Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Metal-Free Chloroamidation of Indoles with Sulfonamides and NaClO

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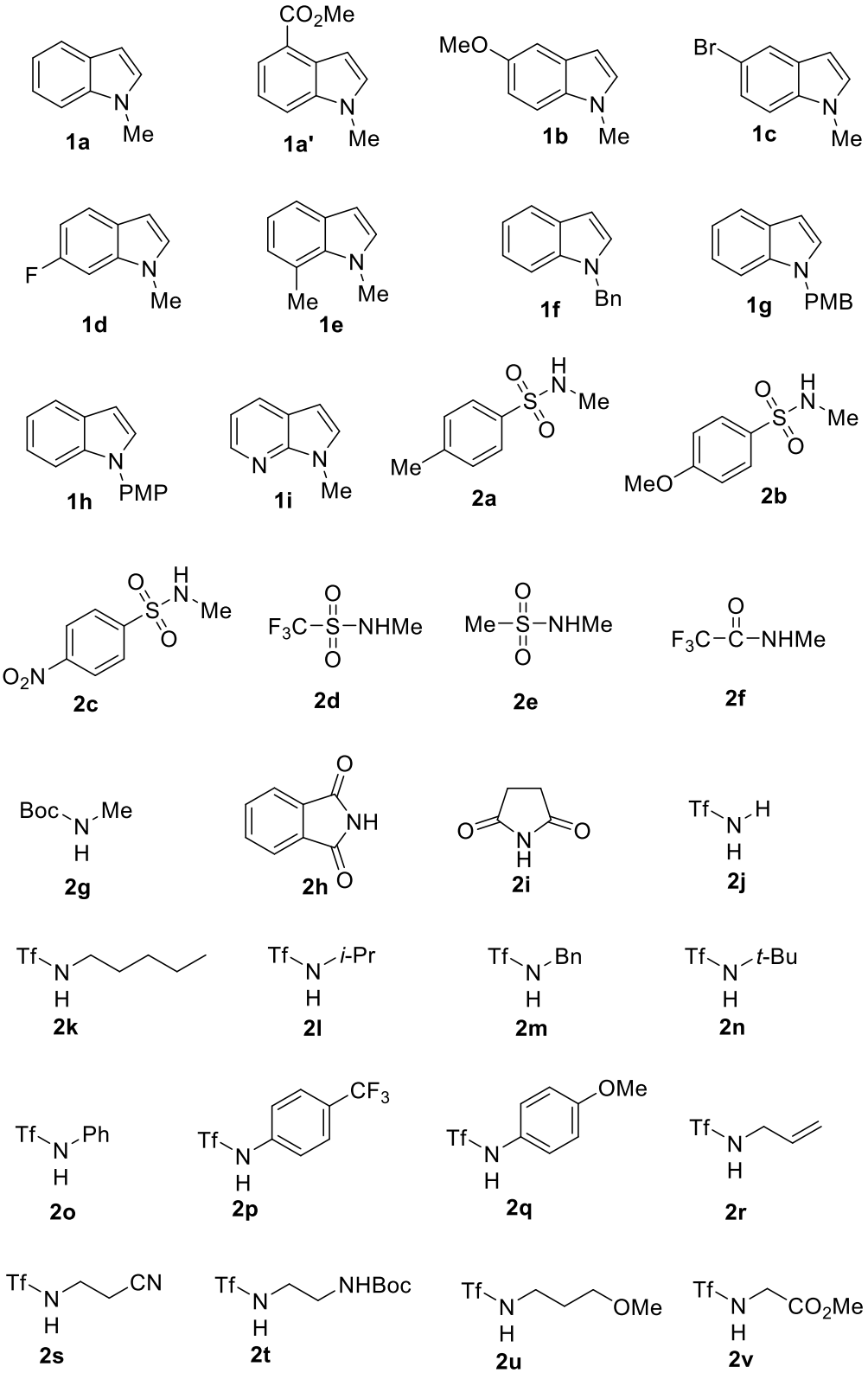
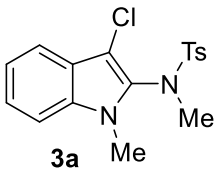
1. General Methods

NaClO (Sodium hypochlorite solution reagent grade, available chlorine 4.00-4.99%) was purchased from Sigma Aldrich. All solvents were used without further purification. Thin layer chromatography (TLC) was performed on EMD precoated plates (silica gel 60 F254, Art 5715) and visualized by fluorescence quenching under UV light and by staining with phosphomolybdic acid or potassium permanganate, respectively. Column chromatography was performed on EMD Silica Gel 60 (300–400 Mesh) using a forced flow of 0.5–1.0 bar. ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) and ^{19}F (376 MHz) were measured on a Bruker AVANCE III–400 spectrometer. Chemical shifts are expressed in parts per million (ppm) with respect to the residual solvent peak. Coupling constants are reported as Hertz (Hz), signal shapes and splitting patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Infrared (IR) spectra were recorded on a Nicolet 6700 spectrophotometer and are reported as wavenumber (cm^{-1}).

2. Starting materials and products





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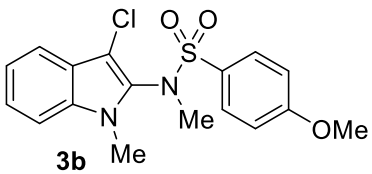

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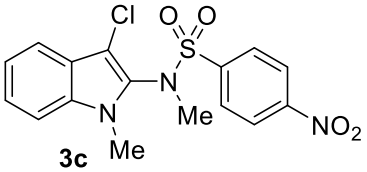

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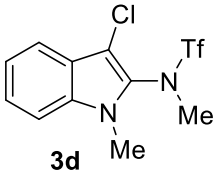

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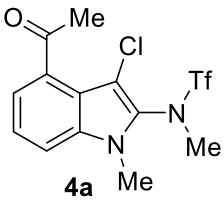

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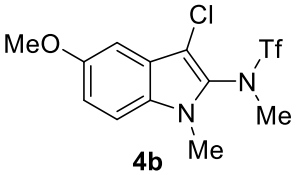

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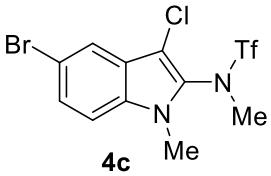

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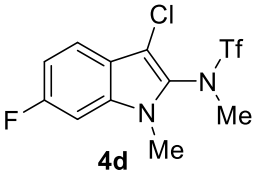

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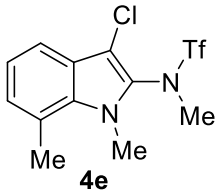

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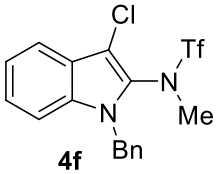

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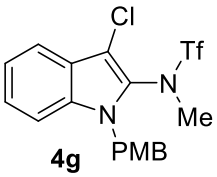

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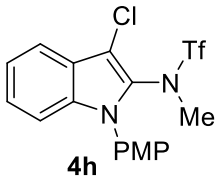

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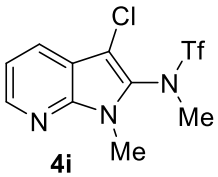

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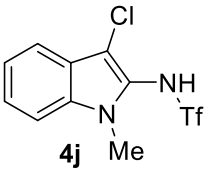

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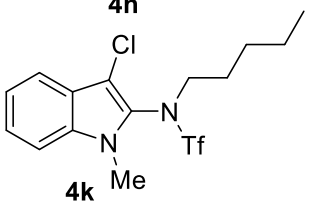

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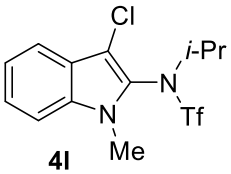

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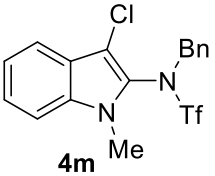

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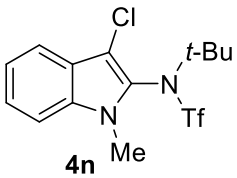

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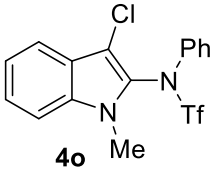

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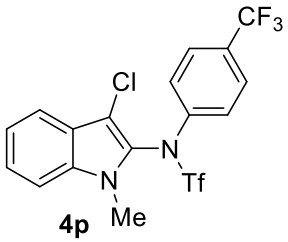

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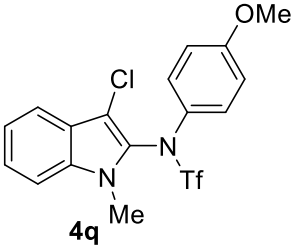

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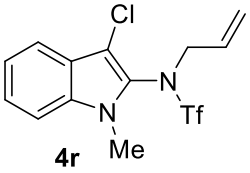

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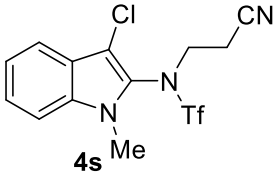

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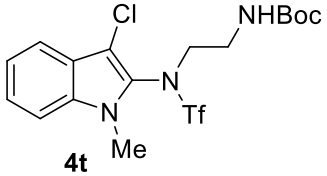

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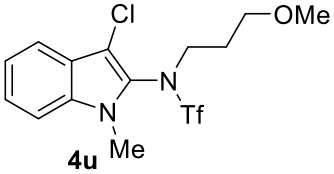

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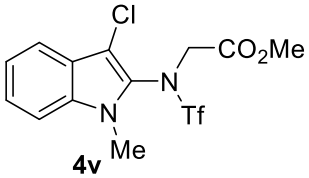

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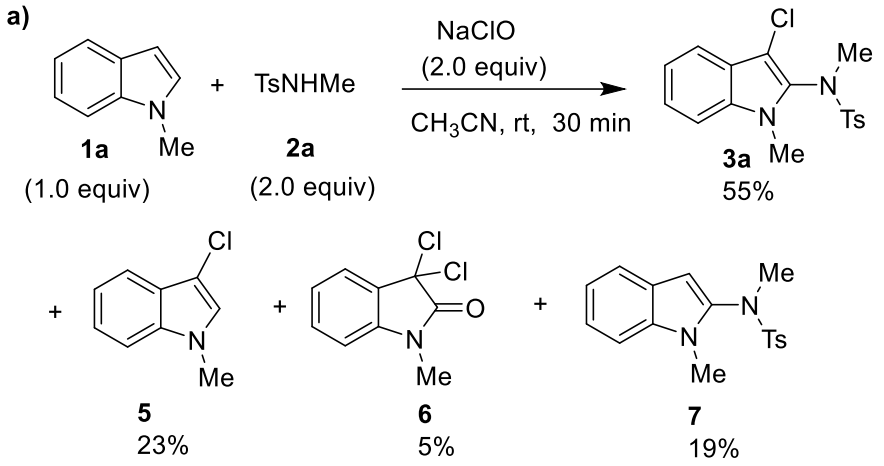
3. Mechanism Studies



A 10 mL round bottom flask was equipped with a rubber septum and magnetic stir bar and was charged with 1a (0.2mmol, 26.9 mmol), **2a** (0.4 mmol, 75.6 mg), NaClO (0.4 mmol, 0.52 mL) in CH_3CN (4 mL) at room temperature for 10 min. **3a**[1] (55%), **5**[2] (23%), **6**[3] (5%) and **7**[4] (19%) was obtained which are in ^1H NMR yields by analysis of the crude reaction mixture with CH_2Br_2 as an internal standard. Substrate **5**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.32 – 7.23 (m, 2H), 7.17 (ddd, *J* = 8.0, 6.5, 1.5 Hz, 1H), 7.01 (s, 1H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.87, 125.76, 125.30, 122.65, 119.95, 118.38, 109.57, 104.37, 32.95; MS (ESI): 166.05 for $[M+H]^+$. Substrate **6**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (ddd, *J* = 7.6, 1.3, 0.6 Hz, 1H), 7.42 (td, *J* = 7.8, 1.3 Hz, 1H), 7.19 (td, *J* = 7.6, 1.0 Hz, 1H), 6.87 (dt, *J* = 7.9, 0.7 Hz, 1H), 3.27 (s, 3H); ^{13}C NMR (100 MHz, CDCl3) δ 168.92, 140.67, 131.93, 129.28, 124.81, 124.24, 109.15, 27.08; MS (ESI): 215.95 for $[M+H]^+$. Substrate **7**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.3 Hz, 2H), 7.53 – 7.44 (m, 1H), 7.36 – 7.27 (m, 1H), 7.26 – 7.21 (m, 1H), 7.10 (ddd, J = 8.1, 7.0, 1.2 Hz, 1H), 5.80 (d, J = 0.8 Hz, 1H), 3.79 (s, 3H), 3.16 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, CDCl3): δ 144.19, 136.89, 135.04, 132.79, 129.41, 128.66, 125.84, 122.45, 120.76, 119.88, 109.93, 96.48, 40.39, 29.41, 21.67; MS (ESI): 315.05 for $[M+H]^+$.

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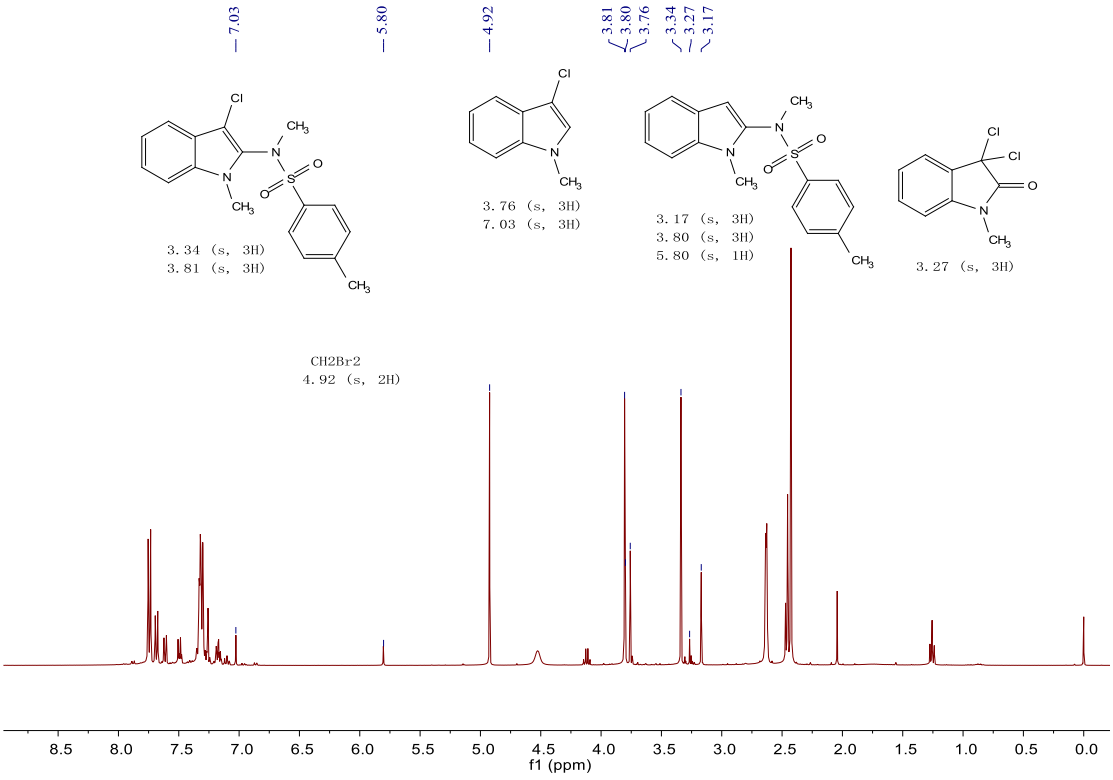
[1] Liu, X.-Y.; Gao, P.; Shen, Y.-W.; Liang, Y.-M. *Org. Lett.* **2011**, *13*, 4196.
[2] Peng, X.; Shao, X.-F.; Liu, Z.-Q. *Tetrahedron Lett.* **2013**, *54*, 3079.
[3] Murphy, G. K.; Abbas, F. Z.; Poulton, A. V. *Adv. Synth. Catal.* **2014**, *356*, 2919.
[4] Tong, K.; Liu, X.; Zhang, Y.; Yu, S. *Chem. Eur. J.* **2016**, *22*, 15669.



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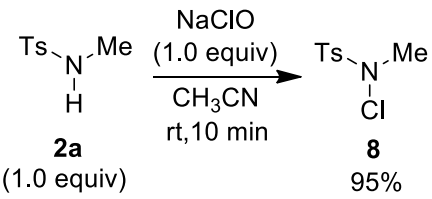
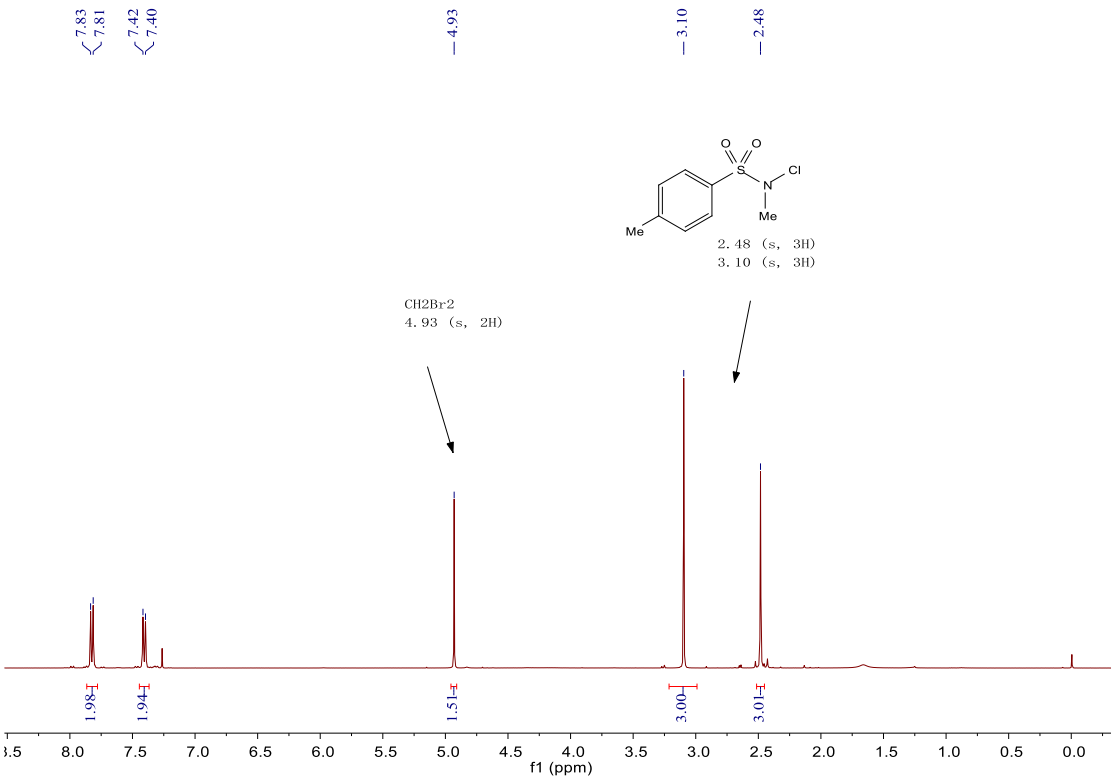


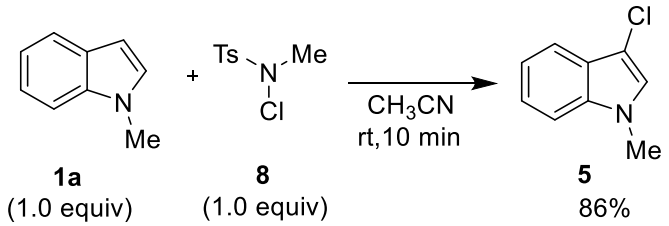
2a
(1.0 equiv)

8
95%

A 10 mL round bottom flask was equipped with a rubber septum and magnetic stir bar and was charged with **2a** (0.2 mmol, 37.0 mg), NaClO (0.2 mmol, 0.39 mL) in CH_3CN (4 mL) at room temperature for 10 min. **8**[5] was obtained in ^1H NMR 95% yields by analysis of the crude reaction mixture with CH_2Br_2 as an internal standard. ^1H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 7.7 Hz, 2H), 3.10 (s, 3H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, CDCl3): δ 145.66, 129.85, 129.73, 128.38, 45.44, 21.74; MS (ESI): 342.00 for $[M+Na]^+$.

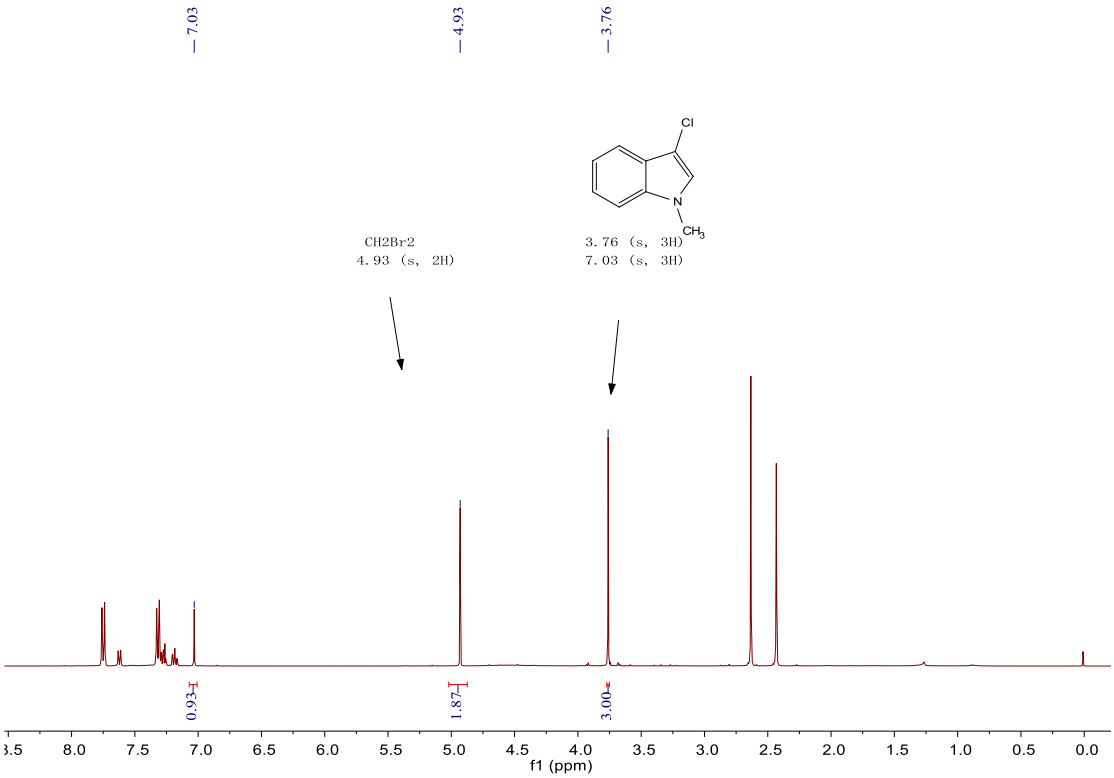
[5] Heuger, G.; Göttlich, R. *Beilstein. J. Org. Chem.* **2015**, *11*, 1226.

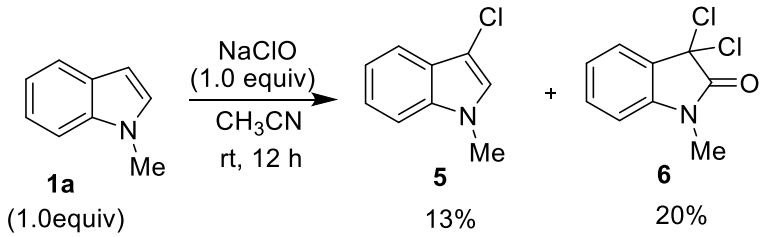




1a (1.0 equiv) **8** (1.0 equiv) **5** 86%

A 10 mL round bottom flask was equipped with a rubber septum and magnetic stir bar and was charged with **1a** (0.2 mmol, 27.5 mg), **8** (0.2 mmol, 43.9 mg) in CH_3CN (4 mL) at room temperature for 10 min. **5** was obtained in ^1H NMR 86% yields by analysis of the crude reaction mixture with CH_2Br_2 as an internal standard.



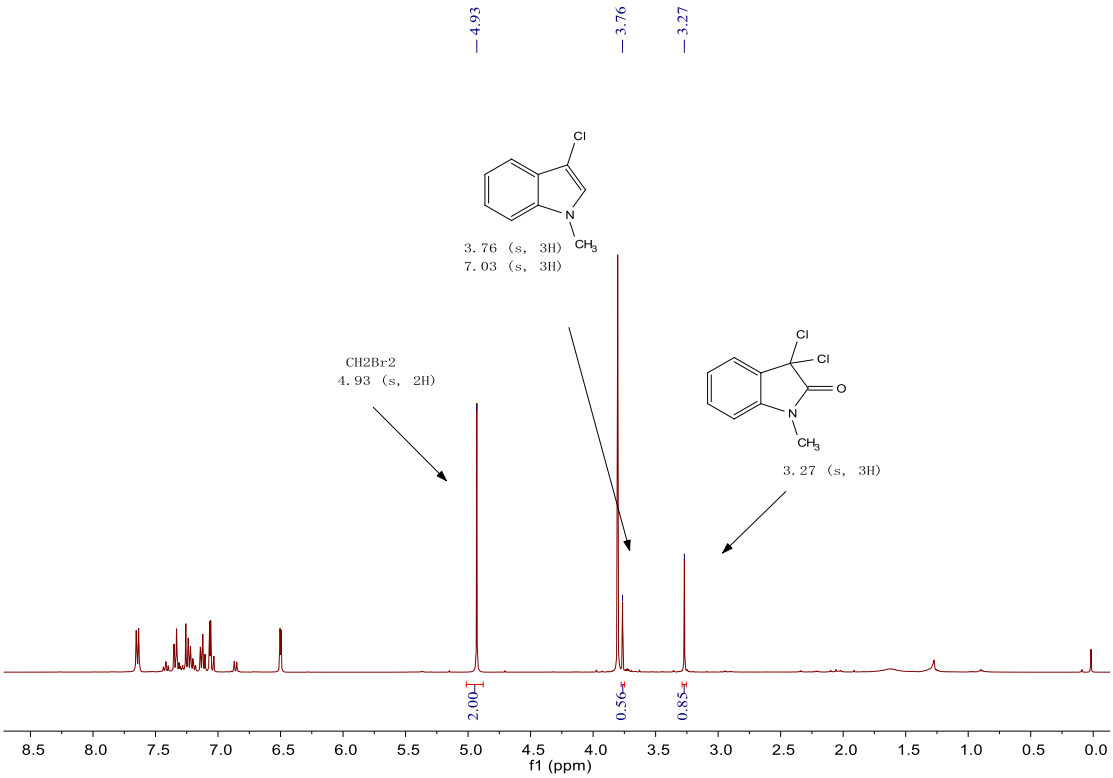


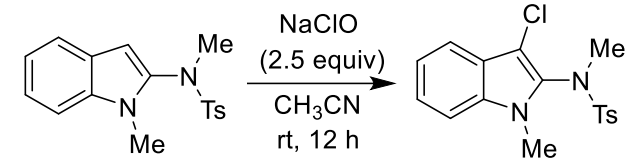
1a
(1.0equiv)

5
13%

6
20%

A 10 mL round bottom flask was equipped with a rubber septum and magnetic stir bar and was charged with **1a** (0.2 mmol, 26.6 mg), NaClO (0.2 mmol, 0.26 mL) in CH_3CN (4 mL) at room temperature for 12 h. **5** (13%) and **6** (20%) were obtained by ^1H NMR analysis of the crude reaction mixture with CH_2Br_2 as an internal standard.

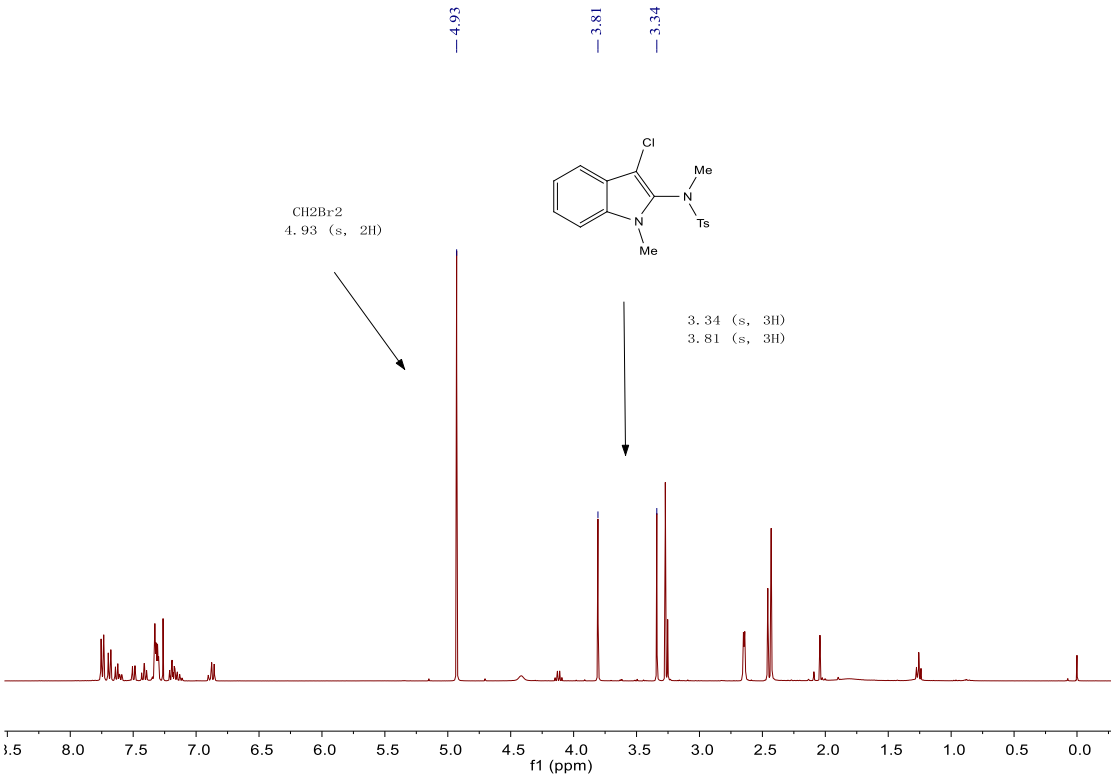


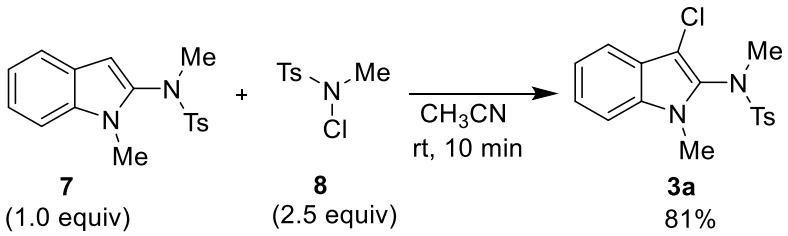


7
(1.0 equiv)

3a
37%

A 10 mL round bottom flask was equipped with a rubber septum and magnetic stir bar and was charged with **7** (0.2 mmol, 34.0 mg), NaClO (0.5 mmol, 0.65 mL) in CH_3CN (4 mL) at room temperature for 12 h. **3a** was obtained (37%) by ^1H NMR analysis of the crude reaction mixture with CH_2Br_2 as an internal standard.



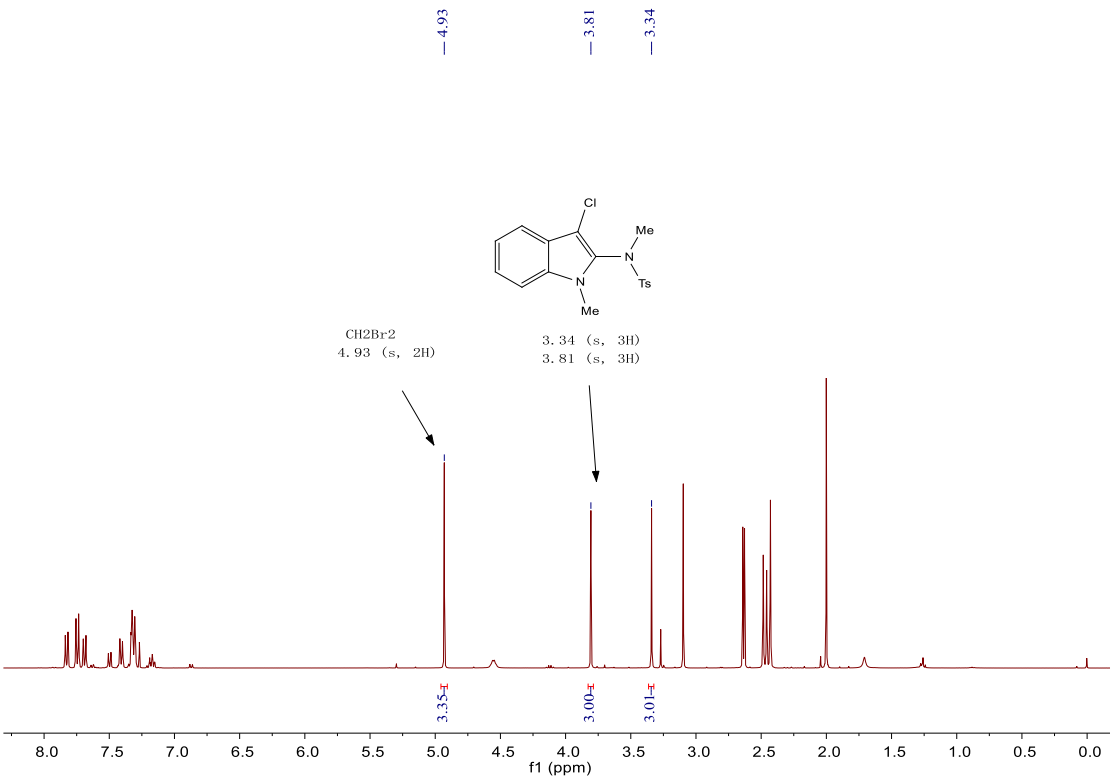


7
(1.0 equiv)

8
(2.5 equiv)

3a
81%

A 10 mL round bottom flask was equipped with a rubber septum and magnetic stir bar and was charged with **7** (0.2 mmol, 32.3 mg), **8** (0.5 mmol, 102.8 mg) in CH_3CN (4 mL) at room temperature for 10 min. **3a** (81%) was obtained by ^1H NMR analysis of the crude reaction mixture with by analysis of the crude reaction mixture with CH_2Br_2 as an internal standard.



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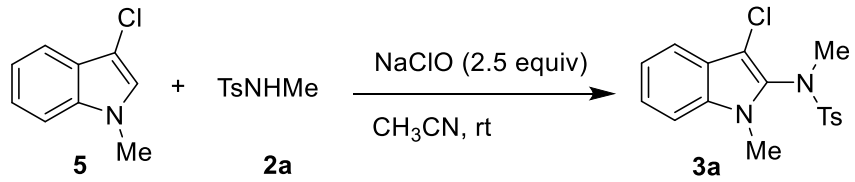
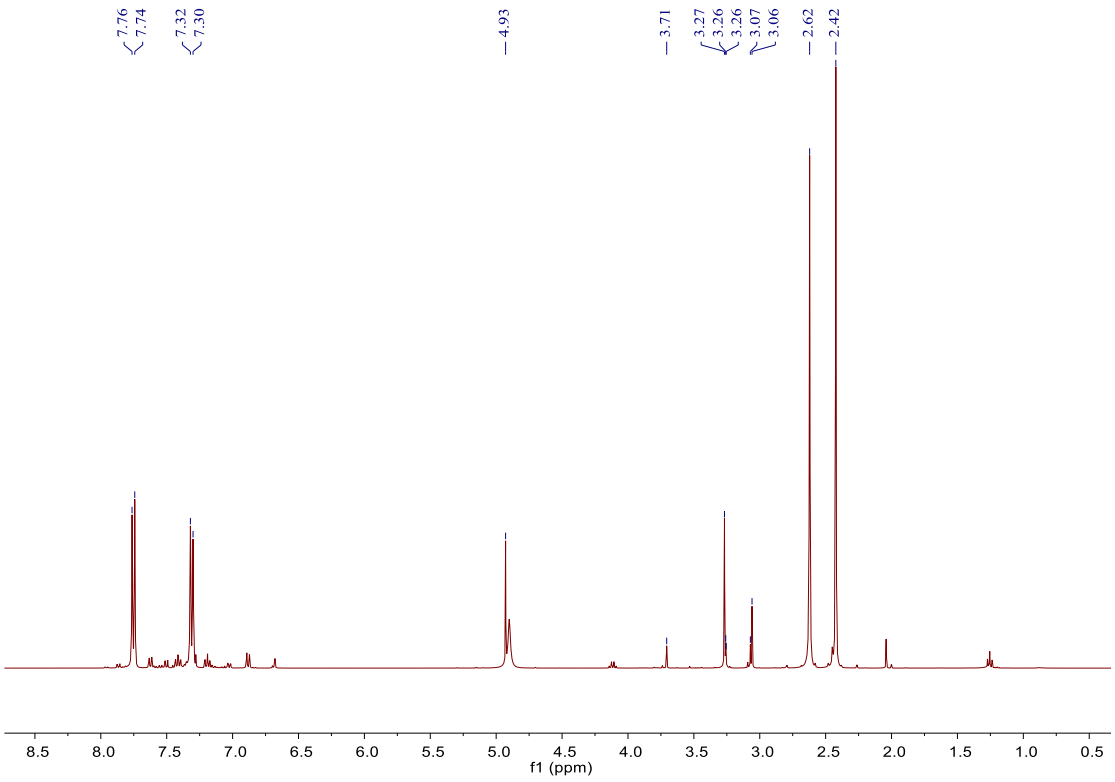


A 10 mL round bottom flask was equipped with a rubber septum and magnetic stir bar and was charged with **5** (0.2 mmol, 34.1 mg), **2a** (0.6 mmol, 113.4 mg) in CH_3CN (4 mL) at room temperature for 30 min. **3a** was not observed by ^1H NMR analysis of the crude reaction mixture with by analysis of the crude reaction mixture with CH_2Br_2 as an internal standard.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7.32
7.30
4.93
3.71
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3.26
3.07
3.06
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2.42
8.5
8.0
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6.5
6.0
5.5
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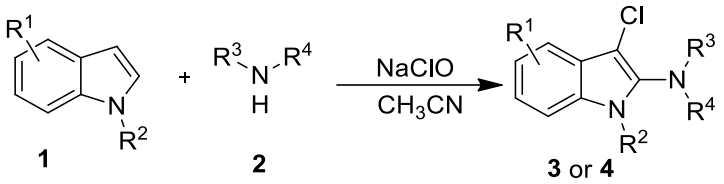
0.5
f1 (ppm)

4. General Procedure



A 10 mL round bottom flask equipped with a rubber septum and magnetic stir bar was charged with indole **1** (0.2 mmol, 1.0 equiv), amide **2** (0.6 mmol, 3.0 equiv), NaClO (0.5 mmol, 2.5 equiv) in CH_3CN (4 mL) at room temperature for 30 min. Then the mixture was poured into a separatory funnel containing 5 mL of H_2O and 5 mL of ethyl acetate. The layers were separated and the aqueous layer was extracted with ethyl acetate (2 × 5 mL). The combined organic layers were dried with Na_2SO_4 and concentrated under reduced pressure after filtration. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 50:1) to afford the desired product indole derivative **3** or **4**.

Notes:

NaClO (Sodium hypochlorite solution reagent grade, available chlorine 4.00 - 4.99%) was purchased from Sigma-Aldrich. Product Number: 239305

CAS Number: 7681-52-9

MDL: MFCD00011120

Formula: NaClO

Formula Weight: 74.44 g/mol

Composition available chlorine, 4.00 - 4.99%

Density 1.097 g/mL at 25 °C

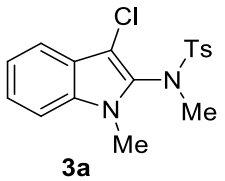
Storage Temperature: 2 - 8 °C

M [ClO-] = available chlorine * d / 0.070906

M [ClO-] = 0.05* 1.097 / 0.070906 = 0.775M

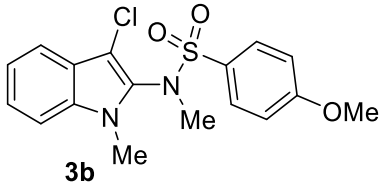
(The above data was provided by Sigma-Aldrich)

5. Data for Compounds.



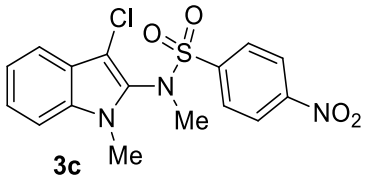
3a

N-(3-chloro-1-methyl-1H-indol-2-yl)-N,4-dimethylbenzenesulfonamide (3a): According to the General Procedure, **3a** was obtained as a white solid (49.6 mg, 72%) from **1a**, **2a** and NaClO. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.29 – 7.37 (m, 4H), 7.16 – 7.21 (m, 1H), 3.35 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.22, 134.90, 133.70, 131.16, 129.75, 128.19, 123.75, 123.69, 120.37, 118.30, 110.13, 101.16, 37.87, 30.00, 21.67; IR (neat, cm^{-1}): 1599.42, 1550.71, 1466.81, 1385.62, 1344.29, 1236.78, 1088.98, 1067.15, 960.74, 923.51; MS (ESI): 349.05 for $[M+H]^+$.



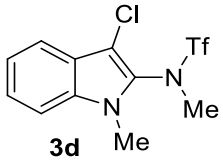
3b

N-(3-chloro-1-methyl-1H-indol-2-yl)-4-methoxy-N-methylbenzenesulfonamide (3b): According to the General Procedure, **3b** was obtained as a white solid (54.4 mg, 73%) from **1a**, **2b** and NaClO. m.p. 47 – 48 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 – 7.67 (m, 2H), 7.50 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.35 –7 .27 (m, 2H), 7.20 – 7.13 (m, 1H), 7.00 – 6.92 (m, 2H), 3.87 (s, 3H), 3.80 (s, 3H), 3.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.61, 133.70, 131.27, 130.31, 129.41, 123.76, 123.68, 120.37, 118.30, 114.34, 110.16, 100.99, 55.68, 37.86, 30.01; IR (neat, cm^{-1}): 1595.17, 1496.61, 1468.40, 1385.62, 1347.05, 1258.68, 1233.31, 1151.66, 1090.69, 1064.74; HRMS (ESI): m/z calcd for $C_{17}H_{18}ClN_2O_3S$ $[M+H]^+$ 365.0727, found 365.0721.



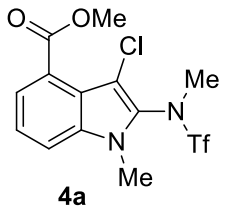
3c

N-(3-chloro-1-methyl-1H-indol-2-yl)-N-methyl-4-nitrobenzenesulfonamide (3c): According to the General Procedure, **3c** was obtained as a yellow solid (66.0 mg, 83%) from **1a**, **2c** and NaClO. m.p. 140 – 141 ^{o}C; ^{1}H NMR (400 MHz, CDCl3): δ 8.37 – 8.32 (m, 2H), 8.05 – 7.91 (m, 2H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.36 – 7.34 (m, 2H), 7.21 – 7.17 (m, 1H), 3.82 (s, 3H), 3.41 (s, 3H); ^{13}C NMR (100 MHz, CDCl3): δ 150.58, 143.56, 133.81, 129.92, 129.42, 124.35, 124.25, 123.51, 120.78, 118.48, 110.28, 101.52, 38.33, 30.08; IR (neat, cm-1): 1602.13, 1528.32, 1469.03, 1346.67, 1234.73, 1160.58, 1087.25, 1009.45, 966.15; HRMS (ESI): m/z calcd for C16H15ClN3O4S [M+H]+ 380.0472, found 380.0466.



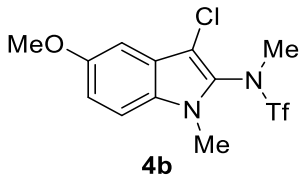
3d

N-(3-chloro-1-methyl-1H-indol-2-yl)-1,1,1-trifluoro-N-methylmethanesulfonamide (3d): According to the General Procedure, **3d** was obtained as a white solid (63.9 mg, 97%) from **1a**, **2d** and NaClO. m.p. 68 – 69 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 – 7.61 (d, *J* = 8.4 Hz, 1H), 7.39 – 7.28 (m, 2H), 7.26 – 7.19 (m, 1H), 3.72 (s, 3H), 3.51 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -74.07; ^{13}C NMR (100 MHz, CDCl3): δ 133.84, 128.13, 124.67, 123.53, 121.06, 119.67 (q, J = 321.6 Hz), 118.98, 110.20, 103.47, 40.04, 29.92; IR (thin film, cm-1): 1556.12, 1469.52, 1423.51, 1402.87, 1382.83, 1334.20, 1222.21, 1180.47, 1123.36, 1059.04; HRMS (ESI): m/z calcd for C11H11ClN2O2S [M+H]+ 327.0182, found 327.0176.



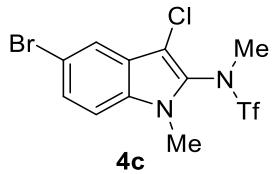
4a

Methyl-3-chloro-1-methyl-2-((1,1,1-trifluoro-N-methylmethyl)sulfonamido)-1H-indole-4-carboxylate (4a): According to the General Procedure, **4a** was obtained as a white solid (60.7 mg, 78%) from **1a'**, **2d** and NaClO. m.p. 151 – 153 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (dd, *J* = 7.4, 1.0 Hz, 1H), 7.48 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.36 (dd, *J* = 8.4, 7.4 Hz, 1H), 3.98 (s, 3H), 3.75 (s, 3H), 3.52 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -74.06; ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.74, 134.48, 130.49, 124.80, 123.53, 123.36, 120.09, 119.68 (q, *J* =321.4 Hz), 113.77, 103.52, 52.17, 39.78, 30.25; IR (neat, cm^{-1}): 2955.26, 1730.94, 1542.59, 1464.11, 1402.01, 1382.99, 1280.07, 1183.58, 953.96; HRMS (ESI): m/z calcd for $C_{13}H_{13}ClF_3N_2O_4S$ $[M+H]^+$ 385.0237, found 385.0230.



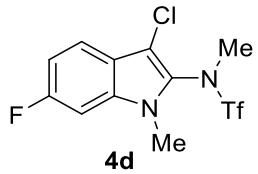
4b

N-(3-chloro-5-methoxy-1-methyl-1H-indol-2-yl)-1,1,1-trifluoro-N-methylmethanesulfonamide (4b): According to the General Procedure, **4b** was obtained as a white solid (68.2 mg, 93%) from **1b**, **2d** and NaClO. m.p. 123 – 125 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 – 7.18 (m, 1H), 7.05 – 6.97 (m, 2H), 3.87 (s, 3H), 3.69 (s, 3H), 3.51 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -74.09; ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.12, 128.93, 128.11, 123.75, 119.91 (dd, *J* = 321.6 Hz), 115.86, 111.36, 102.79, 99.48, 55.81, 40.03, 30.01; IR (neat, cm^{-1}): 1492.33, 1386.17, 1290.90, 1189.6, 1124.47, 1060.87, 1028.33, 947.21, 870.29, 833.26, 793.84; HRMS (ESI): m/z calcd for $C_{12}H_{13}ClF_3N_2O_3S$ $[M+H]^+$ 357.0288, found 357.0282.



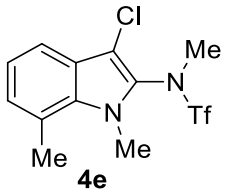
4c

N-(5-bromo-3-chloro-1-methyl-1H-indol-2-yl)-1,1,1-trifluoro-N-methylmethanesulfonamide (4c): According to the General Procedure, **4c** was obtained as a white solid (70.6 mg, 89%) from **1c**, **2d** and NaClO. m.p. 154 – 155 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 1.8 Hz, 1H), 7.42 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.19 (d, *J* = 8.8 Hz, 1H), 3.70 (s, 3H), 3.51 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -74.04; ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.43, 129.08, 127.74, 124.96, 121.52, 119.86 (q, *J* = 321.5 Hz), 114.38, 111.85, 102.84, 39.99, 30.14; IR (neat, cm^{-1}): 1553.41, 1467.33, 1423.51, 1396.78, 1216.09, 1191.60, 1120.80, 1061.38, 1045.66, 974.15, 947.38; HRMS (ESI): m/z calcd for $C_{11}H_{10}BrClF_3N_2O_2S$ $[M+H]^+$ 404.9287, found 404.9281.



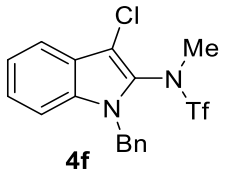
4d

N-(3-chloro-6-fluoro-1-methyl-1H-indol-2-yl)-1,1,1-trifluoro-N-methylmethanesulfonamide (4d): According to the General Procedure, **4d** was obtained as a white solid (50.1 mg, 78%) from **1d**, **2d** and NaClO. m.p. 128 – 129 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (m, 1H), 6.99 (m, 2H), 3.68 (s, 3H), 3.52 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -74.08, -115.71; ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.30 (d, *J* = 240.9 Hz), 132.87 (d, *J* = 12.2 Hz), 127.32 (d, *J* = 3.7 Hz), 119.39 (d, *J* = 10.2 Hz), 119.01, 118.83 (q, *J* = 321.5 Hz), 109.27 (d, *J* = 25.0 Hz), 102.82, 95.56 (d, *J* = 26.7 Hz), 38.99, 29.06; IR (neat, cm^{-1}): 2953.93, 1628.47, 1472.58, 1382.15, 1221.41, 1181.57, 1124.41, 1092.15, 1057.00, 986.30; HRMS (ESI): m/z calcd for $C_{11}H_{10}ClF_4N_2O_2S$ $[M+H]^+$ 345.0088, found 345.0082.



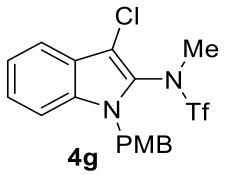
4e

N-(3-chloro-1,7-dimethyl-1H-indol-2-yl)-1,1,1-trifluoro-N-methylmethanesulfonamide (4e): According to the General Procedure, **4e** was obtained as a white solid (65.9 mg, 97%) from **1e**, **2d** and NaClO. m.p. 126 – 128 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 – 7.38 (m, 1H), 7.14 – 6.98 (m, 2H), 3.96 (s, 3H), 3.52 (m, 3H), 2.78 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -74.05; ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.03, 128.36, 127.37, 124.36, 122.09, 121.04, 119.90 (q, J = 321.6 Hz), 116.93, 103.73, 40.02, 32.80, 20.11; IR (neat, cm^{-1}): 1561.53, 1455.99, 1397.04, 1343.87, 1242.62, 1224.31, 1190.04, 1121.29, 1055.63, 947.58, 868.41; HRMS (ESI): m/z calcd for $C_{12}H_{13}ClF_3N_2O_2S$ $[M+H]^+$ 341.0338, found 341.0333.



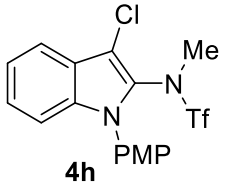
4f

N-(1-benzyl-3-chloro-1H-indol-2-yl)-1,1,1-trifluoro-N-methylmethanesulfonamide (4f): According to the General Procedure, **4f** was obtained as a yellow solid (51.6 mg, 69%) from **1f**, **2d** and NaClO. m.p. 77 – 79 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 – 7.59 (m, 1H), 7.43 – 7.18 (m, 6H), 7.14 – 6.97 (m, 2H), 5.57 – 5.29 (m, 2H), 3.04 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -73.83; ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.63, 133.88, 129.04, 128.16, 128.00, 126.71, 125.06, 123.65, 121.22, 119.92 (q, J = 321.9 Hz), 119.08, 110.68, 104.71, 47.00, 39.63; IR (neat, cm^{-1}): 1461.40, 1396.45, 1387.22, 1347.74, 1244.90, 1119.15, 1060.87, 960.54, 936.38, 795.56; HRMS (ESI): m/z calcd for $C_{17}H_{15}ClF_3N_2O_2S$ $[M+H]^+$ 403.0495, found 403.0489.



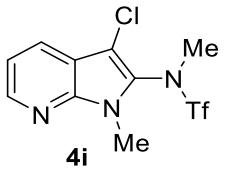
4g

N-(3-chloro-1-(4-methoxybenzyl)-1H-indol-2-yl)-1,1,1-trifluoro-N-methylmethanesulfonamide (4g): According to the General Procedure, **4g** was obtained as a yellow liquid (83.9 mg, 96%) from **1g**, **2d** and NaClO. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.37 – 7.29 (m, 2H), 7.28 – 7.19 (m, 1H), 7.05 – 6.96 (m, 2H), 6.89 – 6.75 (m, 2H), 5.50 – 5.21 (m, 2H), 3.75 (s, 3H), 3.05 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -73.87; ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.28, 133.82, 128.59, 128.15, 128.11, 119.92 (q, *J* = 321.8 Hz), 104.58, 124.98, 123.62, 121.13, 119.04, 114.34, 110.67, 55.28, 46.52, 39.67; IR (neat, cm^{-1}): 1512.98, 1459.71, 1400.39, 1346.40, 1224.70, 1123.75, 1070.89, 1033.13, 963.19, 939.15, 794.83; HRMS (ESI): m/z calcd for $C_{18}H_{17}ClF_3N_2O_3S$ $[M+H]^+$ 433.0601, found 433.0595.



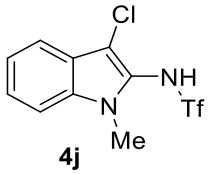
4h

N-(3-chloro-1-(4-methoxyphenyl)-1H-indol-2-yl)-1,1,1-trifluoro-N-methylmethanesulfonamide (4h): According to the General Procedure, **4h** was obtained as a yellow solid (63.4 mg, 78%) from **1h**, **2d** and NaClO. m.p. 97 - 98^{o}C; ^{1}H NMR (400 MHz, Acetone-d_6): δ 7.72 – 7.63 (m, 1H), 7.51-7.42 (m, 2H), 7.38 – 7.25 (m, 2H), 7.21 – 7.05 (m, 3H), 3.92 (s, 3H), 3.57 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -74.21; ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.02, 135.33, 128.96, 127.77, 125.11, 123.53, 121.51, 119.77 (q, *J* = 321.6 Hz), 118.90, 114.81, 111.31, 105.27, 55.56, 40.52; IR (neat, cm^{-1}): 1607.54, 1553.41, 1511.34, 1453.59, 1397.24, 1175.78, 1252.96, 1098.19, 1030.73, 952.27; HRMS (ESI): m/z calcd for $C_{17}H_{15}ClF_3N_2O_3S$ $[M+H]^+$ 419.0444, found 419.0438.



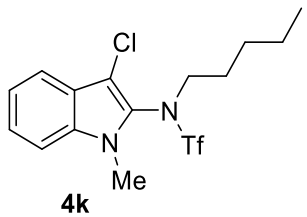
4i

N-(3-chloro-1-methyl-1H-pyrrolo[3,2-b]pyridin-2-yl)-1,1,1-trifluoro-N-methylmethanesulfonamide (4i): According to the General Procedure, **4i** was obtained as a yellow solid (58.7 mg, 90%) from **1i**, **2d** and NaClO. m.p. 98 – 99 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (dd, *J* = 4.7, 1.6 Hz, 1H), 7.94 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.19 (dd, *J* = 7.9, 4.7 Hz, 1H), 3.86 (s, 3H), 3.54 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -74.14; ^{13}C NMR (100 MHz, CDCl3): δ 146.17, 144.24, 128.94, 127.45, 119.83 (q, *J* = 321.3 Hz), 117.29, 116.95, 102.05, 39.96, 28.74; HRMS (ESI): m/z calcd for $C_{10}H_9ClF_3N_3O_2S$ $[M+H]^+$ 328.0134, found 328.0138.



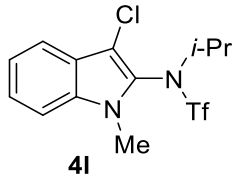
4j

N-(3-chloro-1-methyl-1H-indol-2-yl)-1,1,1-trifluoromethanesulfonamide (4j): According to the General Procedure, **4j** was obtained as a brown solid (41.2 mg, 66%) from **1a**, **2j** and NaClO. m.p. 133 – 134 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.86 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.63 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.54 – 7.41 (m, 2H), 3.53 (s, 3H);^{19}F NMR (376 MHz, DMSO-d_6): δ -74.29; ^{13}C NMR (100 MHz, DMSO-d_6): δ 164.32, 139.21, 133.12, 130.85, 127.42, 124.61, 119.50 (q, *J* = 316.9 Hz), 113.24, 76.18, 31.47; IR (neat, cm^{-1}): 1593.14, 1466.81, 1404.57, 1343.79, 1217.81, 1182.53, 1128.65, 1004.04, 866.02; HRMS (ESI): m/z calcd for $C_{10}H_9ClF_3N_2O_2S$ $[M+H]^+$ 313.0025, found 313.0020.



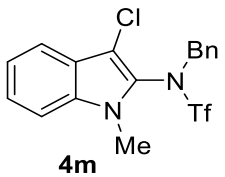
4k

N-(3-chloro-1-methyl-1H-indol-2-yl)-1,1,1-trifluoro-N-pentylmethanesulfonamide (4k): According to the General Procedure, **4k** was obtained as a yellow solid (65.4 mg, 91%) from **1a**, **2k** and NaClO. m.p. 49 – 51 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.0 Hz, 1H), 7.39 – 7.30 (m, 2H), 7.23 (ddd, *J* = 8.0, 6.6, 1.4 Hz, 1H), 3.91 – 3.83 (m, 2H), 3.72 (s, 3H), 1.64 – 1.59 (m, 1H), 1.50 – 1.44 (m, 1H), 1.30 – 1.25 (m, 4H), 0.89 – 0.79 (m, 3H); ^{19}F NMR (376 MHz, CDCl3): δ -74.16; ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.95, 126.60, 124.55, 123.60, 121.01, 119.90 (q, *J* = 321.9 Hz), 118.92, 110.20, 103.80, 53.59, 30.15, 28.60, 28.39, 22.16, 13.84; IR (neat, cm^{-1}): 2957.97, 1464.11, 1396.48, 1204.41, 1186.85, 1126.71, 1056.35, 947.97, 811.47, 752.61; HRMS (ESI): m/z calcd for $C_{15}H_{19}ClF_3N_2O_2S$ $[M+H]^+$ 383.0808, found 383.0803.



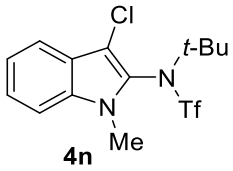
4l

N-(3-chloro-1-methyl-1H-indol-2-yl)-1,1,1-trifluoro-N-isopropylmethanesulfonamide (4l): According to the General Procedure, **4l** was obtained as a yellow solid (60.2 mg, 80%) from **1a**, **2l** and NaClO. m.p. 69 – 70 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.0 Hz, 1H), 7.43 – 7.31 (m, 2H), 7.30 – 7.21 (m, 1H), 4.64 (m, 1H), 3.71 (s, 3H), 1.42 (d, *J* = 6.8 Hz, 3H), 1.28 (d, *J* = 6.7 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -75.01; ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.47, 124.79, 123.82, 121.03, 119.48 (q, *J* = 321.0 Hz) 119.29, 110.23, 106.70, 96.00, 58.83, 30.77, 22.40, 21.99; IR (thin film, cm^{-1}): 1466.81, 1384.18, 1108.23, 1000.82, 967.78, 879.55, 784.83, 746.57; HRMS (ESI): m/z calcd for $C_{13}H_{15}ClF_3N_2O_2S$ $[M+H]^+$ 355.0495, found 355.0489.



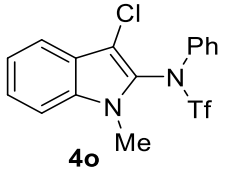
4m

N-benzyl-N-(3-chloro-1-methyl-1H-indol-2-yl)-1,1,1-trifluoromethanesulfonamide (4m): According to the General Procedure, **4m** was obtained as a yellow oil (45.8 mg, 59%) from **1a**, **2m** and NaClO. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.33 – 7.26 (m, 2H), 7.25 – 7.18 (m, 3H), 7.16 – 7.09 (m, 3H), 5.20 (d, *J* = 13.7 Hz, 1H), 4.77 (d, *J* = 13.7 Hz, 1H), 2.99 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -74.21; ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.73, 133.63, 129.71, 129.20, 128.91, 125.97, 124.38, 123.39, 123.17 (q, *J* = 321.6 Hz), 120.85, 118.83, 110.19, 103.58, 56.66, 29.34; IR (neat, cm^{-1}): 1469.52, 1396.69, 1193.27, 1135.6, 1026.27, 968.87, 909.32, 805.48, 742.36, 700.36; HRMS (ESI): m/z calcd for $C_{17}H_{15}ClN_2O_2S$ $[M+H]^+$ 403.0495, found 403.0490.



4n

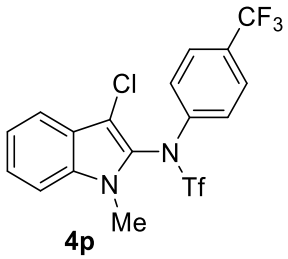
N-(tert-butyl)-N-(3-chloro-1-methyl-1H-indol-2-yl)-1,1,1-trifluoromethanesulfonamide (4n): According to the General Procedure, **4n** was obtained as a yellow solid (34.3 mg, 47%) from **1a**, **2n** and NaClO. m.p. 109 – 110 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.0 Hz, 1H), 7.39 – 7.29 (m, 2H), 7.25 – 7.20 (m, 1H), 3.76 (s, 3H), 1.56 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -73.79; ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.01, 127.39, 124.66, 123.42, 120.98, 119.36 (q, *J* = 322.6 Hz), 119.19, 110.22, 106.58, 70.08, 30.72, 30.54; IR (neat, cm^{-1}): 1558.84, 1461.40, 1387.93, 1366.68, 1328.79, 1236.78, 1135.05, 1101.47, 954.78; HRMS (ESI): m/z calcd for $C_{14}H_{20}ClF_3N_3O_2S$ $[M+NH_4]^+$ 386.0917, found 380.0911.



4o

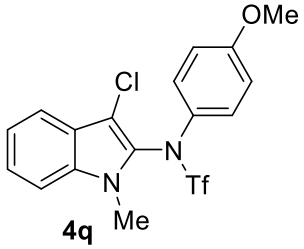
N-(3-chloro-1-methyl-1H-indol-2-yl)-1,1,1-trifluoro-N-phenylmethanesulfonamide (4o): According to the General Procedure, **4o** was obtained as a yellow solid (53.5

mg, 69%) from **1a**, **2o** and NaClO. m.p. 115 – 116 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 – 7.66 (m, 2H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.46 – 7.26 (m, 5H), 7.24 – 7.18 (m, 1H), 3.84 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -72.81; ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.28, 133.90, 129.86, 129.22, 128.04, 127.24, 124.90, 123.69, 121.13, 119.85 (*J* =321.9 Hz), 119.31, 110.17, 104.64, 30.27; IR (neat, cm^{-1}): 1588.59, 1483.05, 1393.74, 1342.32, 1190.77, 1128.53, 987.80, 966.15, 933.68; HRMS (ESI): m/z calcd for $C_{16}H_{13}ClF_3N_2O_2S$ $[M+H]^+$ 389.0338, found 389.0332.



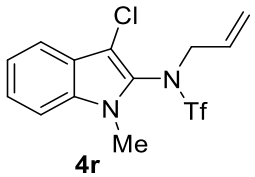
4p

N-(3-chloro-1-methyl-1H-indol-2-yl)-1,1,1-trifluoro-N-(4-(trifluoromethyl)phenyl)methanesulfonamide (4p): According to the General Procedure, **4p** was obtained as a white solid (62.3 mg, 71%) from **1a**, **2p** and NaClO. m.p. 112 – 113 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 – 7.61 (m, 5H), 7.42 – 7.31 (m, 2H), 7.28 – 7.21 (m, 1H), 3.82 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.85 , -72.76; ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.26, 134.05, 130.74 (q, *J* = 33.2 Hz), 127.02 (q, *J* = 3.9 Hz), 126.36, 125.25, 123.58, 123.38 (q, *J* = 270.8 Hz), 121.37, 120.09 (q, *J* = 321.9 Hz), 119.41, 110.25, 105.17, 30.26; IR (neat, cm^{-1}): 1612.95, 1466.81, 1406.03, 1321.75, 1220.54, 1200.20, 1166.42, 1128.79, 1110.09, 1069.66, 993.21, 936.38; HRMS (ESI): m/z calcd for $C_{17}H_{12}ClF_6N_2O_2S$ $[M+H]^+$ 457.0212, found 457.0206.



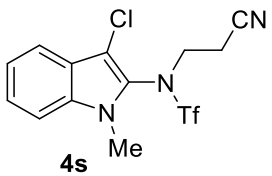
4q

N-(3-chloro-1-methyl-1H-indol-2-yl)-1,1,1-trifluoro-N-(4-methoxyphenyl)methanesulfonamide (4q): According to the General Procedure, **4q** was obtained as a white solid (43.9 mg, 52%) from **1a**, **2q** and NaClO. m.p. 140 – 141 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 – 7.62 (m, 3H), 7.37 – 7.33 (m, 1H), 7.33 – 7.29 (m, 1H), 7.25 – 7.19 (m, 1H), 6.95 – 6.88 (m, 2H), 3.87 (s, 3H), 3.80 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -72.79; ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.08, 137.81, 131.75, 129.28, 128.49, 124.76, 123.68, 121.04 , 119.86 (q, *J* = 322.2 Hz) , 119.24 , 114.88 , 110.10, 104.18, 55.56, 30.22; IR (neat, cm^{-1}): 2960.75, 1468.06, 1396.81, 1221.99, 1203.21, 1126.54, 1055.97, 968.01, 947.65; HRMS (ESI): m/z calcd for $C_{17}H_{15}ClN_2O_3S$ $[M+H]^+$ 419.0444, found 419.0437.



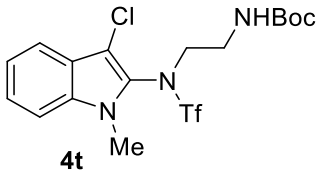
4r

N-allyl-N-(3-chloro-1-methyl-1H-indol-2-yl)-1,1,1-trifluoromethanesulfonamide (4r): According to the General Procedure, **4r** was obtained as a yellow liquid (59.2 mg, 84%) from **1a**, **2r** and NaClO. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.38 – 7.27 (m, 2H), 7.27 – 7.18 (m, 1H), 5.93 – 5.76 (m, 1H), 5.20 – 5.17 (m, 1H), 5.16 – 5.12 (m, 1H), 4.61 – 4.51 (m, 1H), 4.34 (dd, *J* = 14.1, 8.3 Hz, 1H), 3.68 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -74.30; ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.95, 130.26, 126.20, 124.54, 123.47, 122.58, 120.95, 119.84 (q, *J* =321.6 Hz), 118.94, 110.22, 103.99, 55.94, 30.19; IR (neat, cm^{-1}): 1469.52, 1398.00, 1331.50, 1188.31, 1129.36, 1041.93, 966.15, 928.26, 893.08, 746.56; HRMS (ESI): m/z calcd for $C_{13}H_{13}ClF_3N_2O_4S$ $[M+H]^+$ 353.0338, found 353.0333.



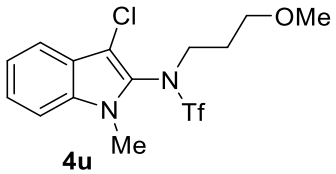
4s

N-(3-chloro-1-methyl-1H-indol-2-yl)-N-(2-cyanoethyl)-1,1,1-trifluoromethanesulfonamide (4s): According to the General Procedure, **4s** was obtained as a white solid (67.8 mg, 92%) from **1a**, **2s** and NaClO. m.p. 65 – 66 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (dt, *J* = 8.2, 1.0 Hz, 1H), 7.42 – 7.32 (m, 2H), 7.28 – 7.22 (m, 1H), 4.26 – 4.09 (m, 2H), 3.76 (s, 3H), 2.76 – 2.62 (m, 1H), 2.61 – 2.50 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -73.70; ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.29, 125.23, 124.92, 123.37, 121.48, 119.78 (q, *J* = 321.8 Hz), 119.02, 115.99, 110.51, 104.27, 48.87, 30.51, 17.91; IR (neat, cm-1): 1466.81, 1399.75, 1346.62, 1282.79, 1224.91, 1193.60, 1138.55, 1087.31, 1048.10, 968.86, 940.61; HRMS (ESI): m/z calcd for $C_{13}H_{12}ClF_3N_3O_2S$ $[M+H]^+$ 366.0291, found 366.0286.



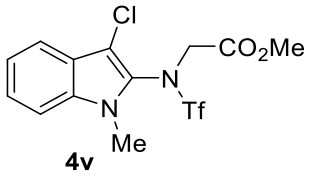
4t

Tert-butyl(2-((N-(3-chloro-1-methyl-1H-indol-2-yl)-1,1,1-trifluoromethyl)sulfonamido)ethyl)carbamate (4t): According to the General Procedure, **4t** was obtained as a white solid (84.0 mg, 93%) from **1a**, **2t** and NaClO. m.p. 119 – 120 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 8.0 Hz, 1H), 7.41 – 7.27 (m, 2H), 7.23 (ddd, *J* = 8.0, 6.9, 1.2 Hz, 1H), 4.83 (brs, 1H), 4.00 (dq, *J* = 20.5, 7.3, 6.4 Hz, 2H), 3.71 (s, 3H), 3.34 – 3.26 (m, 1H), 3.24 – 3.17 (m, 1H), 1.36 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -73.99; ^{13}C NMR (100 MHz, CDCl3): δ 155.63, 134.08, 126.02, 124.81, 123.48, 121.19, 119.83 (q, *J* = 321.9 Hz), 118.95, 110.26, 79.99, 52.28, 39.39, 30.04, 28.21; IR (neat, cm^{-1}): 1684.22, 1522.31, 1465.43, 1396.75, 1320.51, 1286.11, 1224.03, 1185.55, 1118.67, 1058.99; HRMS (ESI): m/z calcd for $C_{17}H_{22}ClF_3N_3O_4S$ $[M+H]^+$ 456.0972, found 456.0967.



4u

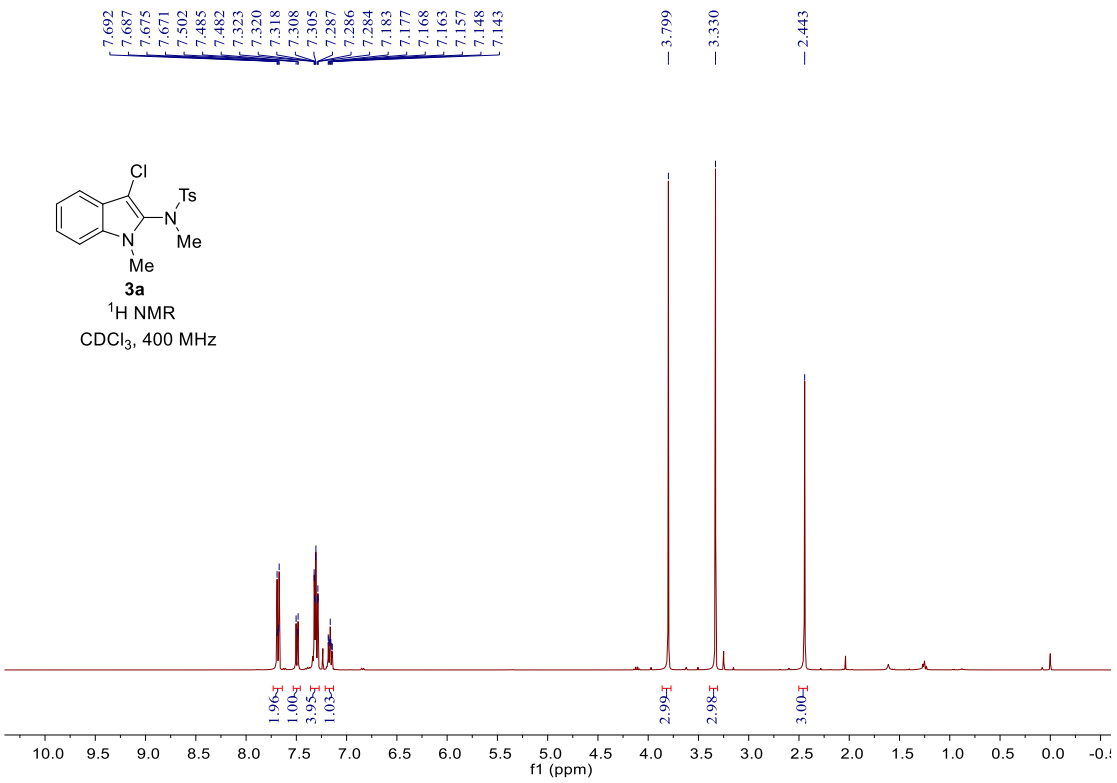
N-(3-chloro-1-methyl-1H-indol-2-yl)-1,1,1-trifluoro-N-(3-methoxypropyl)methanesulfonamide (4u): According to the General Procedure, **4u** was obtained as yellow liquid (71.7 mg, 93%) from **1a**, **2u** and NaClO. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.0 Hz, 1H), 7.40 – 7.29 (m, 2H), 7.26 – 7.20 (m, 1H), 4.09 – 3.86 (m, 2H), 3.72 (s, 3H), 3.42 – 3.32 (m, 2H), 3.27 (s, 3H), 1.96 – 1.83 (m, 1H), 1.83 – 1.68 (m, 1H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -74.21; ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.00, 126.39, 124.66, 123.59, 121.08, 119.87 (q, *J* = 321.8 Hz), 118.96, 110.19, 104.08, 69.10, 58.71, 51.34, 30.10, 29.18; IR (neat, cm^{-1}): 1464.11, 1396.61, 1189.01, 1119.80, 1044.63, 967.96, 879.55, 811.89, 742.97; HRMS (ESI): m/z calcd for $C_{14}H_{17}ClF_3N_2O_3S$ $[M+H]^+$ 385.0601, found 385.0595.

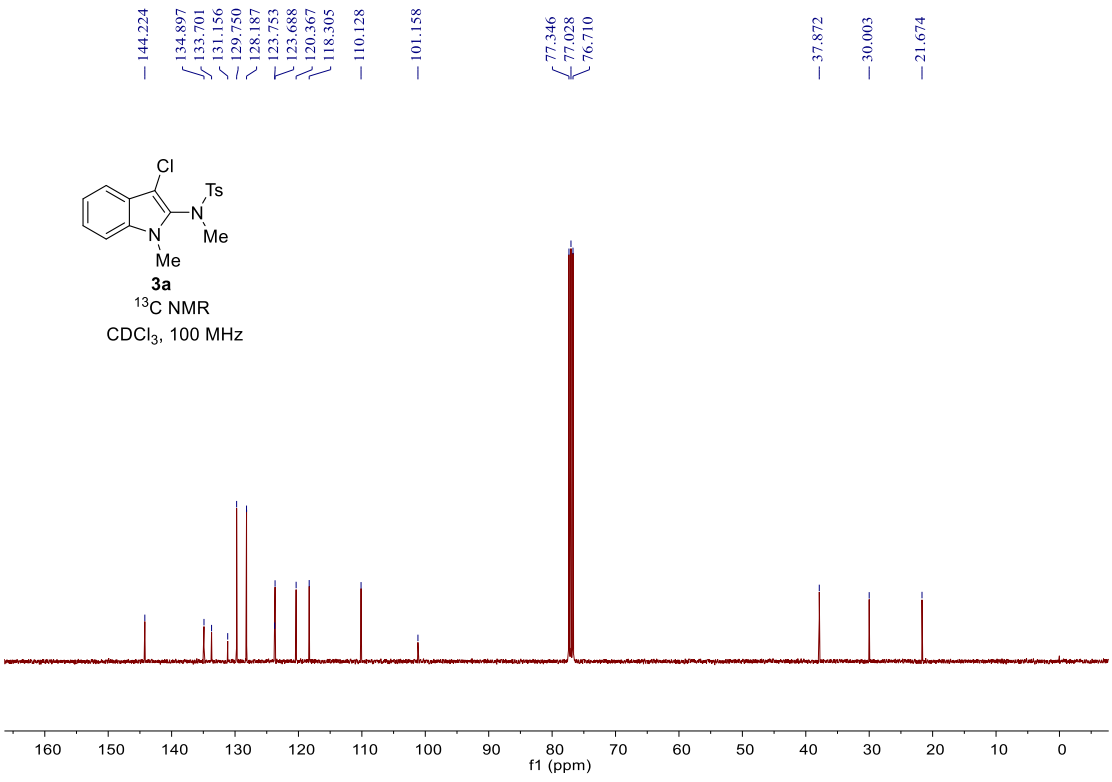


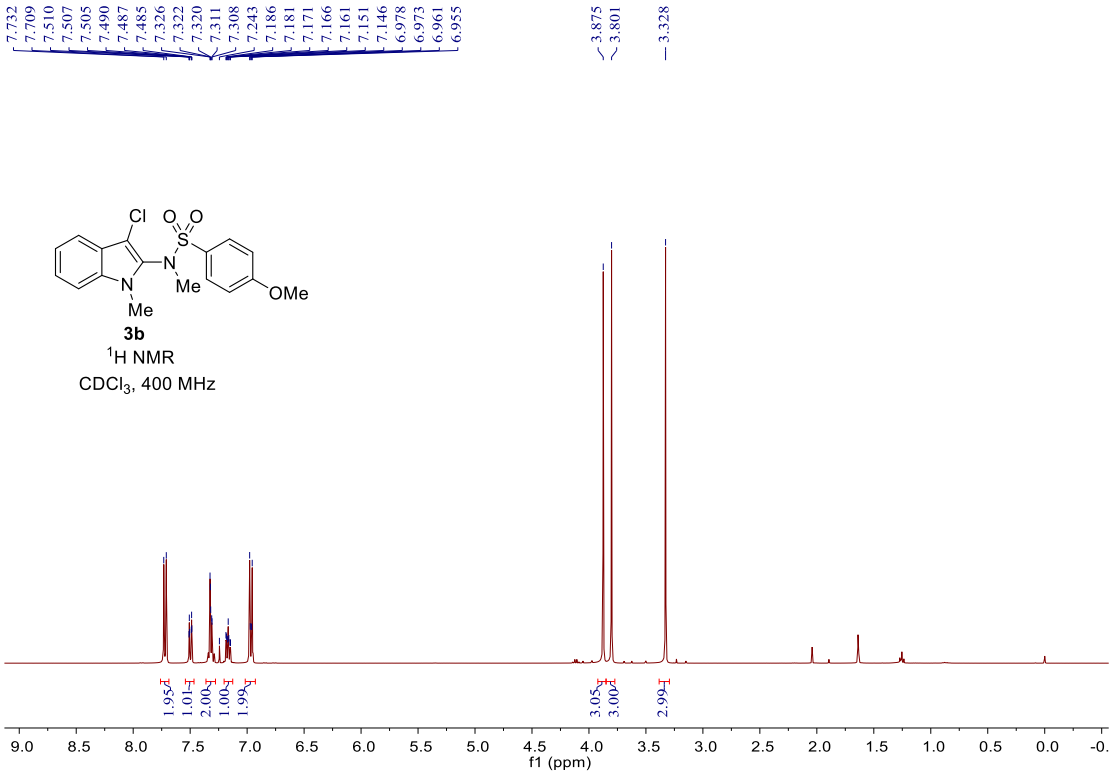
4v

Methyl N-(3-chloro-1-methyl-1H-indol-2-yl)-N-((trifluoromethyl)sulfonyl)glycinate (4v): According to the General Procedure, **4v** was obtained as a white solid (63.7 mg, 83%) from **1a**, **2v** and NaClO. m.p. 95-96 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.40 – 7.33 (m, 2H), 7.25 – 7.19 (m, 1H), 4.81 (d, *J* = 18.2, 1H), 4.52 (d, *J* = 18.2 Hz, 1H), 3.96 (s, 3H), 3.73 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -73.76; ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.66, 134.12, 126.93, 124.71, 123.14, 121.04, 119.87 (q, *J* = 322.1 Hz), 118.73, 110.49, 102.54, 53.09, 52.84, 30.95; IR (neat, cm^{-1}): 1752.12, 1548.00, 1474.93, 1418.10, 1307.14, 1208.67, 1189.96, 1140.00, 1095.11, 971.56, 807.72, 747.14; HRMS (ESI): m/z calcd for $C_{13}H_{13}ClF_3N_2O_4S$ $[M+H]^+$ 385.0237, found 385.0232

6. NMR Spectra for All Compounds



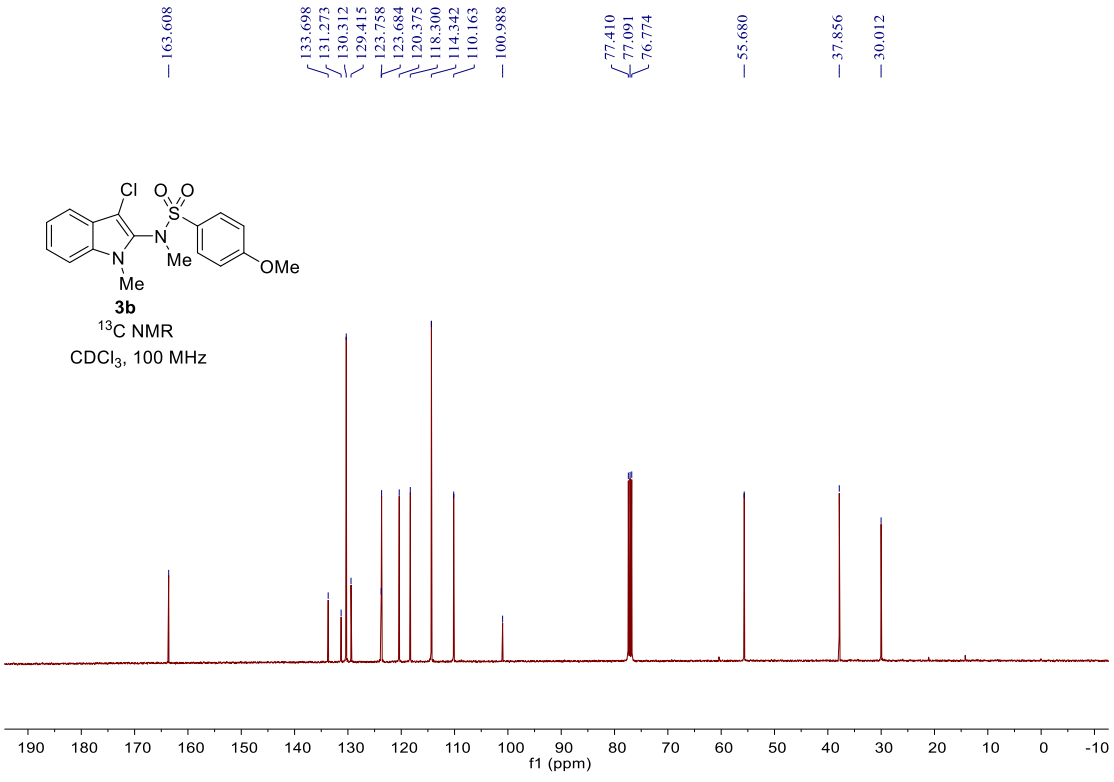




3b

^{1}H NMR

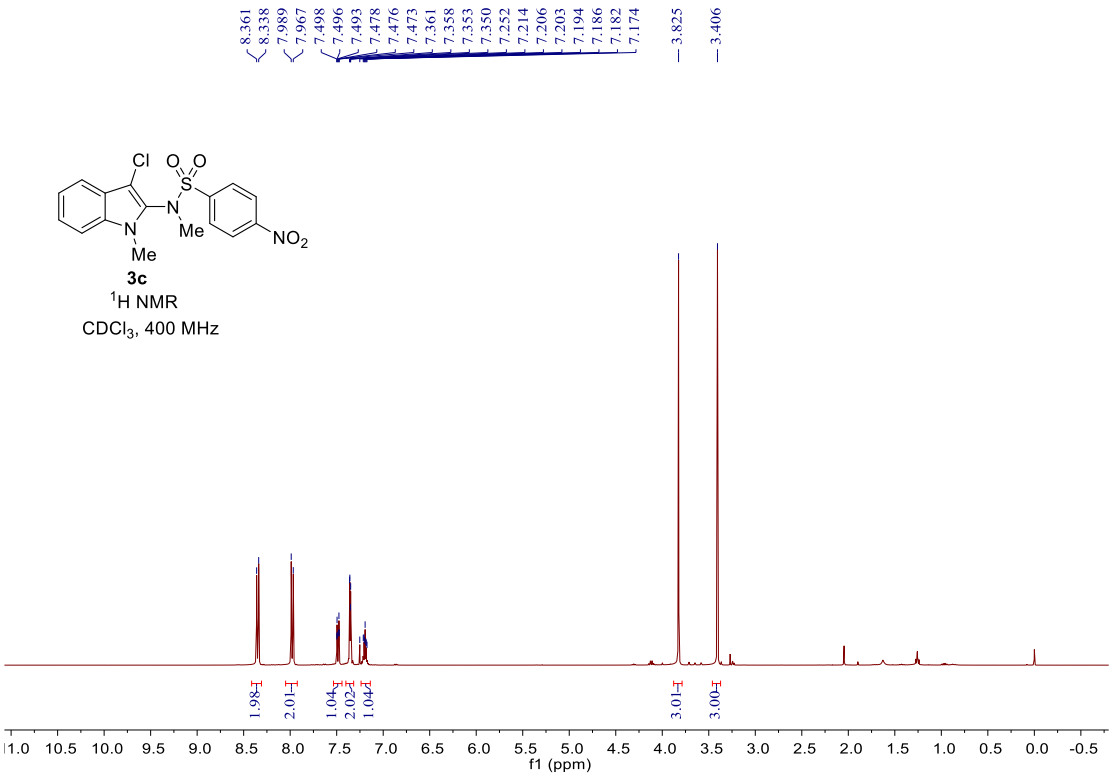
$CDCl_3$, 400 MHz



3b

^{13}C NMR

$CDCl_3$, 100 MHz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7.967
7.498
7.496
7.493
7.478
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7.473
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7.358
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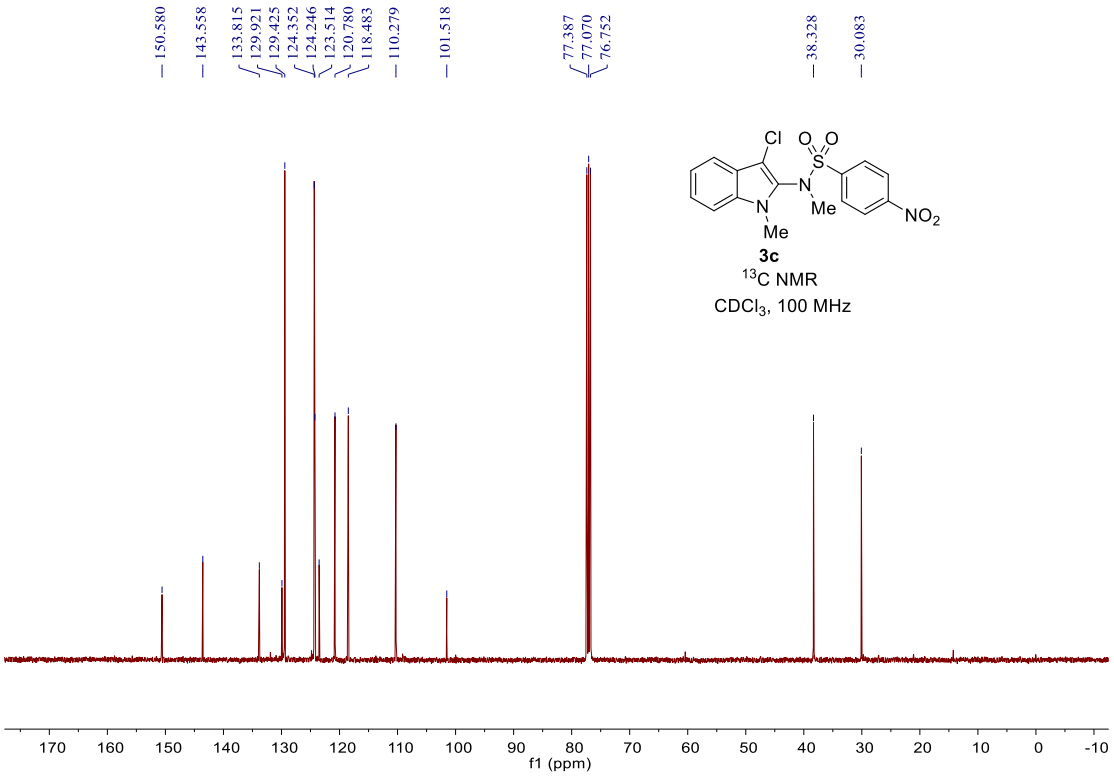
7.350
7.252
7.214
7.206
7.203
7.194
7.186
7.182
7.174
3.825
3.406
Cl
O
O
S
N
Me
N
Me
NO2
3c
1H NMR
CDCl3, 400 MHz
1.98
2.01
1.04
2.02
1.04
3.01
3.00
f1 (ppm)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77.070
76.752
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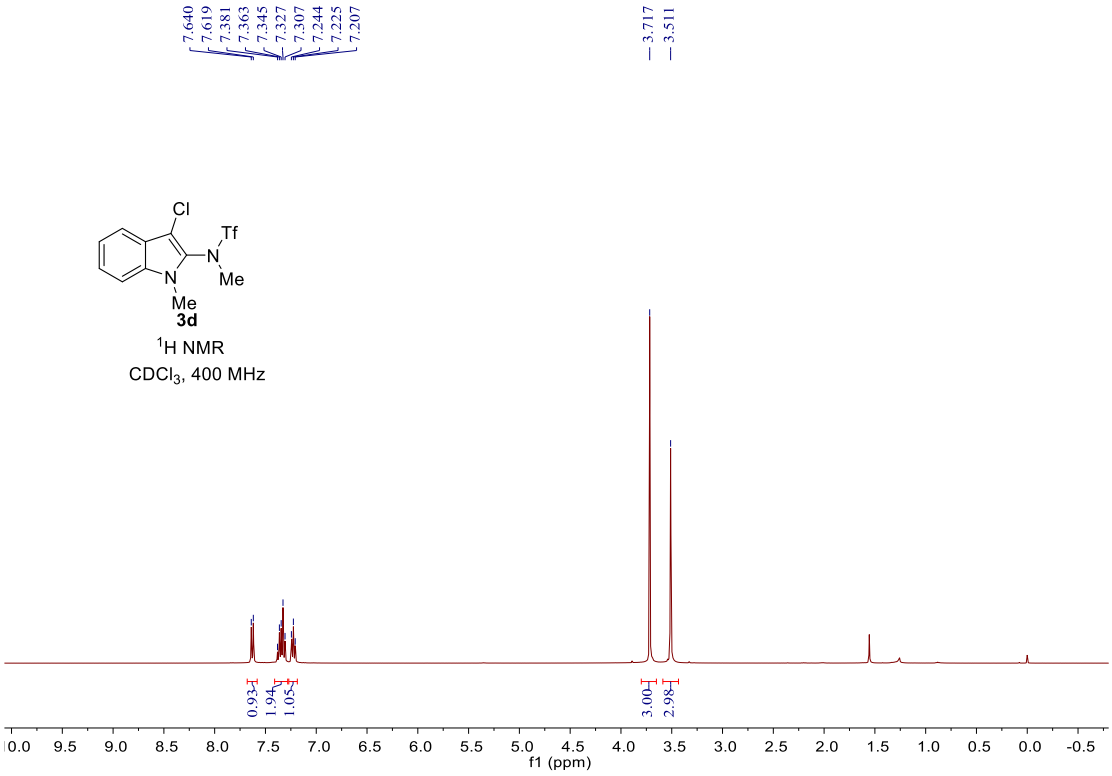
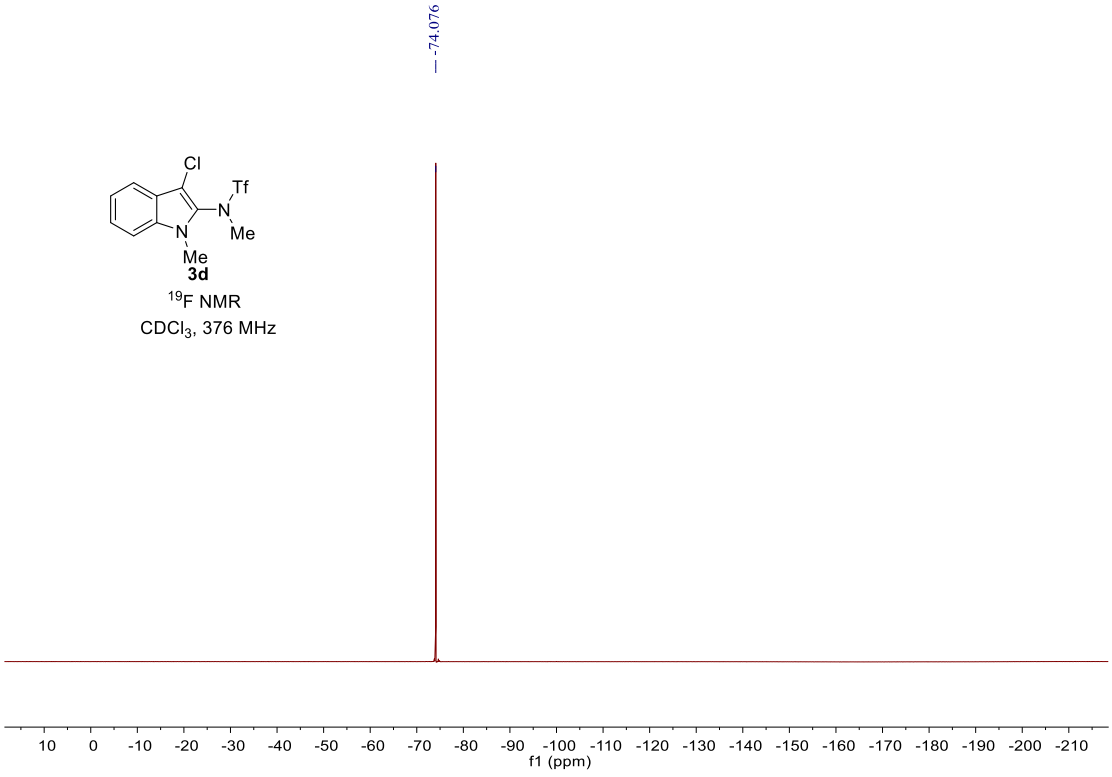
Cl
O
O
S
N
Me
N
Me
NO2
3c
13C NMR
CDCl3, 100 MHz
f1 (ppm)



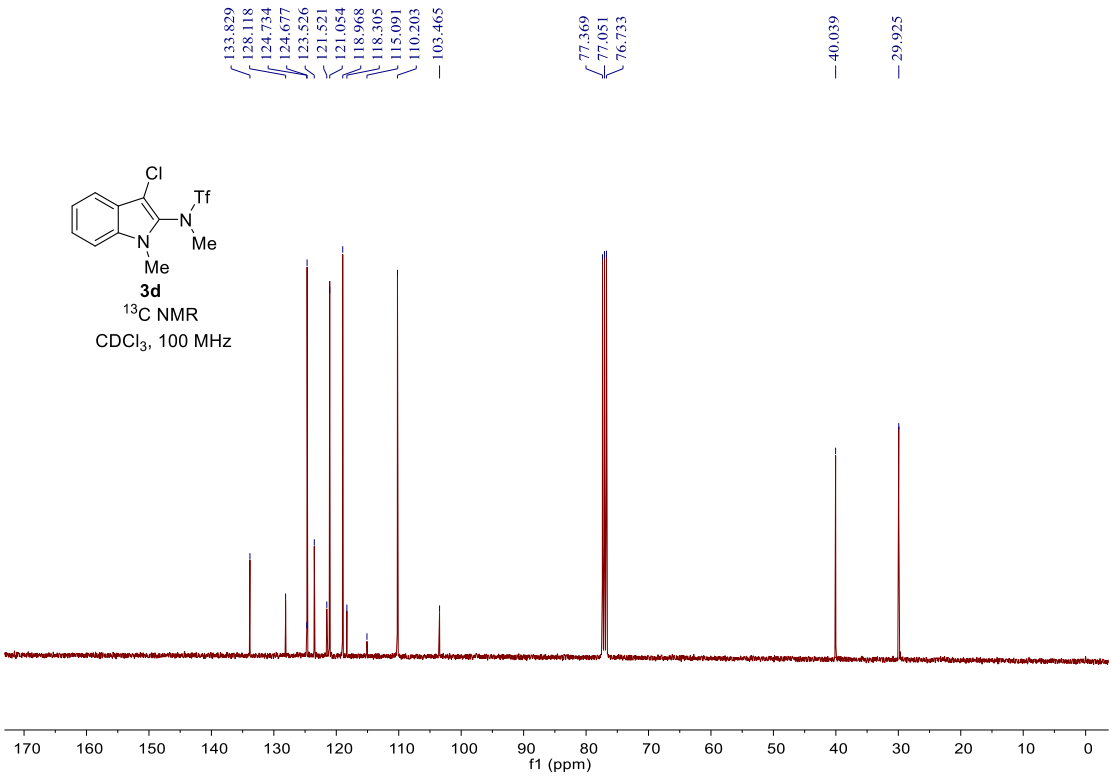
^{1}H NMR

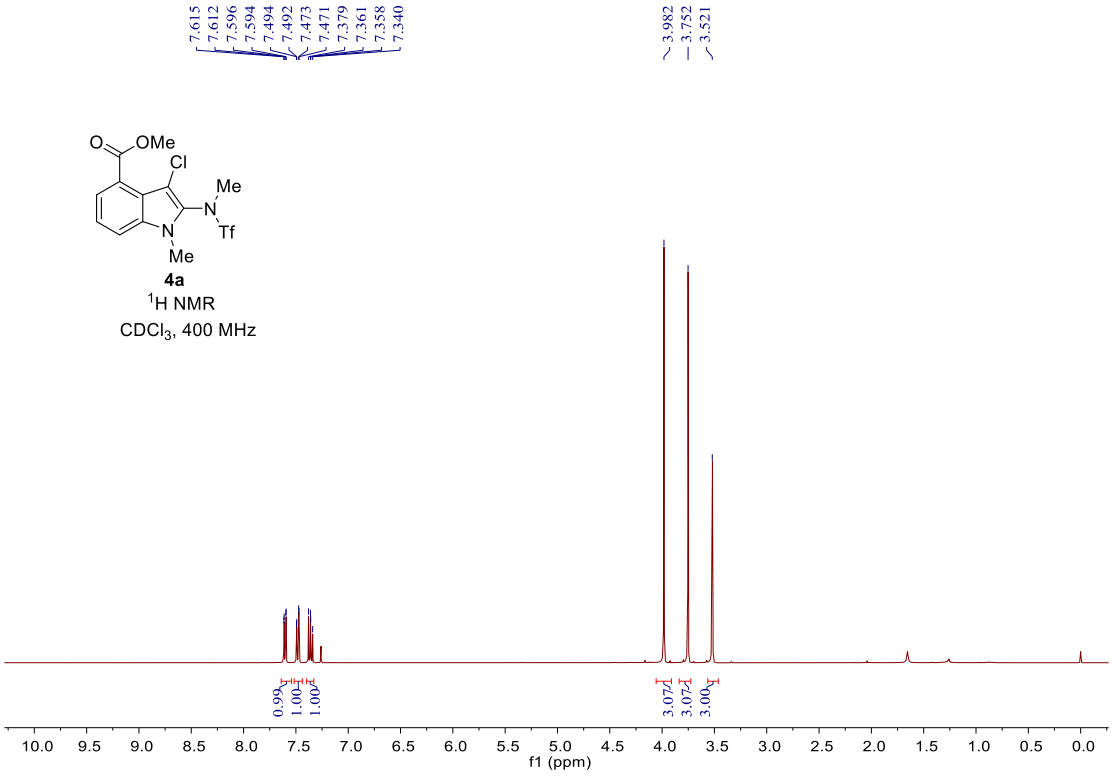
$CDCl_3$, 400 MHz

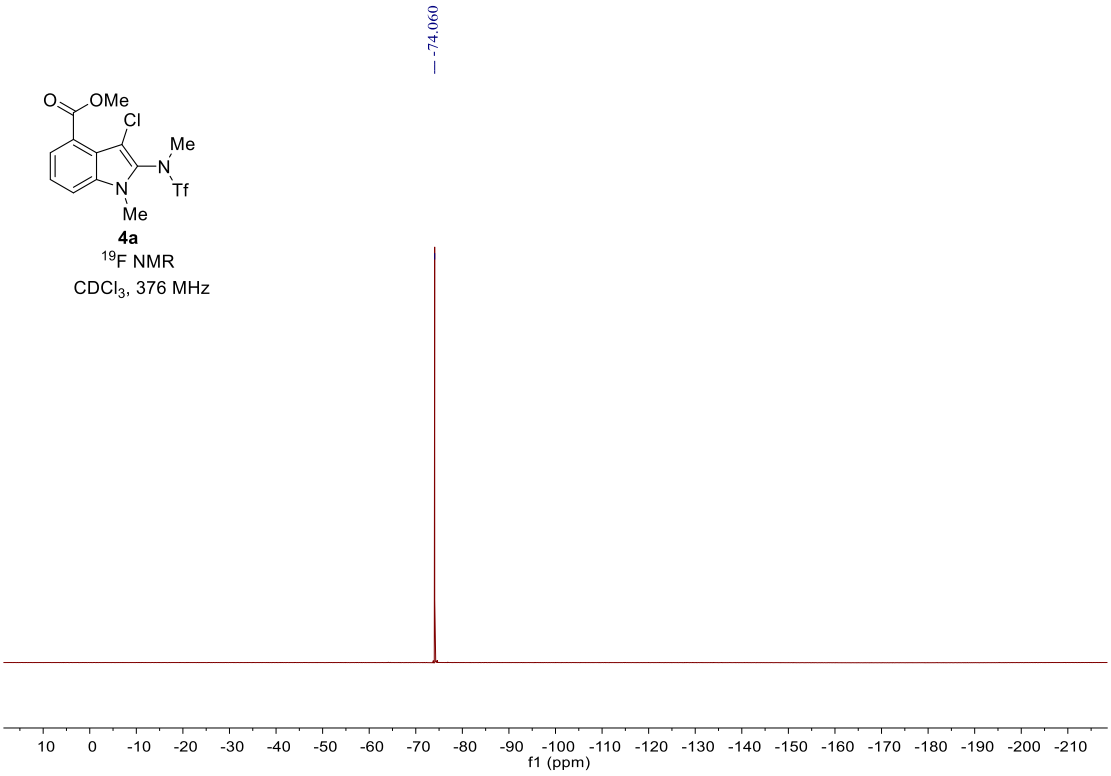


^{19}F NMR

$CDCl_3$, 376 MHz


133.829
128.118
124.734
124.677
123.526
121.521
121.054
118.968
118.305
115.091
110.203
103.465
77.369
77.051
76.733
40.039
29.925
Cl
Tf
N
Me
N
Me
3d
13C NMR
CDCl3, 100 MHz
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

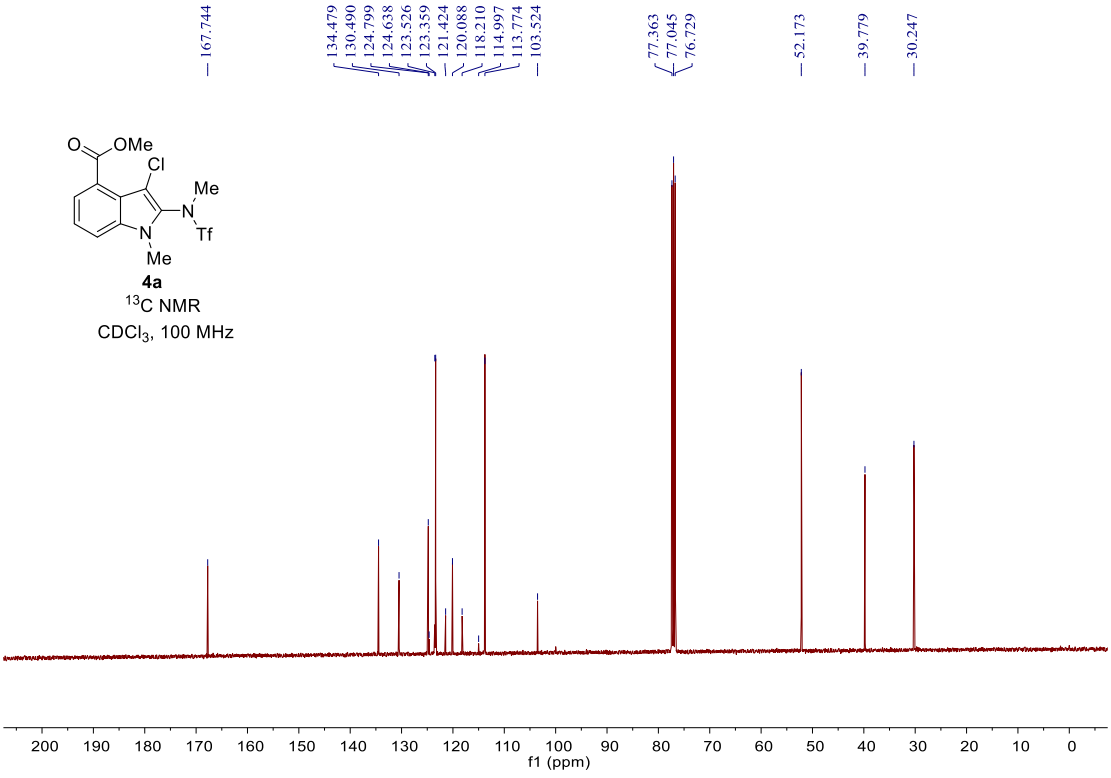

7.615
7.612
7.596
7.594
7.494
7.492
7.473
7.471
7.379
7.361
7.358
7.340
3.982
3.752
3.521
O
OMe
Cl
Me
N
Tf
N
Me
4a
1H NMR
CDCl3, 400 MHz
0.99
1.00
1.00
3.07
3.07
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



4a

^{19}F NMR

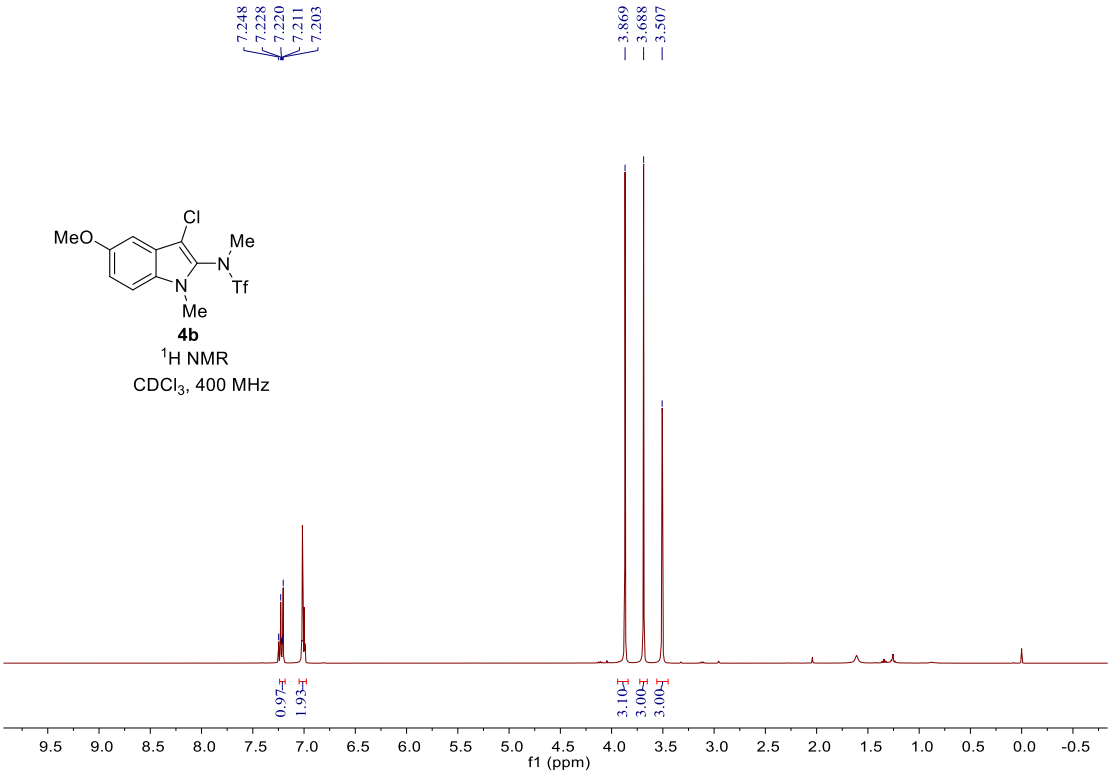
$CDCl_3$, 376 MHz



4a

^{13}C NMR

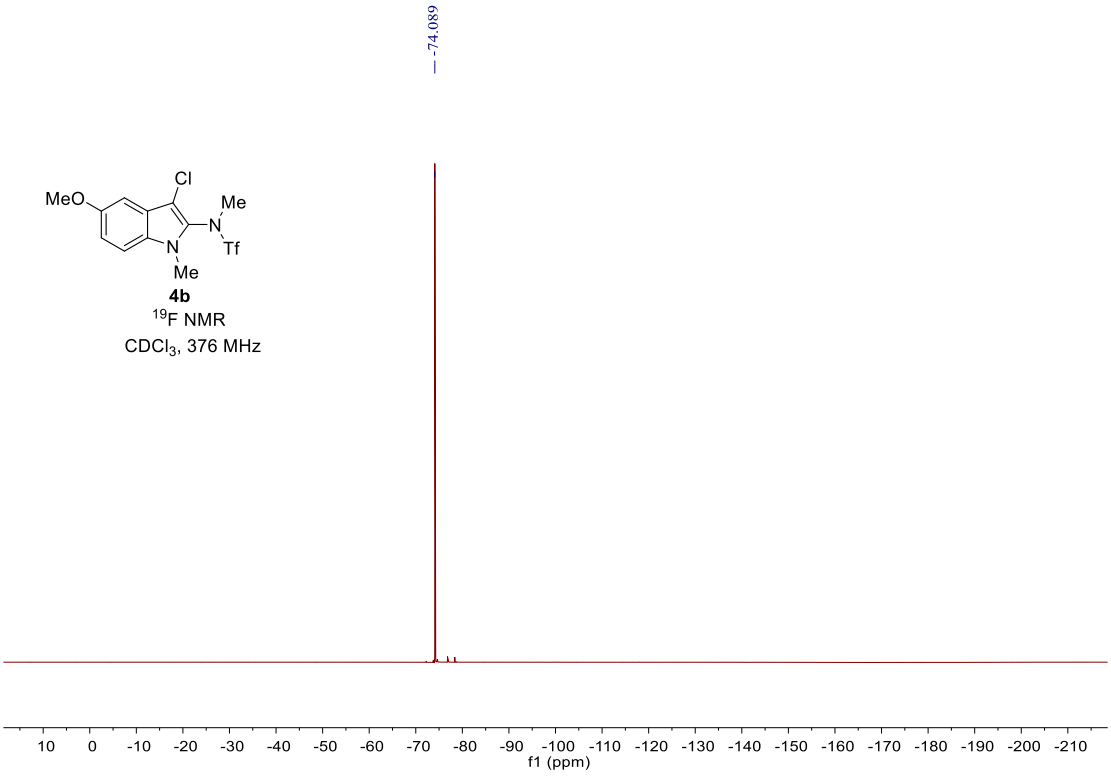
$CDCl_3$, 100 MHz



4b

^{1}H NMR

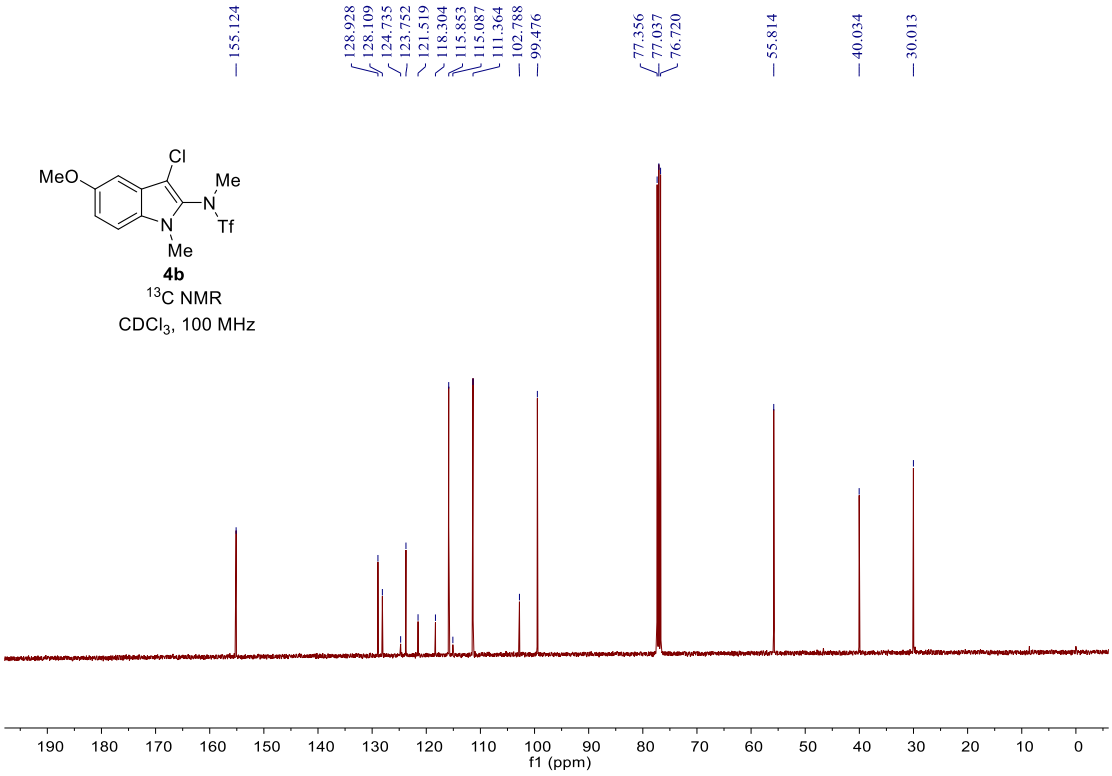
$CDCl_3$, 400 MHz

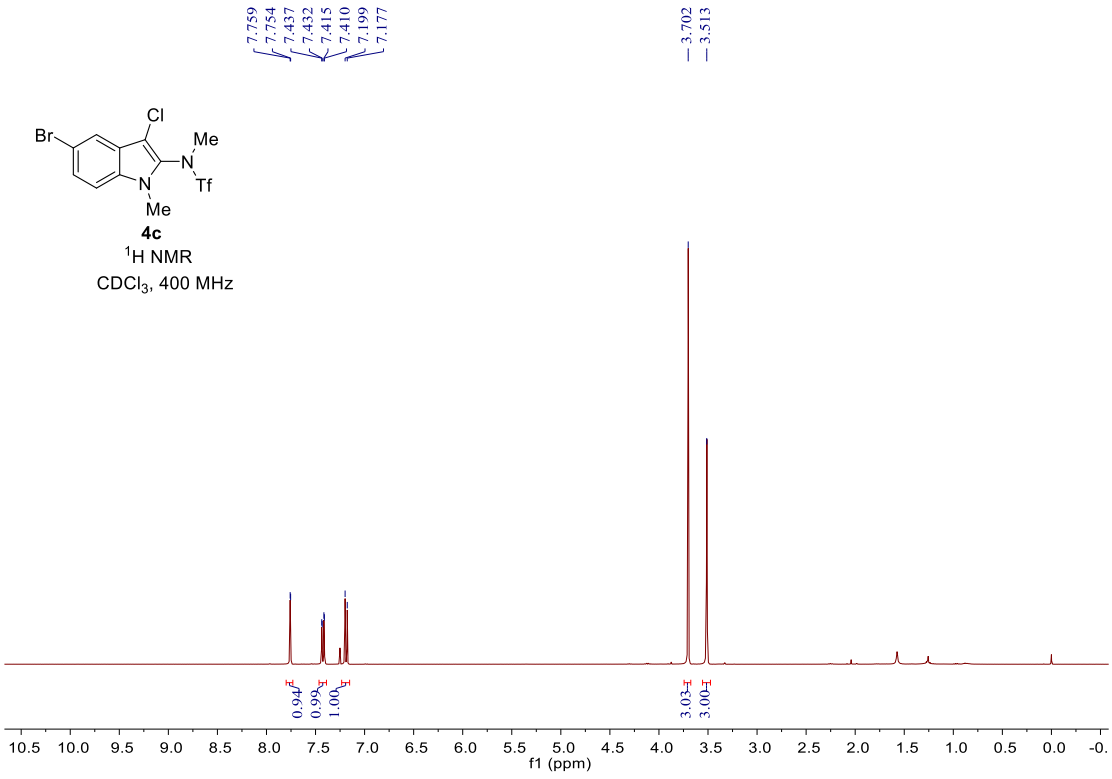


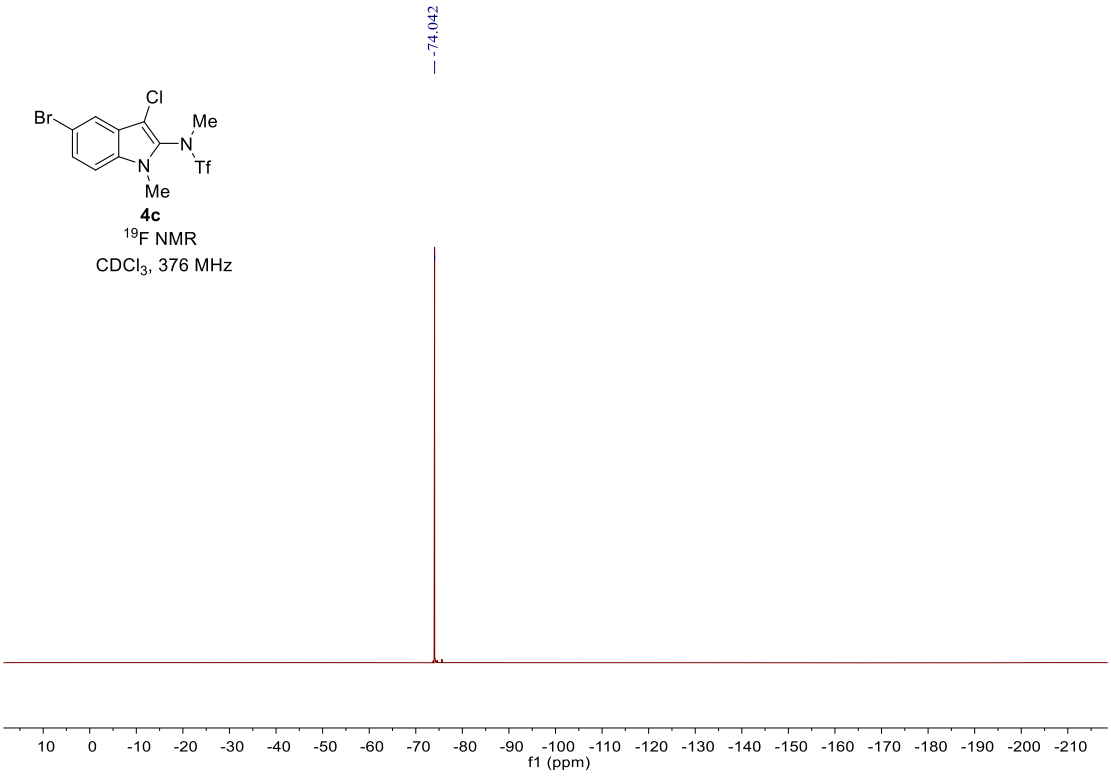
4b

^{19}F NMR

$CDCl_3$, 376 MHz


155.124
128.928
128.109
124.735
123.752
121.519
118.304
115.853
115.087
111.364
102.788
99.476
77.356
77.037
76.720
55.814
40.034
30.013
Cl
MeO
Me
N
Tf
N
Me
4b
13C NMR
CDCl3, 100 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

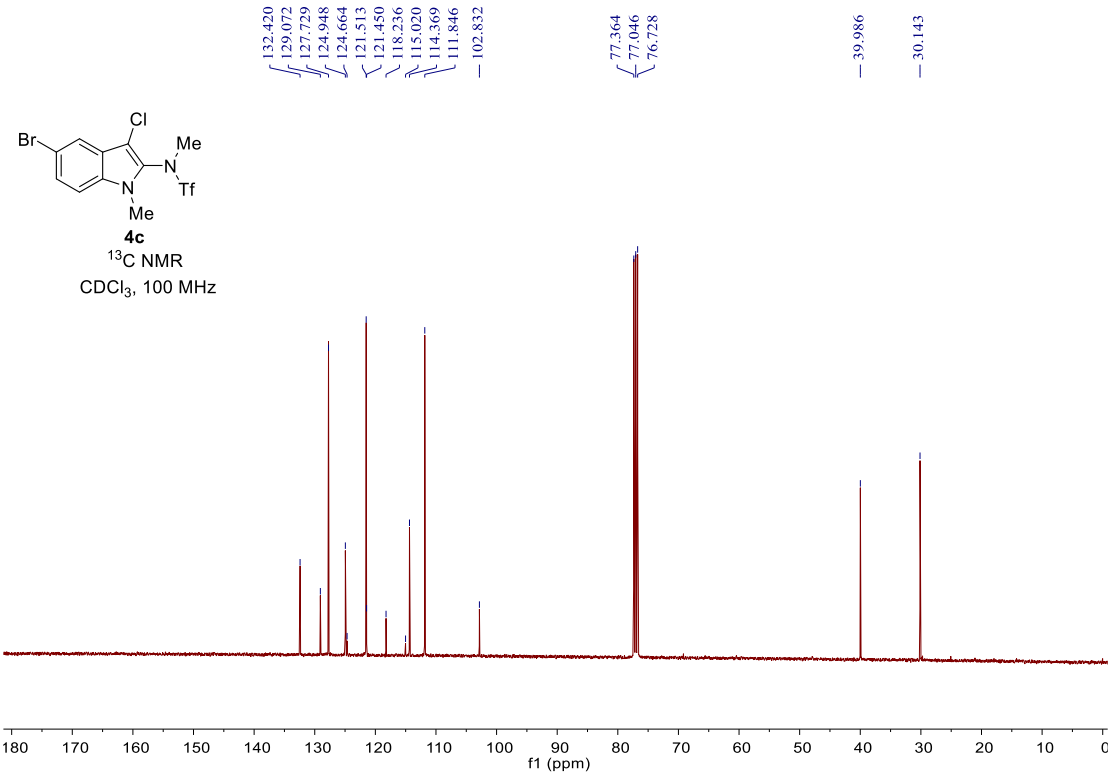

7.759
7.754
7.437
7.432
7.415
7.410
7.199
7.177
3.702
3.513
Cl
Br
Me
N
Tf
N
Me
4c
1H NMR
CDCl3, 400 MHz
0.94
0.99
1.00
3.03
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)



4c

^{19}F NMR

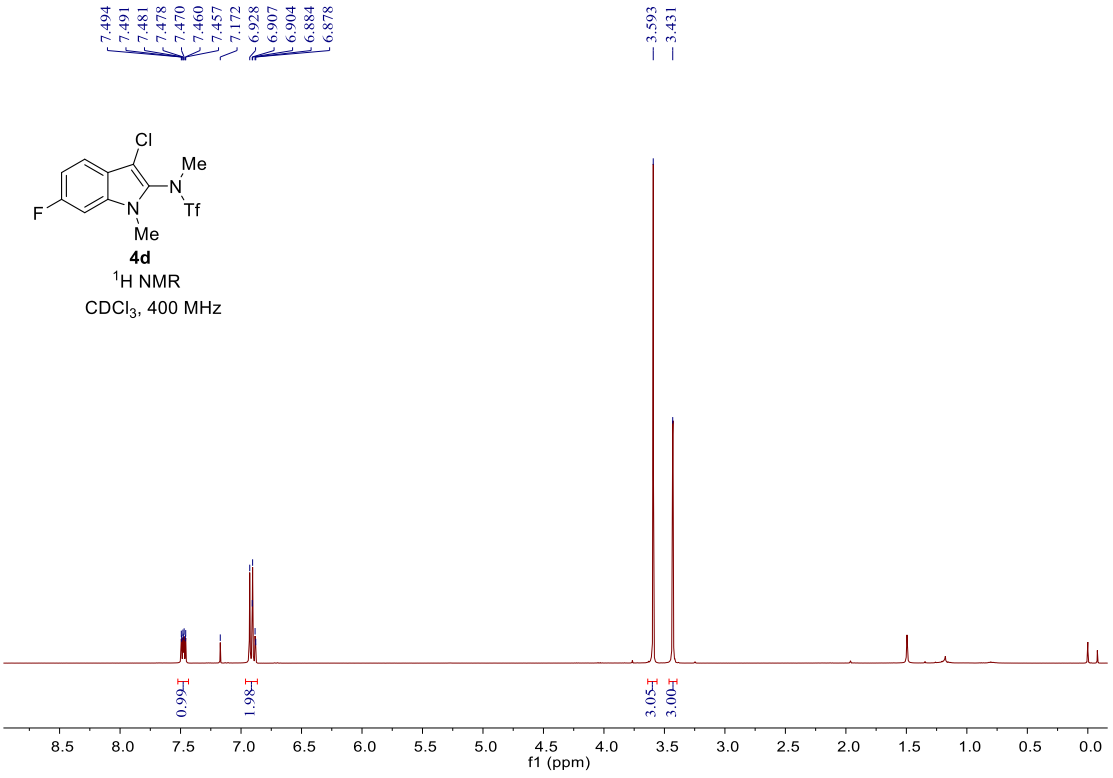
$CDCl_3$, 376 MHz



4c

^{13}C NMR

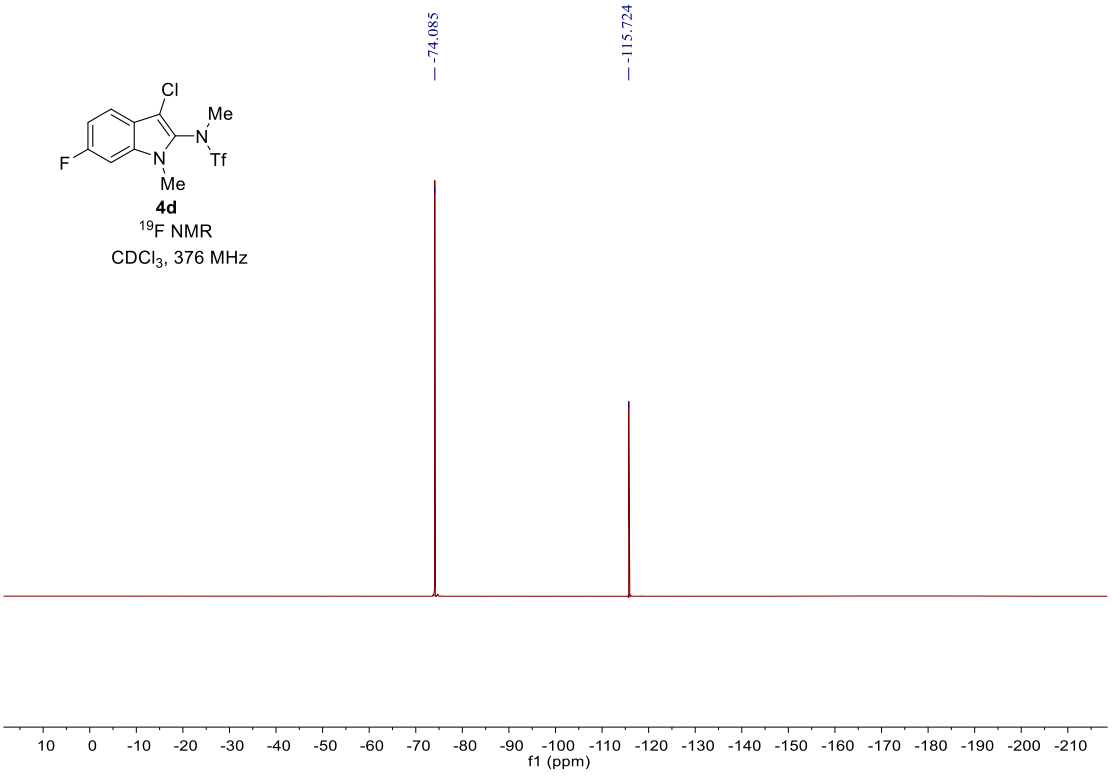
$CDCl_3$, 100 MHz



4d

^{1}H NMR

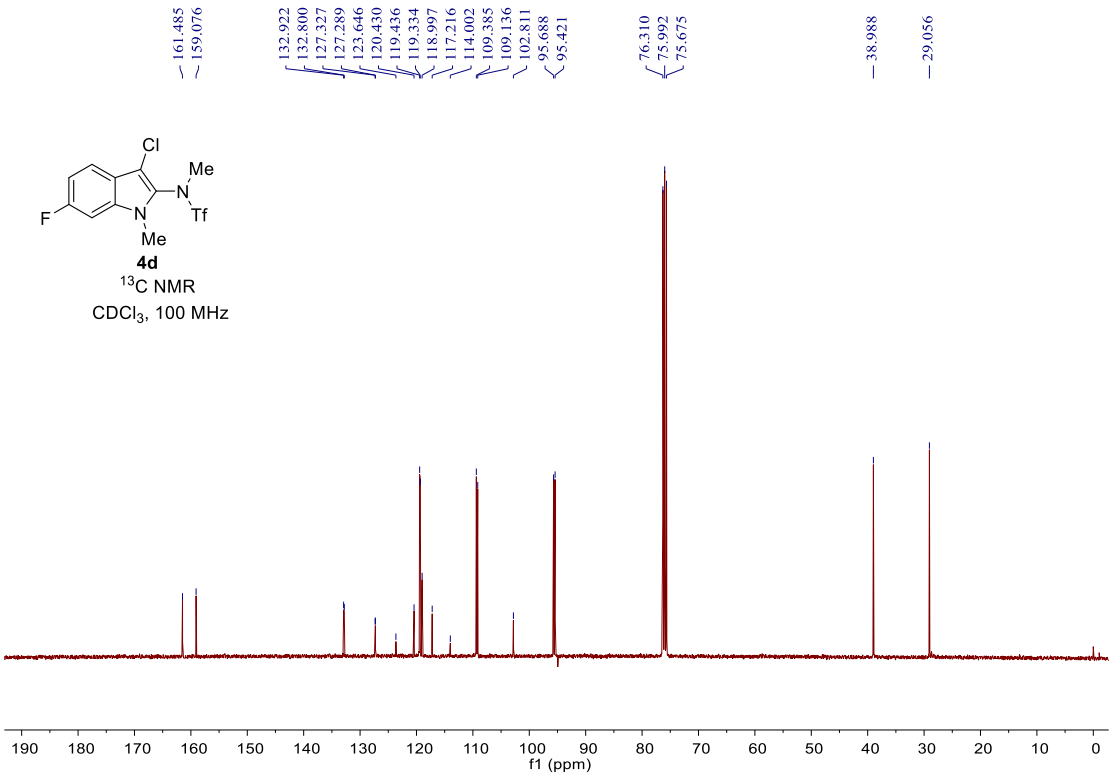
$CDCl_3$, 400 MHz

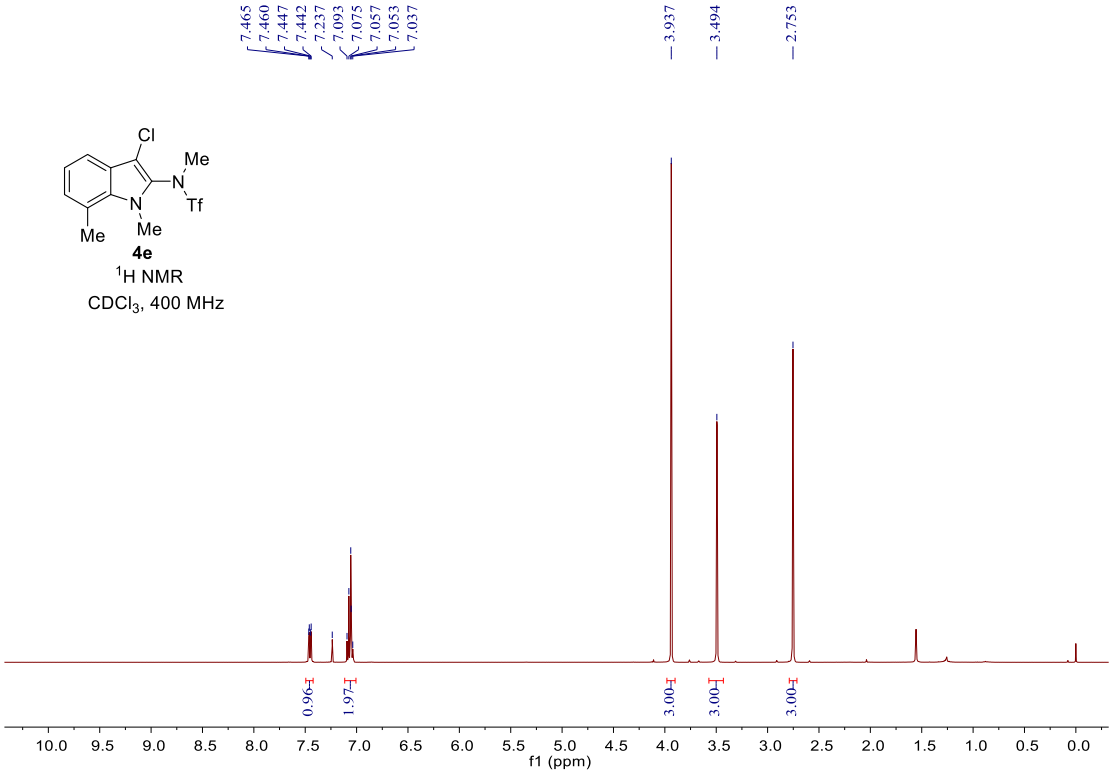


4d

^{19}F NMR

$CDCl_3$, 376 MHz

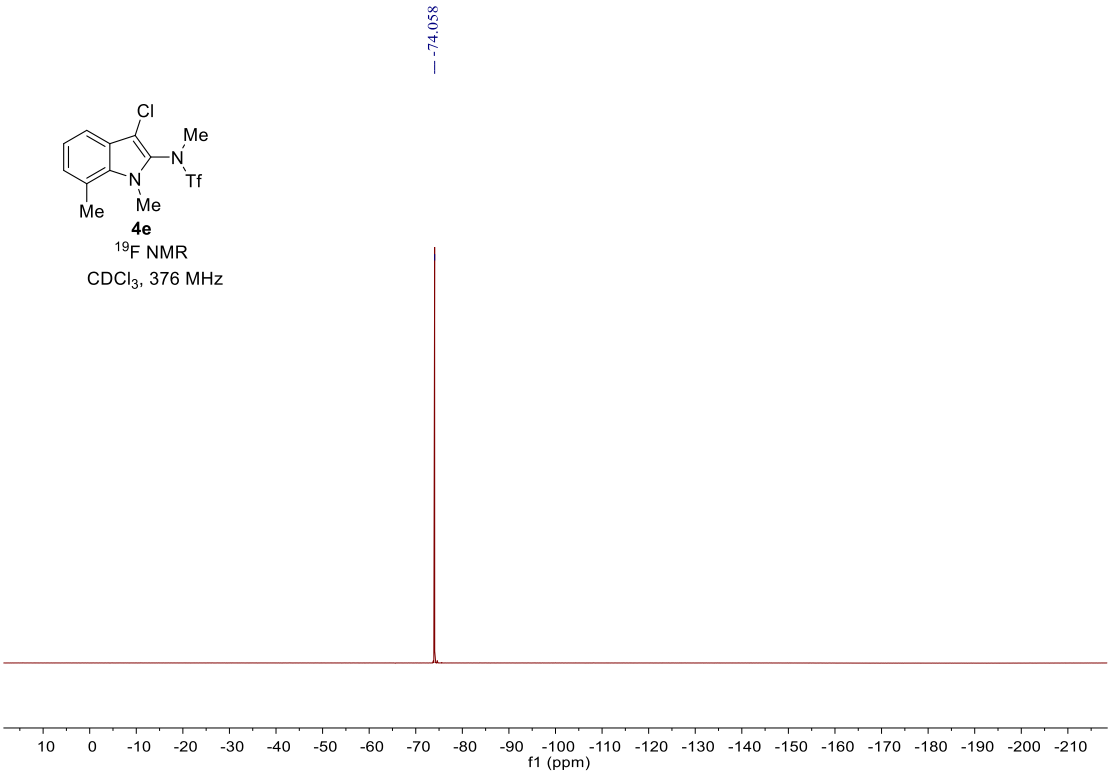

161.485
159.076
132.922
132.800
127.327
127.289
123.646
120.430
119.436
119.334
118.997
117.216
114.002
109.385
109.136
102.811
95.688
95.421
76.310
75.992
75.675
38.988
29.056
Cl
Me
N
Tf
F
N
Me
4d
13C NMR
CDCl3, 100 MHz
f1 (ppm)

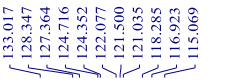

7.465
7.460
7.447
7.442
7.237
7.093
7.075
7.057
7.053
7.037
3.937
3.494
2.753
Cl
Me
N
Tf
N
Me
Me
4e
1H NMR
CDCl3, 400 MHz
0.96
1.97
3.00
3.00
3.00
f1 (ppm)

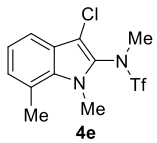
4e

^{19}F NMR

$CDCl_3$, 376 MHz



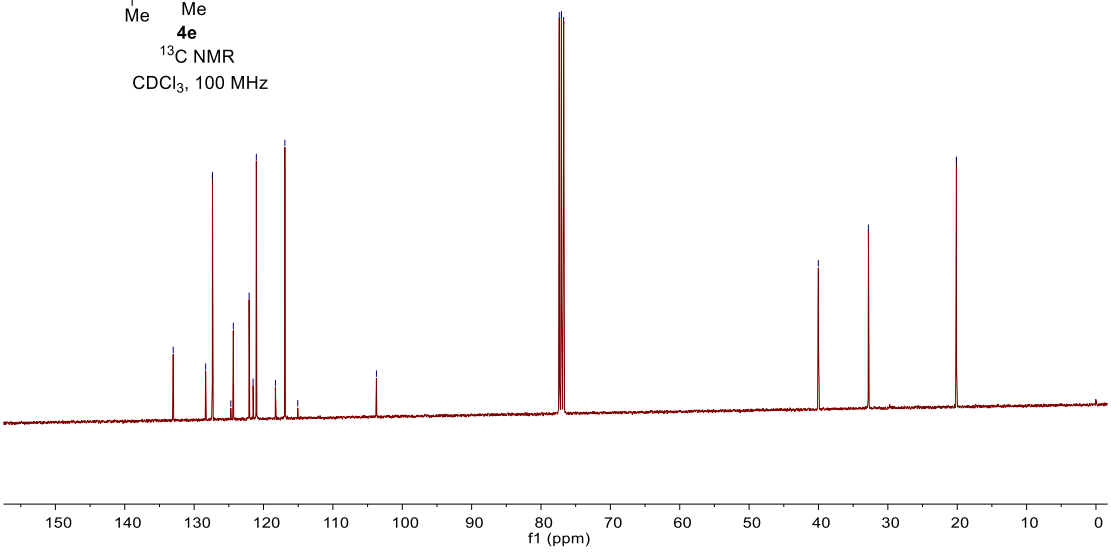


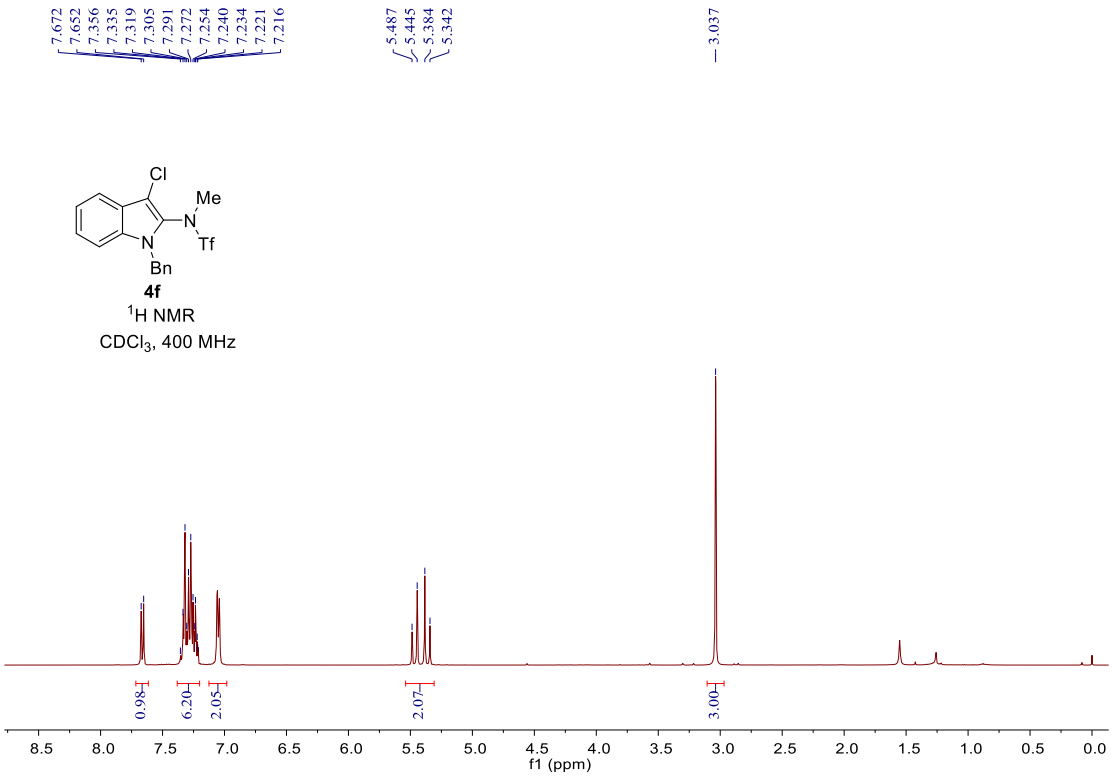


4e

^{13}C NMR

$CDCl_3$, 100 MHz

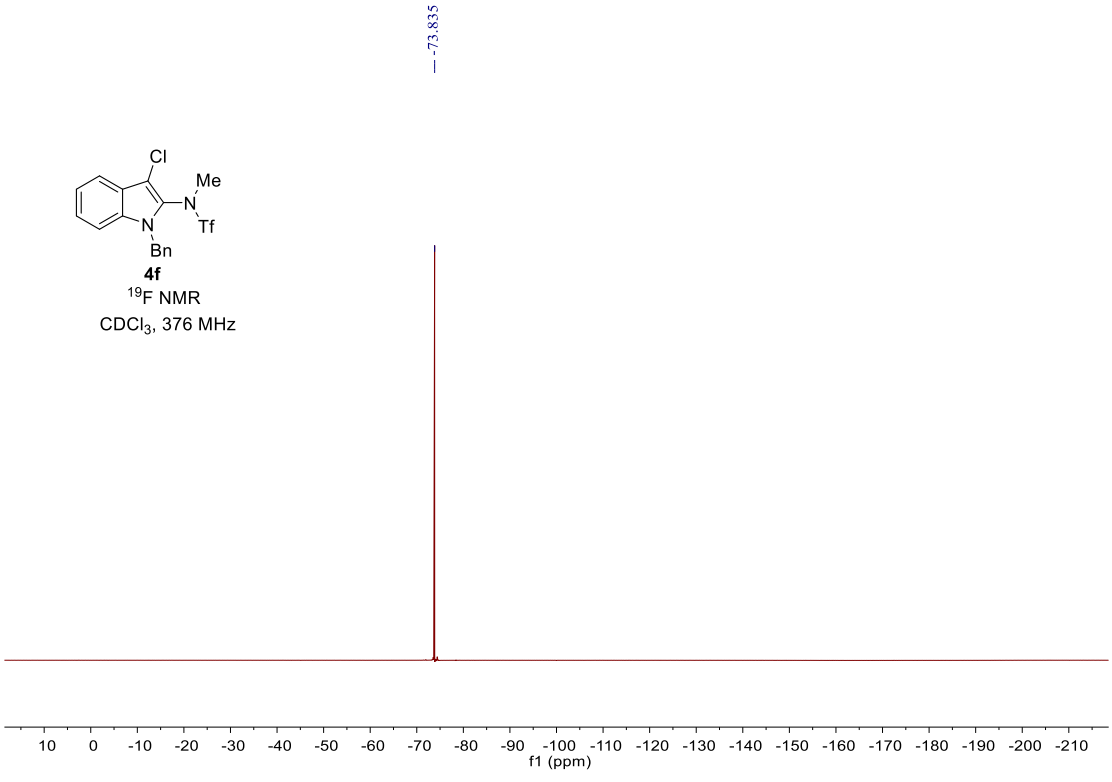




4f

^{1}H NMR

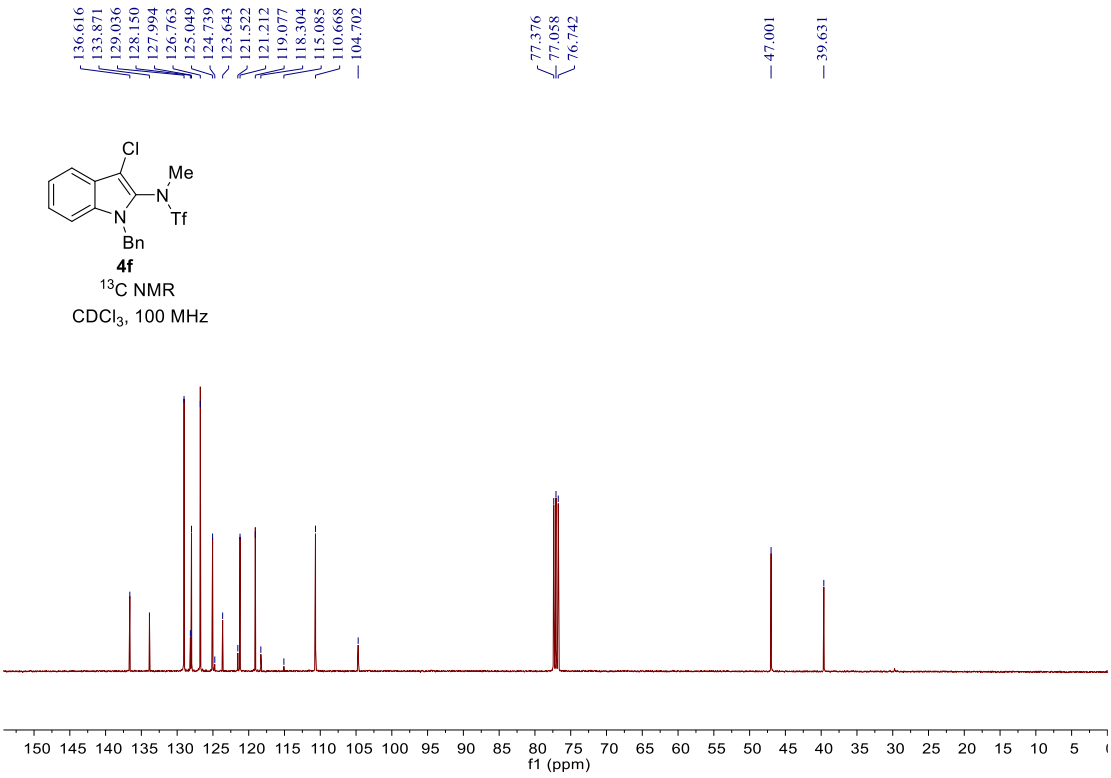
$CDCl_3$, 400 MHz

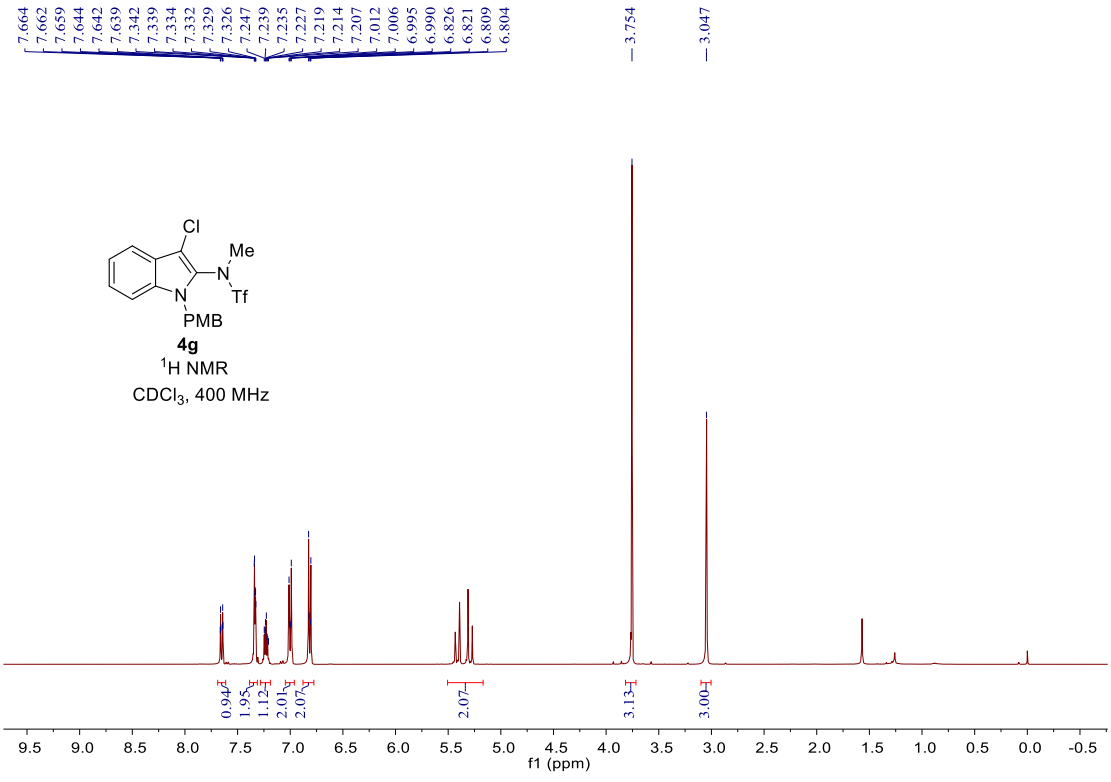


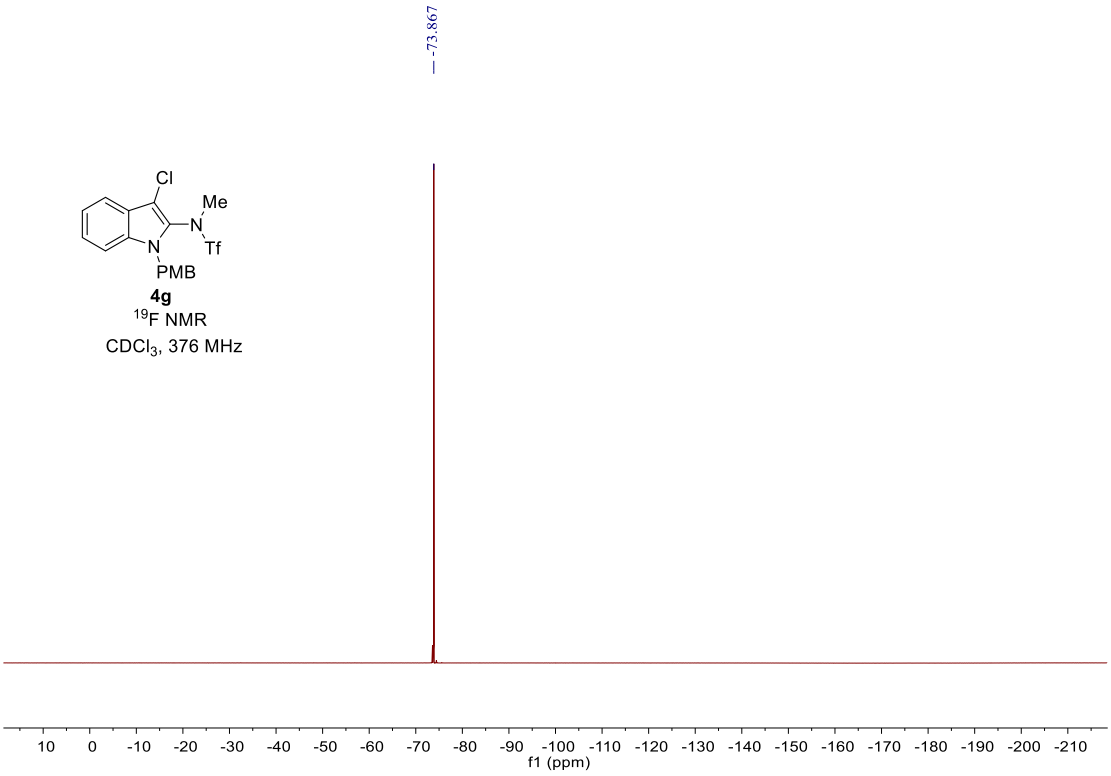
4f

^{19}F NMR

$CDCl_3$, 376 MHz


136.616
133.871
129.036
128.150
127.994
126.763
125.049
124.739
123.643
121.522
121.212
119.077
118.304
115.085
110.668
104.702
77.376
77.058
76.742
47.001
39.631
Cl
Me
N
Tf
N
Bn
4f
13C NMR
CDCl3, 100 MHz
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)

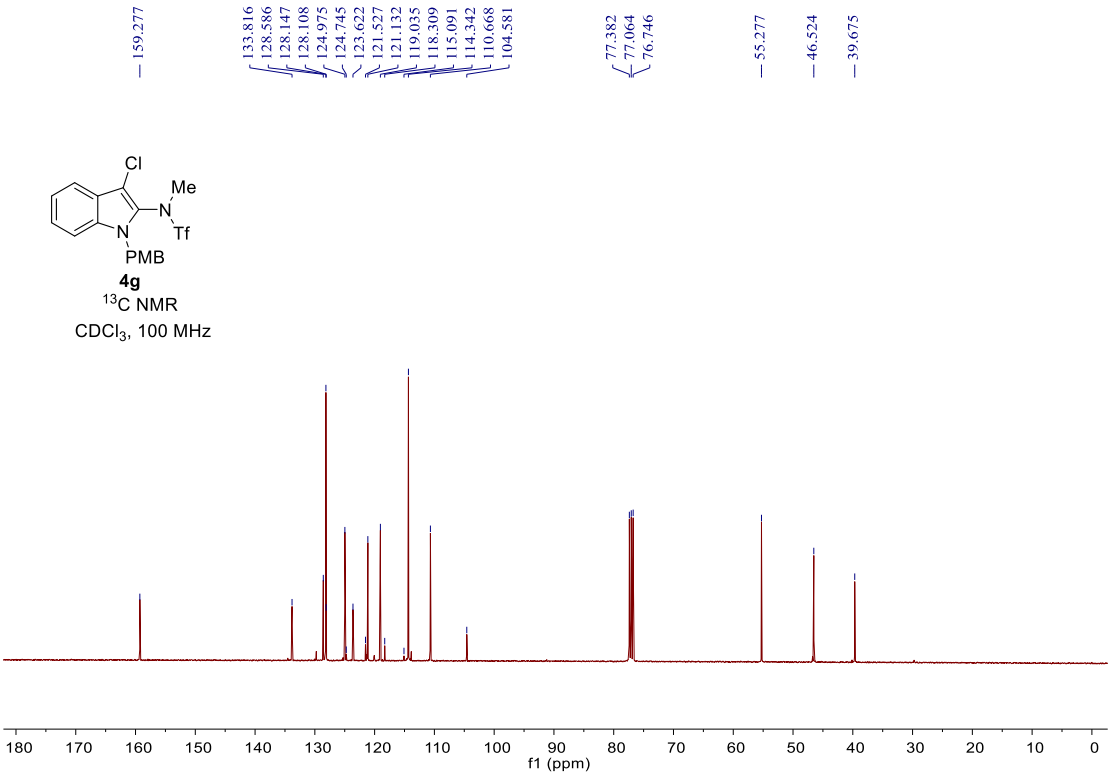

7.664
7.662
7.659
7.644
7.642
7.639
7.342
7.339
7.334
7.332
7.329
7.326
7.247
7.239
7.235
7.227
7.219
7.214
7.207
7.012
7.006
6.995
6.990
6.826
6.821
6.809
6.804
3.754
3.047
Cl
Me
N
Tf
N
PMB
4g
1H NMR
CDCl3, 400 MHz
0.94
1.95
1.12
2.01
2.07
2.07
3.13
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



4g

^{19}F NMR

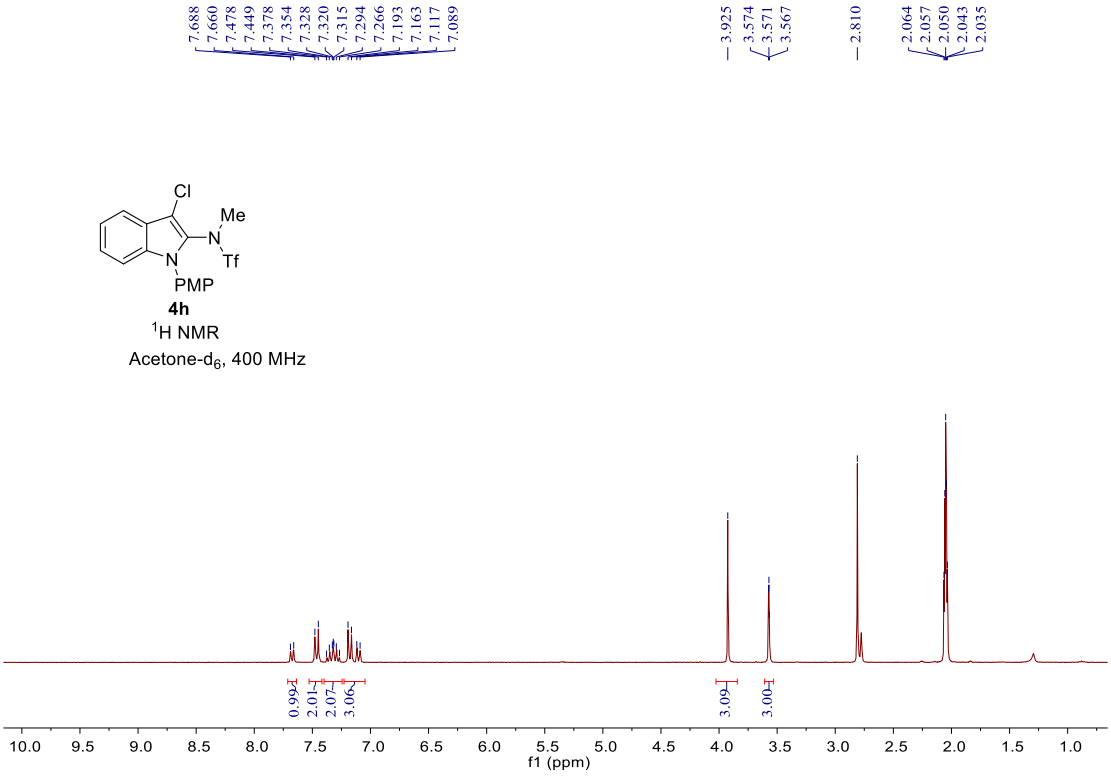
$CDCl_3$, 376 MHz



4g

^{13}C NMR

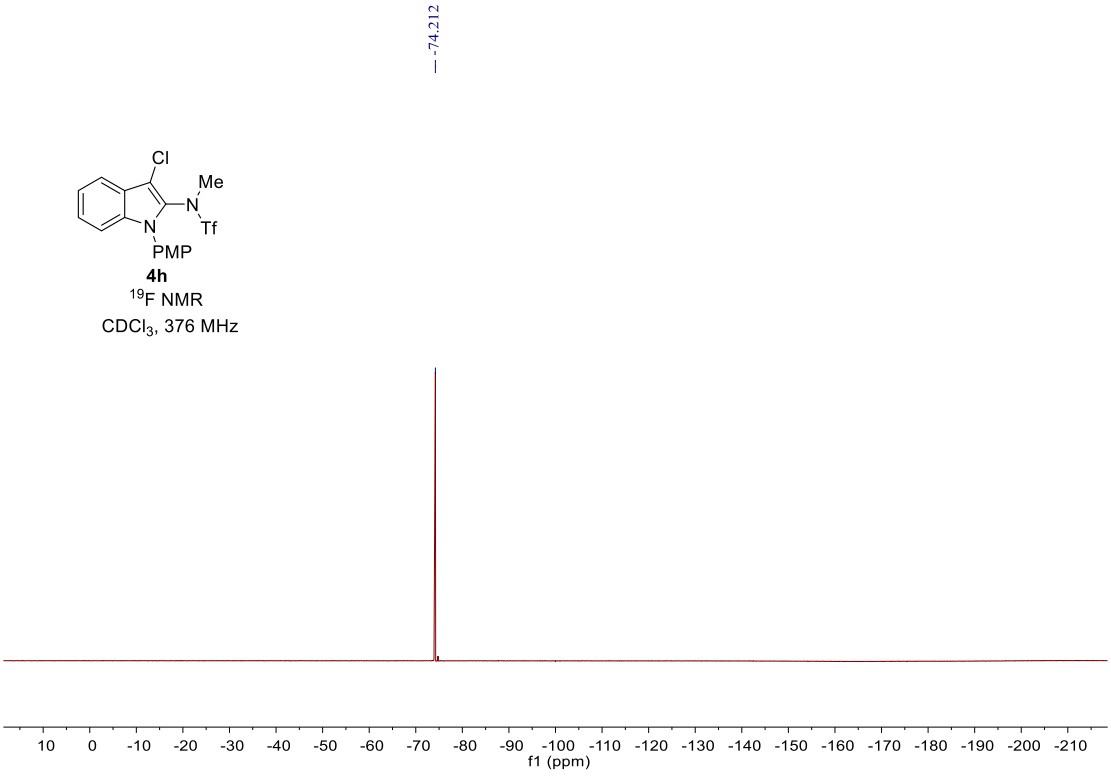
$CDCl_3$, 100 MHz



4h

^{1}H NMR

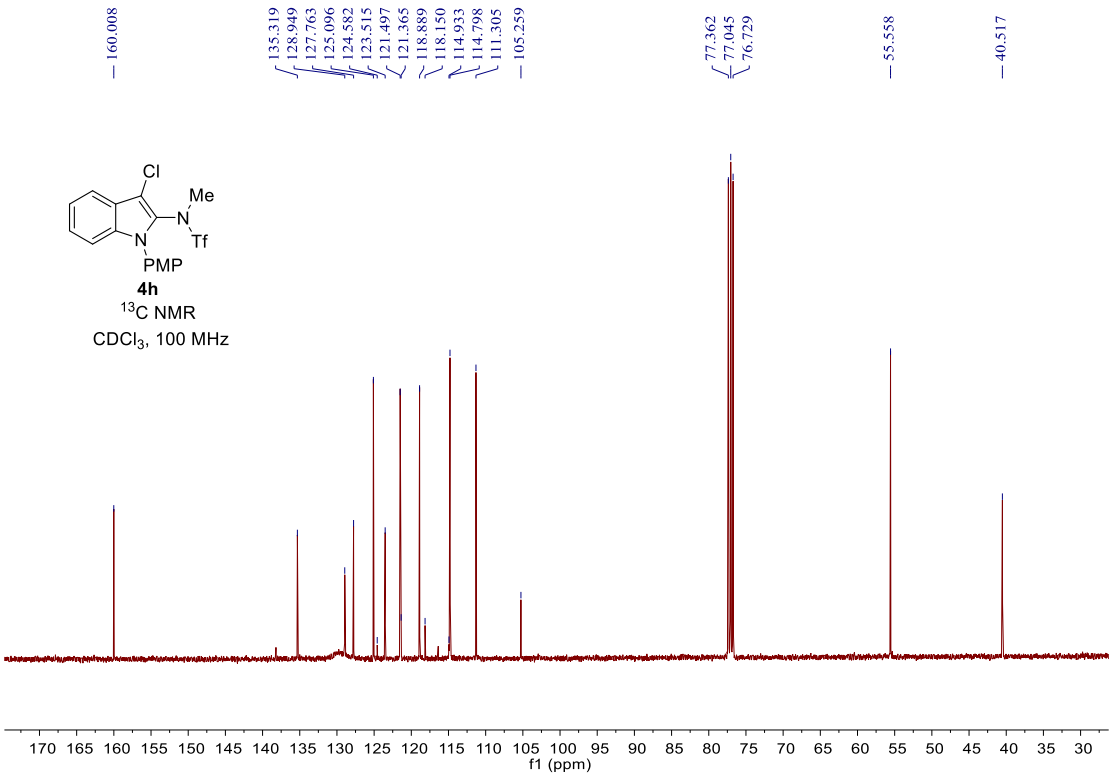
Acetone-d_6, 400 MHz

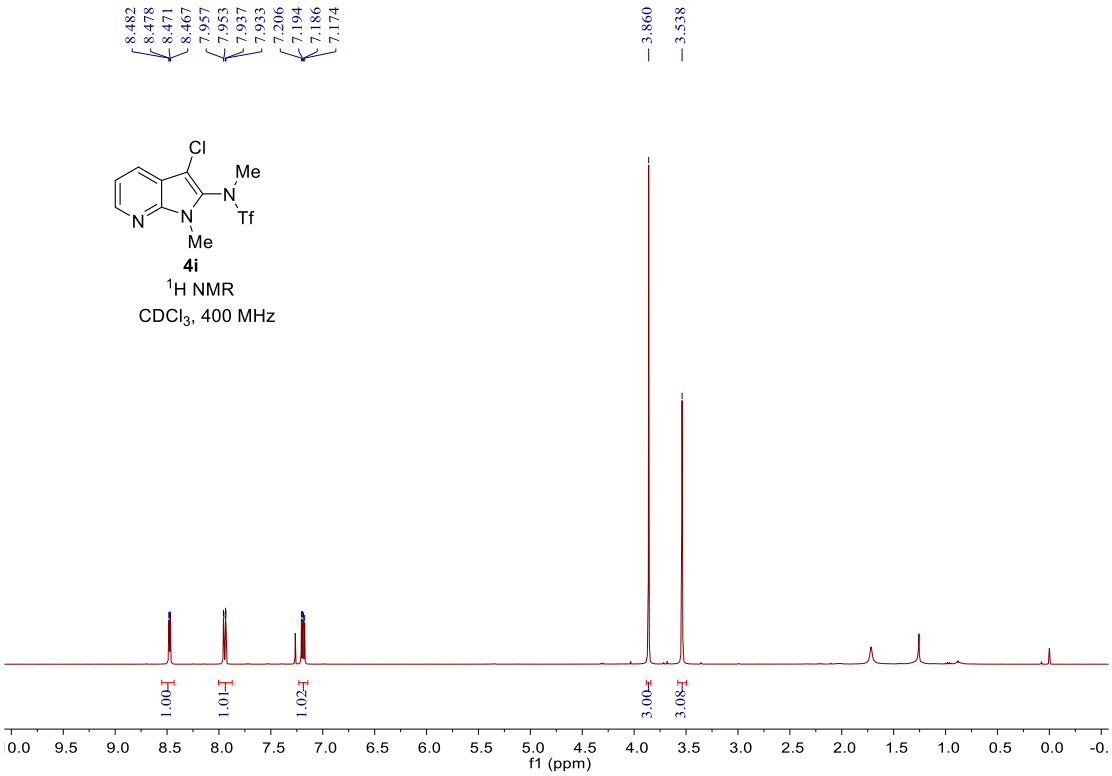


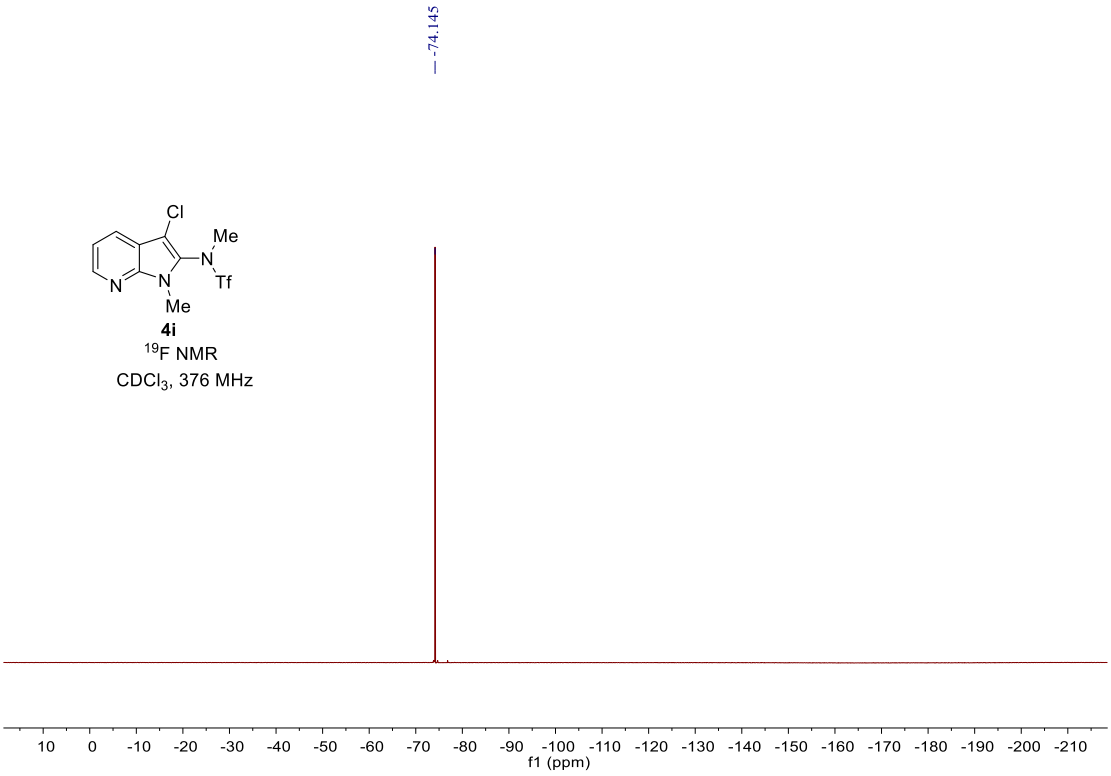
4h

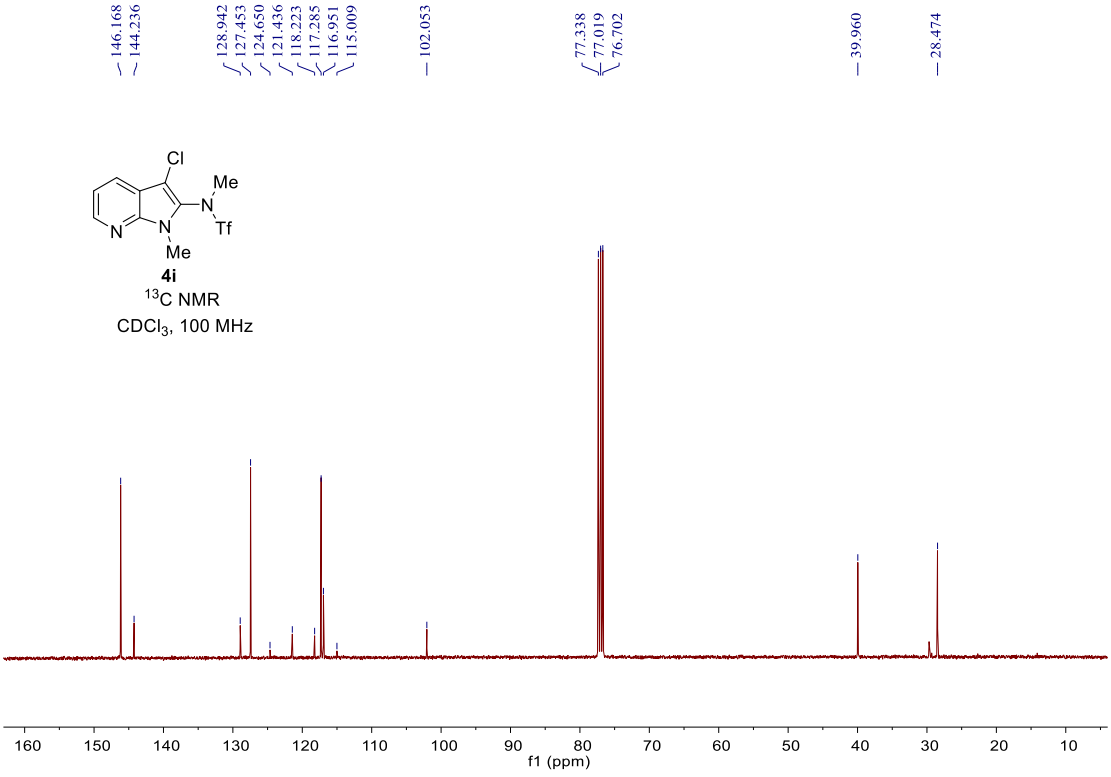
^{19}F NMR

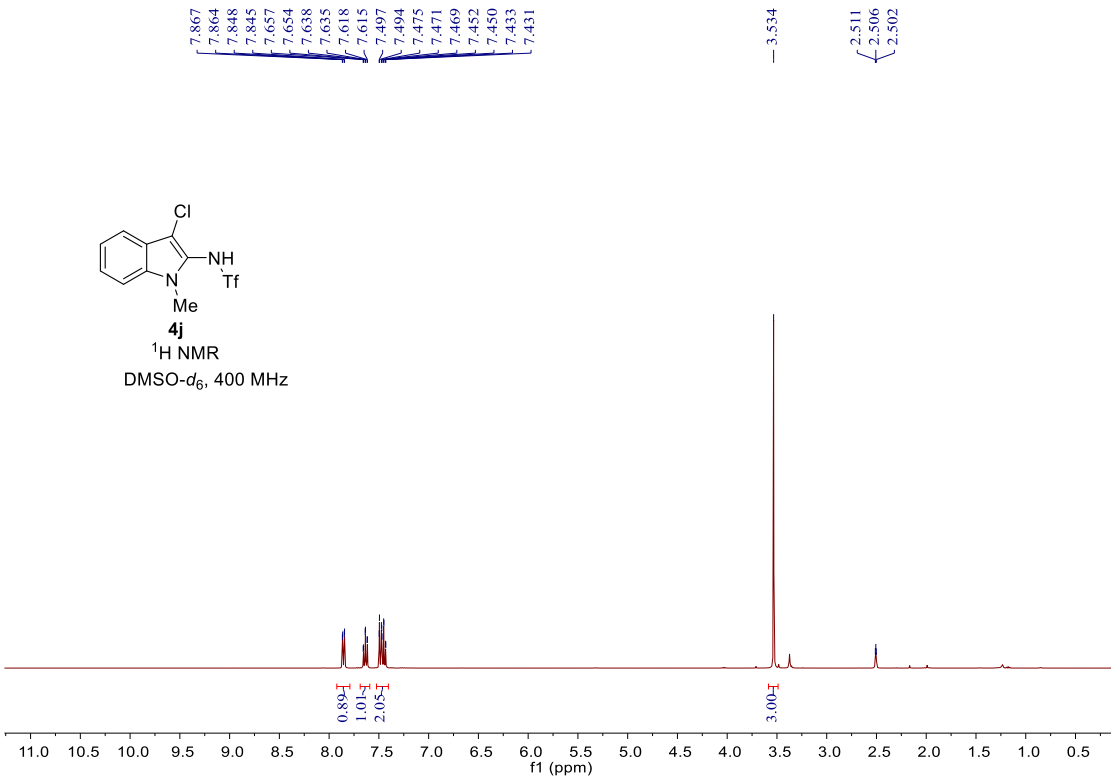
$CDCl_3$, 376 MHz

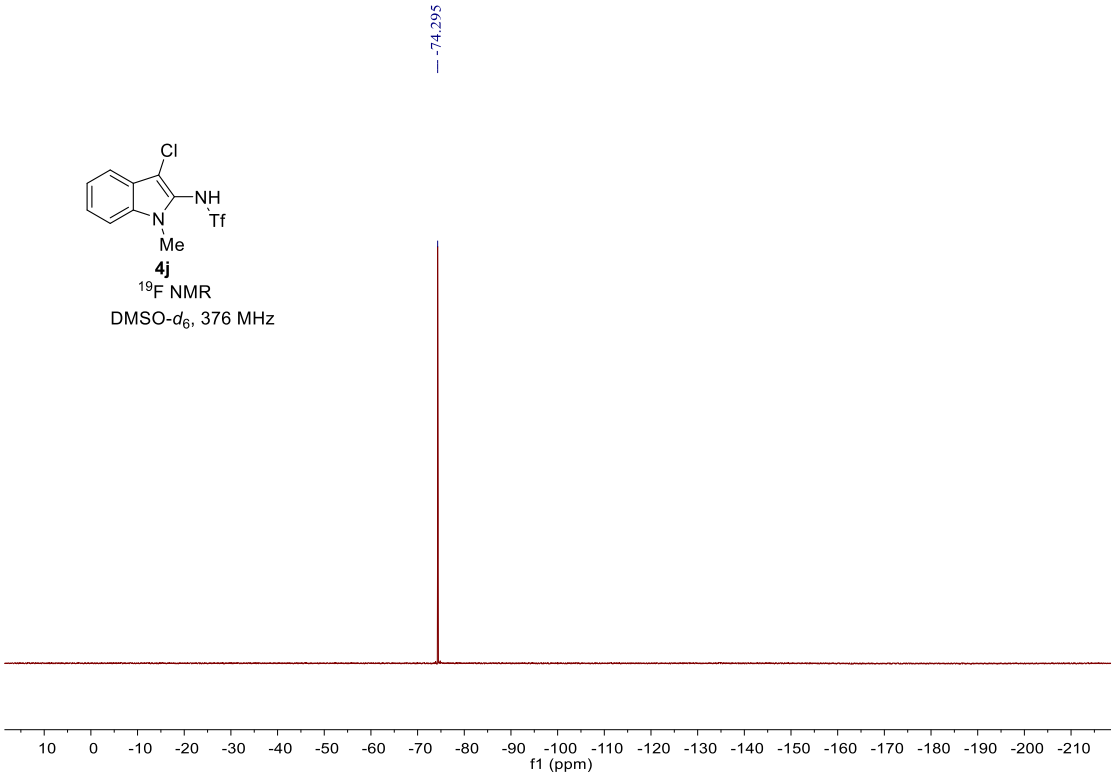

160.008
135.319
128.949
127.763
125.096
124.582
123.515
121.497
121.365
118.889
118.150
114.933
114.798
111.305
105.259
77.362
77.045
76.729
55.558
40.517
Cl
Me
N
Tf
N
PMP
4h
13C NMR
CDCl3, 100 MHz
f1 (ppm)

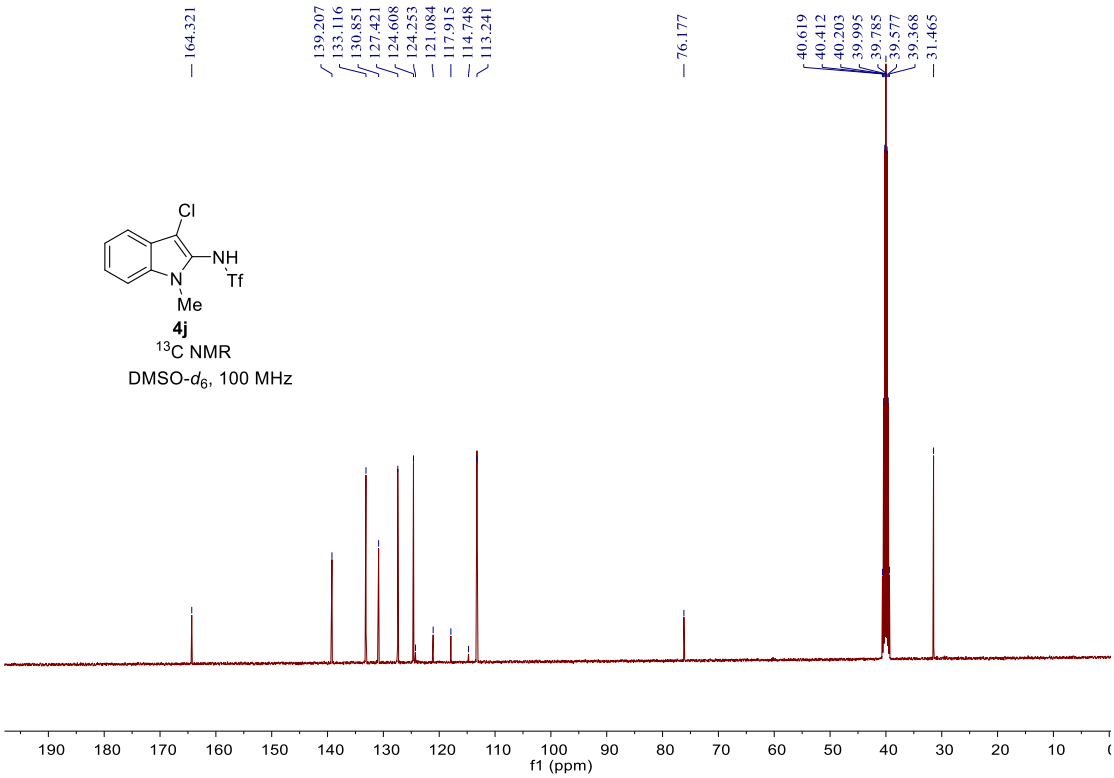

8.482
8.478
8.471
8.467
7.957
7.953
7.937
7.933
7.206
7.194
7.186
7.174
3.860
3.538
Cl
Me
N
Tf
N
N
Me
4i
1H NMR
CDCl3, 400 MHz
1.00
1.01
1.02
3.00
3.08
f1 (ppm)

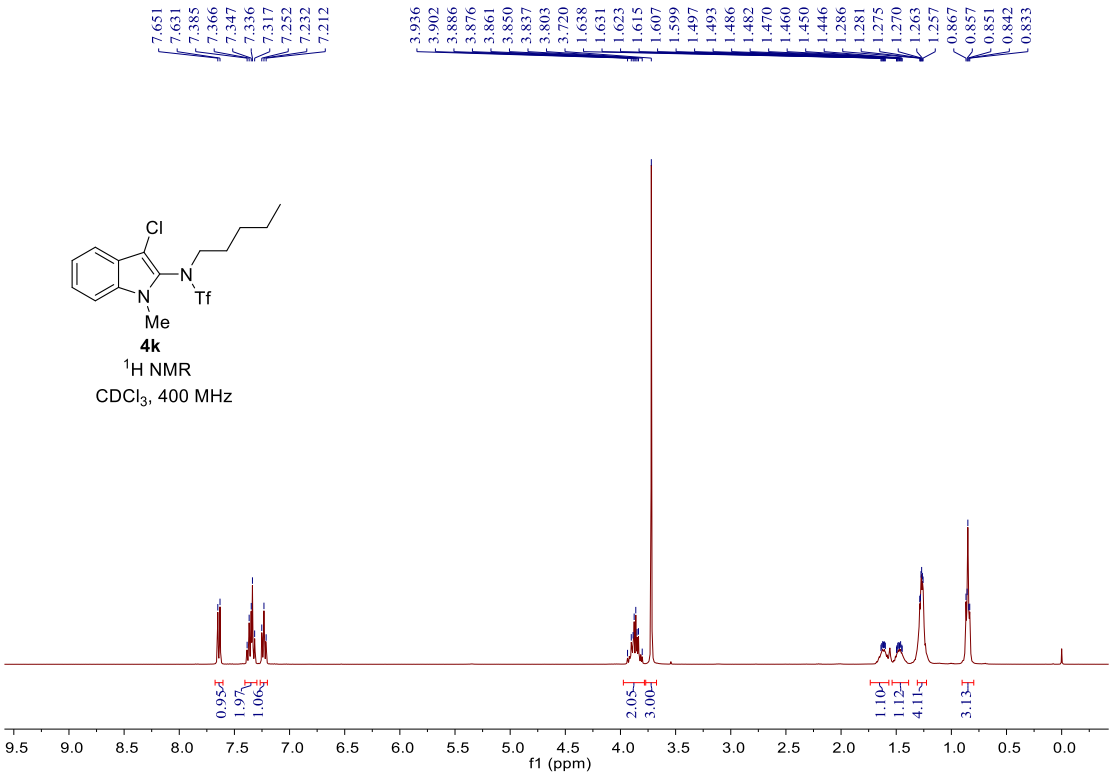

-74.145
Cl
Me
N
Tf
N
N
Me
4i
19F NMR
CDCl3, 376 MHz
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

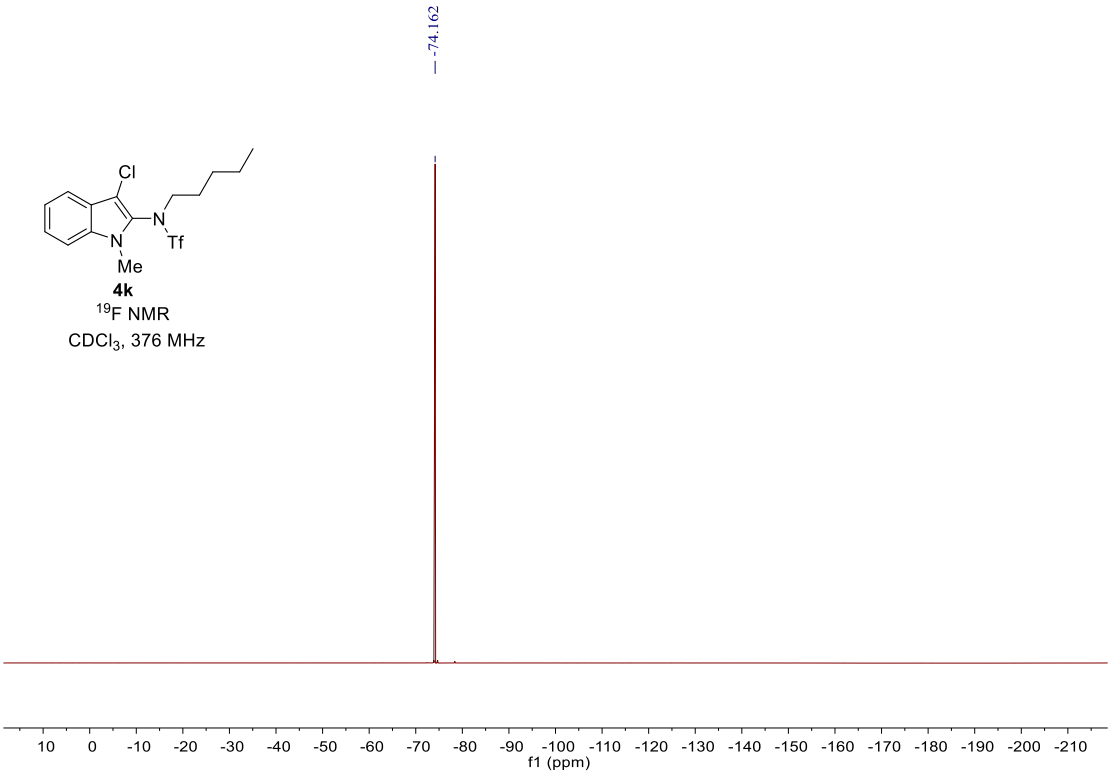

146.168
144.236
128.942
127.453
124.650
121.436
118.223
117.285
116.951
115.009
102.053
77.338
77.019
76.702
39.960
28.474
Cl
Me
N
Tf
N
N
Me
4i
13C NMR
CDCl3, 100 MHz
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

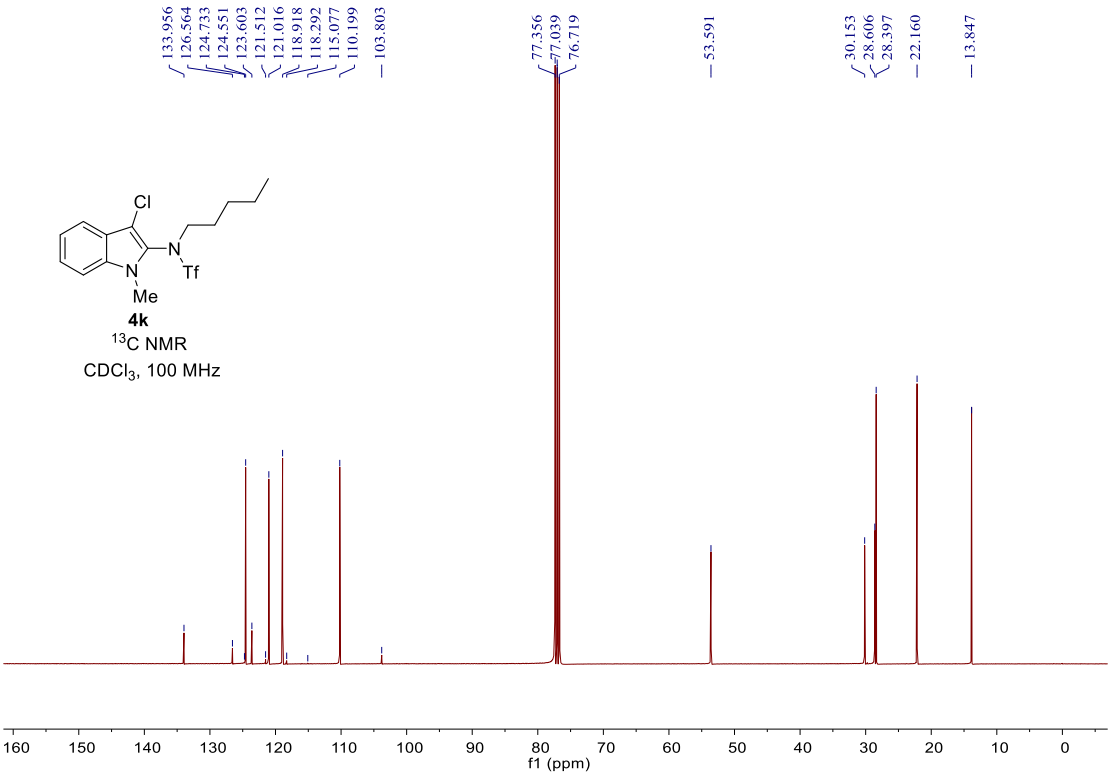

7.867
7.864
7.848
7.845
7.657
7.654
7.638
7.635
7.618
7.615
7.497
7.494
7.475
7.471
7.469
7.452
7.450
7.433
7.431
3.534
2.511
2.506
2.502
Cl
NH
Tf
N
Me
4j
1H NMR
DMSO-d6, 400 MHz
0.89
1.01
2.05
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

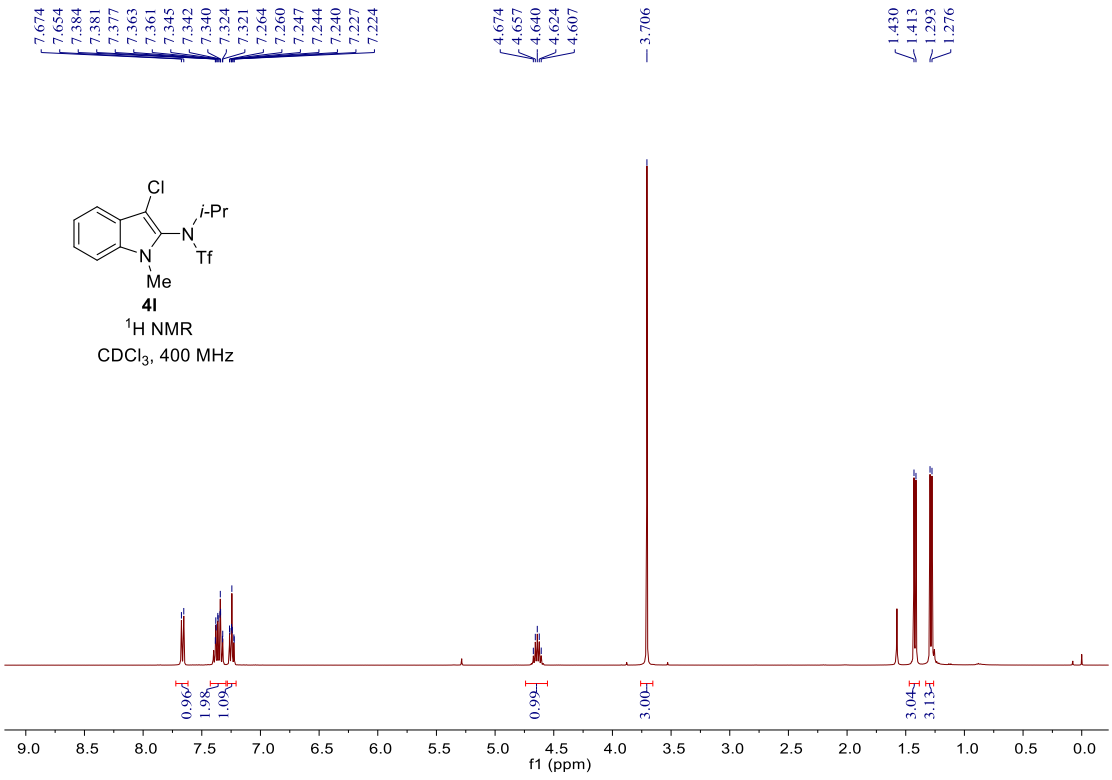

-74.295
Cl
NH
Tf
N
Me
4j
19F NMR
DMSO-d6, 376 MHz
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

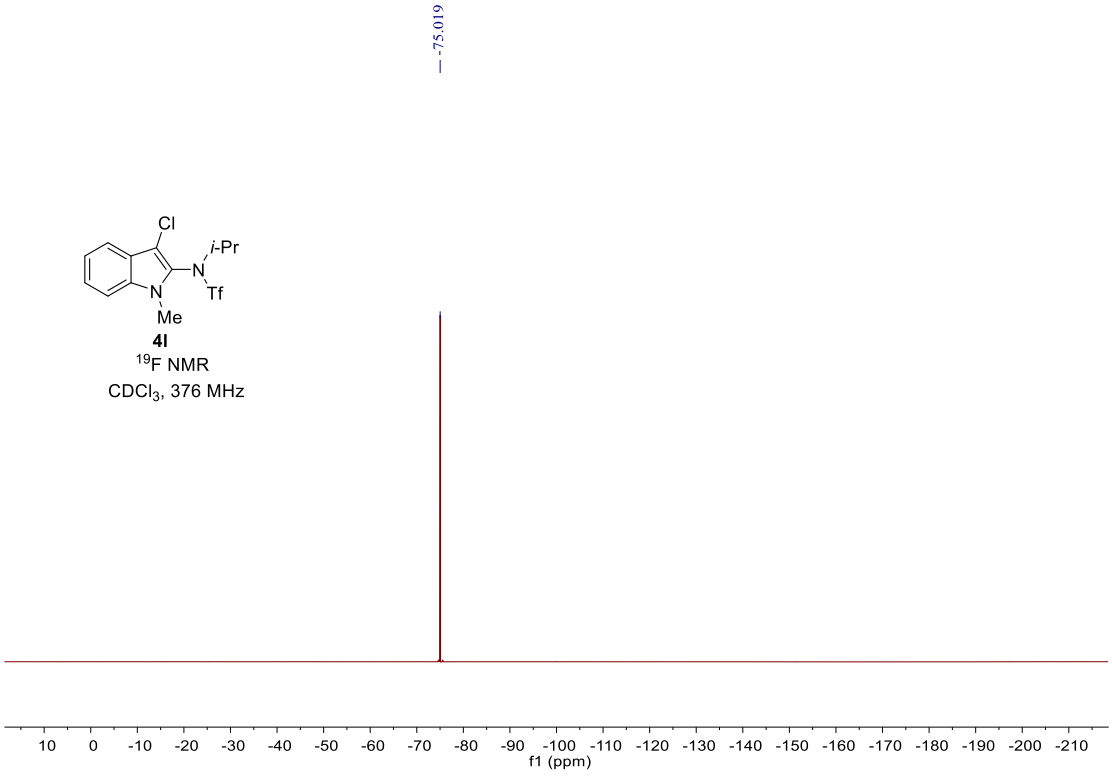

164.321
139.207
133.116
130.851
127.421
124.608
124.253
121.084
117.915
114.748
113.241
76.177
40.619
40.412
40.203
39.995
39.785
39.577
39.368
31.465
Cl
NH
Tf
N
Me
4j
13C NMR
DMSO-d6, 100 MHz
f1 (ppm)

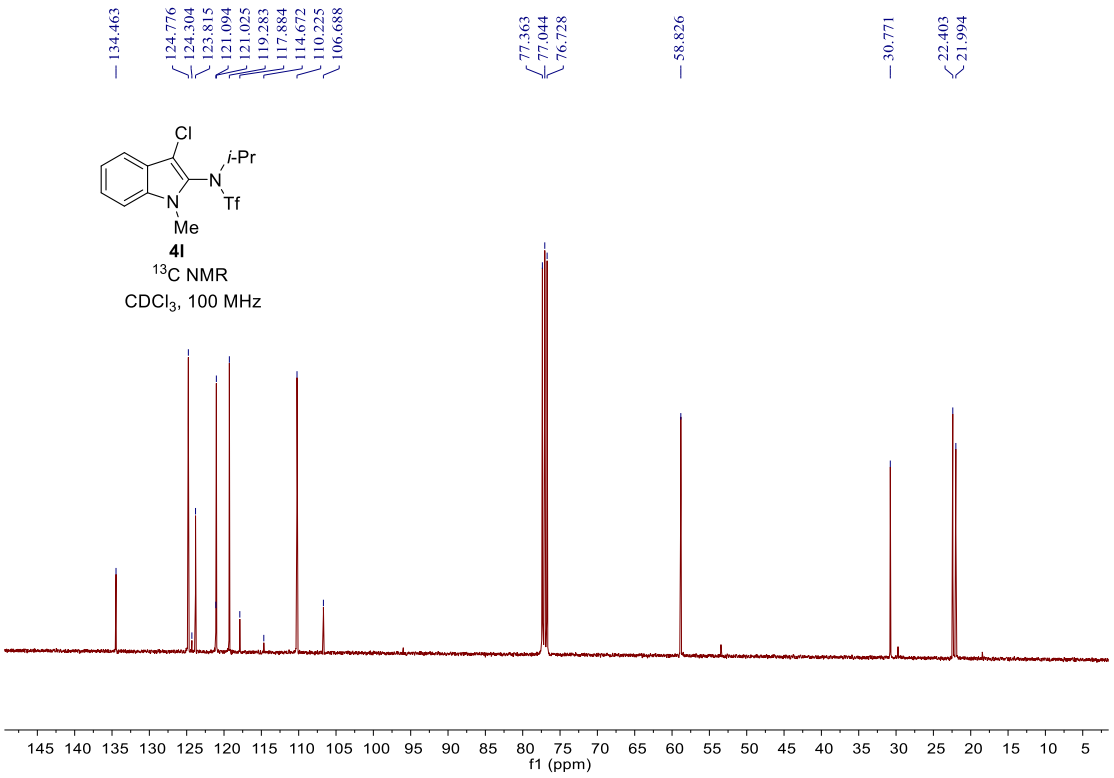

7.651
7.631
7.385
7.366
7.347
7.336
7.317
7.252
7.232
7.212
3.936
3.902
3.886
3.876
3.861
3.850
3.837
3.803
3.720
1.638
1.631
1.623
1.615
1.607
1.599
1.497
1.493
1.486
1.482
1.470
1.460
1.450
1.446
1.286
1.281
1.275
1.270
1.263
1.257
0.867
0.857
0.851
0.842
0.833
Cl
N
Tf
Me
4k
1H NMR
CDCl3, 400 MHz
0.95
1.97
1.06
2.05
3.00
1.10
1.12
4.11
3.13
f1 (ppm)


-74.162
Cl
N
Tf
N
Me
4k
19F NMR
CDCl3, 376 MHz
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


133.956
126.564
124.733
124.551
123.603
121.512
121.016
118.918
118.292
115.077
110.199
103.803
77.356
77.039
76.719
53.591
30.153
28.606
28.397
22.160
13.847
Cl
N
Tf
N
Me
4k
13C NMR
CDCl3, 100 MHz
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.674
7.654
7.384
7.381
7.377
7.363
7.361
7.345
7.342
7.340
7.324
7.321
7.264
7.260
7.247
7.244
7.240
7.227
7.224
4.674
4.657
4.640
4.624
4.607
3.706
1.430
1.413
1.293
1.276
Cl
i-Pr
N
Tf
N
Me
4l
1H NMR
CDCl3, 400 MHz
0.96
1.98
1.09
0.99
3.00
3.04
3.13
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)

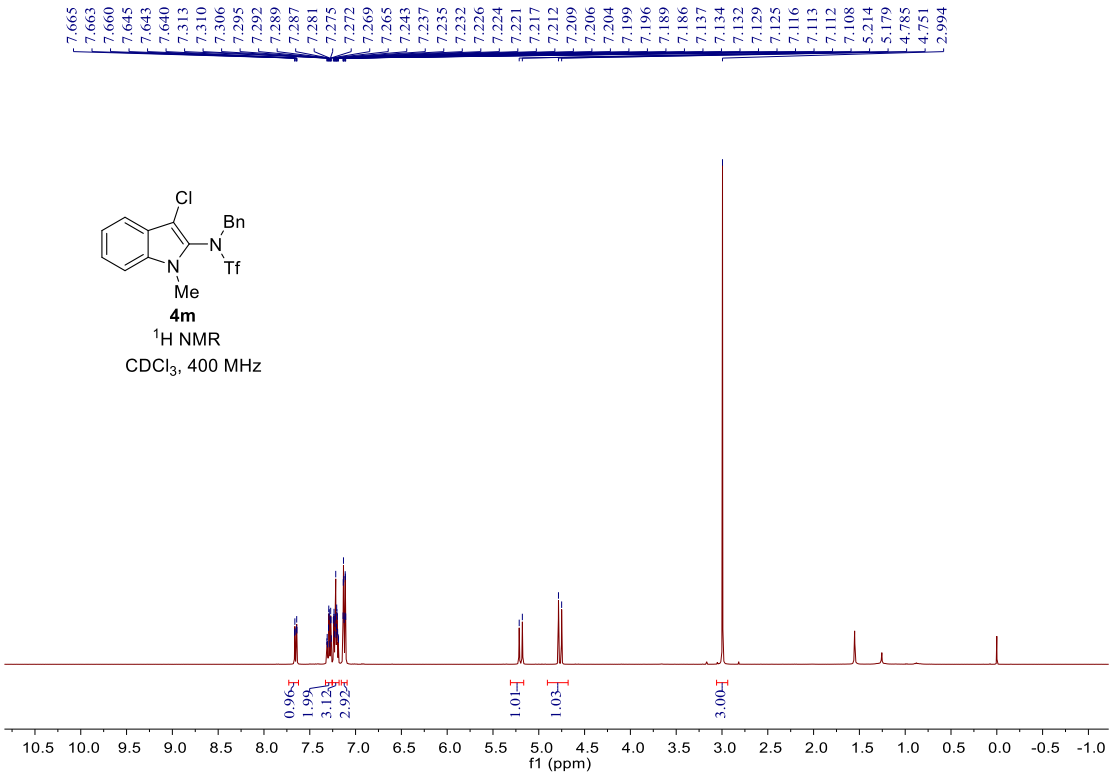

-75.019
Cl
i-Pr
N
Tf
N
Me
4l
19F NMR
CDCl3, 376 MHz
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)



4l

^{13}C NMR

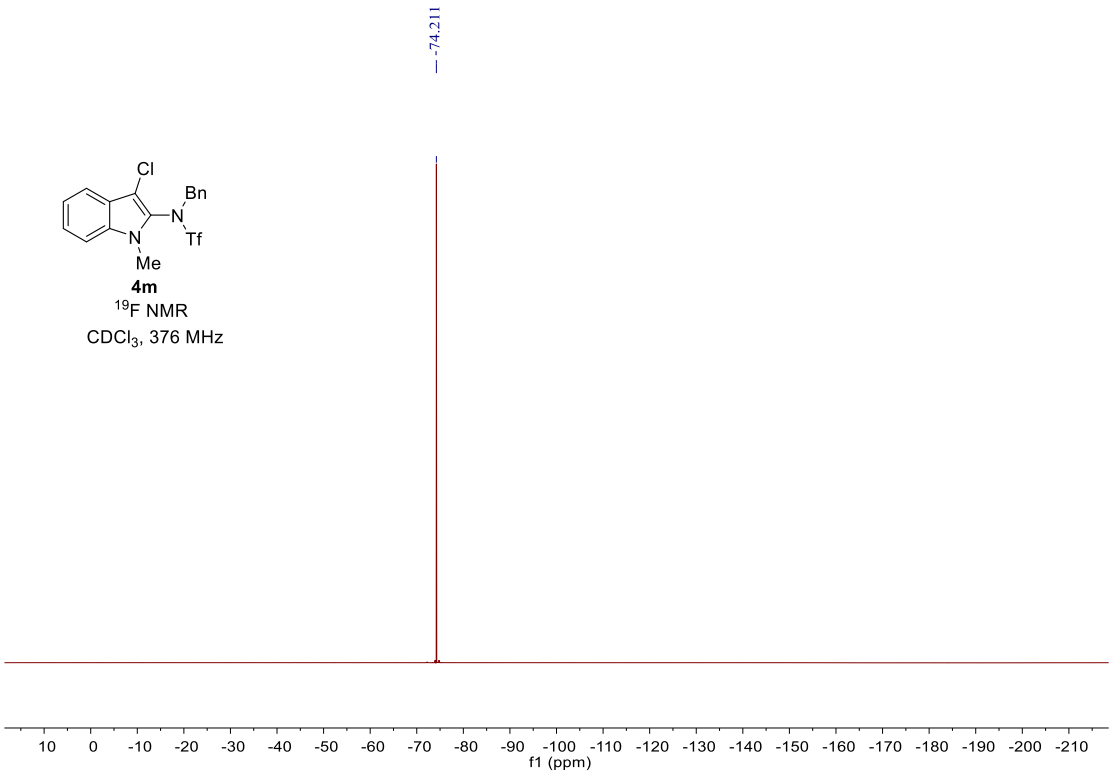
$CDCl_3$, 100 MHz

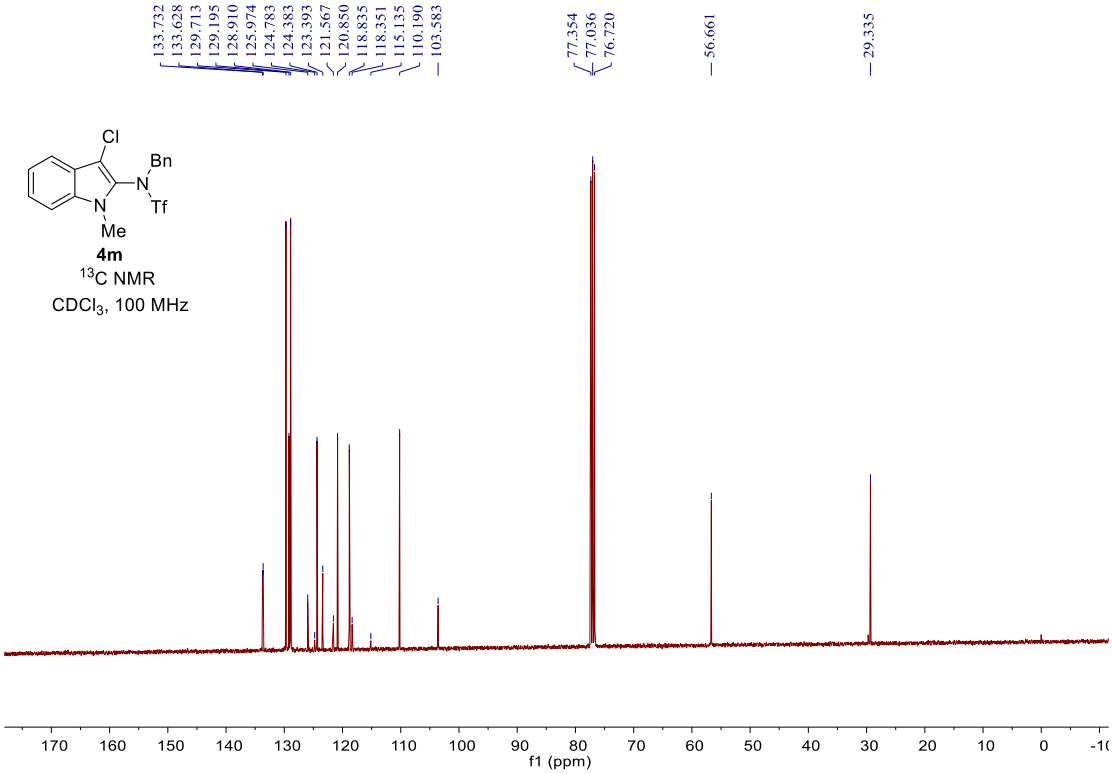


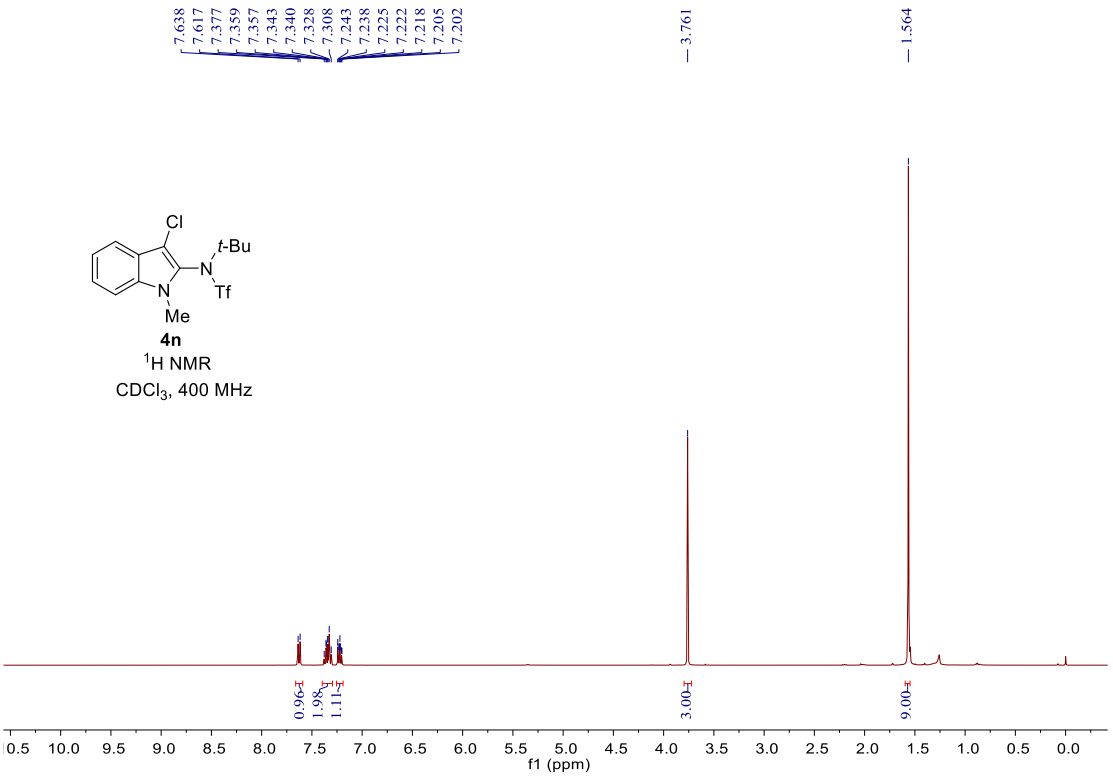
4m

^{1}H NMR

$CDCl_3$, 400 MHz


-74.211
Cl
Bn
N
N
Tf
Me
4m
19F NMR
CDCl3, 376 MHz
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

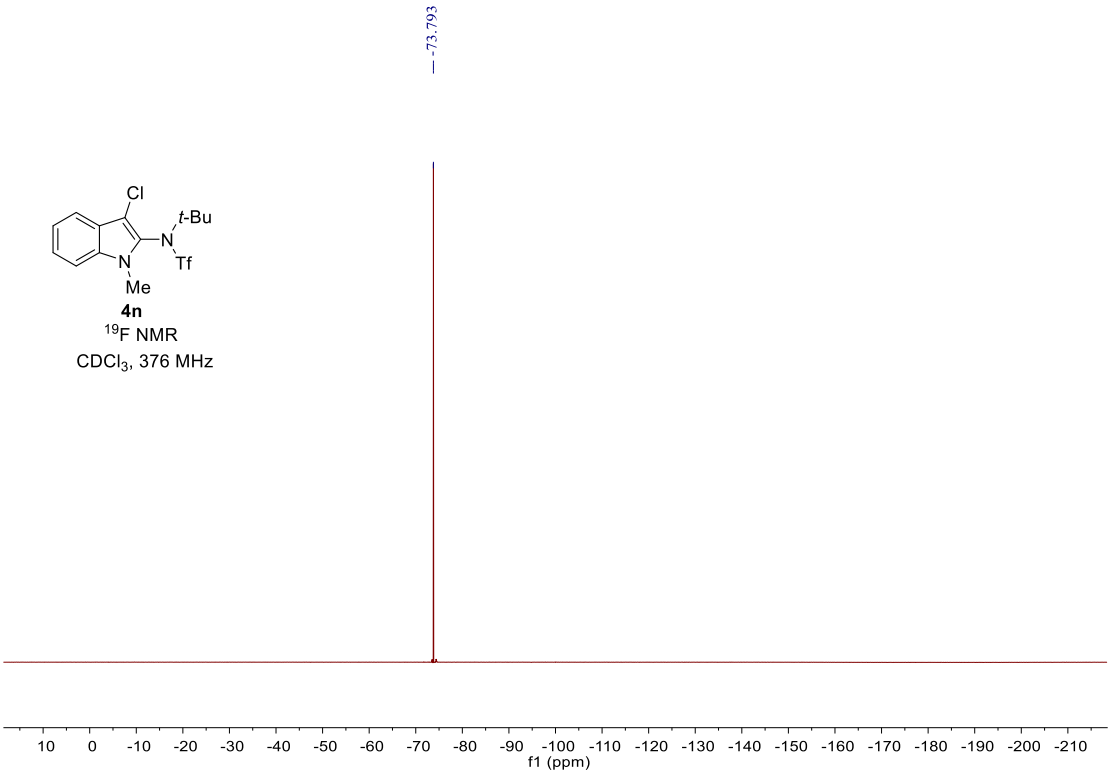

133.732
133.628
129.713
129.195
128.910
125.974
124.783
124.383
123.393
121.567
120.850
118.835
118.351
115.135
110.190
103.583
77.354
77.036
76.720
56.661
29.335
Cl
Bn
N
N
Tf
Me
4m
13C NMR
CDCl3, 100 MHz
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



4n

^{1}H NMR

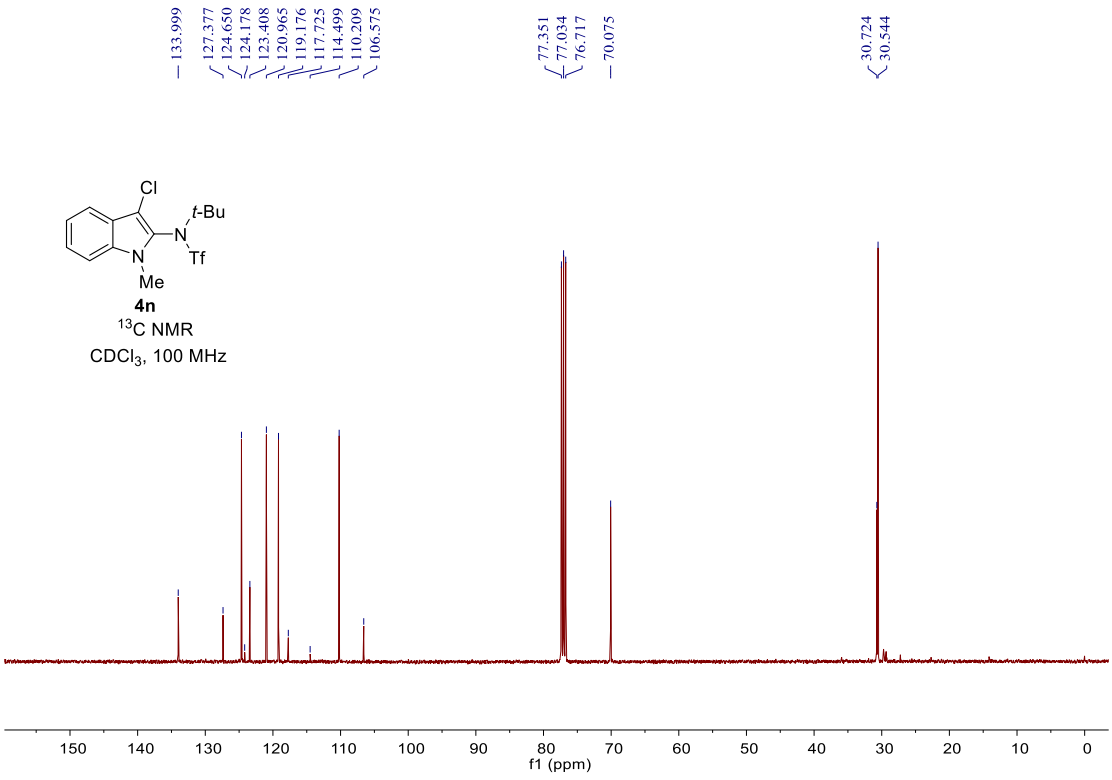
$CDCl_3$, 400 MHz

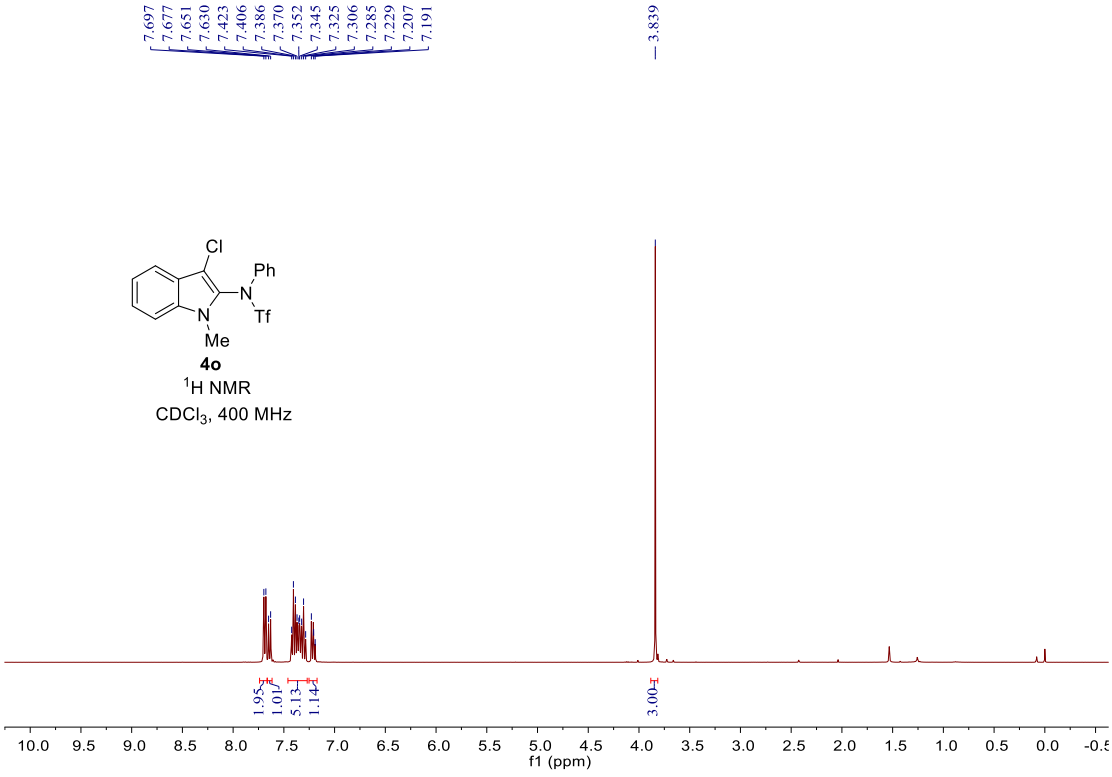


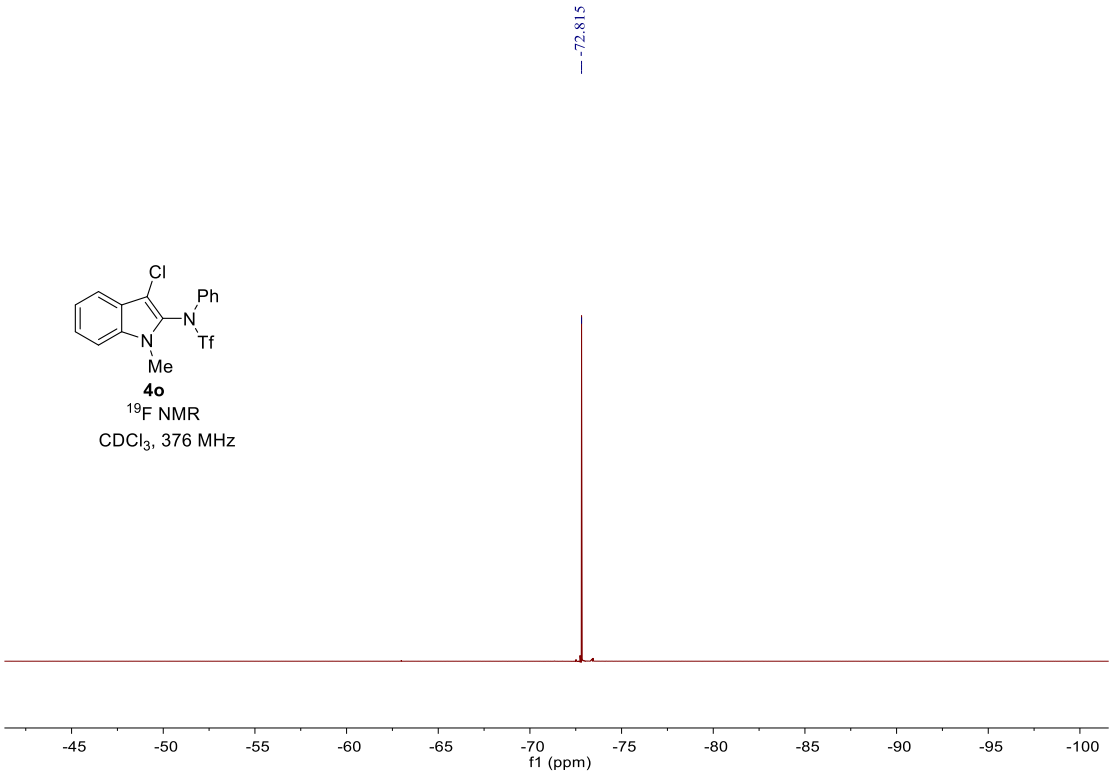
4n

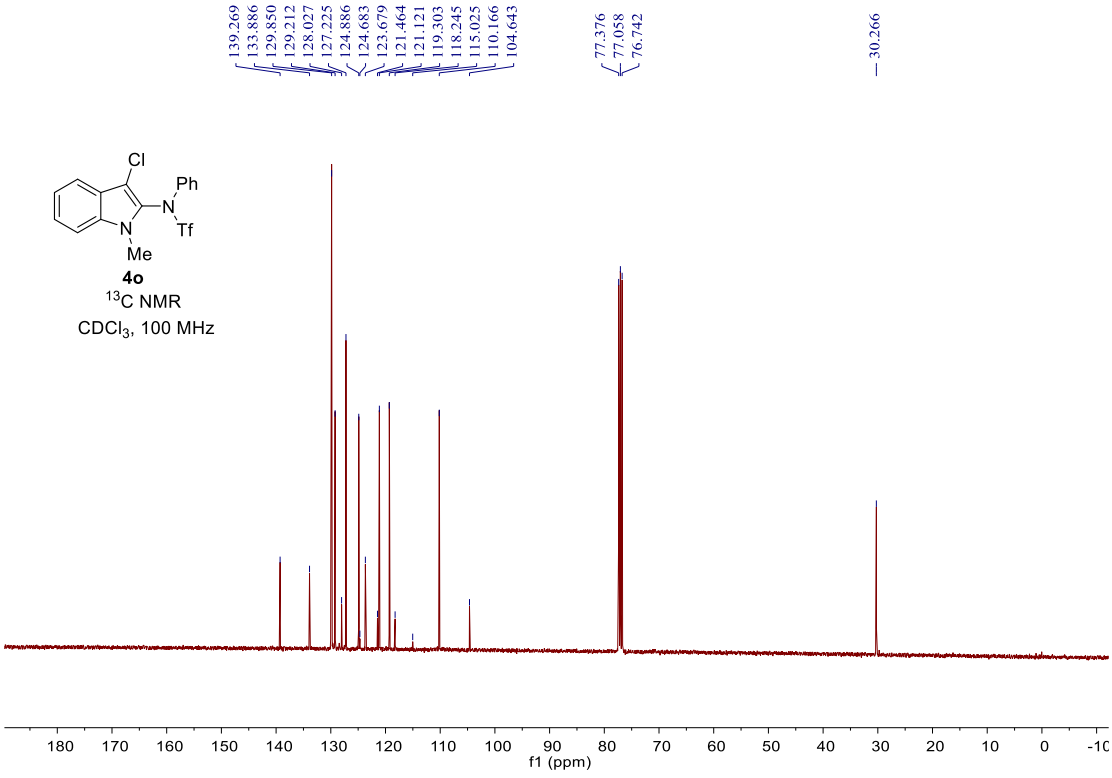
^{19}F NMR

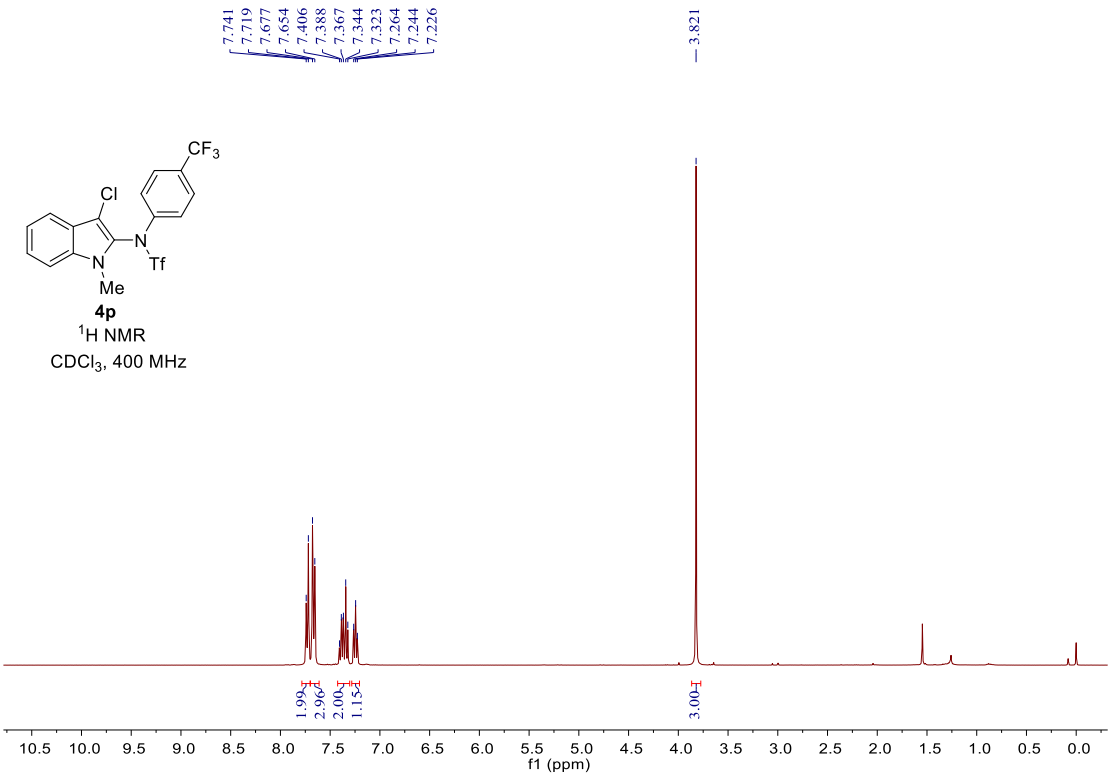
$CDCl_3$, 376 MHz

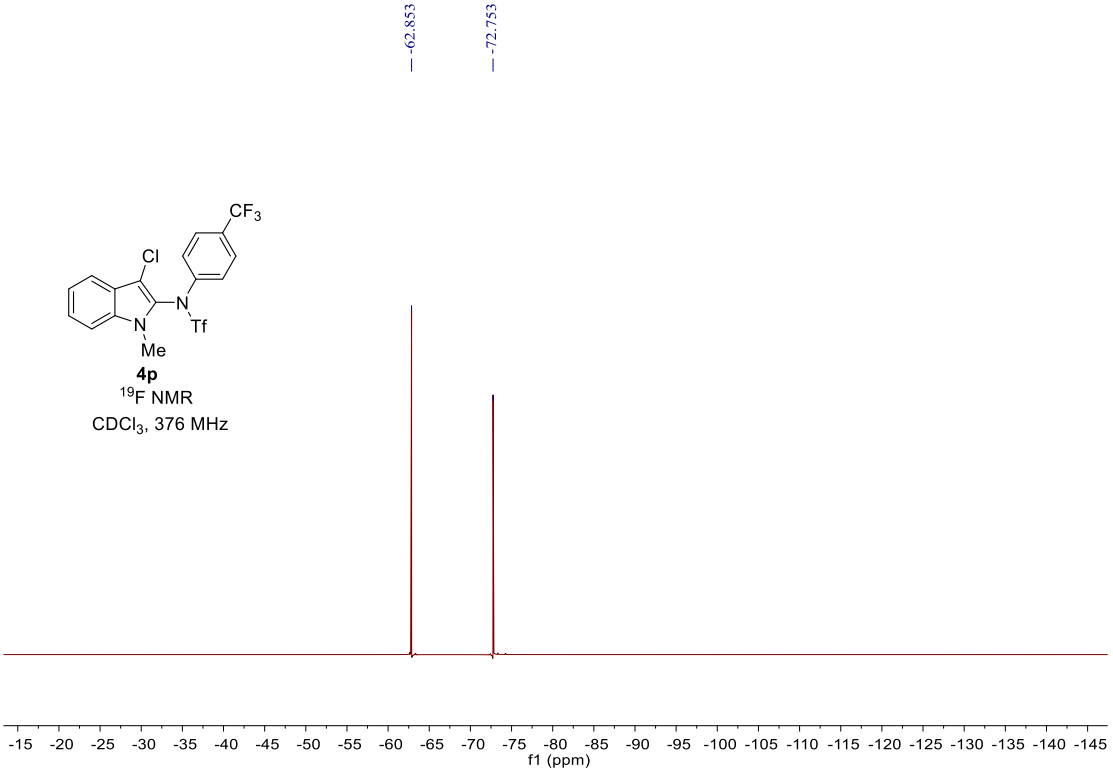

133.999
127.377
124.650
124.178
123.408
120.965
119.176
117.725
114.499
110.209
106.575
77.351
77.034
76.717
70.075
30.724
30.544
Cl
t-Bu
N
Tf
N
Me
4n
13C NMR
CDCl3, 100 MHz
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

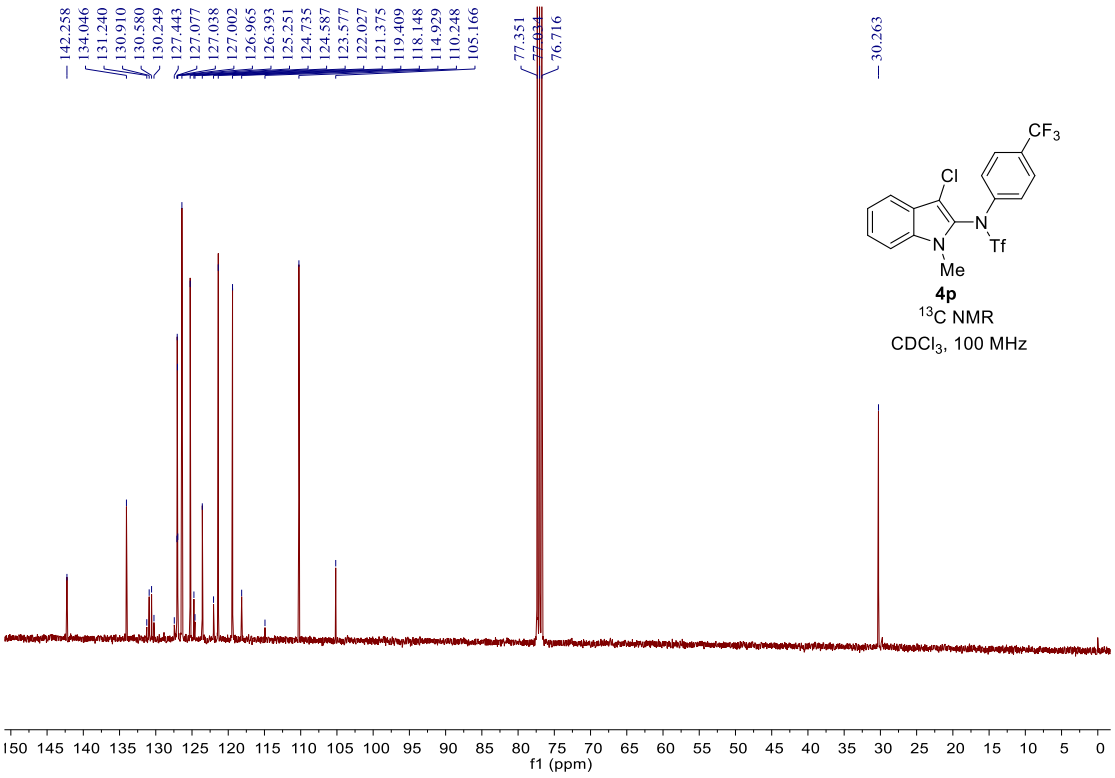

7.697
7.677
7.651
7.630
7.423
7.406
7.386
7.370
7.352
7.345
7.325
7.306
7.285
7.229
7.207
7.191
3.839
Cl
Ph
N
Tf
N
Me
4o
1H NMR
CDCl3, 400 MHz
1.95
1.01
5.13
1.14
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


-72.815
Cl
Ph
N
Tf
N
Me
4o
19F NMR
CDCl3, 376 MHz
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
f1 (ppm)


139.269
133.886
129.850
129.212
128.027
127.225
124.886
124.683
123.679
121.464
121.121
119.303
118.245
115.025
110.166
104.643
77.376
77.058
76.742
30.266
Cl
Ph
N
Tf
N
Me
4o
13C NMR
CDCl3, 100 MHz
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.741
7.719
7.677
7.654
7.406
7.388
7.367
7.344
7.323
7.264
7.244
7.226
3.821
CF3
Cl
N
Tf
N
Me
4p
1H NMR
CDCl3, 400 MHz
1.99
2.96
2.00
1.15
3.00
10.5 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)

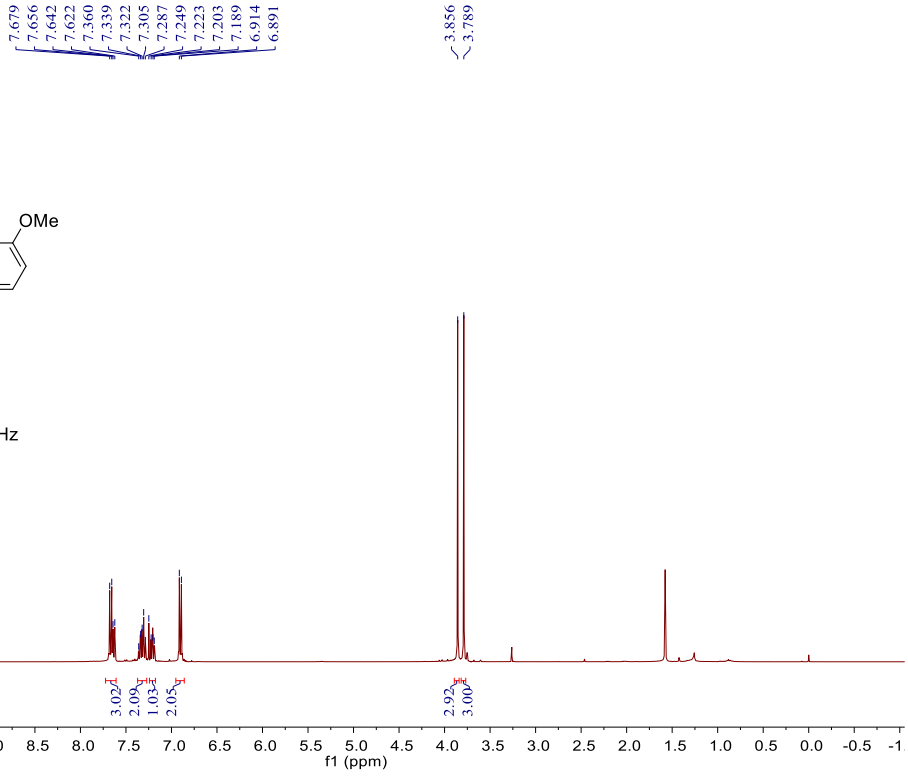

-62.853
-72.753
CF3
Cl
N
Tf
N
Me
4p
19F NMR
CDCl3, 376 MHz
-15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145
f1 (ppm)



4p

^{13}C NMR

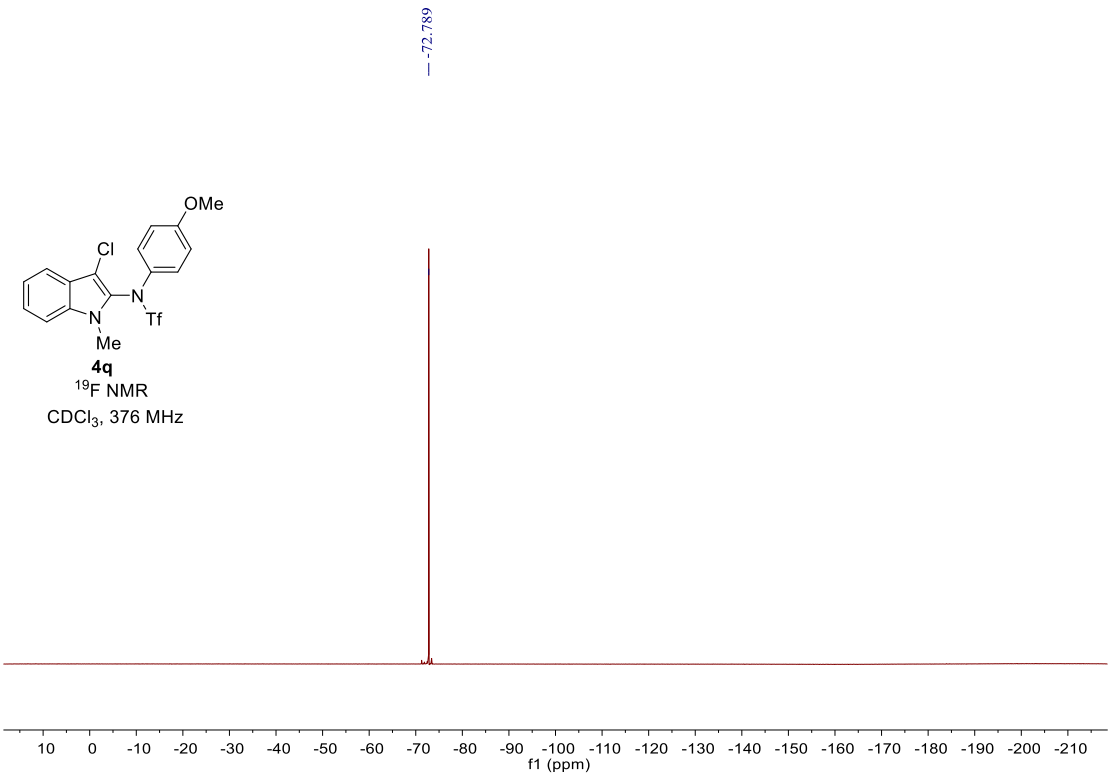
$CDCl_3$, 100 MHz

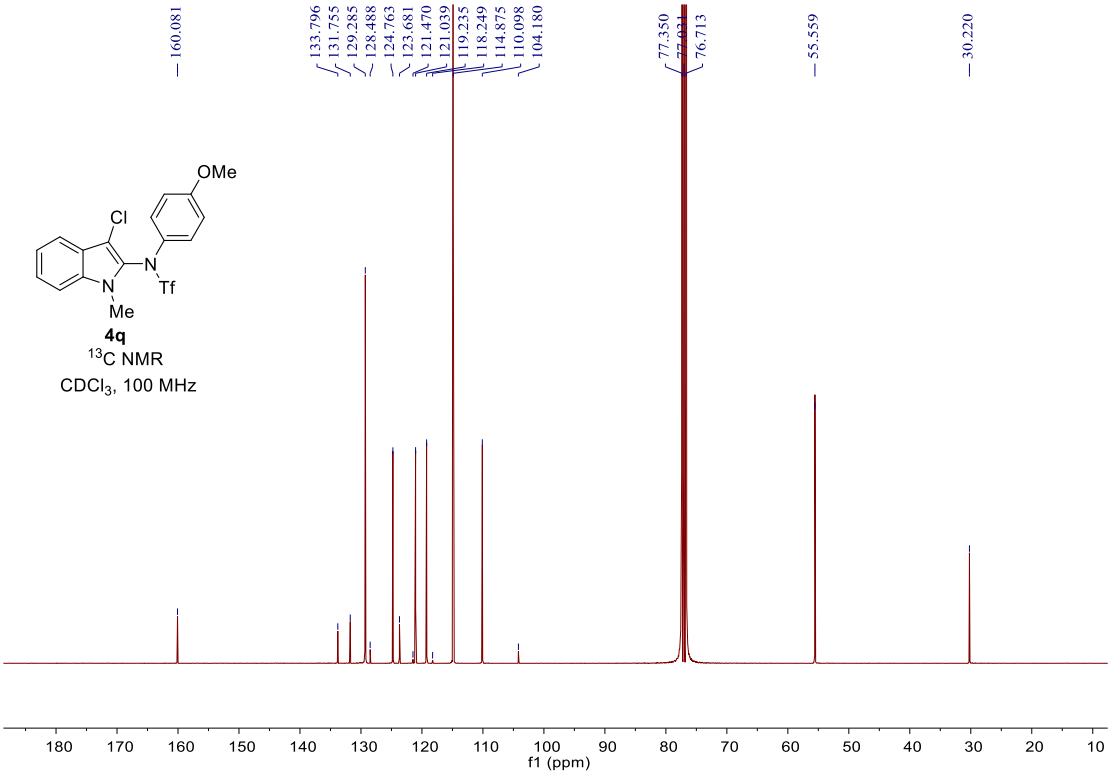


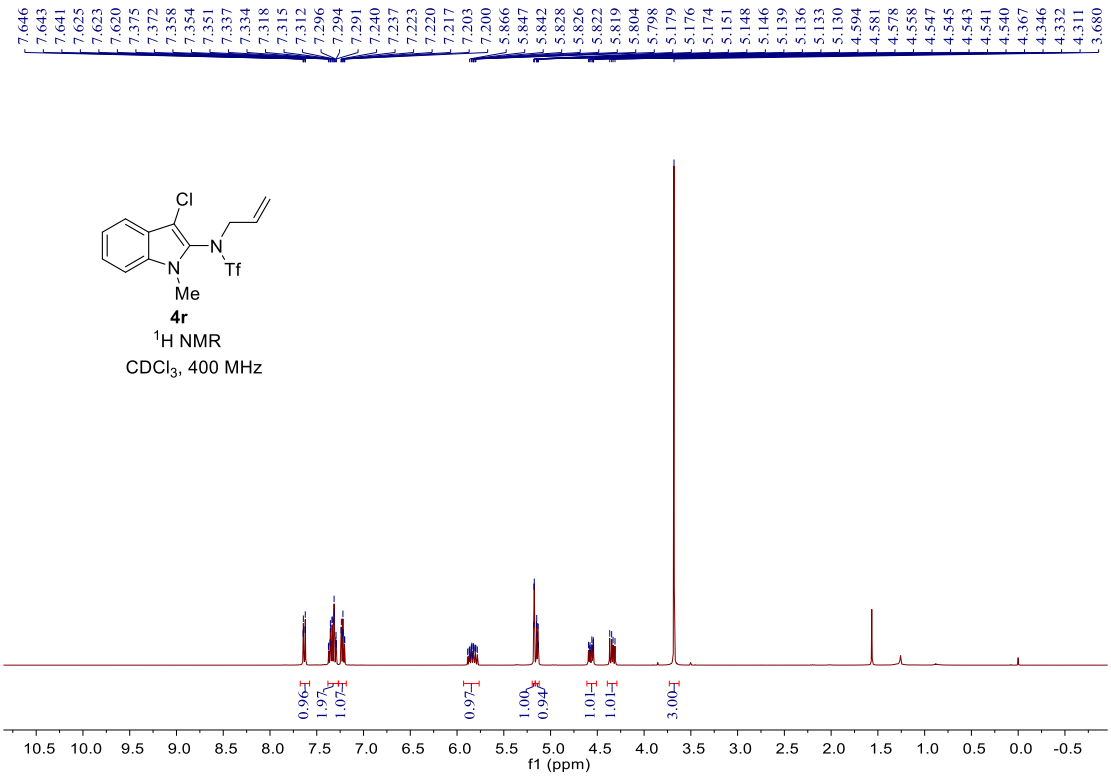
4q

^{1}H NMR

$CDCl_3$, 400 MHz


-72.789
OMe
Cl
N
Tf
N
Me
4q
19F NMR
CDCl3, 376 MHz
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


160.081
133.796
131.755
129.285
128.488
124.763
123.681
121.470
121.039
119.235
118.249
114.875
110.098
104.180
77.350
77.031
76.713
55.559
30.220
OMe
Cl
N
Tf
N
Me
4q
13C NMR
CDCl3, 100 MHz
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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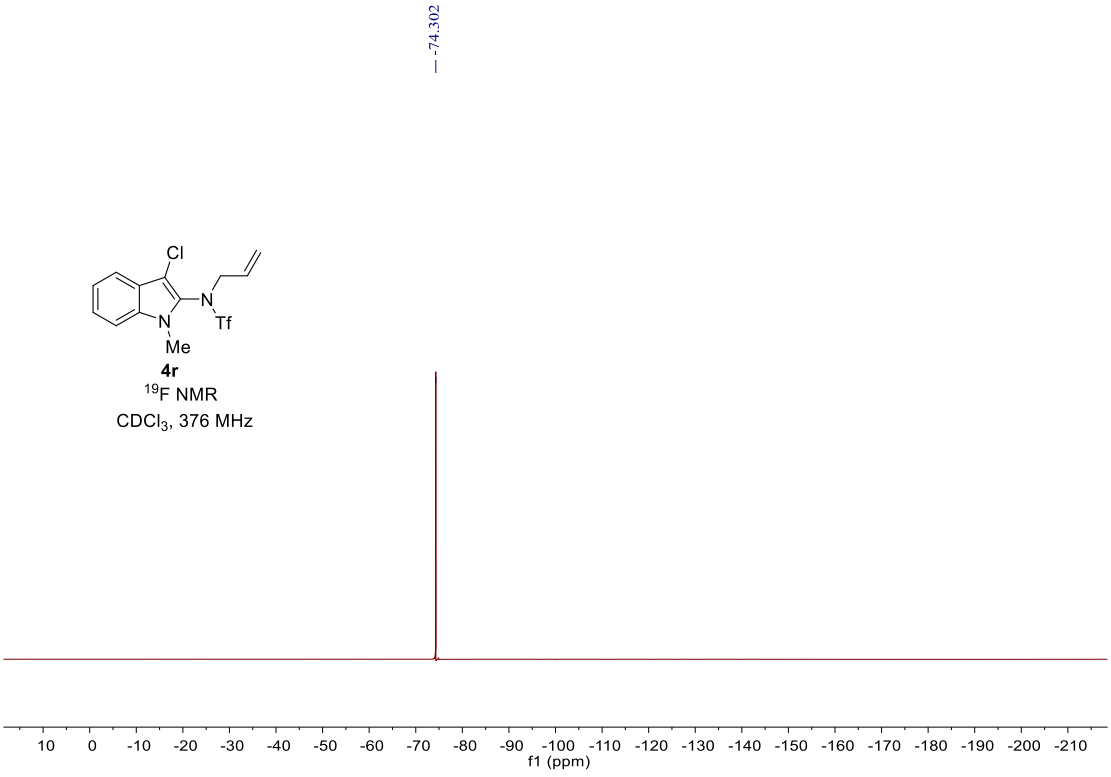
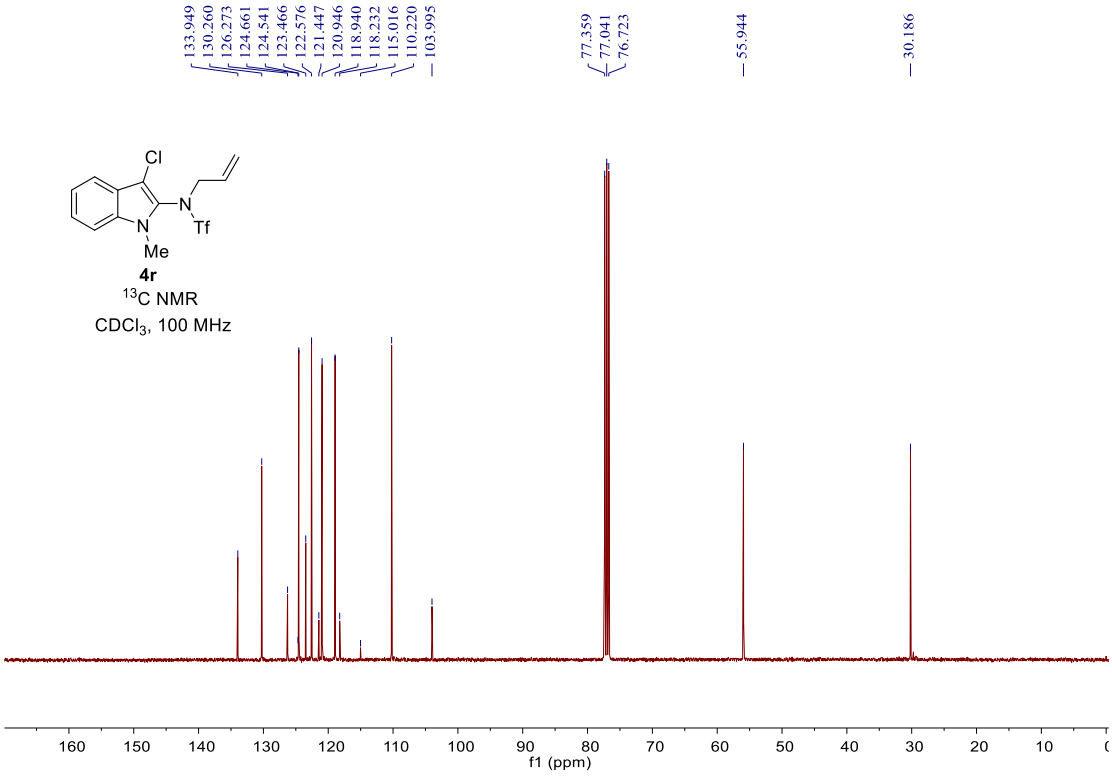
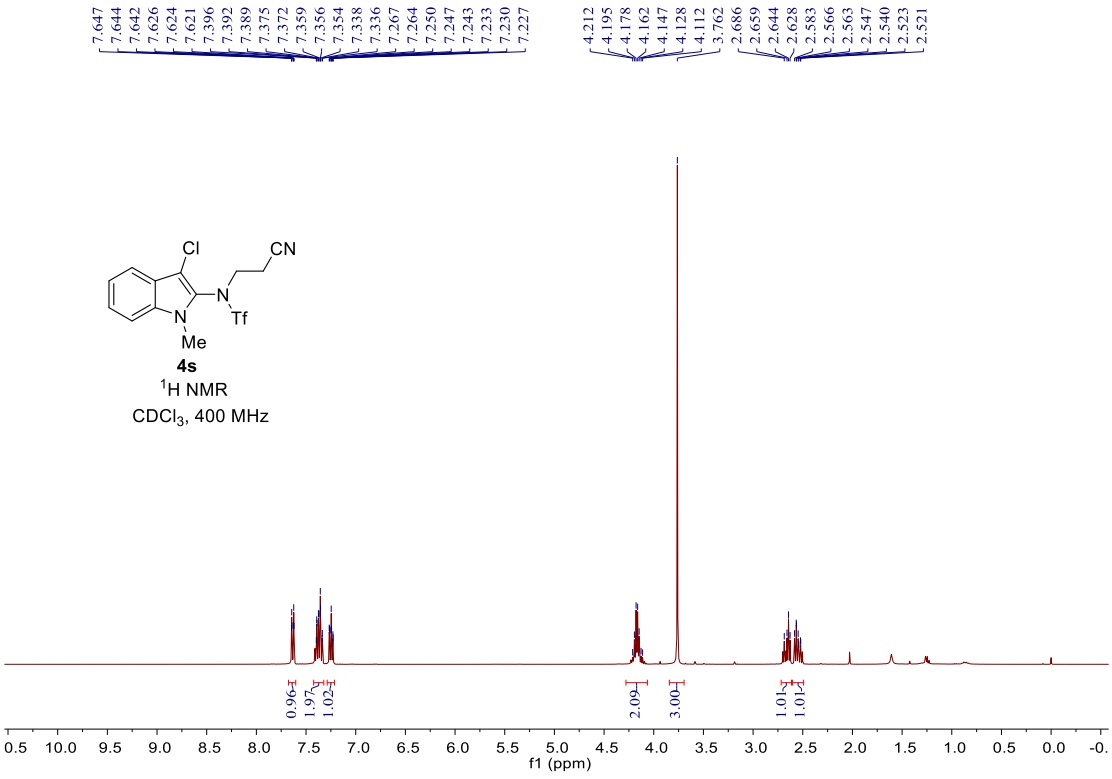
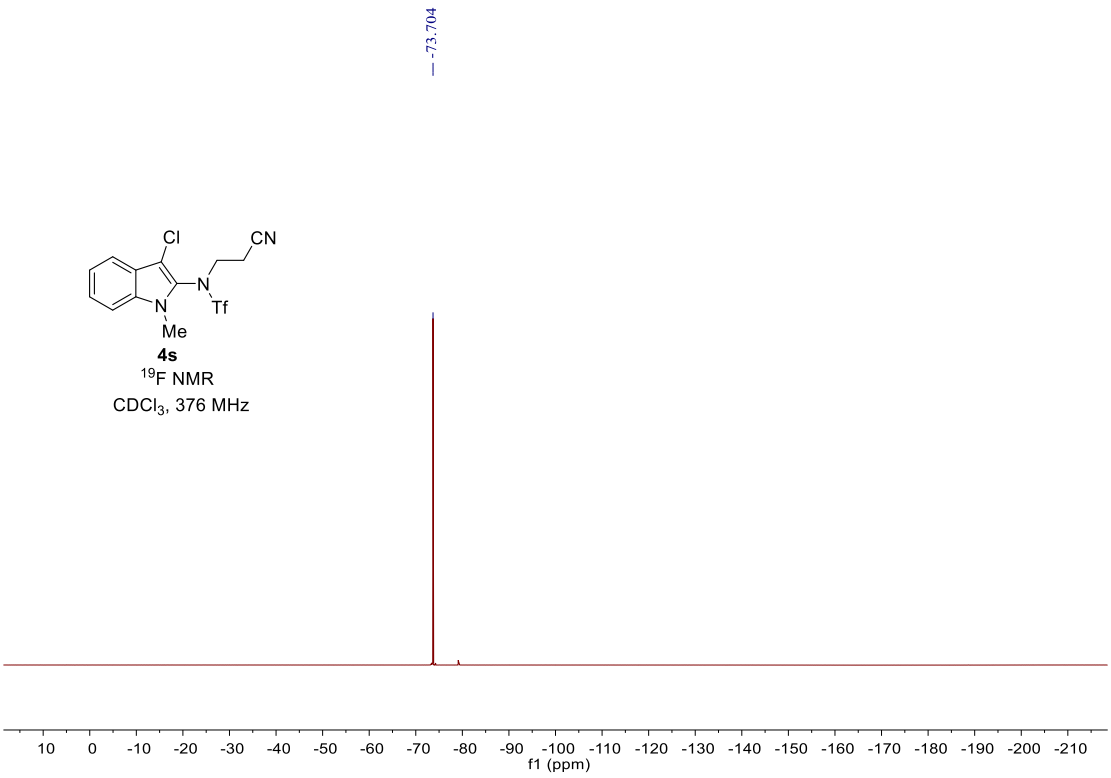
7.643
7.641
7.625
7.623
7.620
7.375
7.372
7.358
7.354
7.351
7.337
7.334
7.318
7.315
7.312
7.296
7.294
7.291
7.240
7.237
7.223
7.220
7.217
7.203
7.200
5.866
5.847
5.842
5.828
5.826
5.822
5.819
5.804
5.798
5.179
5.176
5.174
5.151
5.148
5.146
5.139
5.136
5.133
5.130
4.594
4.581
4.578
4.558
4.547
4.545
4.543
4.541
4.540
4.367
4.346
4.332
4.311
3.680
Cl
N
Tf
N
Me
4r
1H NMR
CDCl3, 400 MHz
0.96
1.97
1.07
0.97
1.00
0.94
1.01
1.01
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


-74.302
Cl
N
Tf
N
Me
4r
19F NMR
CDCl3, 376 MHz
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


133.949
130.260
126.273
124.661
124.541
123.466
122.576
121.447
120.946
118.940
118.232
115.016
110.220
103.995
77.359
77.041
76.723
55.944
30.186
Cl
N
Tf
N
Me
4r
13C NMR
CDCl3, 100 MHz
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

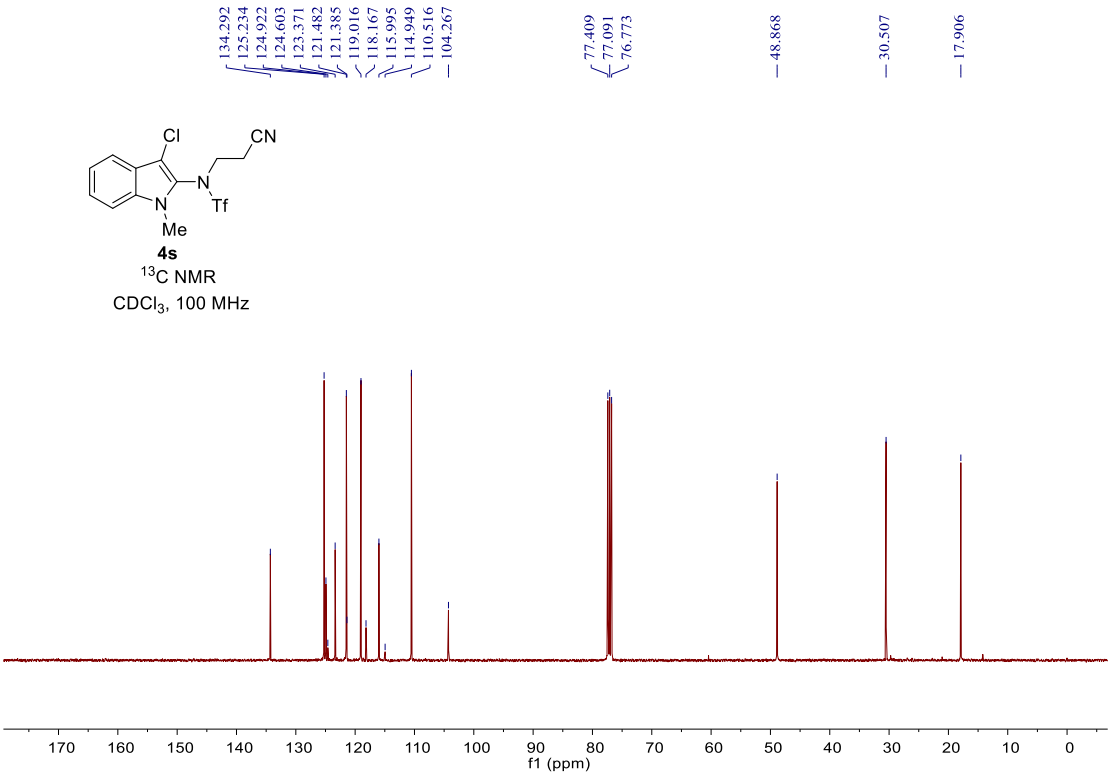

7.647
7.644
7.642
7.626
7.624
7.621
7.396
7.392
7.389
7.375
7.372
7.359
7.356
7.354
7.338
7.336
7.267
7.264
7.250
7.247
7.243
7.233
7.230
7.227
4.212
4.195
4.178
4.162
4.147
4.128
4.112
3.762
2.686
2.659
2.644
2.628
2.583
2.566
2.563
2.547
2.540
2.523
2.521
Cl
CN
N
Tf
N
Me
4s
1H NMR
CDCl3, 400 MHz
0.96
1.97
1.02
2.09
3.00
1.01
1.01
0.5 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)



4s

^{19}F NMR

$CDCl_3$, 376 MHz



4s

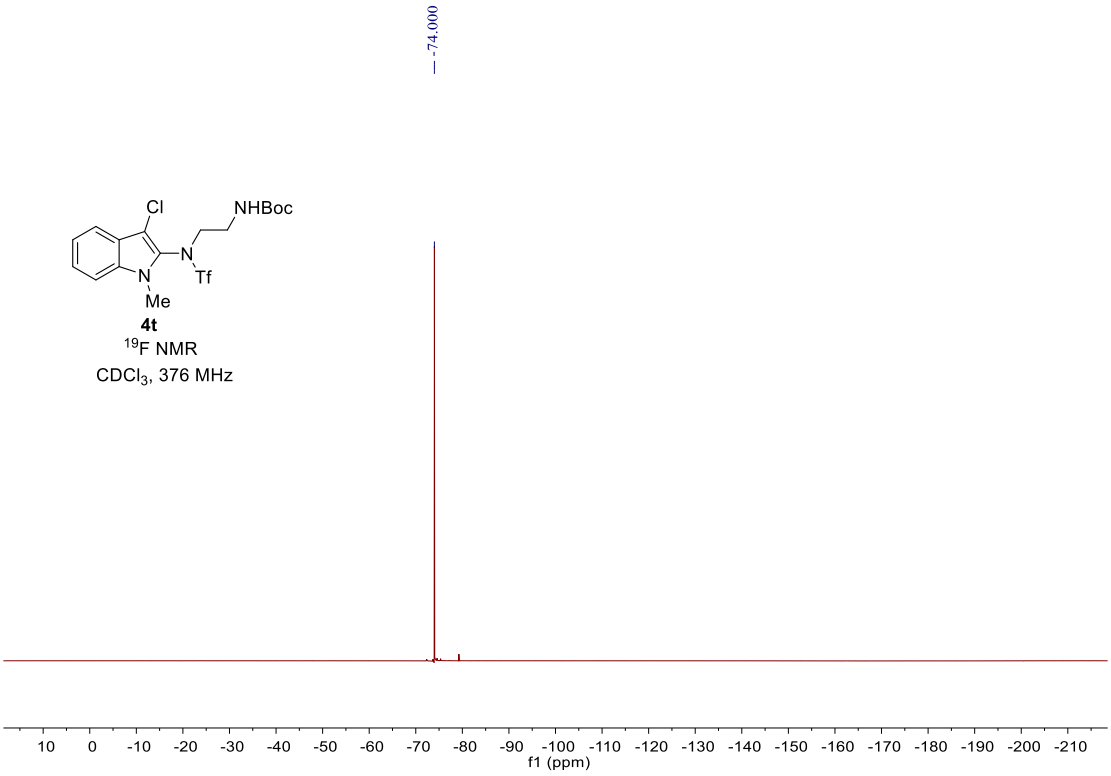
^{13}C NMR

$CDCl_3$, 100 MHz

4t

^{19}F NMR

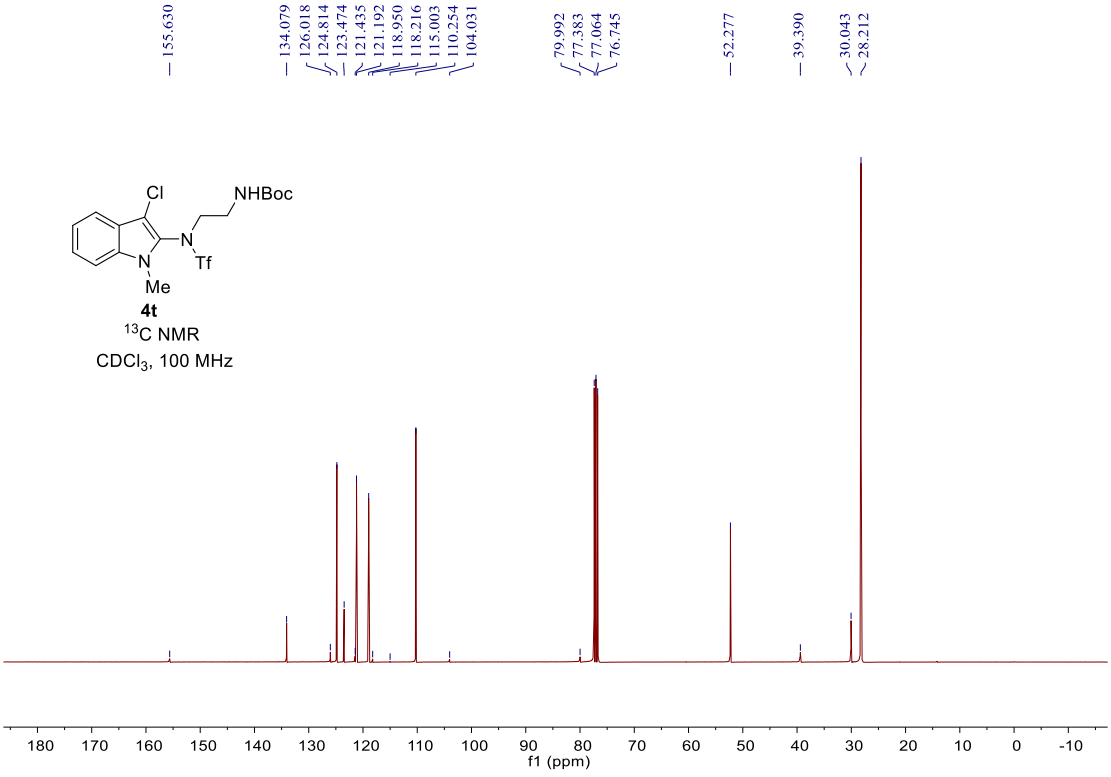
$CDCl_3$, 376 MHz

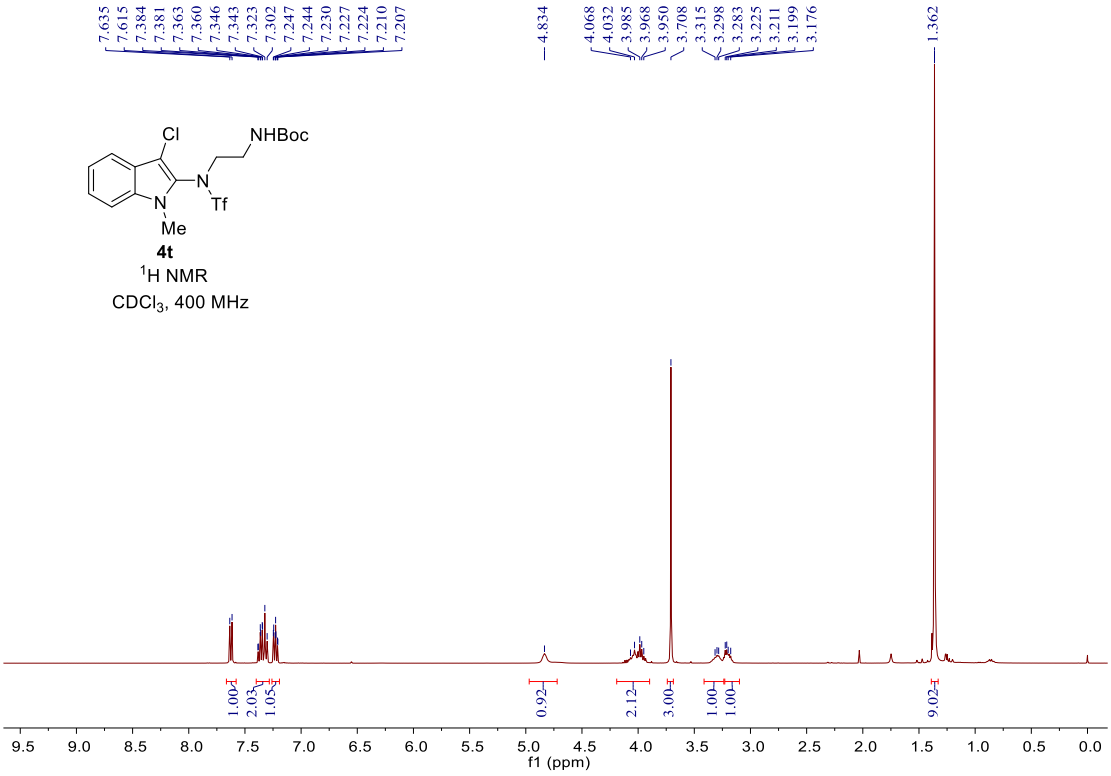


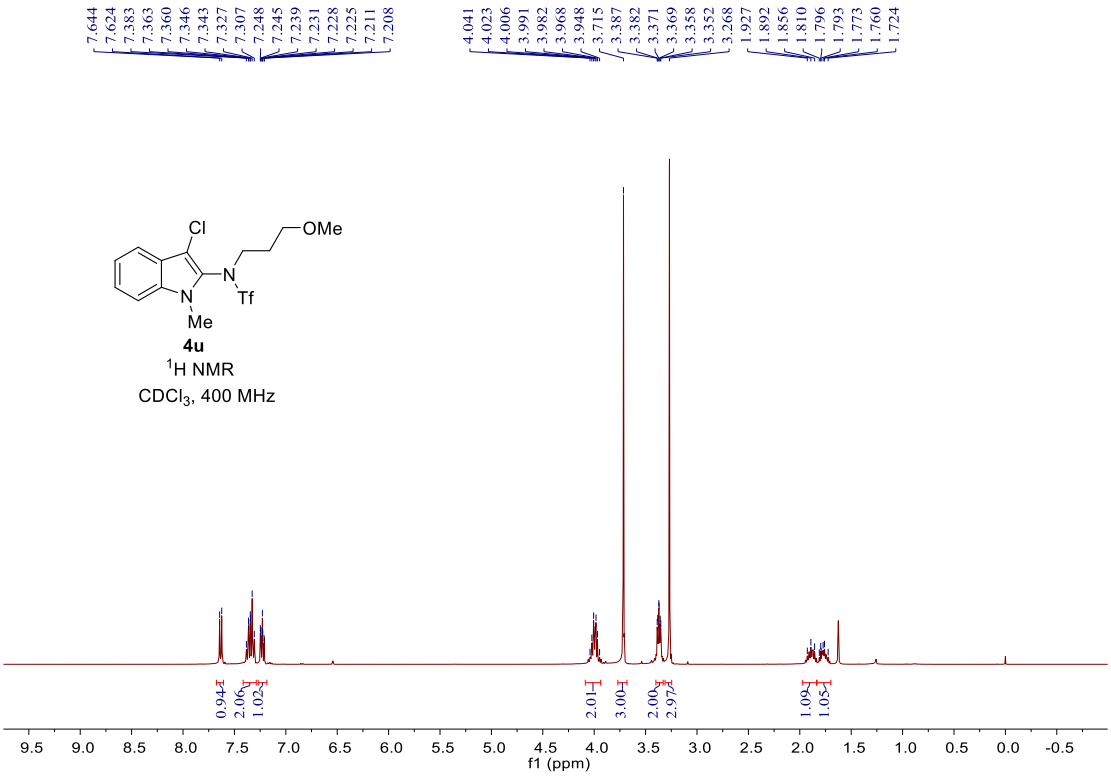
4t

^{13}C NMR

$CDCl_3$, 100 MHz



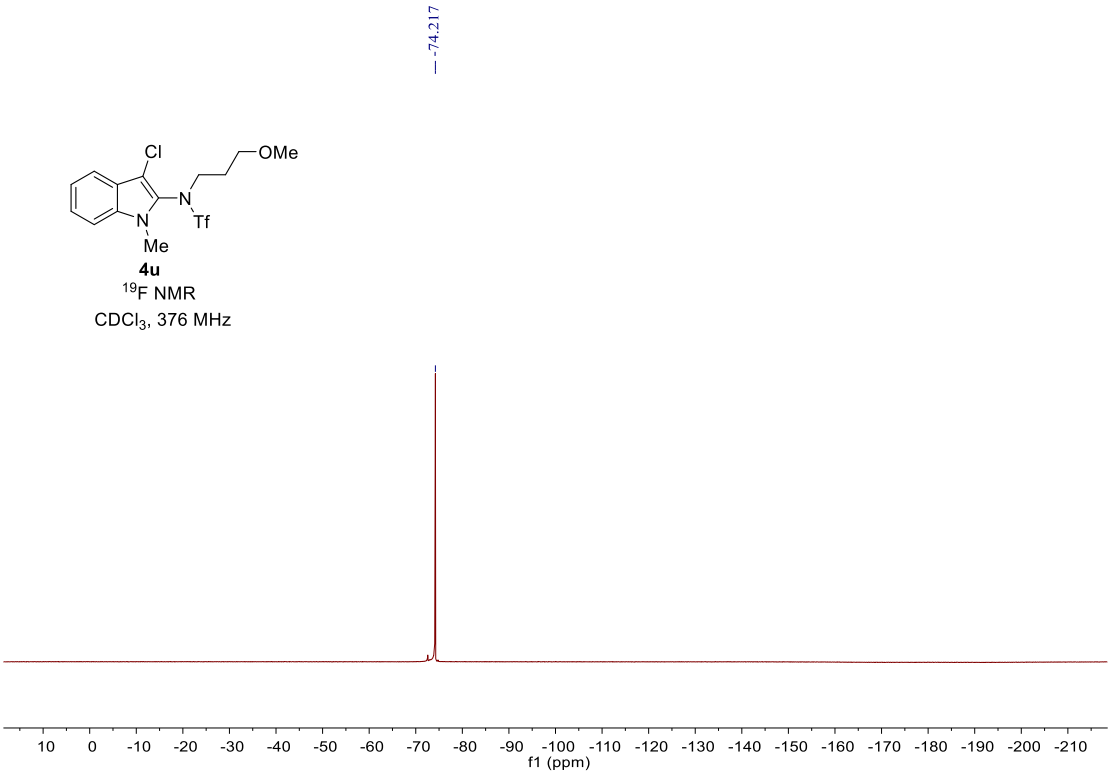

7.635
7.615
7.384
7.381
7.363
7.360
7.346
7.343
7.323
7.302
7.247
7.244
7.230
7.227
7.224
7.210
7.207
4.834
4.068
4.032
3.985
3.968
3.950
3.708
3.315
3.298
3.283
3.225
3.211
3.199
3.176
1.362
Cl
NHBoc
N
Tf
N
Me
4t
1H NMR
CDCl3, 400 MHz
1.00
2.03
1.05
0.92
2.12
3.00
1.00
1.00
9.02
f1 (ppm)


7.644
7.624
7.383
7.363
7.360
7.346
7.343
7.327
7.307
7.248
7.245
7.239
7.231
7.228
7.225
7.211
7.208
4.041
4.023
4.006
3.991
3.982
3.968
3.948
3.715
3.387
3.382
3.371
3.369
3.358
3.352
3.268
1.927
1.892
1.856
1.810
1.796
1.793
1.773
1.760
1.724
Cl
OMe
N
Tf
N
Me
4u
1H NMR
CDCl3, 400 MHz
0.94
2.06
1.02
2.01
3.00
2.00
2.97
1.09
1.05
f1 (ppm)

4u

^{19}F NMR

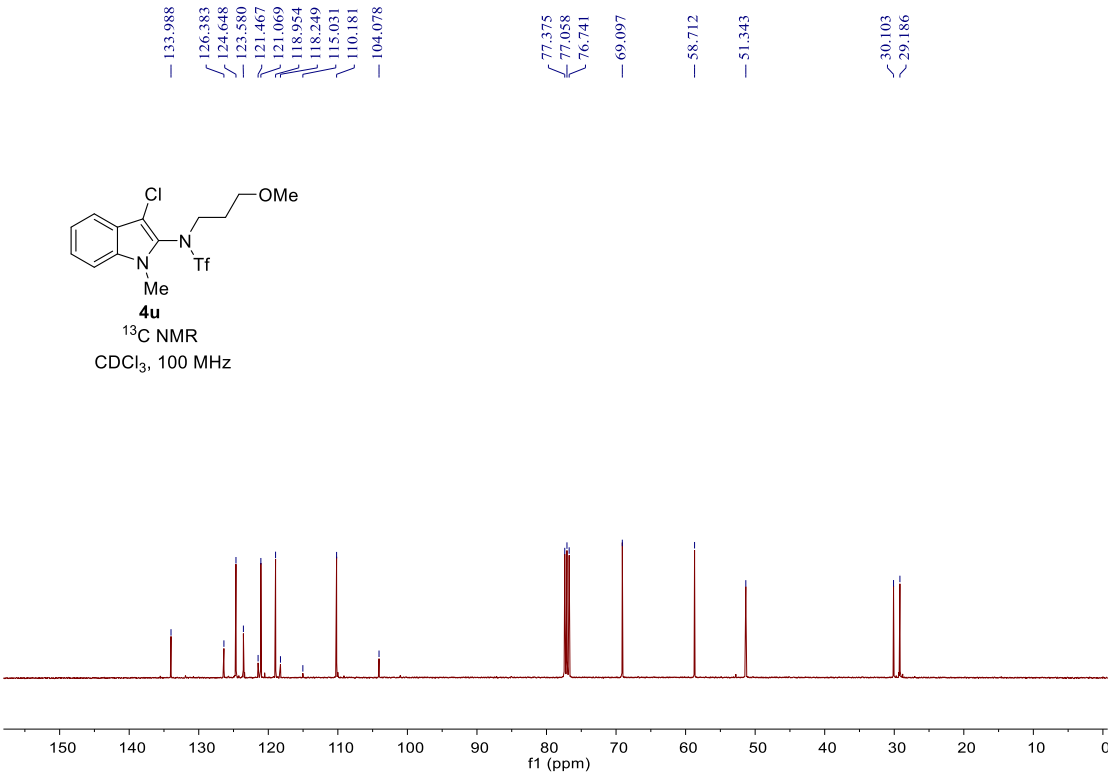
$CDCl_3$, 376 MHz

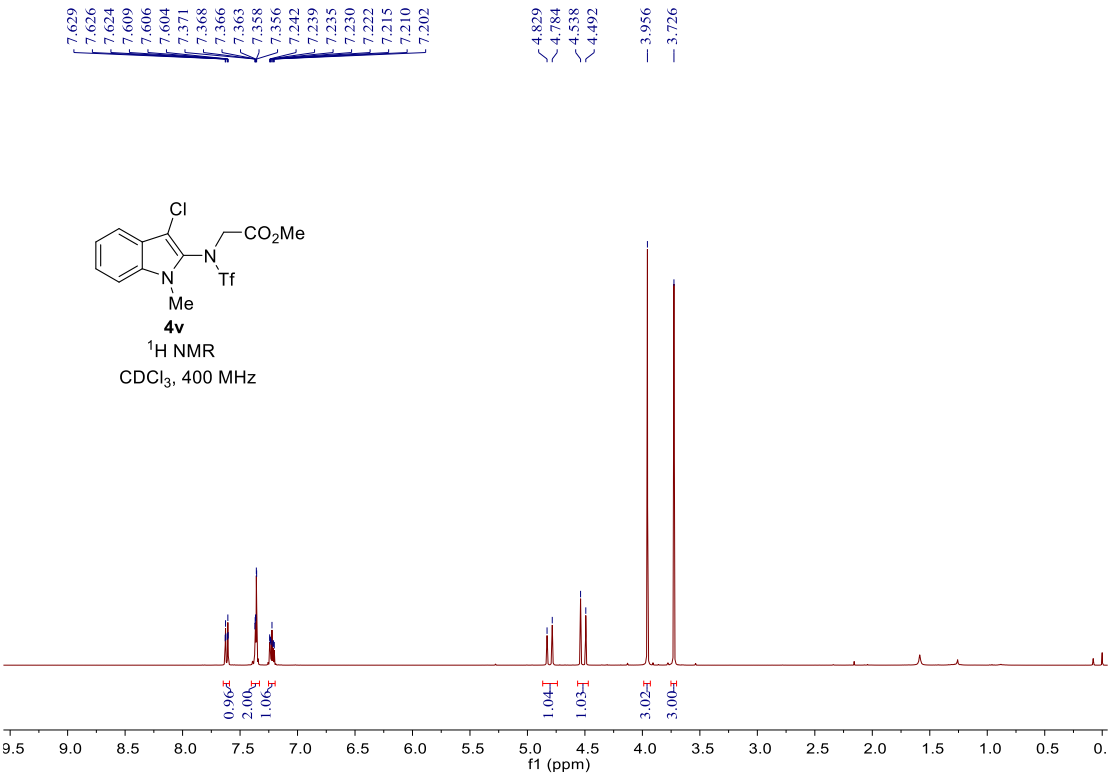


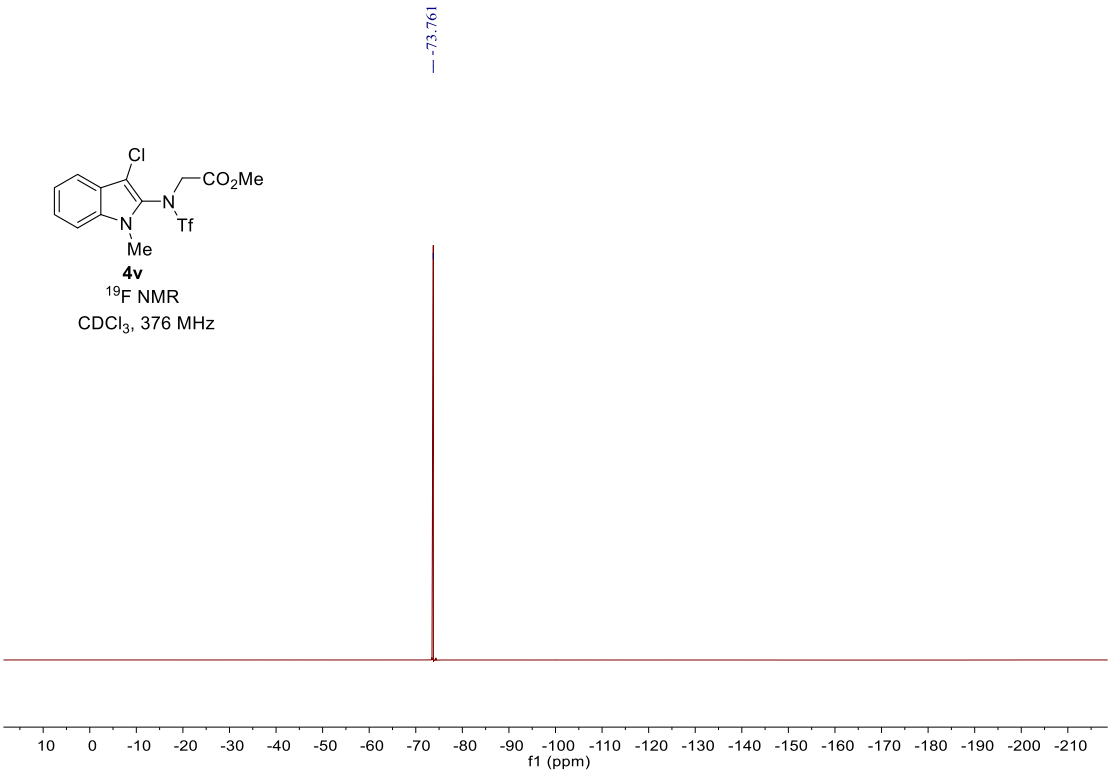
4u

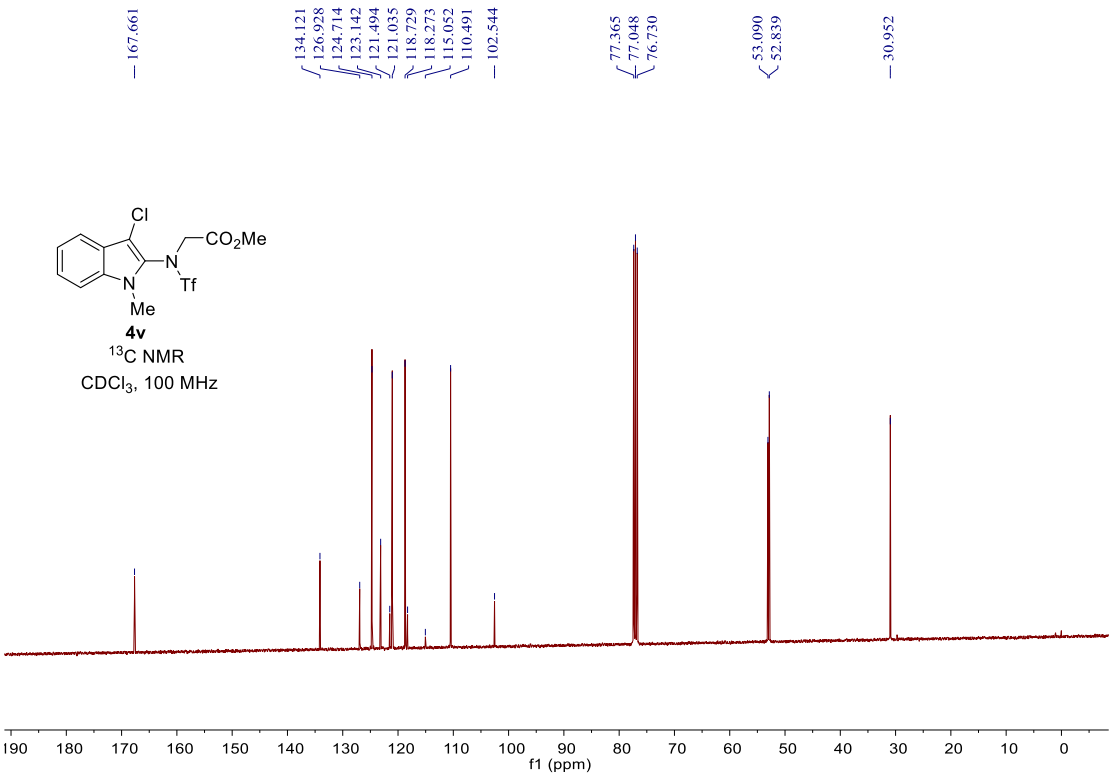
^{13}C NMR

$CDCl_3$, 100 MHz




7.629
7.626
7.624
7.609
7.606
7.604
7.371
7.368
7.366
7.363
7.358
7.356
7.242
7.239
7.235
7.230
7.222
7.215
7.210
7.202
4.829
4.784
4.538
4.492
3.956
3.726
Cl
CO2Me
N
Tf
N
Me
4v
1H NMR
CDCl3, 400 MHz
0.96
2.00
1.06
1.04
1.03
3.02
3.00
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.
f1 (ppm)


-73.761
Cl
CO2Me
N
Tf
N
Me
4v
19F NMR
CDCl3, 376 MHz
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


167.661
134.121
126.928
124.714
123.142
121.494
121.035
118.729
118.273
115.052
110.491
102.544
77.365
77.048
76.730
53.090
52.839
30.952
Cl
CO2Me
N
Tf
N
Me
4v
13C NMR
CDCl3, 100 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)