Supplementary Information

Rh(III)-catalyzed synthesis of 1-aminoindole derivatives from 2-acetyl-1-arylhydrazines and diazo compounds in water

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1. General Informations: All the reactions were carried out under argon atmosphere using standard Schlenk technique. ^{1}H NMR (400 M Hz), ^{19}F (376 M Hz), and ^{13}C NMR (101 M Hz) were recorded on a Bruker AV400 NMR spectrometer with $CDCl_3$ or DMSO-d_6 as solvent. Chemical shifts of ^{1}H, ^{19}F, and ^{13}C NMR spectra are reported in parts per million (ppm). The residual solvent signals were used as references and the chemical shifts converted to the TMS scale (DMSO-d_6: δ H =2.50 ppm, δ C =39.52 ppm; $CDCl_3$: δ H = 7.26 ppm, δ C = 77.00 ppm). All coupling constants (J values) were reported in Hertz (Hz). Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), doublet of doublet of doublets (ddd), doublet of triplets (dt), triplet (t), triplet of doublets (td), quartet (q), and multiplet (m). Column chromatography was performed on silica gel 200-300 mesh. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm). HRMS were done on Varian 7.0 T FTICR-mass spectrometer. $[Cp^*RhCl_2]_2$ was prepared from $RhCl_3 \cdot xH_2O$ following a literature procedure.[1] $[Cp^*Rh(OAc)_2]$ was prepared from $[Cp^*RhCl_2]_2$ following a literature procedure.[2] Unless otherwise noted below, all other compounds have been reported in the literature or are commercially available from Alfa Aesar China (Beijing) Chemical Co., Ltd. without any further purification.

2. General Procedure: Preparation of 2-acetyl-1-arylhydrazines and diazo compounds Substrates

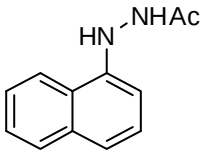
The 2-acetyl-1-arylhydrazines substrates **1a-1d**, **1f-1j**, **1n-1o**, and **1r-1s** were prepared following the same procedure described by F. Glorius et al.[3] **1e** was synthesized following the known procedure.[4] **1k-1m**, **1p-1q**, and **1t-1v** were prepared according to the following procedure:

The corresponding arylhydrazine hydrochloride salt (13 mmol) was dissolved in 1N NaOH (25 mL) and THF (7 mL), then acetic anhydride (1.3 g, 13 mmol) was added dropwise. After stirring for 1 h, EtOAc (25 mL) was added, and the organic layer was separated. The aqueous layer was extracted with EtOAc (3×25 mL). The combined extracts were dried over anhydrous $MgSO_4$. After removal of solvents under reduced pressure, the resulting solid was washed with diethyl ether (20 mL), and purified by short column chromatography on silica

gel (using eluent : EtOAc / Petroleum ether =1/1 (v/v)).

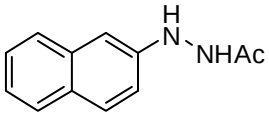
Diazo compounds **2a**, **2b**, **2d**, **2h**, **2i**;[5] **2c**, **2f**;[6] **2e**;[7] **2g**, **2j**[8] were all reported previously.

N'-(naphthalen-1-yl) acetohydrazide (1k)



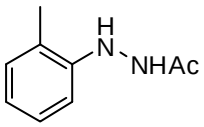
Following the general procedure, this compound was isolated as a grey solid (1.56 g, 60% yield). NMR showed the compounds to be a mixture of two rotamers (ratio: approx 1/0.14). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.80 and 9.13 (2×bs, 1H), 8.62 and 8.22 (2×bs, 1H), 8.18-8.20 (d, J = 8.0 Hz, 1H), 7.80-7.82 (d, J = 7.4 Hz, 1H), 7.44-7.47 (t, 2H), 7.28-7.32 (t, 2H), 6.69-6.71 (d, J = 6.6 Hz, 1H), 1.99 and 1.89 (2×s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6): δ169.0, 144.1, 133.8, 127.9, 136.3, 125.7, 124.4, 122.0, 121.7, 118.2, 104.9, 20.7. IR (cm^{-1}): ν 3243, 3044, 1653, 1624, 1521, 1400, 1373, 795, 767, 668. HRMS (ESI): Calcd for $C_{12}H_{13}N_2O$ $[M+H]^+$: 201.1028, Found: 201.1023. Mp: 139-141 ^{o}C.

N'-(naphthalen-2-yl) acetohydrazide (1l)



Following the general procedure, this compound was isolated as an off-white solid (1.60 g, 61% yield). NMR showed the compounds to be a mixture of two rotamers (ratio: approx 1/0.16). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.75 (bs, 1H), 7.98 (bs, 1H), 7.63-7.70 (m, 4H), 6.92-7.35 (m, 5H), 1.964 and 1.904 (2×s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6): δ169.0, 147.1, 134.3, 128.4, 127.8, 127.5, 126.1, 125.8, 122.1, 116.1 104.5, 20.7. IR (cm^{-1}): ν 3295, 3046, 1673, 1632, 1522, 1369, 1218, 811, 746, 599. HRMS (ESI): Calcd for $C_{12}H_{13}N_2O$ $[M+H]^+$: 201.1028, Found: 201.1026. Mp: 169-171 ^{o}C.

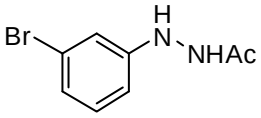
N'-(o-tolyl) acetohydrazide (1m)



Following the general procedure, this compound was isolated as a yellow solid (1.40 g, 66% yield). NMR showed the compounds to be a mixture of two rotamers (ratio: approx 1/0.15). ^{1}H NMR (400 MHz, DMSO-d_6): δ

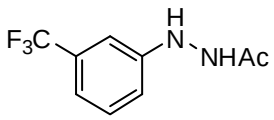
9.62-9.63 (d, J = 2.1 Hz, 1H), 6.98-7.02 (q, 3H), 6.61-6.66 (m, 2H), 2.13 (2×s, 3H), 1.91 (2×s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6): δ168.9, 146.7, 129.9, 126.3, 121.6, 118.4, 110.8, 20.6, 17.2. IR (cm^{-1}): ν 3229, 3020, 1688, 1652, 1500, 1251, 752, 623. HRMS (ESI): Calcd for $C_9H_{13}N_2O$ $[M+H]^+$: 165.1028, Found: 165.1019. Mp: 98-100 °C.

N'-(3-bromophenyl) acetohydrazide (1p)



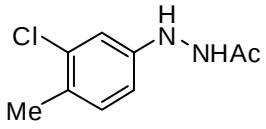
Following the general procedure, this compound was isolated as a white solid (2.37 g, 80% yield). NMR showed the compounds to be a mixture of two rotamers (ratio: approx 10/1). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.70 (bs, 1H), 7.97 (bs, 1H), 7.05-7.09 (t, 1H), 6.82-6.84 (d, 2H), 6.67-6.69 (d, 1H), 1.90 and 1.85 (2×s, 3H).^{13}C NMR (101 MHz, DMSO-d_6): δ 169.1, 151.1, 130.6, 122.0, 120.6, 114.1, 111.0, 20.6. IR (cm^{-1}): ν 3294, 3010, 1653, 1593, 1501, 1471, 1247, 860, 771, 677, 572. HRMS (ESI): Calcd for $C_8H_{10}BrN_2O$ $[M+H]^+$: 228.9977, Found: 228.9973. Mp: 138-140 °C.

N'-(3-(trifluoromethyl)phenyl) acetohydrazide (1q)



Following the general procedure, this compound was isolated as a white solid (1.7 g, 60% yield). NMR showed the compounds to be a mixture of two rotamers (ratio: approx 10/1). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.76 (bs, 1H), 8.15 (bs, 1H), 7.33-7.37 (t, 1H), 6.94-7.01 (m, 3H), 1.92 and 1.86 (2×s, 3H).^{13}C NMR (101 MHz, DMSO-d_6): δ169.2, 150.0, 129.8, 115.5, 114.4，114.3，107.7, 107.7, 20.5. ^{19}F NMR (DMSO-d_6, 376 MHz): δ -61.38 (s). IR (cm^{-1}): ν 3305, 3029, 1655, 1616, 1344, 1123, 1068, 791, 677. HRMS (ESI): Calcd for $C_9H_{10}F_3N_2O$ $[M+H]^+$: 219.0745, Found: 219.0742. Mp: 134-136 °C.

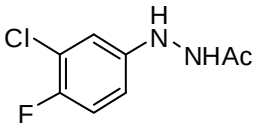
N'-(3-chloro-4-methylphenyl) acetohydrazide (1t)



Following the general procedure, this compound was isolated as a white solid (1.8 g, 70% yield). NMR showed the compounds to be a mixture of two rotamers (ratio: approx 9/1). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.64 (bs, 1H), 7.78 (bs, 1H), 7.06-7.08 (d, 1H), 6.70 (s, 1H), 6.58-6.60 (d, 1H), 2.18(s, 3H), 1.90 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6): δ169.1, 148.9, 133.3, 131.2, 124.3, 111.99, 111.2, 20.6, 18.5. IR (cm^{-1}): ν 3302, 3054, 3027, 1643, 1503, 1368, 1291, 1039, 811,

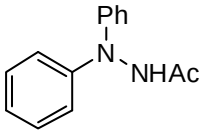
696. HRMS (ESI): Calcd for $C_9H_{12}ClN_2O$ $[M+H]^+$: 199.0638, Found: 199.0631. Mp: 125-127 °C.

N'-(3-chloro-4-fluorophenyl) acetohydrazide (1u)



Following the general procedure, this compound was isolated as a white solid (1.61 g, 80% yield). NMR showed the compounds to be a mixture of two rotamers (ratio: approx 10/1). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.71 (bs, 1H), 7.90 (bs, 1H), 7.15-7.20 (t, 1H), 6.78-6.79 (t, 1H), 6.66-6.68 (m, 1H), 1.91 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6): δ169.2, 150.5 (d, J_{C-F} = 235.9 Hz), 146.8, 119.3 (d, J_{C-F} = 90.5 Hz), 116.8 (d, J_{C-F} = 21.8 Hz), 112.7, 112.0 (d, J_{C-F} = 6.6 Hz), 20.5. ^{19}F NMR (DMSO-d_6, 376 MHz): δ -130.68 (s). IR (cm^{-1}): ν 3294, 3011, 1645, 1602, 1496, 1373, 1214, 1050, 858. 707. HRMS (ESI): Calcd for $C_8H_9ClFN_2O$ $[M+H]^+$: 203.0387, Found: 203.0379. Mp: 140-142 °C.

N', N'-diphenylacetohydrazide (1v)



Following the general procedure, this compound was isolated as a white solid (1.13 g, 49% yield). NMR showed the compounds to be a mixture of two rotamers (ratio: approx 6/1). ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.55 (bs, 1H), 7.26-7.37 (m, 4H), 7.06-7.11 (t, 5H), 6.95-6.99 (t, 2H), 1.94 and 1.90 (2×s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6): δ174.5, 168.7, 146.2, 145.8, 129.3, 129.0, 122.9, 122.0, 119.0, 118.6, 20.5, 19.5. IR (cm^{-1}): ν 3269, 3034, 1671, 1526, 1495, 1367, 746, 698, 691, 628. HRMS (ESI): Calcd for $C_8H_9ClFN_2O$ $[M+H]^+$: 227.1184, Found: 227.1179. Mp: 192-194 °C.

3. Experimental Procedure and Characterization of products

3.1 General Procedure: Rh(III)-catalyzed cyclization of 2-acetyl-1-arylhydrazine with diazo compounds.

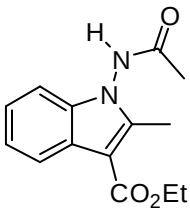
A mixture of 2-acetyl-1-arylhydrazine 1 (0.6 mmol, 1.2 equiv), $[Cp^*RhCl_2]_2$ (7.725 mg, 0.0125 mmol, 2.5 mol%) and CsOAc (24 mg, 0.125 mmol, 25 mol%) were weighted in a sealed tube equip with a stir bar. Water (3 mL), HOAc (15 mg, 0.25 mmol, 50 mol%) and diazo compounds 2 (0.5 mmol, 1 equiv) were added successively. The mixture were sealed

and stirred at 100 °C for 1 h under Ar. Afterwards, it was cooled to room temperature, water was filtered off under reduced pressure and the solid residue was washed with water thoroughly and dried. It is generally enough pure for the white solid. If the products contain some colours, they can be further purified by a short column chromatography on silica gel using EtOAc/petroleum ether = 1/1 as eluent to afford the desired pure products.

3.2 General procedure for the gram scale preparation of ethyl 1-acetamido-2-methyl-1H-indole-3-carboxylate (3aa)

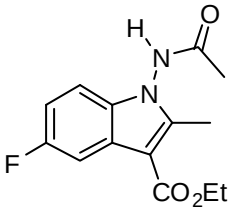
A mixture of 2-acetyl-1-phenylhydrazine **1a** (901.08 mg, 6 mmol, 1.2 equiv), $[Cp^*RhCl_2]_2$ (77.25 mg, 0.125 mmol, 2.5 mol%) and CsOAc (240 mg, 1.25 mmol, 25 mol%) were weighted in a 100 mL sealed tube equip with a stir bar. Water (30 mL), HOAc (150 mg, 2.5 mmol, 50 mol%) and ethyl diazoacetoacetate **2a** (780 mg, 5 mmol, 1 equiv) were added successively. The mixture were sealed and stirred at 100 °C for 1 h under Ar. Afterwards, it was cooled to room temperature, water was filtered off under reduced pressure and the solid residue was washed with water thoroughly, dried to afford the spectroscopically pure product **3aa** 1.16g (89% yield).

Ethyl 1-acetamido-2-methyl-1H-indole-3-carboxylate (3aa)



Following the general procedure, the titled compound was isolated as a white solid (118 mg, 91% yield). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.27 (s, 1H), 7.98-8.00 (m, 1H), 7.28-7.30 (q, 1H), 7.20-7.23 (m, 2H), 4.28-4.34 (q, 2H), 2.52 (s, 3H), 2.16 (s, 3H), 1.34-1.38 (t, 3H). ^{13}C NMR (DMSO-d_6, 101 MHz): δ 169.1, 164.6, 145.2, 135.2, 123.8, 122.4, 122.0, 120.5, 109.1, 101.8, 59.1, 20.4, 14.36, 10.7. IR (cm^{-1}): ν 3252, 2989, 1701, 1672, 1556, 1408, 1214, 1166, 733, 550. HRMS (ESI): Calcd for $C_{14}H_{17}N_2O_3$ $[M+H]^+$: 261.1239, Found: 261.1239. Mp: 177-179 °C.

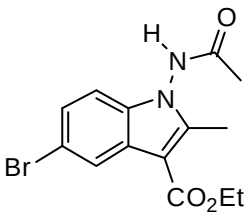
Ethyl 1-acetamido-5-fluoro-2-methyl-1H-indole-3-carboxylate (3ba)



Following the general procedure, the titled compound was isolated as a white solid (125 mg, 90% yield). ^{1}H NMR (DMSO-d_6, 400 MHz): δ

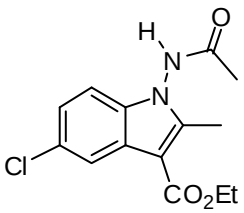
11.31 (s, 1H), 7.65-7.68 (d, J = 9.8 Hz, 1H), 7.31-7.34 (q, 1H), 7..5-7.10 (t, 1H), 4.29-4.34 (q, 2H), 2.52 (s, 3H), 2.16 (s, 3H), 1.34-1.37 (t, 3H), ^{13}C NMR (DMSO-d_6, 101 MHz): δ 169.2, 164.3, 158.7 (d, J_{C-F} = 234.4 Hz), 146.9, 131.8, 124.5 (d, J_{C-F} = 11.0 Hz), 110.6 (d, J_{C-F} = 3.4 Hz), 110.4 (d, J_{C-F} = 12.4 Hz), 105.7 (d, J_{C-F} = 25.4 Hz), 102.0 (d, J_{C-F} = 3.6 Hz), 59.3, 20.4, 14.3, 10.9. ^{19}F NMR (DMSO-d_6, 376 MHz): δ -121.33 (s). IR (cm^{-1}): ν 3255, 2991, 1701, 1672, 1550, 1476, 1257, 1167, 864, 781. HRMS (ESI): Calcd for $C_{14}H_{16}FN_2O_3$ $[M+H]^+$: 279.1145, Found: 279.1145. Mp: 198-200 °C.

Ethyl 1-acetamido-5-bromo-2-methyl-1H-indole-3-carboxylate (3ca)



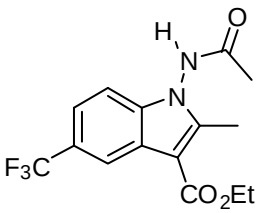
Following the general procedure, the titled compound was isolated as a beige solid (137 mg, 81% yield). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.34 (s, 1H), 8.11 (s, 1H), 7.36-7.38 (d, J = 8.6 Hz, 1H), 7.29-7.32 (d, J = 8.6 Hz, 1H), 4.30-4.35 (q, 2H), 2.52 (s, 3H), 2.16 (s, 3H), 1.34-1.38 (t, 3H), ^{13}C NMR (DMSO-d_6, 101 MHz): δ 169.2, 164.2, 146.6, 134.1, 125.6, 125.1, 122.7, 114.8, 111.4, 101.5, 59.4, 20.4, 14.4, 10.8. IR (cm^{-1}): ν 3190, 3012, 1701, 1691, 1683, 1539, 1456, 1269, 1176, 800, 782. HRMS (ESI): Calcd for $C_{14}H_{16}BrN_2O_3$ $[M+H]^+$: 339.0344, Found: 339.0344. Mp: 203-205 °C.

Ethyl 1-acetamido-5-chloro-2-methyl-1H-indole-3-carboxylate (3da)



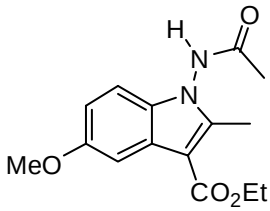
Following the general procedure, the titled compound was isolated as a white solid (122 mg, 82% yield). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.34 (s, 1H), 7.96 (s, 1H), 7.36-7.40 (d, J = 8.6 Hz, 1H), 7.24-7.26 (d, J = 8.6 Hz, 1H), 4.30-4.35 (q, 2H), 2.52 (s, 3H), 2.16 (s, 3H), 1.34-1.37 (t, 3H), ^{13}C NMR (DMSO-d_6, 101 MHz): δ 169.2, 164.2, 146.8, 133.9, 126.7, 124.9, 122.5, 119.7, 110.9, 101.6, 59.4, 20.4, 14.4, 10.8. IR (cm^{-1}): ν 3235, 2991, 1696, 1671, 1565, 1329, 1110, 904, 807, 689. HRMS (ESI): Calcd for $C_{14}H_{16}ClN_2O_3$ $[M+H]^+$: 295.0849, Found: 295.0847. Mp: 185-187 °C.

Ethyl 1-acetamido-2-methyl-5-(trifluoromethyl)-1H-indole-3-carboxylate (3ea)



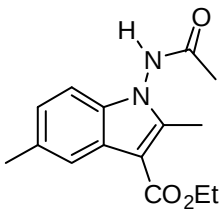
Following the general procedure, the titled compound was isolated as a yellow solid (125 mg, 76% yield). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.45 (s, 1H), 8.32 (s, 1H), 7.54 (s, 2H), 4.32-4.37 (q, 2H), 2.56 (s, 3H), 2.18 (s, 3H), 1.35-1.38 (t, 3H). ^{13}C NMR (DMSO-d_6, 101 MHz): δ 169.2, 164.1, 147.6, 137.0, 126.4, 123.3 (q, J_{C-F} = 92.3 Hz), 119.2, 117.7, 117.7, 110.3, 102.6, 59.6, 20.4, 14.2, 10.8. ^{19}F NMR (DMSO-d_6, 376 MHz): δ -59.09 (s). IR (cm^{-1}): ν 3193, 3018, 2978, 2935, 1565, 1691, 1540, 1457, 1270, 804. HRMS (ESI): Calcd for $C_{15}H_{16}F_3N_2O_3$ $[M+H]^+$: 329.1113, Found: 329.1112. Mp: 165-167 °C.

Ethyl 1-acetamido-5-methoxy-2-methyl-1H-indole-3-carboxylate (3fa)



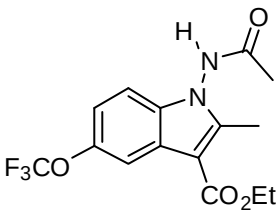
Following the general procedure, the titled compound was isolated as a white solid (117 mg, 81% yield). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.23 (s, 1H), 7.50-7.51 (d, J = 2.4 Hz, 1H), 7.19-7.21 (d, J = 8.8 Hz, 1H), 6.84-6.86 (q, J = 11.3 Hz, 1H), 4.28-4.33 (q, 2H), 2.51 (s, 3H), 2.15 (s, 3H), 1.35-1.39 (t, 3H). ^{13}C NMR (DMSO-d_6, 101 MHz): δ 169.1, 164.7, 155.5, 145.3, 130.2, 124.7, 111.6, 109.9, 103.0, 101.5, 59.1, 55.3, 20.4, 14.4, 10.9. IR (cm^{-1}): ν 3260, 2981, 1695, 1670, 1478, 1202, 1171, 669. HRMS (ESI): Calcd for $C_{15}H_{19}N_2O_4$ $[M+H]^+$: 291.1345, Found: 291.1344. Mp: 200-202 °C.

Ethyl 1-acetamido-2,5-dimethyl-1H-indole-3-carboxylate (3ga)



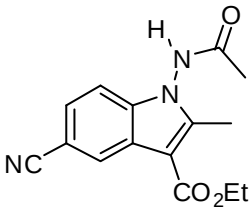
Following the general procedure, the titled compound was isolated as a white solid (114 mg, 83% yield). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.22 (s, 1H), 7.79 (s, 1H), 7.16-7.18 (d, J = 8.3 Hz, 1H), 7.02-7.04 (d, J = 8.2 Hz, 1H), 4.28-4.33 (q, 2H), 2.41 (s, 3H), 2.15 (s, 3H), 1.34-1.38 (t, 3H). ^{13}C NMR (DMSO-d_6, 101 MHz): δ 169.1, 164.7, 145.1, 133.6, 130.81, 124.1, 123.8, 120.4, 108.8, 101.4, 59.1, 21.3, 20.4, 14.4, 10.8. IR (cm^{-1}): ν 3231, 2980, 1691, 1651, 1541, 1466, 1411, 1375, 1267, 1063, 801, 783. HRMS (ESI): Calcd for $C_{15}H_{19}N_2O_3$ $[M+H]^+$: 275.1396, Found: 275.1396. Mp: 168-170 °C.

Ethyl 1-acetamido-2-methyl-5-(trifluoromethoxy)-1H-indole-3-carboxylate (3ha)



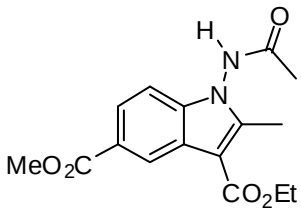
Following the general procedure, prolong reaction time to 2h, the titled compound was isolated as a white solid (151 mg, 87% yield). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.38 (s, 1H), 7.90 (s, 1H), 7.42-7.44 (d, J = 8.8 Hz, 1H), 7.21-7.23 (d, J = 8.7 Hz, 1H), 4.30-4.35 (q, 2H), 2.54 (s, 3H), 2.18 (s, 3H), 1.34-1.38 (t, 3H). ^{13}C NMR (DMSO-d_6, 101MHz): δ 169.2, 164.1, 147.3, 144.0, 133.7, 124.2, 120.3 ($J_{C\text{-}F}$ = 254.7 Hz), 116.1, 112.6, 110.7, 102.2, 59.5, 20.4, 14.2, 10.9. ^{19}F NMR (DMSO-d_6, 376 MHz): δ -56.98 (s). IR (cm^{-1}): ν 3245, 2982, 1705, 1674, 1559, 1470, 1372, 1261, 1174, 1154, 789. HRMS (ESI): Calcd for $C_{15}H_{16}F_3N_2O_4$ $[M+H]^+$: 345.1062, Found: 345.1063. Mp: 155-157 °C.

Ethyl 1-acetamido-5-cyano-2-methyl-1H-indole-3-carboxylate (3ia)



Following the general procedure, the titled compound was isolated as a white solid (109 mg, 76% yield). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.46 (s, 1H), 8.36 (s, 1H), 7.63-7.65 (d, J = 8.4 Hz, 1H), 7.53-7.55 (d, J = 8.4 Hz, 1H), 4.33-4.38 (q, 2H), 2.56 (s, 3H), 2.18 (s, 3H), 1.36-1.39 (t, 3H), ^{13}C NMR (DMSO-d_6, 101 MHz): δ 169.2, 163.9, 148.0, 137.2, 125.8, 125.4, 123.6, 120.0, 110.8, 104.5, 102.5, 59.7, 20.4, 14.3, 10.8. IR (cm^{-1}): ν 3290, 2987, 2224, 1696, 1458, 1247, 1173, 1128, 817, 668. HRMS (ESI): Calcd for $C_{15}H_{16}N_3O_3$ $[M+H]^+$: 286.1192, Found: 286.1192. Mp: 182-184 °C.

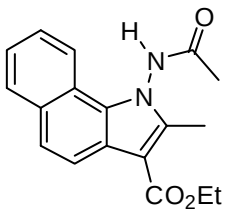
3-ethyl 5-methyl 1-acetamido-2-methyl-1H-indole-3,5-dicarboxylate (3ja)



Following the general procedure, the solid residue was purified by a short column chromatography using EtOAc/petroleum ether = 1/10 ~ 1/1 (v/v) as eluent. The titled compound was isolated as a white solid (140 mg, 88% yield). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.41 (s, 1H), 8.70 (s, 1H), 7.84-7.86 (d, J = 8.5 Hz, 1H), 7.41-7.43 (d, J = 8.6 Hz, 1H), 4.32-4.37 (q, 2H), 2.54 (s, 3H), 2.18 (s, 3H), 1.36-1.39 (t, 3H). ^{13}C NMR (DMSO-d_6, 101 MHz): δ 169.2, 166.8, 164.2, 147.1, 137.9, 123.6, 123.5, 122.7, 109.4, 102.9, 59.5, 51.9, 20.4, 14.3, 10.9.

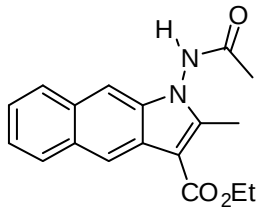
(One signal missing due to overlap). IR (cm^{-1}): ν 3242, 2986, 1716, 1696, 1677, 1556, 1433, 1170, 765. HRMS (ESI): Calcd for $C_{16}H_{19}N_2O_5$ $[M+H]^+$: 319.1294, Found: 319.1295. Mp: 186-188 °C.

Ethyl 1-acetamido-2-methyl-1H-benzo[g]indole-3-carboxylate (3ka)



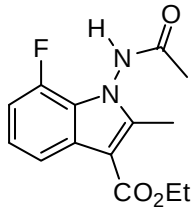
Following the general procedure, prolong reaction time to 12h, the titled compound was isolated as a white solid (17 mg, 11% yield). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.86 (s, 1H), 8.49-8.51 (d, *J* = 8.5 Hz, 1H), 8.20-8.22 (d, *J* = 8.7 Hz, 1H), 7.99-8.01 (d, *J* = 8.1 Hz, 1H), 7.69-7.71 (d, *J* = 8.8 Hz, 1H), 7.57-7.60 (t, 1h), 7.46-7.50 (t, 1H), 4.33-4.39 (q, 2H), 2.58 (s, 3H), 2.29 (s, 3H), 1.38-1.41 (t, 3H). ^{13}C NMR (DMSO-d_6, 101 MHz): δ 169.1, 164.7, 143.7, 130.6, 128.8, 127.9, 126.1, 124.2, 122.8, 121.0, 120.9, 120.0, 119.6, 103.4, 59.4, 20.6, 14.4, 10.7. IR (cm^{-1}): ν 3249, 2976, 1701, 1668, 1553, 1521, 1403, 8110, 745. HRMS (ESI): Calcd for $C_{18}H_{19}N_2O_3$ $[M+H]^+$: 311.1396 ， Found: 311.1392 . Mp: 196-198 °C.

Ethyl 1-acetamido-2-methyl-1H-benzo[f]indole-3-carboxylate (3la)



Following the general procedure, the solid residue was purified by a short column chromatography using EtOAc/petroleum ether = 1/10 to 1/1 (v/v) as eluent. The titled compound was isolated as a white solid (121 mg, 78% yield). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.37 (s, 1H), 8.53 (s, 1H), 7.98-8.04 (q, 2H), 7.81 (s, 1H), 7.38-7.46 (m, 2H), 4.36-4.41 (q, 2H), 2.62 (s, 3H), 2.22 (s, 3H), 1.40-1.44 (t, 3H), ^{13}C NMR (DMSO-d_6, 101 MHz): δ 169.3, 164.6, 150.4, 135.8, 129.8, 128.2, 127.3, 124.8, 124.4, 123.6, 118.3, 104.7, 101.0, 59.3, 20.53, 14.5, 11.3. IR (cm^{-1}): ν 3246, 2980, 1694, 16718, 1566, 1262, 1174, 1124, 737. HRMS (ESI): Calcd for $C_{18}H_{19}N_2O_3$ $[M+H]^+$: 311.1396, Found: 311.1395. Mp: 179-181 °C.

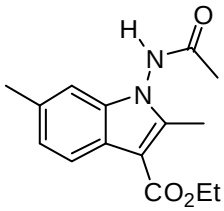
Ethyl 1-acetamido-7-fluoro-2-methyl-1H-indole-3-carboxylate (3na)



Following the general procedure, prolong reaction time to 2 h, the titled compound was isolated as a white solid (115 mg, 83% yield). ^{1}H NMR

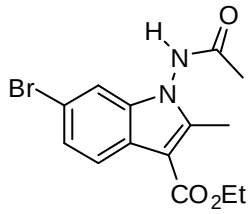
(DMSO-d_6, 400 MHz): δ 11.46 (s, 1H), 7.81-7.83 (s, 1H), 7.13-7.18 (m, 1H), 7.00-7.05 (q, 1H), 4.29-4.34 (q, 2H), 2.51 (s, 3H), 2.11 (s, 3H), 1.34-1.37 (t, 3H). ^{13}C NMR (DMSO-d_6, 101 MHz): δ 169.4, 164.3, 148.2 (d, J_{C-F} = 244.0 Hz), 146.6, 127.7, 122.8 (d, J_{C-F} = 8.5 Hz), 122.3 (d, J_{C-F} = 6.5 Hz), 116.8 (d, J_{C-F} = 3.4 Hz), 108.6 (d, J_{C-F} = 16.8 Hz), 102.8, 59.4, 20.2, 14.3, 10.5. ^{19}F NMR (DMSO-d_6, 376 MHz): δ -140.30 (s) IR (cm^{-1}): ν 3252, 2988, 1703, 1672, 1582, 1258, 1244, 1194, 790, 725, 553. HRMS (ESI): Calcd for $C_{14}H_{16}FN_2O_3$ $[M+H]^+$: 279.1145, Found: 279.1138. Mp: 183-185 °C.

Ethyl 1-acetamido-2,6-dimethyl-1H-indole-3-carboxylate (3oa)



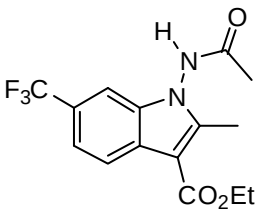
Following the general procedure, the titled compound was isolated as a white solid (114 mg, 83% yield). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.21 (s, 1H), 7.84-7.86 (d, J = 7.8Hz, 1H), 7.08 (s, 1H), 7.02-7.04 (d, J = 8.2 Hz, 1H), 4.27-4.32 (q, 2H), 2.40 (s, 3H), 2.16 (s, 3H), 1.33-1.37 (t, 3H). ^{13}C NMR (DMSO-d_6, 101 MHz): δ 169.1, 164.7, 144.6, 135.6, 131.9, 123.6, 121.7, 120.3, 108.9, 101.7, 59.1, 21.2, 20.4, 14.4, 10.7. IR (cm^{-1}): ν 3247, 2990, 2912, 1704, 1674, 1557, 1406, 1192, 1130, 807, 553. HRMS (ESI): Calcd for $C_{15}H_{19}N_2O_3$ $[M+H]^+$: 275.1396, Found: 275.1393. Mp: 152-154 °C.

Ethyl 1-acetamido-6-bromo-2-methyl-1H-indole-3-carboxylate (3pa)



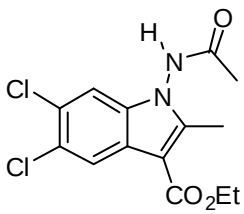
Following the general procedure, the solid residue was purified by a short column chromatography using EtOAc/petroleum ether = 1/10 ~ 1/1 (v/v) as eluent. The titled compound was isolated as a beige solid (144 mg, 85% yield). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.29 (s, 1H), 7.9-7.92 (d, J = 8.5 Hz, 1H), 7.57 (s, 1H), 7.35-7.37 (dd, J = 1.6 Hz, 1.7 Hz, 1H), 4.28-4.34 (q, 2H), 2.51 (s, 3H), 2.17 (s, 3H), 1.33-1.37 (t, 3H). ^{13}C NMR (DMSO-d_6, 101 MHz): δ 169.3, 164.3, 146.2, 136.2, 125.0, 122.9, 122.3, 115.3, 112.04, 102.1, 59.4, 20.5, 14.4, 10.8. IR (cm^{-1}): ν 3244, 2929, 1701, 1672, 1554, 1466, 1261, 809, 564. HRMS (ESI): Calcd for $C_{14}H_{16}BrN_2O_3$ $[M+H]^+$: 339.0344, Found: 339.0343. Mp: 213-215 °C.

Ethyl 1-acetamido-2-methyl-6-(trifluoromethyl)-1H-indole-3-carboxylate (3qa)



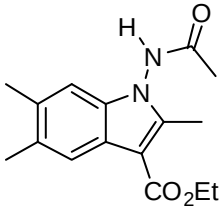
Following the general procedure, the titled compound was isolated as a yellow solid (121 mg, 74% yield). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.41 (s, 1H), 8.17-8.19 (d, J = 8.3 Hz, 1H), 7.71 (s, 1H), 7.53-7.55 (d, J = 8.4 Hz, 1H), 4.31-4.37 (q, 2H), 2.56 (s, 3H), 2.19 (s, 3H), 1.35-1.39 (t, 3H). ^{13}C NMR (DMSO-d_6, 101 MHz): δ 169.4, 164.1, 148.4, 134.5, 126.6, 123.1 (q, $J_{C\text{-}F}$ = 90.9 Hz), 121.4, 118.5, 106.7, 106.7, 102.3, 59.5, 20.5, 14.3, 10.9. ^{19}F NMR (DMSO-d_6, 376 MHz): δ -59.06 (s). IR (cm^{-1}): ν 3246, 2989, 1704, 1676, 1557, 1334, 1540, 1152, 1104, 825. HRMS (ESI): Calcd for $C_{15}H_{16}F_3N_2O_3$ [M+H]$^+$: 329.1113, Found: 329.1114. Mp: 220-222 ^{o}C.

Ethyl 1-acetamido-5,6-dichloro-2-methyl-1H-indole-3-carboxylate (3ra)



Following the general procedure, the titled compound was isolated as a white solid (149 mg, 90% yield). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.36 (s, 1H), 8.10 (s, 1H), 7.73 (s, 1H), 4.30-4.35 (q, 2H), 2.52 (s, 3H), 2.16 (s, 3H), 1.34-1.37 (t, 3H). ^{13}C NMR (DMSO-d_6, 101 MHz): δ 169.8, 164.4, 148.2, 134.9, 125.8, 125.3, 124.1, 121.9, 111.8, 102.2, 60.1, 20.0, 14.8, 11.4. IR (cm^{-1}): ν 3229, 2982, 2910, 1704, 1672, 1552, 1457, 1171, 1062, 878, 632. HRMS (ESI): Calcd for $C_{14}H_{15}Cl_2N_2O_3$ [M+H]$^+$: 329.0460, Found: 329.0456. Mp: 229-231 ^{o}C.

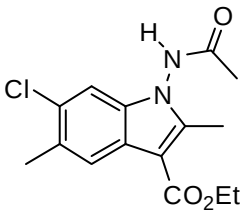
Ethyl 1-acetamido-2,5,6-trimethyl-1H-indole-3-carboxylate (3sa)



Following the general procedure, prolong reaction time to 2h, the solid residue was purified by a short column chromatography using EtOAc/petroleum ether = 1/2~1/1 (v/v) as eluent. The titled compound was obtained as a white solid (104 mg, 72% yield). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.20 (s, 1H), 7.76 (s, 1H), 7.07 (s, 1H), 4.29-4.34 (q, 2H), 2.53 (s, 3H), 2.33 (s, 6H), 2.17 (s, 3H), 1.36-1.39 (t, 3H). ^{13}C NMR (DMSO-d_6, 101 MHz): δ 169.1, 164.8, 144.1, 134.1, 131.1, 130.2, 122.1, 120.8, 109.3, 101.3, 59.0, 20.4, 19.9, 19.9, 14.4, 11.7. IR (cm^{-1}): ν

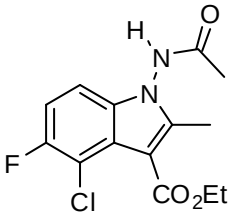
3246, 2979, 2938, 1696, 1674, 1556, 1189, 1126, 579. HRMS (ESI): Calcd for $C_{16}H_{21}N_2O_3$ $[M+H]^+$: 289.1152, Found: 289.1151. Mp: 167-169 °C.

Ethyl 1-acetamido-6-chloro-2,5-dimethyl-1H-indole-3-carboxylate (3ta)



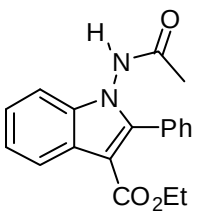
Following the general procedure, the titled compound was isolated as a white solid (131 mg, 85% yield). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.24 (s, 1H), 7.92 (s, 1H), 7.42 (s, 1H), 4.28-4.33 (q, 2H), 2.50 (s, 3H), 2.41 (s, 3H), 2.16 (s, 3H), 1.34-1.37 (t, 3H). ^{13}C NMR (DMSO-d_6, 101 MHz): δ 169.2, 164.3, 146.1, 134.4, 128.7, 128.2, 123.0, 109.4, 101.6, 59.3, 20.5, 20.1, 19.9, 14.4, 10.8. IR (cm^{-1}): ν 3247, 2990, 2912, 1704, 1674, 1557, 1406, 1192, 1130, 807, 553. HRMS (ESI): Calcd for $C_{15}H_{18}ClN_2O_3$ $[M+H]^+$:309.1006, Found: 309.1004. Mp: 226-228 °C.

Ethyl 1-acetamido-4-chloro-5-fluoro-2-methyl-1H-indole-3-carboxylate (3ua)



Following the general procedure, the titled compound was isolated as a white solid (115 mg, 73% yield). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.33 (s, 1H), 7.80-7.83 (d, J = 10.1 Hz, 1H), 7.65-7.66 (d, J = 6.3 Hz, 1H), 4.29-4.34 (q, 2H), 2.51 (s, 3H), 2.16 (s, 3H), 1.34-1.37 (t, 3H).^{13}C NMR (DMSO-d_6, 101 MHz): δ 169.3, 164.0, 154.7, 152.4, 147.6, 131.8, 123.0 (d, $J_{C\text{-}F}$ = 25.2 Hz), 114.9 (d, $J_{C\text{-}F}$ = 21.1 Hz), 107.1 (d, $J_{C\text{-}F}$ = 25.2 Hz), 102.1, 59.5, 20.5, 14.3, 10.9. ^{19}F NMR (DMSO-d_6, 376 MHz): δ -124.21 (s). IR (cm^{-1}): ν 3250, 2991, 1704, 1672, 1550, 1474, 1411, 1177, 864, 781, 555. HRMS (ESI): Calcd for $C_{14}H_{15}ClFN_2O_3$ $[M+H]^+$: 313.0755, Found: 313.0756. Mp: 179-181 °C.

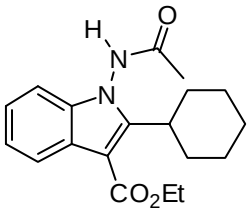
Ethyl 1-acetamido-2-phenyl-1H-indole-3-carboxylate (3ab)



Following the general procedure, the solid residue was purified by a short column chromatography using EtOAc/petroleum ether = 1/5~1/1 (v/v) as eluent. The titled compound was isolated as a white solid (114 mg, 71% yield). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.22 (s, 1H), 8.11-8.13 (q, 1H),

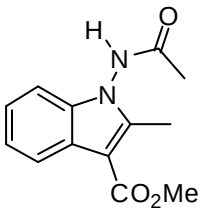
7.42-7.48 (m, 5H), 7.30-7.38 (m, 3H), 4.11-4.16 (q, 2H), 1.92 (s, 3H), 1.10-1.14 (t, 3H). ^{13}C NMR (DMSO-d_6, 101 MHz): δ 169.1, 163.8, 145.8, 135.7, 130.2, 129.3, 129.0, 127.5, 124.0, 123.5, 122.5, 121.2, 109.8, 103.2, 59.1, 20.2, 14.0. IR (cm^{-1}): ν 3254, 3024, 2984, 1681, 1458, 1409, 1185, 1042, 757. HRMS (ESI): Calcd for $C_{19}H_{19}N_2O_3$ $[M+H]^+$: 323.1396, Found: 323.1393. Mp: 178-180 °C.

Ethyl 1-acetamido-2-cyclohexyl-1H-indole-3-carboxylate (3ac)



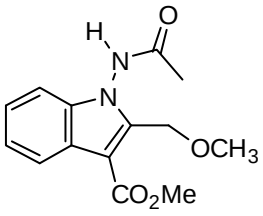
Following the general procedure, the titled compound was isolated as a white solid (115 mg, 70% yield). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.29 (s, 1H), 8.00-8.02 (t, 1H), 7.19-7.22 (t, 3H), 4.30-4.35 (q, 2H), 2.18 (s, 3H), 1.60-2.14 (m, 8H), 1.37-1.40 (t, 3H), 1.30-1.33 (m, 3H). ^{13}C NMR (DMSO-d_6, 101 MHz): δ 169.7, 165.0, 152.5, 135.7, 124.6, 123.1, 122.5, 121.6, 109.8, 102.0, 59.8, 36.1, 29.4 (d, J = 6.6 Hz), 26.9, 25.9, 21.0, 14.9. IR (cm^{-1}): ν 3254, 2928, 2853, 1695, 1683, 1529, 1257, 1160, 1114, 753. HRMS (ESI): Calcd for $C_{19}H_{25}N_2O_3$ $[M+H]^+$: 329.1865, Found: 329.1864. Mp: 196-198 °C.

Methyl 1-acetamido-2-methyl-1H-indole-3-carboxylate (3ad)



Following the general procedure, the titled compound was isolated as a white solid (112 mg, 91% yield). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.24 (s, 1H), 7.95-7.96 (d, J = 6.2 Hz, 1H), 7.18-7.26 (t, 3H), 3.81 (s, 3H), 2.50 (s, 3H), 2.13 (s, 3H). ^{13}C NMR (DMSO-d_6, 101 MHz): δ 169.6, 165.6, 145.8, 135.7, 124.3, 123.0, 122.5, 121.0, 109.6, 102.2, 51.2, 20.9, 11.3. IR (cm^{-1}): ν 3241, 2988, 2950, 1697, 1673, 1370, 1272, 1214, 1162, 784, 736. HRMS (ESI): Calcd for $C_{13}H_{15}N_2O_3$ $[M+H]^+$: 247.1083, Found: 247.1079. Mp: 160-162 °C.

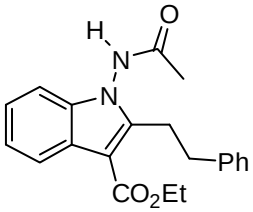
Methyl 1-acetamido-2-(methoxymethyl)-1H-indole-3-carboxylate (3ae)



Following the general procedure, reaction time was shortened to 0.5h, the titled compound was isolated as a white solid (132 mg, 95% yield). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.40 (s, 1H), 8.05-8.09 (t, 1H),

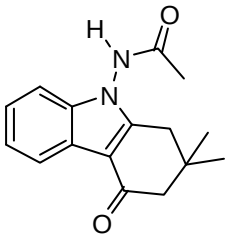
7.27-7.32 (q, 3H), 4.98-5.01 (d, J = 11.4 Hz, 1H), 4.54-4.57 (d, J = 11.6Hz, 1H), 3.88 (s, 3H), 3.28 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (DMSO-d_6, 101 MHz): δ 169.1, 164.6, 142.2, 135.7, 123.7, 123.3, 122.4, 121.4, 109.7, 104.2, 61.8, 57.6, 51.0, 20.4. IR (cm^{-1}): ν 3250, 2985, 1682, 1458, 1262, 1185, 1167, 750. HRMS (ESI): Calcd for $C_{14}H_{16}NaN_2O_4$ $[M+Na]^+$: 299.1008, Found: 299.1002. Mp: 199-201 °C.

Ethyl 1-acetamido-2-phenethyl-1H-indole-3-carboxylate (3af)



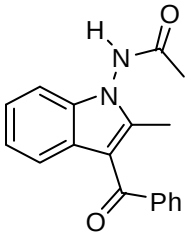
Following the general procedure, the titled compound was isolated as a white solid (130 mg, 74% yield). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.40 (s, 1H), 8.03-8.05 (t, 1H), 7.32-7.35 (t, 3H), 7.25-7.27 (d, 5H), 4.30-4.35 (q, 2H), 3.29-3.37 (td, 1H), 3.08-3.16 (td, 1H), 2.87-2.94 (td, 1H), 2.76-2.83 (td, 1H), 2.24 (s, 3H), 1.35-1.38 (t, 3H). ^{13}C NMR (DMSO-d_6, 101 MHz): δ 169.4, 164.4, 147.9, 140.9, 135.3, 128.5, 128.1, 126.1, 123.9, 122.8, 122.2, 120.8, 109.4, 101.8, 59.3, 34.5, 27.0, 20.5, 14.4. IR (cm^{-1}): ν 3259, 3059, 3024, 2982, 2926, 1701, 1669, 1551, 1255, 1213, 1173, 742, 696. HRMS (ESI): Calcd for $C_{21}H_{23}N_2O_3$ $[M+H]^+$: 351.1709, Found: 351.1705. Mp: 149-151 °C.

N-(2, 2-dimethyl-4-oxo-3, 4-dihydro-1H-carbazol-9(2H)-yl) acetamide (3ag)



Following the general procedure, the titled compound was isolated as a white solid (98 mg, 73% yield). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.33 (s, 1H), 7.98-8.00 (q, 1H), 7.21-7.34 (m, 3H), 2.61-2.78 (q, 2H), 2.38-2.41 (t, 2H), 2.16 (s, 3H), 1.09 (s, 6H). ^{13}C NMR (DMSO-d_6, 101 MHz): δ 192.3, 169.1, 151.7, 136.5, 123.0, 122.6, 122.0, 120.2, 109.4, 108.8, 51.7, 34.9, 34.2, 28.1, 28.0, 20.4. IR (cm^{-1}): ν 3213, 2956, 1717, 1624, 1524, 1456, 1241, 1173, 761, 550. HRMS (ESI): Calcd for $C_{16}H_{19}N_2O_2$ $[M+H]^+$: 271.1447, Found: 271.1445. Mp: 224-226 °C.

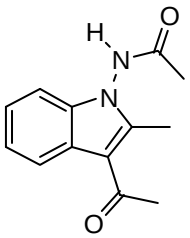
N-(3-benzoyl-2-methyl-1H-indol-1-yl) acetamide (3ah)



A mixture of 2-acetyl-1-phenylhydrazine **1a** (90.108 mg, 0.6 mmol, 1.2 equiv), $[Cp^*RhCl_2]_2$ (7.725 mg, 0.0125 mmol, 2.5 mol%) and

2-diazo-1-phenylbutane-1,3-dione **2h** (94.1 mg, 0.5 mmol, 1 equiv) and CsOAc (24 mg, 0.125 mmol, 25 mol%) were weighted in a sealed tube equip with a stir bar. Water (3 mL), HOAc (15 mg, 0.25 mmol, 50 mol%) were added successively. The mixture were sealed with a Teflon-lined cap and stirred at 100 °C for 1 h under Ar. Afterwards, it was cooled to room temperature, CH_2Cl_2 (10mL) was added to the tube and it was shaked vigorously. The organic layer was separated, the aqueous layer was extracted by CH_2Cl_2 (10 mL) once. The combined organic extracts were dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The resulting solid was purified by a short column chromatography on silica gel (eluent: EtOAc/petroleum ether = 1:1 (v/v)). The titled compound was isolated as a beige solid (70 mg, 48% yield). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.32 (s, 1H), 7.11-7.64 (m, 9H), 2.24 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (DMSO-d_6, 101 MHz): δ 191.7, 169.3, 144.7, 140.9, 135.3, 131.7, 128.5, 128.2, 124.3, 122.7, 122.0, 120.1, 111.2, 109.2, 20.4, 11.4. IR (cm^{-1}): ν 3221, 3018, 1713, 1622, 1521, 1385, 907, 748, 725. HRMS (ESI): Calcd for $C_{18}H_{17}N_2O_2$ $[M+H]^+$: 293.1290, Found: 293.1285. Mp: 194-196 °C.

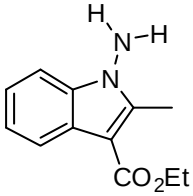
N-(3-acetyl-2-methyl-1H-indol-1-yl) acetamide (3ah)



Following the general procedure, the resulting solid was purified by a short column chromatography on silica gel (eluent: EtOAc/petroleum ether = 2:1 (v/v)). The titled compound was isolated as a white solid (83 mg, 72% yield). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.30 (s, 1H), 8.08 (s, 1H), 7.23-7.29 (d, *J* = 25.8 Hz, 3H), 2.58 (s, 3H), 2.54 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (DMSO-d_6, 101 MHz): δ 193.4, 169.1, 144.6, 135.2, 123.8, 122.5, 122.3, 120.7, 112.1, 109.2, 31.2, 20.4, 11.6. IR (cm^{-1}): ν 3506, 1687, 1626, 1412, 1400, 1276, 1165, 775. HRMS (ESI): Calcd for $C_{13}H_{15}N_2O_2$ $[M+H]^+$: 231.1134, Found: 231.1132. Mp: 100-102 °C.

3.3 General procedure for the deprotected reaction of 3aa[9]

Ethyl 1-amino-2-methyl-1H-indole-3-carboxylate

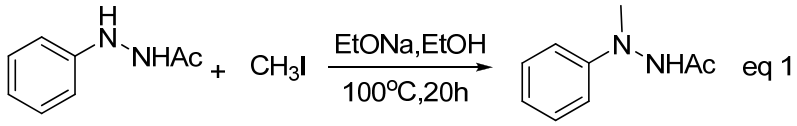


A 25 mL Schlenk tube was charged with Ethyl 1-acetamido-2-methyl-1H-indole-3-carboxylate (**3aa**) (60.1 mg, 0.23 mmol, 1 equiv) and 4N HCl (1.0 mL) dissolved in CH_3OH (1.0 mL) was added

subsequently, the solution was sealed with a Teflon-lined cap and heated to reflux (in an 80 ^{o}C oil bath) for 3 h. After cooling to room temperature, the reaction was quenched by saturated aqueous solution of sodium bicarbonate (5 mL). Concentrated and the aqueous layer was extracted with CH_2Cl_2 until no obvious fluorescence of the aqueous phase was observed under a UV lamp. The combined organic extract was dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure to give the crude product. The crude product was purified by silica gel chromatography (eluting with EtOAc/petroleum ether = 1:2 (v/v)) to give the titled compound in 87% yield (43.5 mg) as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.09-8.11 (q, 1H), 7.30-7.33 (q, 1H), 7.22-7.26 (m, 2H), 4.36-4.41 (q, 2H), 4.32-4.33 (bs, 2H), 2.72(s, 3H), 1.43-1.46 (t, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 166.0, 146.4, 136.6, 124.6, 122.1, 122.0, 121.2, 108.2, 101.7, 59.4, 14.6, 11.2. HRMS (ESI): Calcd for $C_{12}H_{15}N_2O_2$ $[M+H]^+$: 219.1134, Found: 219.1132. Mp: 90-92 ^{o}C.

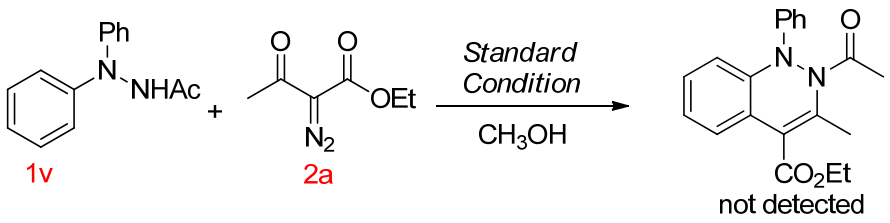
4. Mechanistic Studies:

1. Tested which N-H bond is more acidic.



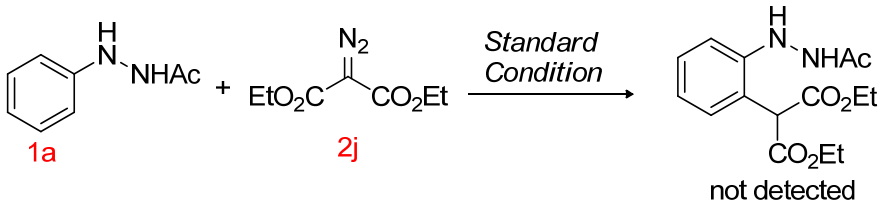
Following the same procedure described by Liang et al.,[10] freshly cut Na (58 mg, 2.5 mmol, 1 equiv) was added to absolute ethanol (1.5 mL) in a sealed tube to get a clear solution. N'-phenylacetohydrazide (375.4 mg, 2.5 mmol, 1 equiv) was added to the resulting solution, and then iodomethane was added. The resulting solution was sealed and kept in 100 ^{o}C in the dark for 20 h. The solution was concentrated and the residue was dissolved in CH_2Cl_2 (5 mL), and then washed with water, dried over anhydrous $MgSO_4$, filtered, and concentrated. Purification by chromatography on silica gel provided the product.

2. Tested whether six member ring can be formed.



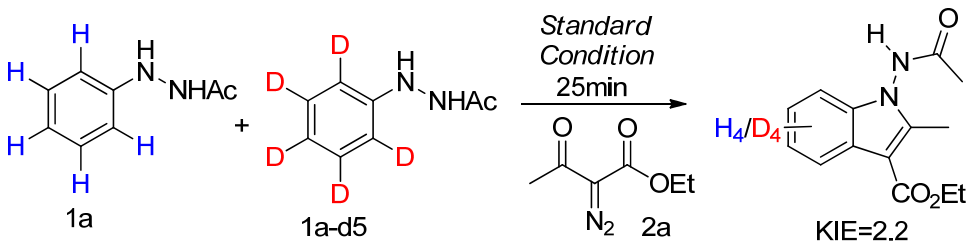
A mixture of N',N'-diphenylacetohydrazide **1v** (135.76 mg, 0.6 mmol, 1.2 equiv), $[Cp^*RhCl_2]_2$ (7.725 mg, 0.0125 mmol, 2.5 mol%) and CsOAc (24 mg, 0.125 mmol, 25 mol%) were weighted in a Schlenk tube equip with a stir bar. CH_3OH (3 mL), HOAc (15 mg, 0.25 mmol, 50 mol%) and ethyl diazoacetoacetate **2a** (78 mg, 0.5 mmol, 1 equiv) were added successively. The mixture were sealed with a Teflon-lined cap and stirred at 100 ^oC for 12 h under Ar. Afterwards, it was cooled to room temperature, no reaction was detected by TLC analysis, no product was obtained and the starting material **1v** was recovered which demonstrated that the six member ring is not favored.

3. Tested whether carbene inserted product can be formed.

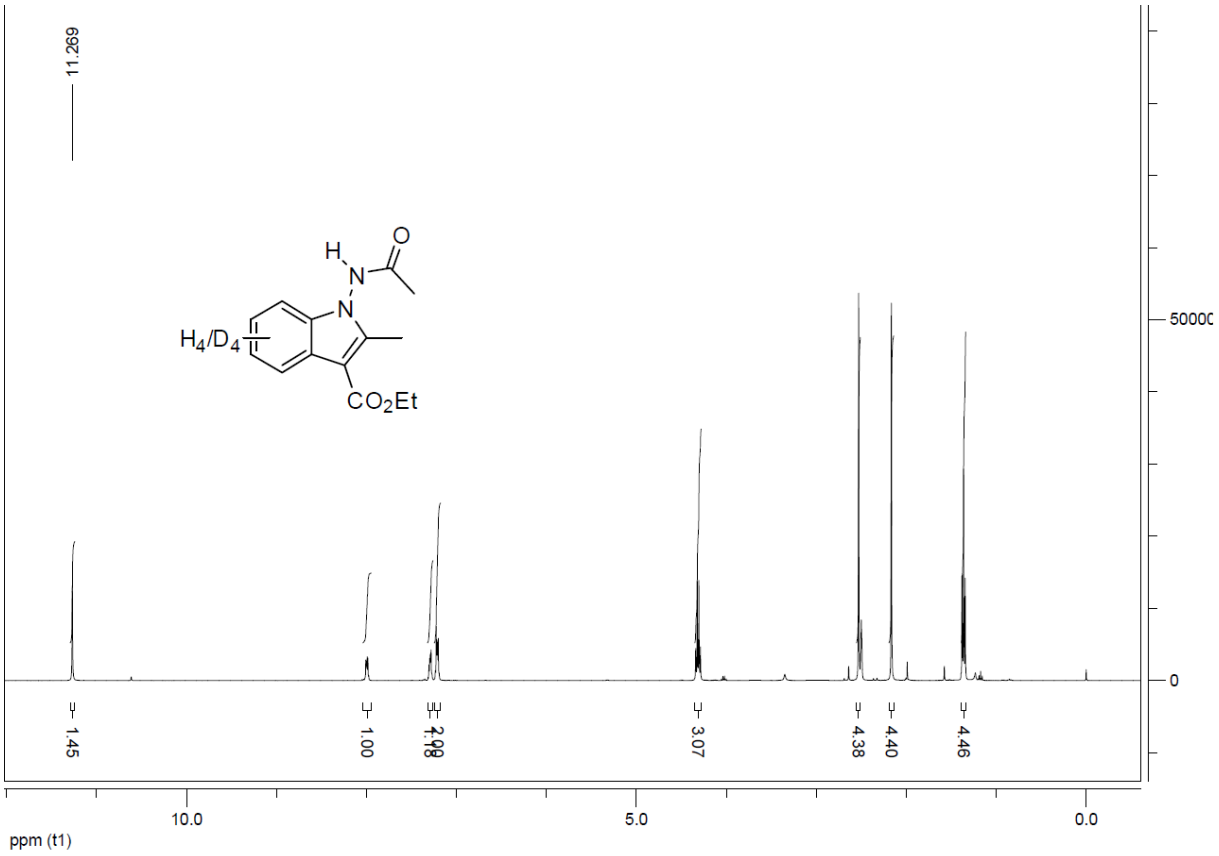


A mixture of 2-acetyl-1-phenylhydrazine **1a** (90.1 mg, 0.6 mmol, 1.2 equiv), $[Cp^*RhCl_2]_2$ (7.725 mg, 0.0125 mmol, 2.5 mol%) and CsOAc (24 mg, 0.125 mmol, 25 mol%) were weighted in a Schlenk tube equip with a stir bar. Water (3 mL), HOAc (15 mg, 0.25 mmol, 50 mol%) and diethyl 2-diazomalonate **2j** (93.1 mg, 0.5 mmol, 1 equiv) were added successively. The mixture were sealed and stirred at 100 ^oC for 1 h under Ar. Afterwards, it was cooled to room temperature, no reaction was detected by TLC analysis and the starting materials were recovered. This indicated that the condensation step may play a vital role in the reaction.

4. Intermolecular Kinetic Isotope Effect.

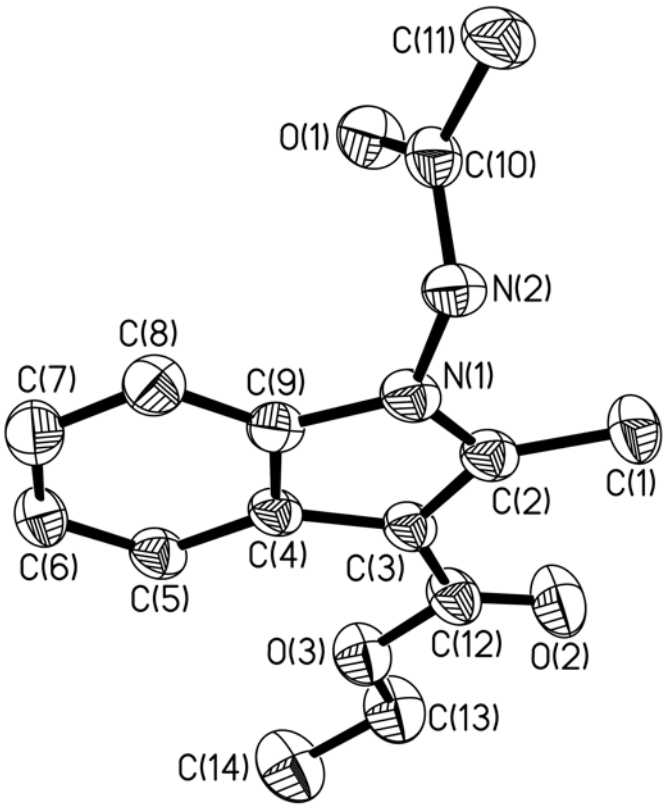


A mixture of 2-acetyl-1-phenylhydrazine **1a** (90.108 mg, 0.6 mmol, 1.2 equiv), 2-acetyl-1-(2, 3, 4, 5, 6-pentadeueriophenyl)hydrazine d^5-**1a** (93.108 mg, 0.6 mmol, 1.2 equiv), $[Cp^*RhCl_2]_2$ (7.725 mg, 0.0125 mmol, 2.5 mol%) and CsOAc (24 mg, 0.125 mmol, 25 mol%) were weighted in a Schlenk tube equip with a stir bar. Water (3 mL), HOAc (15 mg, 0.25 mmol, 50 mol%) and ethyl diazoacetoacetate (78 mg, 0.5 mmol, 1 equiv) were added successively. The mixture were sealed with a Teflon-lined cap and stirred at 100 °C for 25 min. Afterwards, it was cooled in ice bath and the water was filtered off immediately. The solid residue was washed with water thoroughly, and purified by passing through a short pad of silica gel with EtOAc as eluent. The ratio of **3aa**/d^4-**3aa** was indicated to be 2.2:1 by ^{1}H NMR (see below), thus the KIE value was determined to be 2.2.



5. X-ray Crystallography: Data collection was performed on a Rigaku Saturn 70 CCD diffractometer equipped with a rotating anode system by using graphite-monochromated $Mo_{K\alpha}$ radiation (ω-2θ scans). Semiempirical absorption corrections were applied for all complexes. The structures were solved by direct methods and refined by full-matrix least-squares. All calculations were done using the SHELXL-97 program system. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned idealized positions and were included in structure factor calculations.

CCDC- 983540 (**3aa**) contains the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



6. References:

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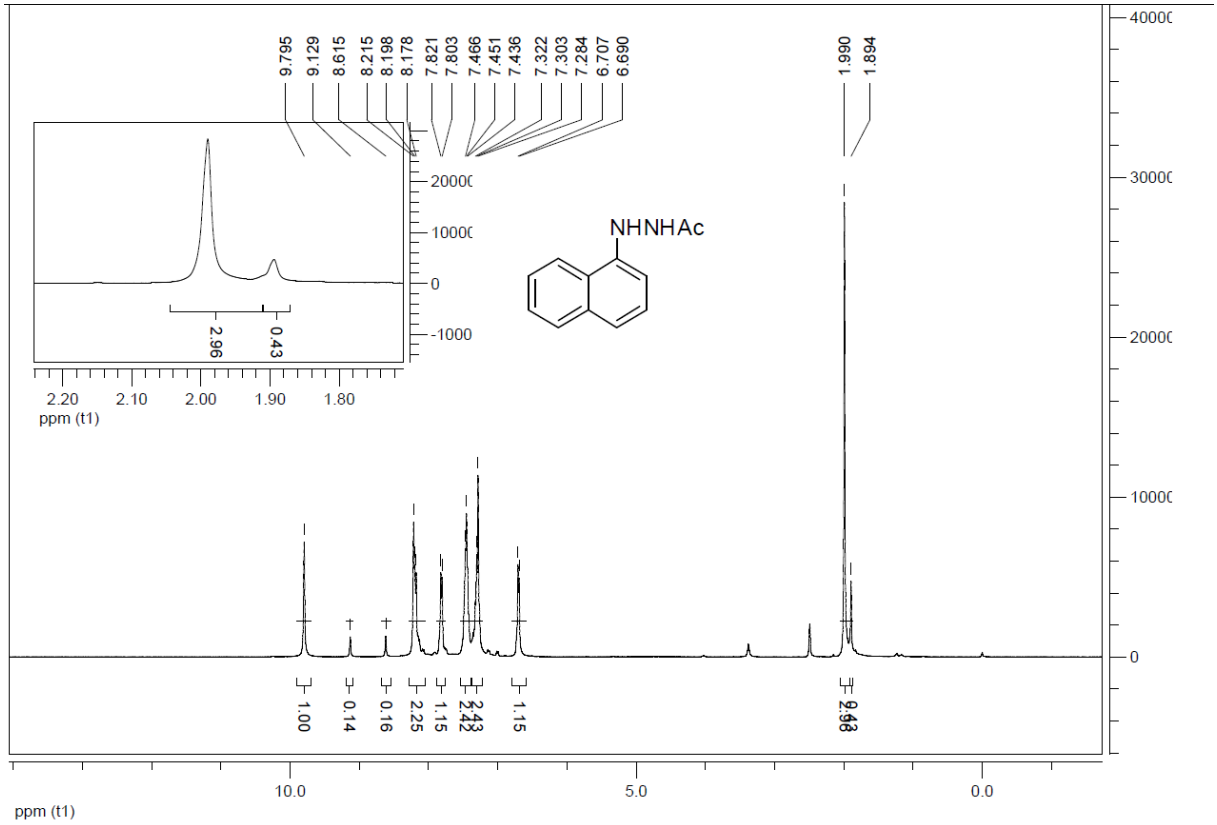
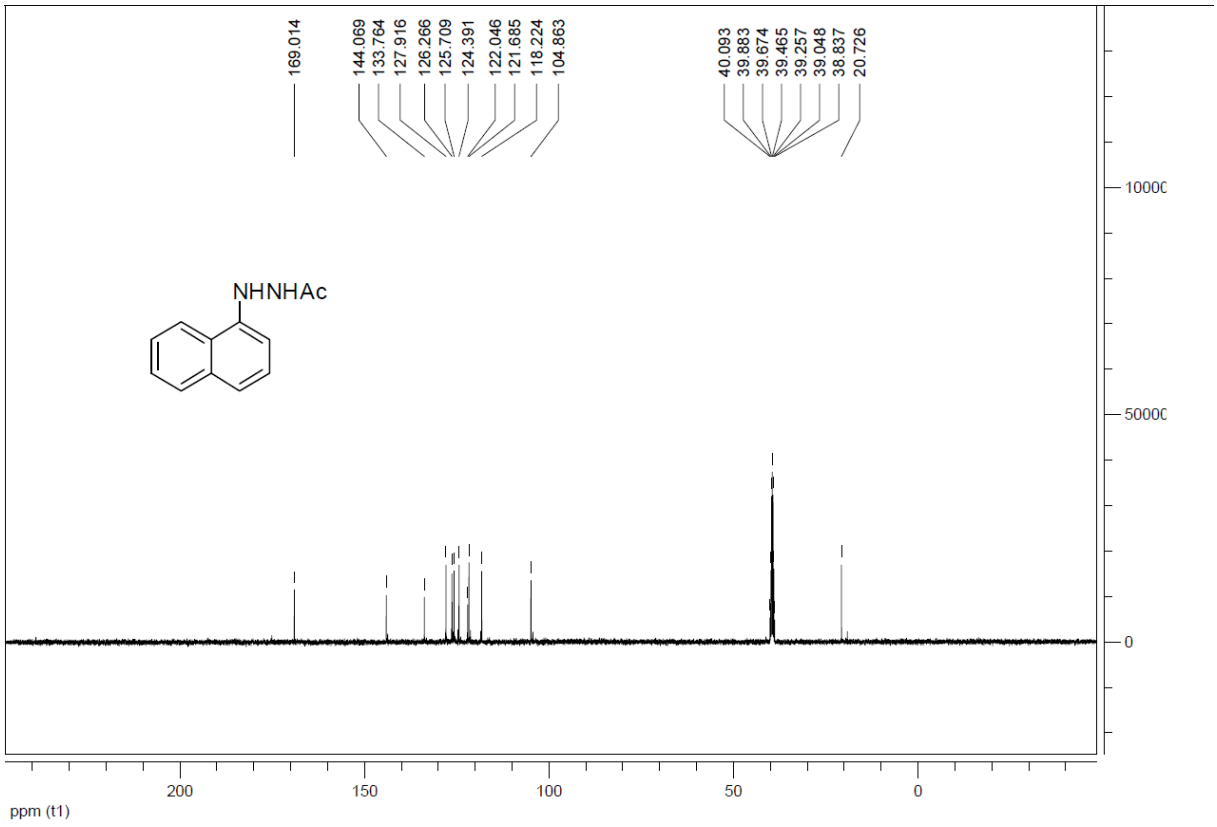
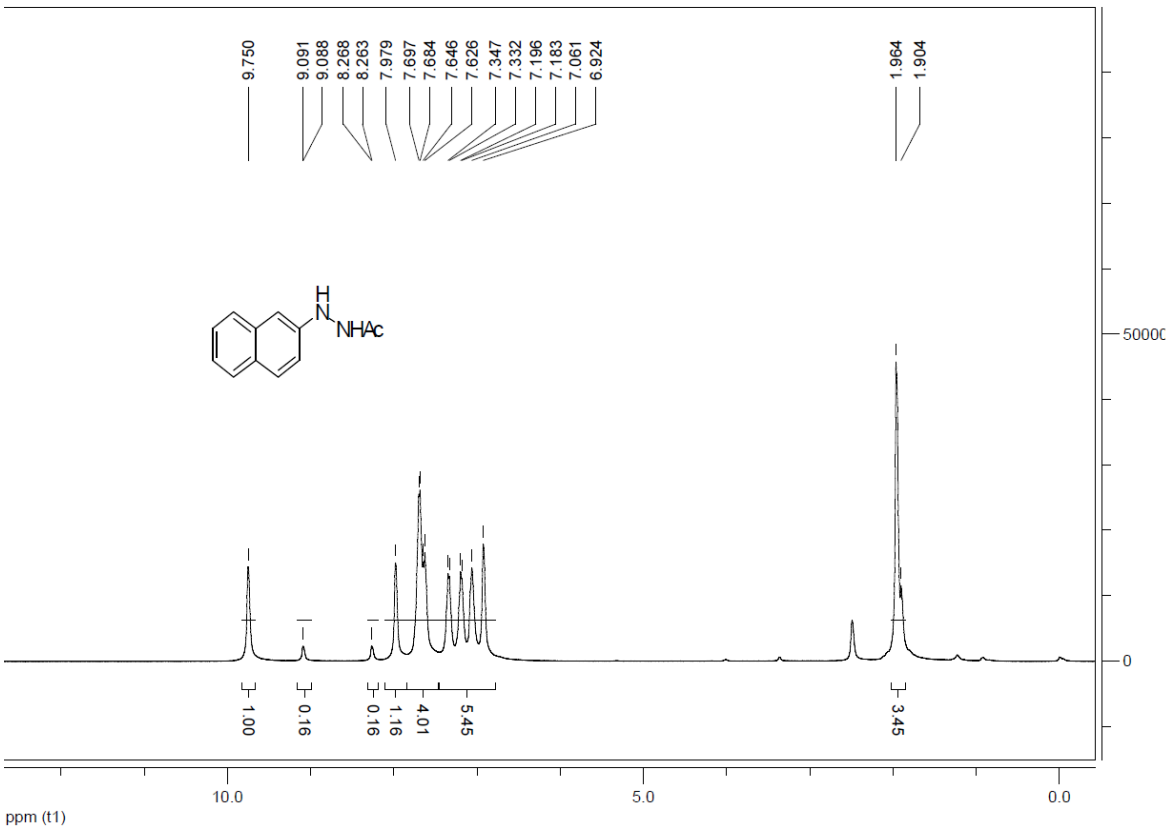
7. NMR Spectra



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7.183
7.061
6.924
1.964
1.904
NHAc
1.00
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1.16
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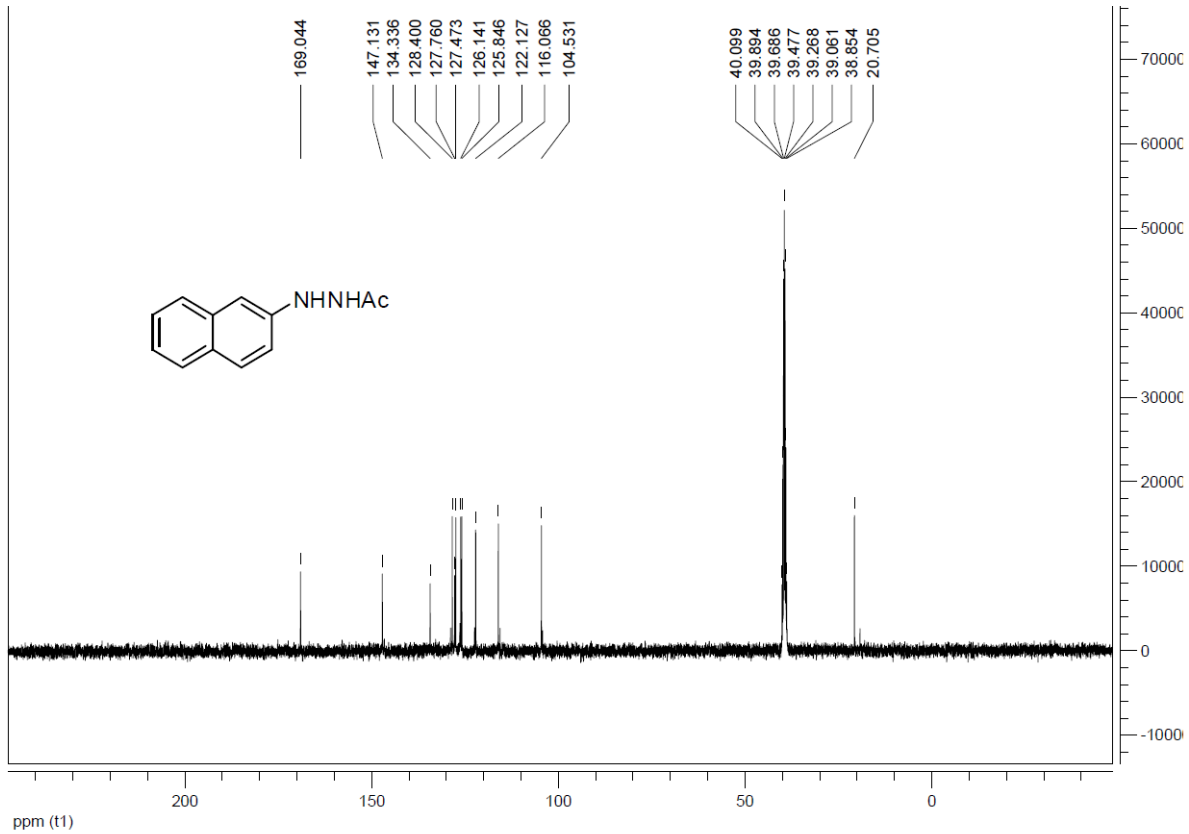
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39.686
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39.268
39.061
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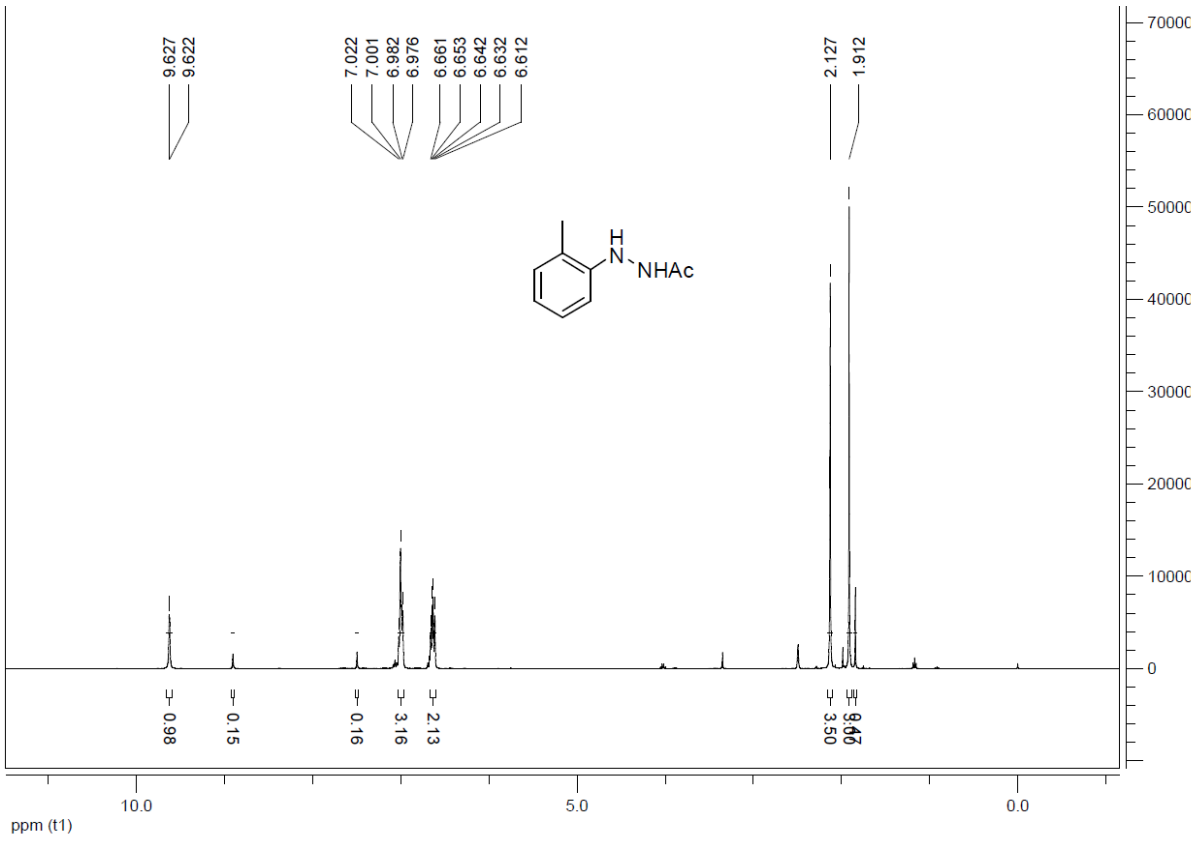
ppm (t1)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H
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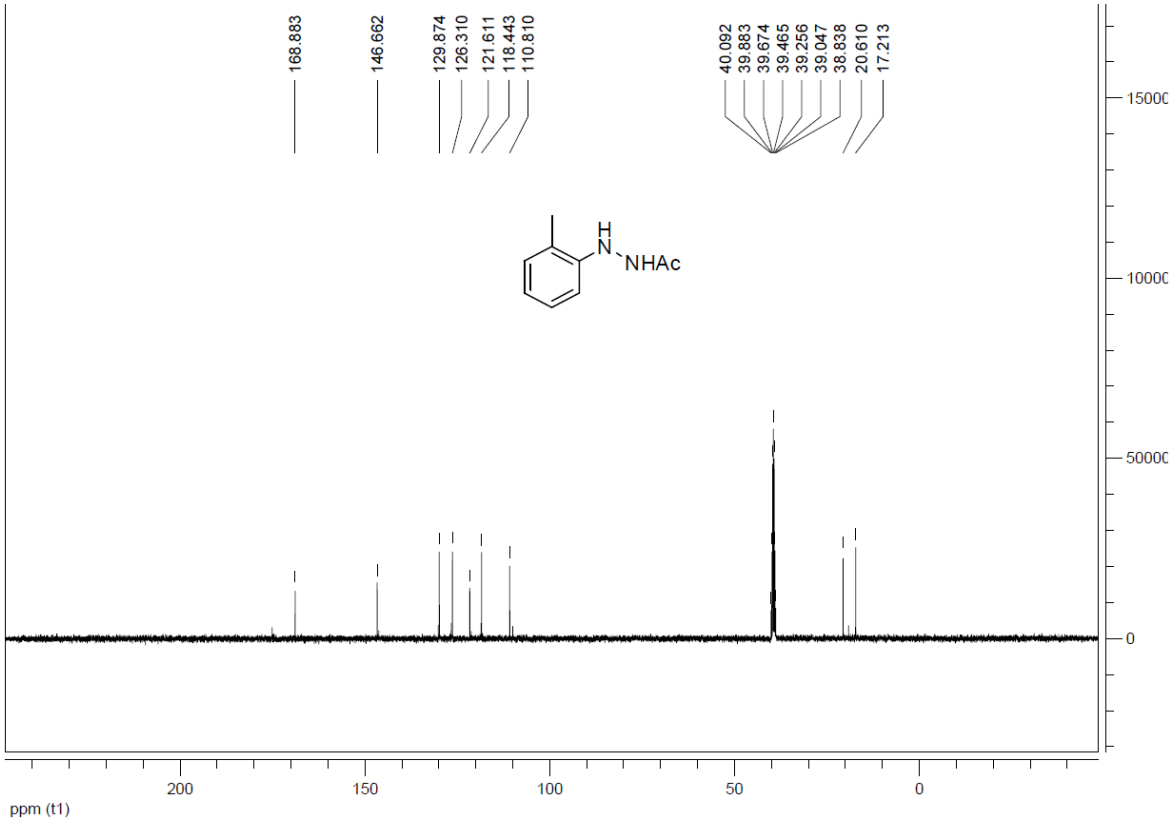
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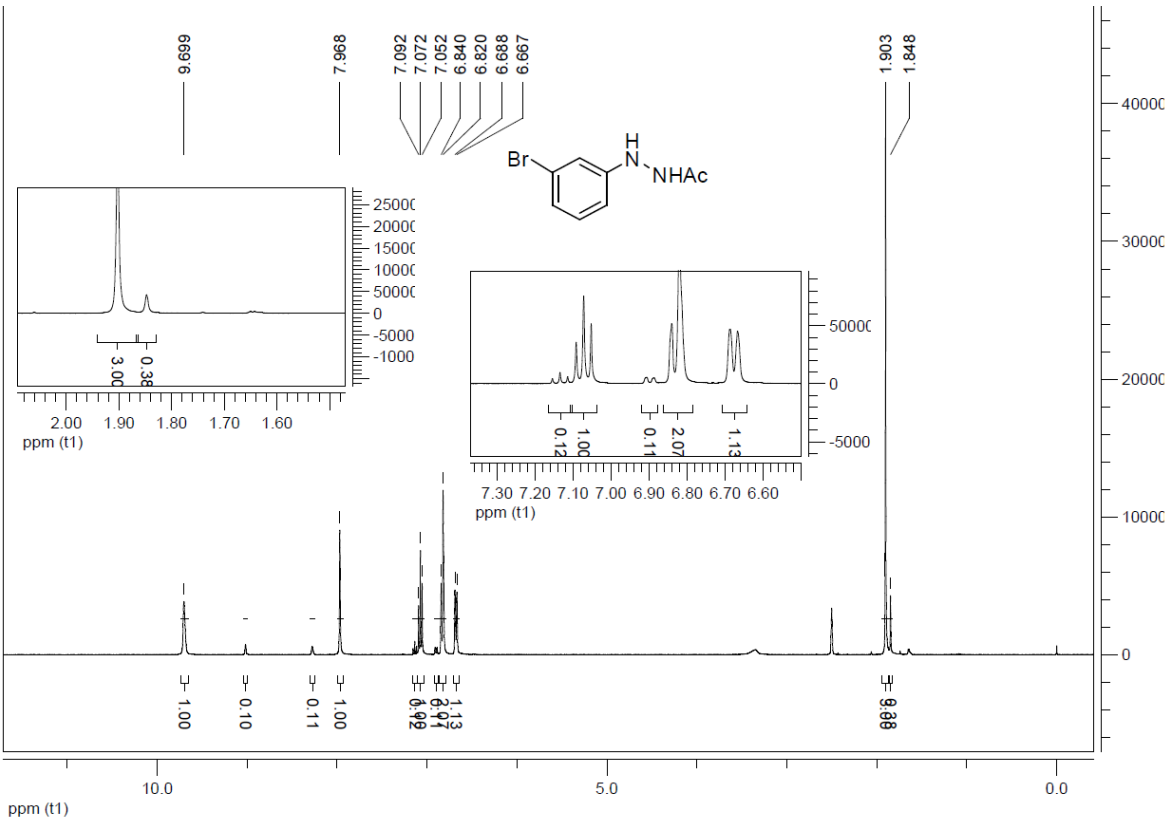
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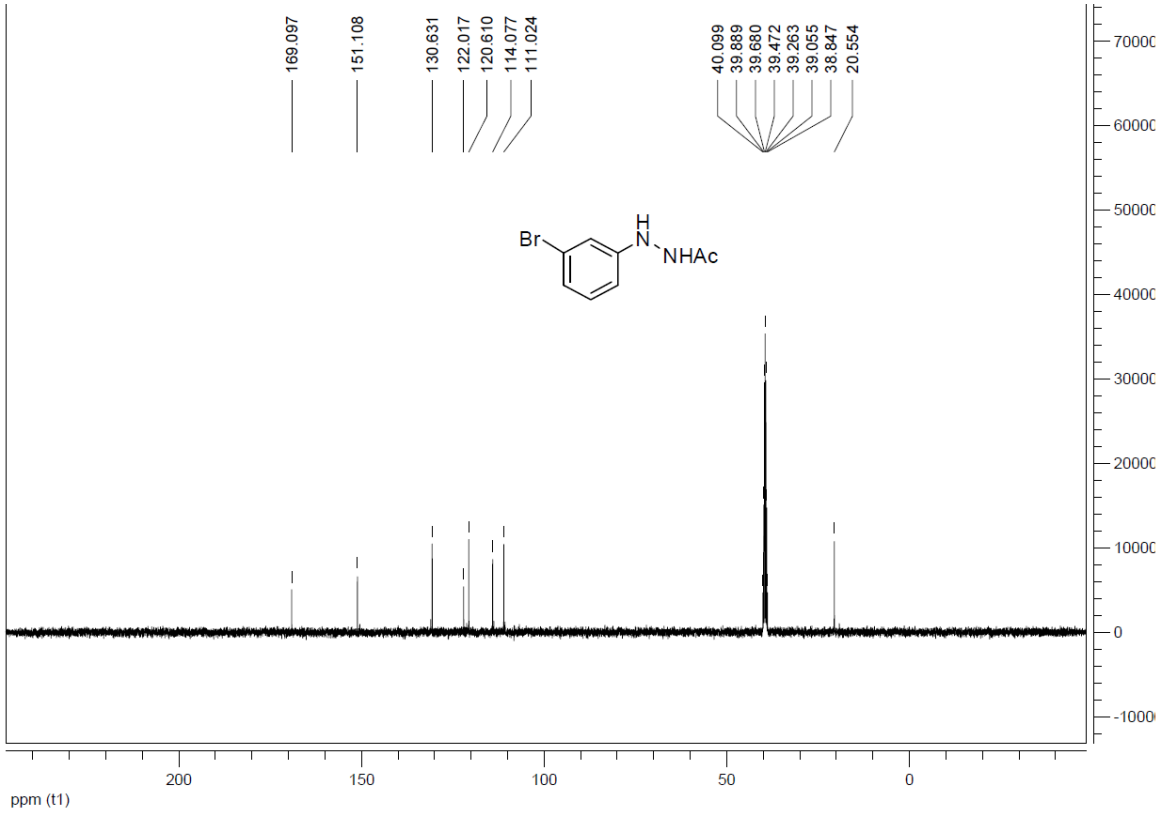
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NHAc
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50
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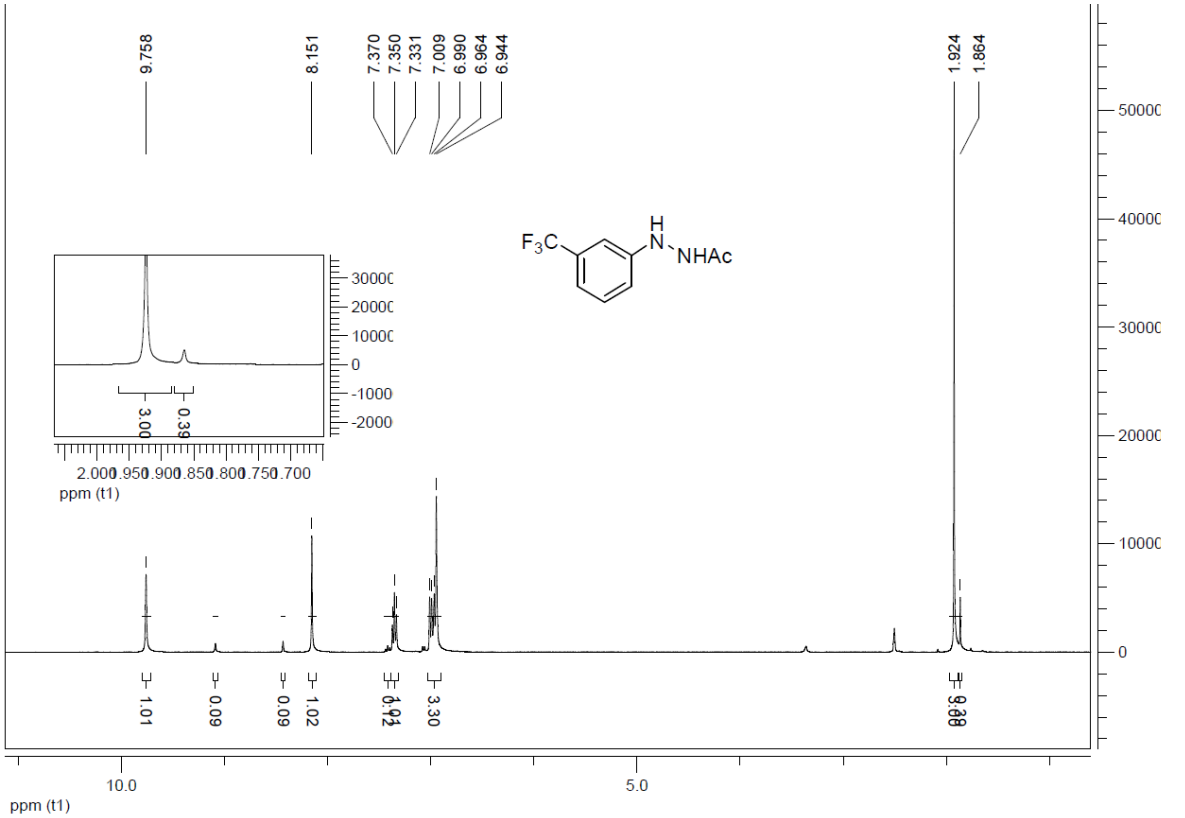
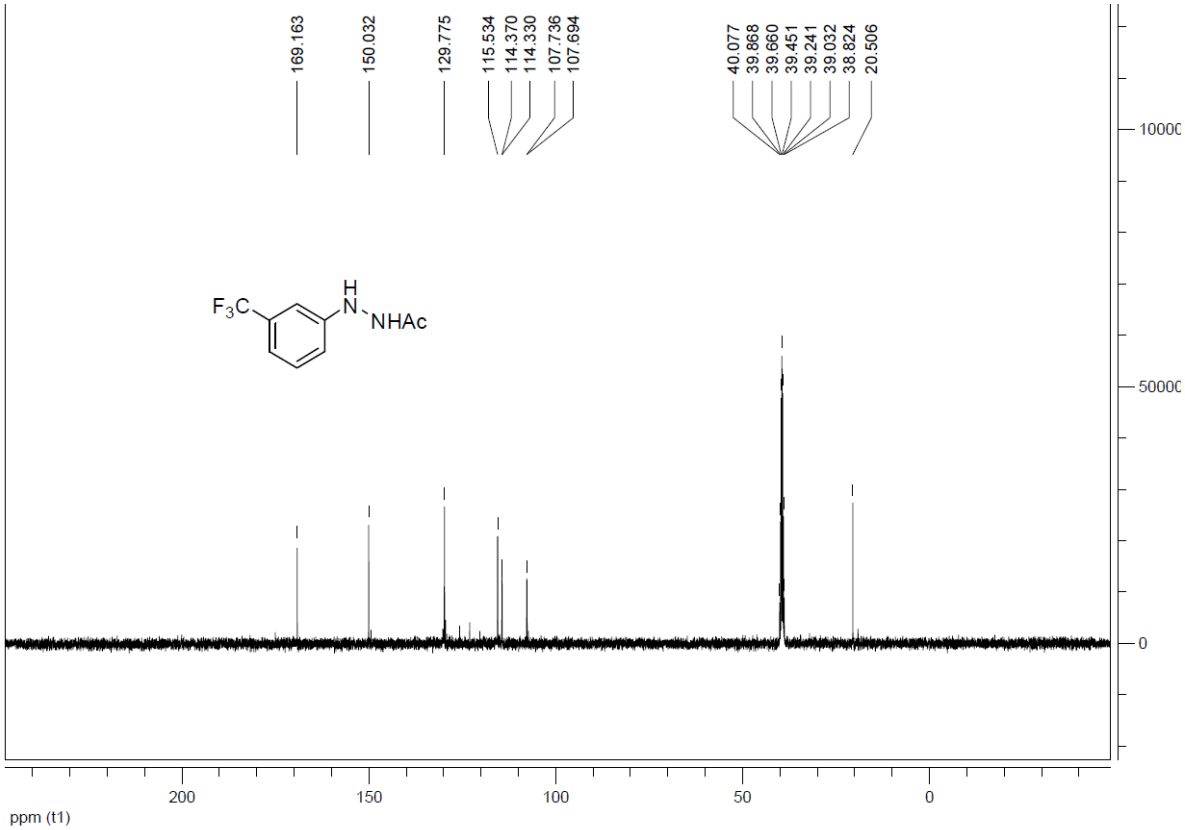
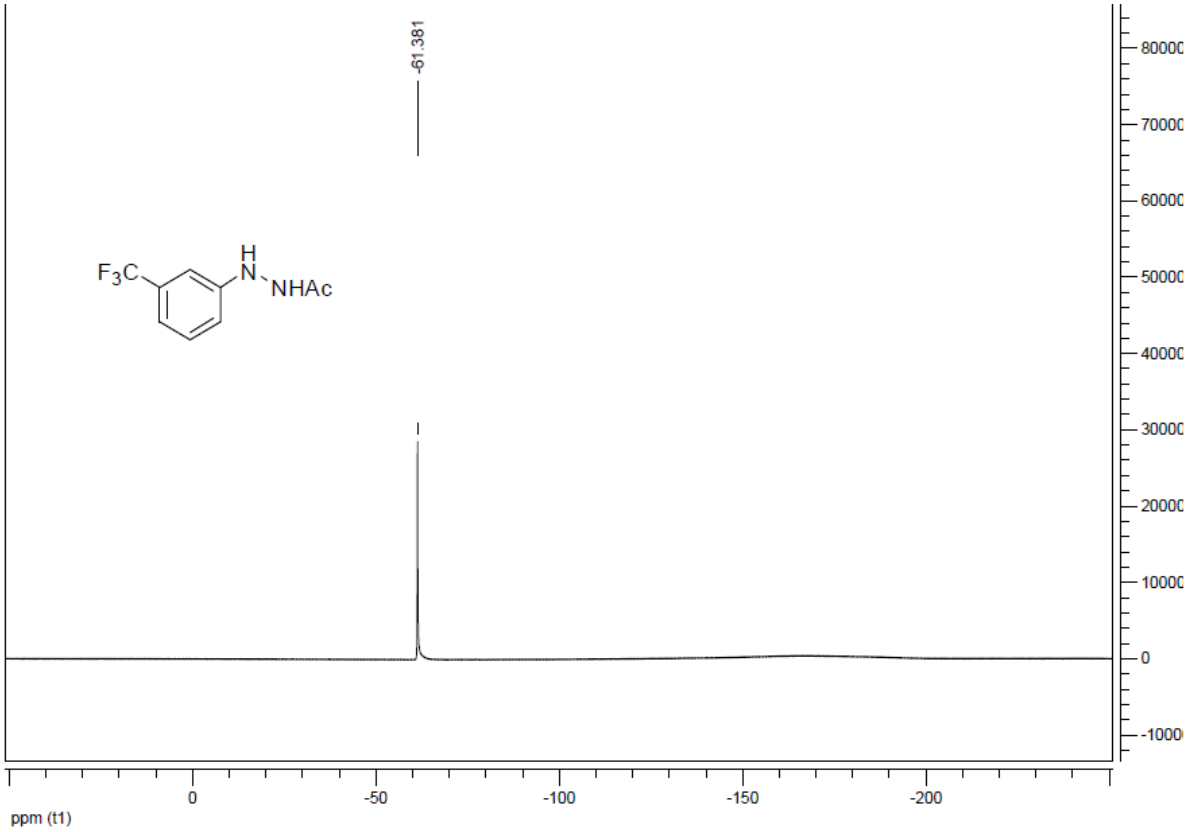

9.758
8.151
7.370
7.350
7.331
7.009
6.990
6.964
6.944
1.924
1.864
F3C
H
N
NHAc
3.00
0.39
2.000.950.900.850.800.750.700
ppm (t1)
1.01
0.09
0.09
1.02
0.13
3.30
9.08
10.0
5.0
ppm (t1)


169.163
150.032
129.775
115.534
114.370
114.330
107.736
107.694
40.077
39.868
39.660
39.451
39.241
39.032
38.824
20.506
F3C
H
N
NHAc
200
150
100
50
0
ppm (t1)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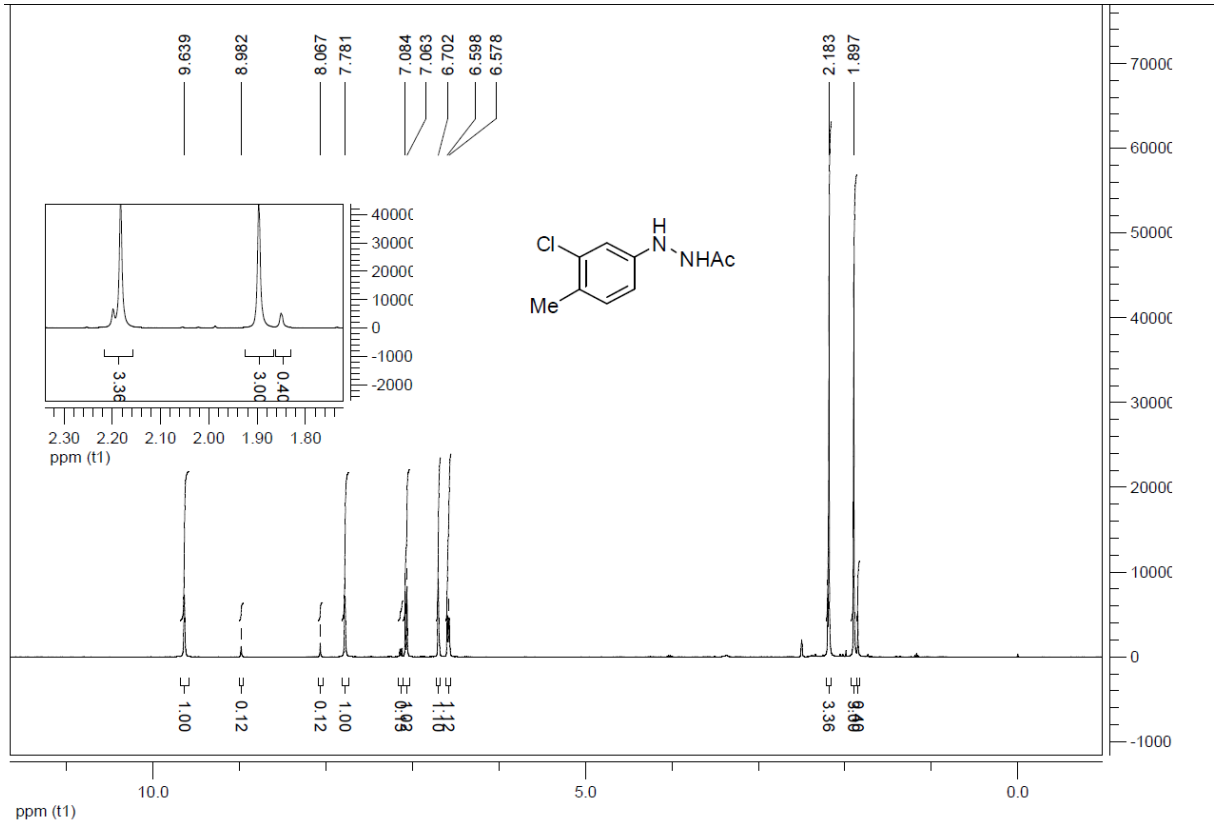
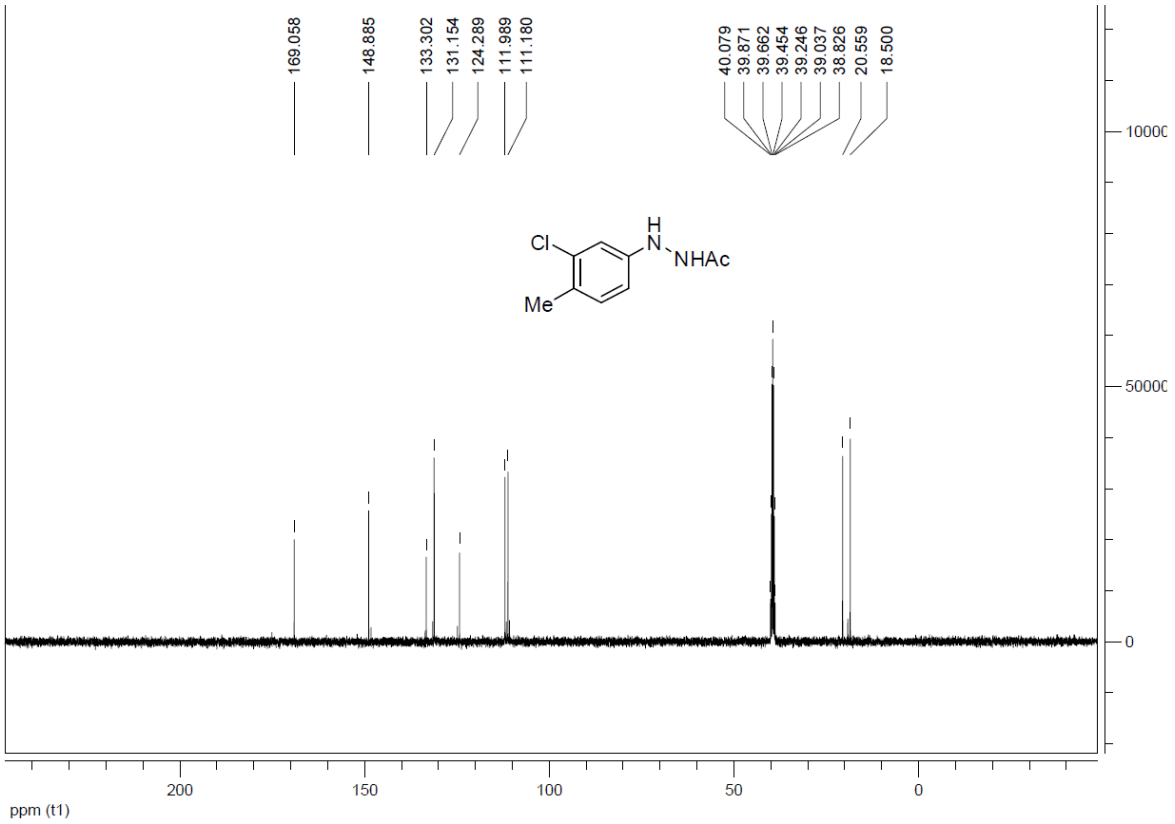
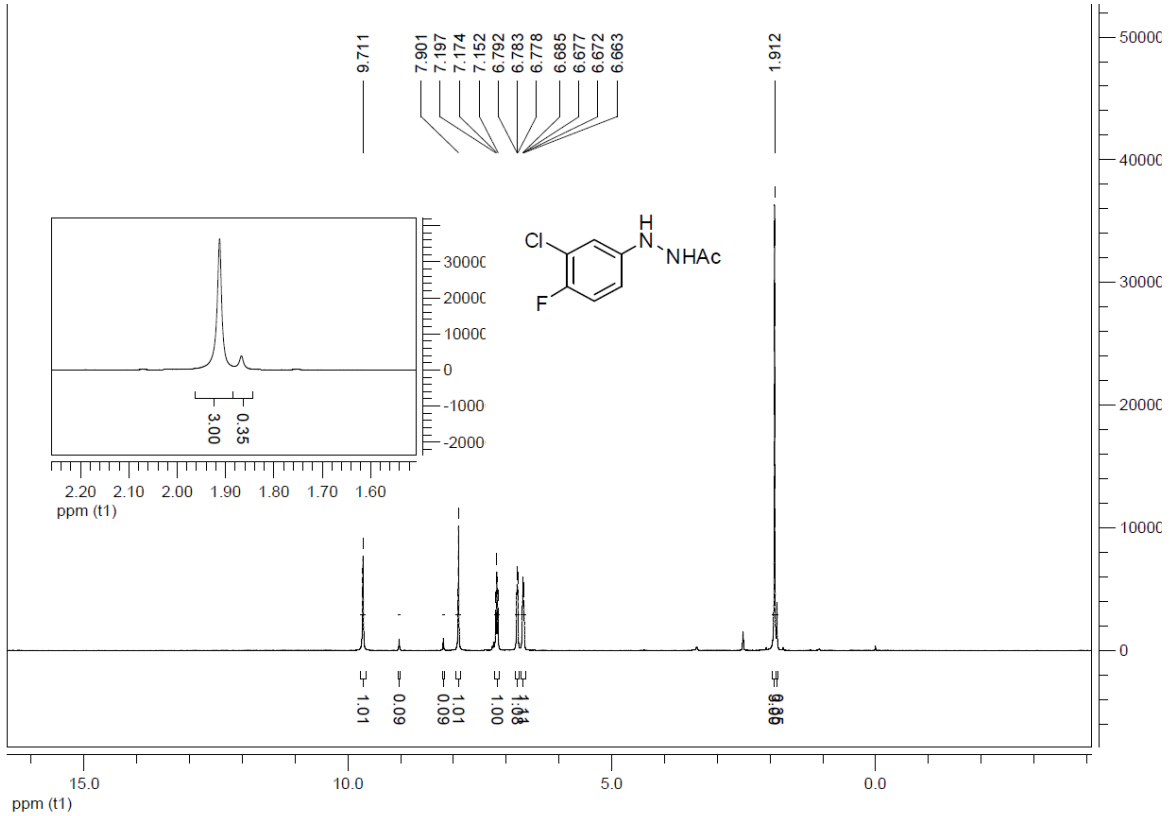
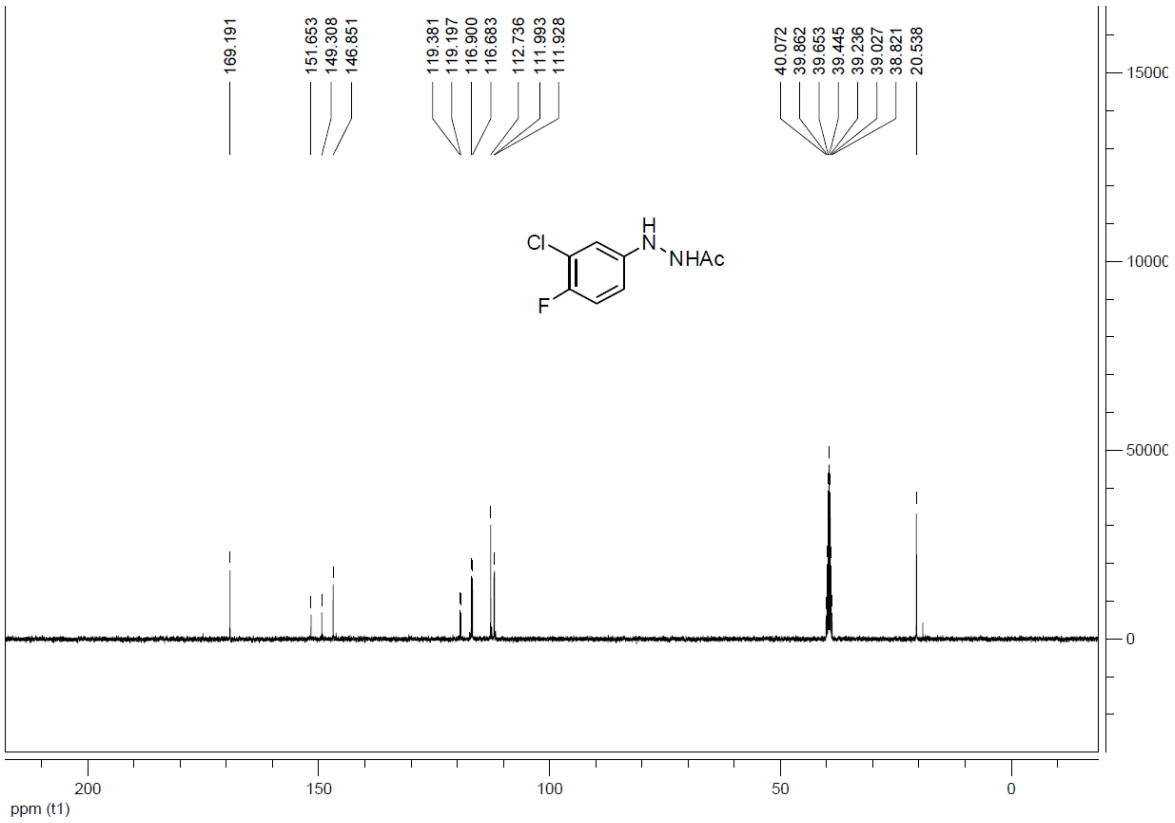
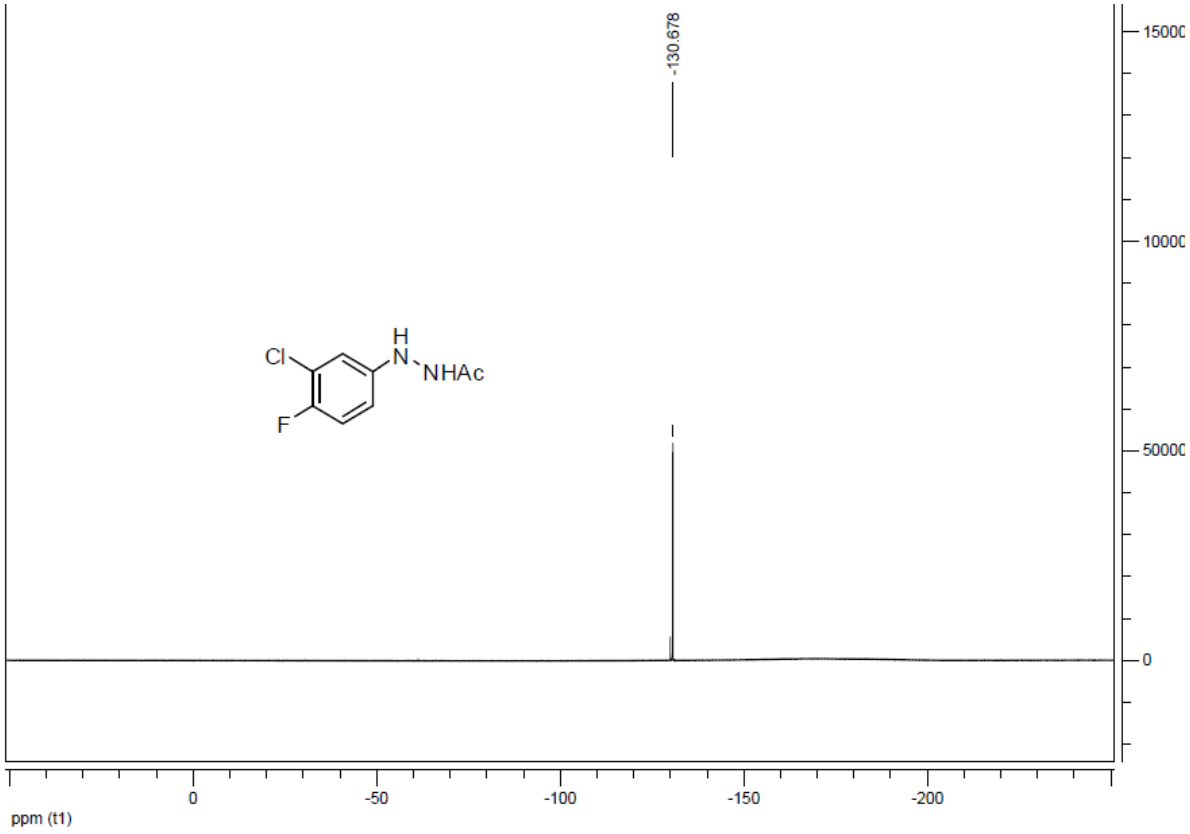
N
NHAc
ppm (t1)


9.639
8.982
8.067
7.781
7.084
7.063
6.702
6.598
6.578
2.183
1.897
Cl
Me
H
N
NHAc
3.36
3.00
0.40
2.30 2.20 2.10 2.00 1.90 1.80
ppm (t1)
1.00
0.12
0.12
1.00
1.16
3.36
10.0
5.0
0.0
ppm (t1)


169.058
148.885
133.302
131.154
124.289
111.989
111.180
40.079
39.871
39.662
39.454
39.246
39.037
38.826
20.559
18.500
Cl
Me
H
N
NHAc
10000
50000
0
200
150
100
50
0
ppm (t1)


9.711
7.901
7.197
7.174
7.152
6.792
6.783
6.778
6.685
6.677
6.672
6.663
1.912
Cl
F
H
N
NHAc
3.00
0.35
30000
20000
10000
0
-1000
-2000
2.20 2.10 2.00 1.90 1.80 1.70 1.60
ppm (t1)
1.01
0.09
0.09
1.01
1.00
50000
40000
30000
20000
10000
0
15.0
10.0
5.0
0.0
ppm (t1)


169.191
151.653
149.308
146.851
119.381
119.197
116.900
116.683
112.736
111.993
111.928
40.072
39.862
39.653
39.445
39.236
39.027
38.821
20.538
Cl
F
H
N
NHAc
150000
100000
50000
0
200
150
100
50
0
ppm (t1)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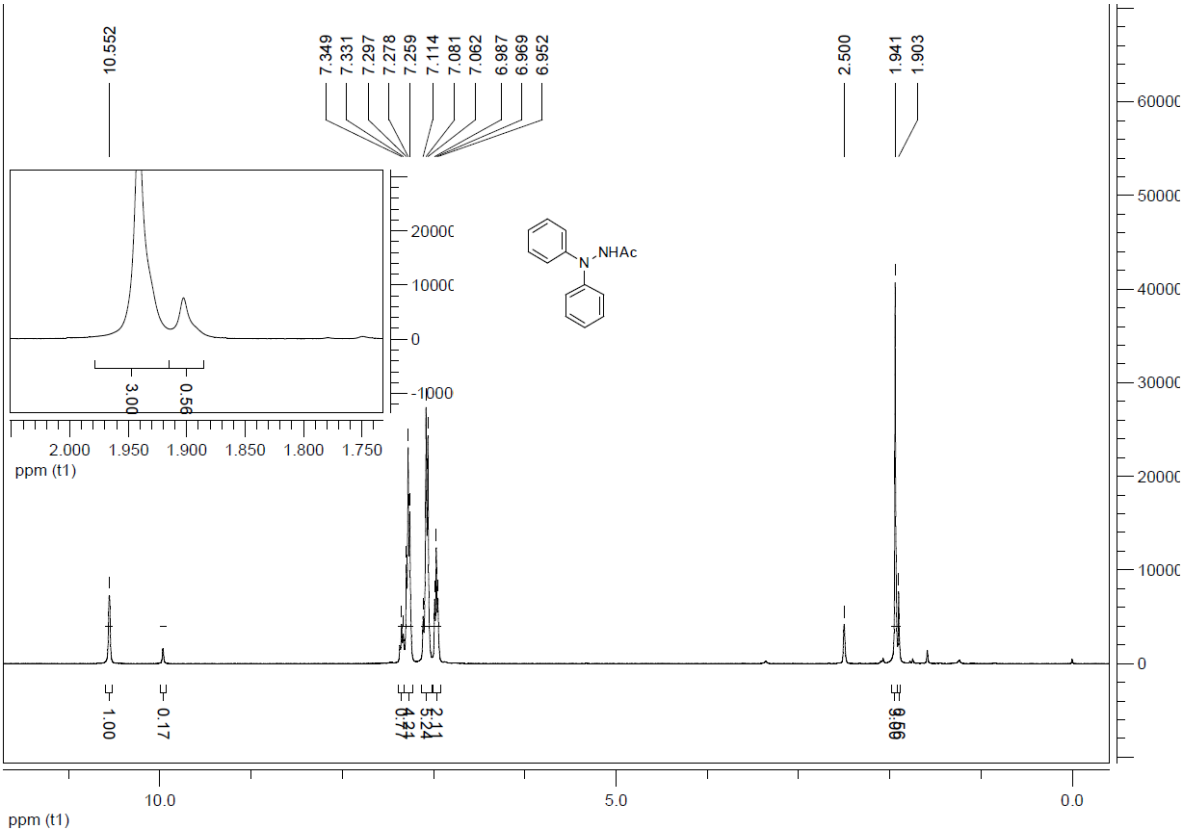
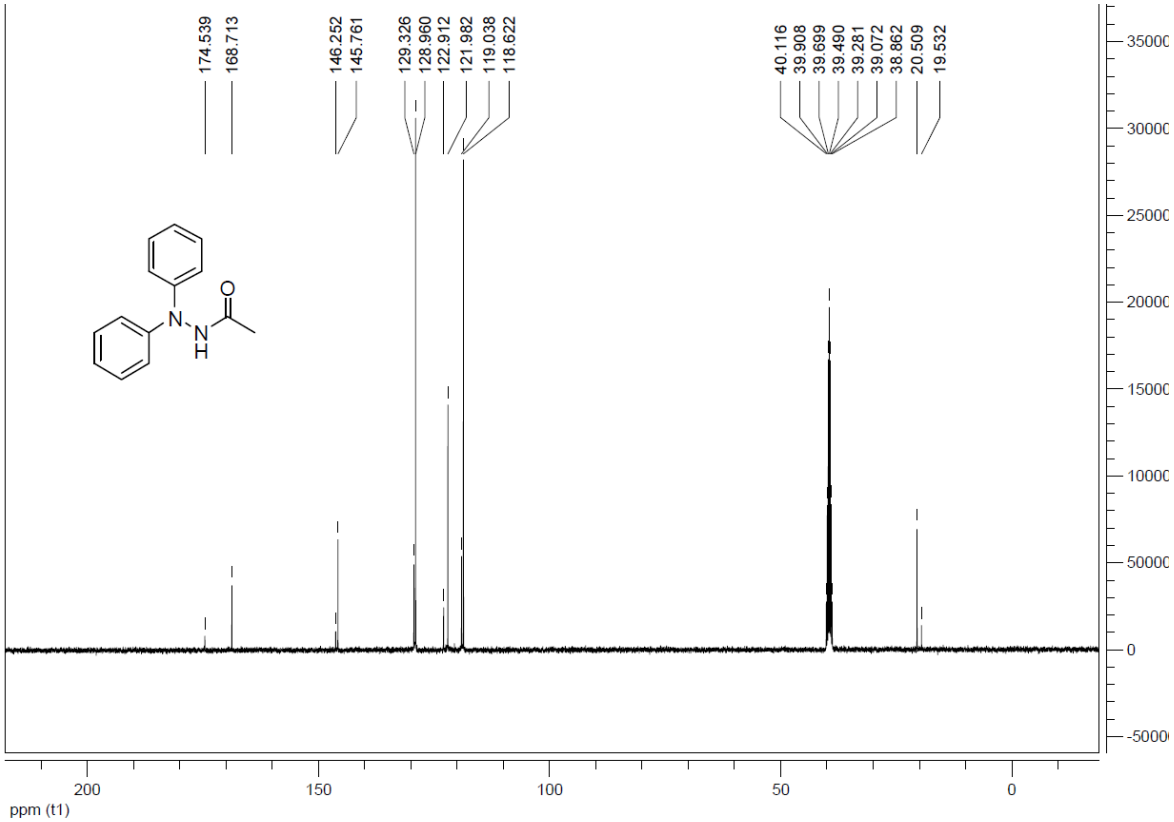
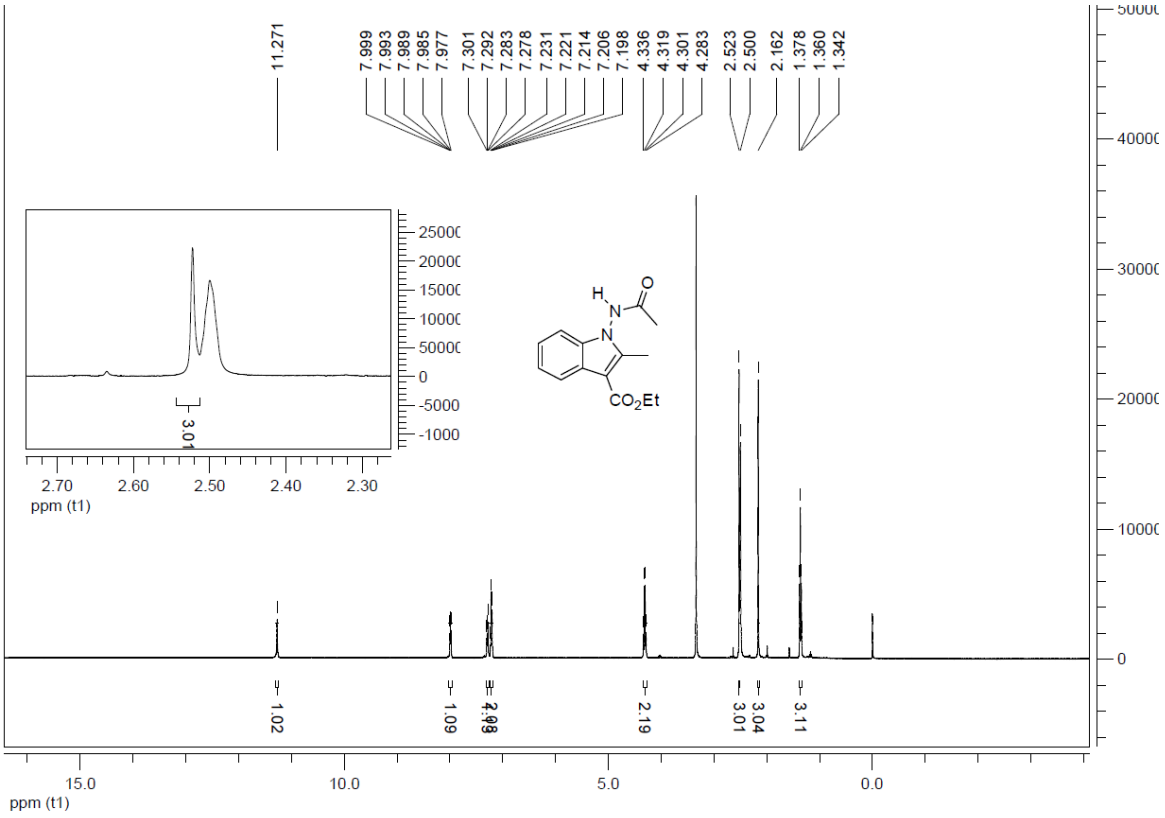
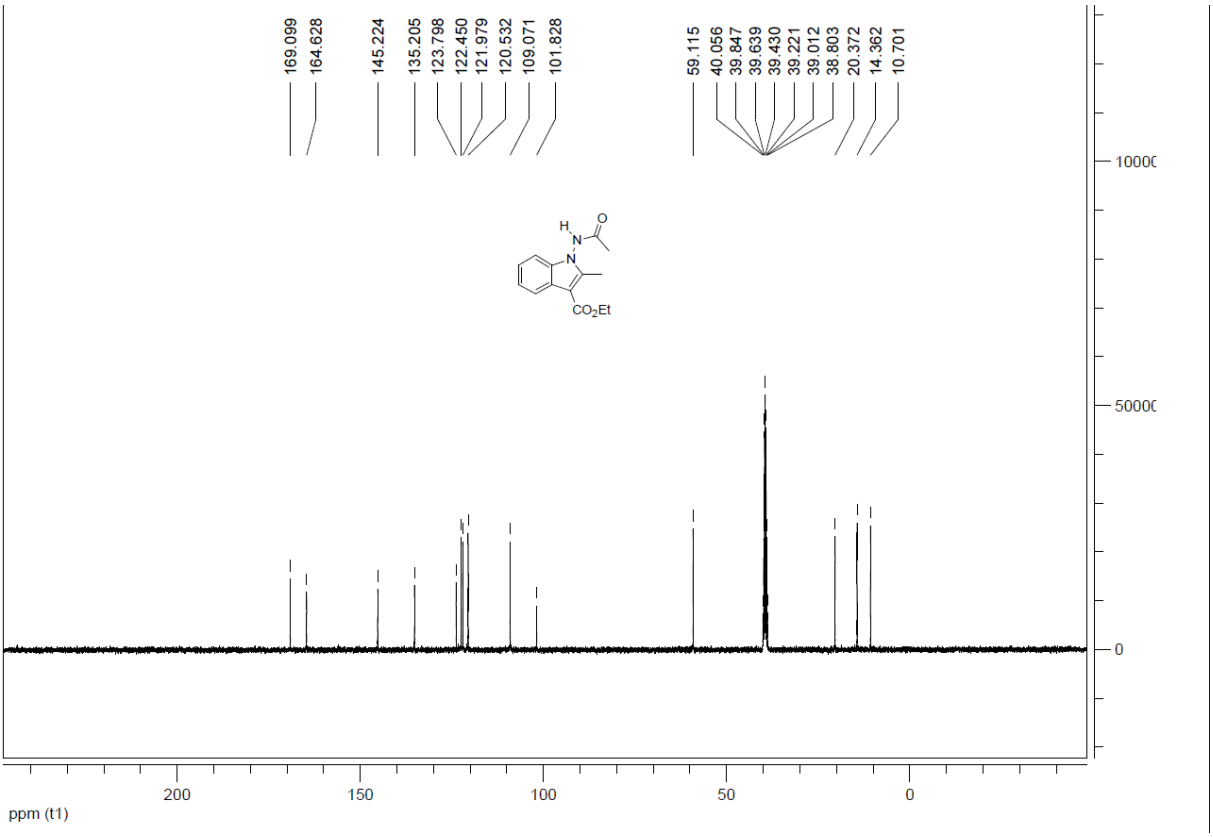
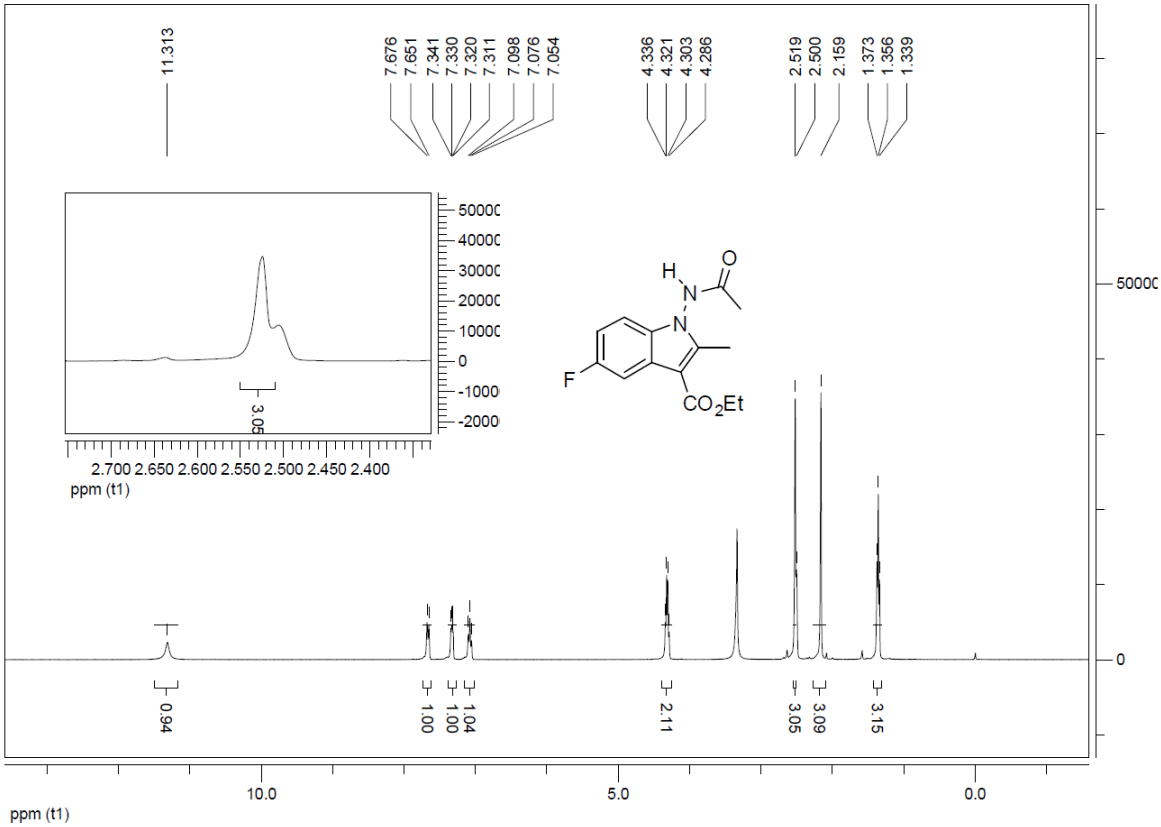
F
H
N
NHAc
150000
100000
50000
0
0
-50
-100
-150
-200
ppm (t1)

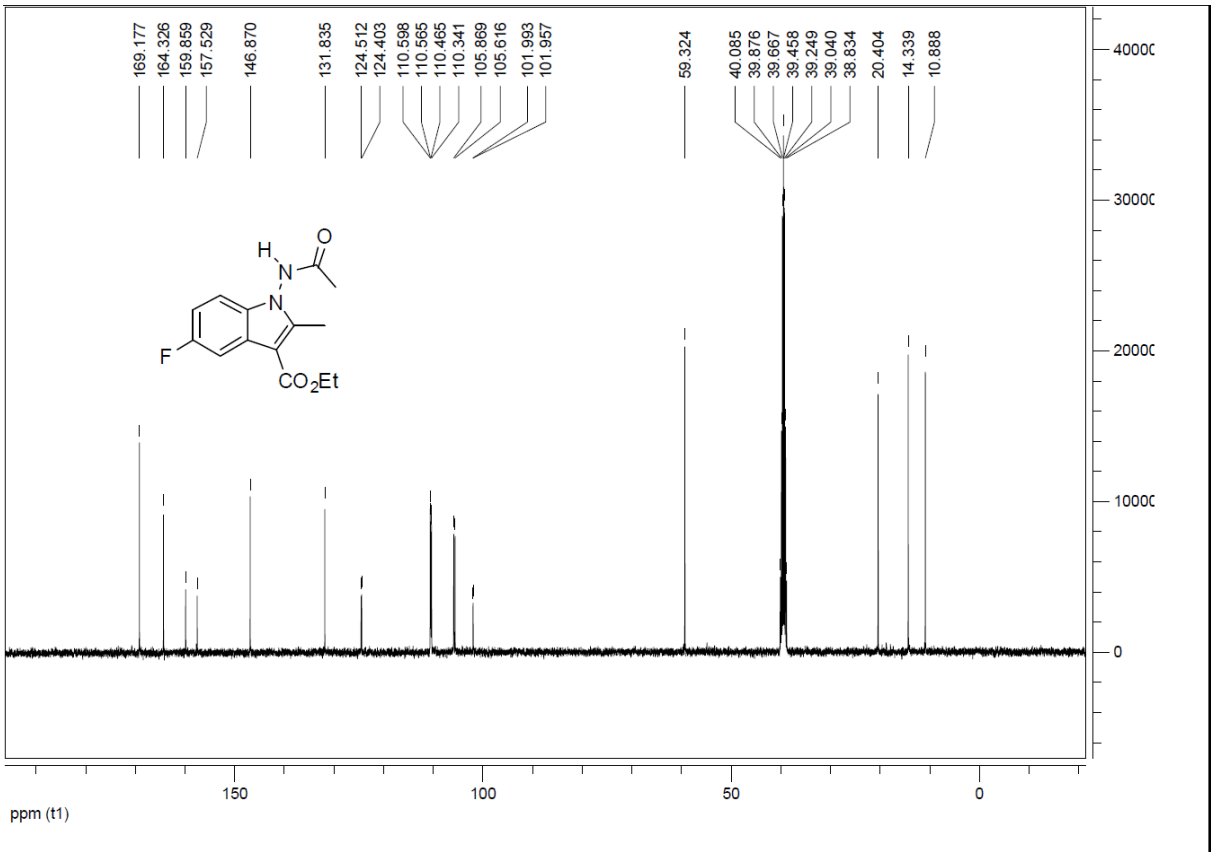

10.552
7.349
7.331
7.297
7.278
7.259
7.114
7.081
7.062
6.987
6.969
6.952
2.500
1.941
1.903
NHAc
3.00
0.56
2.000 1.950 1.900 1.850 1.800 1.750
ppm (t1)
1.00
0.17
2.24
2.21
9.66
10.0
5.0
0.0
ppm (t1)

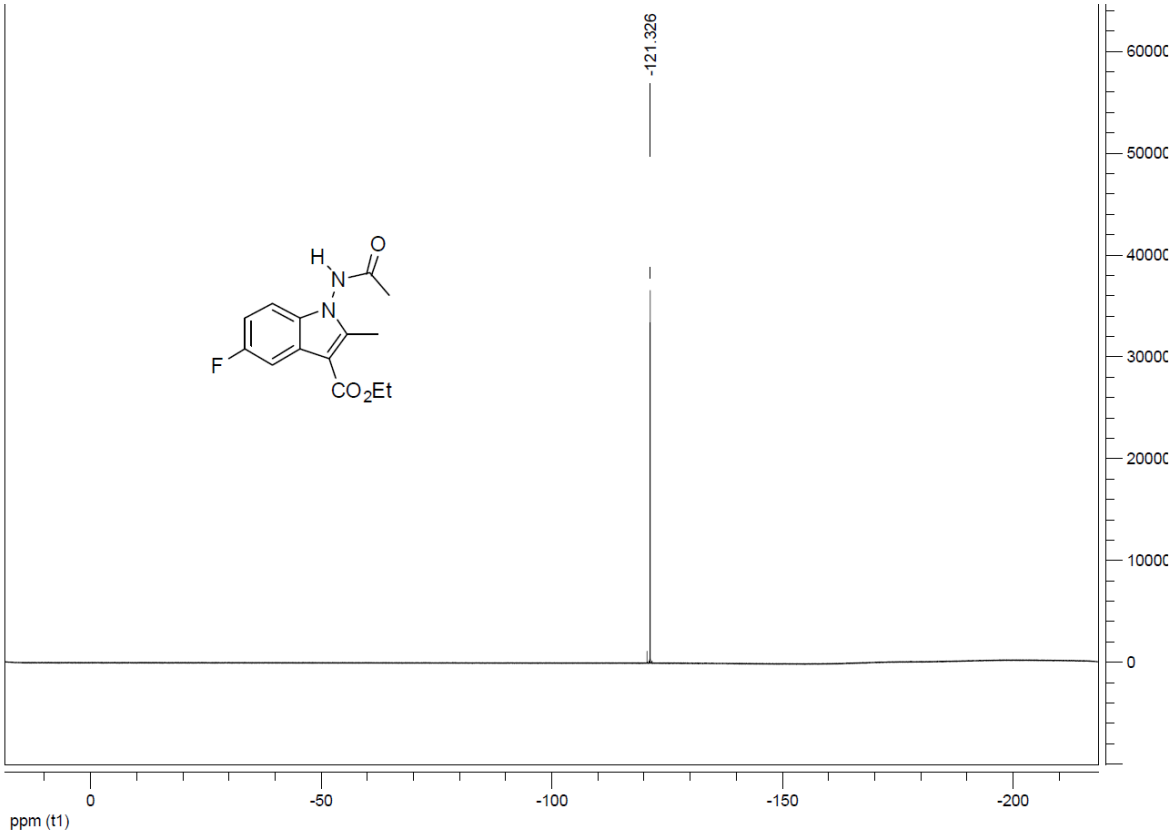

174.539
168.713
146.252
145.761
129.326
128.960
122.912
121.982
119.038
118.622
40.116
39.908
39.699
39.490
39.281
39.072
38.862
20.509
19.532
O
N
N
H
200
150
100
50
0
ppm (t1)

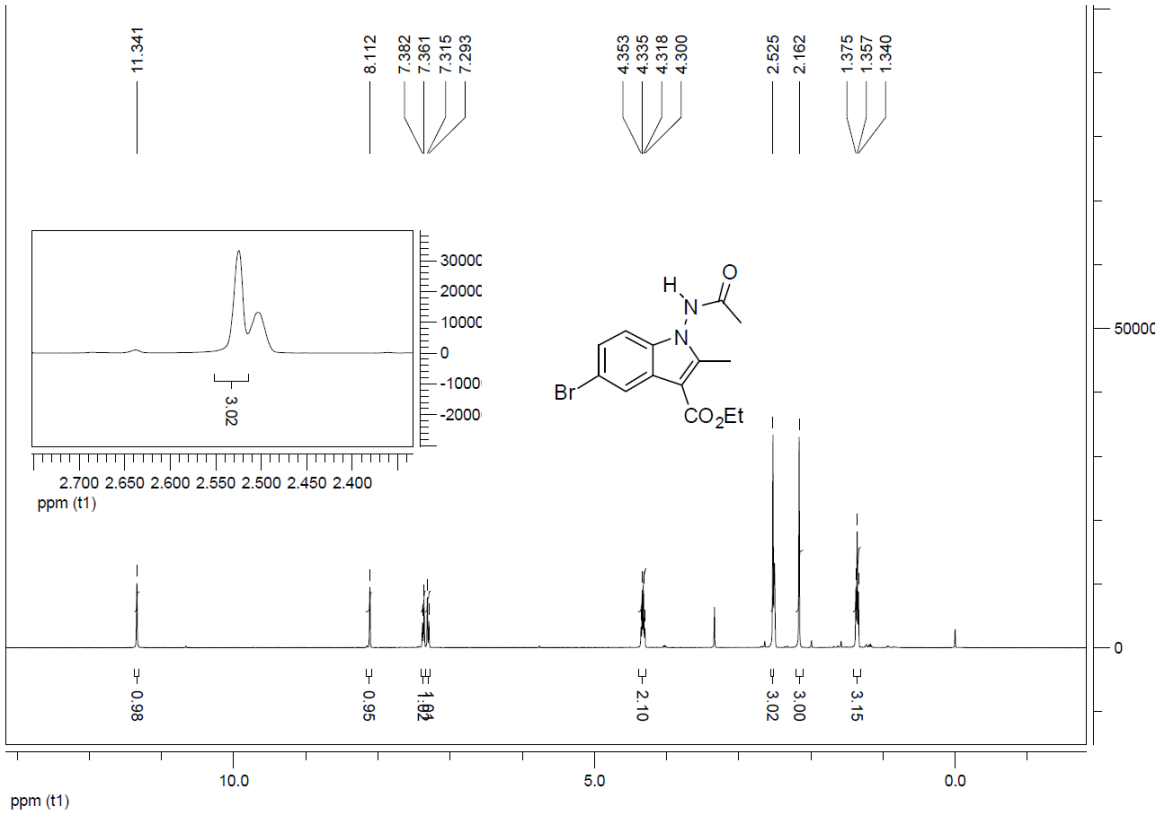

11.271
7.999
7.993
7.989
7.985
7.977
7.301
7.292
7.283
7.278
7.231
7.221
7.214
7.206
7.198
4.336
4.319
4.301
4.283
2.523
2.500
2.162
1.378
1.360
1.342
3.01
2.70
2.60
2.50
2.40
2.30
ppm (t1)
1.02
1.09
2.19
3.01
3.04
3.11
15.0
10.0
5.0
0.0
ppm (t1)

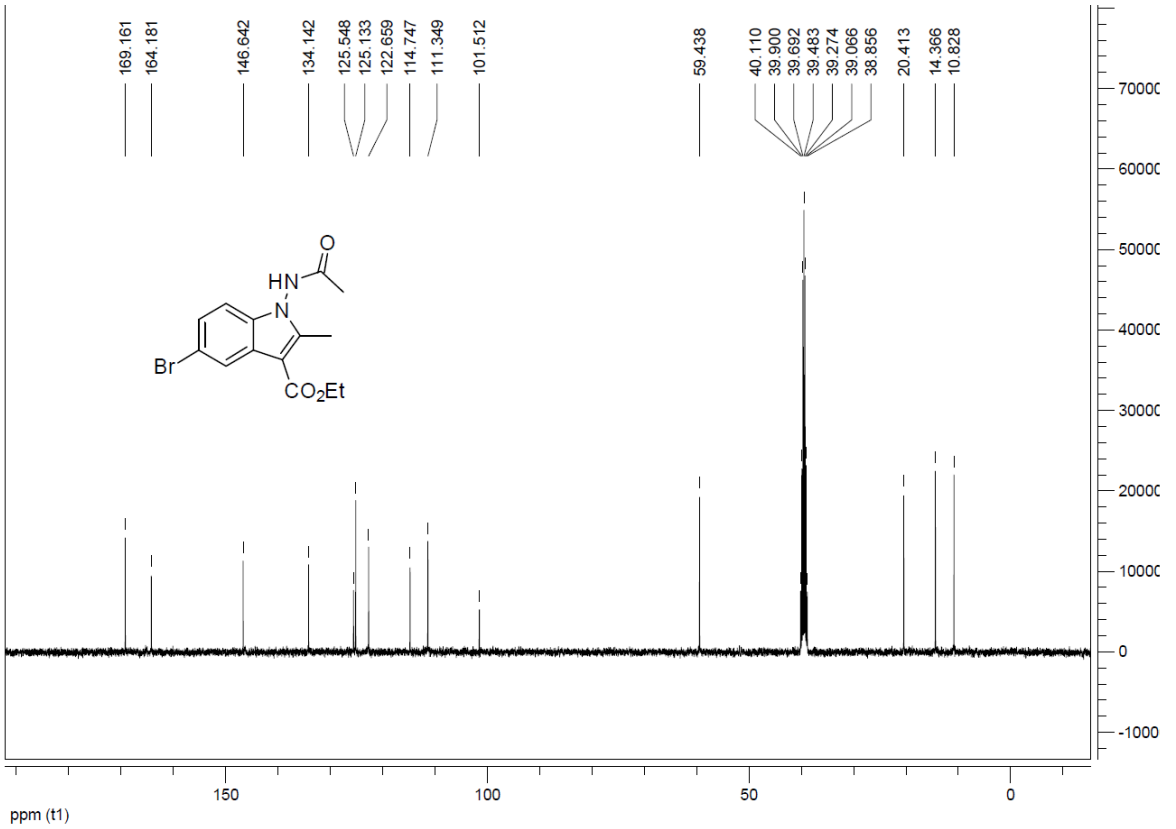

169.099
164.628
145.224
135.205
123.798
122.450
121.979
120.532
109.071
101.828
59.115
40.056
39.847
39.639
39.430
39.221
39.012
38.803
20.372
14.362
10.701
200
150
100
50
0
ppm (t1)

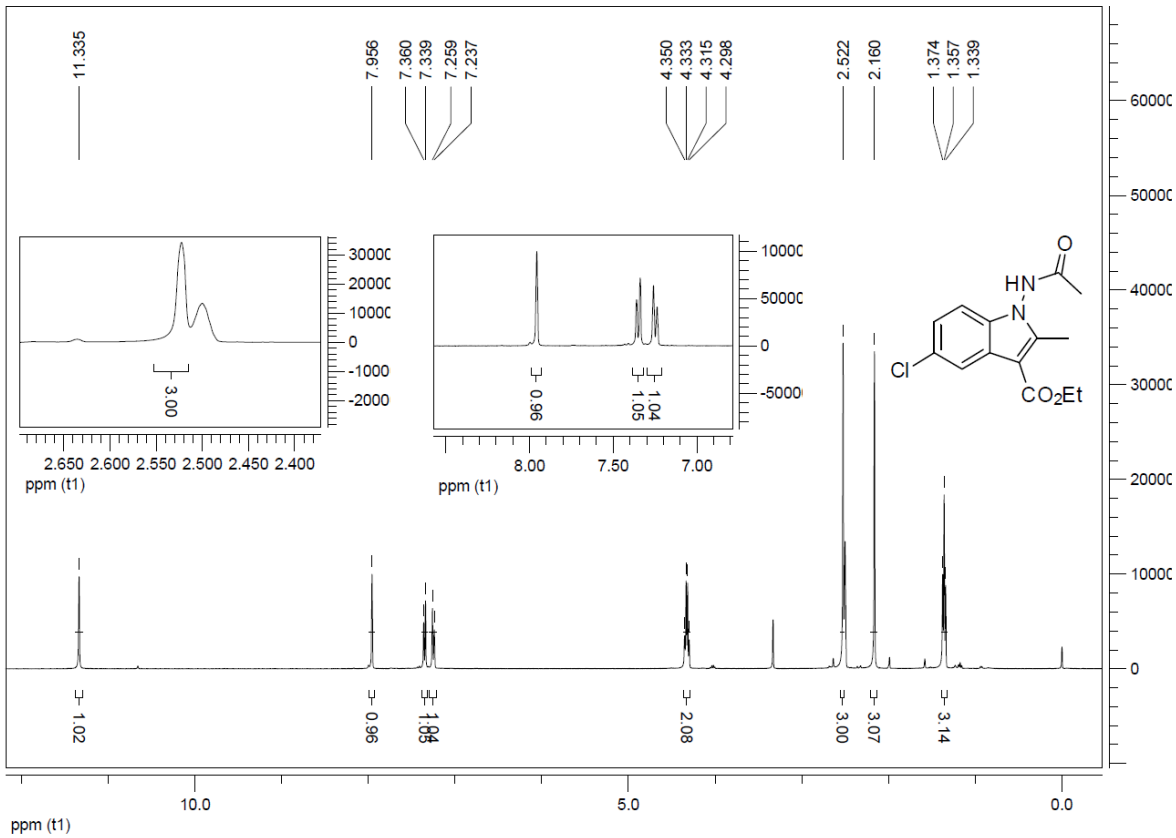

11.313
7.676
7.651
7.341
7.330
7.320
7.311
7.098
7.076
7.054
4.336
4.321
4.303
4.286
2.519
2.500
2.159
1.373
1.356
1.339
3.05
2.700 2.650 2.600 2.550 2.500 2.450 2.400
ppm (t1)
0.94
1.00
1.00
1.04
2.11
3.05
3.09
3.15
10.0
5.0
0.0
ppm (t1)


169.177
164.326
159.859
157.529
146.870
131.835
124.512
124.403
110.598
110.565
110.465
110.341
105.869
105.616
101.993
101.957
59.324
40.085
39.876
39.667
39.458
39.249
39.040
38.834
20.404
14.339
10.888
150
100
50
0
ppm (t1)


-121.326
F
CO2Et
ppm (t1)


11.341
8.112
7.382
7.361
7.315
7.293
4.353
4.335
4.318
4.300
2.525
2.162
1.375
1.357
1.340
Br
CO2Et
3.02
0.98
0.95
2.10
3.02
3.00
3.15
ppm (t1)


169.161
164.181
146.642
134.142
125.548
125.133
122.659
114.747
111.349
101.512
59.438
40.110
39.900
39.692
39.483
39.274
39.066
38.856
20.413
14.366
10.828
HN
O
N
Br
CO2Et
ppm (t1)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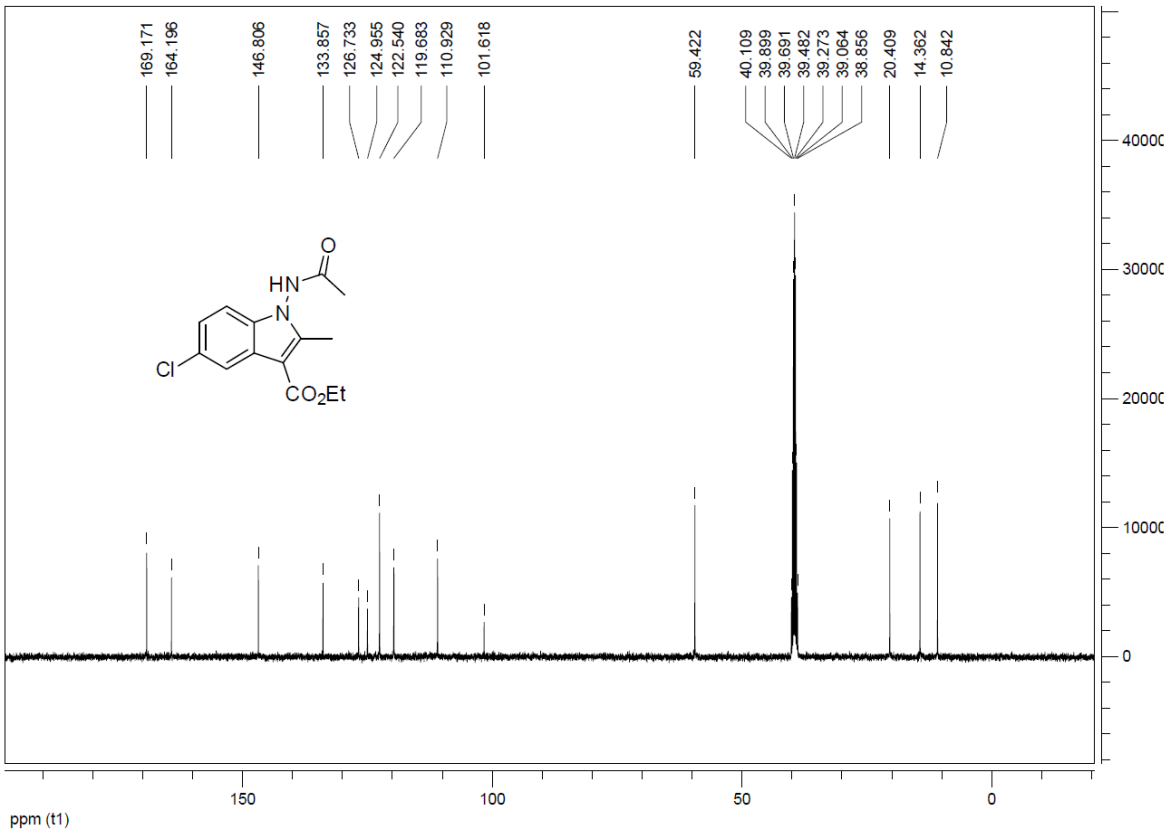
7.360
7.339
7.259
7.237
4.350
4.333
4.315
4.298
2.522
2.160
1.374
1.357
1.339
HN
O
N
Cl
CO2Et
3.00
0.96
1.04
1.02
0.96
1.04
2.08
3.00
3.07
3.14
ppm (t1)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124.955
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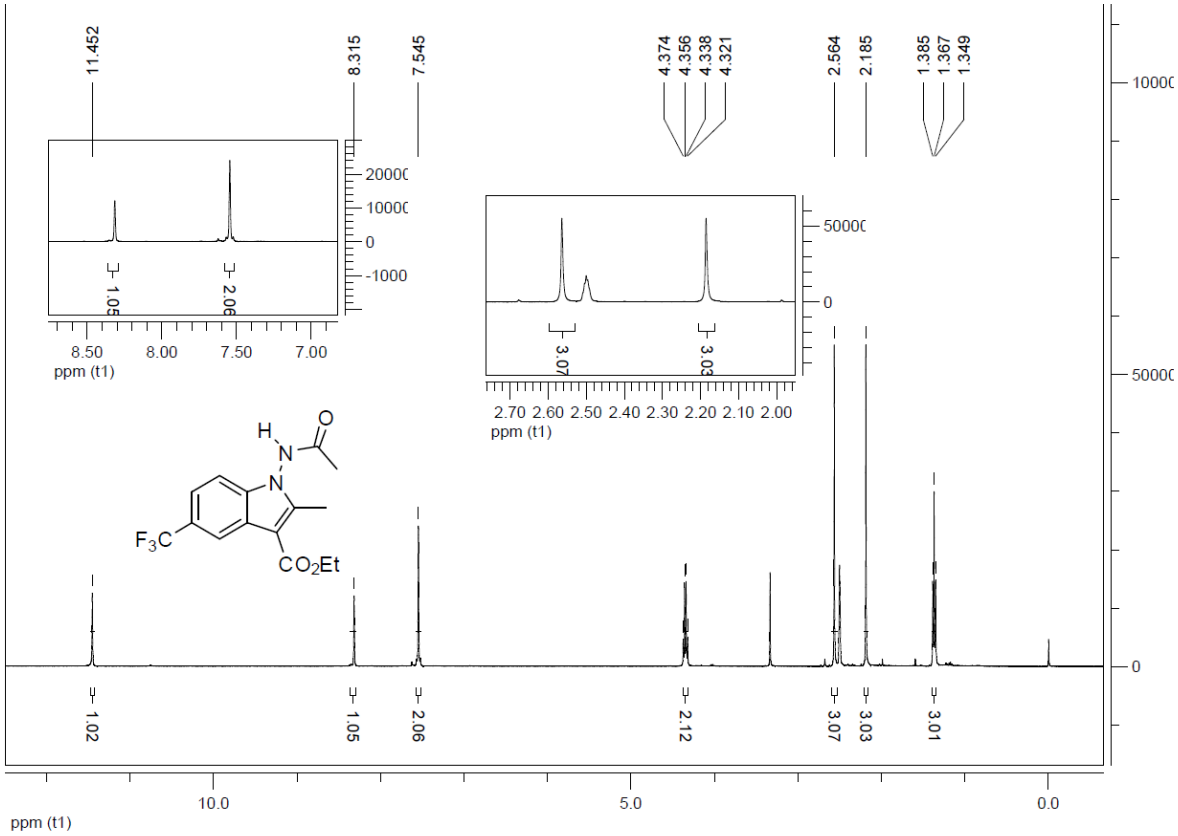
119.683
110.929
101.618
59.422
40.109
39.899
39.691
39.482
39.273
39.064
38.856
20.409
14.362
10.842
HN
O
N
Cl
CO2Et
ppm (t1)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7.545
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4.356
4.338
4.321
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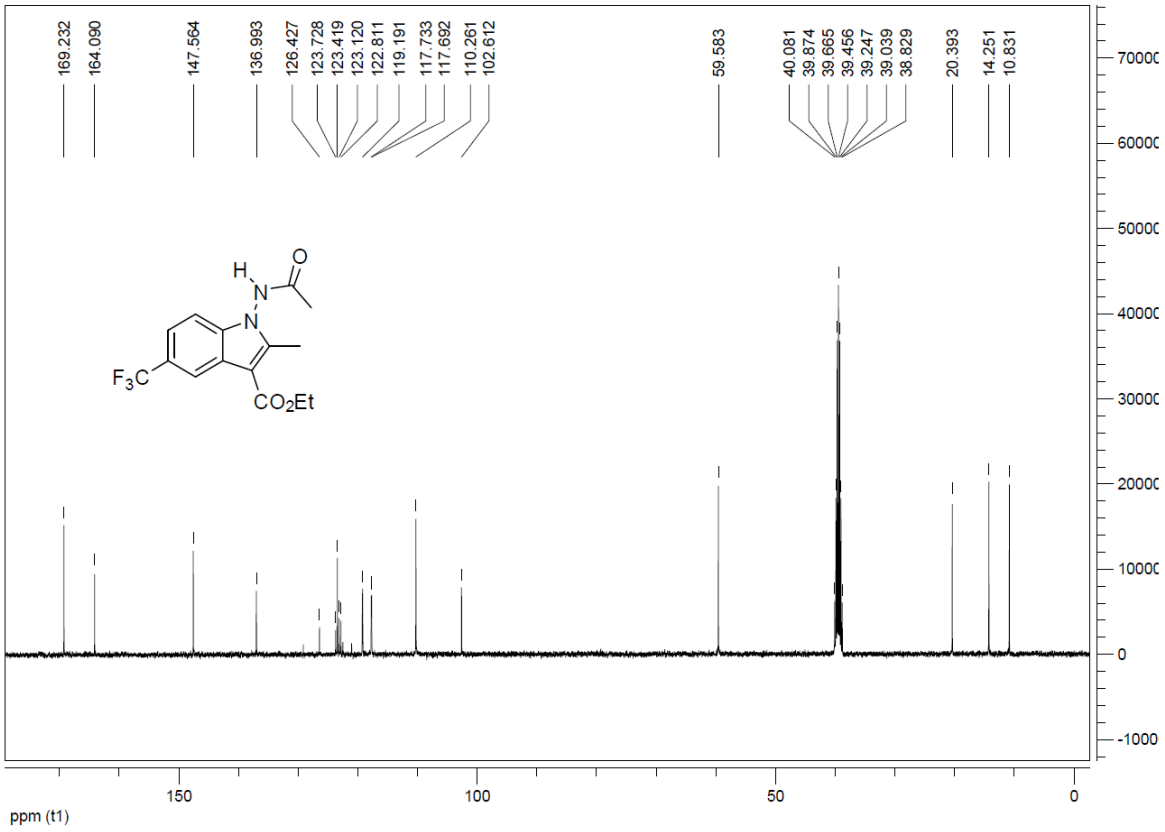
2.185
1.385
1.367
1.349
1.02
1.05
2.06
2.12
3.07
3.03
3.01
H
N
O
F3C
CO2Et
ppm (t1)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136.993
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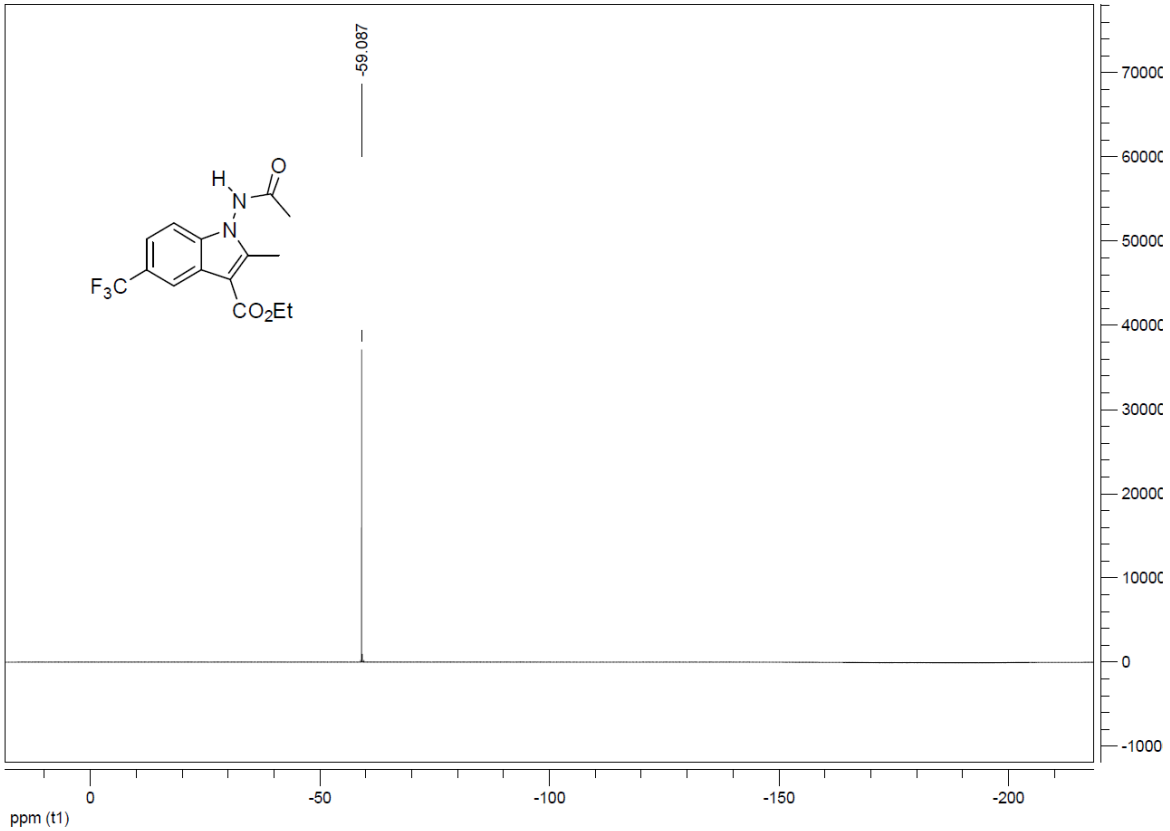
123.728
123.419
123.120
122.811
119.191
117.733
117.692
110.261
102.612
59.583
40.081
39.874
39.665
39.456
39.247
39.039
38.829
20.393
14.251
10.831
H
N
O
N
F3C
CO2Et
150
100
50
0
ppm (t1)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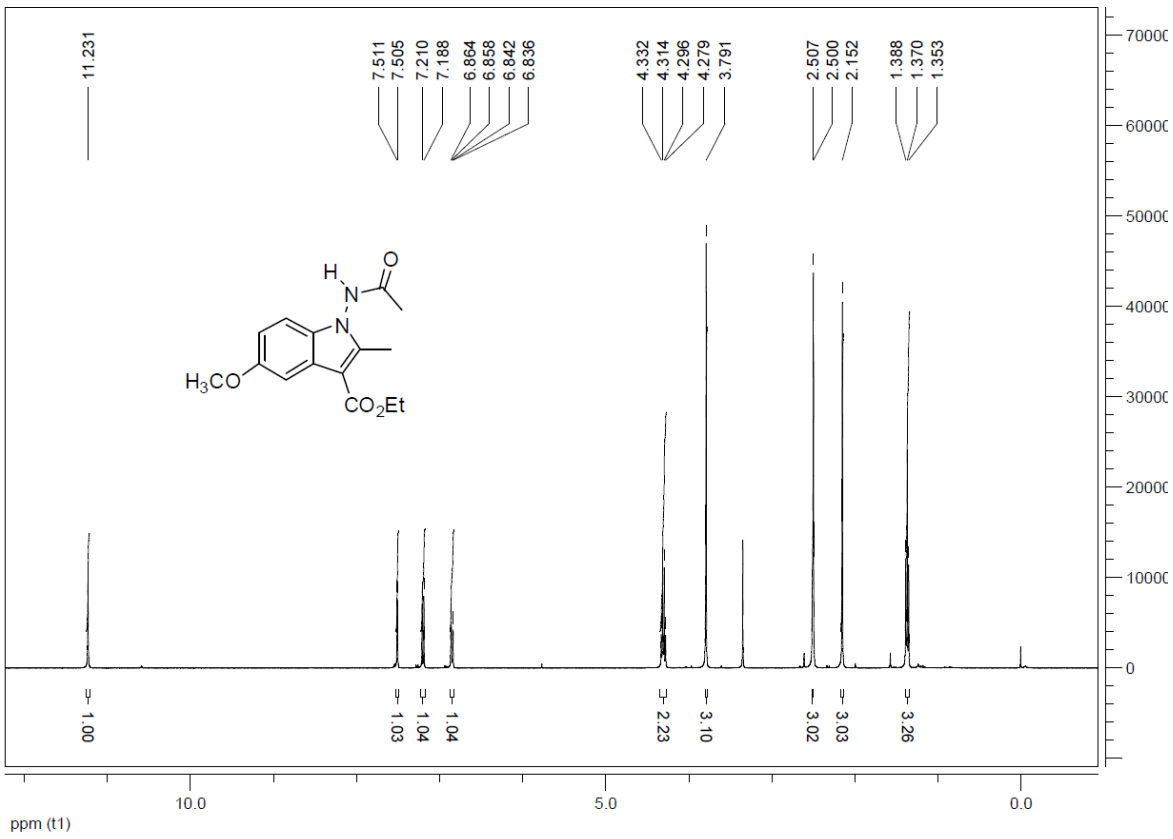
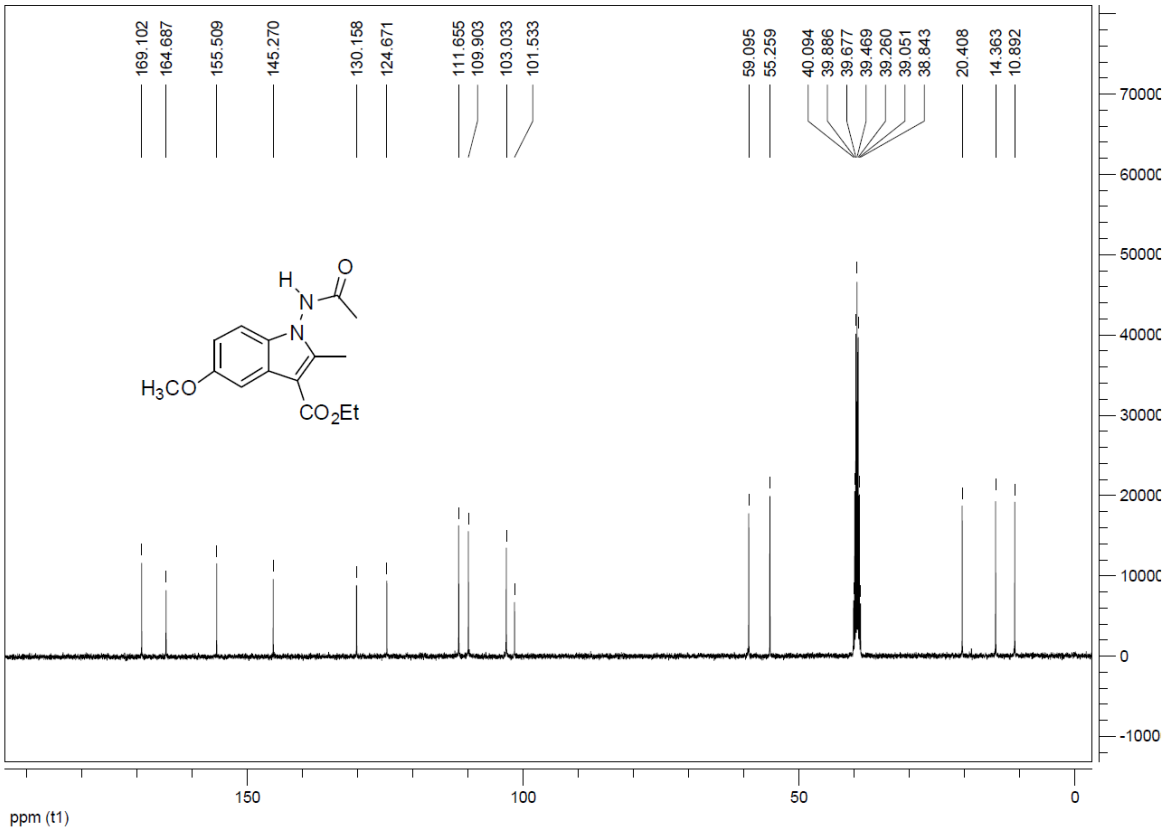
O
N
F3C
CO2Et
0
-50
-100
-150
-200
ppm (t1)


11.231
7.511
7.505
7.210
7.188
6.864
6.858
6.842
6.836
4.332
4.314
4.296
4.279
3.791
2.507
2.500
2.152
1.388
1.370
1.353
1.00
1.03
1.04
1.04
2.23
3.10
3.02
3.03
3.26
H
N
O
N
H3CO
CO2Et
10.0
5.0
0.0
ppm (t1)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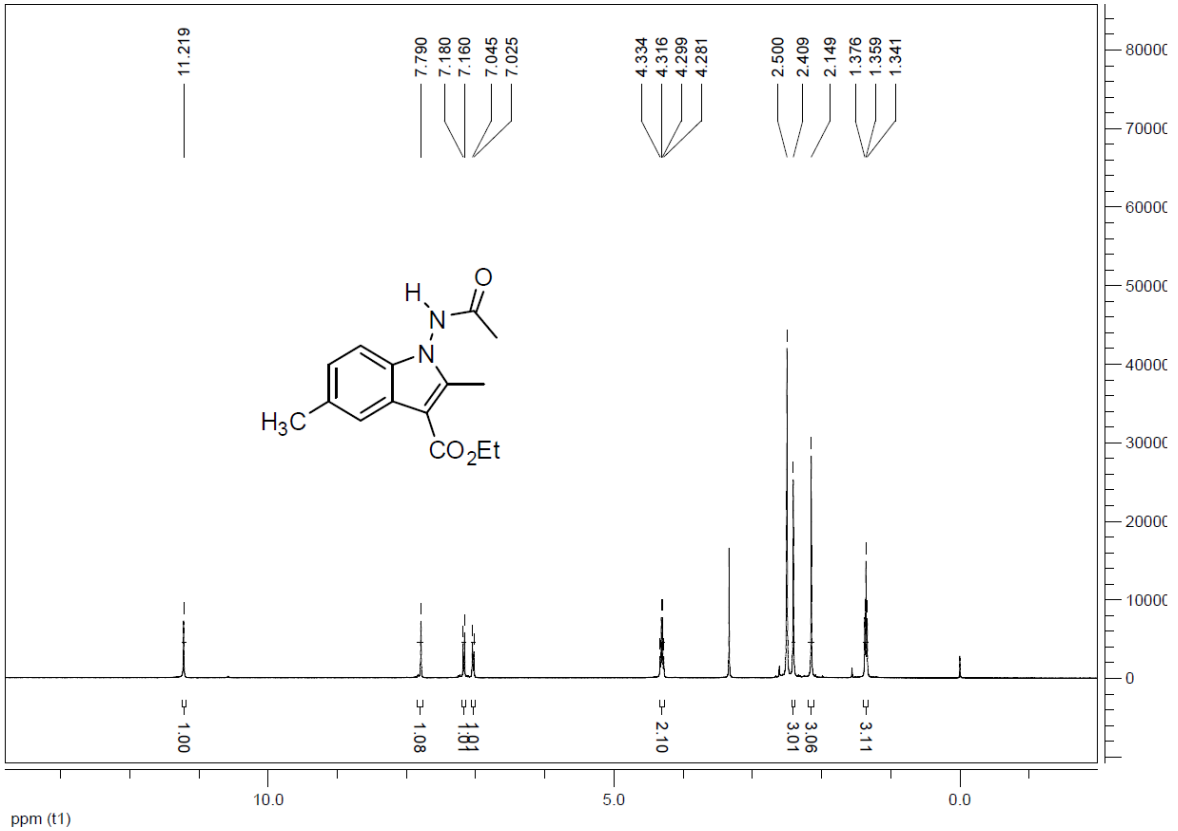
145.270
130.158
124.671
111.655
109.903
103.033
101.533
59.095
55.259
40.094
39.886
39.677
39.469
39.260
39.051
38.843
20.408
14.363
10.892
H
N
O
N
H3CO
CO2Et
150
100
50
0
ppm (t1)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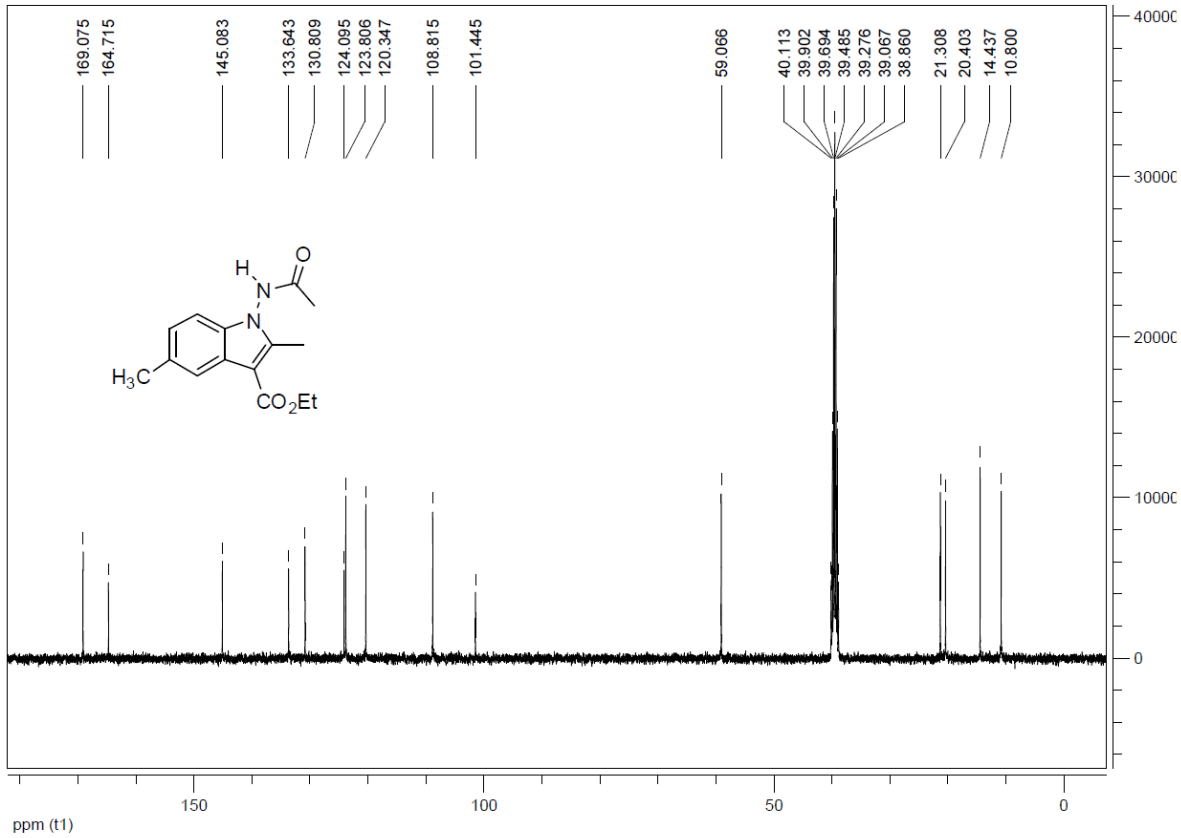
4.316
4.299
4.281
2.500
2.409
2.149
1.376
1.359
1.341
H
N
O
N
H3C
CO2Et
1.00
1.08
1.01
2.10
3.01
3.06
3.11
10.0
5.0
0.0
ppm (t1)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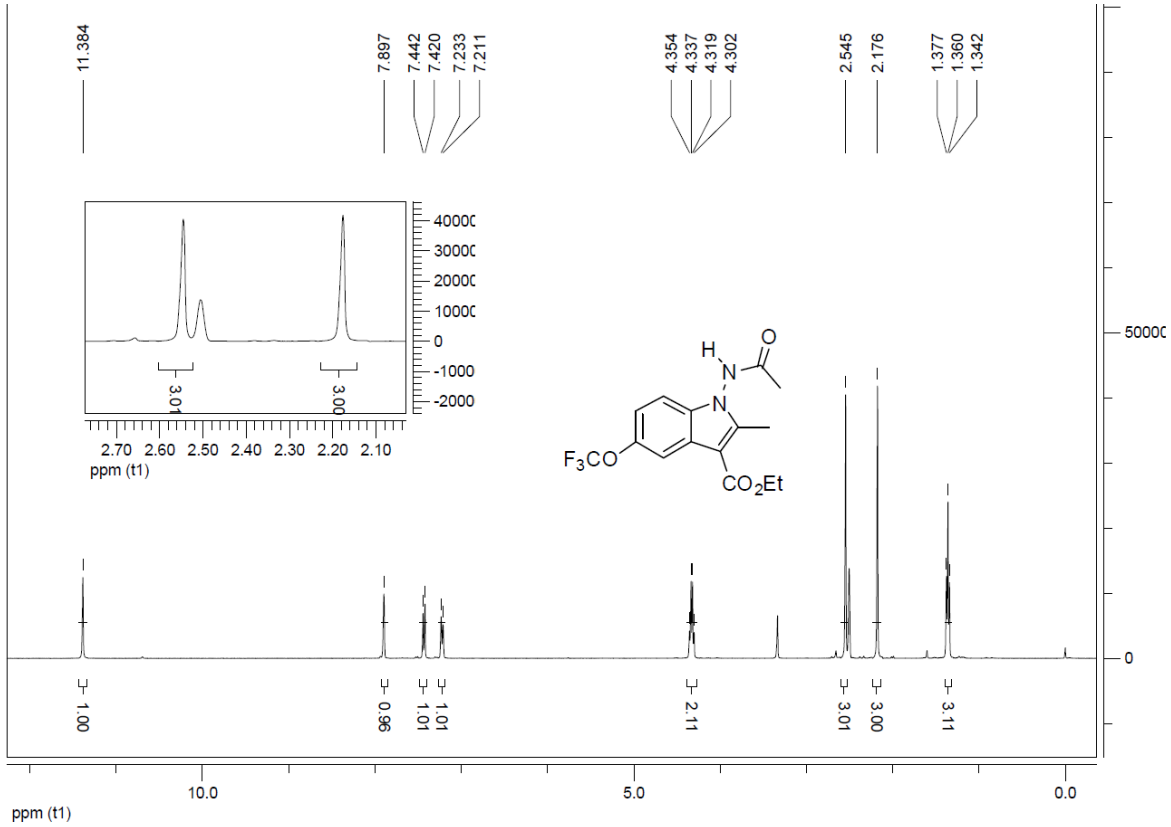
120.347
108.815
101.445
59.066
40.113
39.902
39.694
39.485
39.276
39.067
38.860
21.308
20.403
14.437
10.800
H
N
O
N
H3C
CO2Et
150
100
50
0
ppm (t1)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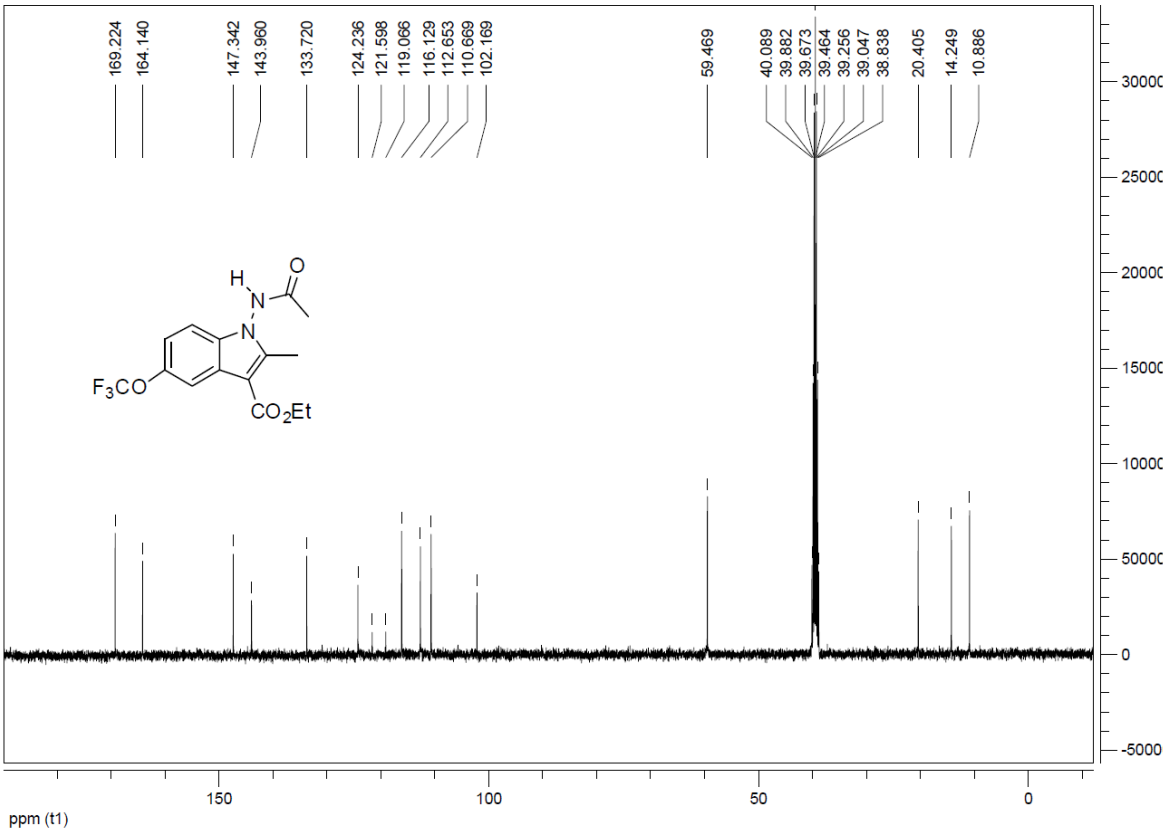
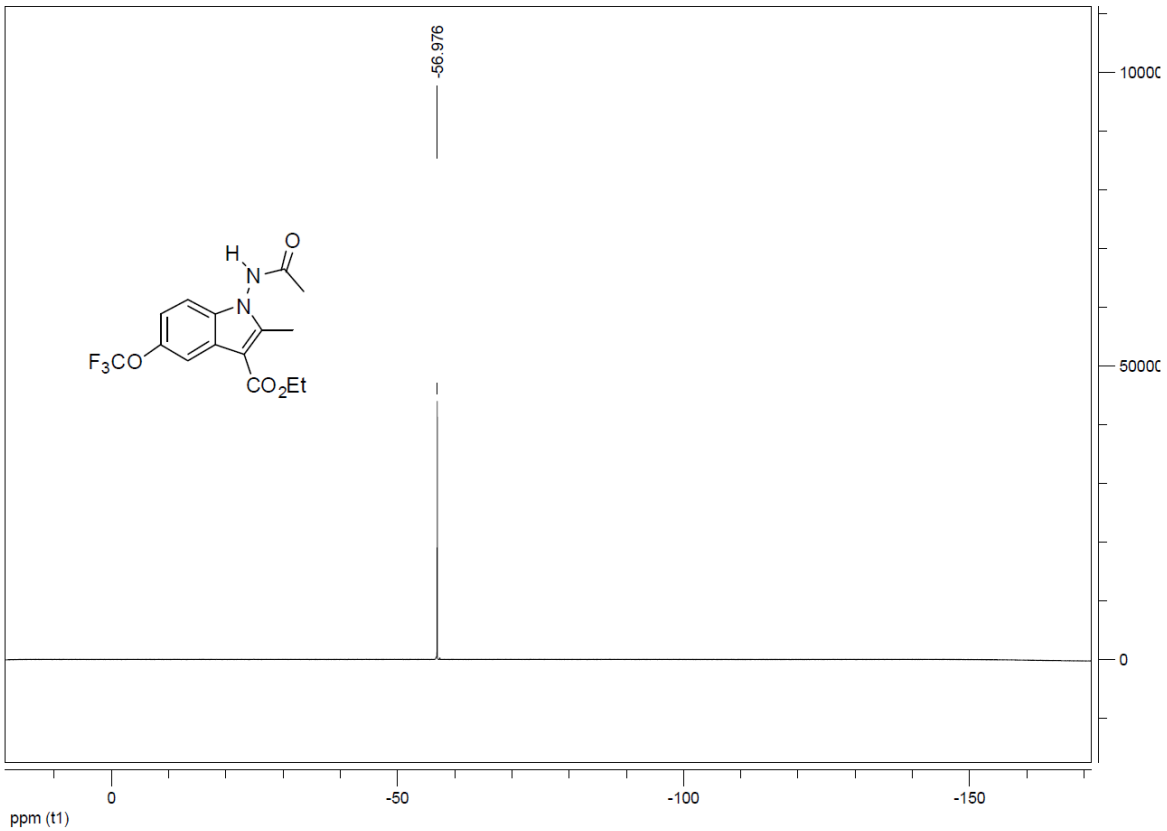
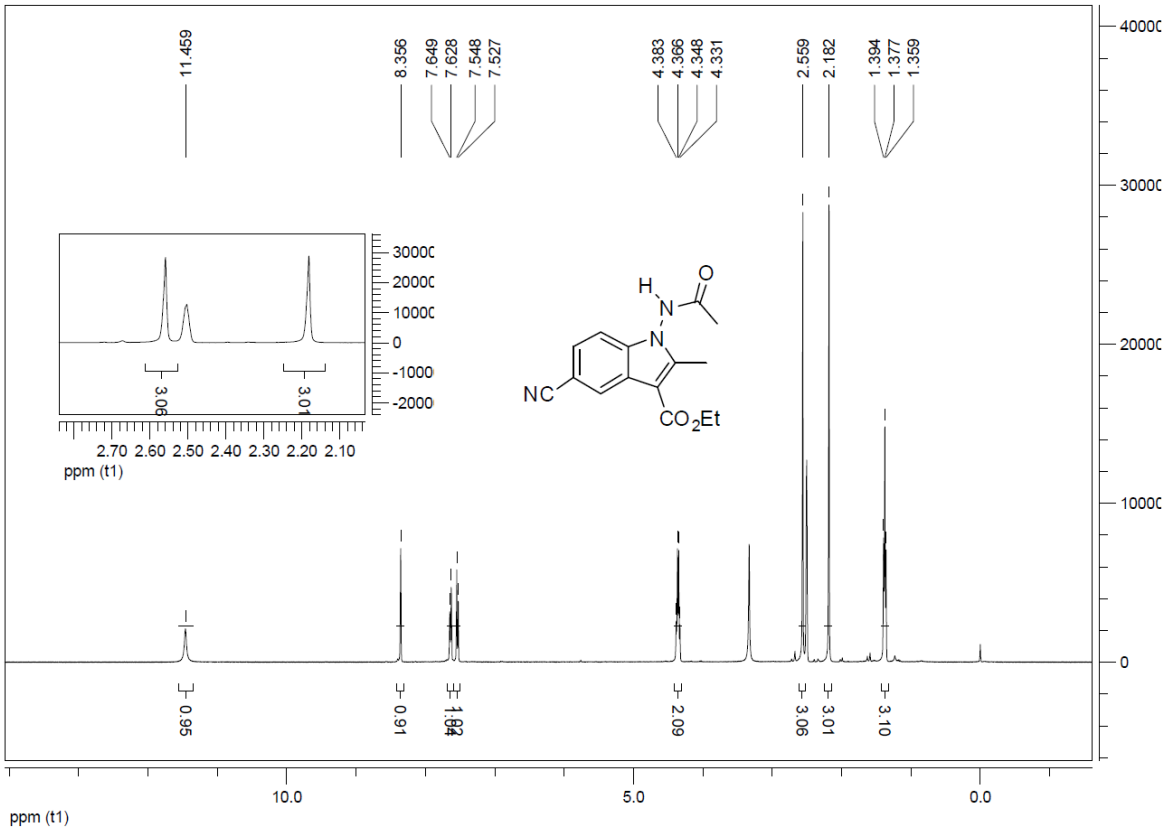
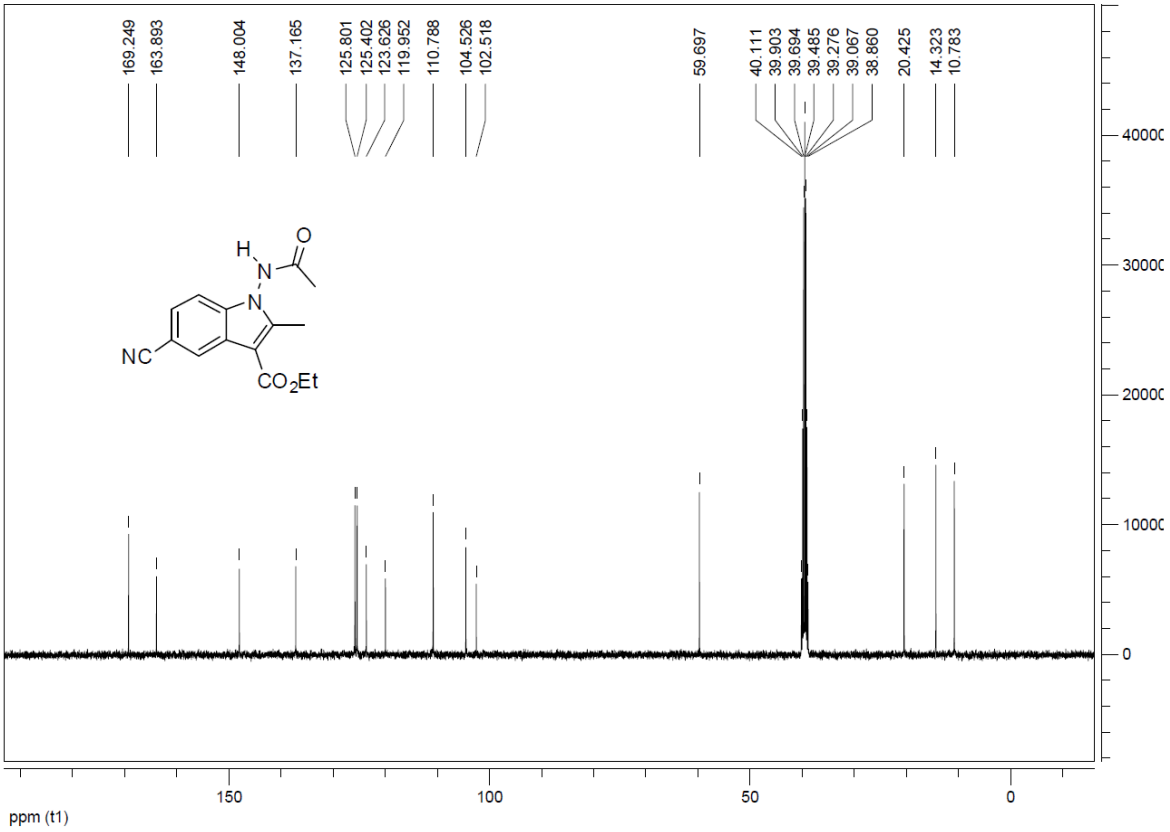
7.233
7.211
4.354
4.337
4.319
4.302
2.545
2.176
1.377
1.360
1.342
3.01
3.00
2.70 2.60 2.50 2.40 2.30 2.20 2.10
ppm (t1)
H
N
O
N
F3CO
CO2Et
1.00
0.96
1.01
1.01
2.11
3.01
3.00
3.11
10.0
5.0
0.0
ppm (t1)


169.224
164.140
147.342
143.960
133.720
124.236
121.598
119.066
116.129
112.653
110.669
102.169
59.469
40.089
39.882
39.673
39.464
39.256
39.047
38.838
20.405
14.249
10.886
H
N
O
N
F3CO
CO2Et
150
100
50
0
ppm (t1)


-56.976
H
N
O
N
F3CO
CO2Et
10000
5000
0
0
-50
-100
-150
ppm (t1)


11.459
8.356
7.649
7.628
7.548
7.527
4.383
4.366
4.348
4.331
2.559
2.182
1.394
1.377
1.359
3.06
3.01
30000
20000
10000
0
-1000
-2000
2.70 2.60 2.50 2.40 2.30 2.20 2.10
ppm (t1)
H
N
O
N
NC
CO2Et
40000
30000
20000
10000
0
0.96
0.91
1.94
2.09
3.06
3.01
3.10
10.0
5.0
0.0
ppm (t1)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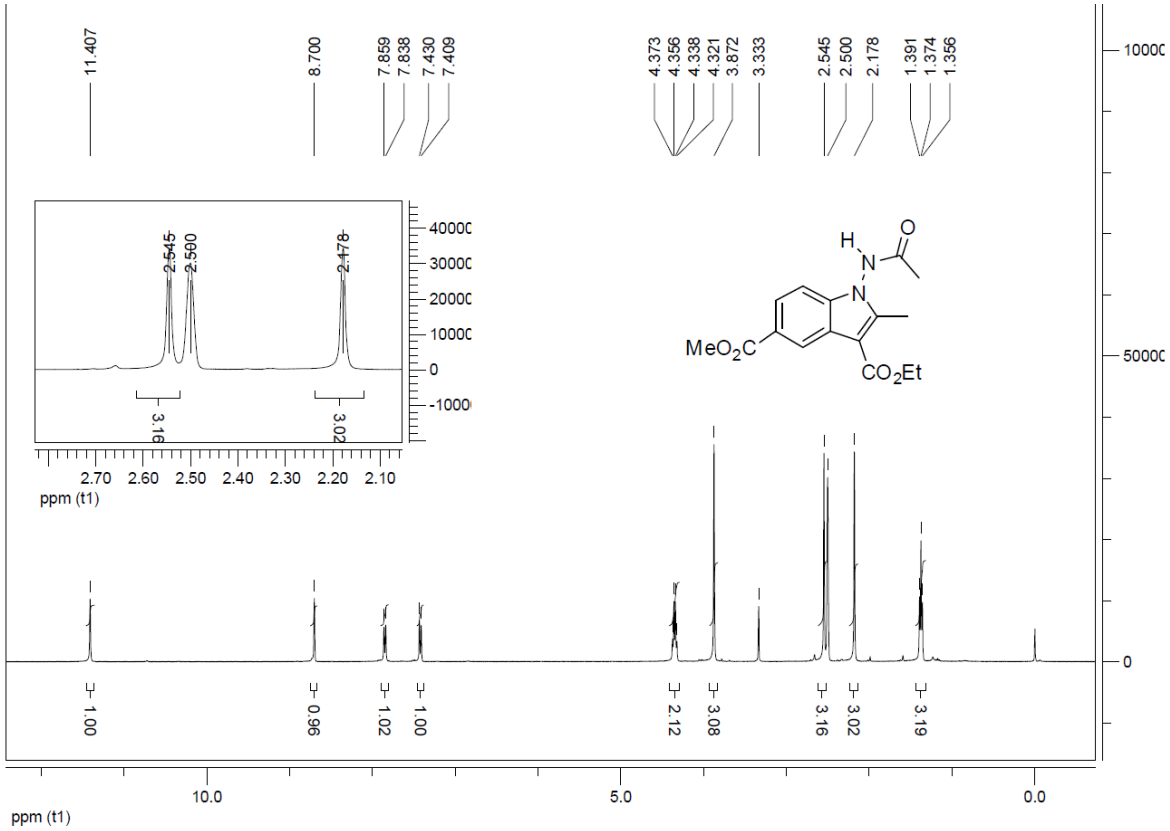
148.004
137.165
125.801
125.402
123.626
119.952
110.788
104.526
102.518
59.697
40.111
39.903
39.694
39.485
39.276
39.067
38.860
20.425
14.323
10.783
NC
CO2Et
ppm (t1)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8.700
7.859
7.838
7.430
7.409
4.373
4.356
4.338
4.321
3.872
3.333
2.545
2.500
2.178
1.391
1.374
1.356
MeO2C
CO2Et
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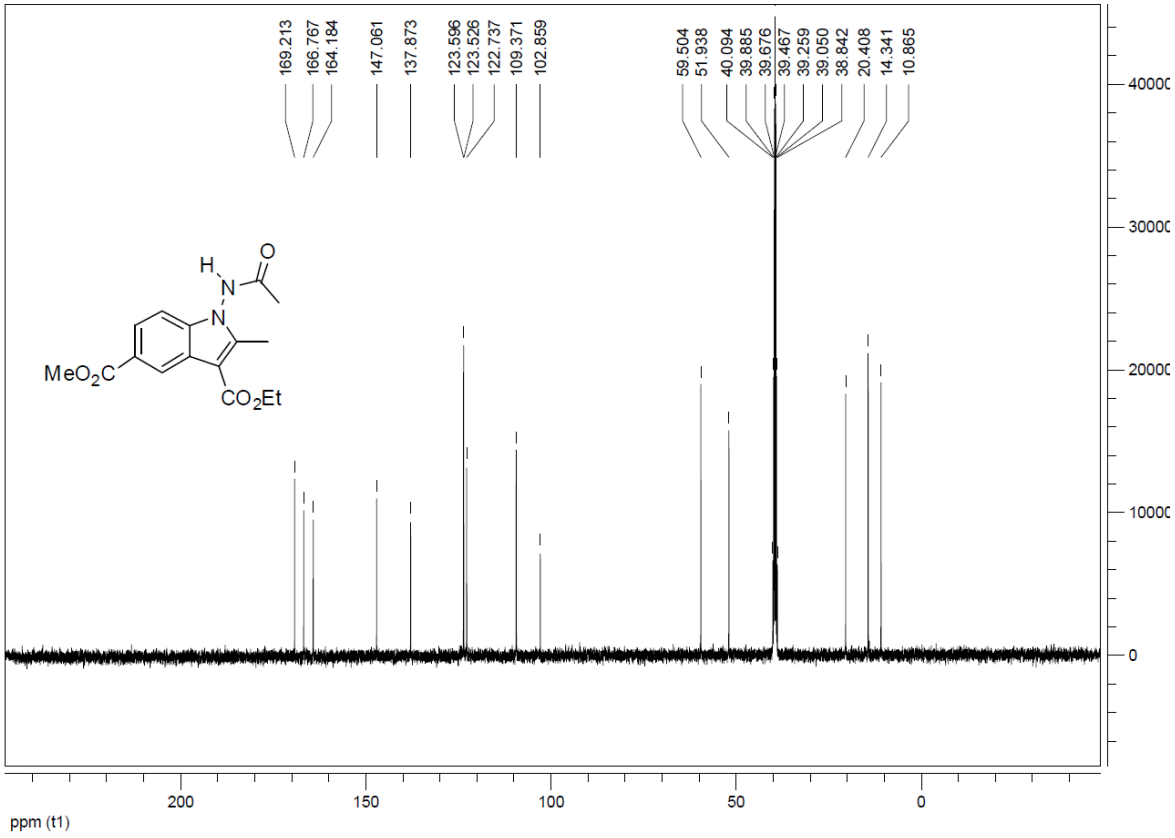
0.96
1.02
1.00
2.12
3.08
3.16
3.02
3.19
ppm (t1)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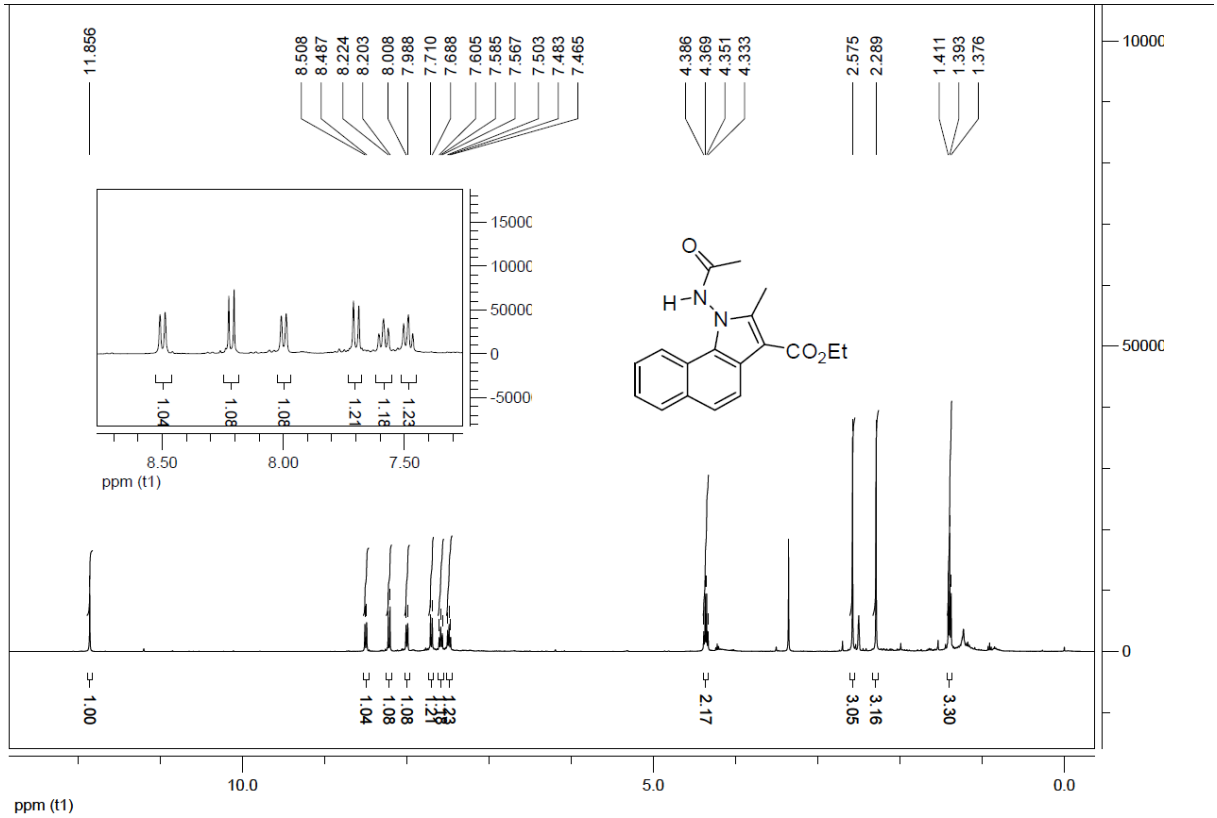
166.767
164.184
147.061
137.873
123.596
123.526
122.737
109.371
102.859
59.504
51.938
40.094
39.885
39.676
39.467
39.259
39.050
38.842
20.408
14.341
10.865
MeO2C
CO2Et
ppm (t1)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8.487
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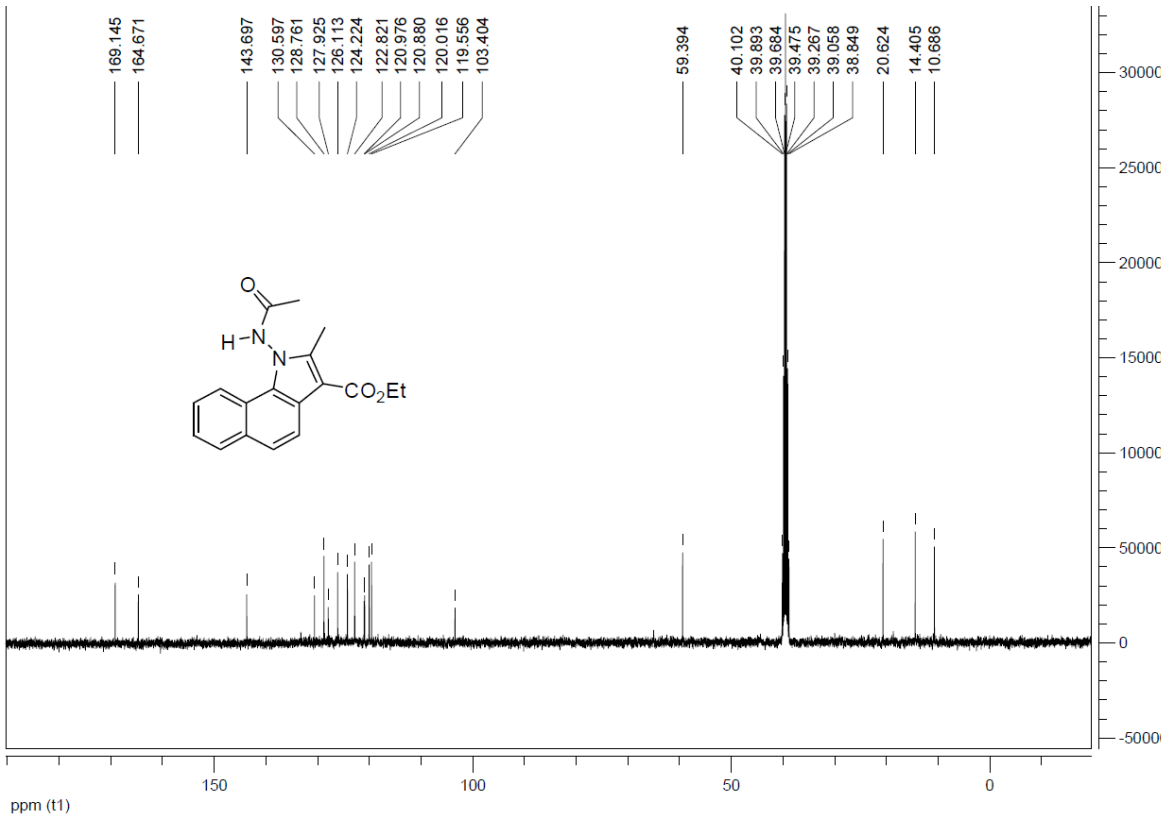
8.203
8.008
7.988
7.710
7.688
7.605
7.585
7.567
7.503
7.483
7.465
4.386
4.369
4.351
4.333
2.575
2.289
1.411
1.393
1.376
CO2Et
1.00
1.04
1.08
2.17
3.05
3.16
3.30
ppm (t1)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164.671
143.697
130.597
128.761
127.925
126.113
124.224
122.821
120.976
120.880
120.016
119.556
103.404
59.394
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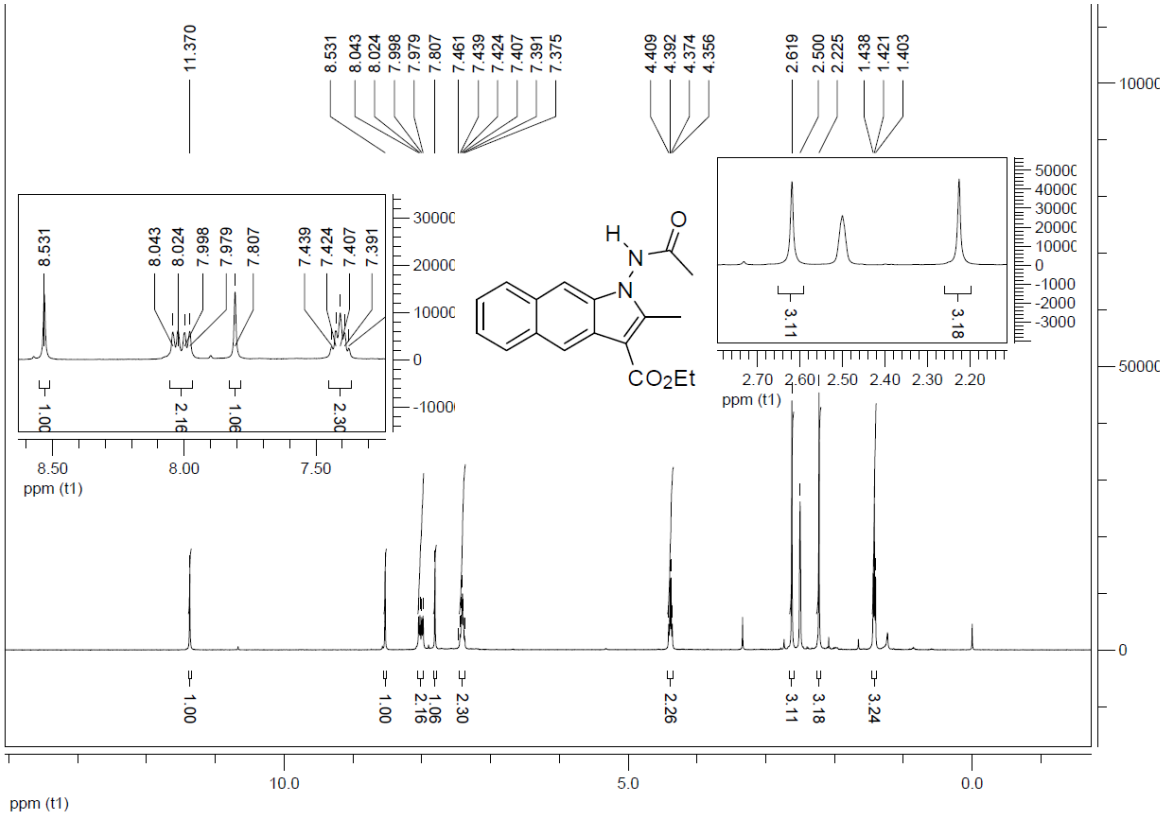
39.475
39.267
39.058
38.849
20.624
14.405
10.686
CO2Et
ppm (t1)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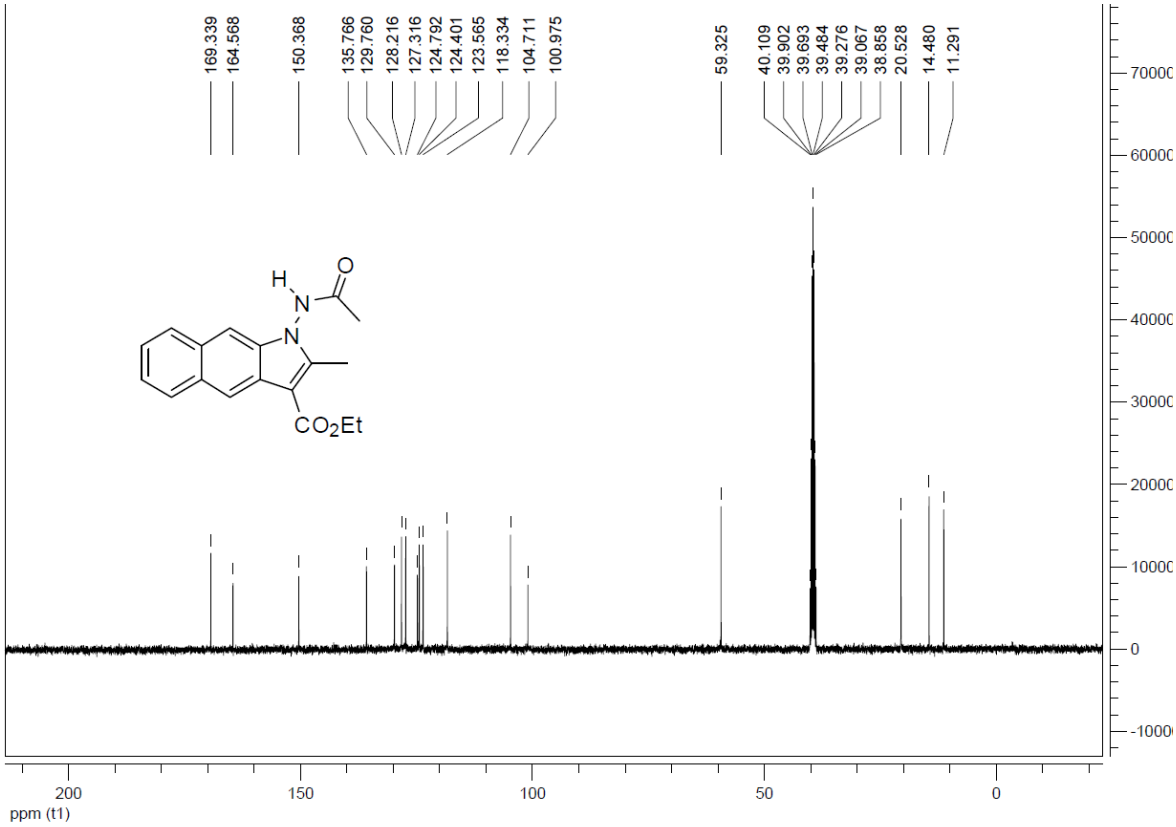
8.531
8.043
8.024
7.998
7.979
7.807
7.461
7.439
7.424
7.407
7.391
7.375
4.409
4.392
4.374
4.356
2.619
2.500
2.225
1.438
1.421
1.403
CO2Et
ppm (t1)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135.766
129.760
128.216
127.316
124.792
124.401
123.565
118.334
104.711
100.975
59.325
40.109
39.902
39.693
39.484
39.276
39.067
38.858
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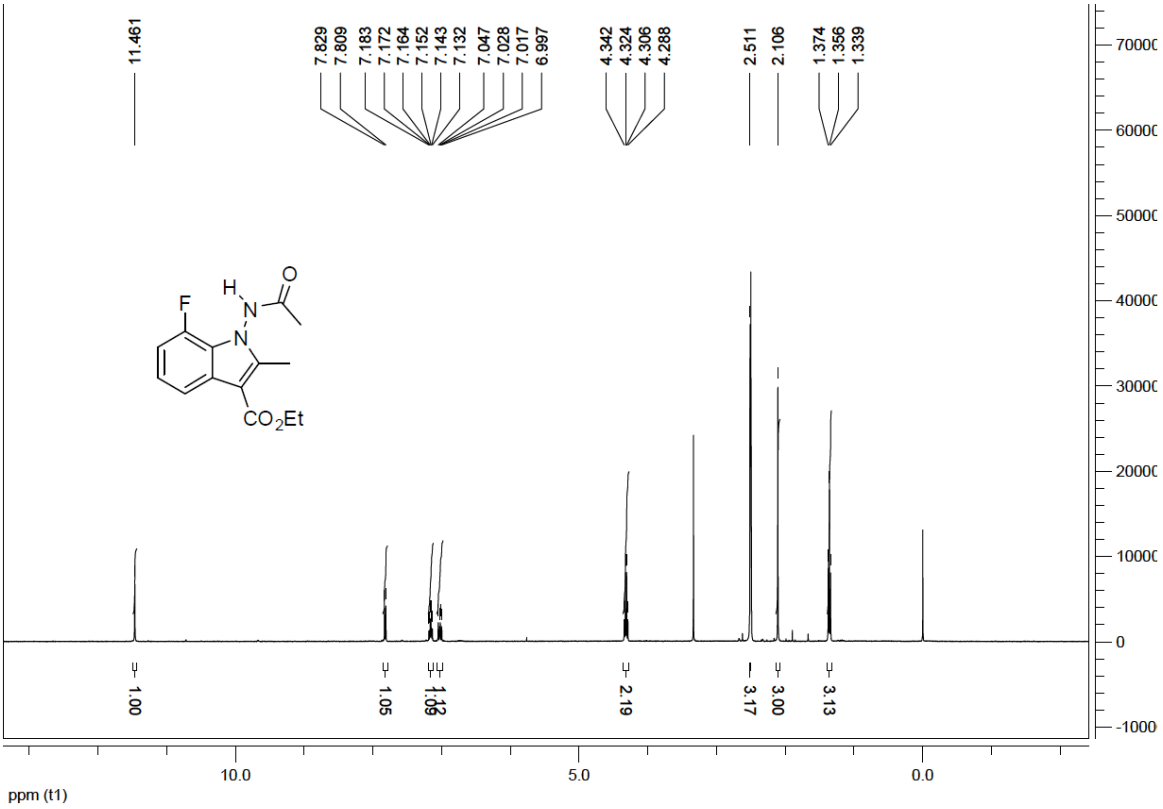
14.480
11.291
H
N
O
N
CO2Et
200
150
100
50
0
ppm (t1)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7.809
7.183
7.172
7.164
7.152
7.143
7.132
7.047
7.028
7.017
6.997
4.342
4.324
4.306
4.288
2.511
2.106
1.374
1.356
1.339
F
H
N
O
N
CO2Et
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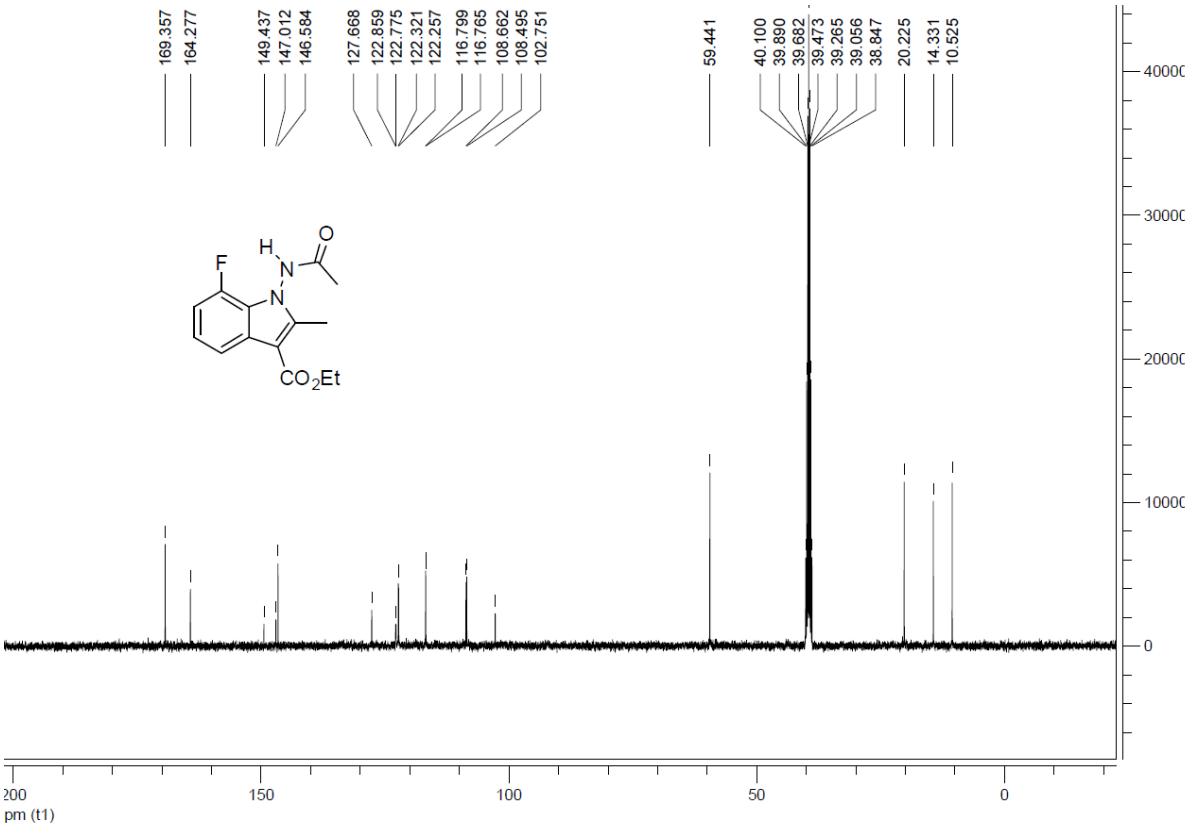
1.05
2.19
3.17
3.00
3.13
10.0
5.0
0.0
ppm (t1)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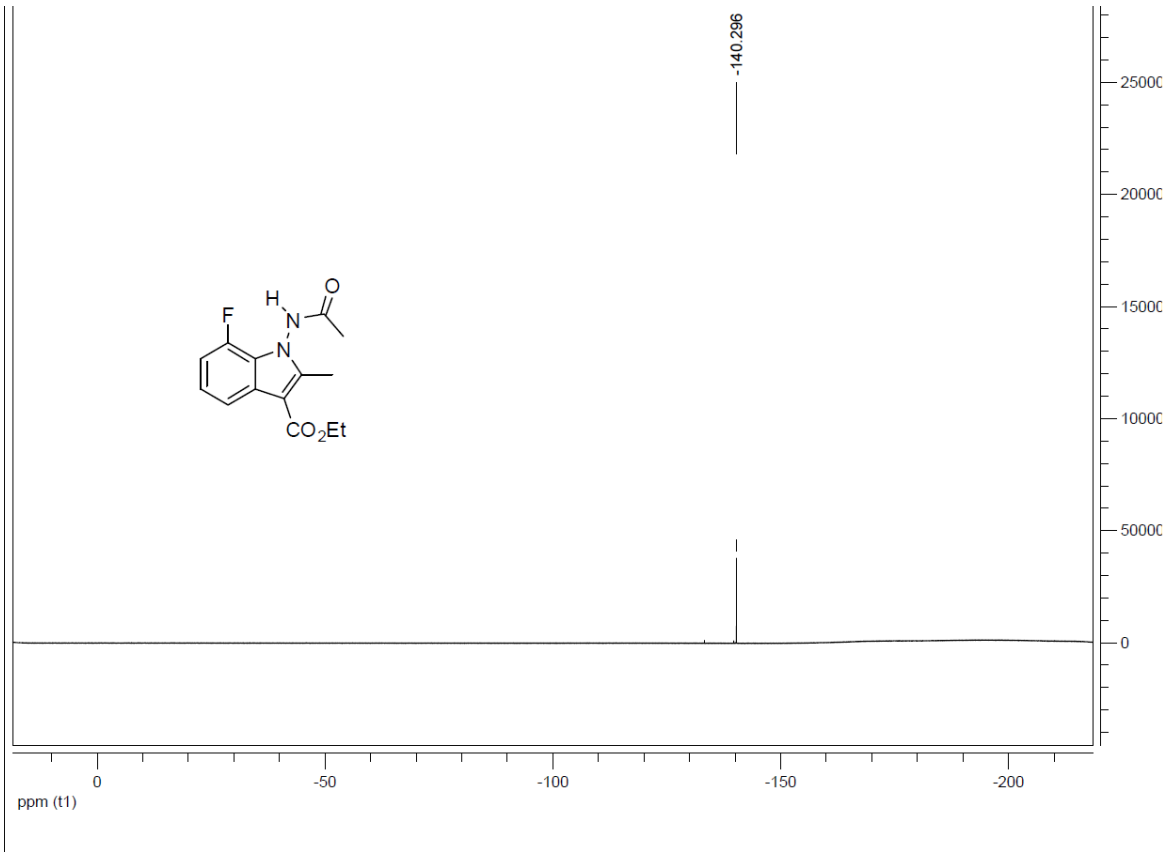
164.277
149.437
147.012
146.584
127.668
122.859
122.775
122.321
122.257
116.799
116.765
108.662
108.495
102.751
59.441
40.100
39.890
39.682
39.473
39.265
39.056
38.847
20.225
14.331
10.525
F
H
N
O
N
CO2Et
40000
30000
20000
10000
0
200
150
100
50
0
pm (t1)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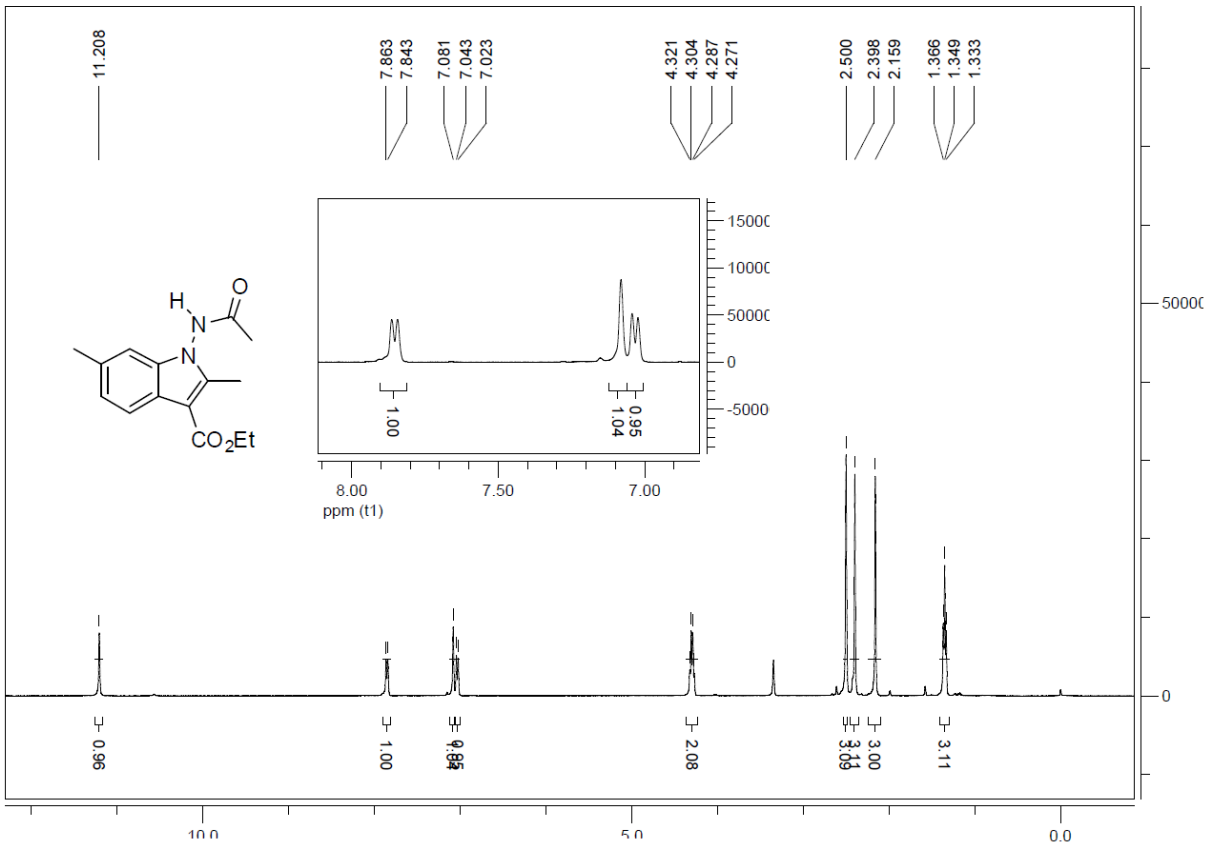
F
H
N
O
N
CO2Et
25000
20000
15000
10000
50000
0
0
-50
-100
-150
-200
ppm (t1)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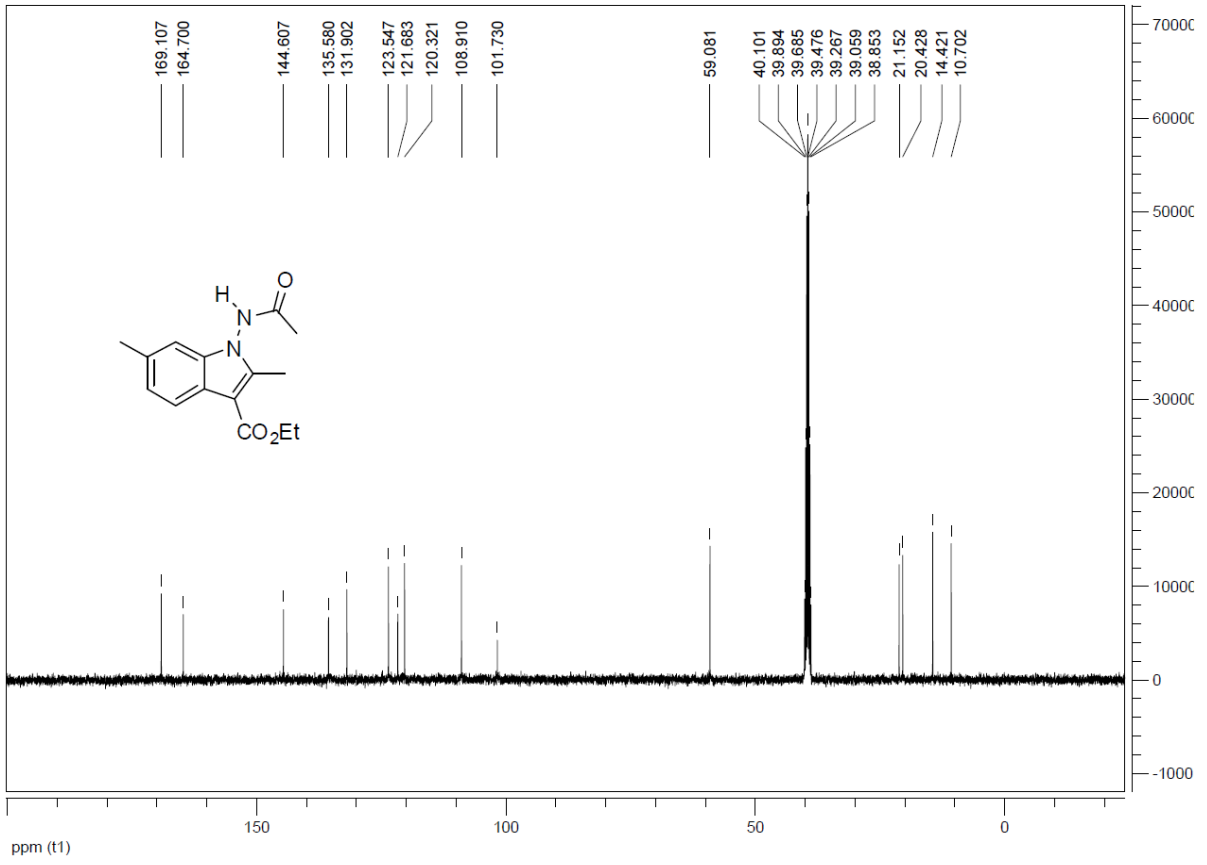
7.843
7.081
7.043
7.023
4.321
4.304
4.287
4.271
2.500
2.398
2.159
1.366
1.349
1.333
H
N
O
N
CO2Et
1.00
0.95
1.04
8.00
7.50
7.00
ppm (t1)
0.96
1.00
2.08
3.00
3.11
3.11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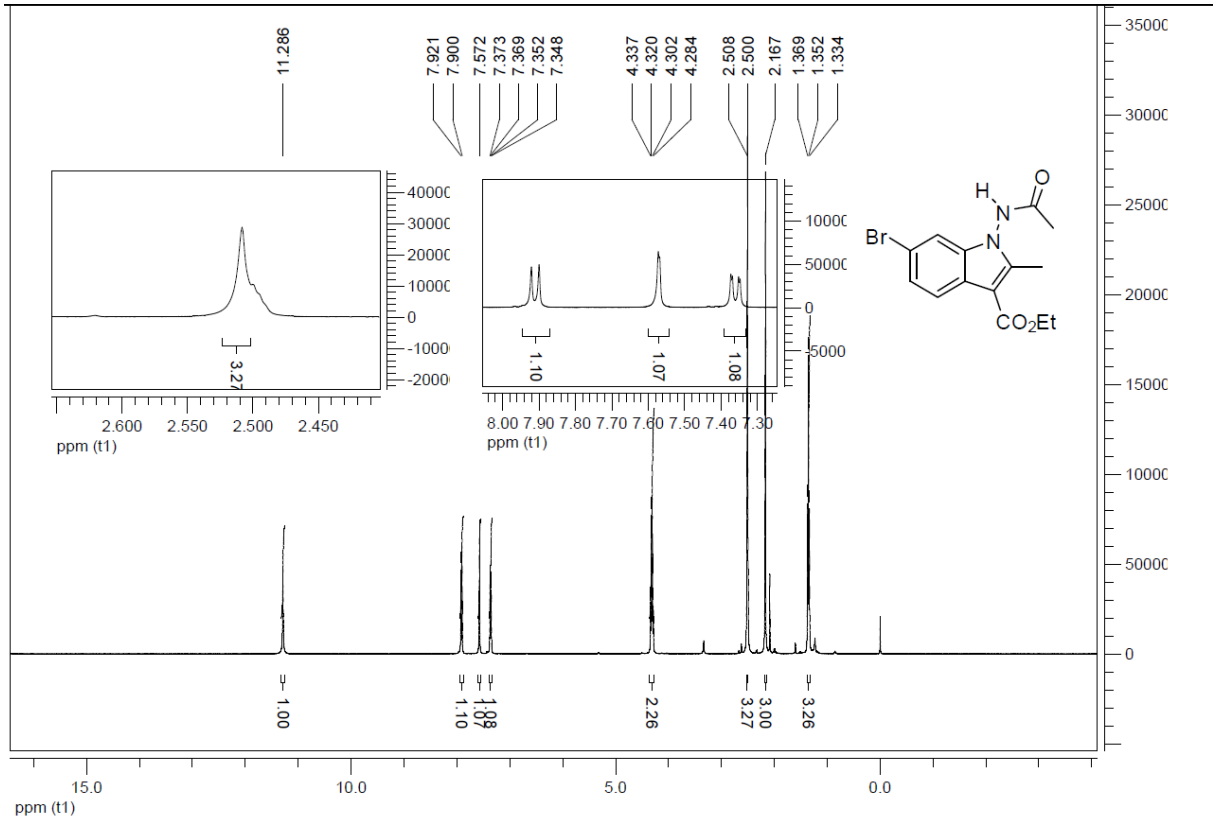
131.902
123.547
121.683
120.321
108.910
101.730
59.081
40.101
39.894
39.685
39.476
39.267
39.059
38.853
21.152
20.428
14.421
10.702
H
N
O
N
CO2Et
150
100
50
0
ppm (t1)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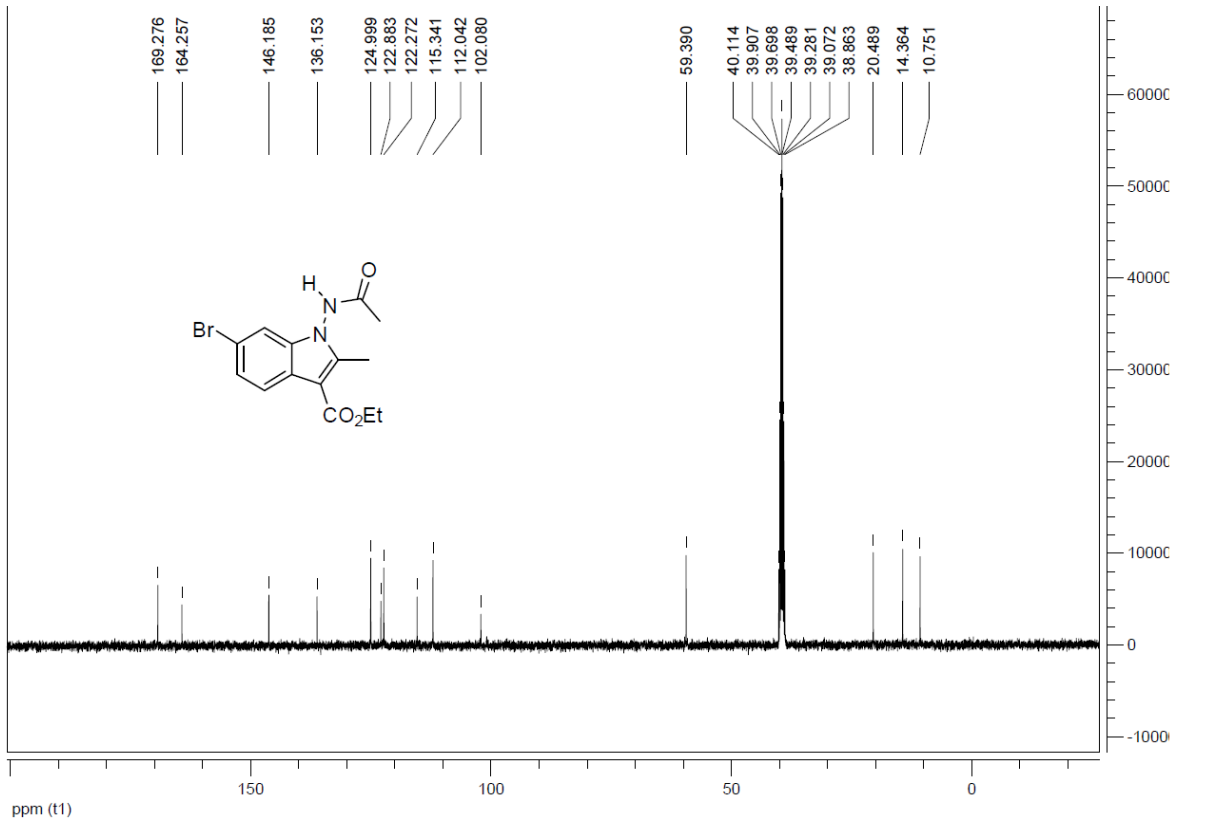
7.900
7.572
7.373
7.369
7.352
7.348
4.337
4.320
4.302
4.284
2.508
2.500
2.167
1.369
1.352
1.334
3.27
1.10
1.07
1.08
2.600 2.550 2.500 2.450
ppm (t1)
8.00 7.90 7.80 7.70 7.60 7.50 7.40 7.30
ppm (t1)
Br
H
N
O
CO2Et
1.00
1.10
1.07
1.08
2.26
3.27
3.00
3.29
15.0
10.0
5.0
0.0
ppm (t1)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122.272
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102.080
59.390
40.114
39.907
39.698
39.489
39.281
39.072
38.863
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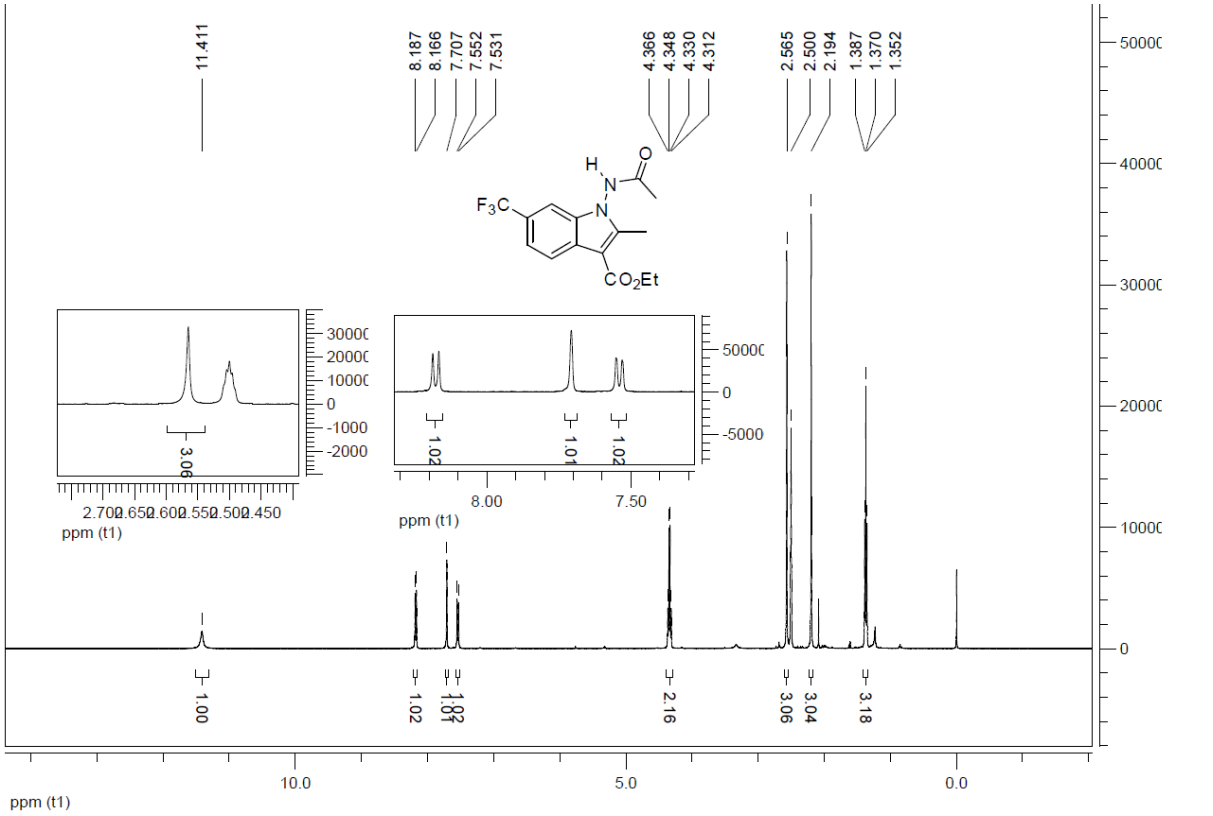
14.364
10.751
Br
H
N
O
CO2Et
150
100
50
0
ppm (t1)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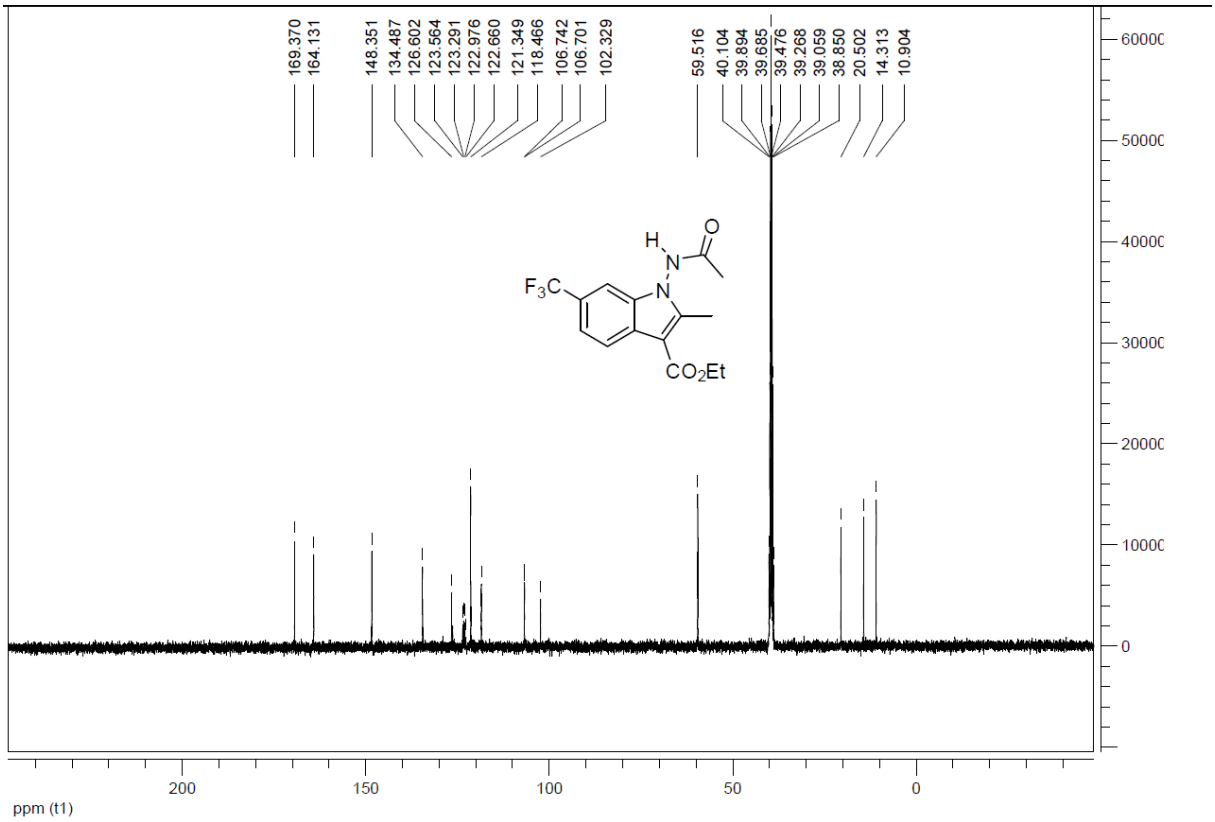
8.187
8.166
7.707
7.552
7.531
4.366
4.348
4.330
4.312
2.565
2.500
2.194
1.387
1.370
1.352
F3C
CO2Et
ppm (t1)
1.00
1.02
1.01
2.16
3.06
3.04
3.18
10.0
5.0
0.0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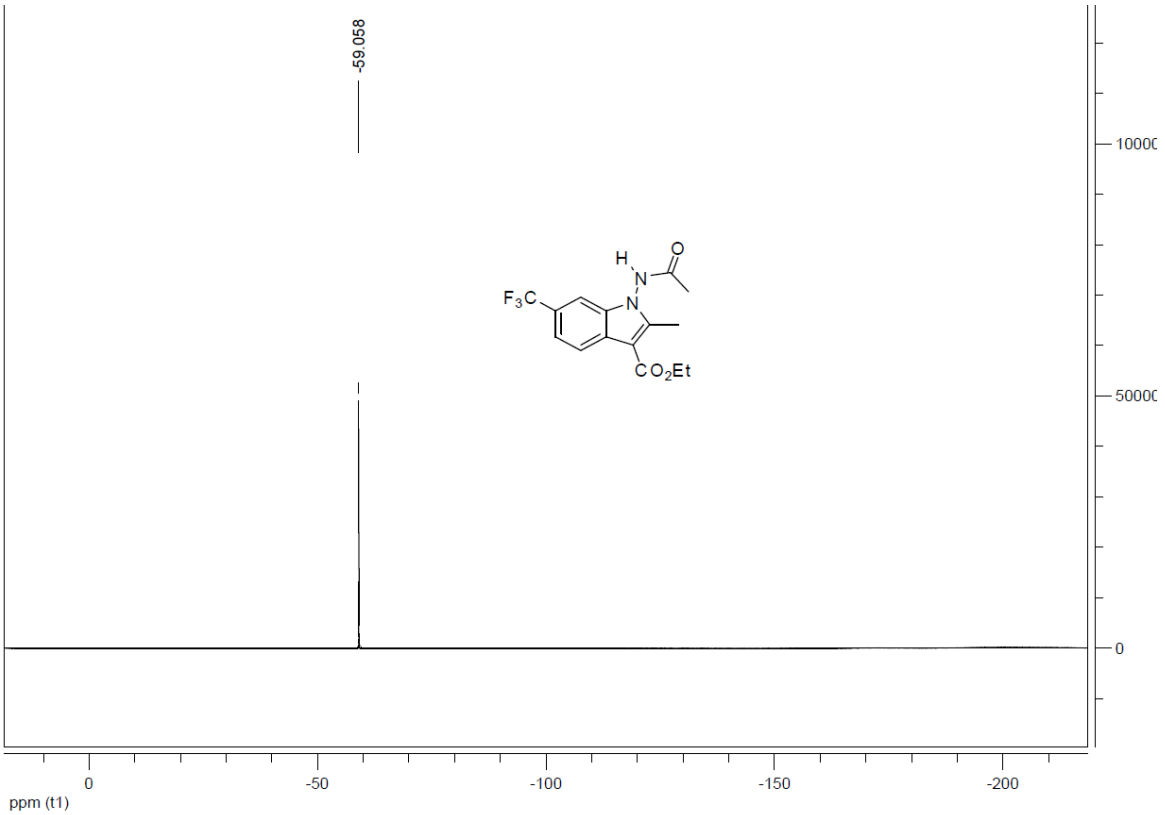
123.291
122.976
122.660
121.349
118.466
106.742
106.701
102.329
59.516
40.104
39.894
39.685
39.476
39.268
39.059
38.850
20.502
14.313
10.904
F3C
CO2Et
ppm (t1)
200
150
100
50
0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0
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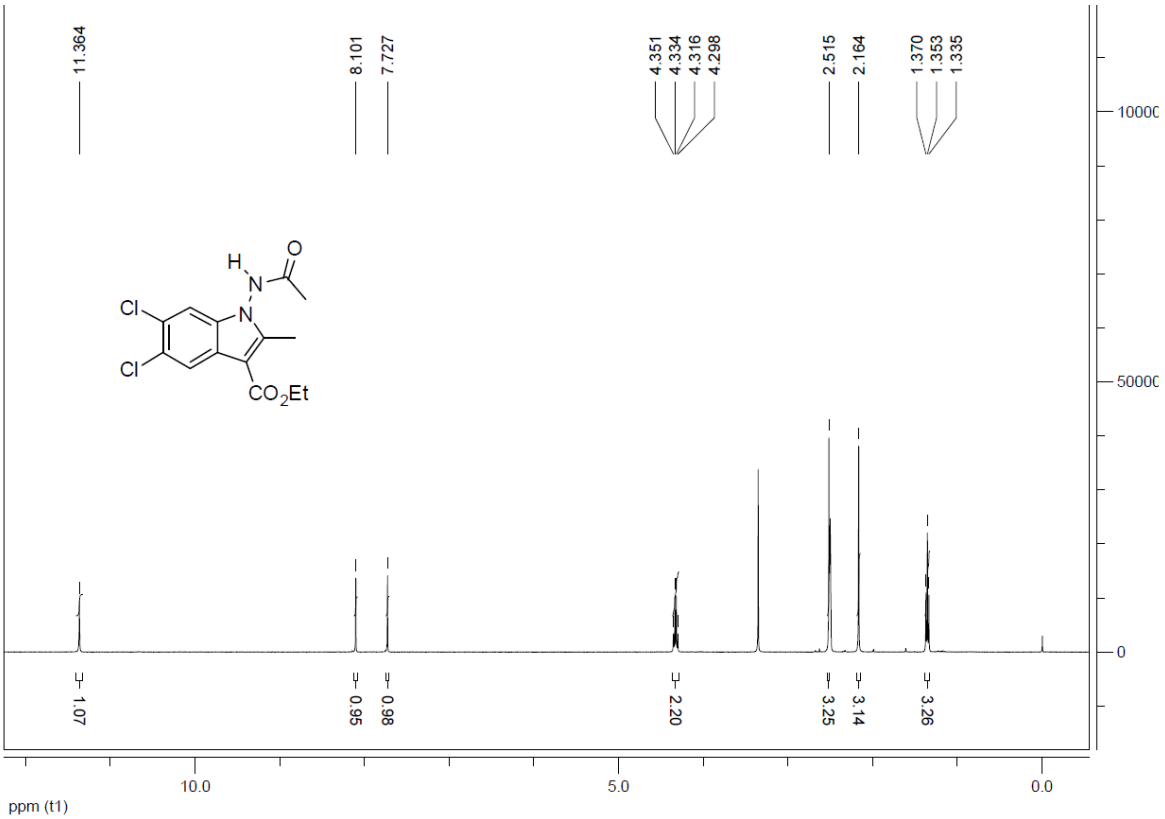
-100
-150
-200
ppm (t1)
H
N
O
F3C
N
CO2Et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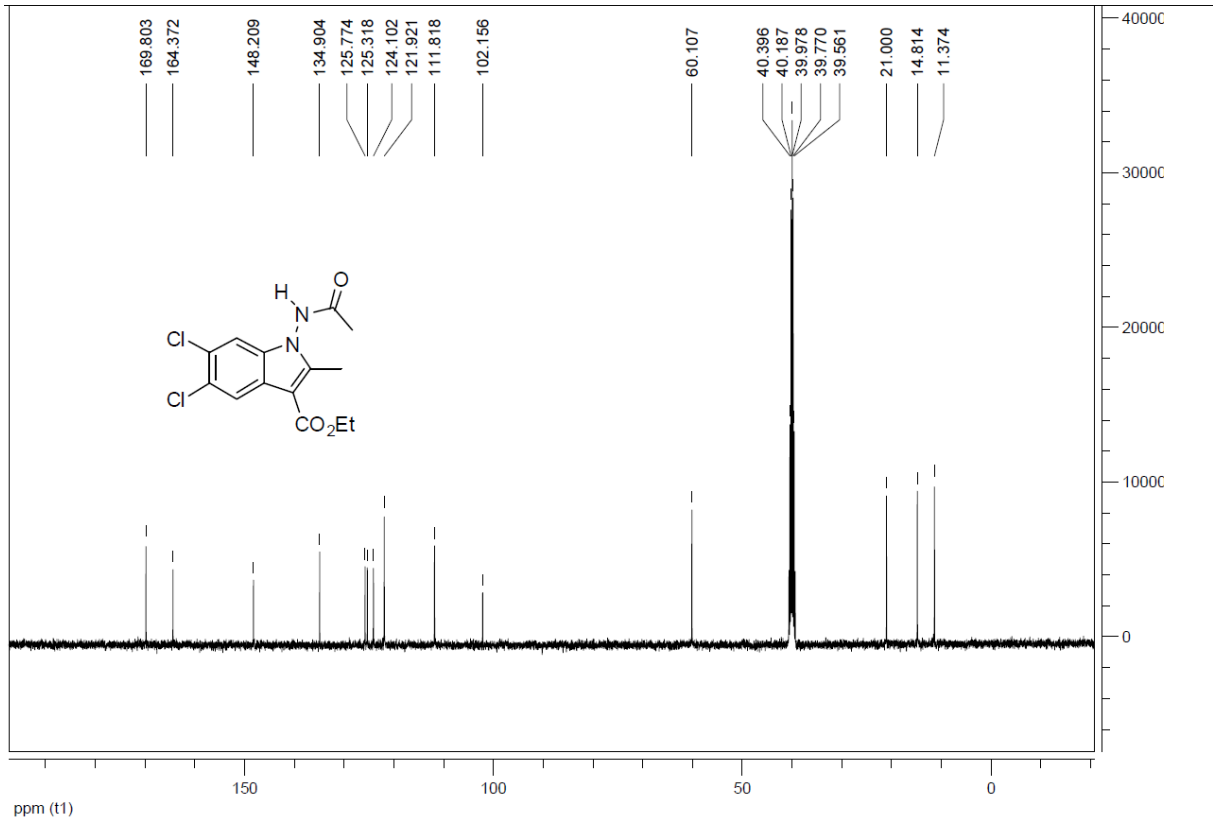
4.298
2.515
2.164
1.370
1.353
1.335
10000
50000
0
1.07
0.95
0.98
2.20
3.25
3.14
3.26
10.0
5.0
0.0
ppm (t1)
H
N
O
Cl
Cl
N
CO2Et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125.318
124.102
121.921
111.818
102.156
60.107
40.396
40.187
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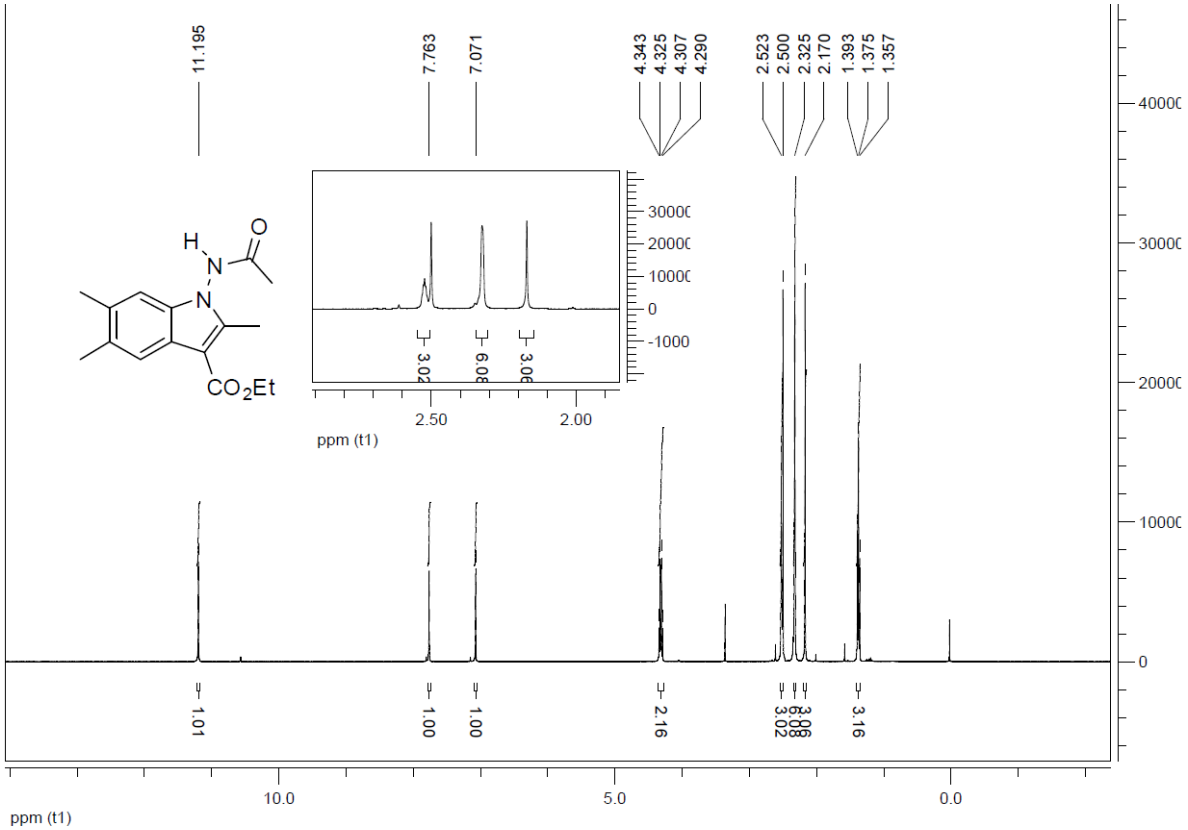
39.770
39.561
21.000
14.814
11.374
Cl
Cl
H
N
O
N
CO2Et
ppm (t1)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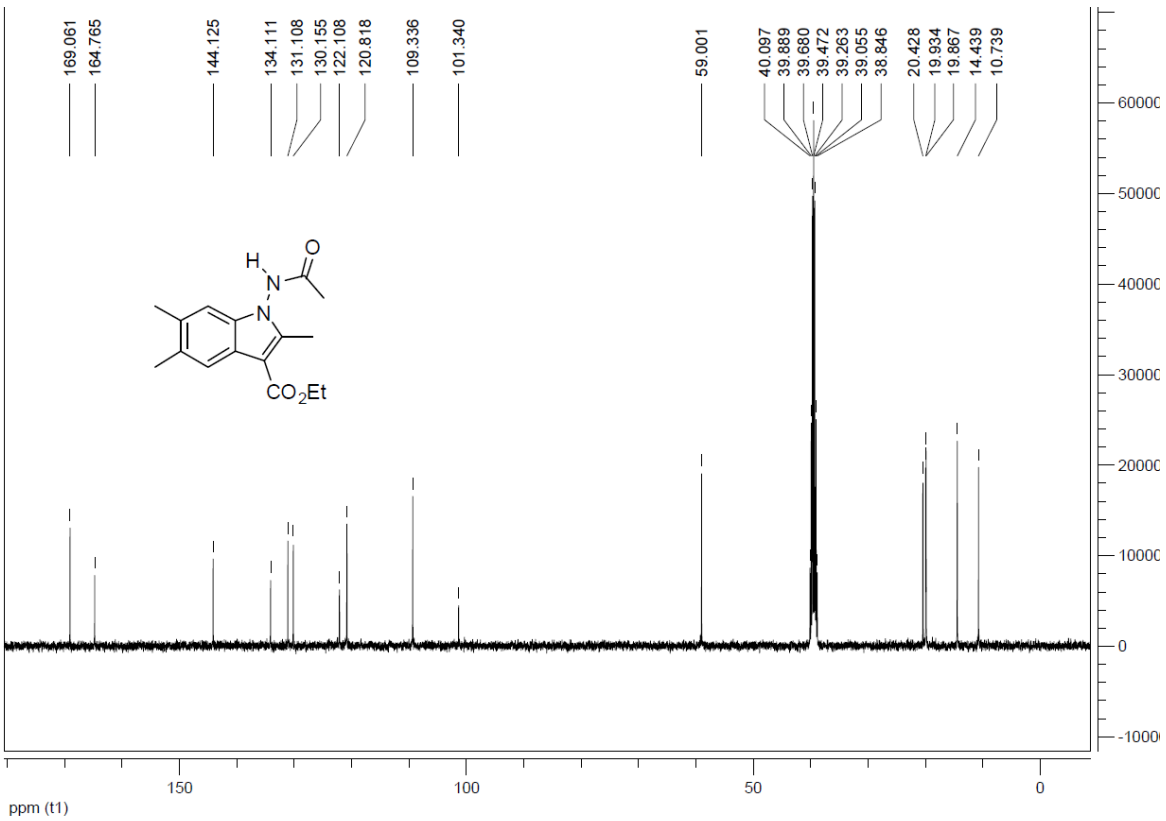
2.500
2.325
2.170
1.393
1.375
1.357
H
N
O
N
CO2Et
3.02
6.08
3.06
ppm (t1)
1.01
1.00
1.00
2.16
3.02
3.06
3.16
ppm (t1)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131.108
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120.818
109.336
101.340
59.001
40.097
39.889
39.680
39.472
39.263
39.055
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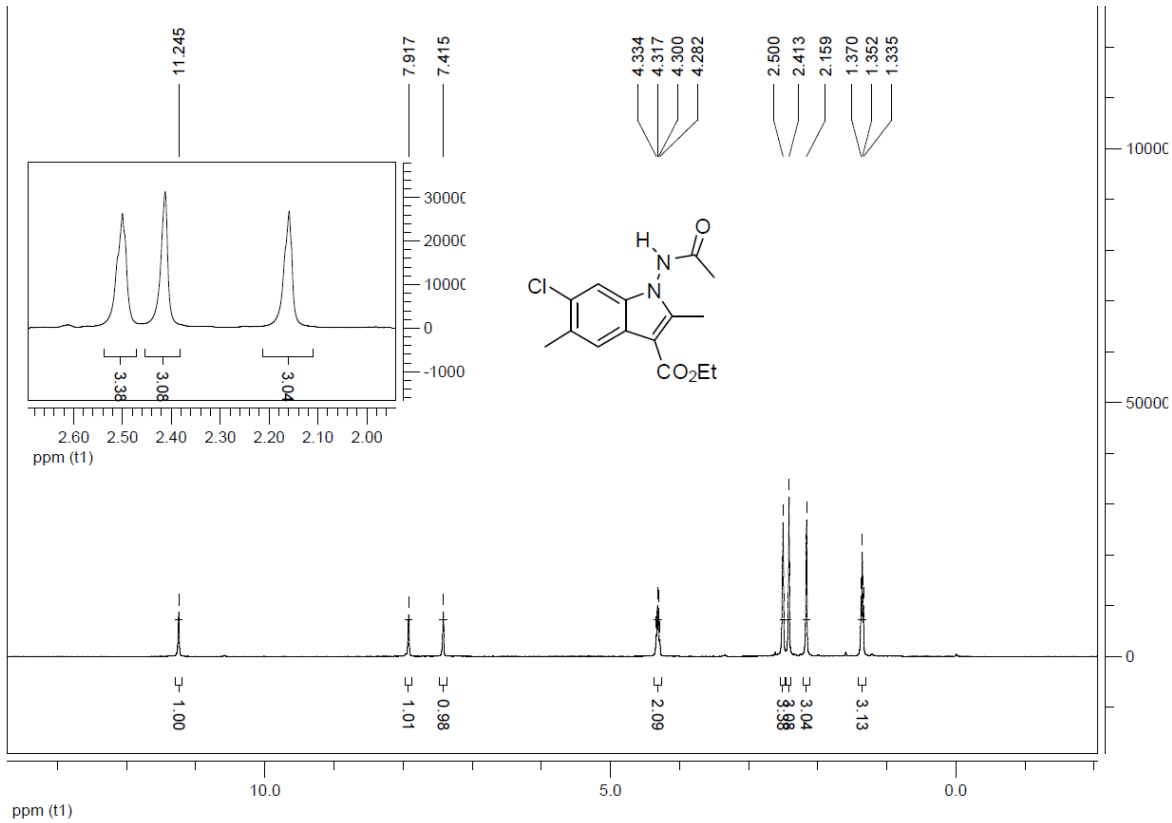
19.934
19.867
14.439
10.739
H
N
O
N
CO2Et
ppm (t1)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2.159
1.370
1.352
1.335
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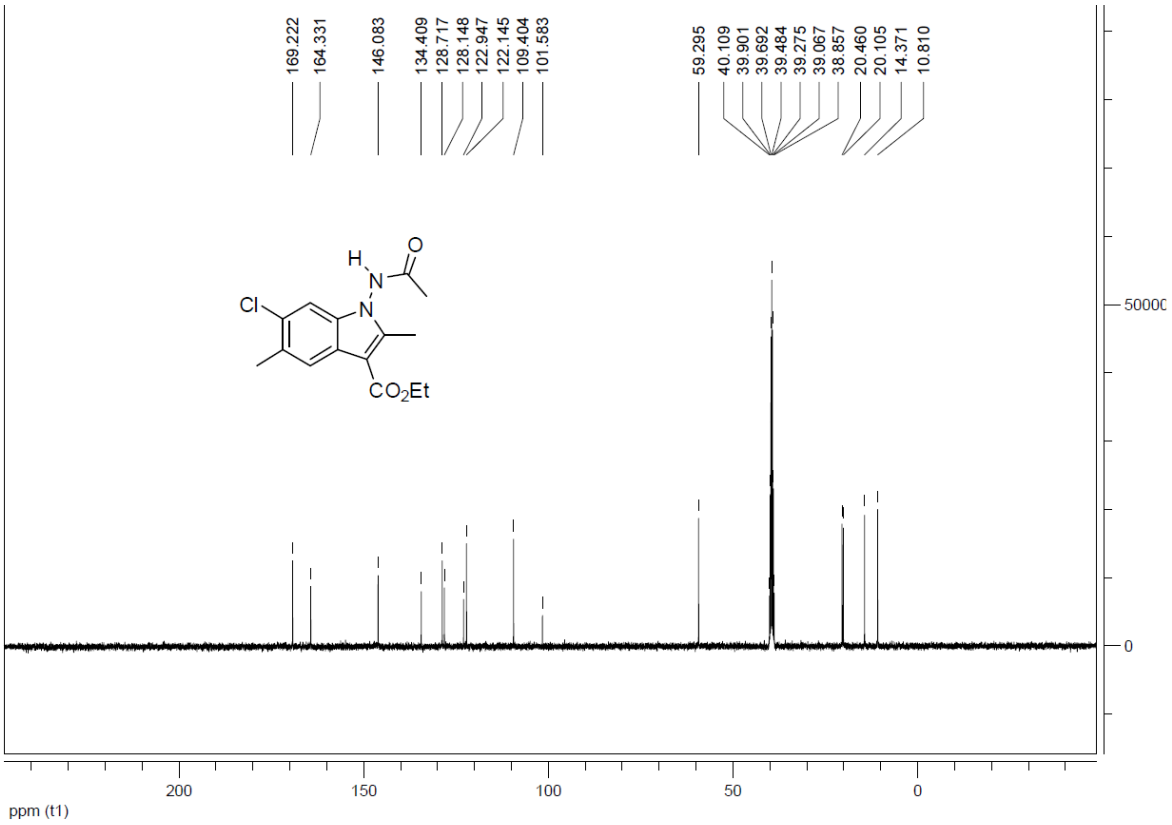
3.08
3.04
Cl
CO2Et
1.00
1.01
0.98
2.09
3.13
ppm (t1)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122.145
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101.583
59.295
40.109
39.901
39.692
39.484
39.275
39.067
38.857
20.460
20.105
14.371
10.810
H
N
O
Cl
N
CO2Et
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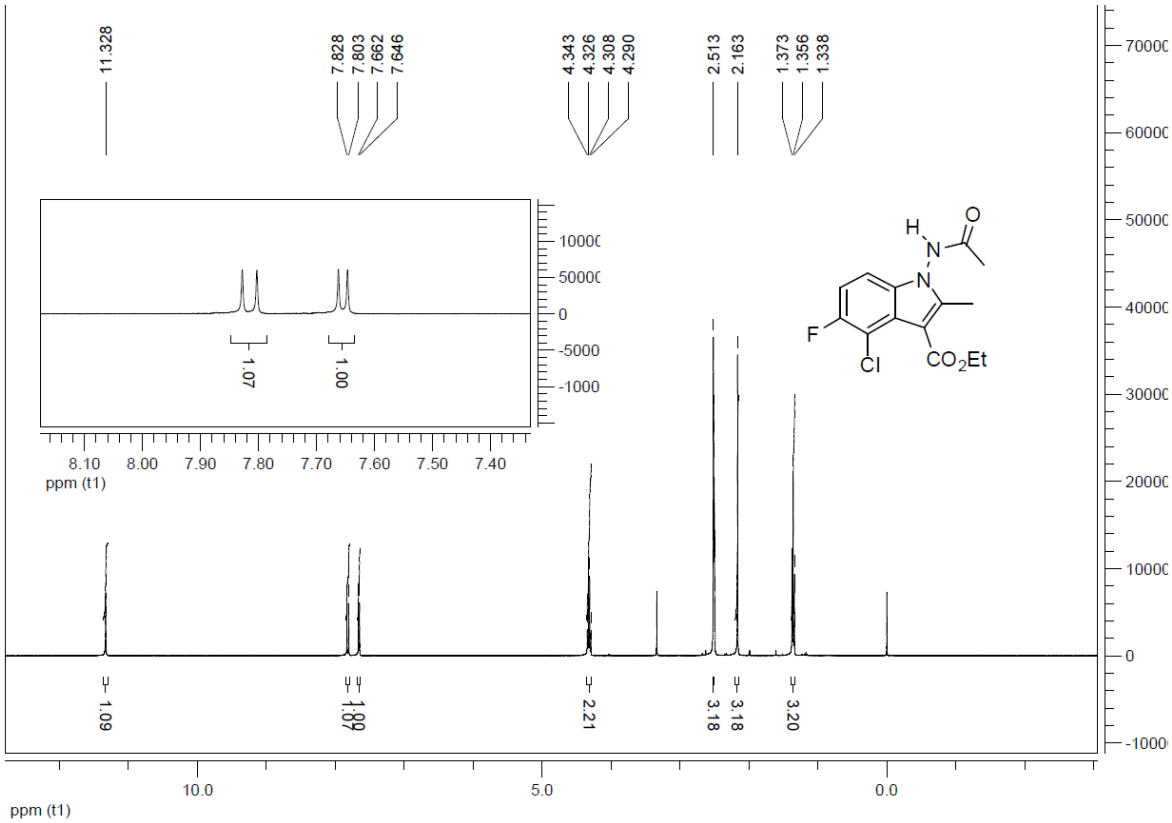
0
200
150
100
50
0
ppm (t1)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7.803
7.662
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4.326
4.308
4.290
2.513
2.163
1.373
1.356
1.338
1.07
1.00
10000
5000
0
-5000
-1000
8.10
8.00
7.90
7.80
7.70
7.60
7.50
7.40
ppm (t1)
H
N
O
F
Cl
CO2Et
70000
60000
50000
40000
30000
20000
10000
0
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1.07
1.00
2.21
3.18
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10.0
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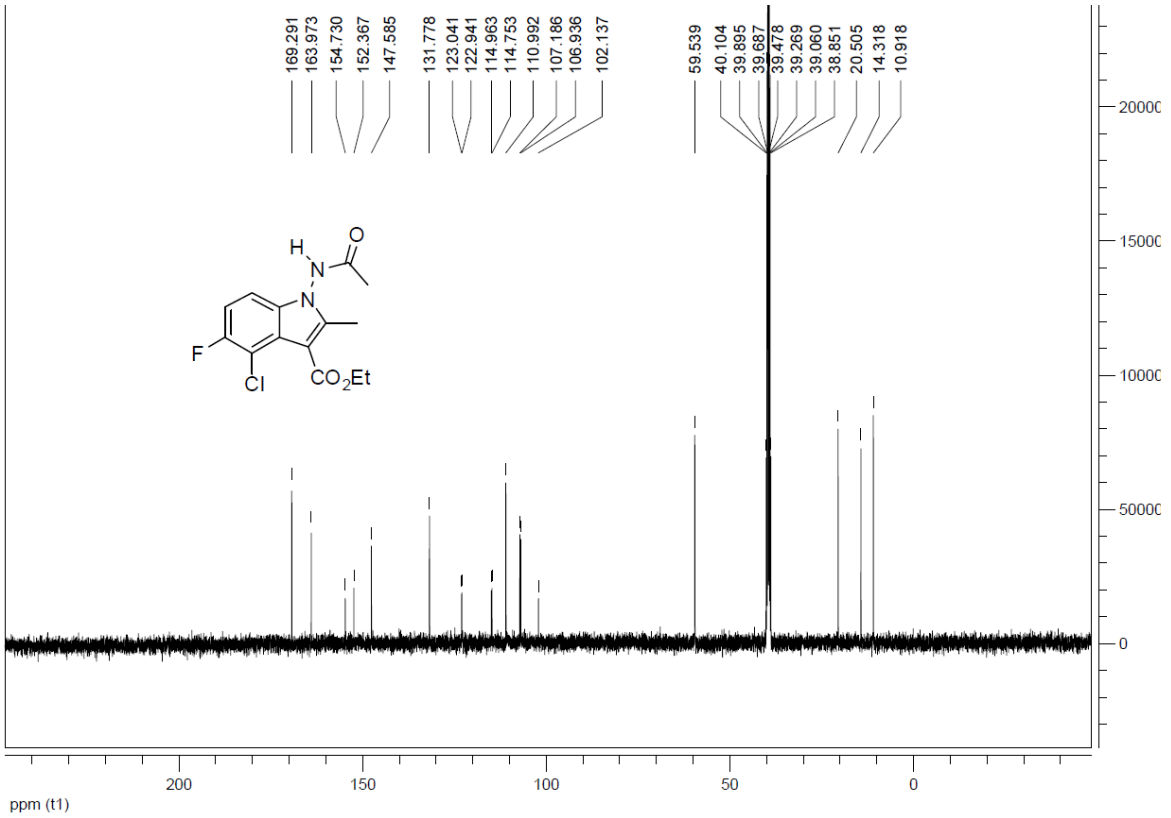
ppm (t1)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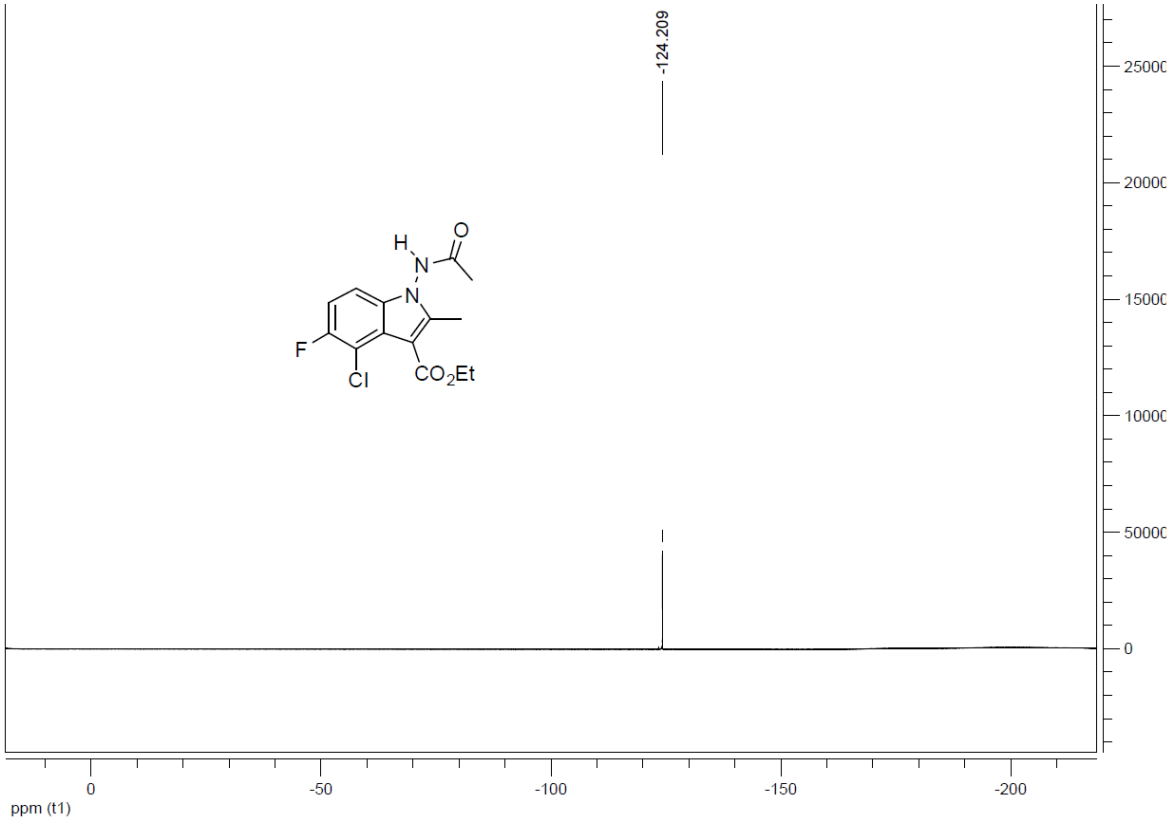
152.367
147.585
131.778
123.041
122.941
114.963
114.753
110.992
107.186
106.936
102.137
59.539
40.104
39.895
39.687
39.478
39.269
39.060
38.851
20.505
14.318
10.918
H
N
O
N
F
Cl
CO2Et
20000
15000
10000
5000
0
200
150
100
50
0
ppm (t1)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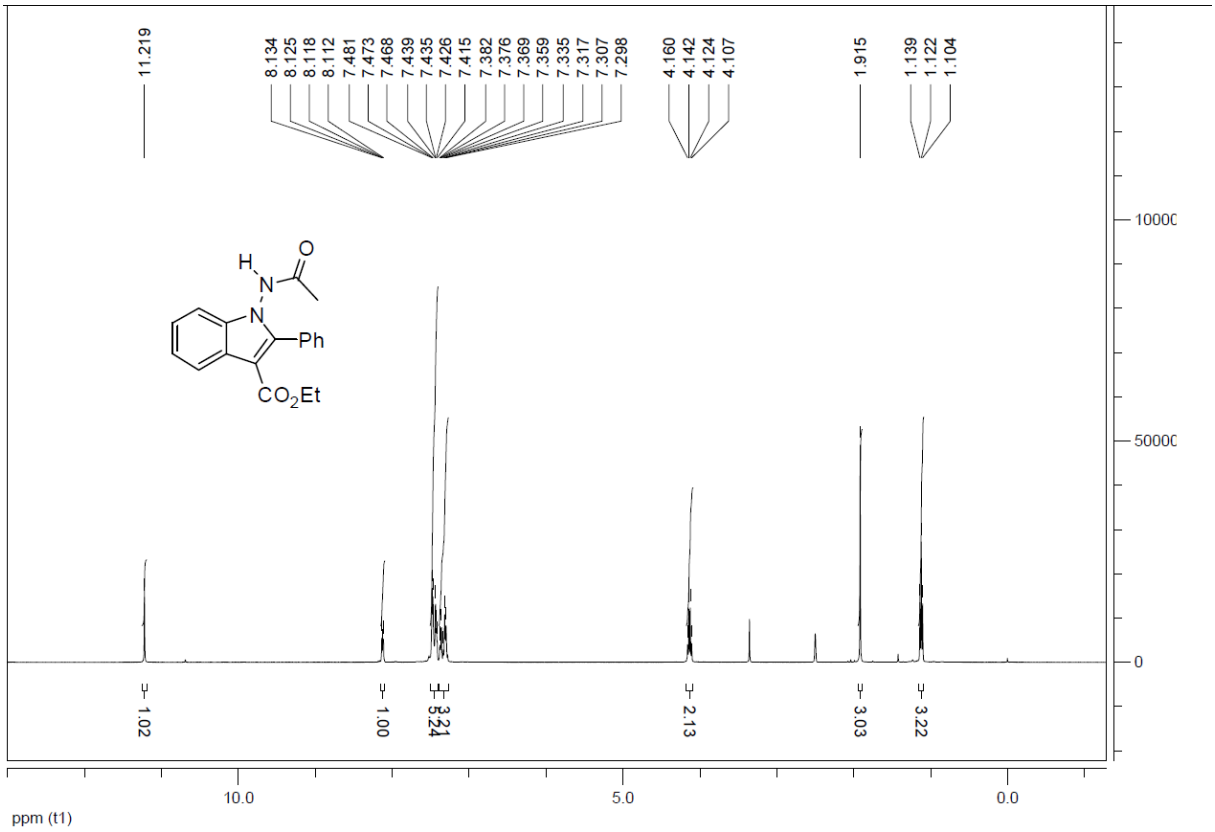
H
N
O
N
F
Cl
CO2Et
25000
20000
15000
10000
5000
0
0
-50
-100
-150
-200
ppm (t1)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7.435
7.426
7.415
7.382
7.376
7.369
7.359
7.335
7.317
7.307
7.298
4.160
4.142
4.124
4.107
1.915
1.139
1.122
1.104
H
N
O
N
Ph
CO2Et
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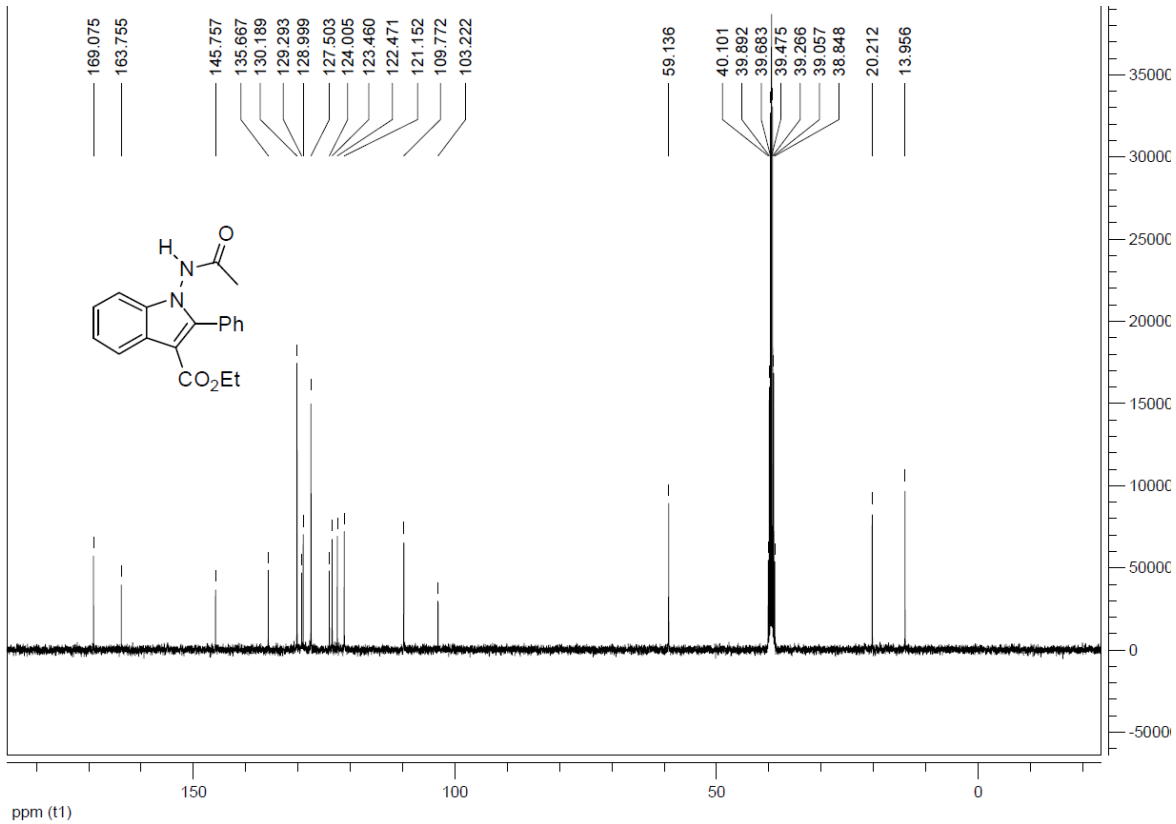
1.00
3.21
2.13
3.03
3.22
10.0
5.0
0.0
ppm (t1)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123.460
122.471
121.152
109.772
103.222
59.136
40.101
39.892
39.683
39.475
39.266
39.057
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20.212
13.956
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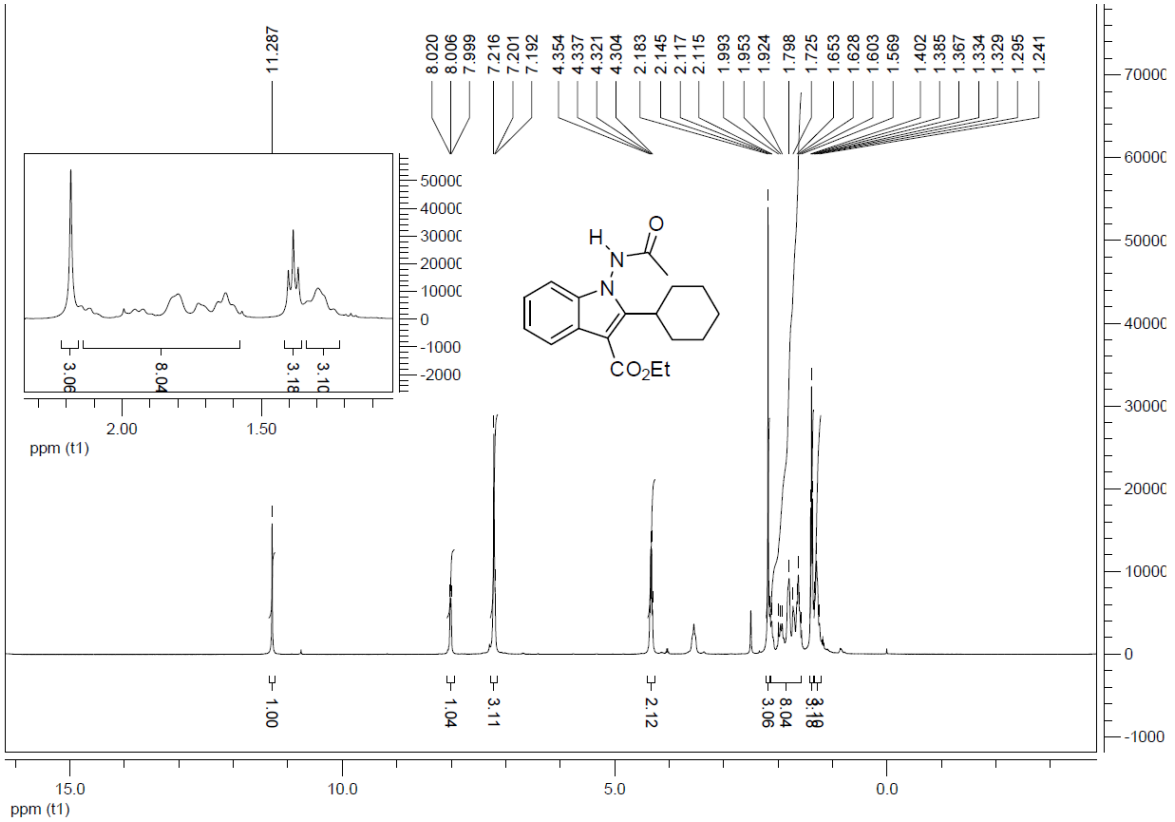
O
N
Ph
CO2Et
150
100
50
0
ppm (t1)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4.321
4.304
2.183
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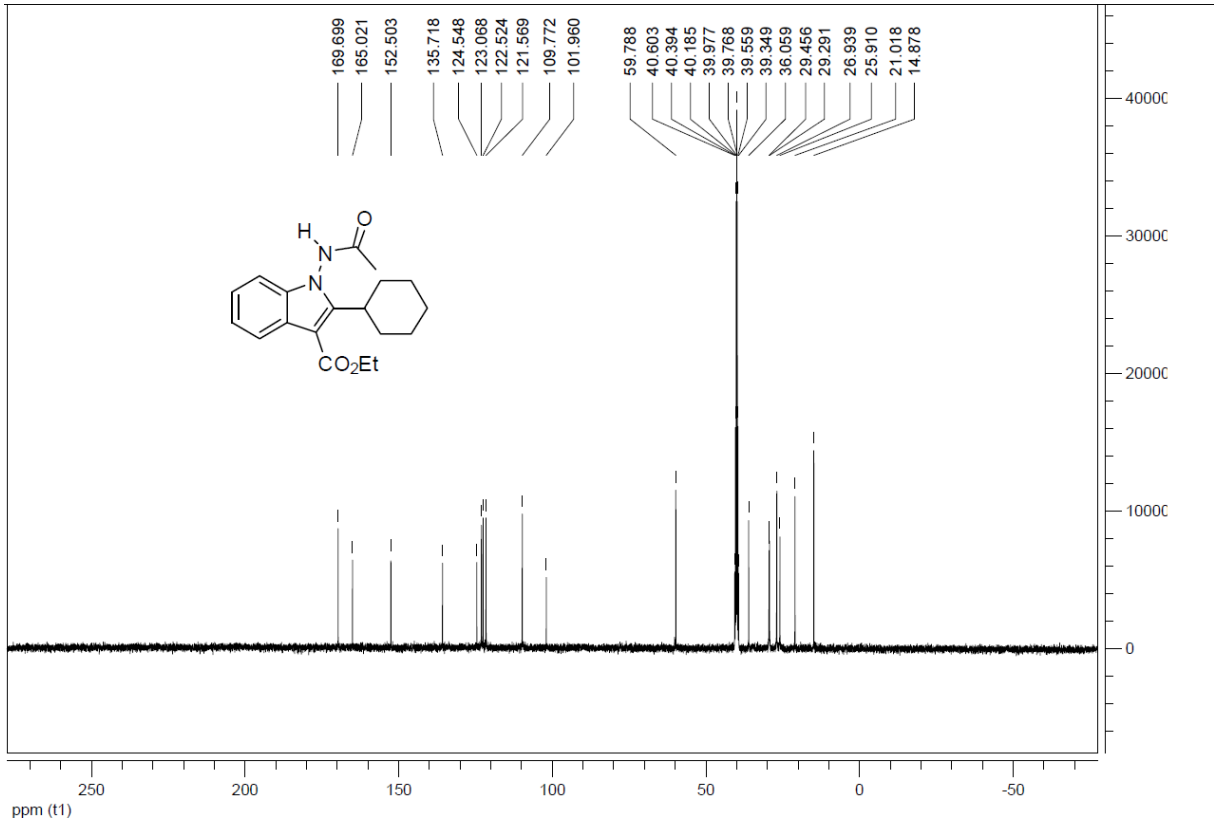
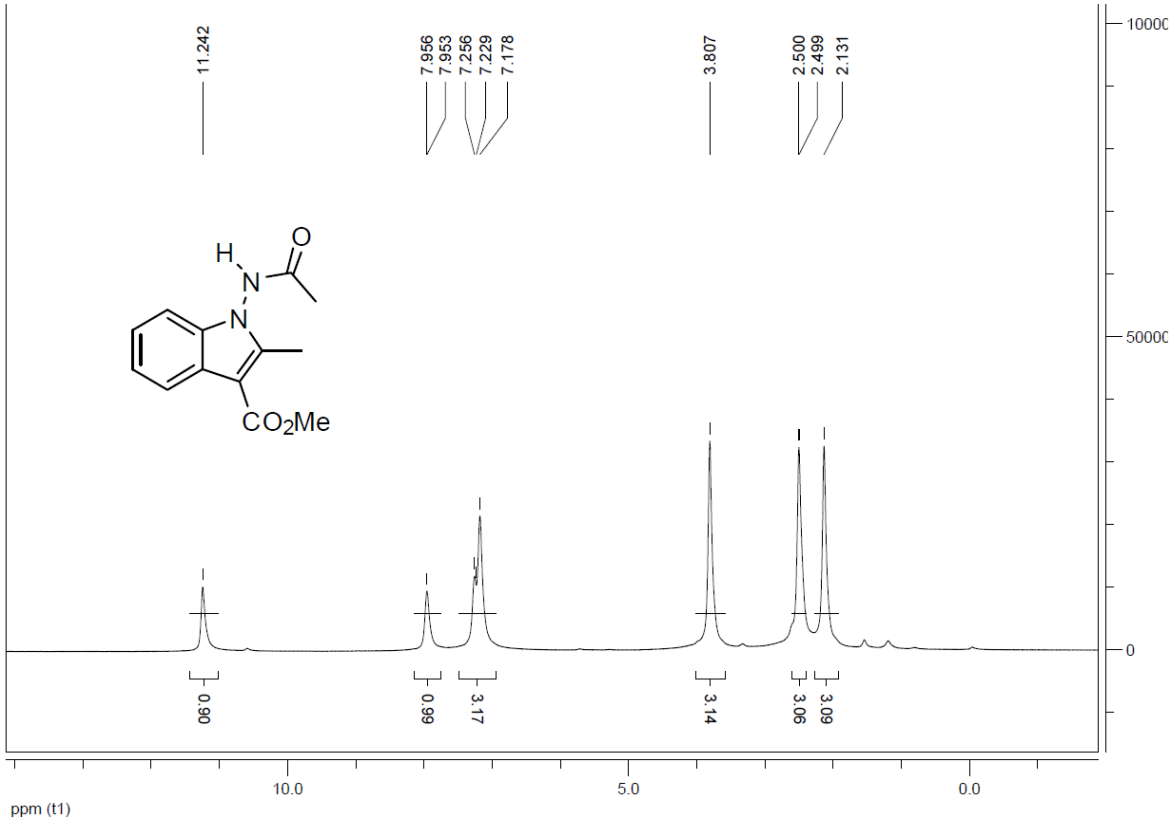
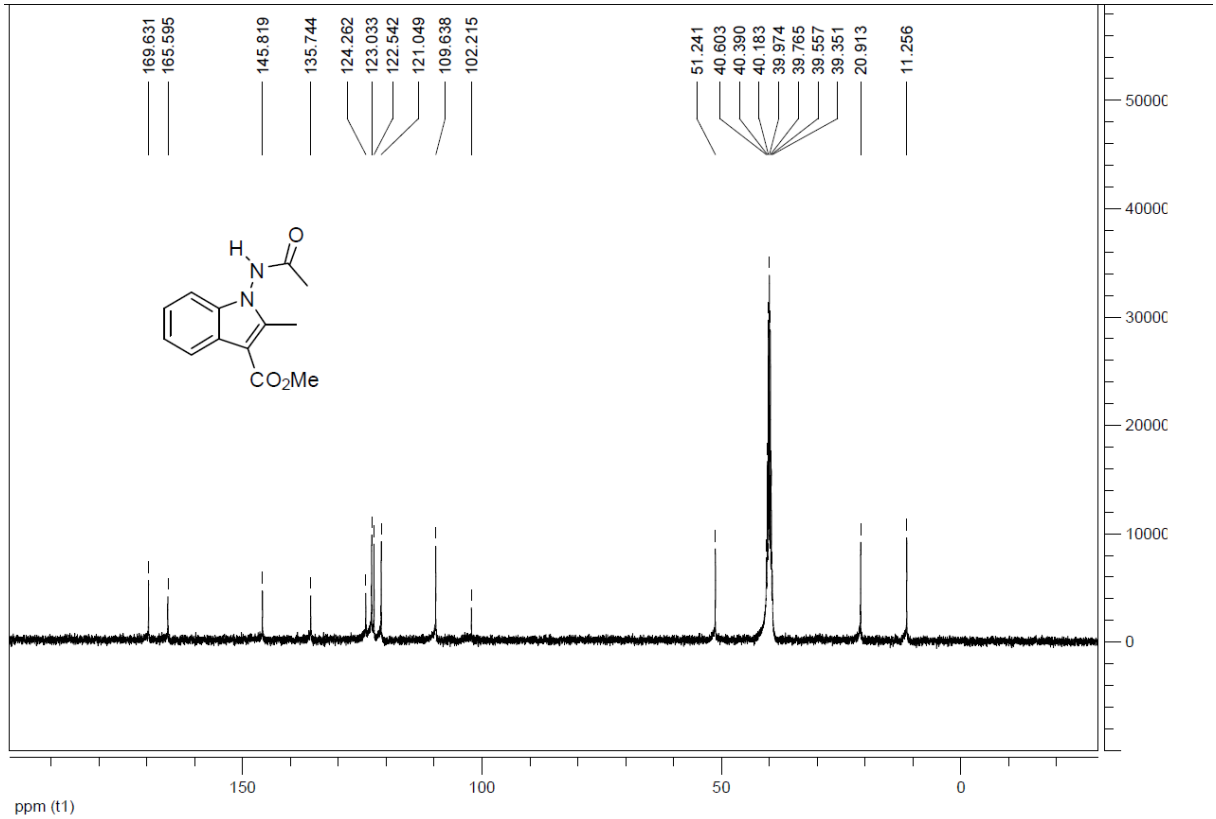
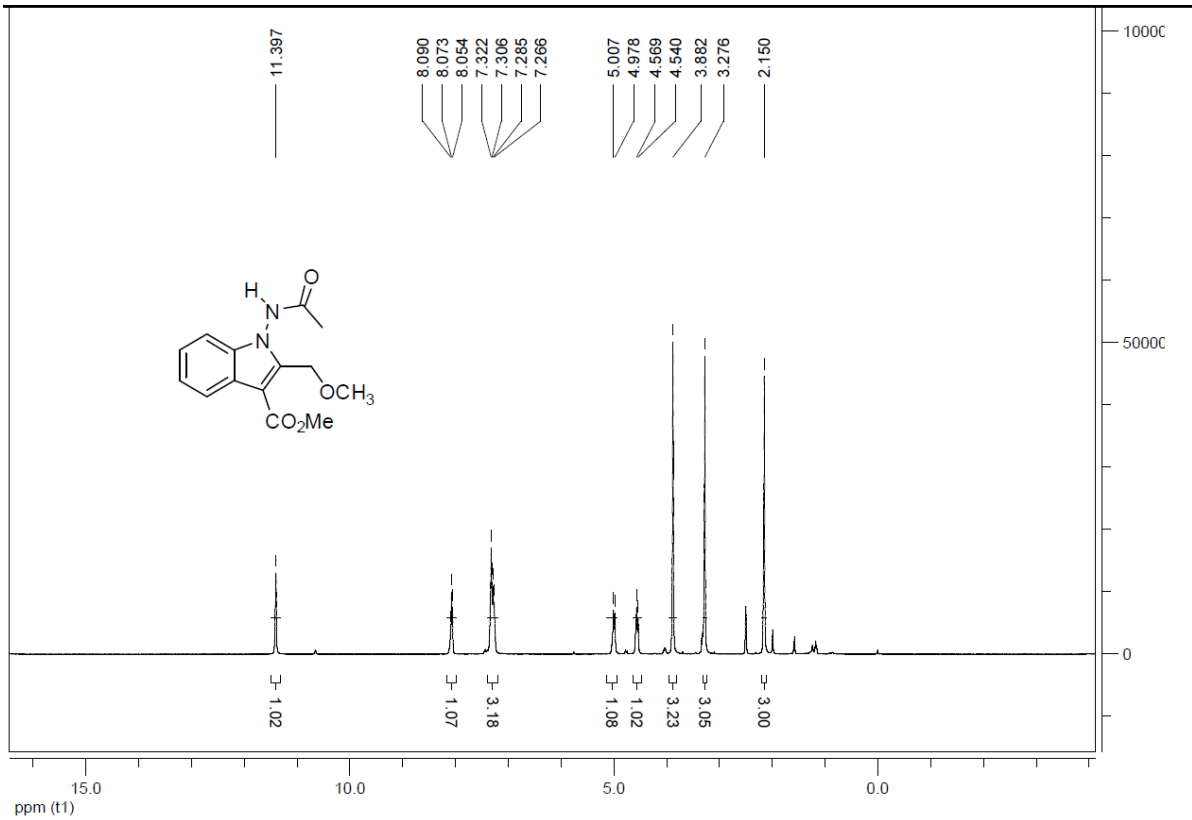
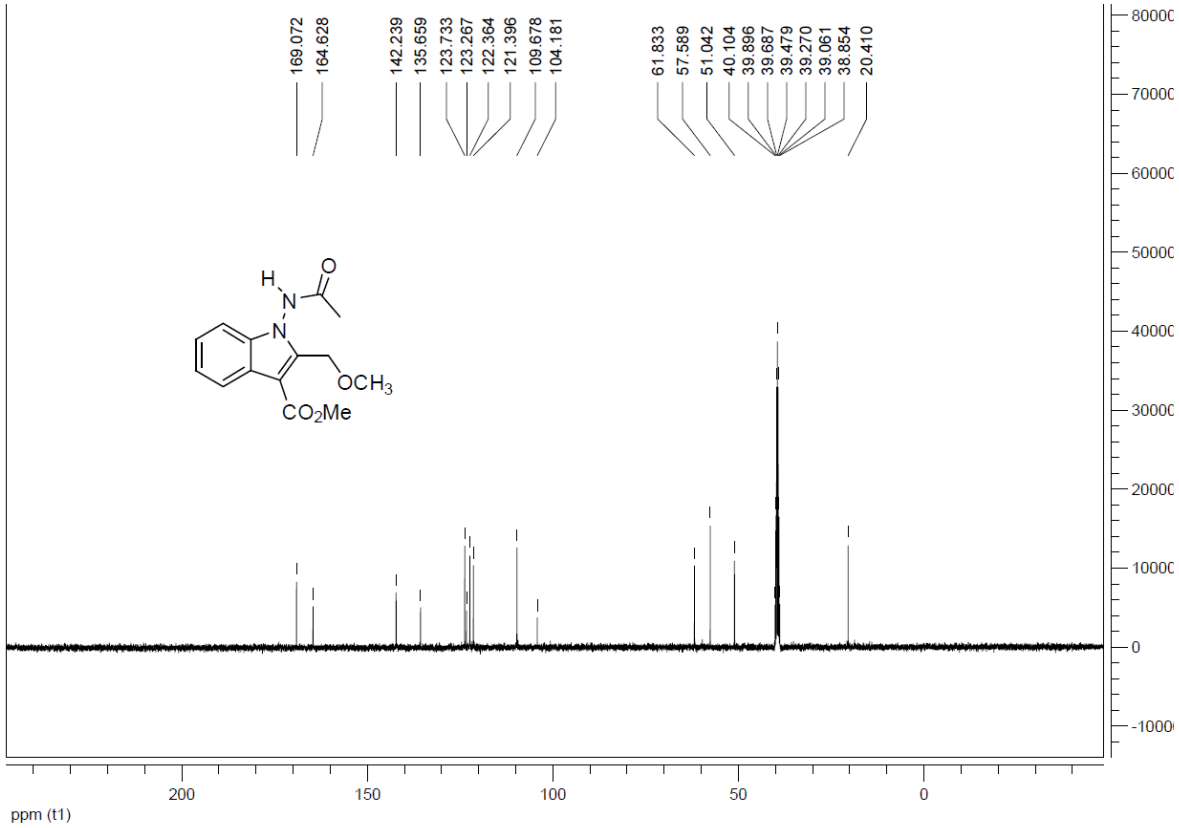
2.117
2.115
1.993
1.953
1.924
1.798
1.725
1.653
1.628
1.603
1.569
1.402
1.385
1.367
1.334
1.329
1.295
1.241
3.06
8.04
3.18
3.10
2.00
1.50
ppm (t1)
1.00
1.04
3.11
2.12
3.06
8.04
3.18
15.0
10.0
5.0
0.0
ppm (t1)
H
N
N
O
CO2Et

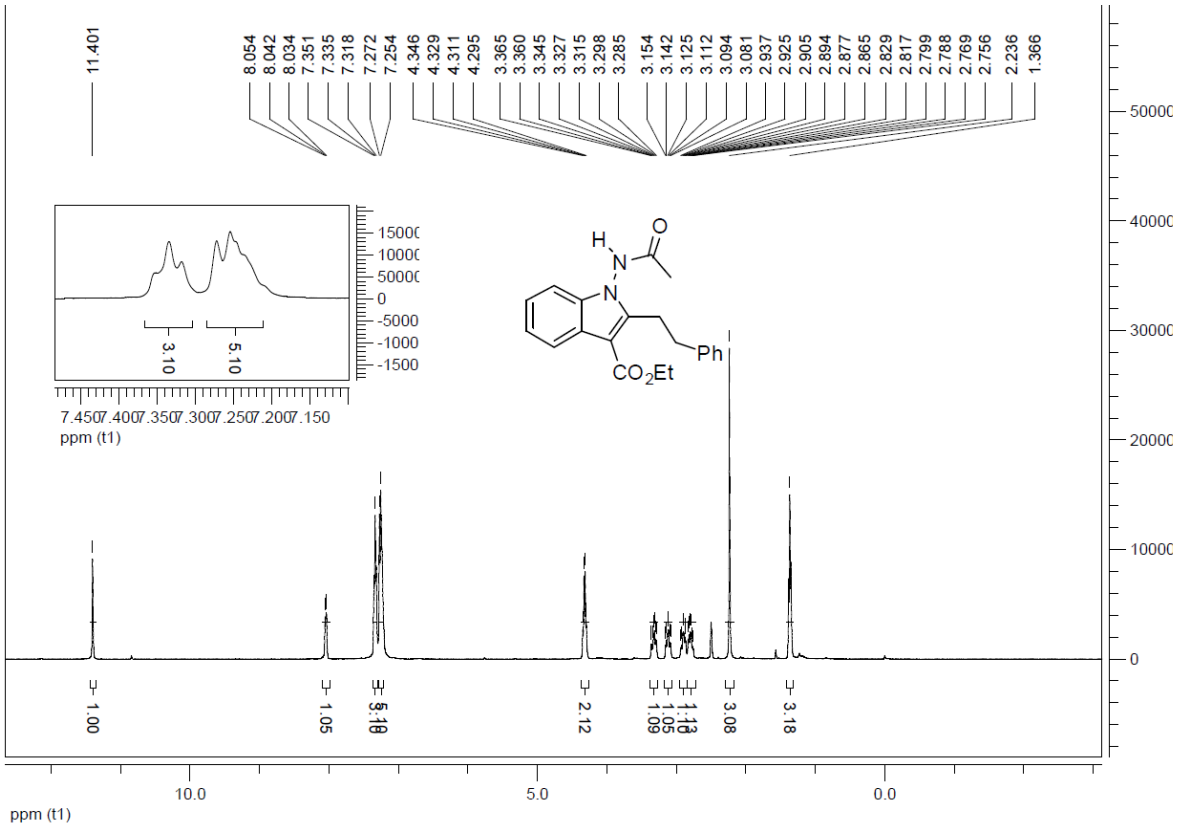

169.699
165.021
152.503
135.718
124.548
123.068
122.524
121.569
109.772
101.960
59.788
40.603
40.394
40.185
39.977
39.768
39.559
39.349
36.059
29.456
29.291
26.939
25.910
21.018
14.878
250
200
150
100
50
0
-50
ppm (t1)
H
N
N
O
CO2Et

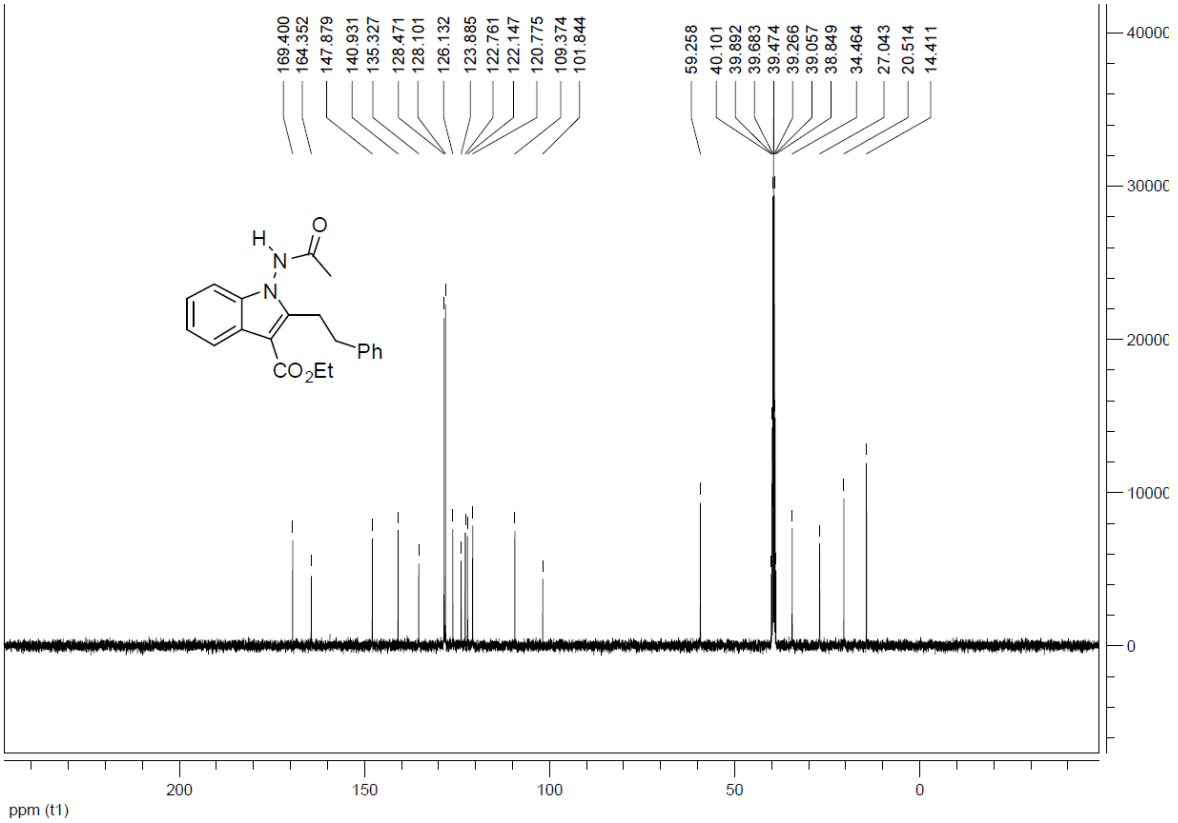

11.242
7.956
7.953
7.256
7.229
7.178
3.807
2.500
2.499
2.131
H
N
O
N
CO2Me
0.90
0.99
3.17
3.14
3.06
3.09
10.0
5.0
0.0
ppm (t1)

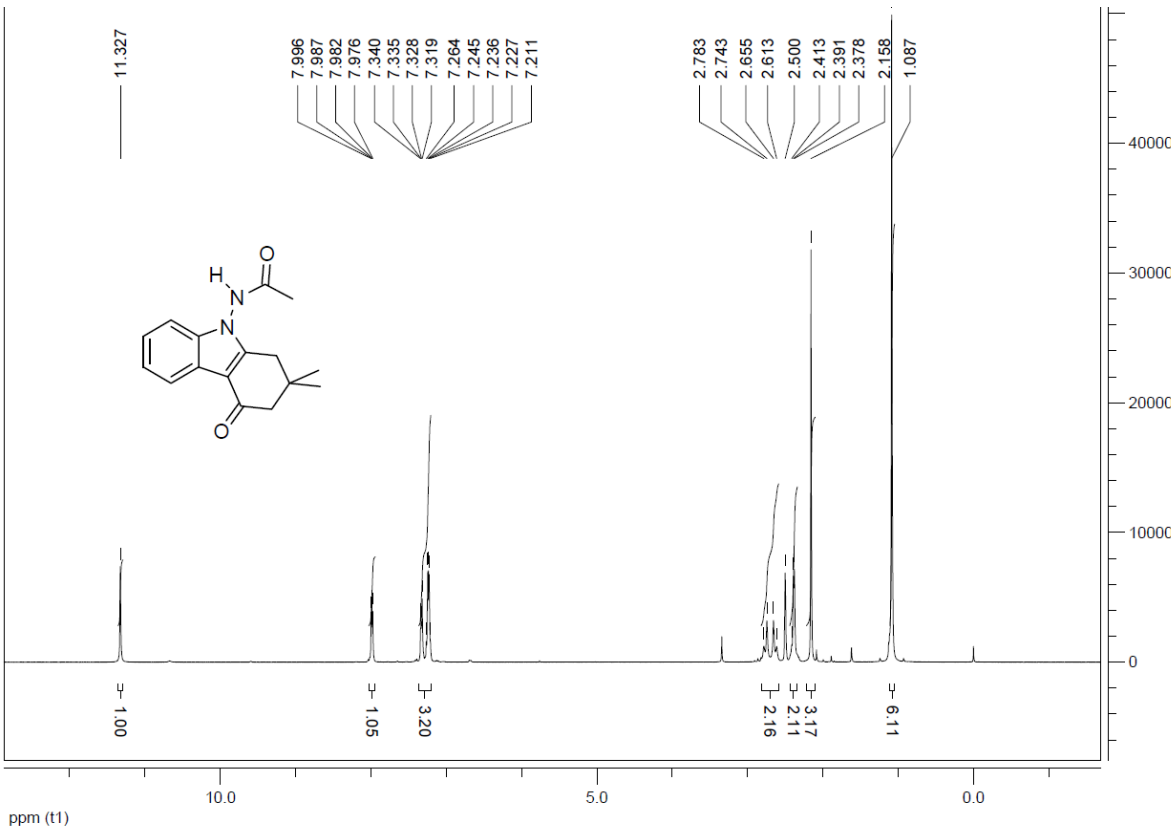

169.631
165.595
145.819
135.744
124.262
123.033
122.542
121.049
109.638
102.215
51.241
40.603
40.390
40.183
39.974
39.765
39.557
39.351
20.913
11.256
H
N
O
N
CO2Me
150
100
50
0
ppm (t1)

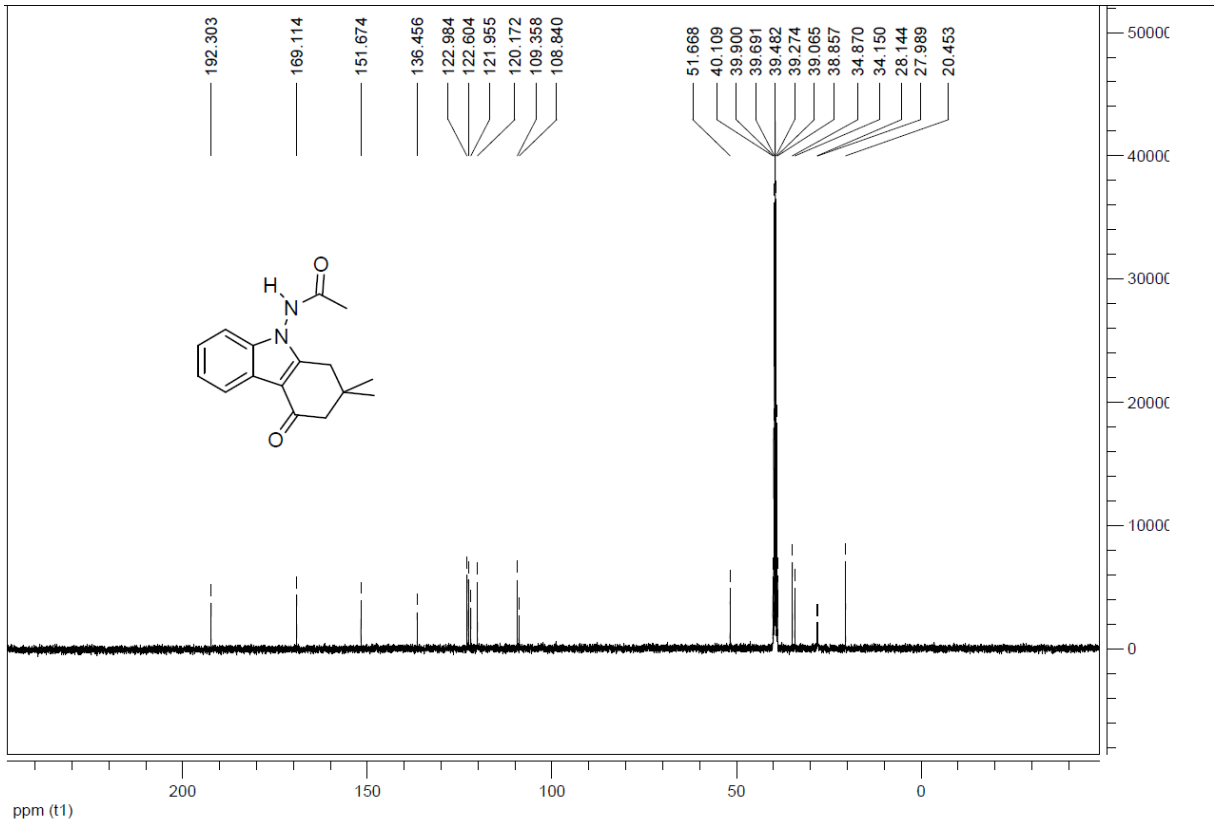

11.397
8.090
8.073
8.054
7.322
7.306
7.285
7.266
5.007
4.978
4.569
4.540
3.882
3.276
2.150
1.02
1.07
3.18
1.08
1.02
3.23
3.05
3.00
ppm (t1)

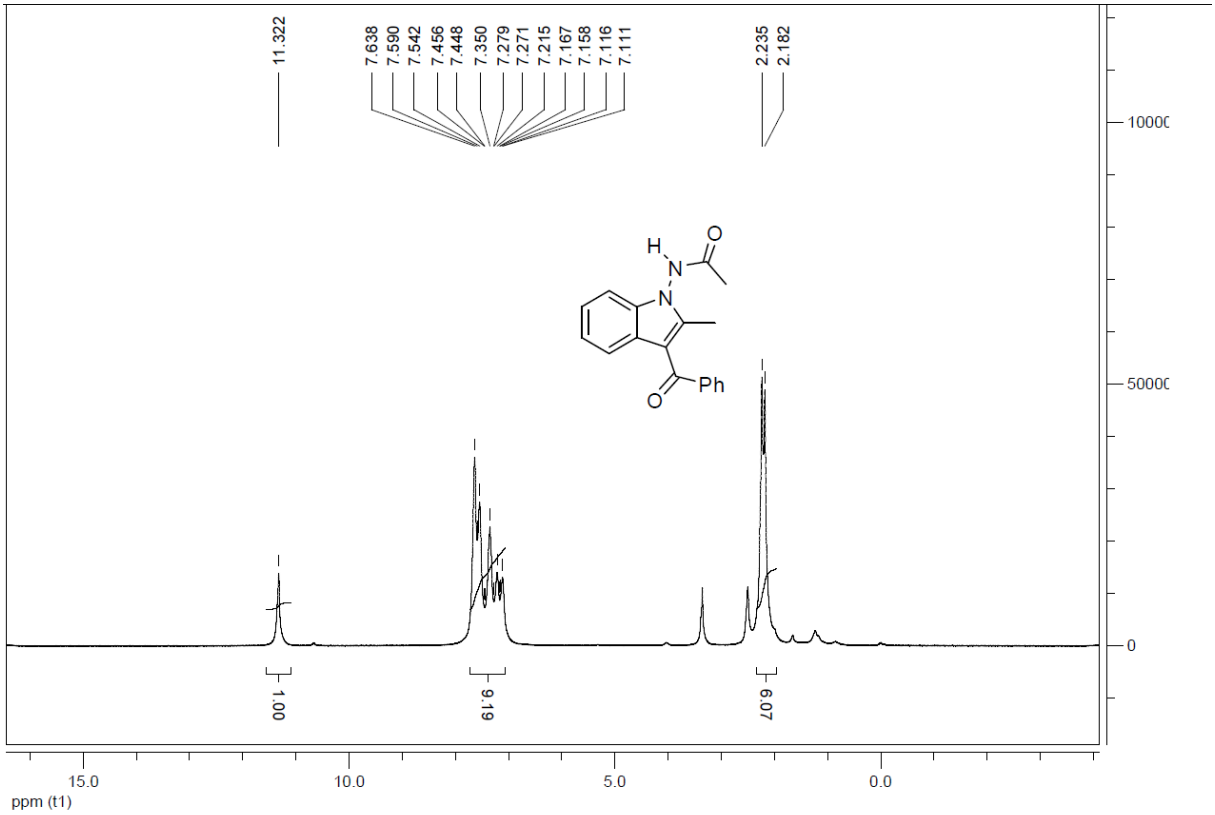

169.072
164.628
142.239
135.659
123.733
123.267
122.364
121.396
109.678
104.181
61.833
57.589
51.042
40.104
39.896
39.687
39.479
39.270
39.061
38.854
20.410
ppm (t1)

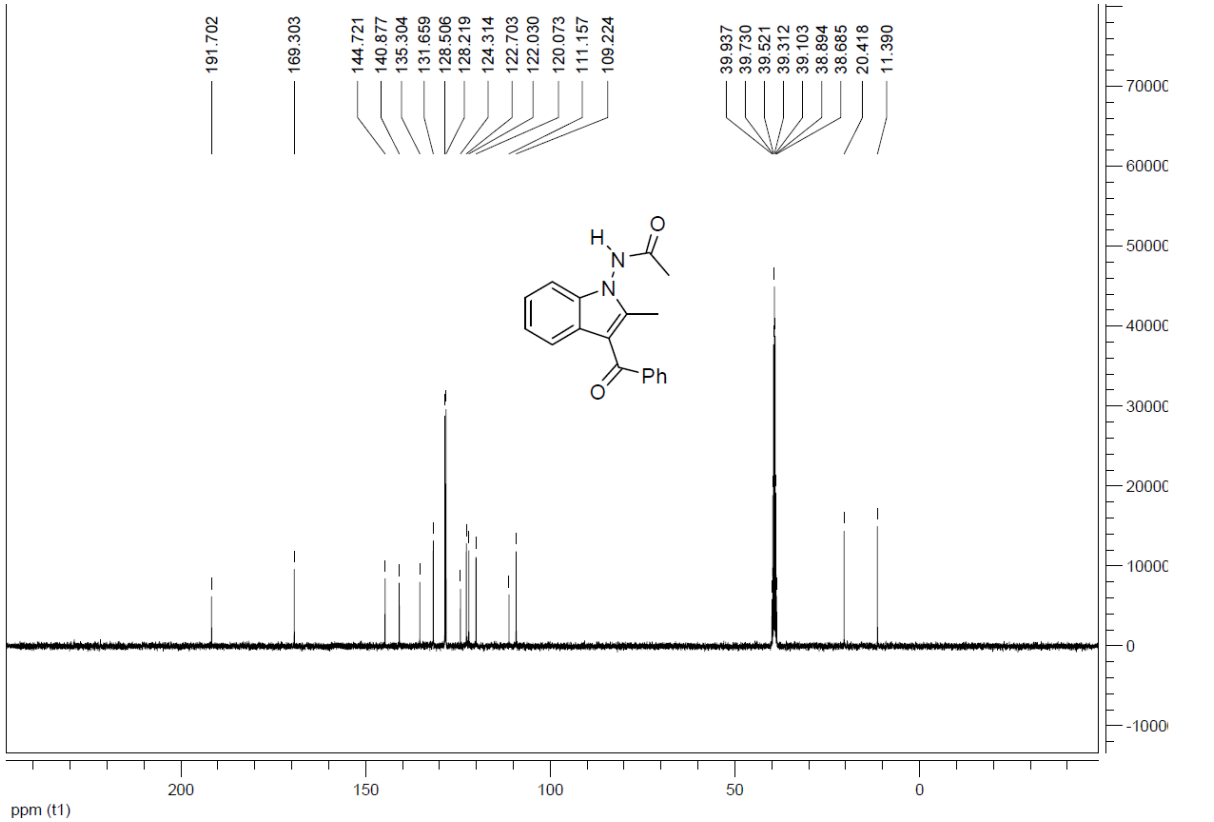

11.401
8.054
8.042
8.034
7.351
7.335
7.318
7.272
7.254
4.346
4.329
4.311
4.295
3.365
3.360
3.345
3.327
3.315
3.298
3.285
3.154
3.142
3.125
3.112
3.094
3.081
2.937
2.925
2.905
2.894
2.877
2.865
2.829
2.817
2.799
2.788
2.769
2.756
2.236
1.366
3.10
5.10
7.450 7.400 7.350 7.300 7.250 7.200 7.150
ppm (t1)
1.00
1.05
5.10
2.12
1.09
1.05
3.08
3.18
10.0
5.0
0.0
ppm (t1)

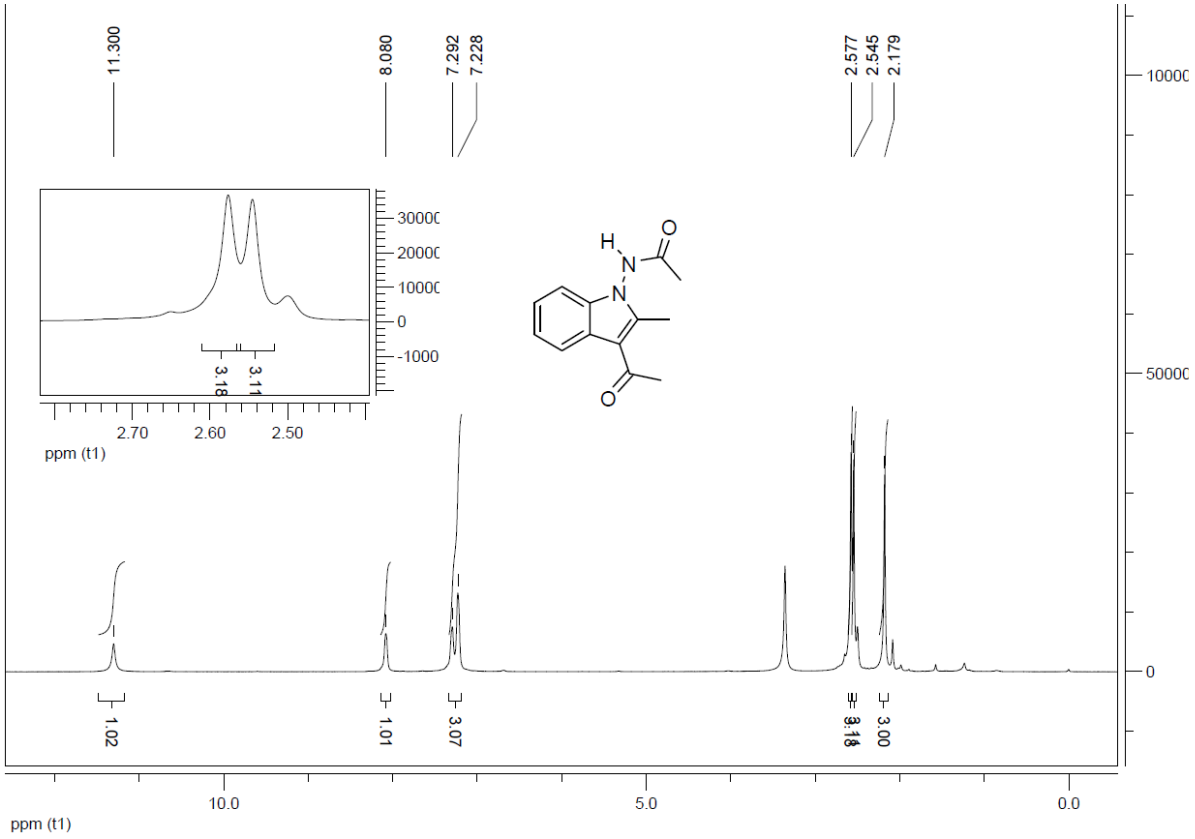

169.400
164.352
147.879
140.931
135.327
128.471
128.101
126.132
123.885
122.761
122.147
120.775
109.374
101.844
59.258
40.101
39.892
39.683
39.474
39.266
39.057
38.849
34.464
27.043
20.514
14.411
200
150
100
50
0
ppm (t1)

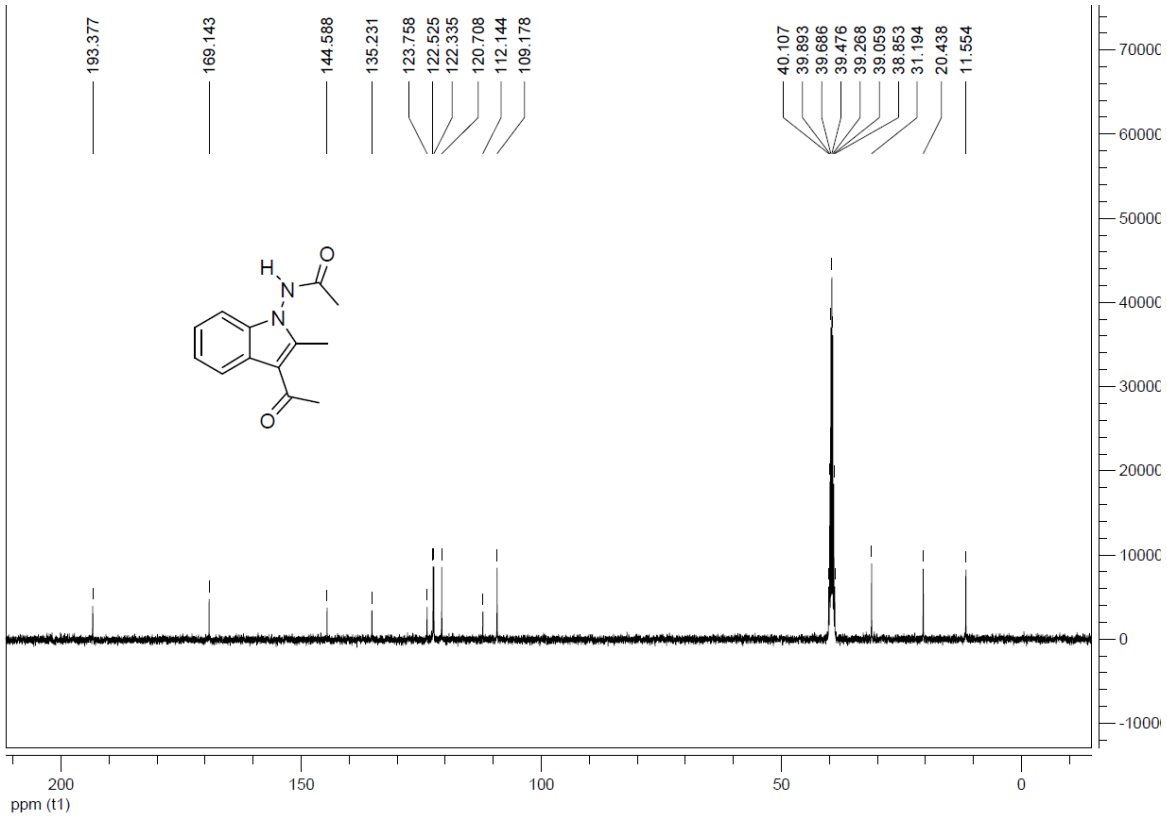

11.327
7.996
7.987
7.982
7.976
7.340
7.335
7.328
7.319
7.264
7.245
7.236
7.227
7.211
2.783
2.743
2.655
2.613
2.500
2.413
2.391
2.378
2.158
1.087
1.00
1.05
3.20
2.16
2.11
3.17
9.11
10.0
5.0
0.0
ppm (t1)

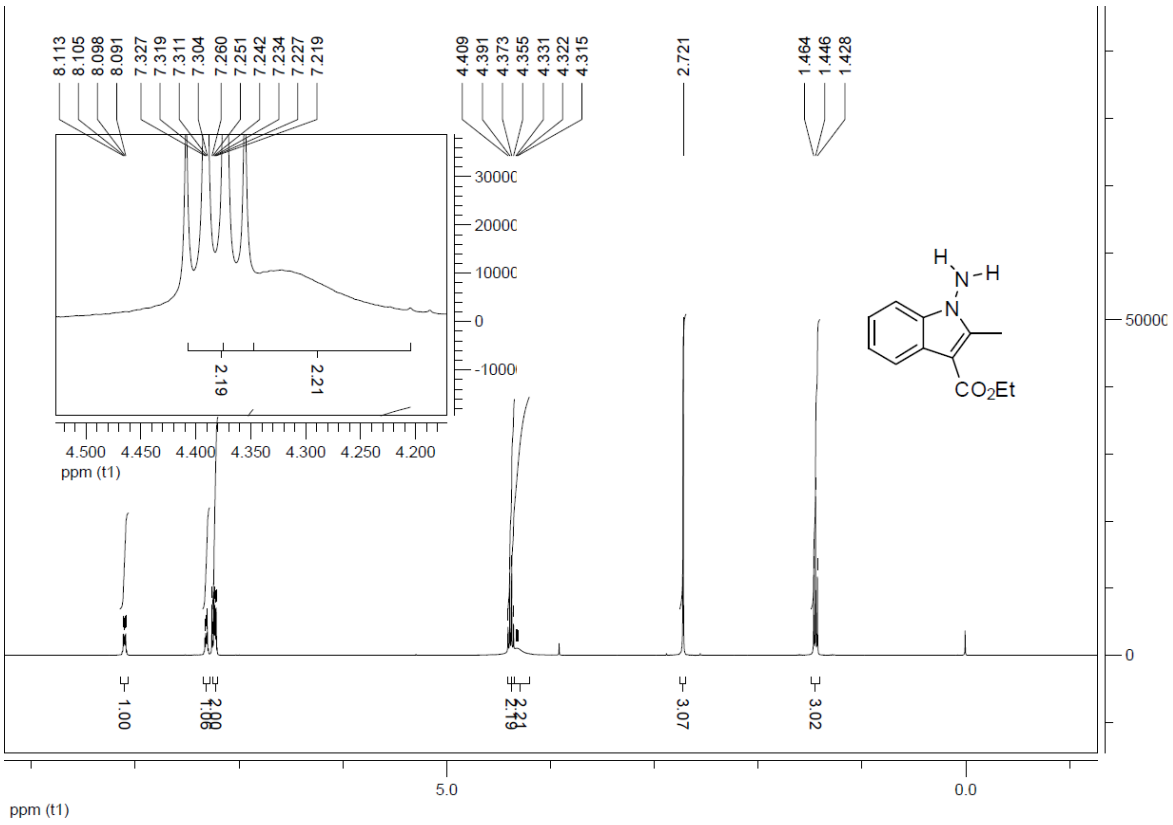

192.303
169.114
151.674
136.456
122.984
122.604
121.955
120.172
109.358
108.840
51.668
40.109
39.900
39.691
39.482
39.274
39.065
38.857
34.870
34.150
28.144
27.989
20.453
200
150
100
50
0
ppm (t1)

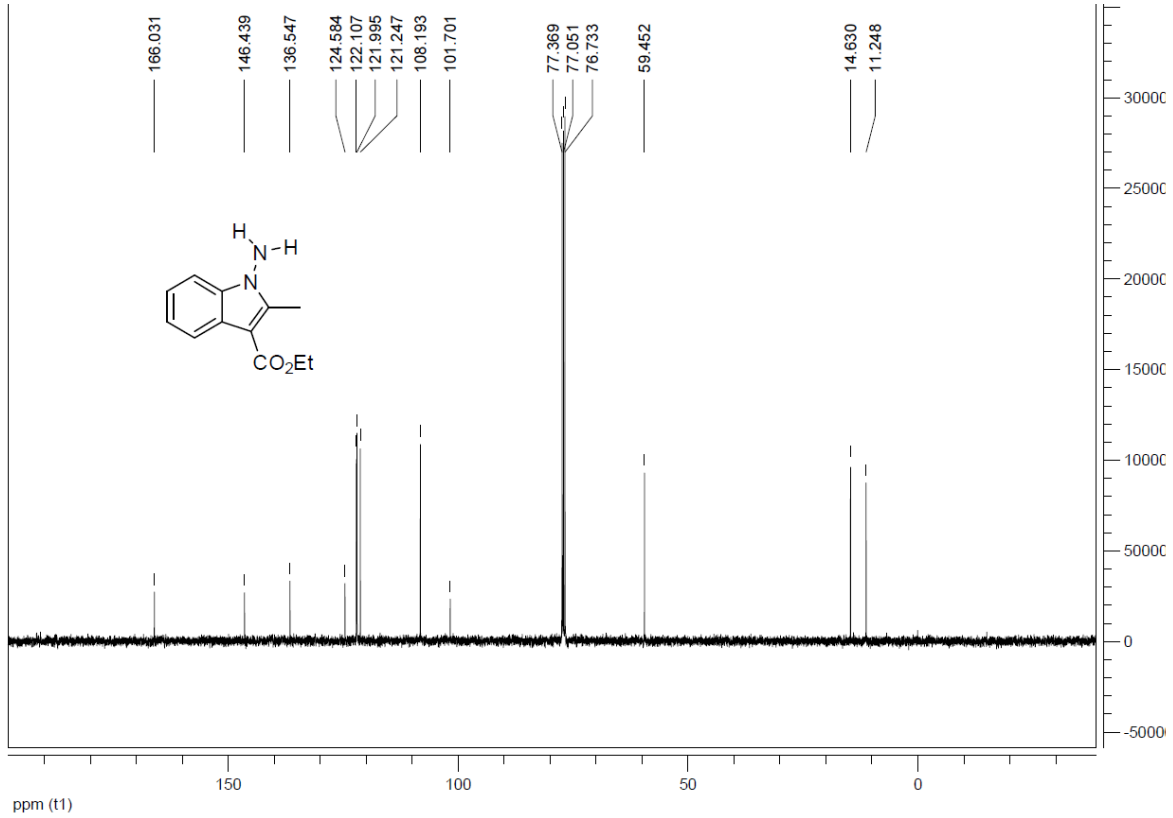

11.322
7.638
7.590
7.542
7.456
7.448
7.350
7.279
7.271
7.215
7.167
7.158
7.116
7.111
2.235
2.182
H
N
O
N
Ph
O
1.00
9.19
6.07
15.0
10.0
5.0
0.0
ppm (t1)


191.702
169.303
144.721
140.877
135.304
131.659
128.506
128.219
124.314
122.703
122.030
120.073
111.157
109.224
39.937
39.730
39.521
39.312
39.103
38.894
38.685
20.418
11.390
H
N
O
N
Ph
O
200
150
100
50
0
ppm (t1)


11.300
8.080
7.292
7.228
2.577
2.545
2.179
3.18
3.11
2.70
2.60
2.50
ppm (t1)
1.02
1.01
3.07
3.18
3.00
10.0
5.0
0.0
ppm (t1)


193.377
169.143
144.588
135.231
123.758
122.525
122.335
120.708
112.144
109.178
40.107
39.893
39.686
39.476
39.268
39.059
38.853
31.194
20.438
11.554
200
150
100
50
0
ppm (t1)


8.113
8.105
8.098
8.091
7.327
7.319
7.311
7.304
7.260
7.251
7.242
7.234
7.227
7.219
4.409
4.391
4.373
4.355
4.331
4.322
4.315
2.721
1.464
1.446
1.428
2.19
2.21
4.500 4.450 4.400 4.350 4.300 4.250 4.200
ppm (t1)
1.00
2.00
2.21
3.07
3.02
5.0
0.0
ppm (t1)
CO2Et


166.031
146.439
136.547
124.584
122.107
121.995
121.247
108.193
101.701
77.369
77.051
76.733
59.452
14.630
11.248
150
100
50
0
ppm (t1)
CO2Et