Supporting Information

for

$BF_3{\cdot}OEt_2$ Catalyzed chemoselective C=C bond cleavage of α,β-enones: An unexpected synthesis of 3-alkylated oxindoles and spiro-indolooxiranes

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CONTENTS

General information

Melting points were determined on a capillary melting point apparatus and uncorrected. The solid compounds were crystalized using ethyl acetate and hexane as solvents. IR spectra were recorded using ATR technique on a Bruker Alpha FT-IR spectrophotometer. All compounds were fully characterized. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded at 400 MHz using $CDCl_3$ in ppm (δ) related to tetramethylsilane (δ=0.00) as an internal standard and are reported as follows; chemical shift (ppm), multiplicity (br = broad, s = singlet, d = doublet, t = triplet, dd = doublet of doublet, m = multiplet), ABq = AB quartet and coupling constant (Hz). Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded at 100 MHz in $CDCl_3$. Chemical shifts are reported in delta (δ) units, parts per million (ppm) relative to the center of the triplet at 77.7 ppm for $CDCl_3$. Carbon types were determined from ^{13}C NMR and DEPT experiments. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.7 ppm). High-resolution mass analyses were performed using the electrospray ionization (ESI) technique on a Thermo Exactive Orbitrap mass spectrometer. All solvents are commercial grade(LR) without distillation. Thin-layer chromatography was performed on silica or alumina plates and components visualized by observation under iodine/UV light at 254 nm. Column chromatography was performed on silica gel (100-200 mesh). All the reactions were conducted in oven-dried glassware under a positive pressure of nitrogen with magnetic stirring. Acetophenone, aldehyde and $BF_3{\cdot}Et_2O$ were purchased from M/s Aldrich and M/s Alfa Aesar and used as provided. The diazoamides[1] and chalcones[2] were prepared according to the literature.

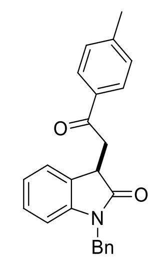
Experimental Section

General experimental procedure for the synthesis of alkylated oxindoles 3

To a solution of diazoamide **1** (1.0 equiv) and chalcone **2** (1.0 equiv) in $CHCl_3$ (5 mL) was added 10 mol% of $BF_3{\cdot}OEt_2$. The reaction mixture was stirred at 0 °C under the open-air atmosphere and monitored by TLC until the disappearance of the diazoamide. After the appropriate period, the reaction mixture was diluted with $CHCl_3$ (10 mL) and water (15 mL). The organic phase was separated and the aqueous layer was washed with $CHCl_3$ (10 mL). The concentration of the combined organic layers under reduced pressure afforded the crude product, which was purified by column chromatography using silica gel to afford the corresponding product **3**.

Synthesis of 1-benzyl-3-[2-(4-methylphenyl)-2-oxoethyl]-1,3-dihydro-2*H*-indol-2-one (3a)

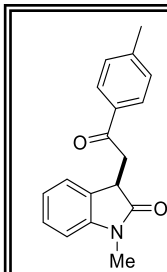
To a solution of 1-benzyl-3-diazo-1,3-dihydro-2*H*-indol-2-one (**1a**) (100 mg, 0.40 mmol) and (2*E*)-1-(4-methylphenyl)-3-phenylprop-2-en-1-one (**2a**) (90 mg, 0.40 mmol) in $CHCl_3$ (5 mL) was added 10 mol% of $BF_3{\cdot}OEt_2$. The reaction mixture was stirred at 0 °C under an open-air atmosphere to afford **3a** (103 mg, 73%) as a colorless crystalline solid according to general procedure. R_f = 0.39 (EtOAc/hexane = 1:4, v/v); mp 146-147 °C; IR (neat): ν_{max} 2922, 1708, 1684, 1607, 1462, 1354, 745 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ = 2.40 (s, 3H, CH_3), 3.44 (dd, J_1 = 18 Hz, J_2 = 9 Hz, 1H, CH), 3.86 (dd, J_1 = 18.1 Hz, J_2 = 2.9 Hz, 1H, CH), 4.16 (dd, J_1 = 8.8 Hz, J_2 = 2.3 Hz,1H, CH), 4.97 (s, 2H, CH_2), 6.73 (d, *J* = 7.6 Hz, 1H, ArH), 6.92-6.96 (m, 1H, ArH), 7.12-7.15 (m, 1H, ArH), 7.23-7.37 (m, 8H, ArH), 7.89 (d, *J* = 8 Hz, 2H, ArH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 21.7, 40.0, 41.3, 44.0, 109.1, 122.5, 124.5, 127.4, 127.6, 128.0, 128.3, 128.8, 129.2, 129.4, 134.0, 135.0, 143,5, 144.4, 177.9, 196.5 ppm; HRMS (ESI) Calculated for $C_{24}H_{21}NO_2$ $(M+H)^+$: 356.1651 found: 356.1644.



3a

Synthesis of 1-methyl-3-[2-(4-methylphenyl)-2-oxoethyl]-1,3-dihydro-2*H*-indol-2-one (3b)

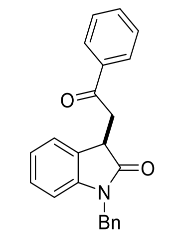
To a solution of 3-diazo-1-methyl-1,3-dihydro-2*H*-indol-2-one (**1b)** (100 mg, 0.58 mmol) and (2*E*)-1-(4-methylphenyl)-3-phenylprop-2-en-1-one (**2a)** (128, 0.58 mmol) in $CHCl_3$ (5 mL) was added 10 mol% of $BF_3{\cdot}OEt_2$. The reaction mixture was stirred at 0 °C under an open-air atmosphere to afford **3b** (110 mg, 68%) as a colorless crystalline solid according to general procedure. R_f = 0.25 (EtOAc/hexane = 1:4, v/v); mp 198-199 °C; IR (neat): ν_{max} 2923, 1704, 1606, 1467, 1345, 1263, 1090, 735 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ = 2.40 (s, 3H, CH_3), 3.26 (s, 3H, CH_3), 3.36 (dd, J_1 = 18 Hz, J_2 = 9.2 Hz, 1H, CH), 3.80 (dd, J_1 = 18 Hz, J_2 = 2.8 Hz, 1H, CH), 4.07 (d, *J* = 9.2 Hz, 1H, CH), 6.85 (d, *J* = 7.6 Hz, 1H, ArH), 6.98 (t, *J* = 7.6 Hz, 1H, ArH), 7.25-7.29 (m,4H, ArH), 7.87 (d, J = 8 Hz, 2H, ArH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 21.7, 26.4, 40.0, 41.2, 108.0, 122.5, 124.5, 128.1, 128.3, 129.2, 129.4, 133.9, 144.3, 144.4, 177.9, 196.6 ppm; HRMS (ESI) Calculated for $C_{18}H_{17}NO_2$ $(M+H)^+$: 280.1338 found: 280.1333.



3b

Synthesis of 1-benzyl-3-(2-oxo-2-phenylethyl)-1,3-dihydro-2*H*-indol-2-one (3c)[3]

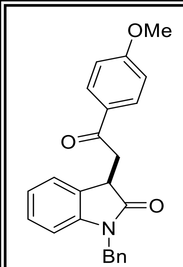
To a solution of 1-benzyl-3-diazo-1,3-dihydro-2*H*-indol-2-one (**1a**) (100 mg, 0.40 mmol) and (2*E*)-1,3-diphenylprop-2-en-1-one (**2b**) (83 mg, 40 mmol) in $CHCl_3$ (5 mL) was added 10 mol% of $BF_3{\cdot}OEt_2$. The reaction mixture was stirred at 0 °C under an open-air atmosphere to afford **3c** (99 mg, 73%) as a colorless crystalline solid according to general procedure. R_f = 0.34 (EtOAc/hexane = 1:4, v/v); mp 162-163 °C; IR (neat): ν_{max} 3057, 2914, 1702, 1605, 1356, 1216, 744 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ = 3.47 (dd, J_1 = 27.2 Hz, J_2 = 9.0 Hz, 1H, CH), 3.89 (dd, J_1 = 18.4 Hz, J_2 = 3.2 Hz, 1H, CH), 4.17 (dd, J_1 = 8.8 Hz, J_2 = 2.8 Hz, 1H, CH), 4.97 (s, 2H, CH_2), 6.74 (d, J = 7.6 Hz, 1H, ArH), 6.95 (t, J = 7.6 Hz, 1H, ArH), 7.14 (t, J = 7.6 Hz, 1H, ArH), 7.25-7.38 (m, 6H, ArH) 7.45-7.49 (m, 2H, ArH), 7.56-7.59 (m, 1H, ArH), 7.98-8.01 (m, 2H, ArH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 40.1, 41.3, 44.0, 109.1, 122.6, 124.4, 127.4, 127.7, 128.1, 128.2, 128.8, 128.9, 129.1, 133.5, 136.0, 136.4, 143.5, 177.9, 196.9 ppm; HRMS (ESI) Calculated for $C_{23}H_{19}NO_2$ $(M+H)^+$: 342.1494 found: 342.1485.



3c

Synthesis of 1-benzyl-3-[2-(4-methoxyphenyl)-2-oxoethyl]-1,3-dihydro-2*H*-indol-2-one (3d)[4]

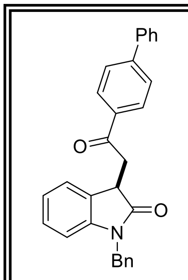
To a solution of 1-benzyl-3-diazo-1,3-dihydro-2*H*-indol-2-one (**1a**) (100 mg, 0.40 mmol) and (2*E*)-1-(4-methoxyphenyl)-3-phenylprop-2-en-1-one (**2c**) (95 mg, 0.40 mmol) in $CHCl_3$ (5 mL) was added 10 mol% of $BF_3{\cdot}OEt_2$. The reaction mixture was stirred at 0 °C under an open-air atmosphere to afford **3d** (105 mg, 71%) as a colorless crystalline solid according to general procedure. R_f = 0.18 (EtOAc/hexane = 1:4, v/v); mp 166-167 °C; IR (neat): ν_{max} 2924, 1705, 1674, 1595, 1359, 1165 698 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ = 3.42 (dd, J_1 = 18.0 Hz, J_2 = 9.0 Hz, 1H, CH), 3.82 (d, J = 2.8 Hz, 1H, CH), 3.87 (s, 3H, CH_3), 4.17 (d, J = 7.6 Hz, 1H, CH), 4.97 (s, 2H, CH_2), 6.73 (d, J = 7.6 Hz, 1H, ArH), 6.93-6.97 (m, 3H, ArH), 7.14 (t, J = 7.6 Hz, 1H, ArH), 7.24-7.37 (m, 6H, ArH), 7.98 (d, J = 8.8 Hz, 2H, ArH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 39.7, 41.4, 44.0, 55.5, 109.0, 113.9, 122.5, 124.5, 127.4, 127.6, 128.0, 129.3, 129.5, 130.5, 136.0, 143.4, 163.8, 178.0, 195.3 ppm; HRMS (ESI) Calculated for $C_{24}H_{21}NO_3$ $(M+H)^+$: 372.1600 found: 372.1594



3d

Synthesis of 3-[2-([1,1'-biphenyl]-4-yl)-2-oxoethyl]-1-benzyl-1,3-dihydro-2*H*-indol-2-one (3f)[5]

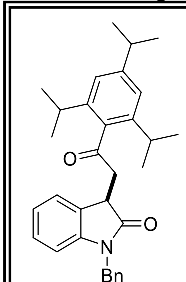
To a solution of 1-benzyl-3-diazo-1,3-dihydro-2*H*-indol-2-one (**1a**) (100 mg, 0.40 mmol) and (*2E)*-1-([1,1'-biphenyl]-4-yl)-3-phenylprop-2-en-1-one (**2d**) (114 mg, 0.40 mmol) in $CHCl_3$ (5 mL) was added 10 mol% of $BF_3 \cdot OEt_2$. The reaction mixture was stirred at 0 °C under an open-air atmosphere to afford **3f** (105 mg, 63%) as a colorless crystalline solid according to general procedure. R_f = 0.30 (EtOAc/hexane = 1:4, v/v); mp 161-162 °C; IR (neat): ν_{max} 2921, 1707, 1605, 1481, 1353, 1273, 753 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ = 3.43 (dd, J_1 = 18.1 Hz, J_2 = 9.0 Hz, 1H, CH), 3.85 (dd, J_1 = 18.1 Hz, J_2 = 3.0 Hz, 1H, CH), 4.12 (dd, J_1 = 8.8 Hz, J_2 = 2.5 Hz, 1H, CH), 4.91 (s, 2H, CH_2), 6.67 (d, J = 7.6 Hz, 1H, ArH), 6.89 (t, J = 7.6 Hz, 1H, ArH), 7.08 (t, J = 7.6 Hz, 1H, ArH), 7.17-7.41 (m, 9H, ArH), 7.54-7.63 (m, 4H), 8.00 (d, J = 8.4 Hz, 2H, ArH)) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 40.1, 41.3, 44.0, 109.1, 122.6, 124.5, 127.3, 127.7, 128.1, 128.4, 128.8, 129.0, 129.1, 135.1, 135.9, 139.8, 143.5, 146.2, 177.9, 196.5 ppm; HRMS (ESI) Calculated for $C_{29}H_{23}NO_2$ $(M+Na)^+$: 440.1626 found: 440.1621.



3f

Synthesis of 1-benzyl-3-[2-oxo-2-(2,4,6-trimethylphenyl)ethyl]-1,3-dihydro-2*H*-indol-2-one (3g)

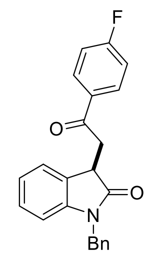
To a solution of 1-benzyl-3-diazo-1,3-dihydro-2*H*-indol-2-one (**1a**) (100 mg, 0.40 mmol) and (2*E*)-3-phenyl-1-(2,4,6-triisopropylphenyl)prop-2-en-1-one (**2e**) (134 mg, 0.40 mmol) in $CHCl_3$ (5 mL) was added 10 mol% of $BF_3 \cdot OEt_2$. The reaction mixture was stirred at 0 °C under an open-air atmosphere to afford **3g** (106 mg, 57%) as a colorless amorphous solid according to general procedure. R_f = 0.51 (EtOAc/hexane = 1.5:3.5, v/v); mp 116-117 °C; IR (neat): ν_{max} 2961, 1706, 1610, 1461, 1354, 1211, 1008, 741 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ = 1.06-1.16 (m, 18H, CH_3), 2.56-2.65 (m, 2H, CH_2), 2.76-2.83 (m, 1H, CH), 3.14 (dd, J_1 = 19.0 Hz, J_2 = 8.2 Hz, 1H, CH), 3.50 (dd, J_1 = 18.6 Hz, J_2 = 3.0 Hz, 1H, CH), 3.97-3.99 (m, 1H, CH), 4.87 (ABq, $\Delta\delta_{AB}$ = 0.08, J = 15.7 Hz, 2H, CH_2), 6.66 (d, J = 7.6 Hz, 1H,ArH), 6.91-6.94 (m, 3H, ArH), 7.06-7.28 (m, 7H, ArH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 24.0, 30.8, 34.4, 41.1, 44.0, 47.3, 109.2, 121.2, 122.3, 124.1. 127.4, 127.6, 128.1, 128.8, 136.0, 136.5, 143.7, 143.9, 149.9, 177.5, 207.5 ppm; HRMS (ESI) Calculated for $C_{32}H_{37}NO_2$ $(M+H)^+$: 468.2903 found: 468.2897.



3g

Synthesis of 1-benzyl-3-[2-(4-fluorophenyl)-2-oxoethyl]-1,3-dihydro-2*H*-indol-2-one (3i)

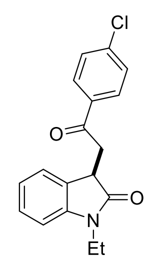
To a solution of 1-benzyl-3-diazo-1,3-dihydro-2*H*-indol-2-one (**1a**) (100 mg, 0.40 mmol) and (2*E*)-1-(4-fluorophenyl)-3-phenylprop-2-en-1-one (**2f**) (90 mg, 0.40 mmol) in $CHCl_3$ (5 mL) was added 10 mol% of $BF_3 \cdot OEt_2$. The reaction mixture was stirred at 0 °C under an open-air atmosphere to afford **3i** (90 mg, 63%) as a colorless crystalline solid according to general procedure. R_f = 0.24 (EtOAc/hexane = 1:4, v/v); mp 127-128 °C; IR (neat): ν_{max} 2918, 1699, 1601, 1354, 1221, 1160, 841, 739 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 3.45 (dd, J_1 = 18.2 Hz, J_2 = 8.8 Hz, 1H, CH), 3.86 (dd, J_1 = 18.2 Hz, J_2 = 3.1 Hz, 1H, CH), 4.16 (dd, J_1 = 8.8 Hz, J_2 = 2.7 Hz, 1H, CH), 4.98 (s, 2H, CH_2), 6.75 (d, J = 7.6 Hz, 1H, ArH), 6.96 (t, J = 7.6 Hz, 1H, ArH), 7.13-7.18 (m, 3H, ArH), 7.23-7.37 (m, 6H, ArH), 8.01-8.05 (m, 2H, ArH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 40.0, 41.3, 44.0, 109.1, 115.9 (d, J = 22 Hz), 122.6, 124.4, 127.4, 127.8, 128.1, 128.8, 129.0, 130.9 (d, J = 10 Hz), 132.8 (d, J = 2 Hz), 135.9, 143.5, 166 (d, J = 254 Hz), 177.7, 195.3 ppm; HRMS (ESI) Calculated for $C_{23}H_{18}FNO_2$ $(M+H)^+$: 360.1400 found: 360.1390.



3i

Synthesis of 3-[2-(4-chlorophenyl)-2-oxoethyl]-1-ethyl-1,3-dihydro-2*H*-indol-2-one (3j)

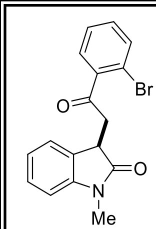
To a solution of 3-diazo-1-ethyl-1,3-dihydro-2*H*-indol-2-one (**1c**) (100 mg, 0.53 mmol) and (2*E*)-1-(4-chlorophenyl)-3-phenylprop-2-en-1-one (**2g**) (130 mg, 0.53 mmol) in $CHCl_3$ (5 mL) was added 10 mol% of $BF_3 \cdot OEt_2$. The reaction mixture was stirred at 0 °C under an open-air atmosphere to afford **3j** (109 mg, 65%) as a colorless amorphous solid according to general procedure. R_f = 0.32 (EtOAc/hexane = 1:4, v/v); mp 151-152 °C; IR (neat): ν_{max} 2920, 1705, 1609, 1487, 1356, 1219, 748 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 1.31 (t, J = 7.6 Hz, 3H, CH_3), 3.36 (dd, J_1 = 18.4 Hz, J_2 = 9.2 Hz, 1H, CH), 3.76-3.85 (m, 3H, CH_2/CH), 4.04 (dd, J_1 = 9 Hz, J_2 = 2.9 Hz, 1H, CH), 6.88 (d, J = 7.6 Hz, 1H, ArH), 6.96-7.00 (m, 1H, ArH), 7.23-7.29 (m, 2H, ArH), 7.43-7.45 (m, 2H, ArH), 7.91 (d, J = 8.8 Hz, 2H, ArH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 12.7, 34.9, 40.0, 41.2, 108.2, 122.3, 124.5, 128.1, 129.0, 129.2, 129.6, 134.7, 139.9, 143.4, 177.1, 195.8 ppm; HRMS (ESI) Calculated for $C_{18}H_{16}{}^{35}ClNO_2$ $(M+H)^+$: 314.0948 found: 314.0931.



3j

Synthesis of 3-[2-(2-bromophenyl)-2-oxoethyl]-1-methyl-1,3-dihydro-2*H*-indol-2-one (3k)

To a solution of 3-diazo-1-methyl-1,3-dihydro-2*H*-indol-2-one (**1b**) (100 mg, 0.58 mmol) and (2*E*)-1-(2-bromophenyl)-3-phenylprop-2-en-1-one (**2h**) (115 mg, 0.58 mmol) in $CHCl_3$ (5 mL) was added 10 mol% of $BF_3 \cdot OEt_2$. The reaction mixture was stirred at 0 °C under an open-air atmosphere to afford **3k** (120 mg, 60%) as a colorless crystalline solid according to general procedure. R_f = 0.40 (EtOAc/hexane = 1:4, v/v); mp 184-185 °C; IR (neat): ν_{max} 3056, 2922, 1693,

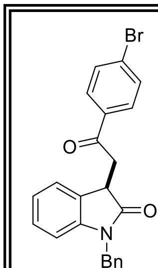


3k

1609, 1353, 1215, 1104, 735 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 3.30 (s, 3H, CH_3), 3.50 (dd, J_1 = 18.4 Hz, J_2 = 8.8 Hz, 1H, CH), 3.91 (dd, J_1 = 18.4 Hz, J_2 = 3.2 Hz, 1H, CH), 4.10 (dd, J_1 = 18.4 Hz, J_2 = 3.2 Hz, 1H, CH), 6.90-7.05 (m, 2H, ArH), 7.26-7.34 (m, 2H, ArH), 7.73 (t, J = 8 Hz, 1H, ArH), 8.32-8.47 (m, 2H, ArH), 8.81-8.82 (m, 1H, ArH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 26.5, 40.2, 41.0, 108.3, 122.6, 123.1, 124.2, 127.7, 128.4, 128.6, 130.1, 133.7, 137.5, 144.4, 148.5, 177.3, 195.09 ppm; HRMS (ESI) Calculated for $C_{17}H_{14}{}^{79}BrNO_2$ $(M+H)^+$: 344.0286 found: 344.0282.

Synthesis of 1-benzyl-3-[2-(4-bromophenyl)-2-oxoethyl]-1,3-dihydro-2*H*-indol-2-one (3l)[4]

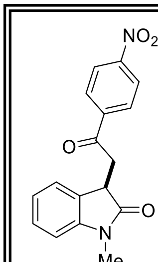
To a solution of 1-benzyl-3-diazo-1,3-dihydro-2*H*-indol-2-one (**1a**) (100 mg, 0.40 mmol) and (2*E*)-1-(4-bromophenyl)-3-phenylprop-2-en-1-one (**2i**) (115 mg, 0.40 mmol) in $CHCl_3$ (5 mL) was added 10 mol% of $BF_3{\cdot}OEt_2$. The reaction mixture was stirred at 0 °C under an open-air atmosphere to afford **3l** (106 mg, 63%) as a colorless crystalline solid according to general procedure. R_f = 0.46 (EtOAc/hexane = 1:4, v/v); mp 132-133 °C; IR (neat): ν_{max} 2922, 1693, 1609, 1353, 1215, 1104, 735 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 3.44 (dd, J_1 = 18 Hz, J_2 = 8.8 Hz, 1H, CH), 3.85 (dd, J_1 = 18 Hz, J_2 = 3 Hz, 1H, CH), 4.15 (dd, J_1 = 8.4 Hz, J_2 = 2,4 Hz, 1H, CH), 4.97 (s, 2H, CH_2), 6.75 (d, J = 7.6 Hz, 1H, ArH), 6.96 (t, J = 7.6 Hz, 1H, ArH), 7.14-7.37 (m, 7H, ArH), 7.62 (d, J = 8.4 Hz, 2H, ArH), 7.86 (d, J = 8.8 Hz, 2H, ArH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 40.0, 41.2, 44.0, 109.2, 122.6, 124.3, 127.4, 127.7, 128.1, 128.78, 128.84, 129.7, 132.1, 135.0, 135.9, 143.5, 177.7, 195.9 ppm; HRMS (ESI) Calculated for $C_{23}H_{18}{}^{79}BrNO_2$ $(M-H)^+$: 418.0448 found: 418.0451.



3l

Synthesis of 1-methyl-3-[2-(4-nitrophenyl)-2-oxoethyl]-1,3-dihydro-2*H*-indol-2-one (3m)

To a solution of 3-diazo-1-methyl-1,3-dihydro-2*H*-indol-2-one (**1b**) (100 mg, 0.58 mmol) and (2*E*)-1-(4-nitrophenyl)-3-phenylprop-2-en-1-one (**2j**) (101 mg, 0.58 mmol) in $CHCl_3$ (5 mL) was added 10 mol% of $BF_3{\cdot}OEt_2$. The reaction mixture was stirred at 0 °C under an open-air atmosphere to afford **3m** (91 mg, 51%) as a colorless crystalline solid according to general procedure. R_f = 0.18 (EtOAc/hexane = 1.5:3.5, v/v); mp 131-132 °C; IR (neat): ν_{max} 2928, 1696, 1610, 1468, 1347, 1215, 1091, 749 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 3.13 (s, 3H, CH_3), 3.24 (dd, J_1 = 18.4 Hz, J_2 = 8.8 Hz, 1H, CH), 3.62 (dd, J_1 = 18.4 Hz, J_2 = 3.6 Hz, 1H, CH), 3.97 (dd, J_1 = 8.7 Hz, J_2 = 3.4 Hz, 1H, CH), 6.91-6.95 (m, 1H, ArH), 7.17-7.35 (m, 5H, ArH), 7.48-7.50 (m, 1H,

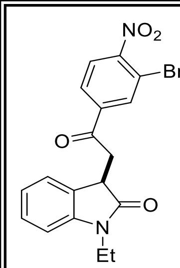


3m

ArH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 26.5, 41.4, 43.7, 108.2, 118.4, 122.6, 124.5, 127.6, 128.3, 128.6, 128.9, 132.0, 133.9, 140.6, 144.3, 177.2, 200.9 ppm; HRMS (ESI) Calculated for $C_{17}H_{14}N_2O_4$ $(M+H)^+$: 311.1032 found: 311.1043.

Synthesis of 3-[2-(3-bromo-4-nitrophenyl)-2-oxoethyl]-1-ethyl-1,3-dihydro-2*H*-indol-2-one (3n)

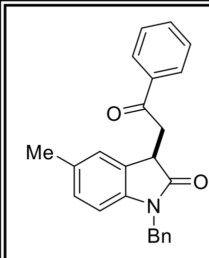
To a solution of 3-diazo-1-ethyl-1,3-dihydro-2*H*-indol-2-one (**1c**) (100 mg, 0.53 mmol) and (2*E*)-1-(3-bromo-4-nitrophenyl)-3-phenylprop-2-en-1-one (**2k**) (176 mg, 0.53 mmol) in $CHCl_3$ (5 mL) was added 10 mol% of $BF_3{\cdot}OEt_2$. The reaction mixture was stirred at 0 °C under an open-air atmosphere to afford **3n** (71 mg, 33%) as a colorless crystalline solid according to general procedure. R_f = 0.15 (EtOAc/hexane = 1.5:3.5, v/v); mp 201-202 °C; IR (neat): ν_{max} 2929, 1695, 1604, 1535, 1353, 1217, 1029,738 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 1.32 (t, J = 7.2 Hz, 3H, CH_3), 3.41 (dd, J_1 = 18.4 Hz, J_2 = 8.4 Hz, 1H, CH), 3.78-3.85 (m, 3H, CH_2/CH), 4.03 (dd, J_1 = 8.4 Hz, J_2 = 3.2 Hz, 1H, CH), 6.90 (d, J = 7.6 Hz, 1H, ArH), 7.00 (t, J = 7.6 Hz, 1H, ArH), 7.21-7.31 (m, 2H, ArH), 7.88 (d, J = 7.9 Hz, 1H, ArH), 7.98-8.01 (m, 1H, ArH), 8.4 (d, J = 1.6 Hz, 1H, ArH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 12.6, 35.0, 40.1, 41.0, 108.4, 120.2, 122.5, 124.3, 125.1, 128.4, 128.6, 131.9, 135.8, 136.2, 143.5, 150.1, 176.7, 194.1 ppm; HRMS (ESI) Calculated for $C_{18}H_{15}{}^{79}BrN_2O_4$ $(M+H)^+$: 403.0293 found: 403.0285.



3n

Synthesis of 1-benzyl-5-methyl-3-(2-oxo-2-phenylethyl)-1,3-dihydro-2*H*-indol-2-one (3p)[3]

To a solution of 1-benzyl-3-diazo-5-methyl-1,3-dihydro-2*H*-indol-2-one (**1d**) (100 mg, 0.38 mmol) and (2*E*)-1,3-diphenylprop-2-en-1-one (**2b**) (176 mg, 0.38 mmol) in $CHCl_3$ (5 mL) was added 10 mol% of $BF_3{\cdot}OEt_2$. The reaction mixture was stirred at 0 °C under an open-air atmosphere to afford **3p** (100 mg, 74%) as a colorless crystalline solid according to general procedure. R_f = 0.39 (EtOAc/hexane = 1:4, v/v); mp 161-162 °C; IR (neat): ν_{max} 2913, 1698, 1599, 1493, 1445, 1353, 1185,728 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 2.29 (s, 3H, CH_3), 3.53 (dd, J_1 = 18.2 Hz, J_2 = 9 Hz, 1H, CH), 3.95 (dd, J_1 = 18.2 Hz, J_2 = 3.0 Hz, 1H, CH), 4.20-4.22 (m, 1H, CH), 5.02 (s, 2H, CH_2), 6.68 (d, J = 8 Hz, 1H, ArH), 7.00 (d, J = 8 Hz, 1H, ArH), 7.13 (s, 1H, ArH), 7.30-7.65 (m, 8H, ArH), 8.07 (d J = 8 Hz, 2H, ArH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 21.1, 40.2, 41.3, 44.0, 108.9, 125.28, 125.33, 127.4,

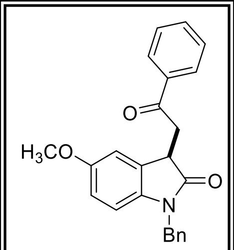


3p

127.6, 128.3, 128.76, 128.82, 129.2, 132.2, 133.5, 136.0, 136.4, 141.0, 177.8, 197.0 ppm; HRMS (ESI) Calculated for $C_{24}H_{21}NO_2$ $(M+H)^+$: 356.1651 found: 356.1646.

Synthesis of 1-benzyl-5-methoxy-3-(2-oxo-2-phenylethyl)-1,3-dihydro-2*H*-indol-2-one (3q)

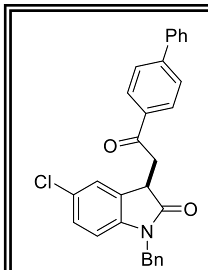
To a solution of 1-benzyl-3-diazo-5-methoxy-1,3-dihydro-2*H*-indol-2-one (**1e**) (100 mg, 0.36 mmol) and (2*E*)-1,3-diphenylprop-2-en-1-one (**2b**) (75 mg, 0.36 mmol) in $CHCl_3$ (5 mL) was added 10 mol% of $BF_3{\cdot}OEt_2$. The reaction mixture was stirred at 0 °C under an open-air atmosphere to afford **3q** (96 mg, 72%) as a colorless crystalline solid according to general procedure. R_f = 0.18 (EtOAc/hexane = 1:4, v/v); mp 173-174 °C; IR (neat): ν_{max} 2923, 1701, 1599, 1445, 1363, 1187, 1147, 725 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ = 3.52 (dd, J_1 = 18.2 Hz, J_2 = 9.0 Hz,1H, CH), 3.74 (s, 3H, CH_3), 3.94 (dd, J_1 = 18.2 Hz, J_2 = 2.8 Hz, 1H, CH), 4.19-4.21 (m, 1H, CH), 5.00, (s, 2H, CH_2), 6.66-6.73 (m, 2H, ArH), 6.95 (s, 1H, ArH), 7.30-7.40 (m, 5H, ArH), 7.52 (t, J = 7.6 Hz, 2H, ArH), 7.61-765 (m, 1H, ArH), 8.05 (d, J = 7.2 Hz, 2H, ArH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 40.2, 41.7, 44.1, 55.8, 109.4, 112.0, 112.3, 127.3, 127.6, 128.2, 128.75, 128.82, 130.5, 133.5, 136.0, 136.3, 136.9, 155.9, 177.5, 196.9 ppm; HRMS (ESI) Calculated for $C_{24}H_{21}NO_3$ $(M+H)^+$: 372.1600 found: 372.1623.



3q

Synthesis of 3-[2-([1,1'-biphenyl]-4-yl)-2-oxoethyl]-5-chloro-1-benzyl-1,3-dihydro-2*H* -indol-2-one (3r)

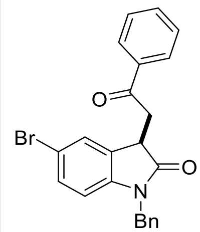
To a solution of 1-benzyl-5-chloro-3-diazo-1,3-dihydro-2*H*-indol-2-one (**1f**) (100 mg, 0.35 mmol) and (2*E*)-1-([1,1'-biphenyl]-4-yl)-3-phenylprop-2-en-1-one (**2d**) (100 mg, 0.35 mmol) in $CHCl_3$ (10 mL) was added 10 mol% of $BF_3{\cdot}OEt_2$. The reaction mixture was stirred at 0 °C under an open-air atmosphere to afford **3r** (108 mg, 68%) as a colorless crystalline solid according to general procedure. R_f = 0.26 (EtOAc/hexane = 1.5:.3.5, v/v); mp 178-179 °C; IR (neat): ν_{max} 2919, 1707, 1681, 1601, 1483, 1352, 1263, 805 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ = 3.49-3.57 (m, 1H, CH), 3.94 (dd, J_1 = 18.4 Hz, J_2 = 2.8 Hz, 1H, CH), 4.15 (d, J = 5.6 Hz, 1H, CH), 4.97 (s, 2H, CH_2), 6.33-6.65 (m, 1H, ArH), 7.12 (d, J = 6.8 Hz, 1H, ArH), 7.25-7.49 (m, 9H, ArH), 7.62-7.71 (m, 4H, ArH), 8.05-8.08 (m, 2H, ArH), ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 39.9, 41.2, 44.1, 110.0, 124.9, 127.30, 127.33, 127.4, 127.8, 127.95, 128.01, 128.4, 128.8, 128.9, 129.0, 130.8, 134.8, 135.5, 139.8, 142.1, 146.4, 177.3, 196.1 ppm; HRMS (ESI) Calculated for $C_{29}H_{22}{}^{35}ClNO_2$ $(M+Na)^+$: 474.1237 found: 474.1244.



3r

Synthesis of 1-benzyl-5-bromo-3-(2-oxo-2-phenylethyl)-1,3-dihydro-2*H*-indol-2-one (3s)

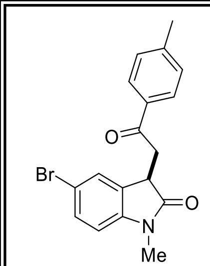
To a solution of 1-benzyl-5-bromo-3-diazo-1,3-dihydro-2*H*-indol-2-one (**1g**) (100 mg, 0.30 mmol) and (2*E*)-1,3-diphenylprop-2-en-1-one (**2b**) (56 mg, 0.30 mmol) in $CHCl_3$ (5 mL) was added 10 mol% of $BF_3{\cdot}OEt_2$. The reaction mixture was stirred at 0 °C under an open-air atmosphere to afford **3s** (81 mg, 63%) as a colorless crystalline solid according to general procedure. R_f = 0.46 (EtOAc/hexane = 1:4, v/v); mp 162-163 °C; IR (neat): ν_{max} 2917, 1707, 1602, 1483, 1350, 1289, 1217, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 3.55 (dd, J_1 = 18.4 Hz, J_2 = 8.8 Hz, 1H, CH), 3.95 (dd, J_1 = 18.4 Hz, J_2 = 2.4 Hz, 1H, CH), 4.18 (d, J = 8 Hz, 1H, CH), 5.00 (s, 2H, CH_2), 6.64 (d, J = 8.4 Hz, 1H, ArH), 7.30-7.66 (m, 10H, ArH), 8.04 (d, J = 7.6 Hz, 2H, ArH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 39.9, 41.2, 44.1, 110.5, 115.3, 127.3, 127.6, 127.8, 128.3, 128.8, 128.9, 130.9, 131.1, 133.7, 135.4, 136.1, 142.5, 177.2, 196.5 ppm; HRMS (ESI) Calculated for $C_{23}H_{18}{}^{79}BrNO_2$ $(M+Na)^+$: 442.0420 found: 442.0419



3s

Synthesis of 5-bromo-1-methyl-3-[2-(4-methylphenyl)-2-oxoethyl]-1,3-dihydro-2*H*-indol-2-one (3t)

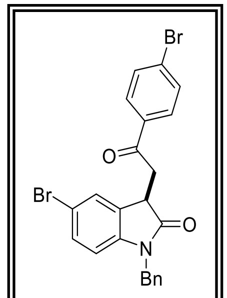
To a solution of 5-bromo-3-diazo-1-methyl-1,3-dihydro-2*H*-indol-2-one (**1h**) (100mg, 0.40 mmol) and (2*E*)-1-(4-methylphenyl)-3-phenylprop-2-en-1-one (**2a**) (89 mg, 0.40 mmol) in $CHCl_3$ (5 mL) was added 10 mol% of $BF_3{\cdot}OEt_2$. The reaction mixture was stirred at 0 °C under an open-air atmosphere to afford **3t** (93mg, 65%) as a colorless crystalline solid according to general procedure. R_f = 0.35 (EtOAc/hexane = 1:4, v/v); mp 153-154 °C; IR (neat): ν_{max} 2917, 1711, 1606, 1483, 1345, 1098, 806 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 2.42 (s, 3H, CH_3), 3.25 (s, 3H, CH3), 3.39 (dd, J_1 = 18.4 Hz, J_2 = 8.8 Hz, 1H, CH), 3.82 (dd, J_1 = 18.3 Hz, J_2 = 2.9 Hz, 1H, CH), 4.03-4.05 (m, 1H, CH), 6.73 (d, J = 8.4 Hz, 1H, ArH), 7.27-7.41 (m, 4H, ArH), 7.87 (d, J = 8.4 Hz, 2H, ArH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 21.7, 26.5, 39.8, 41.2, 109.4, 115.2, 127.7, 128.3, 129.4, 130.9, 131.2, 133.7, 143.4, 144.6, 177.2, 196.2 ppm; HRMS (ESI) Calculated for $C_{18}H_{16}{}^{79}BrNO_2$ $(M+H)^+$: 358.0443 found: 358.0437.



3t

Synthesis of 1-benzyl-5-bromo-3-[2-(4-bromophenyl)-2-oxoethyl]-1,3-dihydro-2*H*-indol-2-one (3u)

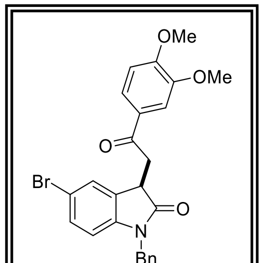
To a solution of 1-benzyl-5-bromo-3-diazo-1,3-dihydro-2*H*-indol-2-one (**1g**) (100 mg, 0.30 mmol) and (2*E*)-1-(4-bromophenyl)-3-phenylprop-2-en-1-one (**2i**) (137 mg, 0.30 mmol) in $CHCl_3$ (5 mL) was added 10 mol% of $BF_3{\cdot}OEt_2$. The reaction mixture was stirred at 0 °C under an open-air atmosphere to afford **3u** (76mg, 51%) as a colorless crystalline solid according to general procedure. R_f = 0.54 (EtOAc/hexane = 1:4, v/v); mp 148-149 °C; IR (neat): ν_{max} 2920, 1710, 1586, 1482, 1348, 1169, 809 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ = 3.39 (dd, J_1 = 18.4 Hz, J_2 = 8.4 Hz, 1H, CH), 3.77 (dd, J_1 = 18.4 Hz, J_2 = 3.2 Hz, 1H, CH), 4.00-4.02 (m, 1H, CH), 4.87 (ABq, $\Delta\delta_{AB}$ = 0.02, J = 15.8 Hz, 2H, CH_2), 6.51 (d, J = 8.4 Hz, 1H, ArH), 7.16-7.28 (m, 7H, ArH), 7.54 (d, J = 8.4 Hz, 2H, ArH), 7.77 (d, J = 8.4 Hz, 2H, ArH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 39.8, 41.2, 44.1, 110.6, 115.4, 127.3, 127.5, 127.8, 128.9, 129.0, 129.7, 130.9, 131.0, 132.1, 134.8, 135.4, 142.5, 177.0, 195.5 ppm; HRMS (ESI) Calculated for $C_{23}H_{17}{}^{79}Br^{81}BrNO_2$ $(M+H)^+$: 499.9684 found: 499.9683



3u

Synthesis of 5-bromo-3-[2-(3,4-dimethoxyphenyl)-2-oxoethyl]-1-benzyl-1,3-dihydro-2*H*-indol-2-one (3v)

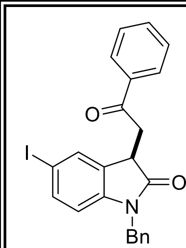
To a solution of 1-benzyl-5-bromo-3-diazo-1,3-dihydro-2*H*-indol-2-one (**1g**) (100 mg, 0.30 mmol) and (2*E*)-1-(3,4-dimethoxyphenyl)-3-phenylprop-2-en-1-one (**2l**) (137 mg, 0.30 mmol) in $CHCl_3$ (5 mL) was added 10 mol% of $BF_3{\cdot}OEt_2$. The reaction mixture was stirred at 0 °C under an open-air atmosphere to afford **3v** (86mg, 60%) as a colorless amorphous solid according to general procedure. R_f = 0.11 (EtOAc/hexane = 1.5:3.5, v/v); mp 123-124 °C; IR (neat): ν_{max} 2943, 1710, 1670, 1487, 1343, 1273, 730 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ = 3.64 (dd, J_1 = 19 Hz, J_2 = 8.1 Hz, 1H, CH), 3.83 (s, 3H, CH_3), 3.92-3.98 (m, 4H, CH_3/CH), 4.11 (dd, J_1 = 7.6 Hz, J_2 = 2.8 Hz, 1H, CH), 5.00 (ABq, $\Delta\delta_{AB}$ = 0.08, J = 15.7 Hz, 2H, CH_2), 6.62 (d, J = 8 Hz, 1H, ArH), 6.96 (d, J = 8.8 Hz, 1H, ArH), 7.09-7.12 (m, 1H, ArH), 7.28-7.42 (m, 8H, ArH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 41.8, 44.0, 44.8, 55.86, 55.92, 110.4, 113.2, 113.8, 115.2, 121.4, 126.7, 127.3, 127.7, 128.9, 130.6, 131.5, 135.6. 142.6, 153.5, 153.8, 177.5, 197.5 ppm; HRMS (ESI) Calculated for $C_{25}H_{22}{}^{79}BrNO_4$ $(M+H)^+$: 480.0810 found: 480.0805.



3v

Synthesis of 1-benzyl-5-iodo-3-(2-oxo-2-phenylethyl)-1,3-dihydro-2*H*-indol-2-one (3w)

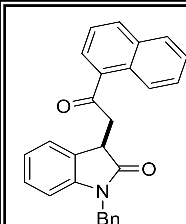
To a solution of 1-benzyl-3-diazo-5-iodo-1,3-dihydro-2*H*-indol-2-one (**1i**) (100 mg, 0.27 mmol) and (2*E*)-1,3-diphenylprop-2-en-1-one (**2b**) (56 mg, 0.27 mmol) in $CHCl_3$ (5 mL) was added 10 mol% of $BF_3{\cdot}OEt_2$. The reaction mixture was stirred at 0 °C under an open-air atmosphere to afford **3w** (74 mg, 59%) as a colorless crystalline solid according to general procedure. R_f = 0.43 (EtOAc/hexane = 1:4, v/v); mp 196-197 °C; IR (neat): ν_{max} 2918, 1705, 1598, 1483, 1351, 1215, 1175, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 3.56 (dd, J_1 = 18.4 Hz, J_2 = 8.4 Hz, 1H, CH), 3.94 (dd, J_1 = 18.4 Hz, J_2 = 2.8 Hz, 1H, CH), 4.15-4.17 (m, 1H, CH), 5.00 (s, 2H, CH_2), 6.55 (d, J = 8 Hz, 1H, ArH), 7.30-7.67 (m, 10H, ArH), 8.04 (d, J = 7.6 Hz, 2H, ArH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 39.9, 41.0, 44.0, 85.3, 111.1, 127.3, 127.8, 128.3, 128.8, 128.9, 131.5, 133.1, 133.7, 135.5, 136.1, 136.9, 143.3, 177.0, 196.4 ppm; HRMS (ESI) Calculated for $C_{23}H_{18}INO_2$ $(M+H)^+$: 468.0460 found: 468.0464.



3w

Synthesis of 1-benzyl-3-[2-(naphthalen-1-yl)-2-oxoethyl]-1,3-dihydro-2*H*-indol-2-one (3x)

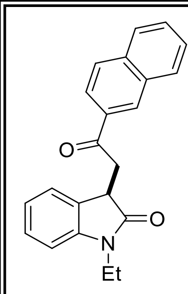
To a solution of 1-benzyl-3-diazo-1,3-dihydro-2*H*-indol-2-one (**1a**) (100 mg, 0.40 mmol) and (2*E*)-1-(naphthalen-1-yl)-3-phenylprop-2-en-1-one (**2m**) (163 mg, 0.40 mmol) in $CHCl_3$ (5 mL) was added 10 mol% of $BF_3{\cdot}OEt_2$. The reaction mixture was stirred at 0 °C under an open-air atmosphere to afford **3x** (110 mg, 70%) as a colorless crystalline solid according to general procedure. R_f = 0.44 (EtOAc/hexane = 1.5:3.5, v/v); mp 161-162 °C; IR (neat): ν_{max} 2919, 1703, 1608, 1355, 1217, 1170, 746 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 3.53 (dd, J_1 = 18 Hz, J_2 = 8.8 Hz, 1H, CH), 3.92-3.98 (m, 1H, CH), 4.24 (dd, J_1 = 8.8 Hz, J_2 = 2.8 Hz, 1H, CH), 5.03 (s, 2H, CH_2), 6.79 (d, J = 7.6 Hz, 1H, ArH), 7.00 (t, J = 7.6 Hz, 1H, ArH), 7.20 (t, J = 7.6 Hz, 1H, ArH), 7.29-7.65 (m, 11H, ArH), 8.04-8.06 (m, 2H, ArH), ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 40.1, 41.3, 44.0, 109.1, 122.6, 124.4, 127.4, 127.6, 128.0, 128.2, 128.75. 128.84, 129.1,133.5, 135.9, 136.4, 143.5, 177.9, 196.9 ppm; HRMS (ESI) Calculated for $C_{27}H_{21}NO_2$ $(M+H)^+$: 392.1651 found: 392.1653.



3x

Synthesis of 1-ethyl-3-[2-(naphthalen-2-yl)-2-oxoethyl]-1,3-dihydro-2*H*-indol-2-one (3y)

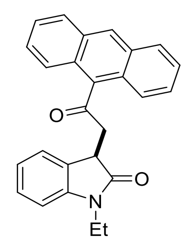
To a solution of 3-diazo-1-ethyl-1,3-dihydro-2*H*-indol-2-one (**1c**) (100 mg, 0.53 mmol) and (2*E*)-1-(naphthalen-2-yl)-3-phenylprop-2-en-1-one (**2n**) (137 mg, 0.53 mmol) in $CHCl_3$ (5 mL) was added 10 mol% of $BF_3{\cdot}OEt_2$. The reaction mixture was stirred at 0 °C under an open-air atmosphere to afford **3y** (113mg, 65%) as a colorless amorphous solid according to general procedure. R_f = 0.39 (EtOAc/hexane = 1:4, v/v); mp 111-112 °C; IR (neat): ν_{max} 2978, 1699, 1609, 1462, 1358, 1227, 1133, 739 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ = 1.27 (t, J = 7.2 Hz, 3H, CH), 3.48 (dd, J_1 = 17.9 Hz, J_2 = 8.7 Hz, 1H, CH), 3.75-3.88 (m, 3H, CH/CH_2), 4.13 (dd, J_1 = 8.4 Hz, J_2 = 3.2 Hz, 1H, CH), 6.84 (d, J = 7.6 Hz, 1H, ArH), 7.00 (t, J = 7.6 Hz, 1H, ArH), 7.24-7.59 (m, 5H, ArH), 7.83-7.96 (m, 3H, ArH), 8.61 (d, J = 8.4 Hz, 1H, ArH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 12.7, 34.9, 41.8, 43.1, 108.3, 122.4, 124.4, 124.5, 125.8, 126.6, 128.07, 128.12, 128.2, 128.5, 129.3, 130.1, 133.1, 134.0, 135.1, 143.5, 177.2, 201.0 ppm; HRMS (ESI) Calculated for $C_{22}H_{19}NO_2$ $(M+H)^+$: 330.1494 found: 330.1486.



3y

Synthesis of 3-[2-(anthracen-9-yl)-2-oxoethyl]-1-ethyl-1,3-dihydro-2*H*-indol-2-one (3z)

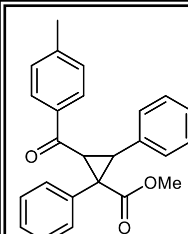
To a solution of 3-diazo-1-ethyl-1,3-dihydro-2*H*-indol-2-one (**1c**) (100 mg, 0.53 mmol) and (2*E*)-1-(anthracen-9-yl)-3-phenylprop-2-en-1-one (**2o**) (163 mg, 0.53 mmol) in $CHCl_3$ (5 mL) was added 10 mol% of $BF_3{\cdot}OEt_2$. The reaction mixture was stirred at 0 °C under an open-air atmosphere to afford **3z** (106 mg, 53%) as a colorless amorphous solid according to general procedure. R_f = 0.41 (EtOAc/hexane = 1.5:3.5, v/v); mp 121-122 °C; IR (neat): ν_{max} 2979, 1702, 1609, 1462, 1366, 1273, 737 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ = 1.34, (t, J = 7.2 Hz, 3H, CH_3), 3.66 (dd, J_1 = 19.6 Hz, J_2 = 7.4 Hz, 1H, CH), 3.77-3.96 (m, 3H, CH/CH_2) 4.07 (dd, J_1 = 7.2 Hz, J_2 = 3.2 Hz, 1H, CH), 6.95 (d, J = 7.6 Hz, 1H, ArH), 7.16 (t, J = 7.6 Hz, 1H, ArH), 7.36 (t, J = 7.6 Hz, 1H, ArH) 7.44-7.53 (m, 5H, ArH), 7.78-7.80 (m, 2H, ArH), 7.98-8.01 (m, 2H, ArH), 8.46 (s, 1H, ArH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 12.5, 35.0, 41.3, 46.7, 108.5, 122.30, 122.33, 124.1, 124.2, 125.6, 126.98, 127.03, 128.3, 128.8, 129.0, 131.0, 134.9, 144.0, 177.0, 207.0 ppm; HRMS (ESI) Calculated for $C_{26}H_{21}NO_2$ $(M+H)^+$: 380.1651 found: 380.1629.



3z

Synthesis of methyl 2-(4-methylbenzoyl)-1,3-diphenylcyclopropane-1-carboxylate (3aa)[6]

To a solution of methyl 2-diazo-2-phenylacetate (**1k**) (100 mg, 0.57 mmol) and (2*E*)-1-(4-methylphenyl)-3-phenylprop-2-en-1-one (**2a)** (126 mg, 0.57 mmol) in $CHCl_3$ (5 mL) was added 10 mol% of $BF_3{\cdot}OEt_2$. The reaction mixture was stirred at 0 °C under an open-air atmosphere to afford **6a** (44 mg, 21%) as a colorless amorphous solid according to general procedure. R_f = 0.8 (EtOAc/hexane = 0.5:4.5, v/v); mp 157-158 °C; IR (neat): ν_{max} 2951, 1715,

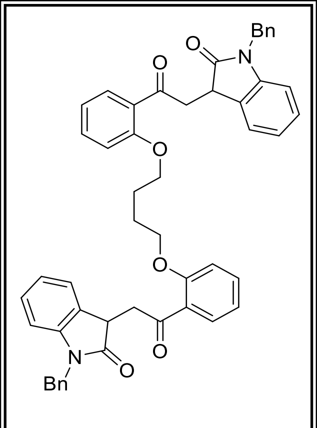


3aa

1670, 1445, 1263, 1180, 716 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 2.49 (s, 3H, CH_3), 3.46 (s, 3H, CH_3), 4.03 (d, J = 7.2 Hz, 1H, CH), 4.45 (d, J = 7.2 Hz, 1H, CH), 7.29-7.43 (m, 12H, ArH), 8.06 (d, J = 8 Hz, 2H, ArH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 21.8, 35.2, 35.4, 48.7, 52.7, 127.3, 127.9, 128.3, 128.4, 128.6, 128.8, 129.5, 130.1, 134.8, 135.3, 135.5, 144.2, 170.0, 193.5 ppm; HRMS (ESI) Calculated for $C_{25}H_{23}O_3$ $(M+H)^+$: 371.1647 found: 371.1607.

Synthesis of 3,3'-(((butane-1,4-diylbis(oxy))bis(2,1-phenylene))bis(2-oxoethane-2,1-diyl))bis(1-benzylindolin-2-one) (6a)

To a solution of 1-benzyl-3-diazo-1,3-dihydro-2*H*-indol-2-one (**1a**) (100 mg, 0.40 mmol) and (2*E*,2'*E*)-1,1'-((butane-1,4-diylbis(oxy))bis(2,1-phenylene))bis(3-phenylprop-2-en-1-one) (**5a**) (101 mg, 0.20 mmol) in $CHCl_3$ (5 mL) was added 10 mol% of $BF_3{\cdot}OEt_2$. The reaction mixture was stirred at 0 °C under an open-air atmosphere to afford **6a** (182 mg, 59%) as a colorless crystalline solid according to general procedure. R_f = 0.28 (EtOAc/hexane = 1.5:3.5, v/v); mp 187-188 °C; IR (neat): ν_{max} 2927, 1707, 1672, 1599, 1454, 1356, 1291, 1236, 753 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 1.73 (s, 1H, CH), 2.31-2.34 (m, 1H, CH), 3.44 (dd, J_1 = 18.4 Hz, J_2 = 9.2 Hz, 1H, CH), 3.90 (dd, J_1 = 18.4 Hz, J_2 = 3.2 Hz, 1H, CH), 4.12-4.28 (m, 3H, CH_2), 4.86-4.92 (m, 2H, CH_2), 6.69 (d, J = 7.6 Hz, 1H, ArH), 6.88-6.99 (m, 3H, ArH), 7.08-7.13 (m, 1H, ArH), 7.22-7.42 (m, 7H, ArH), 7.75 (d, J = 7.6 Hz, 1H, ArH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 29.2, 41.7, 43.9, 45.3, 65.1, 109.0, 112.6, 121.0, 122.5, 124.4, 127.3, 127.5, 127.6, 127.9, 128.8, 129.3, 130.5, 134.1, 136.0, 143.4, 157.9, 177.9, 198.7 ppm (due to the C_2 Symmetry we observed half-half the signal); HRMS (ESI) Calculated for $C_{50}H_{44}N_2O_6$ $(M+K)^+$: 807.2863 found: 807.2852.

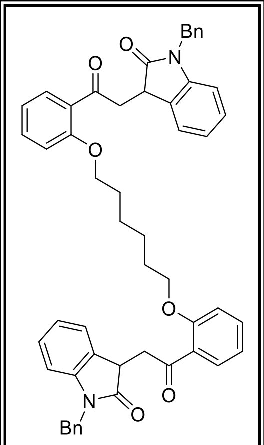


6a

Synthesis of (((hexane-1,6-diylbis(oxy))bis(2,1-phenylene))bis(2-oxoethane-2,1-diyl))bis(1-benzylindolin-2-one) (6b)

To a solution of 1-benzyl-3-diazo-1,3-dihydro-2*H*-indol-2-one (**1a**) (100 mg, 0.40 mmol) and (2*E*,2'*E*)-1,1'-((hexane-1,6-diylbis(oxy))bis(2,1-phenylene))bis(3-phenylprop-2-en-1-one) (**5b**) (106 mg, 0.2 mmol) in $CHCl_3$ (5 mL) was added 10 mol% of $BF_3{\cdot}OEt_2$. The reaction mixture was stirred at 0 °C under an open-air atmosphere to afford **6b** (179 mg, 56%) as a colorless crystalline solid according to general procedure. R_f = 0.30 (EtOAc/hexane = 1.5:3.5, v/v); mp

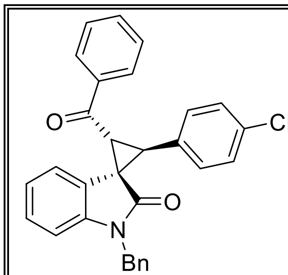
210-211 °C; IR (neat): ν_{max} 2931, 1709, 1671, 1602, 1457, 1356, 753 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ = 1.50 (s, 2H, CH_2), 1.83 (s, 2H, CH_2), 3.54-3.60 (m, 1H, CH_2), 3.90-3.60 (m, 4H, CH_2), 4.88-5.02 (m, 2H, CH_2), 6.69-6.71 (m, 1H, ArH), 6.92-6.99 (m, 3H, ArH), 7.09-7.13 (m, 1H, ArH), 7.21-7.30 (m, 6H, ArH), 7.41-7.45 (m, 1H, ArH), 7.77 (d, J = 7.6 Hz, 1H, ArH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 26.1, 29.1, 42.0, 44.0, 45.3, 68.5, 109.1, 112.4, 120.6, 122.6, 124.3, 127.2, 127.6, 127.8, 128.8, 129.6, 130.4, 130.7, 134.1, 135.8, 143.3, 158.6, 178.4, 198.5 ppm (due to the C_2 Symmetry we observed half-half the signal); HRMS (ESI) Calculated for $C_{52}H_{48}N_2O_6$ $(M+H)^+$: 797.3591 found: 797.3588.



6b

Synthesis of 2-benzoyl-3-(4-chlorophenyl)-1'-ethylspiro[cyclopropane-1,3'-indol]-2'(1'*H*)-one (7a)

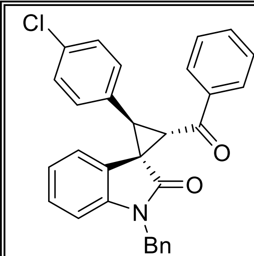
To a solution of $InCl_3$ (20 mol%) in 6:2 mL water and THF were added 1-benzyl-3-diazo-1,3-dihydro-2*H*-indol-2-one (**1a**) (100 mg, 0.40 mmol) and (2*E*)-1-(4-chlorophenyl)-3-phenylprop-2-en-1-one (**2g**) (97 mg, 0.40 mmol) under an air atmosphere. The reaction mixture was stirred at ambient temperature for 24 h and extracted with ethyl acetate. The organic phase was dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by chromatographic purification (Hexane/EtOAc) to afford the desired cyclopropane product **7a** (154 mg, 83%) as a colorless crystalline solid. R_f = 0.31 (EtOAc/hexane = 1:4, v/v); mp 225-226 °C; IR (neat): ν_{max} 3057, 1708, 1673, 1606, 1357, 1179, 1091, 739 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ = 4.13 (d, J = 8 Hz, 1H, CH), 4.31 (d, J = 8.4 Hz, 1H, CH), 4.93 (ABq, $\Delta\delta_{AB}$ = 0.06, J = 15.6 Hz, 2H, CH_2), 6.76 (d, J = 7.6 Hz, 1H, ArH), 6.94 (t, J = 7.6 Hz, 1H, ArH), 7.11 (t, J = 7.6 Hz, 1H, ArH), 7.21-7.41 (m, 12H, ArH), 7.51-7.55 (m, 1H, ArH), 7.93 (d, J = 7.6 Hz, 1H, ArH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 38.6, 41.4, 44.1, 109.2, 122.0, 122.6, 125.7, 127.3, 127.7, 128.4, 128.5, 128.8, 128.9, 130.7, 131.9, 133.5, 133.9, 136.0, 136.9, 142.9, 172.0, 192.7 ppm; HRMS (ESI) Calculated for $C_{30}H_{22}{}^{35}ClNO_2$ $(M+H)^+$: 464.1417 found: 464.1412.



7a

Synthesis of 2-benzoyl-3-(4-chlorophenyl)-1'-methylspiro[cyclopropane-1,3'-indol]-2'(1'H)-one (7b)

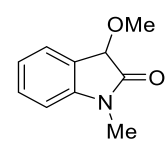
To a solution of 1-benzyl-3-diazo-1,3-dihydro-2*H*-indol-2-one (**1a**) (100 mg, 0.40 mmol) and dimethyl phosphite (40 μL, 0.44 mmol) in 2.0 mL THF was added to a flame-dried round bottom flask equipped with a magnetic stirring bar under argon. The solution was cooled to -30 °C and 0.5 M KHMDS in toluene (110 μL, 0.48 mmol, 1.2 equiv) was added dropwise, after additional 10 min, a solution of (2*E*)-1-(4-chlorophenyl)-3-phenylprop-2-en-1-one (**2g**) (97 mg, 0.40 mmol) in 1.0 mL THF was added dropwise. The reaction was allowed to proceed at the same temperature and was monitored by TLC. Once the α,β-unsaturated ketone was fully consumed the reaction mixture was quenched with saturated aqueous ammonium chloride. After being warmed to ambient temperature, the mixture was extracted with ethyl acetate. The organic phase was dried over Na_2SO_4 and concentrated *in vacuo.* The residue was purified by chromatographic purification (Hexane/EtOAc) to afford the desired cyclopropane product **7b** (132 mg, 71%) as a colorless crystalline solid. R_f = 0.31 (EtOAc/hexane = 1:4, v/v); mp 196-197 °C; IR (neat): ν_{max} 2922, 1706, 1605, 1459, 1353, 1175, 741 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ = 3.67 (d, *J* = 8.4 Hz, 1H, CH), 4.22 (d, *J* = 8.0 Hz, 1H, CH), 4.59 (d, *J* = 15.6 Hz, 1H, CH), 5.19 (d, *J* = 15.6 Hz, 1H, CH), 6.18 (d, *J* = 7.6 Hz, 1H, ArH), 6.79-6.85 (m, 2H, ArH), 7.02 (d, *J* = 6.8 Hz, 1H, ArH), 7.02-7.39 (m, 11H, ArH), 7.78 (d, *J* = 8.4 Hz, 2H, ArH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 37.5, 39.3, 41.7, 44.0, 109.3, 121.3, 122.1, 125.2, 127.3, 127.7, 127.8, 128.0, 128.7, 129.2, 129.8, 129.9, 133.5, 134.8, 135.8, 139.9, 143.2, 172.5, 190.7 ppm; HRMS (ESI) Calculated for $C_{30}H_{22}{}^{35}ClNO_2$ $(M+H)^+$: 464.1417 found: 464.1410.



7b

Synthesis of 3-methoxy-1-methyl-1,3-dihydro-2*H*-indol-2-one (8)[7]

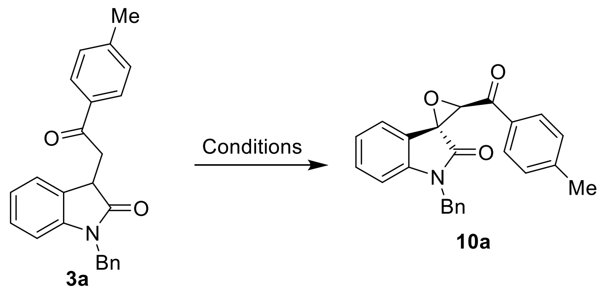
To a solution of 3-diazo-1-methyl-1,3-dihydro-2*H*-indol-2-one (**1b**) (100 mg, 0.58 mmol), (2*E*)-1-(4-methylphenyl)-3-phenylprop-2-en-1-one (**2a**) (90 mg, 0.58 mmol) and methanol (23 μL, 0.58 mmol) in $CHCl_3$ (5 mL) was added 10 mol% of $BF_3{\cdot}OEt_2$. The reaction mixture was stirred at 0 °C temperature to afford product **8** (88 mg, 86%) as a light yellow amorphous solid. R_f = 0.46 (EtOAc/hexane = 1.5:3.5, v/v); mp 131-132 °C; IR (neat): ν_{max} 2927, 1705, 1612, 1467, 1350, 1019, 752 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ = 3.19 (s, 3H, CH_3), 3.52 (s, 3H, CH_3), 4.86 (s, 1H, CH), 6.82 (d, *J* = 7.8 Hz, 1H, ArH), 7.10 (t, *J* = 7.6 Hz, 1H, ArH), 7.32-7.36 (m, 1H, ArH), 7.38-7.42 (m, 1H,



8

ArH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 26.0, 56.1, 76.7, 108.4, 122.9, 125.3, 130.0 144.3, 174.3 ppm.

Table 2. Optimization of reaction conditions of spiro-indolooxiranes **10a**

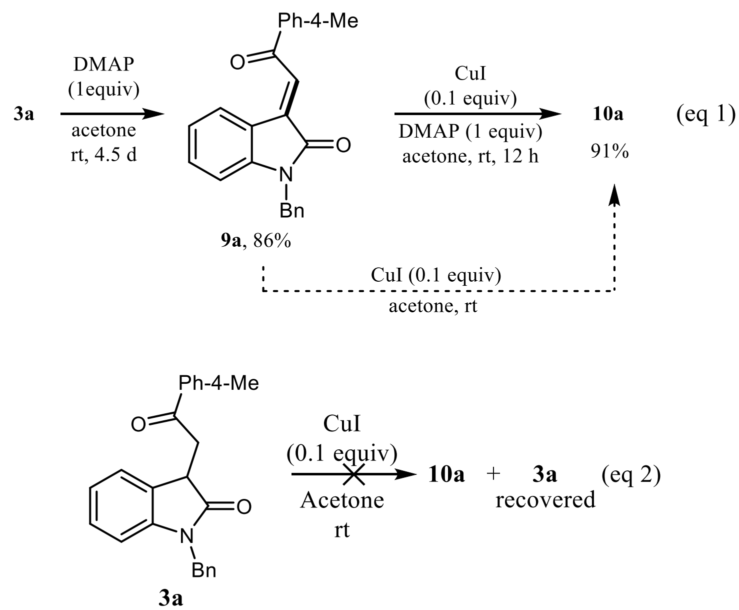


Entry	Catalyst	Base	Solvent	Temp. (°C)	Yield[b] %
1	$NiBr_2$	TEA	PhMe	rt	35
2	$FeCl_3$	TEA	PhMe	rt	22
3	$CuCl_2$	TEA	PhMe	rt	30
4	CuBr	TEA	PhMe	rt	46
5	CuI	TEA	PhMe	rt	61
6	CuI	DBU	PhMe	rt	20
7	CuI	DMAP	PhMe	rt	68
8	CuI	DABCO	PhMe	rt	nr[c]
9	CuI	DMAP	THF	rt	39
10	CuI	DMAP	DMF	rt	15
11	**CuI**	**DMAP**	**Acetone**	**rt**	**91**
12	CuI	DMAP	DCM	rt	nr[c]
13	CuI	DMAP	Acetone	50	44
14[d]	CuI	DMAP	Acetone	rt	nr[c]

[a]Reaction conditions: 10 mol% catalyst, **3a** (0.13 mmol, 1.0 equiv.), base (0.13 mmol, 1.0 equiv.), solvent (4.0 mL), at room temperature, for 15 h under an open air atmosphere. [b]Isolated yield. [c]The reaction was conducted at 50 °C. [d]The reaction carried out under argon atmosphere.

Further to develop the synthesis of spiro-indolooxiranes, the required 3-alkylated oxindole **3a** was synthesized from diazoamide. The reaction of 3-alkylated oxindole **3a** was initially studied with triethylamine (TEA) in the presence of various catalysts, solvents and the results were summarized in Table 2. Our initial investigation began with the epoxide formation of 3-alkylated oxindole **3a** dissolved in 4 mL of toluene at room temperature for 13 hours in the presence of 10 mol% of $NiBr_2$ and 1.0 equiv. of trimethylamine the desired spiro-indolooxirane **10a** was isolated in 35% yield (Table 2, entry 1). Moreover, $FeCl_3$ didn't improve the yield of product **10a** (Table 2, entry 2). In order to optimize the reaction conditions, various copper catalysts, such as

$CuCl_2$, CuBr, or CuI, were examined; however, CuI enhanced the yield of product **10a** (Table 2, entry 5). Then optimize various bases such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 4-Dimethylaminopyridine (DMAP), and 1,4-diazabicyclo[2.2.2]octane (DABCO). Among the bases screening indicated that DMAP was optimal to give spiro-indolooxirane **10a** in 68% yield (Table 2, entry 7). Successively, the screening of solvents (Table 2, entries 9–12) revealed that acetone was the optimum choice in terms of isolated yield of product **10a**. The above reaction was carried out at 50 °C afforded product **10a** in 44% yield (Table 2, entry 13).

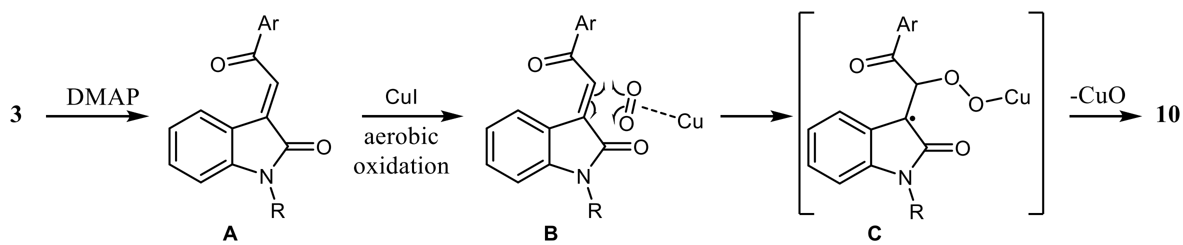


Scheme 8. Control experiments for **10a**

The reaction was carried out under argon atmosphere however, the desired product **10a** was not formed (Table 2, entry 13). Thus, the optimized reaction conditions for the formation of product **10a** were found to be 10 mol% of CuI and DMAP in acetone at room temperature, as indicated in Table 2, entry 11.

To understand the reaction mechanism of this epoxidation transformation, few control experiments were performed. When the reaction was carried out with 3-alkylated oxindole **3a** at room temperature in the presence of DMAP, the formation of oxindole-derived α,β-unsaturated enamide **9a** was successfully isolated in 86% yield. The oxindole-derived α,β-unsaturated enamide **9a** was converted into spiro-indolooxirane **10a** (Scheme 8, eq 1). Similarly, the reaction was carried out with CuI didn't give the desired product **10a**, but the subsequent addition of 1 equiv of DMAP delivered the desired product **10a** (Scheme 8, eq 2). In order to study mechanistic pathway for the reaction, we examined the reaction between 3-alkylated oxindole **3a** (1 equiv) and CuI (0.1 equiv) in the presence of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) did not afford the desired product **10a**. This suggests a radical pathway for this transformation.

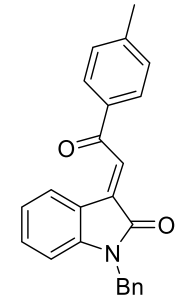
A plausible mechanism for the formation of spiro-indolooxiranes **10** from 3-alkylated oxindoles **3** is depicted in Scheme 9. Under mild basic conditions, the protons at the CH_{α} and CH_{β} position of **3** is amenable for oxidation to provide the intermediate **A**. Copper-bound dioxygen is able to activate superoxide to insert into the α,β-unsaturated enamide **B** to form 2-oxyindolenylperoxo radical intermediate **C**, which triggers the O-O bond cleavage reaction leading to spiro-indolooxiranes **10**.



Scheme 9. Plausible reaction mechanism for **10**.

General experimental procedure for the synthesis of spiro-indolooxiranes 10

A mixture of DMAP (1.0 equiv) and copper iodide (0.1 equiv) in 4 mL acetone was stirred at room temperature for 5 minutes. Then, 3-alkylated oxindole **3** (1.0 equiv) was added to the reaction mixture and stirred for 15-24 h. The mixture was then quenched with water and extracted with ethyl acetate (3×10 mL). The concentration of the combined organic layers under reduced pressure afforded the crude product, which was purified by column chromatography using silica gel to afford the corresponding product **10**.



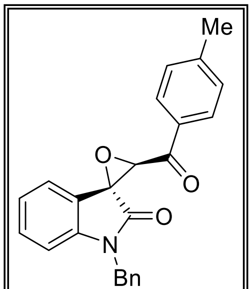
9a

Synthesis of (3*E*)-1-benzyl-3-[2-(4-methylphenyl)-2-oxoethylidene]-1,3-dihydro-*2H*-indol-2-one (9a)

To a solution of DMAP (0.14 mmol) in acetone (4 mL) was added 1-benzyl-3-[2-(4-methylphenyl)-2-oxoethyl]-1,3-dihydro-2*H*-indol-2-one (**3a**) (50 mg, 0.14 mmol) the reaction mixture was stirred at room temperature to afford **9a** (42 mg, 86%) as a colorless amorphous solid according to general procedure. R_f = 0.46 (EtOAc/hexane = 1:4, v/v); mp 141-142 °C; IR (neat): ν_{max} 2922, 1701, 1659, 1596, 1482, 1345, 1228, 692 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 2.33 (s, 3H, CH_3), 5.00 (s, 2H, CH_2), 6.64 (d, J = 8 Hz, 1H, ArH), 7.11 (d. J = 8 Hz, 1H, ArH), 7.30-7.37 (m, 6H, ArH), 7.57-7.61 (m, 2H, ArH), 7.67-6.68 (m, 1H, ArH), 7.98 (s, 1H, ArH), 8.16-8.19 (m, 3H, ArH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 21.1, 44.0, 109.03, 120.3, 126.4, 127.3, 127.7, 128.3, 128.85, 128.92, 132.4, 133.0, 133.8, 135.6, 136.8, 137.7, 143.0, 168.2, 191.3 ppm; HRMS (ESI) Calculated for $C_{24}H_{19}NO_2$ $(M+H)^+$: 354.1494 found: 354.1504.

Synthesis of 1-benzyl-3'-(4-methylbenzoyl)spiro[indole-3,2'-oxiran]-2(1*H*)-one (10a)

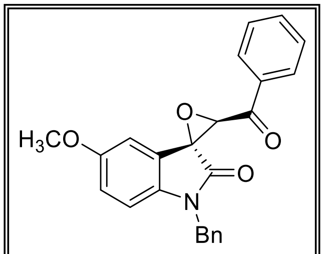
To a solution of DMAP (17 mg, 0.14 mmol) and copper iodide (3 mg, 0.014 mmol) in acetone (4 mL) was added 1-benzyl-3-[2-(4-methylphenyl)-2-oxoethyl]-1,3-dihydro-2*H*-indol-2-one (**3a**) (50 mg, 0.14 mmol) the reaction mixture was stirred at room temperature to afford **10a** (49 mg, 95%) as a colorless crystalline solid according to general procedure. R_f = 0.35 (EtOAc/hexane = 1:4, v/v); mp 198-199-174 °C; IR (neat): ν_{max} 2923, 1701, 1599, 1445, 1363, 1187, 1147, 725 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 2.40 (s, 3H, CH_3), 5.02 (d, J = 4.4 Hz, 3H, NCH_2/OCH), 6.77 (d, J = 8 Hz, 1H, ArH), 6.92 (t, J = 7.6 Hz, 1H, ArH), 7.12 (d, J = 7.6 Hz, 1H, ArH), 7.19-7.37 (m, 10H, ArH), 7.85 (d, J = 8.4 Hz, 2H, ArH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 21.9, 44.5, 60.9, 64.0, 110.0, 119.4, 123.3, 124.5, 127.3, 128.0, 128.5, 129.0, 129.7, 130.9, 132.7, 135.1, 144.5, 145.7, 170.5, 190.2 ppm; HRMS (ESI) Calculated for $C_{24}H_{19}NO_3$ $(M+H)^+$: 370.1443 found: 370.1437.



10a

Synthesis of 3'-benzoyl-1-benzyl-5-methoxyspiro[indole-3,2'-oxiran]-2(1*H*)-one (10b)

To a solution of DMAP (16 mg, 0.13 mmol) and copper iodide (3 mg, 0.013 mmol) in acetone (4 mL) was added 1-benzyl-3-diazonio-5-methoxy-2-oxo-2,3-dihydro-1*H*-indol-3-ide (**3q**) (50 mg, 0.13 mmol) the reaction mixture was stirred at room temperature to afford **10b** (47 mg, 91%) as a colorless amorphous solid according to general procedure. R_f = 0.23 (EtOAc/hexane = 1:4, v/v); mp 148-149 °C; IR (neat): ν_{max} 2923, 1701, 1599, 1445, 1363, 1187, 1147, 725 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 3.57 (s, 3H, CH_3), 4.91 (s, 2H, CH_2), 4.97 (s, 1H, CH), 6.59-6.67 (m, 3H, ArH), 7.19-7.56 (m, 8H, ArH), 7.88 (d, J = 7.6 Hz, 2H, ArH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 44.6, 55.7, 61.2, 64.01, 110.7, 110.8, 116.4, 120.4, 127.3, 128.0, 128.4, 129.0, 129.1, 134.5, 135.15, 135.19,

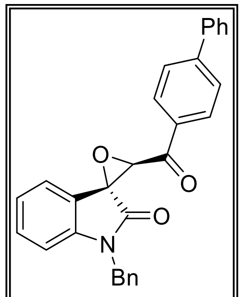


10b

137.7, 156.2, 170.2, 190.70 ppm; HRMS (ESI) Calculated for $C_{24}H_{19}NO_4$ $(M+H)^+$: 386.1392 found: 386.1386.

Synthesis of 3'-([1,1'-biphenyl]-4-carbonyl)-1-benzylspiro[indole-3,2'-oxiran]-2(1*H*)-one (10c)

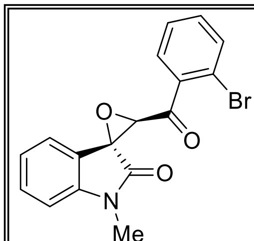
To a solution of DMAP (15 mg, 0.12 mmol) and copper iodide (3 mg, 0.012 mmol) in acetone (4 mL) was added 3-[2-([1,1'-biphenyl]-4-yl)-2-oxoethyl]-1-benzyl-1,3-dihydro-2*H*-indol-2-one (**3f**) (50 mg, 0.12 mmol) the reaction mixture was stirred at room temperature to afford **10c** (45 mg, 87%) as a colorless crystalline solid according to general procedure. R_f = 0.37 (EtOAc/hexane = 1:4, v/v); mp 210-211 °C; IR (neat): ν_{max} 2923, 1701, 1599, 1445, 1363, 1187, 1147, 725 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ = 5.07 (s, 2H, CH_2), 5.12 (s, 1H, CH), 6.96 (d, J = 0.8 Hz, 1H, ArH), 6.98-7.00 (m, 1H, ArH), 7.19-7.21 (m, 1H, ArH), 7.25-7.29 (m, 1H, ArH), 7.33-7.53 (m, 7H, ArH), 7.63-7.74 (m, 5H, ArH), 8.07 (d, J = 8.4 Hz, 2H, ArH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 44.5, 61.0, 64.1, 110.0, 119.4, 123.3, 124.6, 127.3, 127.4, 127.6, 128.0, 128.6, 129.0, 129.1, 131.0, 133.8, 135.1, 139.4, 144.6, 147.3, 170.5, 190.2 ppm; HRMS (ESI) Calculated for $C_{29}H_{21}NO_3$ $(M+Na)^+$: 454.1419 found: 454.1414.



10c

Synthesis of 3'-(2-bromobenzoyl)-1-methylspiro[indole-3,2'-oxiran]-2(1*H*)-one (10d)

To a solution of DMAP (18 mg, 0.16 mmol) and copper iodide (3 mg, 0.016 mmol) in acetone (4 mL) was added 3-[2-(2-bromophenyl)-2-oxoethyl]-1-methyl-1,3-dihydro-2*H*-indol-2-one (**3k**) (50 mg, 0.16 mmol) the reaction mixture was stirred at room temperature to afford **10d** (42 mg, 79%) as a colorless crystalline solid according to general procedure. R_f = 0.31 (EtOAc/hexane = 1:4, v/v); mp 167-169 °C; IR (neat): ν_{max} 2923, 1701, 1599, 1445, 1363, 1187, 1147, 725 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ = 3.22 (s, 3H, CH_3), 4.81 (s, 1H, CH), 6.81-6.85 (m, 1H, ArH), 6.96 (t, J = 7.6 Hz, 1H, ArH), 7.24-7.34 (m, 4H, ArH), 7.48-7.53 (m, 2H, ArH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 26.9, 62.7, 65.4, 109.0, 119.3, 120.5, 123.3, 124.8, 127.9, 131.0, 131.2, 133.7, 134.2, 137.8, 145.5, 170.1, 193.2 ppm; HRMS (ESI) Calculated for $C_{17}H_{12}{}^{79}BrNO_3$ $(M+H)^+$: 358.0079 found: 358.0083.

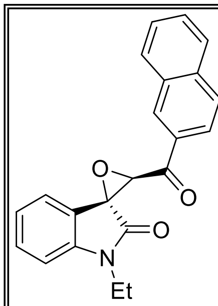


10d

Synthesis of 1-ethyl-3'-(naphthalene-2-carbonyl)spiro[indole-3,2'-oxiran]-2(1*H*)-one (10e)

To a solution of DMAP (18 mg, 0.15 mmol) and copper iodide (3 mg, 0.015 mmol) in acetone (4 mL) was added 1-ethyl-3-[2-(naphthalen-2-yl)-2-oxoethyl]-1,3-dihydro-2*H*-indol-2-one (**3y**) (50 mg, 0.15 mmol) the reaction mixture was stirred at room temperature to afford **10e** (44 mg, 85%)

as a colorless amorphous solid according to general procedure. R_f = 0.38 (EtOAc/hexane = 1:4, v/v); mp 135-136 °C; IR (neat): ν_{max} 2923, 1701, 1599, 1445, 1363, 1187, 1147, 725 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ = 1.40 (t, *J* = 7.2 Hz, 3H, CH_3), 3.82-3.98 (m, 2H, CH_2), 4.99 (s, 1H, CH), 6.95-6.99 (m, 2H, ArH), 7.26-8.10 (m, 8H, ArH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 12.8, 35.6, 61.6, 65.0, 109.2, 119.6, 123.1, 124.4, 124.8, 125.5, 127.0, 128.7, 129.0, 130.1, 130.3, 131.1, 131.9, 134.0, 134.8, 144.6, 169.9, 193.2 ppm; HRMS (ESI) Calculated for $C_{22}H_{17}NO_3$ $(M+H)^+$: 344.1287 found: 344.1286.



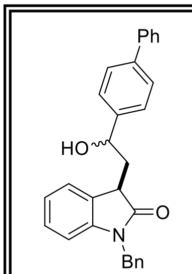
10e

General experimental procedure for the synthesis of 11

A mixture of 3-alkylated oxindoles **3** (4.0 mmol) in dry MeOH (15 mL) was added $NaBH_4$ (8.0 mmol) slowly at 0 °C under nitrogen atmosphere. The reaction mixture was allowed to stir for 5 hours at room temperature and the solvent was evaporated. The mixture was then quenched with water and extracted with ethyl acetate (3×10 mL). The concentration of the combined organic layers under reduced pressure afforded the crude product, which was purified by column chromatography using silica gel to afford the corresponding product **11**.

Synthesis of 3-[2-([1,1'-biphenyl]-4-yl)-2-hydroxyethyl]-1-benzyl-1,3-dihydro-2*H*-indol-2-one (11a)

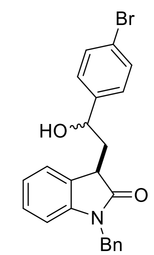
To the stirred solution of 3-[2-([1,1'-biphenyl]-4-yl)-2-oxoethyl]-1-benzyl-1,3-dihydro-*2H*-indol-2-one (**3f**) (50 mg, 0.12 mmol) in dry MeOH (40 mL) was added $NaBH_4$ (14 mg, 0.36 mmol) slowly at 0 °C under nitrogen atmosphere. The reaction mixture was allowed to stir for 2 hours at 0 °C to afford corresponding alcohol **11a** (47 mg, 95%) as a colorless crystalline solid. R_f = 0.15 (EtOAc/hexane = 1.5:3.5, v/v); mp 171-172 °C; IR (neat): ν_{max} 3380, 2991, 1689, 1610, 1485, 1359, 1070, 739 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ = 2.17-2.29 (m, 2H, CH_2), 2.44-2.50 (m, 1H, CH), 3.63-3.77 (m, 1H, CH), 4.83-4.85 (m, 2H, CH_2), 5.14-5.17 (m, 1H, CH), 6.64-6.68 (m, 1H, ArH), 6.91-6.98 (m, 1H, ArH), 7.05-7.12 (m, 1H, ArH), 7.17-7.28 (m, 6H, ArH), 7.35 (t, J = 7.6 Hz, 2H, ArH), 7.44-7.52 (m, 6H, ArH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 39.3, 40.7, 42.6, 43.96, 43.98, 45.1, 71.1, 73.5, 109.3, 109.4, 122.8, 122.9, 123.7, 124.0, 126.1, 126.5, 127.11, 127.14, 127.25, 127.31, 127.37, 127.39, 127.7, 127.8, 128.0, 128.2, 128.8, 128.9, 130.0, 135.6, 135.7, 140.3, 140.6, 140.9, 141.0, 143.0, 143.2, 143.3, 143.5, 179.2 ppm; HRMS (ESI) Calculated for $C_{29}H_{25}NO_2$ $(M+Na)^+$: 442.1783 found: 442.1783.



11a

Synthesis of 1-benzyl-3-[2-(4-bromophenyl)-2-hydroxyethyl]-1,3-dihydro-*2H*-indol-2-one (11b)

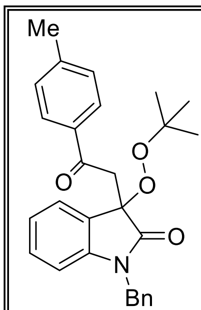
To the stirred solution of 1-benzyl-3-[2-(4-bromophenyl)-2-oxoethyl]-1,3-dihydro-*2H*-indol-2-one (**3l**) (50 mg, 0.12 mmol) in dry MeOH (40 mL) was added $NaBH_4$ (14 mg, 0.36 mmol) slowly at 0 °C under nitrogen atmosphere. The reaction mixture was allowed to stir for 5 hours at room temperature to afford corresponding alcohol **11b** (44 mg, 89%) as a colorless crystalline solid. R_f = 0.12 (EtOAc/hexane = 1.5:3.5 v/v); mp 167-168 °C; IR (neat): ν_{max} 3401, 2923, 1691, 1611, 1485, 1364, 1071, 749 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 2.16-2.34 (m, 2H, CH), 2.47-2.54 (m, 1H, CH), 3.70 (dd, J_1 = 9.6 Hz, J_2 = 3.6 Hz, 1H, CH), 3.84 (dd, J_1 = 9.2 Hz, J_2 = 4.8 Hz, 1H, CH), 4.32 (d, J = 6.4 Hz, 1H, CH), 4.95-5.01 (m, 2H, CH_2), 5.20 (d. J = 6.8 Hz, 1H, CH), 6.77-6.81 (m, 1H, ArH), 7.04-7.39 (m, 10H, ArH), 7.51-7.54 (m, 2H, ArH), ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 39.1, 40.7, 42.4, 43.97, 44.0145.2, 7.07, 73.3, 109.4, 109.5, 121.1, 121.3, 122.9, 123.0, 123.6, 123.9, 127.4, 127.5, 127.76, 127.84, 128.1, 128.3, 128.6, 128.8, 128.87, 128.92, 131.5, 131.6, 135.5, 135.6, 142.9, 143.17, 143.22, 143.5, 179.1, 179.2 ppm; HRMS (ESI) Calculated for $C_{23}H_{20}{}^{81}BrNO_2$ $(M+H)^+$: 424.0735 found: 424.0764.



11b

Synthesis of 3-*tert*-butoxy-1-benzyl-3-[2-(4-methylphenyl)-2-oxoethyl]-1,3-dihydro-2*H*-indol-2-one (12)

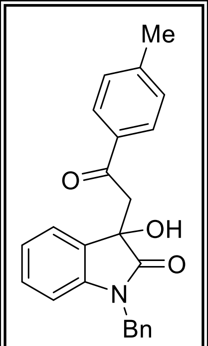
To a solution of $FeCl_3$ (7 mg, 0.04 mmol) and TBHP (55 µL, 0.56 mmol) in acetonitrile (2 mL) was added 1-benzyl-3-[2-(4-methylphenyl)-2-oxoethyl]-1,3-dihydro-*2H*-indol-2-one (**3a**) (50 mg, 0.14 mmol) and the reaction mixture was stirred at room temperature to afford **12** (41 mg, 69%) as a colorless liquid according to general procedure. R_f = 0.38 (EtOAc/hexane = 1:4, v/v); IR (neat): ν_{max} 2923, 1730, 1684, 1611, 1465, 1358, 1181, 1007, 701 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 1.04 (s, 9H, $C(CH_3)_3$), 2.32 (s, 3H, CH_3), 3.71-3.91 (m, 2H, CH_2), 4.66 (d, J = 16 Hz, 1H, NCH), 5.26 (d, J = 16 Hz, 1H, NCH), 6.55 (d, J = 8 Hz, 1H, ArH), 6.85-6.89 (m, 1H, ArH), 7.07-7.33 (m, 10H, ArH), 7.73 (d, J = 8.4 Hz, 2H, ArH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 21.7, 26.4, 42.5, 43.9, 80.7, 82.4, 109.2, 122.0, 124.1, 127.1, 128.3, 128.6, 129.2, 129.7, 134.0, 135.9, 144.3, 144.5, 174.0, 194.2 ppm; HRMS (ESI) Calculated for $C_{28}H_{29}NO_3$ $(M+H)^+$: 444.2175 found: 444.2168.



12

Synthesis of 1-benzyl-3-hydroxy-3-[2-(4-methylphenyl)-2-oxoethyl]-1,3-dihydro-2*H*-indol-2-one (13)

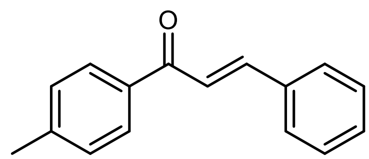
To a solution of 3-tert-butoxy-1-benzyl-3-[2-(4-methylphenyl)-2-oxoethyl]-1,3-dihydro-*2H*-indol-2-one (**12**) (30 mg, 0.07 mmol) in acetonitrile (5 mL) was stirred at reflux conditions for 6 hours to afford **13** (14 mg, 52%) as a colorless crystalline solid. R_f = 0.13 (EtOAc/hexane = 1.5:3.5, v/v); mp 161-162 °C; IR (neat): ν_{max} 3364, 3059, 1680, 1608, 1349, 1174, 1000, 733 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 2.44 (s, 3H, CH_3), 3.63 (d, J = 17.2 Hz, 1H of CH_2), 3.91 (d, J = 17.2 Hz, 1H of CH_2), 4.98 (ABq, $\Delta\delta_{AB}$ = 0.06, J = 15.6 Hz, 2H, CH_2), 6.76 (d, J = 7.2 Hz, 1H, ArH), 7.01-7.04 (m, 1H, ArH), 7.20-7.45 (m, 9H, ArH), 7.84 (d, J = 7.6 Hz, 2H, ArH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 21.7, 44.0, 44.5, 74.6, 109.7, 123.1, 124.0, 127.3, 127.7, 128.4, 128.9, 129.4, 129.8, 130.2, 134.0, 135.6, 142.9, 144.8, 176.7, 197.8 ppm; HRMS (ESI) Calculated for $C_{24}H_{21}NO_3$ $(M+H)^+$: 372.1600 found: 372.1604.



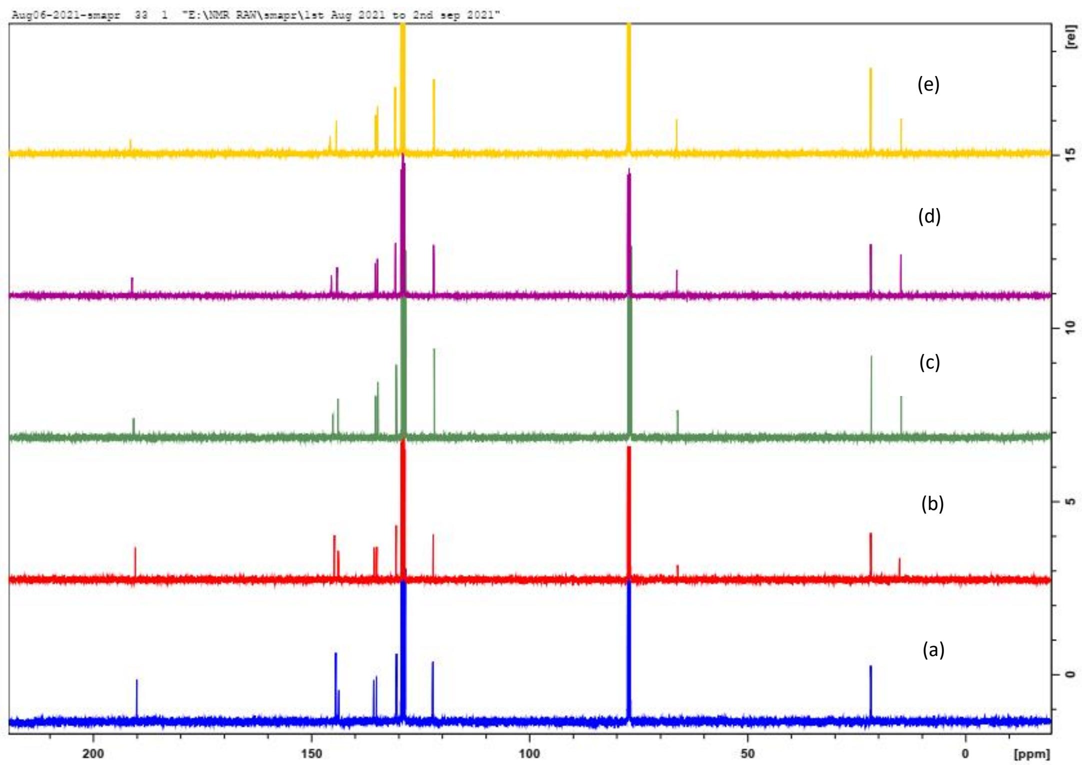
13

NMR-Titration experiments

The ^{13}C NMR titration experiments were performed to investigate the interactions of chalcone **2a** with $BF_3{\cdot}OEt_2$ and the results revealed the presence of binding (Figure S1).



2a



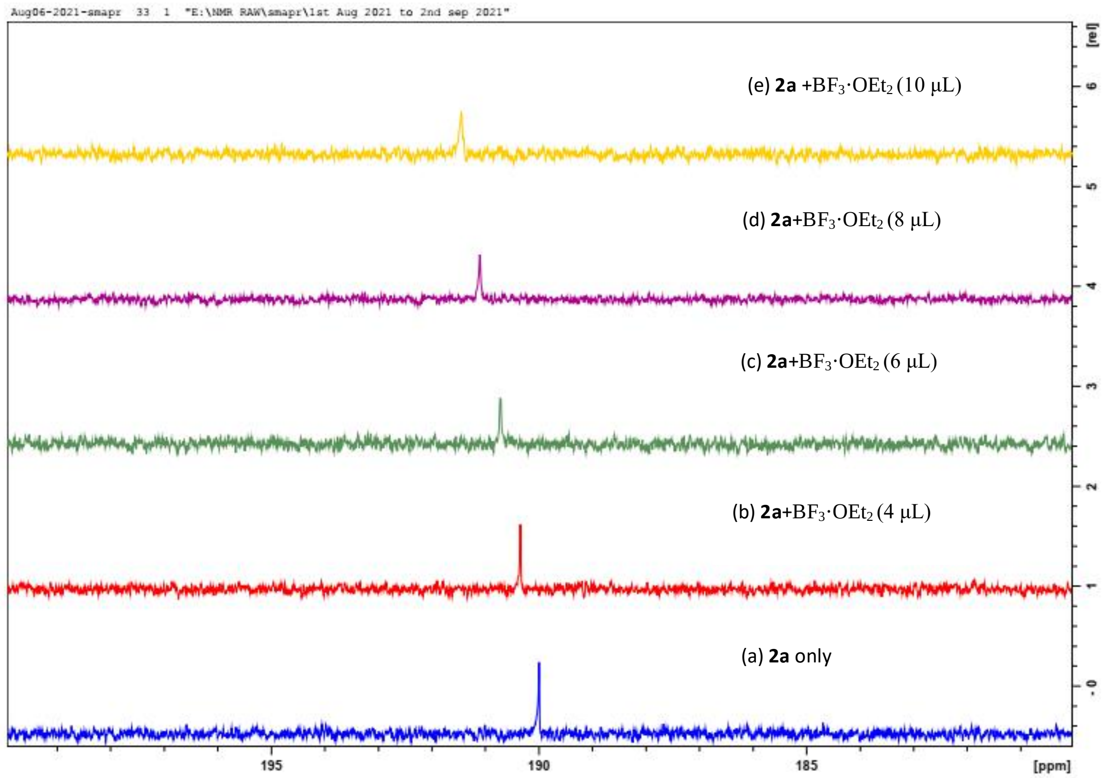


Figure S1. ^{13}C-NMR spectra of chalcone **2a** signals in $CDCl_3$

(a) Chalcone **2a** only.

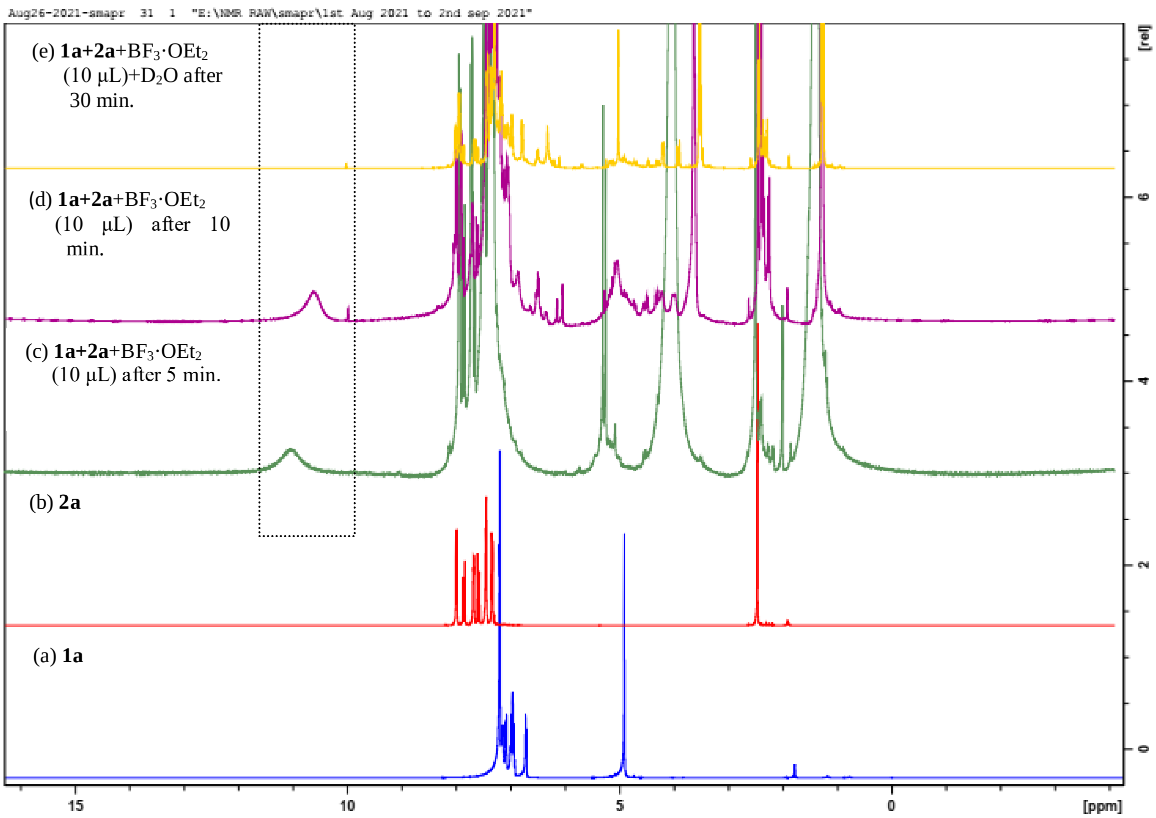
(b) Chalcone **2a** (20 mg) with $BF_3{\cdot}OEt_2$ (4 μL)

(c) Chalcone **2a** (20 mg) with $BF_3{\cdot}OEt_2$ (6 μL)

(d) Chalcone **2a** (20 mg) with $BF_3{\cdot}OEt_2$ (8 μL)

(e) Chalcone **2a** (20 mg) with $BF_3{\cdot}OEt_2$ (10 μL)

Next, the ^{1}H NMR experiments were performed at different time interval to follow the reaction between diazoamide **1a** and chalcone **2a** in the presence of $BF_3{\cdot}OEt_2$ to afford product **3a** with the by-product of benzoic acid determined using D_2O exchange experiment as shown in Figure S2.



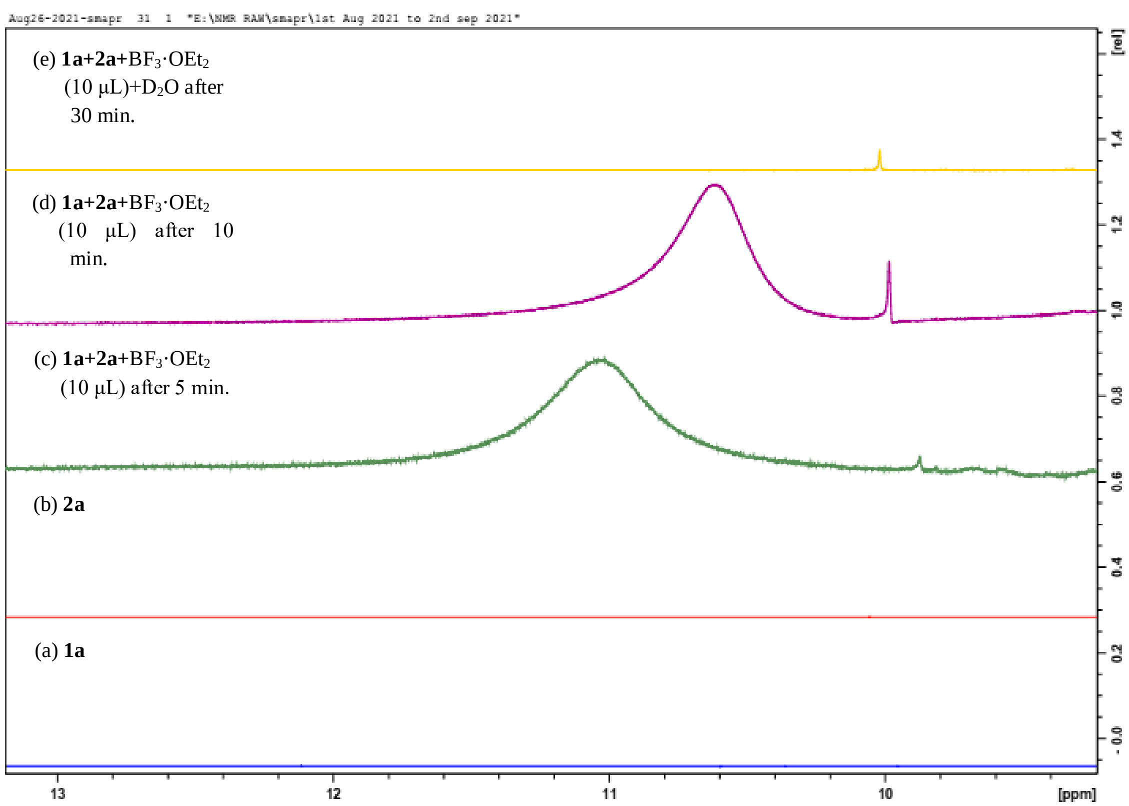


Figure S2. [1]H-NMR spectra of reaction mixture **3a** signals in $CDCl_3$

(a) Diazoamide **1a** (10 mg).

(b) Chalcone **2a** (10 mg).

(c) A mixture of diazoamide **1a** (10 mg), chalcone **2a** (10 mg) with $BF_3 \cdot OEt_2$ (10 µL) after 5 minutes.

(d) A mixture of diazoamide **1a** (10 mg), chalcone **2a** (10 mg) with $BF_3 \cdot OEt_2$ (10 µL) after 10 minutes.

(e) A mixture of diazoamide **1a** (10 mg), chalcone **2a** (10 mg) with $BF_3 \cdot OEt_2$ (10 µL) and 1 drop of D_2O after 30 minutes.

In order to determine the presence of benzoic acid as a byproduct during the formation of product **3a**, NMR experiments at different time interval were recorded between benzaldehyde and $BF_3 \cdot OEt_2$ in $CDCl_3$ as shown in Figure S3. The disappearance of aldehyde at 10.20 ppm with the appearance of benzoic acid as a broad singlet at 11.32 ppm were observed and confirmed with D_2O exchange experiments.

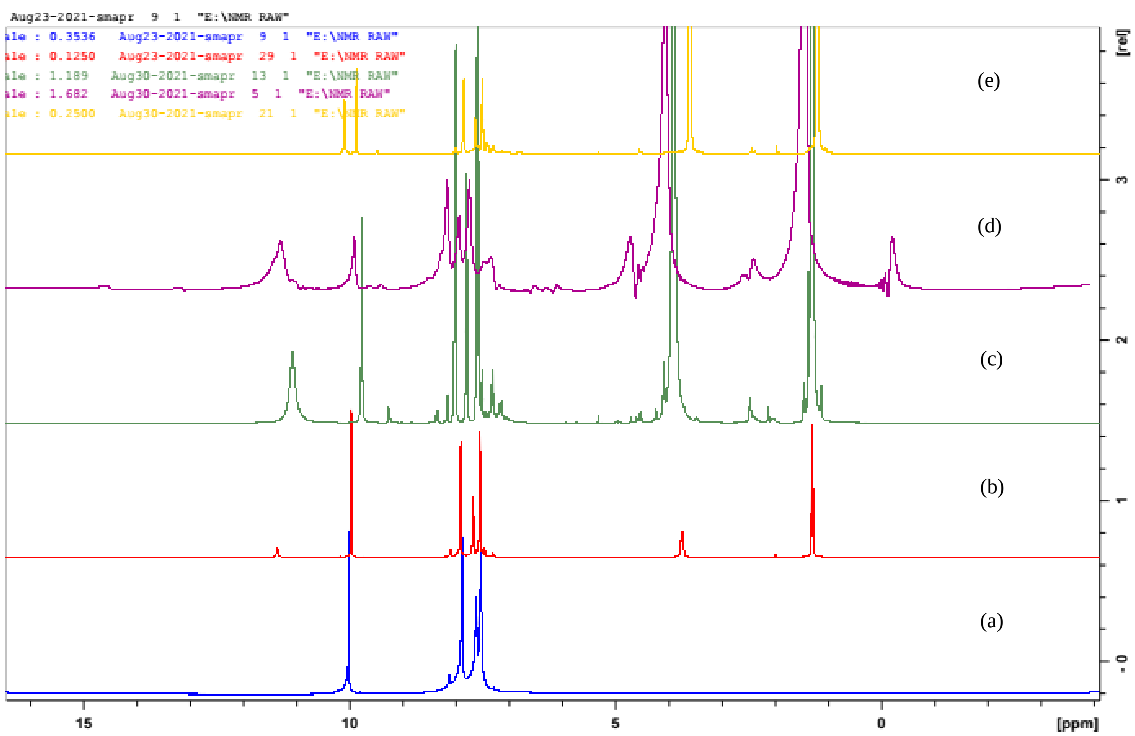


Figure S3. ^{1}H-NMR spectra of benzaldehyde signals in $CDCl_3$

(a) Benzaldehyde only.

(b) Benzaldehyde (20 mg) with $BF_3 \cdot OEt_2$ (5 µL) after 5 minutes.

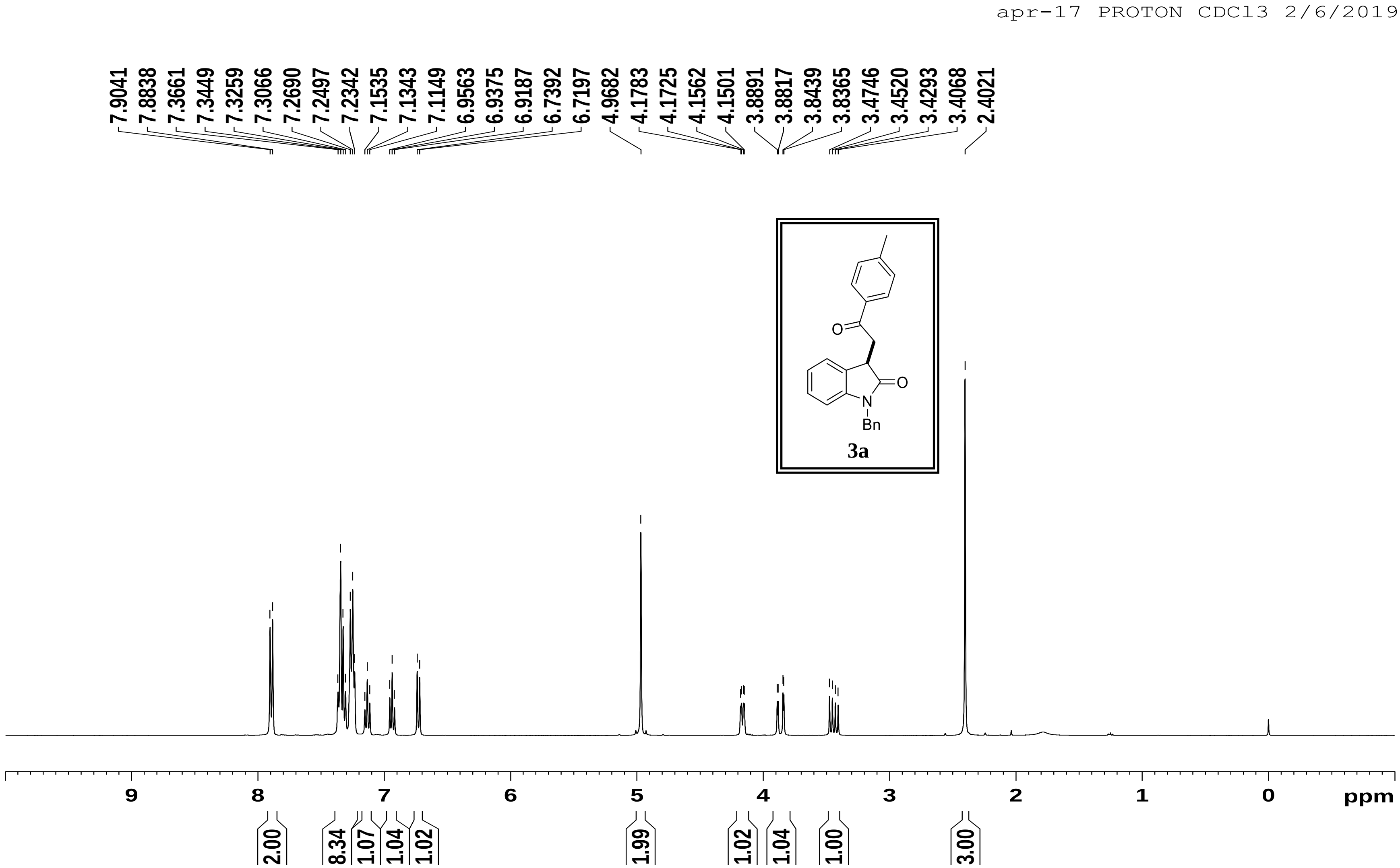
(c) Benzaldehyde (20 mg) with $BF_3 \cdot OEt_2$ (5 µL) after 10 minutes.

(d) Benzaldehyde (20 mg) with $BF_3 \cdot OEt_2$ (5 µL) after 20 minutes.

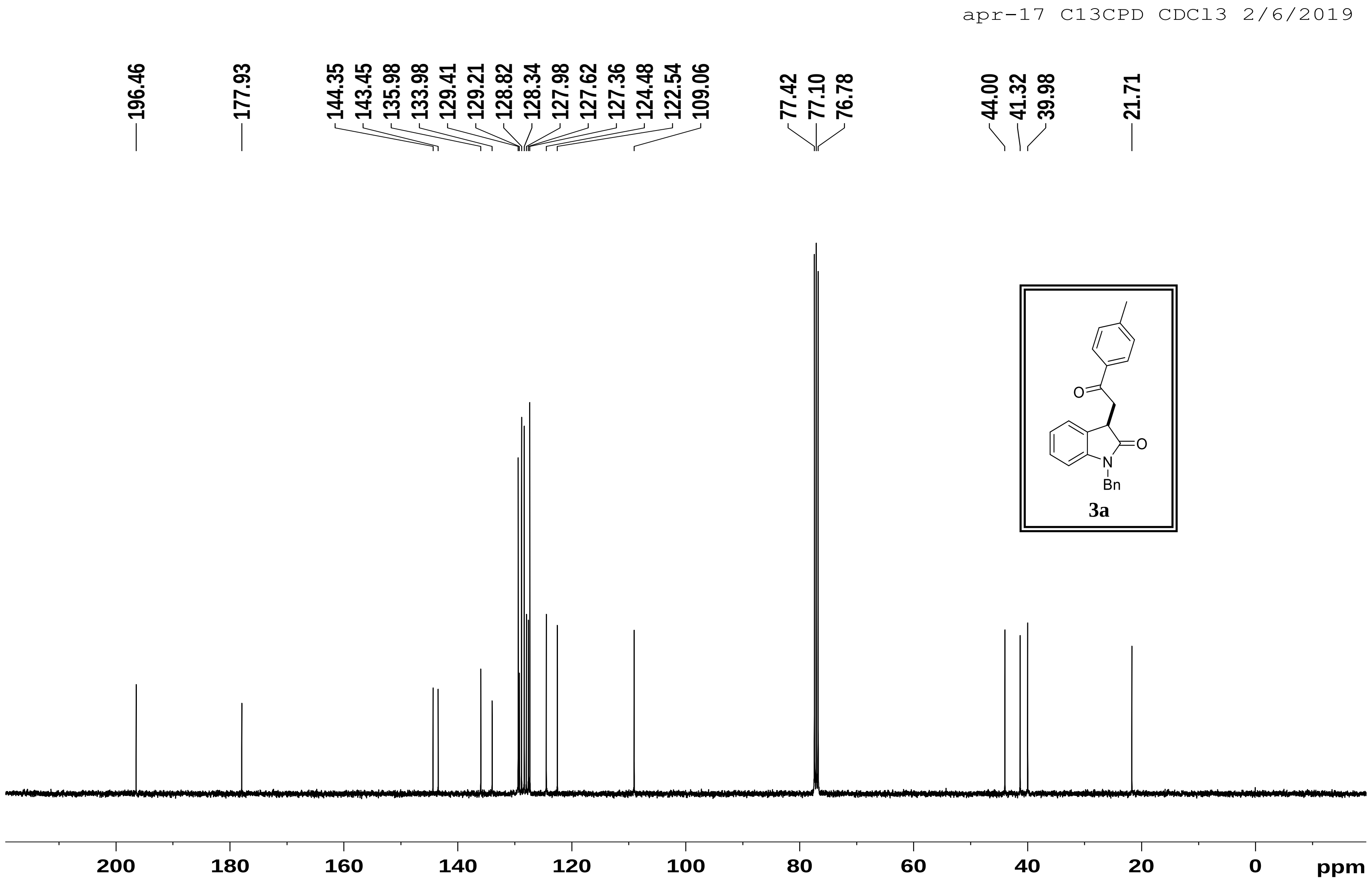
(e) A mixture of benzaldehyde, $BF_3 \cdot OEt_2$ (5 µL) and 1 drop of D_2O after 30 minutes.

Copies of ^{1}H and ^{13}C NMR spectra

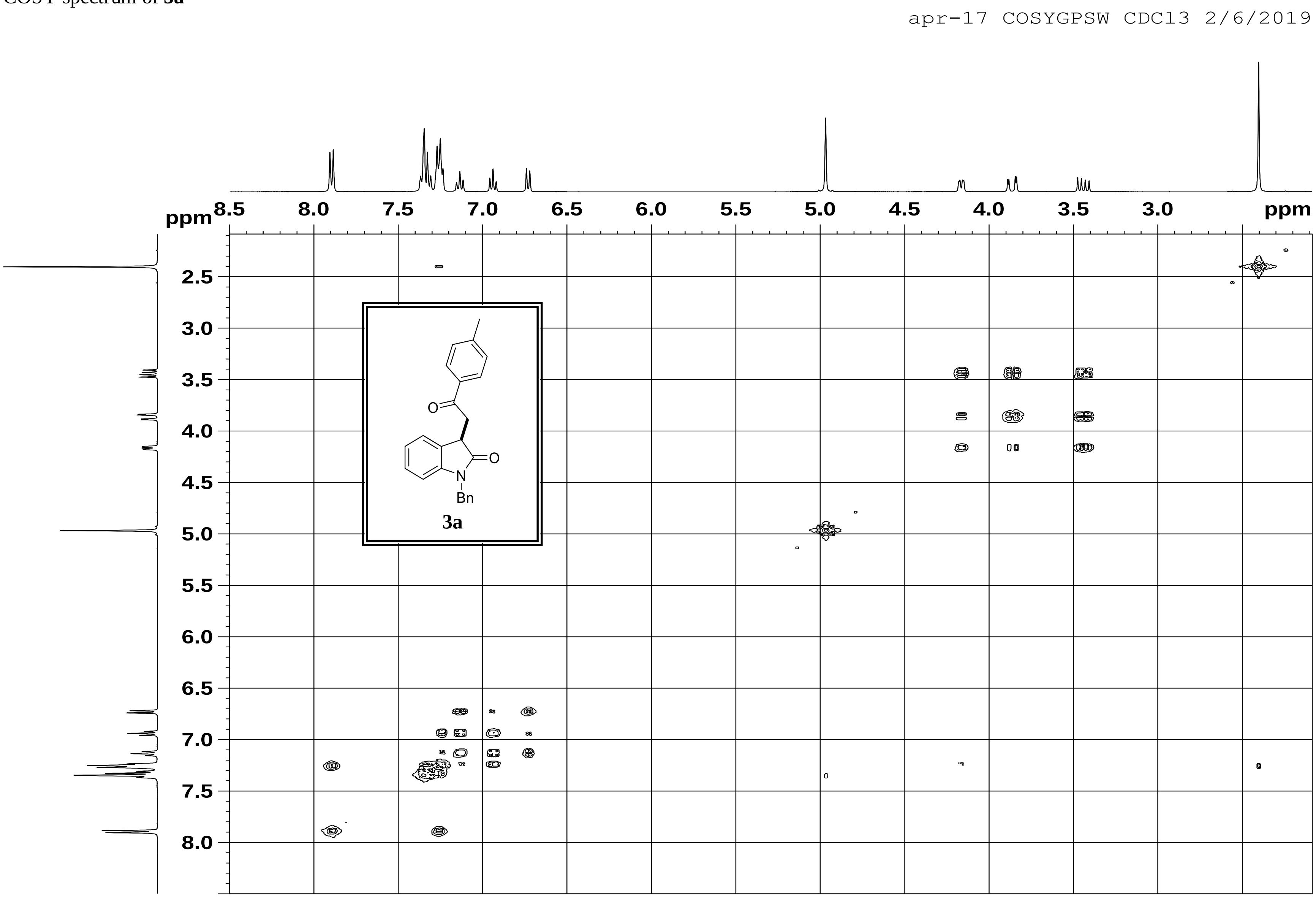
^{1}H NMR spectrum of **3a**



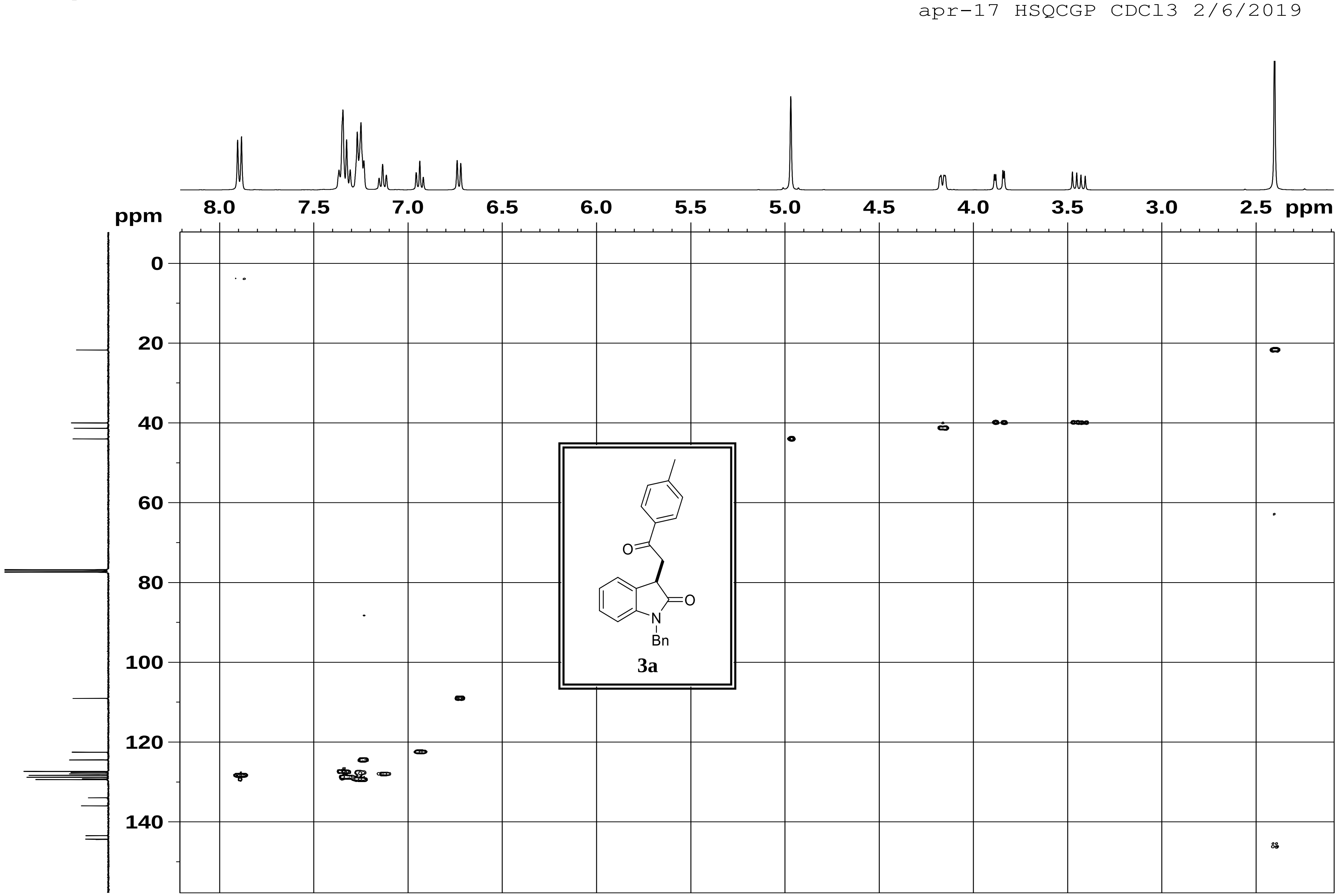
[13]C NMR spectrum of **3a**



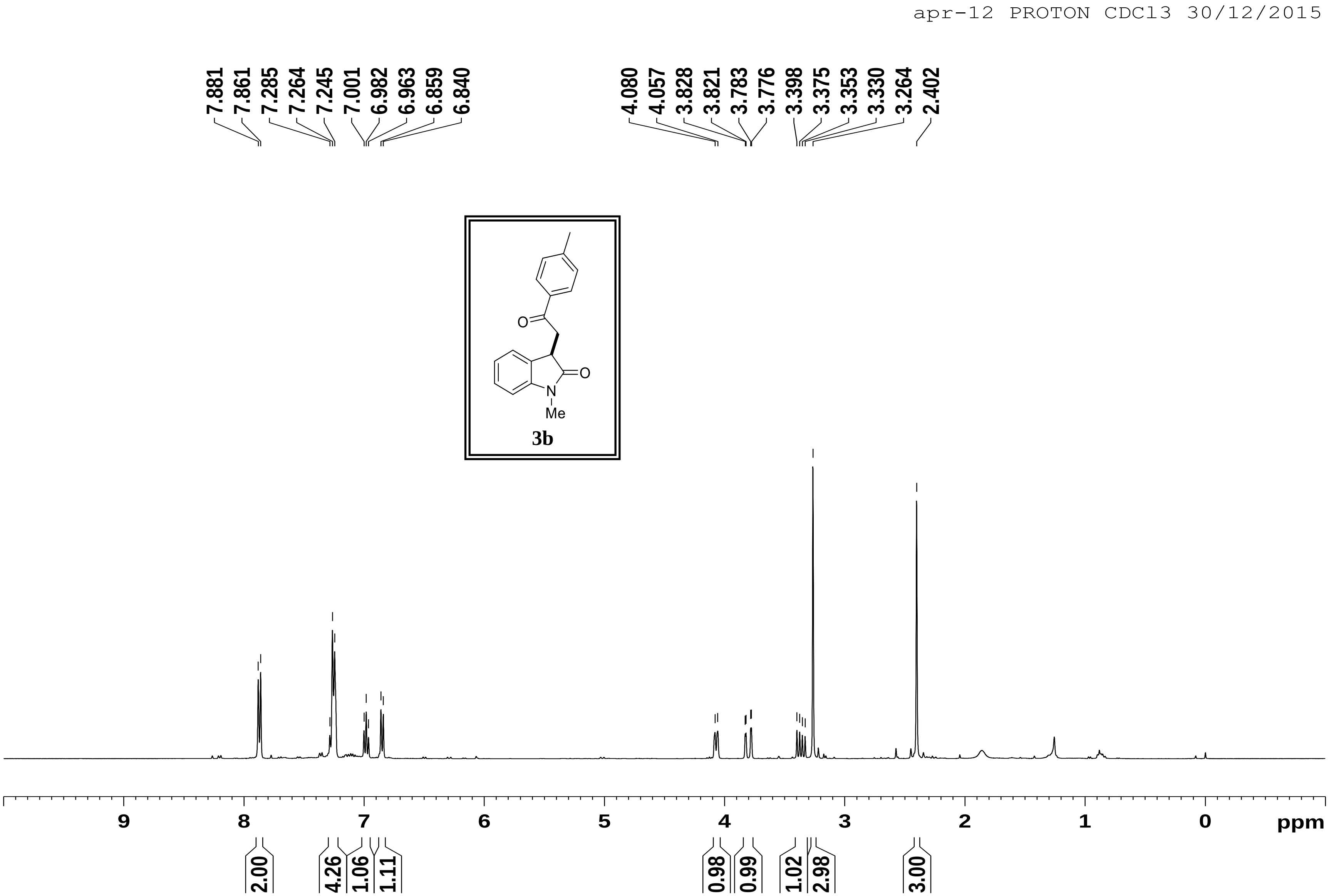
COSY spectrum of **3a**



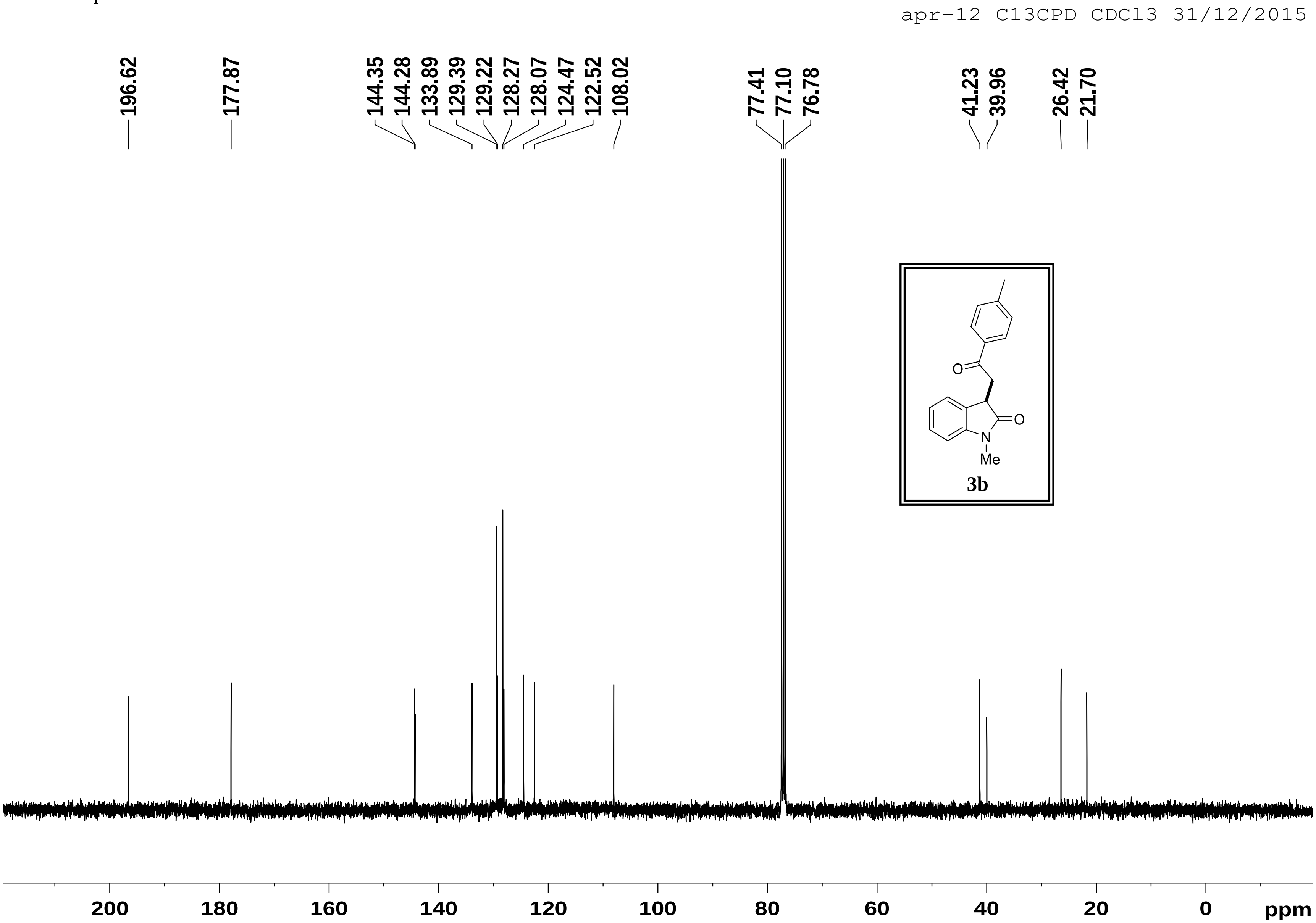
HSQC spectrum of **3a**



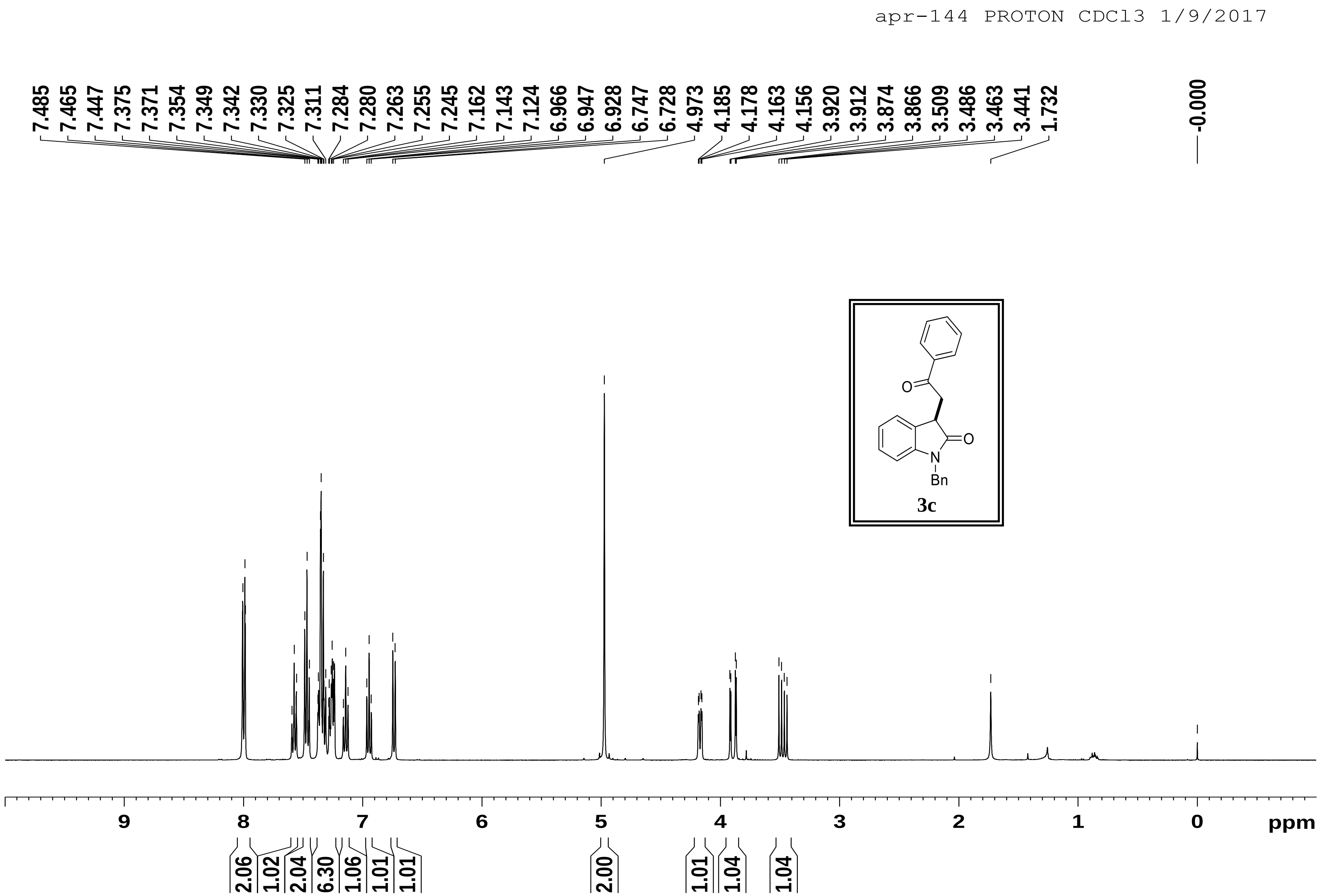
^{1}H NMR spectrum of **3b**



^{13}C NMR spectrum of **3b**

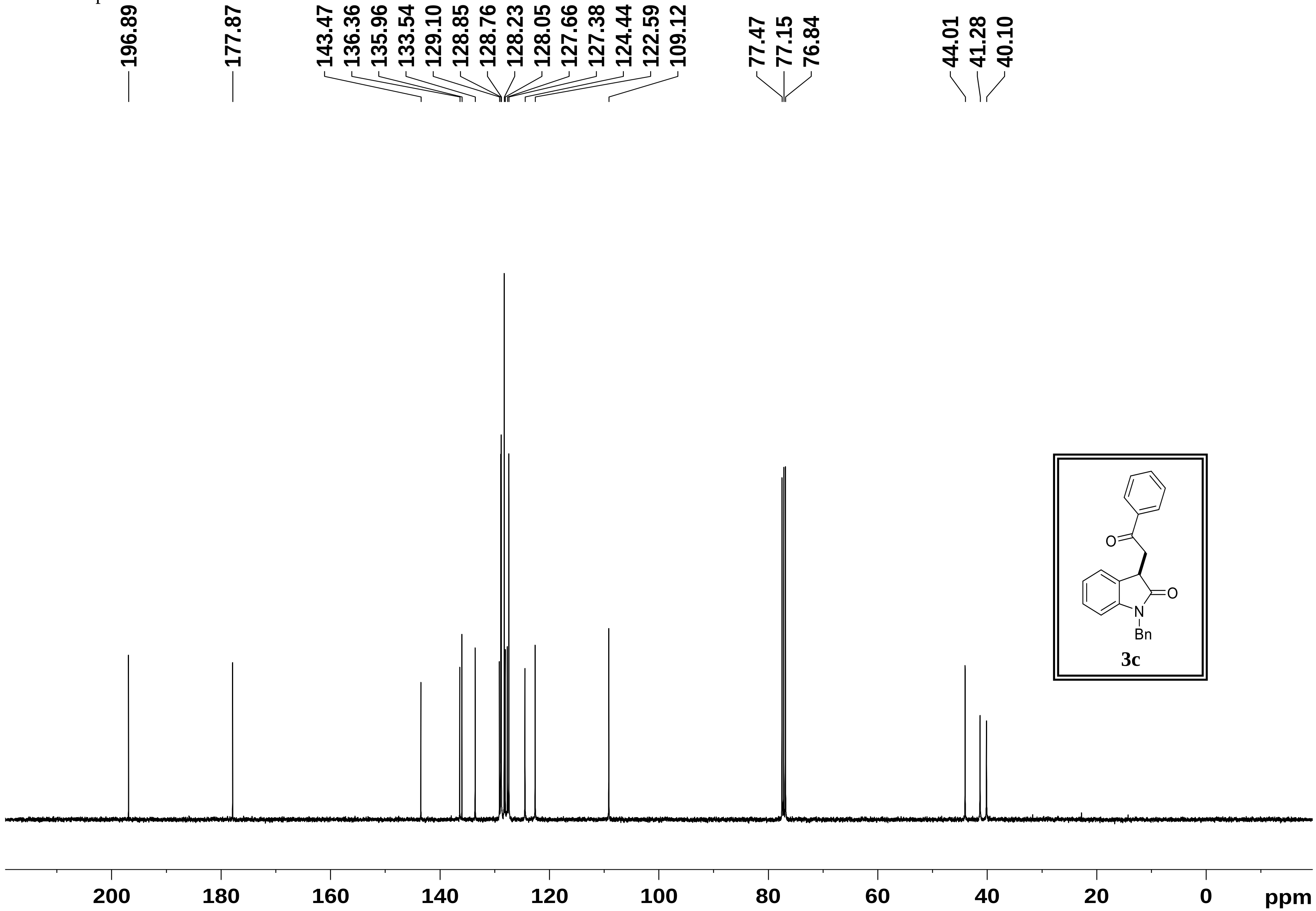


^{1}H NMR spectrum of **3c**

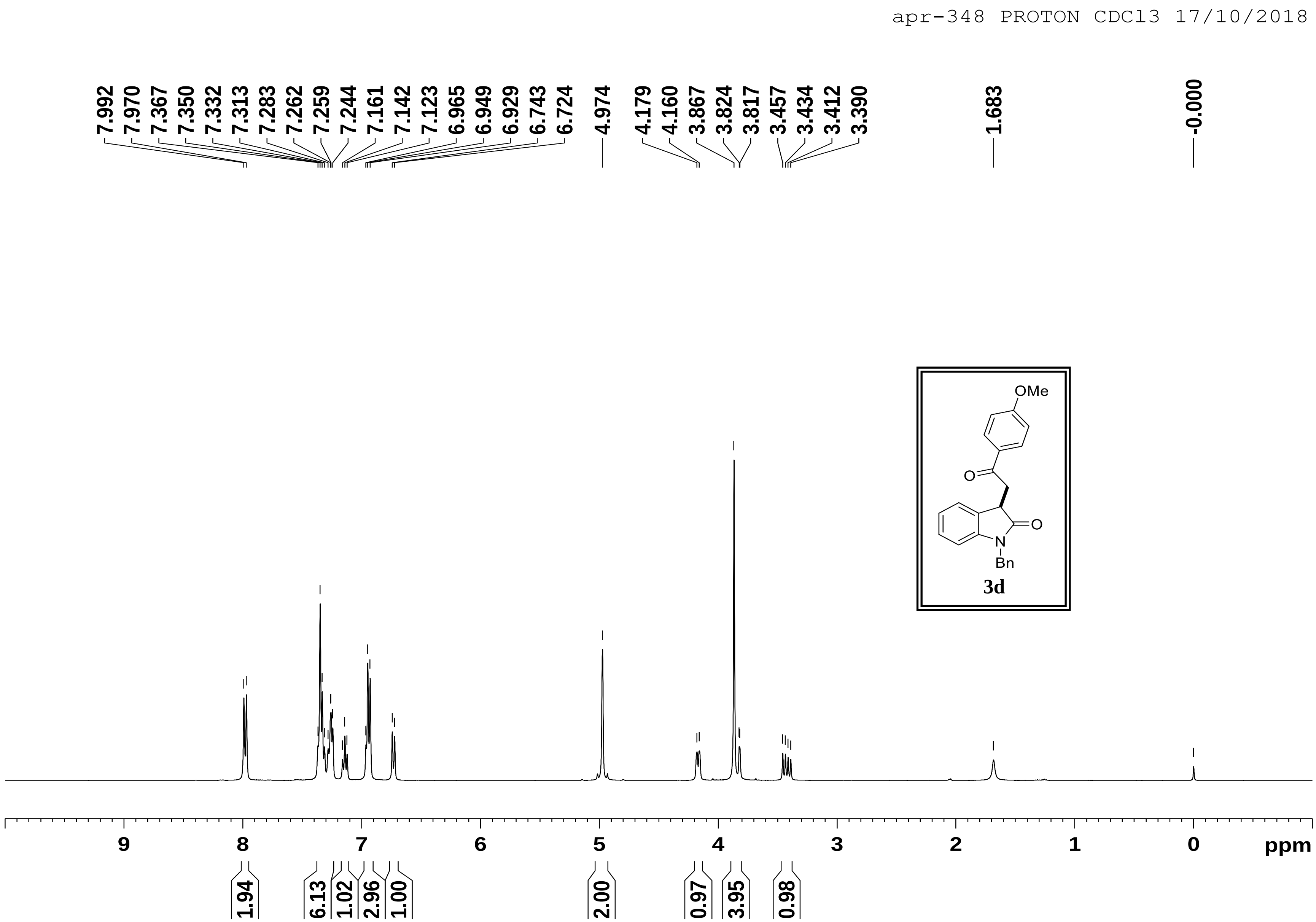


3c

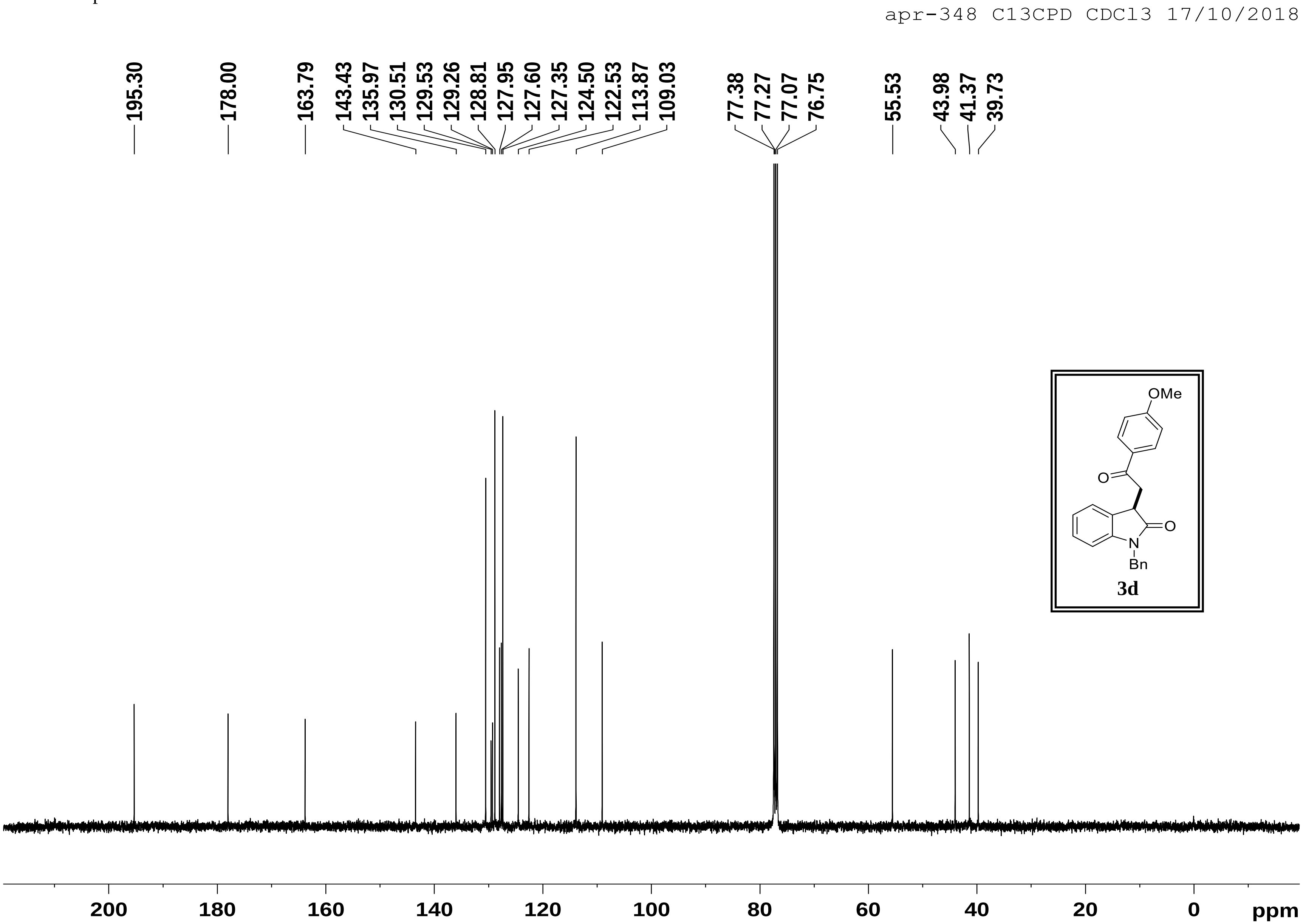
^{13}C NMR spectrum of **3c**



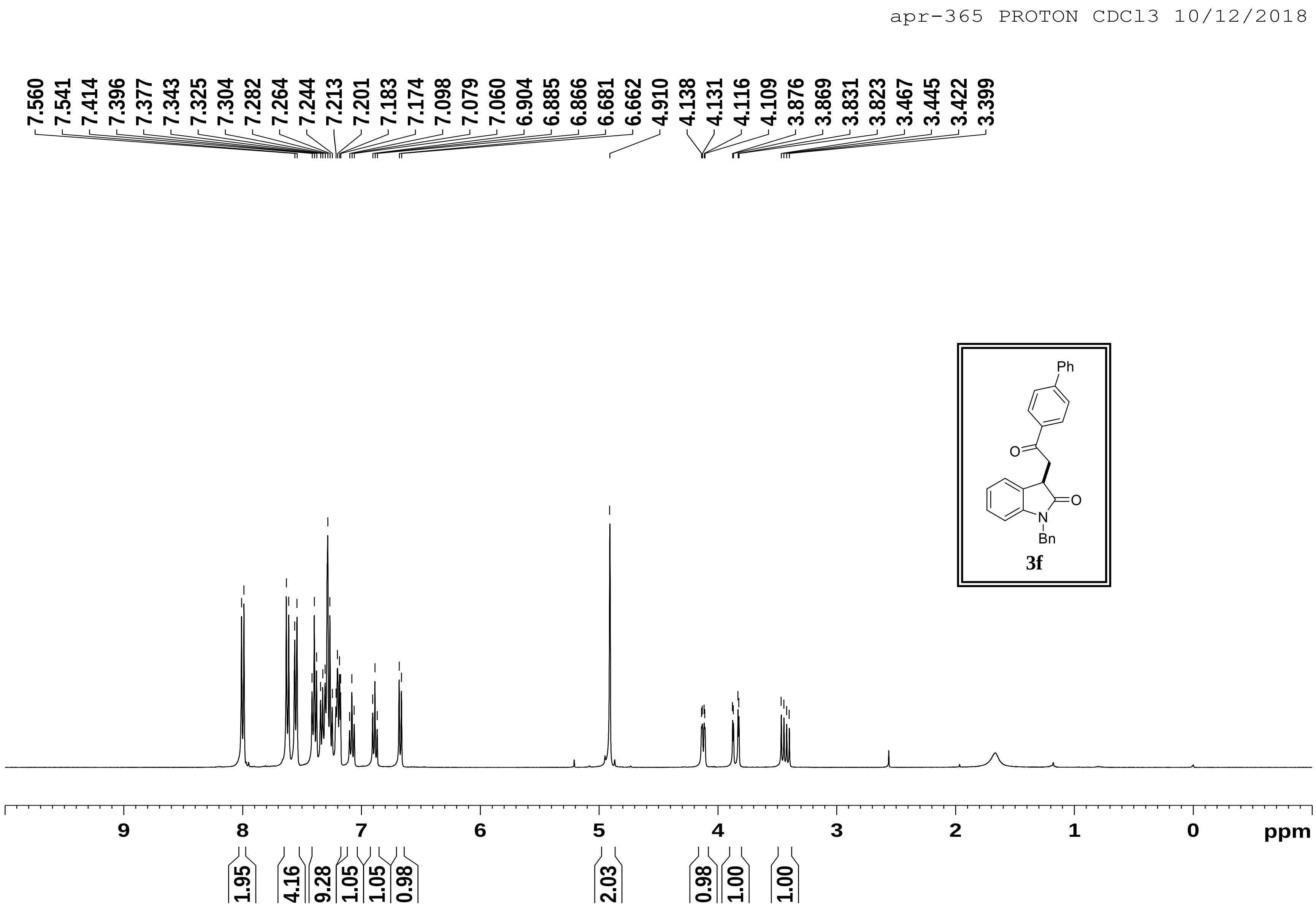
[1]H NMR spectrum of **3d**



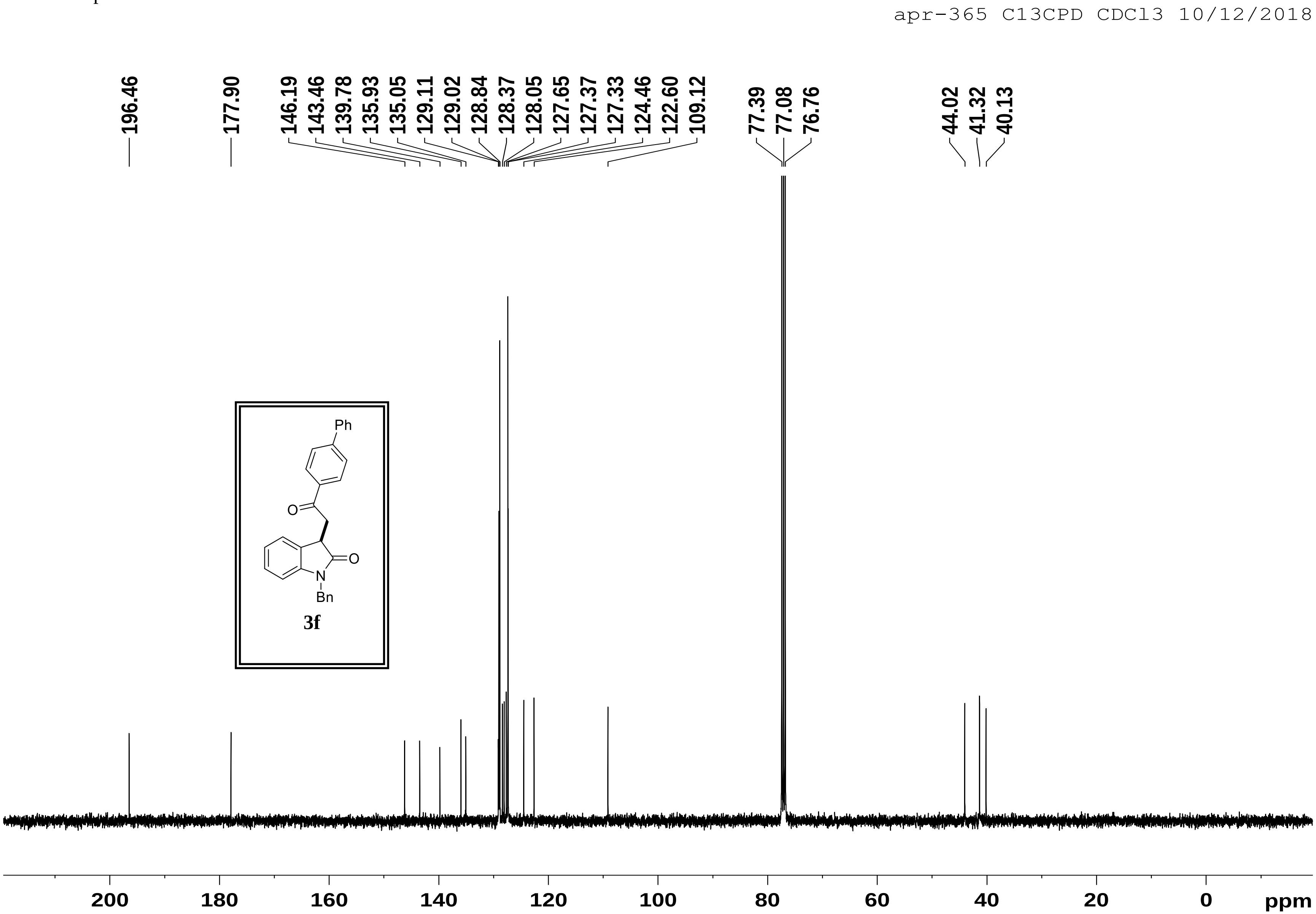
[13]C NMR spectrum of **3d**



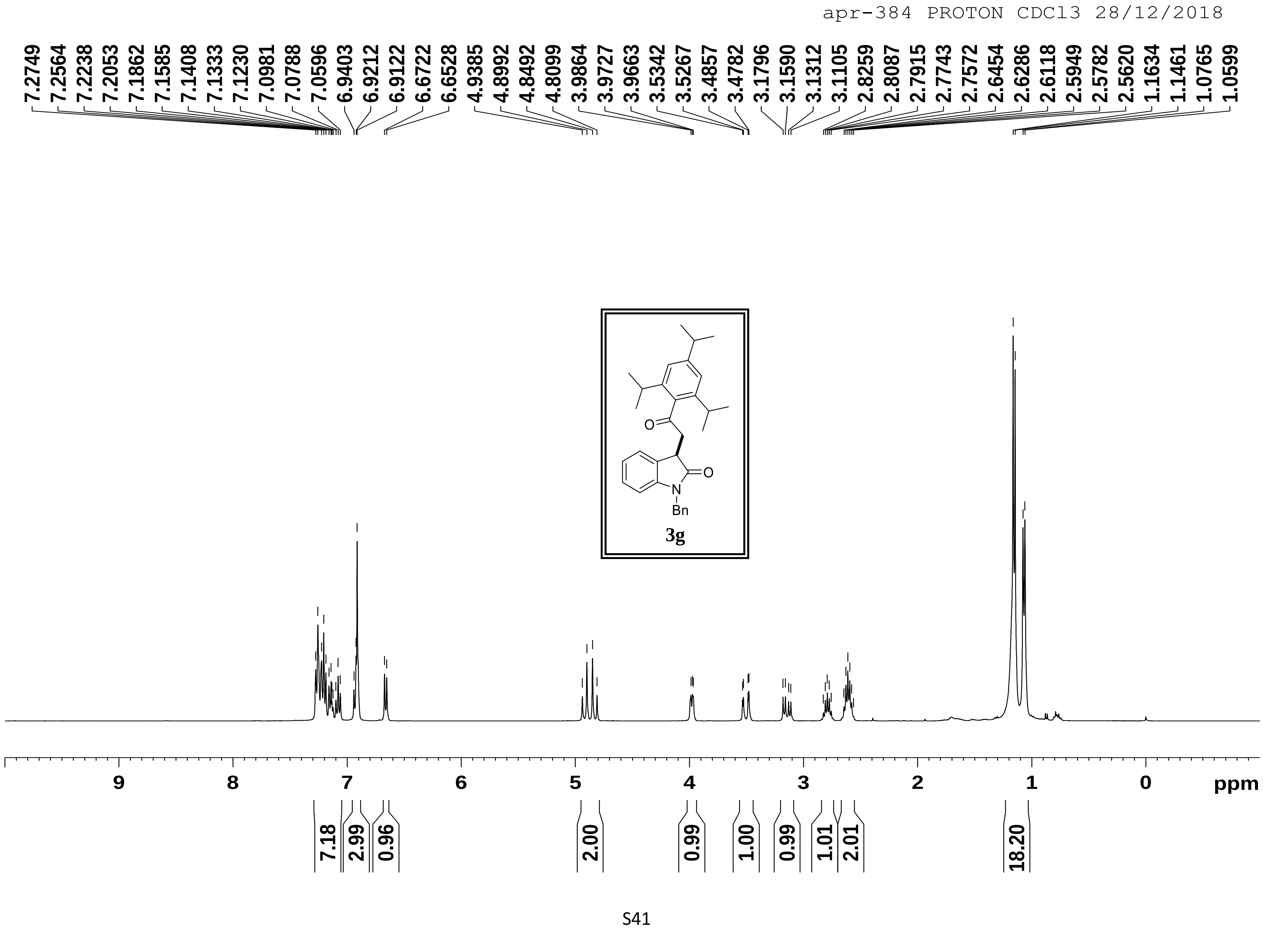
^{1}H NMR spectrum of **3f**



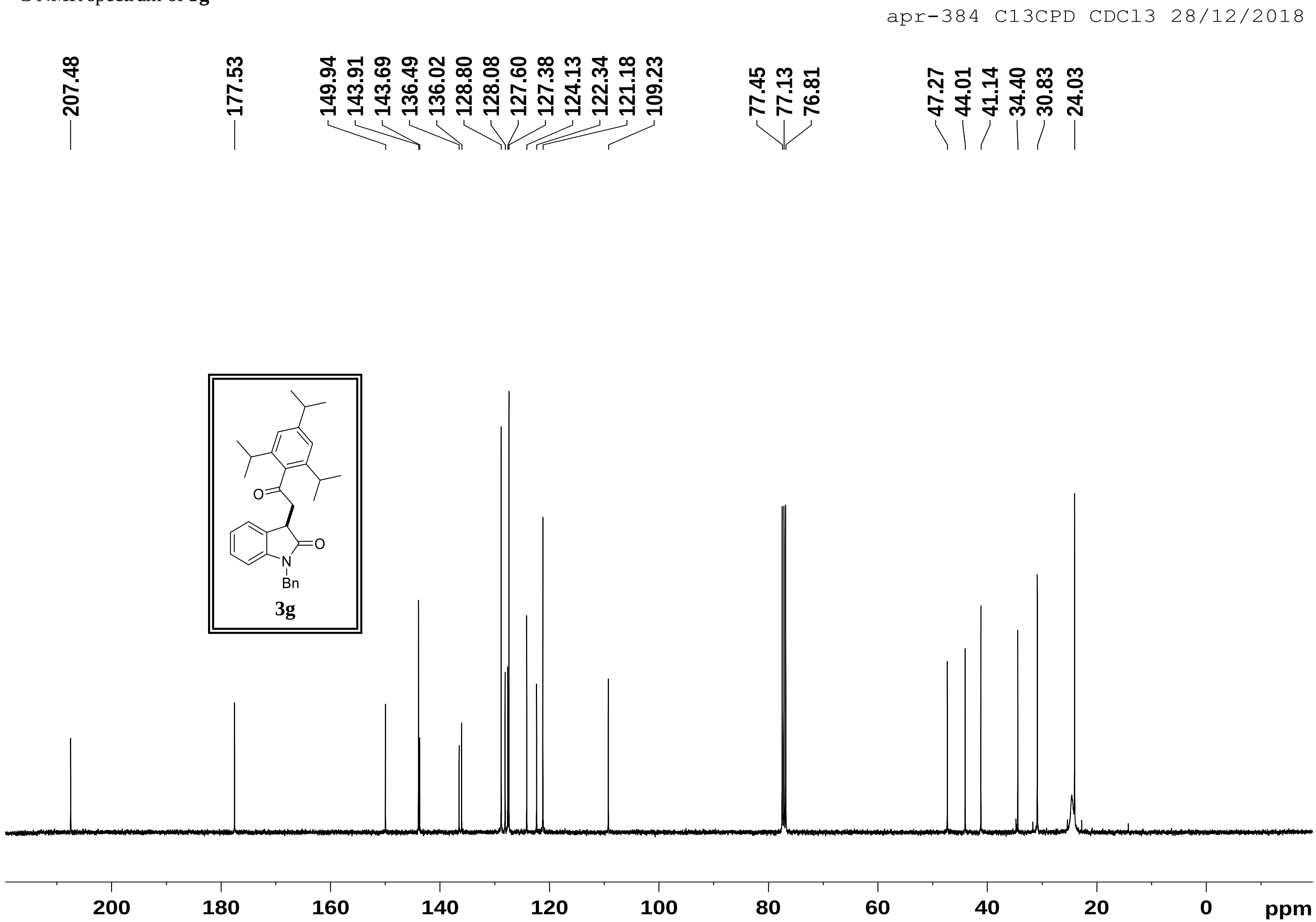
^{13}C NMR spectrum of **3f**



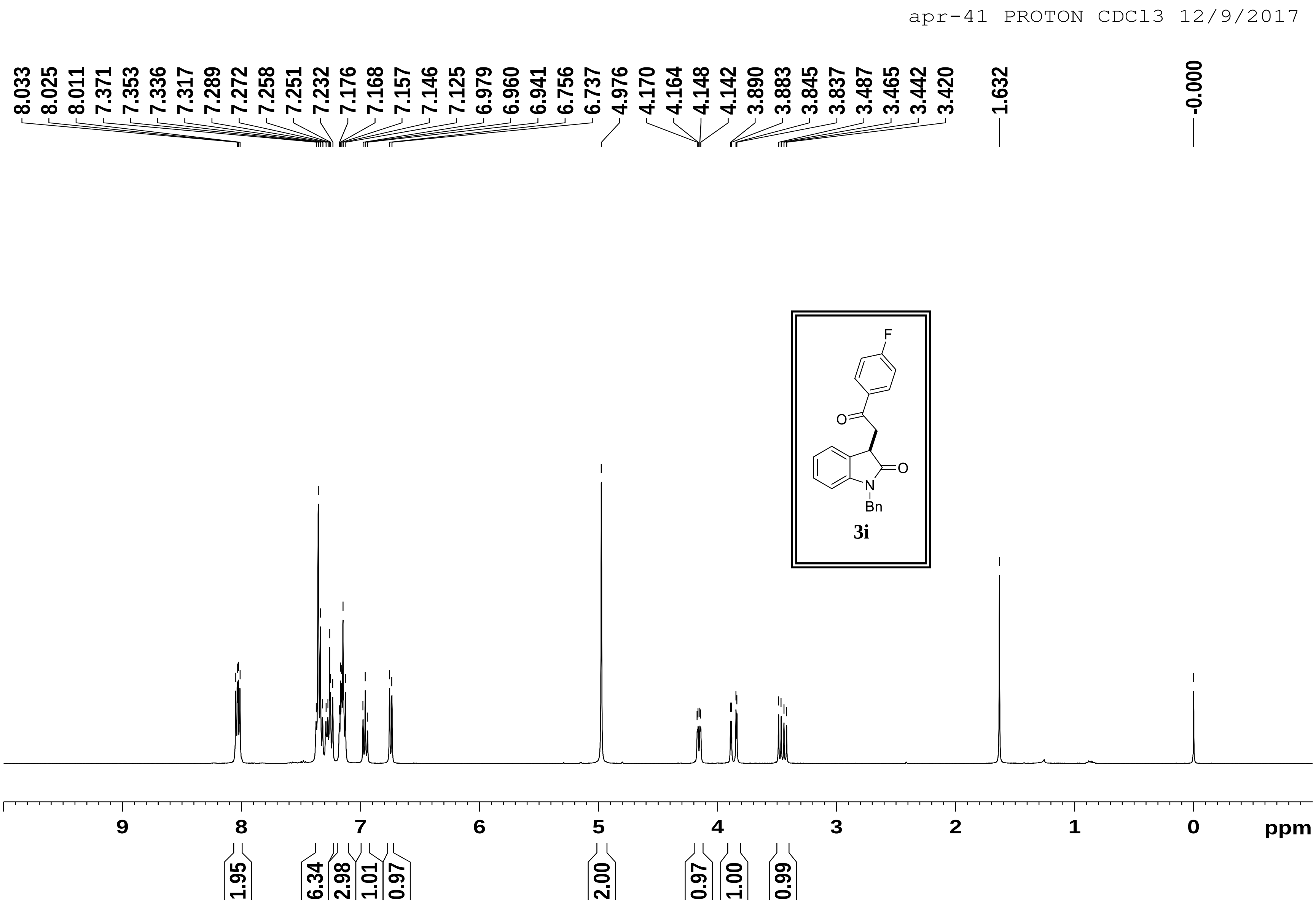
^{1}H NMR spectrum of **3g**



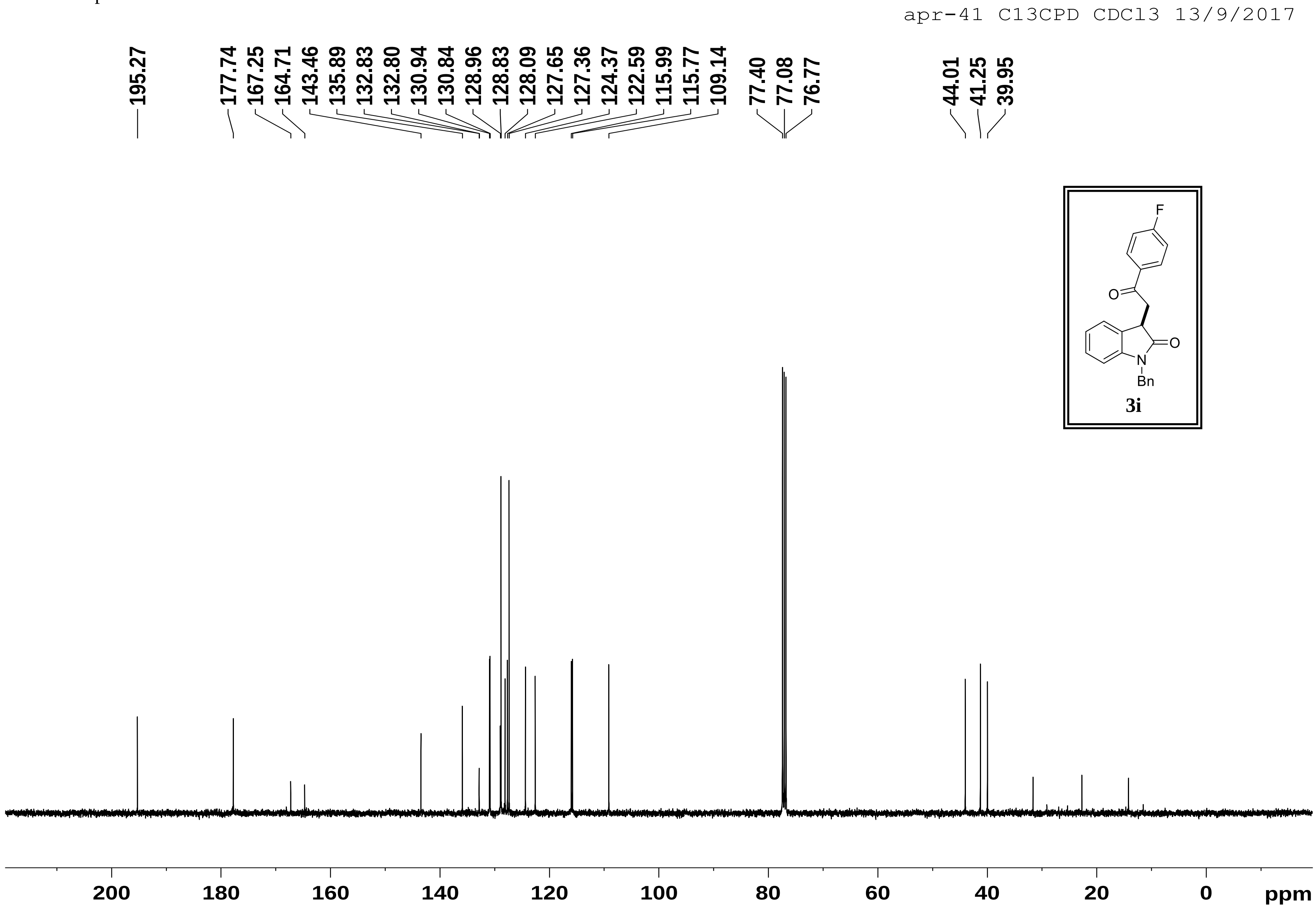
[13]C NMR spectrum of **3g**



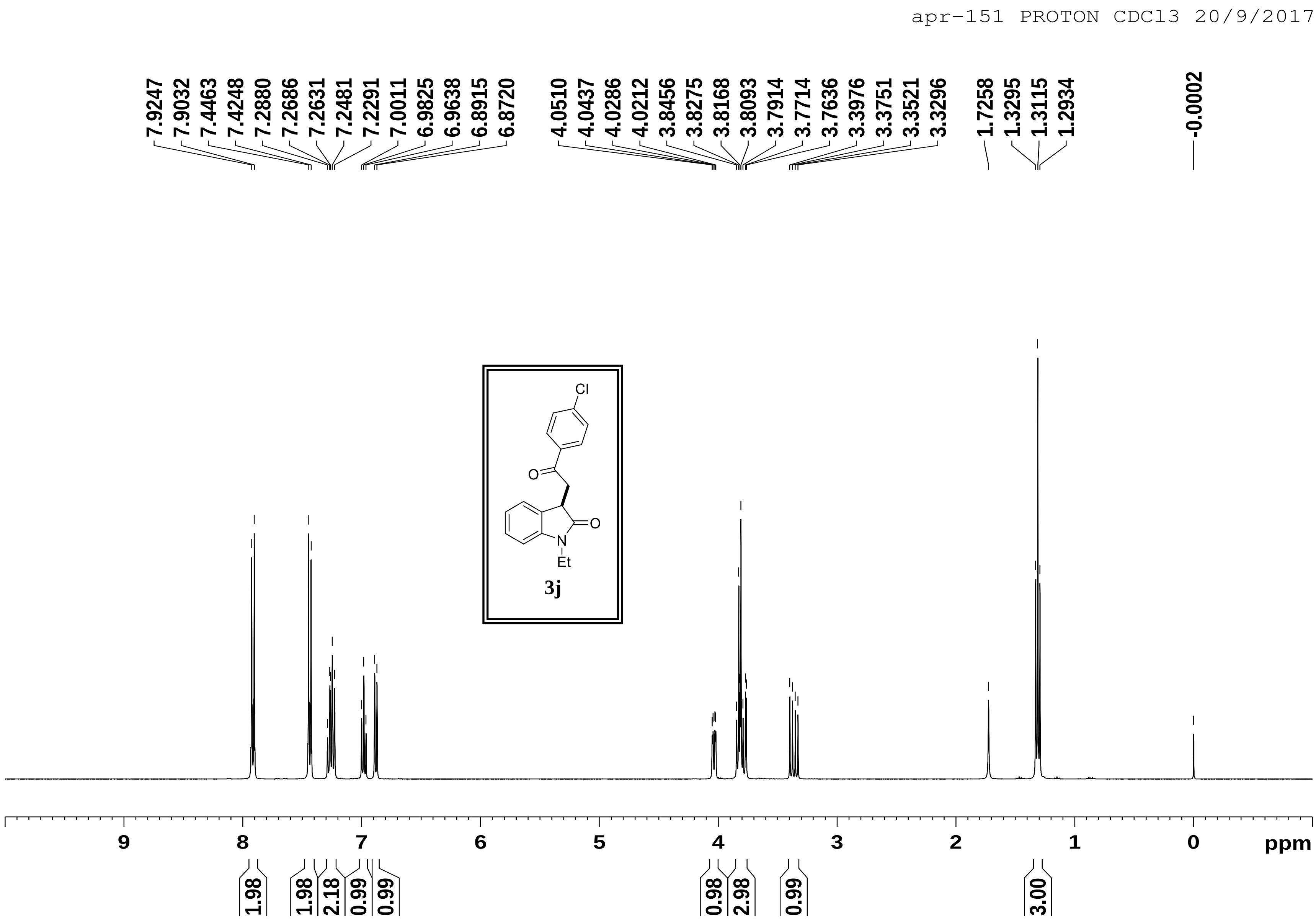
[1]H NMR spectrum of **3i**



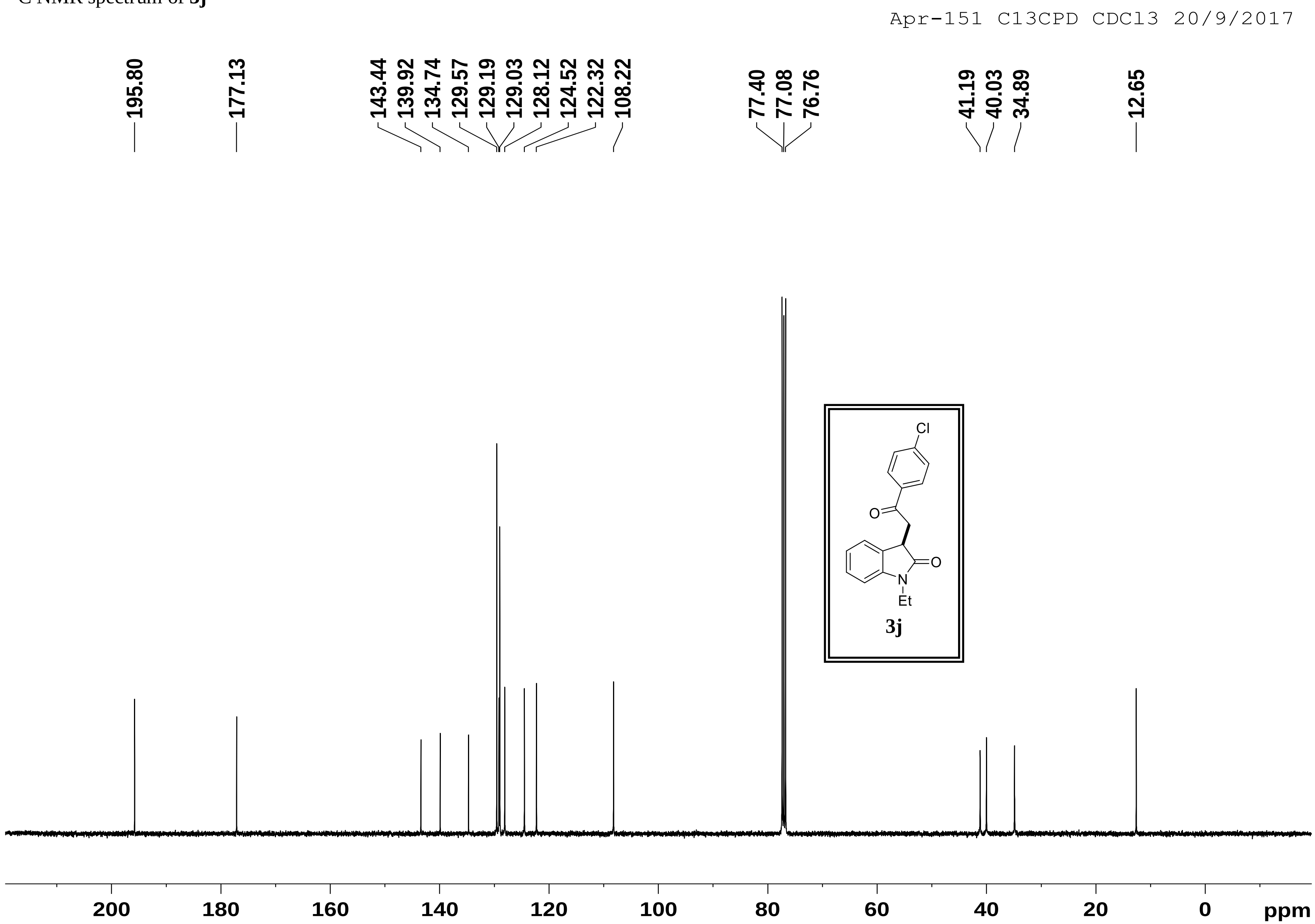
^{13}C NMR spectrum of **3i**



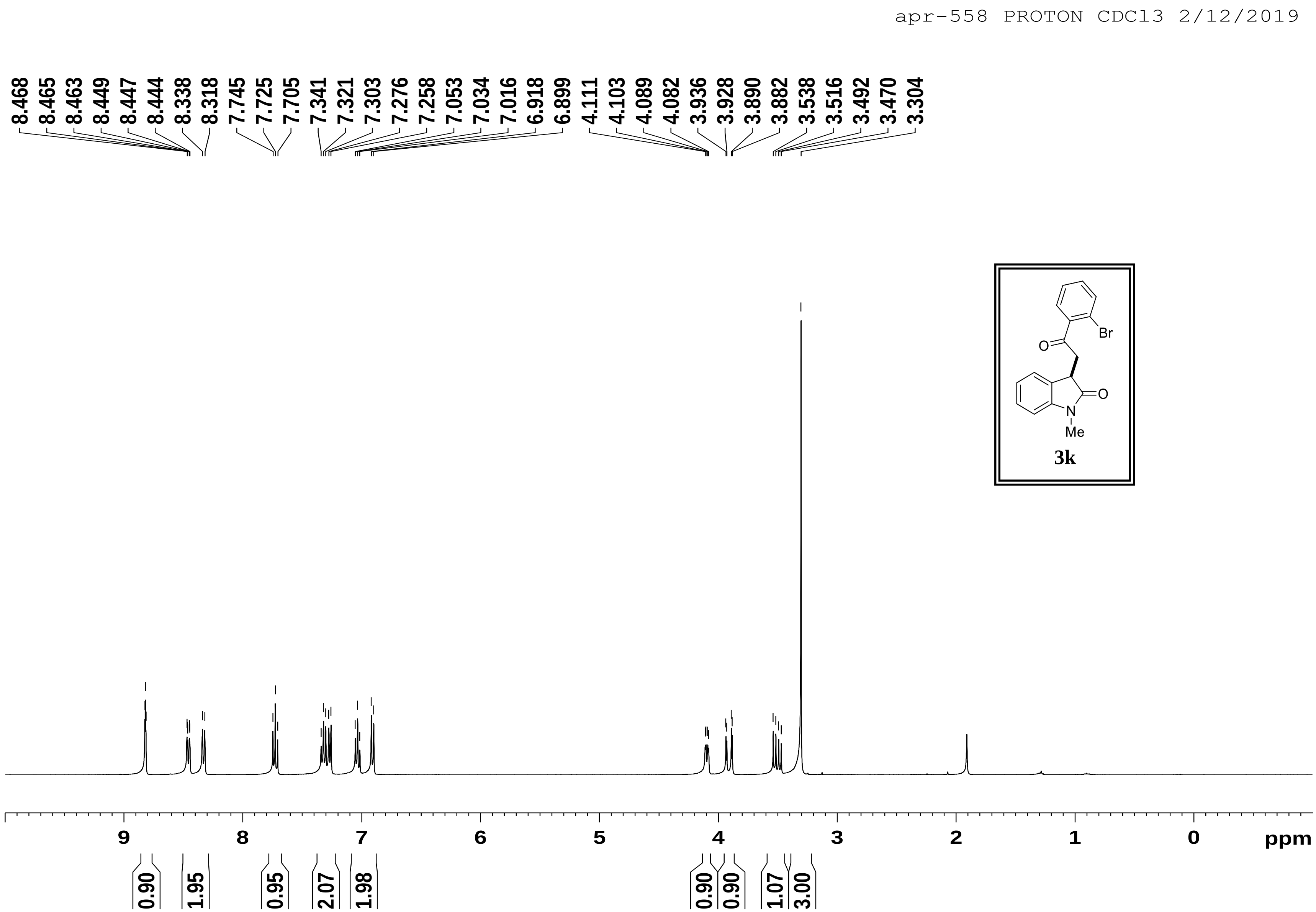
^{1}H NMR spectrum of **3j**



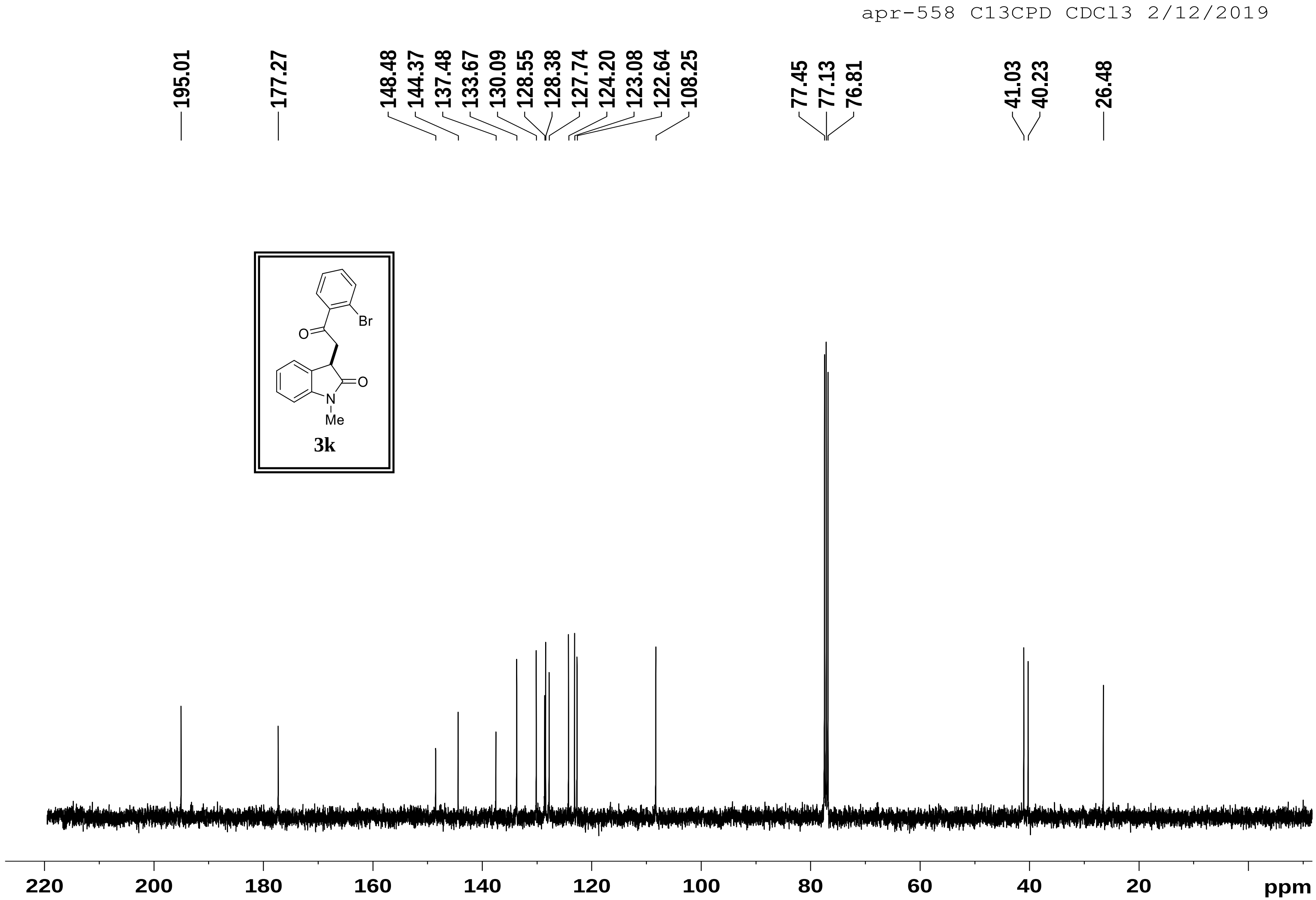
^{13}C NMR spectrum of **3j**



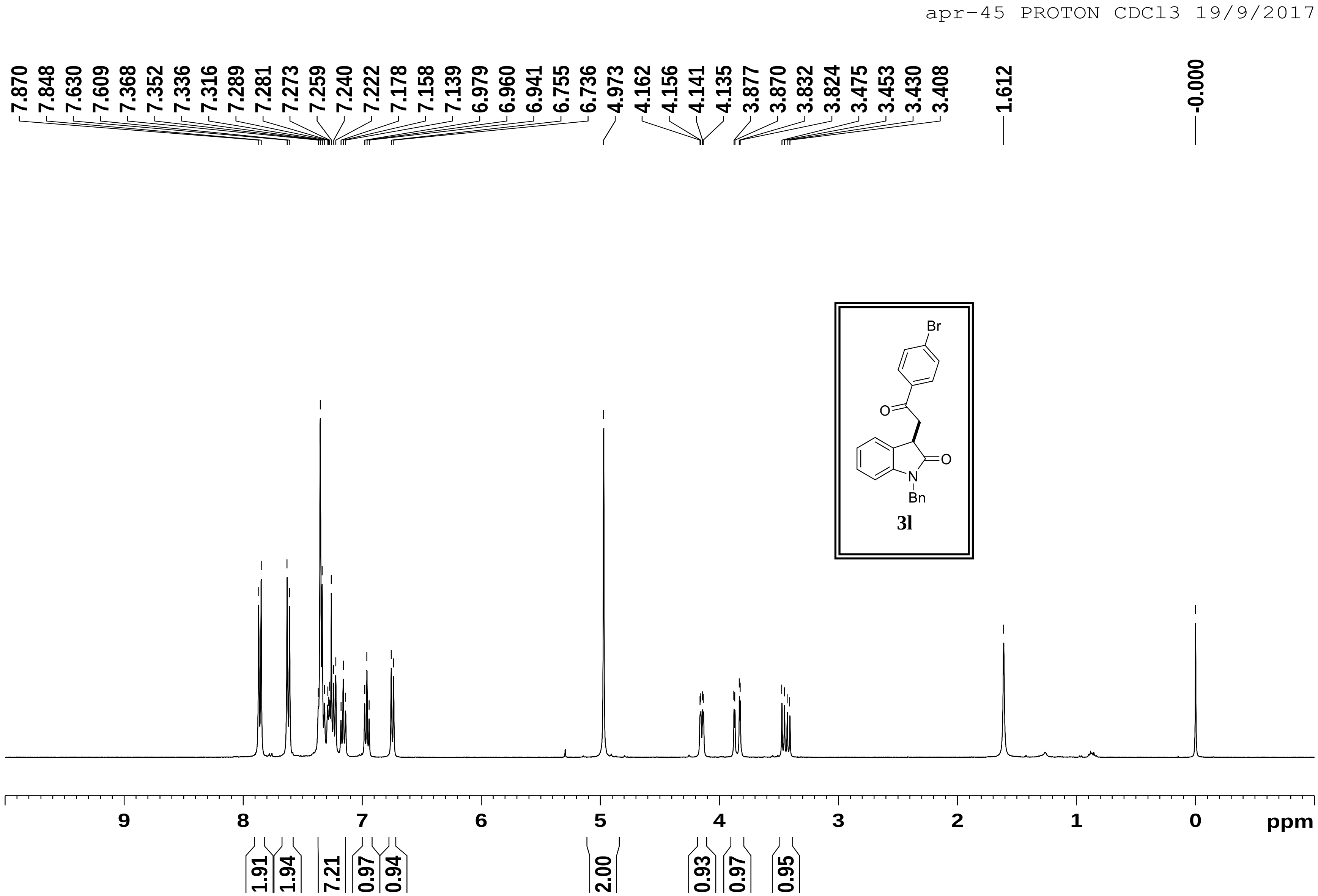
^{1}H NMR spectrum of **3k**



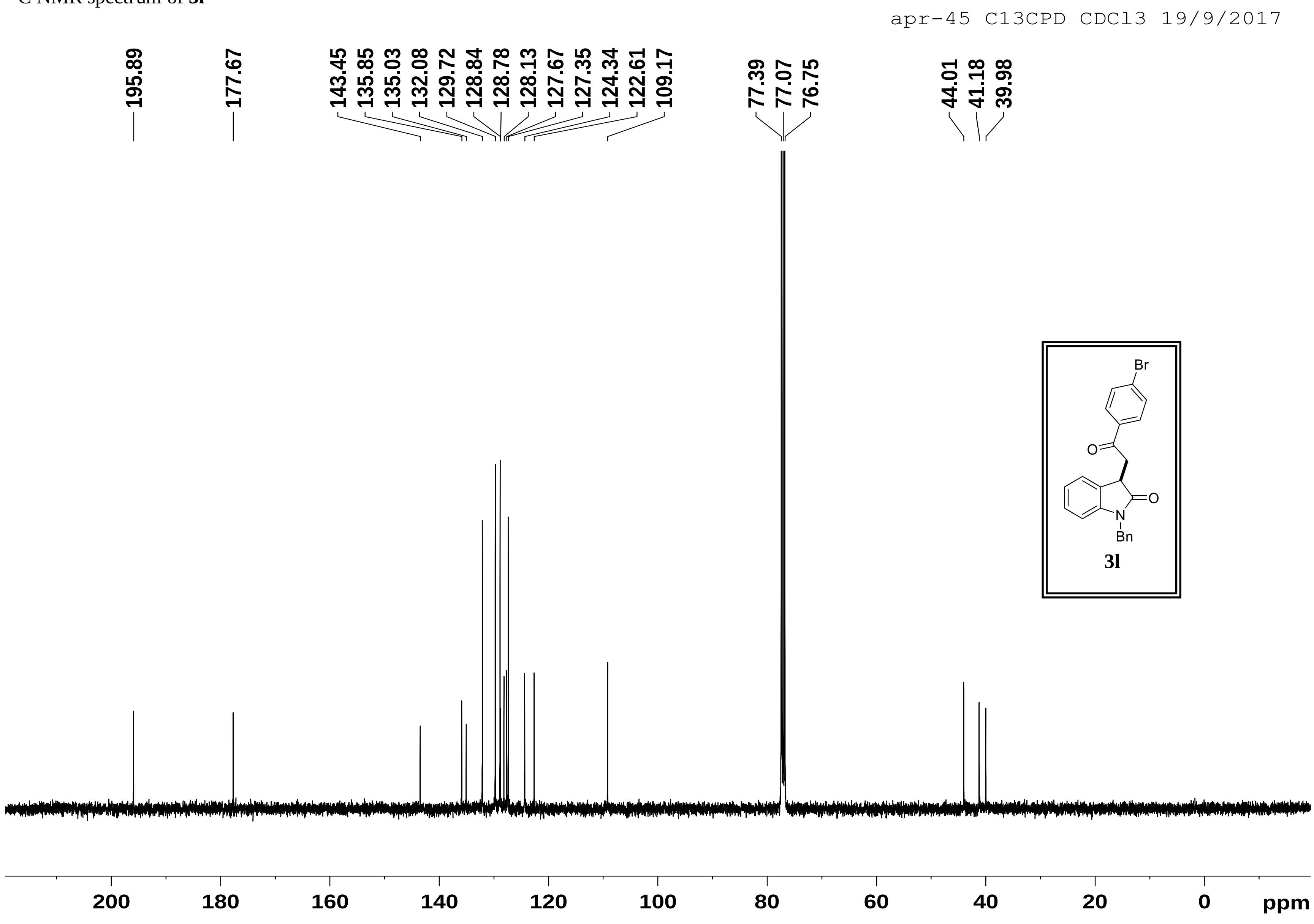
^{13}C NMR spectrum of **3k**



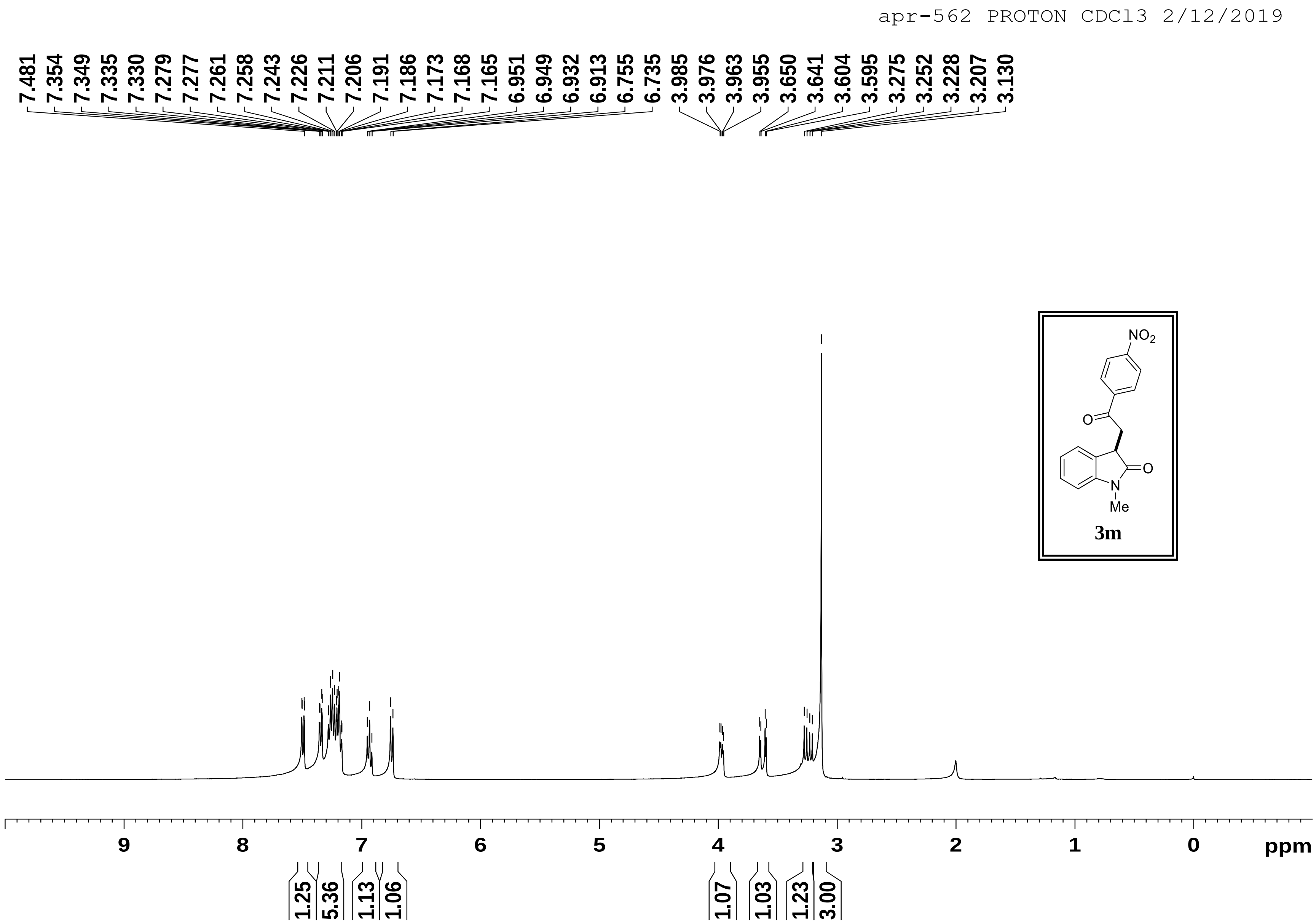
[1]H NMR spectrum of **3l**



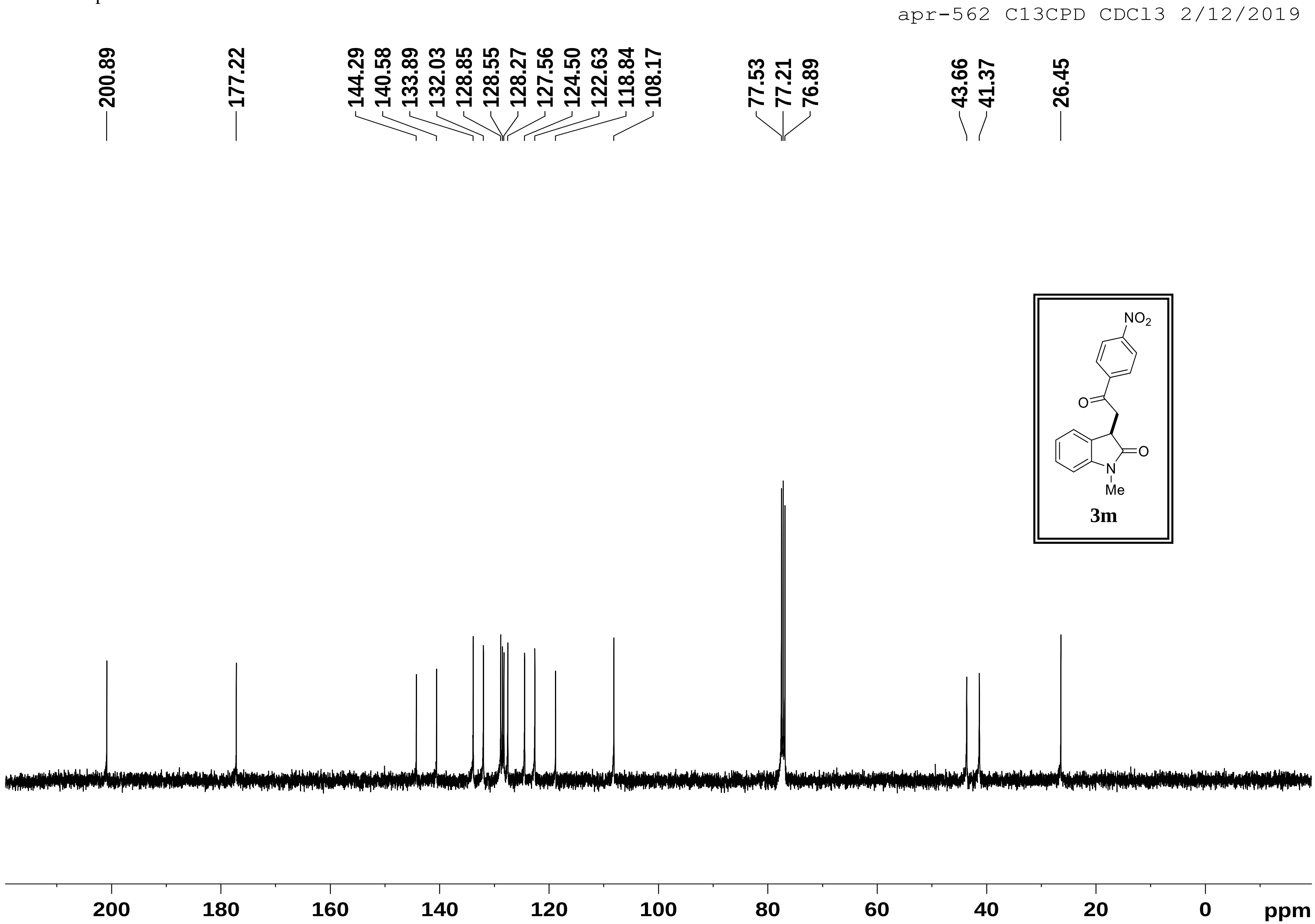
^{13}C NMR spectrum of **3l**



[1]H NMR spectrum of **3m**

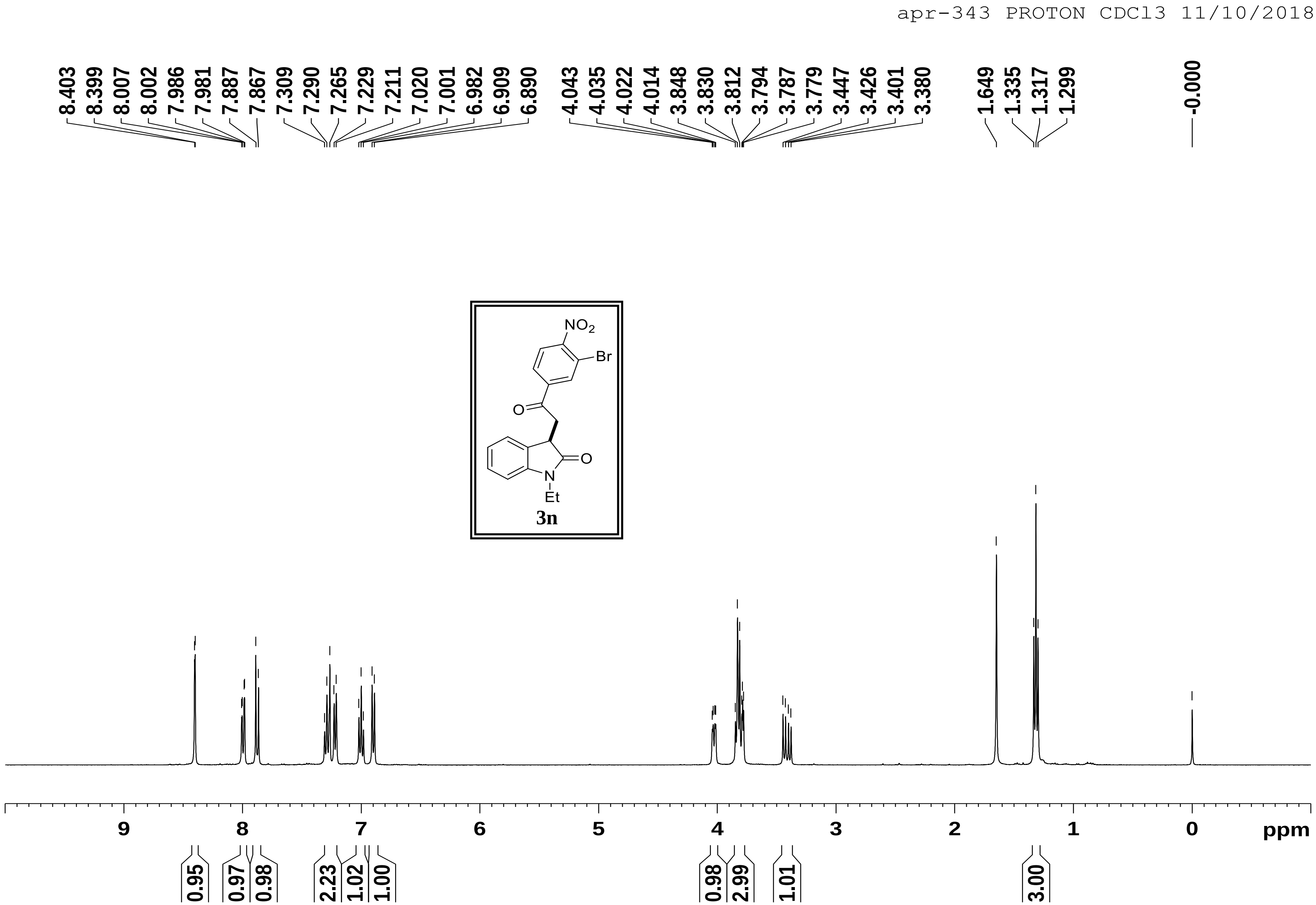


^{13}C NMR spectrum of **3m**

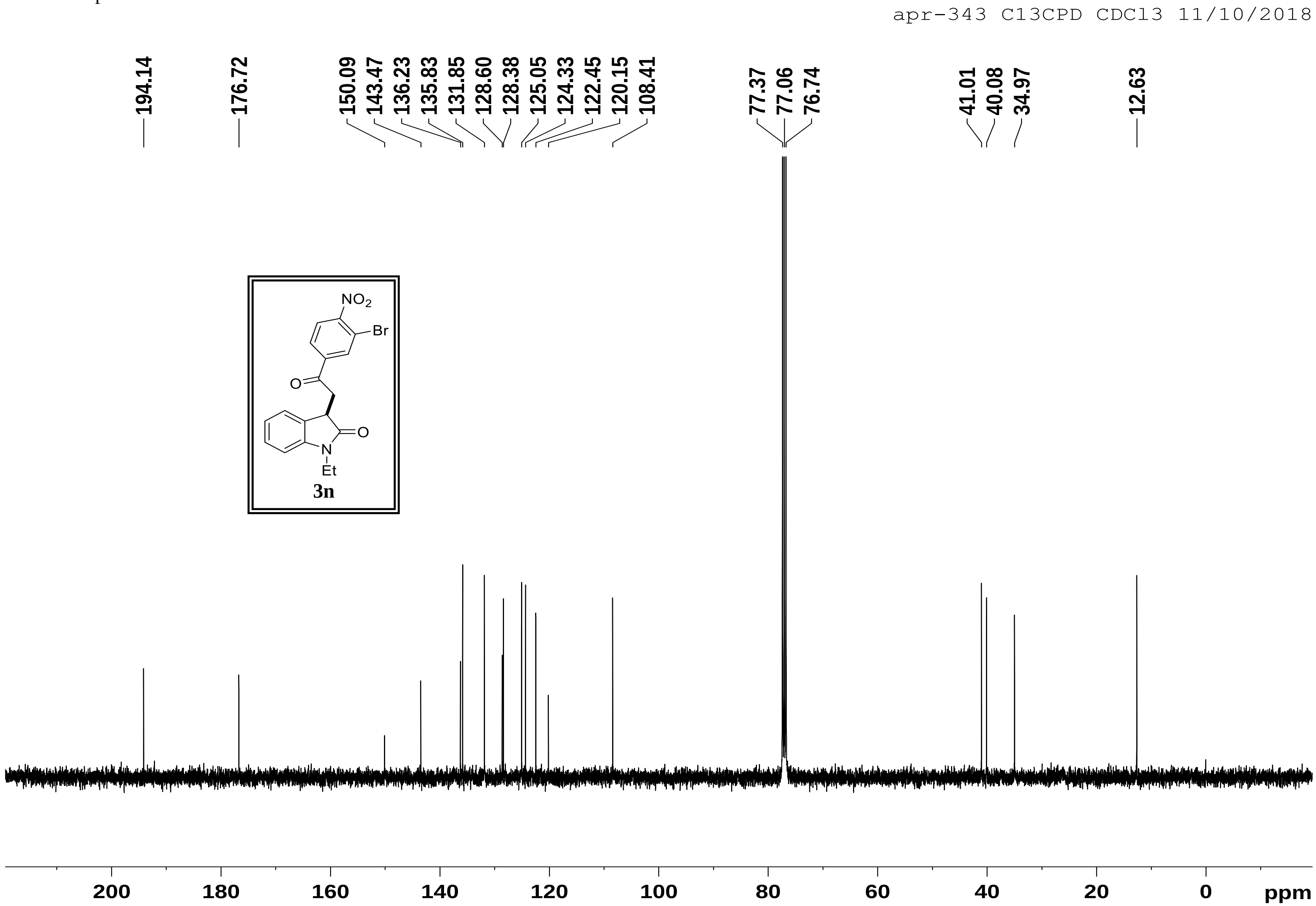


3m

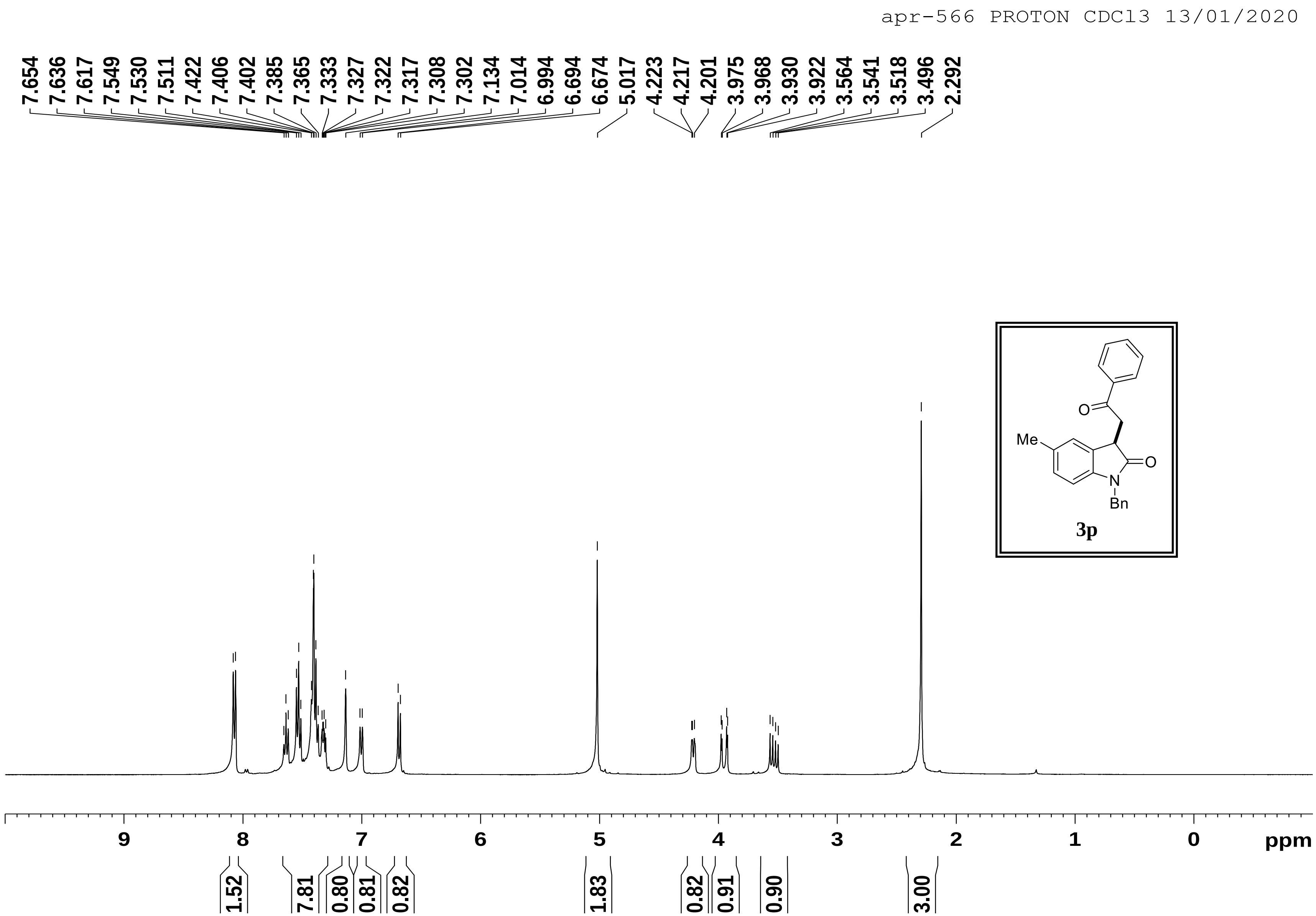
^{1}H NMR spectrum of **3n**



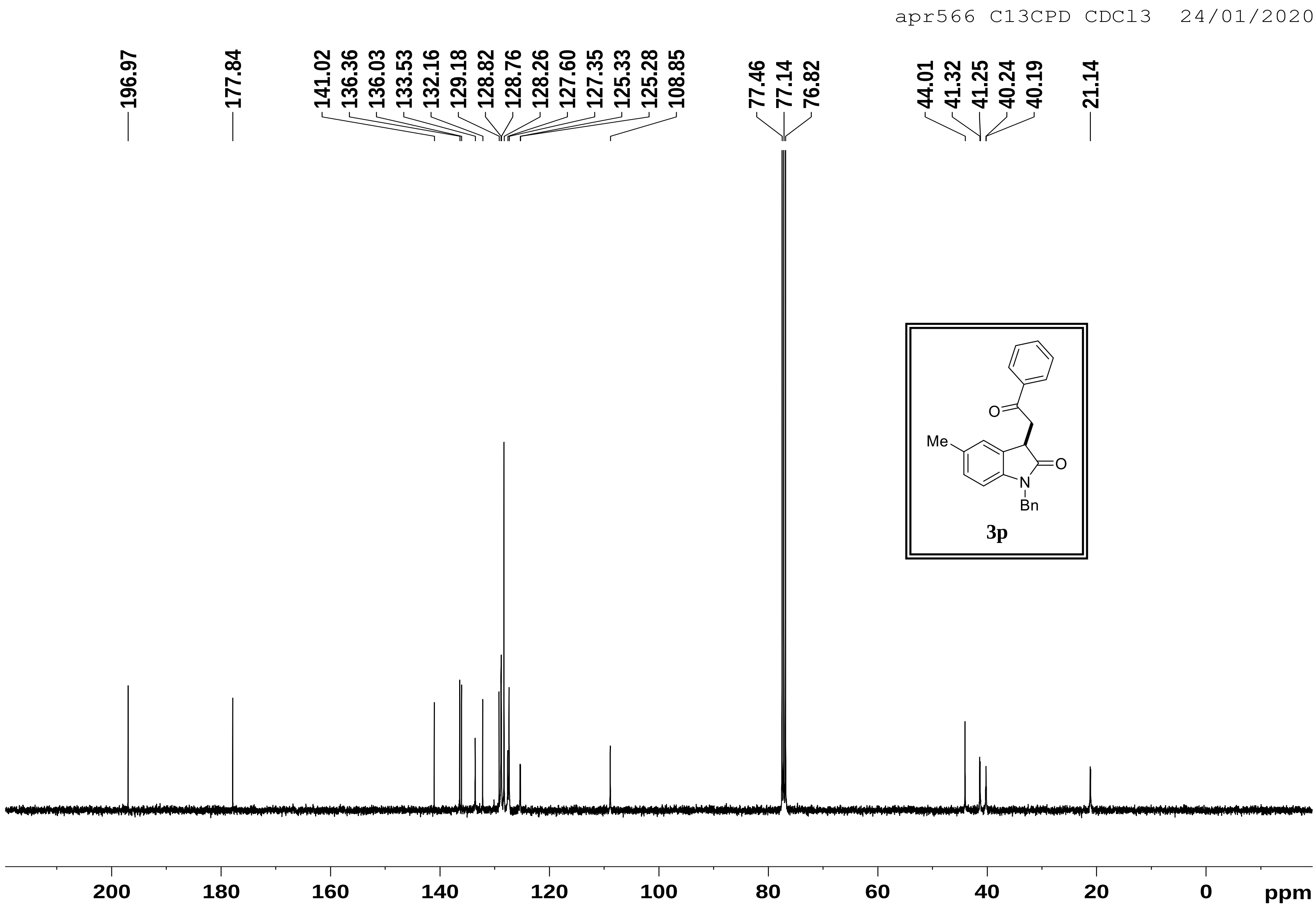
^{13}C NMR spectrum of **3n**



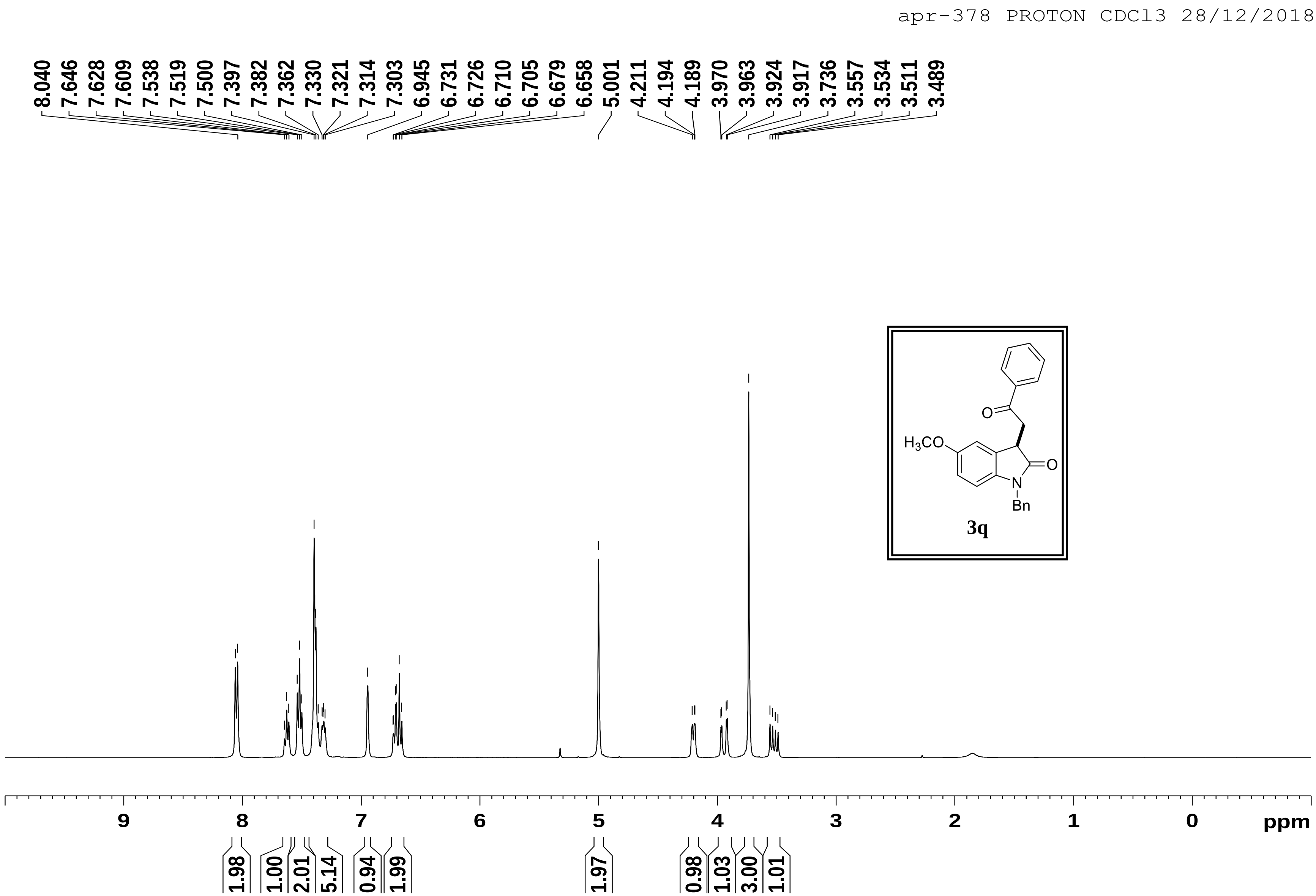
^{1}H NMR spectrum of **3p**



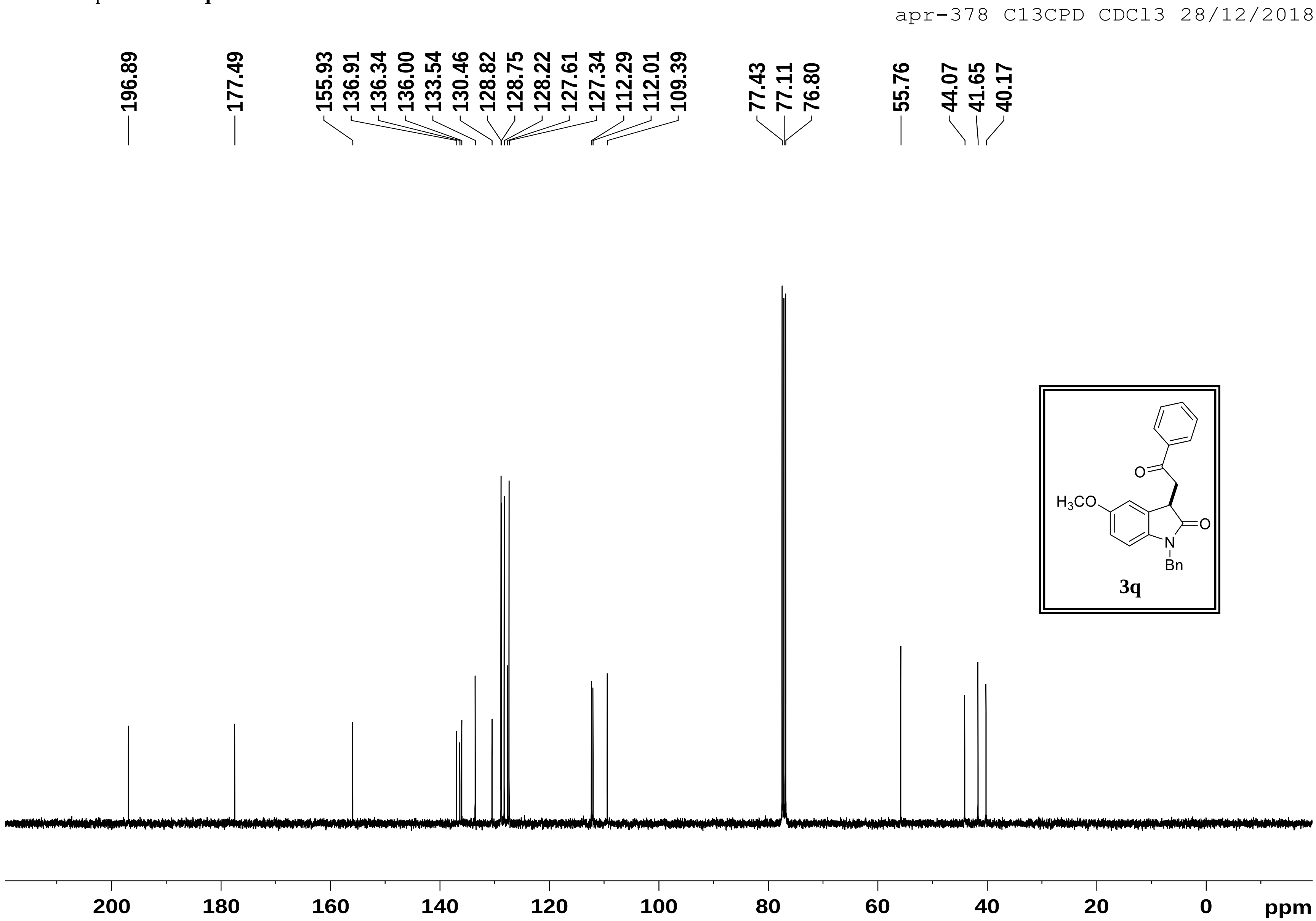
[13]C NMR spectrum of **3p**



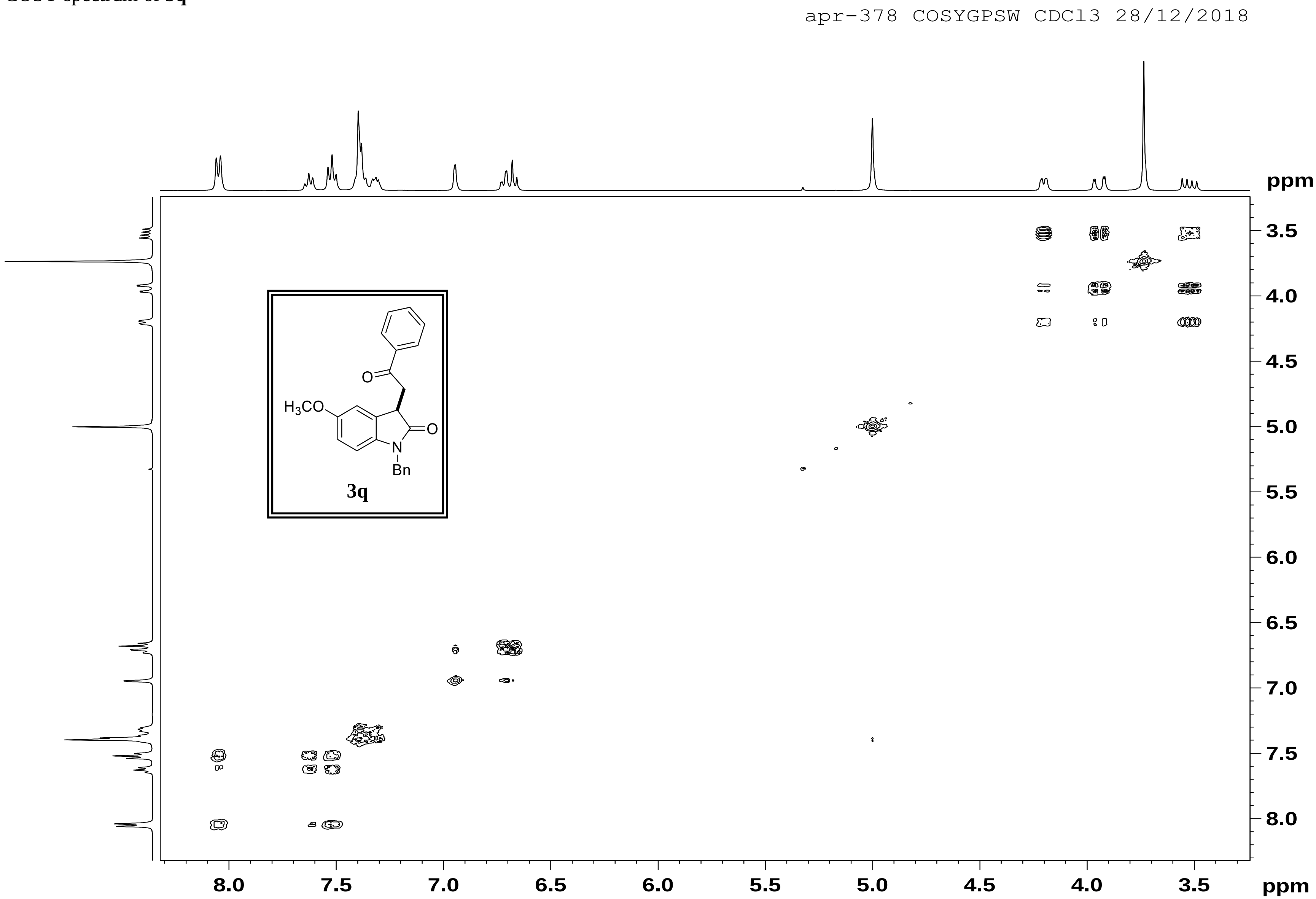
^{1}H NMR spectrum of **3q**



^{13}C NMR spectrum of **3q**

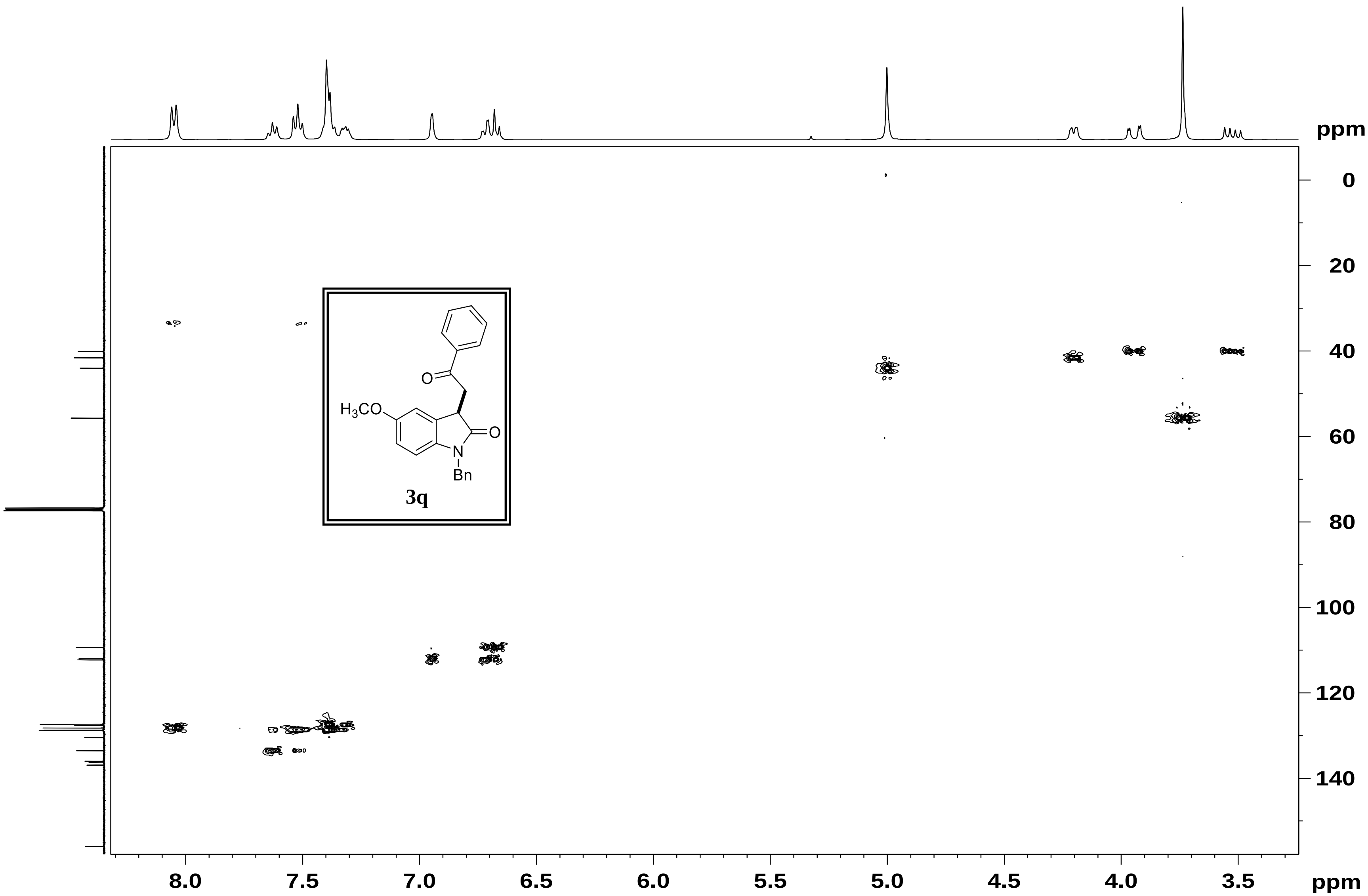


COSY spectrum of **3q**

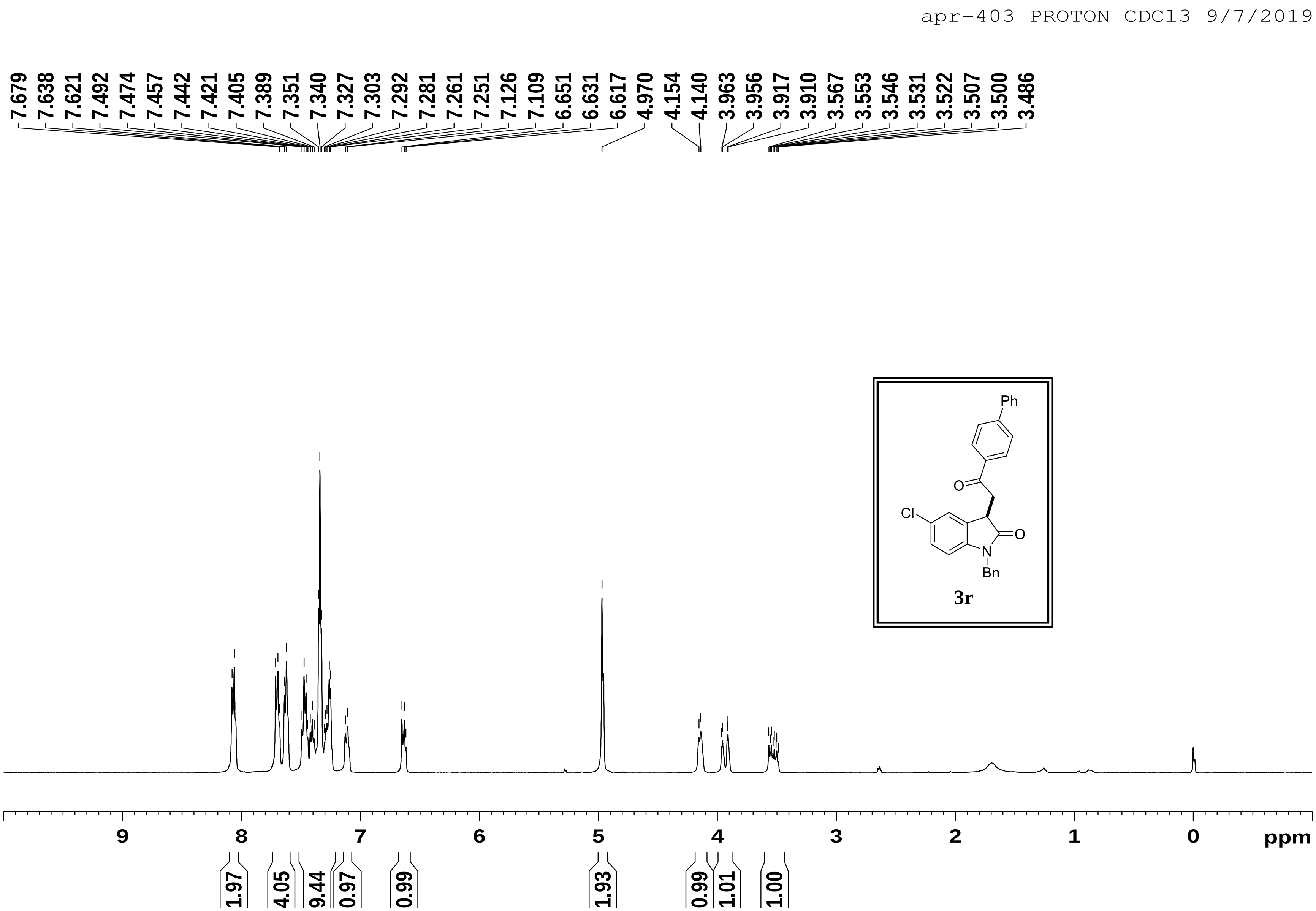


HSQC spectrum of **3q**

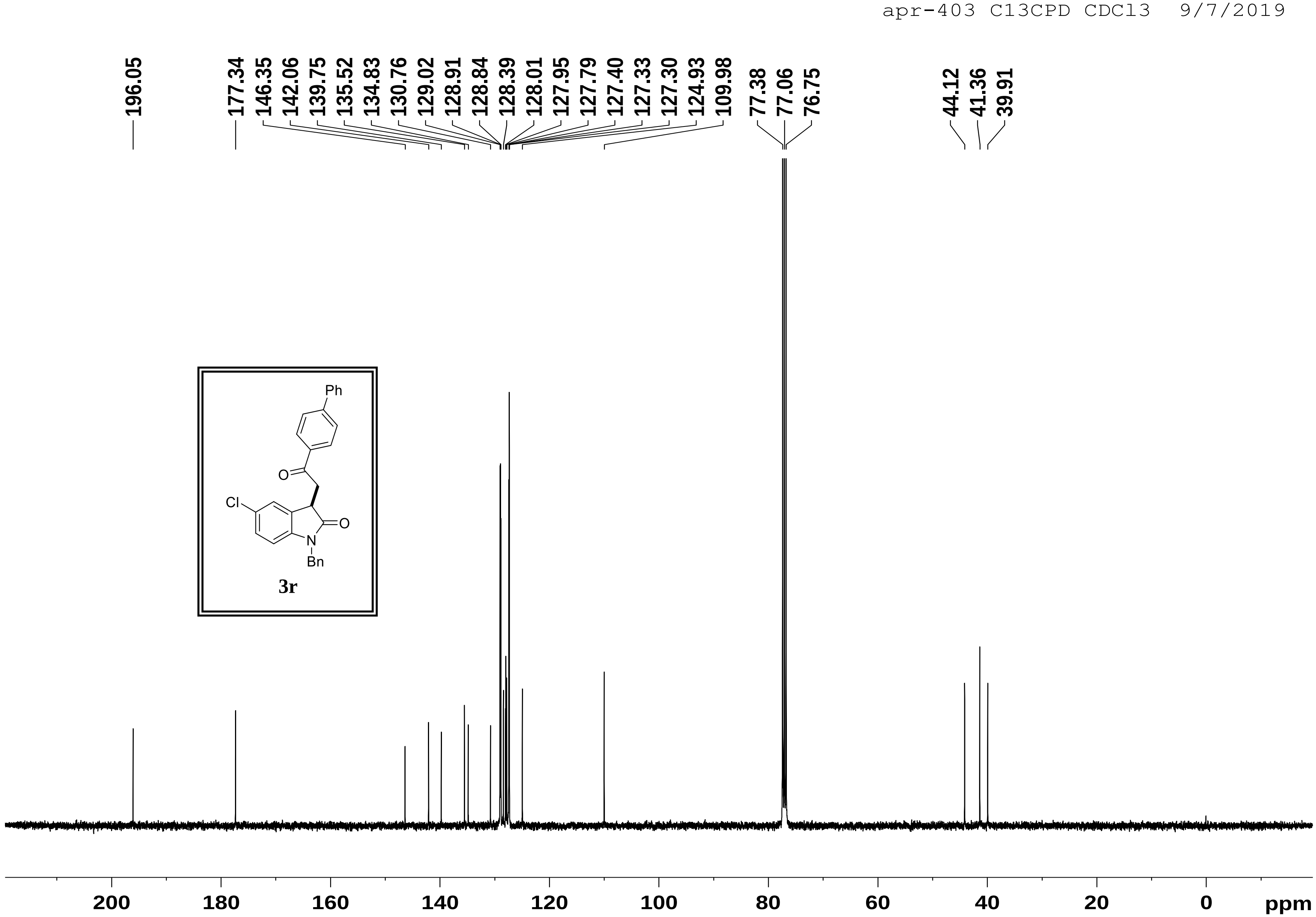
apr-378 HSQCGP CDCl3 28/12/20118



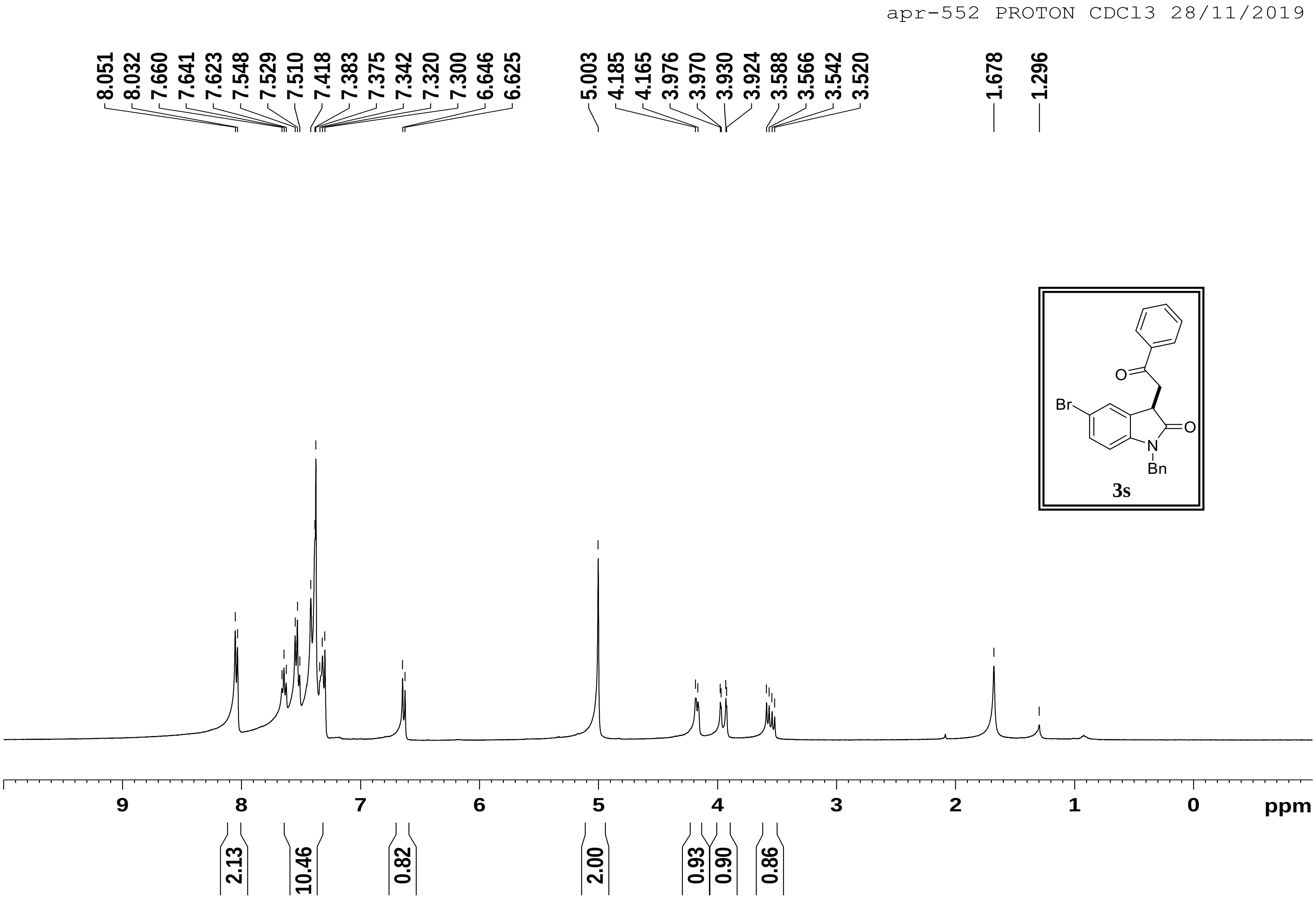
[1]H NMR spectrum of **3r**



^{13}C NMR spectrum of **3r**

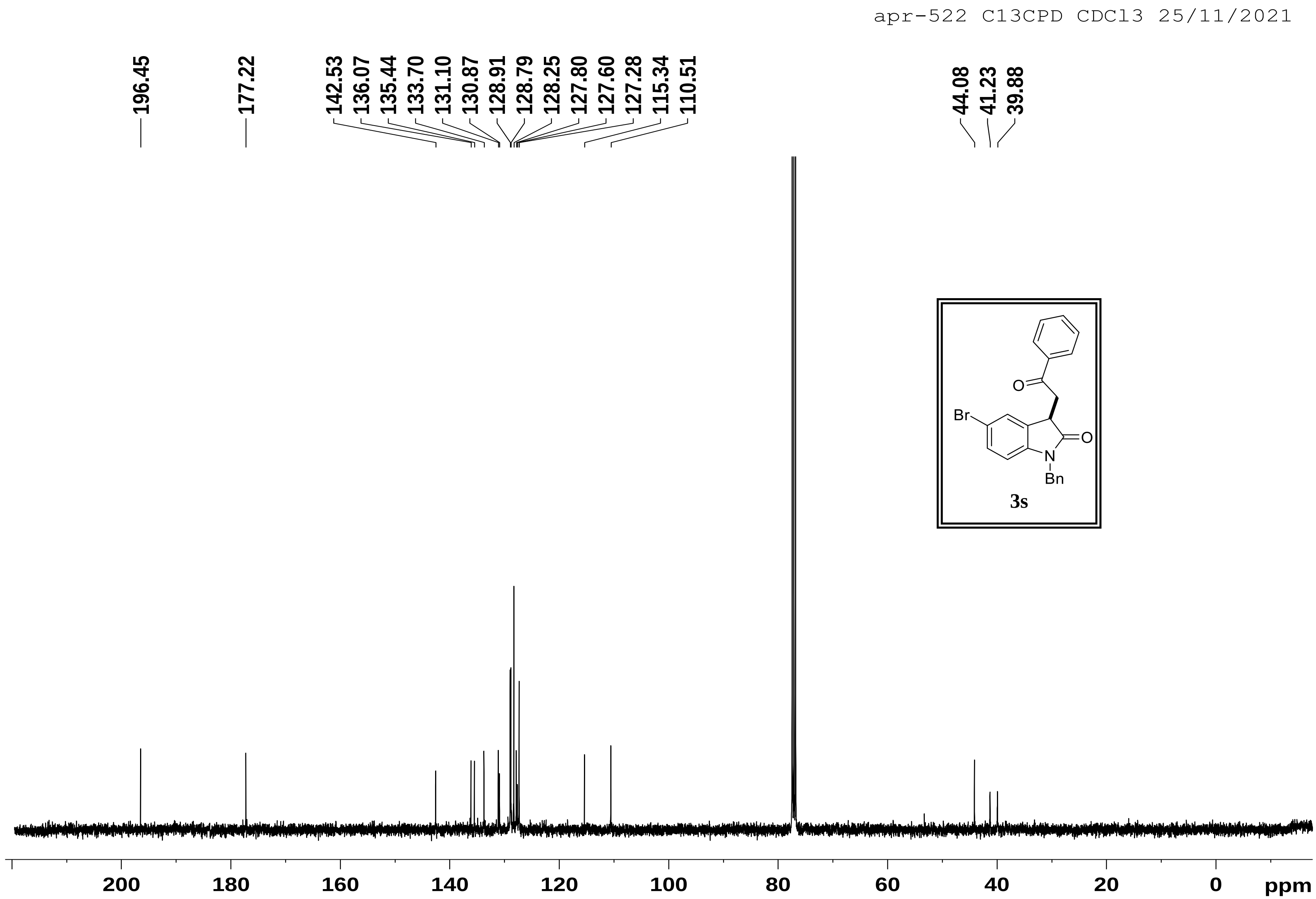


[1]H NMR spectrum of **3s**

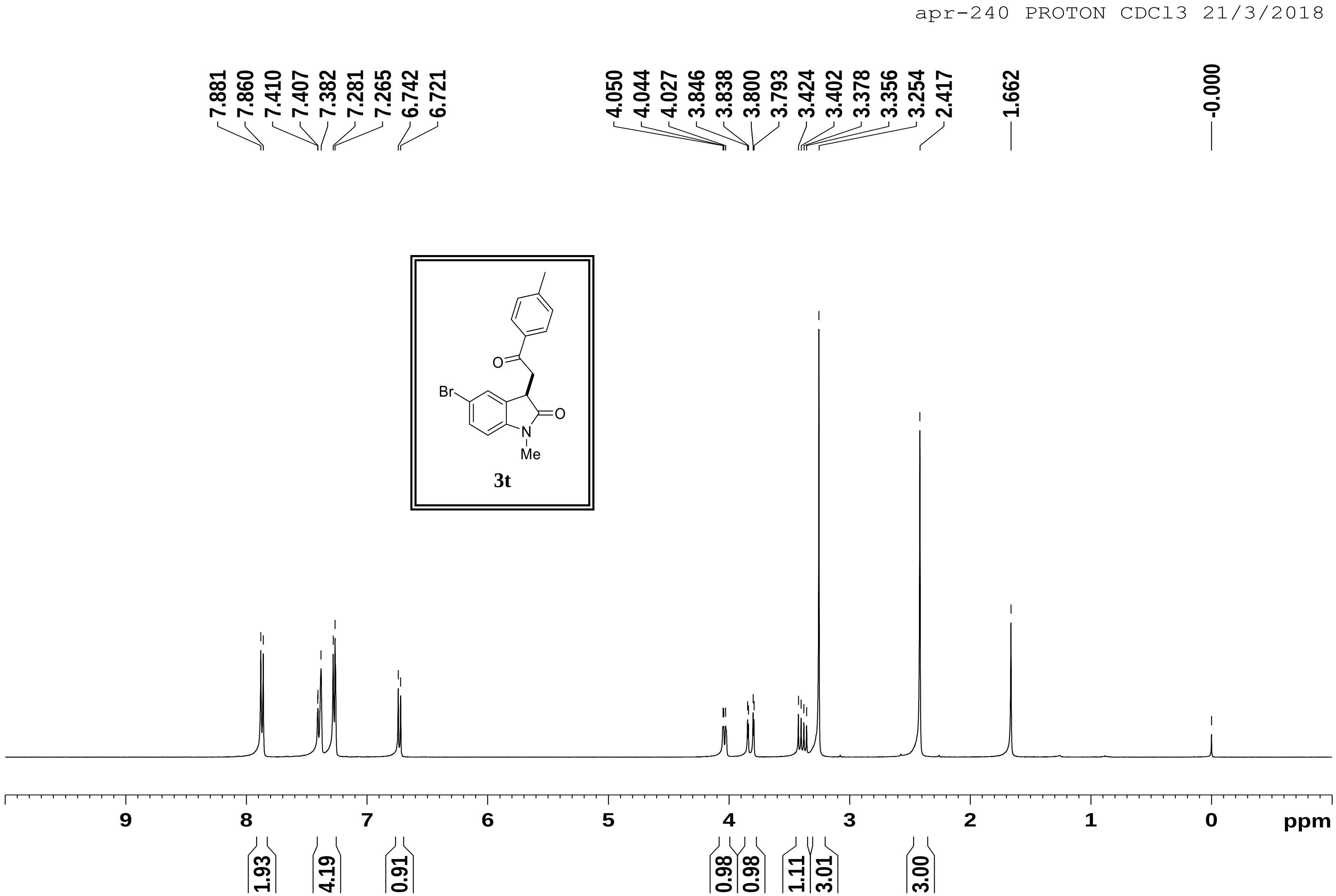


3s

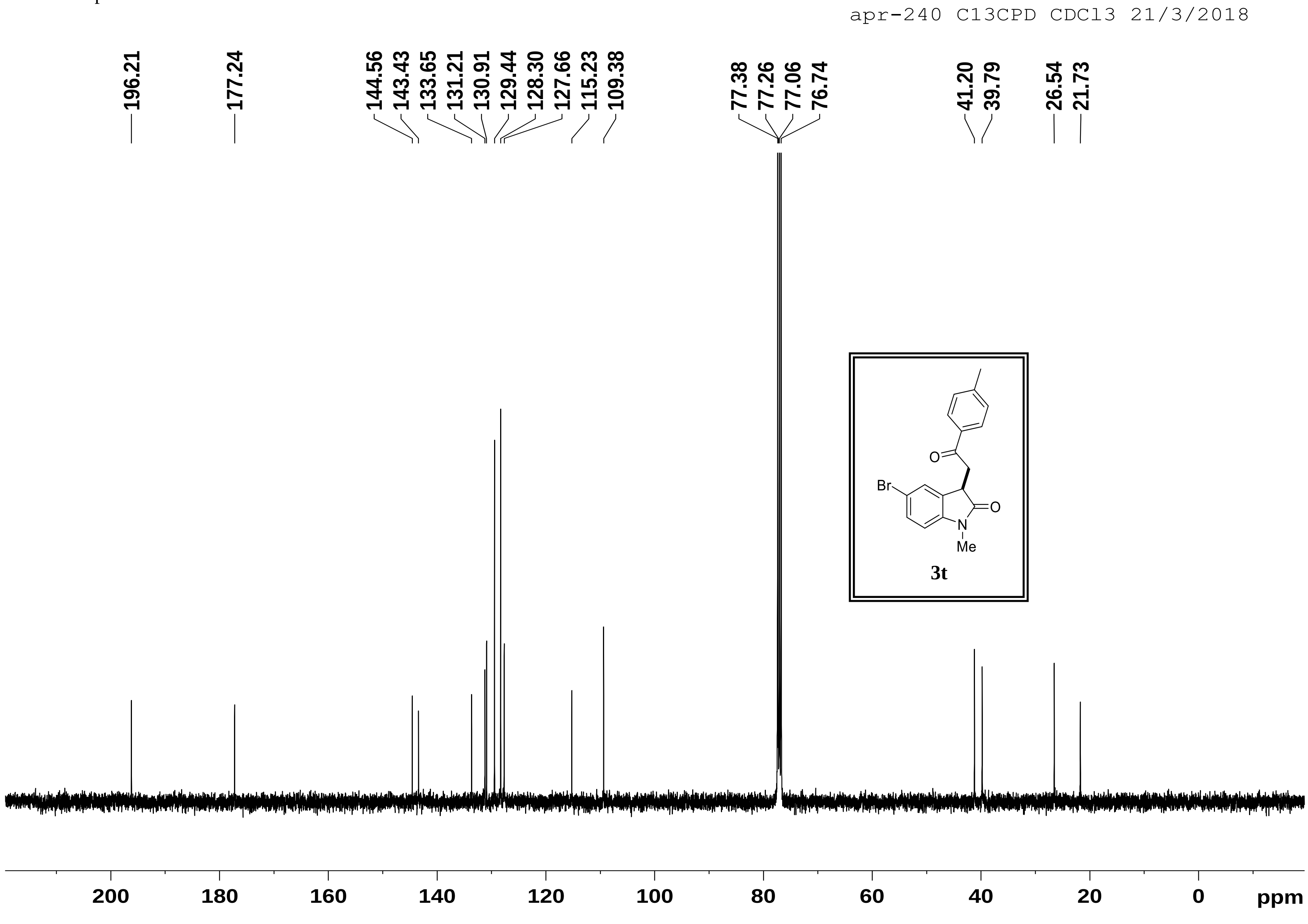
^{13}C NMR spectrum of **3s**



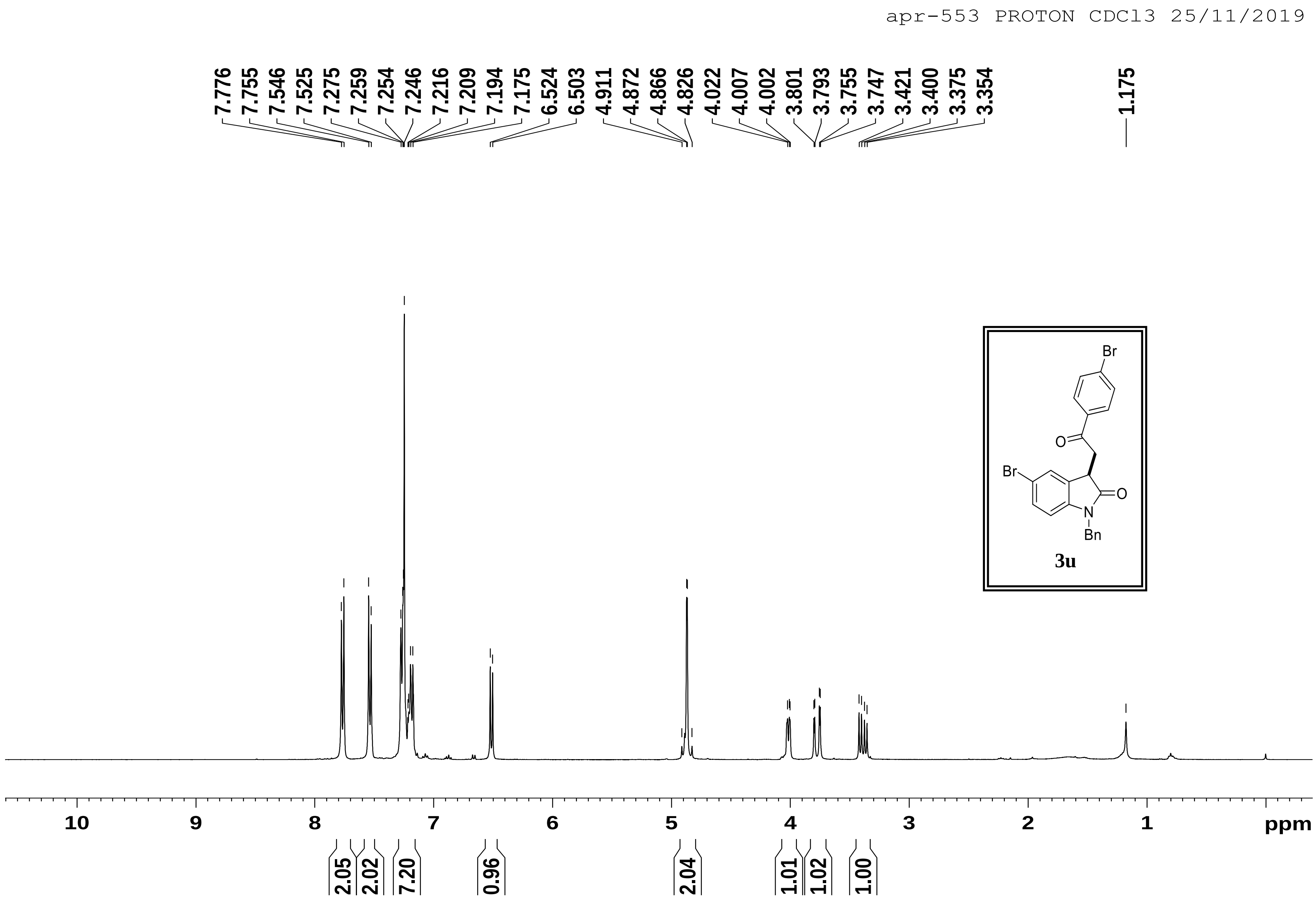
^{1}H NMR spectrum of **3t**



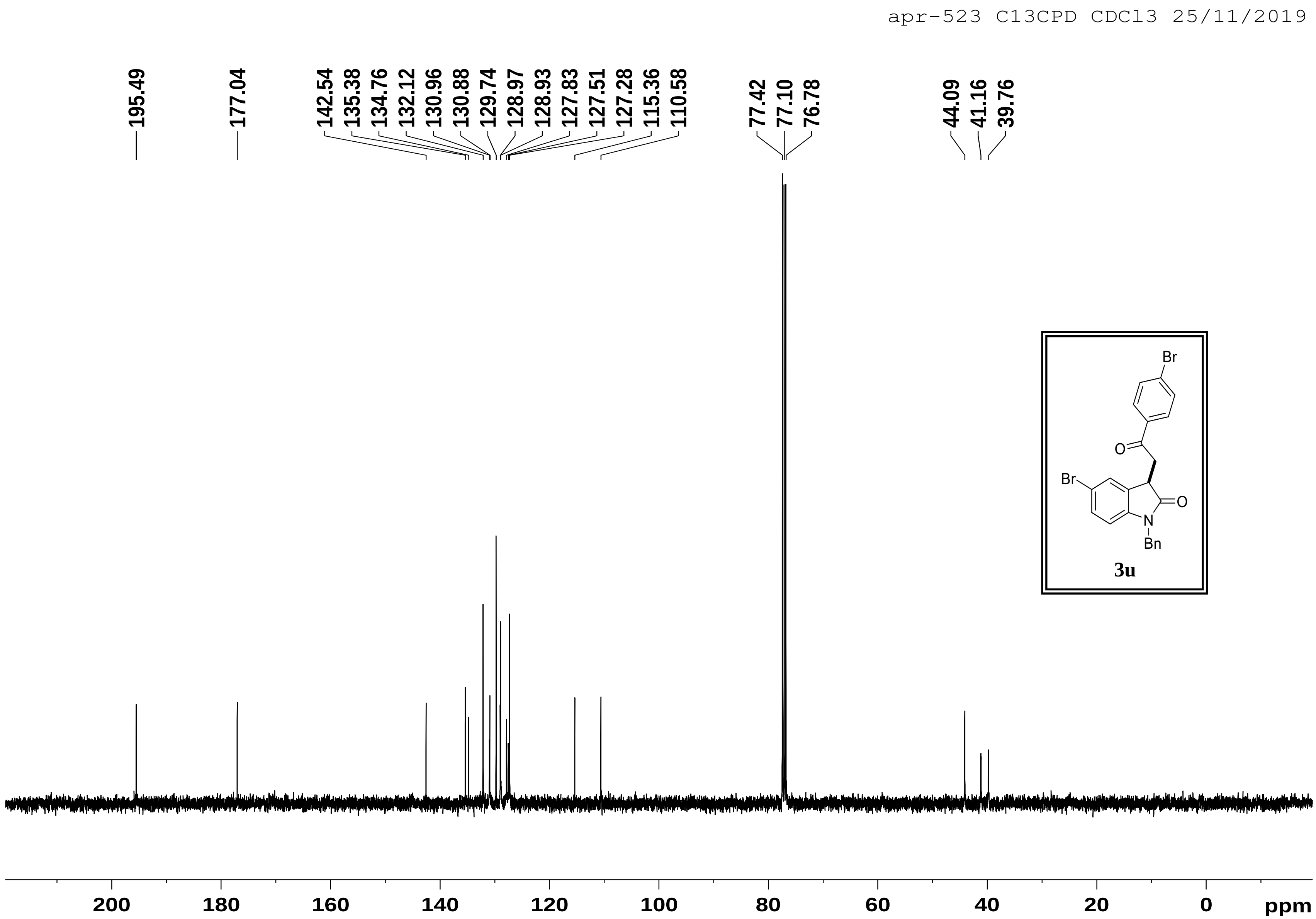
[13]C NMR spectrum of **3t**



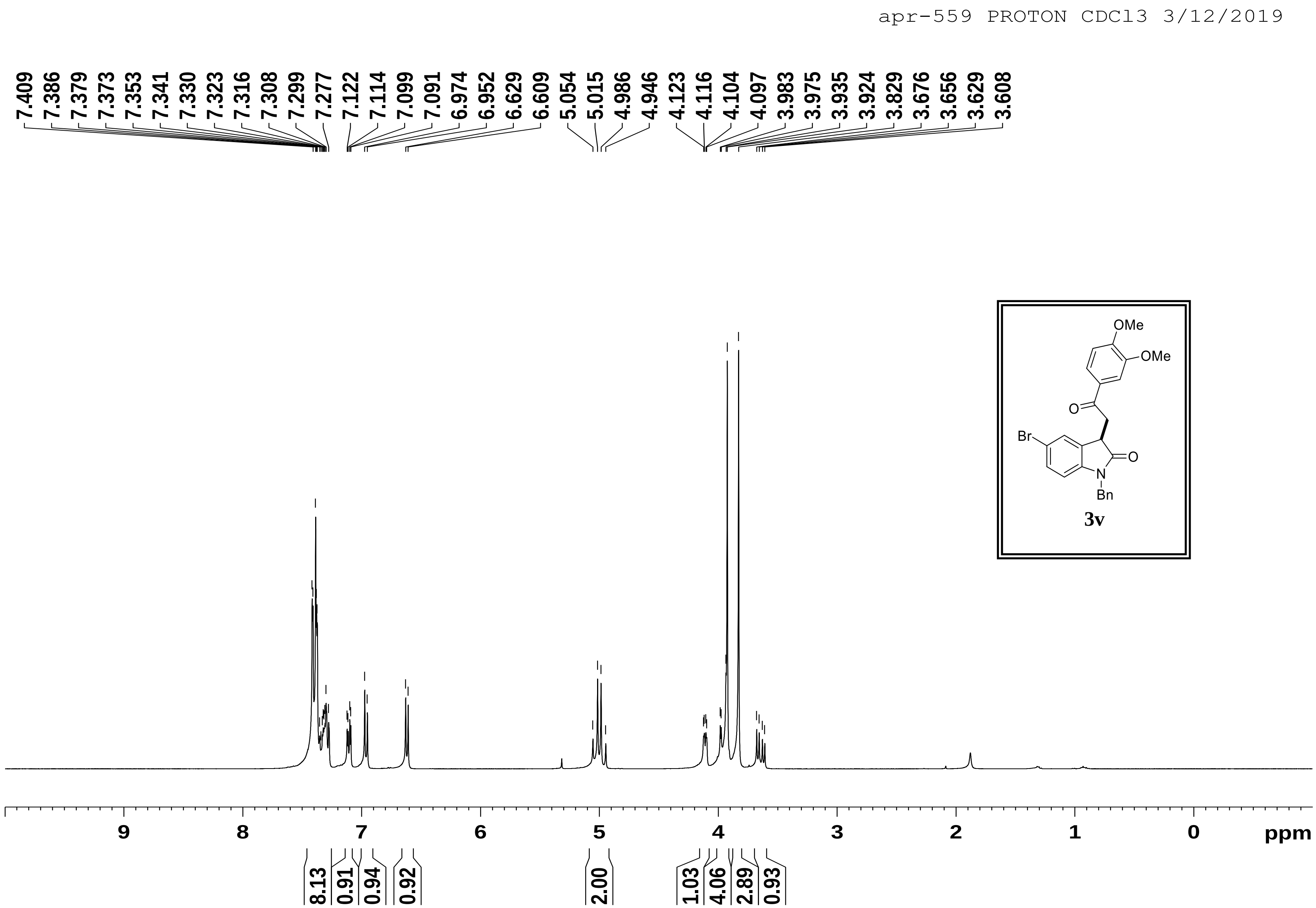
[1]H NMR spectrum of **3u**



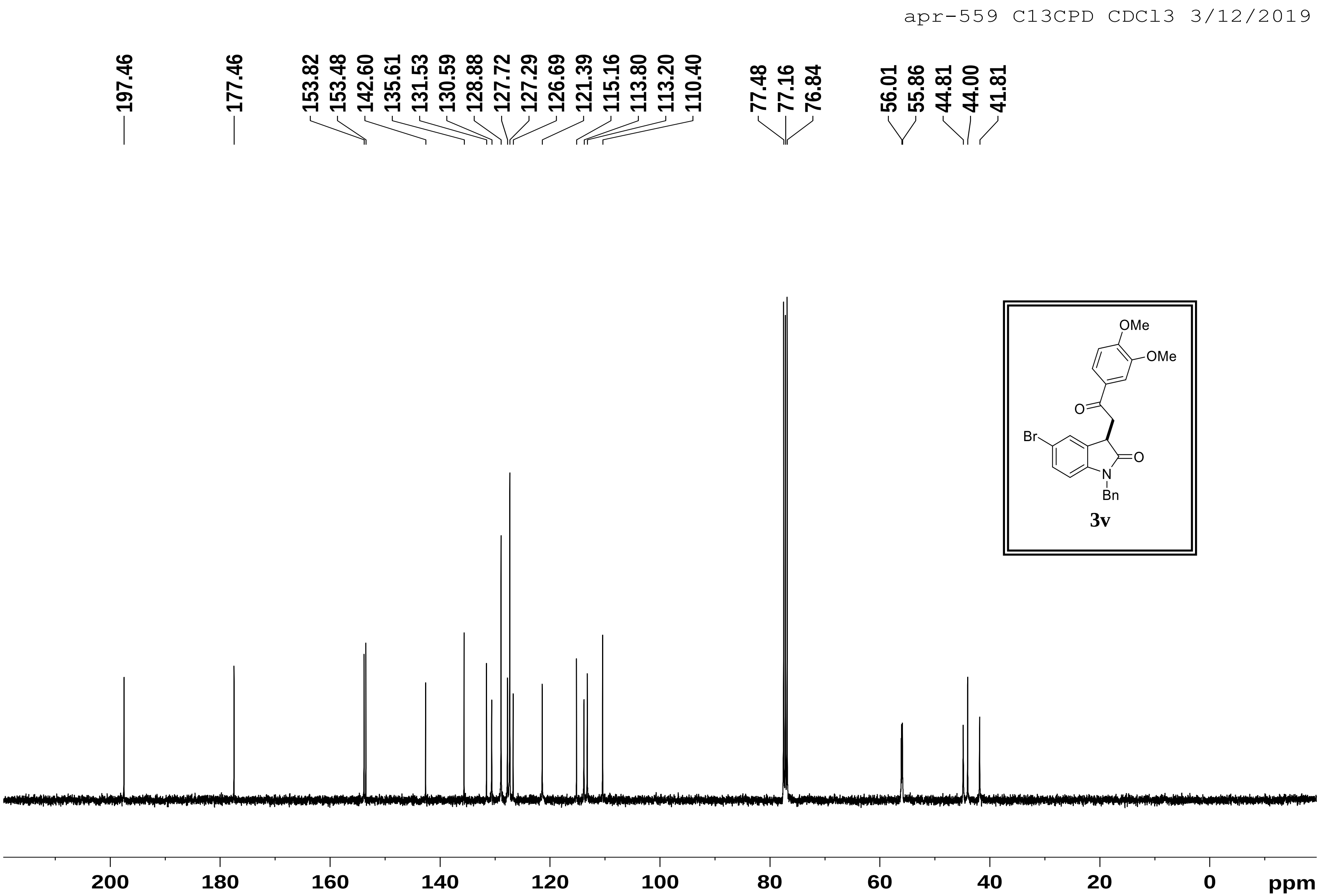
^{13}C NMR spectrum of **3u**



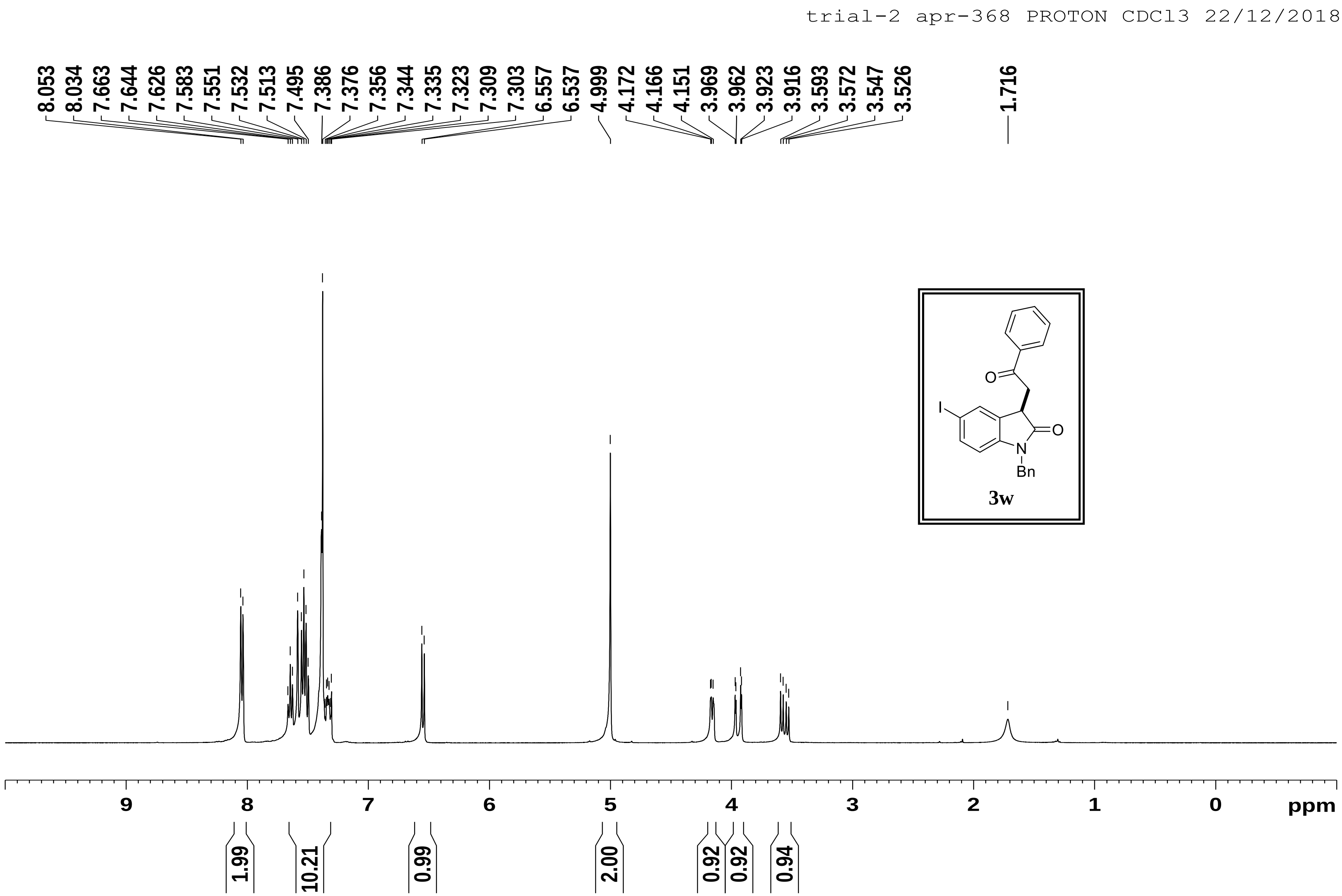
^{1}H NMR spectrum of **3v**



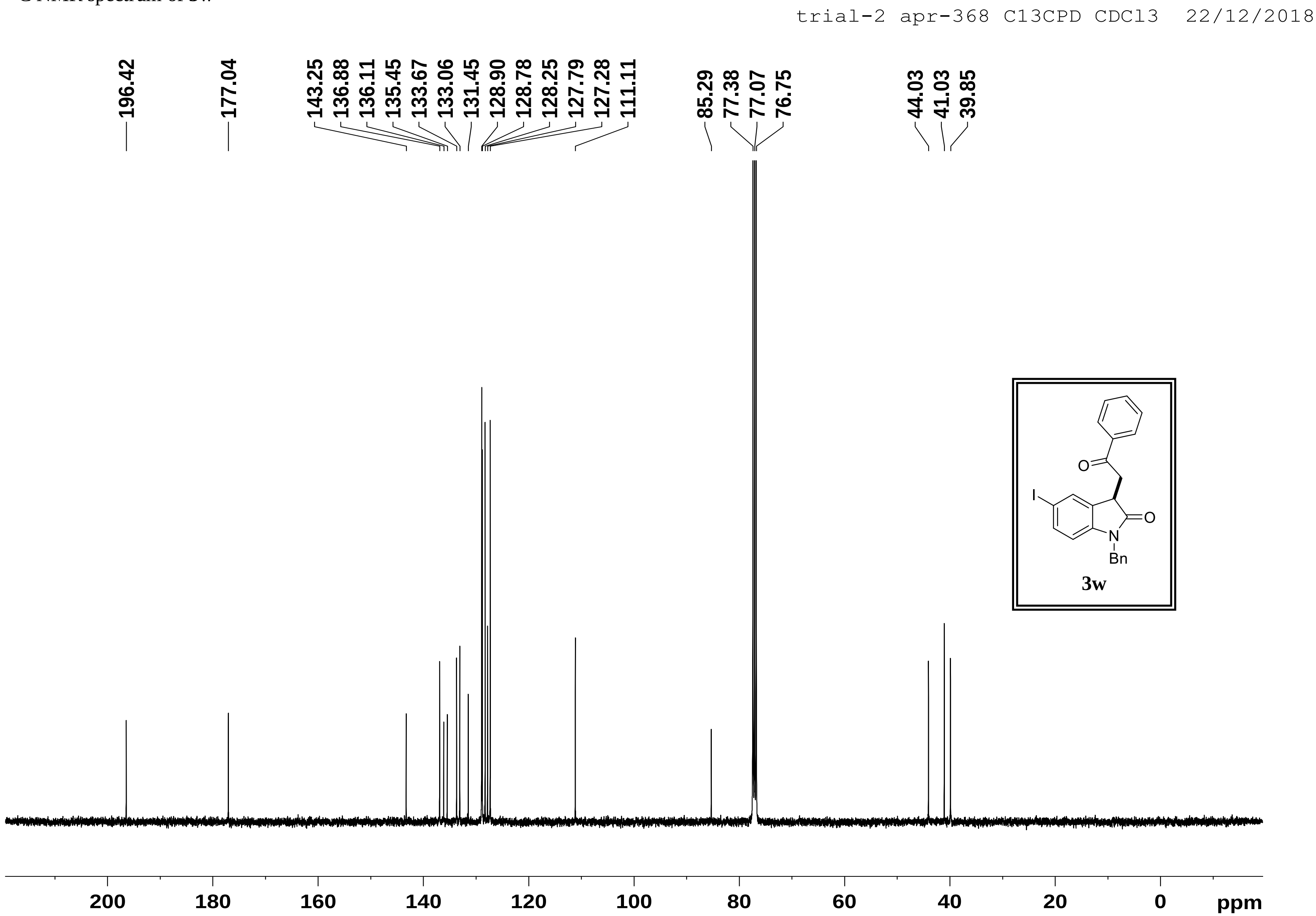
^{13}C NMR spectrum of **3v**



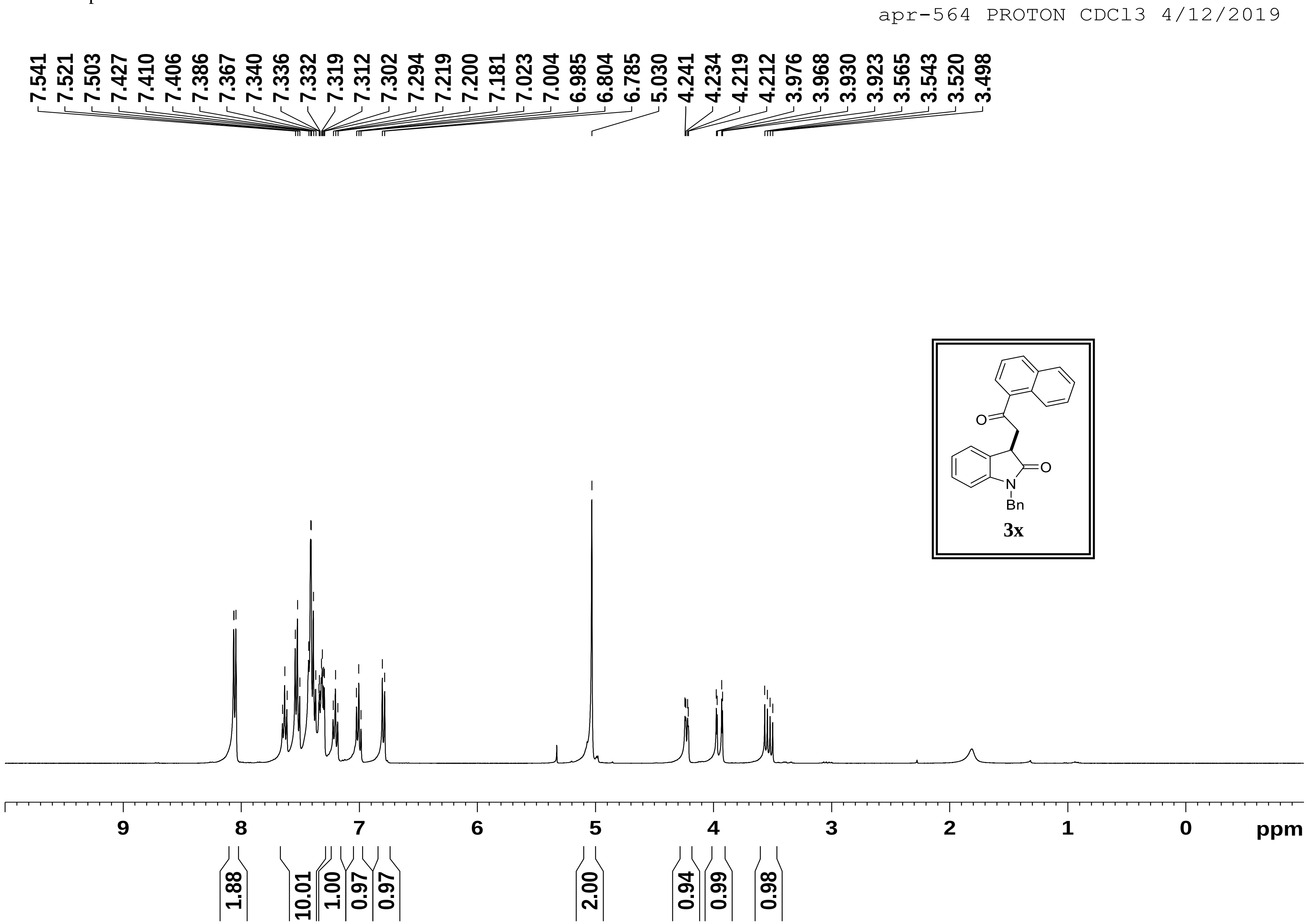
^{1}H NMR spectrum of **3w**



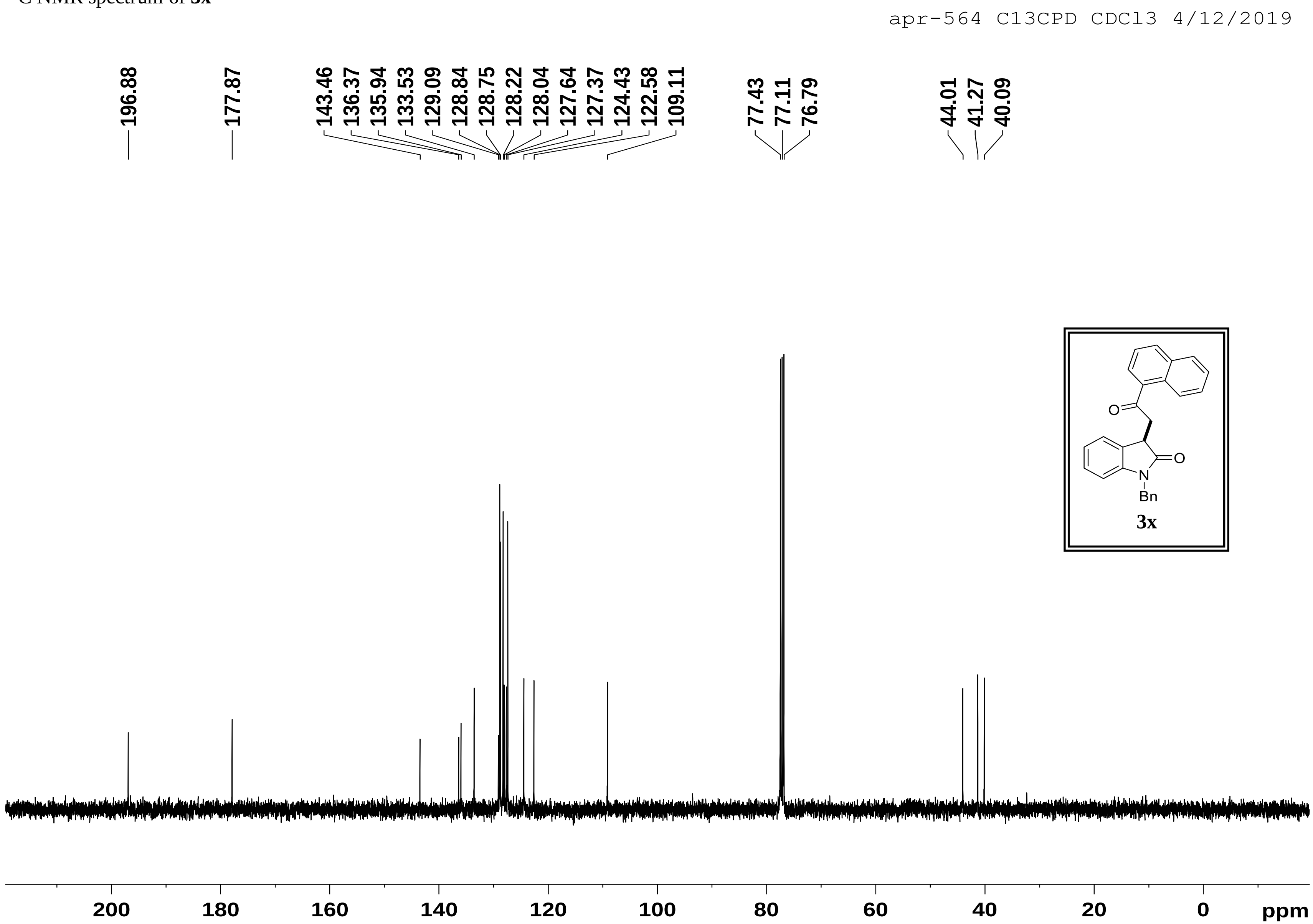
^{13}C NMR spectrum of **3w**



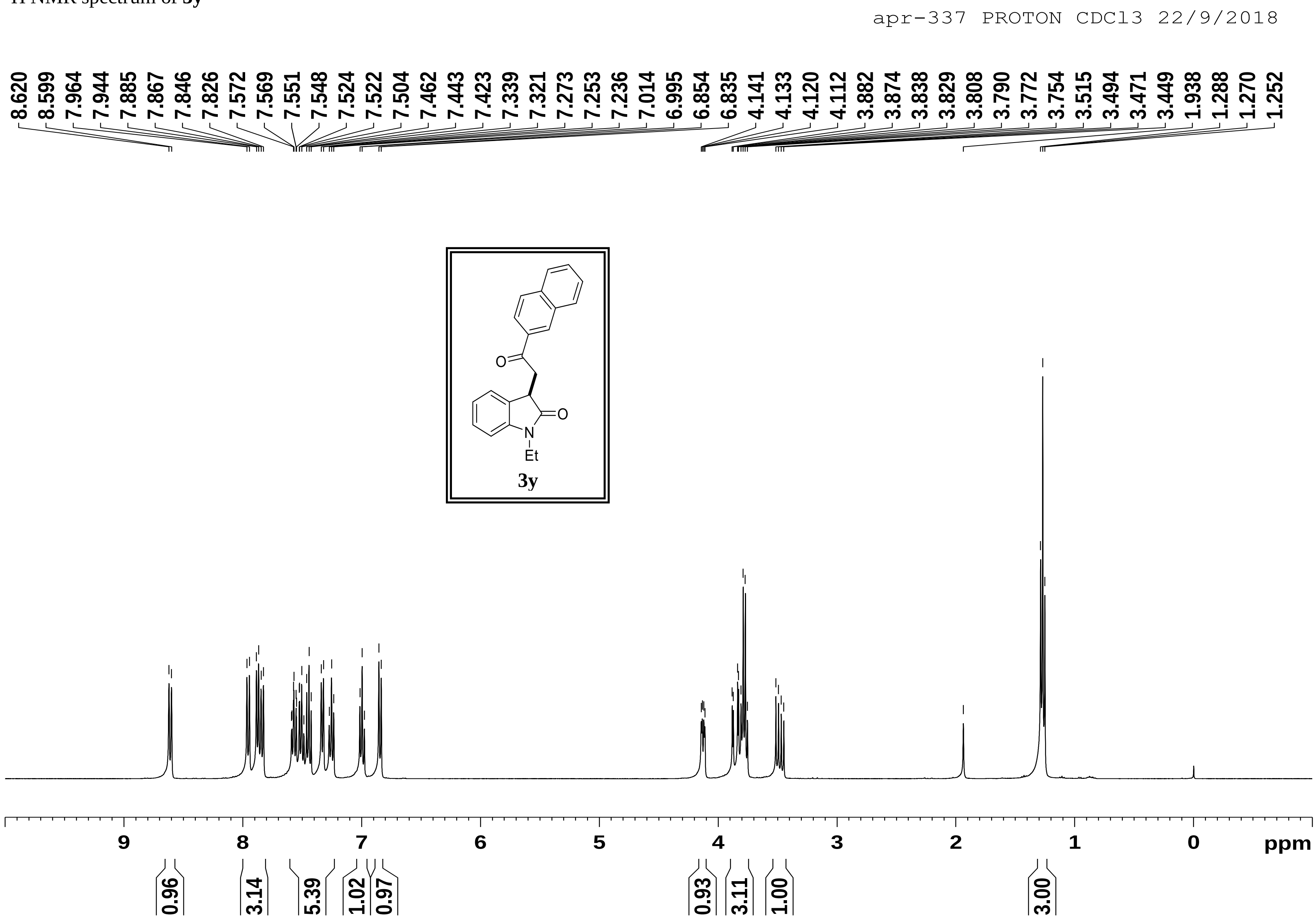
^{1}H NMR spectrum of **3x**



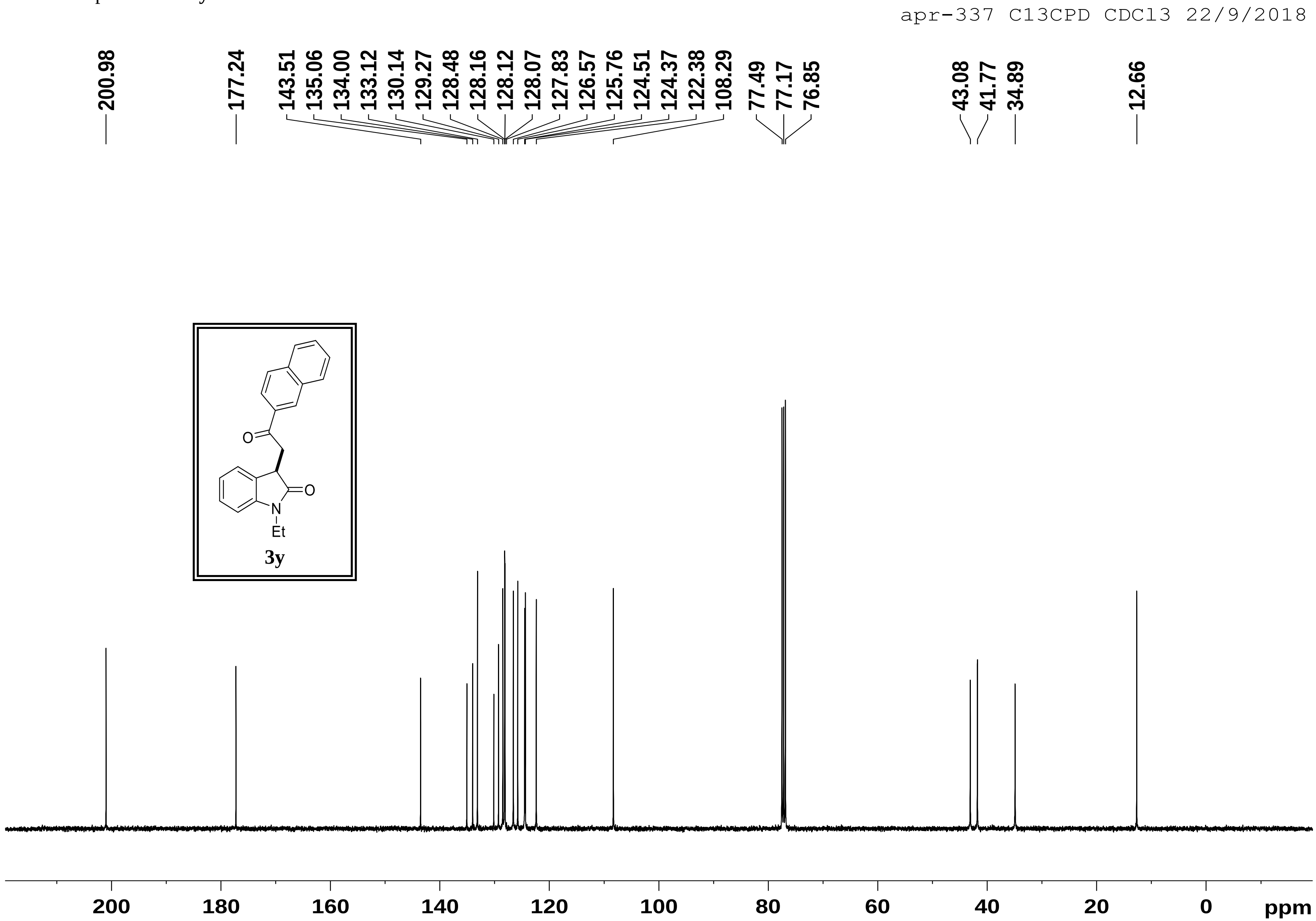
^{13}C NMR spectrum of **3x**



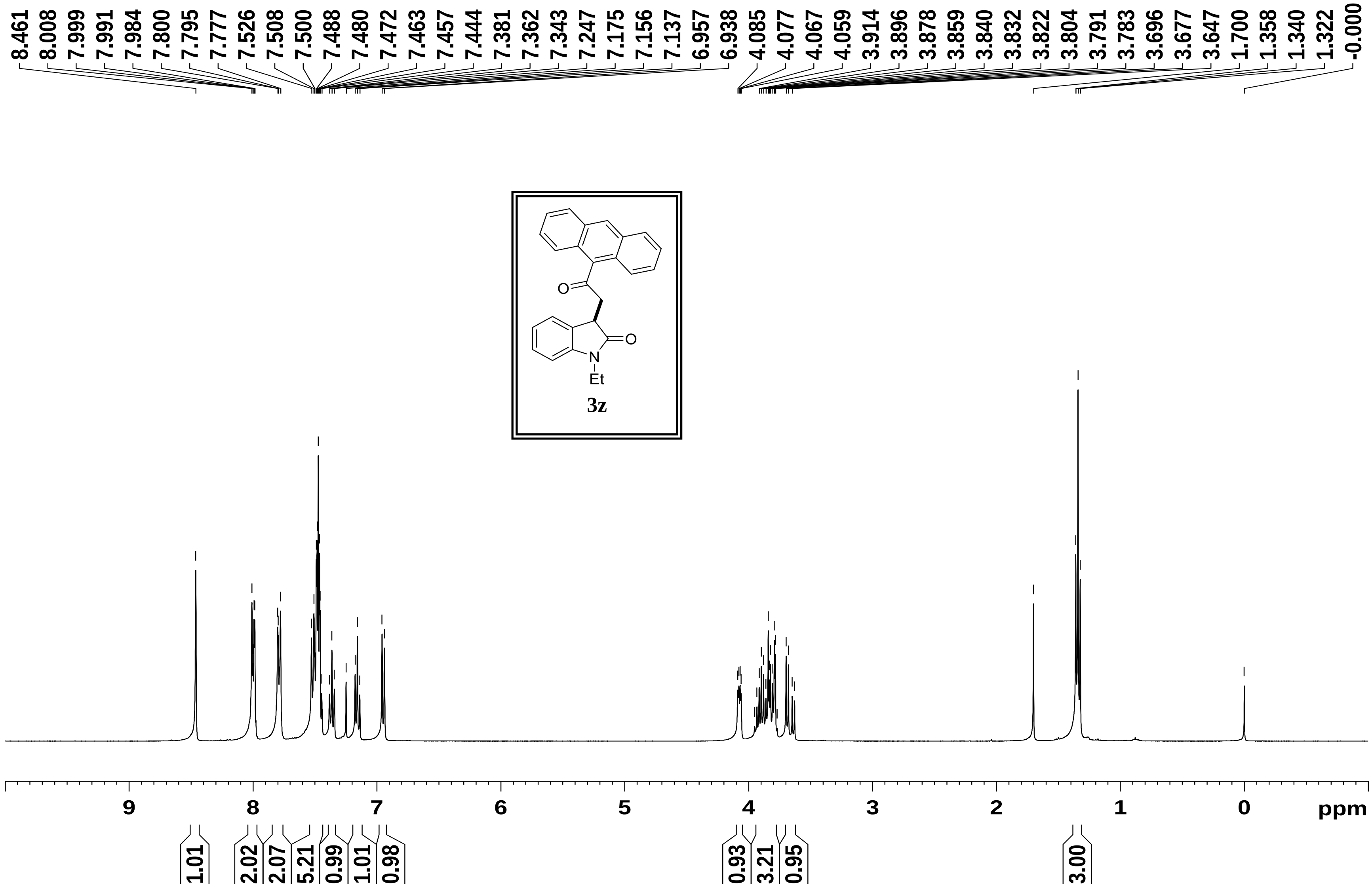
[1]H NMR spectrum of **3y**



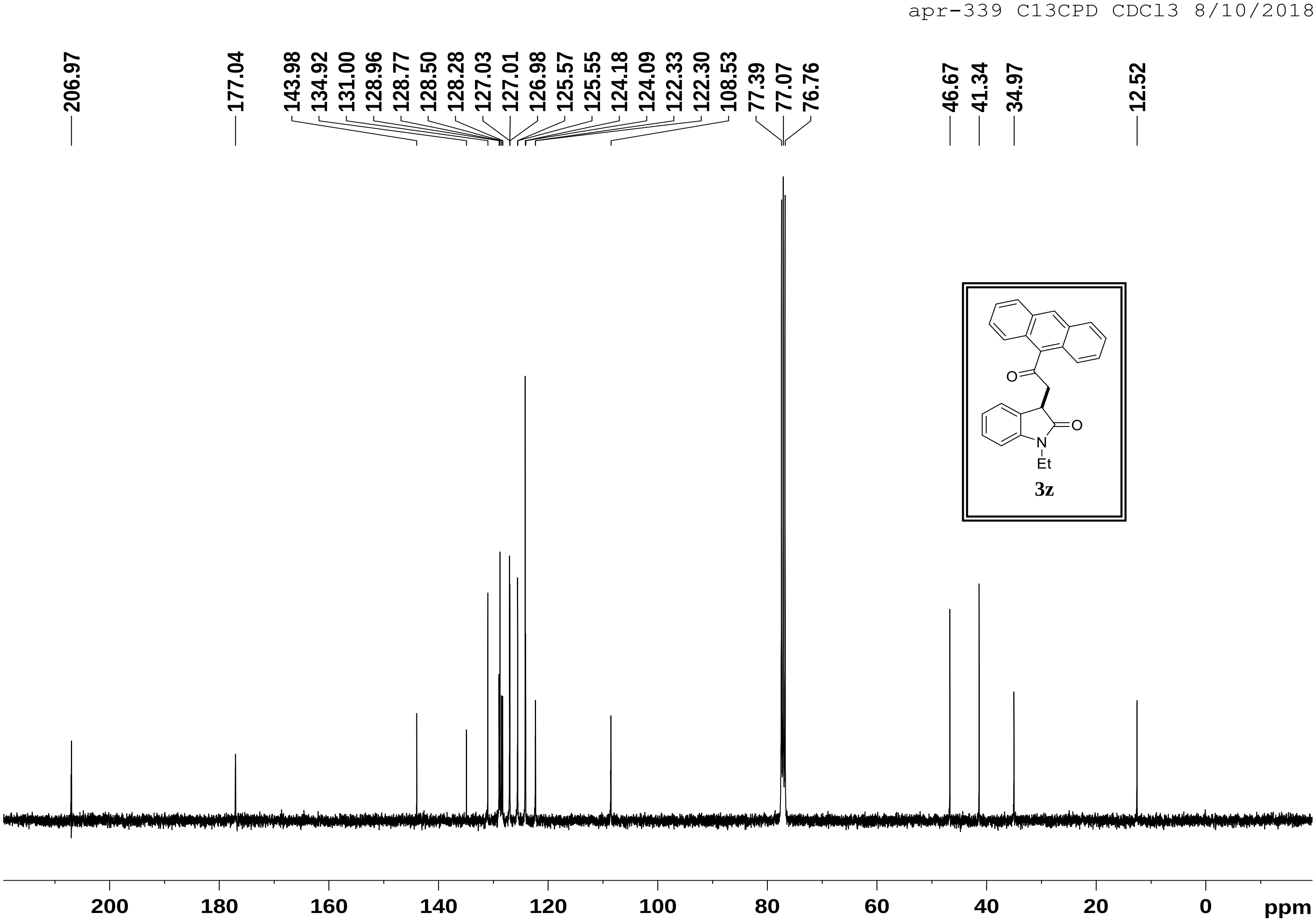
^{13}C NMR spectrum of **3y**



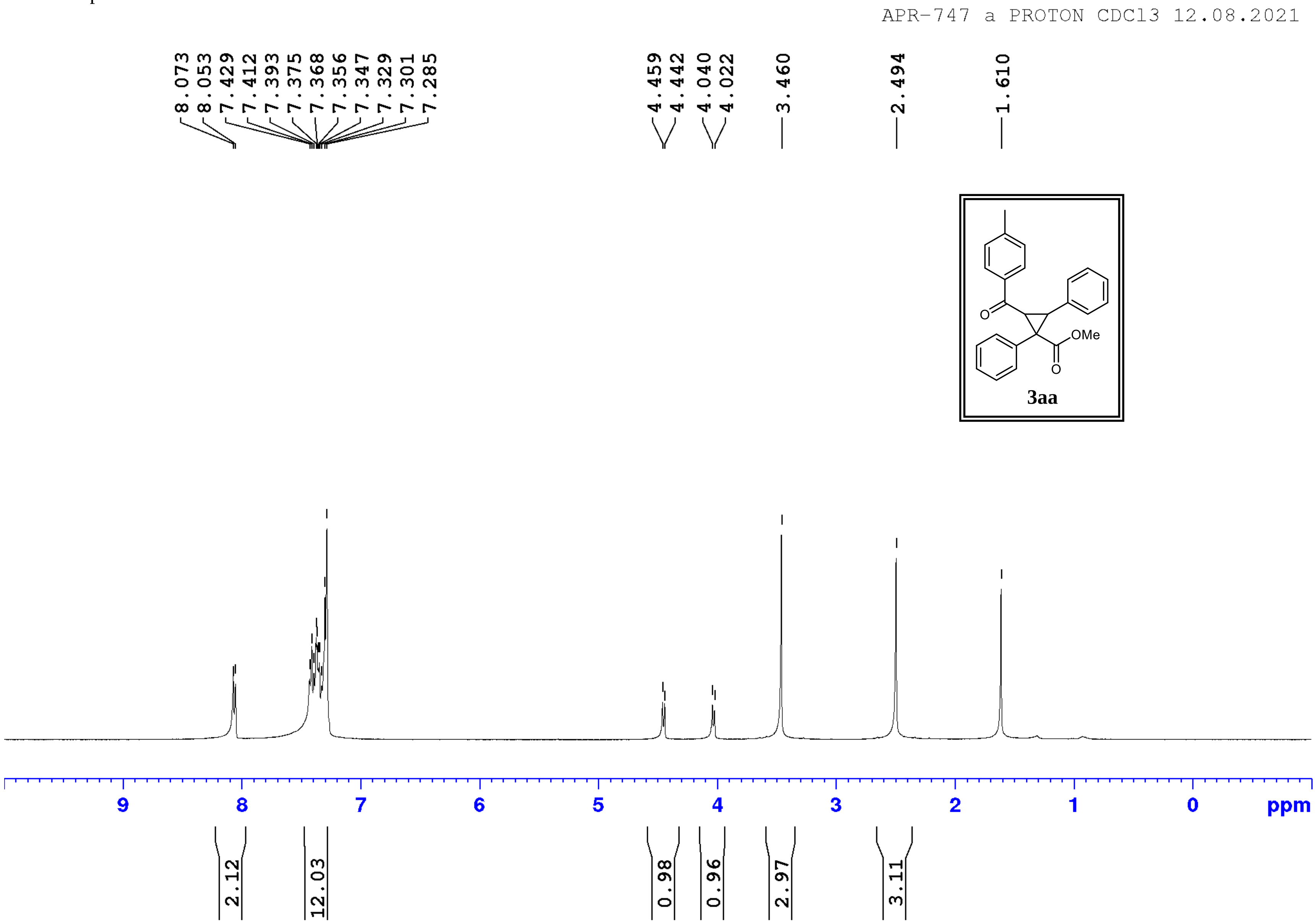
[1]H NMR spectrum of **3z**



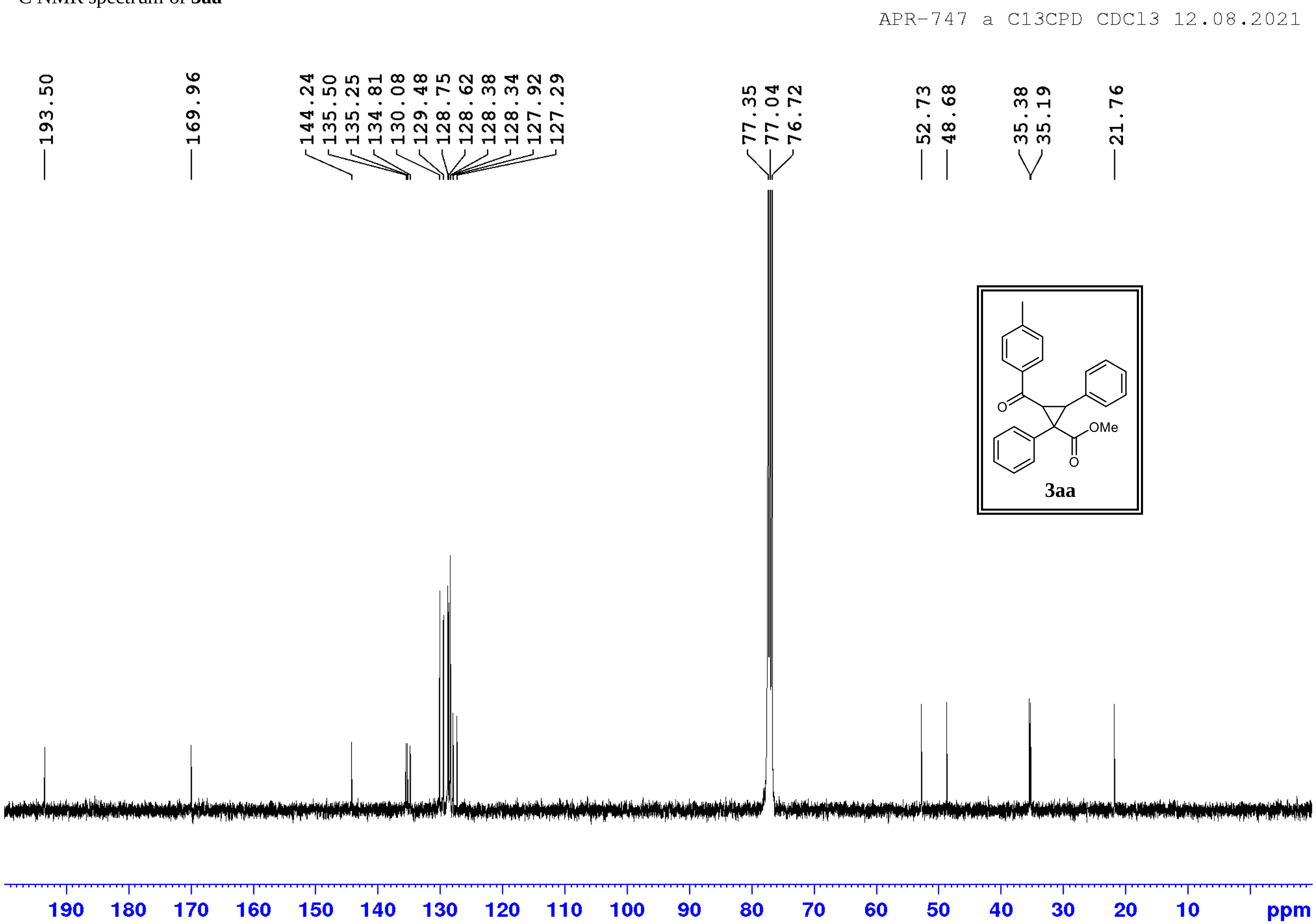
^{13}C NMR spectrum of **3z**



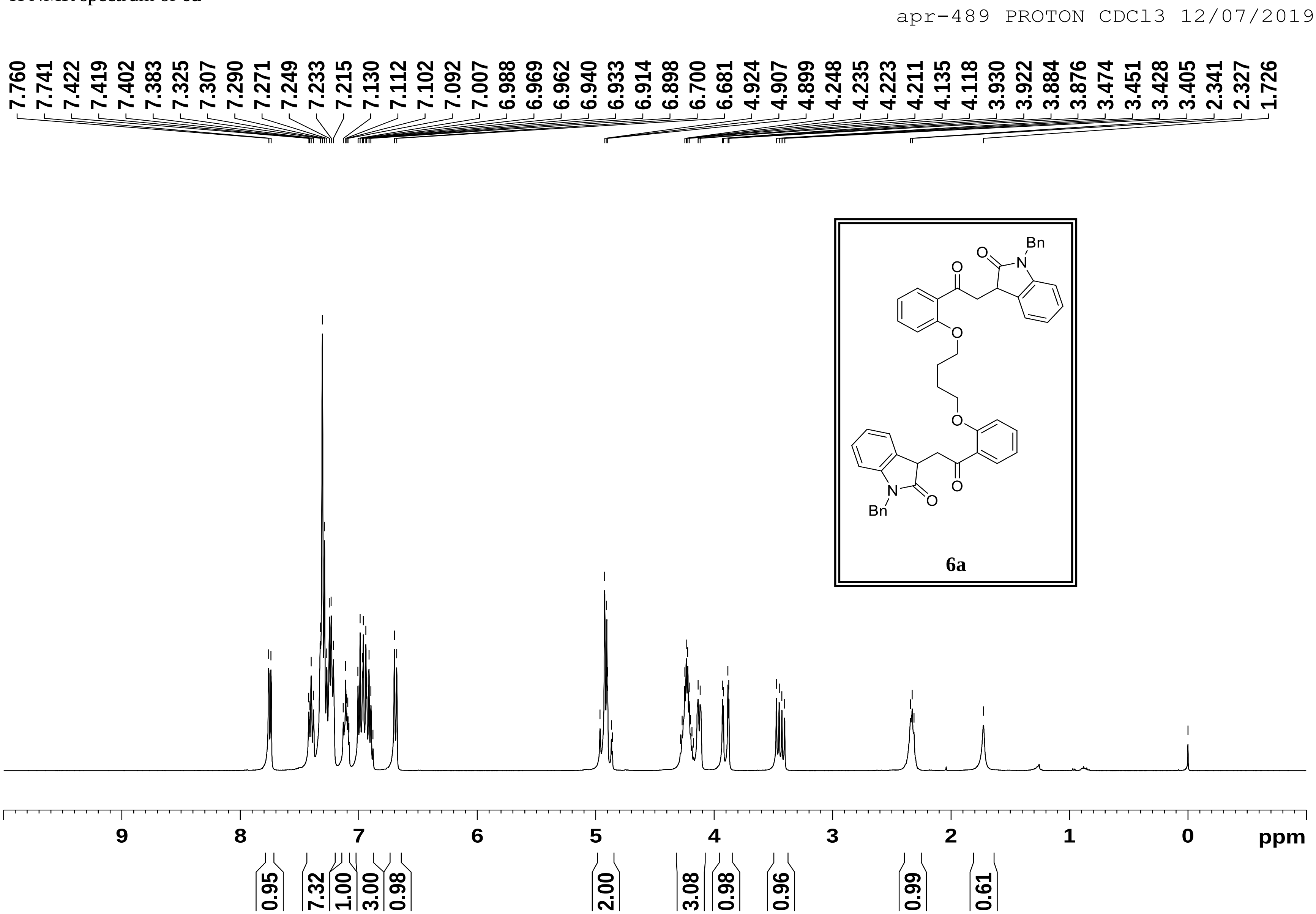
^{1}H NMR spectrum of **3aa**



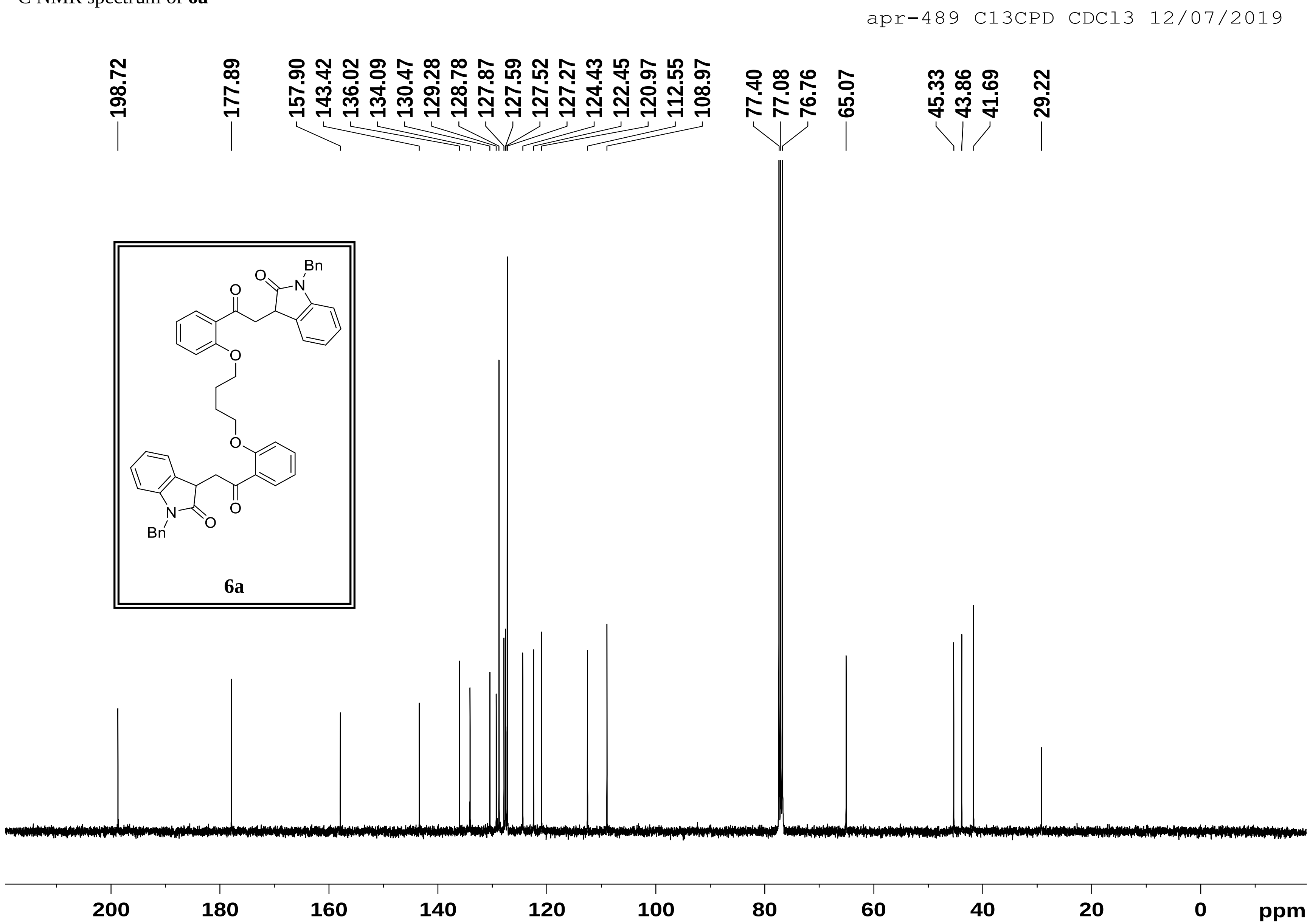
^{13}C NMR spectrum of **3aa**



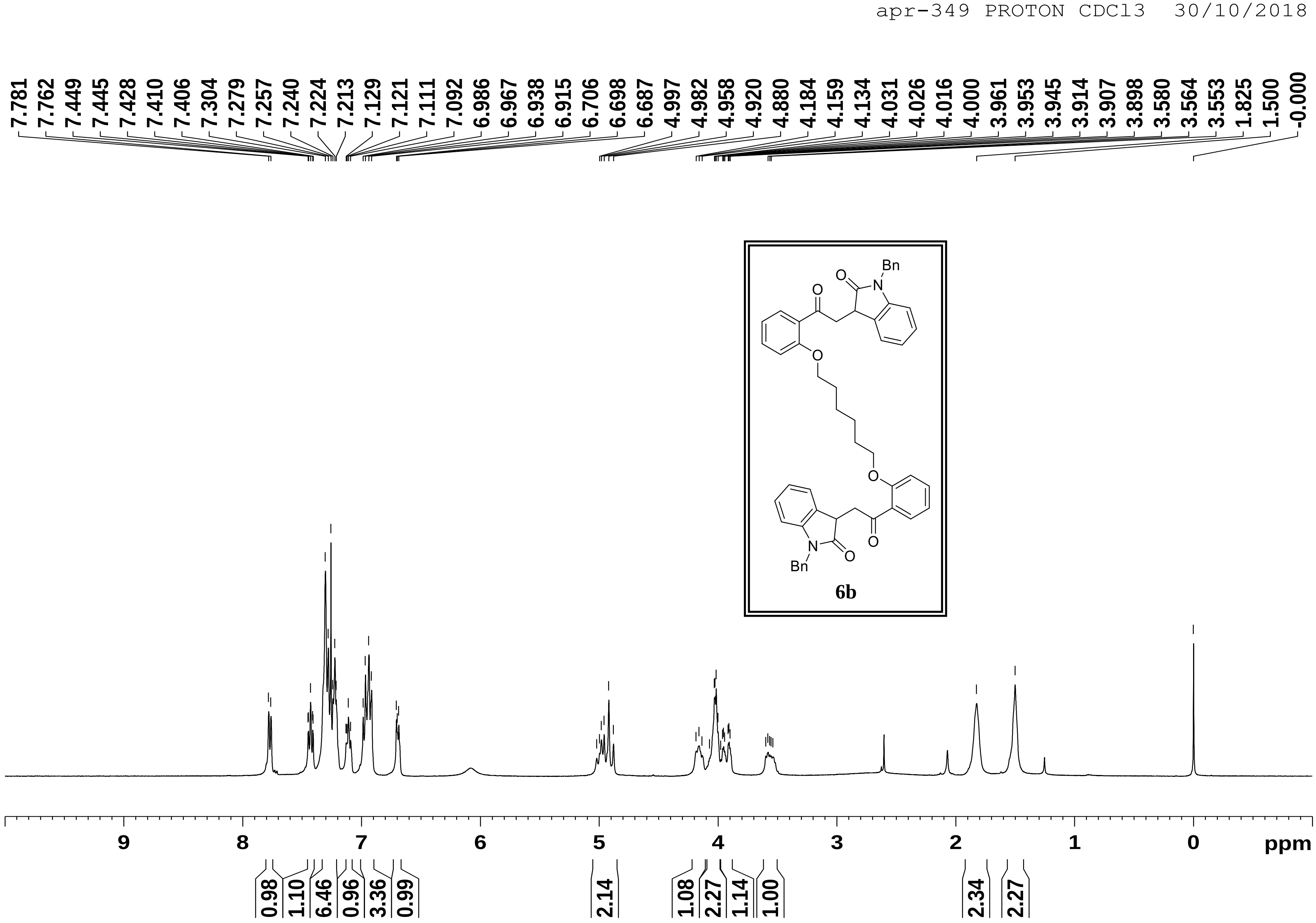
^{1}H NMR spectrum of **6a**



^{13}C NMR spectrum of **6a**

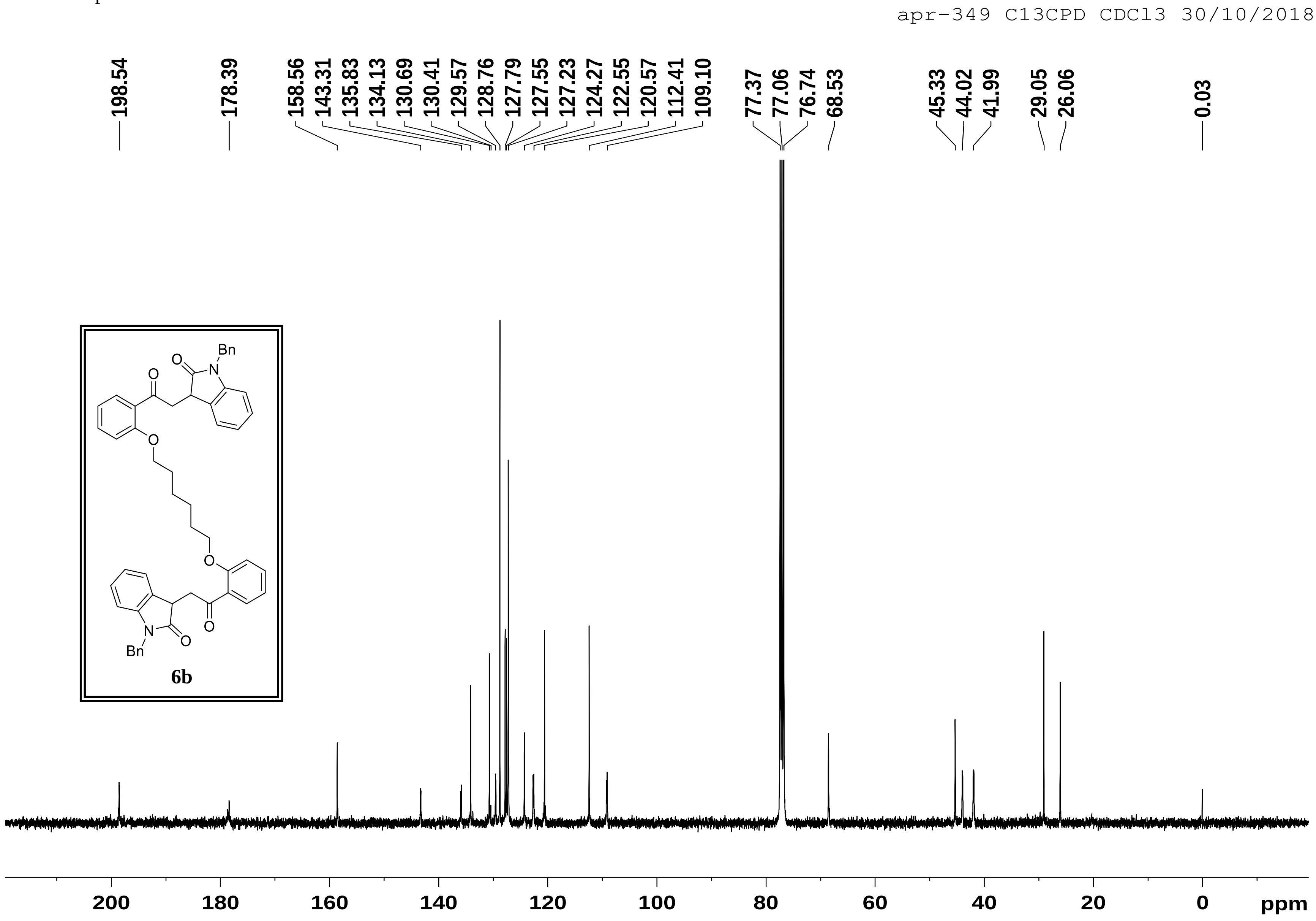


^{1}H NMR spectrum of **6b**

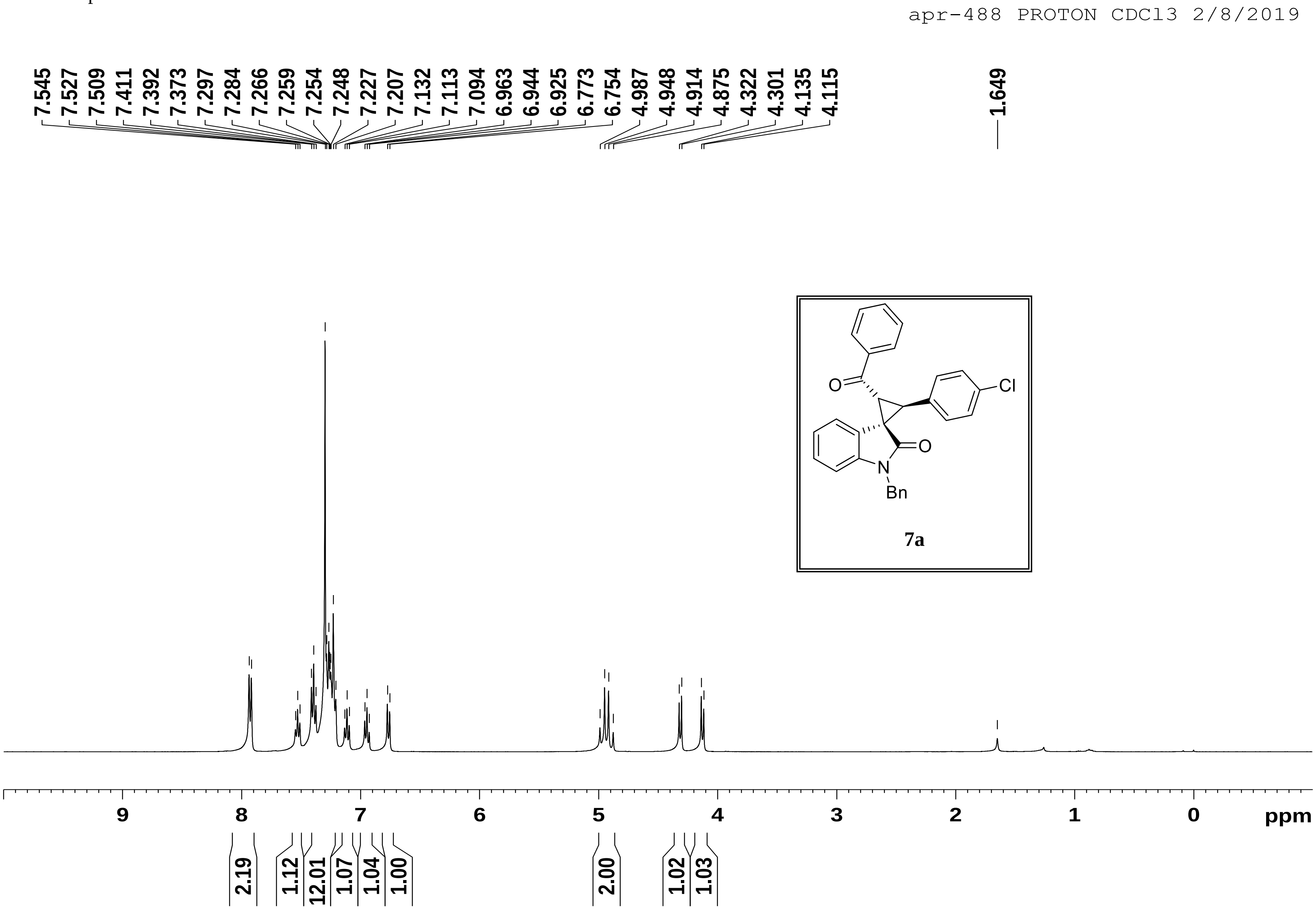


6b

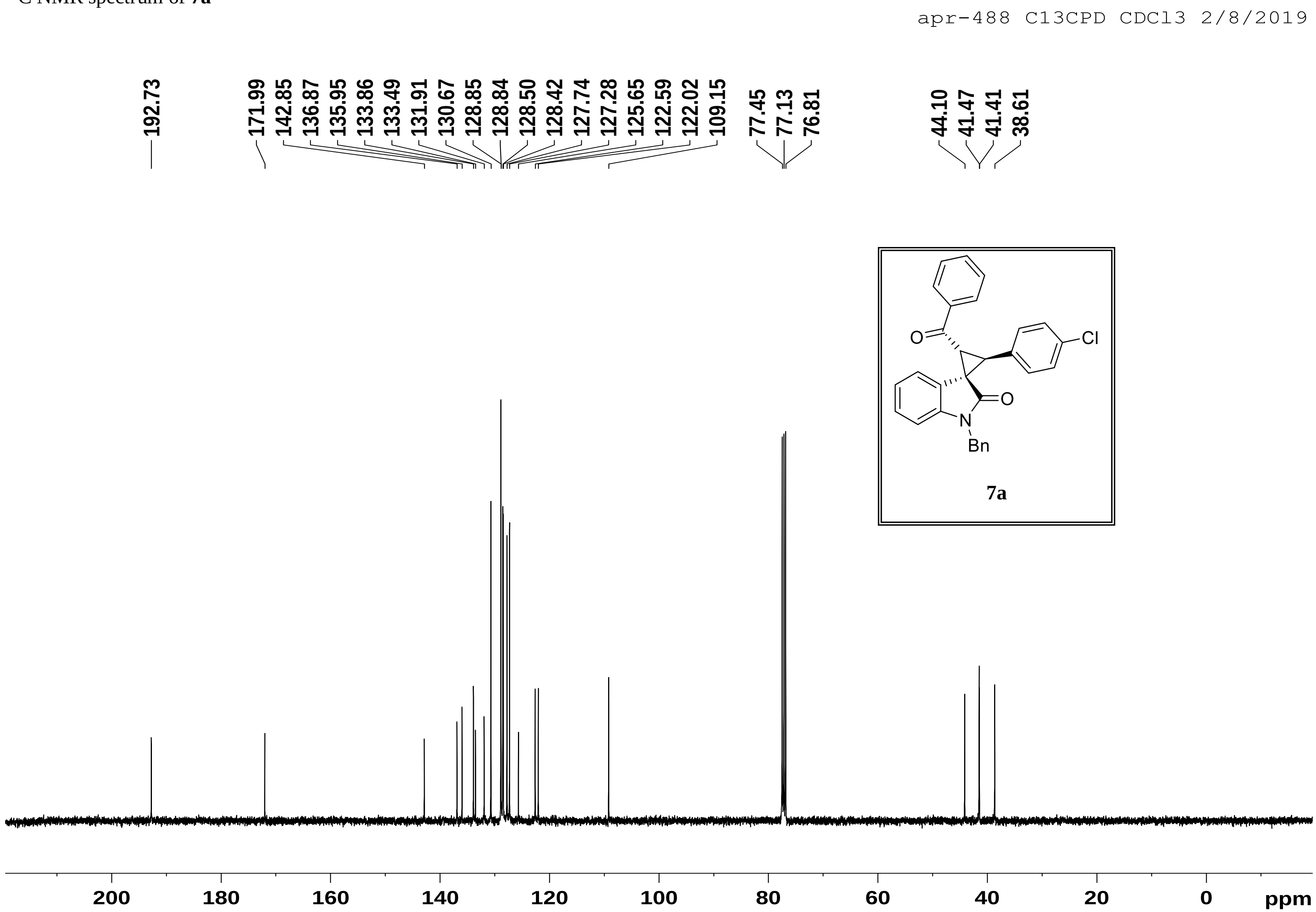
^{13}C NMR spectrum of **6b**



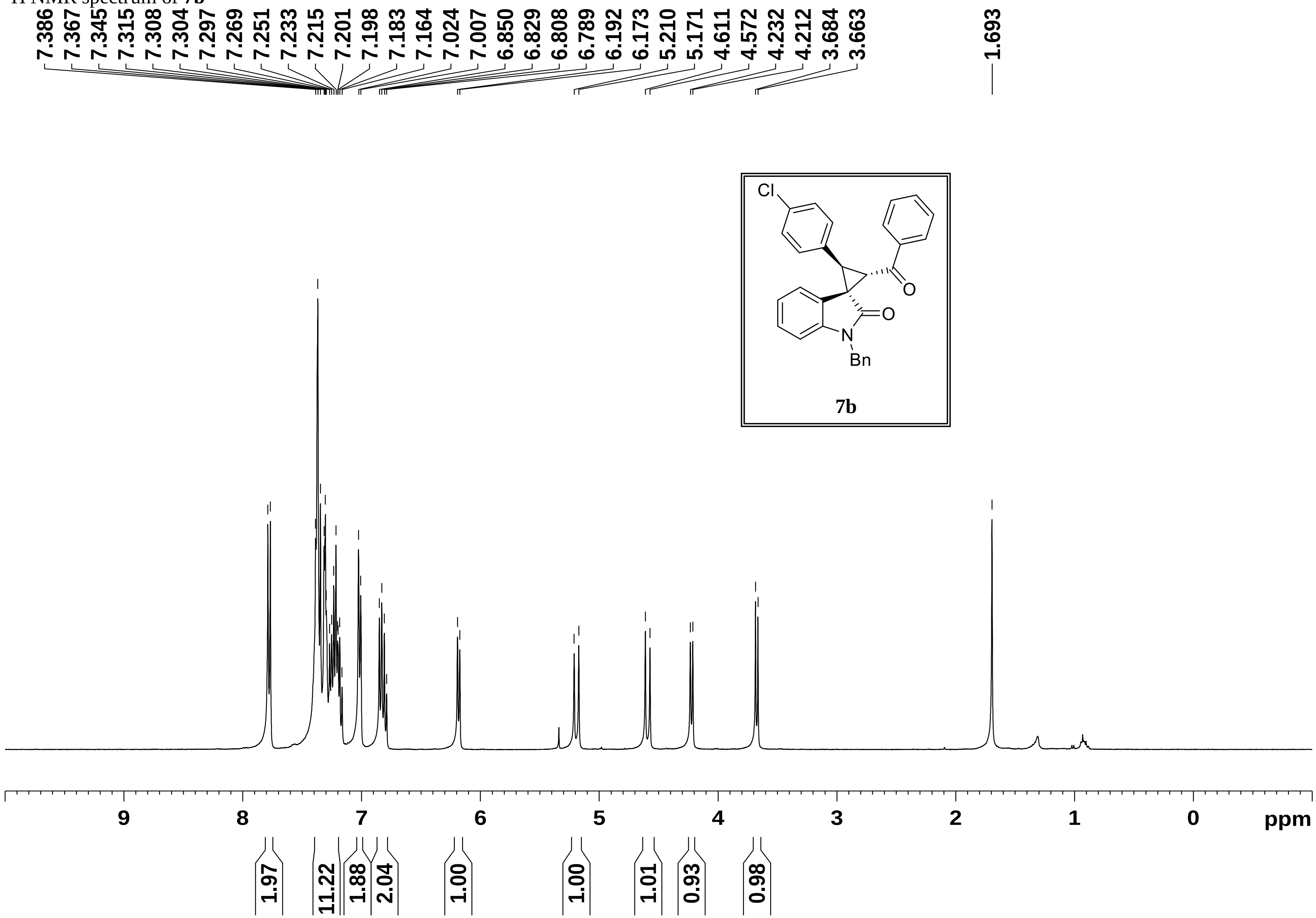
[1]H NMR spectrum of **7a**



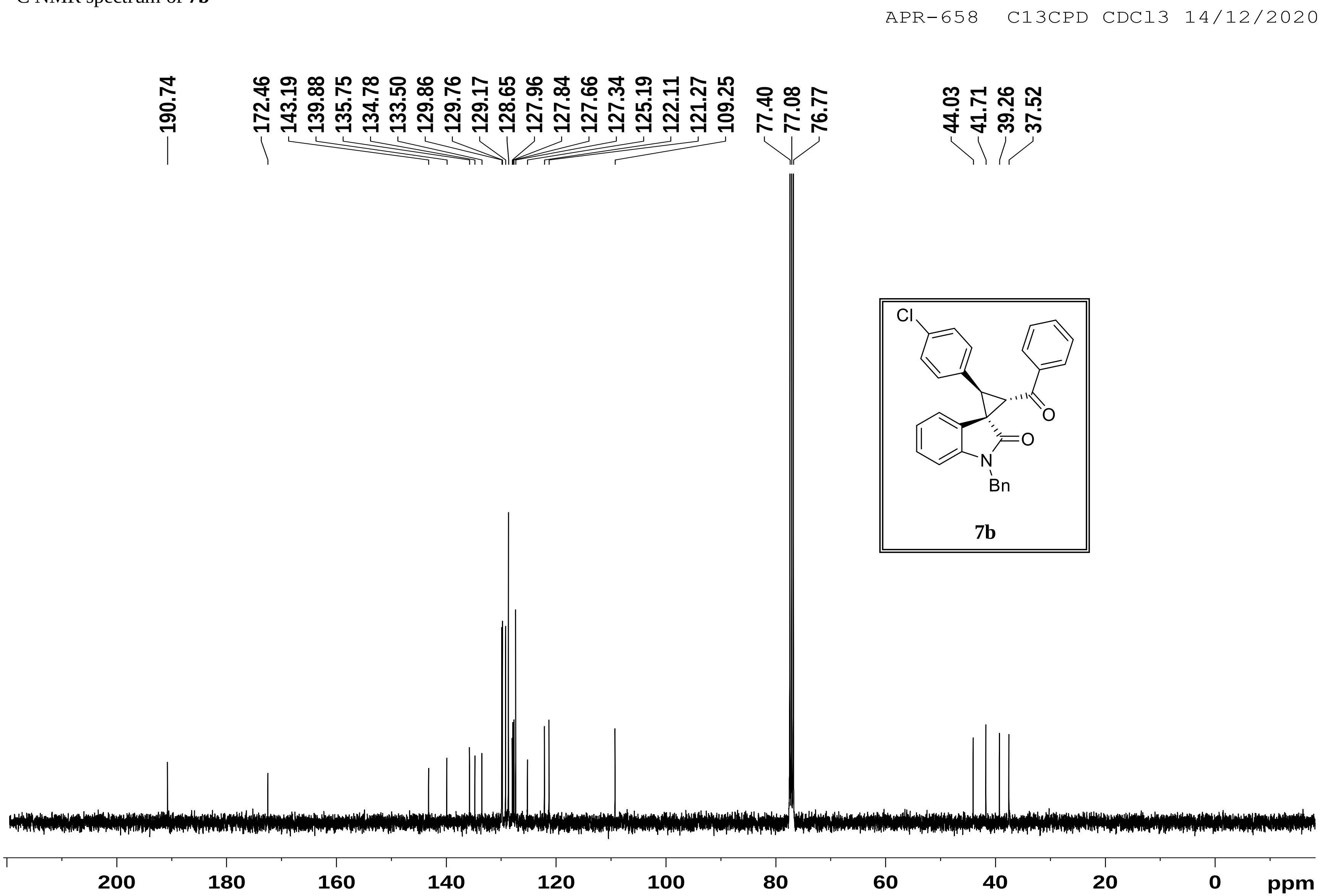
^{13}C NMR spectrum of **7a**



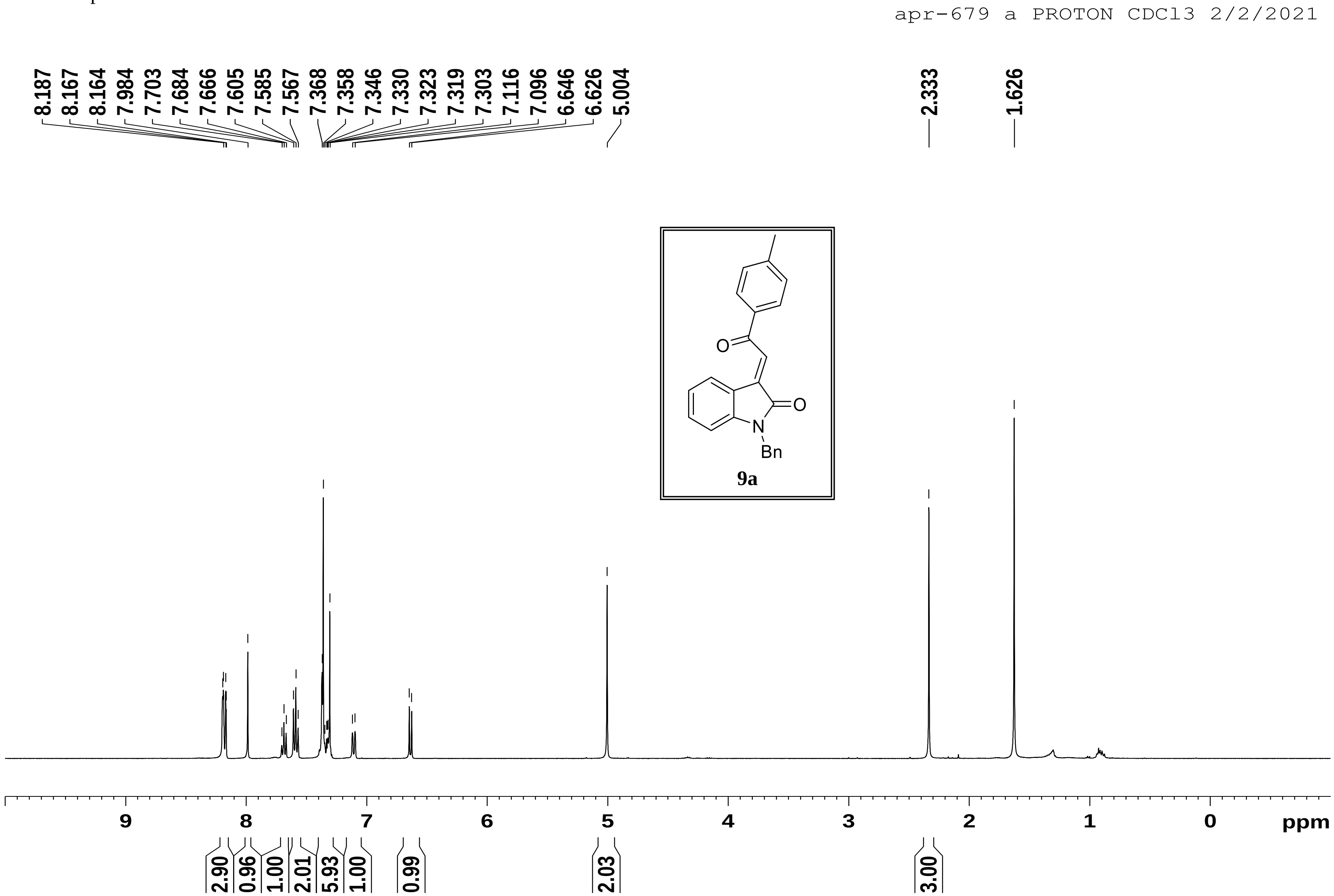
^{1}H NMR spectrum of **7b**



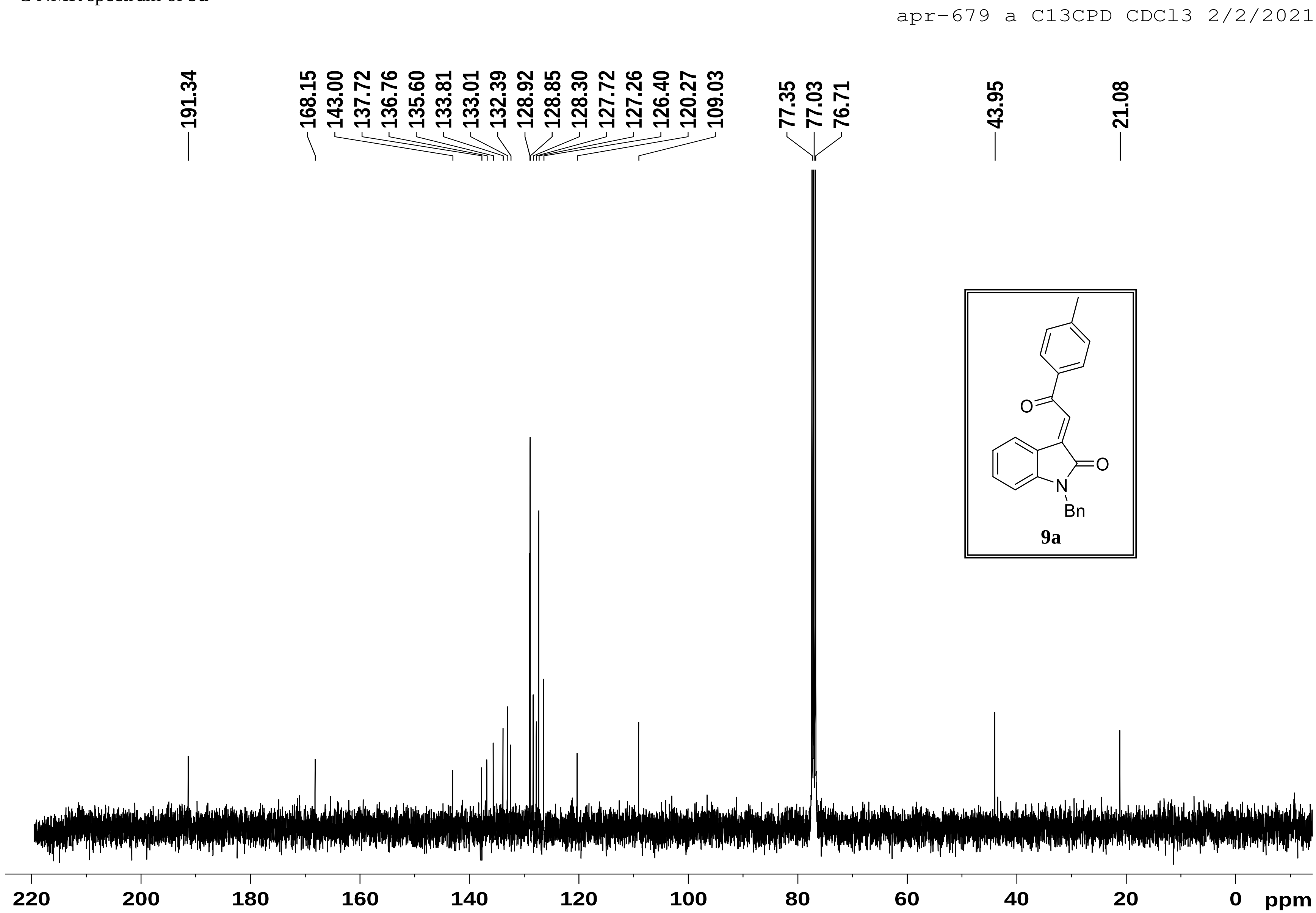
^{13}C NMR spectrum of **7b**



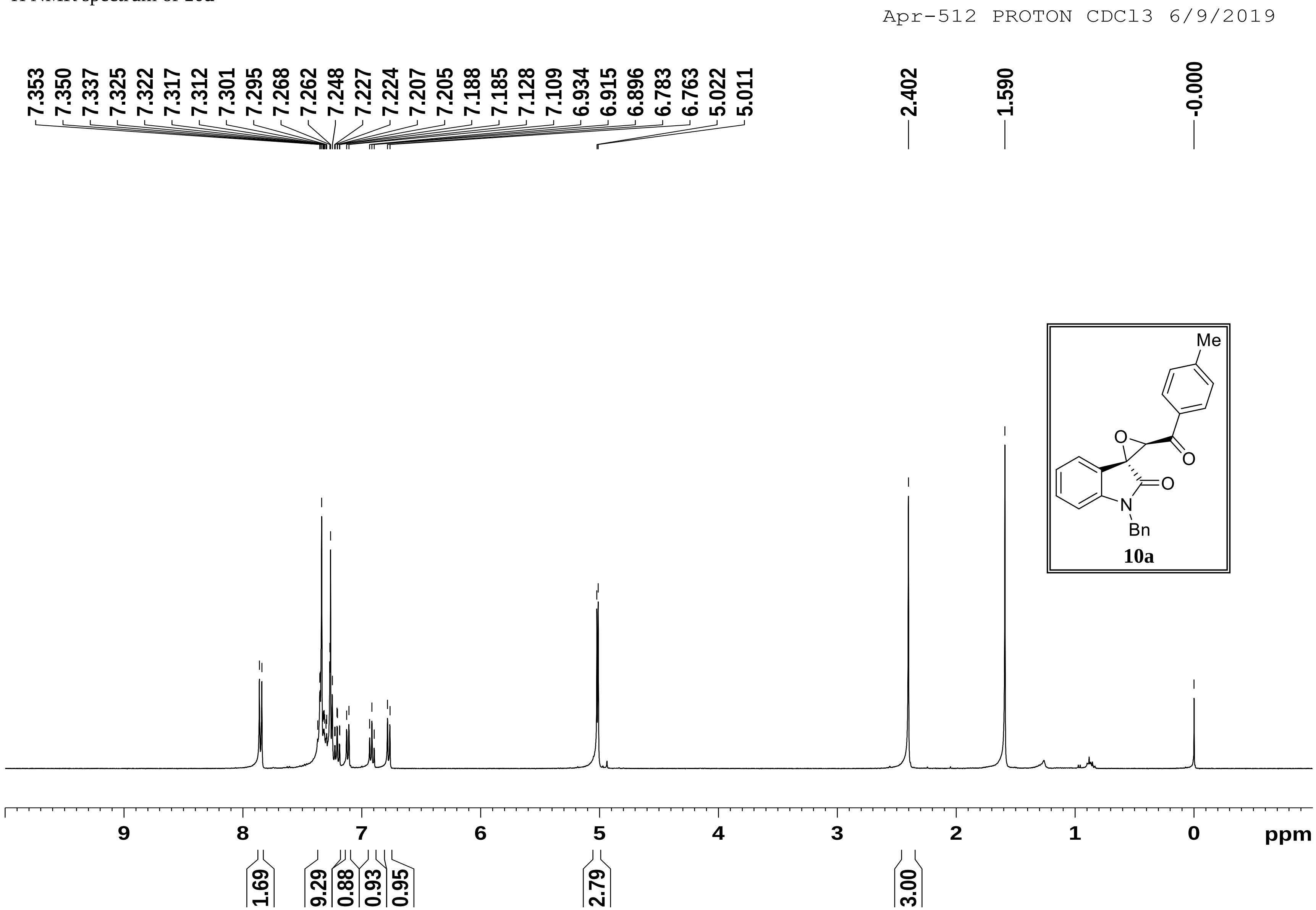
^{1}H NMR spectrum of **9a**



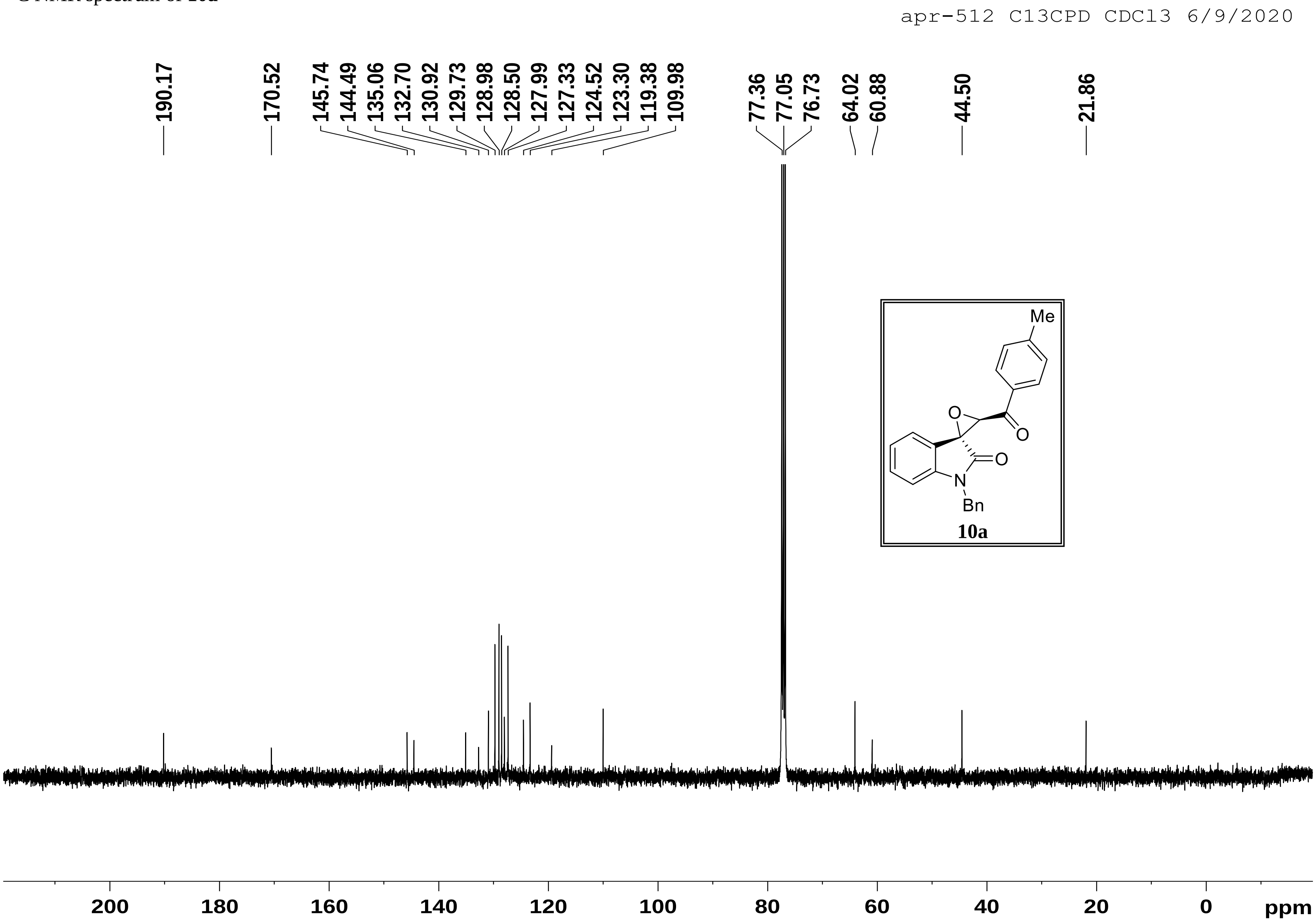
^{13}C NMR spectrum of **9a**



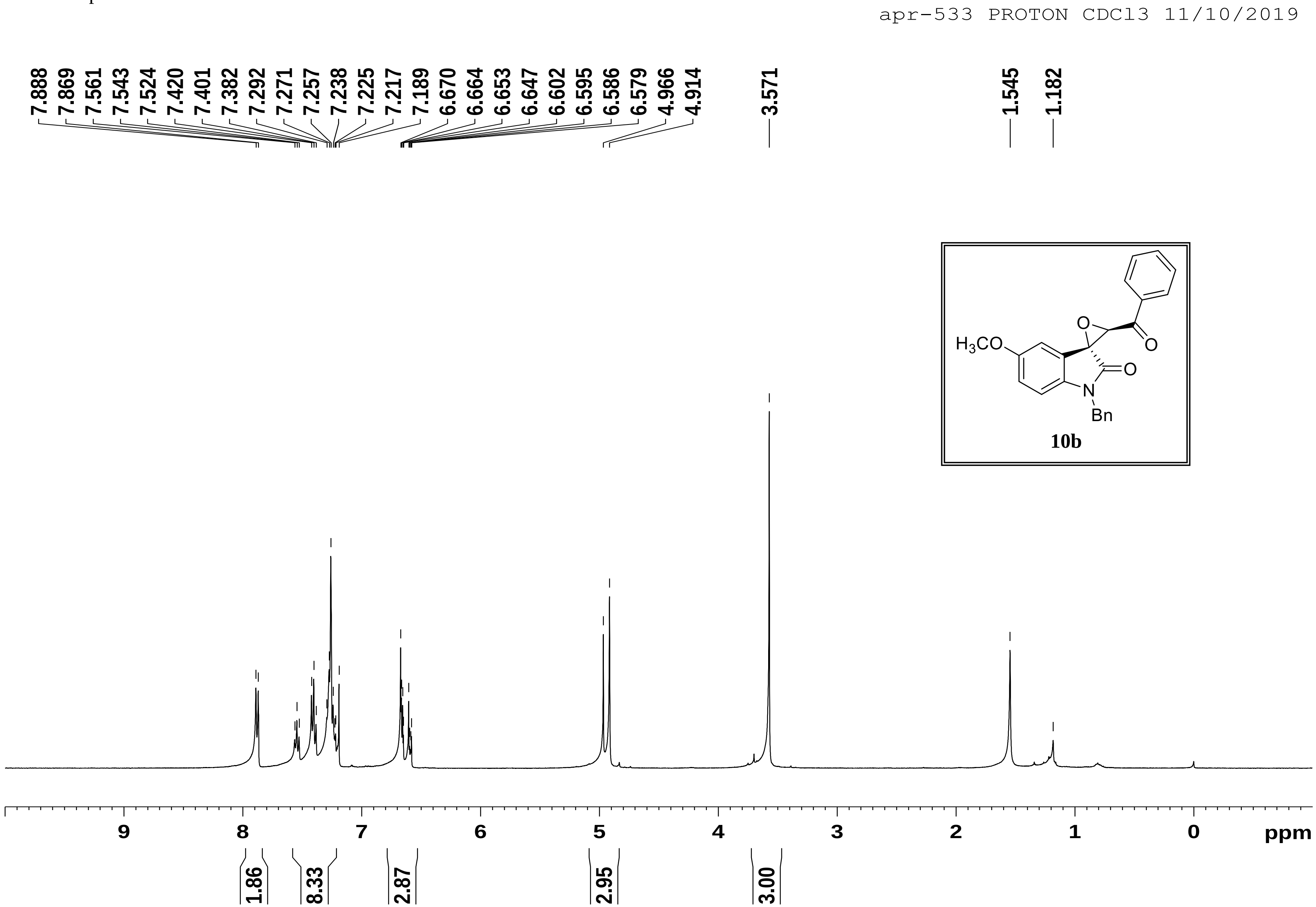
^{1}H NMR spectrum of **10a**



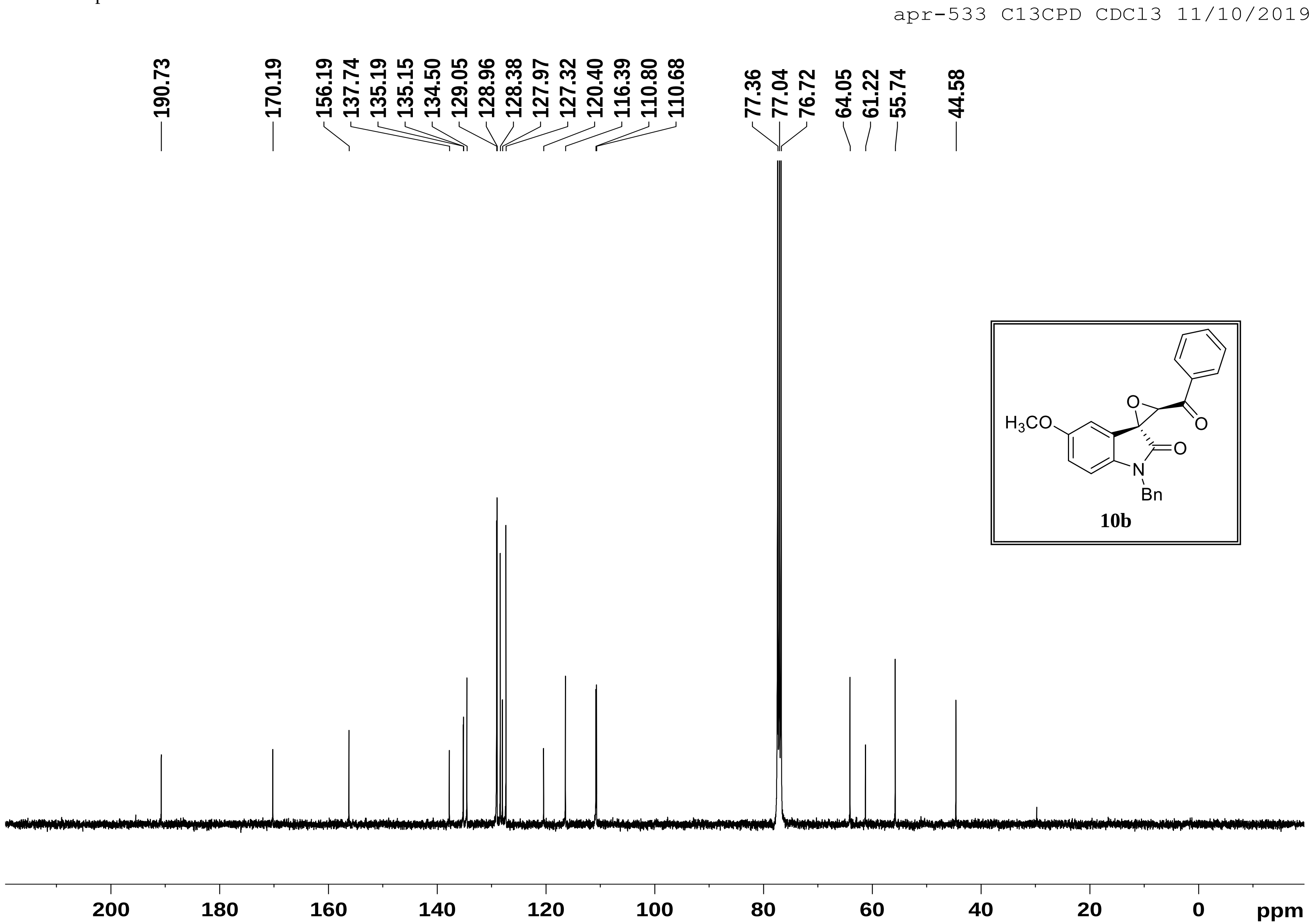
^{13}C NMR spectrum of **10a**



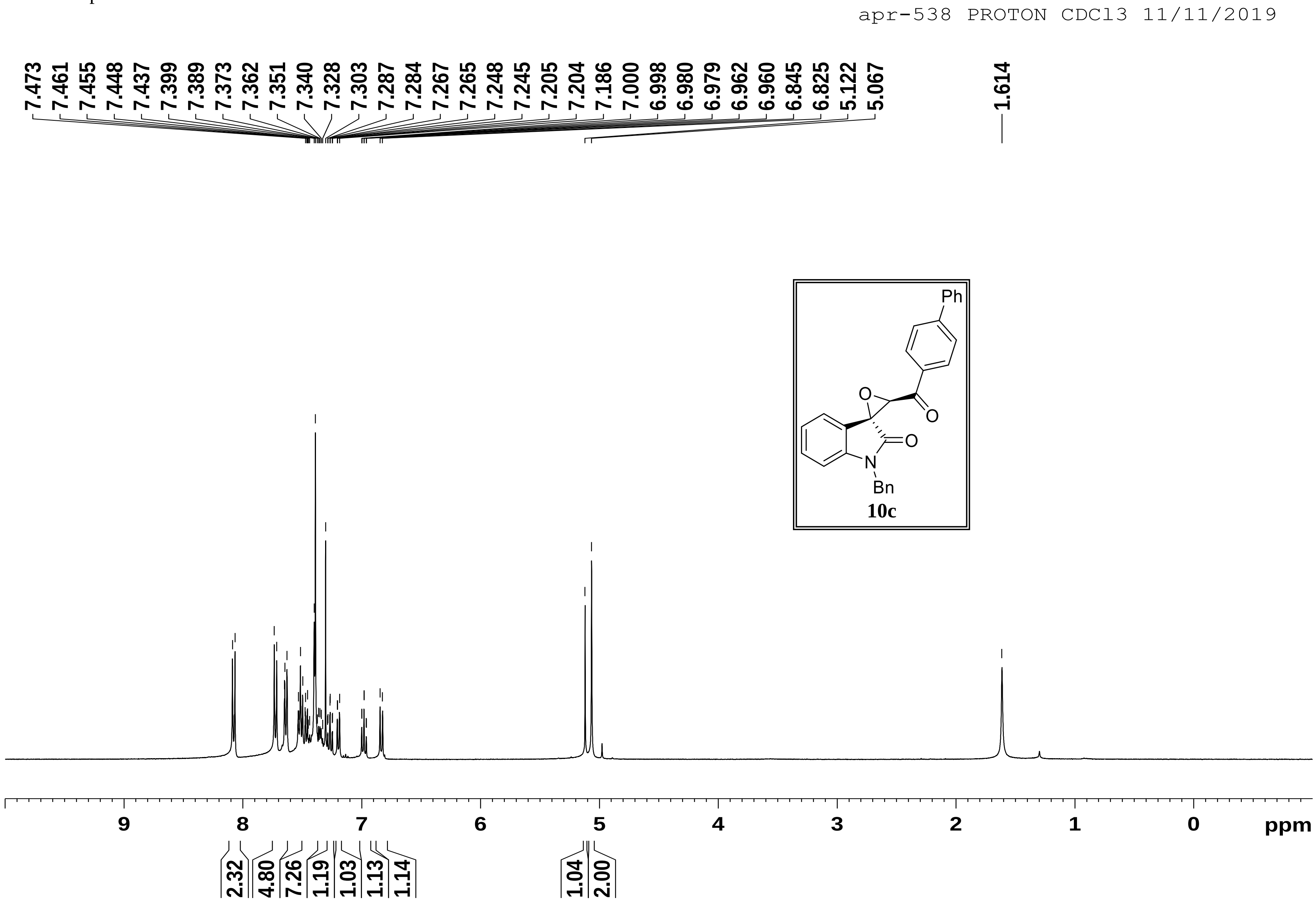
^{1}H NMR spectrum of **10b**



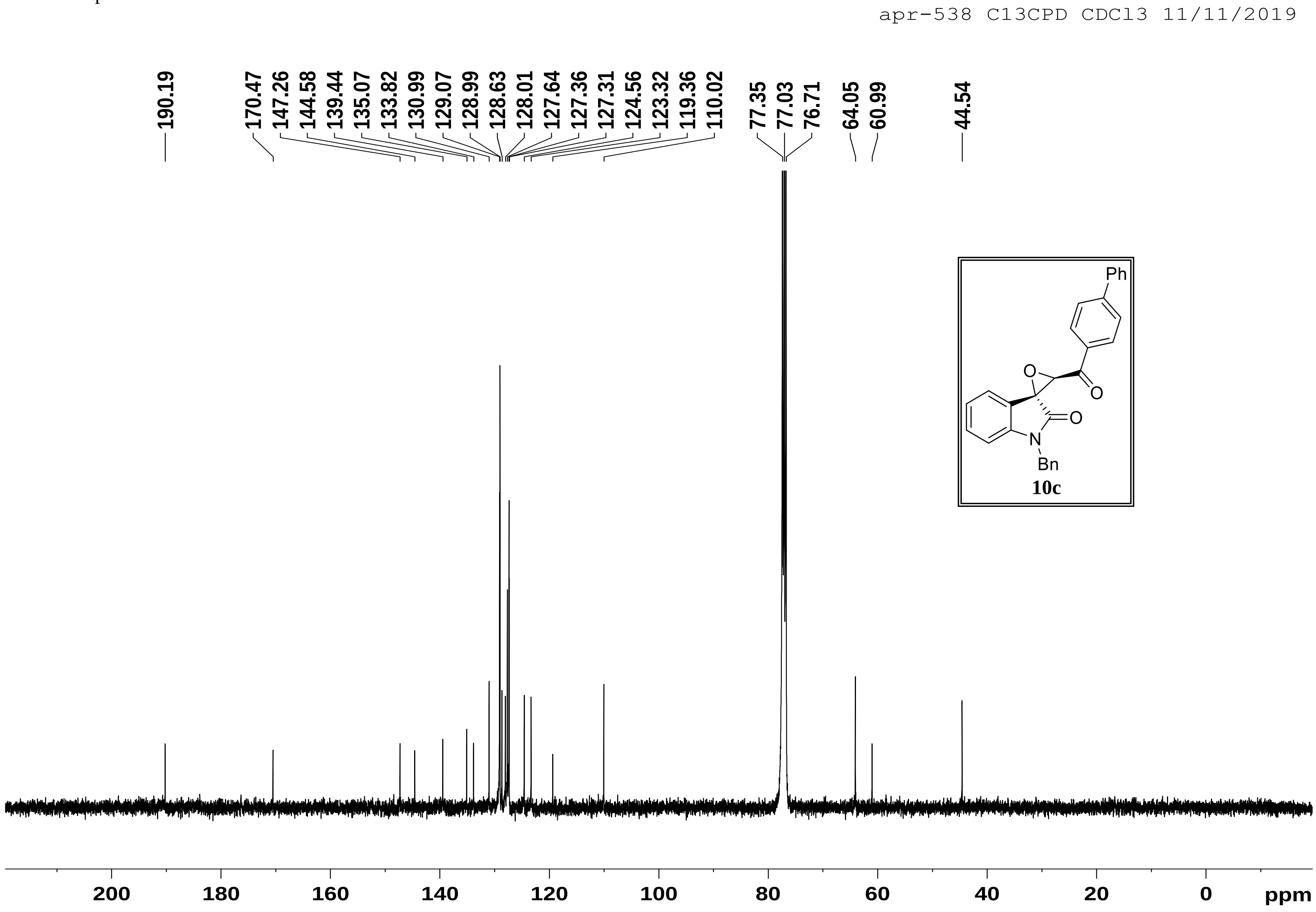
^{13}C NMR spectrum of **10b**



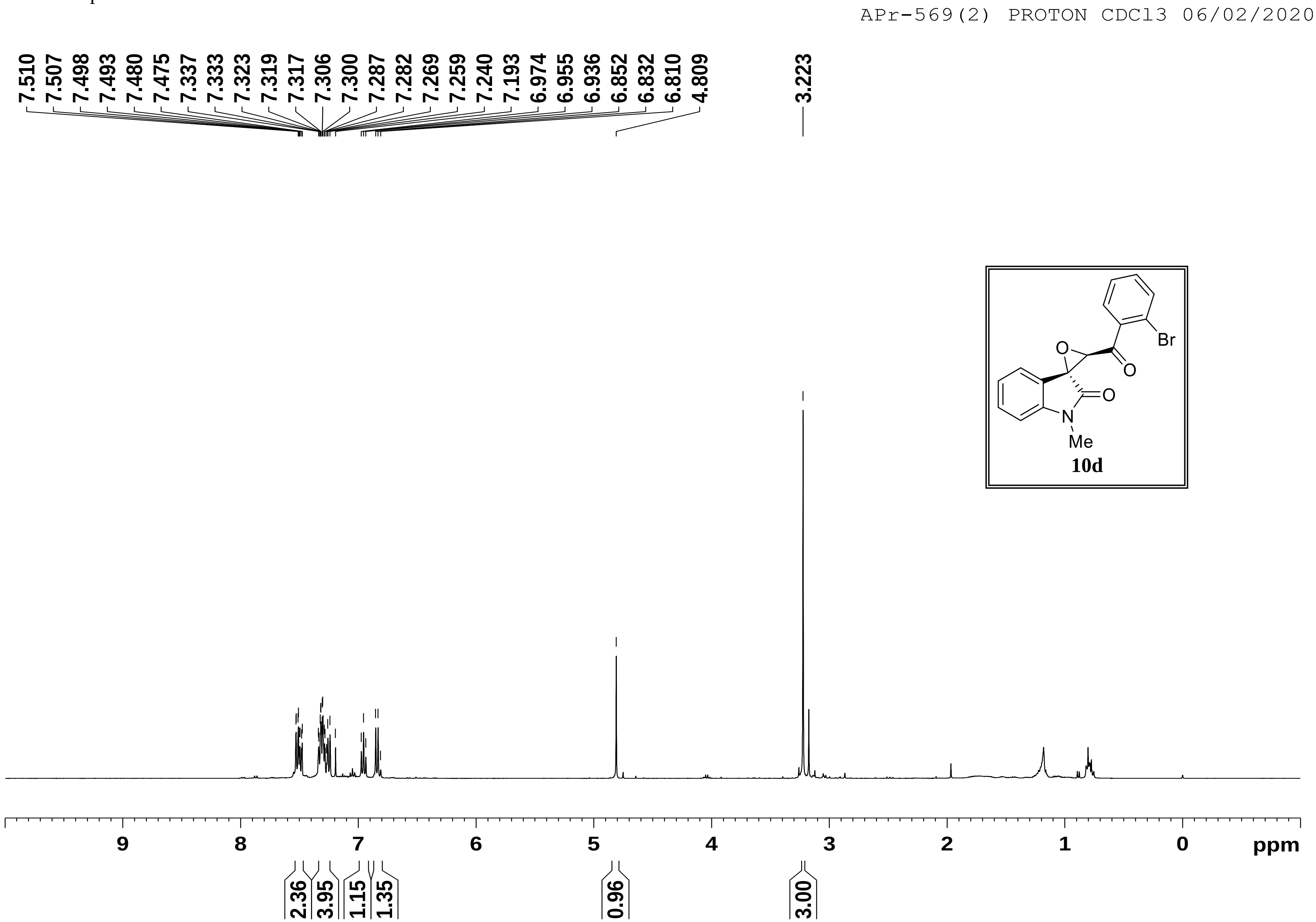
[1]H NMR spectrum of **10c**



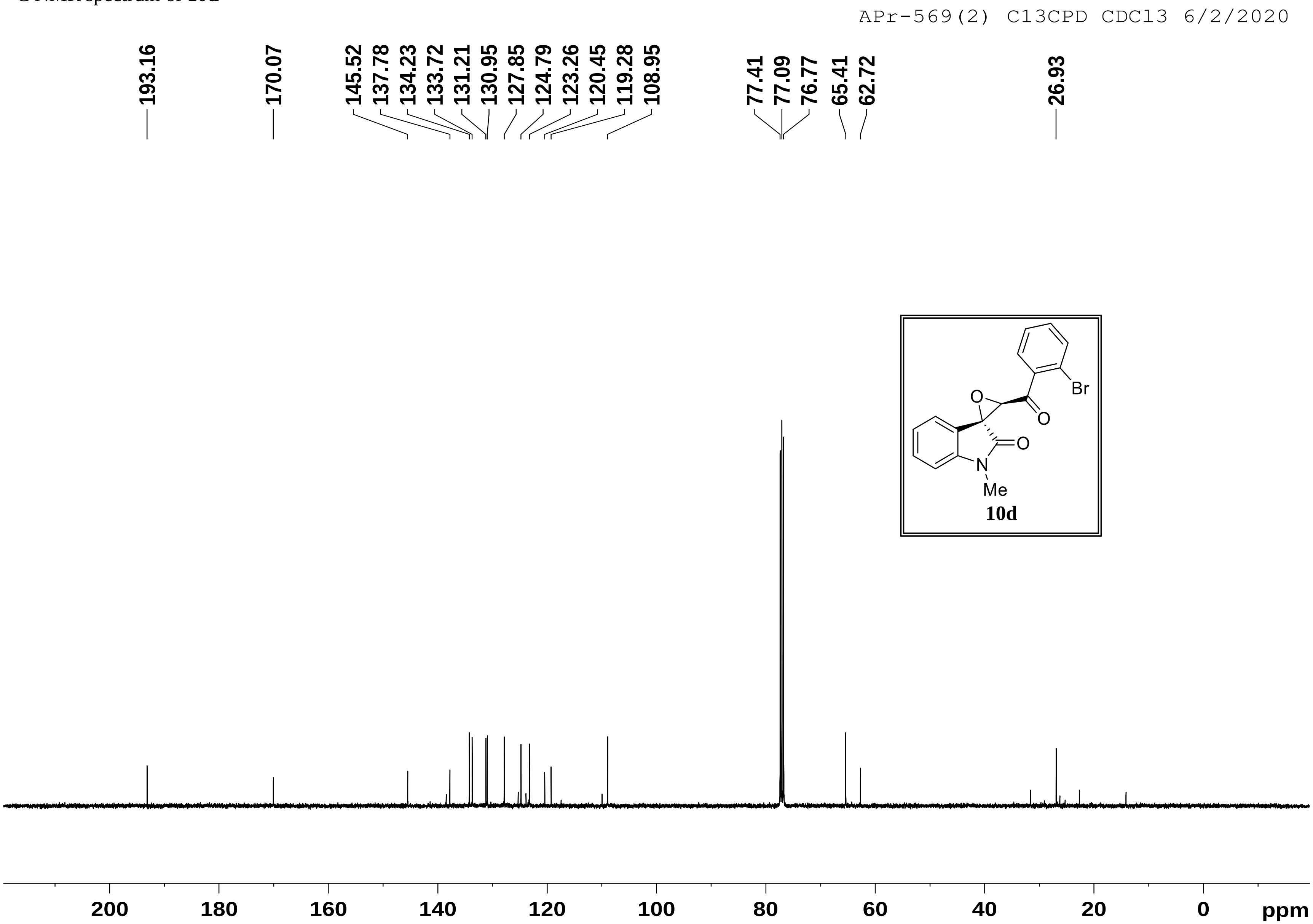
^{13}C NMR spectrum of **10c**



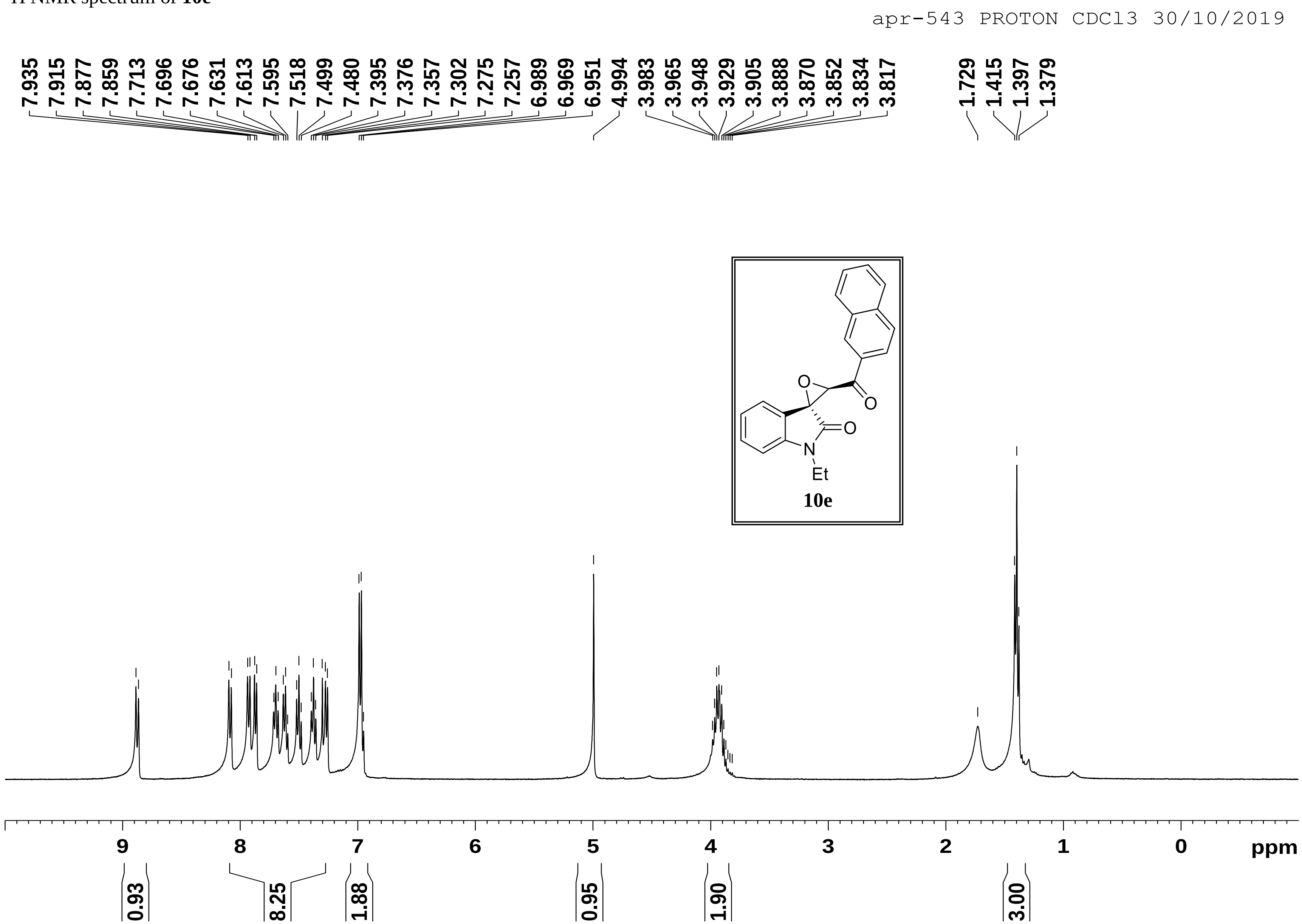
[1]H NMR spectrum of **10d**



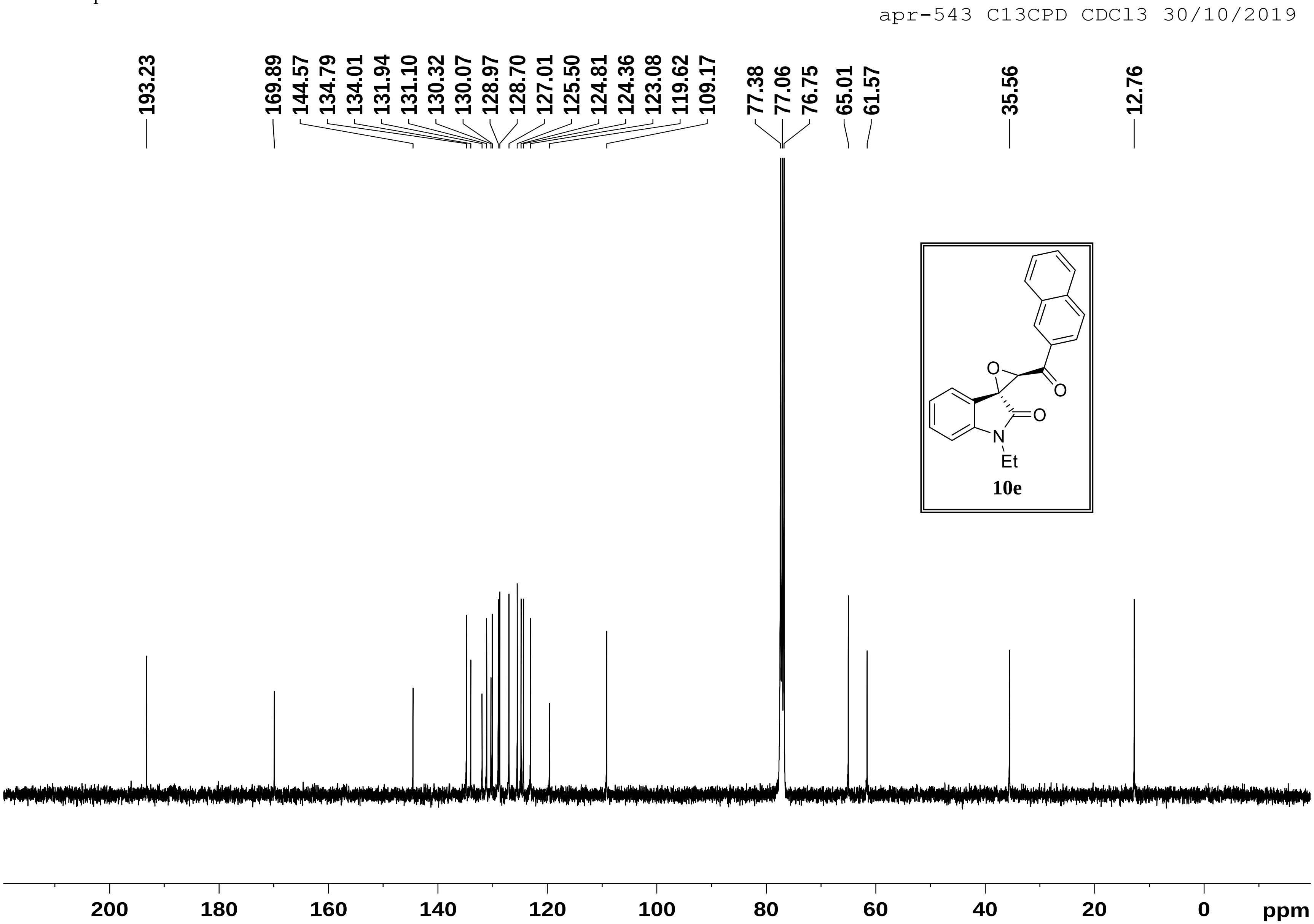
[13]C NMR spectrum of **10d**



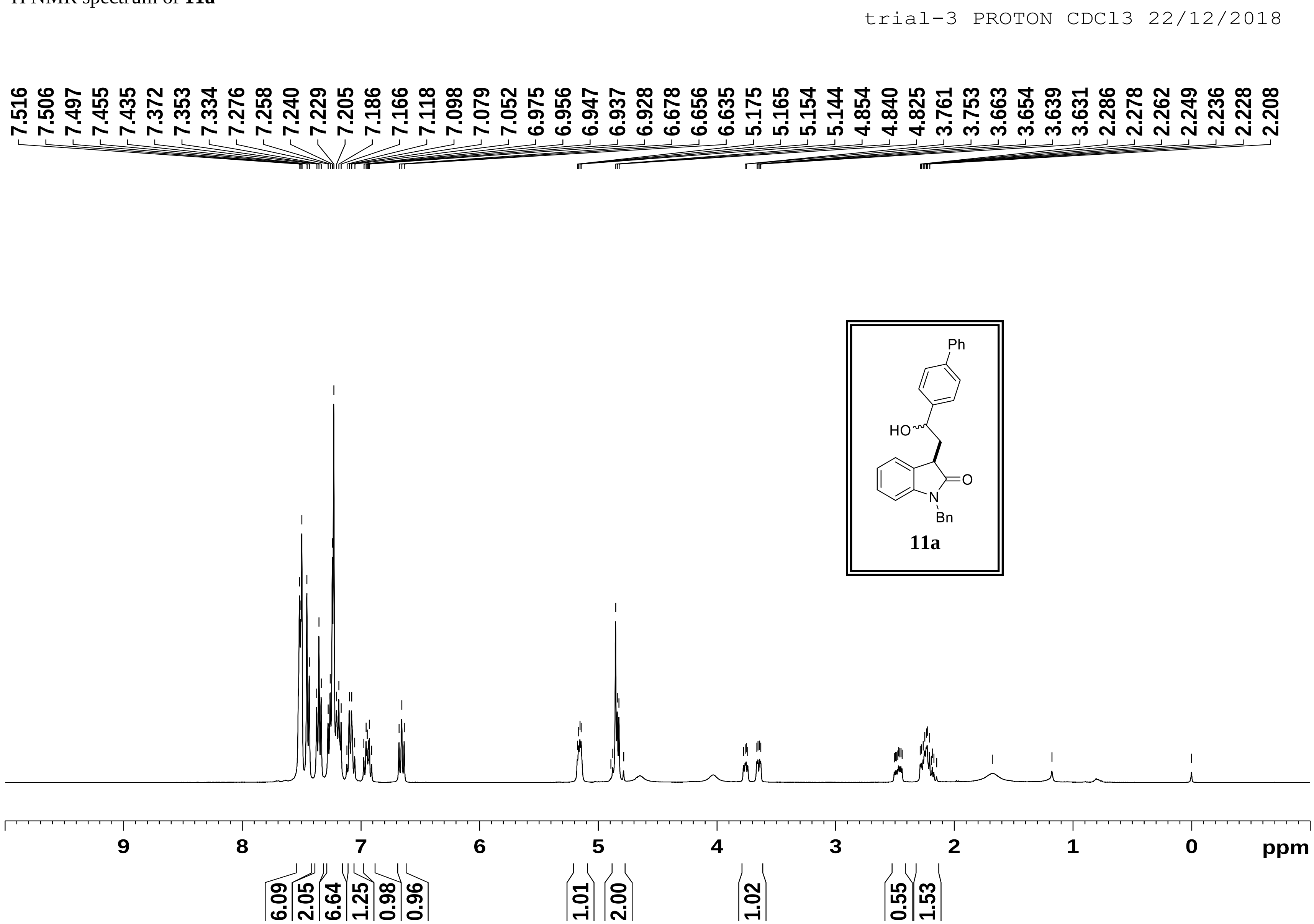
^{1}H NMR spectrum of **10e**



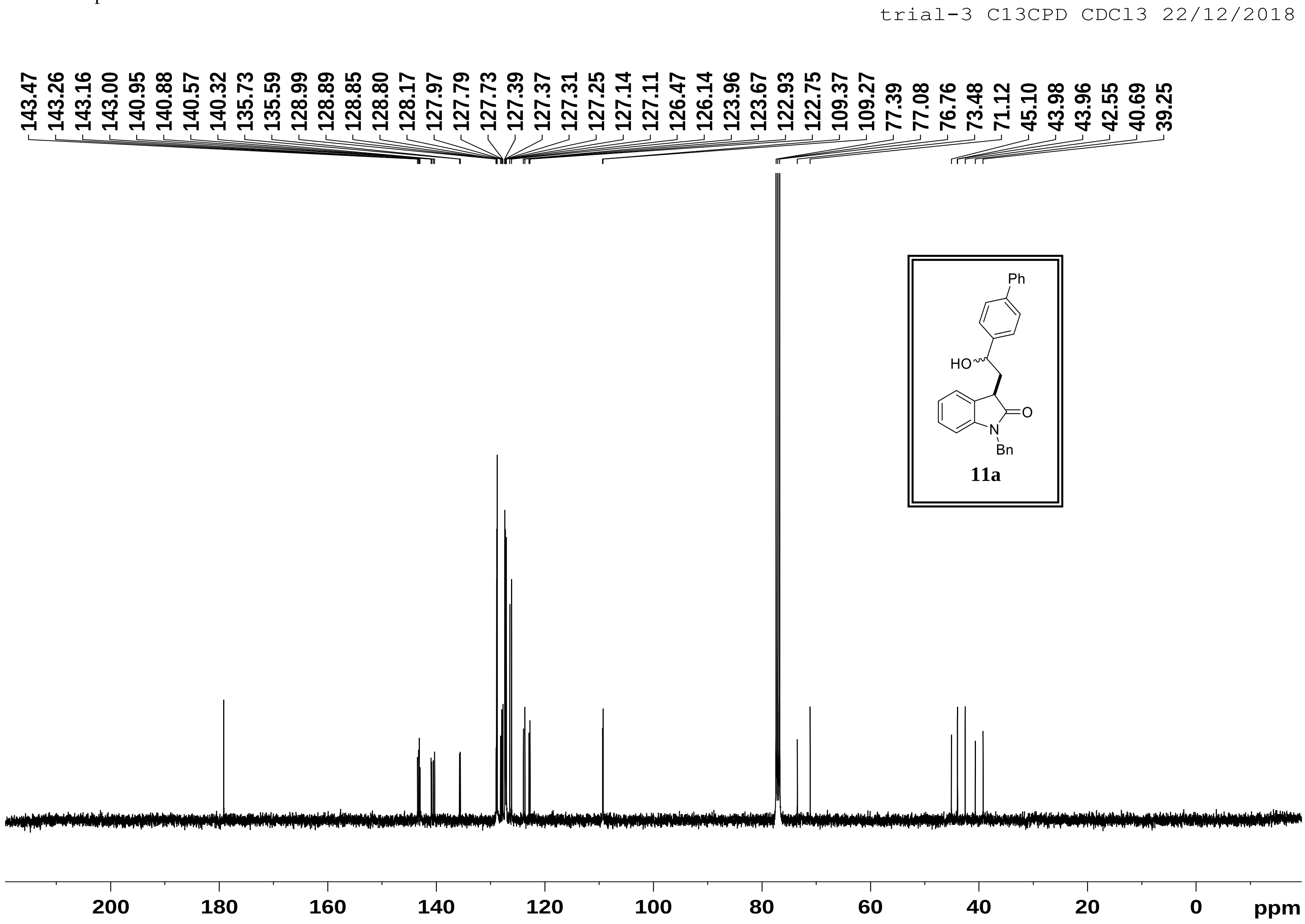
^{13}C NMR spectrum of **10e**



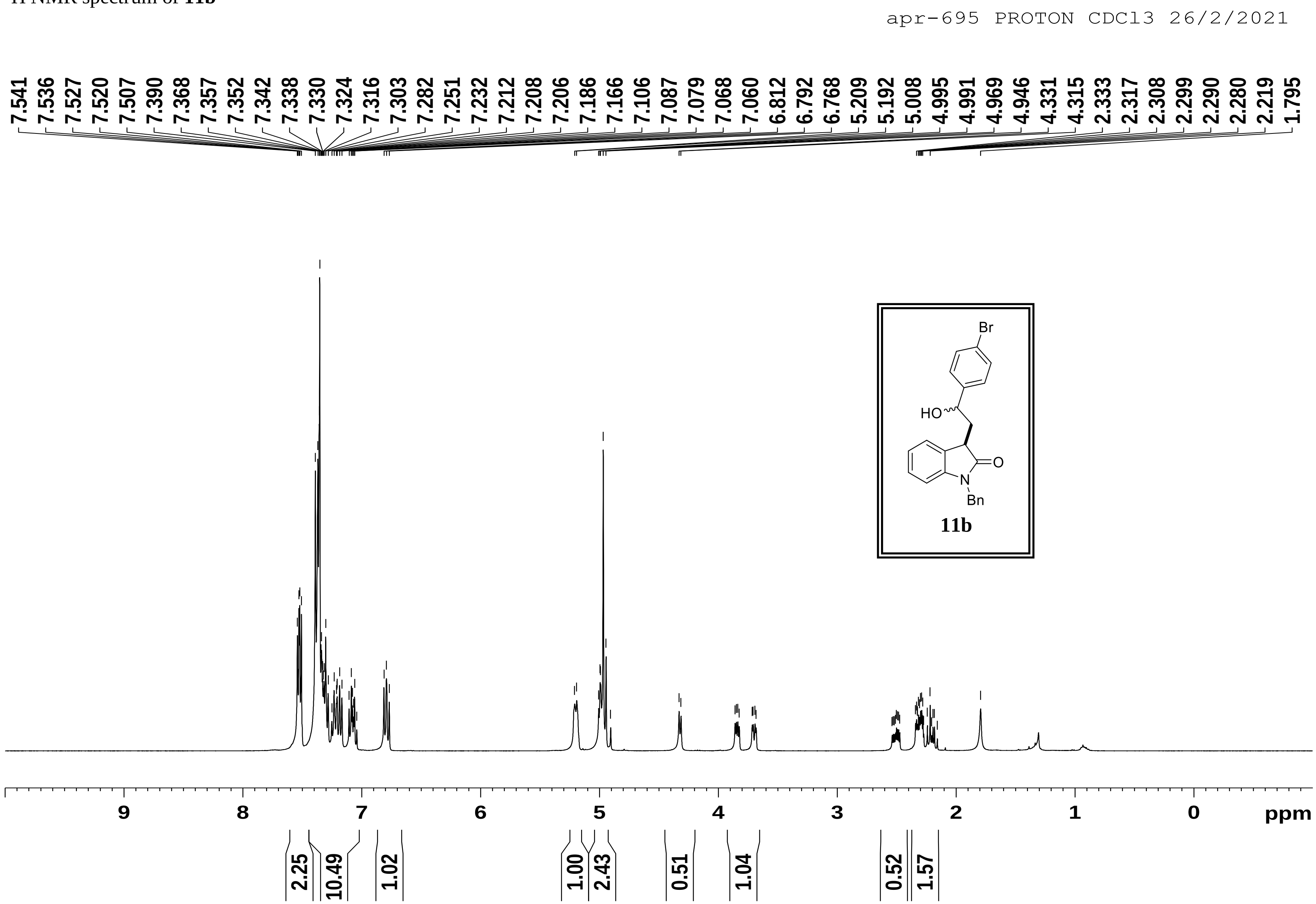
[1]H NMR spectrum of **11a**



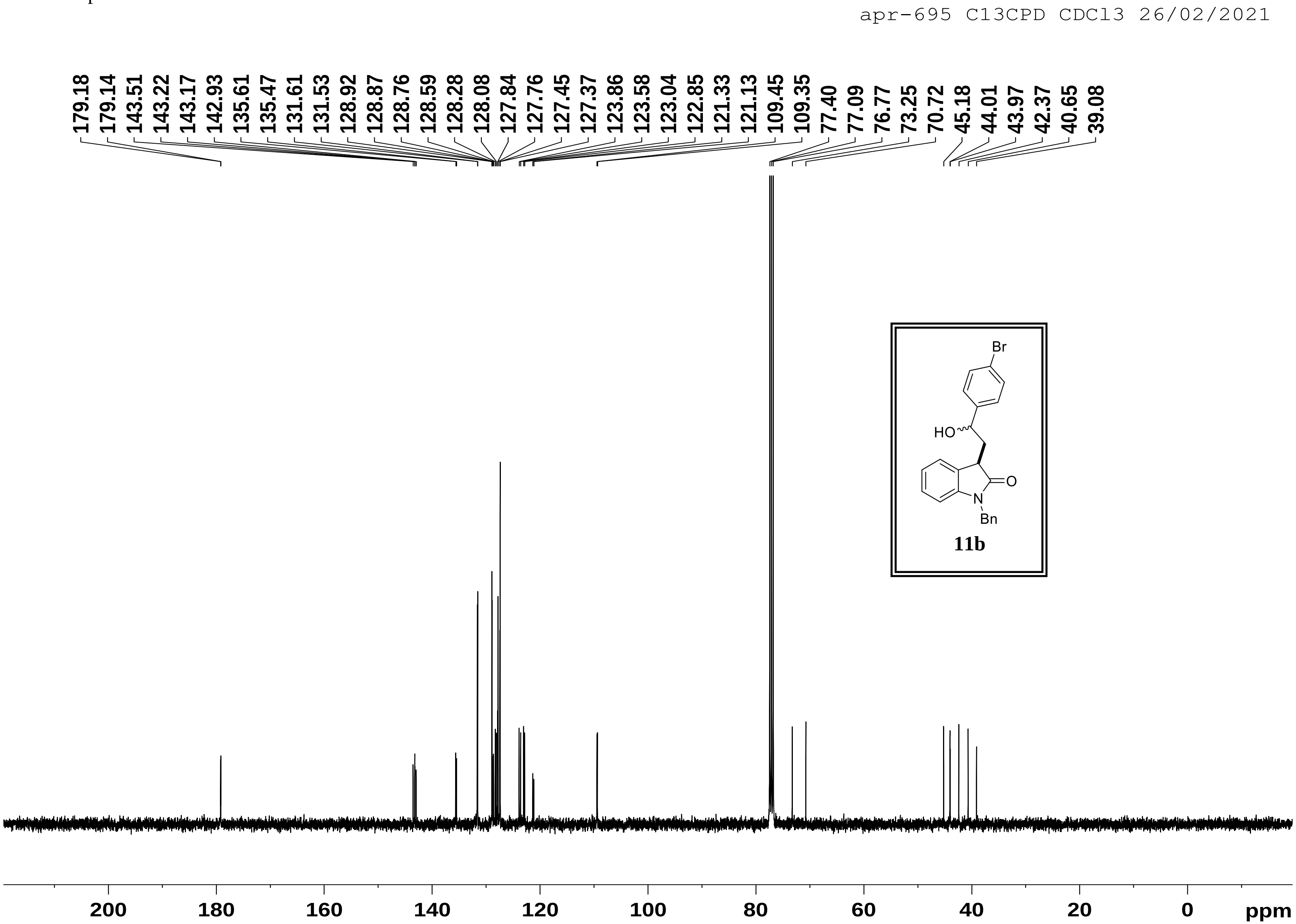
^{13}C NMR spectrum of **11a**



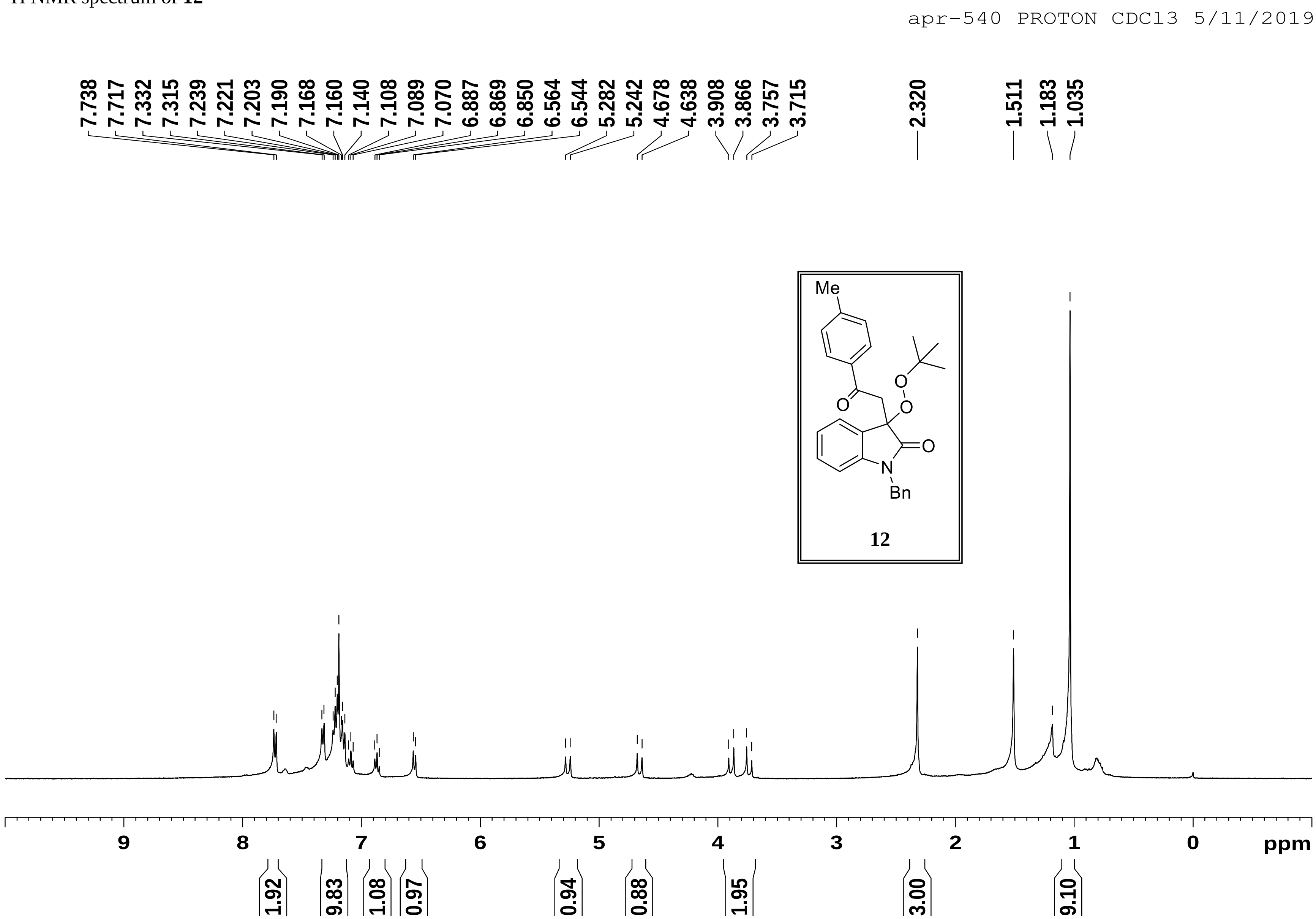
^{1}H NMR spectrum of **11b**



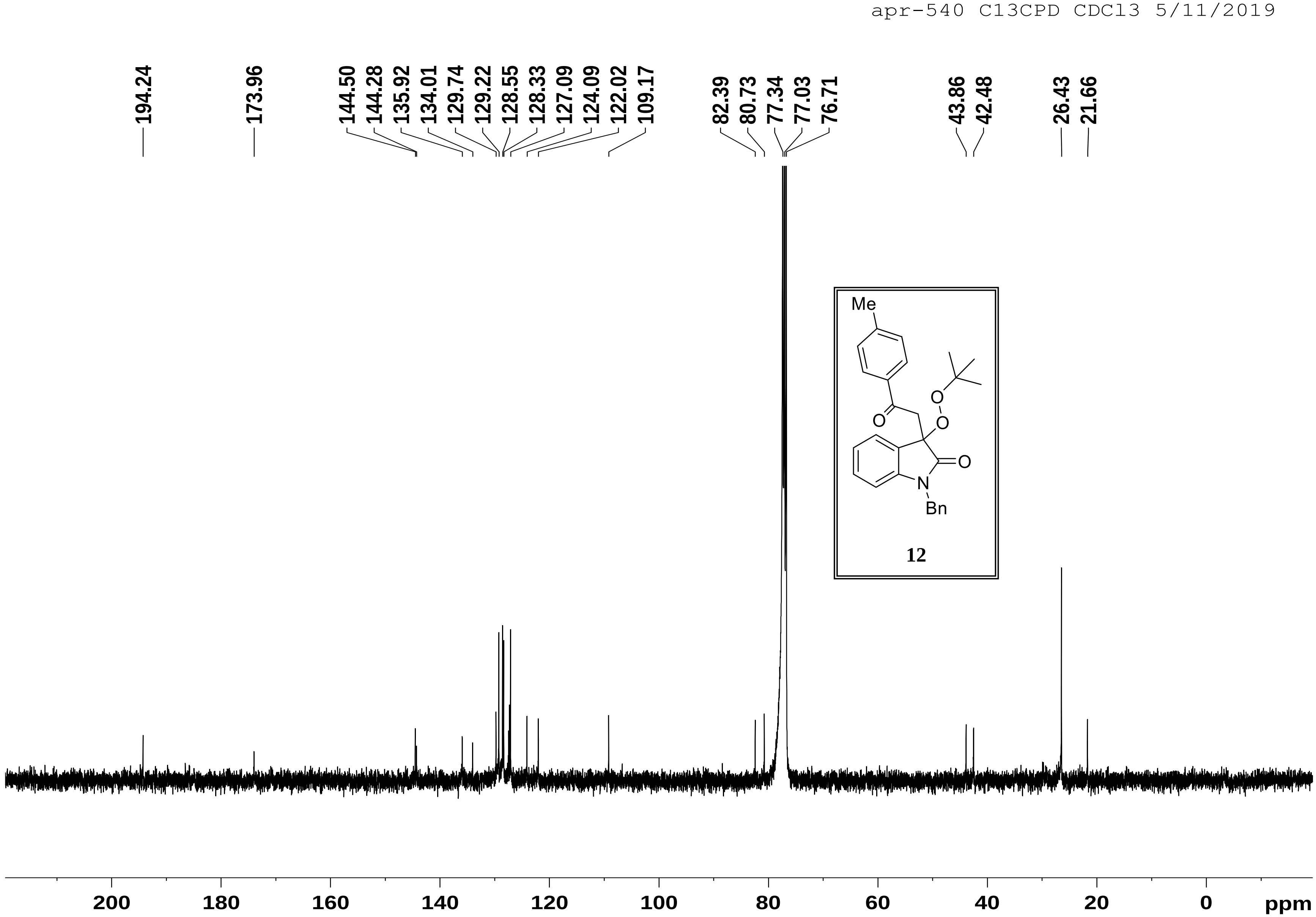
^{13}C NMR spectrum of **11b**



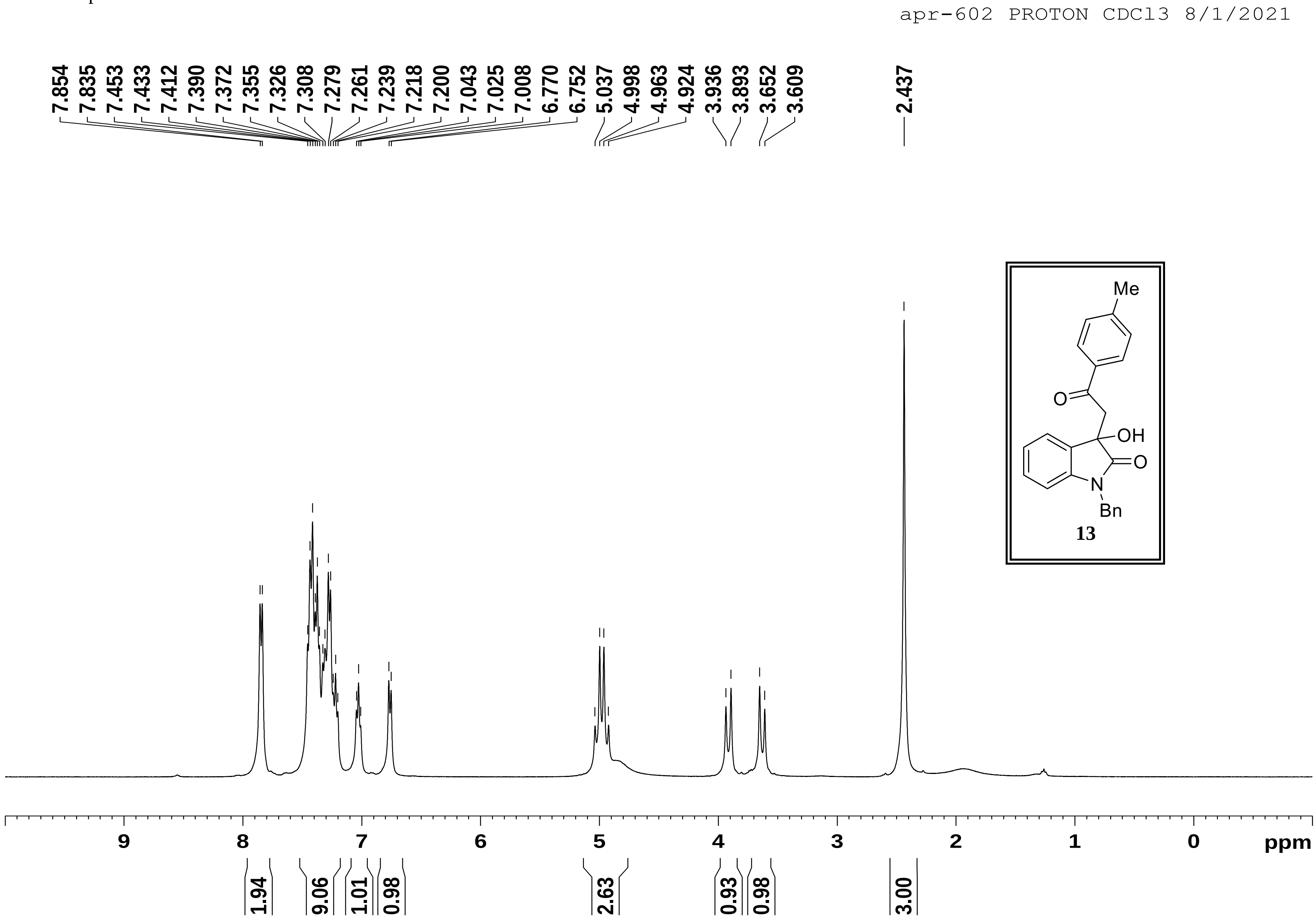
^{1}H NMR spectrum of **12**



^{13}C NMR spectrum of **12**



[1]H NMR spectrum of **13**



^{13}C NMR spectrum of **13**

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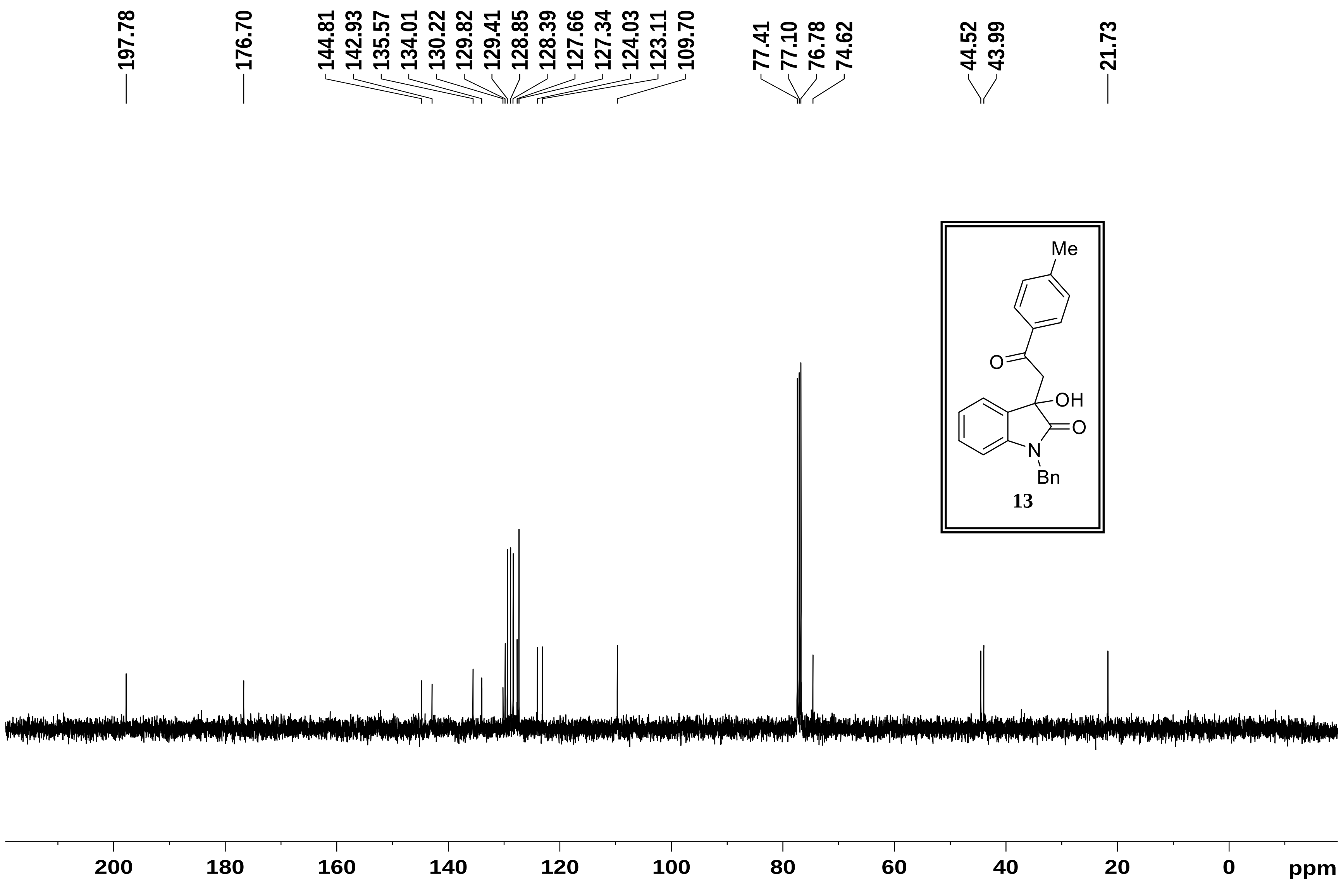

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