Supporting Information

Divergent Construction of 3-(Indol-2-yl)succinimide/maleimide and Fused Benzodiazepine Skeletons from 2-(1*H*-Indol-1-yl)anilines and Maleimides

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I. General experimental information

Unless otherwise noted, all reagents including catalyst [Ru(*p*-cymene)Cl_2]$_2$ were purchased from commercial sources and used without further purification. 2-(1*H*-Indol-1-yl)anilines (**1**) were prepared based on literature procedures.[1] Melting points were recorded with a micro melting point apparatus and uncorrected. The ^{1}H NMR spectra were recorded at 400 MHz or 600 MHz. The ^{13}C NMR spectra were recorded at 100 MHz or 150 MHz. The ^{19}F NMR spectra were recorded at 376 MHz or 565 MHz. Chemical shifts were expressed in parts per million (δ), and were reported as s (singlet), d (doublet), t (triplet), dd (doublet of doublets), m (multiplet), br s (broad singlet), etc. The coupling constants J were given in Hz. High resolution mass spectra (HRMS) were obtained *via* ESI mode by using a MicrOTOF mass spectrometer. All reactions were monitored by thin layer chromatography (TLC) using silica gel plates (silica gel 60 F254 0.25 mm), and components were visualized by observation under UV light (254 and 365 nm).

II. Experimental procedures and spectroscopic data

1. Typical procedure for the synthesis of 3a and spectroscopic data of 3a-3v

To a reaction tube equipped with a stir bar were added 2-(1*H*-indol-1-yl)aniline (**1a**, 41.6 mg, 0.2 mmol), EA (2 mL), *N*-methylmaleimide (**2a**, 33.3 mg, 0.3 mmol), $[Ru(p\text{-cymene})Cl_2]_2$ (6.12 mg, 0.01 mmol), $AgSbF_6$ (13.7 mg, 0.04 mmol) and AcOH (57 μL, 1.0 mmol) with stirring. The mixture was stirred at 80 ℃ under air for 12 h. Upon completion, it was cooled to room temperature, quenched with saturated aqueous solution of $NaHCO_3$ (1 mL), filtered through a pad of celite, and extracted with CH_2Cl_2 (10 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (4:1) as eluent to afford **3a**. **3b**-**3v** were obtained in a similar manner except for that the reaction for the synthesis of **3v** was carried out at 60 ℃.

3-(1-(2-Aminophenyl)-1*H*-indol-2-yl)-1-methylpyrrolidine-2,5-dione (3a)

Eluent: petroleum ether/ethyl acetate (4:1). Yellow solid (43.4 mg, 68%, dr = 0.6:0.4), mp 90.2-92.1 ℃. ^1H NMR (600 MHz, $CDCl_3$): δ 7.62-7.60 (m, 1H), 7.30-7.27 (m, 1.4H), 7.15-7.13 (m, 2H), 7.02 (d, J = 7.8 Hz, 0.6H), 6.96-6.94 (m, 1H), 6.88-6.80 (m, 2H), 6.57 (s, 0.6H), 6.56 (s, 0.4H), 4.13-4.08 (m, 1H), 3.54 (br s, 2H), 2.96-2.83 (m, 5H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 176.8, 176.0, 175.7, 175.6, 144.8, 144.5, 138.0, 137.6, 136.0, 135.9, 130.6, 130.5, 130.4, 130.3, 127.7, 127.6, 122.7, 121.8, 121.7, 120.9, 120.8, 120.7, 120.6, 119.0, 118.7, 116.7, 116.3, 110.5, 110.4, 102.4, 101.7, 39.2, 39.0, 36.4, 35.9, 25.1. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{17}N_3O_2Na$ 342.1213; Found 342.1207.

3-(1-(2-Aminophenyl)-6-methyl-1*H*-indol-2-yl)-1-methylpyrrolidine-2,5-dione (3b)

Eluent: petroleum ether/ethyl acetate (4:1). White solid (40.0 mg, 60%, dr = 0.55:0.45), mp 180.8-181.9 ℃. ^1H NMR (600 MHz, $CDCl_3$): δ 7.48 (d, J = 7.8 Hz, 1H), 7.30-7.26 (m, 1.55H), 7.02 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 0.45H), 6.98 (d, J = 7.8 Hz, 1H), 6.89-6.81 (m, 2H), 6.74 (s, 0.55H), 6.73 (s, 0.45H), 6.52 (s, 0.45H), 6.51 (s, 0.55H), 4.11-4.06 (m, 1H), 3.70 (s, 0.9H), 3.41 (s, 1.1H), 2.95-2.83 (m, 5H), 2.38 (s, 3H). $^{13}C\{^1H\}$ NMR (150

MHz, $CDCl_3$): δ 176.9, 176.0, 175.8, 175.7, 144.9, 144.6, 138.4, 138.0, 135.2, 135.1, 132.7, 130.6, 130.5, 130.4, 130.3, 125.5, 125.4, 122.6, 122.5, 122.0, 121.9, 120.4, 120.3, 118.9, 118.6, 116.6, 116.2, 110.3, 110.2, 102.2, 101.6, 39.2, 39.0, 36.4, 35.9, 25.1, 21.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{20}N_3O_2$ 334.1550; Found 334.1543.

3-(1-(2-Aminophenyl)-6-methoxy-1*H*-indol-2-yl)-1-methylpyrrolidine-2,5-dione (3c)

Eluent: petroleum ether/ethyl acetate (4:1). White solid (39.8 mg, 57%, dr = 0.6:0.4), mp 200.1-202.0 ℃. ^1H NMR (600 MHz, $CDCl_3$): δ 7.47 (d, J = 9.0 Hz, 1H), 7.31-7.27 (m, 1.6H), 7.03 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 0.4H), 6.89-6.80 (m, 3H), 6.50 (s, 0.4H), 6.49 (s, 0.6H), 6.40 (d, J = 1.8 Hz, 0.6H), 6.39 (d, J = 1.8 Hz, 0.4H), 4.10-4.05 (m, 1H), 3.733 (s, 1.8H), 3.729 (s, 1.2H), 3.71 (s, 0.8H), 3.43 (s, 1.2H), 2.95-2.82 (m, 5H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 176.9, 176.1, 175.8, 175.7, 157.1, 144.8, 144.5, 138.8, 138.4, 134.6, 134.5, 130.6, 130.5, 130.4, 130.3, 121.8, 121.7, 121.4, 121.3, 119.0, 118.7, 116.7, 116.3, 110.8, 110.7, 102.3, 101.7, 93.8, 93.7, 55.7, 39.3, 39.0, 36.4, 35.9, 25.1. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{19}N_3O_3Na$ 372.1319; Found 372.1309.

3-(1-(2-Aminophenyl)-6-fluoro-1*H*-indol-2-yl)-1-methylpyrrolidine-2,5-dione (3d)

Eluent: petroleum ether/ethyl acetate (4:1). White solid (43.8 mg, 65%, dr = 0.5:0.5), mp 215.0-216.2 ℃. ^1H NMR (600 MHz, $CDCl_3$): δ 7.52-7.50 (m, 1H), 7.30-7.27 (m, 1.5H), 7.02-7.01 (m, 0.5H), 6.92-6.81 (m, 3H), 6.65-6.62 (m, 1H), 6.55 (s, 0.5H), 6.54 (s, 0.5H), 4.12-4.07 (m, 1H), 3.71 (s, 1H), 3.41 (s, 1H), 2.97-2.83 (m, 5H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 176.7, 175.9, 175.6, 175.5, 160.3 (d, $^1J_{C\text{-}F}$ = 237.0 Hz), 144.7, 144.4, 138.1 (d, $^3J_{C\text{-}F}$ = 11.9 Hz), 137.7 (d, $^3J_{C\text{-}F}$ = 12.0 Hz), 136.4 (d, $^4J_{C\text{-}F}$ = 2.3 Hz), 136.3 (d, $^4J_{C\text{-}F}$ = 2.7 Hz), 130.8, 130.7, 130.4, 130.1, 124.1, 124.0, 121.6 (d, $^3J_{C\text{-}F}$ = 9.9 Hz), 121.5, 121.48 (d, $^3J_{C\text{-}F}$ = 9.9 Hz), 121.4, 119.1, 118.8, 116.8, 116.4, 109.6 (d, $^2J_{C\text{-}F}$ = 25.8 Hz), 109.5 (d, $^2J_{C\text{-}F}$ = 23.4 Hz), 102.4, 101.8, 97.0 (d, $^2J_{C\text{-}F}$ = 27.2 Hz), 96.9 (d, $^2J_{C\text{-}F}$ = 26.1 Hz), 39.2, 39.0, 36.3, 35.8, 25.1. ^{19}F NMR (565 MHz, $CDCl_3$): δ -119.39 – -119.43 (m). HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{16}FN_3O_2Na$ 360.1119; Found 360.1119.

3-(1-(2-Aminophenyl)-6-chloro-1*H*-indol-2-yl)-1-methylpyrrolidine-2,5-dione (3e)

Eluent: petroleum ether/ethyl acetate (4:1). White solid (45.2 mg, 64%, dr = 0.55:0.45), mp 220.0-221.7 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.50 (d, *J* = 8.4 Hz, 1H), 7.31-7.27 (m, 1.55H), 7.11-7.10 (m, 1H), 7.00 (d, *J* = 6.6 Hz, 0.45H), 6.94 (s, 0.55H), 6.93 (s, 0.45H), 6.88-6.81 (m, 2H), 6.55 (s, 0.45H), 6.54 (s, 0.55H), 4.11-4.06 (m, 1H), 3.70 (s, 0.9H), 3.41 (s, 1.1H), 2.96-2.82 (m, 5H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 176.6, 175.7, 175.5, 175.4, 144.7, 144.4, 138.4, 138.0, 136.8, 136.7, 130.9, 130.8, 130.4, 130.2, 128.7, 126.2, 126.1, 121.6, 121.59, 121.56, 121.1, 119.1, 118.8, 116.9, 116.4, 110.45, 110.41, 102.4, 101.7, 39.2, 38.9, 36.2, 35.7, 25.2. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{16}ClN_3O_2Na$ 376.0823; Found 376.0814.

3-(1-(2-Aminophenyl)-6-bromo-1*H*-indol-2-yl)-1-methylpyrrolidine-2,5-dione (3f)

Eluent: petroleum ether/ethyl acetate (4:1). White solid (48.4 mg, 61%, dr = 0.6:0.4), mp 236.1-236.7 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.56-7.53 (m, 1H), 7.27-7.16 (m, 2.6H), 6.93-6.89 (m, 1.4H), 6.83-6.81 (m, 1H), 6.72-6.63 (m, 2H), 4.93 (s, 1.2H), 4.77 (s, 0.8H), 4.28 (dd, J_1 = 9.6 Hz, J_2 = 5.2 Hz, 0.6H), 4.08-4.04 (m, 0.4H), 2.95-2.84 (m, 2H), 2.81 (s, 1.2H), 2.70 (s, 1.8H). ^{13}C{^{1}H} NMR (100 MHz, DMSO): δ 177.3, 176.6, 176.4, 176.0, 146.3, 139.2, 139.0, 138.4, 138.3, 130.8, 130.6, 130.5, 130.4, 127.1, 126.9, 123.4, 122.5, 120.0, 119.9, 117.0, 116.9, 116.6, 116.4, 115.0, 114.8, 113.1, 112.9, 103.8, 101.2, 38.9, 36.5, 35.0, 25.2, 25.0. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{16}BrN_3O_2Na$ 420.0318; Found 420.0295.

3-(1-(2-Aminophenyl)-6-(trifluoromethyl)-1*H*-indol-2-yl)-1-methylpyrrolidine-2,5-dione (3g)

Eluent: petroleum ether/ethyl acetate (4:1).White solid (57.3 mg, 74%, dr = 0.7:0.3), mp 82.7-84.6 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.4 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.32-7.28 (m, 1.7H), 7.22 (s, 0.7H), 7.21 (s, 0.3H), 7.02-7.01 (m, 0.3H), 6.90-6.82 (m, 2H), 6.63 (s, 0.3H), 6.62 (s, 0.7H), 4.14 (dd, J_1 = 9.6 Hz, J_2 = 5.4 Hz, 0.3H), 4.10 (dd, J_1 = 9.6 Hz, J_2 = 5.4 Hz, 0.7H), 3.72 (br s, 0.6H), 3.42 (br s, 1.4H), 2.97-2.83 (m, 5H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 176.4, 175.6, 175.4, 175.3, 144.7, 144.4, 139.0, 138.9, 136.9, 136.5, 131.1, 131.0, 130.4, 130.2, 130.1, 130.0, 125.0 (q, $^1J_{C\text{-}F}$ = 270.3 Hz), 124.8 (q,$^2J_{C\text{-}F}$ = 31.8 Hz), 121.2, 121.1, 120.8, 120.7, 119.2, 118.9, 117.5 (q, $^3J_{C-F}$ = 3.6 Hz), 117.0, 116.5, 108.0 (q, $^3J_{C-F}$ = 4.4 Hz), 102.5, 101.8, 39.2, 38.9, 36.2, 35.7, 25.18, 25.16. ^{19}F NMR (565 MHz, $CDCl_3$): δ -60.51 (s), -60.52 (s). HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{16}F_3N_3O_2Na$ 410.1087; Found 410.1074.

3-(1-(2-Aminophenyl)-5-methyl-1*H*-indol-2-yl)-1-methylpyrrolidine-2,5-dione (3h)

Eluent: petroleum ether/ethyl acetate (4:1). White solid (44.0 mg, 66%, dr = 0.5:0.5), mp 91.2-93.0 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.38 (s, 1H), 7.28-7.23 (m, 1.5H), 7.00 (dd, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 0.5H), 6.96 (d, J = 8.4 Hz, 1H), 6.85-6.78 (m, 3H), 6.47 (s, 0.5H), 6.46 (s, 0.5H), 4.08-4.04 (m, 1H), 3.69 (br s, 1H), 3.41 (br s, 1H), 2.93-2.81 (m, 5H), 2.42 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 176.8, 176.0, 175.8, 175.7, 144.9, 144.6, 136.4, 136.0, 135.9, 130.5, 130.4, 130.3, 130.2, 130.14, 130.11, 128.0, 127.9, 124.3, 122.0, 121.9, 120.4, 120.3, 118.9, 118.6, 116.6, 116.2, 110.14, 110.12, 101.9, 101.2, 39.2, 39.0, 36.4, 35.9, 25.1, 21.4. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{19}N_3O_2Na$ 356.1369; Found 356.1363.

3-(1-(2-Aminophenyl)-5-methoxy-1*H*-indol-2-yl)-1-methylpyrrolidine-2,5-dione (3i)

Eluent: petroleum ether/ethyl acetate (4:1). White solid (38.4 mg, 55%, dr = 0.5:0.5), mp 90.3-92.0 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.30-7.25 (m, 1.5H), 7.06 (d, J = 1.8 Hz, 1H), 7.01 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 0.5H), 6.87-6.79 (m, 4H), 6.49 (s, 0.5H), 6.48 (s, 0.5H), 4.10-4.05 (m, 1H), 3.84 (s, 3H), 3.70 (s, 1H), 3.40 (s, 1H), 2.96-2.83 (m, 5H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 176.8, 176.0, 175.8, 175.6, 155.0, 154.9, 144.9, 144.6, 136.4, 136.3, 133.2, 132.8, 130.5, 130.4, 130.4, 130.3, 128.1, 128.0, 122.0, 121.9, 118.9, 118.6, 116.7, 116.2, 112.8, 111.24, 111.21, 102.5, 102.4, 101.9, 101.4, 55.94, 55.93, 39.3, 39.0, 36.4, 35.9, 25.1. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{19}N_3O_3Na$ 372.1319; Found 372.1306.

3-(1-(2-Aminophenyl)-5-fluoro-1*H*-indol-2-yl)-1-methylpyrrolidine-2,5-dione (3j)

Eluent: petroleum ether/ethyl acetate (4:1). White solid (48.5 mg, 72%, dr = 0.5:0.5), mp 73.2-74.0 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.30-7.24 (m, 2.5H), 7.01 (dd, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 0.5H), 6.91-6.81 (m, 4H), 6.531 (s, 0.5H), 6.526 (s, 0.5H), 4.11-4.07 (m, 1H), 3.70 (s, 1H), 3.39 (s, 1H), 2.98-2.83 (m, 5H). ^{13}C{^{1}H}

NMR (150 MHz, $CDCl_3$): δ 176.6, 175.8, 175.6, 175.5, 158.6 (d, $^1J_{C-F}$ = 234.3 Hz), 158.5 (d, $^1J_{C-F}$ = 234.3 Hz), 144.8, 144.5, 137.6, 137.5, 134.5, 134.1, 130.7, 130.6, 130.5, 130.2, 128.0 (d, $^3J_{C-F}$ = 7.2 Hz), 127.9 (d, $^3J_{C-F}$ = 7.5 Hz), 121.5, 119.1, 118.7, 116.8, 116.4, 111.2 (d, $^3J_{C-F}$ = 6.3 Hz), 111.18 (d, $^3J_{C-F}$ = 6.5 Hz), 111.16, 111.0, 105.6 (d, $^2J_{C-F}$ = 23.0 Hz), 105.5 (d, $^2J_{C-F}$ = 22.8 Hz), 102.2 (d, $^4J_{C-F}$ = 4.4 Hz), 101.7 (d, $^4J_{C-F}$ = 4.2 Hz), 39.2, 39.0, 36.3, 35.8, 25.2. ^{19}F NMR (565 MHz, $CDCl_3$): δ -123.45 – -123.49 (m), -123.51 – -123.55 (m). HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{16}FN_3O_2Na$ 360.1119; Found 360.1106.

3-(1-(2-Aminophenyl)-5-chloro-1*H*-indol-2-yl)-1-methylpyrrolidine-2,5-dione (3k)

Eluent: petroleum ether/ethyl acetate (4:1). White solid (47.3 mg, 67%, dr = 0.6:0.4), mp 83.9-85.6 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.57 (d, J = 1.8 Hz, 1H), 7.30-7.27 (m, 1.6H), 7.11-7.09 (m, 1H), 7.00 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 0.4H), 6.88-6.81 (m, 3H), 6.52 (s, 0.4H), 6.51 (s, 0.6H), 4.11-4.07 (m, 1H), 3.69 (s, 0.8H), 3.39 (s, 1.2H), 2.98-2.82 (m, 5H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 176.5, 175.7, 175.5, 175.4, 144.7, 144.4, 137.4, 137.3, 136.3, 135.9, 130.8, 130.7, 130.4, 130.1, 128.7, 128.6, 126.53, 126.50, 123.0, 121.3, 120.1, 120.0, 119.1, 118.8, 116.8, 116.4, 111.6, 111.5, 101.9, 101.3, 39.2, 38.9, 36.2, 35.7, 25.2. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{16}ClN_3O_2Na$ 376.0823; Found 376.0820.

3-(1-(2-Aminophenyl)-5-bromo-1*H*-indol-2-yl)-1-methylpyrrolidine-2,5-dione (3l)

Eluent: petroleum ether/ethyl acetate (4:1). White solid (51.6 mg, 65%, dr = 0.6:0.4), mp 80.0-81.5 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.73 (d, J = 0.6 Hz, 1H), 7.30-7.28 (m, 1.6H), 7.23 (d, J = 9.0 Hz, 1H), 7.00 (d, J = 7.2 Hz, 0.4H), 6.88-6.81 (m, 3H), 6.514 (s, 0.4H), 6.510 (s, 0.6H), 4.12-4.07 (m, 1H), 3.68 (s, 0.8H), 3.38 (s, 1.2H), 2.97-2.82 (m, 5H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 176.5, 175.7, 175.5, 175.4, 144.7, 144.4, 137.2, 137.1, 136.6, 136.2, 130.8, 130.7, 130.4, 130.1, 129.3, 129.2, 125.6, 123.2, 123.1, 121.3, 119.1, 118.8, 116.8, 116.4, 114.1, 114.0, 112.0, 111.9, 101.8, 101.2, 39.1, 38.9, 36.2, 35.7, 25.2. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{16}BrN_3O_2Na$ 420.0318; Found 420.0303.

3-(1-(2-Aminophenyl)-4-methyl-1*H*-indol-2-yl)-1-methylpyrrolidine-2,5-dione (3m)

Eluent: petroleum ether/ethyl acetate (4:1). White solid (37.3 mg, 56%, dr = 0.6:0.4), mp 209.0-209.5 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.30-7.26 (m, 1.4H), 7.07-7.01 (m, 1.6H), 6.94 (d, J = 7.2 Hz, 1H), 6.87-6.77 (m, 3H), 6.59 (s, 0.6H), 6.58 (s, 0.4H), 4.14-4.10 (m, 1H), 3.68 (s, 1.2H), 3.40 (s, 0.8H), 2.93-2.87 (m, 5H), 2.55 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 176.9, 176.1, 175.8, 175.7, 144.8, 144.5, 137.7, 137.3, 135.4, 135.3, 130.6, 130.5, 130.4, 130.3, 130.2, 127.6, 127.5, 122.9, 122.1, 122.0, 121.0, 120.9, 118.9, 118.6, 116.7, 116.3, 108.04, 108.01, 100.9, 100.2, 39.3, 39.0, 36.5, 36.0, 25.1, 18.7. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{19}N_3O_2Na$ 356.1369; Found 356.1354.

3-(1-(2-Aminophenyl)-4-fluoro-1*H*-indol-2-yl)-1-methylpyrrolidine-2,5-dione (3n)

Eluent: petroleum ether/ethyl acetate (4:1). White solid (41.8 mg, 62%, dr = 0.6:0.4), mp 155.0-156.2 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.30-7.26 (m, 1.6H), 7.07-7.03 (m, 1H), 7.01 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 0.4H), 6.88-6.79 (m, 3H), 6.74-6.71 (m, 1H), 6.66 (s, 0.4H), 6.65 (s, 0.6H), 4.12-4.06 (m, 1H), 3.71(br s, 0.8H), 3.42 (br s, 1.2H), 2.97-2.84 (m, 5H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 176.5, 175.7, 175.5, 175.4, 156.2 (d, $^{1}J_{C\text{-}F}$ = 247.7 Hz), 156.1 (d, $^{1}J_{C\text{-}F}$ = 248.1 Hz), 144.7, 144.4, 140.4 (d, $^{3}J_{C\text{-}F}$ = 11.7 Hz), 140.0 (d, $^{3}J_{C\text{-}F}$ = 10.4 Hz), 136.1, 136.0, 130.8, 130.7, 130.4, 130.1, 123.3, 123.2, 121.5, 121.4, 119.0, 118.7, 116.84 (d, $^{2}J_{C\text{-}F}$ = 21.3 Hz), 116.83, 116.8 (d, $^{2}J_{C\text{-}F}$ = 22.2 Hz), 116.4, 106.6 (d, $^{4}J_{C\text{-}F}$ = 3.0 Hz), 106.5 (d, $^{4}J_{C\text{-}F}$ = 3.3 Hz), 105.7 (d, $^{2}J_{C\text{-}F}$ = 18.6 Hz), 105.6 (d, $^{2}J_{C\text{-}F}$ = 18.9 Hz), 98.4, 97.7, 39.2, 38.9, 36.3, 35.7, 25.2. ^{19}F NMR (565 MHz, $CDCl_3$): δ -122.12 (dd, J_1 = 10.2 Hz, J_2 = 5.7 Hz), -122.16 ((dd, J_1 = 9.6 Hz, J_2 = 5.1 Hz)). HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{16}FN_3O_2Na$ 360.1119; Found 360.1100.

3-(1-(2-Aminophenyl)-7-fluoro-1*H*-indol-2-yl)-1-methylpyrrolidine-2,5-dione (3o)

Eluent: petroleum ether/ethyl acetate (4:1). Yellow solid (39.8 mg, 59%, dr = 0.55:0.45), mp 137.8-138.7 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.30 (m, 1.45H), 7.24-7.21 (m, 1H), 7.06-6.99 (m, 1.55H), 6.83-6.75 (m, 3H), 6.57 (s, 1H), 4.07-4.01 (m, 1H), 3.57 (br s, 2H), 2.90-2.81 (m, 5H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 176.6, 175.8, 175.6, 175.4, 149.7 (d, $^{1}J_{C\text{-}F}$ = 246.2 Hz), 149.6 (d, $^{1}J_{C\text{-}F}$ = 246.3 Hz), 144.7, 144.6, 137.5, 137.4, 131.6 (d, $^3J_{C-F}$ = 8.7 Hz), 131.5 (d, $^3J_{C-F}$ = 8.6 Hz), 130.6, 130.5, 130.0, 129.9, 125.6 (d, $^2J_{C-F}$ = 35.7 Hz), 125.5 (d, $^2J_{C-F}$ = 35.4 Hz), 123.4, 123.3, 121.0 (d, $^4J_{C-F}$ = 2.4 Hz), 120.9 (d, $^4J_{C-F}$ = 3.9 Hz), 118.6, 118.3, 116.6 (d, $^3J_{C-F}$ = 6.4 Hz), 116.5 (d, $^3J_{C-F}$ = 7.3 Hz), 116.4, 116.0, 108.5 (d, $^2J_{C-F}$ = 16.9 Hz), 108.4 (d, $^2J_{C-F}$ = 17.0 Hz), 103.2, 102.5, 39.0, 38.7, 36.3, 35.9, 25.2, 25.1. ^{19}F NMR (376 MHz, $CDCl_3$): δ -135.64 (d, J = 10.5 Hz), -135.83 (d, J = 11.3 Hz). HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{16}FN_3O_2Na$ 360.1119; Found 360.1108.

3-(1-(2-Aminophenyl)-7-chloro-1*H*-indol-2-yl)-1-methylpyrrolidine-2,5-dione (3p)

Eluent: petroleum ether/ethyl acetate (4:1). White solid (46.6 mg, 66%, dr = 0.5:0.5), mp 134.6-136.0 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.51-7.50 (m, 1H), 7.30 (td, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 0.5H), 7.27-7.25 (m, 1H), 7.13-7.12 (m, 1H), 7.06-7.02 (m, 1.5H), 6.85-6.76 (m, 2H), 6.59 (s, 0.5H), 6.58 (s, 0.5H), 4.05-4.01 (m, 1H), 3.47 (br s, 2H), 2.97-2.86 (m, 5H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 176.6, 175.8, 175.6, 175.5, 145.6, 145.5, 138.0, 137.9, 133.0, 132.6, 131.1, 131.0, 130.8, 130.7, 130.6, 130.4, 124.3, 124.2, 123.2, 122.9, 121.43, 121.40, 119.6, 119.5, 118.5, 118.1, 117.1, 117.0, 116.1, 115.7, 103.3, 102.5, 39.2, 38.9, 36.4, 35.9, 25.2, 25.1. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{16}ClN_3O_2Na$ 376.0823; Found 376.0813.

3-(1-(2-Amino-5-chlorophenyl)-1*H*-indol-2-yl)-1-methylpyrrolidine-2,5-dione (3q)

Eluent: petroleum ether/ethyl acetate (4:1). White solid (40.9 mg, 58%, dr = 0.6:0.4), mp 82.1-83.6 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.62-7.61 (m, 1H), 7.36 (d, J = 1.8 Hz, 0.6H), 7.27 (d, J = 2.4 Hz, 0.6H), 7.25 (d, J = 1.8 Hz, 0.4H), 7.19-7.15 (m, 2H), 7.04 (d, J = 2.4 Hz, 0.4H), 6.97-6.94 (m, 1H), 6.83 (d, J = 8.4 Hz, 0.4H), 6.80 (d, J = 9.0 Hz, 0.6H), 6.59 (s, 0.4H), 6.57 (s, 0.6H), 4.11 (dd, J_1 = 9.6 Hz, J_2 = 5.4 Hz, 0.4H), 4.07 (dd, J_1 = 9.6 Hz, J_2 = 4.8 Hz, 0.6H), 3.76 (s, 0.8H), 3.43 (s, 1.2H), 3.05-2.83 (m, 5H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 176.6, 175.8, 175.5, 175.4, 143.7, 143.2, 137.8, 137.3, 135.9, 135.5, 130.6, 130.5, 130.4, 129.9, 127.8, 123.03, 123.01, 123.0, 122.7, 122.6, 121.14, 121.11, 120.9, 120.8, 117.6, 117.1, 110.4, 110.3, 102.9, 101.8, 39.1, 38.7, 36.3, 35.7, 25.23, 25.21. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{16}ClN_3O_2Na$ 376.0823; Found 376.0816.

3-(1-(2-Amino-5-bromophenyl)-1*H*-indol-2-yl)-1-methylpyrrolidine-2,5-dione (3r)

Eluent: petroleum ether/ethyl acetate (4:1). White solid (47.7 mg, 60%, dr = 0.5:0.5), mp 102.3-103.5 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62-7.59 (m, 1H), 7.49 (d, *J* = 2.0 Hz, 0.5H), 7.40-7.36 (m, 1H), 7.19-7.14 (m, 2.5H), 6.97-6.93 (m, 1H), 6.79-6.73 (m, 1H), 6.58 (s, 0.5H), 6.56 (s, 0.5H), 4.12-4.05 (m, 1H), 3.78 (br s, 1H), 3.46 (br s, 1H), 3.09-2.80 (m, 5H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 176.6, 175.8, 175.5, 175.4, 144.2, 143.7, 137.8, 137.3, 135.9, 135.5, 133.4, 133.3, 133.2, 132.8, 127.4, 123.0, 123.0, 122.9, 121.2, 121.1, 120.9, 120.8, 118.0, 117.5, 110.4, 110.3, 109.6, 109.2, 102.9, 101.8, 39.1, 38.7, 36.3, 35.7, 25.3, 25.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{17}BrN_3O_2$ 398.0499; Found 398.0491.

3-(1-(2-Amino-4-methoxyphenyl)-1*H*-indol-2-yl)-1-methylpyrrolidine-2,5-dione (3s)

Eluent: petroleum ether/ethyl acetate (4:1). White solid (39.1 mg, 56%, dr = 0.55:0.45), mp 82.4-84.0 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.61-7.59 (m, 1H), 7.21 (d, *J* = 8.4 Hz, 0.45H), 7.16-7.12 (m, 2H), 6.98-6.95 (m, 1H), 6.93 (d, *J* = 8.4 Hz, 0.55H), 6.55 (s, 0.55H), 6.54 (s, 0.45H), 6.42 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 0.45H), 6.39-6.36 (m, 1.55H), 4.13-4.08 (m, 1H), 3.82 (s, 1.35H), 3.81 (s, 1.65H), 3.68 (s, 1.1H), 3.38 (s, 0.9H), 2.99-2.84 (m, 5H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 176.8, 176.0, 175.8, 175.6, 161.2, 145.9, 145.6, 138.3, 137.9, 136.3, 136.2, 131.4, 131.1, 127.7, 127.6, 122.6, 120.73, 120.70, 120.67, 120.6, 115.0, 114.9, 110.43, 110.40, 104.7, 104.5, 102.0, 101.4, 101.3, 101.2, 55.4, 39.2, 38.9, 36.4, 36.0, 25.1. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{19}N_3O_3Na$ 372.1319; Found 372.1317.

3-(1-(2-Aminophenyl)-1*H*-indol-2-yl)-1-ethylpyrrolidine-2,5-dione (3t)

Eluent: petroleum ether/ethyl acetate (4:1). White solid (40.0 mg, 60%, dr = 0.7:0.3), mp 201.0-202.2 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63-7.60 (m, 1H), 7.33-7.26 (m, 1.3H), 7.17-7.13 (m, 2H), 7.04 (dd, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 0.7H), 6.97-6.95 (m, 1H), 6.89-6.80 (m, 2H), 6.55 (s, 1H), 4.11-4.06 (m, 1H), 3.57-3.48 (m, 2H), 3.13 (br s, 2H), 2.98-2.81 (m, 2H), 1.17-1.12 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 176.5, 175.8, 175.5, 175.4, 144.9, 144.5, 137.9, 137.5, 136.3, 136.2, 130.6, 130.5, 130.4, 130.2, 127.8, 127.7, 122.7, 121.9, 120.8, 120.79, 120.7, 120.6, 119.0, 118.8, 116.7, 116.3, 110.5, 110.4, 101.8, 101.4, 39.0, 38.8, 36.4, 36.2, 34.14, 34.10, 13.00, 12.97. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{19}N_3O_2Na$ 356.1369; Found 356.1352.

3-(1-(2-Aminophenyl)-1*H*-indol-2-yl)-1-benzylpyrrolidine-2,5-dione (3u)

Eluent: petroleum ether/ethyl acetate (4:1). White solid (41.1 mg, 52%, dr = 0.5:0.5), mp 94.0-95.0 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.58-7.57 (m, 1H), 7.35-7.34 (m, 2H), 7.29-7.23 (m, 4.5H), 7.14-7.11 (m, 2H), 7.00 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 0.5H), 6.95-6.93 (m, 1H), 6.86-6.83 (m, 1H), 6.79-6.73 (m, 1H), 6.47 (s, 0.5H), 6.46 (s, 0.5H), 4.62-4.56 (m, 2H), 4.06-4.03 (m, 1H), 3.67 (s, 1H), 3.36 (s, 1H), 2.92-2.79 (m, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 176.3, 175.7, 175.4, 175.2, 144.9, 144.5, 137.9, 137.5, 136.3, 136.2, 135.7, 135.6, 130.6, 130.5, 130.4, 130.2, 128.9, 128.8, 128.7, 128.1, 128.0, 127.8, 127.7, 122.7, 121.8, 121.7, 120.83, 120.81, 120.8, 120.7, 119.0, 118.7, 116.7, 116.3, 110.6, 110.4, 101.8, 101.3, 42.8, 42.7, 39.0, 38.8, 36.4, 36.3. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{21}N_3O_2Na$ 418.1526; Found 418.1503.

3-(1-(2-Aminophenyl)-1*H*-pyrrol-2-yl)-1-methylpyrrolidine-2,5-dione (3v)

Eluent: petroleum ether/ethyl acetate (4:1). Yellow syrup (33.9 mg, 63%, dr = 0.45:0.55). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.20 (d, J = 7.8 Hz, 0.45H), 7.11 (t, J = 7.8 Hz, 1H), 6.92 (d, J = 7.2 Hz, 0.55H), 6.71-6.59 (m, 3H), 6.20-6.19 (m, 1H), 6.08-6.07 (m, 1H), 3.85-3.80 (m, 1H), 3.76 (br s, 1.1H), 3.44 (br s, 0.9H), 2.85-2.66 (m, 5H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 176.5, 175.6, 175.0, 174.9, 143.2, 143.0, 129.0, 128.9, 128.4, 128.1, 127.8, 127.7, 123.6, 123.5, 122.2, 121.9, 117.3, 117.0, 115.3, 114.8, 108.2, 106.8, 106.6, 37.5, 37.3, 35.5, 35.3, 24.0, 23.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{16}N_3O_2$ 270.1237; Found 270.1238.

2. Typical procedure for the synthesis of 4a and spectroscopic data of 4a-4y

To a reaction tube equipped with a stir bar were added 2-(1*H*-indol-1-yl)aniline (**1a**, 41.6 mg, 0.2 mmol), EA (2 mL), *N*-methylmaleimide (**2a**, 33.3 mg, 0.3 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (6.12 mg, 0.01 mmol), $AgSbF_6$ (13.7 mg, 0.04 mmol) and AcOH (57 μL, 1.0 mmol) with stirring. The mixture was stirred at 80 ℃ under air for 12 h. After being cooled to room temperature, it was added with $BF_3·Et_2O$ (49 μL, 0.4 mmol). The resulting mixture was stirred at 100 ℃ under air for 10 h. Upon completion, it was cooled to ambient temperature, quenched with saturated aqueous solution of $NaHCO_3$ (1 mL), filtered through a pad of celite, and extracted with CH_2Cl_2 (10 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (6:1) as eluent to afford **4a**. **4b-4y** were obtained in a similar manner except for that the reaction for the synthesis of **4y** was carried out at 60 ℃ and 80 ℃ for the two steps, respectively.

11-Methyl-13,13*a*-dihydrobenzo[2,3]pyrrolo[2',3':5,6][1,4]diazepino[1,7-*a*]indol-12(11*H*)-one (4a)

Eluent: petroleum ether/ethyl acetate (6:1). White solid (33.1 mg, 55%), mp 178.1-178.9 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 7.62 (d, J = 8.4 Hz, 2H), 7.42 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.38-7.34 (m, 1H), 7.29-7.25 (m, 1H), 7.23-7.15 (m, 2H), 6.37 (s, 1H), 4.02-4.00 (m, 1H), 3.21-3.04 (m, 5H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 175.2, 161.6, 140.2, 139.9, 136.6, 129.9, 128.9, 127.7, 126.8, 125.0, 124.8, 122.7, 121.2, 120.9, 111.1, 98.0, 34.8, 31.9, 26.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{16}N_3O$ 302.1288; Found 302.1278.

3,11-Dimethyl-13,13*a*-dihydrobenzo[2,3]pyrrolo[2',3':5,6][1,4]diazepino[1,7-*a*]indol-12(11*H*)-one (4b)

Eluent: petroleum ether/ethyl acetate (6:1). White solid (32.1 mg, 51%), mp 172.0-173.5 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.77 (d, J = 7.8 Hz, 1H), 7.50 (d, J = 7.8 Hz, 1H), 7.43-7.40 (m, 2H), 7.35 (t, J = 7.8 Hz, 1H), 7.28 (t, J = 7.8 Hz, 1H), 7.01 (d, J = 7.8 Hz, 1H), 6.31 (s, 1H), 3.99 (d, J = 8.4 Hz, 1H), 3.18-3.04 (m, 5H), 2.45 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 175.3, 161.7, 140.2. 139.4, 137.0, 132.6, 130.0, 127.7, 126.7, 125.1, 124.7, 122.9, 120.5, 111.0, 97.8, 34.8, 31.9, 26.3, 22.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{18}N_3O$ 316.1444; Found 316.1438.

3-Methoxy-11-methyl-13,13*a*-dihydrobenzo[2,3]pyrrolo[2',3':5,6][1,4]diazepino[1,7-*a*]indol-12(11*H*)-one (4c)

Eluent: petroleum ether/ethyl acetate (6:1). White solid (28.5 mg, 43%), mp 185.4-186.6 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.76 (d, J = 7.8 Hz, 1H), 7.49 (d, J = 8.4 Hz, 1H), 7.41 (d, J = 7.8 Hz, 1H), 7.36 (t, J = 7.8 Hz, 1H), 7.27 (t, J = 7.8 Hz, 1H), 7.12 (s, 1H), 6.84 (dd, J_1 = 8.4 Hz, J_1 = 1.8 Hz, 1H), 6.29 (s, 1H), 3.99 (d, J = 8.4 Hz, 1H), 3.81 (s, 3H), 3.16-3.04 (m, 5H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 175.3, 161.9, 156.8, 140.3, 139.1, 137.4, 129.9, 127.7, 126.8, 124.8, 124.7, 123.0, 121.4, 110.8, 97.8, 95.1, 55.8, 34.7, 31.9, 26.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{18}N_3O_2$ 332.1394; Found 332.1382.

3-Fluoro-11-methyl-13,13*a*-dihydrobenzo[2,3]pyrrolo[2',3':5,6][1,4]diazepino[1,7-*a*]indol-12(11*H*)-one (4d)

Eluent: petroleum ether/ethyl acetate (6:1). White solid (35.1 mg, 55%), mp 188.5-189.8 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.71 (d, J = 7.8 Hz, 1H), 7.53 (dd, J_1 = 8.4 Hz, J_2 = 5.4 Hz, 1H), 7.42 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 7.37 (t, J = 7.8 Hz, 1H), 7.32-7.27 (m, 2H), 6.94 (td, J_1 = 9.0 Hz, J_2 = 1.8 Hz, 1H), 6.35 (s, 1H), 4.02 (d, J = 8.4 Hz, 1H), 3.18-3.06 (m, 5H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 175.1, 161.7, 160.1 (d, $^1J_{C\text{-}F}$ = 237.5 Hz), 140.4 (d, $^4J_{C\text{-}F}$ = 4.2 Hz), 140.2, 136.6 (d, $^3J_{C\text{-}F}$ = 12.0 Hz), 129.6, 127.8, 127.1, 125.3, 125.0, 124.5, 121.6 (d, $^3J_{C\text{-}F}$ = 9.8 Hz), 109.8 (d, $^2J_{C\text{-}F}$ = 24.9 Hz), 97.9, 97.8 (d, $^2J_{C\text{-}F}$ = 27.2 Hz), 34.8, 31.8, 26.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ -119.18 (td, J_1 = 9.8 Hz, J_2 = 6.0 Hz,). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{15}FN_3O$ 320.1194; Found 320.1187.

3-Chloro-11-methyl-13,13*a*-dihydrobenzo[2,3]pyrrolo[2',3':5,6][1,4]diazepino[1,7-*a*]indol-12(11*H*)-one (4e)

Eluent: petroleum ether/ethyl acetate (6:1). White solid (37.5 mg, 56%), mp 236.1-236.6 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 7.6 Hz, 1H), 7.60 (s, 1H), 7.50 (d, J = 8.4 Hz, 1H), 7.43-7.35 (m, 2H), 7.31-7.27 (m, 1H), 7.12 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H), 6.34 (s, 1H), 3.98 (d, J = 7.2 Hz, 1H), 3.17-3.03 (m, 5H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 175.0, 161.6, 140.7, 140.2, 136.9, 129.4, 128.6, 127.8, 127.4, 127.2, 125.0, 124.8, 121.8, 121.7, 111.1, 98.0, 34.8, 31.8, 26.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{15}ClN_3O$ 336.0898; Found 336.0879.

3-Bromo-11-methyl-13,13*a*-dihydrobenzo[2,3]pyrrolo[2',3':5,6][1,4]diazepino[1,7-*a*]indol-12(11*H*)-one (4f)

Eluent: petroleum ether/ethyl acetate (6:1). White solid (37.1 mg, 49%), mp 232.8-233.0 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.76 (s, 1H), 7.72 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 7.47 (d, J = 8.4 Hz, 1H), 7.42 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 7.40-7.37 (m, 1H), 7.32-7.29 (m, 1H), 7.27 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H), 6.35 (s, 1H), 4.00-3.98 (m, 1H), 3.16 (dd, J_1 = 18.0 Hz, J_2 = 2.4 Hz, 1H), 3.12 (s, 3H), 3.08 (dd, J_1 = 18.6 Hz, J_2 = 9.0 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 175.0, 161.5, 140.5, 140.2, 137.3, 129.3, 127.8, 127.7, 127.3, 125.0, 124.8, 124.4, 122.1, 116.2, 114.0, 98.0, 34.7, 31.8, 26.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{15}BrN_3O$ 380.0393; Found 380.0373.

11-Methyl-3-(trifluoromethyl)-13,13*a*-dihydrobenzo[2,3]pyrrolo[2',3':5,6][1,4]diazepino[1,7-*a*]indol-12(11*H*)-one (4g)

Eluent: petroleum ether/ethyl acetate (6:1). White solid (45.0 mg, 61%), mp 211.0-213.0 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.89 (s, 1H), 7.74 (d, J = 7.8 Hz, 1H), 7.70 (d, J = 7.8 Hz, 1H), 7.45-7.41 (m, 3H), 7.35-7.33 (m, 1H), 6.45 (s, 1H), 4.05 (d, J = 7.8 Hz, 1H), 3.22-3.10 (m, 5H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ. 174.9, 161.4, 142.4, 140.3, 135.6, 131.3, 129.2, 127.9, 127.5, 125.2, 125.0 (q, $^1J_{C\text{-}F}$ = 269.8 Hz), 124.79, 124.77 (q, $^2J_{C\text{-}F}$ = 31.8 Hz), 121.3, 117.8 (q, $^3J_{C\text{-}F}$ = 3.9 Hz), 108.6 (q, $^3J_{C\text{-}F}$ = 3.9 Hz), 98.1, 34.9, 31.8, 26.4. ^{19}F NMR (565 MHz, $CDCl_3$): δ -60.60 (s). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{15}F_3N_3O$ 370.1162; Found 370.1151.

2,11-Dimethyl-13,13*a*-dihydrobenzo[2,3]pyrrolo[2',3':5,6][1,4]diazepino[1,7-*a*]indol-12(11*H*)-one (4h)

Eluent: petroleum ether/ethyl acetate (6:1). White solid (33.4 mg, 53%), mp 239.4-240.5 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J = 8.0 Hz, 1H), 7.49 (d, J = 8.4 Hz, 1H), 7.41-7.39 (m, 2H), 7.33 (t, J = 7.6 Hz, 1H), 7.25 (t, J = 7.2 Hz, 1H), 7.02 (d, J = 8.4 Hz, 1H), 6.27 (s, 1H), 3.95 (d, J = 8.0 Hz, 1H), 3.15 (dd, J_1 = 18.4 Hz, J_2 = 2.4 Hz, 1H), 3.10 (s, 3H), 3.03 (dd, J_1 = 18.0 Hz, J_2 = 8.8 Hz, 1H), 2.43 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 175.3, 161.6, 140.1, 139.9, 134.9, 130.6, 130.0, 129.2, 127.7, 126.6, 124.9, 124.8, 124.2, 120.6, 110.8, 97.6, 34.8, 31.9, 26.3, 21.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{18}N_3O$ 316.1444; Found 316.1434.

2-Methoxy-11-methyl-13,13*a*-dihydrobenzo[2,3]pyrrolo[2',3':5,6][1,4]diazepino[1,7-*a*]indol-12(11*H*)-one (4i)

Eluent: petroleum ether/ethyl acetate (6:1). White solid (27.8 mg, 42%), mp 229.7-230.8 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 7.6 Hz, 1H), 7.50 (d, J = 8.8 Hz, 1H), 7.40 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 7.35-7.31 (m, 1H), 7.27-7.23 (m, 1H), 7.06 (d, J = 2.0 Hz, 1H), 6.85 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 1H), 6.27 (s, 1H), 3.93 (d, J = 7.6 Hz, 1H), 3.83 (s, 3H), 3.14 (dd, J_1 = 18.4 Hz, J_2 = 2.8 Hz, 1H), 3.10 (s, 3H), 3.04 (dd, J_1 = 18.4 Hz, J_2 = 9.2 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 175.2, 161.5, 155.0, 140.2, 140.0, 131.7, 130.0, 129.6, 127.7, 126.6, 124.81, 124.77, 112.5, 112.0, 102.6, 97.7, 55.9, 34.8, 31.9, 26.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{18}N_3O_2$ 332.1394; Found 332.1391.

2-Fluoro-11-methyl-13,13*a*-dihydrobenzo[2,3]pyrrolo[2',3':5,6][1,4]diazepino[1,7-*a*]indol-12(11*H*)-one (4j)

Eluent: petroleum ether/ethyl acetate 6:1). White solid (38.3 mg, 60%), mp 214.8-215.8 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.72-7.71 (m, 1H), 7.53 (dd, J_1 = 9.0 Hz, J_2 = 4.2 Hz, 1H), 7.42 (dd, J_1 = 7.8 Hz, J_2 = 0.6 Hz, 1H), 7.38-7.35 (m, 1H), 7.29-7.24 (m, 2H), 6.94 (td, J_1 = 9.0 Hz, J_2 = 2.4 Hz, 1H), 6.33 (s, 1H), 3.98 (d, J = 7.8 Hz, 1H), 3.16 (dd, J_1 = 18.0 Hz, J_2 = 2.4 Hz, 1H), 3.12 (s, 3H), 3.07 (dd, J_1 = 18.6 Hz, J_2 = 9.0 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 175.1, 161.5, 158.4 (d, $^{1}J_{C\text{-}F}$ = 235.8 Hz), 141.3, 140.1, 133.1, 129.7, 129.4 (d, $^{3}J_{C\text{-}F}$

= 9.0 Hz), 127.8, 127.0, 124.9, 124.7, 112.0 (d, $^{3}J_{C-F}$ = 9.0 Hz), 110.8 (d, $^{2}J_{C-F}$ = 25.2 Hz), 105.8 (d, $^{2}J_{C-F}$ = 23.1 Hz), 97.9 (d, $^{4}J_{C-F}$ = 4.1 Hz), 34.8, 31.8, 26.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ -122.65 (td, J_1 = 9.0 Hz, J_2 = 4.1 Hz). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{15}FN_3O$ 320.1194; Found 320.1178.

2-Chloro-11-methyl-13,13*a*-dihydrobenzo[2,3]pyrrolo[2',3':5,6][1,4]diazepino[1,7-*a*]indol-12(11*H*)-one (4k)

Eluent: petroleum ether/ethyl acetate (6:1). Yellow solid (34.2 mg, 51%), mp 209.2-210.4 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.69 (d, J = 8.4 Hz, 1H), 7.56 (d, J = 1.8 Hz, 1H), 7.51 (d, J = 9.0 Hz, 1H), 7.42 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H), 7.38-7.36 (m, 1H), 7.29-7.26 (m, 1H), 7.14 (dd, J_1 = 9.0 Hz, J_2 = 1.8 Hz, 1H), 6.30 (s, 1H), 3.98 (d, J = 7.8 Hz, 1H), 3.15 (dd, J_1 = 18.0 Hz, J_2 = 2.4 Hz, 1H), 3.11 (s, 3H), 3.07 (dd, J_1 = 18.0 Hz, J_2 = 9.0 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 175.0, 161.5, 141.1, 140.2, 134.9, 130.0, 129.5, 127.8, 127.1, 126.7, 124.9, 124.8, 122.9, 120.3, 112.2, 97.5, 34.8, 31.8, 26.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{15}ClN_3O$ 336.0898; Found 336.0883.

2-Bromo-11-methyl-13,13*a*-dihydrobenzo[2,3]pyrrolo[2',3':5,6][1,4]diazepino[1,7-*a*]indol-12(11*H*)-one (4l)

Eluent: petroleum ether/ethyl acetate (6:1). Yellow solid (41.7 mg, 55%), mp 203.7-204.7 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.73 (d, J = 1.8 Hz, 1H), 7.69 (dd, J_1 = 7.8 Hz, J_2 = 0.6 Hz, 1H), 7.47 (d, J = 9.0 Hz, 1H), 7.42 (dd, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H), 7.39-7.36 (m, 1H), 7.29-7.26 (m, 2H), 6.31 (s, 1H), 3.99 (d, J = 7.8 Hz, 1H), 3.16 (dd, J_1 = 18.6 Hz, J_2 = 3.0 Hz, 1H), 3.12 (s, 3H), 3.08 (dd, J_1 = 18.0 Hz, J_2 = 9.0 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 175.0, 161.5, 141.0, 140.2, 135.2, 130.6, 129.5, 127.8, 127.2, 125.5, 124.9, 124.8, 123.4, 114.2, 112.6, 97.4, 34.8, 31.8, 26.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{15}BrN_3O$ 380.0393; Found 380.0381.

1,11-Dimethyl-13,13*a*-dihydrobenzo[2,3]pyrrolo[2',3':5,6][1,4]diazepino[1,7-*a*]indol-12(11*H*)-one (4m)

Eluent: petroleum ether/ethyl acetate (6:1). White solid (25.8 mg, 41%), mp 218.5-218.9 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 8.0 Hz, 1H), 7.47 (d, J = 8.4 Hz, 1H), 7.41 (d, J = 7.6 Hz, 1H), 7.35 (t, J = 7.2 Hz, 1H), 7.29-7.25 (m, 1H), 7.13 (t, J = 7.6 Hz, 1H), 6.98 (d, J = 6.8 Hz, 1H), 6.39 (s, 1H), 4.03 (d, J = 8.8 Hz, 1H) 3.25-3.06 (m, 5H), 2.55 (s, 3H),. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 175.3, 161.7, 140.2, 139.3, 136.4, 130.4, 130.0, 128.7, 127.6, 126.8, 125.1, 124.8, 122.8, 121.4, 108.7, 96.4, 34.8, 31.9, 26.3, 18.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{18}N_3O$ 316.1444; Found 316.1444.

1-Fluoro-11-methyl-13,13*a*-dihydrobenzo[2,3]pyrrolo[2',3':5,6][1,4]diazepino[1,7-*a*]indol-12(11*H*)-one (4n)

Eluent: petroleum ether/ethyl acetate (6:1). White solid (32.5 mg, 51%), mp 182.7-183.7 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.74 (d, J = 7.8 Hz, 1H), 7.43-7.37 (m, 3H), 7.28 (t, J = 7.8 Hz, 1H), 7.14-7.11 (m, 1H), 6.86-6.83 (m, 1H), 6.48 (s, 1H), 4.01 (d, J = 8.4 Hz, 1H), 3.20 (dd, J_1 = 18.6 Hz, J_2 = 2.4 Hz, 1H), 3.13-3.08 (m, 4H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 175.0, 161.7, 156.1 (d, $^{1}J_{C-F}$ = 246.0 Hz), 140.2, 139.9, 138.9 (d, $^{3}J_{C-F}$ = 10.5 Hz), 129.6, 127.8, 127.2, 125.0, 124.9, 123.2 (d, $^{3}J_{C-F}$ = 7.5 Hz), 118.0 (d, $^{2}J_{C-F}$ = 21.9 Hz), 107.2 (d, $^{4}J_{C-F}$ = 3.9 Hz), 106.0 (d, $^{2}J_{C-F}$ = 17.4 Hz), 93.9, 34.7, 31.8, 26.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ -121.94 – -121.98 (m). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{15}FN_3O$ 320.1194; Found 320.1194.

1-Chloro-11-methyl-13,13*a*-dihydrobenzo[2,3]pyrrolo[2',3':5,6][1,4]diazepino[1,7-*a*]indol-12(11*H*)-one (4o)

Eluent: petroleum ether/ethyl acetate (6:1). White solid (34.8 mg, 52%), mp 191.1-191.8 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.72 (d, J = 7.2 Hz, 1H), 7.52 (d, J = 8.4 Hz, 1H), 7.43 (d, J = 7.8 Hz, 1H), 7.38 (t, J = 7.2 Hz, 1H), 7.28 (t, J = 7.2 Hz, 1H), 7.18 (d, J = 7.2 Hz, 1H), 7.13 (t, J = 7.2 Hz, 1H), 6.51 (s, 1H), 4.03 (d, J = 8.4 Hz, 1H) 3.23 (d, J = 18.0 Hz, 1H), 3.13-3.09 (m, 4H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 175.0, 161.6, 140.5, 140.3, 137.2, 129.5, 127.8, 127.7, 127.3, 126.1, 125.0, 124.9, 123.2, 120.9, 109.8, 96.6, 34.8, 31.8, 26.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{15}ClN_3O$ 336.0898; Found 336.0890.

4-Fluoro-11-methyl-13,13*a*-dihydrobenzo[2,3]pyrrolo[2',3':5,6][1,4]diazepino[1,7-*a*]indol-12(11*H*)-one (4p)

Eluent: petroleum ether/ethyl acetate (6:1). White solid (33.8 mg, 53%), mp 172.6-173.0 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.47 (t, *J* = 7.8 Hz, 1H), 7.39 (d, *J* = 7.8 Hz, 1H), 7.35-7.33 (m, 2H), 7.24-7.21 (m, 1H), 7.11-7.08 (m, 1H), 6.95-6.92 (m, 1H), 6.45 (s, 1H), 3.95 (d, *J* = 7.8 Hz, 1H), 3.17-3.14 (m, 4H), 3.08 (dd, J_1 = 18.0 Hz, J_2 = 9.0 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 175.0, 161.9, 149.3 (d, $^1J_{C-F}$ = 247.3 Hz), 142.4, 140.2, 132.7 (d, $^3J_{C-F}$ = 3.8 Hz), 130.1 (d, $^4J_{C-F}$ = 2.1 Hz), 127.0, 126.8 (d, $^5J_{C-F}$ = 7.1 Hz), 126.2, 124.3 (d, $^2J_{C-F}$ = 8.4 Hz), 124.2, 121.5 (d, $^3J_{C-F}$ = 7.2 Hz), 116.6 (d, $^4J_{C-F}$ = 3.3 Hz), 109.1 (d, $^2J_{C-F}$ = 19.2 Hz), 99.5 (d, $^4J_{C-F}$ = 2.1 Hz), 34.6, 32.0, 26.4. ^{19}F NMR (565 MHz, $CDCl_3$): δ -121.97 – -122.01 (m). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{15}FN_3O$ 320.1194; Found 320.1189.

4-Chloro-11-methyl-13,13*a*-dihydrobenzo[2,3]pyrrolo[2',3':5,6][1,4]diazepino[1,7-*a*]indol-12(11*H*)-one (4q)

Eluent: petroleum ether/ethyl acetate (6:1). White solid (33.5 mg, 50%), mp 173.0-174.0 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (dd, J_1 = 8.0 Hz, J_2 = 0.8 Hz, 1H), 7.36-7.33 (m, 2H), 7.30-7.16 (m, 3H), 7.11 (t, *J* = 8.0 Hz, 1H), 6.48 (d, *J* = 1.2 Hz, 1H), 3.96-3.93 (m, 1H), 3.18-3.12 (m, 4H), 3.07 (dd, J_1 = 18.4 Hz, J_2 = 8.8 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 175.0, 162.5, 144.1, 141.0, 132.8, 131.9, 129.5, 129.0, 127.1, 125.6, 125.0, 123.3, 121.9, 119.4, 117.7, 99.9, 34.7, 32.0, 26.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{15}ClN_3O$ 336.0898; Found 336.0890.

8-Methoxy-11-methyl-13,13*a*-dihydrobenzo[2,3]pyrrolo[2',3':5,6][1,4]diazepino[1,7-*a*]indol-12(11*H*)-one (4r)

Eluent: petroleum ether/ethyl acetate (6:1). White solid (27.2 mg, 41%), mp 201.0-202.8 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 9.2 Hz, 1H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.22-7.13 (m, 2H), 6.93 (d, *J* = 2.8 Hz, 1H), 6.84 (dd, J_1 = 8.8 Hz, J_2 = 2.8 Hz, 1H), 6.35 (s, 1H), 4.00 (d, *J* = 8.4 Hz, 1H), 3.88 (s, 3H), 3.18 (dd, J_1 = 18.4 Hz, J_2 = 2.4 Hz, 1H), 3.10-3.03 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 175.6, 162.3, 158.5, 141.7, 139.9, 137.0, 129.1, 126.2, 123.5, 122.9, 121.32, 121.26, 112.2, 111.5, 111.3, 97.8, 56.1, 35.3, 32.2, 26.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{18}N_3O_2$ 332.1394; Found 332.1385.

7-Fluoro-11-methyl-13,13*a*-dihydrobenzo[2,3]pyrrolo[2',3':5,6][1,4]diazepino[1,7-*a*]indol-12(11*H*)-one (4s)

Eluent: petroleum ether/ethyl acetate (6:1). Red solid (30.6 mg, 48%), mp 117.0-118.0 ℃. ^1H NMR (600 MHz, $CDCl_3$): δ 7.64-7.62 (m, 2H), 7.51 (dd, J_1 = 9.0 Hz, J_2 = 1.8 Hz, 1H), 7.38 (dd, J_1 = 8.4 Hz, J_2 = 6.0 Hz, 1H), 7.24 (d, J = 8.4 Hz, 1H), 7.19 (t, J = 7.2 Hz, 1H), 7.10-7.07 (m, 1H), 6.38 (s, 1H), 4.01 (d, J = 8.4 Hz, 1H), 3.18 (d, J = 18.6 Hz, 1H), 3.10-3.07 (m, 4H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 175.0, 161.5, 159.1 (d, $^1J_{C\text{-}F}$ = 243.0 Hz), 139.6, 136.6 (d, $^4J_{C\text{-}F}$ = 2.7 Hz), 136.4, 130.5 (d, $^3J_{C\text{-}F}$ = 10.5 Hz), 129.1 (d, $^3J_{C\text{-}F}$ = 8.1Hz), 129.0, 123.0, 121.6, 121.1, 114.0 (d, $^2J_{C\text{-}F}$ = 21.6 Hz), 111.6 (d, $^2J_{C\text{-}F}$ = 24.9 Hz), 110.9, 98.6, 34.7, 31.9, 26.3. ^{19}F NMR (565 MHz, $CDCl_3$): δ -116.62 – -116.66 (m). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{15}FN_3O$ 320.1194; Found 320.1186.

7-Chloro-11-methyl-13,13*a*-dihydrobenzo[2,3]pyrrolo[2',3':5,6][1,4]diazepino[1,7-*a*]indol-12(11*H*)-one (4t)

Eluent: petroleum ether/ethyl acetate (6:1). White solid (30.1 mg, 45%), mp 234.9-235.3 ℃. ^1H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, J = 2.0 Hz, 1H), 7.63 (d, J = 8.4 Hz, 2H), 7.36-7.30 (m, 2H), 7.28-7.24 (m, 1H), 7.20 (t, J = 7.6 Hz, 1H), 6.39 (s, 1H), 4.01 (dd, J_1 = 8.8 Hz, J_2 = 1.6 Hz, 1H), 3.19 (dd, J_1 = 18.4 Hz, J_2 = 2.8 Hz, 1H), 3.13-3.06 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 175.0, 161.9, 139.6, 138.8, 136.4, 130.7, 129.7, 129.0, 128.9, 126.9, 124.7, 123.1, 121.6, 121.1, 110.9, 98.7, 34.8, 31.9, 26.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{15}ClN_3O$ 336.0898; Found 336.0891.

7-Bromo-11-methyl-13,13*a*-dihydrobenzo[2,3]pyrrolo[2',3':5,6][1,4]diazepino[1,7-*a*]indol-12(11*H*)-one (4u)

Eluent: petroleum ether/ethyl acetate (6:1). Red solid (34.9 mg, 46%), mp 243.8-244.7 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.91 (s, 1H), 7.61 (d, J = 7.8 Hz, 2H), 7.45 (d, J = 7.2 Hz, 1H), 7.28-7.24 (m, 2H), 7.19 (t, J = 7.2 Hz, 1H), 6.38 (s, 1H), 3.98 (d, J = 8.4 Hz, 1H), 3.17 (d, J = 18.0 Hz, 1H), 3.10-3.06 (m, 4H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 175.0, 161.9, 139.6, 139.3, 136.4, 131.0, 129.8, 129.2, 129.0, 127.6, 123.1, 121.6, 121.1, 117.1, 110.8, 98.7, 34.8, 31.9, 26.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{15}BrN_3O$ 380.0393; Found 380.0390.

11-Ethyl-13,13*a*-dihydrobenzo[2,3]pyrrolo[2',3':5,6][1,4]diazepino[1,7-*a*]indol-12(11*H*)-one (4v)

Eluent: petroleum ether/ethyl acetate (6:1). White solid (31.5 mg, 50%), mp 179.5-180.5 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.78 (d, J = 7.8 Hz, 1H), 7.65-7.63 (m, 2H), 7.41 (d, J = 7.2 Hz, 1H), 7.36 (t, J = 7.8 Hz, 1H), 7.27 (t, J = 7.8 Hz, 1H), 7.22 (t, J = 7.8 Hz, 1H), 7.18 (t, J = 7.2 Hz, 1H), 6.38 (s, 1H), 4.00 (d, J = 8.4 Hz, 1H), 3.78-3.73 (m, 1H), 3.69-3.64 (m, 1H), 3.17 (dd, J_1 = 18.0 Hz, J_2 = 2.4 Hz, 1H), 3.07 (dd, J_1 = 18.6 Hz, J_2 = 8.4 Hz, 1H), 1.19 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 175.0, 161.0, 140.2, 140.0, 136.6, 129.9, 129.0, 127.7, 126.7, 124.9, 124.7, 122.6, 121.1, 120.9, 111.1, 97.9, 35.0, 34.7, 31.9, 12.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{18}N_3O$ 316.1444; Found 316.1433.

11-Benzyl-13,13*a*-dihydrobenzo[2,3]pyrrolo[2',3':5,6][1,4]diazepino[1,7-*a*]indol-12(11*H*)-one (4w)

Eluent: petroleum ether/ethyl acetate (6:1). Gray solid (31.7 mg, 42%), mp 249.5-250.1 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.77 (d, J = 7.8 Hz, 1H), 7.63 (d, J = 8.4 Hz, 2H), 7.42-7.39 (m, 3H), 7.35-7.33 (m, 1H), 7.27-7.20 (m, 5H), 7.17 (t, J = 7.8 Hz, 1H), 6.38 (s, 1H), 4.86 (d, J = 13.8 Hz, 1H), 4.74 (d, J = 14.4 Hz, 1H), 4.01 (d, J = 8.4 Hz, 1H), 3.19 (dd, J_1 = 18.6 Hz, J_2 = 2.4 Hz, 1H), 3.08 (dd, J_1 = 18.0 Hz, J_2 = 9.0 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 175.0, 160.8, 140.1, 139.9, 136.6, 136.0, 129.9, 129.0, 128.8, 128.5, 127.8, 127.7, 126.7, 124.9, 124.8, 122.6, 121.1, 120.9, 111.1, 98.1, 43.5, 34.8, 31.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{20}N_3O$ 378.1601; Found 378.1599.

11-Isobutyl-13,13*a*-dihydrobenzo[2,3]pyrrolo[2',3':5,6][1,4]diazepino[1,7-*a*]indol-12(11*H*)-one (4x)

Eluent: petroleum ether/ethyl acetate (6:1). White solid (30.8 mg, 45%), mp 240.4-241.5 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, J = 7.6 Hz, 1H), 7.65-7.62 (m, 2H), 7.39 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.37-7.33 (m, 1H), 7.29-7.27 (m, 1H), 7.22-7.16 (m, 2H), 6.38 (s, 1H), 4.00 (d, J = 7.6 Hz, 1H), 3.53 (dd, J_1 = 13.2 Hz, J_2 = 7.6 Hz, 1H), 3.44 (dd, J_1 = 13.2 Hz, J_2 = 7.6 Hz, 1H), 3.19 (dd, J_1 = 18.4 Hz, J_2 = 2.4 Hz, 1H), 3.08 (dd, J_1 = 18.4 Hz, J_2 = 9.2 Hz, 1H), 2.19-2.09 (m, 1H), 0.84-0.80 (m, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 175.5, 161.6, 140.3, 140.1, 136.5, 129.8, 129.0, 127.7, 126.7, 124.9, 124.6, 122.5, 121.1, 120.9, 111.1, 97.7, 47.1, 34.6, 31.7, 26.5, 20.1, 20.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{22}N_3O$ 344.1757; Found 344.1757.

10-Methyl-12,12a-dihydrobenzo[*b*]dipyrrolo[1,2-*d*:3',2'-*f*][1,4]diazepin-11(10*H*)-one (4y)

Eluent: petroleum ether/ethyl acetate (6:1). Yellow solid (26.1 mg, 52%), mp 127.2-128.0 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.46 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H), 7.36-7.34 (m, 1H), 7.30 (td, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 1H), 7.23-7.20 (m, 1H), 7.08-7.07 (m, 1H), 6.36-6.35 (m, 1H), 6.02-6.01 (m, 1H), 3.83 (dd, J_1 = 8.4 Hz, J_2 = 3.0 Hz, 1H), 3.14 (s, 3H), 3.11-3.02 (m, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 175.5, 161.6, 138.6, 131.9, 131.6, 128.0, 126.6, 125.3, 123.8, 121.5, 110.4, 104.2, 34.3, 32.2, 26.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{14}N_3O$ 252.1131; Found 252.1134.

3. Typical procedure for the synthesis of 5a and spectroscopic data of 5a-5f[2]

To a reaction tube equipped with a stir bar were added **3a** (63.8 mg, 0.2 mmol), DMF (2 mL), DEAD (31.5 μL, 0.2 mmol) and K_2CO_3 (138.2 mg, 1 mmol) with stirring. The mixture was stirred at room temperature for 2 h. Afterwards, it was quenched with water, filtered through a pad of celite, and extracted with CH_2Cl_2 (10 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (6:1) as eluent to afford **5a**. **5b-5f** were obtained in a similar manner.

3-(1-(2-Aminophenyl)-1*H*-indol-2-yl)-1-methyl-1*H*-pyrrole-2,5-dione (5a)

Eluent: petroleum ether/ethyl acetate (6:1). Yellow solid (39.9 mg, 63%), mp 197.5-198.4 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (s, 1H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.26-7.25 (m, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 7.2 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.90-6.85 (m, 2H), 5.54 (s, 1H), 3.50 (br s, 2H), 2.98 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 171.3, 170.5, 144.2, 140.5, 134.4, 131.0, 129.7, 128.2, 127.9, 126.0, 122.7, 122.5, 121.6, 119.3, 118.7, 116.6, 112.7, 110.7, 23.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{16}N_3O_2$ 318.1237; Found 318.1228.

3-(1-(2-Aminophenyl)-6-methyl-1*H*-indol-2-yl)-1-methyl-1*H*-pyrrole-2,5-dione (5b)

Eluent: petroleum ether/ethyl acetate (6:1). Yellow solid (46.5 mg, 70%), mp 195.4-195.8 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.89 (s, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.35-7.32 (m, 1H), 7.07 (dd, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 1H), 7.01 (d, *J* = 7.8 Hz, 1H), 6.90-6.86 (m, 2H), 6.76 (s, 1H), 5.47 (s, 1H), 3.52 (s, 2H), 2.96 (s, 3H), 2.39 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 171.4, 170.6, 144.3, 141.0, 136.7, 134.5, 130.9, 129.7, 127.8, 125.9, 123.7, 122.7, 122.3, 119.3, 117.7, 116.6, 112.8, 110.4, 23.8, 22.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{18}N_3O_2$ 332.1394; Found 332.1381.

3-(1-(2-Aminophenyl)-5-methyl-1*H*-indol-2-yl)-1-methyl-1*H*-pyrrole-2,5-dione (5c)

Eluent: petroleum ether/ethyl acetate (6:1). Yellow solid (40.5 mg, 61%), mp 198.7-199.7 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.85 (s, 1H), 7.51 (s, 1H), 7.34-7.31 (m, 1H), 7.09 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H), 7.06 (dd, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 1H), 6.89-6.85 (m, 3H), 5.51 (s, 1H), 3.50 (s, 2H), 2.98 (s, 3H), 2.44 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 171.4, 170.5, 144.2, 139.1, 134.5, 131.0, 130.9, 129.6, 128.2, 128.1, 127.9, 122.7, 122.0, 119.3, 118.3, 116.6, 112.2, 110.4, 23.8, 21.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{18}N_3O_2$ 332.1394; Found 332.1385.

3-(1-(2-Aminophenyl)-4-fluoro-1*H*-indol-2-yl)-1-methyl-1*H*-pyrrole-2,5-dione (5d)

Eluent: petroleum ether/ethyl acetate (6:1). Yellow solid (38.2 mg, 57%), mp 218.3-220.5 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.00 (s, 1H), 7.37-7.34 (m, 1H), 7.20-7.17 (m, 1H), 7.09 (dd, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 1H), 6.92-6.88 (m, 2H), 6.86-6.83 (m, 1H), 6.78 (d, J = 8.4 Hz, 1H), 5.57 (s, 1H), 3.51 (s, 2H), 3.01 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 171.1, 170.2, 157.2 (d, $^1J_{C-F}$ = 250.8 Hz), 144.0, 142.5 (d, $^3J_{C-F}$ = 10.4 Hz), 134.0, 131.2, 129.5, 128.1, 126.5 (d, $^3J_{C-F}$ = 7.7 Hz), 122.2, 119.6, 119.4, 117.6 (d, $^2J_{C-F}$ = 23.0 Hz), 116.7, 108.3, 106.8 (d, $^4J_{C-F}$ = 2.6 Hz), 106.1 (d, $^2J_{C-F}$ = 18.5 Hz), 23.9. ^{19}F NMR (565 MHz, $CDCl_3$): δ -119.46 – -119.48 (m). HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{14}FN_3O_2Na$ 358.0962; Found 358.0954.

3-(1-(2-Aminophenyl)-7-chloro-1*H*-indol-2-yl)-1-methyl-1*H*-pyrrole-2,5-dione (5e)

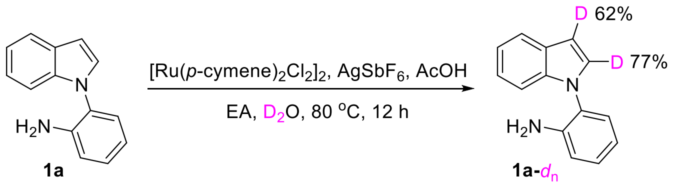
Eluent: petroleum ether/ethyl acetate (6:1). Yellow solid (46.6 mg, 66%), mp 191.1-193.0 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.97 (s, 1H), 7.67 (d, J = 8.4 Hz, 1H), 7.34 (t, J = 7.8 Hz, 1H), 7.25 (d, J = 7.2 Hz, 1H), 7.10 (t, J = 7.8 Hz, 1H), 7.07 (d, J = 7.8 Hz, 1H), 6.85-6.82 (m, 2H), 5.48 (s, 1H), 3.56 (s, 2H), 3.02 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 171.1, 170.4, 145.2, 135.2, 133.8, 131.3, 130.6, 130.4, 129.8, 127.3, 123.9, 122.0, 121.5, 120.3, 118.8, 117.5, 116.0, 113.0, 23.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{15}ClN_3O_2$ 352.0847; Found 352.0844.

3-(1-(2-Amino-5-chlorophenyl)-1*H*-indol-2-yl)-1-methyl-1*H*-pyrrole-2,5-dione (5f)

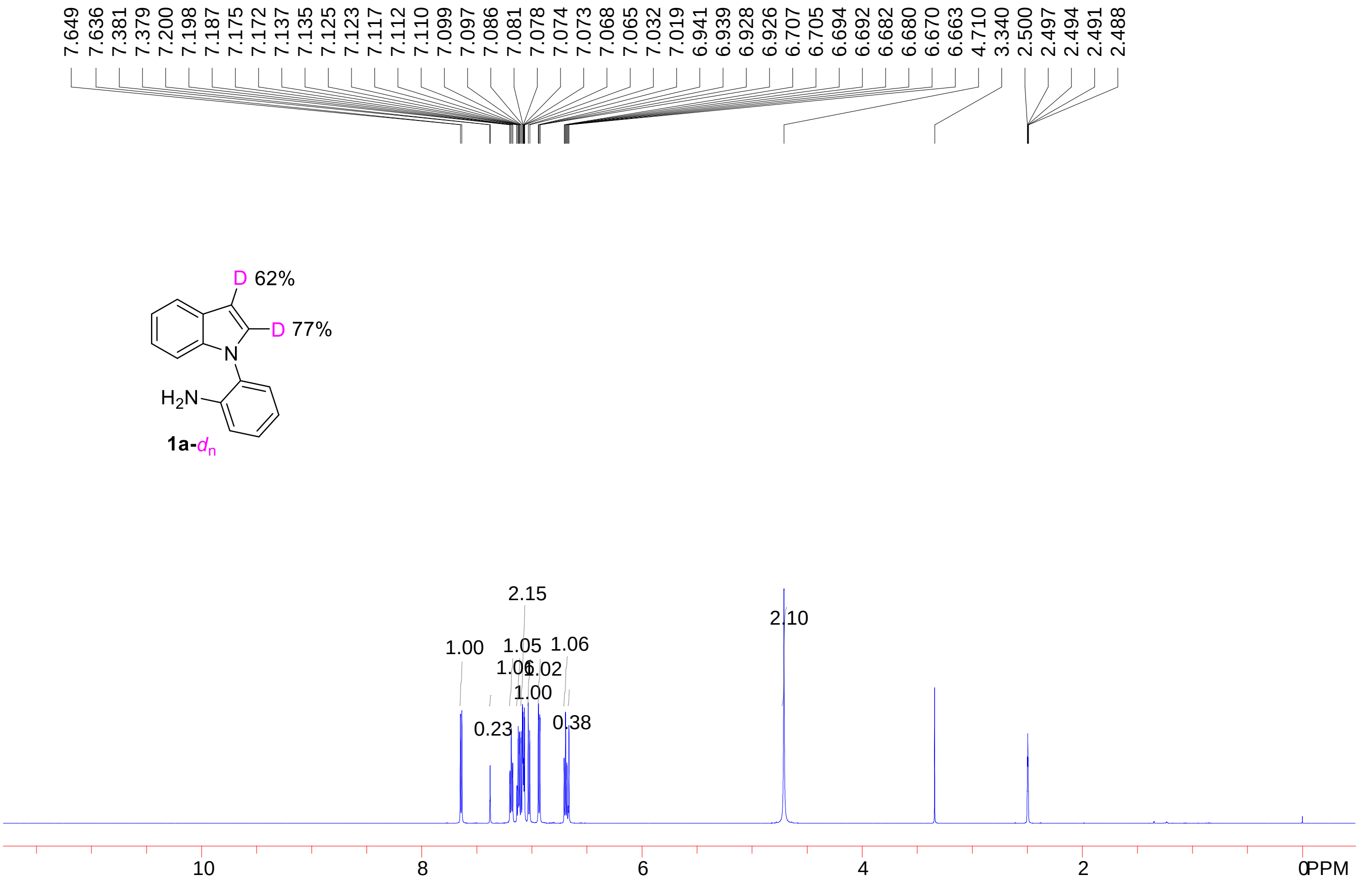
Eluent: petroleum ether/ethyl acetate (6:1). Yellow solid (41.8 mg, 60%), mp 191.3-191.6 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.93 (s, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.33-7.28 (m, 2H), 7.20 (t, *J* = 1.2 Hz, 1H), 7.10 (d, *J* = 2.4 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 6.85 (d, *J* = 9.0 Hz, 1H), 5.63 (s, 1H), 3.57 (s, 2H), 3.00 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 171.1, 170.3, 143.0, 140.4, 134.2, 131.0, 129.4, 128.0, 127.9, 126.3, 123.3, 123.2, 122.8, 121.9, 118.8, 117.4, 113.2, 110.6, 23.9. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{14}ClN_3O_2Na$ 374.0667; Found 374.0657.

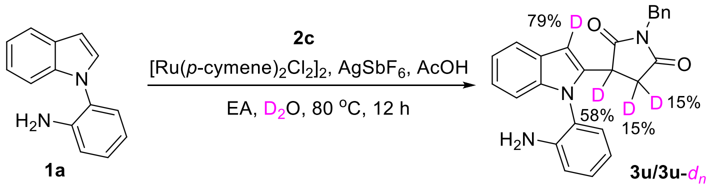
III. Mechanism studies

1. Studies on the reversibility of C−H bond cleavage

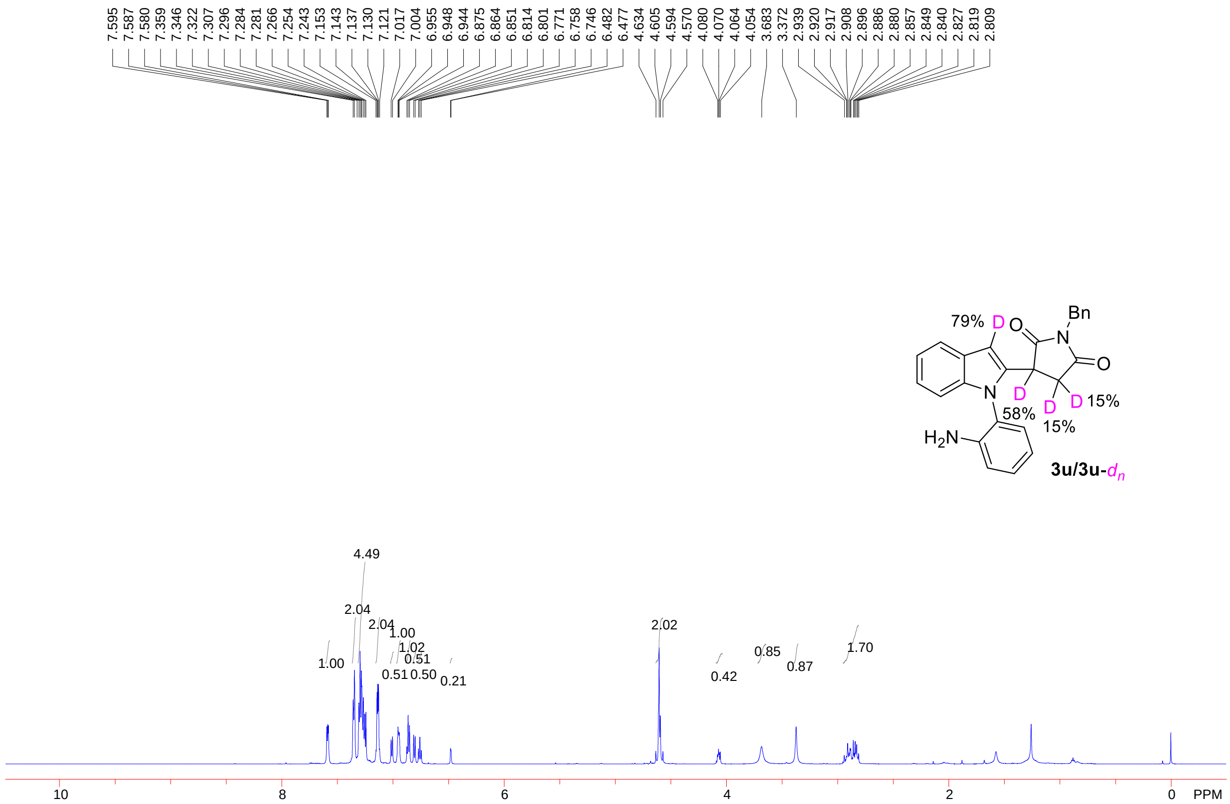


To a reaction tube equipped with a stir bar were charged with 2-(1*H*-indol-1-yl)aniline (**1a**, 41.6 mg, 0.2 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (6.12 mg, 0.01 mmol), $AgSbF_6$ (13.7 mg, 0.04 mmol), AcOH (57 μL, 1.0 mmol), EA (2 mL) and D_2O (72 μL, 4 mmol). The tube was sealed, and the resulting mixture was stirred at 80 ℃ under air for 12 h. Upon analyzing the ^{1}H NMR spectrum of the resulting mixture, the deuteration percentages at the α- and β-position of the indole moiety of **1a** were calculated as 77% and 62%.

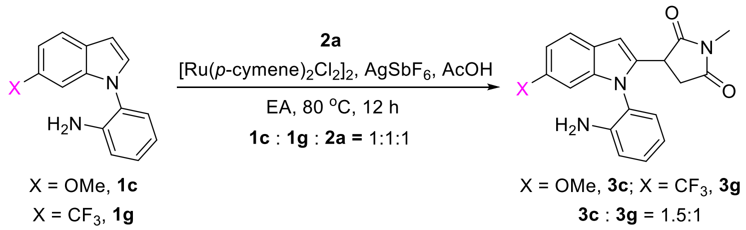




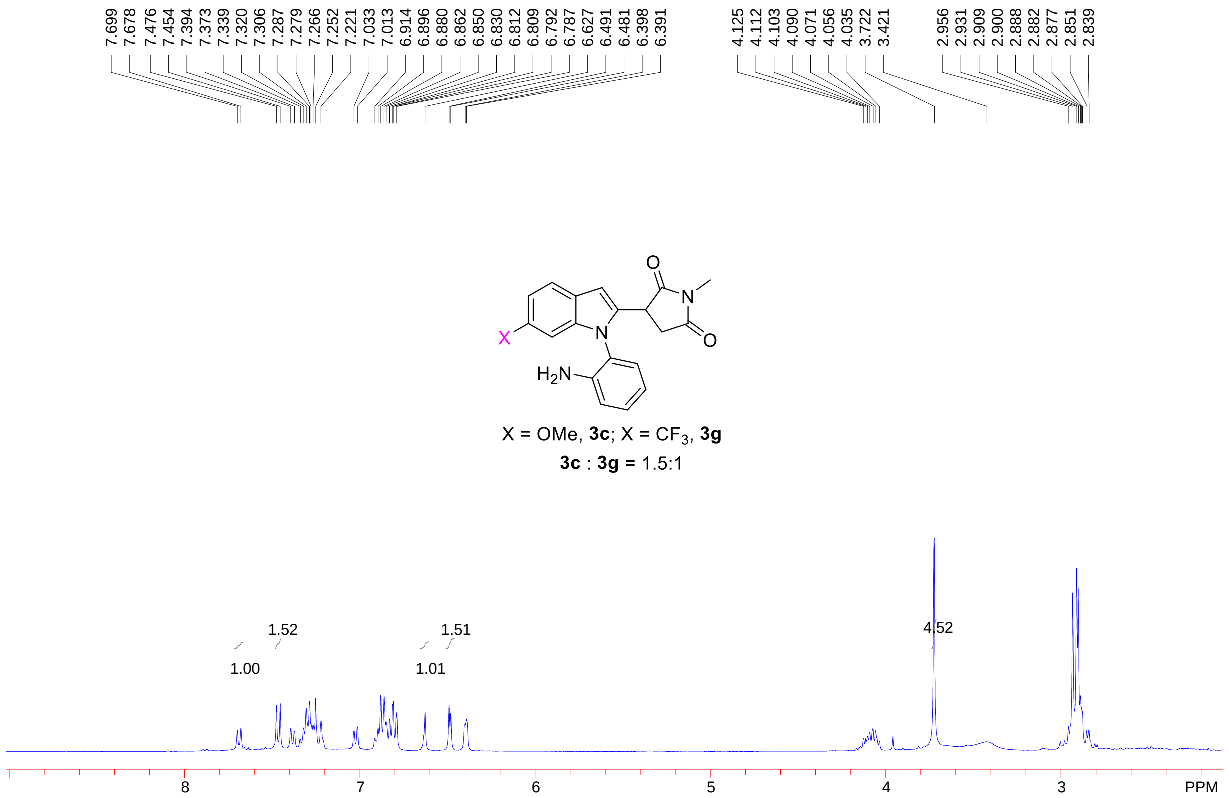
To a reaction tube equipped with a stir bar were added 2-(1*H*-indol-1-yl)aniline (**1a**, 41.6 mg, 0.2 mmol), EA (2 mL), D_2O (72 μL, 4 mmol), *N*-benzyl maleimide (**2c**, 56.2 mg, 0.3 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (6.12 mg, 0.01 mmol), $AgSbF_6$ (13.7 mg, 0.04 mmol) and AcOH (57 μL, 1.0 mmol) with stirring. The mixture was stirred at 80 ℃ under air for 12 h. Afterwards, it was cooled to room temperature, quenched with saturated aqueous solution of $NaHCO_3$ (1 mL), filtered through a pad of celite, and extracted with CH_2Cl_2 (10 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (4:1) as eluent to afford afford a mixture of **3u** and **3u**-d_n. Upon analyzing the ^{1}H NMR spectrum of the mixture, the deuteration percentages on the secondary and tertiary carbon center of the succinimide unit of **3u** were calculated to be 15% and 58%. Meanwhile, 79% deuteration on the β-position of the indole scaffold was also observed.



2. Electronic competition experiment



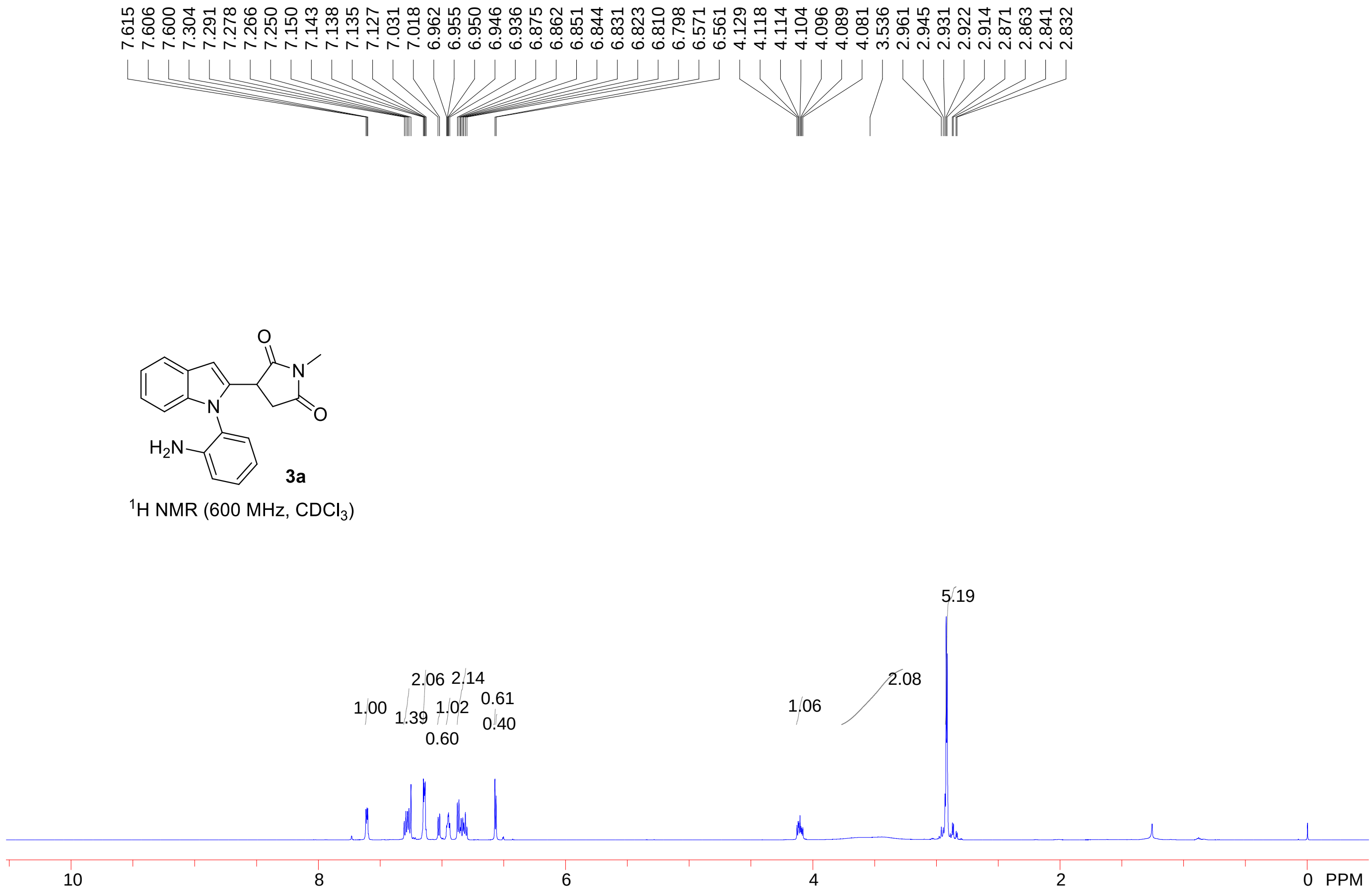
To a reaction tube equipped with a stir bar were added 2-(6-methoxy-1*H*-indol-1-yl)aniline (**1c**, 47.6 mg, 0.2 mmol), 2-(6-(trifluoromethyl)-1*H*-indol-1-yl)aniline (**1g**, 55.3 mg, 0.2 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (6.12 mg, 0.01 mmol), $AgSbF_6$ (13.7 mg, 0.04 mmol), AcOH (57 μL, 1.0 mmol), EA (2 mL) and *N*-methylmaleimide (**2a**, 22.2 mg, 0.2 mmol). The mixture was stirred at 80 ℃ under air for 12 h. Afterwards, it was cooled to room temperature, quenched with saturated aqueous solution of $NaHCO_3$ (1 mL), filtered through a pad of celite, and extracted with CH_2Cl_2 (10 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (4:1) as eluent to afford a mixture of **3c** and **3g**. Upon analyzing the ^{1}H NMR spectrum of the mixture, the ratio of **3c** to **3g** was determined to be about 1.5:1.



IV. Cell antiproliferative activity assay

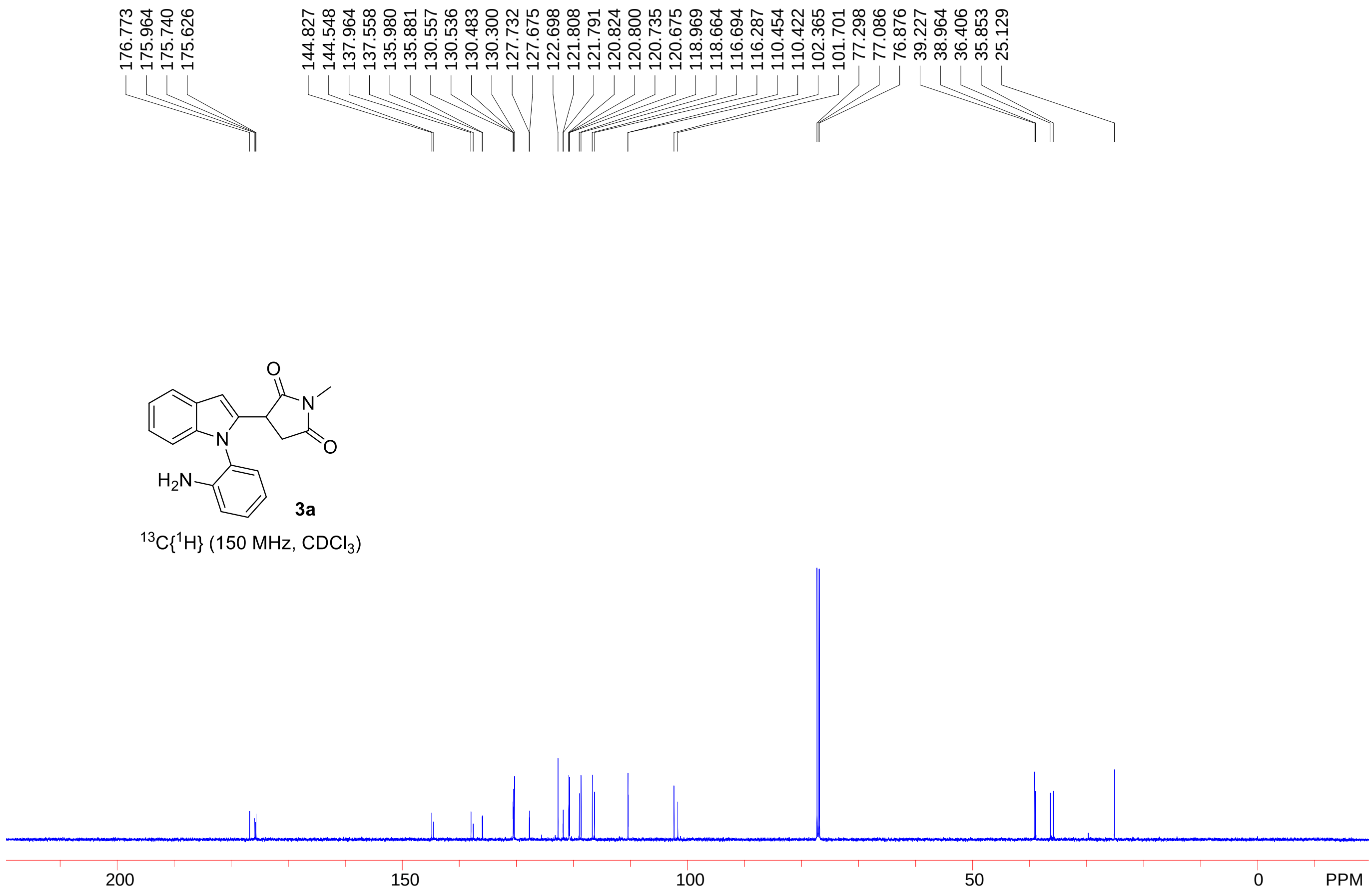
Cell antiproliferative activity was evaluated by the CellTiter-Glo (Promega, USA) assay. Make 1000× compounds solution in DMSO, Add 1 μL 1000 × compounds to 49 μL growth medium to make 20 × compounds. Dilute cell suspensions in growth medium to desired density and 95 μL were taken to 96-well plate. Add 5 μL 20 × compounds into 96-well plate according to the plate map. Final DMSO concentration in each well was 0.1%. Then the cell was incubated at 37 ℃, 5% CO_2 for 72 h. Equilibrate the assay plate to room temperature before measurement. Add 20 μL of CellTiter-Glo® Reagent into each well. Mix contents for 2 minutes on an orbital shaker to induce cell lysis. Incubate at room temperature for 10 minutes to stabilize luminescent signal. Record luminescence using EnVision Multilabel Reader (PerkinElmer). Cell viability (CV%) was calculated relative to vehicle (DMSO) treated control wells using following fromula: Cell viability(%) = (RLU compound -RLU blank)/(RLU control-RLU blank)*100%. The IC_{50} values were calculated using GraphPad Prism 6.0 software, fitting to a 4-parameter equation to generate concentration response curves. All assays were conducted with two parallel samples and two repetitions, and 5-fluorouracil was used as the positive control.

V. NMR spectra of 3a-3v



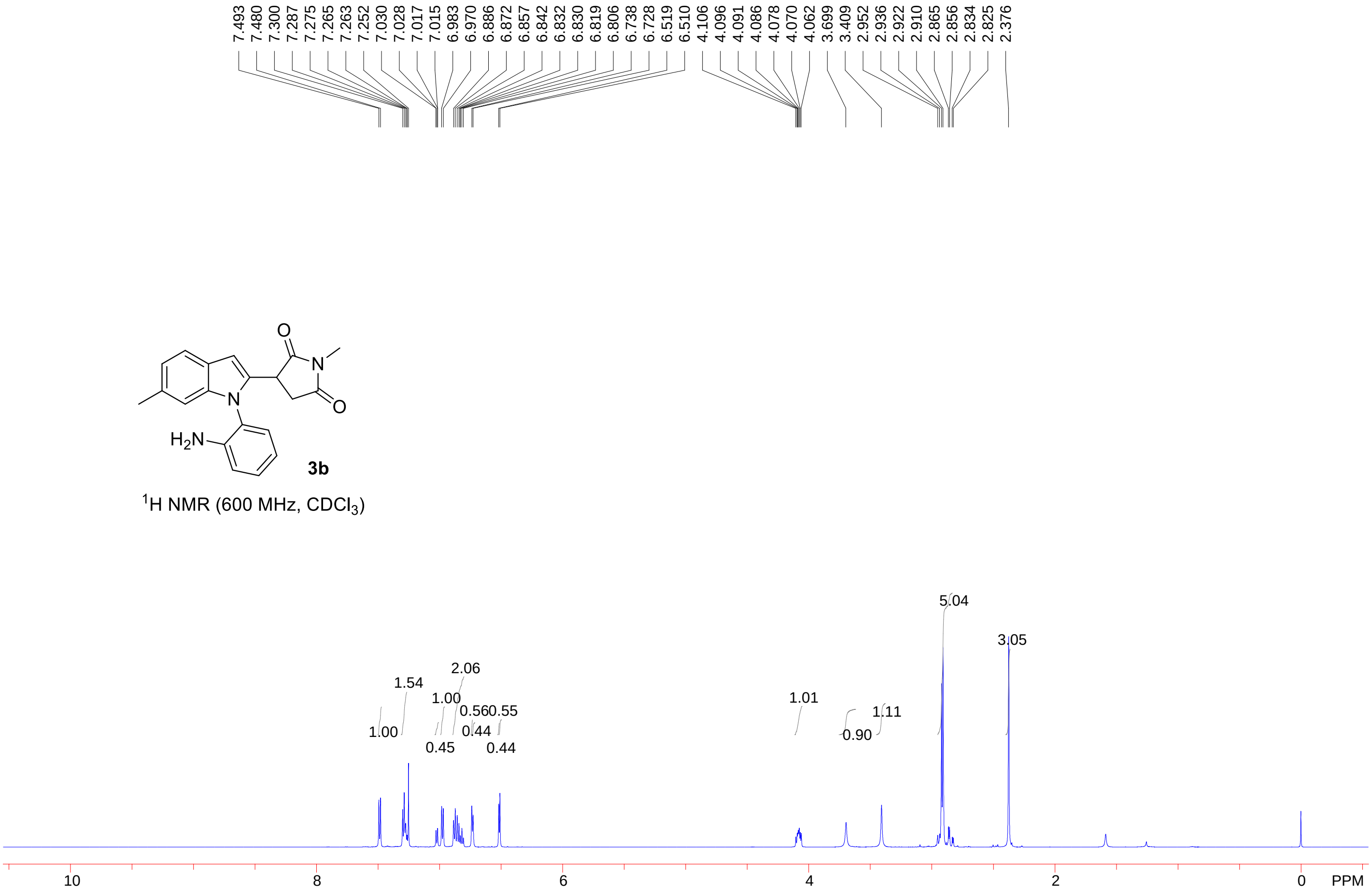
3a

^{1}H NMR (600 MHz, $CDCl_3$)



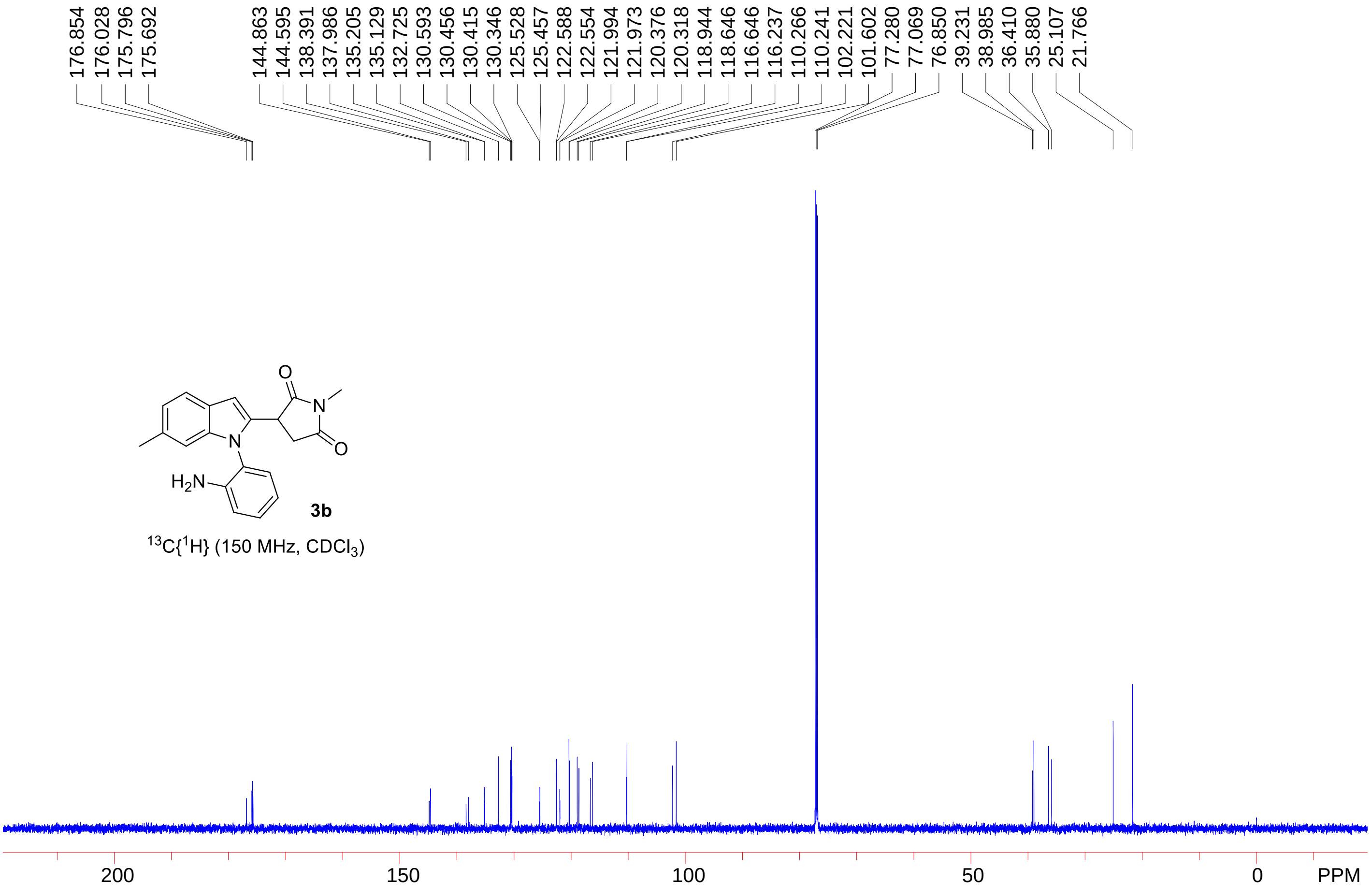
3a

$^{13}C\{^1H\}$ (150 MHz, $CDCl_3$)



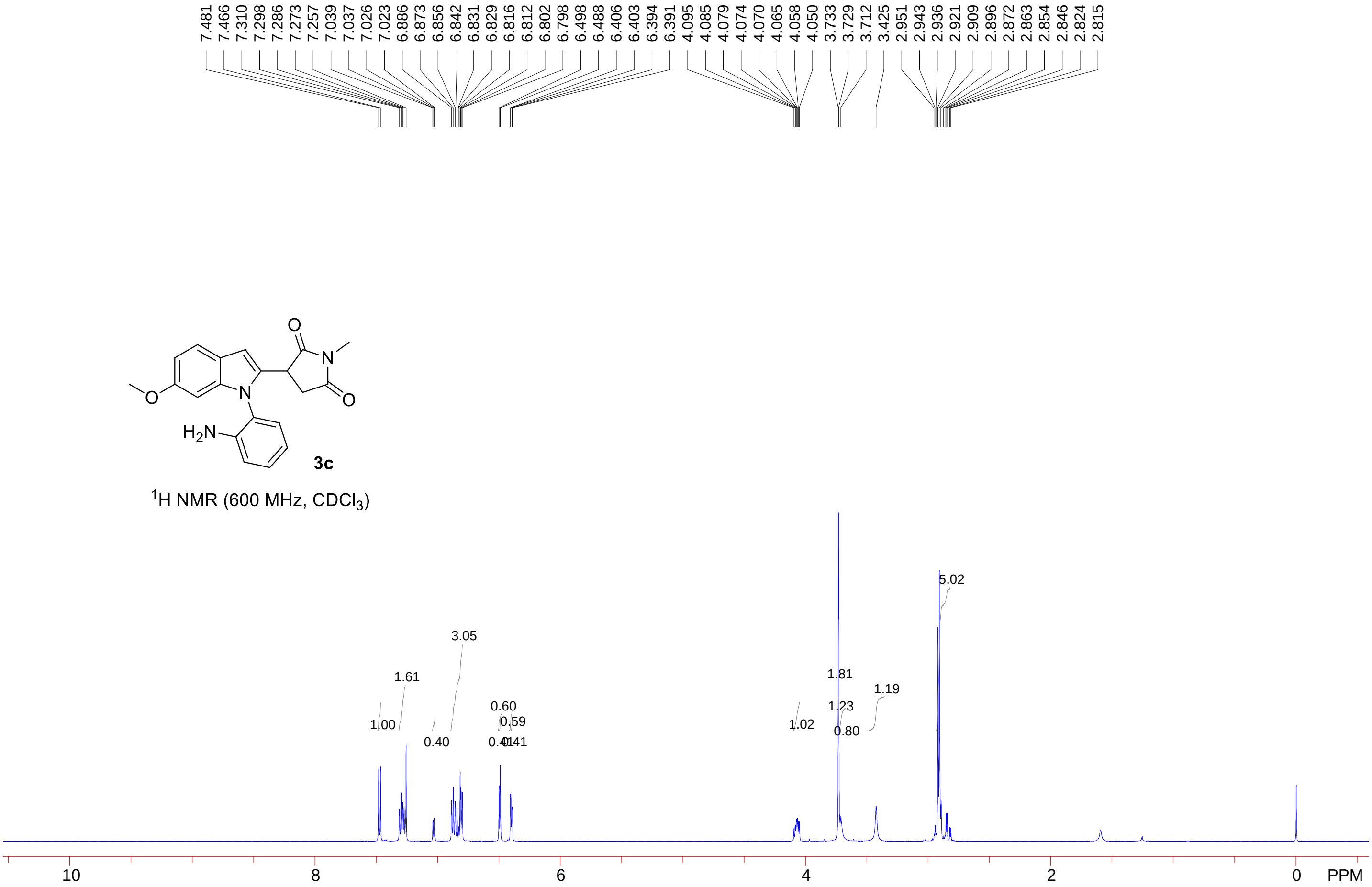
3b

^1H NMR (600 MHz, $CDCl_3$)



3b

$^{13}C\{^1H\}$ (150 MHz, $CDCl_3$)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6.829
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4.065
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3.712
3.425
2.951
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2.936
2.921
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2.896
2.872
2.863
2.854
2.846
2.824
2.815
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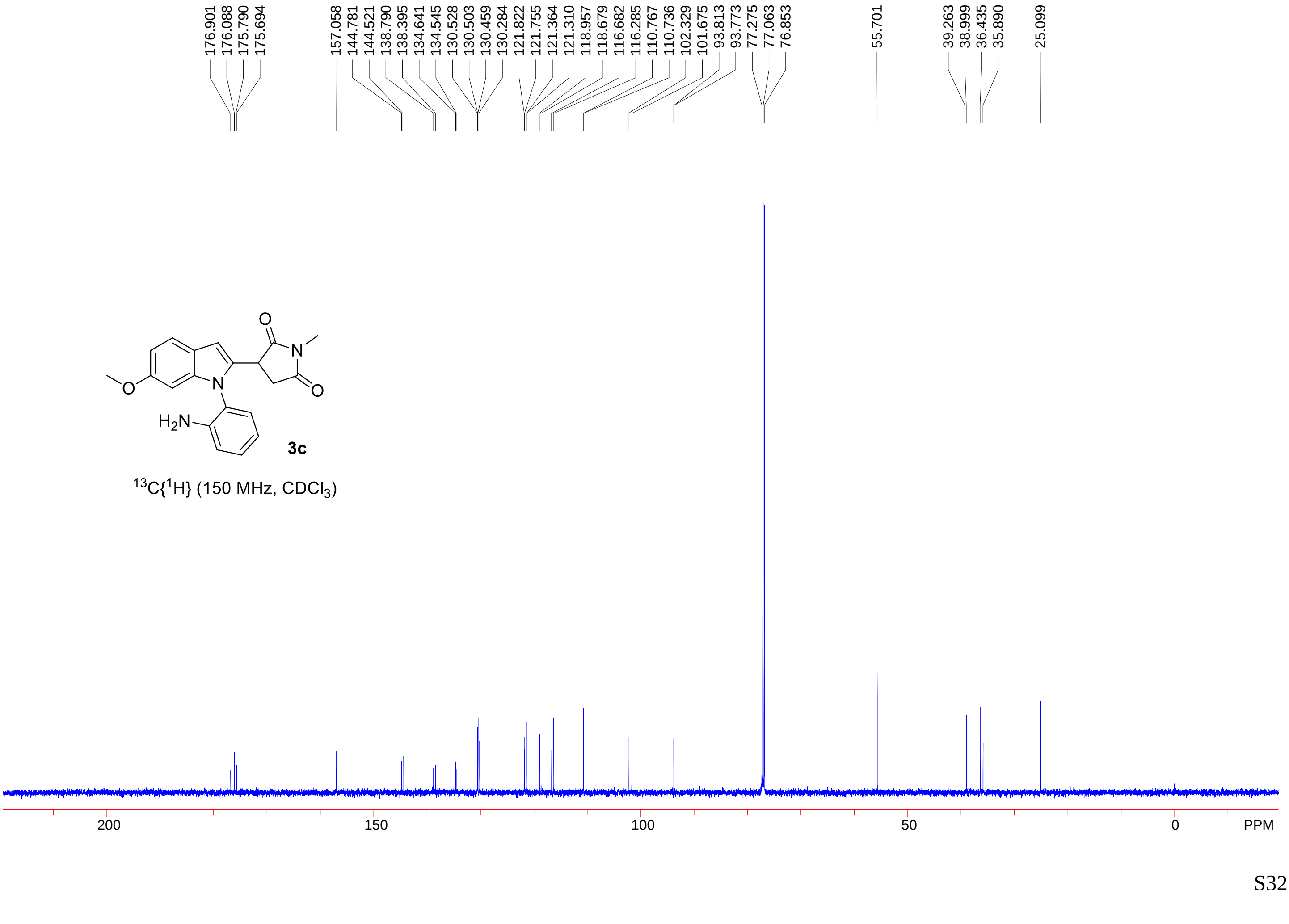
N
O
O
N
H_2N
3c
^{1}H NMR (600 MHz, $CDCl_3$)
5.02
3.05
1.61
1.81
1.19
0.60
1.23
0.59
1.00
1.02
0.80
0.40
0.41
0.41
10
8
6
4
2
0
PPM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O
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O
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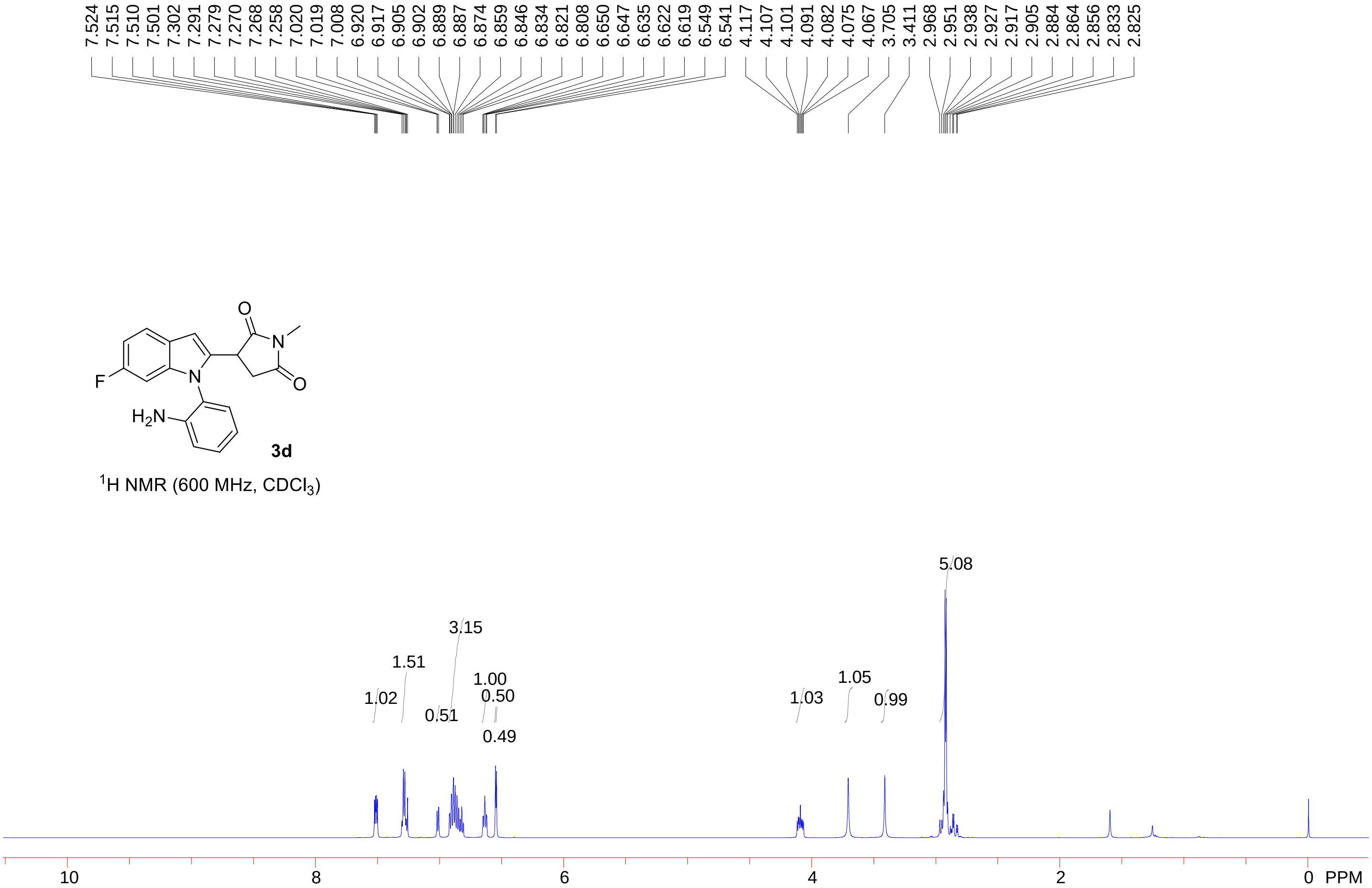
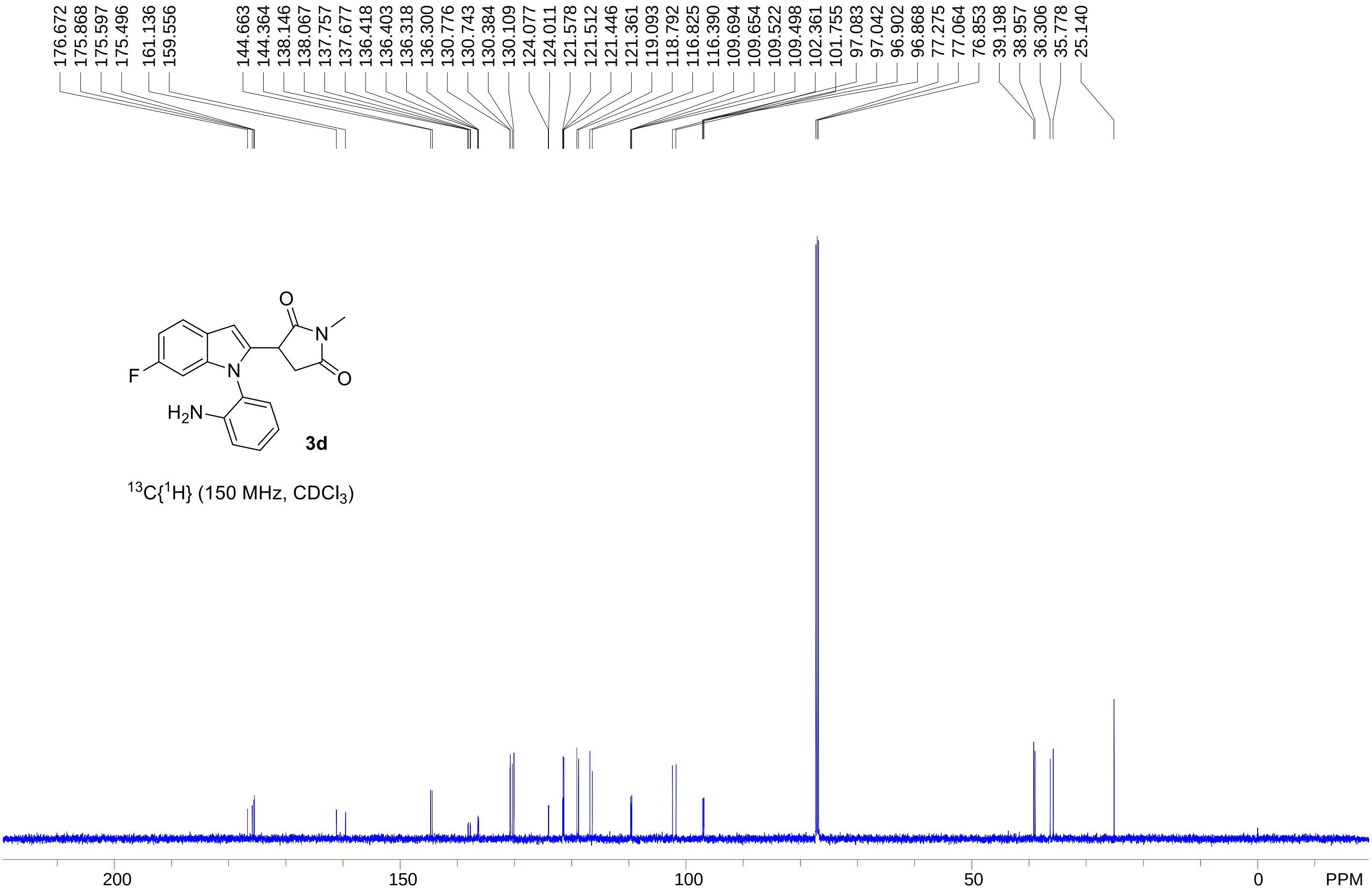
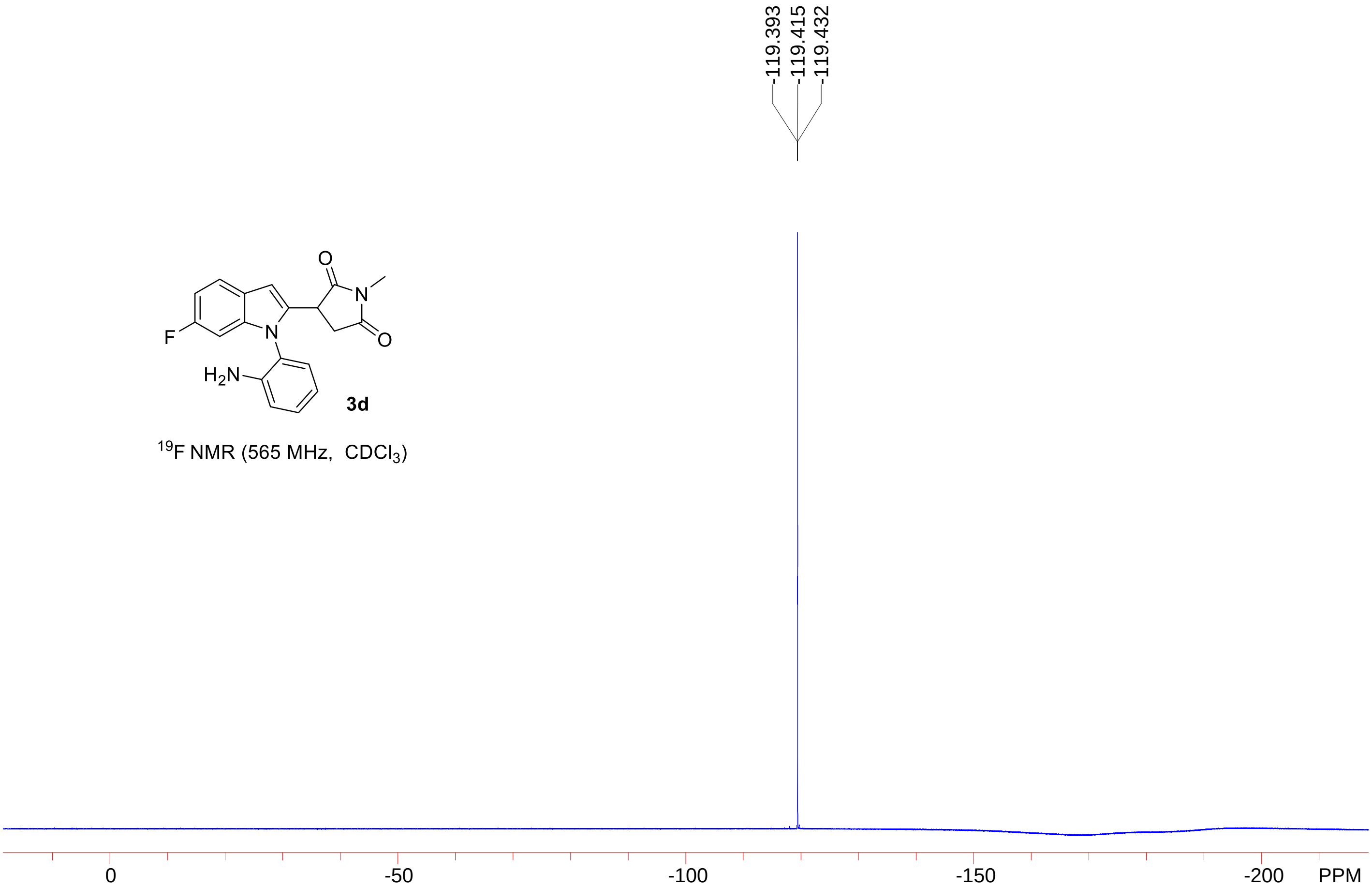
200
150
100
50
0
PPM

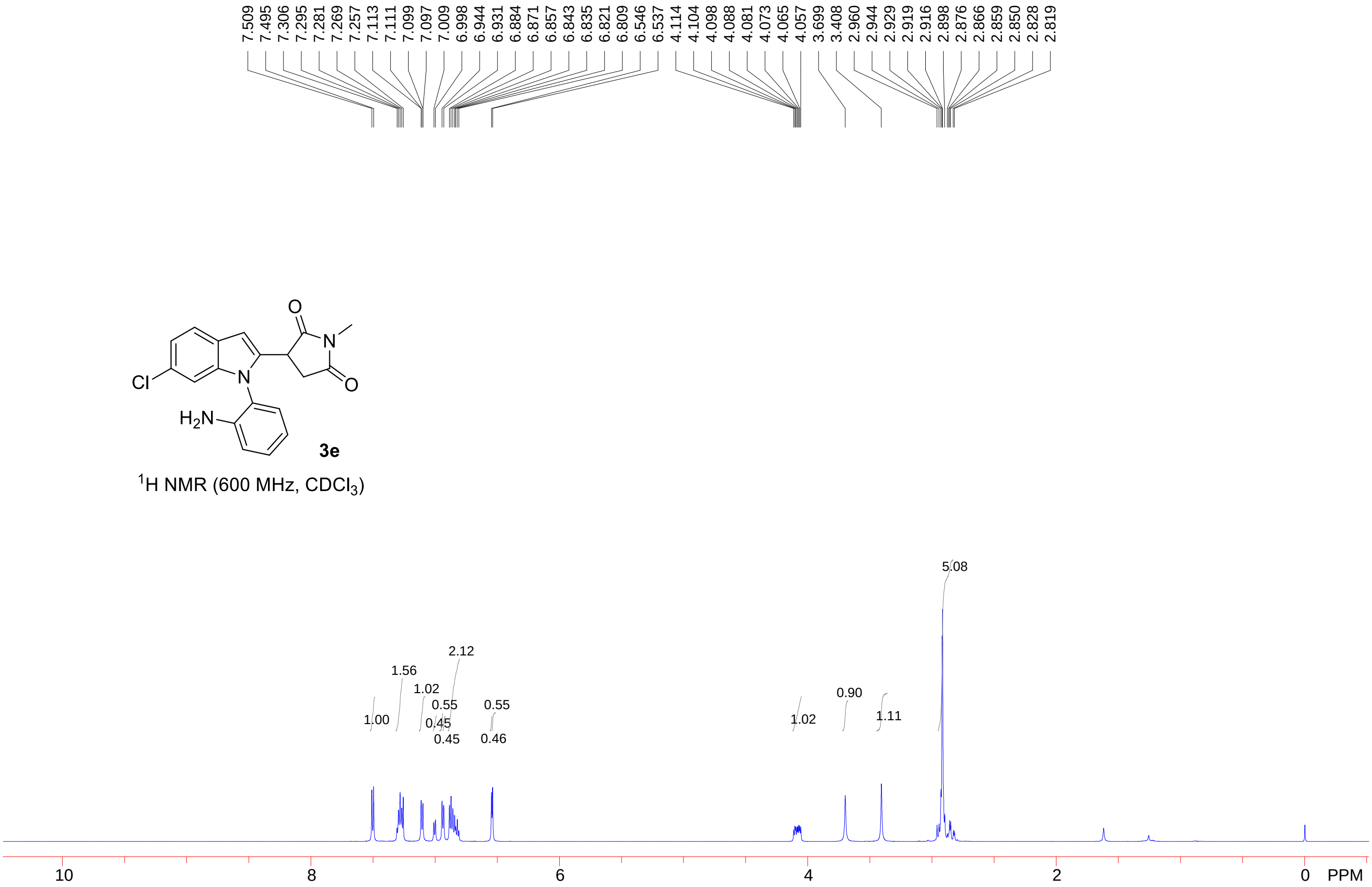

7.524 7.515 7.510 7.501 7.302 7.291 7.279 7.270 7.268 7.258 7.020 7.019 7.008 6.920 6.917 6.905 6.902 6.889 6.887 6.874 6.859 6.846 6.834 6.821 6.808 6.650 6.647 6.635 6.622 6.619 6.549 6.541 4.117 4.107 4.101 4.091 4.082 4.075 4.067 3.705 3.411 2.968 2.951 2.938 2.927 2.917 2.905 2.884 2.864 2.856 2.833 2.825
O
N
F
N
O
H_2N
3d
^{1}H NMR (600 MHz, $CDCl_3$)
5.08
3.15
1.51
1.00
1.02
0.50
0.51
0.49
1.05
1.03
0.99
10
8
6
4
2
0 PPM

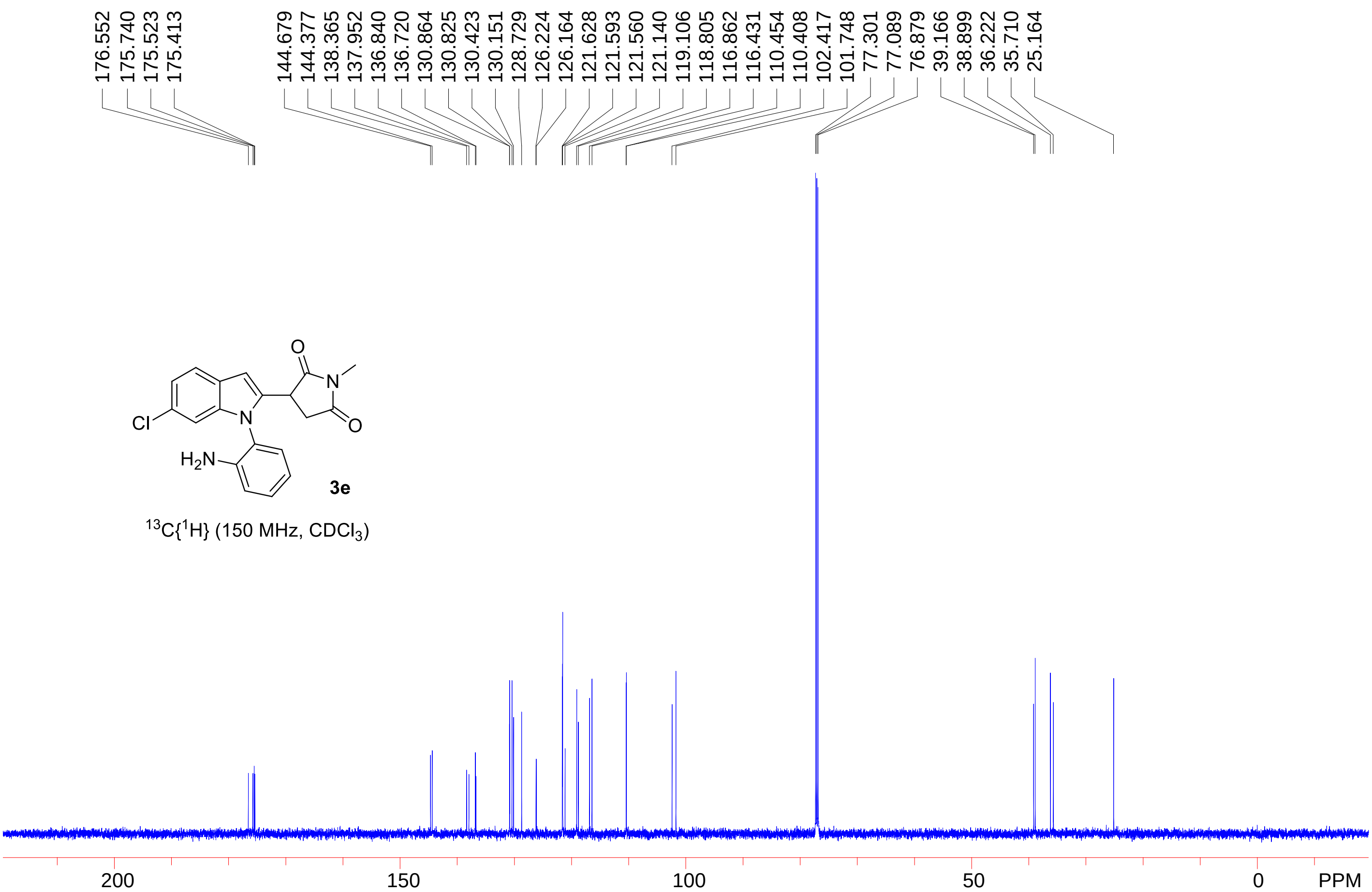

176.672 175.868 175.597 175.496 161.136 159.556 144.663 144.364 138.146 138.067 137.757 137.677 136.418 136.403 136.318 136.300 130.776 130.743 130.384 130.109 124.077 124.011 121.578 121.512 121.446 121.361 119.093 118.792 116.825 116.390 109.694 109.654 109.522 109.498 102.361 101.755 97.083 97.042 96.902 96.868 77.275 77.064 76.853 39.198 38.957 36.306 35.778 25.140
O
N
F
N
O
H_2N
3d
^{13}C{^{1}H} (150 MHz, $CDCl_3$)
200
150
100
50
0
PPM

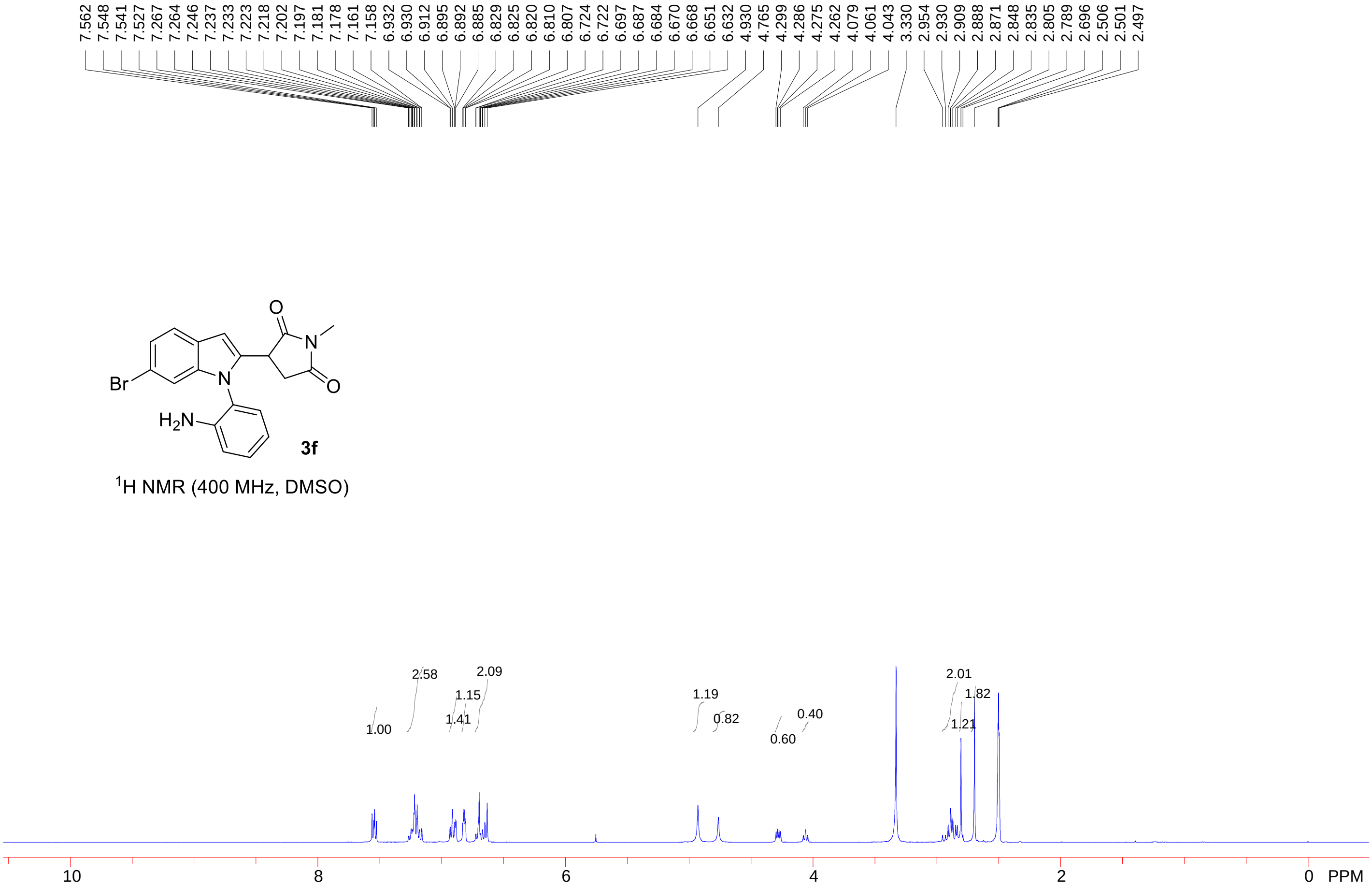
3d

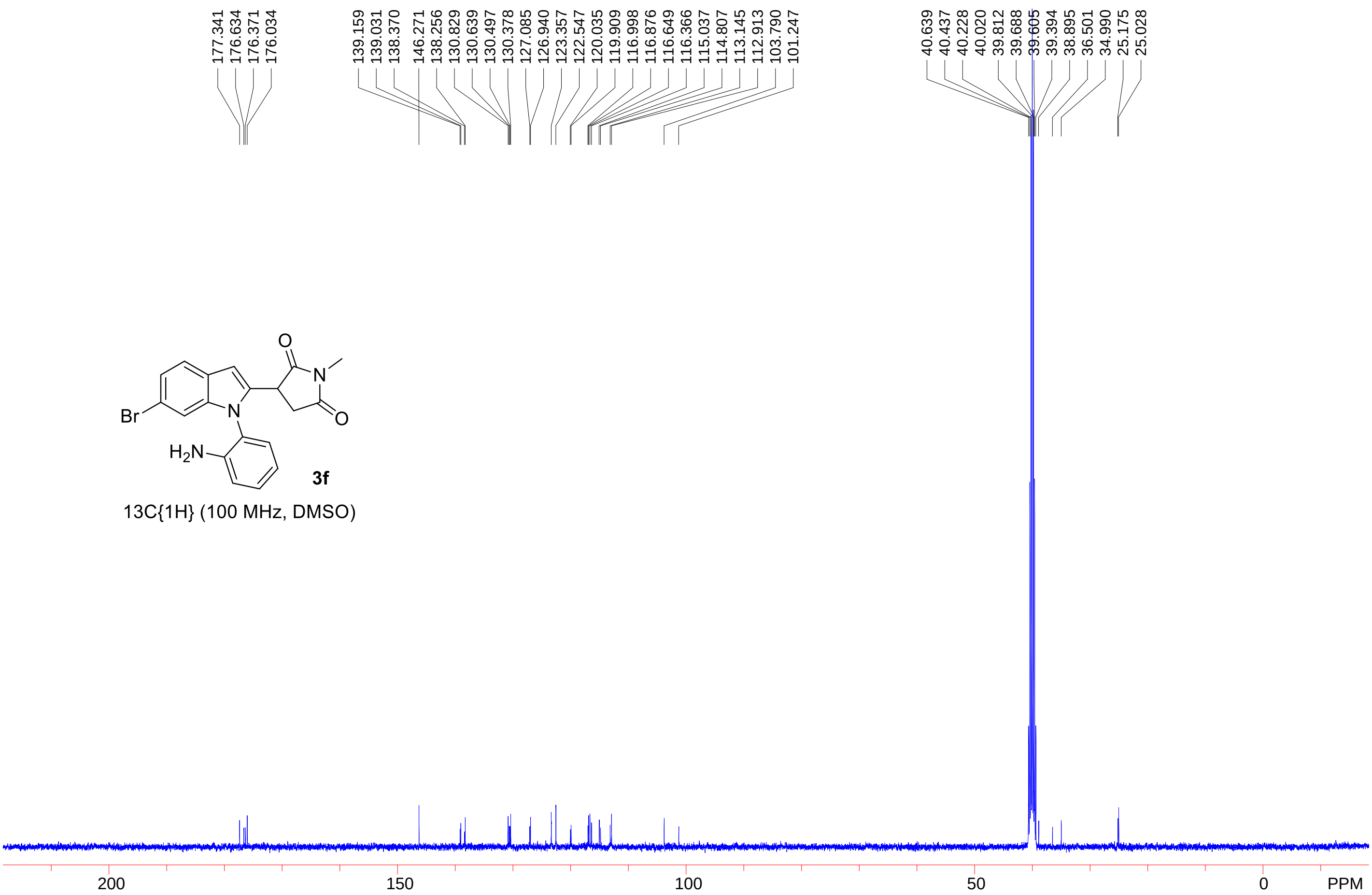
^{19}F NMR (565 MHz, $CDCl_3$)

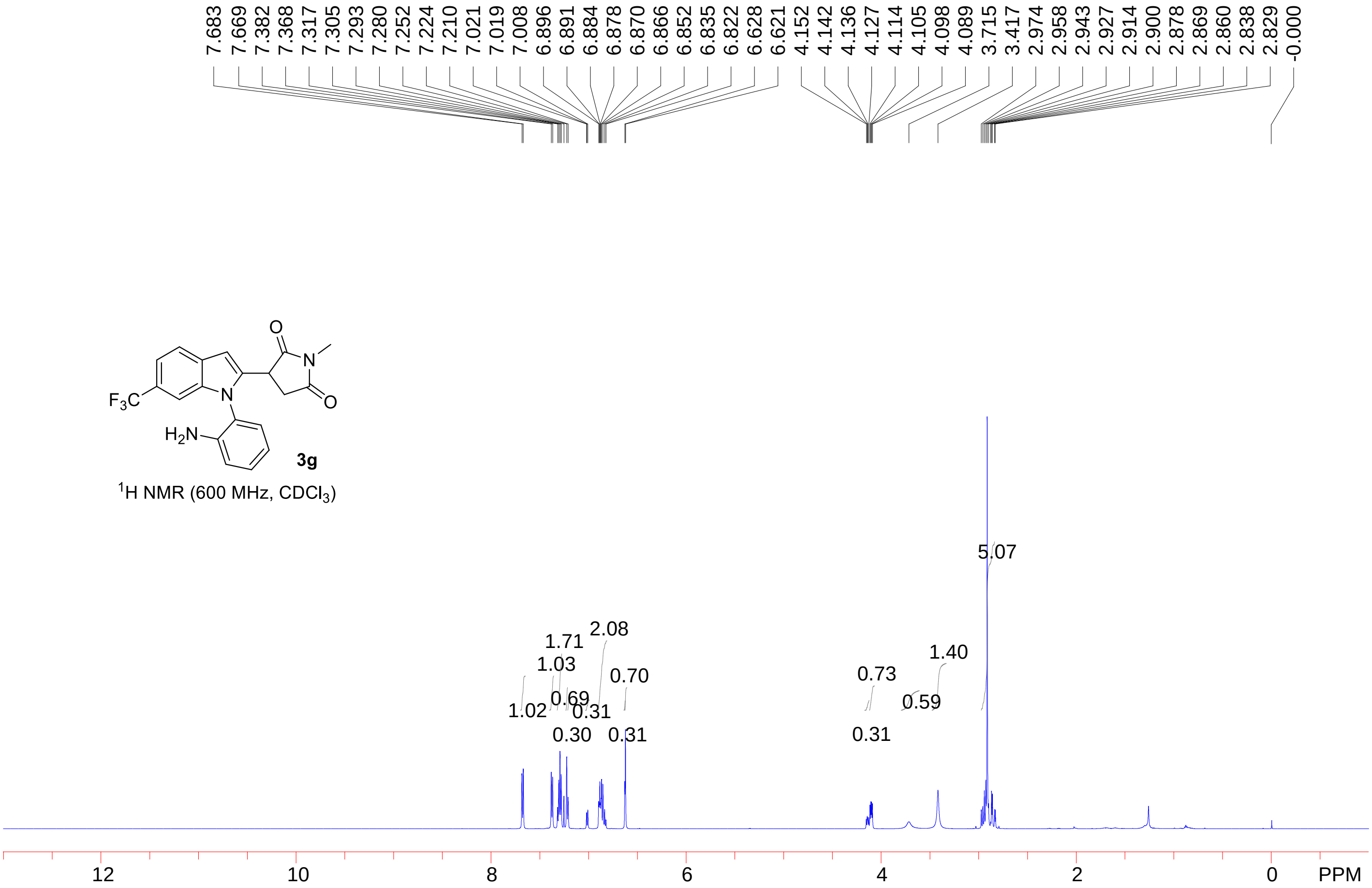


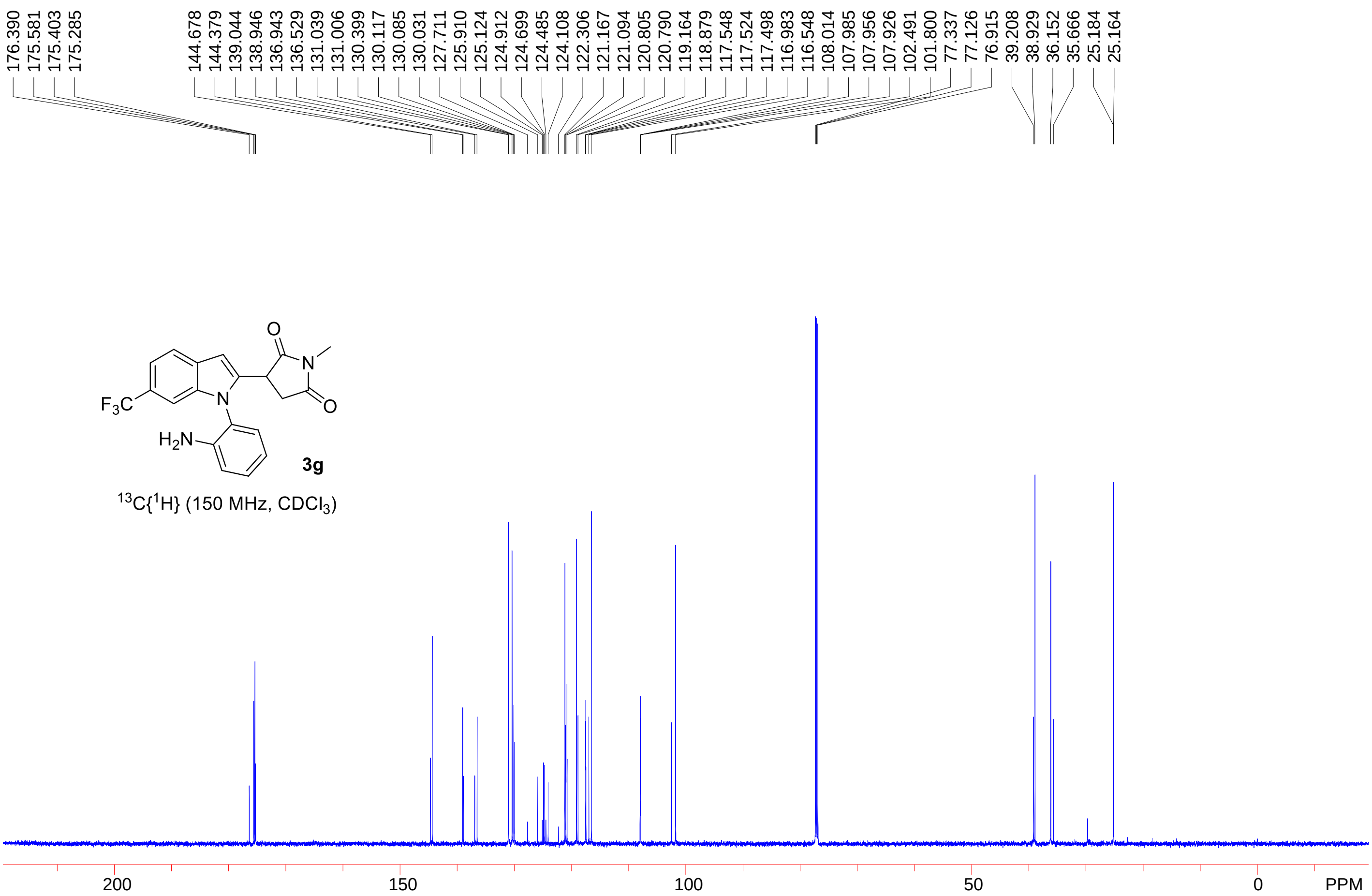

7.509
7.495
7.306
7.295
7.281
7.269
7.257
7.113
7.111
7.099
7.097
7.009
6.998
6.944
6.931
6.884
6.871
6.857
6.843
6.835
6.821
6.809
6.546
6.537
4.114
4.104
4.098
4.088
4.081
4.073
4.065
4.057
3.699
3.408
2.960
2.944
2.929
2.919
2.916
2.898
2.876
2.866
2.859
2.850
2.828
2.819
Cl
N
O
O
N
H2N
3e
1H NMR (600 MHz, CDCl3)
5.08
2.12
1.56
1.02
0.55
0.55
1.00
0.45
0.45
0.46
1.02
0.90
1.11
10
8
6
4
2
0
PPM

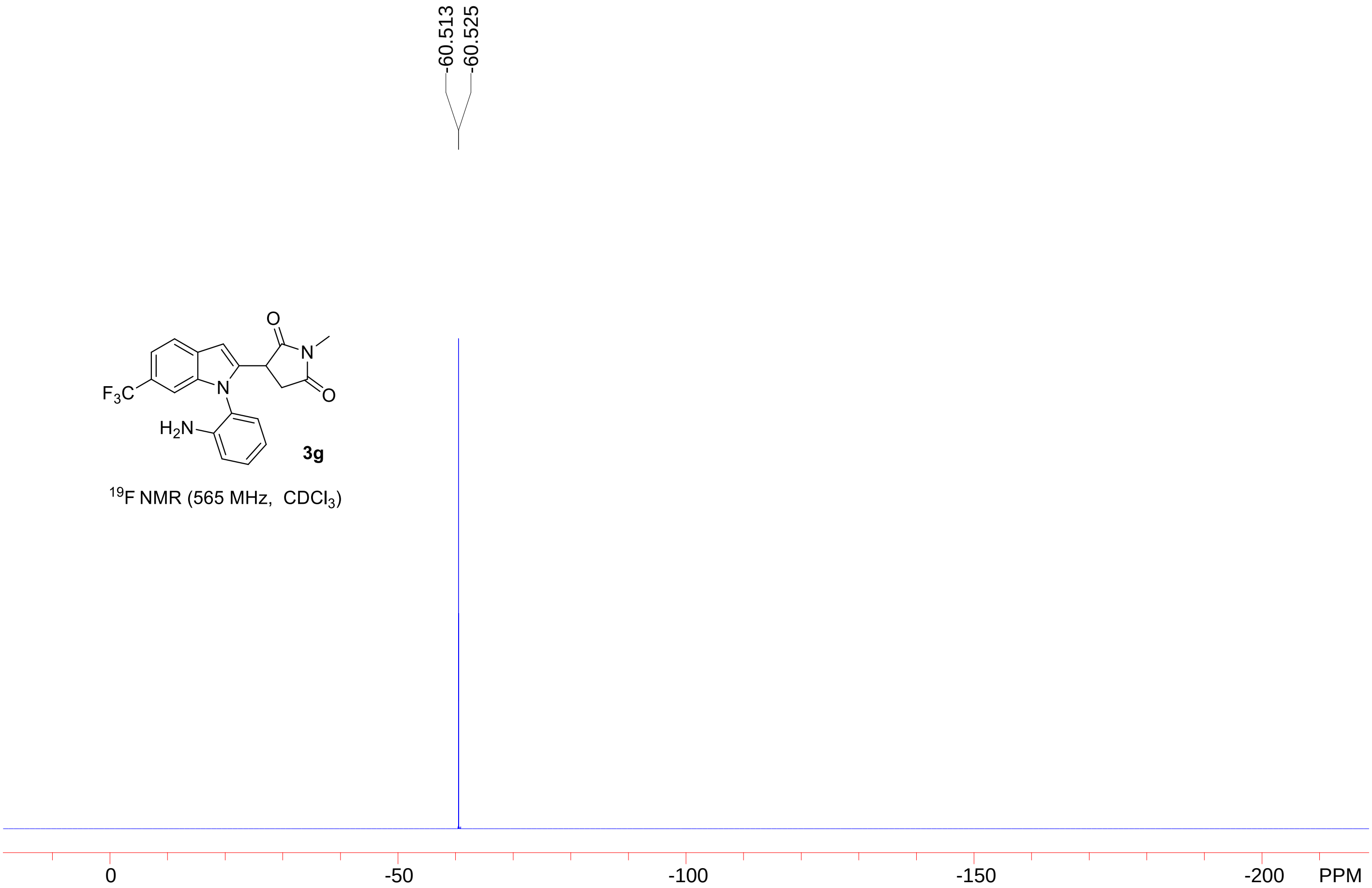

176.552
175.740
175.523
175.413
144.679
144.377
138.365
137.952
136.840
136.720
130.864
130.825
130.423
130.151
128.729
126.224
126.164
121.628
121.593
121.560
121.140
119.106
118.805
116.862
116.431
110.454
110.408
102.417
101.748
77.301
77.089
76.879
39.166
38.899
36.222
35.710
25.164
Cl
N
O
O
N
H2N
3e
13C{1H} (150 MHz, CDCl3)
200
150
100
50
0
PPM


7.562 7.548 7.541 7.527 7.267 7.264 7.246 7.237 7.233 7.223 7.218 7.202 7.197 7.181 7.178 7.161 7.158 6.932 6.930 6.912 6.895 6.892 6.885 6.829 6.825 6.820 6.810 6.807 6.724 6.722 6.697 6.687 6.684 6.670 6.668 6.651 6.632 4.930 4.765 4.299 4.286 4.275 4.262 4.079 4.061 4.043 3.330 2.954 2.930 2.909 2.888 2.871 2.848 2.835 2.805 2.789 2.696 2.506 2.501 2.497
Br
O
N
O
H_2N
3f
^{1}H NMR (400 MHz, DMSO)
1.00 2.58 1.41 1.15 2.09 1.19 0.82 0.60 0.40 2.01 1.21 1.82
10 8 6 4 2 0 PPM


177.341 176.634 176.371 176.034
139.159 139.031 138.370 146.271 138.256 130.829 130.639 130.497 130.378 127.085 126.940 123.357 122.547 120.035 119.909 116.998 116.876 116.649 116.366 115.037 114.807 113.145 112.913 103.790 101.247
40.639 40.437 40.228 40.020 39.812 39.688 39.605 39.394 38.895 36.501 34.990 25.175 25.028
Br
O
N
O
H_2N
3f
13C{1H} (100 MHz, DMSO)
200 150 100 50 0 PPM

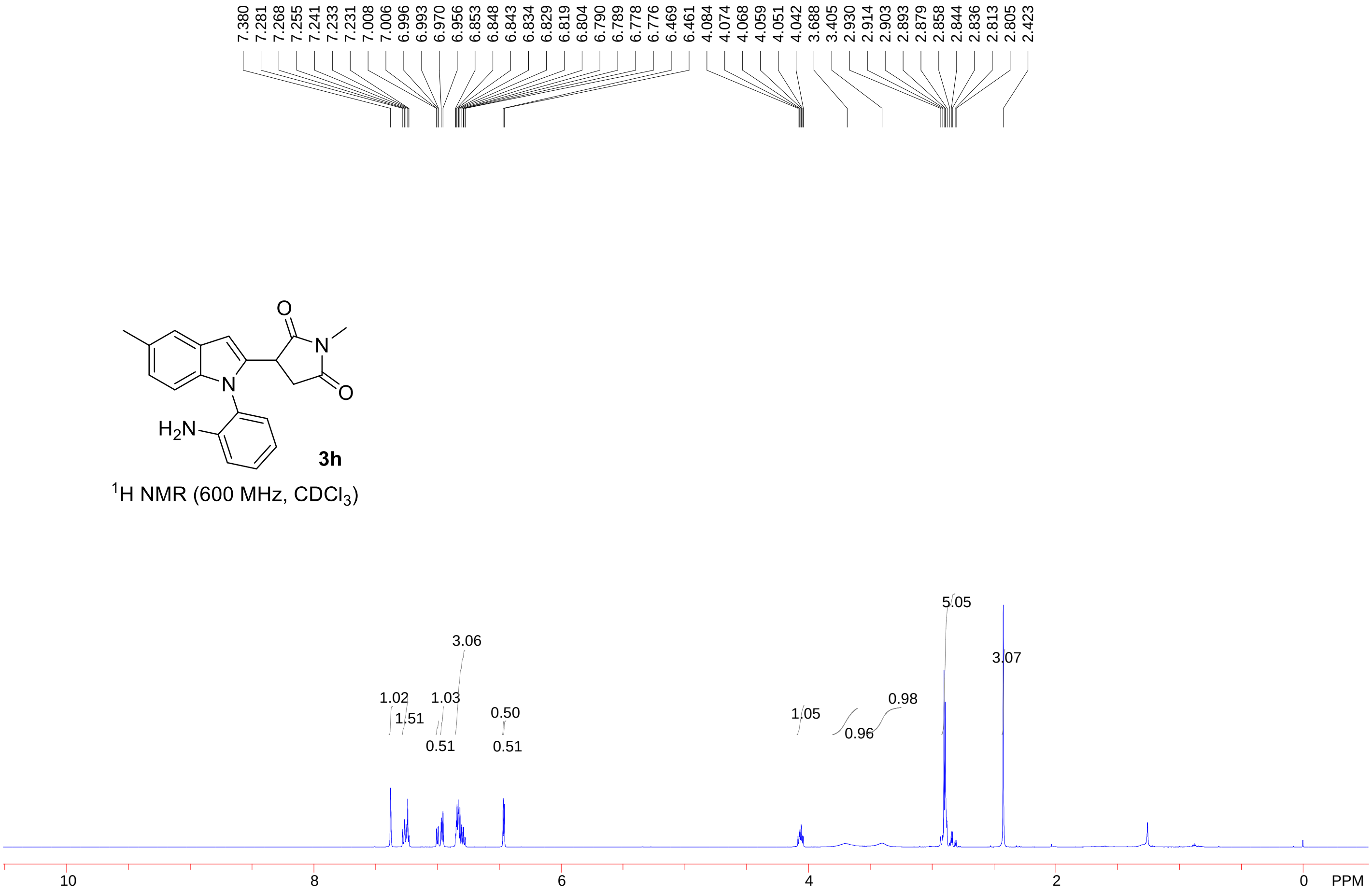

7.683 7.669 7.382 7.368 7.317 7.305 7.293 7.280 7.252 7.224 7.210 7.021 7.019 7.008 6.896 6.891 6.884 6.878 6.870 6.866 6.852 6.835 6.822 6.628 6.621 4.152 4.142 4.136 4.127 4.114 4.105 4.098 4.089 3.715 3.417 2.974 2.958 2.943 2.927 2.914 2.900 2.878 2.869 2.860 2.838 2.829 -0.000
F3C
H2N
N
O
3g
1H NMR (600 MHz, CDCl3)
5.07
1.71 2.08
1.03
0.70
1.40
0.73
0.69
0.59
1.02
0.31
0.30
0.31
0.31
12 10 8 6 4 2 0 PPM


176.390 175.581 175.403 175.285 144.678 144.379 139.044 138.946 136.943 136.529 131.039 131.006 130.399 130.117 130.085 130.031 127.711 125.910 125.124 124.912 124.699 124.485 124.108 122.306 121.167 121.094 120.805 120.790 119.164 118.879 117.548 117.524 117.498 116.983 116.548 108.014 107.985 107.956 107.926 102.491 101.800 77.337 77.126 76.915 39.208 38.929 36.152 35.666 25.184 25.164
F3C
H2N
N
O
3g
13C{1H} (150 MHz, CDCl3)
200 150 100 50 0 PPM



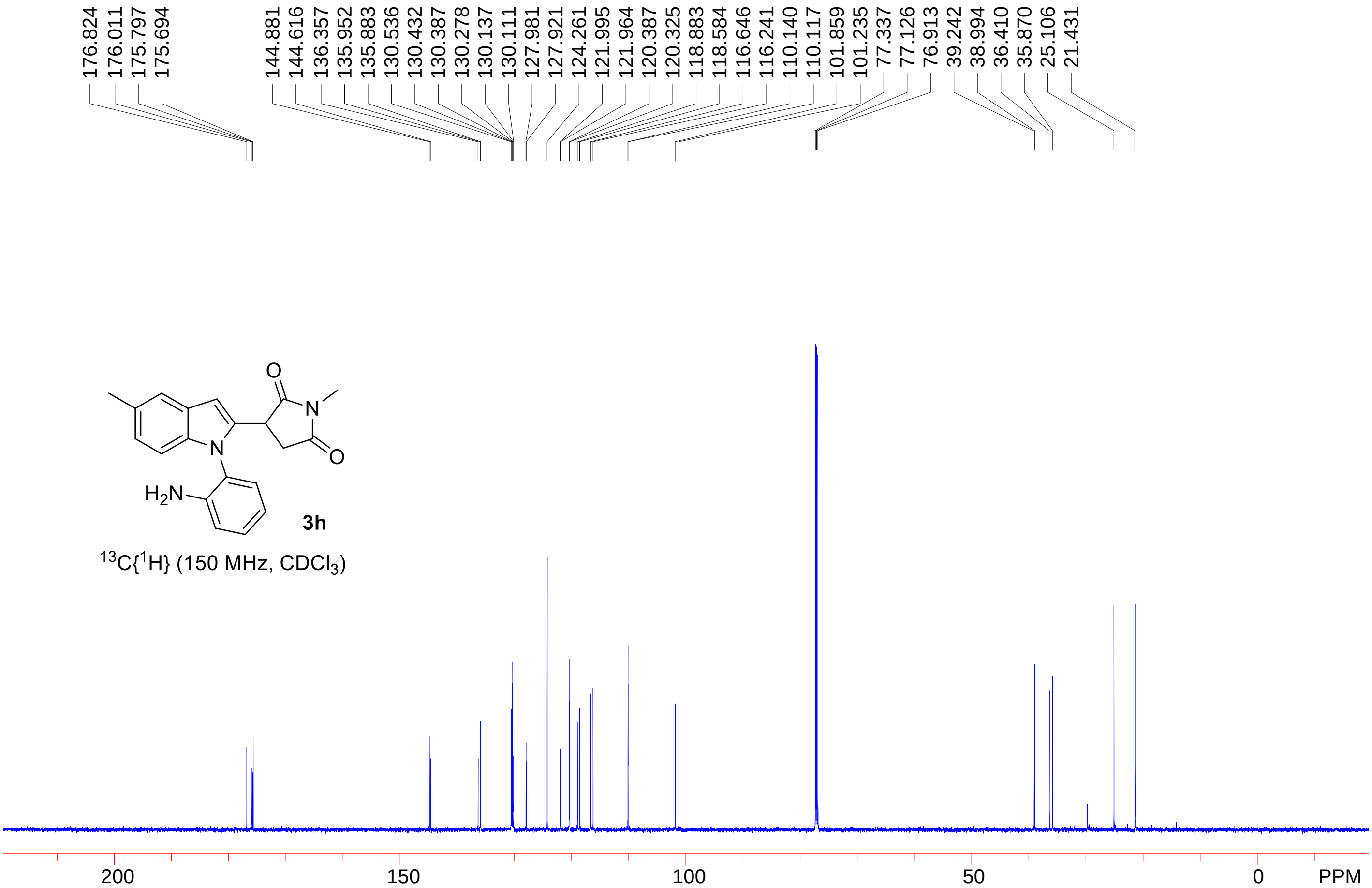
3g

^{19}F NMR (565 MHz, CDCl$_3$)



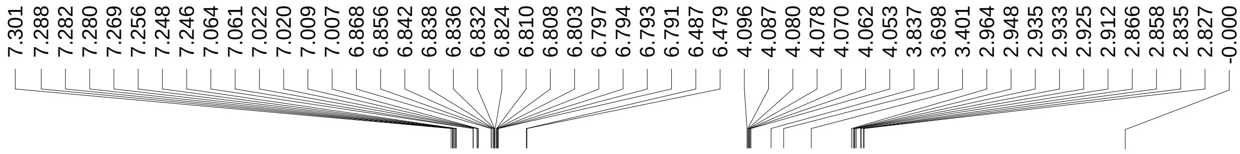
3h

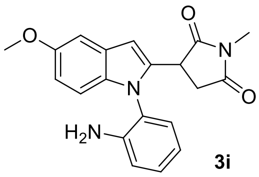
^{1}H NMR (600 MHz, $CDCl_3$)



3h

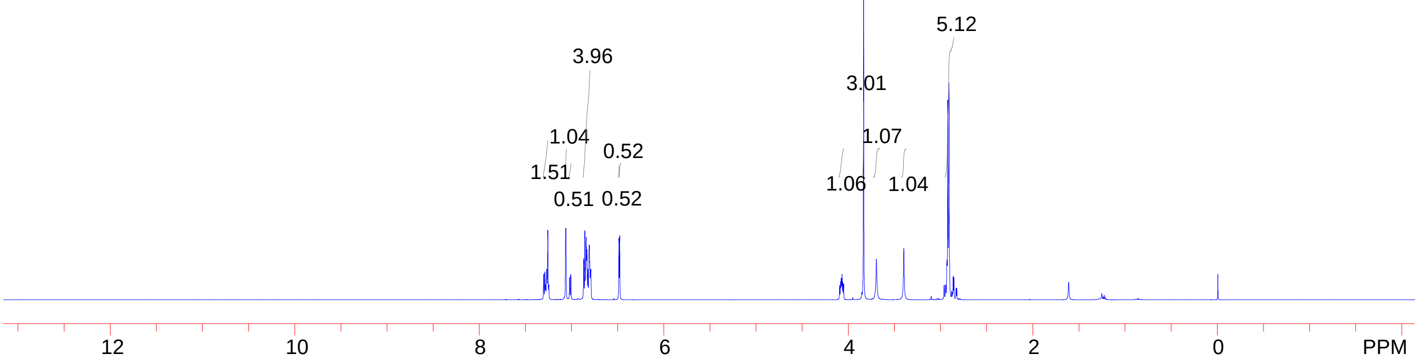
^{13}C{^{1}H} (150 MHz, $CDCl_3$)

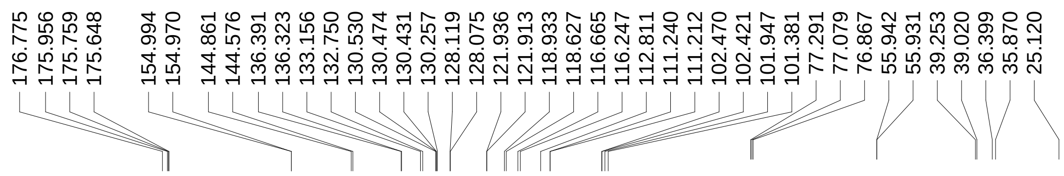


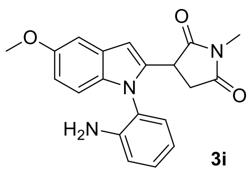


3i

^{1}H NMR (600 MHz, $CDCl_3$)

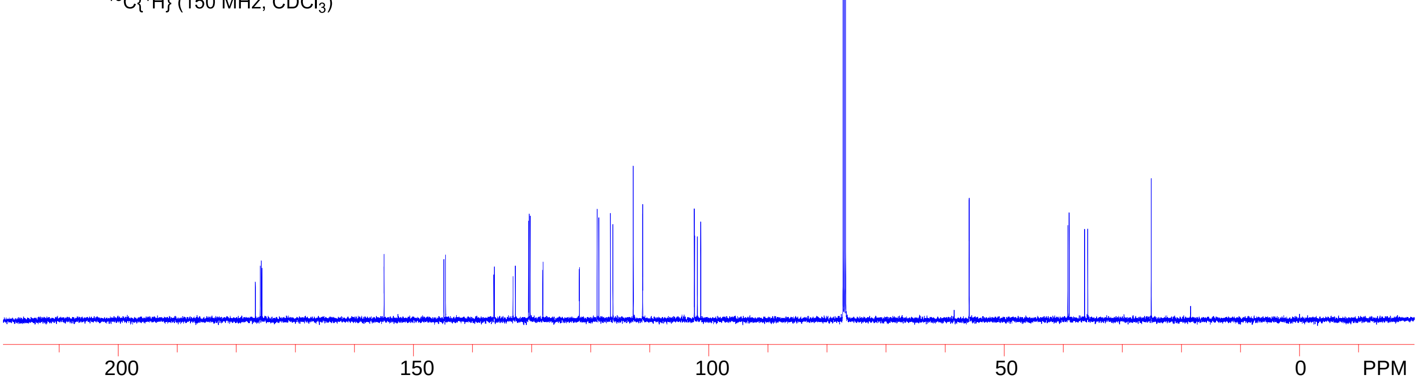


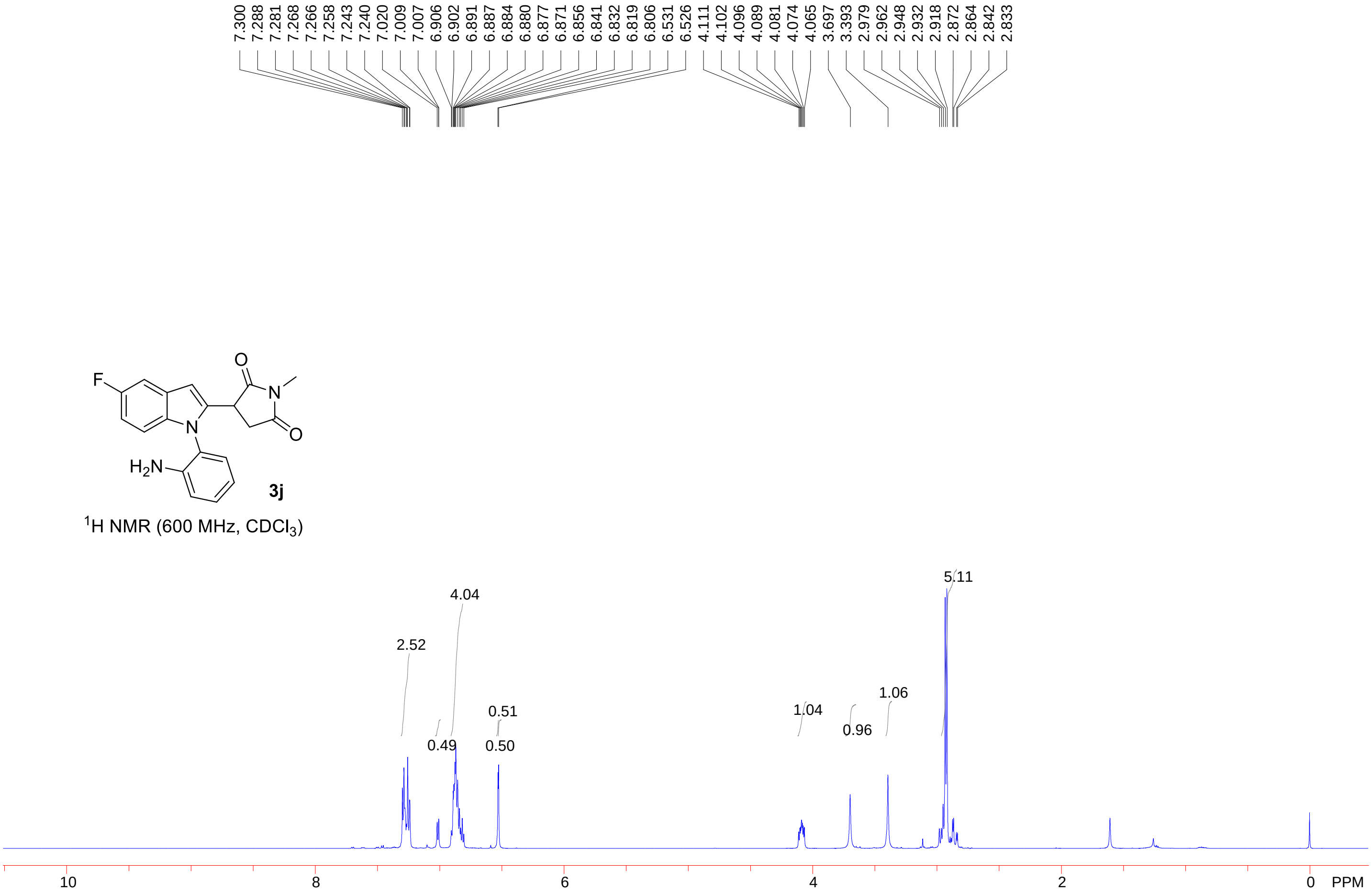


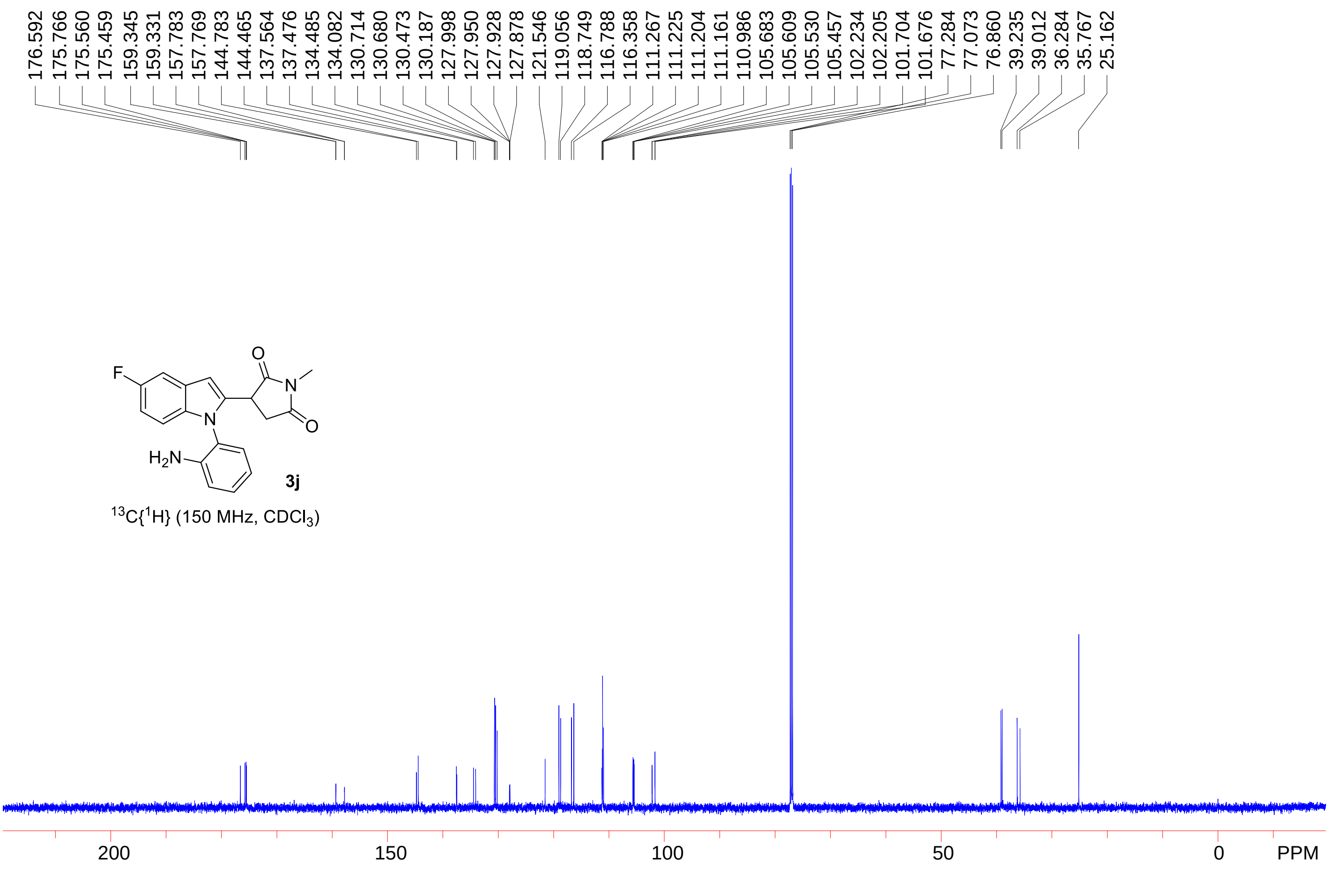


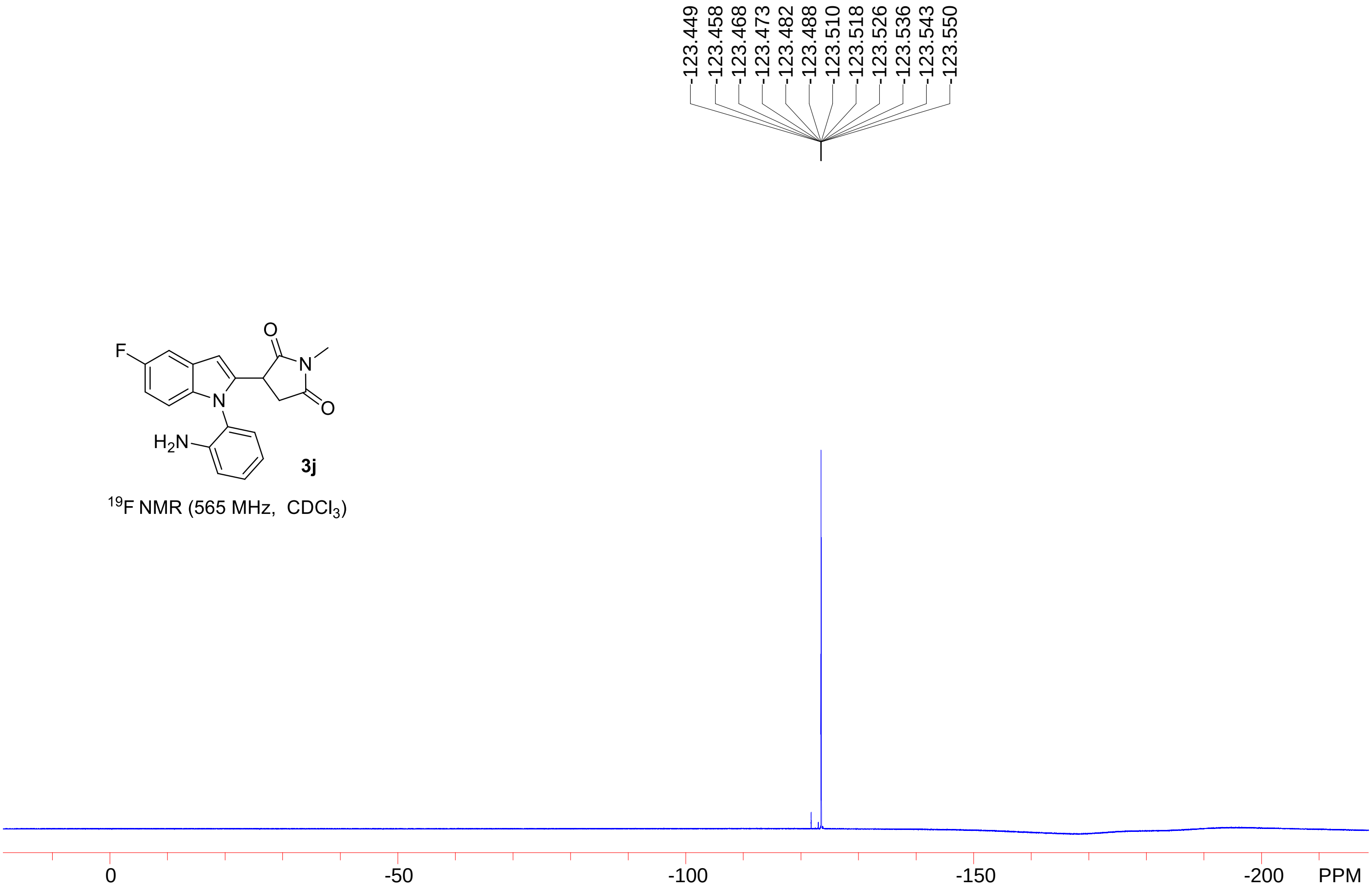
3i

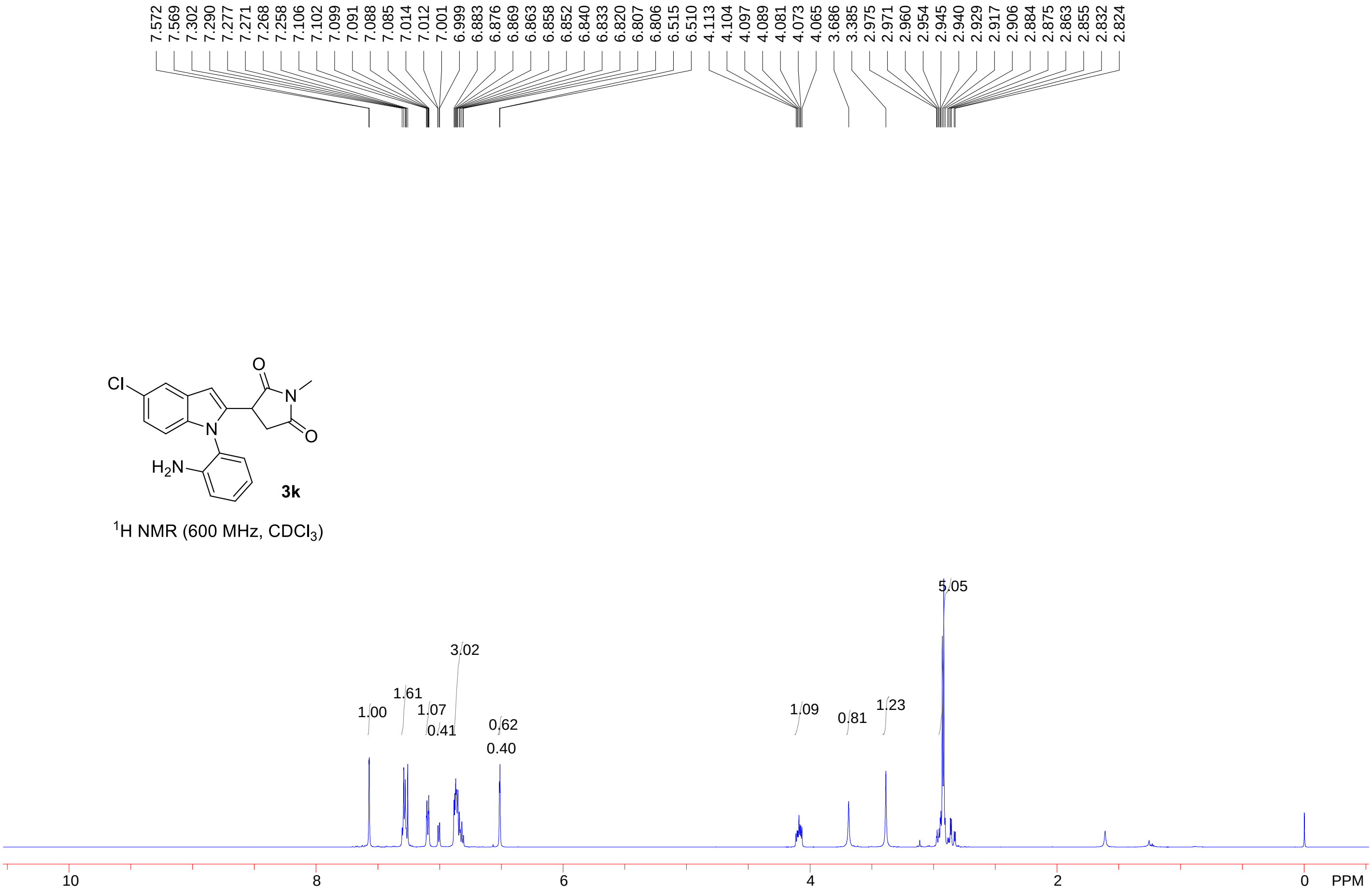
$^{13}C\{^{1}H\}$ (150 MHz, $CDCl_3$)

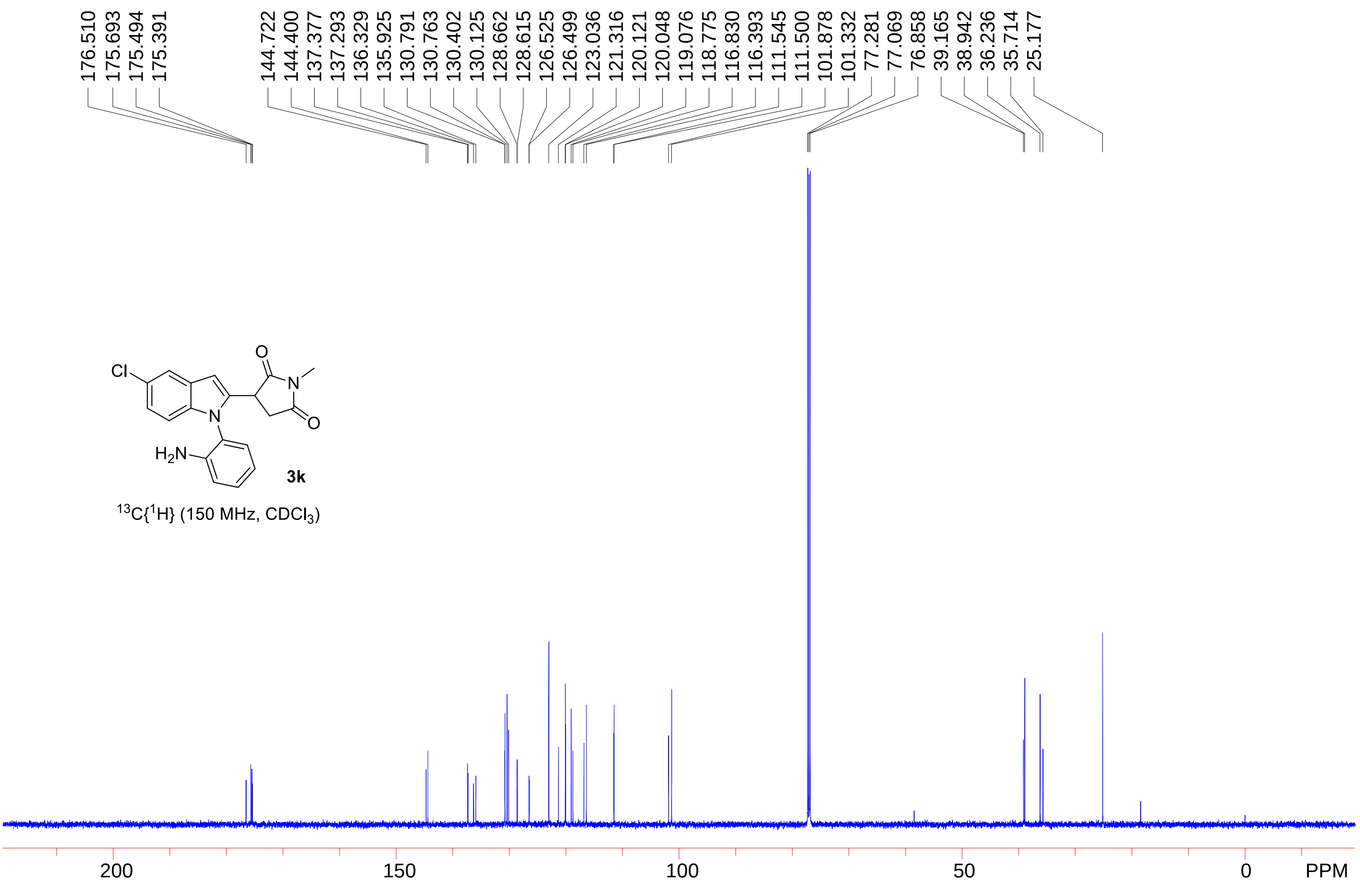


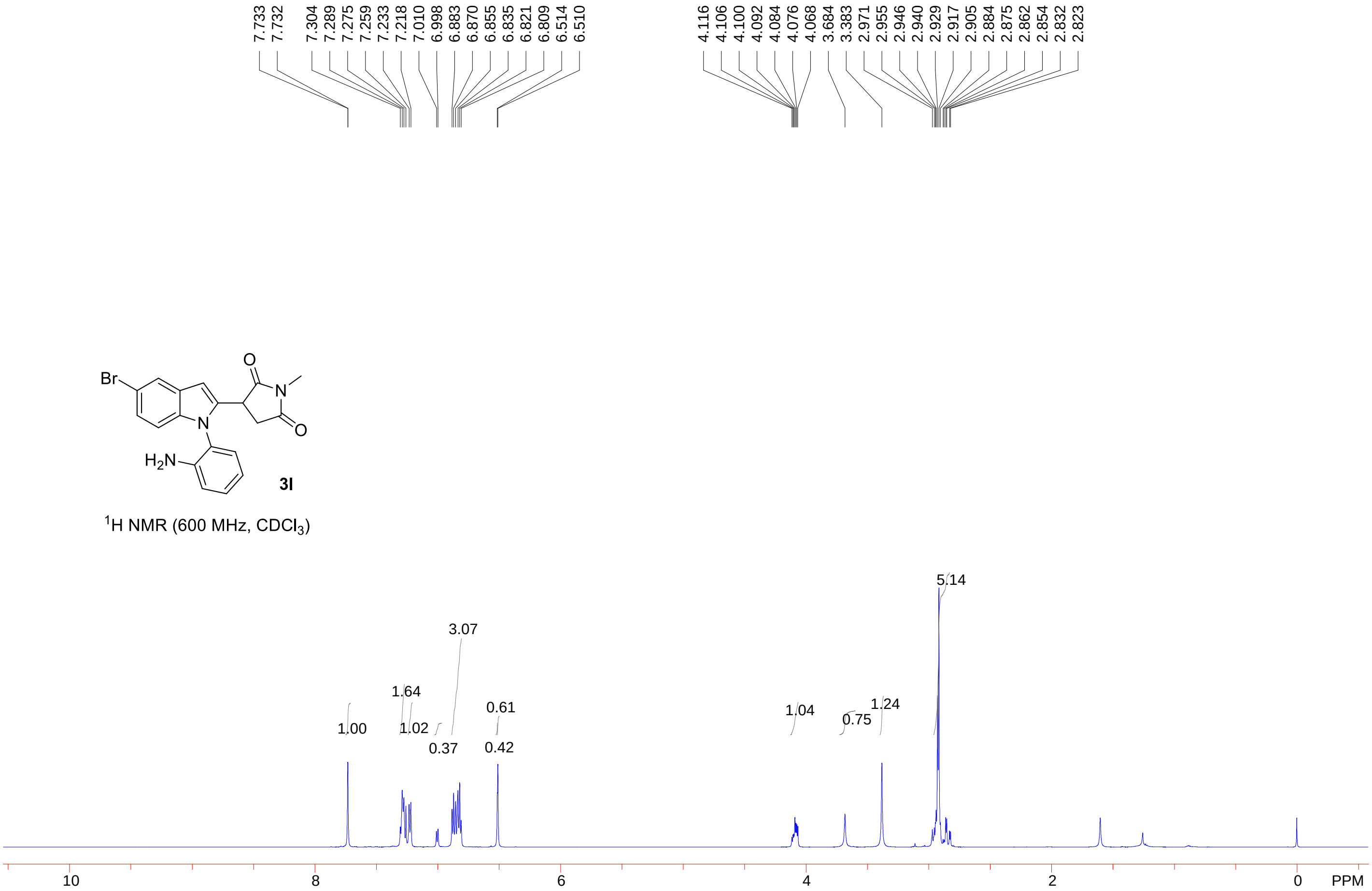

7.300 7.288 7.281 7.268 7.266 7.258 7.243 7.240 7.020 7.009 7.007 6.906 6.902 6.891 6.887 6.884 6.880 6.877 6.871 6.856 6.841 6.832 6.819 6.806 6.531 6.526 4.111 4.102 4.096 4.089 4.081 4.074 4.065 3.697 3.393 2.979 2.962 2.948 2.932 2.918 2.872 2.864 2.842 2.833
F
O
N
N
O
H_2N
3j
^1H NMR (600 MHz, $CDCl_3$)
2.52
4.04
0.49
0.51
0.50
1.04
0.96
1.06
5.11
10
8
6
4
2
0
PPM


176.592 175.766 175.560 175.459 159.345 159.331 157.783 157.769 144.783 144.465 137.564 137.476 134.485 134.082 130.714 130.680 130.473 130.187 127.998 127.950 127.928 127.878 121.546 119.056 118.749 116.788 116.358 111.267 111.225 111.204 111.161 110.986 105.683 105.609 105.530 105.457 102.234 102.205 101.704 101.676 77.284 77.073 76.860 39.235 39.012 36.284 35.767 25.162
F
O
N
N
O
H_2N
3j
$^{13}C\{^1H\}$ (150 MHz, $CDCl_3$)
200
150
100
50
0
PPM


-123.449
-123.458
-123.468
-123.473
-123.482
-123.488
-123.510
-123.518
-123.526
-123.536
-123.543
-123.550
F
O
N
O
N
H2N
3j
19F NMR (565 MHz, CDCl3)
0
-50
-100
-150
-200
PPM


7.572 7.569 7.302 7.290 7.277 7.271 7.268 7.258 7.106 7.102 7.099 7.091 7.088 7.085 7.014 7.012 7.001 6.999 6.883 6.876 6.869 6.863 6.858 6.852 6.840 6.833 6.820 6.807 6.806 6.515 6.510 4.113 4.104 4.097 4.089 4.081 4.073 4.065 3.686 3.385 2.975 2.971 2.960 2.954 2.945 2.940 2.929 2.917 2.906 2.884 2.875 2.863 2.855 2.832 2.824
Cl
O
N
O
N
H2N
3k
1H NMR (600 MHz, CDCl3)
5.05
3.02
1.61
1.00
1.07
0.41
0.62
0.40
1.09
0.81
1.23
10
8
6
4
2
0
PPM


176.510 175.693 175.494 175.391
144.722 144.400 137.377 137.293 136.329 135.925 130.791 130.763 130.402 130.125 128.662 128.615 126.525 126.499 123.036 121.316 120.121 120.048 119.076 118.775 116.830 116.393 111.545 111.500 101.878 101.332 77.281 77.069 76.858 39.165 38.942 36.236 35.714 25.177
Cl
O
N
O
N
H2N
3k
13C{1H} (150 MHz, CDCl3)
200
150
100
50
0
PPM


7.733
7.732
7.304
7.289
7.275
7.259
7.233
7.218
7.010
6.998
6.883
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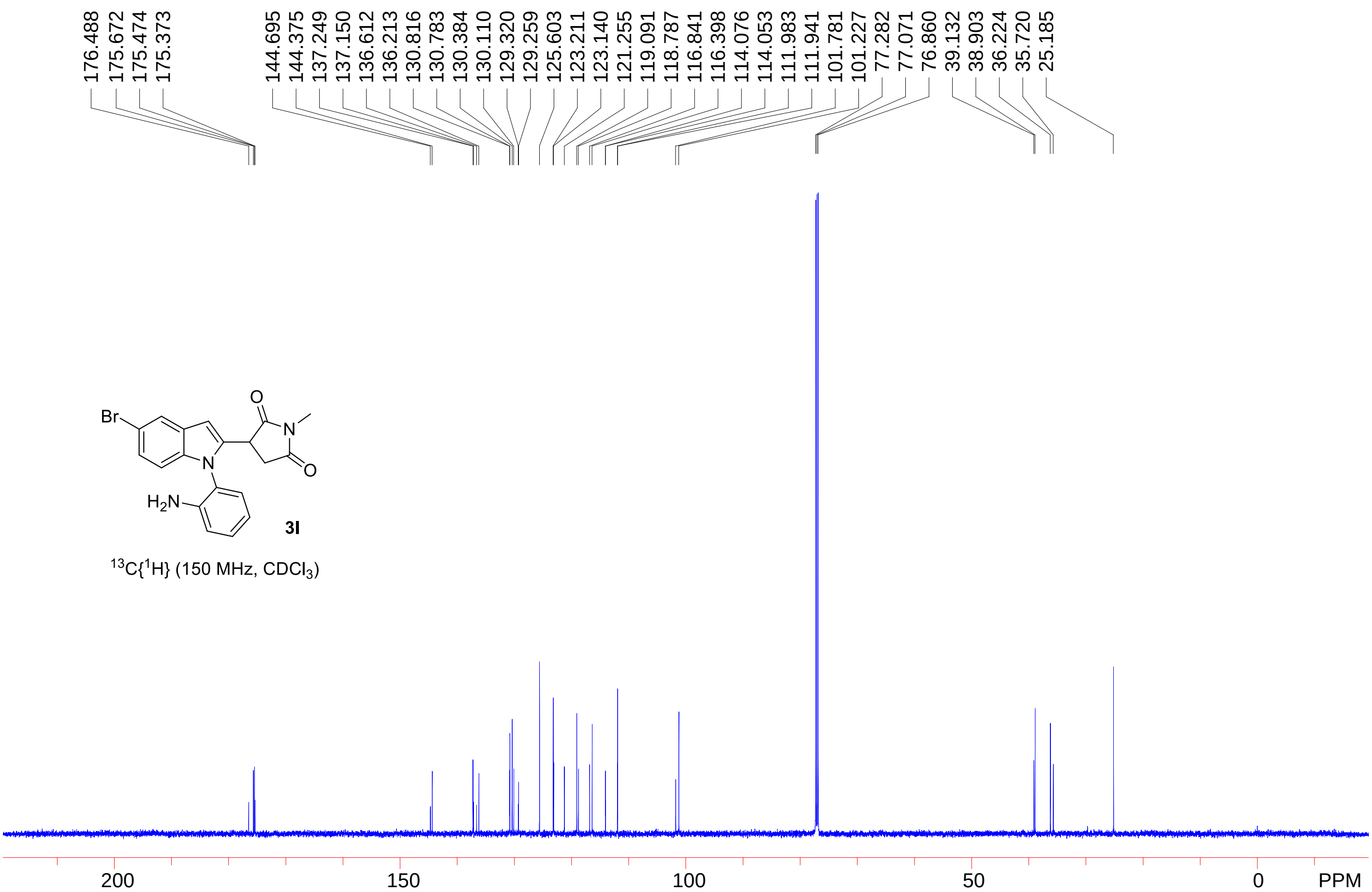
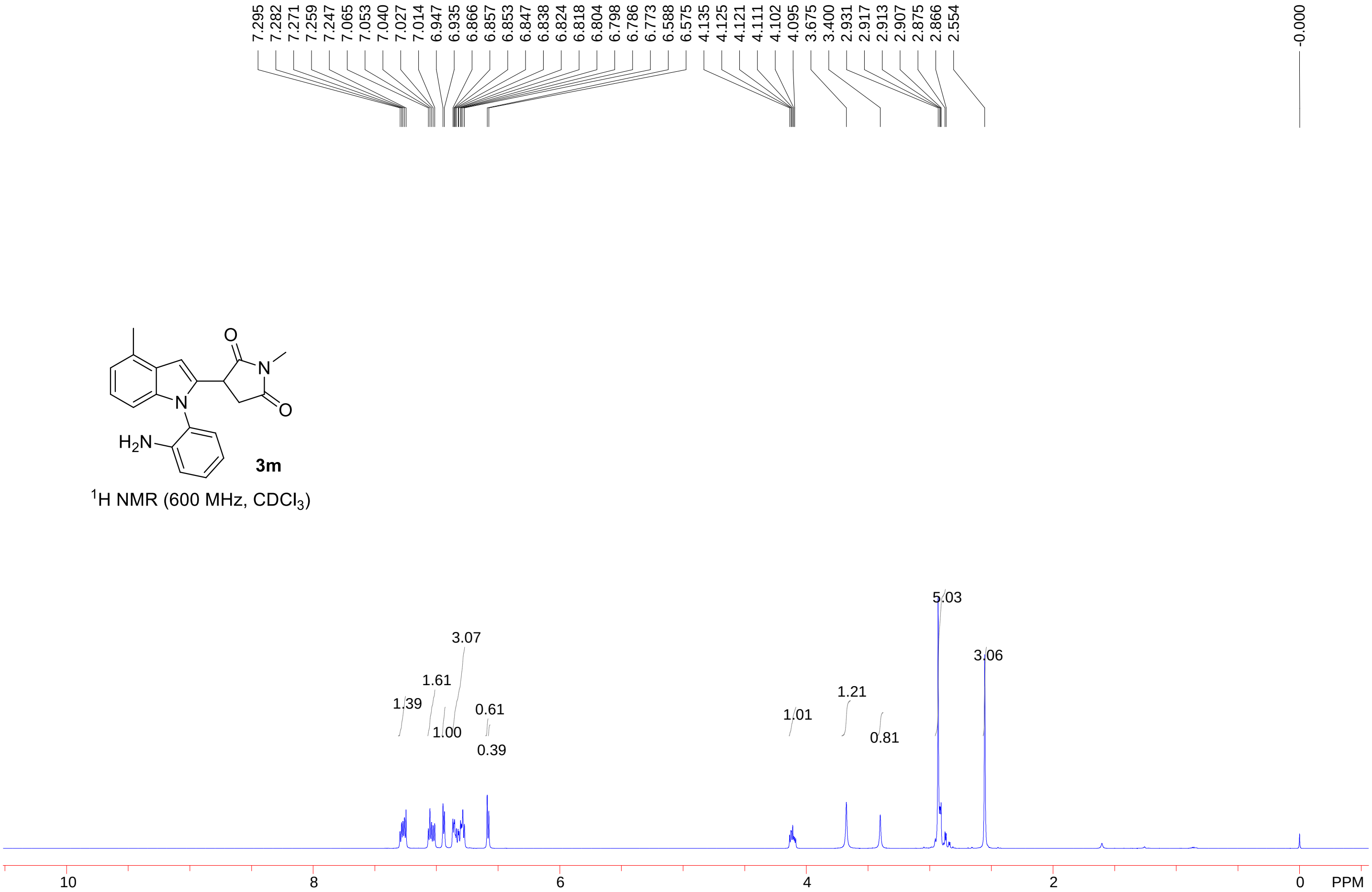
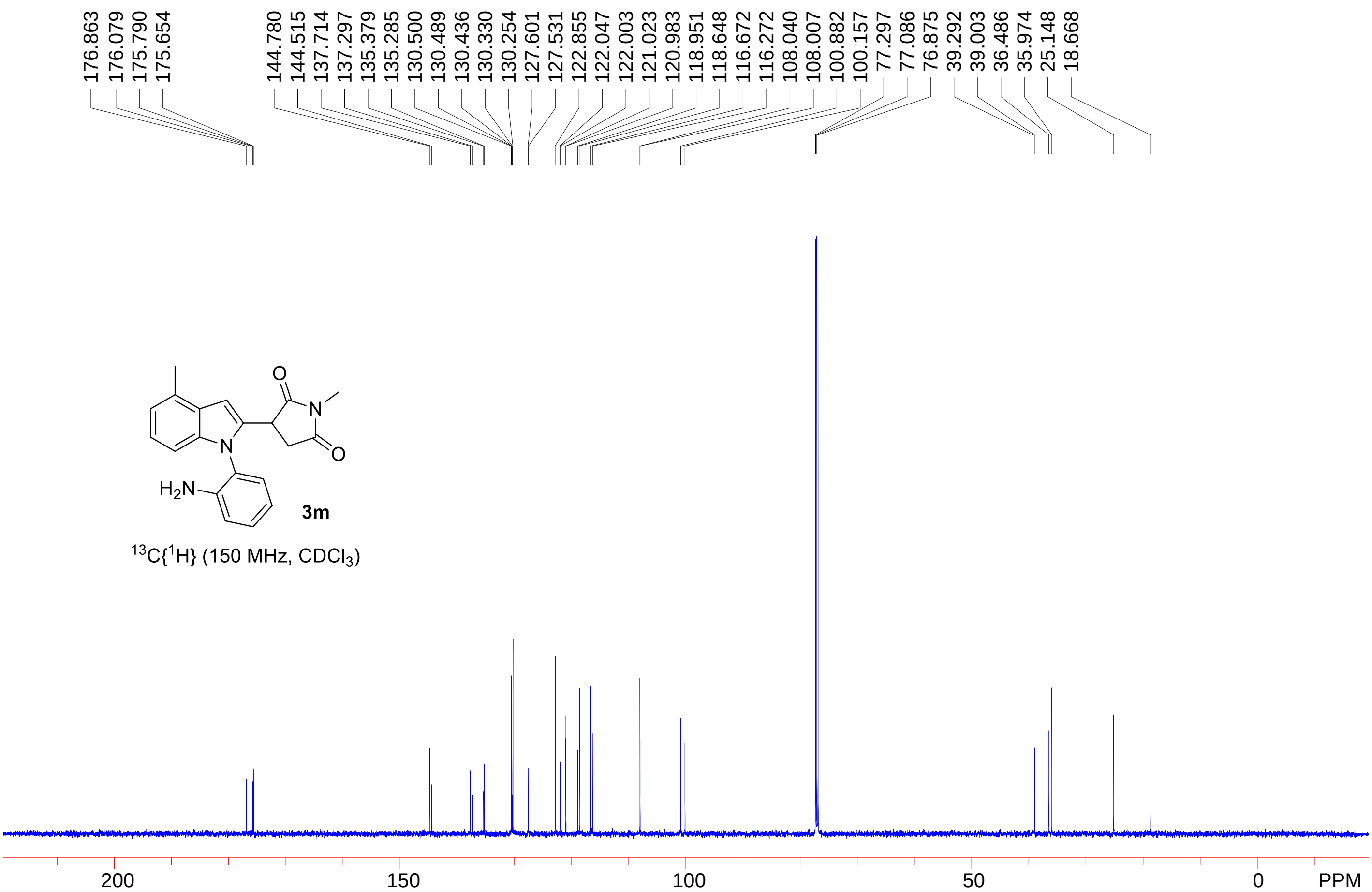
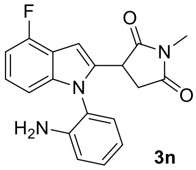
6.855
6.835
6.821
6.809
6.514
6.510
4.116
4.106
4.100
4.092
4.084
4.076
4.068
3.684
3.383
2.971
2.955
2.946
2.940
2.929
2.917
2.905
2.884
2.875
2.862
2.854
2.832
2.823
Br
O
N
O
N
H2N
3l
1H NMR (600 MHz, CDCl3)
1.00
1.64
1.02
0.37
3.07
0.61
0.42
1.04
0.75
1.24
5.14
10
8
6
4
2
0
PPM


176.488
175.672
175.474
175.373
144.695
144.375
137.249
137.150
136.612
136.213
130.816
130.783
130.384
130.110
129.320
129.259
125.603
123.211
123.140
121.255
119.091
118.787
116.841
116.398
114.076
114.053
111.983
111.941
101.781
101.227
77.282
77.071
76.860
39.132
38.903
36.224
35.720
25.185
Br
O
N
O
N
H2N
3l
13C{1H} (150 MHz, CDCl3)
200
150
100
50
0
PPM

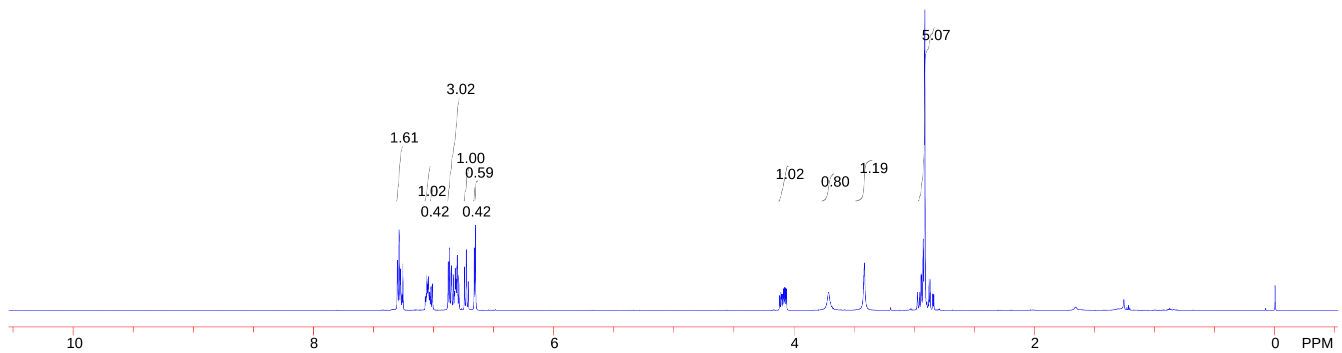

7.295 7.282 7.271 7.259 7.247 7.065 7.053 7.040 7.027 7.014 6.947 6.935 6.866 6.857 6.853 6.847 6.838 6.824 6.818 6.804 6.798 6.786 6.773 6.588 6.575 4.135 4.125 4.121 4.111 4.102 4.095 3.675 3.400 2.931 2.917 2.913 2.907 2.875 2.866 2.554
-0.000
O
N
O
N
H2N
3m
1H NMR (600 MHz, CDCl3)
1.39 1.61 3.07 1.00 0.61 0.39 1.01 1.21 0.81 5.03 3.06
10 8 6 4 2 0 PPM

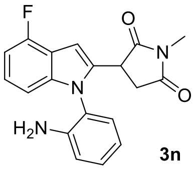

176.863 176.079 175.790 175.654 144.780 144.515 137.714 137.297 135.379 135.285 130.500 130.489 130.436 130.330 130.254 127.601 127.531 122.855 122.047 122.003 121.023 120.983 118.951 118.648 116.672 116.272 108.040 108.007 100.882 100.157 77.297 77.086 76.875 39.292 39.003 36.486 35.974 25.148 18.668
O
N
O
N
H2N
3m
13C{1H} (150 MHz, CDCl3)
200 150 100 50 0 PPM



3n

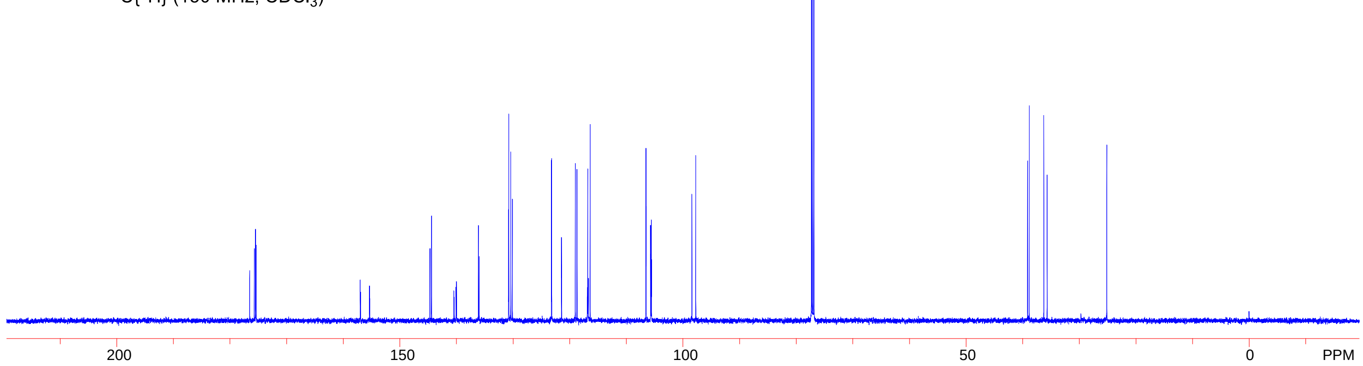
^{1}H NMR (600 MHz, $CDCl_3$)

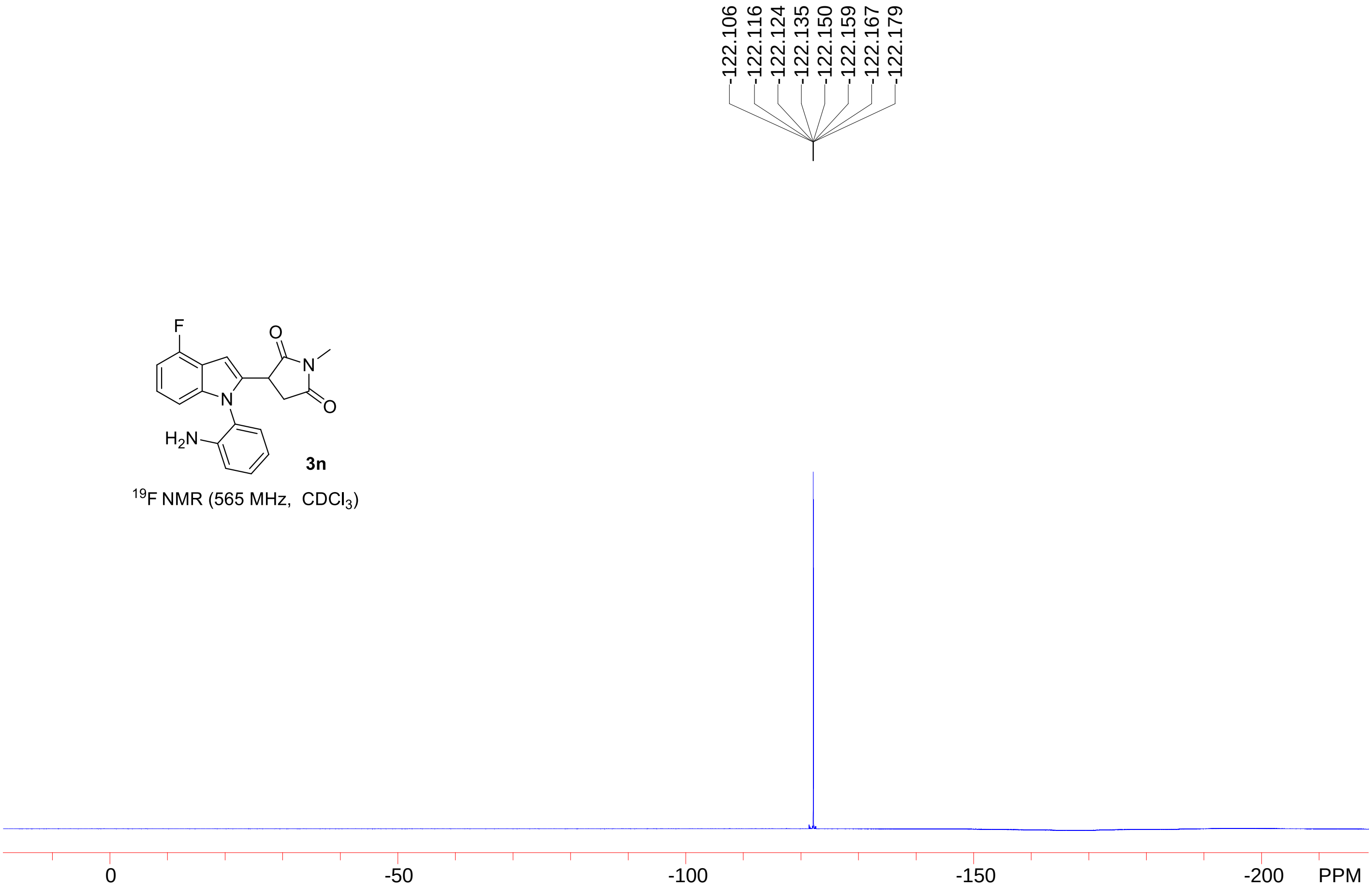




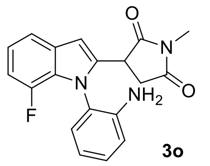
3n

$^{13}C\{^1H\}$ (150 MHz, $CDCl_3$)



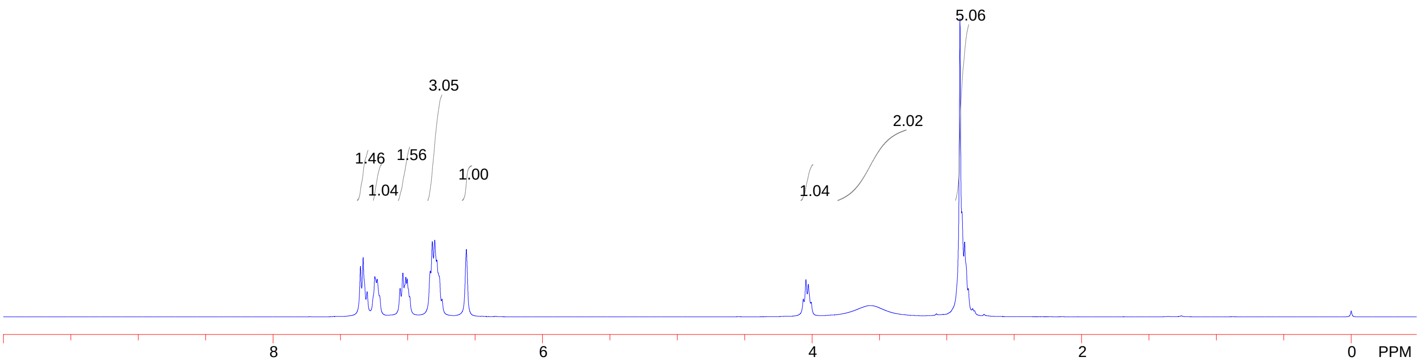


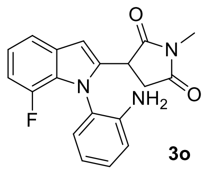
-122.106
-122.116
-122.124
-122.135
-122.150
-122.159
-122.167
-122.179
F
O
N
O
N
H_2N
3n
^{19}F NMR (565 MHz, $CDCl_3$)
0
-50
-100
-150
-200
PPM



3o

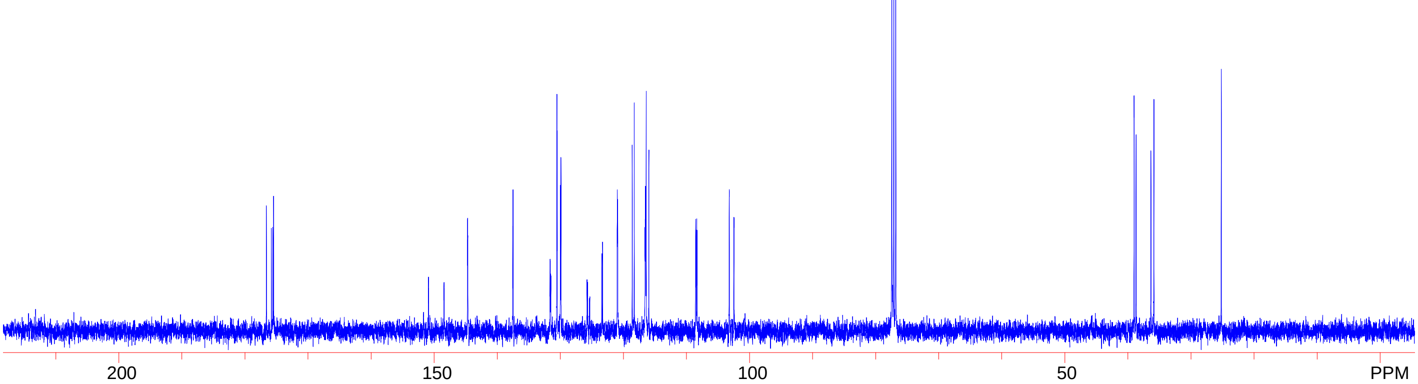
^{1}H NMR (400 MHz, $CDCl_3$)

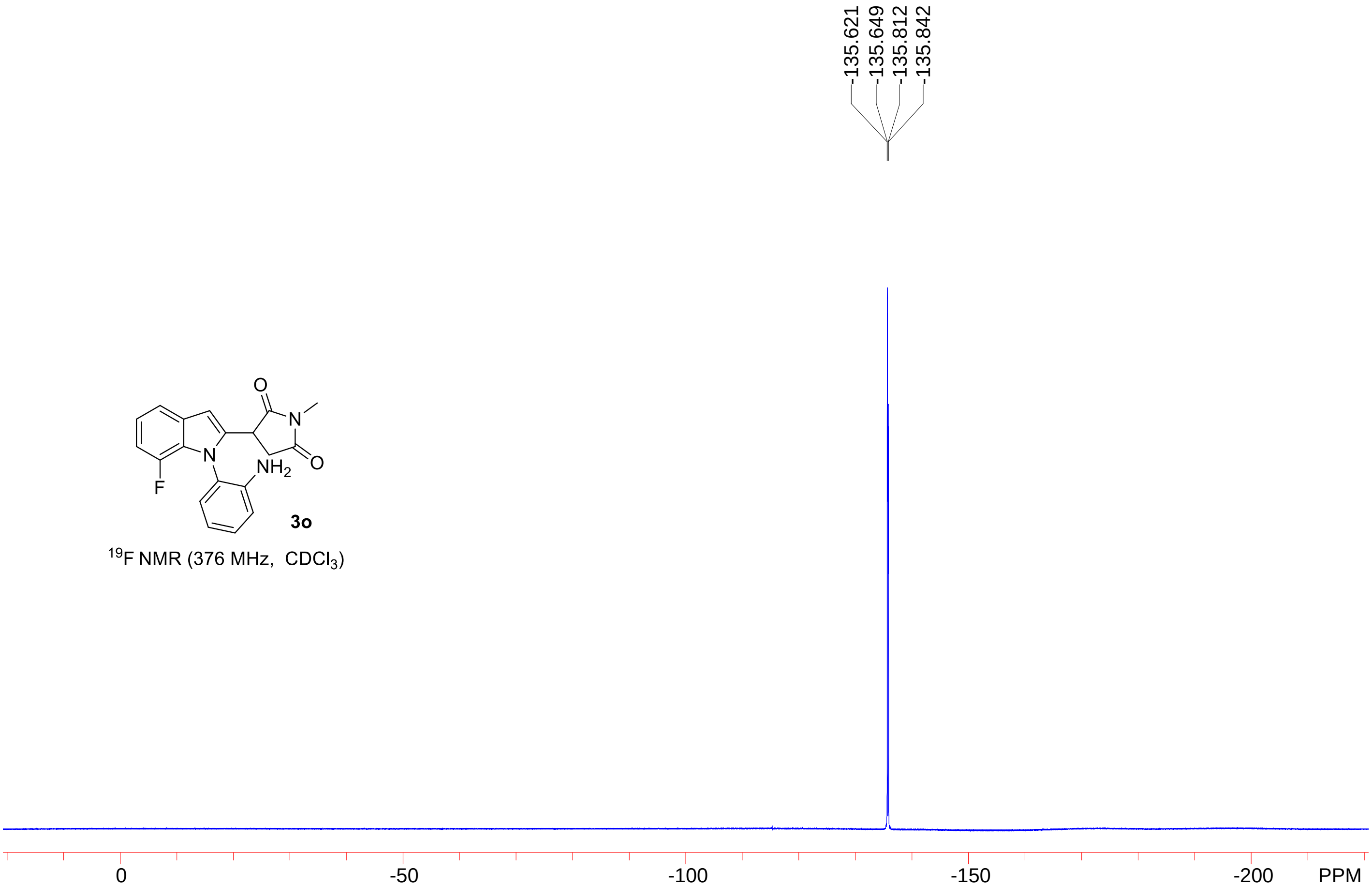


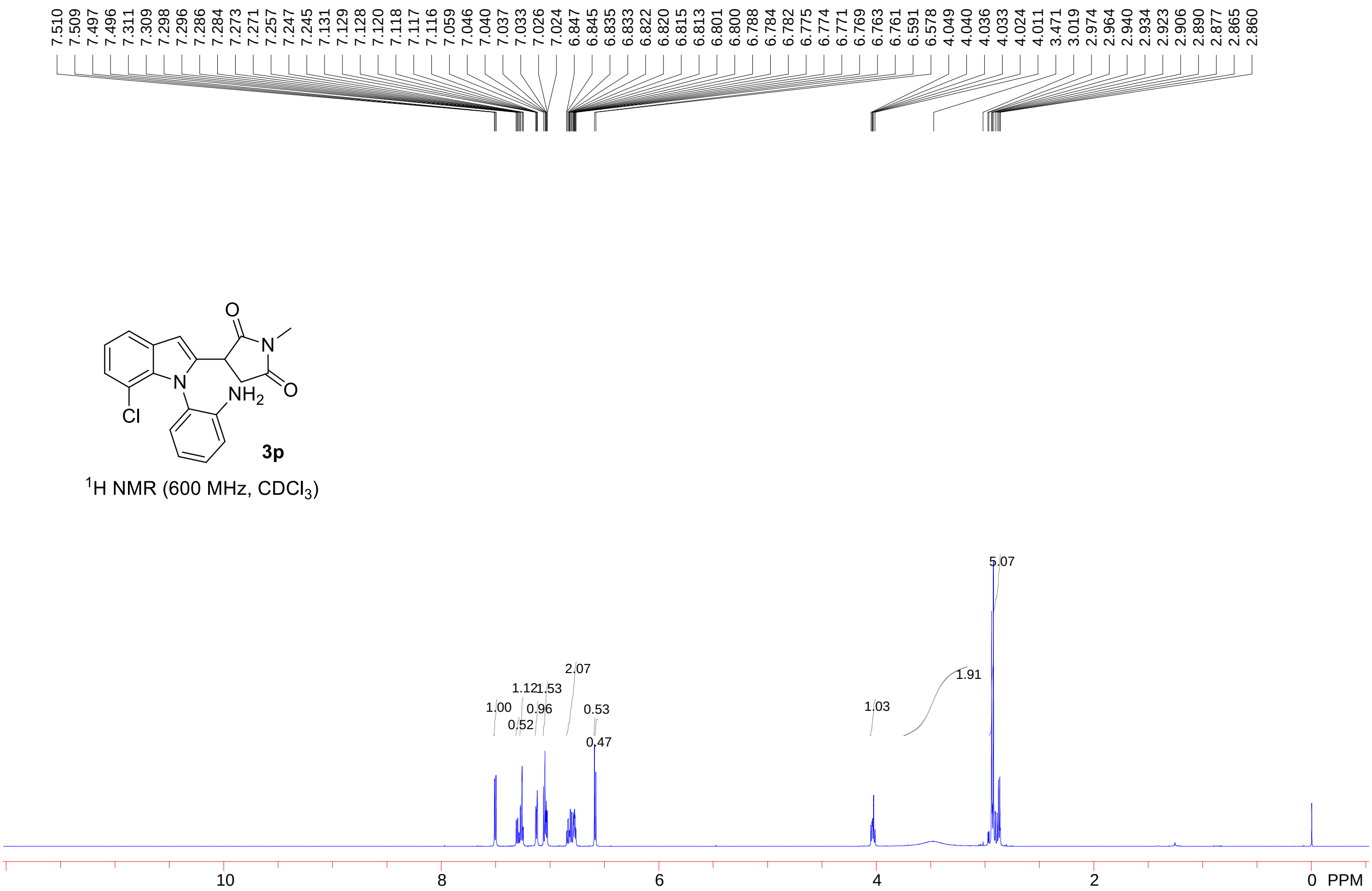


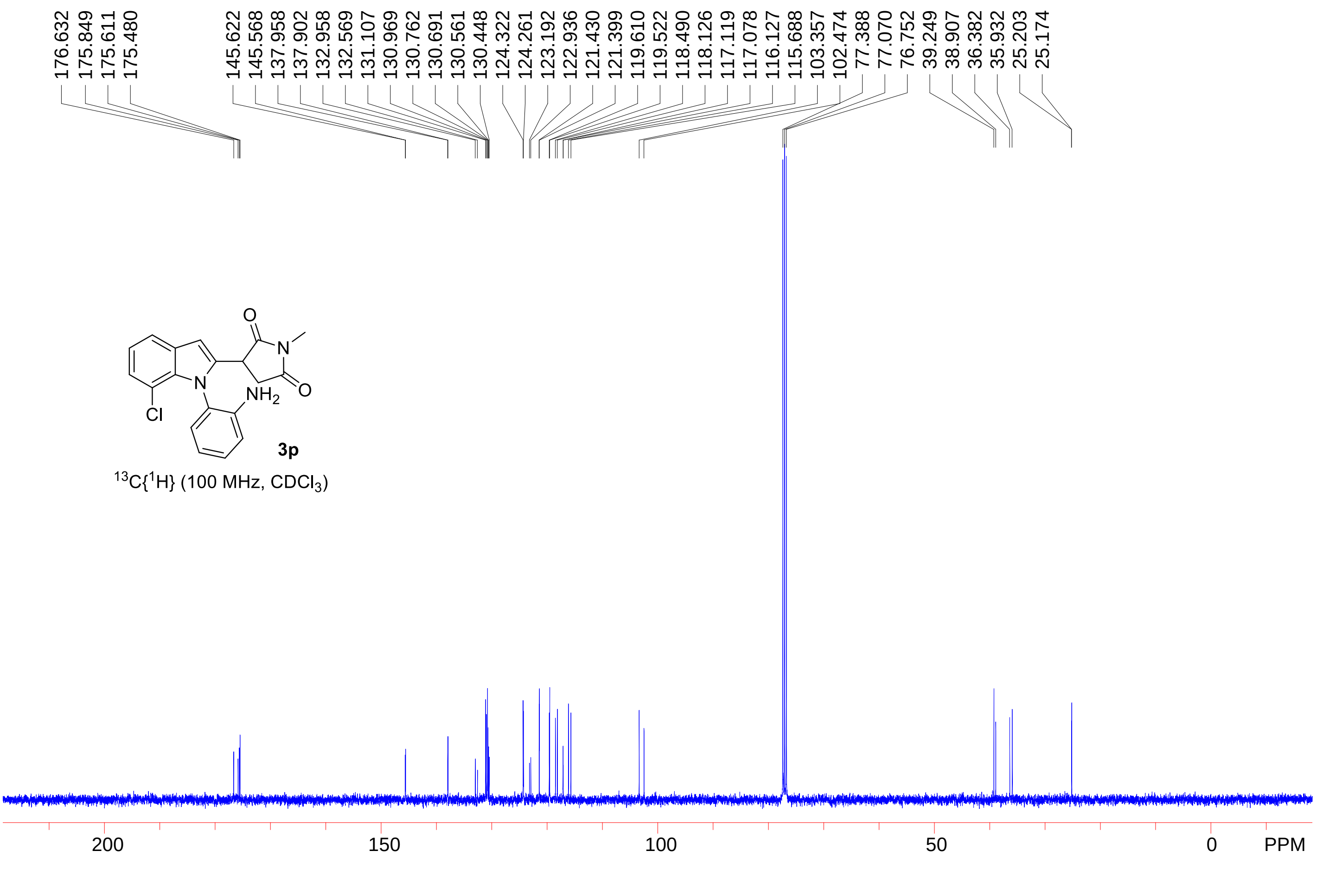
3o

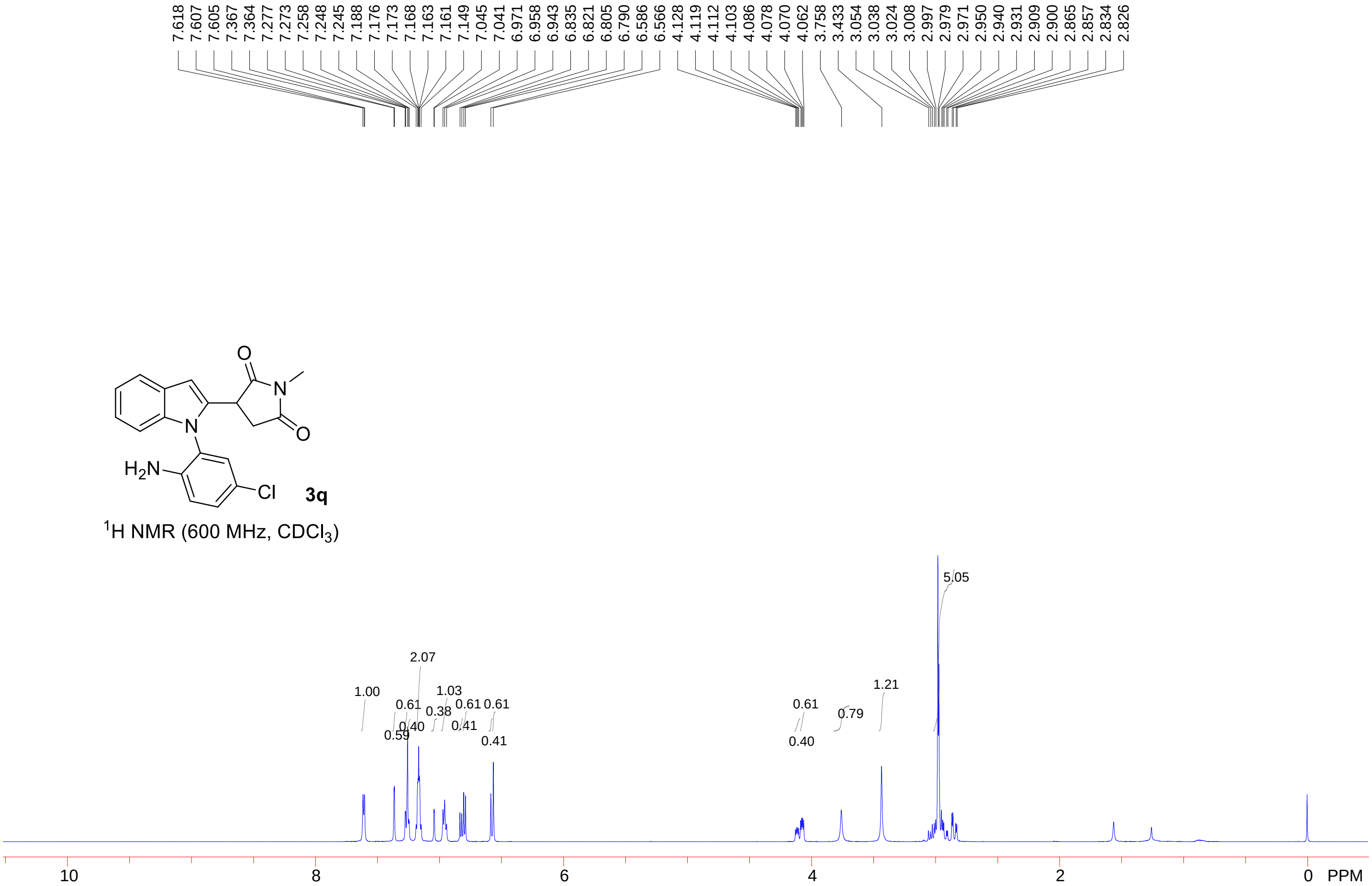
$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$)




-135.621
-135.649
-135.812
-135.842
O
N
O
NH2
N
F
3o
19F NMR (376 MHz, CDCl3)
0
-50
-100
-150
-200
PPM

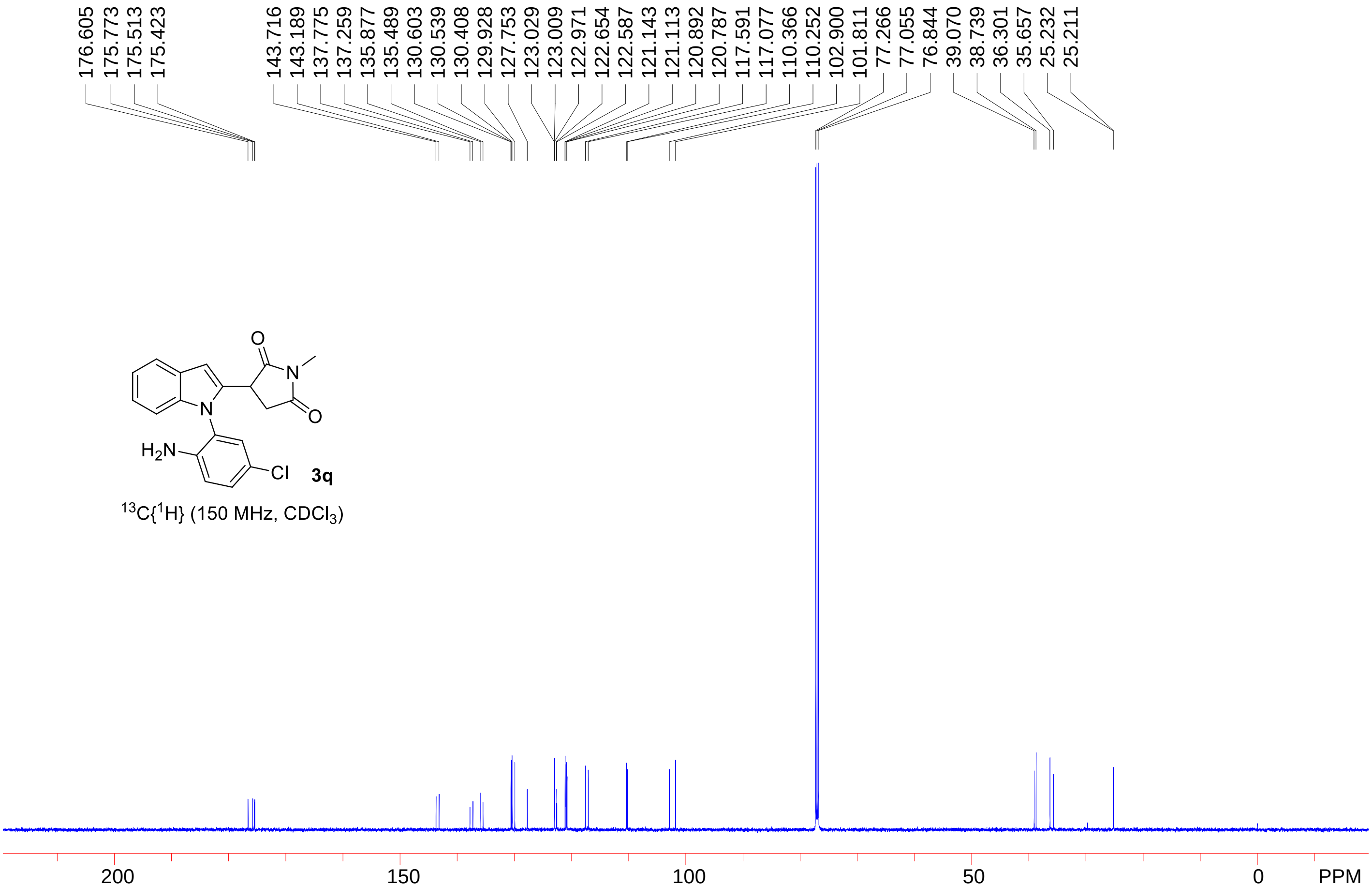

3p
^{1}H NMR (600 MHz, CDCl$_3$)


3p
^{13}C{^{1}H} (100 MHz, CDCl$_3$)



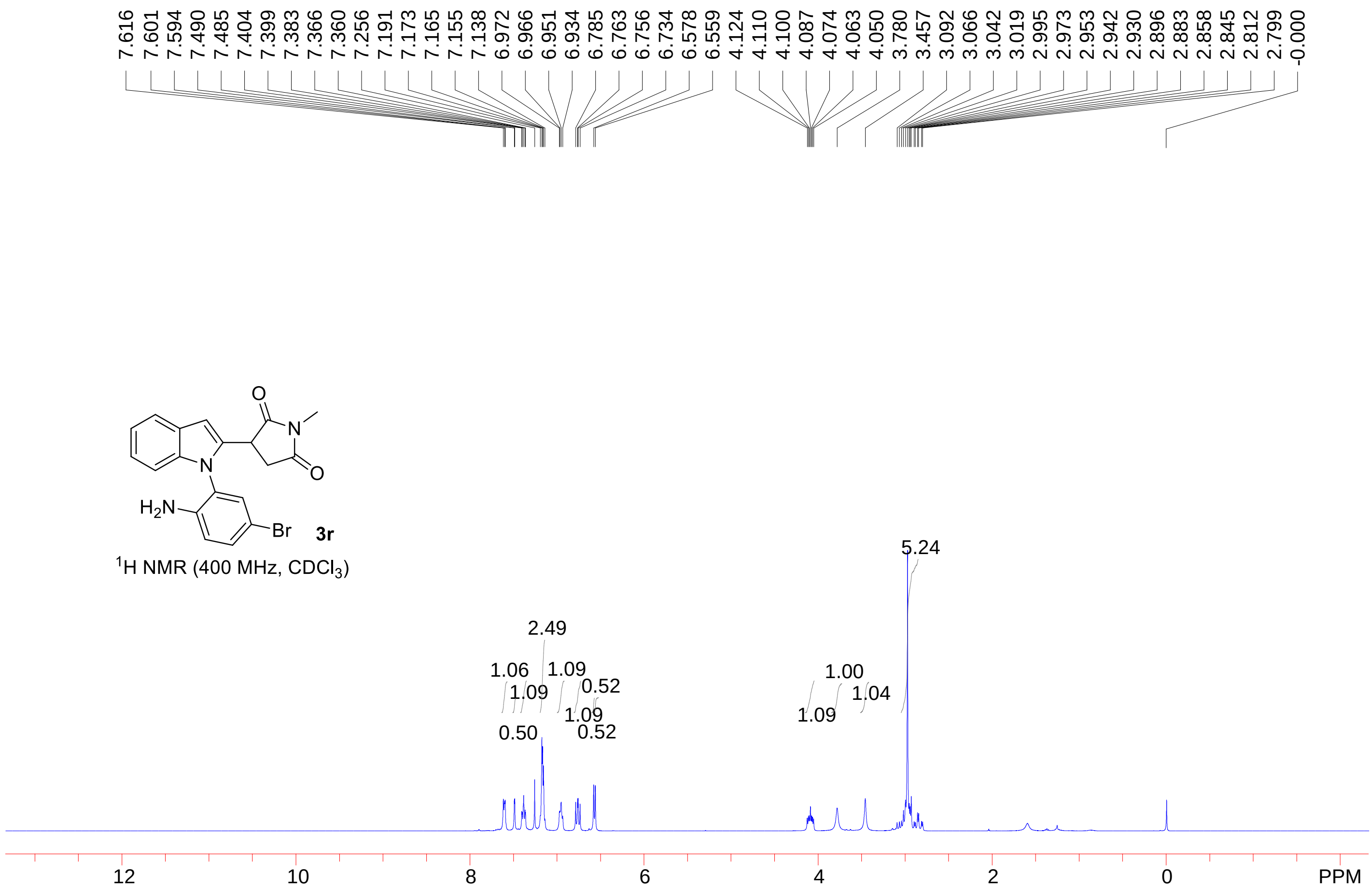
3q

^{1}H NMR (600 MHz, $CDCl_3$)

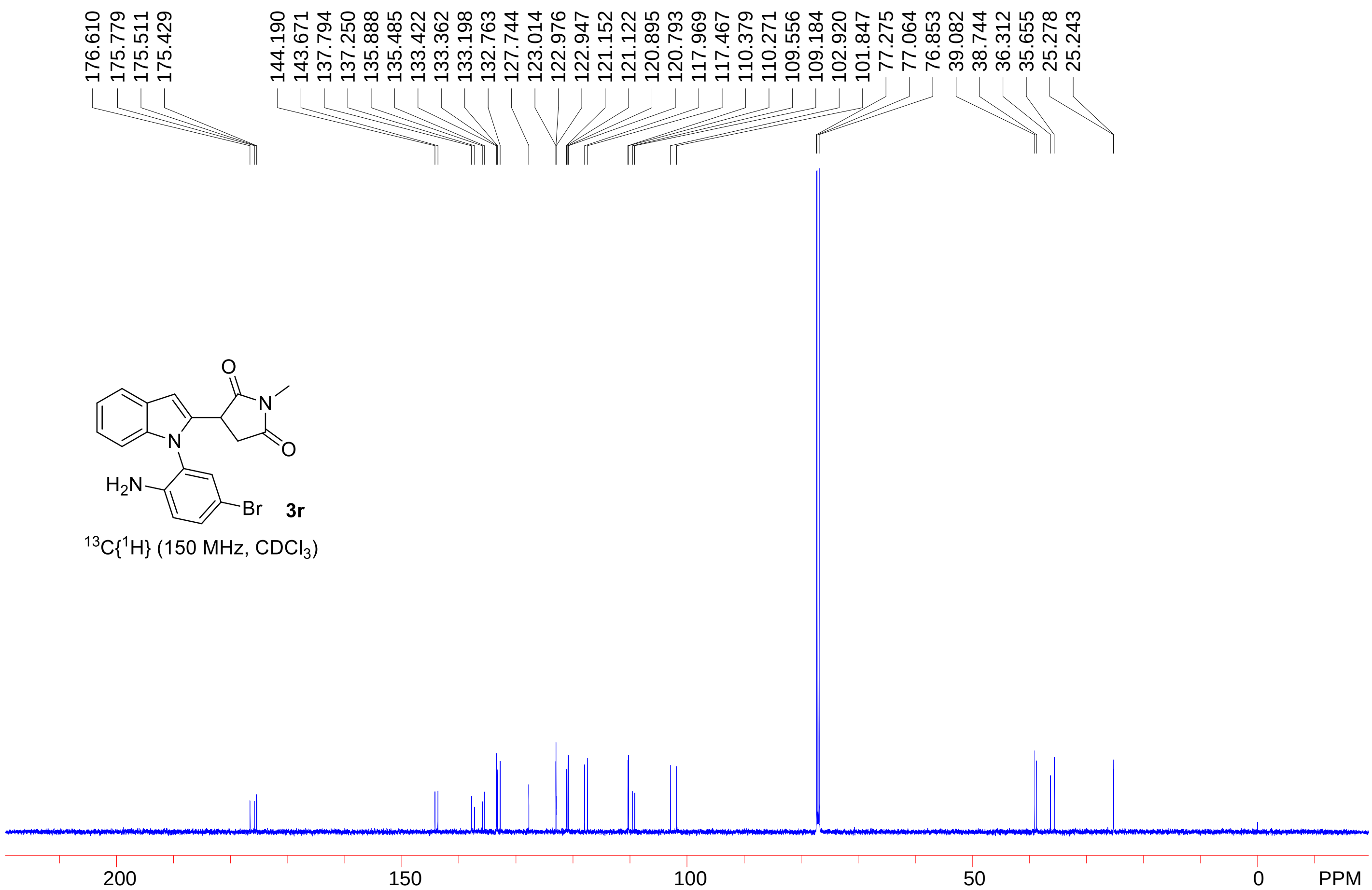


3q

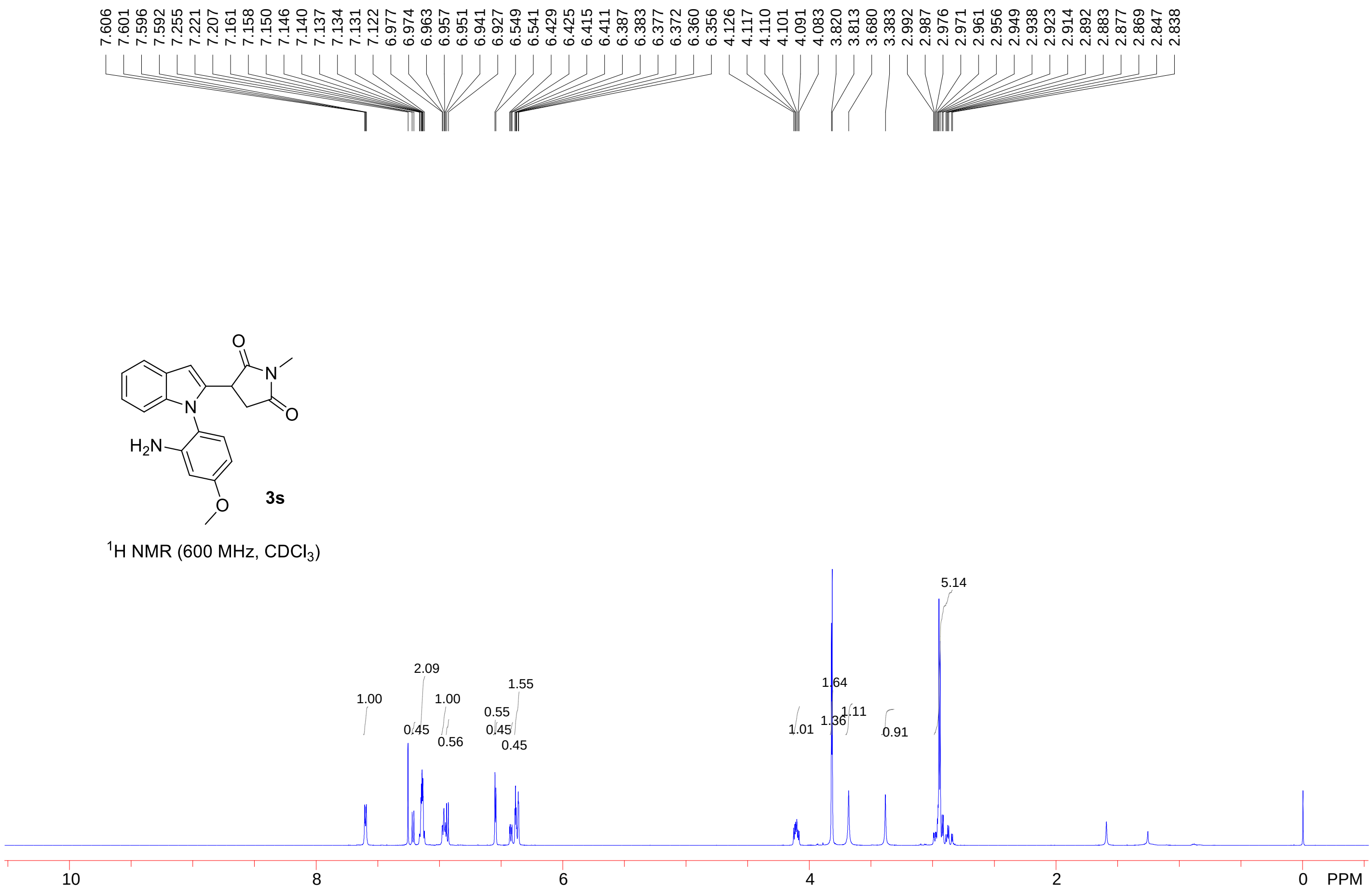
$^{13}C\{^{1}H\}$ (150 MHz, $CDCl_3$)

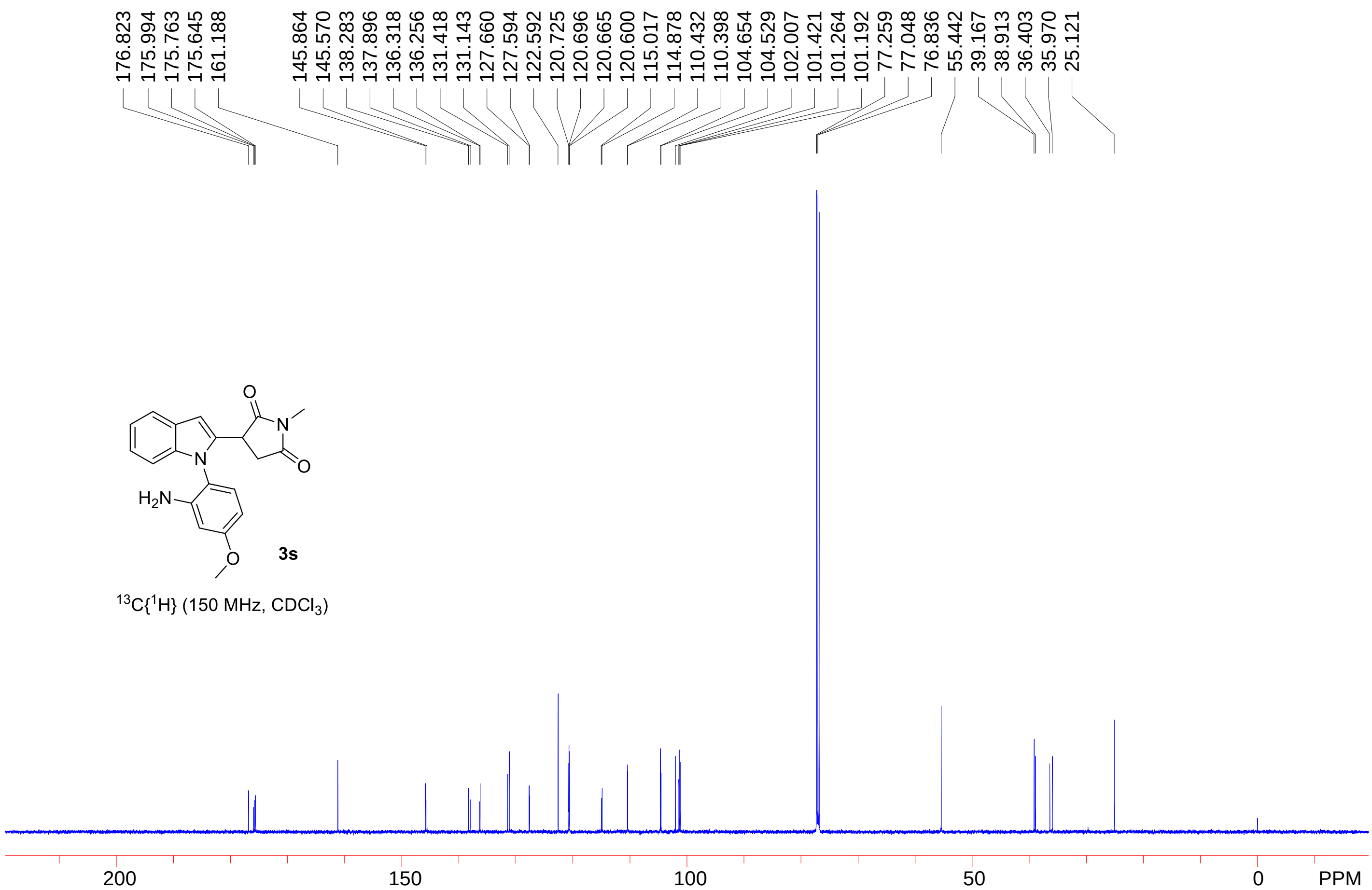


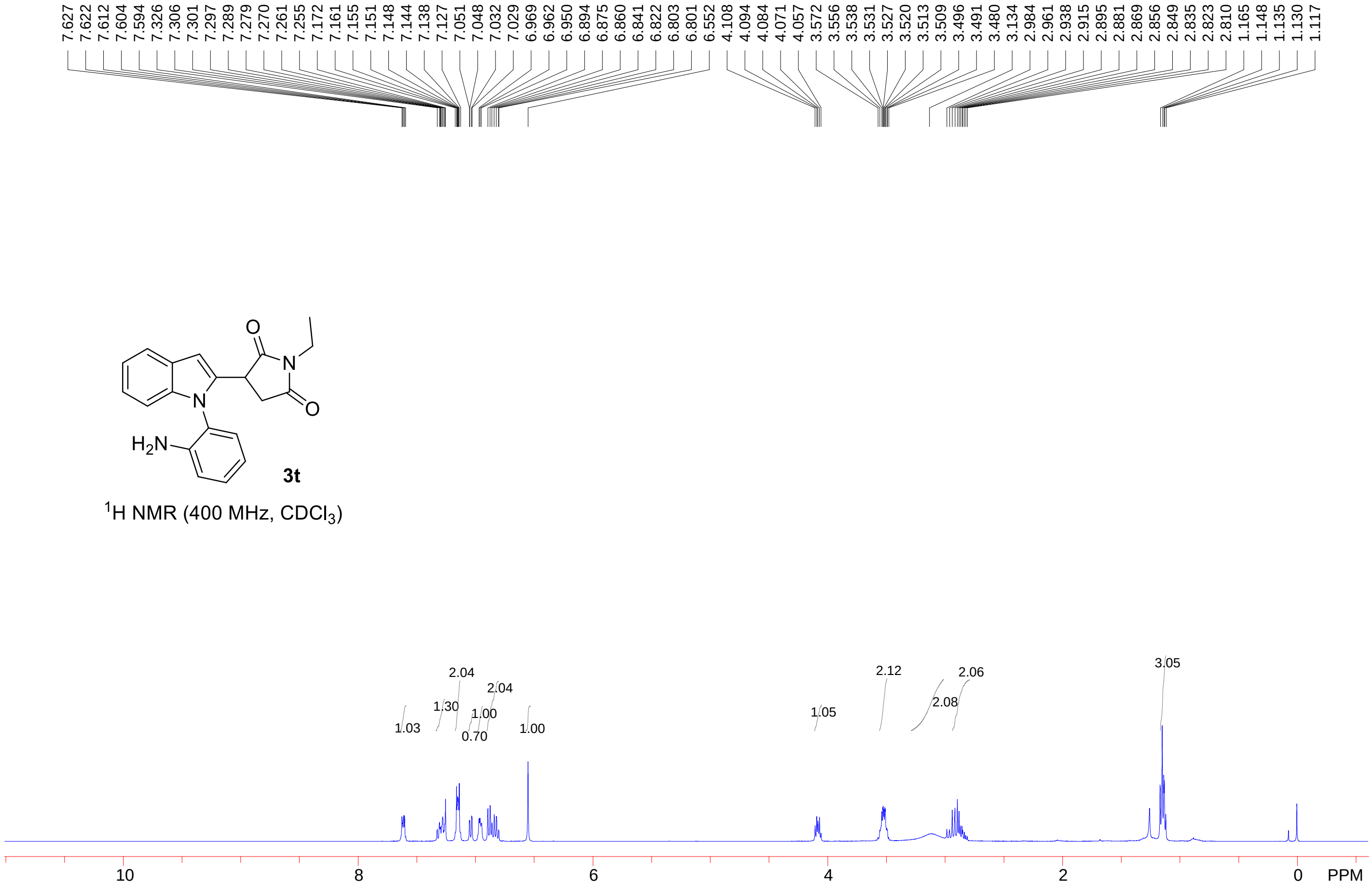
7.616
7.601
7.594
7.490
7.485
7.404
7.399
7.383
7.366
7.360
7.256
7.191
7.173
7.165
7.155
7.138
6.972
6.966
6.951
6.934
6.785
6.763
6.756
6.734
6.578
6.559
4.124
4.110
4.100
4.087
4.074
4.063
4.050
3.780
3.457
3.092
3.066
3.042
3.019
2.995
2.973
2.953
2.942
2.930
2.896
2.883
2.858
2.845
2.812
2.799
-0.000
H2N
Br
3r
1H NMR (400 MHz, CDCl3)
5.24
2.49
1.06
1.09
1.09
0.52
1.09
0.50
0.52
1.00
1.04
1.09
12
10
8
6
4
2
0
PPM



176.610
175.779
175.511
175.429
144.190
143.671
137.794
137.250
135.888
135.485
133.422
133.362
133.198
132.763
127.744
123.014
122.976
122.947
121.152
121.122
120.895
120.793
117.969
117.467
110.379
110.271
109.556
109.184
102.920
101.847
77.275
77.064
76.853
39.082
38.744
36.312
35.655
25.278
25.243
H2N
Br
3r
13C{1H} (150 MHz, CDCl3)
200
150
100
50
0
PPM

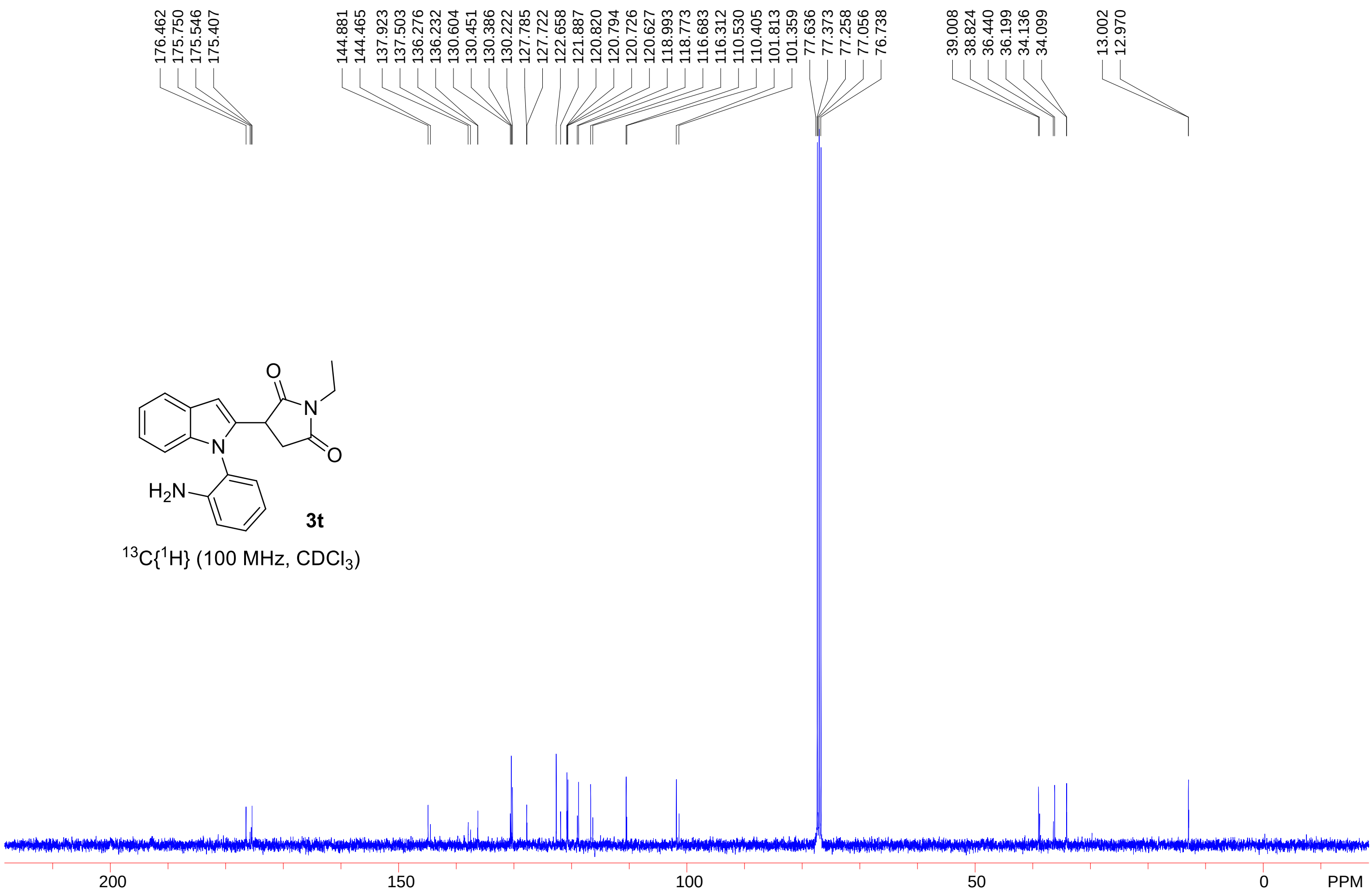

7.606 7.601 7.596 7.592 7.255 7.221 7.207 7.161 7.158 7.150 7.146 7.140 7.137 7.134 7.131 7.122 6.977 6.974 6.963 6.957 6.951 6.941 6.927 6.549 6.541 6.429 6.425 6.415 6.411 6.387 6.383 6.377 6.372 6.360 6.356 4.126 4.117 4.110 4.101 4.091 4.083 3.820 3.813 3.680 3.383 2.992 2.987 2.976 2.971 2.961 2.956 2.949 2.938 2.923 2.914 2.892 2.883 2.877 2.869 2.847 2.838
3s
1H NMR (600 MHz, CDCl3)
1.00 2.09 0.45 1.00 0.56 0.55 0.45 1.55 0.45 1.01 1.64 1.36 1.11 0.91 5.14
10 8 6 4 2 0 PPM


176.823 175.994 175.763 175.645 161.188 145.864 145.570 138.283 137.896 136.318 136.256 131.418 131.143 127.660 127.594 122.592 120.725 120.696 120.665 120.600 115.017 114.878 110.432 110.398 104.654 104.529 102.007 101.421 101.264 101.192 77.259 77.048 76.836 55.442 39.167 38.913 36.403 35.970 25.121
3s
13C{1H} (150 MHz, CDCl3)
200 150 100 50 0 PPM



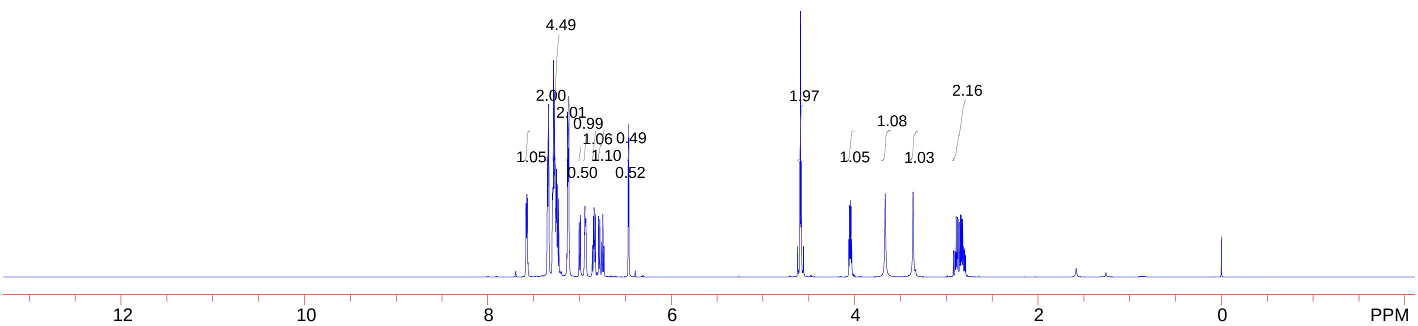
3t

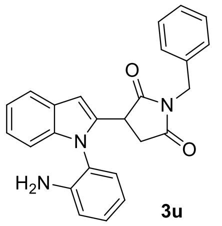
^{1}H NMR (400 MHz, $CDCl_3$)



3t

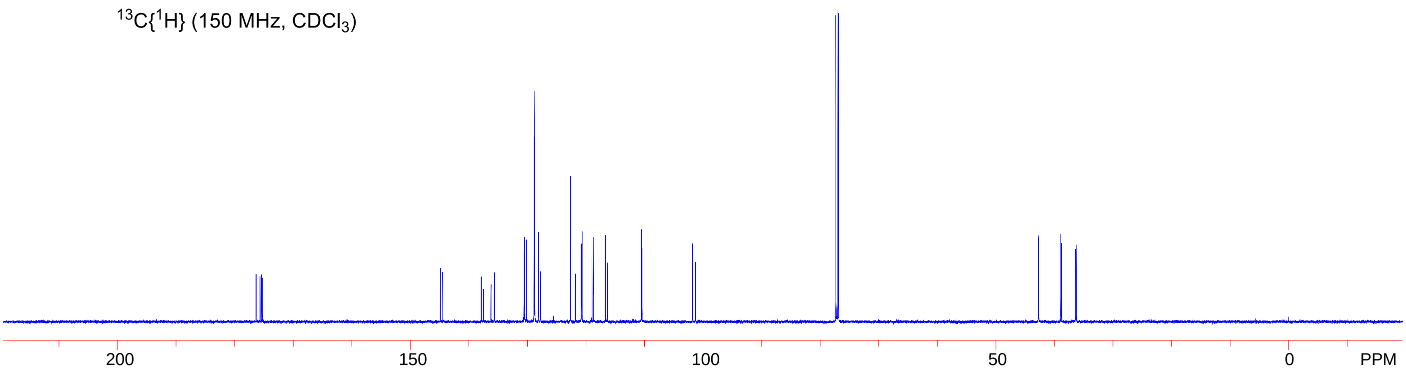
^{13}C{^{1}H} (100 MHz, $CDCl_3$)

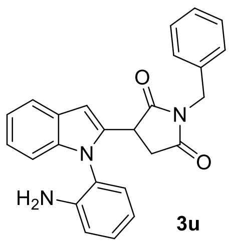




3u

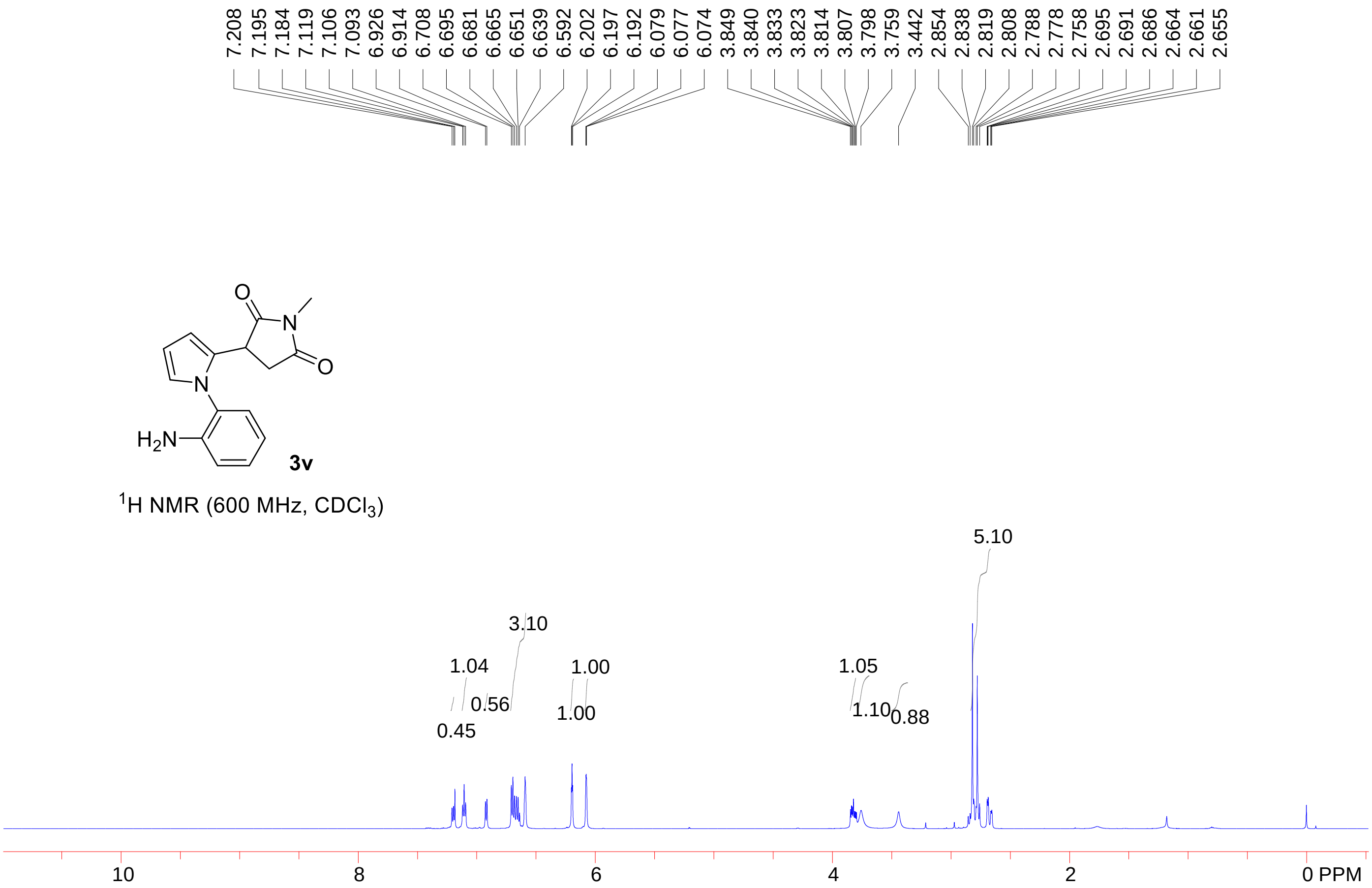
^{1}H NMR (600 MHz, $CDCl_3$)





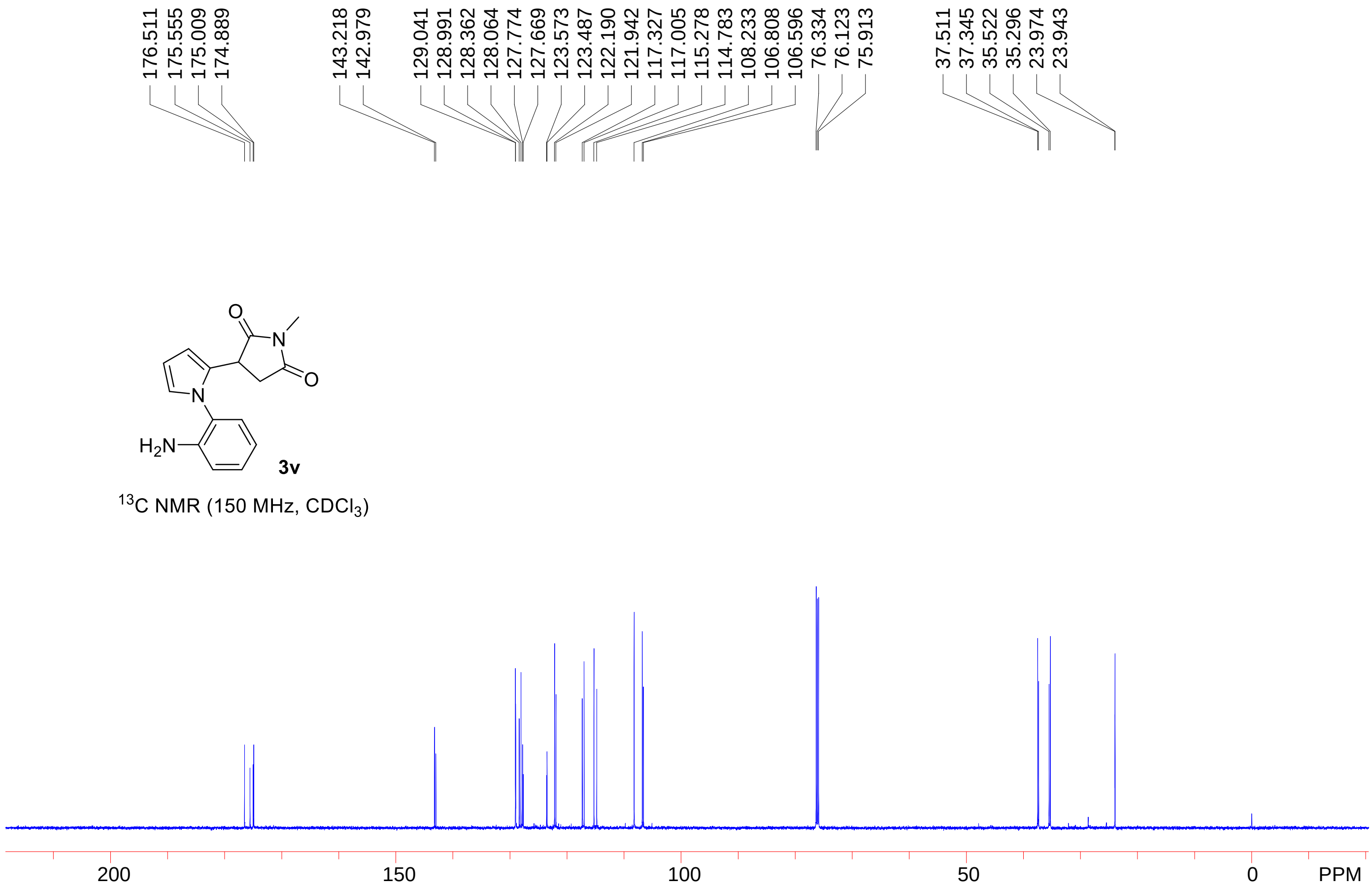
3u

^{13}C{^{1}H} (150 MHz, $CDCl_3$)



3v

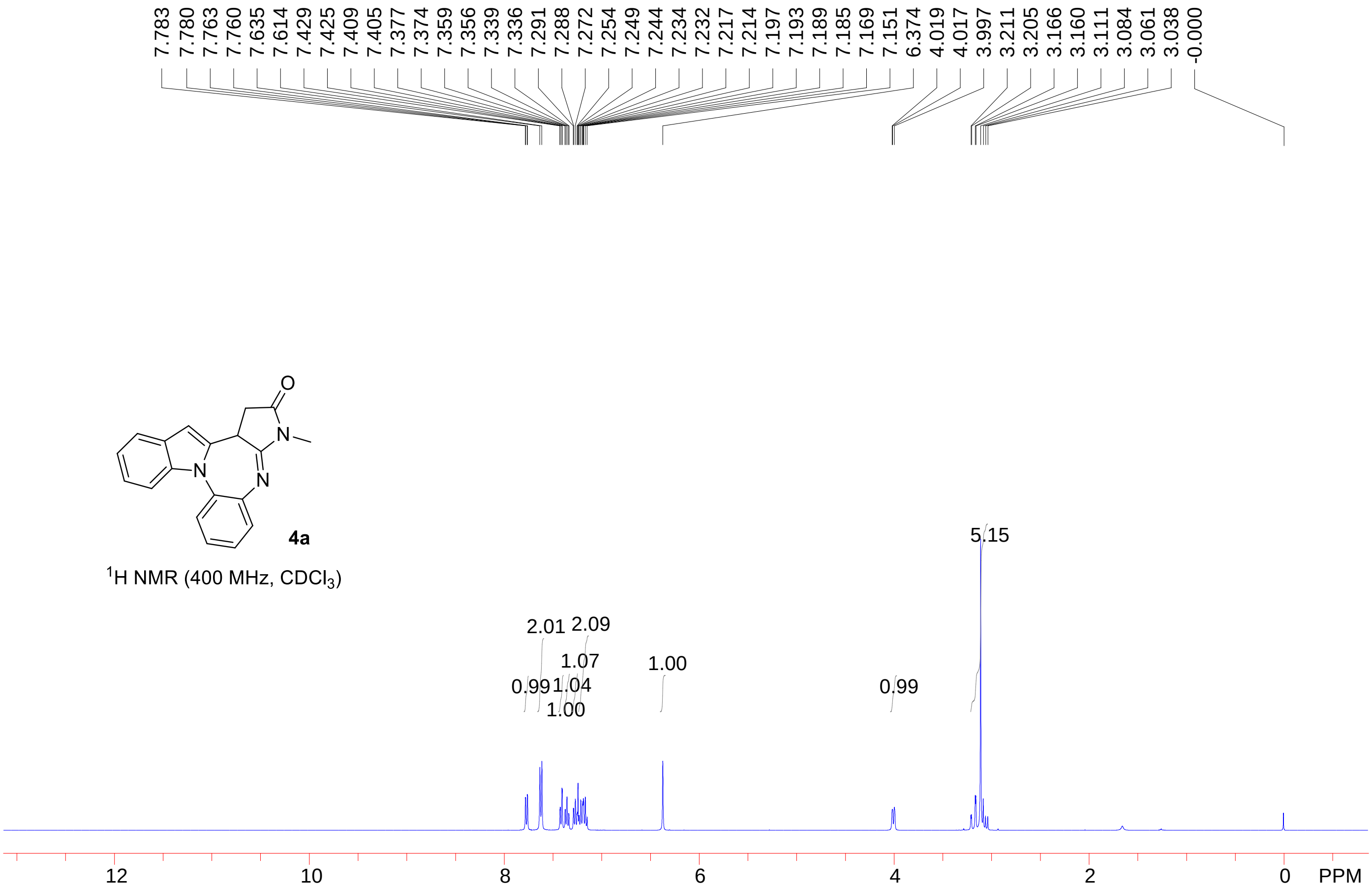
^{1}H NMR (600 MHz, $CDCl_3$)

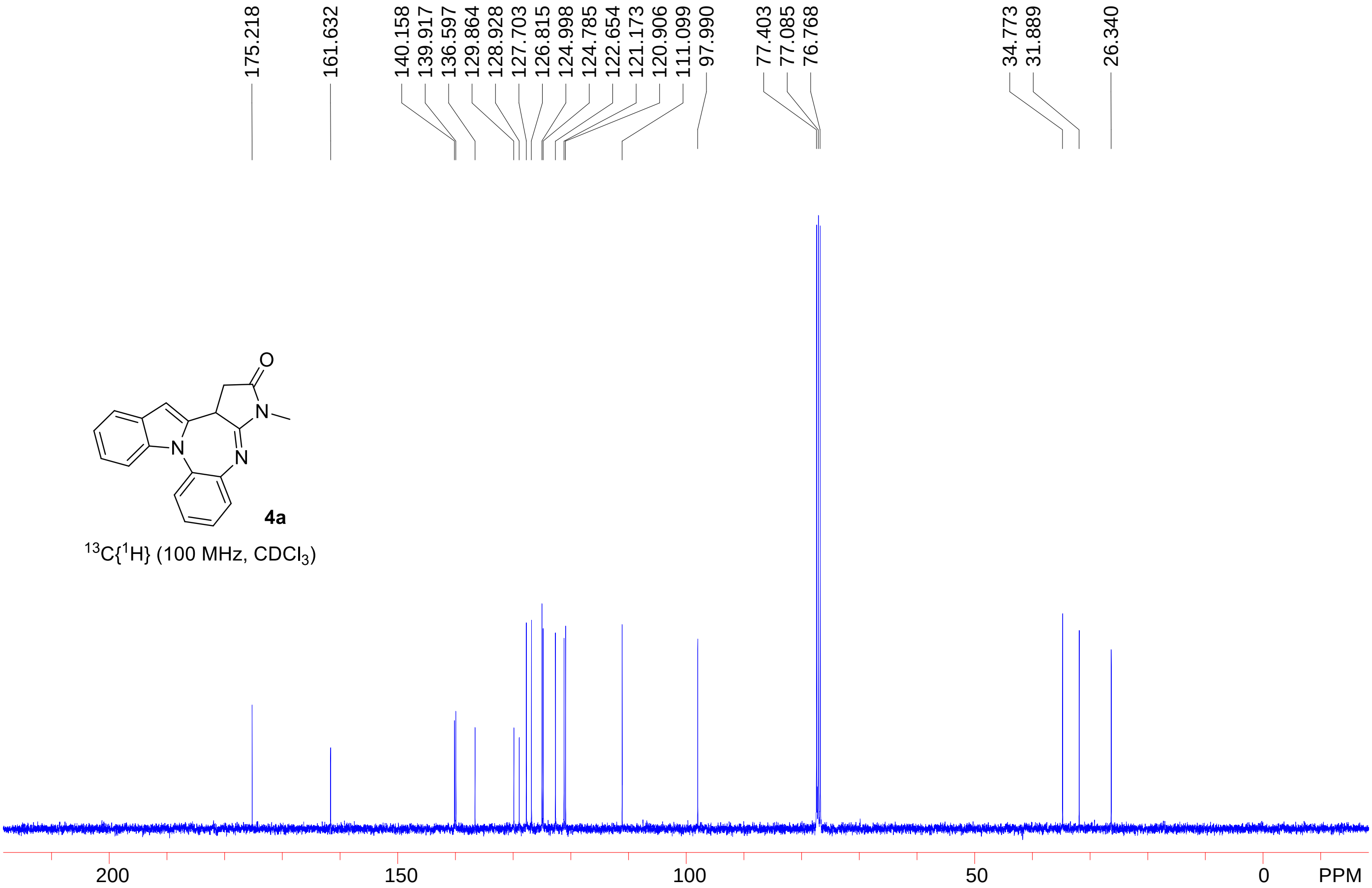


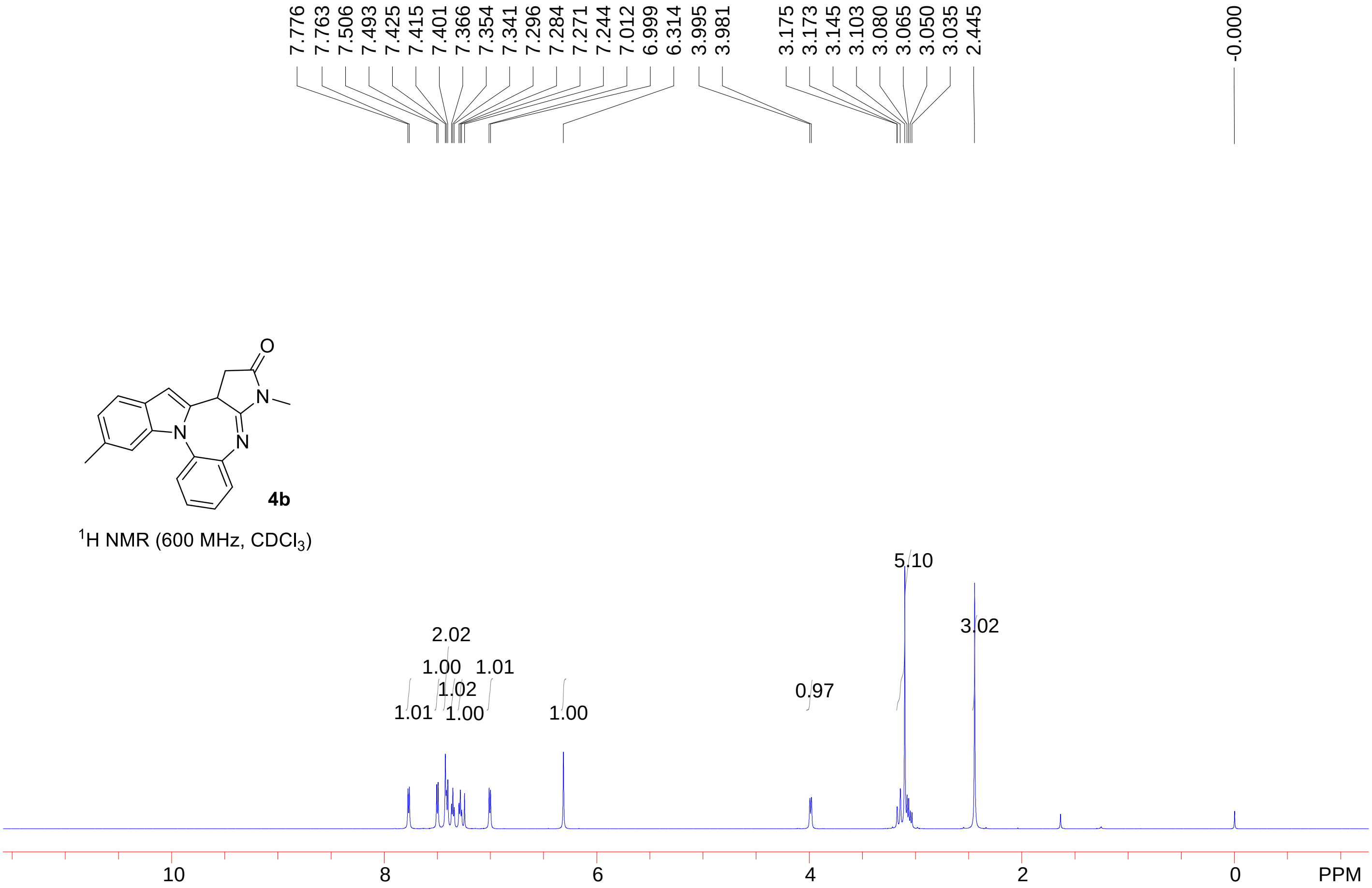
3v

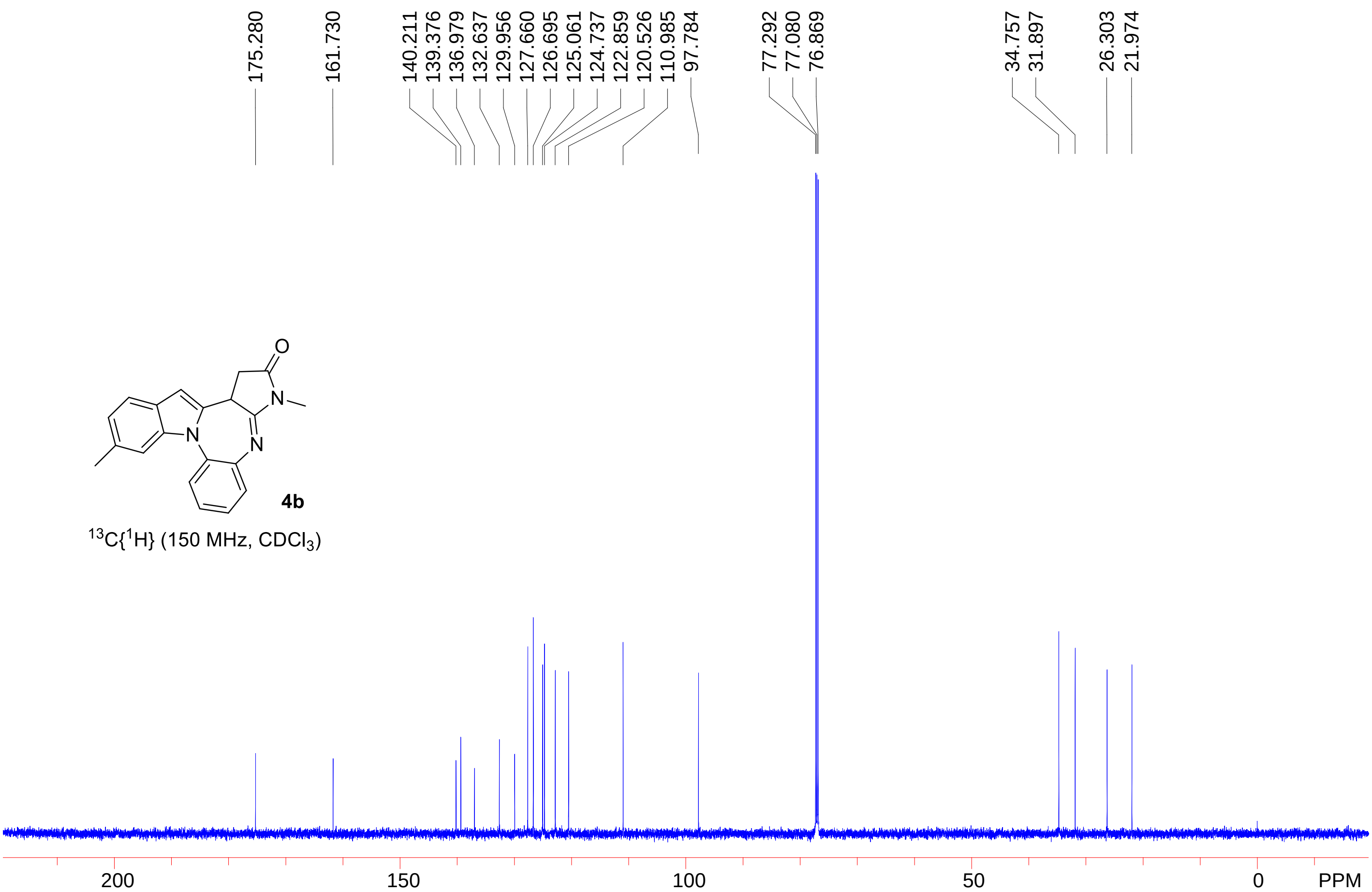
^{13}C NMR (150 MHz, $CDCl_3$)

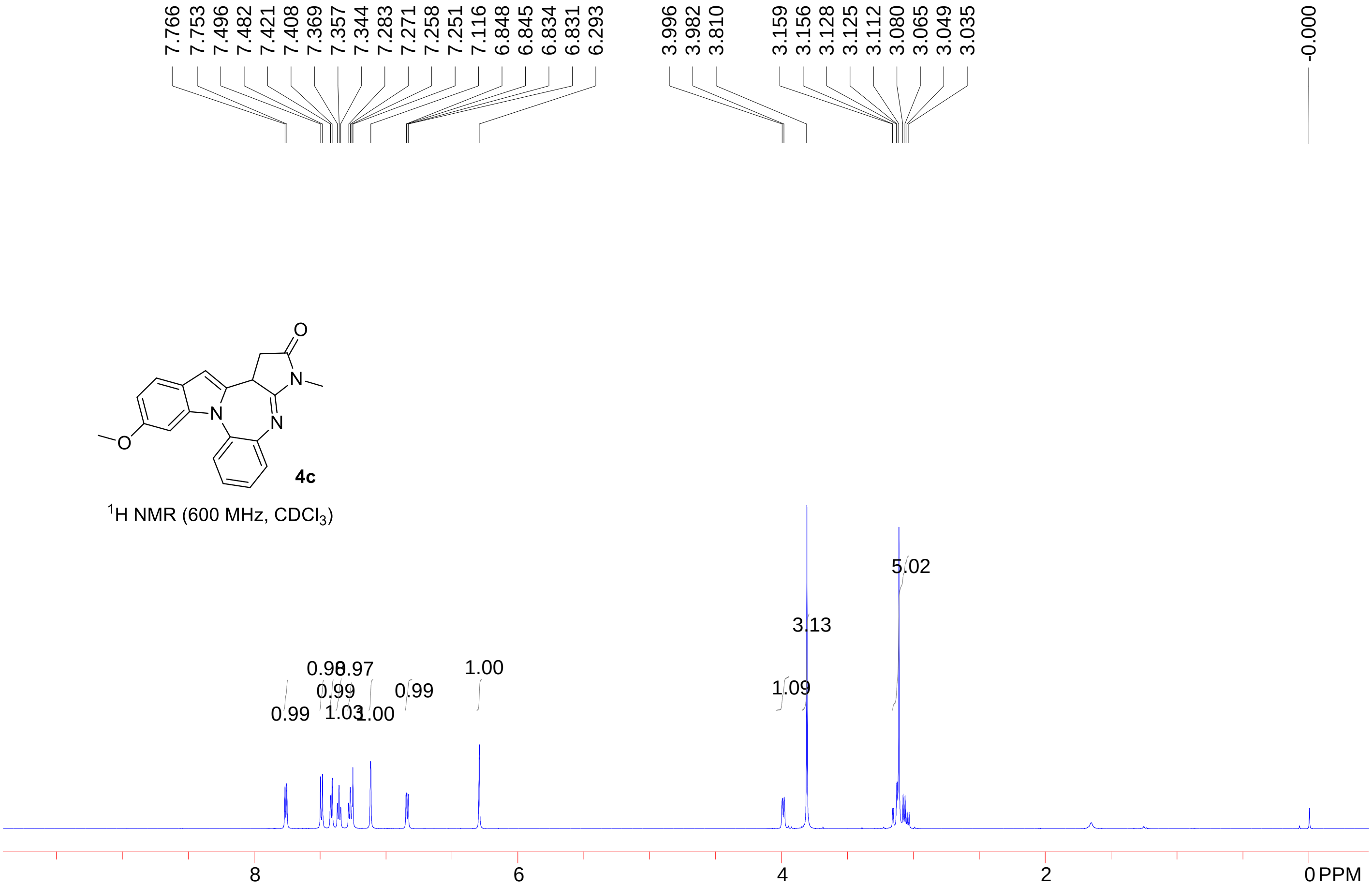
VI. NMR spectra of 4a-4y

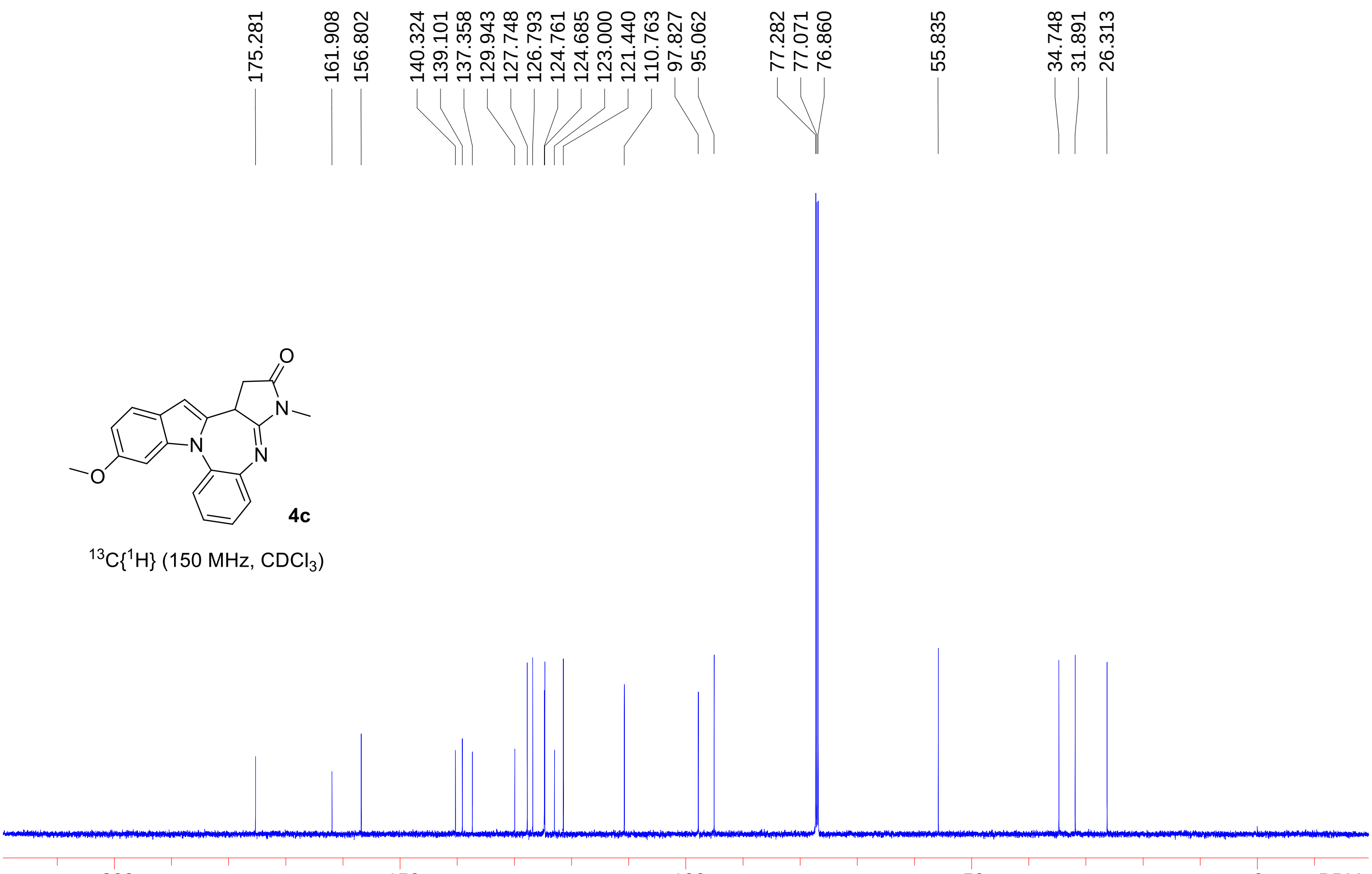


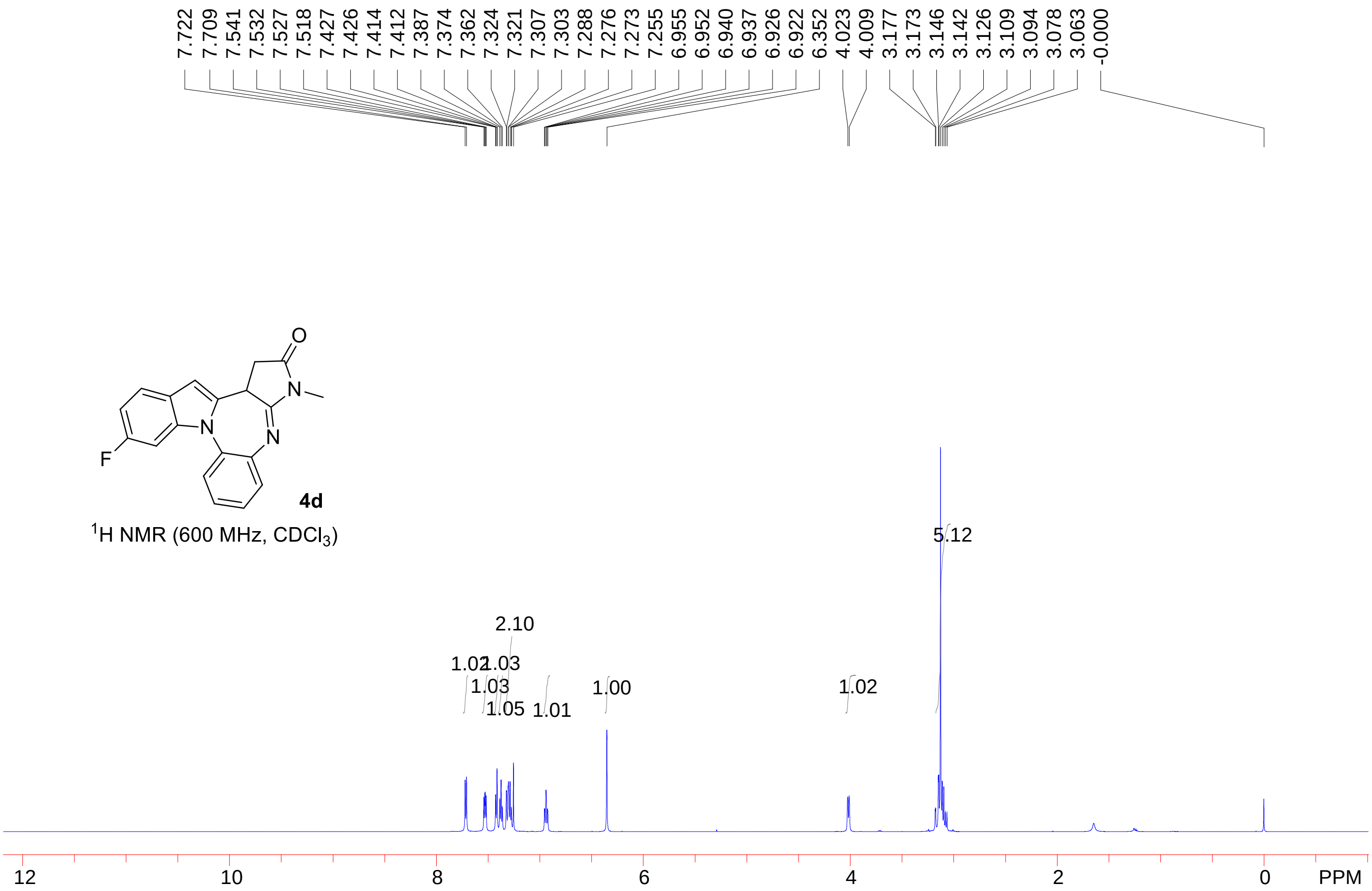


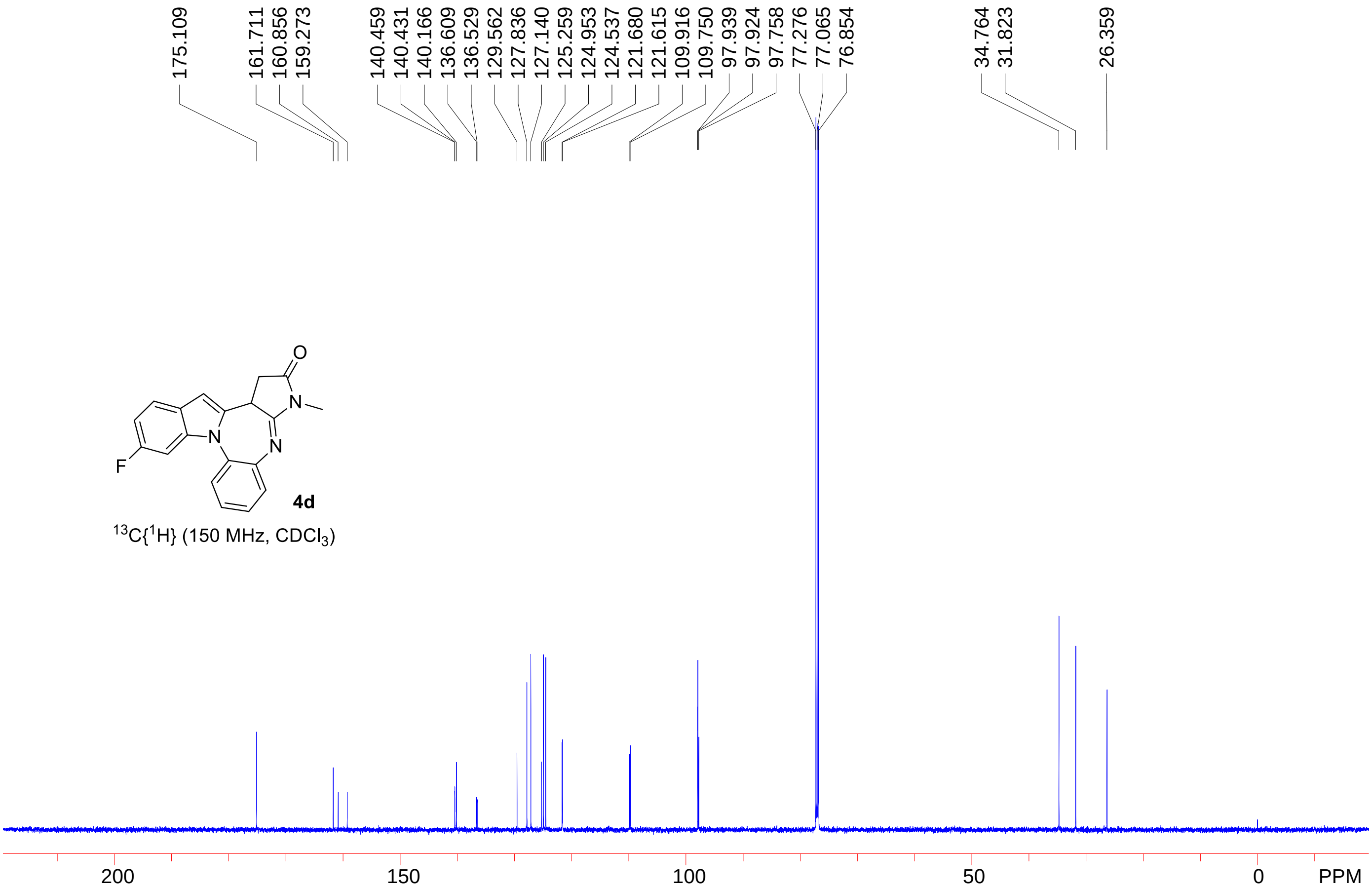

7.776
7.763
7.506
7.493
7.425
7.415
7.401
7.366
7.354
7.341
7.296
7.284
7.271
7.244
7.012
6.999
6.314
3.995
3.981
3.175
3.173
3.145
3.103
3.080
3.065
3.050
3.035
2.445
-0.000
O
N
N
N
4b
^{1}H NMR (600 MHz, CDCl$_3$)
5.10
3.02
2.02
1.00
1.01
1.02
1.01
1.00
1.00
0.97
10
8
6
4
2
0
PPM

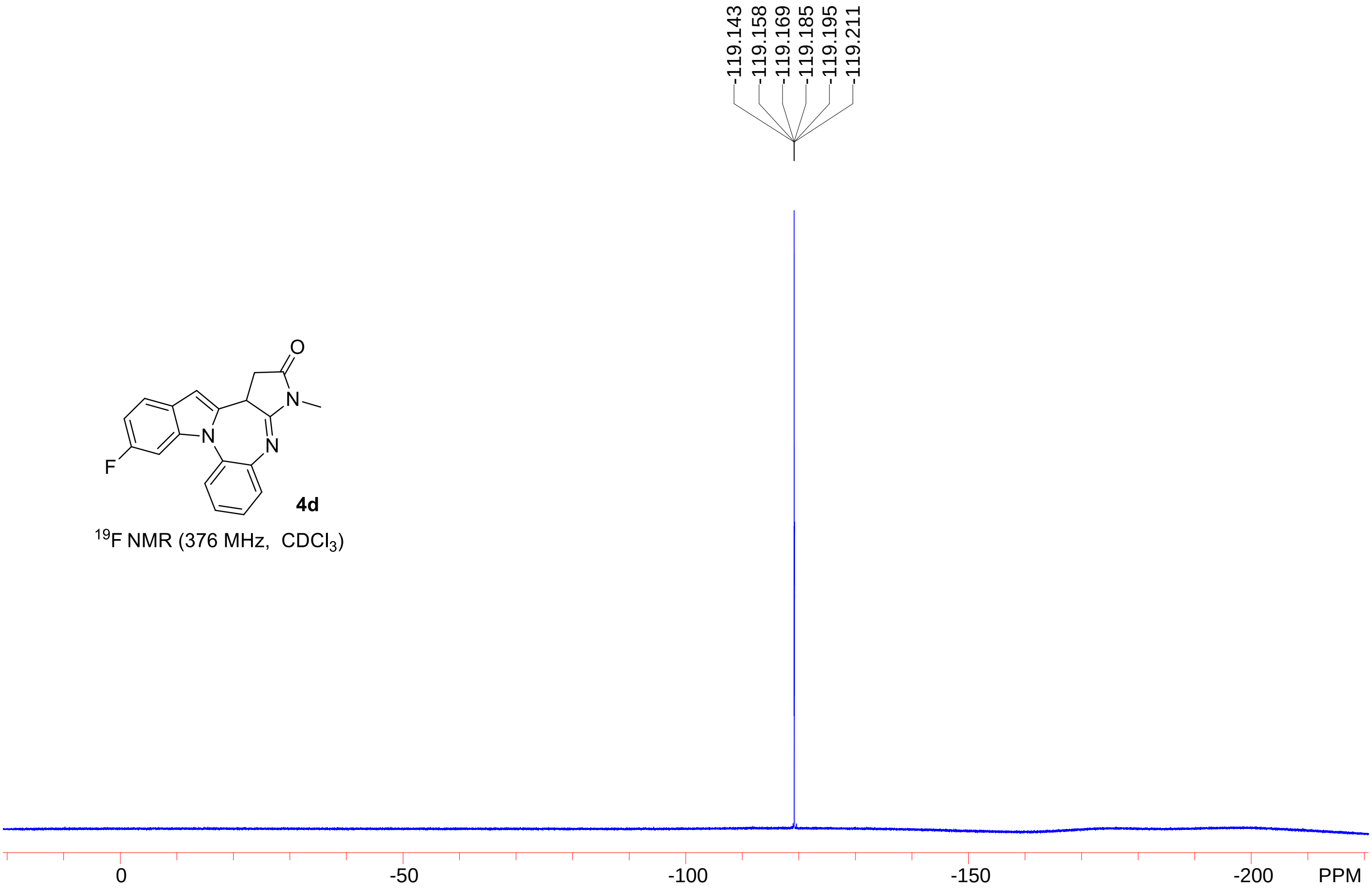

175.280
161.730
140.211
139.376
136.979
132.637
129.956
127.660
126.695
125.061
124.737
122.859
120.526
110.985
97.784
77.292
77.080
76.869
34.757
31.897
26.303
21.974
O
N
N
N
4b
^{13}C{^{1}H} (150 MHz, CDCl$_3$)
200
150
100
50
0
PPM


7.766 7.753 7.496 7.482 7.421 7.408 7.369 7.357 7.344 7.283 7.271 7.258 7.251 7.116 6.848 6.845 6.834 6.831 6.293
3.996 3.982 3.810
3.159 3.156 3.128 3.125 3.112 3.080 3.065 3.049 3.035
-0.000
O
N
N
N
O
4c
^{1}H NMR (600 MHz, CDCl$_3$)
0.99 0.98 0.97 0.99 1.03 1.00 0.99 1.00
1.09 3.13 5.02
8
6
4
2
0 PPM


175.281
161.908 156.802
140.324 139.101 137.358 129.943 127.748 126.793 124.761 124.685 123.000 121.440 110.763 97.827 95.062
77.282 77.071 76.860
55.835
34.748 31.891 26.313
O
N
N
N
O
4c
^{13}C{^{1}H} (150 MHz, CDCl$_3$)
200
150
100
50
0
PPM

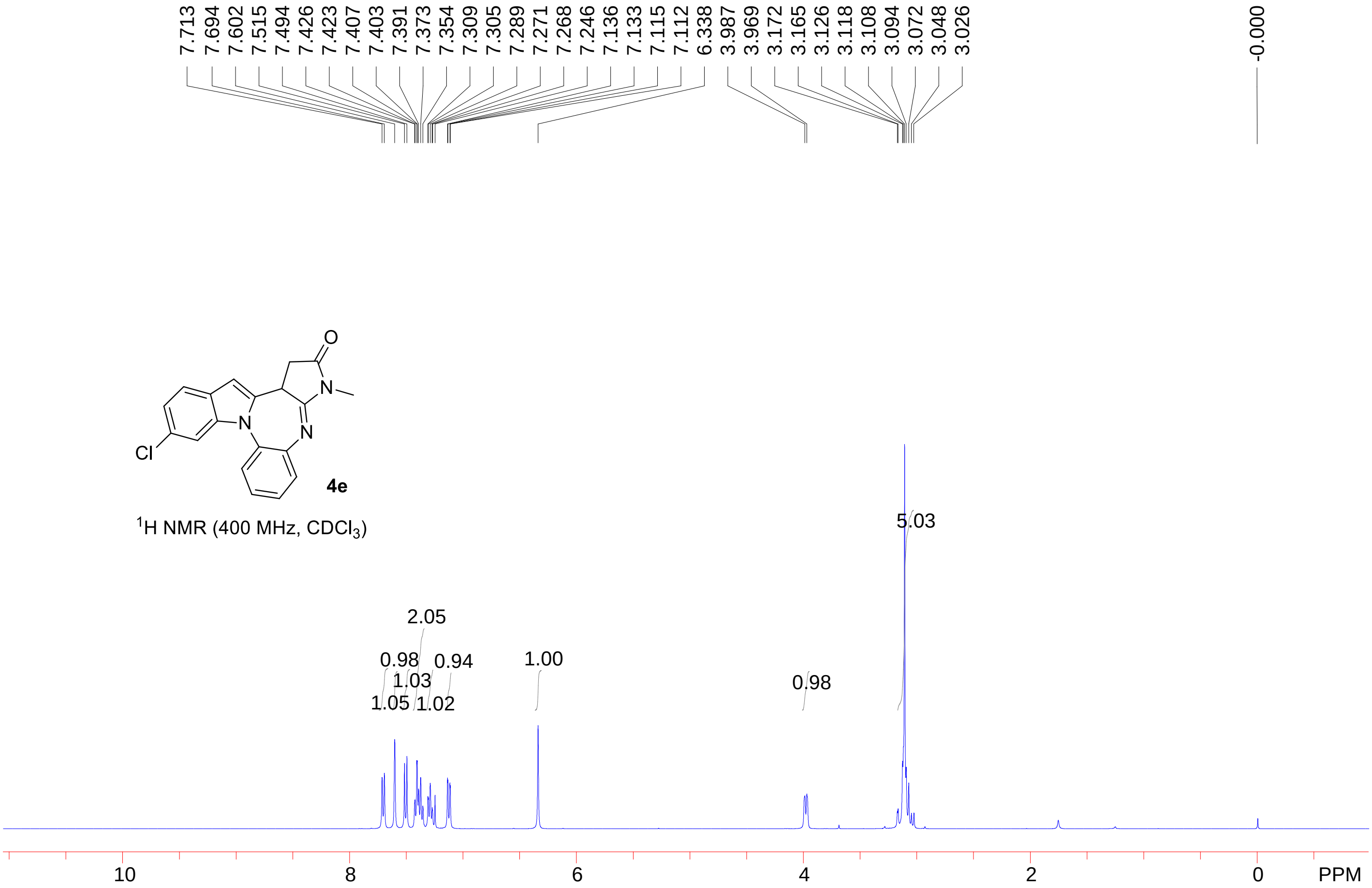

7.722
7.709
7.541
7.532
7.527
7.518
7.427
7.426
7.414
7.412
7.387
7.374
7.362
7.324
7.321
7.307
7.303
7.288
7.276
7.273
7.255
6.955
6.952
6.940
6.937
6.926
6.922
6.352
4.023
4.009
3.177
3.173
3.146
3.142
3.126
3.109
3.094
3.078
3.063
-0.000
F
N
O
N
N
4d
^{1}H NMR (600 MHz, CDCl$_3$)
5.12
2.10
1.02
1.03
1.03
1.05
1.01
1.00
1.02
12
10
8
6
4
2
0
PPM

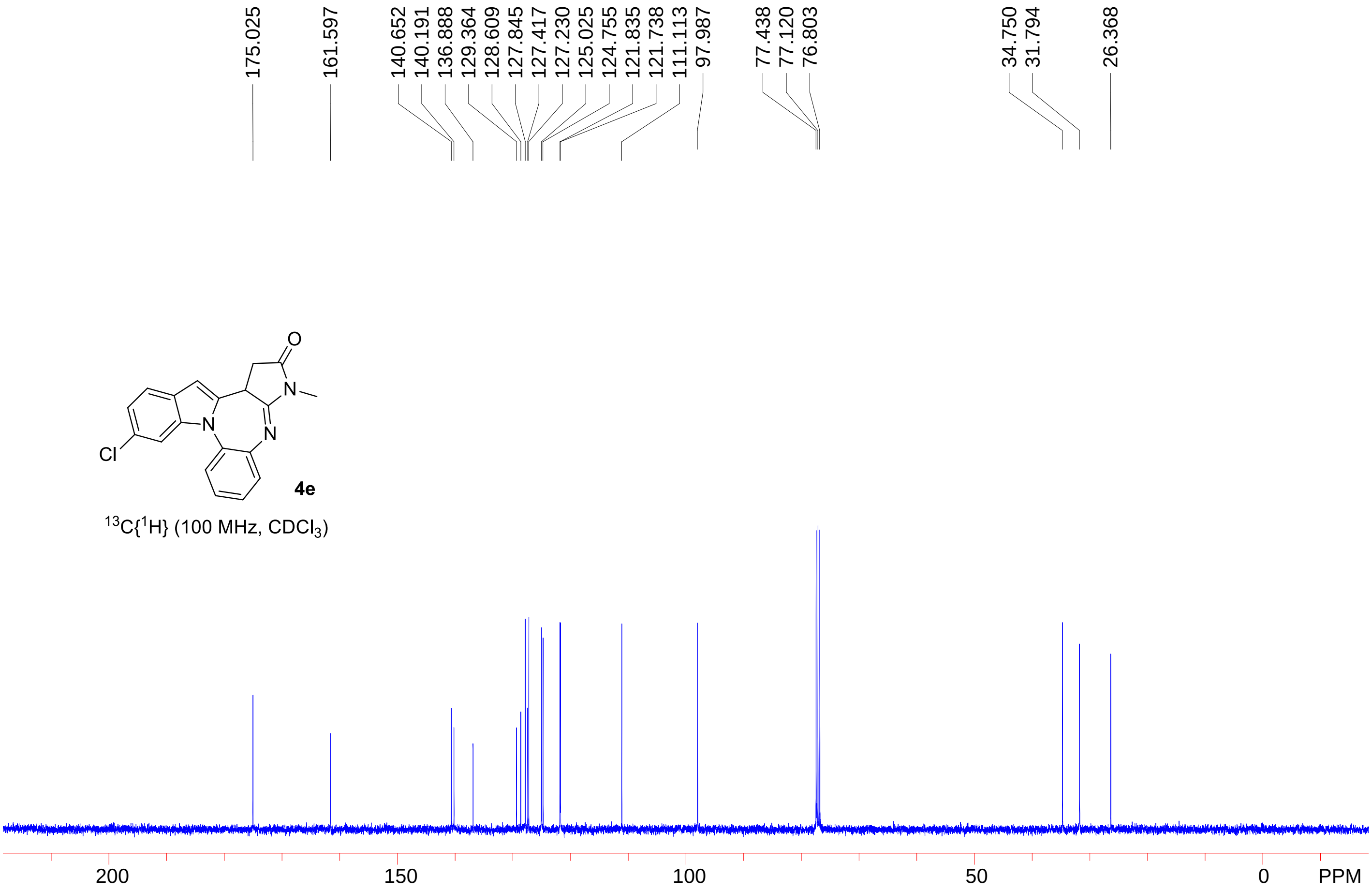

175.109
161.711
160.856
159.273
140.459
140.431
140.166
136.609
136.529
129.562
127.836
127.140
125.259
124.953
124.537
121.680
121.615
109.916
109.750
97.939
97.924
97.758
77.276
77.065
76.854
34.764
31.823
26.359
F
N
O
N
N
4d
^{13}C{^{1}H} (150 MHz, CDCl$_3$)
200
150
100
50
0
PPM

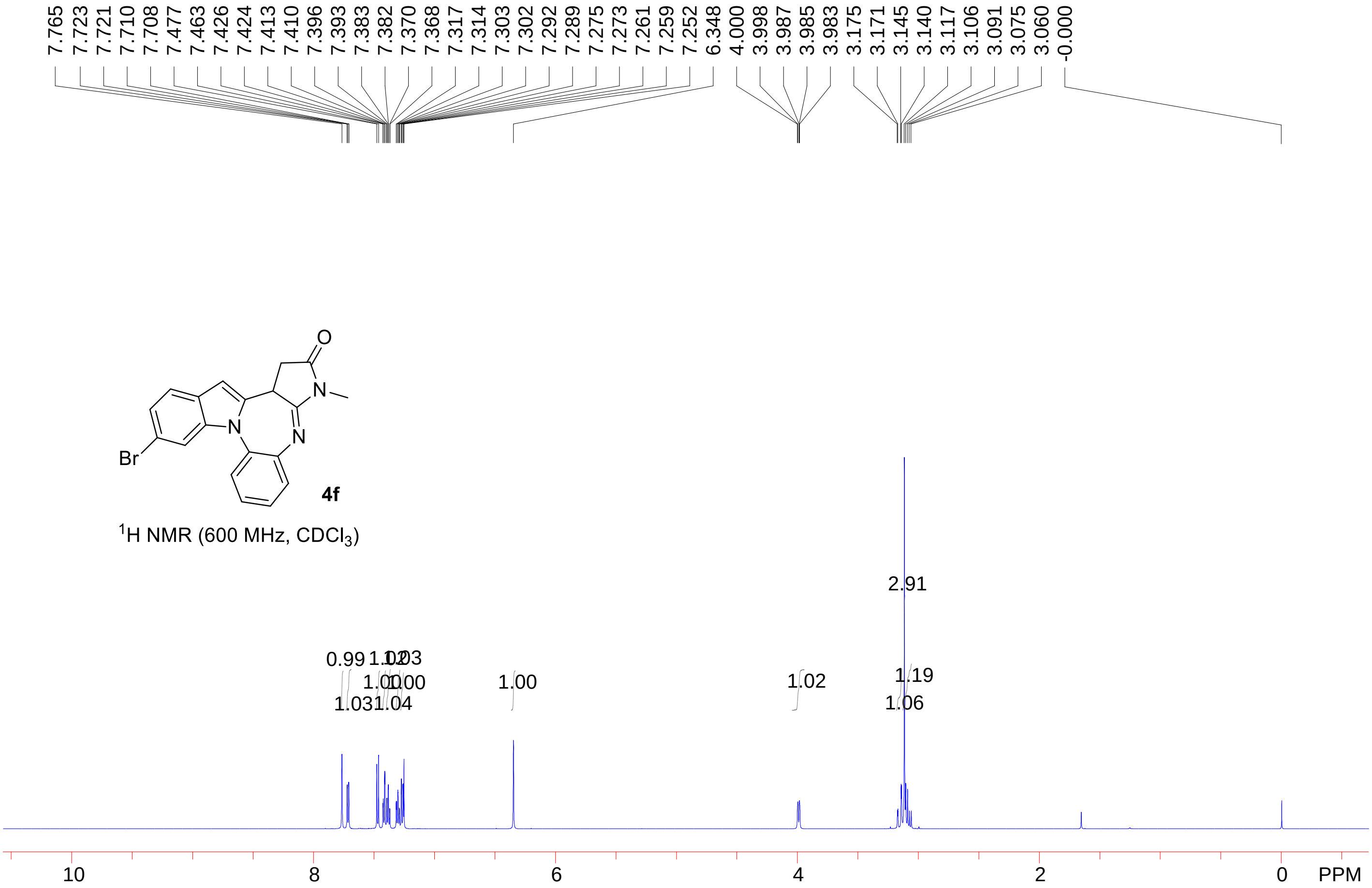


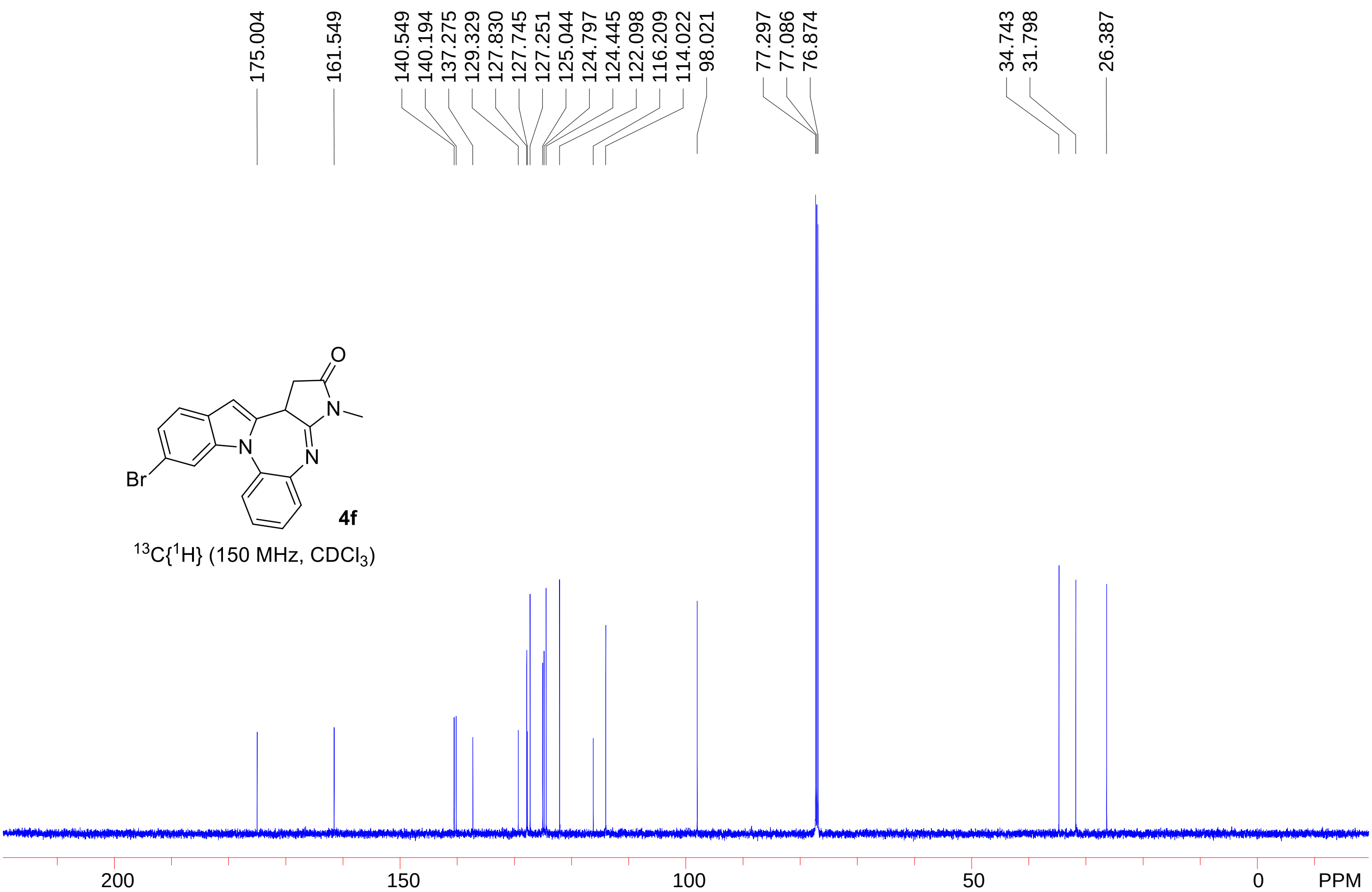
4d

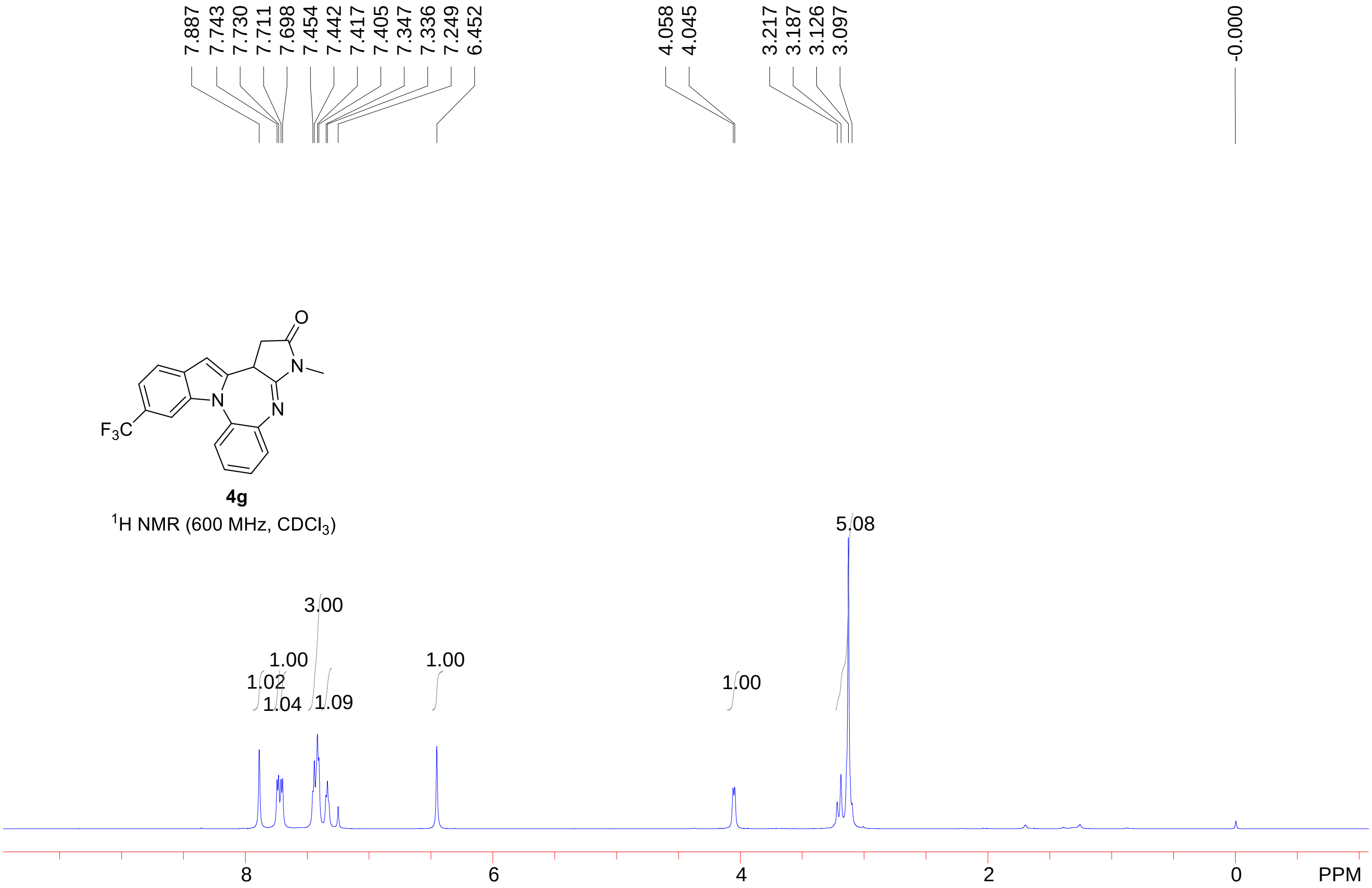
^{19}F NMR (376 MHz, $CDCl_3$)

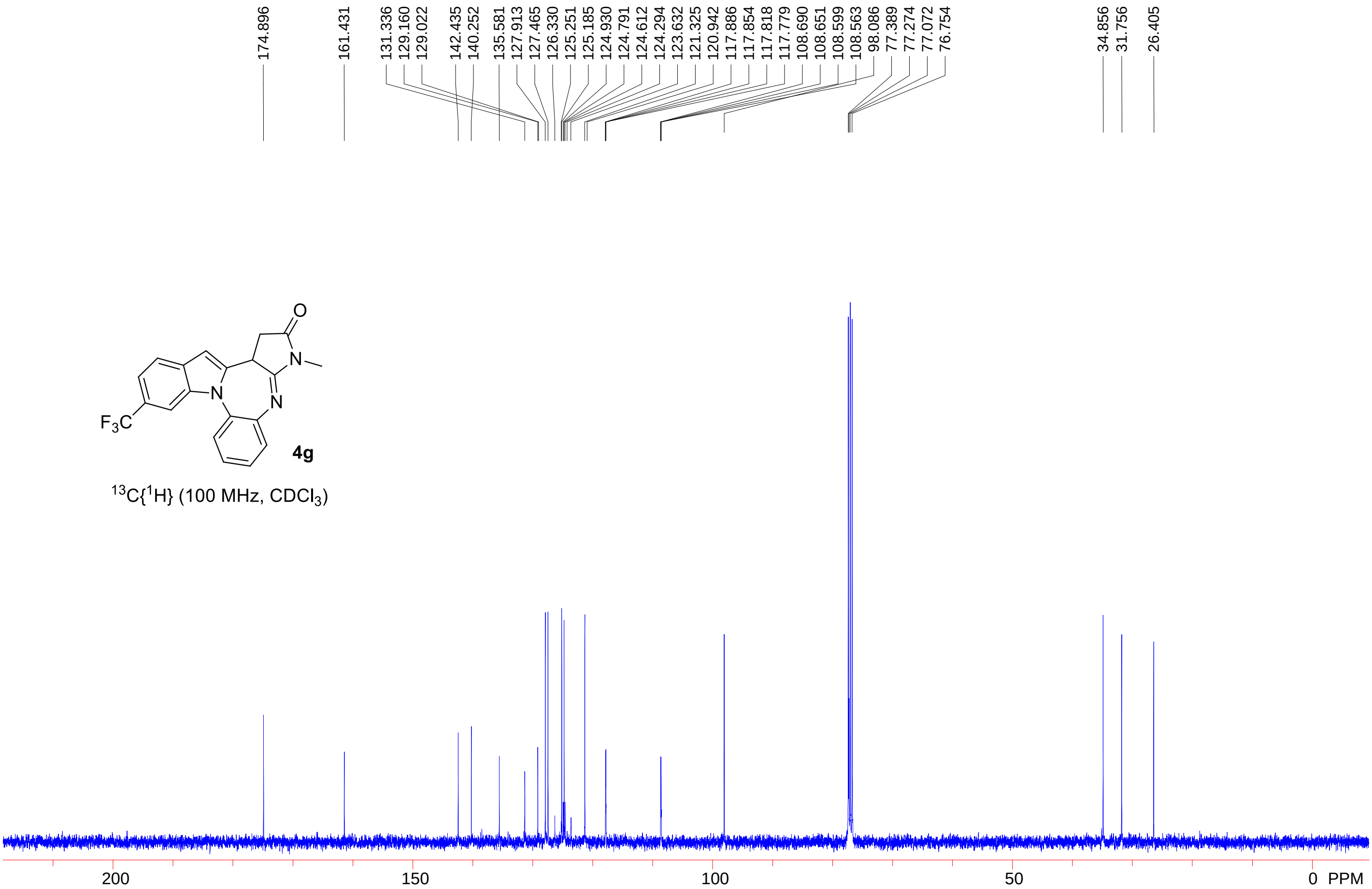

7.713
7.694
7.602
7.515
7.494
7.426
7.423
7.407
7.403
7.391
7.373
7.354
7.309
7.305
7.289
7.271
7.268
7.246
7.136
7.133
7.115
7.112
6.338
3.987
3.969
3.172
3.165
3.126
3.118
3.108
3.094
3.072
3.048
3.026
-0.000
O
N
N
N
Cl
4e
^{1}H NMR (400 MHz, $CDCl_3$)
5.03
2.05
0.98
0.94
1.03
1.05
1.02
1.00
0.98
10
8
6
4
2
0
PPM

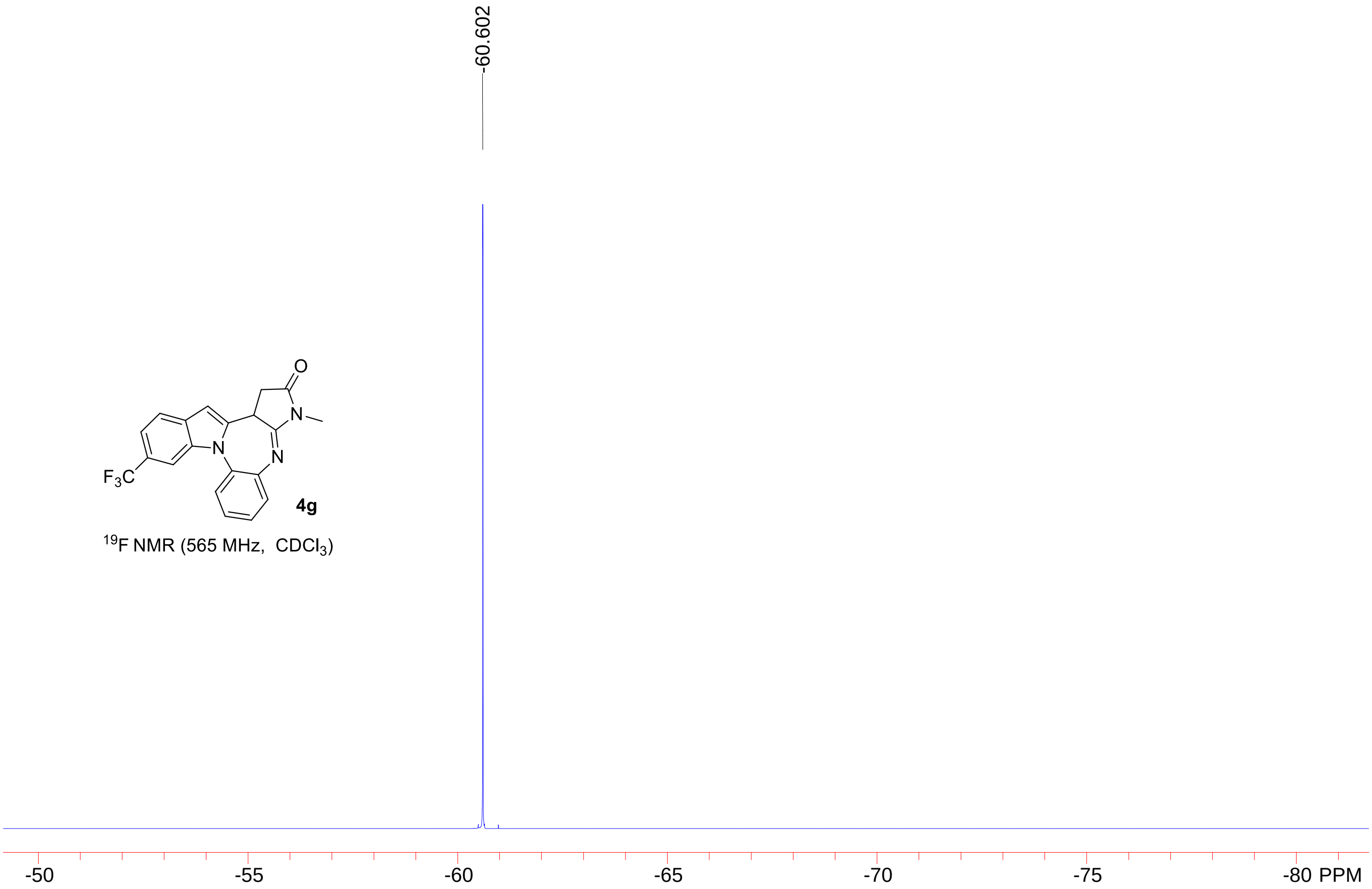

175.025
161.597
140.652
140.191
136.888
129.364
128.609
127.845
127.417
127.230
125.025
124.755
121.835
121.738
111.113
97.987
77.438
77.120
76.803
34.750
31.794
26.368
O
N
N
N
Cl
4e
$^{13}C\{^1H\}$ (100 MHz, $CDCl_3$)
200
150
100
50
0
PPM


7.765 7.723 7.721 7.710 7.708 7.477 7.463 7.426 7.424 7.413 7.410 7.396 7.393 7.383 7.382 7.370 7.368 7.317 7.314 7.303 7.302 7.292 7.289 7.275 7.273 7.261 7.259 7.252 6.348 4.000 3.998 3.987 3.985 3.983 3.175 3.171 3.145 3.140 3.117 3.106 3.091 3.075 3.060 -0.000
O
N
N
N
Br
4f
1H NMR (600 MHz, CDCl3)
0.99 1.02 1.03 1.01 1.00 1.03 1.04 1.00 1.02 2.91 1.19 1.06
10
8
6
4
2
0
PPM

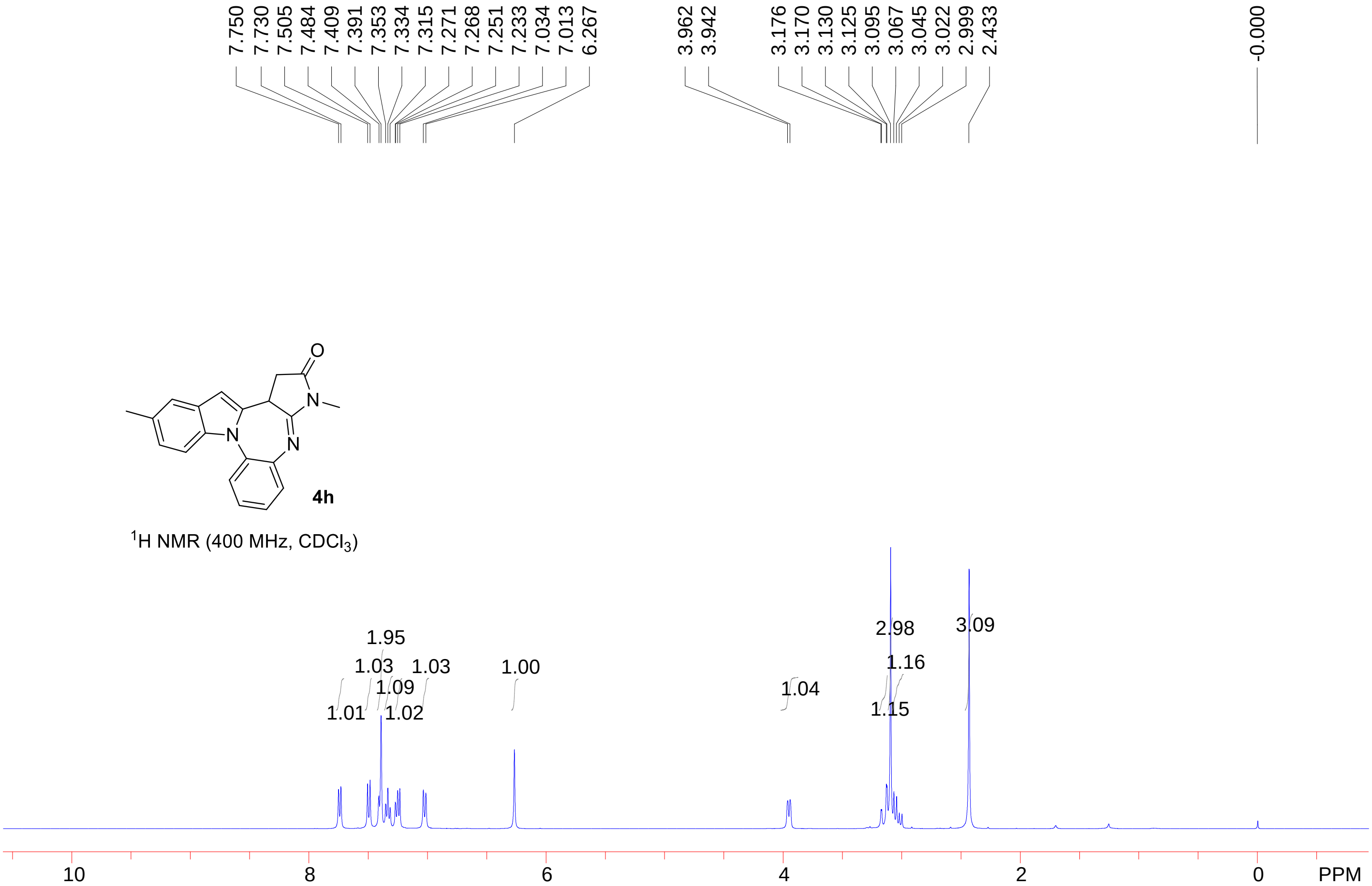

175.004 161.549 140.549 140.194 137.275 129.329 127.830 127.745 127.251 125.044 124.797 124.445 122.098 116.209 114.022 98.021 77.297 77.086 76.874 34.743 31.798 26.387
O
N
N
N
Br
4f
13C{1H} (150 MHz, CDCl3)
200
150
100
50
0
PPM

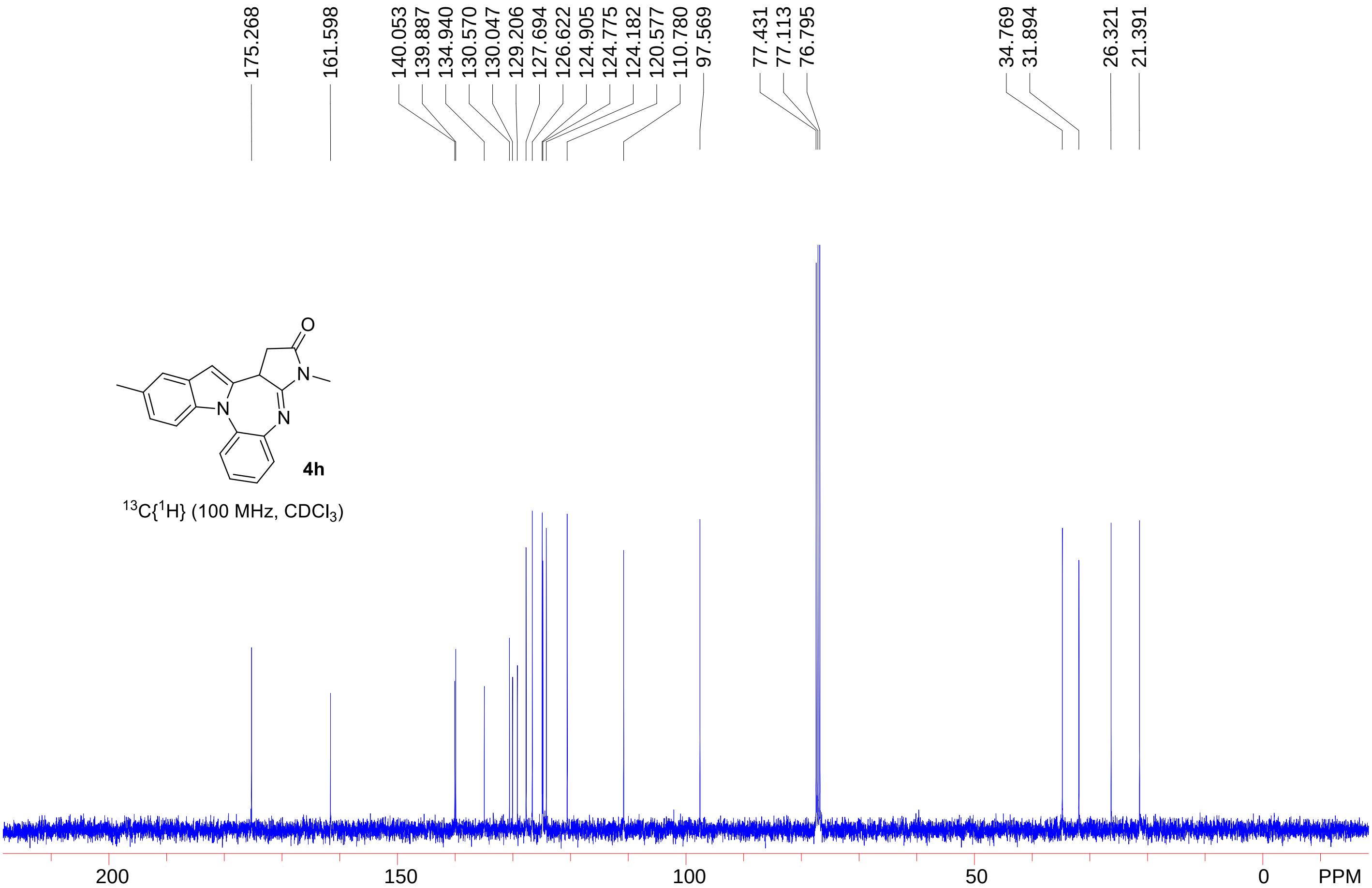

7.887 7.743 7.730 7.711 7.698 7.454 7.442 7.417 7.405 7.347 7.336 7.249 6.452
4.058 4.045
3.217 3.187 3.126 3.097
-0.000
O
N
N
N
F3C
4g
1H NMR (600 MHz, CDCl3)
5.08
3.00
1.00
1.02
1.04
1.09
1.00
1.00
8
6
4
2
0
PPM

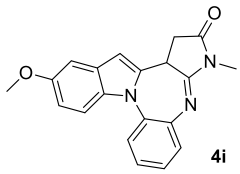

174.896
161.431
131.336 129.160 129.022
142.435 140.252 135.581 127.913 127.465 126.330 125.251 125.185 124.930 124.791 124.612 124.294 123.632 121.325 120.942 117.886 117.854 117.818 117.779 108.690 108.651 108.599 108.563 98.086 77.389 77.274 77.072 76.754
34.856 31.756 26.405
O
N
N
N
F3C
4g
13C{1H} (100 MHz, CDCl3)
200
150
100
50
0 PPM



-60.602
O
N
N
N
F3C
4g
19F NMR (565 MHz, CDCl3)
-50
-55
-60
-65
-70
-75
-80 PPM

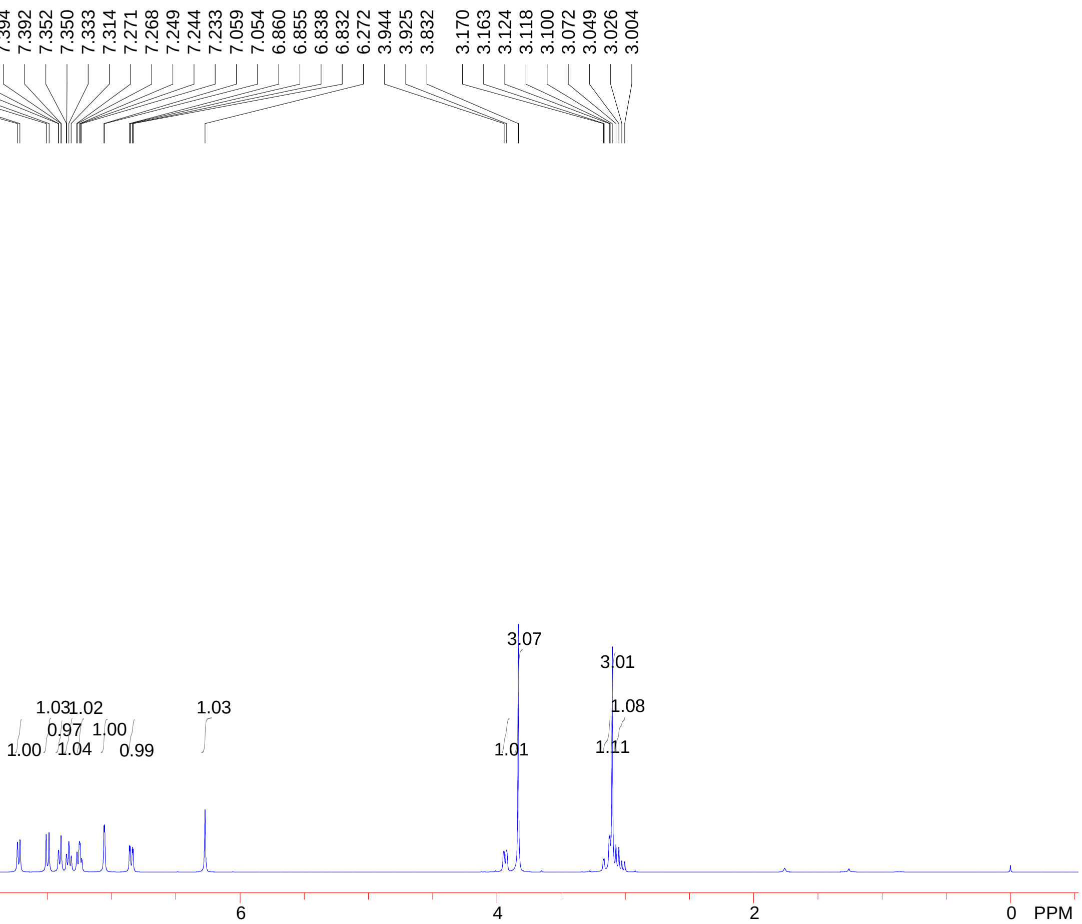

7.750
7.730
7.505
7.484
7.409
7.391
7.353
7.334
7.315
7.271
7.268
7.251
7.233
7.034
7.013
6.267
3.962
3.942
3.176
3.170
3.130
3.125
3.095
3.067
3.045
3.022
2.999
2.433
-0.000
4h
1H NMR (400 MHz, CDCl3)
1.95
1.03
1.03
1.00
1.09
1.01
1.02
1.04
2.98
3.09
1.16
1.15
10
8
6
4
2
0
PPM

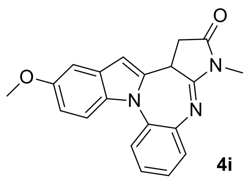

175.268
161.598
140.053
139.887
134.940
130.570
130.047
129.206
127.694
126.622
124.905
124.775
124.182
120.577
110.780
97.569
77.431
77.113
76.795
34.769
31.894
26.321
21.391
4h
13C{1H} (100 MHz, CDCl3)
200
150
100
50
0
PPM



4i

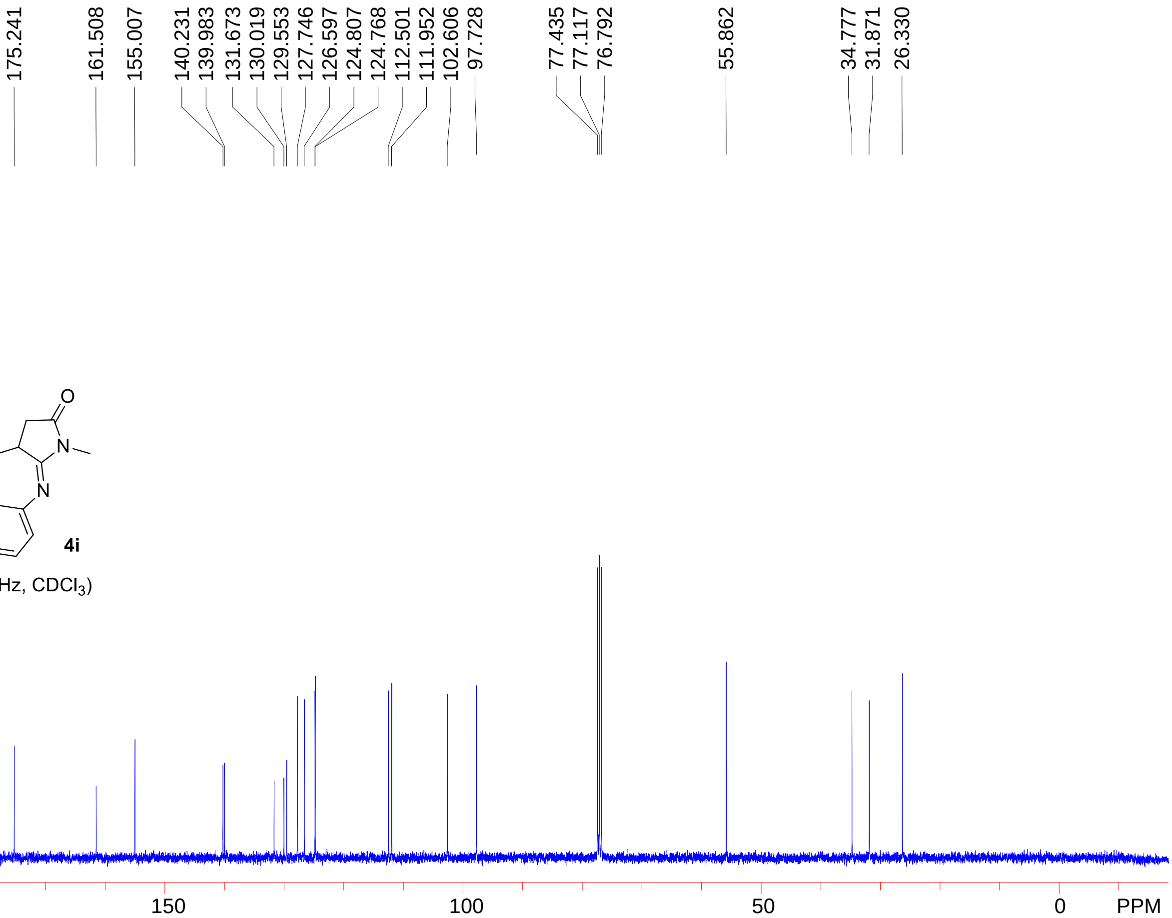
^1H NMR (400 MHz, $CDCl_3$)

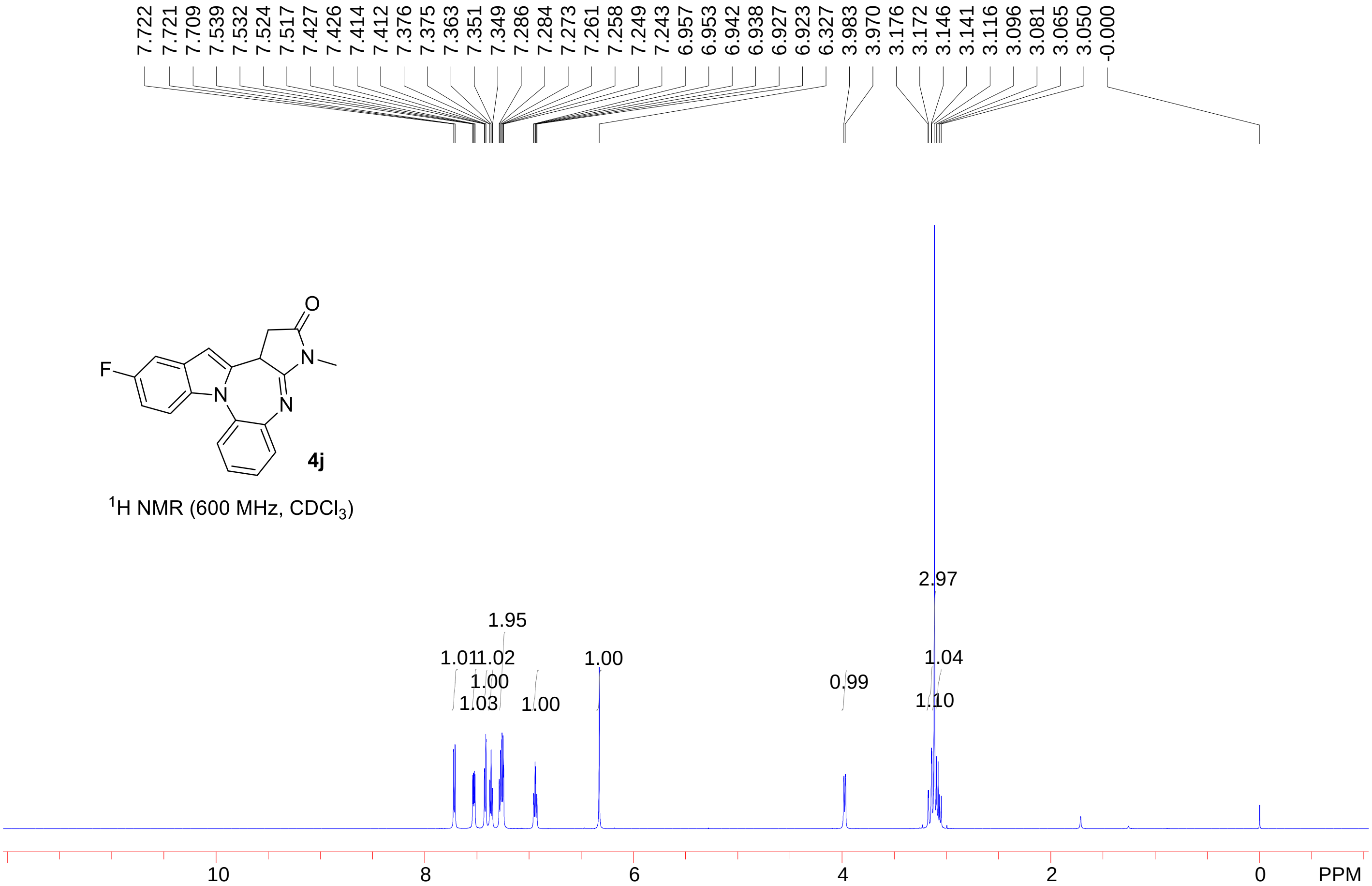


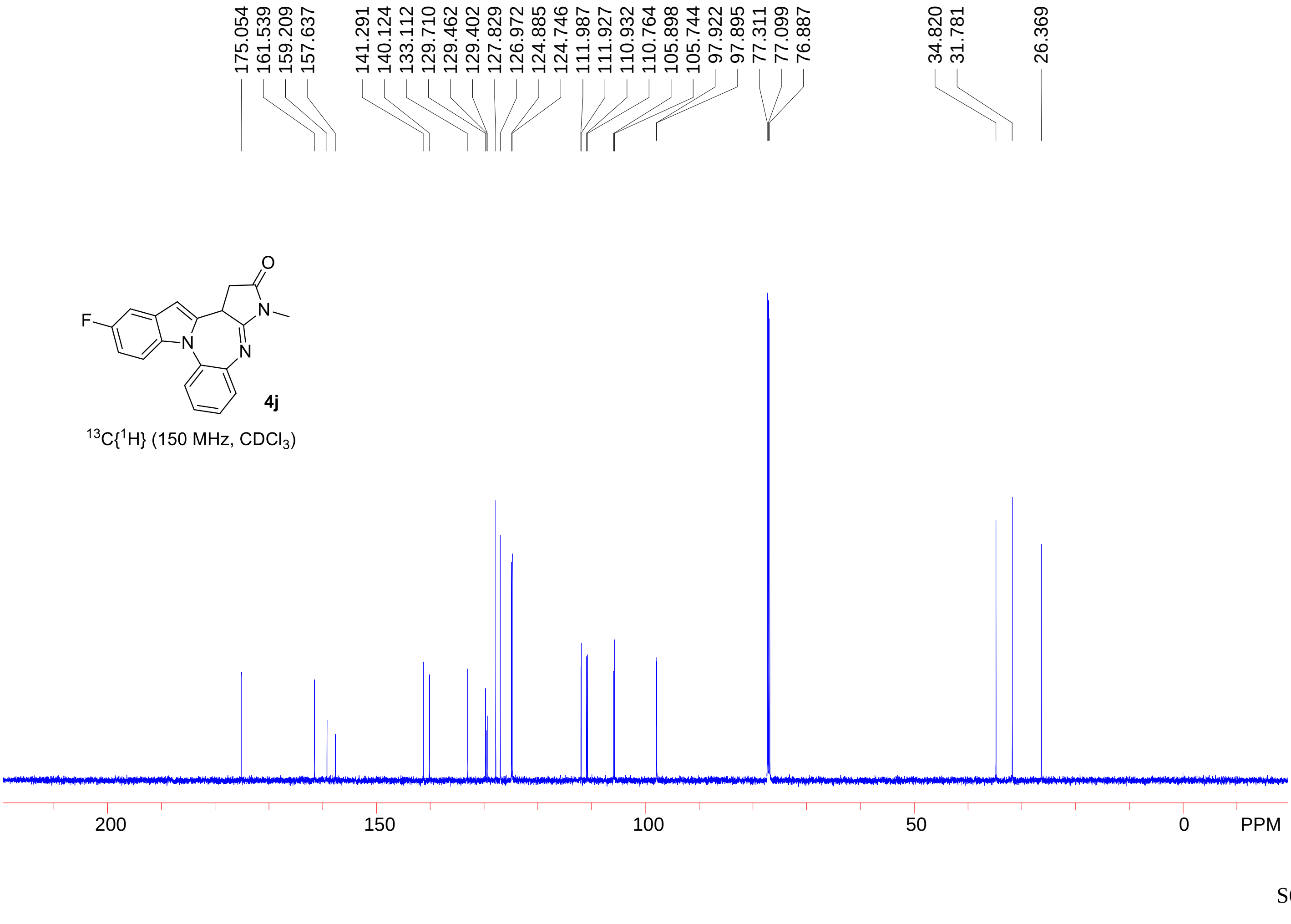


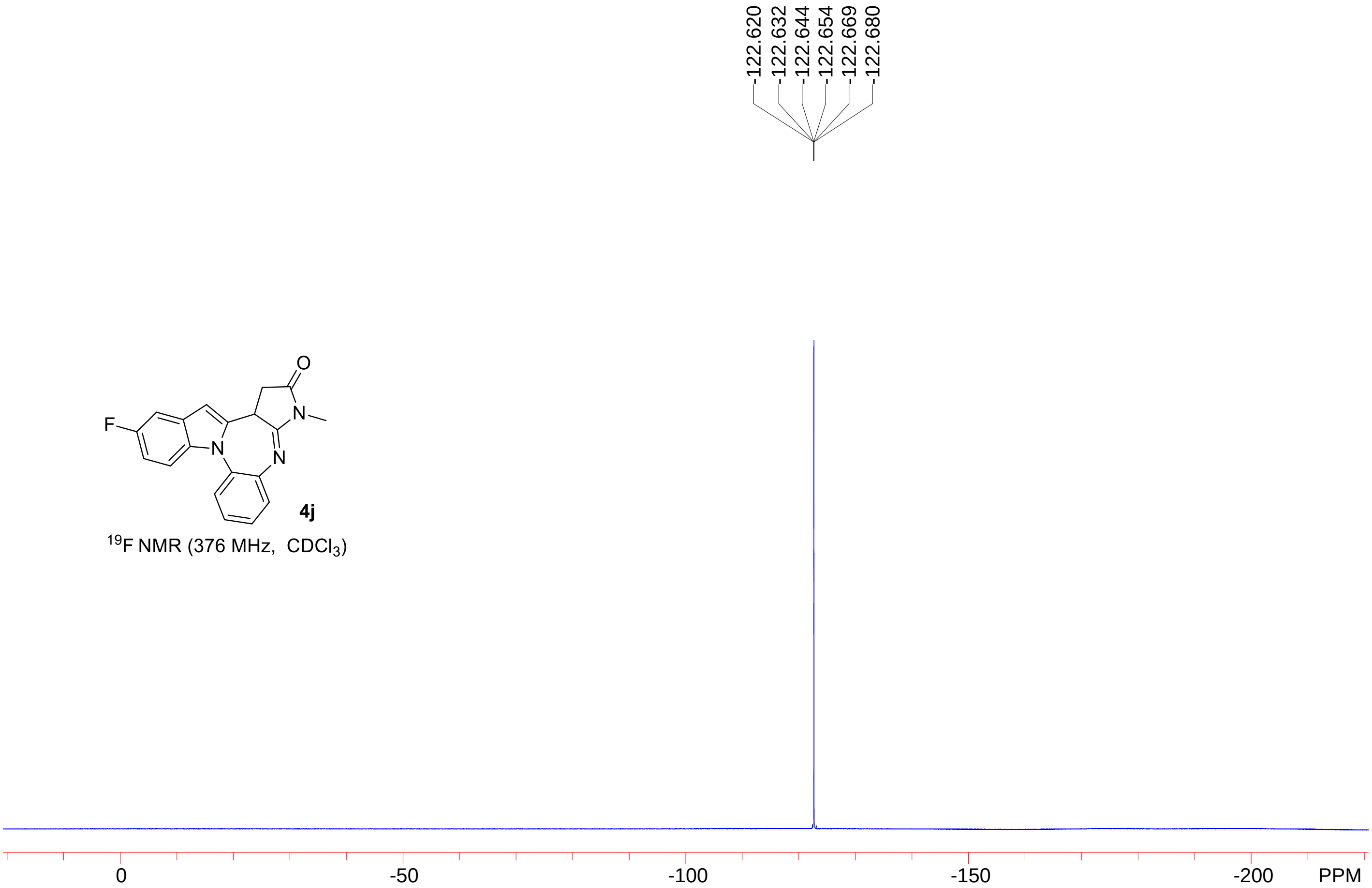
4i

$^{13}C\{^1H\}$ (100 MHz, $CDCl_3$)

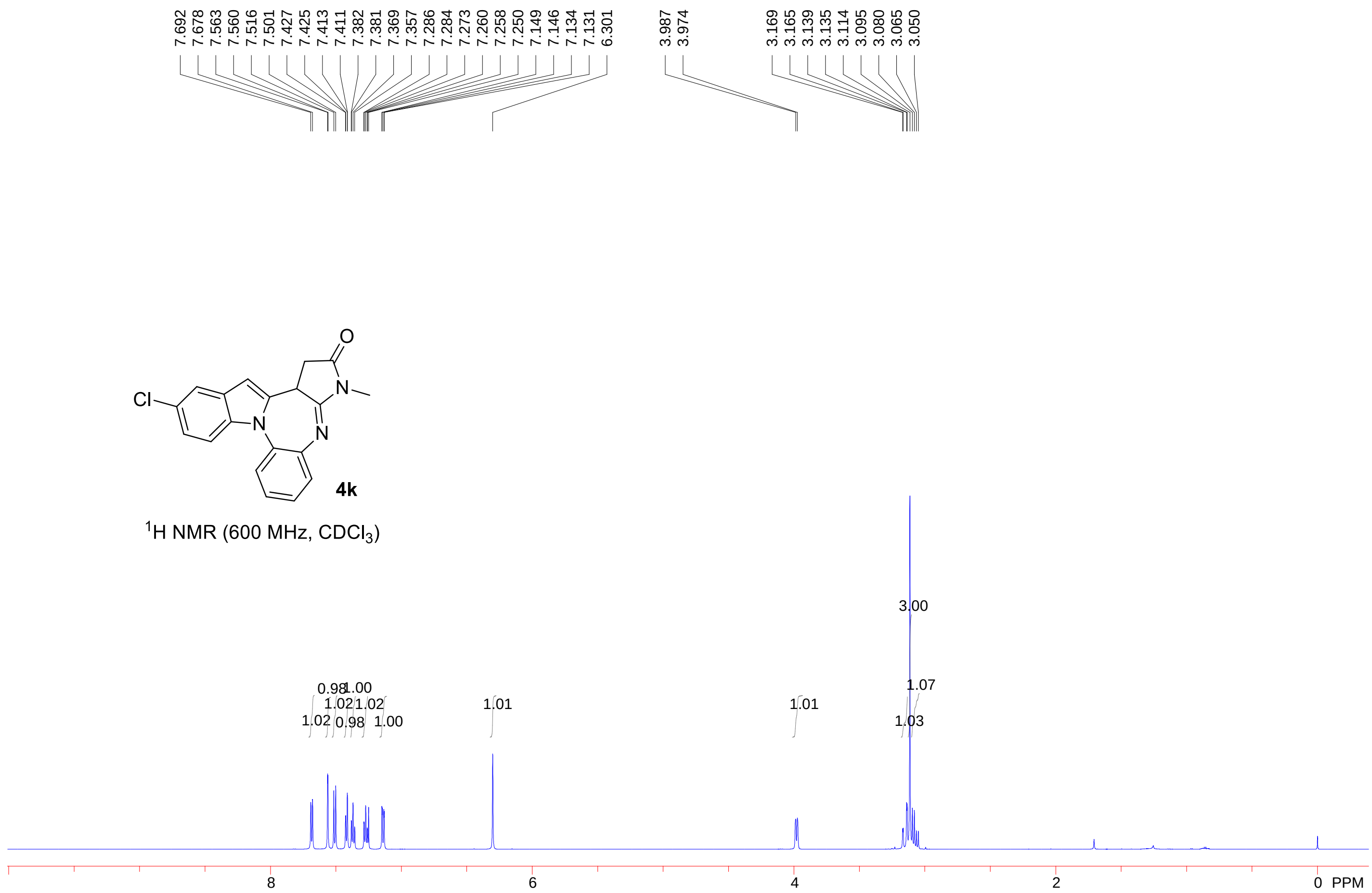


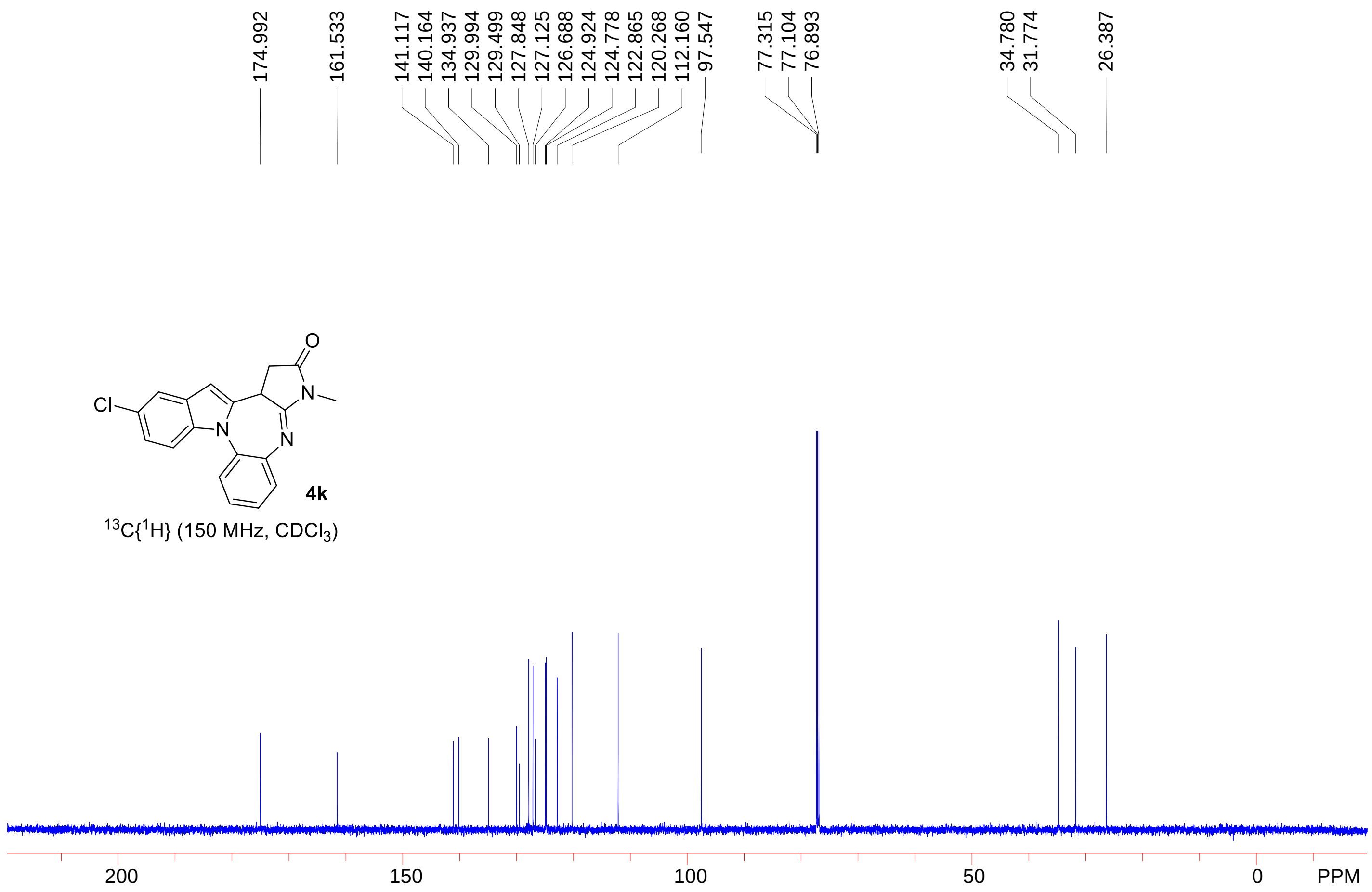

7.722
7.721
7.709
7.539
7.532
7.524
7.517
7.427
7.426
7.414
7.412
7.376
7.375
7.363
7.351
7.349
7.286
7.284
7.273
7.261
7.258
7.249
7.243
6.957
6.953
6.942
6.938
6.927
6.923
6.327
3.983
3.970
3.176
3.172
3.146
3.141
3.116
3.096
3.081
3.065
3.050
-0.000
F
O
N
N
N
4j
1H NMR (600 MHz, CDCl3)
2.97
1.95
1.01
1.02
1.00
1.03
1.00
1.00
0.99
1.04
1.10
10
8
6
4
2
0
PPM

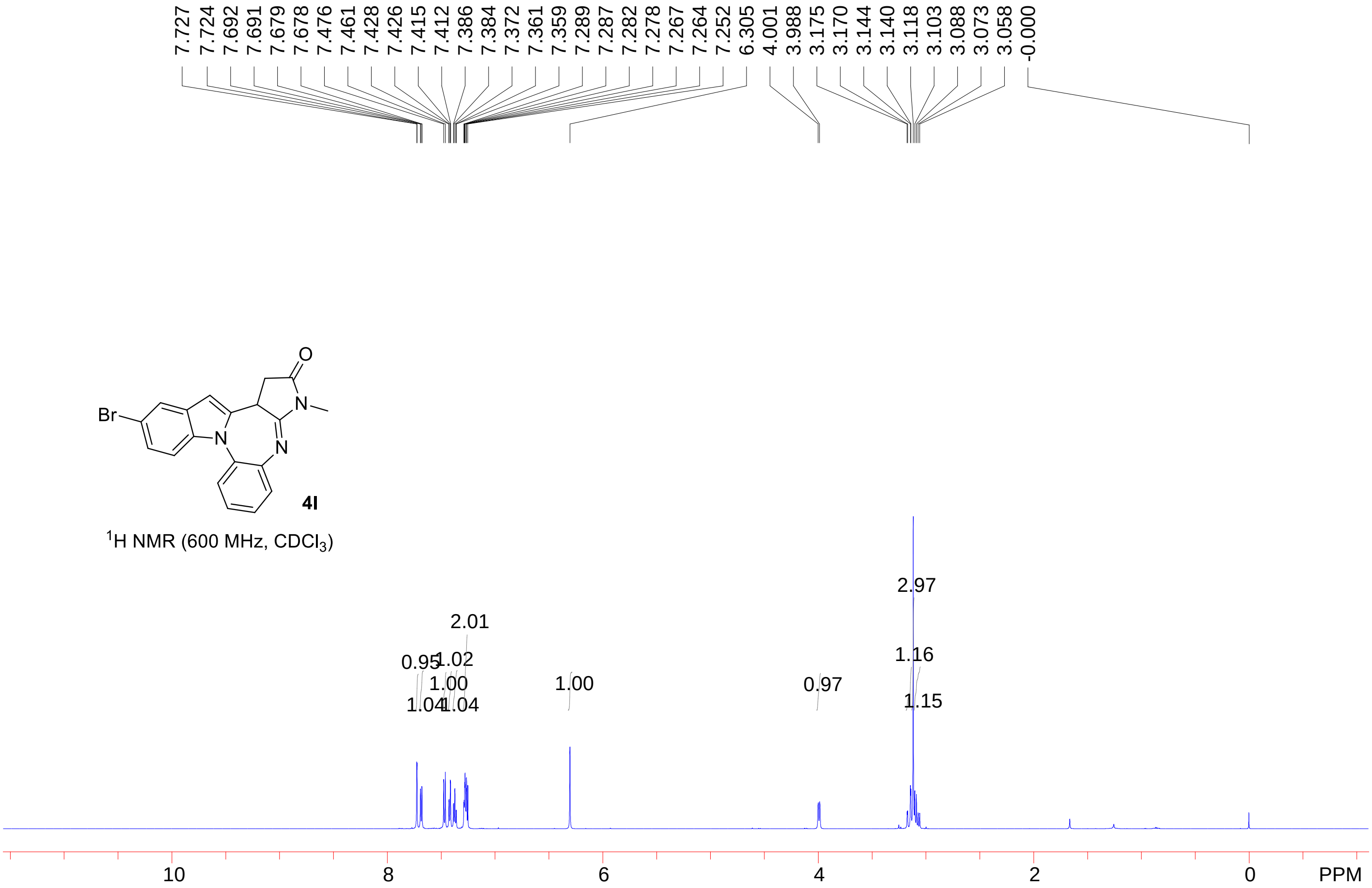

175.054
161.539
159.209
157.637
141.291
140.124
133.112
129.710
129.462
129.402
127.829
126.972
124.885
124.746
111.987
111.927
110.932
110.764
105.898
105.744
97.922
97.895
77.311
77.099
76.887
34.820
31.781
26.369
F
O
N
N
N
4j
13C{1H} (150 MHz, CDCl3)
200
150
100
50
0
PPM



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

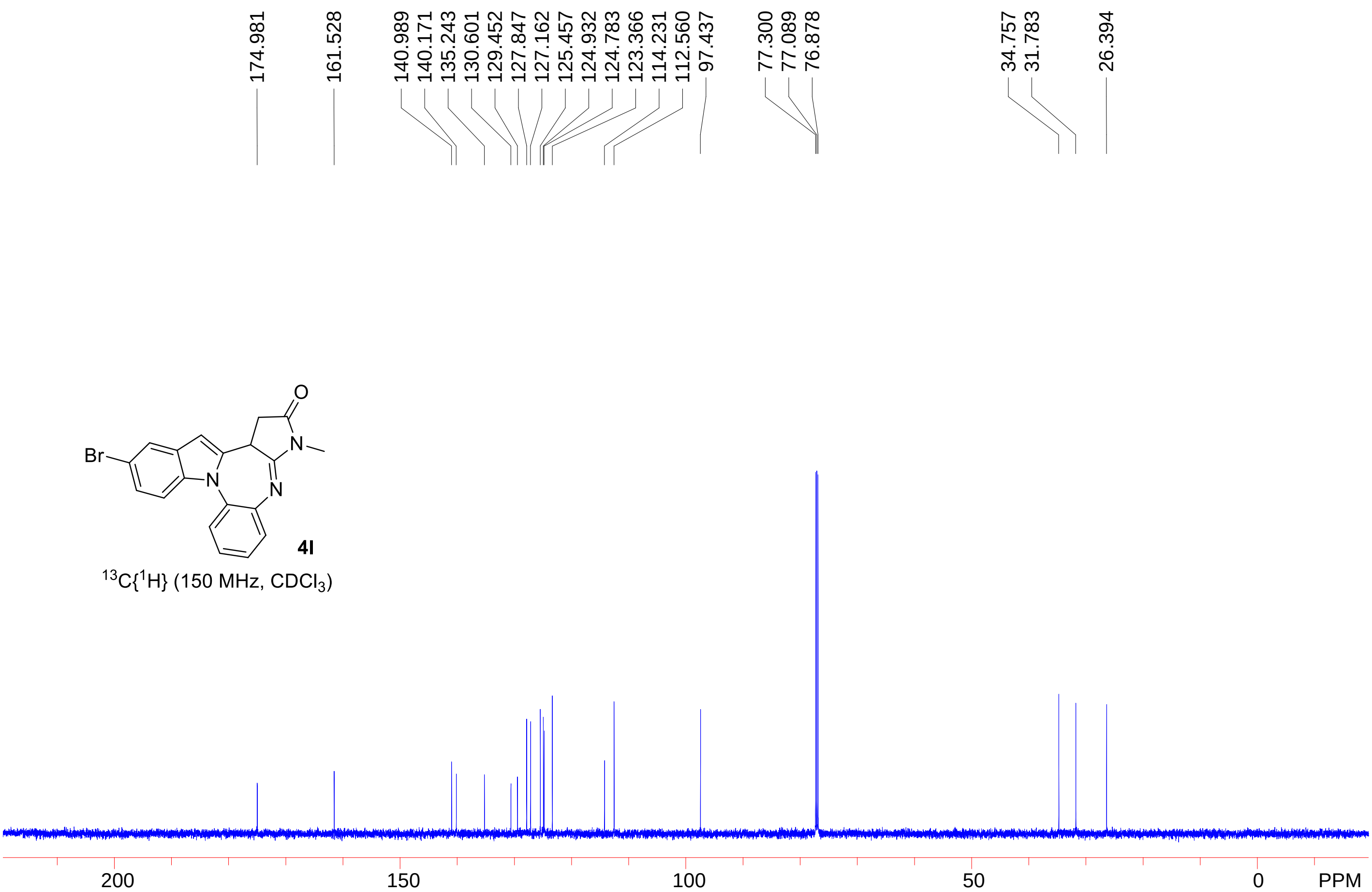

7.692 7.678 7.563 7.560 7.516 7.501 7.427 7.425 7.413 7.411 7.382 7.381 7.369 7.357 7.286 7.284 7.273 7.260 7.258 7.250 7.149 7.146 7.134 7.131 6.301
3.987 3.974
3.169 3.165 3.139 3.135 3.114 3.095 3.080 3.065 3.050
Cl
O
N
N
N
4k
^{1}H NMR (600 MHz, CDCl$_3$)
3.00
0.98 1.00
1.02 1.02
1.02 0.98 1.00
1.01
1.01
1.07
1.03
8
6
4
2
0 PPM


174.992
161.533
141.117 140.164 134.937 129.994 129.499 127.848 127.125 126.688 124.924 124.778 122.865 120.268 112.160 97.547
77.315 77.104 76.893
34.780 31.774
26.387
Cl
O
N
N
N
4k
^{13}C{^{1}H} (150 MHz, CDCl$_3$)
200
150
100
50
0
PPM



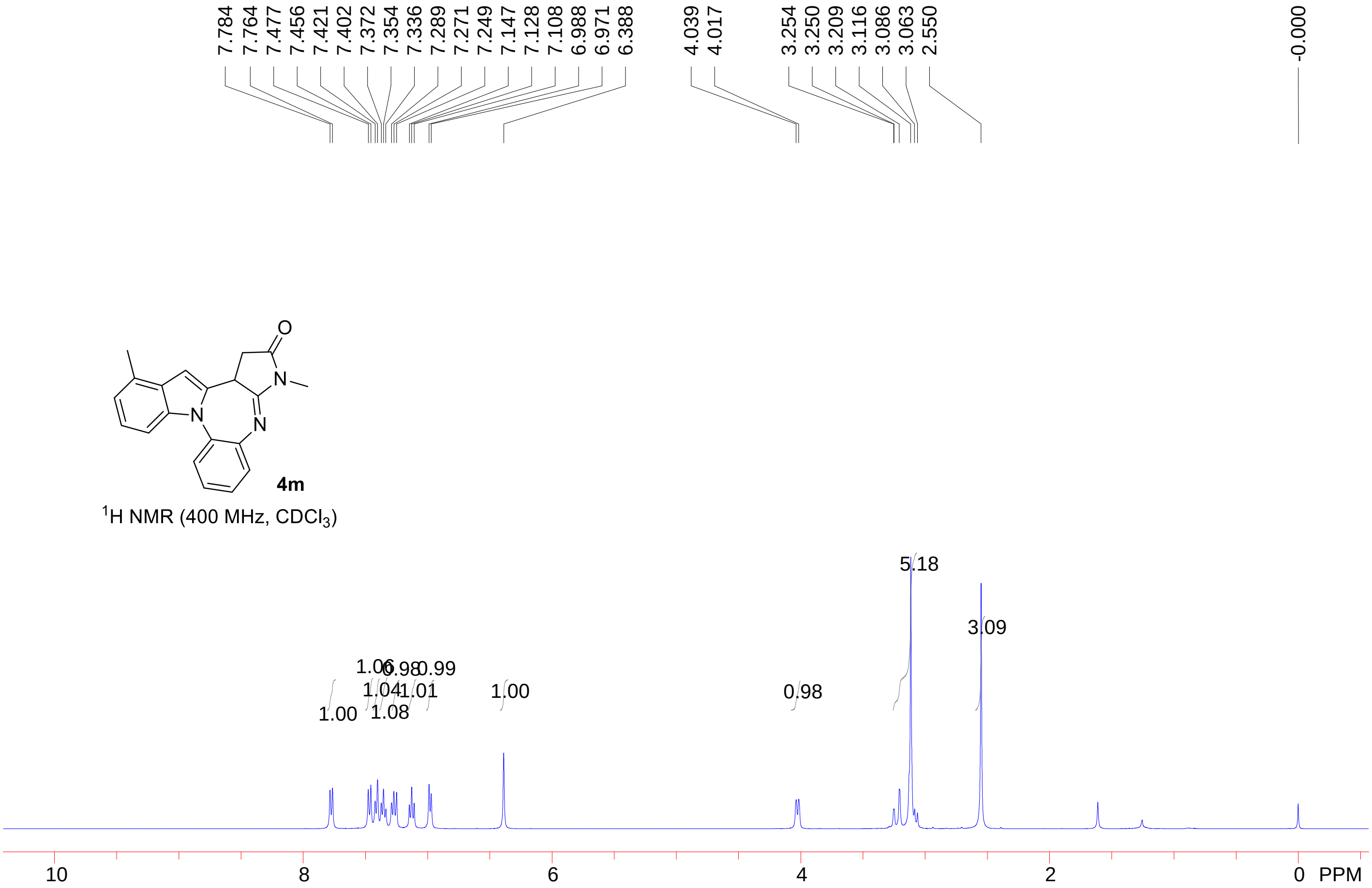
4l

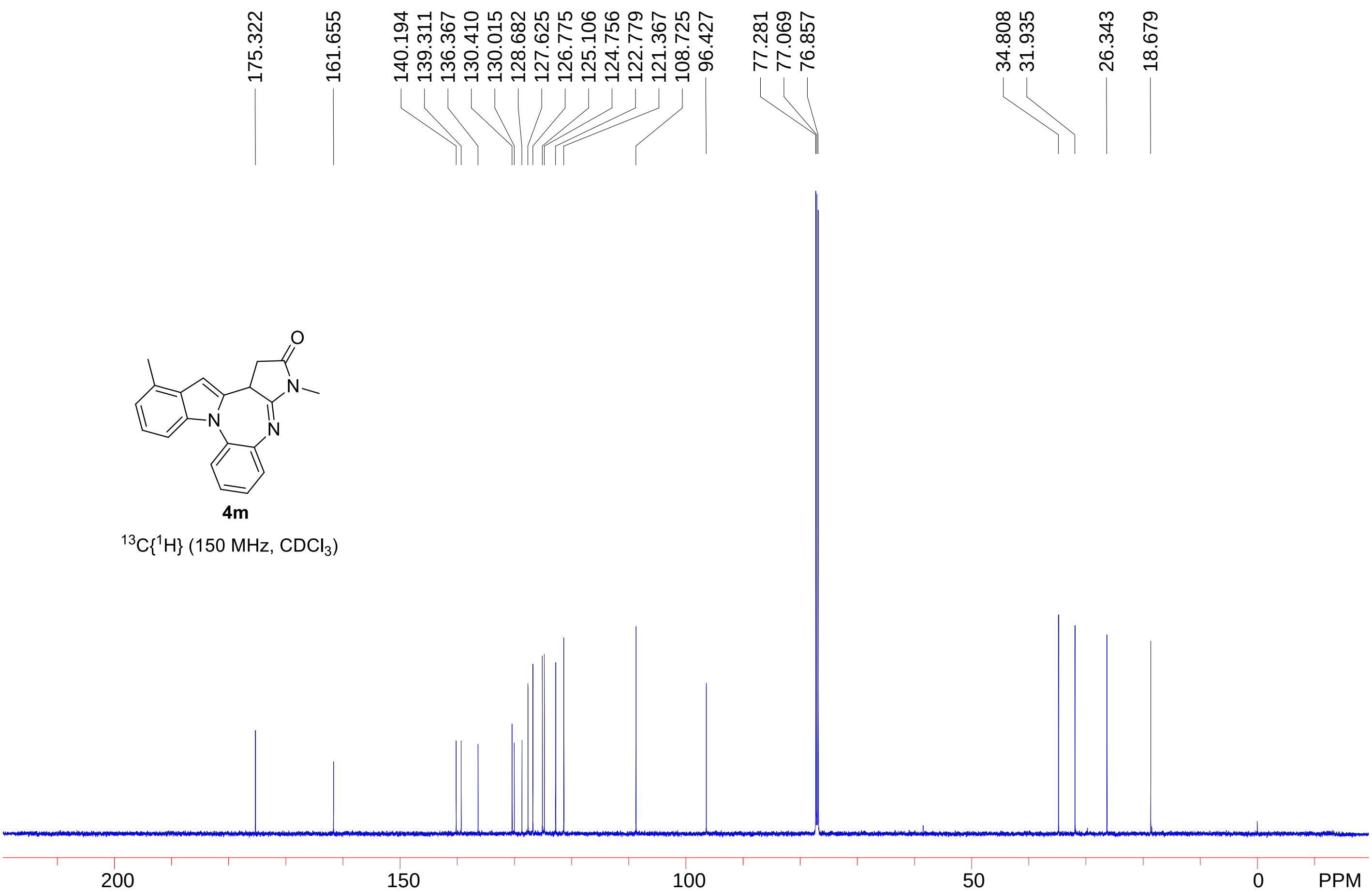
^{1}H NMR (600 MHz, $CDCl_3$)

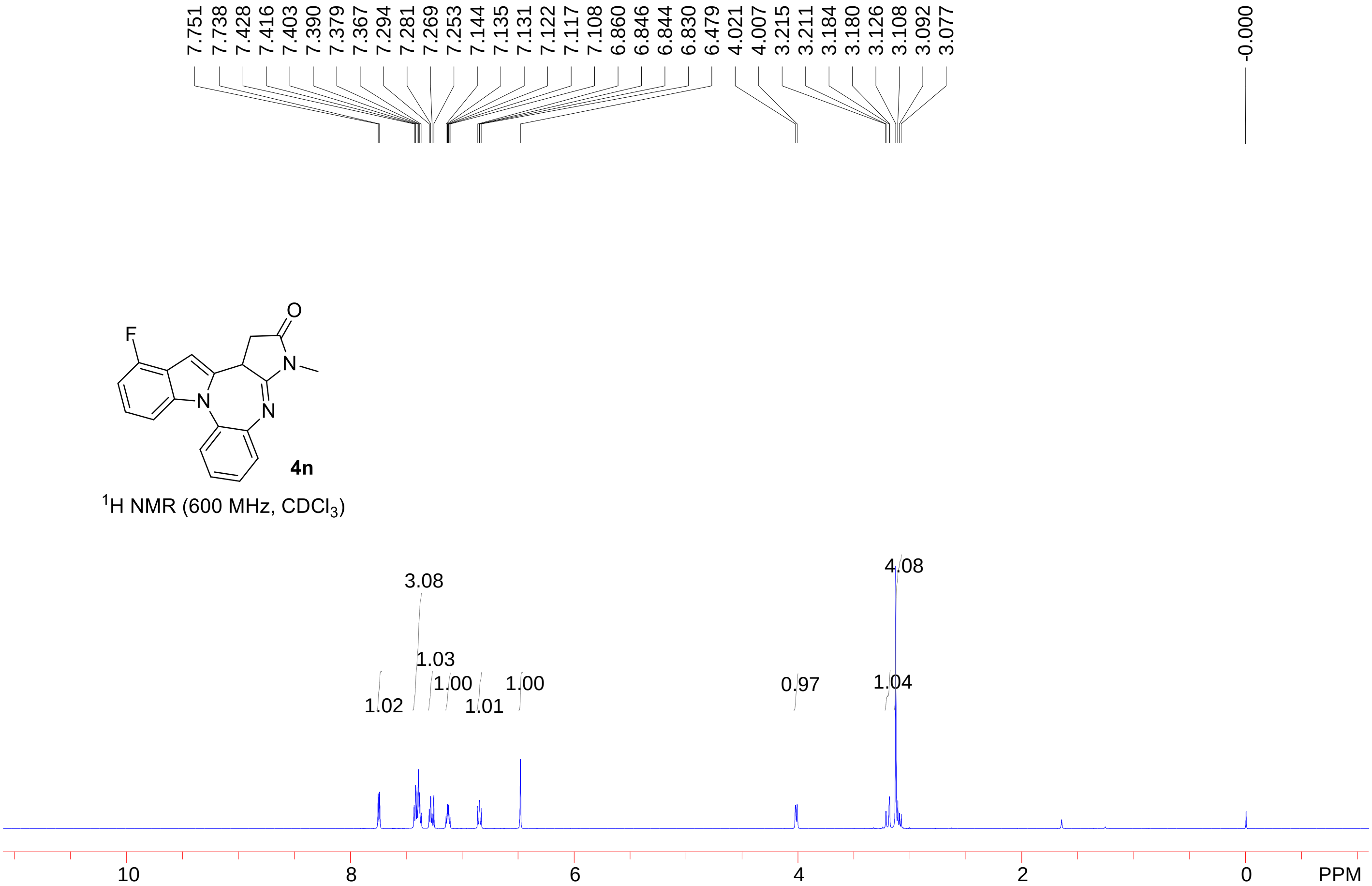


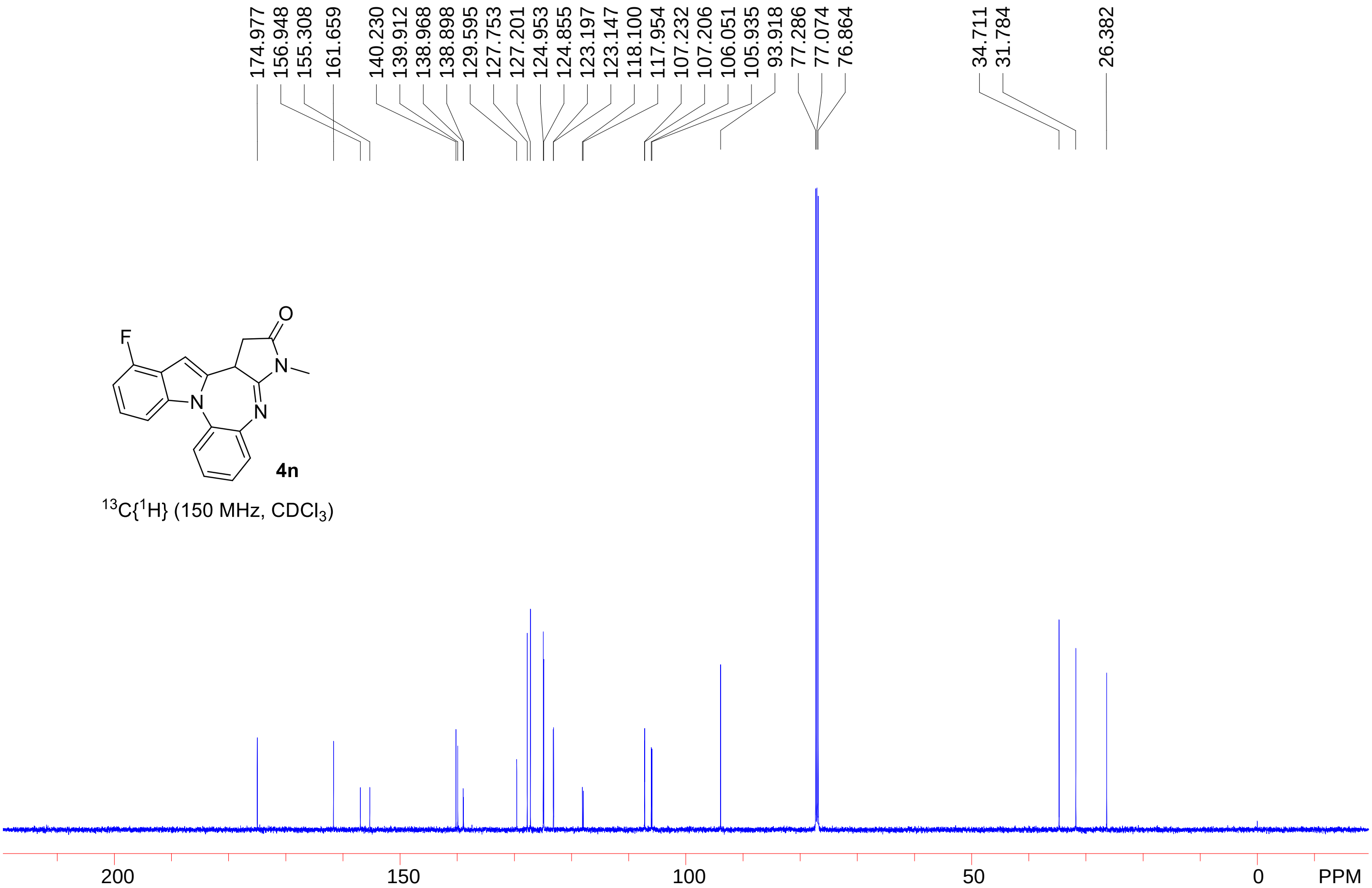
4l

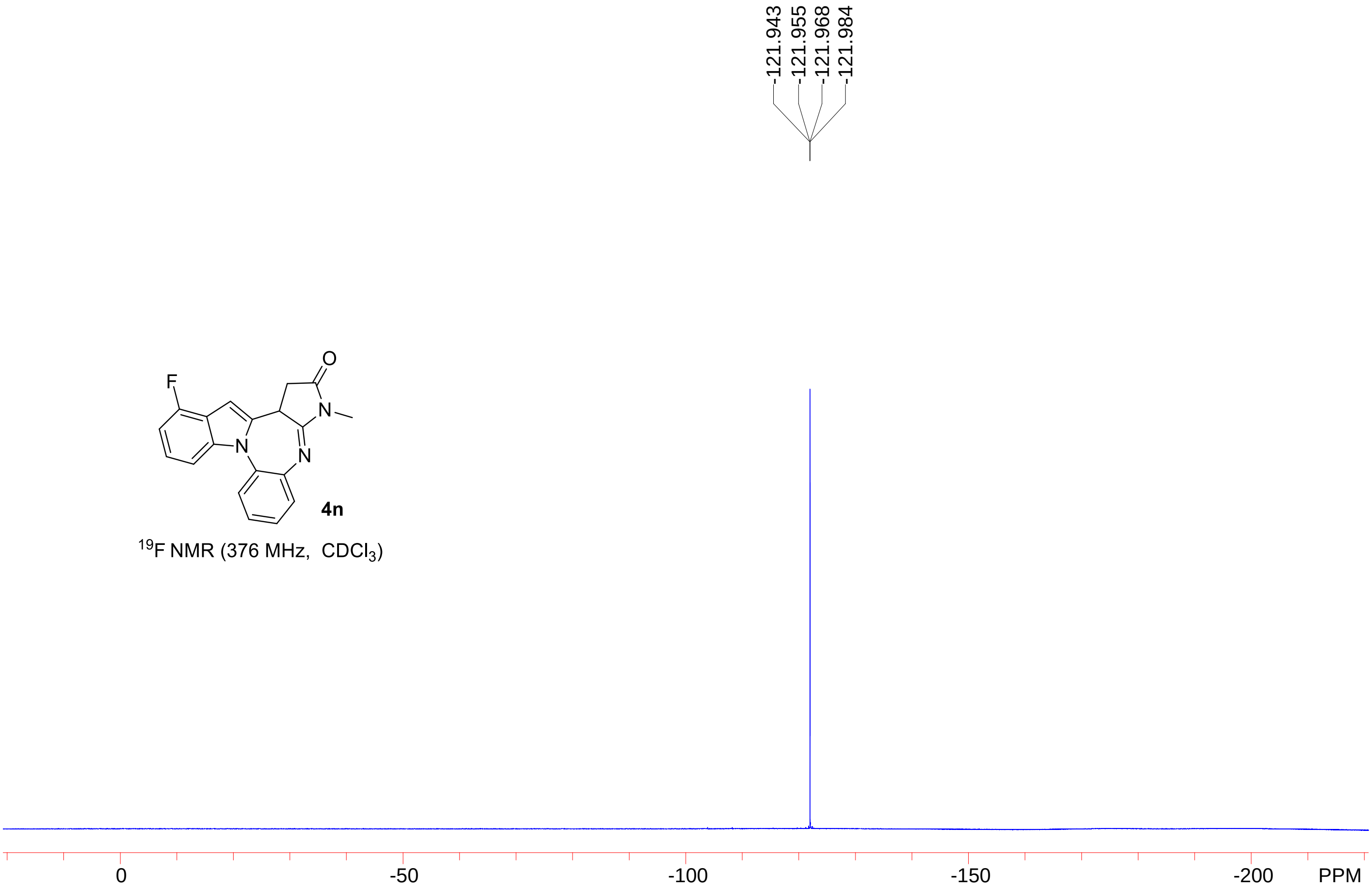
$^{13}C\{^{1}H\}$ (150 MHz, $CDCl_3$)

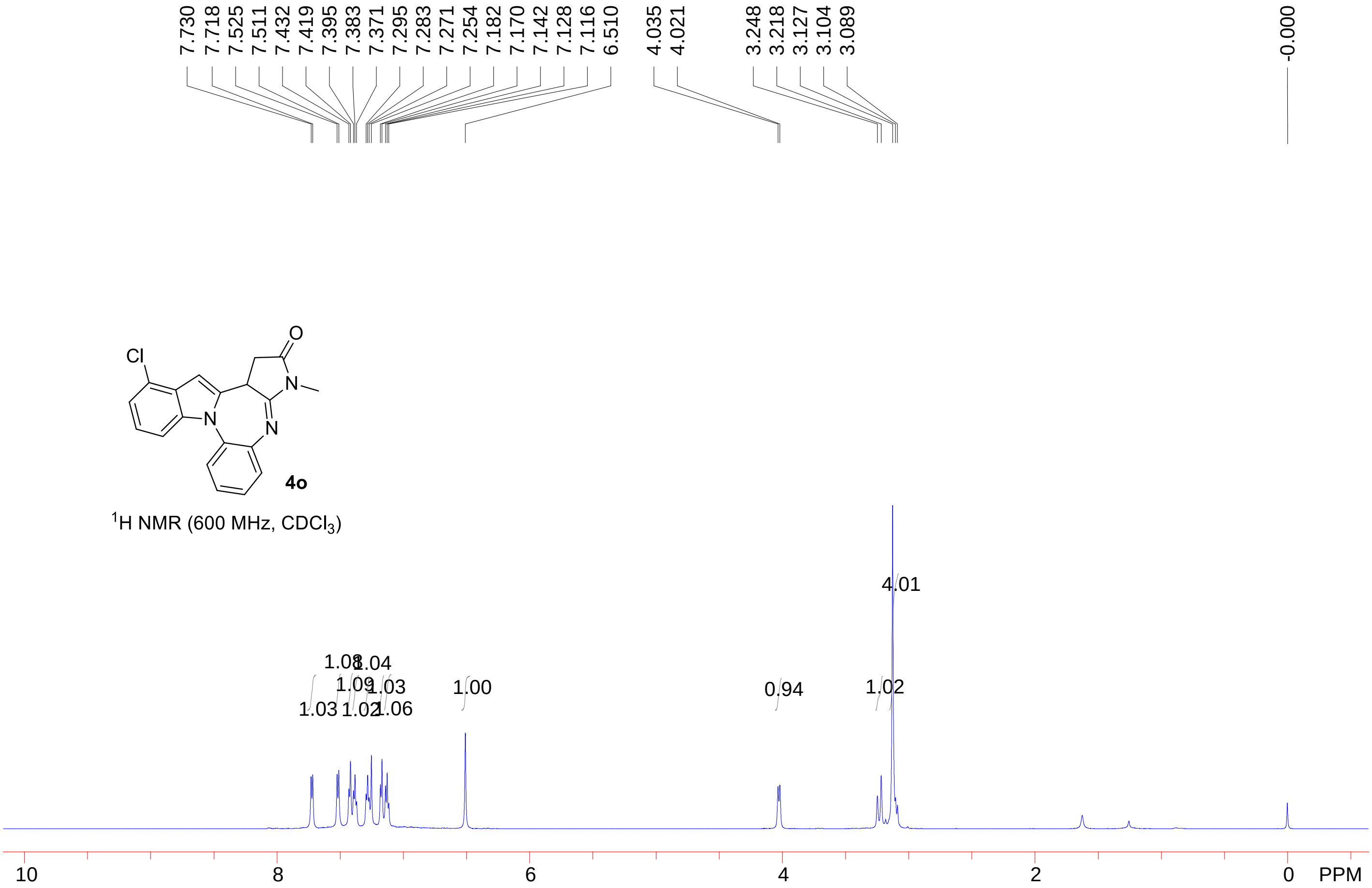

7.784
7.764
7.477
7.456
7.421
7.402
7.372
7.354
7.336
7.289
7.271
7.249
7.147
7.128
7.108
6.988
6.971
6.388
4.039
4.017
3.254
3.250
3.209
3.116
3.086
3.063
2.550
-0.000
4m
^{1}H NMR (400 MHz, CDCl$_3$)
5.18
3.09
1.06
0.98
0.99
1.04
1.01
1.00
1.08
1.00
0.98
10
8
6
4
2
0 PPM

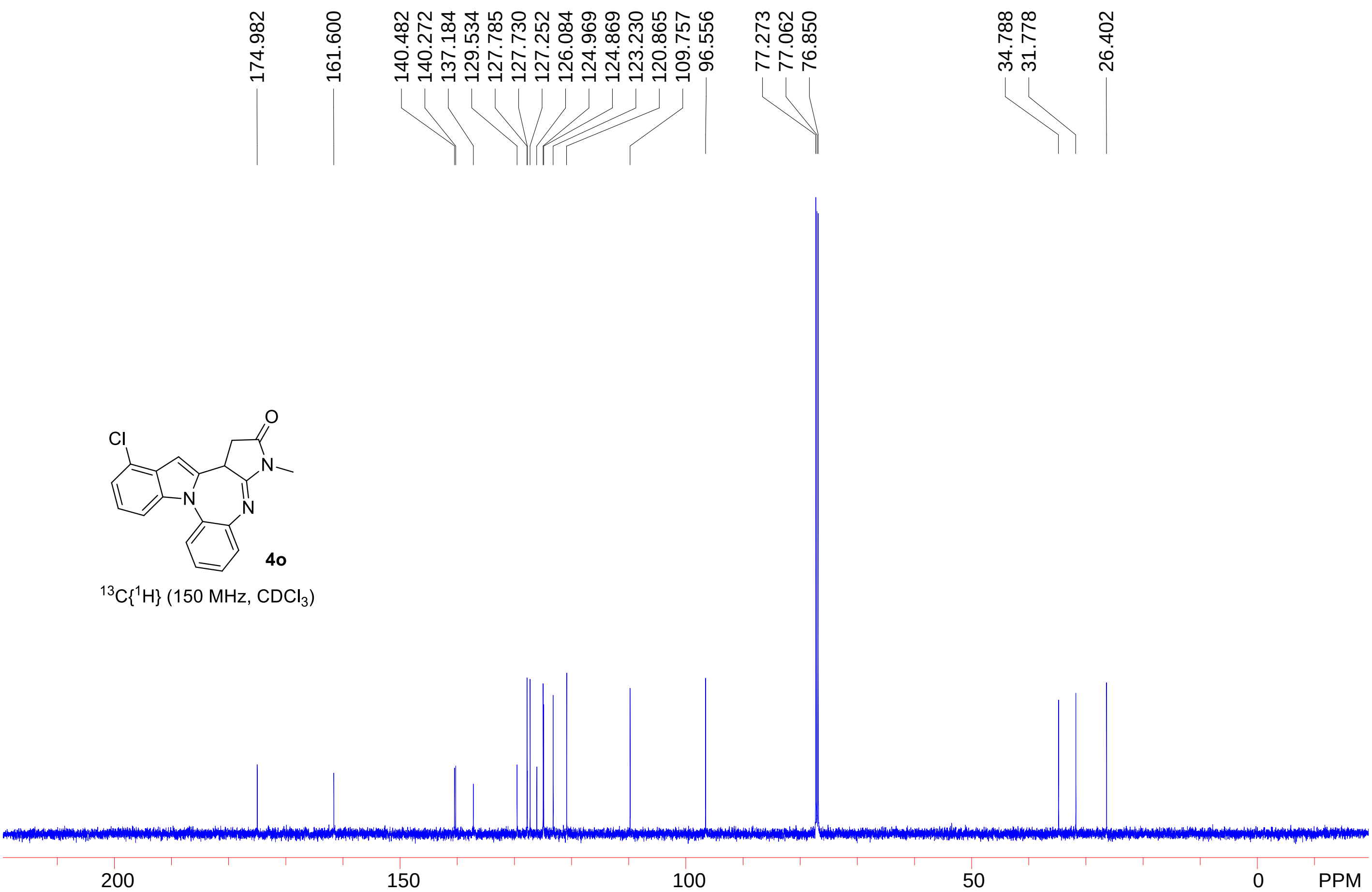

175.322
161.655
140.194
139.311
136.367
130.410
130.015
128.682
127.625
126.775
125.106
124.756
122.779
121.367
108.725
96.427
77.281
77.069
76.857
34.808
31.935
26.343
18.679
4m
^{13}C{^{1}H} (150 MHz, CDCl$_3$)
200
150
100
50
0
PPM

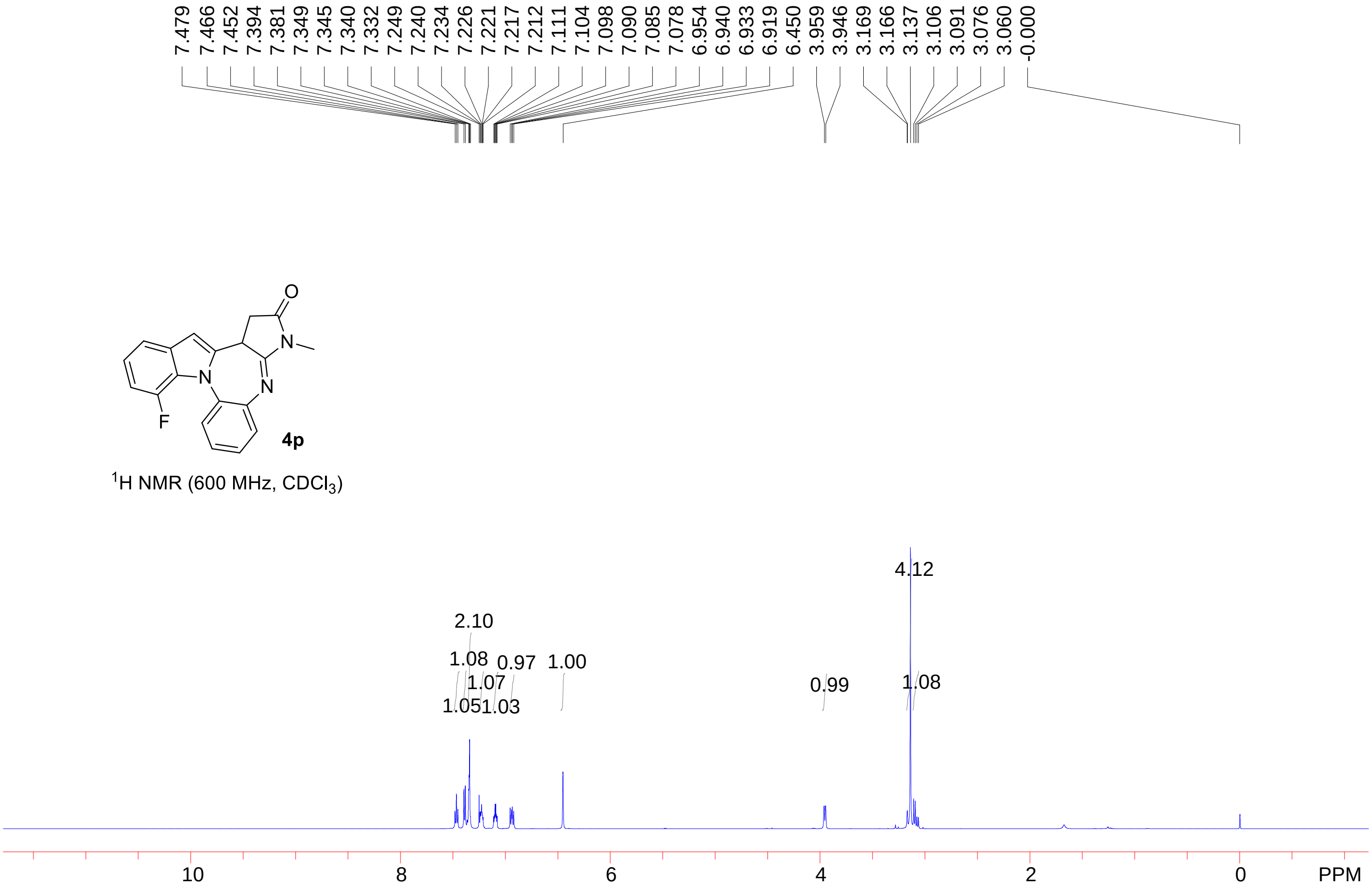

7.751 7.738 7.428 7.416 7.403 7.390 7.379 7.367 7.294 7.281 7.269 7.253 7.144 7.135 7.131 7.122 7.117 7.108 6.860 6.846 6.844 6.830 6.479 4.021 4.007 3.215 3.211 3.184 3.180 3.126 3.108 3.092 3.077
-0.000
F
O
N
N
N
4n
^{1}H NMR (600 MHz, $CDCl_3$)
3.08
4.08
1.03
1.00
1.00
1.02
1.01
0.97
1.04
10
8
6
4
2
0
PPM


174.977 156.948 155.308 161.659 140.230 139.912 138.968 138.898 129.595 127.753 127.201 124.953 124.855 123.197 123.147 118.100 117.954 107.232 107.206 106.051 105.935 93.918 77.286 77.074 76.864
34.711 31.784
26.382
F
O
N
N
N
4n
$^{13}C\{^1H\}$ (150 MHz, $CDCl_3$)
200
150
100
50
0
PPM

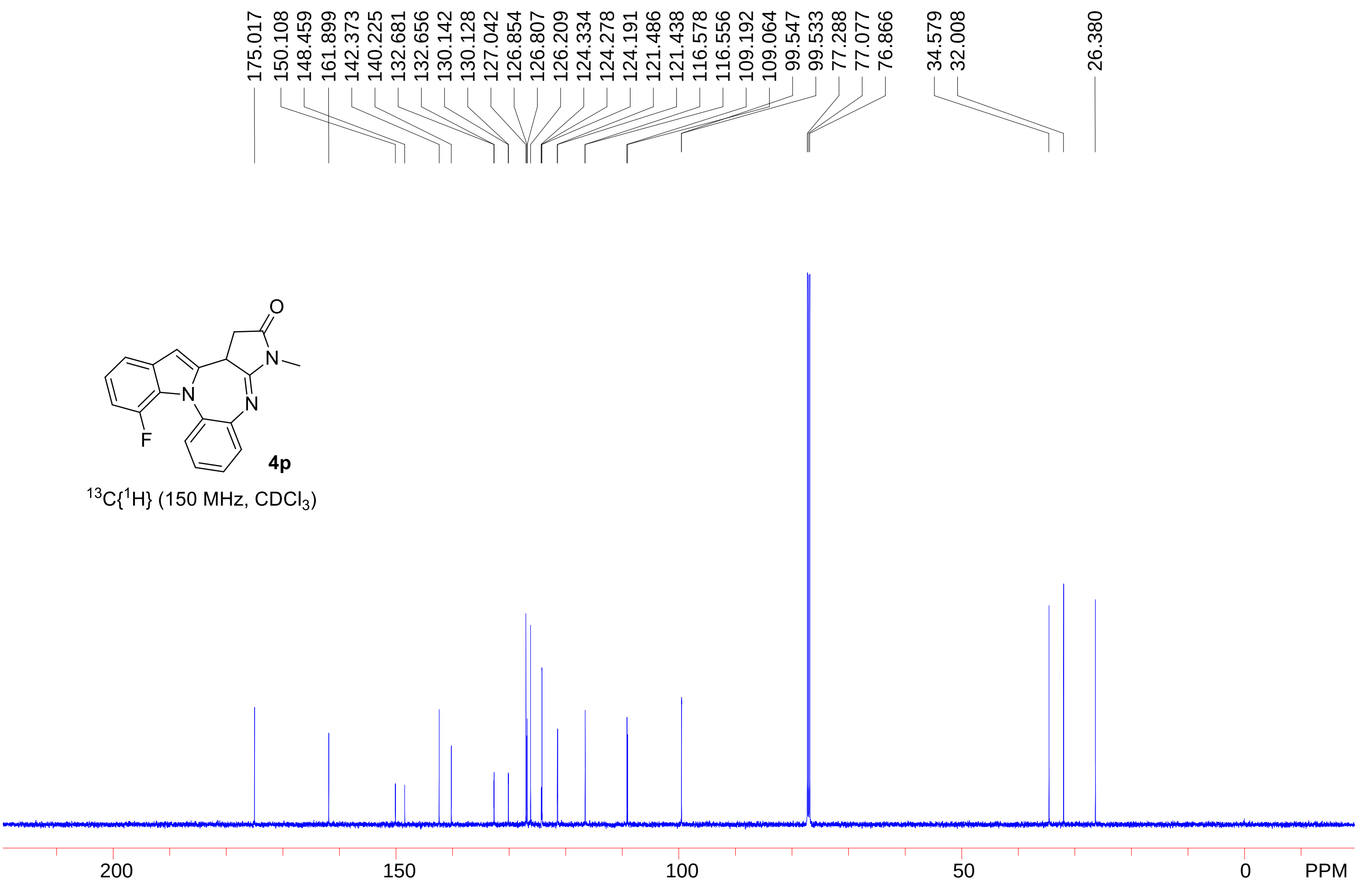

-121.943
-121.955
-121.968
-121.984
F
O
N
N
N
4n
19F NMR (376 MHz, CDCl3)
0
-50
-100
-150
-200
PPM


7.730
7.718
7.525
7.511
7.432
7.419
7.395
7.383
7.371
7.295
7.283
7.271
7.254
7.182
7.170
7.142
7.128
7.116
6.510
4.035
4.021
3.248
3.218
3.127
3.104
3.089
-0.000
Cl
O
N
N
N
4o
^{1}H NMR (600 MHz, $CDCl_3$)
4.01
1.08
1.04
1.09
1.03
1.03
1.02
1.06
1.00
0.94
1.02
10
8
6
4
2
0
PPM

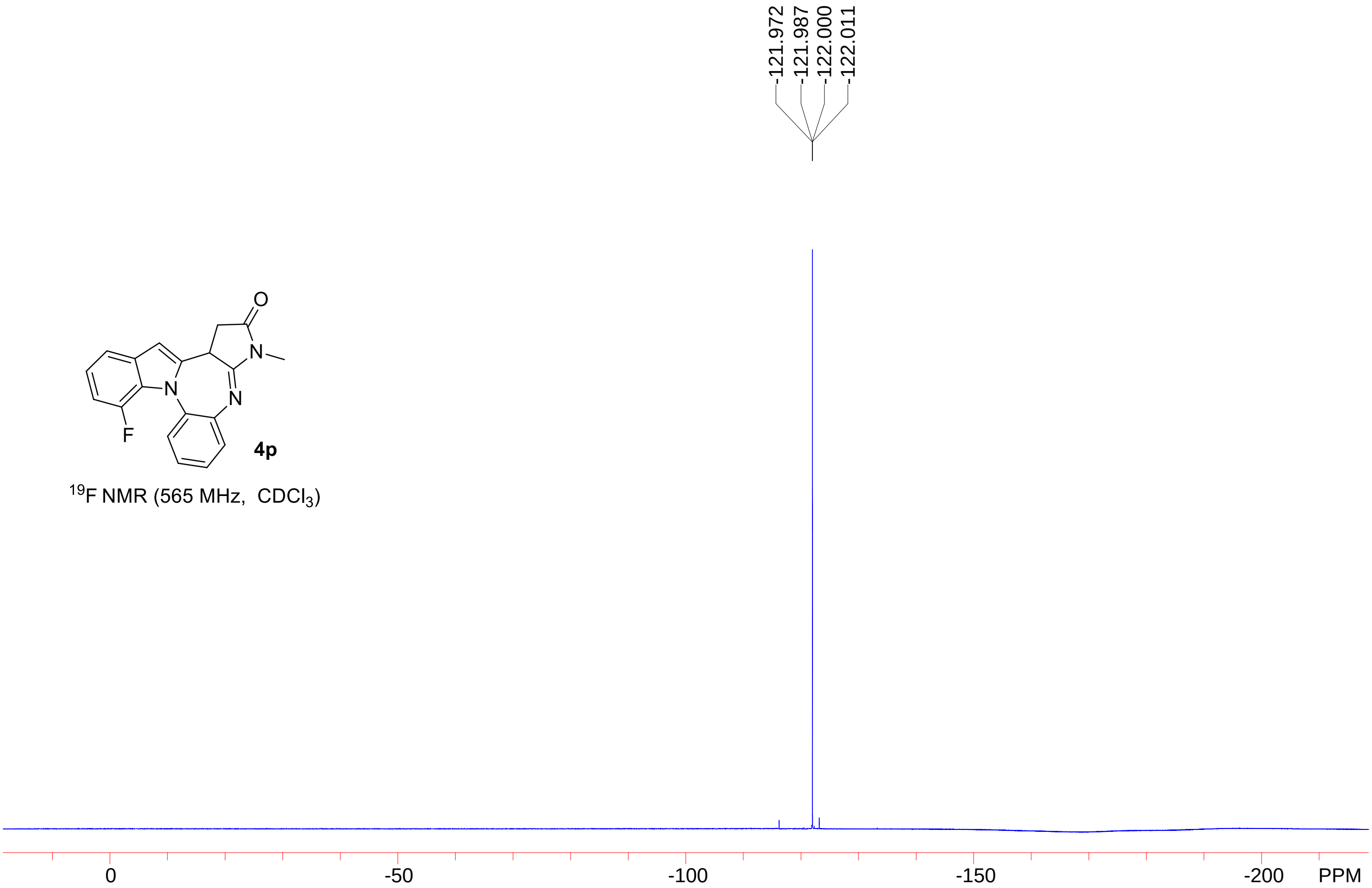

174.982
161.600
140.482
140.272
137.184
129.534
127.785
127.730
127.252
126.084
124.969
124.869
123.230
120.865
109.757
96.556
77.273
77.062
76.850
34.788
31.778
26.402
Cl
O
N
N
N
4o
^{13}C{^{1}H} (150 MHz, $CDCl_3$)
200
150
100
50
0
PPM



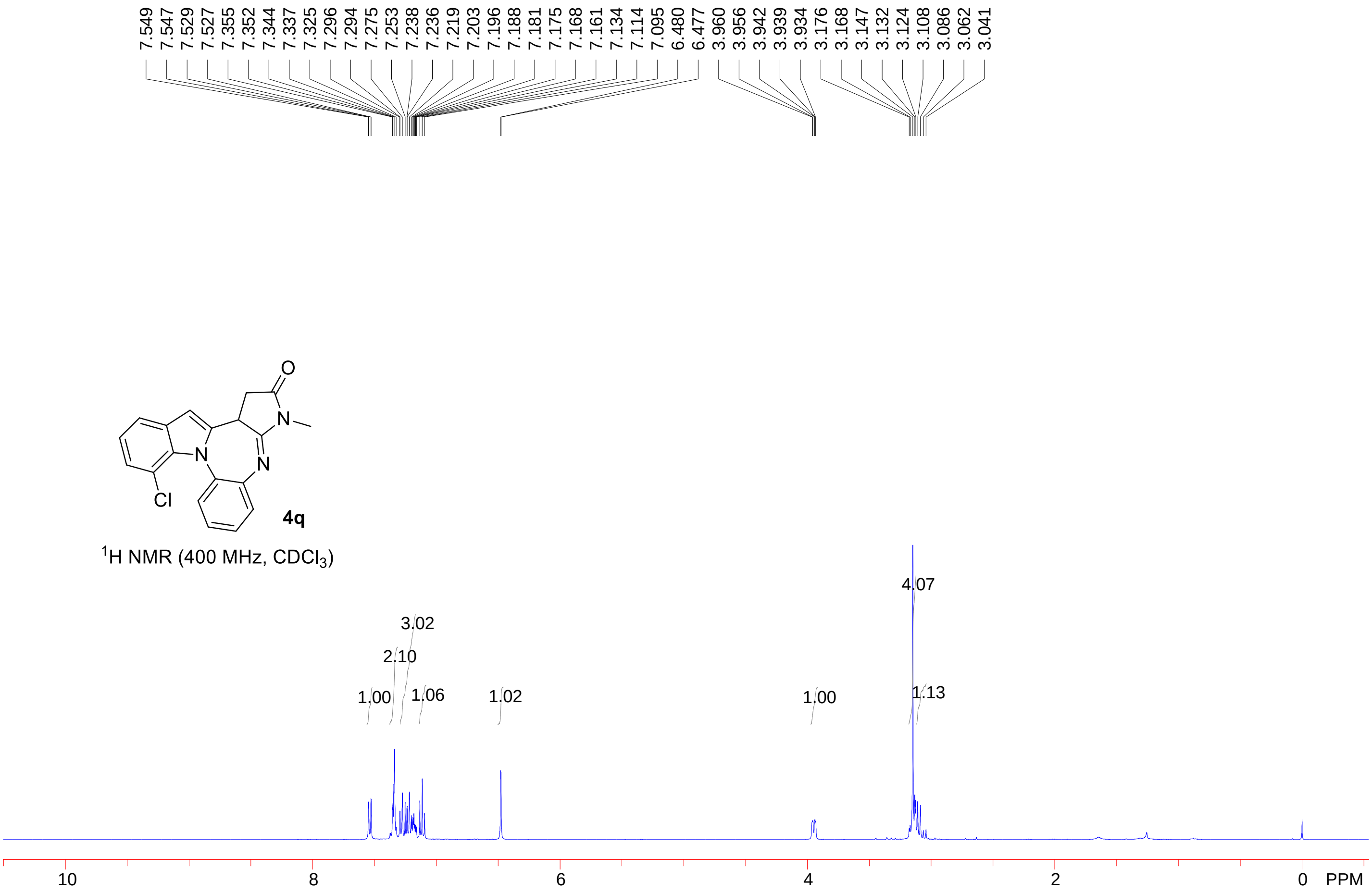
^{1}H NMR (600 MHz, $CDCl_3$)

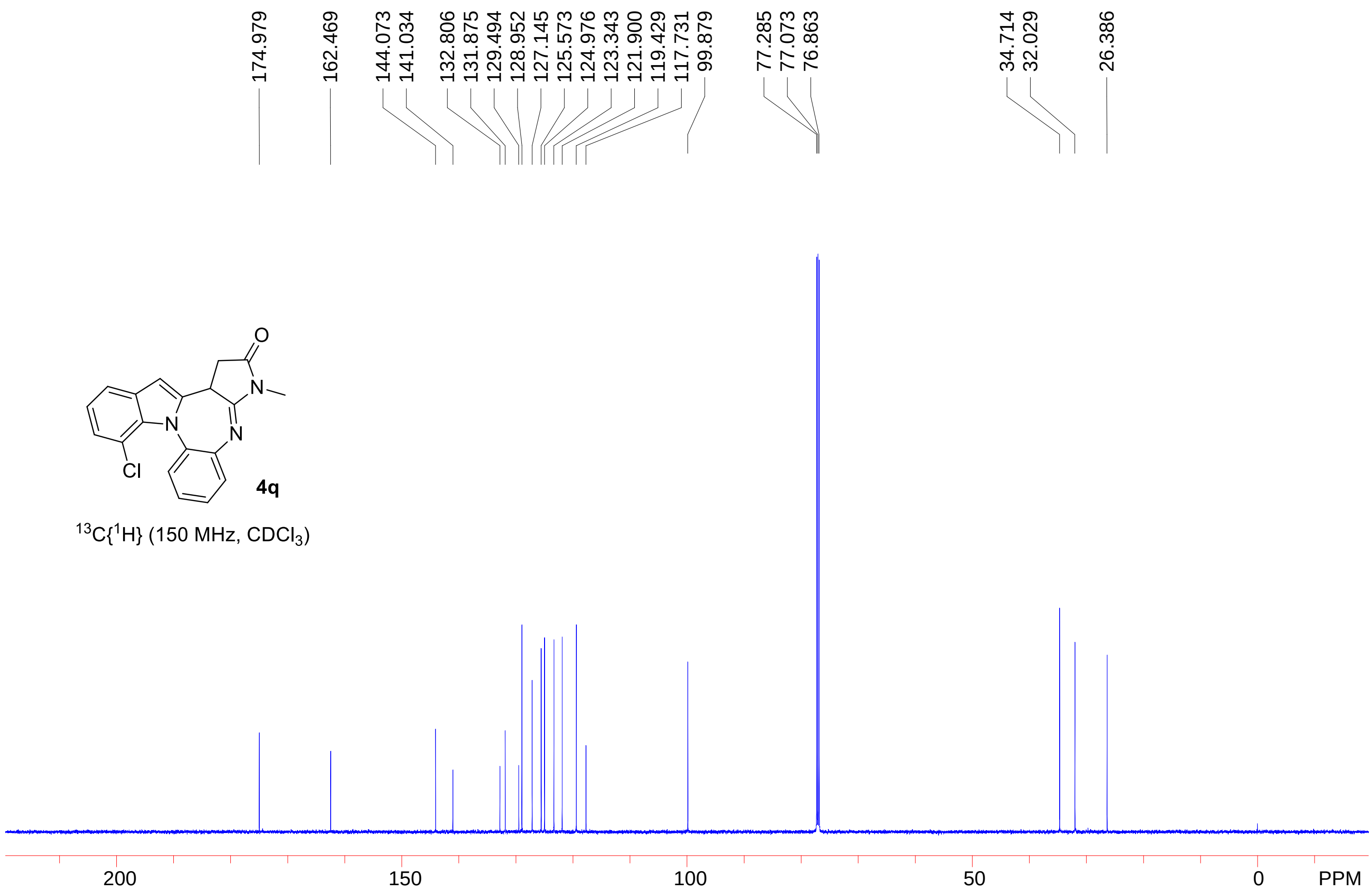


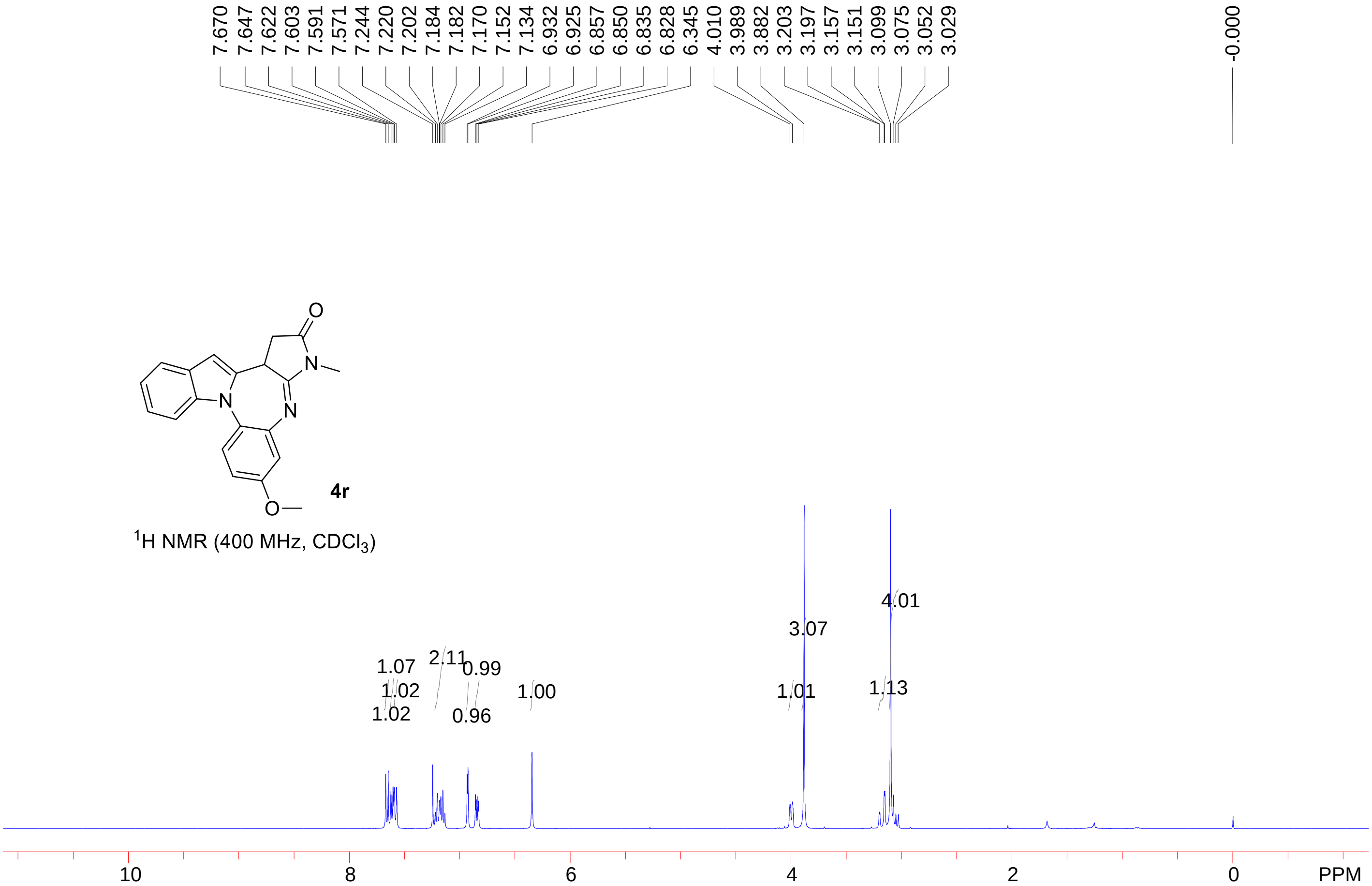
$^{13}C\{^1H\}$ (150 MHz, $CDCl_3$)

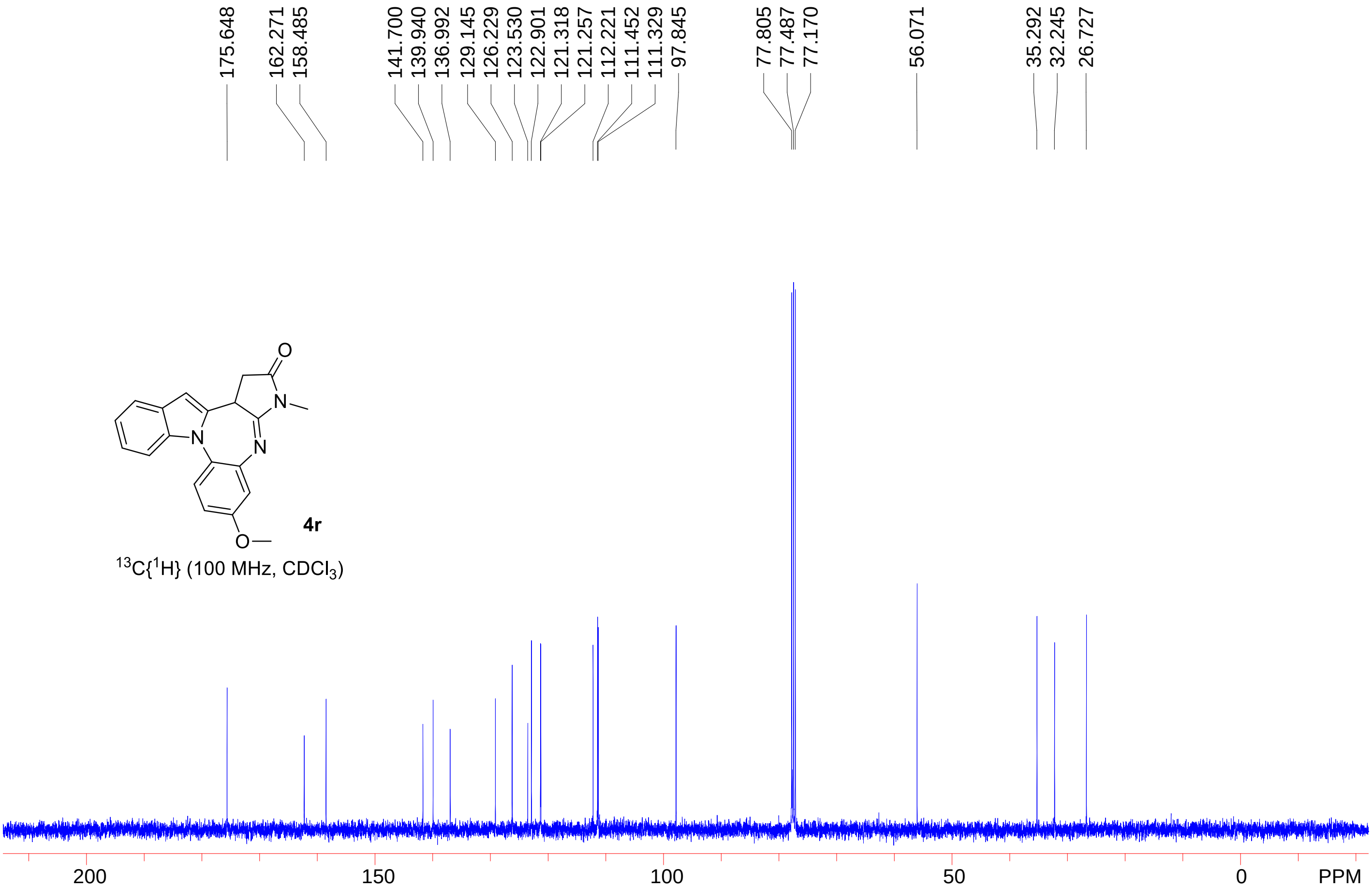


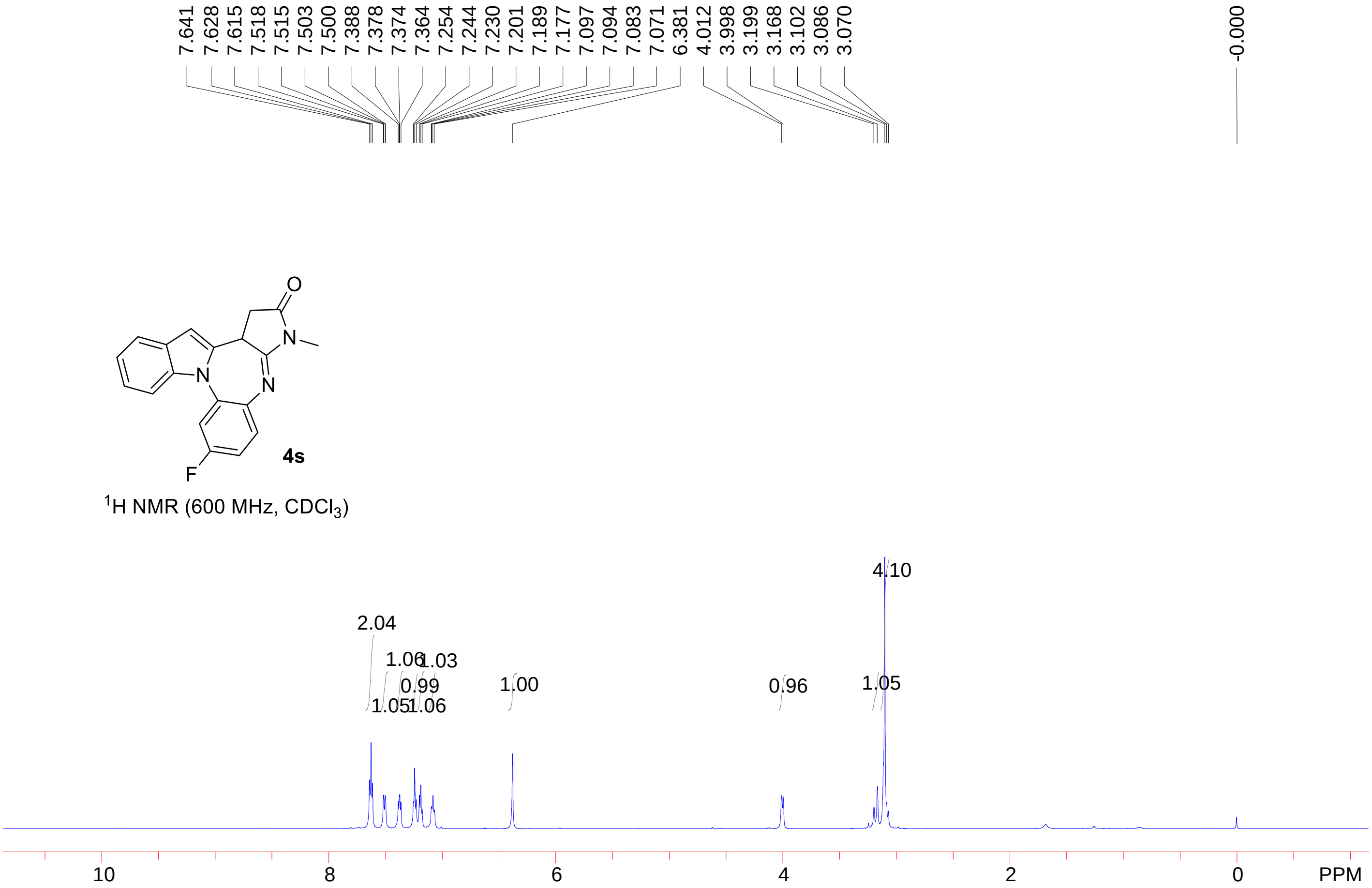
-121.972
-121.987
-122.000
-122.011
F
N
N
N
O
4p
^{19}F NMR (565 MHz, $CDCl_3$)
0
-50
-100
-150
-200
PPM

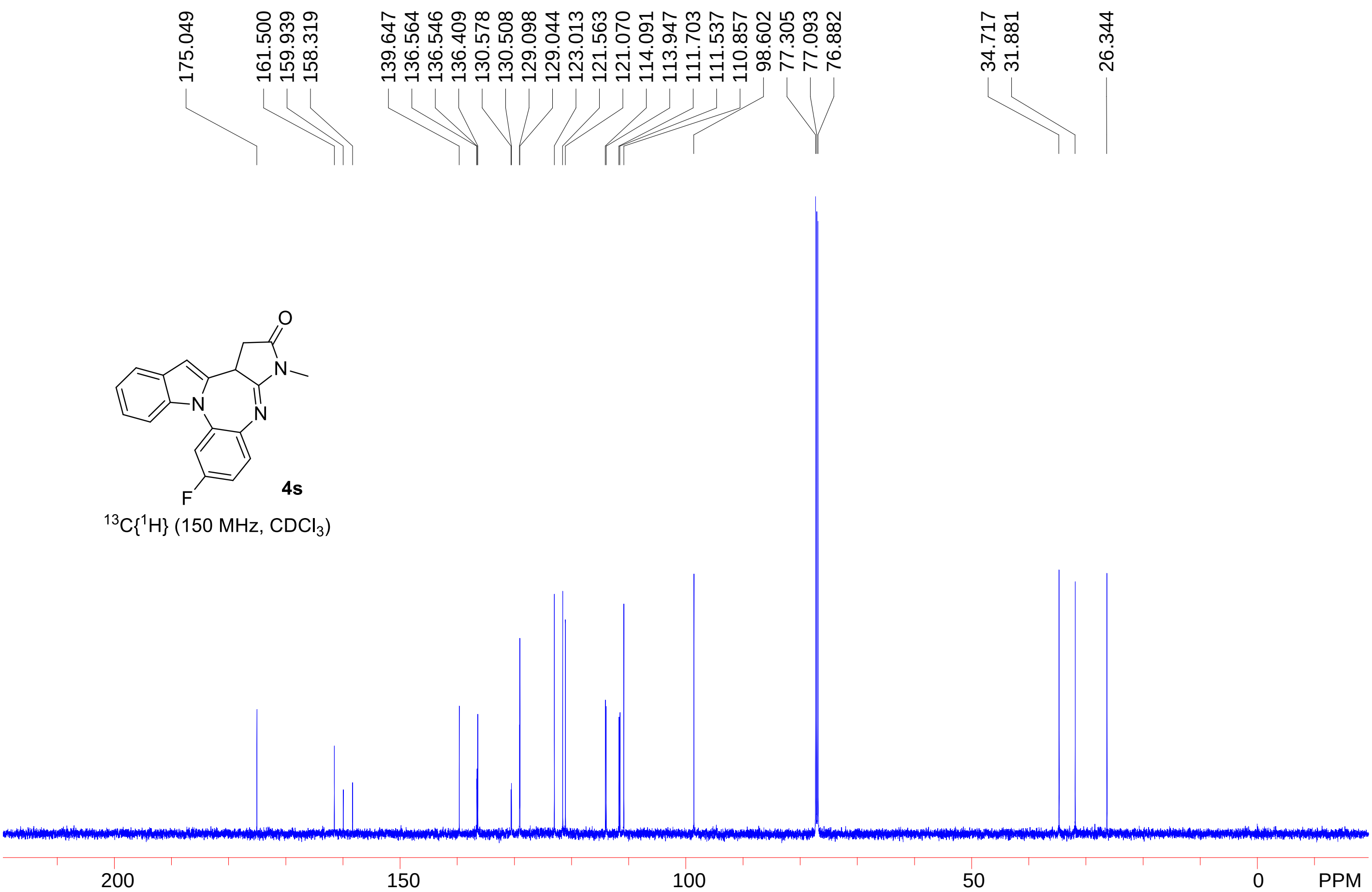

7.549
7.547
7.529
7.527
7.355
7.352
7.344
7.337
7.325
7.296
7.294
7.275
7.253
7.238
7.236
7.219
7.203
7.196
7.188
7.181
7.175
7.168
7.161
7.134
7.114
7.095
6.480
6.477
3.960
3.956
3.942
3.939
3.934
3.176
3.168
3.147
3.132
3.124
3.108
3.086
3.062
3.041
O
N
N
N
Cl
4q
^{1}H NMR (400 MHz, $CDCl_3$)
4.07
3.02
2.10
1.00
1.06
1.02
1.00
1.13
10
8
6
4
2
0
PPM

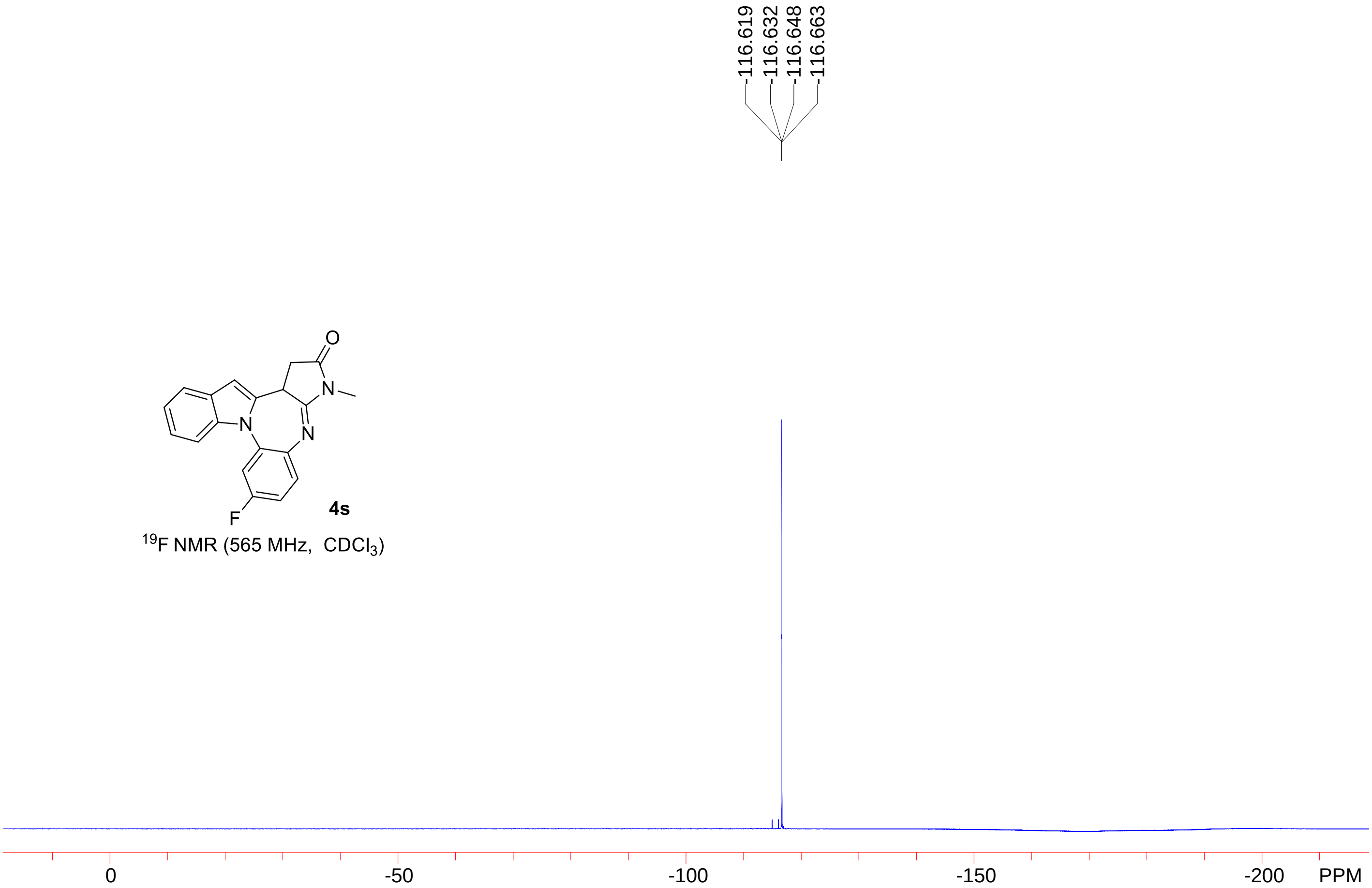

174.979
162.469
144.073
141.034
132.806
131.875
129.494
128.952
127.145
125.573
124.976
123.343
121.900
119.429
117.731
99.879
77.285
77.073
76.863
34.714
32.029
26.386
O
N
N
N
Cl
4q
$^{13}C\{^{1}H\}$ (150 MHz, $CDCl_3$)
200
150
100
50
0
PPM


7.670 7.647 7.622 7.603 7.591 7.571 7.244 7.220 7.202 7.184 7.182 7.170 7.152 7.134 6.932 6.925 6.857 6.850 6.835 6.828 6.345 4.010 3.989 3.882 3.203 3.197 3.157 3.151 3.099 3.075 3.052 3.029
-0.000
O
N
N
N
4r
1H NMR (400 MHz, CDCl3)
1.07
1.02
1.02
2.11
0.99
0.96
1.00
1.01
3.07
4.01
1.13
10
8
6
4
2
0
PPM

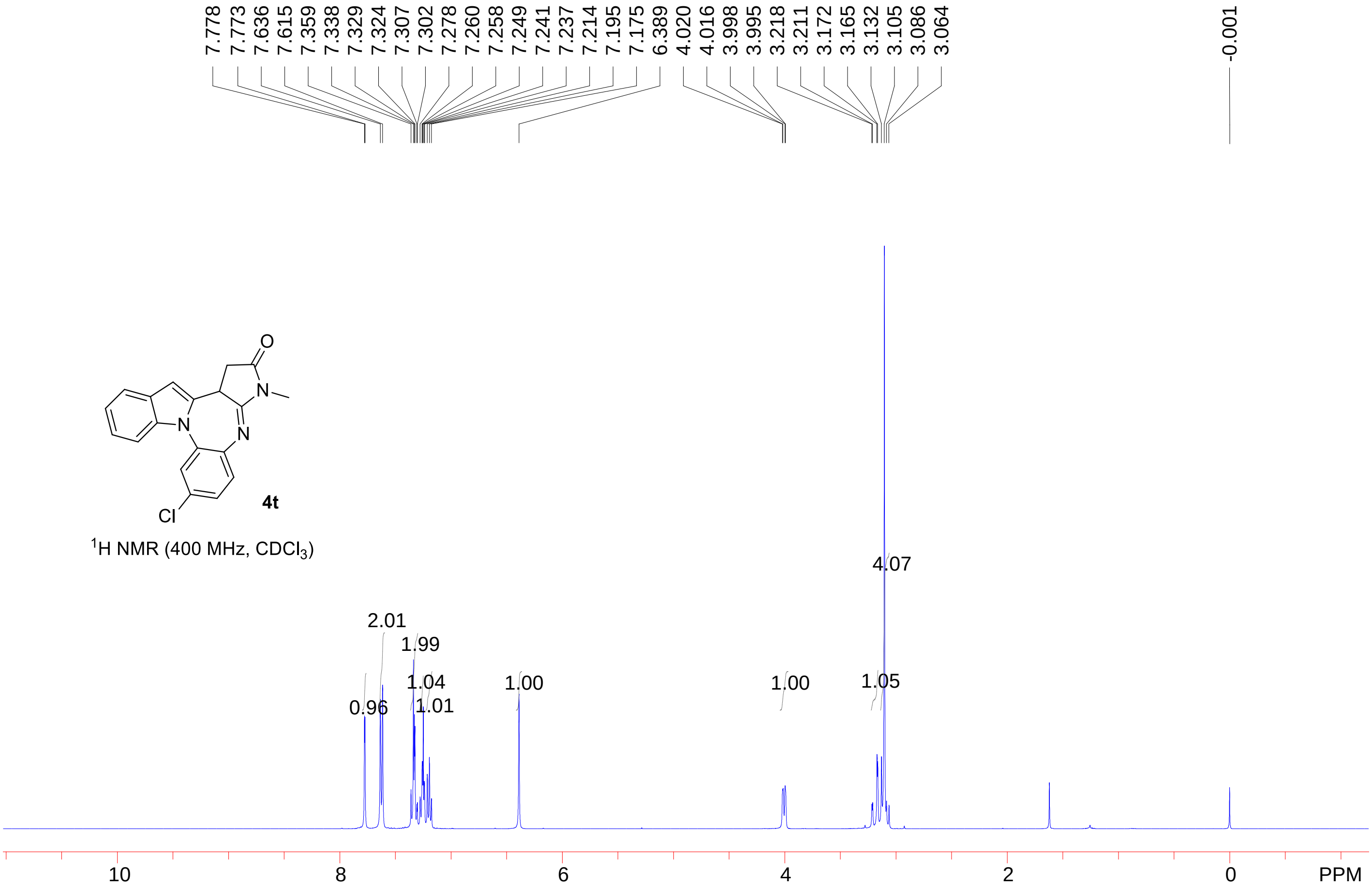

175.648
162.271 158.485
141.700 139.940 136.992 129.145 126.229 123.530 122.901 121.318 121.257 112.221 111.452 111.329 97.845
77.805 77.487 77.170
56.071
35.292 32.245 26.727
O
N
N
N
4r
13C{1H} (100 MHz, CDCl3)
200
150
100
50
0
PPM


7.641
7.628
7.615
7.518
7.515
7.503
7.500
7.388
7.378
7.374
7.364
7.254
7.244
7.230
7.201
7.189
7.177
7.097
7.094
7.083
7.071
6.381
4.012
3.998
3.199
3.168
3.102
3.086
3.070
-0.000
O
N
N
N
F
4s
1H NMR (600 MHz, CDCl3)
4.10
2.04
1.06
1.03
0.99
1.05
1.06
1.00
0.96
1.05
10
8
6
4
2
0
PPM

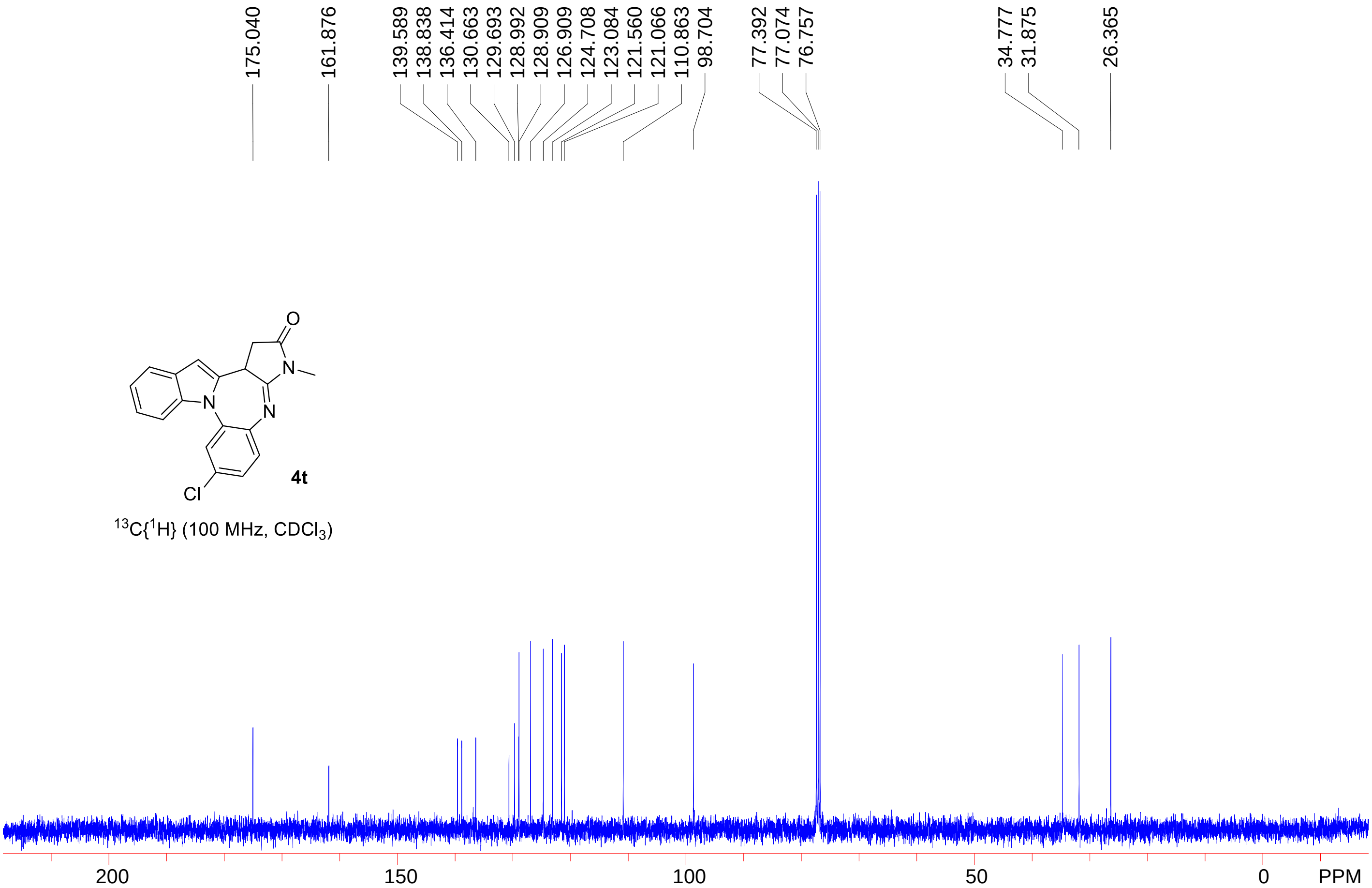

175.049
161.500
159.939
158.319
139.647
136.564
136.546
136.409
130.578
130.508
129.098
129.044
123.013
121.563
121.070
114.091
113.947
111.703
111.537
110.857
98.602
77.305
77.093
76.882
34.717
31.881
26.344
O
N
N
N
F
4s
13C{1H} (150 MHz, CDCl3)
200
150
100
50
0
PPM



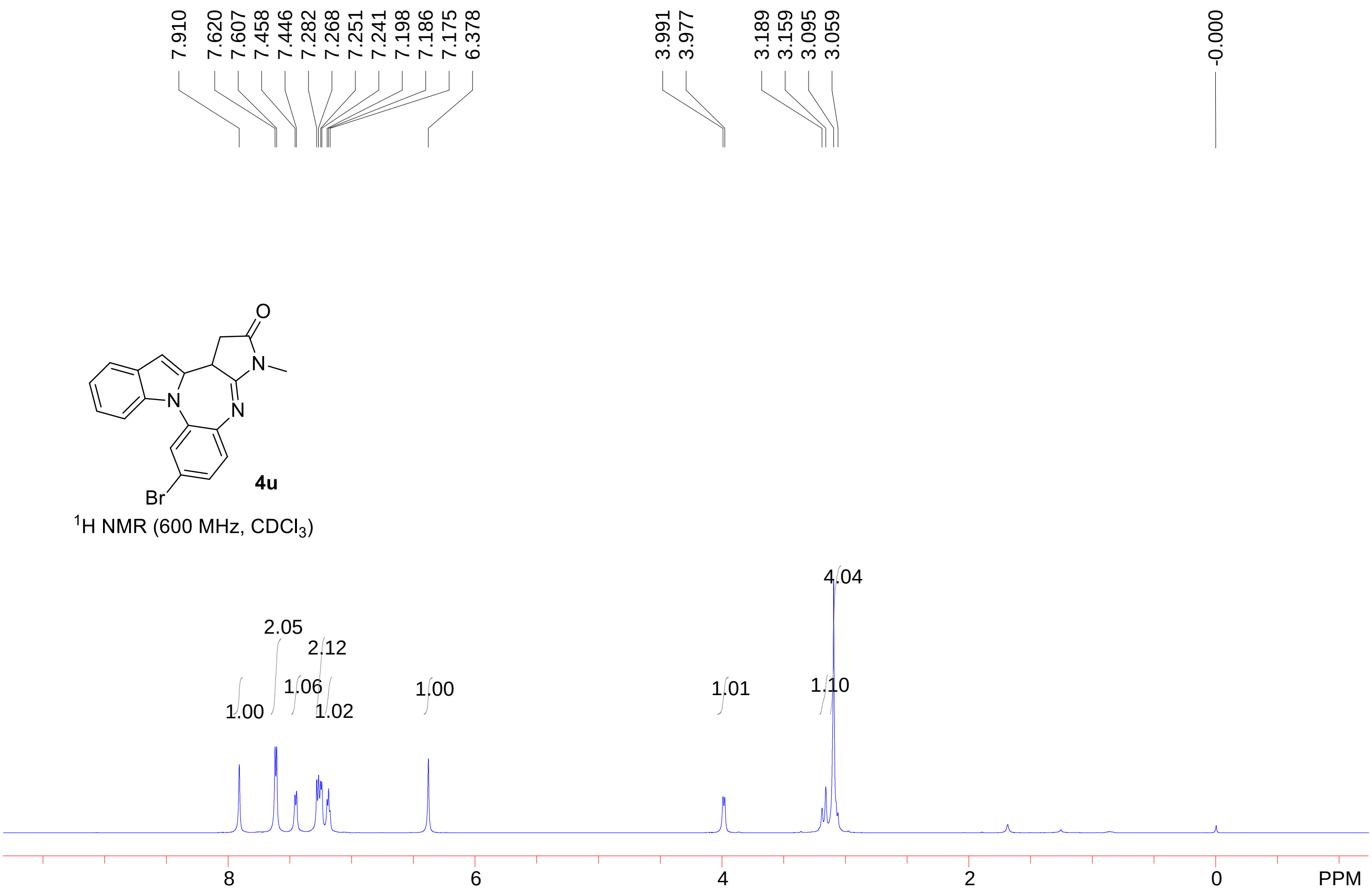
-116.619
-116.632
-116.648
-116.663
O
N
N
N
F
4s
19F NMR (565 MHz, CDCl3)
0
-50
-100
-150
-200
PPM

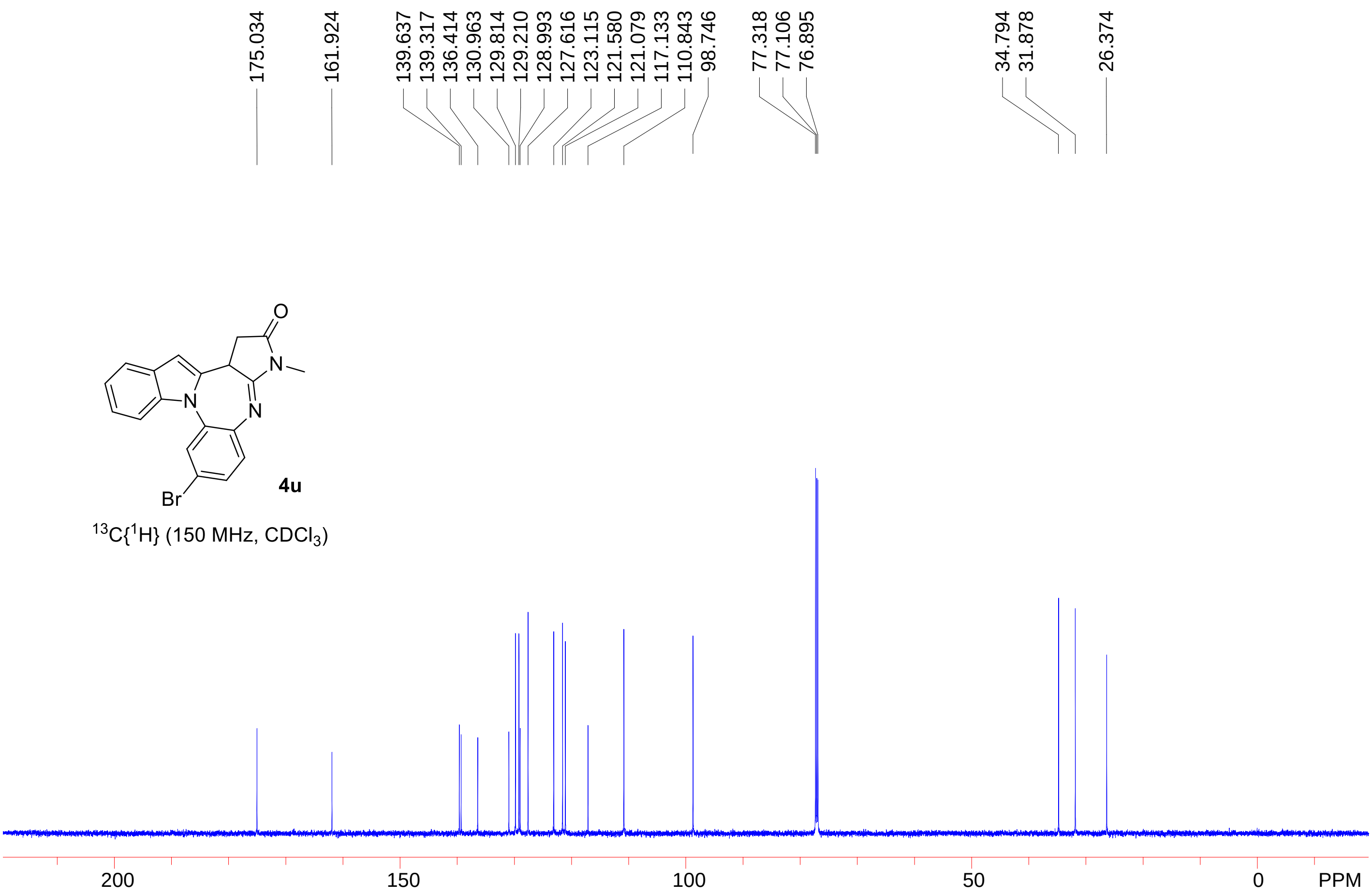


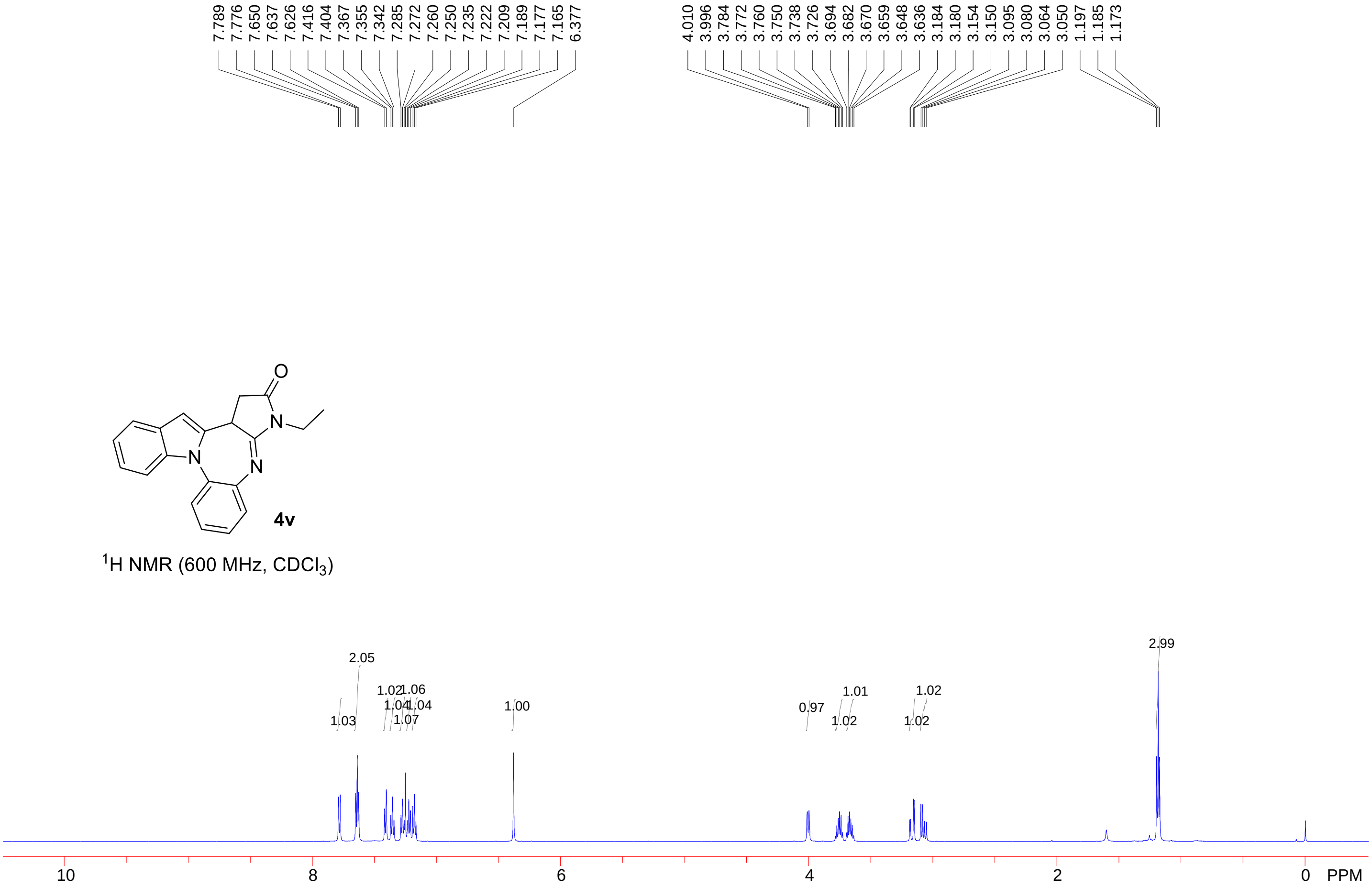
^{1}H NMR (400 MHz, $CDCl_3$)



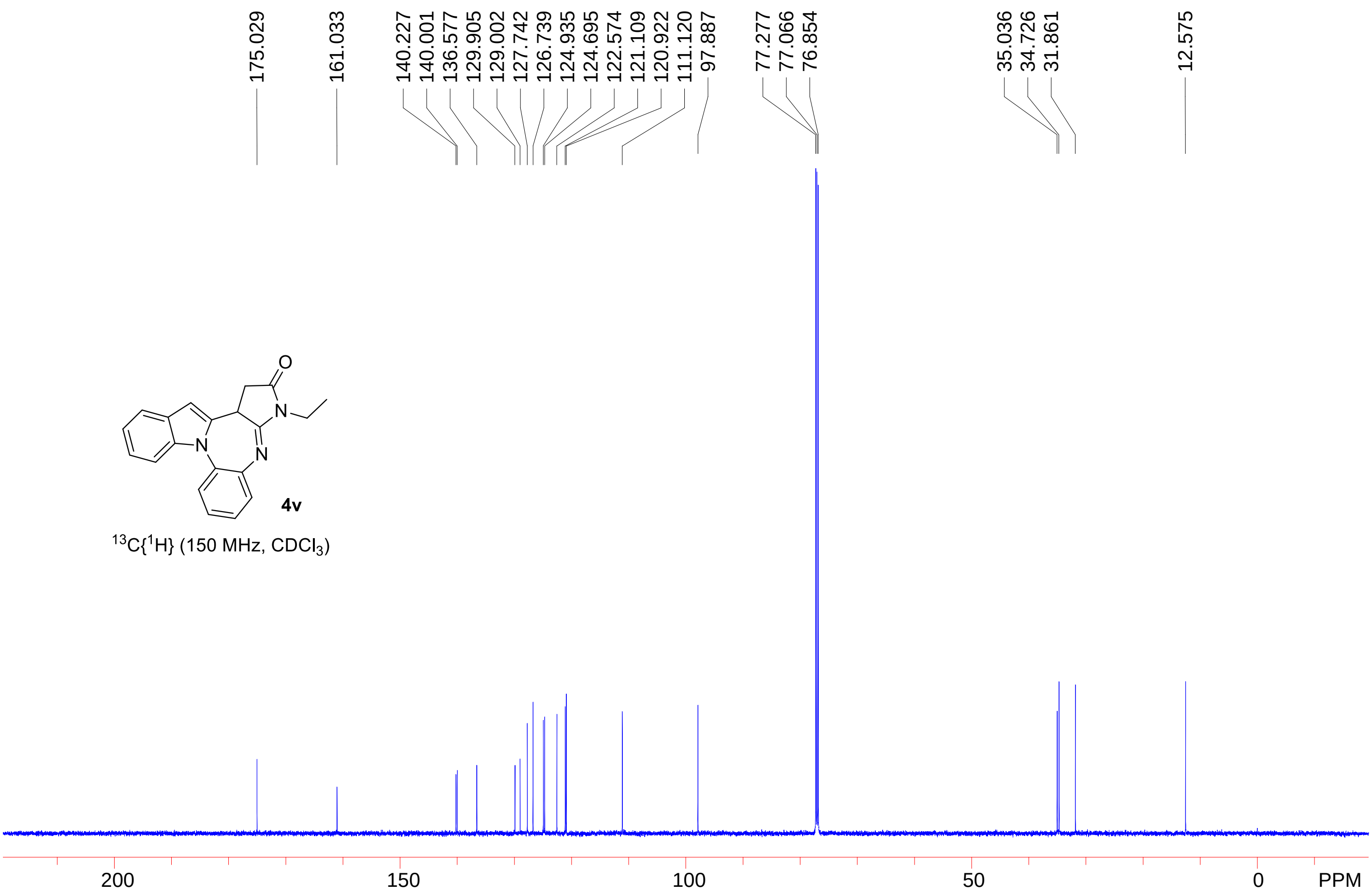
$^{13}C\{^1H\}$ (100 MHz, $CDCl_3$)


7.910
7.620
7.607
7.458
7.446
7.282
7.268
7.251
7.241
7.198
7.186
7.175
6.378
3.991
3.977
3.189
3.159
3.095
3.059
-0.000
O
N
N
N
Br
4u
^{1}H NMR (600 MHz, $CDCl_3$)
4.04
2.05
2.12
1.06
1.00
1.02
1.00
1.01
1.10
8
6
4
2
0
PPM

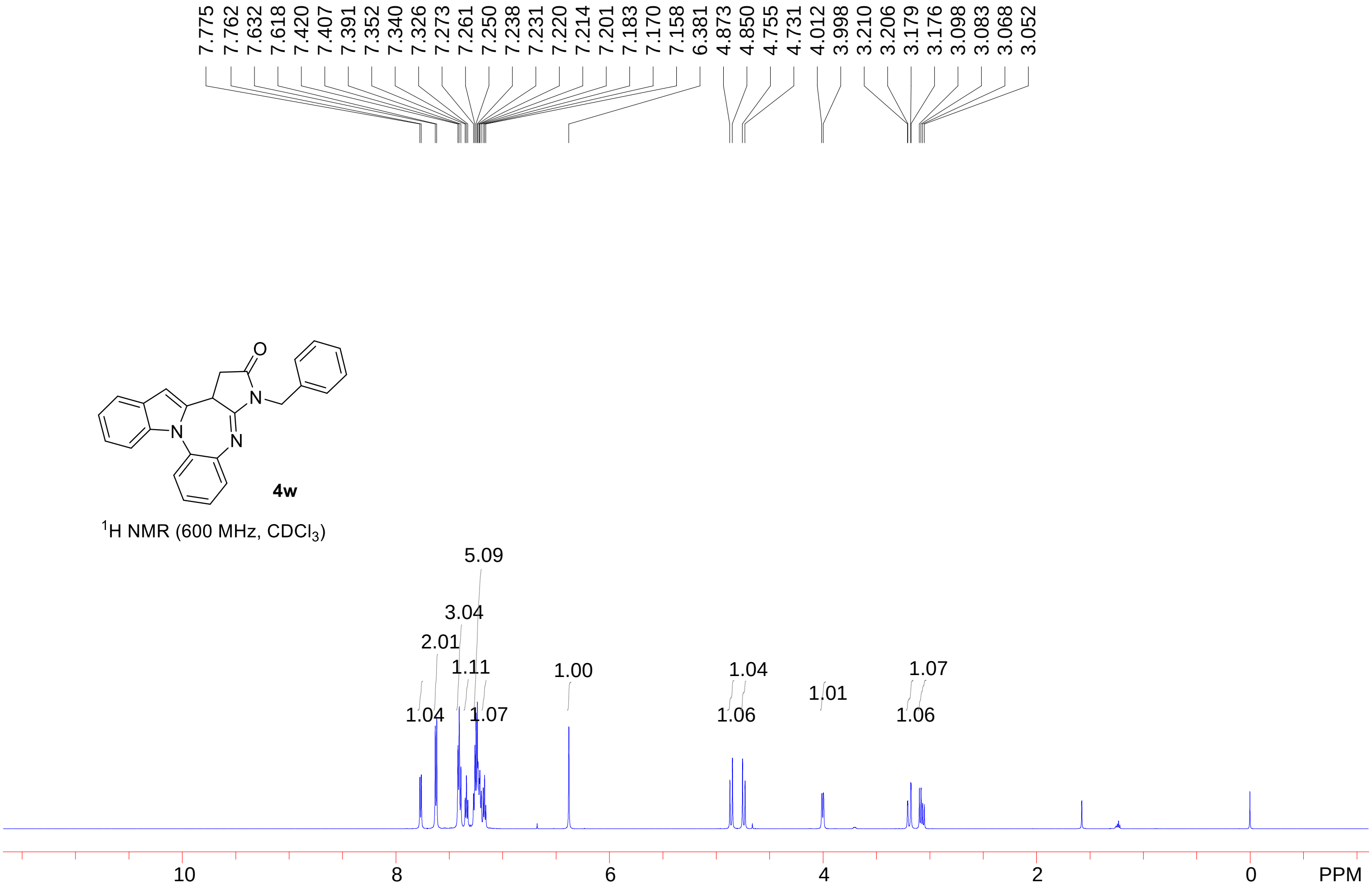

175.034
161.924
139.637
139.317
136.414
130.963
129.814
129.210
128.993
127.616
123.115
121.580
121.079
117.133
110.843
98.746
77.318
77.106
76.895
34.794
31.878
26.374
O
N
N
N
Br
4u
$^{13}C\{^{1}H\}$ (150 MHz, $CDCl_3$)
200
150
100
50
0
PPM



^{1}H NMR (600 MHz, $CDCl_3$)

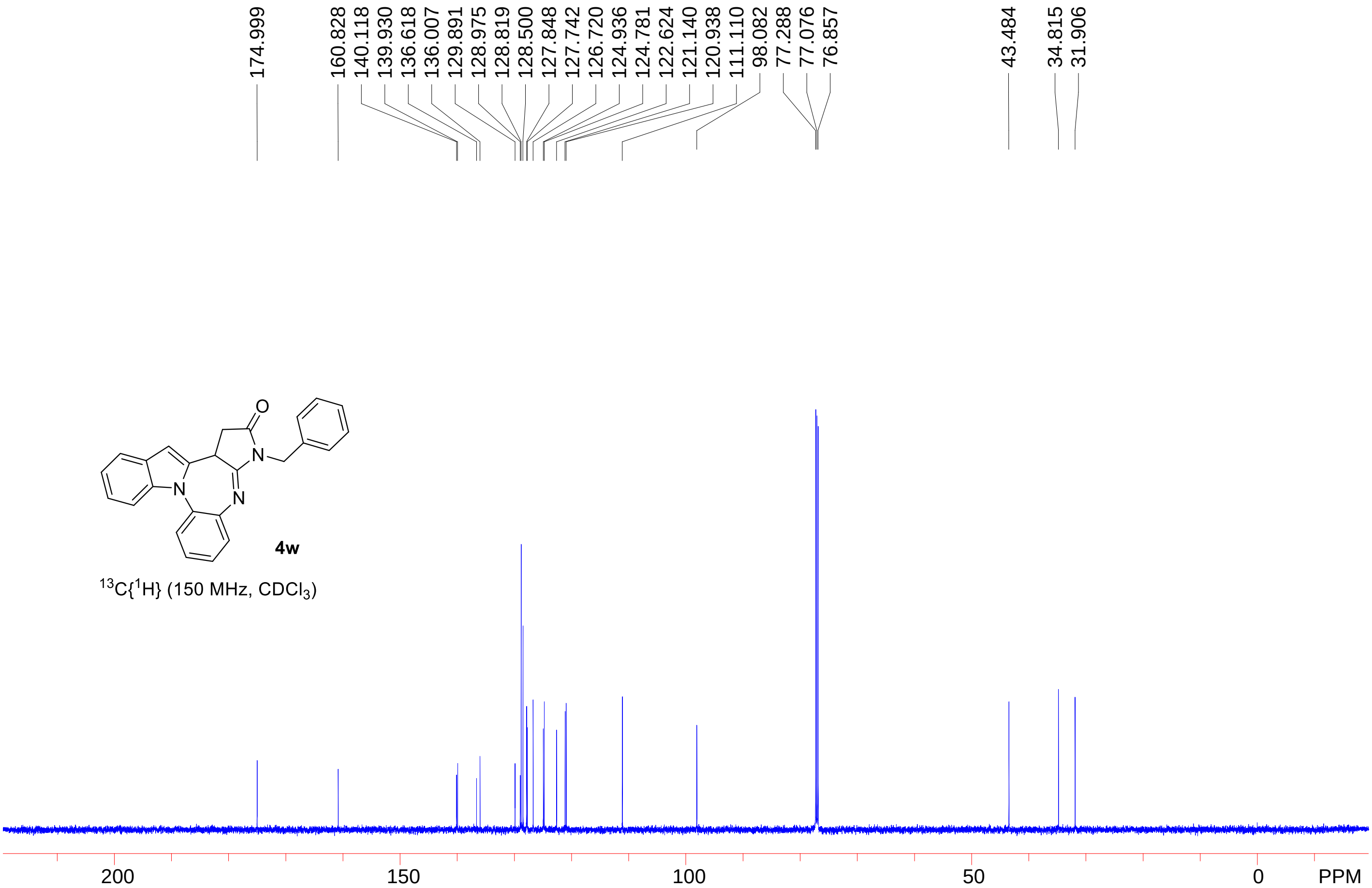


$^{13}C\{^{1}H\}$ (150 MHz, $CDCl_3$)



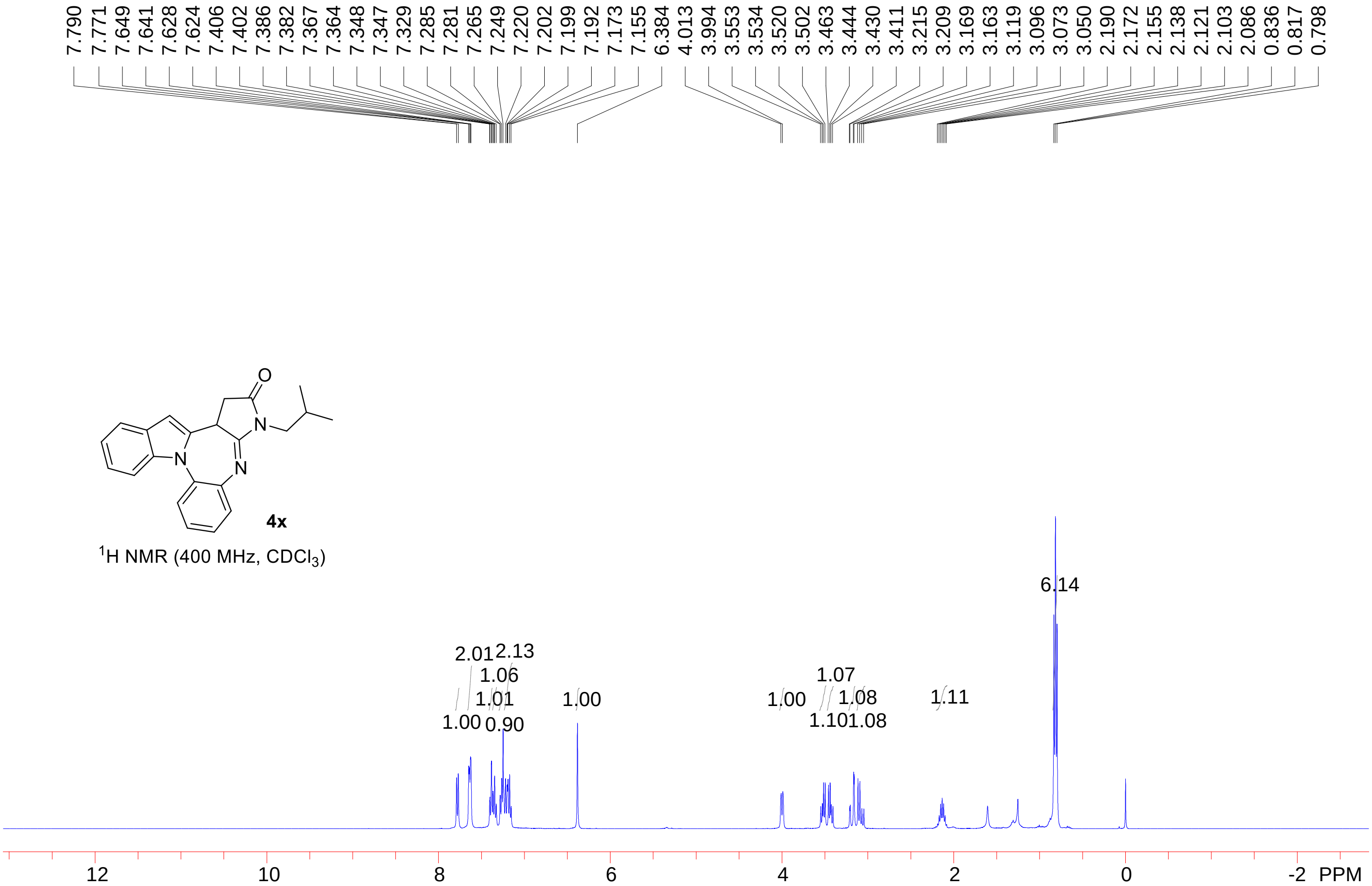
4w

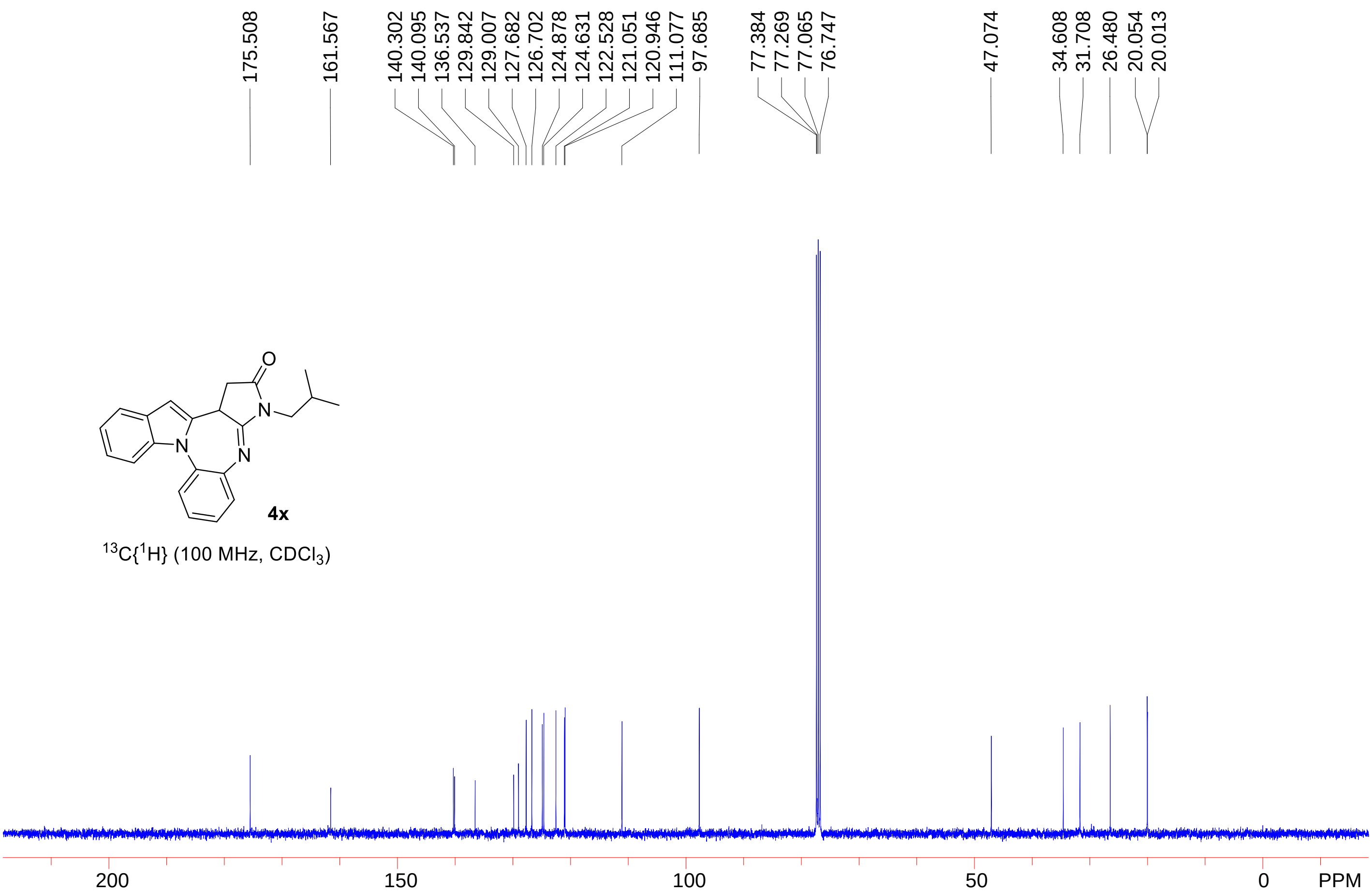
^{1}H NMR (600 MHz, $CDCl_3$)

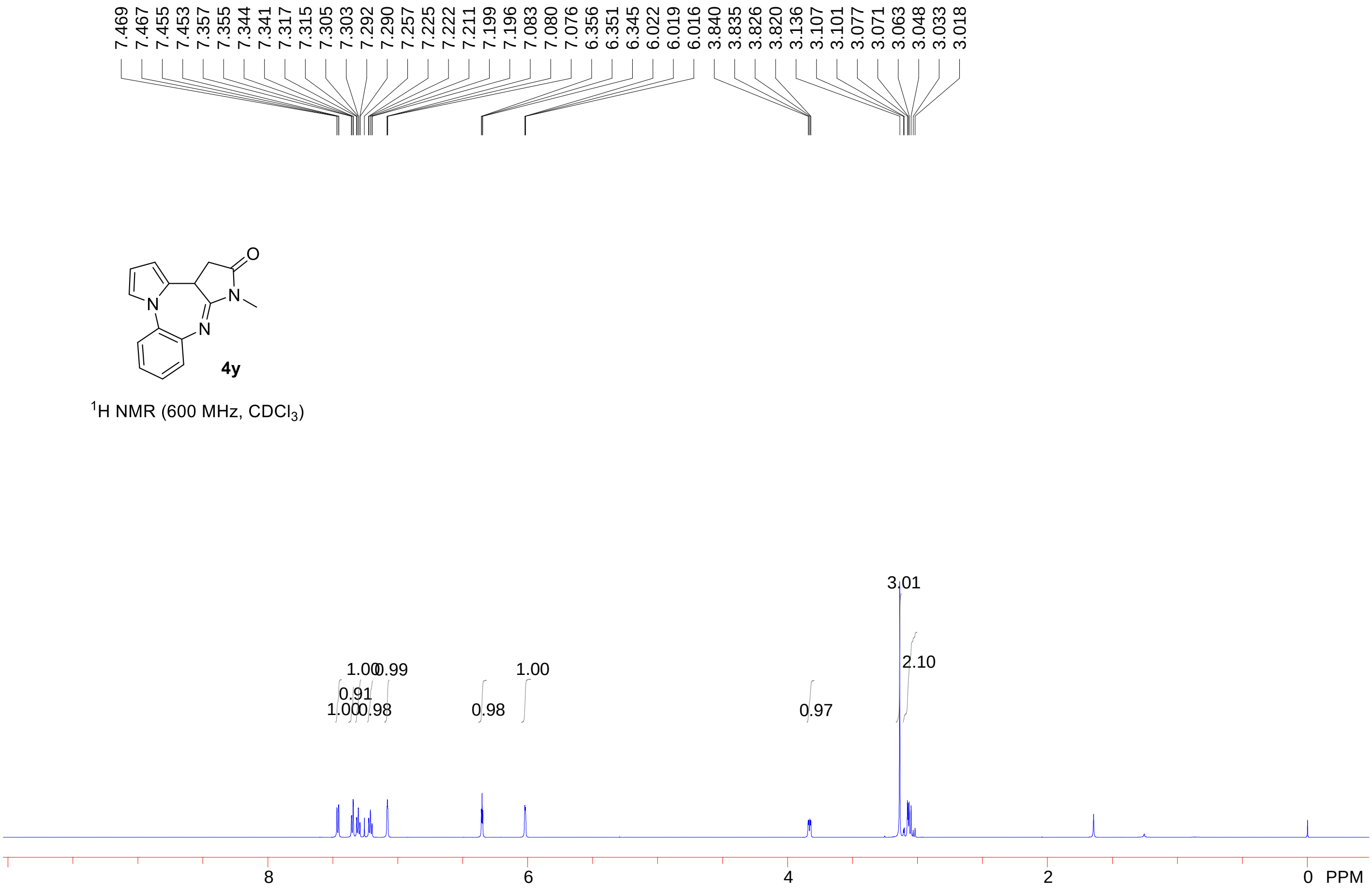


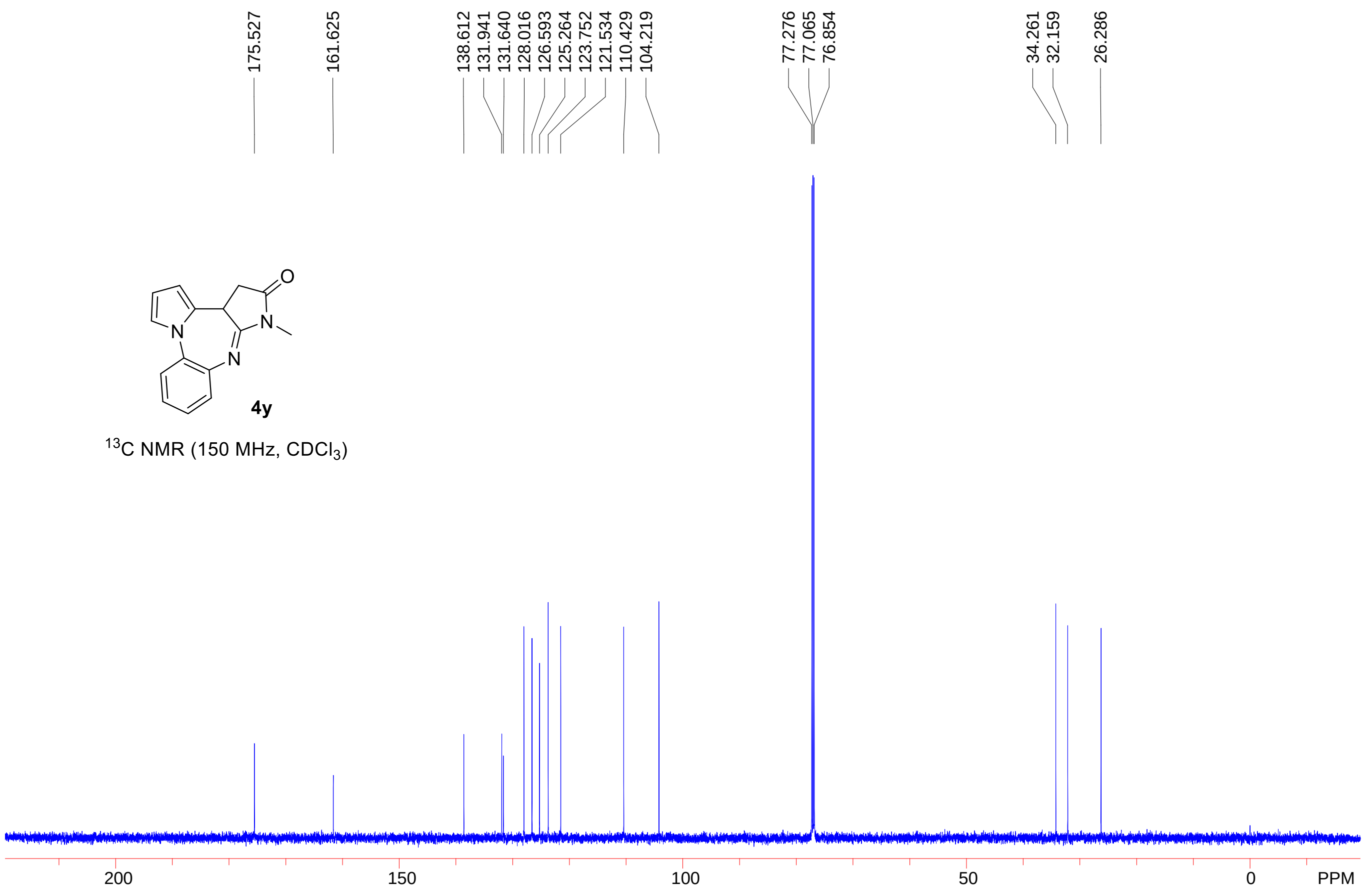
4w

$^{13}C\{^{1}H\}$ (150 MHz, $CDCl_3$)

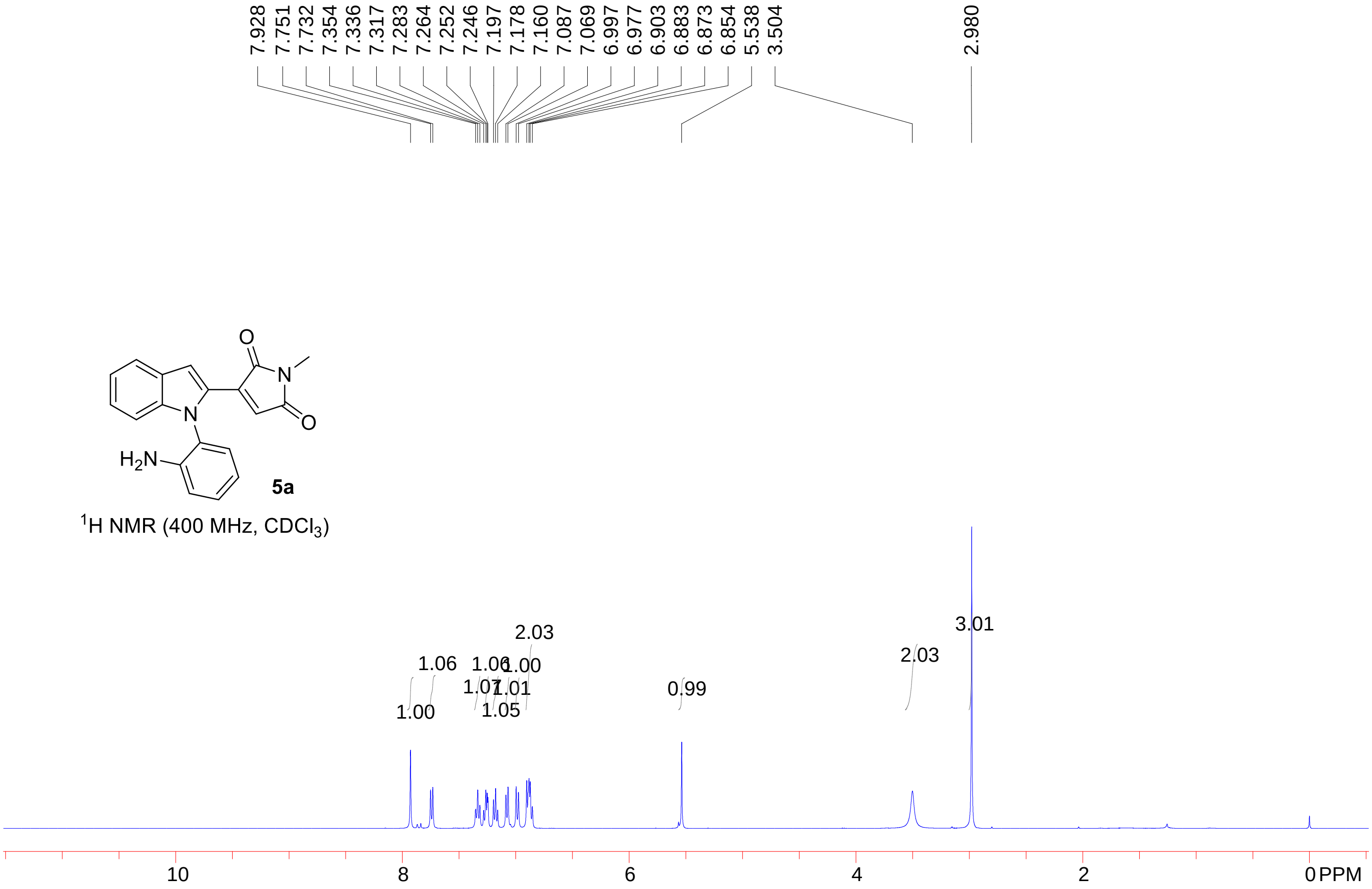

7.790 7.771 7.649 7.641 7.628 7.624 7.406 7.402 7.386 7.382 7.367 7.364 7.348 7.347 7.329 7.285 7.281 7.265 7.249 7.220 7.202 7.199 7.192 7.173 7.155 6.384 4.013 3.994 3.553 3.534 3.520 3.502 3.463 3.444 3.430 3.411 3.215 3.209 3.169 3.163 3.119 3.096 3.073 3.050 2.190 2.172 2.155 2.138 2.121 2.103 2.086 0.836 0.817 0.798
O
N
N
N
4x
^{1}H NMR (400 MHz, CDCl$_3$)
6.14
2.01 2.13
1.06
1.01
1.00 0.90
1.00
1.00
1.07
1.08
1.10 1.08
1.11
12 10 8 6 4 2 0 -2 PPM

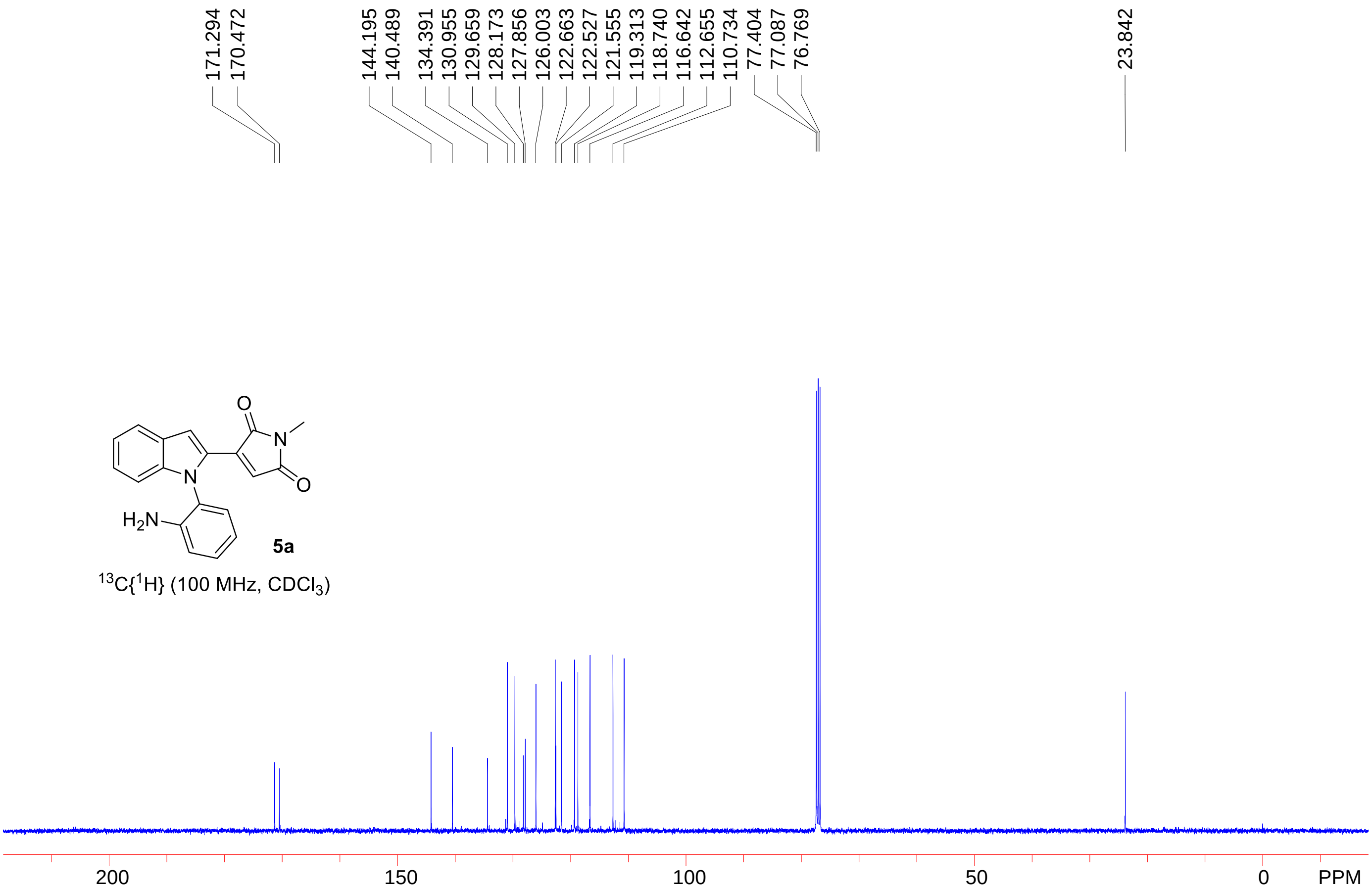

175.508 161.567 140.302 140.095 136.537 129.842 129.007 127.682 126.702 124.878 124.631 122.528 121.051 120.946 111.077 97.685 77.384 77.269 77.065 76.747 47.074 34.608 31.708 26.480 20.054 20.013
O
N
N
N
4x
^{13}C{^{1}H} (100 MHz, CDCl$_3$)
200 150 100 50 0 PPM

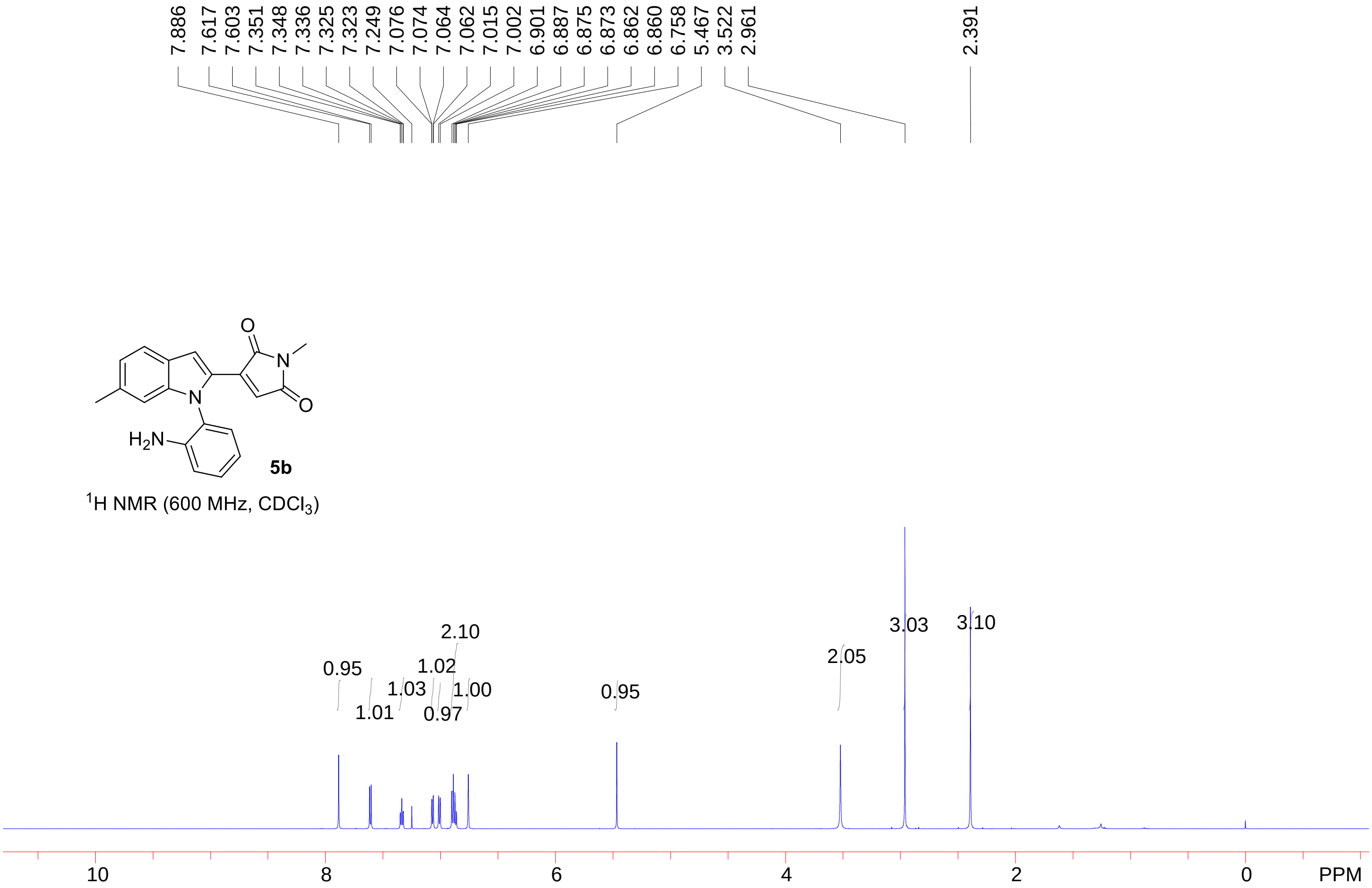

7.469
7.467
7.455
7.453
7.357
7.355
7.344
7.341
7.317
7.315
7.305
7.303
7.292
7.290
7.257
7.225
7.222
7.211
7.199
7.196
7.083
7.080
7.076
6.356
6.351
6.345
6.022
6.019
6.016
3.840
3.835
3.826
3.820
3.136
3.107
3.101
3.077
3.071
3.063
3.048
3.033
3.018
4y
^{1}H NMR (600 MHz, $CDCl_3$)
3.01
2.10
1.00
0.99
0.91
1.00
0.98
0.98
1.00
0.97
8
6
4
2
0
PPM

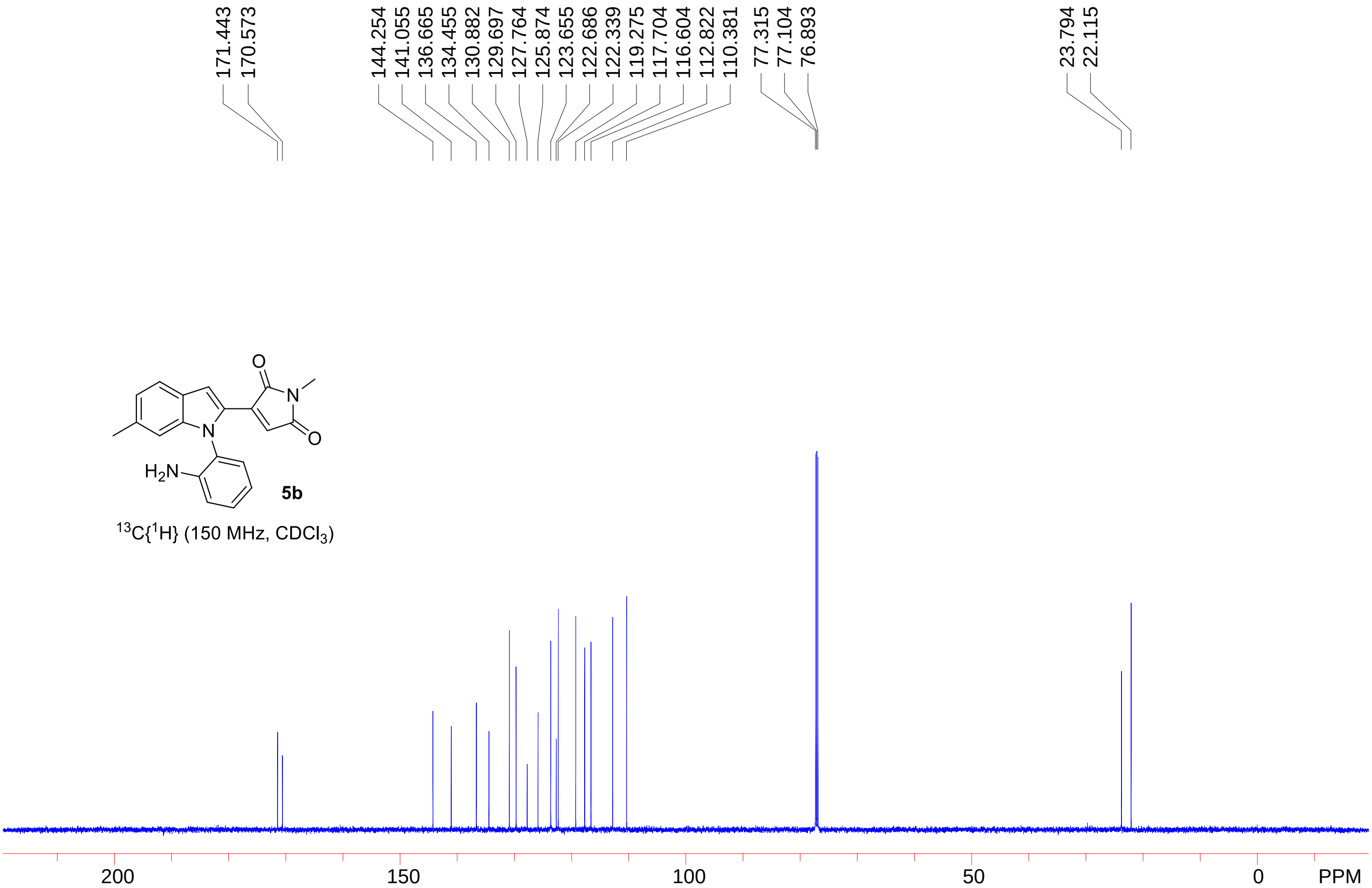

175.527
161.625
138.612
131.941
131.640
128.016
126.593
125.264
123.752
121.534
110.429
104.219
77.276
77.065
76.854
34.261
32.159
26.286
4y
^{13}C NMR (150 MHz, $CDCl_3$)
200
150
100
50
0
PPM

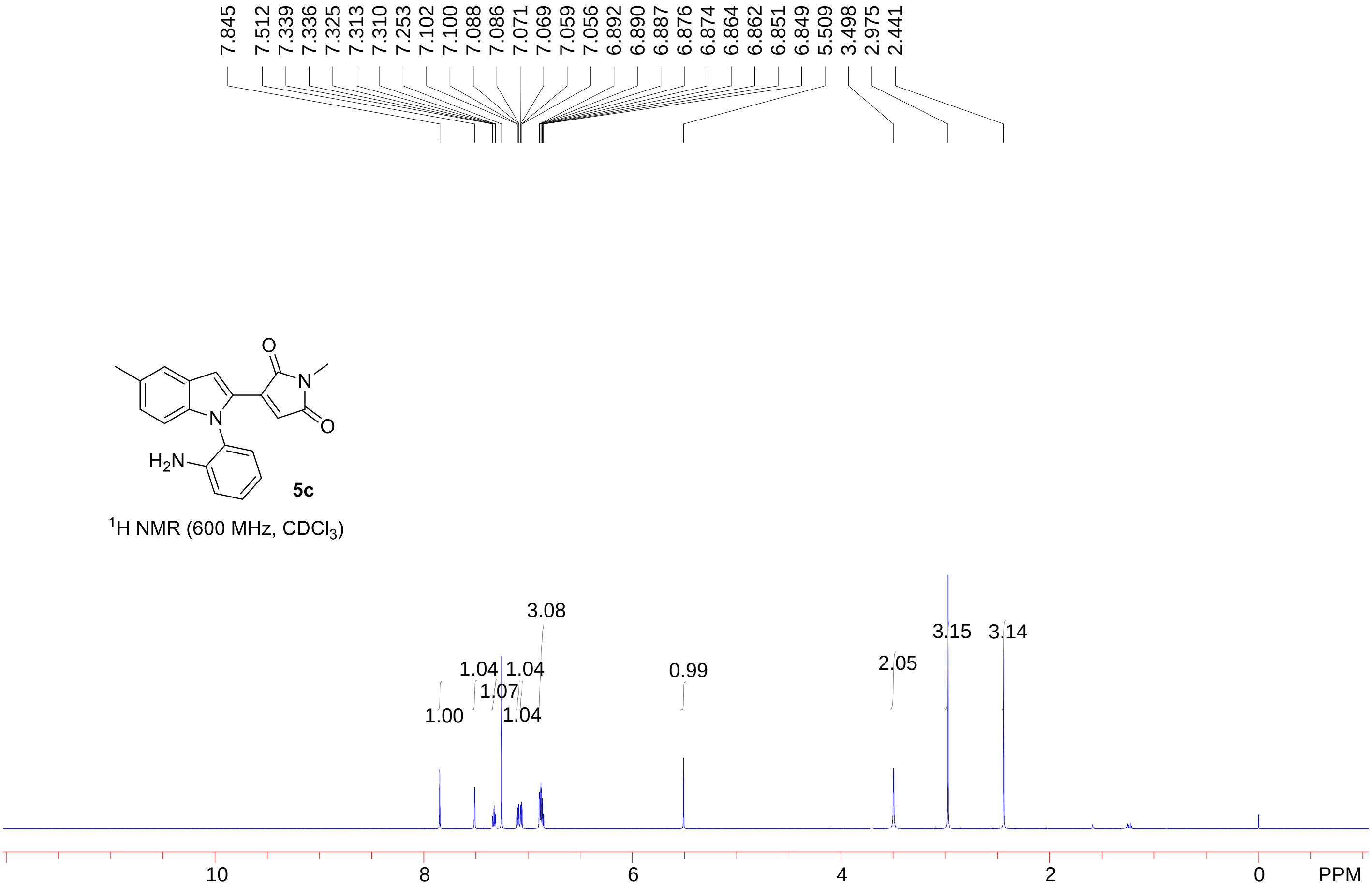
VII. NMR spectra of 5a-5f



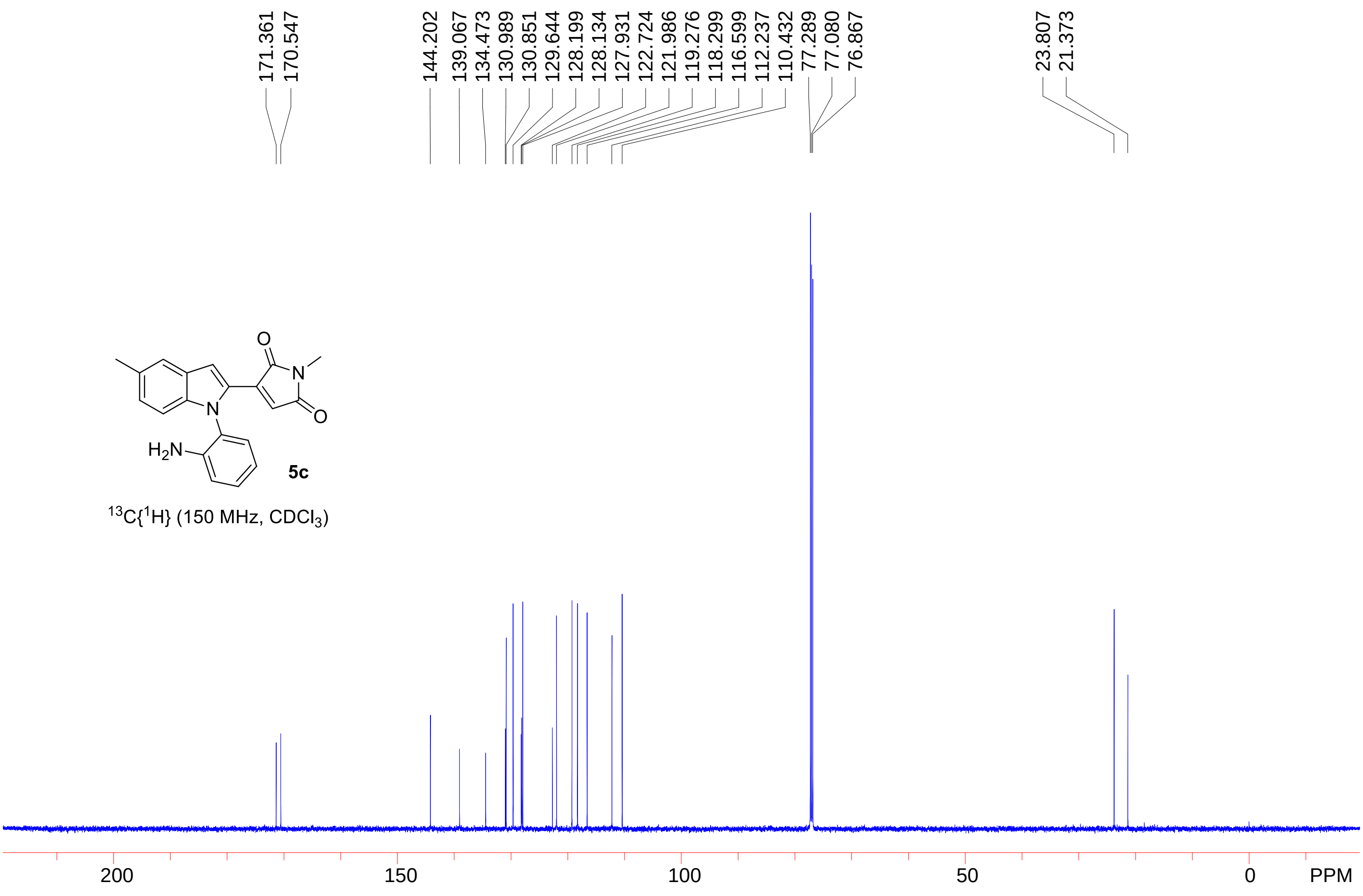



7.886
7.617
7.603
7.351
7.348
7.336
7.325
7.323
7.249
7.076
7.074
7.064
7.062
7.015
7.002
6.901
6.887
6.875
6.873
6.862
6.860
6.758
5.467
3.522
2.961
2.391
O
N
O
N
H2N
5b
1H NMR (600 MHz, CDCl3)
0.95
1.01
1.03
1.02
2.10
0.97
1.00
0.95
2.05
3.03
3.10
10
8
6
4
2
0
PPM

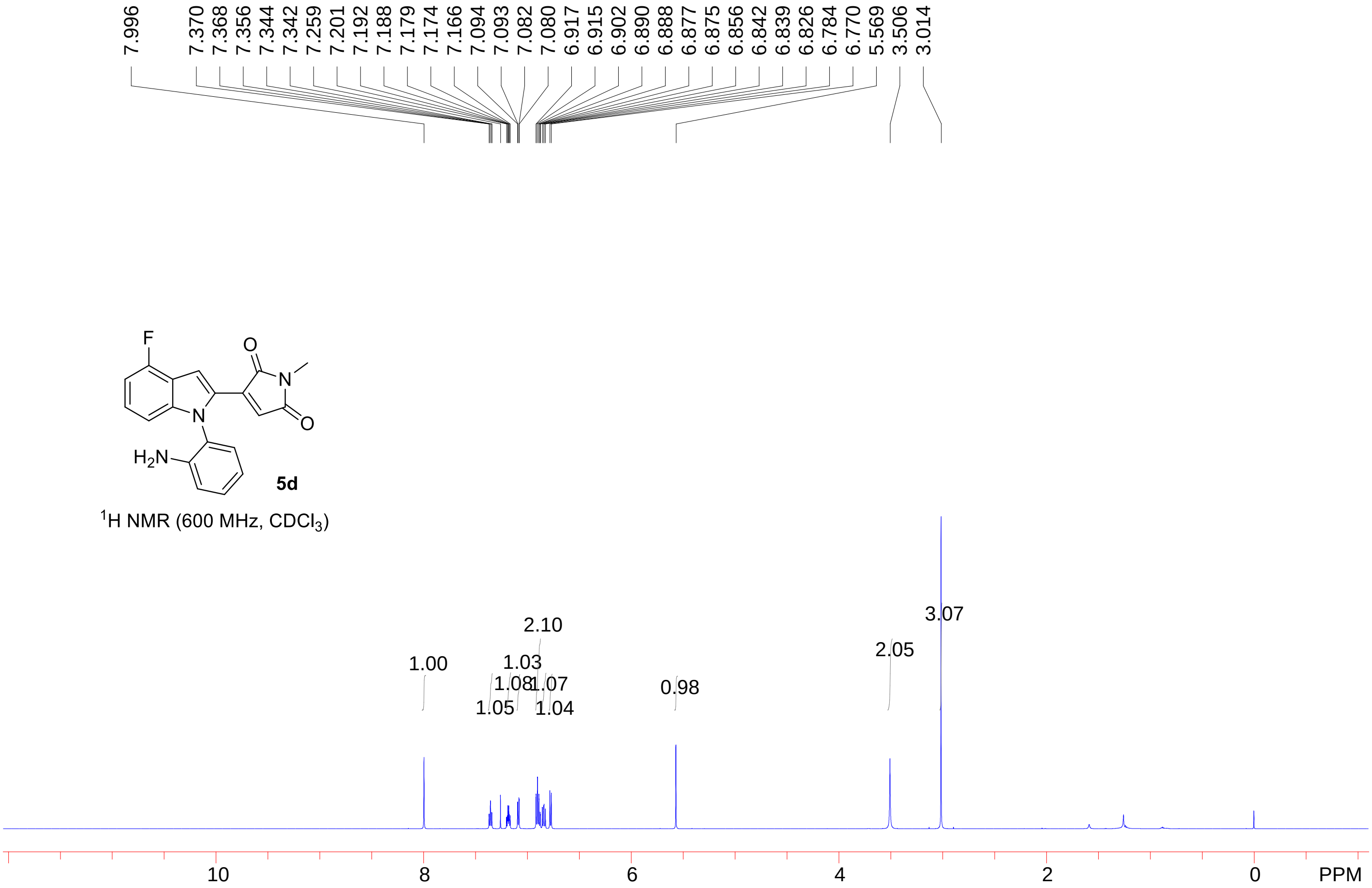

171.443
170.573
144.254
141.055
136.665
134.455
130.882
129.697
127.764
125.874
123.655
122.686
122.339
119.275
117.704
116.604
112.822
110.381
77.315
77.104
76.893
23.794
22.115
O
N
O
N
H2N
5b
13C{1H} (150 MHz, CDCl3)
200
150
100
50
0
PPM

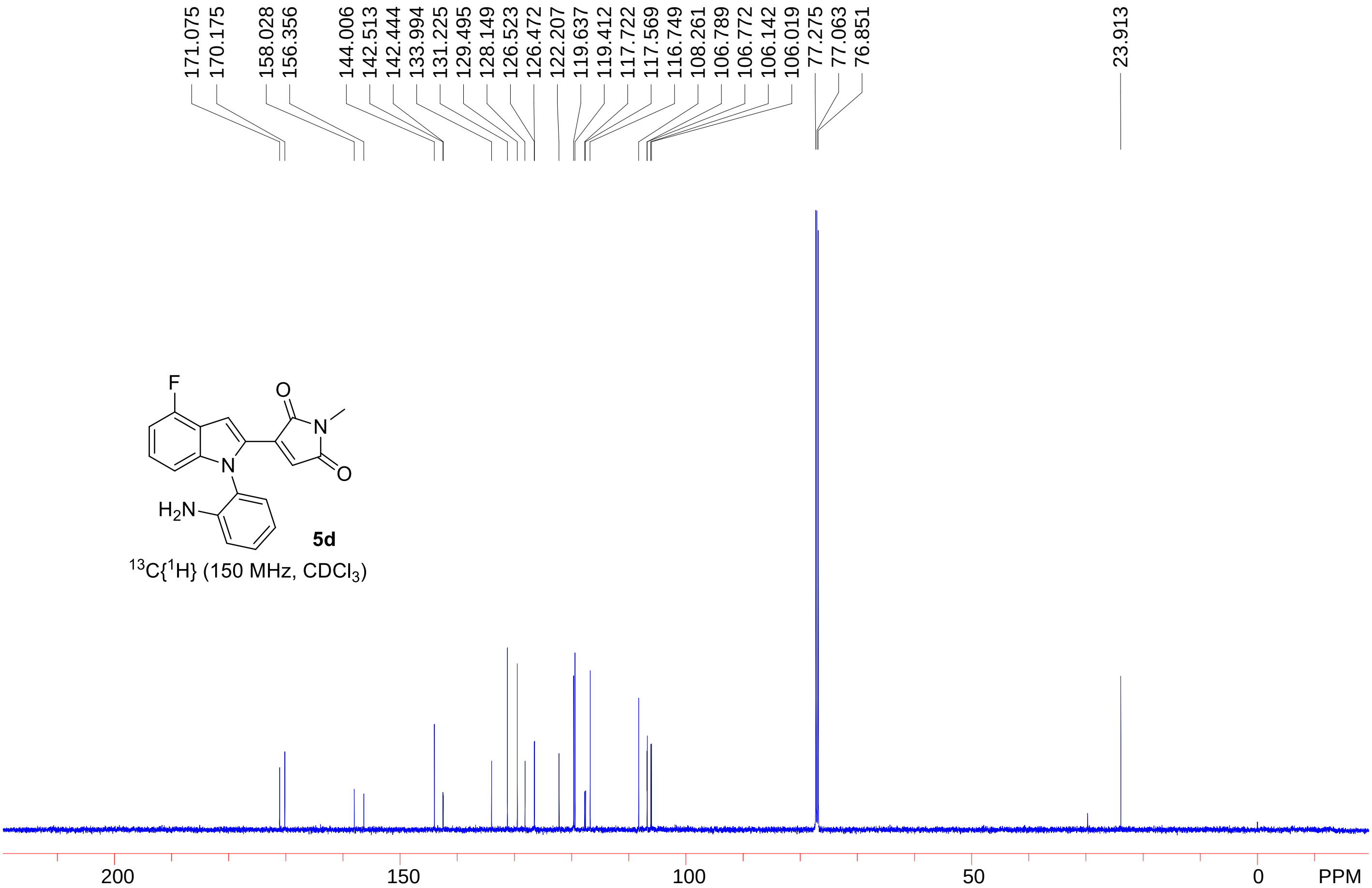


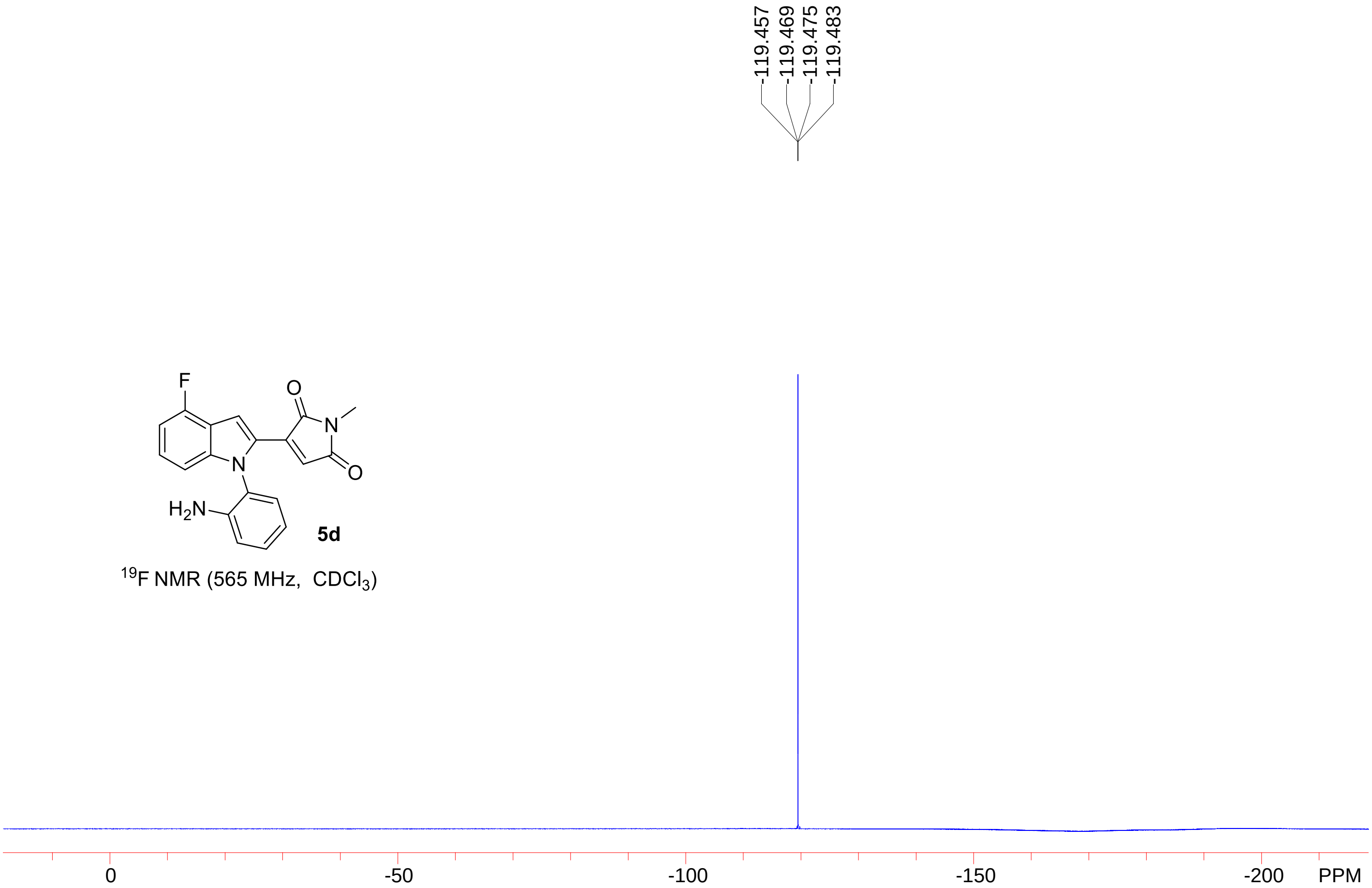
^{1}H NMR (600 MHz, $CDCl_3$)



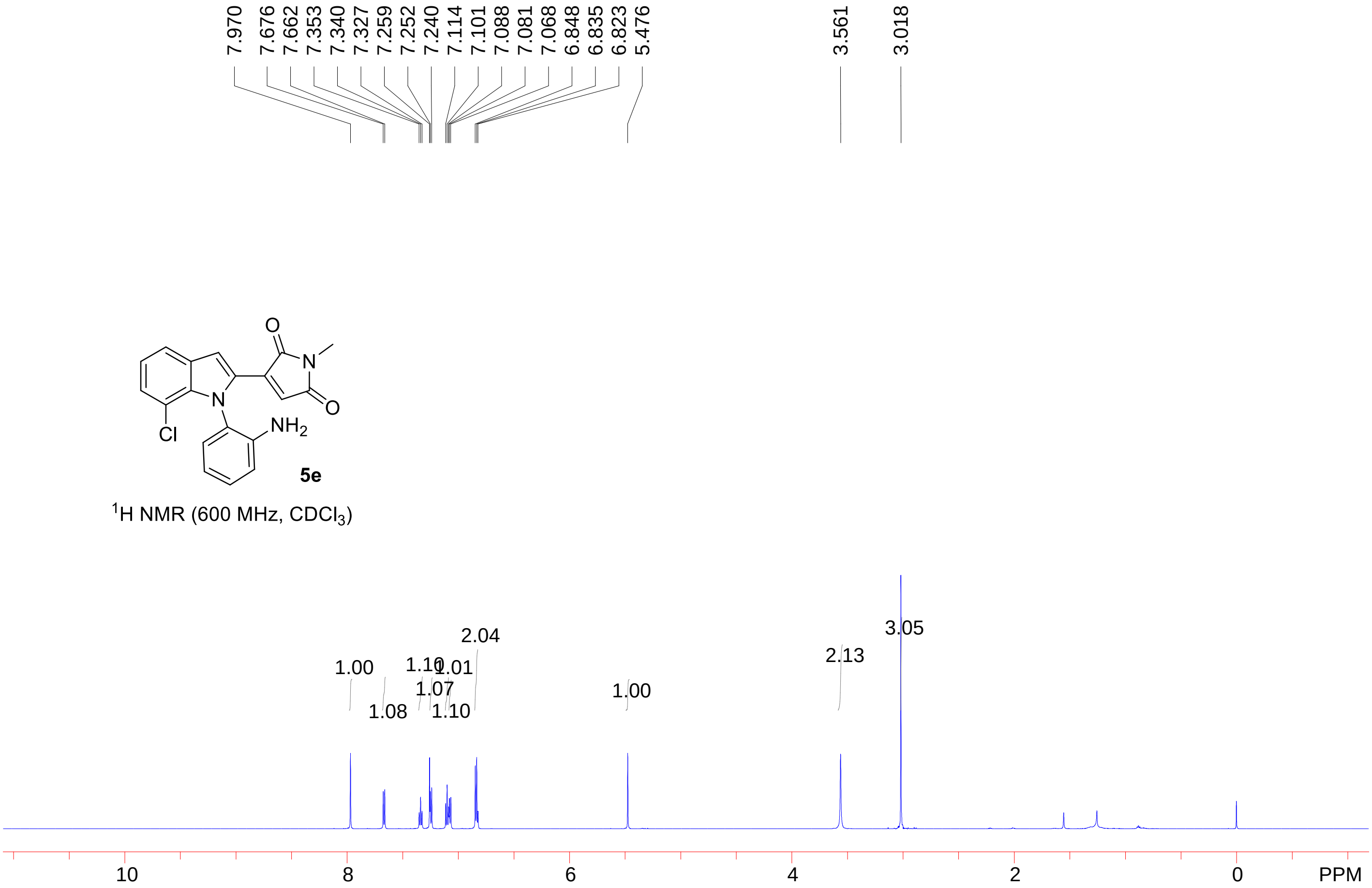
^{13}C{^{1}H} (150 MHz, $CDCl_3$)

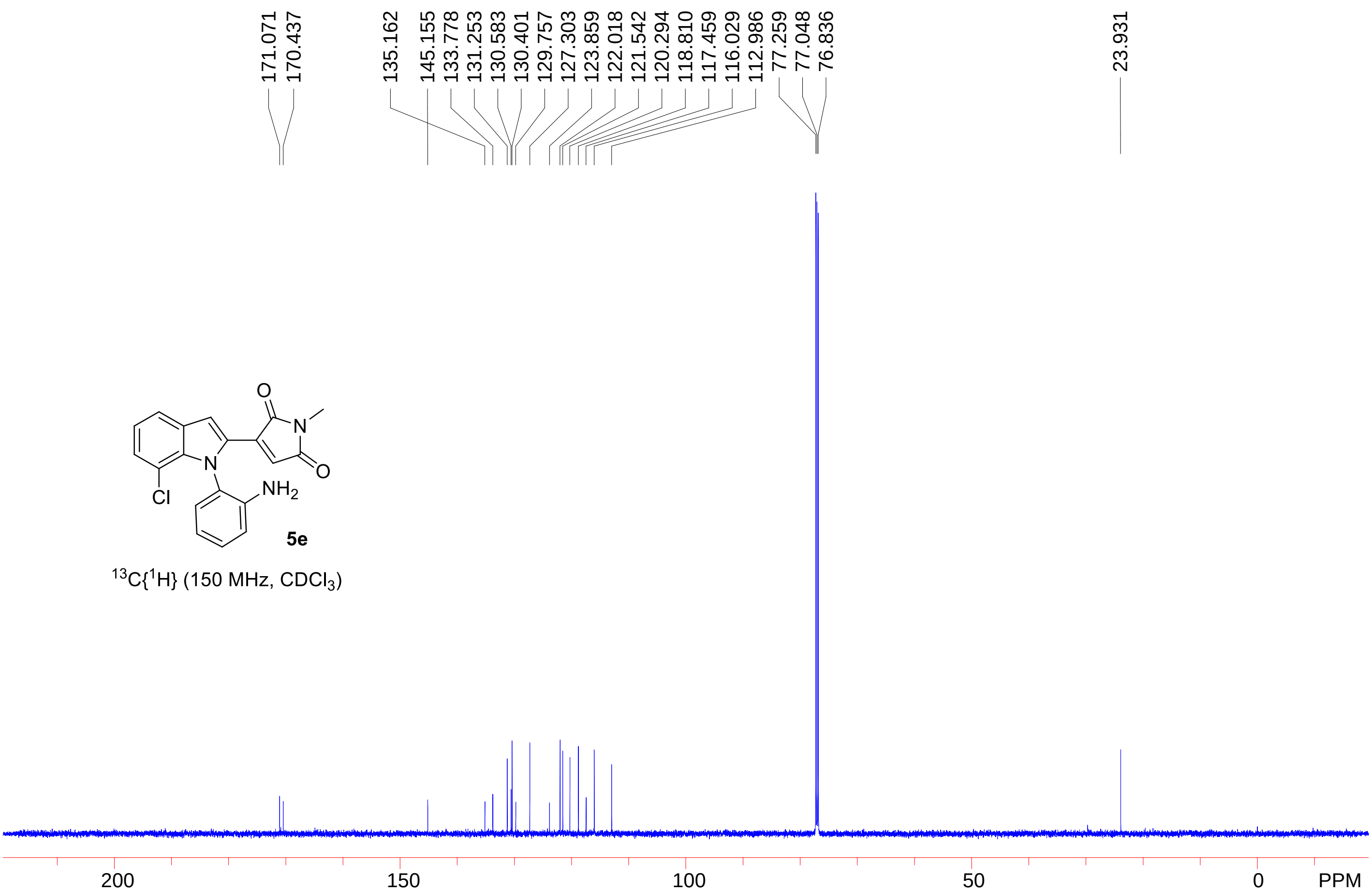

7.996
7.370
7.368
7.356
7.344
7.342
7.259
7.201
7.192
7.188
7.179
7.174
7.166
7.094
7.093
7.082
7.080
6.917
6.915
6.902
6.890
6.888
6.877
6.875
6.856
6.842
6.839
6.826
6.784
6.770
5.569
3.506
3.014
F
O
N
N
H2N
O
5d
1H NMR (600 MHz, CDCl3)
1.00
2.10
1.03
1.08
1.07
1.05
1.04
0.98
2.05
3.07
10
8
6
4
2
0
PPM

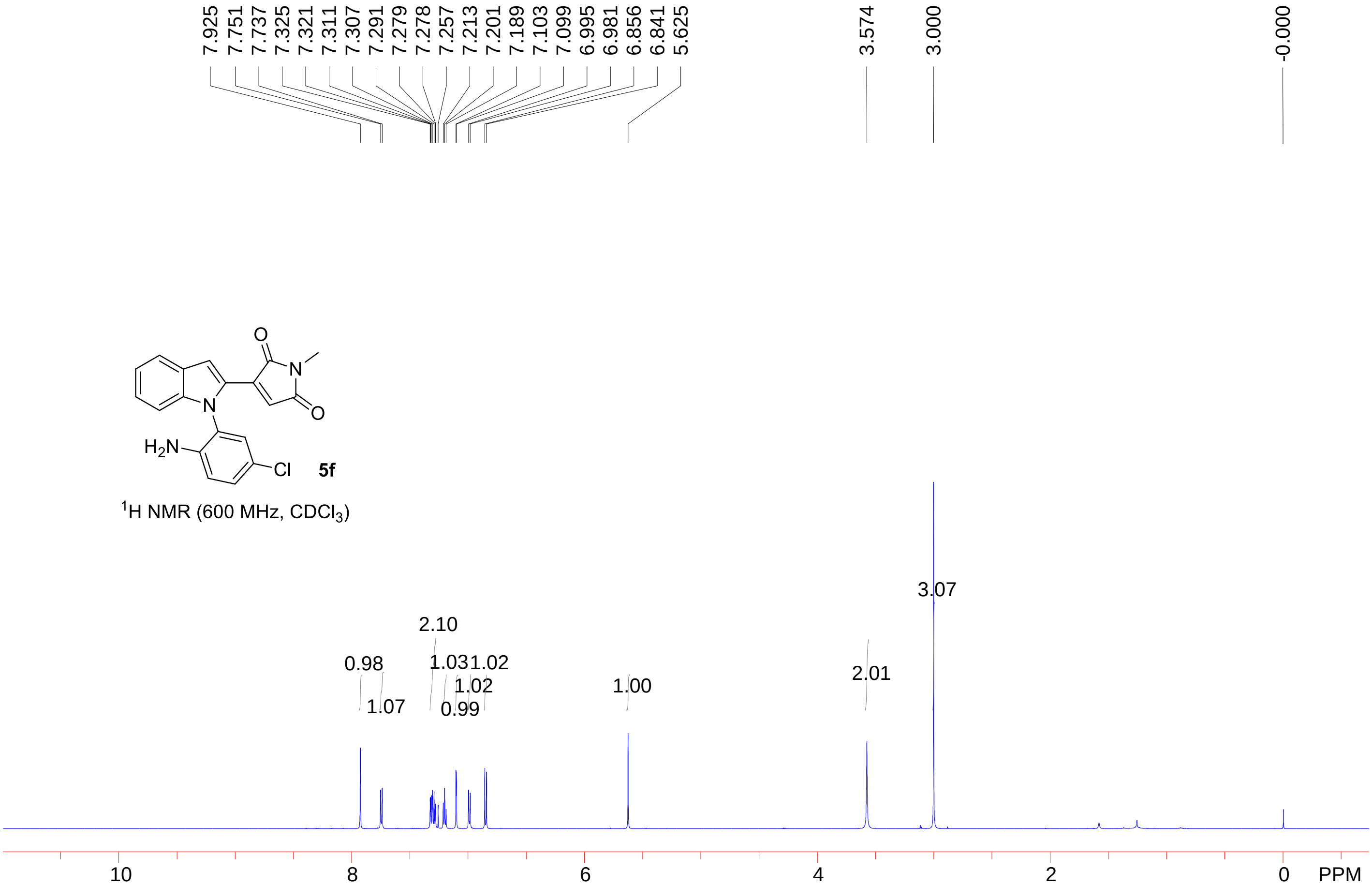

171.075
170.175
158.028
156.356
144.006
142.513
142.444
133.994
131.225
129.495
128.149
126.523
126.472
122.207
119.637
119.412
117.722
117.569
116.749
108.261
106.789
106.772
106.142
106.019
77.275
77.063
76.851
23.913
F
O
N
N
H2N
O
5d
13C{1H} (150 MHz, CDCl3)
200
150
100
50
0
PPM

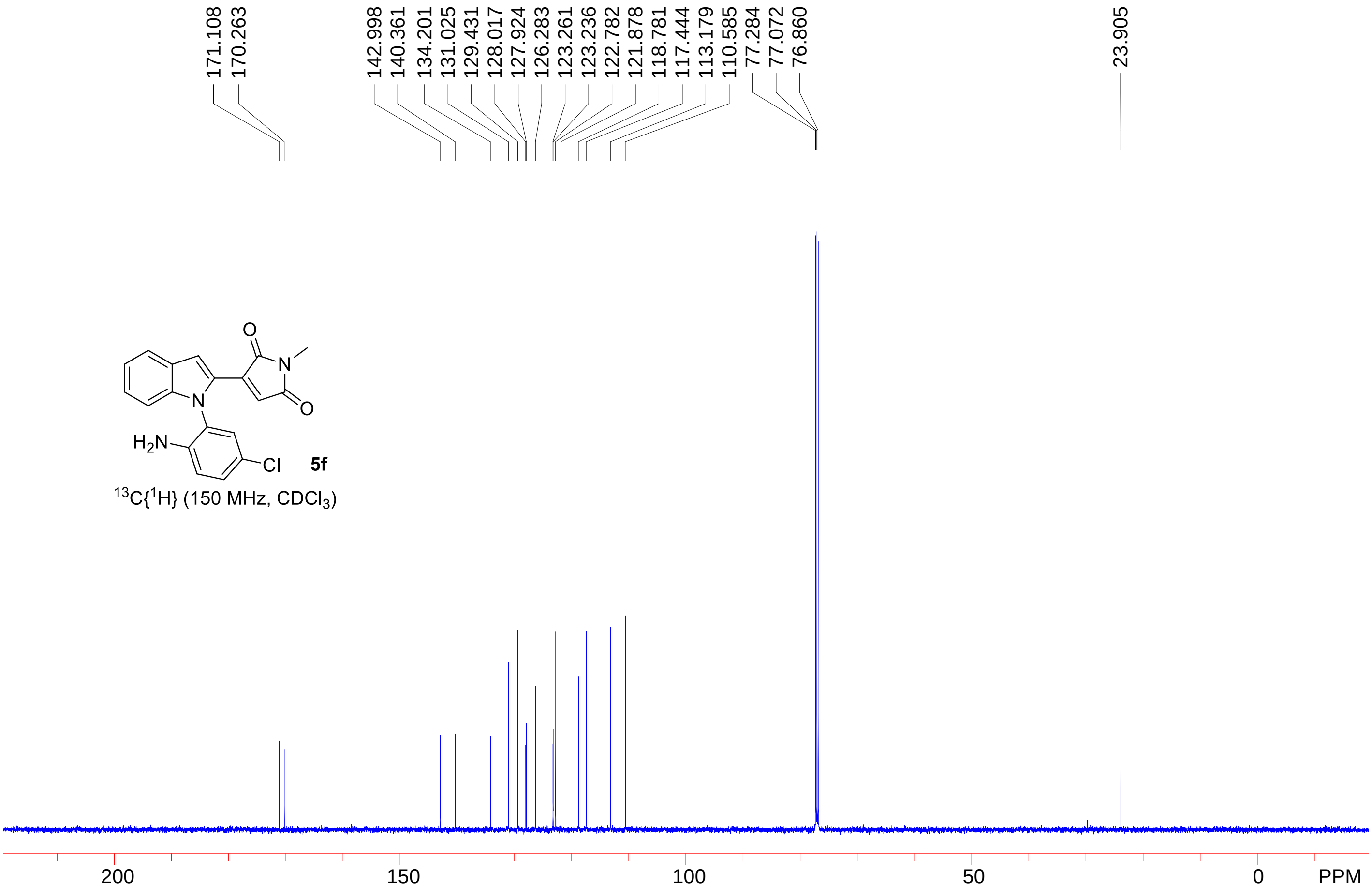


^{19}F NMR (565 MHz, $CDCl_3$)

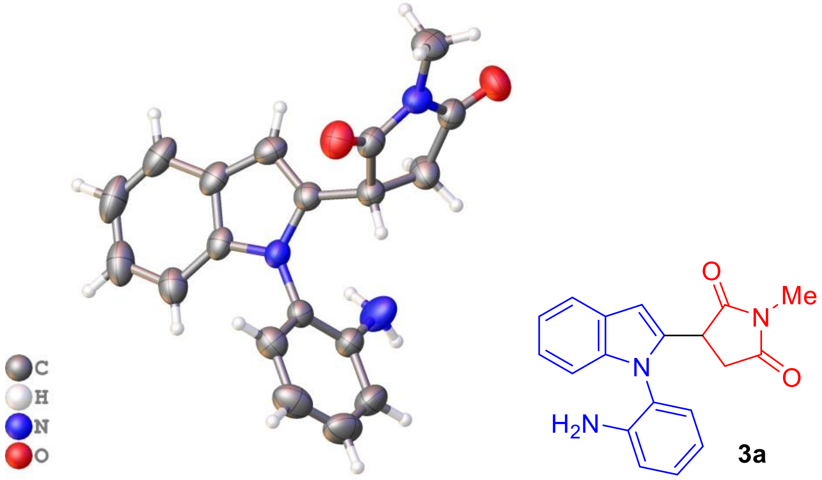

7.970 7.676 7.662 7.353 7.340 7.327 7.259 7.252 7.240 7.114 7.101 7.088 7.081 7.068 6.848 6.835 6.823 5.476
3.561 3.018
Cl
N
O
NH2
5e
1H NMR (600 MHz, CDCl3)
1.00 1.08 1.10 1.07 1.01 1.10 2.04 1.00 2.13 3.05
10 8 6 4 2 0 PPM


171.071 170.437 135.162 145.155 133.778 131.253 130.583 130.401 129.757 127.303 123.859 122.018 121.542 120.294 118.810 117.459 116.029 112.986 77.259 77.048 76.836 23.931
Cl
N
O
NH2
5e
13C{1H} (150 MHz, CDCl3)
200 150 100 50 0 PPM


7.925
7.751
7.737
7.325
7.321
7.311
7.307
7.291
7.279
7.278
7.257
7.213
7.201
7.189
7.103
7.099
6.995
6.981
6.856
6.841
5.625
3.574
3.000
-0.000
O
N
O
N
H2N
Cl
5f
1H NMR (600 MHz, CDCl3)
3.07
2.10
0.98
1.031.02
1.02
1.07
0.99
1.00
2.01
10
8
6
4
2
0
PPM


171.108
170.263
142.998
140.361
134.201
131.025
129.431
128.017
127.924
126.283
123.261
123.236
122.782
121.878
118.781
117.444
113.179
110.585
77.284
77.072
76.860
23.905
O
N
O
N
H2N
Cl
5f
13C{1H} (150 MHz, CDCl3)
200
150
100
50
0
PPM

VIII. X-ray crystal structure and data of 3a



3a

Fig. S1 X-ray crystal structure of **3a** with 50% ellipsoid probability

X-ray structure determination. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent from a petroleum ether/ethyl acetate (4:1) solution of **3a**. Crystal data collection and refinement parameters of **3a** are summarized in Table S1. Intensity data were collected at 293 K on a SuperNova Dual diffractometer using mirror-monochromated Cu Kα radiation, λ = 1.54184 Å. The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections based on the multi-scan technique. Using Olex2, the structure was solved with the SHELXS structure solution program using Direct Methods and refined with the SHELXL refinement package using Least Squares minimisation. Nonhydrogen atoms were refined with anisotropic displacement parameters. The H-atoms were either located or calculated and subsequently treated with a riding model.

Table S1 Crystallographic data and structure refinement results of **3a**

Empirical formula	$C_{19}H_{17}N_3O_2$
Formula weight	319.35
Temp, K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a, Å	11.5596(3)
b, Å	10.6483(2)
c, Å	14.4503(3)

α (°)	90
β (°)	112.178(3)
γ (°)	90
Volume, Å^3	1647.09(7)
Z	4
d_{calc}, g cm^{-3}	1.288
λ, Å	1.54184
μ, mm^{-1}	0.691
No. of data collected	7714
No. of unique data	3141
R_{int}	0.0223
Goodness-of-fit on F^2	1.147
R_1, wR_2 ($I > 2\sigma(I)$)	0.0551, 0.1639
R_1, wR_2 (all data)	0.0647, 0.1691

IX. X-ray crystal structure and data of 4a

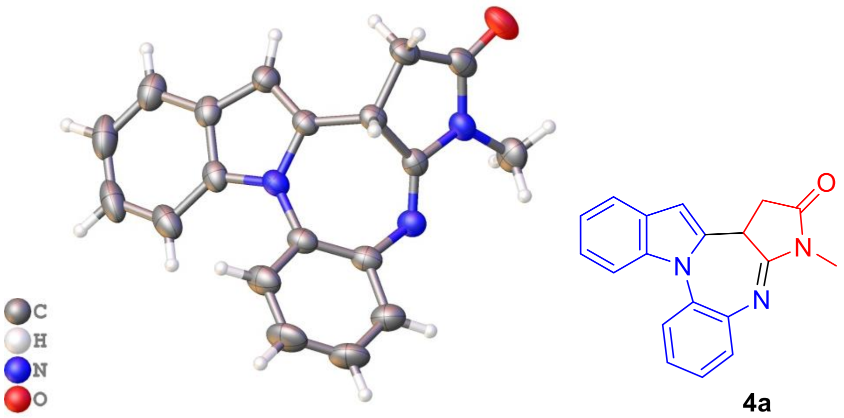


Fig. S2 X-ray crystal structure of **4a** with 50% ellipsoid probability

X-ray structure determination. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent from a petroleum ether/ethyl acetate (4:1) solution of **4a**. Crystal data collection and refinement parameters of **4a** are summarized in Table S2. Intensity data were collected at 293 K on a SuperNova Dual diffractometer using mirror-monochromated Cu Kα radiation, λ = 1.54184 Å. The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections based on the multi-scan technique. Using Olex2, the structure was solved with the SHELXS structure solution program using Direct Methods and refined with the SHELXL refinement package using Least Squares minimisation. Nonhydrogen atoms were refined with anisotropic displacement parameters. The H-atoms were either located or calculated and subsequently treated with a riding model.

Table S2 Crystallographic data and structure refinement results of **4a**

Empirical formula	$C_{19}H_{15}N_3O$
Formula weight	301.34
Temp, K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a, Å	8.6573(2)
b, Å	8.6388(2)
c, Å	19.5245(4)
α (°)	90

β (°)	96.868(2)
γ (°)	90
Volume, Å^3	1449.73(6)
Z	4
d_{calc}, g cm^{-3}	1.381
λ, Å	1.54184
μ, mm^{-1}	0.701
No. of data collected	6282
No. of unique data	2751
R_{int}	0.0200
Goodness-of-fit on F^2	1.257
R_1, wR_2 ($I > 2\sigma(I)$)	0.0529, 0.1427
R_1, wR_2 (all data)	0.0668, 0.1474

X. References

1. T. U. Thikekar and C.-M. Sun, Palladium-Catalyzed Regioselective Synthesis of 1,2-Fused-Indole Diazepines via [5+2] Annulation of *o*-Indoloanilines with Alkynes, *Adv. Synth. Catal.*, **2017**, *359*, 3388-3396.
2. A. Mandal, H. Sahoo, S. Dana and M. Baidya, Ruthenium(II)-Catalyzed Hydroarylation of Maleimides Using Carboxylic Acids as a Traceless Directing Group, *Org. Lett.*, **2017**, *19*, 4138-4141.