Supporting Information

Linker modified immobilized pipearzine based catalyst on ordered short channel mesoporous silica as an effective recyclable catalyst in base catalyzed organic transformations of isatins

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Methods and Materials

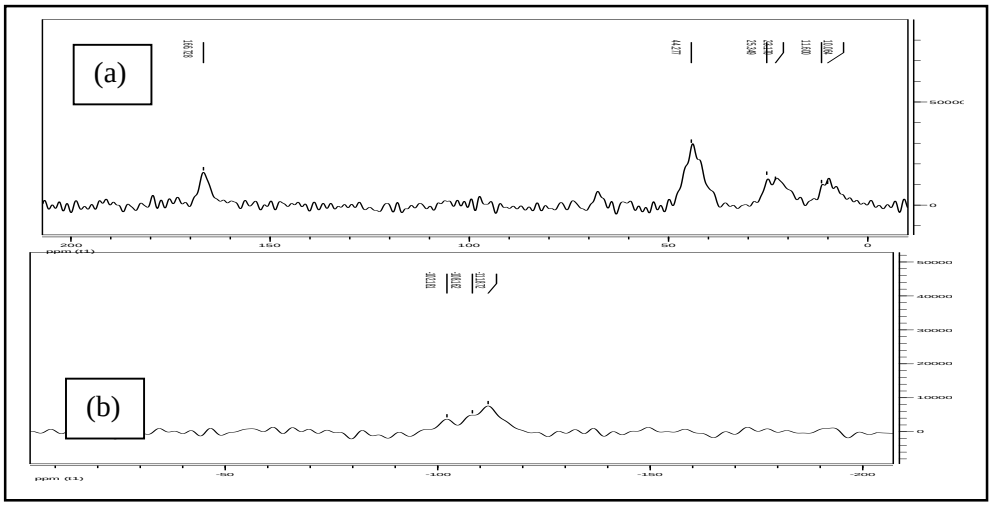
Different ketones (purchased from TCI Chemicals) and reagents were used as received. All the isatin derivatives were purchased from Sigma Aldrich. Malononitrile was purchased from S D fine chemicals, India and used as received. Solvents used mainly THF was used as such. NMR spectra were obtained with a Bruker F113V spectrometer (200 and 500 MHz) and were referenced internally with tetramethylsilane (TMS). Splitting patterns were reported as s, singlet; d, doublet; dd, doublet of doublet; t, triplet; q, quartet; m, multiplet; br, broad. For the purification of product flash chromatography was performed using silica gel 100–200 mesh.

Hammet indicator experiment AFMS and IMPC

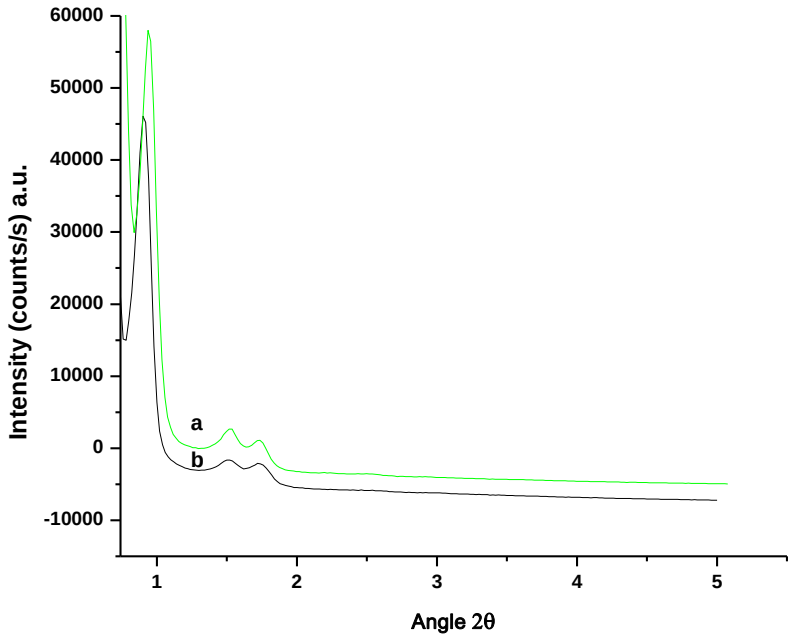
Basicity of the catalyst was determined by using Hammett Indicator Experiment[1]. In the determination of Basicity 100 mg of Support Material (**AFMS**) Solid Catalyst (**IMPC**) was dissolved in 4 mL of Benzene separately. 0.2 mL of Hammett Indicator BTB (12.8 mg diluted in 10 mL of Benzene) was then added to both the above solution containing **AFMS** and **IMPC**. Both the solutions was then tritrated with .1N solution of Benzoic Acid in benzene. The end point was then noted with sharp color change from light green to light yellow. The amount of Benzoic acid (.1N) consumed for **AFMS** and **IMPC** was (30 µL) and (360 µL) respectively. The basicity was calculated and expressed in units of

mmoles/g from the titre of 0.1 N benzoic acid acid required for the amount of solid sample, which was found to be **.029mmol/g** for **AFMS** and 0.360mmol/g for **IMPC**.

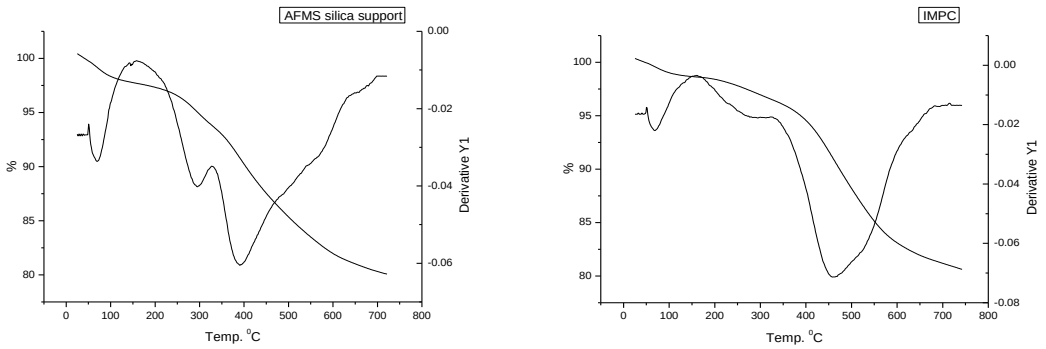
Solid state ^{13}C NMR (a) and ^{29}Si-NMR (b) spectra of IMPC



PXRD pattern of support material AFMS (**a**) and immobilized melamine piperazine core IMPC (**b**)

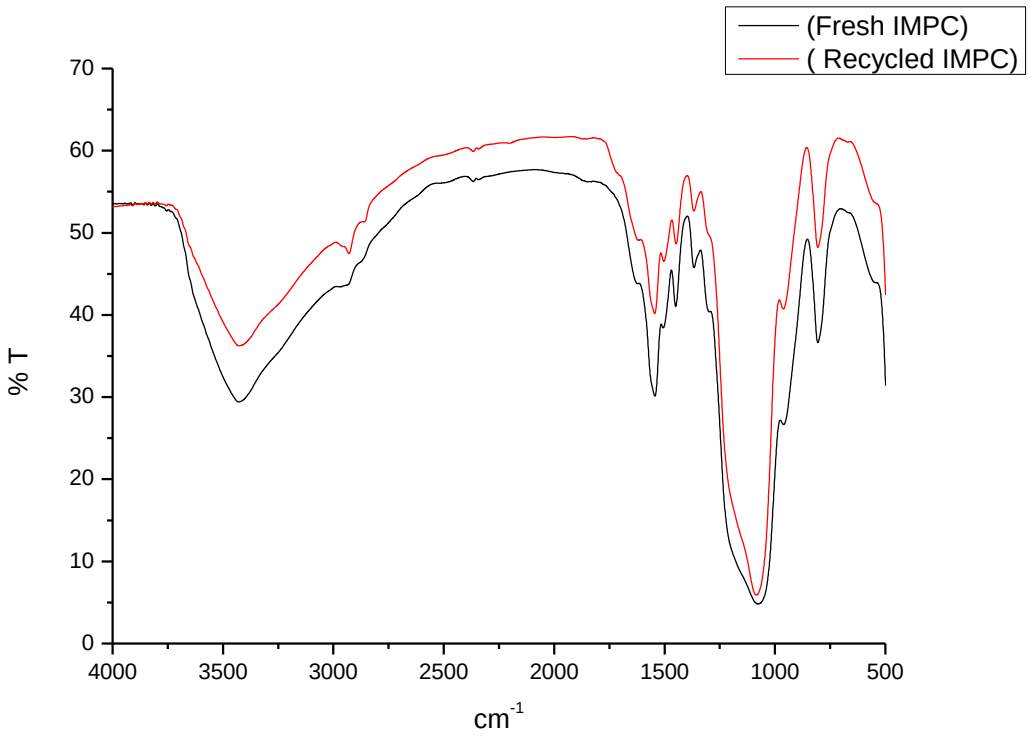


TGA Profile of the Silica Support (a) and Melamine Piperazine Core IMPC (b)

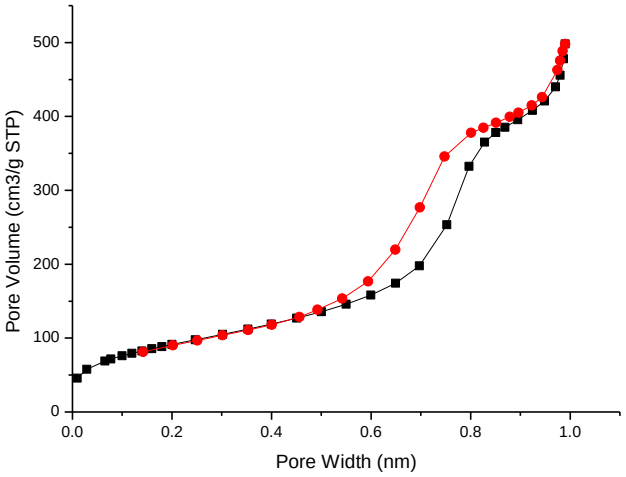


(a) (b)

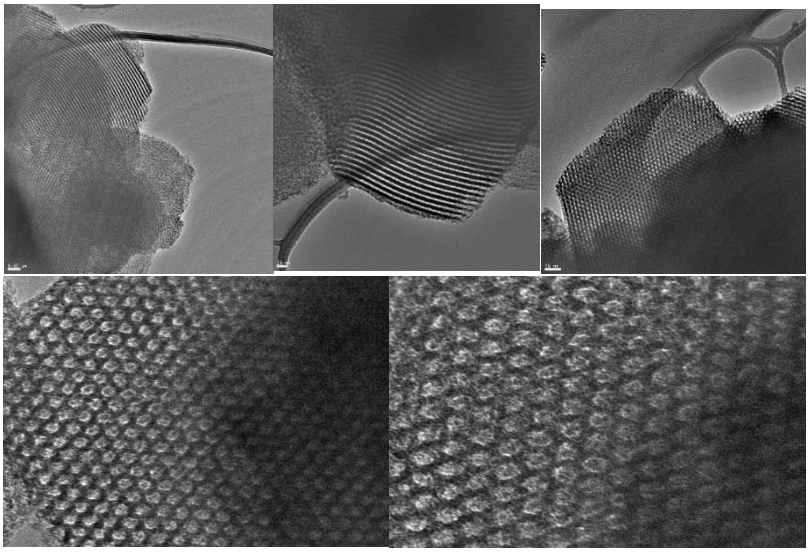
IR profile of the Fresh catalyst IMPC and Recycled IMPC



N_2 adsorption and desorption isotherm of Recycled Catalyst (IMPC)

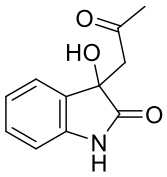


TEM Images of the recycled catalyst IMPC



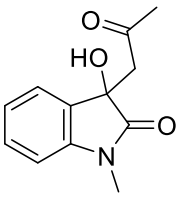
Compound Characterization Data- Cross Aldol Condensation (3aa-3hf)

3-hydroxy-3-(2-oxopropyl)indolin-2-one (3aa)[2]



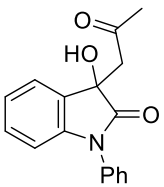
White Solid, yield 98%; ^{1}H NMR (200 MHz, d_6-DMSO): δ 10.22 (s, 1H)**,** 7.13-7.26 (dd, *J* = 7.40, 10.40 Hz, 2H), 6.86-6.93 (t, *J* = 7.40 Hz, 1H), 6.76-6.80 (d, *J* = 7.60 Hz, 1H), 5.98 (s, 1H), 3.32 (d, *J* = 16.40 Hz, 1H), 3.04 (d, *J* = 16.60 Hz, 1H), 2.00 (s, 3H) ppm; ^{13}C NMR (50 MHz, d_6-DMSO): δ 205.12, 178.12, 142.47, 131.46, 128.94, 123.64, 121.20, 109.39, 72.62, 50.22, 30.51 ppm; TOF–MS (ESI+Na^+) Calcd. for ($C_{11}H_{11}NO_3$+Na^+) 228.07, Found: 228.01.

3-hydroxy-1-methyl-3-(2-oxopropyl)indolin-2-one (3ba)[3a,b]



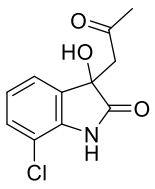
White Solid, Yield 90% , ^{1}H NMR (500 MHz, d_6-DMSO): δ 7.26-7.30 (m, 2H), 6.97-7.00 (t, *J* = 7.50 Hz, 1H), 6.95 (d, *J* = 8.00 Hz, 1H), 6.08 (s, 1H), 3.36 (d, *J* = 16.50 Hz, 1H), 3.09 (s, 3H), 3.06 (br, 1H), 1.98 (s, 3H) ppm; ^{13}C NMR (125 MHz, d_6-DMSO): δ 205.17, 176.51, 144.03, 130.86, 129.16, 123.23, 121.97, 108.26, 72.34, 50.40, 30.44, 25.89 ppm; TOF–MS (ESI+H^+) Calcd. for ($C_{12}H_{13}NO_3$+H^+) 220.08, Found: 220.01

3-hydroxy-3-(2-oxopropyl)-1-phenylindolin-2-one (3ca)



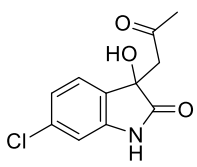
White Solid, Yield 92%, ^{1}H NMR (500 MHz, d_6-DMSO): δ 7.57-7.60 (t, *J* = 7.70 Hz, 2H)**,** 7.39-7.47 (m, 4H), 7.20-7.23 (t, *J* = 7.70 Hz, 1H), 7.03-7.06 (t, *J* = 7.50 Hz, 1H), 6.68 (d, *J* = 8.00 Hz, 1H), 6.27 (s, 1H), 3.54 (d, *J* = 17.00 Hz, 1Hz), 3.25 (d, *J* = 17.00 Hz, 1H), 2.02 (s, 3H) ppm; ^{13}C NMR (125 MHz, d_6-DMSO): δ 205.44, 176.09, 143.92, 134.61, 130.69, 129.52, 129.10, 127.80, 126.47, 123.73, 122.49, 108.61, 72.27, 50.89, 30.19 ppm; TOF-MS (ESI+Na^+) Calcd. for ($C_{17}H_{15}NO_3$+Na^+) 304.11, Found: 304.26.

7-chloro-3-hydroxy-3-(2-oxopropyl)indolin-2-one (3da)[3b]



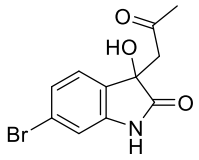
White solid, yield 95%, ^{1}H NMR (500 MHz, d_6-DMSO): δ 10.65 (s, 1H), 7.25 (d, *J* = 8.00 Hz, 1Hz), 7.22 (d, *J*=7.00 Hz, 1H), 6.91-6.94 (t, *J* = 7.50 Hz, 1H), 6.14 (s, 1H), 3.34 (brs, 1H), 3.11 (d, *J* = 17.00 Hz, 1H), 2.0 (s, 3H) ppm; ^{13}C NMR (125 MHz, d_6-DMSO): δ 205.25, 178.05, 140.30, 133.54, 128.88, 122.57, 122.15, 113.57, 73.02, 50.10, 30.26 ppm; TOF–MS (ESI+Na^+) Calcd. for ($C_{11}H_{10}ClNO_3$+Na^+) 262.03, Found: 262.19.

6-chloro-3-hydroxy-3-(2-oxopropyl)indolin-2-one (3ea)[4]



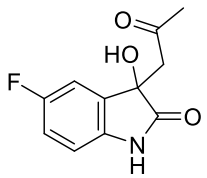
White Solid, Yield 94%, ^{1}H NMR (500 MHz, d_6-DMSO): δ 10.38 (s, 1H), 7.26 (d, *J* = 8.00 Hz, 1H), 6.96 (d, *J* = 8.00 Hz, 1H), 6.79 (s, 1H), 6.07 (s, 1H), 3.35 (d, *J* = 17.00 Hz, 1Hz), 3.07 (d, *J* = 17.50 Hz, 1H), 2.00 (s, 3H) ppm; ^{13}C NMR (125 MHz, d_6-DMSO): δ 205.24, 178.08, 144.18, 133.11, 130.48, 125.08, 120.84, 109.43, 72.11, 49.98, 30.33 ppm; TOF-MS (ESI+Na^+) Calcd. for exact ($C_{11}H_{10}ClNO_3$+Na^+) 262.03, Found: 262.22.

6-bromo-3-hydroxy-3-(2-oxopropyl)indolin-2-one (3fa)[4]



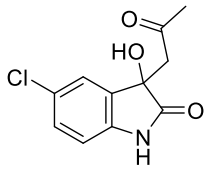
White Solid, Yield 91%, ^{1}H NMR (500 MHz, d_6-DMSO): δ 10.39 (s, 1H), 7.20 (d, *J* = 7.80 Hz, 1H), 7.07-7.11 (m, 1H), 6.94 (d, *J* = 1.60 Hz, 1H), 6.11 (s, 1H), 3.30 (br, 1H), 3.10 (d, *J* = 17.20 Hz, 1H), 2.00 (s, 3H) ppm; ^{13}C NMR (125 MHz, d_6-DMSO): δ 205.13, 177.89, 144.29, 130.88, 125.42, 123.69, 121.43, 112.11, 72.13, 49.91, 30.28 ppm; TOF-MS (ESI-H^+) Calcd. for exact ($C_{11}H_{10}BrNO_3$-H^+) 281.98, Found: 282.14.

5-fluoro-3-hydroxy-3-(2-oxopropyl)indolin-2-one (3ga)[3b,4]



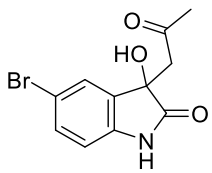
White Solid, Yield 93%, ^{1}H NMR (200 MHz, d_6-DMSO): δ 10.24 (s, 1H), 7.11-7.17 (dd, *J* = 2.60, 5.60 Hz, 1H), 6.94-7.05 (m, 1H), 6.72-6.79 (dd, *J* = 4.40, 4.00 Hz, 1H), 6.10 (s, 1H), 3.36 (d, *J*=17.00 Hz, 1H), 3.07 (d, *J* = 17.00 Hz, 1H), 2.01 (s, 3H) ppm; ^{13}C NMR (125 MHz, d_6-DMSO): δ 205.23, 178.16, 158.75, 156.87, 138.73, 133.36, 133.30, 115.08, 114.90, 111.69, 111.50, 110.10, 110.04, 72.84, 49.98, 30.37 ppm; TOF-MS (ESI+Na^+) Calcd. for ($C_{11}H_{10}FNO_3$+Na^+) 246.06, Found: 246.19.

5-chloro-3-hydroxy-3-(2-oxopropyl)indolin-2-one (3ha)[3b]



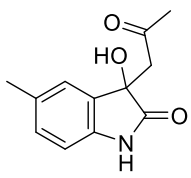
White Solid, Yield 94%, ^{1}H NMR (500 MHz, d_6-DMSO): δ 10.35 (s, 1H), 7.31 (s, 1H), 7.21-7.22 (d, *J* = 8.50 Hz, 1Hz), 6.79 (d, *J* = 8.00 Hz, 1H), 6.10 (s, 1H), 3.40 (br, 1H), 3.08 (d, *J* = 17.00 Hz, 1H), 2.01 (s, 3H) ppm; ^{13}C NMR (125 MHz, d_6-DMSO): δ 205.28, 177.85, 141.53, 133.69, 128.63, 125.16, 123.91, 110.77, 72.56, 49.89, 30.25 ppm; TOF-MS (ESI+Na^+) Calcd. for ($C_{11}H_{10}ClNO_3$+Na^+) 262.03, Found: 262.09.

5-bromo-3-hydroxy-3-(2-oxopropyl)indolin-2-one (3ia)[4]



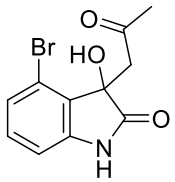
White Solid, Yield 90%, ^{1}H NMR (500 MHz, d_6-DMSO): δ 10.37 (s, 1H), 7.43 (s, 1H), 7.34-7.36 (s, *J* = 8.00 Hz, 1H), 6.74-6.76 (d, *J* = 8.00 Hz, 1H), 6.11 (s, 1H), 3.37 (br, 1H), 3.08 (d, *J* = 17.50 Hz, 1H), 2.00 (s, 3H) ppm; ^{13}C NMR (125 MHz, d_6-DMSO): δ 205.35, 177.75, 141.97, 134.12, 131.52, 126.62, 126.92, 112.92, 111.38, 72.55, 49.91, 30.27 ppm; TOF-MS (ESI+Na^+) Calcd. for ($C_{11}H_{10}BrNO_3$+Na^+) 305.98, Found: 305.99.

3-hydroxy-5-methyl-3-(2-oxopropyl)indolin-2-one (3ja)[4]



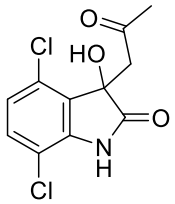
White Solid, Yield 90%, ^{1}H NMR (200 MHz, d_6-DMSO): δ 10.10 (s, 1H), 7.05 (s, 1H), 6.95-6.99 (d, *J* = 8.00 Hz, 1H), 6.64-6.68 (d, *J* = 8.00 Hz, 1H), 5.93 (s, 1H), 3.28 (d, *J* = 17.00 Hz, 1H), 3.02 (d, *J* = 16.50 Hz, 1H), 2.22 (s, 3H), 2.00 (s, 3H) ppm; ^{13}C NMR (125 MHz, d_6-DMSO): δ 205.11, 178.11, 139.97, 131.52, 129.93, 129.06, 124.29, 109.11, 72.68, 50.24, 30.50, 20.63 ppm; TOF-MS (ESI+Na^+) Calcd. for ($C_{11}H_{10}ClNO_3$+Na^+) 242.09, Found: 242.19.

4-bromo-3-hydroxy-3-(2-oxopropyl)indolin-2-one (3ka)[5a,b]



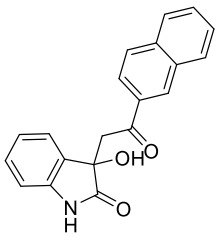
White Solid, Yield 88% , ^{1}H NMR (500 MHz, d_6-DMSO): δ 10.46 (s, 1H), 7.11 (t, *J* =7.70 Hz, 1H), 7.04 (d, *J* = 8.00 Hz, 1H), 6.79 (d, *J* = 7.50 Hz, 1H), 6.12 (s, 1H), 3.75 (d, *J* =17.0 Hz, 1H), 3.14 (d, *J* = 7.50 Hz, 1H), 2.10 (s, 3H) ppm; ^{13}C NMR (125 MHz, d_6-DMSO): δ 205.08, 177.32, 145.06, 130.88, 129.02, 125.07, 118.21, 108.92, 73.95, 48.29, 30.04 ppm; TOF-MS (ESI+Na^+) Calcd. for ($C_{11}H_{10}BrNO_3$+Na^+) 305.98, Found: 305.94.

4, 7-dichloro-3-hydroxy-3-(2-oxopropyl)indolin-2-one (3la)[6]



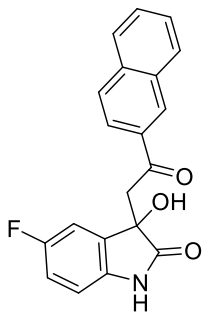
White Solid, Yield 92%, ^{1}H NMR (200 MHz, d_6-DMSO): δ 10.90 (s, 1H), 7.29 (d, *J* = 8.80 Hz, 1H), 6.92 (d, *J* = 8.80 Hz, 1H), 6.30 (s, 1H), 3.74 (d, *J* = 17.60 Hz, 1H), 3.25 (d, *J* = 17.80 Hz, 1H), 2.03 (s, 3H) ppm; ^{13}C NMR (125 MHz, d_6-DMSO): δ 205.26, 177.19, 142.31, 130.35, 128.96, 128.23, 123.13, 112.68, 73.94, 48.37, 29.83 ppm; TOF-MS (ESI+H^+) Calcd. for ($C_{11}H_9Cl_2NO_3$+H^+) 274.00, Found: 274.10.

3-hydroxy-3-(2-(naphthalen-2-yl)-2-oxoethyl)indolin-2-one (3ab)[7]



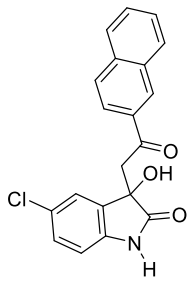
White Solid, Yield 90%, ^{1}H NMR (500 MHz, d_6-DMSO): δ 10.31 (s, 1H), 8.70 (s, 1H), 8.14 (d, *J* = 8.00 Hz, 1H), 7.97 (t, *J* = 7.50 Hz, 2H), 7.82 (d, *J* = 8.50 Hz, 1H), 7.63-7.68 (m, 2H), 7.31 (d, *J* = 7.00 Hz, 1H), 7.16 (t, *J* = 7.50 Hz, 1H), 6.82-6.86 (m, 2H), 6.13 (s, 1H), 4.25 (d, *J* = 17.50 Hz, 1H), 3.73 (d, *J* = 17.50 Hz, 1H) ppm.; ^{13}C NMR (125 MHz, d_6-DMSO): δ 196.40, 178.35, 142.91, 135.02, 133.41, 132.06, 131.69, 130.25, 129.65, 128.91, 128.74, 128.22, 127.58, 126.92, 123.60, 123.10, 121.10, 109.38, 73.10, 45.72 ppm; TOF-MS (ESI+Na^+) Calcd. for exact ($C_{20}H_{15}NO_3^+$) 340.11, Found: 340.18.

5-fluoro-3-hydroxy-3-(2-(naphthalen-2-yl)-2-oxoethyl)indolin-2-one (3gb)



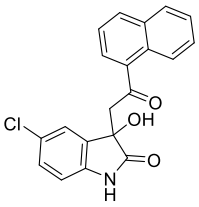
White Solid, Yield 92%, ^{1}H NMR (500 MHz, d_6-DMSO): δ 10.35 (s, 1H), 8.69 (s, 1H), 8.15 (d, *J* = 8.00 Hz, 1H), 7.99 (d, *J* = 8.00 Hz, 2H), 7.84 (d, *J* = 8.00 Hz, 1H), 7.63-7.68 (m, 2H), 7.26 (d, *J* = 7.50 Hz, 1H), 6.99-7.02 (t, *J* = 8.00 Hz, 1H), 6.83 (br, 1H), 6.27 (s, 1H), 4.29 (d, *J* = 7.50, 1H), 3.78 (d, *J* = 17.50 Hz, 1H) ppm; ^{13}C NMR (125 MHz, d_6-DMSO): δ 196.91, 178.83, 159.20, 157.32, 139.56, 135.54, 134.06, 134.00, 133.78, 132.53, 130.76, 130.13, 129.27, 128.73, 128.09, 127.45, 123.58, 115.50, 115.32, 112.18, 111.99, 110.55, 110.49, 73.85, 46.18 ppm; TOF-MS (ESI+Na^+) Calcd. for exact ($C_{20}H_{14}FNO_3$+Na^+) 358.10, Found: 358.18.

5-chloro-3-hydroxy-3-(2-(naphthalen-2-yl)-2-oxoethyl)indolin-2-one (3hb)



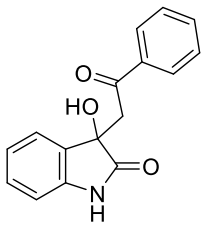
White Solid, Yield 95% , ^{1}H NMR (500 MHz, d_6-DMSO): δ 10.47 (s, 1H), 8.70 (s, 1H), 8.15 (d, *J* = 7.50 Hz, 1H), 7.99 (d, *J* = 8.00 Hz, 2H), 7.85 (d, *J* = 8.50 Hz, 1H), 7.64-7.68 (m, 2H), 7.44 (s, 1H), 7.24 (d, *J* = 8.00 Hz, 1H), 6.87 (d, *J* = 8.00 Hz, 1H), 6.29 (s, 1H), 4.34 (d, *J* = 17.50 Hz, 1H), 3.80 (d, *J*=17.50 Hz, 1H) ppm; ^{13}C NMR (125 MHz, d_6-DMSO): δ 196.49, 178.09, 141.87, 135.07, 133.93, 133.21, 132.04, 130.32, 129.66, 128.79, 128.64, 128.25, 127.61, 126.96, 125.15, 123.97, 123.09, 110.81, 73.15, 45.73 ppm; TOF-MS (ESI+Na^+) Calcd. for exact ($C_{20}H_{14}ClNO_3$+Na^+) 374.06 Found 374.11

3-hydroxy-3-(2-(naphthalen-1-yl)-2-oxoethyl)indolin-2-one (3hc)



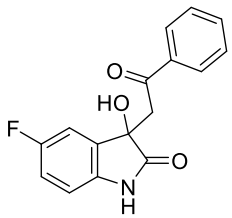
White Solid, Yield 85%, ^{1}H NMR (500 MHz, d_6-DMSO): δ 10.47 (s, 1H), 8.10-8.14 (m, 3H), 7.98 (d, *J* = 6.50 Hz, 1H), 7.53-7.61 (m, 4H), 7.44 (s, 1H), 7.23 (d, *J* = 6.50 Hz, 1H), 6.84 (d, *J* = 7.50 Hz, 1H), 6.28 (s, 1H), 4.18 (d, *J* = 17.00 Hz, 1H), 3.74 (d, *J* = 17.00 Hz, 1H) ppm; ^{13}C NMR (125 MHz, d_6-DMSO): δ 201.25, 178.53, 142.22, 135.00, 134.19, 133.81, 133.26, 129.54, 129.18, 129.01, 128.93, 128.22, 126.85, 125.73, 125.32, 125.23, 124.59, 111.35, 73.80, 49.35 ppm; TOF-MS (ESI-H^+) Calcd. for exact ($C_{20}H_{14}ClNO_3$-H^+) 350.07, Found: 350.30.

3-hydroxy-3-(2-oxo-2-phenylethyl)indolin-2-one (3ad)[3b,18]



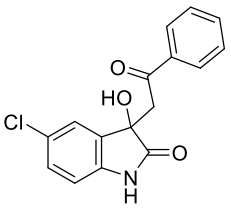
White Solid, Yield 90% , ^{1}H NMR (500 MHz, d_6-DMSO): δ 10.26 (s, 1H), 7.88 (d, *J* = 8.00 Hz, 1H), 7.62 (t, *J* = 7.50 Hz, 1H), 7.47-7.50 (m, 2H), 7.27 (d, *J* = 7.00 Hz, 1H), 7.16 (t, *J* = 7.50 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.07 (s, 1H), 4.06 (d, *J* = 17.50 Hz, 1H), 3.58 (d, *J* = 17.50 Hz, 1H) ppm; ^{13}C NMR (125 MHz, d_6-DMSO): δ 196.43, 178.29, 142.89, 136.08, 133.42, 131.68, 128.88, 128.74, 128.62, 123.86, 123.57, 123.51, 121.08, 109.36, 72.94, 45.69 ppm; TOF-MS (ESI+H^+) Calcd. for exact ($C_{16}H_{13}NO_3$+H^+) 268.09, Found: 268.04

5-fluoro-3-hydroxy-3-(2-oxo-2-phenylethyl)indolin-2-one (3gd)[8a,b]



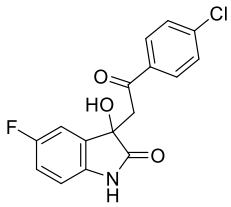
White Solid, Yield 86%, ^{1}H NMR (500 MHz, d_6-DMSO): δ 10.31 (s, 1H), 7.88-7.89 (br, d, 2H), 7.62-7.65 (t, *J* = 7.50 Hz, 1H), 7.49-7.52 (t, *J* = 8.00 Hz, 2H), 7.20-7.22 (m, 1H), 7.01-6.97 (m, 1H), 6.79-6.81 (m, 1H), 6.21 (s, 1H), 4.09-4.12 (d, *J* = 17.50 Hz, 1H), 3.60-3.64 (d, *J* = 18.00 Hz, 1H) ppm; ^{13}C NMR (125 MHz, d_6-DMSO): δ 196.48, 178.30, 156.85, 139.06, 135.98, 133.48, 128.72, 127.88, 115.00, 114.82, 111.65, 111.45, 110.06, 110.00, 73.23, 45.66 ppm; TOF-MS (ESI+Na^+) Calcd. for exact ($C_{16}H_{12}FNO_3$+Na^+) 308.08, Found: 308.19.

5-chloro-3-hydroxy-3-(2-oxo-2-phenylethyl)indolin-2-one (3hd)[8b]



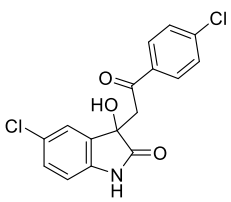
White Solid, Yield 88%, ^{1}H NMR (500 MHz, d_6-DMSO): δ 10.46 (s, 1H), 7.88-7.89 (d, *J* = 7.50 Hz, 2H), 7.61-7.64 (t, *J* = 7.50 Hz, 1H), 7.48-7.51 (t, *J* = 7.50 Hz, 2H), 7.29-7.31 (d, *J* = 7.50 Hz, 1H), 6.90-6.92 (dd, *J* = 6.00, 2.00 Hz, 1H), 6.84 (d, *J* = 2.00 Hz, 1H), 6.20 (s, 1H), 4.09-4.12 (d, *J* = 18.00 Hz, 1H), 3.61-3.65 (d, *J* = 18.00 Hz, 1H) ppm; ^{13}C NMR (125 MHz, d_6-DMSO): δ 196.53, 178.27, 144.54, 135.89, 133.53, 133.12, 130.73, 128.73, 127.88, 125.02, 120.80, 109.48, 72.54, 45.69 ppm; TOF-MS (ESI+Na^+) Calcd. for exact ($C_{16}H_{12}FNO_3$+Na^+) 324.05, Found: 324.09

3-(2-(4-chlorophenyl)-2-oxoethyl)-5-fluoro-3-hydroxyindolin-2-one (3ge)



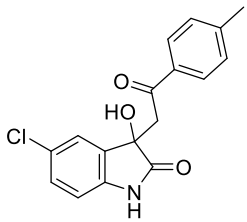
White Solid, Yield 85%, ^{1}H NMR (200 MHz, d_6-DMSO): δ 10.32 (s, 1H), 7.92 (s,1H), 7.88 (s,1H), 7.59, (s, 1H), 7.55 (s,1H), 7.17 (dd, *J* = 2.40, 5.80 Hz, 1H), 6.95-7.05 (m, 1H), 6.77-6.83 (m, 1H), 6.25 (s, 1H), 4.08 (d, *J* = 17.60 Hz), 3.70 (br, 1H) ppm; ^{13}C NMR (125 MHz, d_6-DMSO): δ 195.48, 178.11, 158.66, 156.78, 138.93, 138.32, 134.66, 133.37, 133.31, 129.79, 128.73, 114.73, 114.98, 111.66, 114.47, 110.01, 109.95, 73.17, 45.59 ppm; TOF-MS (ESI+Na^+) Calcd. for exact ($C_{16}H_{11}ClFNO_3$+Na^+) 342.04, Found: 342.01.

5-chloro-3-(2-(4-chlorophenyl)-2-oxoethyl)-3-hydroxyindolin-2-one (3he)



White Solid, Yield 87% , ^{1}H NMR (200 MHz, d_6-DMSO): δ 10.4 (s, 1H), 7.92 (s, 1H), 7.88 (s, 1H), 7.60 (s, 1H), 7.55 (s, 1H), 7.37 (d, *J* = 2.00 Hz, 1H), 7.2 (dd, *J* = 2.00, 6.50 Hz, 1H), 6.83 (d, *J* = 8.20 Hz, 1H), 6.26 (s, 1H), 4.13 (d, *J* = 18.00 Hz, 1H), 3.65 (br, 1H) ppm; ^{13}C NMR (125 MHz, d_6-DMSO): δ 195.54, 177.84, 141.72, 136.35, 134.57, 133.70, 129.80, 128.72, 128.28, 125.09, 123.93, 110.73, 72.93, 45.58 ppm; TOF-MS (ESI+H^+) Calcd. for exact ($C_{16}H_{11}Cl_2NO_3$+H^+) 336.01, Found: 336.22.

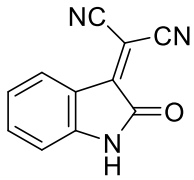
5-chloro-3-hydroxy-3-(2-oxo-2-(p-tolyl)ethyl)indolin-2-one (3hf)



White Solid, Yield 80%, ^{1}H NMR (500 MHz, d_6-DMSO): δ 10.25 (s, 1H), 7.78 (s, 1H), 7.76 (s, 1H), 7.30 (s, 1H), 7.28 (s, 1H), 7.24-7.26 (d, *J* = 7.50 Hz, 1H), 7.15 (t, *J* = 7.50 Hz, 1H), 6.84 (t, *J* = 7.50 Hz, 1H), 6.80 (d, *J* = 8.00 Hz, 1H), 6.04 (s, 1H), 4.03 (d, *J* = 17.50 Hz, 1H), 3.55 (d, *J* = 17.50 Hz, 1H), 2.35 (s, 3H) ppm; ^{13}C NMR (125 MHz, d_6-DMSO): δ 196.39, 178.82, 144.28, 143.42, 134.19, 132.25, 129.71, 129.35, 128.48, 124.01, 121.55, 109.84, 73.45, 46.08, 21.61 ppm; TOF-MS (ESI+H^+) Calcd. for exact ($C_{17}H_{14}ClNO_3$+H^+) 316.06, Found: 316.09

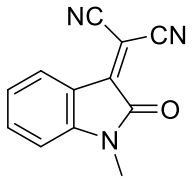
Compound Characterization Data (Knoevenagel Condensation 4a-4k)

2-(2-oxoindolin-3-ylidene)malononitrile (4a)[9a,b]



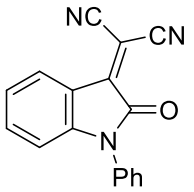
Red Solid, Yield 99%, ^{1}H NMR (500 MHz, d_6-DMSO): δ 11.20 (s, 1H), 7.83 (d, *J* = 3.00 Hz, 1H,), 7.54 (t, *J* = 7.75 Hz, 1H,), 7.09 (t, *J* = 7.75 Hz, 1H) 6.91 (d, *J* = 8.00 Hz, 1H) ppm; ^{13}C NMR (125 MHz, d_6-DMSO): δ 163.7, 150.5, 146.4, 137.9, 125.8, 122.9, 118.5, 113.0, 111.7, 111.5, 80.5 ppm; TOF-MS (ESI+Na^+) Calcd. for exact ($C_{11}H_5N_3O$+Na^+) 218.04, Found: 218.06.

2-(1-methyl-2-oxoindolin-3-ylidene)malononitrile (4b)[9a]



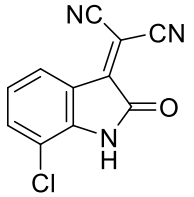
Red Solid, Yield 96%, ^{1}H NMR (200 MHz, d_6-DMSO): δ 7.92 (d, *J* = 7.80 Hz, 1H), 7.66 (t, *J* = 7.70 Hz, 1H), 7.18 (dd, 2H), 3.15 (s, 3H) ppm; ^{13}C NMR (125 MHz, d_6-DMSO): δ 162.36, 149.75, 147.12, 137.65, 125.42, 123.38, 117.93, 112.87, 112.03, 113.36, 110.47, 81.14, 26.21 ppm; TOF-MS (ESI+H^+) Exact Calcd. for ($C_{12}H_7N_3O$+H^+) 210.06, Found: 210.19.

2-(2-oxo-1-phenylindolin-3-ylidene)malononitrile (4c)



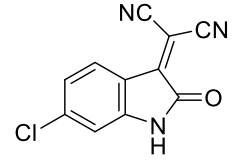
Red Solid, Yield 94%, ^{1}H NMR (200 MHz, d_6-DMSO): δ 8.06 (d, *J* = 7.60 Hz, 1H), 7.66-7.46 (m, 7H), 7.31-7.23(t, *J* = 6.00 Hz, 1H), 6.84 (d, *J* = 8.20 Hz, 1H) ppm; ^{13}C NMR (125 MHz, d_6-DMSO): δ 161.92, 149.83, 146.96, 137.66, 132.58, 129.79, 128.83, 126.65, 125.73, 123.93, 118.17, 112.93, 111.39, 110.66, 81.2 ppm; TOF-MS (ESI+) Calcd. for ($C_{17}H_9N_3O$) 271.07, Found: 271.24.

2-(7-chloro-2-oxoindolin-3-ylidene)malononitrile (4d)



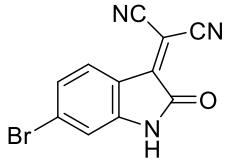
Red Solid, Yield 98% , ^{1}H NMR (200 MHz, d_6-DMSO): δ 11.69 (s, 1H), 7.88 (d, *J* = 7.80 Hz, 1H), 7.69 (d, *J* = 8.20 Hz, 1H), 7.17 (t, *J* = 8.00 Hz, 1H,) ppm; ^{13}C NMR (125 MHz, d_6-DMSO): δ 163.62, 150.06, 143.62, 136.59, 124.17, 123.89, 120.28, 115.61, 112.63, 111.19, 81.98 ppm; TOF-MS (ESI+H^+) Calcd. for exact ($C_{11}H_4ClN_3O$+H^+) 229.00, Found: 229.04

2-(6-chloro-2-oxoindolin-3-ylidene)malononitrile (4e)



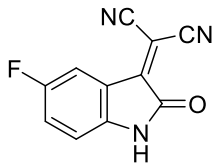
Red Solid, Yield 95%, ^{1}H NMR (200 MHz, d_6-DMSO): δ 11.39 (s, 1H), 7.89 (d, *J* = 8.40 Hz, 1H), 7.24 (d, *J* = 8.40 Hz, IH), 7.0 (s, 1H) ppm; ^{13}C NMR (125 MHz, d_6-DMSO): δ 163.69, 149.42, 147.45, 141.86, 127.06, 122.92, 117.49, 112.85, 111.60, 111.33, 80.89 ppm; TOF-MS (ESI+Na^+) Exact. Calcd for ($C_{11}H_4ClN_3O$+Na^+) 229.00, Found: 229.92.

2-(6-bromo-2-oxoindolin-3-ylidene)malononitrile (4f)



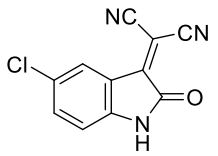
Brown Red Solid, Yield 98%, ^{1}H NMR (200 MHz, d_6-DMSO): δ 11.37 (s, 1H), 7.79 (d, *J* = 8.20 Hz, 1H), 7.40-7.35 (dd, 1H), 7.14 (d, *J* = 1.6 Hz, 1H) ppm; ^{13}C NMR (125 MHz, d_6-DMSO): δ 163.59, 149.62, 147.28, 131.22, 126.99, 117.78, 114.42, 112.90, 111.41, 80.96 ppm; TOF-MS (ESI-H^+) Exact Calcd. for ($C_{11}H_4BrN_3O$-H^+) 272.95, Found: 272.05.

2-(5-fluoro-2-oxoindolin-3-ylidene)malononitrile (4g)[9b]



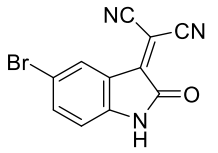
Red Solid, Yield 97% , ^{1}H NMR (200 MHz, d_6-DMSO): δ 11.25 (s, 1H), 7.43-7.60 (m, 2H), 6.94-7.00 (dd, *J* = 4.40 Hz, 1H) ppm; ^{13}C NMR (125 MHz, d_6-DMSO): δ 163.36, 149.52, 145.11, 136.86, 126.43, 124.65, 119.86, 113.21, 112.61, 111.07, 82.20 ppm; TOF-MS (ESI-H^+) Exact Calcd. for ($C_{11}H_4FN_3O$-H^+) 212.03, Found: 212.92.

2-(5-chloro-2-oxoindolin-3-ylidene)malononitrile (4h)[9a,b]



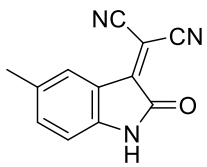
Red Solid, Yield 96%, ^{1}H NMR (200 MHz, d_6-DMSO): δ 11.37 (s, 1H), 7.77 (d, *J* = 2.00 Hz, 1H), 7.66 (m, 1H), 7.00 (d, *J* = 8.40 Hz, 1H) ppm; ^{13}C NMR (125 MHz, d_6-DMSO): δ 163.59, 158.40, 156.49, 150.10, 142.94, 124.51, 124.32, 119.11, 119.05, 112.94, 112.88, 112.57, 111.97, 111.77, 111.12, 82.18 ppm; TOF-MS (ESI-H^+) Calcd. for exact ($C_{11}H_4ClN_3O$-H^+) 228.00, Found: 228.06.

2-(5-bromo-2-oxoindolin-3-ylidene)malononitrile (4i)[9a,b]



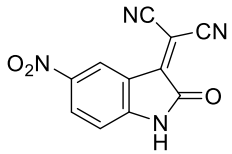
Brown Red Solid, Yield 99%, ^{1}H NMR (200 MHz, d_6-DMSO): δ 11.37 (s, 1H), 7.92 (d, *J* = 1.80 Hz, 1H), 7.78 (dd, *J* = 2.00, 6.4 Hz 1H), 6.93 (d, *J* = 8.40 Hz, 1H) ppm; ^{13}C NMR (125 MHz, d_6-DMSO): δ 163.50, 149.51, 147.23, 131.20, 126.92, 125.76, 117.71, 114.38, 112.82, 111.31, 80.90 ppm; TOF-MS (ESI-H^+) Exact Calcd. for ($C_{11}H_4BrN_3O$-H^+) 271.95, Found: 271.99.

2-(5-methyl-2-oxoindolin-3-ylidene)malononitrile (4j)



Red Solid, Yield 96%, ^{1}H NMR (200 MHz, d_6-DMSO): δ 11.10 (s, 1H), 7.66 (s, 1H), 7.42 (d, *J* = 7.84 Hz, 1H), 6.87 (d, *J* = 8.00 Hz, 1H) 2.28 (s, 3H) ppm; ^{13}C NMR (125 MHz, d_6-DMSO): δ 163.66, 150.43, 144.33, 138.43, 131.82, 125.59, 118.53, 112.93, 111.41, 80.14, 20.34 ppm; TOF-MS (ESI+H^+) Exact Calcd. for ($C_{12}H_7N_3O$+H^+) 210.06, Found: 210.22.

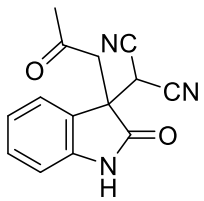
2-(5-nitro-2-oxoindolin-3-ylidene)malononitrile (4k)[9b]



Red Solid, Yield 94%, ^{1}H NMR (200 MHz, d_6-DMSO): δ 11.91 (s, 1H), 8.42-8.44 (m, 1H), 7.0 (s, 1H), 7.14 (d, *J* = 3.40 Hz, IH) ppm; ^{13}C NMR (125 MHz, d_6-DMSO): δ 163.94, 151.12, 149.20, 142.33, 132.62, 120.62, 118.71, 112.43, 111.86, 110.86, 83.39 ppm; TOF-MS (ESI+H^+) Exact Calcd. for ($C_{11}H_4N_4O_3$+H^+) 241.02, Found: 241.08.

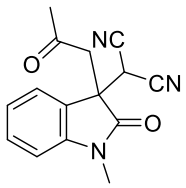
Compound Characterization Data (conjugate addition of acetone to isatylidene malononitriles adducts) (5a-5k)

2-(2-oxo-3-(2-oxopropyl)indolin-3-yl)malononitrile (5a)[10a,b]



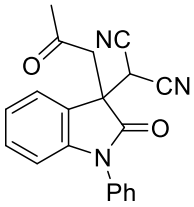
White solid, Yield 95% , ^{1}H NMR (200 MHz, d_6-DMSO): δ 10.97 (s, 1H), 7.26-7.38 (m, 2H), 6.91-7.06 (m, 2H), 5.52 (s, 1H), 3.60 (d, *J* = 17.80 Hz, 1H), 3.2 (br, 1H), 2.04 (s, 3H) ppm; ^{13}C NMR (125 MHz, d_6-DMSO): δ 203.58, 175.34, 143.00, 129.90, 126.50, 123.35, 121.96, 111.56, 111.20, 110.12, 48.20, 45.63, 30.02, 29.82 ppm; TOF-MS (ESI+Na^+) Exact Calcd. for ($C_{14}H_{11}N_3O_2$+Na^+) 276.09, Found: 276.15.

2-(1-methyl-2-oxo-3-(2-oxopropyl)indolin-3-yl)malononitrile (5b)



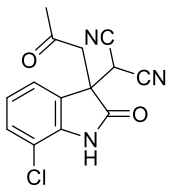
White solid, Yield 90% , ^{1}H NMR (200 MHz, d_6-DMSO): δ 7.37-7.45 (m, 2H), 7.07-7.17 (m, 2H), 5.56 (s, 1H), 3.63-3.72 (d, *J* = 18.0 Hz, 1H), 3.29-3.38 (d, *J* = 17.80 Hz, 1H), 2.03 (s, 3H) ppm; ^{13}C NMR (125 MHz, d_6-DMSO): δ 203.55, 173.75, 144.42, 130.06, 125.75, 123.05, 122.67, 111.39, 111.43, 111.10, 109.13, 47.82, 45.75, 30.00, 29.72, 26.46 ppm; TOF-MS (ESI+Na^+) Exact Calcd. for ($C_{15}H_{13}N_3O_2$+Na^+) 290.10, Found: 290.24.

2-(2-oxo-3-(2-oxopropyl)-1-phenylindolin-3-yl)malononitrile (5c)



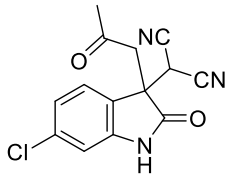
White solid, Yield 88% , ^{1}H NMR (500 MHz, d_6-DMSO): δ 7.62-7.65 (m, 2H), 7.51-7.55 (m, 2H), 7.40-7.41 (d, *J* = 8.0 Hz, 2H), 7.34-7.37 (t, *J* = 8.00 Hz, 1H), 7.16-7.19 (t, *J* = 8.00 Hz, 1H), 6.76-6.78 (d, *J* = 8.00 Hz, 1H), 5.69 (s, 1H), 3.82-3.85 (d, *J* = 18.50 Hz, 1H), 3.46-3.50 (d, *J* = 18.50 Hz, 1H), 2.10 (s, 3H) ppm; ^{13}C NMR (125 MHz, d_6-DMSO): δ 203.93, 173.55, 144.43, 133.79, 130.19, 129.91, 128.66, 126.51, 125.54, 123.54, 123.26, 111.40, 111.07, 109.37, 47.94, 46.29, 30.33, 29.62 ppm; TOF-MS (ESI+H^+) Exact Calcd. for ($C_{20}H_{15}N_3O_2$+H^+) 330.12, Found: 330.17.

2-(7-chloro-2-oxo-3-(2-oxopropyl)indolin-3-yl)malononitrile (5d)[10a]



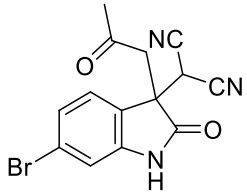
White solid, Yield 92% , ^{1}H NMR (200 MHz, d_6-DMSO): δ 11.44 (s, 1H), 7.33-7.41 (t, *J* = 8.00 Hz, 2H), 7.02-7.10 (t, *J* = 7.80 Hz, 1H), 5.55 (s, 1H), 3.63-3.72 (d, *J* = 18.00 Hz, 1H), 3.39 (br, 1H), 2.06 (s, 3H) ppm; ^{13}C NMR (125 MHz, d_6-DMSO): δ 203.70, 175.31, 140.82, 129.98, 128.38, 123.30, 122.05, 114.30, 111.28, 110.97, 48.90, 45.81, 29.92, 29.66 ppm; TOF-MS (ESI+H^+) Exact Calcd. for ($C_{14}H_{10}ClN_3O_2$+H^+) 288.05, Found: 288.13.

2-(6-chloro-2-oxo-3-(2-oxopropyl)indolin-3-yl)malononitrile (5e)[10a]



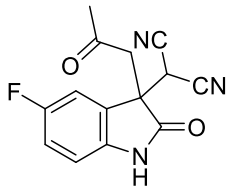
White solid, Yield 92% , ^{1}H NMR (200 MHz, d_6-DMSO): δ 11.19 (s, 1H), 7.39-7.38 (d, *J* = 8.00 Hz, 1H), 7.10-7.12 (t, *J* = 8.00 Hz, 1H), 6.97 (s, 1H) 5.55 (s, 1H), 3.63-3.67 (d, *J* = 18.5 Hz, 1H), 3.34-3.30 (d, *J* = 18.50 Hz, 1H), 2.05 (s, 3H) ppm; ^{13}C NMR (125 MHz, d_6-DMSO): δ 203.70, 175.35, 144.56, 134.29, 125.49, 124.95, 121.75, 111.35, 111.00, 110.17, 47.98, 45.64, 29.80, 29.68 ppm; TOF-MS (ESI+H^+) Exact Calcd. for ($C_{14}H_{10}ClN_3O_2$+H^+) 288.05, Found: 288.05.

2-(6-bromo-2-oxo-3-(2-oxopropyl)indolin-3-yl)malononitrile (5f)[10b]



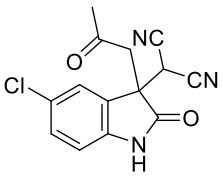
White solid, Yield 93%, ^{1}H NMR (500 MHz, d_6-DMSO): δ 11.17 (s, 1H), 7.33 (d, *J*=8.00 Hz, 1H), 7.26 (dd, *J* = 1.50, 6.50 Hz, 1H), 7.09 (d, *J* = 2.00 Hz, 1H), 5.56 (s, 1H), 3.67 (d, *J* = 18.00 Hz, 1H), 3.3 (brs, 1H), 2.05 (s, 3H) ppm; ^{13}C NMR (125 MHz, d_6-DMSO): δ 203.65, 175.18, 144.65, 125.90, 125.25, 124.59, 122.62, 112.83, 111.31, 110.96, 47.93, 45.56, 29.64 ppm; TOF-MS (ESI+H^+) Exact Calcd. for ($C_{14}H_{10}BrN_3O_2$+H^+) 330.99, Found: 330.84

2-(5-fluoro-2-oxo-3-(2-oxopropyl)indolin-3-yl)malononitrile (5g)[10a,b]



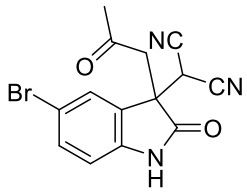
White solid, Yield 92%, ^{1}H NMR (200 MHz, d_6-DMSO): δ 11.01, 7.25-7.31 (dd, *J* = 2.4, 5.8 Hz, 1H), 7.10-7.20 (m, 1H), 6.90-6.96 (m, 1H), (s, 1H), 3.62- 3.71 (d, *J* = 18.00 Hz, 1H), 3.26-3.35 (d, *J* = 18.00 Hz, 1H), 2.06 (s, 3H) ppm; ^{13}C NMR (125 MHz, d_6-DMSO): δ 203.63, 175.29, 158.70, 156.81, 139.34, 128.15, 128.09, 116.34, 116.16, 111.66, 111.46, 111.31, 110.98, 48.58, 45.57, 29.84, 29.66 ppm; TOF-MS (ESI+H^+) Exact Calcd for ($C_{14}H_{10}FN_3O_2$-H^+) 270.08, Found: 270.00

2-(5-chloro-2-oxo-3-(2-oxopropyl)indolin-3-yl)malononitrile (5h)[10a,b]



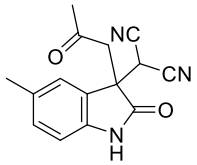
White solid, Yield 90%, ^{1}H NMR (500 MHz, d_6-DMSO): δ 11.17 (s, 1H), 7.47 (d, *J* = 2.50 Hz, 1H), 7.39 (dd, *J* = 2.00, 6.50 Hz, 1H), 6.98 (d, *J* = 8.50 Hz, 1H) 5.55 (s, 1H), 3.71 (d, *J* = 18.00 Hz, 1H), 3.34 (d, *J* = 18.00 Hz, 1H), 2.07 (s, 3H) ppm; ^{13}C NMR (125 MHz, d_6-DMSO): δ 203.84, 175.21, 142.11, 129.91, 128.63, 125.94, 123.85, 111.64, 111.36, 111.02, 48.44, 45.70, 29.91, 29.68 ppm; TOF-MS (ESI+Na^+) Exact Calcd. for ($C_{14}H_{10}ClN_3O_2$+Na^+) 310.05, Found: 310.13.

2-(5-bromo-2-oxo-3-(2-oxopropyl)indolin-3-yl)malononitrile (5i)[10a,b]



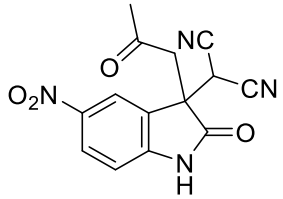
White solid, Yield 88%, ^{1}H NMR (500 MHz, d_6-DMSO): δ 11.15 (s, 1H), 7.58 (d, *J* = 1.5 Hz, 1H), 7.48-7.58 (dd, *J* = 2.00, 6.00 Hz, 1H), 6.91 (d, *J* = 8.00 Hz, 1H), 5.57 (s, 1H), 3.68-3.72 (d, *J* = 18.00 Hz, 1H), 3.3 (brs, 1H), 2.07 (s, 3H) ppm; ^{13}C NMR (125 MHz, d_6-DMSO): δ 203.68, 174.95, 142.42, 132.57, 128.94, 126.43, 113.40, 111.95, 111.26, 110.93, 48.21, 45.59, 29.79, 29.56 ppm; TOF-MS (ESI+H^+) Exact Calcd. for ($C_{14}H_{10}BrN_3O_2$+H^+) 330.99, Found: 330.91

2-(5-methyl-2-oxo-3-(2-oxopropyl)indolin-3-yl)malononitrile (5j)[10a,b]



White solid, Yield 85%, ^{1}H NMR (500 MHz, d_6-DMSO): δ 10.90 (s, 1H), 7.19 (s, 1H), 7.13 (d, *J* = 8.00 Hz, 1H), 6.85 (d, *J* = 8.00 Hz, 1H), 5.47 (s, 1H), 3.58 (d, *J* = 18.00 Hz, 1H), 3.28 (d, *J* = 18.00 Hz, 1H), 2.26 (s, 3H), 2.05 (s, 3H) ppm; ^{13}C NMR (125 MHz, d_6-DMSO): δ 203.69, 175.40, 140.60, 131.00, 130.27, 126.24, 123.95, 111.67, 111.29, 109.99, 48.34, 45.73, 30.16, 29.91, 20.80 ppm; TOF-MS (ESI+Na^+) Exact Calcd. for ($C_{15}H_{13}N_3O_2$+Na^+) 290.10, Found: 290.20.

2-(5-nitro-2-oxo-3-(2-oxopropyl)indolin-3-yl)malononitrile (5k)[10a]



White solid, Yield 85%, ^{1}H NMR (500 MHz, d_6-DMSO): δ 11.75, 8.38 (s, 1H), 8.30 (d, *J* = 8.50 Hz, 1H), 7.17 (d, *J* = 8.50 Hz, 1H), 5.72 (s, 1H), 3.41 (brs, 1H), 2.08 (s, 1H) ppm; ^{13}C NMR (125 MHz, d_6-DMSO): δ 203.91, 175.86, 149.55, 142.21, 127.54, 127.16, 119.75, 111.04, 110.75, 110.19, 48.09, 45.83, 29.50, 29.40 ppm; TOF-MS (ESI^+) Exact Calcd. for ($C_{15}H_{13}N_3O_2$+M^+) 298.07, Found: 298.13.

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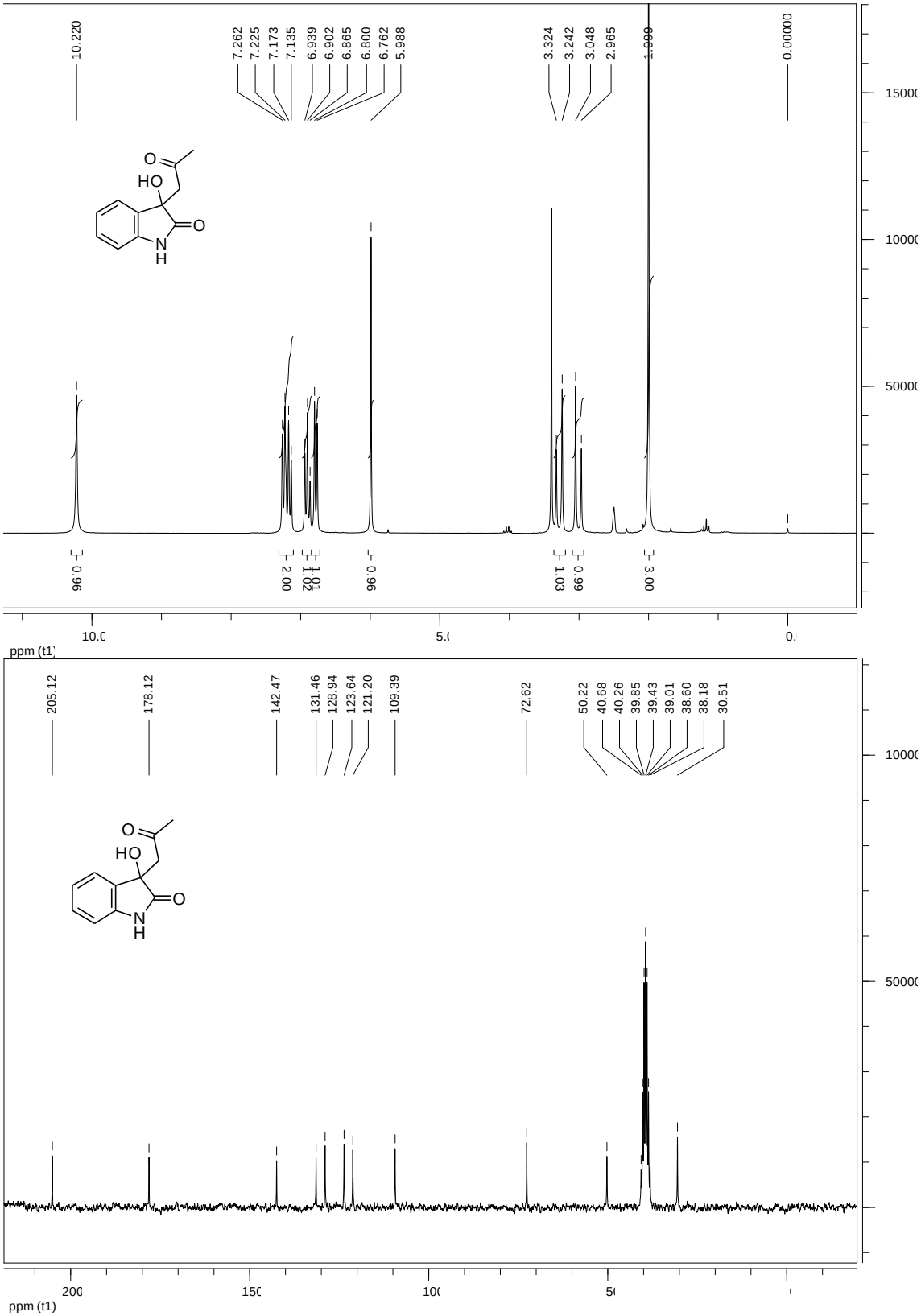
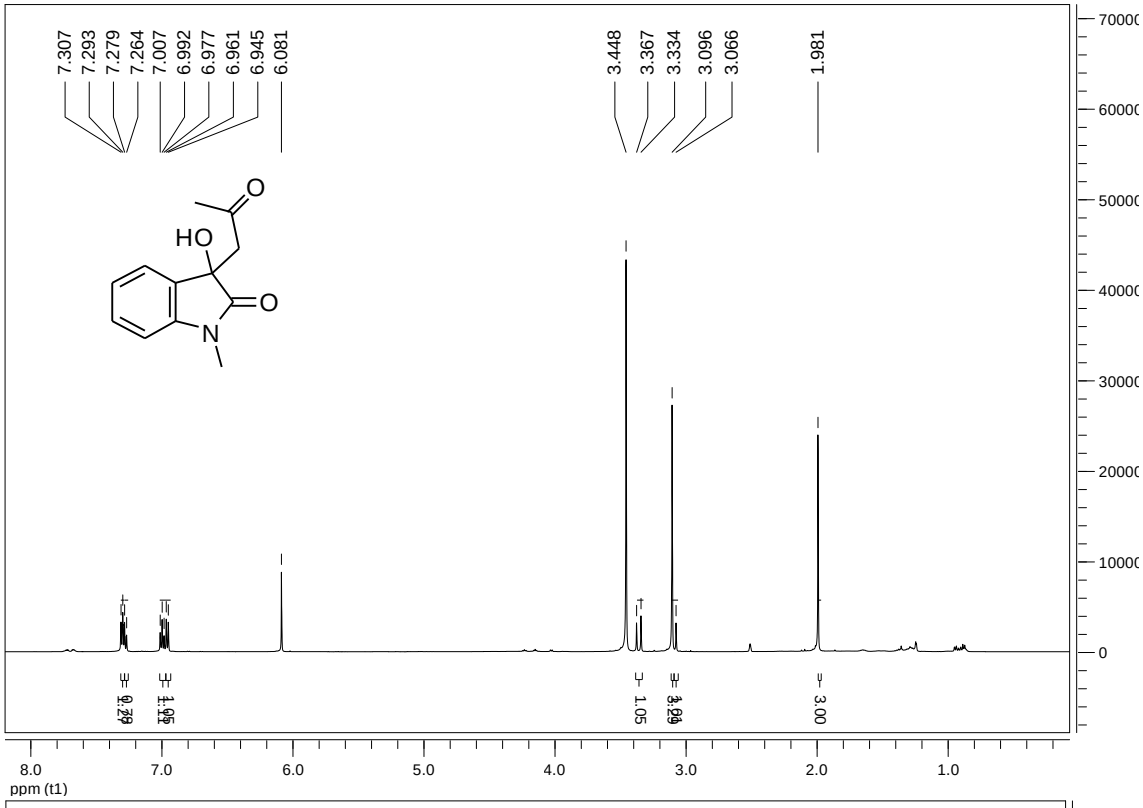
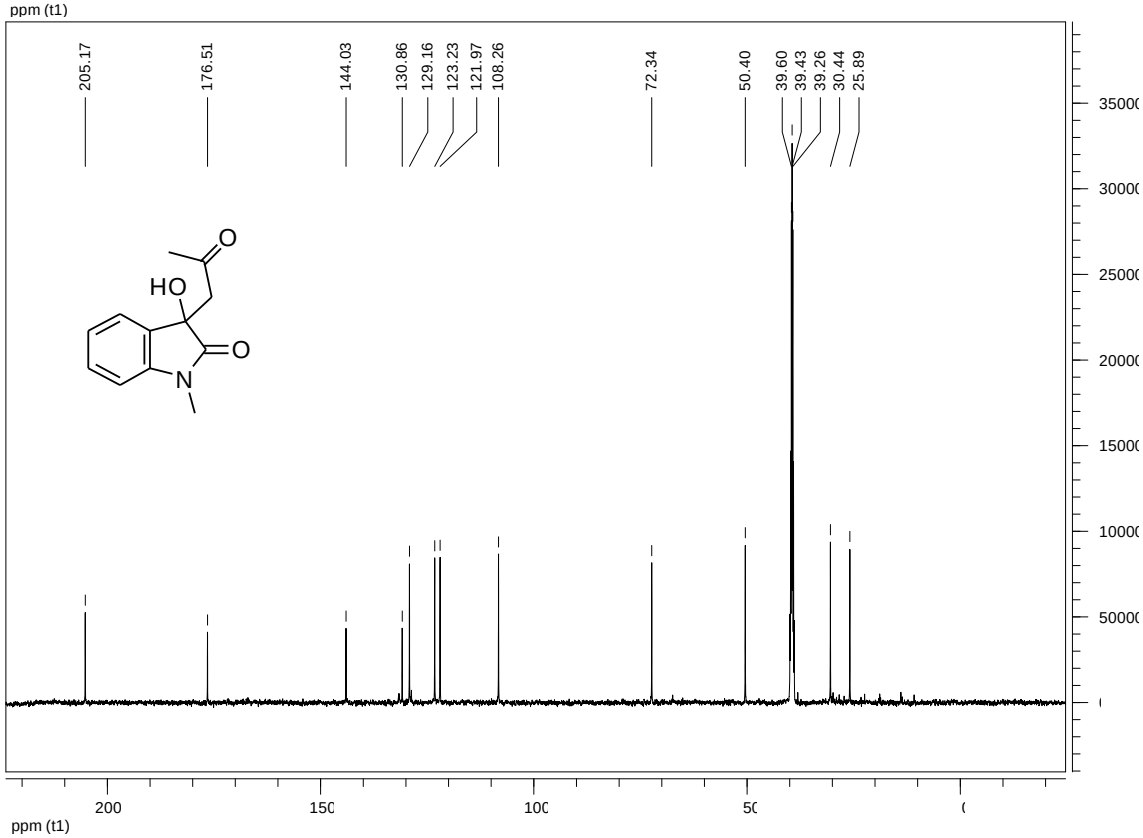
^{1}H and ^{13}C NMR spectra of (**3aa**)

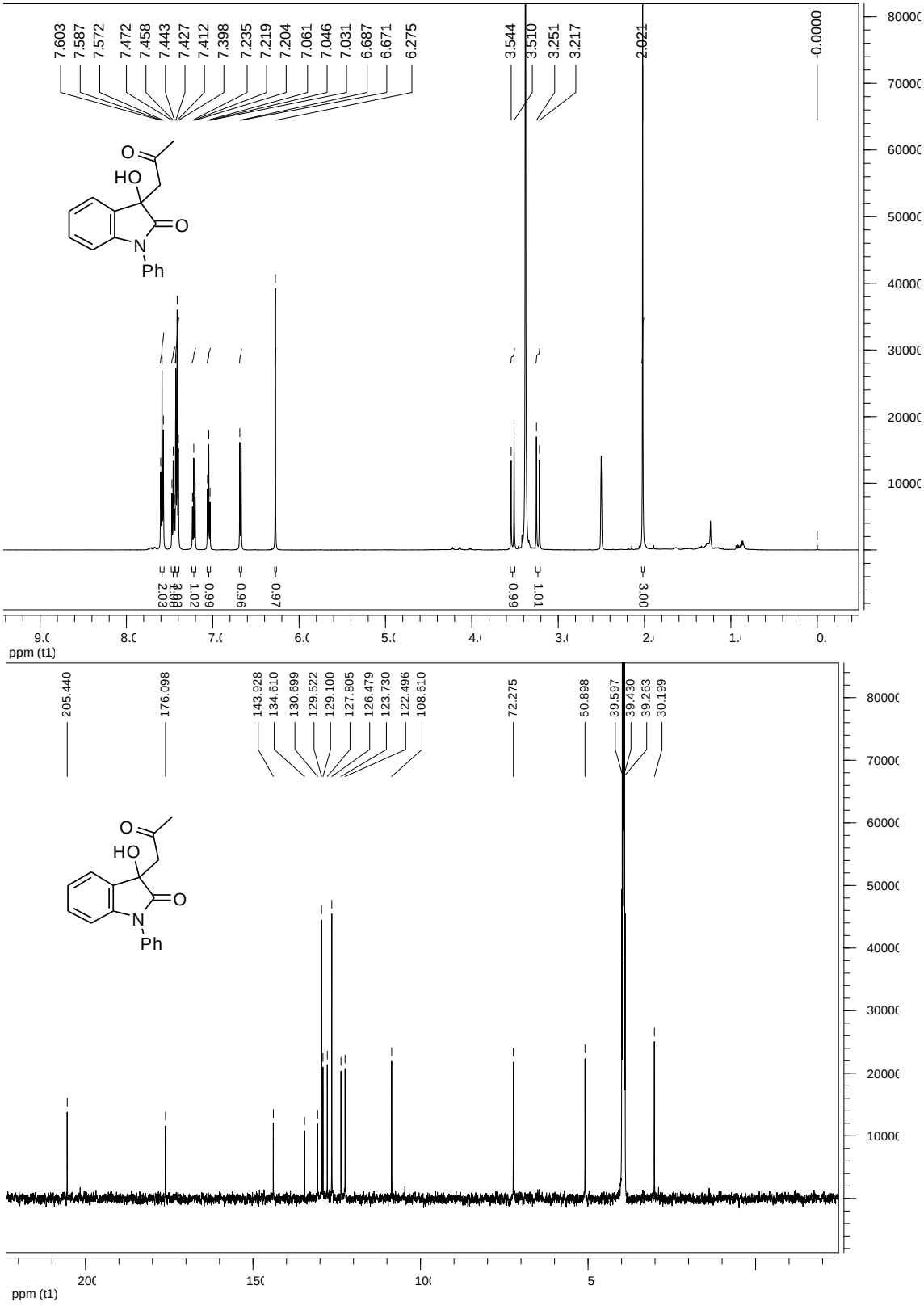


^{1}H and ^{13}C NMR spectra of (**3ba**)

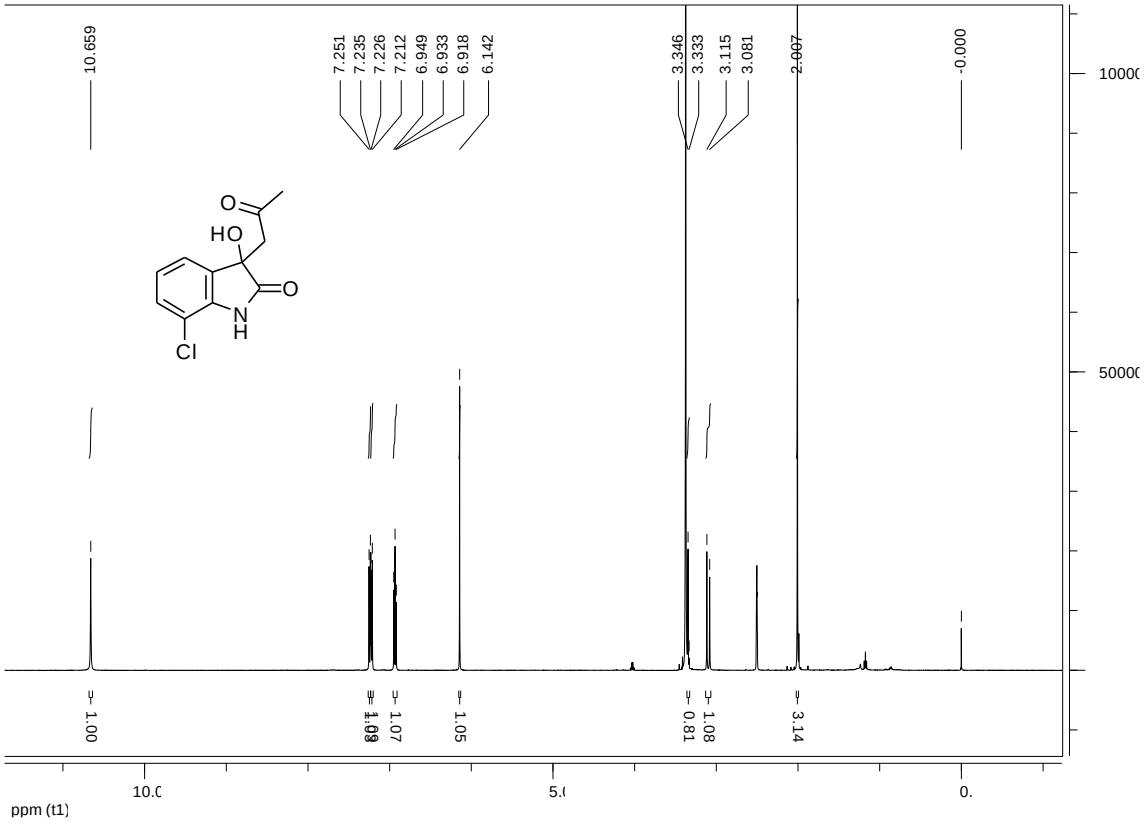


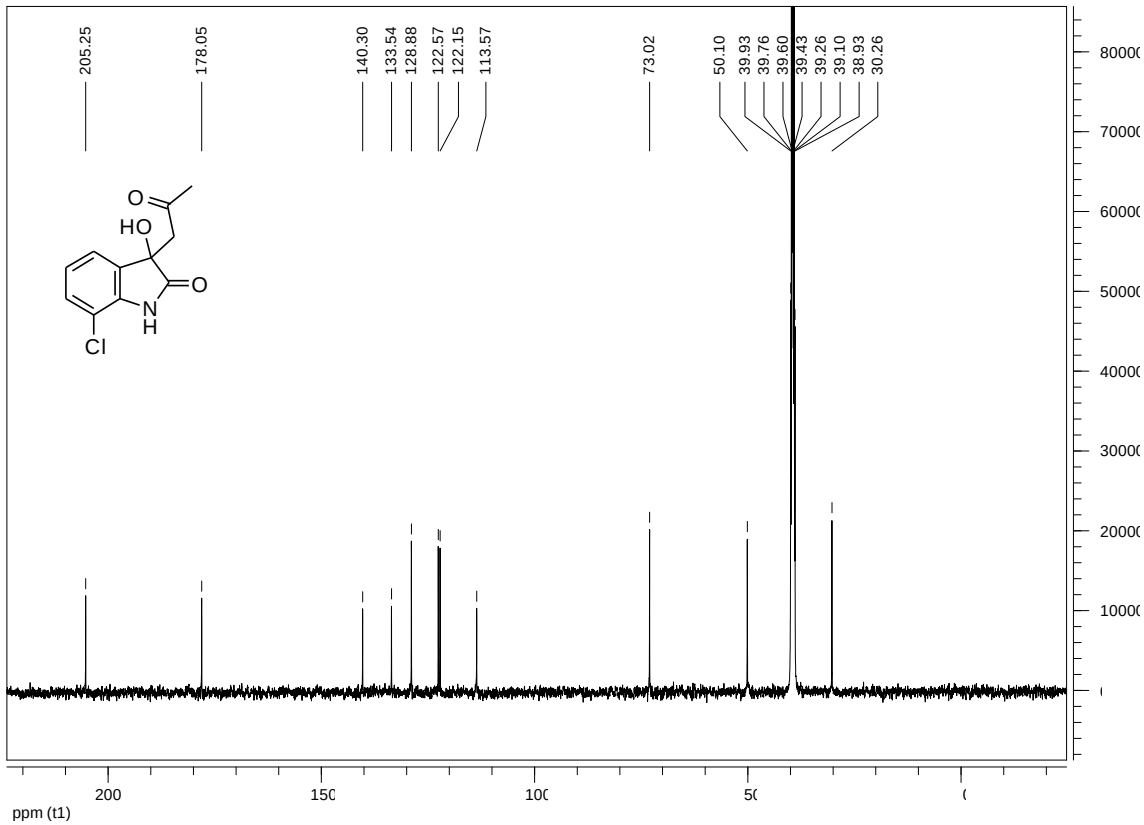


^{1}H and ^{13}C NMR spectra of (**3ca**)

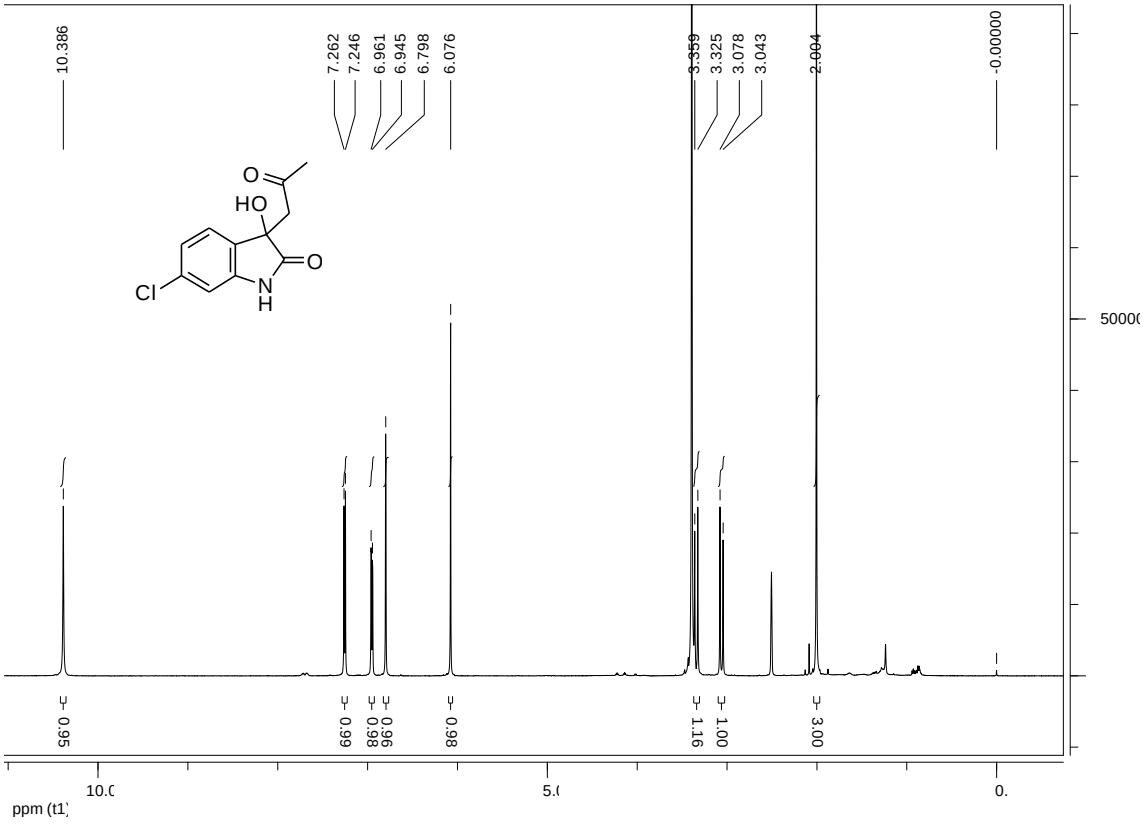


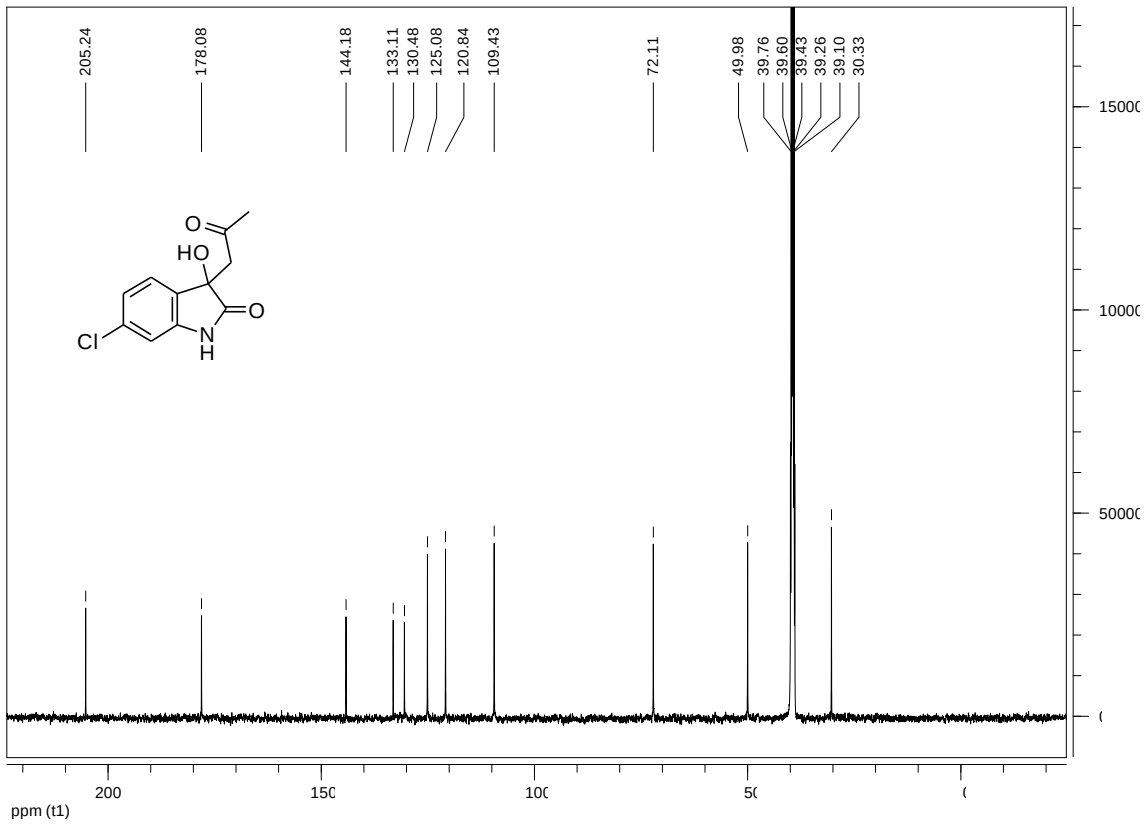
^{1}H and ^{13}C NMR spectra of (**3da**)



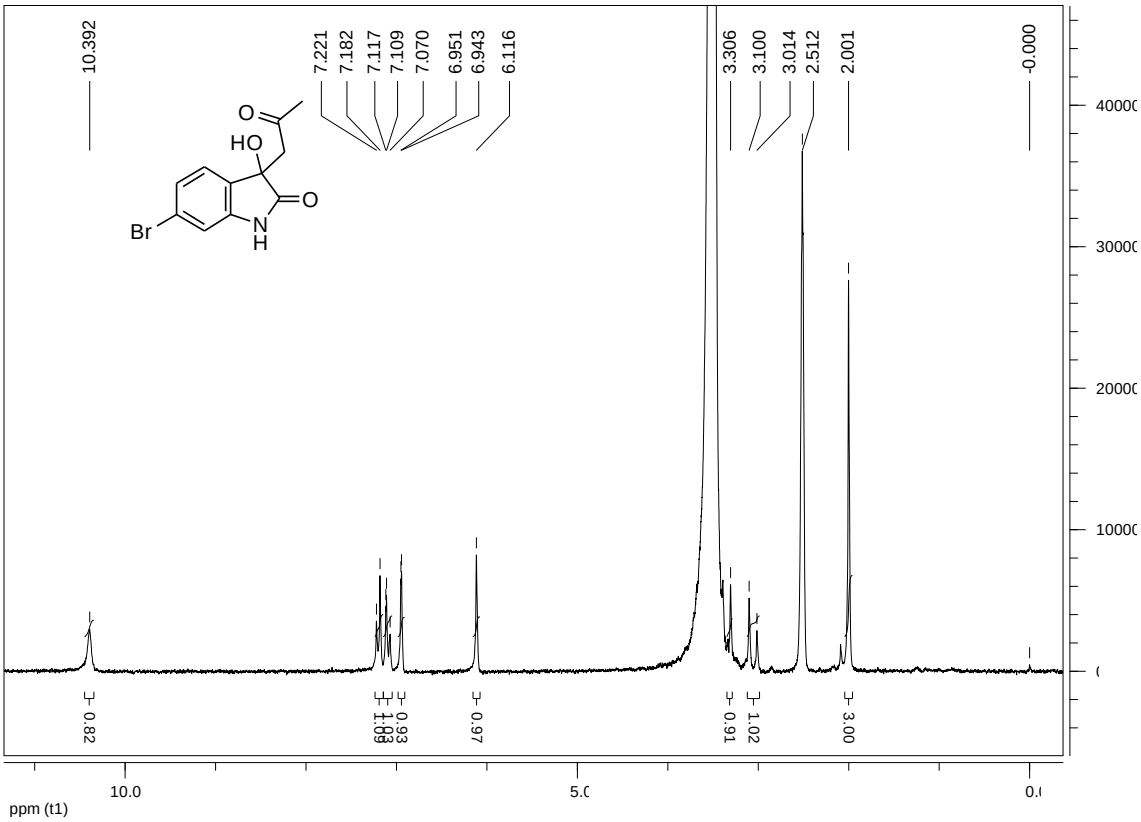


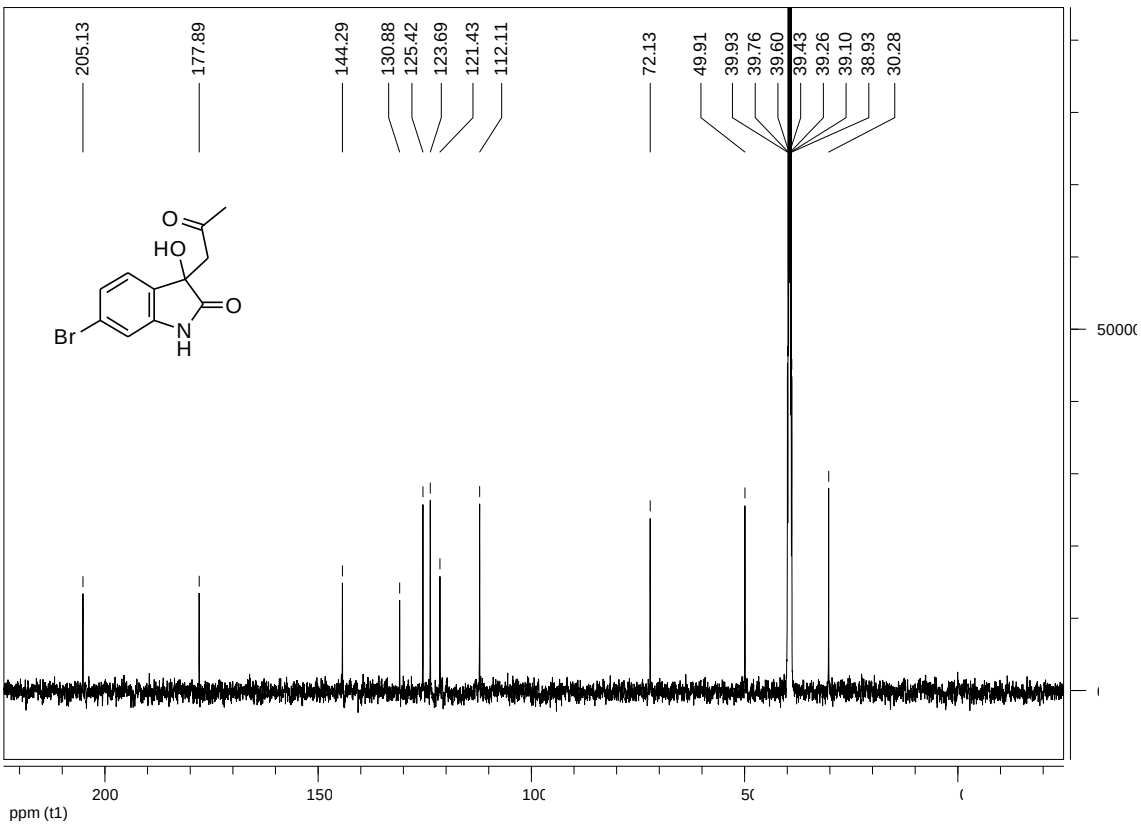
^{1}H and ^{13}C NMR spectra of (**3ea**)



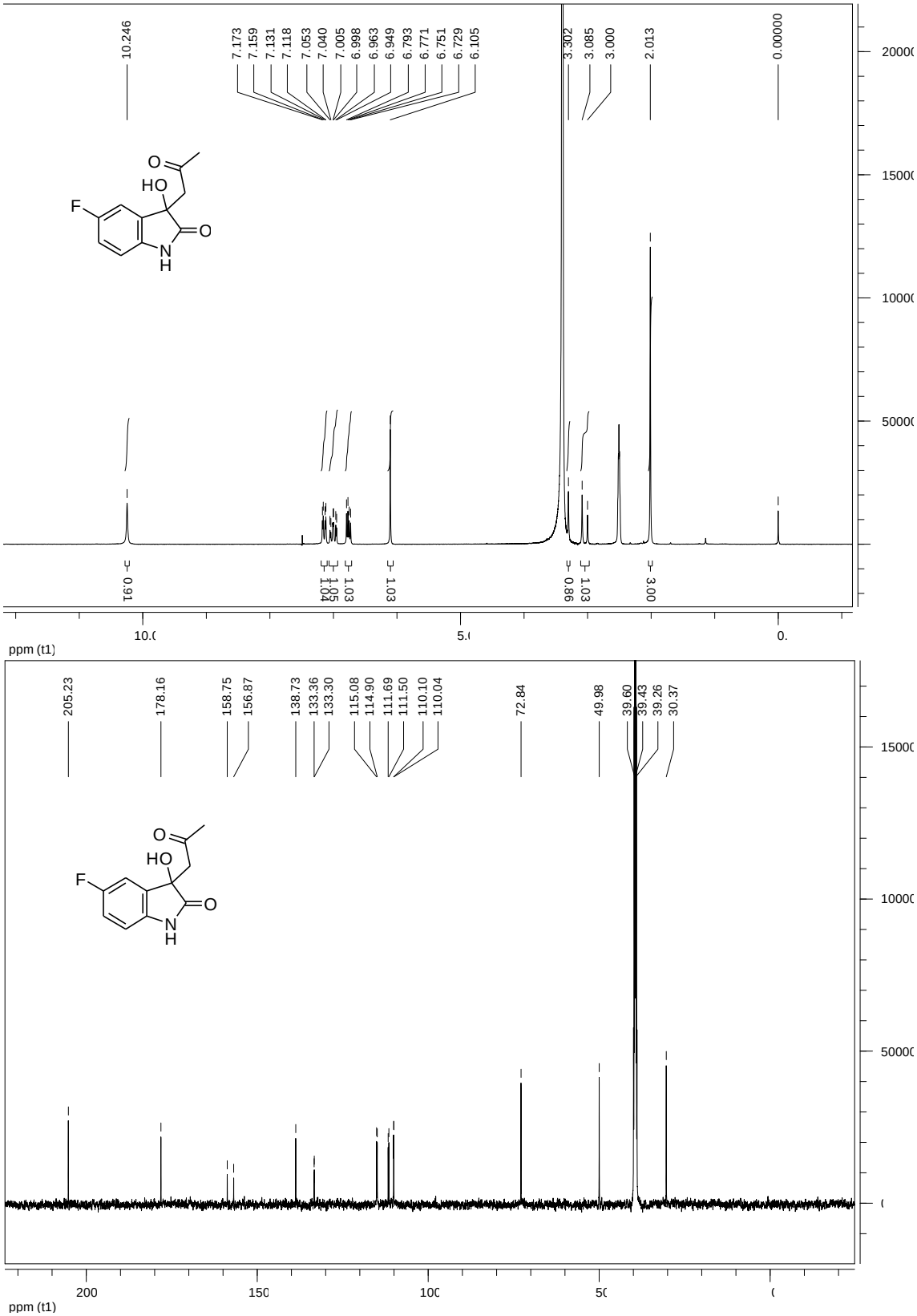


^{1}H and ^{13}C NMR spectra of (**3fa**)

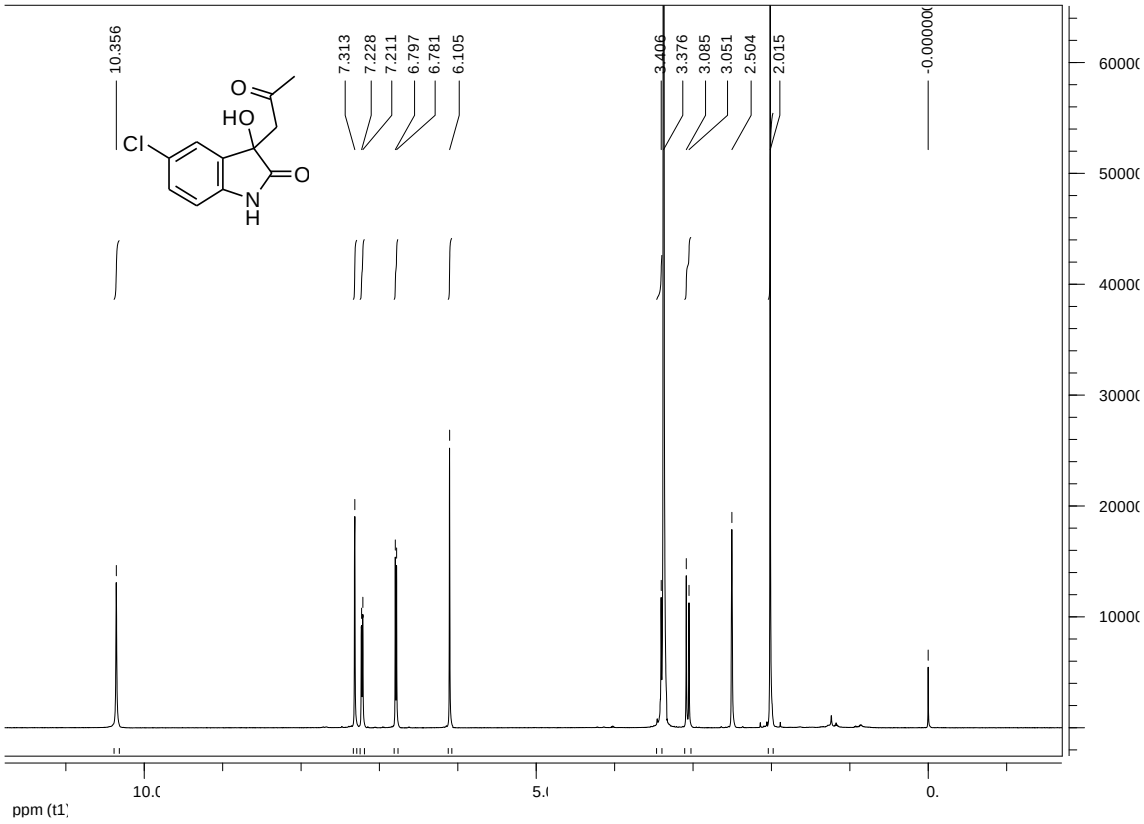


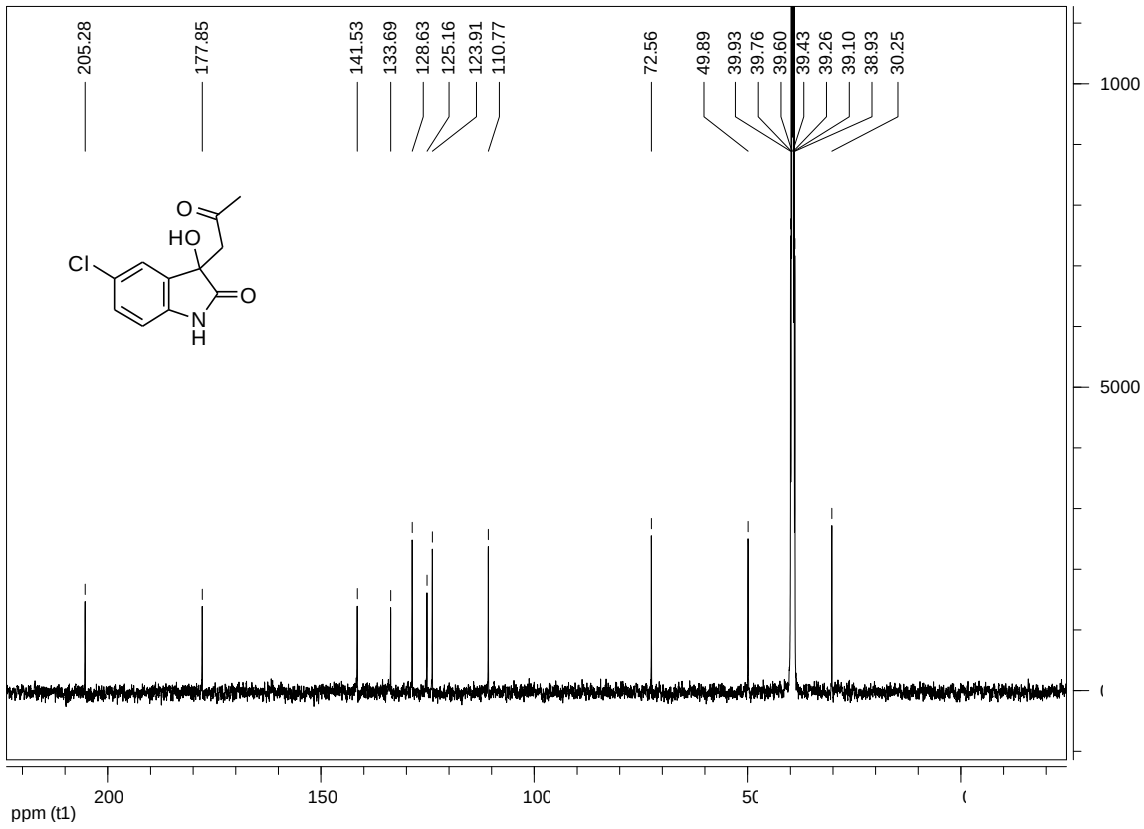


^{1}H and ^{13}C NMR spectra of (**3ga**)

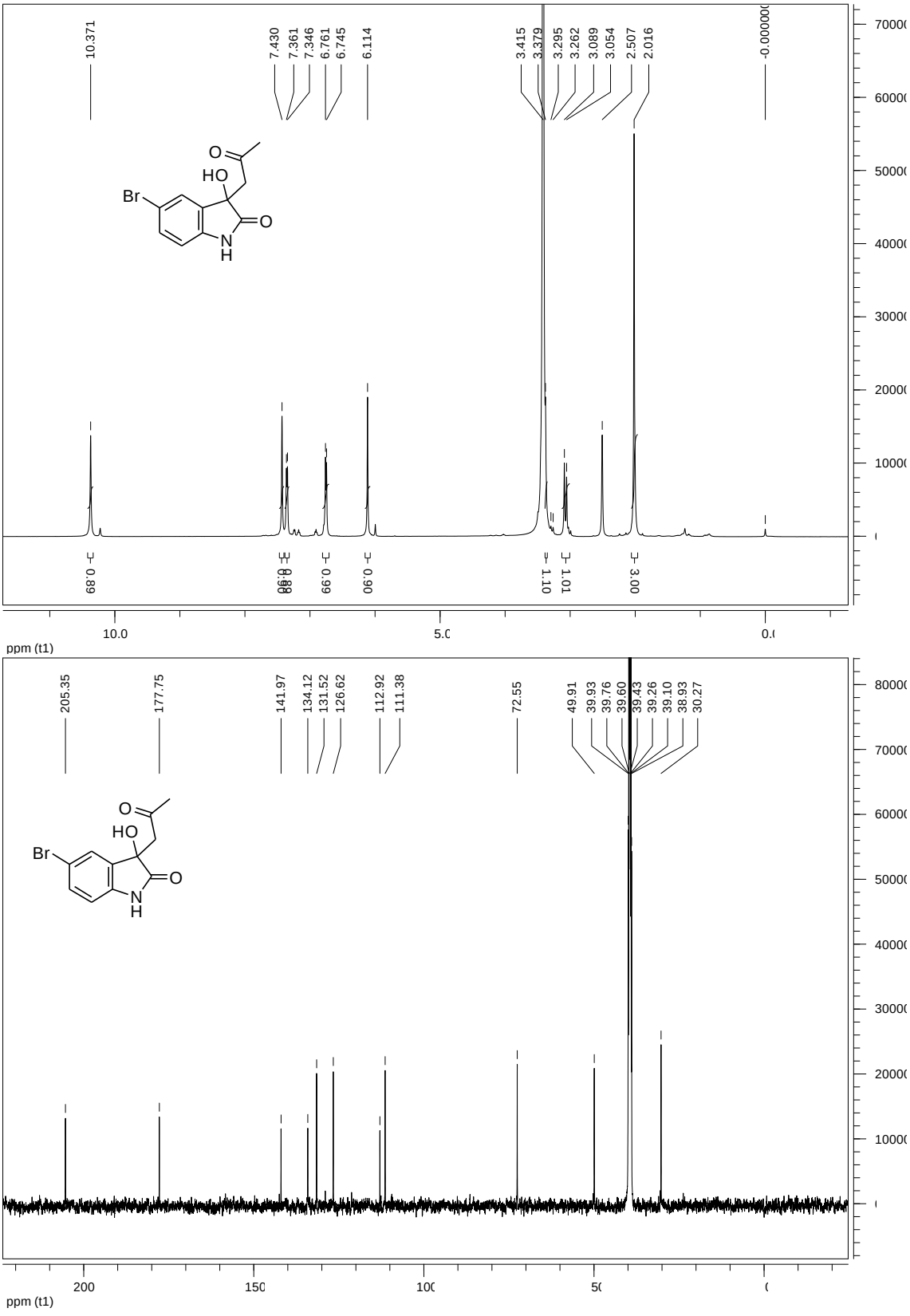


^{1}H and ^{13}C NMR spectra of (**3ha**)

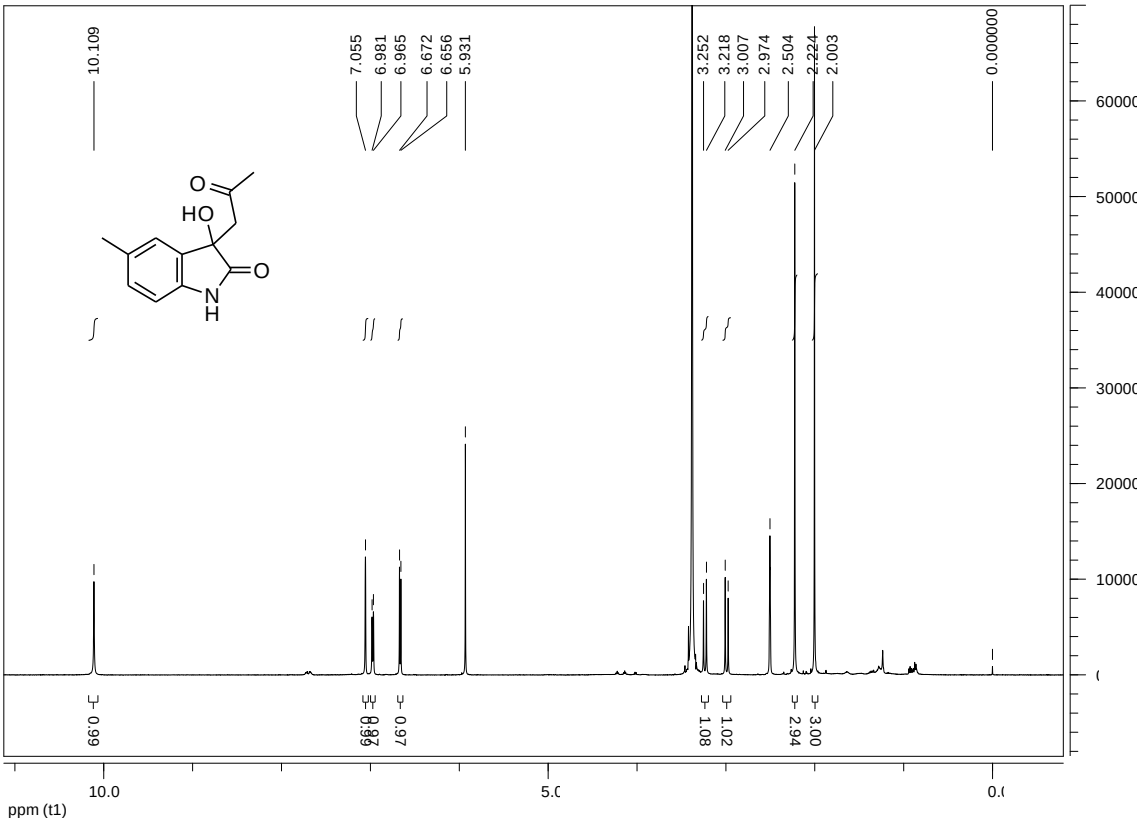


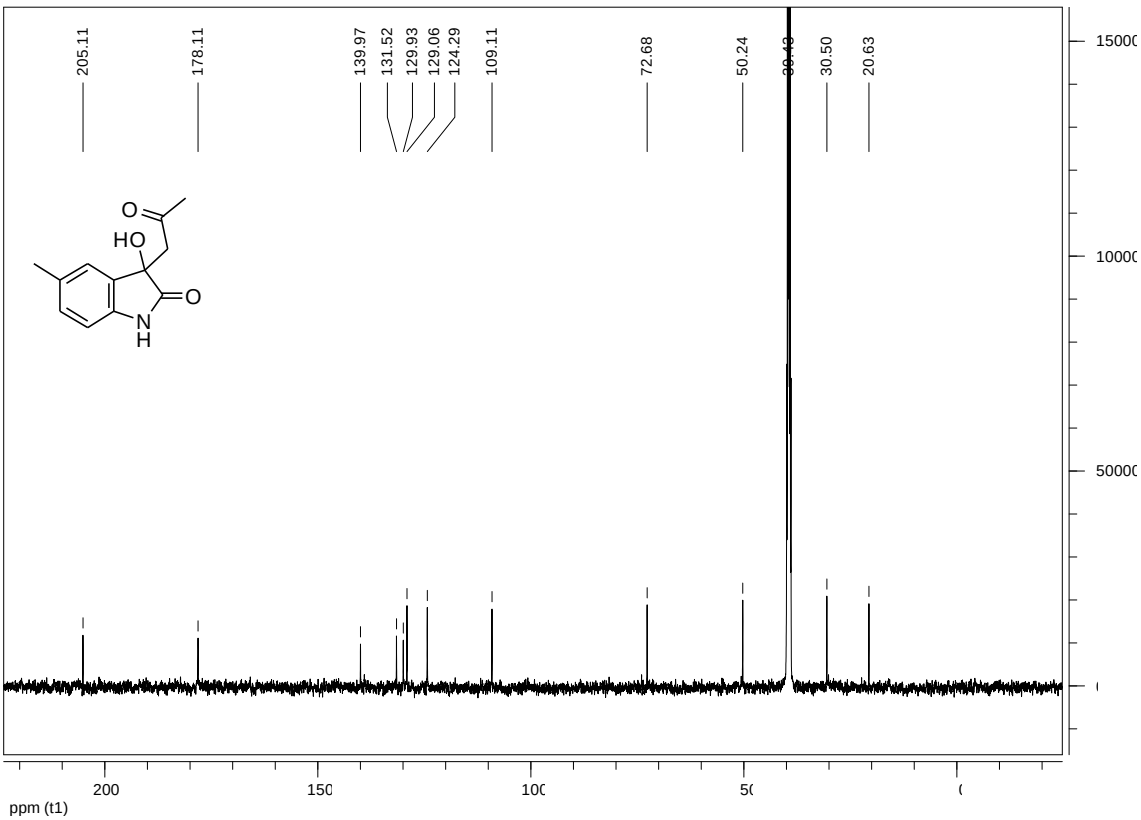


^{1}H and ^{13}C NMR spectra of (**3ia**)

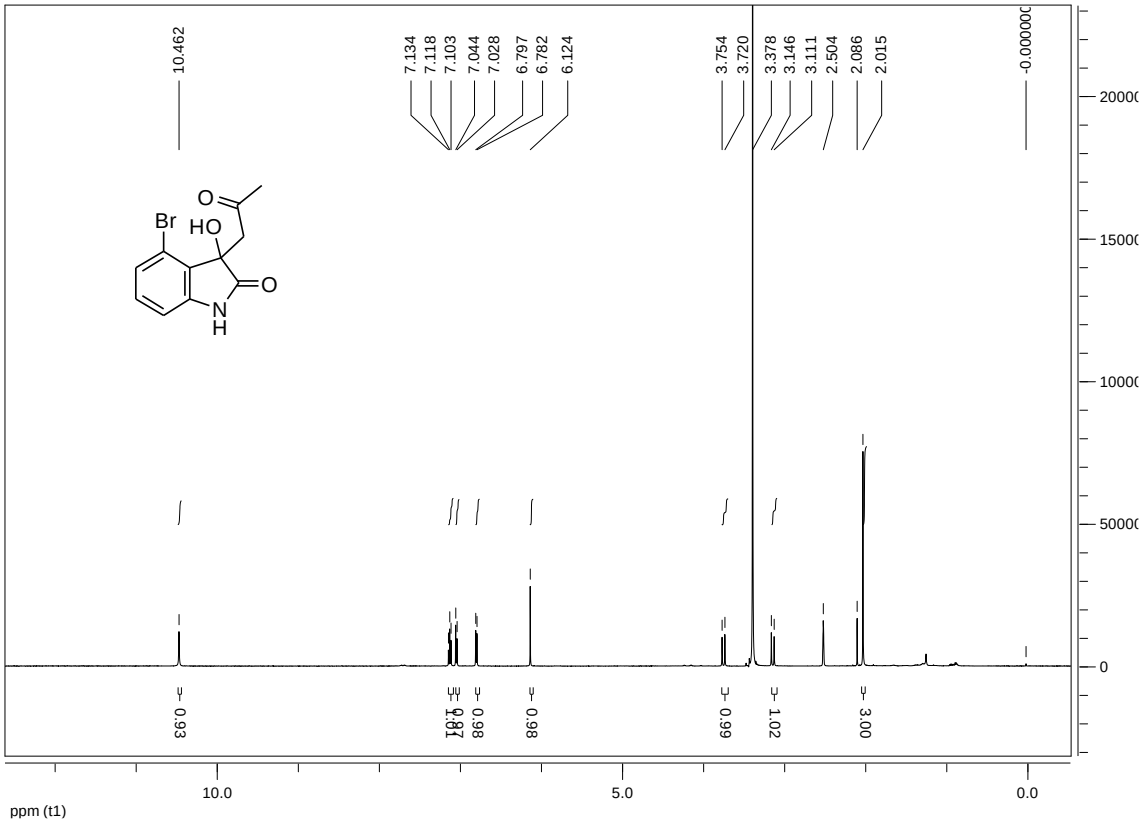


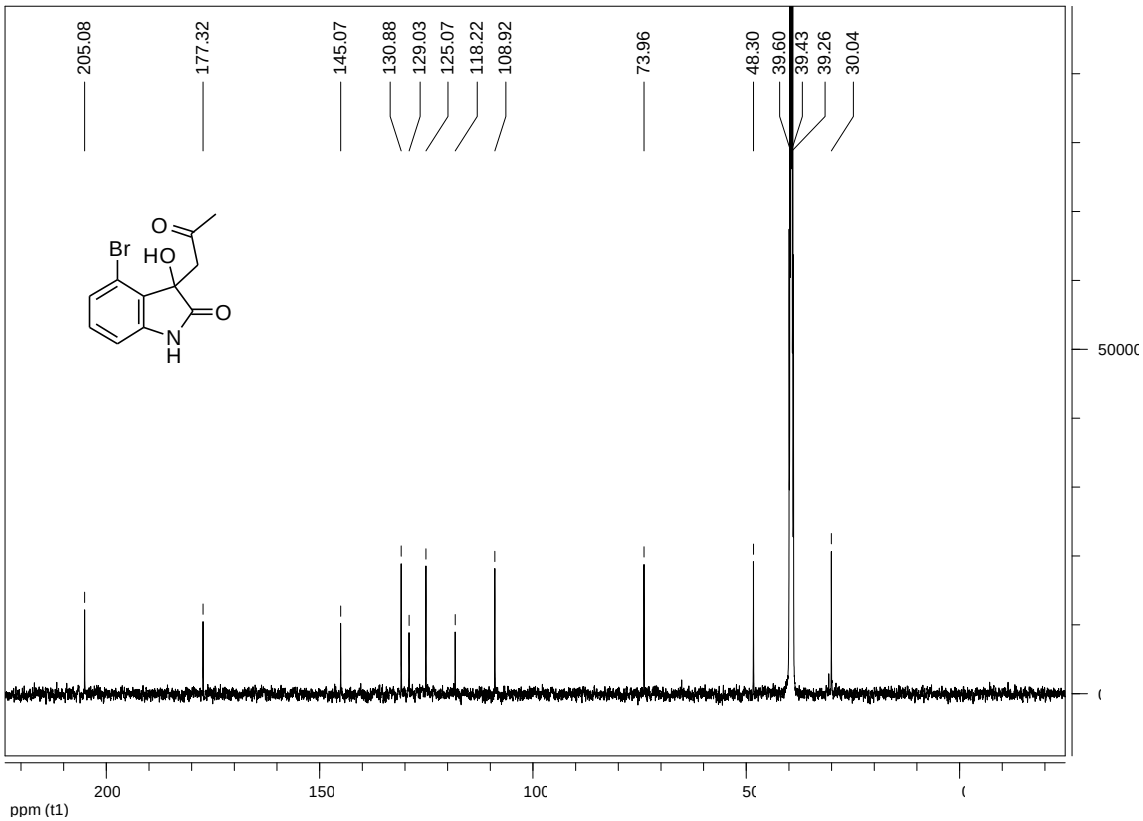
^{1}H and ^{13}C NMR spectra of (**3ja**)



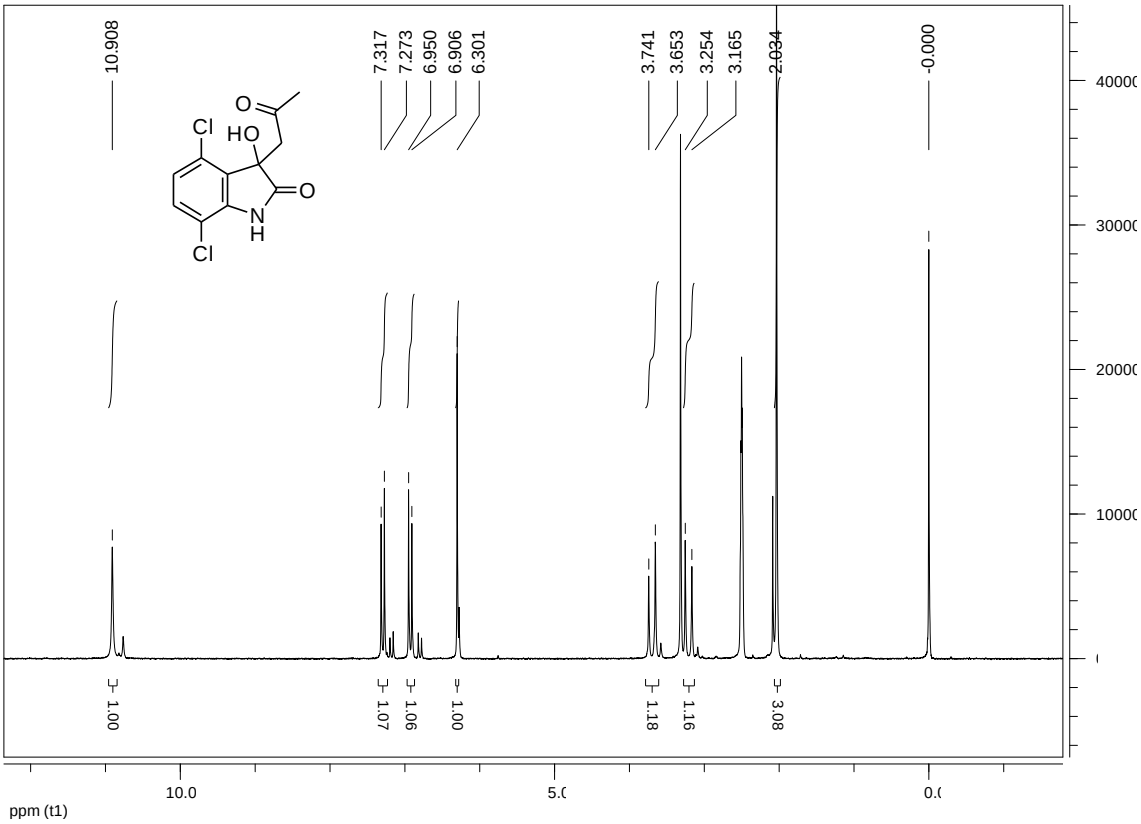


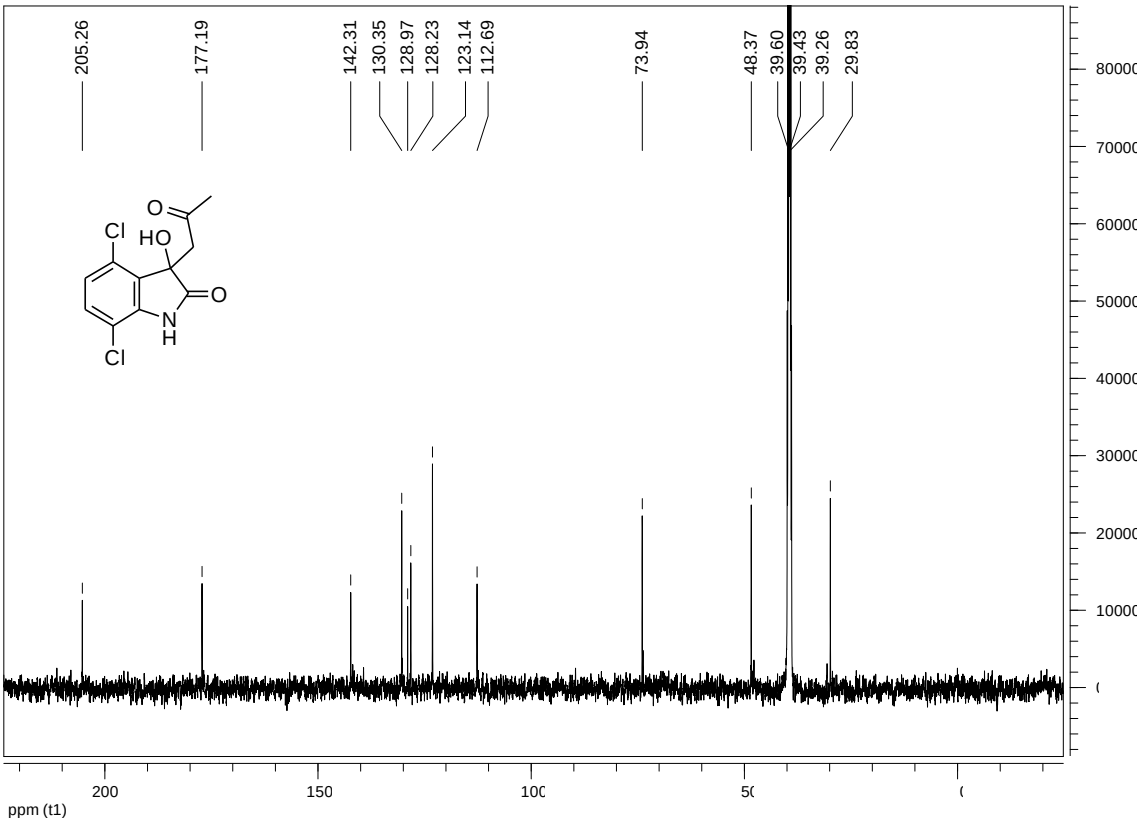
^{1}H and ^{13}C NMR spectra of (**3ka**)



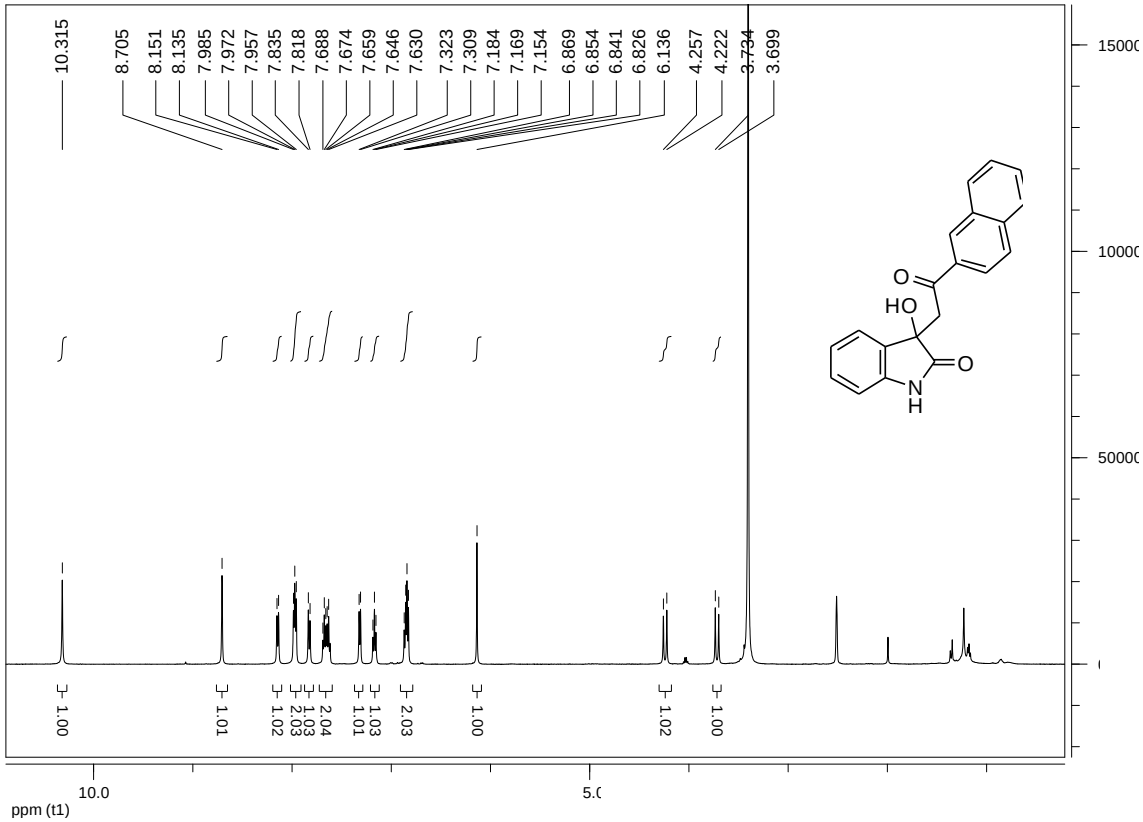


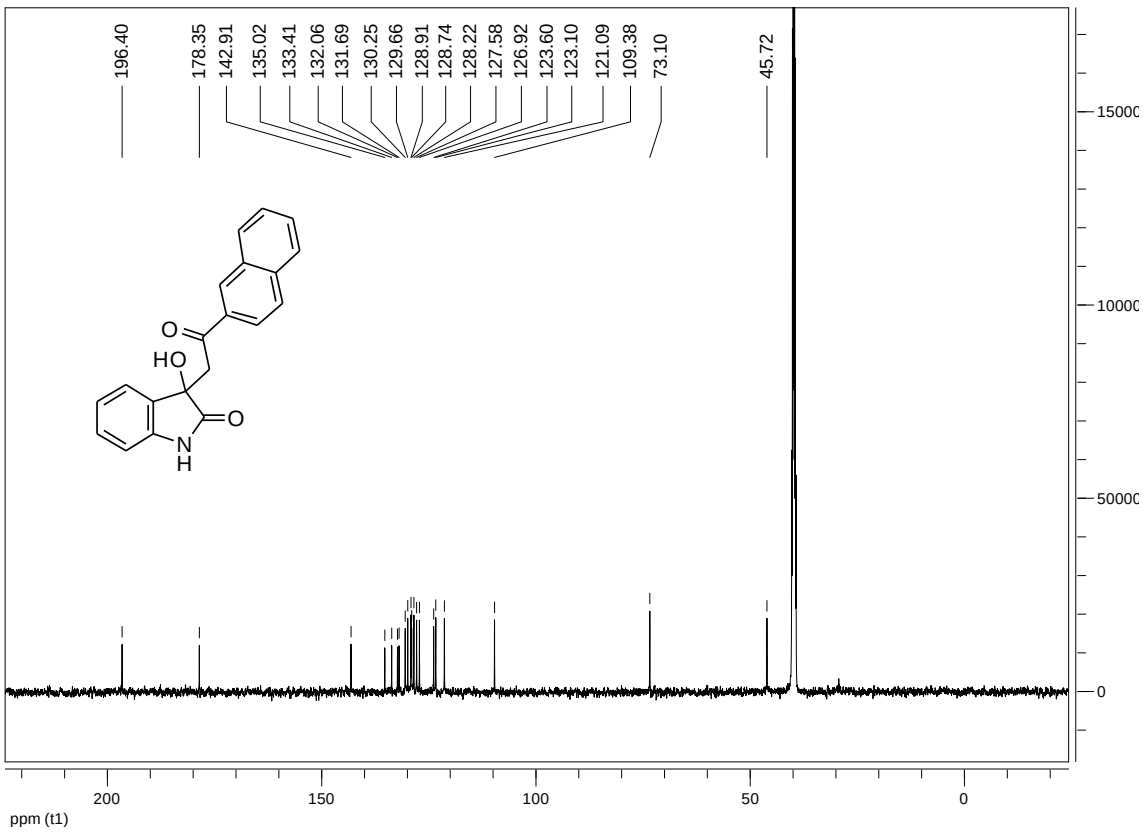
^{1}H and ^{13}C NMR spectra of (**3la**)



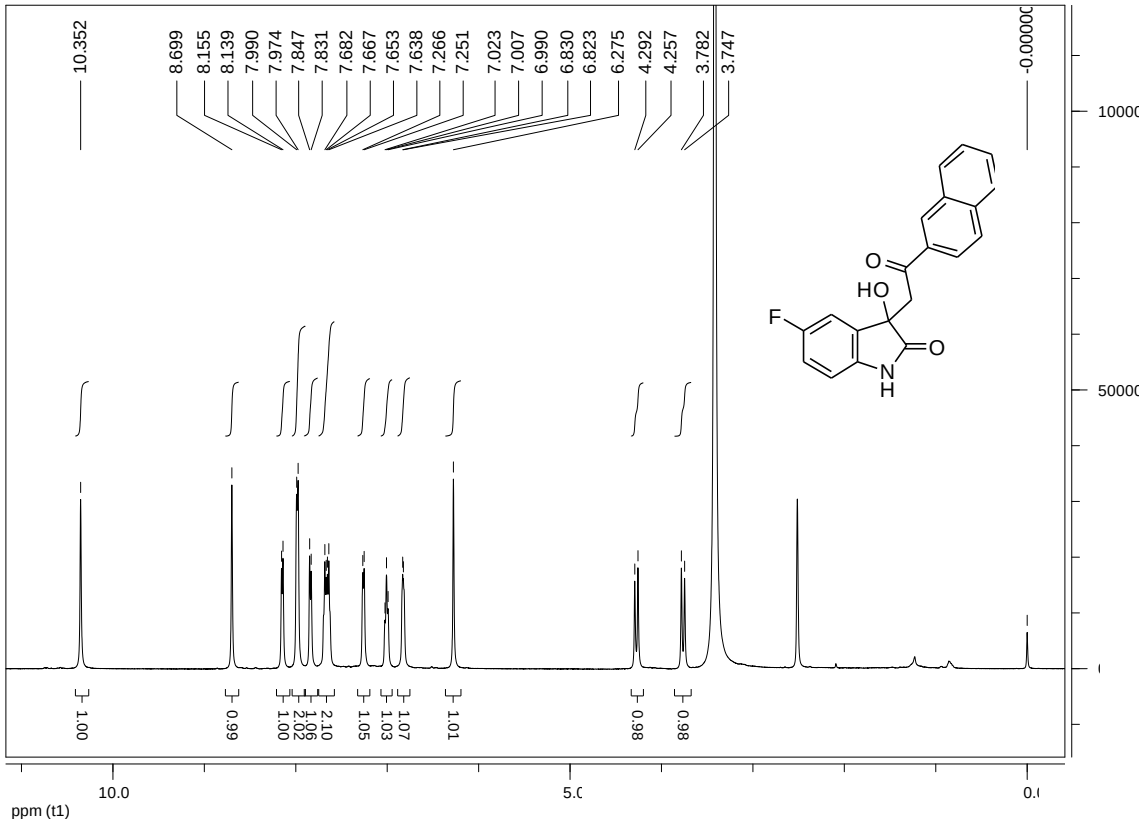


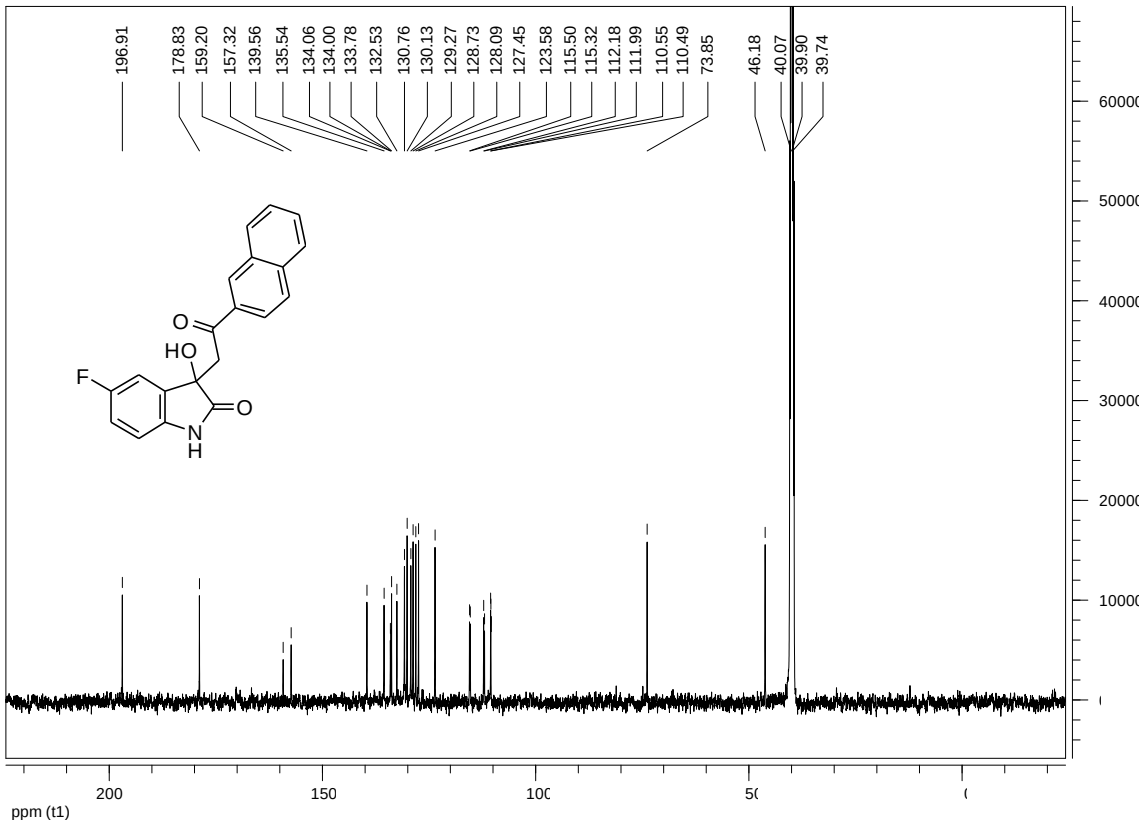
^{1}H and ^{13}C NMR spectra of (**3ab**)



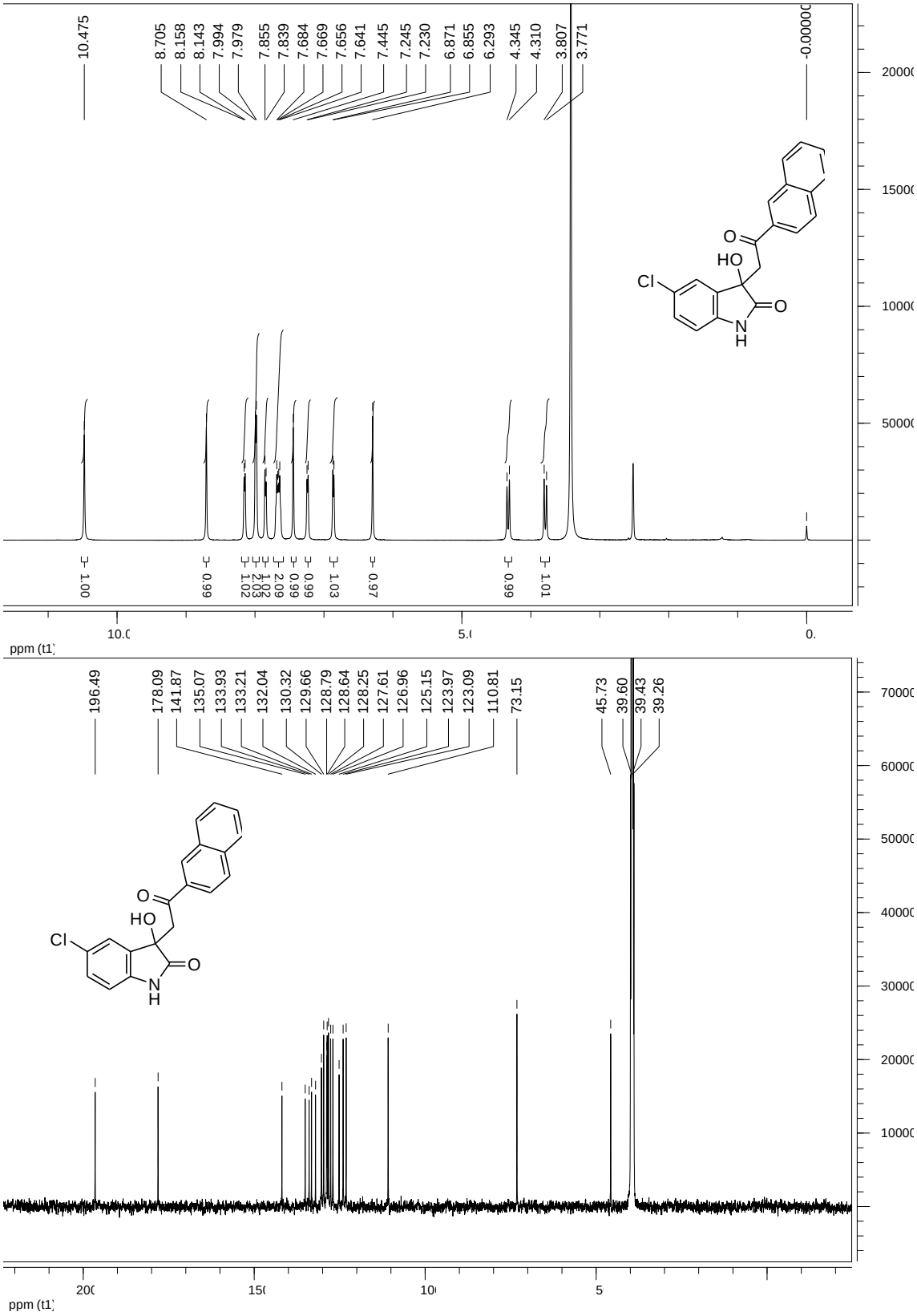


^{1}H and ^{13}C NMR spectra of (**3gb**)

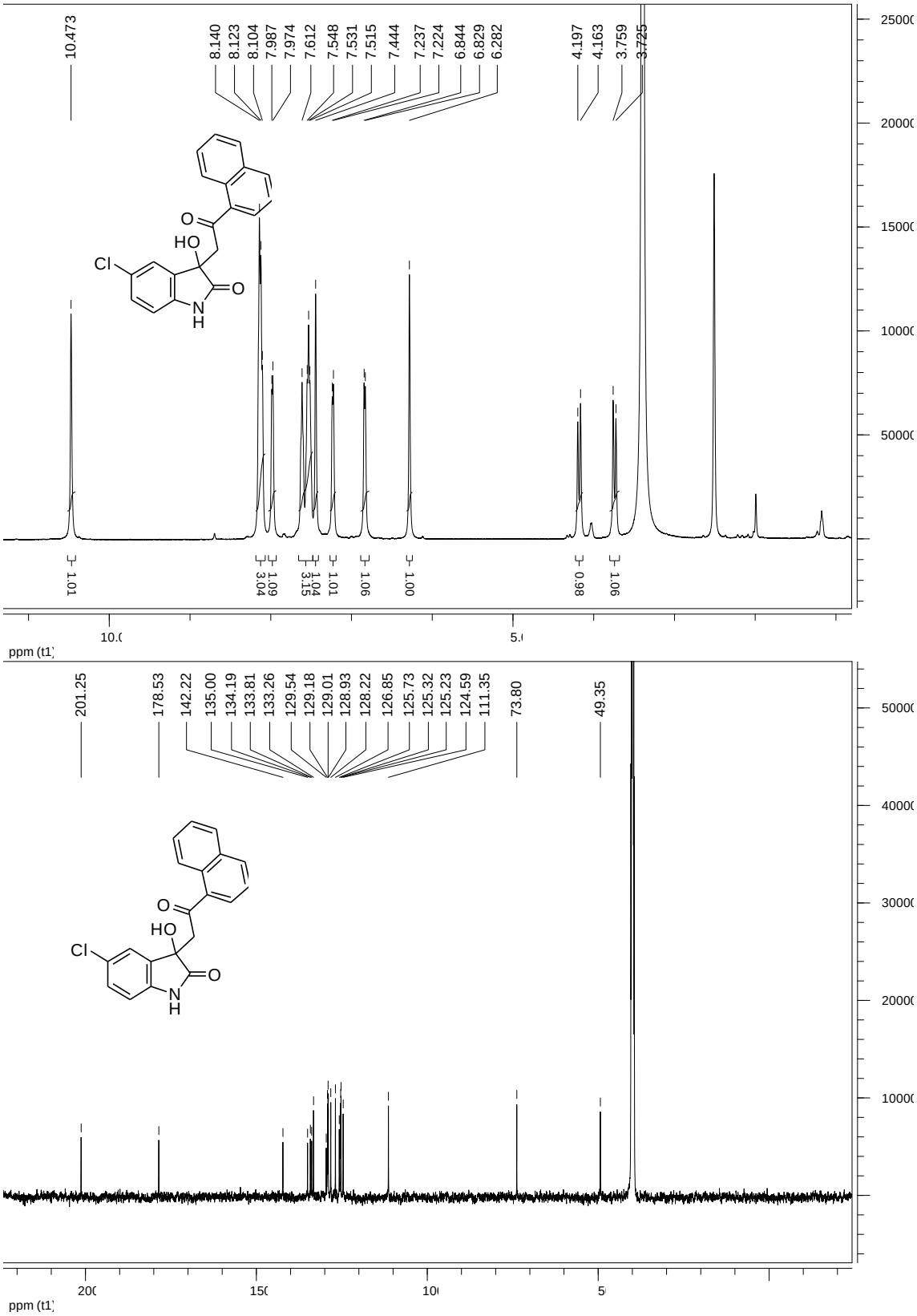




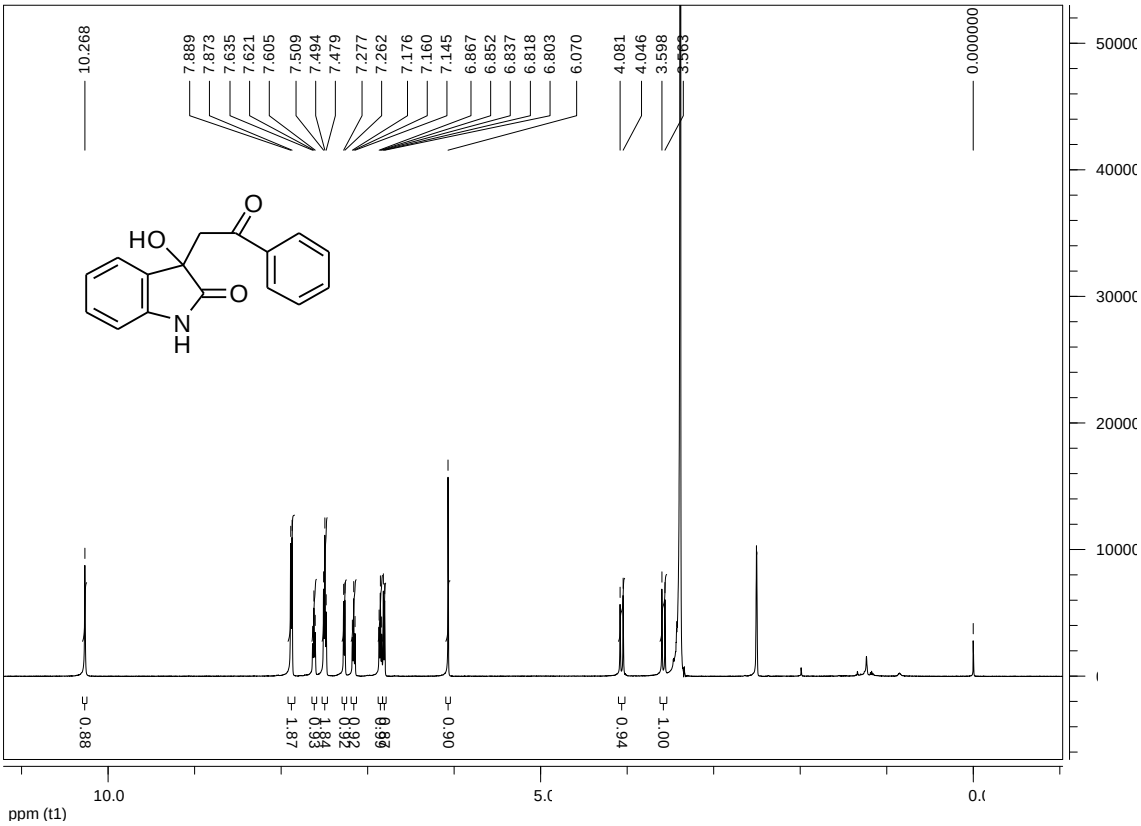
^{1}H and ^{13}C NMR spectra of (**3hb**)

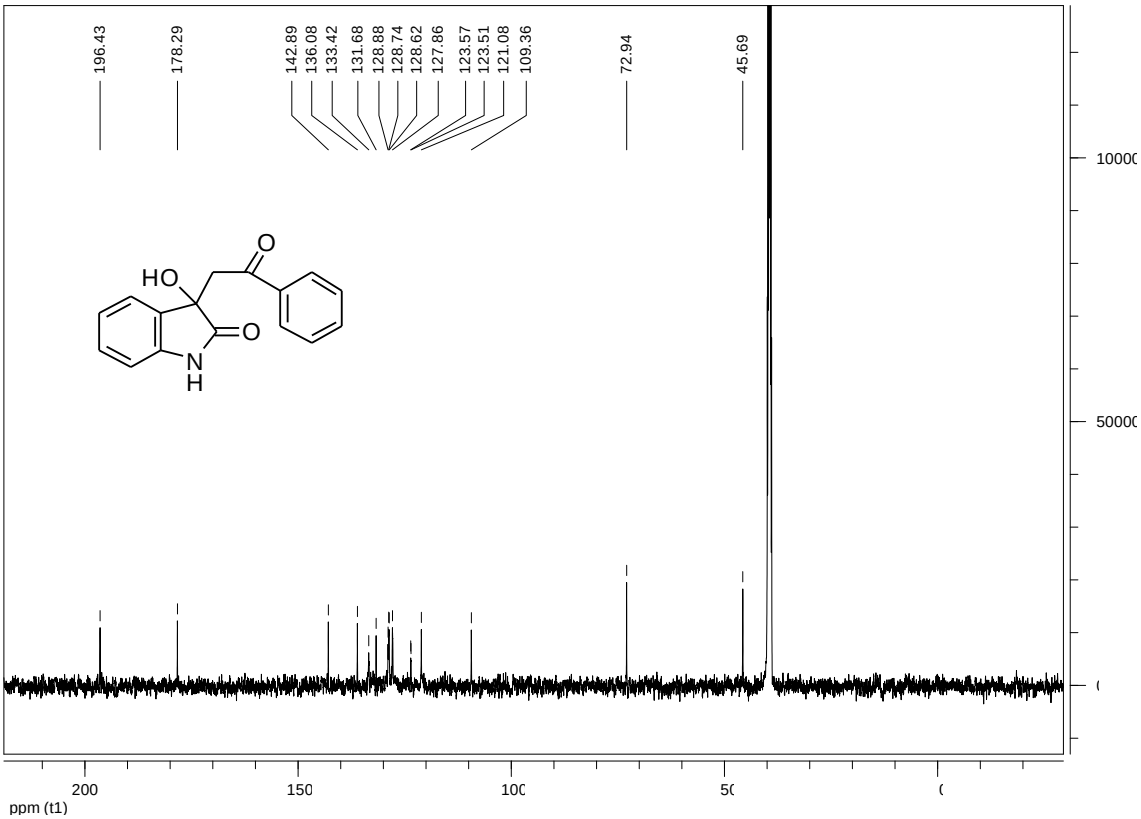


^{1}H and ^{13}C NMR spectra of (**3hc**)

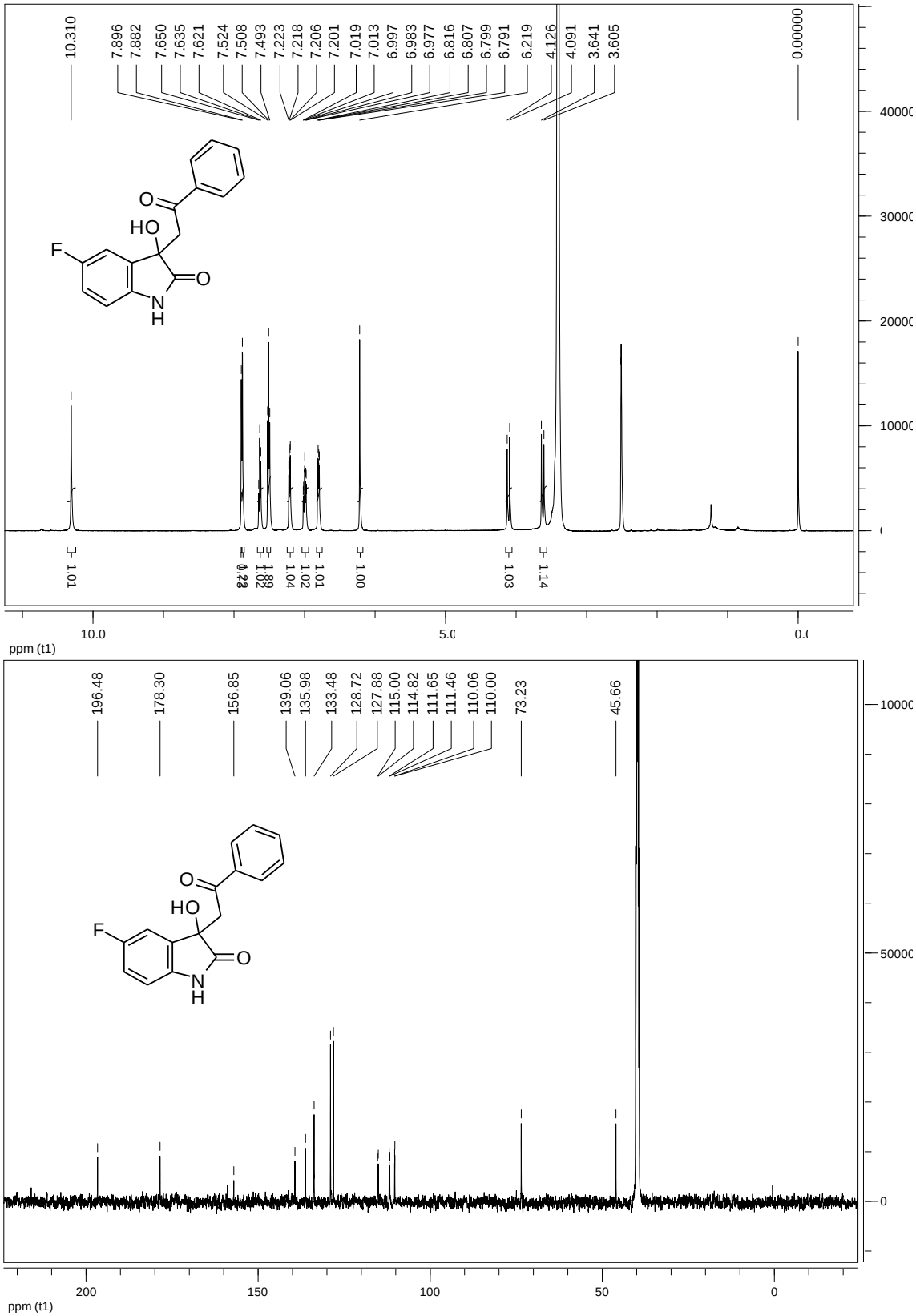


^{1}H and ^{13}C NMR spectra of (**3ad**)

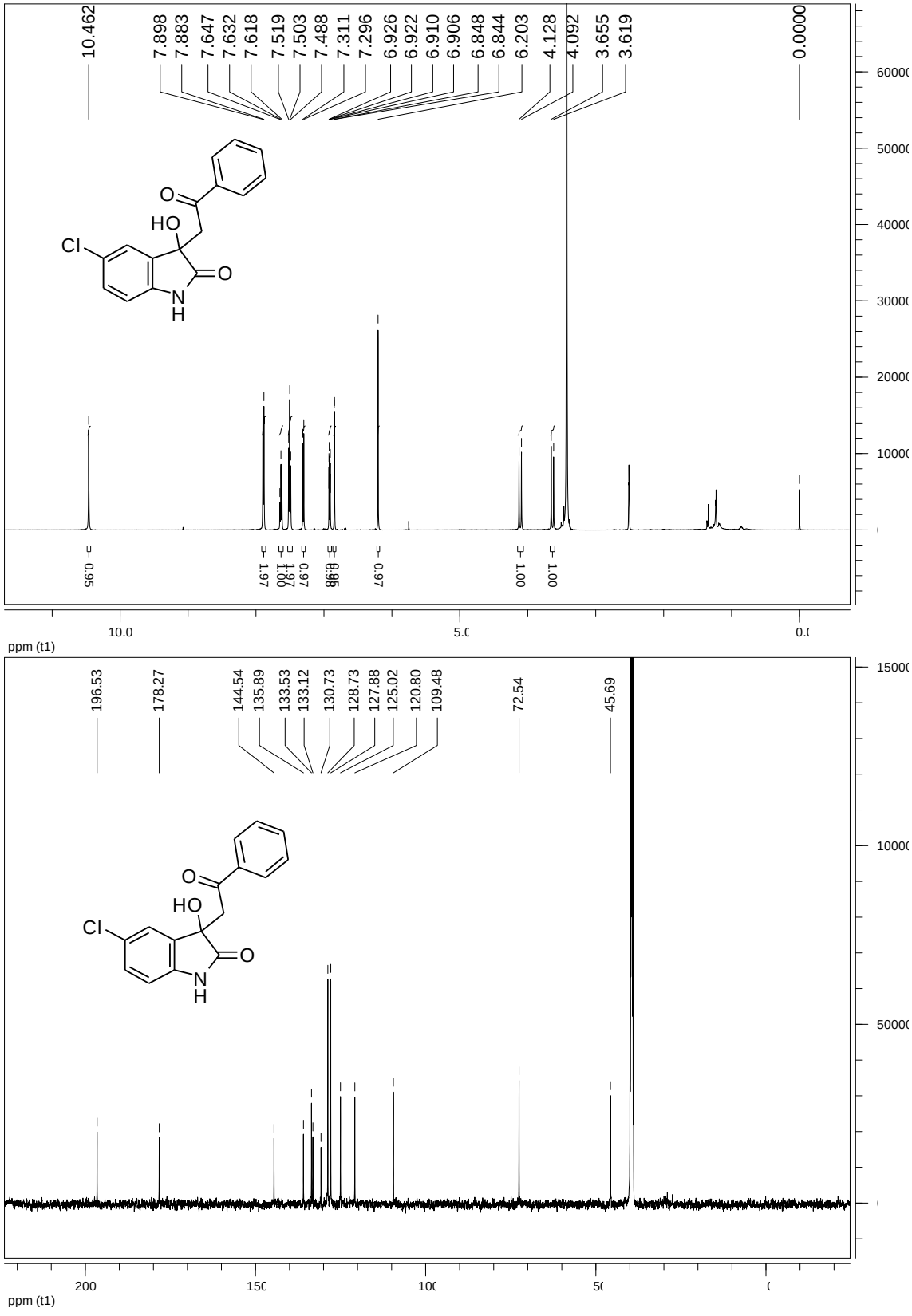




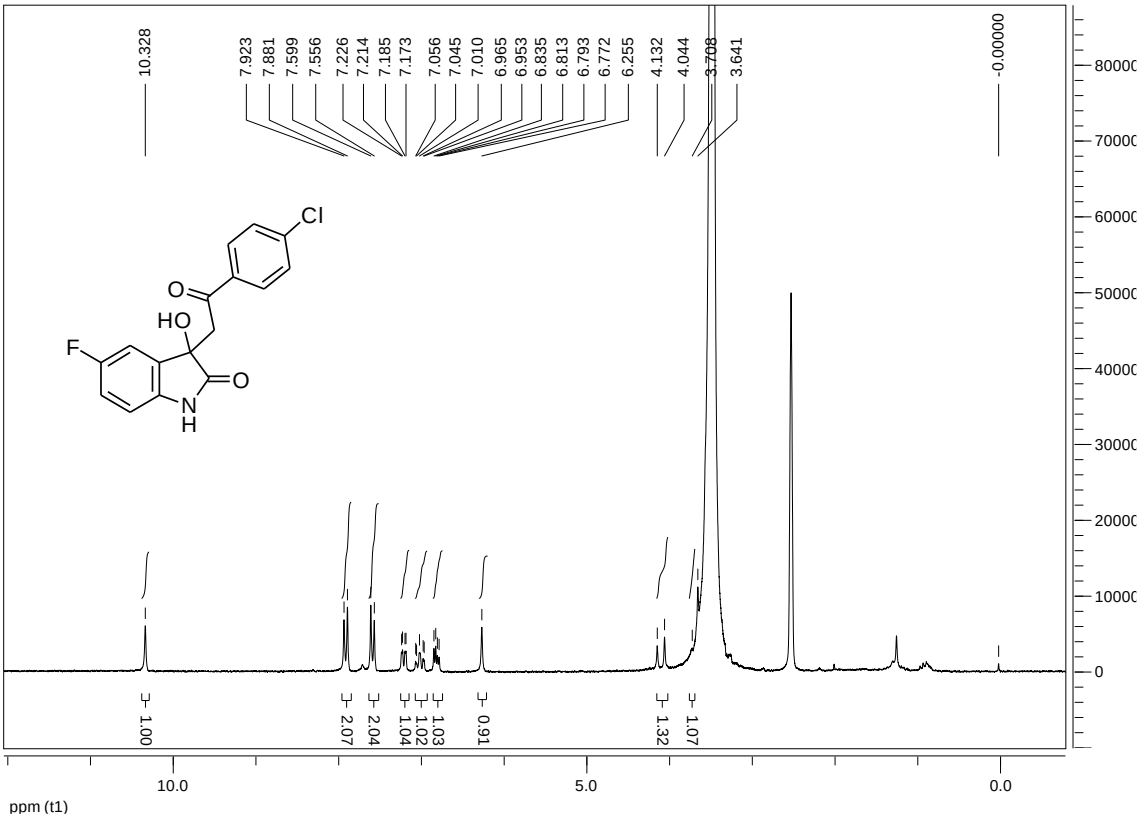
^{1}H and ^{13}C NMR spectra of (**3gd**)

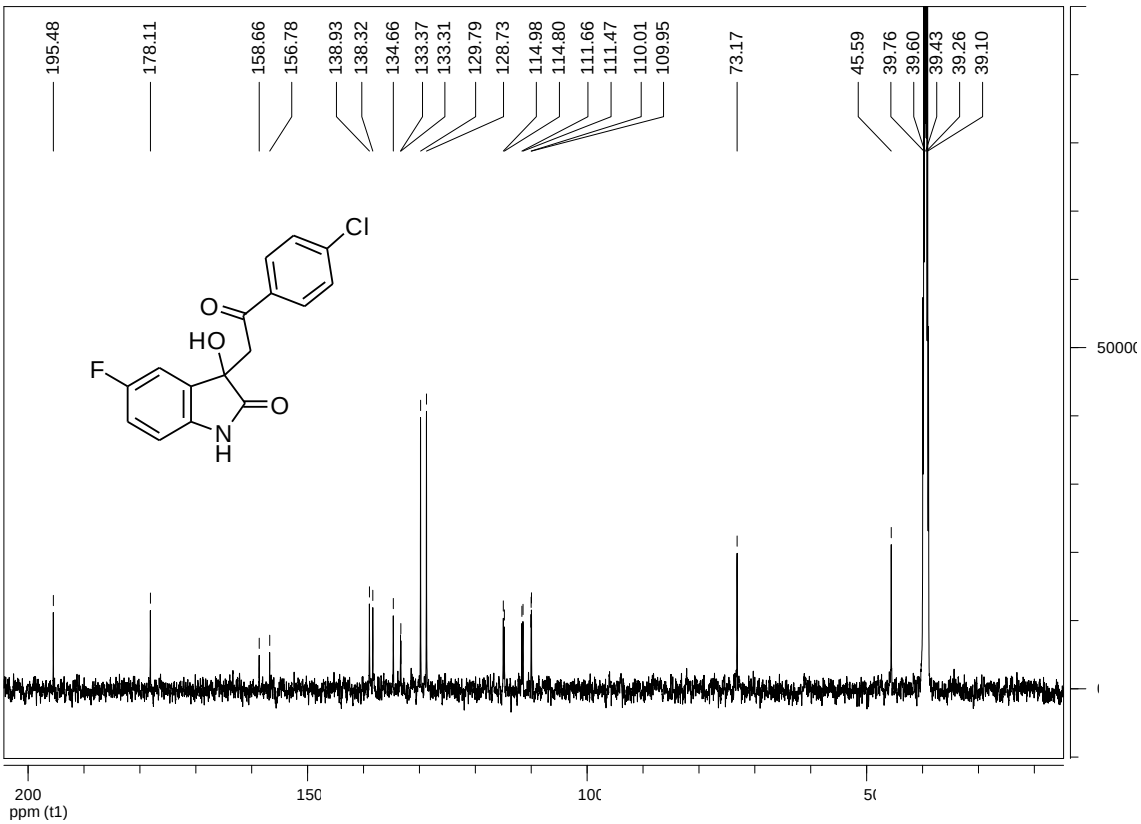


^{1}H and ^{13}C NMR spectra of (**3hd**)

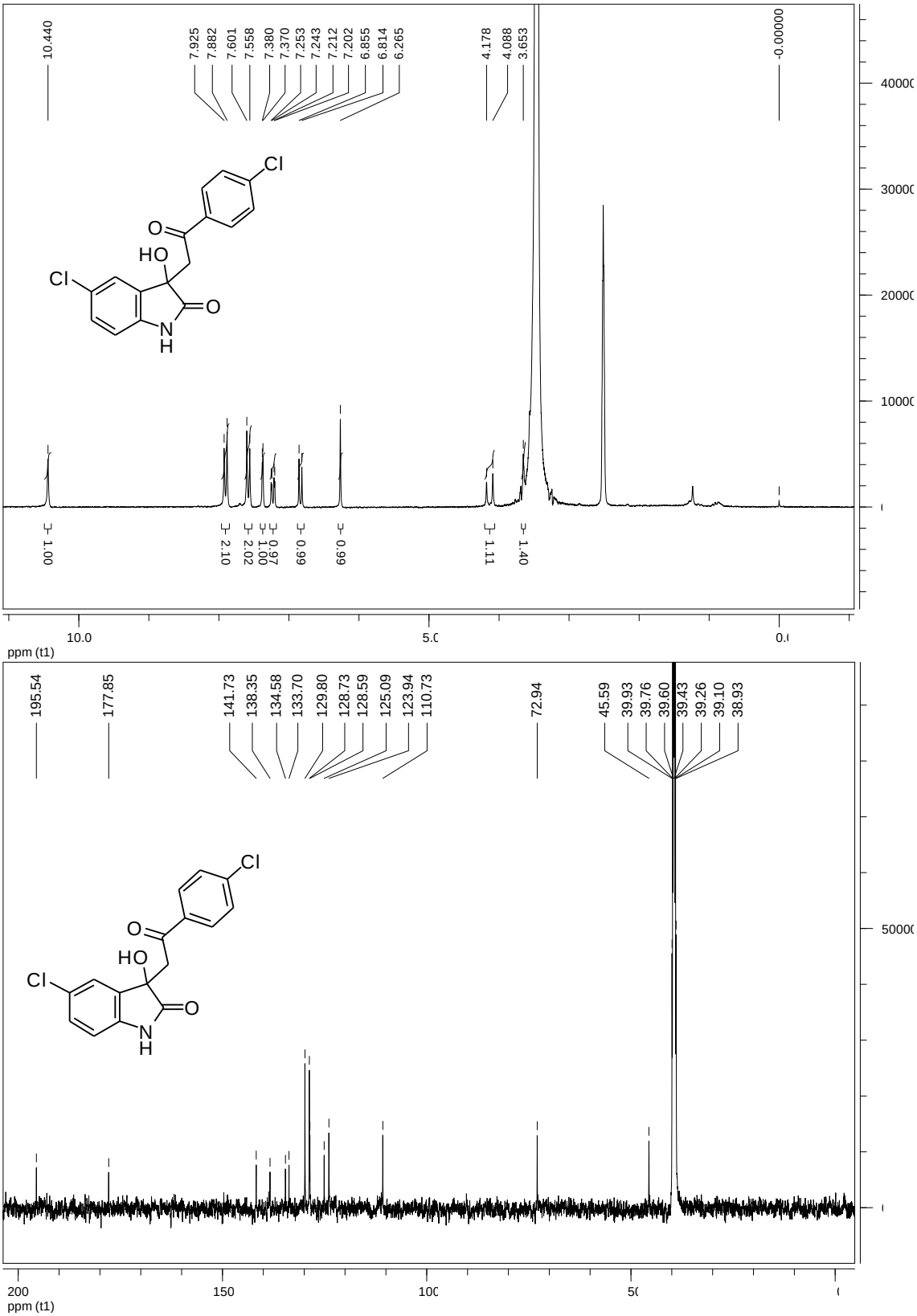


^{1}H and ^{13}C NMR spectra of (**3ge**)

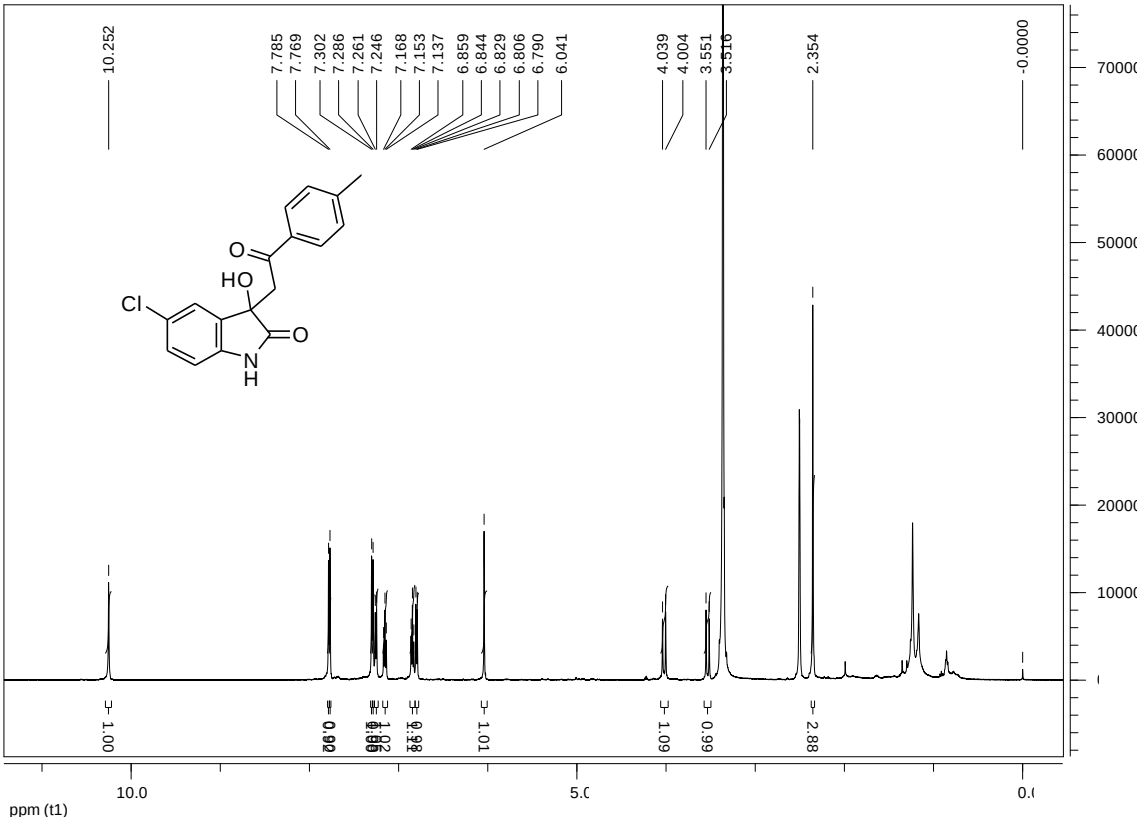


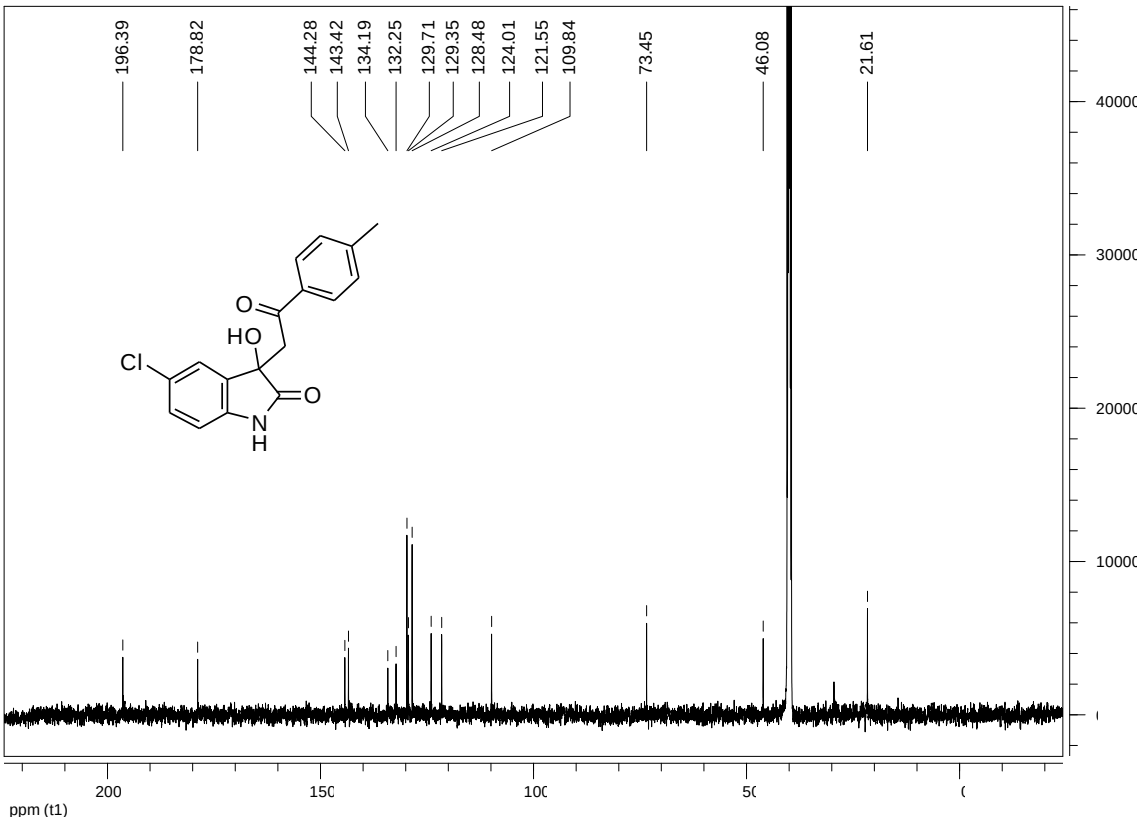


^{1}H and ^{13}C NMR spectra of (**3he**)

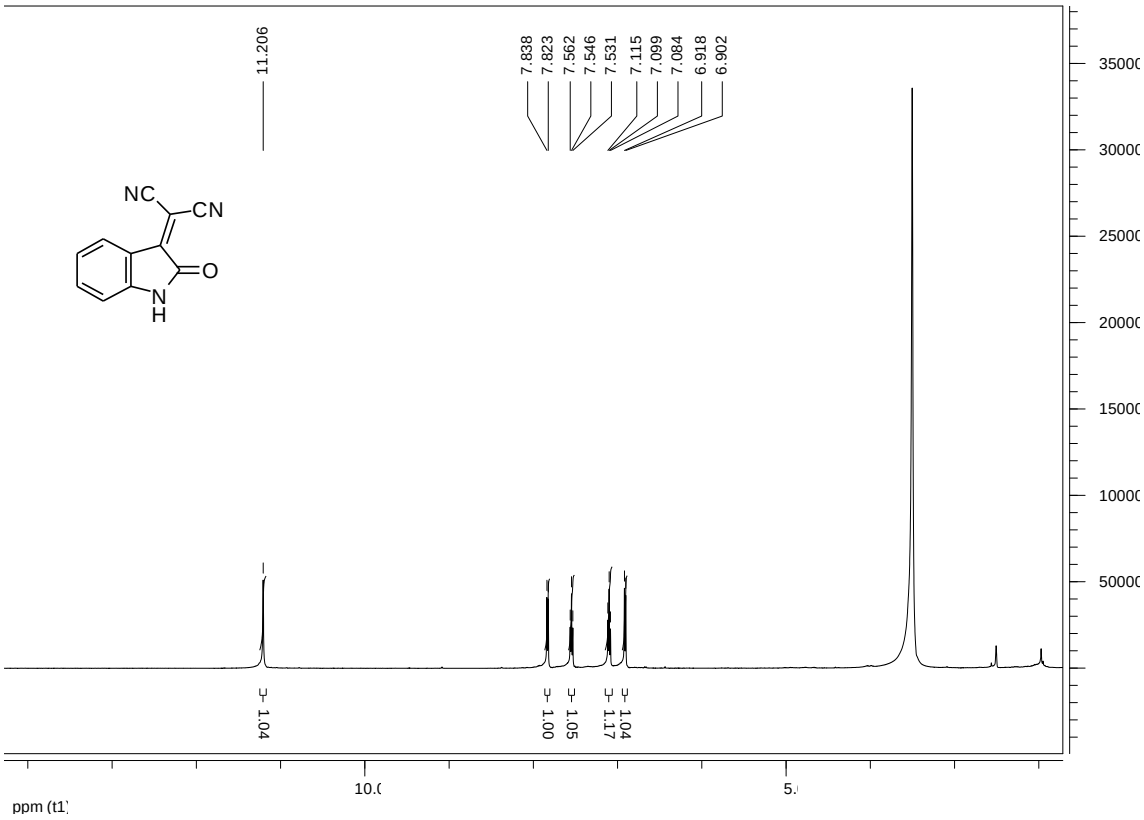


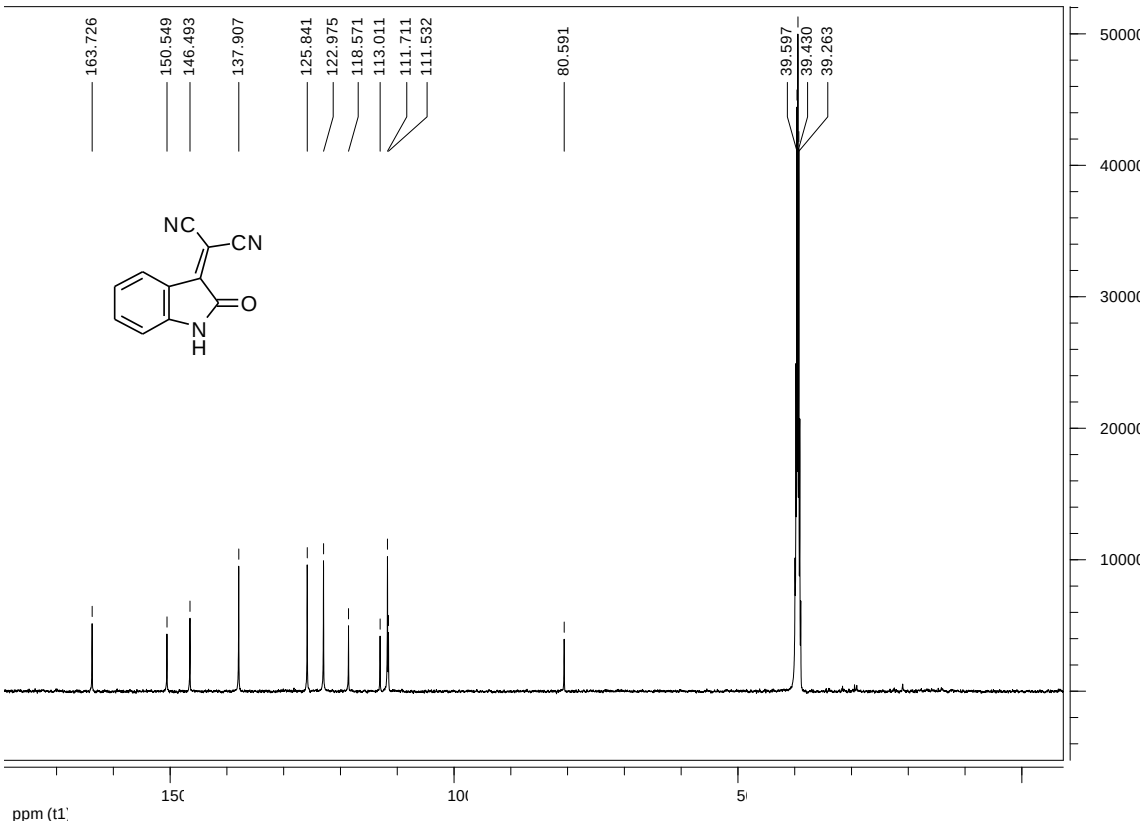
^{1}H and ^{13}C NMR spectra of (**3hf**)



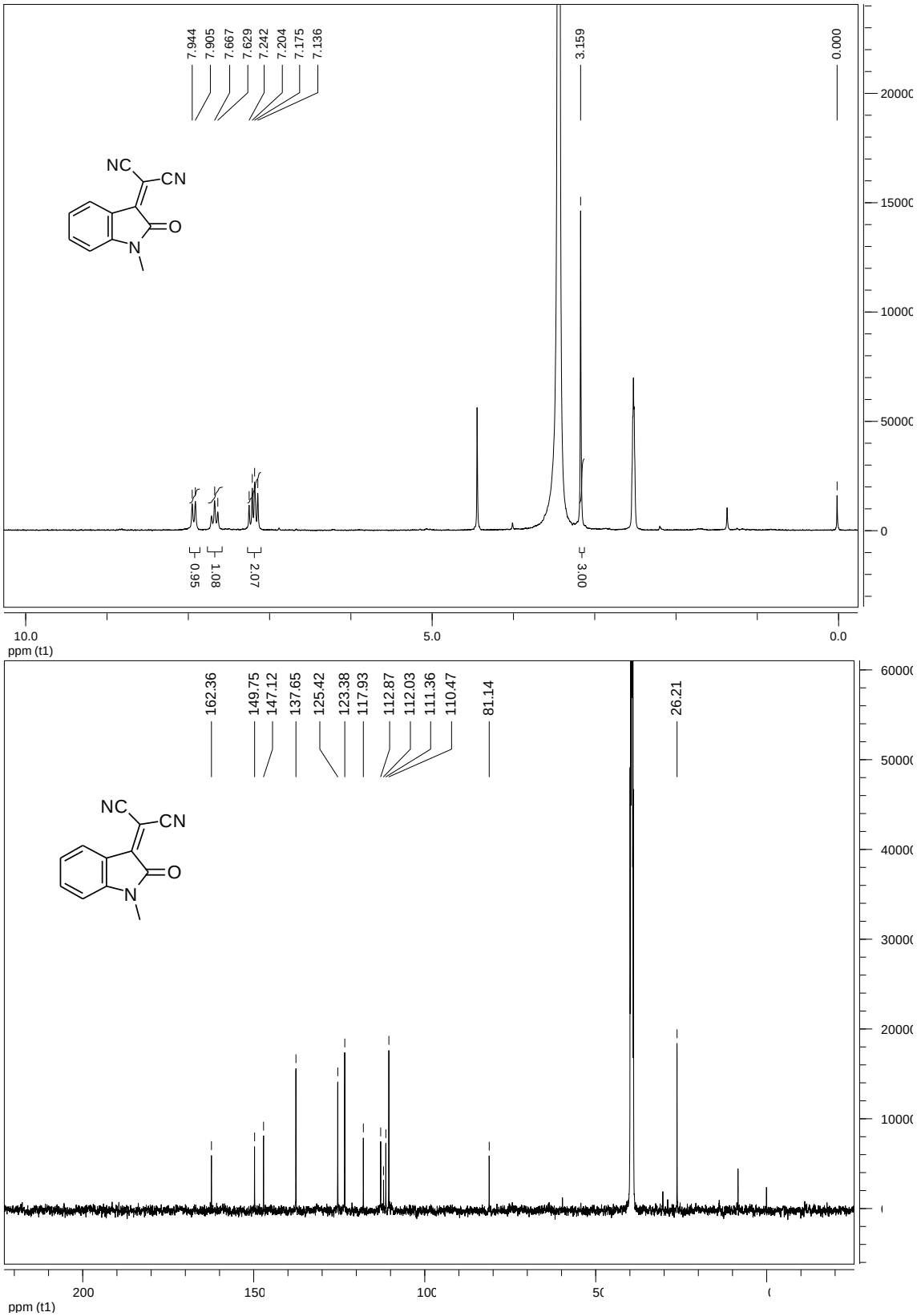


^{1}H and ^{13}C NMR spectra of (**4a**)

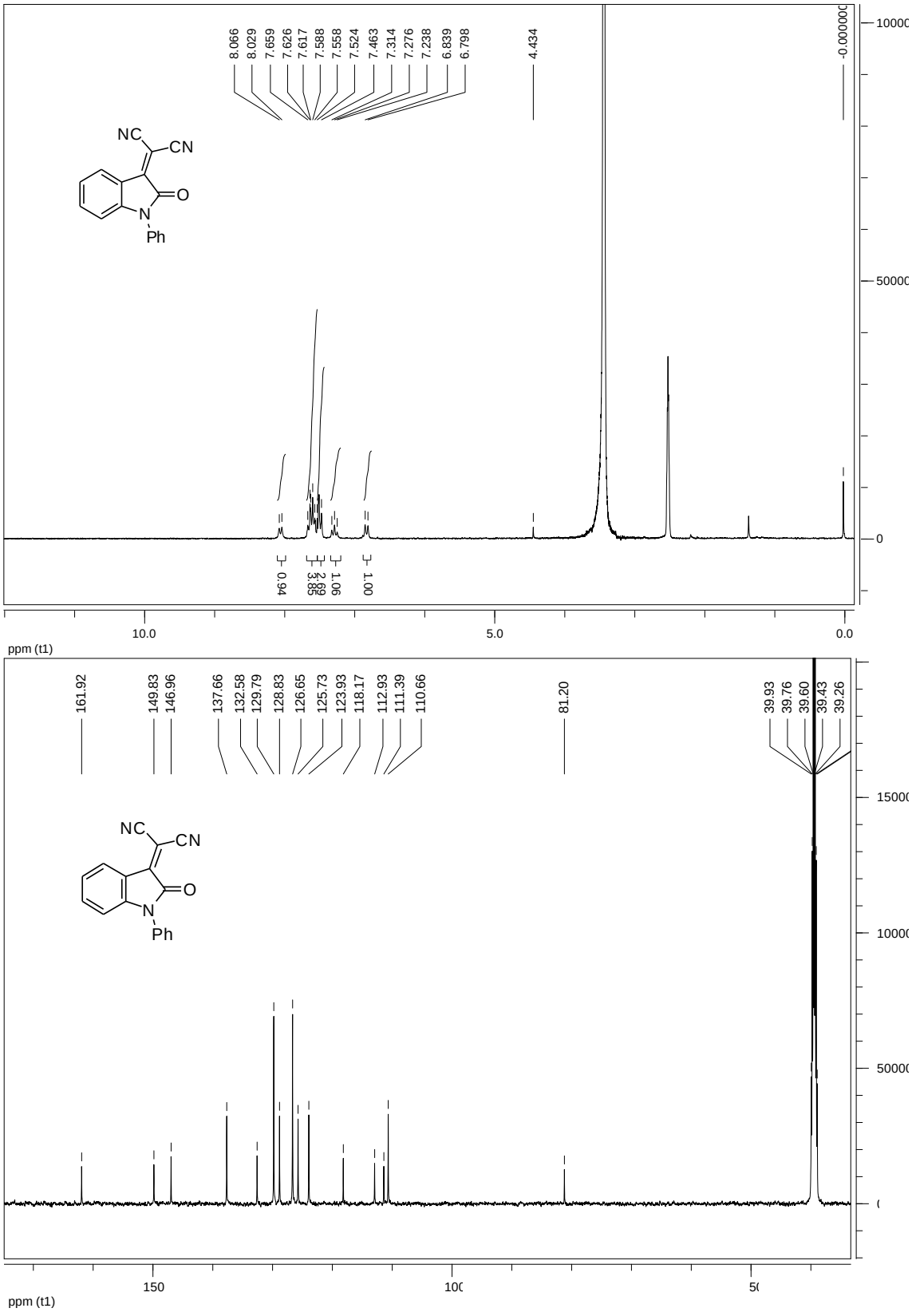




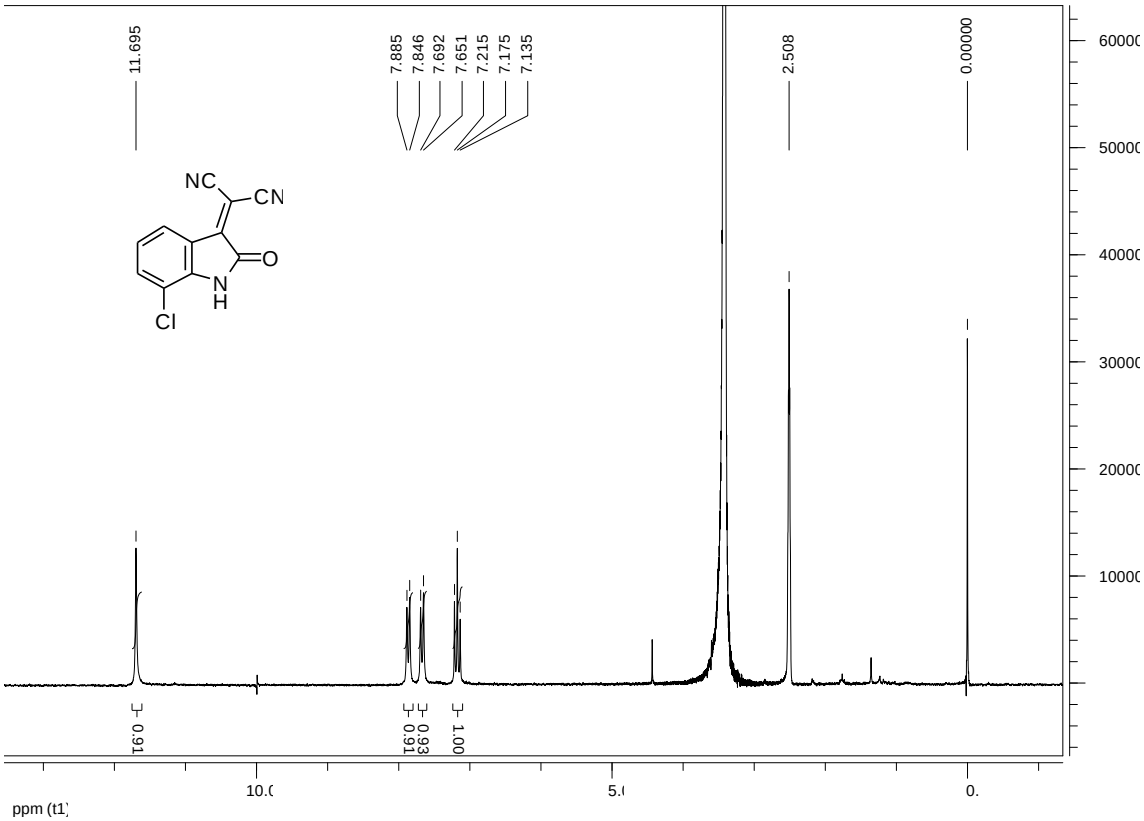
^{1}H and ^{13}C NMR spectra of (**4b**)

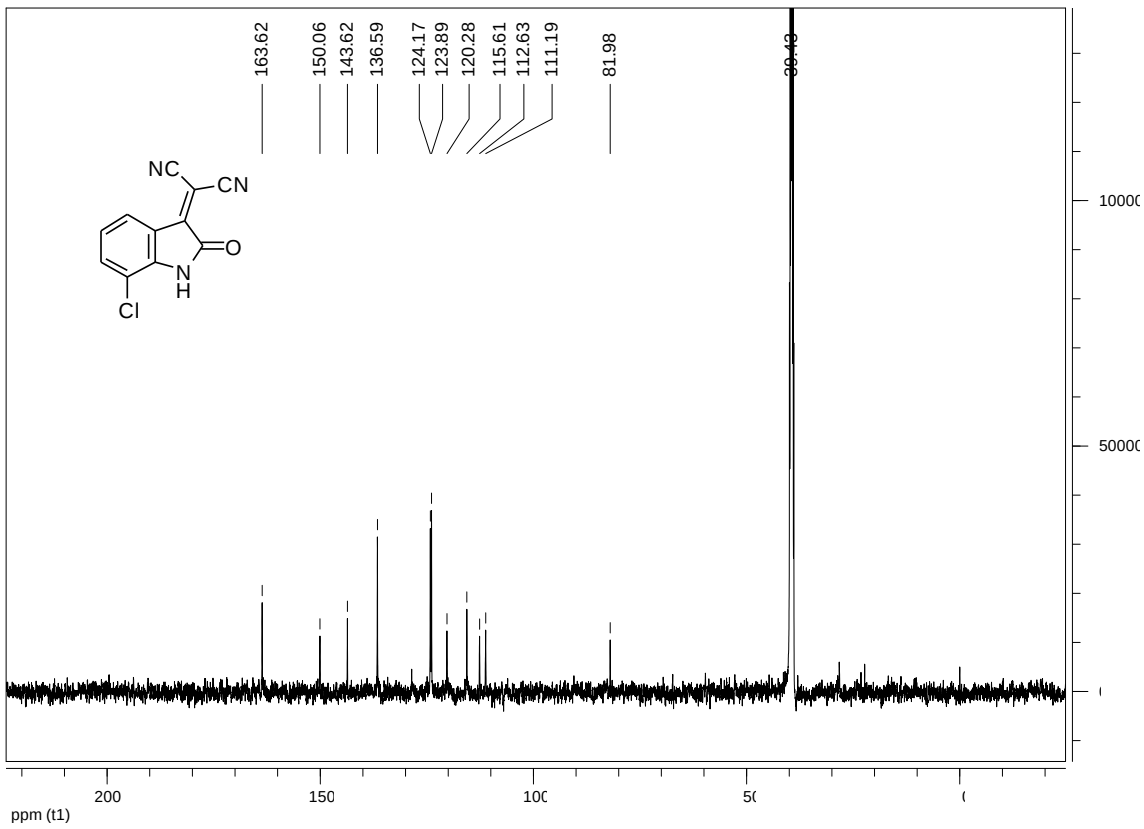


^{1}H and ^{13}C NMR spectra of (**4c**)

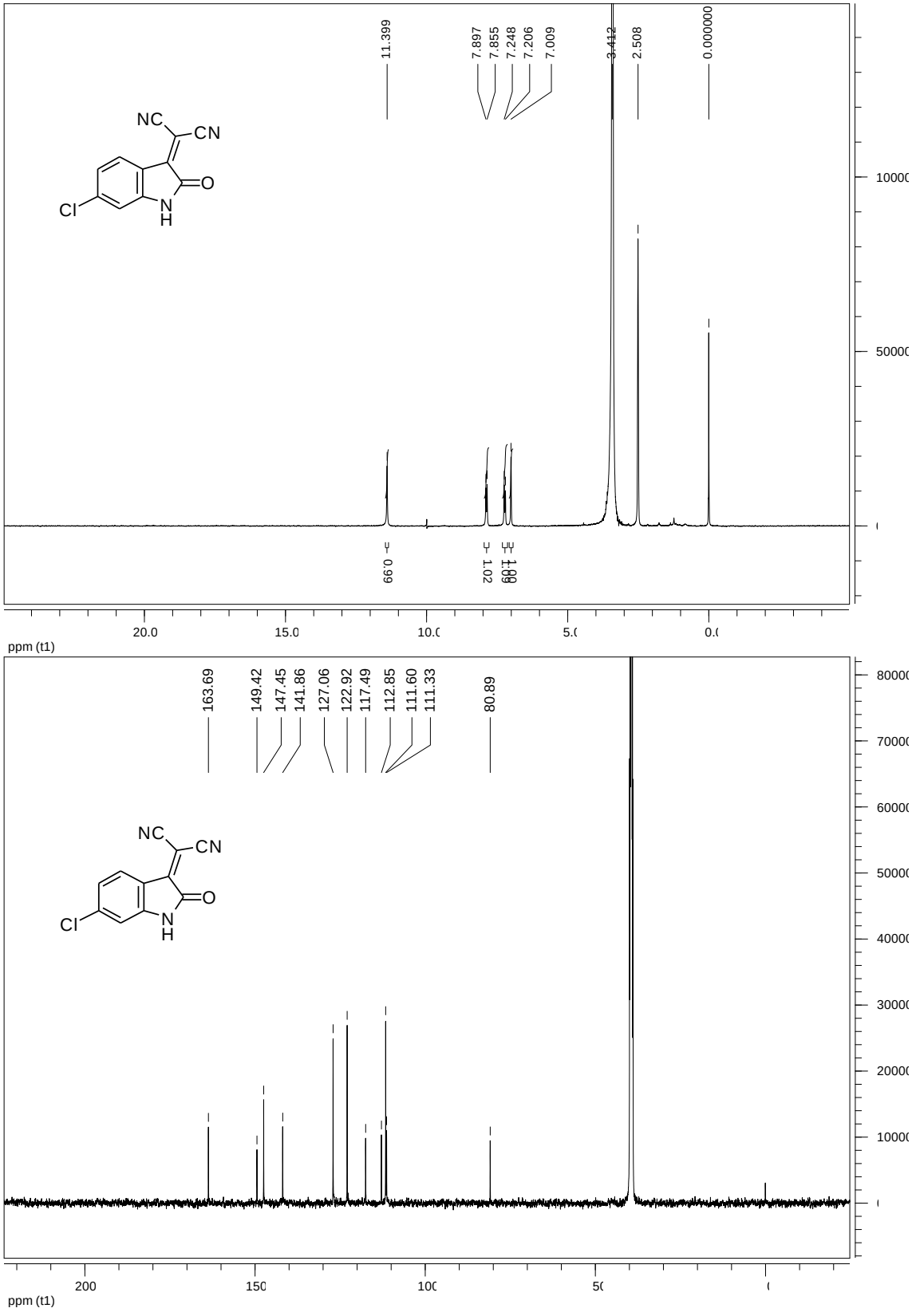


^{1}H and ^{13}C NMR spectra of (**4d**)

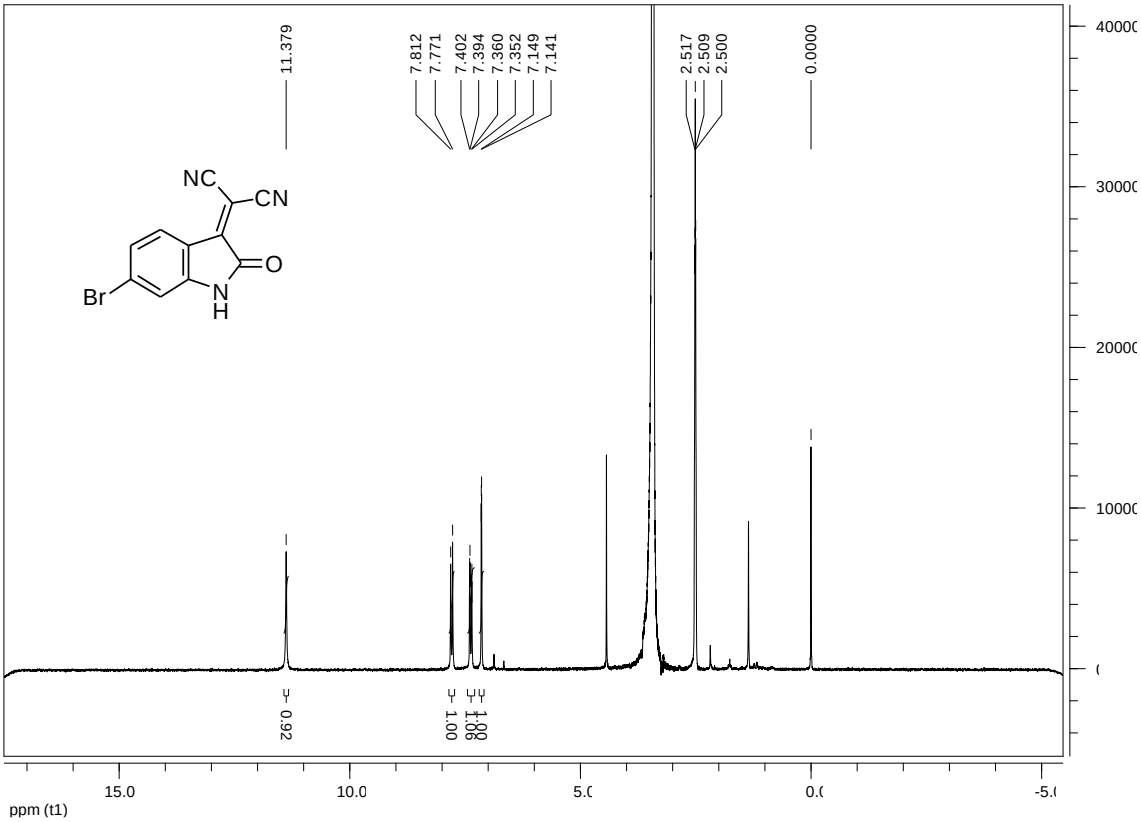


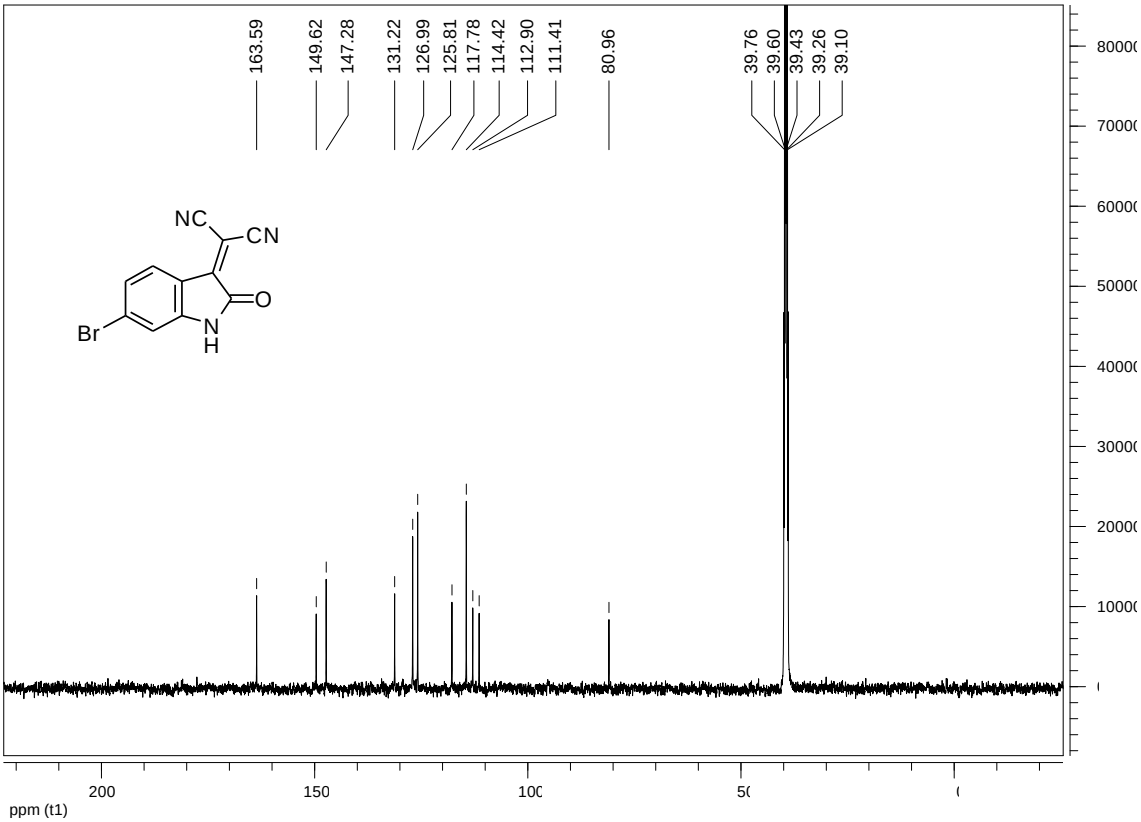


^{1}H and ^{13}C NMR spectra of (**4e**)

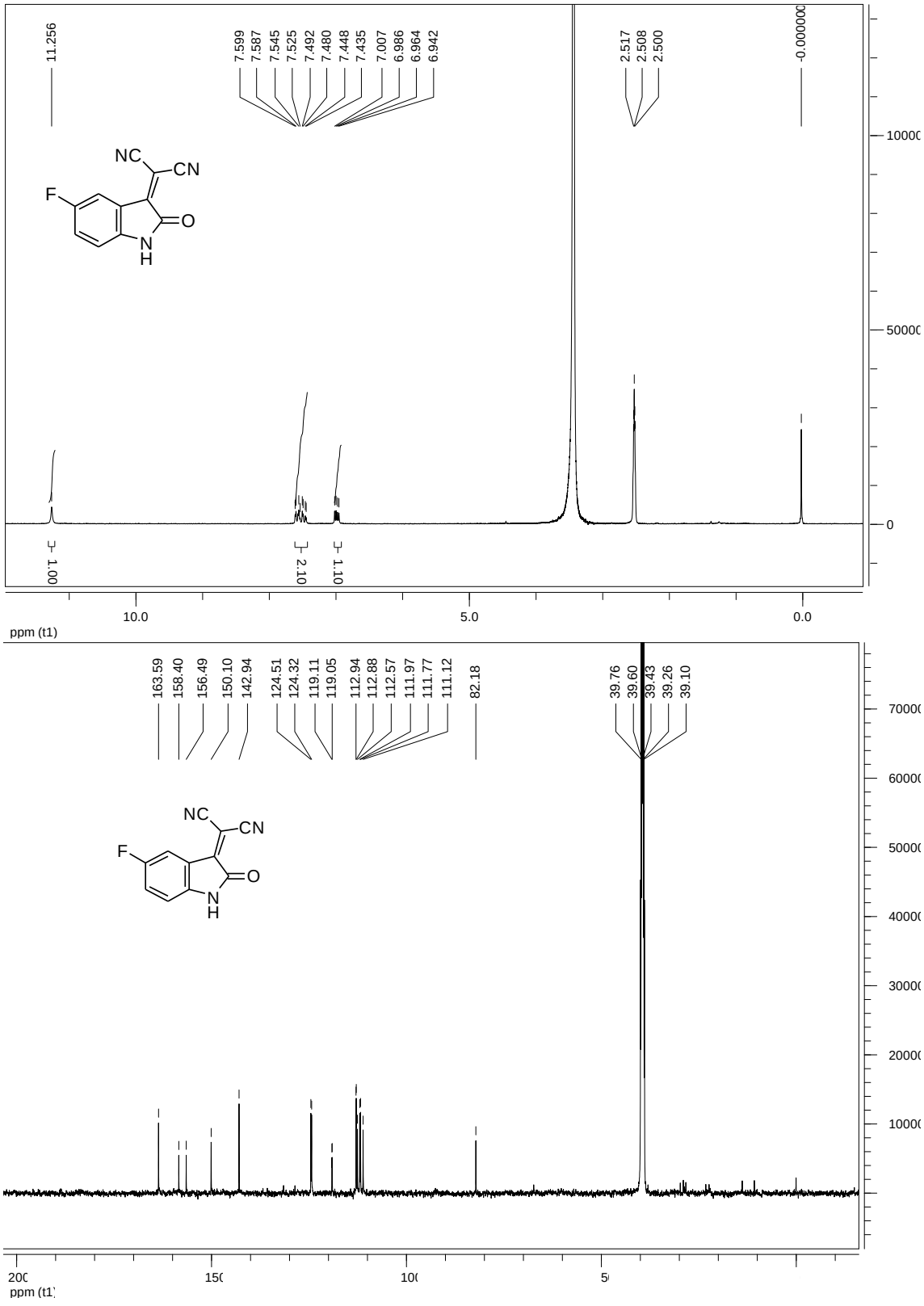


^{1}H and ^{13}C NMR spectra of (**4f**)

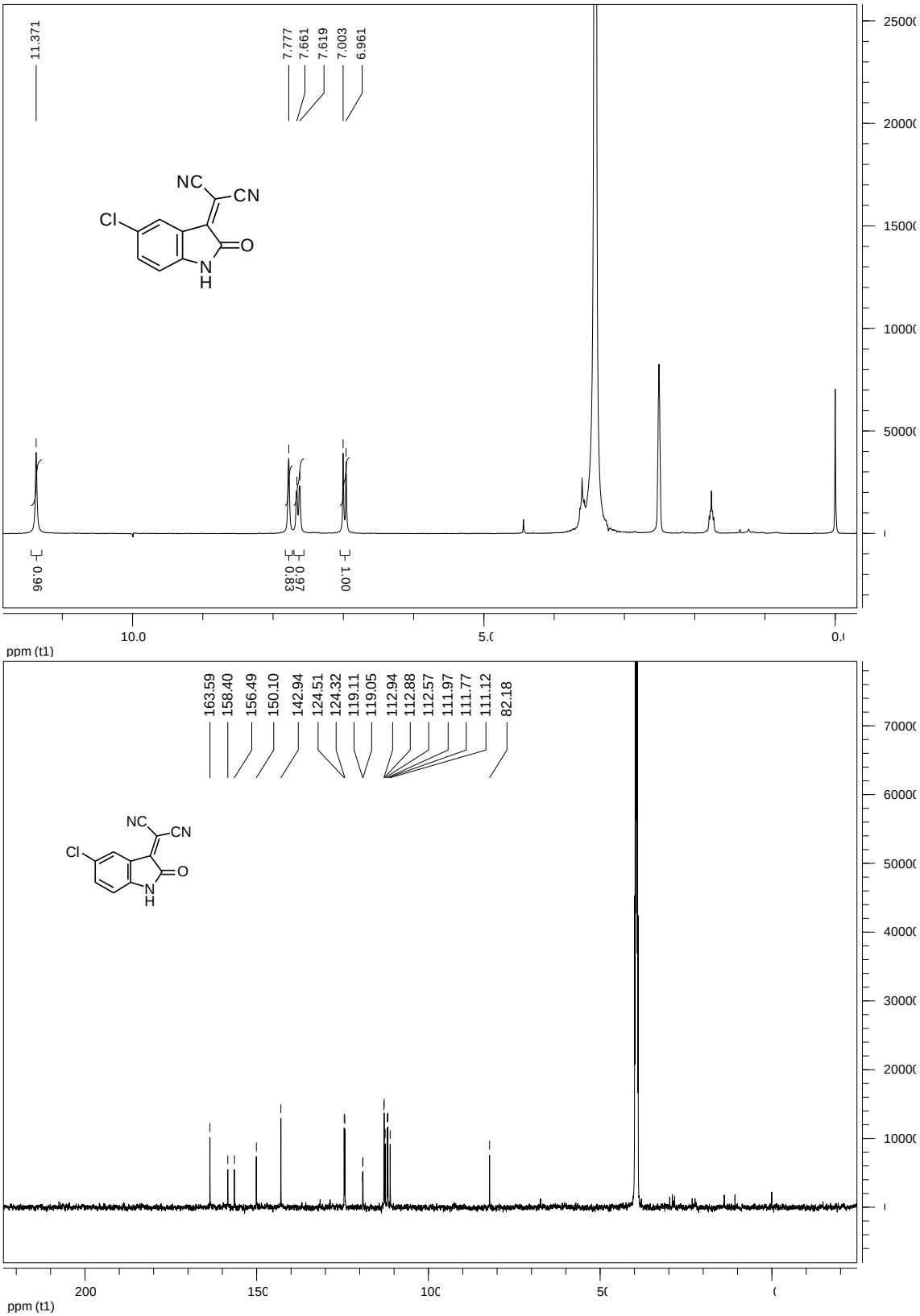




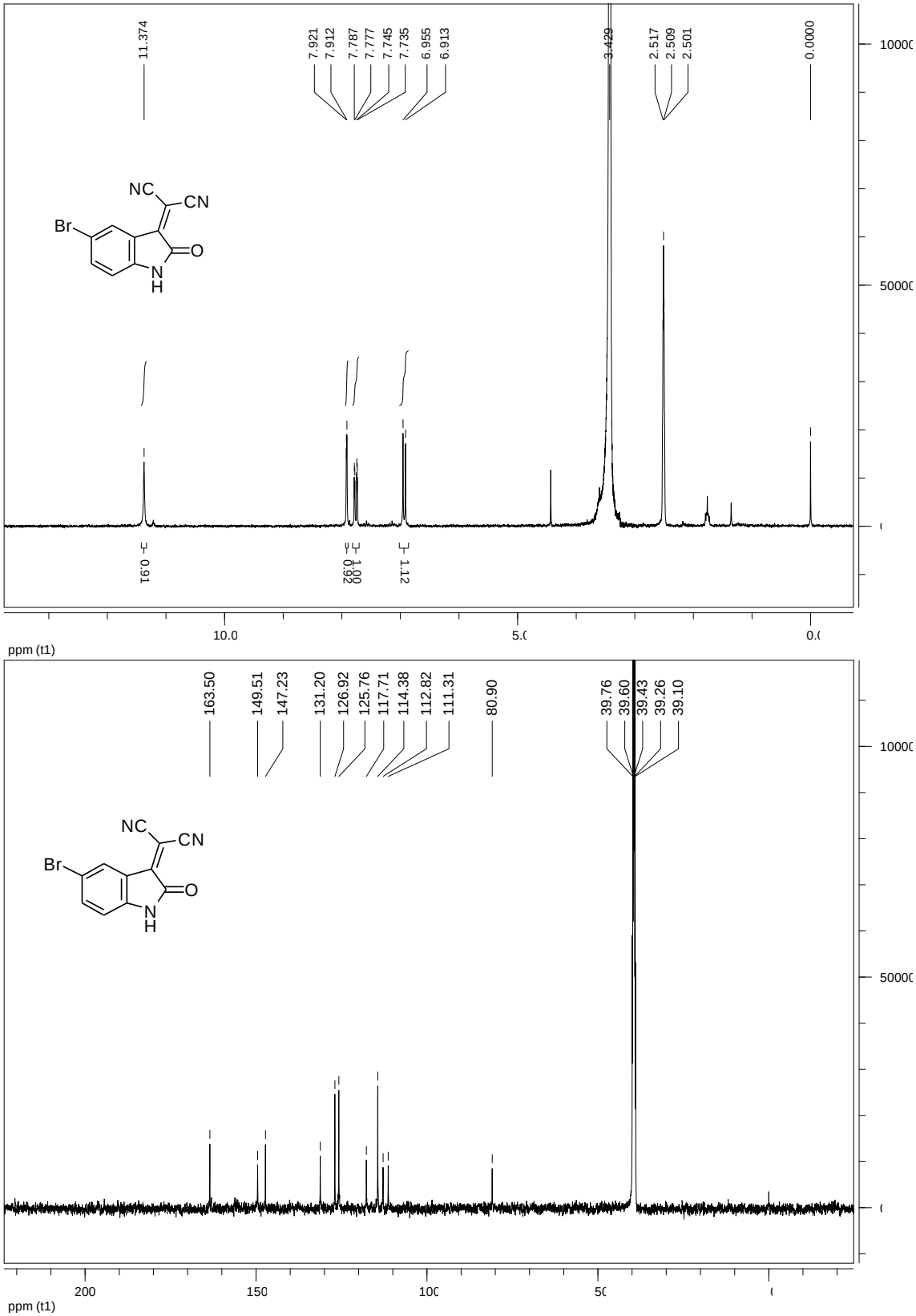
^{1}H and ^{13}C NMR spectra of (**4g**)



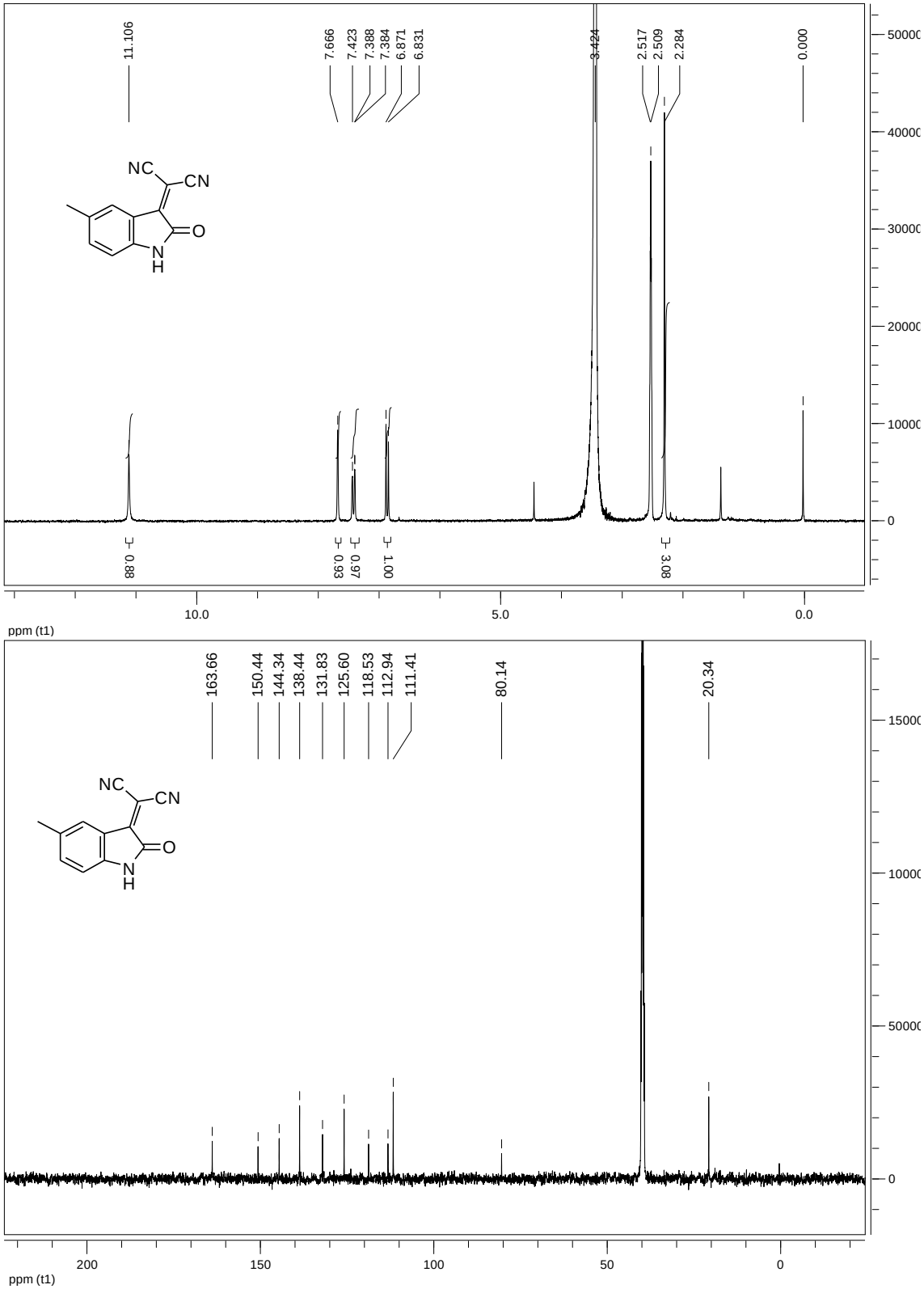
^{1}H and ^{13}C NMR spectra of (**4h**)



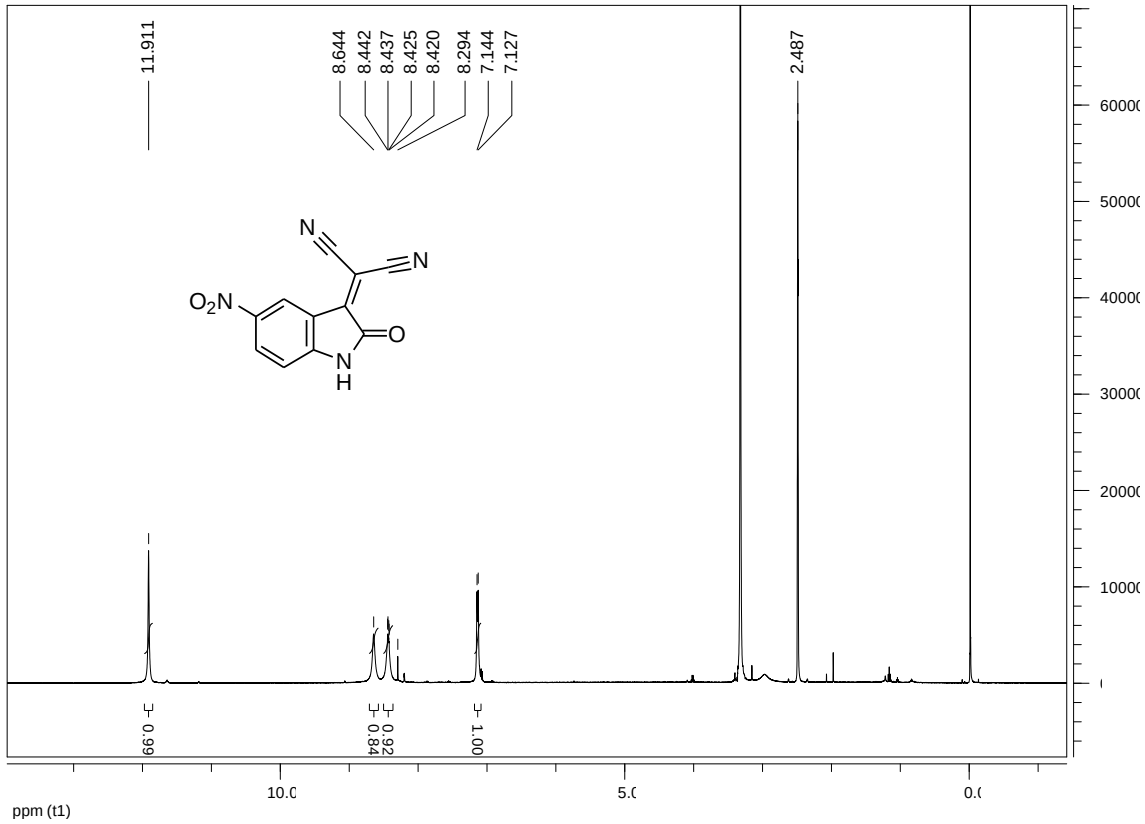
^{1}H and ^{13}C NMR spectra of (**4i**)

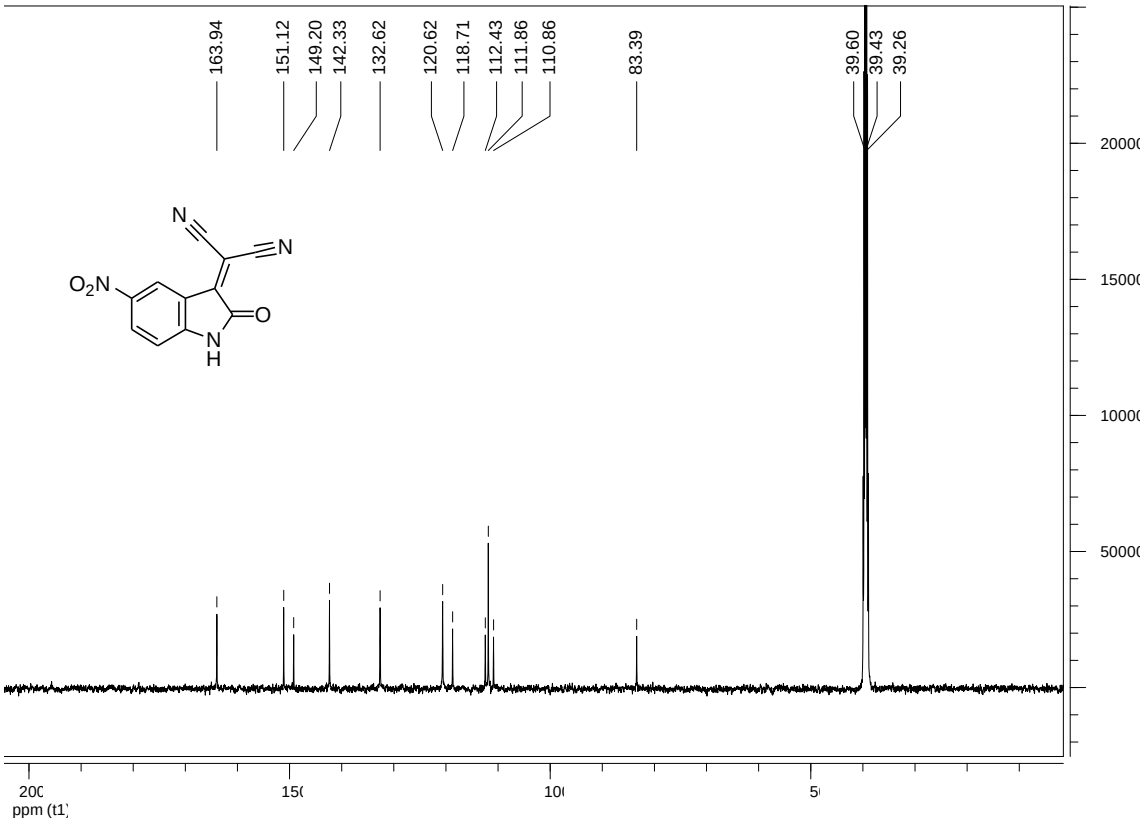


^{1}H and ^{13}C NMR spectra of (**4j**)

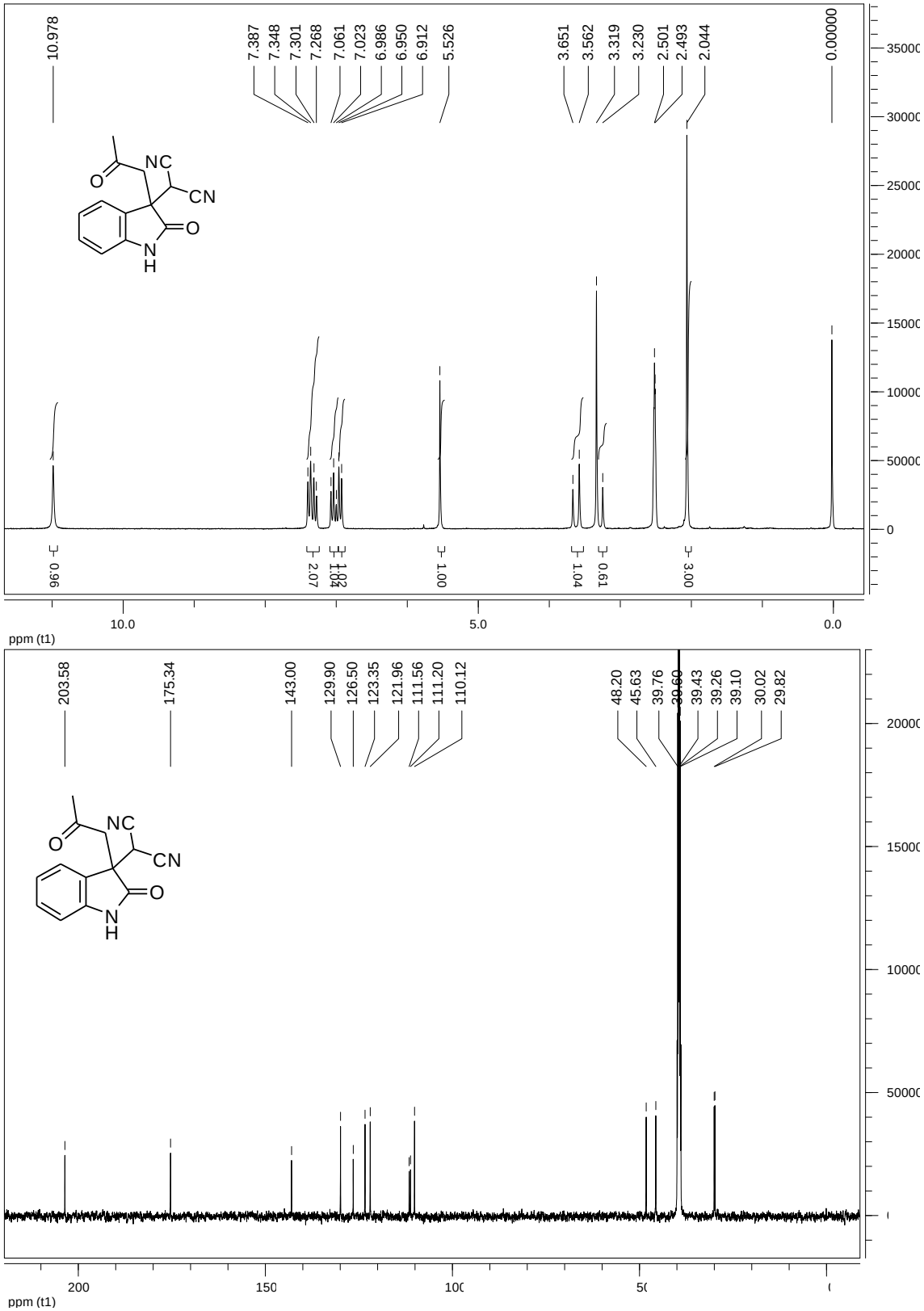


^{1}H and ^{13}C NMR spectra of (**4k**)

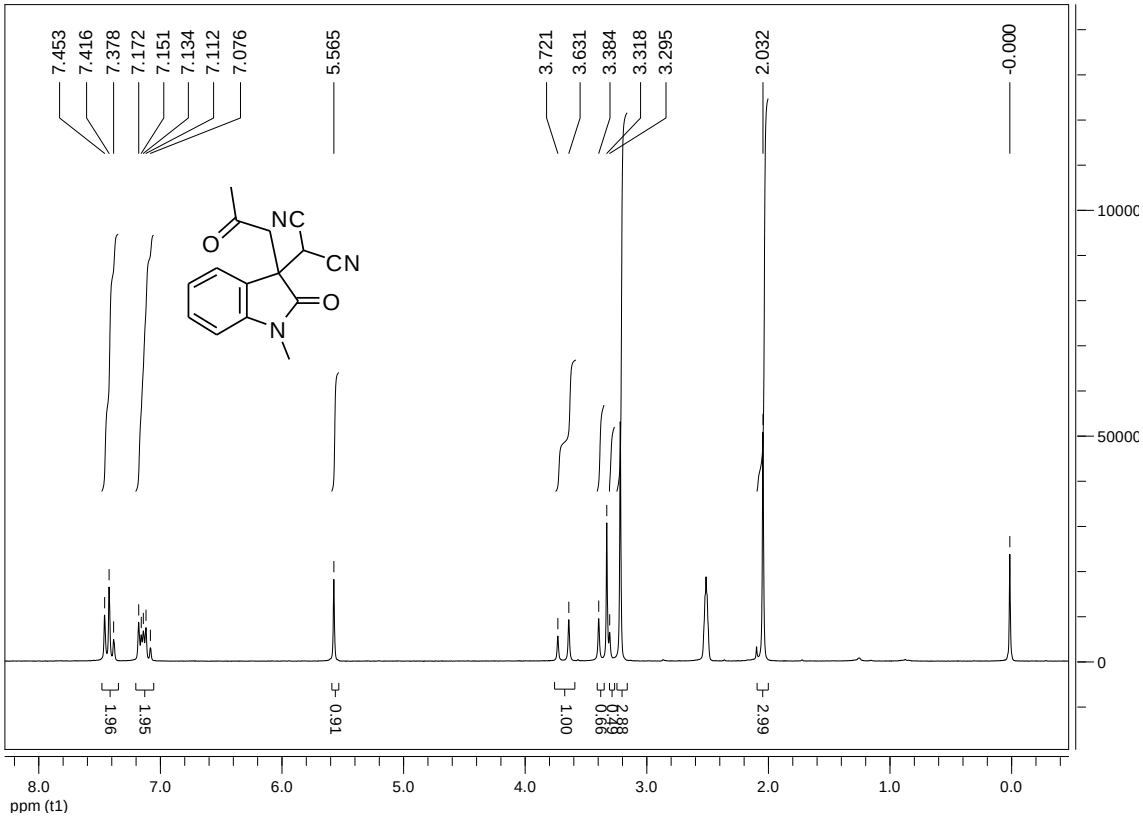


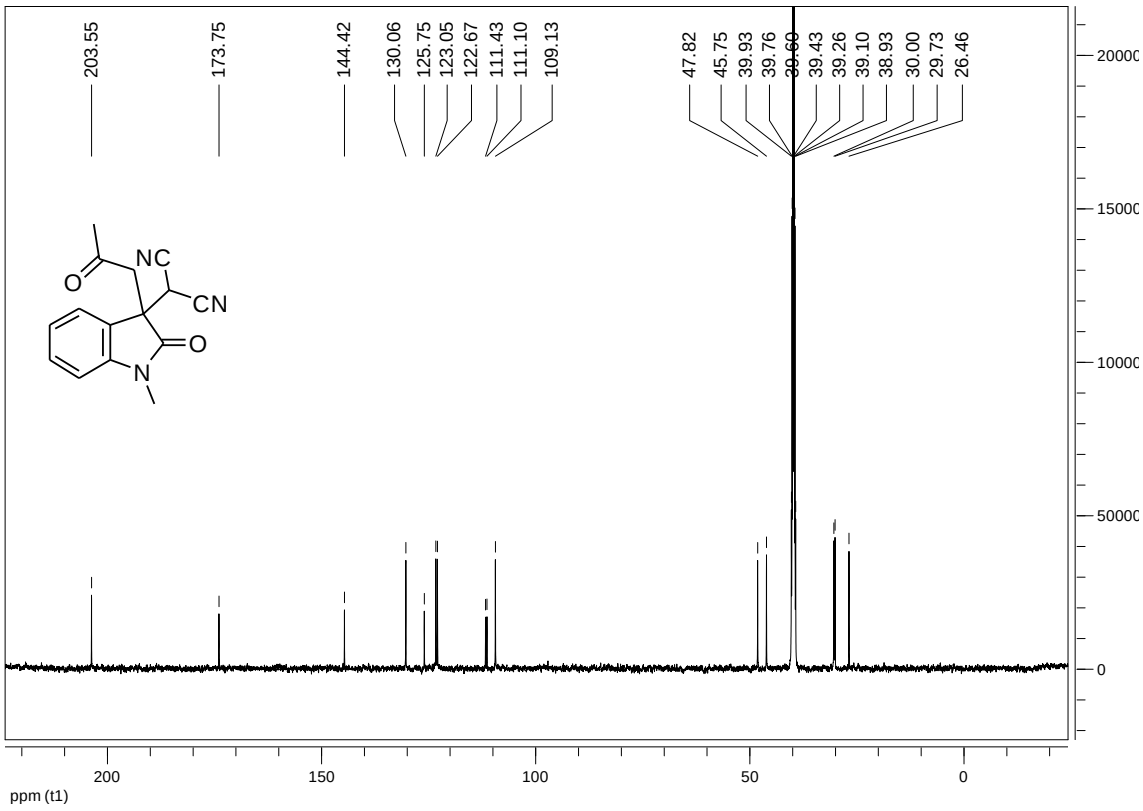


^{1}H and ^{13}C NMR spectra of (**5a**)

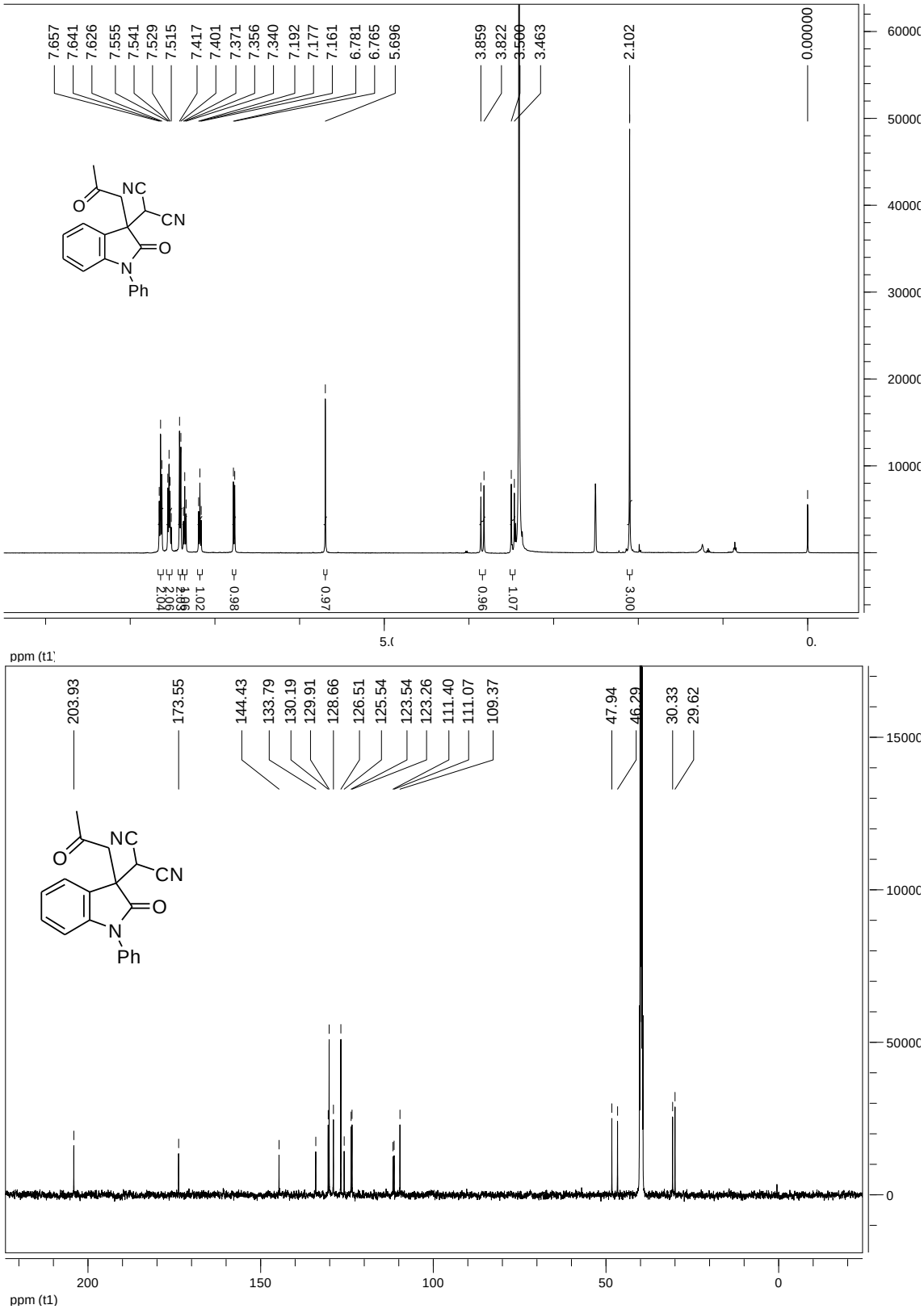


^{1}H and ^{13}C NMR spectra of (**5b**)

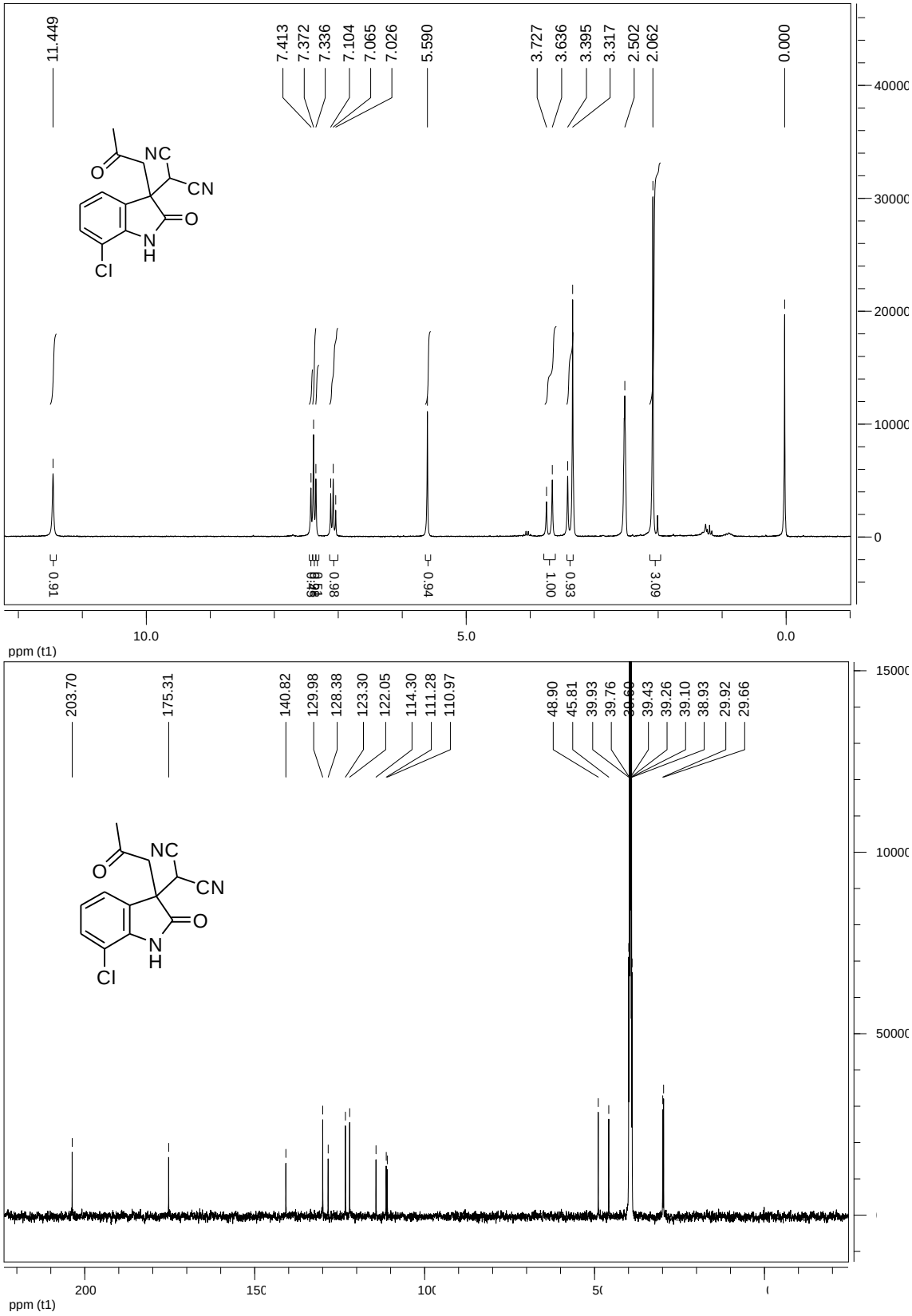




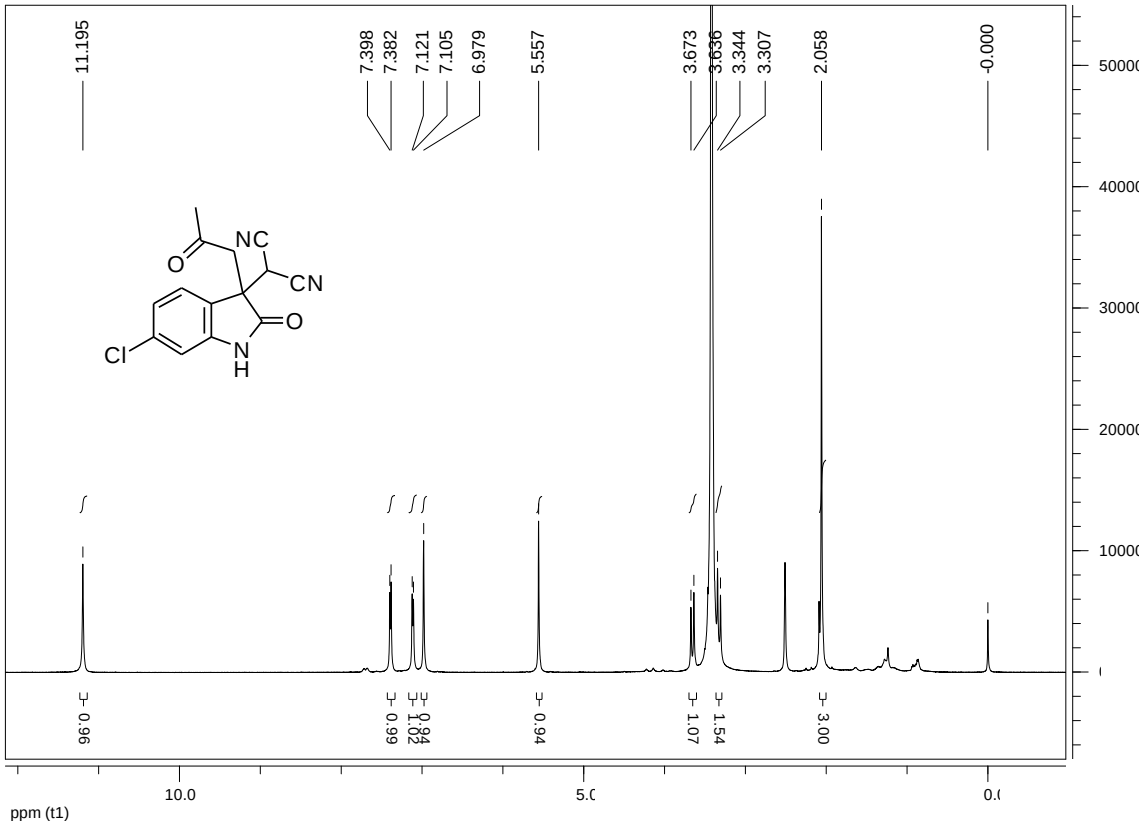
^{1}H and ^{13}C NMR spectra of (**5c**)

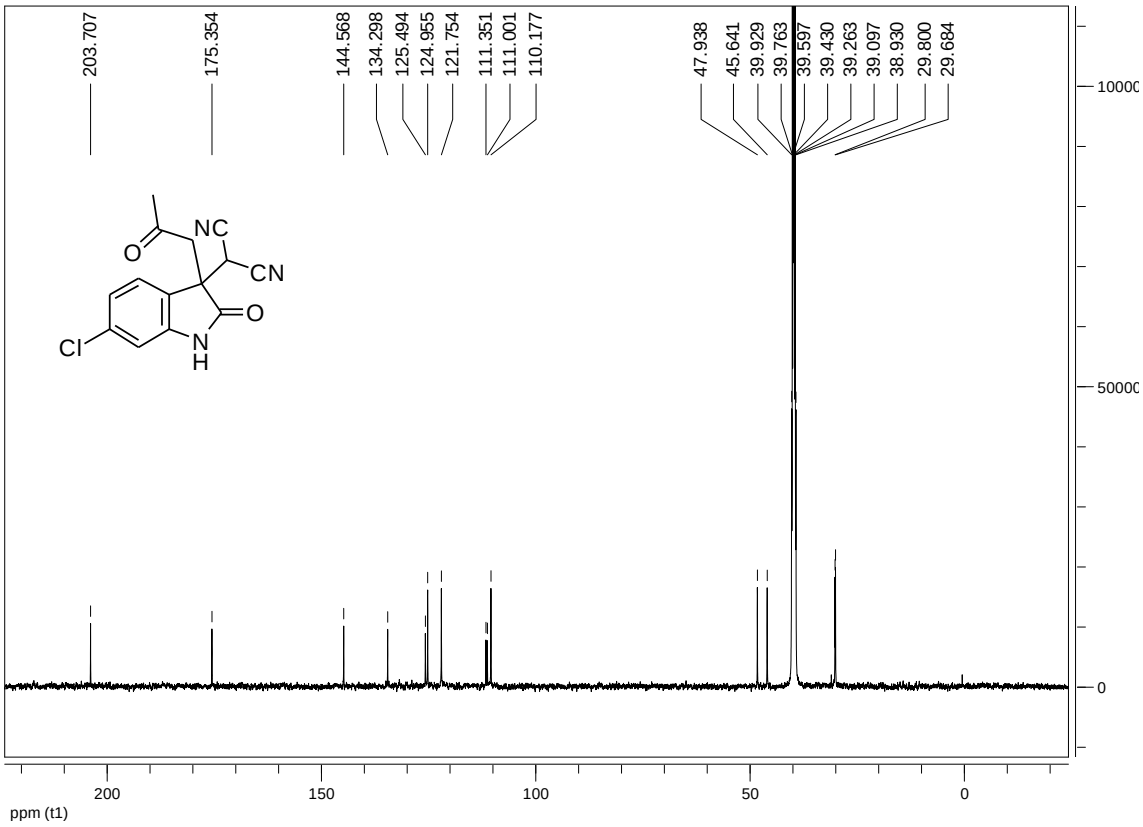


^{1}H and ^{13}C NMR spectra of (**5d**)

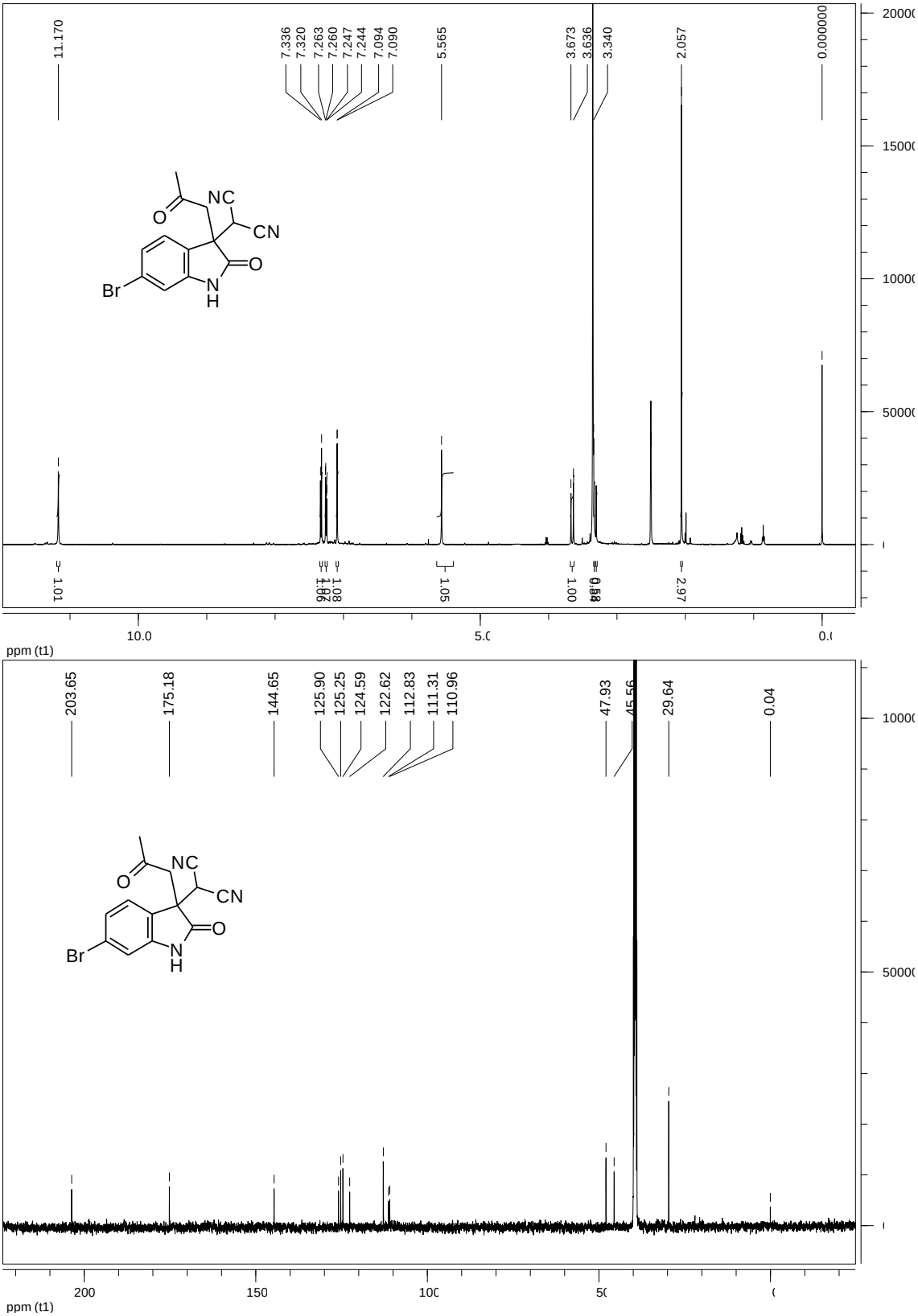


^{1}H and ^{13}C NMR spectra of (**5e**)

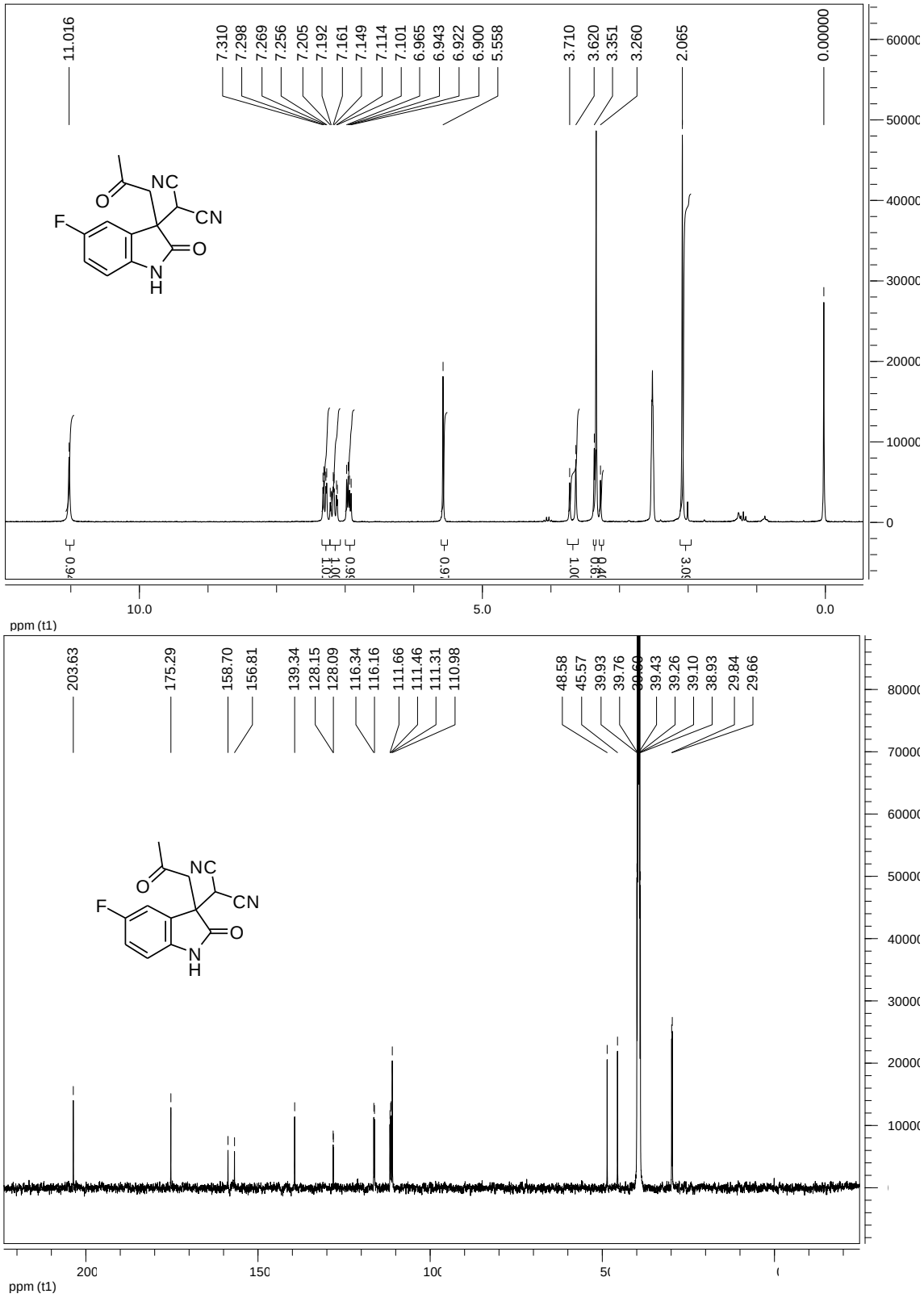




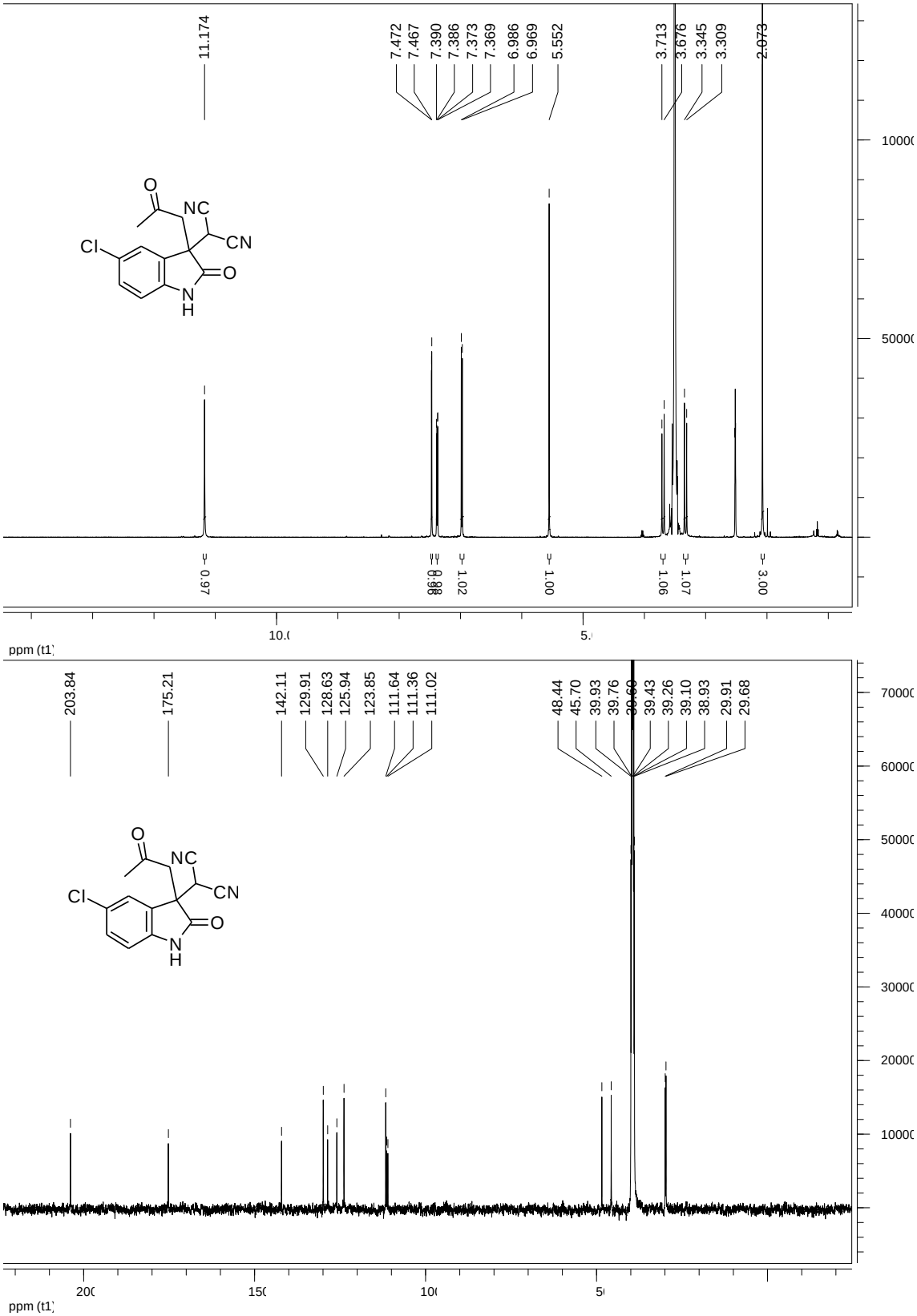
^{1}H and ^{13}C NMR spectra of (**5f**)



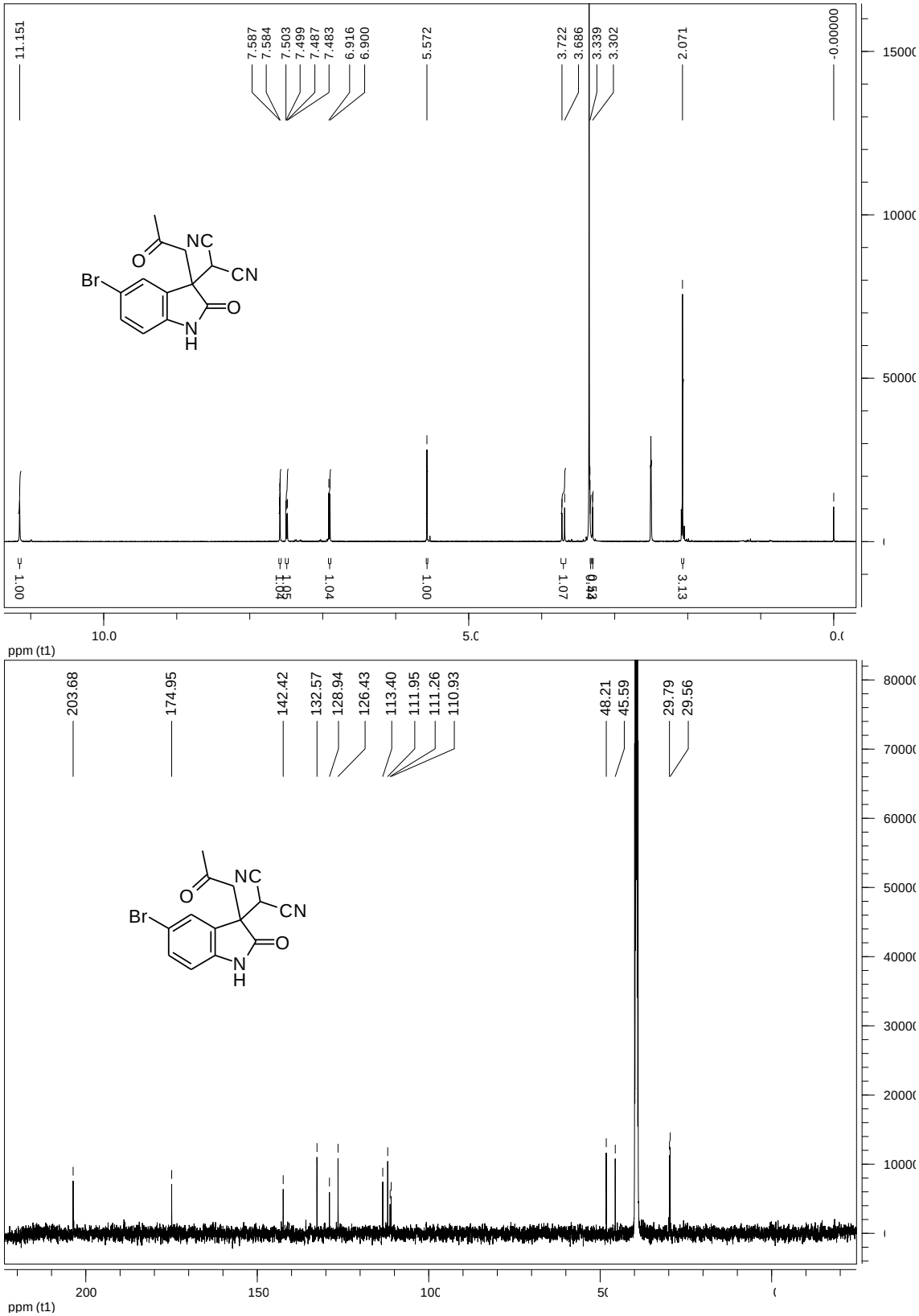
^{1}H and ^{13}C NMR spectra of (**5g**)



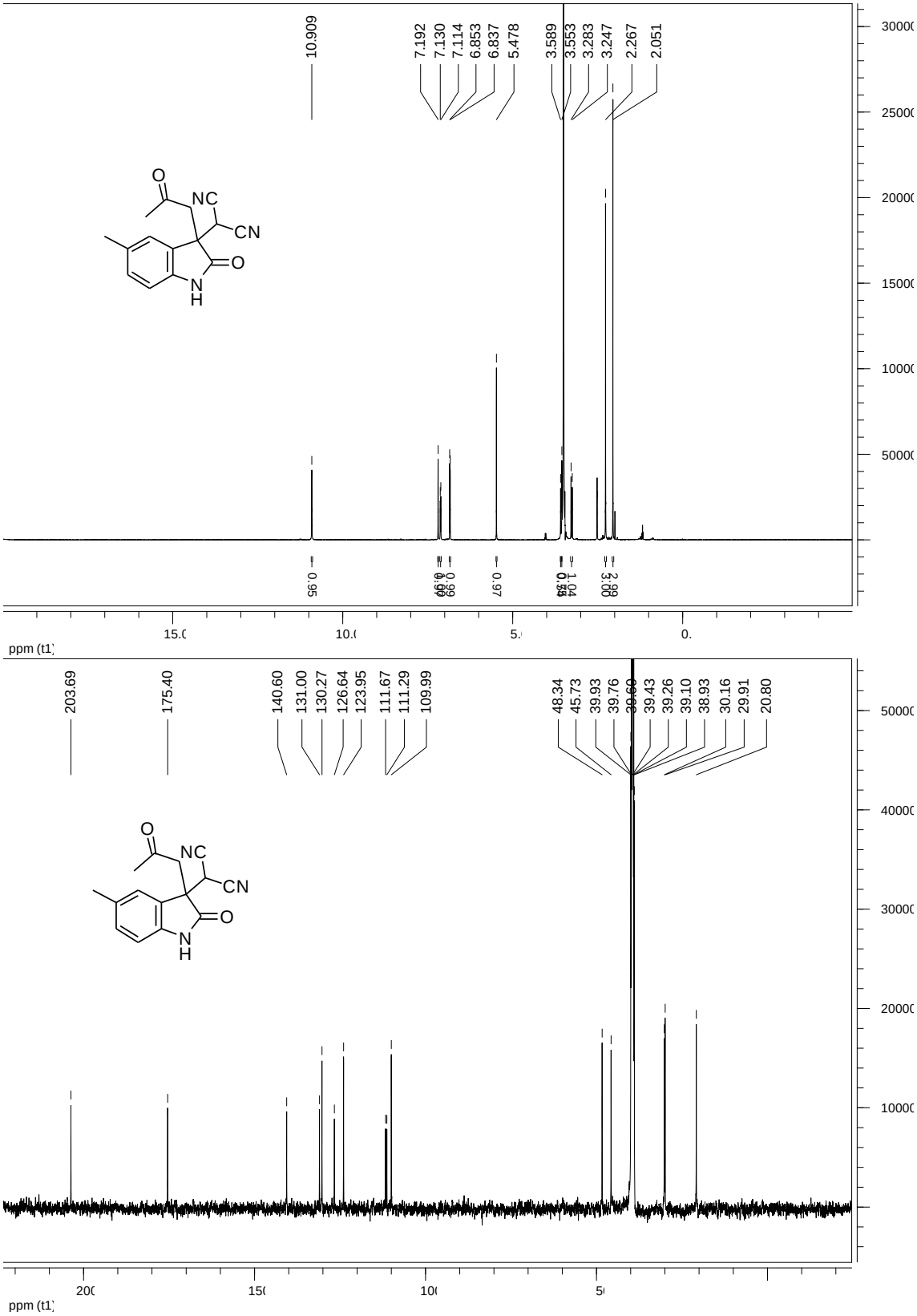
^{1}H and ^{13}C NMR spectra of (**5h**)



^{1}H and ^{13}C NMR spectra of (**5i**)



^{1}H and ^{13}C NMR spectra of (**5j**)



^{1}H and ^{13}C NMR spectra of (**5k**)