

BF₃·OEt₂ catalyzed decarbonylative arylation/C-H functionalization of diazoamides with arylaldehydes: Synthesis of substituted 3-aryloxindoles

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General information

Melting points were determined on a capillary melting point apparatus and uncorrected. IR spectra were recorded using ATR technique on a Bruker Alpha FT-IR spectrophotometer. All compounds were fully characterized. Proton nuclear magnetic resonance (^1H NMR) spectra were recorded at 400 MHz using CDCl_3 in ppm (δ) related to tetramethylsilane ($\delta=0.00$) as an internal standard and are reported as follows; chemical shift (ppm), multiplicity (s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, ABq = AB quartet, m = multiplet) 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 : $\delta_{\text{H}} = 7.26$ ppm, $\delta_{\text{C}} = 77.7$ ppm). High resolution mass analyses were performed using electrospray ionization (ESI) technique on a Thermo Exactive Orbitrap mass spectrometer. All solvents were purified by distillation following standard procedure. 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. aldehyde and were purchased from M/s Aldrich and M/s Alfa Aesar used as provided. The diazoamides¹ was prepared according to the literature method.

Experimental Section

General experimental procedure for the synthesis of α -aryloxindoles (**3**, **6** and **7**)

An oven-dried single neck round bottom flask (50 mL) containing a solution diazoamides **1** (1 equiv.) and appropriate aldehydes **2** or **5** (1 or 0.5 equiv.) in dichloromethane (DCM, 5 mL) under an open-air atmosphere and the reaction mixture was stirred at 0 °C. After 10 minutes, 20 mol% of $\text{BF}_3 \cdot \text{OEt}_2$ was transferred using 100 μL pipette to the reaction mixture. The reaction mixture was stirred and monitored using TLC until the disappearance of the diazoamide. After the appropriate period, the reaction mixture was allowed to room temperature and then DCM (20 mL) and water (20 mL) were added. The organic phase was separated and the aqueous layer was washed with DCM (20 mL). The combined organic layers were washed with brine solution and dried over sodium sulphate. 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 products **3**, **6** and **7**.

General experimental procedure for reaction conditions of 3a under inert atmosphere

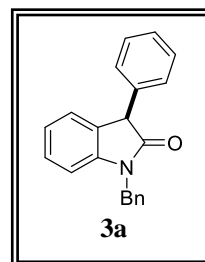
An oven-dried double neck round bottom flask (50 mL) was put under vacuum and flushed with an argon atmosphere for two times. Diazoamide **1a** (1 equiv.) and benzaldehyde **2a** (1.1 equiv.) were dissolved in 5 mL of dry DCM and added to the reaction mixture into the round bottom flask. After 10 minutes, 20 mol% was transferred using 100 μ L pipette to the reaction mixture. The reaction mixture was stirred and monitored using TLC until the disappearance of the diazoamide **1a**. After the appropriate period, the reaction mixture was allowed to room temperature and then DCM (20 mL) and water (20 mL) were added. The organic phase was separated and the aqueous layer was washed with DCM (20 mL). The combined organic layers were washed with brine solution and dried over sodium sulphate. 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 **3a**.

General experimental procedure for gram scale experiments for 3b and 3y

An oven-dried double neck round bottom flask (100 mL) containing a solution of the appropriate aldehyde **2** (1.1 equiv) in dichloromethane (DCM, 5 mL) under an open-air atmosphere and the reaction mixture was stirred at 0 °C. After 10 minutes, 20 mol% of $\text{BF}_3 \cdot \text{OEt}_2$ was transferred using 100 μ L pipette to the reaction mixture. Then added a solution of 3-diazoindol-2-one **1** (1 equiv) in (DCM, 10 mL) using syringe pump with the rate of addition of 5 mL/h. The reaction mixture was stirred and monitored using TLC until the disappearance of the diazoamide. After the appropriate period, the reaction mixture was allowed to room temperature and then DCM (40 mL) and water (40 mL) were added. The organic phase was separated and the aqueous layer was washed with DCM (20 mL). The combined organic layers were washed with brine solution and dried over sodium sulphate. 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 products **3b** and **3y**.

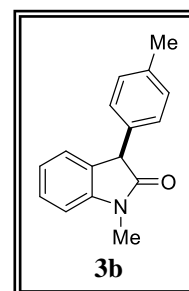
Synthesis of 1-benzyl-3-phenyl-1,3-dihydro-2H-indol-2-one (3a)²

To a solution of 1-benzyl-3-diazo-1,3-dihydro-2*H*-indol-2-one (**1a**) (100 mg, 0.40 mmol) and benzaldehyde (**2a**) (47 mg, 0.44 mmol) in CH₂Cl₂ (5 mL) was added 20 mol% of BF₃·OEt₂. The reaction mixture was stirred at 0°C under the open-air atmosphere to afford (**3a**) (106 mg, 88%) as a white solid according to general procedure. R_f = 0.46 (EtOAc/hexane = 1:4, v/v); mp 114-115 °C; IR (neat): ν_{max} 3033, 1707, 1607, 1485, 1347, 1187, 744746 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ = 4.80 (s, 1H, CH), (ABq, Δδ_{AB} = 0.10, J = 15.6 Hz, 2H, CH₂), 6.89 (d, J = 8 Hz, 1H, ArH), 7.08-7.12 (m, 1H, ArH), 7.24-7.46 (m, 12H, ArH) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ = 44.0, 52.2, 109.3, 122.9, 125.2, 127.5, 127.7, 127.8, 128.4, 128.6, 128.9, 129.0, 129.1, 136.0, 136.9, 143.6, 176.2 ppm; HRMS (ESI) Calculated for C₂₁H₁₇NO (M+H)⁺: 300.1388 found: 300.1383.



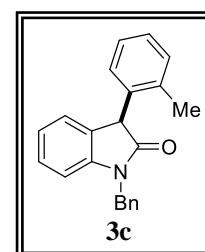
Synthesis of 1-methyl-3-(4-methylphenyl)-1,3-dihydro-2*H*-indol-2-one (**3b**)²

To a solution of 3-diazo-1-methyl-1,3-dihydro-2*H*-indol-2-one (**1b**) (100 mg, 0.58 mmol) and 4-methylbenzaldehyde (**2b**) (70 mg, 0.64 mmol) in CH₂Cl₂ (5 mL) was added 20 mol% of BF₃·OEt₂. The reaction mixture was stirred at 0°C under the open-air atmosphere to afford (**3b**) (124 mg, 90%) as a white solid according to general procedure. R_f = 0.41 (EtOAc/hexane = 1:4, v/v); mp 92-93 °C; IR (neat): ν_{max} 2920, 1703, 1601, 1485, 1350, 1015, 744 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ = 2.31 (s, 3H, CH₃), 3.23 (s, 3H, CH₃), 4.56 (s, 1H, CH), 6.88 (d, J = 7.6 Hz, 1H, ArH), 7.02-7.16 (m, 6H ArH), 7.31 (t, J = 7.6 Hz, 1H, ArH) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ = 21.2, 26.5, 51.7, 108.2, 122.7, 125.0, 128.3, 128.4, 129.1, 129.6, 133.7, 137.3, 144.5, 176.2 ppm; HRMS (ESI) Calculated for C₁₆H₁₅NO (M+H)⁺: 238.1232 found: 238.1260.



Synthesis of 1-benzyl-3-(2-methylphenyl)-1,3-dihydro-2*H*-indol-2-one (**3c**)³

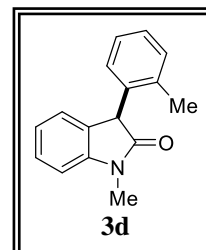
To a solution of 1-benzyl-3-diazo-1,3-dihydro-2*H*-indol-2-one (**1a**) (100 mg, 0.40 mmol) and 2-methylbenzaldehyde (**2c**) (53 mg, 0.44 mmol) in CH₂Cl₂ (5 mL) was added 20 mol% of BF₃·OEt₂. The reaction mixture was stirred at 0°C under the open-air atmosphere to afford (**3c**) (79 mg, 63%) as a white solid according to general procedure. R_f = 0.5 (EtOAc/hexane = 1:4, v/v); mp 86-87 °C; IR (neat): ν_{max} 2923, 1711, 1610, 1487, 1350, 1187, 748 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ = 2.49 (bs, 3H, CH₃), 4.96 (s, 3H, CH₂/CH), 6.79- 7.34 (m, 13H, ArH) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ = 20.0, 44.0, 109.1, 122.8, 124.7, 126.4, 127.6,



127.7, 128.2, 128.8, 129.3, 131.1, 135.5, 136.0, 137.3, 143.5, 176.3 ppm; HRMS (ESI) Calculated for C₂₂H₁₉NO(M+H)⁺: 314.1545 found: 314.1548.

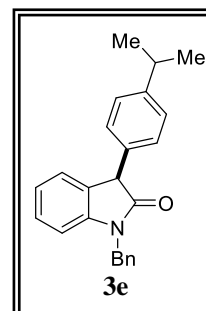
Synthesis of 1-methyl-3-(2-methylphenyl)-1,3-dihydro-2H-indol-2-one (**3d**)⁴

To a solution of 3-diazo-1-methyl-1,3-dihydro-2H-indol-2-one (**1b**) (100 mg, 0.58 mmol) and 1-methylbenzaldehyde (**2c**) (70 mg, 0.64 mmol) in CH₂Cl₂ (5 mL) was added 20 mol% of BF₃·OEt₂. The reaction mixture was stirred at 0°C under the open-air atmosphere to afford (**3d**) (84 mg, 61%) as a white solid according to general procedure. R_f = 0.38 (EtOAc/hexane = 1:4, v/v); mp 131-132 °C; IR (neat): ν_{max} 2992, 1683, 1607, 1466, 1252, 1088, 739 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ = 2.33 (bs, 3H, CH₃), 3.19 (s, 3H, CH₃), 4.76 (s, 1H, CH), 6.81-6.85 (m, 1H, ArH), 6.93-7.26 (m, 7H, ArH) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ = 19.8, 26.5, 108.1, 122.8, 124.6, 126.4, 127.7, 128.3, 129.3, 131.0, 135.5, 137.2, 144.4, 176.2 ppm; HRMS (ESI) Calculated for C₁₆H₁₅NO(M+H)⁺: 238.1232 found: 238.1234.



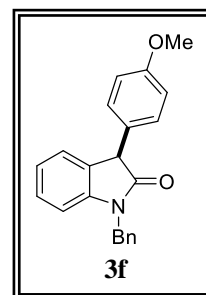
Synthesis of 1-benzyl-3-[4-(propan-2-yl)phenyl]-1,3-dihydro-2H-indol-2-one (**3e**)

To a solution of 1-benzyl-3-diazo-1,3-dihydro-2H-indol-2-one (**1a**) (100 mg, 0.40 mmol) and 4-isopropylbenzaldehyde (**2d**) (65 mg, 0.44 mmol) in CH₂Cl₂ (5 mL) was added 20 mol% of BF₃·OEt₂. The reaction mixture was stirred at 0°C under the open-air atmosphere to afford (**3e**) (110 mg, 81%) as a white solid according to general procedure. R_f = 0.52 (EtOAc/hexane = 1:4, v/v); mp 146-147 °C; IR (neat): ν_{max} 2922, 1706, 1607, 1488, 1353, 1018, 746 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ = 1.23 (d, J = 7.2 Hz, 6H, 2CH₃), 2.84-2.94 (m, 1H, CH), 4.68 (s, 1H, CH), 4.94 (ABq, Δδ_{AB} = 0.10, J = 16 Hz, 2H, CH₂), 6.77 (d, J = 7.6, 1H, ArH), 7.00 (t, J = 7.5 Hz, 1H, ArH), 7.13-7.21 (m, 6H, ArH), 7.24-7.32 (m, 5H, ArH) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ = 23.99, 24.02, 33.9, 44.0, 51.8, 109.2, 122.8, 125.2, 127.1, 127.4, 127.7, 128.3, 128.4, 128.8, 129.1, 134.0, 136.0, 143.6, 148.2, 176.4 ppm; HRMS (ESI) Calculated for C₂₄H₂₃NO(M+H)⁺: 342.1858 found: 342.1862.



Synthesis of 1-benzyl-3-(4-methoxyphenyl)-1,3-dihydro-2H-indol-2-one (**3f**)⁵

To a solution of 1-benzyl-3-diazo-1,3-dihydro-2H-indol-2-one (**1a**) (100 mg, 0.40 mmol) and 4-methoxybenzaldehyde (**2e**) (60 mg, 0.44 mmol) in CH₂Cl₂ (5 mL) was added 20 mol% of BF₃·OEt₂. The reaction mixture was stirred at 0°C under the open-air atmosphere to afford (**3f**) (112 mg, 85%) as a white solid according to general procedure. R_f = 0.3 (EtOAc/hexane = 1:4, v/v); mp 108-109 °C; IR (neat): ν_{max} 2924, 1708, 1606, 1489, 1353,

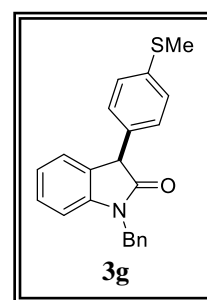


1098, 747 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ = 3.79 (s, 3H, CH_3), 4.65 (s, 1H, CH), 4.93 (ABq, $\Delta\delta_{AB}$ = 0.09, J = 15.6 Hz, 2H, CH_2), 6.77 (d, J = 8 Hz, 1H, ArH), 6.87 (d, J = 8.8 Hz, 2H, ArH), 7.01 (t, J = 7.6 Hz, 1H, ArH), 7.13-7.21 (m, 4H, ArH), 7.24-7.31 (m, 5H, ArH) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ = 44.0, 51.3, 55.4, 109.2, 114.5, 122.8, 125.1, 127.4, 127.7, 128.3, 128.79, 128.83, 129.2, 129.5, 136.0, 143.6, 159.1, 176.5 ppm; HRMS (ESI) Calculated for $\text{C}_{22}\text{H}_{19}\text{NO}_2(\text{M}+\text{H})^+$: 330.1494 found: 330.1485.

Synthesis of 1-benzyl-3-[4-(methylsulfanyl)phenyl]-1,3-dihydro-2H-indol-2-one (**3g**)

To a solution of 1-benzyl-3-diazo-1,3-dihydro-2H-indol-2-one (**1a**) (100 mg, 0.40 mmol) and 4-(methylthio)benzaldehyde (**2f**) (67 mg, 0.44 mmol) in CH_2Cl_2 (5 mL) was added 20 mol% of $\text{BF}_3 \cdot \text{OEt}_2$. The reaction mixture was stirred at 0°C under the open-air atmosphere to afford

(**3g**) (115 mg, 83%) as a white solid according to general procedure. R_f = 0.33 (EtOAc/hexane = 1:4, v/v); mp 123-124 $^\circ\text{C}$; IR (neat): ν_{max} 2921, 1705, 1607, 1347, 1089, 1015, 737 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ = 2.31 (s, 3H, CH_3), 4.53 (s, 1H, CH), 4.80 (ABq, $\Delta\delta_{AB}$ = 0.11, J = 15.6 Hz, 2H, CH_2), 6.66 (d, J = 8 Hz, 1H, ArH), 6.88 (t, J = 7.6 Hz, 1H, ArH), 7.00-7.19 (m, 11H, ArH) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ = 15.9, 44.0, 51.6,

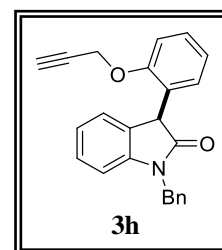


109.4, 122.9, 125.2, 127.2, 127.5, 127.8, 128.5, 128.8, 128.9, 129.0, 133.6, 136.0, 138.0, 143.6, 176.1 ppm; HRMS (ESI) Calculated for $\text{C}_{22}\text{H}_{19}\text{NOS}(\text{M}+\text{H})^+$: 346.1266 found: 346.1268.

Synthesis of 1-benzyl-3-{2-[(prop-2-yn-1-yl)oxy]phenyl}-1,3-dihydro-2H-indol-2-one (**3h**)

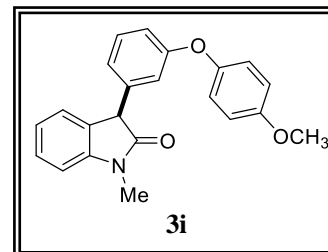
To a solution of 1-benzyl-3-diazo-1,3-dihydro-2H-indol-2-one (**1a**) (100 mg, 0.40 mmol) and 2-[(prop-2-yn-1-yl)oxy]benzaldehyde (**2g**) (70 mg, 0.44 mmol) in CH_2Cl_2 (5 mL) was added 20 mol% of $\text{BF}_3 \cdot \text{OEt}_2$. The reaction mixture was stirred at 0°C under the open-air atmosphere to afford (**3h**) (99 mg, 70%) as a white solid according to general

procedure. R_f = 0.28 (EtOAc/hexane = 1:4, v/v); mp 121-122 $^\circ\text{C}$; IR (neat): ν_{max} 3287, 2922, 2121, 1706, 1607, 1488, 1353, 1018, 746 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ = 2.45 (t, J = 2.2 Hz, 1H, CH), 4.51 (s, 2H, CH_2), 4.92-5.06 (m, 3H, CH_2/CH), 6.76 (d, J = 7.6, 1H, ArH), 6.91-7.07 (m, 4H, ArH), 7.13-7.17 (m, 2H, ArH), 7.25-7.41 (m, 6H, ArH) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ = 44.1, 48.2, 56.5, 75.5, 78.6, 108.8, 113.3, 122.1, 122.5, 124.2, 126.7, 127.6, 127.8, 128.8, 128.9, 129.7, 130.6, 136.3, 143.4, 155.8, 176.6 ppm; HRMS (ESI) Calculated for $\text{C}_{24}\text{H}_{19}\text{NO}_2(\text{M}+\text{H})^+$: 354.1494 found: 354.2231.



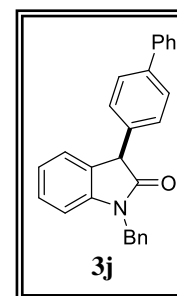
Synthesis of 3-[3-(4-methoxyphenoxy)phenyl]-1-methyl-1,3-dihydro-2*H*-indol-2-one (**3i**)

To a solution of 3-diazo-1-methyl-1,3-dihydro-2*H*-indol-2-one (**1b**) (100 mg, 0.58 mmol) and 3-(4-methoxyphenoxy)benzaldehyde (**2h**) (145 mg, 0.64 mmol) in CH₂Cl₂ (5 mL) was added 20 mol% of BF₃·OEt₂. The reaction mixture was stirred at 0°C under the open-air atmosphere to afford (**3i**) (160 mg, 80%) as a white solid according to general procedure. R_f = 0.27 (EtOAc/hexane = 1:4, v/v); mp 136-137 °C; IR (neat): ν_{max} 2928, 1683, 1607, 1466, 1343, 1088, 739 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ = 3.25 (s, 3H, CH₃), 3.80 (s, 3H, CH₃), 4.56 (s, 1H, CH), 6.78-7.08 (m, 9H, ArH), 7.16-7.34 (m, 3H, ArH) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ = 26.5, 51.9, 55.7, 108.2, 114.9, 116.3, 118.1, 120.9, 122.4, 122.8, 125.0, 128.5, 128.6, 130.0, 138.5, 144.5, 149.9, 160.0, 158.8, 175.7 ppm; HRMS (ESI) Calculated for C₂₂H₁₉NO₃(M+H)⁺: 346.1443 found:346.1443.



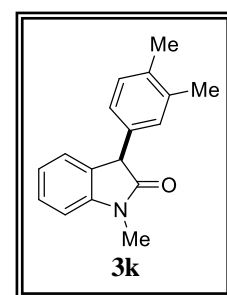
Synthesis of 1-benzyl-3-([1,1'-biphenyl]-4-yl)-1,3-dihydro-2*H*-indol-2-one (**3j**)⁶

To a solution of 1-benzyl-3-diazo-1,3-dihydro-2*H*-indol-2-one (**1a**) (100 mg, 0.40 mmol) and [1,1'-biphenyl]-4-carbaldehyde (**2i**) (80 mg, 0.44 mmol) in CH₂Cl₂ (5 mL) was added 20 mol% of BF₃·OEt₂. The reaction mixture was stirred at 0°C under the open-air atmosphere to afford (**3j**) (99 mg, 66%) as a white solid according to general procedure. R_f = 0.65 (EtOAc/hexane = 1:4, v/v); mp 118-119 °C; IR (neat): ν_{max} 2923, 1708, 1609, 1480, 1350, 1085, 736 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ = 4.87-4.95 (m, 3H, CH₂/CH), 6.71-7.62 (m, 18H, ArH) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ = 44.0, 109.0, 122.7, 124.7, 127.3, 127.5, 127.7, 128.0, 128.1, 128.8, 129.9, 130.6, 130.9, 135.1, 136.1, 140.8, 143.4, 177.0 ppm; HRMS (ESI) Calculated for C₂₇H₂₁NO(M+H)⁺: 376.1701 found: 376.1696.



Synthesis of 3-(3,4-dimethylphenyl)-1-methyl-1,3-dihydro-2*H*-indol-2-one (**3k**)⁷

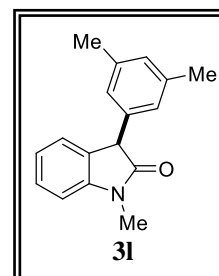
To a solution of 3-diazo-1-methyl-1,3-dihydro-2*H*-indol-2-one (**1b**) (100 mg, 0.58 mmol) and 3,4-dimethylbenzaldehyde (**2j**) (85 mg, 0.64 mmol) in CH₂Cl₂ (5 mL) was added 20 mol% of BF₃·OEt₂. The reaction mixture was stirred at 0°C under the open-air atmosphere to afford (**3k**) (121 mg, 83%) as a white solid according to general procedure. R_f = 0.37 (EtOAc/hexane = 1:4, v/v); mp 94-95 °C; IR (neat): ν_{max} 2926, 1707, 1608, 1480, 1350, 1085, 736 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ = 2.19 (s, 6H, 2CH₃), 3.21 (s, 3H, CH₃), 4.50 (s, 1H, CH), 6.84-6.94 (m, 3H, ArH), 7.00-7.06 (m, 2H, ArH), 7.12 (d, J = 7.2Hz, 1H, ArH), 7.26-7.30 (m, 1H, ArH) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ = 19.5, 19.9, 26.5,



51.8, 108.2, 122.8, 125.0, 125.9, 128.4, 129.3, 129.7, 130.2, 134.1, 136.0, 137.2, 144.5, 176.4 ppm; HRMS (ESI) Calculated for C₁₇H₁₇NO(M+H)⁺: 252.1388 found: 252.1383.

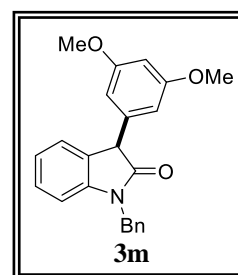
Synthesis of 3-(3,5-dimethylphenyl)-1-methyl-1,3-dihydro-2H-indol-2-one (**3l**)⁷

To a solution of 3-diazo-1-methyl-1,3-dihydro-2H-indol-2-one (**1b**) (100 mg, 0.58 mmol) and 3,5-dimethylbenzaldehyde (**2k**) (85 mg, 0.64 mmol) in CH₂Cl₂ (5 mL) was added 20 mol% of BF₃·OEt₂. The reaction mixture was stirred at 0°C under the open-air atmosphere to afford (**3l**) (130 mg, 89%) as a white solid according to general procedure. R_f = 0.38 (EtOAc/hexane = 1:4, v/v); mp 97-98 °C; IR (neat): ν_{max} 2924, 1706, 1609, 1465, 1342, 1255, 1023, 747 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ = 2.17 (s, 6H, CH₃), 3.14 (s, 3H, CH₃), 4.66 (s, 1H, CH), 6.76-6.81 (m, 2H, ArH), 6.89-6.95 (m, 4H, ArH), 7.17-7.21 (m, 1H, ArH) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ = 19.7, 21.1, 26.4, 108.1, 122.8, 124.6, 127.1, 128.2, 129.5, 131.9, 132.5, 137.3, 144.4, 176.4 ppm; HRMS (ESI) Calculated for C₁₇H₁₇NO (M+H)⁺: 252.1388 found: 252.1382.



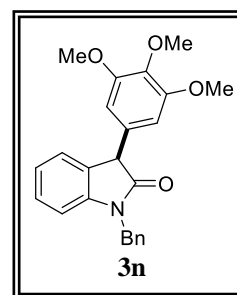
Synthesis of 1-benzyl-3-(3,5-dimethoxyphenyl)-1,3-dihydro-2H-indol-2-one (**3m**)

To a solution of 1-benzyl-3-diazo-1,3-dihydro-2H-indol-2-one (**1a**) (100 mg, 0.40 mmol) and 3,5-dimethoxybenzaldehyde (**2l**) (73 mg, 0.44 mmol) in CH₂Cl₂ (5 mL) was added 20 mol% of BF₃·OEt₂. The reaction mixture was stirred at 0°C under the open-air atmosphere to afford (**3m**) (109 mg, 85%) as a white solid according to general procedure. R_f = 0.17 (EtOAc/hexane = 1:4, v/v); mp 130-131 °C; IR (neat): ν_{max} 2936, 1708, 1606, 1460, 1247, 1024, 731 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ = 3.79 (s, 3H, CH₃), 3.84 (s, 3H, CH₃), 4.63 (s, 1H, CH), 4.93 (ABq, Δδ_{AB} = 0.16, J = 15.6 Hz, 2H, CH₂), 6.71-6.84 (m, 4H, ArH), 7.01 (t, J = 7.6 Hz, 1H, ArH), 7.16-7.33 (m, 7H, ArH) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ = 43.9, 51.6, 55.9, 56.0, 109.2, 111.5, 120.7, 122.8, 125.2, 127.5, 127.7, 128.4, 128.8, 129.1, 129.2, 136.1, 143.5, 148.6, 149.3, 176.4 ppm; HRMS (ESI) Calculated for C₂₃H₂₁NO₃ (M+H)⁺: 360.1600 found: 360.1595.



Synthesis of 1-benzyl-3-(3,4,5-trimethoxyphenyl)-1,3-dihydro-2H-indol-2-one (**3n**)

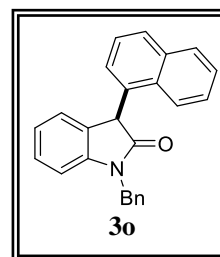
To a solution of 1-benzyl-3-diazo-1,3-dihydro-2H-indol-2-one (**1a**) (100 mg, 0.40 mmol) and 3,4,5-trimethoxybenzaldehyde (**2m**) (86 mg, 0.44 mmol) in CH₂Cl₂ (5 mL) was added 20 mol% of BF₃·OEt₂. The reaction mixture was stirred at 0°C under the open-air atmosphere to afford (**3n**)



(125 mg, 80%) as a white solid according to general procedure. $R_f = 0.22$ (EtOAc/hexane = 1:4, v/v); mp 151-152 °C; IR (neat): ν_{\max} 2922, 1708, 1609, 1480, 1350, 1085, 736 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) $\delta = 3.49$ (s, 3H, CH_3), 3.84 (d, $J = 2.8$ Hz, 6H, 2CH_3), 4.73 (s, 1H, CH), 4.98 (ABq, $\Delta\delta_{AB} = 0.16$, $J = 15.6$ Hz, 2H, CH_2), 6.62-7.32 (m, 11H, ArH) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) $\delta = 44.0, 48.7, 56.1, 60.5, 60.7, 107.2, 108.9, 122.4, 123.6, 124.2, 124.9, 127.6, 127.9, 128.7, 130.2, 136.2, 142.5, 143.5, 152.1, 153.7, 176.9$ ppm; HRMS (ESI) Calculated for $\text{C}_{24}\text{H}_{23}\text{NO}_4$ ($\text{M}+\text{H}$) $^+$: 390.1705 found: 390.1700.

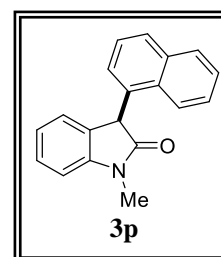
Synthesis of 1-benzyl-3-(naphthalen-1-yl)-1,3-dihydro-2H-indol-2-one (**3o**)^{8a}

To a solution of 1-benzyl-3-diazo-1,3-dihydro-2H-indol-2-one (**1a**) (100 mg, 0.40 mmol) and 1-naphthaldehyde (**2n**) (70 mg, 0.44 mmol) in CH_2Cl_2 (5 mL) was added 20 mol% of $\text{BF}_3 \cdot \text{OEt}_2$. The reaction mixture was stirred at 0°C under the open-air atmosphere to afford (**3o**) (99 mg, 71%) as a white semi-solid according to general procedure. $R_f = 0.43$ (EtOAc/hexane = 1:4, v/v); mp 65-66 °C; IR (neat): ν_{\max} 2926, 1706, 1607, 1346, 1170, 1017, 733 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) $\delta = 4.97$ -5.28 (m, 2H, CH_2), 5.68 (bs, 1H, CH), 6.92-7.18 (m, 4H, ArH), 7.25-7.74 (m, 9H, ArH), 7.86-7.95 (m, 2H, ArH), 8.45 (bs, 1H, ArH) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) $\delta = 44.2, 52.3, 109.4, 122.9, 124.2, 125.3, 125.6, 126.0, 126.2, 126.3, 126.6, 127.5, 127.8, 128.3, 128.9, 129.6, 132.9, 133.6, 134.3, 134.4, 136.1, 143.7, 176.2$ ppm; HRMS (ESI) Calculated for $\text{C}_{25}\text{H}_{19}\text{NO}$ ($\text{M}+\text{H}$) $^+$: 350.1545 found: 350.1540.



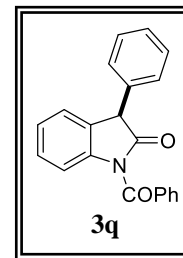
Synthesis of 1-Methyl-3-(naphthalen-1-yl)-1,3-dihydro-2H-indol-2-one (**3p**)^{8b}

To a solution of 3-diazo-1-methyl-1,3-dihydro-2H-indol-2-one (**1b**) (100 mg, 0.58 mmol) and 1-naphthaldehyde (**2n**) (99 mg, 0.64 mmol) in CH_2Cl_2 (5 mL) was added 20 mol% of $\text{BF}_3 \cdot \text{OEt}_2$. The reaction mixture was stirred at 0°C under the open-air atmosphere to afford (**3p**) (101 mg, 64%) as a white semi-solid according to general procedure. $R_f = 0.57$ (EtOAc/hexane = 1:4, v/v); mp 153-154 °C; IR (neat): ν_{\max} 3053, 1711, 1610, 1470, 1346, 752 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) $\delta = 3.39$ (s, 3H, CH_3), 5.57 (bs, 1H, CH), 6.98-7.69 (m, 10H, ArH), 7.76 (bs, 1H, ArH) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) $\delta = 26.6, 52.3, 108.4, 122.9, 124.1, 124.8, 125.6, 126.0, 126.6, 127.6, 127.7, 127.9, 128.4, 128.6, 129.0, 129.5, 134.4, 144.6, 176.2$ ppm; HRMS (ESI) Calculated for $\text{C}_{19}\text{H}_{15}\text{NO}$ ($\text{M}+\text{Na}$) $^+$: 296.1051 found: 296.1054.



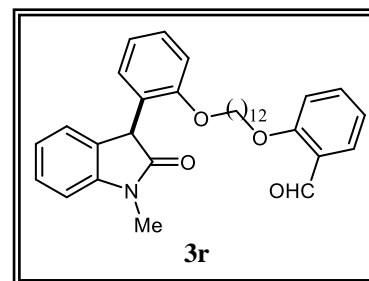
Synthesis of 1-benzoyl-3-phenyl-1,3-dihydro-2H-indol-2-one (**3q**)

To a solution of 1-benzoyl-3-diazo-1,3-dihydro-2*H*-indol-2-one (**1c**) (100 mg, 0.38 mmol) and benzaldehyde (**2a**) (44 mg, 0.42 mmol) in CH₂Cl₂ (5 mL) was added 20 mol% of BF₃·OEt₂. The reaction mixture was stirred at 0°C under the open-air atmosphere to afford (**3q**) (72 mg, 61%) as a white solid according to general procedure. R_f = 0.43 (EtOAc/hexane = 1:4, v/v); mp 173-174 °C; IR (neat): ν_{max} 2924, 1746, 1681, 1597, 1462, 1278, 1151, 730 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ = 4.77 (s, 1H, CH), 7.17-7.37 (m, 10H, ArH), 7.45-7.50 (m, 1H, ArH), 7.60-7.62 (m, 2H, ArH), 7.86 (d, *J* = 8 Hz, 1H, ArH) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ = 52.6, 115.2, 125.2, 125.3, 128.09, 128.12, 128.3, 128.5, 128.9, 129.1, 129.3, 132.9, 134.1, 136.0, 141.0, 169.6, 175.3 ppm; HRMS (ESI) Calculated for C₂₁H₁₅NO₂ (M+H)⁺: 314.1181 found: 314.1178.



Synthesis of 2-((12-(2-(1-methyl-2-oxoindolin-3-yl)phenoxy)dodecyl)oxy)benzaldehyde (**3r**)

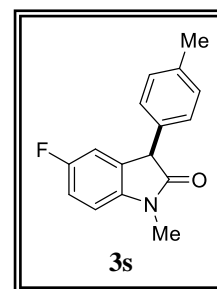
To a solution of 3-diazo-1-methyl-1,3-dihydro-2*H*-indol-2-one (**1b**) (100 mg, 0.58 mmol) and 2,2'-(dodecane-1,12-diylbis(oxy))dibenzaldehyde (**2o**) (119 mg, 0.29 mmol) in CH₂Cl₂ (5 mL) was added 20 mol% of BF₃·OEt₂. The reaction mixture was stirred at 0°C under the open-air atmosphere to afford (**3r**) (199 mg, 65%) as a white solid according to general procedure. R_f = 0.1 (EtOAc/hexane = 1:4, v/v); mp 64-65 °C; IR (neat): ν_{max} 2927, 1690, 1600, 1462, 1243, 753 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ = 1.15-1.49 (m, 18H, 9CH₂), 1.83-1.87 (m, 2H, CH₂), 3.28 (s, 3H, CH₃), 3.72 (s, 1H, 1/2CH₂), 3.86-3.88 (m, 1H, 1/2CH₂), 4.06-4.09 (m, 2H, CH₂), 4.72 (s, 1H, CH), 6.81-7.01 (m, 6H, ArH), 7.18-7.26 (m, 4H, ArH), 7.51-7.55 (m, 1H, ArH), 7.83 (d, *J* = 7.6 Hz, 1H, ArH), 10.52 (s, 1H, CHO) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ = 25.9, 26.1, 26.4, 29.1, 29.2, 29.36, 29.43, 29.5, 29.58, 29.6, 68.0, 68.6, 107.5, 111.8, 112.5, 120.5, 120.6, 122.3, 123.8, 125.0, 125.6, 127.7, 128.3, 128.6, 129.0, 129.9, 131.0, 135.9, 144.3, 156.9, 161.6, 176.8, 189.9 ppm; HRMS (ESI) Calculated for C₃₄H₄₁NO₄ (M+H)⁺: 528.3114 found: 528.3109.



Synthesis of 5-fluoro-1-methyl-3-(4-methylphenyl)-1,3-dihydro-2*H*-indol-2-one (**3s**)

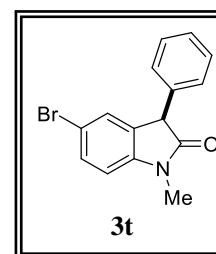
To a solution of 3-diazo-5-fluoro-1-methyl-1,3-dihydro-2*H*-indol-2-one (**1d**) (100 mg, 0.52 mmol) and 4-methylbenzaldehyde (**2b**) (69 mg, 0.58 mmol) in CH₂Cl₂ (5 mL) was added 20 mol% of BF₃·OEt₂. The reaction mixture was stirred at 0°C under the open-air atmosphere to afford (**3s**) (110 mg, 83%) as a white solid according to general procedure. R_f = 0.2

(EtOAc/hexane = 1:4, v/v); mp 156-157 °C; IR (neat): ν_{\max} 2925, 1703, 1612, 1489, 1345, 1268, 1123, 814 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ = 2.38 (s, 3H, CH_3), 3.28 (s, 3H, CH_3), 4.61 (s, 1H, CH), 6.84-6.87 (m, 1H, ArH), 6.95-6.97 (m, 1H, ArH), 7.04-7.21 (m, 5H, ArH) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ = 21.2, 26.6, 52.0, 108.6 (d, J = 8 Hz), 113.1 (d, J = 25 Hz), 114.6 (d, J = 24 Hz), 128.3, 129.7, 130.7 (d, J = 9 Hz), 133.1, 137.5, 140.5, 159.3 (d, J = 239 Hz), 175.8 ppm; HRMS (ESI) Calculated for $\text{C}_{16}\text{H}_{14}\text{FNO}$ ($\text{M}+\text{H}$) $^+$: 256.1138 found: 256.1139.



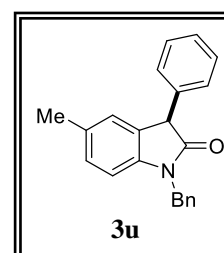
Synthesis of 5-bromo-1-methyl-3-phenyl-1,3-dihydro-2H-indol-2-one (3t)

To a solution of 5-bromo-3-diazo-1-methyl-1,3-dihydro-2H-indol-2-one (**1e**) (100 mg, 0.40 mmol) and benzaldehyde (**2a**) (46 mg, 0.44 mmol) in CH_2Cl_2 (5 mL) was added 20 mol% of $\text{BF}_3 \cdot \text{OEt}_2$. The reaction mixture was stirred at 0°C under the open-air atmosphere to afford (**3t**) (94 mg, 78%) as a white solid according to general procedure. R_f = 0.33 (EtOAc/hexane = 1:4, v/v); mp 177-178 °C; IR (neat): ν_{\max} 2923, 1695, 1599, 1485, 1337, 1095, 725 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ = 3.28 (s, 3H, CH_3), 4.64 (s, 1H, CH), 6.82 (d, J = 8.4 Hz, 1H, ArH), 7.22-7.24 (m, 2H, ArH), 7.30-7.41 (m, 4H, ArH), 7.49 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H, ArH) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ = 26.6, 52.0, 109.7, 115.4, 127.9, 128.2, 128.4, 129.1, 130.9, 131.3, 135.9, 143.5, 175.4 ppm; HRMS (ESI) Calculated for $\text{C}_{15}\text{H}_{12}^{79}\text{BrNO}$ ($\text{M}+\text{H}$) $^+$: 302.0181 found: 302.0183.



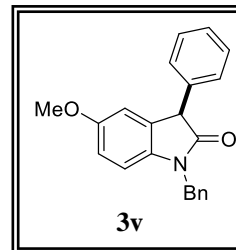
Synthesis of 1-benzyl-5-methyl-3-phenyl-1,3-dihydro-2H-indol-2-one (3u)⁹

To a solution of 1-benzyl-3-diazo-5-methyl-1,3-dihydro-2H-indol-2-one (**1f**) (100 mg, 0.38 mmol) and benzaldehyde (**2a**) (44 mg, 0.42 mmol) in CH_2Cl_2 (5 mL) was added 20 mol% of $\text{BF}_3 \cdot \text{OEt}_2$. The reaction mixture was stirred at 0°C under the open-air atmosphere to afford (**3u**) (109 mg, 92%) as a white solid according to general procedure. R_f = 0.49 (EtOAc/hexane = 1:4, v/v); mp 97-98 °C; IR (neat): ν_{\max} 2920, 1705, 1606, 1493, 1341, 1283, 698 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ = 2.34 (s, 3H, CH_3), 4.76 (s, 1H, CH), 5.01 (ABq, $\Delta\delta_{AB}$ = 0.1, J = 15.6 Hz, 2H, CH_2), 6.76 (d, J = 7.6 Hz, 1H, ArH), 7.06-7.09 (m, 2H, ArH), 7.32-7.44 (m, 10H, ArH) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ = 21.1, 44.0, 52.3, 109.0, 126.0, 127.4, 127.66, 127.67, 128.57, 128.64, 128.9, 129.0, 129.1, 132.4, 136.1, 137.1, 141.2, 176.2 ppm; HRMS (ESI) Calculated for $\text{C}_{22}\text{H}_{19}\text{NO}$ ($\text{M}+\text{H}$) $^+$: 314.1545 found: 314.1546.



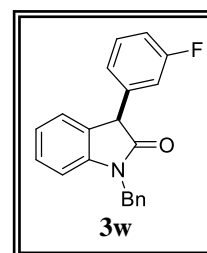
Synthesis of 1-benzyl-5-methoxy-3-phenyl-1,3-dihydro-2H-indol-2-one (**3v**)⁹

To a solution of 1-benzyl-3-diazo-5-methoxy-1,3-dihydro-2H-indol-2-one (**1g**) (100 mg, 0.36 mmol) and benzaldehyde (**2a**) (42 mg, 0.40 mmol) in CH₂Cl₂ (5 mL) was added 20 mol% of BF₃·OEt₂. The reaction mixture was stirred at 0°C under the open-air atmosphere to afford (**3v**) (101 mg, 85%) as a white solid according to general procedure. R_f = 0.31 (EtOAc/hexane = 1:4, v/v); mp 86-87 °C; IR (neat): ν_{max} 2926, 1702, 1600, 1489, 1341, 1176, 1027, 728 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ = 3.76 (s, 3H, CH₃), 4.75 (s, 1H, CH), 4.98 (ABq, Δδ_{AB} = 0.09, J = 15.6 Hz, 2H, CH₂), 6.72-6.84 (m, 3H, ArH), 7.28-7.40 (m, 10H, ArH) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ = 44.1, 52.6, 55.8, 109.6, 112.3, 112.9, 127.4, 127.7, 128.5, 128.8, 129.0, 130.3, 136.0, 136.8, 137.1, 156.2, 175.9 ppm; HRMS (ESI) Calculated for C₂₂H₁₉NO₂ (M+H)⁺: 330.1494 found: 330.1484.



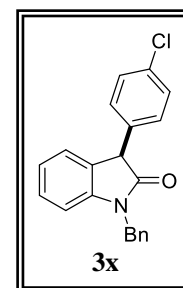
Synthesis of 1-benzyl-3-(3-fluorophenyl)-1,3-dihydro-2H-indol-2-one (**3w**)

To a solution of 1-benzyl-3-diazo-1,3-dihydro-2H-indol-2-one (**1a**) (100 mg, 0.40 mmol) and 3-fluorobenzaldehyde (**2p**) (55 mg, 0.44 mmol) in CH₂Cl₂ (5 mL) was added 20 mol% of BF₃·OEt₂. The reaction mixture was stirred at 0°C under the open-air atmosphere to afford (**3w**) (84 mg, 66%) as a white solid according to general procedure. R_f = 0.39 (EtOAc/hexane = 1:4, v/v); mp 141-142 °C; IR (neat): ν_{max} 2927, 1708, 1608, 1478, 1348, 1261, 1018, 734 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ = 4.70 (s, 1H, CH), 4.94 (ABq, Δδ_{AB} = 0.07, J = 15.6 Hz, 2H, CH₂), 6.80 (d, J = 8.0 Hz, 1H, ArH), 6.92 (d, J = 9.6 Hz, 1H, ArH), 6.97-7.06 (m, 3H, ArH), 7.15-7.35 (m, 8H, ArH) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ = 44.1, 51.7, 109.4, 114.7 (d, J = 21 Hz), 115.5 (d, J = 22 Hz), 122.9, 124.3 (d, J = 3 Hz), 125.2, 127.4, 127.8, 128.2, 128.6, 128.9, 130.4 (d, J = 9 Hz), 135.8, 139.0 (d, J = 7 Hz), 143.6, 163.1 (d, J = 245 Hz), 175.5 ppm; HRMS (ESI) Calculated for C₂₁H₁₆FNO (M+H)⁺: 318.1294 found: 318.1297.



Synthesis of 1-benzyl-3-(4-chlorophenyl)-1,3-dihydro-2H-indol-2-one (**3x**)⁸

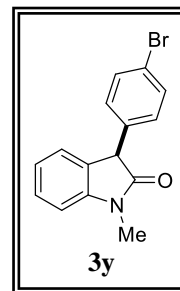
To a solution of 1-benzyl-3-diazo-1,3-dihydro-2H-indol-2-one (**1a**) (100 mg, 0.40 mmol) and 4-chlorobenzaldehyde (**2q**) (62 mg, 0.44 mmol) in CH₂Cl₂ (5 mL) was added 20 mol% of BF₃·OEt₂. The reaction mixture was stirred at 0°C under the open-air atmosphere to afford (**3x**) (93 mg, 70%) as a white solid according to general procedure. R_f = 0.35 (EtOAc/hexane = 1:4, v/v); mp 125-126 °C; IR (neat): ν_{max} 2923, 1709, 1608, 1489, 1352, 1018, 748 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ = 4.62 (s, 1H, CH), 4.85 (ABq, Δδ_{AB} = 0.10, J = 15.6 Hz, 2H, CH₂), 6.97-7.06 (m, 3H, ArH), 7.15-7.35 (m, 8H, ArH) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ = 44.1, 51.7, 109.4, 114.7 (d, J = 21 Hz), 115.5 (d, J = 22 Hz), 122.9, 124.3 (d, J = 3 Hz), 125.2, 127.4, 127.8, 128.2, 128.6, 128.9, 130.4 (d, J = 9 Hz), 135.8, 139.0 (d, J = 7 Hz), 143.6, 163.1 (d, J = 245 Hz), 175.5 ppm; HRMS (ESI) Calculated for C₂₁H₁₆ClNO (M+H)⁺: 318.1044 found: 318.1047.



CH₂), 6.61 (d, *J* = 8.4 Hz, 1H, ArH), 7.06-7.25 (m, 12H, ArH) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ = 44.1, 52.1, 110.2, 125.6, 127.3, 127.9, 128.0, 128.2, 128.35, 128.44, 128.9, 129.2, 130.6, 135.5, 136.0, 142.1, 175.7 ppm; HRMS (ESI) Calculated for C₂₁H₁₆³⁵CINO (M+H)⁺: 334.0999 found: 334.0999.

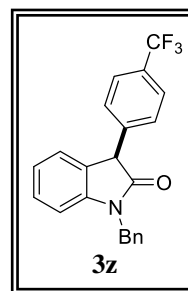
Synthesis of 3-(4-bromophenyl)-1-methyl-1,3-dihydro-2H-indol-2-one (**3y**)¹⁰

To a solution of 3-diazo-1-methyl-1,3-dihydro-2H-indol-2-one (**1b**) (100 mg, 0.58 mmol) and 4-bromobenzaldehyde (**2r**) (118 mg, 0.44 mmol) in CH₂Cl₂ (5 mL) was added 20 mol% of BF₃·OEt₂. The reaction mixture was stirred at 0°C under the open-air atmosphere to afford (**3y**) (125 mg, 72%) as a white solid according to general procedure. *R*_f = 0.26 (EtOAc/hexane = 1:4, v/v); mp 167-168 °C; IR (neat): ν_{max} 2921, 1688, 1606, 1484, 1345, 1081, 750 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ = 3.22 (s, 3H, CH₃), 4.54 (s, 1H, CH), 6.89 (d, *J* = 7.6 Hz, 1H, ArH), 7.04-7.14 (m, 4H, ArH), 7.33 (t, *J* = 7.6 Hz, 1H, ArH), 7.43 (d, *J* = 7.6 Hz, 2H, ArH) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ = 26.6, 51.4, 108.4, 121.7, 122.9, 125.1, 128.2, 128.8, 130.2, 132.0, 135.7, 144.5, 175.4 ppm; HRMS (ESI) Calculated for C₁₅H₁₂⁷⁹BrNO (M+H)⁺: 302.0181 found: 302.0179.



Synthesis of 1-benzyl-3-[4-(trifluoromethyl)phenyl]-1,3-dihydro-2H-indol-2-one (**3z**)¹¹

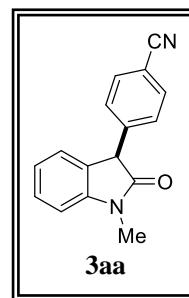
To a solution of 1-benzyl-3-diazo-1,3-dihydro-2H-indol-2-one (**1a**) (100 mg, 0.40 mmol) and 4-(trifluoromethyl)benzaldehyde (**2s**) (77 mg, 0.44 mmol) in CH₂Cl₂ (5 mL) was added 20 mol% of BF₃·OEt₂. The reaction mixture was stirred at 0°C under the open-air atmosphere to afford (**3z**) (110 mg, 75%) as a white solid according to general procedure. *R*_f = 0.43 (EtOAc/hexane = 1:4, v/v); mp 110-111 °C; IR (neat): ν_{max} 2925, 1712, 1611, 1486, 1324, 1118, 745 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ = 4.77 (s, 1H, CH), 4.95 (ABq, $\Delta\delta_{AB}$ = 0.08, *J* = 15.6 Hz, 2H, CH₂), 6.83 (d, *J* = 7.6 Hz, 1H, ArH), 7.03-7.07 (m, 1H, ArH), 7.15 (d, *J* = 7.2 Hz, 1H, ArH), 7.23-7.37 (m, 8H, ArH), 7.61 (d, *J* = 8.0 Hz, 2H, ArH) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ = 44.1, 51.8, 109.5, 123.0, 124.1 (q, *J* = 270 Hz, CF₃), 125.2, 125.9 (q, *J* = 4 Hz), 127.4, 127.8, 127.9, 128.8, 128.9, 130.0 (q, *J* = 32 Hz), 135.7, 140.7, 143.6, 175.3 ppm; HRMS (ESI) Calculated for C₂₂H₁₆F₃NO (M+H)⁺: 368.1262 found: 368.1268.



Synthesis of 4-(1-methyl-2-oxo-2,3-dihydro-1H-indol-3-yl)benzotrile (**3aa**)¹²

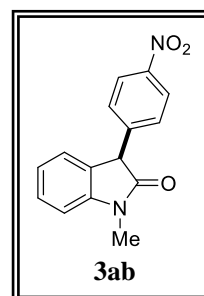
To a solution of 3-diazo-1-methyl-1,3-dihydro-2H-indol-2-one (**1b**) (100 mg, 0.58 mmol) and 4-formylbenzotrile (**2t**) (84 mg, 0.64 mmol) in CH₂Cl₂ (5 mL) was added 20 mol% of BF₃·OEt₂. The reaction mixture was stirred at 0°C under the open-air atmosphere to afford

(3aa) (98 mg, 68%) as a white solid according to general procedure. $R_f = 0.3$ (EtOAc/hexane = 1:4, v/v); mp 161-162 °C; IR (neat): ν_{\max} 2918, 2221, 1695, 1607, 1469, 1344, 1080, 749 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) $\delta = 3.26$ (s, 3H, CH_3), 4.67 (s, 1H, CH), 6.93 (d, $J = 8.0$ Hz, 1H, ArH), 7.09-7.16 (m, 2H, ArH), 7.34-7.40 (m, 3H, ArH), 7.63 (d, $J = 8.4$ Hz, 2H, ArH) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) $\delta = 26.6, 51.8, 108.6, 111.6, 118.6, 123.1, 125.1, 127.3, 129.1, 129.3, 132.6, 141.9, 144.5, 174.6$ ppm; HRMS (ESI) Calculated for $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}$ (M-H) $^+$: 247.0871 found: 247.0888.



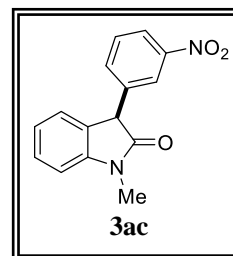
Synthesis of 1-methyl-3-(4-nitrophenyl)-1,3-dihydro-2H-indol-2-one (**3ab**)¹³

To a solution of 3-diazo-1-methyl-1,3-dihydro-2H-indol-2-one (**1b**) (100 mg, 0.58 mmol) and benzaldehyde (**2u**) (96 mg, 0.64 mmol) in CH_2Cl_2 (5 mL) was added 20 mol% of $\text{BF}_3 \cdot \text{OEt}_2$. The reaction mixture was stirred at 0°C under the open-air atmosphere to afford (**3ab**) (110 mg, 71%) as a white solid according to general procedure. $R_f = 0.21$ (EtOAc/hexane = 1.5:3.5, v/v); mp 186-187 °C; IR (neat): ν_{\max} 2922, 1706, 1607, 1488, 1353, 1018, 746 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) $\delta = 3.26$ (s, 3H, CH_3), 4.61 (s, 1H, CH), 6.90 (d, $J = 7.6$ Hz, 1H, ArH), 7.07 (t, $J = 7.6$ Hz, 1H, ArH), 7.16-7.21 (m, 3H, ArH), 7.28-7.35 (m, 3H, ArH) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) $\delta = 26.6, 66.1, 109.0, 122.7, 123.3, 125.5, 125.7, 129.0, 131.0, 143.3, 143.9, 147.9, 173.0$ ppm; HRMS (ESI) Calculated for $\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_3$ (M+H) $^+$: 269.0926 found: 269.0921.



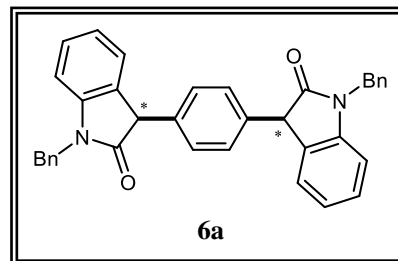
Synthesis of 1-methyl-3-(3-nitrophenyl)-1,3-dihydro-2H-indol-2-one (**3ac**)¹⁴

To a solution of 3-diazo-1-methyl-1,3-dihydro-2H-indol-2-one (**1a**) (100 mg, 0.58 mmol) and 3-nitrobenzaldehyde (**2v**) (96 mg, 0.64 mmol) in CH_2Cl_2 (5 mL) was added 20 mol% of $\text{BF}_3 \cdot \text{OEt}_2$. The reaction mixture was stirred at 0°C under the open-air atmosphere to afford (**3ac**) (98 mg, 63%) as a white solid according to general procedure. $R_f = 0.21$ (EtOAc/hexane = 1.5:3.5, v/v); mp 150-151 °C; IR (neat): ν_{\max} 2935, 1724, 1610, 1520, 1344, 1093, 1013, 737 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) $\delta = 3.32$ (s, 3H, CH_3), 4.77 (s, 1H, CH), 6.99 (d, $J = 7.6$ Hz, 1H, ArH), 7.16-7.22 (m, 2H, ArH), 7.44 (t, $J = 7.6$ Hz, 1H, ArH), 7.56-7.60 (m, 1H, ArH), 7.66-7.68 (m, 1H, ArH), 8.09 (s, 1H, ArH), 8.21 (dd, $J_1 = 8.0$ Hz, $J_2 = 0.8$ Hz, 1H, ArH) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) $\delta = 26.7, 51.4, 108.7, 122.8, 123.2, 123.3, 125.1, 127.2, 129.2, 129.9, 135.0, 138.6, 144.5, 148.6, 174.8$ ppm; HRMS (ESI) Calculated for $\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_3$ (M+H) $^+$: 269.0926 found: 269.0919.



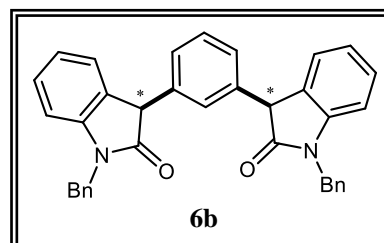
Synthesis of 3,3'-(1,4-phenylene)bis(1-benzyl-1,3-dihydro-2H-indol-2-one) (**6a**)

To a solution of 1-benzyl-3-diazo-1,3-dihydro-2H-indol-2-one (**1a**) (100 mg, 0.40 mmol) and terephthalaldehyde (**5a**) (27 mg, 0.20 mmol) in CH₂Cl₂ (5 mL) was added 20 mol% of BF₃·OEt₂. The reaction mixture was stirred at 0°C under the open-air atmosphere to afford (**6a**) (71 mg, 68%) as a white solid according to general procedure. R_f = 0.35 (EtOAc/hexane = 2:3, v/v); mp 207-209 °C; IR (neat): ν_{max} 2924, 1707, 1609, 1480, 1350, 741 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ = 4.62-4.63 (m, 2H, 2CH), 4.78-4.94 (m, 4H, 2CH₂), 6.69-6.72 (m, 2H, ArH), 6.93-6.96 (m, 2H, ArH), 7.08-7.25 (m, 18H, ArH) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ = 44.0, 51.7, 109.2, 122.8, 125.27, 125.32, 127.4, 127.7, 128.4, 128.7, 128.8, 129.1, 135.88, 135.91, 136.04, 136.1, 143.56, 143.59, 175.97, 176.0 ppm; HRMS (ESI) Calculated for C₃₆H₂₈N₂O₂ (M+H)⁺: 521.2229 found: 521.2220.



Synthesis of 3,3'-(1,3-phenylene)bis(1-benzyl-1,3-dihydro-2H-indol-2-one) (**6b**)

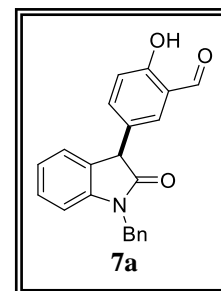
To a solution of 1-benzyl-3-diazo-1,3-dihydro-2H-indol-2-one (**1a**) (100 mg, 0.40 mmol) and isophthalaldehyde (**5b**) (27 mg, 0.20 mmol) in CH₂Cl₂ (5 mL) was added 20 mol% of BF₃·OEt₂. The reaction mixture was stirred at 0°C under the open-air atmosphere to afford (**6b**) (48 mg, 46%) as a white solid according to general procedure. R_f = 0.35 (EtOAc/hexane = 2:3, v/v); mp 187-188 °C; IR (neat): ν_{max} 2924, 1705, 1609, 1489, 1352, 1174, 739 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ = 4.72 (s, 1H, CH), 4.79 (s, 1H, CH), 4.92-5.06 (m, 4H, 2CH₂), 6.82-6.85 (m, 2H, ArH), 7.06-7.09 (m, 2H, ArH), 7.19-7.37 (m, 18H, ArH) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ = 44.0, 51.93, 51.94, 109.24, 109.28, 122.86, 122.92, 125.30, 125.33, 127.1, 127.36, 127.38, 127.67, 127.70, 127.73, 128.4, 128.5, 128.6, 128.9, 129.5, 129.6, 130.2, 135.86, 135.89, 137.31, 137.32, 143.5, 175.9, 176.0 ppm; HRMS (ESI) Calculated for C₃₆H₂₈N₂O₂ (M+Na)⁺: 543.2048 found: 543.2081.



Synthesis of 5-(1-benzyl-2-oxo-2,3-dihydro-1H-indol-3-yl)-2-hydroxybenzaldehyde (**7a**)

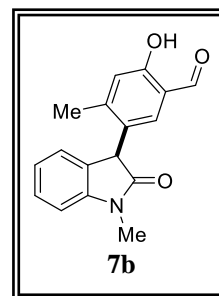
To a solution of 1-benzyl-3-diazo-1,3-dihydro-2H-indol-2-one (**1a**) (100 mg, 0.40 mmol) and 2-hydroxybenzaldehyde (**2x**) (54 mg, 0.44 mmol) in CH₂Cl₂ (5 mL) was added 20 mol% of BF₃·OEt₂. The reaction mixture was stirred at 0°C under the open-air atmosphere to afford (**7a**) (103 mg, 75%) as a white solid according to general procedure. R_f = 0.41 (EtOAc/hexane = 2:3, v/v); mp 157-158 °C; IR (neat): ν_{max} 3057, 1707, 1655, 1609, 1482,

1350, 1278, 1195, 737 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ = 4.75 (s, 1H, CH), 4.99 (ABq, $\Delta\delta_{AB}$ = 0.05, J = 15.6 Hz, 2H, CH_2), 6.89 (d, J = 7.6 Hz, 1H, ArH), 7.03 (d, J = 8.8 Hz, 1H, ArH), 7.11 (t, J = 7.6 Hz, 1H, ArH), 7.23 (d, J = 7.2 Hz, 1H, ArH), 7.28-7.37 (m, 6H, ArH), 7.42-7.45 (m, 1H, ArH), 7.49 (d, J = 2.4 Hz, 1H, ArH), 9.88 (s, 1H, CHO), 11.05 (s, 1H, OH) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ = 44.1, 50.8, 109.6, 118.5, 120.7, 123.1, 125.2, 127.5, 127.9, 128.0, 128.2, 128.8, 128.9, 133.4, 135.8, 137.0, 143.6, 161.2, 175.8, 196.5 ppm; HRMS (ESI) Calculated for $\text{C}_{22}\text{H}_{17}\text{NO}_3$ ($\text{M}+\text{H}$) $^+$: 344.1287 found: 344.1288.



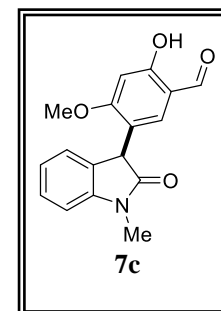
Synthesis of 2-hydroxy-4-methyl-5-(1-methyl-2-oxo-2,3-dihydro-1H-indol-3-yl)benzaldehyde (7b)

To a solution of 3-diazo-1-methyl-1,3-dihydro-2H-indol-2-one (**1b**) (100 mg, 0.58 mmol) and 2-hydroxy-4-methylbenzaldehyde (**2y**) (87 mg, 0.64 mmol) in CH_2Cl_2 (5 mL) was added 20 mol% of $\text{BF}_3\cdot\text{OEt}_2$. The reaction mixture was stirred at 0°C under the open-air atmosphere to afford (**7b**) (132 mg, 81%) as a white solid according to general procedure. R_f = 0.22 (EtOAc/hexane = 2:3, v/v); mp 183-184 $^\circ\text{C}$; IR (neat): ν_{max} 2924, 1704, 1651, 1613, 1464, 1345, 1264, 740 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ = 2.46 (bs, 3H, CH_3), 3.32 (s, 3H, CH_3), 4.84 (s, 1H, CH), 6.91-7.13 (m, 5H, ArH), 7.30-7.43 (m, 1H, ArH), 9.74 (s, 1H, CHO), 10.97 (s, 1H, OH) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ = 20.7, 26.5, 108.4, 119.1, 119.8, 123.0, 124.5, 127.5, 128.4, 128.7, 144.4, 148.4, 160.9, 175.8, 195.7 ppm; HRMS (ESI) Calculated for $\text{C}_{17}\text{H}_{15}\text{NO}_3$ ($\text{M}+\text{H}$) $^+$: 282.1130 found: 282.1124.



Synthesis of 2-hydroxy-4-methoxy-5-(1-methyl-2-oxo-2,3-dihydro-1H-indol-3-yl)benzaldehyde (7c)

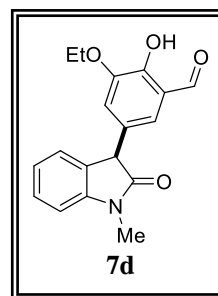
To a solution of 3-diazo-1-methyl-1,3-dihydro-2H-indol-2-one (**1b**) (100 mg, 0.58 mmol) and 2-hydroxy-4-methoxybenzaldehyde (**2z**) (97 mg, 0.64 mmol) in CH_2Cl_2 (5 mL) was added 20 mol% of $\text{BF}_3\cdot\text{OEt}_2$. The reaction mixture was stirred at 0°C under the open-air atmosphere to afford (**7c**) (146 mg, 85%) as a white solid according to general procedure. R_f = 0.33 (EtOAc/hexane = 2:3, v/v); mp 165-166 $^\circ\text{C}$; IR (neat): ν_{max} 2920, 1694, 1640, 1463, 1349, 1204, 745 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ = 3.34 (s, 3H, CH_3), 3.85 (s, 3H, CH_3), 4.87 (s, 1H, CH), 6.50 (s, 1H, ArH), 6.92-7.11 (m, 3H, ArH), 7.26-7.36 (m, 2H, ArH), 9.69 (s, 1H, CHO), 11.57 (s, 1H, OH) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ = 26.5,



47.0, 56.3, 99.7, 108.0, 114.7, 118.7, 122.7, 124.0, 128.2, 129.0, 134.9, 144.2, 164.3, 164.6, 176.2, 194.4 ppm; HRMS (ESI) Calculated for C₁₇H₁₅NO₄ (M+H)⁺: 298.1079 found: 298.1055.

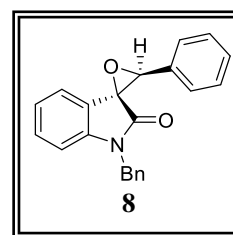
Synthesis of 4-ethoxy-5-(1-ethyl-2-oxo-2,3-dihydro-1*H*-indol-3-yl)-2-hydroxybenzaldehyde (**7d**)

To a solution of 3-diazo-1-methyl-1,3-dihydro-2*H*-indol-2-one (**1b**) (100 mg, 0.58 mmol) and 3-ethoxy-2-hydroxybenzaldehyde (**2aa**) (106 mg, 0.64 mmol) in CH₂Cl₂ (5 mL) was added 20 mol% of BF₃·OEt₂. The reaction mixture was stirred at 0 °C under the open-air atmosphere to afford (**7d**) (132 mg, 73%) as a white solid according to general procedure. R_f = 0.30 (EtOAc/hexane = 2:3, v/v); mp 143-144 °C; IR (neat): ν_{max} 2927, 1703, 1641, 1611, 1466, 1348, 1254, 739 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ = 1.49 (t, *J* = 6.8 Hz, 3H, CH₃), 3.28 (s, 3H, CH₃), 4.08-4.13 (m, 2H, CH₂), 5.22 (bs, 1H, CH), 6.45 (bs, 1H, ArH), 6.97-7.44 (m, 5H, ArH), 10.54 (bs, 1H, CHO), 12.36 (bs, 1H, OH) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ = 14.7, 26.7, 46.0, 64.8, 108.7, 118.5, 118.6, 123.0, 125.4, 127.1, 128.9, 130.0, 144.3, 147.5, 154.4, 174.9, 176.8, 195.6 ppm; HRMS (ESI) Calculated for C₁₈H₁₇NO₄ (M+H)⁺: 312.1236 found: 312.1214.



Synthesis of 1-benzyl-3'-phenylspiro[indole-3,2'-oxiran]-2(1*H*)-one (**8**)

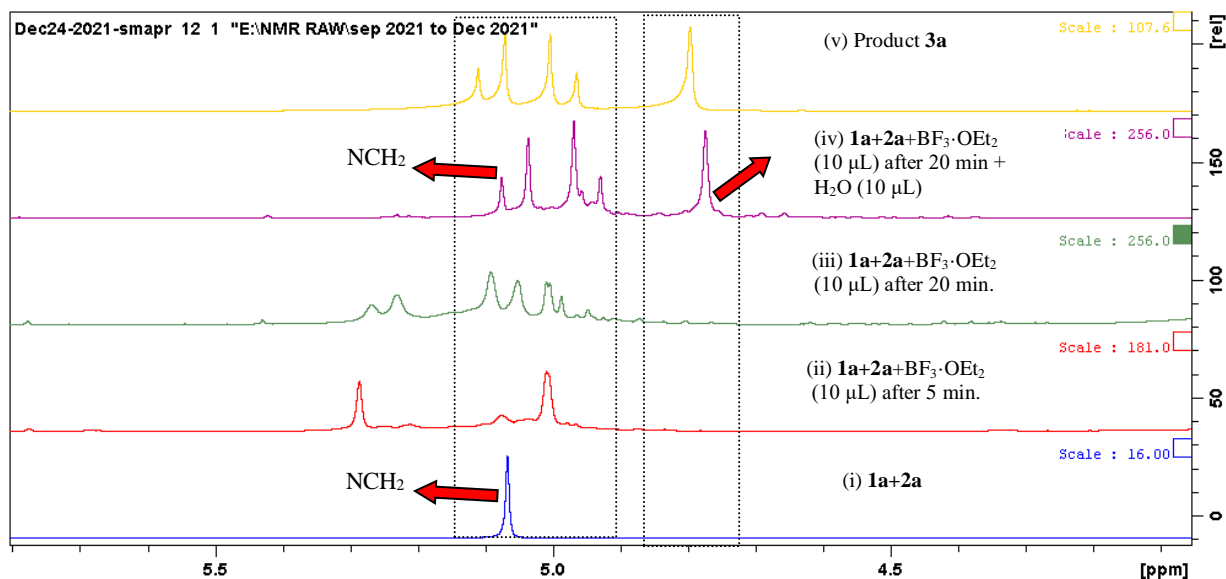
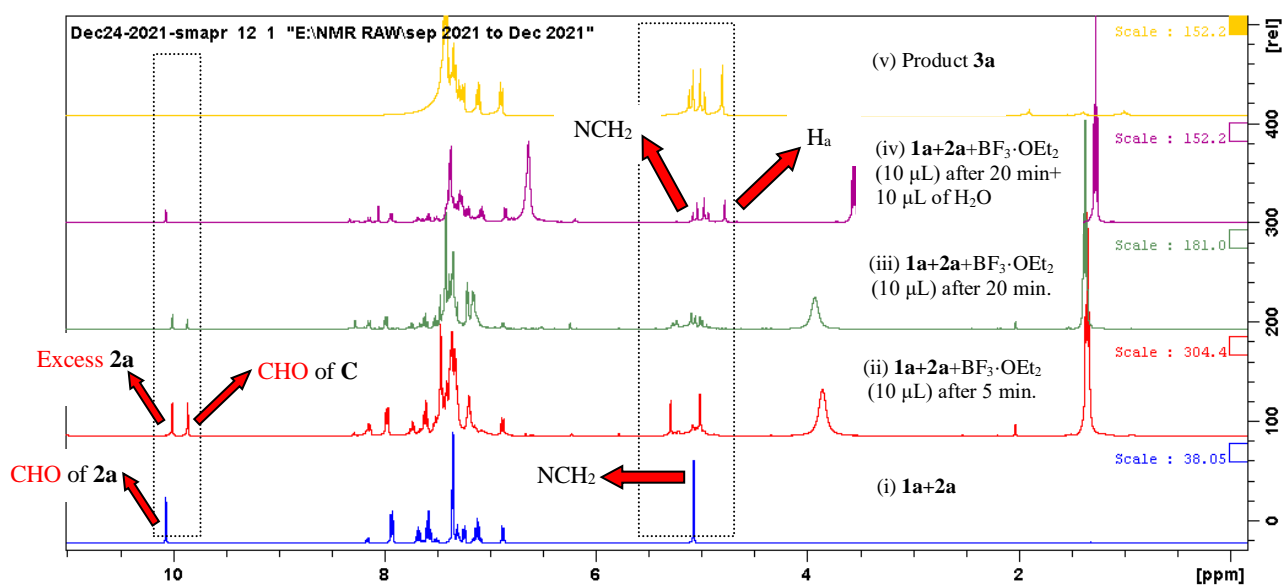
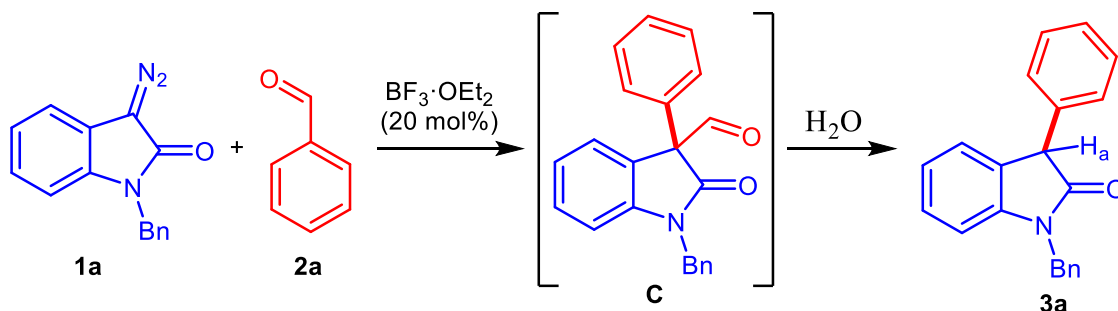
A solution of 1-benzyl-3-diazo-1,3-dihydro-2*H*-indol-2-one (**1a**) (100 mg, 0.40 mmol) in dry dichloroethane (5 mL) was added dropwise to a solution containing benzaldehyde (**2a**) (47 mg, 0.44 mmol) dissolved in dry DCE (5 mL) and rhodium(II) acetate (1 mol%) at 60 °C for the period of 2 h to afford (**8**) (120 mg, 92%) as a white solid. R_f = 0.42 (EtOAc/hexane = 1:4, v/v); mp 123-124 °C; IR (neat): ν_{max} 3054, 1726, 1614, 1461, 1354, 1176, 736 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ = 4.60 (s, 1H, CH), 4.71 (ABq, Δδ_{AB} = 0.15, *J* = 15.6 Hz, 2H, CH₂), 6.67 (d, *J* = 7.6 Hz, 1H, ArH), 6.94-6.98 (m, 1H, ArH), 7.10-7.32 (m, 10H, ArH), 7.52-7.54 (m, 2H, ArH) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ = 44.2, 62.0, 67.8, 109.8, 121.8, 122.8, 123.6, 127.5, 127.6, 127.8, 127.9, 128.87, 128.91, 130.2, 131.9, 135.6, 143.8, 170.1 ppm; HRMS (ESI) Calculated for C₂₂H₁₇NO₂ (M+Na)⁺: 350.1157 found: 350.1158.



NMR experiments for the reaction of **1a** and **2a**

To find out the insight into the mechanism, an experiment was planned in a NMR tube. Towards this, an equimolar amount of diazoamide **1a** and benzaldehyde **2a** was dissolved in CDCl₃ and the ¹H-NMR spectrum was recorded at different time intervals. Initially, -NCH₂

and -CHO protons appeared as a singlet at 5.07 and 10.06 ppm, respectively [Figure S1(i)]. A new aldehyde peak was observed at 9.85 ppm after the addition of 10 μ L of $\text{BF}_3 \cdot \text{OEt}_2$ into the NMR tube [Figure S1(ii), (iii)]. Then, the peak at 9.85 ppm disappeared after the addition of 10 μ L of water into the NMR tube and the formation of a singlet at 4.77 ppm [Figure S1(iv)] that is responsible for H_a proton of **3a**.



Expansion for NCH₂ peak

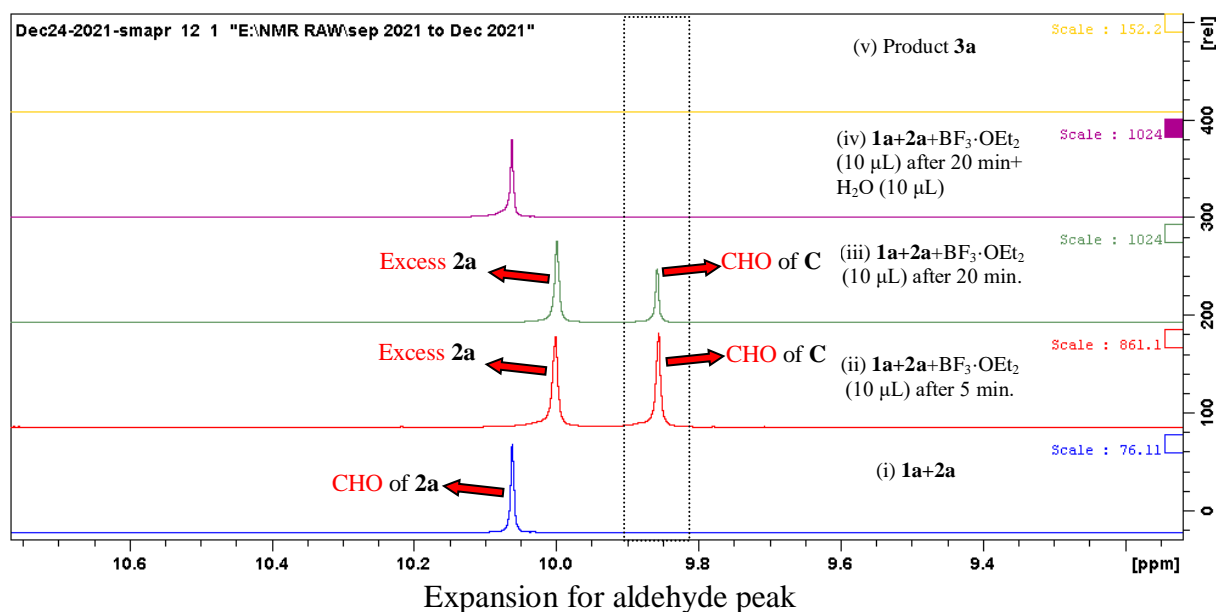


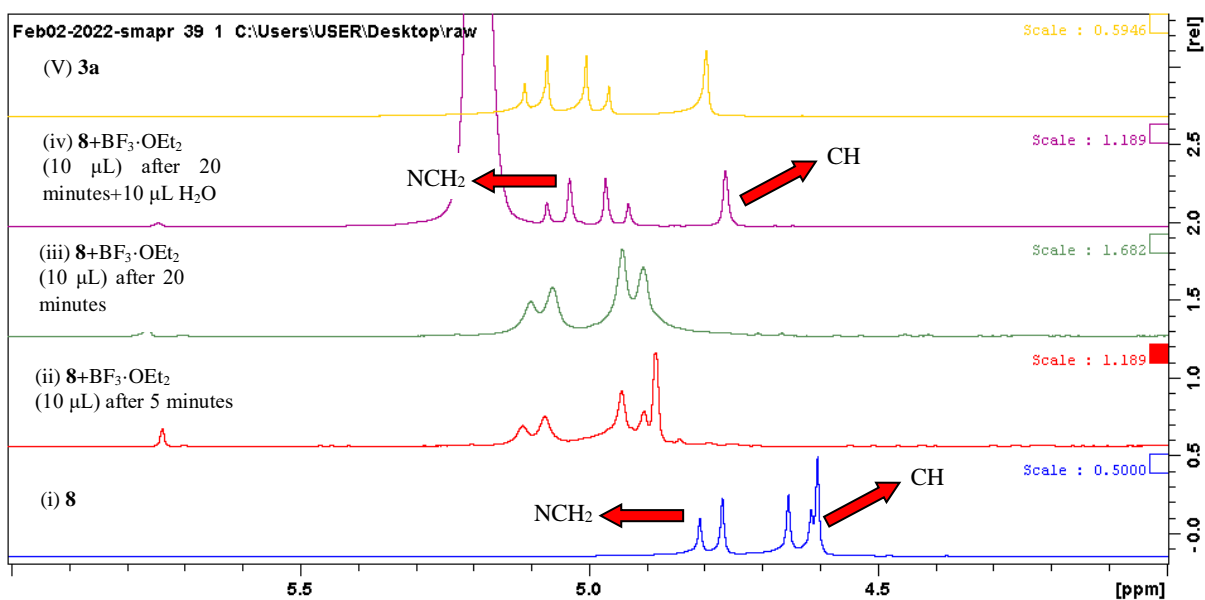
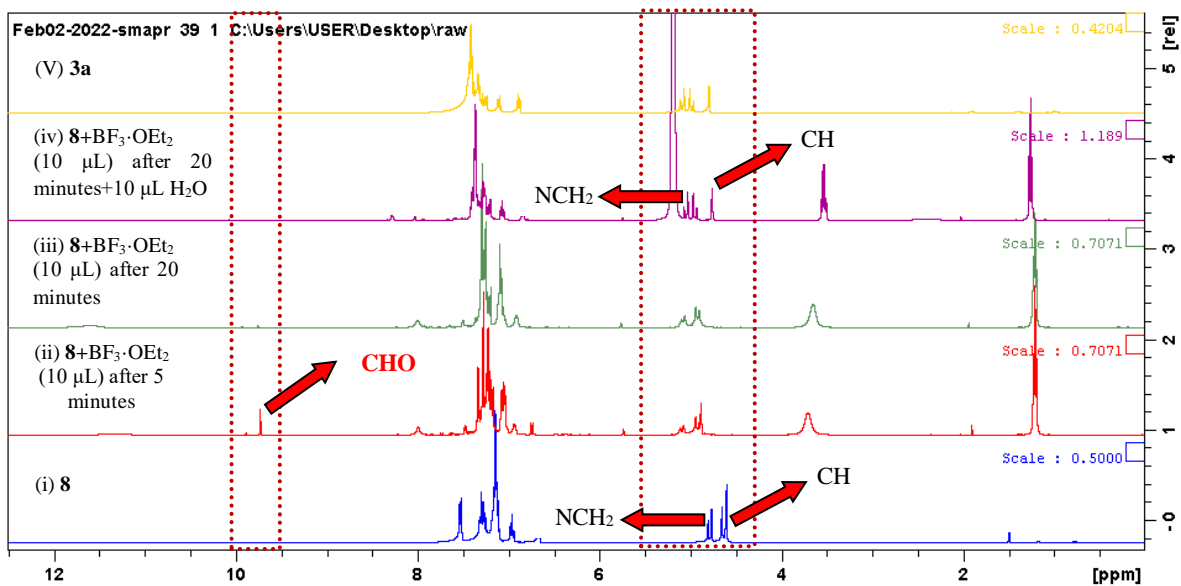
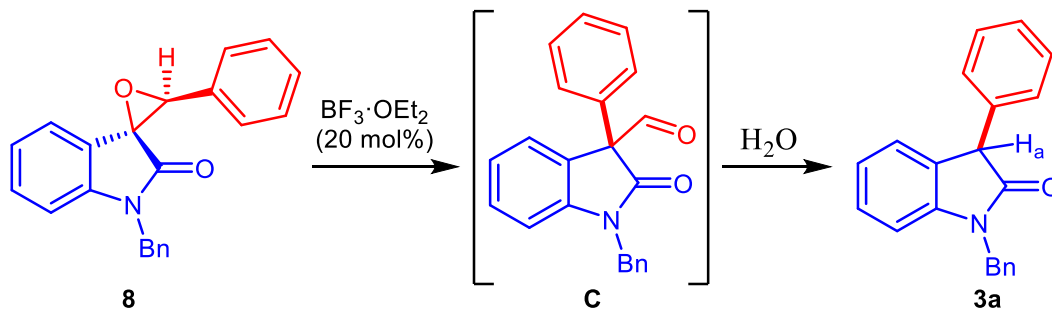
Figure S1. ¹H-NMR spectra of reaction mixture **3a** signals in CDCl₃

- (i) A mixture of diazoamide **1a** (10 mg) and benzaldehyde **2a** (5 mg)
- (ii) A mixture of diazoamide **1a** (10 mg), benzaldehyde **2a** (5 mg) and BF₃·OEt₂ (10 μL) after 5 minutes
- (iii) A mixture of diazoamide **1a** (10 mg), and benzaldehyde **2a** (5 mg) and BF₃·OEt₂ (10 μL) after 20 minutes
- (iv) A mixture of diazoamide **1a** (10 mg), benzaldehyde **2a** (5 mg), BF₃·OEt₂ (10 μL) and H₂O (10 μL)
- (v) Isolated product **3a**

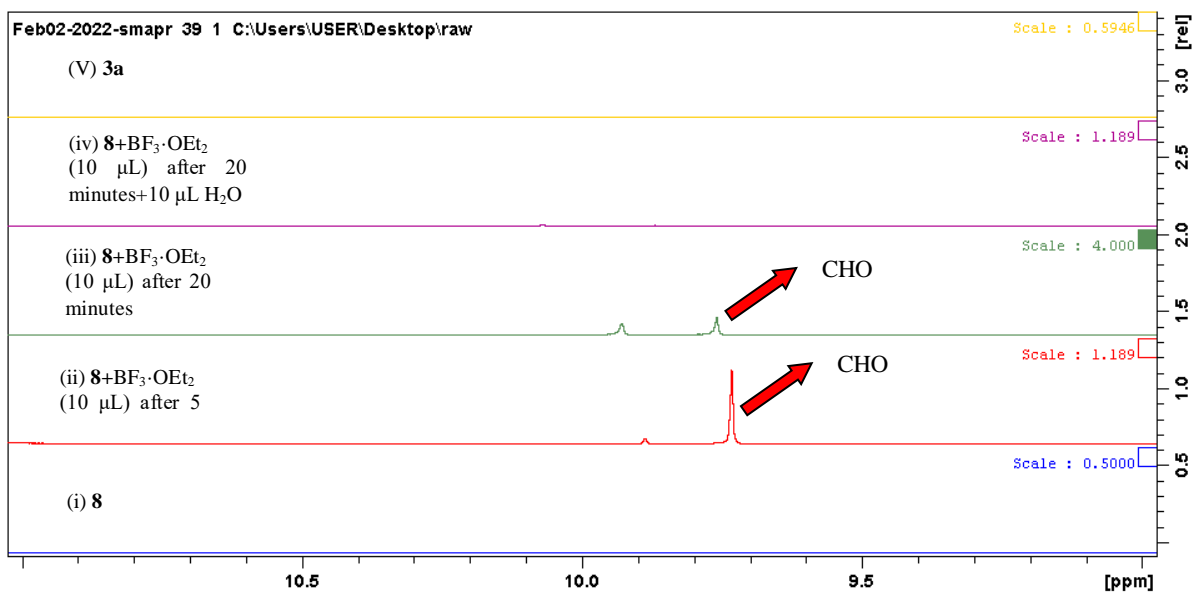
NMR experiments for the reaction of epoxide **8**

To find out the insight into the mechanism, an experiment was planned in a NMR tube. Towards this, spiro-indolooxirane **8** was dissolved in CDCl₃ and the ¹H-NMR spectrum was recorded at different time intervals. Initially, -NCH₂ and -CH protons appeared as an AB quartet and a singlet at 4.71 and 4.60 ppm, respectively [Figure S2(i)]. A new aldehyde peak was observed at 9.73 ppm after the addition of 10 μL of BF₃·OEt₂ into the NMR tube [Figure S2(ii), (iii)]. Then, the peak at 9.73 ppm disappeared after the addition of 10 μL of water into the NMR tube and the formation of a singlet at 4.78 ppm [Figure S2(iv)] that is responsible for H_a proton of **3a**.

H_a



Expansion for **NCH₂** peak



Expansion for aldehyde peak

Figure S2. ¹H-NMR spectra of reaction mixture **3a** signals in CDCl₃

(i) Epoxide **8**

(ii) A mixture of epoxide **8** (20 mg) and BF₃·OEt₂ (10 μL) after 5 minutes

(iii) A mixture of epoxide **8** (20 mg) and BF₃·OEt₂ (10 μL) after 20 minutes

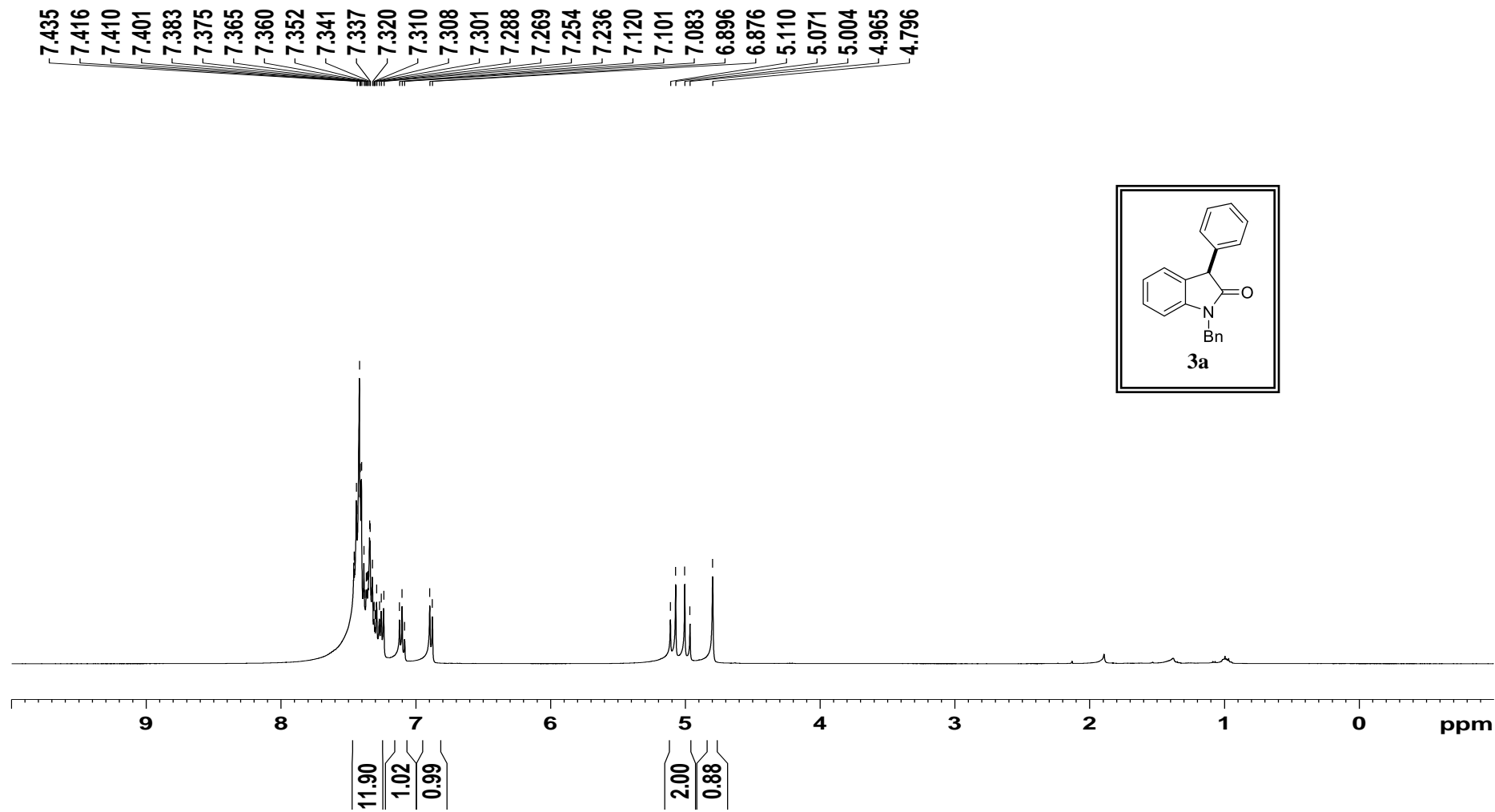
(iv) A mixture of epoxide **8** (20 mg) and BF₃·OEt₂ (10 μL) after 20 minutes and H₂O (10 μL)

(v) Isolated product **3a**

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

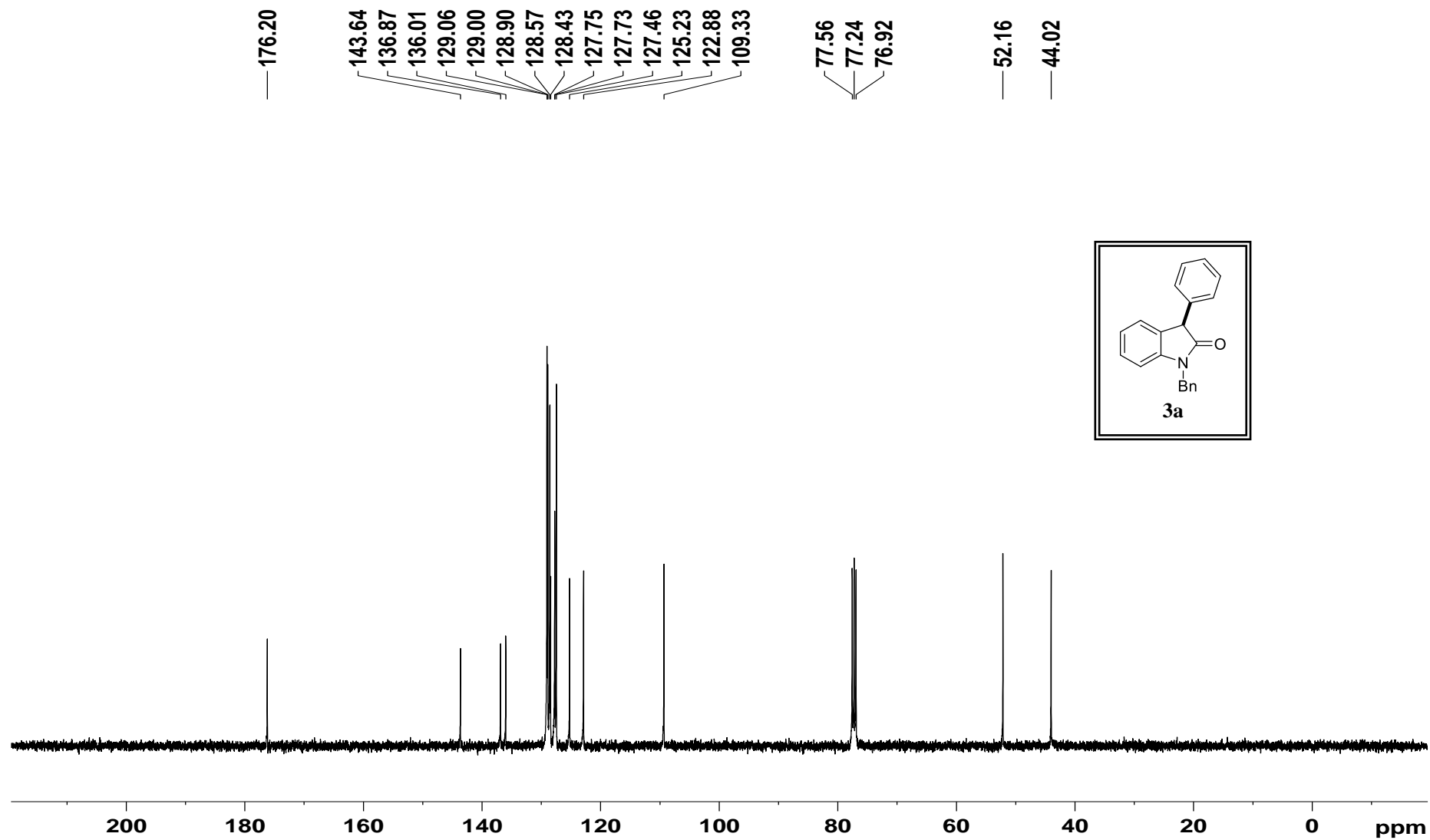
^1H NMR spectrum of 3a

apr-541 recemic PROTON CDCl3 7/11/2019



¹³C NMR spectrum of **3a**

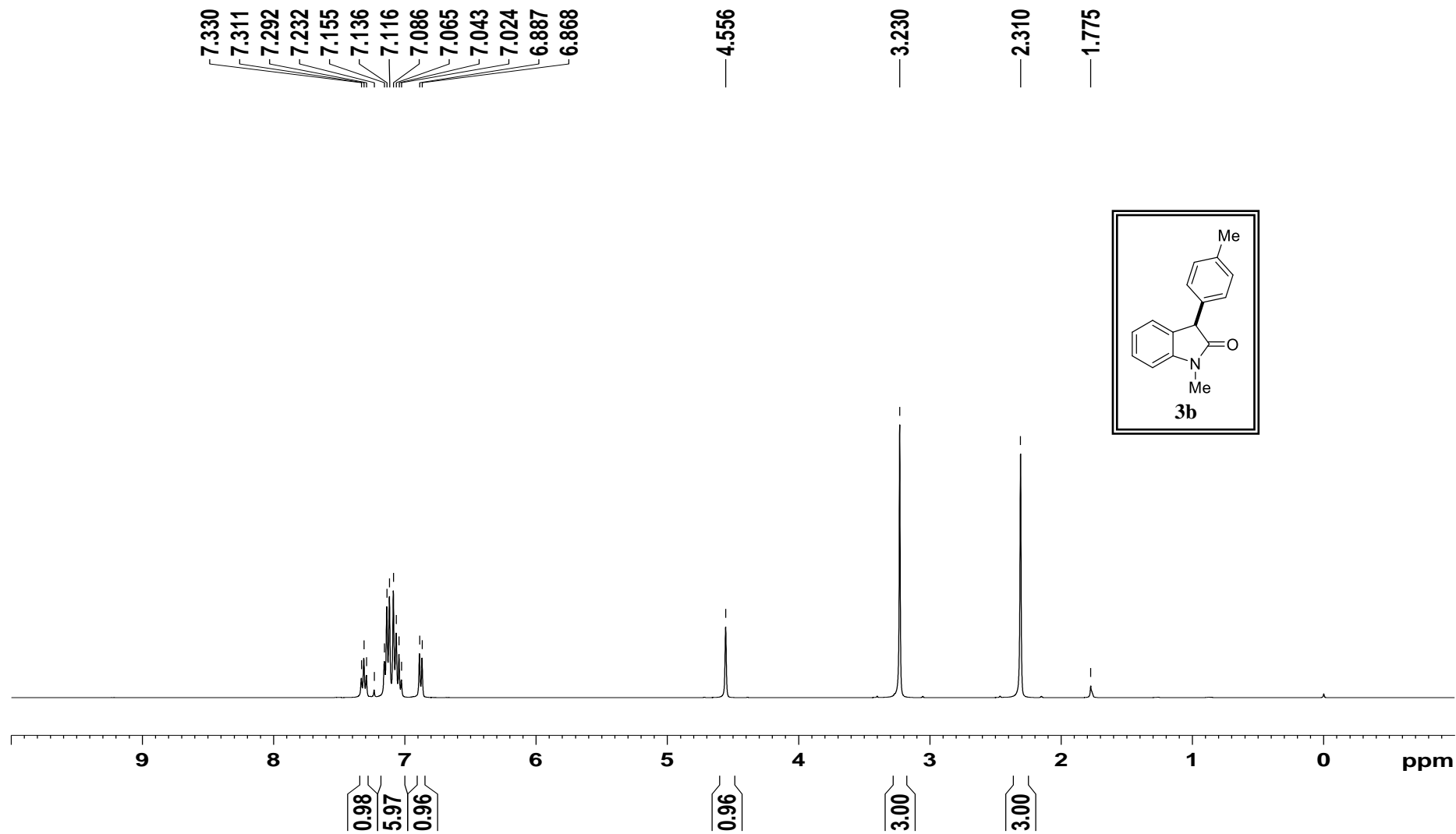
apr-541 recemic C13CPD CDC13 7/11/2019



S23

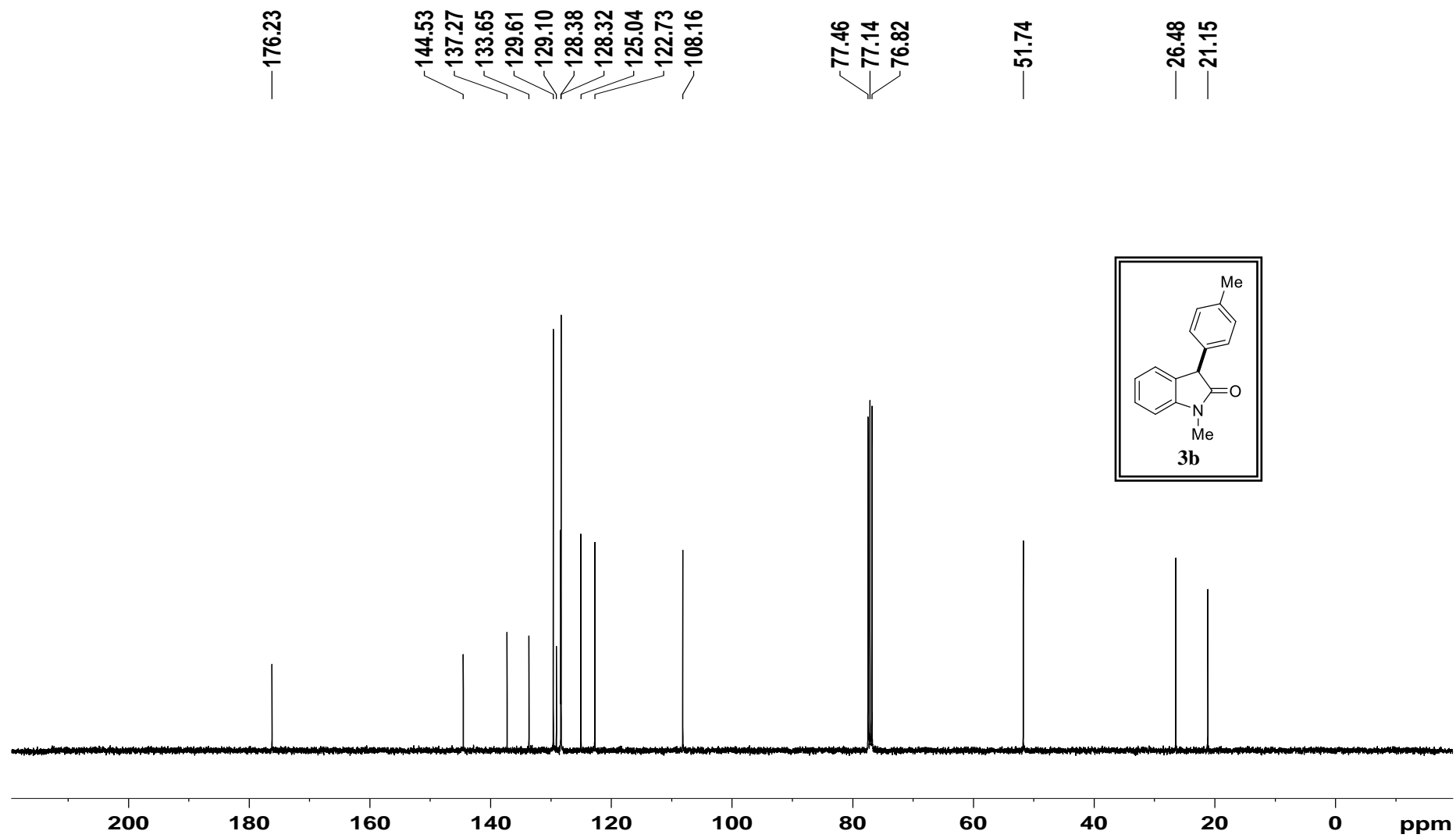
¹H NMR spectrum of **3b**

apr-414 PROTON CDCl3 11/3/2019



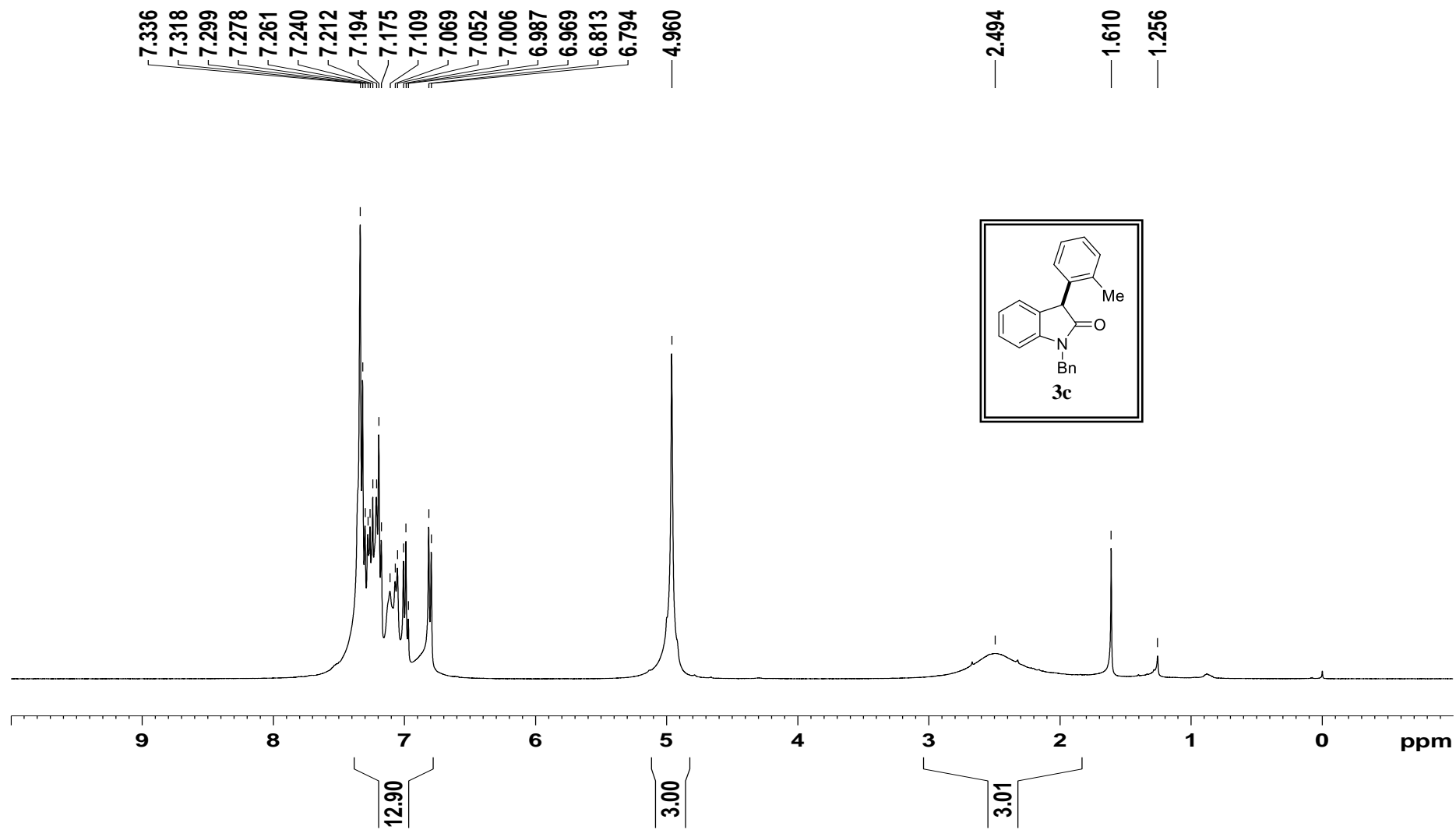
¹³C NMR spectrum of **3b**

apr-414 C13CPD CDC13 11/3/2019



¹H NMR spectrum of **3c**

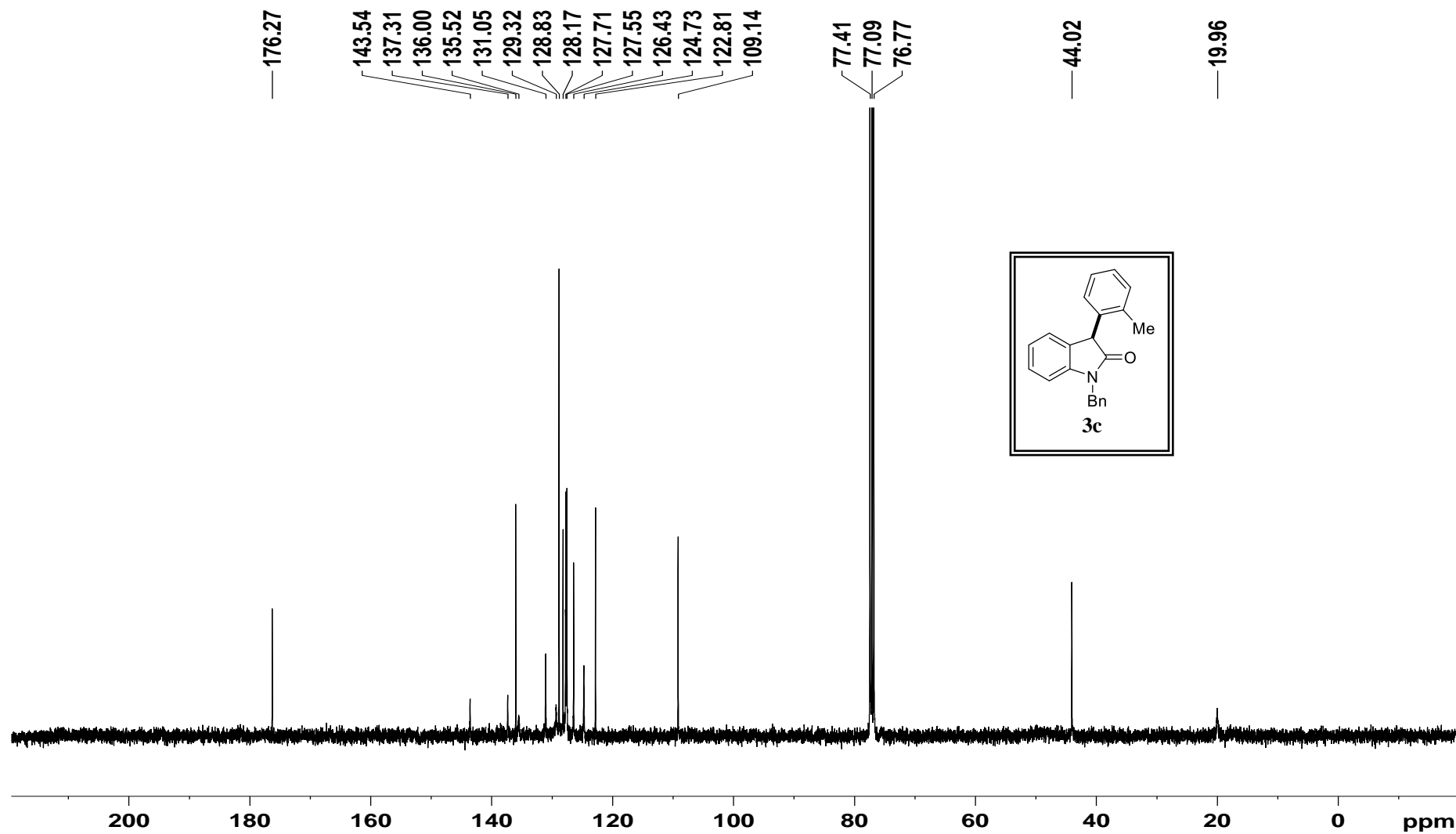
apr-421 PROTON CDC13 2/8/2019



S26

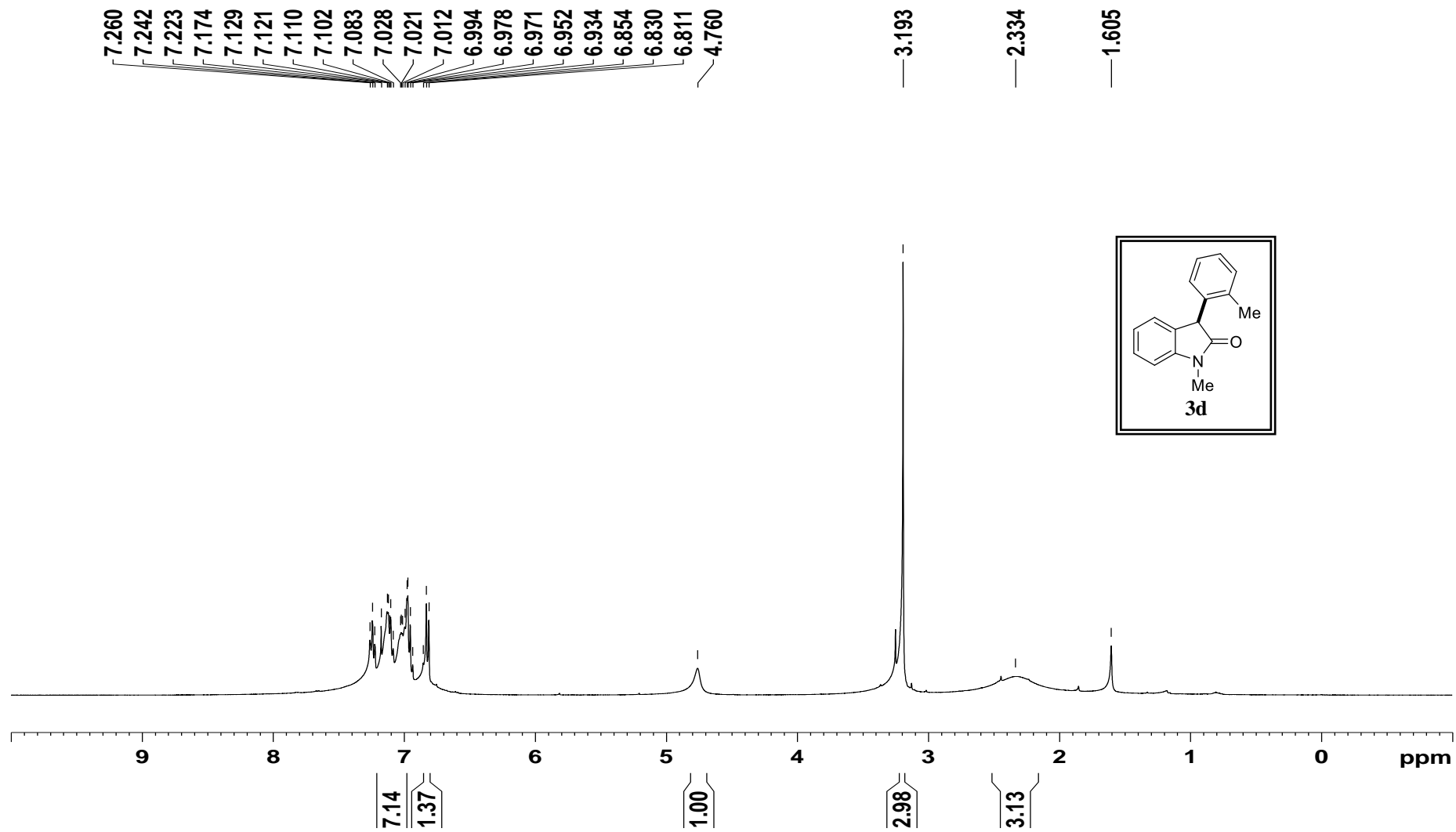
^{13}C NMR spectrum of **3c**

apr-421 C13CPD CDC13 6/8/2019



¹H NMR spectrum of **3d**

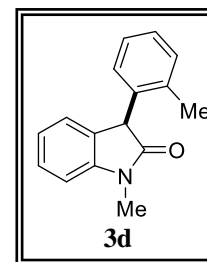
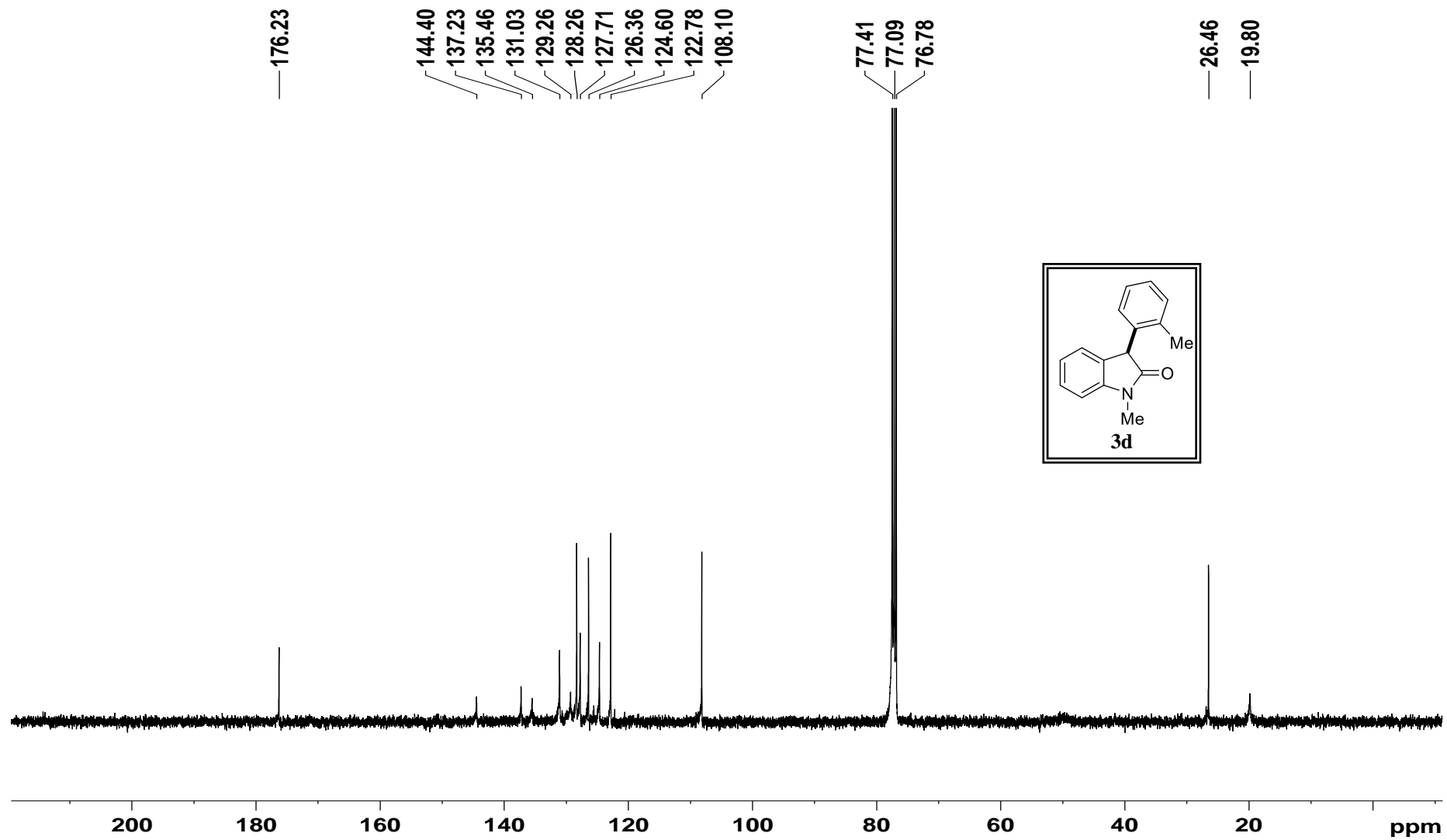
apr-515 PROTON CDC13 25/9/2019



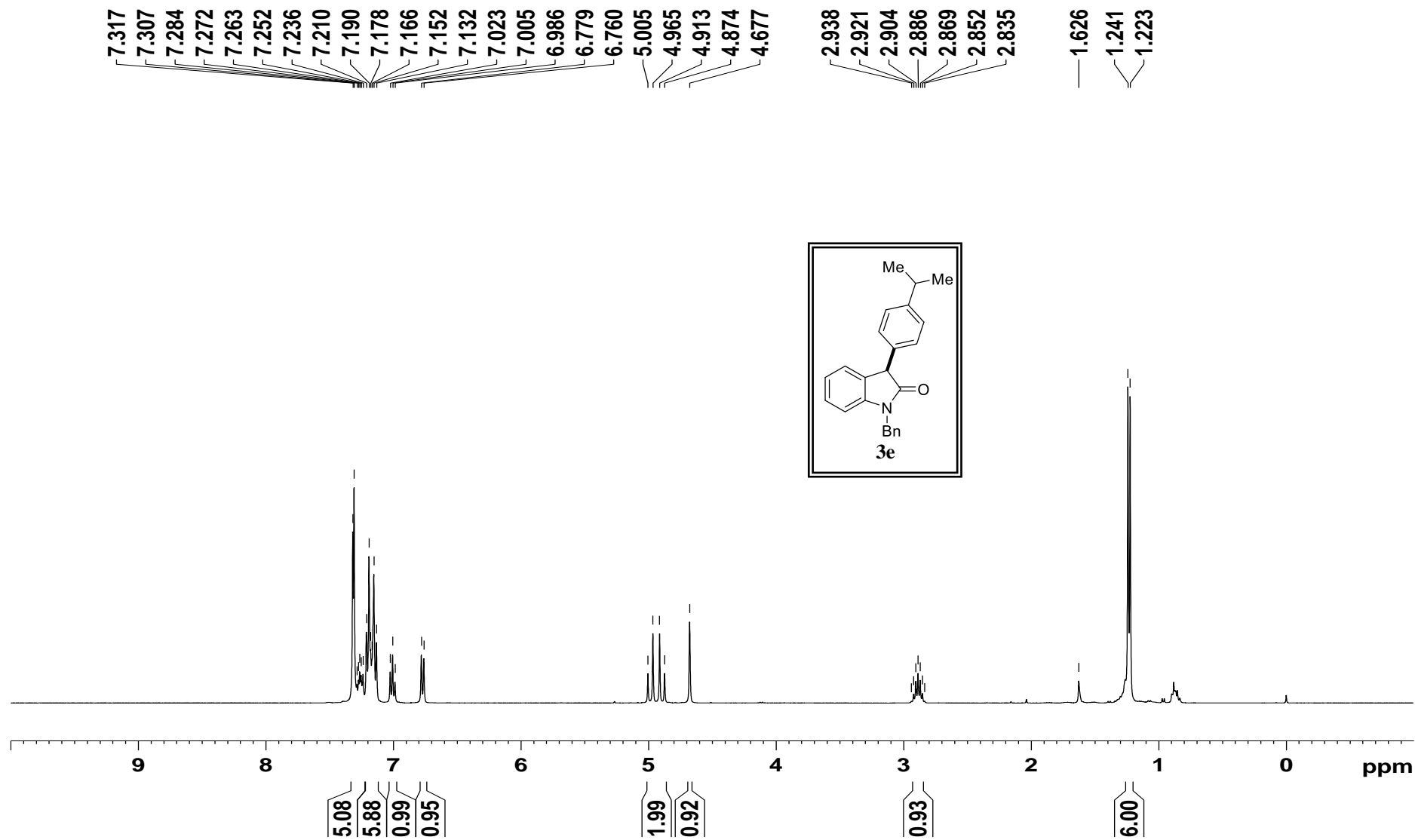
S28

¹³C NMR spectrum of **3d**

apr-515 C13CPD CDC13 25/9/2019

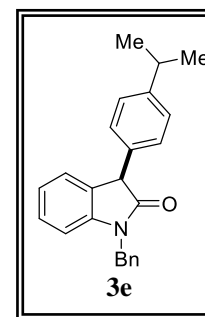
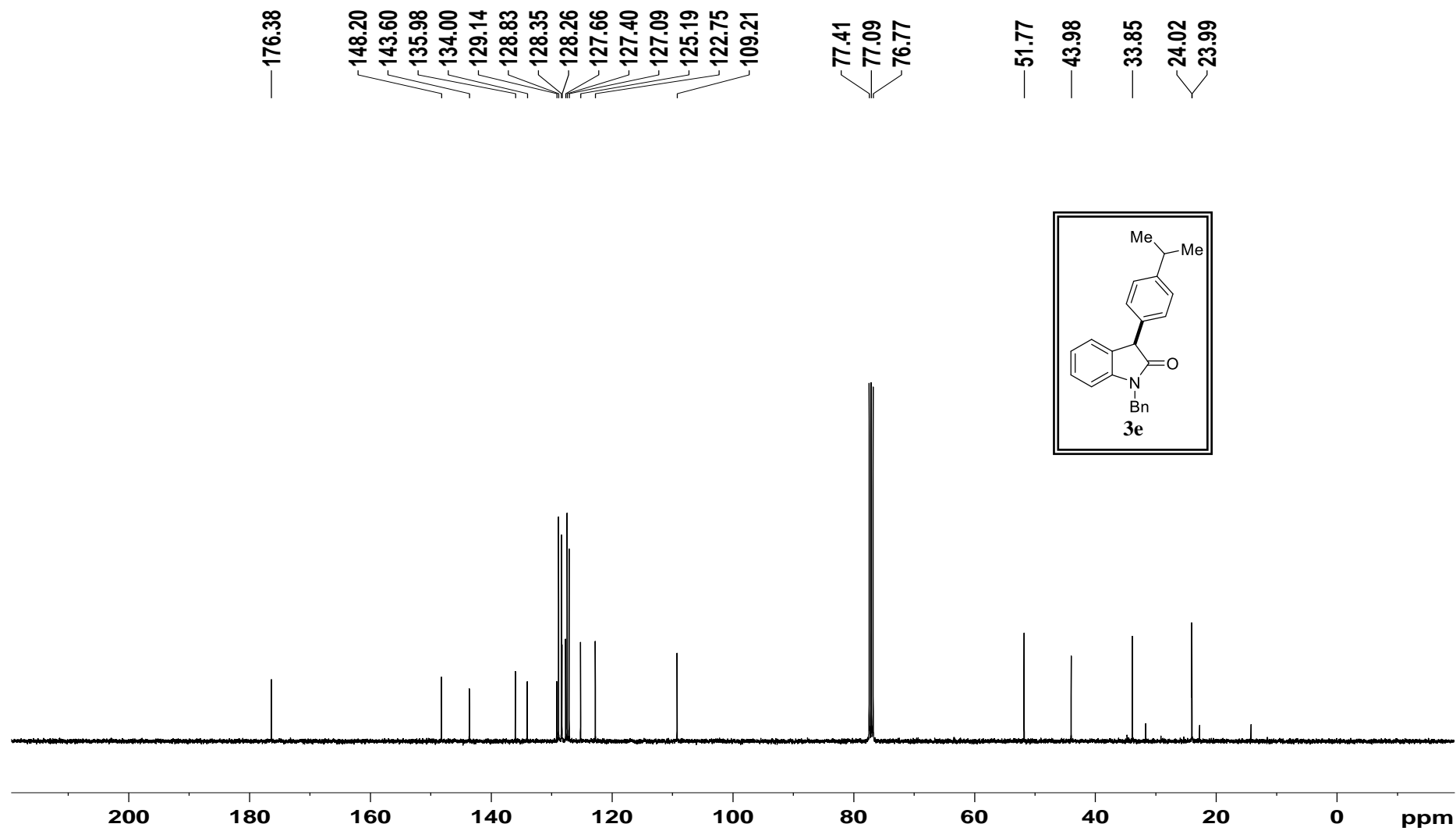


¹H NMR spectrum of 3e



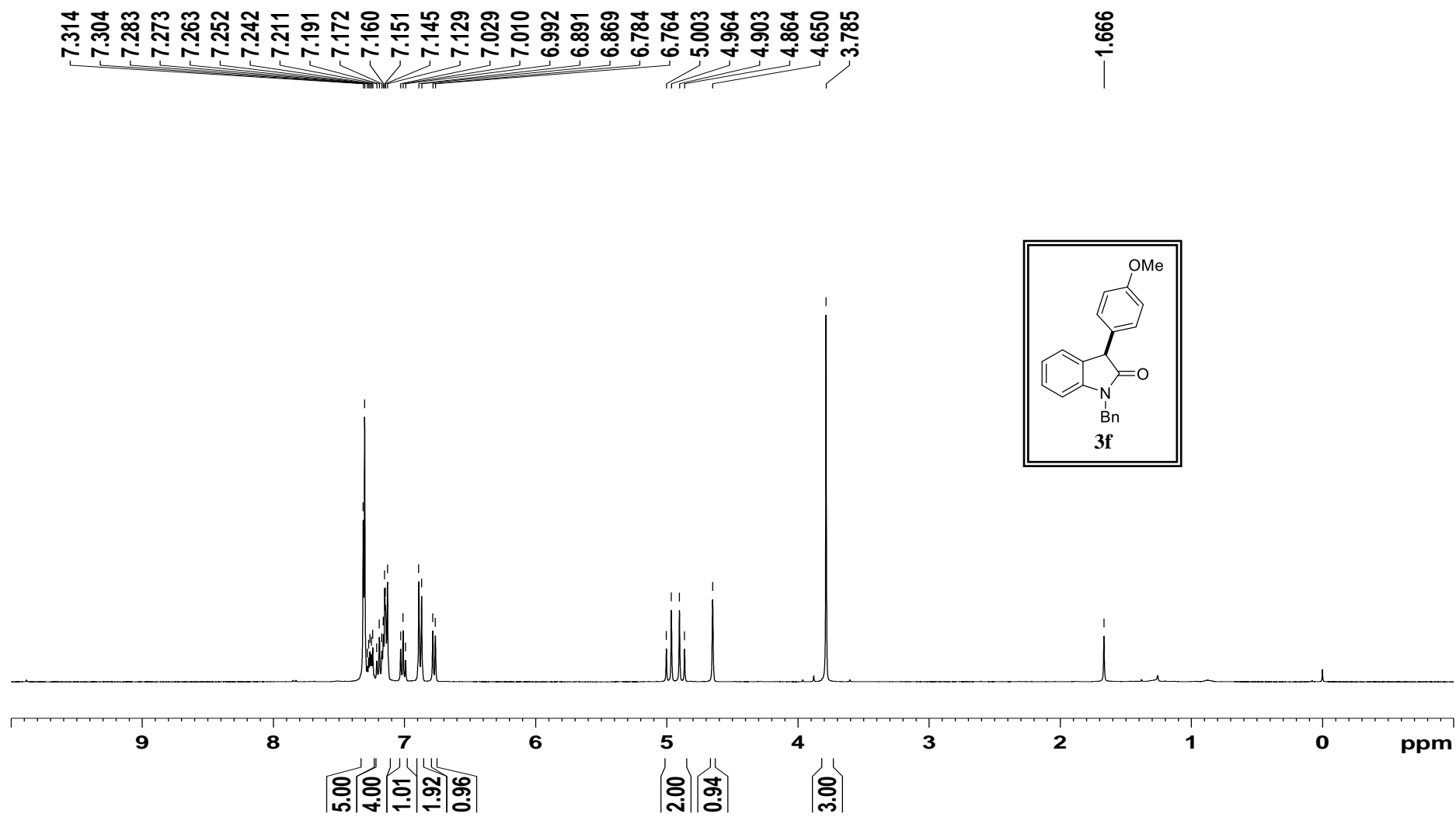
¹³C NMR spectrum of **3e**

apr-424 C13CPD CDC13 23/03/2019



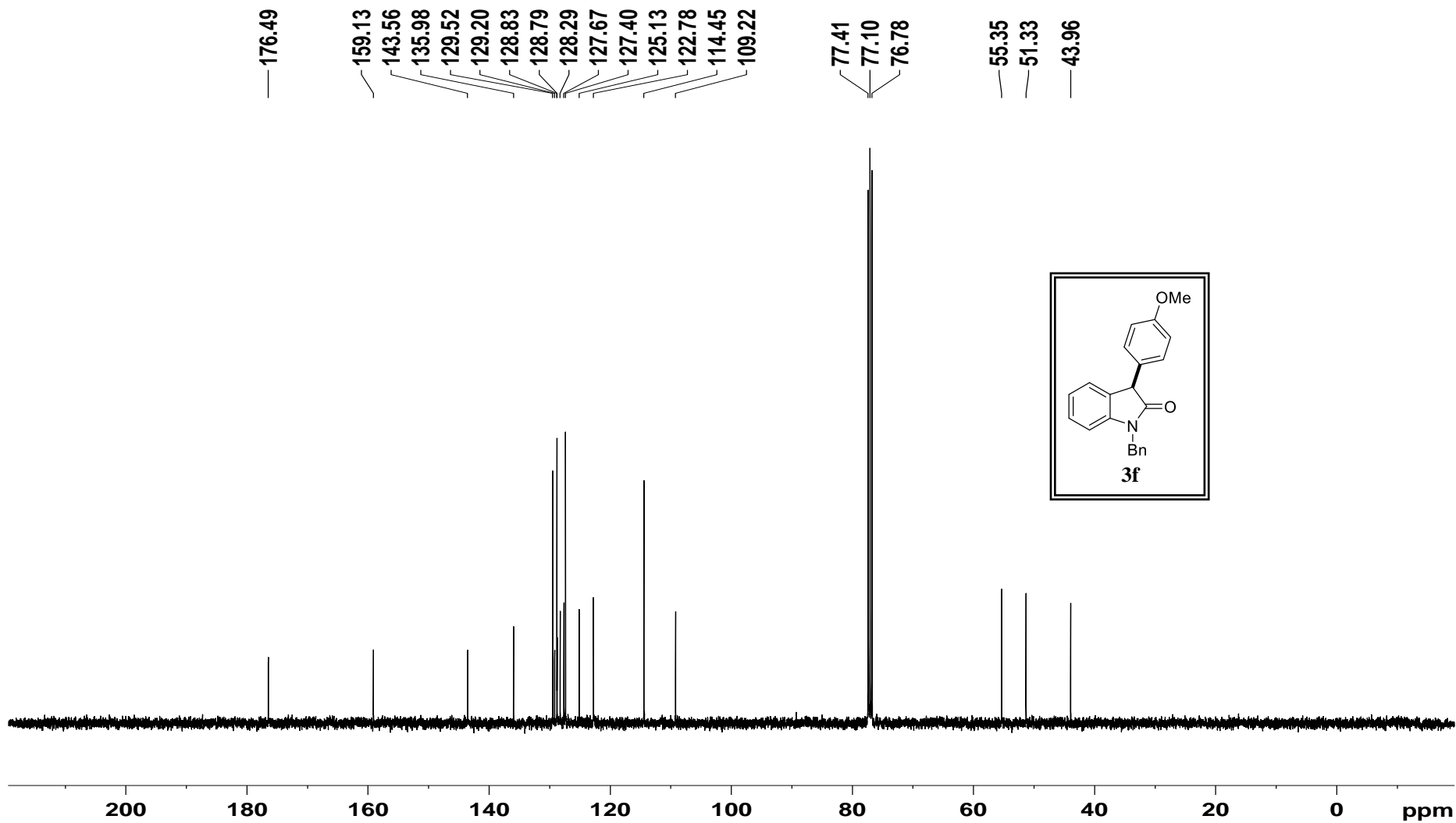
¹H NMR spectrum of **3f**

apr-412 PROTON CDC13 14/03/2019



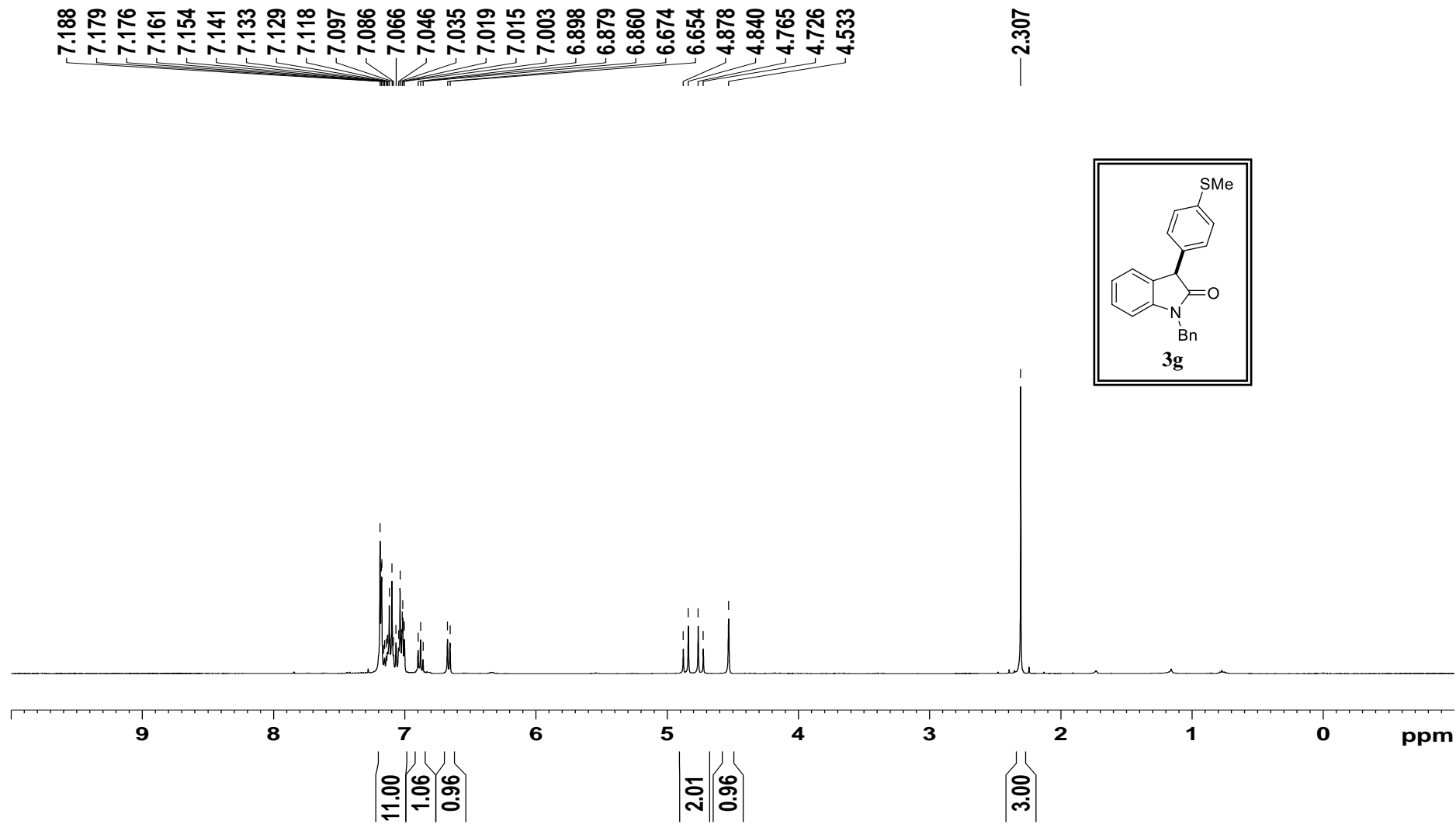
^{13}C NMR spectrum of **3f**

apr-412 C13CPD CDC13 14/03/2019



¹H NMR spectrum of 3g

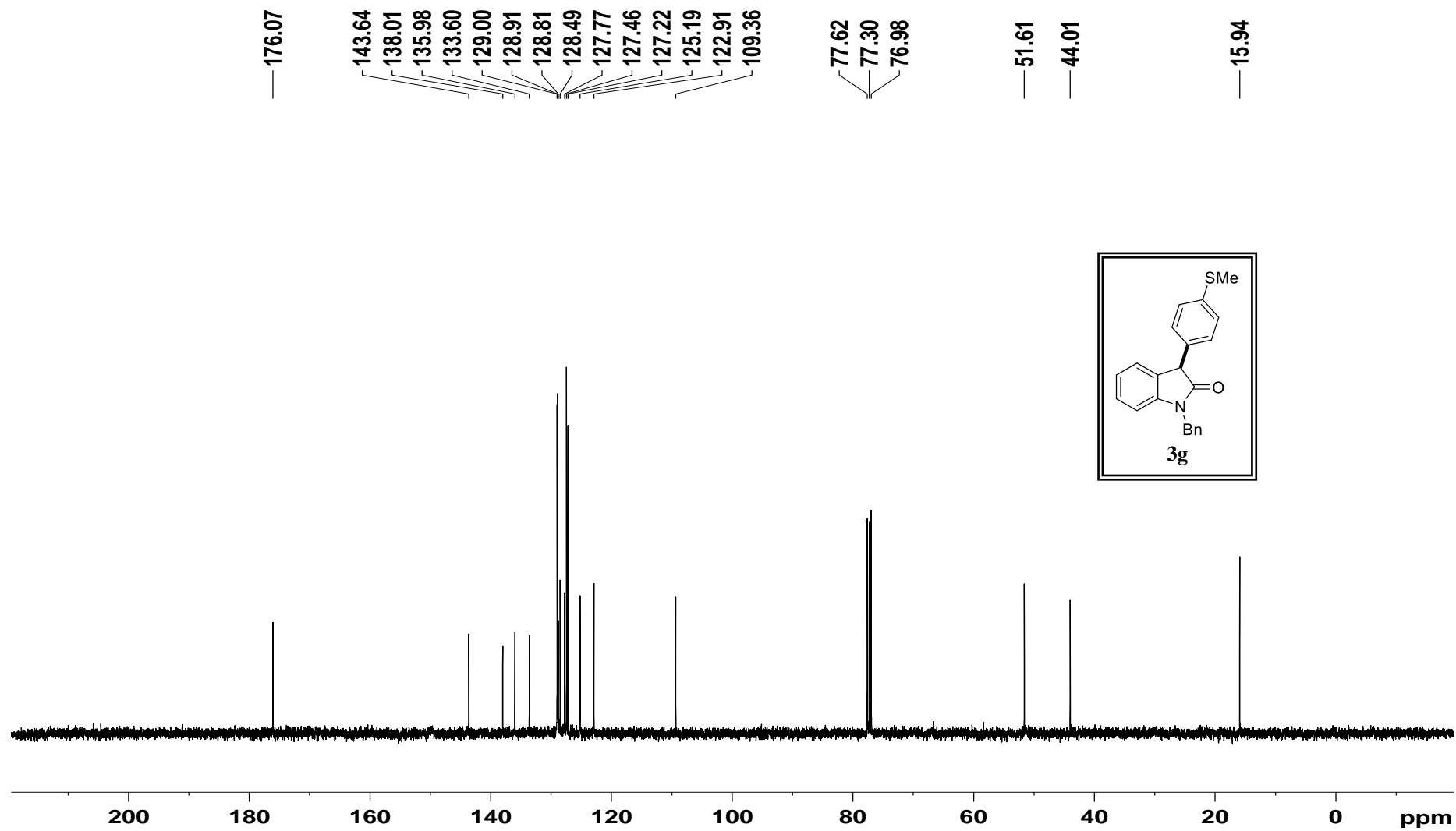
apr-581 PROTON CDC13 30/1/2020



S34

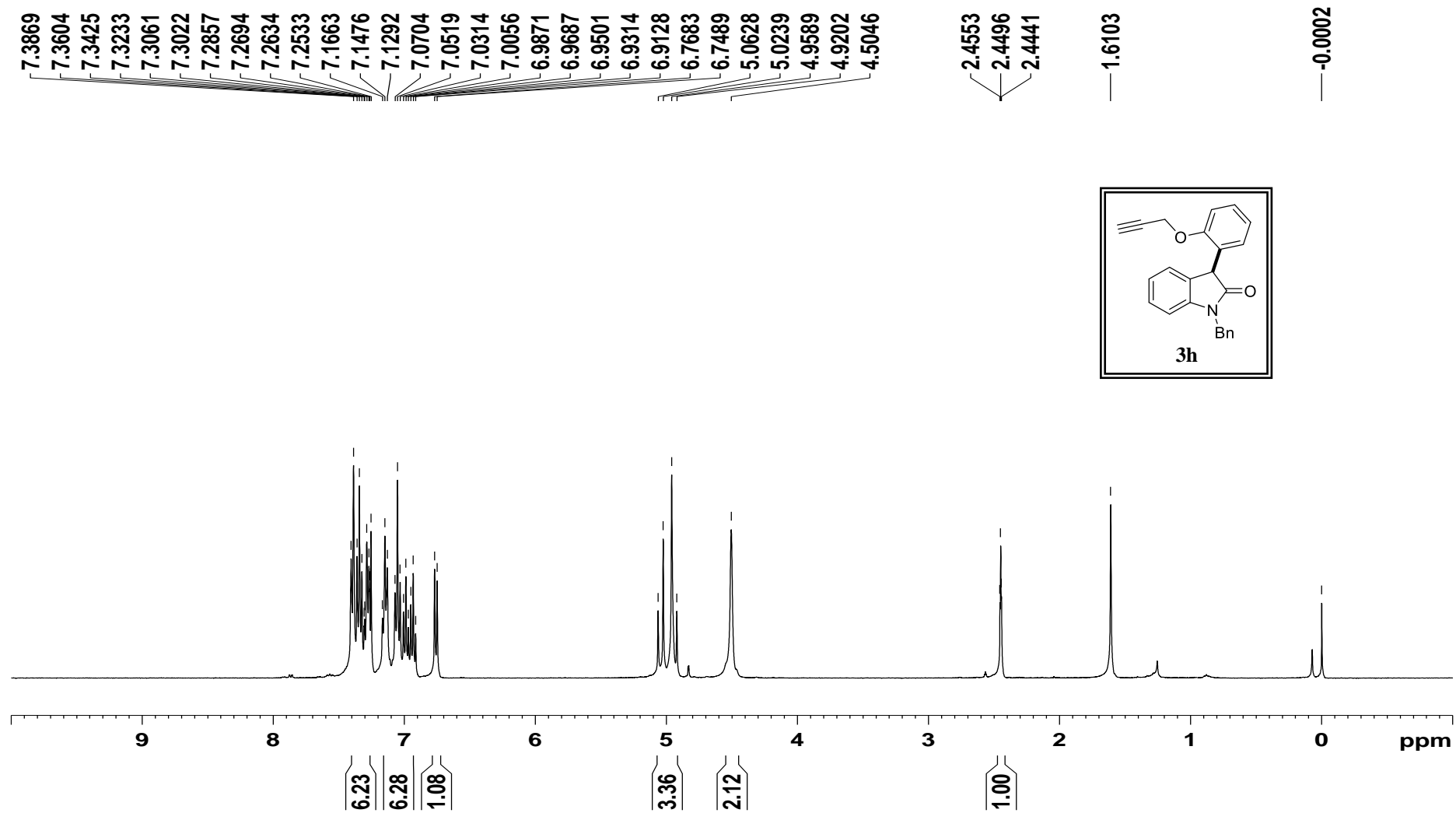
¹³C NMR spectrum of **3g**

apr-581 C13CPD CDC13 30/01/2020



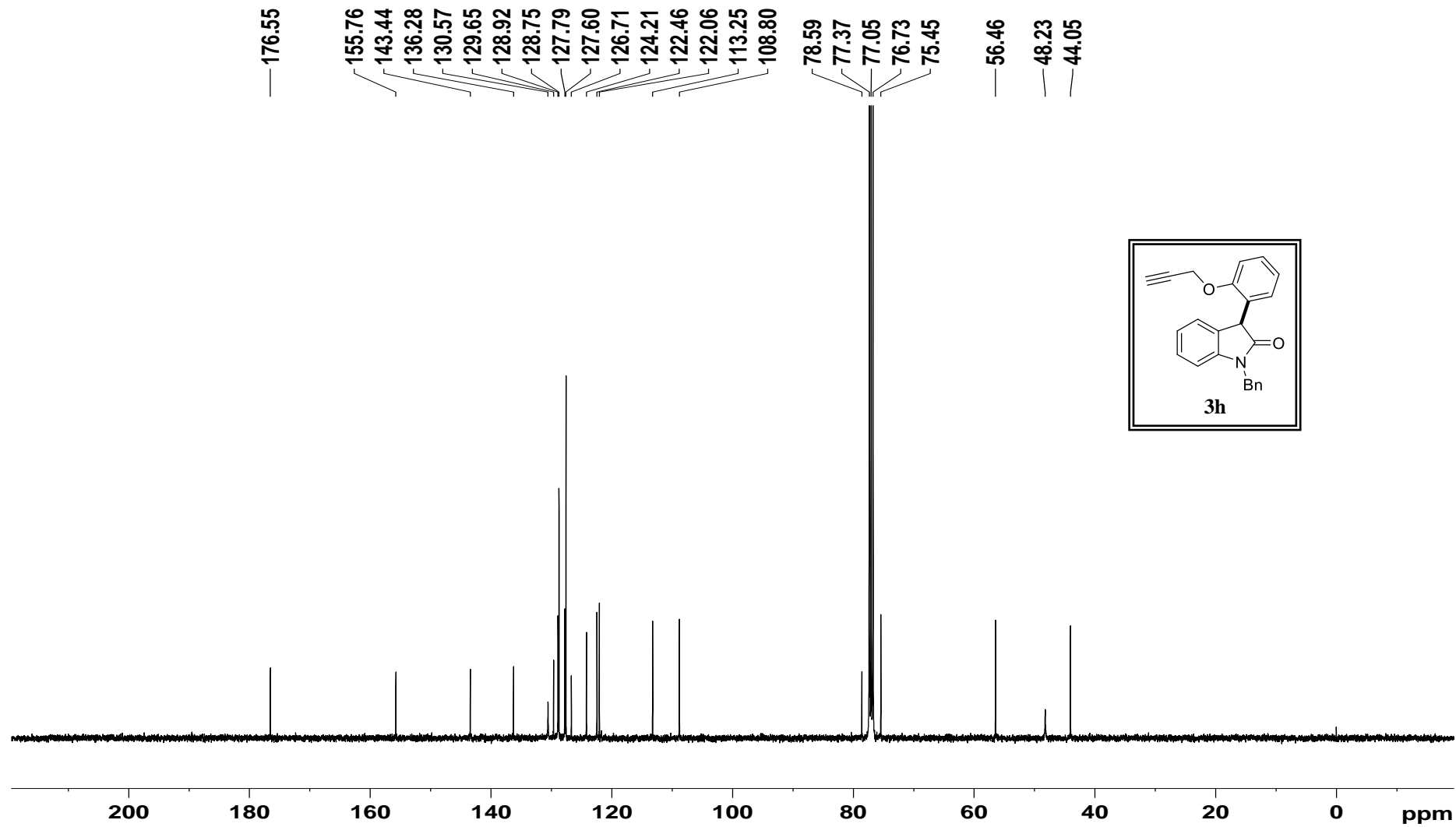
¹H NMR spectrum of **3h**

apr-401 PROTON CDCl3 15/2/2019



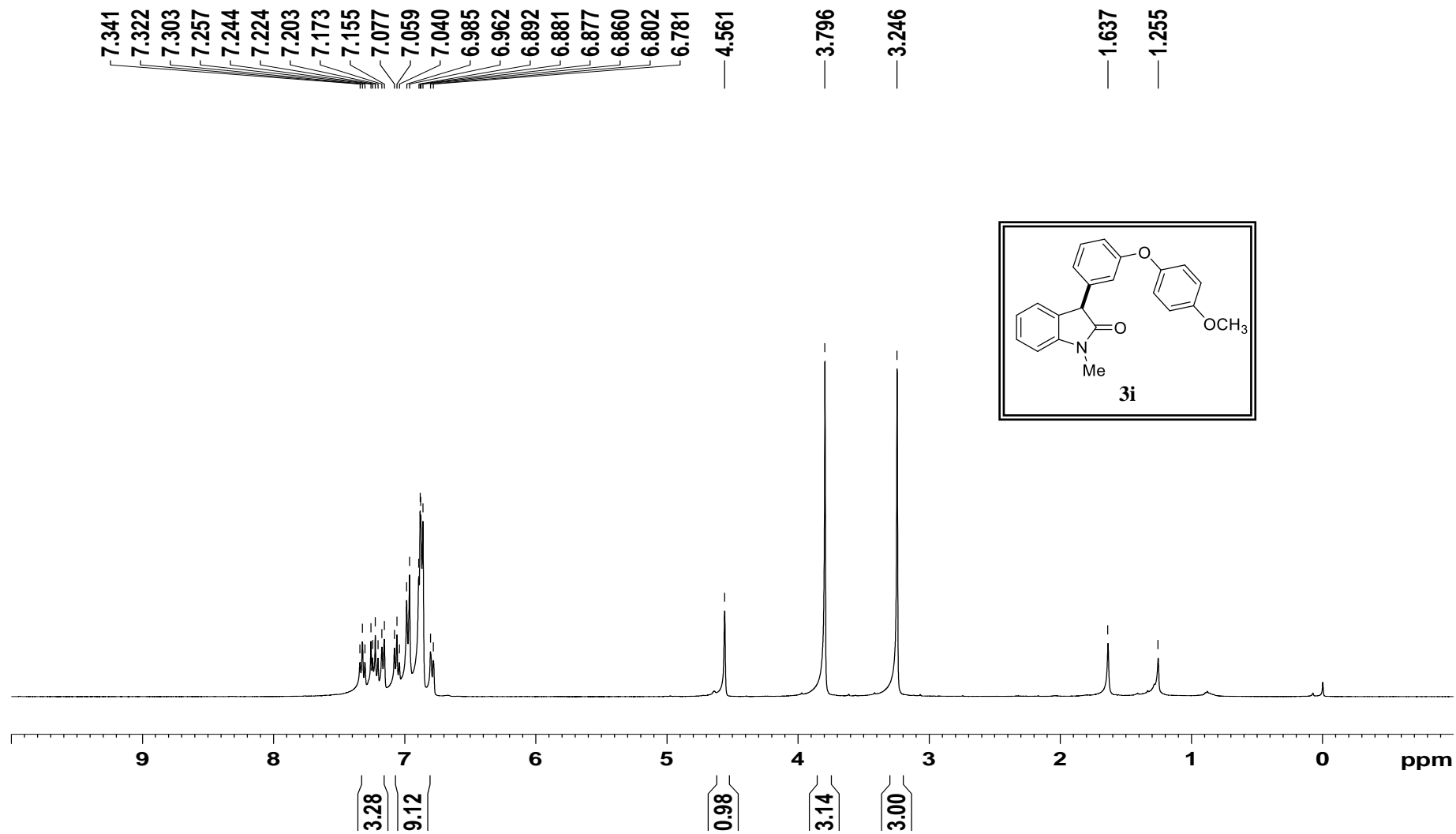
¹³C NMR spectrum of **3h**

apr-401 C13CPD CDC13 15/2/2019



¹H NMR spectrum of **3i**

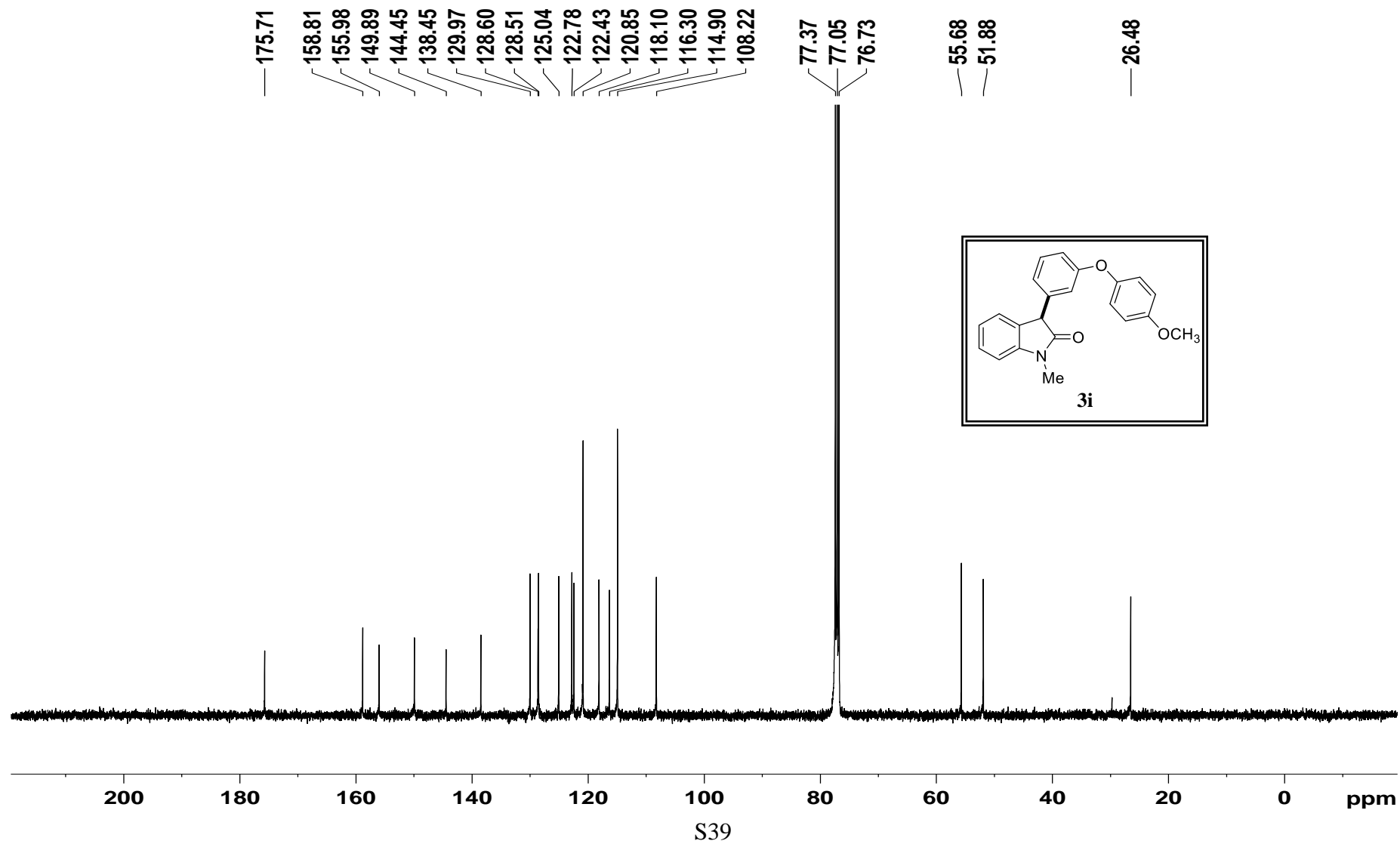
apr-462 PROTON CDC13 30/5/2019



S38

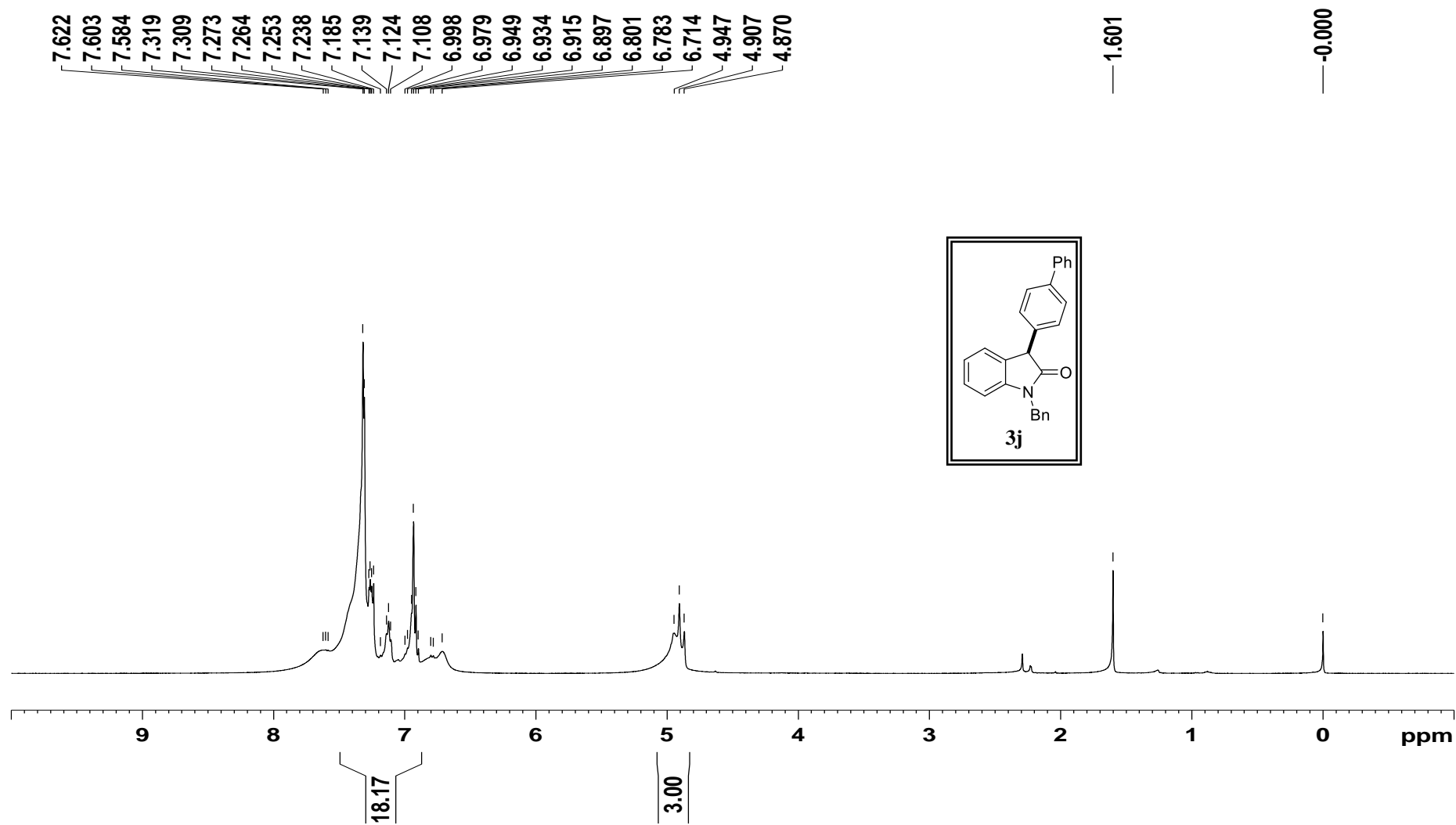
¹³C NMR spectrum of **3i**

apr-462 C13CPD CDC13 31/5/2019



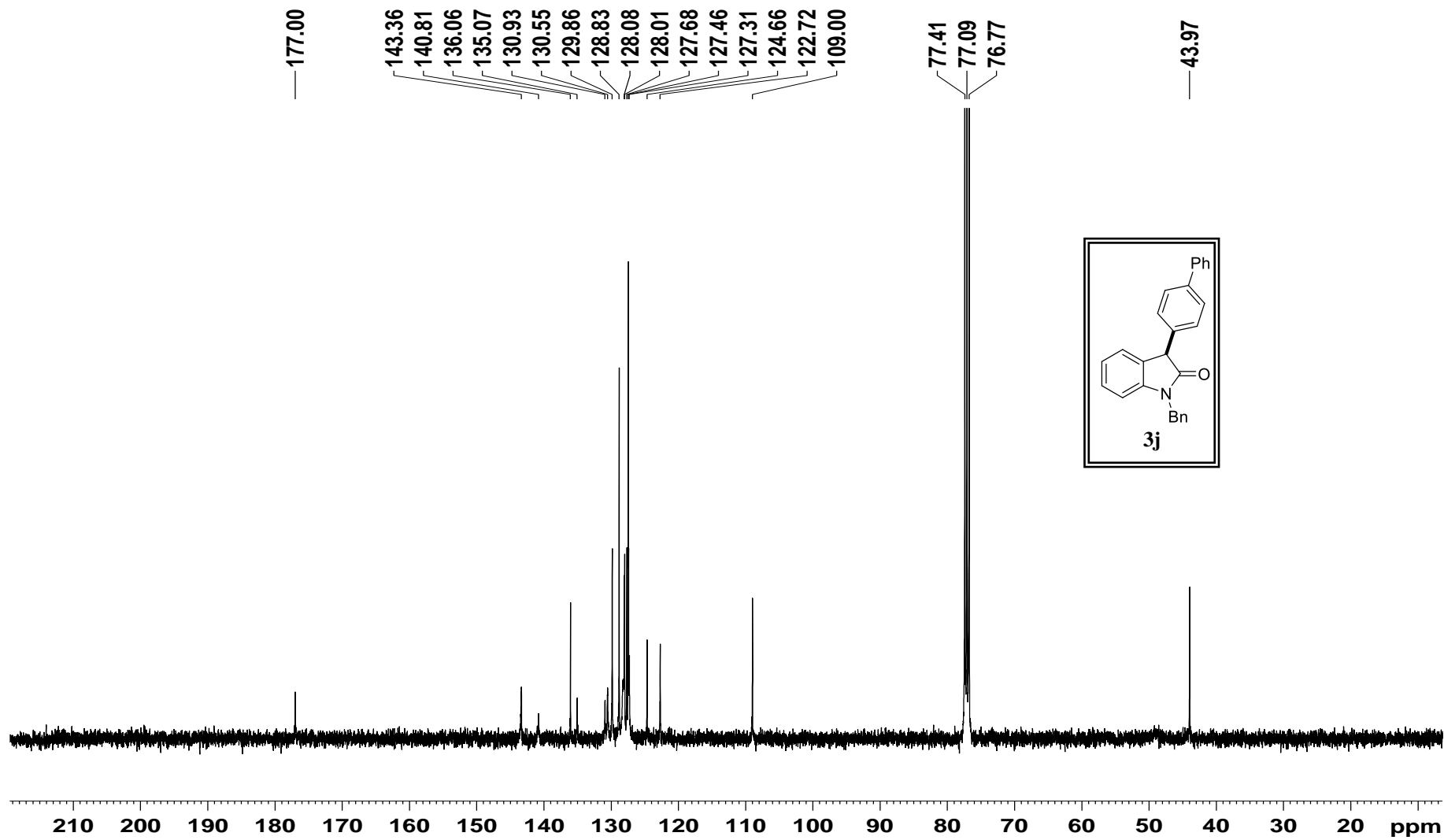
¹H NMR spectrum of **3j**

apr-504 PROTON CDC13 21/8/2019



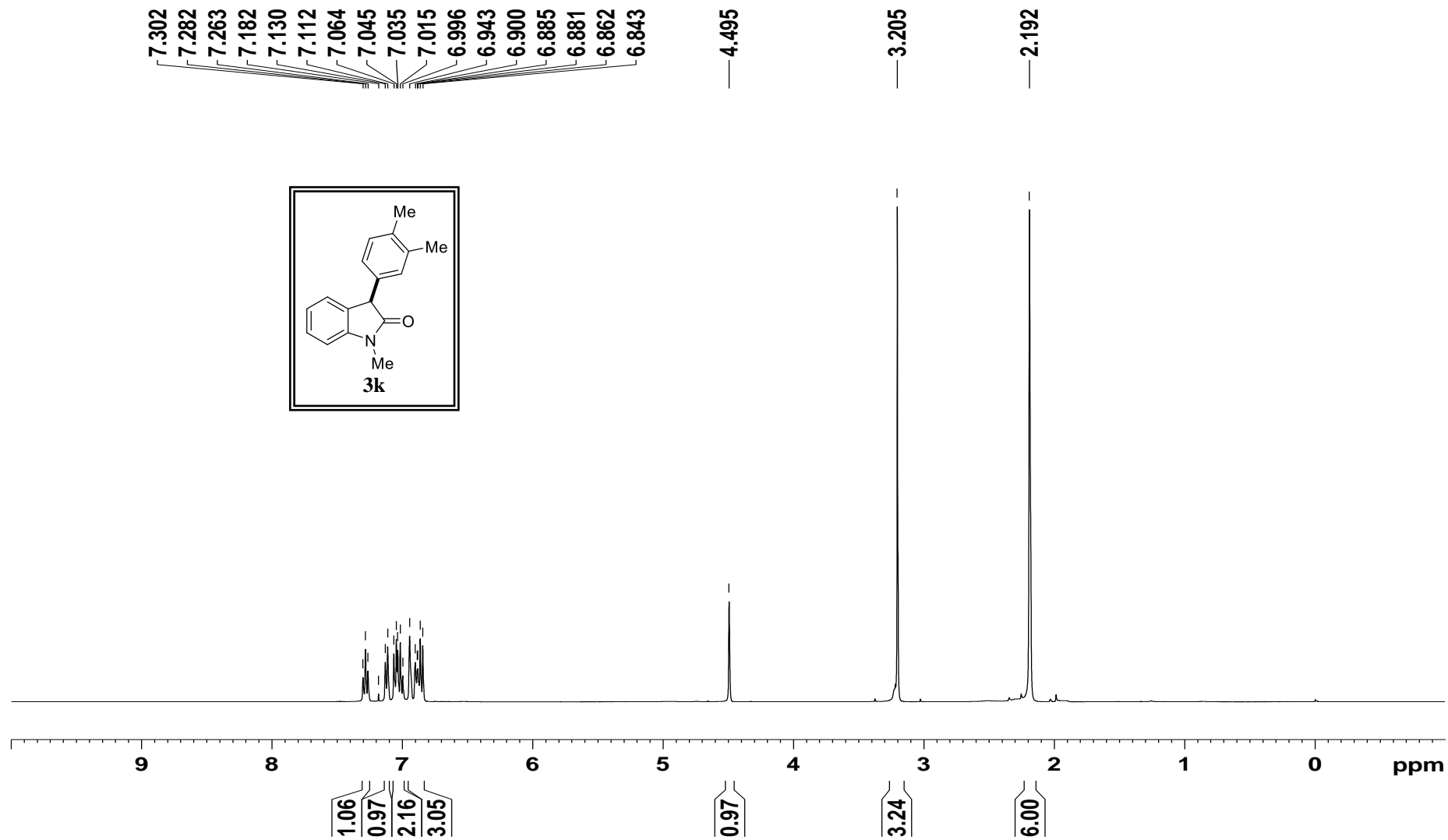
¹³C NMR spectrum of **3j**

apr-504 C13CPD CDC13 21/8/2019



¹H NMR spectrum of **3k**

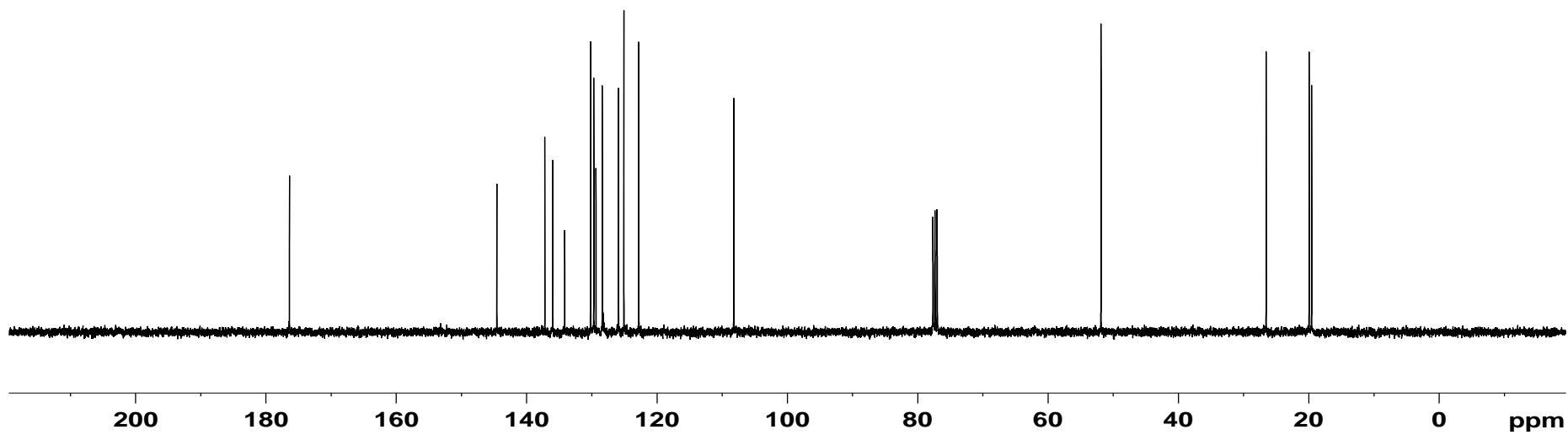
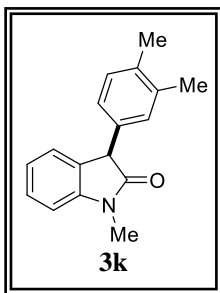
apr-501 PROTON CDC13 16/8/2019



¹³C NMR spectrum of **3k**

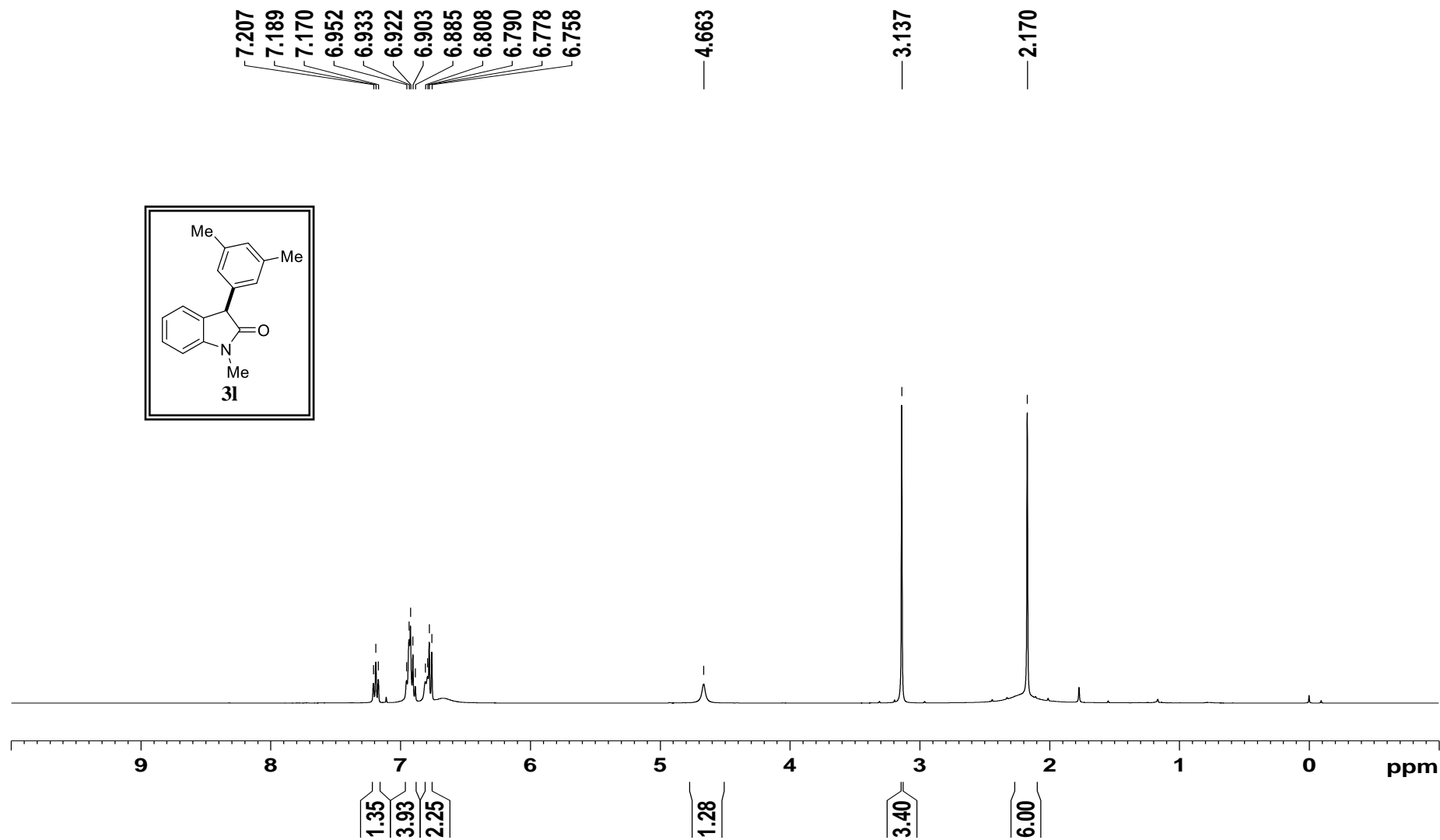
apr-501 C13CPD CDC13 16/8/2019

176.37
144.54
137.18
135.98
134.13
130.17
129.67
129.32
128.37
125.89
125.04
122.77
108.19
77.65
77.33
77.01
51.84
26.50
19.90
19.53



¹H NMR spectrum of **31**

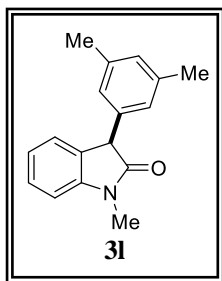
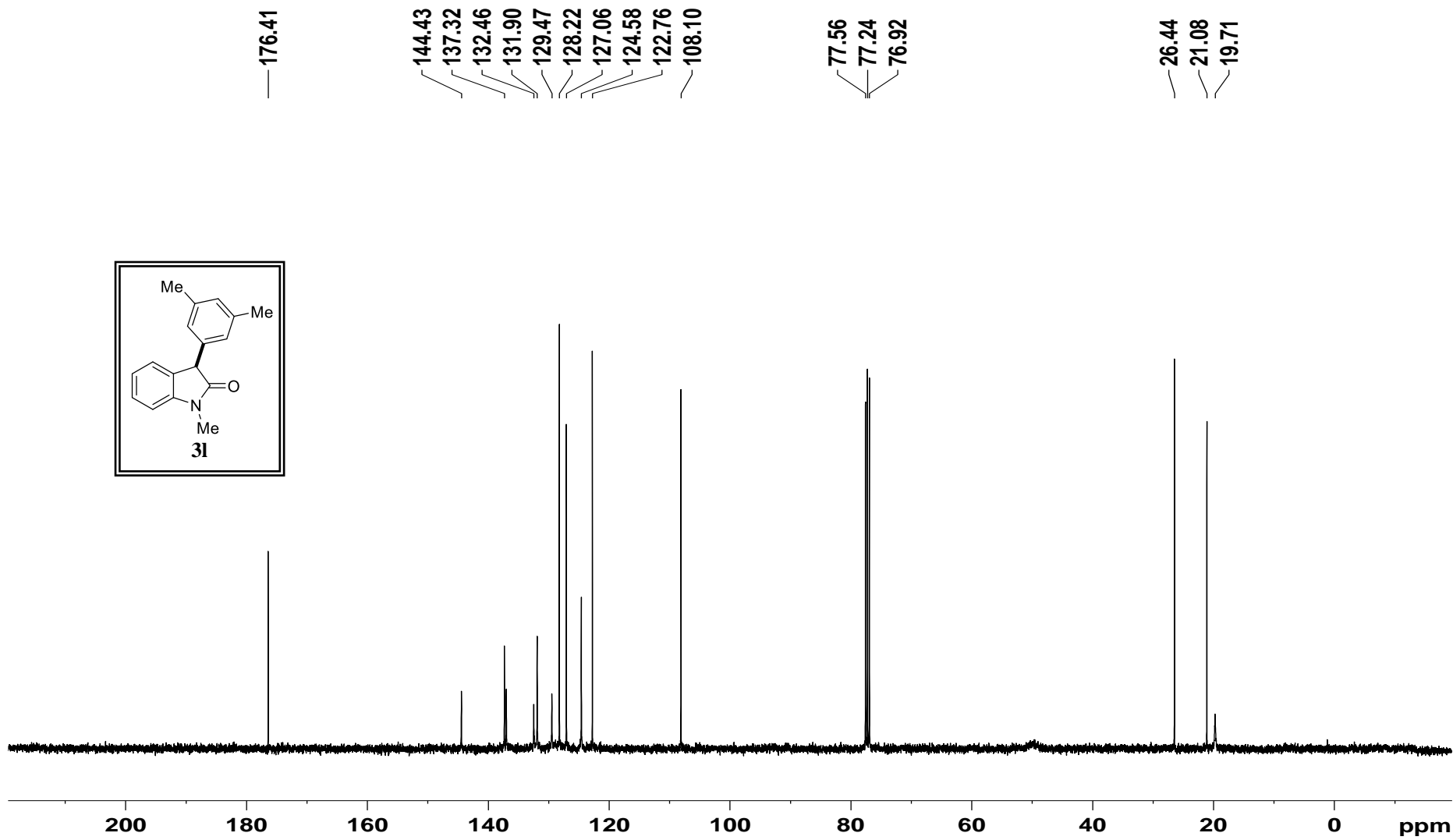
Apr-500 PROTON CDCl₃ 9/8/2019



S44

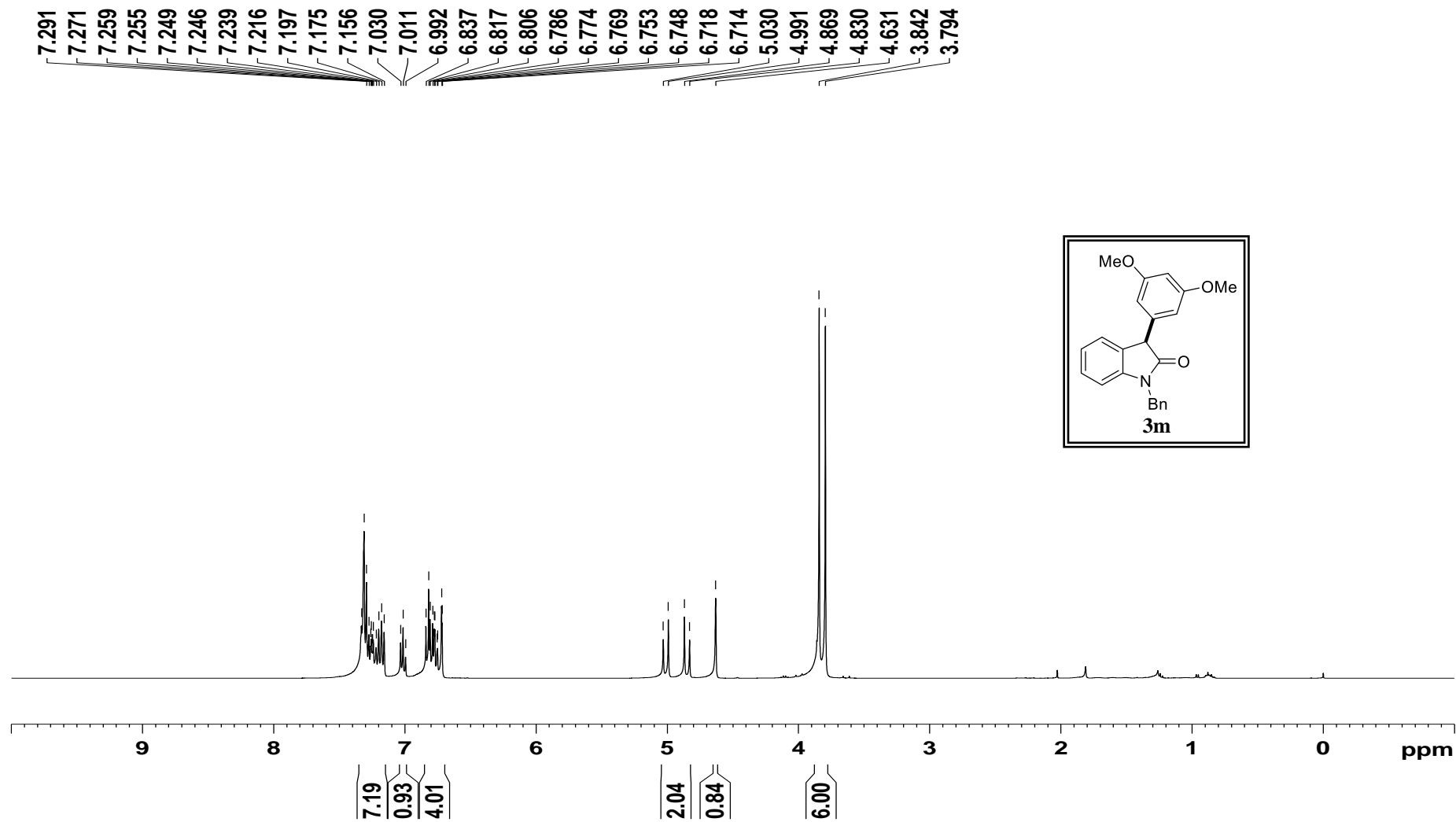
¹³C NMR spectrum of **31**

Apr-500 C13CPD CDC13 9/8/2019



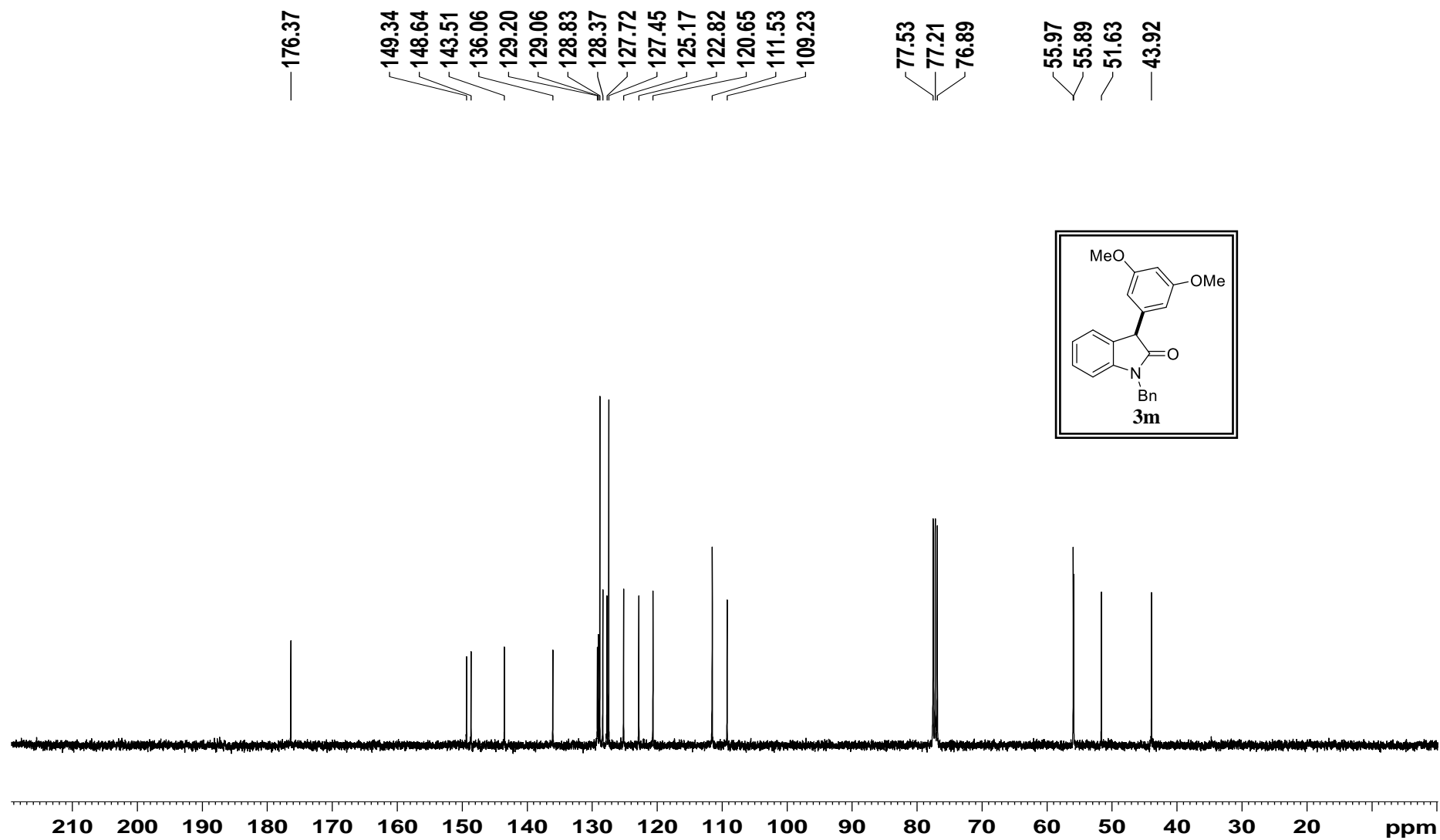
¹H NMR spectrum of **3m**

apr-502 PROTON CDC13 16/8/2019



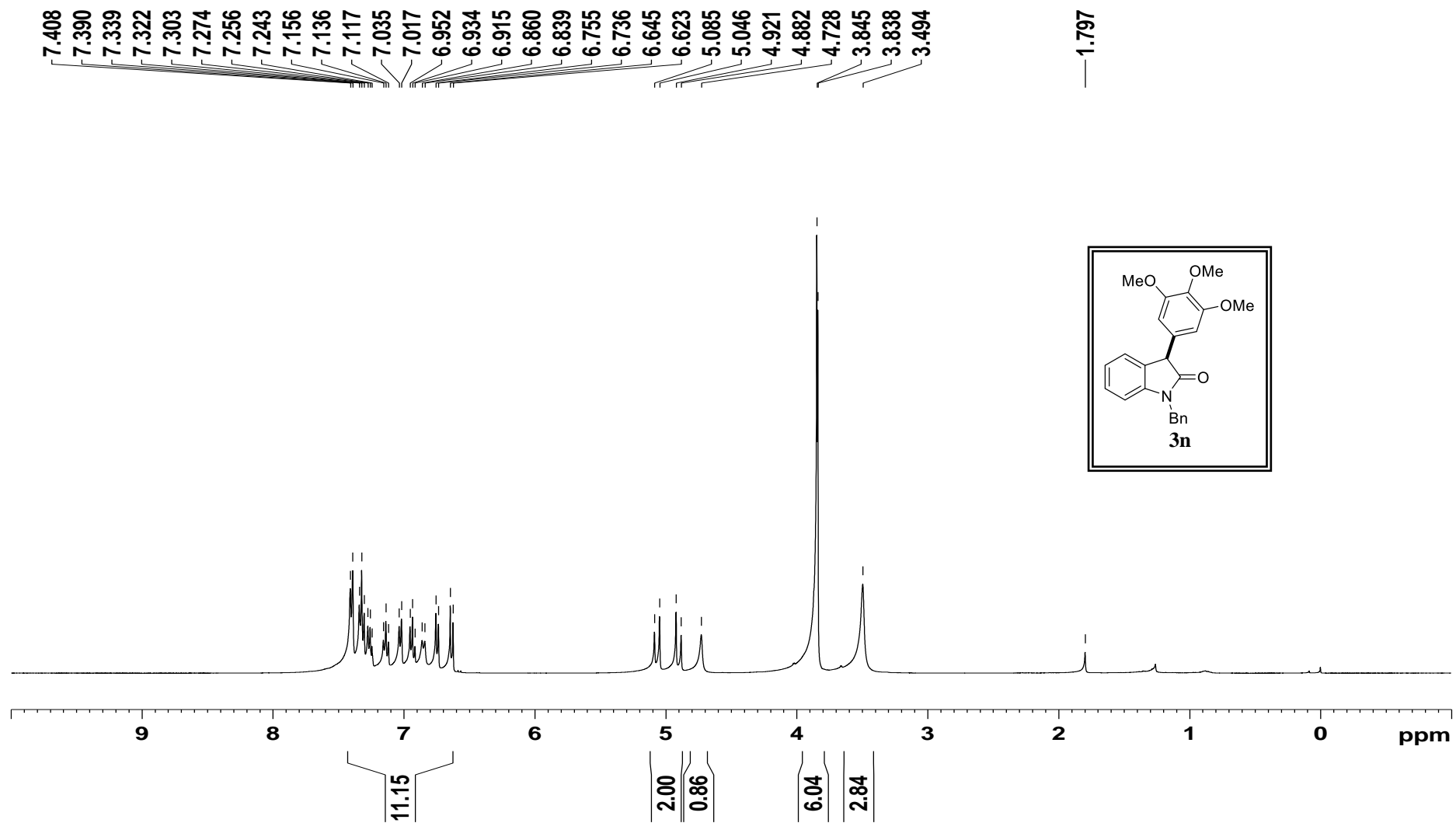
¹³C NMR spectrum of **3m**

apr-502 C13CPD CDC13 16/8/2019



¹H NMR spectrum of **3n**

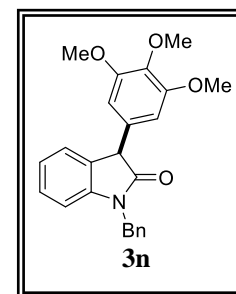
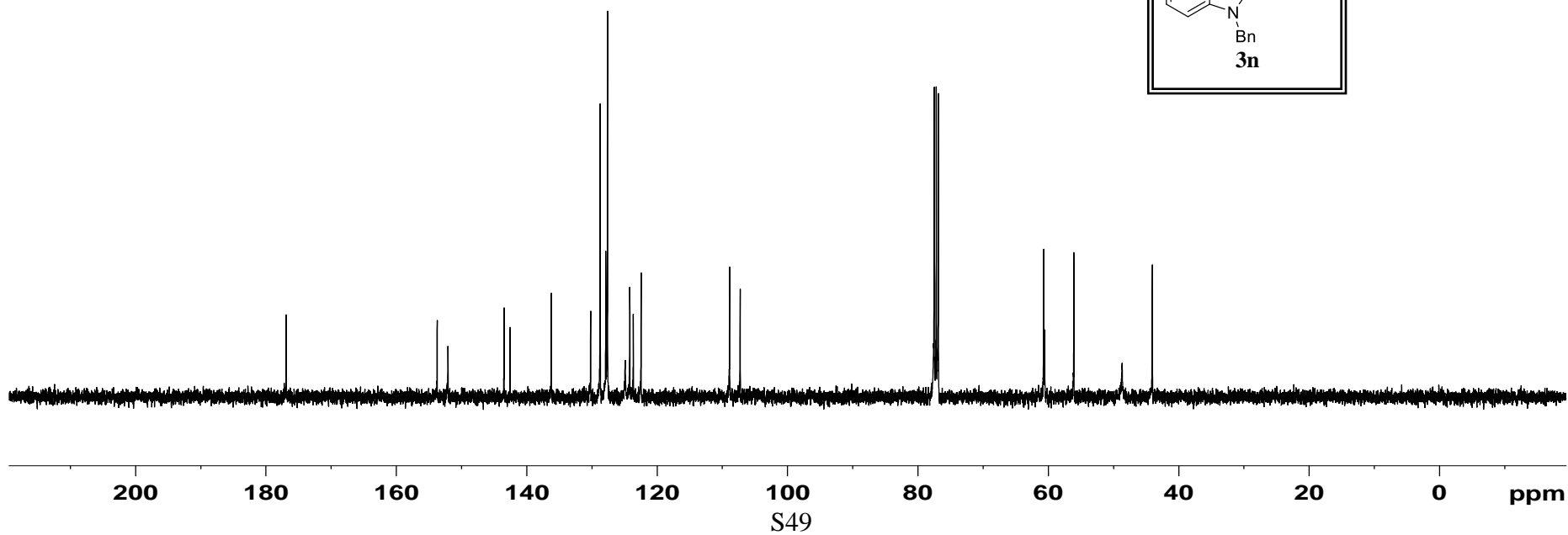
apr-503 PROTON CDC13 21/8/2019



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

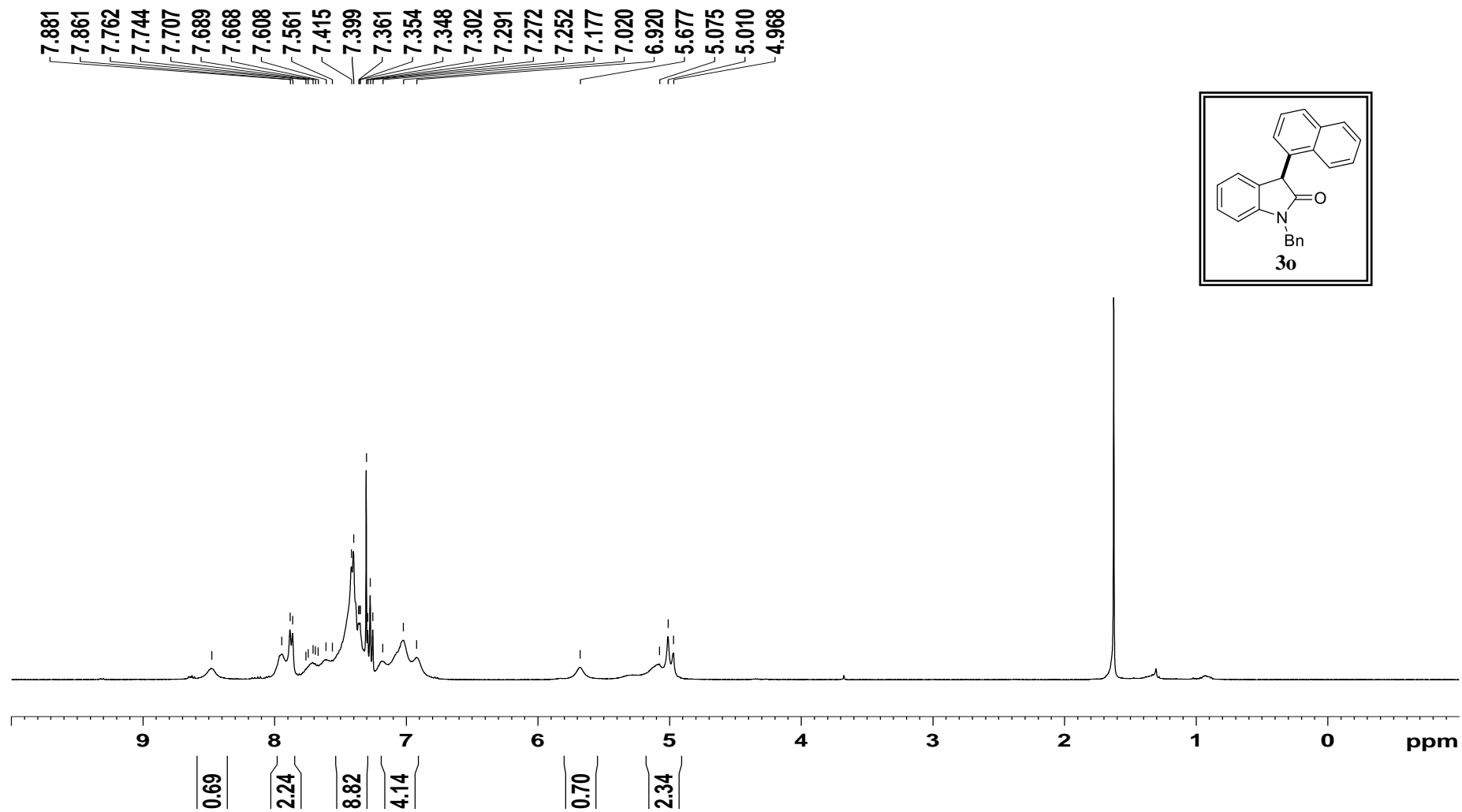
apr-503 C13CPD CDC13 21/8/2019

176.88
153.72
152.06
143.46
142.52
136.22
130.19
128.71
127.86
127.59
124.86
124.17
123.64
122.44
108.88
107.24
77.48
77.17
76.85
60.70
60.53
56.06
48.68
44.02



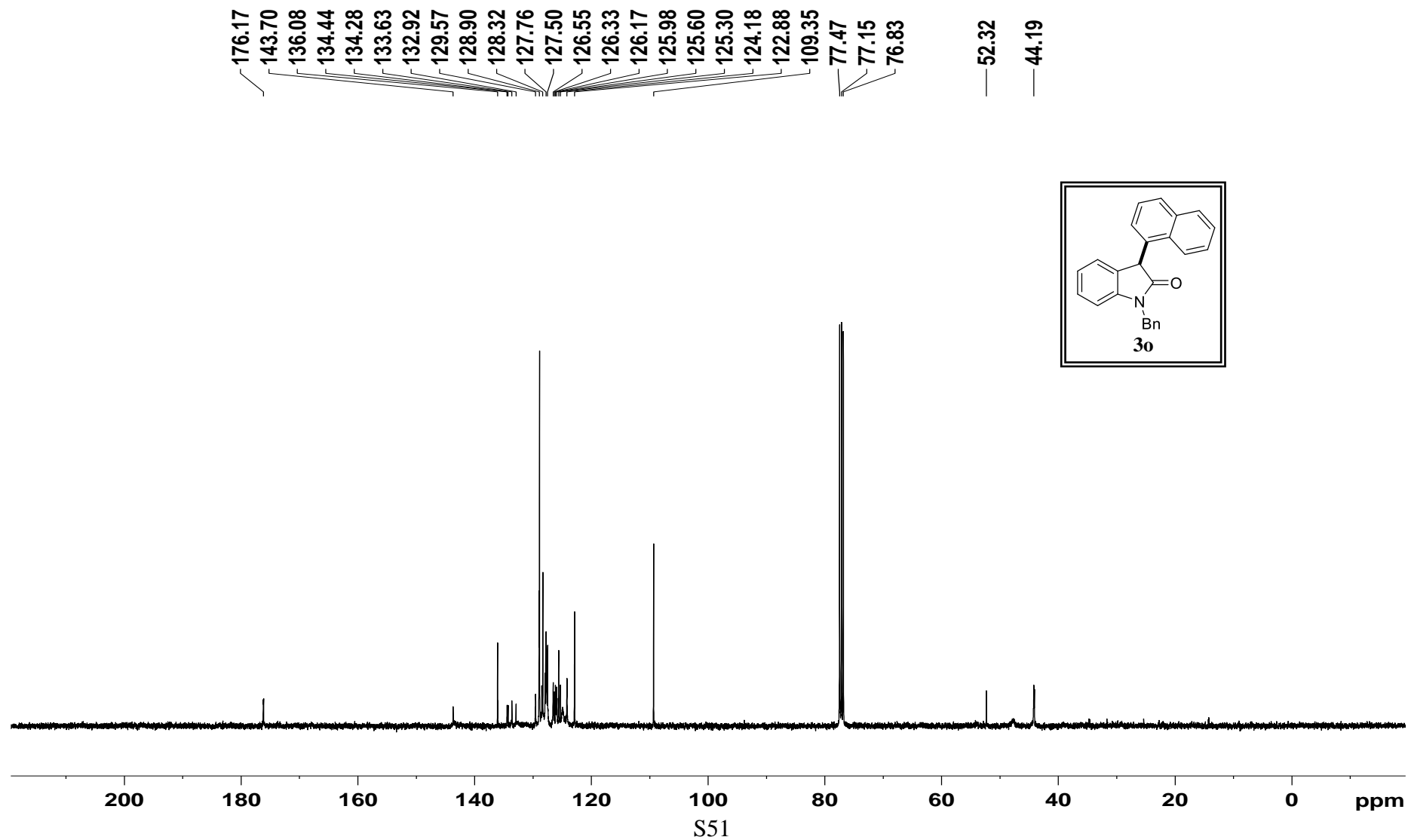
¹H NMR spectrum of **30**

apr-620 PROTON CDC13 9/2/2022



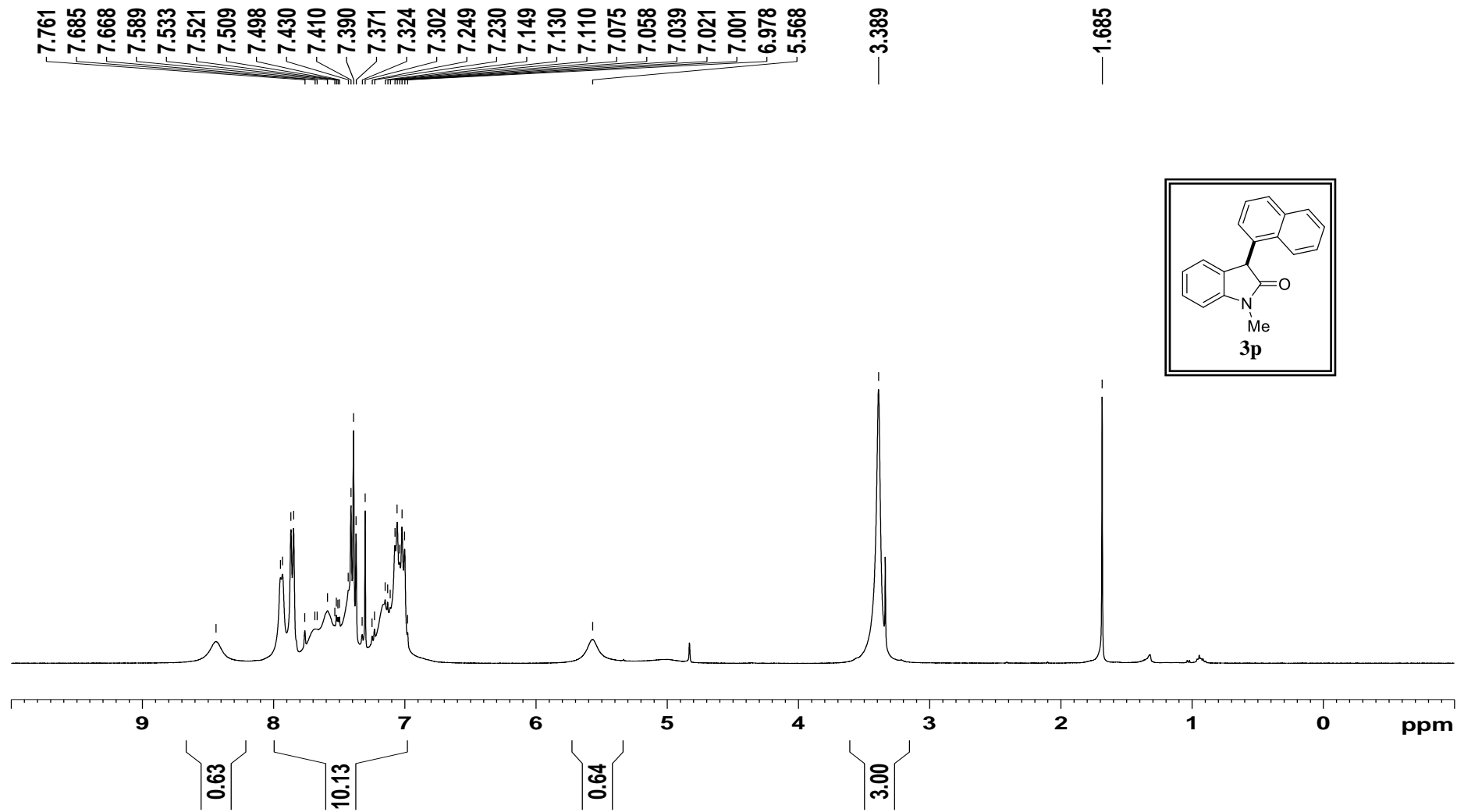
¹³C NMR spectrum of **30**

apr-620 C13CPD CDC13 15/7/2020



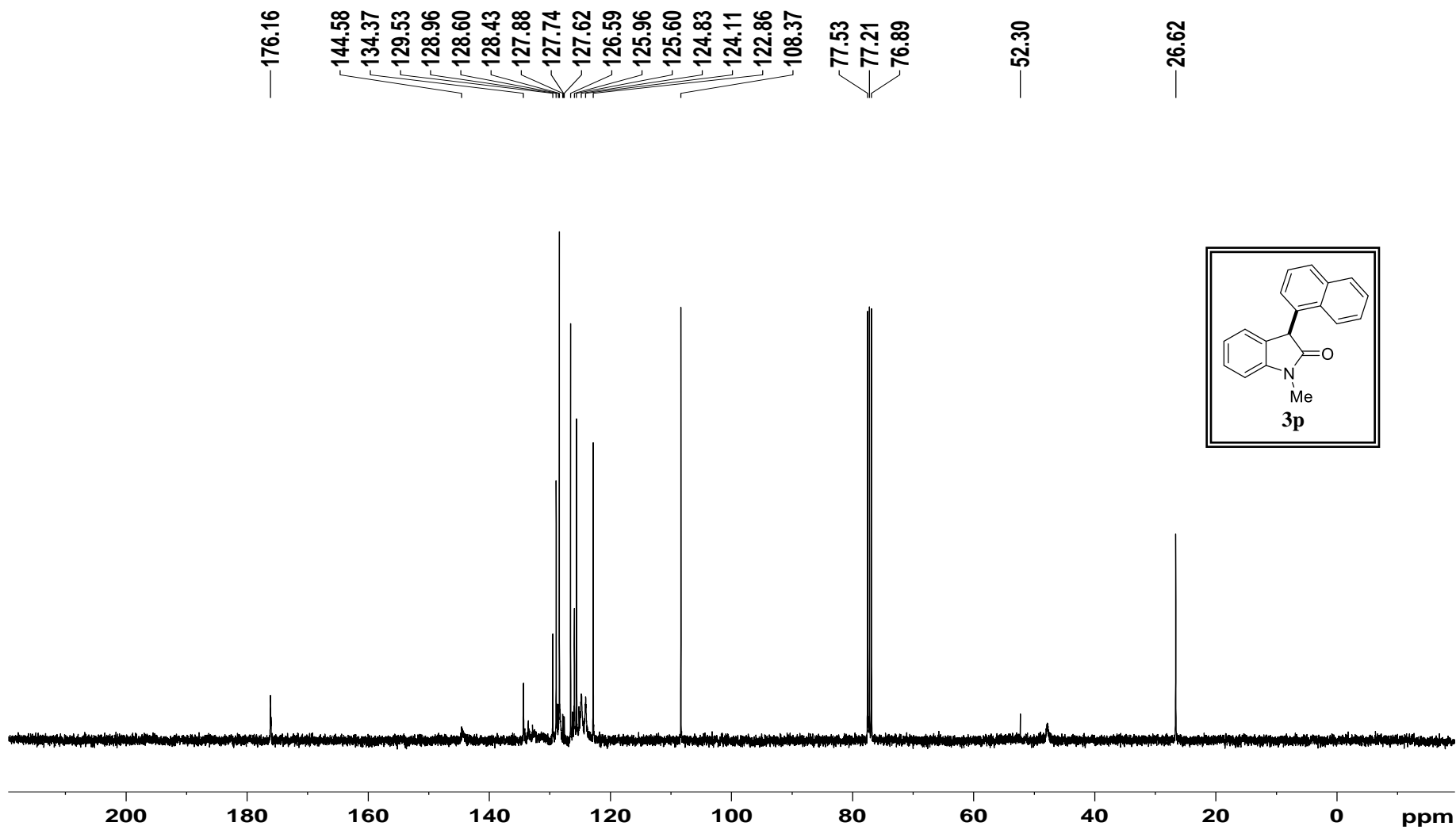
¹H NMR spectrum of **3p**

APR-819 PROTON CDC13 15/2/2022



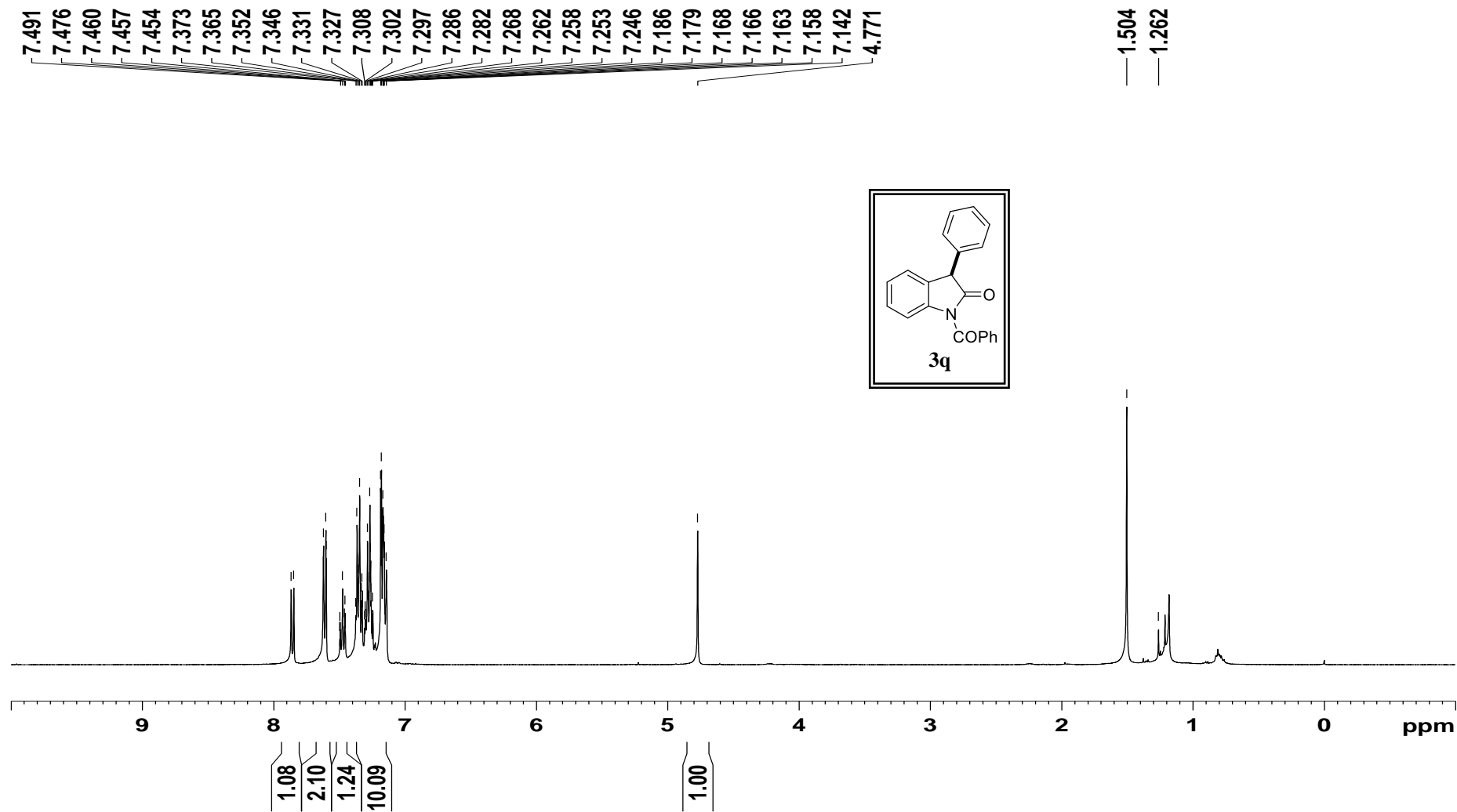
¹³C NMR spectrum of **3p**

apr-819 C13CPD CDC13 15/2/2022



¹H NMR spectrum of **3q**

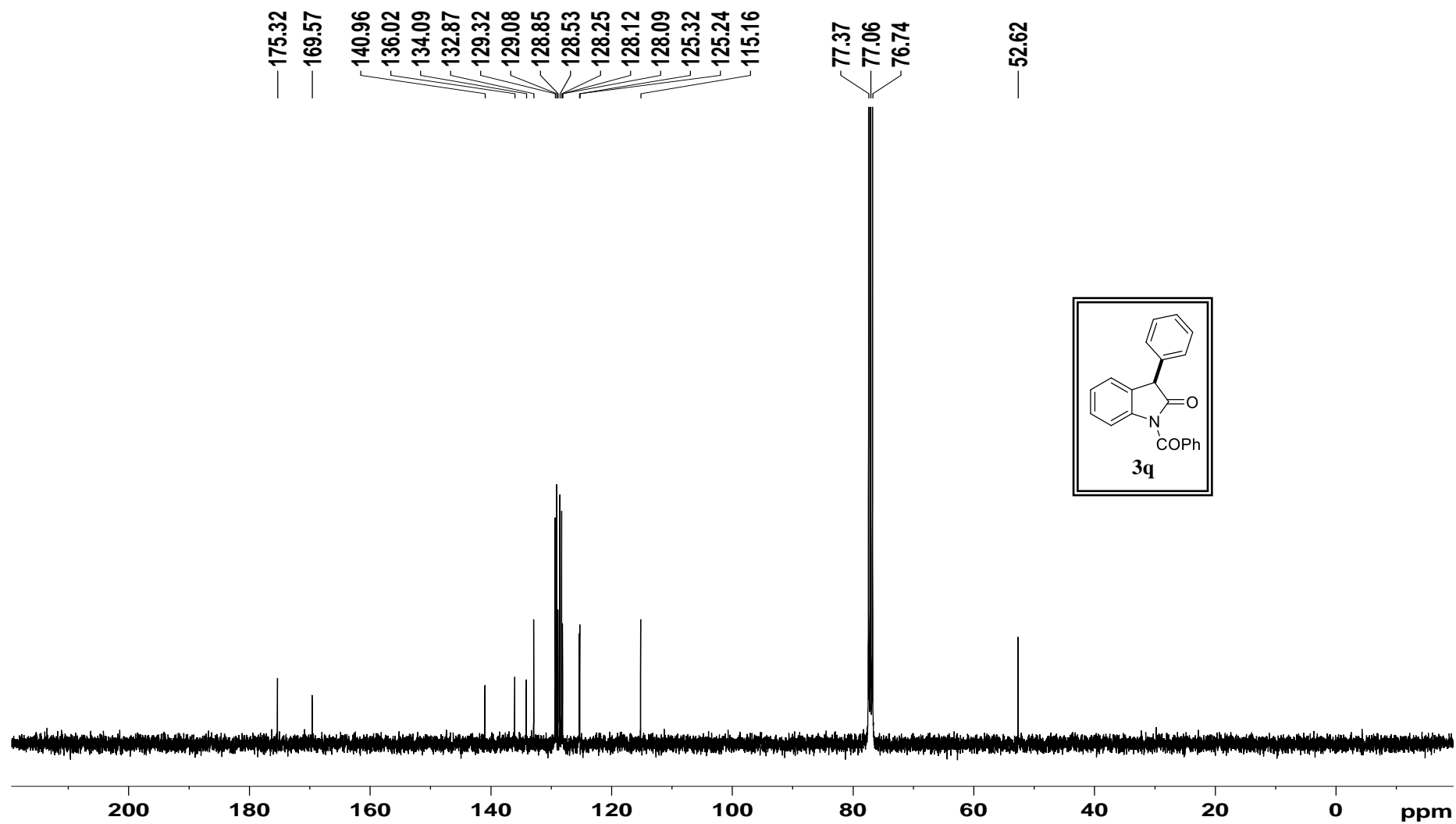
apr-704 PROTON CDC13 2/3/2021



S54

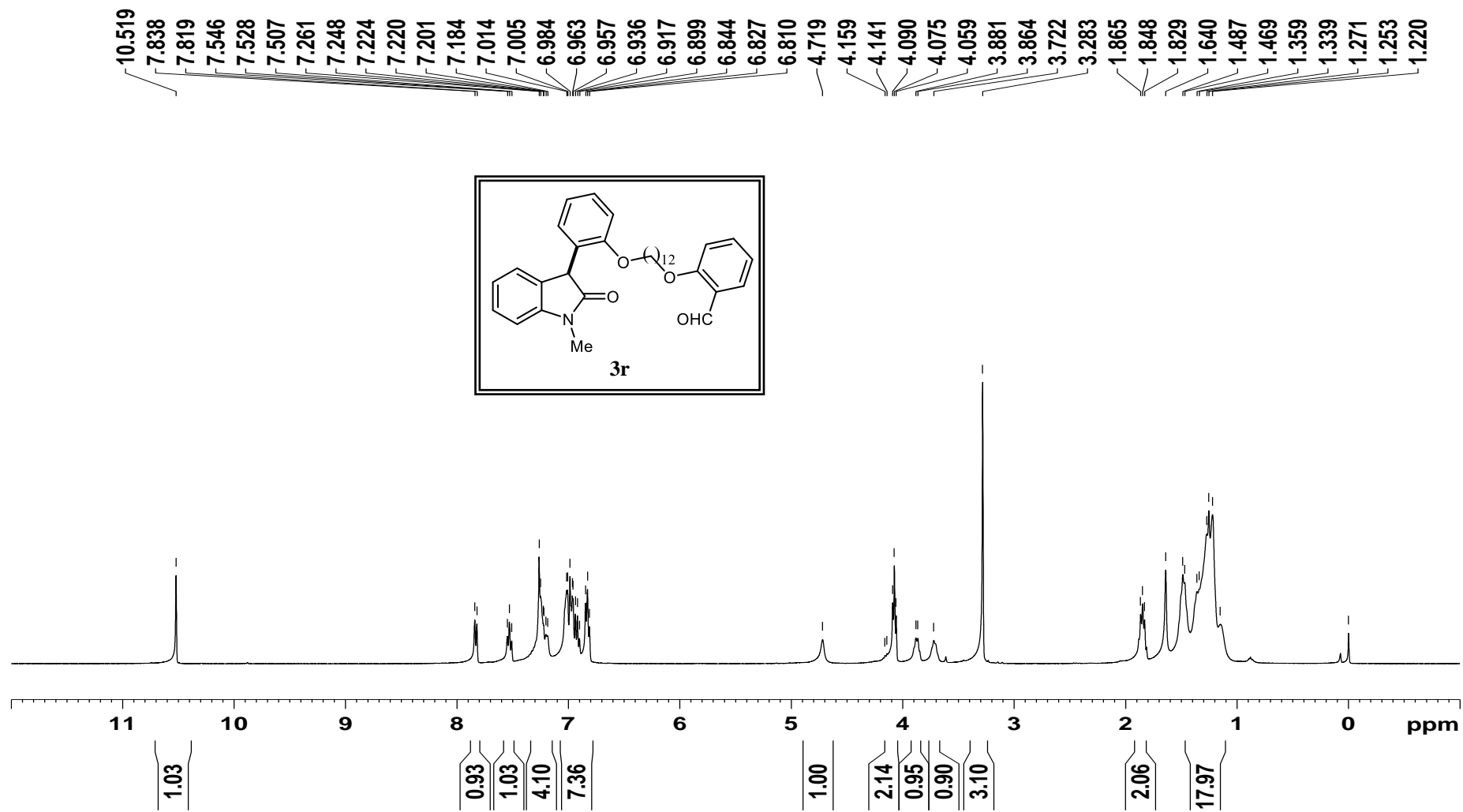
¹³C NMR spectrum of **3q**

apr-704 C13CPD CDC13 2/9/2021



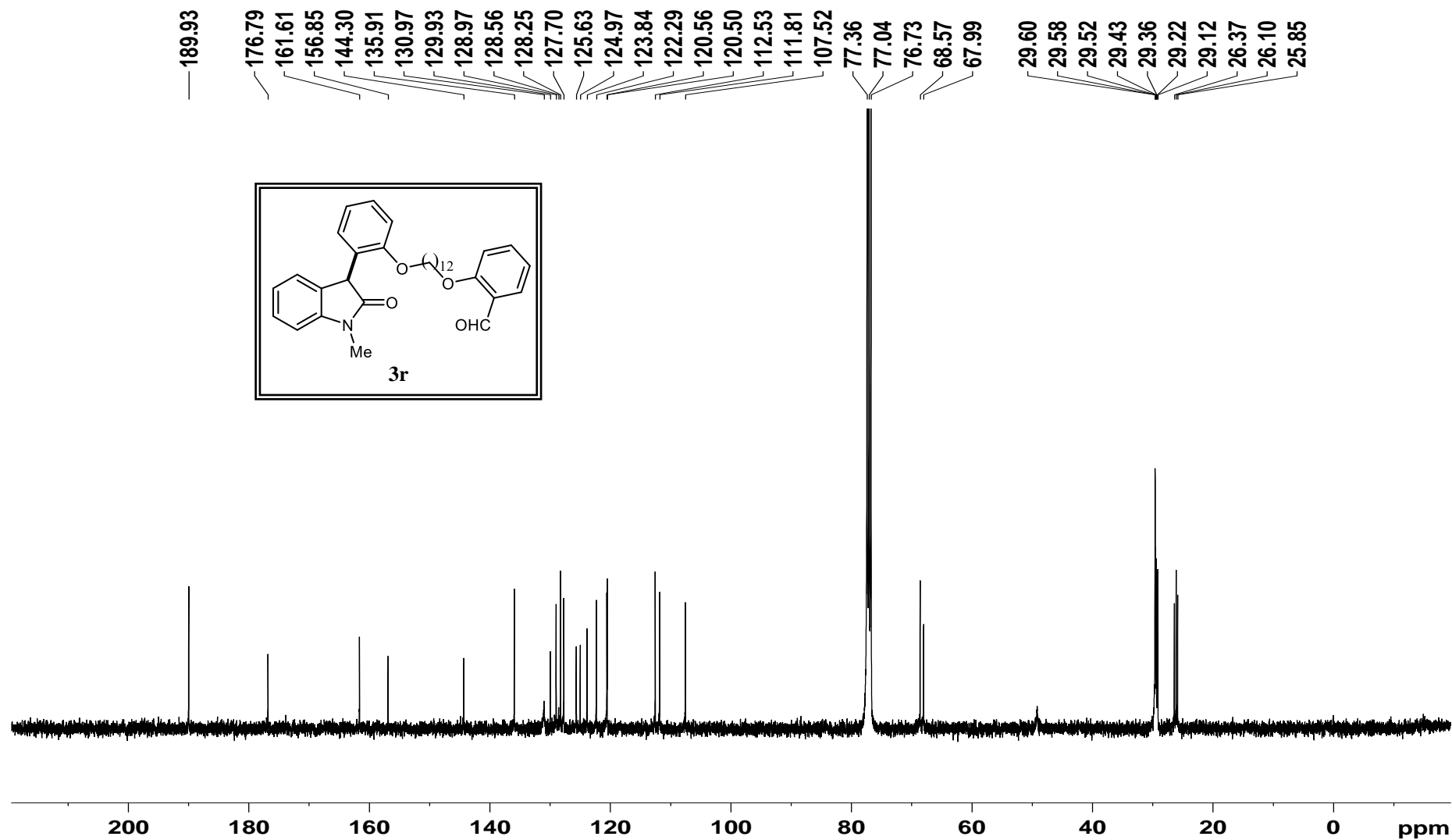
¹H NMR spectrum of 3r

apr-440 PROTON CDC13 12/04/2019

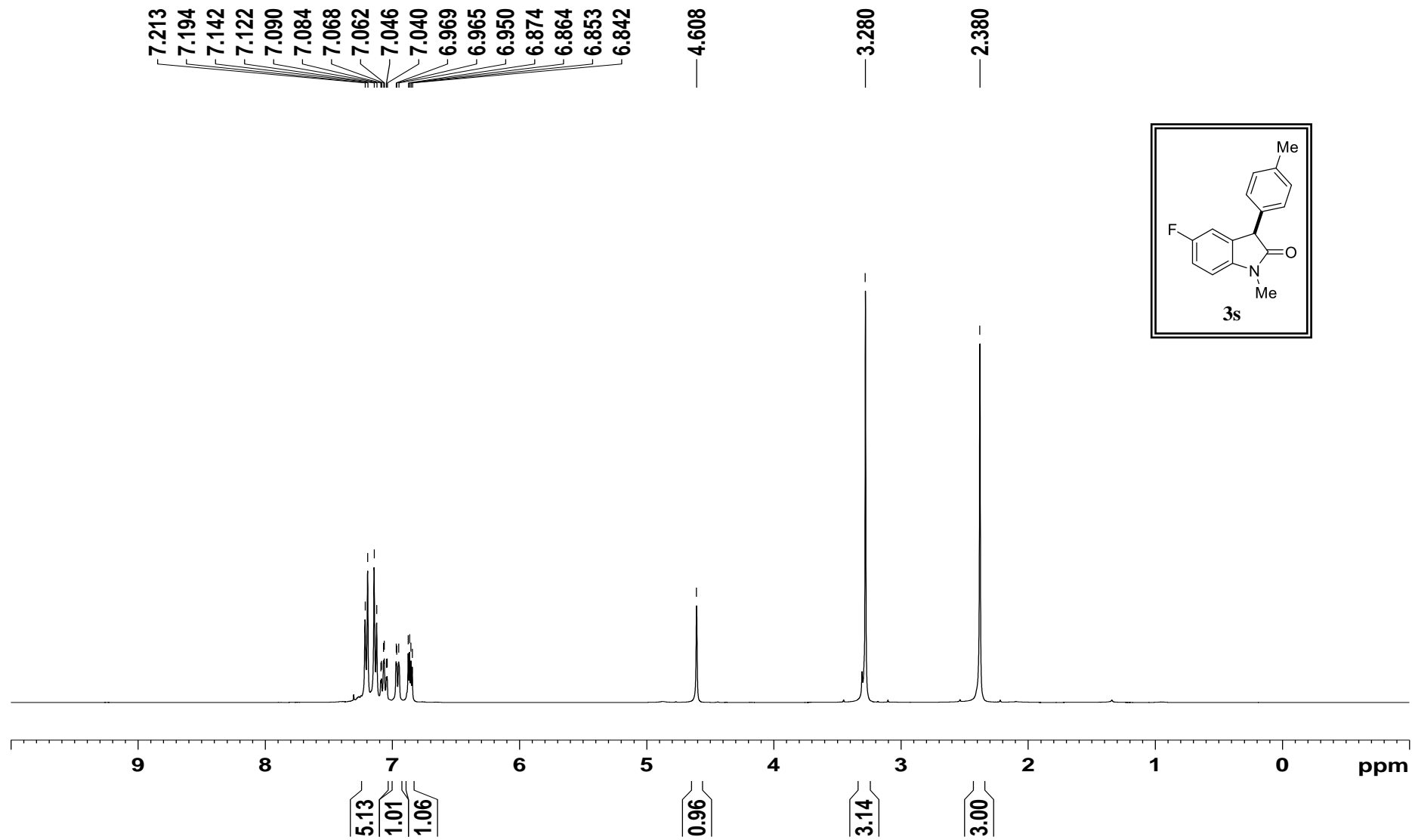


¹³C NMR spectrum of 3r

apr-440 C13CPD CDC13 12/04/2019

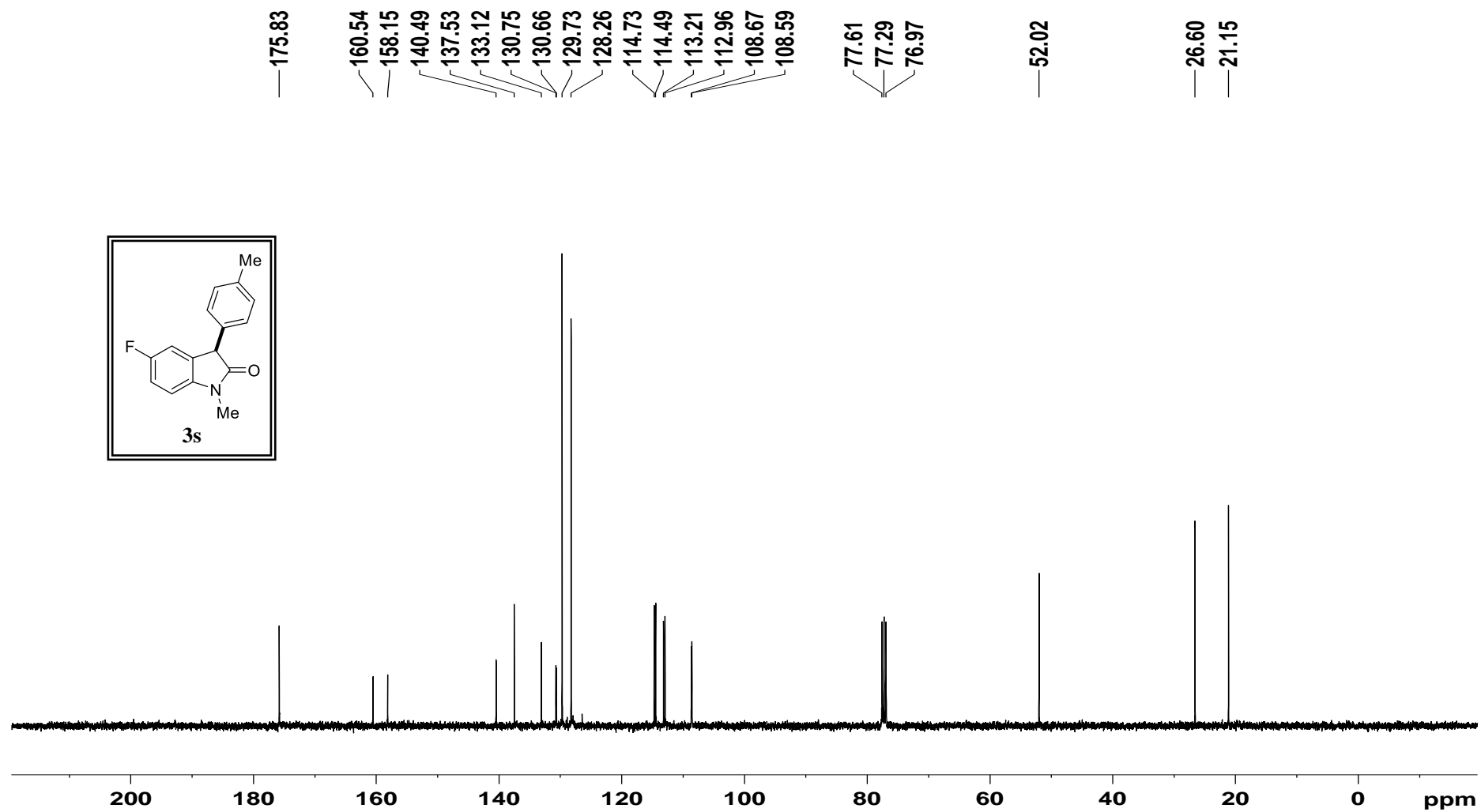


¹H NMR spectrum of 3s



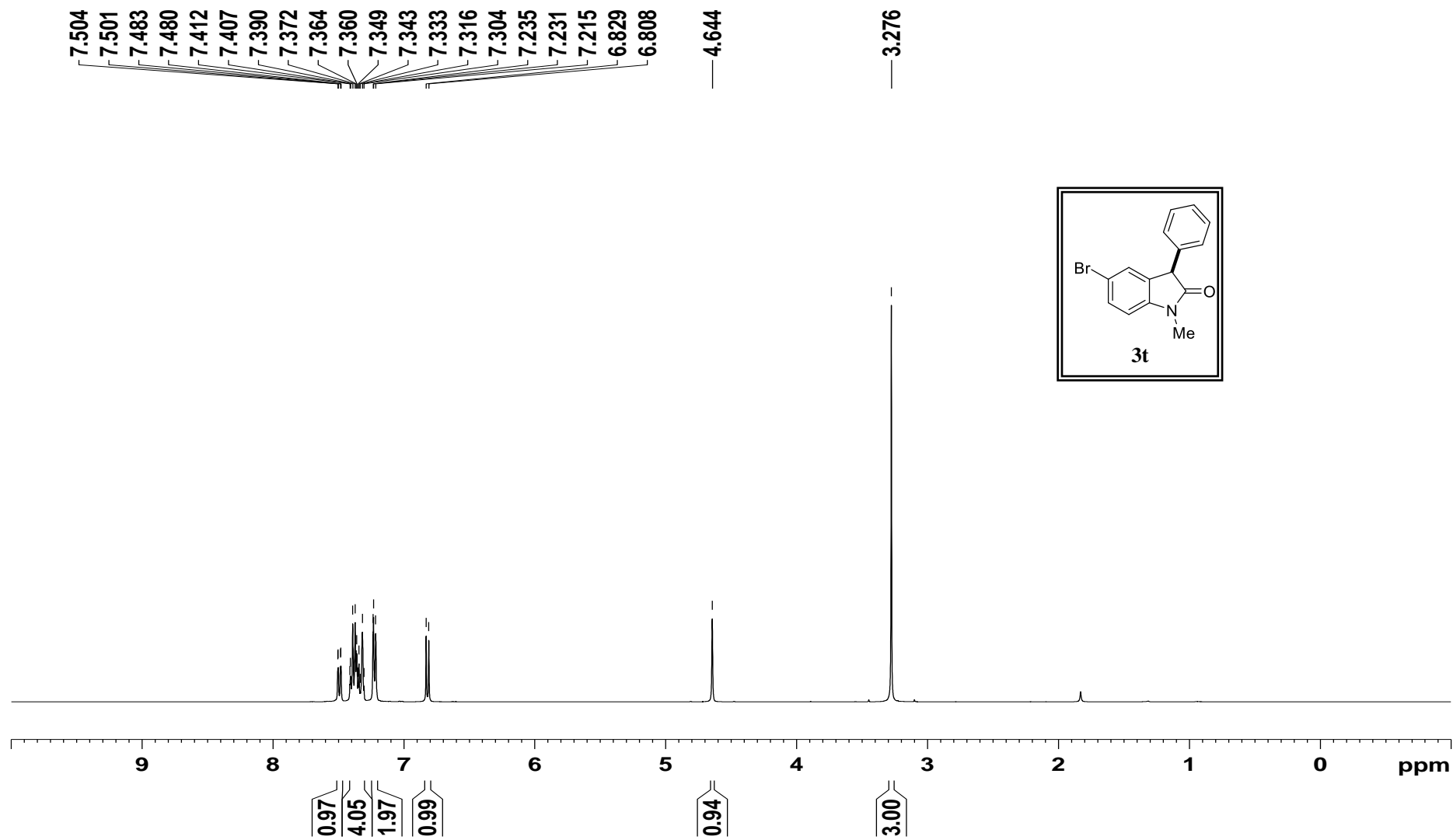
¹³C NMR spectrum of 3s

apr-775 C13CPD CDC13 29/9/2021



¹H NMR spectrum of 3t

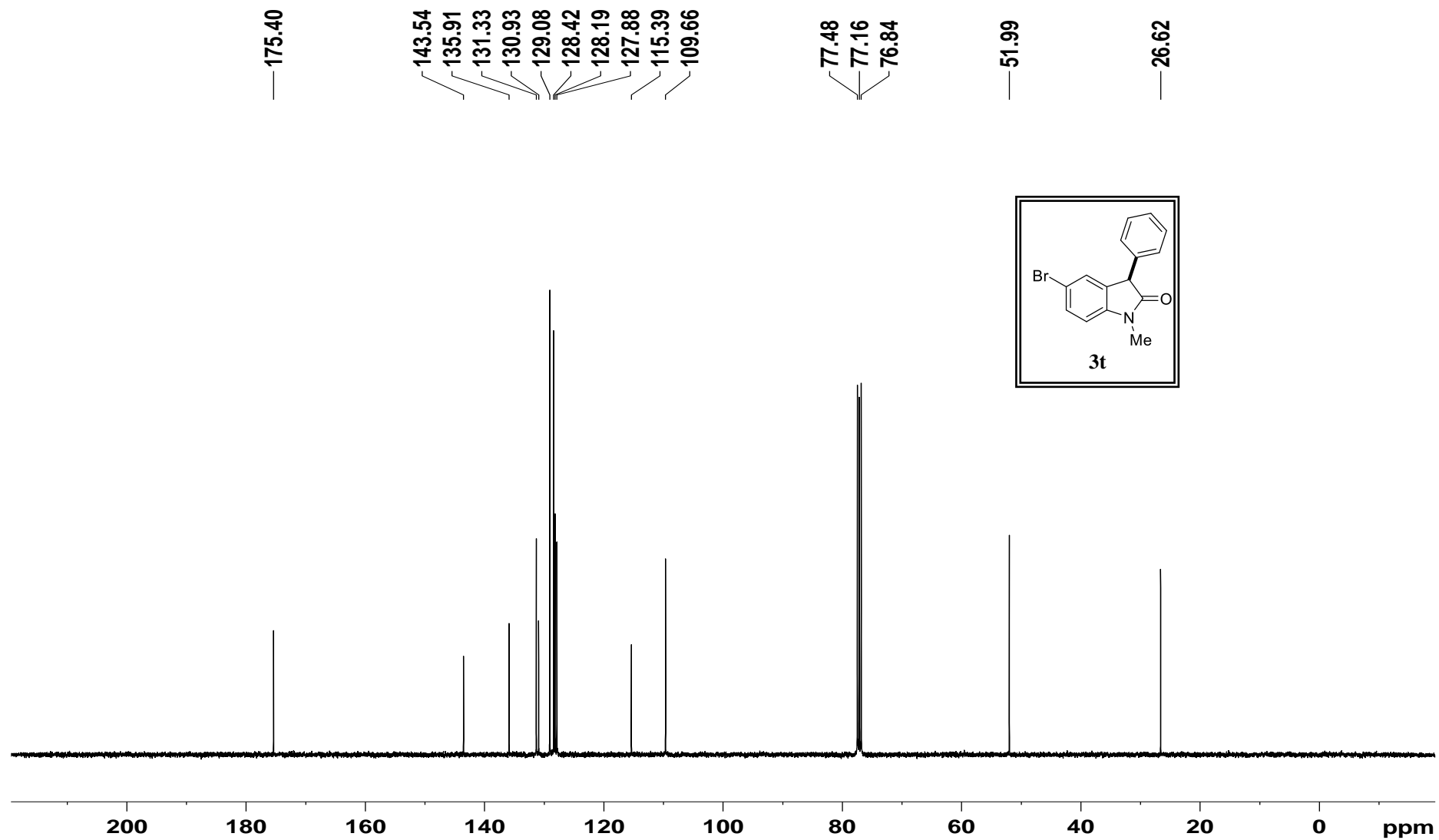
apr-774 PROTON CDC13 29/9/2021



S60

¹³C NMR spectrum of **3t**

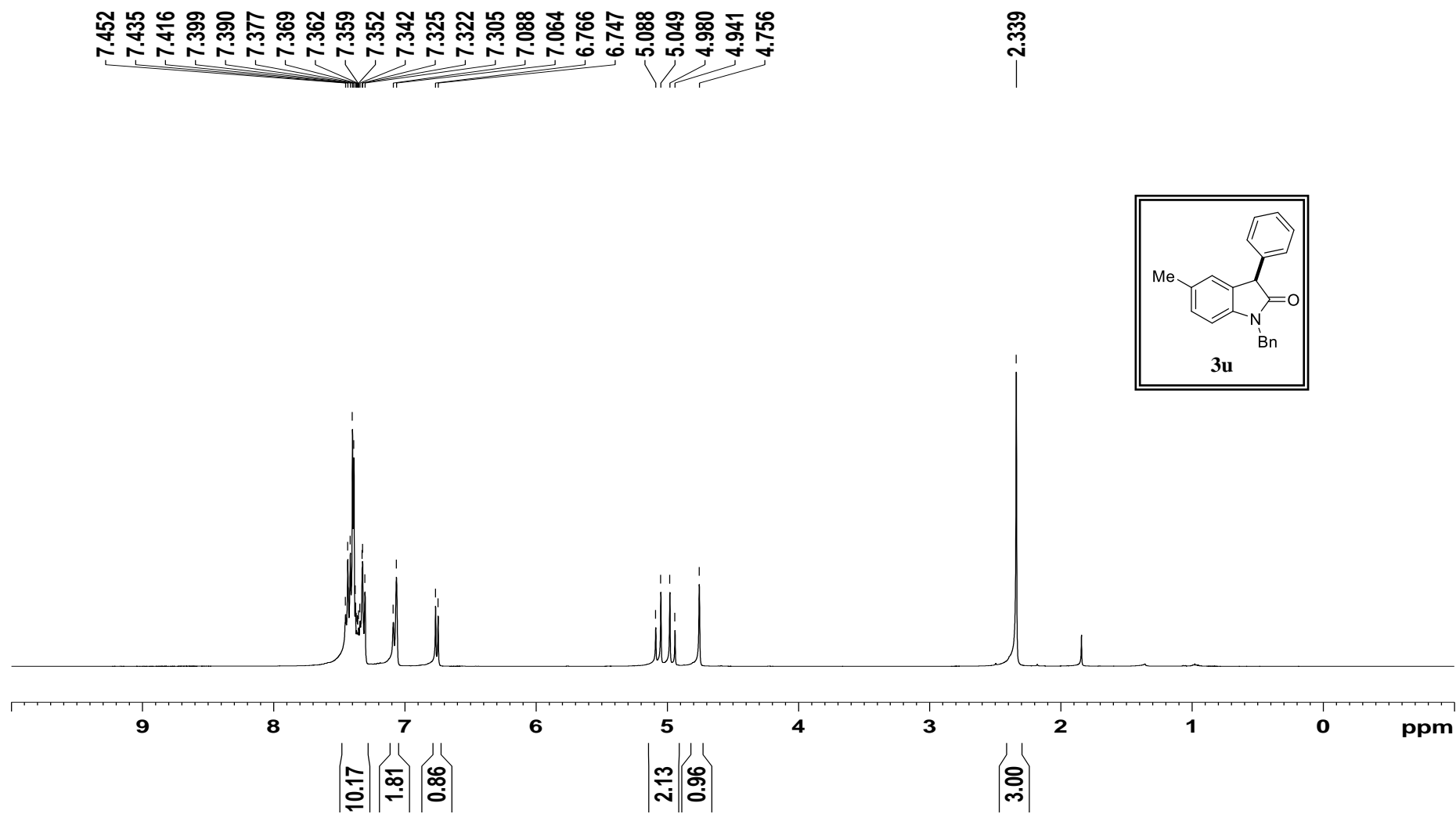
apr-774 C13CPD CDC13 29/9/2021



S61

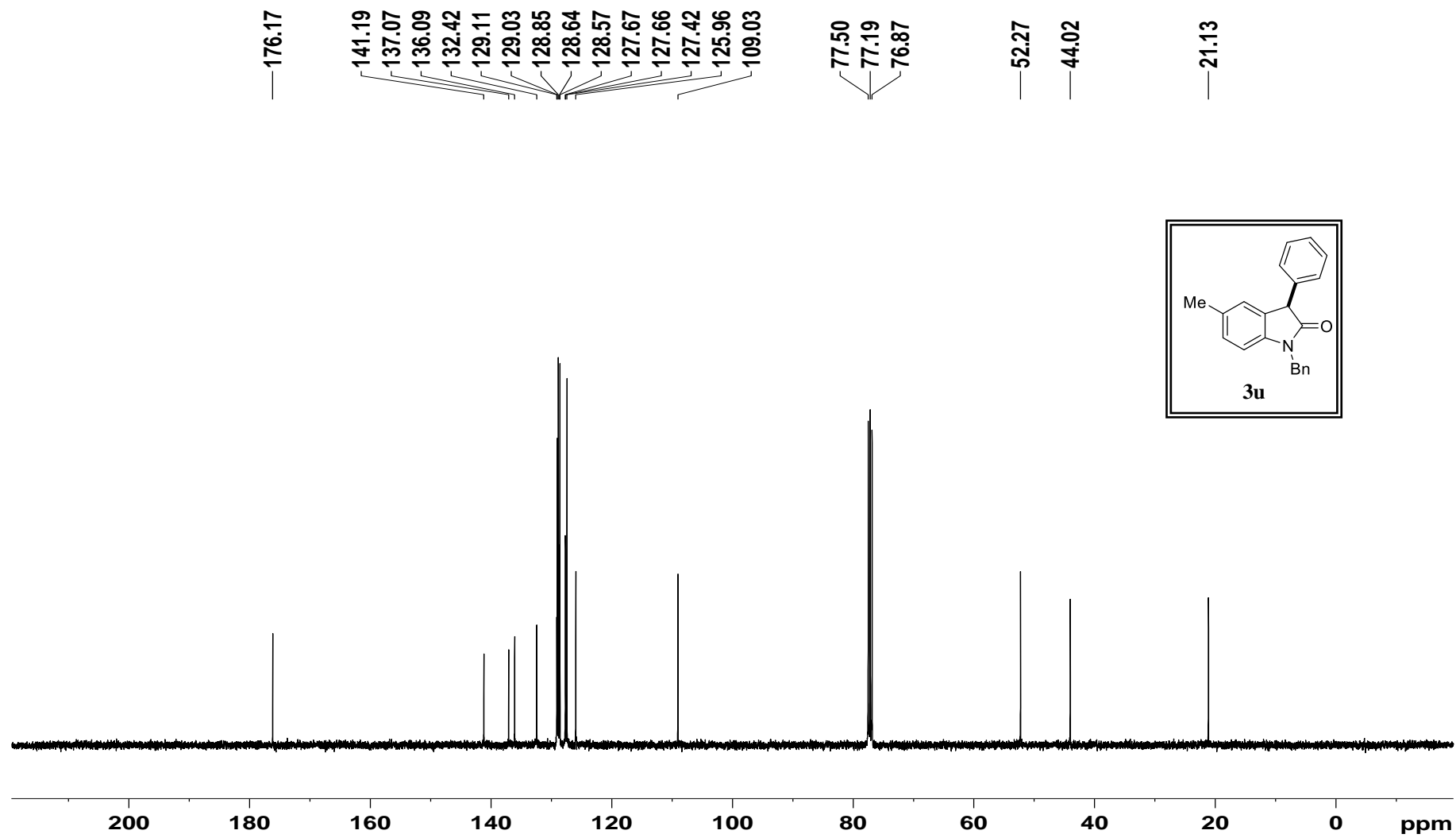
¹H NMR spectrum of **3u**

apr-780 PROTON CDCl3 4/10/2021



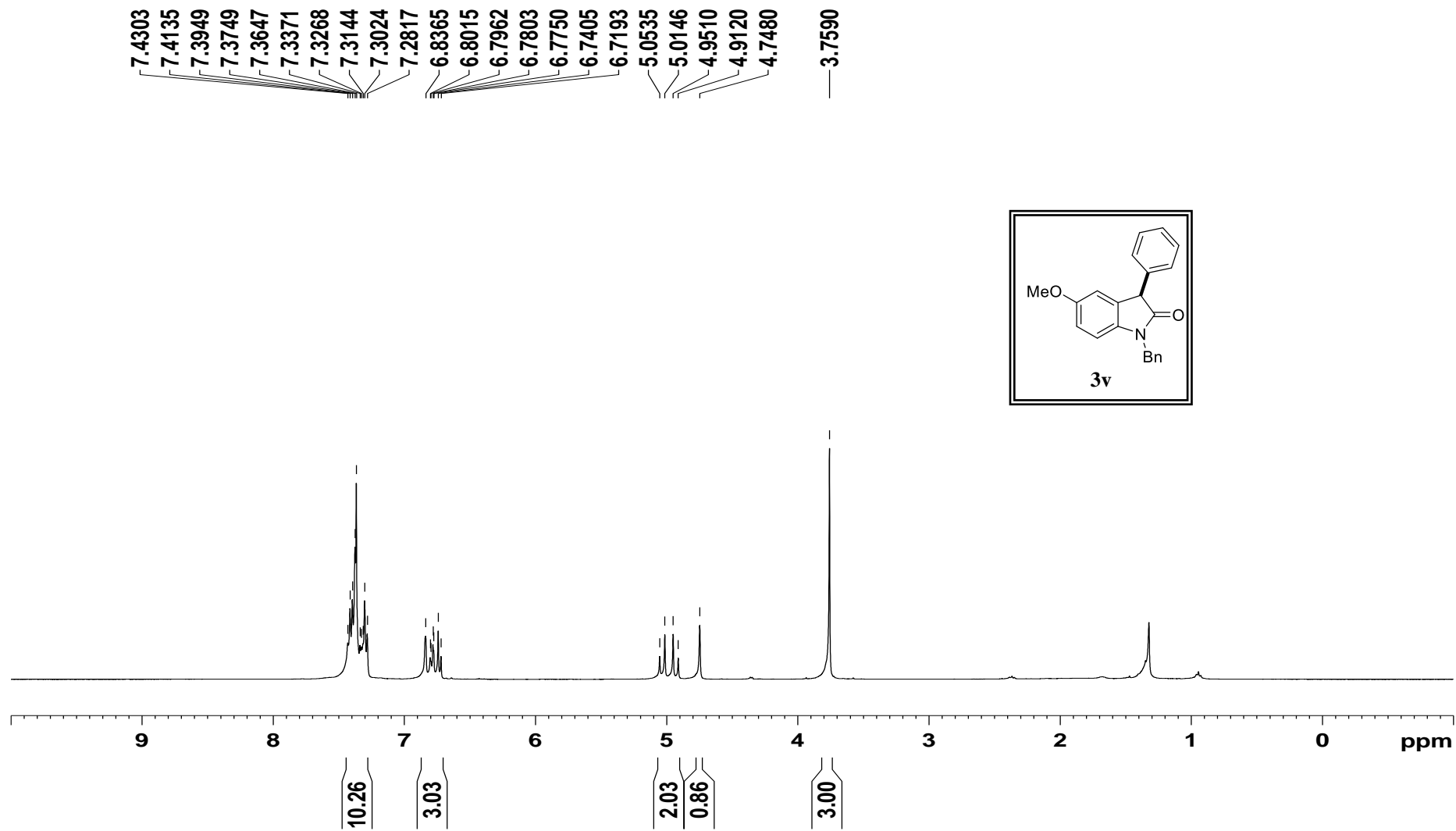
¹³C NMR spectrum of **3u**

apr-780 C13CPD CDC13 4/10/2021



¹H NMR spectrum of **3v**

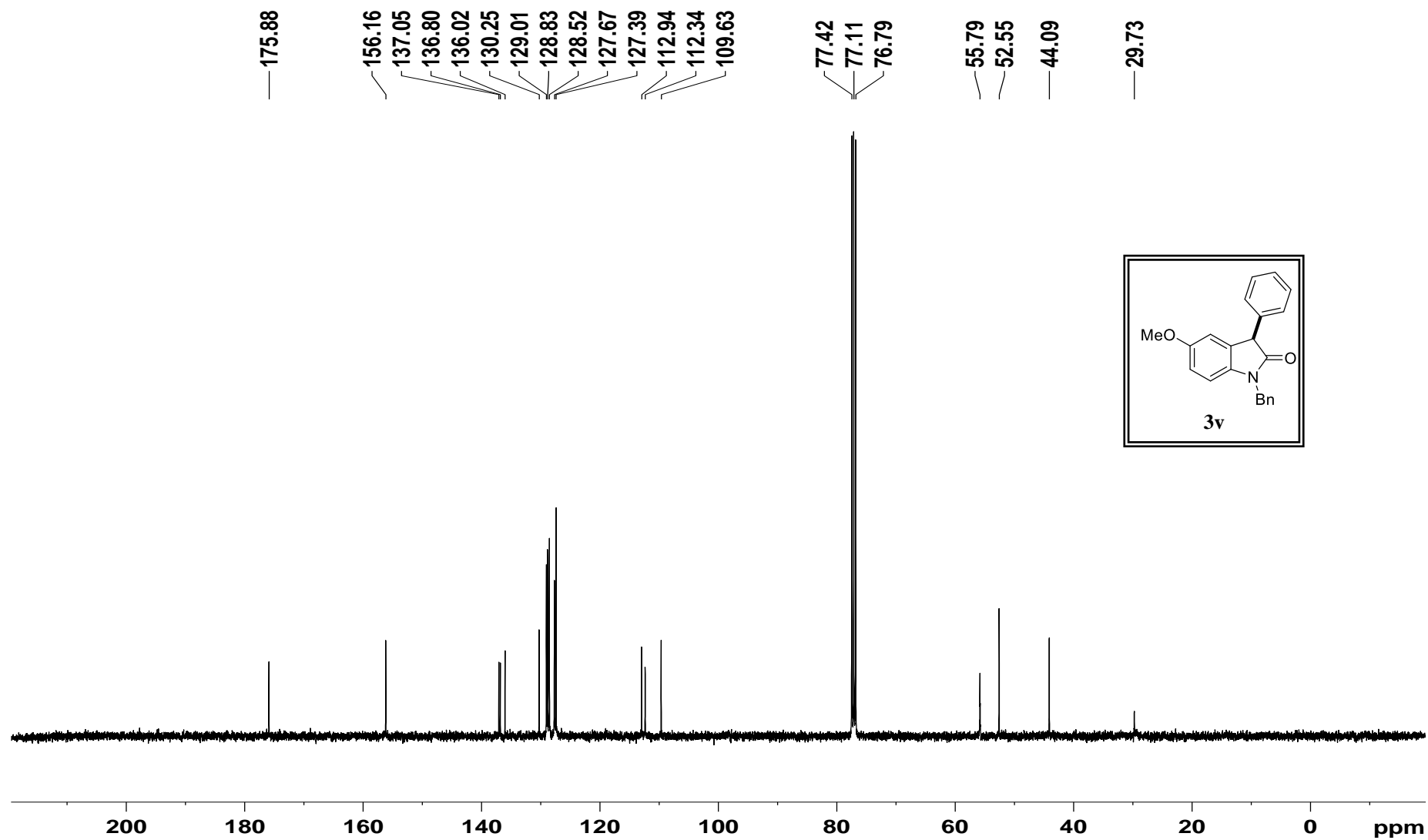
apr-785 PROTON CDCl₃ 11/10/2021



S64

¹³C NMR spectrum of **3v**

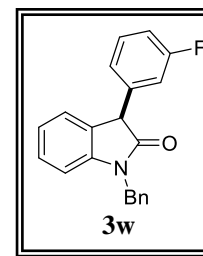
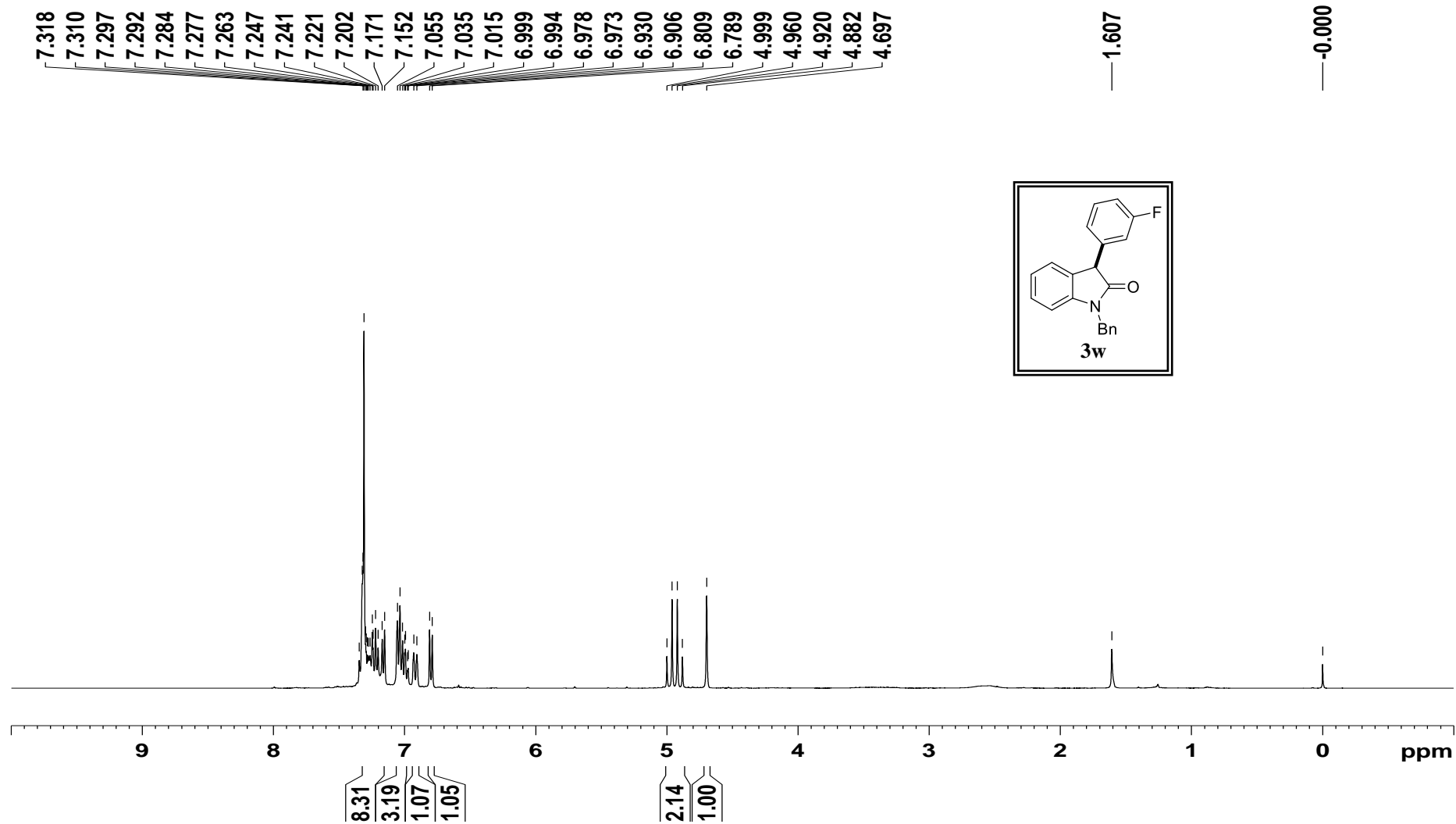
apr-785 C13CPD CDC13 11/10/2021



S65

¹H NMR spectrum of 3w

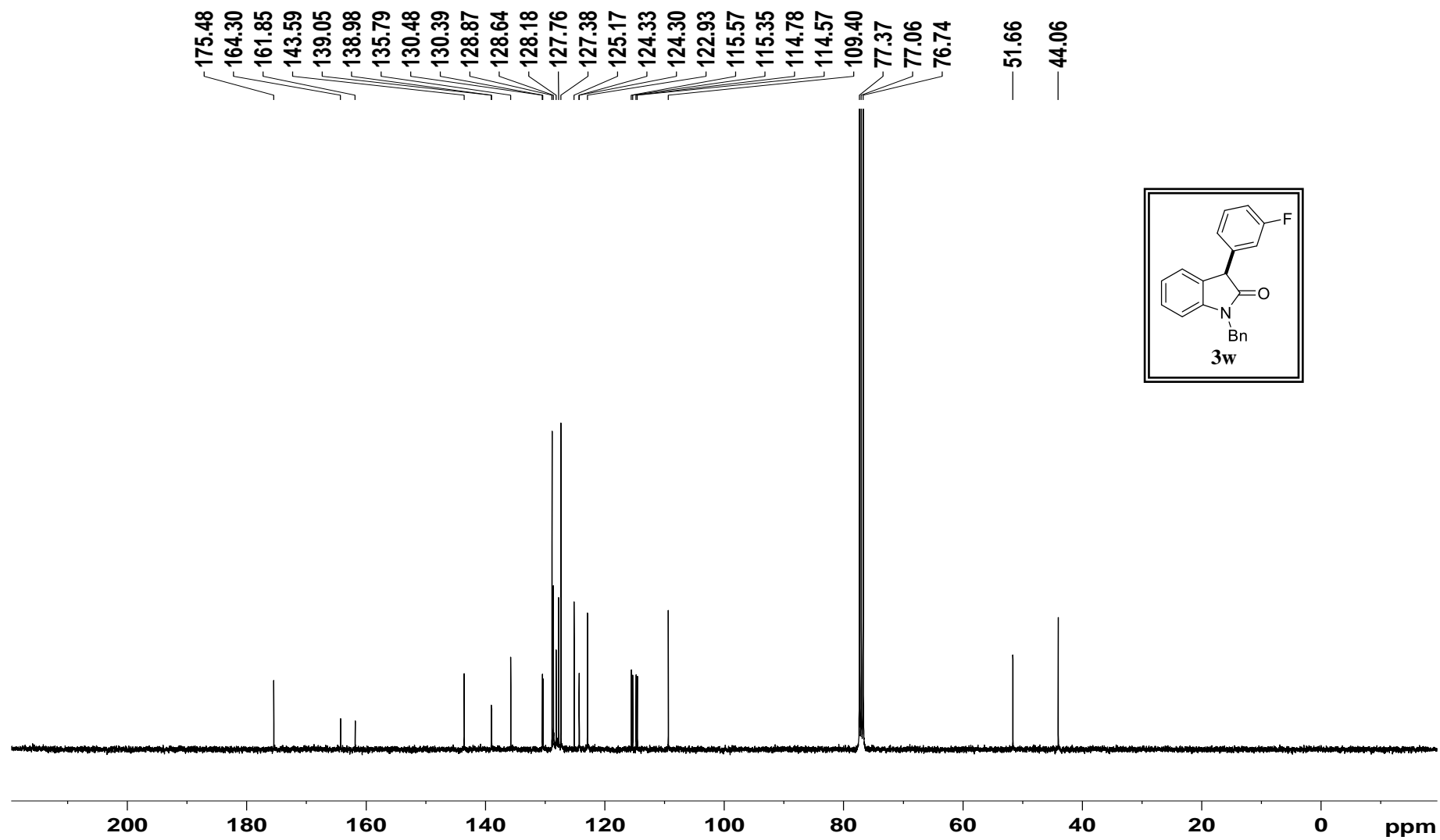
apr426 PROTON CDCl3 25/03/2019



S66

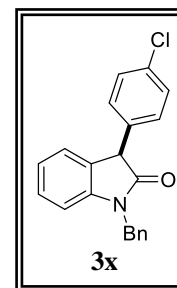
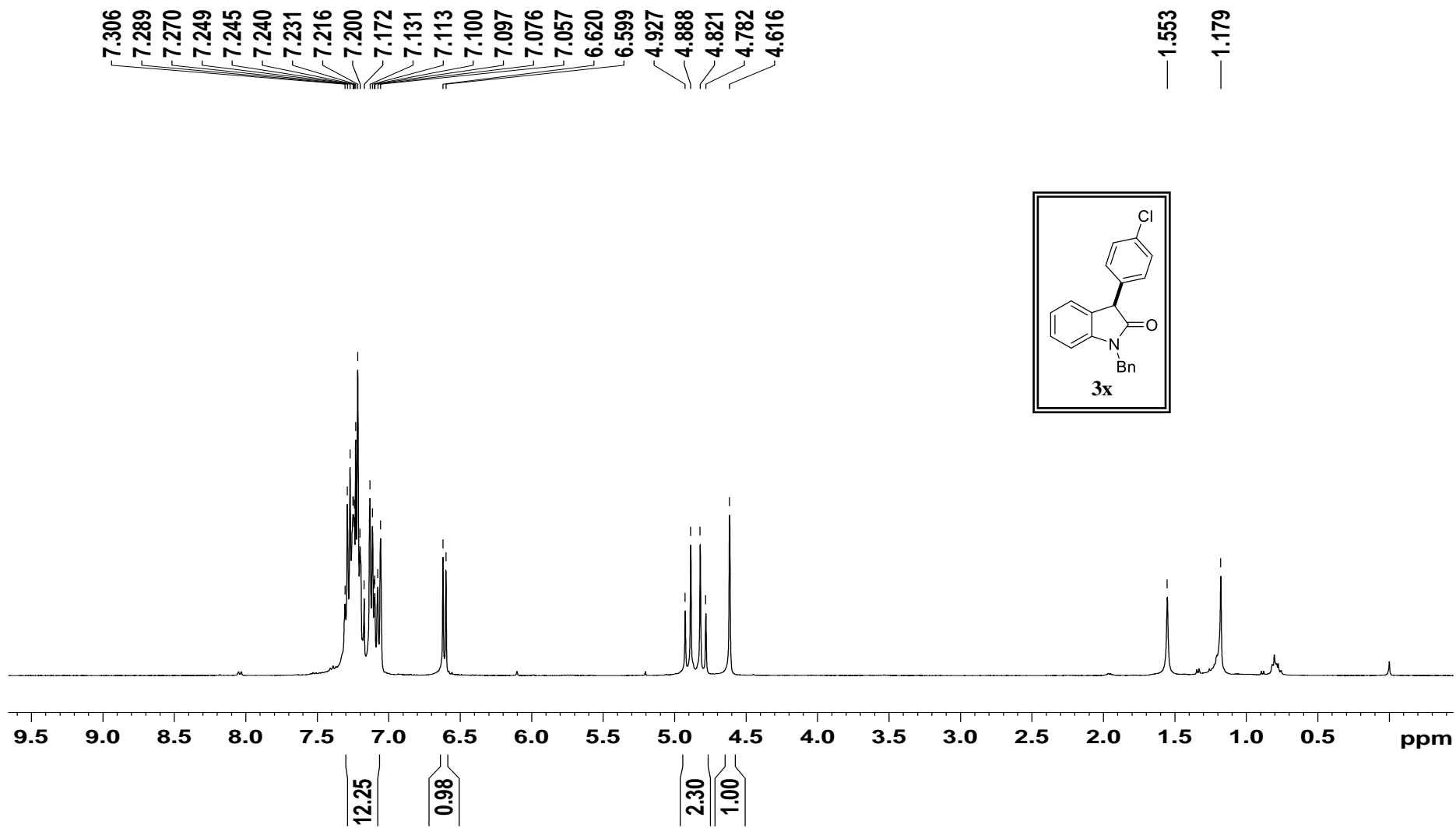
^{13}C NMR spectrum of **3w**

apr426 C13CPD CDC13 25/03/2019



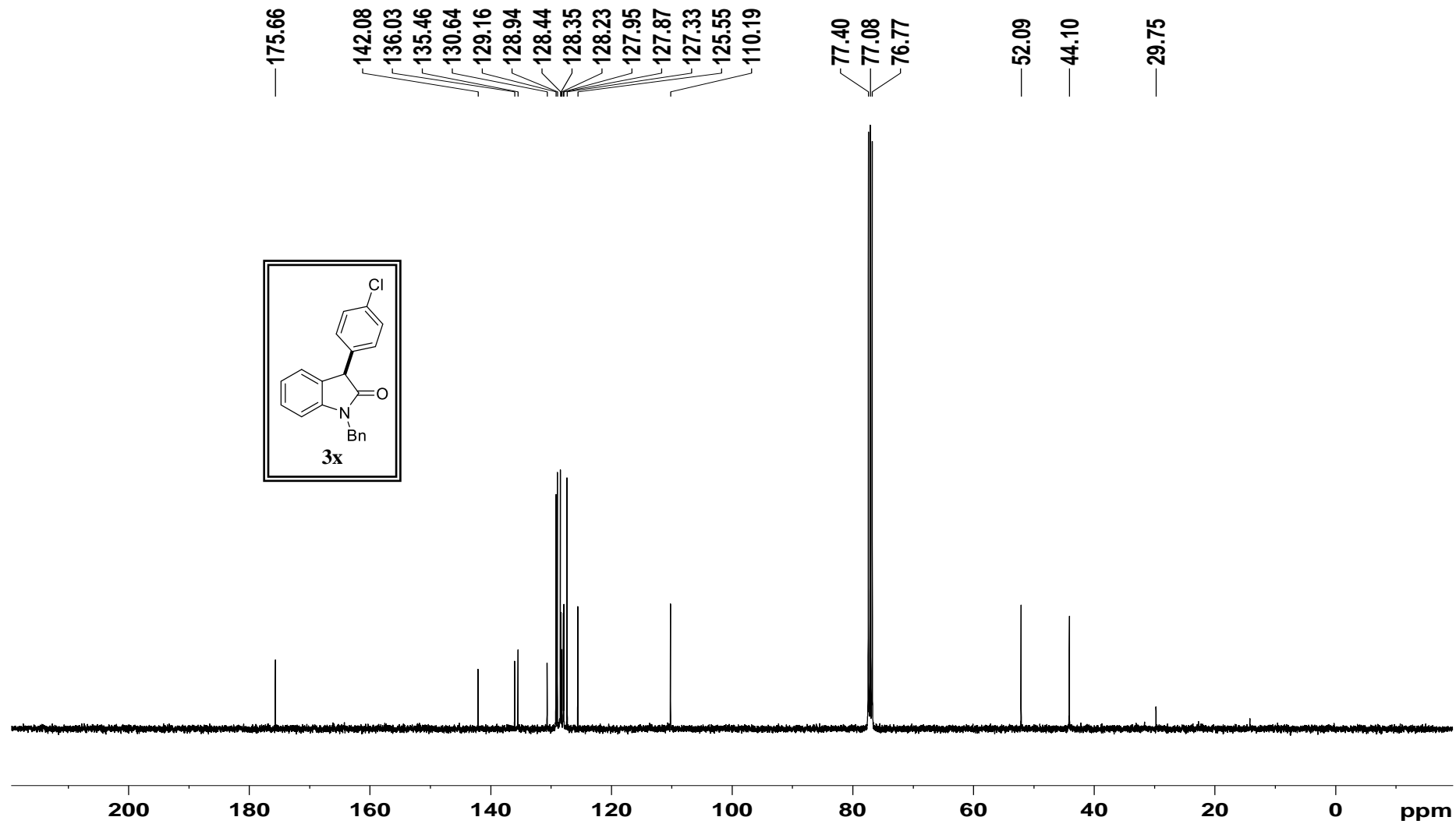
¹H NMR spectrum of 3x

apr-527 PROTON CDCl3 25/10/2019



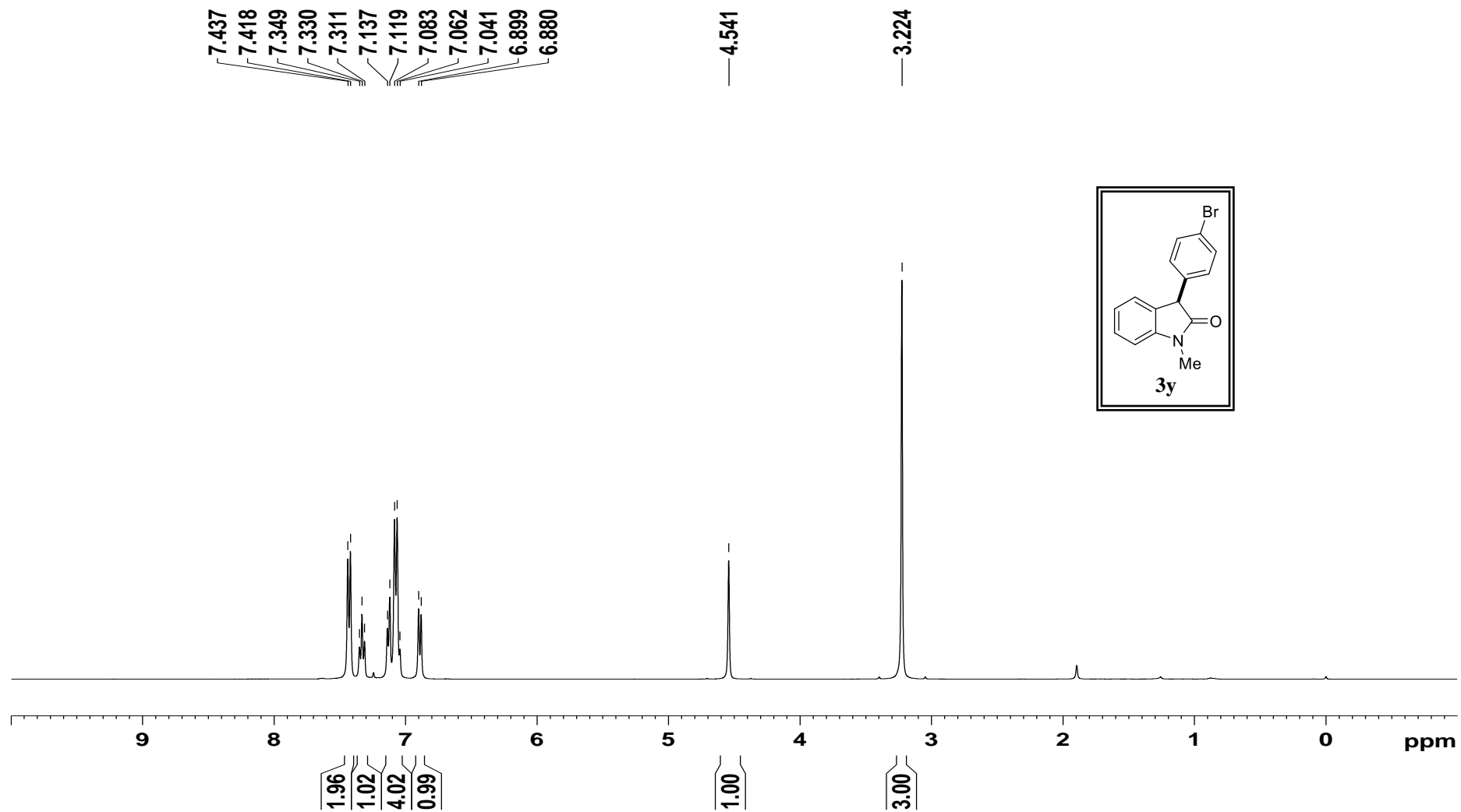
¹³C NMR spectrum of **3x**

apr-527 C13CPD CDC13 25/10/2019



¹H NMR spectrum of **3y**

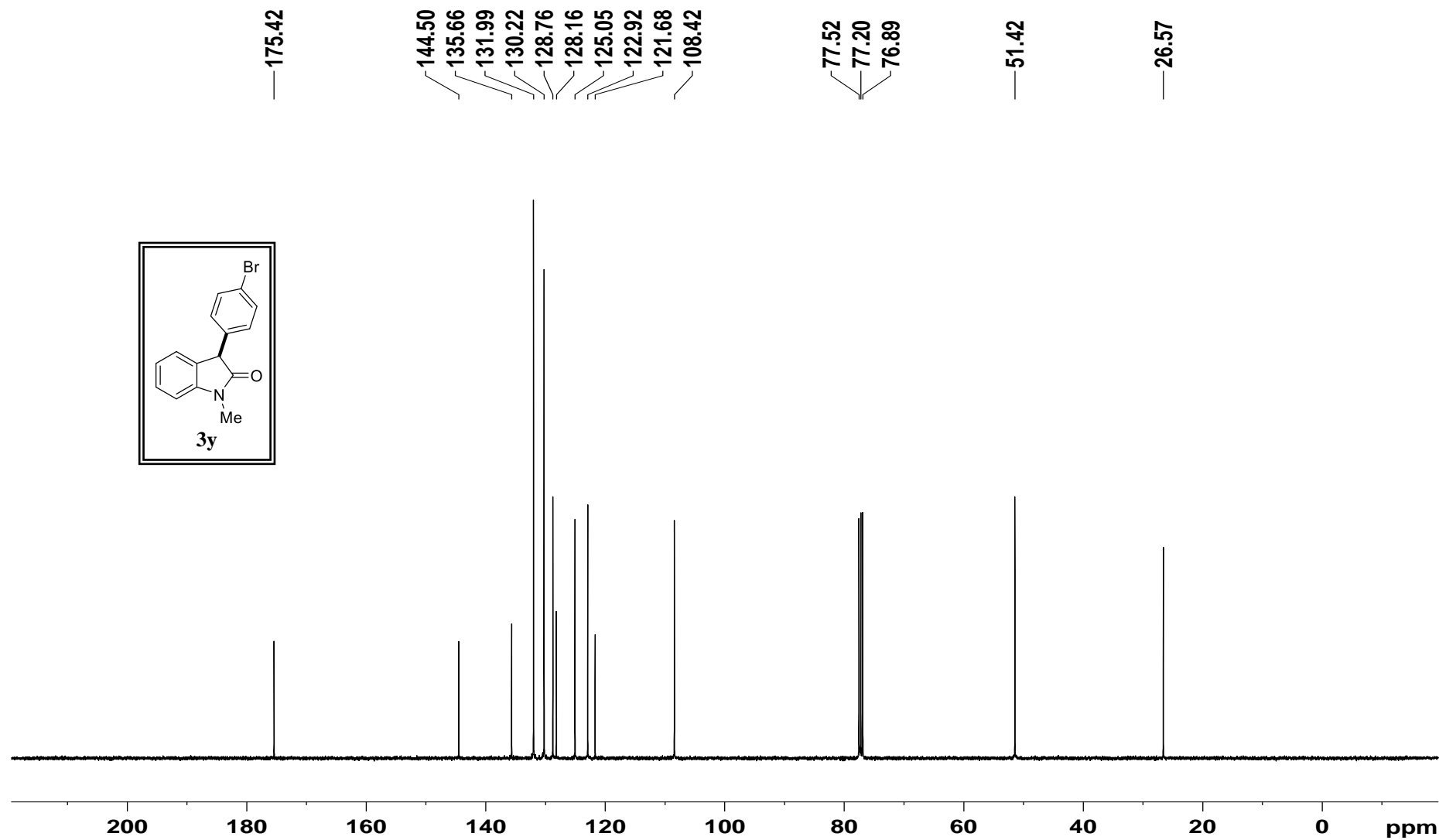
apr-425 PROTON CDC13 26/03/2019



S70

¹³C NMR spectrum of **3y**

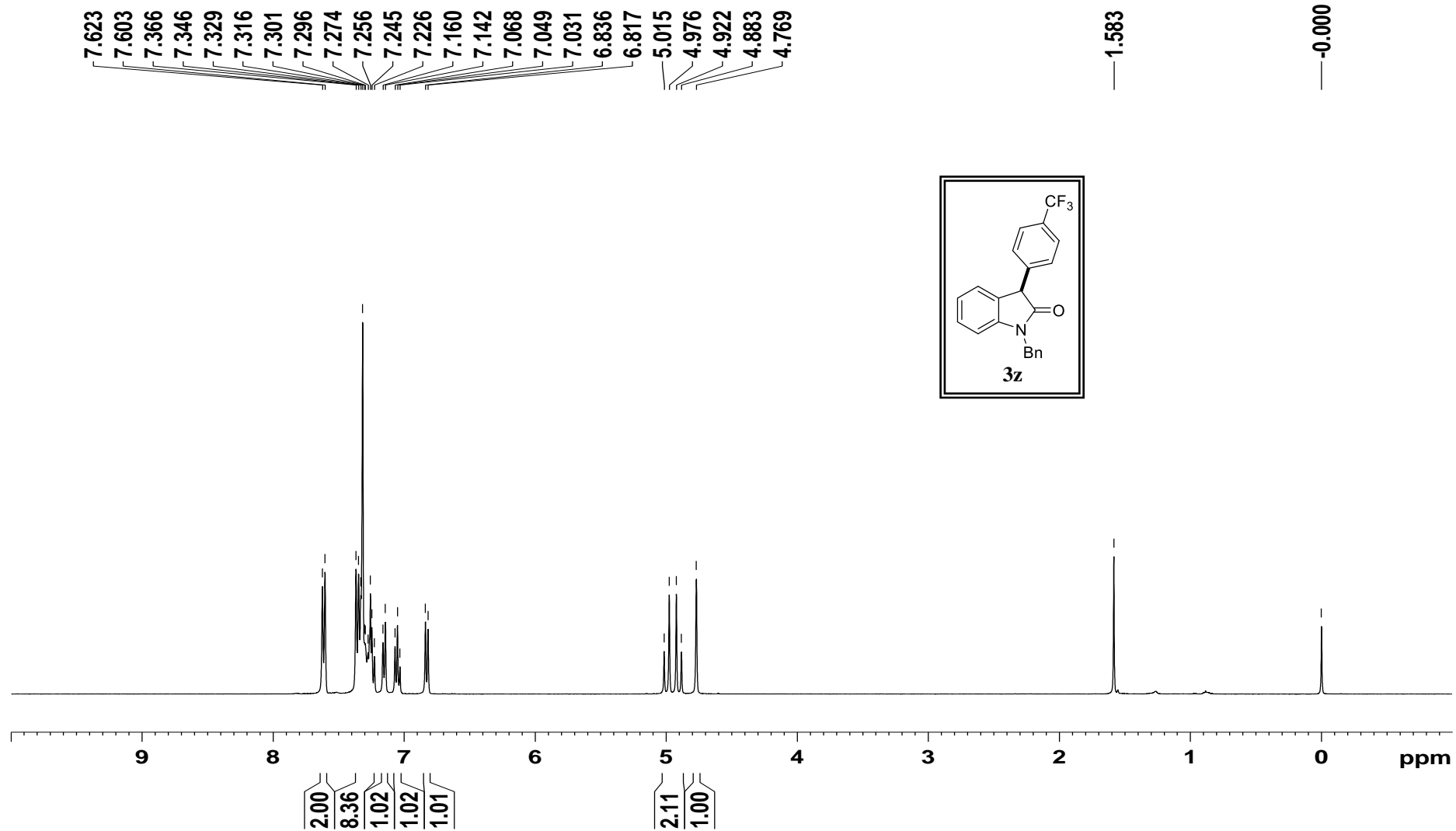
apr-425 C13CPD CDC13 25/03/2019



S71

¹H NMR spectrum of **3z**

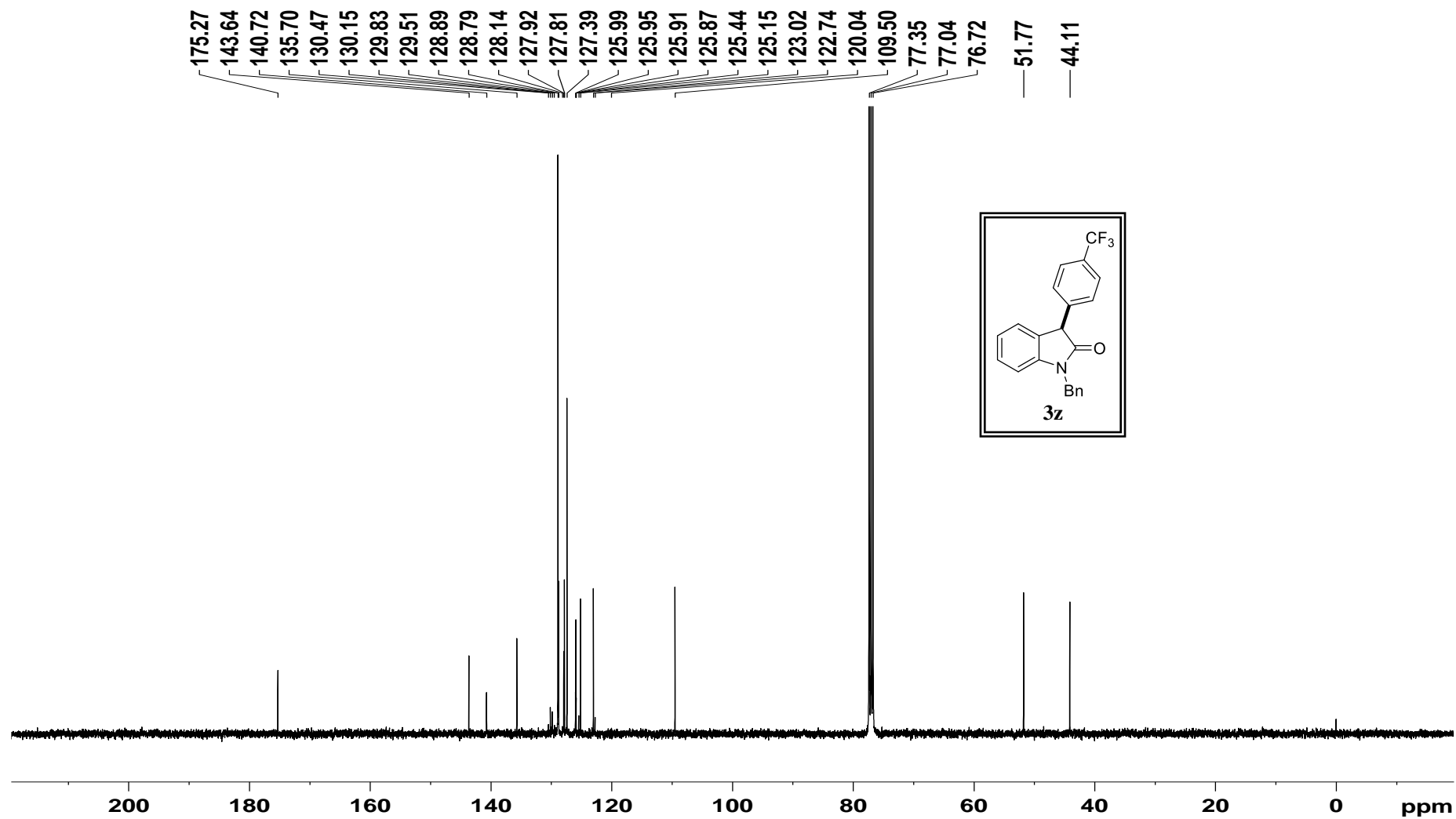
apr435 PROTON CDC13 4/04/2019



S72

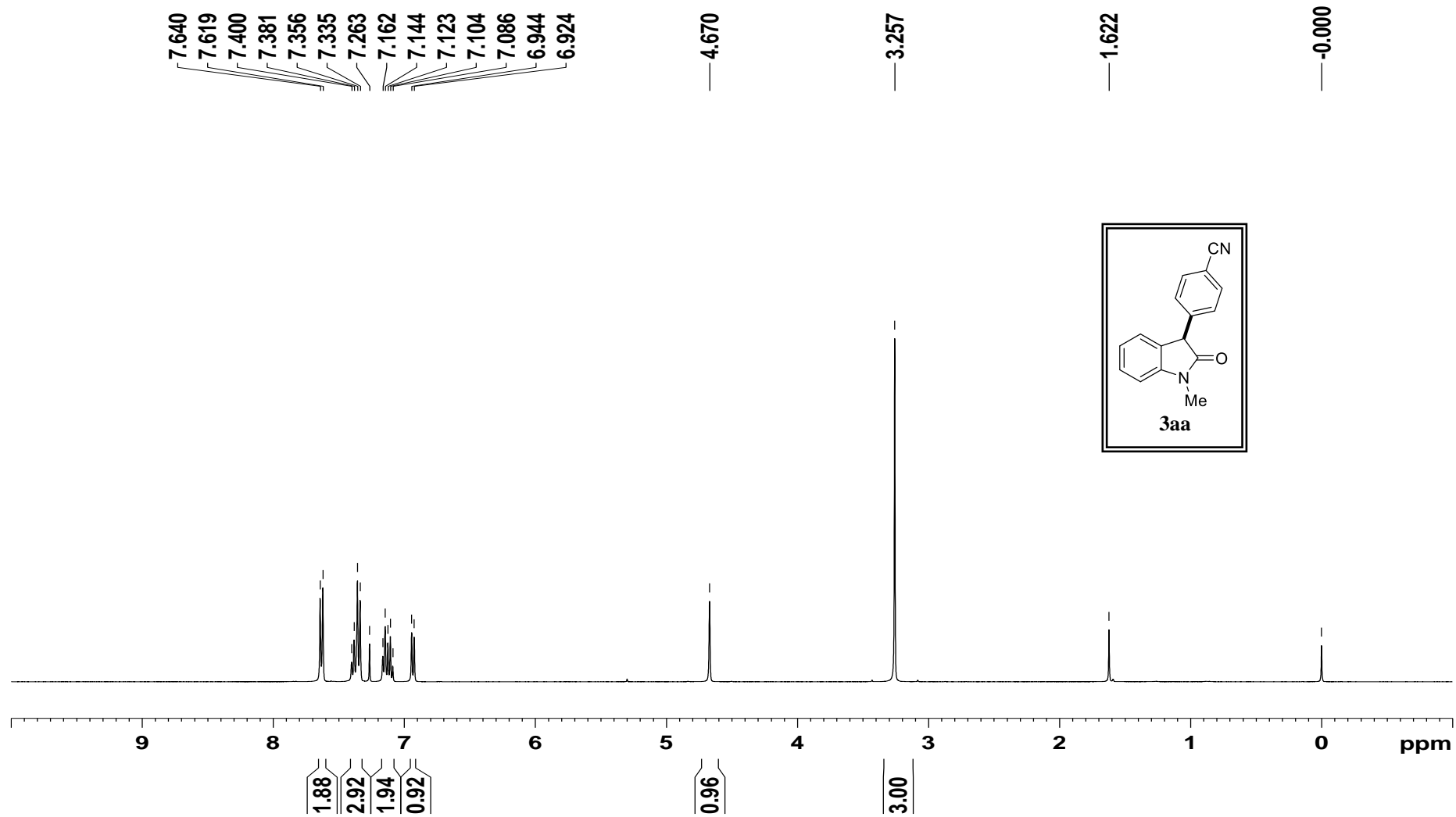
¹³C NMR spectrum of **3z**

apr-435 C13CPD CDC13 8/2/2022



¹H NMR spectrum of **3aa**

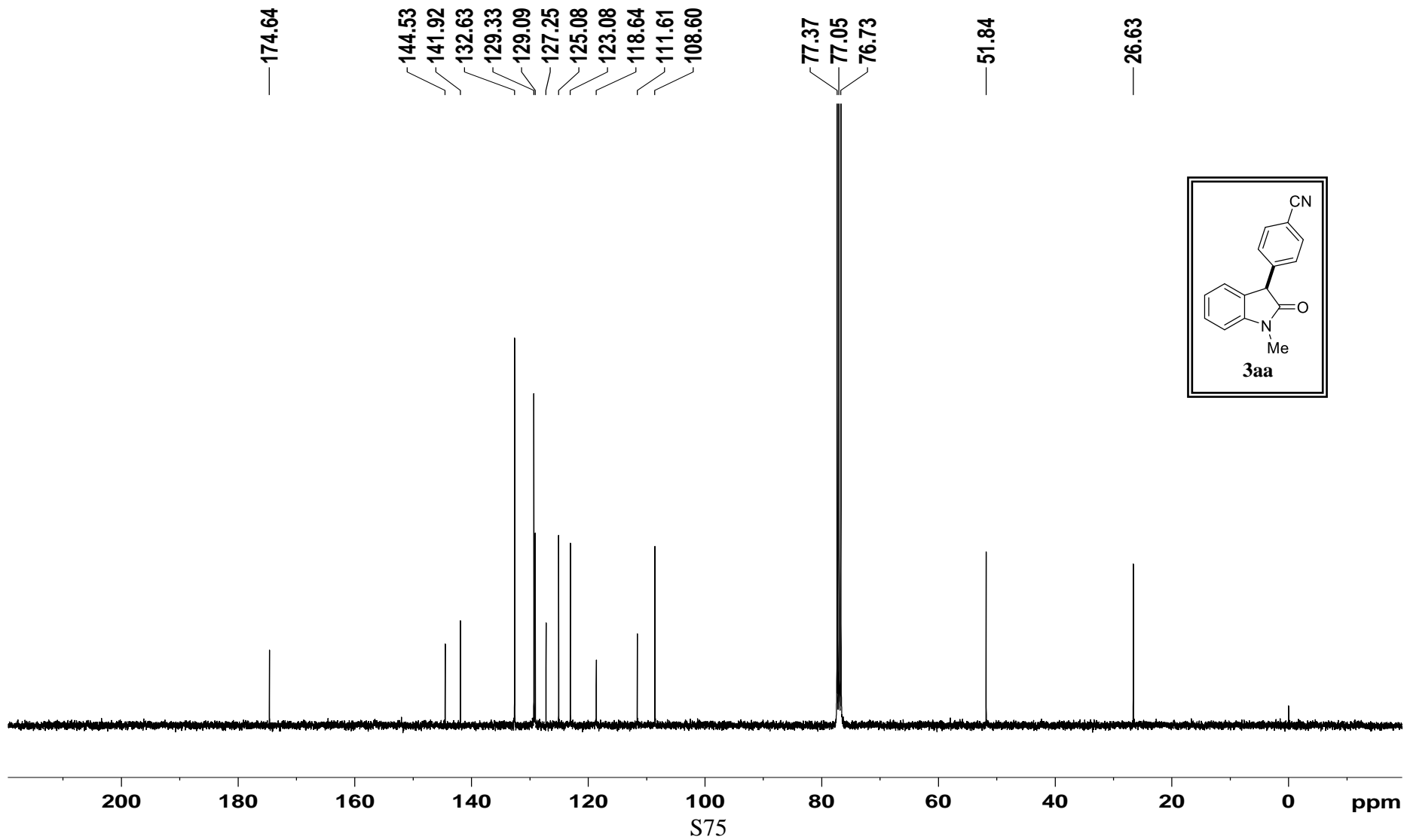
apr-427 PROTON CDC13 23/03/2019



S74

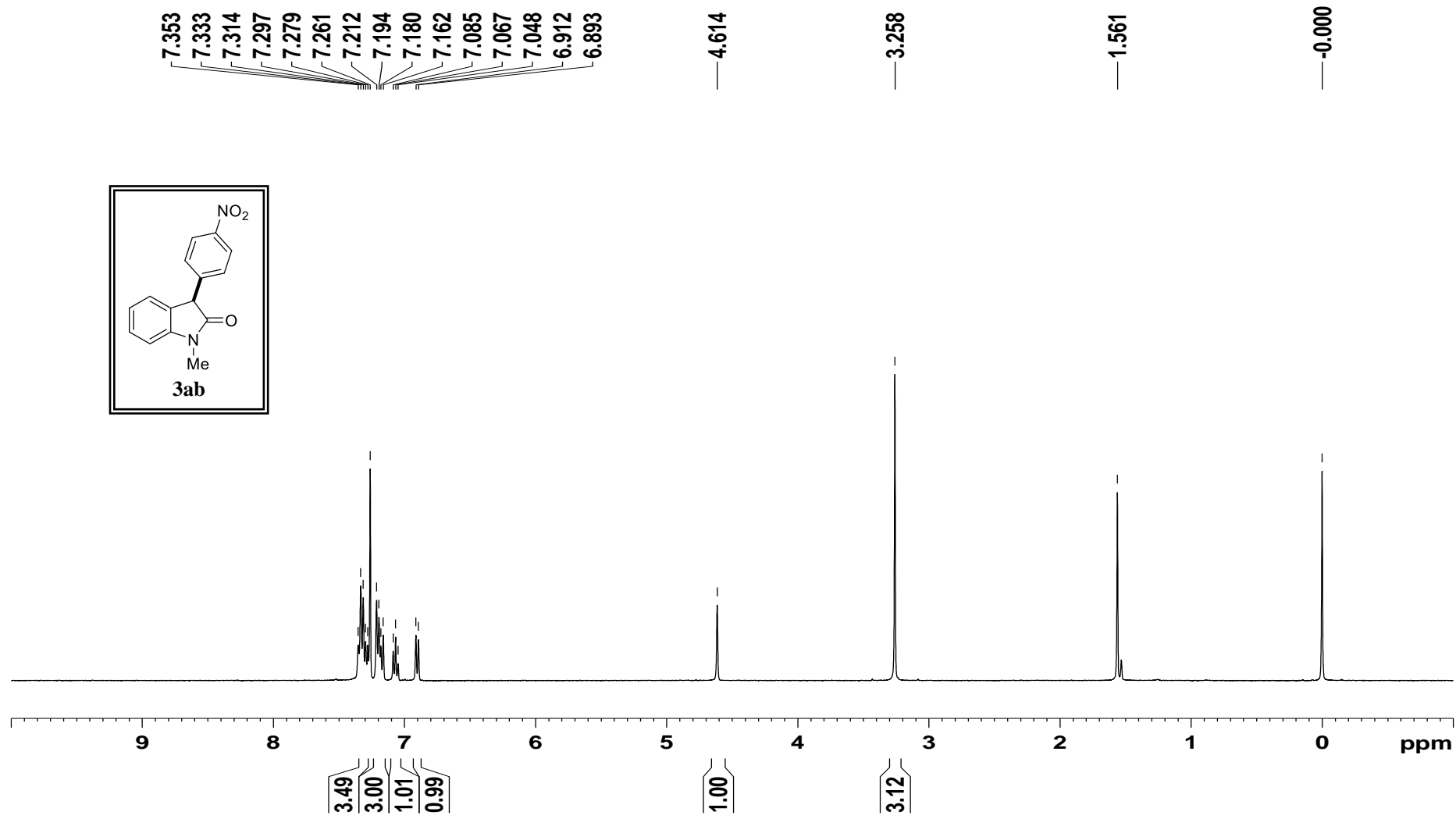
¹³C NMR spectrum of **3aa**

apr-427 C13CPD CDC13 23/03/2019



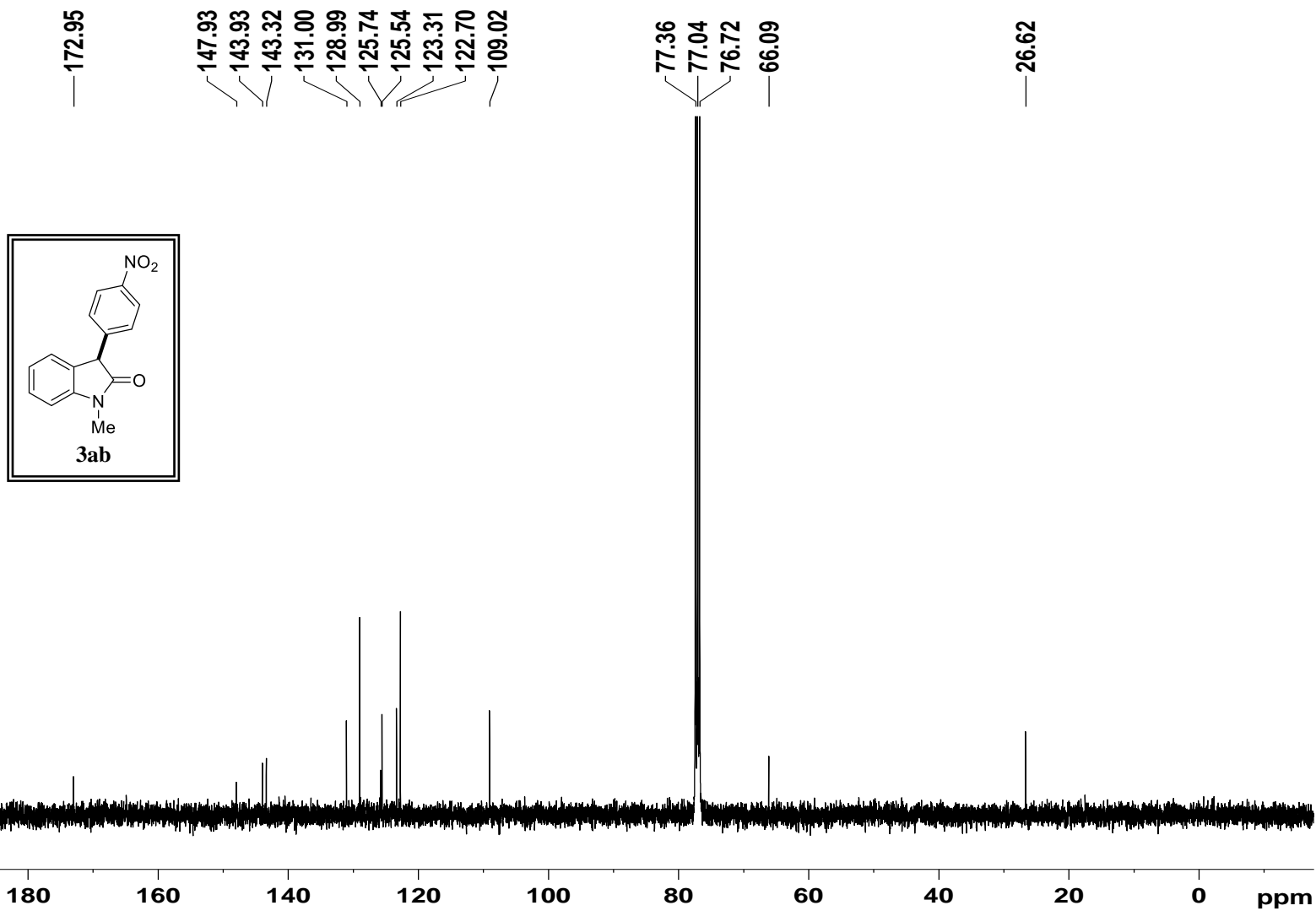
¹H NMR spectrum of **3ab**

apr-409 a PROTON CDCl₃ 5/3/2019



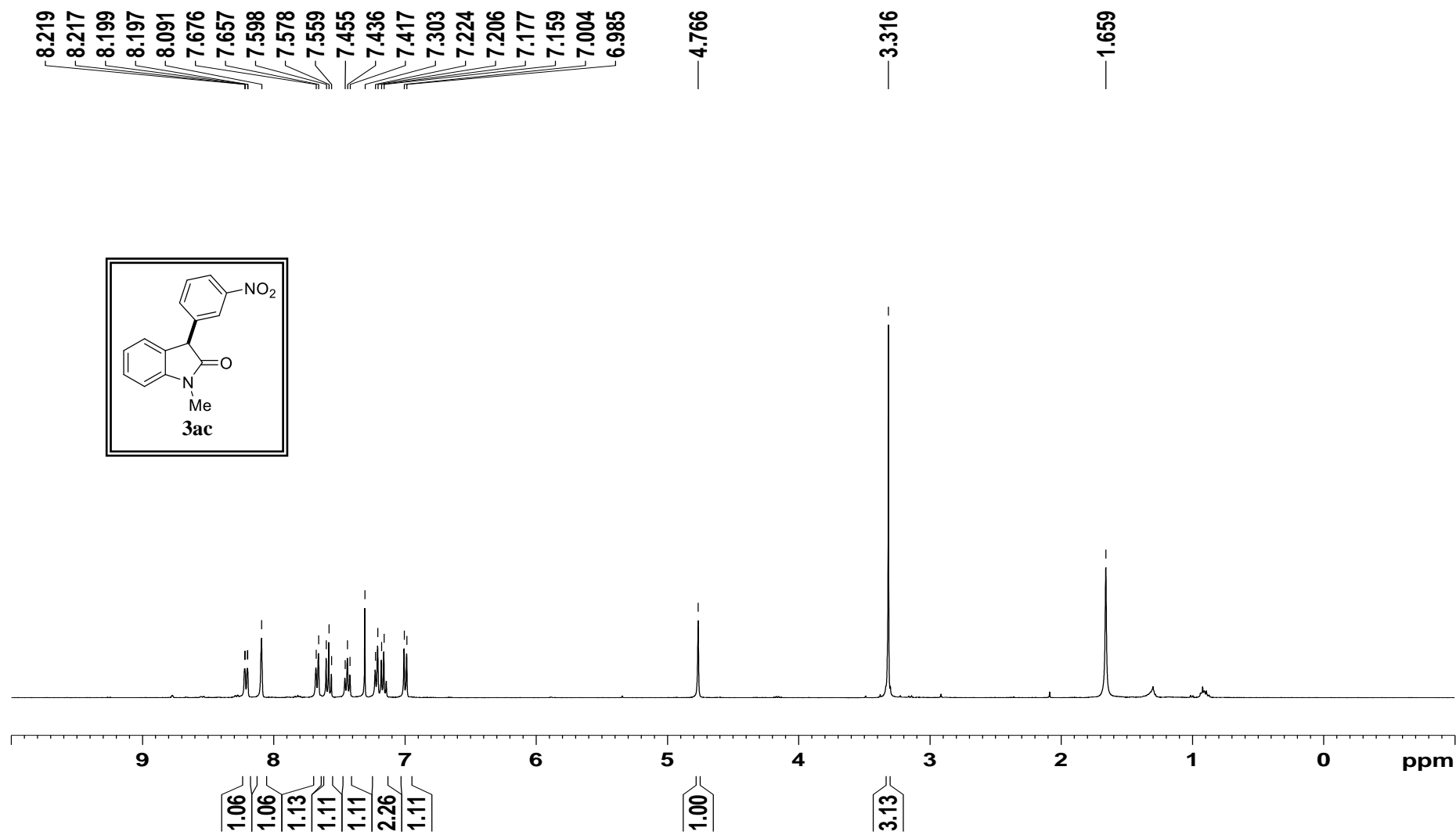
¹³C NMR spectrum of **3ab**

apr-409 a C13CPD CDC13 31/7/2020



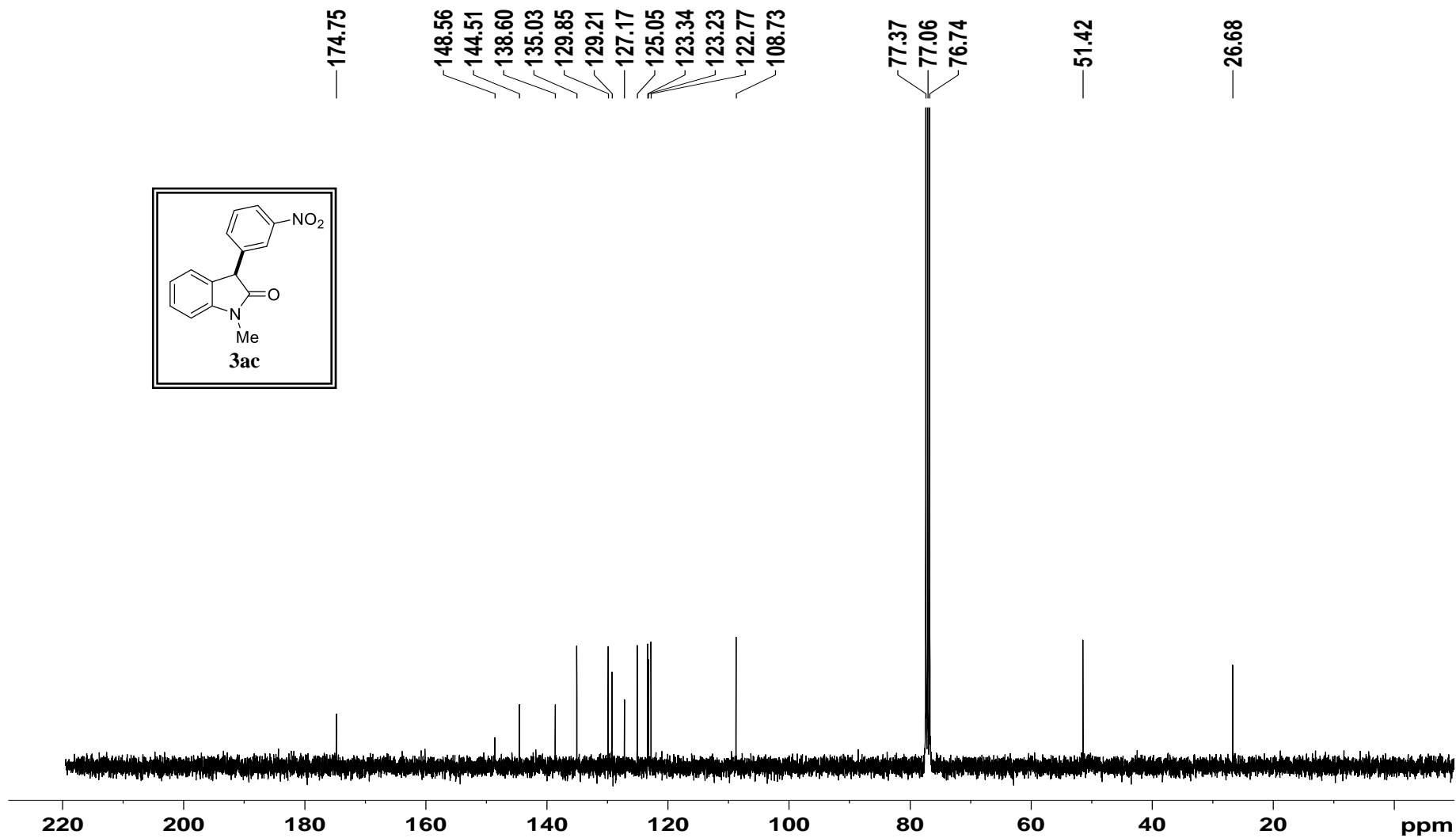
¹H NMR spectrum of **3ac**

APR -636 PROTON CDC13 05/01/2021



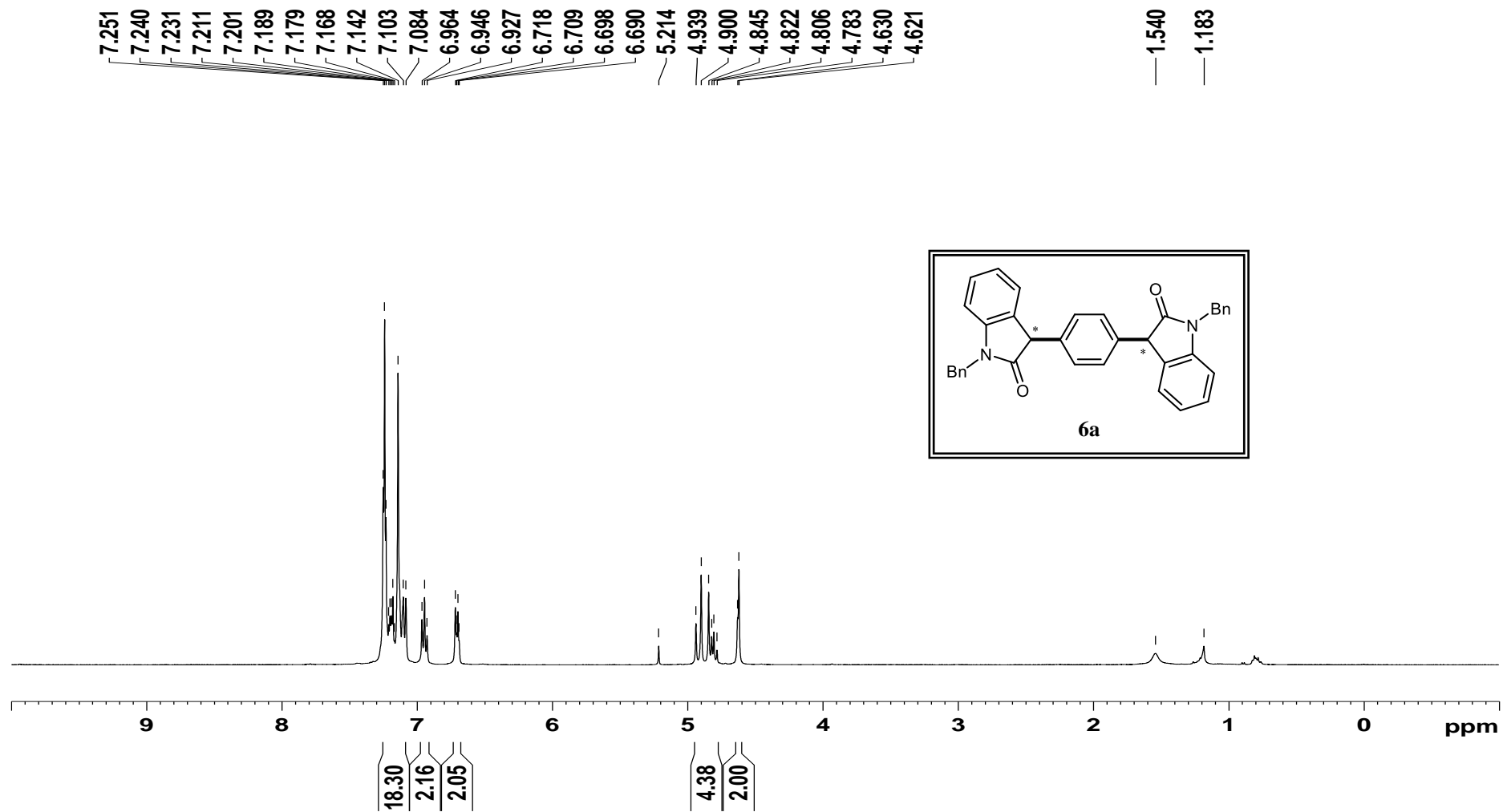
¹³C NMR spectrum of **3ac**

APR -636 C13CPD CDC13 5/1/2021



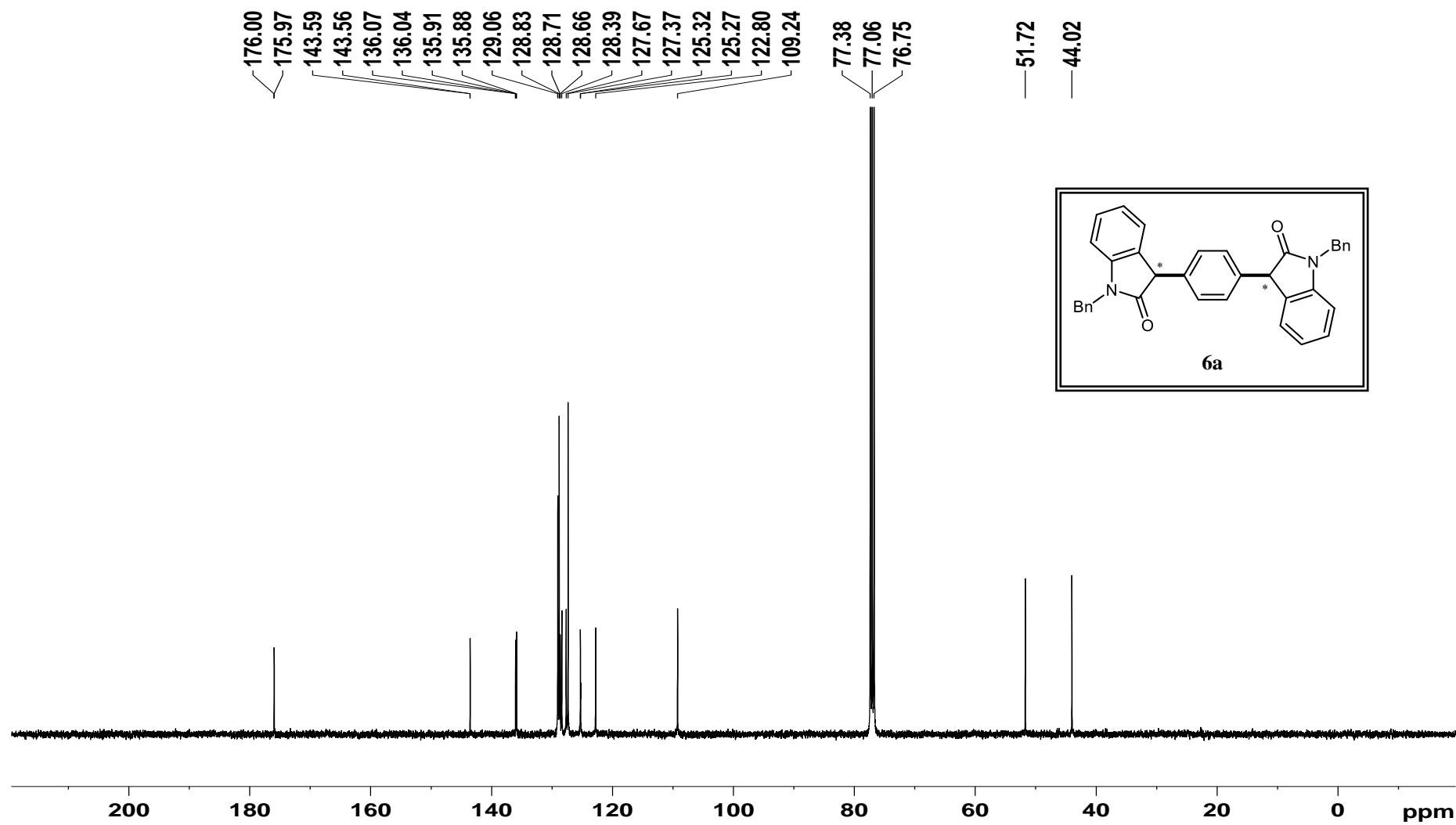
¹H NMR spectrum of **6a**

apr-612 PROTON CDCl₃ 14/7/2022



¹³C NMR spectrum of **6a**

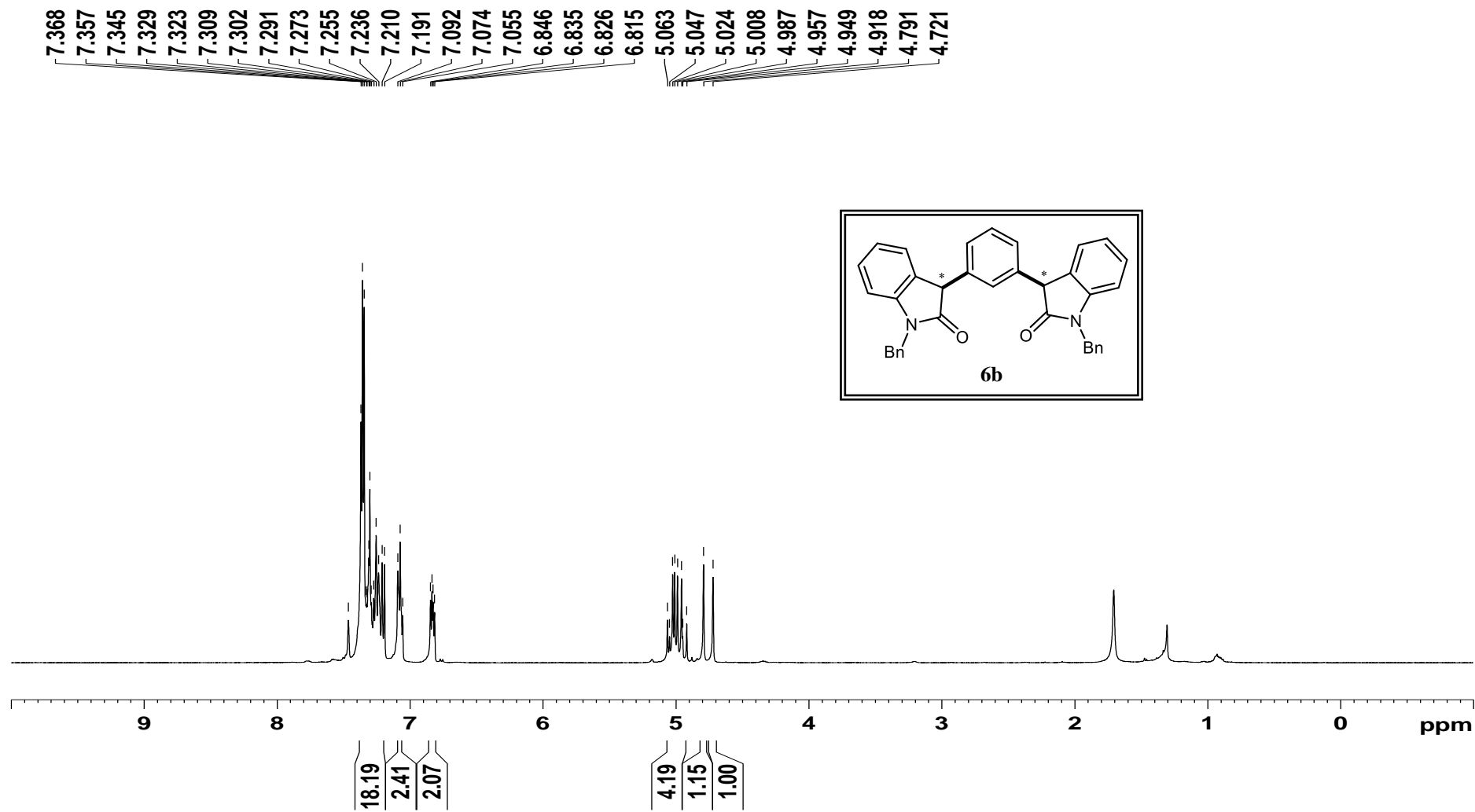
apr-612 C13CPD CDC13 14/7/2022



S81

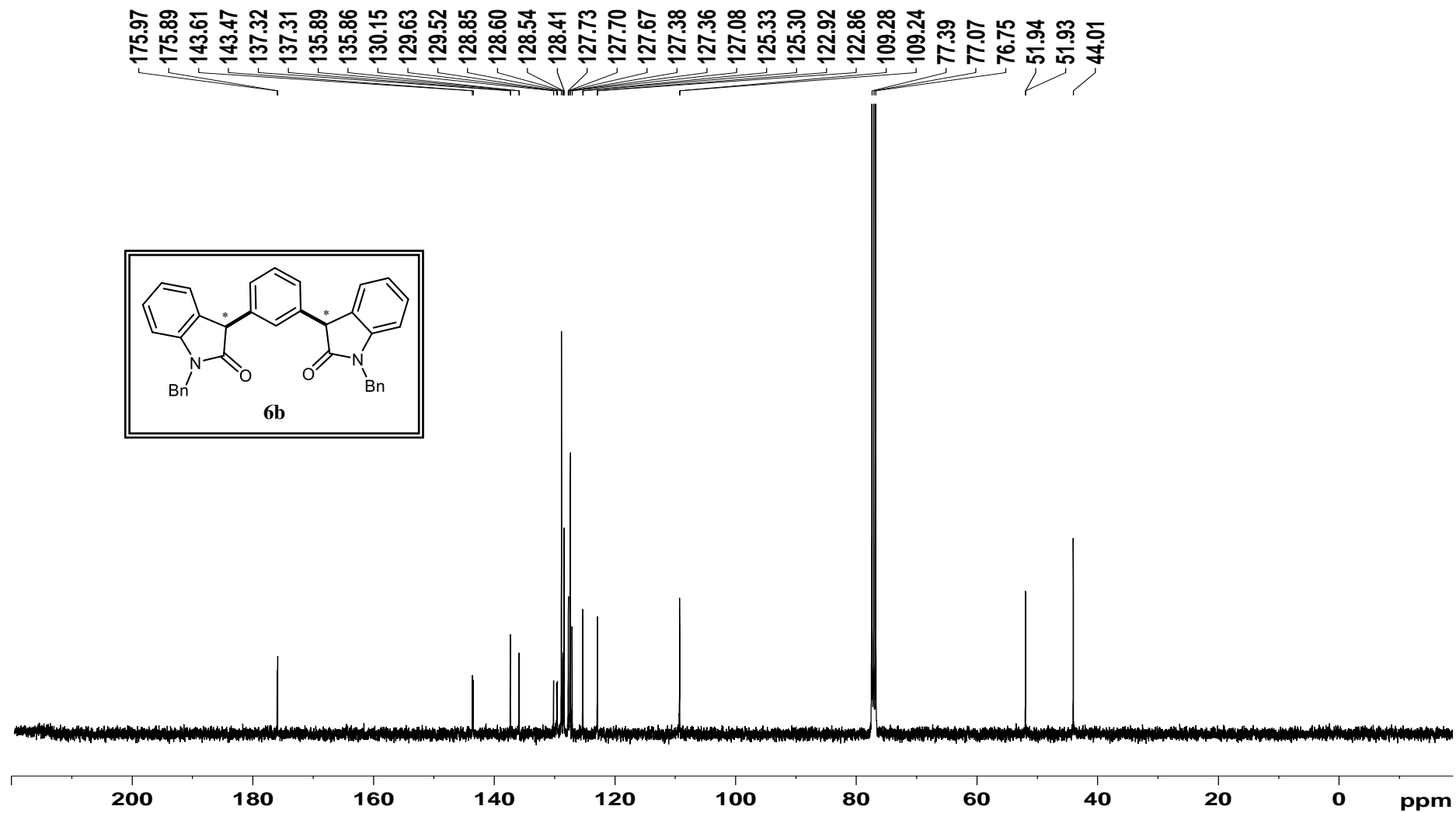
¹H NMR spectrum of **6b**

apr-682 b PROTON CDC13 7/2/2022



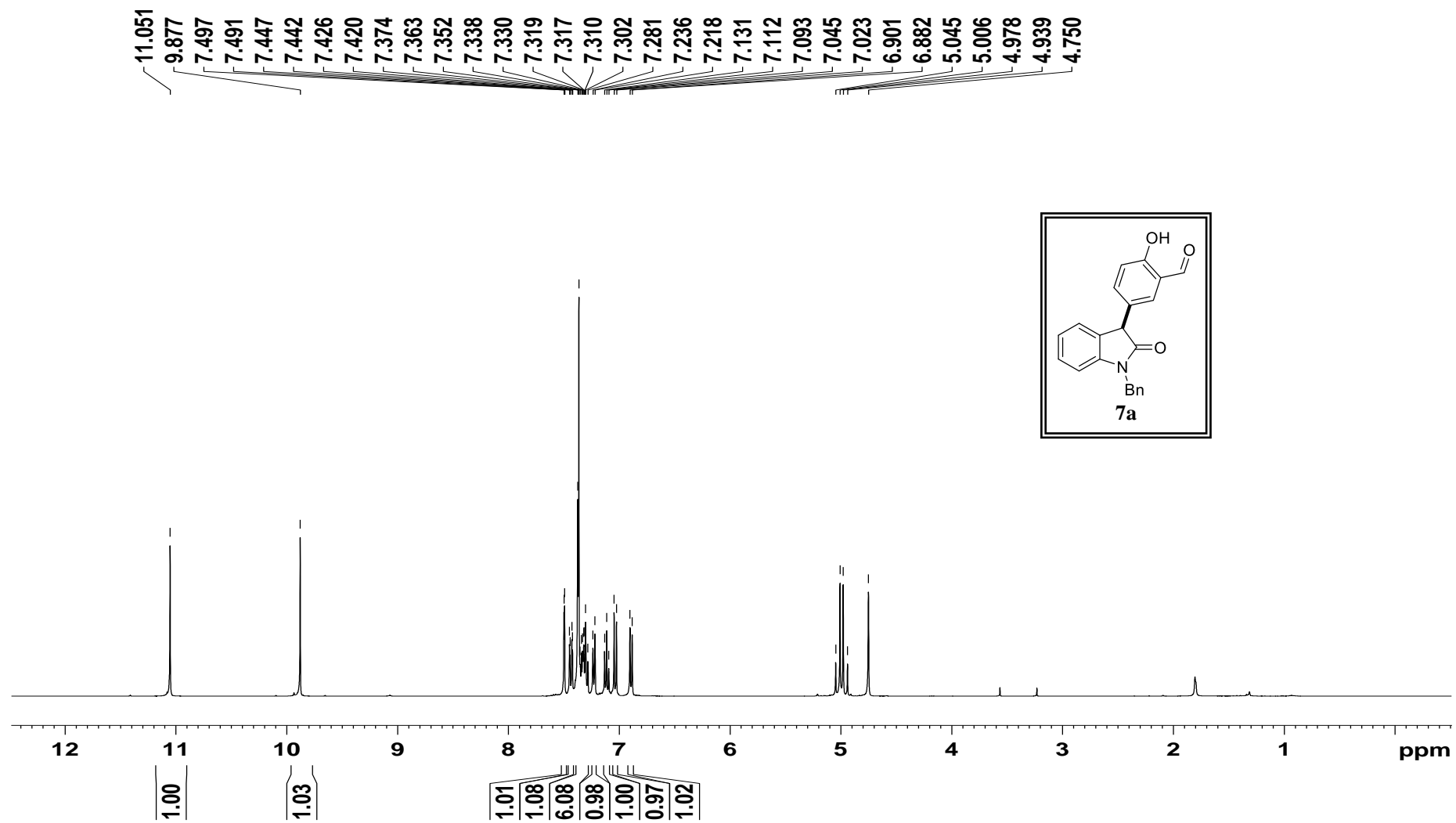
^{13}C NMR spectrum of **6b**

apr-682 b C13CPD CDC13 7/2/2022



¹H NMR spectrum of **7a**

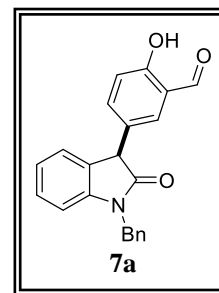
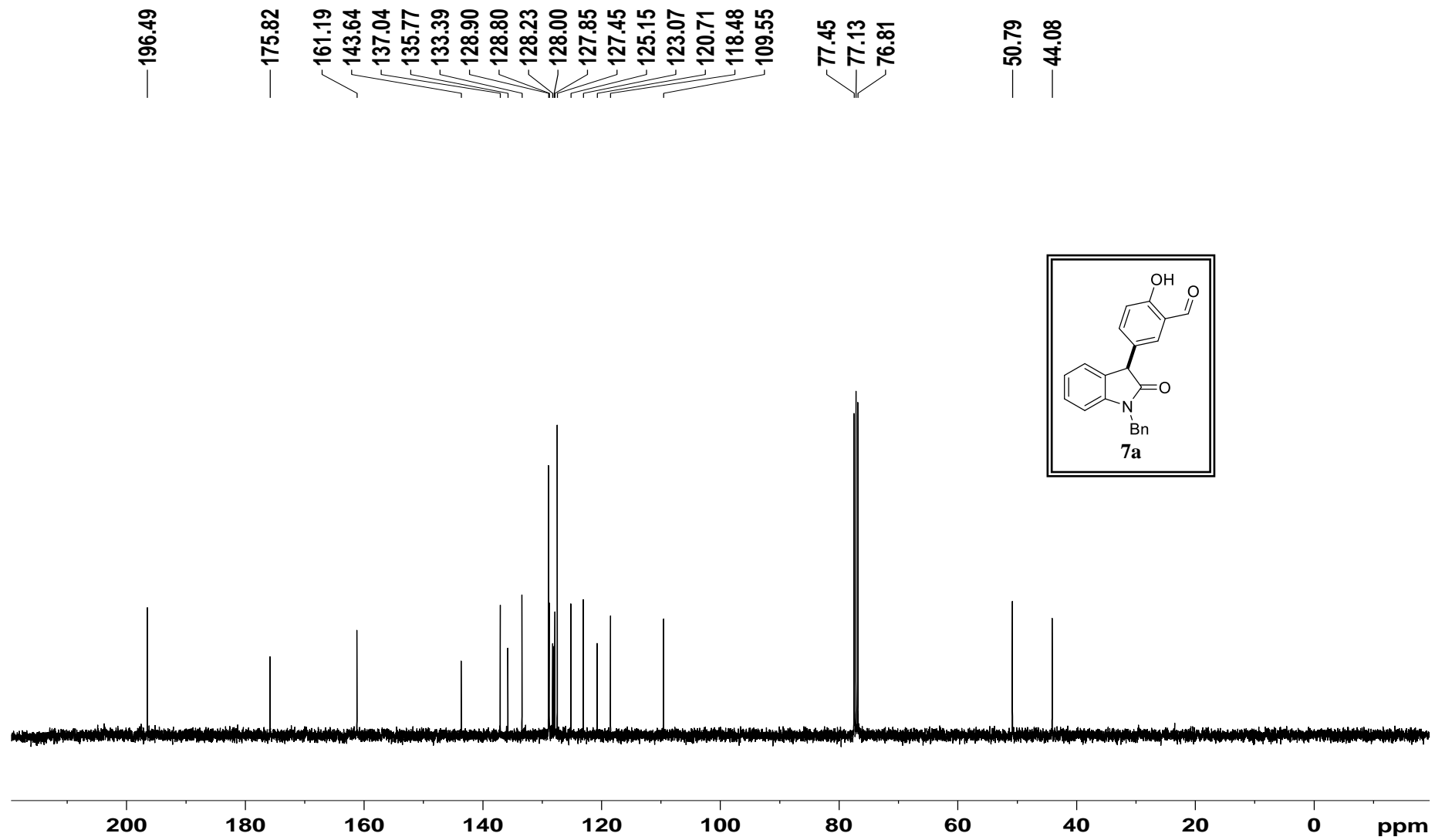
apr-705 PROTON CDC13 9/3/2021



S84

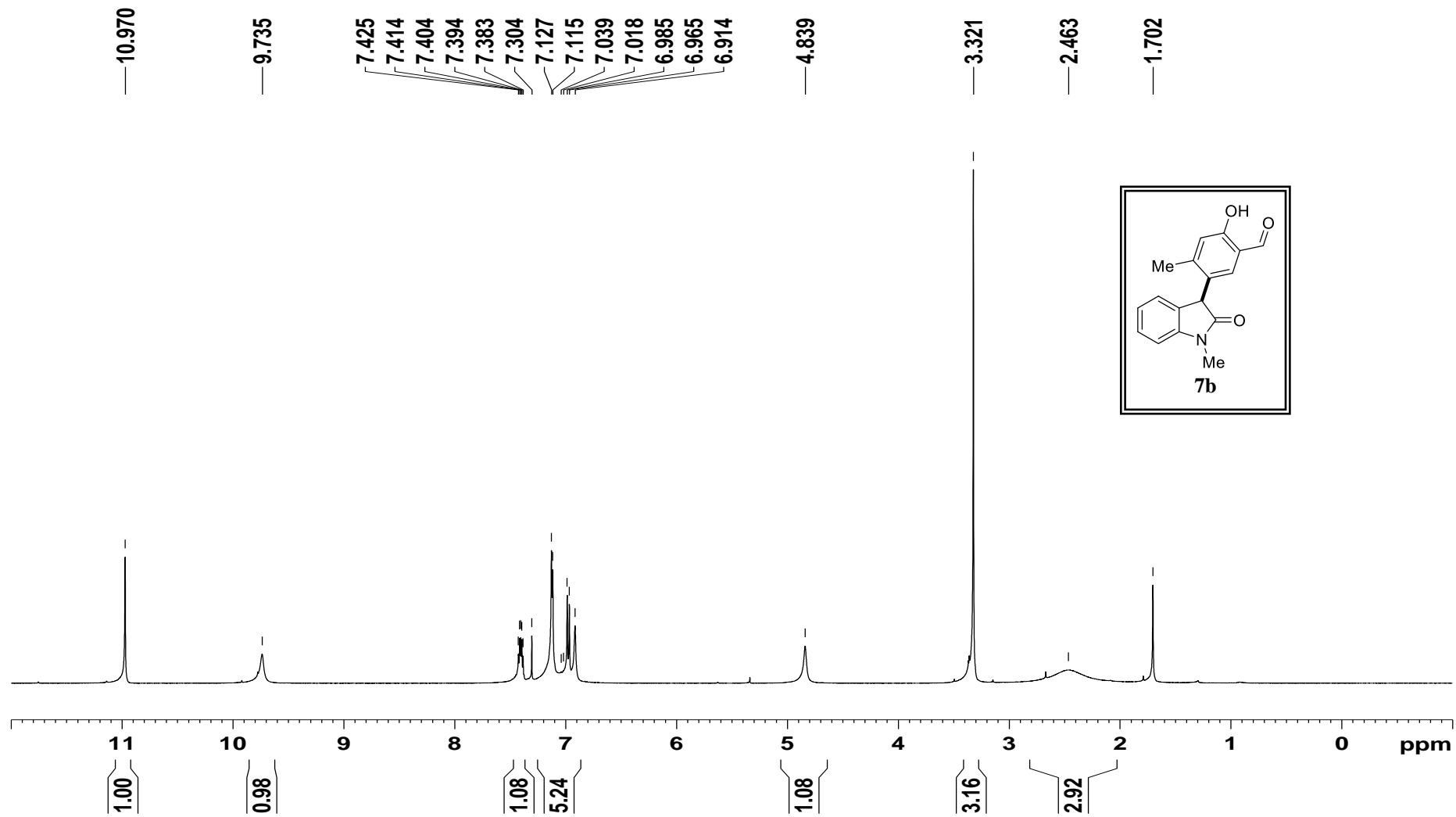
¹³C NMR spectrum of **7a**

apr-705 C13CPD CDC13 9/3/2021



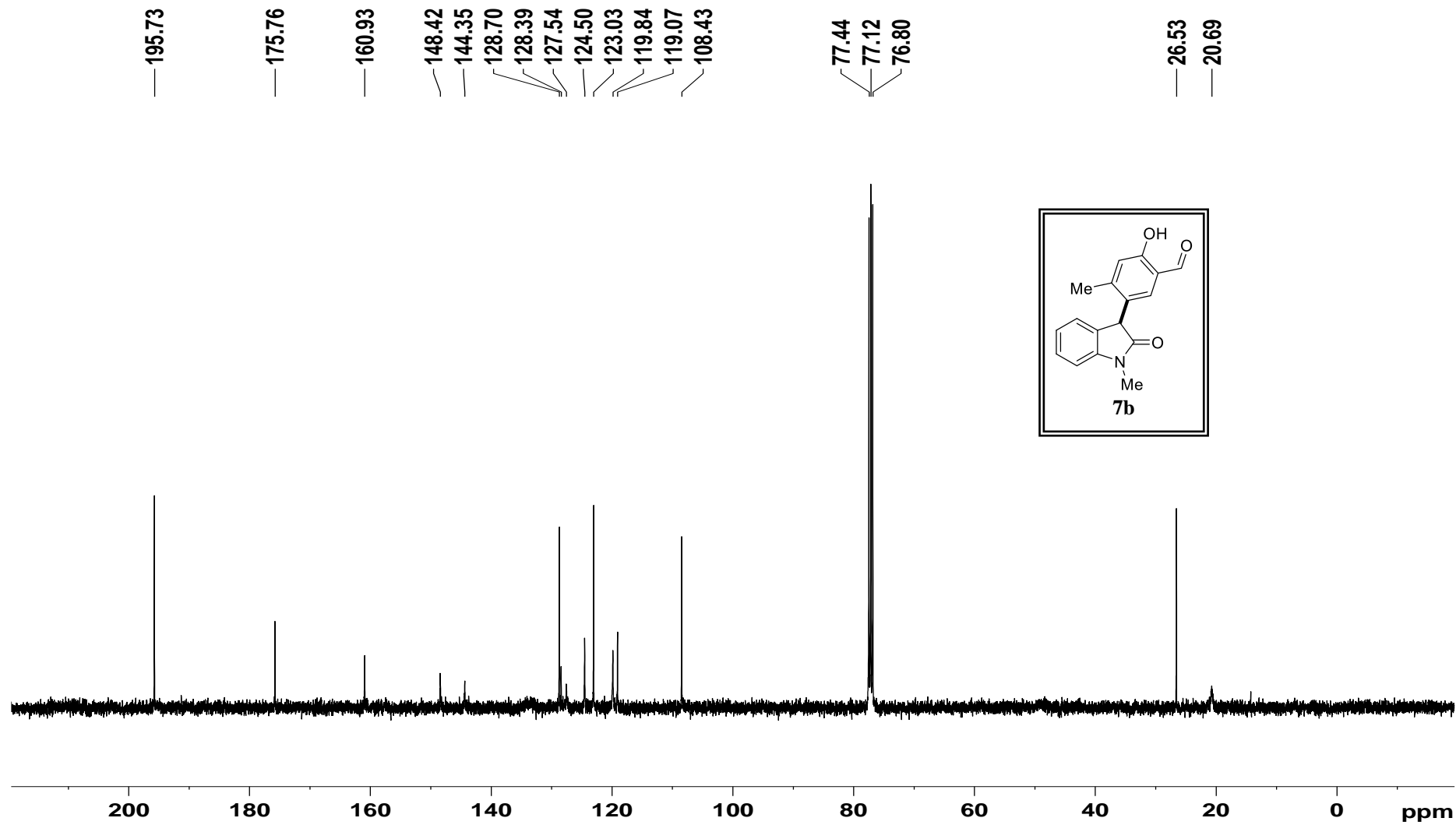
¹H NMR spectrum of **7b**

apr-737 PROTON CDC13 26/4/2021



¹³C NMR spectrum of **7b**

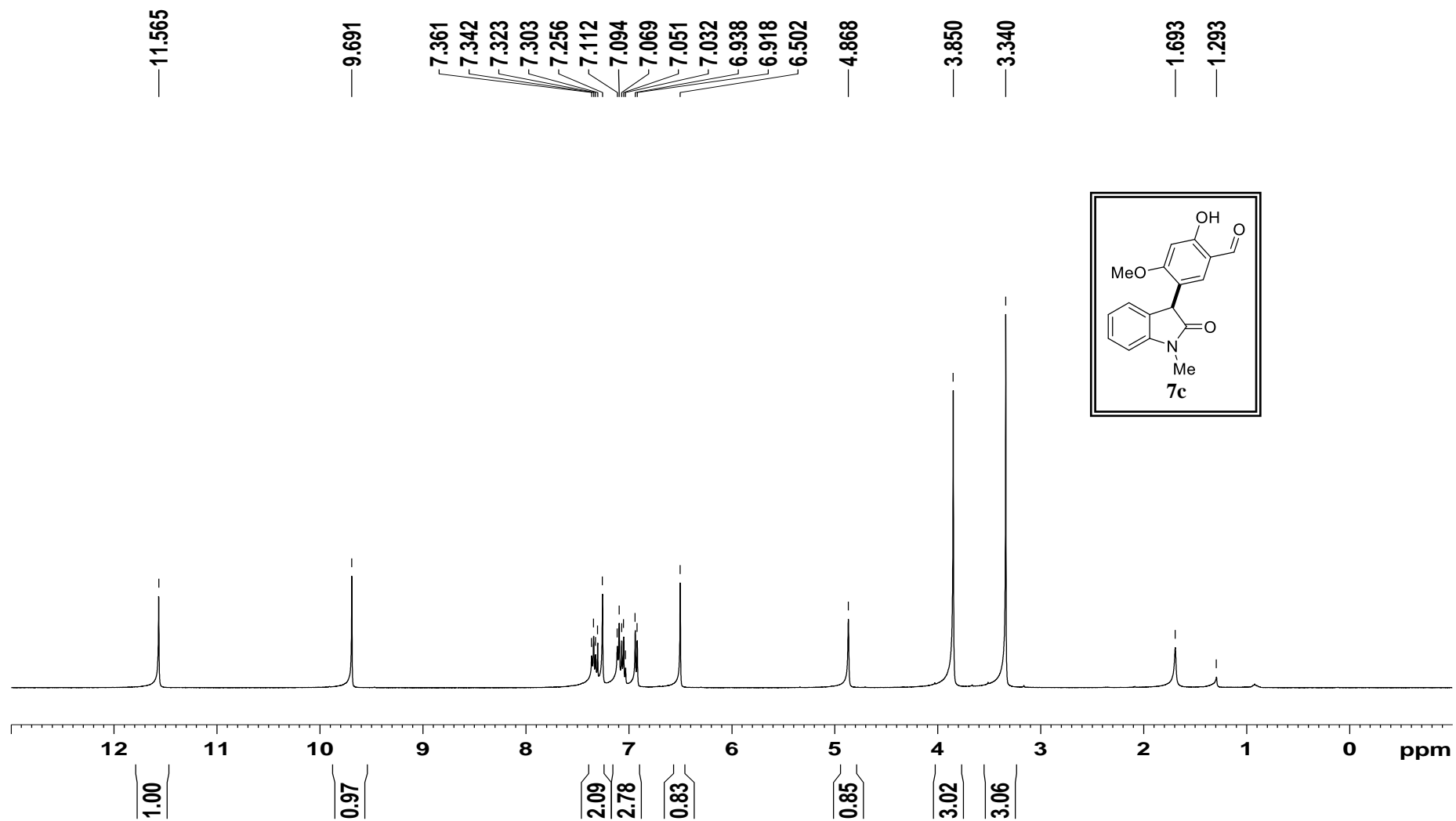
apr-737 C13CPD CDC13 28/4/2021



S87

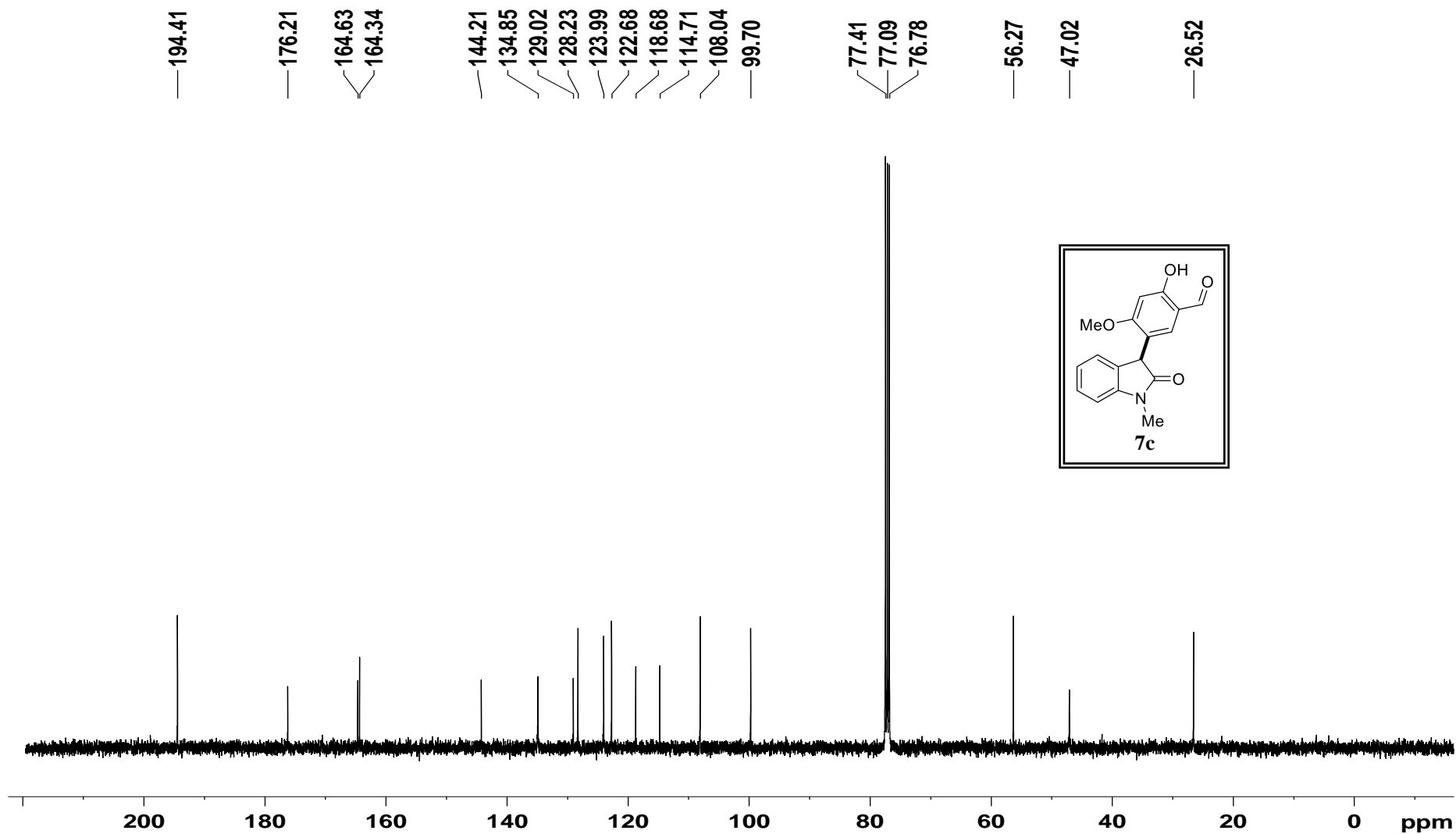
¹H NMR spectrum of **7c**

apr-735 PROTON CDC13 26/4/2021



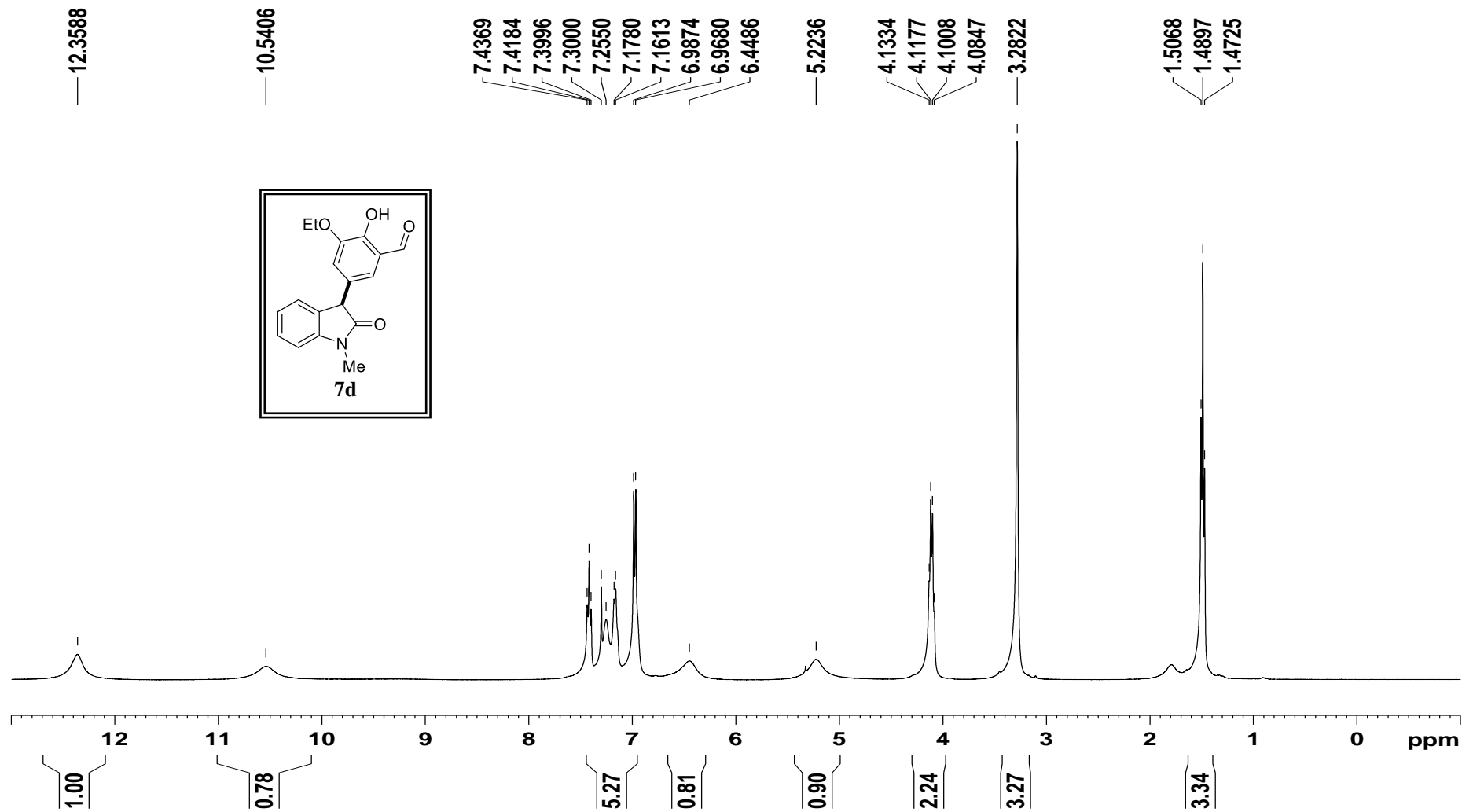
¹³C NMR spectrum of 7c

apr-737 C13CPD CDC13 28/4/2021



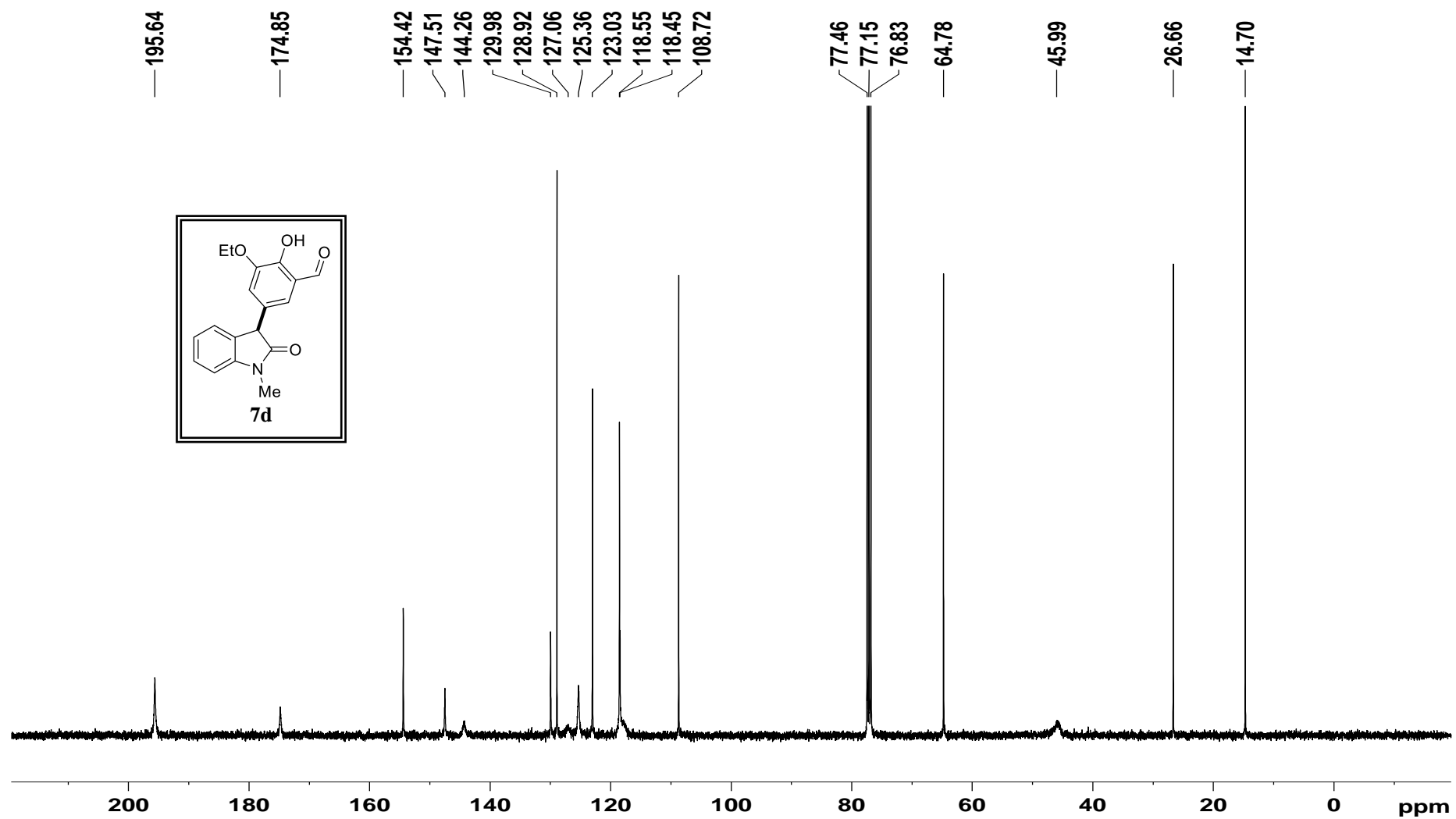
¹H NMR spectrum of **7d**

apr-739 PROTON CDC13 7/2/2022



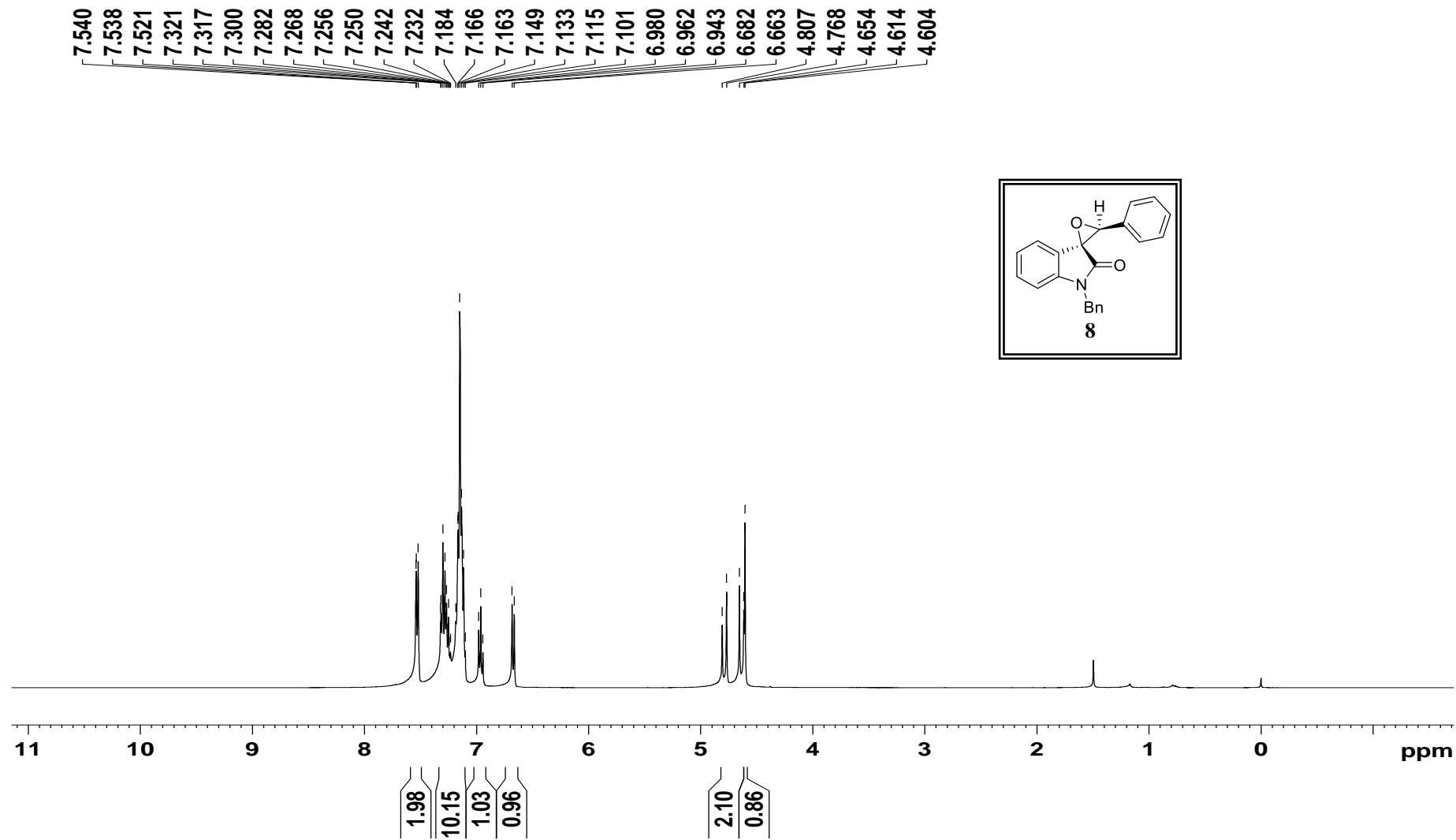
¹³C NMR spectrum of **7d**

APR-739 C13CPD CDC13 3/2/2022



¹H NMR spectrum of **8**

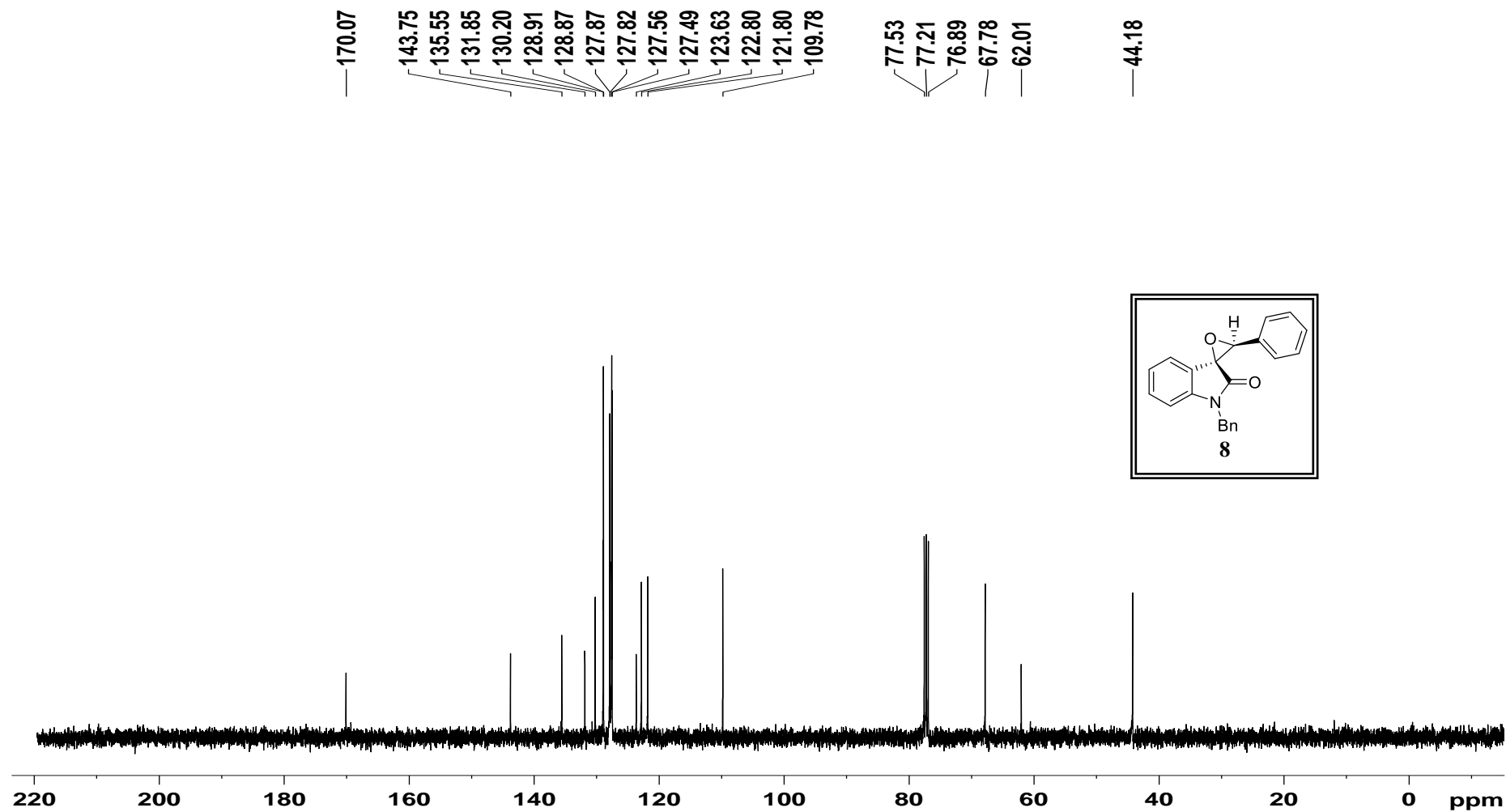
apr-815 PROTON CDCl₃ 2/2/2022



S92

¹³C NMR spectrum of **8**

apr-815 C13CPD CDC13 2/2/2022



References

1. M. P. Cava, R. L. Little and D. R. Naipier, *J. Am. Chem. Soc.* 1958, **80**, 2257.
2. J-T, Xia and X-P. Hu, *Org. Lett.* 2020, **22**, 1102.
3. C-K. Mai, M. F. Sammons and T. Sammakia, *Org. Lett.* 2010, **12**, 2306.
4. A. Vignesh, W. Kaminsky and N. Dharmaraj, *Chem. Cat. Chem.* 2017, **9**, 910.
5. C. Zhai, D. Xing, C. Jing, J. Zhou, C. Wang, D. Wang and W. Hu, *Org. Lett.* 2014, **16**, 2934.
6. B. M. Trost, J. Xie and J. D. Sieber, *J. Am. Chem. Soc.* 2011, **133**, 20611.
7. J. Duan and F. Y. Kwong, *J. Org. Chem.* 2017, **82**, 6468.
8. (a) M. J. Durbin and M. C. Willis, *Org. Lett.* 2008, **10**, 1413; (b) J. Duan, and F. Y. Kwong, *J. Org. Chem.* 2017, **82**, 6468.
9. A. Kondoh, A. Takei and M. Terada, *Synlett*, 2016, **27**, 1848.
10. B. M. Trost, J. T. Masters and A. C. Burns, *Angew. Chem.* 2013, **125**, 2316.
11. P. Rodríguez-Ferrer, D. Naharro, A. Maestro, J. M. Andrés and R. Pedrosa, *Eur. J. Org. Chem.* 2019, 6539.
12. B. M. Trost and Y. Zhang, *J. Am. Chem. Soc.* 2007, **129**, 14548.
13. M. Sattar, V. Rathore, C. D. Prasad and S. Kumar, *Chem. Asian J.* 2017, **12**, 734.
14. C. Peng, W. Zhang, G. Yan and J. Wang, *Org. Lett.* 2009, **11**, 1667.