Electronic Supplementary Material (ESI) for ChemComm.

Nitrostyrenes as 1,4-*CCNO*-Dipoles: Diastereoselective Formal [4+1] Cycloaddition of Indoles

Alexander V. Aksenov,*,† Nicolai A. Aksenov,† Dmitrii A. Aksenov,† Vladislav F. Khamraev,† and Michael Rubin*,†,‡

†Department of Chemistry, North Caucasus Federal University, 1a Pushkin St., Stavropol 355009, Russian Federation

‡Department of Chemistry, University of Kansas, 1567 Irving Hill Road, Lawrence, Kansas 66045, United States

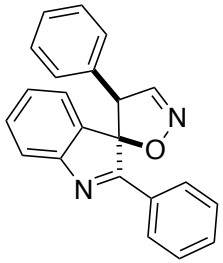
Supporting Information

Table of Contents

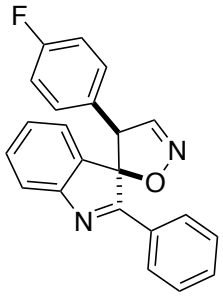
General Information

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance-III spectrometer (400 or 100 MHz, respectively) equipped with BBO probe in $CDCl_3$ or DMSO-d_6, using TMS as internal standard. High-resolution mass spectra were registered with a Bruker Maxis spectrometer (electrospray ionization, in MeCN solution, using HCO_2Na–HCO_2H for calibration). Melting points were measured with a Stuart smp30 apparatus. All reactions were performed in oven-dried 3 mL Weaton microreactor equipped with magnetic spin-vane and Mininert valve, employing magnetic stirring. Reaction progress and purity of isolated compounds were controlled by TLC on Silufol UV-254 plates, eluting with hexanes/EtOAc mixture 4:1. Indoles **4d**,[1] **4h**,[2] and **4j**,[3] as well as nitroalkene **3e**[4] were synthesized according to known procedures. All other reagents and solvents were purchased from commercial vendors and used as received.

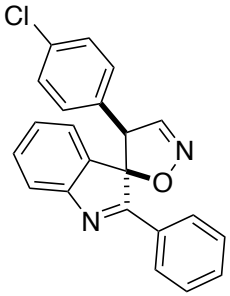
Preparative procedures.



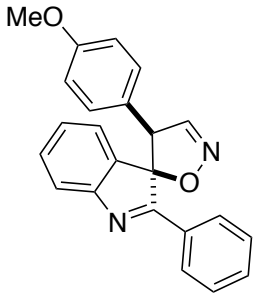
(3*R,4'*S**)-2,4'-Diphenyl-4'*H*-spiro[indole-3,5'-isoxazole]** (**2aa**), **Typical Procedure**: Reaction vessel was charged with 2-phenyl-1*H*-indole (**4a**) (97 mg, 0.50 mmol), (2-nitrovinyl)benzene (**3a**) (82 mg, 0.55 mmol), phosphorous acid (150 mg), and formic acid (500 mg). The mixture was vigorously stirred for 2 h at room temperature. Resulting dark-red homogenous solution was poured into water (50 mL), and the formed precipitate was filtered and washed consecutively with water (4 times), 10% aqueous ammonia, and once again with water. After drying, the resulting crystalline material was sufficiently pure for any practical purposes, but it couls be additionally purified by Flash column chromatography on Silica gel eluting with a mixture of hexane and ethyl acetate (4:1), or by re-crystallization from a mixture of hexane and benzene (1:1). The titled material was obtained as light-grey solid, m.p. 103-105 ^{o}C (benzene/hexanes), R_f 0.47 (hexanes/EtOAc, 1:4). Yield 156 mg, (0.48 mmol, 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.70 (d, *J* = 1.6 Hz, 1H), 7.59 – 7.49 (m, 3H), 7.40 (d, *J* = 7.7 Hz, 1H), 7.15 (td, *J* = 7.6, 1.3 Hz, 1H), 7.12 – 7.08 (m, 3H), 6.94 (d, *J* = 6.7 Hz, 1H), 6.91 – 6.82 (m, 3H), 5.10 (d, *J* = 1.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.4, 152.9, 149.5, 135.7, 133.1, 131.8, 131.7, 130.1, 129.2 (2C), 128.7 (2C), 128.4 (2C), 128.2, 127.8 (2C), 126.0, 124.7, 121.2, 97.7, 61.8; FT IR (film, cm^{-1}): 3059, 3034, 2360, 1691, 1657, 1561, 1544, 1461, 1198; HRMS (ES TOF) calc`d for $C_{22}H_{16}N_2NaO$ $(M+Na)^+$ 347.1155, found 347.1167 (3.4 ppm).



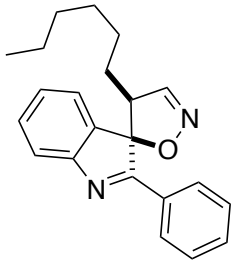
(3*R,4'*S**)-4'-(4-Fluorophenyl)-2-phenyl-4'*H*-spiro[indole-3,5'-isoxazole]** (**2ab**): This compound was obtained via Typical Procedure from 2-phenyl-1*H*-indole (**4a**) (97 mg, 0.50 mmol) and 1-fluoro-4-(2-nitrovinyl)benzene (**3b**) (92 mg, 0.55 mmol). The titled material was obtained as light yellow crystals, m.p. 94-96 °C (benzene/hexanes), R_f 0.41 (hexanes/EtOAc, 1:4). Yield 161 mg (0.47 mmol, 94%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (dd, *J* = 7.9, 1.5 Hz, 2H), 7.68 (d, *J* = 1.5 Hz, 1H), 7.61 – 7.49 (m, 3H), 7.42 (d, *J* = 7.7 Hz, 1H), 7.22 – 7.15 (m, 1H), 6.96 – 6.88 (m, 2H), 6.86 – 6.76 (m, 4H), 5.08 (d, *J* = 1.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.2, 162.3 (d, *J* = 242.1 Hz), 161.1, 152.9, 149.2, 135.6, 131.9, 131.5, 130.2, 129.4 (d, *J* = 8.2 Hz), 129.2 (2C), 128.9 (2C, d, *J* = 3.3 Hz), 128.3 (2C), 126.2, 124.5, 121.3, 115.7 (2C, d, *J* = 21.8 Hz), 97.7, 61.0; FT IR (film, cm^{-1}): 3062, 2923, 2855, 2210, 1696, 1603, 1509, 1460, 1235, 1160, 1104; HRMS (ES TOF) calc'd for $C_{22}H_{16}FN_2O$ $(M+H)^+$ 343.1241, found 343.1231 (2.9 ppm); calc'd for $C_{22}H_{15}FN_2ONa$ $(M+Na)^+$ 365.1061, found 365.1058 (0.8 ppm);



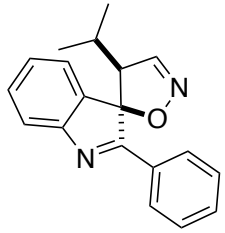
(3*R,4'*S**)-4'-(4-Chlorophenyl)-2-phenyl-4'*H*-spiro[indole-3,5'-isoxazole]** (**2ac**): This compound was obtained via Typical Procedure from 2-phenyl-1*H*-indole (**4a**) (97 mg, 0.50 mmol) and 1-chloro-4-(2-nitrovinyl)benzene (**3c**) (101 mg, 0.55 mmol). The titled material was obtained as yellow crystals, m.p. 125-128 °C (benzene/ hexanes), R_f 0.22 (hexanes/benzene, 5:2). Yield 148 mg. (0.42 mmol, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.1 Hz, 2H), 7.67 (s, 1H), 7.59 – 7.49 (m, 3H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.23 – 7.14 (m, 1H), 7.08 (d, *J* = 8.1 Hz, 2H), 6.93 (d, *J* = 4.0 Hz, 2H), 6.78 (d, *J* = 8.1 Hz, 2H), 5.06 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.1, 152.7, 149.0, 135.4, 134.1, 131.9, 131.6, 131.4, 130.4, 129.3 (2C), 129.0 (2C), 128.9 (2C), 128.3 (2C), 126.3, 124.5, 121.4, 97.6, 61.1; FT IR (film, cm^{-1}): 3649, 3568, 3061, 2360, 1682, 1652, 1513, 1455, 1242; HRMS (ES TOF) calc`d for $C_{22}H_{15}ClN_2NaO$ $(M+Na)^+$ 381.0765, found 381.0763 (0.5 ppm).



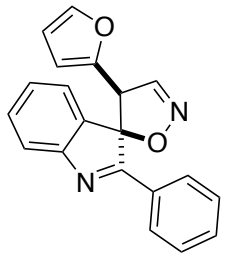
(3*R,4'*S**)-4'-(4-Methoxyphenyl)-2-phenyl-4'*H*-spiro[indole-3,5'-isoxazole]** (**2ad**): This compound was obtained via Typical Procedure from 2-phenyl-1*H*-indole (**4a**) (97 mg, 0.50 mmol) and 1-methoxy-4-(2-nitro-vinyl)benzene (**3d**) (99 mg, 0.55 mmol). The titled material was obtained as grey crystals, m.p. 122-123 °C (benzene/hexanes), R_f 0.20 (benzene). Yield 152 mg, (0.43 mmol, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (dd, *J* = 7.6, 1.4 Hz, 2H), 7.65 (d, *J* = 1.1 Hz, 1H), 7.53 (q, *J* = 6.1 Hz, 3H), 7.41 (d, *J* = 7.7 Hz, 1H), 7.16 (t, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 7.0 Hz, 1H), 6.91 (t, *J* = 7.4 Hz, 1H), 6.77 (d, *J* = 8.6 Hz, 2H), 6.62 (d, *J* = 8.6 Hz, 2H), 5.05 (s, 1H), 3.66 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.4, 159.2, 152.9, 149.9, 135.8, 131.7, 131.7, 130.0, 129.1 (2C), 129.0 (2C), 128.3 (2C), 126.1, 125.0, 124.7, 121.2, 114.0 (2C), 97.8, 61.2, 55.2; FT IR (film, cm^{-1}): 3069, 2829, 2363, 1895, 1689, 1614, 1513, 1456, 1250, 1179, 1033; HRMS (ES TOF) calc`d for $C_{23}H_{18}N_2NaO_2$ $(M+Na)^+$ 377.1260, found 377.1263 (0.7 ppm).



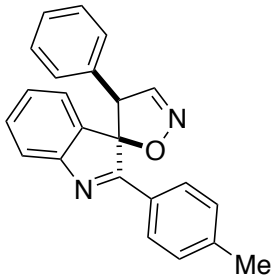
(3*R,4'*S**)-4'-Hexyl-2-phenyl-4'H-spiro[indole-3,5'-isoxazole]** (**2ae**): This compound was obtained via Typical Procedure from 2-phenyl-1*H*-indole (**4a**) (97 mg, 0.50 mmol) and 1-nitrooct-1-ene (**3e**) (86 mg, 0.55 mmol). The titled material was obtained as yellowish oil, R_f 0.33 (hexane/acetone 6:1). Yield 122 mg (0.37 mmol, 73%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.03 (m, 2H), 7.61 (d, *J* = 7.7 Hz, 1H), 7.53 – 7.44 (m, 3H), 7.44 – 7.38 (m, 2H), 7.37 – 7.33 (m, 1H), 7.22 (td, *J* = 7.5, 1.0 Hz, 1H), 3.73 (td, *J* = 7.9, 1.4 Hz, 1H), 1.50 (tdd, *J* = 13.2, 6.7, 4.1 Hz, 1H), 1.29 – 1.18 (m, 1H), 1.12 – 0.78 (m, 8H), 0.75 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.7, 153.4, 151.1, 135.8, 131.6, 131.5, 130.4, 128.9 (2C), 128.1 (2C), 126.2, 124.0, 121.7, 96.4, 56.2, 31.2, 28.7, 28.3, 27.5, 22.3, 13.9; FT IR (film, cm^{-1}): 3043, 2979, 2972, 2930, 2882, 1719, 1614, 1543, 1453, 1374, 1355, 1262, 1033; HRMS (ES TOF) calc`d for $C_{22}H_{25}N_2O$ $(M+H)^+$ 333.1961, found 333.1969 (2.3 ppm); calc`d for $C_{22}H_{24}N_2NaO$ $(M+Na)^+$ 355.1781, found 355.1783 (0.5 ppm).



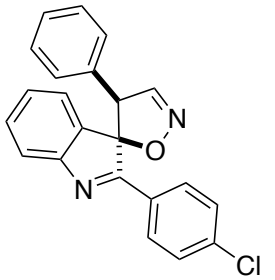
(3*R,4'*S**)-4'-Isopropyl-2-phenyl-4'*H*-spiro[indole-3,5'-isoxazole]** (**2af**): This compound was obtained via Typical Procedure from 2-phenyl-1*H*-indole (**4a**) (97 mg, 0.50 mmol) and 3-methyl-1-nitrobut-1-ene (**3f**) (63 mg, 0.55 mmol). The titled material was obtained as colorless solid, m.p. 148-150 °C (benzene/hexanes), R_f 0.21 (hexane/ acetone 7:1). Yield 103 mg (0.35 mmol, 71%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 6.9 Hz, 2H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.55 – 7.45 (m, 4H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.38 (d, *J* = 7.2 Hz, 1H), 7.22 (t, *J* = 7.4 Hz, 1H), 3.45 (dd, *J* = 11.1, 0.8 Hz, 1H), 1.99 – 1.83 (m, 1H), 1.03 (d, *J* = 6.6 Hz, 3H), 0.29 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.0, 153.9, 150.2, 135.9, 131.8, 131.6, 130.7, 129.0 (2C), 128.2 (2C), 126.5, 123.8, 121.9, 96.3, 63.9, 28.1, 22.5, 20.3; FT IR (film, cm^{-1}): 3039, 2972, 2930, 2874, 1723, 1543, 1456, 1374, 1273, 1036 cm-1; HRMS (ES TOF) calc`d for $C_{19}H_{19}N_2O$ $(M+H)^+$ 291.1492, found 291.1485 (2.5 ppm).



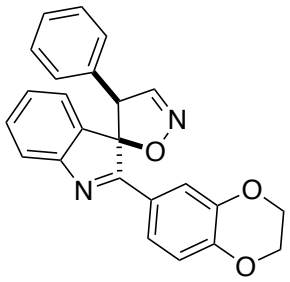
(3*R,4'*R**)-4'-(Furan-2-yl)-2-phenyl-4'*H*-spiro[indole-3,5'-isoxazole]** (**2ag**): This compound was obtained via Typical Procedure from 2-phenyl-1*H*-indole (**4a**) (97 mg, 0.50 mmol) and 2-(2-nitrovinyl)furan (77 mg, 0.55 mmol). The titled material was obtained as yellow oil, R_f 0.21 (hexane/ acetone 6:1). Yield 97 mg (0.31 mmol, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.0 Hz, 2H), 7.61 (d, *J* = 0.8 Hz, 1H), 7.56 – 7.46 (m, 4H), 7.27 (t, *J* = 7.6 Hz, 1H), 7.11 (dd, *J* = 9.0, 4.1 Hz, 2H), 7.01 (d, *J* = 7.5 Hz, 1H), 6.17 – 6.08 (m, 1H), 6.01 (d, *J* = 3.2 Hz, 1H), 5.10 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.5, 153.1, 147.1, 146.0, 142.9, 135.4, 131.8, 131.4, 130.4, 129.2 (2C), 128.2 (2C), 126.3, 124.2, 121.3, 110.6, 109.0, 96.5, 55.9; FT IR (film, cm^{-1}): 3073, 2930, 2855, 1606, 1539, 1505, 1464, 1445, 1318, 1269, 1246, 1201, 1145, 1073; HRMS (ES TOF) calc`d for $C_{20}H_{15}N_2O_2$ $(M+H)^+$ 315.1128, found 315.1137 (2.9 ppm); calc`d for $C_{20}H_{14}N_2NaO_2$ $(M+Na)^+$ 337.0947, found 337.0940 (2.2 ppm).



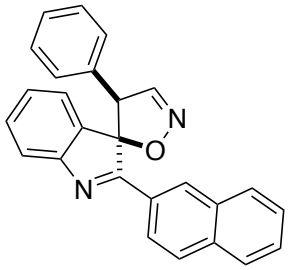
(3*R*,4'S)-4'-phenyl-2-(*p*-tolyl)-4'*H*-spiro[indole-3,5'-isoxazole]** (**2ba**): This compound was obtained via Typical Procedure from 2-(*p*-tolyl)-1*H*-indole (**4b**) (104 mg, 0.50 mmol) and (2-nitrovinyl)benzene (**3a**) (82 mg, 0.55 mmol). The titled material was obtained as light grey solid, m.p. 55-57 °C (benzene/hexanes), R_f 0.27 (hexane/benzene 2:5). Yield 154 mg, (0.46 mmol, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.0 Hz, 2H), 7.70 (s, 1H), 7.38 (d, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.20 – 7.03 (m, 4H), 6.94 (d, *J* = 7.3 Hz, 1H), 6.91 – 6.80 (m, 3H), 5.10 (s, 1H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.3, 153.0, 149.4, 142.4, 135.7, 133.1, 130.0, 129.9 (2C), 128.9, 128.6, 128.3, 128.1, 127.7 (2C), 125.8, 124.6, 121.0, 97.7, 62.0, 21.8; FT IR (film, cm^{-1}): 3032, 2882, 2589, 2364, 1925, 1813, 1614, 1543, 1516, 1456, 1190; HRMS (ES TOF) calc`d for $C_{23}H_{18}N_2NaO$ $(M+Na)^+$: 361.1311, found 361.1311 (0.2 ppm).



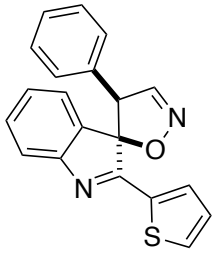
(3*R*,4'S)-2-(4-Chlorophenyl)-4'-phenyl-4'*H*-spiro[indole-3,5'-isoxazole]** (**2ca**): This compound was obtained via Typical Procedure from 2-(4-chlorophenyl)-1*H*-indole (**4c**) (114 mg, 0.50 mmol) and (2-nitrovinyl)benzene (**3a**) (82 mg, 0.55 mmol). The titled material was obtained as light-yellow solid, m.p. 152-153 °C (benzene/ hexanes), R_f 0.32 (hexane/benzene 2:5). Yield 154 mg (0.43 mmol, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.4 Hz, 2H), 7.71 (s, 1H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 7.7 Hz, 1H), 7.10 (d, *J* = 4.4 Hz, 4H), 6.97 – 6.79 (m, 4H), 5.04 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.2, 152.8, 149.6, 138.0, 135.6, 132.9, 130.2, 130.1, 129.6 (2C), 129.5 (2C), 128.7 (2C), 128.3, 127.7 (2C), 126.2, 124.7, 121.3, 97.6, 61.7; FT IR (film, cm^{-1}): 2994, 2360, 1749, 1655, 1490, 1456, 1377, 1250, 1096; HRMS (ES TOF) calc`d for $C_{22}H_{16}ClN_2O$ $(M+H)^+$ 359.0946, found 359.0940 (1.4 ppm); calc`d for $C_{22}H_{15}ClN_2NaO$ $(M+Na)^+$ 381.0765, found 381.0751 (3.7 ppm).



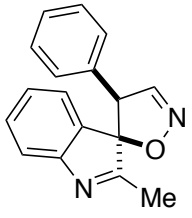
(3*R*,4'S)-2-(2,3-Dihydrobenzo[*b*][1,4]dioxin-6-yl)-4'-phenyl-4'*H*-spiro[indole-3,5'-isoxazole]** (**2da**): This compound was obtained via Typical Procedure from 2-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)-1*H*-indole (**4d**) (126 mg, 0.50 mmol) and (2-nitrovinyl)benzene (**3a**) (82 mg, 0.55 mmol). The titled material was obtained as yellow solid, m.p. 116-119 °C (benzene/hexanes); R_f 0.22 (hexane/benzene 2:5). Yield 141 mg (0.37 mmol, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 2H), 7.68 (s, 1H), 7.34 (d, *J* = 7.8 Hz, 1H), 7.18 – 7.05 (m, 4H), 6.99 (d, *J* = 8.3 Hz, 1H), 6.92 (d, *J* = 7.4 Hz, 1H), 6.87 – 6.80 (m, 3H), 5.12 (s, 1H), 4.31 (d, *J* = 5.6 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.7, 153.0, 149.5, 147.0, 143.9, 135.6, 133.1, 130.0, 128.6 (2C), 128.1, 127.7 (2C), 125.6, 125.0, 124.5, 122.1, 120.8, 118.0, 117.4, 97.6, 64.8, 64.3, 62.1; FT IR (film, cm^{-1}): 3065, 2360, 1681, 1565, 1513, 1288, 1246, 1066; HRMS (ES TOF) calc`d for $C_{24}H_{19}N_2O_3$ $(M+H)^+$ 383.1390, found 383.1393 (0.8 ppm); calc`d for $C_{24}H_{18}N_2NaO_3$ $(M+Na)^+$ 405.1210, found 405.1208 (0.3 ppm).



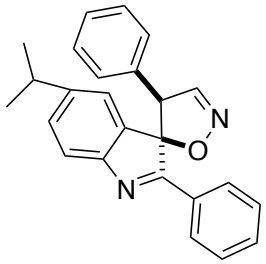
(3*R,4'*S**)-2-(Naphthalen-2-yl)-4'-phenyl-4'*H*-spiro[indole-3,5'-isoxazole]** (**2ea**): This compound was obtained via Typical Procedure from 2-(naphthalen-2-yl)-1*H*-indole (**4e**) (122 mg, 0.50 mmol) and (2-nitrovinyl)benzene (**3a**) (82 mg, 0.55 mmol). The titled material was obtained as green solid, m.p. 154-156 °C (benzene/hexanes), R_f 0.32 (benzene). Yield 144 mg (0.38 mmol, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.35 (d, *J* = 8.6 Hz, 1H), 8.04 – 7.95 (m, 2H), 7.91 (d, *J* = 7.6 Hz, 1H), 7.76 (s, 1H), 7.64 – 7.54 (m, 2H), 7.45 (d, *J* = 7.7 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.14 – 7.05 (m, 3H), 7.00 (d, *J* = 7.2 Hz, 1H), 6.94 – 6.83 (m, 3H), 5.19 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.3, 152.9, 149.6, 135.8, 134.9, 133.1, 133.0, 130.1, 129.4, 129.0, 129.0, 128.8, 128.6 (2C), 128.2, 128.0, 127.9, 127.7 (2C), 126.9, 126.0, 124.9, 124.6, 121.2, 97.8, 62.2. FT IR (film, cm^{-1}): 3058, 2360, 1693, 1509, 1456, 1231, 909; HRMS (ES TOF) calc`d for $C_{26}H_{18}N_2NaO$ $(M+Na)^+$ 397.1311, found 397.1324 (3.2 ppm).



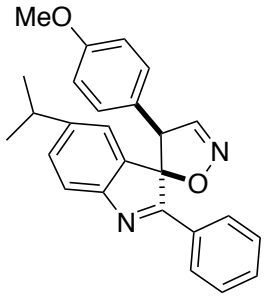
(3*R,4'*S**)-4'-Phenyl-2-(thiophen-2-yl)-4'*H*-spiro[indole-3,5'-isoxazole]** (**2fa**): This compound was obtained via Typical Procedure from 2-(thiophen-2-yl)-1*H*-indole (**4f**) (100 mg, 0.50 mmol) and (2-nitrovinyl)benzene (**3a**) (82 mg, 0.55 mmol). The titled material was obtained as green solid, m.p. 57-60 °C (benzene/hexanes), R_f 0.27 (benzene). Yield 119 mg (0.36 mmol, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 1.6 Hz, 1H), 7.69 (dd, *J* = 3.8, 1.0 Hz, 1H), 7.62 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.37 (dt, *J* = 7.7, 0.8 Hz, 1H), 7.20 (dd, *J* = 5.0, 3.8 Hz, 1H), 7.15 – 7.08 (m, 4H), 6.91 – 6.79 (m, 4H), 5.19 (d, *J* = 1.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 153.2, 149.2, 135.4, 135.0, 133.1, 131.3, 130.3, 130.1, 128.7 (2C), 128.7, 128.3, 127.8 (2C), 125.7, 124.7, 120.9, 97.1, 62.9; FT IR (film, cm^{-1}): 3080, 2360, 1753, 1550, 1505, 1423, 1243, 1190, 1059 cm-1; HRMS (ES TOF): calc`d for $C_{20}H_{14}N_2NaOS$ $(M+Na)^+$ 353.0719, found 353.0706 (3.8 ppm).



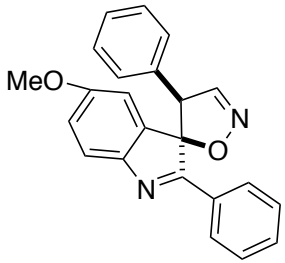
(3*R,4'*S**)-2-Methyl-4'-phenyl-4'*H*-spiro[indole-3,5'-isoxazole]** (**2ga**): This compound was obtained via Typical Procedure from 2-methyl-1*H*-indole (**4g**) (66 mg, 0.50 mmol) and (2-nitrovinyl)benzene (**3a**) (82 mg, 0.55 mmol). The reaction was carried out at 10 °C. The titled material was obtained as red solid, m.p. 64-65°C (benzene/ hexanes), R_f 0.70 (benzene). Yield 58 mg (0.22 mmol, 44%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 1.4 Hz, 1H), 7.24 (d, *J* = 7.7 Hz, 1H), 7.20 – 7.13 (m, 3H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.82 (dd, *J* = 6.4, 2.8 Hz, 2H), 6.65 (t, *J* = 7.5 Hz, 1H), 6.28 (d, *J* = 7.4 Hz, 1H), 4.51 (d, *J* = 1.2 Hz, 1H), 2.27 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.1, 154.25, 149.3, 133.0, 132.8, 130.3, 129.0 (2C), 128.7, 128.5 (2C), 125.6, 125.3, 120.3, 96.4, 58.6, 15.4; FT IR (film, cm^{-1}): 3062, 3039, 2930, 2863, 1726, 1595, 1464, 1381, 1246, 1194, 1074; HRMS (ES TOF) calc'd for $C_{17}H_{15}N_2O$ $(M + H)^+$ 263.1179, found 263.1176 (0.9 ppm).



(3*R,4'*S**)-5-Isopropyl-2,4'-diphenyl-4'*H*-spiro[indole-3,5'-isoxazole]** (**2ha**): This compound was obtained via Typical Procedure from 5-isopropyl-2-phenyl-1*H*-indole (**4h**) (118 mg, 0.50 mmol) and (2-nitrovinyl)benzene (**3a**) (82 mg, 0.55 mmol). The titled material was obtained as grey solid, m.p. 108-110°C (benzene/ hexanes), R_f 0.43 (hexanes/benzene, 2:5). Yield 166 mg, (0.46 mmol, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (dd, *J* = 7.5, 1.7 Hz, 2H), 7.70 (d, *J* = 1.1 Hz, 1H), 7.53 (d, *J* = 6.8 Hz, 3H), 7.30 (d, *J* = 7.9 Hz, 1H), 7.09 (d, *J* = 6.5 Hz, 3H), 7.02 – 6.92 (m, 1H), 6.88 – 6.81 (m, 2H), 6.75 (s, 1H), 5.07 (s, 1H), 2.69 (hept, *J* = 6.9 Hz, 1H), 1.04 (d, *J* = 6.9 Hz, 3H), 1.01 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.6, 150.9, 149.4, 147.1, 135.7, 133.4, 131.8, 131.5, 129.1 (2C), 128.6 (2C), 128.2 (2C), 128.1, 128.1, 127.8 (2C), 122.9, 120.8, 97.5, 61.6, 34.1, 24.3, 23.6; FT IR (film, cm^{-1}): 2960, 2360, 1955, 1670, 1494, 1381, 1186; HRMS (ES TOF) calc`d for $C_{25}H_{23}N_2O$ $(M+H)^+$ 367.1805, found 367.1794 (2.9 ppm).

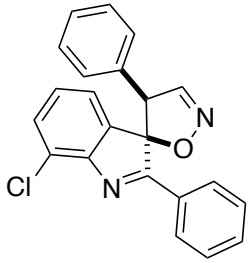


(3*R,4'*S**)-5-Isopropyl-4'-(4-methoxyphenyl)-2-phenyl-4'*H*-spiro[indole-3,5'-isoxazole]** (**2hd**): This compound was obtained via Typical Procedure from 5-isopropyl-2-phenyl-1*H*-indole (**4h**) (118 mg, 0.50 mmol) and 1-methoxy-4-(2-nitrovinyl)benzene (**3d**) (99 mg, 0.55 mmol). The titled material was obtained as green solid, m.p. 61-63°C (benzene/hexanes), R_f 0.33 (Benzene). Yield 166 mg (0.42 mmol, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (dd, *J* = 7.7, 1.9 Hz, 2H), 7.66 (d, *J* = 1.5 Hz, 1H), 7.55 – 7.47 (m, 3H), 7.31 (d, *J* = 7.9 Hz, 1H), 6.98 (dd, *J* = 7.9, 1.5 Hz, 1H), 6.77 (d, *J* = 8.6 Hz, 3H), 6.65 – 6.58 (m, 2H), 5.02 (d, *J* = 1.2 Hz, 1H), 3.66 (s, 3H), 2.71 (hept, *J* = 6.9 Hz, 1H), 1.07 (d, *J* = 6.9 Hz, 3H), 1.04 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.7, 159.3, 151.0, 149.7, 147.1, 135.8, 131.9, 131.5, 129.1 (2C), 129.0 (2C), 128.2 (2C), 128.2, 125.4, 122.9, 120.7, 114.0 (2C), 97.6, 61.1, 55.3, 34.1, 24.3, 23.6; FT IR (film, cm^{-1}): 2957, 2919, 2364, 1749, 1606, 1516, 1254, 1179, 1033; HRMS (ES TOF), calc`d for $C_{26}H_{25}N_2O_2$ $(M+H)^+$ 397.1911, found 397.1901 (2.5 ppm); calc`d for $C_{26}H_{24}N_2NaO_2$ $(M+Na)^+$ 419.1730, found 419.1737 (1.7 ppm).

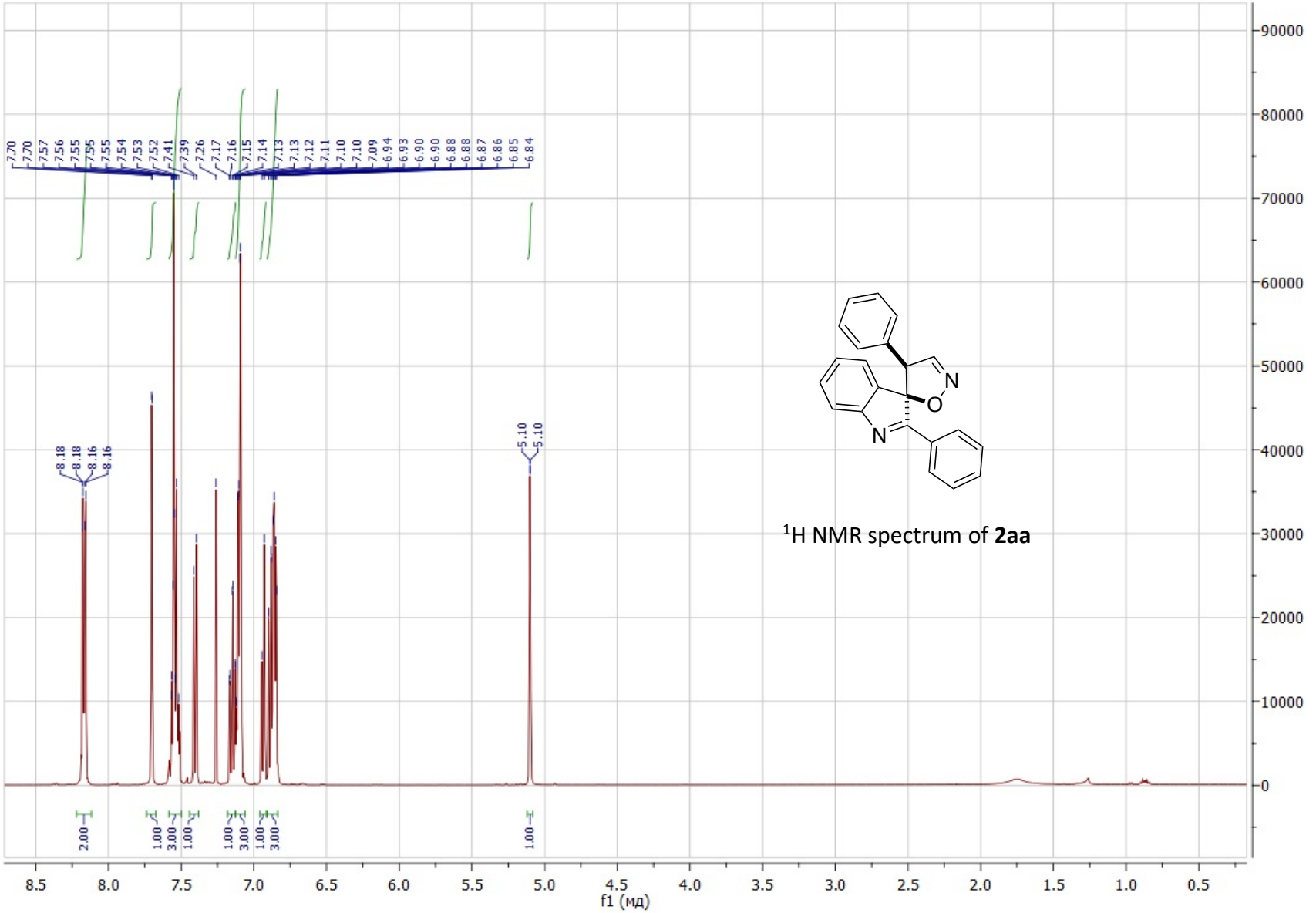


(3*R,4'*S**)-5-methoxy-2,4'-diphenyl-4'*H*-spiro[indole-3,5'-isoxazole]** (**2ia**): This compound was obtained via Typical Procedure from 5-methoxy-2-phenyl-1*H*-indole (**4i**) (112 mg, 0.50 mmol) and (2-nitrovinyl)benzene (**3a**) (82 mg, 0.55 mmol). The titled material was obtained as yellow oil, R_f 0.33 (hexane/acetone 6:1). Yield 160 mg (0.45 mmol, 90%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.08 (m, 2H), 7.71 (d, *J* = 1.6 Hz, 1H), 7.56 – 7.49 (m, 3H), 7.32 (d, *J* = 8.4 Hz, 1H), 7.17 – 7.10 (m, 3H), 6.87 (dd, *J* = 6.5, 3.0 Hz, 2H), 6.66 (dd, *J* = 8.4, 2.5 Hz, 1H), 6.46 (d, *J* = 2.5 Hz, 1H), 5.10 (d, *J* = 1.5 Hz, 1H), 3.61 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.6, 158.3, 149.4, 146.2, 137.2, 133.1, 131.7, 131.5, 129.2 (2C), 128.7 (2C), 128.3, 128.1 (2C), 127.8 (2C), 121.7, 115.3, 111.0, 97.5, 61.7, 55.8; FT IR (film, cm^{-1}): 3065, 3035, 2964, 2934, 2837, 1606, 1546, 1475, 1359, 1292, 1201, 1175, 1028;

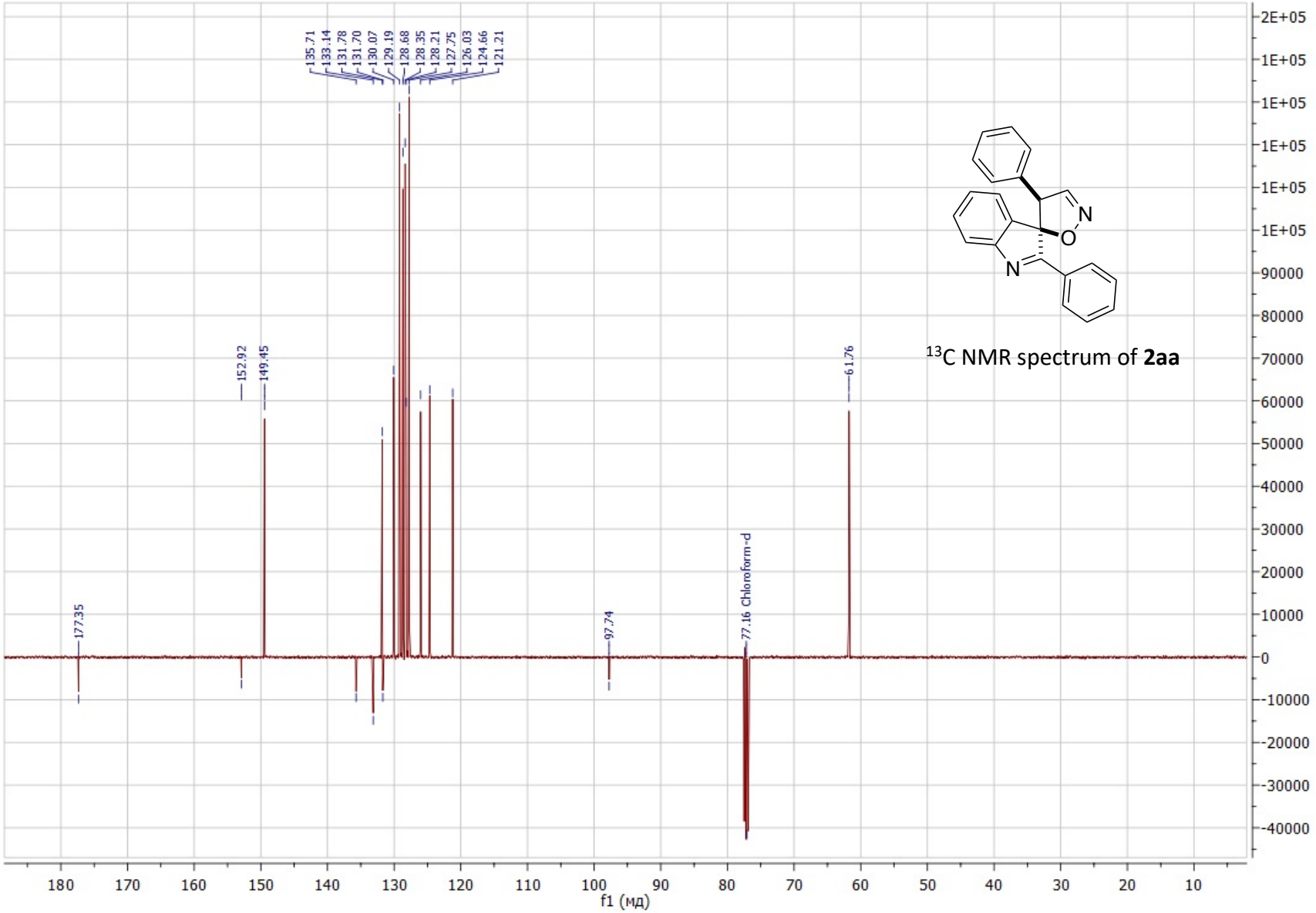
HRMS (ES TOF) calc`d for $C_{23}H_{19}N_2O_2$ $(M+H)^+$ 355.1441, found 355.1438 (0.7 ppm); calc`d for $C_{23}H_{18}N_2NaO_2$ $(M+Na)^+$: 377.1260, found 377.1268, (2.0 ppm).



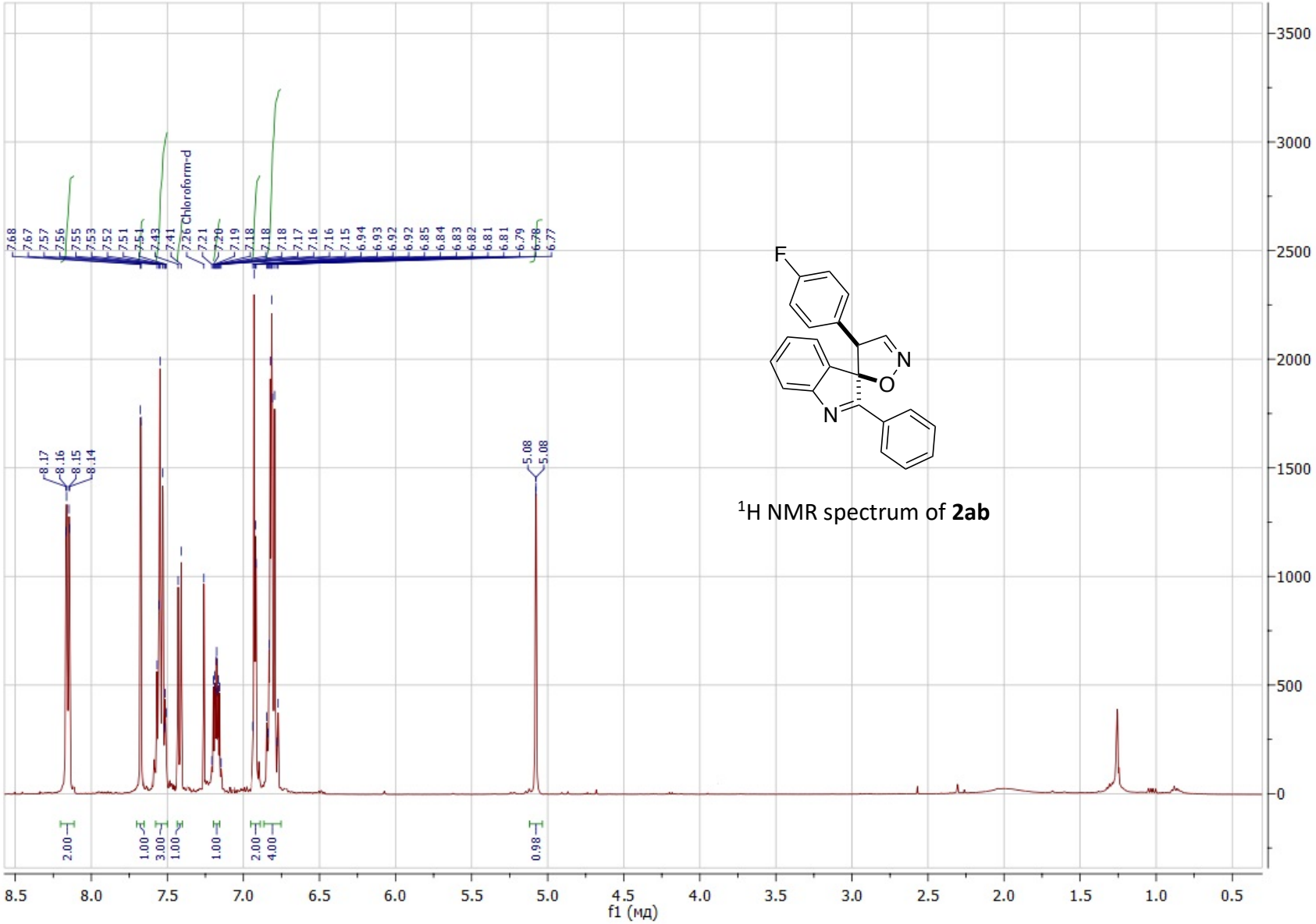
(3*R,*4*'S*)-7-Chloro-2,4'-diphenyl-4'H-spiro[indole-3,5'-isoxazole]** (**2ja**): This compound was obtained via Typical Procedure from 7-chloro-2-phenyl-1*H*-indole (**4j**) (114 mg, 0.50 mmol) and (2-nitrovinyl)benzene (**3a**) (82 mg, 0.55 mmol). The titled material was obtained as pink solid, m.p. 162-165^{o}C (benzene/hexanes), R_f 0.34 (benzene/hexanes 1:0.4). Yield 154 mg, (0.43 mmol, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 7.1 Hz, 2H), 7.70 (s, 1H), 7.59 – 7.50 (m, 3H), 7.16 – 7.09 (m, 4H), 6.89 – 6.78 (m, 4H), 5.12 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.3, 149.7, 149.5, 137.8, 132.8, 132.2, 131.3, 130.6, 129.2 (2C), 128.8 (2C), 128.6 (2C), 128.4, 127.7 (2C), 127.0, 126.3, 123.0, 98.3, 62.2; FT IR (film, cm^{-1}): 2923,2360, 1749, 1531,1460, 1246, 1190, 1044; HRMS (ES TOF) calc`d for $C_{22}H_{15}ClN_2NaO$ $(M+Na)^+$ 381.0765, found 381.0751 (3.8 ppm).



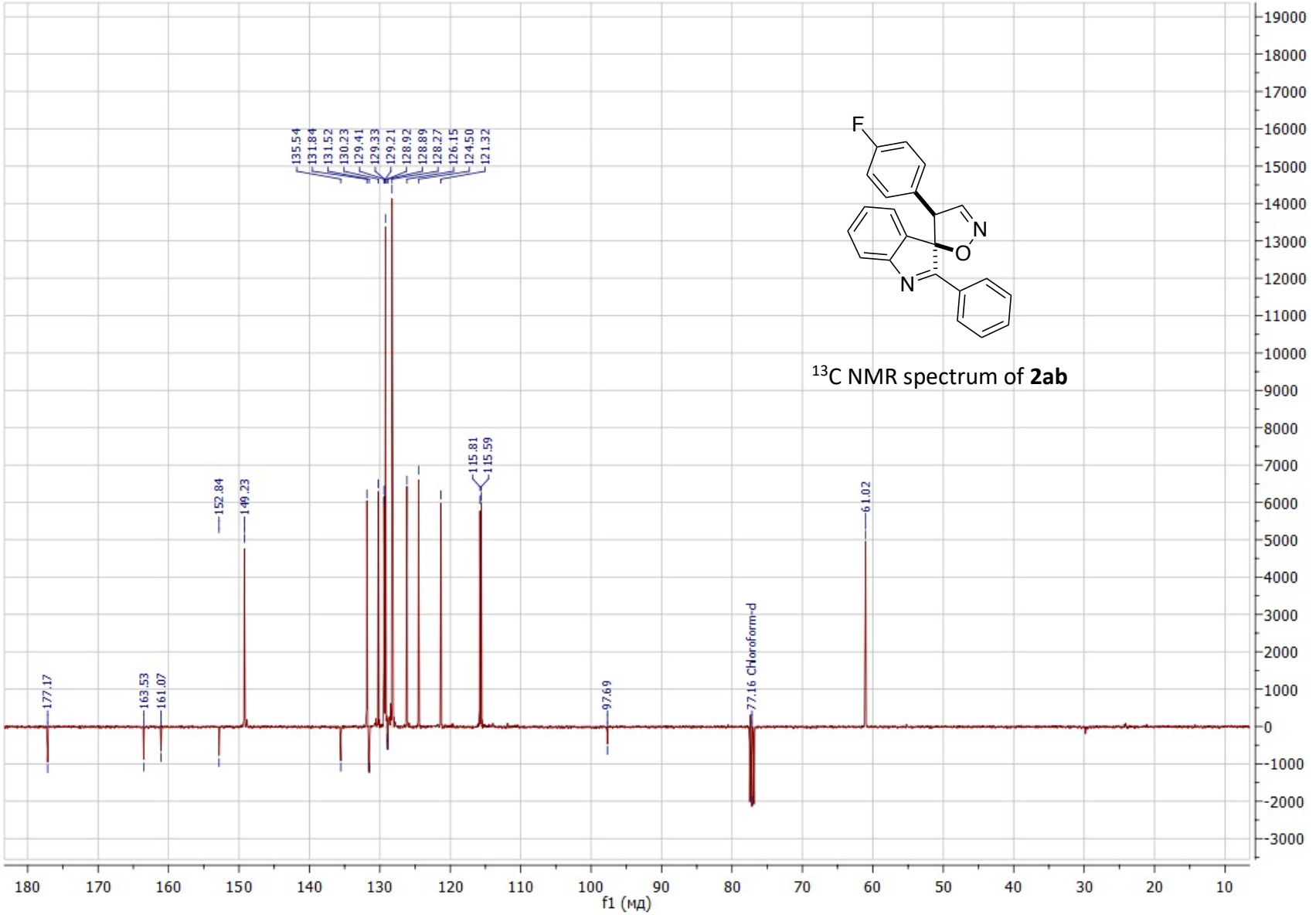
^{1}H NMR spectrum of **2aa**



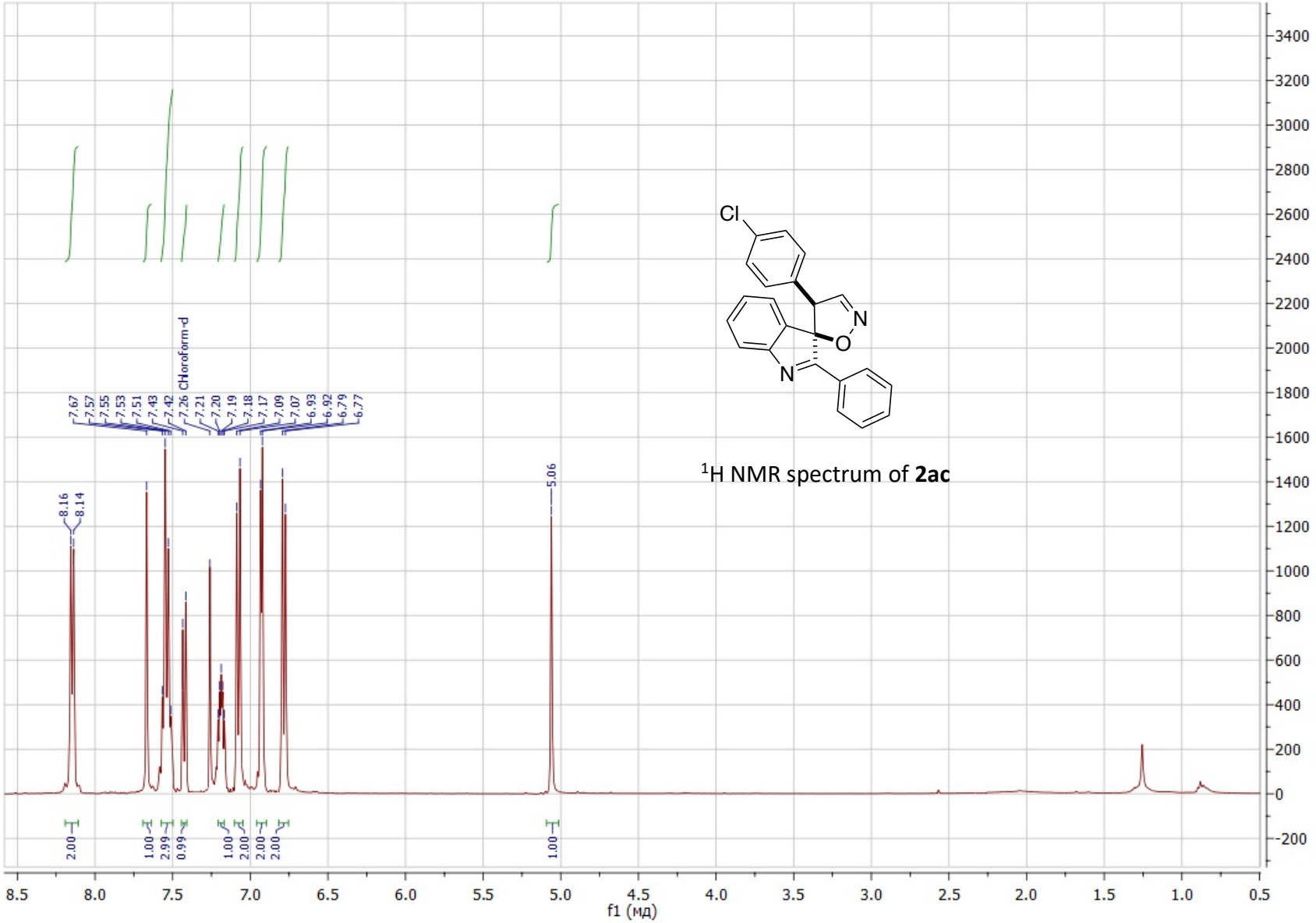
^{13}C NMR spectrum of **2aa**



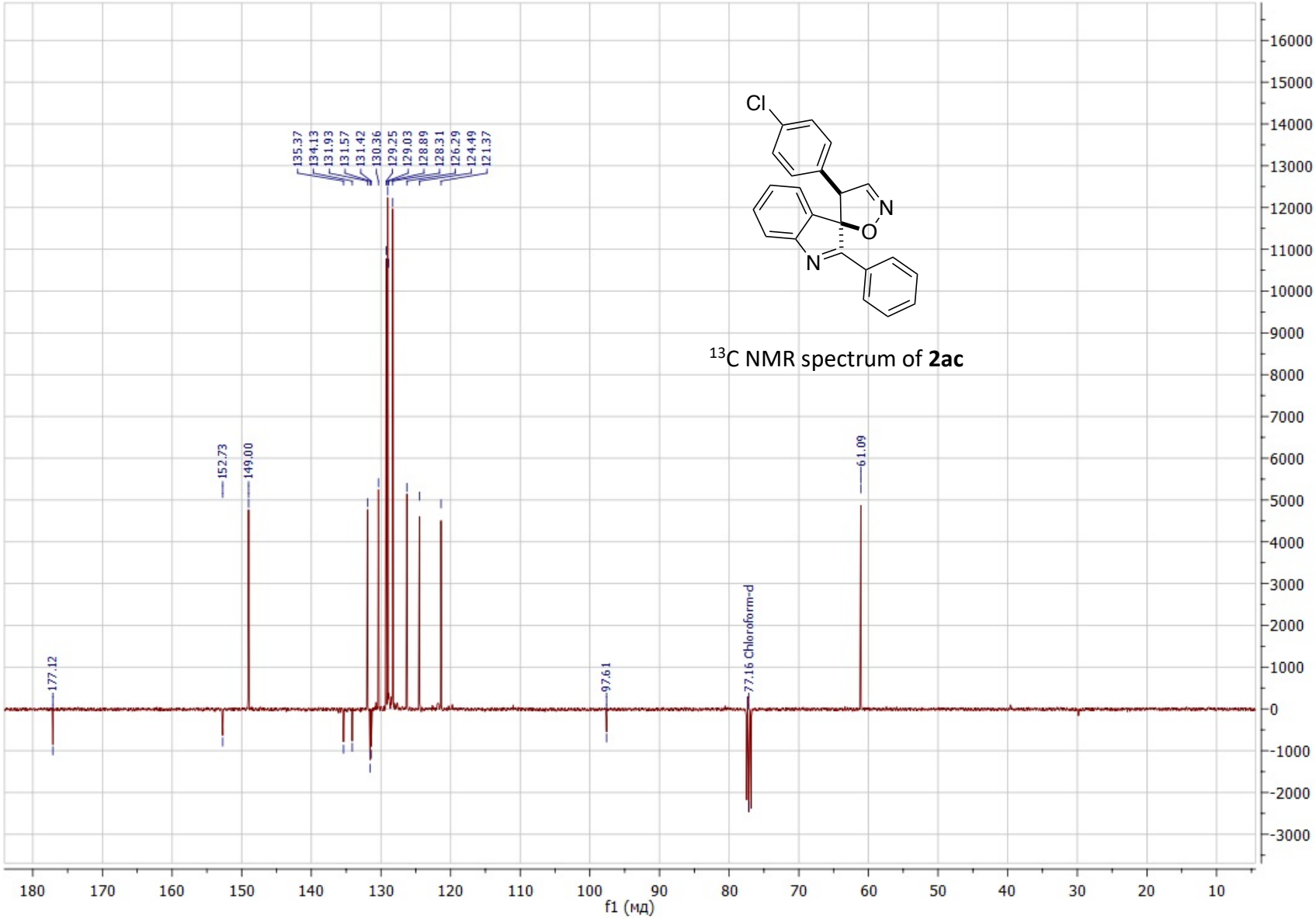
^{1}H NMR spectrum of **2ab**



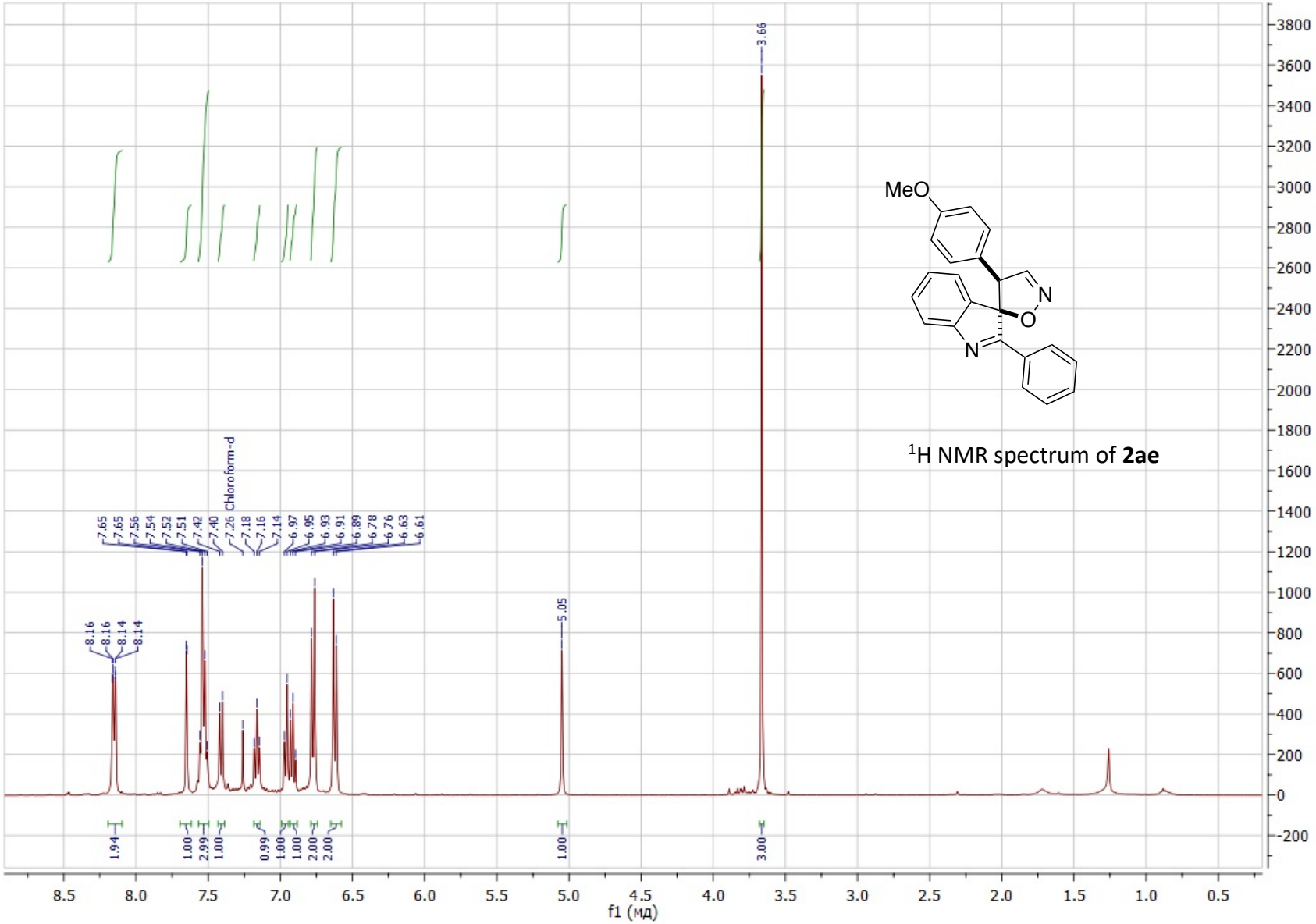
^{13}C NMR spectrum of **2ab**



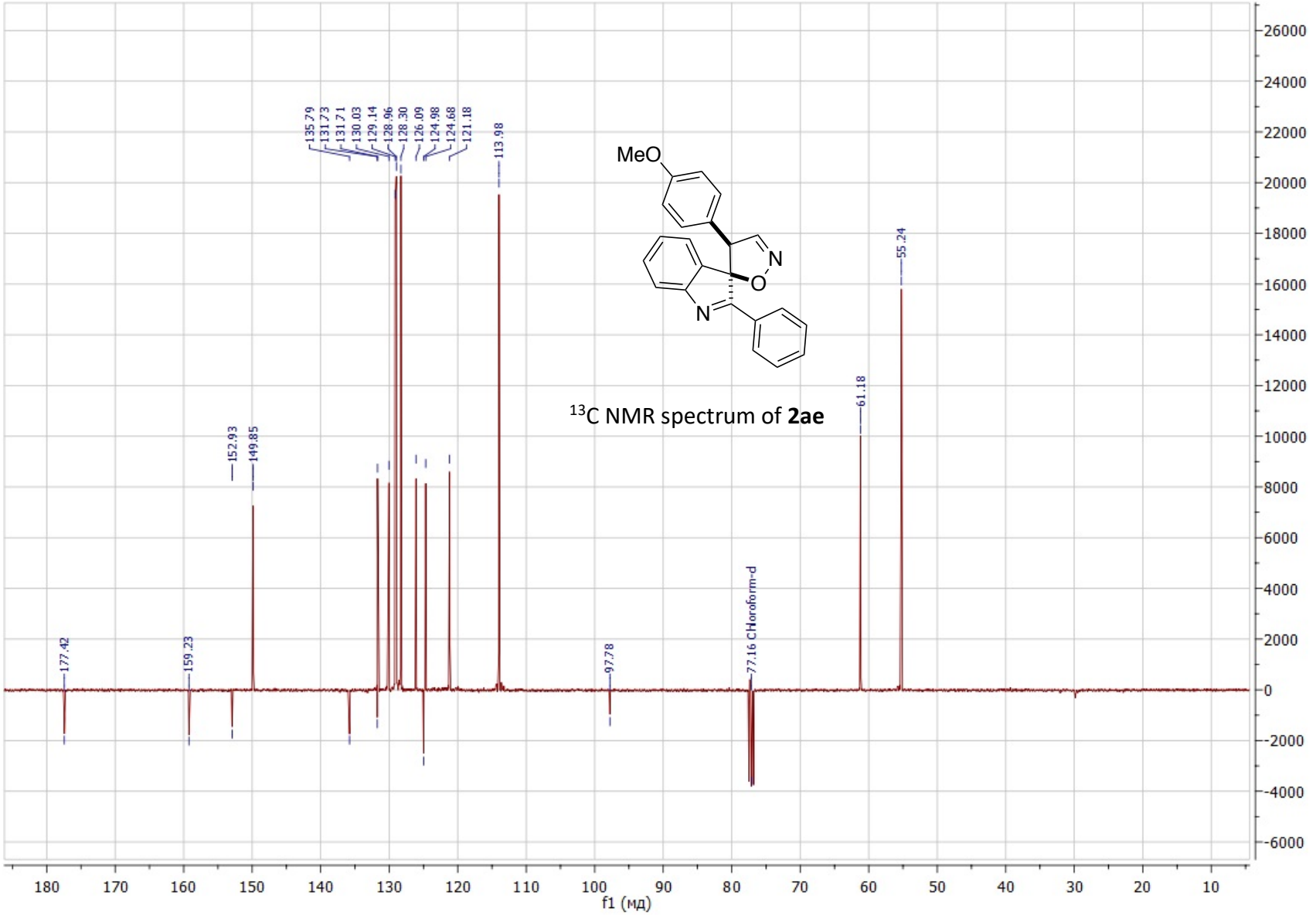
^{1}H NMR spectrum of **2ac**



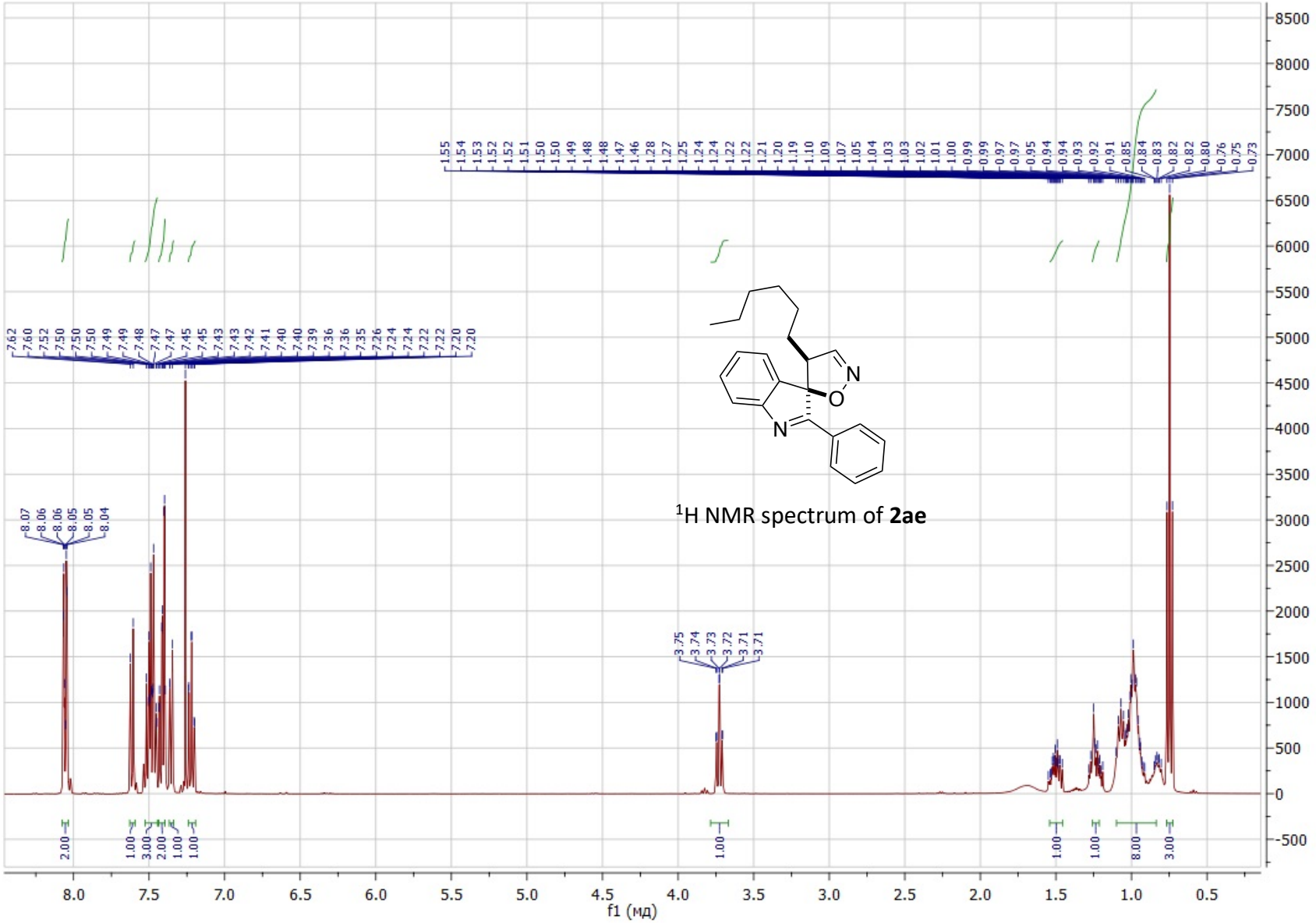
^{13}C NMR spectrum of **2ac**



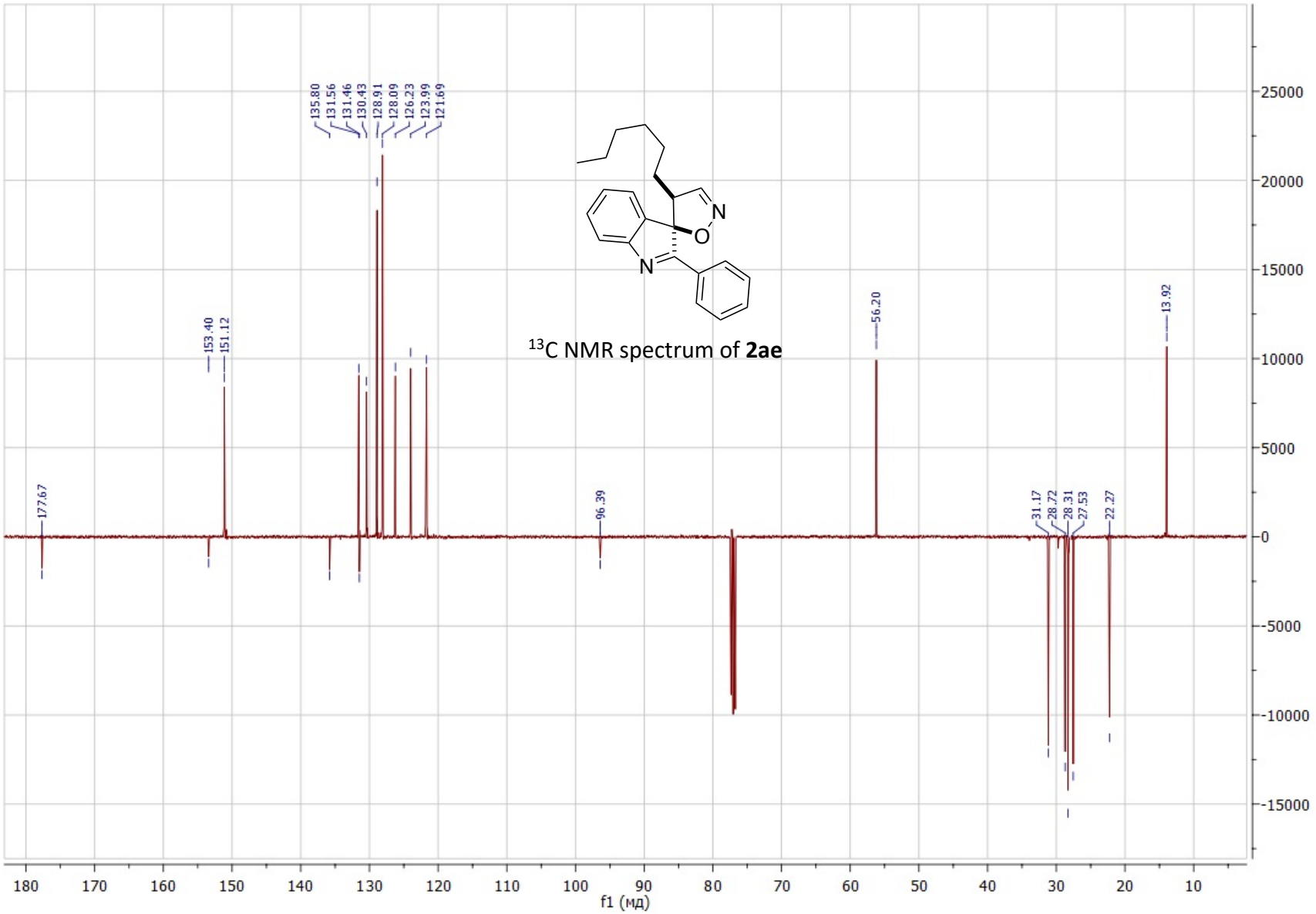
^{1}H NMR spectrum of **2ae**



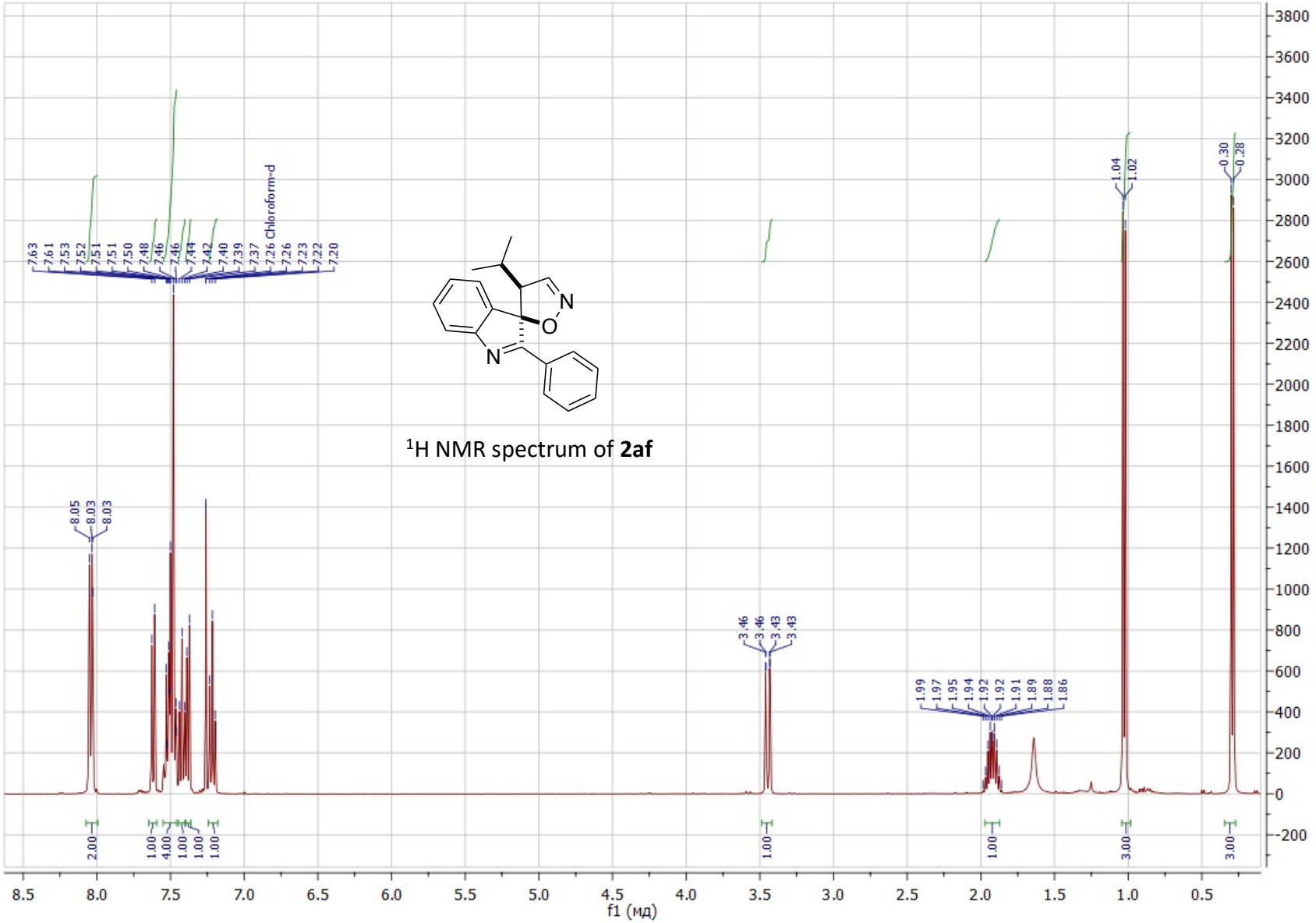
^{13}C NMR spectrum of **2ae**



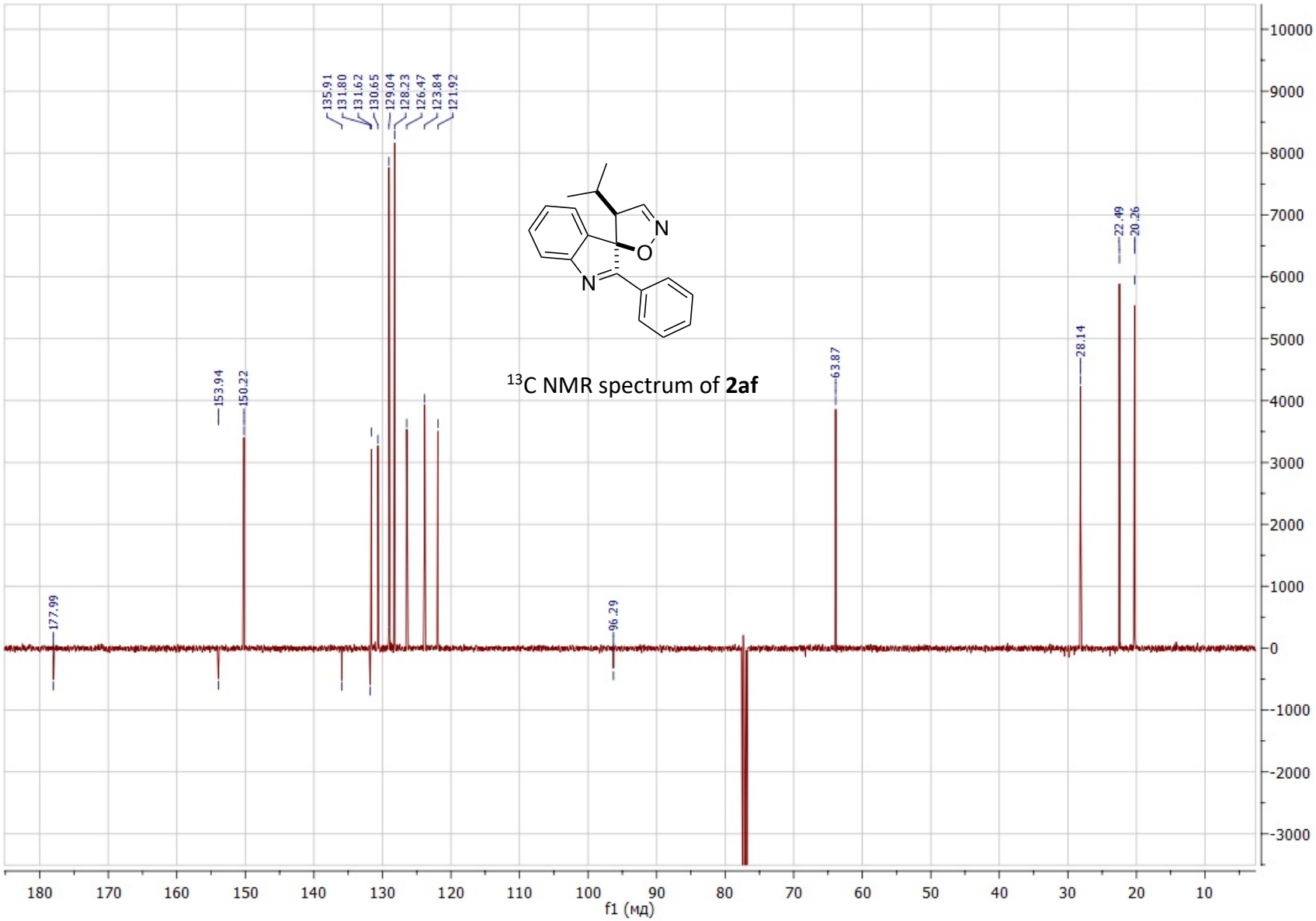
^{1}H NMR spectrum of **2ae**



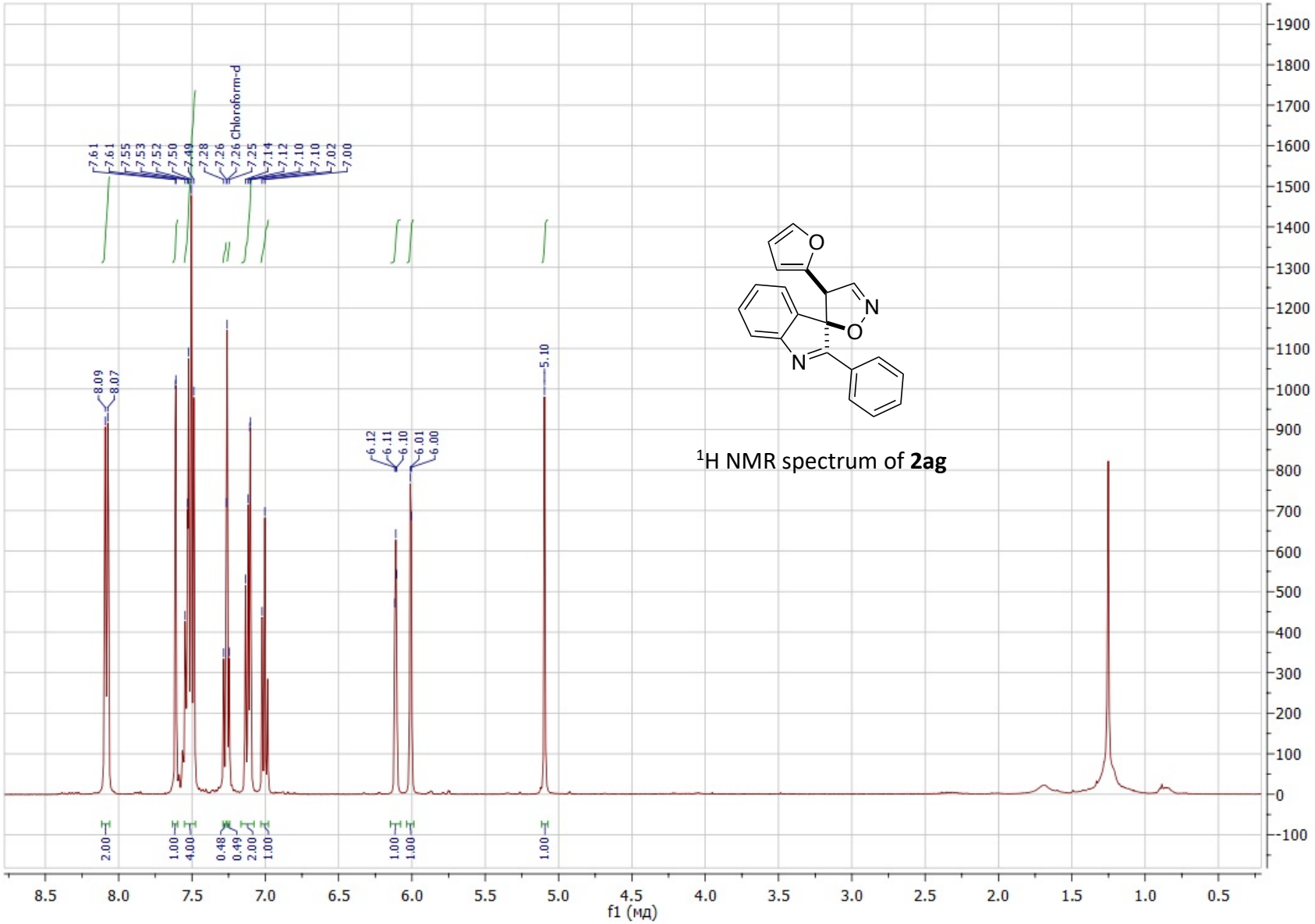
^{13}C NMR spectrum of **2ae**



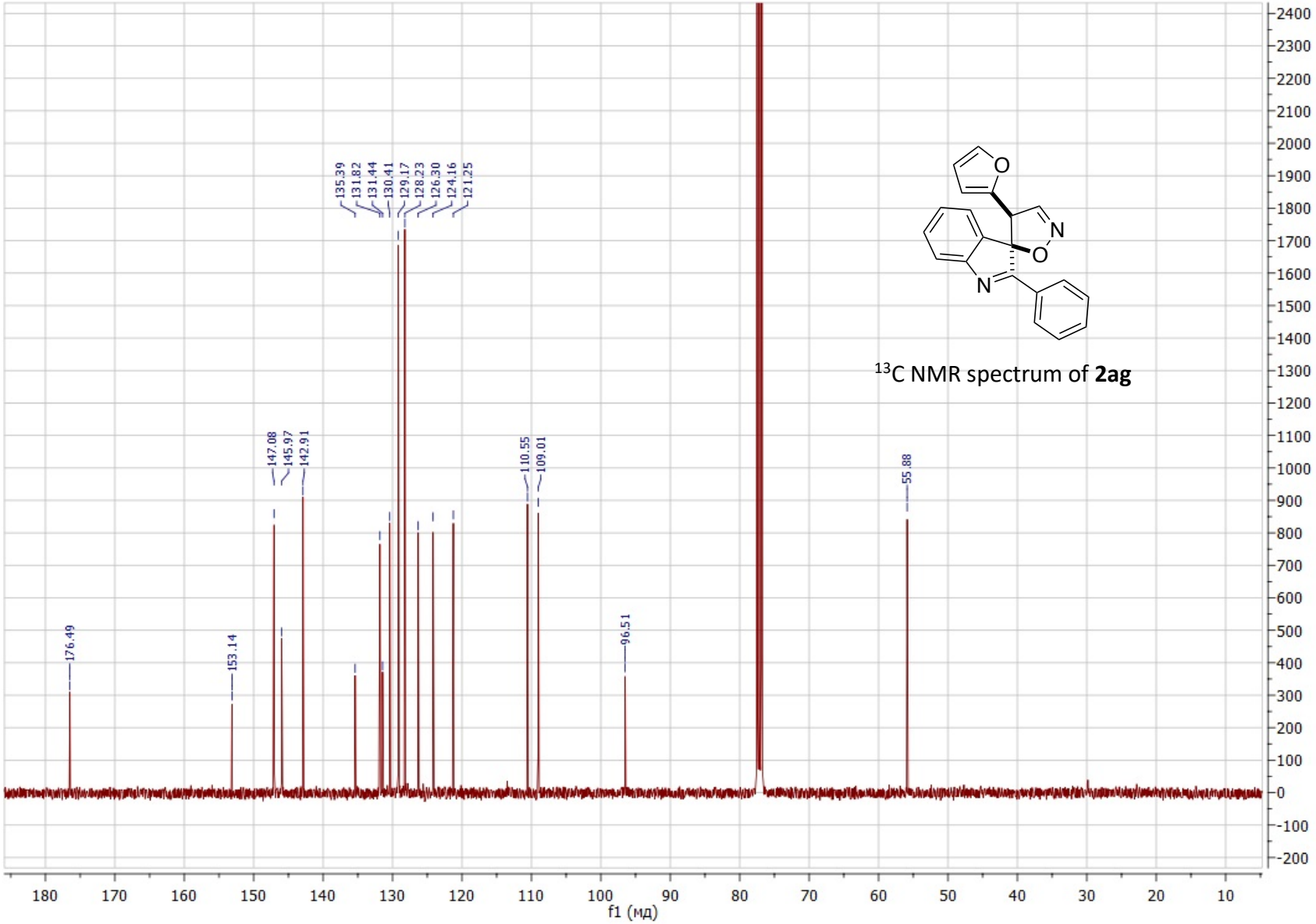
^{1}H NMR spectrum of **2af**



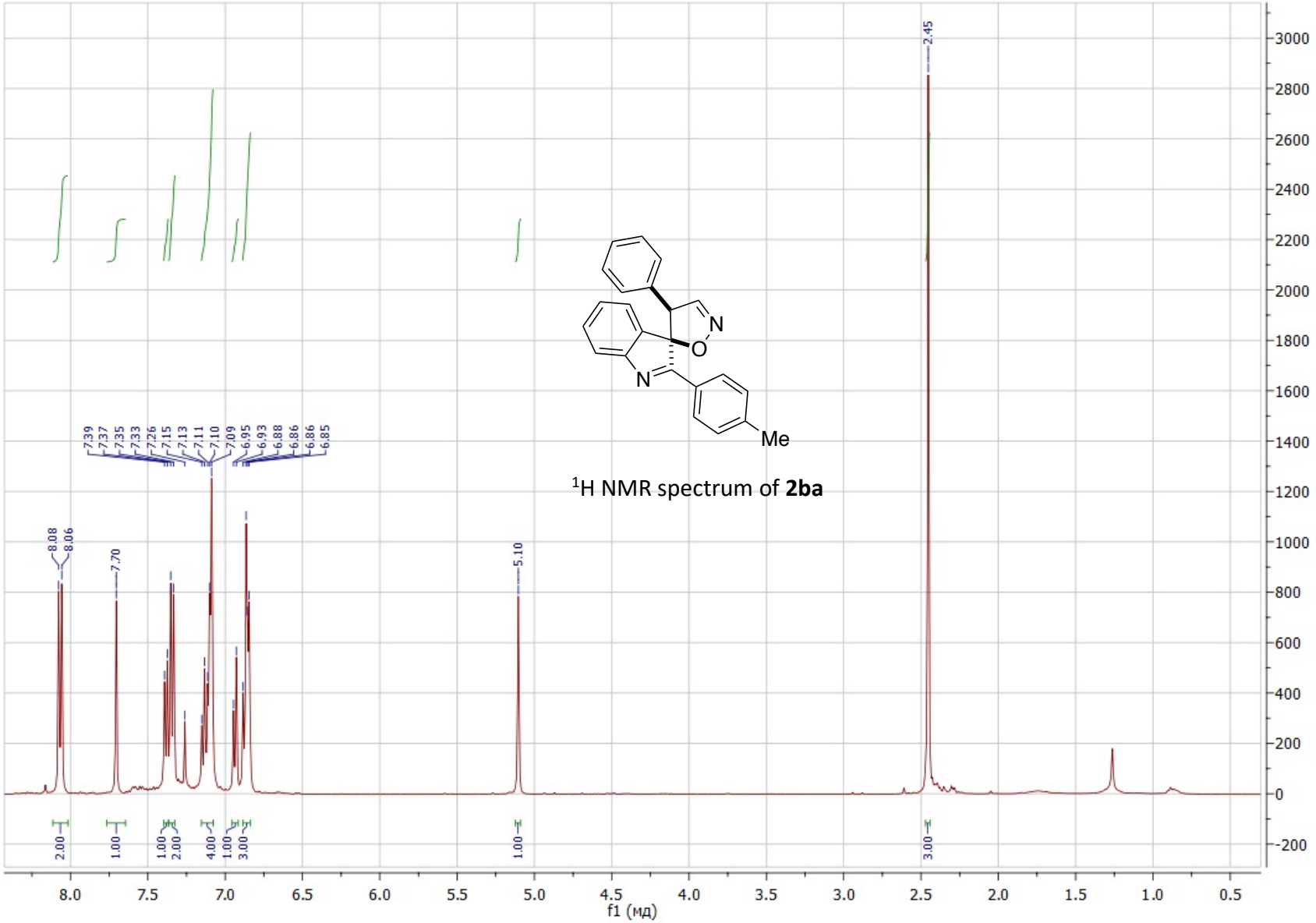
^{13}C NMR spectrum of **2af**



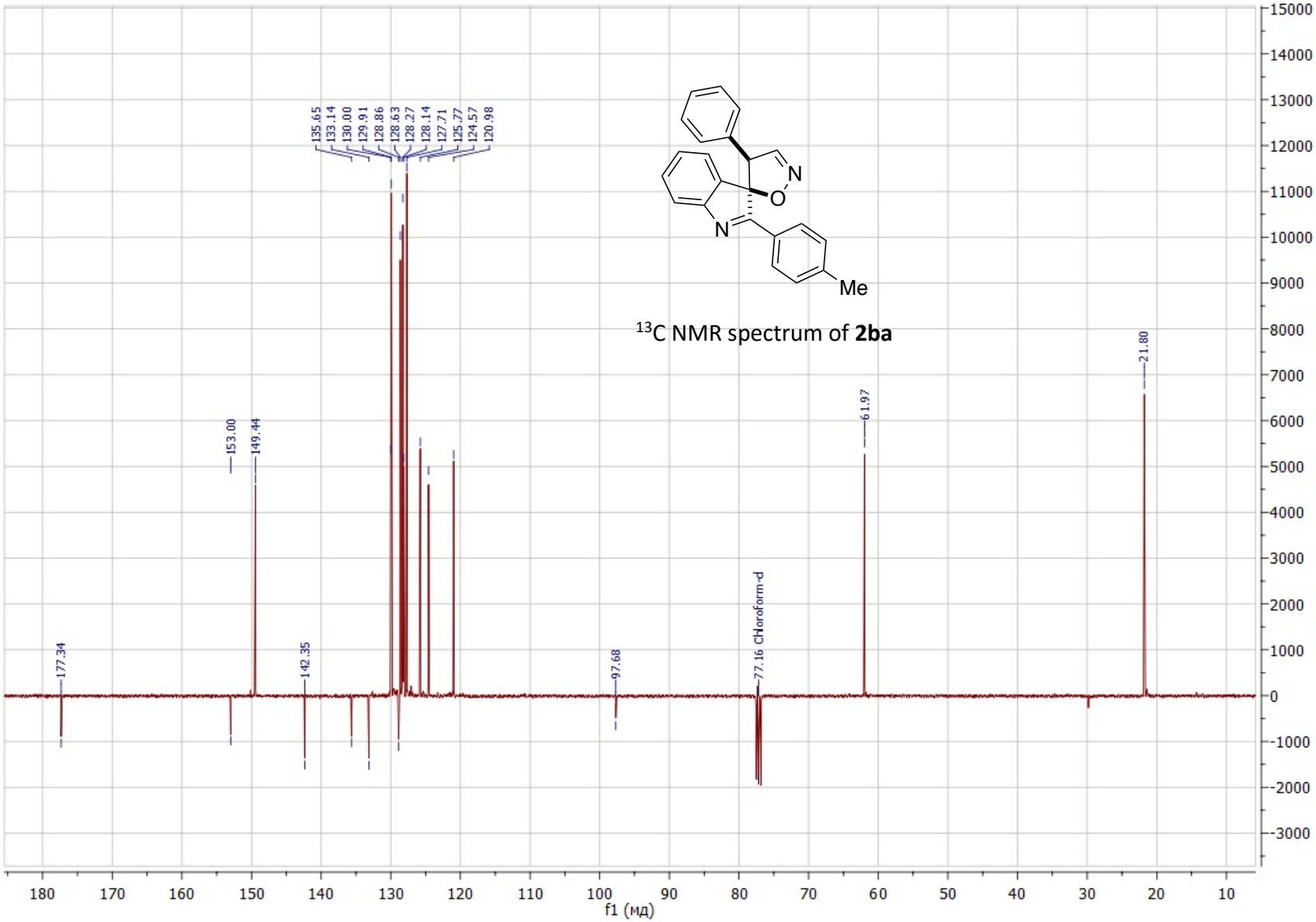
^{1}H NMR spectrum of **2ag**



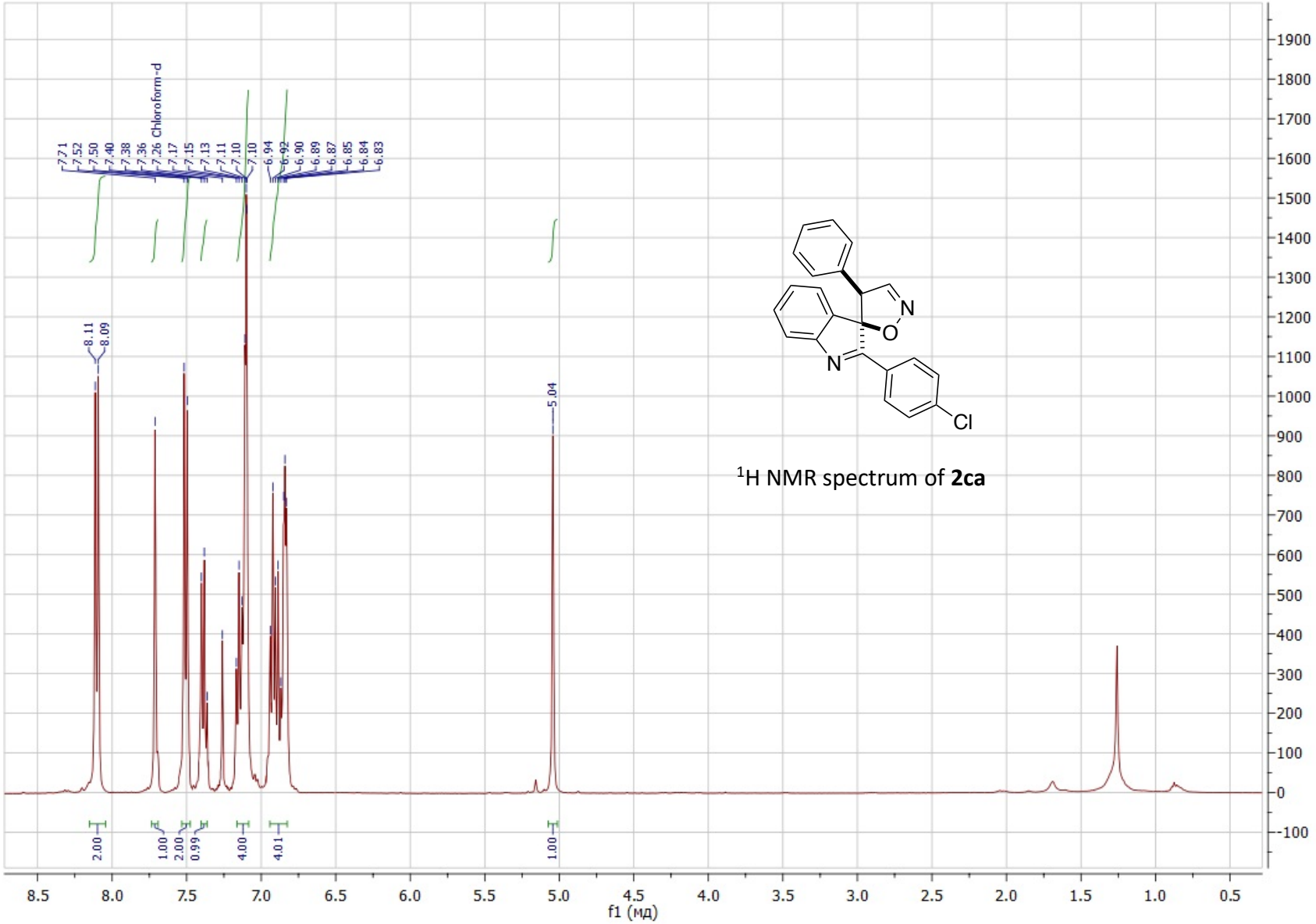
^{13}C NMR spectrum of **2ag**



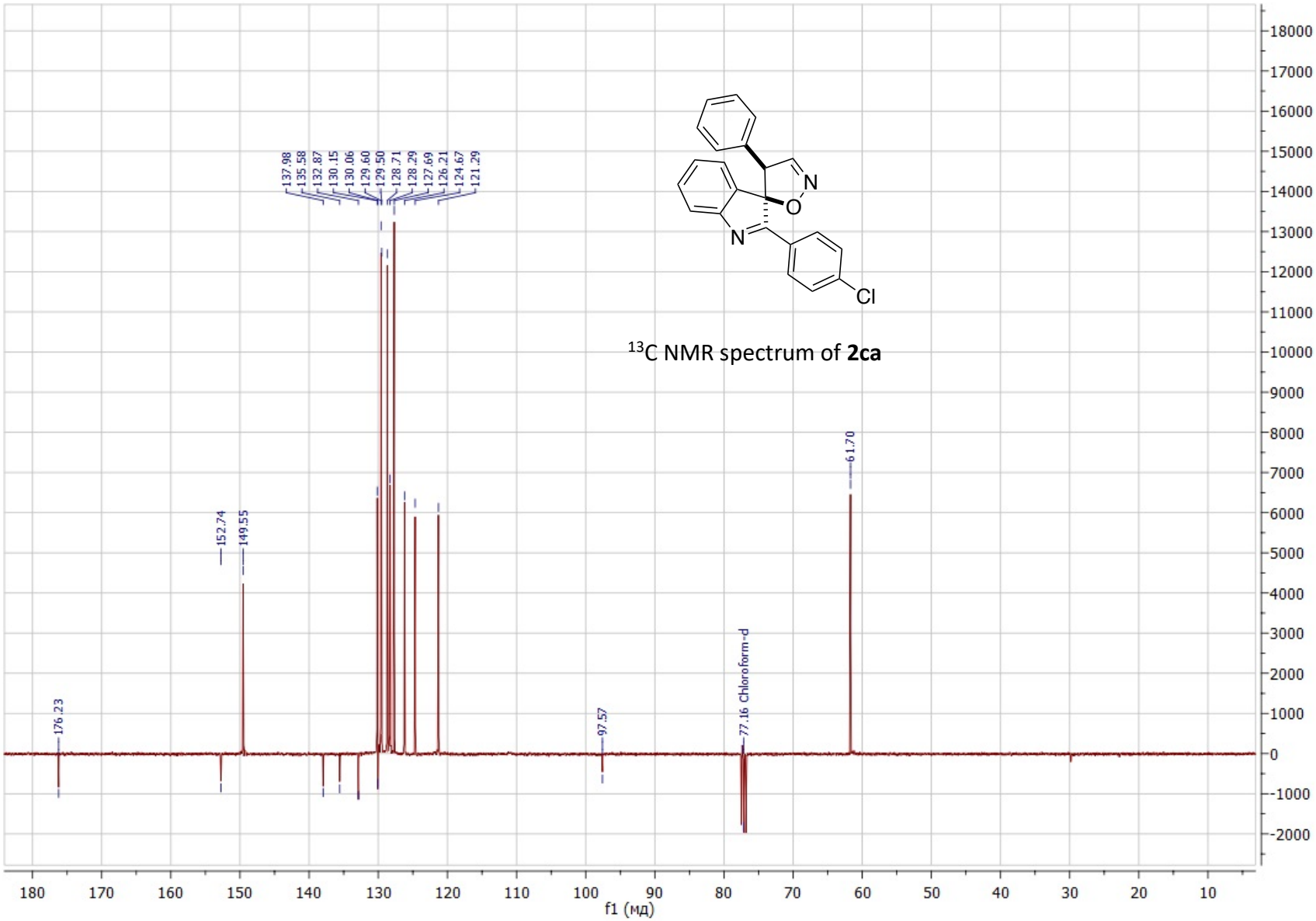
^{1}H NMR spectrum of **2ba**



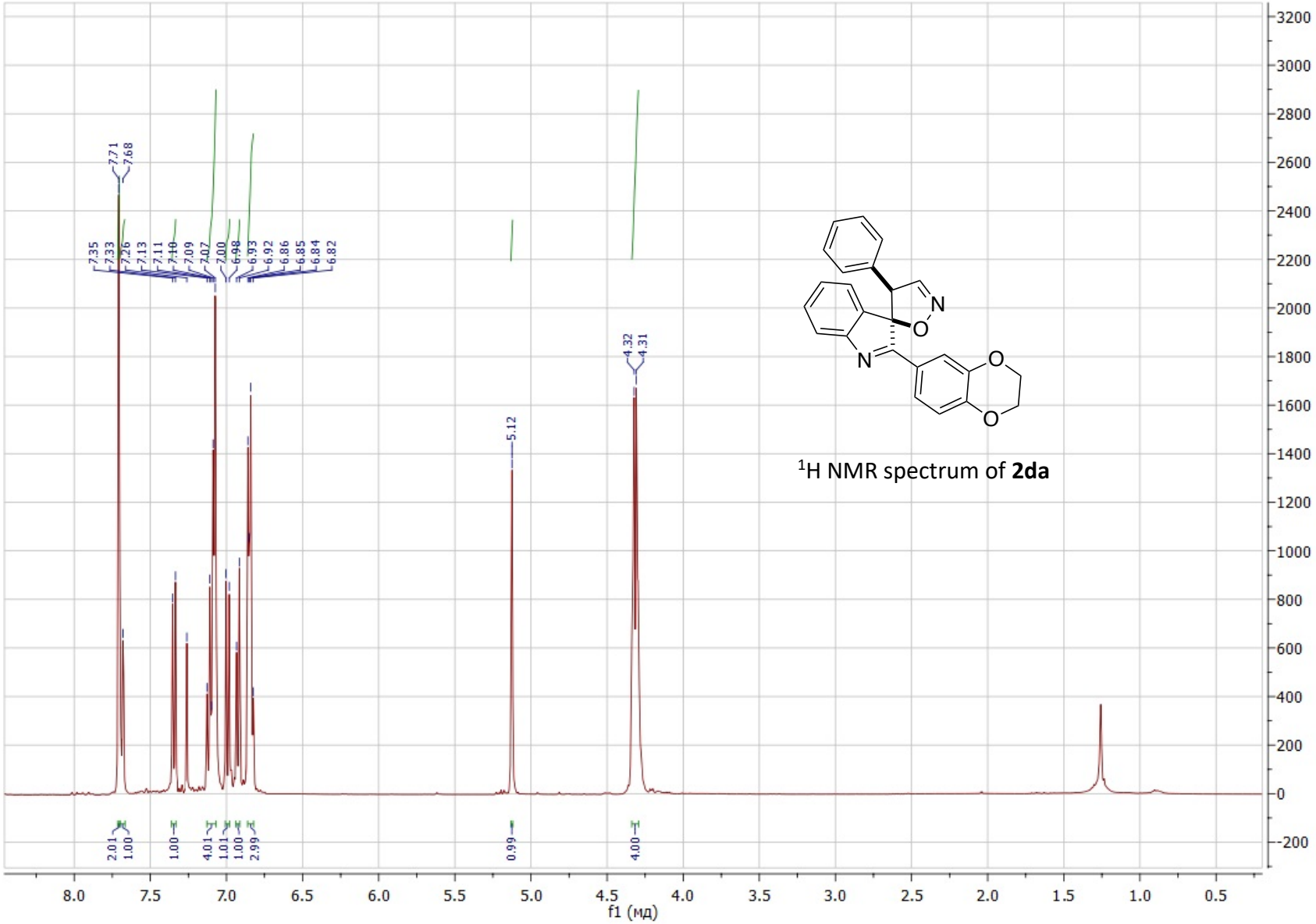
^{13}C NMR spectrum of **2ba**



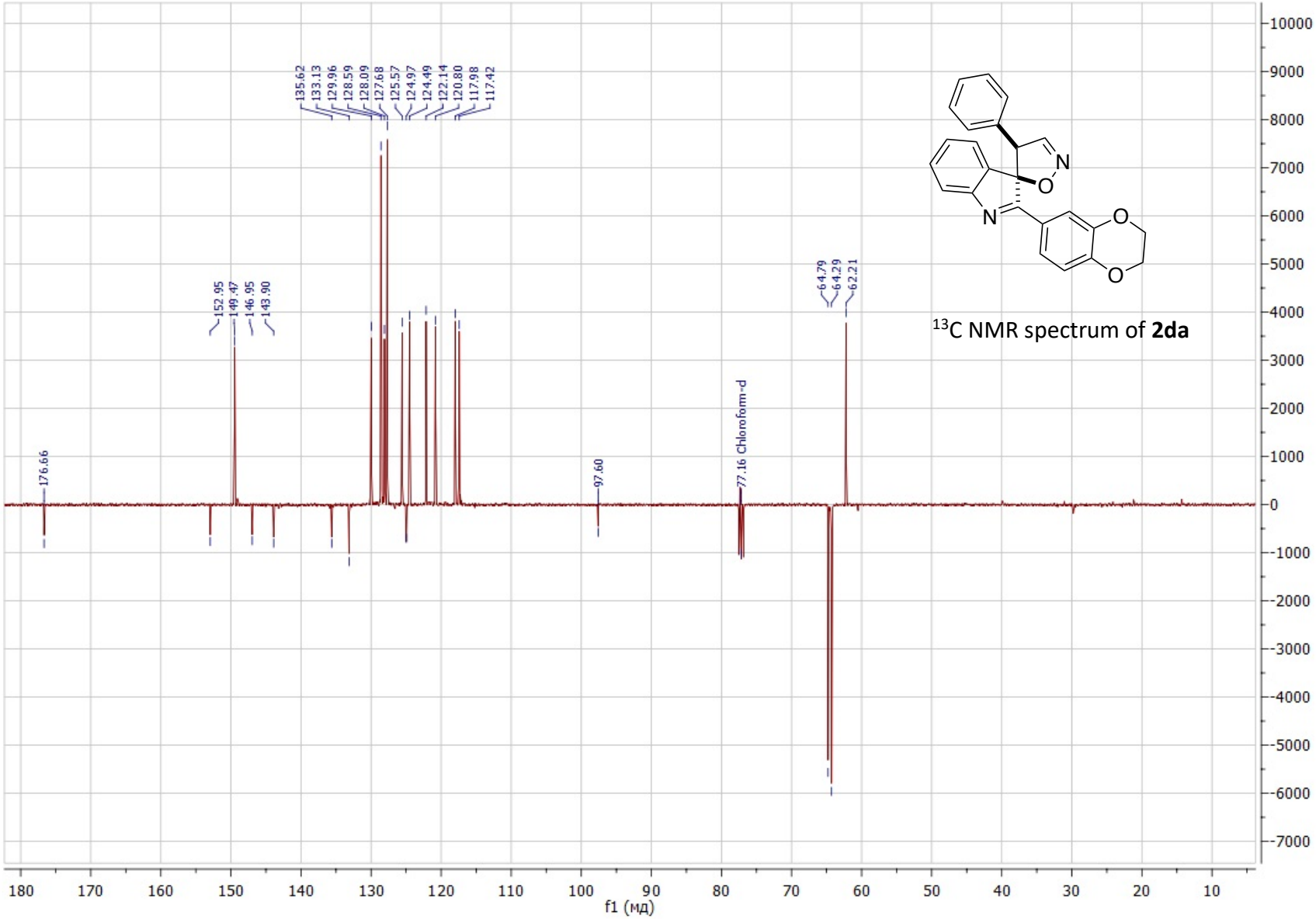
^{1}H NMR spectrum of **2ca**



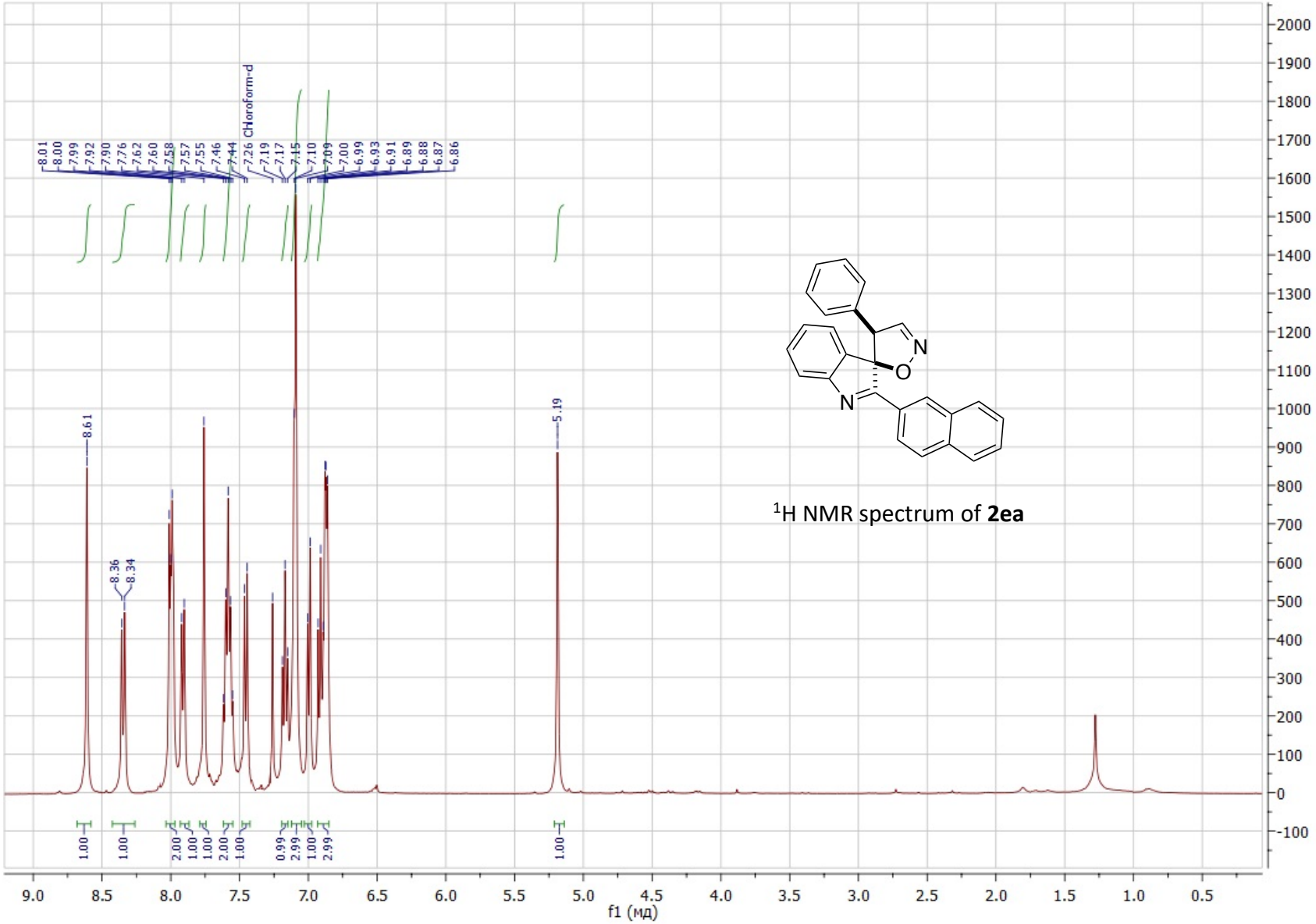
^{13}C NMR spectrum of **2ca**



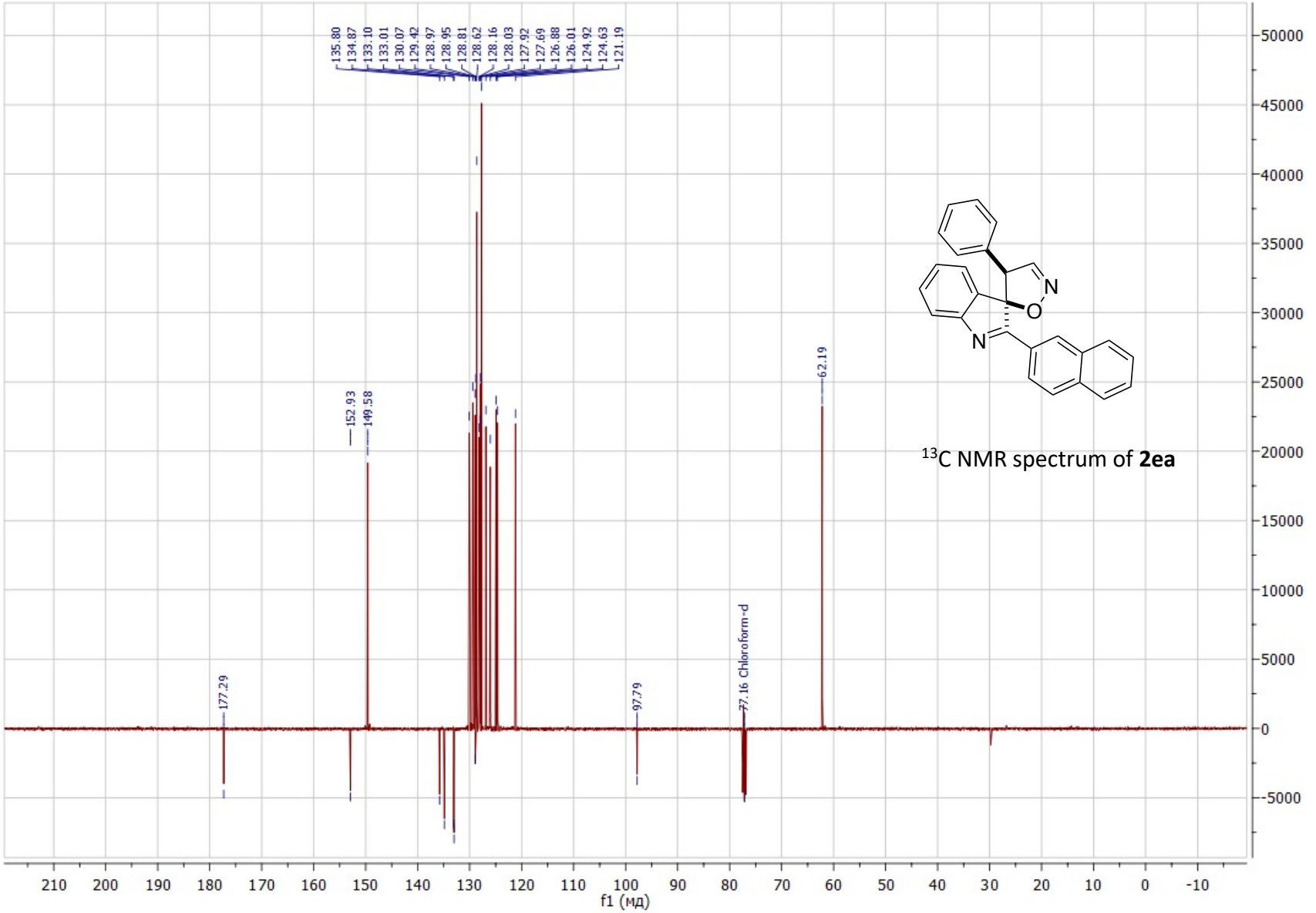
^{1}H NMR spectrum of **2da**



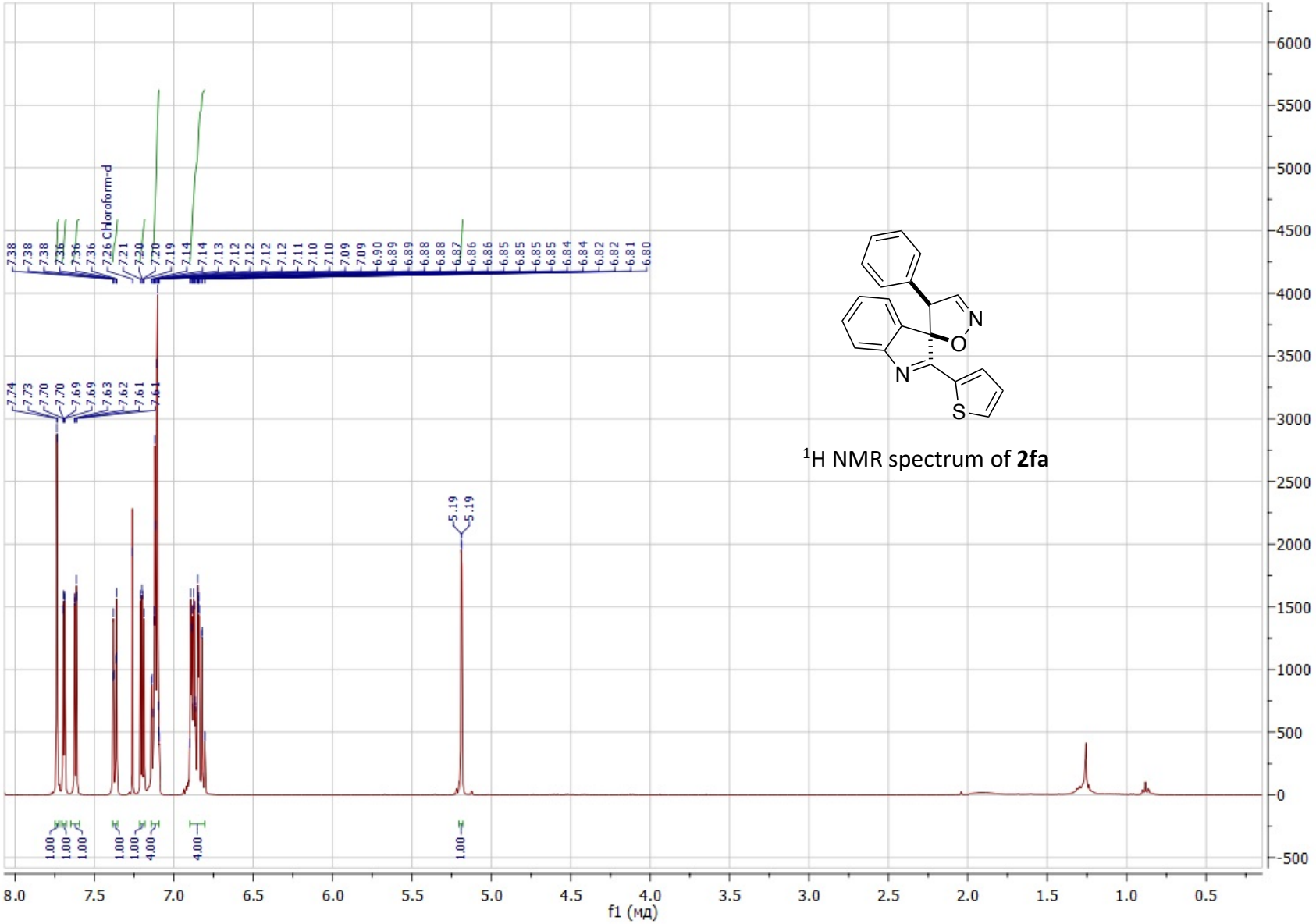
^{13}C NMR spectrum of **2da**



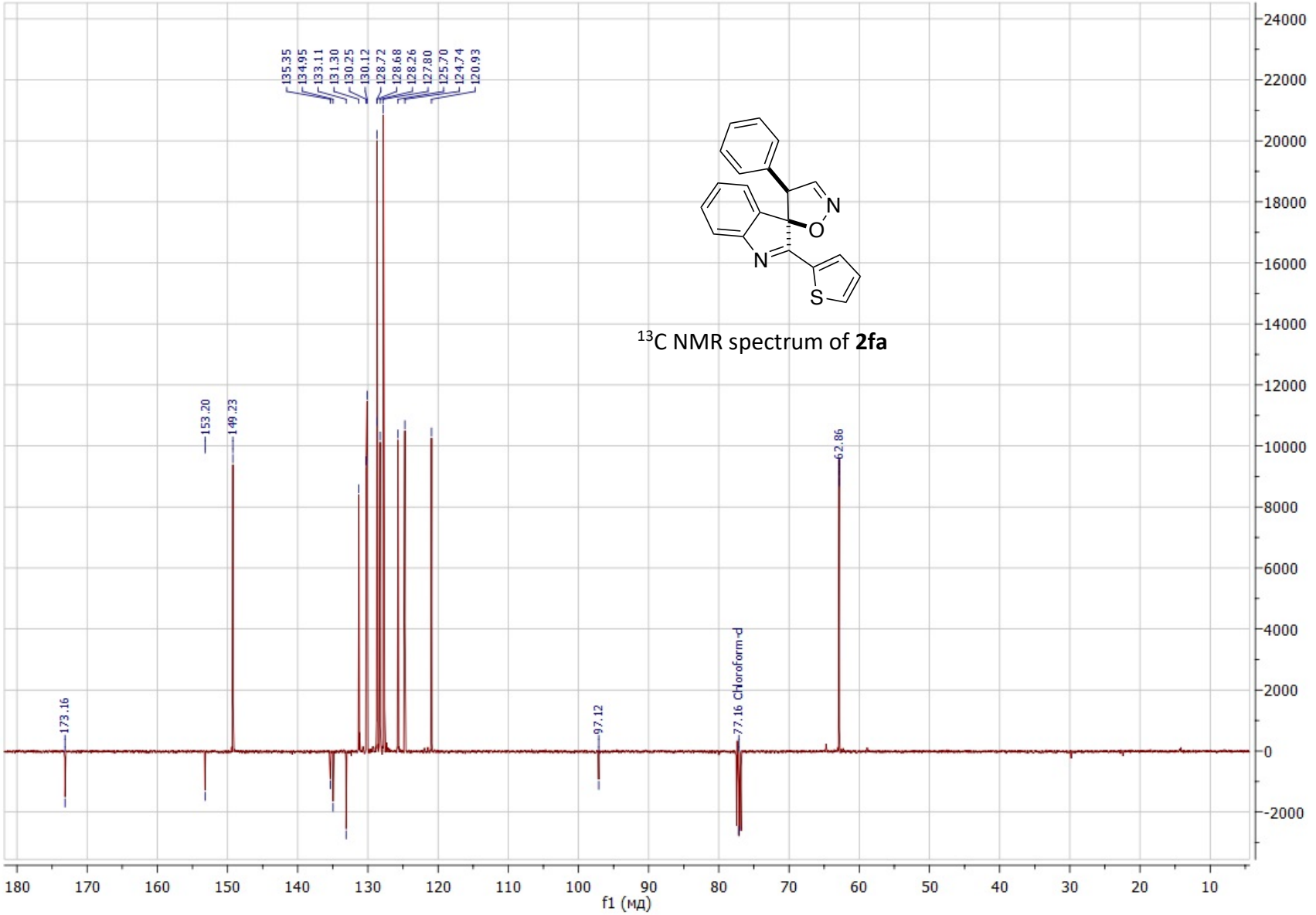
^{1}H NMR spectrum of **2ea**



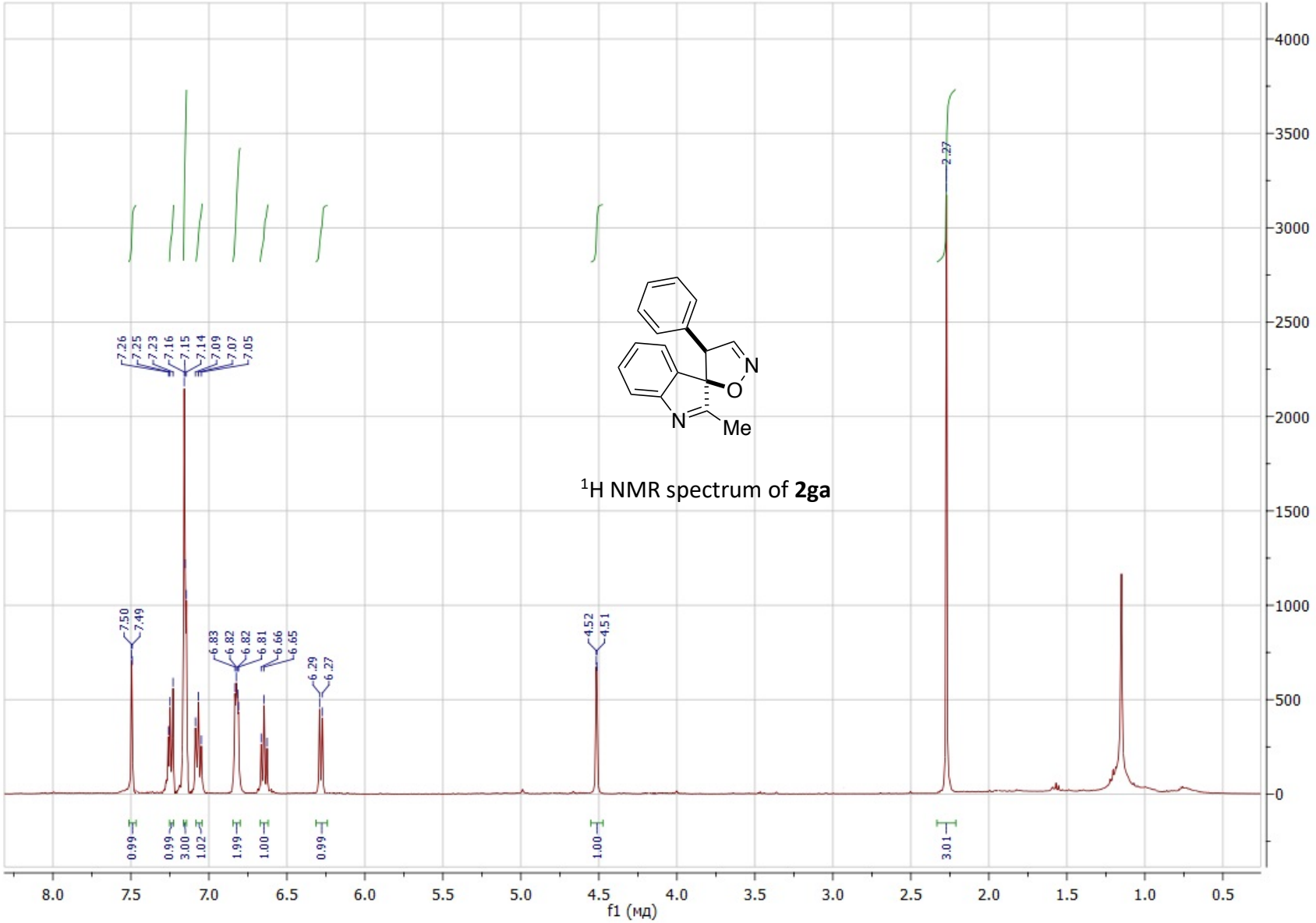
^{13}C NMR spectrum of **2ea**



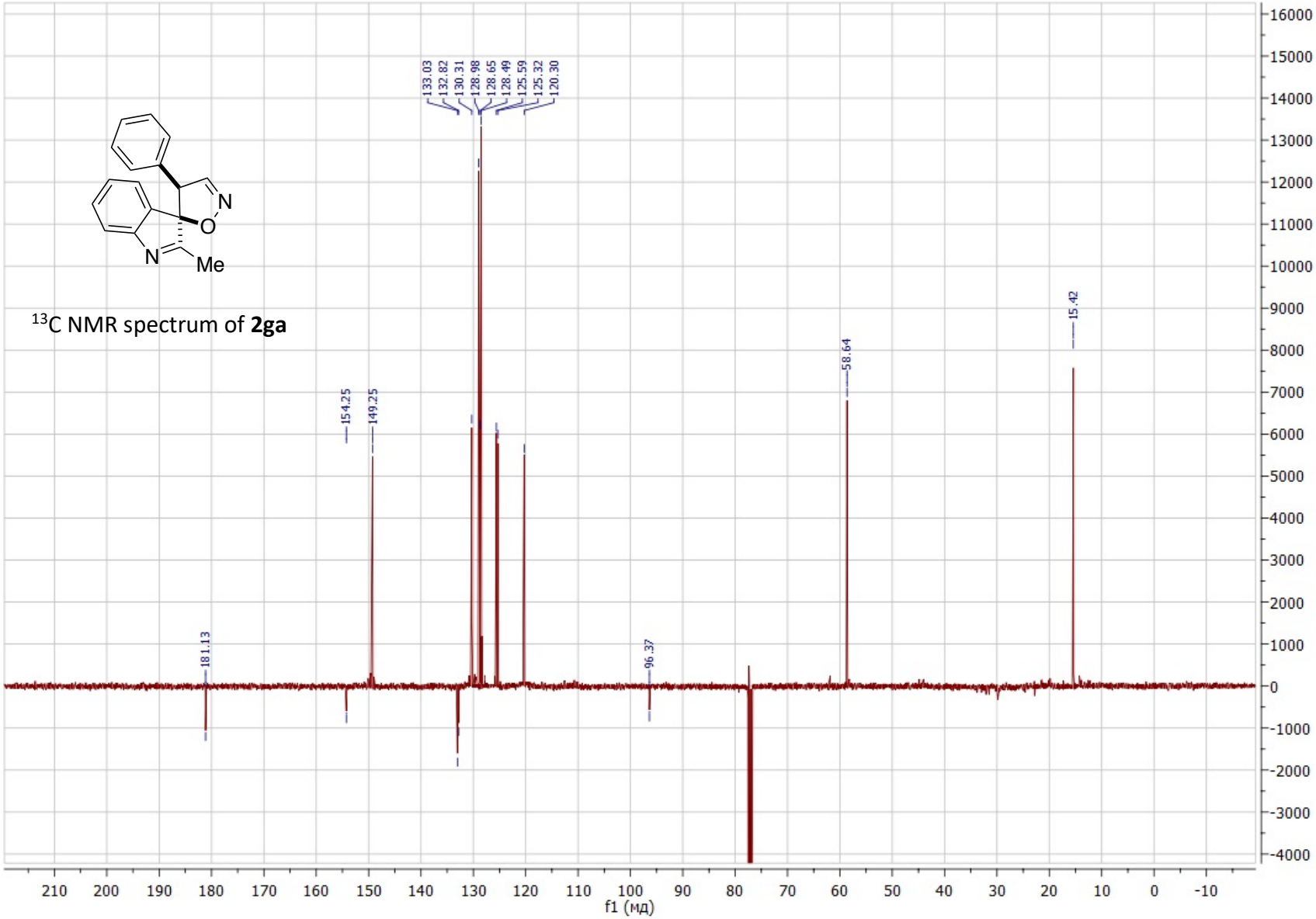
^{1}H NMR spectrum of **2fa**



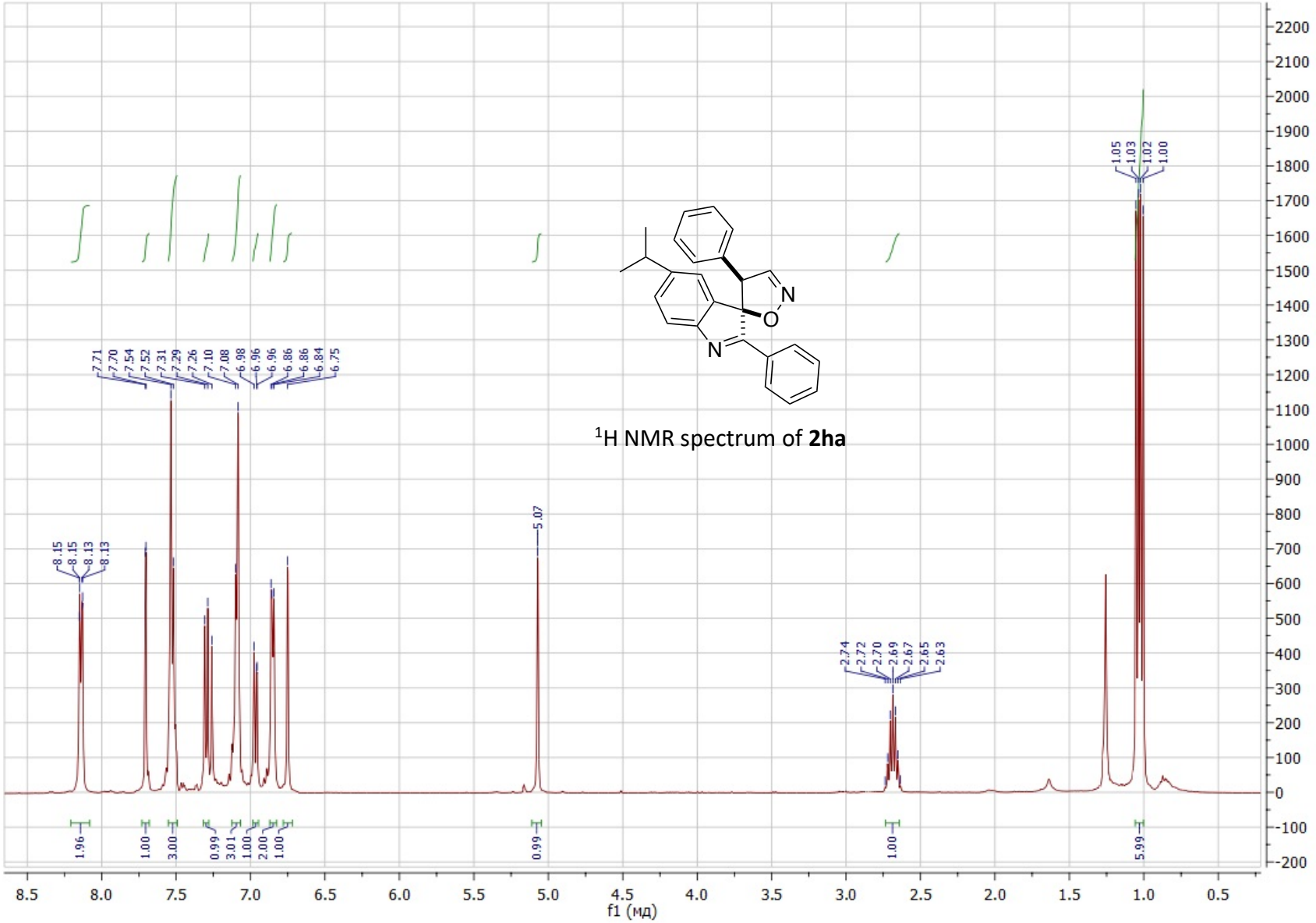
^{13}C NMR spectrum of **2fa**



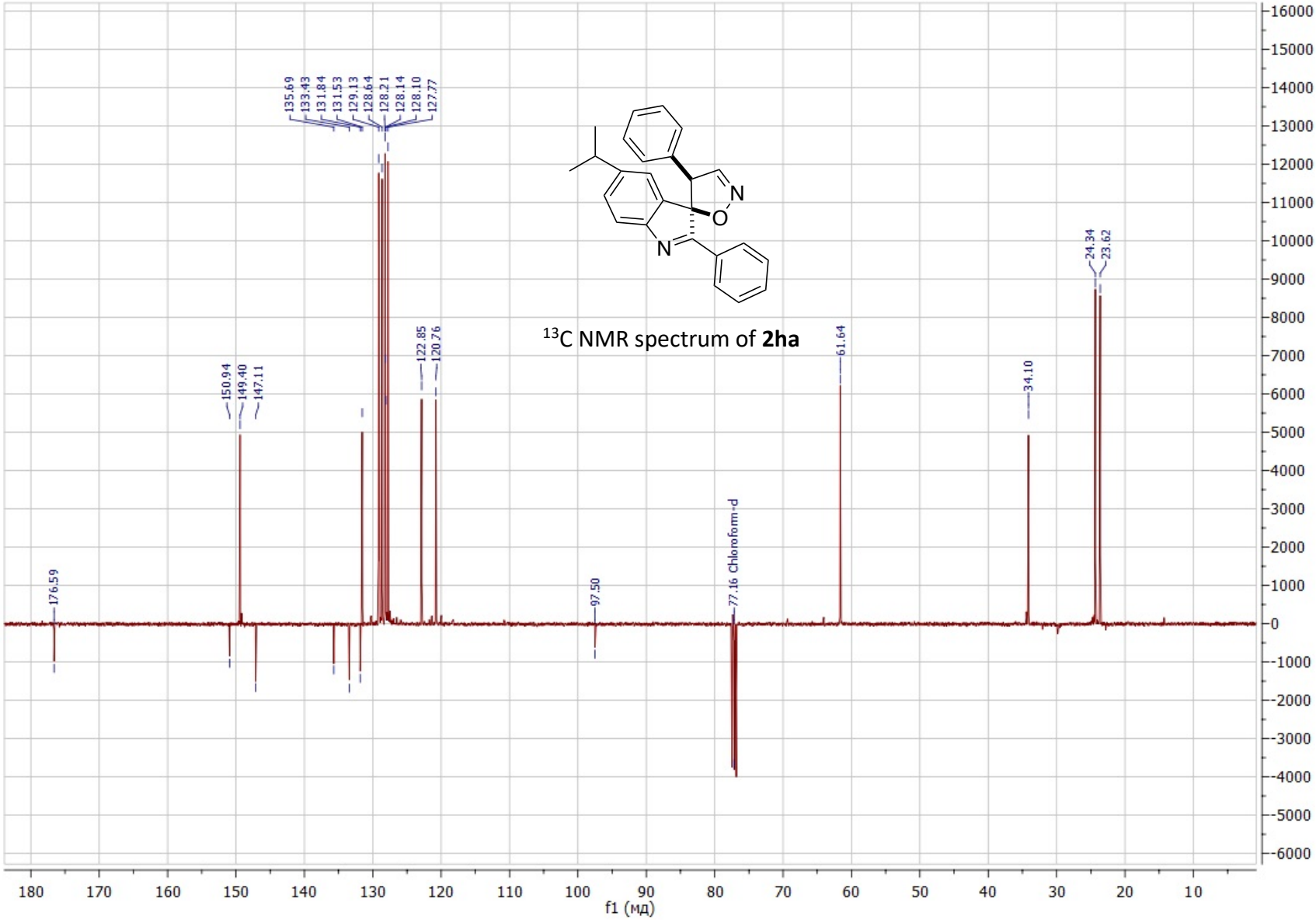
^{1}H NMR spectrum of **2ga**



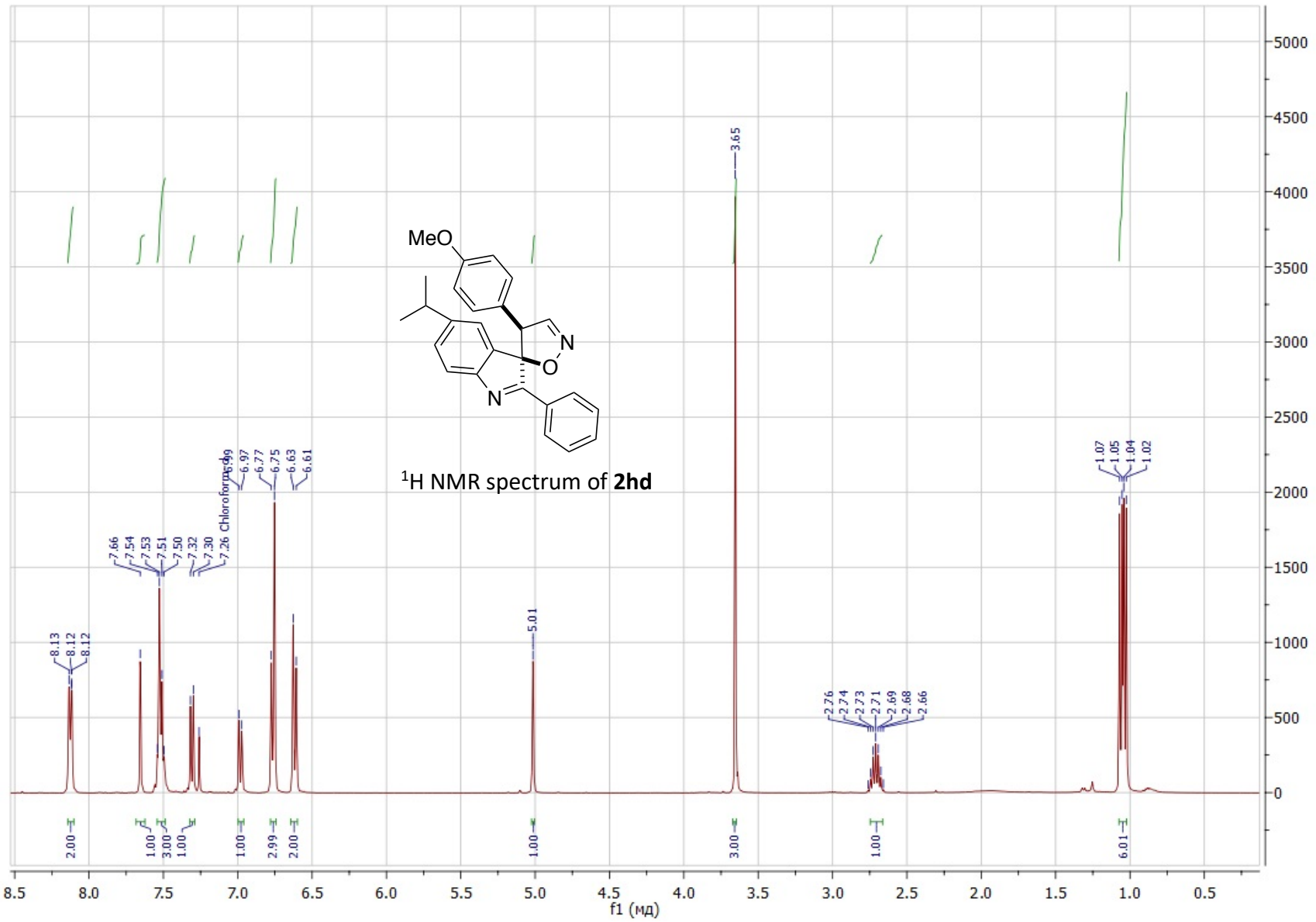
^{13}C NMR spectrum of **2ga**



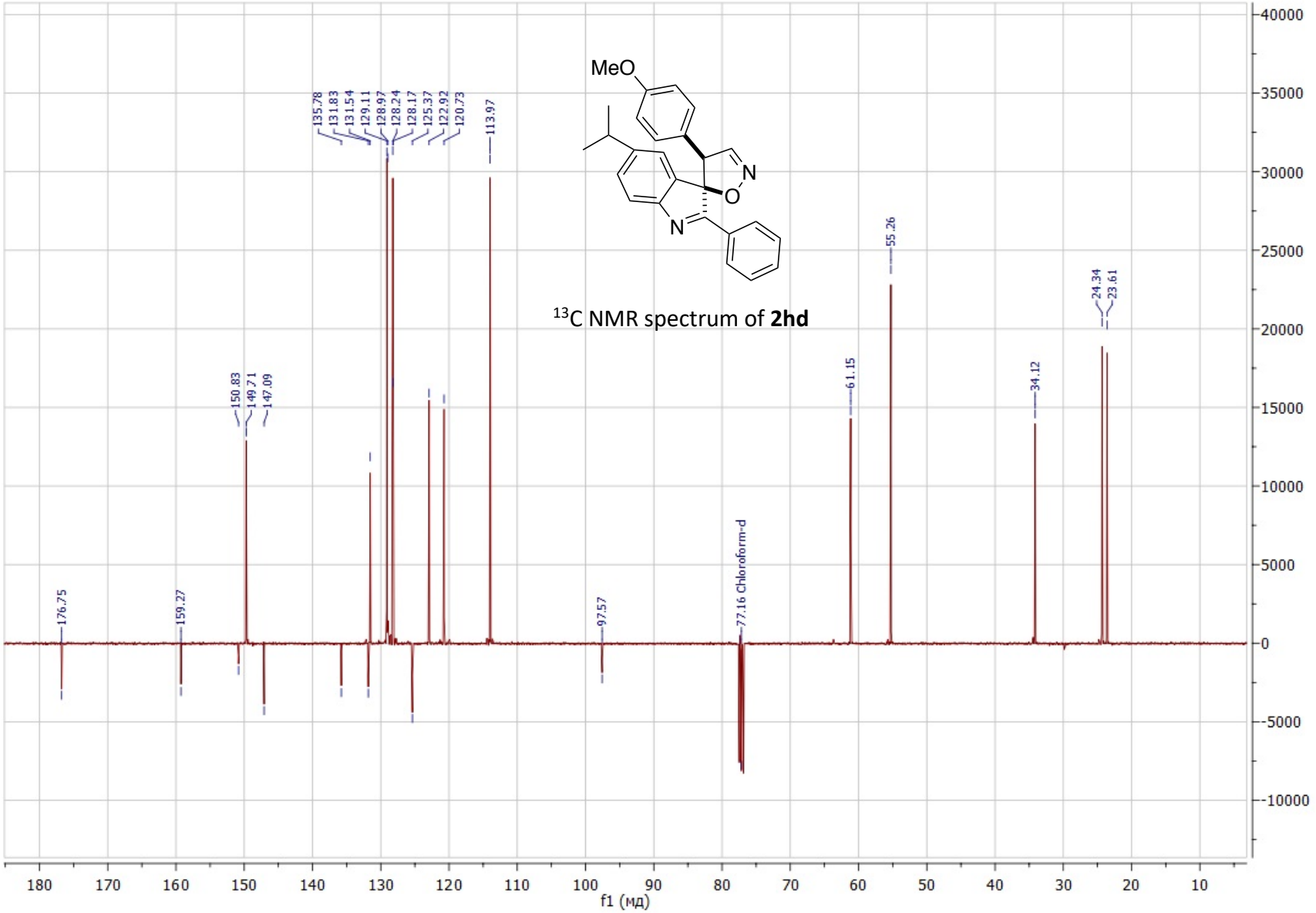
^{1}H NMR spectrum of **2ha**



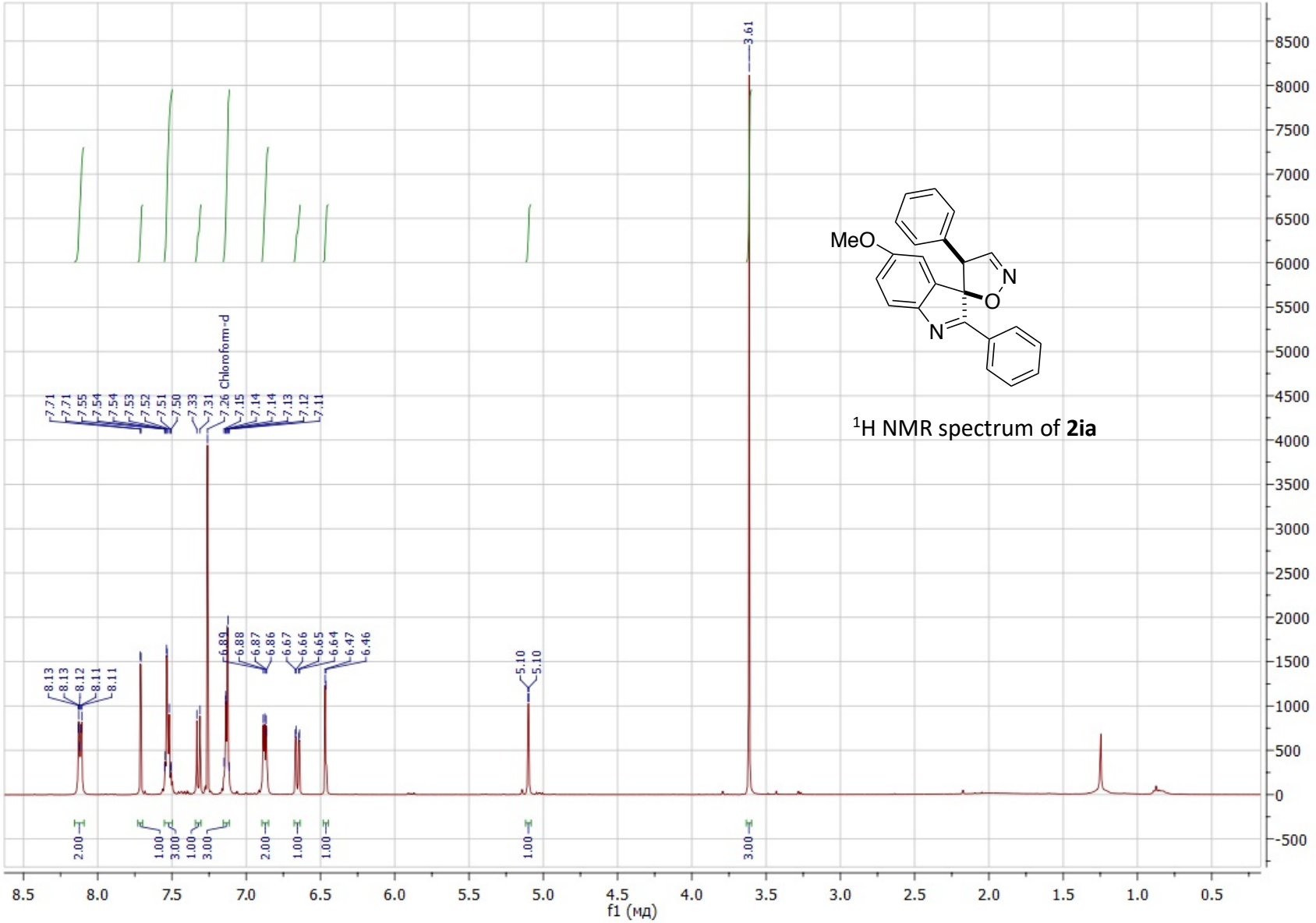
^{13}C NMR spectrum of **2ha**



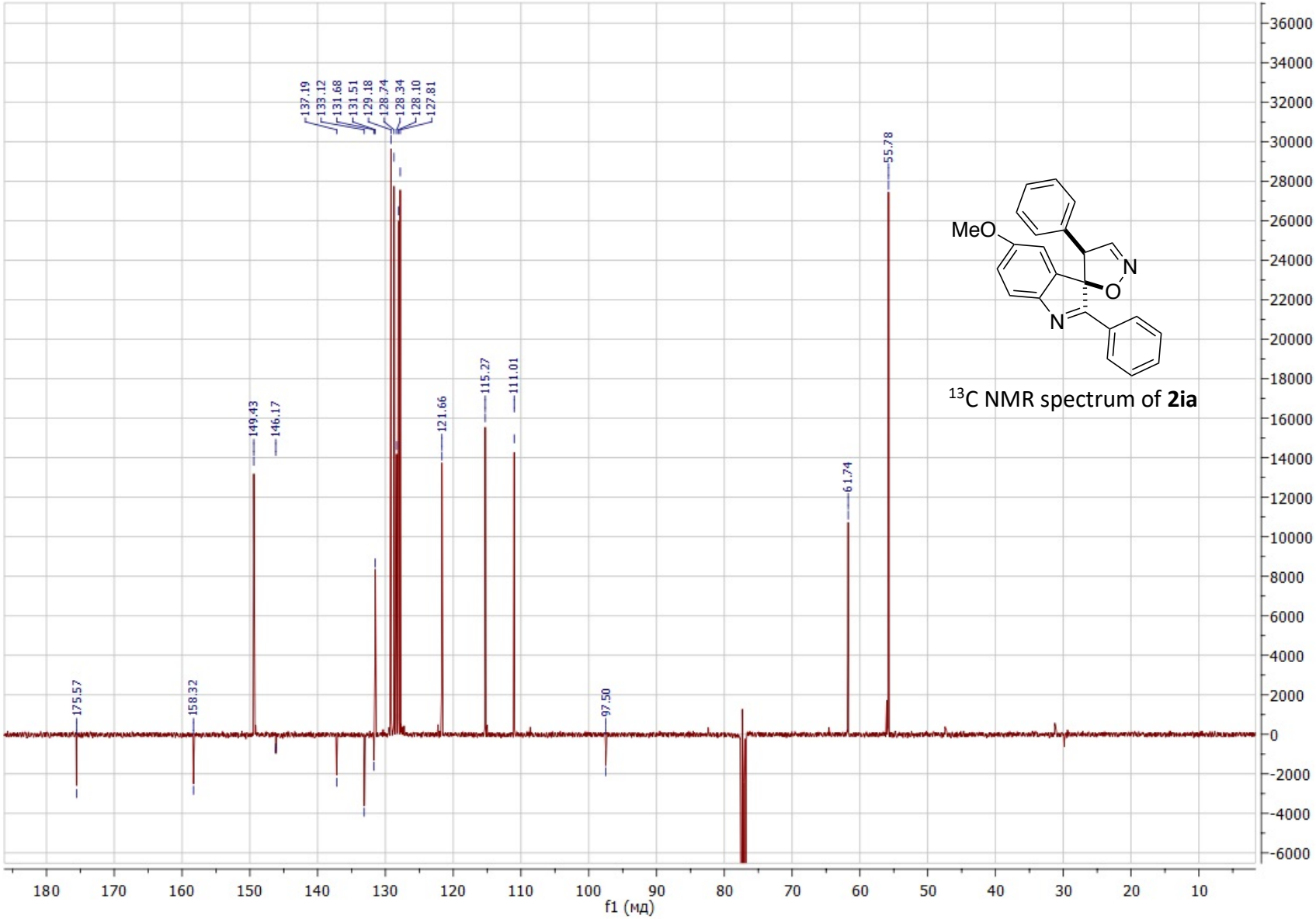
^{1}H NMR spectrum of **2hd**



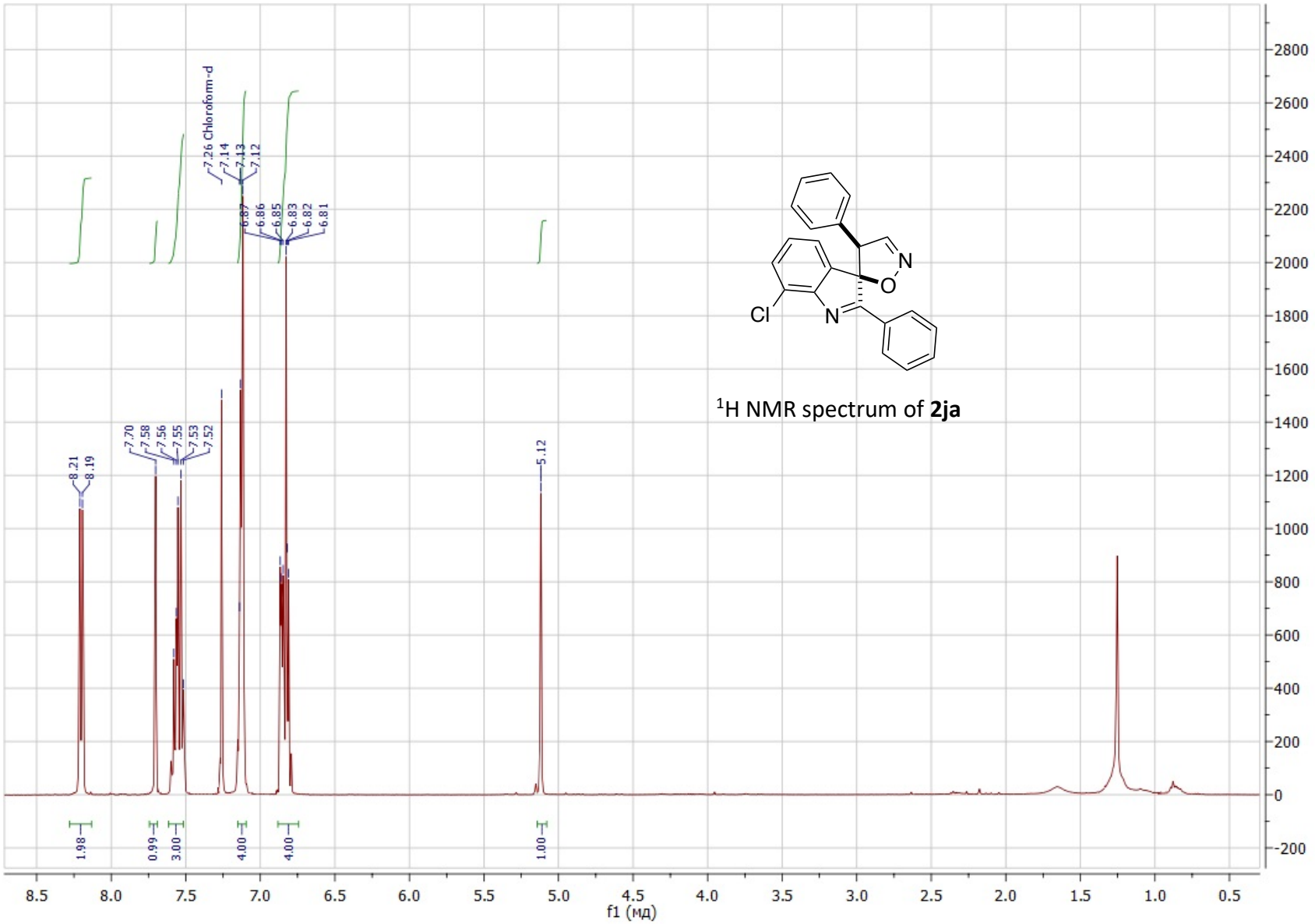
^{13}C NMR spectrum of **2hd**



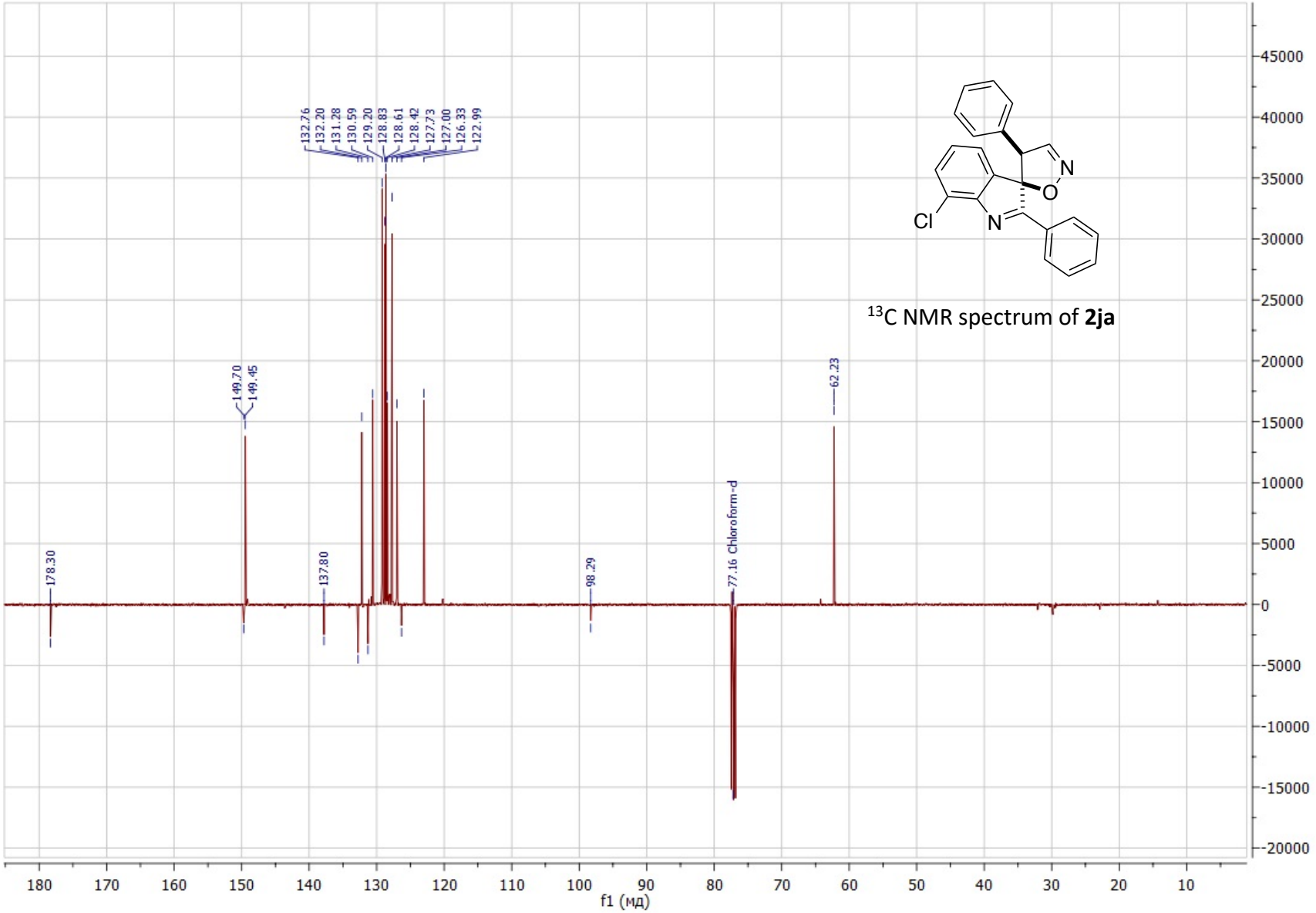
^{1}H NMR spectrum of **2ia**



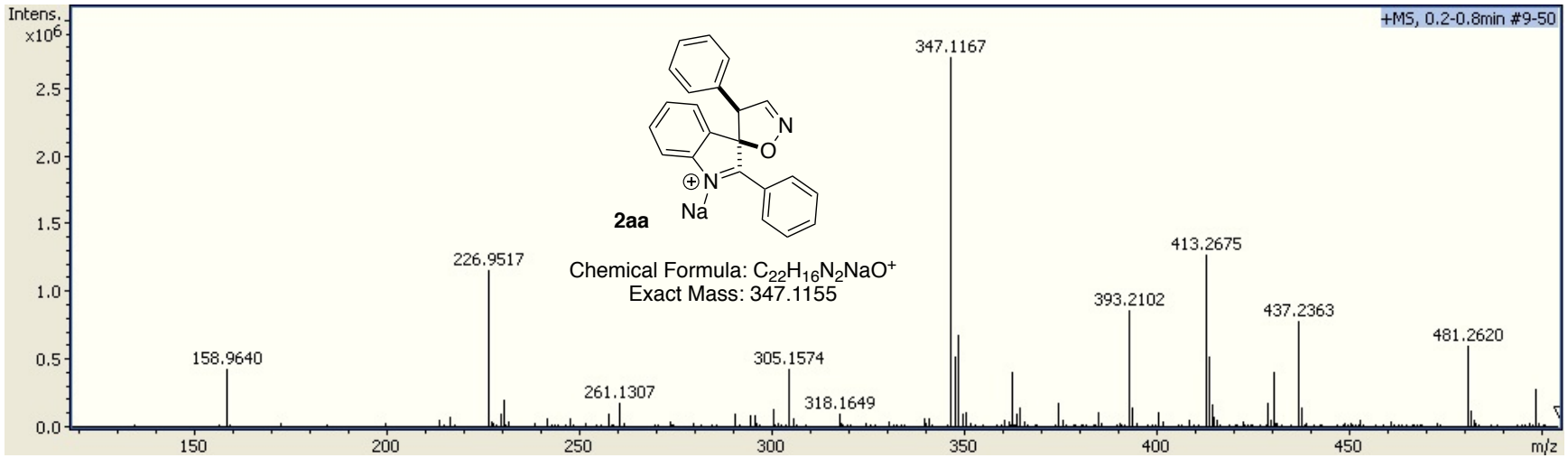
^{13}C NMR spectrum of **2ia**

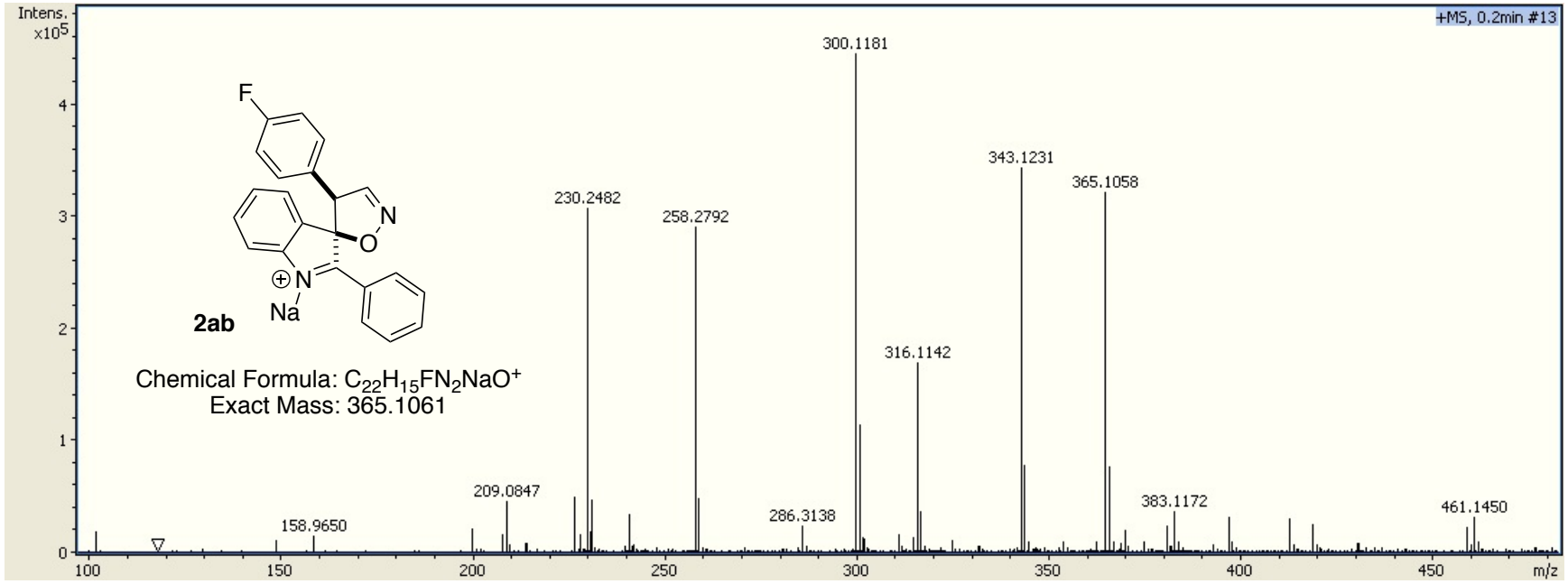


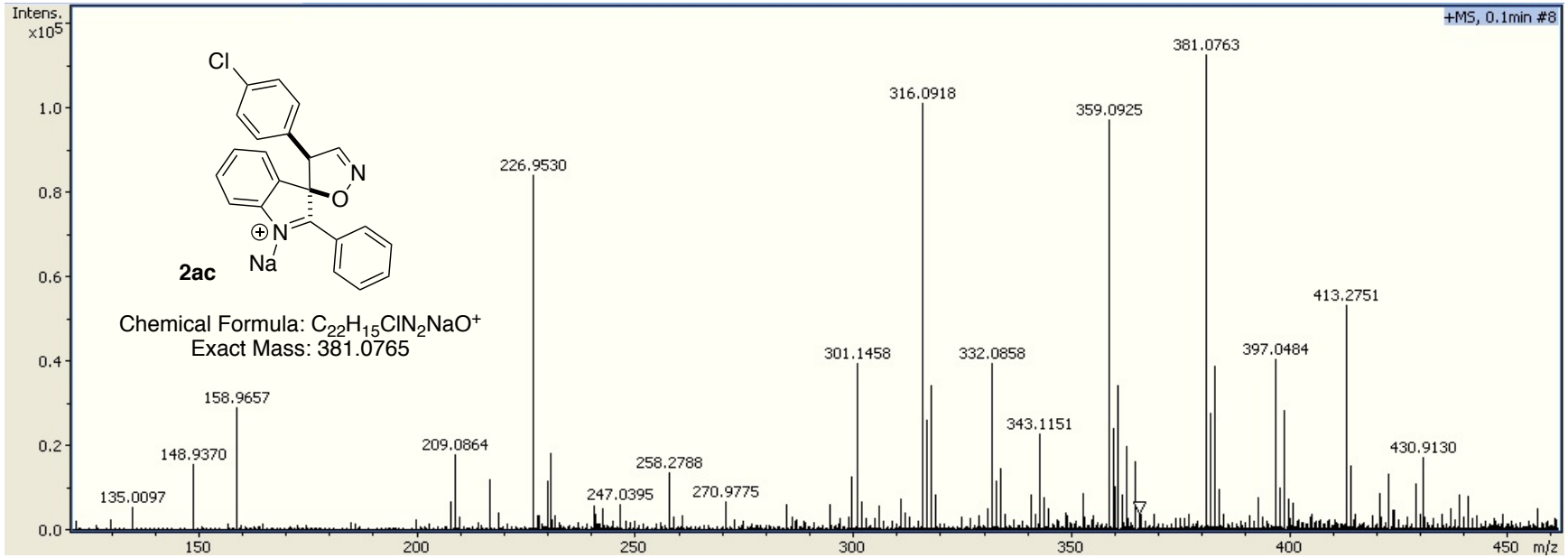
^{1}H NMR spectrum of **2ja**

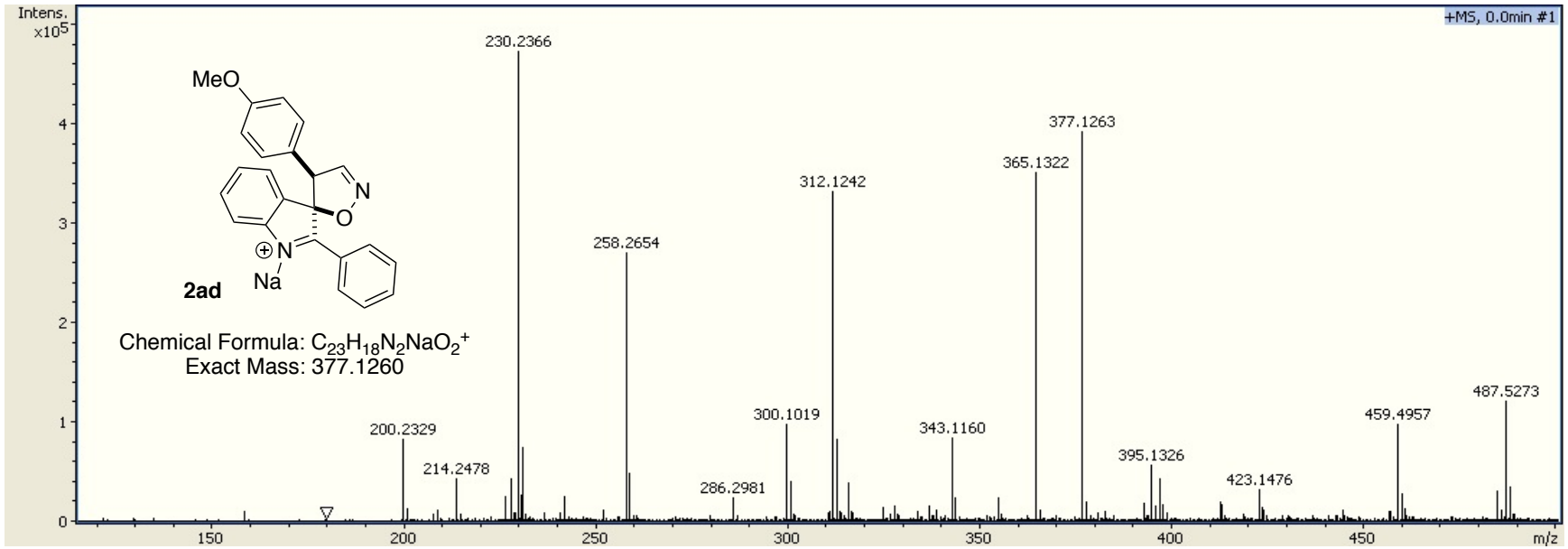


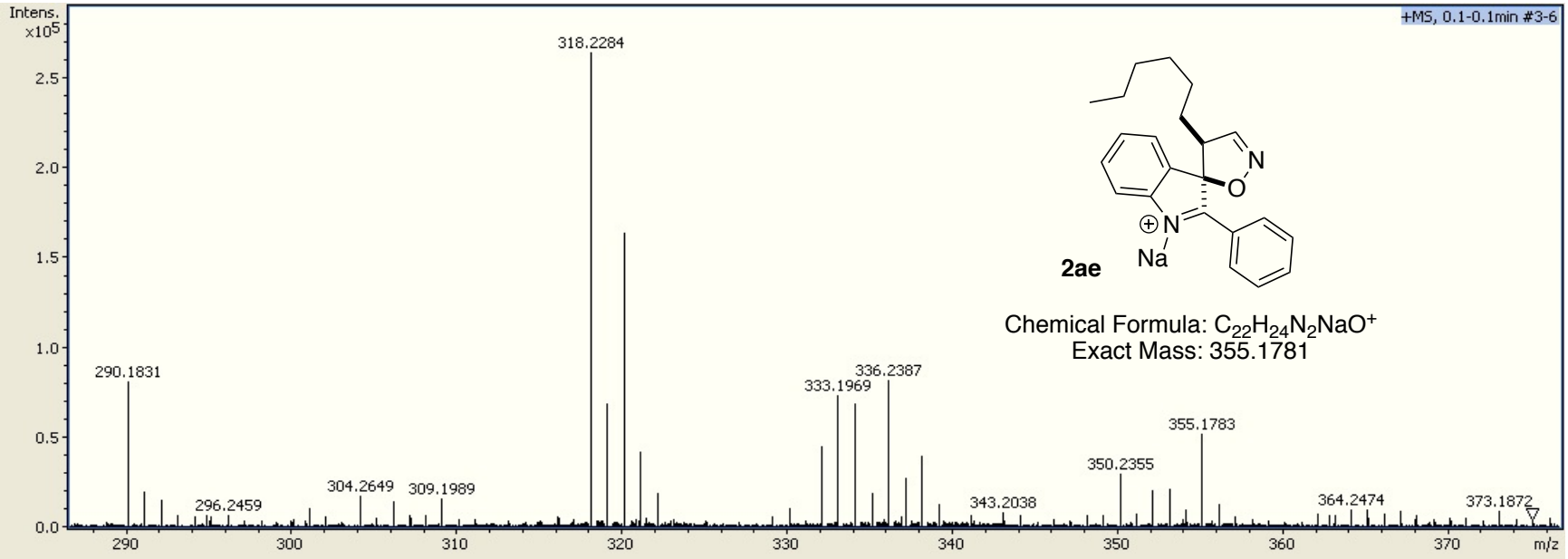
^{13}C NMR spectrum of **2ja**

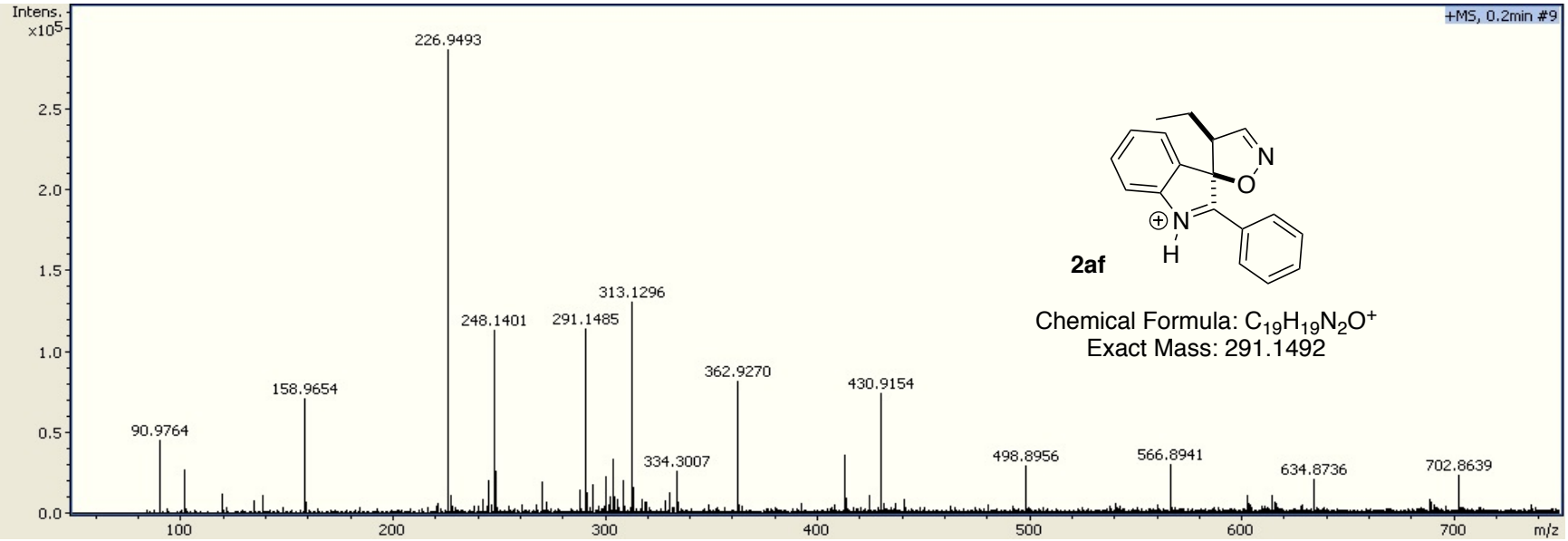

Intens.
x10^6
+MS, 0.2-0.8min #9-50
347.1167
413.2675
226.9517
393.2102
437.2363
481.2620
158.9640
305.1574
261.1307
318.1649
2aa
Chemical Formula: C22H16N2NaO+
Exact Mass: 347.1155
m/z

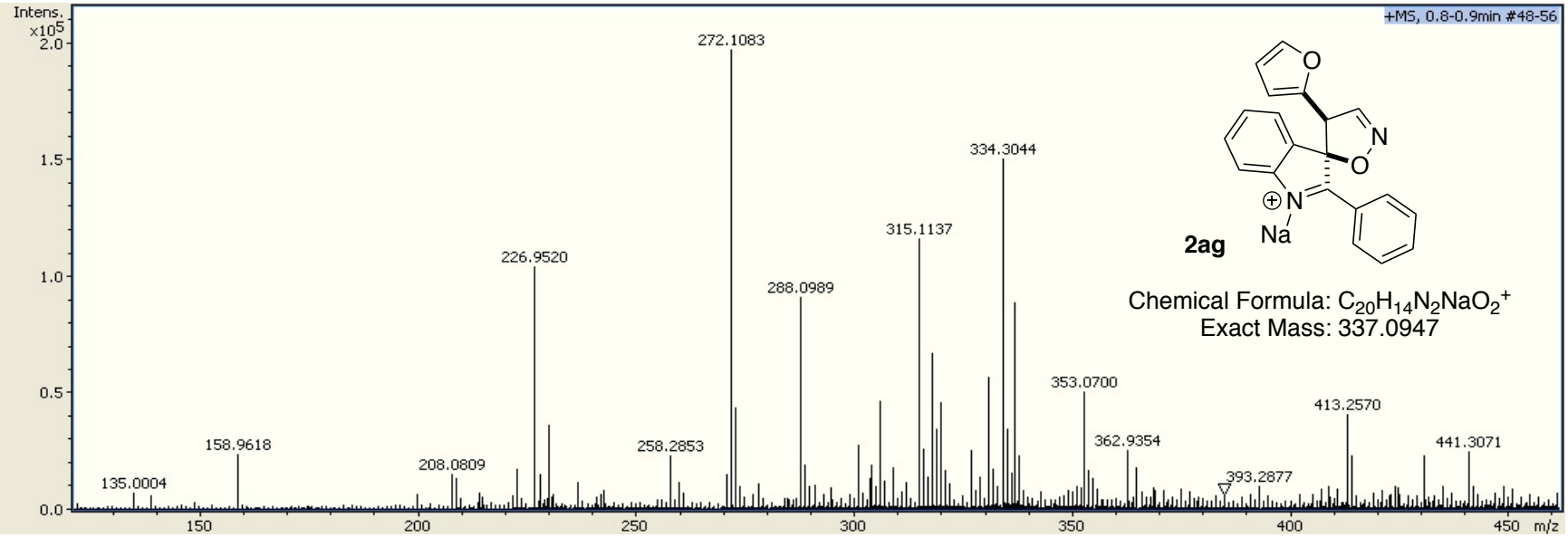

Intens.
x10^5
+MS, 0.2min #13
300.1181
343.1231
365.1058
230.2482
258.2792
316.1142
209.0847
158.9650
286.3138
383.1172
461.1450
2ab
Chemical Formula: C22H15FN2NaO+
Exact Mass: 365.1061
m/z

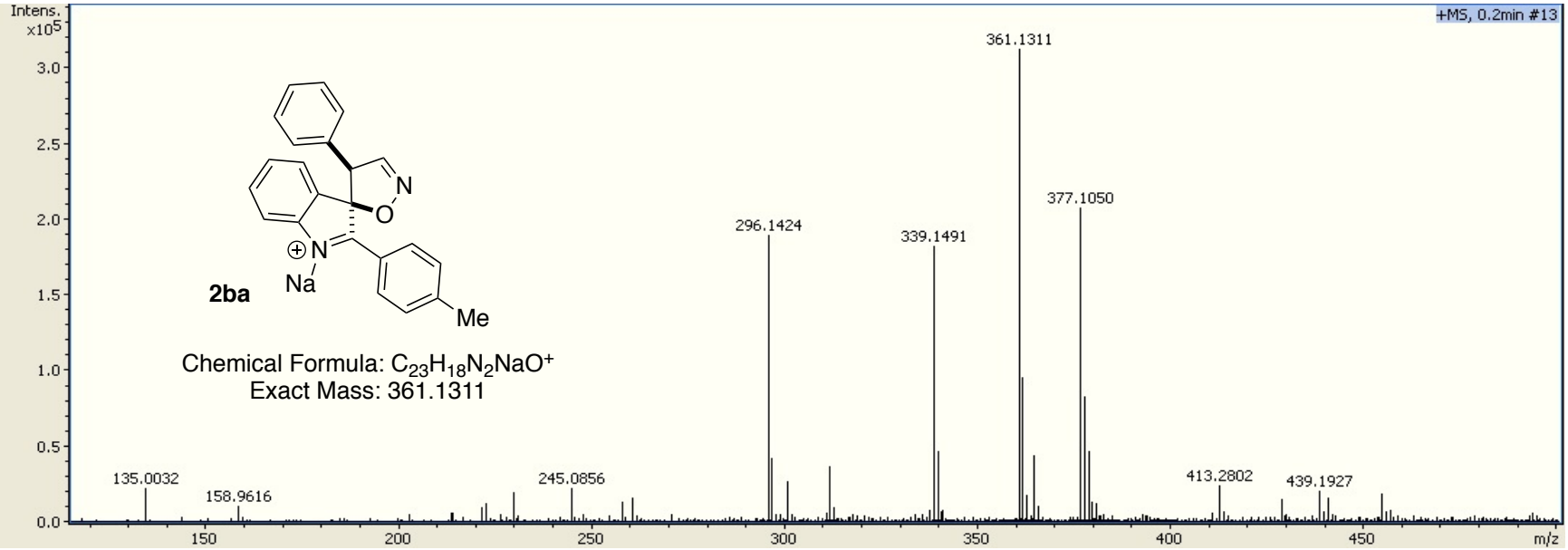

Intens.
x10^5
+MS, 0.1min #8
Cl
N
O
N
Na
2ac
Chemical Formula: C22H15ClN2NaO+
Exact Mass: 381.0765
381.0763
316.0918
359.0925
226.9530
413.2751
301.1458
332.0858
397.0484
158.9657
343.1151
430.9130
148.9370
209.0864
258.2788
135.0097
247.0395
270.9775
m/z

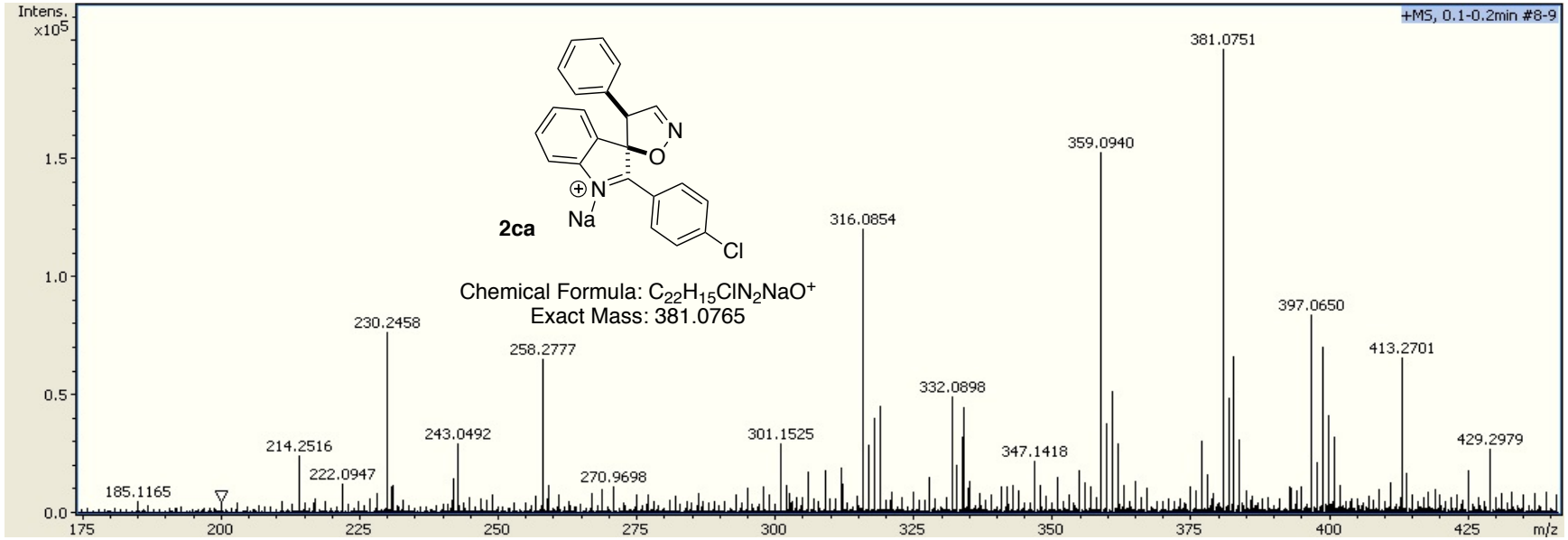

Intens.
x10^5
+MS, 0.0min #1
MeO
N
O
N
Na
2ad
Chemical Formula: C23H18N2NaO2+
Exact Mass: 377.1260
230.2366
377.1263
365.1322
312.1242
258.2654
487.5273
300.1019
459.4957
343.1160
200.2329
395.1326
214.2478
423.1476
286.2981
m/z

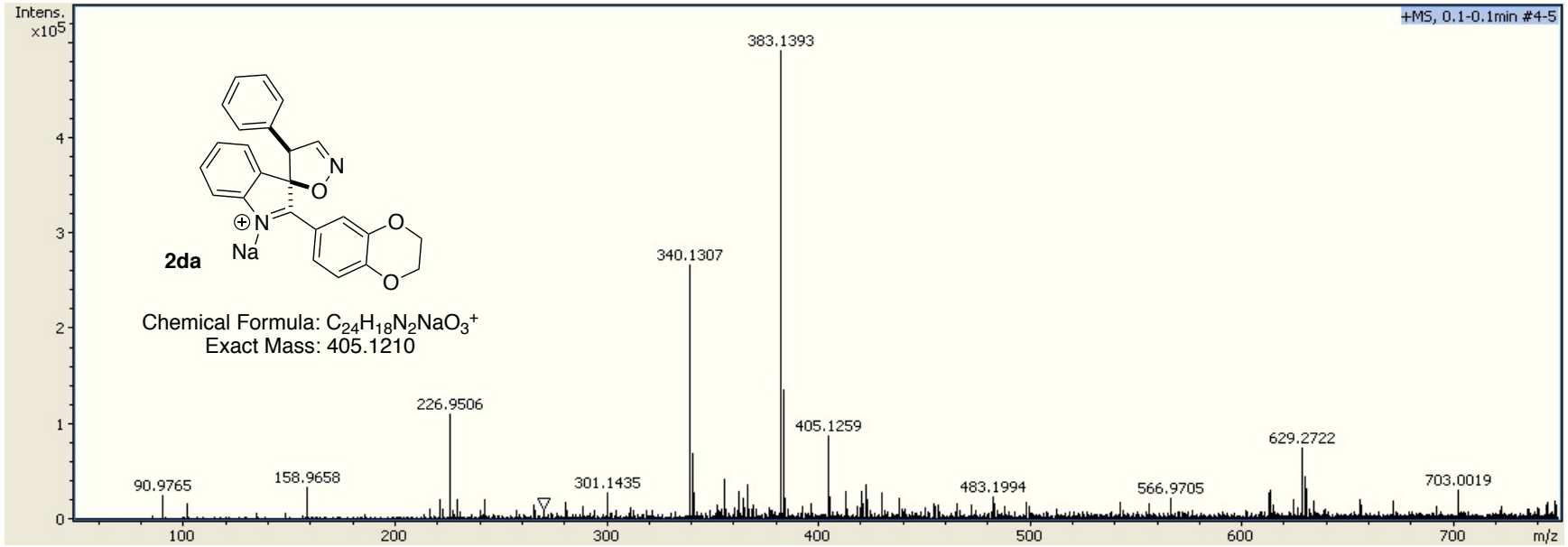

Intens.
x10^5
+MS, 0.1-0.1min #3-6
318.2284
290.1831
296.2459
304.2649
309.1989
333.1969
336.2387
343.2038
350.2355
355.1783
364.2474
373.1872
m/z
2ae
Chemical Formula: C22H24N2NaO+
Exact Mass: 355.1781

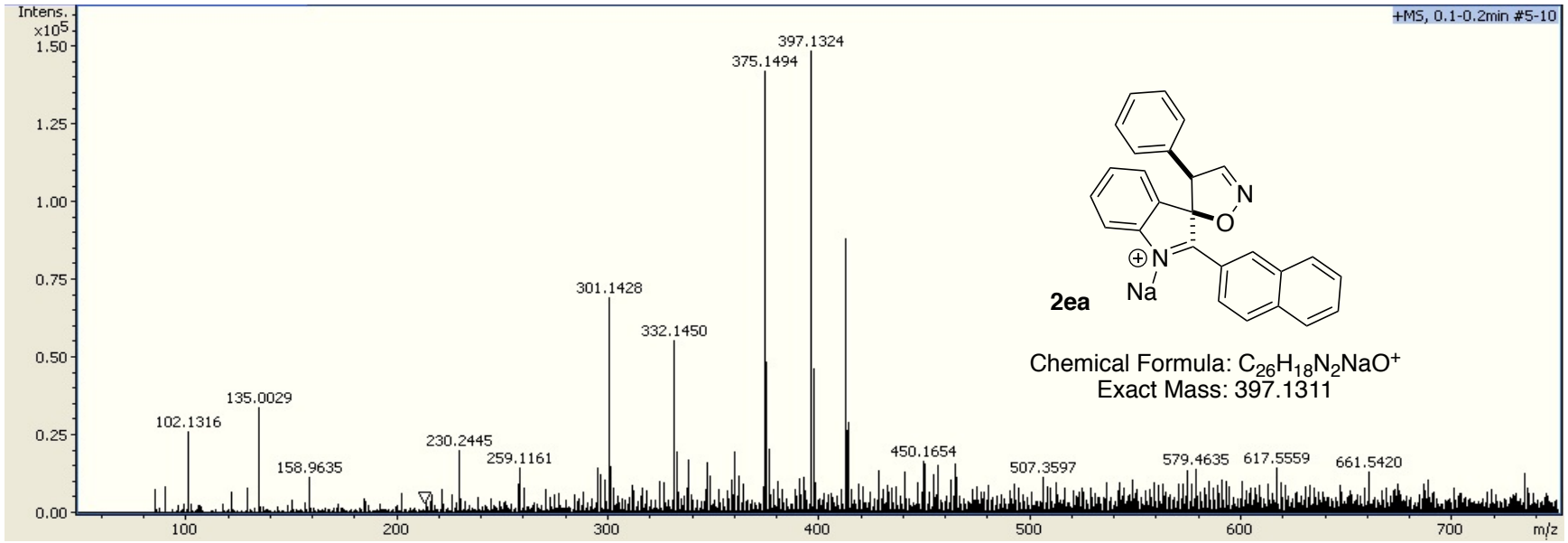

Intens.
x10^5
+MS, 0.2min #9
226.9493
90.9764
158.9654
248.1401
291.1485
313.1296
334.3007
362.9270
430.9154
498.8956
566.8941
634.8736
702.8639
m/z
2af
Chemical Formula: C19H19N2O+
Exact Mass: 291.1492

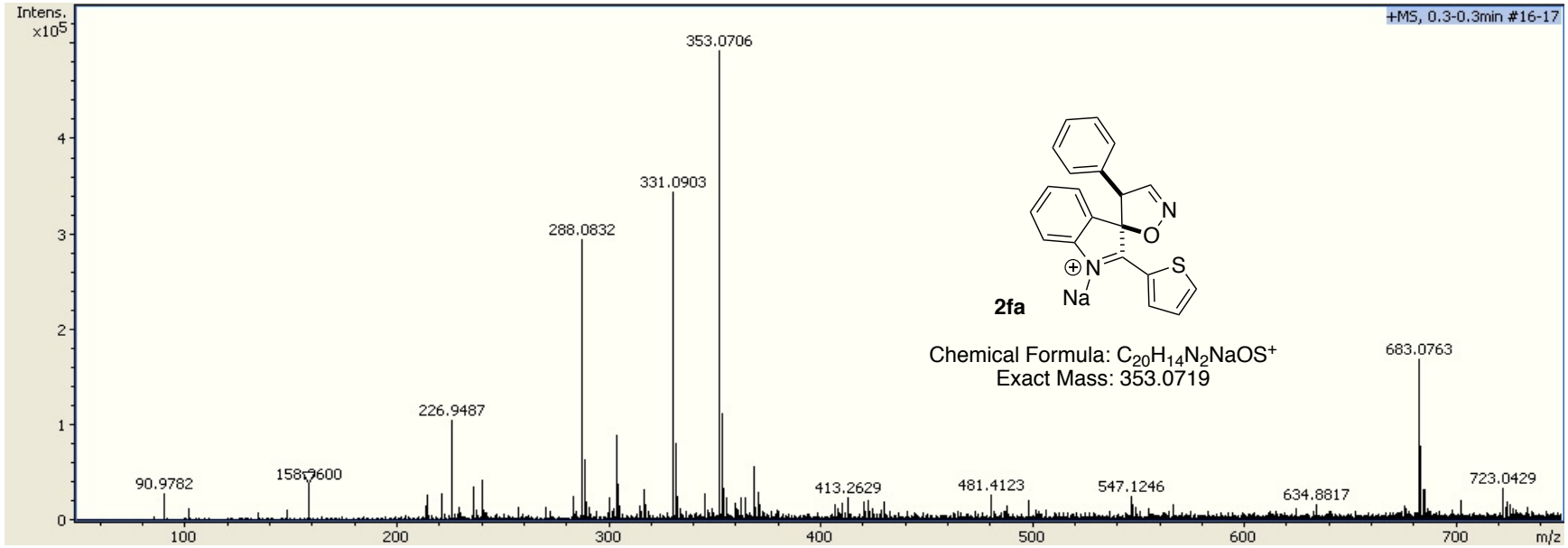

Intens.
x10^5
+MS, 0.8-0.9min #48-56
272.1083
334.3044
315.1137
226.9520
288.0989
353.0700
413.2570
362.9354
441.3071
158.9618
208.0809
258.2853
135.0004
393.2877
2ag
Chemical Formula: C20H14N2NaO2+
Exact Mass: 337.0947
m/z

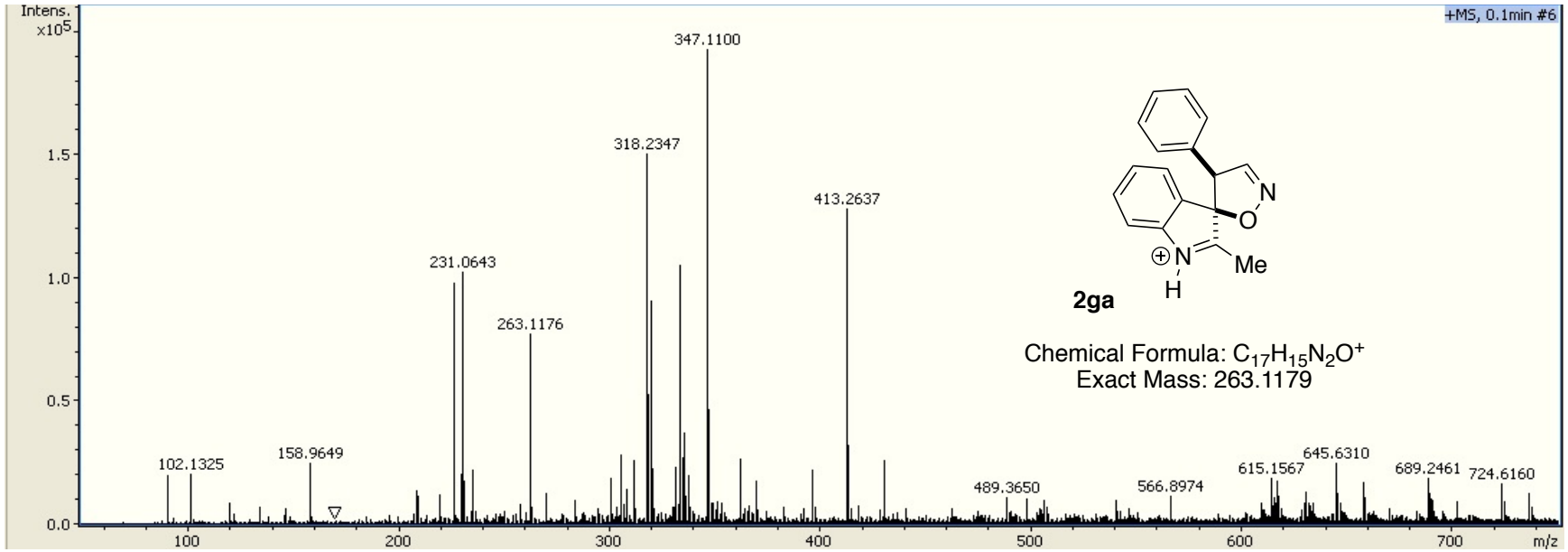

Intens.
x10^5
+MS, 0.2min #13
361.1311
377.1050
296.1424
339.1491
135.0032
158.9616
245.0856
413.2802
439.1927
2ba
Me
Chemical Formula: C23H18N2NaO+
Exact Mass: 361.1311
m/z

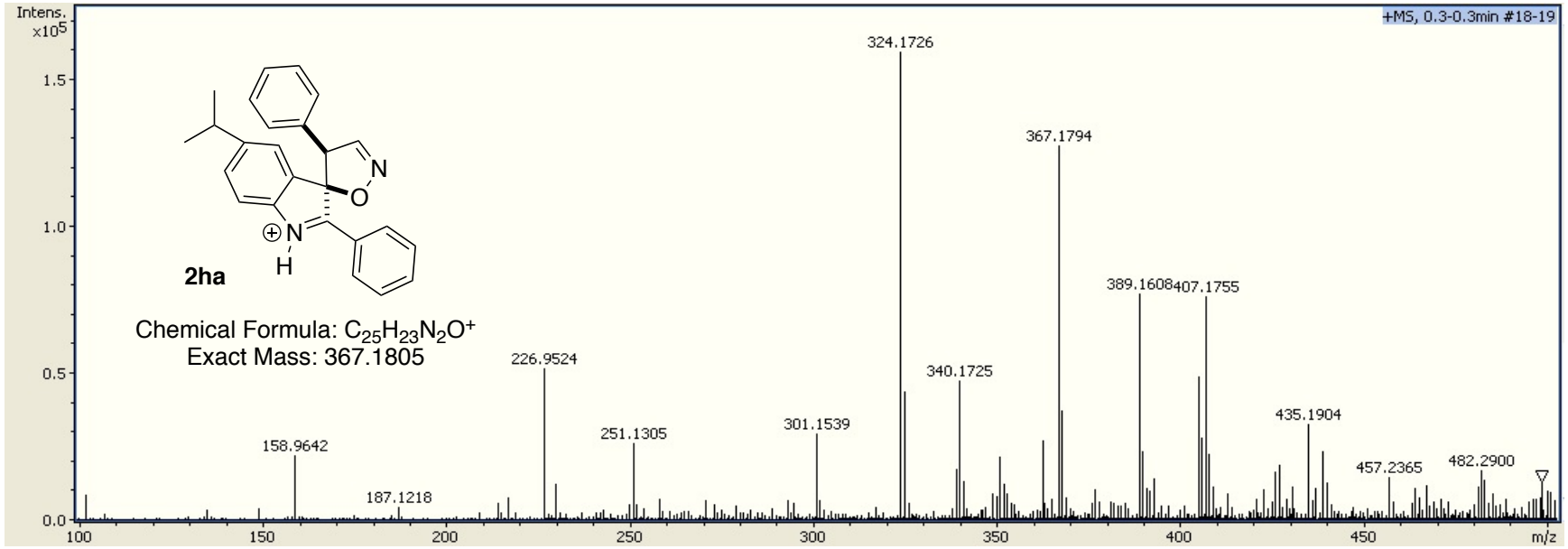

Intens.
x10^5
+MS, 0.1-0.2min #8-9
2ca
Chemical Formula: C22H15ClN2NaO+
Exact Mass: 381.0765
381.0751
359.0940
316.0854
397.0650
413.2701
230.2458
258.2777
332.0898
243.0492
214.2516
222.0947
301.1525
347.1418
429.2979
185.1165
270.9698
m/z

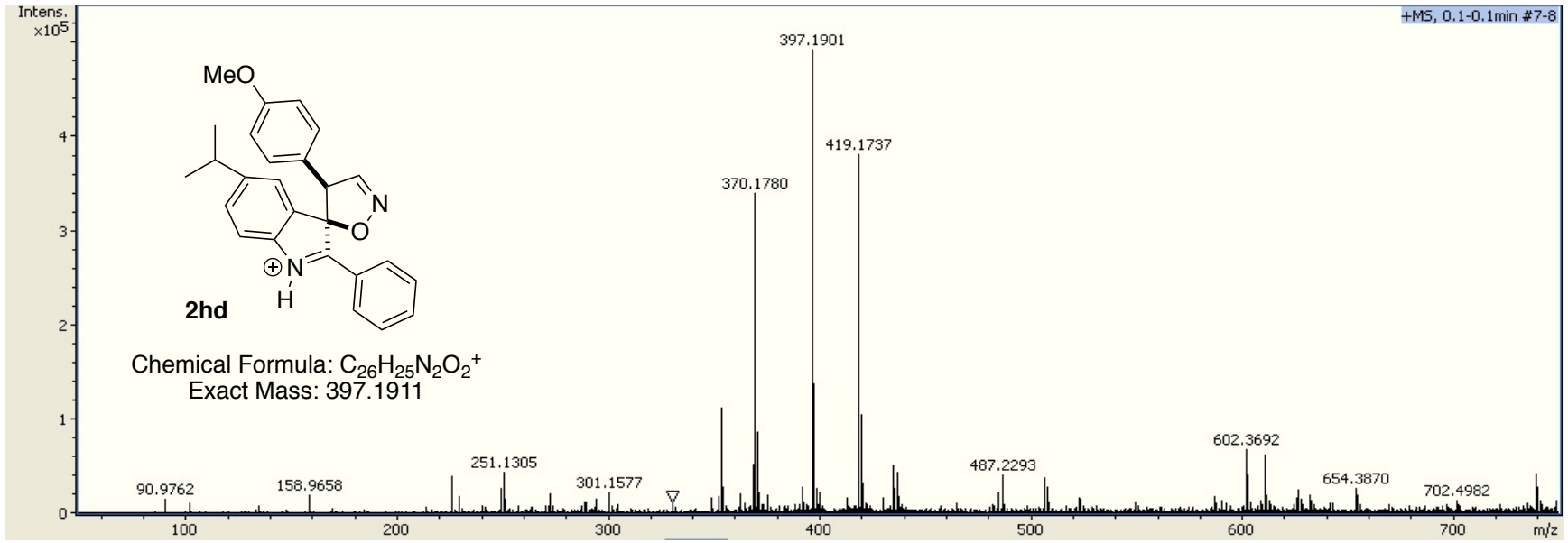

Intens.
x10^5
+MS, 0.1-0.1min #4-5
2da
Chemical Formula: C24H18N2NaO3+
Exact Mass: 405.1210
383.1393
340.1307
226.9506
405.1259
629.2722
90.9765
158.9658
301.1435
483.1994
566.9705
703.0019
m/z

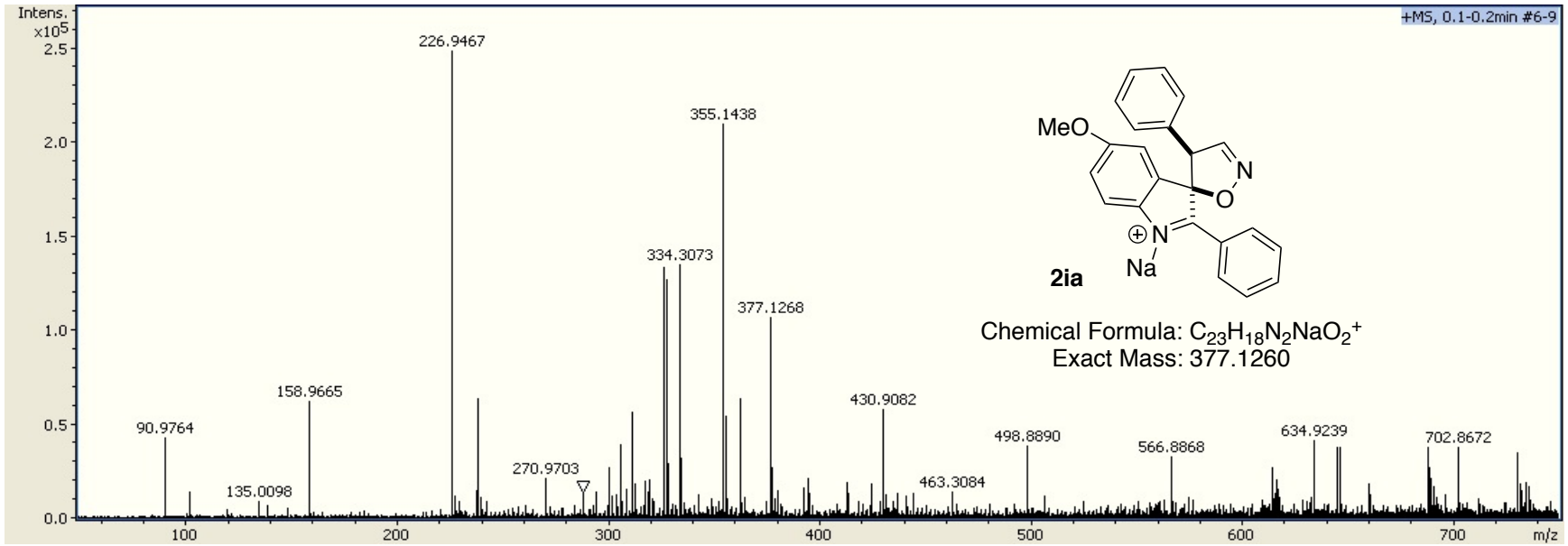

Intens.
x10^5
+MS, 0.1-0.2min #5-10
397.1324
375.1494
301.1428
332.1450
135.0029
102.1316
230.2445
259.1161
158.9635
450.1654
507.3597
579.4635
617.5559
661.5420
m/z
2ea
Chemical Formula: C26H18N2NaO+
Exact Mass: 397.1311

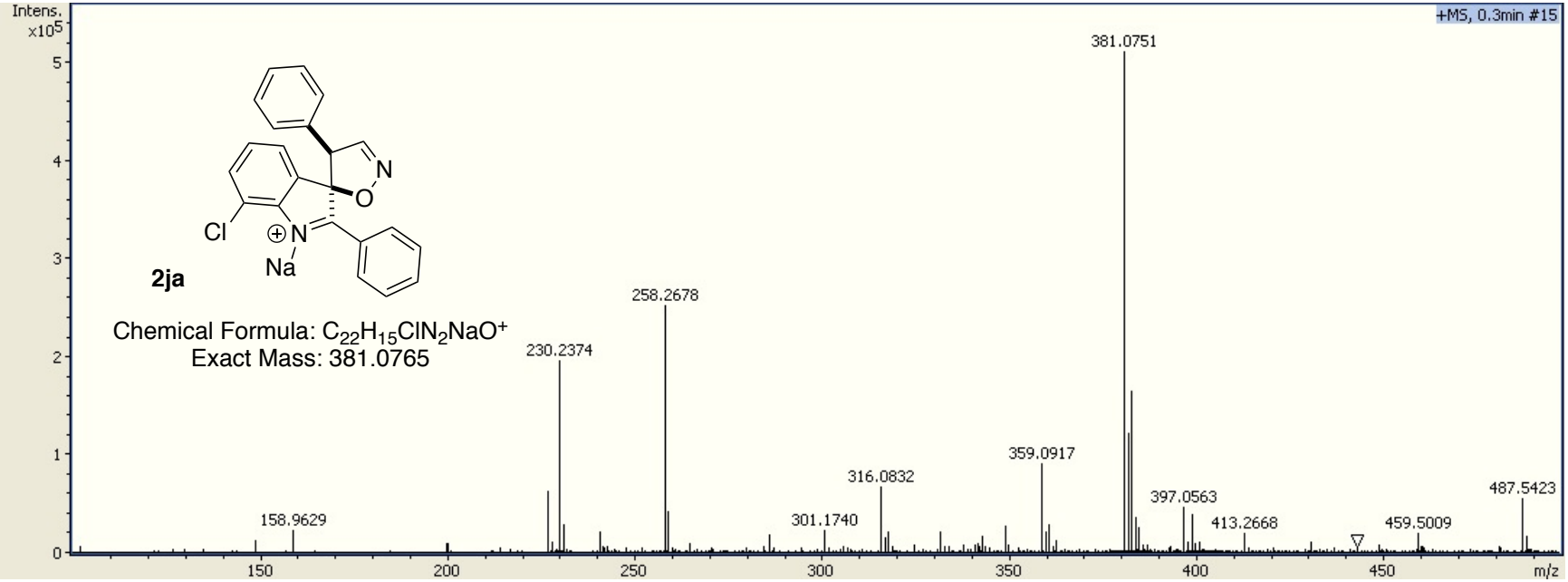

Intens.
x10^5
+MS, 0.3-0.3min #16-17
353.0706
331.0903
288.0832
226.9487
90.9782
158.9600
413.2629
481.4123
547.1246
634.8817
683.0763
723.0429
m/z
2fa
Chemical Formula: C20H14N2NaOS+
Exact Mass: 353.0719


Intens.
x10^5
+MS, 0.1min #6
347.1100
318.2347
413.2637
231.0643
263.1176
102.1325
158.9649
489.3650
566.8974
615.1567
645.6310
689.2461
724.6160
2ga
Chemical Formula: C17H15N2O+
Exact Mass: 263.1179
m/z


Intens.
x10^5
+MS, 0.3-0.3min #18-19
324.1726
367.1794
389.1608
407.1755
226.9524
340.1725
301.1539
251.1305
435.1904
158.9642
187.1218
457.2365
482.2900
2ha
Chemical Formula: C25H23N2O+
Exact Mass: 367.1805
m/z


Intens.
x10^5
+MS, 0.1-0.1min #7-8
MeO
N
O
N
H
2hd
Chemical Formula: C26H25N2O2+
Exact Mass: 397.1911
397.1901
419.1737
370.1780
602.3692
487.2293
654.3870
702.4982
251.1305
301.1577
90.9762
158.9658
m/z


Intens.
x10^5
+MS, 0.1-0.2min #6-9
226.9467
355.1438
334.3073
377.1268
158.9665
90.9764
135.0098
270.9703
430.9082
498.8890
566.8868
634.9239
702.8672
463.3084
MeO
N
O
N
Na
2ia
Chemical Formula: C23H18N2NaO2+
Exact Mass: 377.1260
m/z


Intens.
x10^5
+MS, 0.3min #15
381.0751
258.2678
230.2374
359.0917
316.0832
397.0563
487.5423
158.9629
301.1740
413.2668
459.5009
m/z
2ja
Chemical Formula: C22H15ClN2NaO+
Exact Mass: 381.0765

X-Ray Crystallography

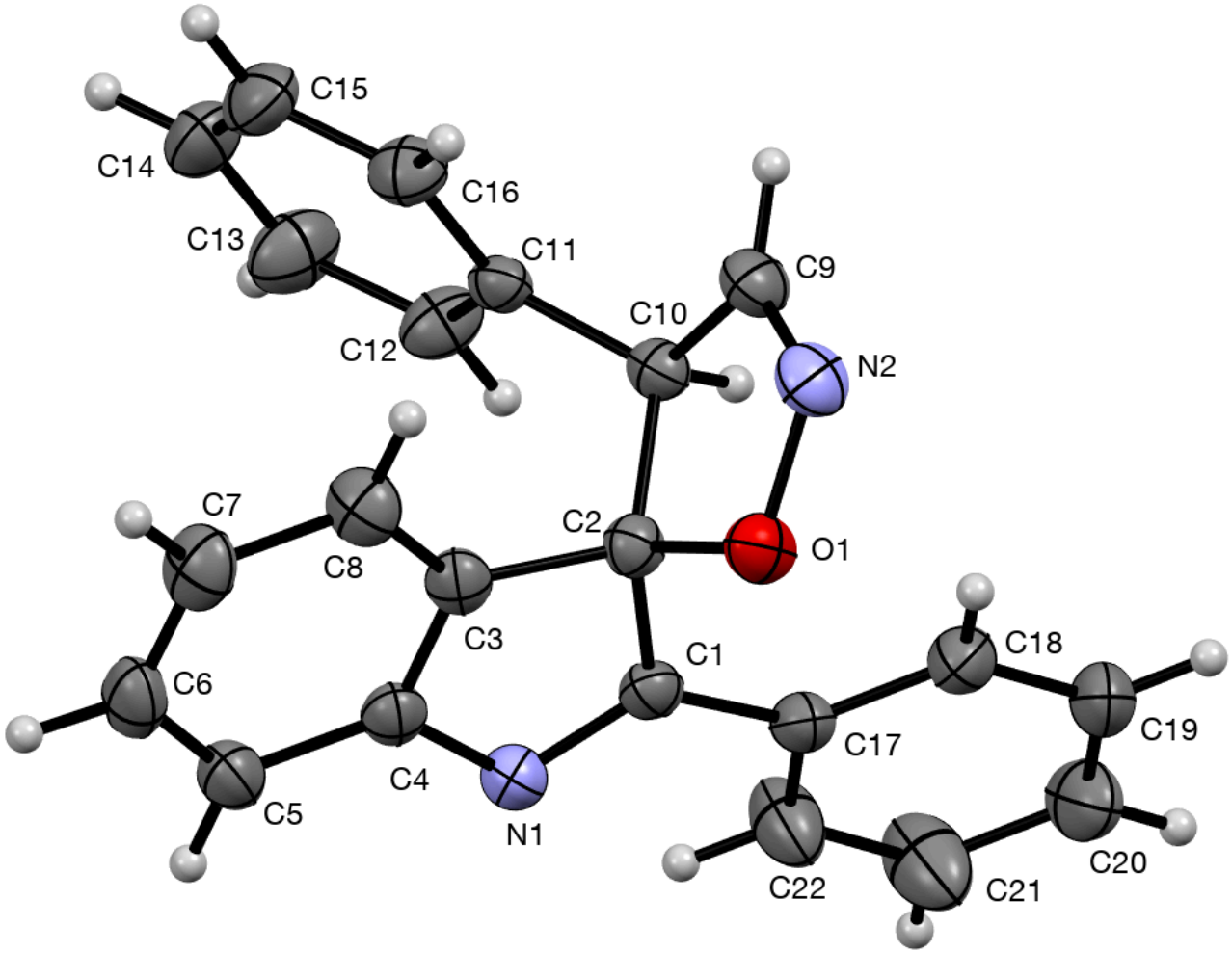


Figure S1. ORTEP drawings of **2aa** (CCDC #1834625, bottom) showing atom numbering schemes and 50% probability ellipsoids.

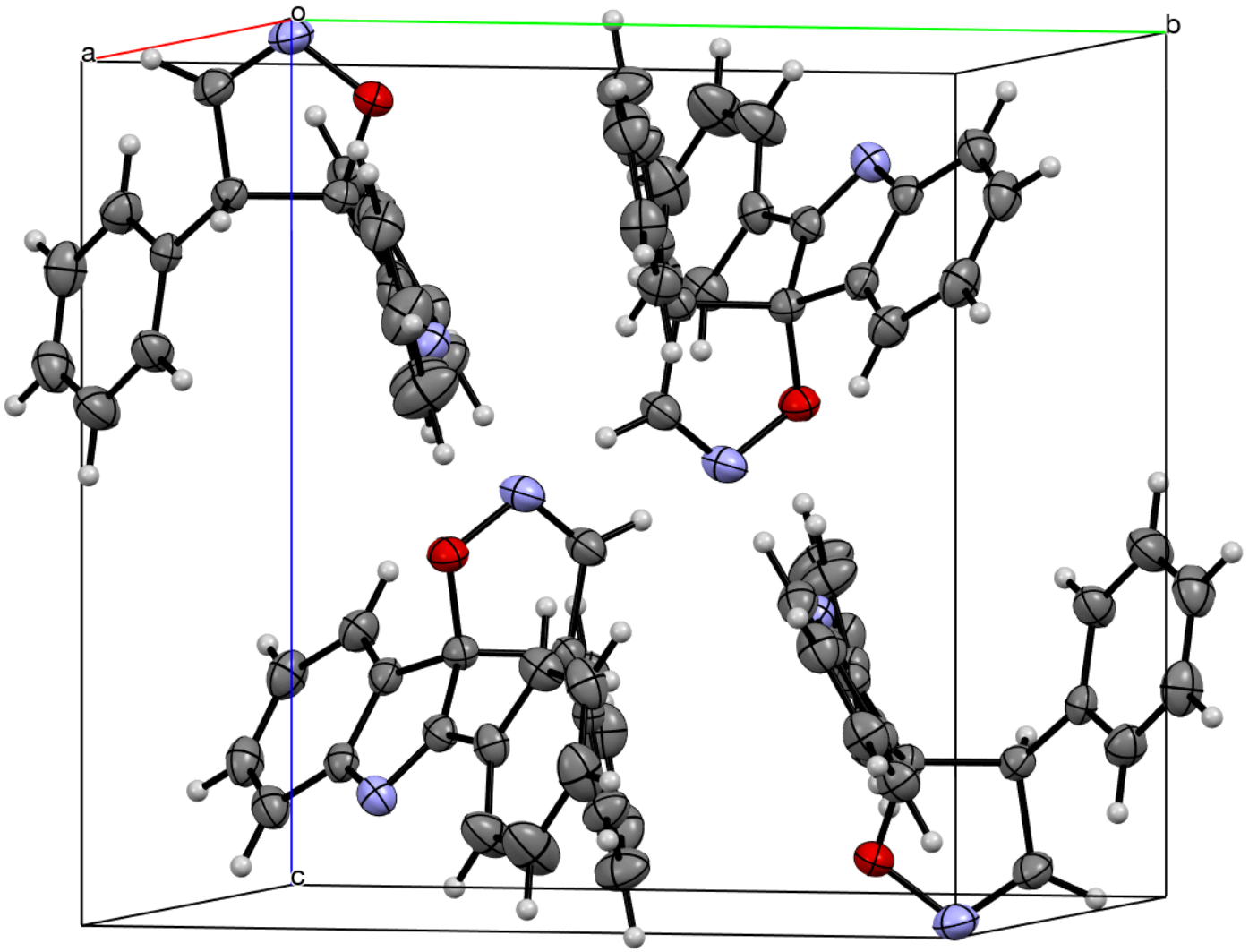


Figure S2. Packing of **2aa** molecules in a crystal lattice.

X-Ray Crystallography data for compound 2aa (CCDC #1834625)

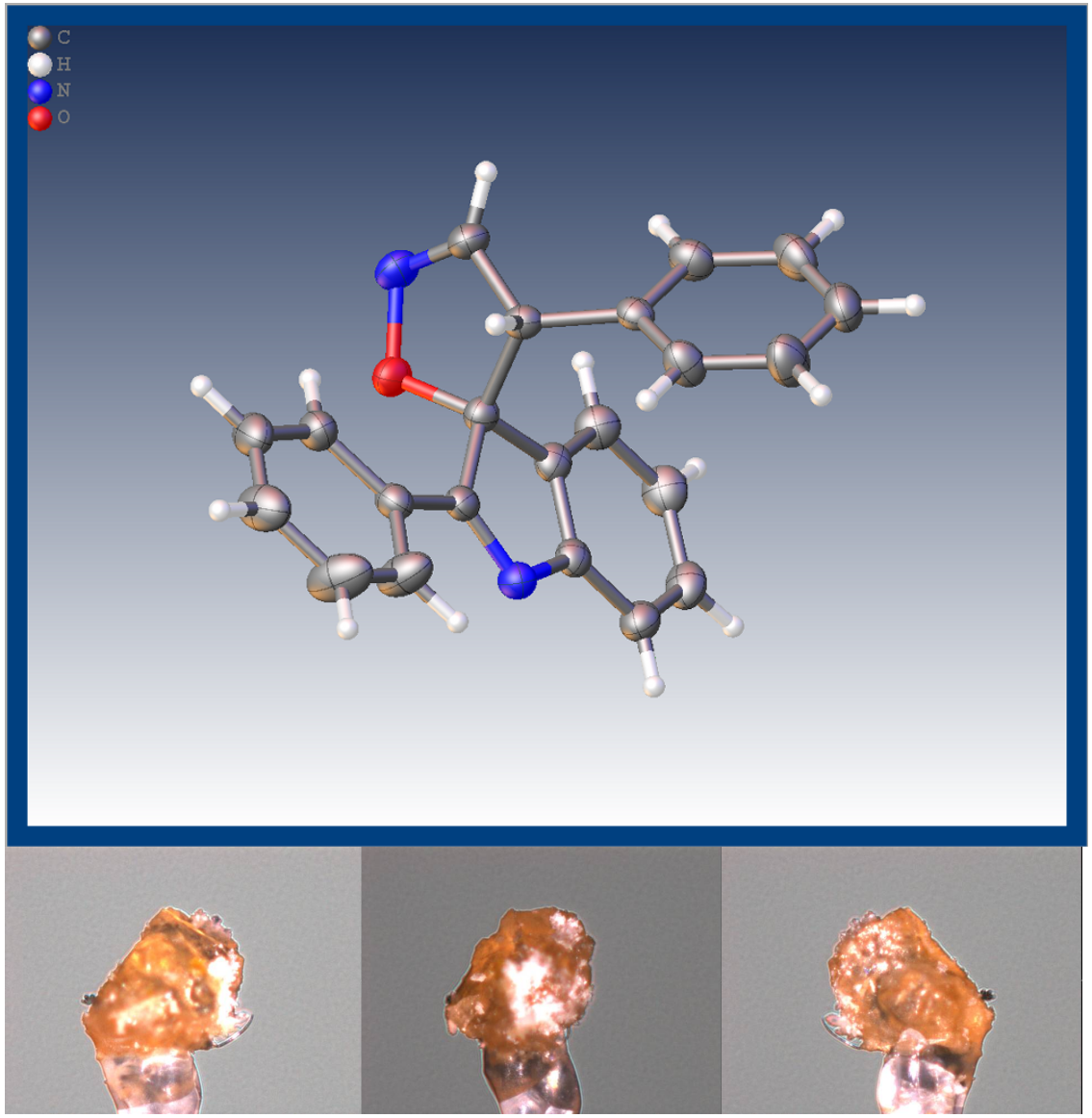


Table S1. Crystal data and structure refinement for 2aa

Identification code	ANNA_SPOIRA_NU_11
Empirical formula	$C_{22}H_{16}N_2O$
Formula weight	324.37
Temperature/K	149.99(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.1571(2)
b/Å	12.4540(2)
c/Å	11.9000(2)
α/°	90
β/°	90.0450(10)
γ/°	90
Volume/Å^3	1653.51(5)
Z	4
ρ_{calc}g/cm^3	1.303
μ/mm^{-1}	0.638
F(000)	680.0
Crystal size/mm^3	0.525 × 0.4 × 0.347
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	10.282 to 151.682
Index ranges	$-10 \leq h \leq 13$, $-13 \leq k \leq 15$, $-14 \leq l \leq 14$
Reflections collected	16080
Independent reflections	3424 [R_{int} = 0.0360, R_{sigma} = 0.0189]
Data/restraints/parameters	3424/0/226
Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0452, wR_2 = 0.1196
Final R indexes [all data]	R_1 = 0.0483, wR_2 = 0.1220
Largest diff. peak/hole / e Å^{-3}	0.32/-0.20

Table S2. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 2aa. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O^1	7235.3(9)	3527.1(7)	5786.5(7)	33.4(2)
N^1	7544.3(10)	2786.4(9)	8576.0(9)	30.9(3)
N^2	7409.4(11)	4422.4(10)	5062.9(9)	37.1(3)
C^2	7710.4(11)	3783.7(10)	6893.2(10)	26.2(3)
C^{11}	8827.8(11)	5516.0(9)	7521.6(10)	26.1(3)
C^{10}	7784.8(11)	5036.7(10)	6896.0(10)	26.6(3)
C^1	6947.5(11)	3366.9(10)	7869.3(10)	27.0(3)
C^3	8871.2(11)	3204.7(10)	7127.4(10)	28.1(3)
C^4	8725.9(11)	2666.3(10)	8137.3(11)	28.2(3)
C^9	7727.9(12)	5226.4(11)	5652.3(11)	34.5(3)
C^{17}	5681.2(11)	3651.0(10)	8066.6(11)	30.1(3)
C^5	9649.5(13)	2078.2(11)	8617.5(12)	35.4(3)
C^8	9939.9(13)	3156.4(12)	6548.7(12)	36.2(3)
C^{18}	4942.3(12)	4051.7(11)	7216.5(12)	36.1(3)
C^6	10736.3(13)	2043.6(12)	8039.9(13)	38.8(3)
C^{16}	9910.8(13)	5764.7(12)	7001.2(12)	36.3(3)
C^{12}	8720.0(13)	5693.9(12)	8663.8(12)	37.6(3)
C^{19}	3736.8(13)	4269.0(12)	7439.1(14)	41.1(3)
C^{14}	10740.7(14)	6344.6(13)	8757.7(14)	45.2(4)
C^7	10876.9(13)	2562.1(12)	7022.3(13)	40.3(3)
C^{15}	10854.7(13)	6178.7(13)	7622.8(15)	43.4(4)
C^{22}	5196.1(14)	3488.6(15)	9126.2(14)	48.5(4)
C^{20}	3274.5(14)	4088.2(14)	8487.7(16)	49.1(4)
C^{13}	9667.7(16)	6103.9(14)	9282.0(14)	48.7(4)
C^{21}	3999.0(16)	3698.7(17)	9335.7(16)	60.0(5)

Table S3. Anisotropic Displacement Parameters ($Å^2×10^3$) for 2aa. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O^1	42.3(5)	32.0(5)	25.9(4)	-1.3(4)	-6.0(4)	-3.9(4)
N^1	30.2(5)	29.7(5)	32.8(6)	3.8(4)	-2.4(4)	-1.3(4)
N^2	42.7(7)	42.4(7)	26.1(5)	5.3(5)	-2.7(5)	-1.0(5)
C^2	27.7(6)	26.3(6)	24.6(6)	-0.5(4)	-1.7(4)	-0.3(5)
C^{11}	26.8(6)	19.7(5)	31.7(6)	1.9(4)	1.6(5)	0.8(4)
C^{10}	28.1(6)	25.2(6)	26.6(6)	2.5(4)	1.4(4)	1.4(5)
C^1	29.9(6)	22.8(6)	28.5(6)	0.2(4)	-3.4(5)	-3.9(5)
C^3	30.7(6)	23.6(6)	30.0(6)	-4.8(5)	-2.7(5)	1.6(5)
C^4	29.3(6)	22.8(6)	32.5(6)	-3.4(5)	-3.4(5)	-1.1(5)
C^9	39.0(7)	34.1(7)	30.3(7)	7.2(5)	-4.4(5)	-1.7(6)
C^{17}	27.8(6)	25.8(6)	36.7(7)	3.5(5)	-0.2(5)	-2.3(5)
C^5	36.4(7)	30.3(7)	39.6(7)	2.7(5)	-6.8(5)	1.6(5)
C^8	36.5(7)	36.0(7)	36.2(7)	-2.9(6)	4.6(5)	5.4(6)
C^{18}	31.4(7)	39.0(7)	37.8(7)	6.0(6)	-3.3(5)	-5.8(6)
C^6	32.0(7)	33.5(7)	50.9(8)	-4.1(6)	-8.1(6)	7.8(6)
C^{16}	35.1(7)	37.1(7)	36.8(7)	2.1(6)	7.3(5)	-2.3(6)
C^{12}	37.7(7)	39.9(7)	35.2(7)	-6.6(6)	6.9(5)	-7.9(6)
C^{19}	30.2(7)	38.7(8)	54.4(9)	8.2(6)	-7.4(6)	-0.1(6)
C^{14}	40.3(8)	39.8(8)	55.6(9)	-2.2(7)	-11.2(7)	-8.9(6)
C^7	32.0(7)	40.1(8)	48.9(8)	-7.6(6)	3.2(6)	7.8(6)
C^{15}	28.5(7)	40.3(8)	61.2(10)	2.5(7)	3.1(6)	-5.7(6)
C^{22}	40.3(8)	62.7(10)	42.6(8)	17.2(7)	6.3(6)	14.5(7)
C^{20}	31.0(7)	49.0(9)	67.3(11)	13.0(8)	8.1(7)	7.1(6)
C^{13}	54.3(9)	52.9(9)	38.9(8)	-9.5(7)	-2.3(7)	-15.5(8)
C^{21}	45.8(9)	77.5(13)	56.8(10)	24.3(9)	19.7(8)	18.8(9)

Table S4. Bond Lengths for 2aa.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O^{1}	N^{2}	1.4222(15)	C^{4}	C^{5}	1.3870(18)
O^{1}	C^{2}	1.4548(14)	C^{17}	C^{18}	1.3967(18)
N^{1}	C^{1}	1.2932(16)	C^{17}	C^{22}	1.387(2)
N^{1}	C^{4}	1.4262(16)	C^{5}	C^{6}	1.395(2)
N^{2}	C^{9}	1.2730(19)	C^{8}	C^{7}	1.399(2)
C^{2}	C^{10}	1.5627(17)	C^{18}	C^{19}	1.397(2)
C^{2}	C^{1}	1.5312(17)	C^{6}	C^{7}	1.381(2)
C^{2}	C^{3}	1.5082(17)	C^{16}	C^{15}	1.386(2)
C^{11}	C^{10}	1.5044(17)	C^{12}	C^{13}	1.385(2)
C^{11}	C^{16}	1.3931(18)	C^{19}	C^{20}	1.369(2)
C^{11}	C^{12}	1.3825(18)	C^{14}	C^{15}	1.372(2)
C^{10}	C^{9}	1.5000(17)	C^{14}	C^{13}	1.383(2)
C^{1}	C^{17}	1.4754(17)	C^{22}	C^{21}	1.384(2)
C^{3}	C^{4}	1.3857(18)	C^{20}	C^{21}	1.380(2)
C^{3}	C^{8}	1.3788(18)			

Table S5. Bond Angles for 2aa

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N^{2}	O^{1}	C^{2}	109.03(9)	C^{3}	C^{4}	N^{1}	112.05(11)
C^{1}	N^{1}	C^{4}	107.23(11)	C^{3}	C^{4}	C^{5}	121.69(12)
C^{9}	N^{2}	O^{1}	108.74(10)	C^{5}	C^{4}	N^{1}	126.24(12)
O^{1}	C^{2}	C^{10}	103.92(9)	N^{2}	C^{9}	C^{10}	115.56(12)
O^{1}	C^{2}	C^{1}	114.20(10)	C^{18}	C^{17}	C^{1}	122.35(12)
O^{1}	C^{2}	C^{3}	111.99(10)	C^{22}	C^{17}	C^{1}	118.94(12)
C^{1}	C^{2}	C^{10}	111.50(10)	C^{22}	C^{17}	C^{18}	118.68(13)
C^{3}	C^{2}	C^{10}	115.56(10)	C^{4}	C^{5}	C^{6}	117.33(13)
C^{3}	C^{2}	C^{1}	100.11(10)	C^{3}	C^{8}	C^{7}	117.91(13)
C^{16}	C^{11}	C^{10}	122.62(12)	C^{17}	C^{18}	C^{19}	119.97(13)
C^{12}	C^{11}	C^{10}	118.83(11)	C^{7}	C^{6}	C^{5}	121.11(13)
C^{12}	C^{11}	C^{16}	118.53(12)	C^{15}	C^{16}	C^{11}	120.29(13)
C^{11}	C^{10}	C^{2}	116.00(10)	C^{11}	C^{12}	C^{13}	120.95(14)
C^{9}	C^{10}	C^{2}	98.80(10)	C^{20}	C^{19}	C^{18}	120.28(14)
C^{9}	C^{10}	C^{11}	117.25(11)	C^{15}	C^{14}	C^{13}	119.48(14)
N^{1}	C^{1}	C^{2}	113.37(11)	C^{6}	C^{7}	C^{8}	121.01(13)
N^{1}	C^{1}	C^{17}	121.54(12)	C^{14}	C^{15}	C^{16}	120.69(14)
C^{17}	C^{1}	C^{2}	124.91(11)	C^{21}	C^{22}	C^{17}	120.89(15)
C^{4}	C^{3}	C^{2}	106.90(11)	C^{19}	C^{20}	C^{21}	120.21(15)
C^{8}	C^{3}	C^{2}	132.17(12)	C^{14}	C^{13}	C^{12}	120.06(15)
C^{8}	C^{3}	C^{4}	120.92(12)	C^{20}	C^{21}	C^{22}	119.96(16)

Table S6. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 2aa.

Atom	*x*	*y*	*z*	U(eq)
H[10]	7030.02	5321.16	7237.18	32
H[9]	7917.09	5901.61	5326.21	41
H[5]	9546.09	1713.61	9311.87	43
H[8]	10036.95	3515.3	5850.22	43
H[18]	5259.02	4176.46	6487.25	43
H[6]	11390.91	1656.87	8351.68	47
H[16]	10002.77	5649.99	6216.74	44
H[12]	7985.37	5532.71	9029.94	45
H[19]	3235.97	4543.3	6860.44	49
H[14]	11393.57	6622.61	9180.04	54
H[7]	11621.13	2514.49	6638.24	48
H[15]	11588.18	6349.4	7259.42	52
H[22]	5692.46	3229.7	9715.97	58
H[20]	2452.54	4231.22	8632.07	59
H[13]	9580.67	6219.93	10066.76	58
H[21]	3675.93	3575.07	10062.65	72

Experimental

Single crystals of $C_{22}H_{16}N_2O$ (**2aa**) were obtained by crystallization from solution in benzene. A suitable crystal was selected and mounted on the glass stick with acrylic glue. The diffraction spectrum was registered on a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer. The crystal was kept at 149.99(10) K during data collection. Using Olex2,[5] the structure was solved with the ShelXT[6] structure solution program using Intrinsic Phasing and refined with the ShelXL[7] refinement package using Least Squares minimization.

Crystal structure determination of 2aa.

Crystal Data for $C_{22}H_{16}N_2O$ (M =324.37 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 11.1571(2) Å, b = 12.4540(2) Å, c = 11.9000(2) Å, β = 90.0450(10)°, V = 1653.51(5) Å^3, Z = 4, T = 149.99(10) K, μ(CuKα) = 0.638 mm^{-1}, $Dcalc$ = 1.303 g/cm^3, 16080 reflections measured (10.282° ≤ 2Θ ≤ 151.682°), 3424 unique (R_{int} = 0.0360, R_{sigma} = 0.0189) which were used in all calculations. The final R_1 was 0.0452 (I > 2σ(I)) and wR_2 was 0.1220 (all data).

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups
2.a Ternary CH refined with riding coordinates:
 C10(H10)
2.b Aromatic/amide H refined with riding coordinates:
 C9(H9), C5(H5), C8(H8), C18(H18), C6(H6), C16(H16), C12(H12), C19(H19),
 C14(H14), C7(H7), C15(H15), C22(H22), C20(H20), C13(H13), C21(H21)
```

Theoretical Modelling

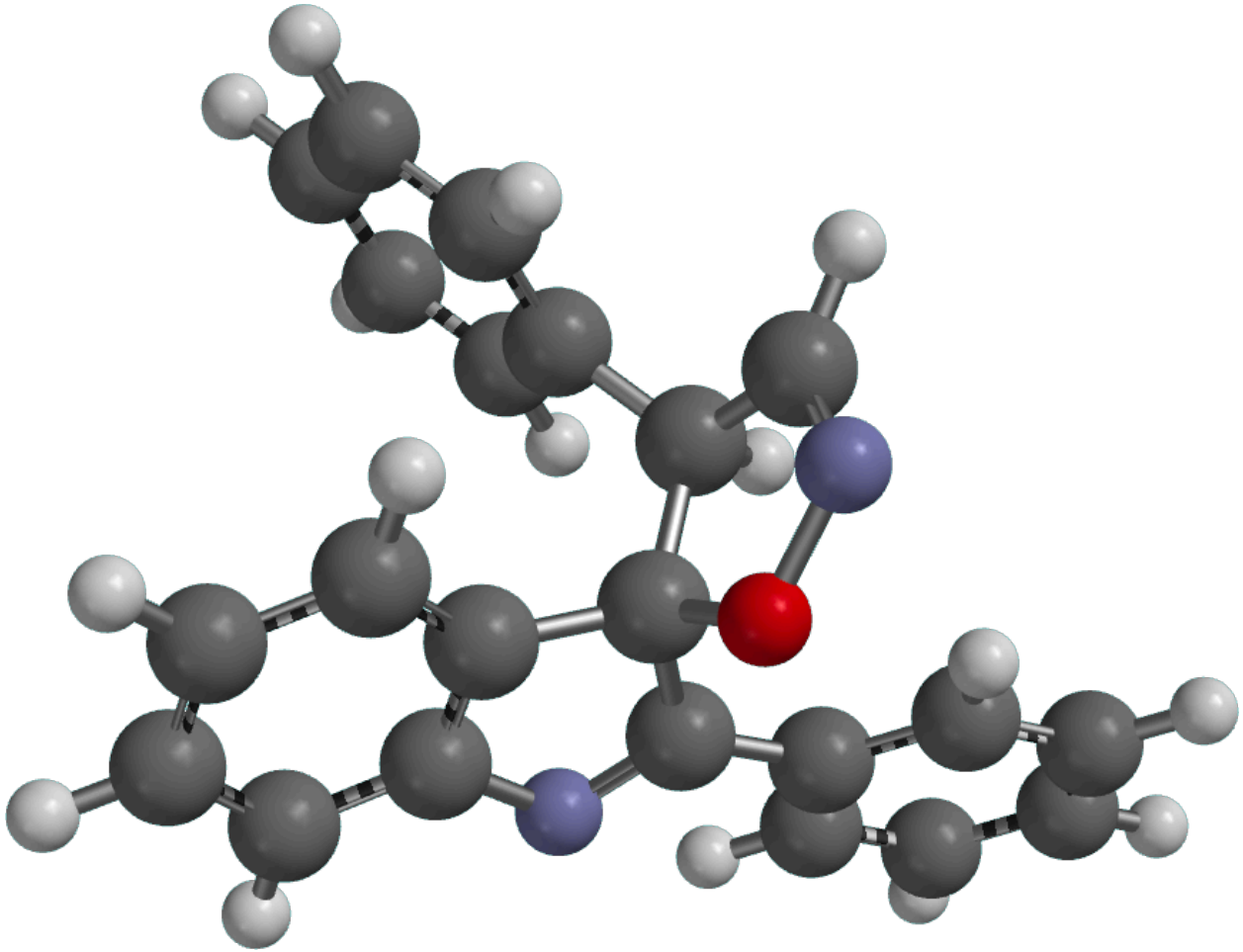


Figure S3. Optimized geometry of **2aa** molecule (DFT, b3lyp 6-311++G**). Number of imaginary frequencies: 0.

Table S7. XYZ coordinates of atoms in optimized geometry of **2aa** structure.

H	3.208132	4.149488	-0.740889	H	-4.978946	-1.466222	1.360885
C	2.567450	3.350825	-0.383994	H	-5.081143	0.159224	-2.612110
C	0.964437	1.295433	0.554842	H	-6.178525	-1.111302	-0.782408
C	1.317647	3.150698	-0.978560	O	-0.568379	0.370440	2.225198
C	2.995804	2.548143	0.674612	C	0.150953	-1.219445	0.583439
C	2.190755	1.507626	1.157612	H	-0.690945	-1.646216	0.025790
C	0.525887	2.122146	-0.486062	C	0.049614	-1.714081	2.003603
H	0.962401	3.781508	-1.784501	H	0.251151	-2.728234	2.326361
H	3.960780	2.734303	1.132029	N	-0.350656	-0.859395	2.855674
H	2.525443	0.899674	1.989444	C	1.417275	-1.591791	-0.163238
N	-0.793337	1.808938	-0.893727	C	3.724621	-2.292730	-1.601763
C	-0.147024	0.310526	0.824422	C	2.620624	-1.849699	0.500688
C	-1.227281	0.848254	-0.148781	C	1.385298	-1.696308	-1.557958
C	-2.580572	0.290821	-0.300921	C	2.530280	-2.037560	-2.273555
C	-5.176275	-0.719964	-0.647628	C	3.765521	-2.199654	-0.212370
C	-3.276279	0.498969	-1.505484	H	2.668233	-1.777766	1.582168
C	-3.211523	-0.426166	0.728246	H	0.457222	-1.508234	-2.088196
C	-4.500632	-0.924302	0.552832	H	2.487057	-2.111287	-3.354404
C	-4.558995	-0.004426	-1.675930	H	4.689165	-2.400227	0.319286
H	-2.791670	1.059850	-2.294828	H	4.615561	-2.564224	-2.156553
H	-2.714456	-0.564538	1.678389				

Parameters:

Formula: $_{C22}H_{16}N_2O$ Dipole moment: 3.63 D

Energy: -1032.88837 au Cv: 311.23 J/molK

ZPE: 850.88 kJ/mol S^o: 511.49 J/molK

H^o: -1032.54771 au G^o: -1032.60580 au

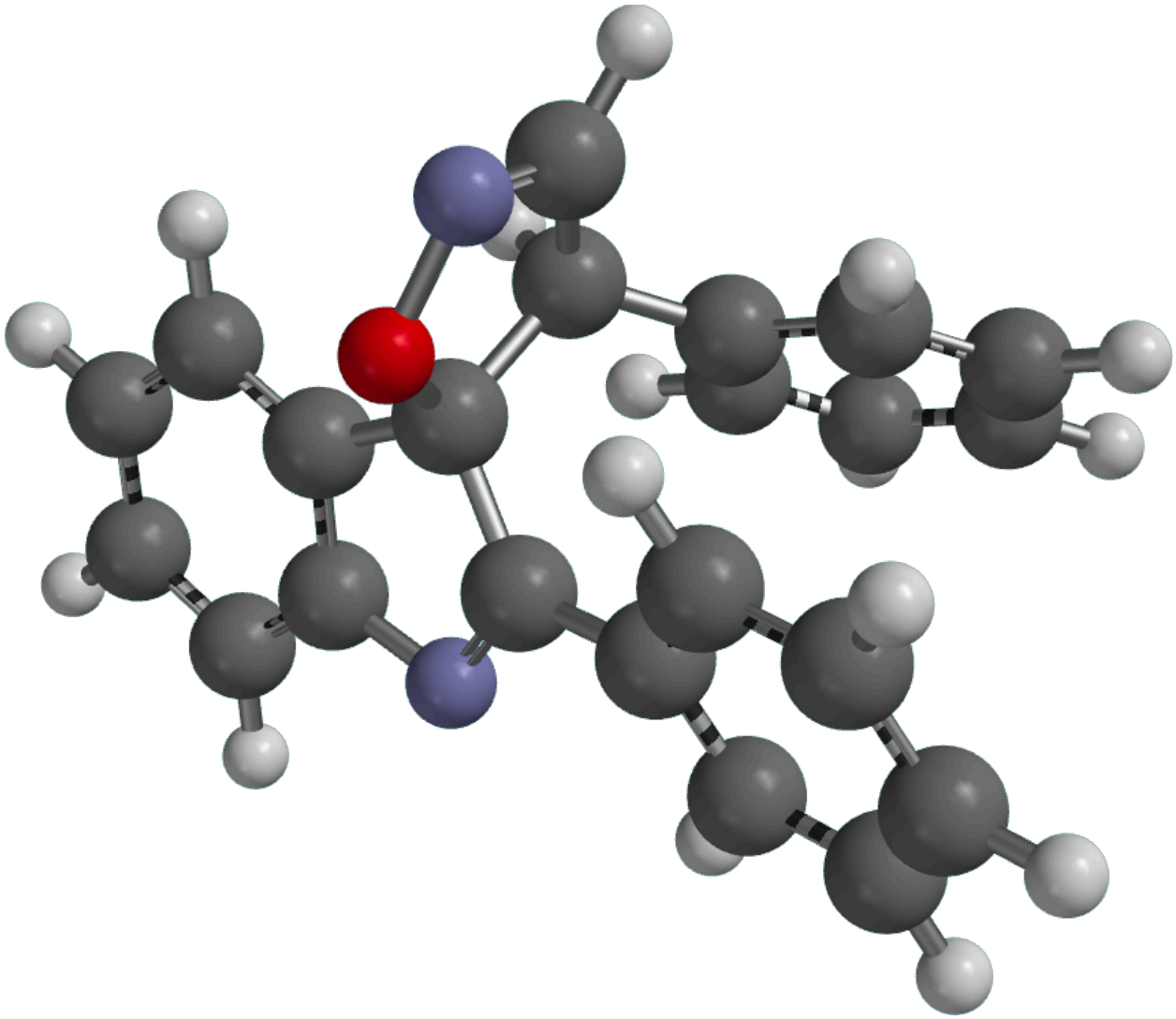


Figure S4. Optimized geometry of *epi*-**2aa** molecule (DFT, b3lyp 6-311++G**). Number of imaginary frequencies: 0.

Table S8. XYZ coordinates of atoms in optimized geometry of ei-**2aa** structure.

H	-5.495914	0.350288	2.043582	H	3.670570	2.472724	-1.730717
C	-4.610985	0.327117	1.417513	H	3.686340	2.107019	2.548236
C	-2.376812	0.252306	-0.212609	H	4.865424	2.671762	0.436534
C	-3.388867	0.769801	1.934445	O	-0.927798	1.063143	-2.034788
C	-4.712492	-0.133761	0.103514	C	-0.464271	-1.142052	-1.206080
C	-3.584951	-0.179570	-0.728784	H	-1.326183	-1.816957	-1.170855
C	-2.281265	0.731855	1.097827	C	-0.143603	-0.881962	-2.652898
H	-3.301176	1.141243	2.948406	H	0.253595	-1.615421	-3.344052
H	-5.674402	-0.455602	-0.278895	N	-0.418887	0.283613	-3.079169
H	-3.671179	-0.531635	-1.751424	C	0.630212	-1.794904	-0.378600
N	-0.975358	1.181858	1.401835	C	2.591280	-3.048824	1.189851
C	-0.984131	0.292538	-0.794621	C	0.278372	-2.491284	0.783649
C	-0.230220	1.006208	0.361556	C	1.977055	-1.743670	-0.748069
C	1.173748	1.446598	0.344396	C	2.950608	-2.368085	0.029192
C	3.836020	2.331840	0.410693	C	1.250695	-3.107278	1.566736
C	1.853197	1.583543	1.567167	H	-0.764503	-2.551154	1.078692
C	1.847057	1.771454	-0.843463	H	2.274355	-1.207115	-1.641910
C	3.167536	2.213755	-0.805558	H	3.990842	-2.316809	-0.272084
C	3.172132	2.015540	1.597808	H	0.960284	-3.638448	2.466564
H	1.329284	1.341211	2.483154	H	3.349125	-3.532919	1.795216
H	1.333750	1.711379	-1.792789				

Parameters:

Formula: $C_{22}H_{16}N_2O$ Dipole moment: 3.61 D
Energy: -1032.88613 au Cv: 305.50 J/molK
ZPE: 861.47 kJ/mol S^o: 507.07 J/molK
H^o: -1032.54169 au G^o: -1032.59927 au

References

(1) Bazile, Y.; De Cointet, P.; Pigerol, C. *J. Heterocycl. Chem.* **1978**, *15*, 859-864.
(2) Bhunia, S. K.; Polley, A.; Natarajan, R.; Jana, R. Chem. Eur. J. **2015**, *21*, 16786-16791.
(3) Lian, X.-L.; Lei, H.; Quan, X.-J.; Ren, Z.-H.; Wang, Y.-Y.; Guan, Z.-H. *Chem. Commun. (Cambridge, UK)* **2013**, *49*, 8196-8198.
(4) Sivcev, V. P.; Volcho, K. P.; Salakhutdinov, N. F.; Anikeev, V. I. *J. Supercrit. Fluids* **2016**, *107*, 179-181.
(5) Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. *J. Appl. Cryst*. **2009**, *42*, 339-341.
(6) Sheldrick, G.M. *Acta Cryst*. **2015**, *A71*, 3-8.
(7) Sheldrick, G.M. *Acta Cryst*. **2015**, *C71*, 3-8.