$ZrCl_4$-promoted facile synthesis of indole derivatives

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Supporting Information

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Experimental Section

General Information. Commercial grade reagents and solvents were used as received from the supplier except where indicated. Dichloroethane (DCE) was distilled from CaH_2 prior to use. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ with 300 MHz NMR spectrometer. ^{1}H NMR and ^{13}C NMR chemical shifts (δ) were reported in units of part per million (ppm), relative to tetramethylsilane (TMS) at δ equal to zero ppm. Coupling constants (*J*) were reported in Hertz (Hz). Infrared spectra were measured using an FT-IR spectrometer and reported in cm^{-1}. Low resolution (LRMS) mass spectra were measured using electron ionization (EI). High resolution (HRMS) mass spectra were obtained using time-of-flight (TOF) via atmospheric pressure chemical ionization (APCI) or electrospray ionization (ESI).

General procedure for the synthesis of aryl azidoacrylate (1a): To a deoxygenated solution of ethyl cinnamate (0.54 g, 3.04 mmol) and NaN_3 (0.30 g, 4.56 mmol) in dry CH_3CN (10 mL) was added a deoxygenated solution of CAN (4.17 g, 7.60 mmol) in dry CH_3CN (25 mL) dropwise at 0 °C for 30 min and the reaction mixture was then warmed to room temperature. The mixture was stirred overnight and quenched with water and extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried (Na_2SO_4) and concentrated. The crude product in dry acetone (15 mL) was treated with KOAc (0.59 g, 6.08 mmol). The reaction mixture was stirred for overnight followed by usual work up and purified by silica gel column chromatography using 10% EtOAc/hexane as eluent to yield 367.3 mg (56%) of (*Z*)-ethyl 2-azido-3-phenylacrylate (**1a**) as a yellow solid: mp 37-38 °C; IR (neat): ν_{max} 2115, 1709, 1617, 1448, 1241 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83-7.80 (m, 2H), 7.41-7.30 (m, 3H), 6.91 (s, 1H), 4.37 (q, 2H, *J* = 7.2 Hz), 1.40 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.5, 133.2, 130.5, 129.3, 128.4, 125.5, 125.3, 62.2, 14.2. APCI-HRMS calcd for $C_{11}H_{11}N_3NaO_2$ $(M+Na)^+$ 240.0744, found 240.0737.

Characterization data of aryl azidoacrylate:

*(Z)-ethyl 2-azido-3-o-tolylacrylate (**1b**)*: Yield 406.1 mg (73%, yellow solid); mp 46-47 °C; IR (neat): ν_{max} 2927, 2118, 1713, 1246 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98-7.93 (m, 1H), 7.27-7.18 (m, 3H), 7.14 (s, 1H), 4.38 (q, 2H, *J* = 7.2 Hz), 2.36 (s, 3H), 1.40 (t, 3H, *J* = 7.2 Hz); ^{13}C

NMR (75 MHz, $CDCl_3$) δ 163.5, 137.5, 131.9, 130.2, 129.6, 129.1, 126.3, 125.8, 123.2, 62.3, 20.1, 14.2. ESI-HRMS calcd for $C_{12}H_{13}N_3NaO_2$ $(M+Na)^+$ 254.0900, found 254.0896.

*(E)-ethyl 2-azido-3-(2-ethylphenyl)acrylate (**1c**)*: Yield 672.8 mg (57%, yellow oil); IR (neat): ν_{max} 2985, 2109, 1710, 1228, 1079 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.93 (dd, 1H, *J* = 8.4, 2.4 Hz), 7.25-7.17 (m, 4H), 4.35 (q, 2H, *J* = 7.2 Hz), 2.68 (q, 2H, *J* = 7.2 Hz), 1.37 (t, 3H, *J* = 7.2 Hz), 1.19 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.3, 143.4, 131.0, 129.6, 129.2, 128.5, 126.2, 125.6, 123.0, 62.1, 26.6, 15.2, 14.0. ESI-HRMS calcd for $C_{13}H_{15}N_3NaO_2$ $(M+Na)^+$ 268.1057, found 268.1056.

*(Z)-ethyl 2-azido-3-(4-tert-butylphenyl)acrylate (**1d**)*: Yield 675.7 mg (49%, light yellow solid); mp 42-43 °C; IR (neat): ν_{max} 2964, 2117, 1710, 1245 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, 2H, *J* = 8.4 Hz), 7.41 (d, 2H, *J* = 8.7 Hz), 6.91 (s, 1H), 4.36 (q, 2H, *J* = 7.2 Hz), 1.40 (t, 3H, *J* = 7.2 Hz), 1.33 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.6, 152.8, 130.43, 130.39, 125.4, 124.8, 62.1, 34.8, 31.1, 14.2. ESI-HRMS calcd for $C_{15}H_{19}N_3NaO_2$ $(M+Na)^+$ 296.1370, found 296.1375.

*(Z)-ethyl 2-azido-3-(biphenyl-4-yl)acrylate (**1e**)*: Yield 522.2 mg (56%, light yellow solid); mp 95-96 °C; IR (neat): ν_{max} 2983, 2119, 1709, 1254 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.90 (d, 2H, *J* = 8.1 Hz), 7.63-7.61 (m, 4H), 7.48-7.43 (m, 2H), 7.39-7.34 (m, 1H), 6.95 (s, 1H), 4.38 (q, 2H, *J* = 7.2 Hz), 1.41 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.5, 141.9, 140.2, 132.2, 131.0, 128.8, 127.7, 127.0, 125.5, 124.8, 62.3, 14.2. EI-MS (rel intensity) 293 (M^+, 5), 265 (30), 192 (100), 149 (66), 71 (16).

*(Z)-ethyl 2-azido-3-(naphthalen-1-yl)acrylate (**1f**)*: Yield 443.9 mg (82%, white solid); mp 66-67 °C; IR (neat): ν_{max} 2114, 1709, 1244, 778 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.09 (d, 1H, *J* = 7.2 Hz), 8.03 (d, 1H, *J* = 8.1 Hz), 7.89-7.84 (m, 2H), 7.68 (s, 1H), 7.59-7.49 (m, 3H), 4.44 (q, 2H, *J* = 7.2 Hz), 1.46 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.4, 133.5, 131.6, 129.7, 129.4, 128.8, 128.1, 127.4, 126.6, 125.9, 125.1, 123.4, 122.2, 62.4, 14.2. ESI-HRMS calcd for $C_{15}H_{13}N_3NaO_2$ $(M+Na)^+$ 290.0900, found 290.0903.

*(Z)-ethyl 2-azido-3-(naphthalen-2-yl)acrylate (**1g**):* Yield 573.4 mg (58%, white solid); mp 77-78 °C; IR (neat): ν_{max} 2110, 1709, 1242, 1080, 745 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.95 (dd, 1H, *J* = 8.7, 1.5 Hz), 7.88-7.80 (m, 3H), 7.53-7.47 (m, 2H), 7.07 (s, 1H), 4.40 (q, 2H, *J* = 7.2 Hz), 1.42 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.6, 133.5, 133.1,

130.9, 130.8, 128.7, 128.0, 127.6, 127.3, 127.1, 126.4, 125.6, 125.3, 62.3, 14.2. ESI-HRMS calcd for $C_{15}H_{13}N_3NaO_2$ $(M+Na)^+$ 290.0900, found 290.0903.

*(Z)-ethyl 2-azido-3-(4-bromophenyl)acrylate (**1h**)*: Yield 391.6 mg (51%, yellow solid); mp 36-37 °C; IR (neat): ν_{max} 2983, 2121, 1714, 1248, 1075 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.64 (d, 2H, *J* = 8.7 Hz), 7.49 (d, 2H, *J* = 8.7 Hz), 6.81 (s, 1H), 4.36 (q, 2H, *J* = 7.2 Hz), 1.39 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.3, 132.1, 131.9, 131.6, 126.2, 123.6, 123.4, 62.4, 14.2. EI-MS (rel intensity) 295 (M^+, 5), 195 (100), 116 (50), 89 (47).

*(Z)-ethyl 2-azido-3-(4-chlorophenyl)acrylate (**1i**)*: Yield 245.0 mg (42%, light yellow oil); IR (neat): ν_{max} 2984, 2218, 1713, 1248 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.77-7.74 (m, 2H), 7.36-7.33 (m, 2H), 6.84 (s, 1H), 4.37 (q, 2H, *J* = 7.2 Hz), 1.40 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.3, 135.1, 131.72, 131.68, 130.9, 128.7, 126.0, 123.7, 62.4, 14.2. EI-MS (rel intensity) 251 (M^+, 5), 151 (100), 114 (26), 89 (28).

*(Z)-ethyl 2-azido-3-(4-fluorophenyl)acrylate (**1j**)*: Yield 1.04 g (82%, light yellow solid); mp 37-38 °C; IR (neat): ν_{max} 2121, 1711, 1233, 833 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.83-7.78 (m, 2H), 7.09-7.02 (m, 2H), 6.85 (s, 1H), 4.36 (q, 2H, *J* = 7.2 Hz), 1.39 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.5, 162.3 (d, J_{CF} = 656 Hz), 132.5 (d, J_{CF} = 33 Hz), 129.4 (d, J_{CF} = 13.2 Hz), 125.1 (d, J_{CF} = 10.2 Hz), 123.9, 115.5 (d, J_{CF} = 86 Hz), 62.2, 14.1. EI-MS (rel intensity) 235 (M^+, 4), 161 (12), 135 (100), 108 (42).

*(Z)-ethyl 2-azido-3-(4-nitrophenyl)acrylate (**1k**):* Yield 327.6 mg (62%, yellow solid); mp 119-120 °C; IR (neat): ν_{max} 2122, 1716, 1518, 1266 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.22 (d, 2H, *J* = 9.0 Hz), 7.96 (d, 2H, *J* = 8.7 Hz), 6.89 (s, 1H), 4.41 (q, 2H, *J* = 7.2 Hz), 1.43 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.8, 147.2, 139.4, 130.9, 129.1, 123.6, 121.4, 62.8, 14.1. EI-MS (rel intensity) 262 (M^+, 1), 167 (22), 149 (87), 84 (100).

*(Z)-ethyl 2-azido-3-(2-bromophenyl)acrylate (**1l**)*: Yield 282.2 mg (56%, light yellow solid); mp 54-55 °C; IR (neat): ν_{max} 2114, 1713, 1243, 1076, 764 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.11 (dd, 1H, *J* = 8.1, 1.5 Hz), 7.60 (dd, 1H, *J* = 8.1, 1.2 Hz), 7.34 (td, 1H, *J* = 7.8, 0.6 Hz), 7.25 (s, 1H), 7.17 (td, 1H, *J* = 7.8, 1.5 Hz), 4.39 (q, 2H, *J* = 7.2 Hz), 1.41 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.2, 132.9, 131.2, 130.2, 127.4, 127.1, 125.2, 123.3, 62.5, 14.1. ESI-HRMS calcd for $C_{11}H_{10}BrN_3NaO_2$ (Br-79) $(M+Na)^+$ 317.9849, found 317.9842.

(*Z)-ethyl 2-azido-3-(2-chlorophenyl)acrylate* ***(1m)***: Yield 351.1 mg (65%, white solid); mp 41-42 °C; IR (neat): ν_{max} 2115, 1713, 1243, 1079 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 (dd, 1H, *J* = 7.8, 1.8 Hz), 7.43 (dd, 1H, *J* = 7.2, 1.2 Hz), 7.34-7.24 (m, 3H), 4.41 (q, 2H, *J* = 7.2 Hz), 1.43 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.2, 134.6, 131.2, 131.0, 130.2, 129.6, 127.4, 126.6, 120.5, 62.5, 14.2 EI-MS (rel intensity) 223 (M^+, 6), 151 (100), 123 (38), 89 (37).

(Z)-ethyl 2-azido-3-(3-chlorophenyl)acrylate ***(1n)***: Yield 495.3 mg (40%, light yellow solid); mp 39-40 °C; IR (neat): ν_{max} 2122, 1713, 1376, 1247, 1083 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.65-7.61 (m, 1H), 7.34-7.27 (m, 2H), 6.81 (s, 1H), 4.37 (q, 2H, *J* = 7.2 Hz), 1.40 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.2, 134.9, 134.3, 130.1, 129.6, 129.2, 128.7, 126.8, 123.2, 62.5, 14.2. EI-MS (rel intensity) 251 (M^+, 5), 177 (47), 151 (100), 116 (41), 89 (26).

(Z)-ethyl 2-azido-3-(3-fluoro-4-methylphenyl)acrylate ***(1o)***: Yield 0.8700 mg (62%, yellow oil); IR (neat): ν_{max} 2969, 2109, 1710, 1228, 1079 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (dd, 1H, *J* = 11.4, 1.2 Hz), 7.38 (dd, 1H, *J* = 7.8, 1.2 Hz), 7.17 (t, 1H, *J* = 7.8 Hz), 6.83 (s, 1H), 4.37 (q, 2H, *J* = 7.2 Hz), 2.29 (d, 3H, *J* = 1.5 Hz), 1.40 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.2, 160.8 (d, J_{CF} = 97 Hz), 132.6, (d, J_{CF} = 34 Hz), 131.1 (d, J_{CF} = 22 Hz), 126.5, 126.4 (d, J_{CF} = 70 Hz), 126.3 (d, J_{CF} = 12 Hz), 125.6, 123.8 (d, J_{CF} = 10 Hz), 116.2 (d, J_{CF} = 95 Hz), 62.2, 14.5 (d, J_{CF} = 13 Hz), 14.0. ESI-HRMS calcd for $C_{12}H_{12}FN_3NaO_2$ $(M+Na)^+$ 272.0806, found 272.0818.

(Z)-ethyl 2-azido-3-(3-methoxyphenyl)acrylate ***(1p)***: Yield 1.35 g (45%, light yellow solid); mp 43-44 °C; IR (neat): ν_{max} 2983, 2106, 1708, 1227, 686 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.35-7.25 (m, 2H), 6.90-6.87 (m, 2H), 4.36 (q, 2H, *J* = 7.2 Hz), 3.82 (s, 3H), 1.39 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.4, 159.4, 134.4, 129.3, 125.7, 125.1, 123.3, 115.4, 115.2, 62.2, 55.2, 14.1. ESI-HRMS calcd for $C_{12}H_{13}N_3NaO_3$ $(M+Na)^+$ 270.0849, found 270.0846.

(Z)-ethyl 2-azido-3-(2-chloro-3,4-dimethoxyphenyl)acrylate ***(1q)***: Yield 365.5 mg (50%, white solid); mp 85-86 °C; IR (neat): ν_{max} 2115, 1709, 1490, 1304, 1040 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (d, 1H, *J* = 9.0 Hz), 7.29 (s, 1H), 6.87 (d, 1H, *J* = 9.0 Hz), 4.38 (q, 2H, *J* = 7.2 Hz), 3.92 (s, 3H), 3.86 (s, 3H), 1.41 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.5,

154.2, 145.5, 129.6, 126.6, 125.8, 124.5, 120.7, 110.0, 62.3, 60.6, 56.1, 14.2. ESI-HRMS calcd for $C_{13}H_{14}ClN_3NaO_4$ (Cl-35) $(M+Na)^+$ 334.0565, found 334.0565.

General procedure for the synthesis of indoles: A mixture of $ZrCl_4$ (153.0 mg, 0.6574 mmol, 1.4 equiv) and $AgNO_3$ (8 mg, 0.0460 mmol, 0.1 equiv) in dry DCE (1 mL) was added with aryl azidoacrylate **1a** (100.0 mg, 0.4604 mmol, 1.0 equiv) at 0 ºC and the reaction mixture was stirred at this temperature for 20 min. The reaction mixture was directly purified by silica gel column packed with 100% hexane and eluted with 10% EtOAc/hexane to yield 65.1 mg (70%) of *ethyl 1H-indole-2-carboxylate (**2a**)* as a white solid: mp 113-114 °C; IR (neat): ν_{max} 3278, 1717, 1652, 1478, 1251 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 9.05 (br s, 1H), 7.68 (dd, 1H, J = 8.1, 0.6 Hz), 7.42 (dd, 1H, J = 8.4, 0.9 Hz), 7.31 (td, 1H, J = 6.9, 0.9 Hz), 7.23 (dd, 1H, J = 2.1, 0.9 Hz), 7.14 (td, 1H, J = 7.8, 0.9 Hz), 4.42 (q, 2H, J = 7.2 Hz), 1.42 (t, 3H, J = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.2, 136.9, 127.5, 125.3, 122.5, 120.7, 111.9, 108.6, 61.0, 14.4. APCI-HRMS calcd for $C_{11}H_{12}NO_2$ $(M+H)^+$ 190.0863, found 190.0857.

Characterization data of indoles:

*ethyl 3-chloro-2-oxo-3-phenylpropanoate (**3a**)*: Yellow oil, IR (neat): ν_{max} 1732, 1240, 1056, 696 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.63-7.56 (m, 4H), 7.49-7.25 (m, 5H), 6.20 (s, 1H), 4.35-4.24 (m, 2H), 1.30 (t, 3H, J = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.8, 160.0, 142.7, 140.0, 131.8, 129.4, 128.9, 127.9, 127.1, 63.2, 61.8, 13.8. ESI-HRMS calcd for $C_{17}H_{15}ClNaO_3$ (Cl-35) $(M+Na)^+$ 325.0602, found 325.0594.

*ethyl 4-methyl-1H-indole-2-carboxylate (**2b**)*: Yield 65.7 mg (75%, white solid); mp 117-118 °C; IR (neat): ν_{max} 3314, 1674, 1527, 1262, 757 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 9.06 (br s, 1H), 7.27-7.19 (m, 3H), 6.95-6.93 (m, 1H), 4.42 (q, 2H, J = 7.2 Hz), 2.57 (s, 3H), 1.42 (t, 3H, J = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.1, 136.7, 132.3, 127.7, 126.8, 125.5, 120.7, 109.4, 107.3, 61.0, 18.6, 14.4. ESI-HRMS calcd for $C_{12}H_{14}NO_2$ $(M+H)^+$ 204.1019, found 204.1019.

*ethyl 4-ethyl-1H-indole-2-carboxylate (**2c**)*: Prepared according to general procedure with a slight modification: a solution of starting material (112.0 mg, 0.4566 mmol) in 0.5 mL DCE was added to a mixture of $ZrCl_4$ and $AgNO_3$ in DCE (1 mL); Yield 68.7 mg (69%, white solid); mp 102-103 °C; IR (neat): ν_{max} 3319, 1673, 1259, 755 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 9.01 (br s, 1H), 7.30 (d, 1H, J = 1.8 Hz), 7.26-7.25 (m, 2H), 7.00-6.94 (m, 1H), 4.42 (q, 2H, J =7.2 Hz), 2.94 (q, 2H, J = 7.2 Hz), 1.43 (t, 3H, J = 7.2 Hz), 1.35 (t, 3H, J = 7.2 Hz); ^{13}C NMR (75 MHz,

$CDCl_3$) δ 162.2, 138.6, 136.9, 126.9, 126.8, 125.6, 118.9, 109.5, 107.1, 61.0, 26.2, 14.8, 14.4. ESI-HRMS calcd for $C_{13}H_{16}NO_2$ $(M+H)^+$ 218.1176, found 218.1184.

*ethyl 6-tert-butyl-1H-indole-2-carboxylate (**2d**)*: Prepared according to general procedure with a slight modification: a solution of starting material (120.0 mg, 0.4390 mmol) in 1.0 mL DCE was added dropwise to a mixture of $ZrCl_4$ and $AgNO_3$ in DCE (1 mL); Yield 74.4 mg (69%, white solid); mp 113-114 °C; IR (neat): ν_{max} 3327, 2958, 1690, 1230 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.93 (br s, 1H), 7.61 (d, 1H, *J* = 8.7 Hz), 7.40 (s, 1H), 7.25 (dd, 1H, *J* = 8.7, 1.5 Hz), 7.18 (dd, 1H, *J* = 2.1, 0.9 Hz), 4.41 (q, 2H, *J* = 7.2 Hz), 1.41 (t, 3H, *J* = 7.2 Hz), 1.38 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.1, 149.0, 137.1, 127.2, 125.2, 122.0, 119.5, 108.4, 107.8, 60.9, 35.0, 31.5, 14.4. ESI-HRMS calcd for $C_{15}H_{20}NO_2$ $(M+H)^+$ 246.1489, found 246.1495.

*ethyl 6-phenyl-1H-indole-2-carboxylate (**2e**)*: Yield 40.1 mg (45%, white solid); mp 116-117 °C; IR (neat): ν_{max} 3310, 1688, 1216, 770 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 9.13 (br s, 1H), 7.74 (d, 1H, *J* = 8.4Hz), 7.66-7.61 (m, 3H), 7.47-7.40 (m, 3H), 7.37-7.32 (m, 1H), 7.25-7.24 (m, 1H), 4.43 (q, 2H, *J* = 7.2 Hz), 1.43 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.0, 141.6, 138.8, 137.4, 128.8, 128.0, 127.4, 127.1, 126.8, 122.8, 120.9, 110.1, 108.5, 61.1, 14.4. ESI-HRMS calcd for $C_{17}H_{16}NO_2$ $(M+H)^+$ 266.1176, found 266.1170.

*ethyl 3-(biphenyl-4-yl)-3-chloro-2-oxopropanoate (**3e**)*: Yield 42.9 mg (42%, Yellow oil); IR (neat): ν_{max} 1732, 1240, 1056, 698 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.24-7.23 (m, 1H), 6.79 (s, 1H), 4.40 (q, 2H, *J* = 7.2 Hz), 3.91 (s, 3H), 3.89 (s, 3H), 1.42 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.9, 153.4, 141.8, 133.4, 126.6, 120.51, 120.47, 107.6, 92.9, 61.1, 61.0, 56.1, 14.3. ESI-HRMS calcd for $C_{13}H_{15}ClNO_4$ (Cl-35) $(M+H)^+$ 284.0684, found 284.0694.

*ethyl 3H-benzo[e]indole-2-carboxylate (**2f**)*: Yield 67.9 mg (80%, white solid); mp 159-160 °C; IR (neat): ν_{max} 3298, 1677, 1191, 758 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 9.47 (br s, 1H), 8.23 (d, 1H, *J* = 8.1 Hz), 7.88 (d, 1H, *J* = 8.1 Hz), 7.75 (dd, 1H, *J* = 1.8, 0.6 Hz), 7.69 (d, 1H, *J* = 9.0 Hz), 7.58 (td, 1H, *J* = 8.1, 1.2 Hz), 7.50 (d, 1H, *J* = 9.0 Hz), 7.45 (td, 1H, *J* = 8.1, 1.2 Hz), 4.46 (q, 2H, *J* = 7.2 Hz), 1.45 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.1, 134.3, 129.4, 128.8, 128.7, 126.9, 126.7, 125.6, 124.2, 123.0, 122.9, 113.0, 117.8, 61.0, 14.4. ESI-HRMS calcd for $C_{15}H_{14}NO_2$ $(M+H)^+$ 240.1019, found 240.1019.

*ethyl 1H-benzo[g]indole-2-carboxylate (**2g**)*: Yield 44.1 mg (48%, white solid); mp 158-159 °C; IR (neat): ν_{max} 3317, 1683, 1211, 743 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 10.2 (br s, 1H), 8.27

(d, 1H, J = 7.5 Hz), 7.91 (dd, 1H, J = 8.7, 1.5 Hz), 7.67 (d, 1H, J = 8.7 Hz), 7.57-7.45 (m, 3H), 7.35 (d, 1H, J = 2.1 Hz), 4.49 (q, 2H, J = 7.2 Hz), 1.46 (t, 3H, J = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.3, 133.0, 132.0, 128.8, 125.8, 125.5, 123.8, 122.0, 121.9, 121.3, 120.7, 110.2, 61.1, 14.5. ESI-HRMS calcd for $C_{15}H_{14}NO_2$ $(M+H)^+$ 240.1019, found 240.1014.

*ethyl 6-bromo-1H-indole-2-carboxylate (**2h**)*: Yield 87.8 mg (79%, white solid); mp 180-181 °C; IR (neat): ν_{max} 3319, 2983, 1695, 1316 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.16 (br s, 1H), 7.59 (s, 1H), 7.54 (d, 1H, J = 8.4 Hz), 7.26 (dd, 1H, J = 8.4, 1.45 Hz), 7.18 (d, 1H, J = 0.9 Hz), 4.43 (q, 2H, J = 7.2 Hz), 1.43 (t, 3H, J = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.8, 137.4, 128.12, 126.3, 124.3, 123.8, 119.0, 114.8, 108.6, 61.3, 14.3. ESI-HRMS calcd for $C_{11}H_{11}BrNO_2$ (Br-79) $(M+H)^+$ 267.9968, found 267.9959.

*ethyl 6-chloro-1H-indole-2-carboxylate (**2i**)*: Yield 34.5 mg (71%, white solid); mp 158-160 °C; IR (neat): ν_{max} 3317, 1693, 1521, 1317 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.24 (br s, 1H), 7.59 (d, 1H, J = 8.7 Hz), 7.42 (s, 1H), 7.19 (d, 1H, J = 1.2 Hz), 7.12 (dd, 1H, J = 8.7, 1.8 Hz), 4.43 (q, 2H, J = 7.2 Hz), 1.43 (t, 3H, J = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.9, 137.1, 131.2, 128.2, 126.0, 123.5, 121.8, 111.7, 108.6, 61.2, 14.3. ESI-HRMS calcd for $C_{11}H_{11}ClNO_2$ (Cl-35) $(M+H)^+$ 224.0473, found 224.0477.

*ethyl 6-fluoro-1H-indole-2-carboxylate (**2j**)*: Yield 61.3 mg (65%, colorless crystal); mp 128-129 °C; IR (neat): ν_{max} 3315, 1684, 1268 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.33 (br s, 1H), 7.61 (dd, 1H, J = 9.0, 5.4 Hz), 7.21-7.20 (m, 1H), 7.10 (dd, 1H, J = 9.6, 2.1 Hz), 6.92 (td, 1H, J = 9.6, 2.4 Hz), 4.43 (q, 2H, J = 7.2 Hz), 1.42 (t, 3H, J = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.3, 161.1 (d, J_{CF} = 630 Hz), 137.1 (d, J_{CF} = 52 Hz), 128.0 (d, J_{CF} = 15 Hz), 124.0, 123.7 (d, J_{CF} = 41 Hz), 110.3 (d, J_{CF} = 101 Hz), 108.8 (d, J_{CF} = 3 Hz), 97.8 (d, J_{CF} = 104 Hz), 61.2, 14.3. ESI-HRMS calcd for $C_{11}H_{11}FNO_2$ $(M+H)^+$ 208.0768, found 208.0778.

*ethyl 6-nitro-1H-indole-2-carboxylate (**2k**)*: Yield 19.0 mg (22%, yellow crystal); mp 154-155 °C; IR (neat): ν_{max} 3320, 1698, 1512, 1321, 1250 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.69 (br s, 1H), 8.34 (s, 1H), 8.05 (dd, 1H, J = 9.0, 2.1 Hz), 7.78 (d, 1H, J = 8.7 Hz), 7.30 (d, 1H, J = 0.9 Hz), 4.49 (q, 2H, J = 7.2 Hz), 1.46 (t, 3H, J = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.3, 145.5, 135.1, 132.4, 131.8, 122.9, 115.8, 108.8, 108.3, 61.9, 14.3. ESI-HRMS calcd for $C_{11}H_{11}N_2O_4$ $(M+H)^+$ 235.0713, found 235.0713.

*ethyl 4-bromo-1H-indole-2-carboxylate (**2l**)*: Yield 61.3 mg (63%, colorless crystal); mp 150-151 °C; IR (neat): ν_{max} 3308, 1689, 1253, 1210, 763 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.55 (br s, 1H), 7.37 (d, 1H, *J* = 8.1 Hz), 7.32 (d, 1H, *J* = 7.2 Hz), 7.27-7.25 (m, 1H), 7.16 (t, 1H, *J* = 7.8 Hz), 4.45 (q, 2H, *J* = 7.2 Hz), 1.44 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.0, 137.0, 128.4, 127.8, 126.0, 123.6, 116.4, 111.1, 108.7, 61.4, 14.3. ESI-HRMS calcd for $C_{11}H_{11}BrNO_2$ (Br-79) $(M+H)^+$ 267.9968, found 267.9962.

*ethyl 4-chloro-1H-indole-2-carboxylate (**2m**)*: Yield 56.4 mg (63%, white solid); mp 139-140 °C; IR (neat): ν_{max} 3316, 1691, 1257, 764 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.68 (br s, 1H), 7.34-7.31 (m, 2H), 7.24-7.21 (m, 2H), 4.45 (q, 2H, *J* = 7.2 Hz), 1.44 (t, 3H, *J* =7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.1, 137.5, 127.8, 127.7, 126.5, 125.7, 120.3, 110.6, 107.0, 61.4, 14.3. ESI-HRMS calcd for $C_{11}H_{11}ClNO_2$ (Cl-35) $(M+H)^+$ 224.0473, found 224.0475.

*ethyl 5-chloro-1H-indole-2-carboxylate (**2nX**)*: Yield 27.7 mg (31%, colorless crystal); mp 160-161 °C; IR (neat): ν_{max} 3311, 1691, 1526, 1255, 770 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.01 (br s, 1H), 7.66-7.65 (m, 1H), 7.35 (d, 1H, *J* = 9.0 Hz), 7.27 (dd, 1H, *J* = 8.7, 2.1 Hz), 7.15 (dd, 1H, *J* = 1.8, 0.6 Hz), 4.42 (q, 2H, *J* = 7.2 Hz), 1.42 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.7, 135.0, 128.7, 128.4, 126.4, 125.8, 121.7, 113.0, 107.9, 61.3, 14.3. ESI-HRMS calcd for $C_{11}H_{10}ClNO_2$ (Cl-35) $(M+H)^+$ 224.0473, found 224.0474.

*ethyl 7-chloro-1H-indole-2-carboxylate (**2nY**)*: Yield 27.1 mg (30%, colorless crystal); mp 98-99 °C; IR (neat): ν_{max} 3321, 1713, 1313, 1241 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.08 (br s, 1H), 7.58 (d, 1H, *J* = 8.1 Hz), 7.32 (dd, 1H, *J* = 7.8, 0.9 Hz), 7.25 (d, 1H, *J* = 2.1 Hz), 7.08 (t, 1H, *J* = 7.8 Hz), 4.43 (q, 2H, *J* = 7.2 Hz), 1.42 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.5, 134.2, 128.7, 128.2, 124.4, 121.5, 121.1, 117.2, 109.3, 62.3, 14.4. ESI-HRMS calcd for $C_{11}H_{11}ClNO_2$ (Cl-35) $(M+H)^+$ 224.0473, found 224.0472.

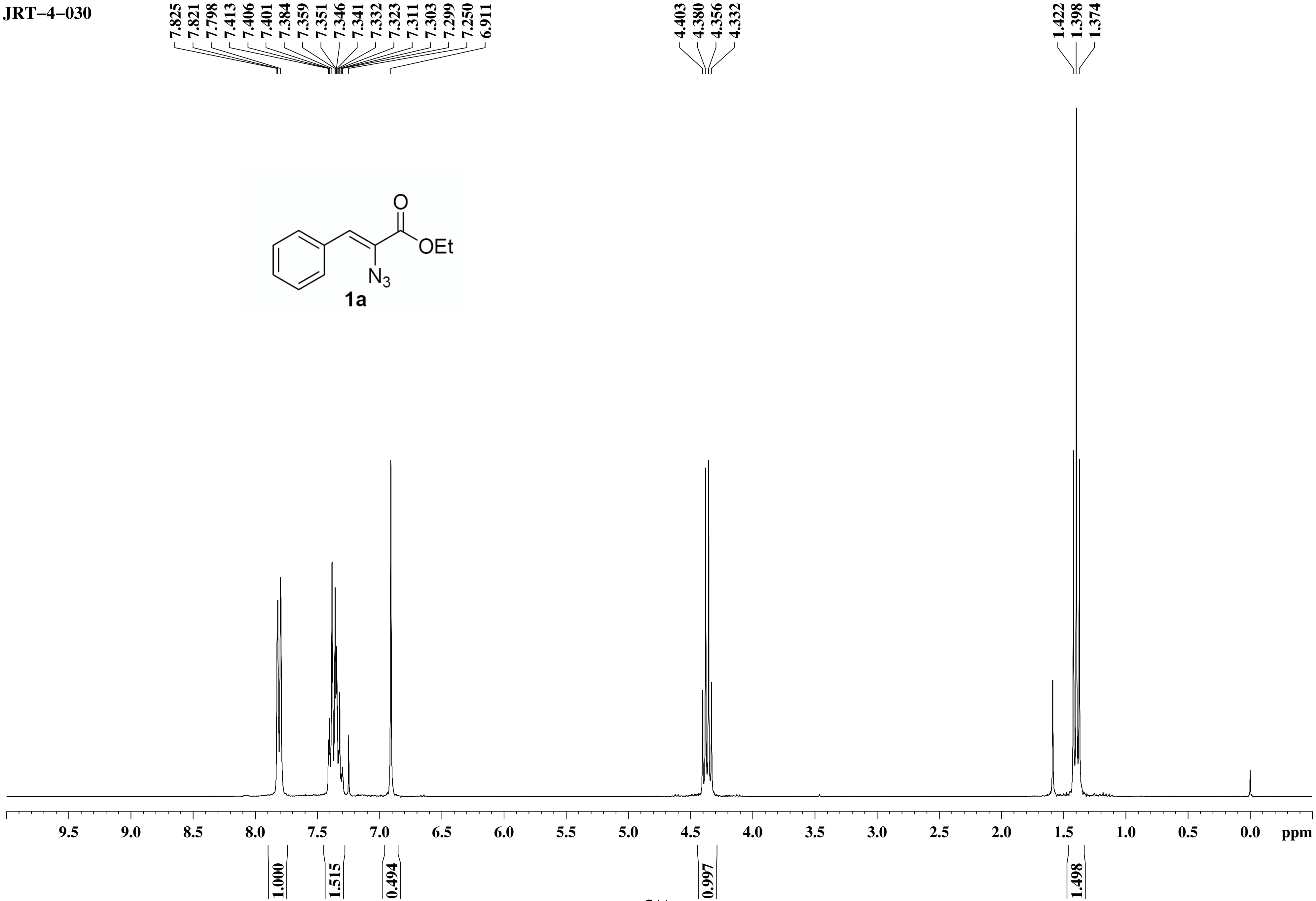
*ethyl 5-fluoro-6-methyl-1H-indole-2-carboxylate (**2oX**)*: Yield 34.4 mg (38%, white solid); mp 141-142 °C; IR (neat): ν_{max} 3319, 1690, 1248, 771 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.16 (br s, 1H), 7.25 (d, 1H, *J* = 9.9 Hz), 7.18 (d, 1H, *J* = 6.3 Hz), 7.13 (dd, 1H, *J* = 2.1, 0.9 Hz), 4.42 (q, 2H, *J* = 7.2 Hz), 2.38 (d, 3H, *J* = 1.8 Hz), 1.41 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.0, 157.3 (d, J_{CF} = 942 Hz), 133.6, 128.0, 125.6, 124.4 (d, J_{CF} = 88 Hz), 113.1 (d, J_{CF} = 22 Hz), 108.4 (d, J_{CF} = 22 Hz), 106.1 (d, J_{CF} = 97 Hz), 61.0, 15.7 (d, J_{CF} = 17 Hz), 14.3. ESI-HRMS calcd for $C_{12}H_{13}FNO_2$ $(M+H)^+$ 222.0925, found 222.0931.

ethyl 7-fluoro-6-methyl-1H-indole-2-carboxylate (***2oY***): Yield 15.8 mg (18%, white solid); mp 114-115 °C; IR (neat): ν_{max} 3310, 1707, 1331 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.15 (br s, 1H), 7.32 (d, 1H, *J* = 8.1 Hz), 7.19 (dd, 1H, *J* = 3.3, 2.4 Hz), 6.92 (dd, 1H, *J* = 7.8, 6.9 Hz), 4.42 (q, 2H, *J* = 7.2 Hz), 2.39 (d, 3H, *J* = 2.1 Hz), 1.42 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.7, 147.5 (d, J_{CF} = 967 Hz), 128.9 (d, J_{CF} = 19 Hz), 127.8, 126.1 (d, J_{CF} = 57 Hz), 124.0 (d, J_{CF} = 13 Hz), 119.2 (d, J_{CF} = 49 Hz), 117.5 (d, J_{CF} = 17 Hz), 109.0 (d, J_{CF} = 9 Hz), 61.1, 14.4, 14.1(d, J_{CF} = 15 Hz). ESI-HRMS calcd for $C_{12}H_{13}FNO_2$ $(M+H)^+$ 222.0925, found 222.0925.

ethyl 5-methoxy-1H-indole-2-carboxylate (***2p***): Prepared according to general procedure with a slight modification: a solution of starting material (100.0 mg, 0.4044 mmol) in 1.5 mL DCE was added dropwise to a mixture of $ZrCl_4$ and $AgNO_3$ in DCE (1 mL); Yield 48.1 mg (54%, colorless crystal); mp 110-111 °C; IR (neat): ν_{max} 3327, 1682, 1527, 1217, 773 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.03 (br s, 1H), 7.31 (d, 1H, *J* = 9.0 Hz), 7.14 (dd, 1H, *J* = 2.1, 0.6 Hz), 7.07 (d, 1H, *J* = 2.4 Hz), 7.02 (dd, 1H, *J* = 8.7, 2.4 Hz), 4.39 (q, 2H, *J* = 7.2 Hz), 3.87 (s, 3H), 1.44 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.0, 154.7, 132.2, 127.85, 127.81, 116.9, 112.8, 108.2, 102.5, 60.9, 55.6, 14.4. ESI-HRMS calcd for $C_{12}H_{14}NO_3$ $(M+H)^+$ 220.0968, found 220.0974.

ethyl 4-chloro-5,6-dimethoxy-1H-indole-2-carboxylate (***2q***): Yield 83.2 mg (88%, colorless crystal); mp 169-170 °C; IR (neat): ν_{max} 3300, 1693, 1272, 1004, 763 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.03 (br s, 1H), 7.24-7.23 (m, 1H), 6.79 (s, 1H), 4.40 (q, 2H, *J* = 7.2 Hz), 3.91 (s, 3H), 3.89 (s, 3H), 1.42 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.9, 153.4, 141.8, 133.4, 126.6, 120.51, 120.47, 107.6, 92.9, 61.1, 61.0, 56.1, 14.3. ESI-HRMS calcd for $C_{13}H_{15}ClNO_4$ (Cl-35) $(M+H)^+$ 284.0684, found 284.0694.

JRT-4-030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6.5
6.0
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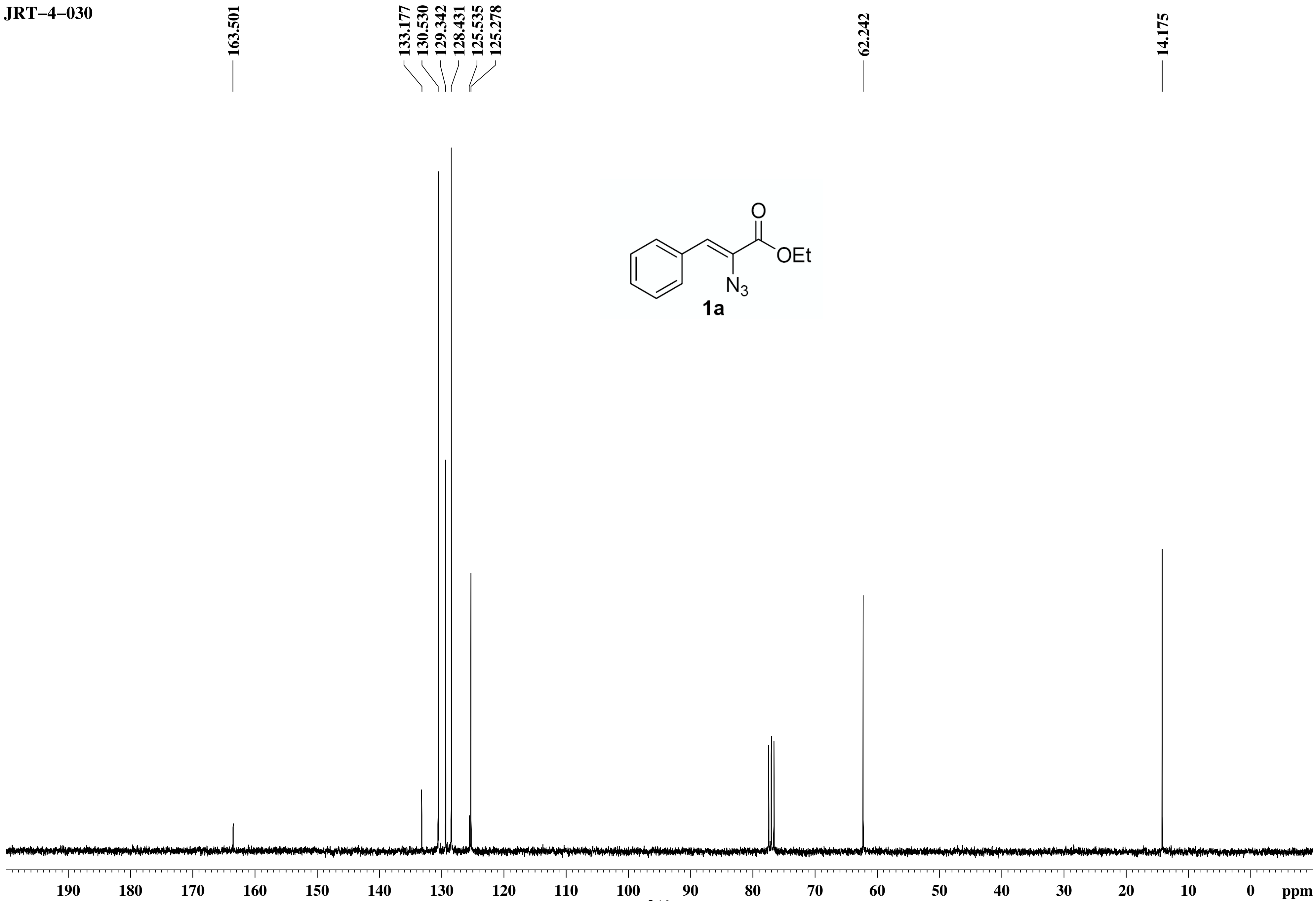
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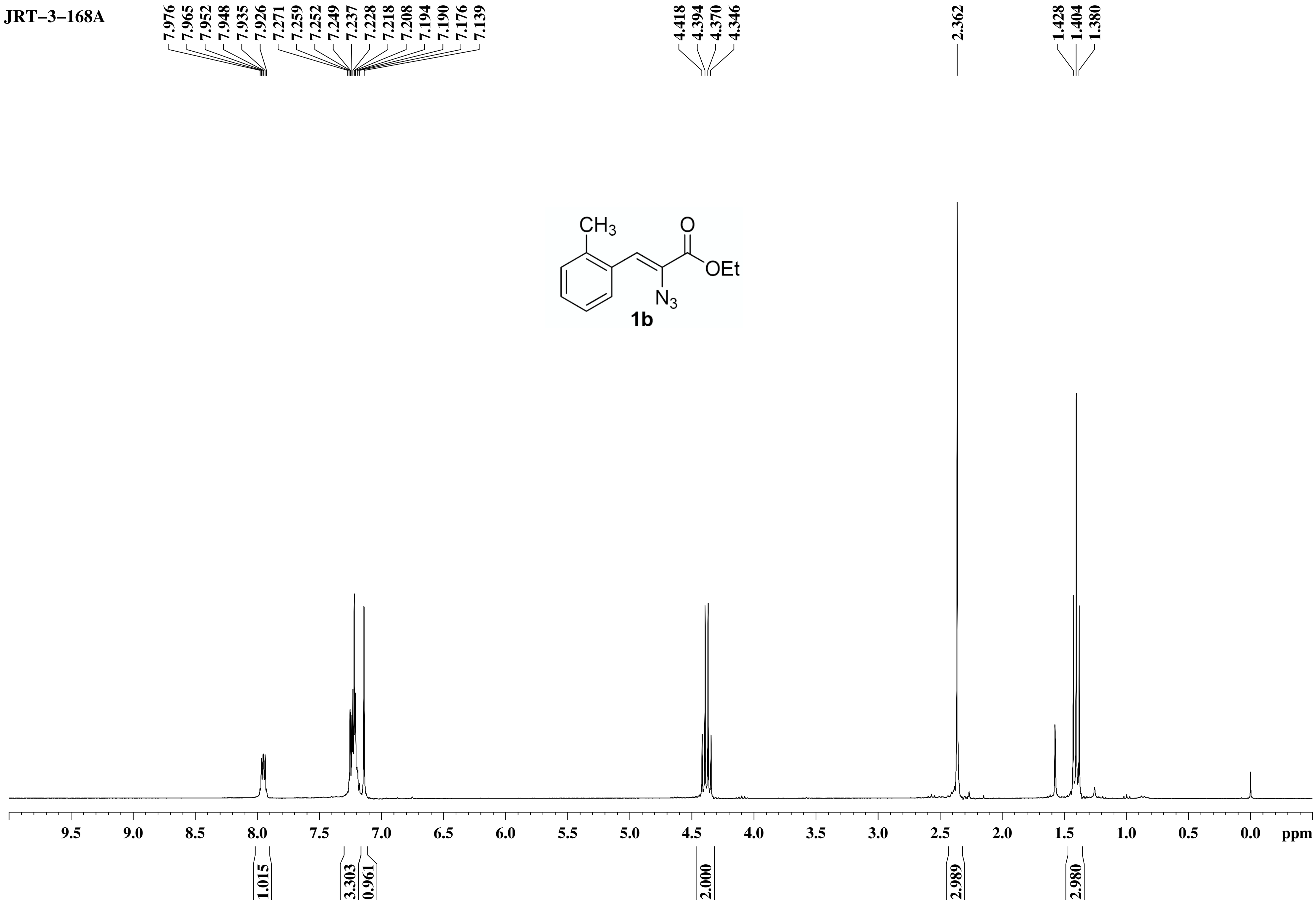

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O
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N3
1b
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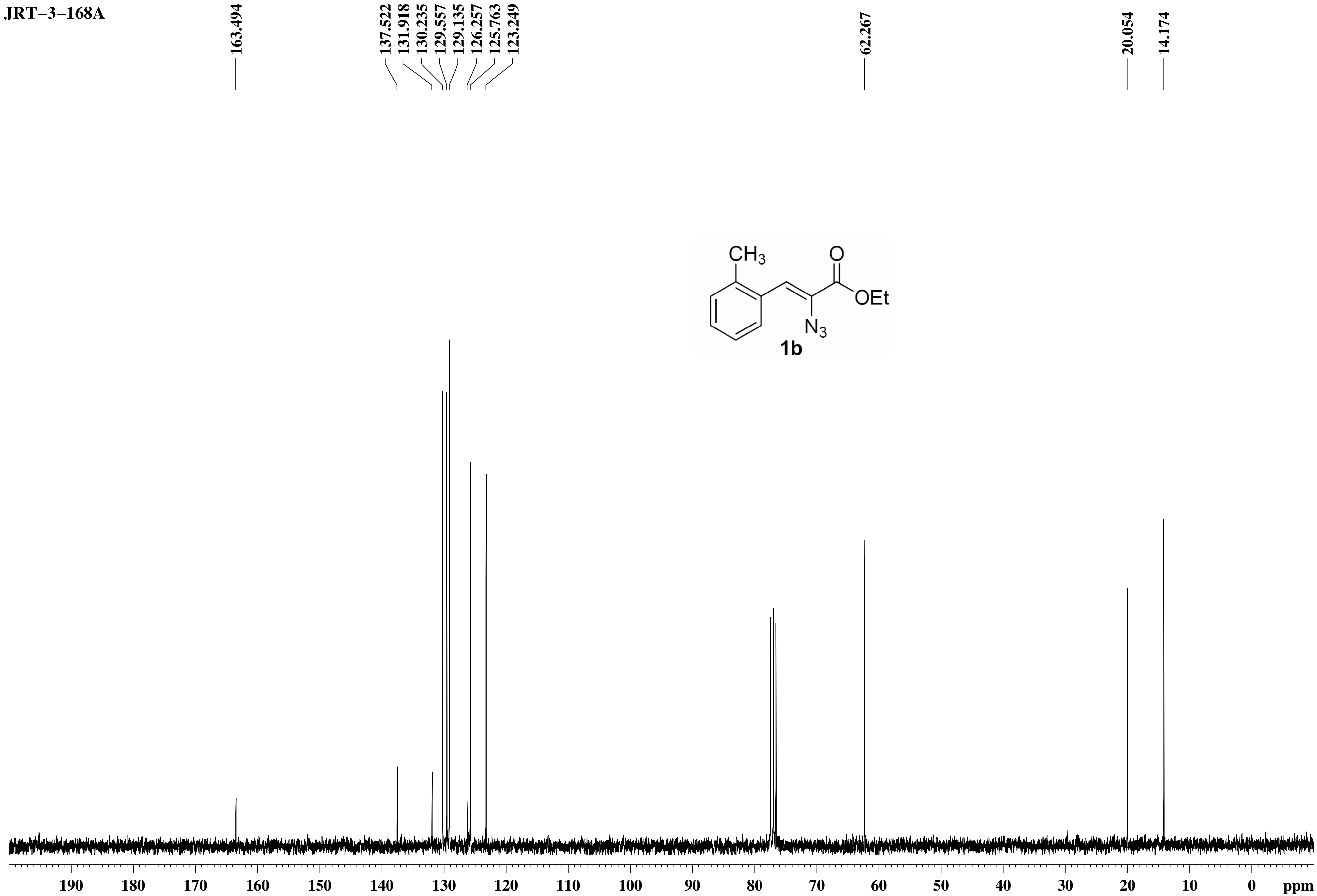
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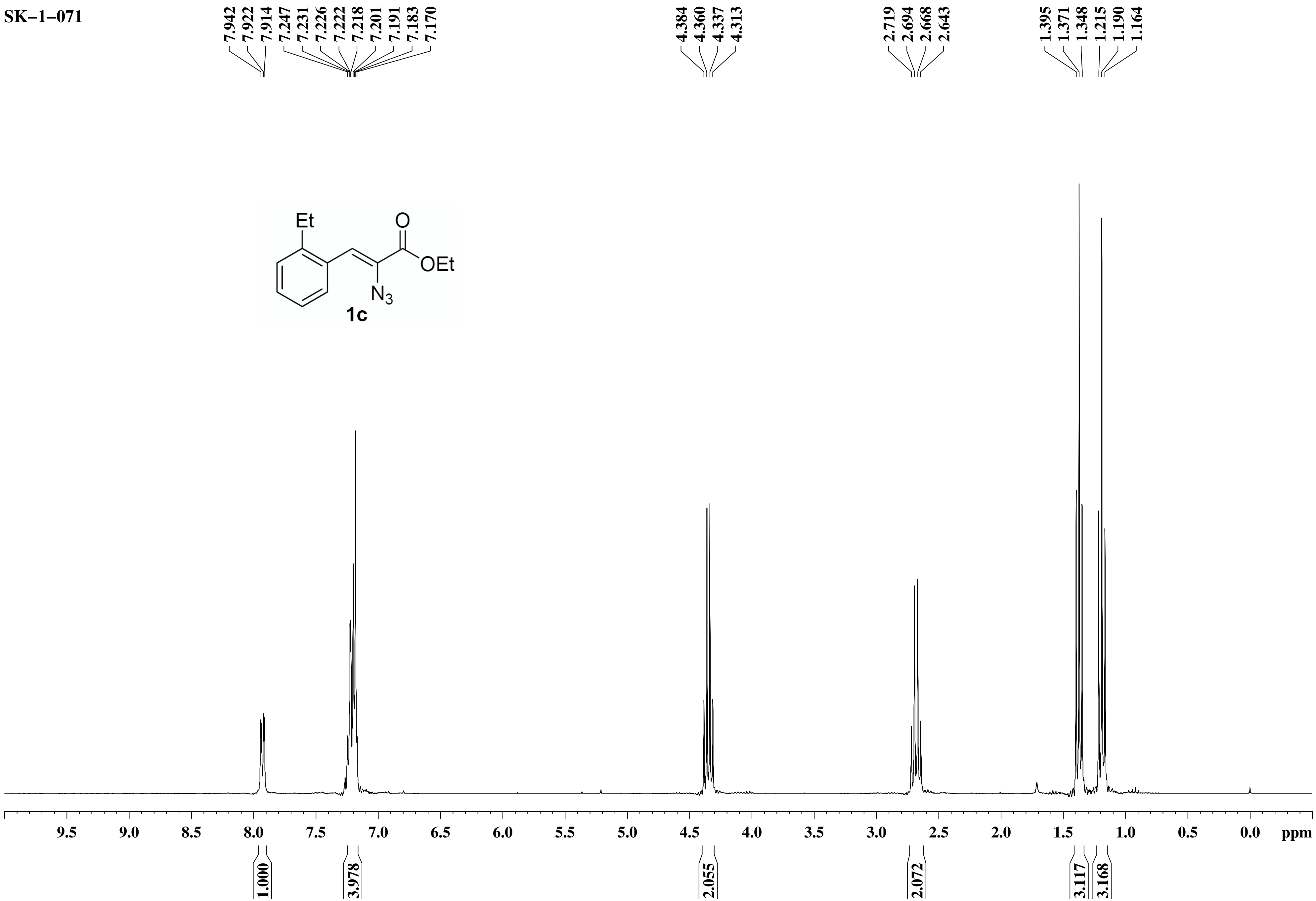
SK−1−071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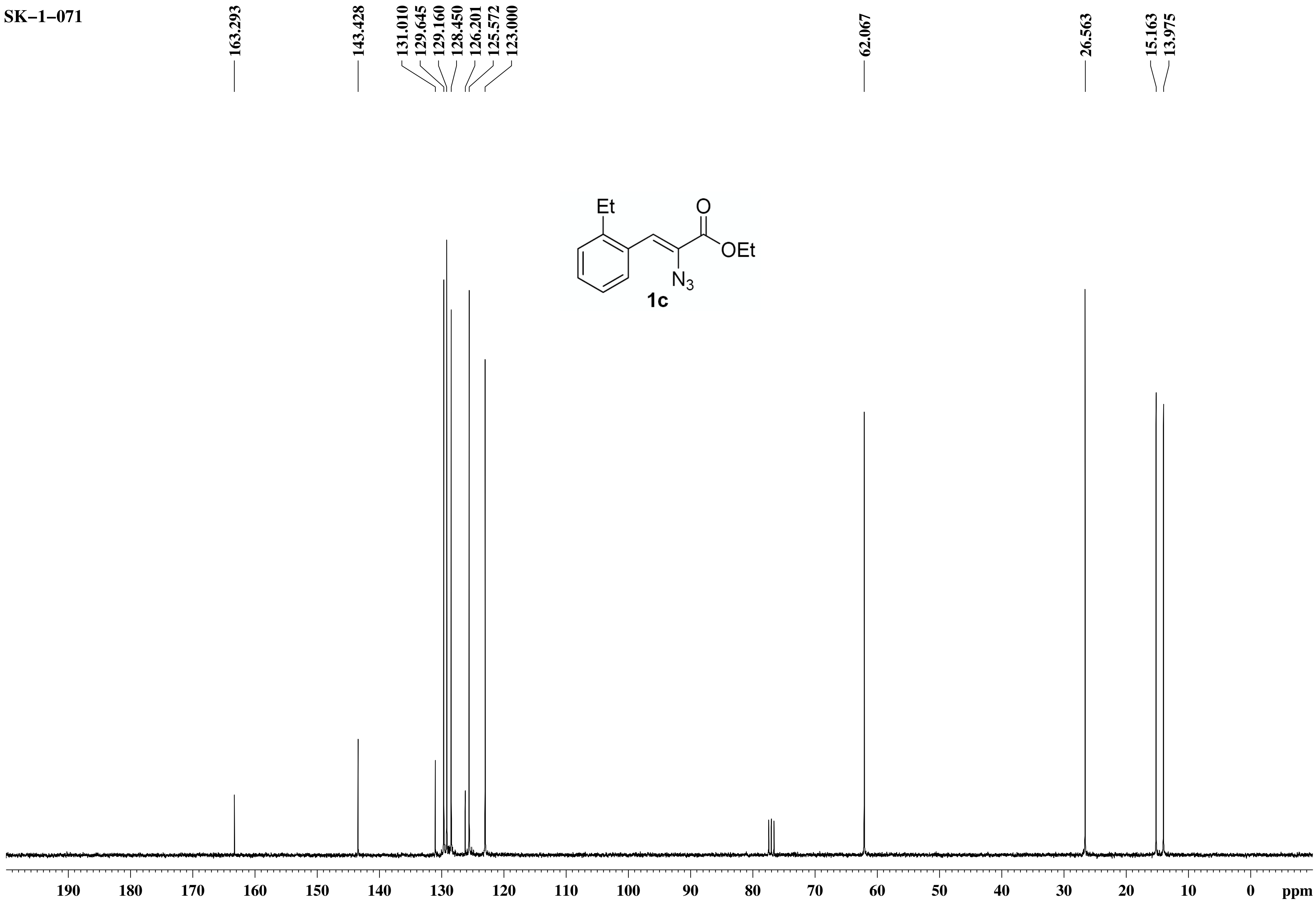
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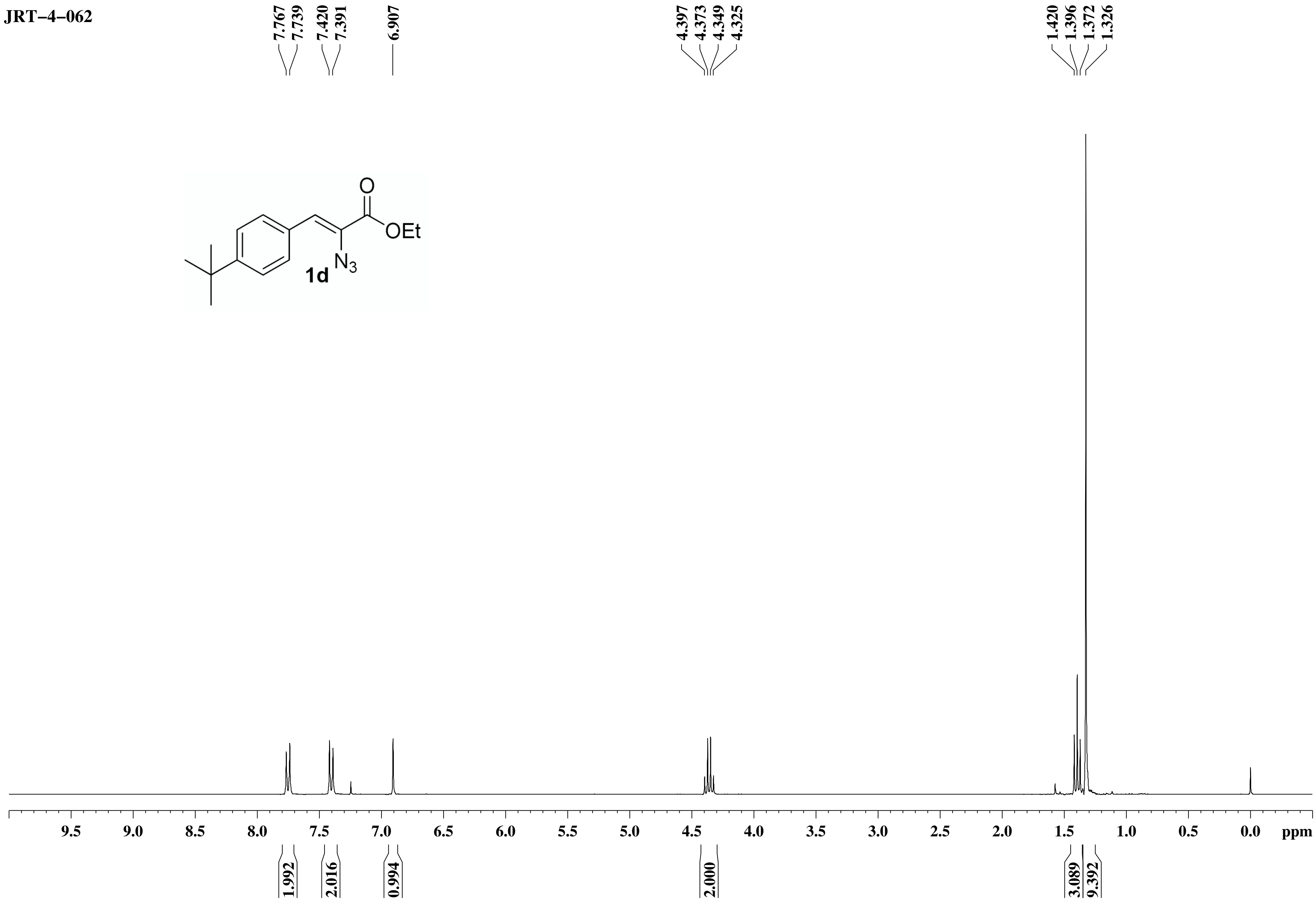
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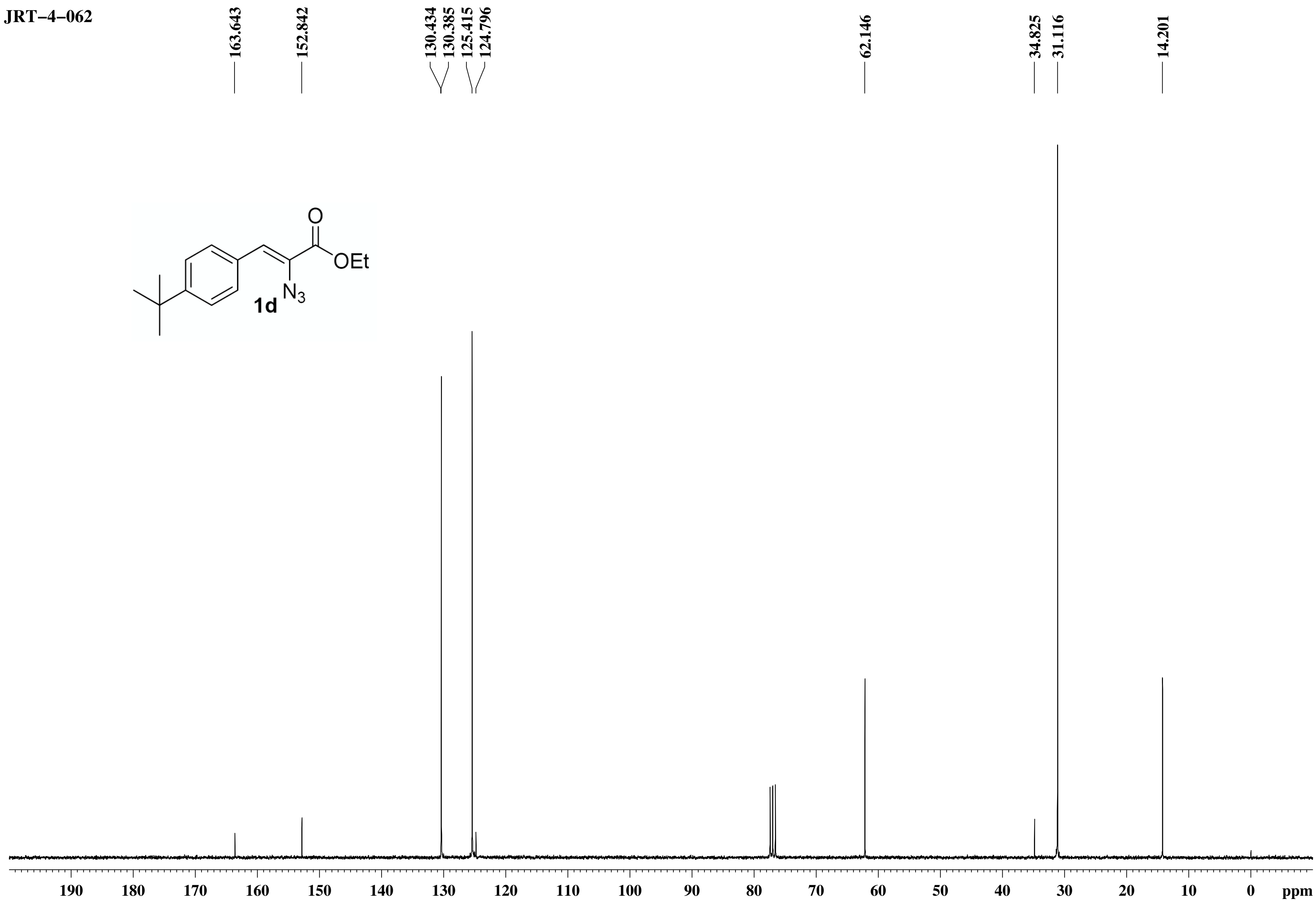
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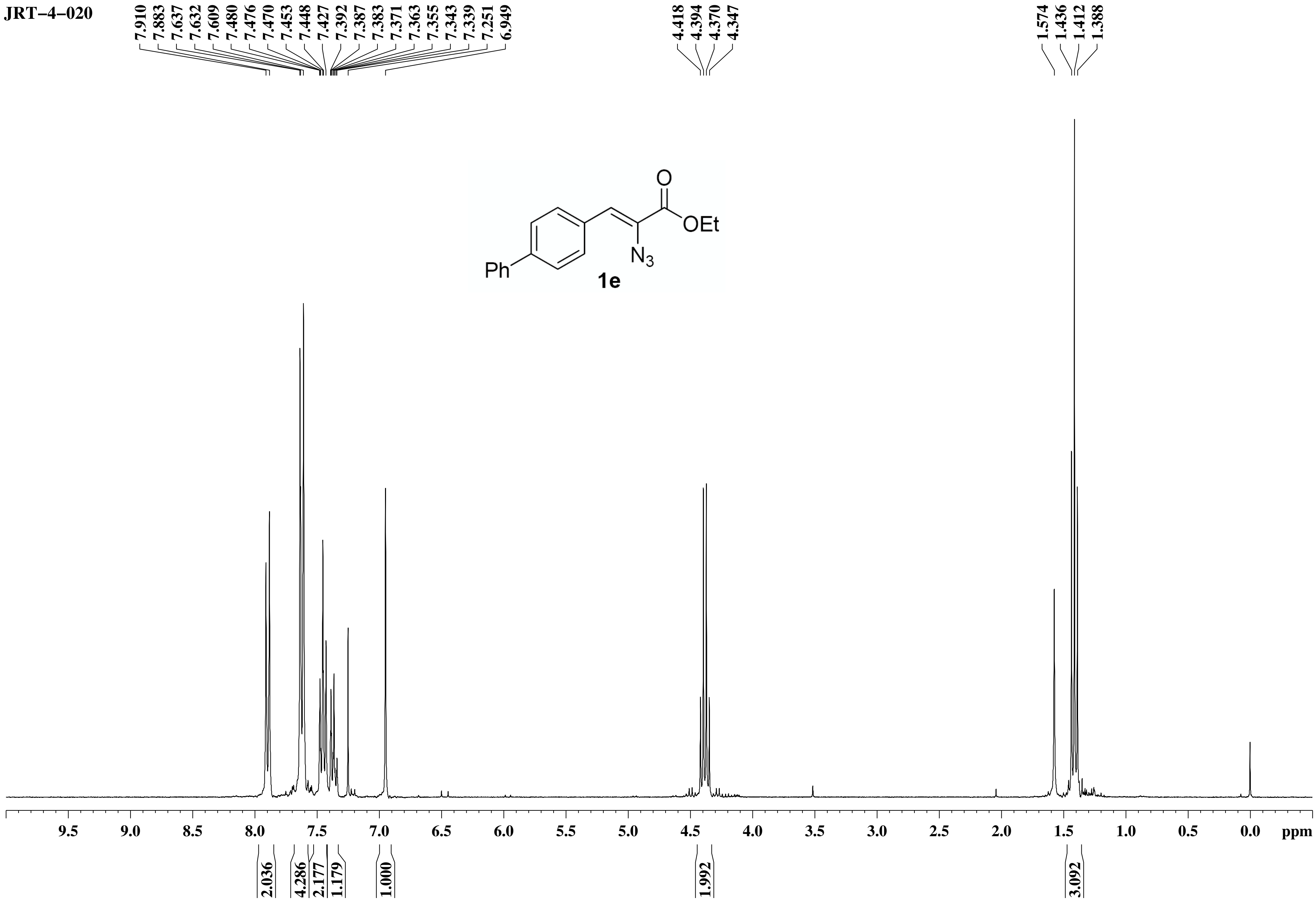
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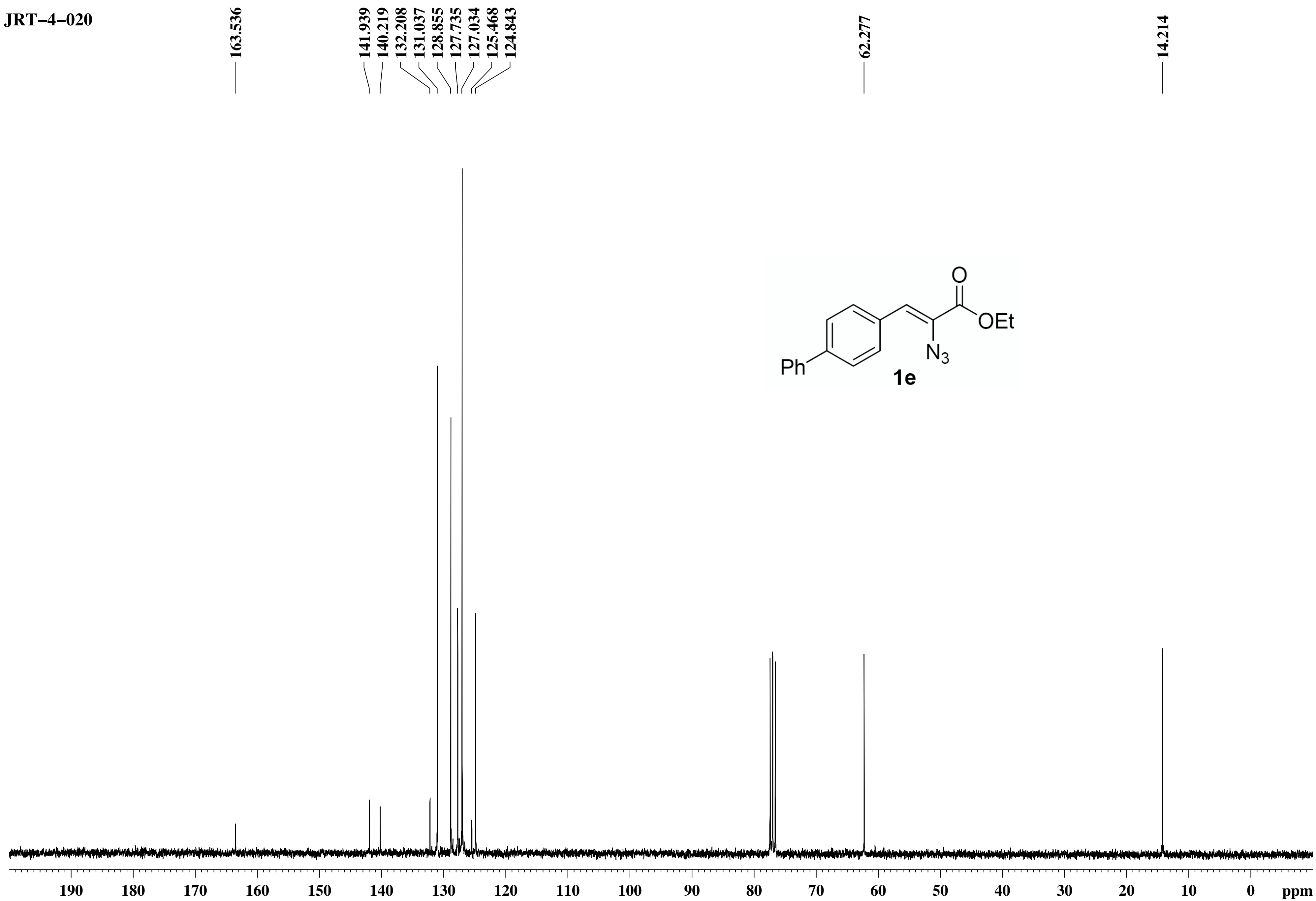
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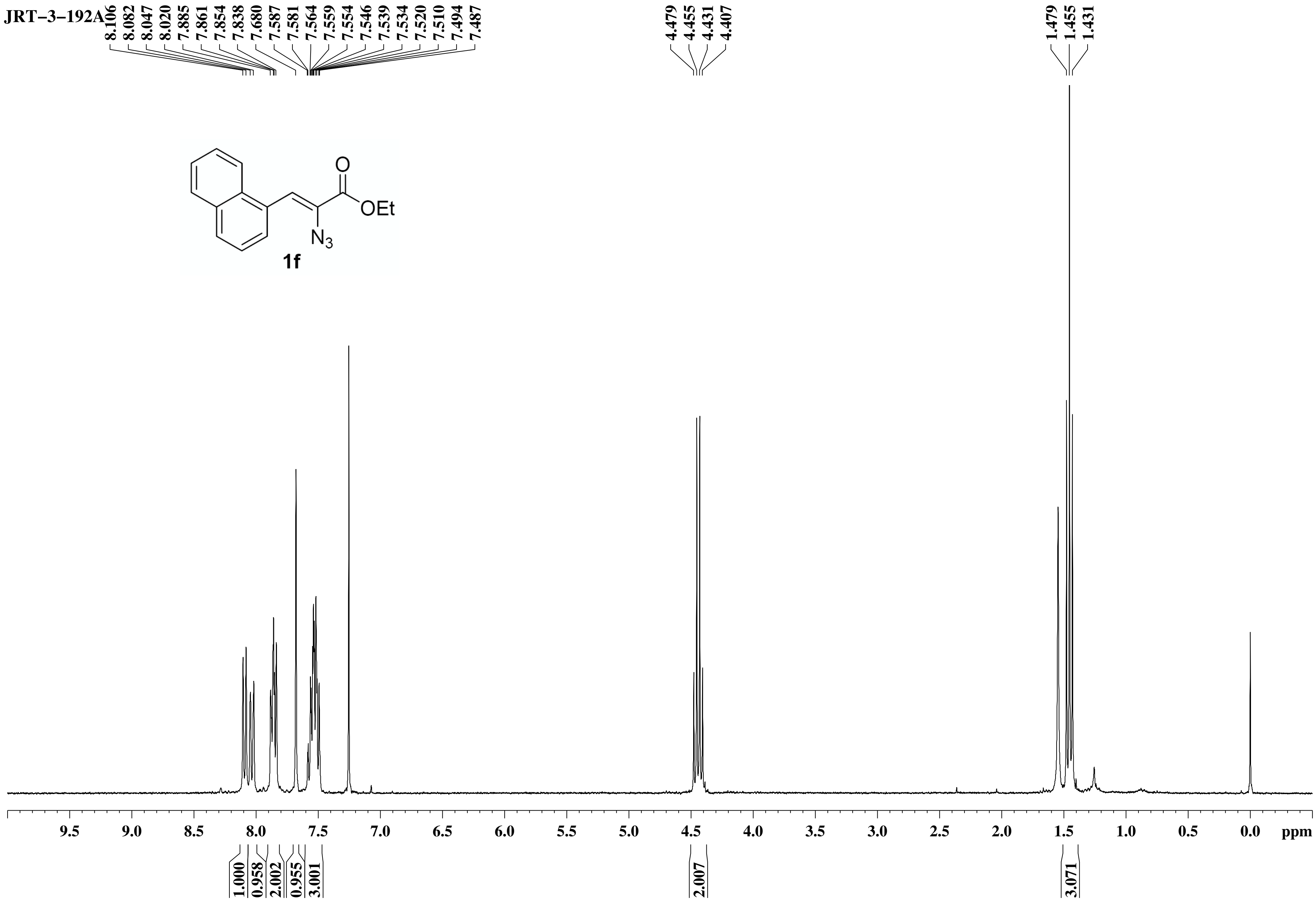
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7.487
4.479
4.455
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4.407
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1.455
1.431
O
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9.5
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6.0
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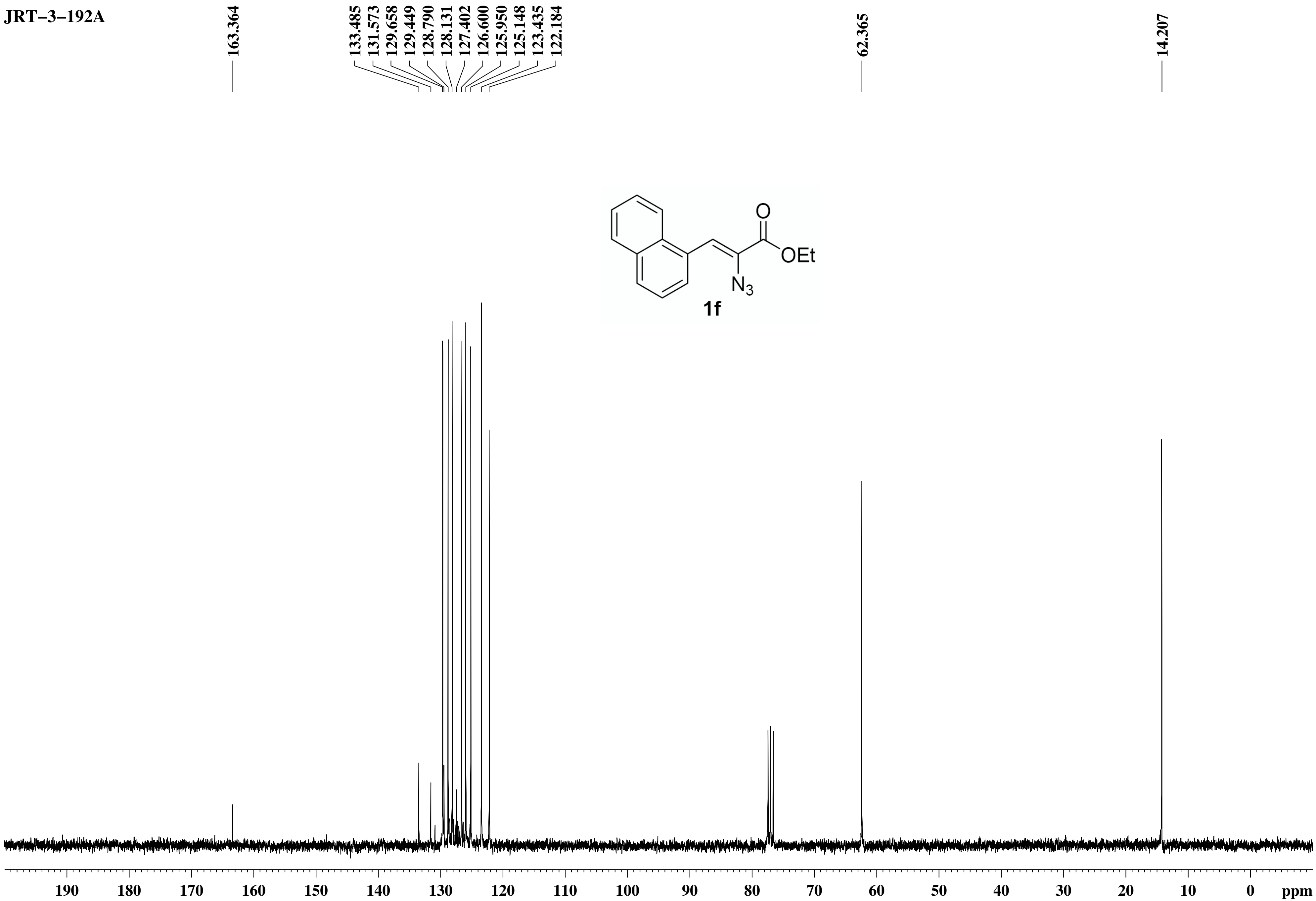
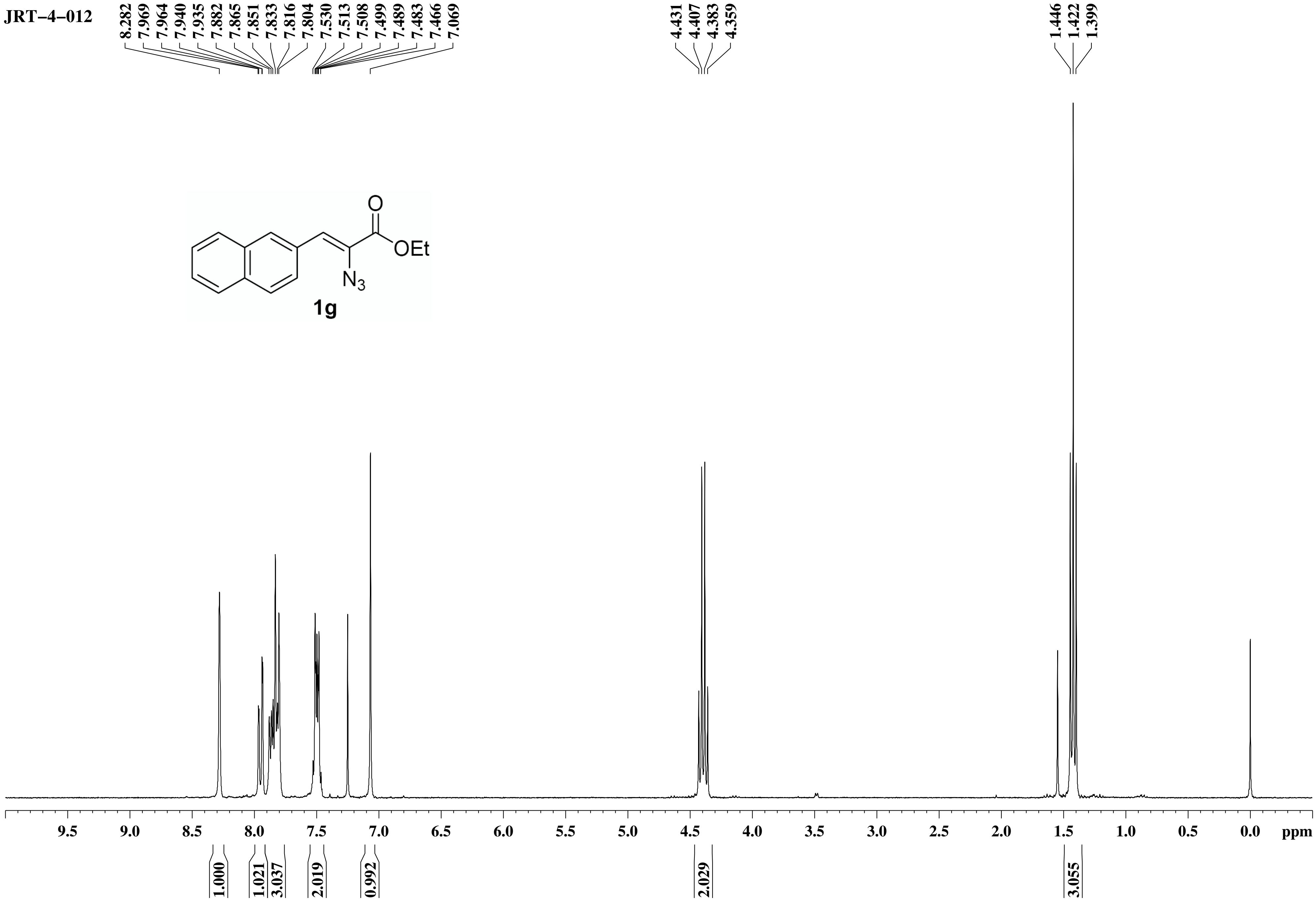
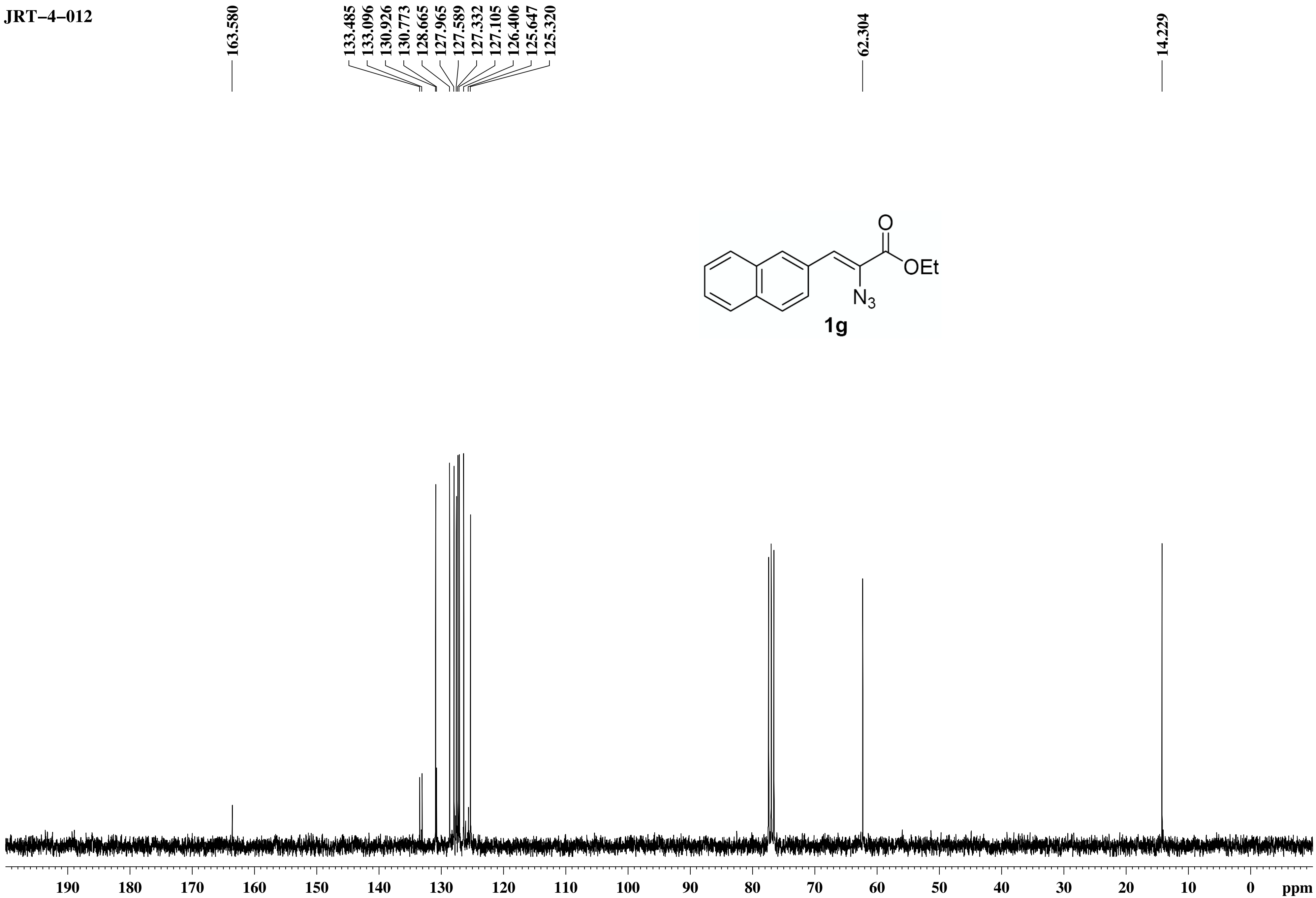
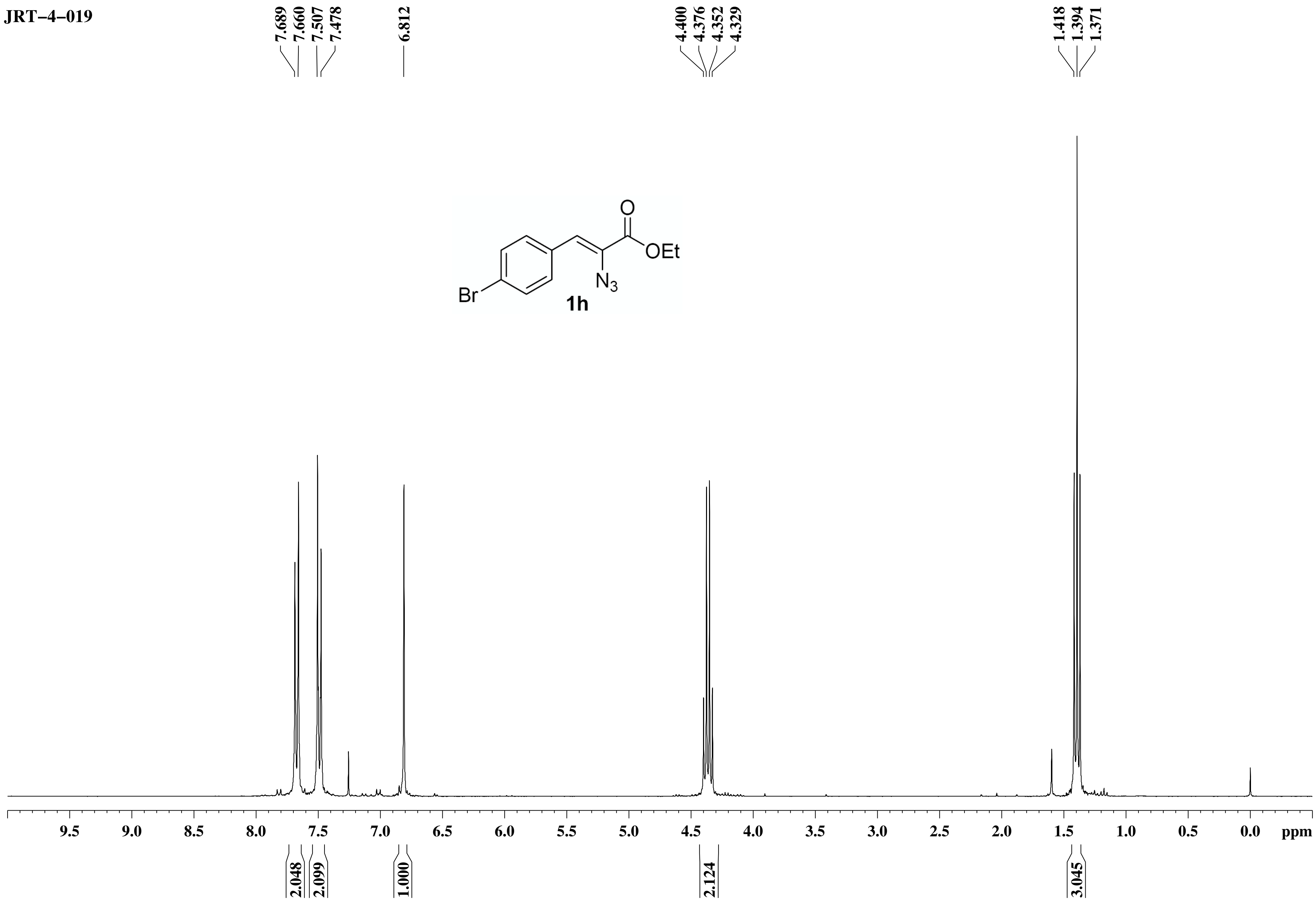
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.000
0.958
2.002
0.955
3.001
2.007
3.071

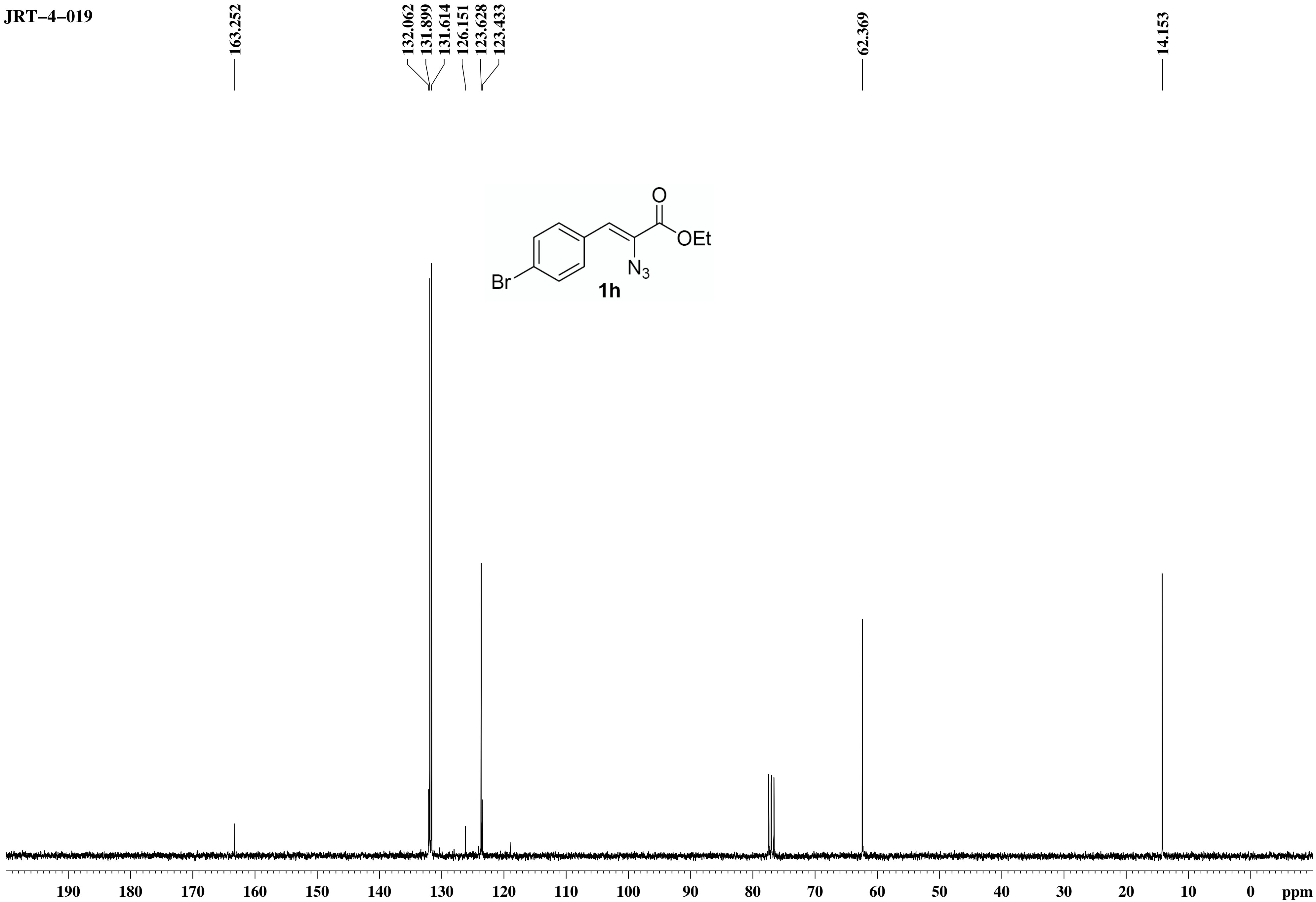
JRT–3–192A



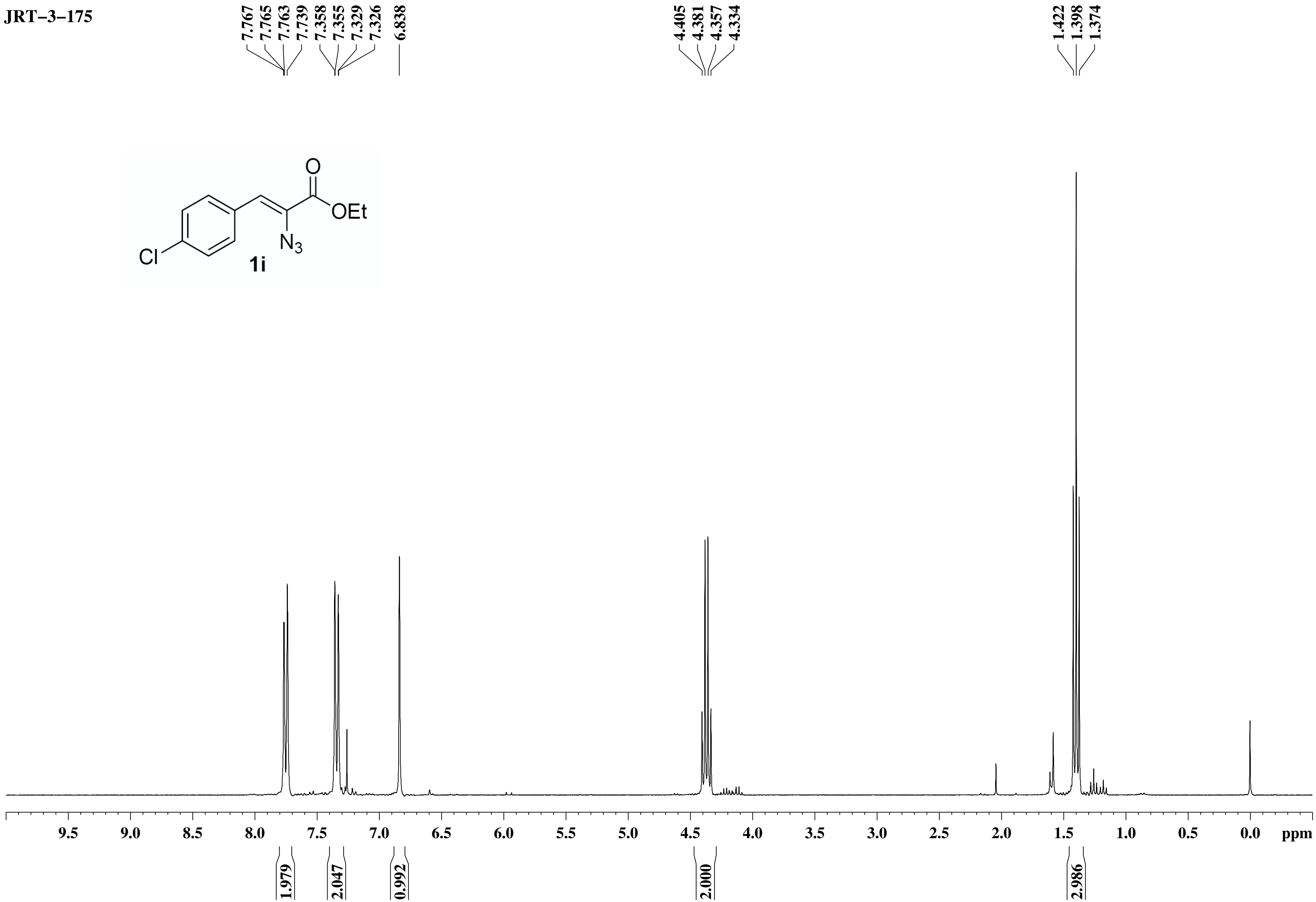

JRT-4-012
8.282
7.969
7.964
7.940
7.935
7.882
7.865
7.851
7.833
7.816
7.804
7.530
7.513
7.508
7.499
7.489
7.483
7.466
7.069
4.431
4.407
4.383
4.359
1.446
1.422
1.399
O
OEt
N3
1g
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.000
1.021
3.037
2.019
0.992
2.029
3.055


JRT−4−012
163.580
133.485
133.096
130.926
130.773
128.665
127.965
127.589
127.332
127.105
126.406
125.647
125.320
62.304
14.229
O
OEt
N3
1g
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

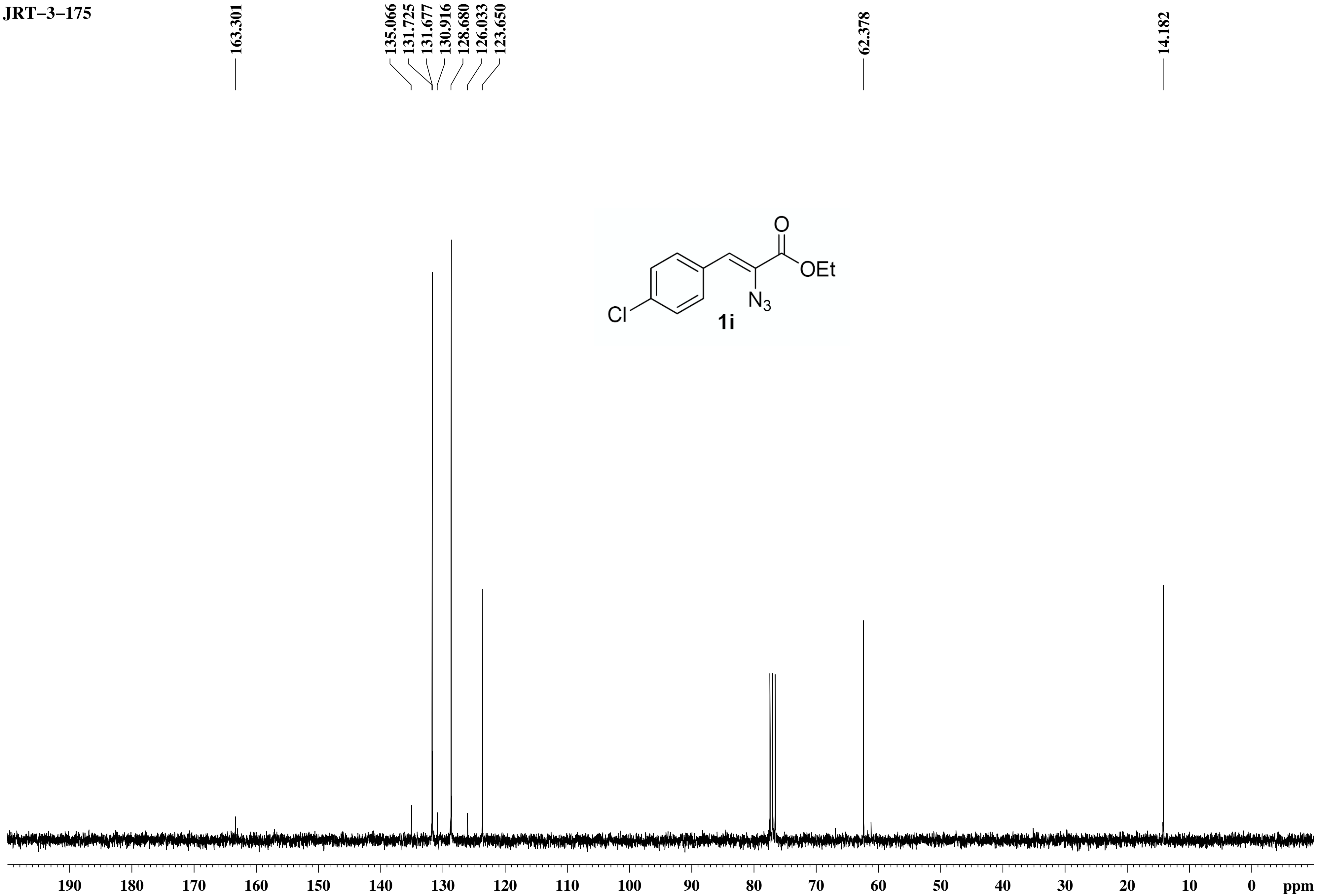

JRT−4−019
7.689
7.660
7.507
7.478
6.812
4.400
4.376
4.352
4.329
1.418
1.394
1.371
O
OEt
N3
Br
1h
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.048
2.099
1.000
2.124
3.045


JRT−4−019
163.252
132.062
131.899
131.614
126.151
123.628
123.433
62.369
14.153
O
OEt
N3
Br
1h
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

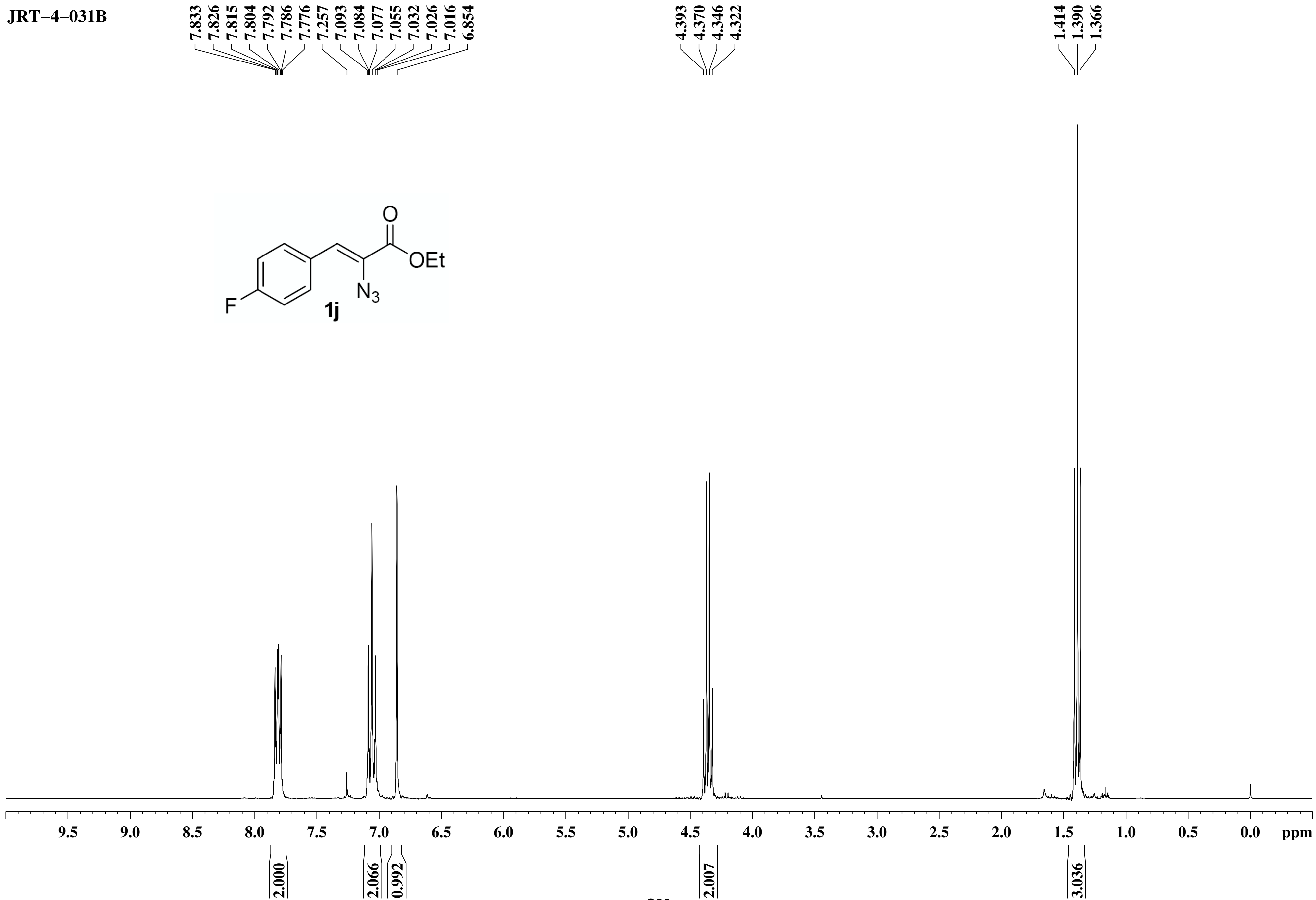
JRT-3-175

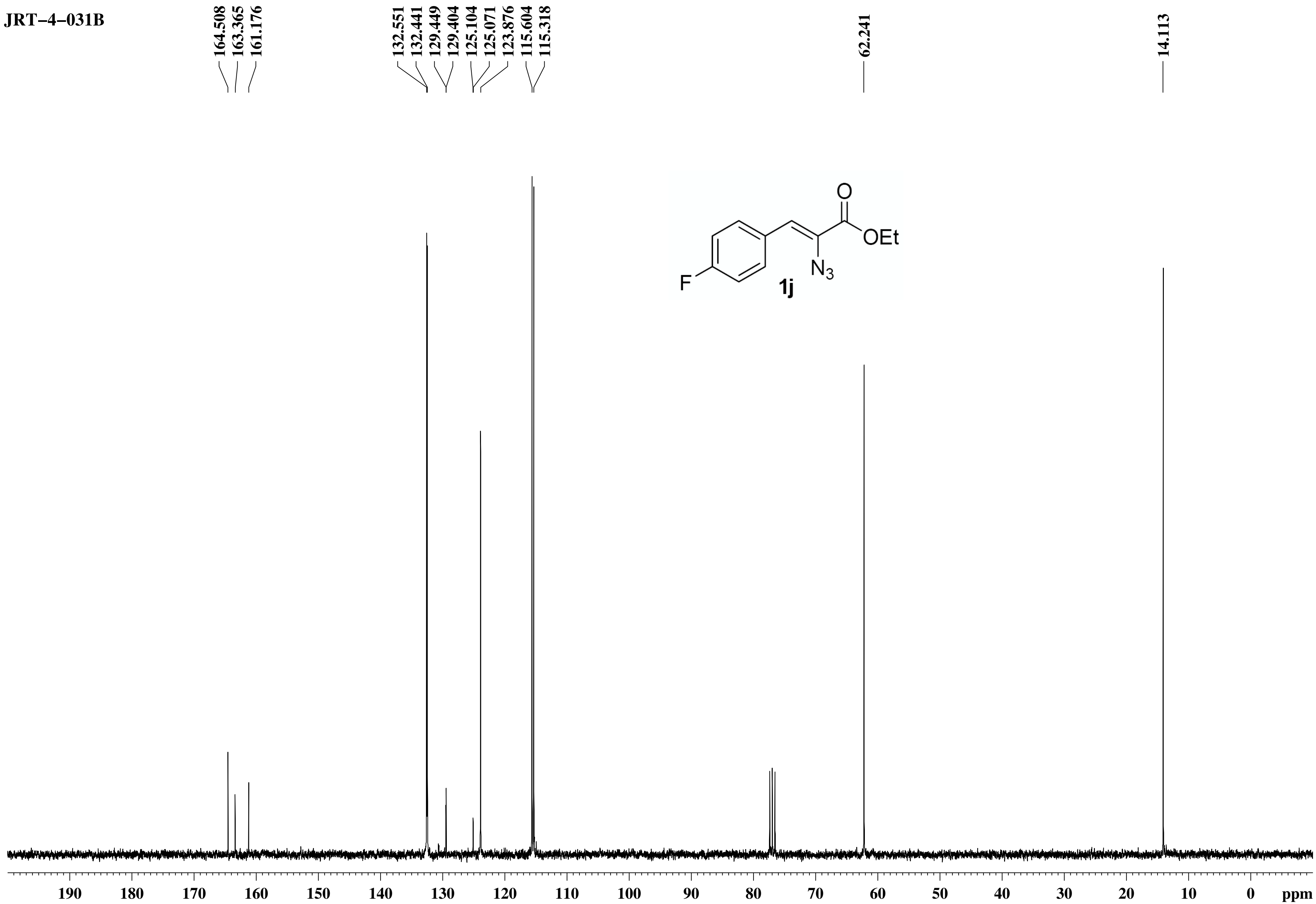

O
OEt
N3
Cl
1i
7.767
7.765
7.763
7.739
7.358
7.355
7.329
7.326
6.838
4.405
4.381
4.357
4.334
1.422
1.398
1.374
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.979
2.047
0.992
2.000
2.986

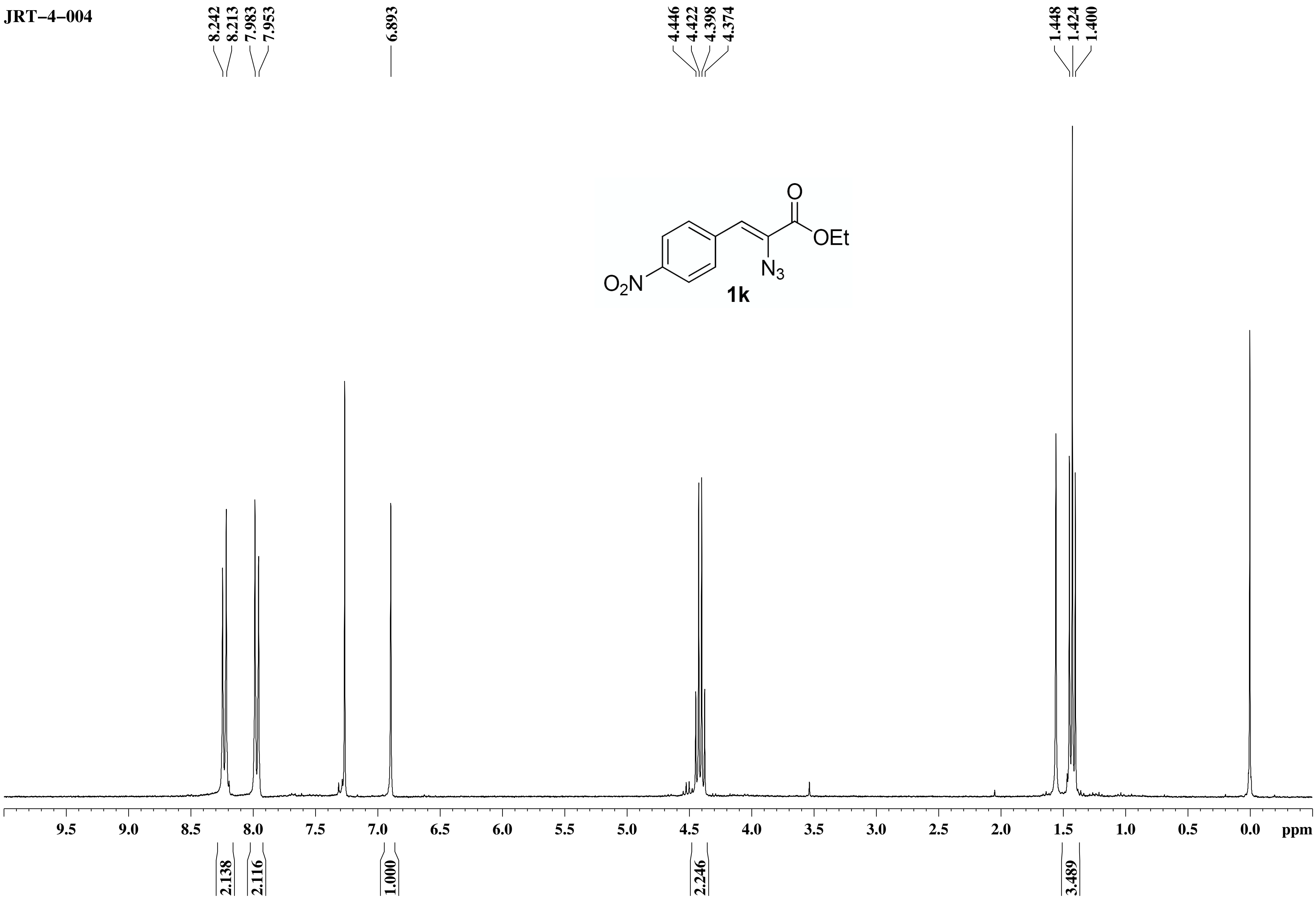
JRT–3–175

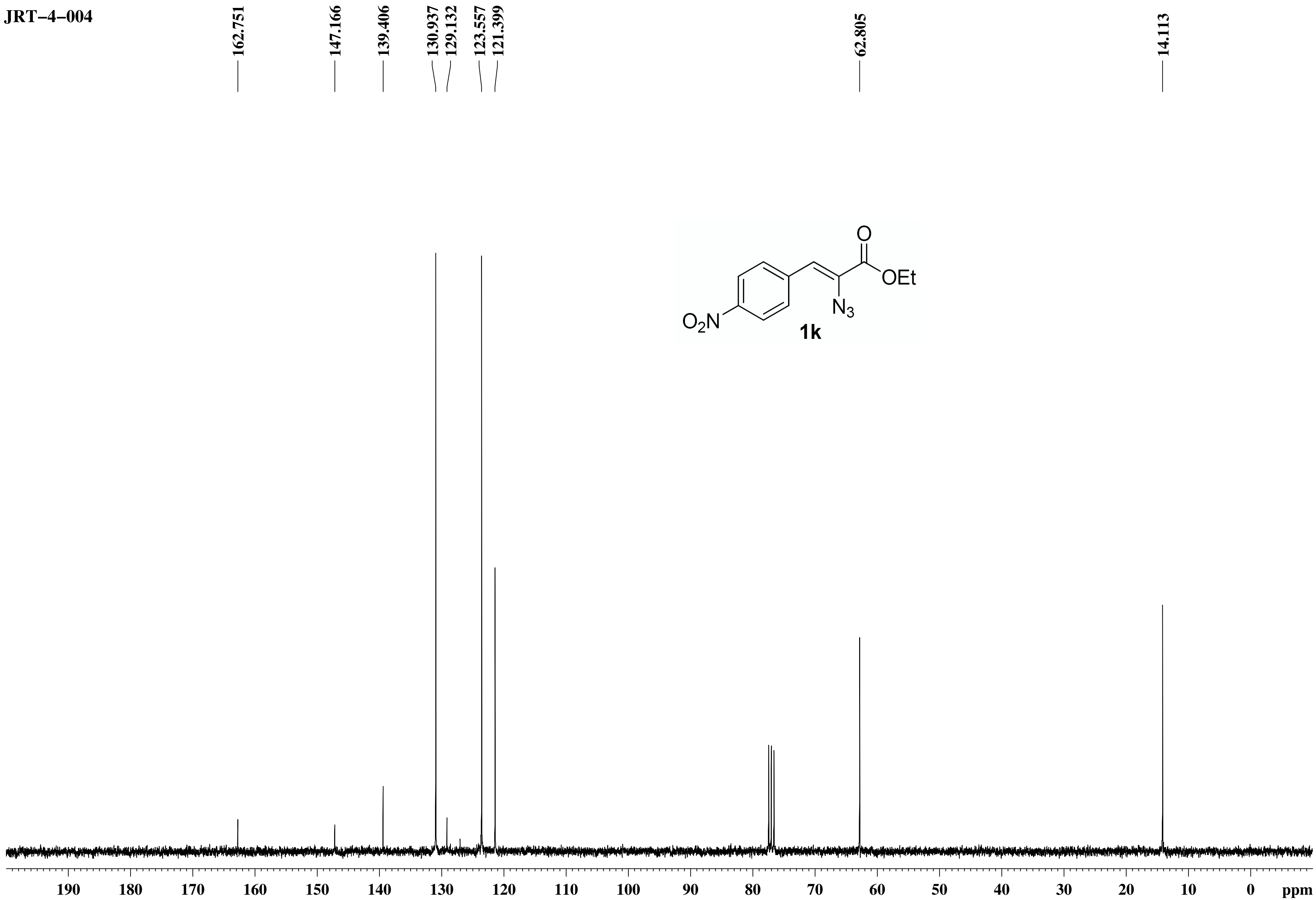

163.301
135.066
131.725
131.677
130.916
128.680
126.033
123.650
62.378
14.182
O
OEt
N3
Cl
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

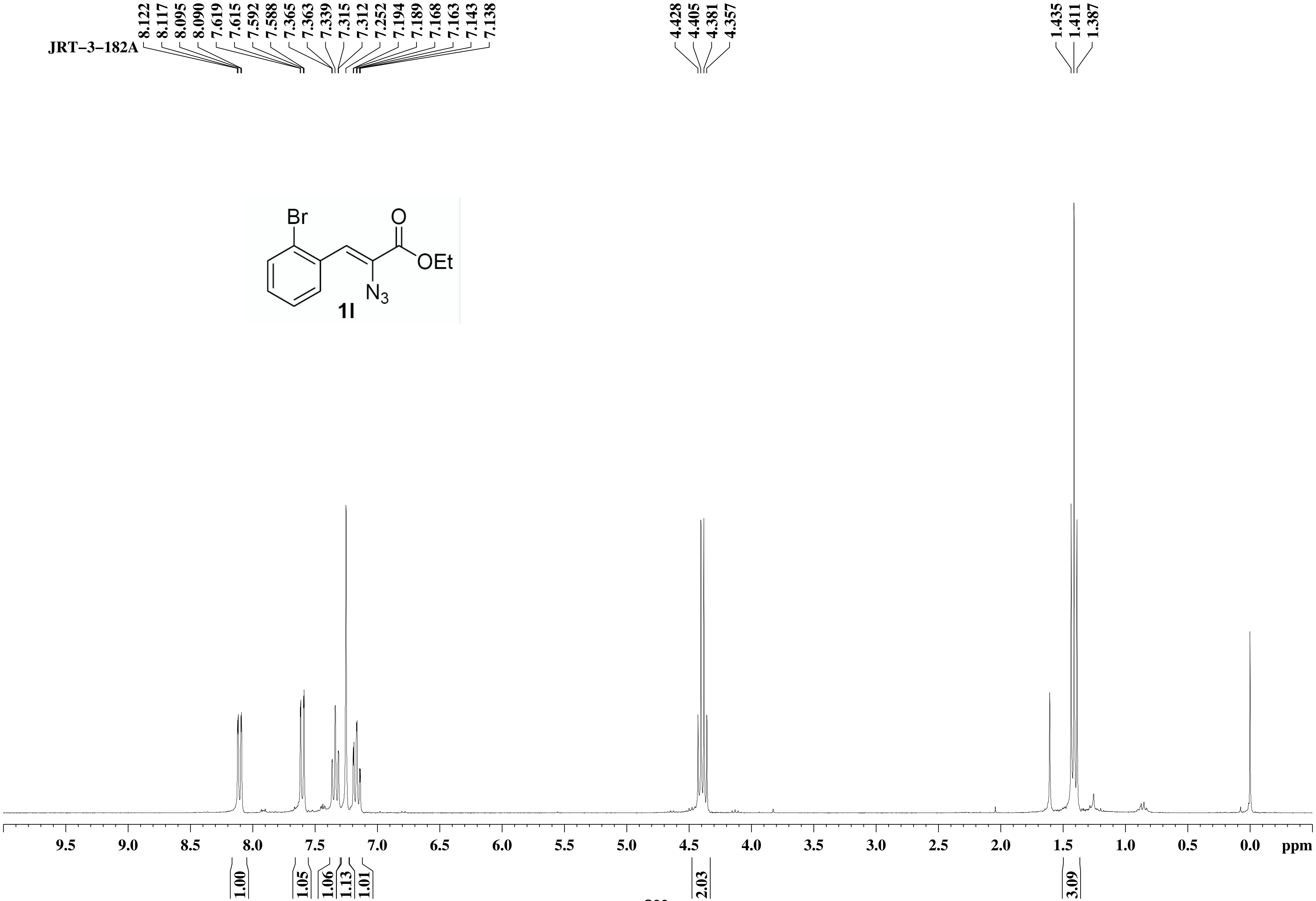
1i

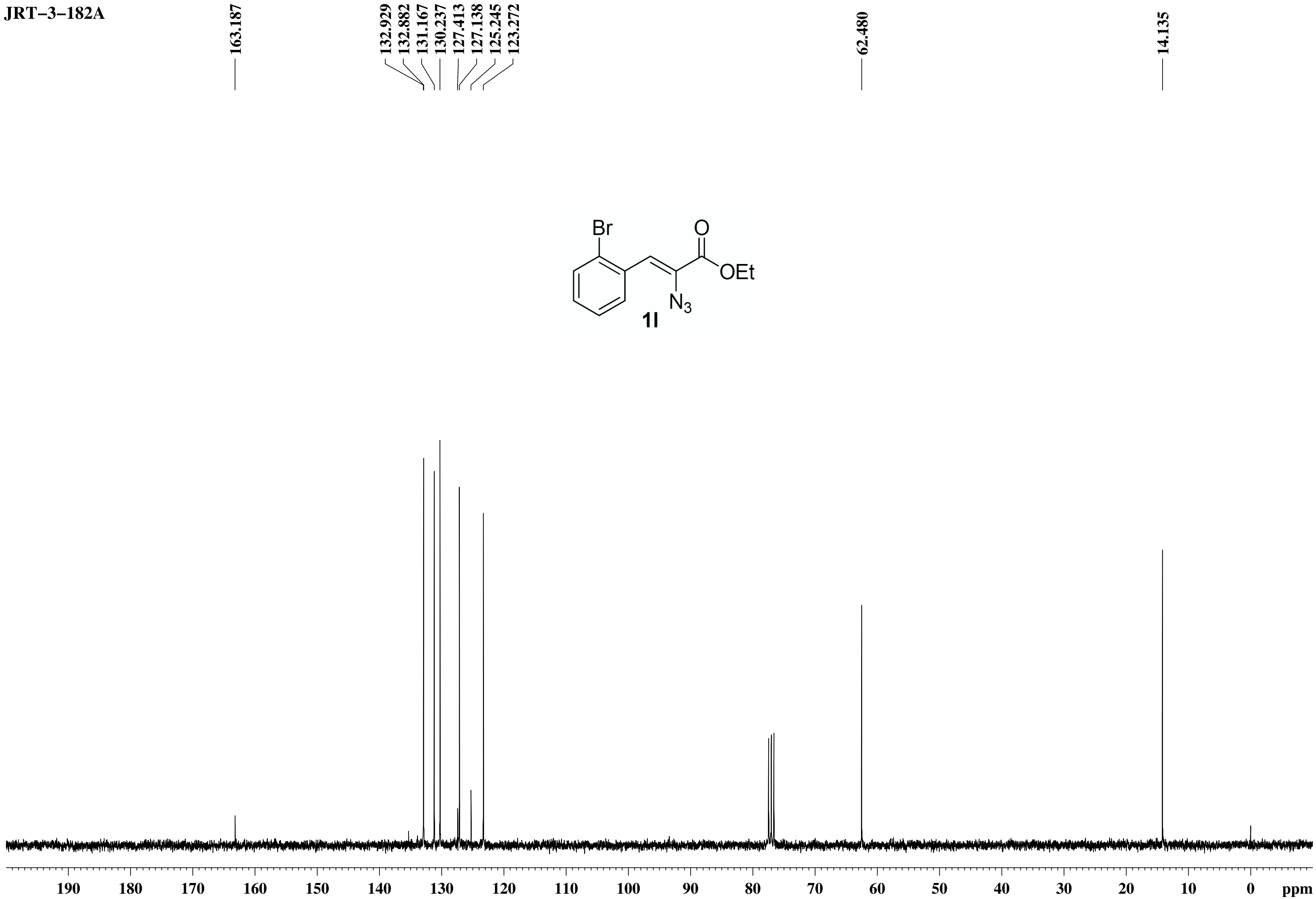

JRT-4-031B
7.833
7.826
7.815
7.804
7.792
7.786
7.776
7.257
7.093
7.084
7.077
7.055
7.032
7.026
7.016
6.854
4.393
4.370
4.346
4.322
1.414
1.390
1.366
O
OEt
N3
F
1j
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.000
2.066
0.992
2.007
3.036


JRT-4-031B
164.508
163.365
161.176
132.551
132.441
129.449
129.404
125.104
125.071
123.876
115.604
115.318
62.241
14.113
O
OEt
N_3
F
1j
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

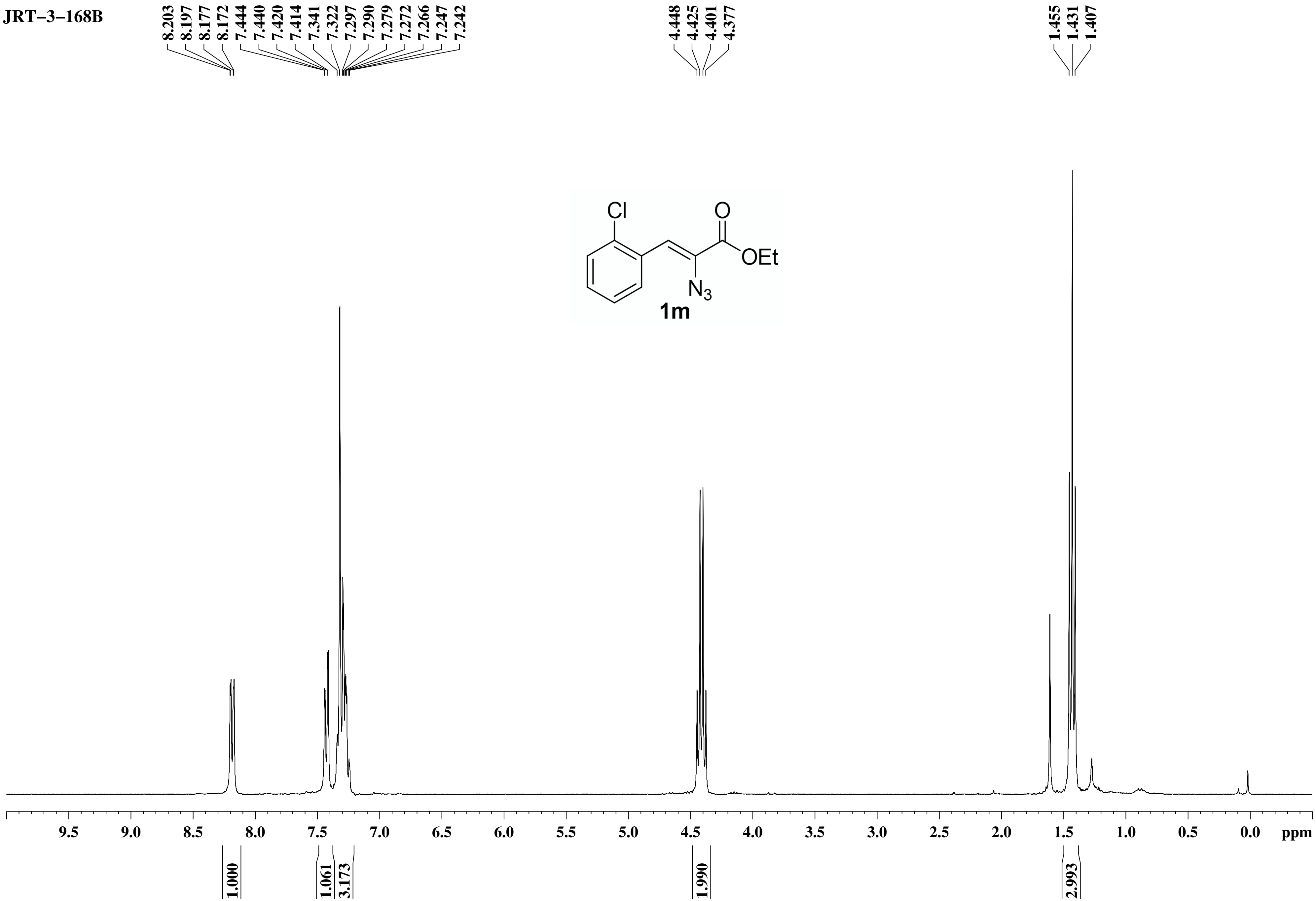

JRT-4-004
8.242
8.213
7.983
7.953
6.893
4.446
4.422
4.398
4.374
1.448
1.424
1.400
O
OEt
O_2N
N_3
1k
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.138
2.116
1.000
2.246
3.489


JRT−4−004
162.751
147.166
139.406
130.937
129.132
123.557
121.399
62.805
14.113
O
OEt
O_2N
N_3
1k
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

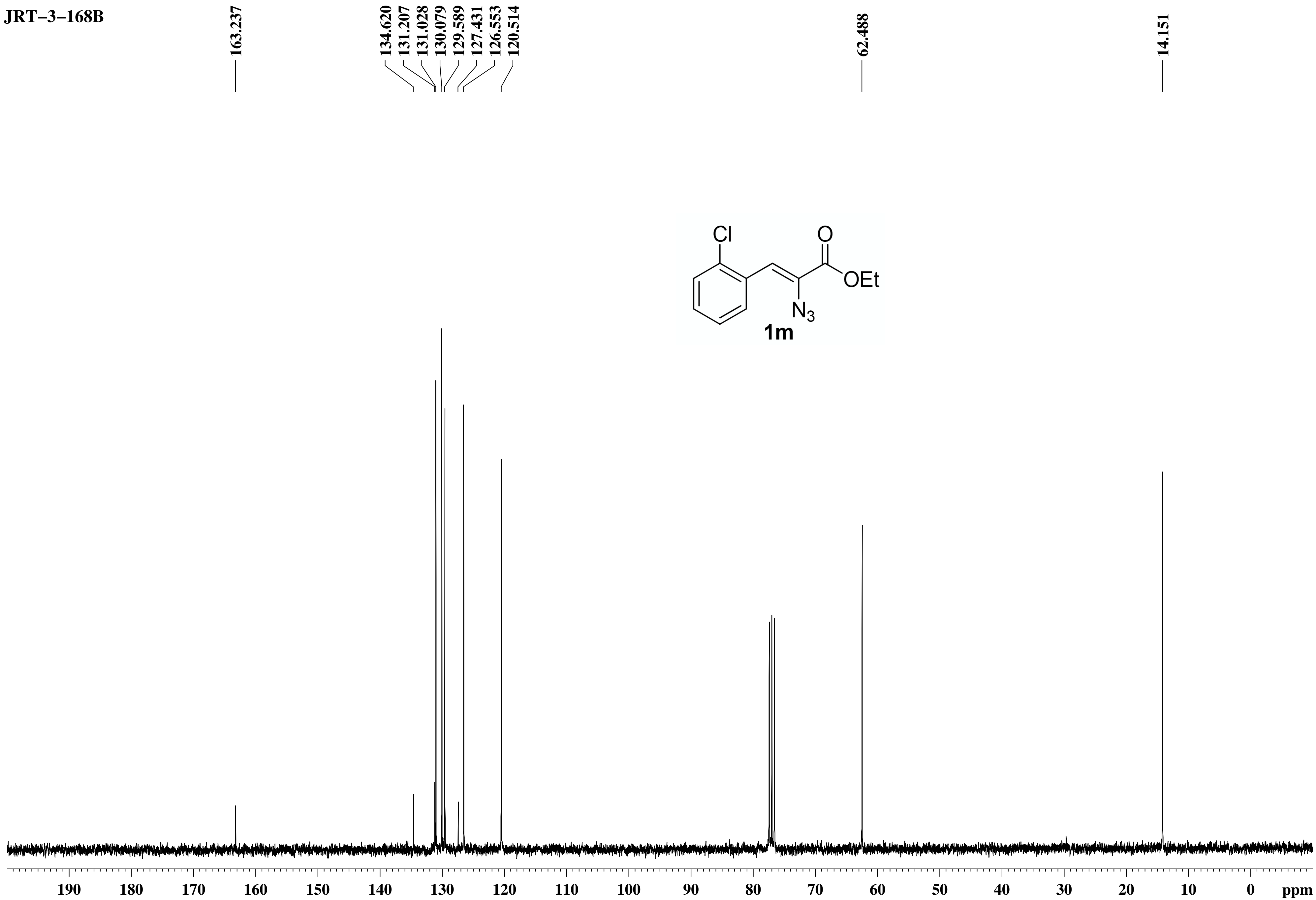

JRT–3–182A
8.122
8.117
8.095
8.090
7.619
7.615
7.592
7.588
7.365
7.363
7.339
7.315
7.312
7.252
7.194
7.189
7.168
7.163
7.143
7.138
4.428
4.405
4.381
4.357
1.435
1.411
1.387
Br
O
OEt
N3
1l
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
1.05
1.06
1.13
1.01
2.03
3.09


JRT–3–182A
163.187
132.929
132.882
131.167
130.237
127.413
127.138
125.245
123.272
62.480
14.135
Br
O
OEt
N3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

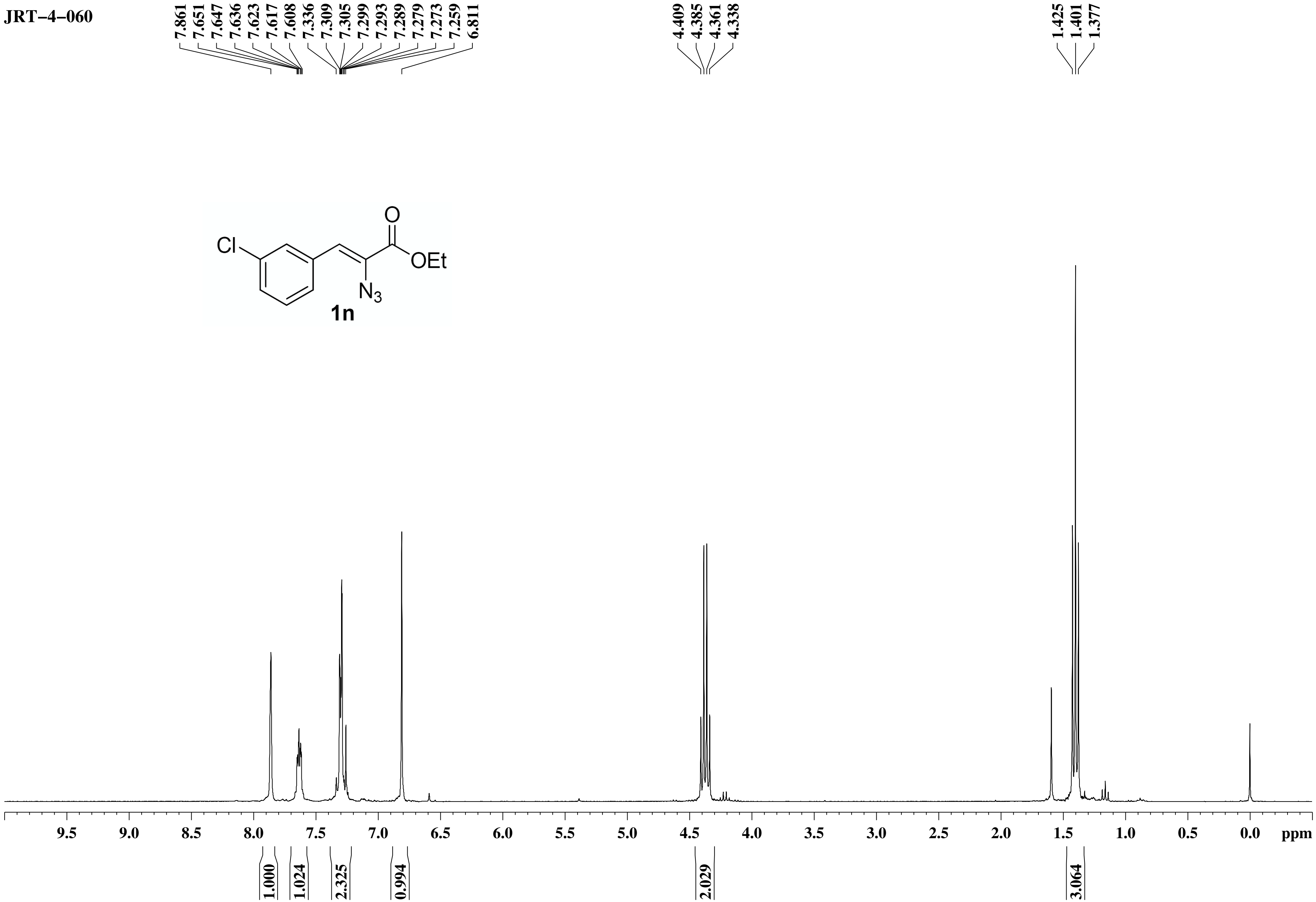
1l


JRT−3−168B
8.203
8.197
8.177
8.172
7.444
7.440
7.420
7.414
7.341
7.322
7.297
7.290
7.279
7.272
7.266
7.247
7.242
4.448
4.425
4.401
4.377
1.455
1.431
1.407
Cl
O
OEt
N3
1m
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.000
1.061
3.173
1.990
2.993

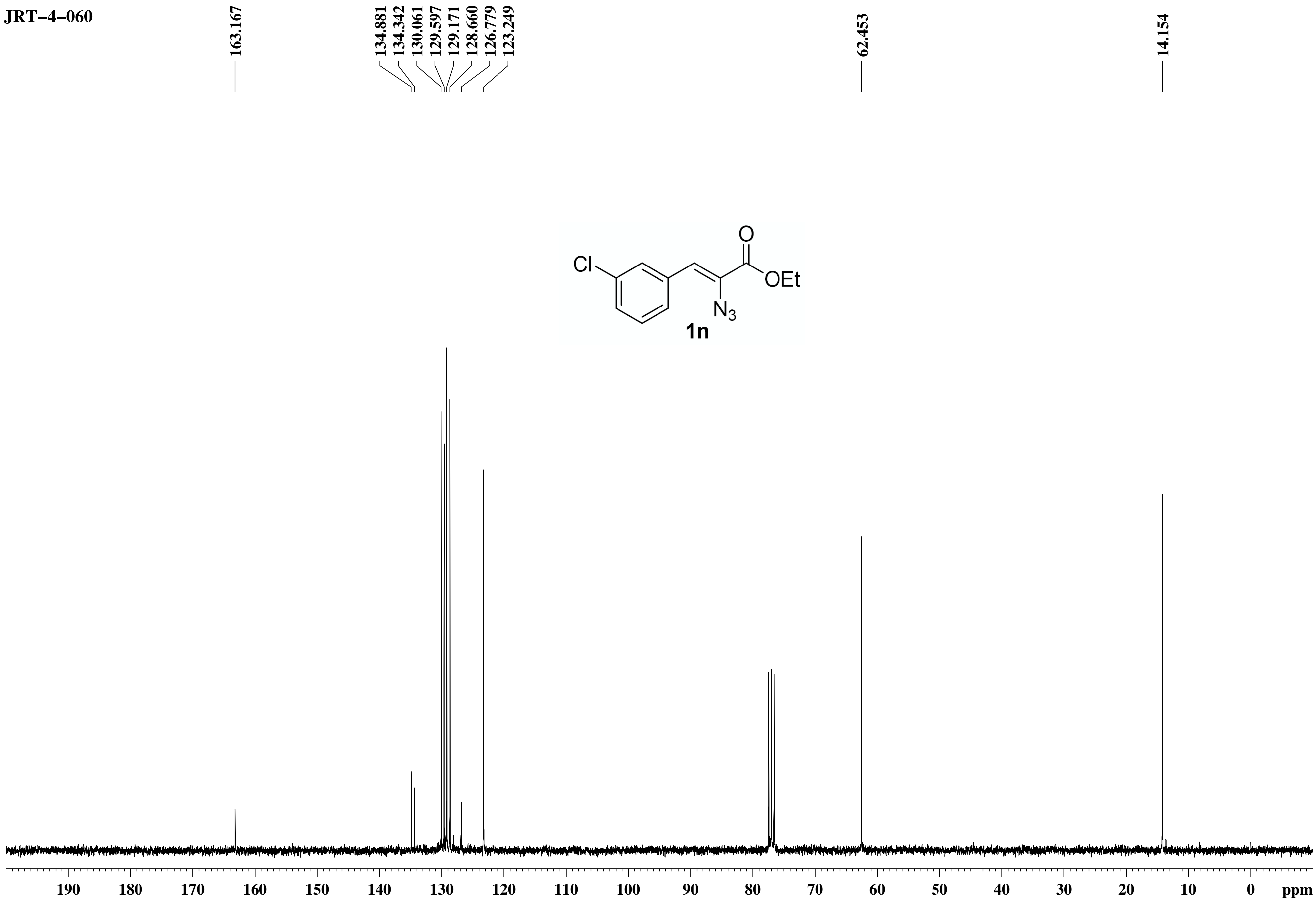
JRT–3–168B


163.237
134.620
131.207
131.028
130.079
129.589
127.431
126.553
120.514
62.488
14.151
Cl
O
OEt
N3
1m
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

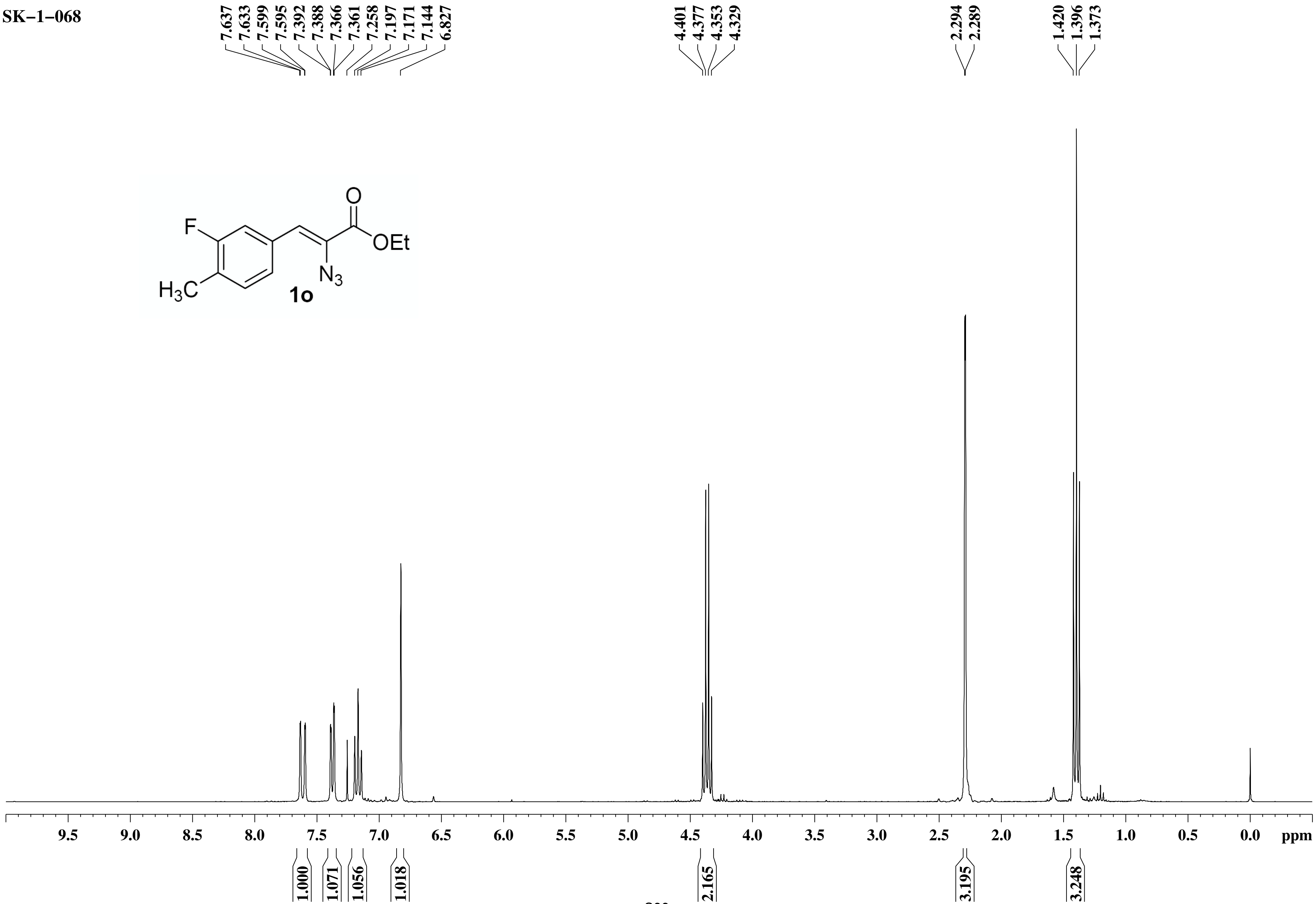
JRT-4-060



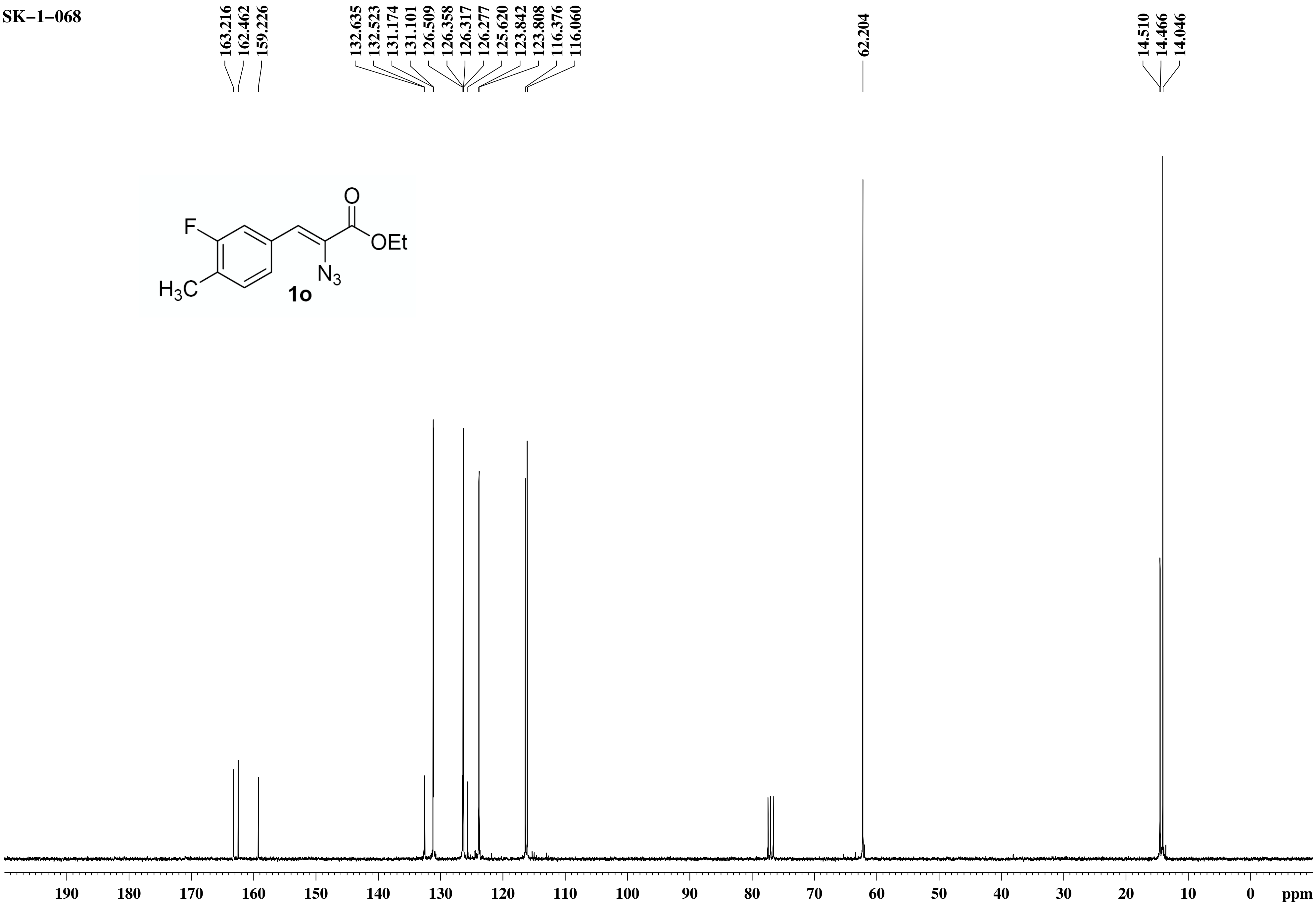
7.861
7.651
7.647
7.636
7.623
7.617
7.608
7.336
7.309
7.305
7.299
7.293
7.289
7.279
7.273
7.259
6.811
4.409
4.385
4.361
4.338
1.425
1.401
1.377
Cl
O
OEt
N3
1n
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.000
1.024
2.325
0.994
2.029
3.064


JRT-4-060
163.167
134.881
134.342
130.061
129.597
129.171
128.660
126.779
123.249
62.453
14.154
Cl
O
OEt
N3
1n
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

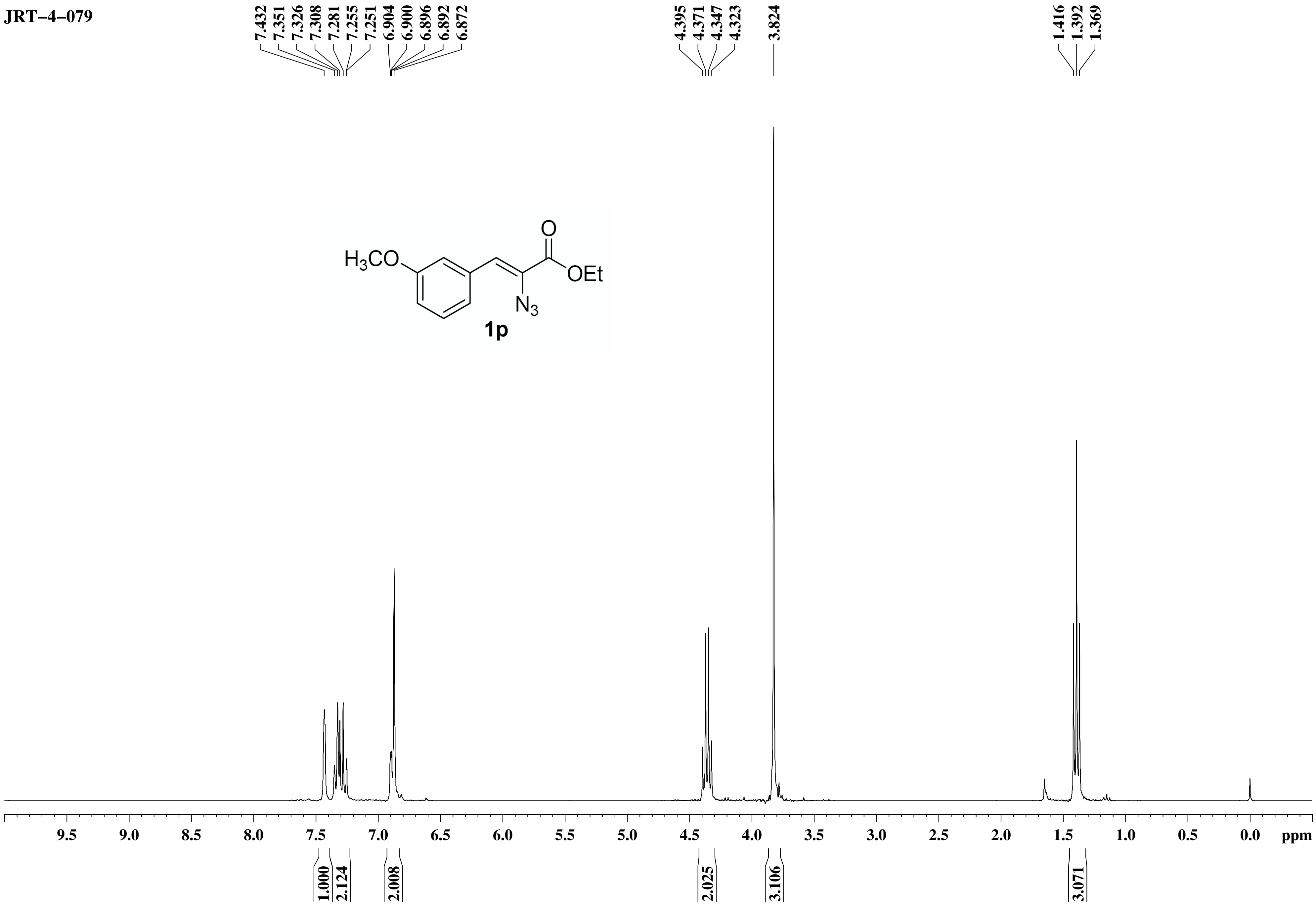
SK−1−068

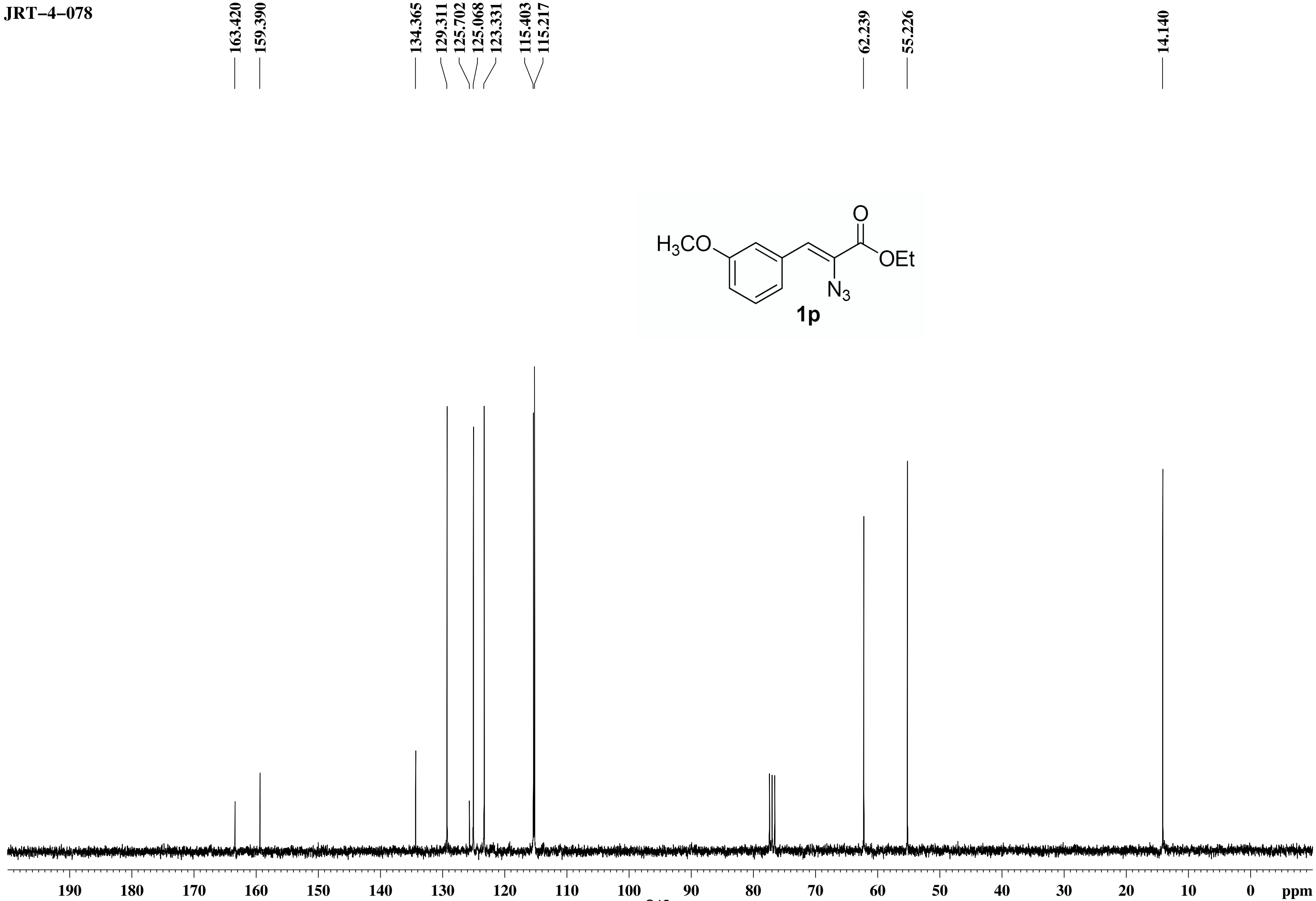


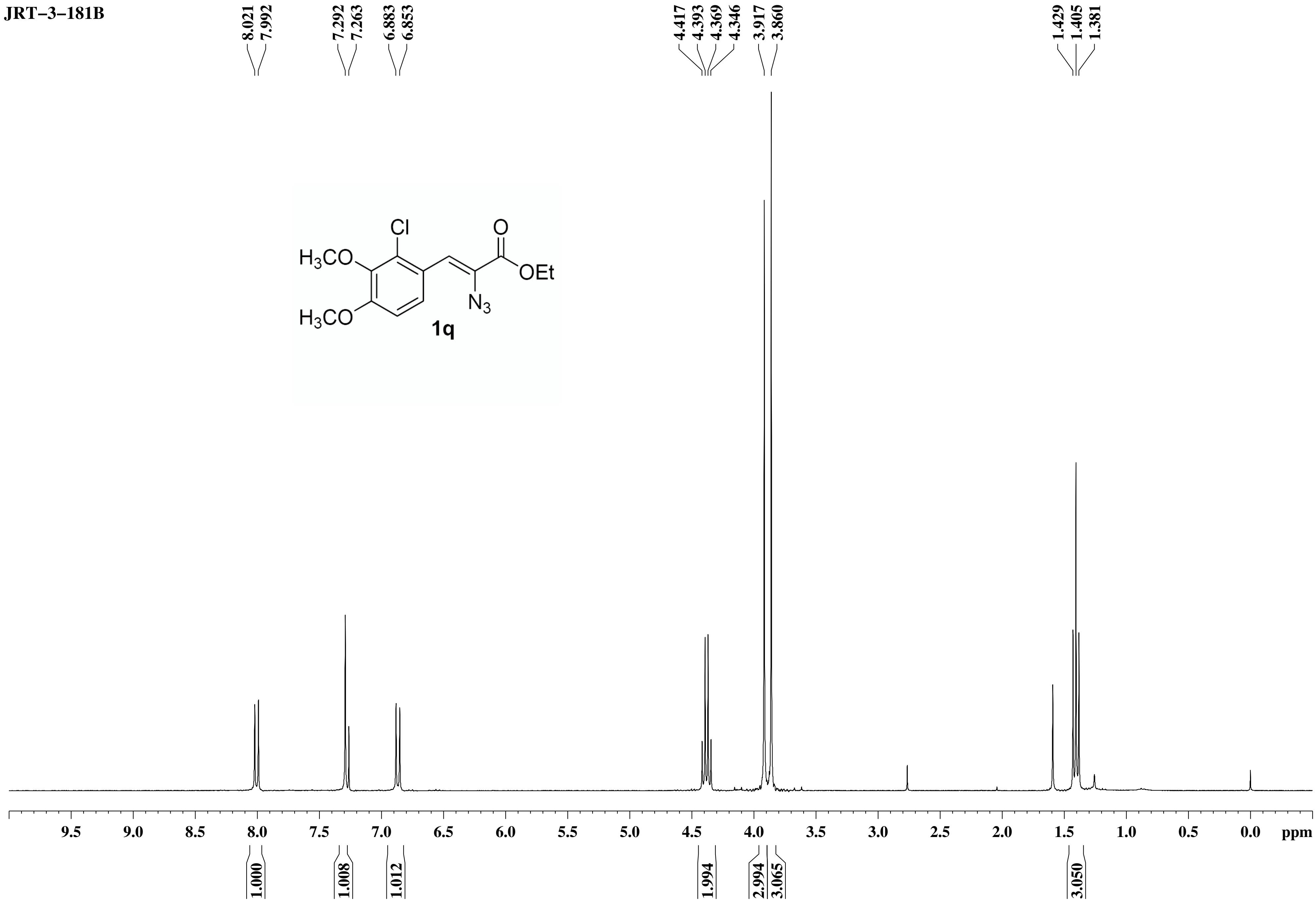
7.637
7.633
7.599
7.595
7.392
7.388
7.366
7.361
7.258
7.197
7.171
7.144
6.827
4.401
4.377
4.353
4.329
2.294
2.289
1.420
1.396
1.373
F
O
OEt
N3
H3C
1o
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.000
1.071
1.056
1.018
2.165
3.195
3.248

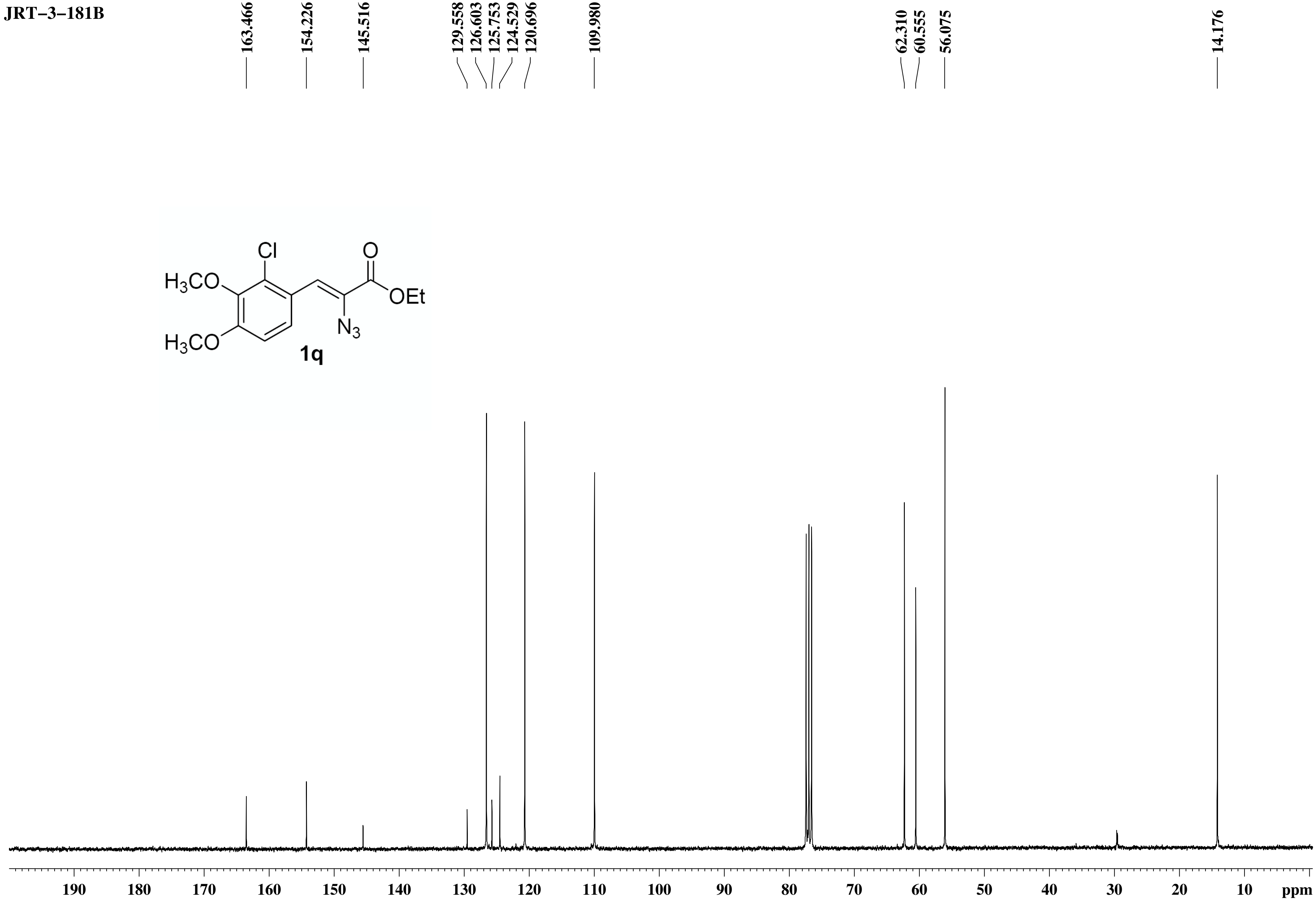

SK−1−068
163.216
162.462
159.226
132.635
132.523
131.174
131.101
126.509
126.358
126.317
126.277
125.620
123.842
123.808
116.376
116.060
62.204
14.510
14.466
14.046
F
O
OEt
N3
H3C
1o
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

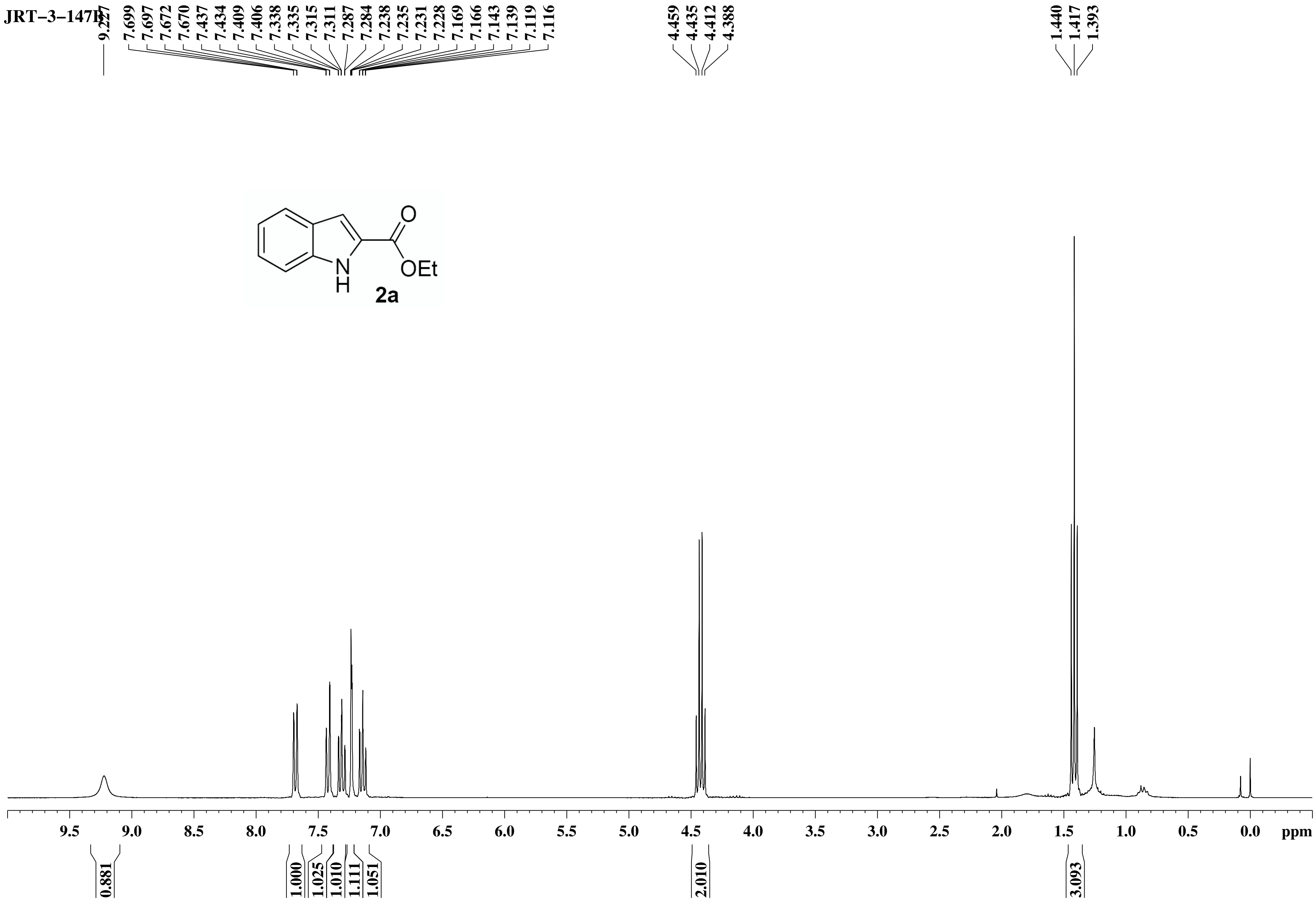
JRT-4-079


7.432
7.351
7.326
7.308
7.281
7.255
7.251
6.904
6.900
6.896
6.892
6.872
4.395
4.371
4.347
4.323
3.824
1.416
1.392
1.369
H3CO
O
OEt
N3
1p
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.000
2.124
2.008
2.025
3.106
3.071

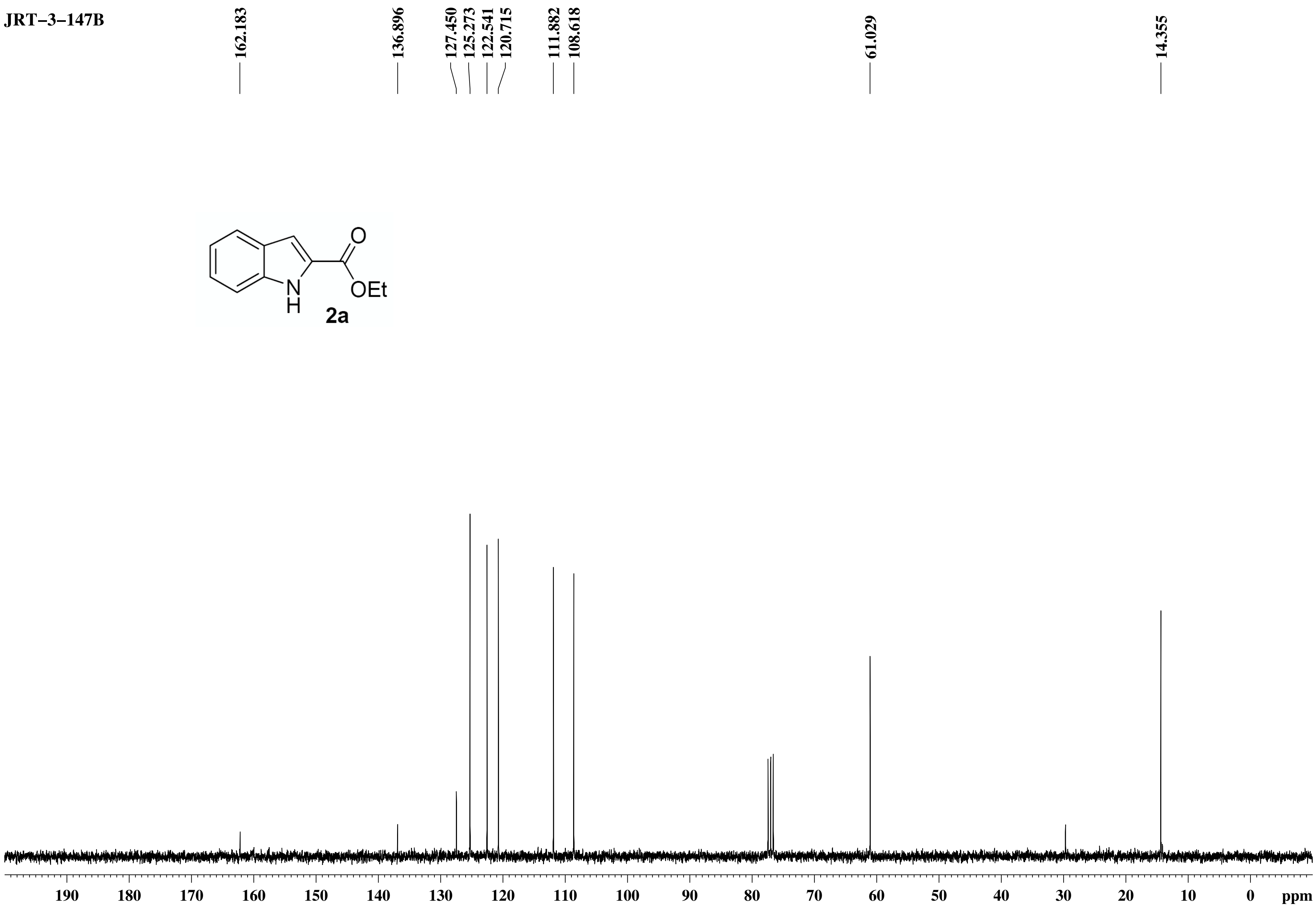

JRT−4−078
163.420
159.390
134.365
129.311
125.702
125.068
123.331
115.403
115.217
62.239
55.226
14.140
H3CO
O
OEt
N3
1p
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


JRT−3−181B
8.021
7.992
7.292
7.263
6.883
6.853
4.417
4.393
4.369
4.346
3.917
3.860
1.429
1.405
1.381
Cl
O
H_3CO
OEt
N_3
H_3CO
1q
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.000
1.008
1.012
1.994
2.994
3.065
3.050

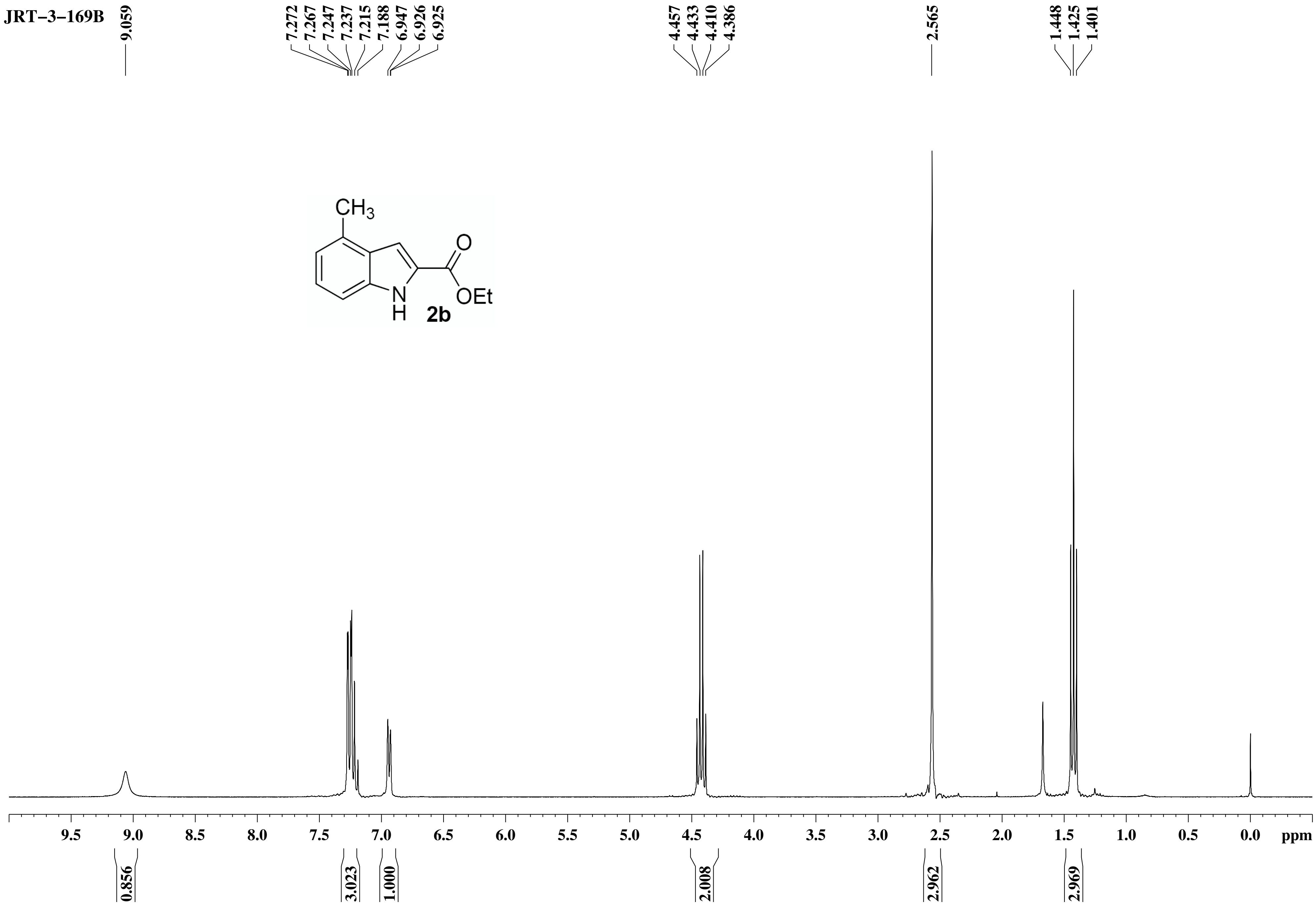

JRT–3–181B
163.466
154.226
145.516
129.558
126.603
125.753
124.529
120.696
109.980
62.310
60.555
56.075
14.176
Cl
O
H_3CO
OEt
N_3
H_3CO
1q
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

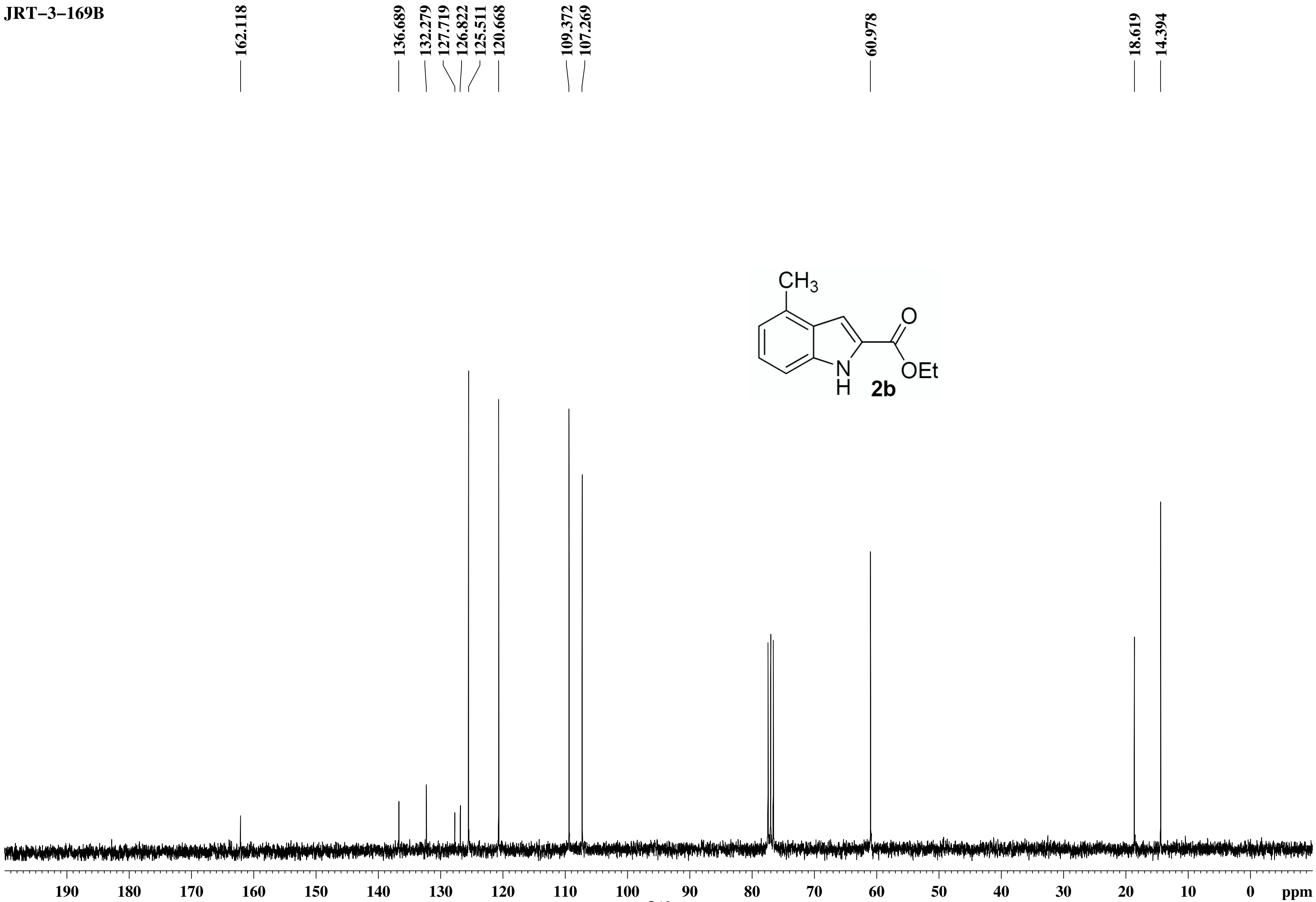

JRT-3-147B
9.227
7.699
7.697
7.672
7.670
7.437
7.434
7.409
7.406
7.338
7.335
7.315
7.311
7.287
7.284
7.238
7.235
7.231
7.228
7.169
7.166
7.143
7.139
7.119
7.116
4.459
4.435
4.412
4.388
1.440
1.417
1.393
O
OEt
N
H
2a
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
0.881
1.000
1.025
1.010
1.111
1.051
2.010
3.093

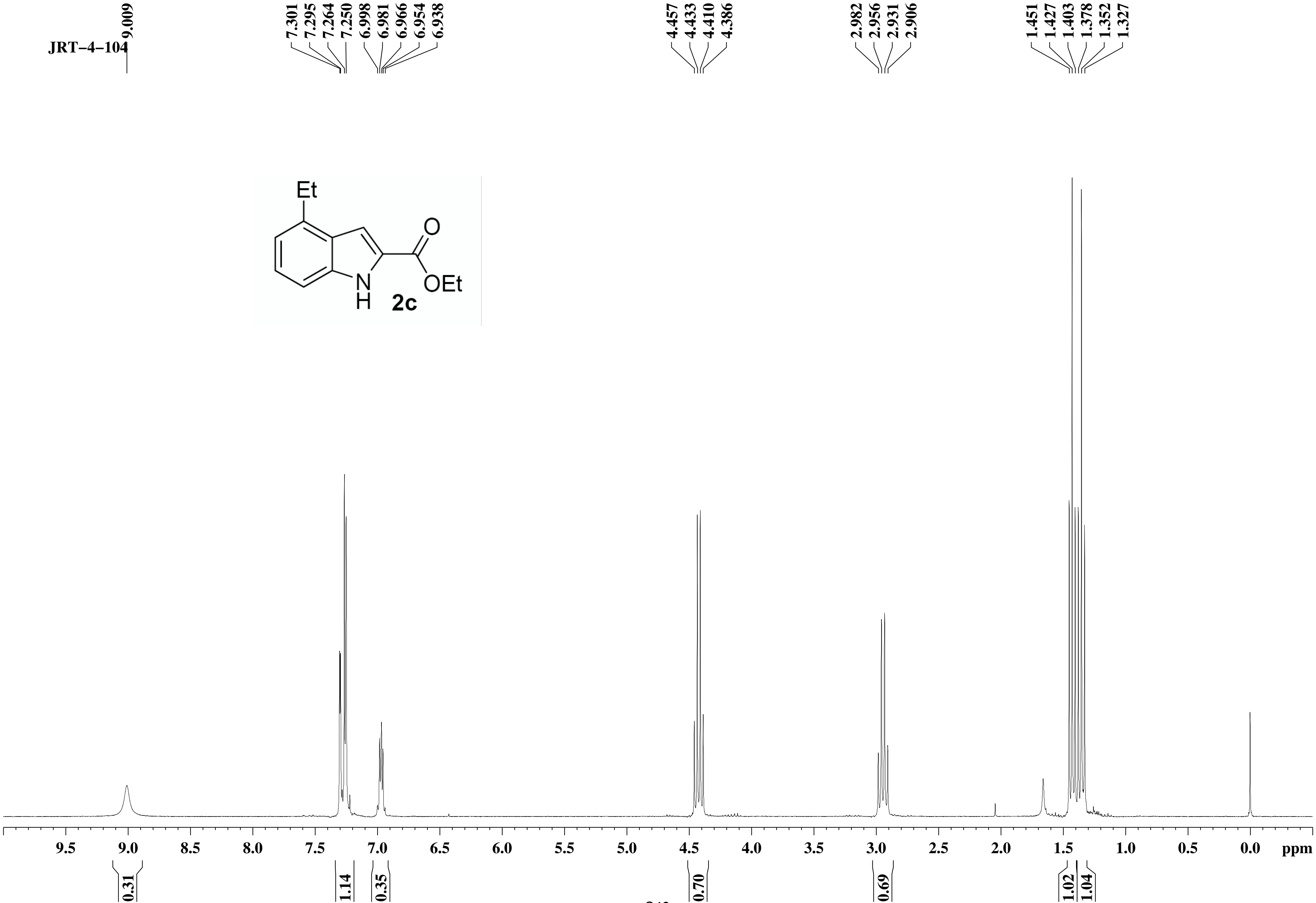
JRT–3–147B


162.183
136.896
127.450
125.273
122.541
120.715
111.882
108.618
61.029
14.355
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
O
N
H
OEt

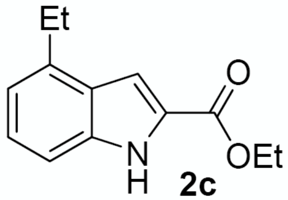
2a


JRT−3−169B
9.059
7.272
7.267
7.247
7.237
7.215
7.188
6.947
6.926
6.925
4.457
4.433
4.410
4.386
2.565
1.448
1.425
1.401
CH3
O
OEt
N
H
2b
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.856
3.023
1.000
2.008
2.962
2.969

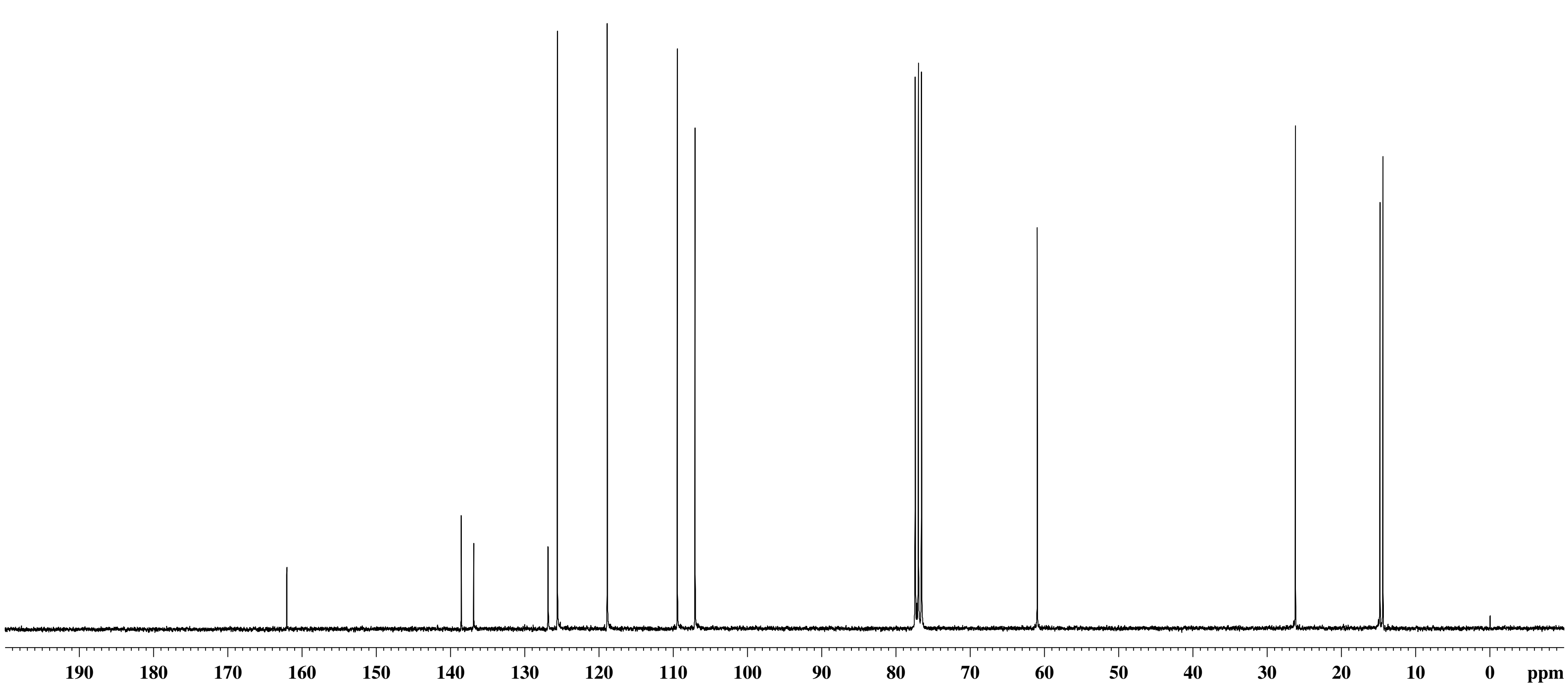

JRT−3−169B
162.118
136.689
132.279
127.719
126.822
125.511
120.668
109.372
107.269
60.978
18.619
14.394
CH3
O
N
H
OEt
2b
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

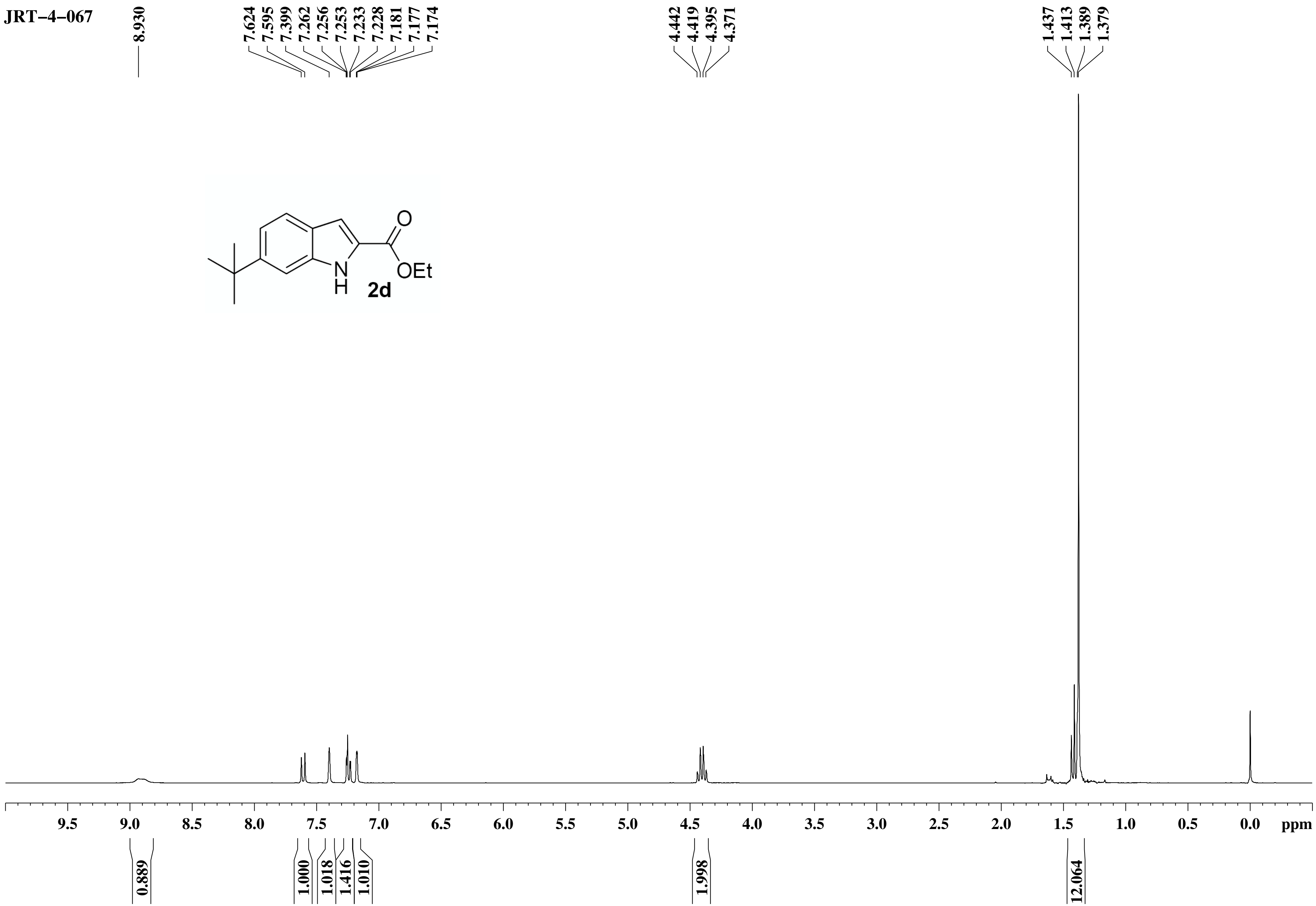

JRT-4-104
9.009
7.301
7.295
7.264
7.250
6.998
6.981
6.966
6.954
6.938
4.457
4.433
4.410
4.386
2.982
2.956
2.931
2.906
1.451
1.427
1.403
1.378
1.352
1.327
Et
O
OEt
N
H
2c
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.31
1.14
0.35
0.70
0.69
1.02
1.04

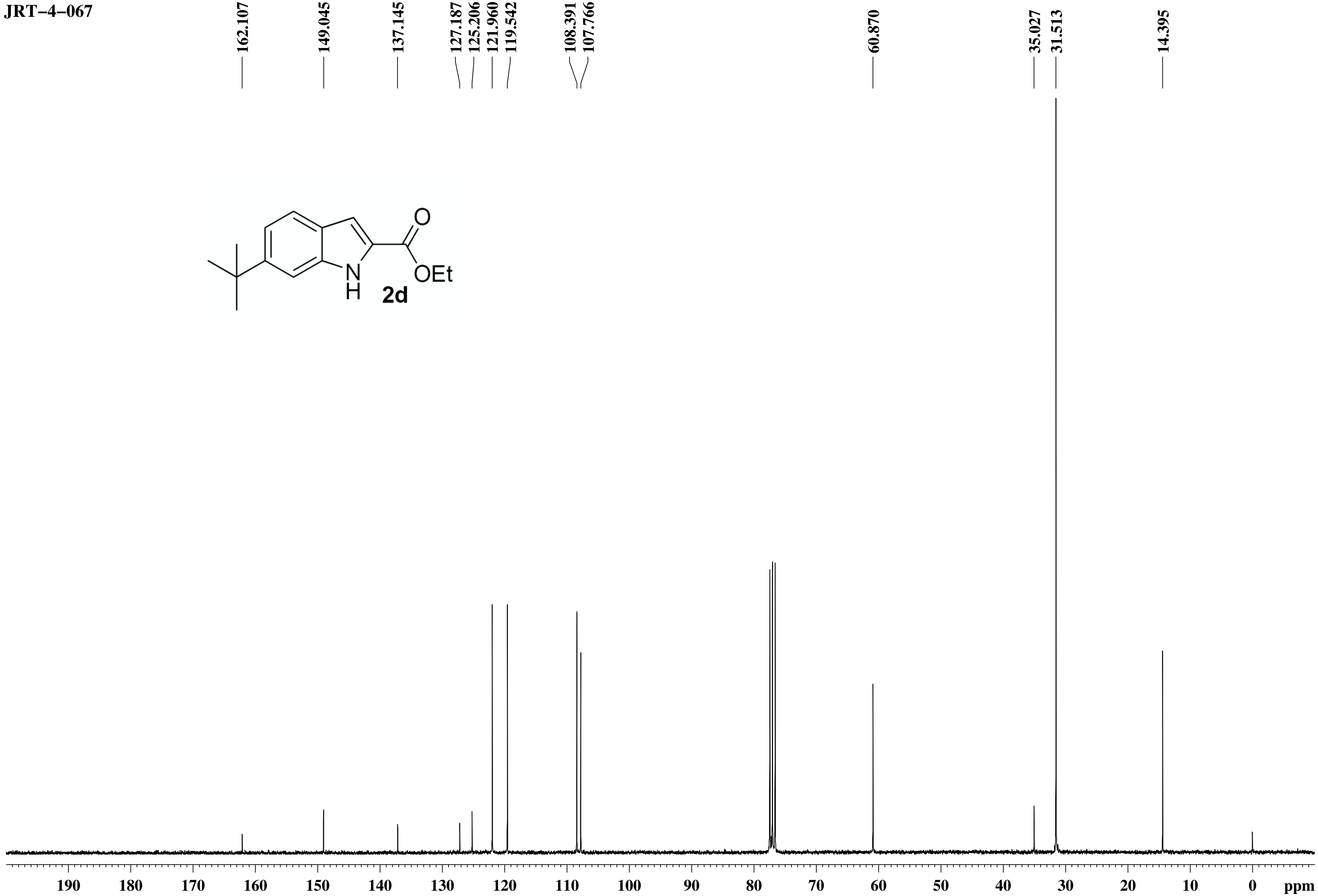
JRT−4−104



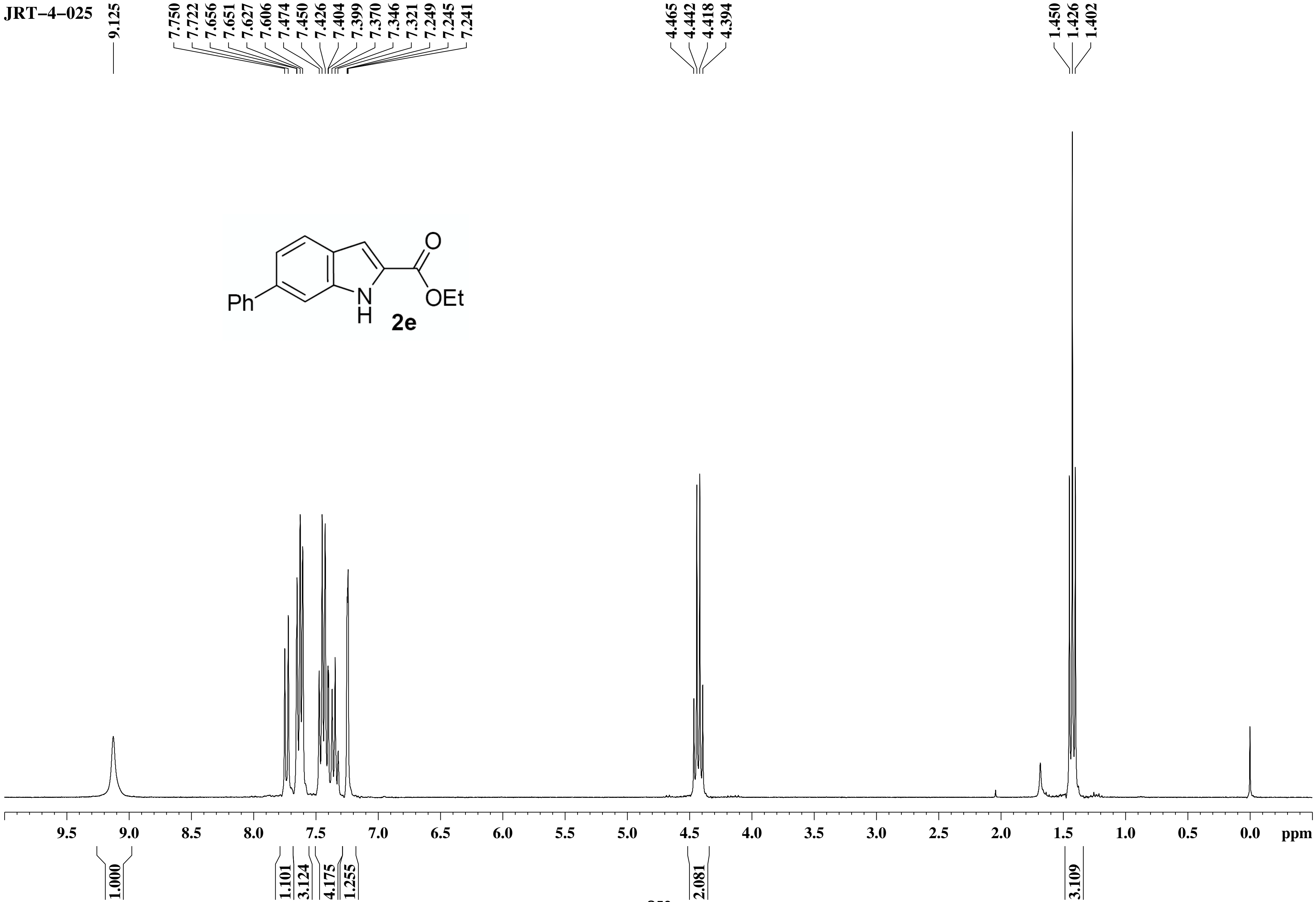
2c


162.082
138.584
136.900
126.910
126.852
125.629
118.907
109.471
107.084
60.974
26.193
14.808
14.404
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


JRT−4−067
8.930
7.624
7.595
7.399
7.262
7.256
7.253
7.233
7.228
7.181
7.177
7.174
4.442
4.419
4.395
4.371
1.437
1.413
1.389
1.379
O
N
H
OEt
2d
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.889
1.000
1.018
1.416
1.010
1.998
12.064

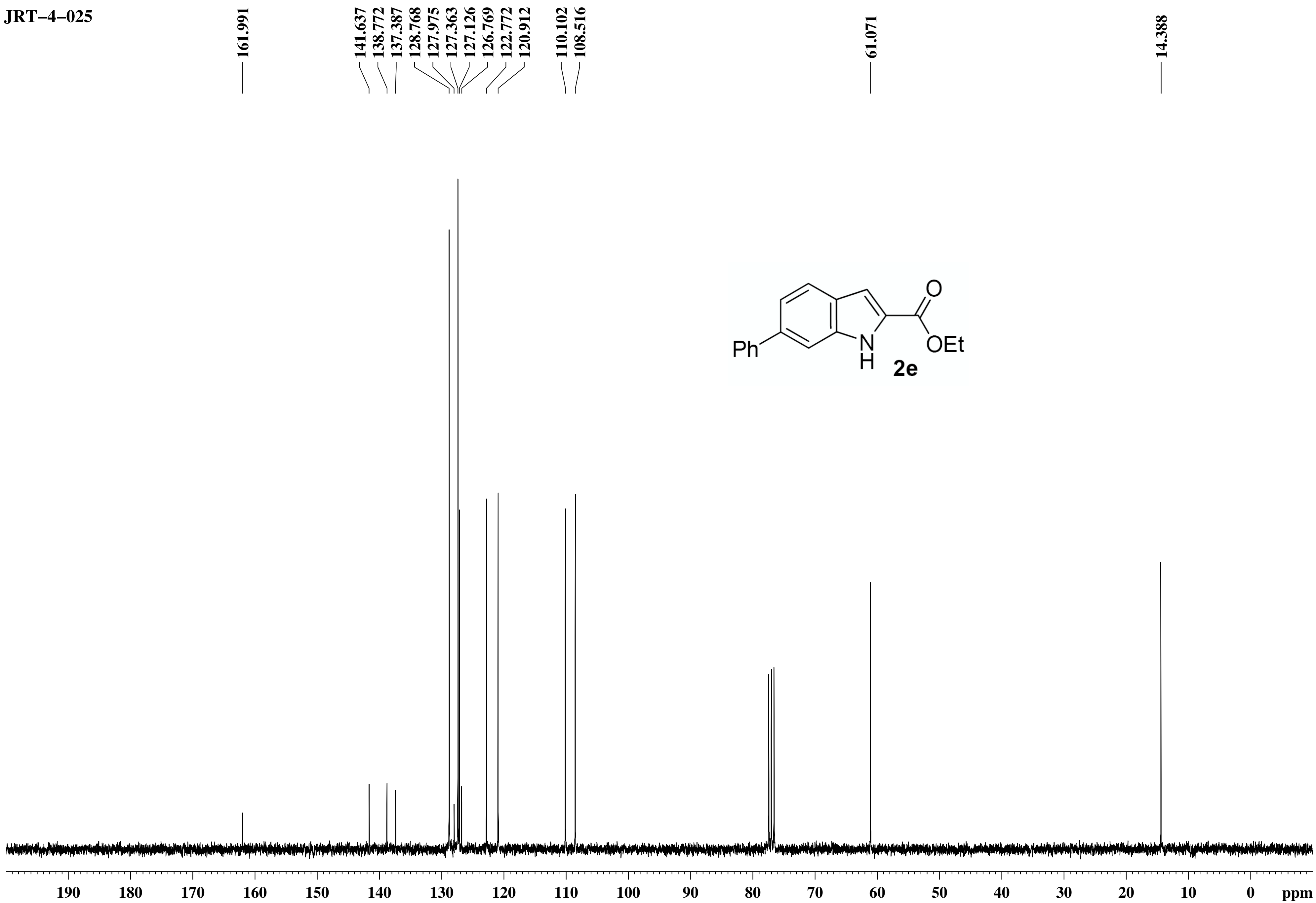

JRT−4−067
162.107
149.045
137.145
127.187
125.206
121.960
119.542
108.391
107.766
60.870
35.027
31.513
14.395
O
OEt
N
H
2d
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

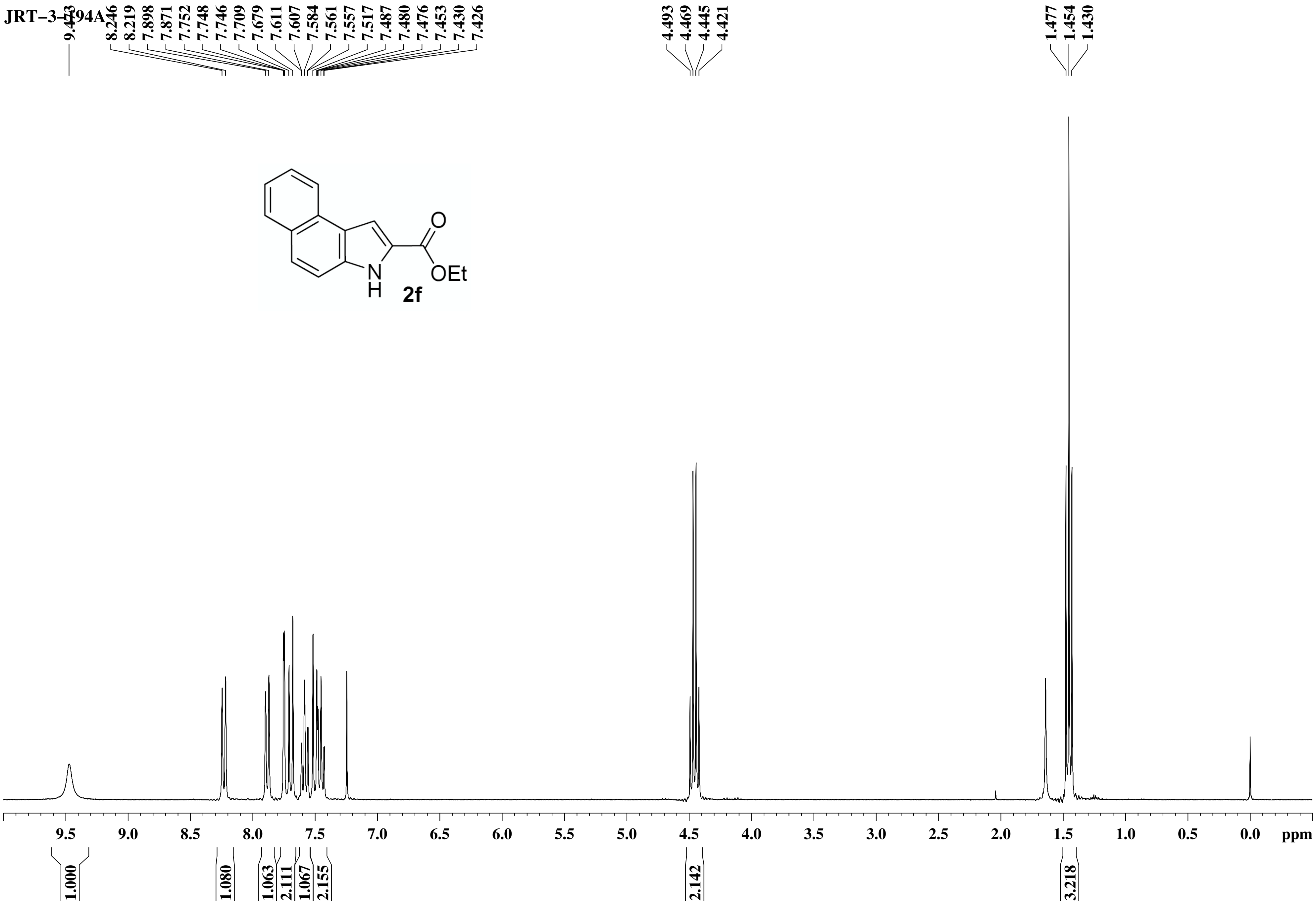
JRT-4-025

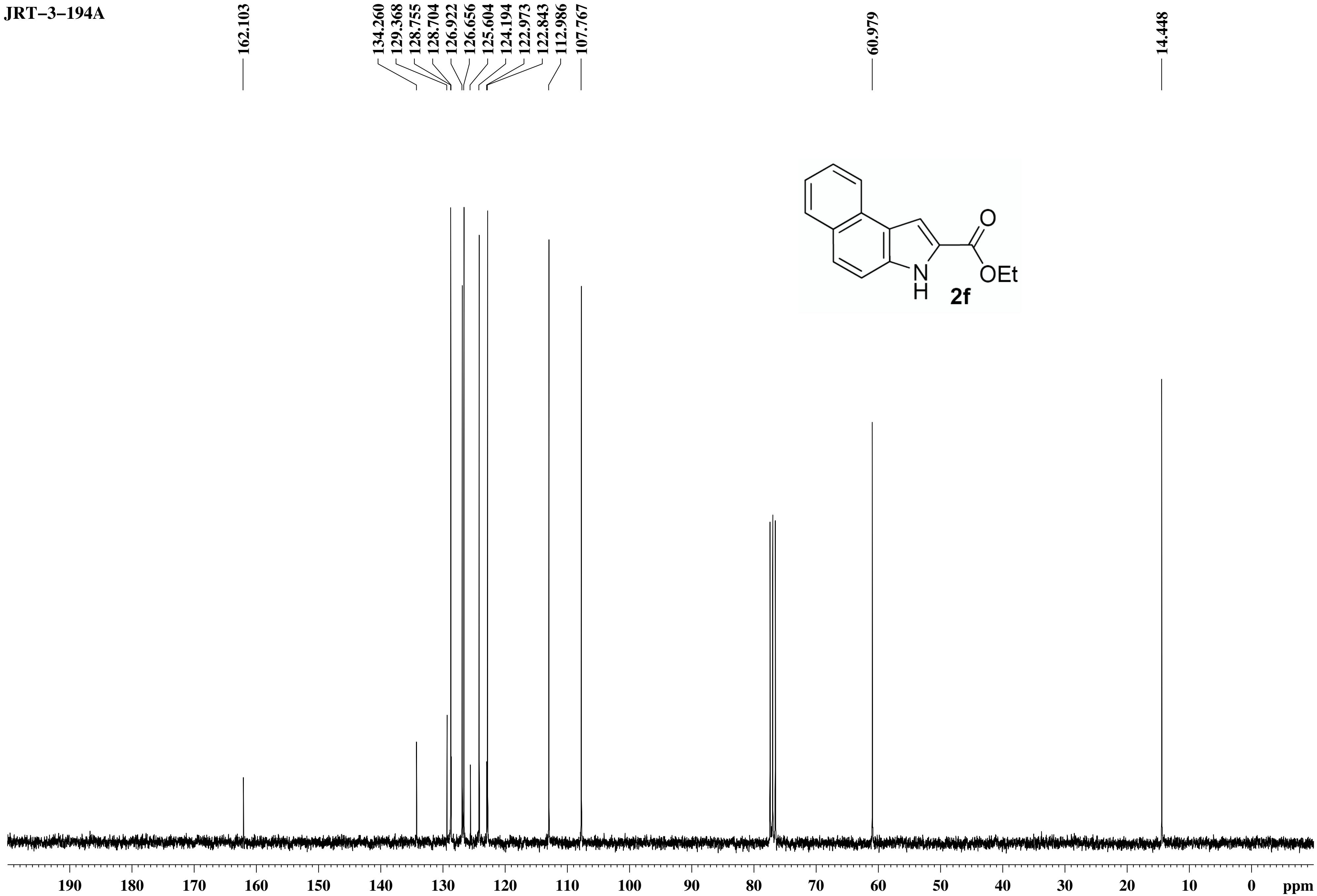


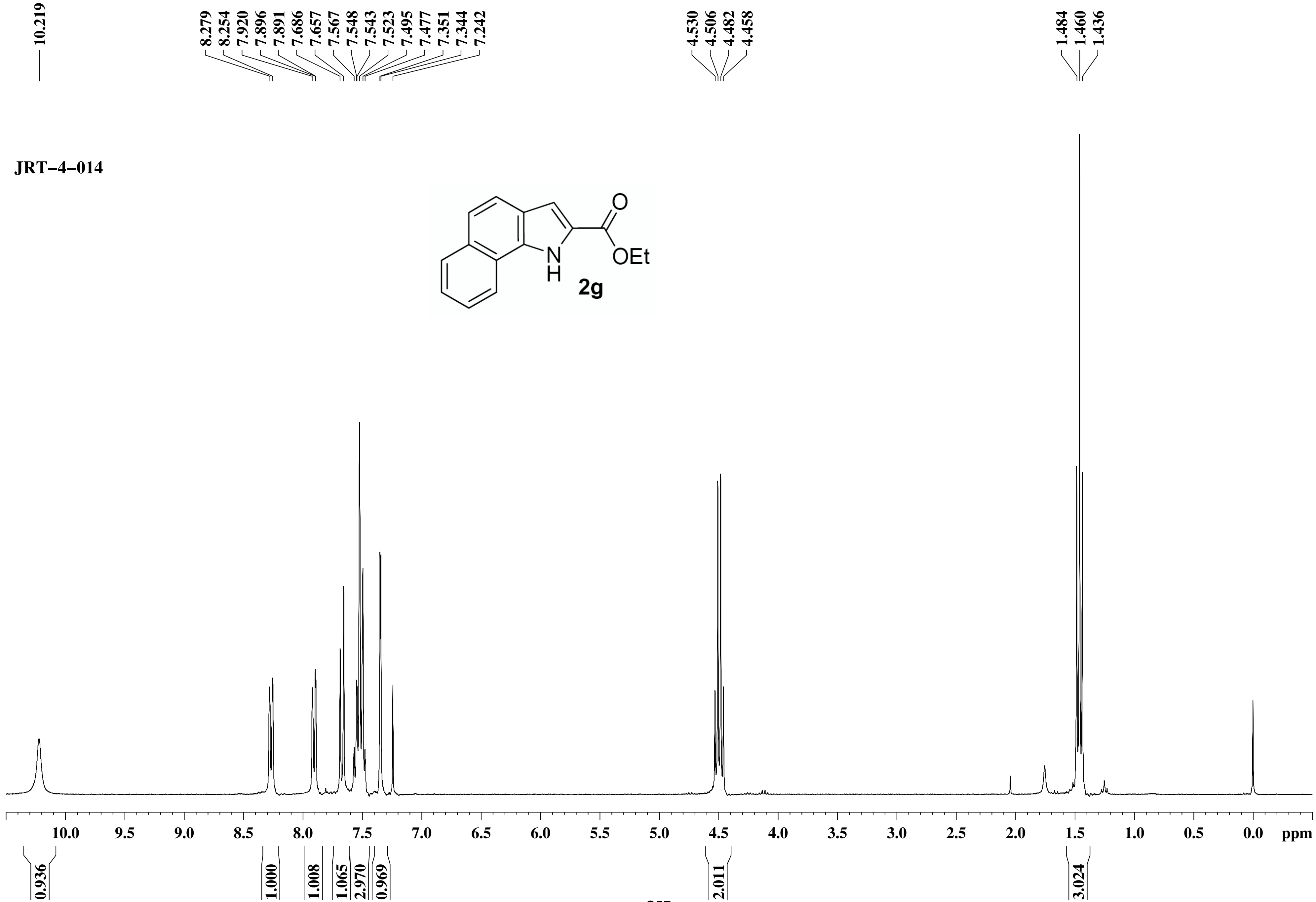
9.125
7.750
7.722
7.656
7.651
7.627
7.606
7.474
7.450
7.426
7.404
7.399
7.370
7.346
7.321
7.249
7.245
7.241
4.465
4.442
4.418
4.394
1.450
1.426
1.402
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.000
1.101
3.124
4.175
1.255
2.081
3.109
Ph
N
H
O
OEt

2e

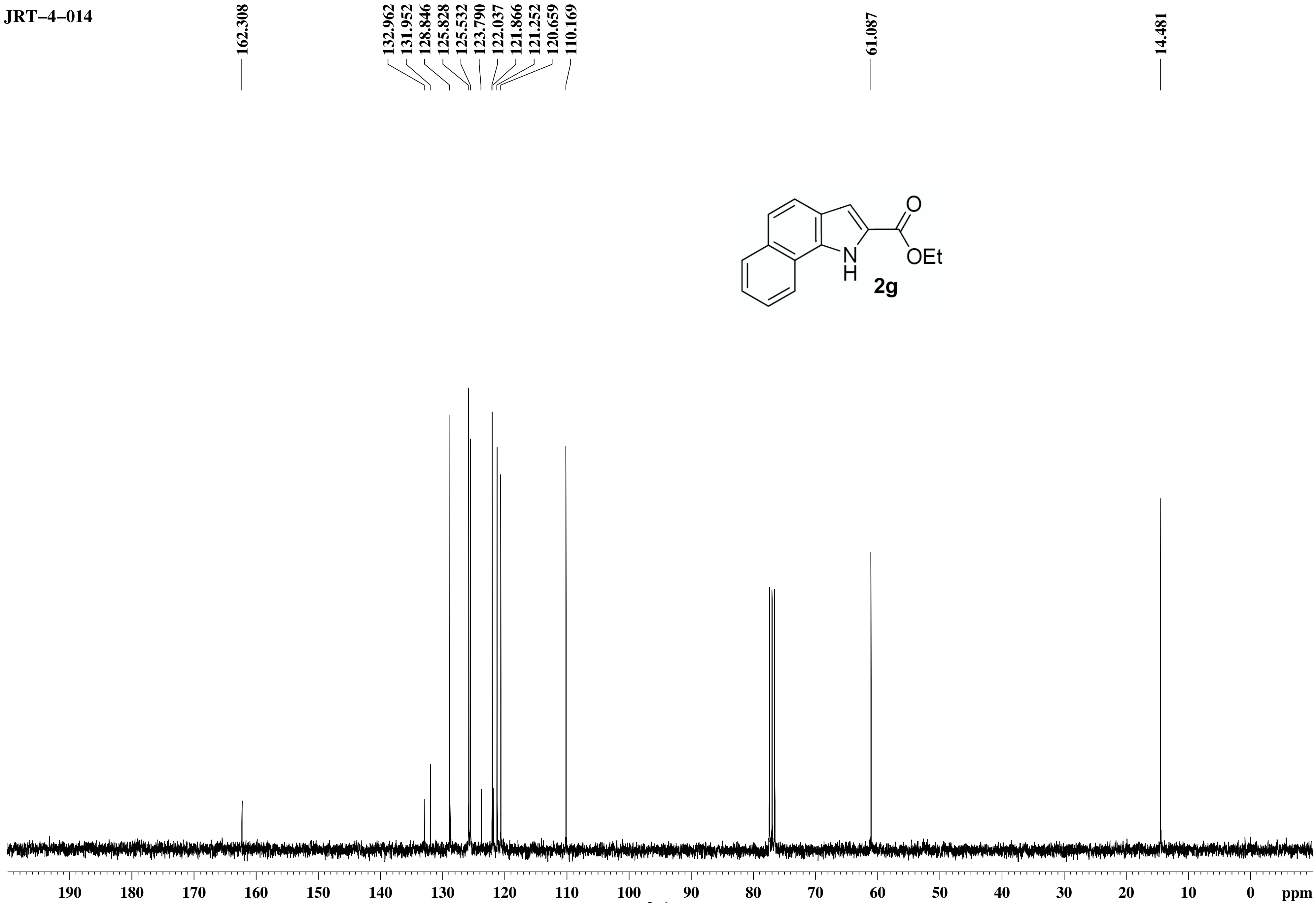

JRT−4−025
161.991
141.637
138.772
137.387
128.768
127.975
127.363
127.126
126.769
122.772
120.912
110.102
108.516
61.071
14.388
O
Ph
N
H
OEt
2e
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

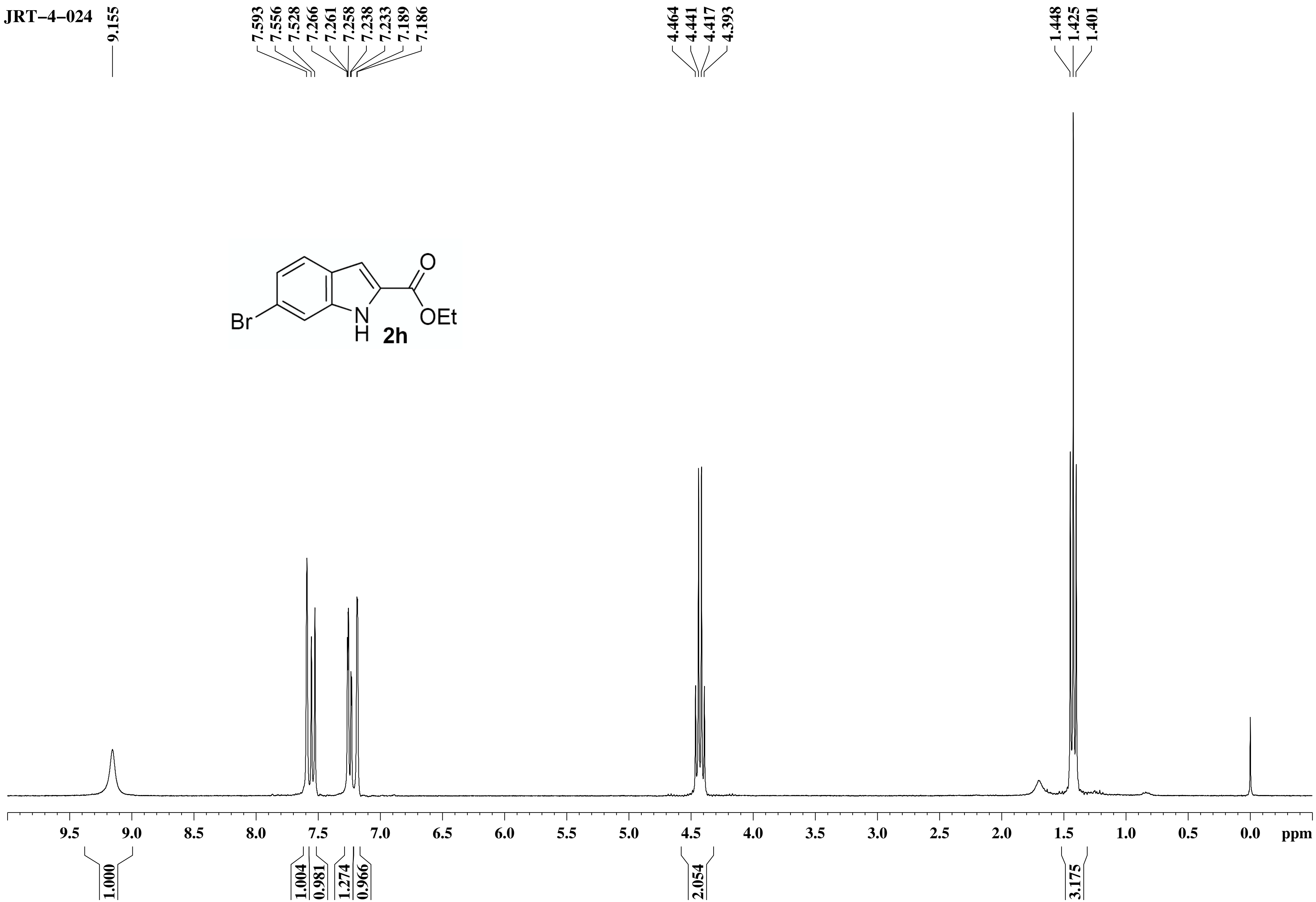

JRT-3-194A
8.246
8.219
7.898
7.871
7.752
7.748
7.746
7.709
7.679
7.611
7.607
7.584
7.561
7.557
7.517
7.487
7.480
7.476
7.453
7.430
7.426
4.493
4.469
4.445
4.421
1.477
1.454
1.430
O
N
H
OEt
2f
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.000
1.080
1.063
2.111
1.067
2.155
2.142
3.218

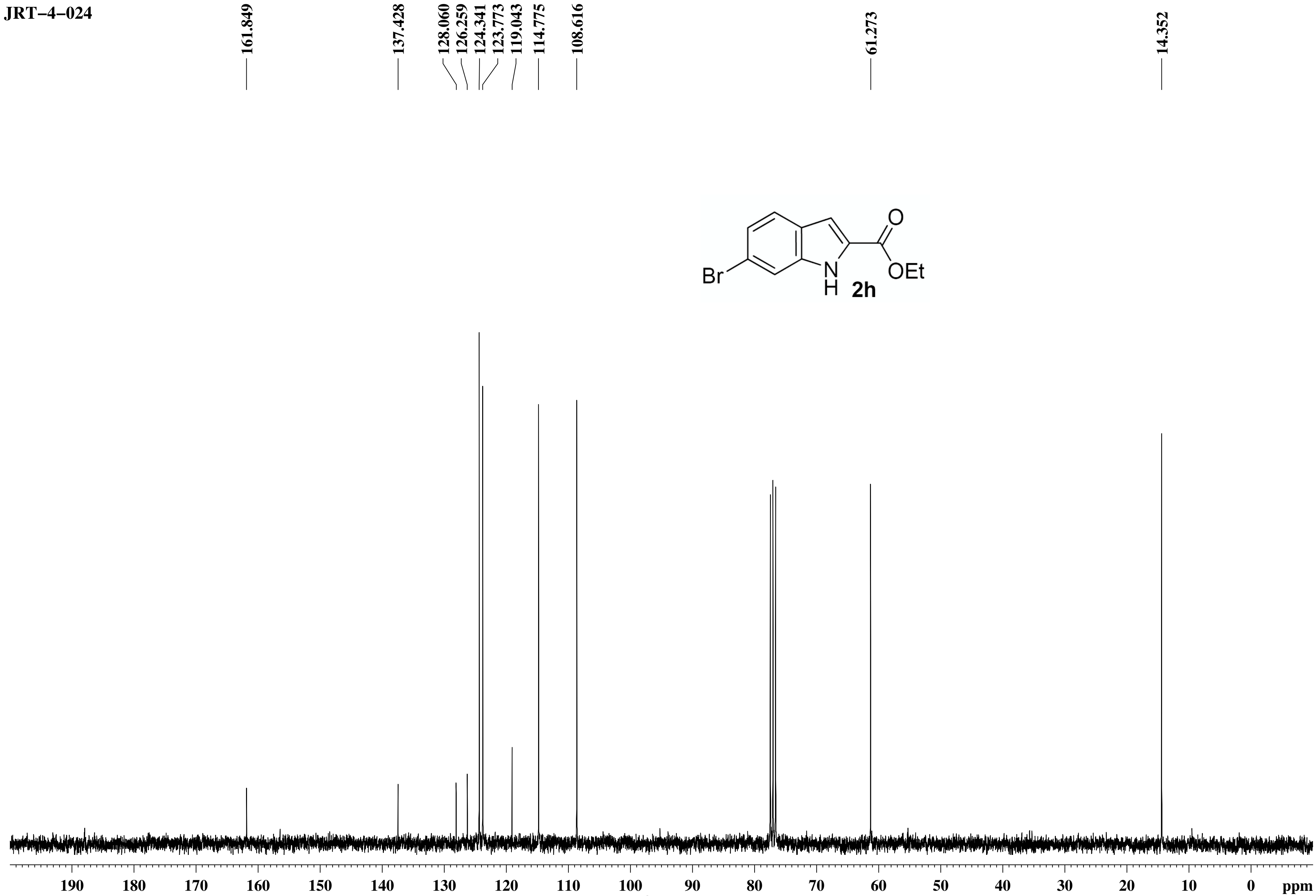

JRT–3–194A
162.103
134.260
129.368
128.755
128.704
126.922
126.656
125.604
124.194
122.973
122.843
112.986
107.767
60.979
14.448
O
OEt
N
H
2f
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



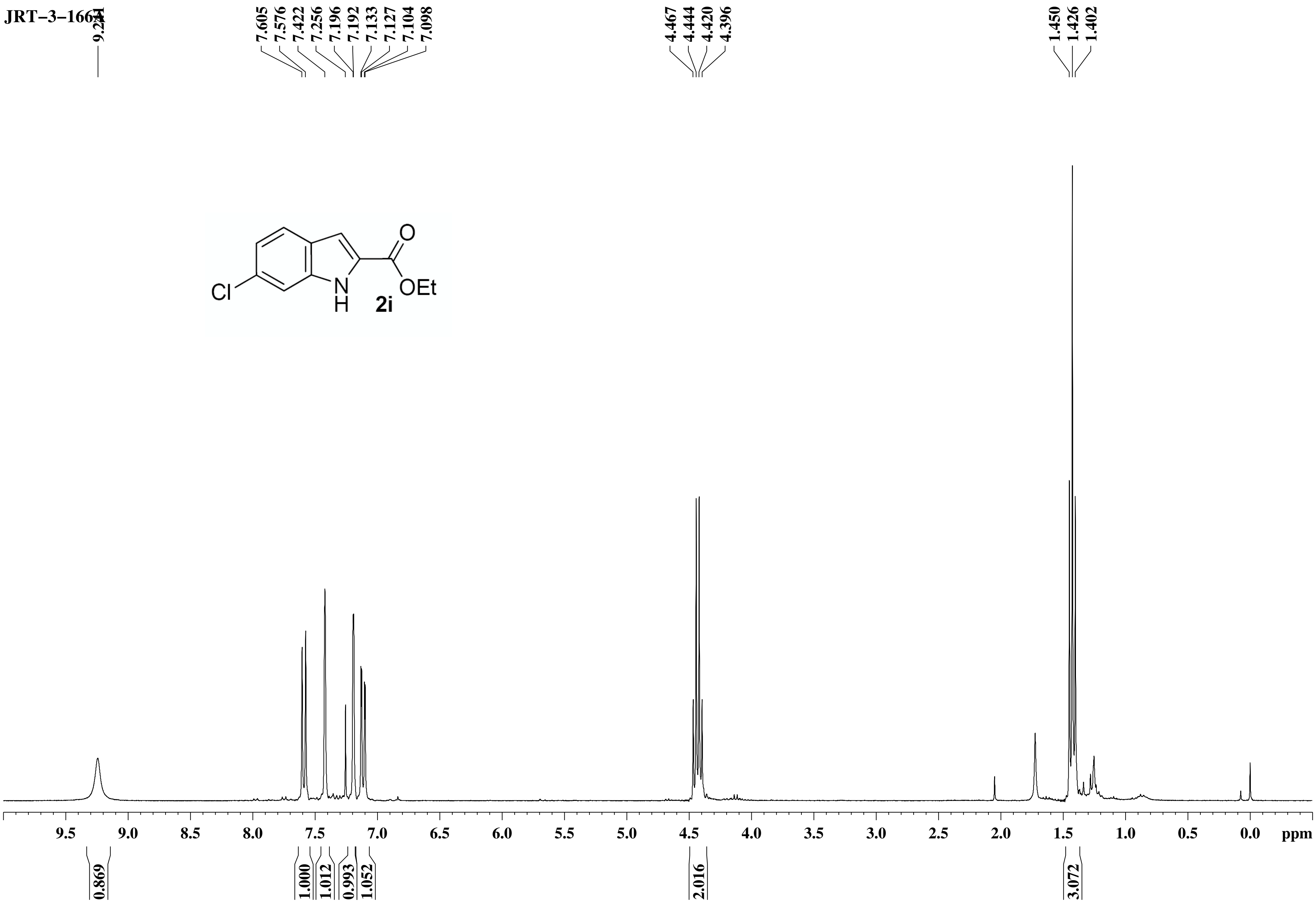
10.219
8.279
8.254
7.920
7.896
7.891
7.686
7.657
7.567
7.548
7.543
7.523
7.495
7.477
7.351
7.344
7.242
4.530
4.506
4.482
4.458
1.484
1.460
1.436
JRT−4−014
O
OEt
N
H
2g
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
0.936
1.000
1.008
1.065
2.970
0.969
2.011
3.024

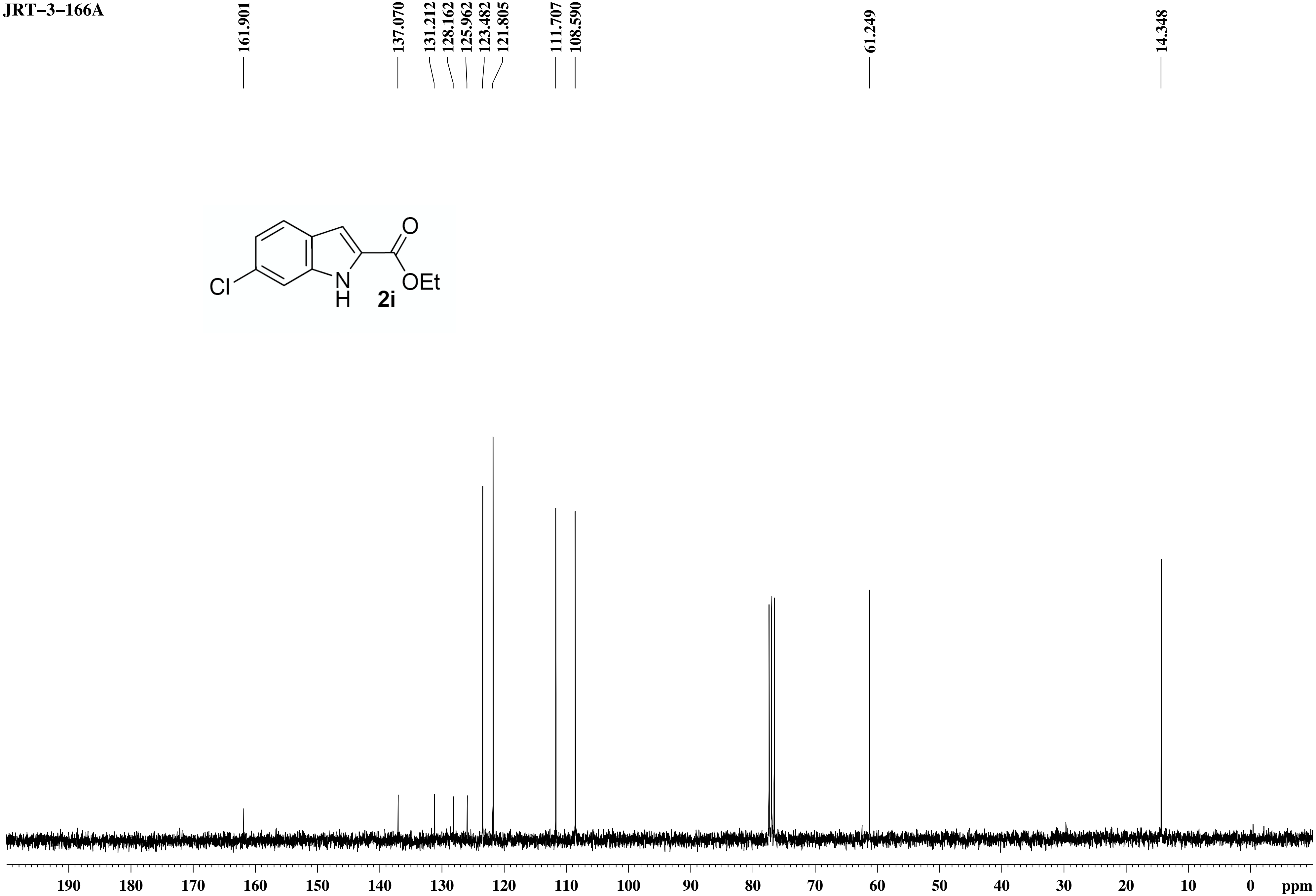

JRT-4-014
162.308
132.962
131.952
128.846
125.828
125.532
123.790
122.037
121.866
121.252
120.659
110.169
61.087
14.481
O
OEt
N
H
2g
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


JRT-4-024
9.155
7.593
7.556
7.528
7.266
7.261
7.258
7.238
7.233
7.189
7.186
4.464
4.441
4.417
4.393
1.448
1.425
1.401
Br
N
H
O
OEt
2h
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.000
1.004
0.981
1.274
0.966
2.054
3.175

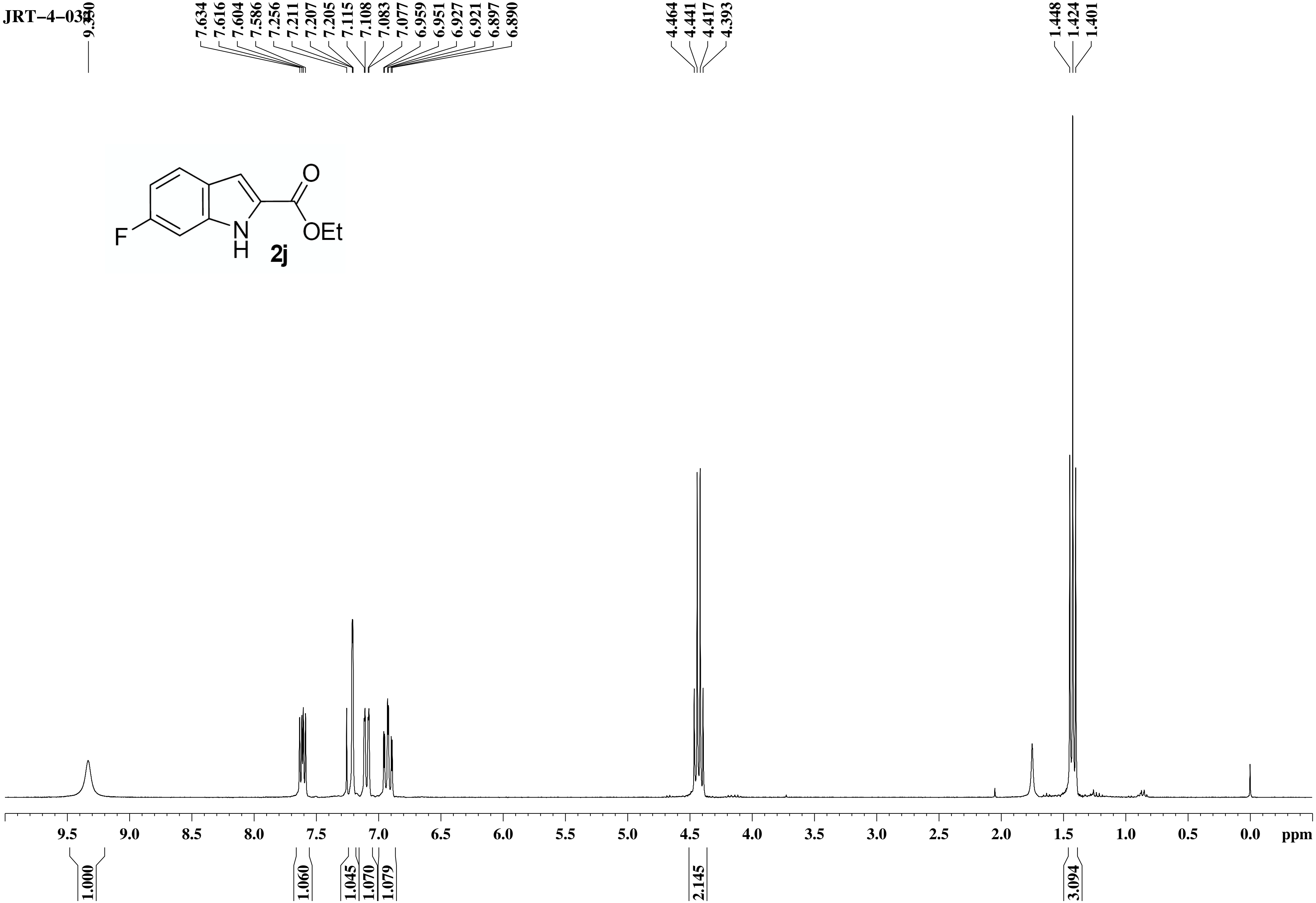

JRT−4−024
161.849
137.428
128.060
126.259
124.341
123.773
119.043
114.775
108.616
61.273
14.352
Br
N
H
O
OEt
2h
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

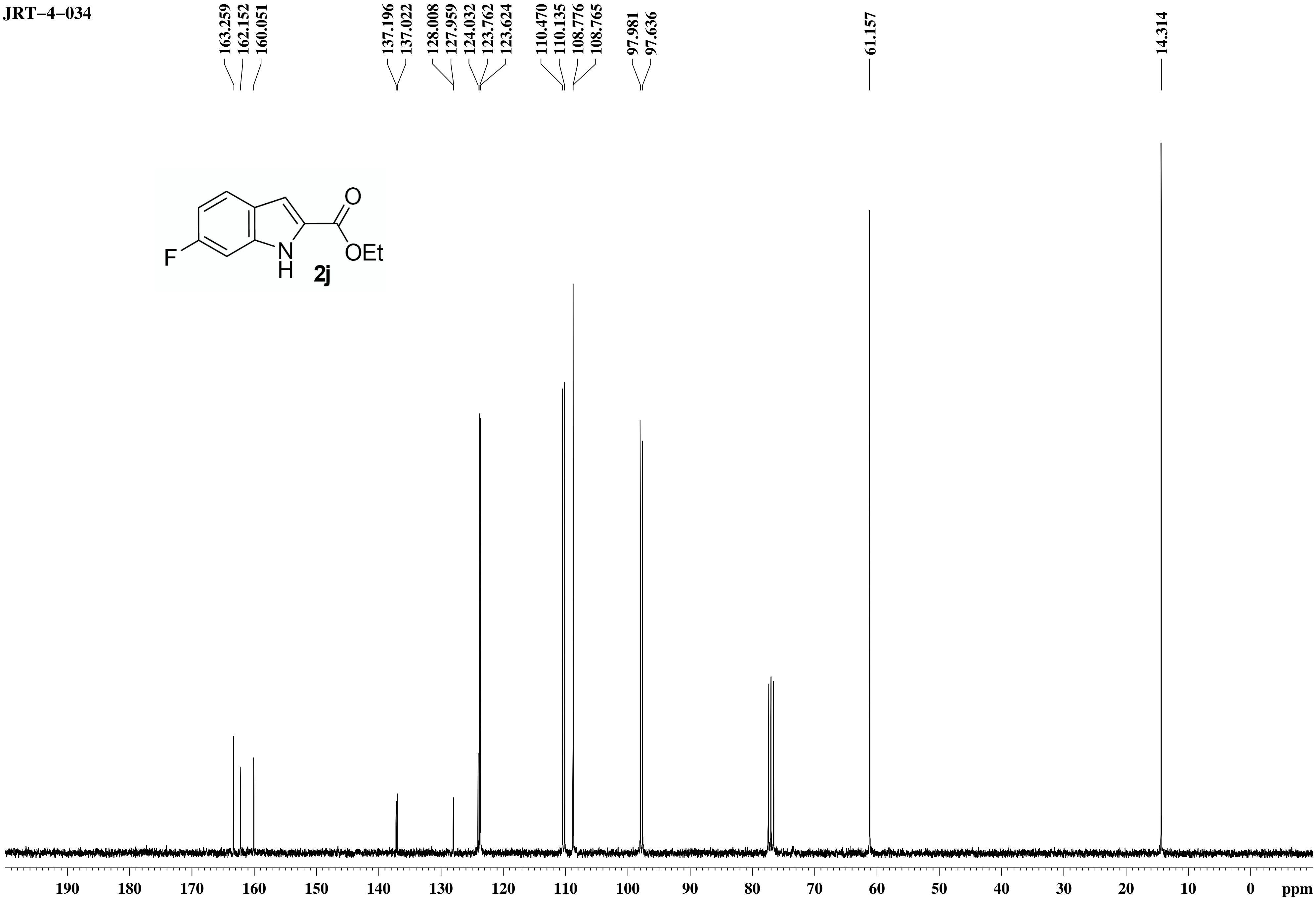
JRT-3-166A

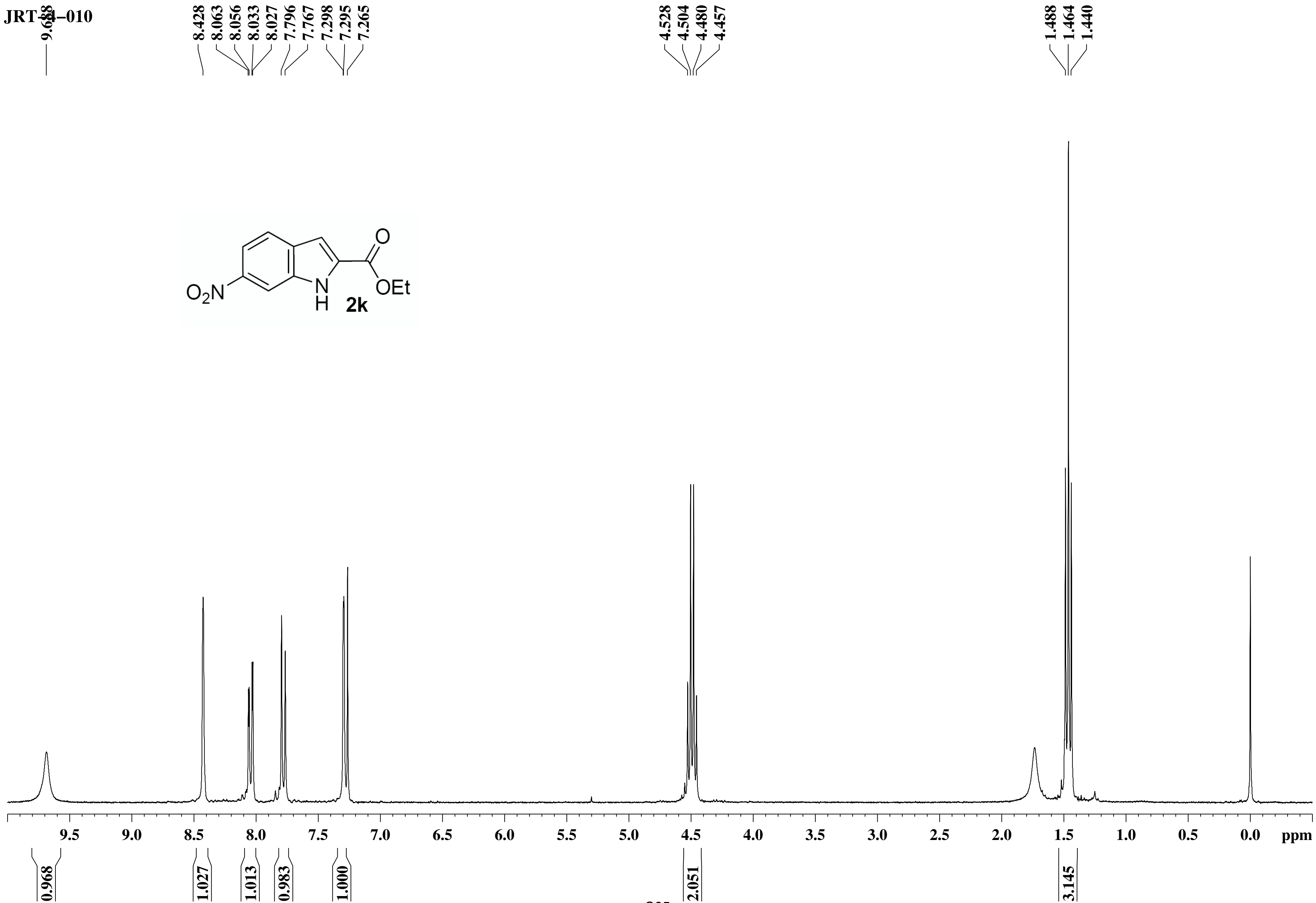

9.241
7.605
7.576
7.422
7.256
7.196
7.192
7.133
7.127
7.104
7.098
4.467
4.444
4.420
4.396
1.450
1.426
1.402
Cl
N
H
O
OEt
2i
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.869
1.000
1.012
0.993
1.052
2.016
3.072

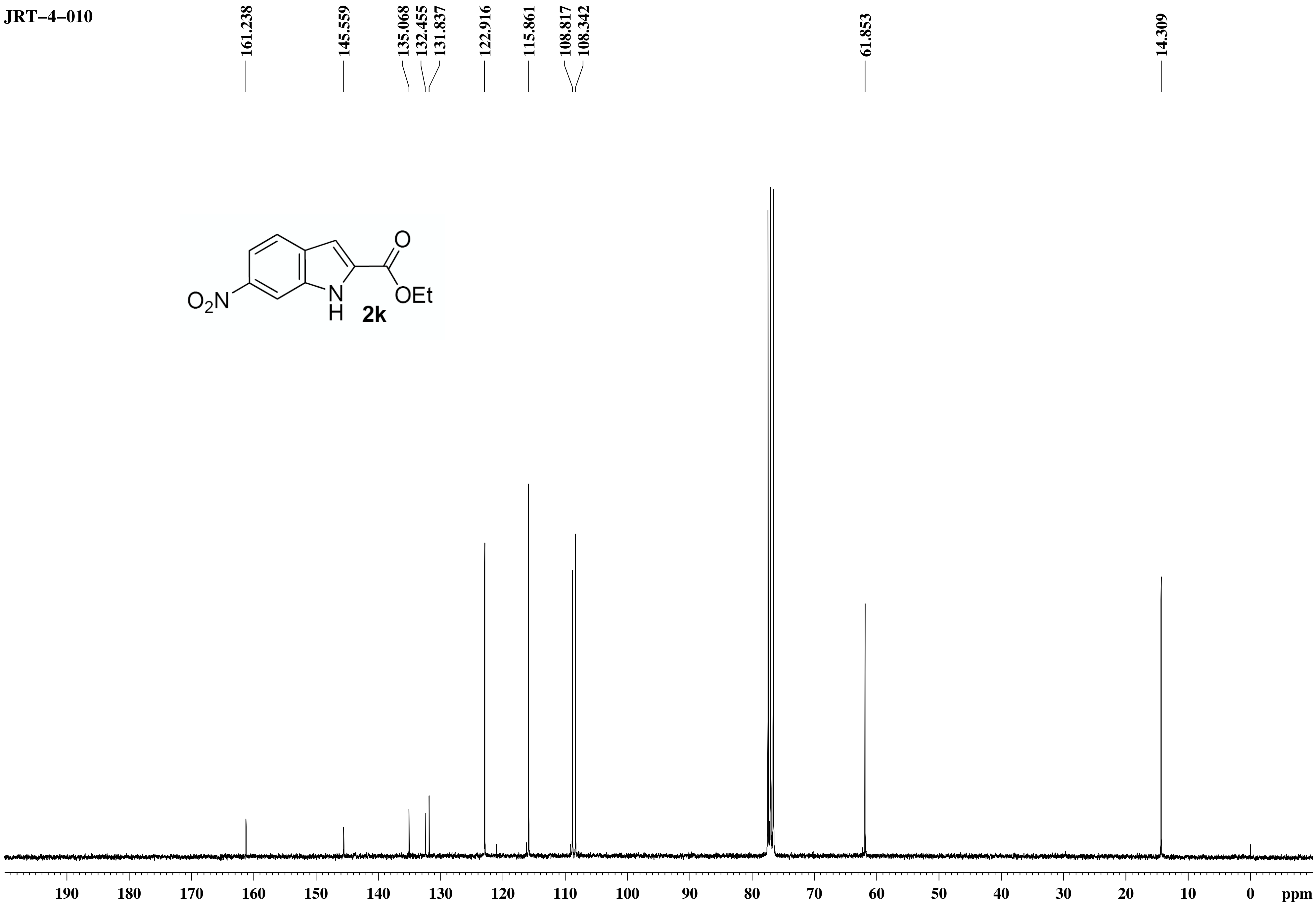

JRT-3-166A
161.901
137.070
131.212
128.162
125.962
123.482
121.805
111.707
108.590
61.249
14.348
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
Cl
N
H
O
OEt

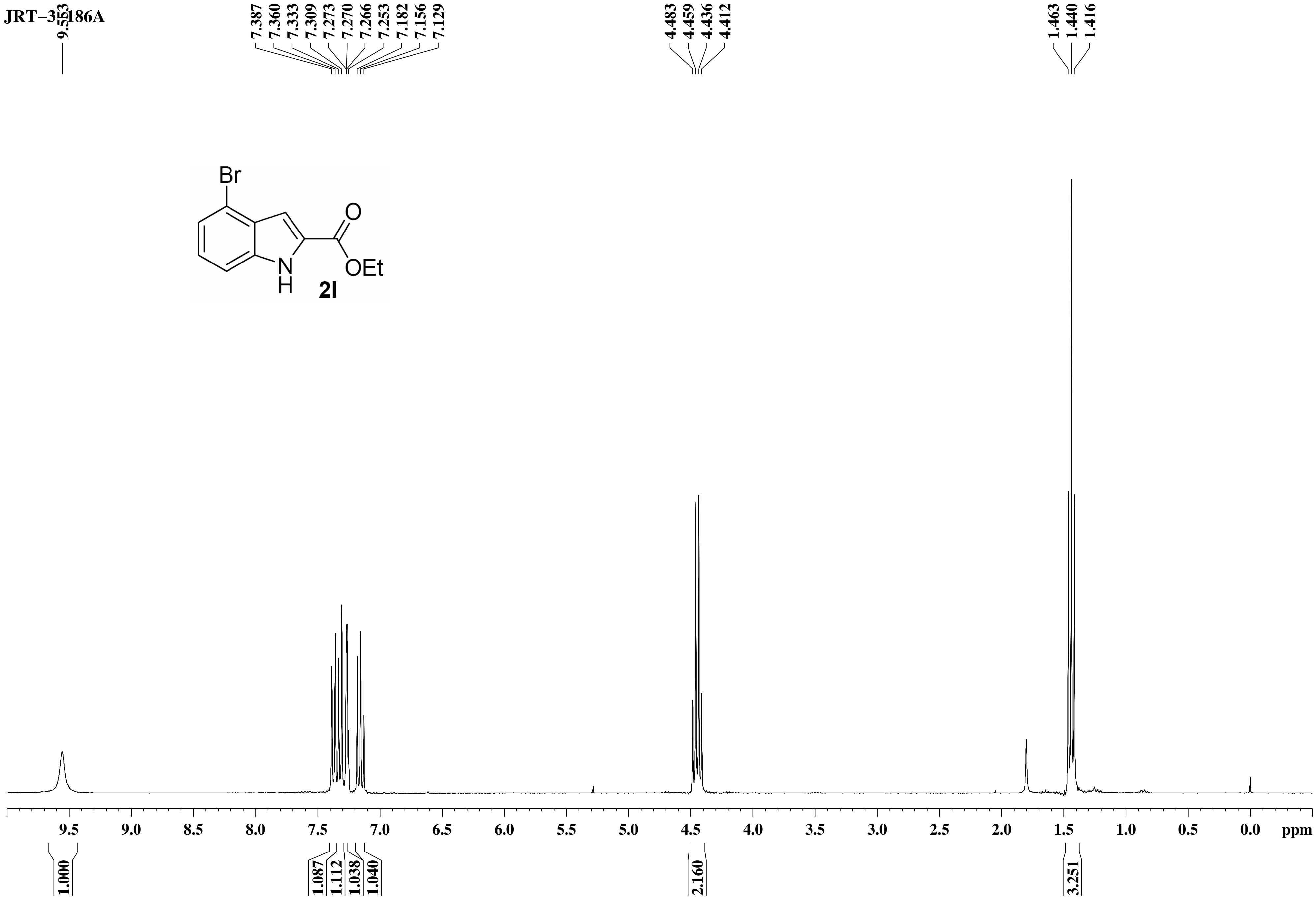
2i

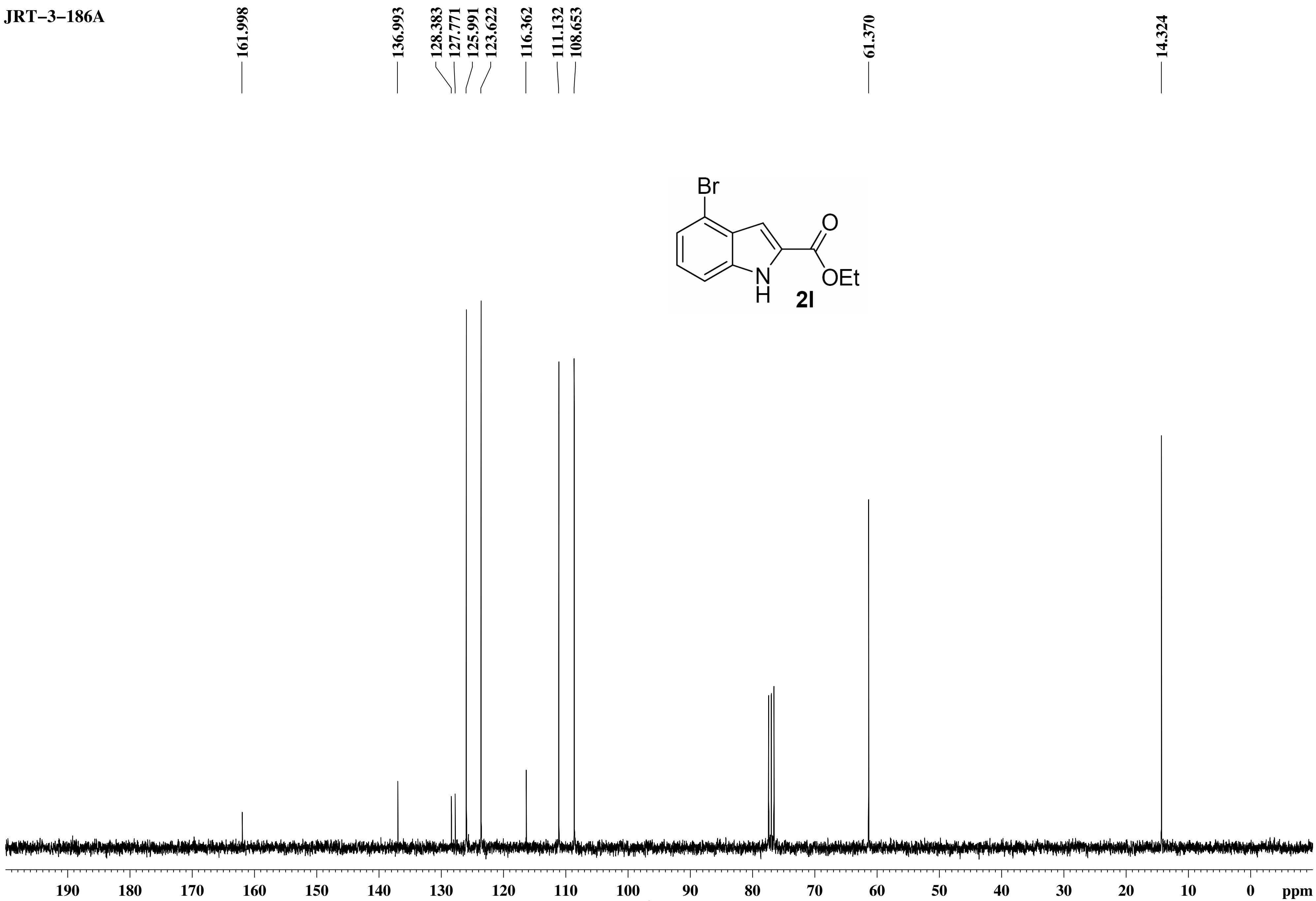

JRT-4-03
9.330
7.634
7.616
7.604
7.586
7.256
7.211
7.207
7.205
7.115
7.108
7.083
7.077
6.959
6.951
6.927
6.921
6.897
6.890
4.464
4.441
4.417
4.393
1.448
1.424
1.401
F
N
H
O
OEt
2j
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.000
1.060
1.045
1.070
1.079
2.145
3.094


JRT-4-034
163.259
162.152
160.051
137.196
137.022
128.008
127.959
124.032
123.762
123.624
110.470
110.135
108.776
108.765
97.981
97.636
61.157
14.314
O
F
N
H
OEt
2j
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

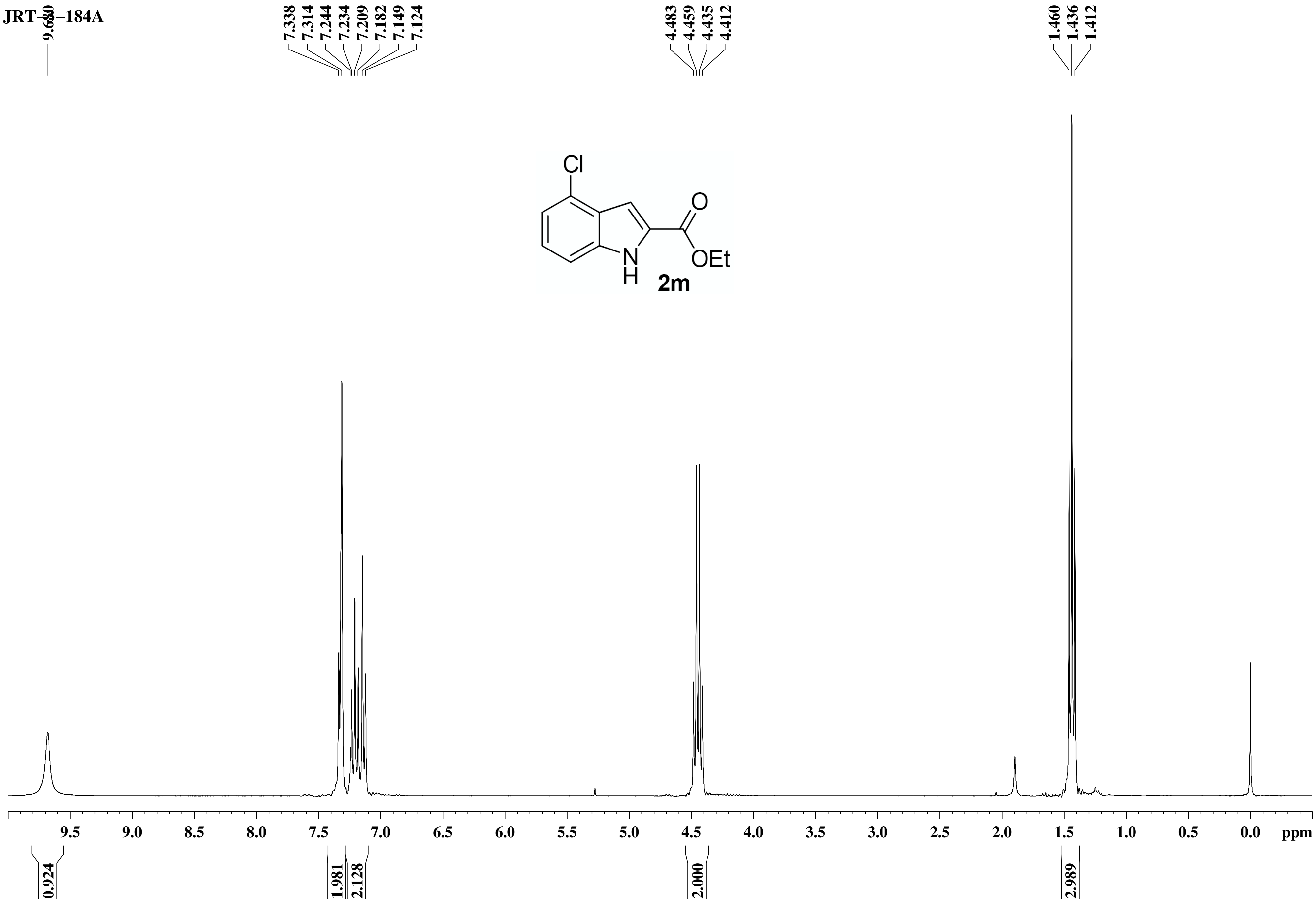

9.688
8.428
8.063
8.056
8.033
8.027
7.796
7.767
7.298
7.295
7.265
4.528
4.504
4.480
4.457
1.488
1.464
1.440
O_2N
N
H
O
OEt
2k
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
0.968
1.027
1.013
0.983
1.000
2.051
3.145


JRT-4-010
161.238
145.559
135.068
132.455
131.837
122.916
115.861
108.817
108.342
61.853
14.309
O
O2N
N
H
OEt
2k
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

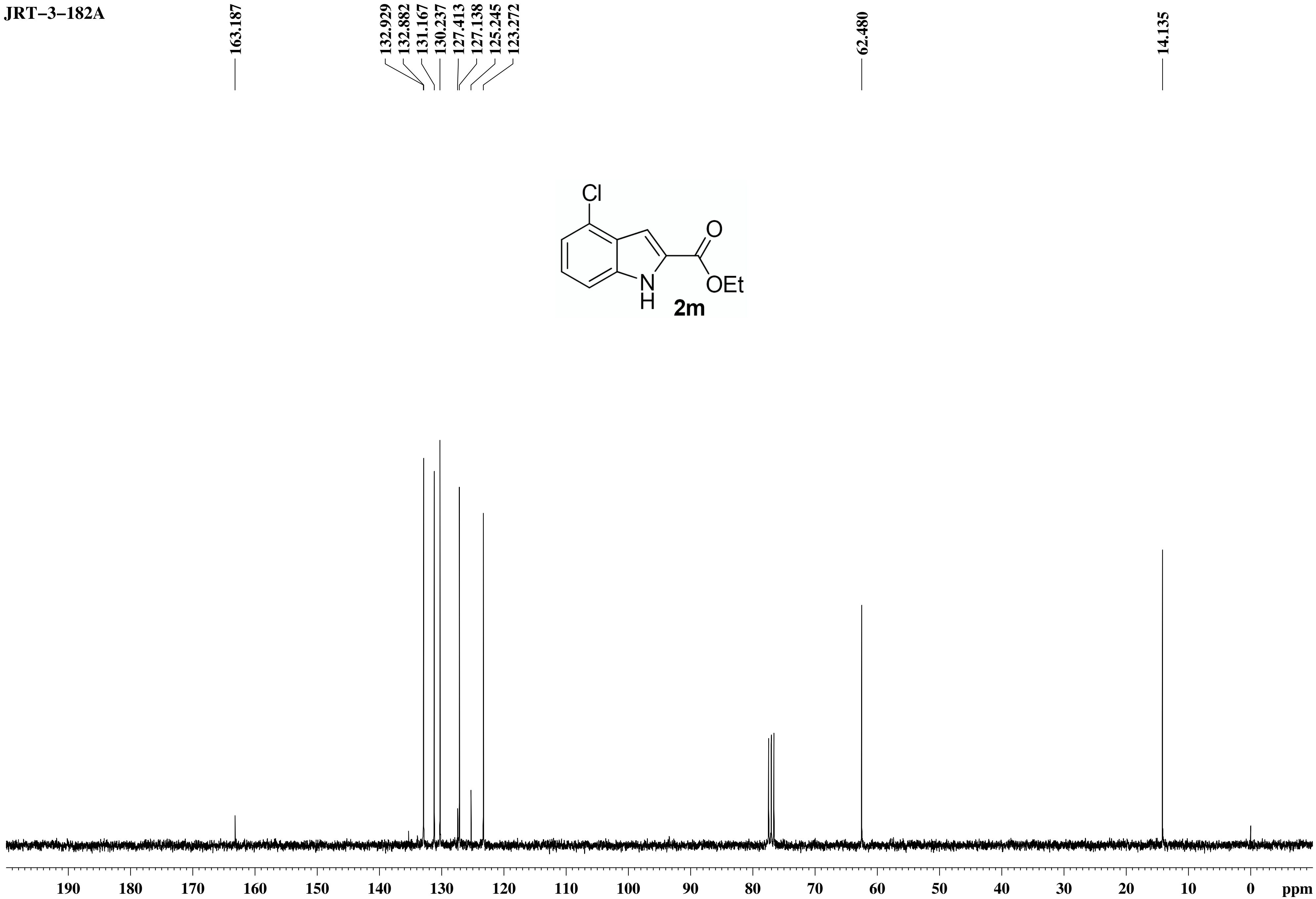

JRT−3−186A
9.553
7.387
7.360
7.333
7.309
7.273
7.270
7.266
7.253
7.182
7.156
7.129
4.483
4.459
4.436
4.412
1.463
1.440
1.416
Br
O
OEt
N
H
2l
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.000
1.087
1.112
1.038
1.040
2.160
3.251

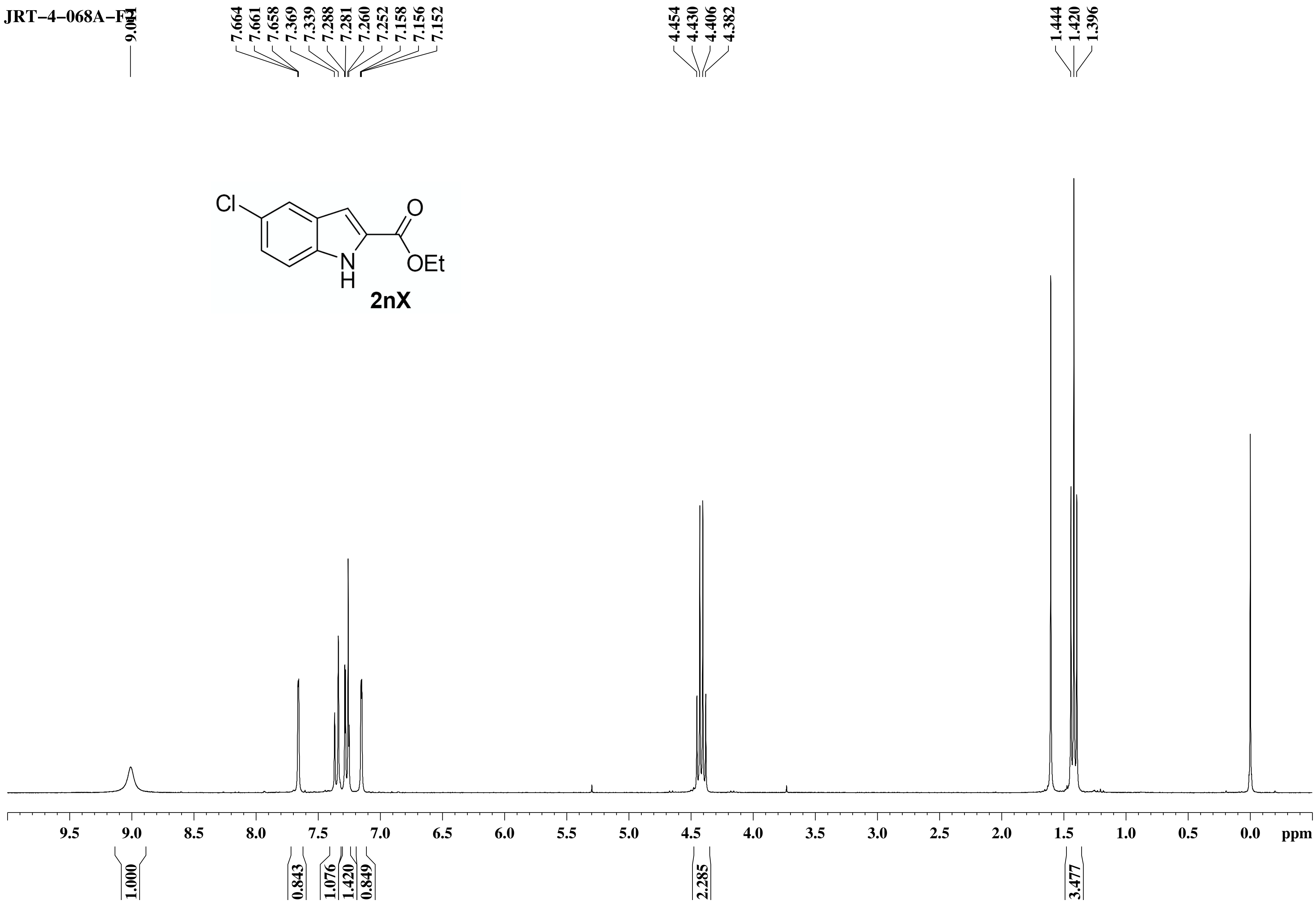

JRT−3−186A
161.998
136.993
128.383
127.771
125.991
123.622
116.362
111.132
108.653
61.370
14.324
Br
O
OEt
N
H
2l
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

JRT-II-184A

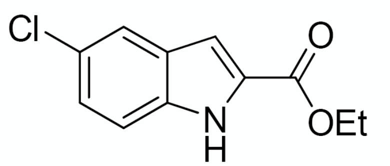


9.680
7.338
7.314
7.244
7.234
7.209
7.182
7.149
7.124
4.483
4.459
4.435
4.412
1.460
1.436
1.412
Cl
O
N
H
OEt
2m
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.924
1.981
2.128
2.000
2.989

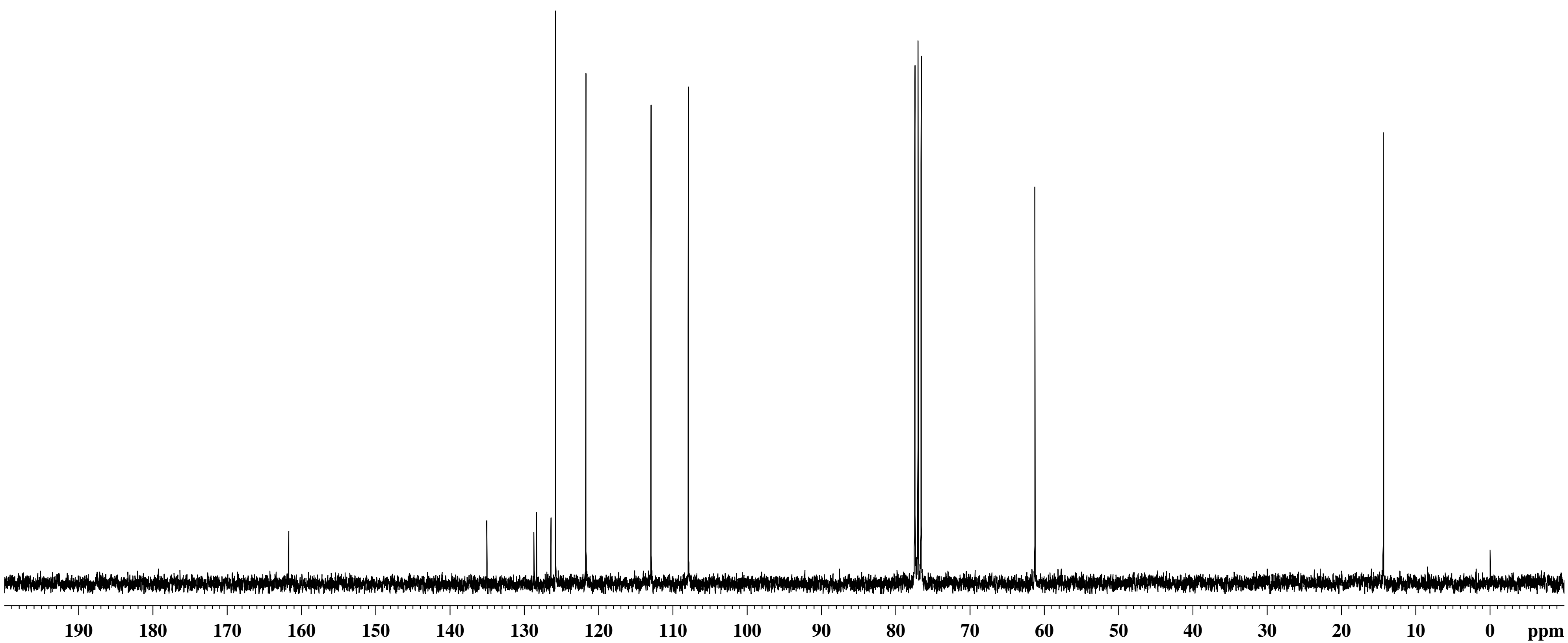

JRT−3−182A
163.187
132.929
132.882
131.167
130.237
127.413
127.138
125.245
123.272
62.480
14.135
Cl
O
OEt
N
H
2m
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

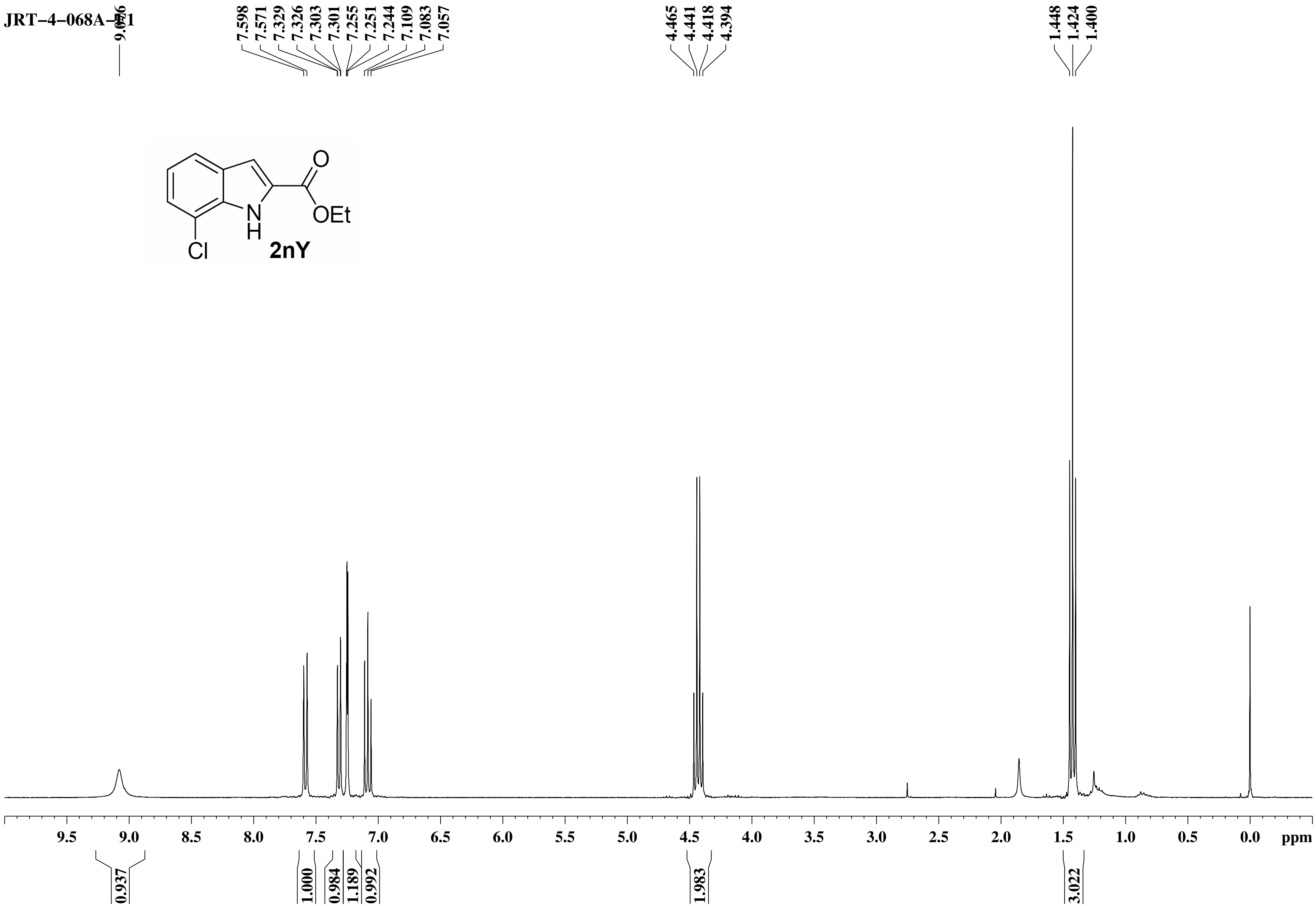

JRT−4−068A−F2
9.01
7.664
7.661
7.658
7.369
7.339
7.288
7.281
7.260
7.252
7.158
7.156
7.152
4.454
4.430
4.406
4.382
1.444
1.420
1.396
Cl
O
OEt
N
H
2nX
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.000
0.843
1.076
1.420
0.849
2.285
3.477

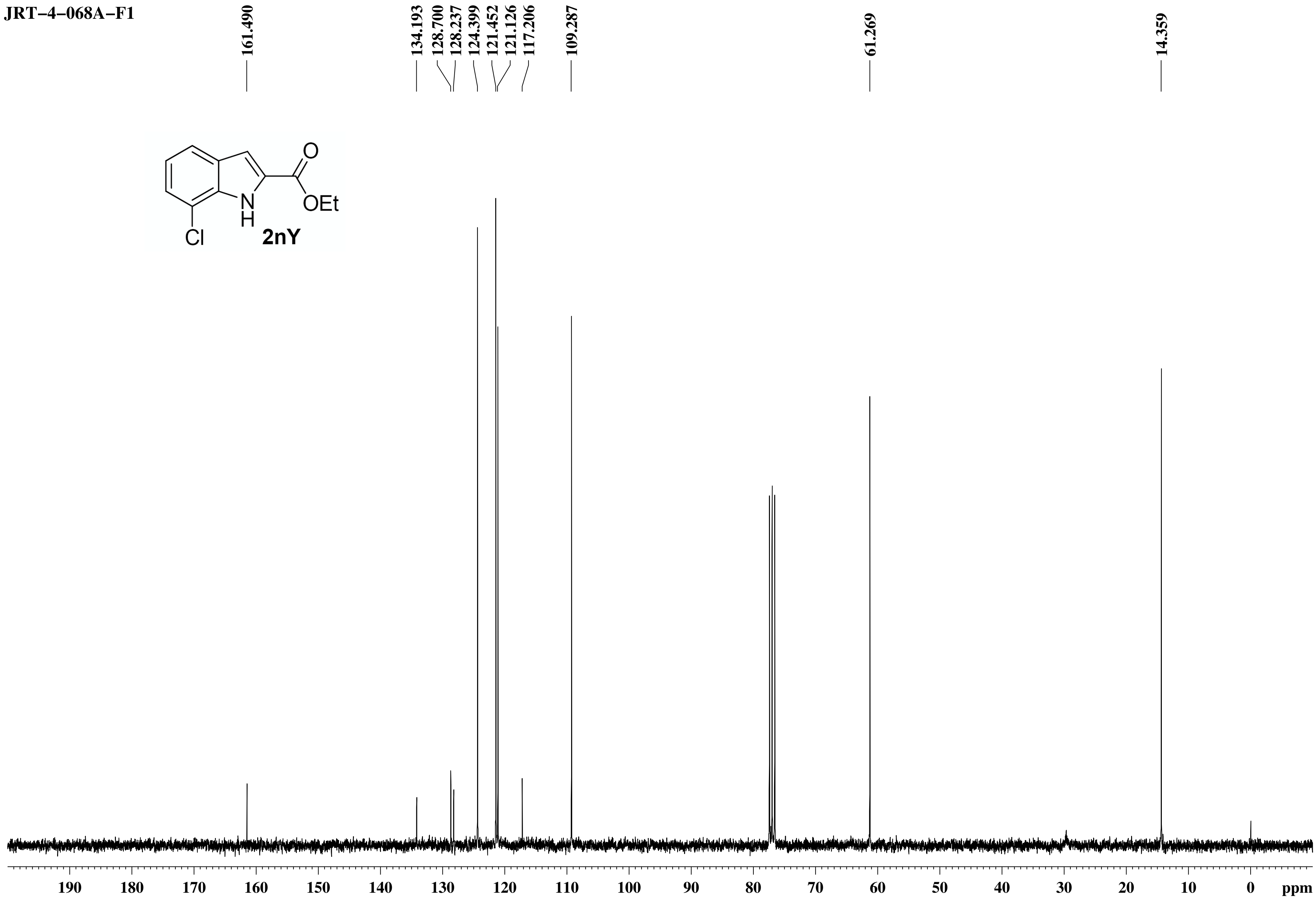
JRT-4-068A-F2

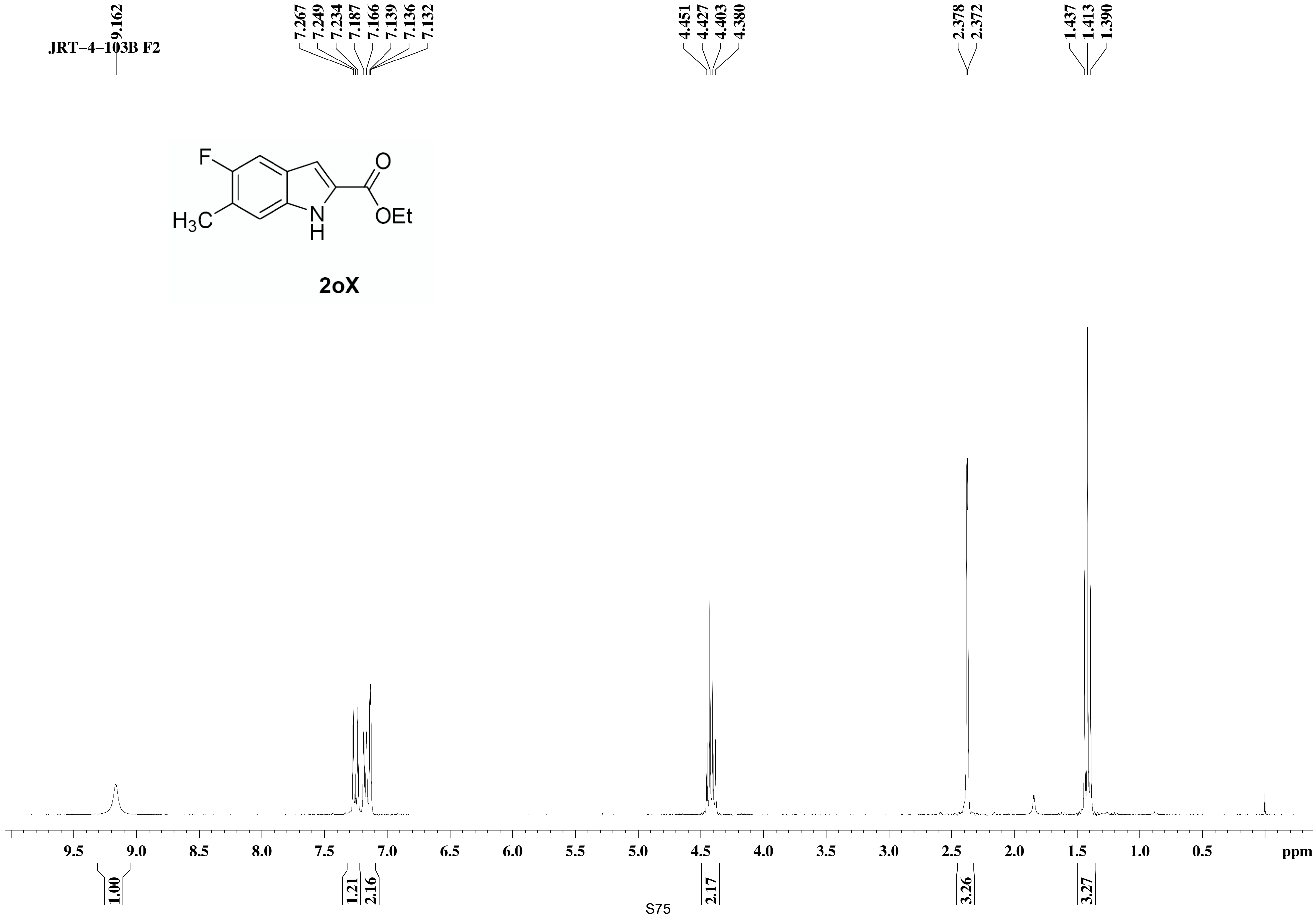


2nX

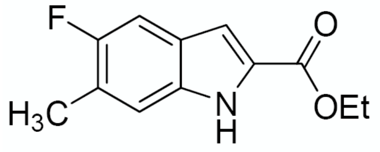



JRT−4−068A−F1
9.076
7.598
7.571
7.329
7.326
7.303
7.301
7.255
7.251
7.244
7.109
7.083
7.057
4.465
4.441
4.418
4.394
1.448
1.424
1.400
O
OEt
N
H
Cl
2nY
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
0.937
1.000
0.984
1.189
0.992
1.983
3.022

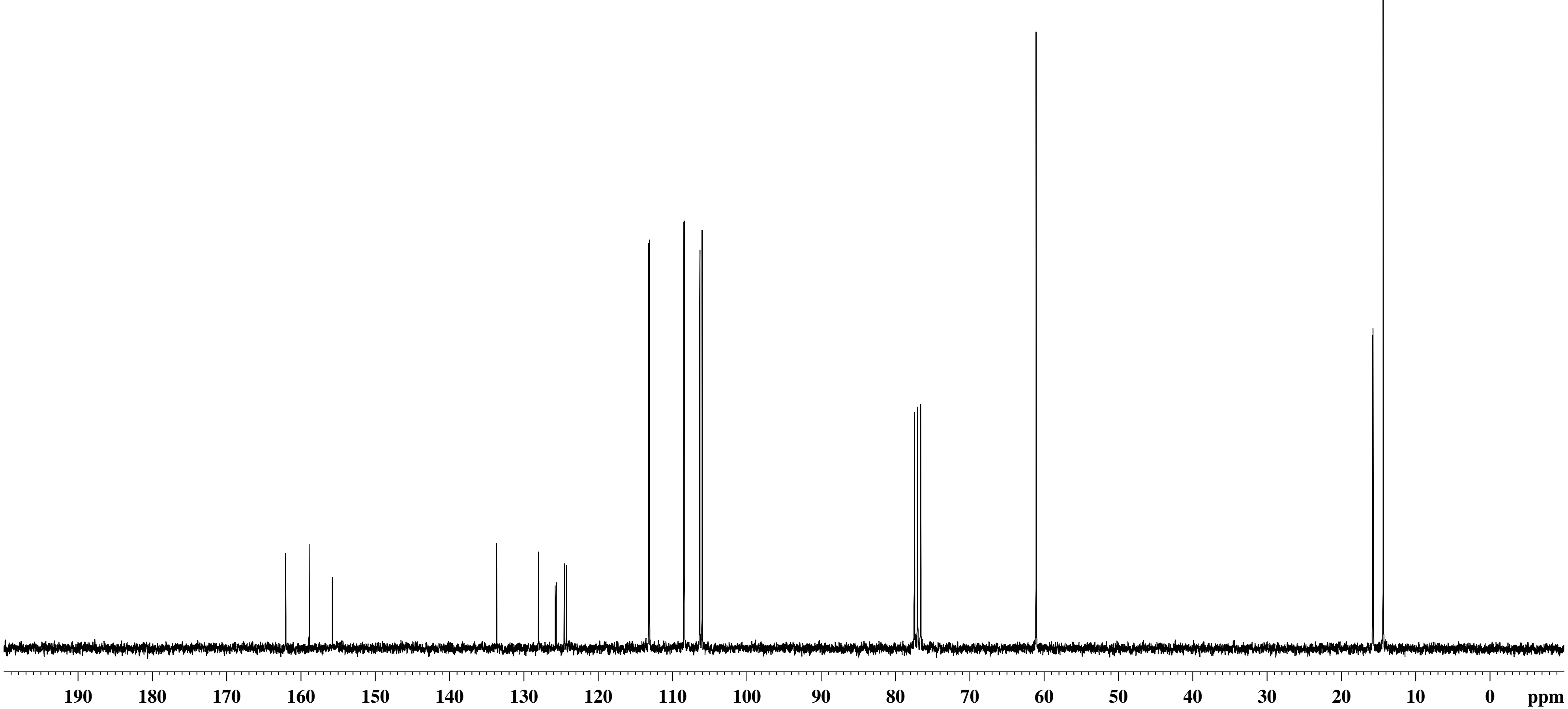

JRT−4−068A−F1
161.490
134.193
128.700
128.237
124.399
121.452
121.126
117.206
109.287
61.269
14.359
O
OEt
N
H
Cl
2nY
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

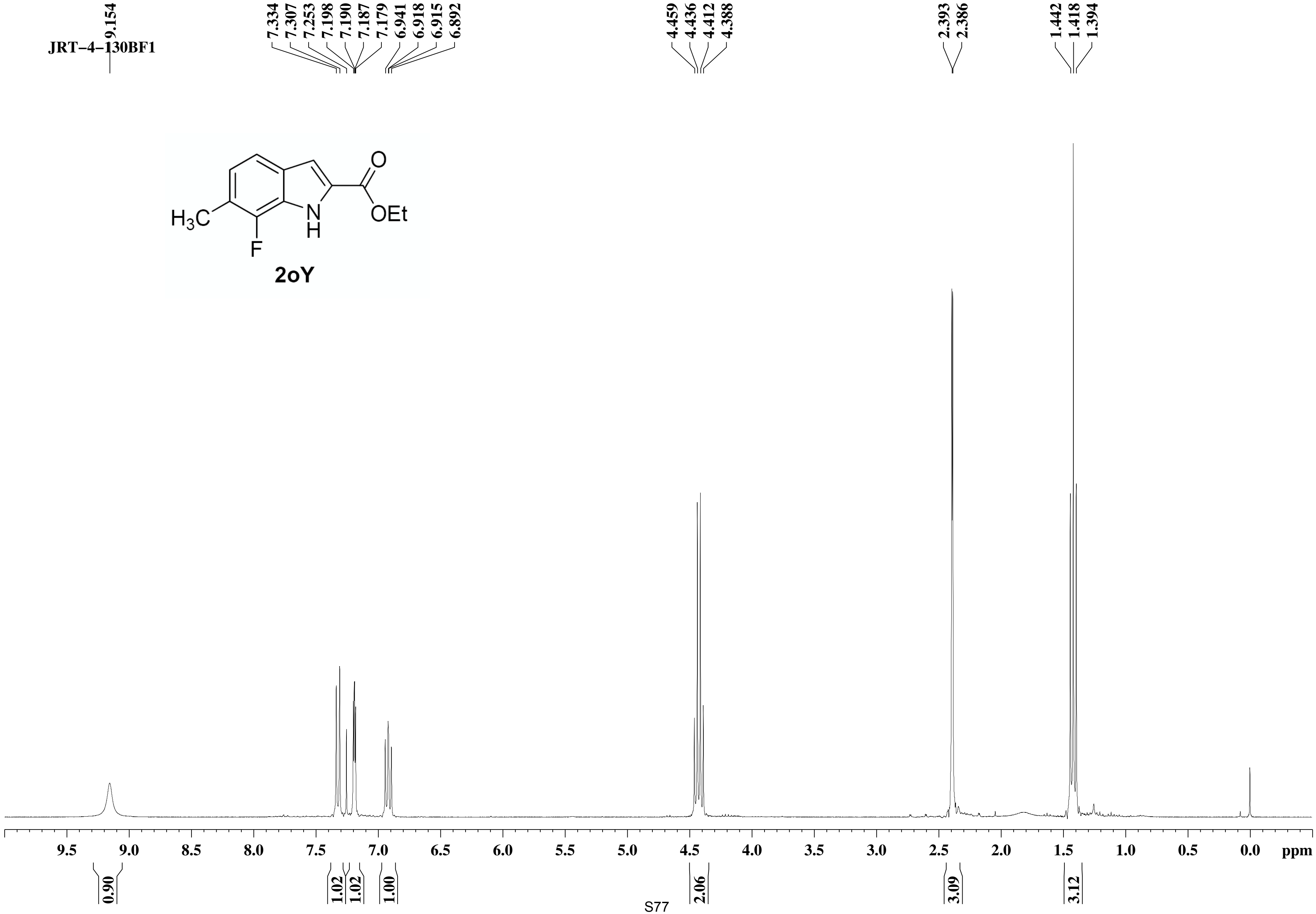

JRT-4-103B F2
9.162
7.267
7.249
7.234
7.187
7.166
7.139
7.136
7.132
4.451
4.427
4.403
4.380
2.378
2.372
1.437
1.413
1.390
F
H3C
N
H
O
OEt
2oX
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
1.21
2.16
2.17
3.26
3.27

JRT–4–103B F2



2oX

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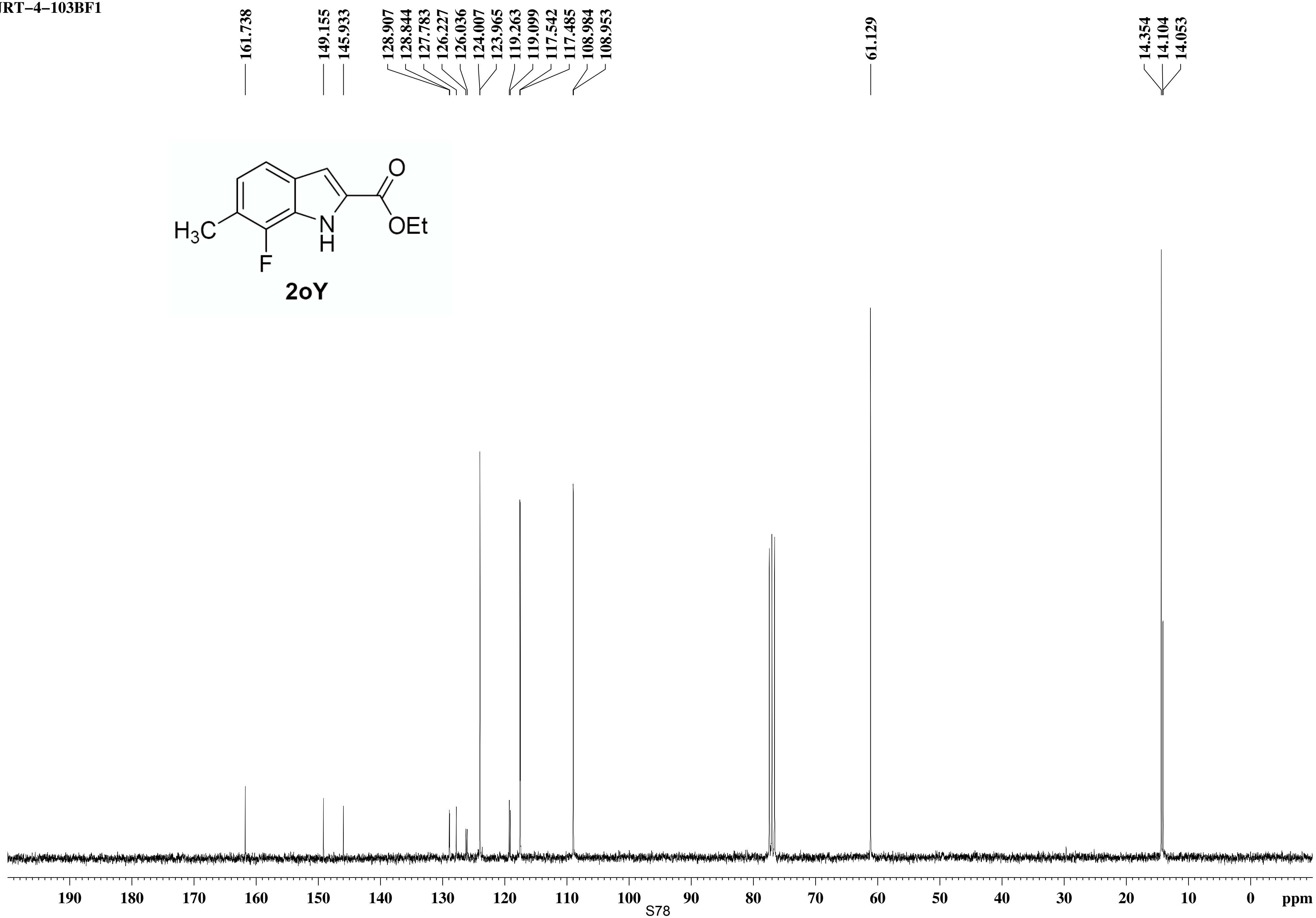
9.154
7.334
7.307
7.253
7.198
7.190
7.187
7.179
6.941
6.918
6.915
6.892
4.459
4.436
4.412
4.388
2.393
2.386
1.442
1.418
1.394
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.90
1.02
1.02
1.00
2.06
3.09
3.12
O
OEt
H3C
N
H
F

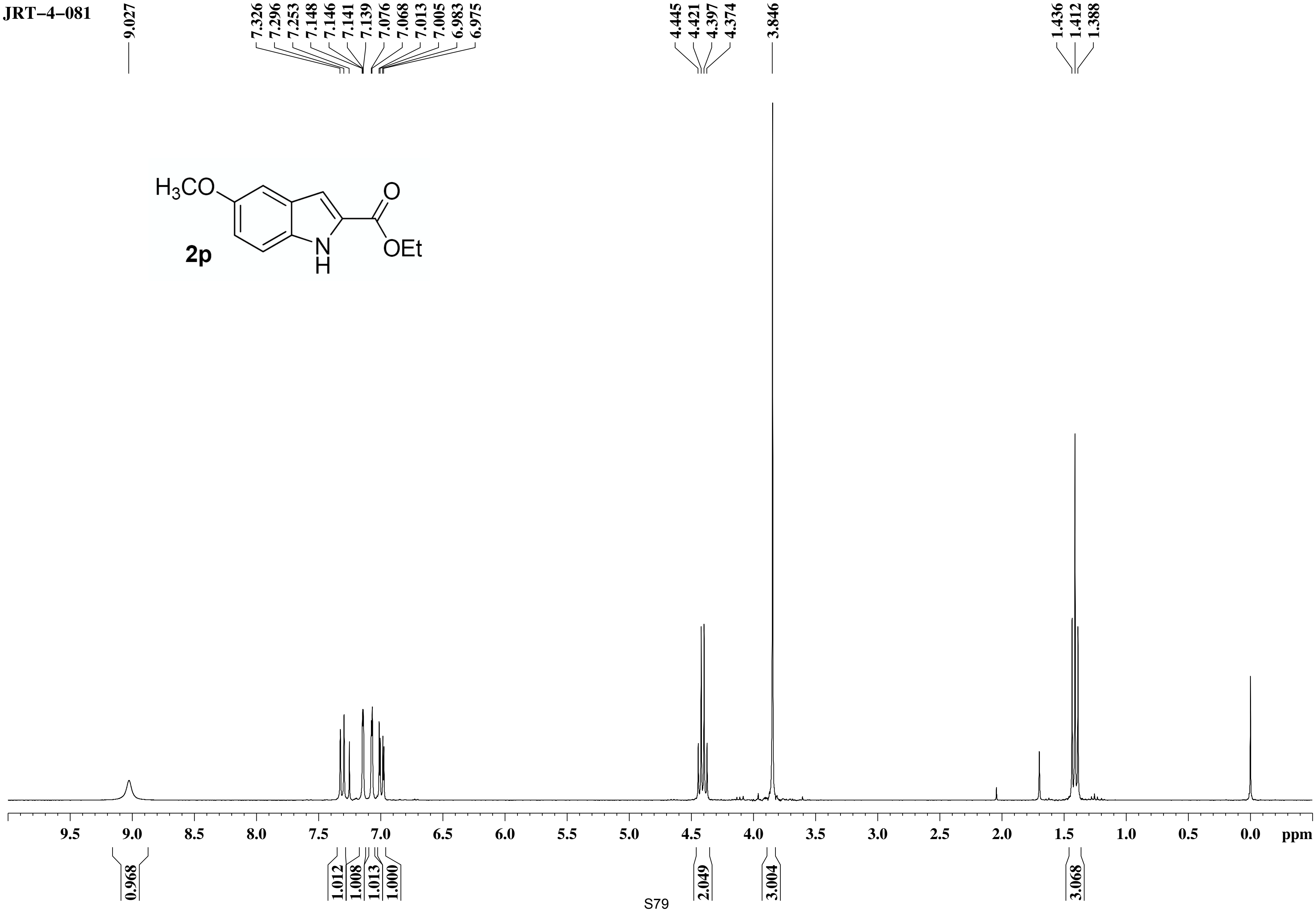
2oY

JRT-4-103BF1



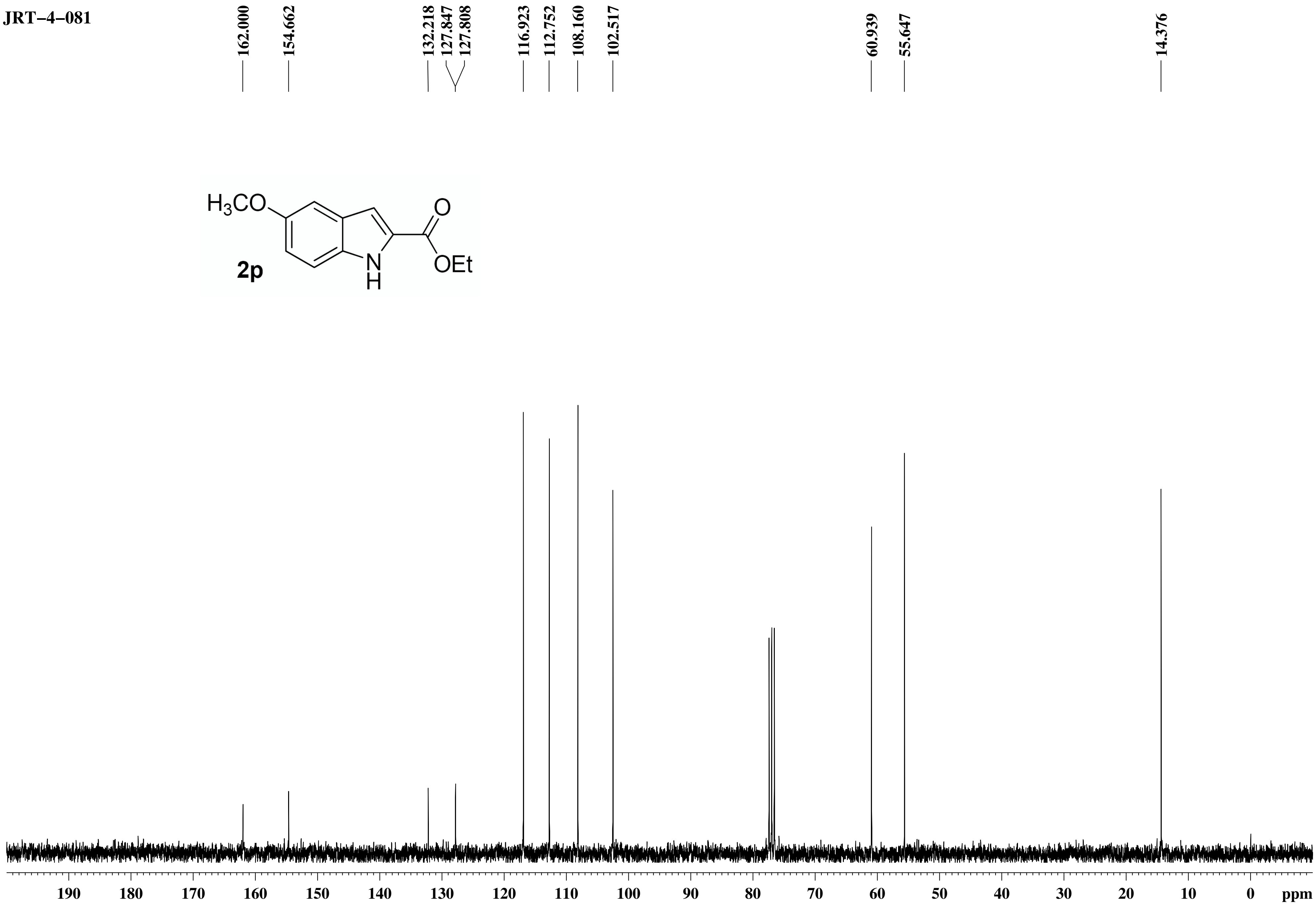
2oY

JRT-4-081

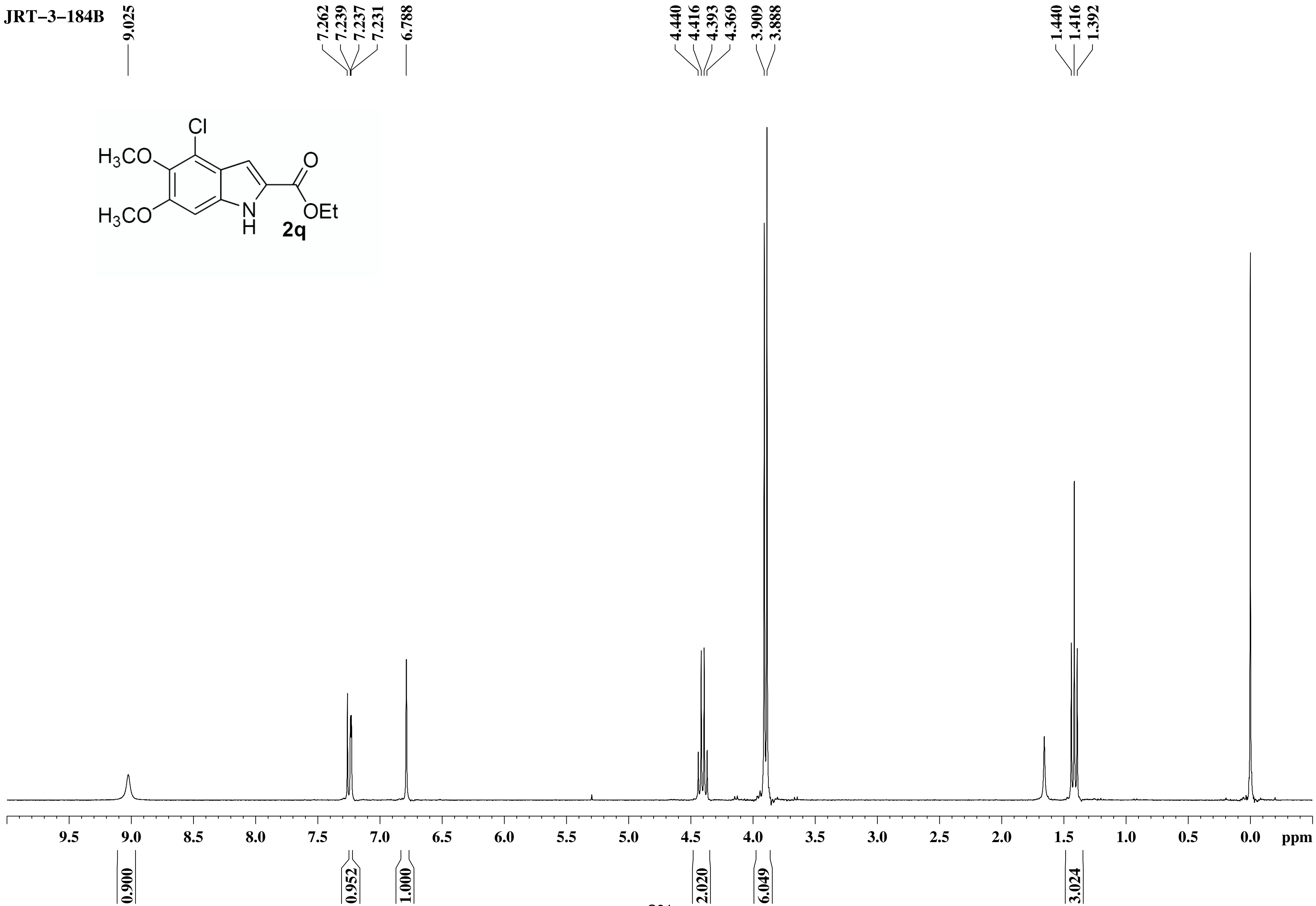


9.027
7.326
7.296
7.253
7.148
7.146
7.141
7.139
7.076
7.068
7.013
7.005
6.983
6.975
4.445
4.421
4.397
4.374
3.846
1.436
1.412
1.388
H3CO
O
OEt
N
H
2p
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
0.968
1.012
1.008
1.013
1.000
2.049
3.004
3.068

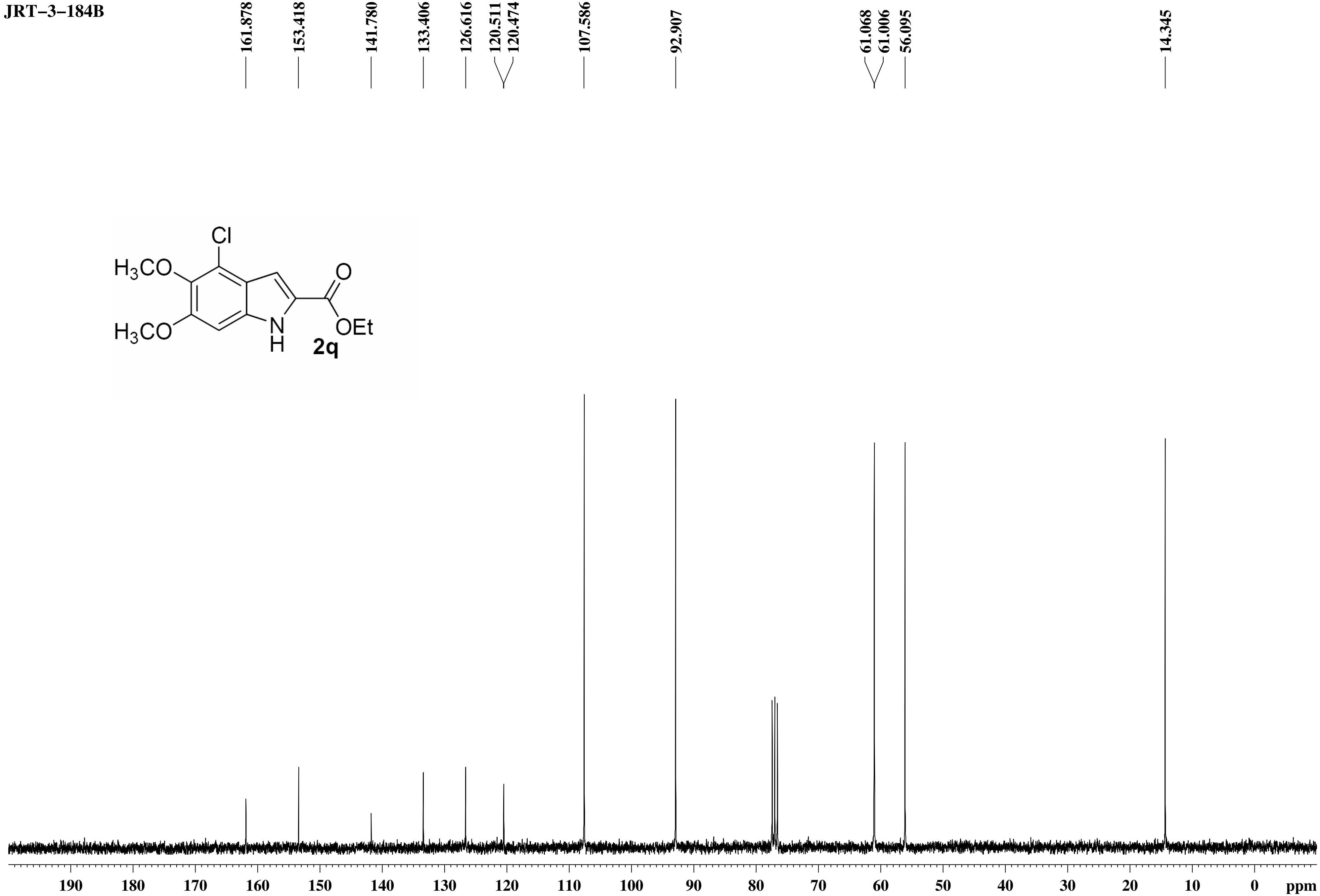
JRT–4–081


162.000
154.662
132.218
127.847
127.808
116.923
112.752
108.160
102.517
60.939
55.647
14.376
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
H3CO
O
OEt
N
H

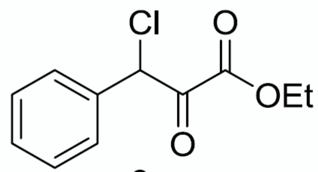
2p


JRT–3–184B
9.025
7.262
7.239
7.237
7.231
6.788
4.440
4.416
4.393
4.369
3.909
3.888
1.440
1.416
1.392
Cl
H_3CO
H_3CO
O
OEt
N
H
2q
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.900
0.952
1.000
2.020
6.049
3.024

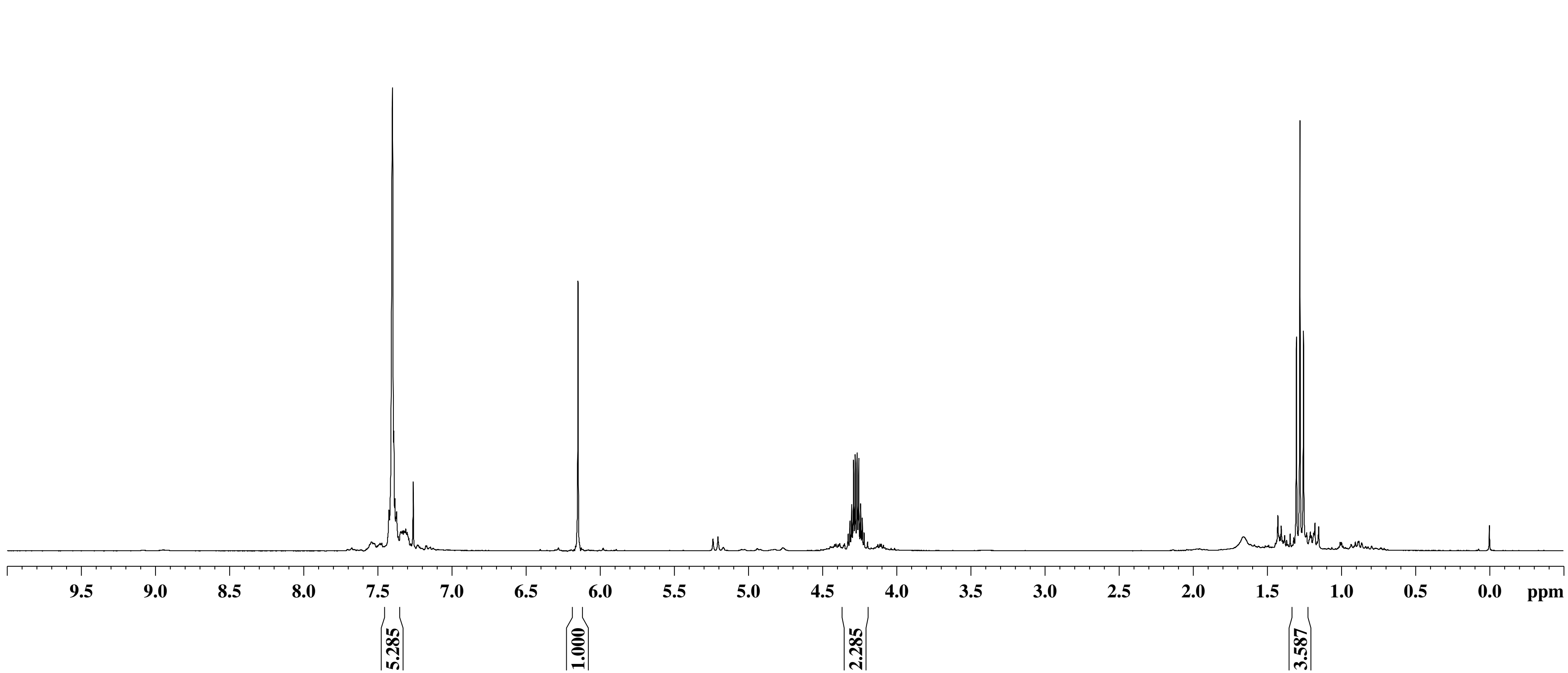
JRT−3−184B


161.878
153.418
141.780
133.406
126.616
120.511
120.474
107.586
92.907
61.068
61.006
56.095
14.345
Cl
H_3CO
H_3CO
O
OEt
N
H
2q
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

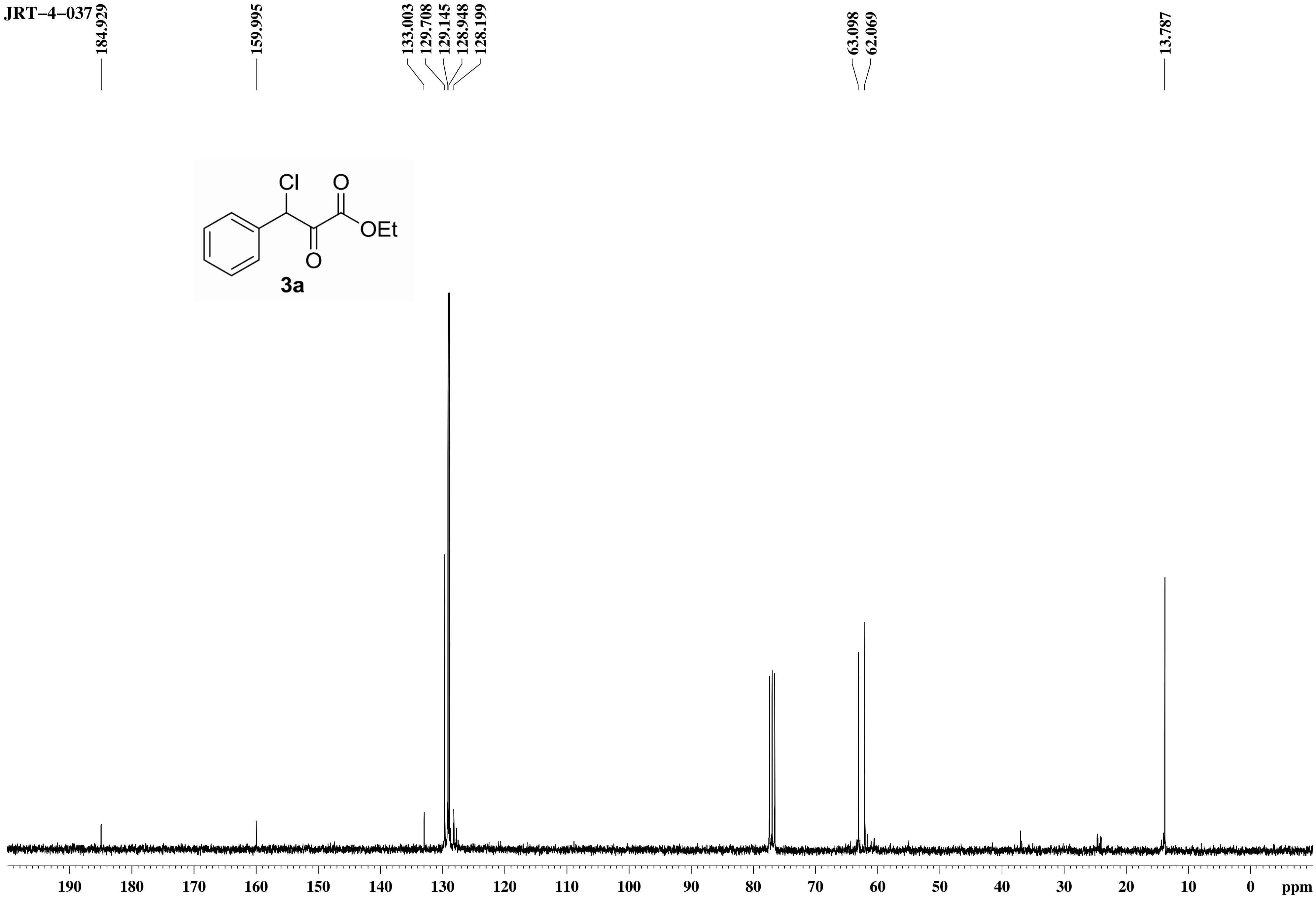
JRT-4-037



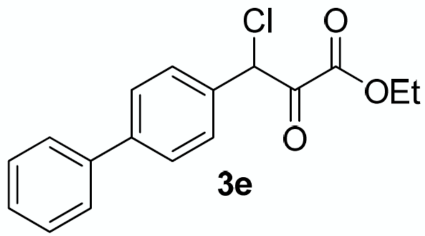
3a



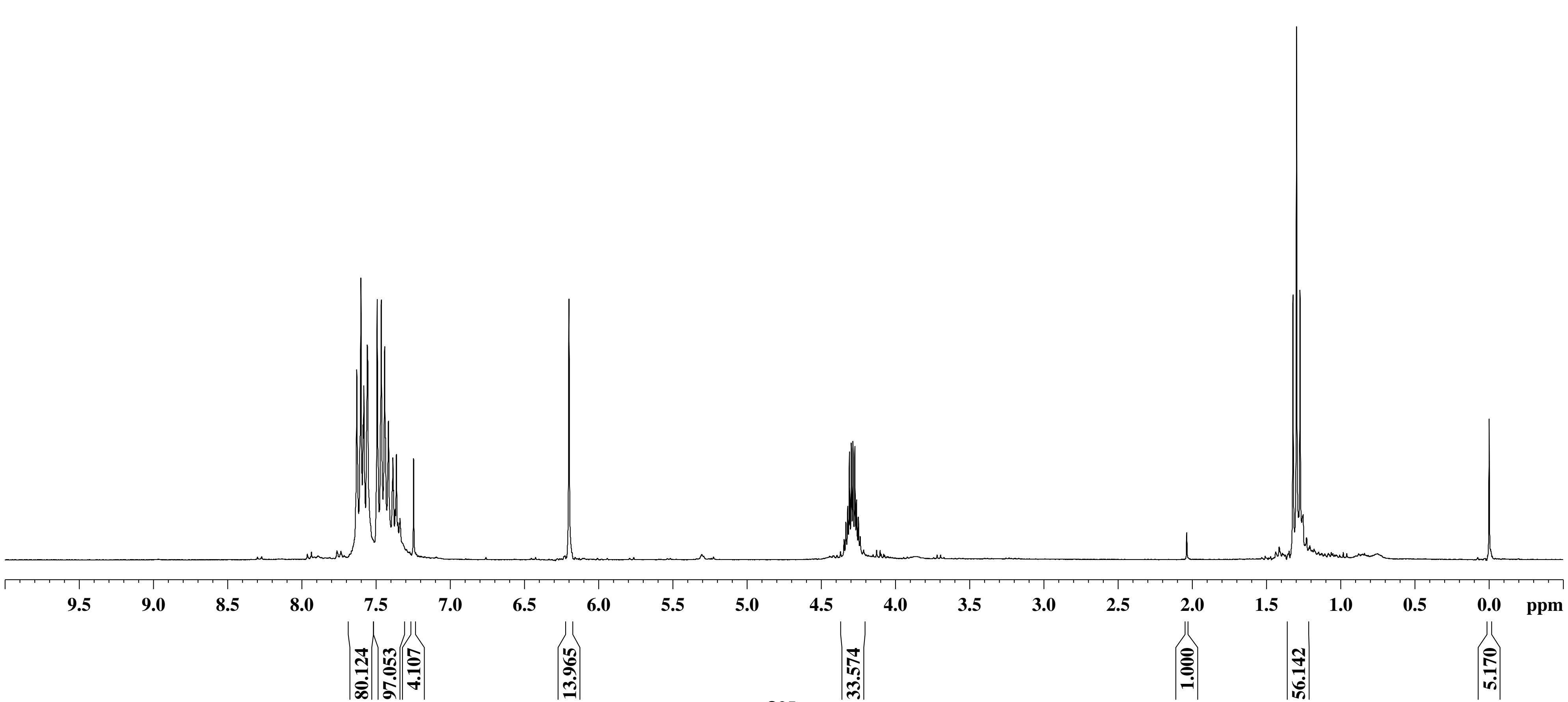
7.400
7.391
6.149
4.326
4.314
4.302
4.290
4.278
4.266
4.255
4.242
4.231
4.219
1.302
1.278
1.254
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
5.285
1.000
2.285
3.587

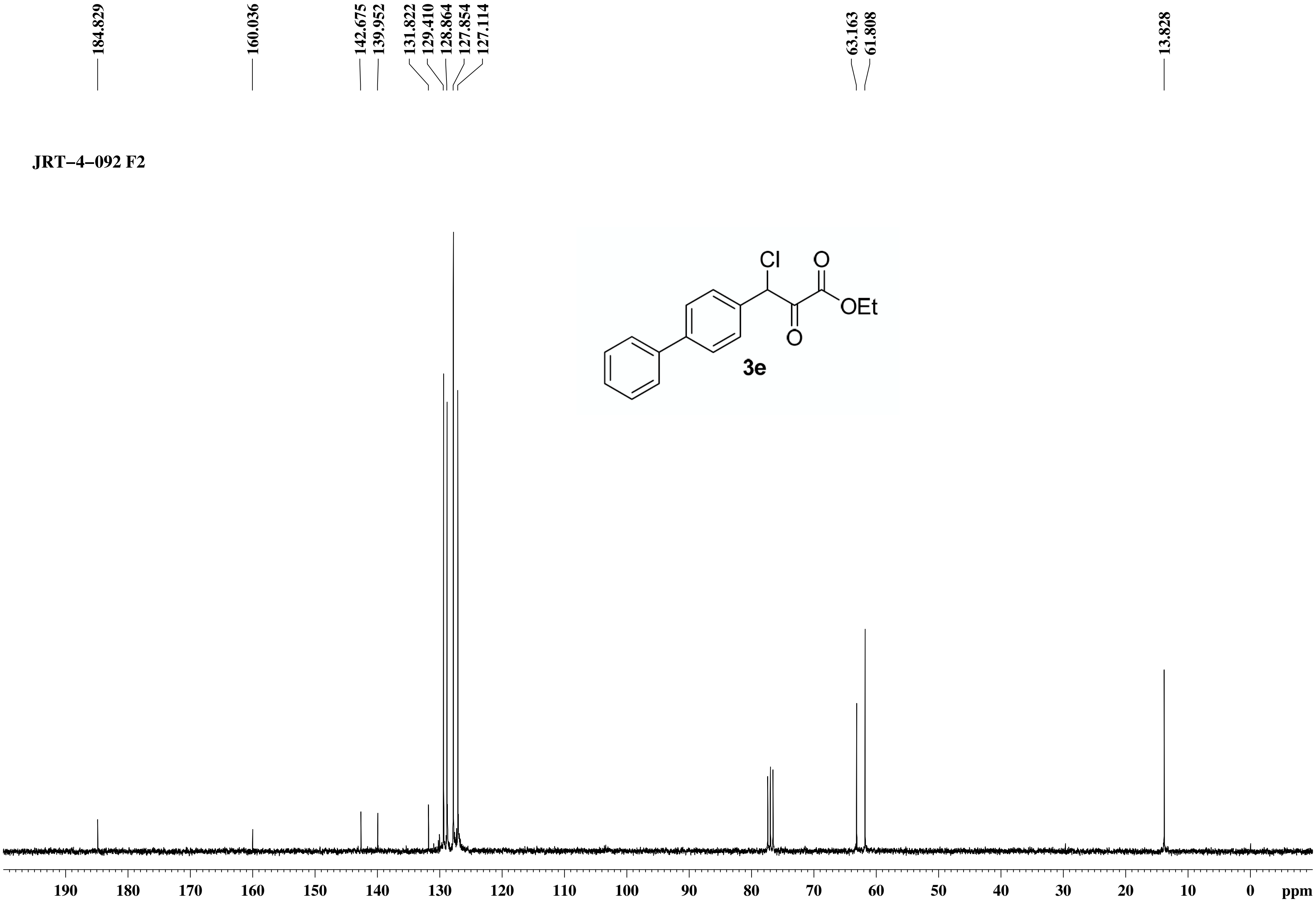

JRT−4−037
184.929
159.995
133.003
129.708
129.145
128.948
128.199
63.098
62.069
13.787
Cl
O
OEt
O
3a
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

JRT-4-092 F2



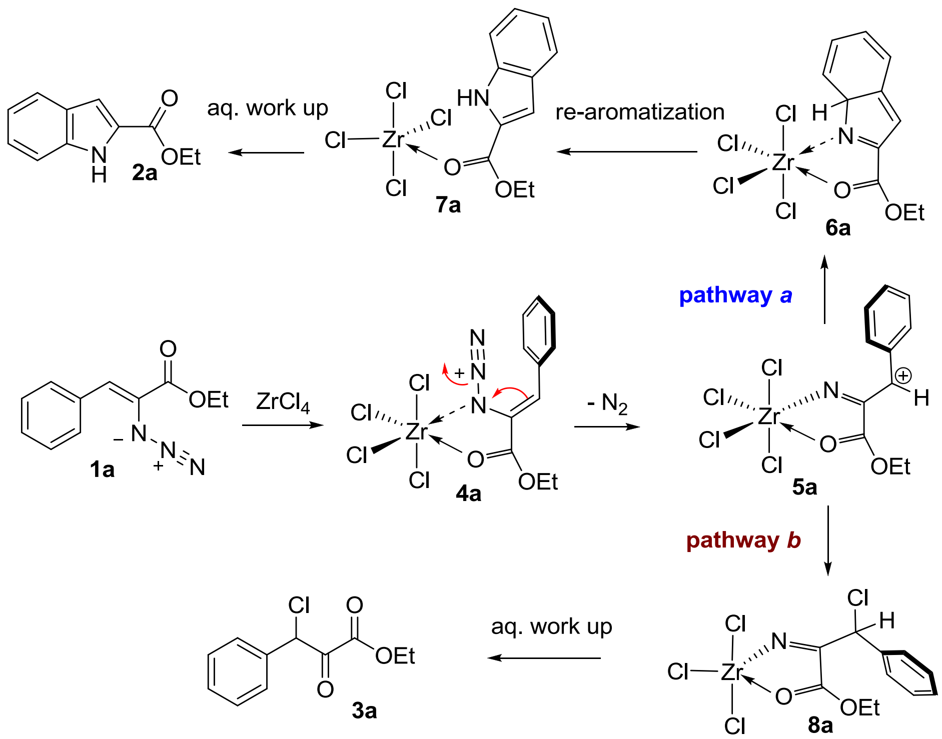
3e




184.829
160.036
142.675
139.952
131.822
129.410
128.864
127.854
127.114
63.163
61.808
13.828
JRT−4−092 F2
Cl
O
OEt
O
3e
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

Quantum chemical calculations[1]

Proposed mechanism for the formations of indole **2a** and by-product **3a**.



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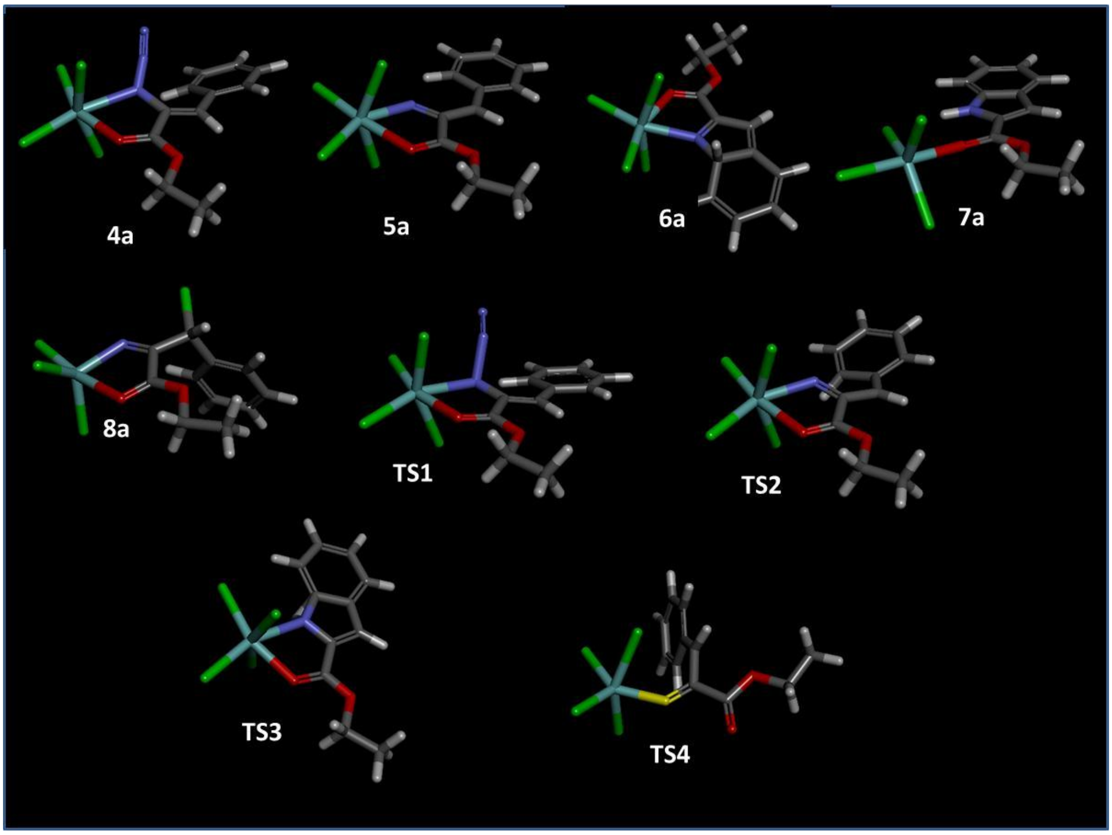
[1] Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Scalmani, G., Barone, V., Mennucci, B., Petersson, G. A., Nakatsuji, H., Caricato, M., Li, X., Hratchian, H. P., Izmaylov, A. F., Bloino, J., Zheng, G., Sonnenberg, J. L., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Jr., J. A. M., Peralta, J. E., Ogliaro, F., Bearpark, M., Heyd, J. J., Brothers, E., Kudin, K. N., Staroverov, V. N., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A., Burant, J. C., Iyengar, S. S., Tomasi, J., Cossi, M., Rega, N., Millam, J. M., Klene, M., Knox, J. E., Cross, J. B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R. E., Yazyev, O., Austin, A. J., Cammi, R., Pomelli, C., Ochterski, J. W., Martin, R. L., Morokuma, K., Zakrzewski, V. G., Voth, G. A., Salvador, P., Dannenberg, J. J., Dapprich, S., Daniels, A. D., Farkas, Ö., Foresman, J. B., Ortiz, J. V., Cioslowski, J., and Fox, D. J. (2009) Gaussian 09, Revision D.01, Gaussian Inc., Wallingford CT.



Complex 4a

atom	X	Y	Z
Zr1	23.7569	-2.2935	6.3457
Cl2	22.2282	-3.605	7.7825
Cl3	25.3233	-1.6362	8.0284
Cl4	25.1111	-1.7682	4.3576
Cl5	22.2133	-0.4673	6.0195
N6	22.4356	-3.456	4.6515
C7	22.6302	-4.8763	4.5522
C8	23.8914	-5.2257	5.2142
O9	24.5148	-4.3672	5.9008
O10	24.3142	-6.4763	5.0822
C11	25.5611	-6.876	5.7981
C12	25.7903	-8.3323	5.469
C13	21.7906	-5.804	4.0196
C14	20.4137	-5.6214	3.5791
C15	19.5562	-4.6746	4.1882
C16	19.8967	-6.4773	2.5822
C17	18.2242	-4.5723	3.7797
C18	18.5702	-6.3563	2.1629
C19	17.7324	-5.4005	2.7586
H20	26.3628	-6.2195	5.4465
H21	25.3963	-6.6913	6.864
H22	26.6985	-8.6807	5.97
H23	25.9151	-8.4742	4.392
H24	24.9522	-8.9463	5.8096
H25	22.2044	-6.8097	3.9484
H26	19.9136	-4.0662	5.0177
H27	20.546	-7.225	2.1324
H28	17.5689	-3.8542	4.2611
H29	18.1853	-7.007	1.3847
H30	16.6988	-5.3111	2.4396
N31	21.8212	-2.8412	3.7287
N32	21.2675	-2.1464	2.9907

Complex 5a

atom	X	Y	Z
Zr1	23.4456	-2.3075	6.198
Cl2	21.6012	-3.5664	7.3427
Cl3	25.0419	-2.0576	7.9943
Cl4	24.8102	-2.0128	4.1566
Cl5	22.304	-0.1916	6.1069
N6	22.3864	-3.5323	4.7117
C7	22.7263	-4.7811	4.4461
C8	23.8969	-5.289	5.2449
O9	24.4202	-4.5234	6.0847
O10	24.3099	-6.5358	5.0112
C11	25.4723	-7.0389	5.7973
C12	25.7302	-8.4518	5.3283
C13	22.095	-5.6303	3.4977
C14	20.9594	-5.3642	2.6937
C15	20.236	-4.1329	2.7365
C16	20.5271	-6.3979	1.8075
C17	19.1257	-3.9598	1.9178
C18	19.4169	-6.2124	0.9946
C19	18.7162	-4.9913	1.0509
H20	26.3093	-6.3592	5.6107
H21	25.2008	-6.9742	6.8554
H22	26.5789	-8.8709	5.8773
H23	25.9682	-8.4713	4.261
H24	24.8582	-9.0876	5.506
H25	22.555	-6.6157	3.3836
H26	20.5791	-3.3558	3.4136
H27	21.0797	-7.3343	1.7774
H28	18.5732	-3.0276	1.9473
H29	19.0889	-6.9967	0.3221
H30	17.8474	-4.844	0.4165

Complex 6a

atom	X	Y	Z
Zr1	32.7967	-20.9188	8.8869
Cl2	32.0711	-22.0383	10.9763
Cl3	34.6343	-19.6742	9.8097
Cl4	33.396	-20.6932	6.5071
Cl5	30.874	-19.453	8.7919
N6	31.5972	-22.7151	7.9956
C7	32.1808	-23.9082	7.9350
C8	33.6016	-23.9077	8.3372
O9	34.1177	-22.8328	8.7348
O10	34.248	-25.0577	8.2448
C11	35.6883	-25.0858	8.6409
C12	36.1613	-26.5039	8.4262
C13	31.3241	-24.9727	7.5104
C14	30.0914	-24.3887	7.28
C15	30.187	-22.9412	7.6832
C16	28.8776	-24.8547	6.6806
C17	29.372	-21.9915	6.8649
C18	28.0043	-23.9184	6.1828
C19	28.2852	-22.491	6.2185
H20	36.2085	-24.3522	8.0171
H21	35.7413	-24.7603	9.6844
H22	37.217	-26.582	8.7027
H23	36.0569	-26.7953	7.3776
H24	35.5905	-27.2031	9.043
H25	31.6229	-26.0015	7.3753
H26	29.7129	-22.8701	8.6948
H27	28.7051	-25.9158	6.5367
H28	29.604	-20.9313	6.9141
H29	27.0994	-24.2465	5.6799
H30	27.6164	-21.8197	5.6908

Complex 7a

atom	X	Y	Z
Zr1	25.3714	-3.1558	7.4978
Cl2	24.8171	-4.844	9.1274
Cl3	26.4086	-1.6628	9.0617
Cl4	27.3584	-3.5117	6.1785
Cl5	23.6972	-1.5141	6.801
N6	22.2157	-3.5804	4.5462
C7	22.7679	-4.8582	4.4474
C8	23.881	-5.2454	5.2510
O9	24.4221	-4.4481	6.0913
O10	24.3321	-6.4868	5.0815
C11	25.4949	-6.9566	5.8881
C12	25.7507	-8.3838	5.4633
C13	22.0693	-5.5968	3.4904
C14	21.0505	-4.7477	2.9794
C15	21.1669	-3.4905	3.6598
C16	20.0377	-4.9211	2.0037
C17	20.3009	-2.4151	3.3876
C18	19.1859	-3.8599	1.7372
C19	19.3192	-2.6191	2.4251
H20	26.3376	-6.2888	5.675
H21	25.2228	-6.8664	6.9461
H22	26.5994	-8.7844	6.0257
H23	25.9863	-8.4365	4.3969
H24	24.8774	-9.0115	5.6608
H25	22.287	-6.6177	3.2134
H26	22.5477	-2.8498	5.176
H27	19.9343	-5.8654	1.4784
H28	20.3954	-1.4671	3.9066
H29	18.4018	-3.9662	0.9945
H30	18.6325	-1.8122	2.1879

Complex 8a

atom	X	Y	Z
Zr1	23.2371	-2.3376	6.0028
Cl2	22.5591	-2.9713	8.2145
Cl3	21.9183	-0.3654	5.6418
Cl4	20.9792	-5.1272	2.3071
Cl5	25.4393	-1.5021	5.5428
N6	22.3996	-3.6074	4.5936
C7	22.7334	-4.8321	4.4289
C8	23.9297	-5.2796	5.2783
O9	24.4079	-4.44	6.0824
O10	24.3842	-6.5077	5.1079
C11	25.5221	-6.9798	5.9532
C12	25.7212	-8.4385	5.6152
C13	22.0582	-5.9009	3.6091
C14	21.2613	-6.8134	4.5081
C15	21.4194	-8.204	4.4036
C16	20.363	-6.2768	5.4473
C17	20.6836	-9.0574	5.2348
C18	19.6289	-7.1312	6.277
C19	19.7889	-8.5214	6.1729
H20	26.3844	-6.351	5.7109
H21	25.2407	-6.8081	6.9967
H22	26.539	-8.847	6.2164
H23	25.9737	-8.5639	4.5588
H24	24.8139	-9.0105	5.8295
H25	22.8082	-6.4746	3.0565
H26	22.1162	-8.6119	3.674
H27	20.2265	-5.1985	5.5112
H28	20.8017	-10.1332	5.1492
H29	18.9334	-6.7166	6.9995
H30	19.2172	-9.1828	6.8166

Complex TS1

atom	X	Y	Z
Zr1	23.602	-2.3744	6.7048
Cl2	22.2013	-3.9199	8.0941
Cl3	25.3871	-2.03	8.2743
Cl4	24.6436	-1.6324	4.6117
Cl5	22.1055	-0.4951	6.8858
N6	22.0311	-3.5492	5.3744
C7	22.4044	-4.8512	5.0024
C8	23.7957	-5.1919	5.3670
O9	24.4921	-4.3697	6.0243
O10	24.2498	-6.3917	5.0154
C11	25.629	-6.77	5.4368
C12	25.8632	-8.1707	4.9212
C13	21.5757	-5.7794	4.4085
C14	20.1719	-5.6652	4.1052
C15	19.3325	-4.6614	4.6594
C16	19.6003	-6.6505	3.2595
C17	17.972	-4.6472	4.3547
C18	18.2437	-6.6173	2.9436
C19	17.4275	-5.6127	3.4908
H20	26.3142	-6.0303	5.0118
H21	25.6678	-6.6962	6.5279
H22	26.8674	-8.501	5.2034
H23	25.7836	-8.2037	3.831
H24	25.1383	-8.8696	5.3476
H25	22.0561	-6.7171	4.1223
H26	19.7544	-3.9368	5.3498
H27	20.2368	-7.4322	2.8504
H28	17.3314	-3.8888	4.7917
H29	17.8171	-7.3674	2.2864
H30	16.3685	-5.5886	3.2533
N31	21.7528	-2.644	3.9544
N32	21.0938	-1.8797	3.4301

Complex TS2

atom	X	Y	Z
Zr1	23.418	-2.2353	6.0427
Cl2	21.634	-3.3699	7.3673
Cl3	24.9755	-1.7497	7.8193
Cl4	24.9256	-2.0678	4.0925
Cl5	22.1547	-0.2265	5.6338
N6	22.4522	-3.5618	4.4998
C7	22.7471	-4.8396	4.4375
C8	23.9162	-5.2661	5.2725
O9	24.4077	-4.4459	6.0796
O10	24.3543	-6.5103	5.099
C11	25.5296	-6.9489	5.907
C12	25.8217	-8.3741	5.5005
C13	21.9363	-5.7503	3.6837
C14	20.7006	-5.2391	3.2903
C15	20.2285	-4.0256	3.9236
C16	20.024	-5.737	2.1255
C17	19.2847	-3.2227	3.2519
C18	19.0662	-4.9554	1.5173
C19	18.7213	-3.6826	2.0668
H20	26.3487	-6.2567	5.689
H21	25.2552	-6.8438	6.9612
H22	26.6808	-8.7471	6.0662
H23	26.0587	-8.4348	4.4347
H24	24.9657	-9.0224	5.7074
H25	22.2873	-6.7454	3.4217
H26	20.3883	-3.8705	4.9907
H27	20.3471	-6.6768	1.6868
H28	18.9573	-2.2923	3.7007
H29	18.5836	-5.2898	0.6056
H30	17.9606	-3.087	1.5712

Complex TS4

atom	X	Y	Z
Zr1	20.8164	-2.6912	3.1457
Cl2	19.5593	-2.4422	5.2154
Cl3	21.6326	-0.5263	2.5642
Cl4	22.1548	-4.1791	1.4523
Cl5	18.8349	-3.3347	1.9006
N6	22.1762	-3.7155	4.3891
C7	22.7236	-4.8695	4.4032
C8	23.9038	-5.2108	5.2868
O9	24.4436	-4.4713	6.0996
O10	24.2732	-6.512	5.046
C11	25.4075	-7.0457	5.826
C12	25.5921	-8.4867	5.4033
C13	22.2835	-5.9276	3.4458
C14	20.9619	-6.4455	3.4332
C15	19.9982	-6.0501	4.4072
C16	20.5811	-7.3377	2.3905
C17	18.6946	-6.5288	4.3257
C18	19.2746	-7.8006	2.3121
C19	18.3314	-7.3927	3.2771
H20	26.284	-6.424	5.6137
H21	25.1641	-6.9408	6.889
H22	26.4243	-8.9329	5.9565
H23	25.8148	-8.5527	4.3343
H24	24.6895	-9.0699	5.6081
H25	23.0455	-6.4036	2.8315
H26	20.2788	-5.3836	5.2185
H27	21.3144	-7.6092	1.6353
H28	17.9579	-6.2186	5.0576
H29	18.9733	-8.4588	1.5052
H30	17.3074	-7.7456	3.2055

TS3

atom	X	Y	Z
H1	18.7463	-1.7167	1.9696
Zr2	23.3368	-2.2065	6.2158
Cl3	21.4735	-3.3924	7.415
Cl4	24.6218	-1.6018	8.1433
Cl5	24.9895	-1.8042	4.4564
Cl6	21.9543	-0.2976	5.6717
N7	22.3022	-3.5161	4.5065
C8	22.7723	-4.8093	4.3601
C9	23.8591	-5.1485	5.2667
O10	24.2362	-4.3002	6.1262
O11	24.402	-6.3499	5.1417
C12	25.5278	-6.7091	6.0529
C13	25.96	-8.1032	5.6636
C14	22.0429	-5.564	3.441
C15	20.9896	-4.7414	2.9796
C16	21.1072	-3.4628	3.6538
C17	19.96	-4.9191	2.0198
C18	20.3505	-2.3219	3.2347
C19	19.1653	-3.8327	1.6994
C20	19.3704	-2.5443	2.2897
H21	26.31	-5.9562	5.9153
H22	25.1504	-6.64	7.0778
H23	26.7897	-8.4203	6.3025
H24	26.2953	-8.1303	4.6233
H25	25.1388	-8.8146	5.7856
H26	22.2468	-6.5904	3.1717
H27	20.9779	-3.589	4.9287
H28	19.8248	-5.8767	1.5284
H29	20.5282	-1.3494	3.6843
H30	18.3783	-3.9431	0.9601