Electronic supplementary information

Iodine-catalyzed thioallylation of indoles using Bunte salts prepared from Baylis-Hillman bromides

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I. General Information: All the reagents were purchased from Sigma-Aldrich, Merck, and Alfa Aesar, and were used as such. Unless otherwise specified, solvents were purified by standard methods. All the reactions were carried out using oven-dried glassware. Organic solutions were concentrated under reduced pressure using a Buchi rotary evaporator. Thin-layer chromatography (TLC) was done using Merck Kieselgel 60GF254 plates (thickness 0.25 mm), and the crude products were purified by column chromatography using silica gel (Merck 100–200 mesh). Visualization of TLC was made using a 254 nm UV light. ^{1}H & ^{13}C Spectra were recorded on a 500 MHz JEOL ECZ 500R FTNMR spectrometer (^{1}H NMR at 500 MHz & ^{13}C NMR at 125 MHz). Chemical shifts are reported in δ/ppm (parts per million) using tetramethylsilane (TMS) as an internal reference. ^{1}H NMR and ^{13}C NMR chemical shifts are given in ppm with respect to the residual $CHCl_3$ peak (δ 7.26 ppm) and $CDCl_3$ peak (δ 77.00 ppm) respectively. High-resolution mass spectrometry (HRMS) was recorded on a SCIEX X500R QTOF (TOF-MS) system.

II. General procedure for the synthesis of Bunte salts 2:

The preparation of the Bunte salts involves the following three steps:

Step I: Preparation of Baylis-Hillman alcohols.[1] A mixture of the aldehyde (10.0 mmol), acrylonitrile (10.5 mmol) and DABCO (50.0 mmol%) was stirred in a glass vessel at RT for 24-48 h. After completion of the reaction (monitored by TLC), the mixture was diluted with diethyl ether (25 mL) and then washed with 0.5 M HCl solution (3 × 30 mL). The organic phase was dried over anhydrous sodium sulphate, filtered and concentrated under reduced pressure to give the product, which was purified by silica gel column chromatography using a mixture of ethyl acetate-n-hexane (1.0:9.0) to give the Baylis-Hillman alcohol.

Step II: Preparation of Baylis-Hillman bromides.[2] To a solution of BH-alcohol (5.0 mmol) in DCM (15 mL) maintained at 0 °C, was added 48% HBr solution (10.0 mmol) drop wise. The resulting mixture was stirred for 10 min, followed by drop-wise addition of conc. H_2SO_4 (10.0 mmol) at the same temperature. The contents were allowed to stir over night at RT. Upon completion of the reaction (TLC), the mixture was shaken with 25 mL aqueous saturated solution of $NaHCO_3$, and then extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phase was dried over anhydrous sodium sulfate, filtered, and concentrated under diminished pressure to afford the

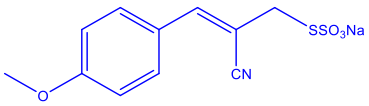
crude product, which was purified by column chromatography using a mixture of ethyl acetate/n-hexane (0.5:9.5) to give the Baylis-Hillman bromides.

Step III: Preparation of Bunte Salts from Baylis-Hillman Bromides.[3]

A mixture of Baylis-Hillman bromide (5.0 mmol, 1.0 equiv.), sodium thiosulfate pentahydrate (6.0 mmol, 1.2 equiv), water (7.5 mL) and methanol (15 mL) was stirred and heated at 50 °C for two hours. The contents were cooled to room temperature and then concentrated on a rotary evaporator under reduced pressure to remove the methanol and water. The residual solid was dissolved in methanol (40 mL), heated to 50 °C (most solid dissolves), and then filtered through Whatman filter paper with the help of a funnel to take out excess sodium thiosulfate and sodium bromide. The filtrate was concentrated under reduced pressure. Trituration of the residue with hexane followed by filtration and drying under vacuum at 50 °C gave the Bunte salt **2** as a white solid.

III. **General procedure for the synthesis of products 3:** A mixture of indole **1**, (1.0 mmol), Bunte salt **2**, (1.0 mmol), I_2 (20 mol %) and DMSO (1.5 mL) was stirred in open air at room temperature for 10 h. After completion of the reaction (monitored by TLC), the mixture was quenched with aqueous solution of sodium thiosulfate pentahydrate (5 mL), and then extracted by ethyl acetate (3 × 5 mL). The combined organic phase was dried over anhydrous sodium sulfate, filtered, concentrated under reduced pressure, and finally purified by silica gel column chromatography using ethyl acetate-n-hexane (1.0:9.0) as eluent to afford the clean product **3**. The structures of all the products were confirmed by ^{1}H & ^{13}C-NMR, NOSEY, and HRMS, with a representative single crystal X-ray analysis.

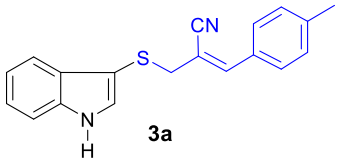
Spectral data of a representative Bunte Salt prepared from Baylis-Hillman Bromide:



White solid; **^{1}H NMR (500 MHz, D_2O):** δ = 3.56 (s, 3H), 3.89 (s, 2H), 6.61 (d, *J* = 8.0 Hz, 2H), 6.90 (s, 1H), 7.36 (d, *J* = 8.5 Hz, 2H). **^{13}C NMR (125 MHz, D_2O):** δ = 39.7, 55.6, 102.9, 104.4, 119.1, 125.9, 130.5, 146.8, 161.0.

Spectral data of the products 3:

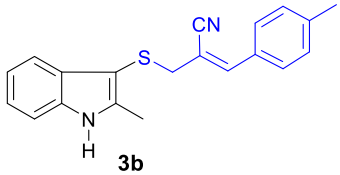
(*E*)-2-(((1*H*-Indol-3-yl)thio)methyl)-3-(*p*-tolyl)acrylonitrile (3a):



3a

Reddish brown viscous liquid (90%, 274 mg); **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 2.33 (s, 3H), 3.52 (s, 2H), 6.17 (s, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.21-7.25 (m, 3H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 7.5 Hz, 1H), 7.79 (d, *J* = 7.5 Hz, 1H), 8.40 (brs, 1H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 21.3, 41.5, 102.8, 106.7, 111.7, 118.5, 118.9, 120.7, 122.7, 128.4, 129.0, 129.3, 130.3, 131.4, 136.2, 140.6, 144.5. **HRMS (TOF MS):** $(M+H)^+$ calcd. for $C_{19}H_{16}N_2S$: 305.1107; found: 305.1110.

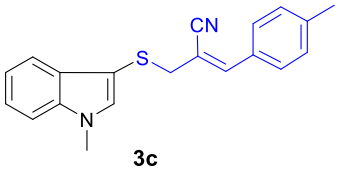
(*E*)-2-(((2-Methyl-1*H*-indol-3-yl)thio)methyl)-3-(*p*-tolyl)acrylonitrile (3b):



3b

Reddish viscous liquid (94%, 299 mg); **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 2.32 (s, 3H), 2.33 (s, 3H), 3.44 (s, 2H), 5.94 (s, 1H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.15 (dd, *J* = 6.0 Hz, *J* = 3.0 Hz, 2H), 7.25-7.27 (m, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.66 (dd, *J* = 6.0 Hz, *J* = 3.0 Hz, 1H), 8.13 (brs, 1H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 12.0, 21.4, 41.3, 99.7, 106.1, 110.8, 118.3, 118.6, 120.6, 122.0, 128.3, 129.4, 130.0, 130.6, 135.3, 140.5, 142.2, 144.0. **HRMS (TOF MS):** $(M+H)^+$ calcd. for $C_{20}H_{18}N_2S$: 319.1264; found: 319.1264.

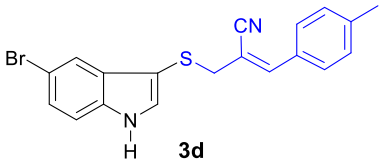
(*E*)-2-(((1-Methyl-1*H*-indol-3-yl)thio)methyl)-3-(*p*-tolyl)acrylonitrile (3c):



3c

Reddish viscous liquid (88%, 280 mg); **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 2.34 (s, 3H), 3.50 (s, 2H), 3.68 (s, 3H), 6.16 (s, 1H), 7.12 (s, 1H), 7.14 (d, *J* = 3.0 Hz, 2H), 7.19-7.22 (m, 1H), 7.25-7.29 (m, 1H), 7.31-7.35 (m, 3H), 7.76 (d, *J* = 7.5 Hz, 1H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 21.4, 32.9, 41.9, 101.2, 106.9, 108.5, 109.7, 119.2, 120.4, 122.4, 128.4, 129.3, 129.7, 130.4, 135.8, 137.0, 140.5, 144.4. **HRMS (TOF MS):** $(M+H)^+$ calcd. For $C_{20}H_{18}N_2S$: 319.1264; found: 319.1264.

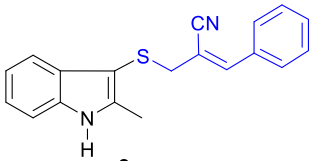
(*E*)-2-(((5-Bromo-1*H*-indol-3-yl)thio)methyl)-3-(*p*-tolyl)acrylonitrile (3d):



3d

Brown solid (78%, 298 mg), mp 121-122 °C; **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 2.34 (s, 3H), 3.51 (s, 2H), 6.21 (s, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.23-7.25 (m, 1H), 7.29-7.32 (m, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.90(d, *J* = 1.5 Hz, 1H), 8.42 (brs, 1H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 21.4, 41.6, 103.0, 106.7, 113.2, 114.4, 118.4, 121.7, 125.9, 128.5, 129.4, 130.3, 130.9, 132.5, 134.9, 140.8, 144.6. **HRMS (TOF MS):** $(M+H)^+$ calcd. for $C_{19}H_{15}N_2S$: 383.0212; found: 383.0217.

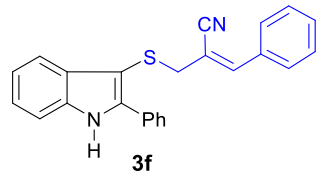
(*E*)-2-(((2-Methyl-1*H*-indol-3-yl)thio)methyl)-3-phenylacrylonitrile (3e):



3e

Reddish viscous liquid (95%, 289 mg); **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 2.38 (s, 3H), 3.49 (s, 2H), 5.99 (s, 1H), 7.17 (d, *J* = 4.5 Hz, 1H), 7.19 (s, 1H), 7.28-7.33 (m, 4H), 7.39-7.40 (m, 2H), 7.67-7.69 (m, 1H), 8.10 (brs, 1H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 12.1, 41.3, 99.8, 107.4, 110.7, 118.4, 120.7, 122.2, 128.4, 127.7, 130.0, 130.1, 133.3, 135.3, 142.2, 143.8. **HRMS (TOF MS):** $(M+H)^+$ calcd. for $C_{19}H_{16}N_2S$: 305.1107; found: 305.1110.

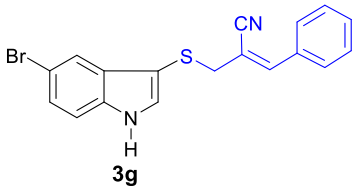
(*E*)-3-Phenyl-2-(((2-phenyl-1*H*-indol-3-yl)thio)methyl)acrylonitrile (3f):



3f

white solid (93%, 340 mg), mp 114-115 °C; **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 3.42 (s, 2H), 6.0 (s, 1H), 7.12 (d, *J* = 7.5 Hz, 2H), 7.20-7.27 (m, 5H), 7.31-7.34 (m, 4H), 7.60-7.62 (m, 2H), 7.80-7.82 (m, 1H), 8.44 (brs, 1H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 41.6, 100.0, 107.0, 111.3, 118.0, 119.3, 121.1, 123.2, 128.2, 128.4, 128.5, 128.5, 128.6, 129.9, 131.0, 131.1, 133.2, 135.5, 142.9, 143.8. **HRMS (TOF MS):** $(M+H)^+$ calcd. for $C_{24}H_{18}N_2S$: 367.1264; found: 367.1267.

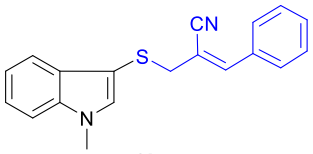
(*E*)-2-(((5-Bromo-1*H*-indol-3-yl)thio)methyl)-3-phenylacrylonitrile (3g):



3g

Brown viscous liquid (80%, 294 mg); **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 3.51 (s, 2H), 6.24 (s, 1H), 7.23-7.33 (m, 6H), 7.44 (d, *J* = 7.5 Hz, 2H), 7.90 (s, 1H), 8.44 (brs, 1H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 41.6, 102.9, 108.0, 113.2, 114.4, 118.2, 121.7, 125.9, 128.5, 128.7, 130.2, 130.9, 132.5, 133.0, 134.8, 144.6. **HRMS (TOF MS):** $(M+H)^+$ calcd. for $C_{18}H_{13}BrN_2S$: 369.0056; found: 369.0057.

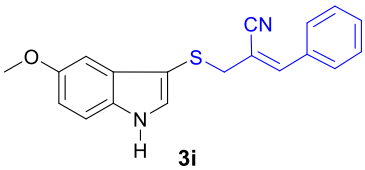
(*E*)-2-(((1-Methyl-1*H*-indol-3-yl)thio)methyl)-3-phenylacrylonitrile (3h):



3h

Brown solid (85%, 258 mg), mp 101-102 °C; **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 3.50 (s, 2H), 3.67 (s, 3H), 6.17 (s, 1H), 7.14 (s, 1H), 7.18 (t, *J* = 7.0 Hz, 1H), 7.24-7.28 (m, 1H), 7.31-7.33 (m, 4H), 7.40-7.42 (m, 2H), 7.76 (d, *J* = 8.0 Hz, 1H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 32.9, 41.8, 101.1, 108.2, 109.7, 118.3, 119.1, 120.5, 122.4, 128.4, 128.6, 129.7, 130.0, 133.1, 135.8, 137.3, 144.3. **HRMS (TOF MS):** $(M+H)^+$ calcd. for $C_{19}H_{16}N_2S$: 305.1107; found: 305.1110.

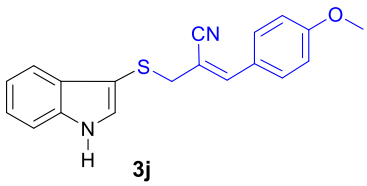
(*E*)-2-(((5-Methoxy-1*H*-indol-3-yl)thio)methyl)-3-phenylacrylonitrile (3i):



3i

Reddish viscous liquid (80%, 256 mg); **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 3.52 (s, 2H), 3.82 (s, 3H), 6.20 (s, 1H), 6.86-6.88 (m, 2H), 7.12-7.15 (m, 1H), 7.20 (d, *J* = 2.5 Hz, 1H), 7.28 (d, *J* = 3.0 Hz, 1H), 7.31-7.34 (m, 2H), 7.40-7,41 (m, 2H), 8.26 (brs, 1H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 41.8, 55.7, 100.3, 102.7, 108.2, 112.5, 113.5, 118.4, 128.4, 128.7, 129.9, 130.1, 131.1, 131.9, 133.2, 144.4, 145.8, 155.2. **HRMS (TOF MS):** $(M+H)^+$ calcd. for $C_{19}H_{16}N_2OS$: 321.1056; found: 321.1056.

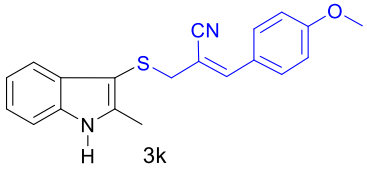
(*E*)-2-(((1*H*-Indol-3-yl)thio)methyl)-3-(4-methoxyphenyl)acrylonitrile (3j):



3j

Reddish brown viscous liquid (93%, 298 mg); **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 3.49 (s, 2H), 3.76 (s, 3H), 6.11 (s, 1H), 6.78 (d, *J* = 8.5 Hz, 2H), 7.17-7.23 (m, 3H), 7.34-7.40 (m, 3H), 7.76 (d, *J* = 8.0 Hz, 1H), 8.40 (brs, 1H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 41.5, 55.3, 103.0, 104.9, 111.7, 114.0, 118.9, 120.7, 122.7, 125.8, 129.0, 130.2, 131.4, 136.2, 144.1, 160.9. **HRMS (TOF MS):** $(M+H)^+$ calcd. for $C_{19}H_{16}N_2OS$: 321.1056; found: 321.1056.

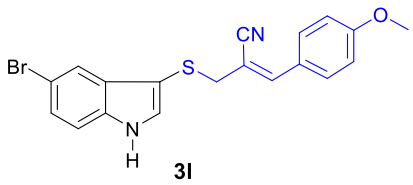
(*E*)-3-(4-Methoxyphenyl)-2-(((2-methyl-1*H*-indol-3-yl)thio)methyl)acrylonitrile (3k):



3k

Reddish brown viscous liquid (95%, 317 mg); **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 2.34 (s, 3H), 3.44 (s, 2H), 3.78(s, 3H), 5.90 (s, 1H), 6.80-6.82 (m, 2H), 7.15-7.17 (m, 2H), 7.26-7.27 (m, 1H), 7.36-7.39 (m, 2H), 7.66-7.68 (m, 1H), 8.15 (brs, 1H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 12.0, 41.4, 55.3, 99.7, 104.3, 114.1, 118.3, 118.9, 120.5, 122.0, 126.1, 130.0, 130.2, 135.3, 142.2, 143.6, 160.9. **HRMS (TOF MS):** $(M+H)^+$ calcd. for $C_{20}H_{18}N_2OS$: 335.1213; found: 335.1223.

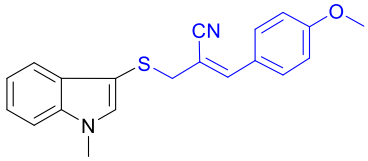
(*E*)-2-(((5-Bromo-1*H*-indol-3-yl)thio)methyl)-3-(4-methoxyphenyl)acrylonitrile (3l):



3l

Brown viscous liquid (78%, 310 mg); **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 3.50 (s, 2H), 3.81 (s, 3H), 6.18 (s, 1H), 6.83-6.89 (m, 2H), 7.24-7.26 (m, 1H), 7.30-7.32 (m, 2H), 7.45-7.47 (m, 2H), 7.90 (d, *J* = 1.5 Hz, 1H), 8.43 (brs, 1H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 41.7, 55.4, 103.1, 104.9, 113.2, 114.1, 114.4, 118.7, 121.8, 125.7, 125.8, 130.4, 131.0, 132.5, 134.8, 144.2, 161.1. **HRMS (TOF MS):** $(M+H)^+$ calcd. for $C_{19}H_{15}BrN_2OS$: 399.0161; found: 399.0172.

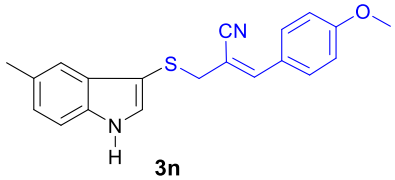
(*E*)-3-(4-Methoxyphenyl)-2-(((1-methyl-1*H*-indol-3-yl)thio)methyl)acrylonitrile (3m):



3m

Light yellow viscous liquid (82%, 274 mg); **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 3.49 (s, 2H), 3.67 (s, 3H), 3.80 (s, 3H), 6.12 (s, 1H), 6.82 (d, *J* = 8.5 Hz, 2H), 7.13 (s, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.24-7.32 (m, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 1H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 32.9, 41.9, 55.3, 101.3, 105.1, 109.7, 114.0, 118.8, 119.2, 120.4, 122.4, 125.9, 129.8, 130.3, 135.7, 137.3, 143.9, 161.0. **HRMS (TOF MS):** $(M+H)^+$ calcd. for $C_{20}H_{18}N_2OS$: 335.1213, found: 335.1223.

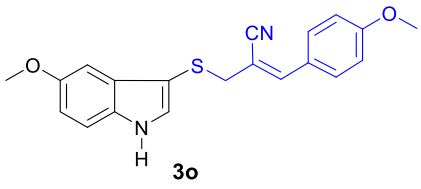
(*E*)-3-(4-Methoxyphenyl)-2-(((5-methyl-1*H*-indol-3-yl)thio)methyl)acrylonitrile (3n):



3n

Reddish viscous liquid (75%, 251 mg); **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 2.44 (s, 3H), 3.50 (s, 2H), 3.80 (s, 3H), 6.12 (s, 1H), 6.81-6.84 (m, 2H), 7.03 (d, *J* = 8.5 Hz, 1H), 7.23-7.26 (m, 2H), 7.42 (d, *J* = 9.0 Hz, 2H), 7.56 (s, 1H), 8.23 (brs,1H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 21.4, 41.7, 55.3, 102.6, 105.1, 111.3, 114.0, 118.7, 118.9, 124.4, 125.9, 130.2, 130.4, 131.4, 134.5, 144.0, 161.0. **HRMS (TOF MS):** $(M+H)^+$ calcd. For $C_{20}H_{18}N_2OS$: 335.1213; found: 335.1223.

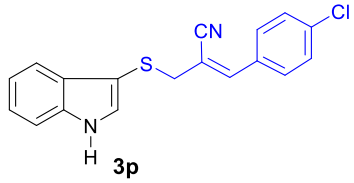
(*E*)-2-(((5-Methoxy-1*H*-indol-3-yl)thio)methyl)-3-(4-methoxyphenyl)acrylonitrile (3o):



3o

Brown viscous liquid (90%, 315 mg); **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 3.48 (s, 2H), 3.77 (s, 3H), 3.81 (s, 3H), 6.13 (s, 1H), 6.79 (d, *J* = 9.0 Hz, 2H), 6.83-6.85 (m, 1H), 7.20-7.23 (m, 3H) 7.38 (d, *J* = 9.0 Hz, 2H), 8.42 (brs, 1H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 41.8, 55.3, 55.7, 100.2, 102.6, 105.0, 112.5, 113.2, 114.0, 118.9, 125.8, 129.9, 130.2, 131.1, 131.9, 144.1, 154.9, 160.9. **HRMS (TOF MS)**: $(M+H)^+$ calcd. for $C_{20}H_{18}N_2O_2S$: 351.1162; found: 351.1162.

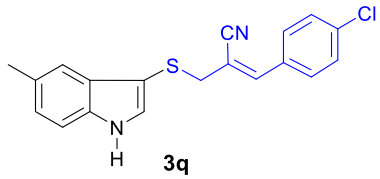
(*E*)-2-(((1*H*-Indol-3-yl)thio)methyl)-3-(4-chlorophenyl)acrylonitrile (3p):



3p

Yellow viscous liquid (85%, 275 mg); **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 3.51 (s, 2H), 6.11 (s, 1H), 7.18-7.27 (m, 5H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 1H), 8.35 (brs, 1H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 41.5, 103.0, 108.7, 111.7, 118.0, 119.0, 120.9, 122.9, 128.9, 129.0, 129.6, 131.3, 131.5, 136.0, 136.2, 142.9. **HRMS (TOF MS)**: $(M+H)^+$ calcd. for $C_{18}H_{13}ClN_2S$: 325.0561; found: 325.0567.

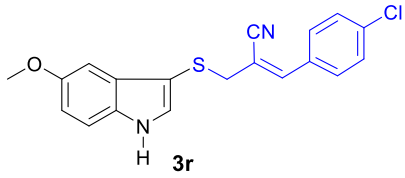
(*E*)-3-(4-Chlorophenyl)-2-(((5-methyl-1*H*-indol-3-yl)thio)methyl)acrylonitrile (3q):



3q

Reddish brown viscous liquid (73%, 247 mg); **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 2.42 (s, 3H), 3.49 (s, 2H), 6.09 (s, 1H), 6.99-7.05 (m, 2H), 7.22 (d, *J* = 3.0 Hz, 1H), 7.24-7.26 (m, 2H), 7.29-7.32 (m, 2H), 7.52 (s, 1H), 8.29 (brs, 1H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 21.4, 41.5, 102.3, 108.7, 111.4, 118.6, 124.5, 128.4, 128.8, 129.4, 129.6, 130.3, 131.4, 134.5, 135.9, 142.8, 144.2. **HRMS (TOF MS)**: $(M+H)^+$ calcd. for $C_{19}H_{15}ClN_2S$: 339.0717; found: 339.0726.

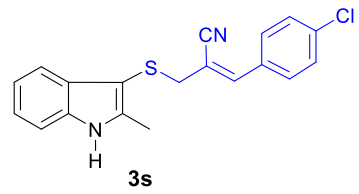
(*E*)-3-(4-Chlorophenyl)-2-(((5-methoxy-1*H*-indol-3-yl)thio)methyl)acrylonitrile (3r):



3r

Light yellow viscous liquid (80%, 283 mg); **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 3.49 (s, 2H), 3.81 (s, 3H), 6.10 (s, 1H), 6.85-6.86 (m, 1H), 7.01-7.05 (m, 1H), 7.18 (s, 1H), 7.23-7.24 (m, 3H), 7.27-7.29 (m, 2H), 8.43 (brs, 1H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 41.7, 55.7, 100.2, 102.3, 108.6, 112.5, 113.2, 118.1, 128.4, 128.8, 129.6, 131.0, 131.5, 131.9, 135.9, 142.9, 155.0. **HRMS (TOF MS)**: $(M+H)^+$ calcd. for $C_{19}H_{15}N_2ClOS$: 355.0667; found: 355.0667.

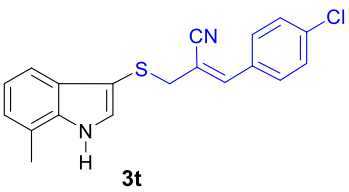
(*E*)-3-(4-Chlorophenyl)-2-(((2-methyl-1*H*-indol-3-yl)thio)methyl)acrylonitrile (3s):



3s

Reddish brown viscous liqiud (89%, 301 mg); **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 2.37 (s, 3H), 3.46 (s, 2H), 5.91 (s, 1H), 7.15-7.19 (m, 2H), 7.25-7.30 (m, 5H), 7.65-7.66 (m, 1H), 8.13 (brs, 1H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 12.0, 41.2, 99.7, 108.0, 110.8, 118.1, 118.4, 120.7, 122.2, 129.0, 129.5, 130.0, 131. 7, 135.3, 136.0, 140.1, 142.4. **HRMS (TOF MS)**: $(M+H)^+$ calcd. for $C_{19}H_{15}ClN_2S$: 339.0717; found: 339.0726.

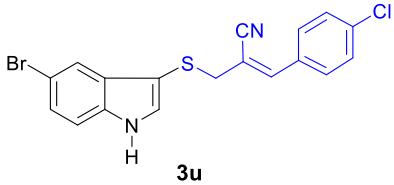
(*E*)-3-(4-Chlorophenyl)-2-(((7-methyl-1*H*-indol-3-yl)thio)methyl)acrylonitrile (3t):



3t

Brown viscous liquid (84%, 284 mg); **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 2.46 (s, 3H), 3.52 (s, 2H), 6.13 (s, 1H), 7.03 (d, *J* = 7.0 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.25-7.27 (m, 3H), 7.32-7.37 (m, 2H),7.60 (d, *J* = 7.5 Hz, 1H), 8.27 (brs, 1H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 16.4, 41.4, 103.5, 108.8, 116.7, 118.0, 121.1, 123.5, 128.6, 128.9, 129.7, 130.3, 131.0, 131.5, 135.8, 136.0, 142.8. **HRMS (TOF MS)**: $(M+H)^+$ calcd. for $C_{19}H_{15}ClN_2S$: 339.0717; found: 339.0726.

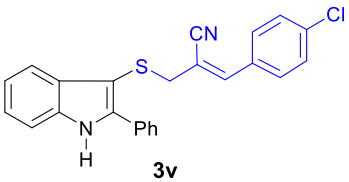
(*E*)-2-(((5-Bromo-1*H*-indol-3-yl)thio)methyl)-3-(4-chlorophenyl)acrylonitrile (3u):



3u

Brown solid (80%, 322 mg), 98-99 °C; **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 3.50 (s, 2H), 6.18 (s, 1H), 7.23-7.30 (m, 5H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.87 (s, 1H), 8.56 (brs, 1H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 41.6, 102.7, 108.6, 113.3, 114.4, 117.9, 121.6, 125.9, 129.0, 129.7, 130.9, 131.3, 132.5, 134.8, 136.1, 143.1. **HRMS (TOF MS)**: $(M+H)^+$ calcd. for $C_{19}H_{15}BrClN_2S$: 402.9666; found: 402.9668.

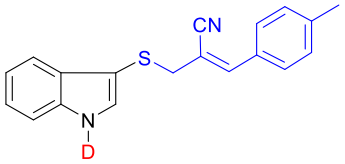
(*E*)-3-(4-Chlorophenyl)-2-(((2-phenyl-1*H*-indol-3-yl)thio)methyl)acrylonitrile (3v):



3v

White solid (90%, 360 mg), mp 154-155 °C; **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 3.43 (s, 2H), 5.91 (s, 1H), 7.04 (d, *J* = 8.0 Hz, 2H), 7.19-7.28 (m, 4H), 7.37 (d, *J* = 6.5 Hz, 4H), 7.64 (d, *J* = 6.0 Hz, 2H), 7.81 (d, *J* = 7.0 Hz, 1H), 8.46 (brs, 1H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 41.6, 100.0, 107.7, 111.3, 117.7, 119.3, 121.2, 123.3, 128.2, 128.7, 129.7, 131.1, 131.6, 135.6, 135.8, 142.2, 142.9. **HRMS (TOF MS)**: $(M+H)^+$ calcd. for $C_{24}H_{17}ClN_2S$: 401.0874; found: 401.0868.

(*E*)-2-(((1*H*-Indol-3-yl-1-*d*)thio)methyl)-3-(*p*-tolyl)acrylonitrile (3a'):

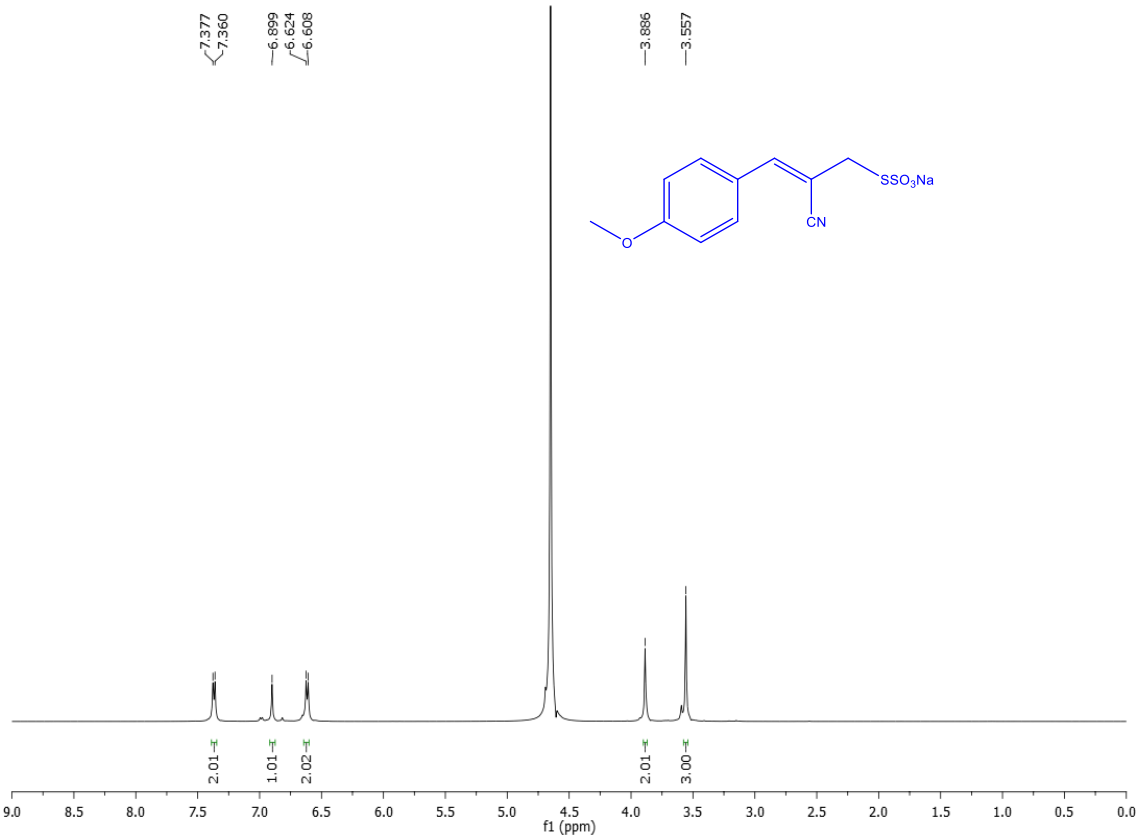


3a'

Reddish brown viscous liquid (90%, 274 mg); **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 2.33 (s, 3H), 3.51 (s, 2H), 6.17 (s, 1H), 7.11 (d, *J* = 7.5 Hz, 2H), 7.21-7.24 (m, 3H), 7.33-7.37 (m, 3H), 7.79 (d, *J* = 7.5 Hz, 1H).

References:

1) A. K. Yadav, A. K. Sharma and K. N. Singh, *Org. Chem. Front*., 2019, **6**, 987-993.
2) (a) D. Basavaiah, A. J. Rao and T. Satyanarayana, *Chem. Rev.,* 2003**, 103**, 811-891; (b) D. Yadav, S. K. Sharma and R. S. Menon, *Org. Biomol. Chem*., 2019, **17,** 4073-4076.
3) (a) J. T. Reeves, K. Camara, Z. S. Han, Y. Xu, H. Lee, C. A. Busacca, Chris H. *Org. Lett.*, 2014, **16**, 1196–1199; (b) H. Distler, *Angew*. *Chem. Int. Ed*., 1967, **6**, 544-553.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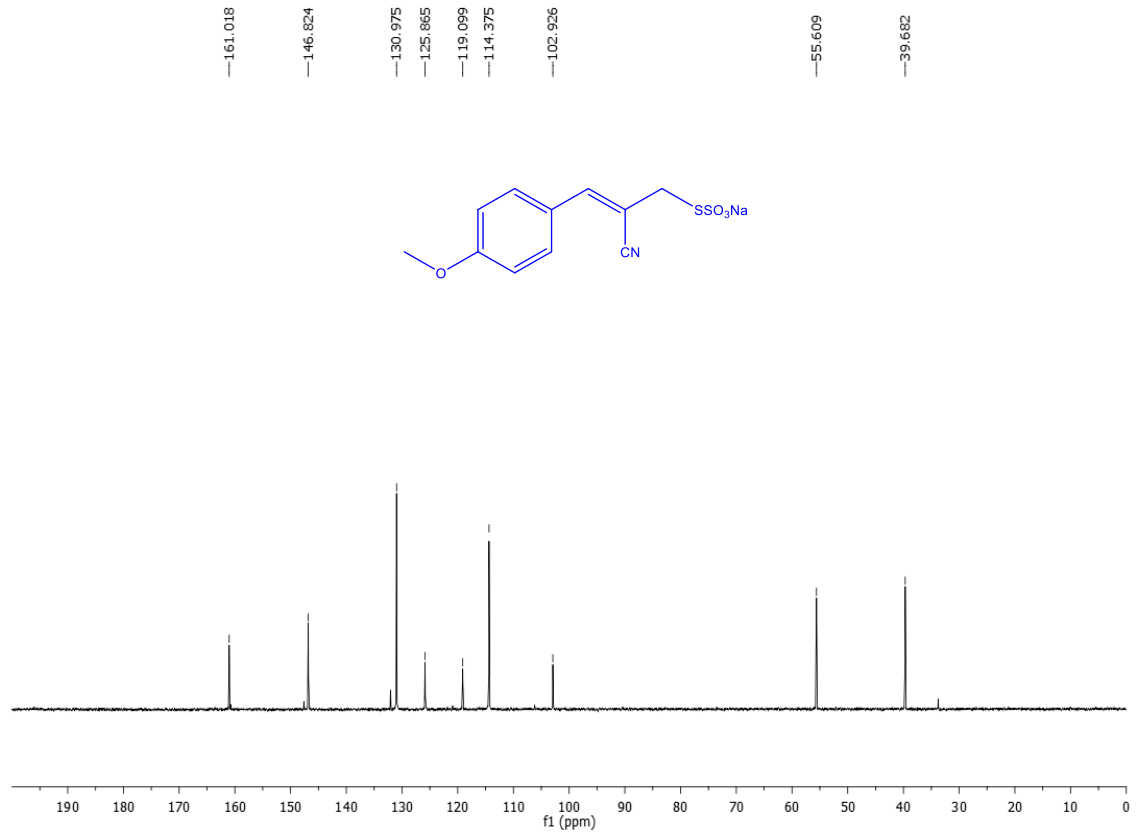
6.899
6.624
6.608
3.886
3.557
SSO3Na
CN
O
2.01
1.01
2.02
2.01
3.00
f1 (ppm)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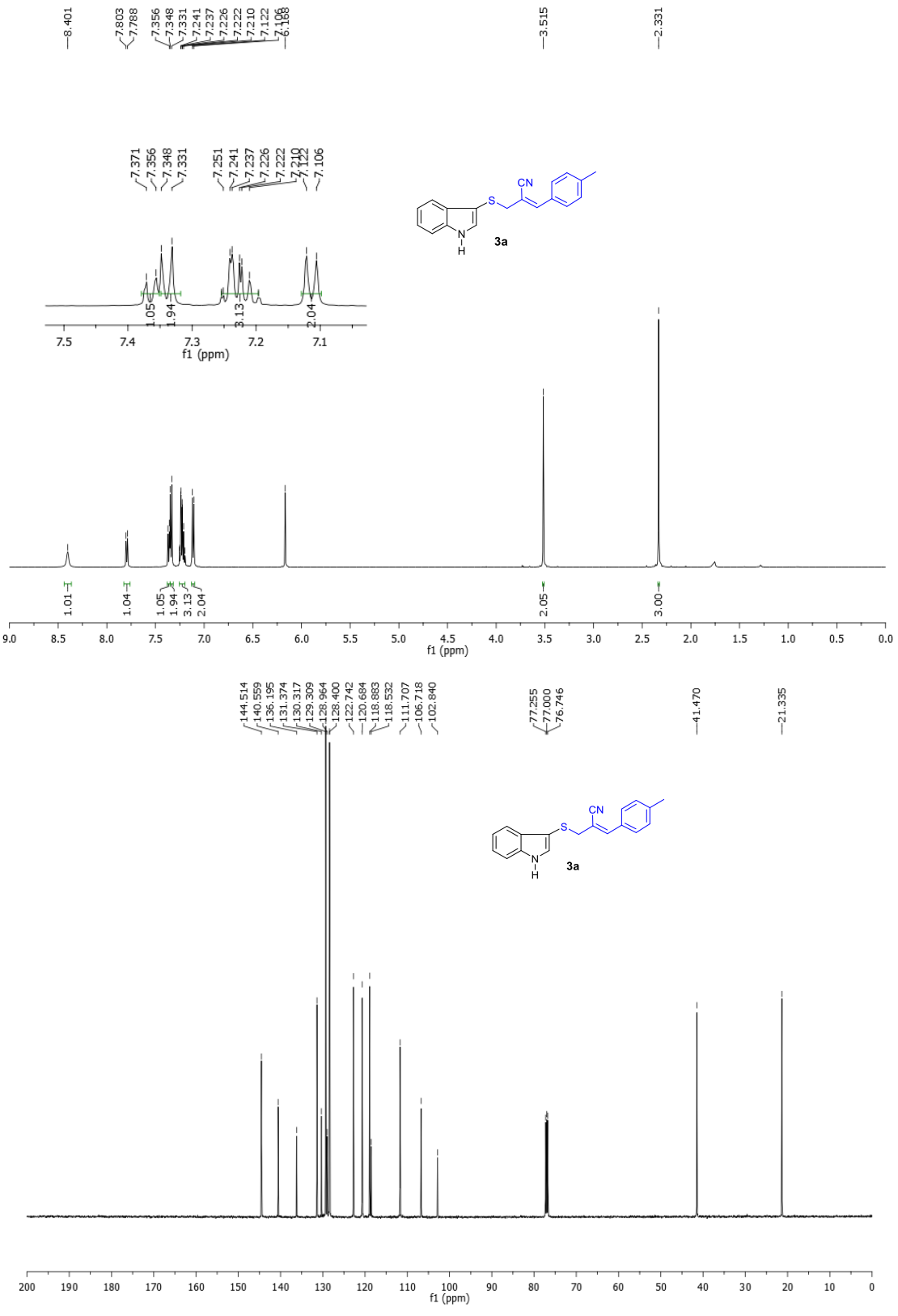
146.824
130.975
125.865
119.099
114.375
102.926
55.609
39.682
SSO3Na
CN
O
f1 (ppm)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7.356
7.348
7.331
7.241
7.237
7.226
7.222
7.210
7.122
7.106
6.168
3.515
2.331
CN
S
N
H
3a
1.01
1.04
1.05
1.94
3.13
2.04
2.05
3.00
f1 (ppm)
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140.559
136.195
131.374
130.317
129.309
128.964
128.400
122.742
120.684
118.883
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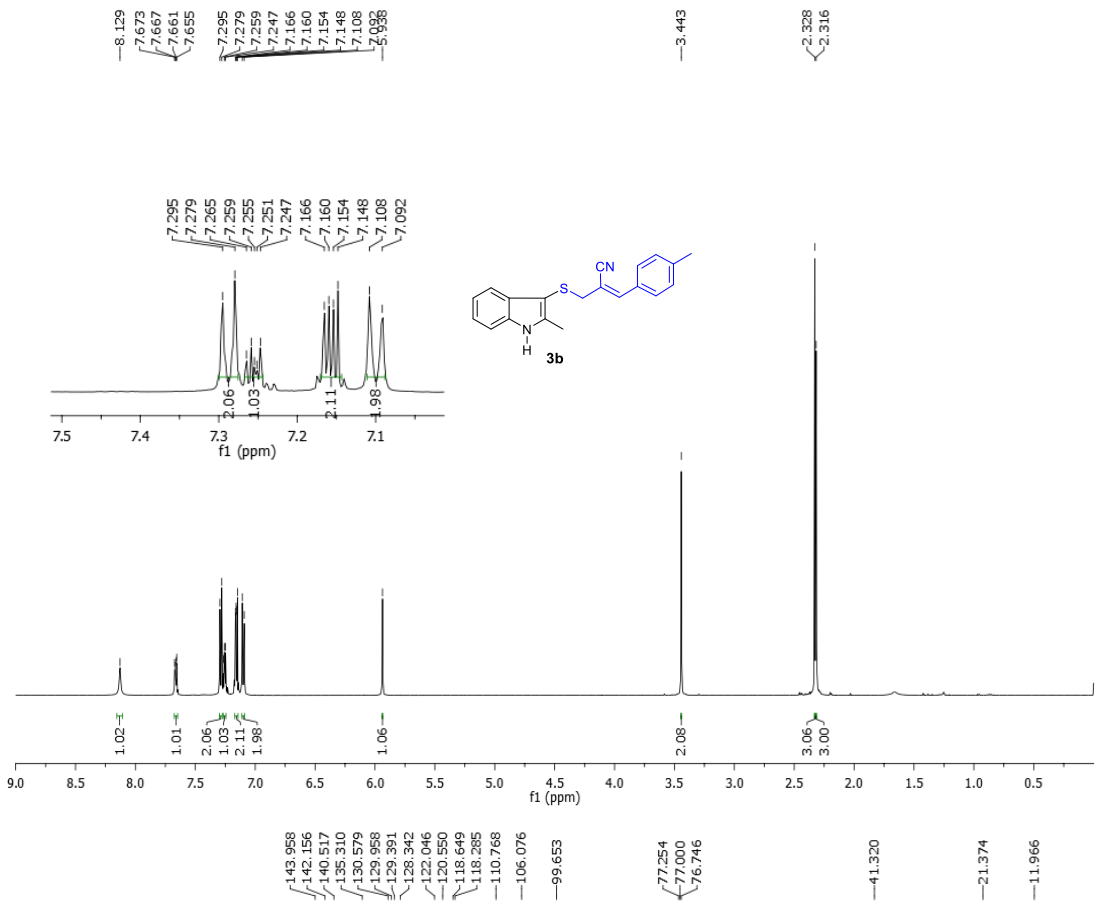
106.718
102.840
77.255
77.000
76.746
41.470
21.335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7.661
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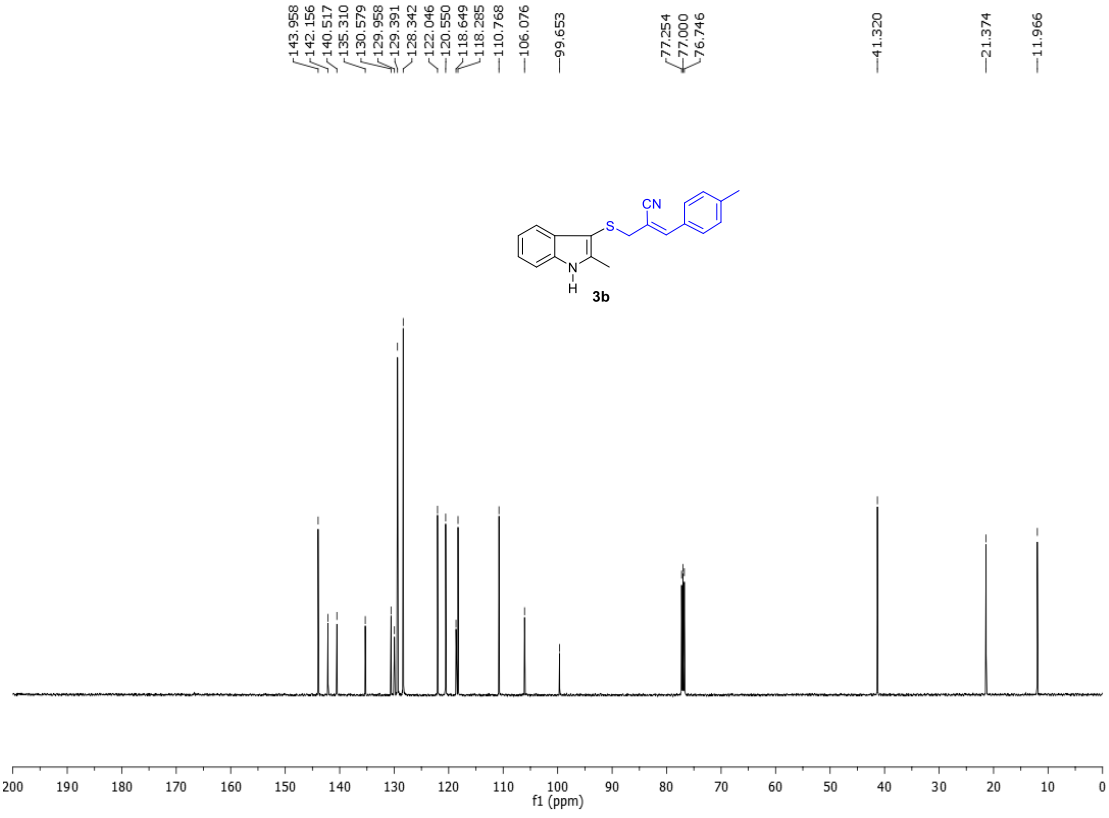
7.259
7.247
7.166
7.160
7.154
7.148
7.108
7.092
5.938
3.443
2.328
2.316
CN
S
N
H
3b
1.02
1.01
2.06
1.03
2.11
1.98
1.06
2.08
3.06
3.00
f1 (ppm)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130.579
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128.342
122.046
120.550
118.649
118.285
110.768
106.076
99.653
77.254
77.000
76.746
41.320
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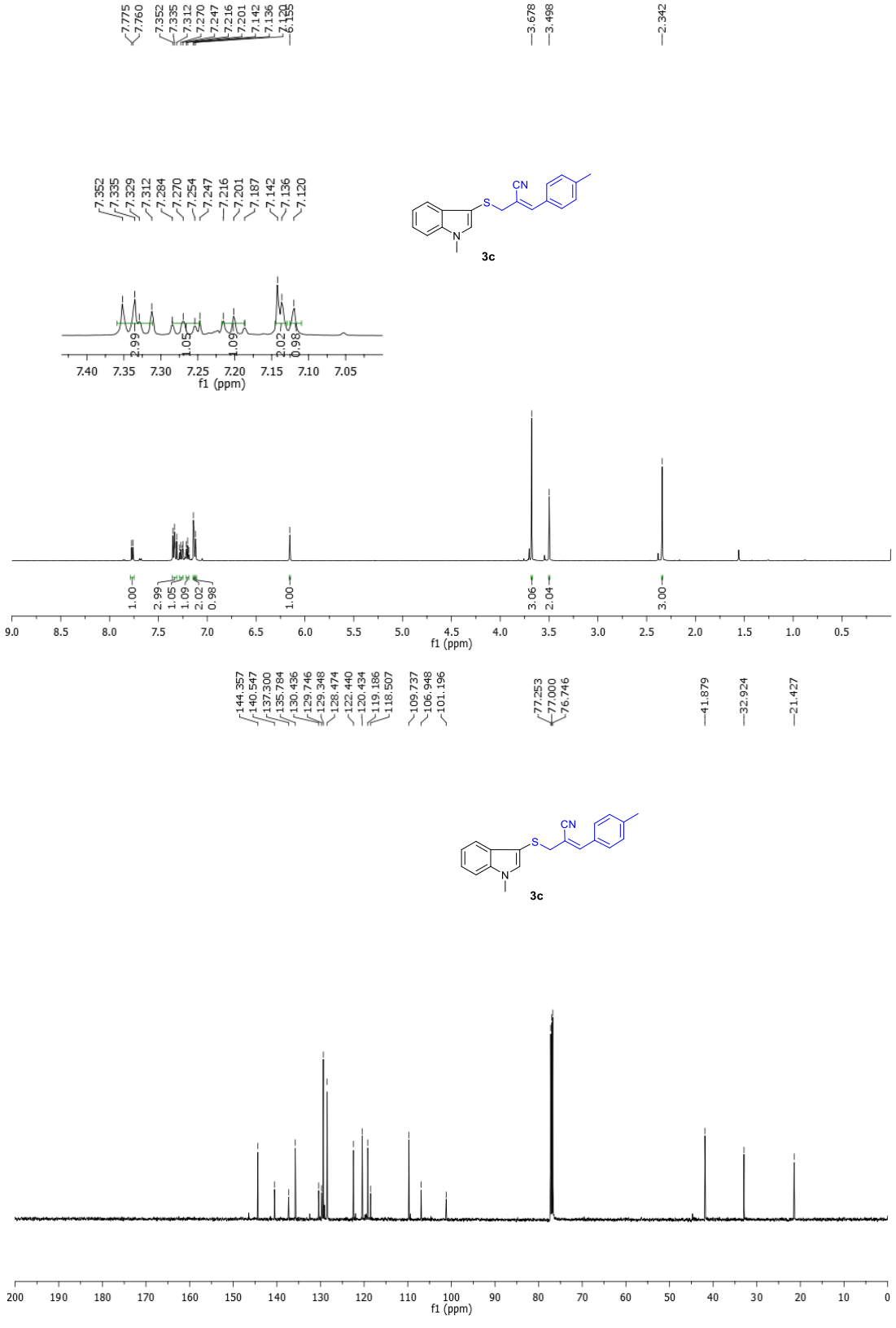
CN
S
N
H
3b
f1 (ppm)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7.216
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7.142
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7.120
6.155
3.678
3.498
2.342
CN
S
N
3c
1.00
2.99
1.05
1.09
2.02
0.98
1.00
3.06
2.04
3.00
f1 (ppm)
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140.547
137.300
135.784
130.436
129.746
129.348
128.474
122.440
120.434
119.186
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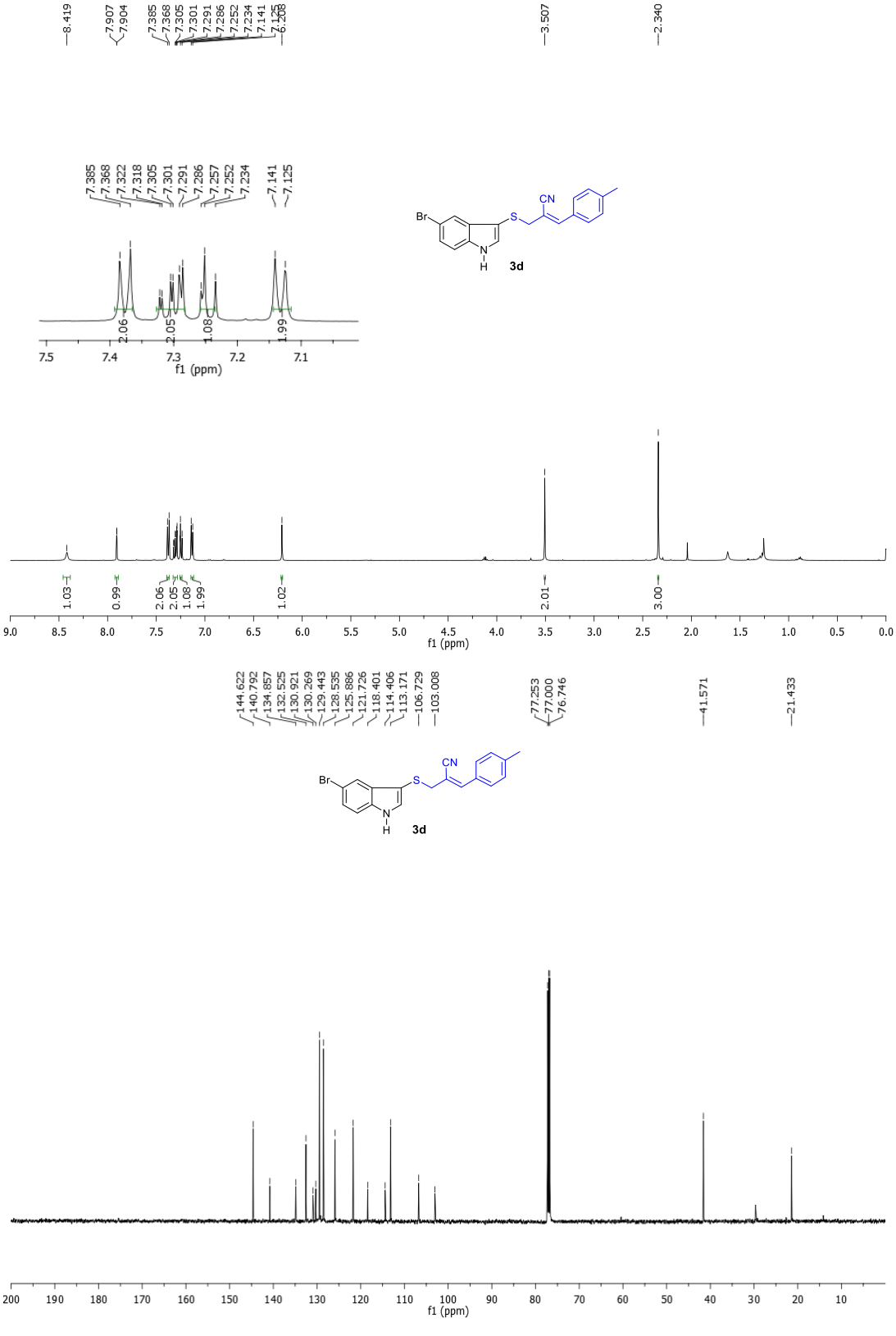
32.924
21.427
f1 (ppm)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7.257
7.252
7.234
7.141
7.125
6.208
3.507
2.340
Br
S
CN
N
H
3d
2.06
2.05
1.08
1.99
7.5
7.4
7.3
7.2
7.1
f1 (ppm)
1.03
0.99
2.06
2.05
1.08
1.99
1.02
2.01
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
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140.792
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132.525
130.921
130.269
129.443
128.535
125.886
121.726
118.401
114.406
113.171
106.729
103.008
77.253
77.000
76.746
41.571
21.433
Br
S
CN
N
H
3d
200
190
180
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160
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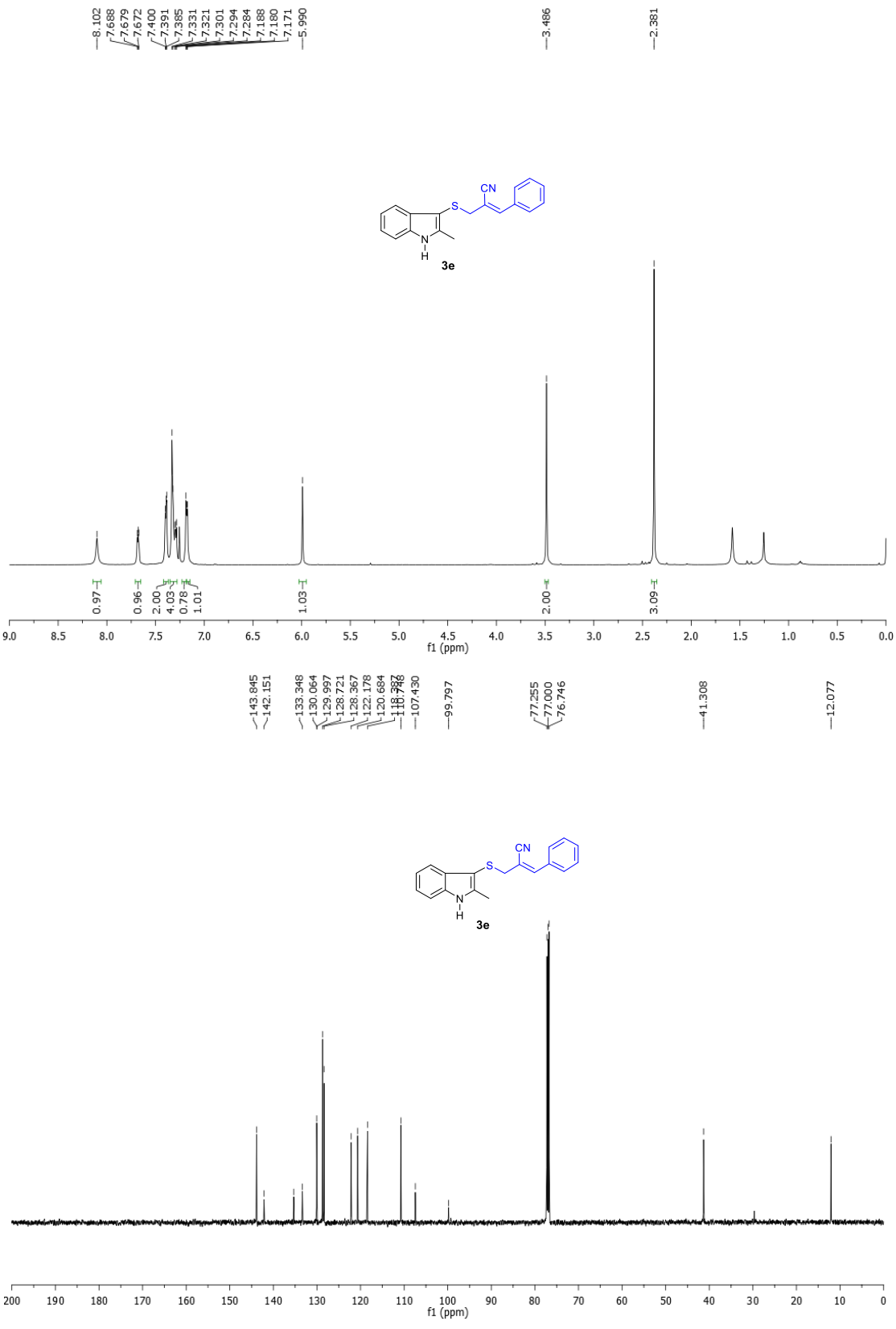
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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7.188
7.180
7.171
5.990
3.486
2.381
CN
S
N
H
3e
0.97
0.96
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4.03
0.78
1.01
1.03
2.00
3.09
f1 (ppm)
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142.151
133.348
130.064
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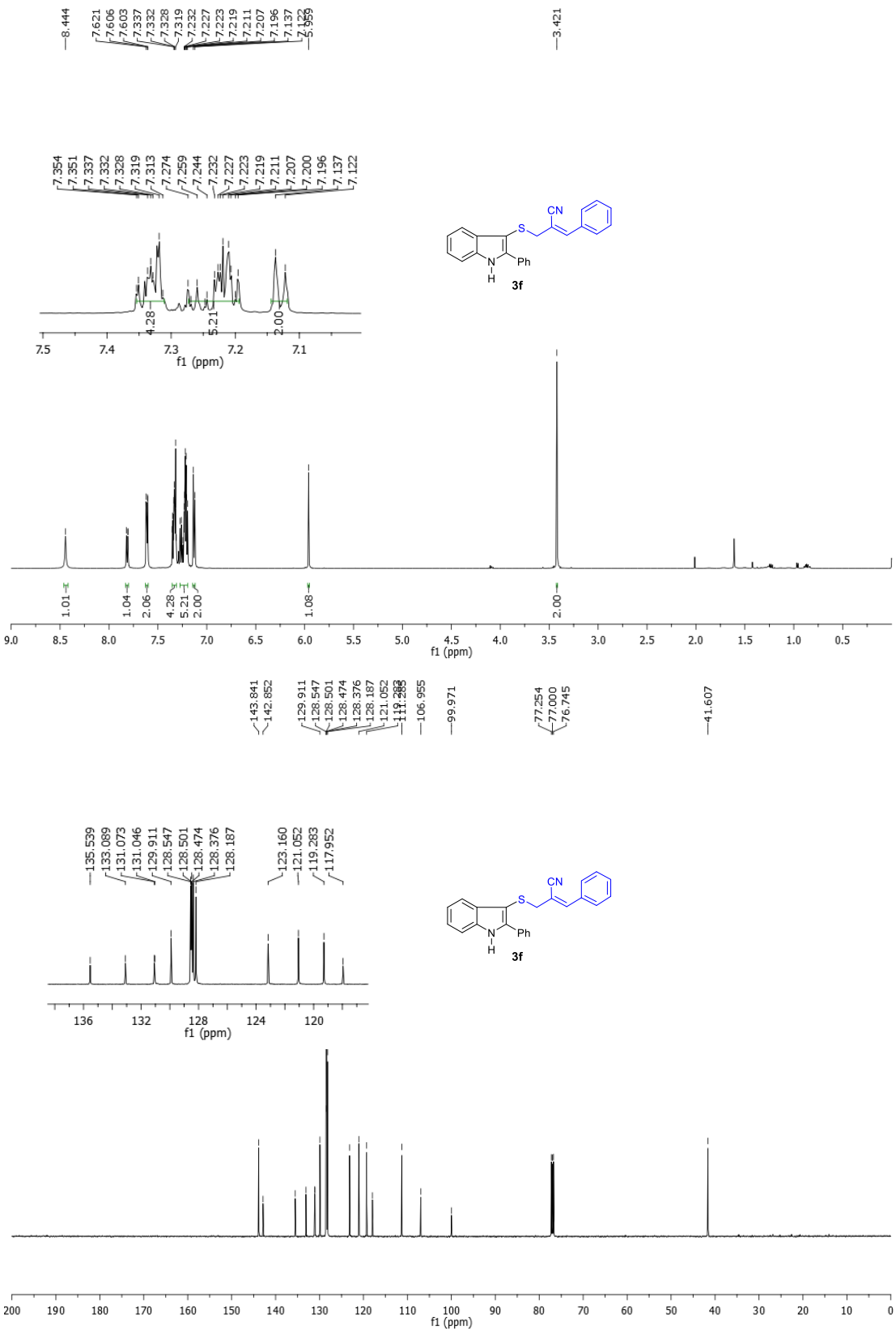
S
N
H
3e
f1 (ppm)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7.207
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7.351
7.337
7.332
7.328
7.319
7.313
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7.259
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7.232
7.227
7.223
7.219
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7.207
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7.137
7.122
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5.21
2.00
7.5
7.4
7.3
7.2
7.1
f1 (ppm)
CN
S
N
H
Ph
3f
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1.04
2.06
4.28
5.21
2.00
1.08
2.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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f1 (ppm)
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128.474
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119.283
117.952
136
132
128
124
120
f1 (ppm)
CN
S
N
H
Ph
3f
200
190
180
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160
150
140
130
120
110
100
90
80
70
60
50
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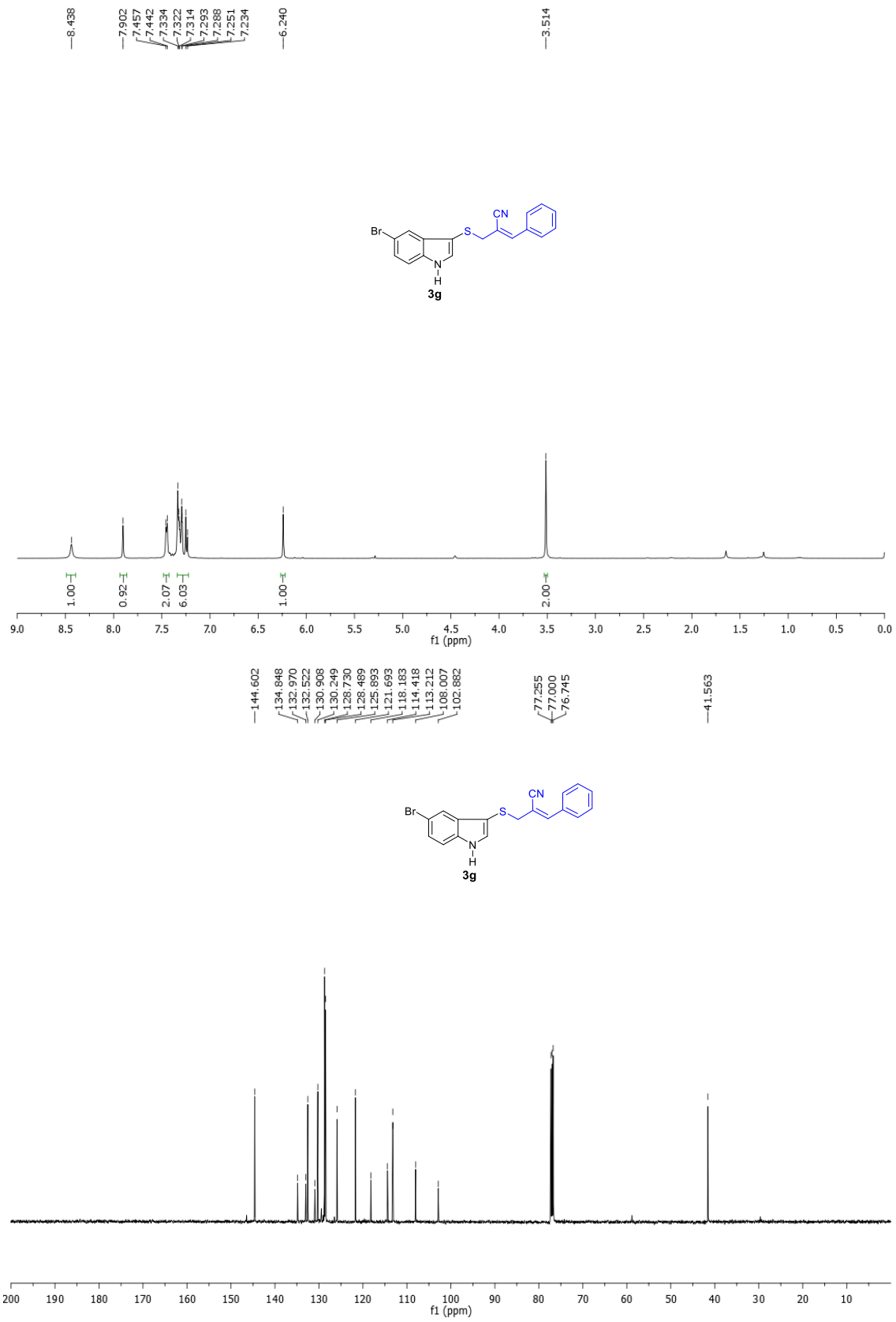
30
20
10
0
f1 (ppm)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S
CN
N
H
3g
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2.07
6.03
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2.00
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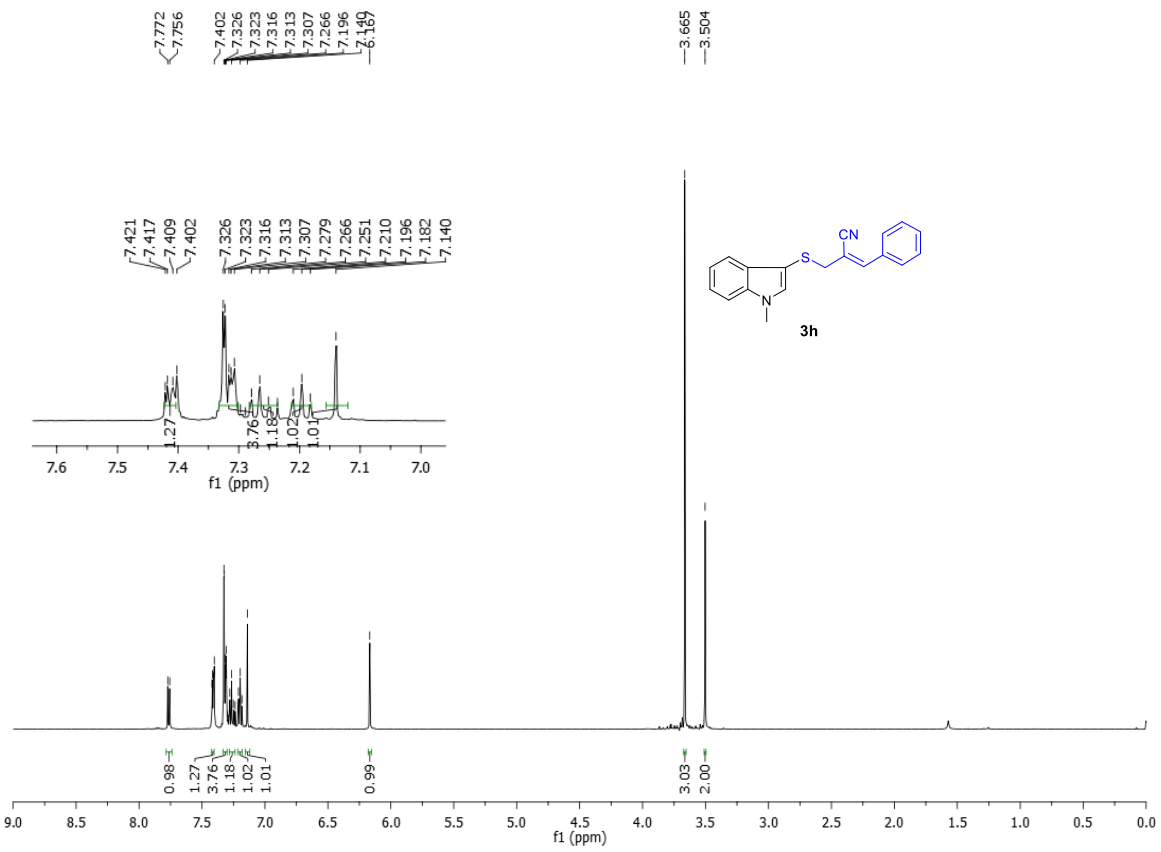
Br
S
CN
N
H
3g
f1 (ppm)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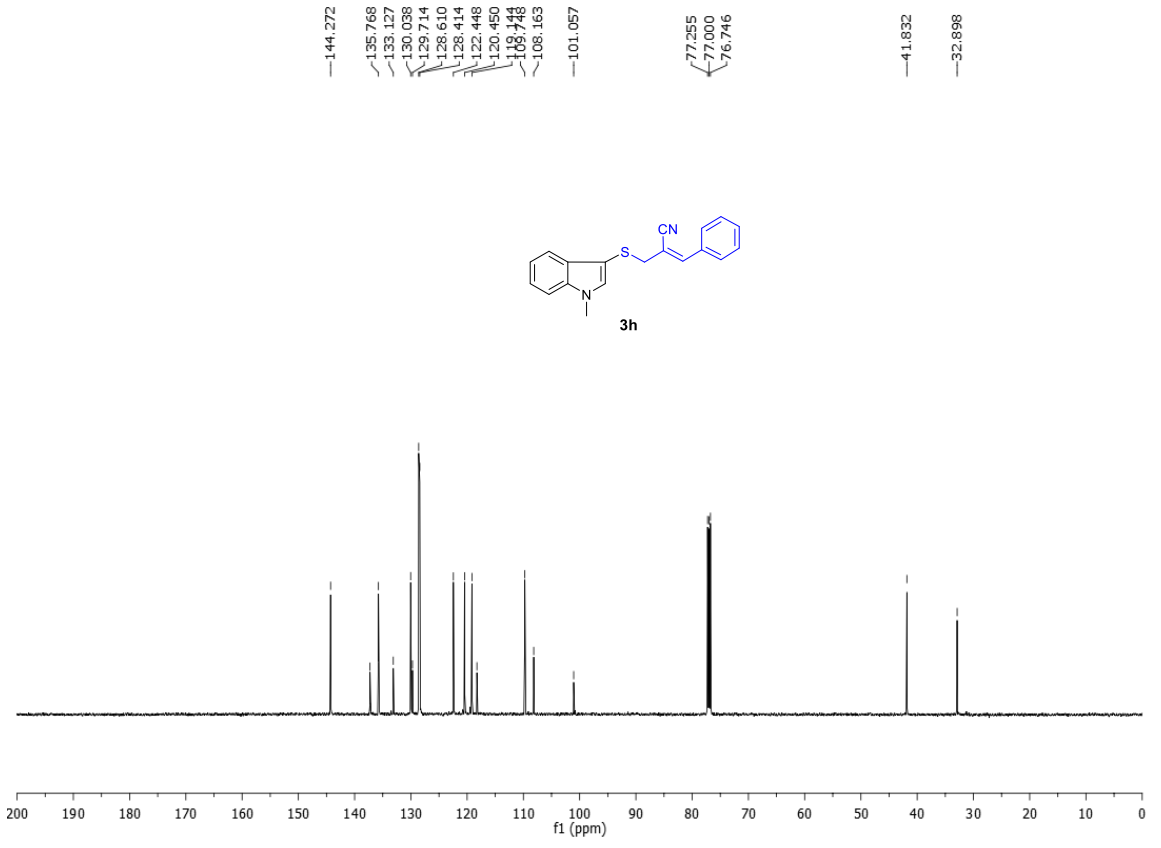
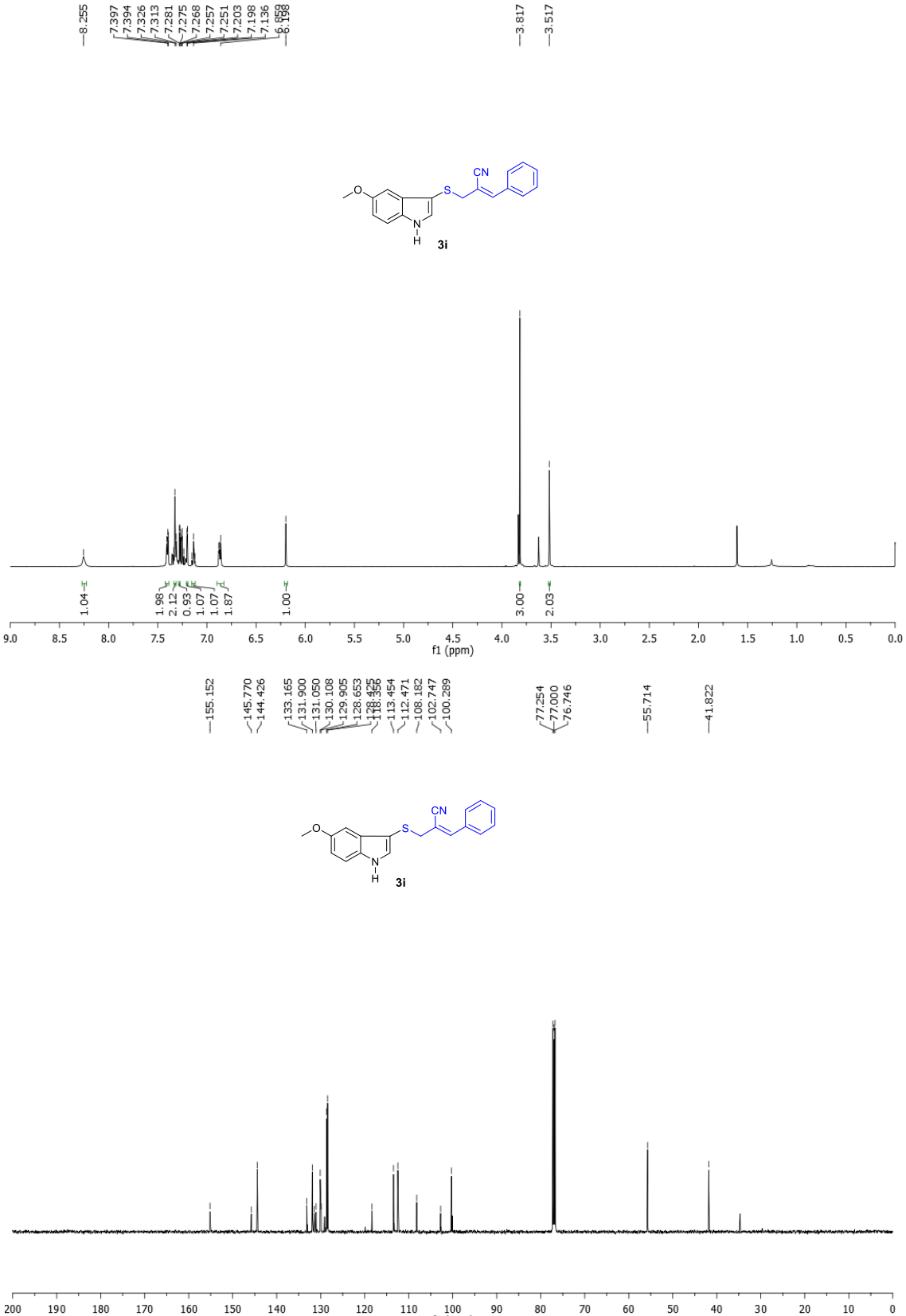
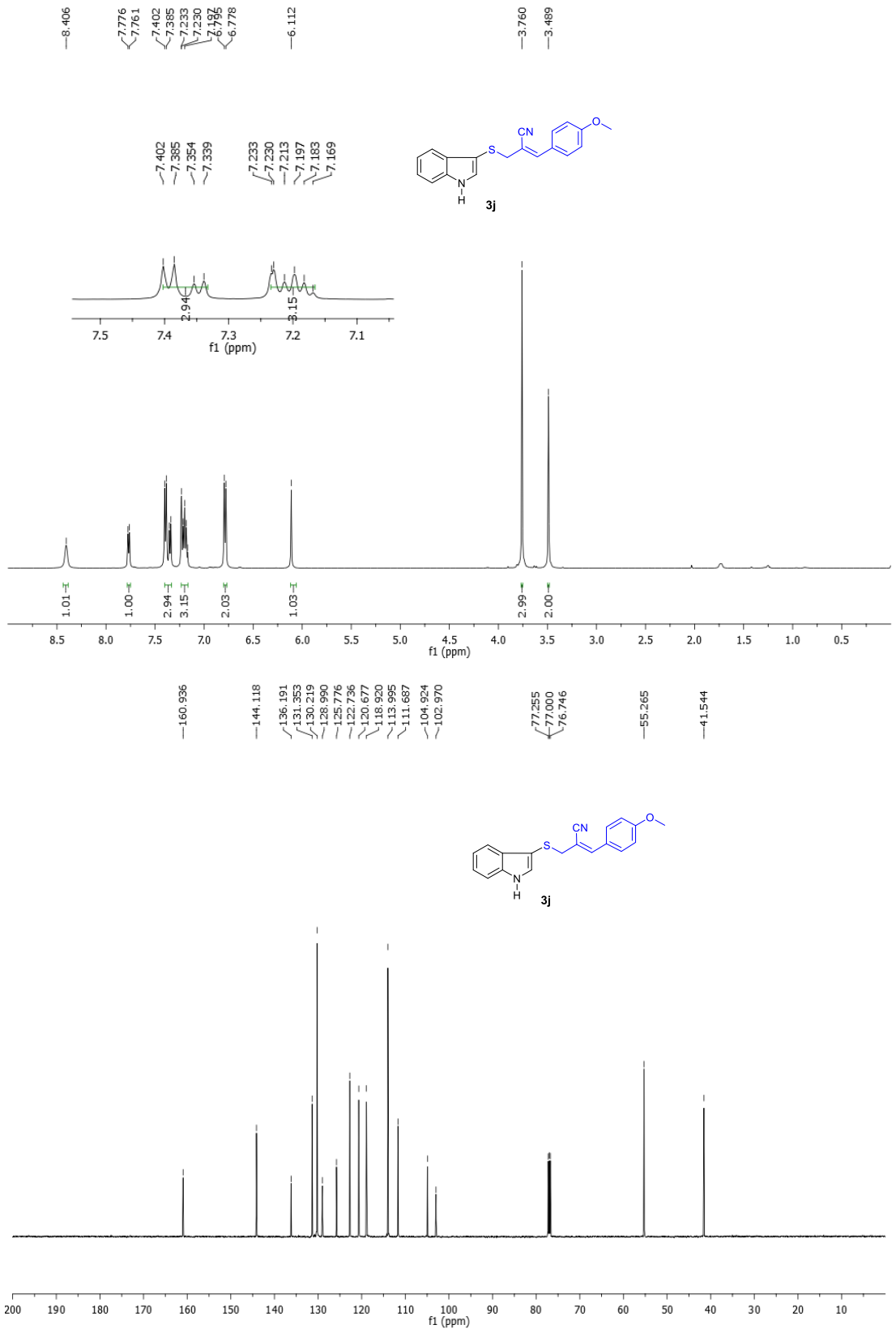
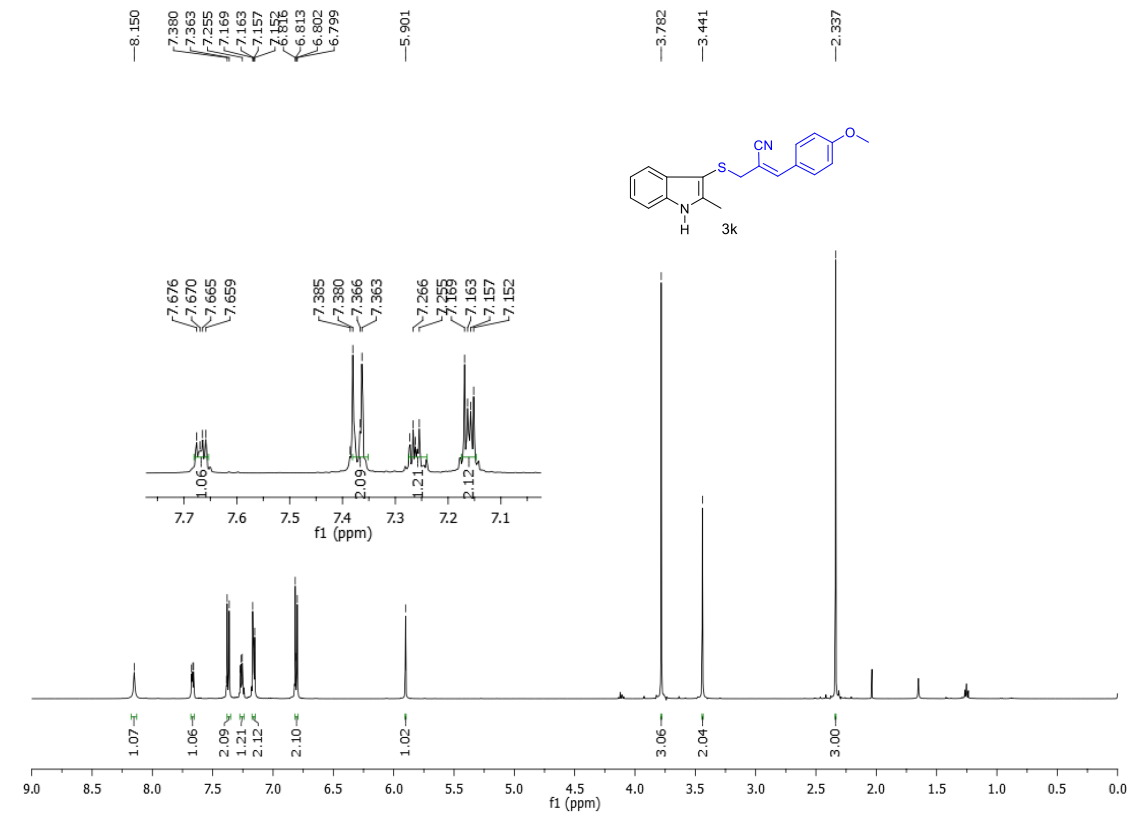
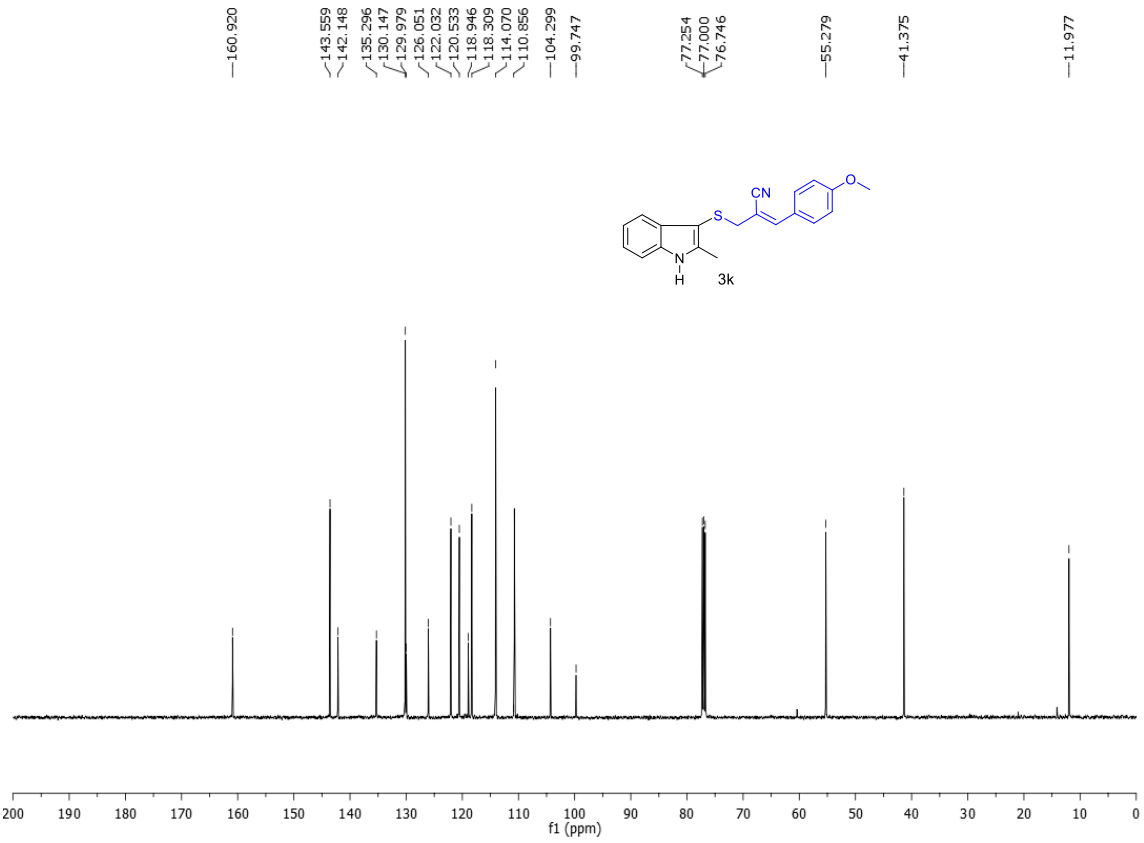
7.417
7.409
7.402
7.326
7.323
7.316
7.313
7.307
7.279
7.266
7.251
7.210
7.196
7.182
7.140
1.27
3.76
1.18
1.02
1.01
7.6
7.5
7.4
7.3
7.2
7.1
7.0
f1 (ppm)
CN
S
N
3h
0.98
1.27
3.76
1.18
1.02
1.01
0.99
3.03
2.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

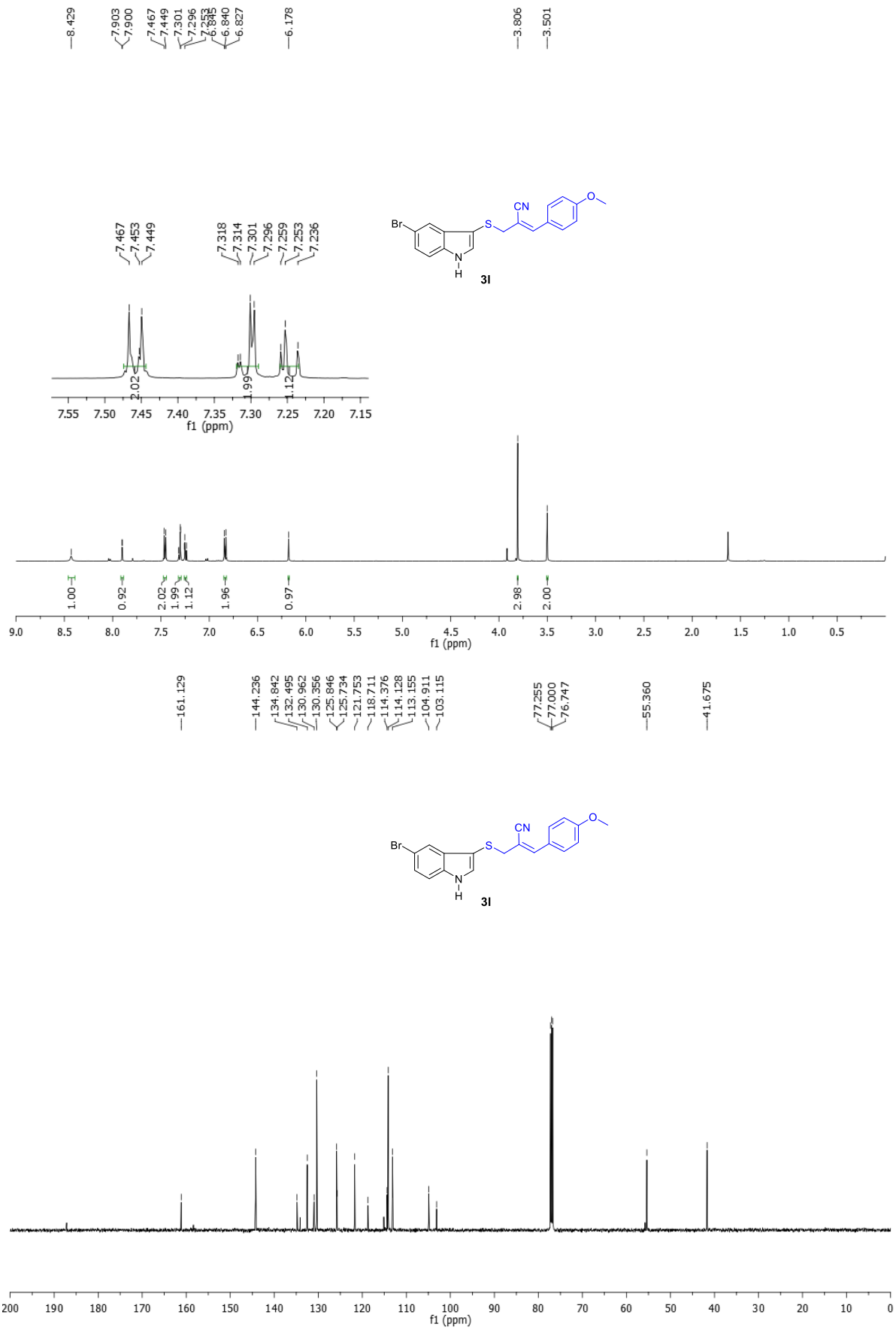

144.272
135.768
133.127
130.038
129.714
128.610
128.414
122.448
120.450
118.144
109.748
108.163
101.057
77.255
77.000
76.746
41.832
32.898
CN
S
N
3h
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

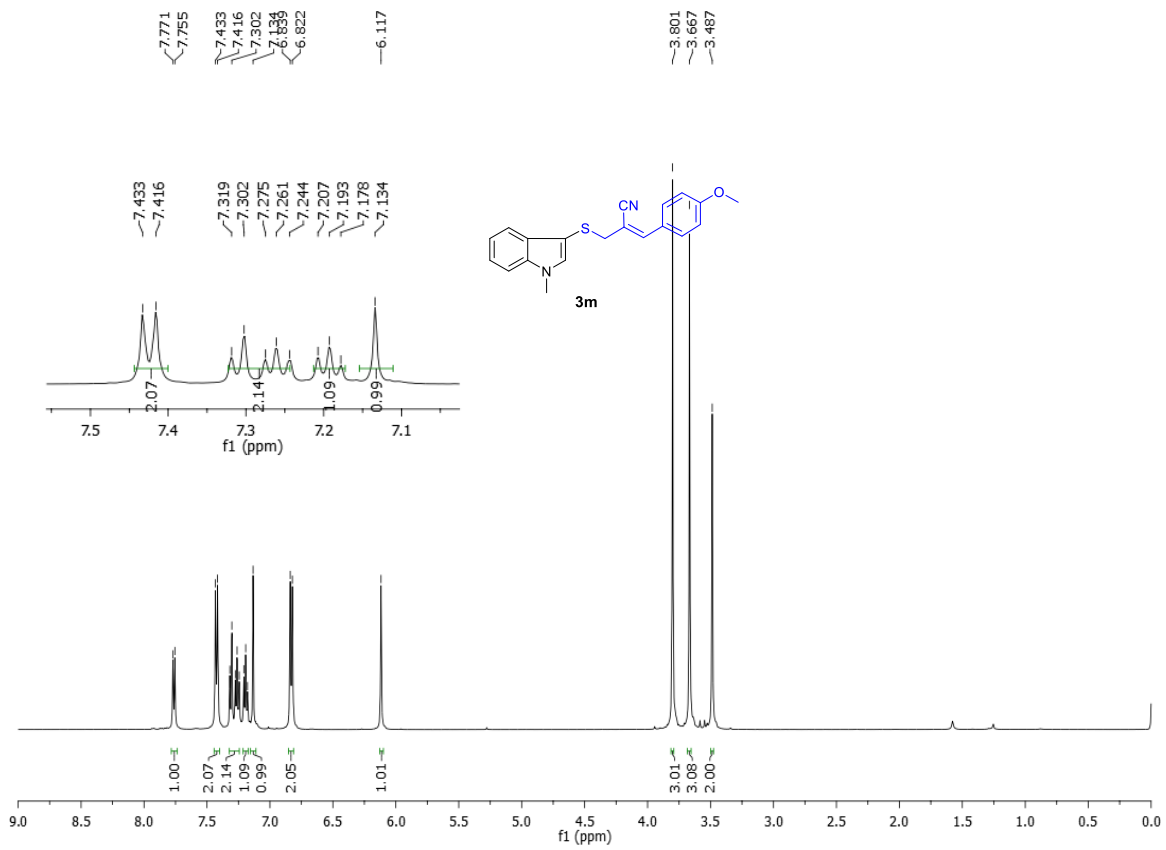

8.255
7.397
7.394
7.326
7.313
7.281
7.275
7.268
7.257
7.251
7.203
7.198
7.136
3.817
3.517
CN
S
O
N
H
3i
1.04
1.98
2.12
0.93
1.07
1.07
1.87
1.00
3.00
2.03
f1 (ppm)
155.152
145.770
144.426
133.165
131.900
131.050
130.108
129.905
128.653
113.454
112.471
108.182
102.747
100.289
77.254
77.000
76.746
55.714
41.822
CN
S
O
N
H
3i
f1 (ppm)

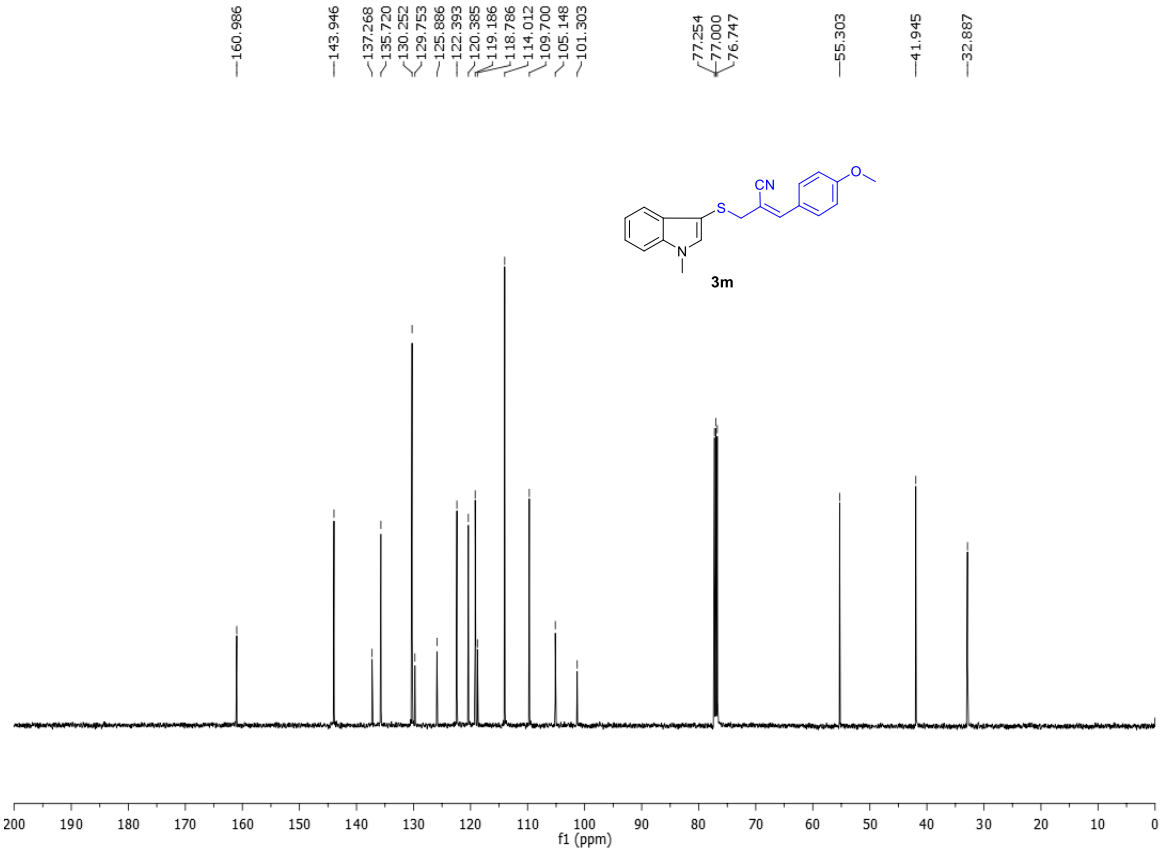

8.406
7.776
7.761
7.402
7.385
7.233
7.230
7.197
7.195
6.778
6.112
3.760
3.489
7.402
7.385
7.354
7.339
7.233
7.230
7.213
7.197
7.183
7.169
CN
O
S
N
H
3j
2.94
3.15
7.5
7.4
7.3
7.2
7.1
f1 (ppm)
1.01
1.00
2.94
3.15
2.03
1.03
2.99
2.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
160.936
144.118
136.191
131.353
130.219
128.990
125.776
122.736
120.677
118.920
113.995
111.687
104.924
102.970
77.255
77.000
76.746
55.265
41.544
CN
O
S
N
H
3j
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

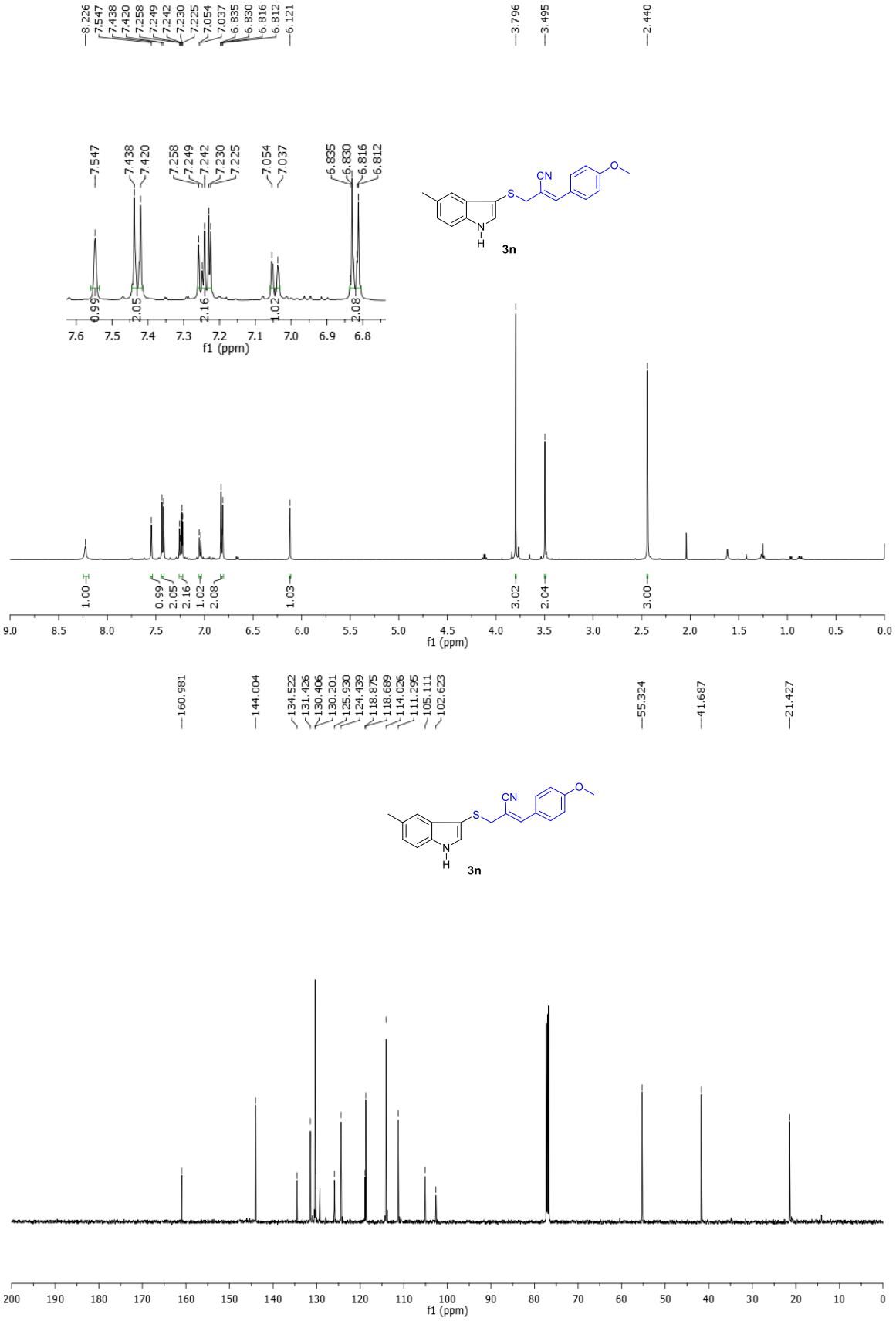

8.150
7.380
7.363
7.255
7.169
7.163
7.157
6.813
6.802
6.799
5.901
3.782
3.441
2.337
CN
S
O
N
H
3k
7.676
7.670
7.665
7.659
7.385
7.380
7.366
7.363
7.266
7.163
7.157
7.152
1.06
2.09
1.21
2.12
f1 (ppm)
1.07
1.06
2.09
1.21
2.12
2.10
1.02
3.06
2.04
3.00
f1 (ppm)

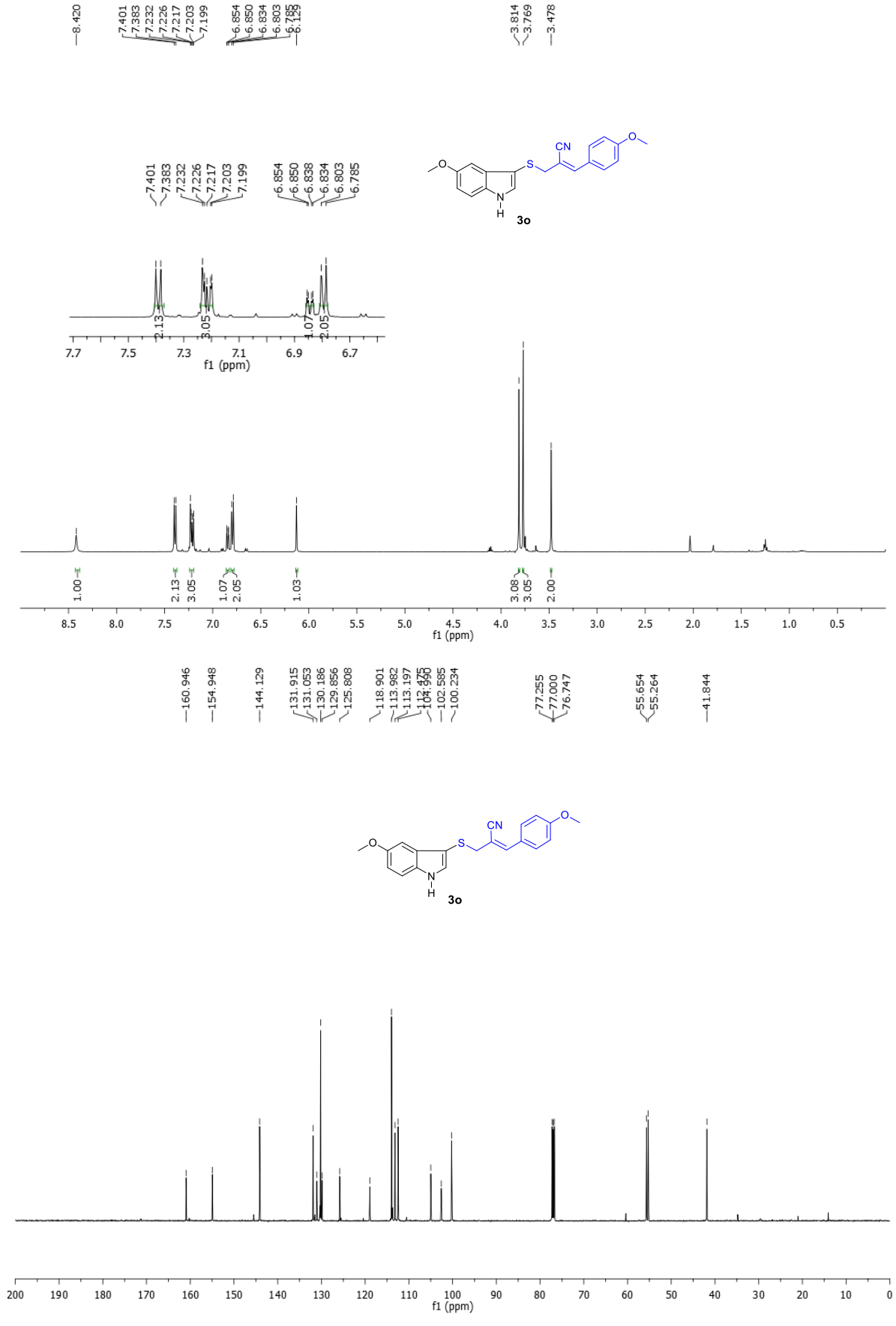

160.920
143.559
142.148
135.296
130.147
129.979
126.051
122.032
120.533
118.946
118.309
114.070
110.856
104.299
99.747
77.254
77.000
76.746
55.279
41.375
11.977
CN
S
O
N
H
3k
f1 (ppm)

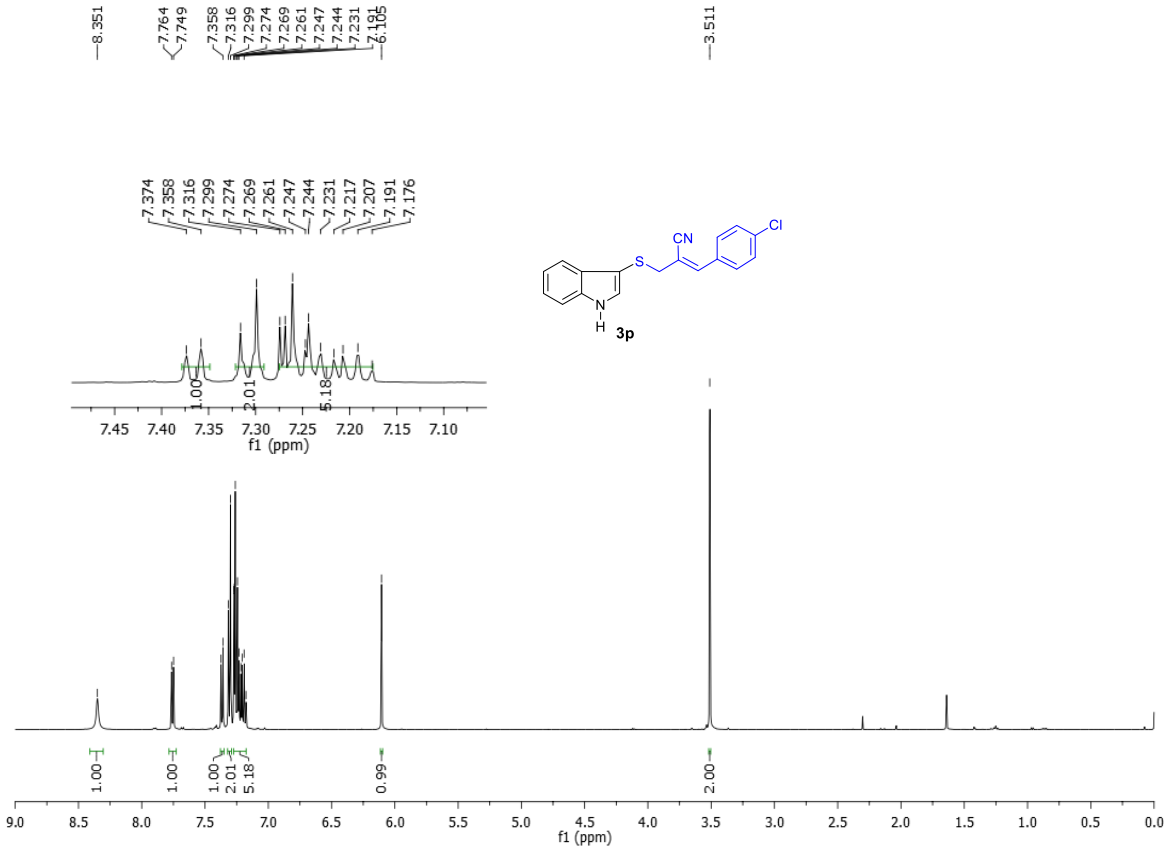

8.429
7.903
7.900
7.467
7.449
7.301
7.296
6.840
6.827
6.178
3.806
3.501
7.467
7.453
7.449
7.318
7.314
7.301
7.296
7.259
7.253
7.236
2.02
1.99
1.12
7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15
f1 (ppm)
Br
S
CN
O
N
H
3l
1.00
0.92
2.02
1.99
1.12
1.96
0.97
2.98
2.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
161.129
144.236
134.842
132.495
130.962
130.356
125.846
125.734
121.753
118.711
114.376
114.128
113.155
104.911
103.115
77.255
77.000
76.747
55.360
41.675
Br
S
CN
O
N
H
3l
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

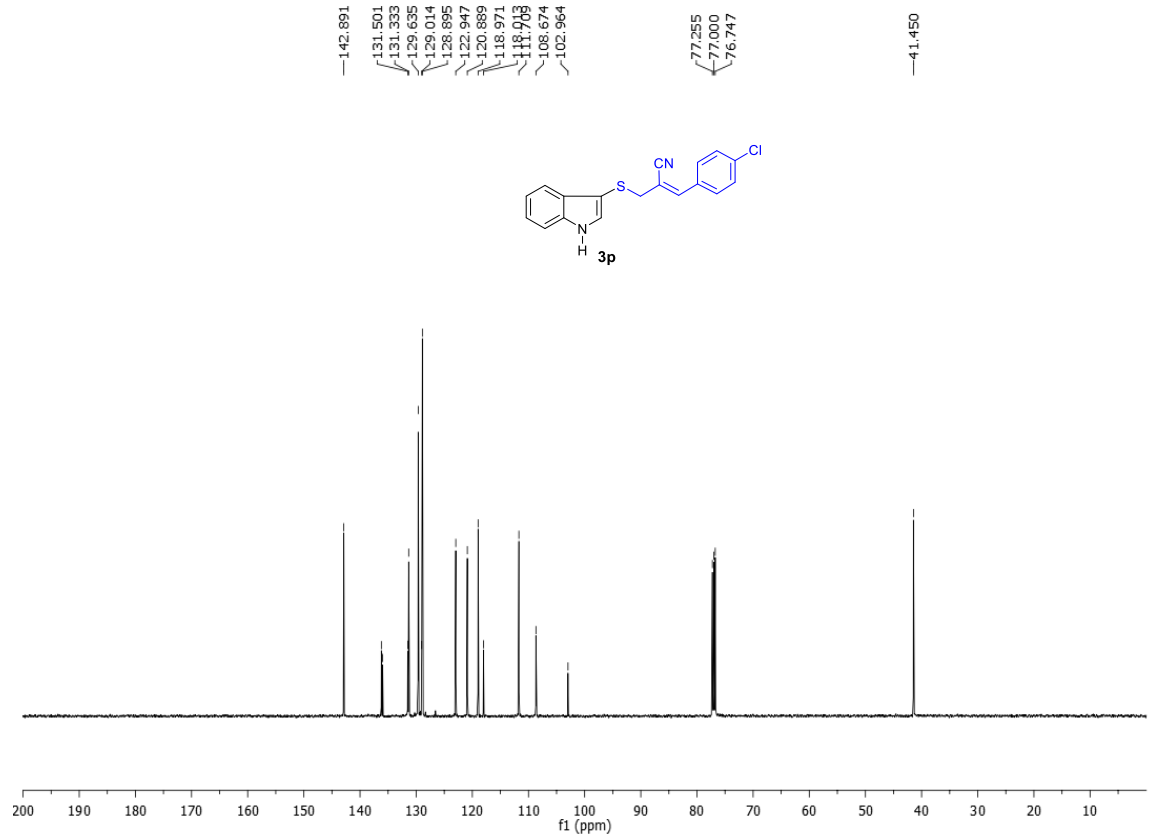

7.771
7.755
7.433
7.416
7.302
7.134
6.839
6.822
6.117
3.801
3.667
3.487
7.433
7.416
7.319
7.302
7.275
7.261
7.244
7.207
7.193
7.178
7.134
2.07
2.14
1.09
0.99
f1 (ppm)
CN
O
S
N
3m
1.00
2.07
2.14
1.09
0.99
2.05
1.01
3.01
3.08
2.00
f1 (ppm)


160.986
143.946
137.268
135.720
130.252
129.753
125.886
122.393
120.385
119.186
118.786
114.012
109.700
105.148
101.303
77.254
77.000
76.747
55.303
41.945
32.887
CN
O
S
N
3m
f1 (ppm)

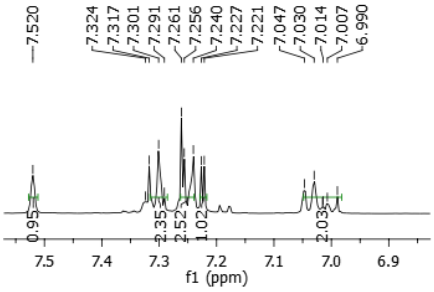

8.226
7.547
7.438
7.420
7.258
7.249
7.242
7.230
7.225
7.054
7.037
6.835
6.830
6.816
6.812
6.121
3.796
3.495
2.440
CN
O
S
N
H
3n
f1 (ppm)
160.981
144.004
134.522
131.426
130.406
130.201
125.930
124.439
118.875
118.689
114.026
111.295
105.111
102.623
55.324
41.687
21.427

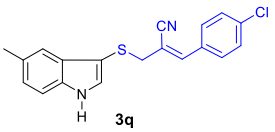

8.420
7.401
7.383
7.232
7.226
7.217
7.203
7.199
6.854
6.850
6.834
6.803
6.785
6.129
3.814
3.769
3.478
CN
S
O
N
H
3o
2.13
3.05
1.07
2.05
f1 (ppm)
1.00
1.03
3.08
160.946
154.948
144.129
131.915
131.053
130.186
129.856
125.808
118.901
113.982
113.197
112.475
104.990
102.585
100.234
77.255
77.000
76.747
55.654
55.264
41.844


8.351
7.764
7.749
7.358
7.316
7.299
7.274
7.269
7.261
7.247
7.244
7.231
7.181
6.105
3.511
7.374
7.358
7.316
7.299
7.274
7.269
7.261
7.247
7.244
7.231
7.217
7.207
7.191
7.176
1.00
2.01
5.18
7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10
f1 (ppm)
CN
Cl
S
N
H
3p
1.00
1.00
1.00
2.01
5.18
0.99
2.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

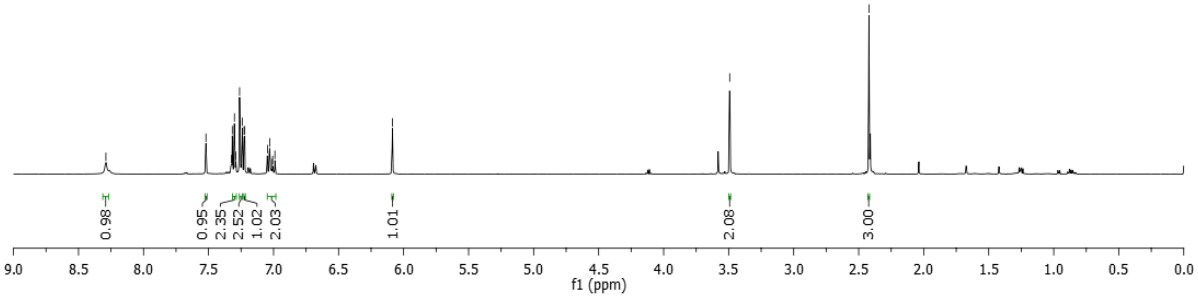

142.891
131.501
131.333
129.635
129.014
128.895
122.947
120.889
118.971
118.013
111.708
108.674
102.964
77.255
77.000
76.747
41.450
CN
Cl
S
N
H
3p
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


8.289
7.520
7.324
7.317
7.301
7.291
7.261
7.256
7.240
7.227
7.221
7.047
7.030
7.007
6.990
6.988
3.492
2.421

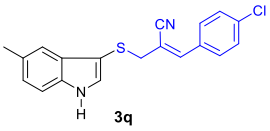

7.520
7.324
7.317
7.301
7.291
7.261
7.256
7.240
7.227
7.221
7.047
7.030
7.014
7.007
6.990
0.95
2.35
2.52
1.02
2.03
7.5
7.4
7.3
7.2
7.1
7.0
6.9
f1 (ppm)


CN
Cl
S
N
H

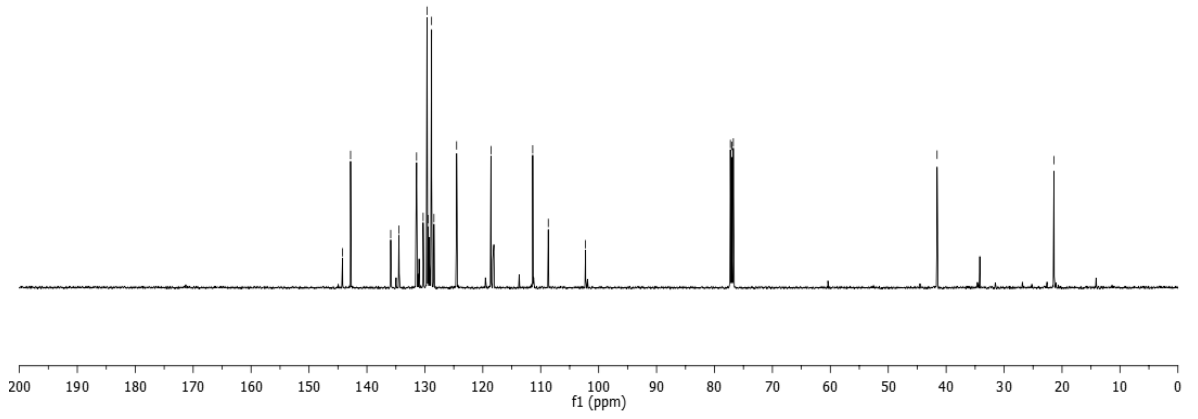
3q


0.98
0.95
2.35
2.52
1.02
2.03
1.01
2.08
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

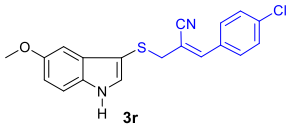

144.214
142.822
131.430
130.296
129.624
129.435
128.839
128.435
124.516
118.597
111.378
108.692
102.260
77.254
77.000
76.746
41.572
21.386


CN
Cl
S
N
H

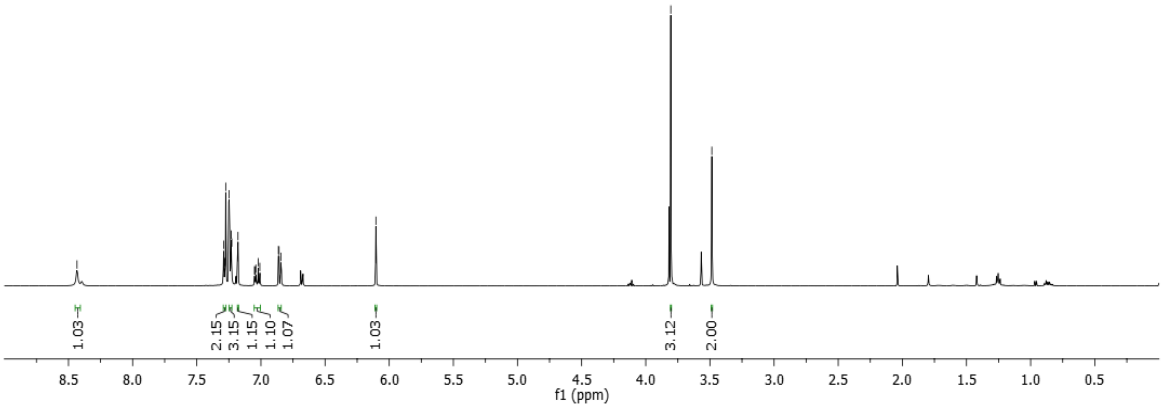
3q

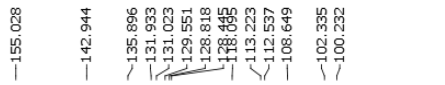

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

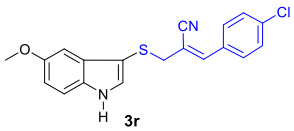

8.434
7.290
7.282
7.274
7.247
7.232
7.227
7.179
7.050
7.046
7.039
7.021
7.008
6.864
6.859
6.845
6.104
3.805
3.485


CN
Cl
O
S
N
H

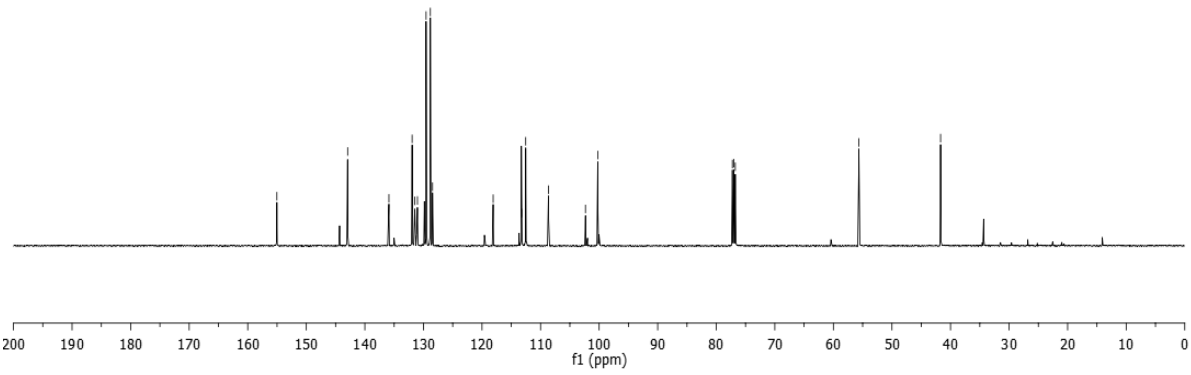
3r

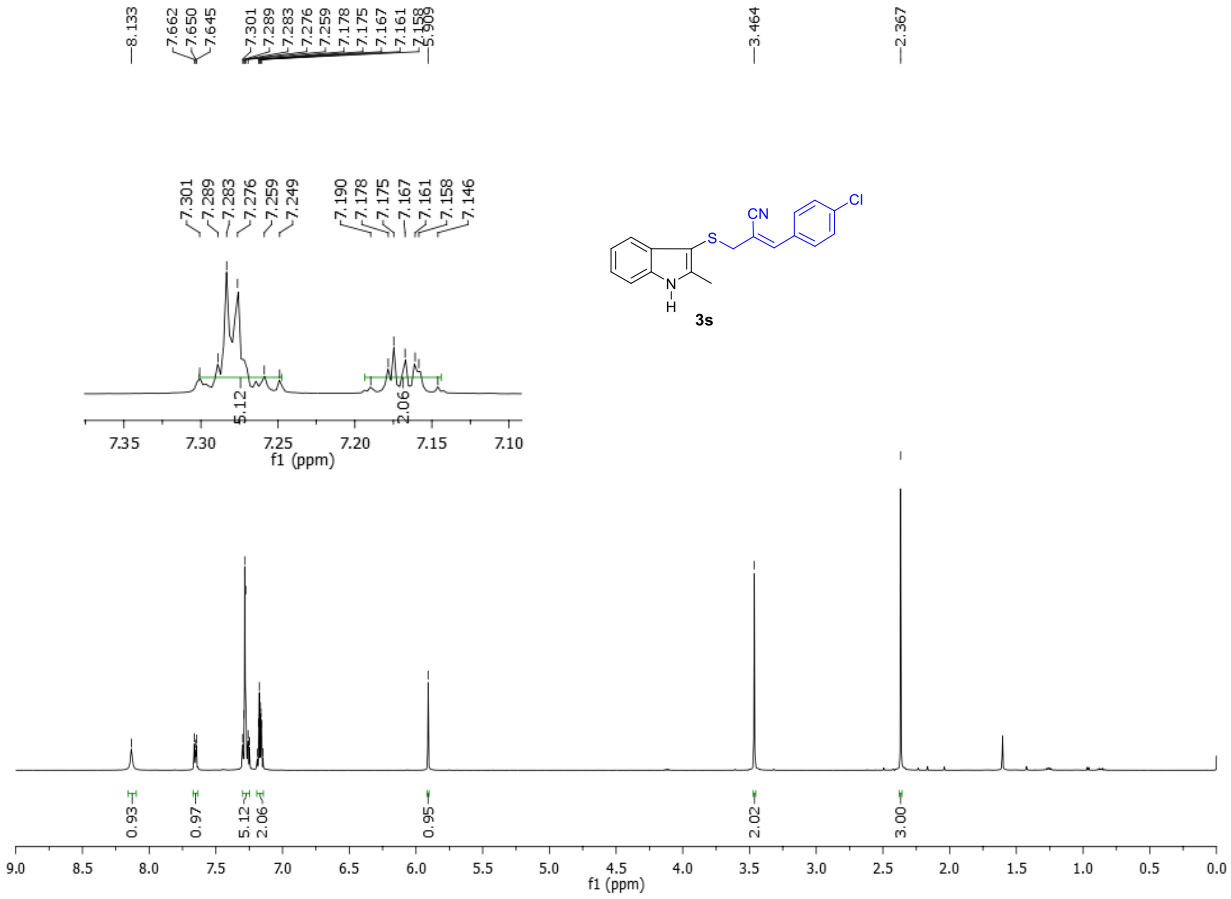

1.03
2.15
3.15
1.15
1.10
1.07
1.03
3.12
2.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

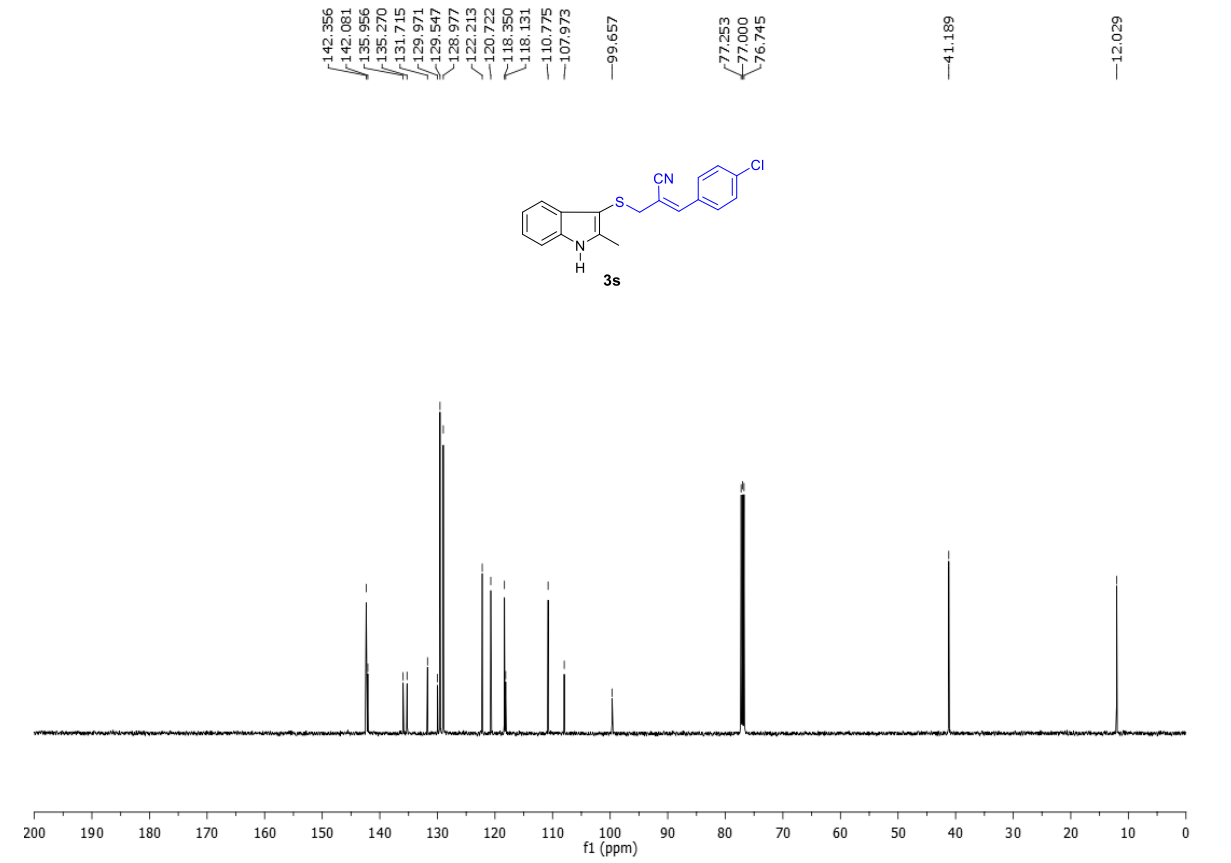

155.028
142.944
135.896
131.933
131.023
129.551
128.818
128.445
128.095
113.223
112.537
108.649
102.335
100.232
77.253
77.000
76.746
55.652
41.696

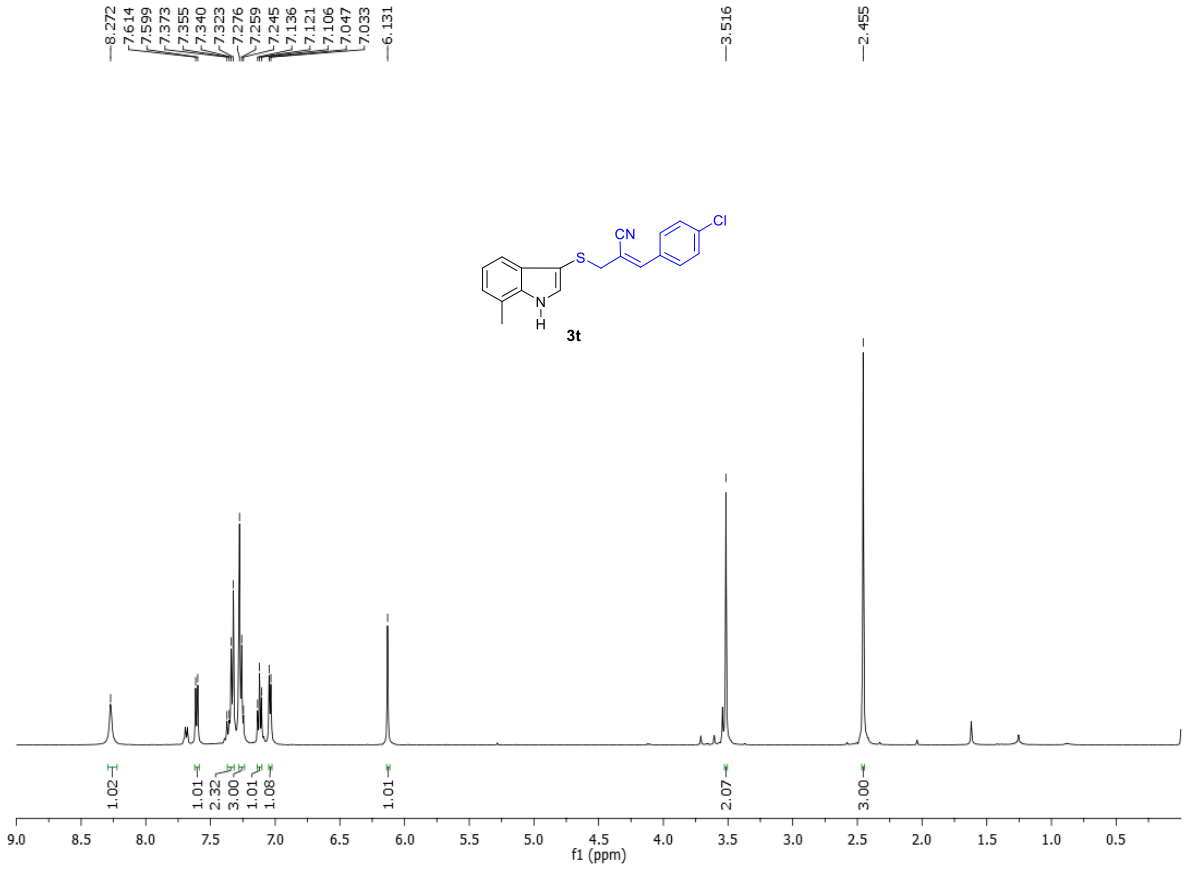

CN
Cl
O
S
N
H

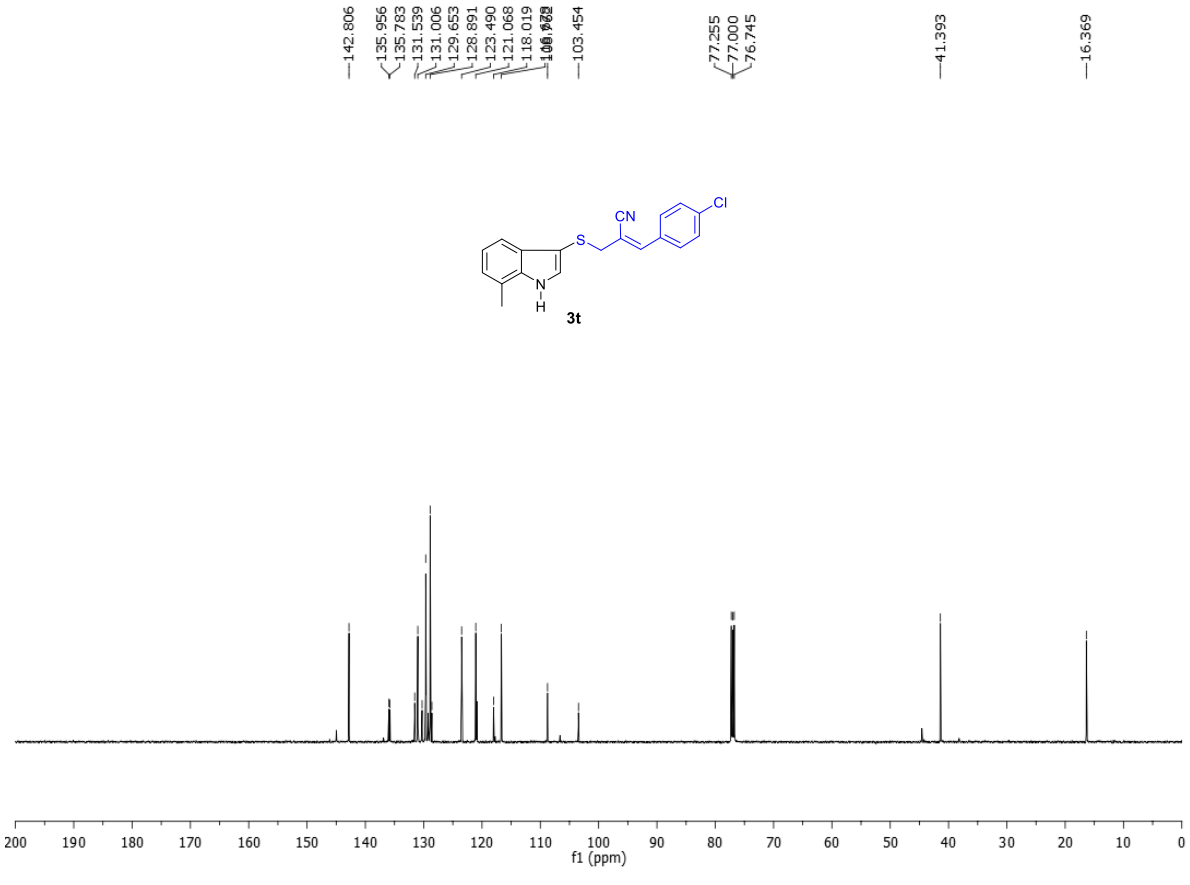
3r

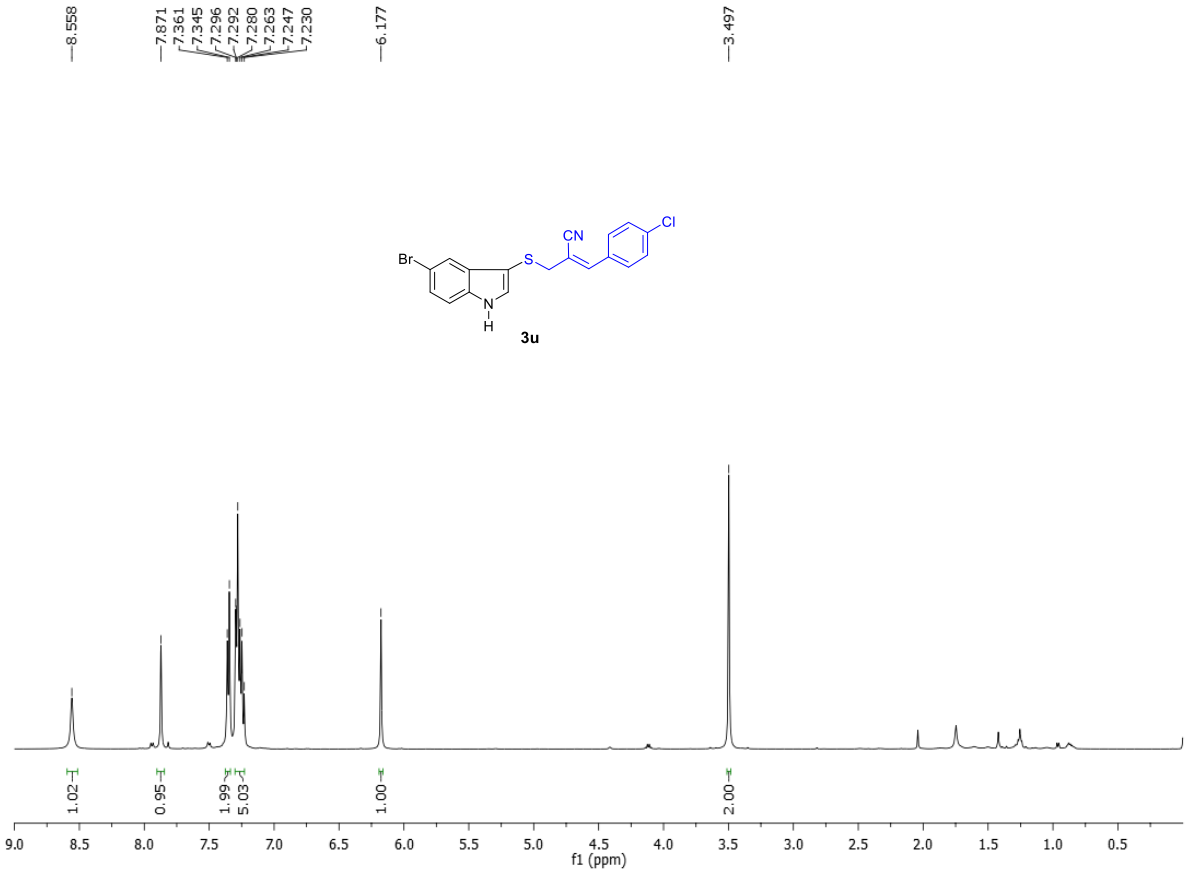

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

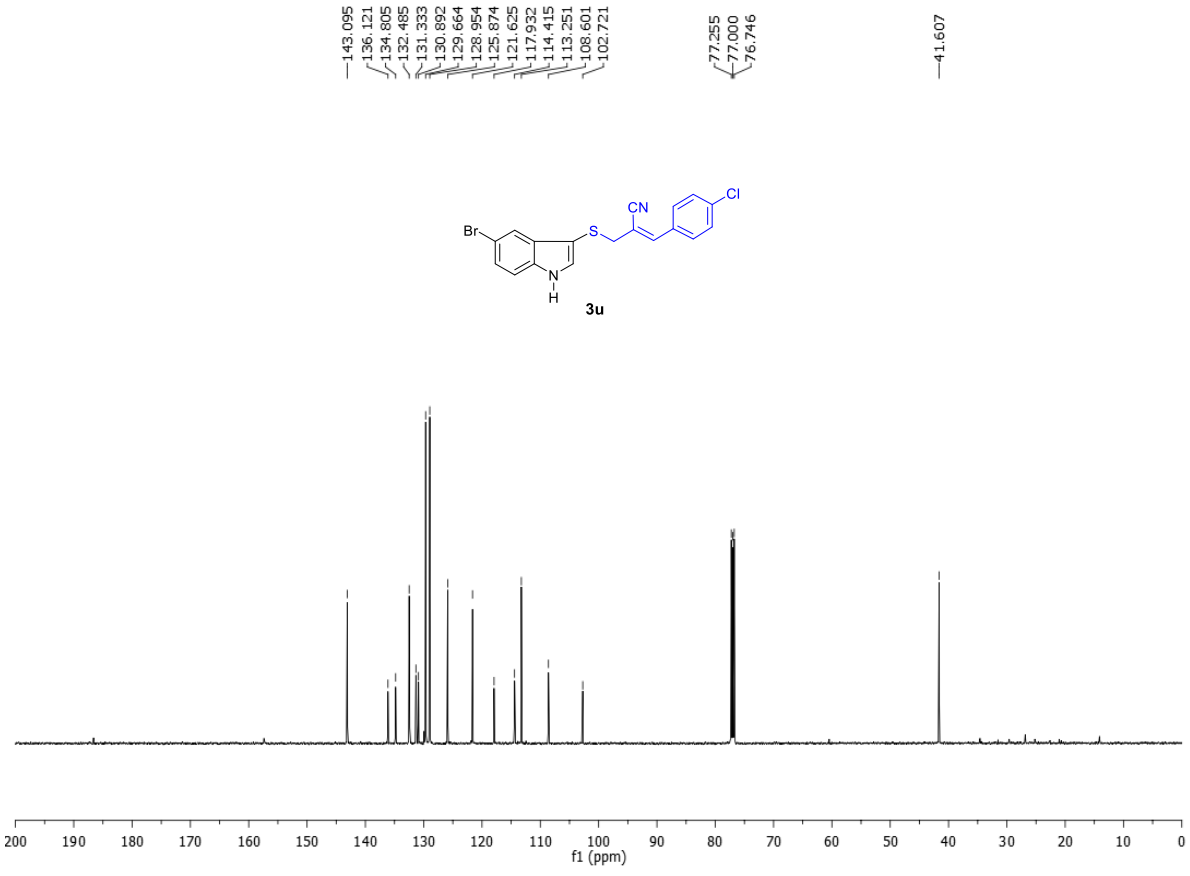

8.133
7.662
7.650
7.645
7.301
7.289
7.283
7.276
7.259
7.178
7.175
7.167
7.161
7.158
5.909
3.464
2.367
7.301
7.289
7.283
7.276
7.259
7.249
7.190
7.178
7.175
7.167
7.161
7.158
7.146
5.12
2.06
7.35
7.30
7.25
7.20
7.15
7.10
f1 (ppm)
CN
Cl
S
N
H
3s
0.93
0.97
5.12
2.06
0.95
2.02
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

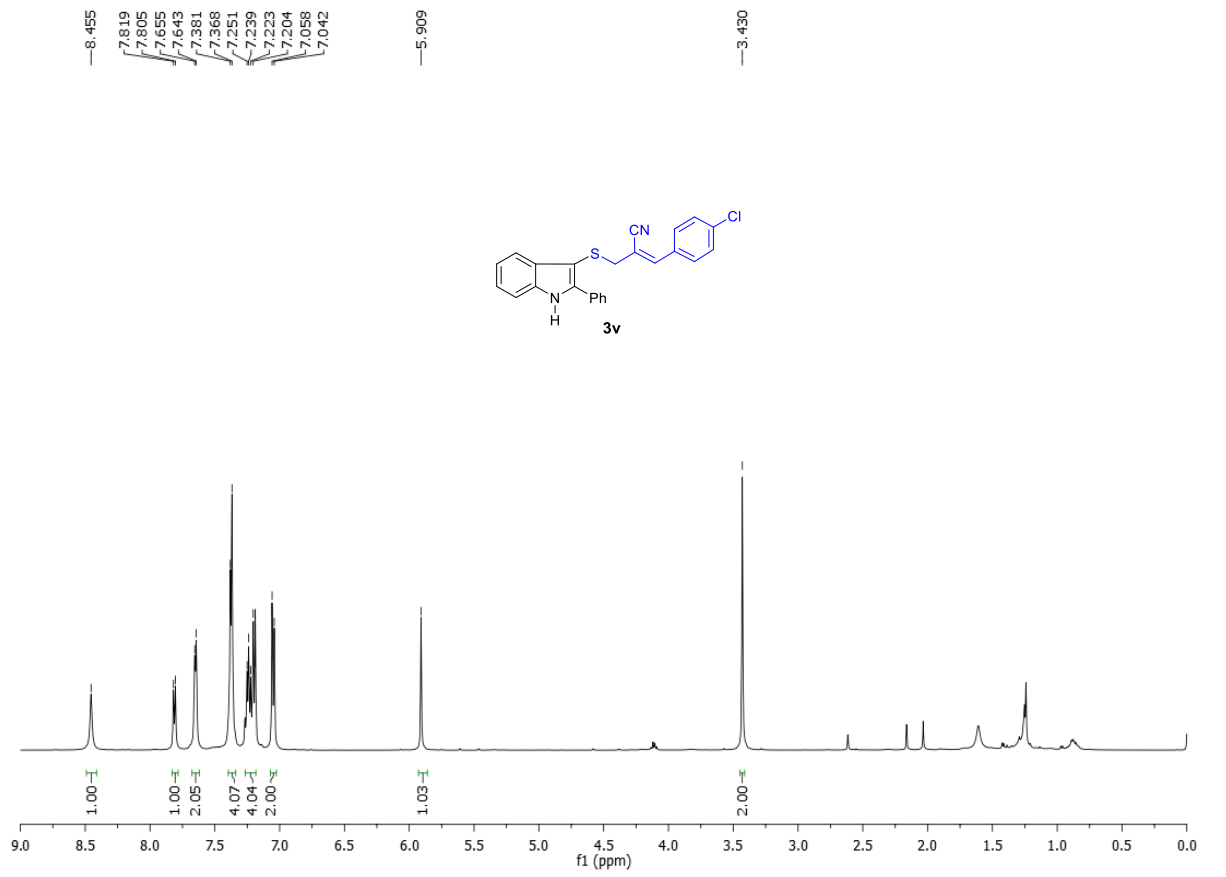

142.356
142.081
135.956
135.270
131.715
129.971
129.547
128.977
122.213
120.722
118.350
118.131
110.775
107.973
99.657
77.253
77.000
76.745
41.189
12.029
CN
Cl
S
N
H
3s
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

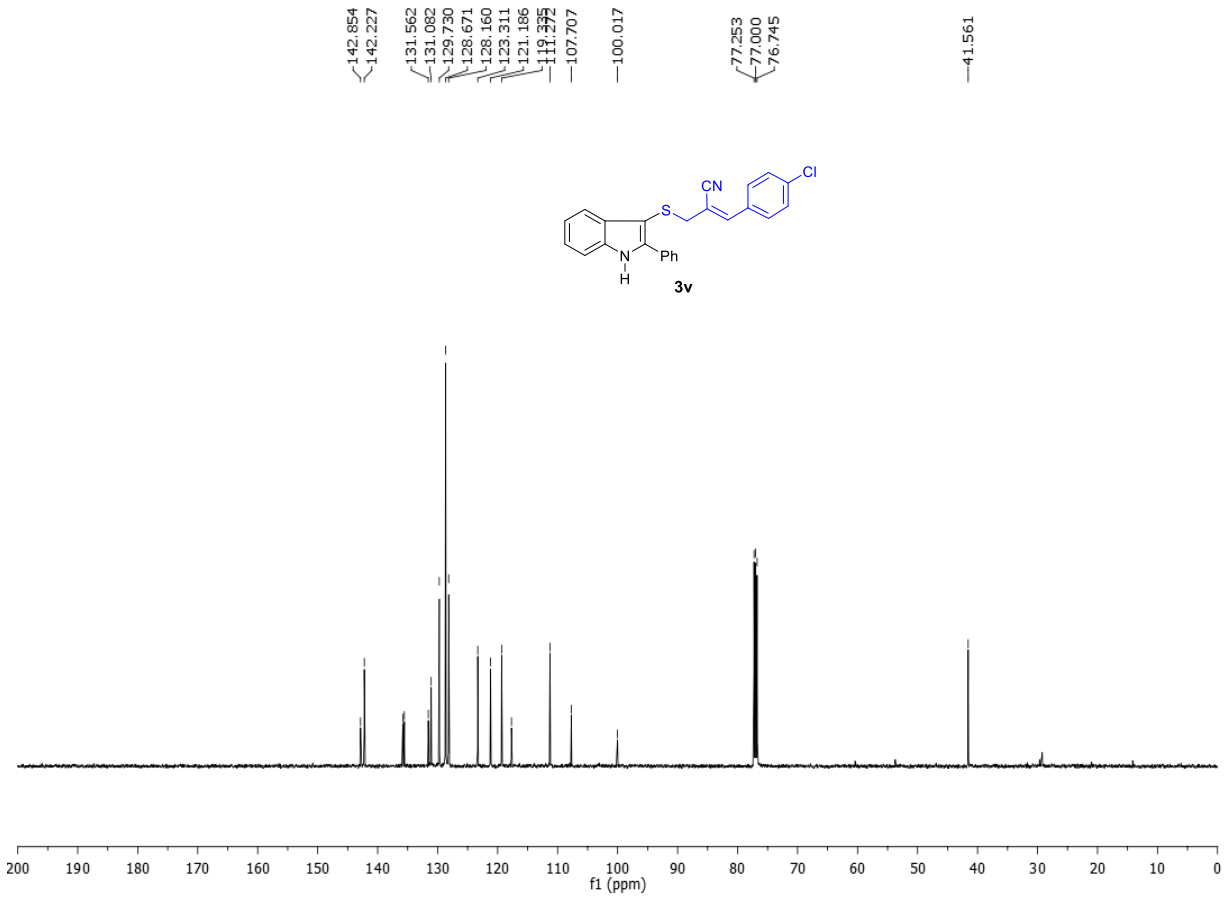

8.272
7.614
7.599
7.373
7.355
7.340
7.323
7.276
7.259
7.245
7.136
7.121
7.106
7.047
7.033
6.131
3.516
2.455
CN
Cl
S
N
H
3t
1.02
1.01
2.32
3.00
1.01
1.08
1.01
2.07
3.00
f1 (ppm)

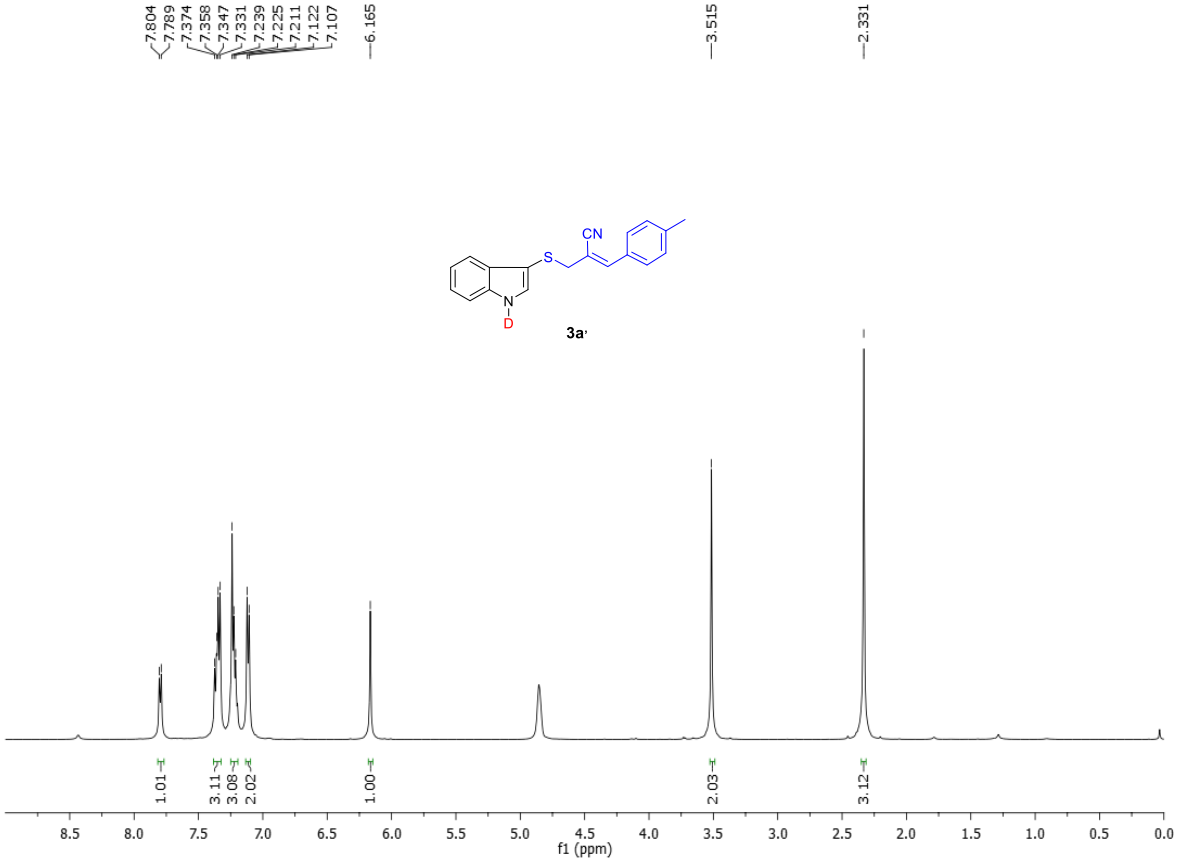

142.806
135.956
135.783
131.539
131.006
129.653
128.891
123.490
121.068
118.019
103.454
77.255
77.000
76.745
41.393
16.369
CN
Cl
S
N
H
3t
f1 (ppm)

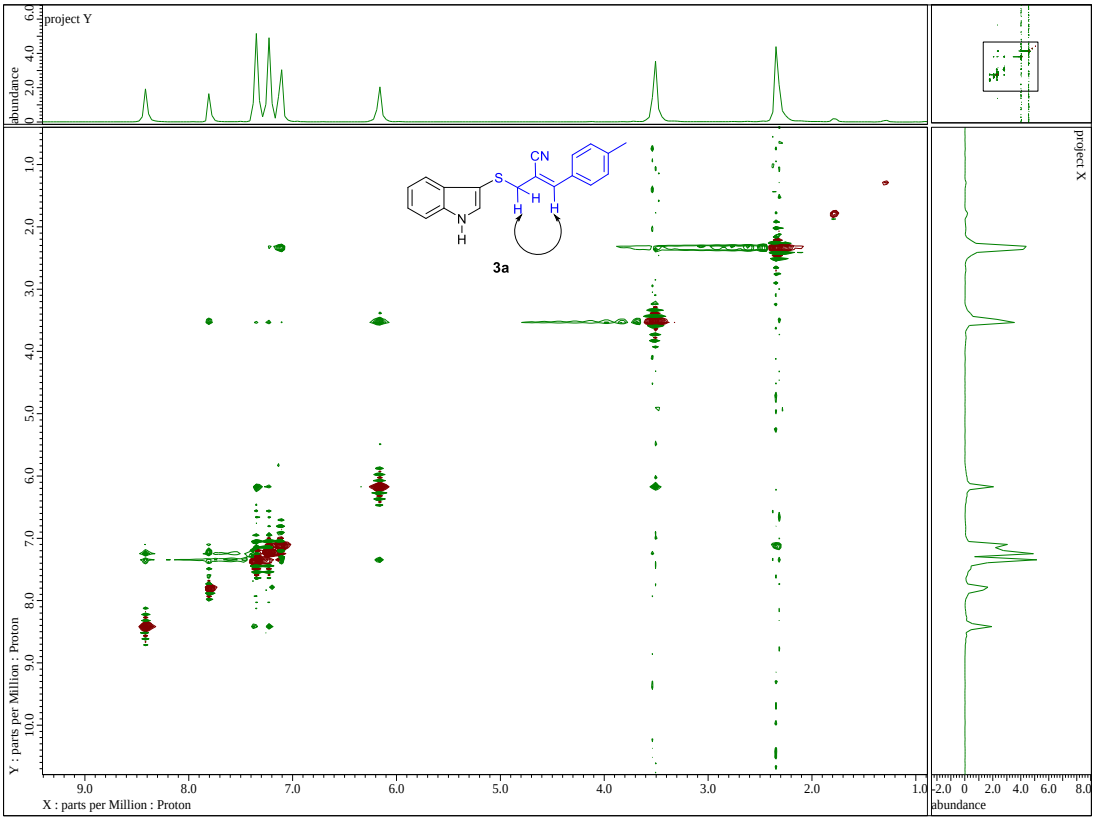

8.558
7.871
7.361
7.345
7.296
7.292
7.280
7.263
7.247
7.230
6.177
3.497
Br
S
CN
Cl
N
H
3u
1.02
0.95
1.99
5.03
1.00
2.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


143.095
136.121
134.805
132.485
131.333
130.892
129.664
128.954
125.874
121.625
117.932
114.415
113.251
108.601
102.721
77.255
77.000
76.746
41.607
Br
S
CN
Cl
N
H
3u
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.455
7.819
7.805
7.655
7.643
7.381
7.368
7.251
7.239
7.223
7.204
7.058
7.042
5.909
3.430
CN
Cl
S
N
H
Ph
3v
1.00
1.00
2.05
4.07
4.04
2.00
1.03
2.00
f1 (ppm)


142.854
142.227
131.562
131.082
129.730
128.671
128.160
123.311
121.186
107.707
100.017
77.253
77.000
76.745
41.561
CN
Cl
S
N
H
Ph
3v
f1 (ppm)


7.804
7.789
7.374
7.358
7.347
7.331
7.239
7.225
7.211
7.122
7.107
6.165
3.515
2.331
CN
S
N
D
3a'
1.01
3.11
3.08
2.02
1.00
2.03
3.12
f1 (ppm)


project Y
abundance
CN
S
N
H
H
H
3a
project X
Y : parts per Million : Proton
X : parts per Million : Proton
abundance