Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Copper-catalyzed synthesis of 1-(2-benzofuryl)-*N*-heteroarenes from *o*-hydroxy-*gem*-(dibromovinyl)benzenes and N-heteroarenes

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Supporting Information

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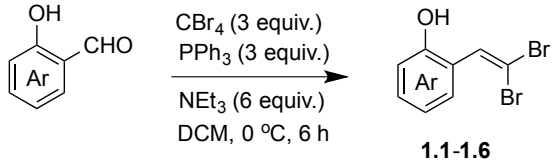
1. General information

All reactions were performed in Schlenk tubes using dry solvents under a nitrogen atmosphere. The *o*-hydroxy-*gem*-(dibromovinyl)benzenes were prepared from salicylaldehyde following the literature method.[1] Purification of the products was performed using 100-200 mesh silica-gel using ethyl acetate/hexane as eluent. ^{1}H NMR and ^{13}C NMR spectra were recorded with JEOL ECS 400 (400 MHz) and 500 (500 MHz). HRMS measurements have been recorded using Electron Ionization (EI) and Electrospray Ionization (ESI) techniques with Waters CAB155 GCT Premier analyzer and Waters HAB 213 Q-TOF Premier analyzer. IR spectra were recorded with PerkinElmer FT-IR. X-ray data were taken from Bruker SMART APEX-II CCD diffractometer.

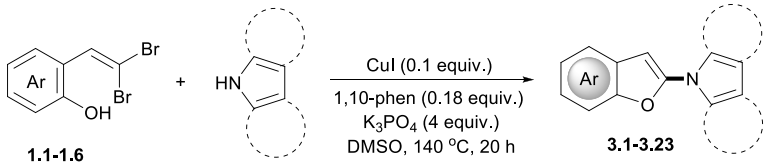
2. Synthesis of *o*-hydroxy-*gem*-(dibromovinyl)benzenes



1.1-1.6

In a three-neck 250 mL round-bottom flask, PPh_3 (66.18 mmol, 6 equiv) was taken in dichloromethane (15 mL) under a nitrogen atmosphere. The vessel was cooled to 0 ^{o}C, after which a solution of CBr_4 (33.24 mmol, 3 equiv) in dichloromethane (15 mL) was added. After 10 minutes, triethylamine (66.18 mmol, 6 equiv) was added dropwise and stirred for additional 5 minutes. After that, salicylaldehyde (11.03 mmol, 1 equiv) in dichloromethane (10 mL) was added dropwise and the reaction mixture was stirred for 6 h at 0 ^{o}C. After that, hexane was added to the mixture and filtered through a silica gel column. The solvent was concentrated and the crude was purified by silica gel column chromatography using hexane as eluent.

3. Synthesis of of 1-(2-benzofuryl)-*N*-heteroarenes

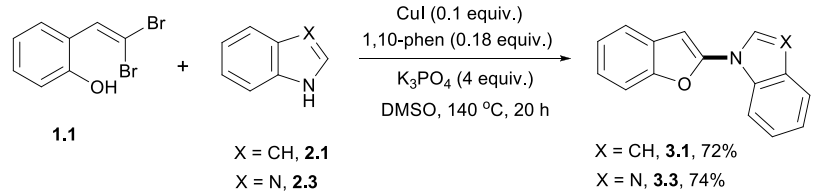


1.1-1.6 **2.1-2.8** **3.1-3.23**

To an oven-dried Schlenk tube, *o*-hydroxy-*gem*-(dibromovinyl)benzene (0.375 mmol, 1 equiv.), K_3PO_4 (1.5 mmol, 4 equiv.), *N*-heteroarene (1.125 mmol, 3 equiv.), CuI (0.037 mmol, 0.1 equiv.), 1,10-phen (0.067 mmol, 0.18 equiv.) and DMSO (3 mL) were added

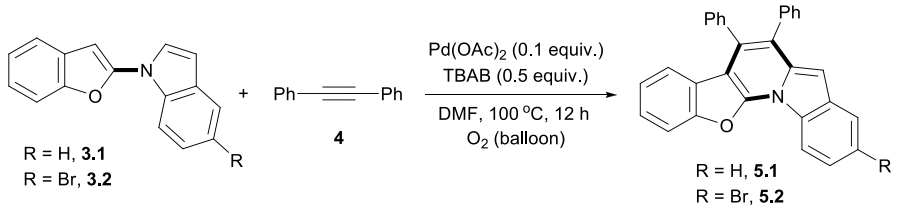
under nitrogen atmosphere. The reaction mixture was stirred in a pre-heated oil bath at 140 ^{o}C for 20 h. After that, the product was extracted with ethyl acetate (30 mL), washed with water (10 mL) and brine solution (10 mL). The organic extract was dried over anhydrous $MgSO_4$ and concentrated. The crude was purified by column chromatography using ethyl acetate/hexane as eluent.

Procedure for higher scale synthesis of 1-(2-benzofuryl)-*N*-heteroarenes 3.1 and 3.3



To an oven-dried Schlenk tube, *o*-hydroxy-*gem*-(dibromovinyl)benzene (3.6 mmol, 1 equiv.), K_3PO_4 (14.4 mmol, 4 equiv.), *N*-heteroarene (10.8 mmol, 3 equiv.), CuI (0.36 mmol, 0.1 equiv.), 1,10-phen (0.648 mmol, 0.18 equiv.) and DMSO (10 mL) were added under nitrogen atmosphere. The reaction mixture was stirred in a pre-heated oil bath at 140 ^{o}C for 20 h. After that, the product was extracted with ethyl acetate (150 mL), washed with water (25 mL) and brine solution (25 mL). The organic extract was dried over anhydrous $MgSO_4$ and concentrated. The crude was purified by column chromatography using ethyl acetate/hexane as eluent.

4. Synthesis of benzofuro-indolo-pyridines



To an oven-dried Schlenk tube, 1-(2-benzofuryl)-*N*-heteroarene (0.171 mmol, 1 equiv.), 1,2-diphenylethyne (0.256 mmol, 1.5 equiv.), TBAB (0.085 mmol, 0.5 equiv.), $Pd(OAc)_2$ (0.017 mmol, 0.1 equiv.) and DMF (2 mL) were added under nitrogen atmosphere. The nitrogen gas present in the Schlenk tube was removed under vacuum and filled with oxygen gas using a oxygen balloon. The reaction mixture was stirred in a pre-heated oil bath at 100 ^{o}C for 12 h. After that, the product was extracted with ethyl acetate (20 mL), washed with water (5 mL) and brine solution (5 mL). The organic extract was dried over anhydrous $MgSO_4$ and concentrated. The crude was purified by column chromatography using ethyl acetate/hexane as eluent.

5. Characterization data

(3.1):[2] White solid (0.064 g, 73%); mp 64-66 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.88–7.86 (m, 1H), 7.71–7.69 (m, 1H), 7.59 (q, J = 3.2, 2.8 Hz, 2H), 7.54–7.52 (m, 1H), 7.39–7.34 (m, 1H), 7.31–7.26 (m, 3H), 6.75 (dd, J = 3.4, 0.8 Hz, 1H), 6.58 (d, J = 0.9 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 151.28, 149.25, 135.02, 129.54, 128.82, 125.83, 123.50, 123.48, 123.45, 121.62, 121.31, 120.35, 111.77, 110.84, 105.88, 90.63 ppm. IR (film, cm^{-1}): 3054, 1622, 1458, 1213, 739. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{16}H_{11}NO$ 233.0841; Found 233.0842.

(3.2): White solid (0.084 g, 72%); mp 88-90 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.81 (d, J = 1.9 Hz, 1H), 7.72 (d, J = 8.8 Hz, 1H), 7.60–7.57 (m, 1H), 7.56 (d, J = 3.4 Hz, 1H), 7.53–7.51 (m, 1H), 7.42 (dd, J = 8.8, 1.9 Hz, 1H), 7.31–7.29 (m, 2H), 6.68–6.67 (m, 1H), 6.56 (s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ = 151.39, 148.71, 133.77, 131.19, 128.56, 127.04, 126.34, 123.86, 123.78, 123.63, 120.50, 114.84, 113.22, 110.91, 105.26, 91.24 ppm. IR (film, cm^{-1}): 3126, 1621, 1457, 1211, 744. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{16}H_{10}BrNO$ 310.9946; Found 310.9940.

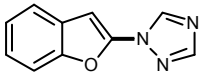
(3.3):[2] White solid (0.069 g, 79%); mp 115-117 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.39 (s, 1H), 7.90 (dd, J = 7.0, 1.3 Hz, 1H), 7.79 (d, J = 7.8 Hz, 1H), 7.65–7.63 (m, 1H), 7.57–7.55 (m, 1H), 7.47–7.31 (m, 4H), 6.74 (d, J = 0.8 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ = 151.67, 145.79, 143.73, 140.70, 132.12, 127.99, 124.61, 124.55, 123.85, 123.69, 120.94, 120.85, 111.36, 111.12, 92.90 ppm. IR (film, cm^{-1}): 3141, 1632, 1499, 1222, 1017, 743. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{11}N_2O$ 235.0871; Found 235.0871.

(3.4):[2] White solid (0.051 g, 74%); mp 57-59 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.05 (s, 1H), 7.57–7.55 (m, 1H), 7.50–7.48 (m, 1H), 7.41 (s, 1H), 7.34–7.28 (m, 2H), 7.22 (s, 1H), 6.52 (d, J = 0.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 151.62, 146.48, 135.16, 130.54, 127.91, 124.45, 123.87, 120.89, 117.03, 111.10, 91.02 ppm. IR (film, cm^{-1}): 3147, 1628, 1490, 1057, 789. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{11}H_9N_2O$ 185.0715; Found 185.0717.

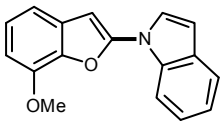
(3.5):[2] White solid (0.085 g, 62%); mp 88-90 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.55–7.52 (m, 1H), 7.50–7.48 (m, 1H), 7.28–7.26 (m, 4H), 6.40–6.39 (m, 2H), 6.37 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 151.30, 150.18, 128.88, 123.48, 123.22, 120.23, 118.78, 111.19, 110.79, 87.49 ppm. IR (film, cm^{-1}): 3133, 1621, 1454, 1008, 724. HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{12}H_9NO$ 183.0684; Found 183.0685.

(3.6): Colourless solid (0.016 g, 17%); mp 85-87 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.77–7.74 (m, 1H), 7.70–7.67 (m, 1H), 7.56 (dd, J = 8.2, 0.9 Hz, 1H), 7.43–7.39 (m, 2H), 7.38–7.28 (m, 3H), 6.79 (d, J = 0.7 Hz, 1H), 2.68 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.60, 151.86, 144.61, 142.41, 135.50, 127.63, 125.23, 123.71, 123.49, 123.29, 121.35, 119.33, 111.45, 110.35, 100.06, 14.62 ppm. IR (film, cm^{-1}): 3058, 1626, 1456, 1247, 743. HRMS (EI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{12}N_2O$ 248.0950; Found 248.0952.

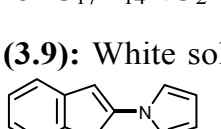
(3.7): White solid (0.045 g, 65%); mp 94-96 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.71 (s, 1H), 8.15 (s, 1H), 7.63–7.60 (m, 1H), 7.53–7.51 (m, 1H), 7.37–7.29 (m, 2H), 6.85 (d, J = 0.9 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.13, 151.83, 145.87, 141.59, 127.63, 125.06, 124.11, 121.48, 111.23, 93.09 ppm. IR (film, cm^{-1}): 3131, 1641, 1398, 1063, 742. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{10}H_8N_3O$ 186.0667; Found 186.0668.



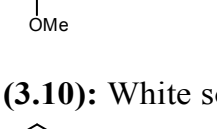
(3.8): White solid (0.067 g, 68%); mp 96-98 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.83 (d, J = 8.2 Hz, 1H), 7.68 (d, J = 7.8 Hz, 1H), 7.62 (d, J = 3.5 Hz, 1H), 7.37–7.33 (m, 1H), 7.26–7.19 (m, 3H), 6.83 (dd, J = 7.1, 2.0 Hz, 1H), 6.73 (d, J = 3.0 Hz, 1H), 6.58 (s, 1H), 4.05 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ = 149.14, 145.03, 140.39, 135.14, 130.48, 129.50, 126.05, 124.15, 123.46, 121.57, 121.26, 112.82, 111.69, 106.35, 105.75, 91.40, 56.15 ppm. IR (film, cm^{-1}): 3034, 1618, 1456, 1213, 1094, 721. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{14}NO_2$ 264.1025; Found 264.1021.



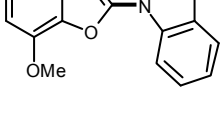
(3.9): White solid (0.052 g, 65%); mp 50-52 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.26–7.24 (m, 2H), 7.17 (t, J = 7.8 Hz, 1H), 7.11 (dd, J = 7.8, 1.1 Hz, 1H), 6.79 (d, J = 7.8 Hz, 1H), 6.36 (t, J = 2.1 Hz, 2H), 6.34 (s, 1H), 4.03 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ = 150.27, 144.95, 140.34, 130.57, 124.15, 119.00, 112.74, 111.11, 106.19, 88.20, 56.12 ppm. IR (film, cm^{-1}): 3120, 2962, 1622, 1477, 1321, 716. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{13}H_{11}NO_2$ 213.0790; Found 213.0797.



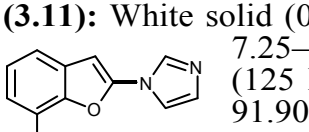
(3.10): White solid (0.065 g, 66%); mp 124-126 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.42 (s, 1H), 7.90 (dd, J = 7.0, 1.5 Hz, 1H), 7.77 (dd, J = 7.3, 1.5 Hz, 1H), 7.46–7.38 (m, 2H), 7.28–7.22 (m, 2H), 6.89 (dd, J = 7.2, 1.9 Hz, 1H), 6.74 (s, 1H), 4.05 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ = 145.68, 145.22, 143.57, 141.00, 140.86, 132.28, 129.64, 124.65, 124.60, 123.72, 120.81, 113.23, 111.34, 107.11, 93.87, 56.11 ppm. IR (film, cm^{-1}): 2965, 1625, 1454, 1216, 726. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{13}N_2O_2$ 265.0977; Found 265.0972.



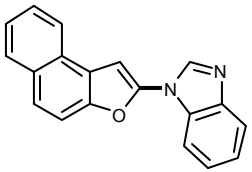
(3.11): White solid (0.07 g, 87%); mp 63-65 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.09 (s, 1H), 7.46 (d, J = 1.4 Hz, 1H), 7.25–7.17 (m, 3H), 6.87 (d, J = 7.9 Hz, 1H), 6.56–6.55 (m, 1H), 4.05 (d, J = 1.6 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ = 146.45, 145.07, 140.83, 135.33, 130.38, 129.52, 124.55, 117.31, 113.12, 106.92, 91.90, 56.00 ppm. IR (film, cm^{-1}): 3401, 2929, 1629, 1482, 1096, 727. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{11}N_2O_2$ 215.0821; Found 215.0829.



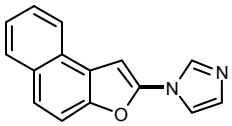
(3.12): White solid (0.07 g, 60%); mp 116-118 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.15 (d, J = 8.2 Hz, 1H), 7.97 (d, J = 8.2 Hz, 1H), 7.82 (d, J = 9.0 Hz, 1H), 7.75–7.67 (m, 2H), 7.63–7.59 (m, 2H), 7.54–7.50 (m, 1H), 7.16 (d, J = 1.9 Hz, 1H), 7.03–6.99 (m, 2H), 6.69 (d, J = 3.3 Hz, 1H), 3.90 (d, J = 1.4 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.26, 148.79, 148.19, 148.17, 130.52, 130.12, 130.09, 128.82, 127.15, 126.41, 124.71, 124.09, 123.41, 113.14, 112.48, 111.72, 105.56, 103.15, 89.72, 89.67, 55.75 ppm. IR (film, cm^{-1}): 2999, 1613, 1477, 1252, 986, 780. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{21}H_{15}NO_2$ 313.1103; Found 313.1105.



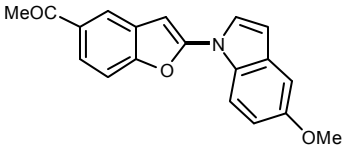
(3.13): White solid (0.071 g, 67%); mp 86-88 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.42 (d, J = 8.6 Hz, 1H), 8.18–8.14 (m, 1H), 8.00–7.97 (m, 1H), 7.93 (d, J = 7.8 Hz, 1H), 7.84–7.78 (m, 2H), 7.72–7.62 (m, 2H), 7.57–7.53 (m, 1H), 7.48–7.40 (m, 2H), 7.22–7.18 (m, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ = 149.10, 144.99, 143.60, 140.90, 132.38, 130.61, 128.96, 127.31, 126.69, 125.62, 125.12, 124.66, 123.74, 123.41, 123.29, 120.86, 111.78, 111.32, 93.03 ppm. IR (film, cm^{-1}): 3055, 1607, 1498, 1194, 987, 743. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{13}N_2O$ 285.1028; Found 285.1026.



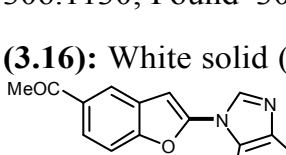
(3.14): White solid (0.061 g, 69%); mp 104-106 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.08 (d, J = 10.1 Hz, 2H), 7.95 (d, J = 8.1 Hz, 1H), 7.75 (d, J = 8.9 Hz, 1H), 7.64-7.59 (m, 2H), 7.52 (t, J = 7.6 Hz, 1H), 7.46 (s, 1H), 7.26 (s, 1H), 6.97 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.84, 145.78, 135.26, 130.57, 130.48, 128.88, 127.23, 126.59, 125.41, 125.06, 123.33, 123.21, 117.27, 111.69, 90.88 ppm. IR (film, cm^{-1}): 3118, 1622, 1485, 1056, 802. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{11}N_2O$ 235.0871; Found 235.0877.



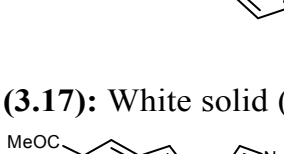
(3.15): White solid (0.08 g, 70%); mp 110-112 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.19 (d, J = 1.7 Hz, 1H), 7.93 (dd, J = 8.6, 1.8 Hz, 1H), 7.75 (d, J = 8.9 Hz, 1H), 7.56–7.53 (m, 2H), 7.14 (d, J = 2.5 Hz, 1H), 7.00 (dd, J = 9.0, 2.5 Hz, 1H), 6.68 (d, J = 3.2 Hz, 1H), 6.56 (s, 1H), 3.89 (s, 3H), 2.68 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 197.62, 155.44, 153.70, 150.68, 133.30, 130.41, 129.70, 129.16, 125.92, 124.12, 121.15, 113.29, 112.56, 110.67, 106.29, 103.36, 89.39, 55.74, 26.81 ppm. IR (film, cm^{-1}): 3132, 2928, 1625, 1479, 1267, 796. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{16}NO_3$ 306.1130; Found 306.1134.



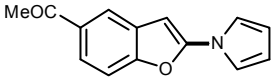
(3.16): White solid (0.078 g, 75%); mp 180-182 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.40 (s, 1H), 8.27 (d, J = 1.6 Hz, 1H), 8.01 (dd, J = 8.7, 1.8 Hz, 1H), 7.90 (dd, J = 7.2, 1.4 Hz, 1H), 7.77 (dd, J = 7.3, 1.2 Hz, 1H), 7.60 (d, J = 8.7 Hz, 1H), 7.47–7.39 (m, 2H), 6.80 (d, J = 0.7 Hz, 1H), 2.69 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 197.30, 154.08, 147.08, 143.67, 140.41, 133.63, 131.78, 128.25, 125.28, 124.87, 123.98, 121.96, 120.99, 111.32, 111.15, 92.82, 26.81 ppm. IR (film, cm^{-1}): 3146, 1679, 1631, 1497, 1300, 1195, 732. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{13}N_2O_2$ 277.0977; Found 277.0971.



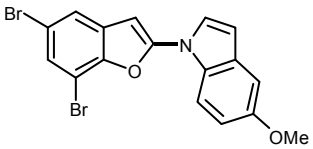
(3.17): White solid (0.074 g, 87%); mp 122-124 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.15 (d, J = 45.4 Hz, 2H), 7.97 (d, J = 8.4 Hz, 1H), 7.54 (d, J = 8.5 Hz, 1H), 7.43 (s, 1H), 7.24 (s, 1H), 6.61 (s, 1H), 2.67 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 197.24, 154.12, 147.70, 135.12, 133.72, 130.78, 128.19, 125.24, 121.93, 116.98, 111.16, 91.28, 26.76 ppm. IR (film, cm^{-1}): 3123, 1680, 1633, 1267, 813, 649. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{11}N_2O_2$ 227.0821; Found 227.0821.



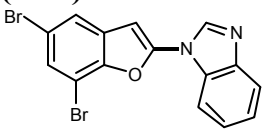
(3.18): White solid (0.052 g, 61%); mp 114-116 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.14 (d, J = 1.8 Hz, 1H), 7.90 (dd, J = 8.5, 1.9 Hz, 1H), 7.49 (d, J = 8.6 Hz, 1H), 7.23 (t, J = 2.2 Hz, 2H), 6.38 (t, J = 2.0 Hz, 3H), 2.66 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 197.55, 153.85, 151.31, 133.35, 129.13, 124.11, 121.18, 118.72, 111.66, 110.72, 87.48, 26.77 ppm. IR (film, cm^{-1}): 3117, 1670, 1632, 1488, 1070, 787. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{14}H_{11}NO_2$ 225.0790; Found 225.0793.



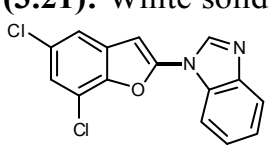
(3.19): White solid (0.079 g, 50%); mp 148-150 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.78 (d, J = 9.0 Hz, 1H), 7.58 (d, J = 1.8 Hz, 1H), 7.54 (d, J = 3.5 Hz, 1H), 7.52 (d, J = 1.8 Hz, 1H), 7.12 (d, J = 2.5 Hz, 1H), 7.00 (dd, J = 9.0, 2.5 Hz, 1H), 6.68 (dd, J = 3.5, 0.7 Hz, 1H), 6.45 (s, 1H), 3.88 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.60, 151.13, 147.35, 131.60, 130.55, 129.60, 128.21, 125.71, 121.80, 116.74, 113.45, 112.81, 106.86, 104.06, 103.54, 88.43, 55.76 ppm. IR (film, cm^{-1}): 3004, 1611, 1477, 1146, 710. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{17}H_{11}Br_2NO_2$ 418.9157; Found 418.9157.



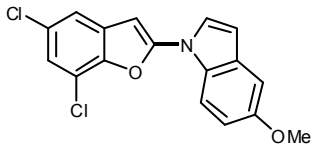
(3.20): White solid (0.106 g, 72%); mp 182-184 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.41 (s, 1H), 7.90 (dd, J = 7.2, 1.3 Hz, 1H), 7.80 (dd, J = 7.7, 1.5 Hz, 1H), 7.69 (d, J = 1.8 Hz, 1H), 7.63 (d, J = 1.8 Hz, 1H), 7.49–7.40 (m, 2H), 6.72 (s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ = 147.98, 147.55, 143.73, 140.27, 131.75, 130.59, 129.82, 125.10, 124.17, 122.69, 121.09, 117.24, 111.48, 104.61, 92.13 ppm. IR (film, cm^{-1}): 3066, 1604, 1206, 840, 740. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_9Br_2N_2O$ 390.9082; Found 390.9084.



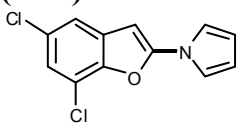
(3.21): White solid (0.098 g, 86%); mp 164-166 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.41 (s, 1H), 7.90 (d, J = 8.4 Hz, 1H), 7.79 (d, J = 7.5 Hz, 1H), 7.49 (d, J = 2.0 Hz, 1H), 7.48–7.40 (m, 2H), 7.34 (d, J = 1.9 Hz, 1H), 6.70 (s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ = 147.74, 146.13, 143.71, 140.27, 131.73, 130.35, 129.92, 125.07, 124.71, 124.16, 121.08, 119.15, 117.35, 111.43, 92.28 ppm. IR (film, cm^{-1}): 3066, 1610, 1498, 1204, 739. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_9Cl_2N_2O$ 303.0092; Found 303.0096.



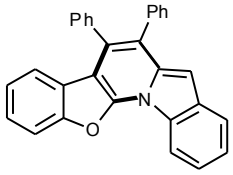
(3.22): White solid (0.096 g, 77%); mp 132-134 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.76 (d, J = 9.0 Hz, 1H), 7.55 (d, J = 3.5 Hz, 1H), 7.39 (d, J = 1.9 Hz, 1H), 7.24 (d, J = 1.9 Hz, 1H), 7.12 (d, J = 2.5 Hz, 1H), 7.00 (dd, J = 9.0, 2.5 Hz, 1H), 6.68 (dd, J = 3.5, 0.6 Hz, 1H), 6.43 (d, J = 0.6 Hz, 1H), 3.88 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ = 155.64, 151.34, 145.52, 131.36, 130.56, 129.65, 129.38, 125.74, 123.17, 118.30, 116.74, 113.44, 112.74, 106.81, 103.58, 88.63, 55.77 ppm. IR (film, cm^{-1}): 2831, 1626, 1479, 1156, 978, 704. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{17}H_{11}Cl_2NO_2$ 331.0167; Found 331.0169.



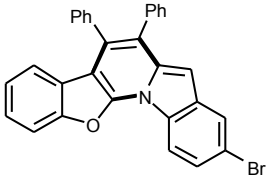
(3.23): White solid (0.05 g, 53%); mp 66-68 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.36–7.35 (m, 1H), 7.24–7.22 (m, 3H), 6.39–6.38 (m, 2H), 6.30 (d, J = 1.5 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ = 151.79, 145.70, 131.32, 129.40, 123.35, 118.83, 118.43, 116.82, 111.95, 87.34 ppm. IR (film, cm^{-1}): 3130, 1627, 1483, 1062, 955, 727. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{12}H_7Cl_2NO$ 250.9905; Found 250.9902.



(5.1): Yellowish green solid (0.048 g, 69%); mp 130-132 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.74–8.70 (m, 1H), 7.79–7.75 (m, 1H), 7.70 (dt, J = 8.2, 0.8 Hz, 1H), 7.47–7.42 (m, 2H), 7.36–7.26 (m, 11H), 7.13 (td, J = 7.6, 1.0 Hz, 1H), 6.86 (ddd, J = 7.9, 1.3, 0.5 Hz, 1H), 6.59 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.31, 148.37, 138.31, 137.08, 136.93, 130.82, 130.60, 130.26, 129.68, 128.56, 128.05, 127.99, 127.41, 127.11, 125.17, 124.87, 123.77, 123.37, 123.30, 120.88, 120.28, 120.23, 114.36, 111.33, 100.93, 95.98 ppm. IR (film, cm^{-1}): 3058, 1626, 1514, 1235, 1188, 734. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{30}H_{20}NO$ 410.1545; Found 410.1541.



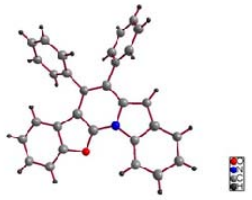
(5.2): Yellowish green solid (0.04 g, 48%); mp 224-226 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.55 (d, J = 8.8 Hz, 1H), 7.88 (d, J = 1.7 Hz, 1H), 7.69 (d, J = 8.2 Hz, 1H), 7.49 (dd, J = 8.8, 1.9 Hz, 1H), 7.34–7.28 (m, 11H), 7.13 (t, J = 7.9 Hz, 1H), 6.85 (d, J = 8.1 Hz, 1H), 6.50 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.37, 147.97, 139.15, 136.83, 136.59, 131.50, 131.20, 130.76, 130.16, 128.13, 128.06, 127.57, 127.27, 127.06, 125.14, 124.66, 123.94, 123.75, 123.62, 122.61, 120.39, 116.97, 115.71, 111.39, 101.51, 95.33 ppm. IR (film, cm^{-1}): 3058, 1628, 1513, 1234, 1179, 698. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{30}H_{19}BrNO$ 488.0650; Found 488.0659.



6. Crystallographic data

Crystal structure determination and refinement

Single crystal of **5.1** coated with light hydrocarbon oil was mounted in the 100 K dinitrogen stream of a Bruker SMART APEX CCD diffractometer equipped with CRYO Industries low-temperature apparatus and intensity data were collected using graphite-monochromated Mo-Kα radiation. The data integration and reduction were processed using the SAINT software. An absorption correction was applied. Structures were solved by direct methods using SHELXS-97 and refined on F^2 by a full-matrix least-squares technique using the SHELXL-97 program package. Non-hydrogen atoms were refined anisotropically. In the refinement, hydrogen atoms were treated as riding atoms using the SHELXL default parameters. The crystal structure refinement parameters are listed in Table 1. All these software packages were a part of the WINGX software package. The X-ray crystallography data have been deposited in Cambridge Crystallography Data Center (CCDC 2040195).



crystal structure of **5.1** (CCDC 2040195)

Sample preparation for crystal growth: The compound **5.1** was dissolved in ethyl acetate solvent. After that, the rectangular-like yellow crystals were grown by slow evaporation of solution **5.1**.

The ellipsoid contour % probability level in the caption for the image of the structure **5.1** is 50%.

Table-1 for compound **5.1**.

Crystal data and structure refinement for 5sepe_0m.

Identification code	shelx	
Empirical formula	C30 H19 N O	
Formula weight	409.46	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 7.4594(4) Å	α = 72.9290(10)°.
	b = 11.1120(5) Å	β = 85.1410(10)°.
	c = 12.7546(6) Å	γ = 80.7110(10)°.
Volume	996.60(8) $Å^3$	
Z	2	
Density (calculated)	1.364 Mg/m^3	
Absorption coefficient	0.082 mm^{-1}	

F(000)	428
Crystal size	0.220 x 0.200 x 0.180 mm^3
Theta range for data collection	4.082 to 25.027°.
Index ranges	-8<=h<=8, -13<=k<=13, -15<=l<=15
Reflections collected	12034
Independent reflections	3498 [R(int) = 0.0460]
Completeness to theta = 25.027°	99.4 %
Absorption correction	Psi-scan
Max. and min. transmission	0.7212 and 0.6745
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3498 / 0 / 289
Goodness-of-fit on F^2	1.065
Final R indices [I>2sigma(I)]	R1 = 0.0430, wR2 = 0.1030
R indices (all data)	R1 = 0.0550, wR2 = 0.1087
Extinction coefficient	n/a
Largest diff. peak and hole	0.249 and -0.388 $e.Å^{-3}$

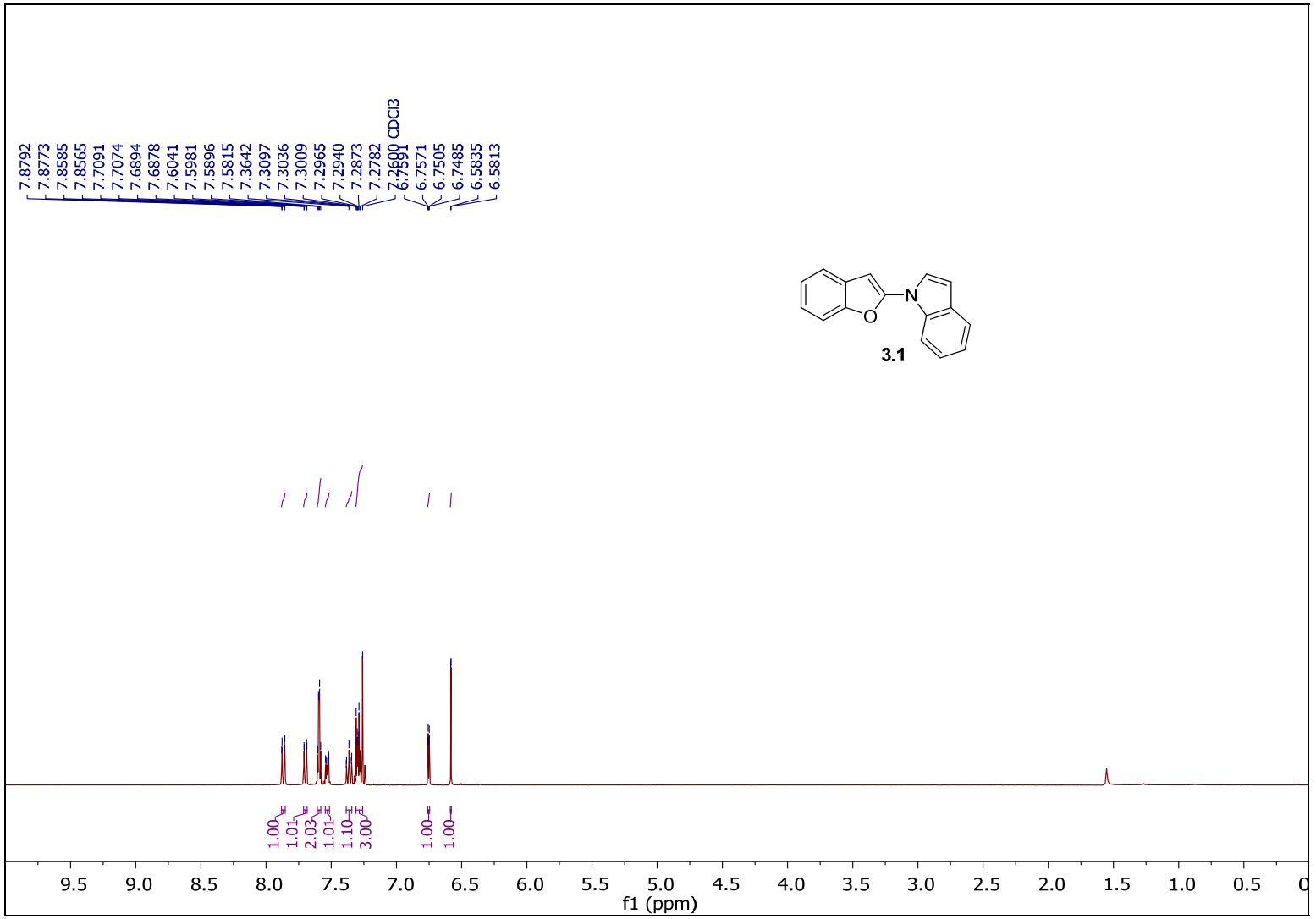
7. References

1 S. G. Newman, A. Aureggi, C. S. Bryan and M. Lautens, *Chem. Commun*., 2009, 5236.

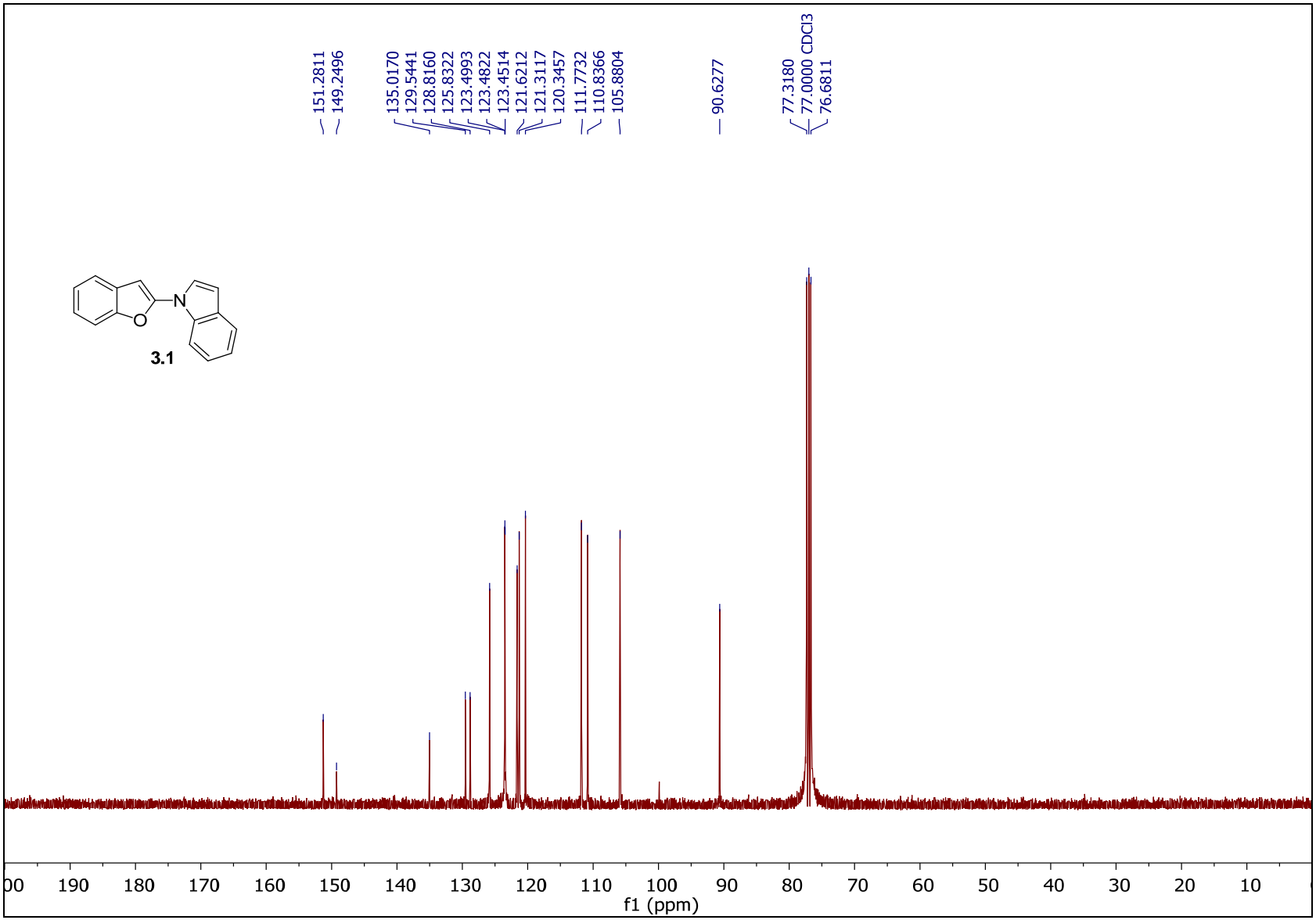
2 M. Hedidi, G. Bentabed-Ababsa, A. Derdour, T. Roisnel, V. Dorcet, F. Chevallier, L. Picot, V. Thiéry and F. Mongin, *Bioorg. Med. Chem*., 2014, **22**, 3498.

3 M. Li, J.-H. Wang, W. Li, C.-D. Lin, L.-B. Zhang and L.-R. Wen, *J. Org. Chem*., 2019, **84**, 8523.

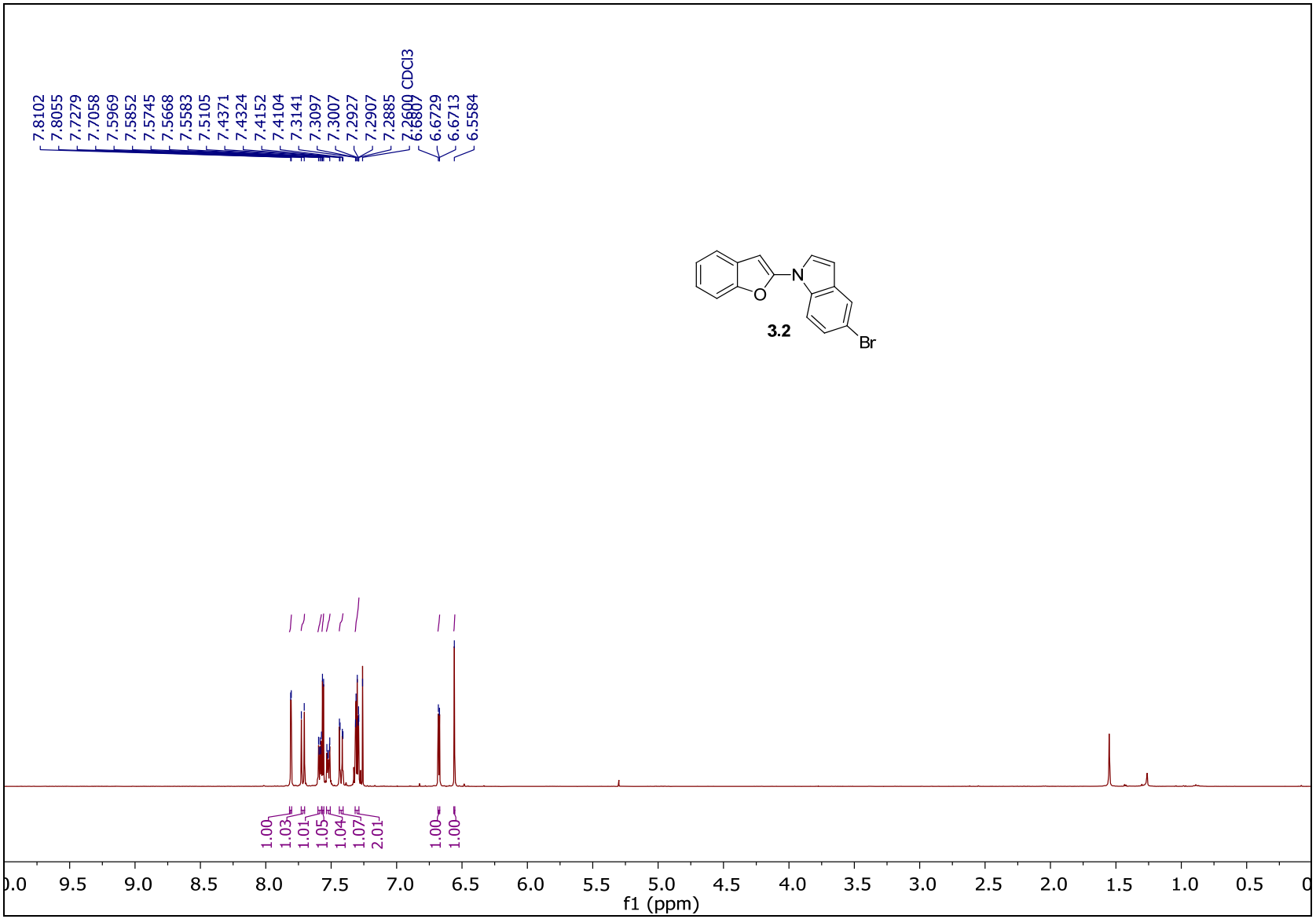
8. ^{1}H NMR, and ^{13}CNMR spectra:



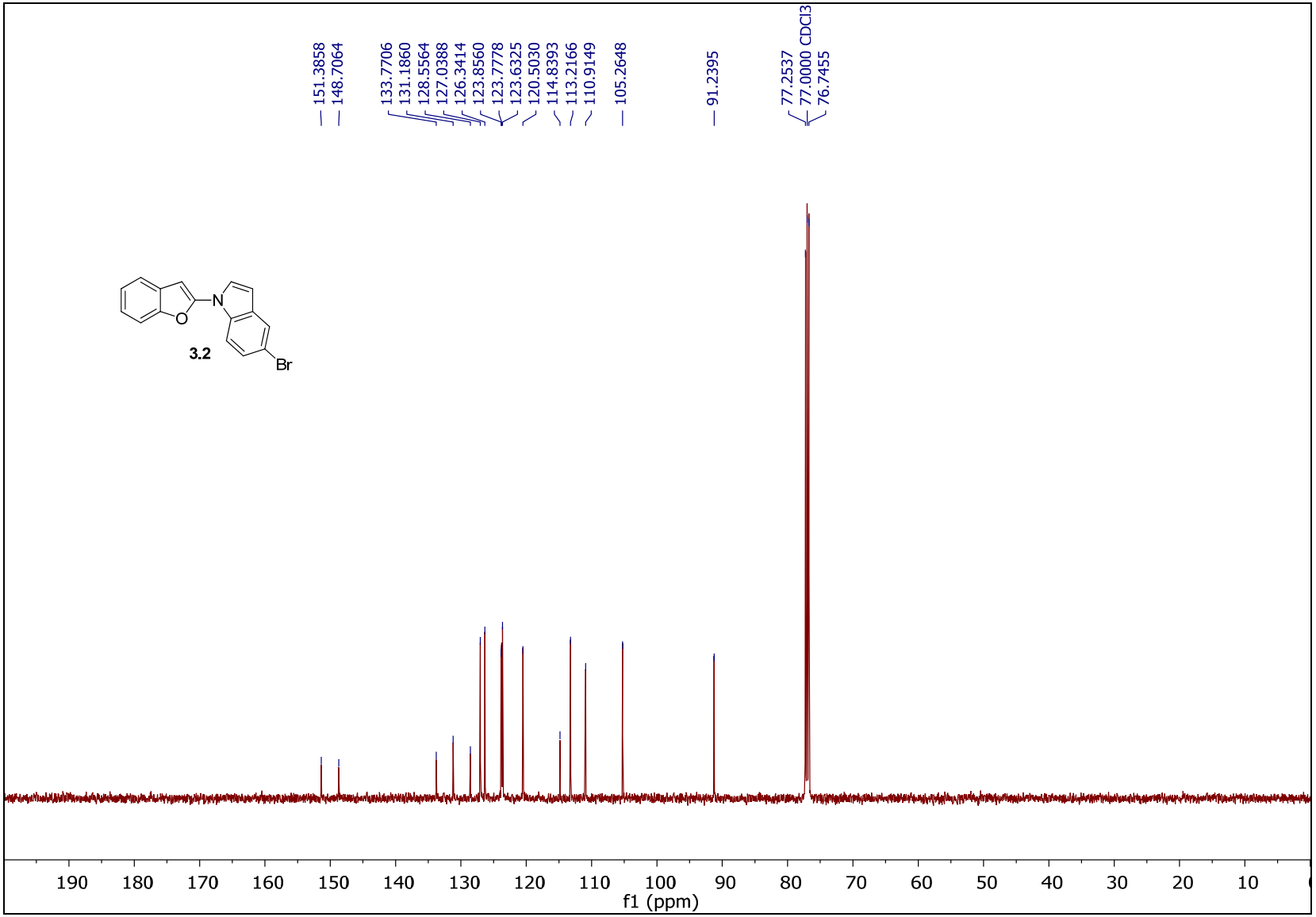
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3.1**



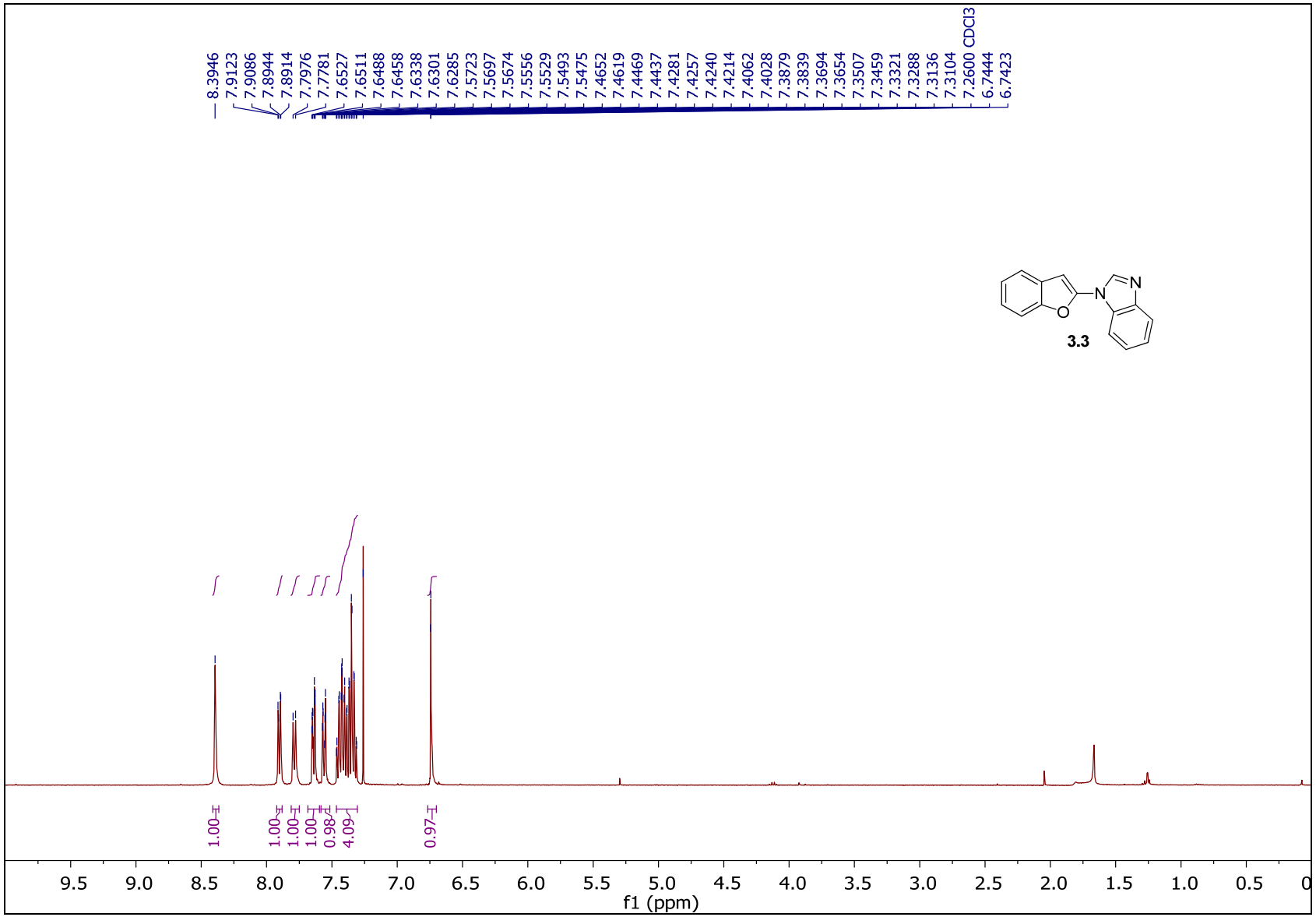
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3.1**



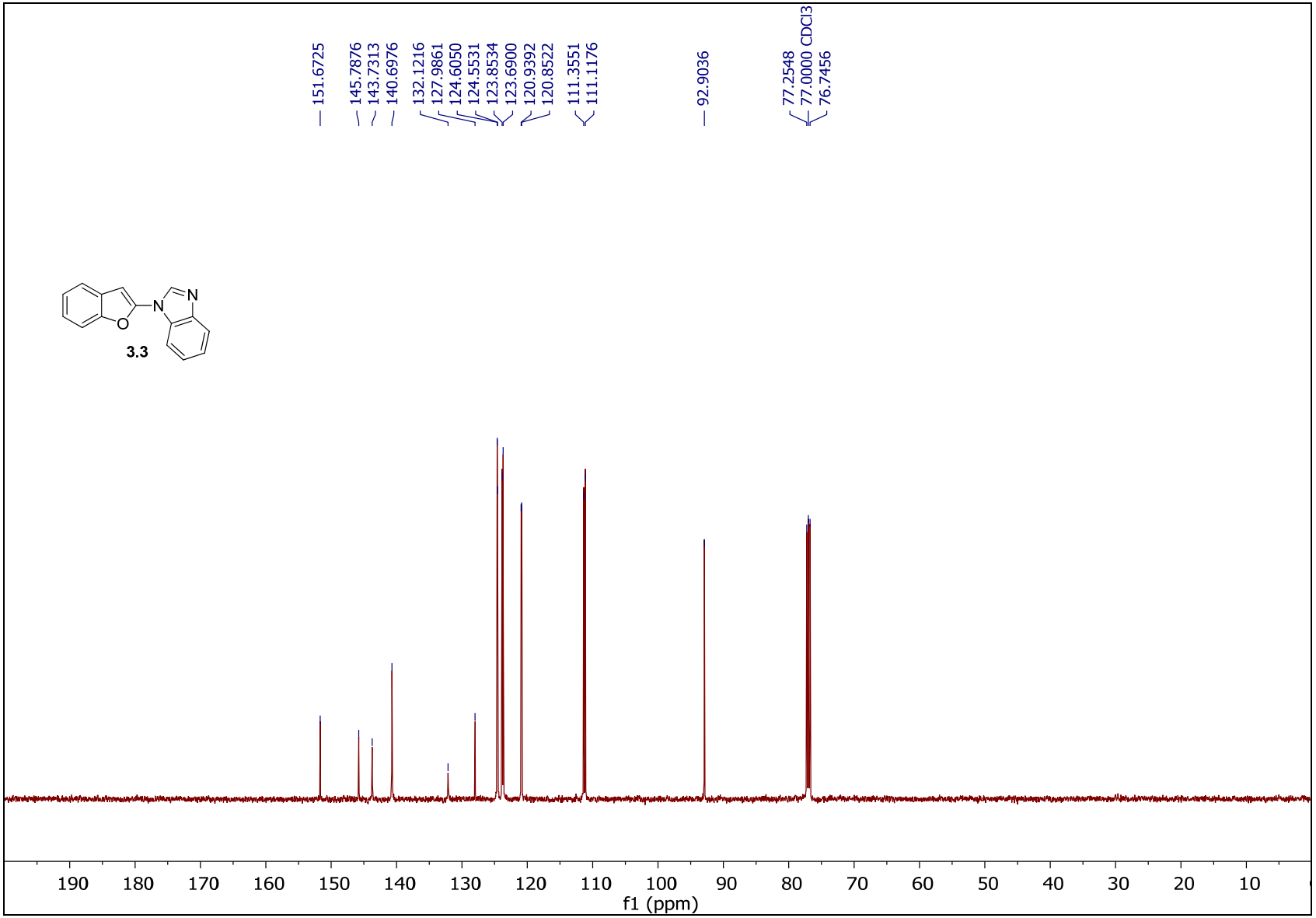
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3.2**



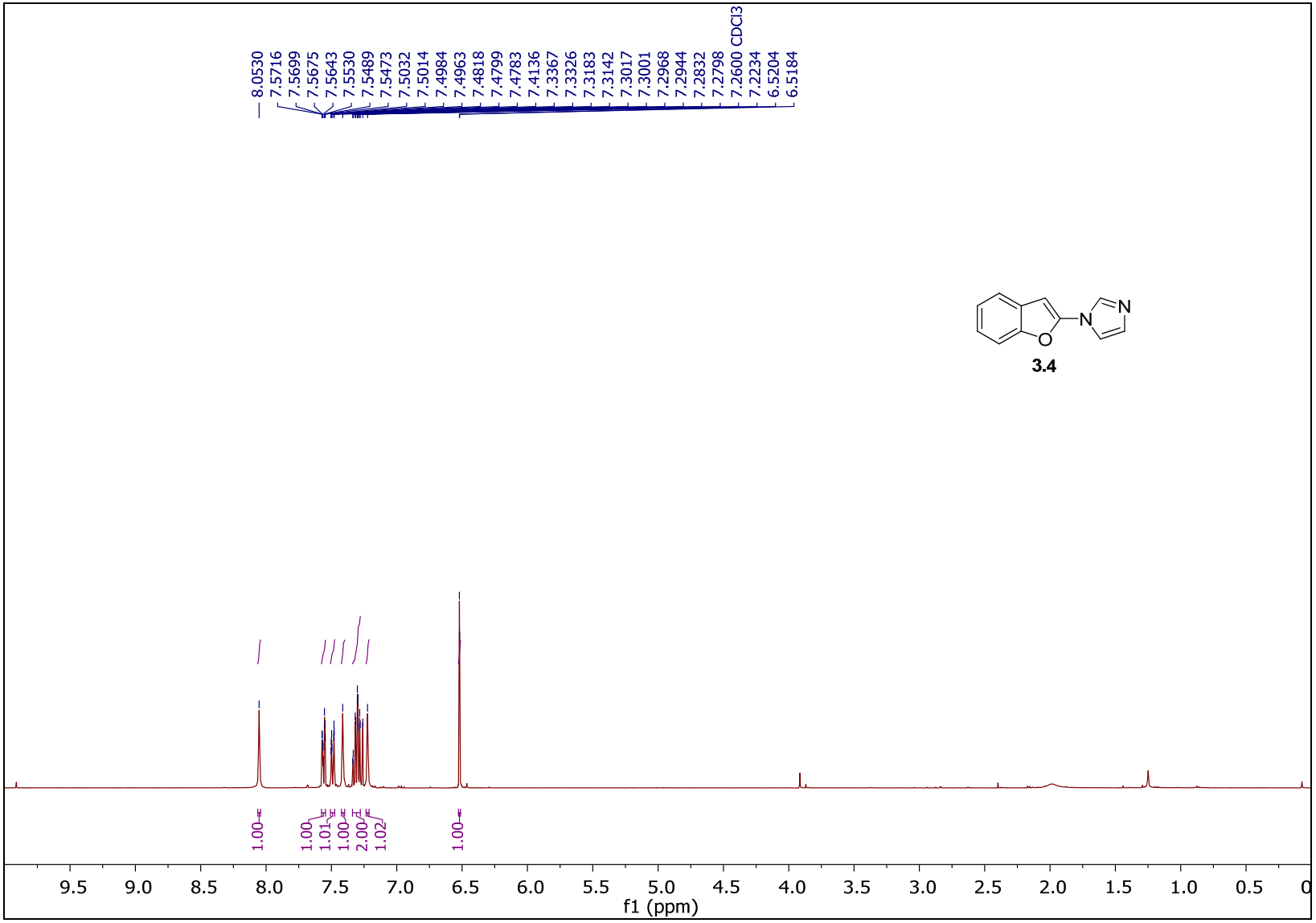
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **3.2**



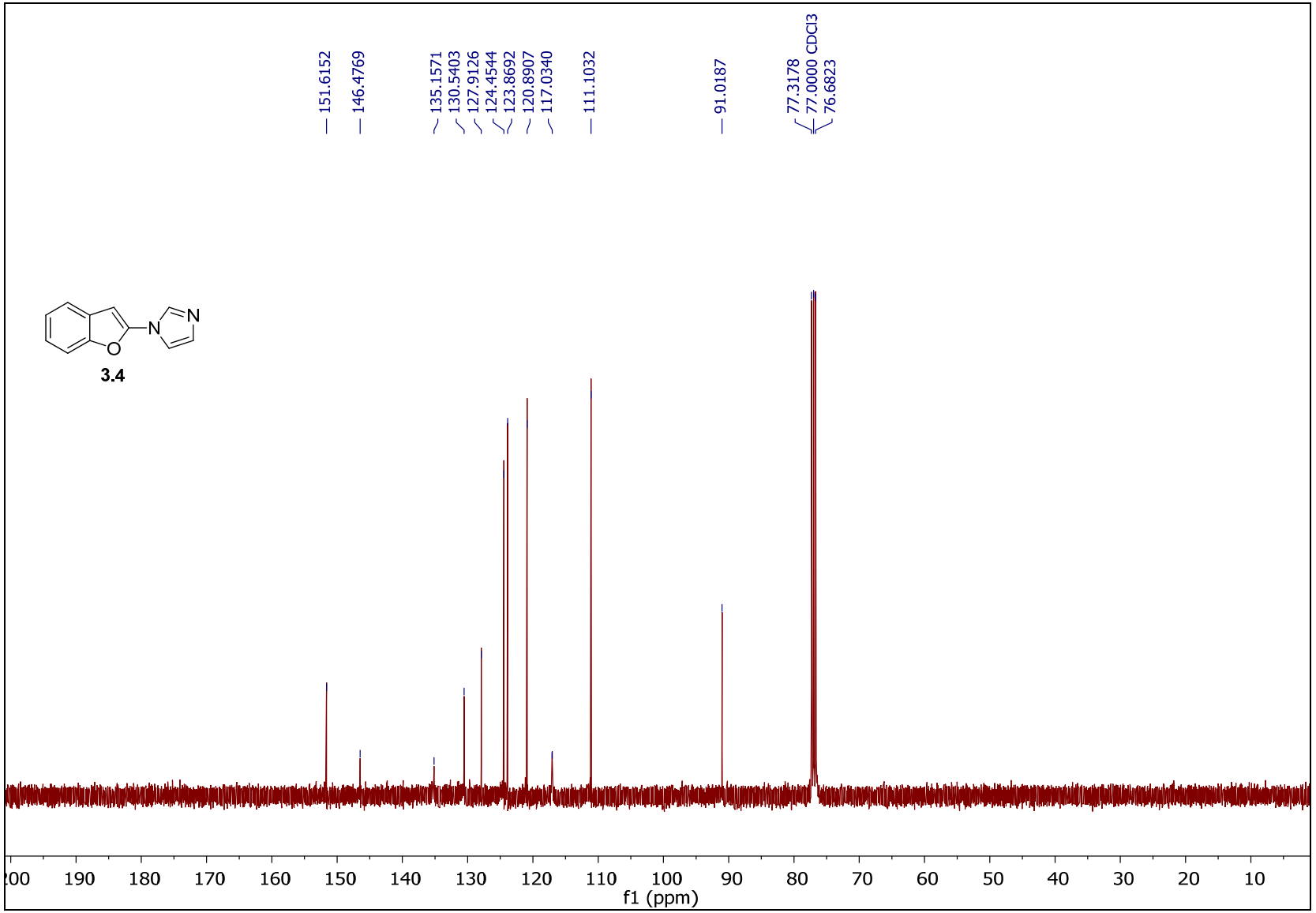
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3.3**



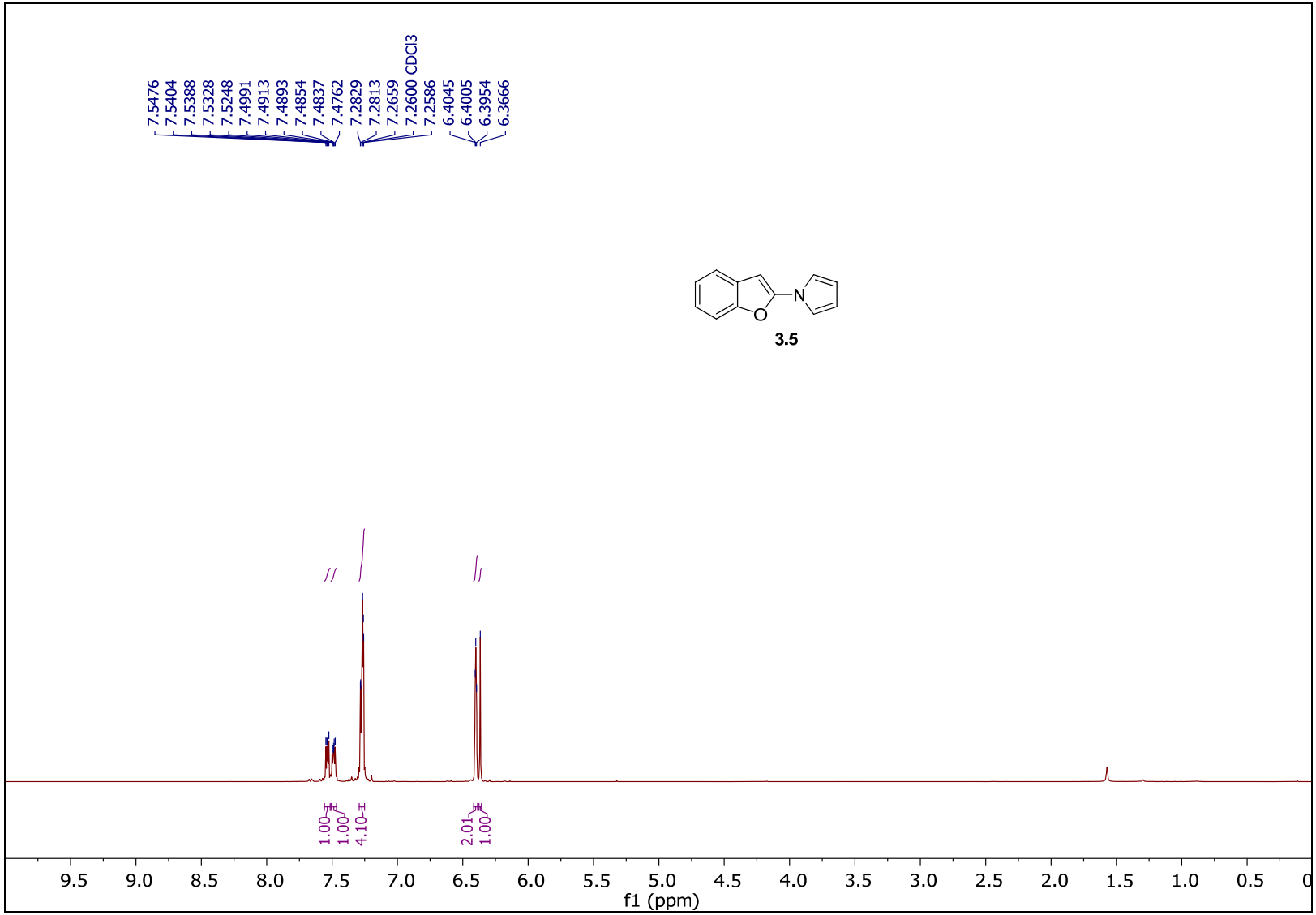
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **3.3**



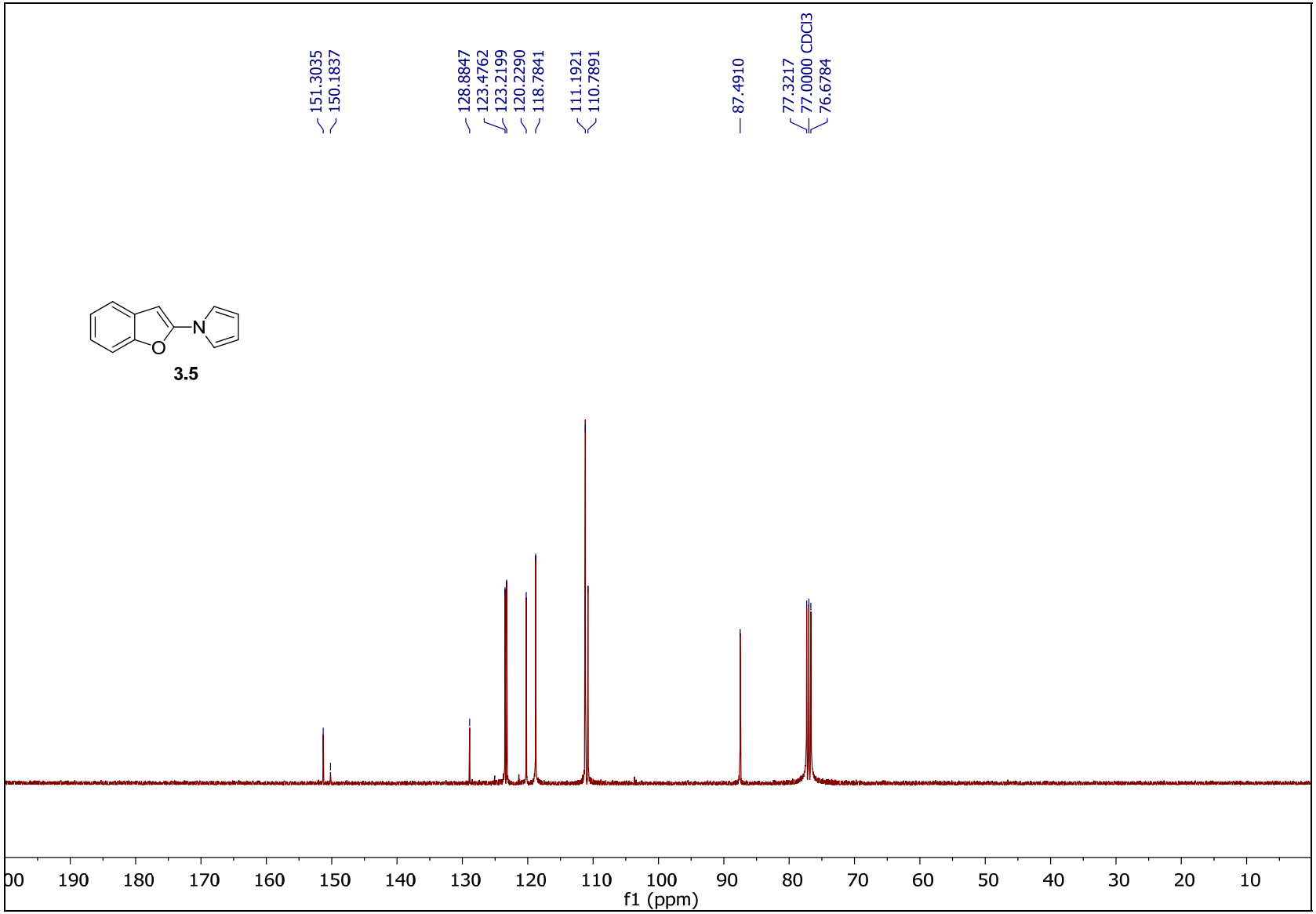
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3.4**



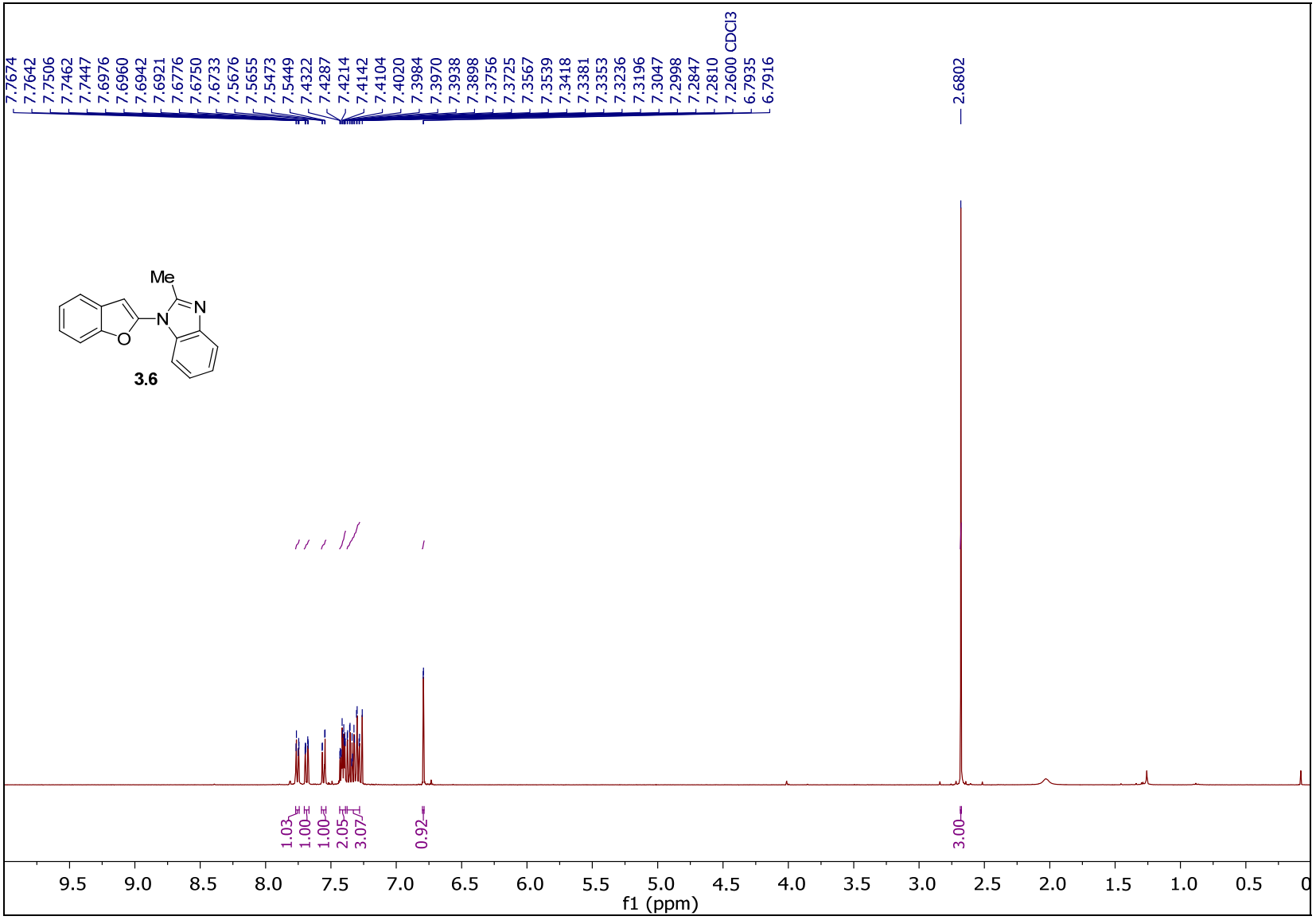
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3.4**



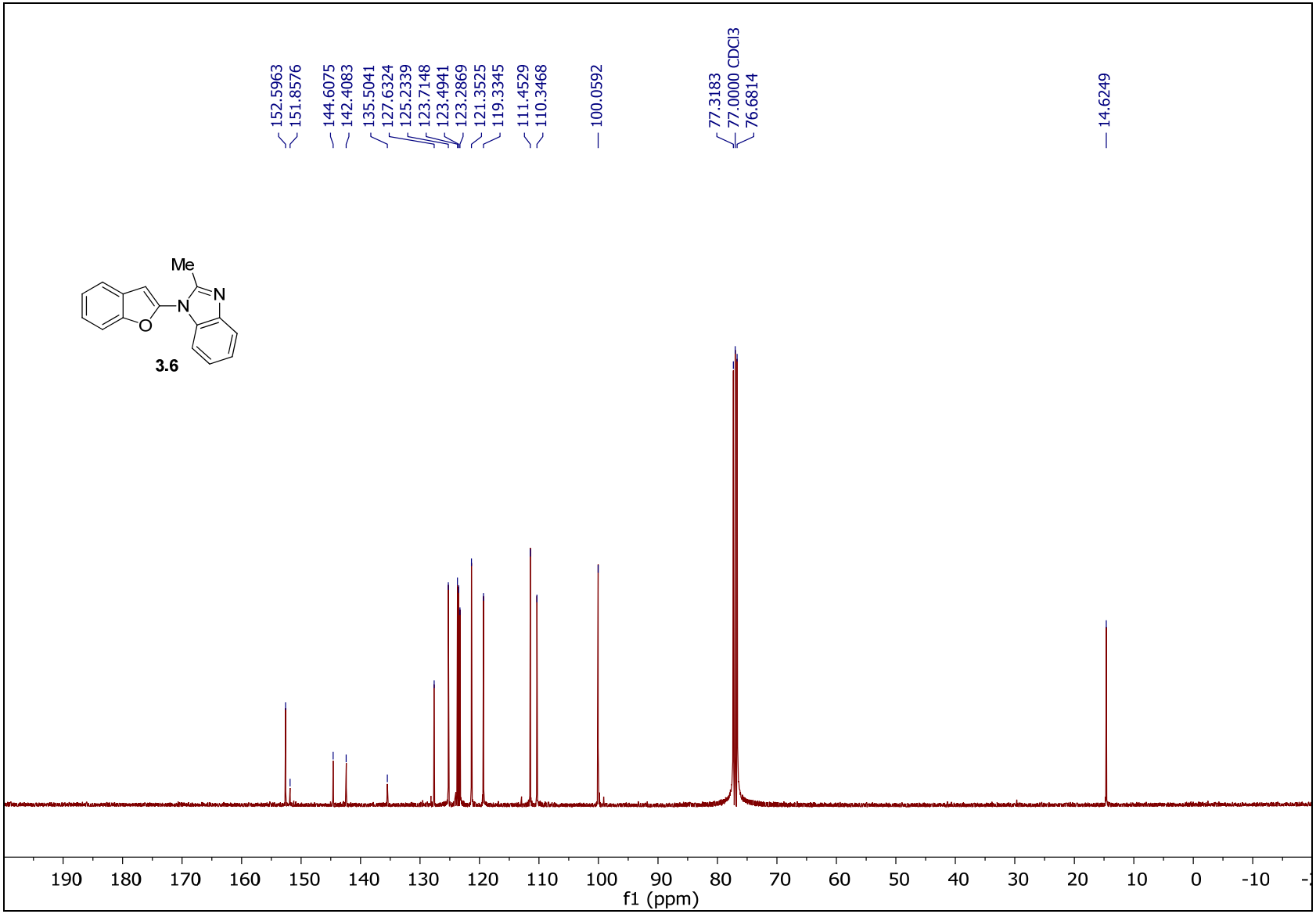
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3.5**



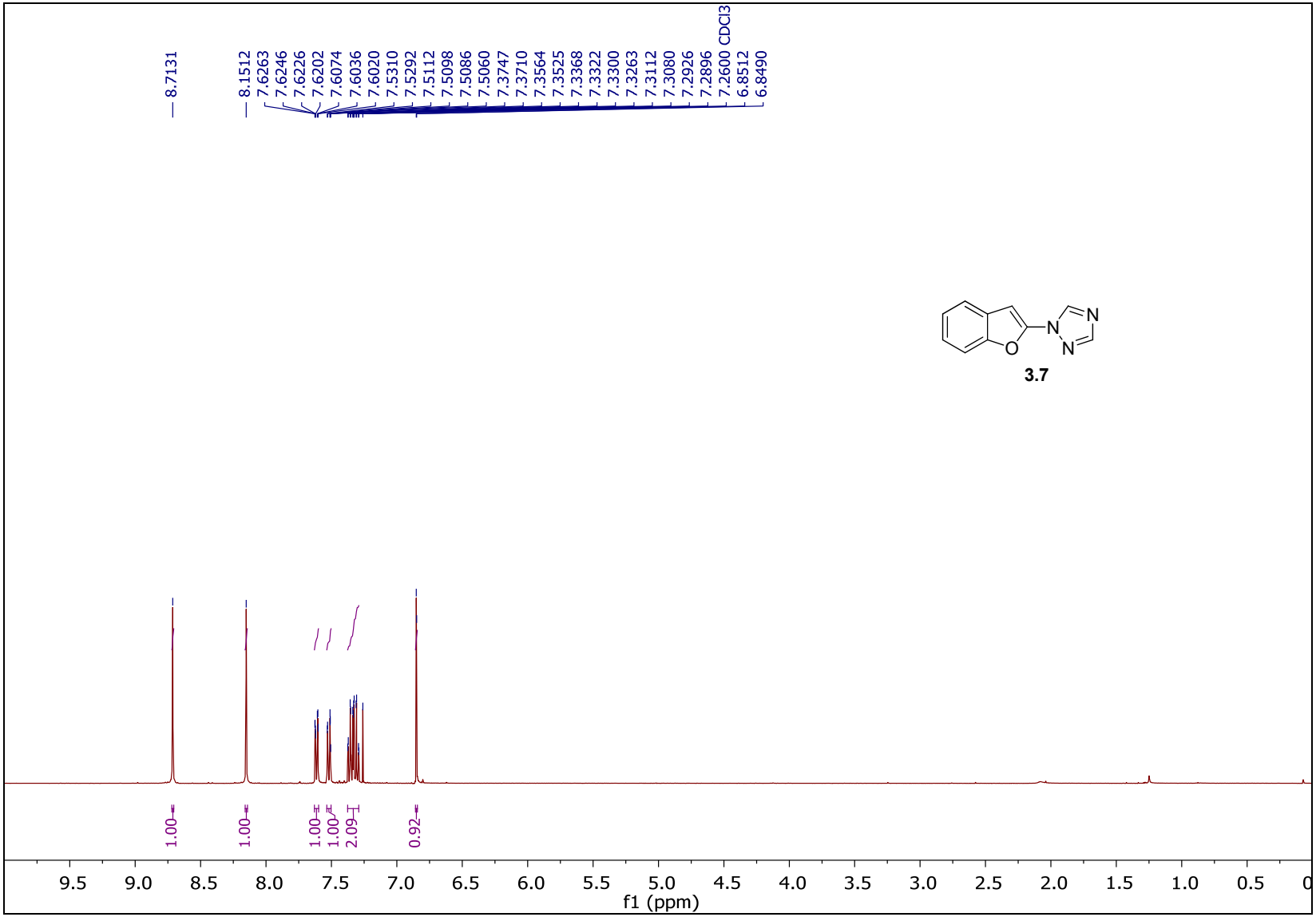
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3.5**



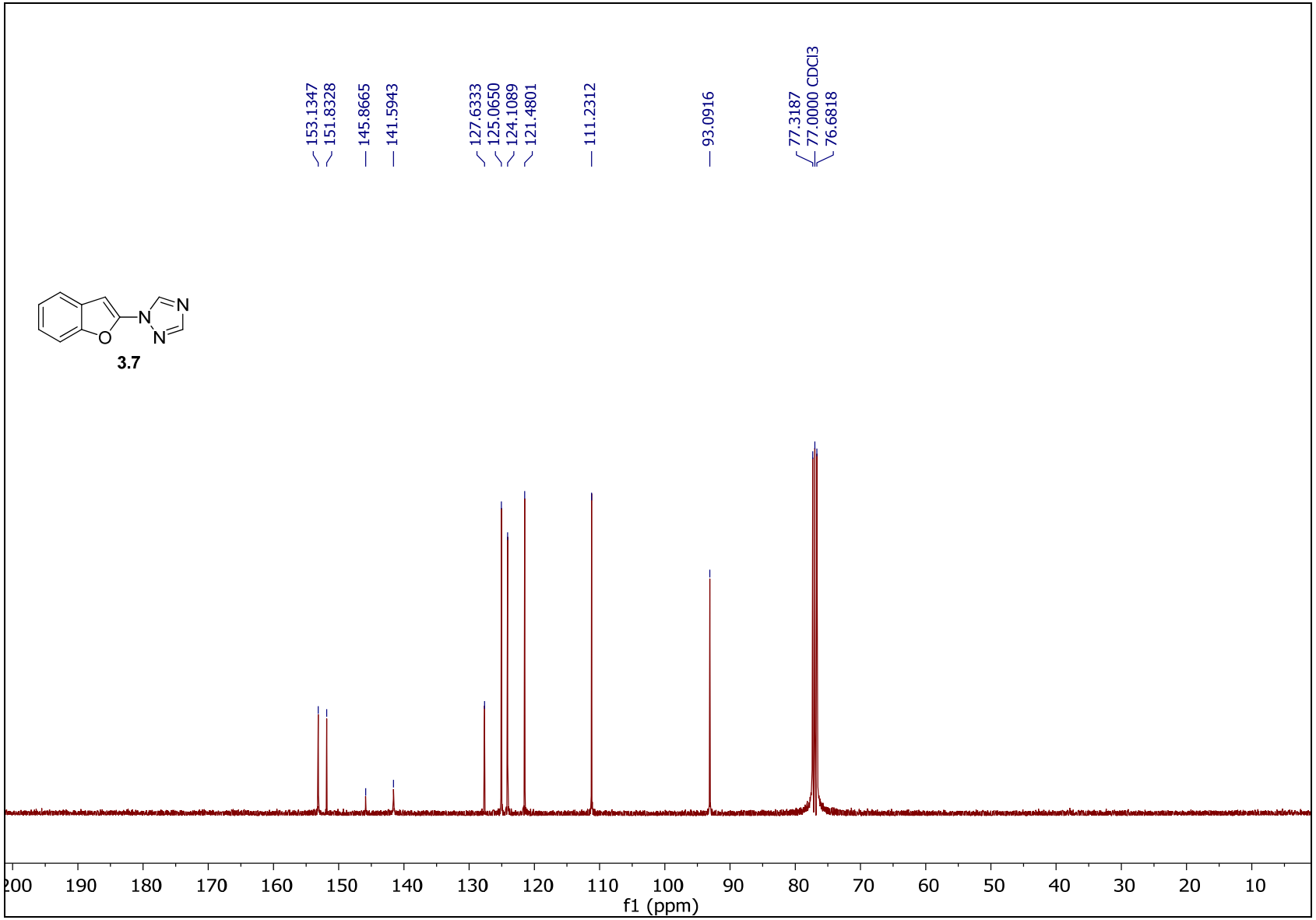
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3.6**



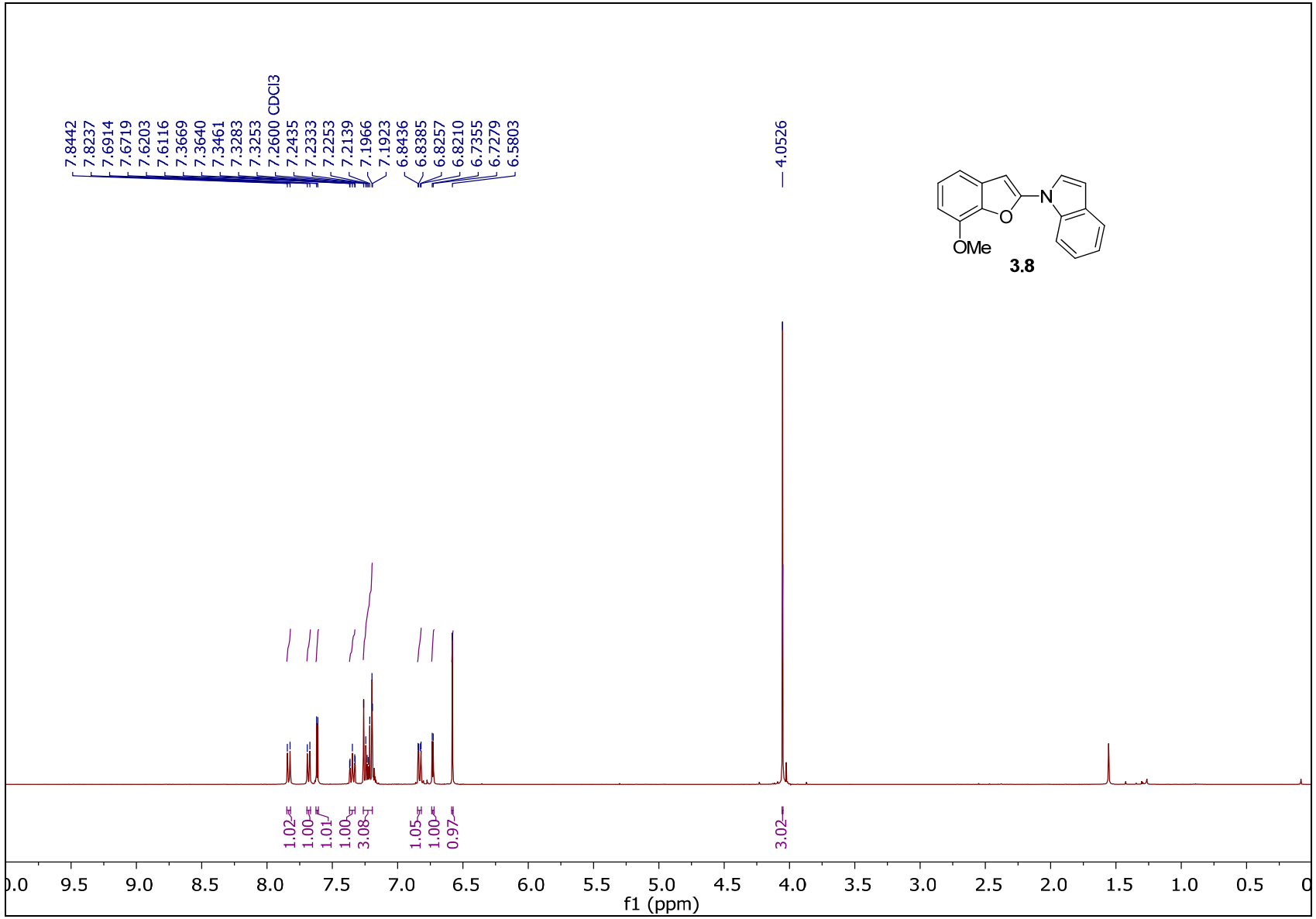
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3.6**



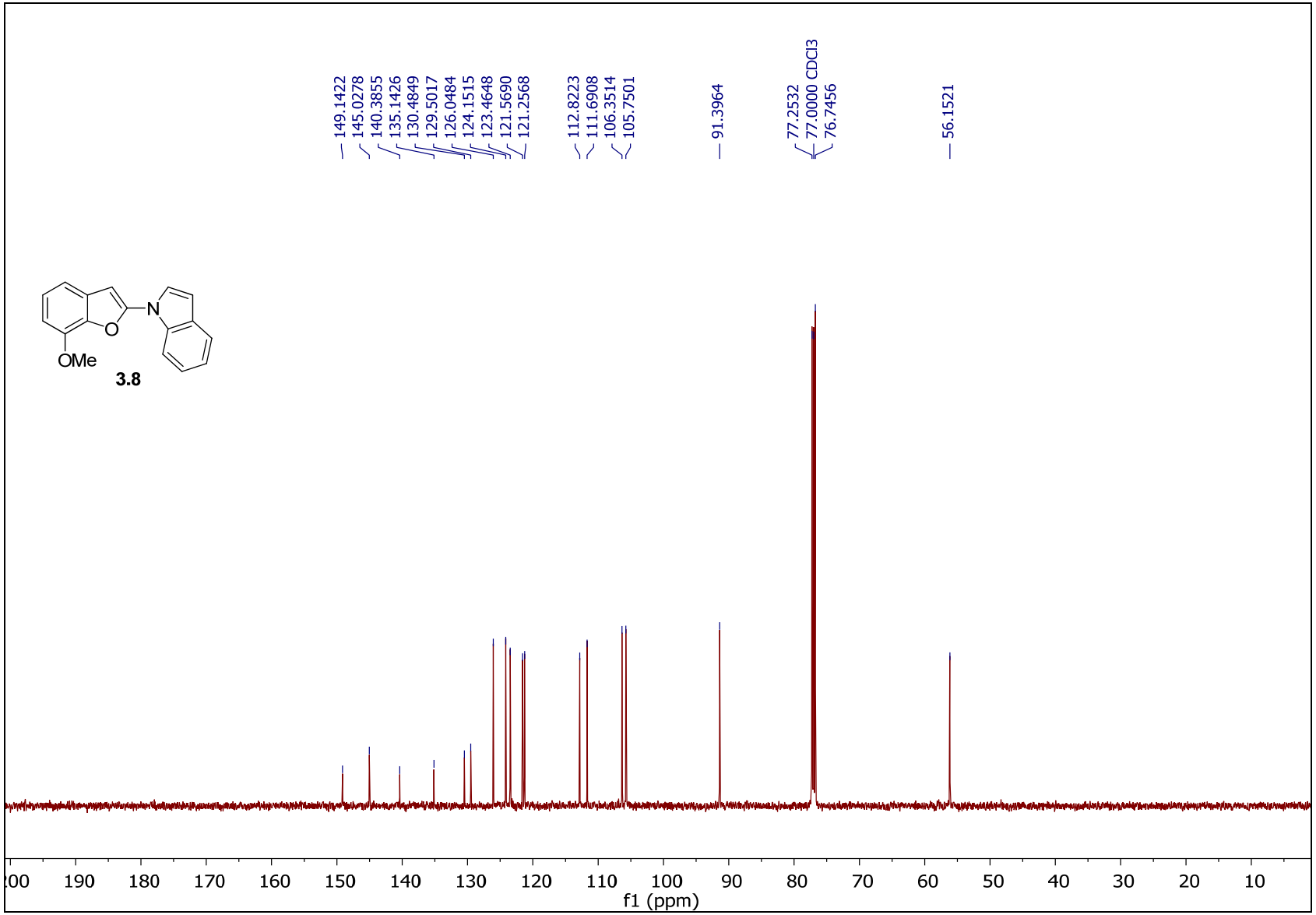
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3.7**



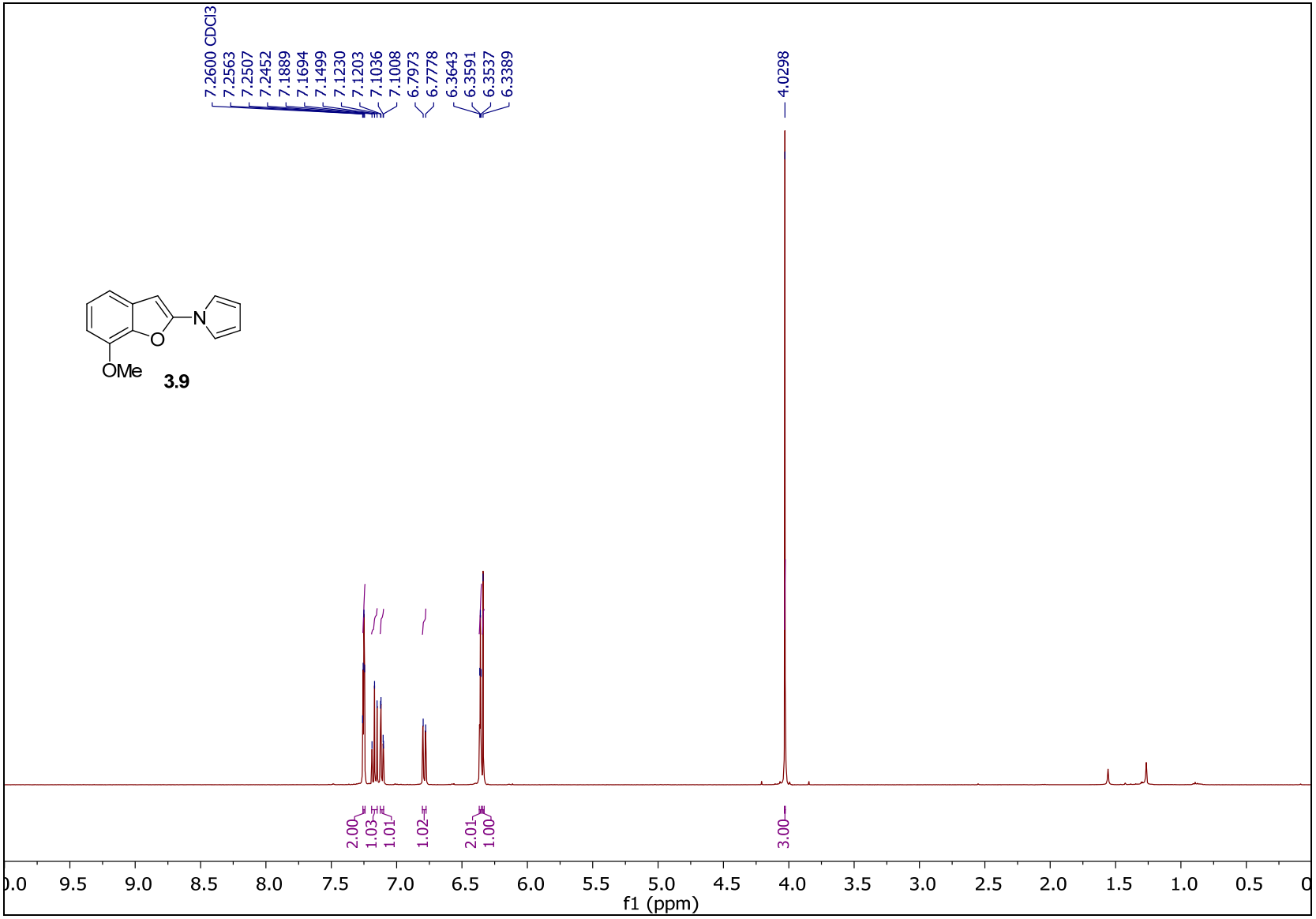
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3.7**



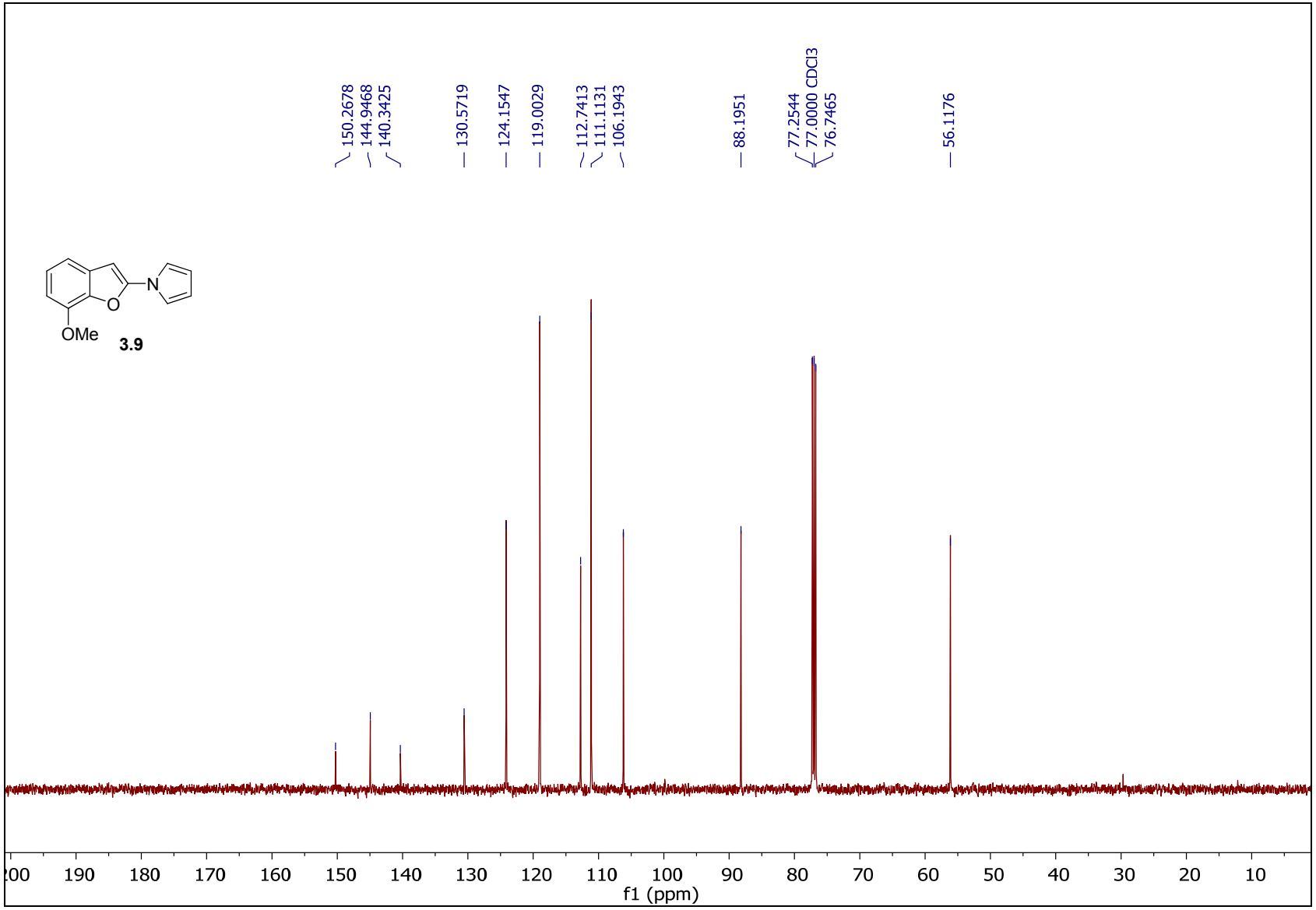
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3.8**



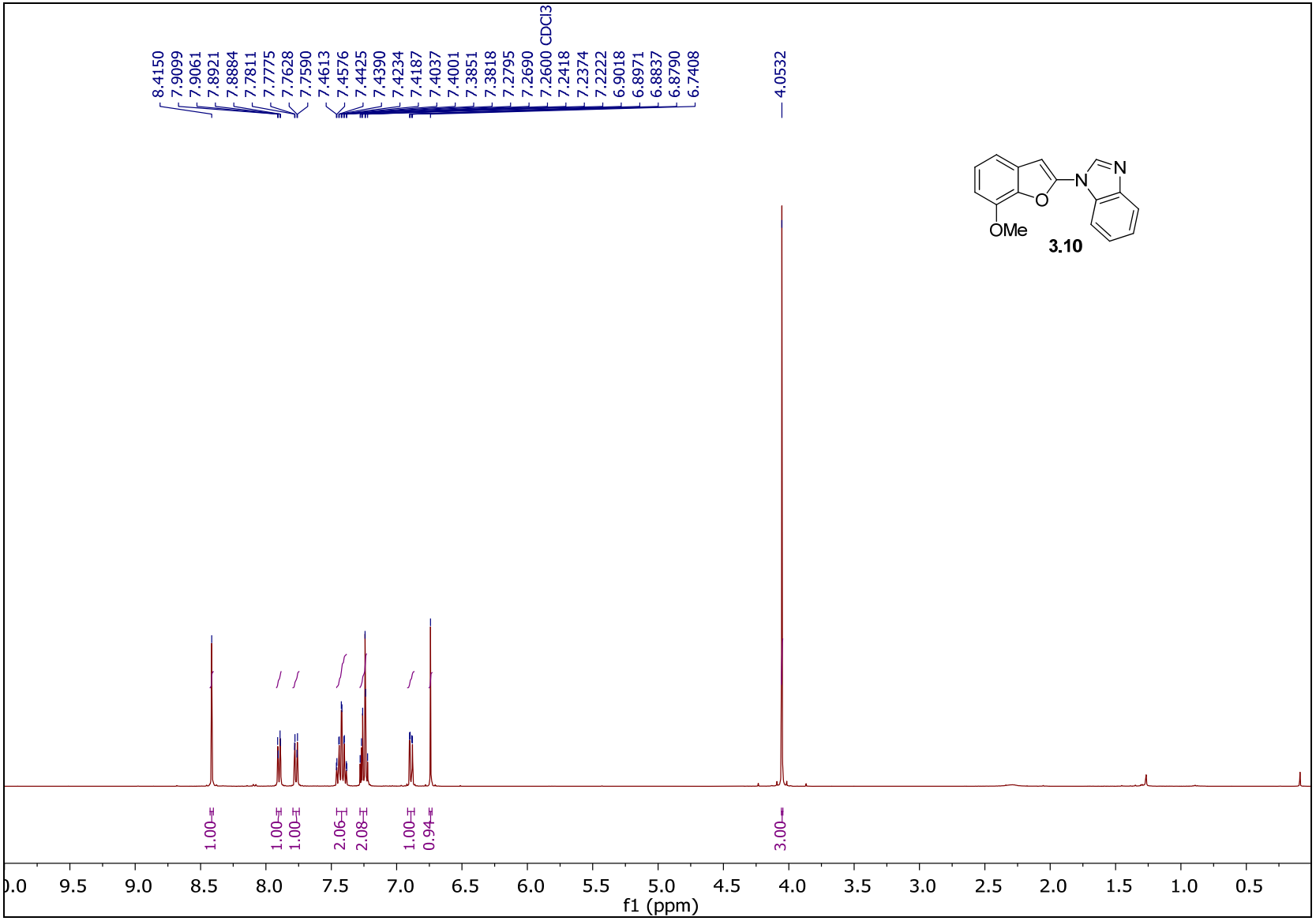
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **3.8**



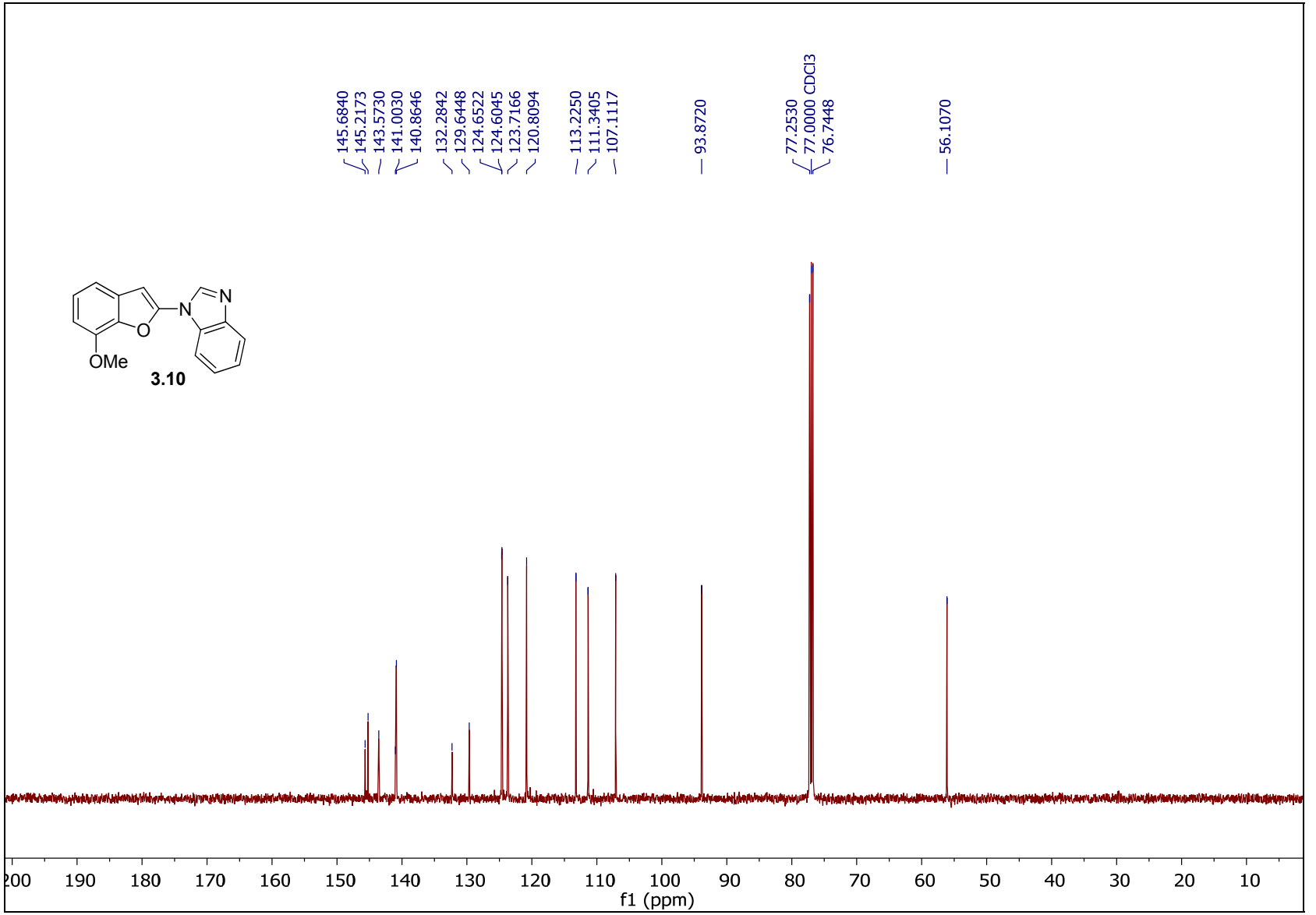
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3.9**



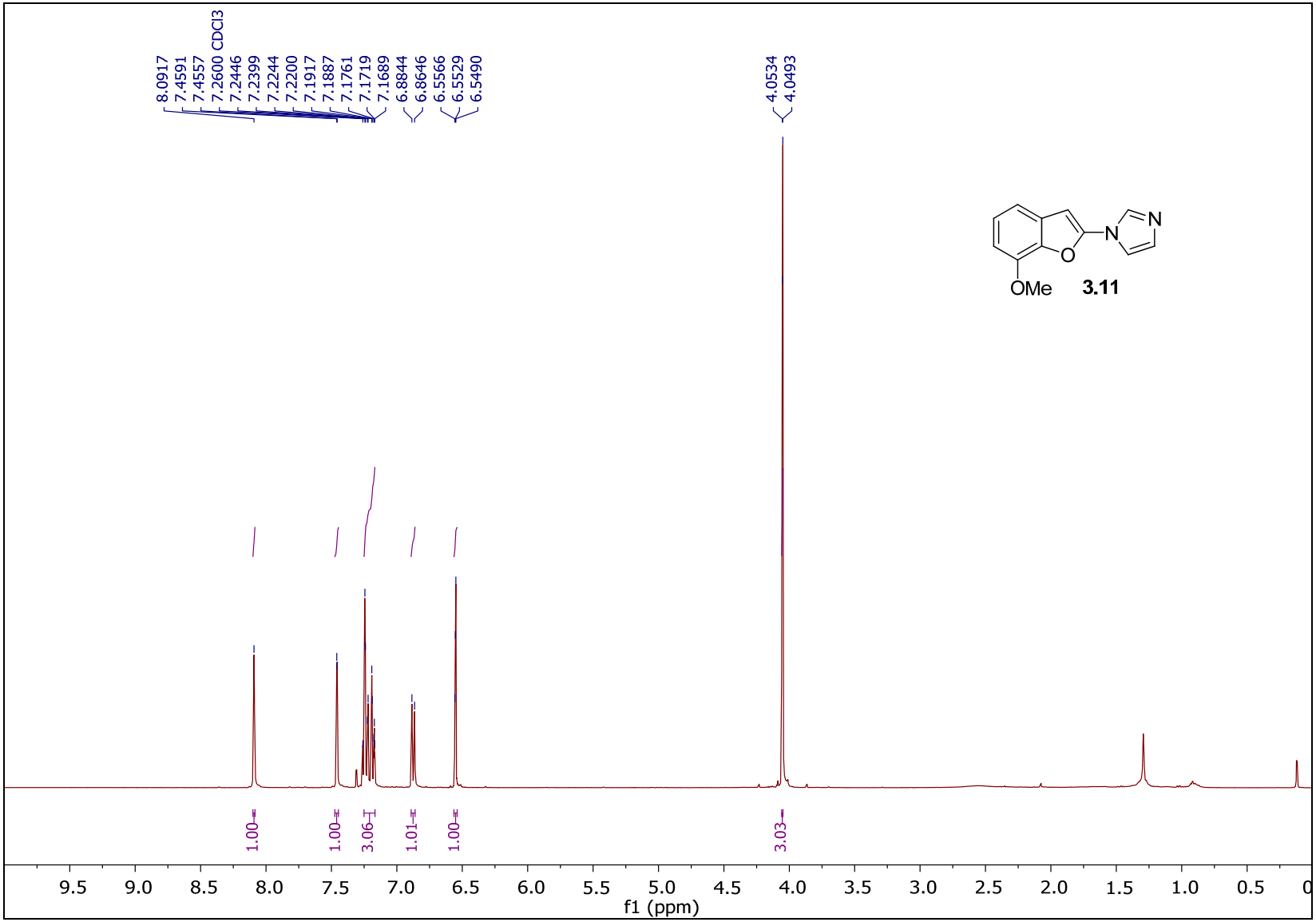
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **3.9**



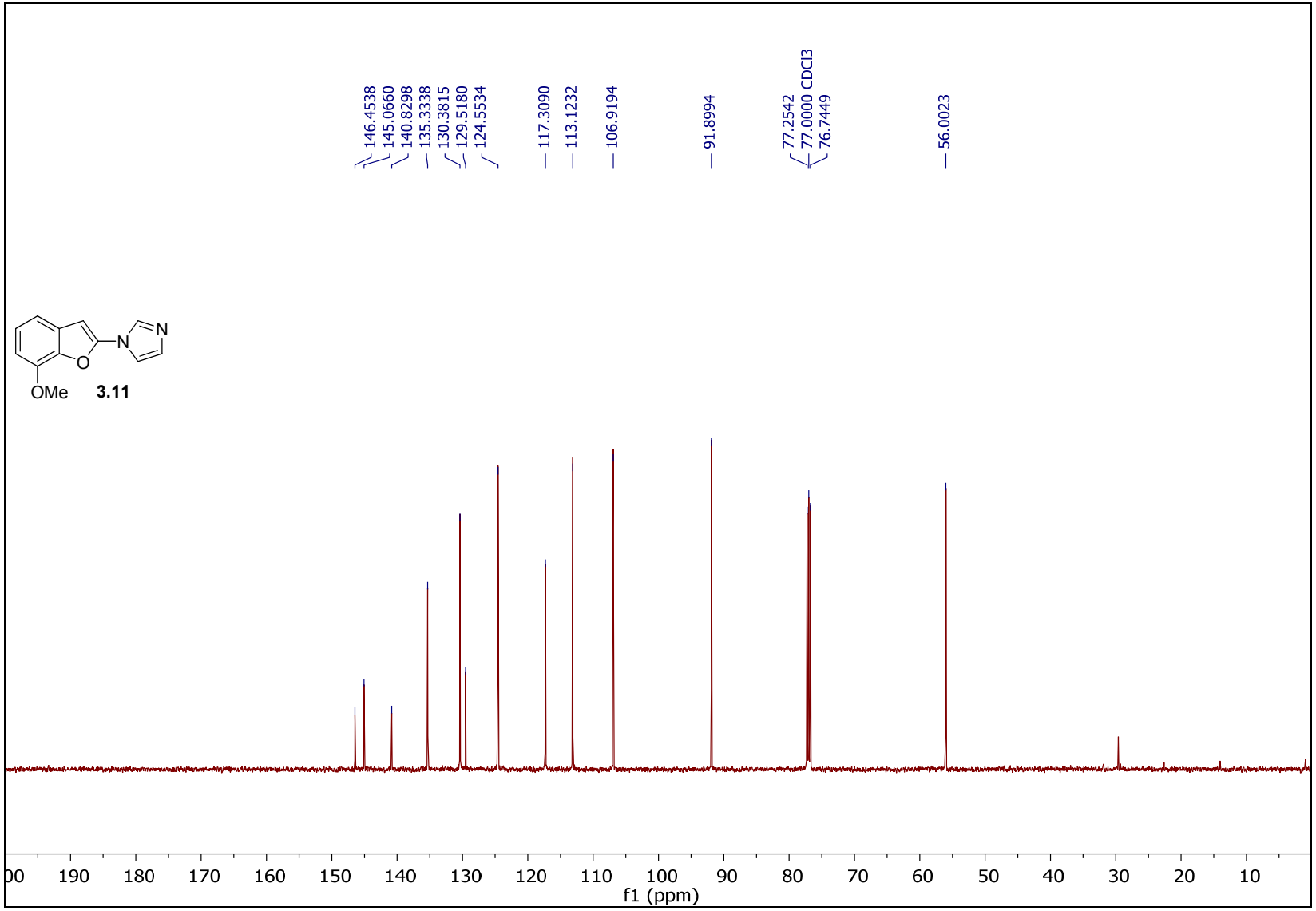
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3.10**



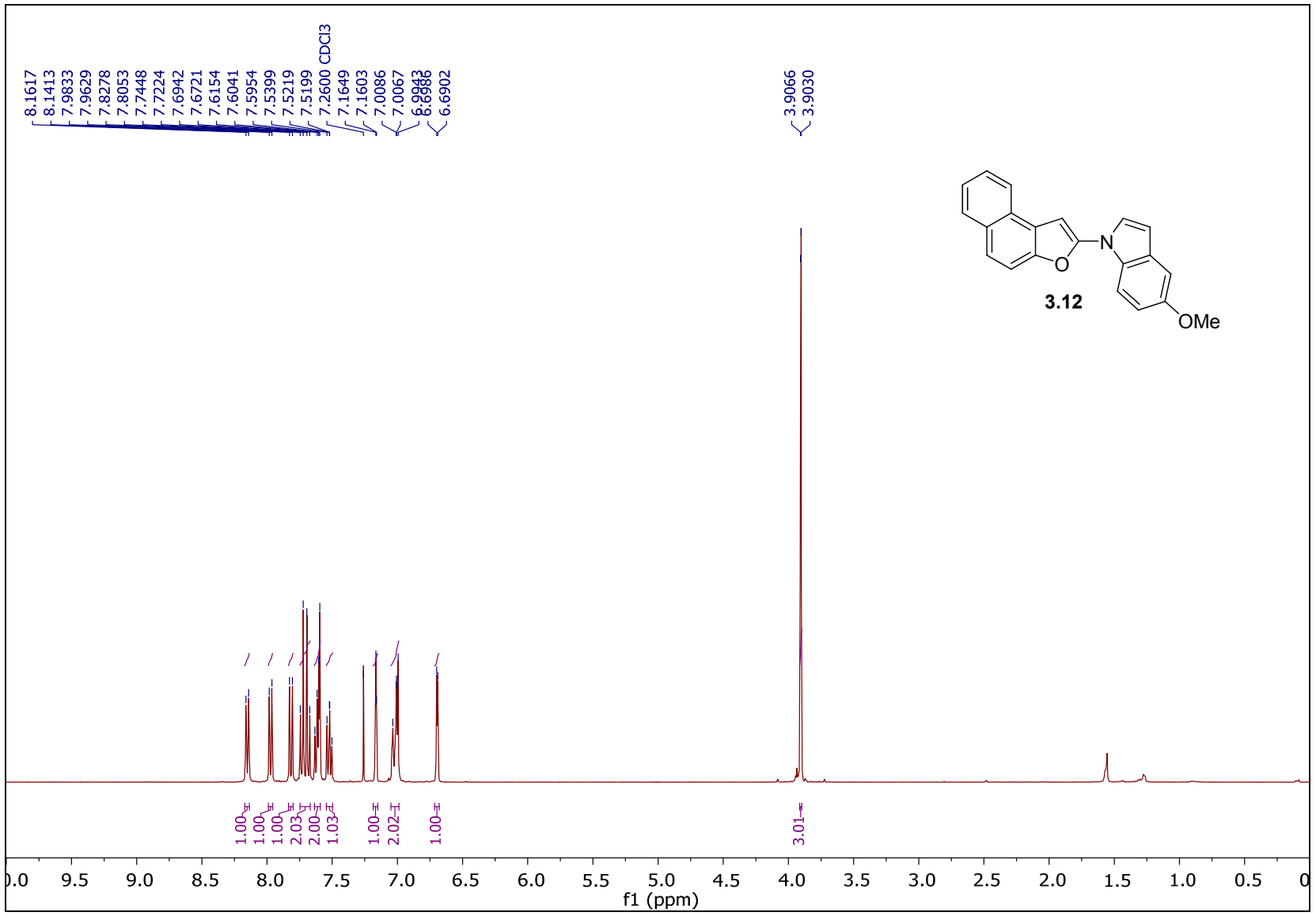
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **3.10**



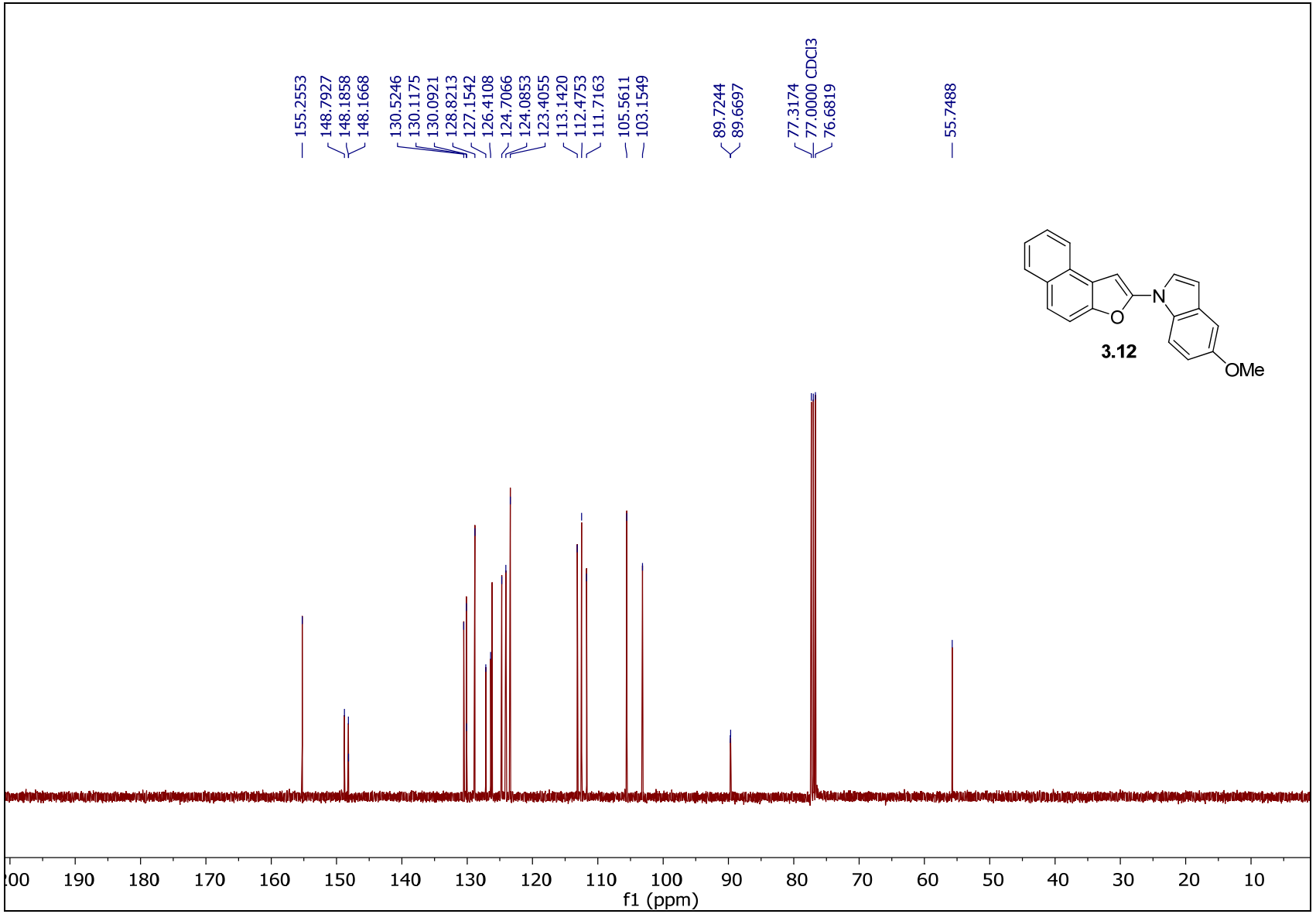
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3.11**



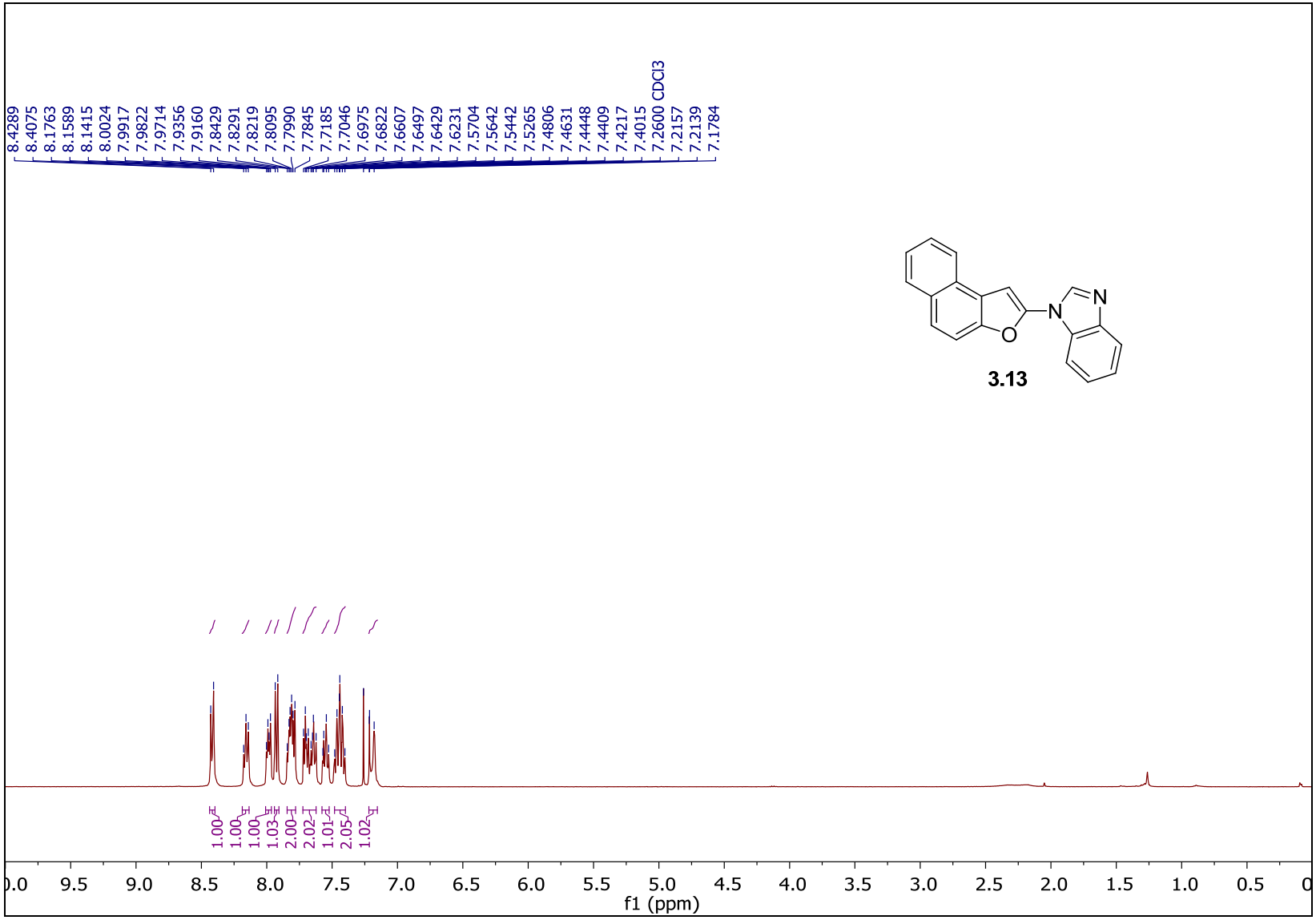
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **3.11**



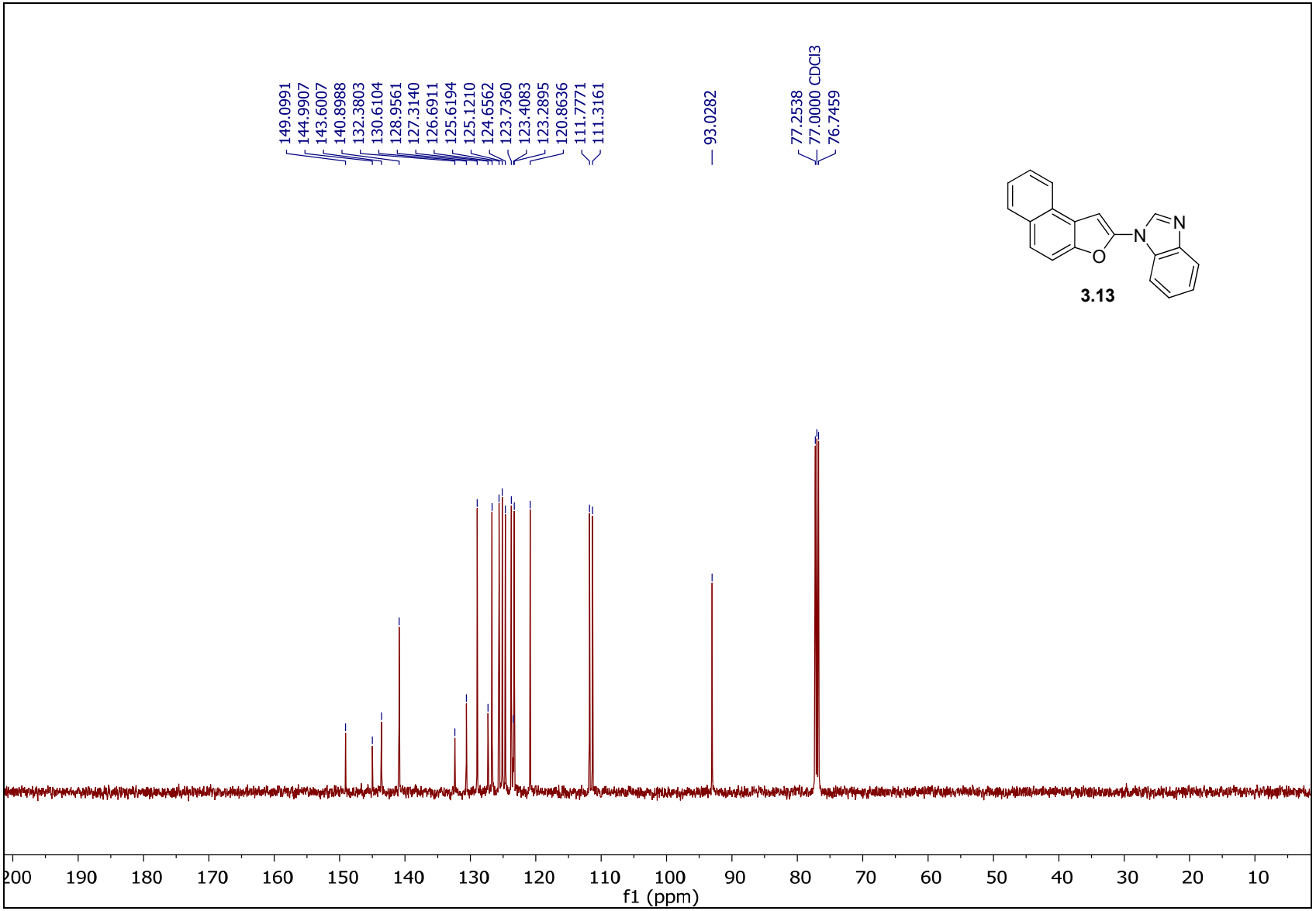
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3.12**



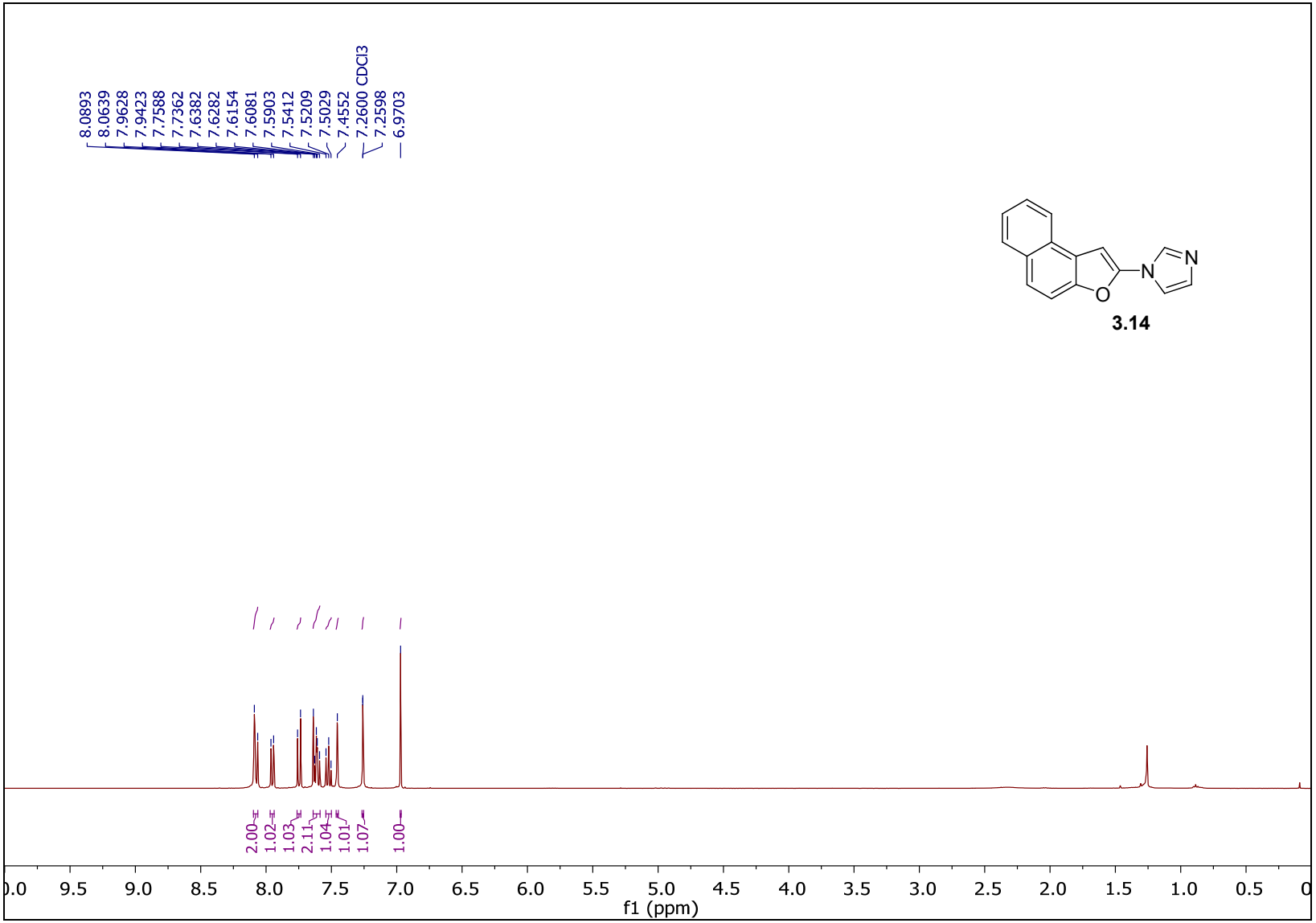
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3.12**



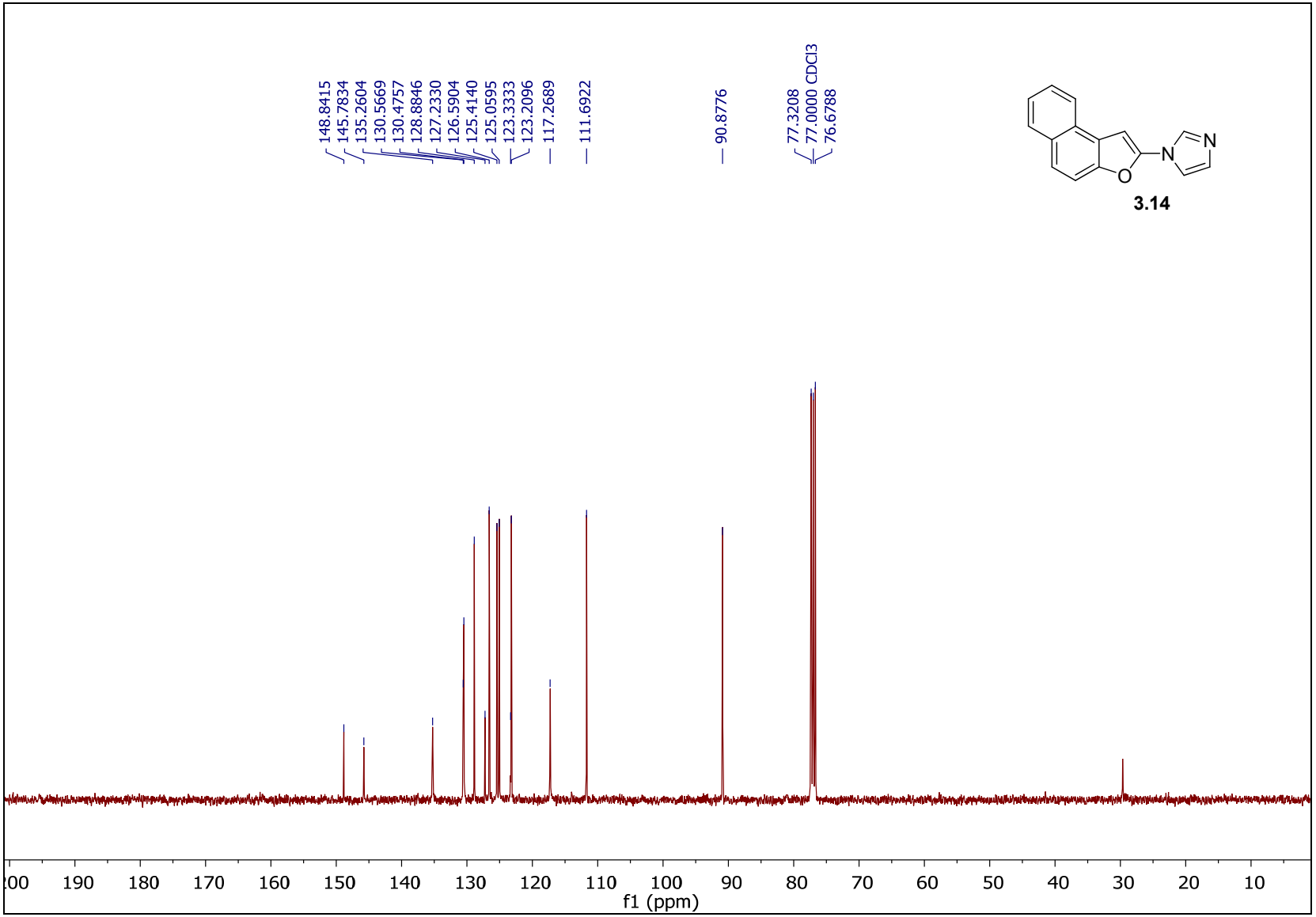
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3.13**



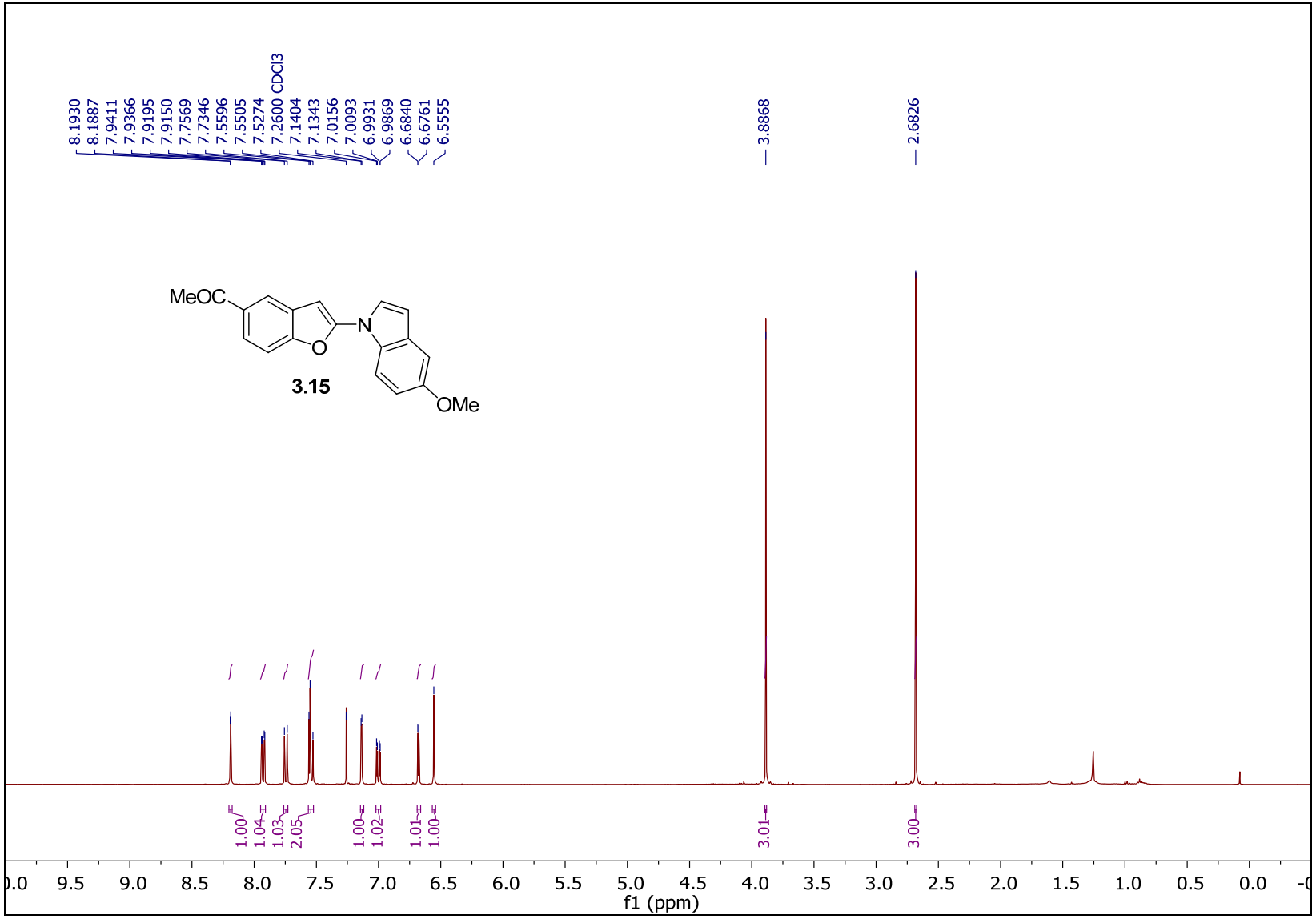
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **3.13**



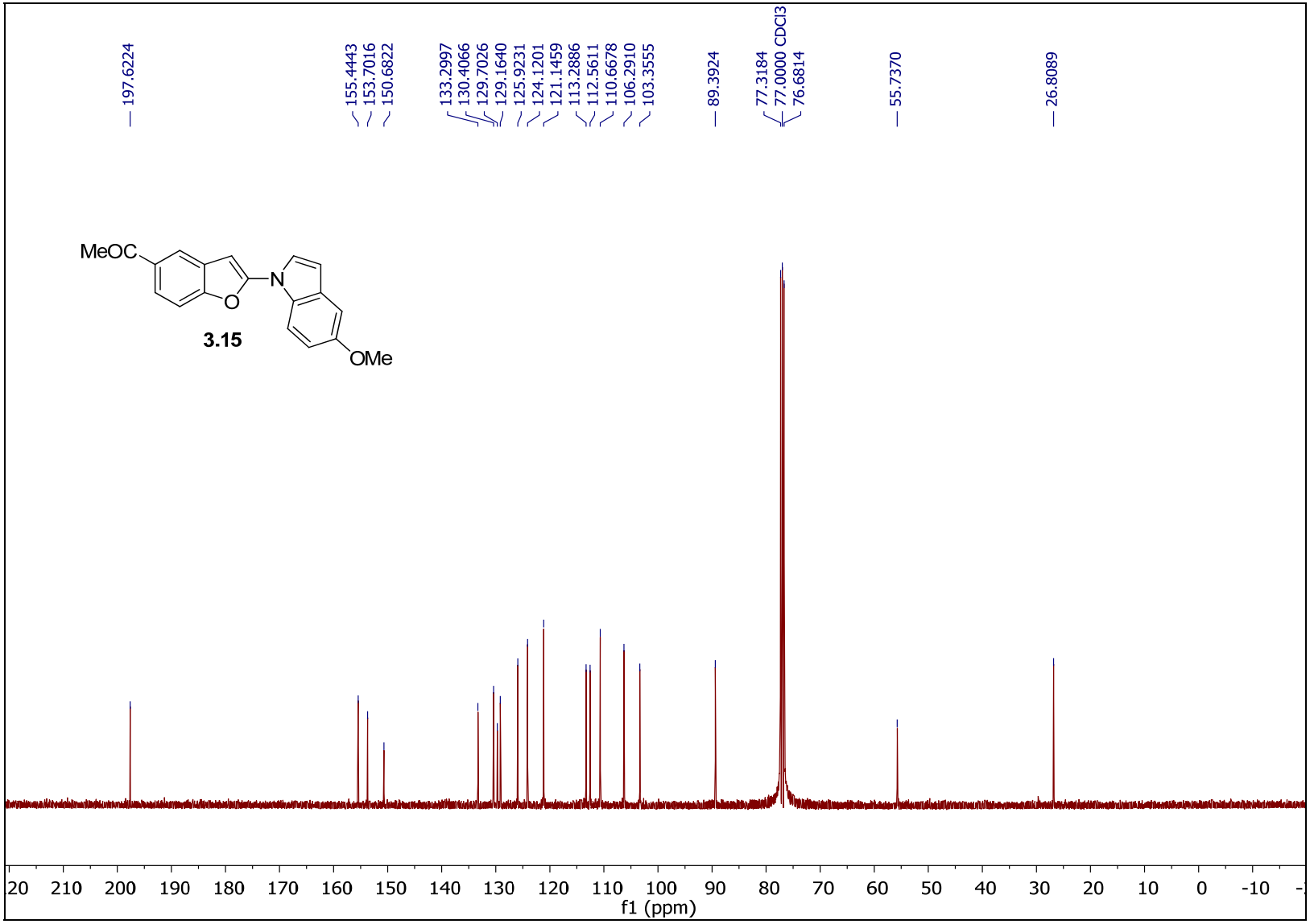
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3.14**



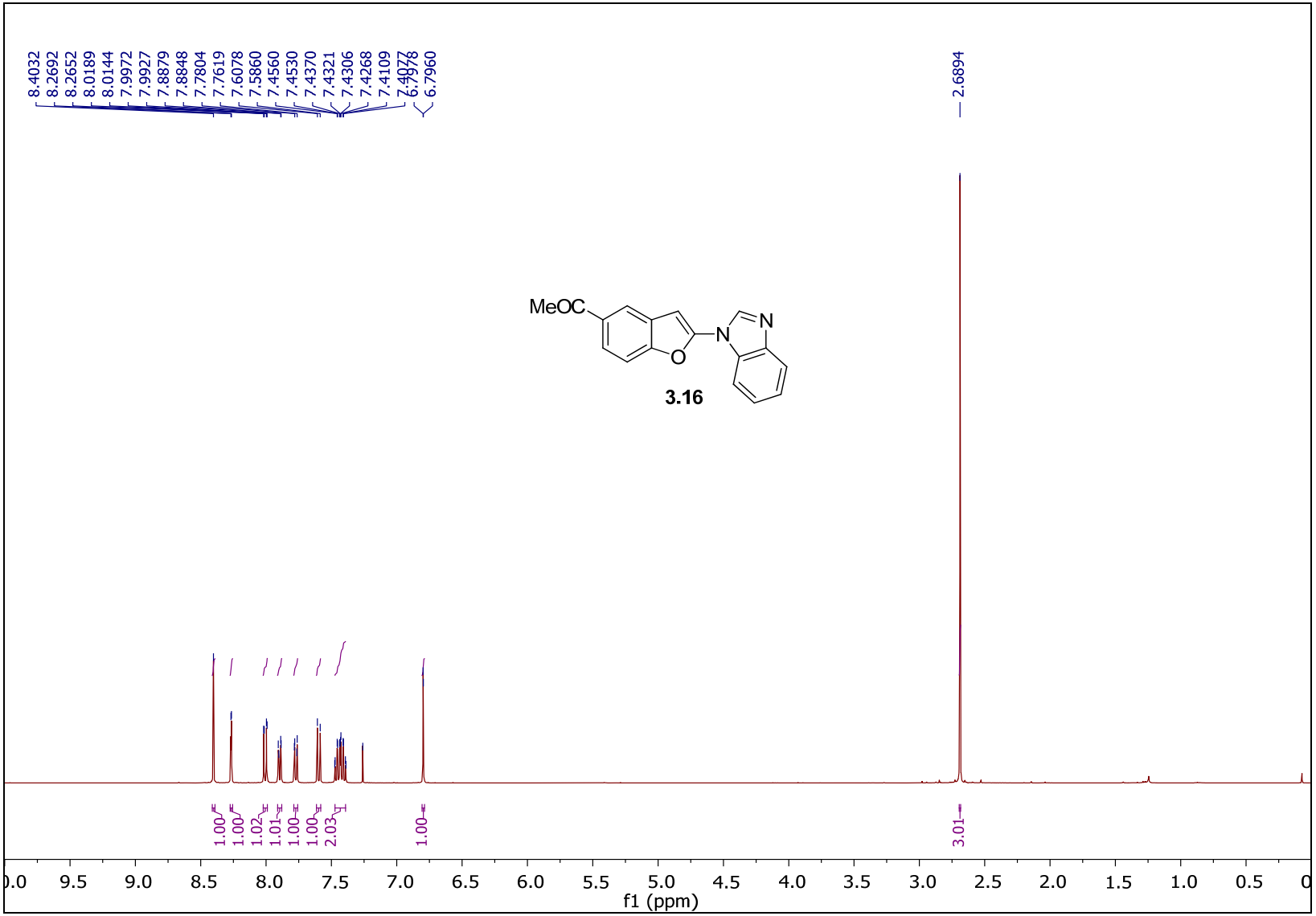
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3.14**



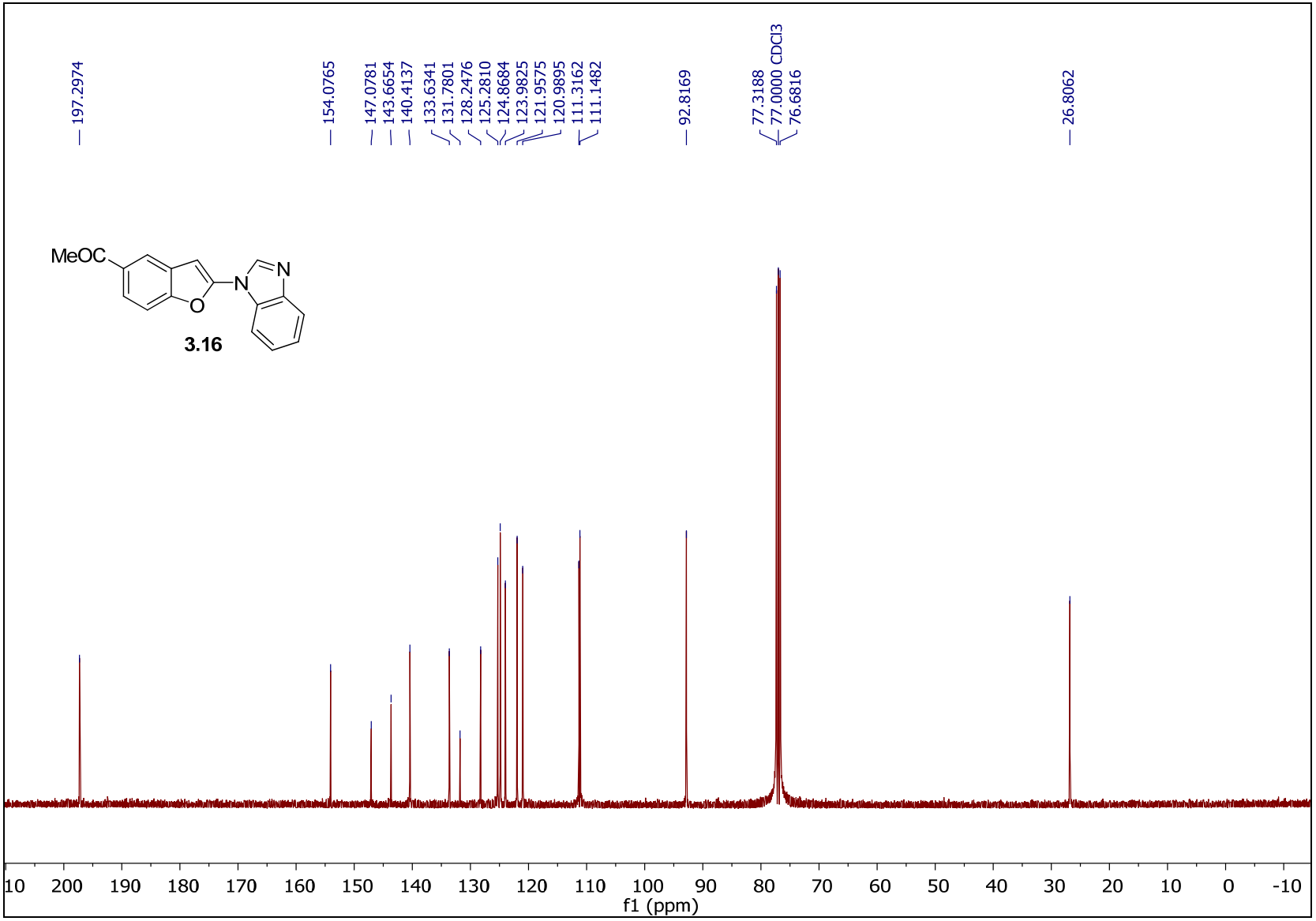
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3.15**



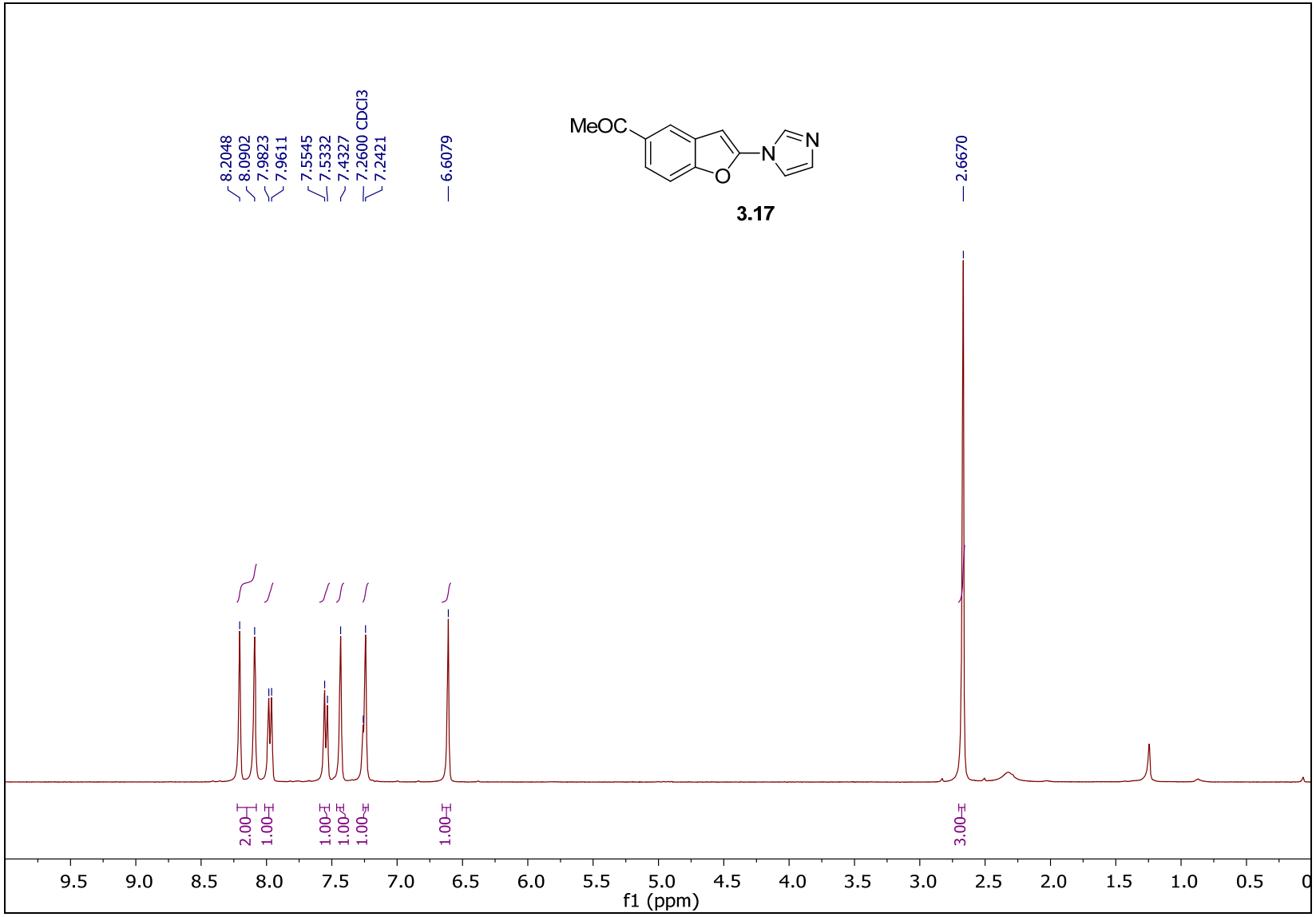
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3.15**



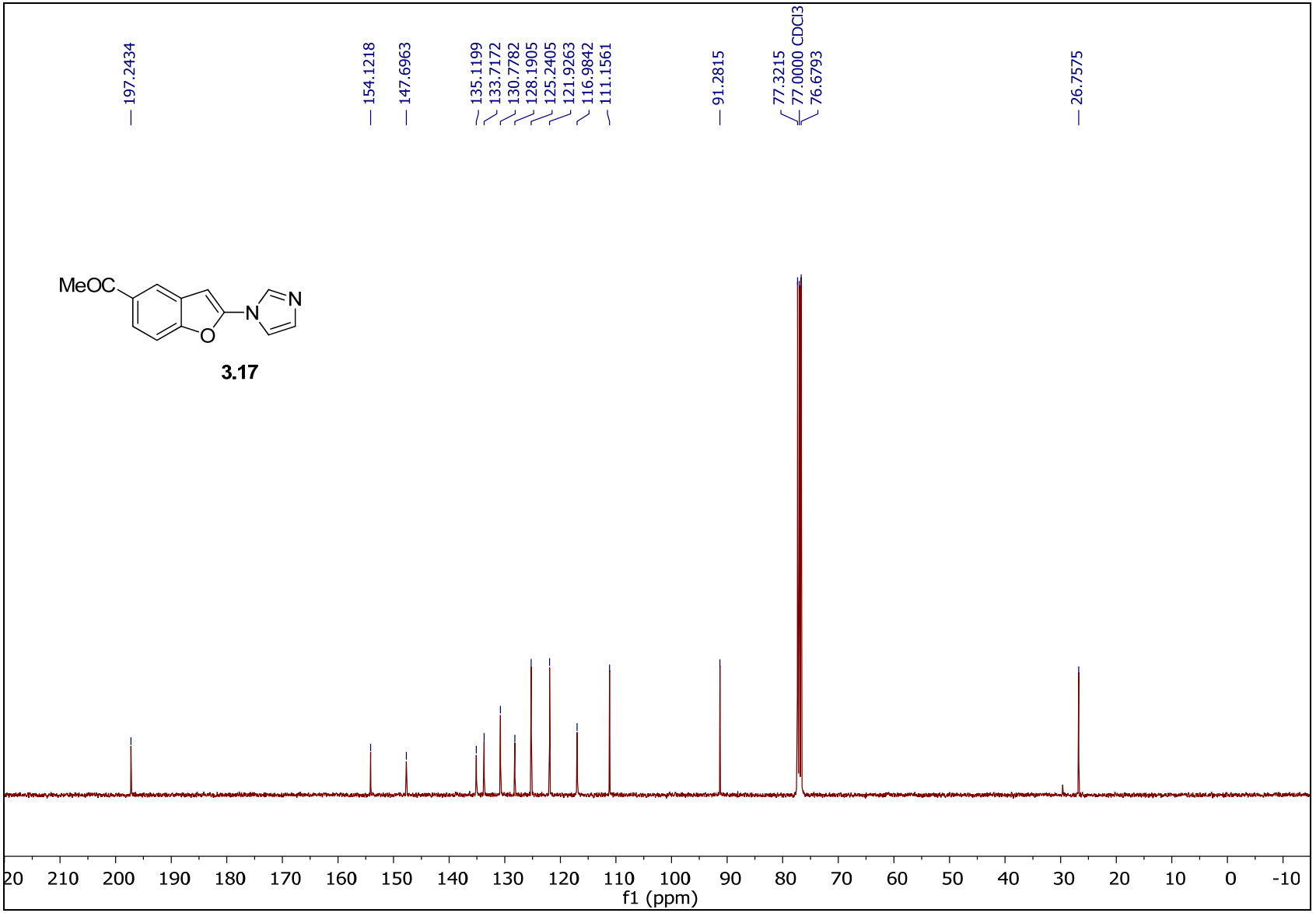
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3.16**



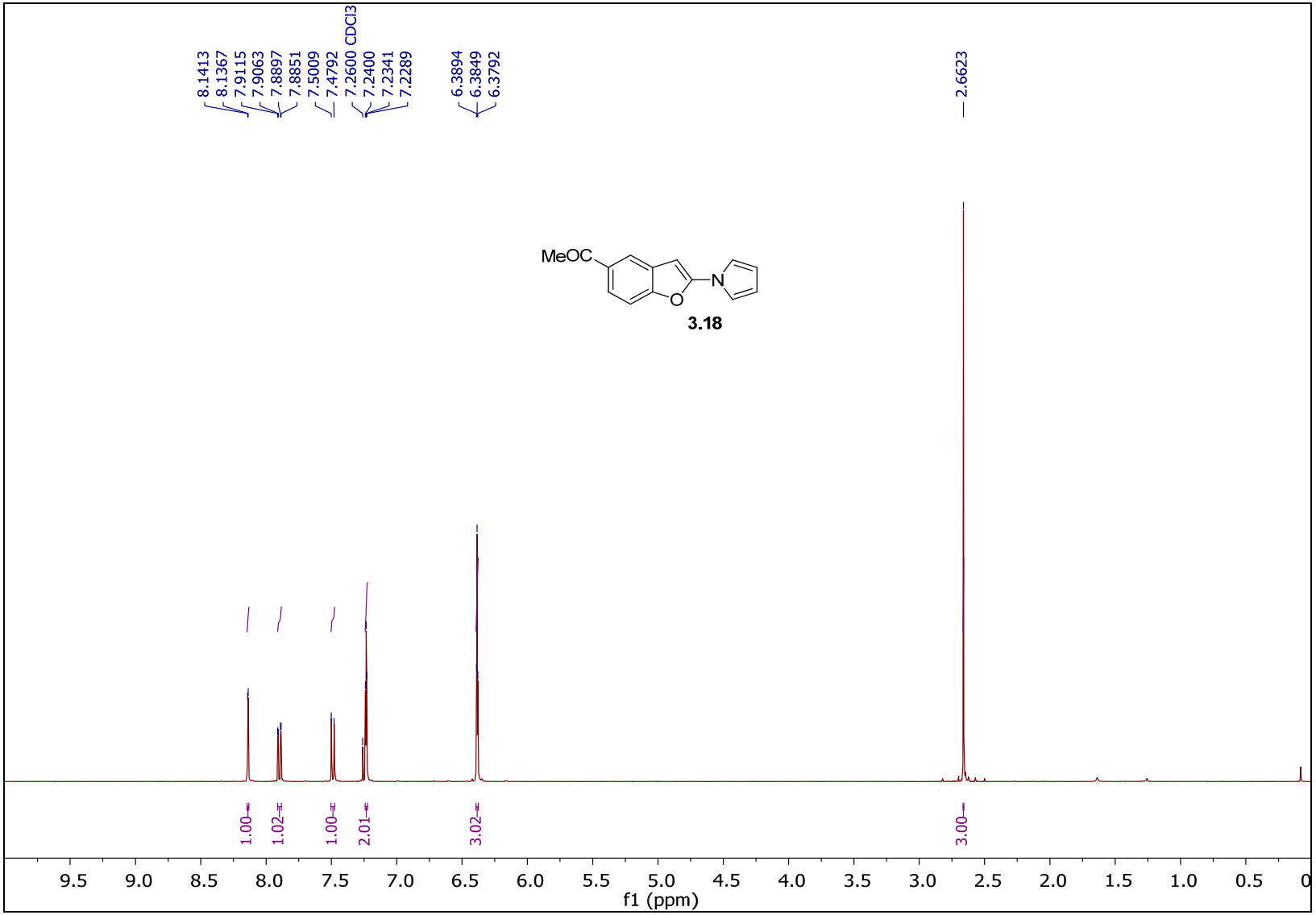
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3.16**



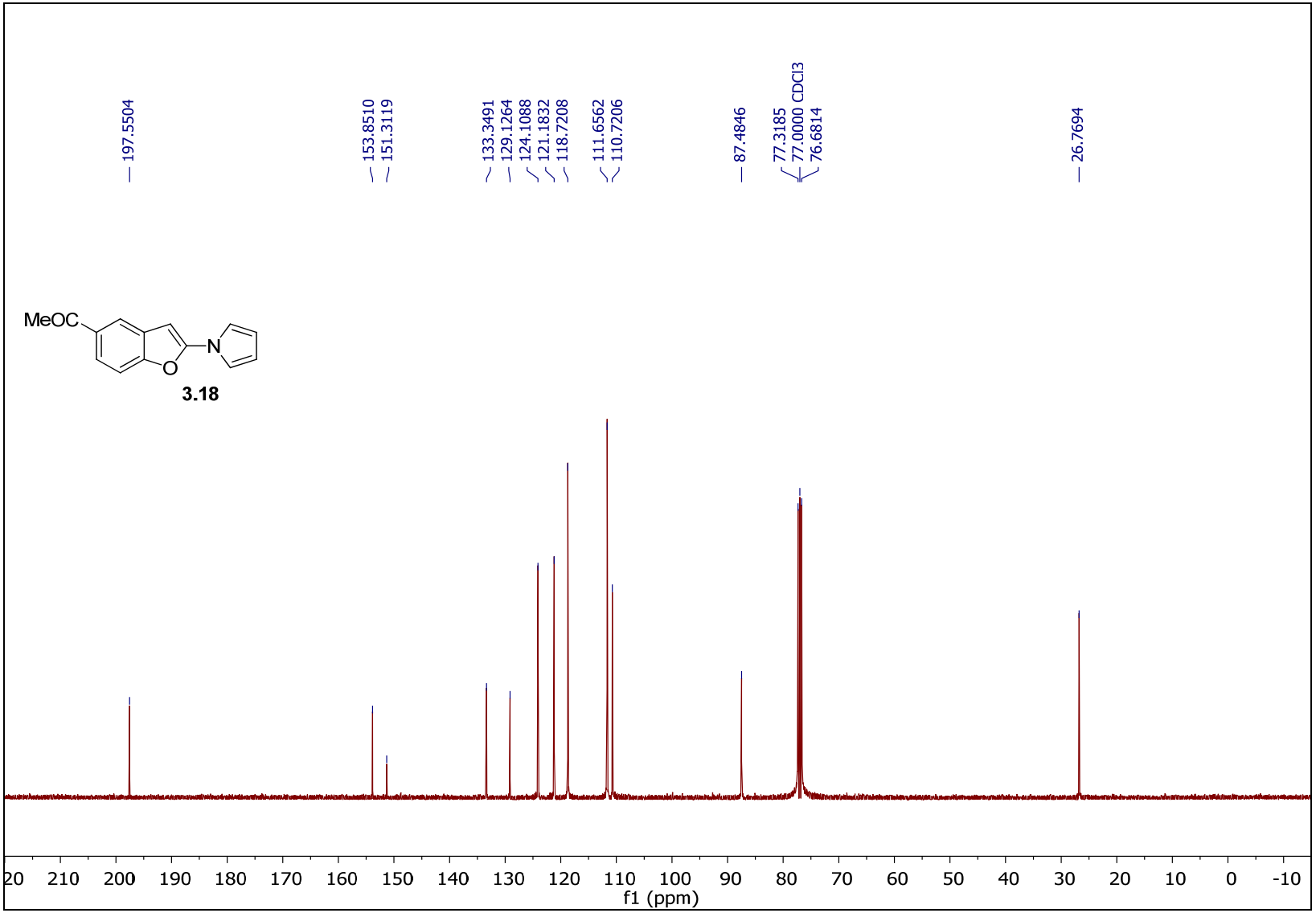
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3.17**



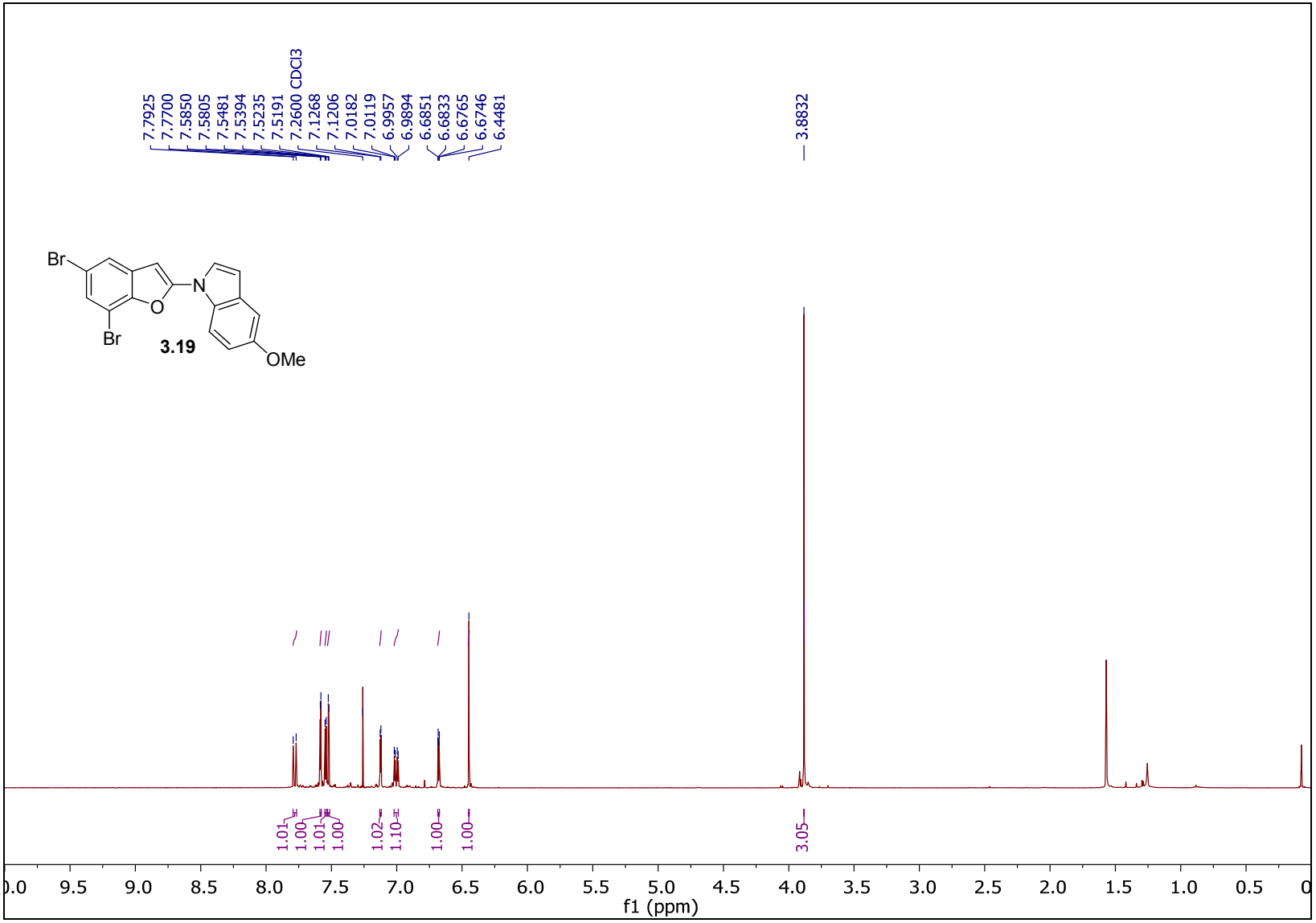
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3.17**



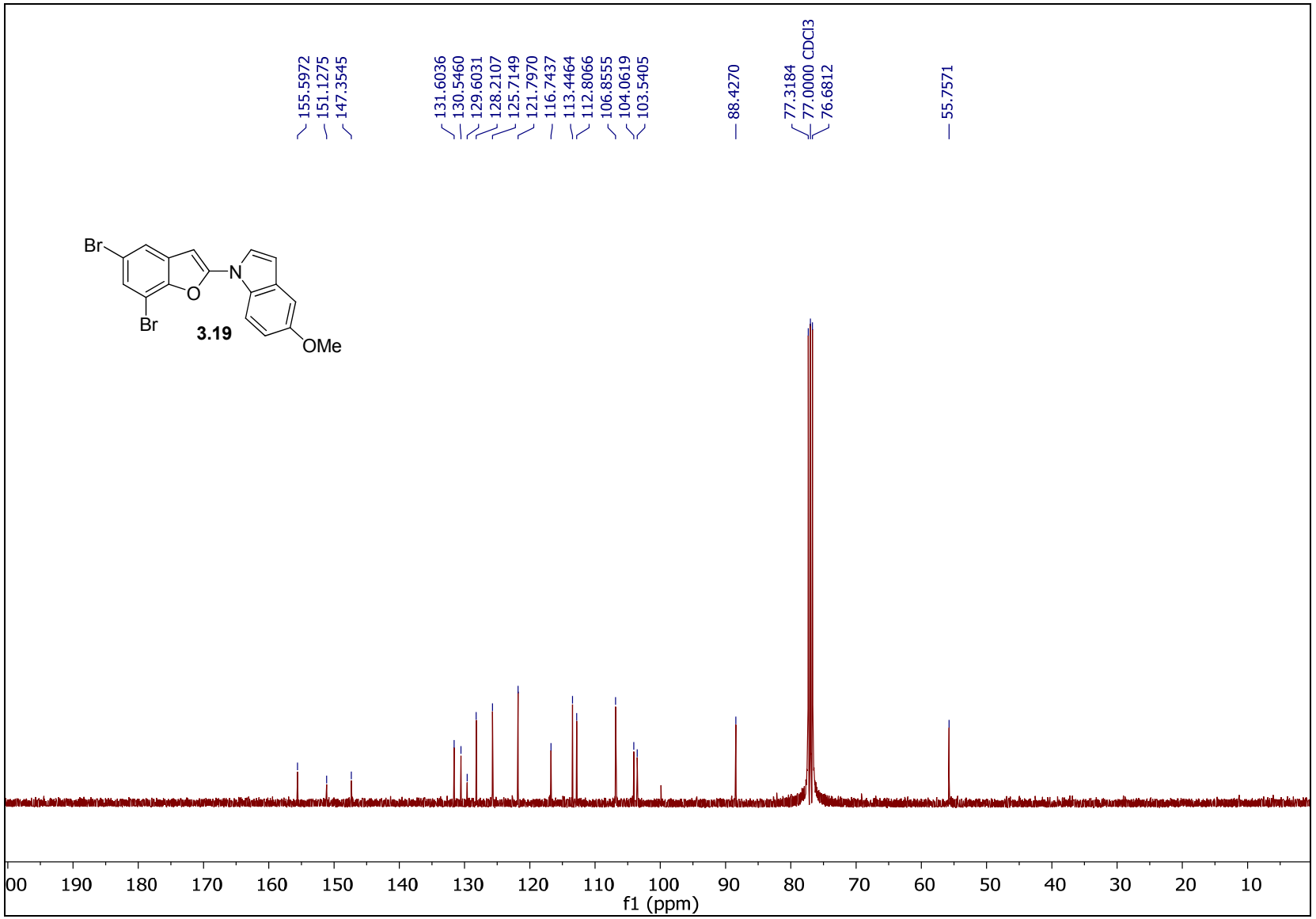
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3.18**



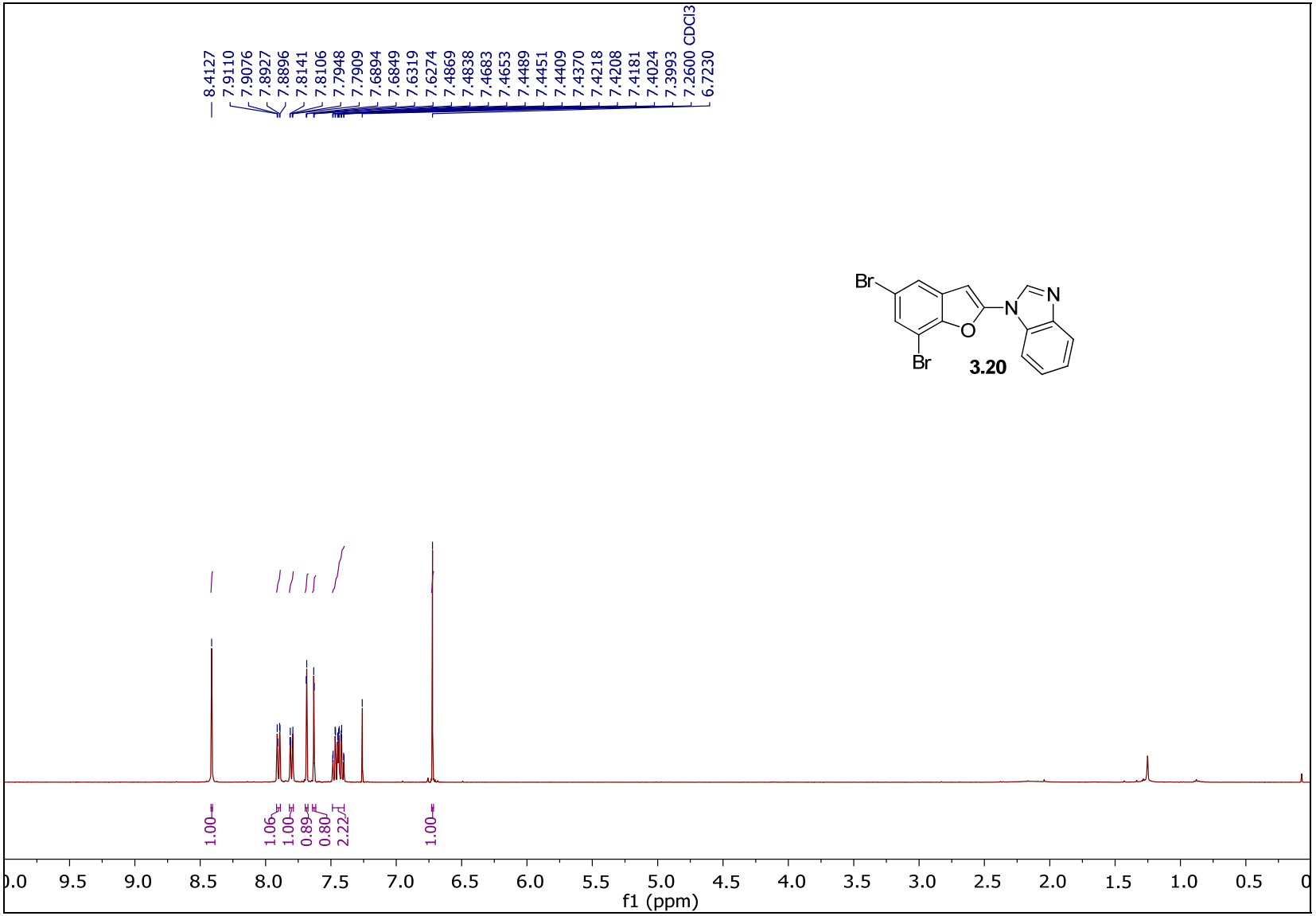
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3.18**



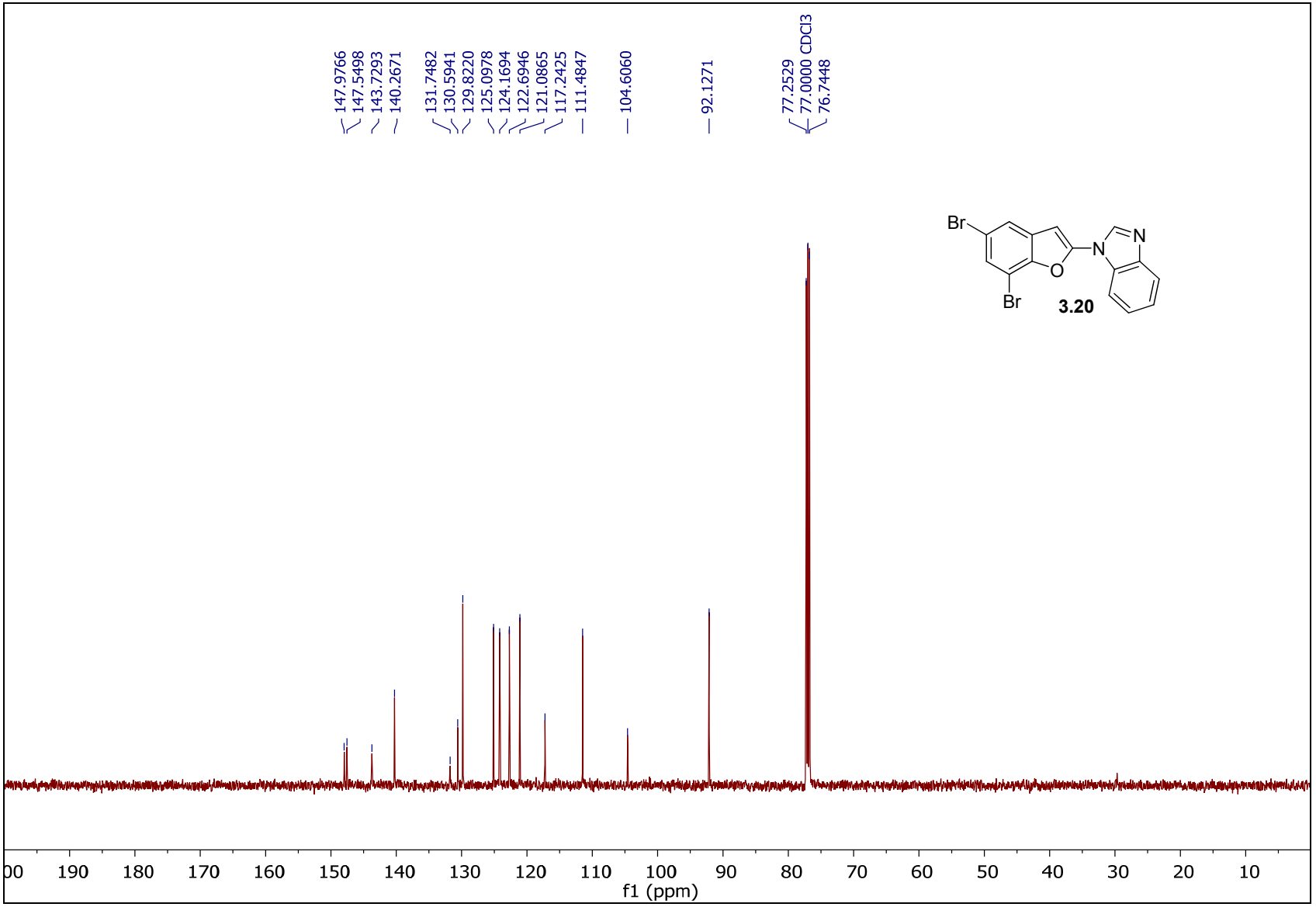
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3.19**



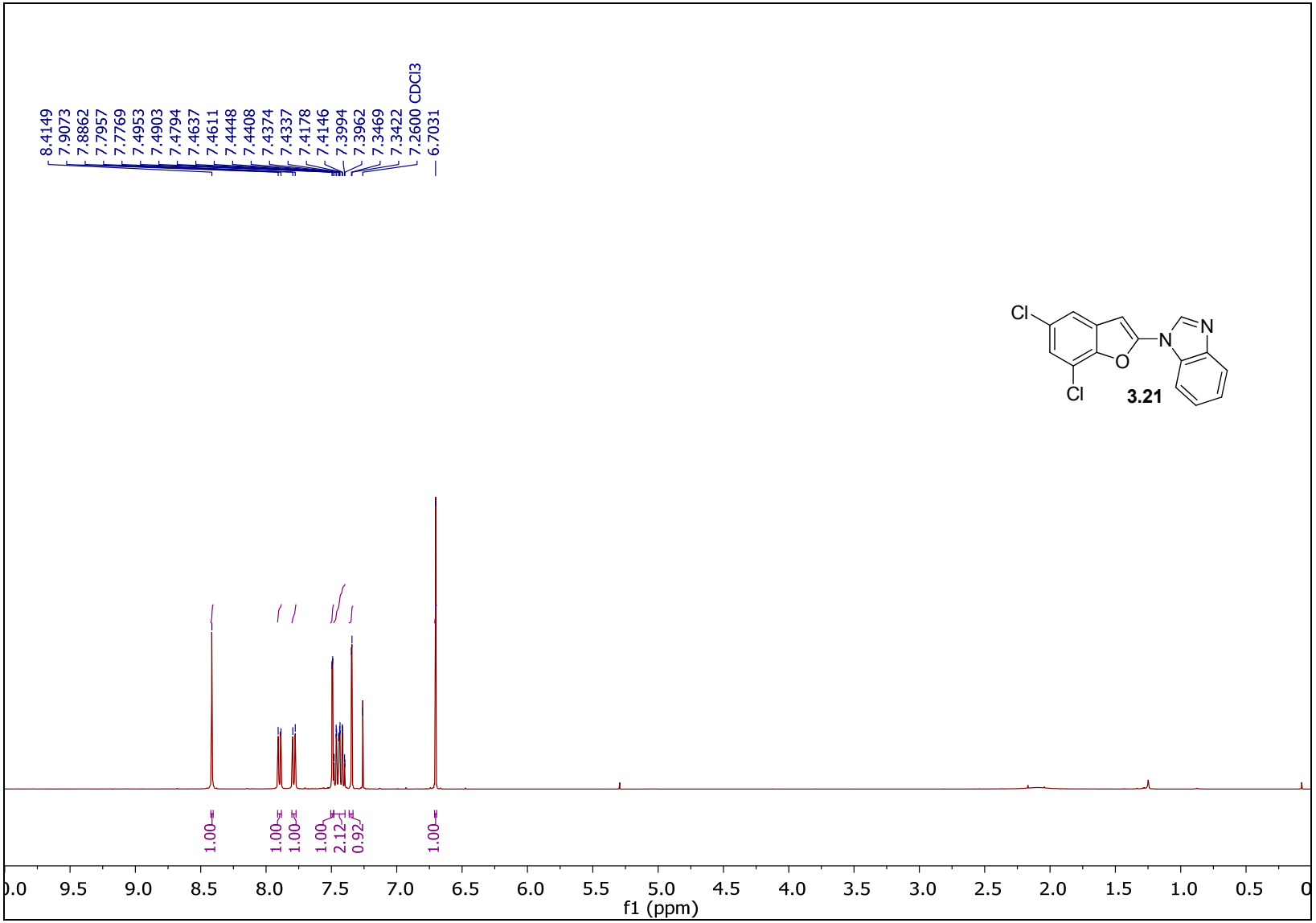
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3.19**



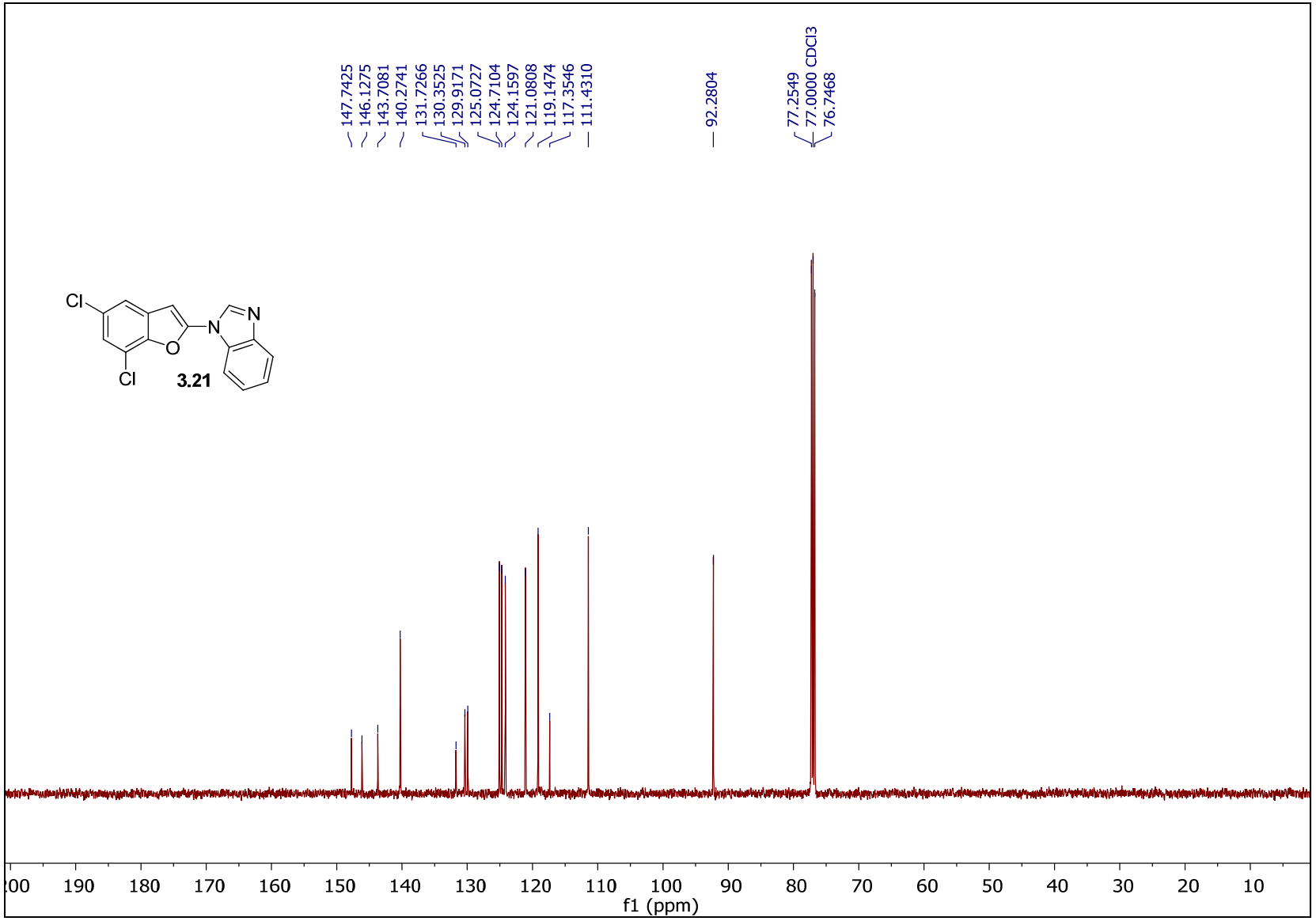
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3.20**



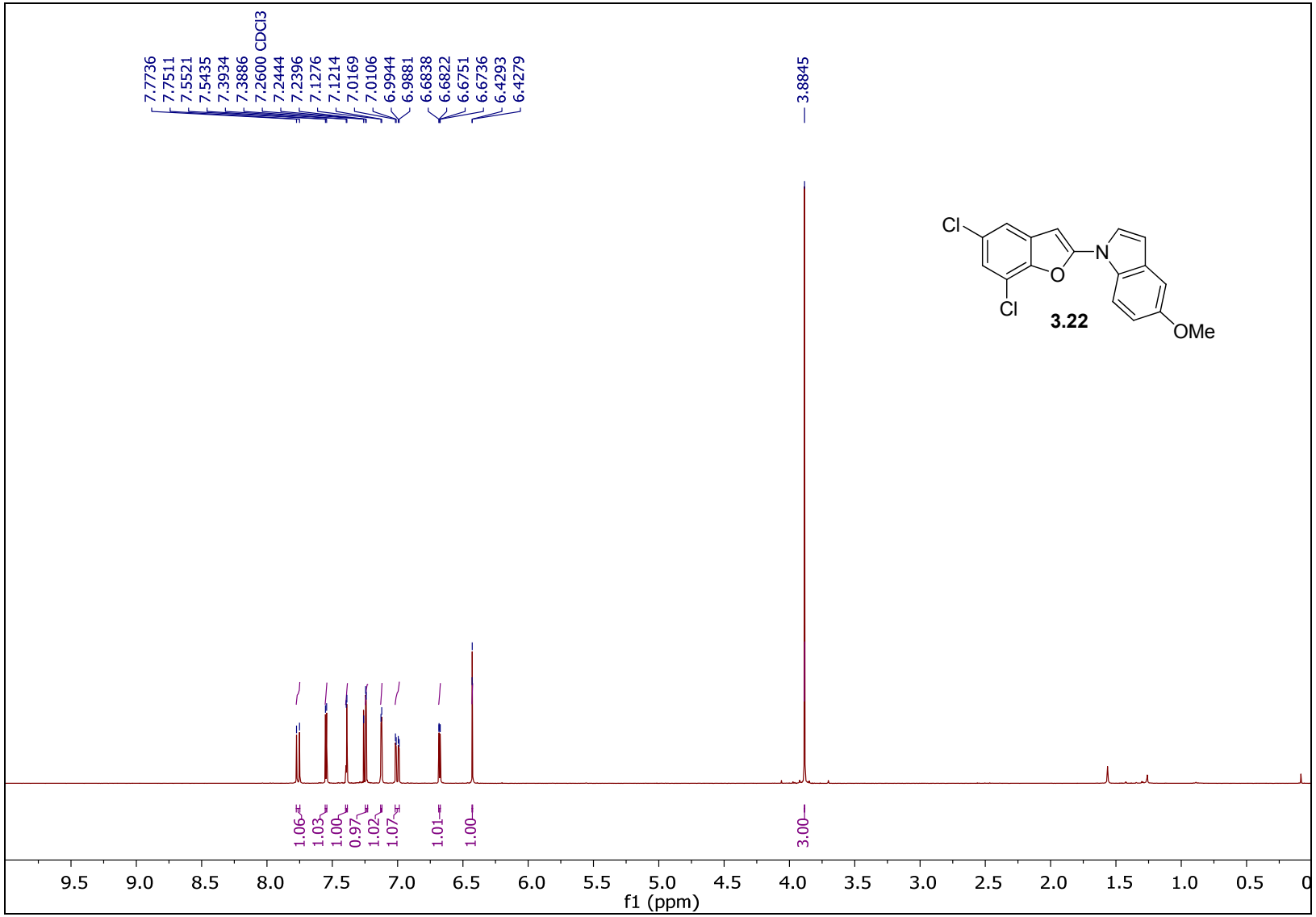
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **3.20**



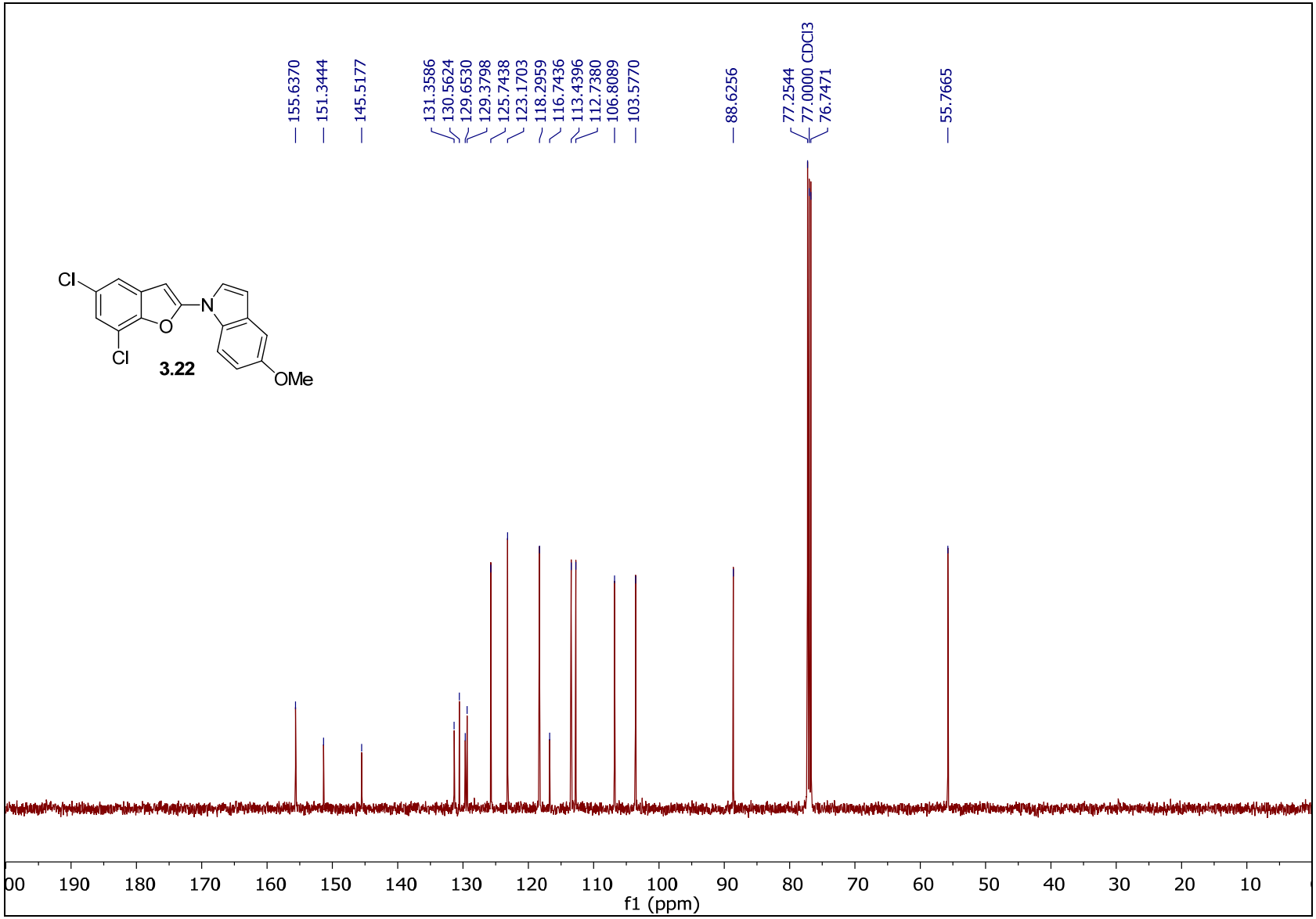
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3.21**



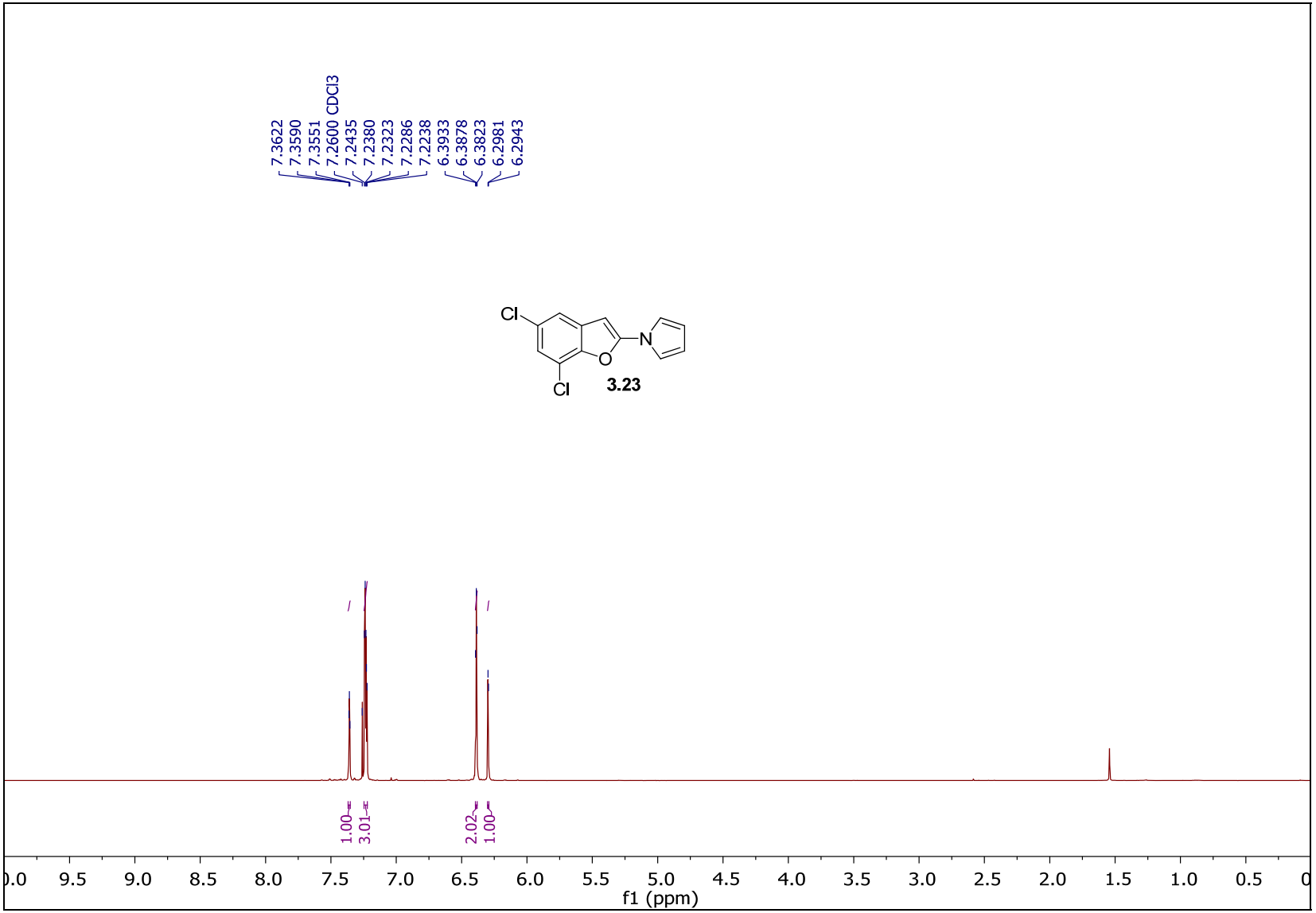
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **3.21**



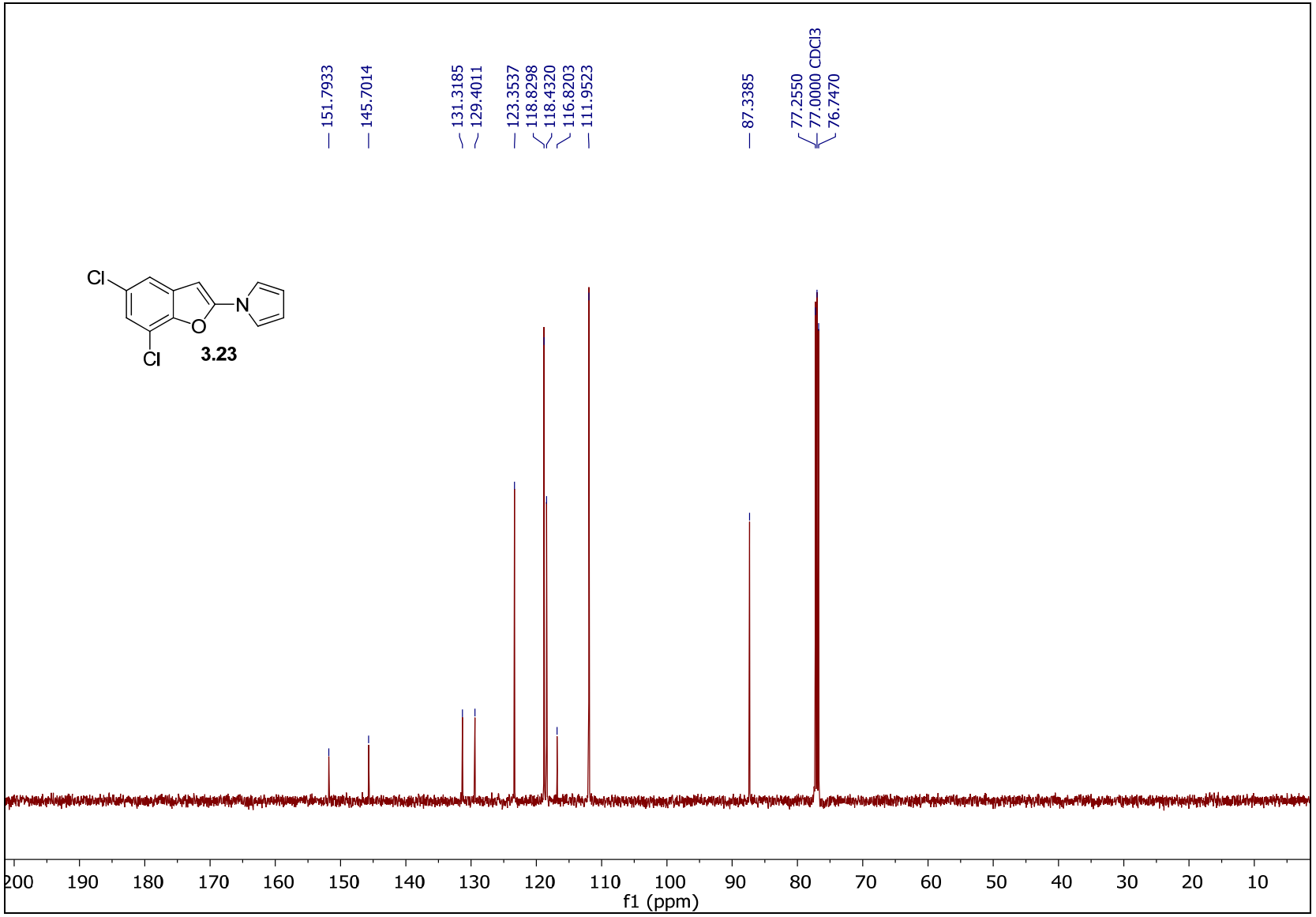
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3.22**



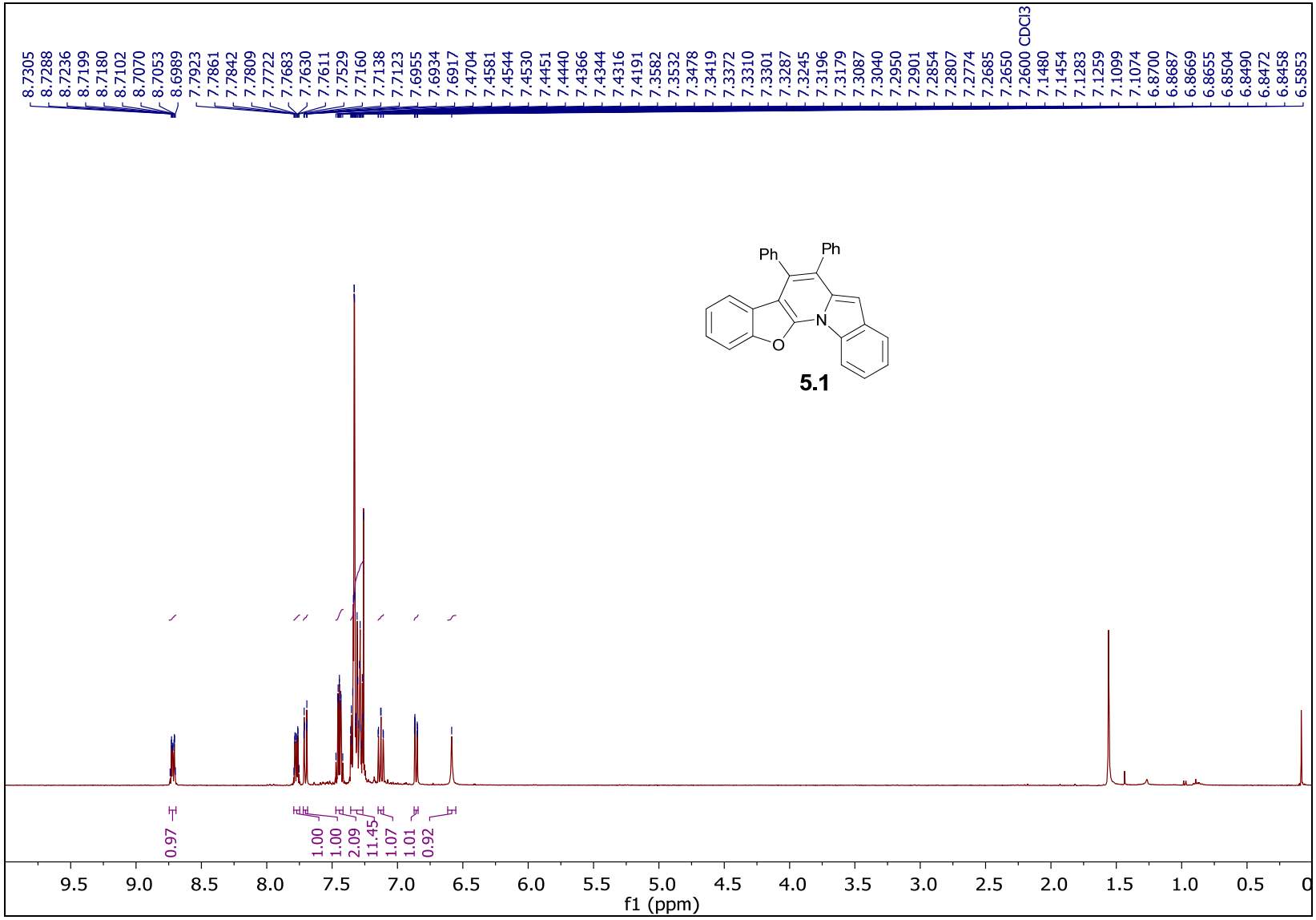
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **3.22**



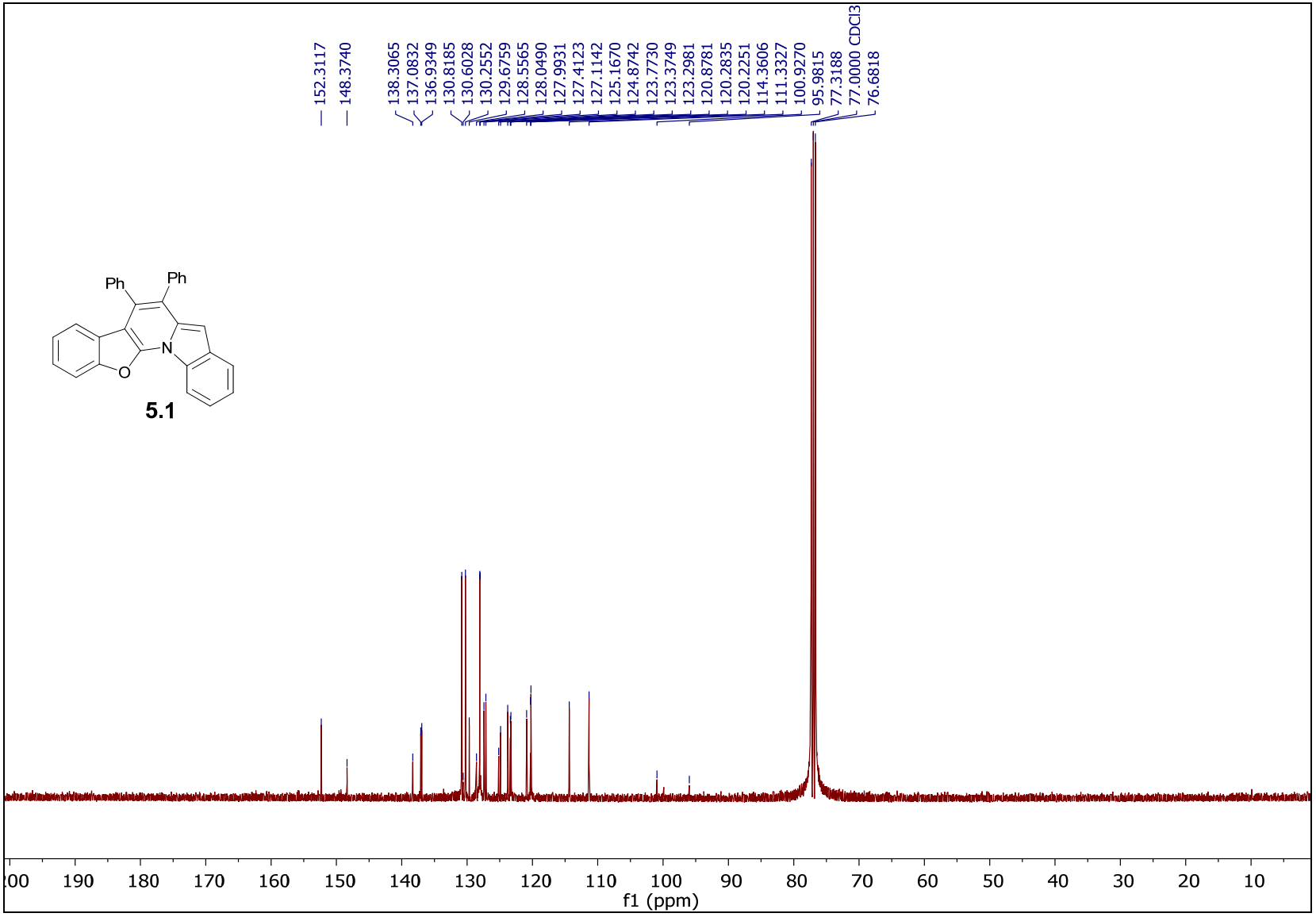
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3.23**



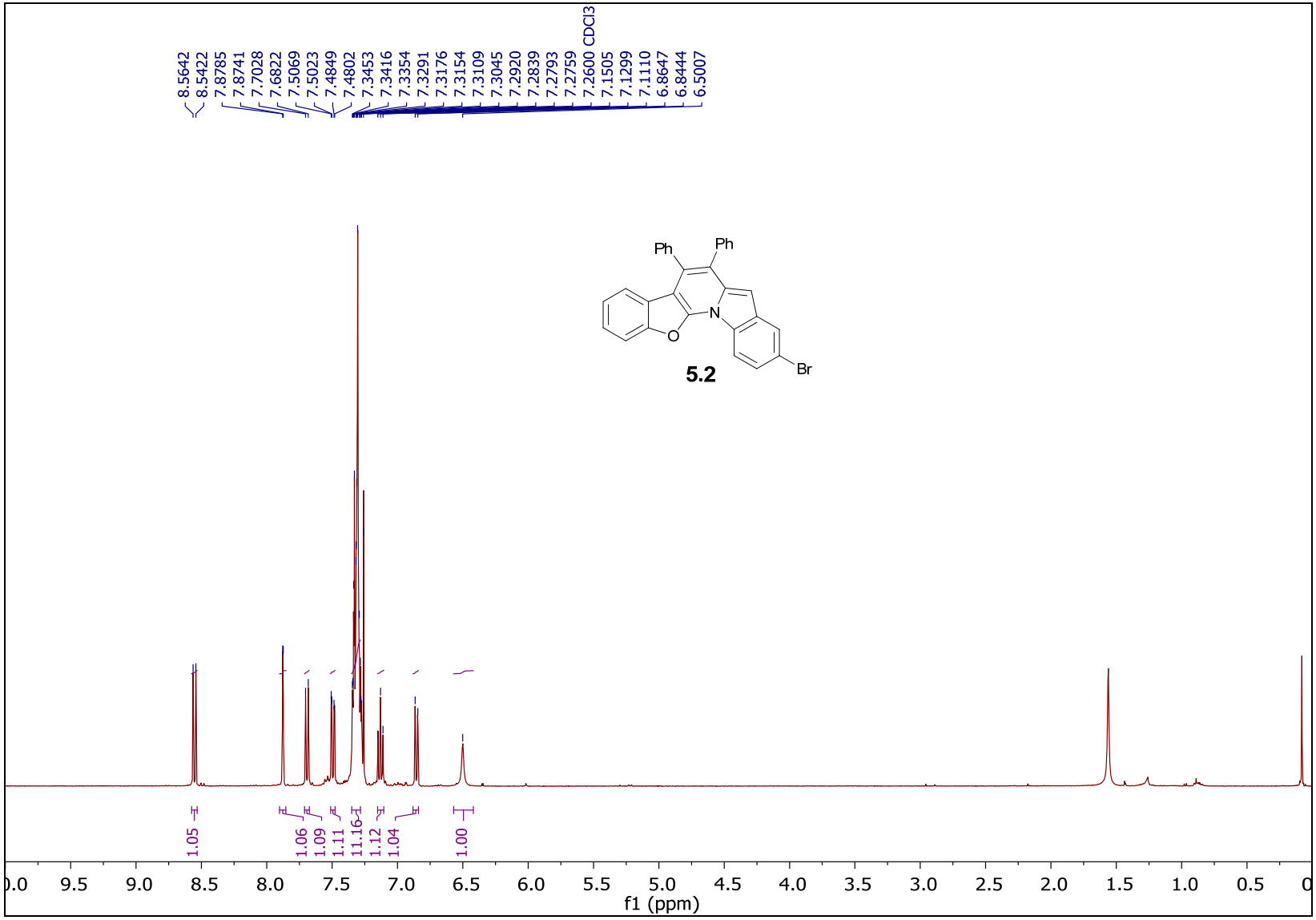
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **3.23**



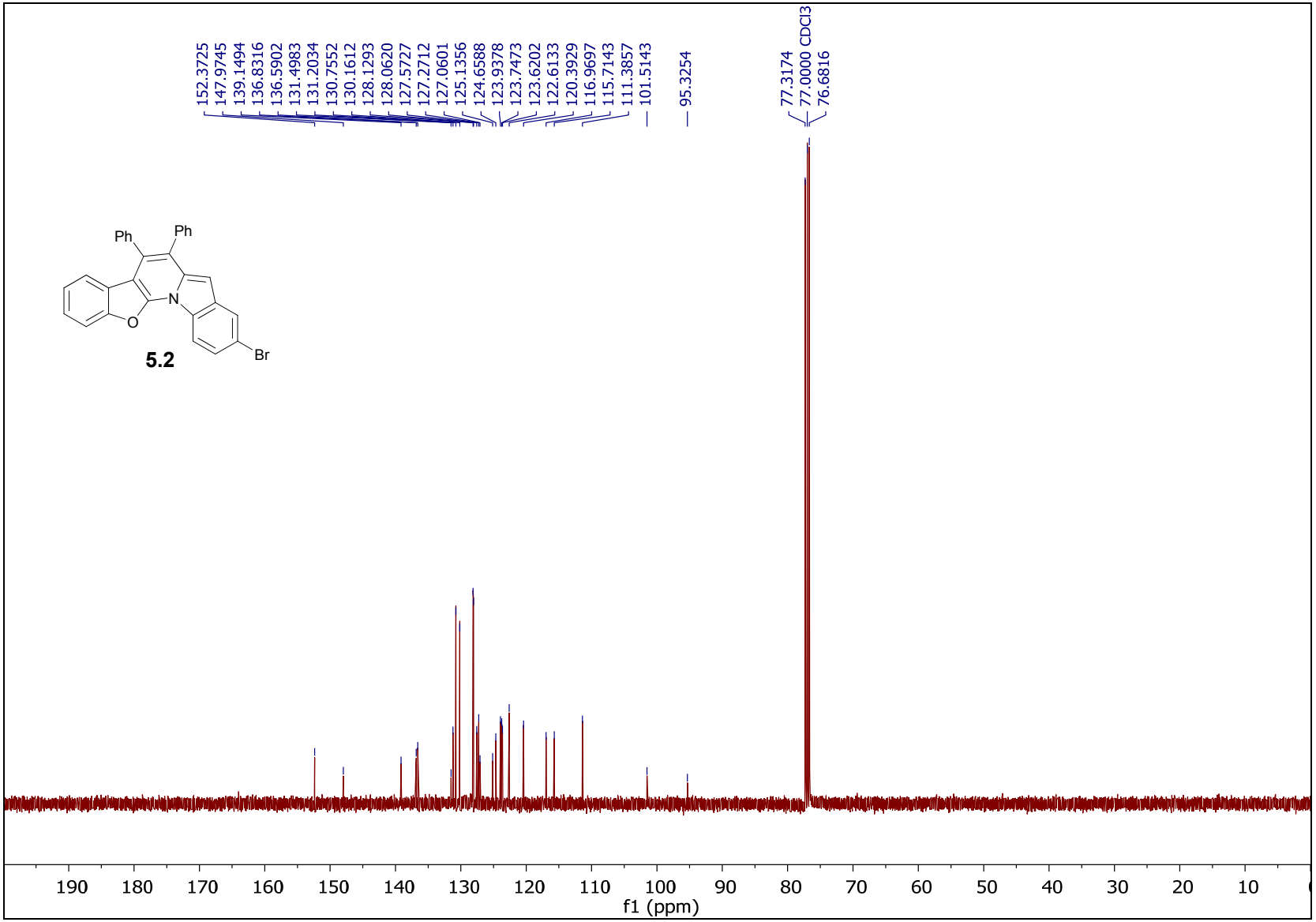
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5.1**



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5.1**

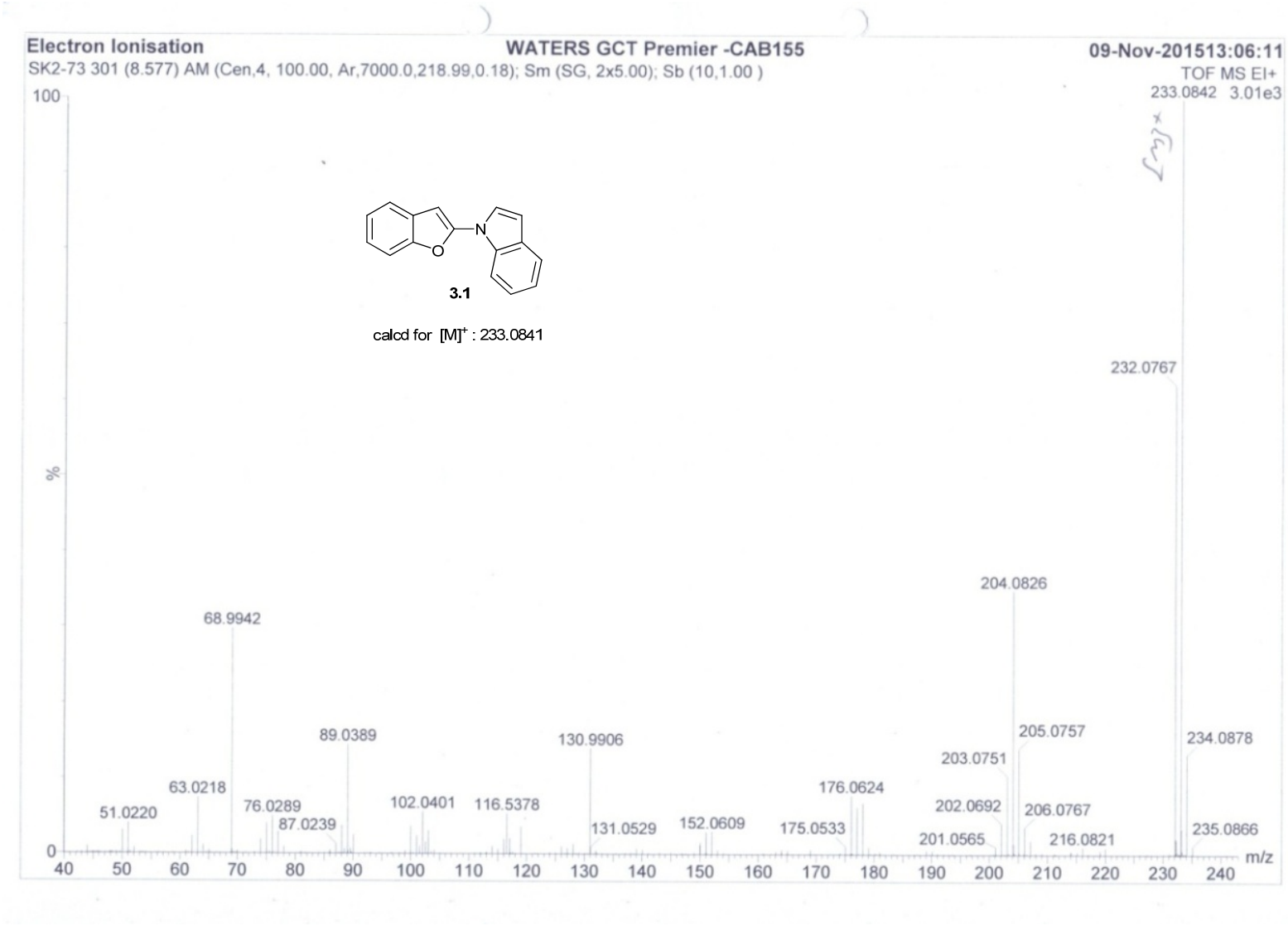


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5.2**

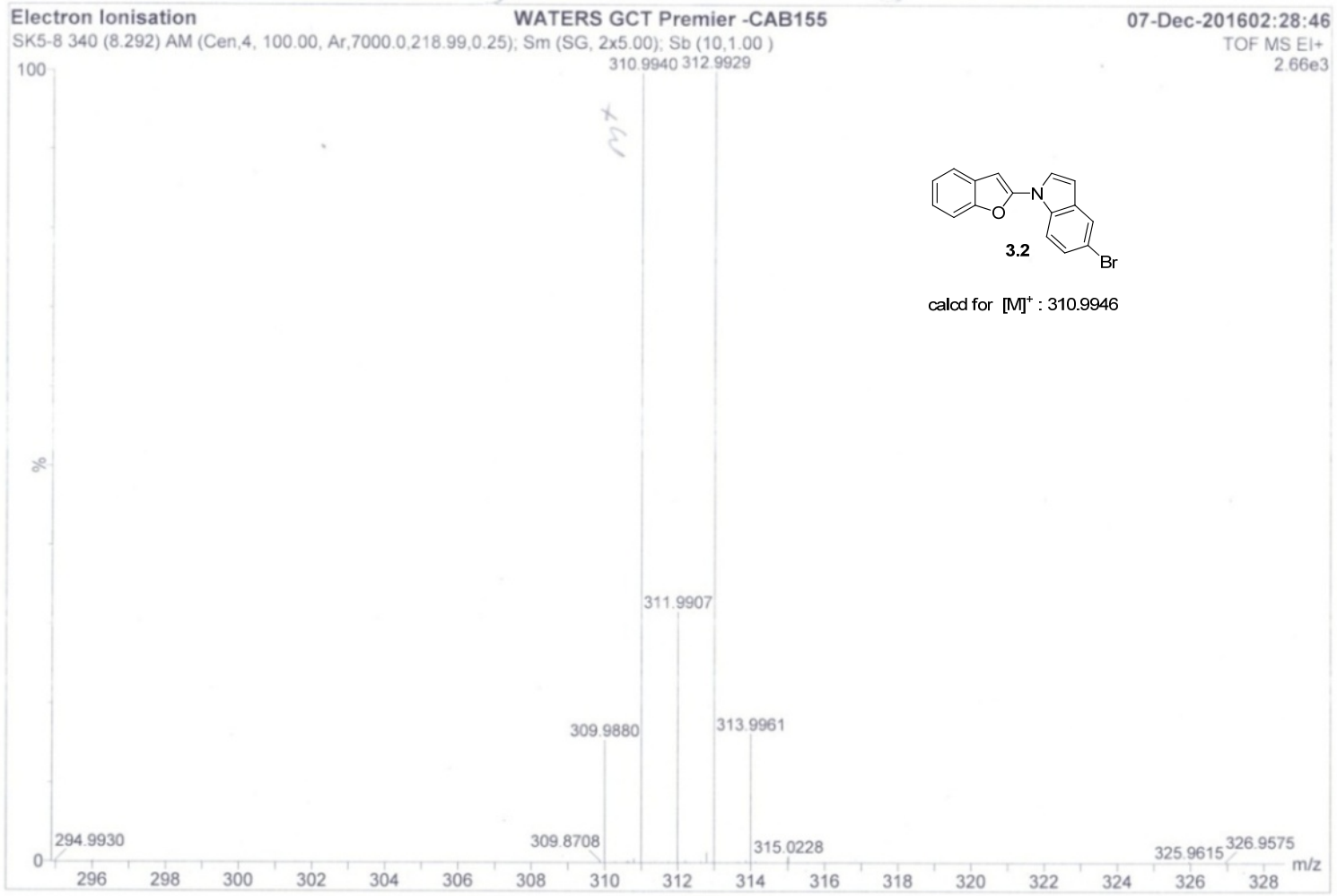


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5.2**

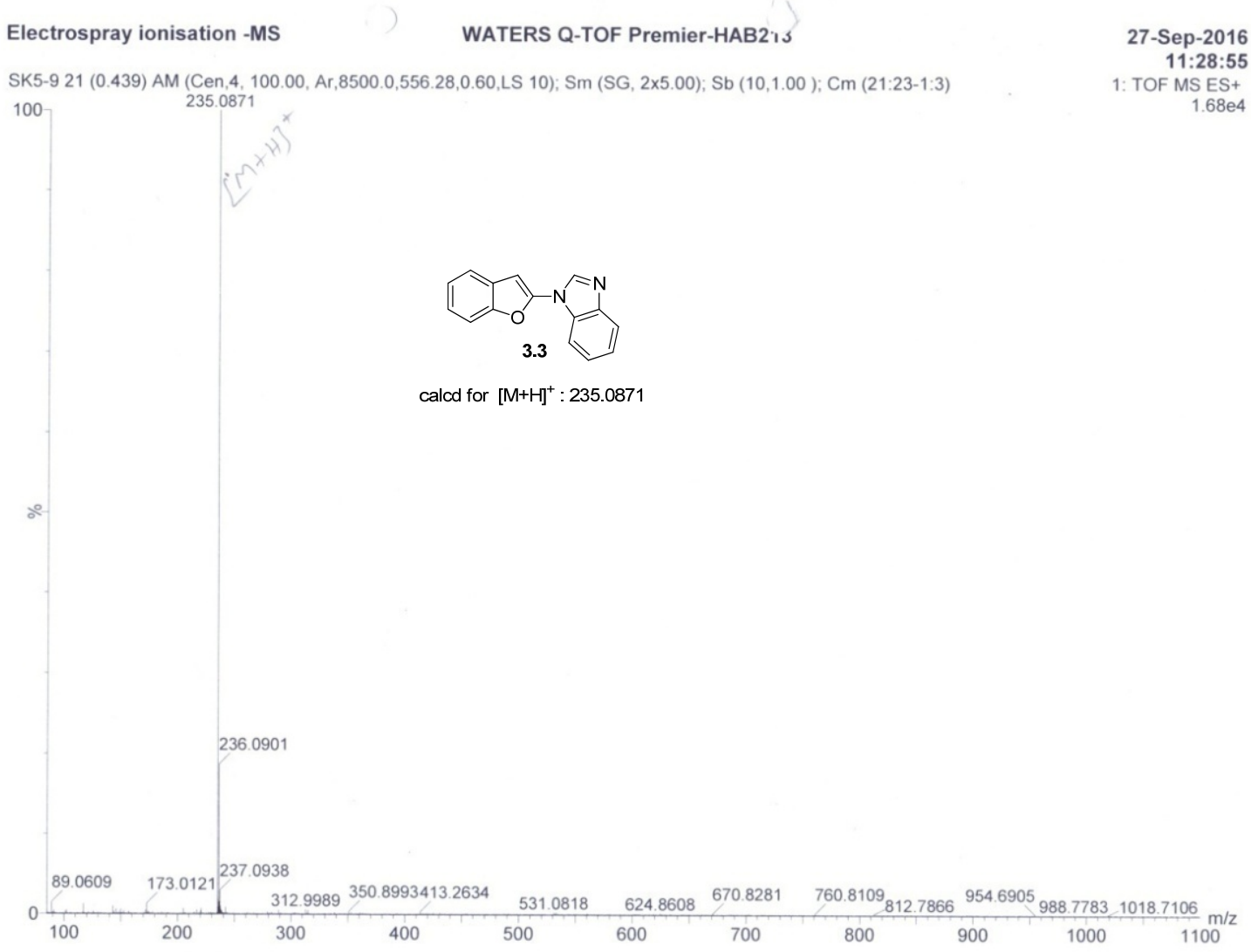
9. HRMS spectra:



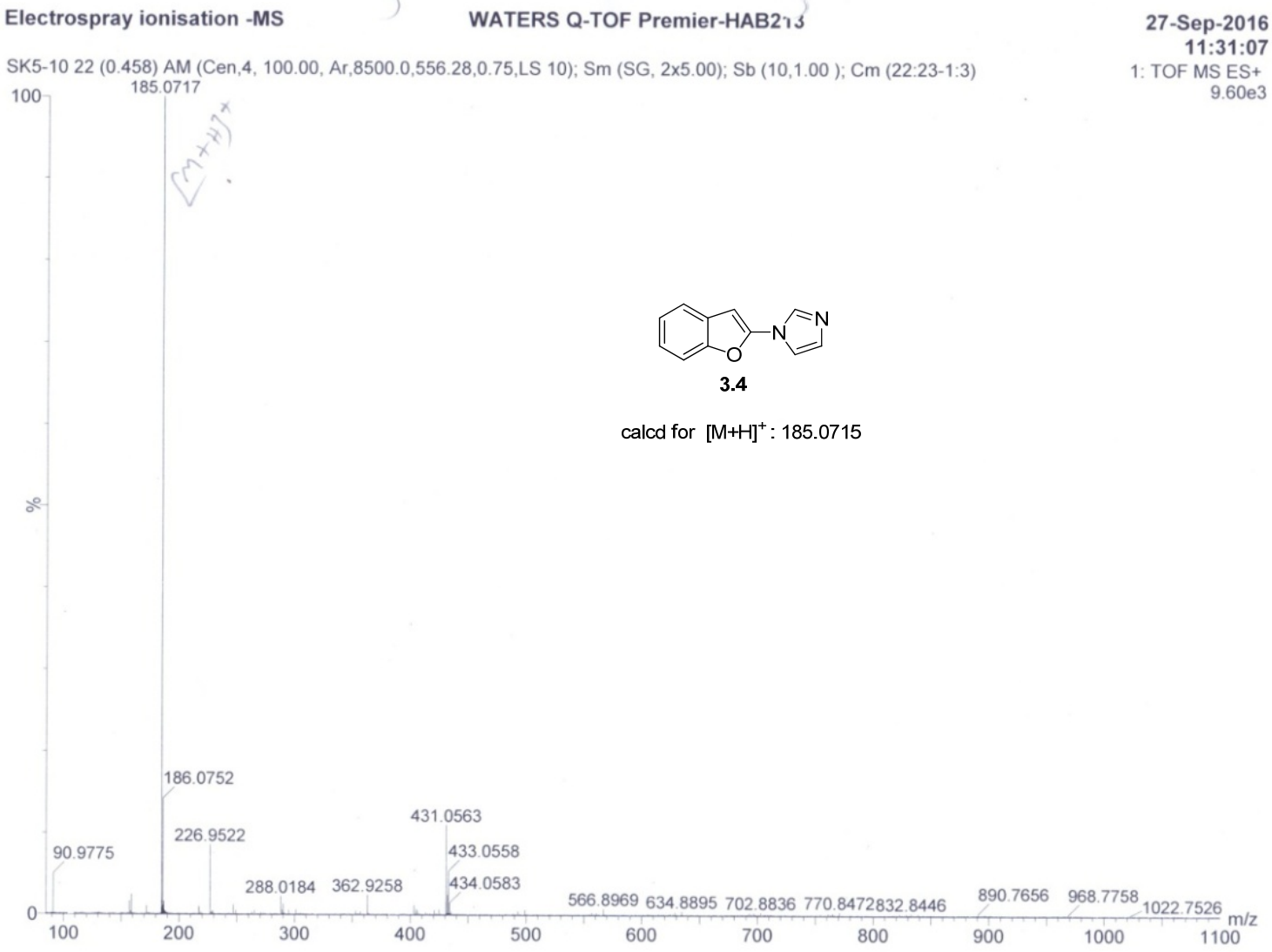
EI (HRMS) spectrum of **3.1**



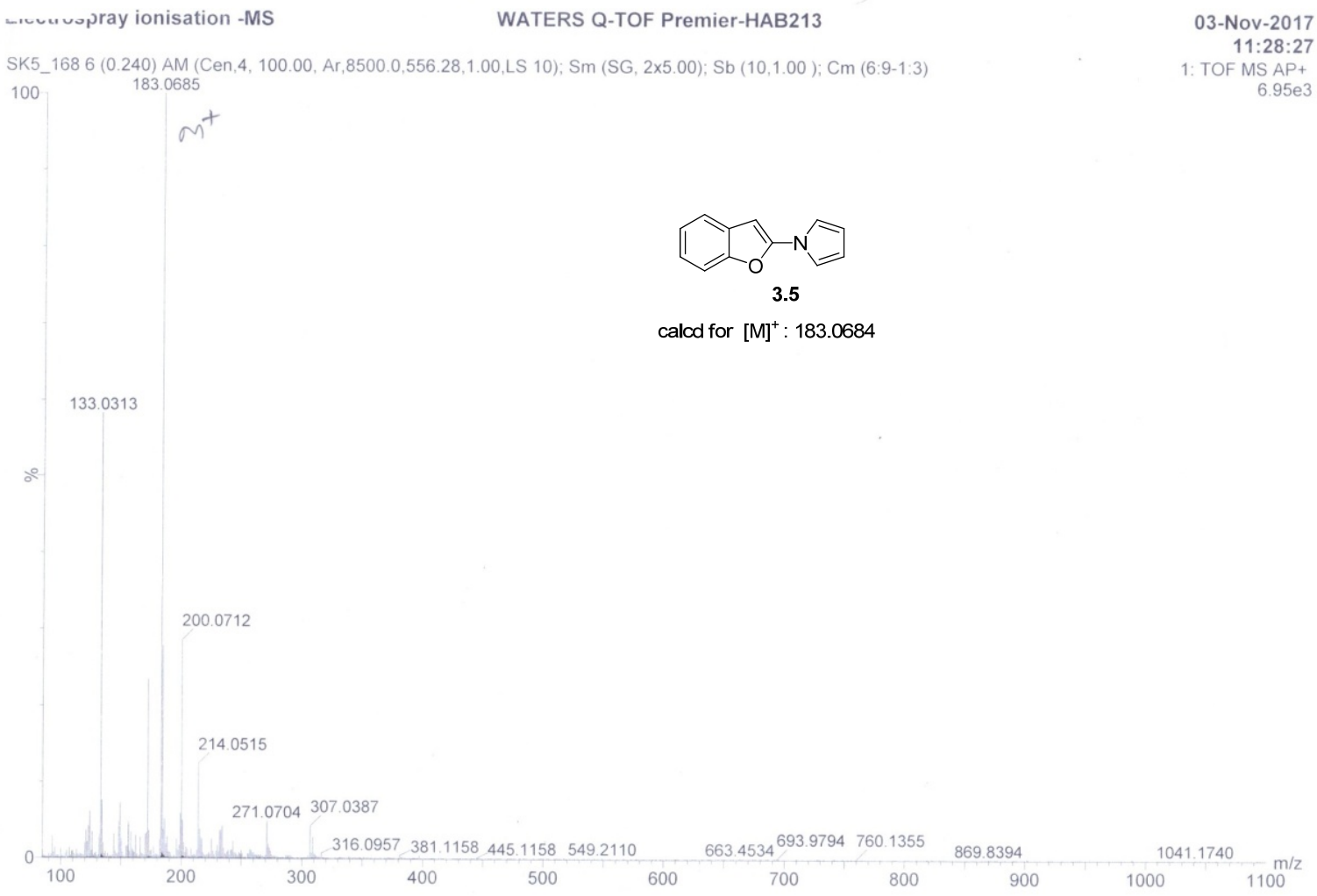
EI (HRMS) spectrum of **3.2**



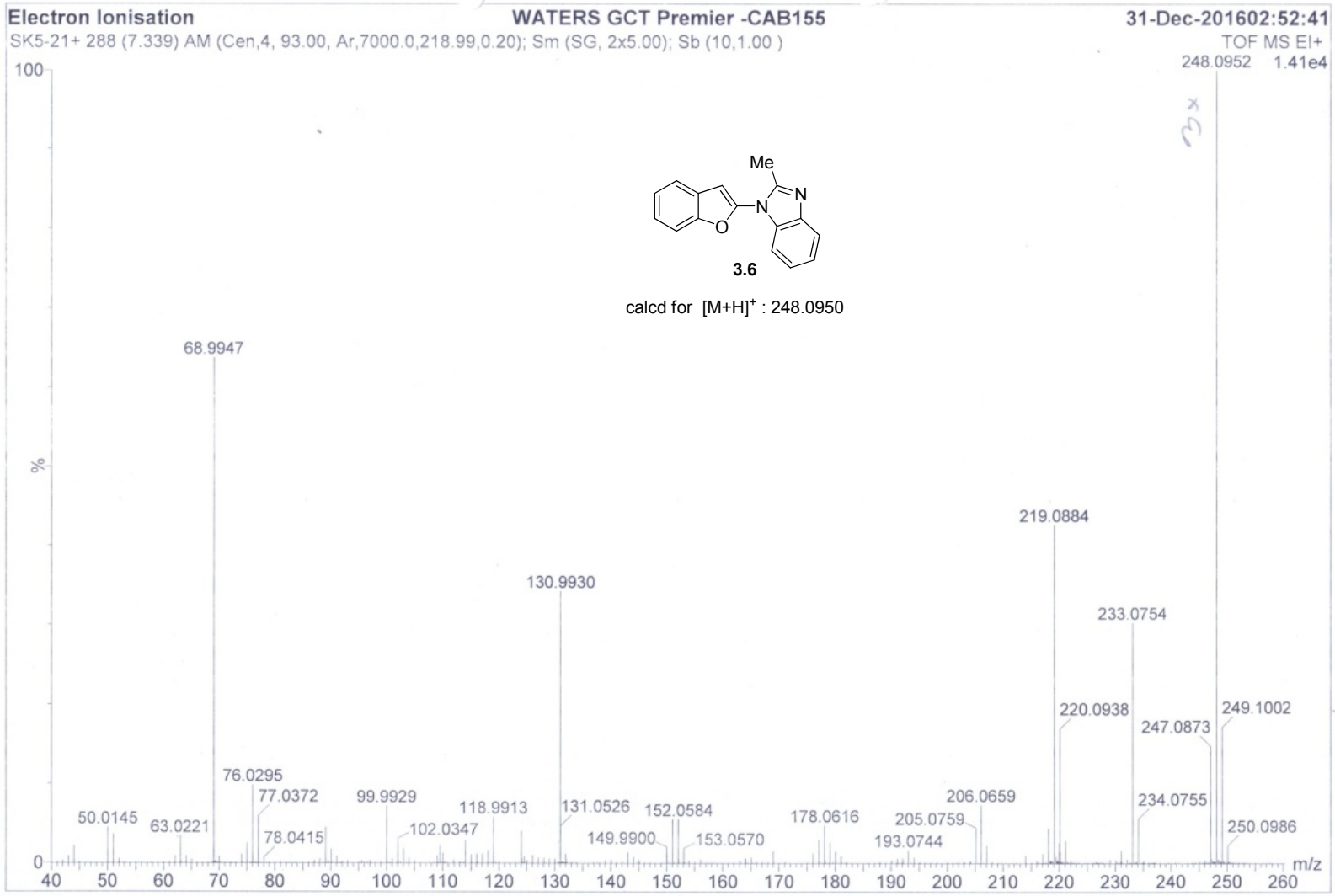
ESI (HRMS) spectrum of **3.3**



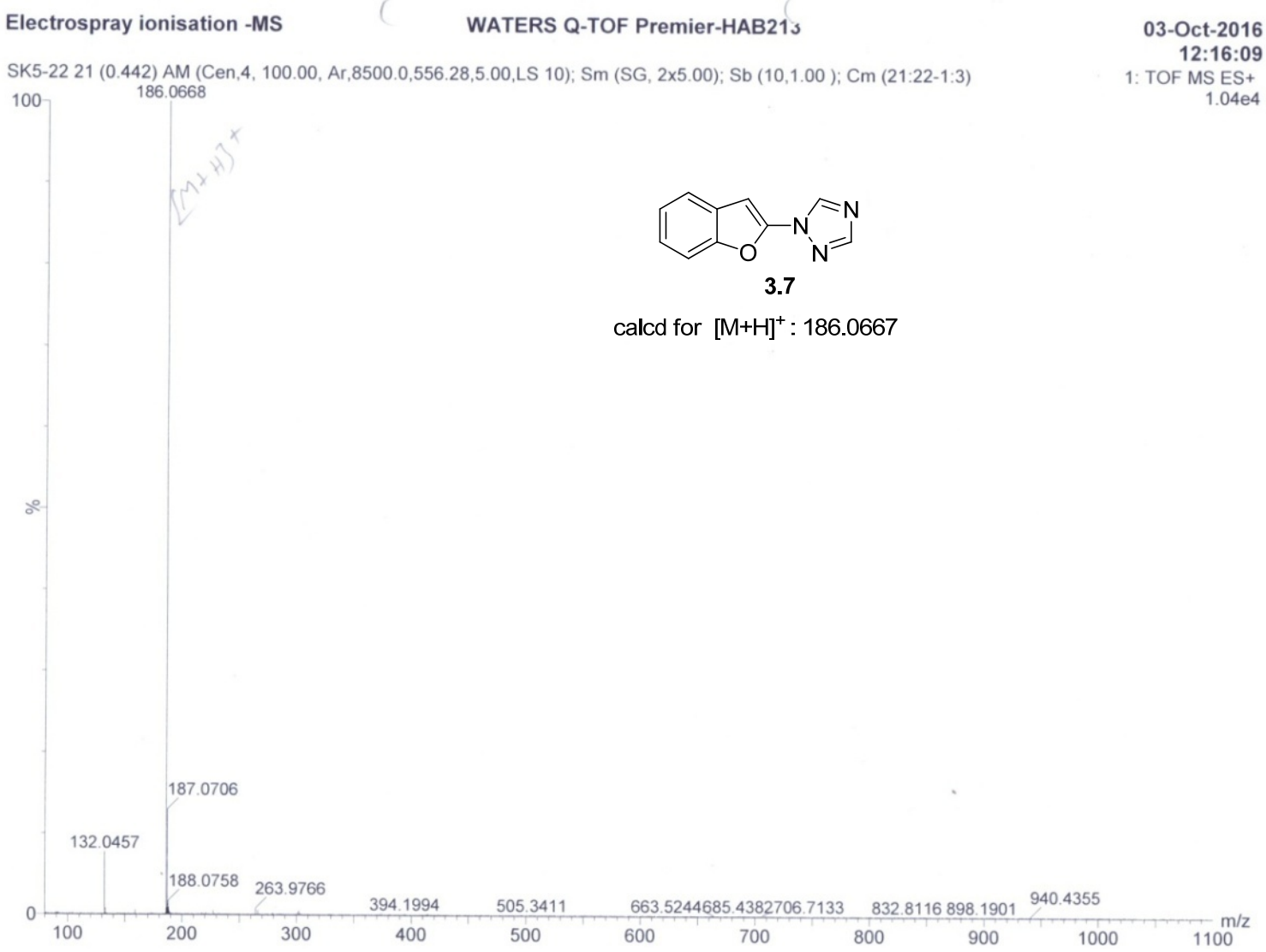
ESI (HRMS) spectrum of **3.4**



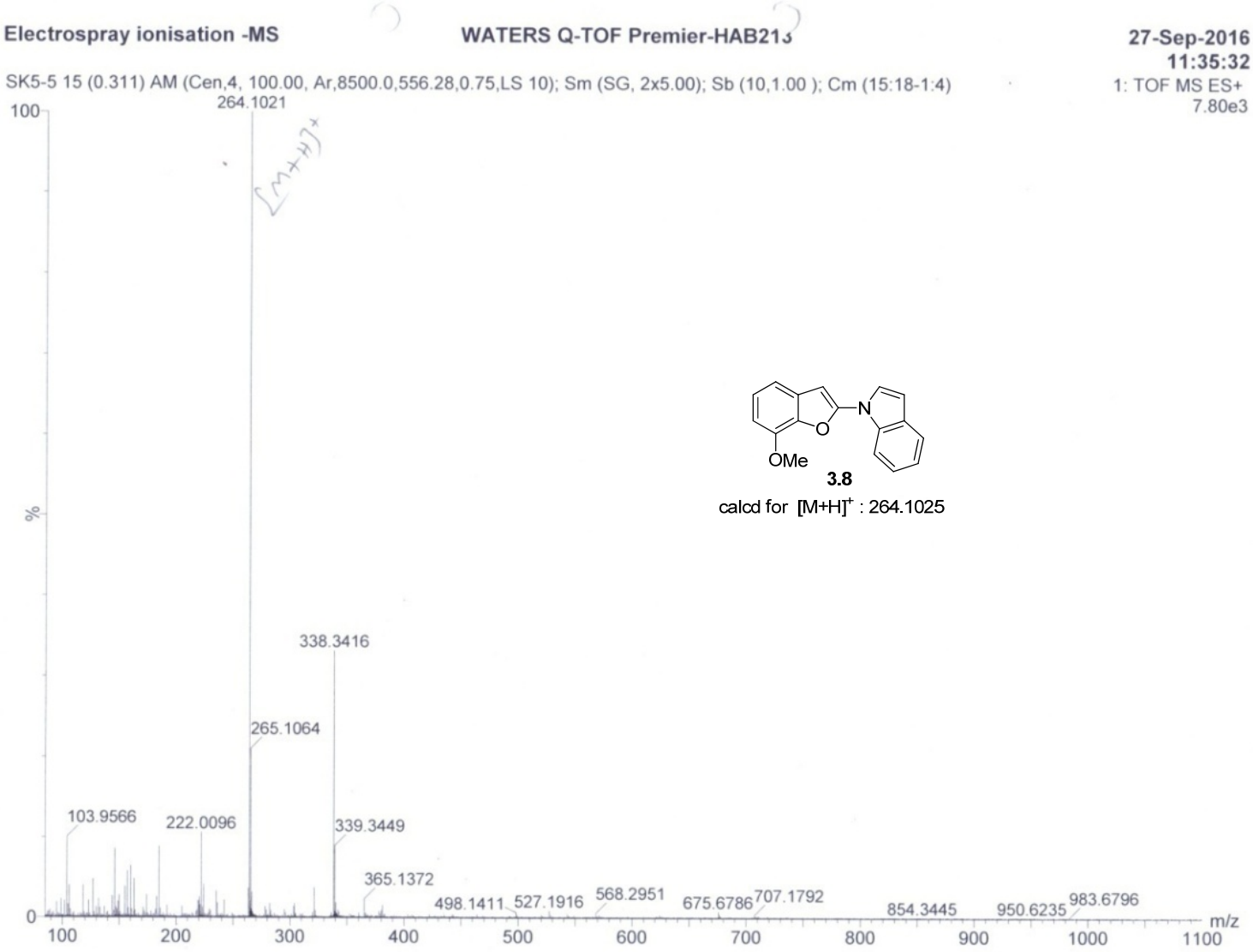
ESI (HRMS) spectrum of **3.5**



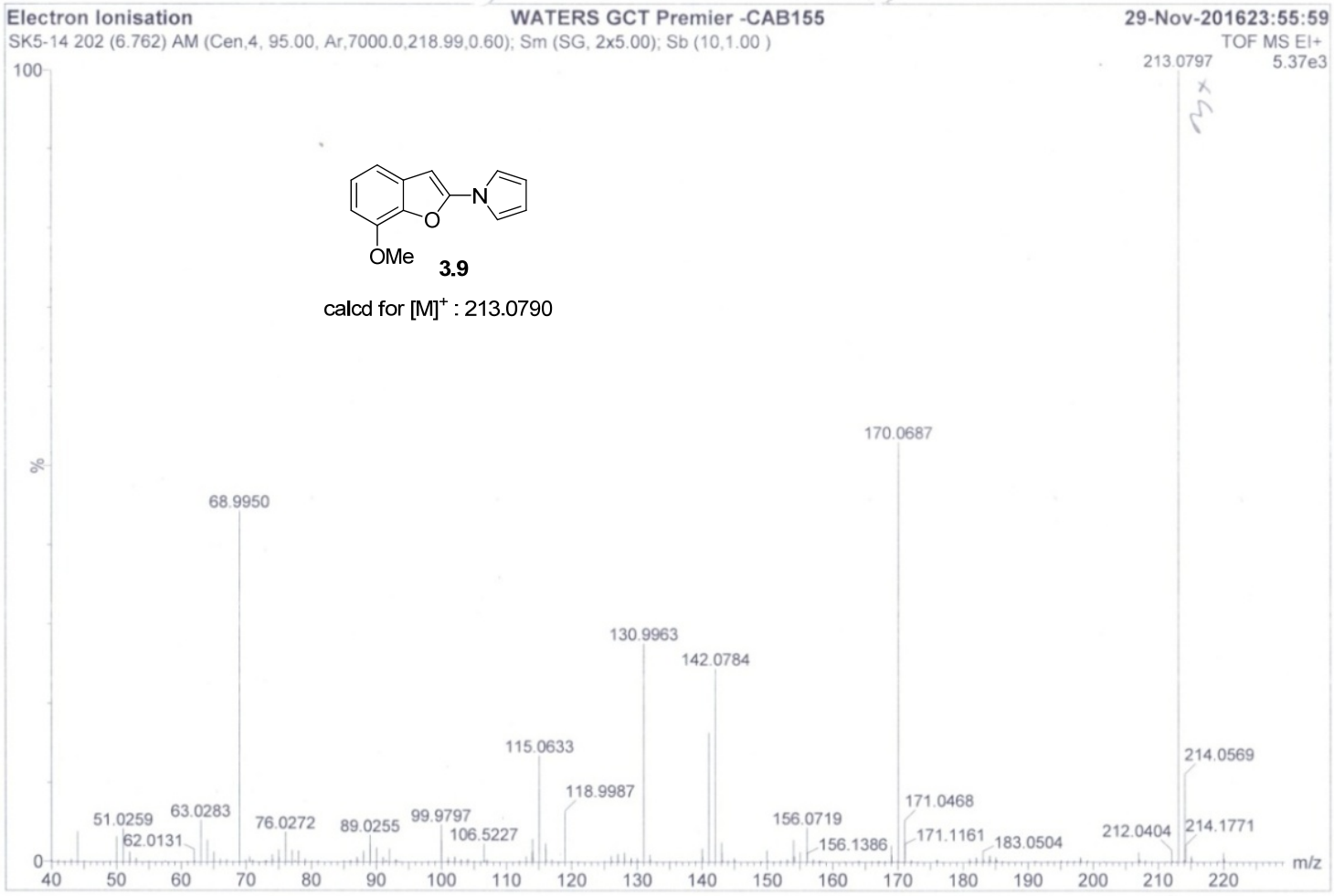
EI (HRMS) spectrum of **3.6**



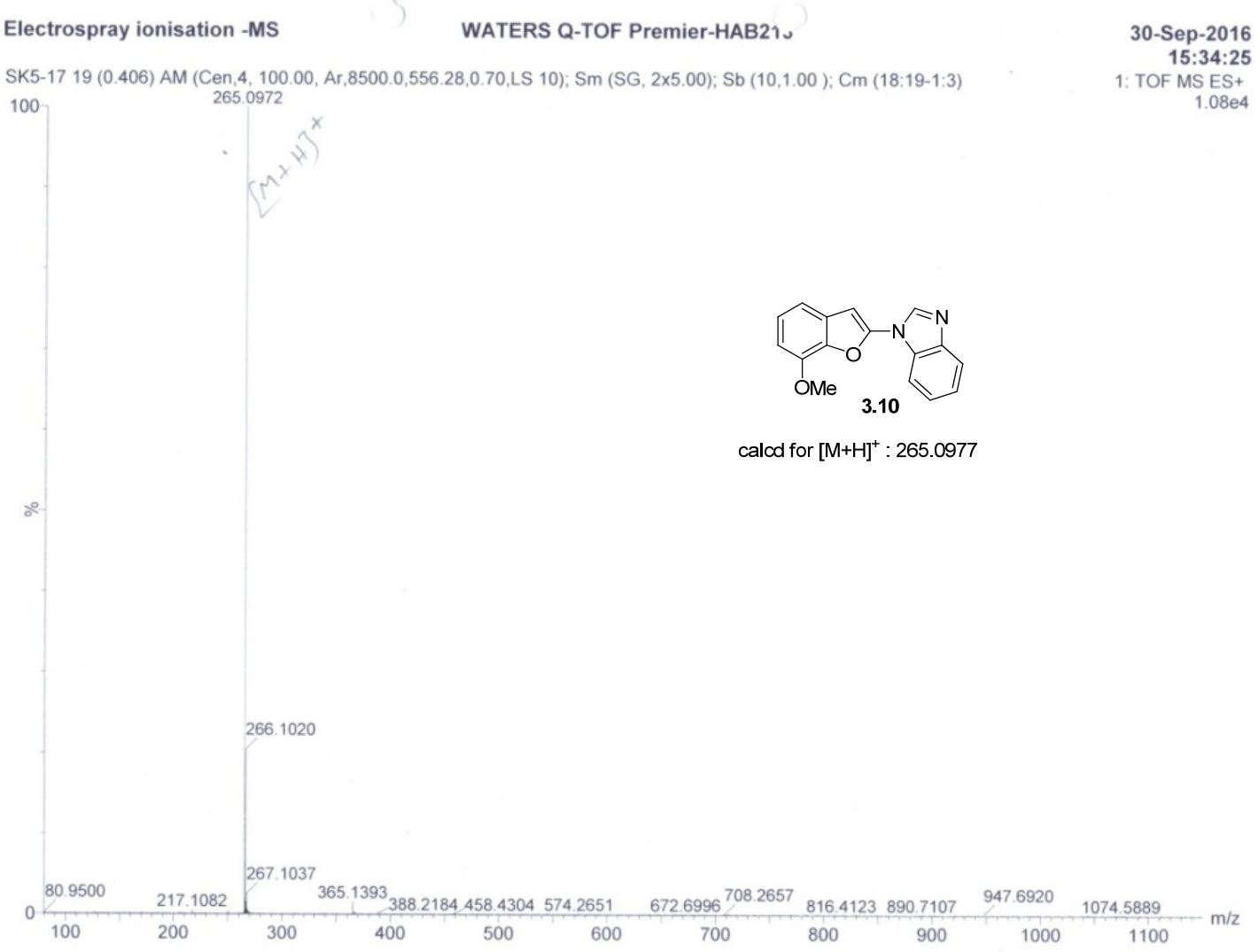
ESI (HRMS) spectrum of **3.7**



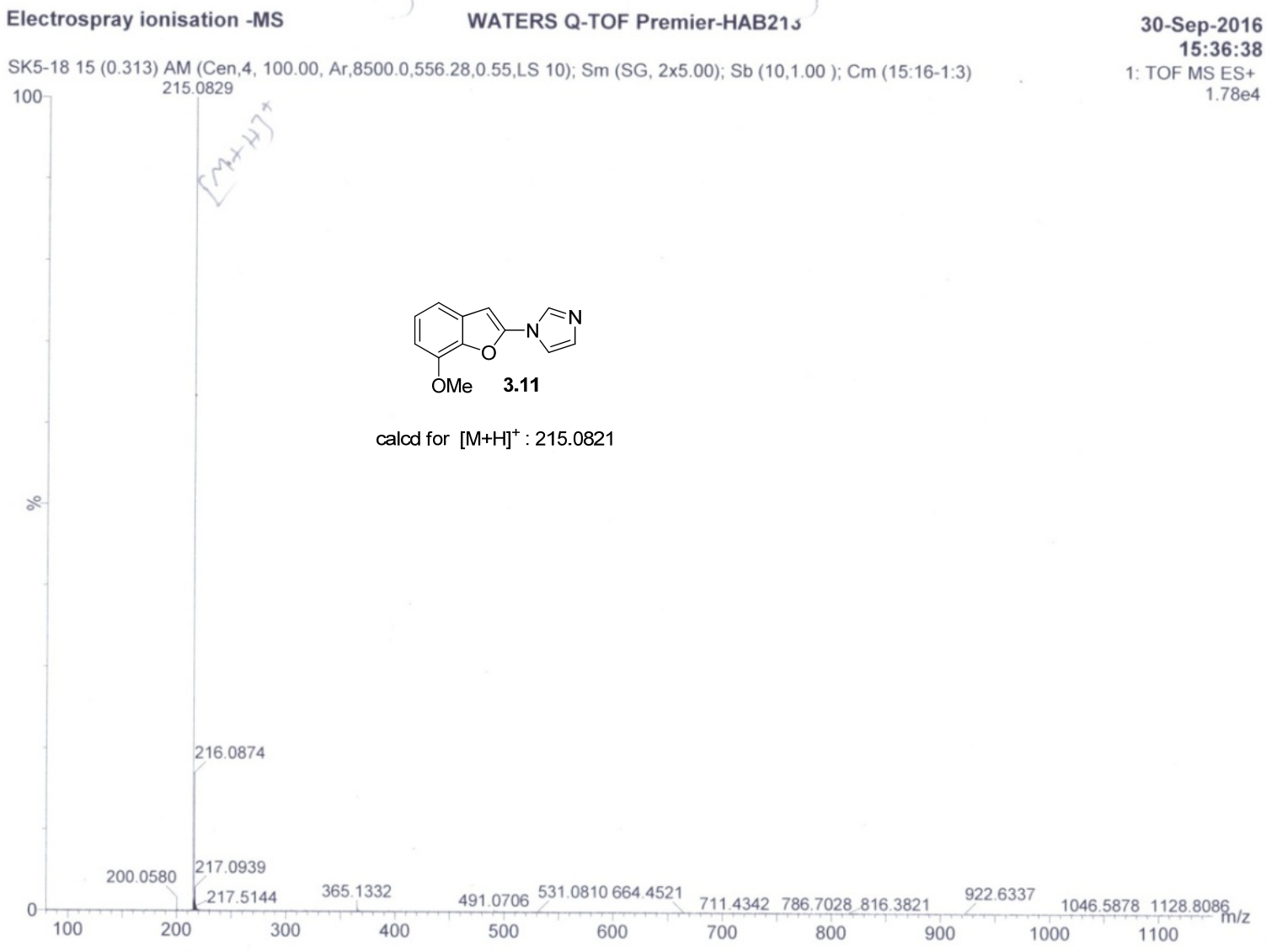
ESI (HRMS) spectrum of **3.8**



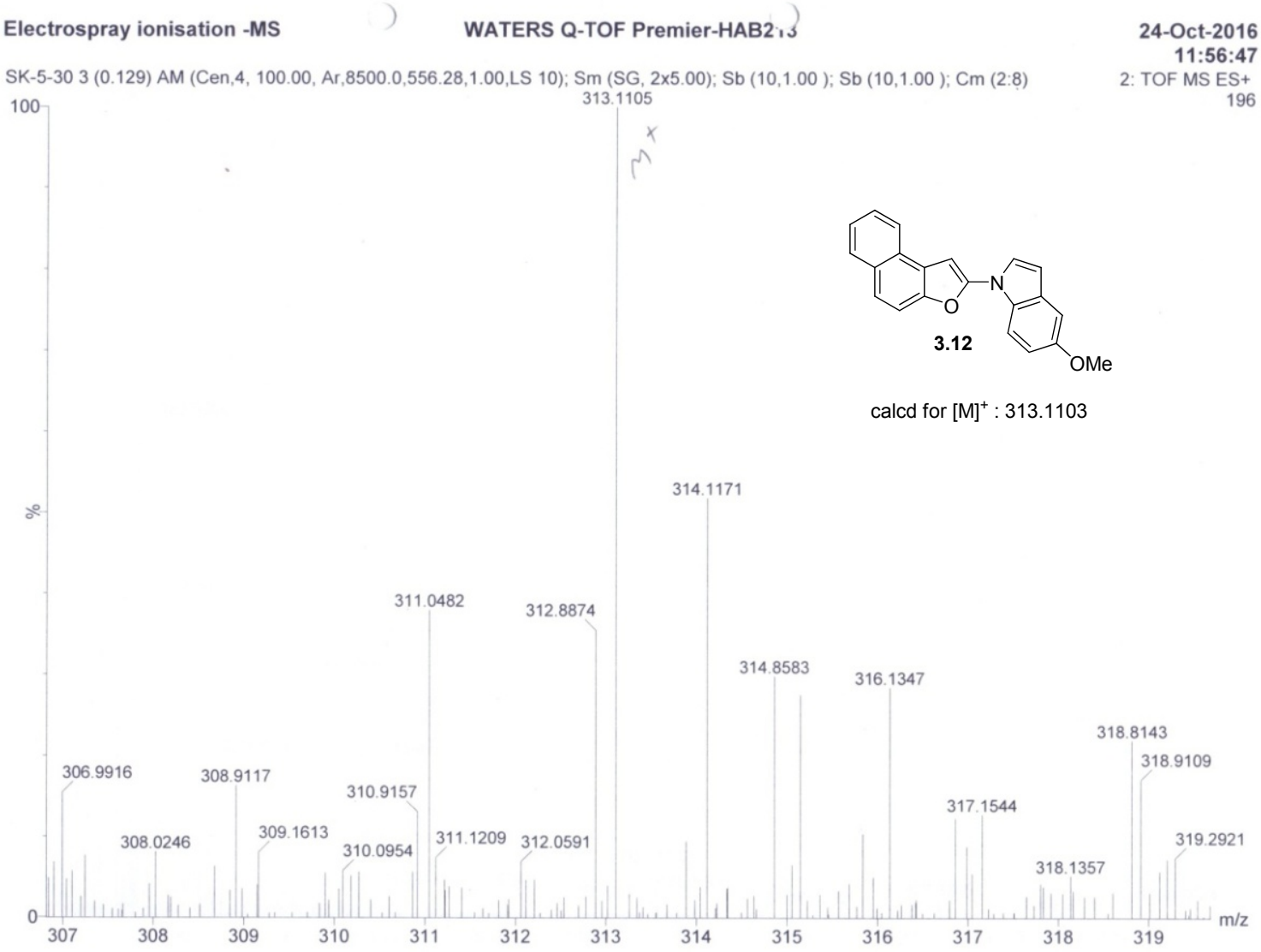
EI (HRMS) spectrum of **3.9**



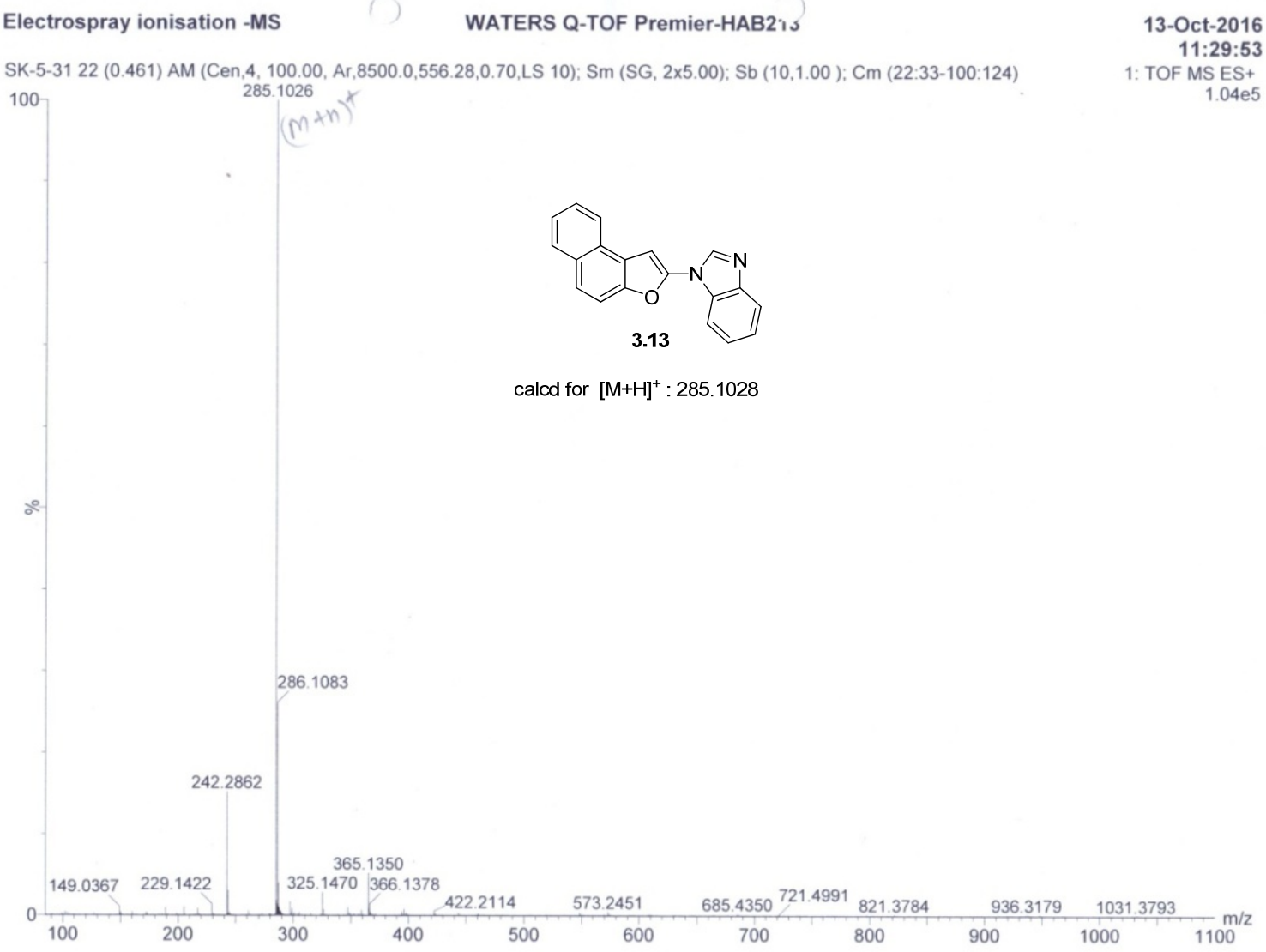
ESI (HRMS) spectrum of **3.10**



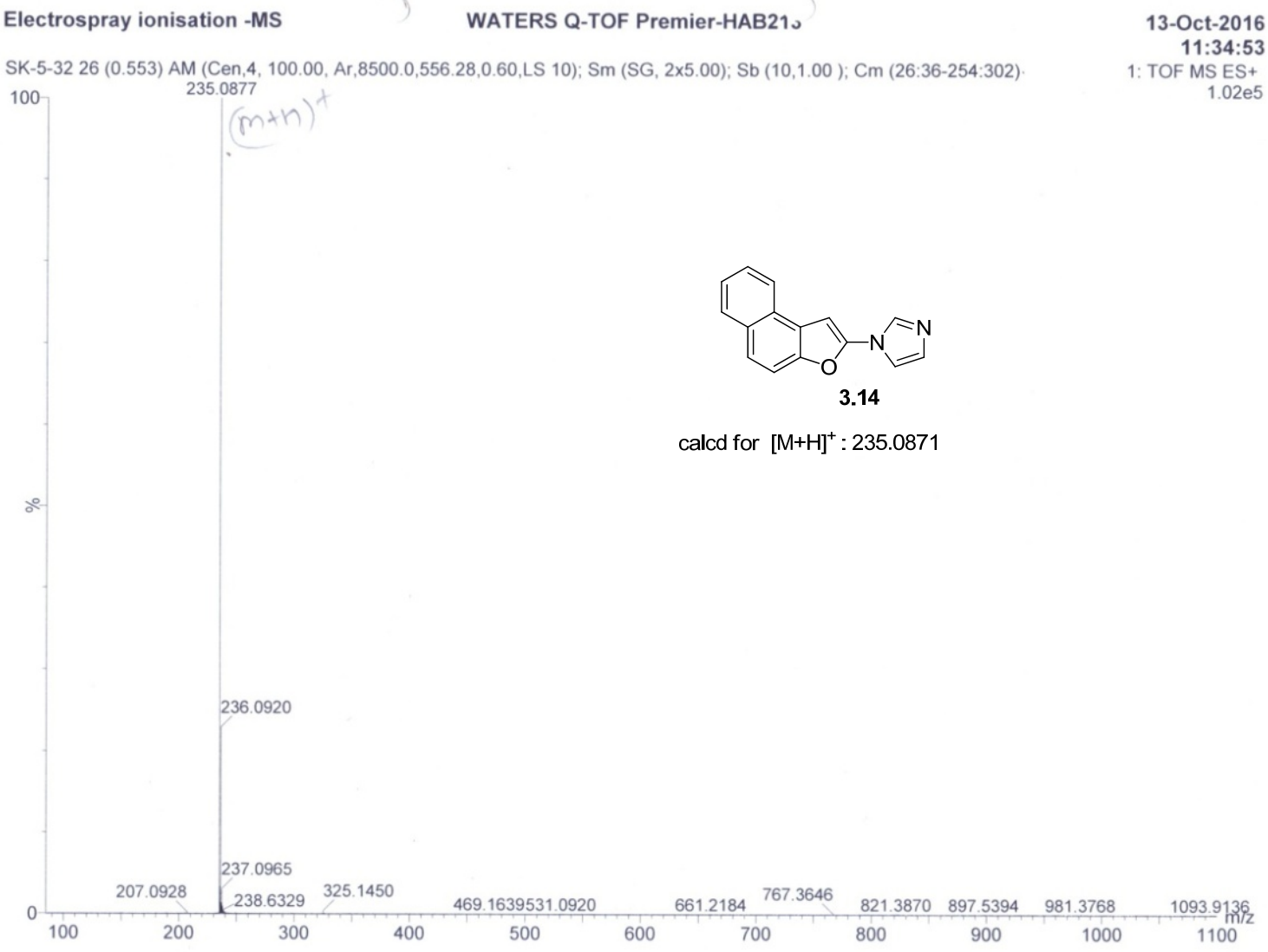
ESI (HRMS) spectrum of **3.11**



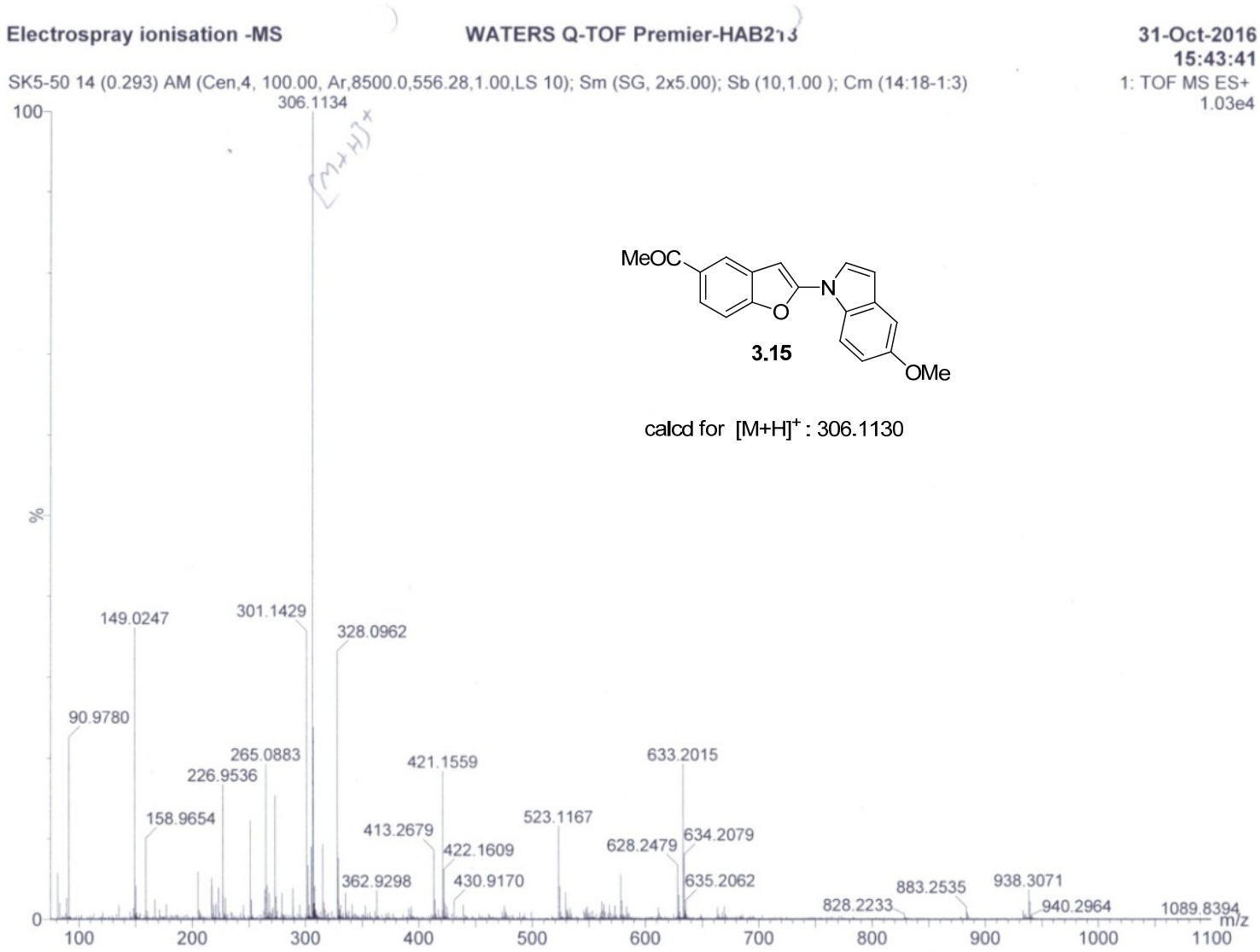
ESI (HRMS) spectrum of **3.12**



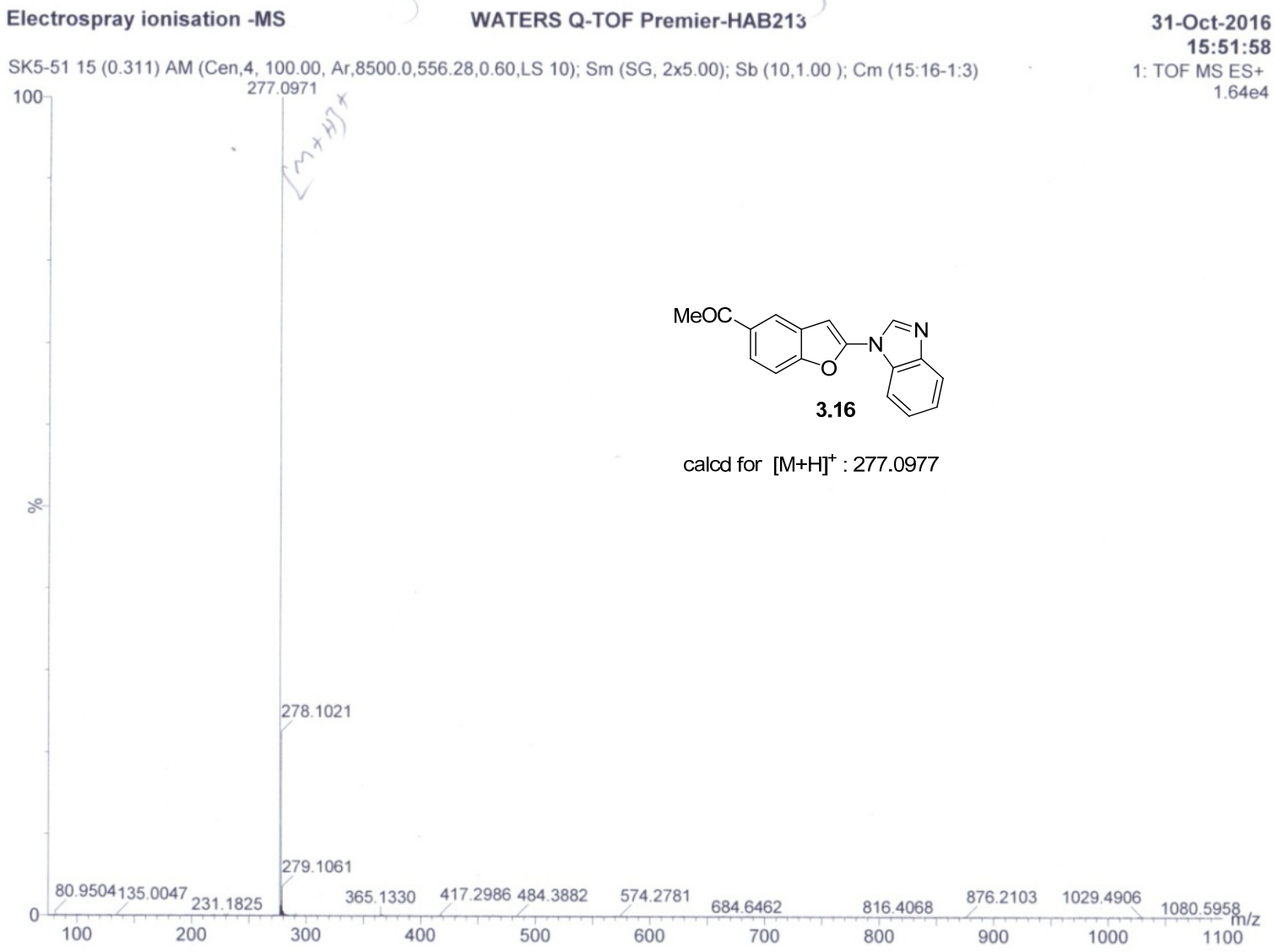
ESI (HRMS) spectrum of **3.13**



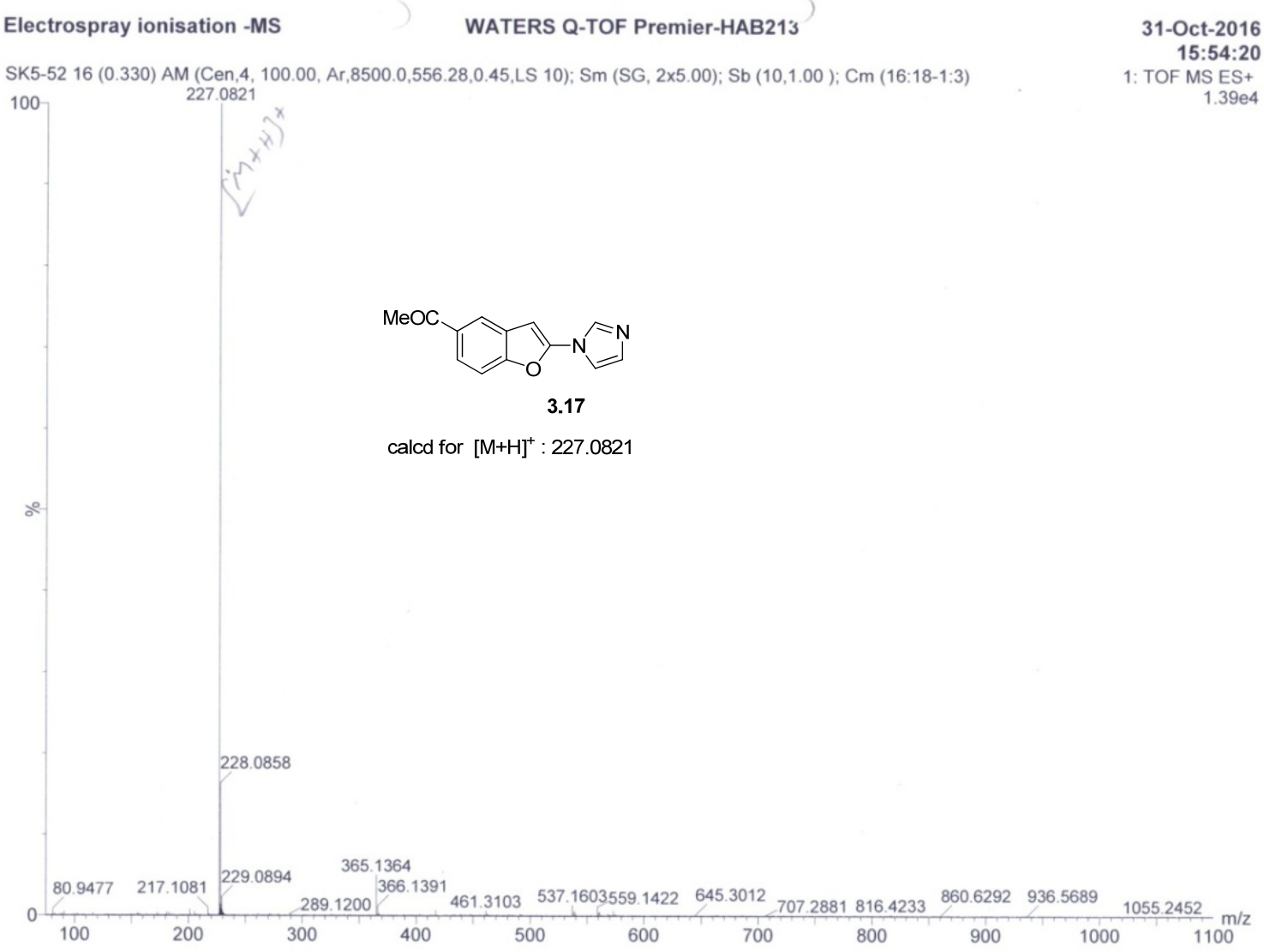
ESI (HRMS) spectrum of **3.14**



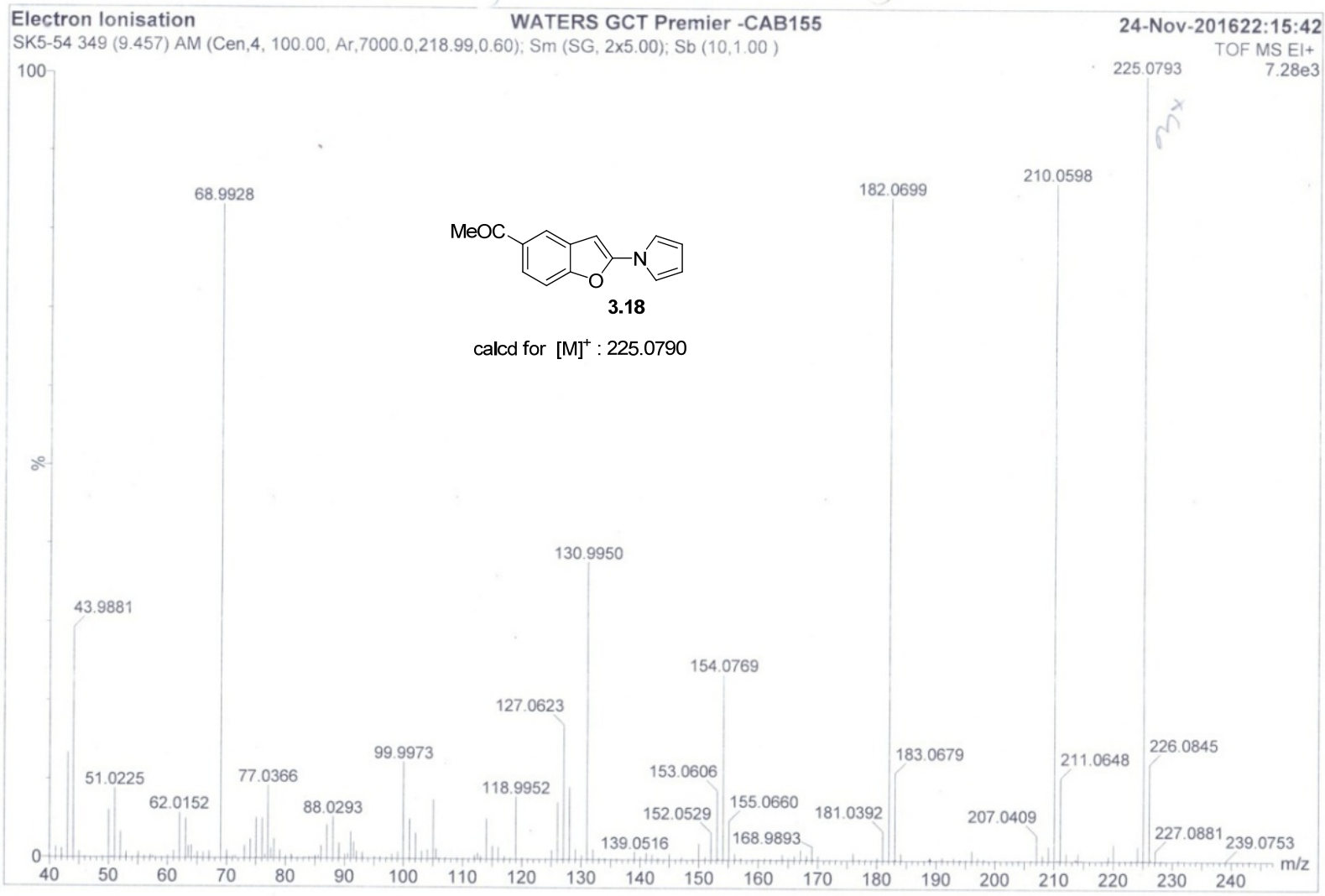
ESI (HRMS) spectrum of **3.15**



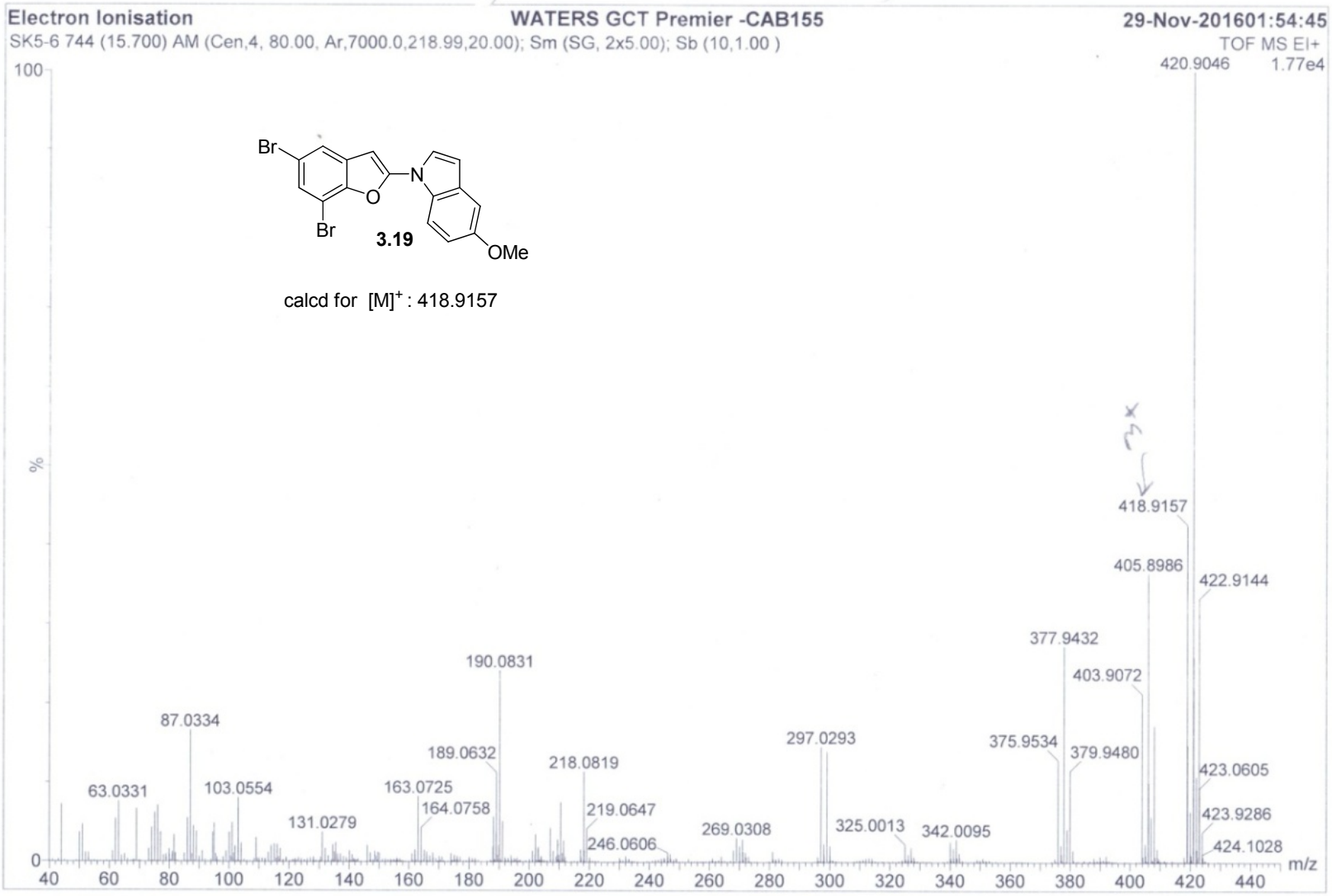
ESI (HRMS) spectrum of **3.16**



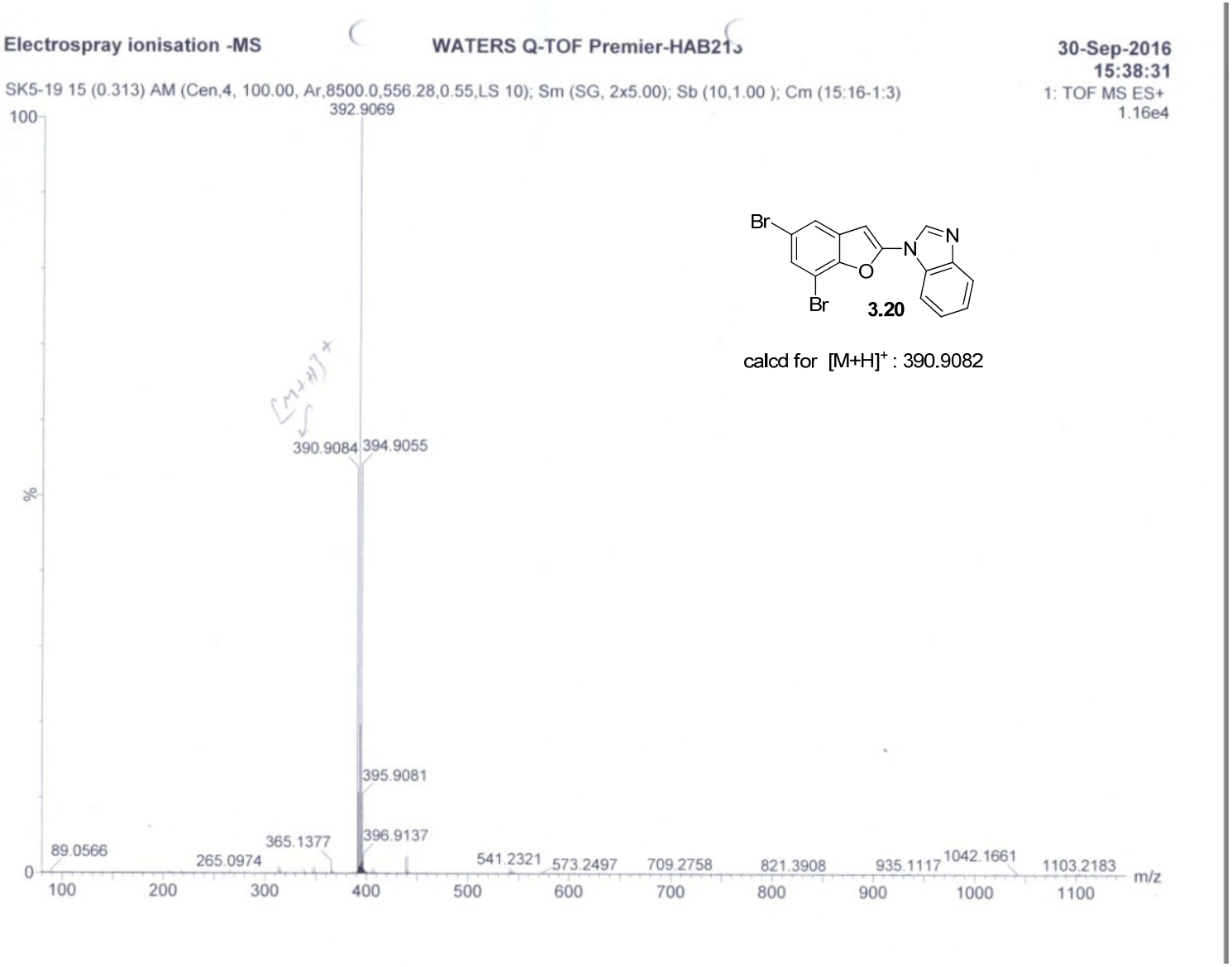
ESI (HRMS) spectrum of **3.17**



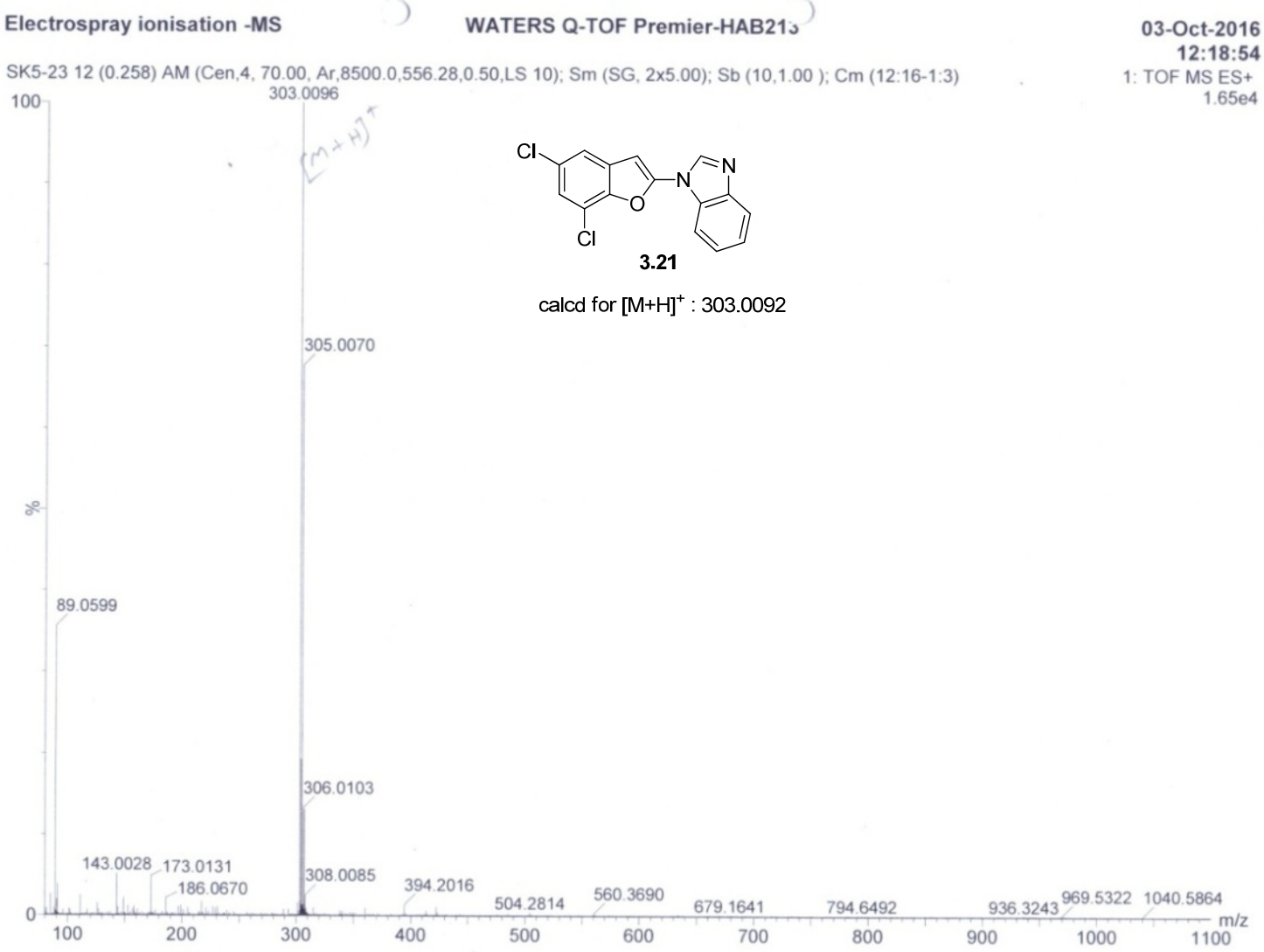
EI (HRMS) spectrum of **3.18**



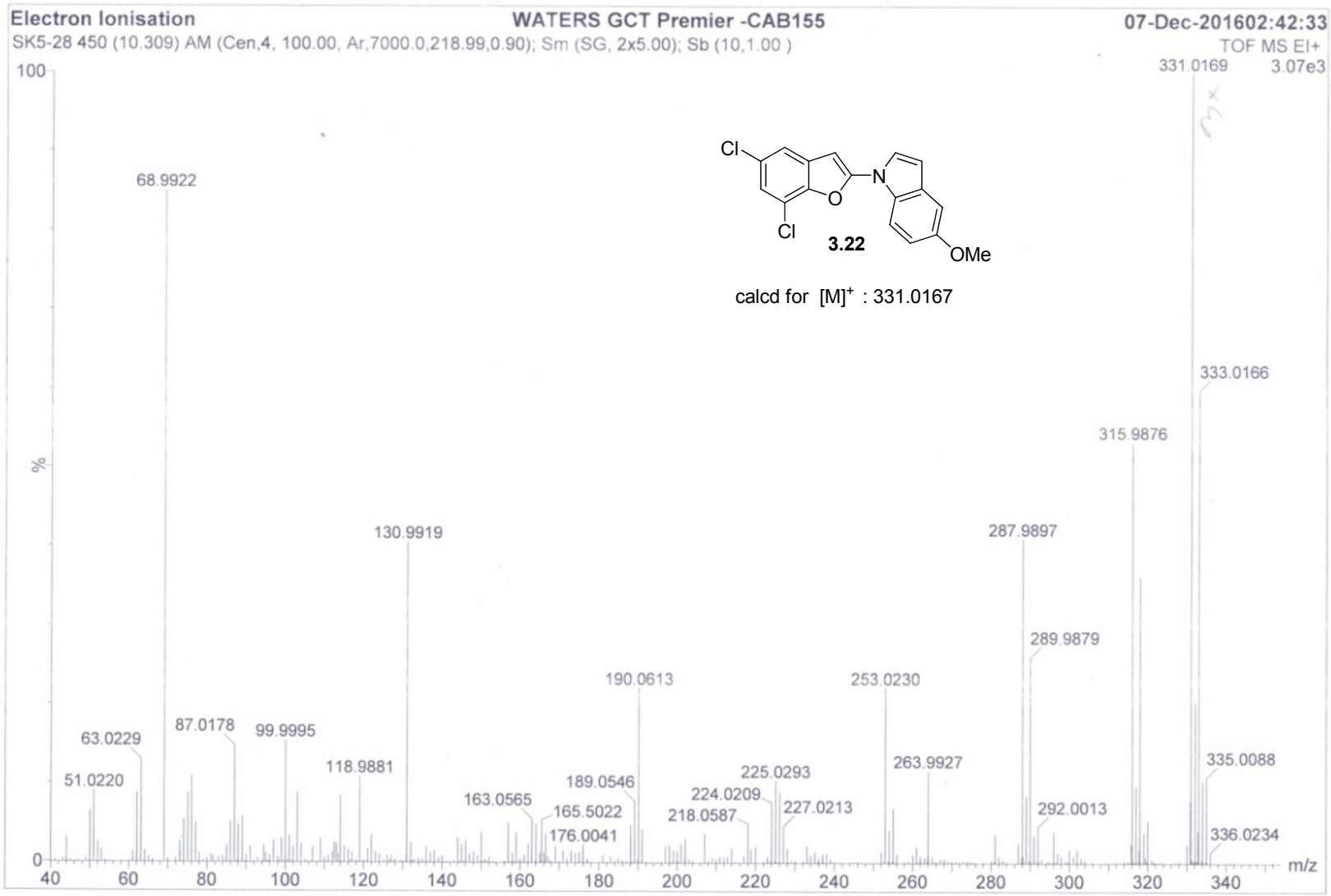
EI (HRMS) spectrum of **3.19**



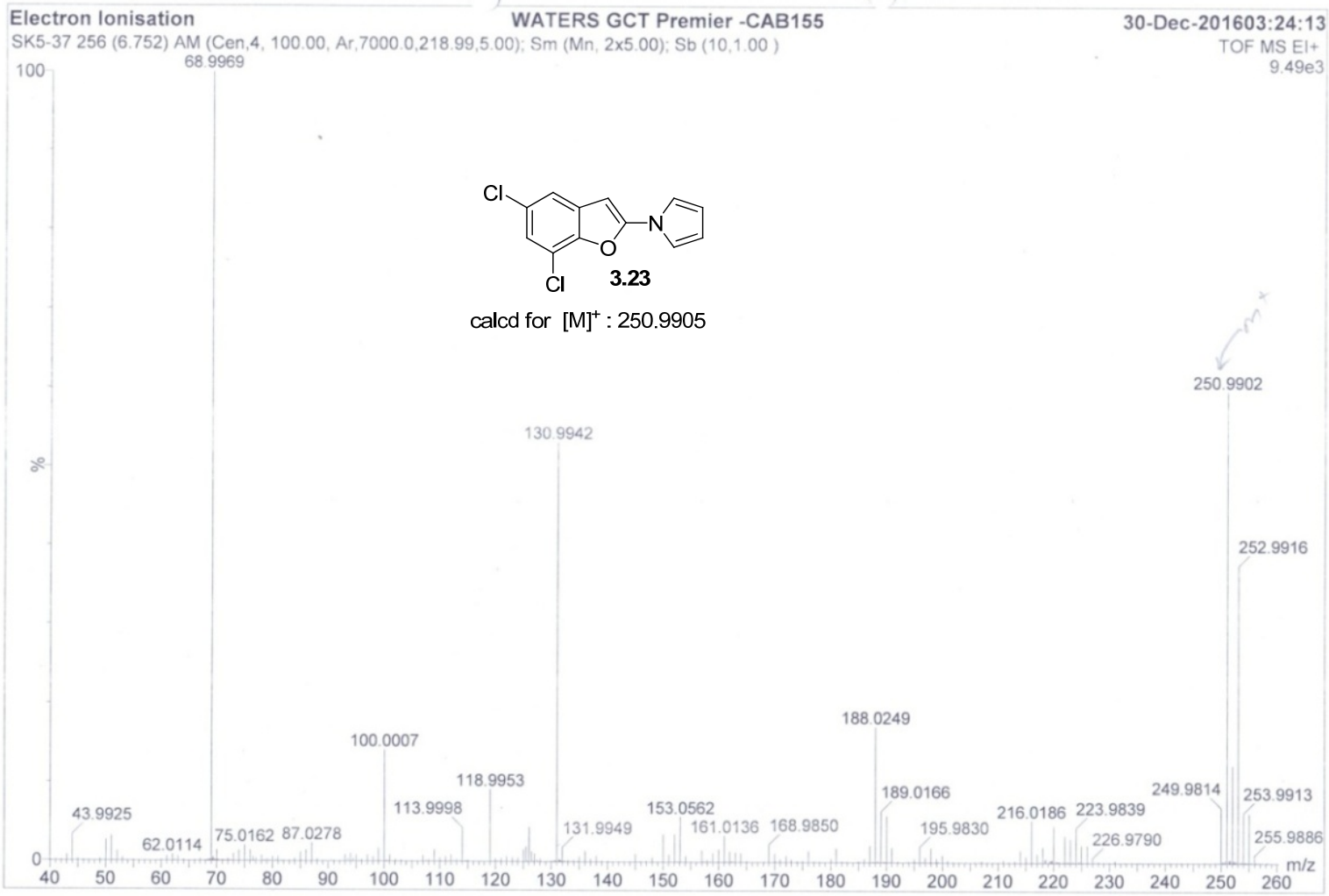
ESI (HRMS) spectrum of **3.20**



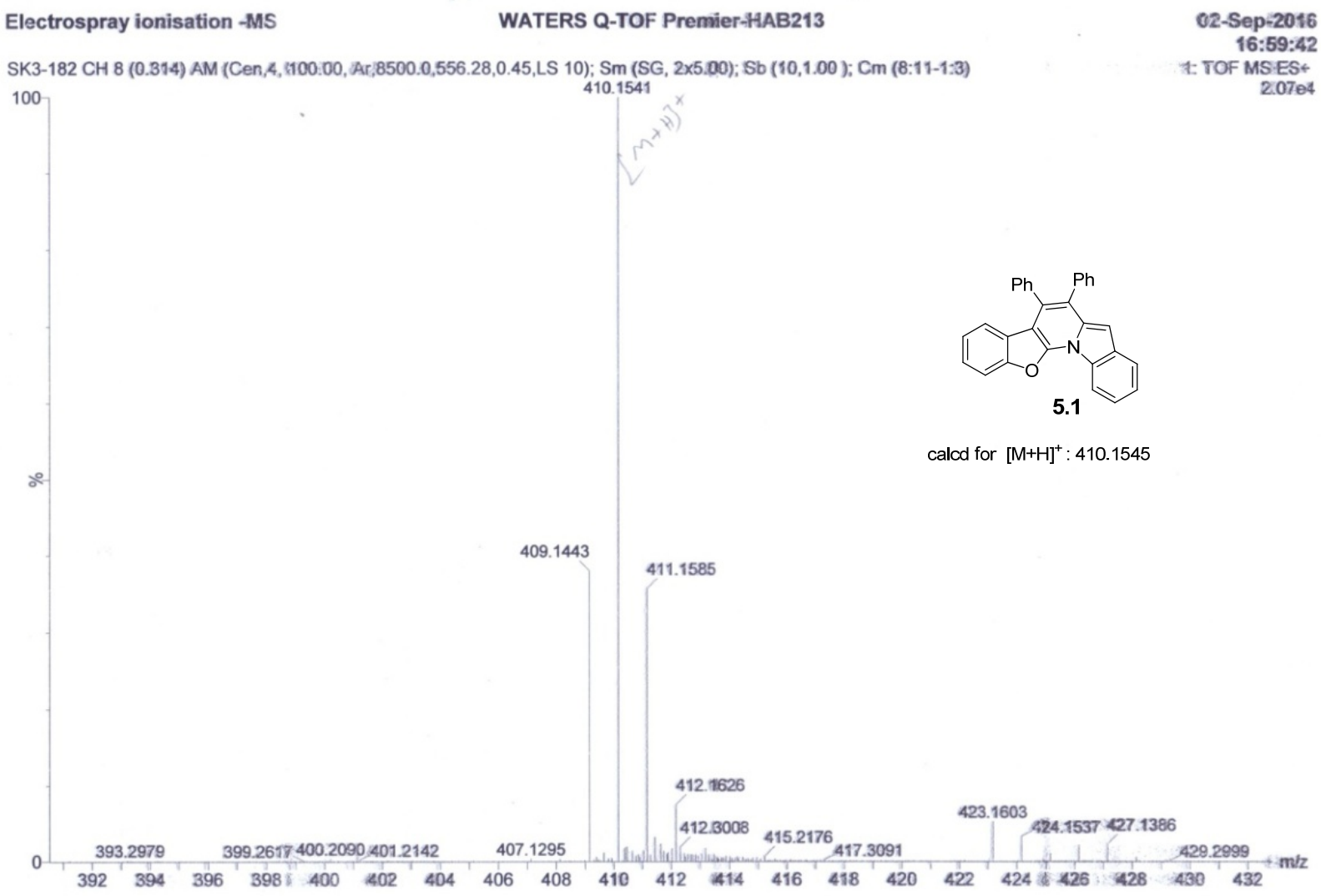
ESI (HRMS) spectrum of **3.21**



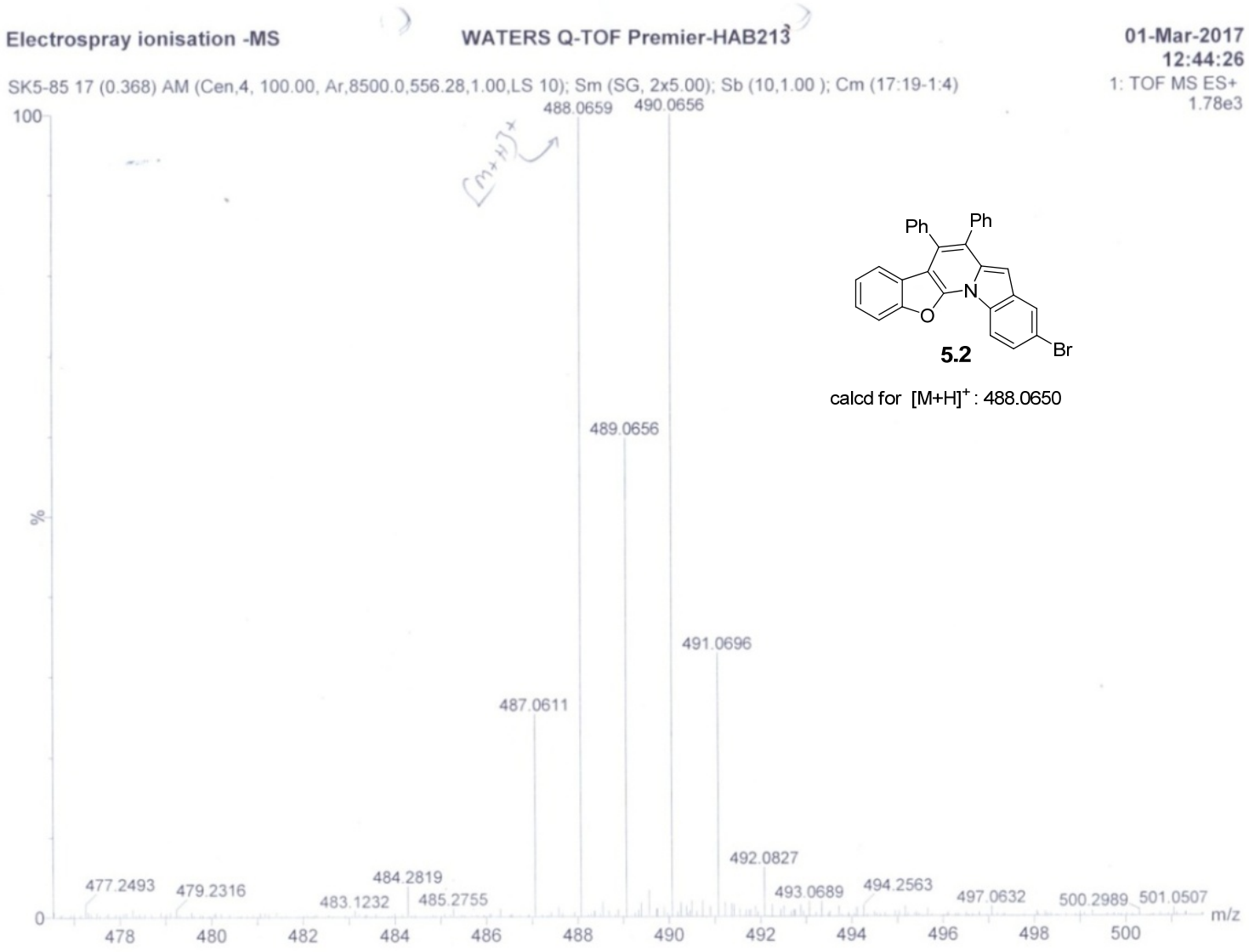
EI (HRMS) spectrum of **3.22**



EI (HRMS) spectrum of **3.23**



ESI (HRMS) spectrum of **5.1**



ESI (HRMS) spectrum of **5.2**