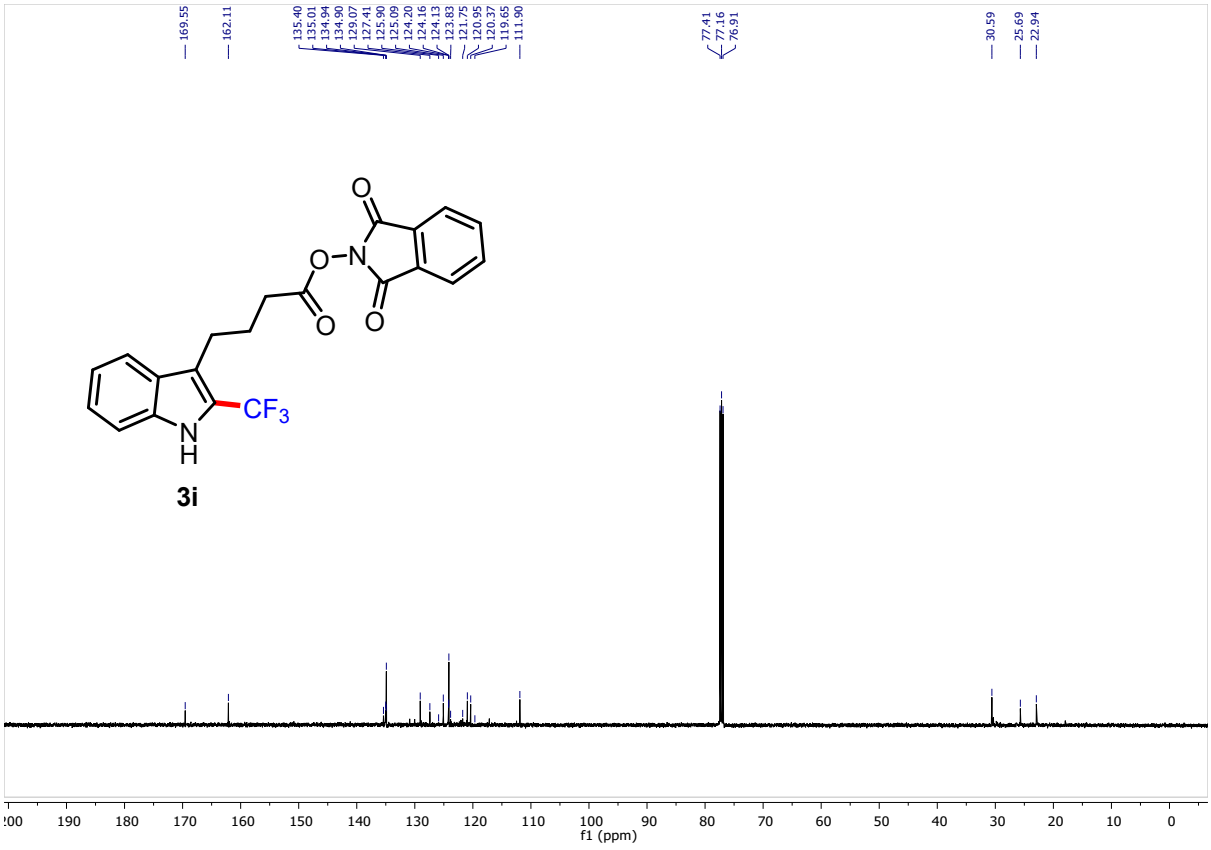

O
O
CF3
N
H
3h
f1 (ppm)



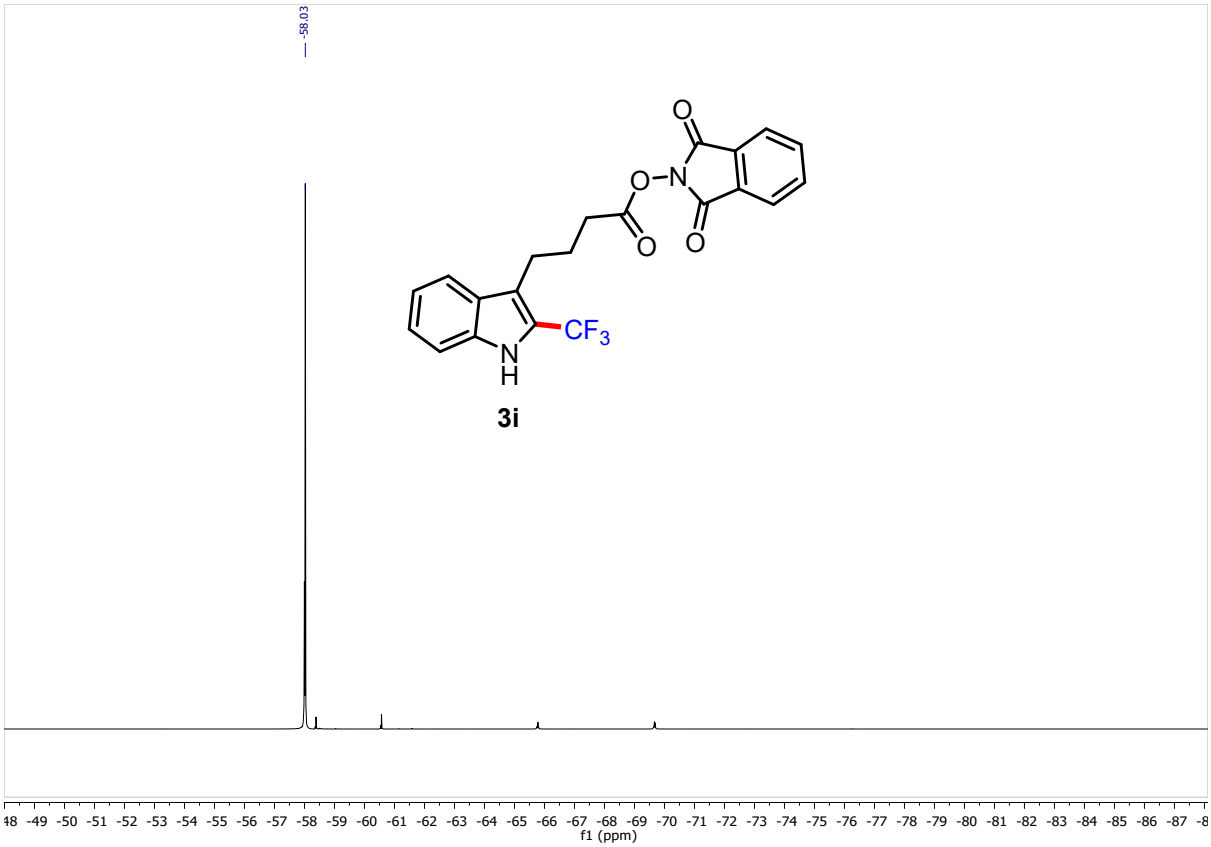
3h

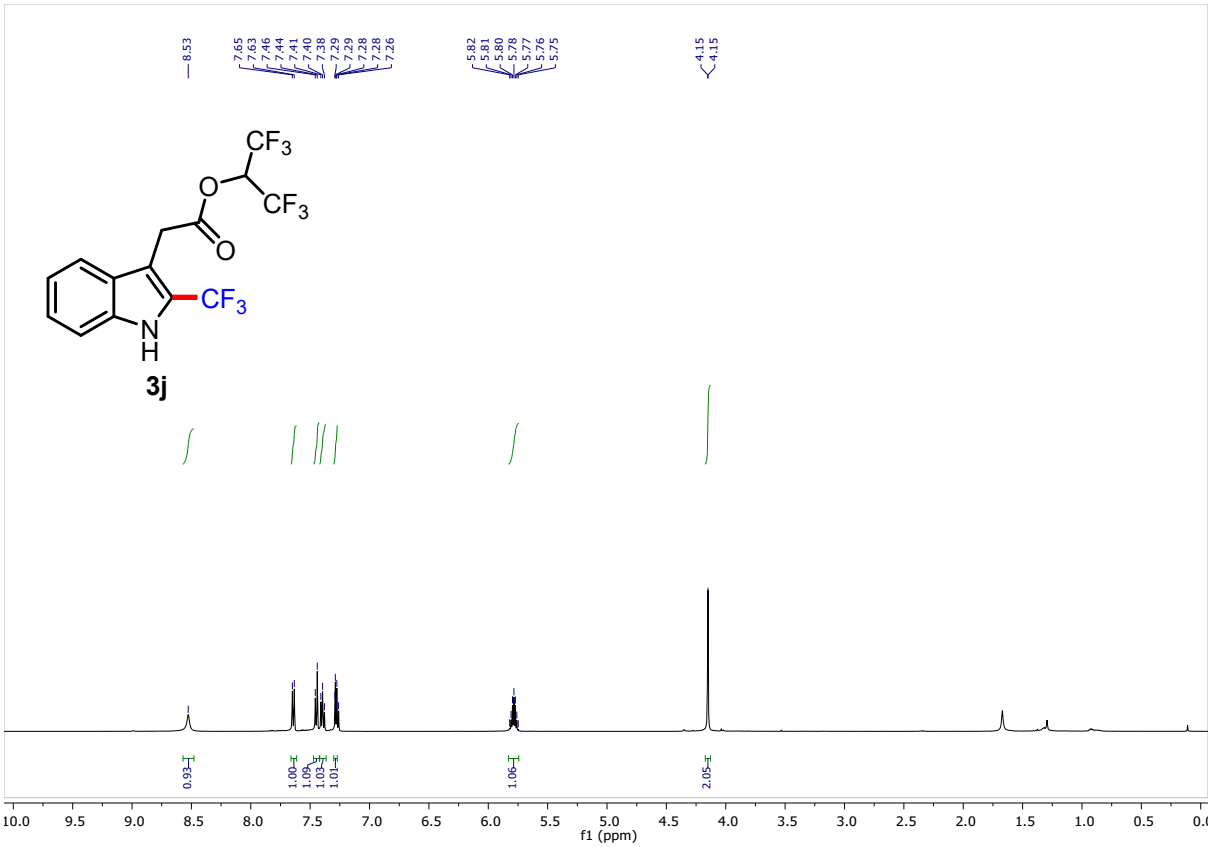

8.36
7.90
7.89
7.89
7.88
7.88
7.80
7.80
7.79
7.79
7.78
7.78
7.73
7.71
7.42
7.40
7.34
7.33
7.31
7.26
7.22
7.21
7.19
3.07
3.07
3.06
3.04
2.75
2.73
2.72
2.20
2.18
2.17
2.15
2.14
O
O
N
O
O
O
CF3
N
H
0.76
2.32
2.42
0.90
0.87
0.85
0.89
2.05
2.06
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

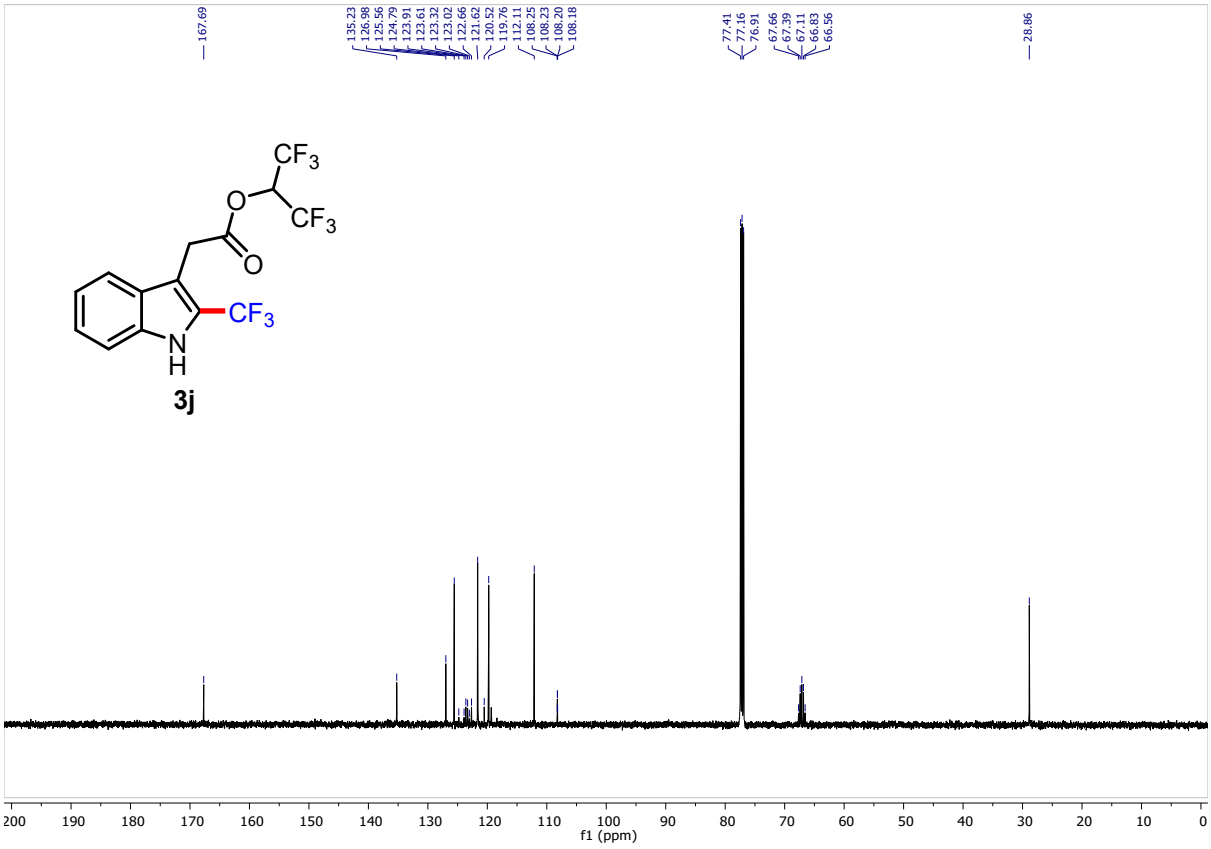
3i

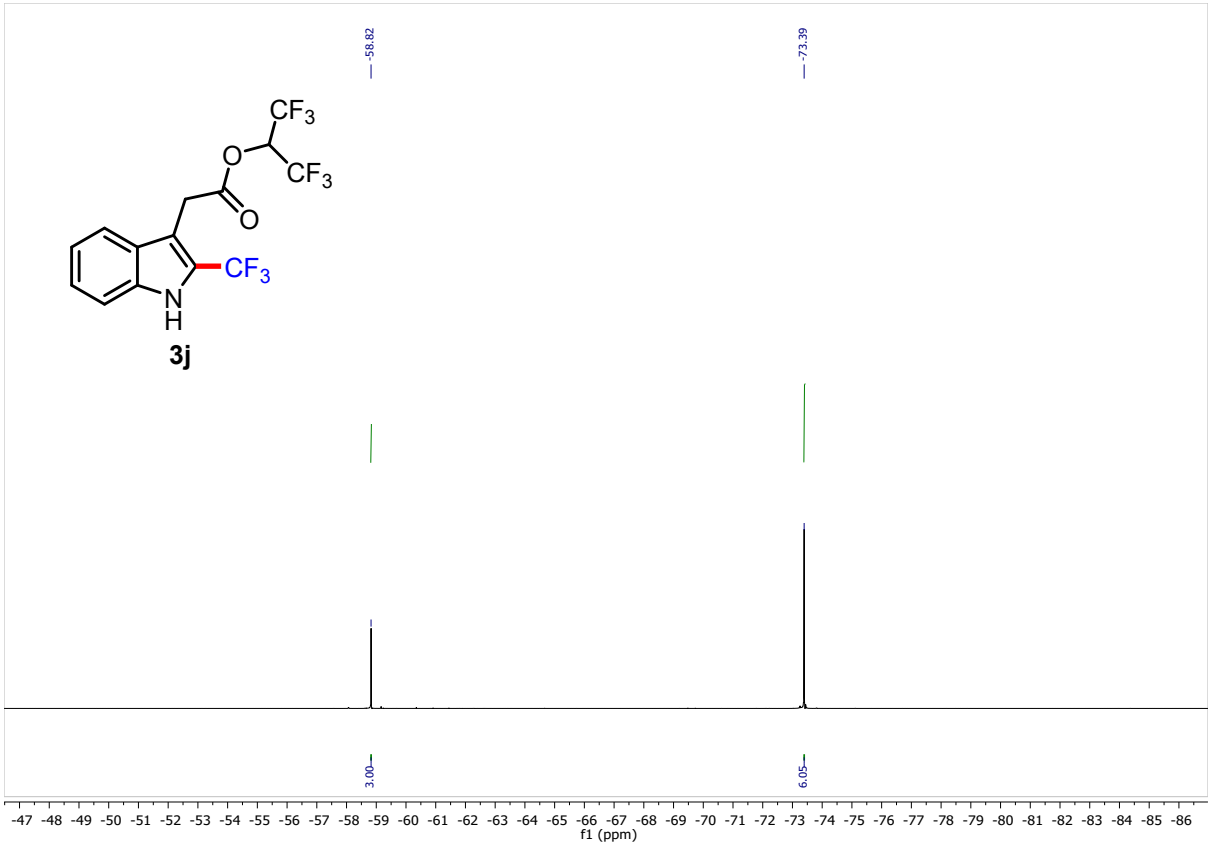

169.55
162.11
135.40
135.01
134.94
134.90
129.07
127.41
125.90
125.09
124.20
124.16
124.13
123.83
121.75
120.95
120.37
119.65
111.90
77.41
77.16
76.91
30.59
25.69
22.94
O
O
N
O
O
O
CF3
N
H
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

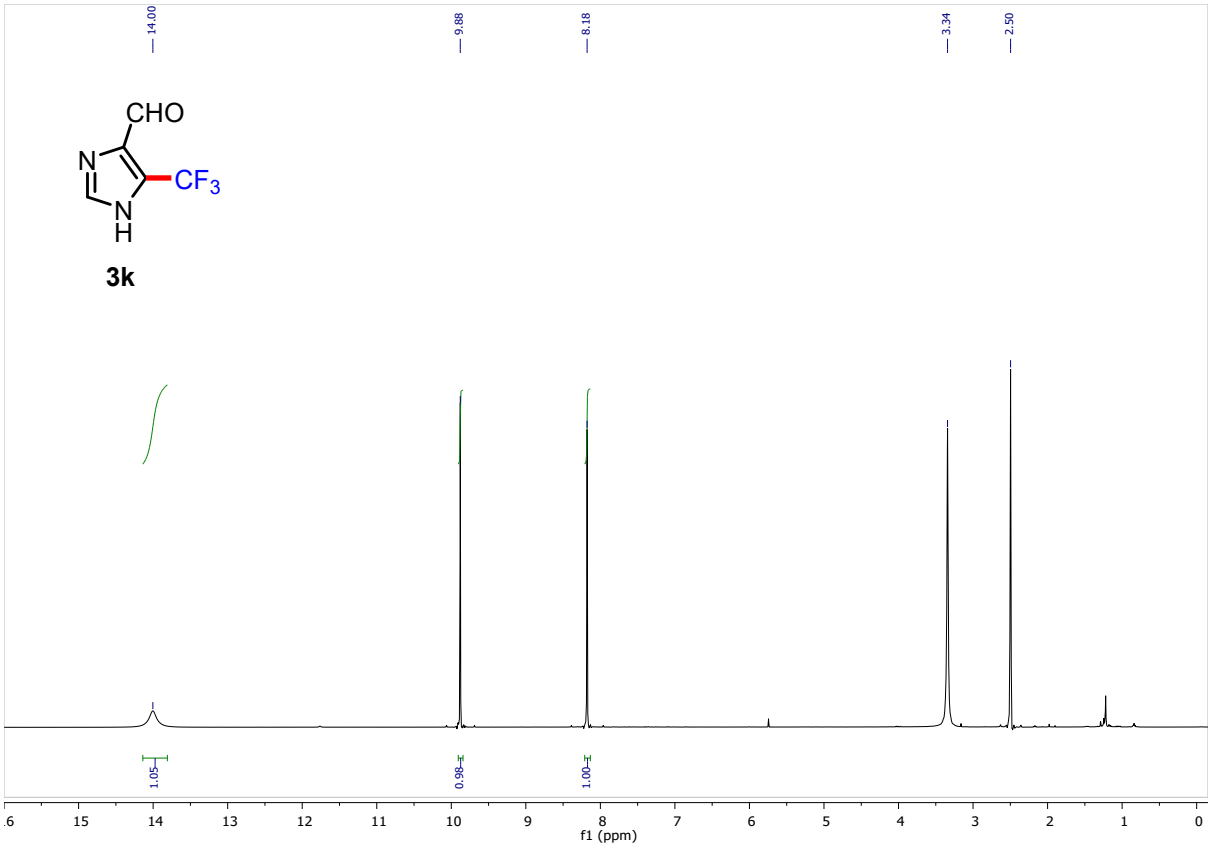
3i

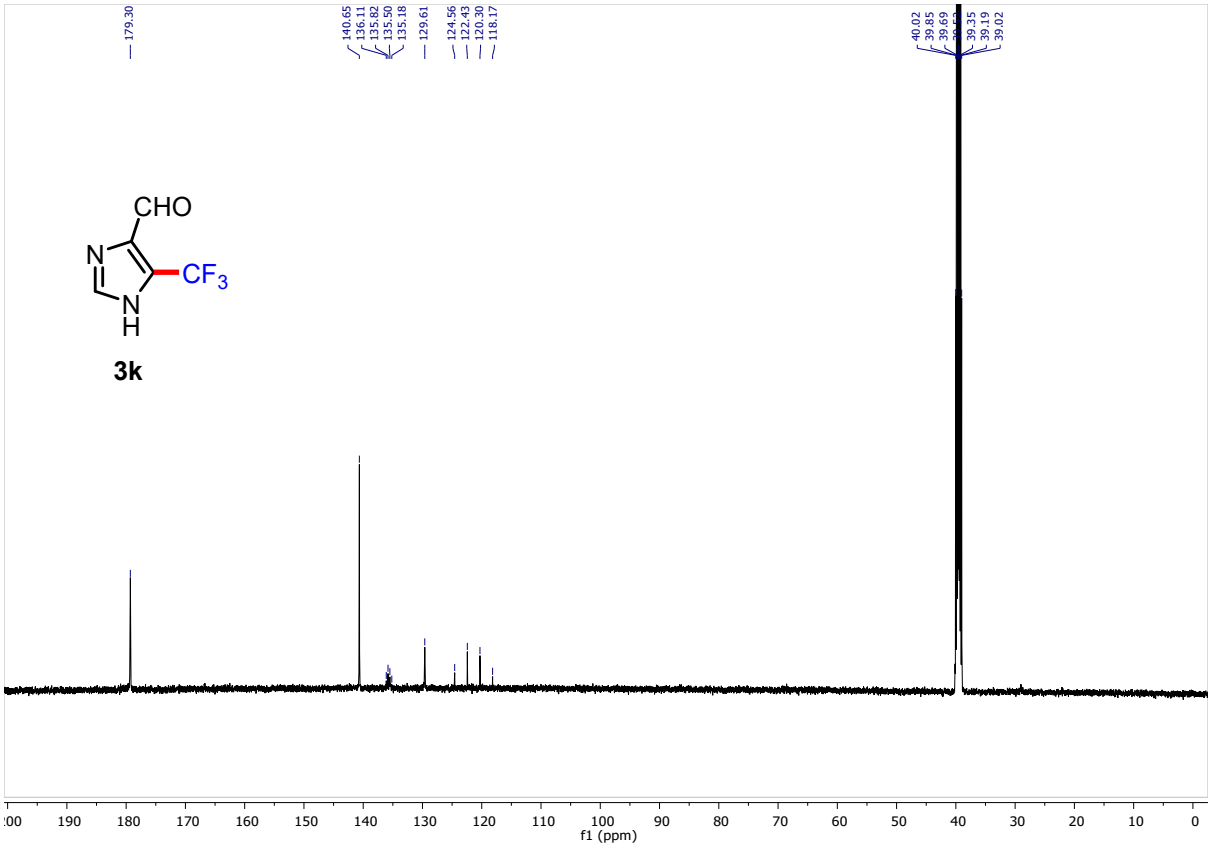

-58.03
O
O-N
O
O
CF3
N
H
3i
f1 (ppm)

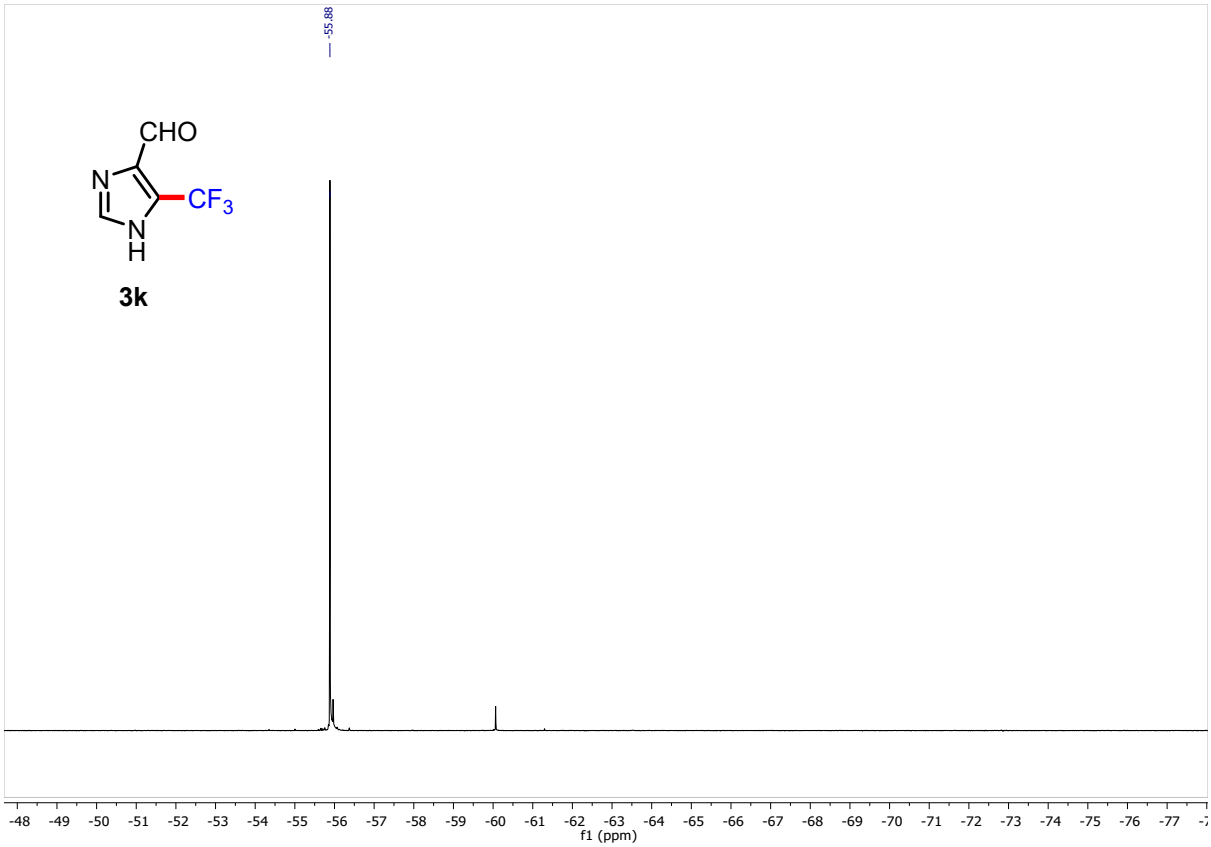

8.53
7.65
7.63
7.46
7.44
7.41
7.40
7.38
7.29
7.29
7.28
7.28
7.26
5.82
5.81
5.80
5.78
5.77
5.76
5.75
4.15
4.15
CF3
O
CF3
O
CF3
N
H
3j
0.93
1.00
1.09
1.03
1.01
1.06
2.05
f1 (ppm)

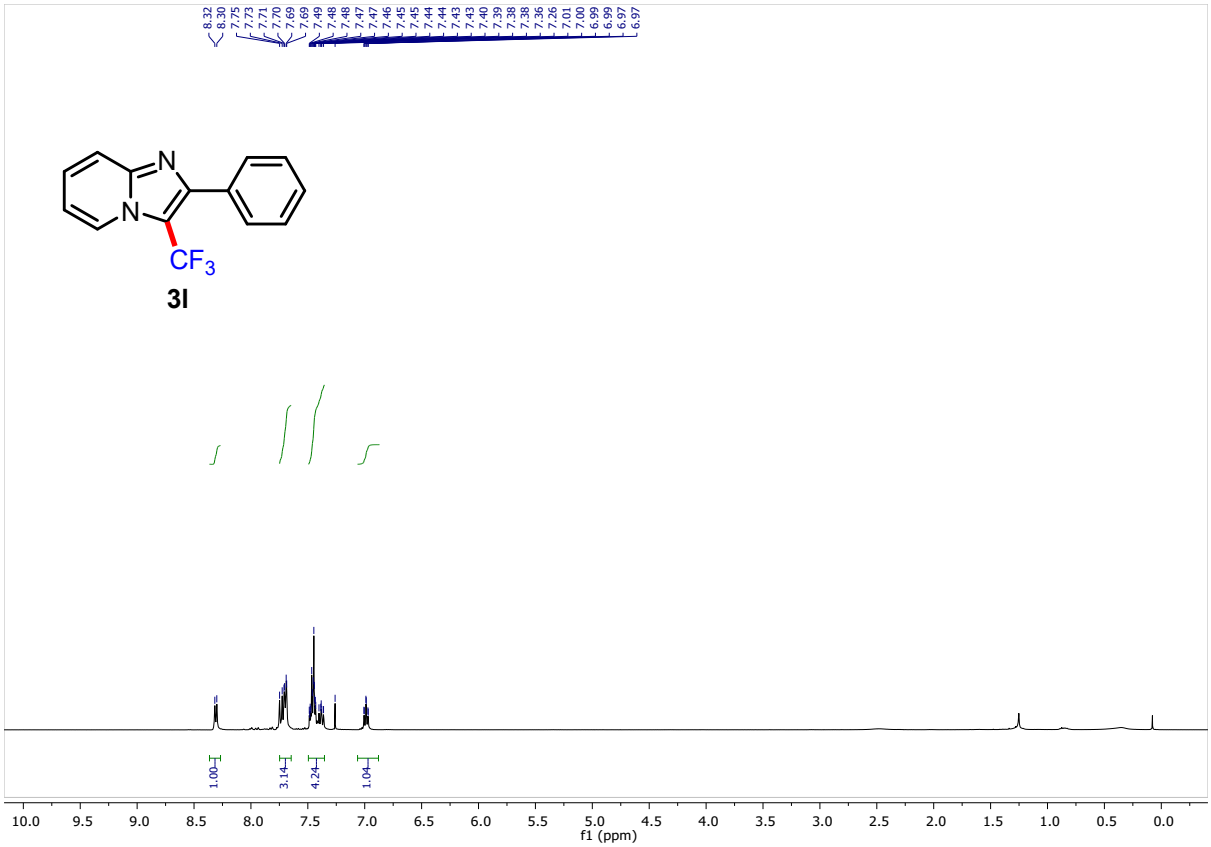

167.69
135.23
126.98
125.56
124.79
123.91
123.61
123.32
123.02
122.66
121.62
120.52
119.76
112.11
108.25
108.23
108.20
108.18
77.41
77.16
76.91
67.66
67.39
67.11
66.83
66.56
28.86
CF3
O
CF3
O
CF3
N
H
3j
f1 (ppm)


-58.82
-73.39
CF3
O
CF3
O
CF3
N
H
3j
3.00
6.05
-47 -48 -49 -50 -51 -52 -53 -54 -55 -56 -57 -58 -59 -60 -61 -62 -63 -64 -65 -66 -67 -68 -69 -70 -71 -72 -73 -74 -75 -76 -77 -78 -79 -80 -81 -82 -83 -84 -85 -86
f1 (ppm)

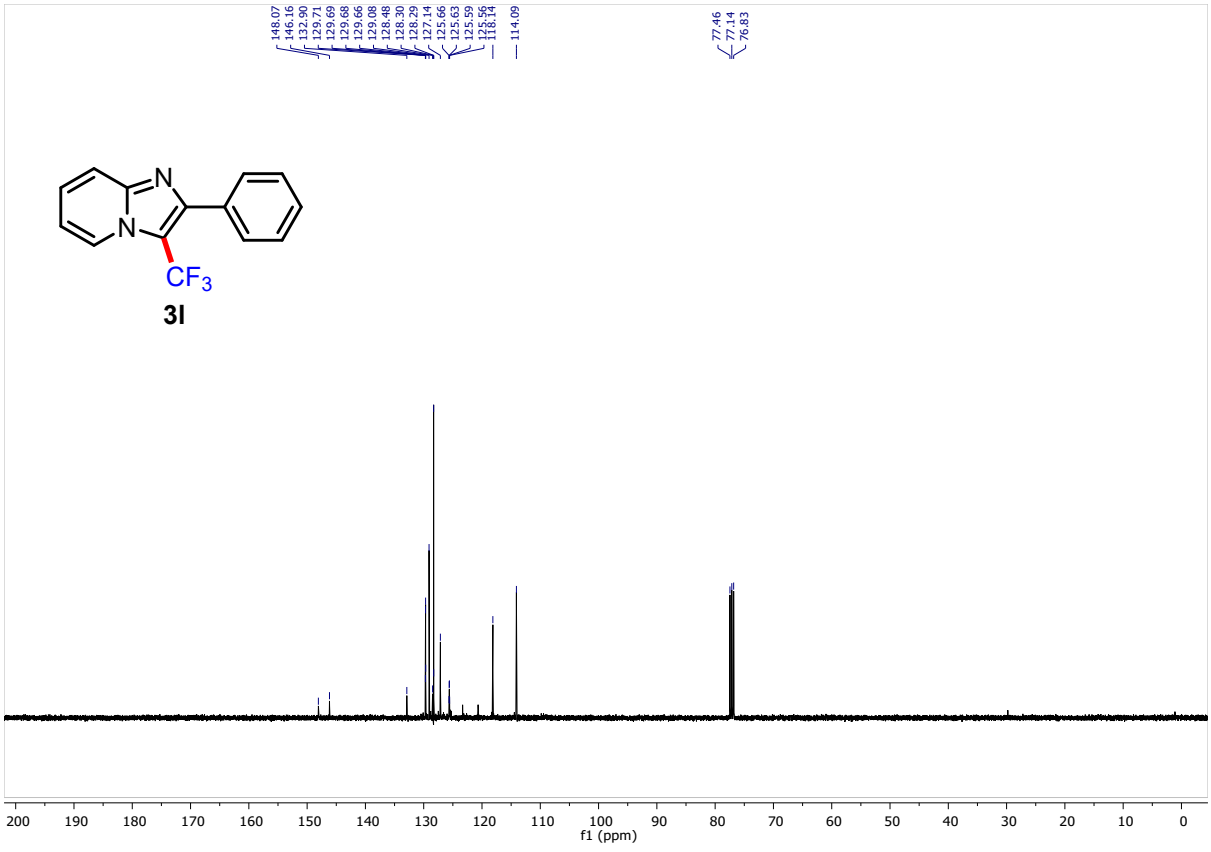

14.00
9.88
8.18
3.34
2.50
CHO
N
CF3
N
H
3k
1.05
0.98
1.00
f1 (ppm)


179.30
140.65
136.11
135.82
135.50
135.18
129.61
124.56
122.43
120.30
118.17
40.02
39.85
39.69
39.35
39.19
39.02
CHO
N
CF3
N
H
3k
f1 (ppm)

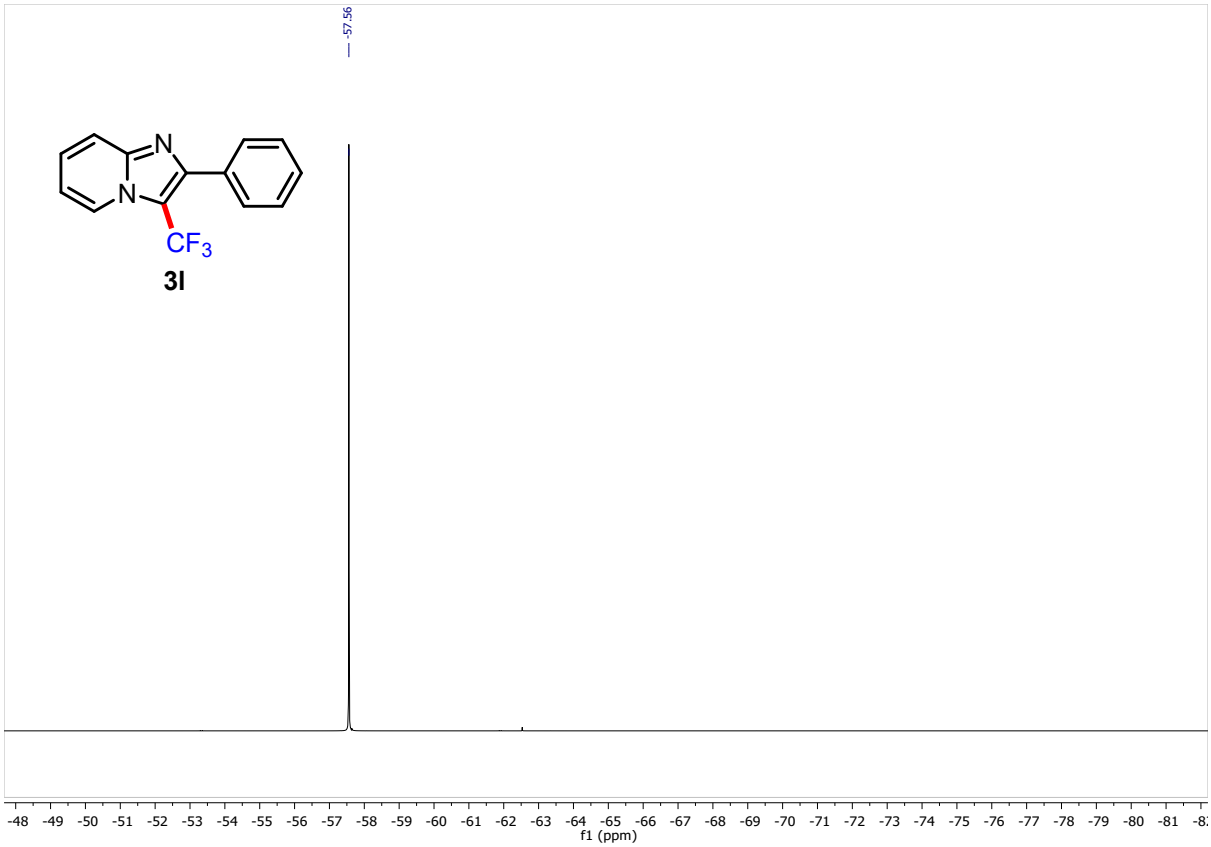

-55.88
CHO
N
CF3
N
H
3k
-48 -49 -50 -51 -52 -53 -54 -55 -56 -57 -58 -59 -60 -61 -62 -63 -64 -65 -66 -67 -68 -69 -70 -71 -72 -73 -74 -75 -76 -77
f1 (ppm)

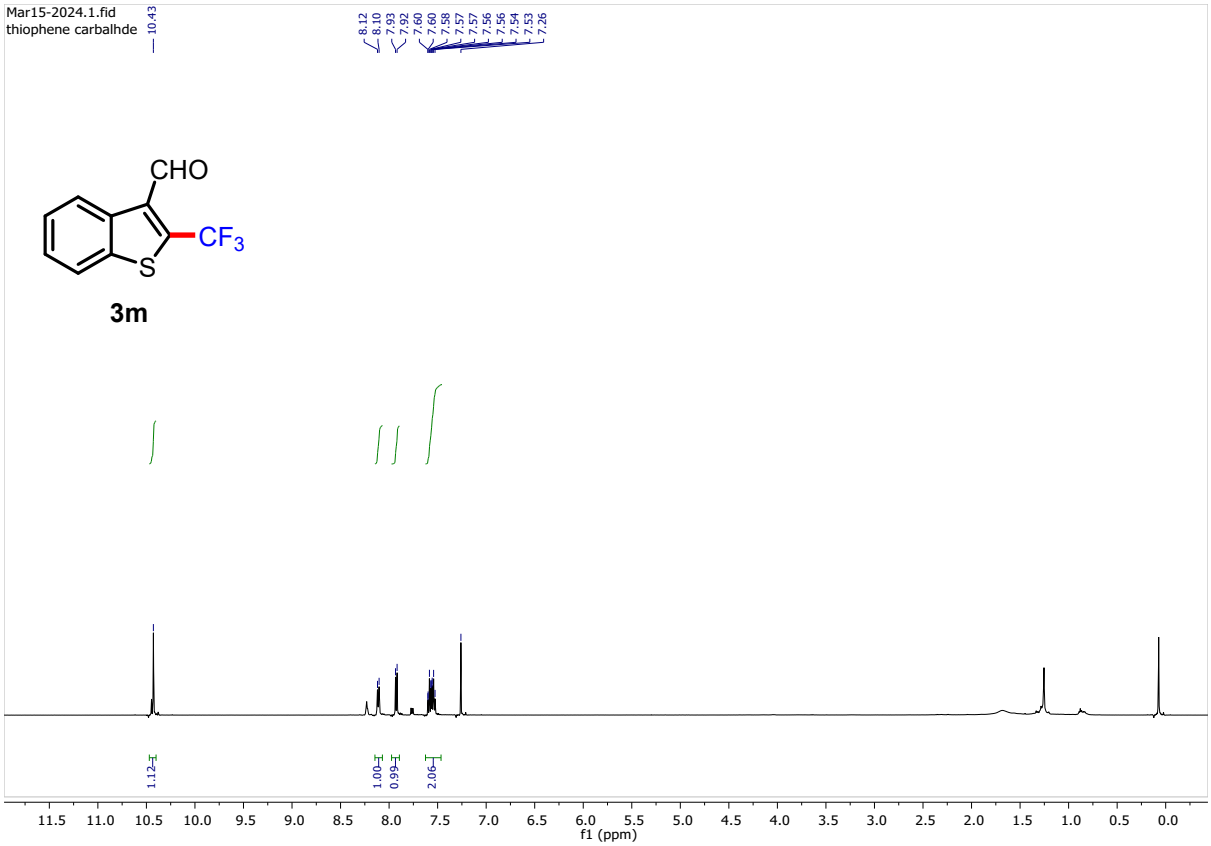

8.32
8.30
7.75
7.73
7.71
7.70
7.69
7.49
7.48
7.48
7.47
7.47
7.46
7.45
7.45
7.44
7.44
7.43
7.43
7.40
7.39
7.38
7.38
7.36
7.26
7.01
7.00
6.99
6.99
6.97
6.97
N
N
CF3
1.00
3.14
4.24
1.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

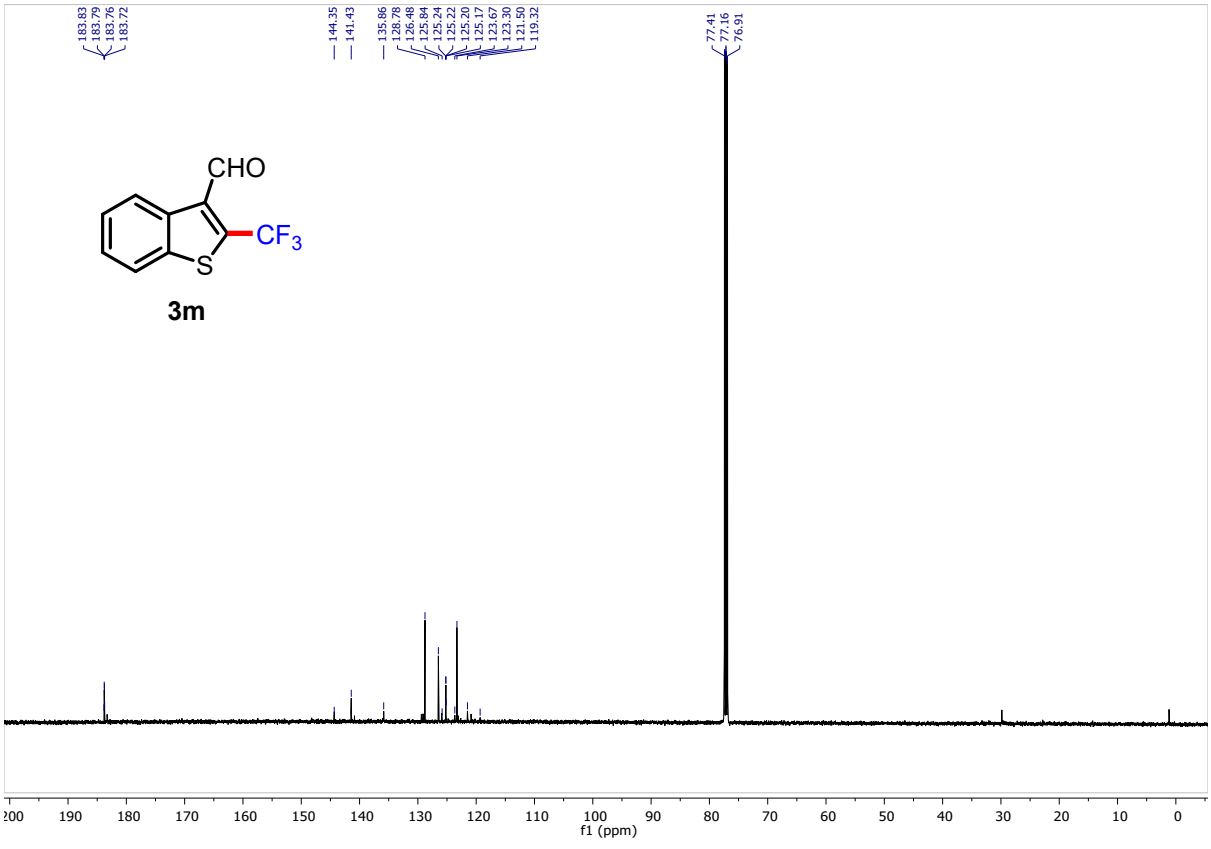
3l

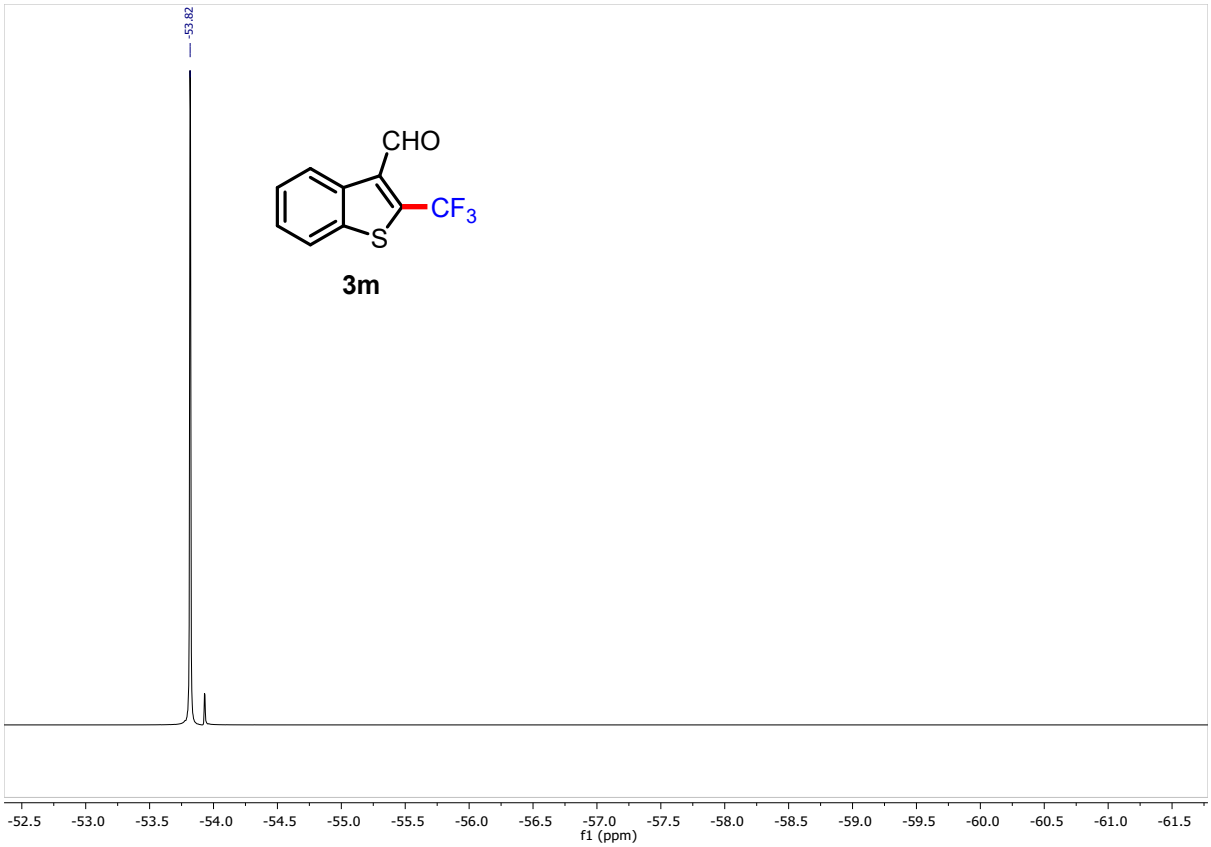

148.07
146.16
132.90
129.71
129.69
129.68
129.66
129.08
128.48
128.30
128.29
127.14
125.66
125.63
125.59
125.56
118.14
114.09
77.46
77.14
76.83
N
N
CF3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

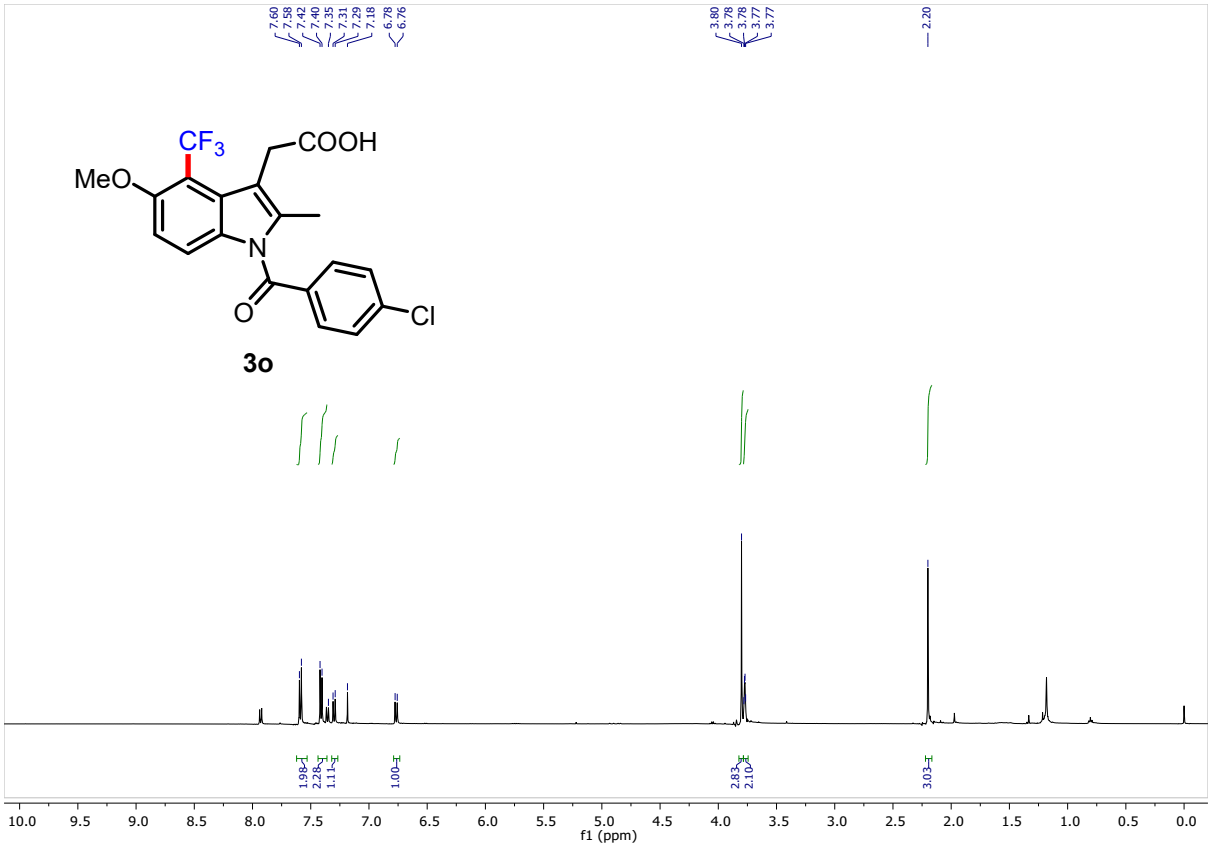
3l

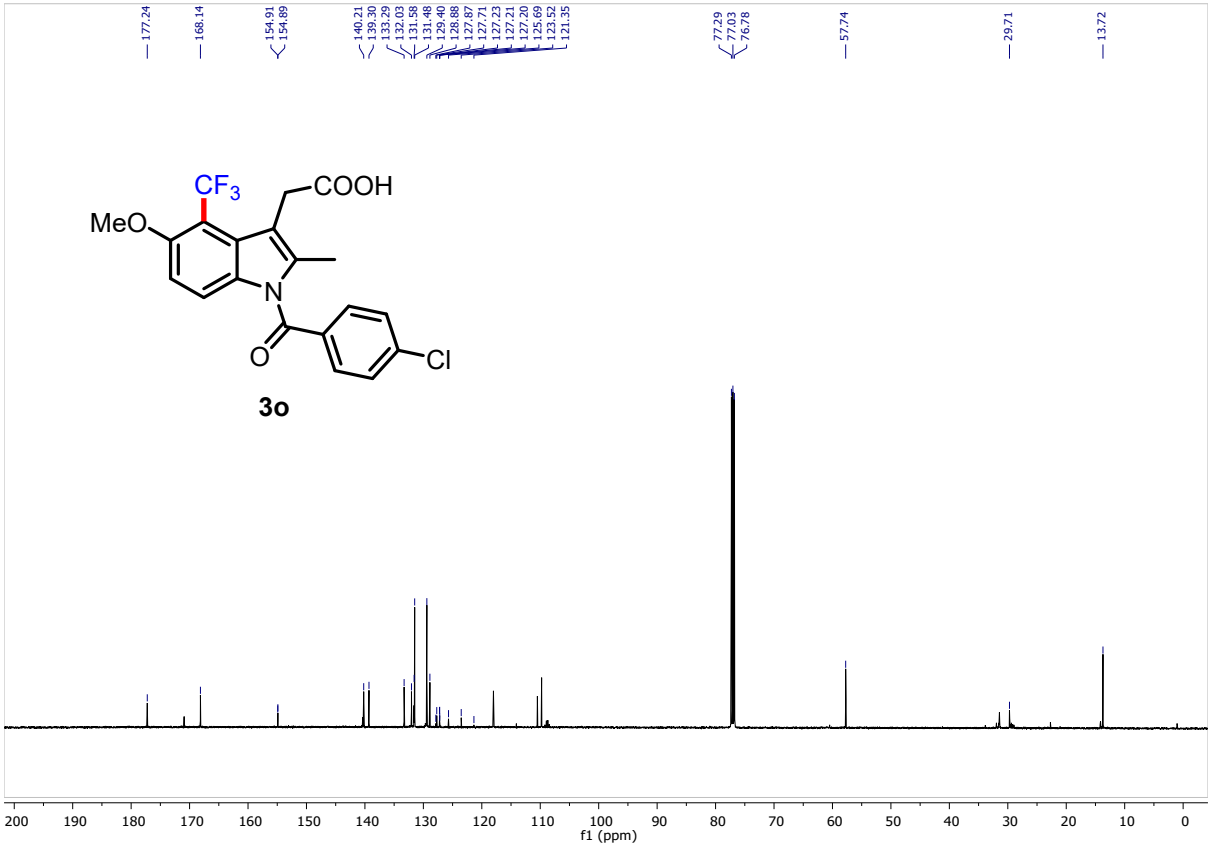

-57.56
N
N
CF3
3l
-48 -49 -50 -51 -52 -53 -54 -55 -56 -57 -58 -59 -60 -61 -62 -63 -64 -65 -66 -67 -68 -69 -70 -71 -72 -73 -74 -75 -76 -77 -78 -79 -80 -81
f1 (ppm)

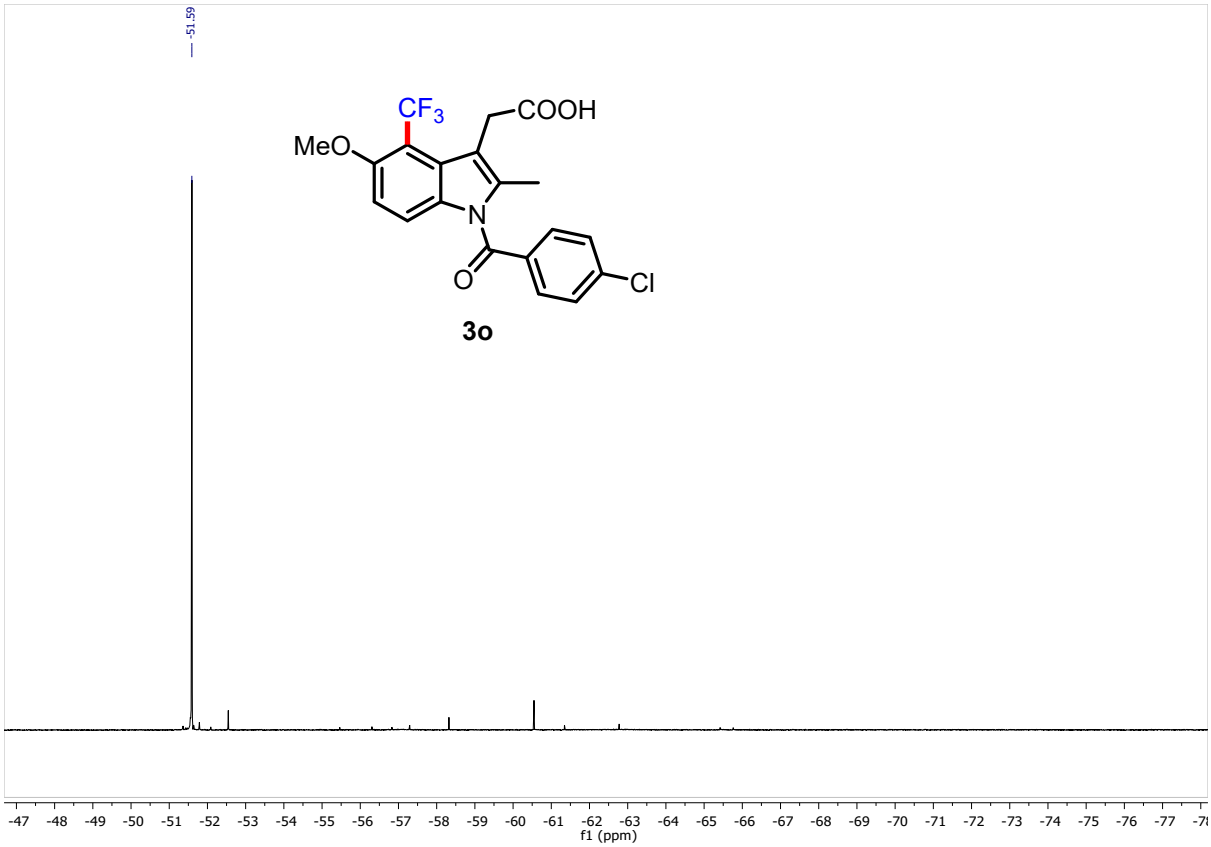

Mar15-2024.1.fid
thiophene carbalhde
10.43
8.12
8.10
7.93
7.92
7.60
7.58
7.57
7.57
7.56
7.56
7.54
7.53
7.26
CHO
CF3
S
3m
1.12
1.00
0.99
2.06
f1 (ppm)

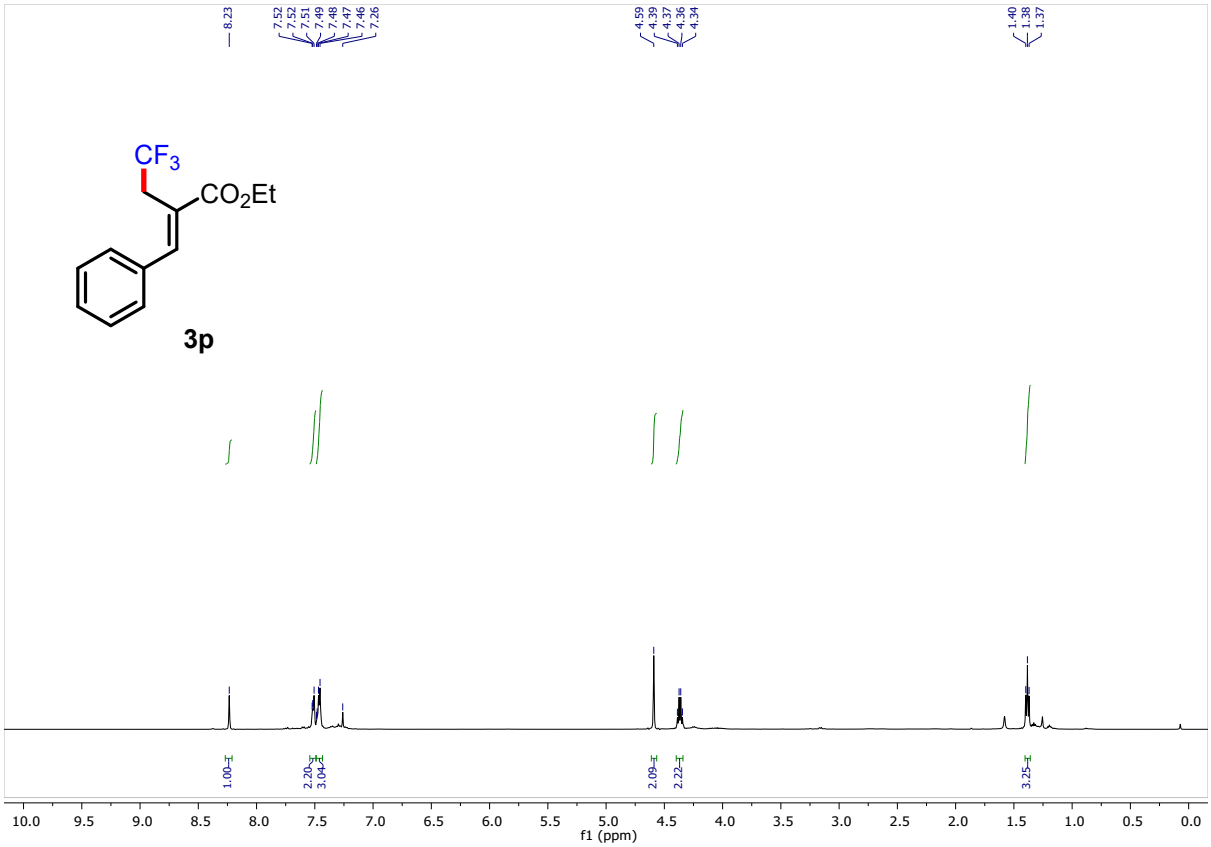

183.83
183.79
183.76
183.72
144.35
141.43
135.86
128.78
126.48
125.84
125.24
125.22
125.20
125.17
123.67
123.30
121.50
119.32
77.41
77.16
76.91
CHO
CF3
S
3m
f1 (ppm)

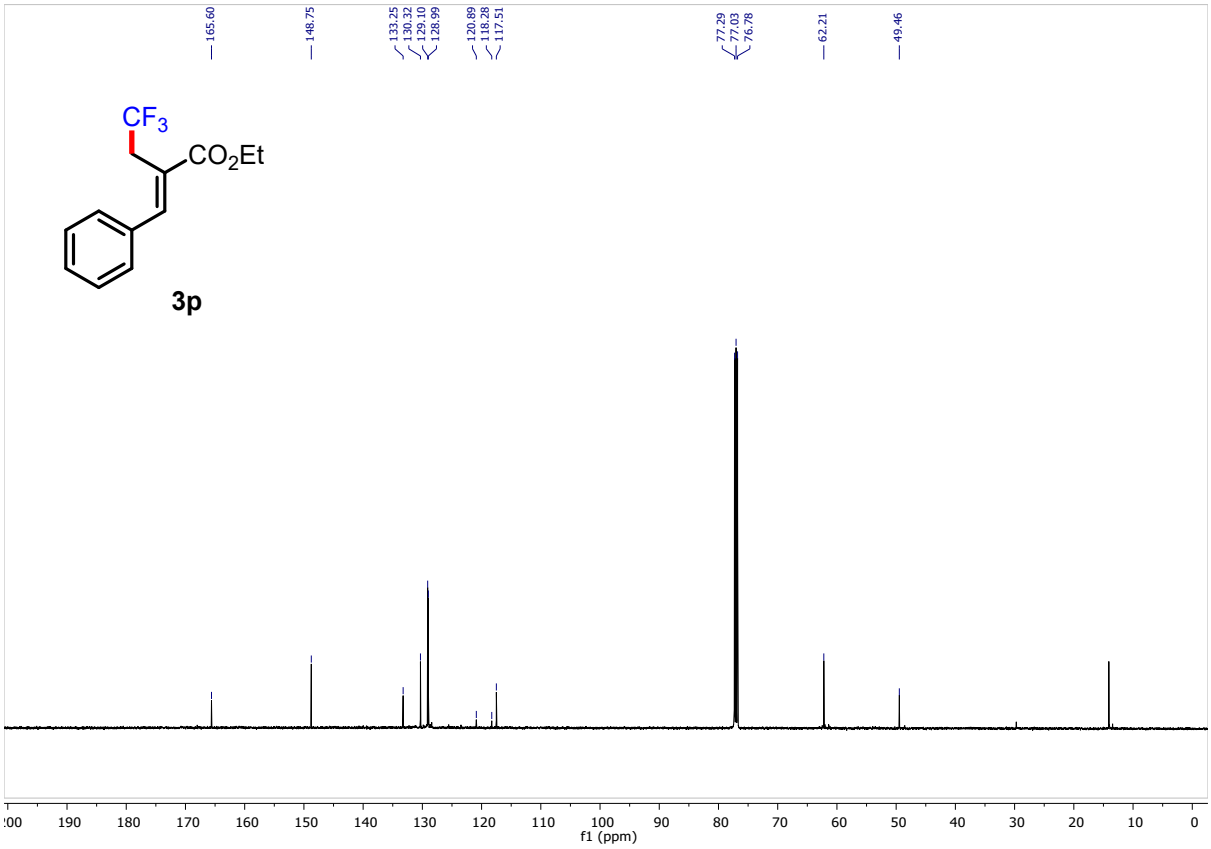

-53.82
CHO
CF3
S
3m
-52.5
-53.0
-53.5
-54.0
-54.5
-55.0
-55.5
-56.0
-56.5
-57.0
-57.5
-58.0
-58.5
-59.0
-59.5
-60.0
-60.5
-61.0
-61.5
f1 (ppm)

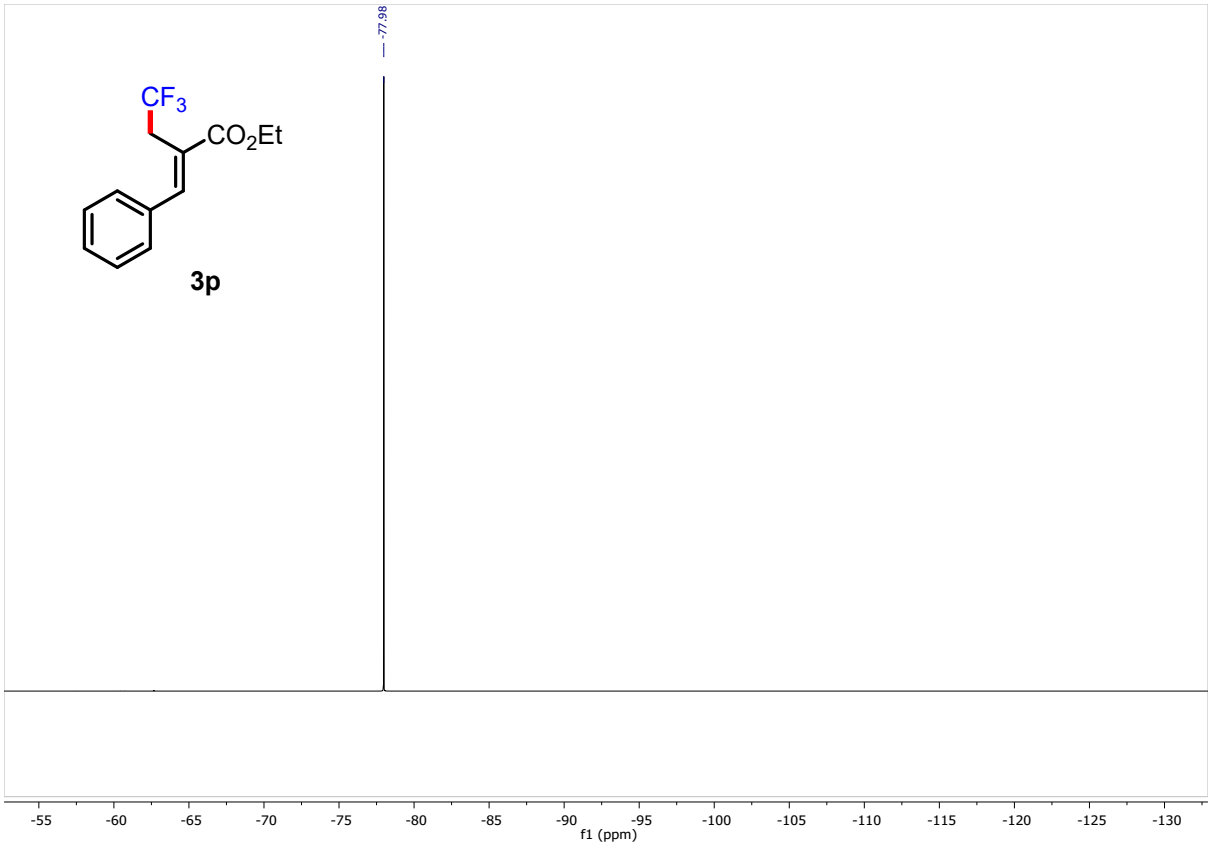

7.60
7.58
7.42
7.40
7.35
7.31
7.29
7.18
6.78
6.76
3.80
3.78
3.78
3.77
3.77
2.20
CF3
COOH
MeO
N
O
Cl
3o
1.98
2.28
1.11
1.00
2.83
2.10
3.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

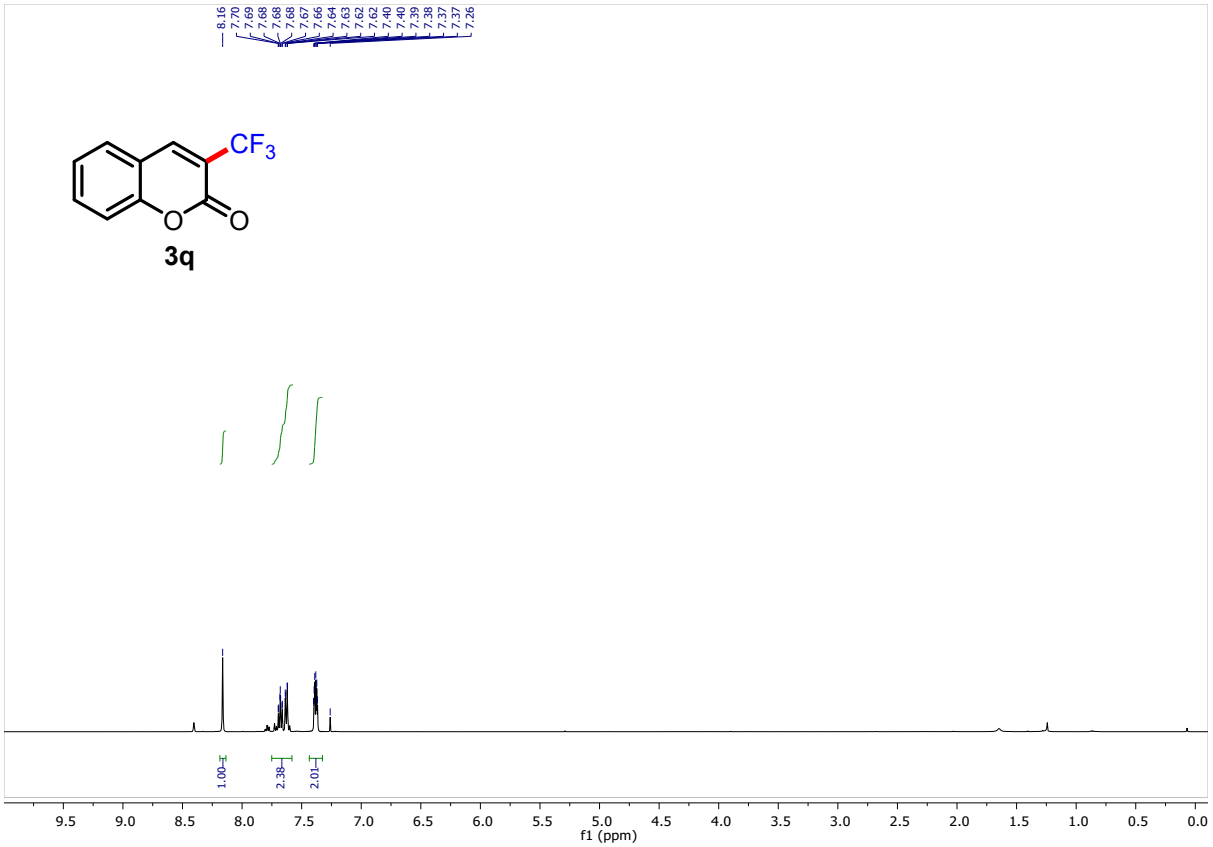

177.24
168.14
154.91
154.89
140.21
139.20
133.29
132.03
131.58
131.46
129.40
128.88
127.87
127.71
127.23
127.21
127.20
125.69
123.52
121.35
77.29
77.03
76.78
57.74
29.71
13.72
CF3
COOH
MeO
N
O
Cl
3o
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

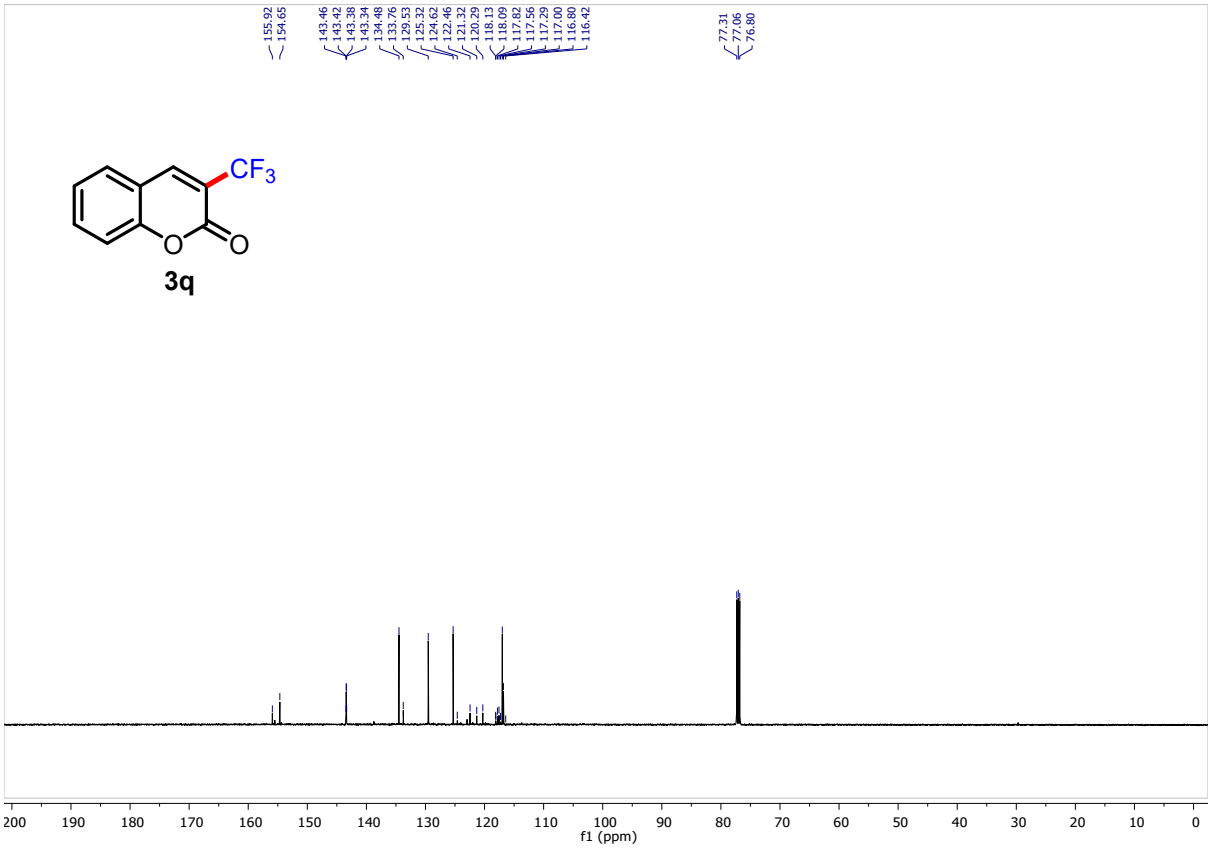

51.59
CF3
COOH
MeO
N
O
Cl
3o
-47 -48 -49 -50 -51 -52 -53 -54 -55 -56 -57 -58 -59 -60 -61 -62 -63 -64 -65 -66 -67 -68 -69 -70 -71 -72 -73 -74 -75 -76 -77
f1 (ppm)

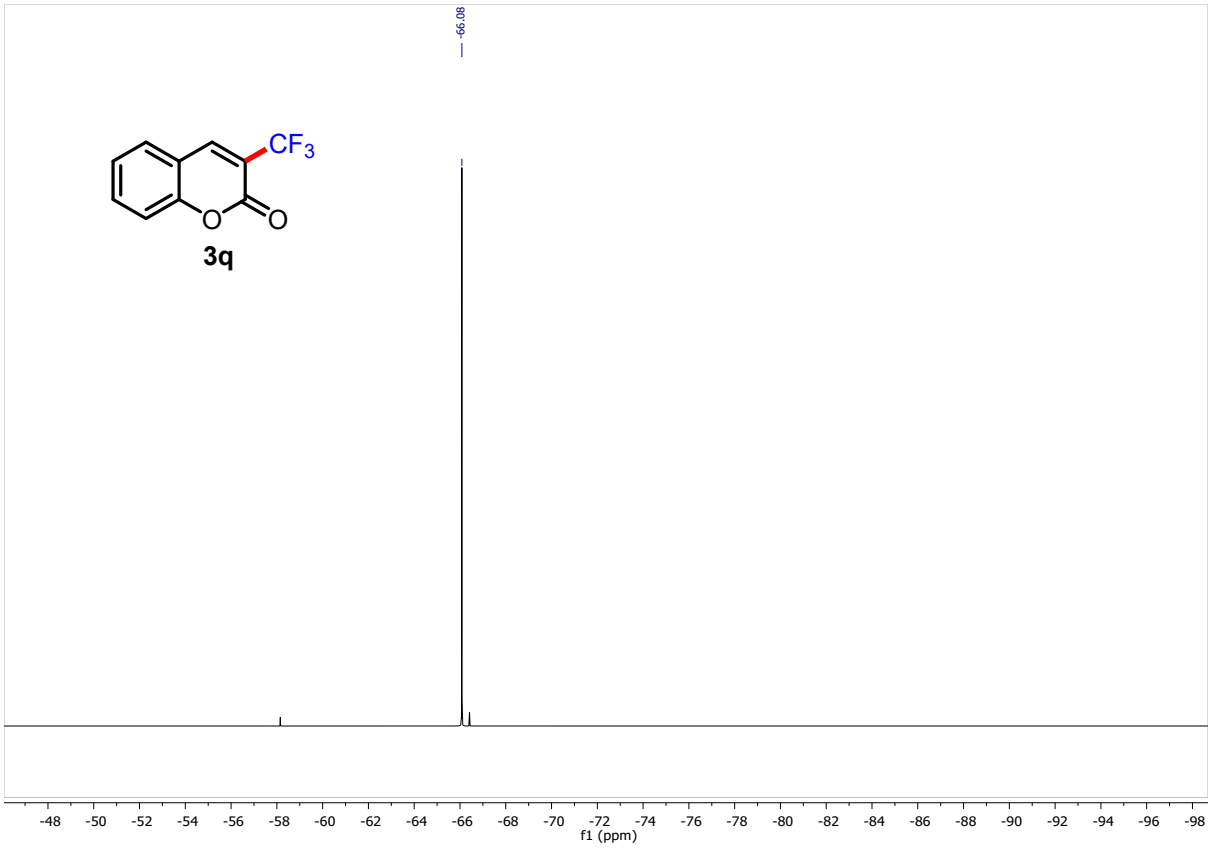

8.23
7.52
7.52
7.51
7.49
7.48
7.47
7.46
7.26
4.59
4.39
4.37
4.36
4.34
1.40
1.38
1.37
CF3
CO2Et
3p
1.00
2.20
3.04
2.09
2.22
3.25
f1 (ppm)

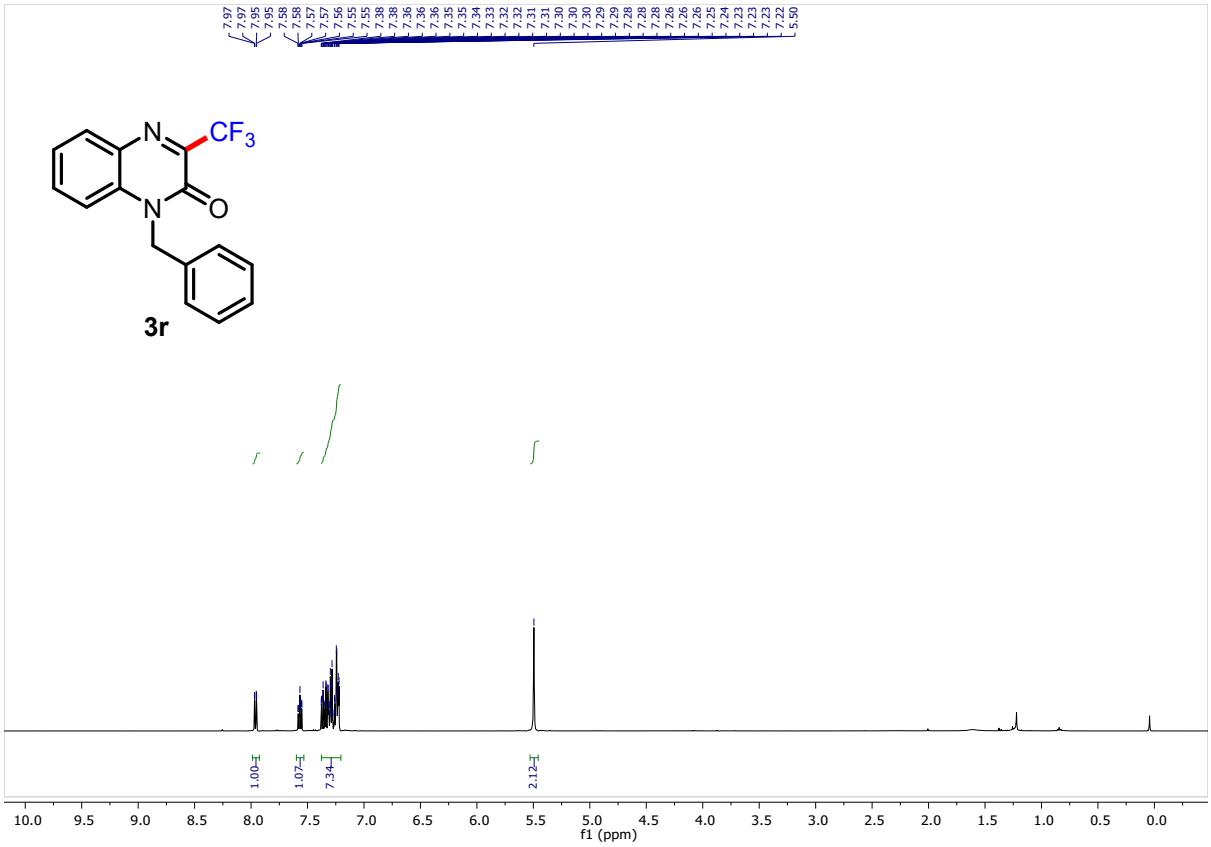

165.60
148.75
133.25
130.32
129.10
128.99
120.89
118.28
117.51
77.29
77.03
76.78
62.21
49.46
CF3
CO2Et
3p
f1 (ppm)

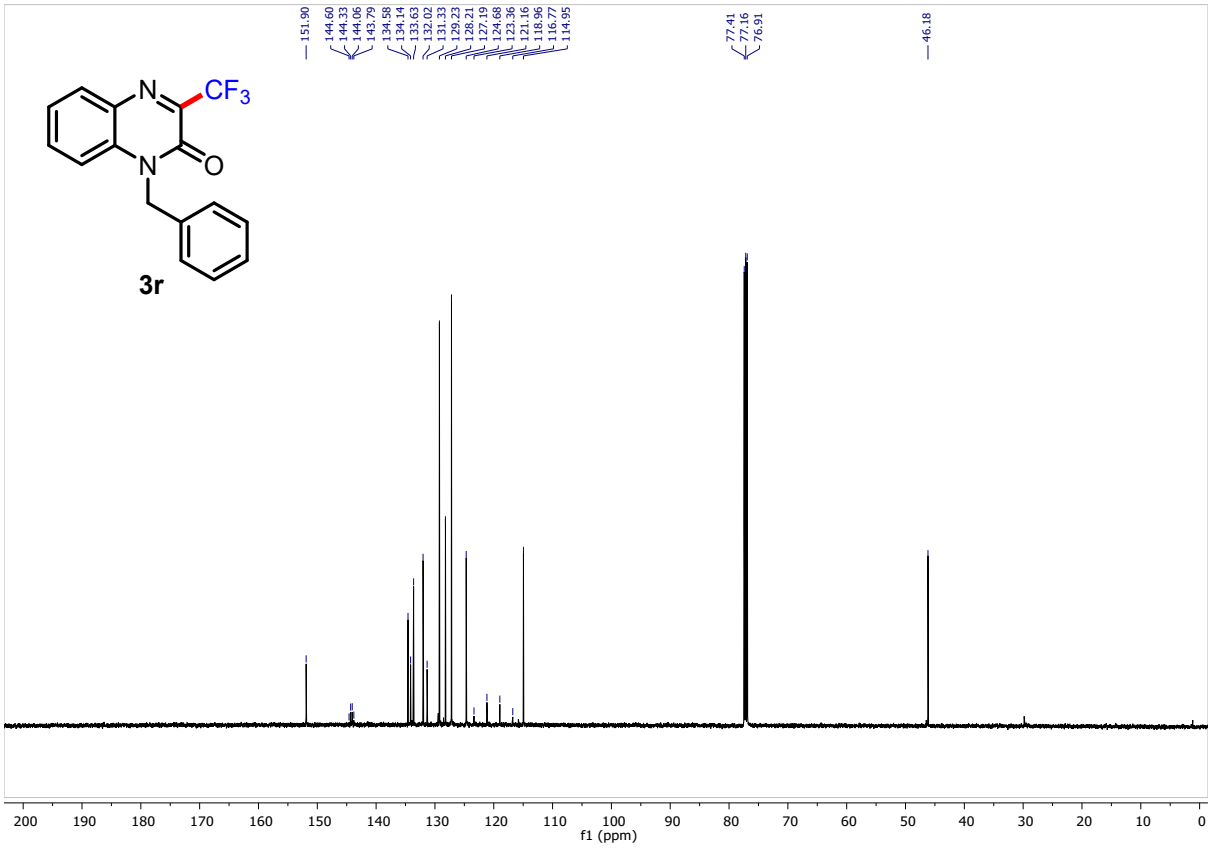

-77.98
CF3
CO2Et
3p
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
f1 (ppm)

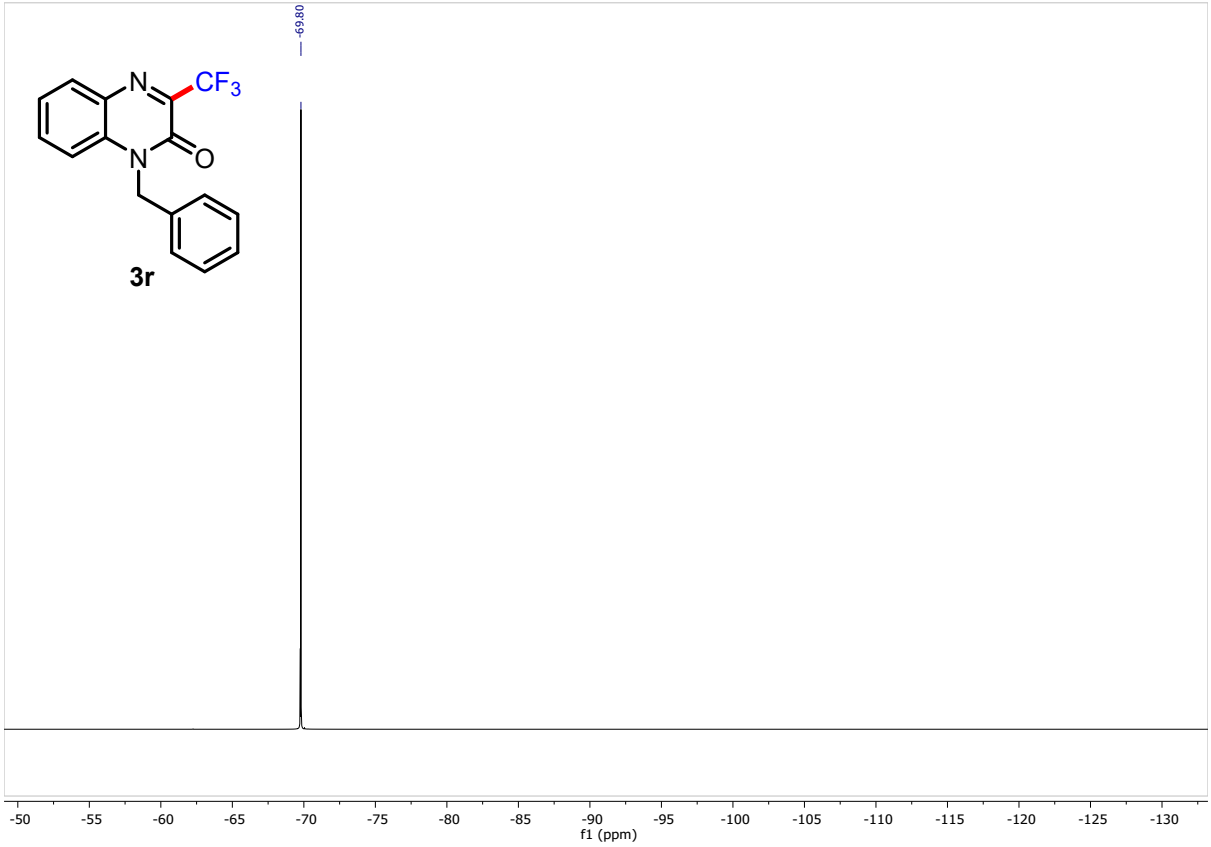

8.16
7.70
7.69
7.68
7.68
7.68
7.67
7.66
7.64
7.63
7.62
7.62
7.40
7.40
7.39
7.38
7.37
7.37
7.26
CF3
O
O
3q
1.00
2.38
2.01
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

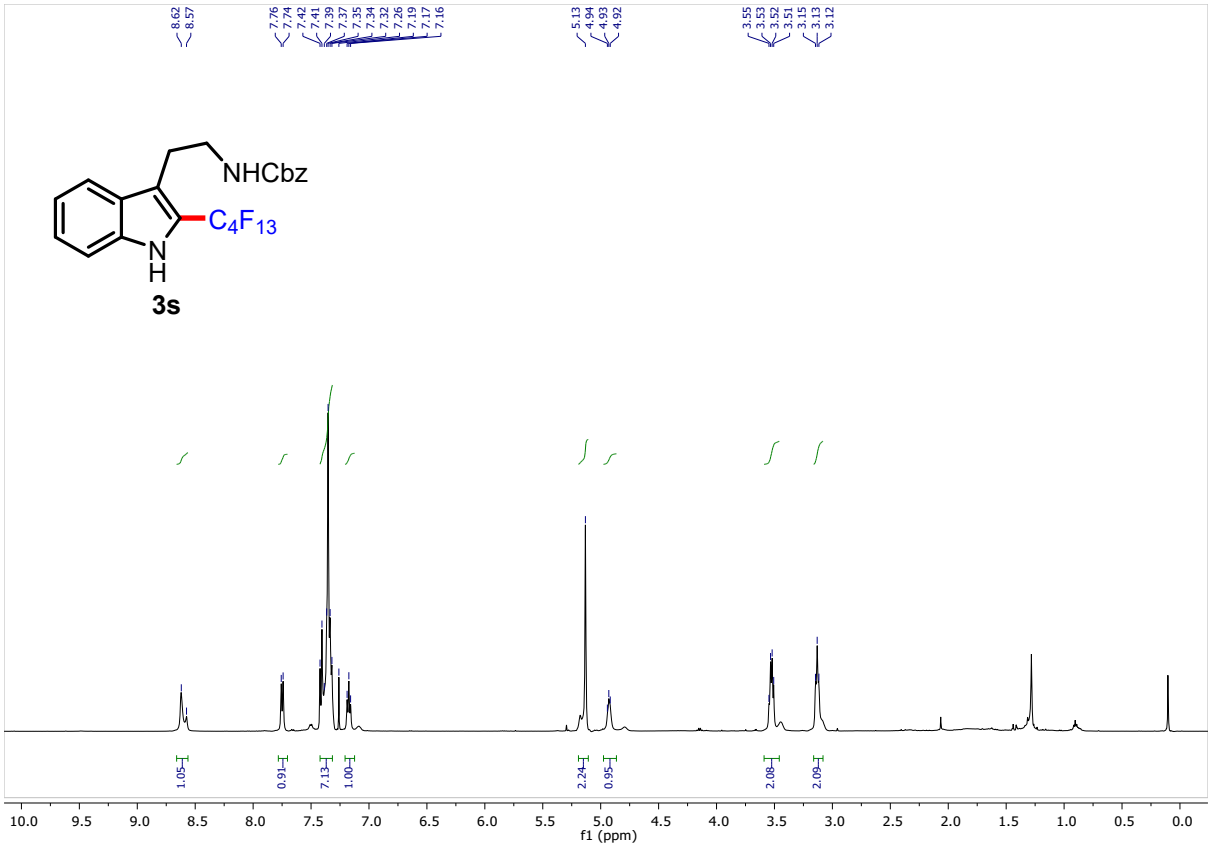

155.92
154.65
143.46
143.42
143.38
143.34
134.48
133.76
129.53
125.32
124.62
122.46
121.32
120.29
118.13
118.09
117.82
117.56
117.29
117.00
116.80
116.42
77.31
77.06
76.80
CF3
O
O
3q
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

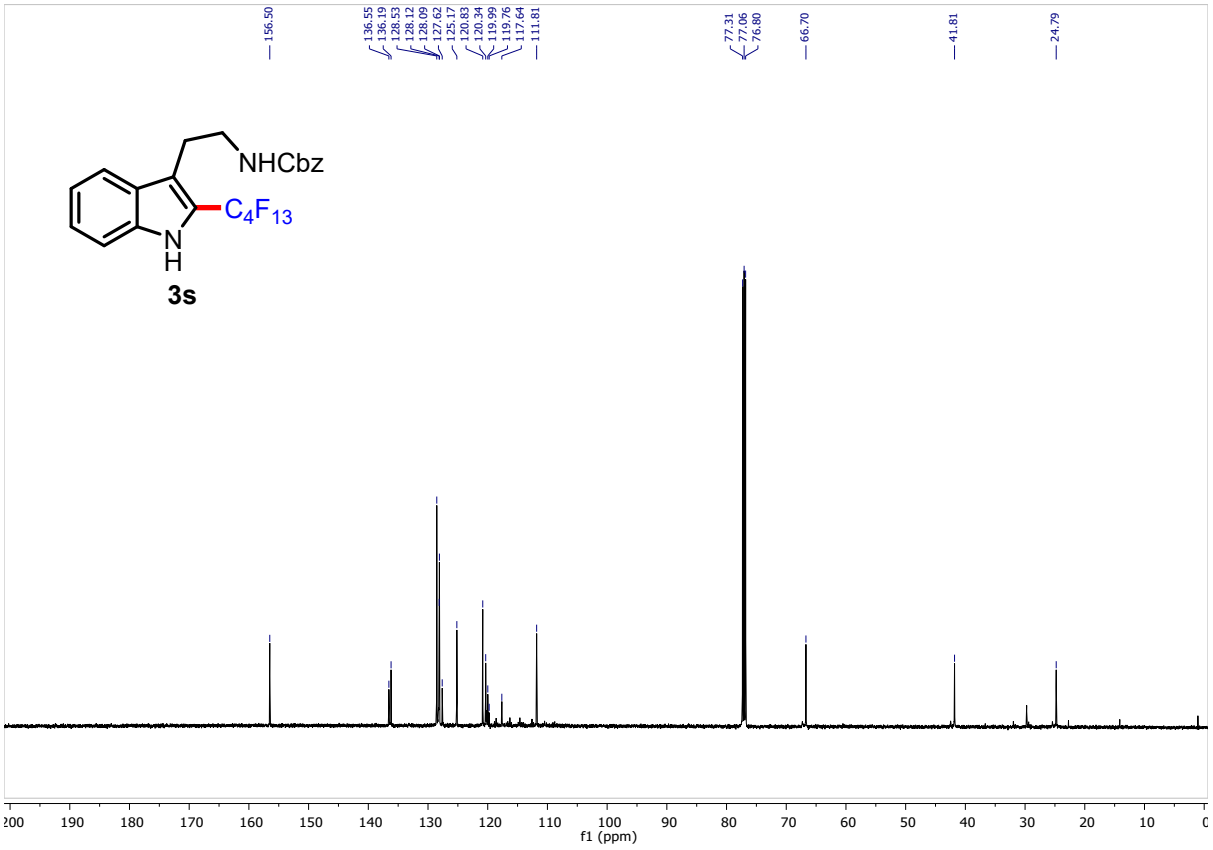

-66.08
CF3
O
O
3q
-48
-50
-52
-54
-56
-58
-60
-62
-64
-66
-68
-70
-72
-74
-76
-78
-80
-82
-84
-86
-88
-90
-92
-94
-96
-98
f1 (ppm)

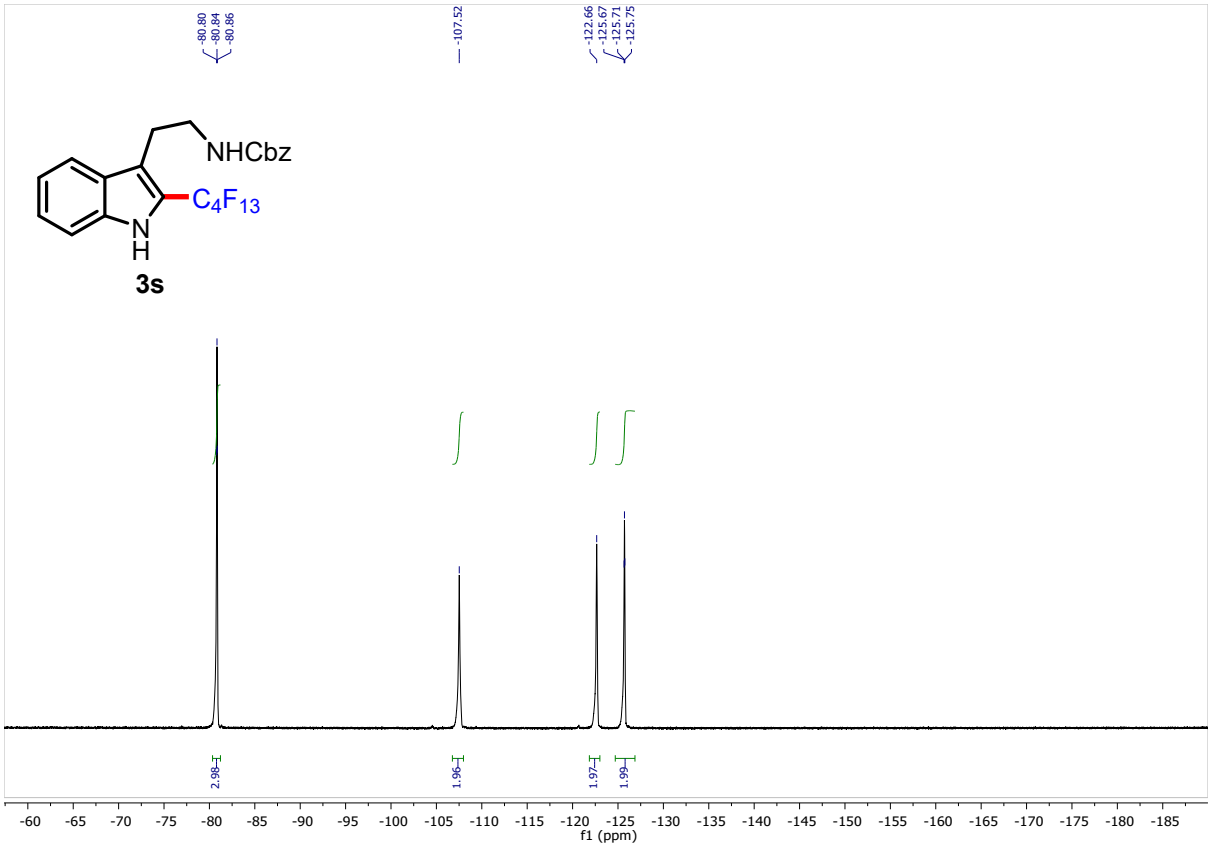

7.97
7.97
7.95
7.95
7.58
7.58
7.57
7.57
7.56
7.55
7.55
7.38
7.38
7.36
7.36
7.36
7.35
7.35
7.34
7.33
7.32
7.32
7.31
7.31
7.30
7.30
7.30
7.29
7.29
7.28
7.28
7.26
7.26
7.26
7.25
7.24
7.23
7.23
7.23
7.22
5.50
N
CF3
N
O
3r
1.00
1.07
7.34
2.12
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

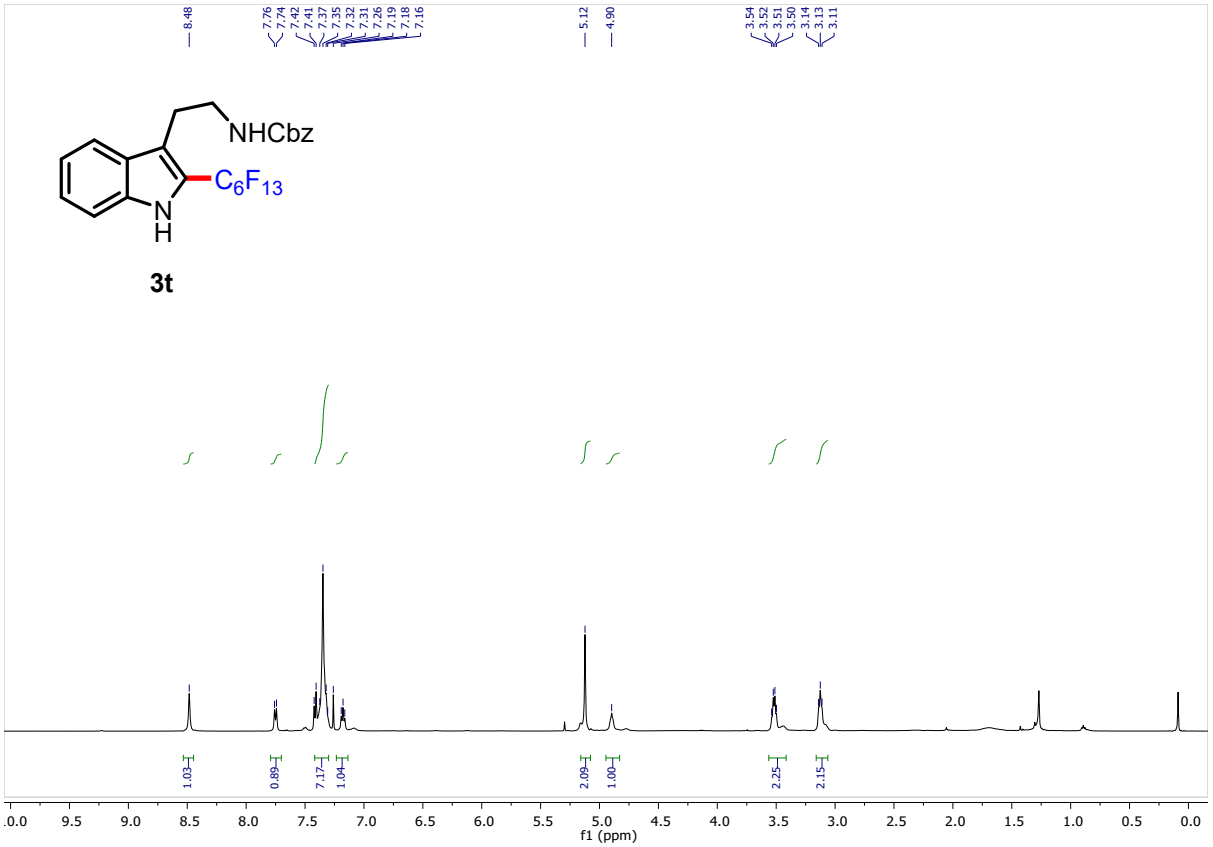

151.90
144.60
144.33
144.06
143.79
134.58
134.14
133.63
132.02
131.33
129.23
128.21
127.19
124.68
123.36
121.16
118.96
116.77
114.95
77.41
77.16
76.91
46.18
N
CF3
N
O
3r
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

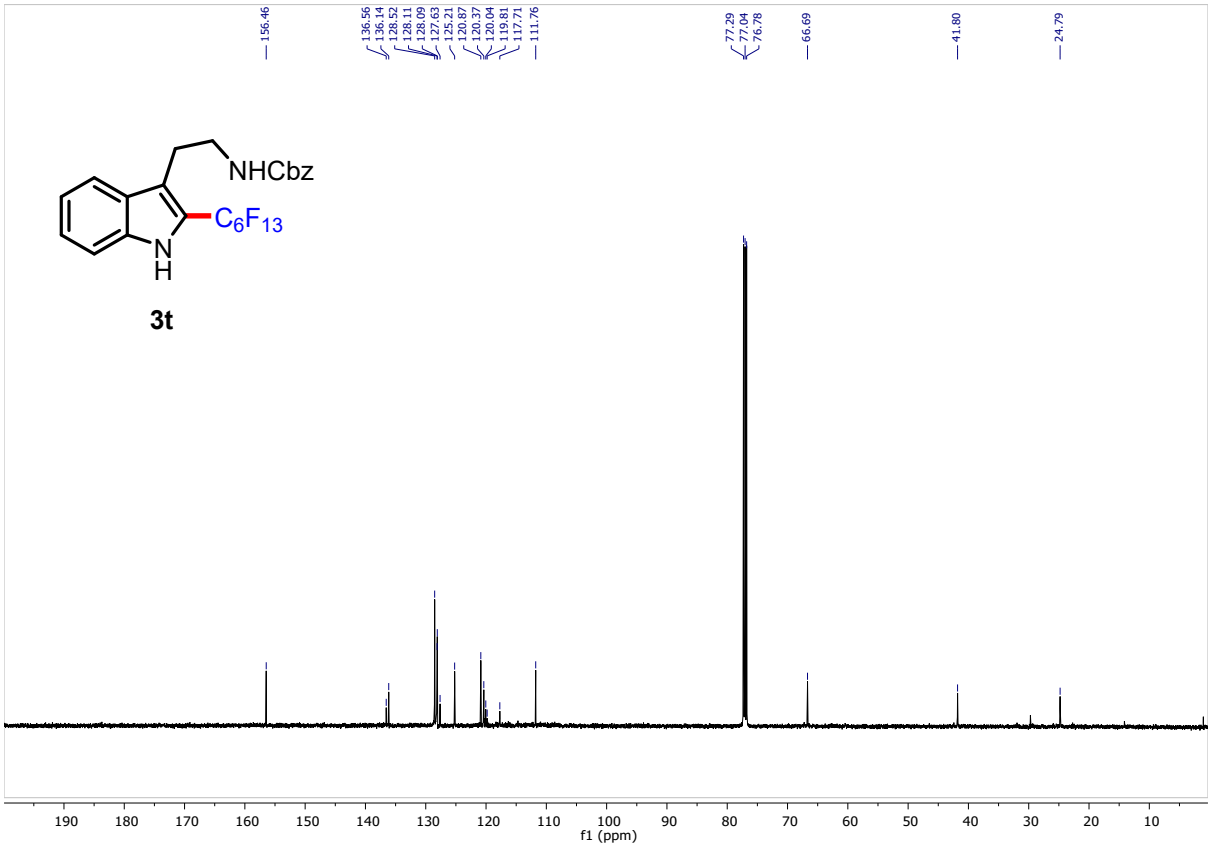

-69.80
N
CF3
N
O
3r
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
f1 (ppm)

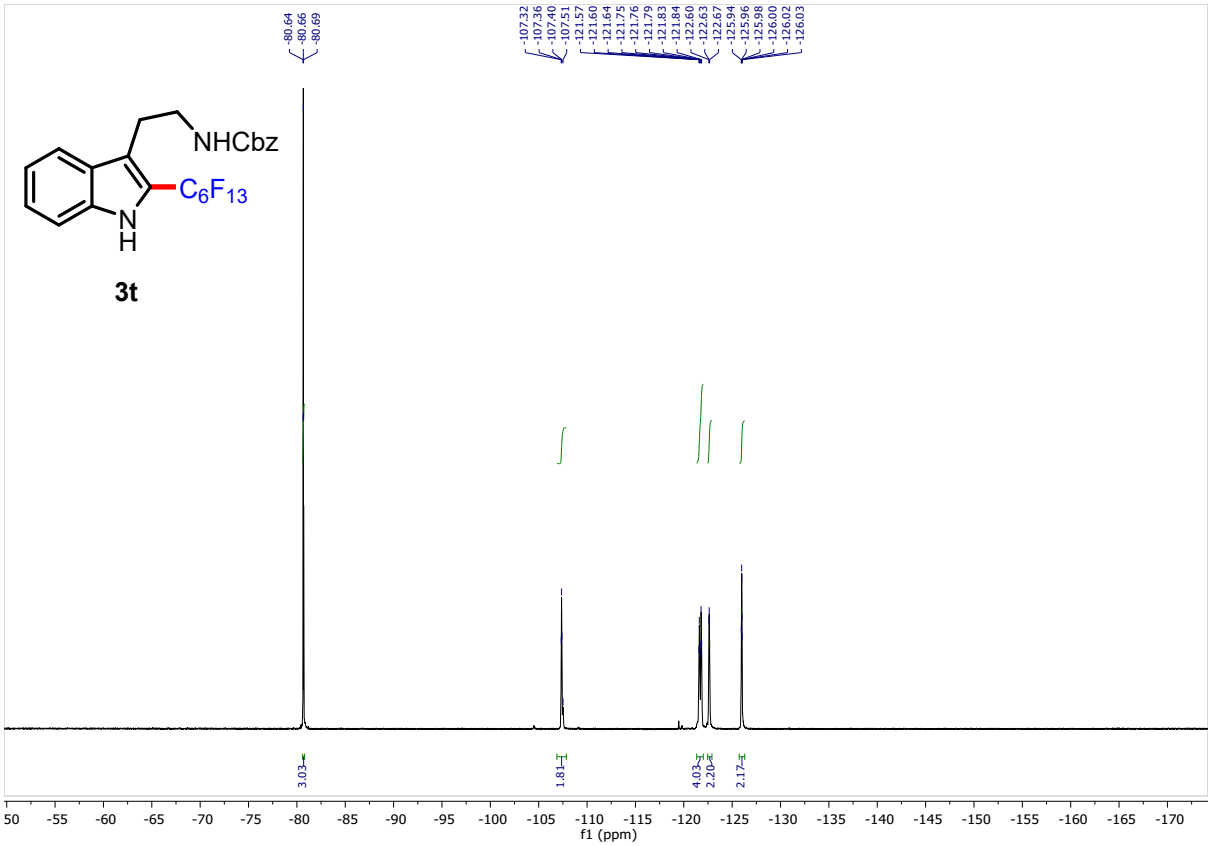

8.62
8.57
7.76
7.74
7.42
7.41
7.39
7.37
7.35
7.34
7.32
7.26
7.19
7.17
7.16
5.13
4.94
4.93
4.92
3.55
3.53
3.52
3.51
3.15
3.13
3.12
NHCbz
C_4F_{13}
N
H
3s
1.05
0.91
7.13
1.00
2.24
0.95
2.08
2.09
f1 (ppm)


156.50
136.55
136.19
128.53
128.12
128.09
127.62
125.17
120.83
120.34
119.99
119.76
117.64
111.81
77.31
77.06
76.80
66.70
41.81
24.79
NHCbz
C_4F_{13}
N
H
3s
f1 (ppm)


-80.80
-80.84
-80.86
-107.52
-122.66
-125.67
-125.71
-125.75
NHCbz
C_4F_{13}
N
H
3s
2.98
1.96
1.97
1.99
-60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185
f1 (ppm)


NHCbz
C_6F_{13}
N
H
3t
f1 (ppm)


NHCbz
C_6F_{13}
N
H
3t
f1 (ppm)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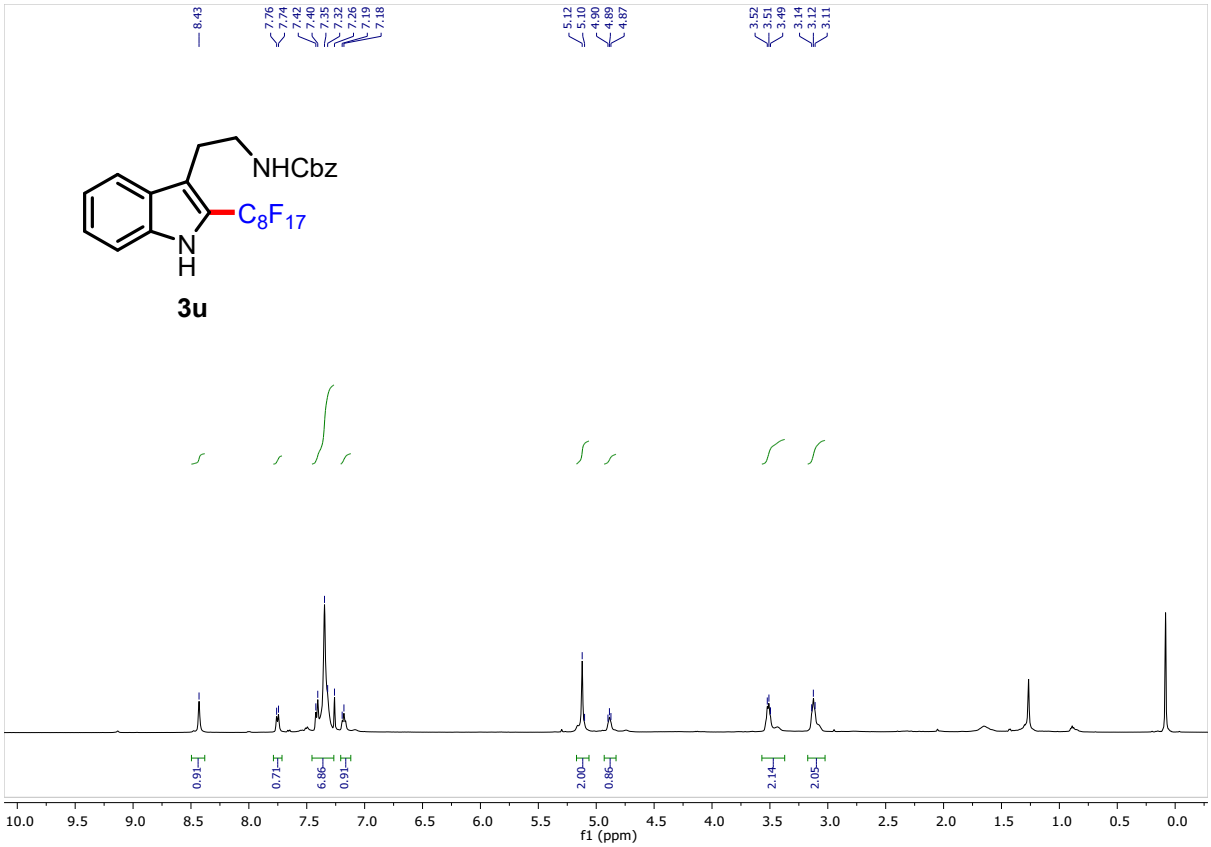
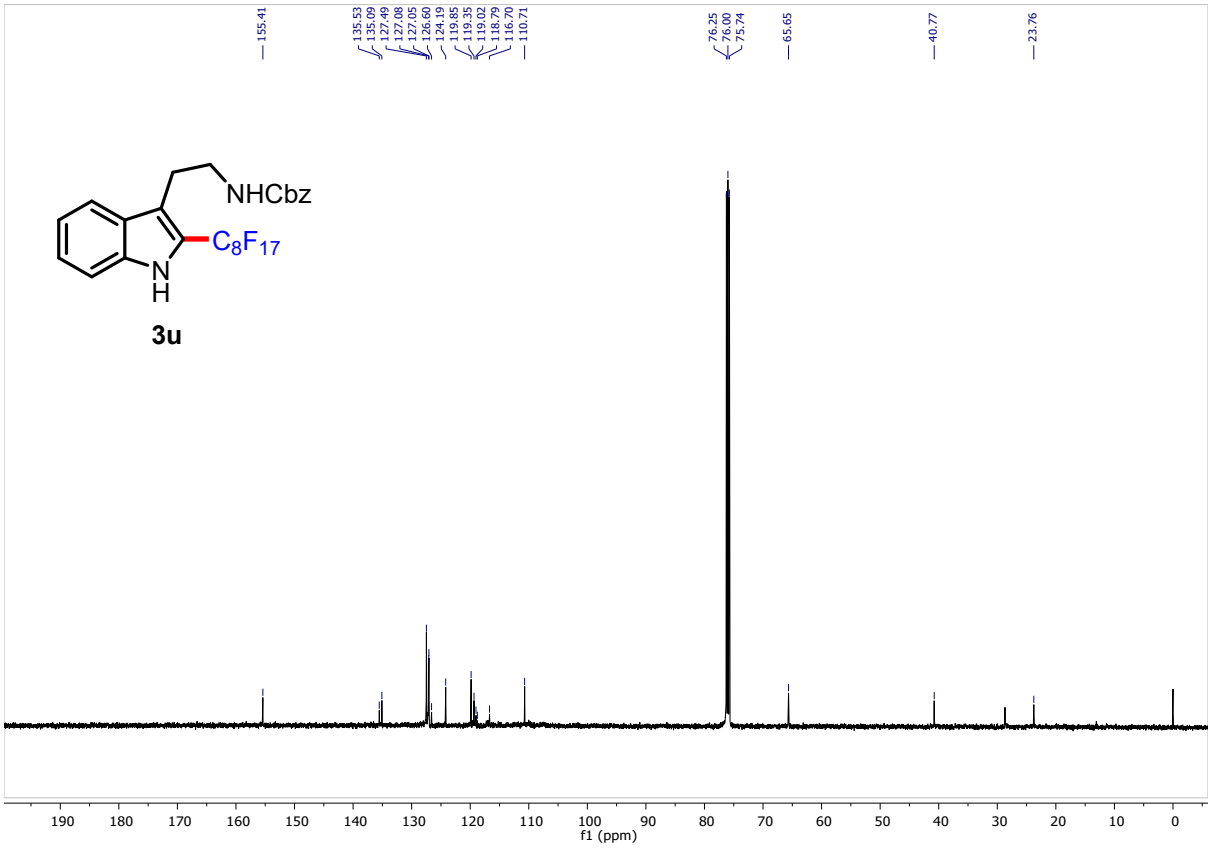
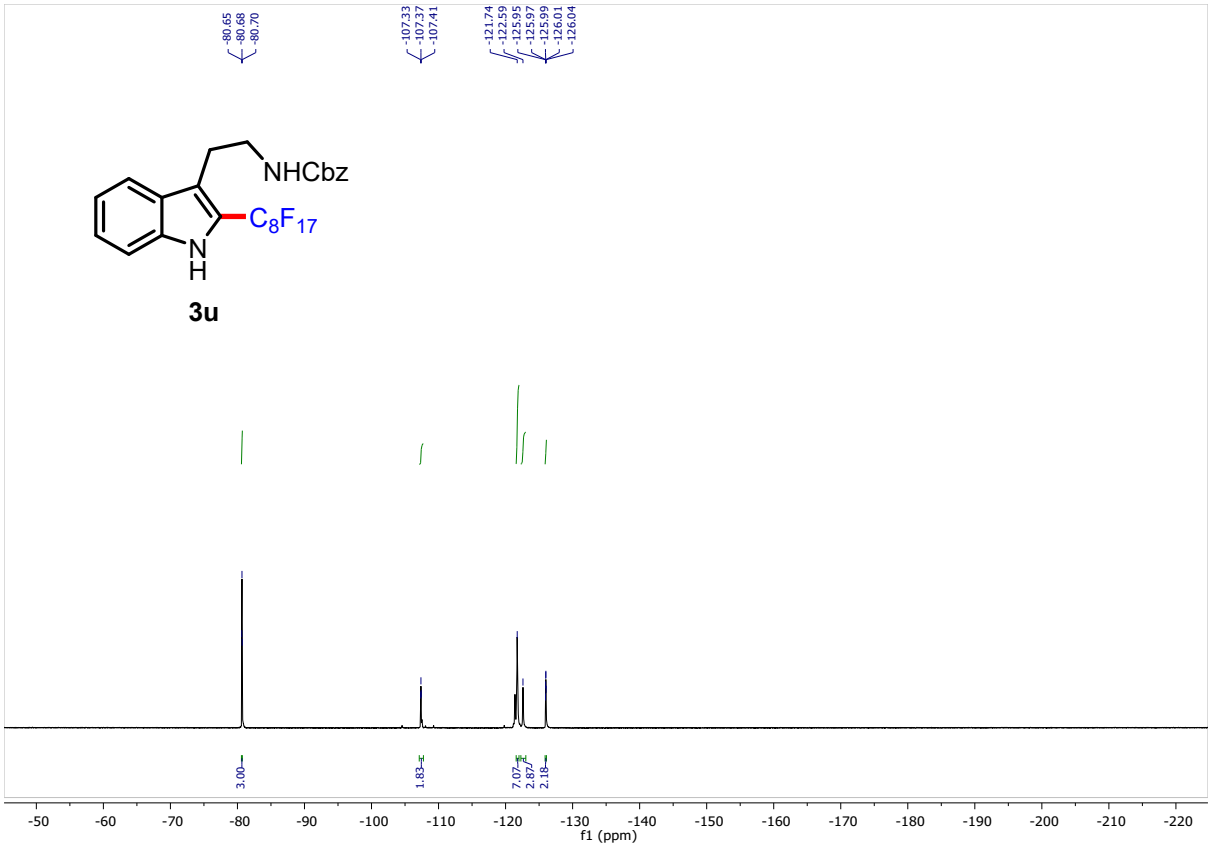
-80.66
-80.69
-107.32
-107.36
-107.40
-107.51
-121.57
-121.60
-121.64
-121.75
-121.76
-121.79
-121.83
-121.84
-122.60
-122.63
-122.67
-125.94
-125.96
-125.98
-126.00
-126.02
-126.03
NHCbz
C_6F_{13}
N
H
3t
3.03
1.81
4.03
2.20
2.17
50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170
f1 (ppm)


8.43
7.76
7.74
7.42
7.40
7.35
7.32
7.26
7.19
7.18
5.12
5.10
4.90
4.89
4.87
3.52
3.51
3.49
3.14
3.12
3.11
NHCbz
C8F17
N
H
3u
0.91
0.71
6.86
0.91
2.00
0.86
2.14
2.05
f1 (ppm)


155.41
135.53
135.09
127.49
127.08
127.05
126.60
124.19
119.85
119.35
119.02
118.79
116.70
110.71
76.25
76.00
75.74
65.65
40.77
23.76
NHCbz
C8F17
N
H
3u
f1 (ppm)


-80.65
-80.68
-80.70
-107.33
-107.37
-107.41
-121.74
-122.59
-125.95
-125.97
-125.99
-126.01
-126.04
NHCbz
C8F17
N
H
3u
3.00
1.83
7.07
2.87
2.18
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
f1 (ppm)