Electronic Supplementary Material (ESI) for RSC Advances.

Surpporting Information

I_2-catalyzed oxidative cyclization synthesis indolizines from aromatic/aliphatic olefins and α-picoline derivatives via $C(_{sp}^2)$-H bond activation

Likui Xiang, Fuming Zhang, Baohua Chen, Xiaobo Pang, Xiaodong Yang, Guosheng Huang, Rulong Yan*

State Key Laboratory of Applied Organic Chemistry, Key laboratory of Nonferrous Metal Chemistry and Resources Utilization of Gansu Province, Department of Chemistry, Lanzhou University, Lanzhou, P. R. China
E-mail: yanrl@lzu.edu.cn, Fax: +86 931 8912596; Tel: +86 931 8912586

Table of Contents

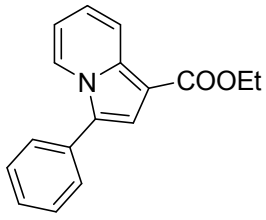
General remark

^{1}H NMR and ^{13}C NMR spectra were recorded on 400MHz and 100MHz in $CDCl_3$. All chemical shifts are given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. All compounds were further characterized by HRMS; copies of their ^{1}H NMR and ^{13}C NMR spectra are provided. Products were purified by flash chromatography on 100–200 mesh silica gels. All melting points were determined without correction. Unless otherwise noted, commercially available reagents and solvents were used without further purification.

Experimental section

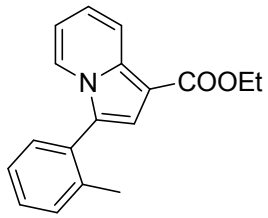
The styrene (**1a/4a**, 2.0 mmol), ethyl 2-(pyridin-2-yl)acetate (**2a**, 1.0 mmol), I_2 (0.05 mmol),TMEDA (0.2 mmol) and TBHP (3.0 mmol) were mixed in NMP(5 mL) and this mixture was at 120 ^{o}C for 4 h. The reaction mixture was cooled down to rt and then extracted with CH_2Cl_2(15 ml×3). The combined organic phase was dried over anhydrous Na_2SO_4. The solvent was evaporated in vacuo and the crude product was purified by column chromatography, eluting with petroleum ether/EtOAc (40:1) to afford the desired indolizines (**3aa/5aa**).

Characterization data of products 3 and 5.



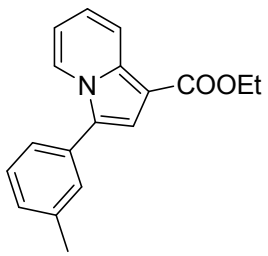
ethyl 3-phenylindolizine-1-carboxylate (3aa).

White solid, melting point: 61-62 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22-8.18 (m, 2 H), 7.48-7.40 (m, 4H), 7.34-7.30 (m, 1 H), 7.23 (s, 1 H), 7.01-6.97 (m, 1 H), 6.64-6.60 (m, 1 H), 4.34-4.29 (q, *J* = 7.2 Hz, 2 H), 1.36-1.33 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 136.4, 131.3, 129.1, 128.6, 128.0, 126.4, 123.4, 122.2, 120.2, 116.1, 112.6, 104.3, 59.5, 14.7. HRMS (ESI) *m/z* calcd for $C_{17}H_{16}NO_2$ $[M+H]^+$: 266.1176, found :266.1172.



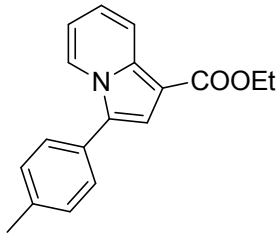
ethyl 3-(o-tolyl)indolizine-1-carboxylate (3ba).

Brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20-8.17 (d, *J* = 12 Hz, 1 H), 7.53-7.51 (d, *J* = 8 Hz, 1 H), 7.32-7.17 (m, 4 H), 7.14 (s, 1 H), 7.00-6.96 (m, 1 H), 6.59-6.56 (m, 1 H), 4.34-4.29 (q, *J* = 7.2 Hz, 2 H), 2.03 (s, 3 H), 1.36-1.32 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 138.5, 135.6, 131.5, 130.5, 130.4, 129.1, 126.2, 125.5, 123.7, 121.9, 120.0, 116.2, 112.4, 103.7, 59.5, 19.6, 14.7. HRMS (ESI) *m/z* calcd for $C_{18}H_{18}NO_2$ $[M+H]^+$: 280.1332, found : 280.1330.



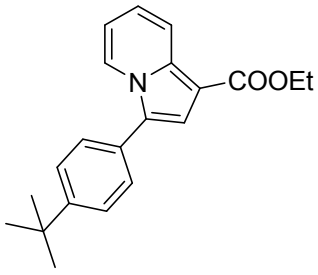
ethyl 3-(m-tolyl)indolizine-1-carboxylate (3ca).

Brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23-8.17 (m, 2 H), 7.33-7.26 (m, 3 H), 7.22 (s, 1 H), 7.15-7.13 (m, 1 H), 7.01-6.97 (m, 1 H), 6.64-6.60 (m, 1 H), 4.34-4.29 (q, *J* = 7.2 Hz, 2 H), 2.35 (s, 3 H), 1.36-1.33 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 138.9, 136.3, 131.2, 129.4, 128.9, 128.8, 126.6, 125.6, 123.5, 122.1, 120.2, 116.0, 112.5, 104.2, 59.5, 21.5, 14.7. HRMS (ESI) *m/z* calcd for $C_{18}H_{18}NO_2$ $[M+H]^+$: 280.1332, found : 280.1335.



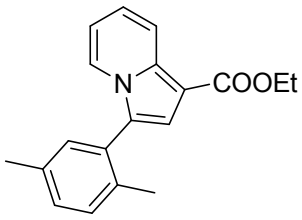
ethyl 3-(p-tolyl)indolizine-1-carboxylate (3da).

Green oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20-8.17 (m, 2 H), 7.37-7.35 (d, *J* = 8 Hz, 2H), 7.24-7.19 (m, 3 H), 7.00-6.96 (m, 1 H), 6.63-6.59 (m, 1 H), 4.34-4.29 (q, *J* = 7.2, 2 H), 2.36 (s, 3 H), 1.36-1.33 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 138.0, 136.2, 129.8, 128.6, 128.3, 126.5, 123.4, 122.0, 120.1, 115.8, 112.4, 104.1, 59.5, 21.3, 14.7. HRMS (ESI) *m/z* calcd for $C_{18}H_{18}NO_2$ $[M+H]^+$: 280.1332, found : 280.1330.



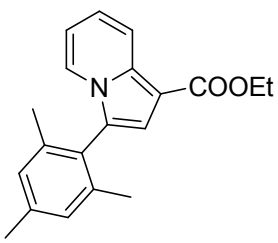
ethyl 3-(4-(tert-butyl)phenyl)indolizine-1-carboxylate (3ea).

White solid, melting point: 118-124 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24-8.17 (m, 2 H), 7.45-7.39 (m, 4H), 7.21 (s, 1 H), 7.00-6.96 (m, 1 H), 6.63-6.59 (m, 1 H), 4.34-4.29 (q, *J* = 7.2 Hz, 2 H), 1.36-1.33 (t, *J* = 7.2 Hz, 3 H), 1.31 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 151.1, 136.2, 128.3, 126.5, 126.0, 123.5, 122.1, 120.1, 115.8, 112.4, 104.1, 59.5, 34.7, 31.3, 14.7. HRMS (ESI) *m/z* calcd for $C_{21}H_{24}NO_2$ $[M+H]^+$: 322.1802, found : 322.1805.



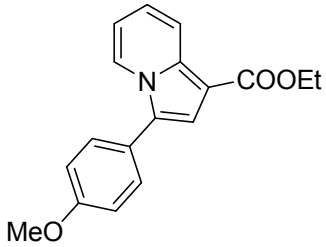
ethyl 3-(2,5-dimethylphenyl)indolizine-1-carboxylate (3fa).

Green oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 -8.17 (m, 1 H), 7.54-7.52 (m, 1H), 7.18-7.07 (m, 4 H), 7.01-6.97 (m, 1 H), 6.60-6.56 (m, 1 H), 4.35-4.29 (q, *J* = 7.2 Hz, 2 H), 2.28 (s, 3 H), 1.98 (s, 3 H), 1.36-1.33 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 135.7, 135.6, 135.2, 132.0, 130.4, 130.2, 129.8, 125.8, 123.8, 121.8, 119.9, 116.1, 112.3, 103.6, 59.5, 20.8, 19.1, 14.7. HRMS (ESI) *m/z* calcd for $C_{19}H_{20}NO_2$ $[M+H]^+$: 294.1489, found : 294.1493.



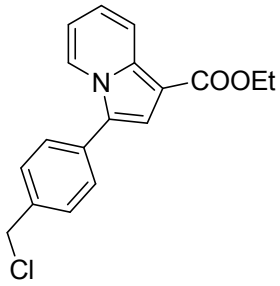
ethyl 3-mesitylindolizine-1-carboxylate (3ga).

Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 -8.16 (m, 1 H), 7.32-7.30 (m, 1H), 7.08 (s, 1 H), 7.01-6.94 (m, 3 H), 6.58-6.54 (m, 1 H), 4.35-4.30 (q, *J* = 7.2 Hz, 2 H), 2.29 (s, 3 H), 1.88 (s, 6 H), 1.38-1.34 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 139.4, 139.0, 135.4, 128.5, 126.8, 124.0, 123.3, 121.7, 119.9, 116.2, 112.3, 103.6, 59.5, 21.2, 19.8, 14.7. HRMS (ESI) *m/z* calcd for $C_{20}H_{22}NO_2$ $[M+H]^+$: 308.1645, found : 308.1643.



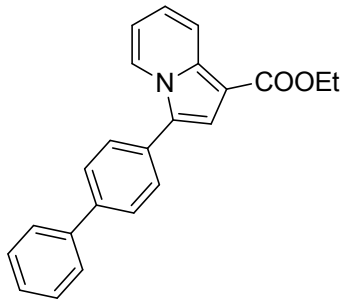
ethyl 3-(4-methoxyphenyl)indolizine-1-carboxylate (3ha).

Brown solid, melting point: 96-98 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18-8.12 (m, 2 H), 7.39-7.37 (d, *J* = 8 Hz, 2H), 7.17 (s, 1 H), 7.00-6.94 (m, 3 H), 6.63-6.59 (m, 1 H), 4.34-4.29 (q, *J* = 7.2 Hz, 2 H), 3.80 (s, 3 H), 1.36-1.33 (t, *J* = 7.2 Hz, 3 H);^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 159.5, 136.1, 130.2, 126.2, 123.6, 123.3, 122.0, 120.1, 115.6, 114.5, 112.4, 104.0, 59.5, 55.4, 14.7. HRMS (ESI) *m/z* calcd for $C_{18}H_{18}NO_3$ $[M+H]^+$: 296.1281, found : 296.1280.



ethyl 3-(4-(chloromethyl)phenyl)indolizine-1-carboxylate (3ia).

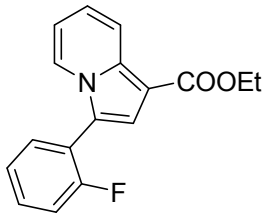
Green oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23-8.19 (m, 2 H), 7.49-7.44 (m, 4 H), 7.24 (s, 1 H), 7.03-6.99 (m, 1 H), 6.67-6.63 (m, 1 H), 4.59 (s, 2 H), 4.35-4.29 (q, *J* = 7.2 Hz, 2 H), 1.37-1.33 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 137.1, 136.5, 131.5, 129.4, 128.8, 125.7, 123.3, 122.4, 120.3, 116.4, 112.8, 104.5, 59.6, 45.9, 14.7. HRMS (ESI) *m/z* calcd for $C_{18}H_{17}ClNO_2$ $[M+H]^+$: 314.0943, found : 314.0940.



ethyl 3-([1,1'-biphenyl]-4-yl)indolizine-1-carboxylate (3ja).

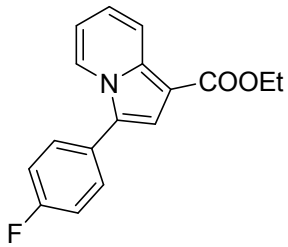
Green solid, melting point: 183-185^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31-8.29 (d, *J* = 8 Hz, 1 H), 8.22-8.20 (d, *J* = 8 Hz, 1 H), 7.67-7.60 (m, 2 H), 7.58-7.55 (m, 4 H), 7.43-7.39 (m, 2 H), 7.34- -7.29 (m, 1 H), 7.19 (s, 1 H), 7.04-7.00 (m, 1 H), 6.68-6.65 (m, 1 H), 4.36-4.30 (q, *J* = 7.2 Hz, 2 H), 1.38-1.34 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 140.8, 140.4, 136.5, 130.2, 128.9, 128.88, 127.8, 127.6, 127.1, 126.1, 123.5, 122.3, 120.3, 116.2, 112.7, 104.4, 59.6, 14.7. HRMS (ESI) *m/z*

calcd for $C_{23}H_{20}NO_2$ $[M+H]^+$: 342.1489, found : 342.1489.



ethyl 3-(2-fluorophenyl)indolizine-1-carboxylate (3ka).

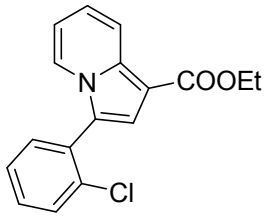
Green oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22-8.20 (d, *J* = 8 Hz, 1 H), 7.82-7.79 (m, 1 H), 7.44-7.33 (m, 2 H), 7.28 (s, 1 H), 7.22-7.13 (m, 2 H), 7.06-7.01 (m, 1 H), 6.68-6.64 (m, 1 H), 4.35-4.29 (q, *J* = 7.2 Hz, 2 H), 1.36-1.33 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 161.4, 158.9, 136.5, 131.98-131.95 (d, *J* = 3 Hz, 1C), 130.3-130.2 (d, *J* = 10 Hz, 1C), 124.8-124.7 (d, *J* = 10 Hz, 1C), 124.33-124.29 (d, *J* = 4 Hz, 1C), 122.4, 120.5, 119.9, 119.0-118.9 (d, *J* = 10 Hz, 1C), 117.5, 116.3-116.1 (d, *J* = 20 Hz, 1C), 112.5, 104.4, 59.6, 14.6. HRMS (ESI) *m/z* calcd for $C_{17}H_{15}FNO_2$ $[M+H]^+$: 284.1081, found : 284.1079.



ethyl 3-(4-fluorophenyl)indolizine-1-carboxylate (3la).

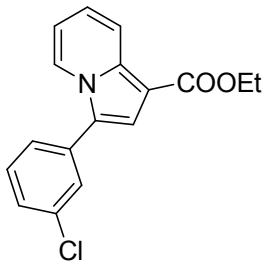
White oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21-8.18 (m, 1 H), 8.12-8.10 (m, 1 H), 7.45-7.42 (m, 2 H), 7.20 (s, 1 H), 7.14-7.10 (m, 2 H), 7.02-6.98 (m, 1 H), 6.66-6.62 (m, 1 H), 4.34-4.29 (q, *J* = 7.2 Hz, 2 H), 1.36-1.33 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 163.7, 161.2,

136.3, 130.6-130.5 (d, J = 10 Hz, 2 C), 127.4-127.3 (d, J = 10 Hz, 1 C) , 125.3, 123.1, 122.2, 120.2, 116.3-116.1 (m, 1 C), 112.7, 104.3, 59.6, 14.7. HRMS (ESI) *m/z* calcd for $C_{17}H_{15}FNO_2$ $[M+H]^+$: 284.1082, found : 284.1085.



ethyl 3-(2-chlorophenyl)indolizine-1-carboxylate (3ma).

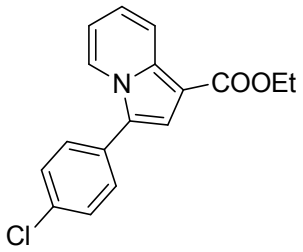
Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22-8.20 (d, J = 8 Hz, 1 H), 7.62-7.60 (d, J = 8 Hz, 1 H), 7.49-7.34 (m, 4 H), 7.33 (s, 1 H), 7.06-7.02(m, 1 H), 6.67-6.63 (m, 1 H), 4.35-4.29 (q, J = 7.2 Hz, 2 H), 1.36-1.33 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 136.0, 135.0, 133.2, 130.17, 130.12, 130.05, 129.4, 128.8, 127.2, 124.3, 123.4, 122.4, 119.9, 117.2, 112.3, 104.0, 59.6, 14.7. HRMS (ESI) *m/z* calcd for $C_{17}H_{15}ClNO_2$ $[M+H]^+$: 300.0786, found : 300.0788.



ethyl 3-(3-chlorophenyl)indolizine-1-carboxylate (3na).

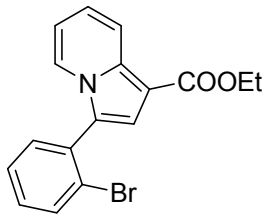
Yellow solid, melting point: 96-98 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20-8.18 (m, 2 H), 7.46 (d, J = 1.2 Hz, 1 H), 7.36-7.27 (m, 3 H), 7.24 (s, 1 H), 7.03-6.99 (m, 1 H), 6.67-6.64 (m, 1 H), 4.34-4.28 (q, J = 7.2 Hz, 2

H), 1.36-1.32 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 136.6, 135.0, 133.1, 130.4, 128.4, 128.0, 126.5, 124.8, 123.2, 122.5, 120.3, 116.7, 112.9, 104.6, 59.6, 14.7. HRMS (ESI) *m/z* calcd for $C_{17}H_{15}ClNO_2$ $[M+H]^+$: 300.0786, found : 300.0785.



ethyl 3-(4-chlorophenyl)indolizine-1-carboxylate (3oa).

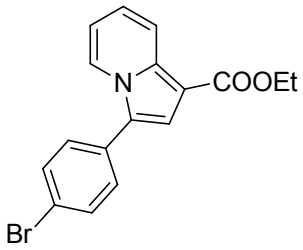
Green solid, melting point: 58-60 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21-8.14 (m, 2 H), 7.42-7.38 (m, 4 H), 7.22 (s, 1 H), 7.03-6.99 (m, 1 H), 6.67-6.63 (m, 1 H), 4.34-4.29 (q, J = 7.2 Hz, 2 H), 1.36-1.33 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 136.5, 133.8, 129.8, 129.7, 129.4, 125.1, 123.1, 122.4, 120.3, 116.4, 112.9, 104.5, 59.6, 14.7. HRMS (ESI) *m/z* calcd for $C_{17}H_{15}ClNO_2$ $[M+H]^+$: 300.0786, found : 300.0783.



ethyl 3-(2-bromophenyl)indolizine-1-carboxylate (3pa).

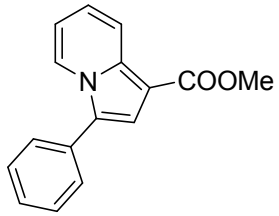
colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22-8.20 (d, J = 8 Hz, 1 H), 7.67-7.65 (d, J = 8 Hz, 1 H), 7.58-7.57 (d, J = 4 Hz, 1 H), 7.36-7.35 (d, J = 4 Hz, 2 H), 7.28-7.23 (m, 2 H), 7.05-7.01 (m, 1 H), 6.66-6.62 (m, 1 H), 4.34-4.29 (q, J = 7.2 Hz, 2 H), 1.36-1.32 (t, J = 7.2 Hz, 3 H); ^{13}C NMR

(100 MHz, $CDCl_3$) δ 165.0, 135.8, 133.5, 133.3, 132.2, 130.4, 127.8, 125.4, 124.8, 124.3, 122.4, 119.9, 117.0, 112.3, 103.8, 59.6, 14.7. HRMS (ESI) *m/z* calcd for $C_{17}H_{15}BrNO_2$ $[M+H]^+$: 344.0281, found : 344.0282.



ethyl 3-(4-bromophenyl)indolizine-1-carboxylate (3qa).

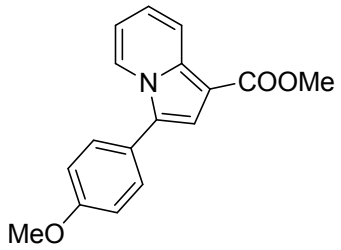
Yellow solid, melting point: 91-93 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.20-8.14 (m, 2 H), 7.56-7.54 (d, *J* = 8 Hz, 2 H), 7.35-7.33 (d, *J* = 8 Hz, 2 H), 7.22 (s, 1 H), 7.03-6.99 (m, 1 H), 6.67-6.63 (m, 1 H), 4.34-4.29 (q, *J* = 7.2 Hz, 2 H), 1.36-1.33 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 136.5, 132.3, 130.2, 130.0, 125.1, 123.1, 122.4, 121.9, 120.3, 116.4, 112.9, 104.5, 59.6, 14.7. HRMS (ESI) *m/z* calcd for $C_{17}H_{15}BrNO_2$ $[M+H]^+$: 344.0281, found : 344.0279.



methyl 3-phenylindolizine-1-carboxylate (3ab).

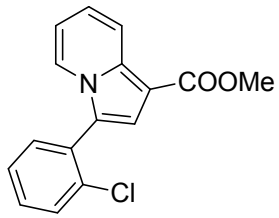
Yellow solid, melting point: 87-88 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.23-8.18 (m, 2 H), 7.48-7.41 (m, 4 H), 7.35-7.31 (m, 1 H), 7.22 (s, 1 H), 7.03-6.99 (m, 1 H), 6.66-6.62 (m, 1 H), 3.85 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 136.4, 131.3, 129.1, 128.7, 128.0, 126.5, 123.4,

122.3, 120.2, 116.0, 112.6, 103.9, 50.9. HRMS (ESI) *m/z* calcd for $C_{16}H_{14}NO_2$ $[M+H]^+$: 252.1019, found : 252.1014.



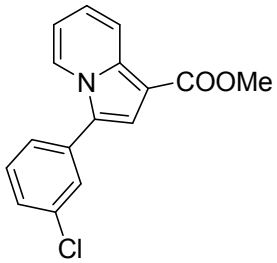
methyl 3-(4-methoxyphenyl)indolizine-1-carboxylate (3hb).

Yellow oil, melting point: 117.3-118.4 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.19-8.13 (m, 2 H), 7.39-7.37 (d, *J* = 8 Hz, 2 H), 7.19 (s, 1 H), 7.01-6.94 (m, 3 H), 6.64-6.61 (m, 1 H), 3.84 (s, 3 H), 3.81 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 159.5, 136.1, 130.2, 126.3, 123.5, 123.4, 122.1, 120.1, 115.5, 114.5, 112.5, 103.6, 55.4, 50.9. HRMS (ESI) *m/z* calcd for $C_{17}H_{16}NO_3$ $[M+H]^+$: 282.1125, found : 282.1129.



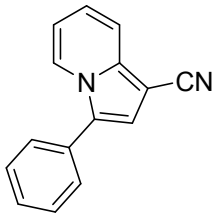
methyl 3-(2-chlorophenyl)indolizine-1-carboxylate (3mb).

Green oil. ^1H NMR (400 MHz, $CDCl_3$) δ 8.22-8.20 (d, *J* = 8 Hz, 1 H), 7.62-7.61 (d, *J* = 4 Hz, 1 H), 7.49-7.47 (m, 1 H), 7.39-7.29 (m, 3 H) 7.23 (s, 1 H), 7.07-7.03 (m, 1 H), 6.67-6.64 (m, 1 H), 3.84 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 136.1, 135.0, 133.2, 130.2-130.0(m, 1C), 127.2, 124.3, 123.4, 122.6, 119.9, 117.1, 112.4, 103.6, 51.0. HRMS (ESI) *m/z* calcd for $C_{16}H_{13}ClNO_2$ $[M+H]^+$: 286.0630, found : 286.0629.



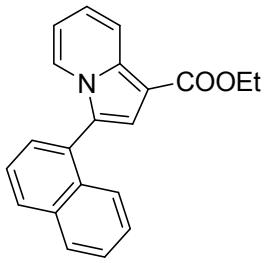
methyl 3-(3-chlorophenyl)indolizine-1-carboxylate (3nb).

Green oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21-8.19 (m, 2 H), 7.47 (s, 1 H), 7.37-7.29 (m, 3 H), 7.23 (s, 1 H), 7.05-7.01 (m, 1 H), 6.70-6.66 (m, 1 H), 3.84 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 136.7, 135.0, 133.0, 130.4, 128.4, 128.1, 126.6, 124.9, 123.2, 122.7, 120.2, 116.6, 113.0, 104.2, 51.0. HRMS (ESI) *m/z* calcd for $C_{16}H_{13}ClNO_2$ $[M+H]^+$: 286.0630, found : 286.0626.



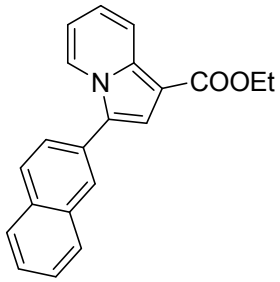
3-phenylindolizine-1-carbonitrile (3ca).

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22-8.20 (d, J = 8 Hz, 1 H), 7.63-7.61 (d, J = 8 Hz, 1 H), 7.45-7.35 (m, 5 H), 7.03-6.98 (m, 2 H), 6.99-6.65 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4. 130.2. 129.3, 128.7, 128.6, 127.0, 123.8, 122.3, 118.3, 116.9, 116.3, 113.1, 82.3. HRMS (ESI) *m/z* calcd for $C_{15}H_{11}N_2$ $[M+H]^+$:219.0917, found : 219.0912.



ethyl 3-(naphthalen-1-yl)indolizine-1-carboxylate (5aa).

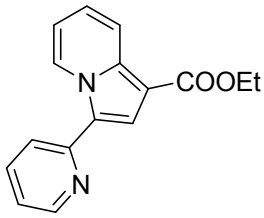
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 -8.23 (d, *J* = 8 Hz, 1 H), 7.90-7.85 (m, 2H), 7.52-7.50 (m, 3 H), 7.49-7.39 (m, 1 H), 7.38-7.30 (m, 3 H), 7.02-6.98 (m, 1 H), 6.52-6.48 (m, 1 H), 4.37-4.31 (q, *J* = 7.2 Hz, 2 H), 1.37-1.34 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 136.0, 133.9, 132.3, 129.5, 129.4, 128.7, 128.5, 126.9, 126.3, 125.7, 125.4, 124.3, 124.2, 122.2, 120.0, 117.5, 112.3, 104.0, 59.6, 14.7. HRMS (ESI) *m/z* calcd for $C_{21}H_{18}NO_2$ $[M+H]^+$: 316.1332, found : 316.1335.



ethyl 3-(naphthalen-2-yl)indolizine-1-carboxylate (5ba).

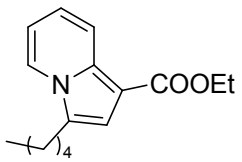
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39-8.38 (d, *J* = 4 Hz, 1 H), 8.31-8.29 (d, *J* = 8 Hz, 1 H), 8.01 (s, 1H), 7.97-7.94 (d, *J* = 12 Hz, 1 H), 7.90-7.86 (m, 2 H), 7.66-7.63 (m, 1 H), 7.56-7.51 (m, 2 H), 7.41 (s, 1 H), 7.12-7.08 (m, 1 H), 6.75-6.71 (m, 1 H), 4.43-4.38 (q, *J* = 7.2 Hz, 2 H), 1.45-1.42 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 136.5, 133.6, 132.8, 128.8, 128.6, 128.0, 127.8, 127.4, 126.7, 126.5,

126.4, 123.4, 122.4, 120.3, 116.5, 112.8, 104.5, 59.6, 14.7. HRMS (ESI) *m/z* calcd for $C_{21}H_{18}NO_2$ $[M+H]^+$: 316.1332, found : 316.1330.



ethyl 3-(pyridin-2-yl)indolizine-1-carboxylate (5ca).

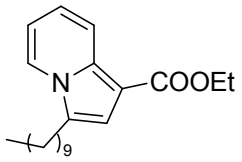
colourless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 10.01-9.99 (d, *J* = 8 Hz, 1 H), 8.57-8.56 (d, *J* = 4 Hz, 1 H), 8.24-8.22 (d, *J* = 8 Hz, 1 H), 7.70 (s, 1 H), 7.66-7.65 (d, *J* = 4 Hz, 2 H), 7.14-7.06 (m, 2 H), 6.82-6.78 (m, 1 H), 4.36-4.31 (q, *J* = 7.2 Hz, 2 H), 1.39-1.35 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 151.9, 148.3, 137.9, 136.6, 127.9, 123.7, 123.6, 121.2, 120.7, 119.4, 117.9, 113.1, 104.6, 59.7, 14.7. HRMS (ESI) *m/z* calcd for $C_{16}H_{15}N_2O_2$ $[M+H]^+$: 267.1128, found : 267.1127.



ethyl 3-pentylindolizine-1-carboxylate (5da).

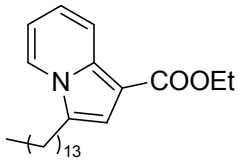
Green oil. ^1H NMR (400 MHz, $CDCl_3$) δ 8.13-8.11 (d, *J* = 8 Hz, 1 H), 7.78-7.76 (d, *J* = 8 Hz, 1 H), 6.97-6.94 (m, 2 H), 6.70-6.66 (m, 1 H), 4.32-4.27 (q, *J* = 7.2 Hz, 2 H), 2.72-2.68 (m, 2 H), 1.75-1.67 (m, 2 H), 1.38-1.29 (m, 7 H), 0.87-0.84 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 135.6, 125.8, 122.7, 121.1, 120.0, 113.6, 112.1, 102.8, 59.4, 31.7, 26.6, 25.7, 22.5, 14.7, 14.0. HRMS calcd for $C_{16}H_{22}NO_2$ $[M+H]^+$:

260.1645; found: 260.1642.



ethyl 3-decylindolizine-1-carboxylate (5ea).

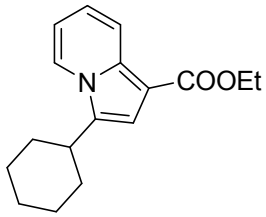
Yellow solid, melting point: 36-37 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 -8.11 (d, *J* = 8 Hz, 1 H), 7.77-7.76 (d, *J* = 4 Hz, 1 H), 6.97-6.93 (m, 2 H), 6.69-6.65 (m, 1 H), 4.32-4.26 (q, *J* = 7.2 Hz, 2 H), 2.71-2.67 (m, 2 H), 1.73-1.63 (m, 2 H), 1.38-1.20 (m, 17 H), 0.83-0.79 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 135.6, 125.8, 122.7, 121.1, 120.0, 113.6, 112.1, 102.8, 59.4, 31.9, 29.61, 29.56, 29.50, 29.45, 29.3, 26.9, 25.7, 22.7, 14.7, 14.1. HRMS (ESI) *m/z* calcd for $C_{21}H_{32}NO_2$ $[M+H]^+$: 330.2428, found : 330.2429.



ethyl 3-tetradecylindolizine-1-carboxylate (5fa).

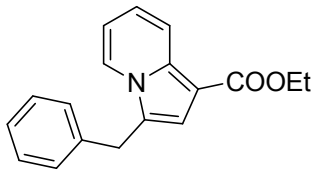
Yellow solid, melting point: 38-40°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13-8.11 (d, *J* = 8 Hz, 1 H), 7.77-7.76 (d, *J* = 4 Hz, 1 H), 6.97-6.93 (m, 2 H), 6.69-6.65 (m, 1 H), 4.32-4.26 (q, *J* = 7.2 Hz, 2 H), 2.71-2.67 (m, 2 H), 1.73-1.66 (m, 2 H), 1.35-1.19 (m, 25 H), 0.82-0.79 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 135.6, 125.8, 122.7, 121.1, 120.0, 113.6, 112.1, 102.8, 59.4, 31.9, 29.70, 29.66, 29.6, 29.51, 29.46, 29.4, 26.9, 25.7, 22.7, 14.7, 14.1. HRMS (ESI) *m/z* calcd for $C_{25}H_{40}NO_2$ $[M+H]^+$:

386.3054, found : 386.3051.



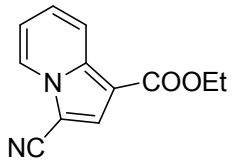
ethyl 3-cyclohexylindolizine-1-carboxylate (5ga).

Colourless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 -8.11 (d, *J* = 12 Hz, 1 H), 7.84-7.82 (d, *J* = 8 Hz, 1 H), 6.96-6.92 (m, 2 H), 6.67-6.64 (m, 1 H), 4.32-4.26 (q, *J* = 7.2 Hz, 2 H), 2.74-2.69 (m, 2 H), 2.03-2.01 (m, 2 H), 1.83-1.72 (m, 3 H), 1.43-1.27 (m, 8 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 135.6, 131.2, 122.8, 121.1, 120.2, 112.0, 111.7, 102.9, 59.4, 35.0, 26.5, 26.3, 14.7. HRMS (ESI) *m/z* calcd for $C_{17}H_{22}NO_2$ $[M+H]^+$: 272.1645, found : 272.1645.



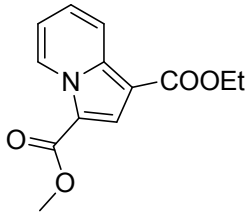
ethyl 3-benzylindolizine-1-carboxylate (5ha).

Red oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16-8.13 (d, *J* = 12 Hz 1 H), 7.66-7.64 (d, *J* = 8 Hz 1 H), 7.25-7.15 (m, 4 H), 7.11-7.09 (d, *J* = 8 Hz 2 H), 7.02 (s, 1 H), 6.98-6.94 (m, 1 H), 6.61-6.56 (m, 1 H), 4.32-4.27 (q, *J* = 7.2 Hz, 2 H), 4.14 (s, 2H), 1.35-1.32 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 136.9, 136.1, 128.8, 128.4, 126.8, 123.5, 123.1, 121.5, 120.0, 116.0, 112.3, 103.0, 59.5, 32.4, 14.7. HRMS (ESI) *m/z* calcd for $C_{18}H_{18}NO_2$ $[M+H]^+$: 280.1332, found : 280.1334.



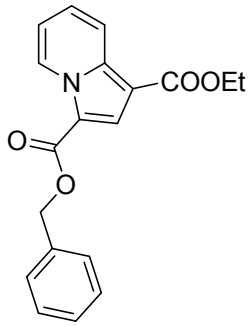
ethyl 3-cyanoindolizine-1-carboxylate (5ja).

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 -8.25 (m, 2 H), 7.73 (s, 1 H), 7.29-7.25 (m, 1H), 6.99-6.95 (m, 1 H), 4.34-4.29 (q, *J* = 7.2 Hz, 2 H), 1.36-1.32 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 137.8, 126.0, 125.7, 125.2, 120.5, 115.0, 112.7, 106.0, 96.6, 60.3, 14.5. HRMS (ESI) *m/z* calcd for $C_{12}H_{11}N_2O_2$ $[M+H]^+$: 215.0815, found : 215.0817.



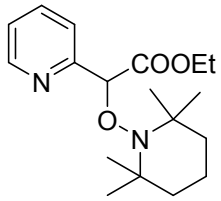
1-ethyl 3-methyl indolizine-1,3-dicarboxylate (5ka).

White solid, melting point: 92-94 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.46-9.44 (m, 1 H), 8.28-8.26 (m, 1 H), 7.92 (s, 1 H), 7.27-7.23 (m, 1 H), 6.94-6.90 (m, 1 H), 4.34-4.28 (q, *J* = 7.2 Hz, 2 H), 3.85 (s, 3 H), 1.36-1.33 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 161.6, 139.1, 127.9, 125.7, 124.4, 119.6, 114.4, 105.3, 59.9, 51.4, 14.6. HRMS (ESI) *m/z* calcd for $C_{13}H_{14}NO_4$ $[M+H]^+$: 248.0917, found : 248.0916.

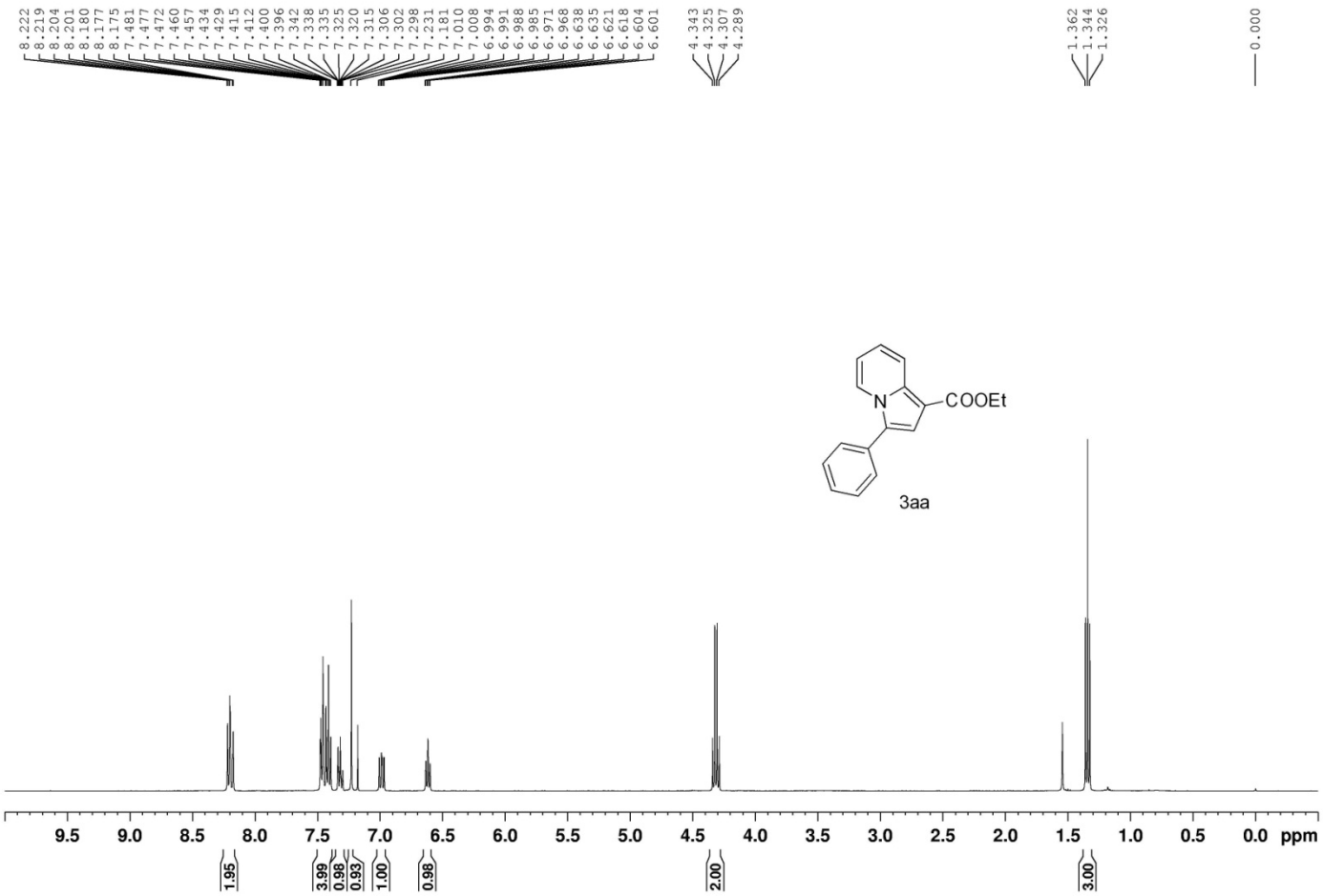


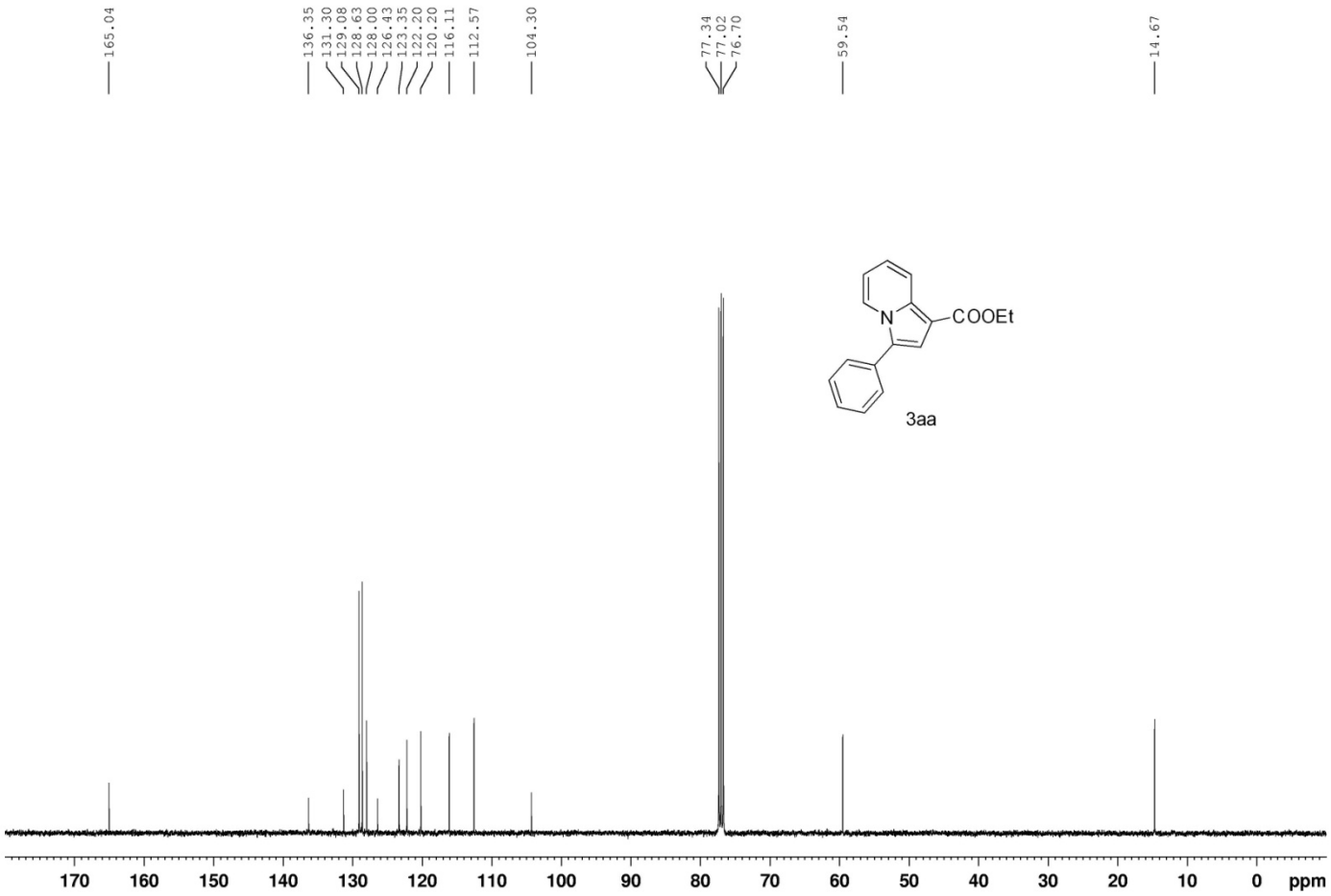
3-benzyl 1-ethyl indolizine-1,3-dicarboxylate (5la).

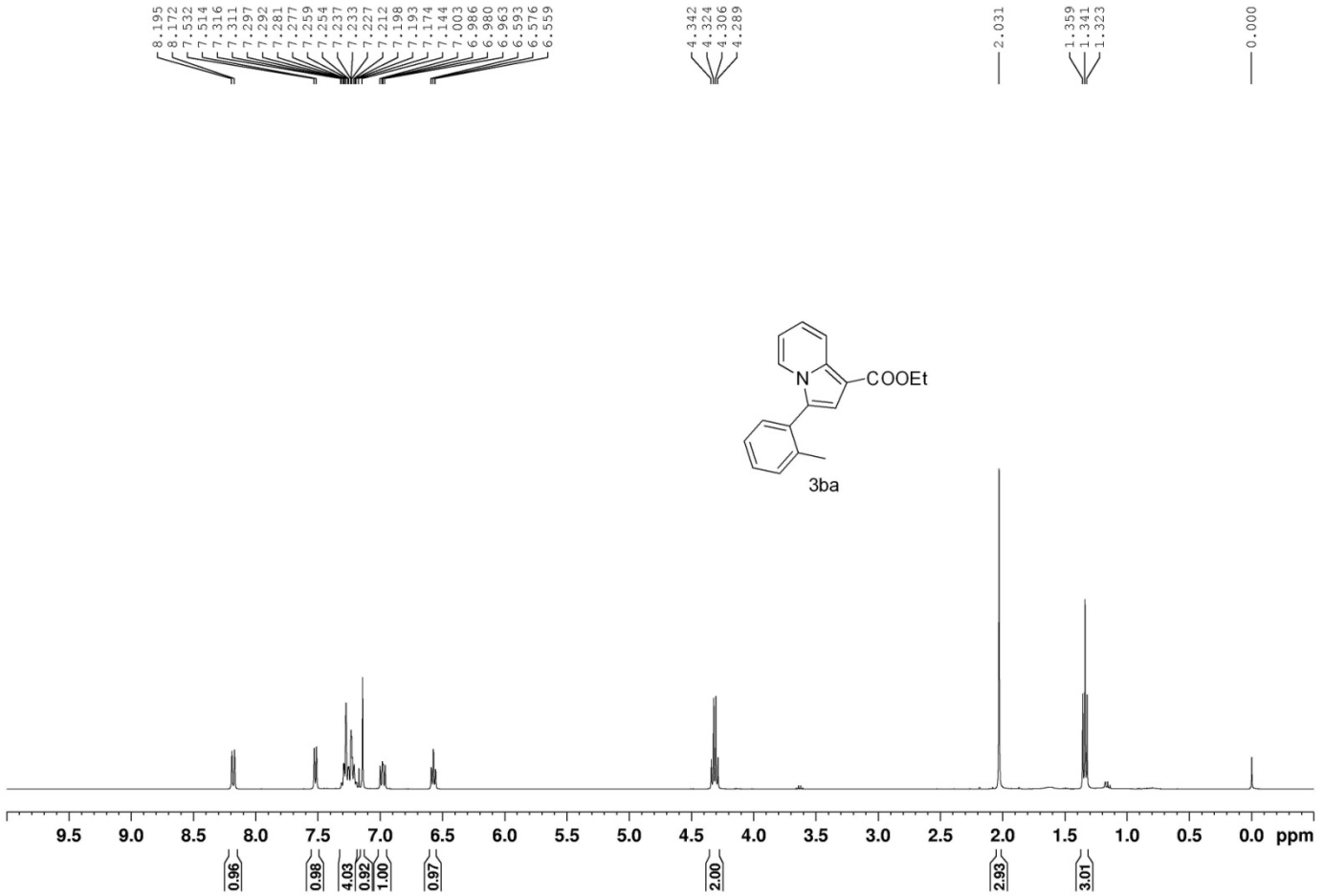
Green oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.47 -9.46 (d, *J* = 4 Hz, 1 H), 8.28-8.26 (d, *J* = 8 Hz, 1 H), 7.96 (s, 1 H), 7.41-7.19 (m, 6 H), 6.93-6.90 (m, 1 H), 5.31 (s, 2 H), 4.33-4.28 (q, J = 7.2 Hz, 2 H), 1.36-1.32 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 160.9, 139.2, 136.2, 128.6, 128.3, 128.2, 128.0, 125.8, 124.6, 119.6, 114.5, 114.3, 105.4, 65.9, 60.0, 14.6. HRMS (ESI) *m/z* calcd for $C_{19}H_{18}NO_4$ $[M+H]^+$: 324.1231, found : 324.1229.

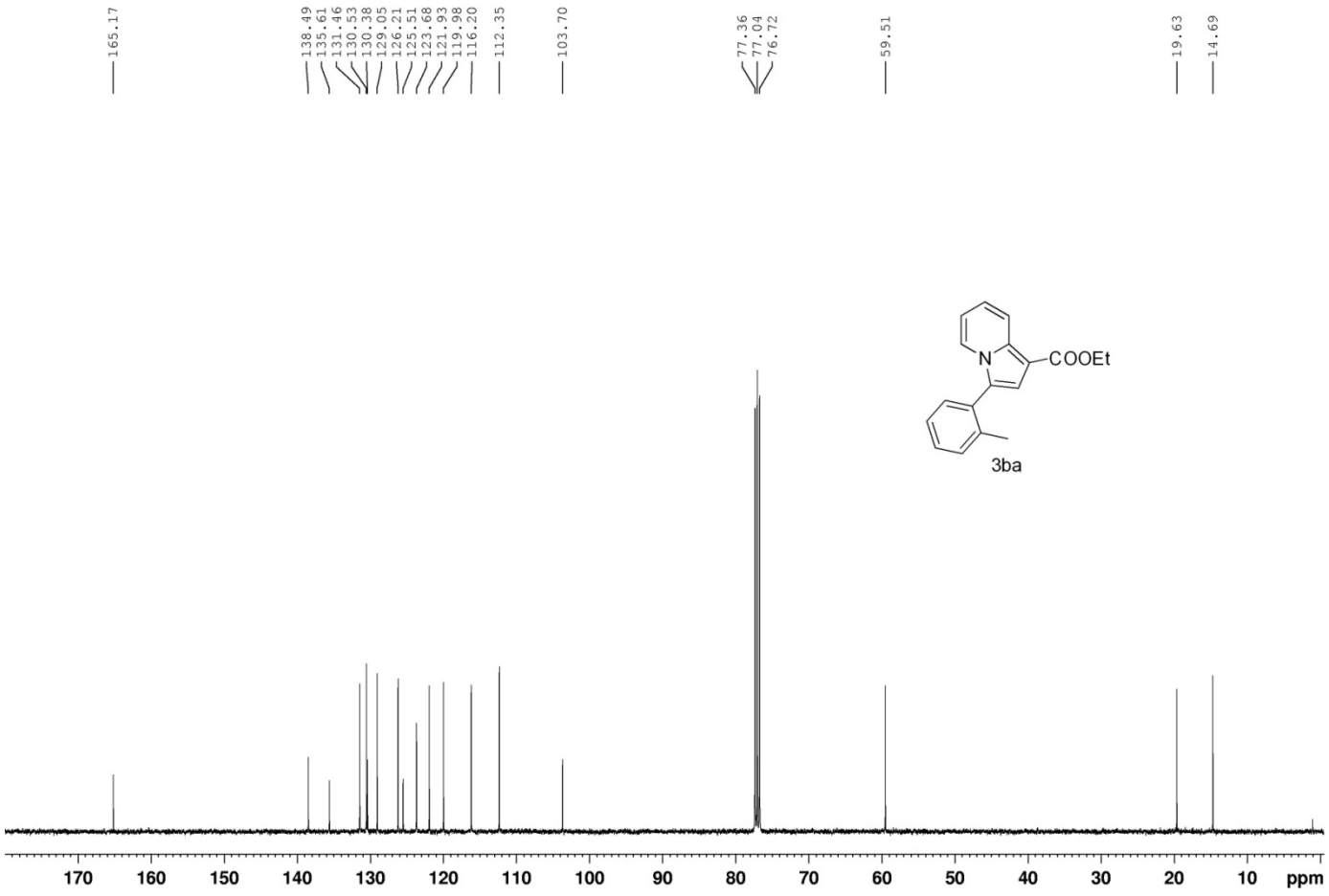


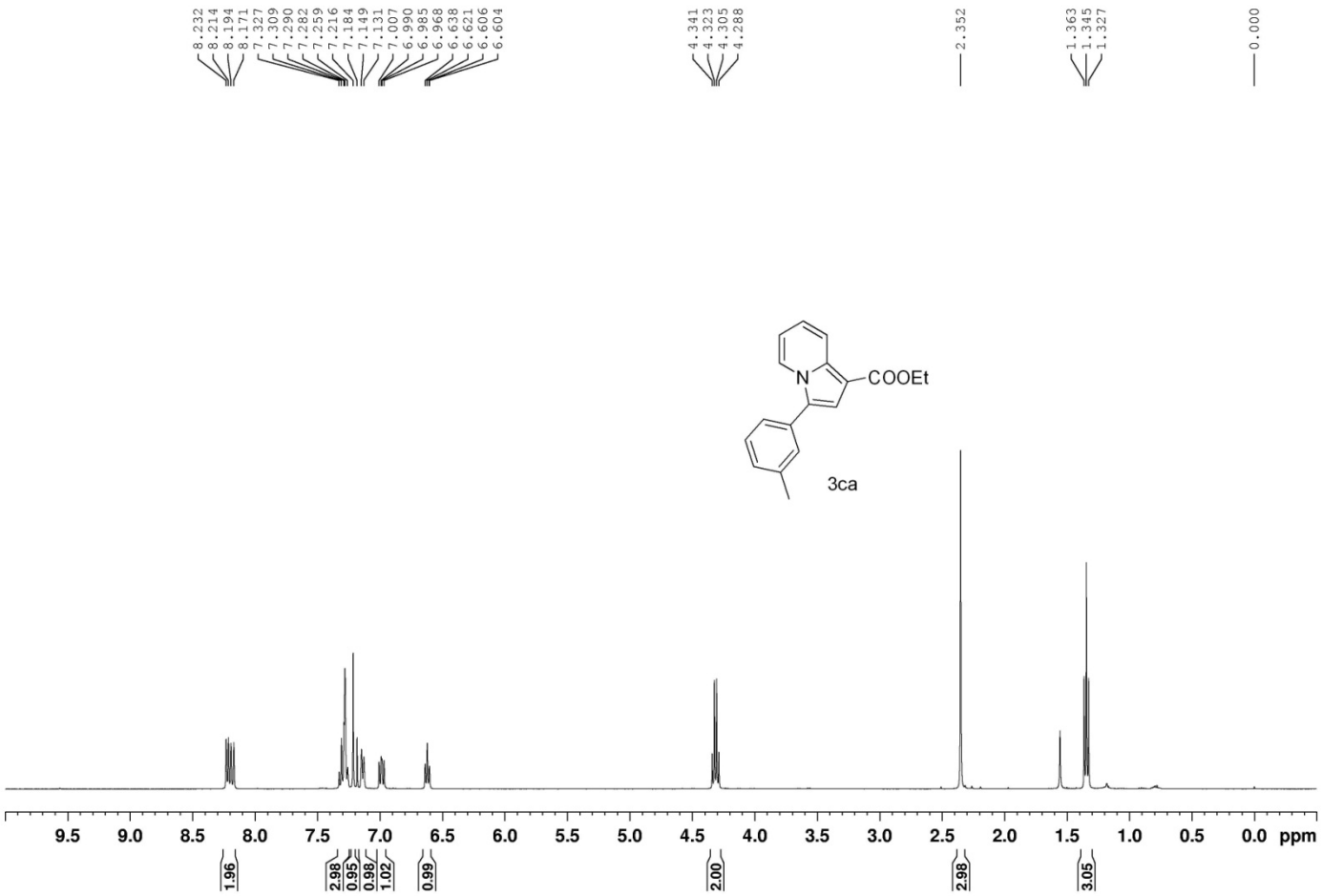
Ethyl 2-(pyridin-2-yl)-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)acetate (A). Green oil . ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49-8.48 (m, 1 H), 7.67-7.63 (m, 1 H), 7.54-7.52 (d, *J* = 8 Hz, 1 H), 7.15-7.12 (m, 1 H), 5.33 (s, 1 H), 4.17-4.03 (m, 2 H), 1.49-1.47 (m, 2 H), 1.42-1.40 (m, 2 H), 1.37-1.14 (m, 8 H), 1.11 (s, 3 H), 1.04 (s, 3 H), 0.63 (s, 3 H).^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 158.0, 149.0, 136.7, 122.8, 121.7, 89.7, 61.0, 60.0, 40.1, 33.2, 32.9, 20.2, 17.1, 14.1. HRMS (ESI) *m/z* calcd for $C_{18}H_{28}N_2O_3K$ $[M+K]^+$: 359.1732, found : 359.1731.

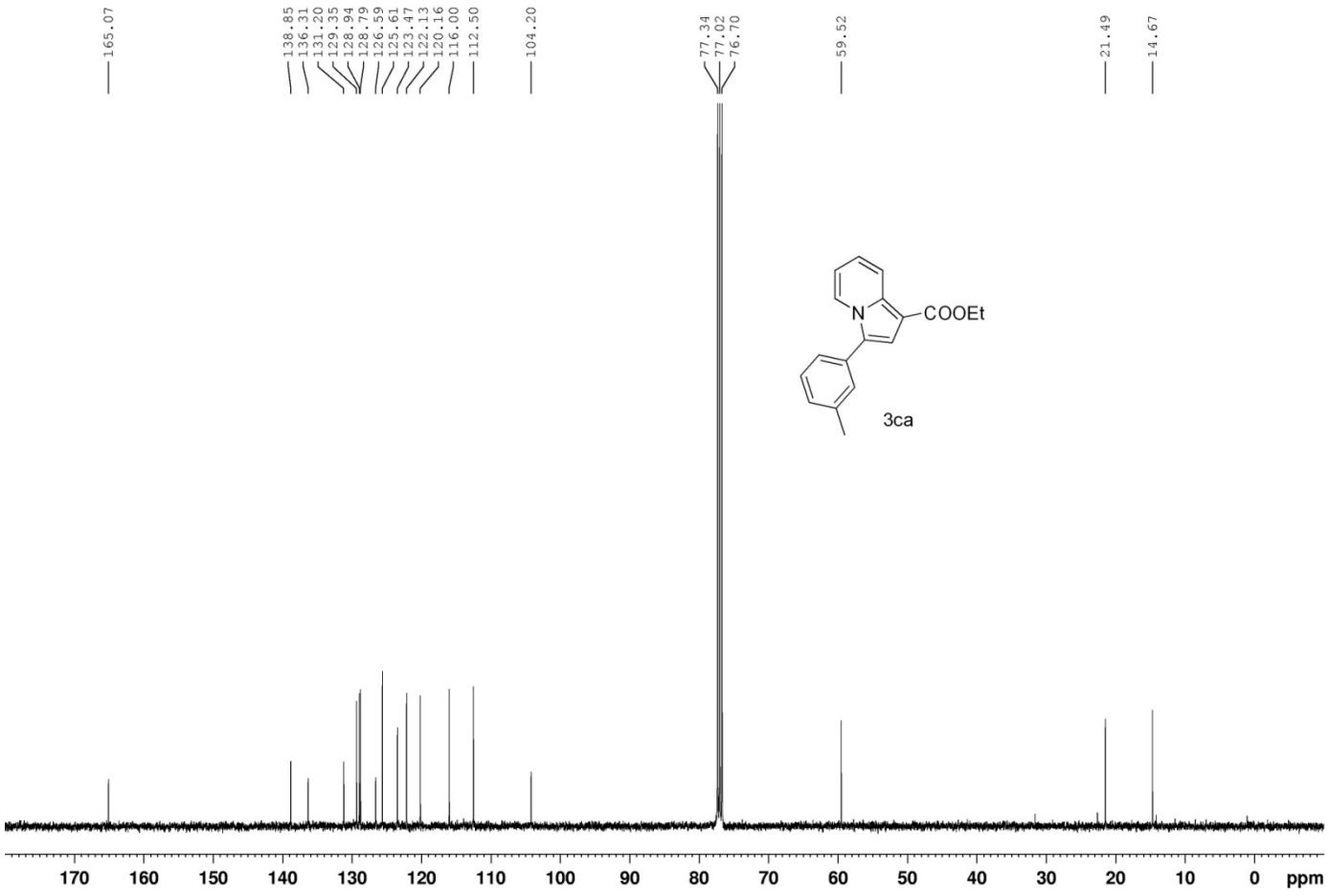

8.222
8.219
8.204
8.201
8.180
8.177
8.175
7.481
7.477
7.472
7.460
7.457
7.434
7.429
7.415
7.412
7.400
7.396
7.342
7.338
7.335
7.325
7.320
7.315
7.306
7.302
7.298
7.231
7.181
7.010
7.008
6.994
6.991
6.988
6.985
6.971
6.968
6.638
6.635
6.621
6.618
6.604
6.601
4.343
4.325
4.307
4.289
1.362
1.344
1.326
0.000
N
COOEt
3aa
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
1.95
3.99
0.98
0.93
1.00
0.98
2.00
3.00

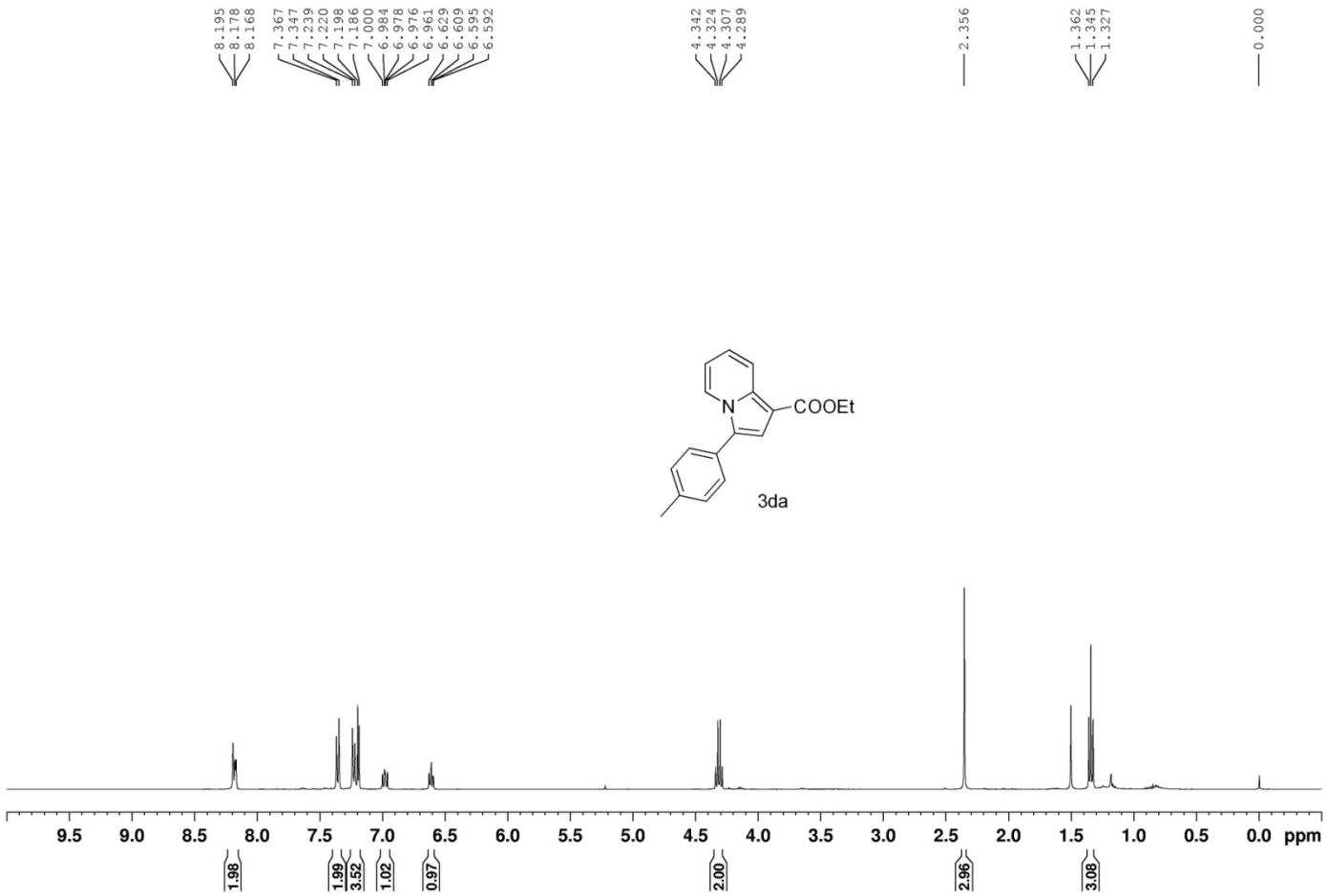

165.04
136.35
131.30
129.08
128.63
128.00
126.43
123.35
122.20
120.20
116.11
112.57
104.30
77.34
77.02
76.70
59.54
14.67
COOEt
N
3aa
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

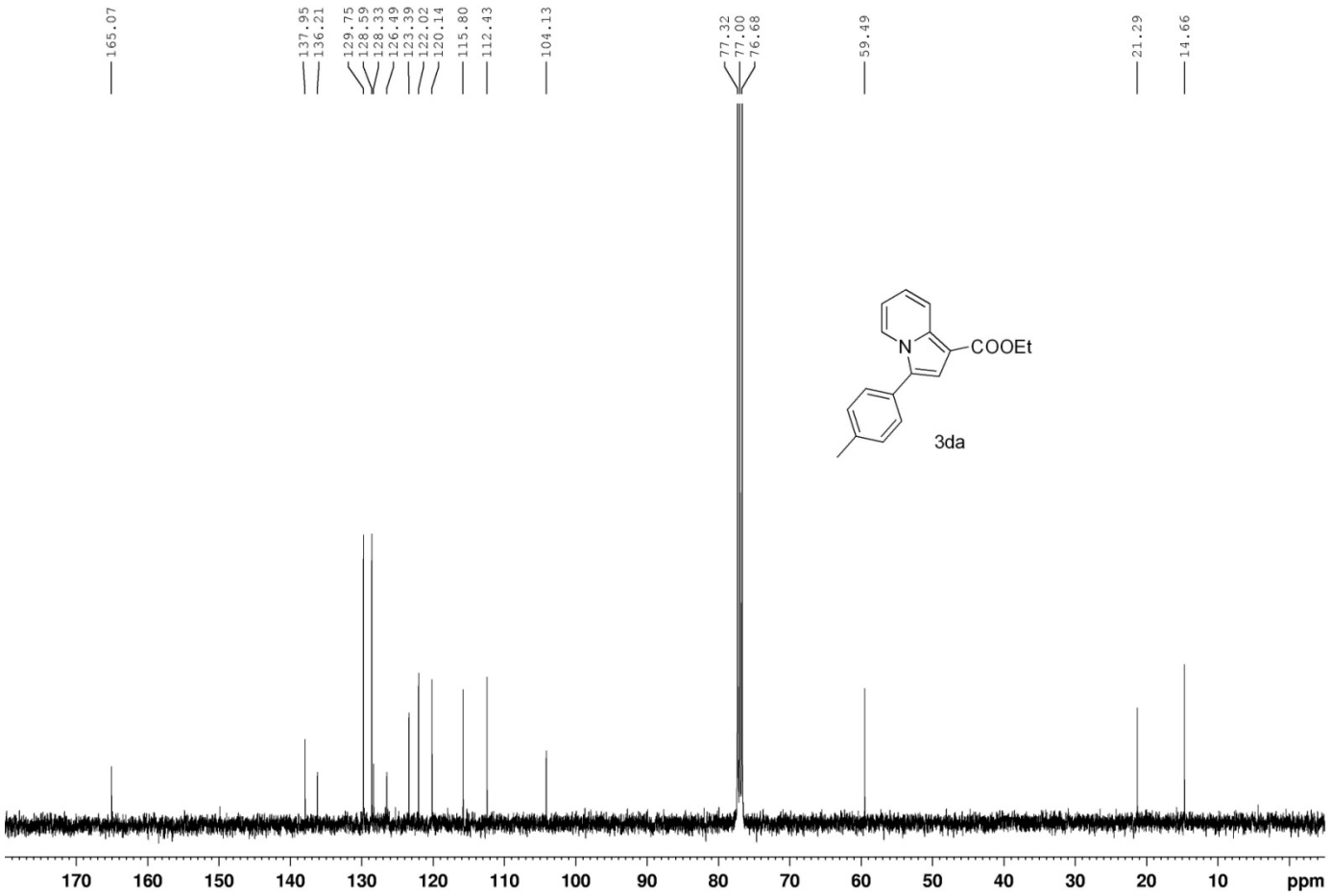

8.195
8.172
7.532
7.514
7.316
7.311
7.297
7.292
7.281
7.277
7.259
7.254
7.237
7.233
7.227
7.212
7.198
7.193
7.174
7.144
7.003
6.986
6.980
6.963
6.593
6.576
6.559
4.342
4.324
4.306
4.289
2.031
1.359
1.341
1.323
0.000
N
COOEt
3ba
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
0.96
0.98
4.03
0.92
1.00
0.97
2.00
2.93
3.01

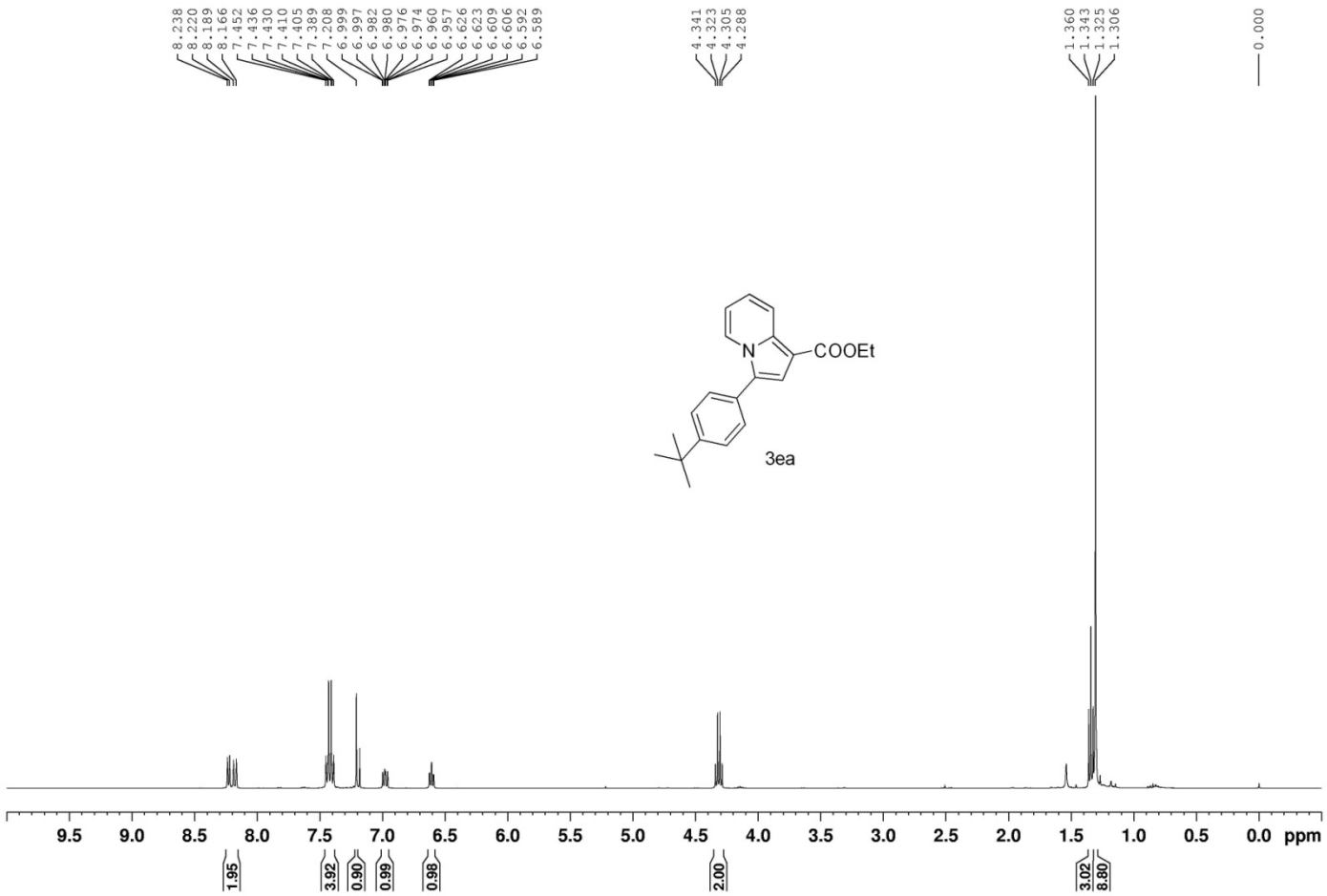

165.17
138.49
135.61
131.46
130.53
130.38
129.05
126.21
125.51
123.68
121.93
119.98
116.20
112.35
103.70
77.36
77.04
76.72
59.51
19.63
14.69
N
COOEt
3ba
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

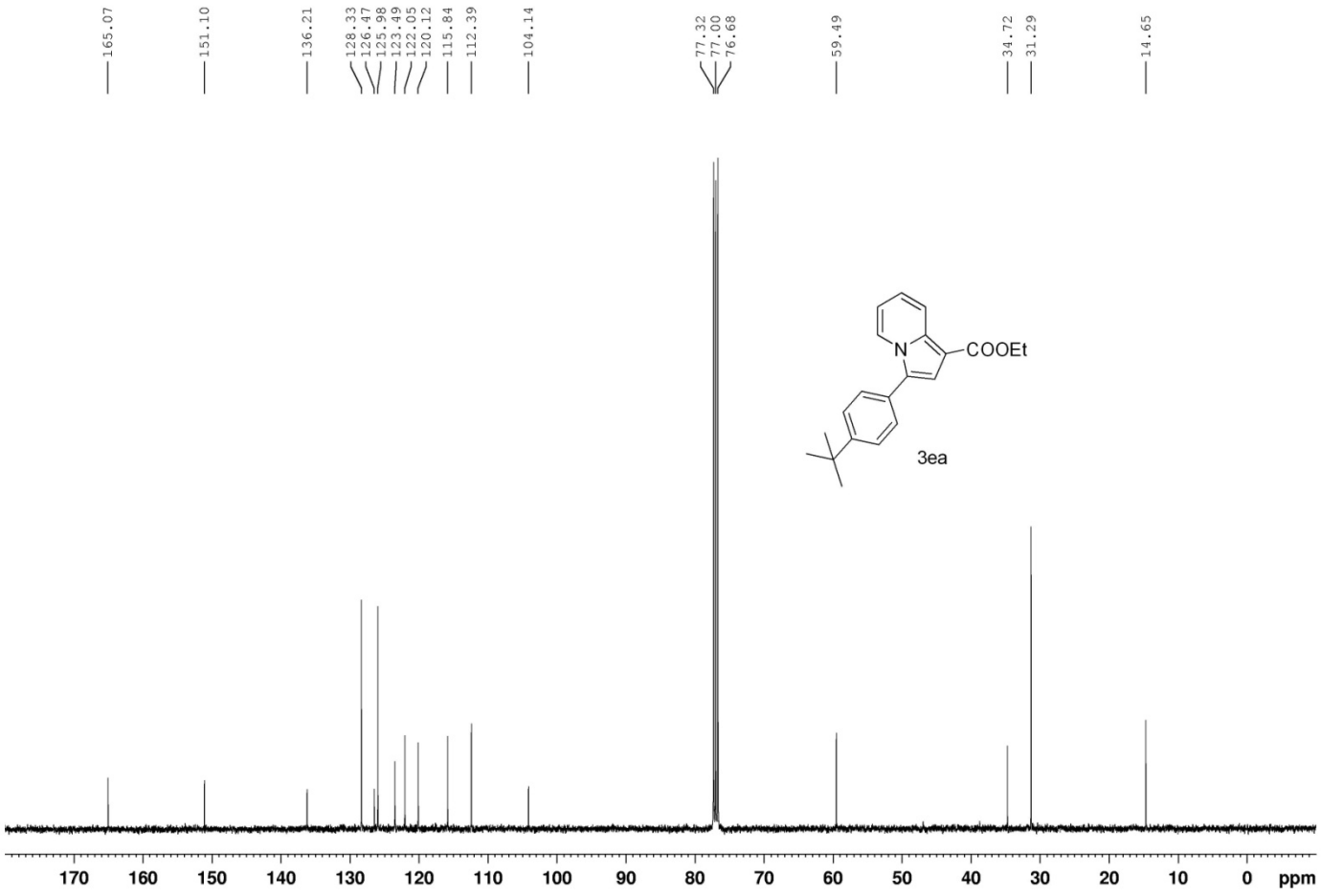

8.232
8.214
8.194
8.171
7.327
7.309
7.290
7.282
7.259
7.216
7.184
7.149
7.131
7.007
6.990
6.985
6.968
6.638
6.621
6.606
6.604
4.341
4.323
4.305
4.288
2.352
1.363
1.345
1.327
0.000
N
COOEt
3ca
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.96
2.98
0.95
0.98
1.02
0.99
2.00
2.98
3.05

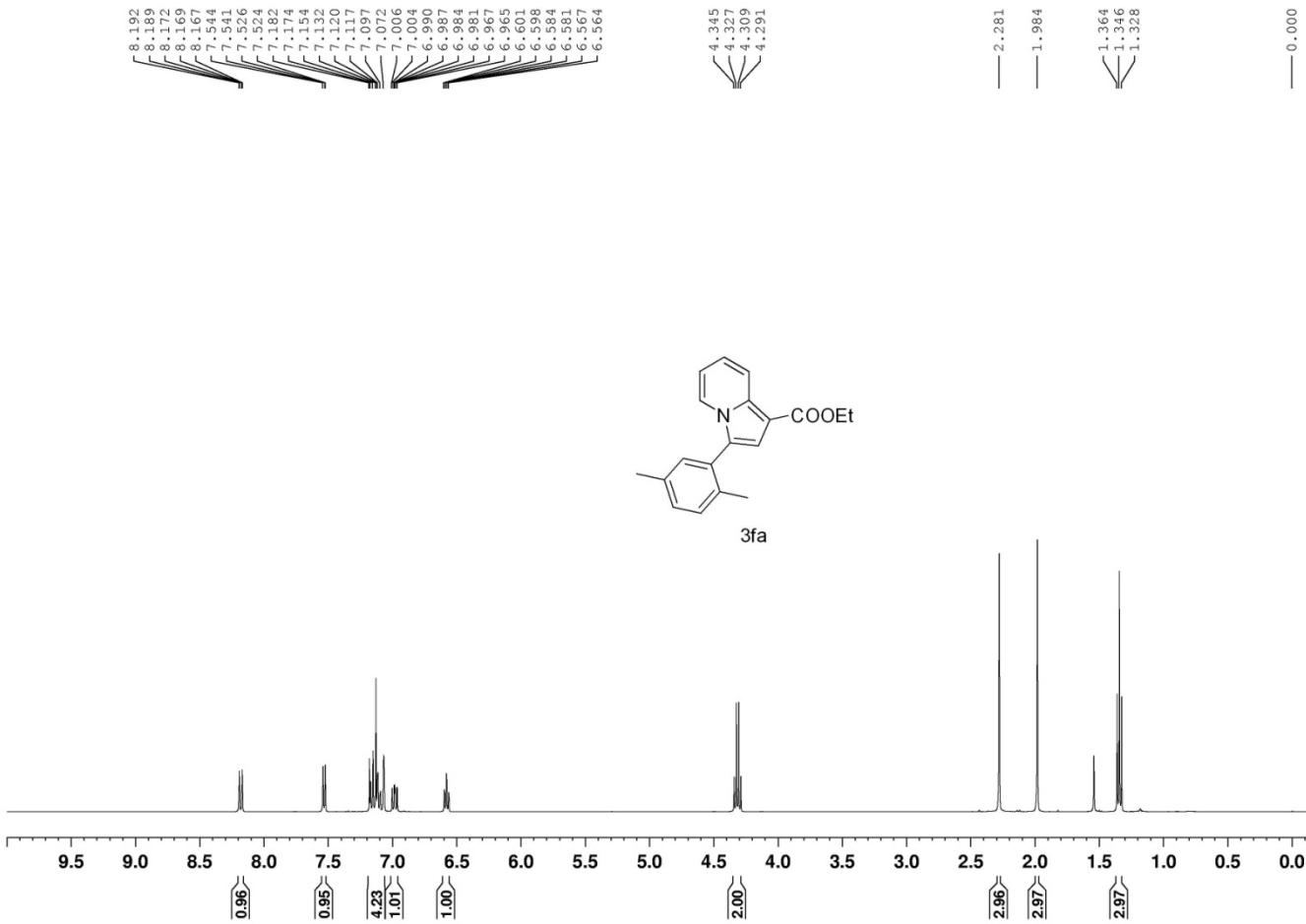

165.07
138.85
136.31
131.20
129.35
128.94
128.79
126.59
125.61
123.47
122.13
120.16
116.00
112.50
104.20
77.34
77.02
76.70
59.52
21.49
14.67
N
COOEt
3ca
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

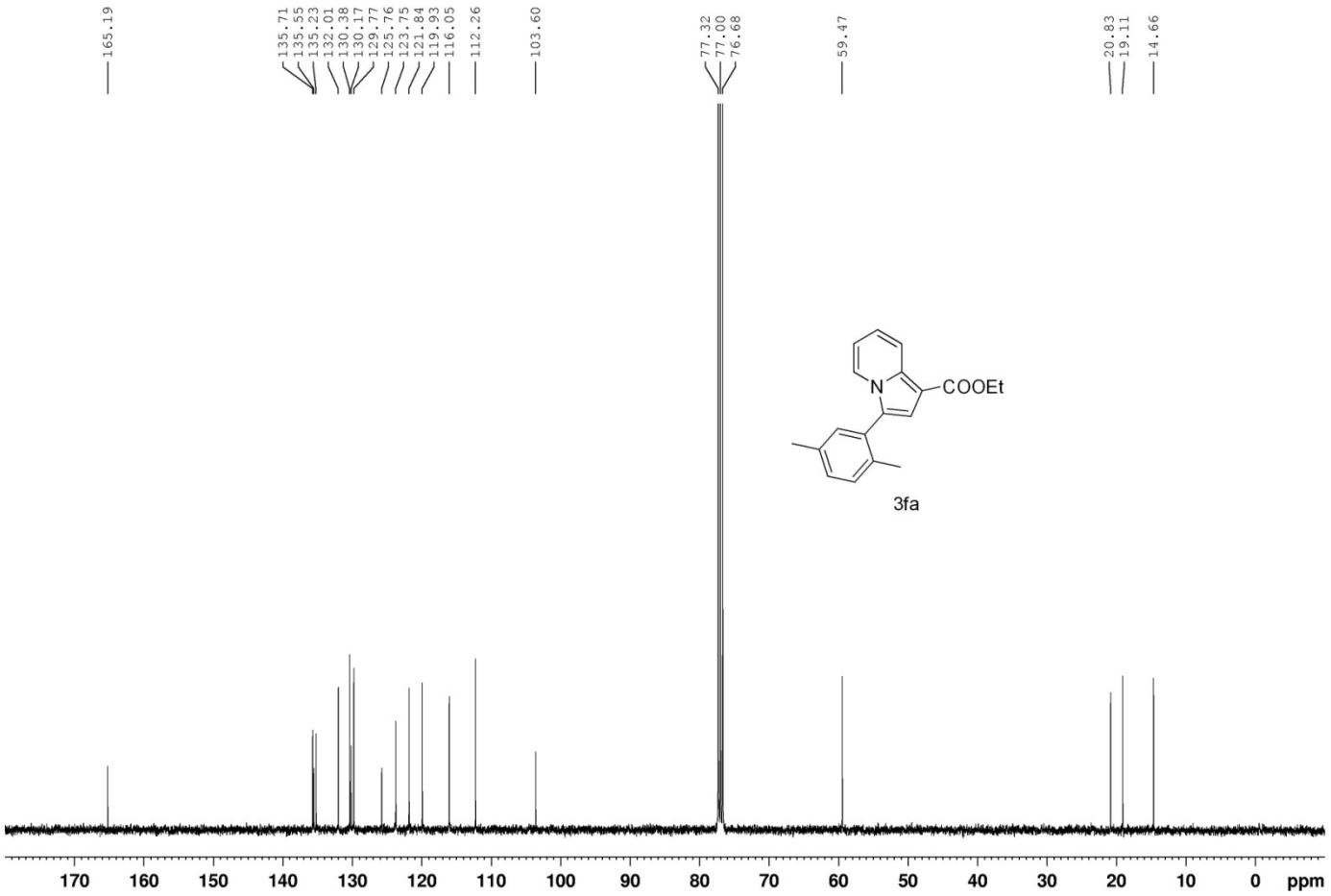

8.195
8.178
8.168
7.367
7.347
7.239
7.220
7.198
7.186
7.000
6.984
6.978
6.976
6.961
6.629
6.609
6.595
6.592
4.342
4.324
4.307
4.289
2.356
1.362
1.345
1.327
0.000
N
COOEt
3da
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.98
1.99
3.52
1.02
0.97
2.00
2.96
3.08

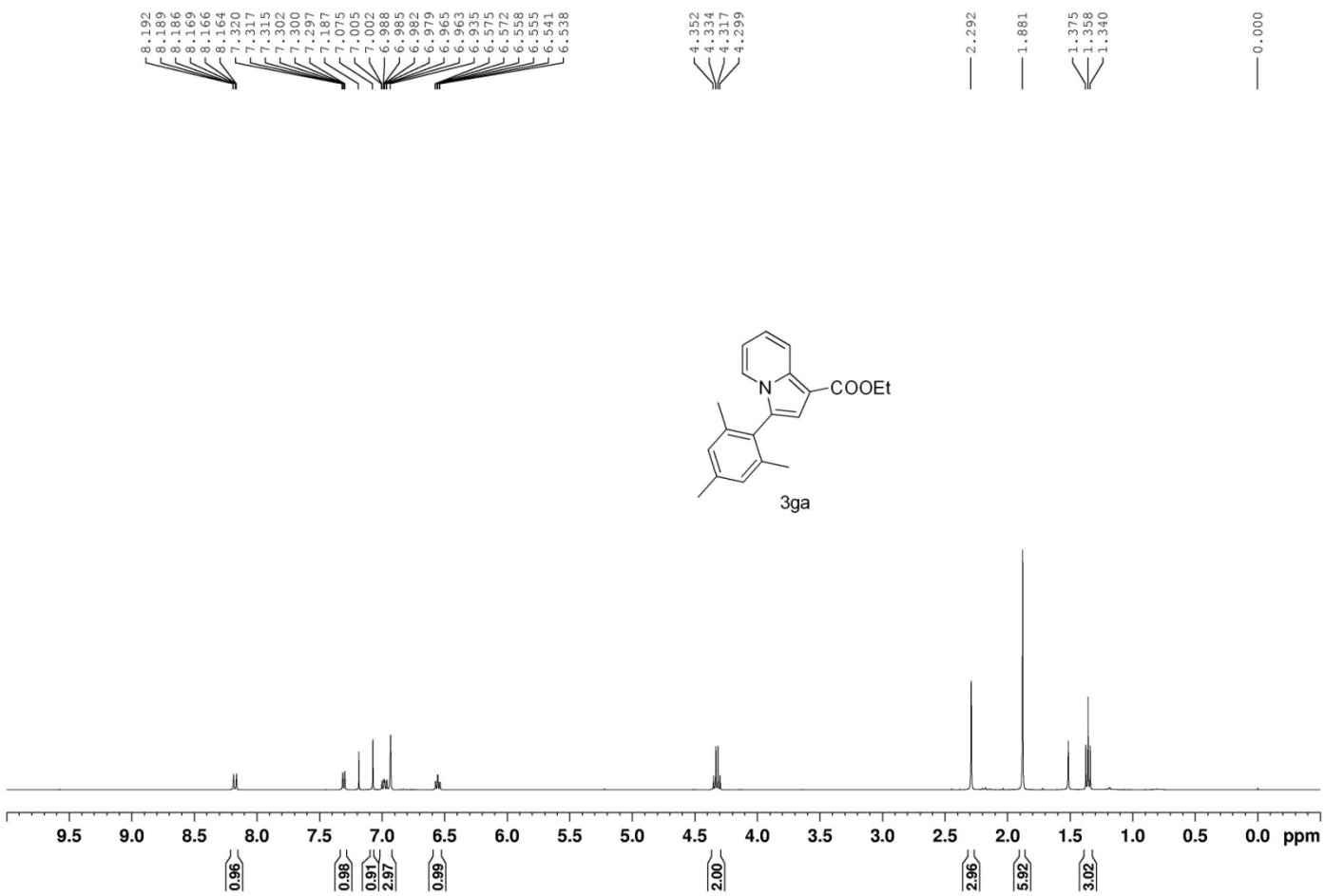

165.07
137.95
136.21
129.75
128.59
128.33
126.49
123.39
122.02
120.14
115.80
112.43
104.13
77.32
77.00
76.68
59.49
21.29
14.66
N
COOEt
3da
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

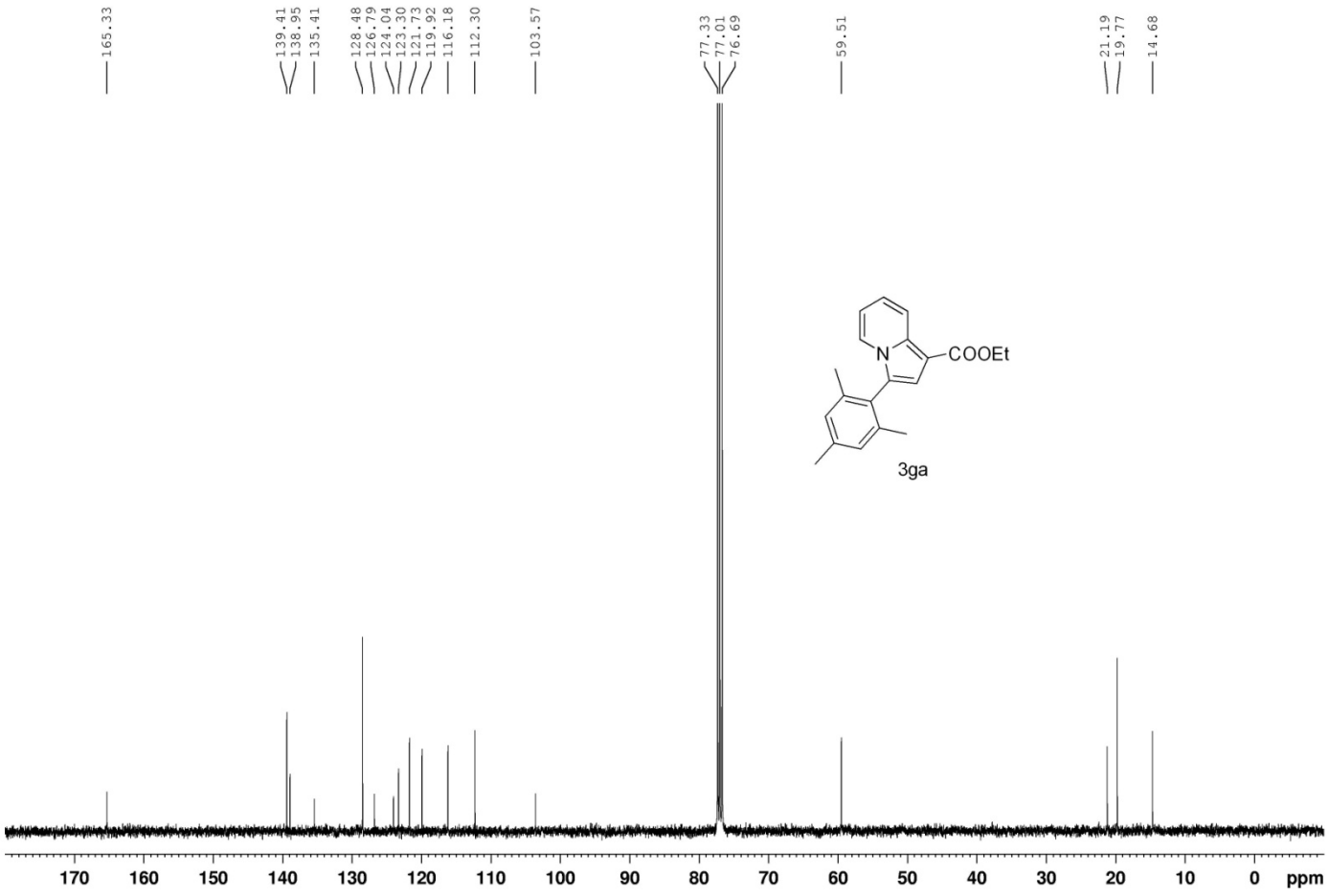

8.238
8.220
8.189
8.166
7.452
7.436
7.430
7.410
7.405
7.389
7.208
6.999
6.997
6.982
6.980
6.976
6.974
6.960
6.957
6.626
6.623
6.609
6.606
6.592
6.589
4.341
4.323
4.305
4.288
1.360
1.343
1.325
1.306
0.000
N
COOEt
3ea
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.95
3.92
0.90
0.99
0.98
2.00
3.02
8.80

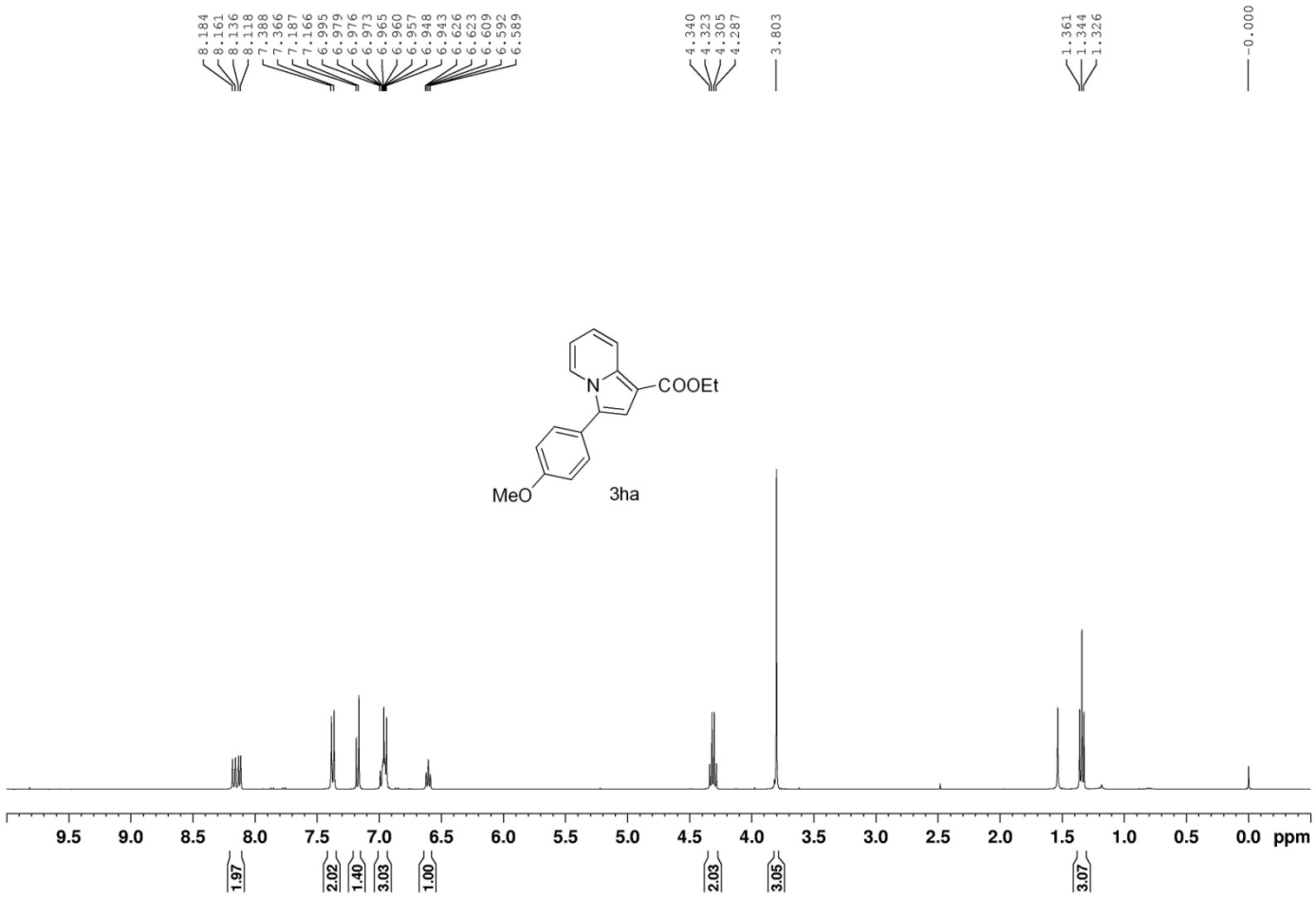

165.07
151.10
136.21
128.33
126.47
125.98
123.49
122.05
120.12
115.84
112.39
104.14
77.32
77.00
76.68
59.49
34.72
31.29
14.65
N
COOEt
3ea
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

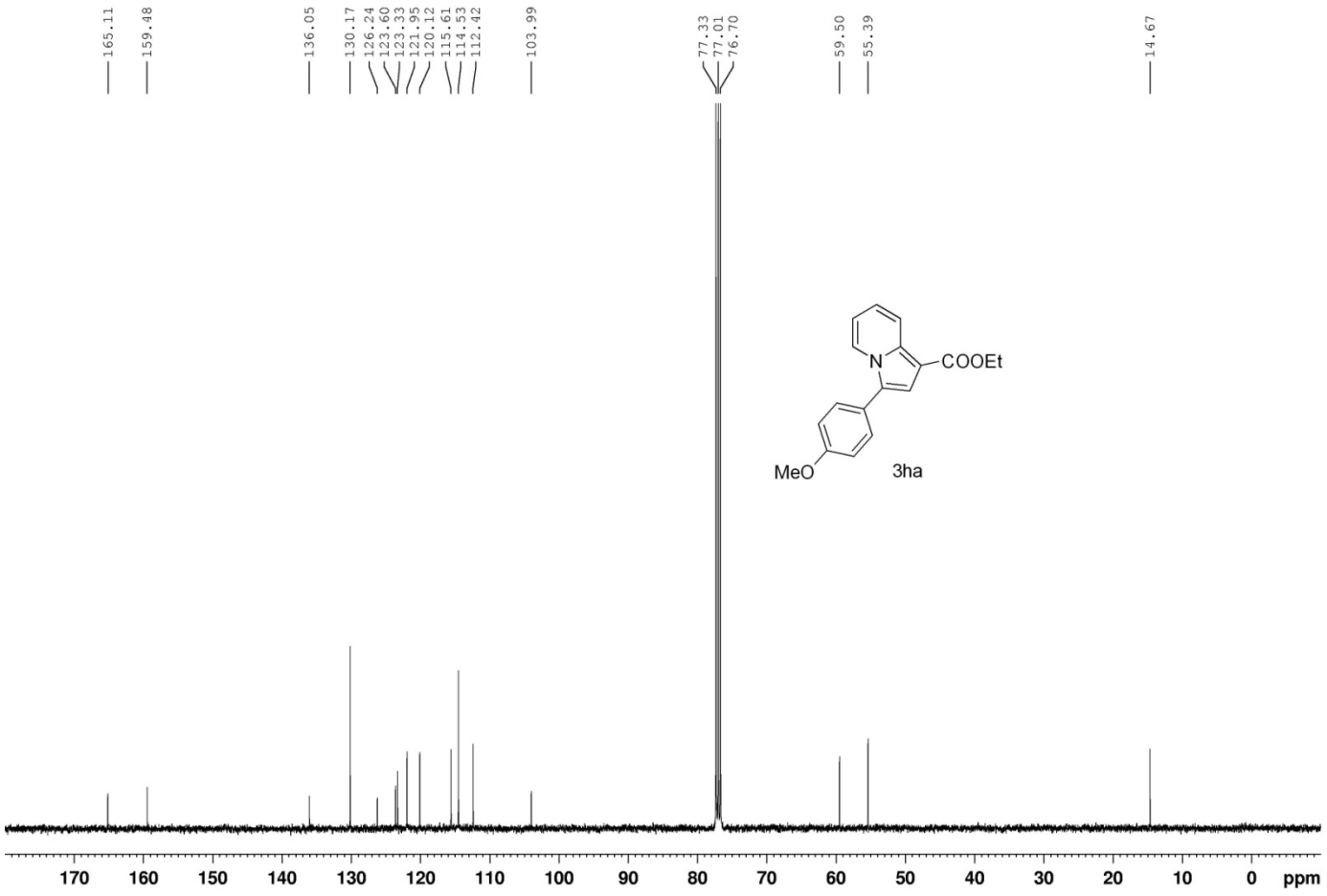

8.192
8.189
8.172
8.169
8.167
7.544
7.541
7.526
7.524
7.182
7.174
7.154
7.132
7.120
7.117
7.097
7.072
7.006
7.004
6.990
6.987
6.984
6.981
6.967
6.965
6.601
6.598
6.584
6.581
6.567
6.564
4.345
4.327
4.309
4.291
2.281
1.984
1.364
1.346
1.328
0.000
N
COOEt
3fa
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
0.96
0.95
4.23
1.01
1.00
2.00
2.96
2.97
2.97

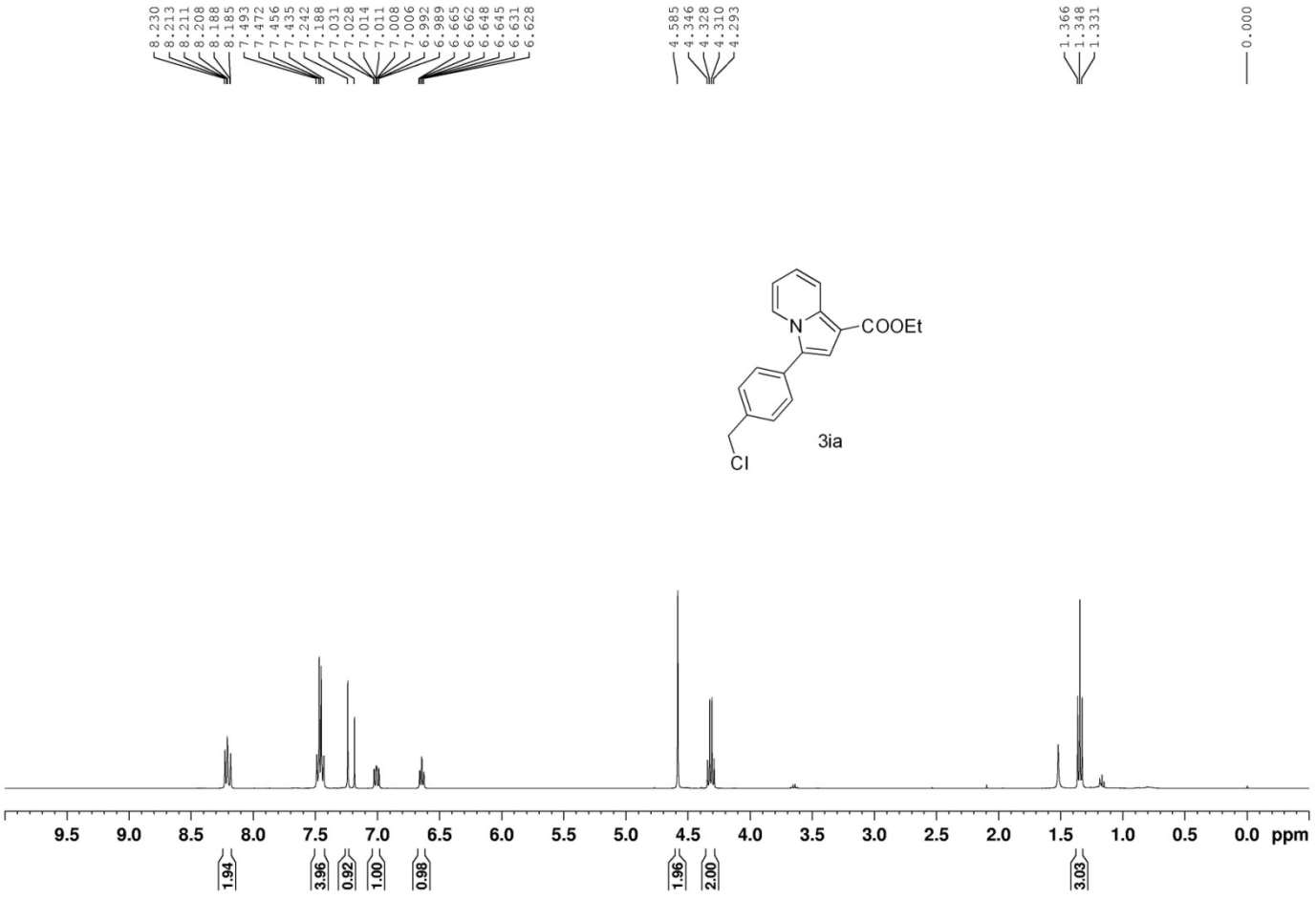

165.19
135.71
135.55
135.23
132.01
130.38
130.17
129.77
125.76
123.75
121.84
119.93
116.05
112.26
103.60
77.32
77.00
76.68
59.47
20.83
19.11
14.66
N
COOEt
3fa
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

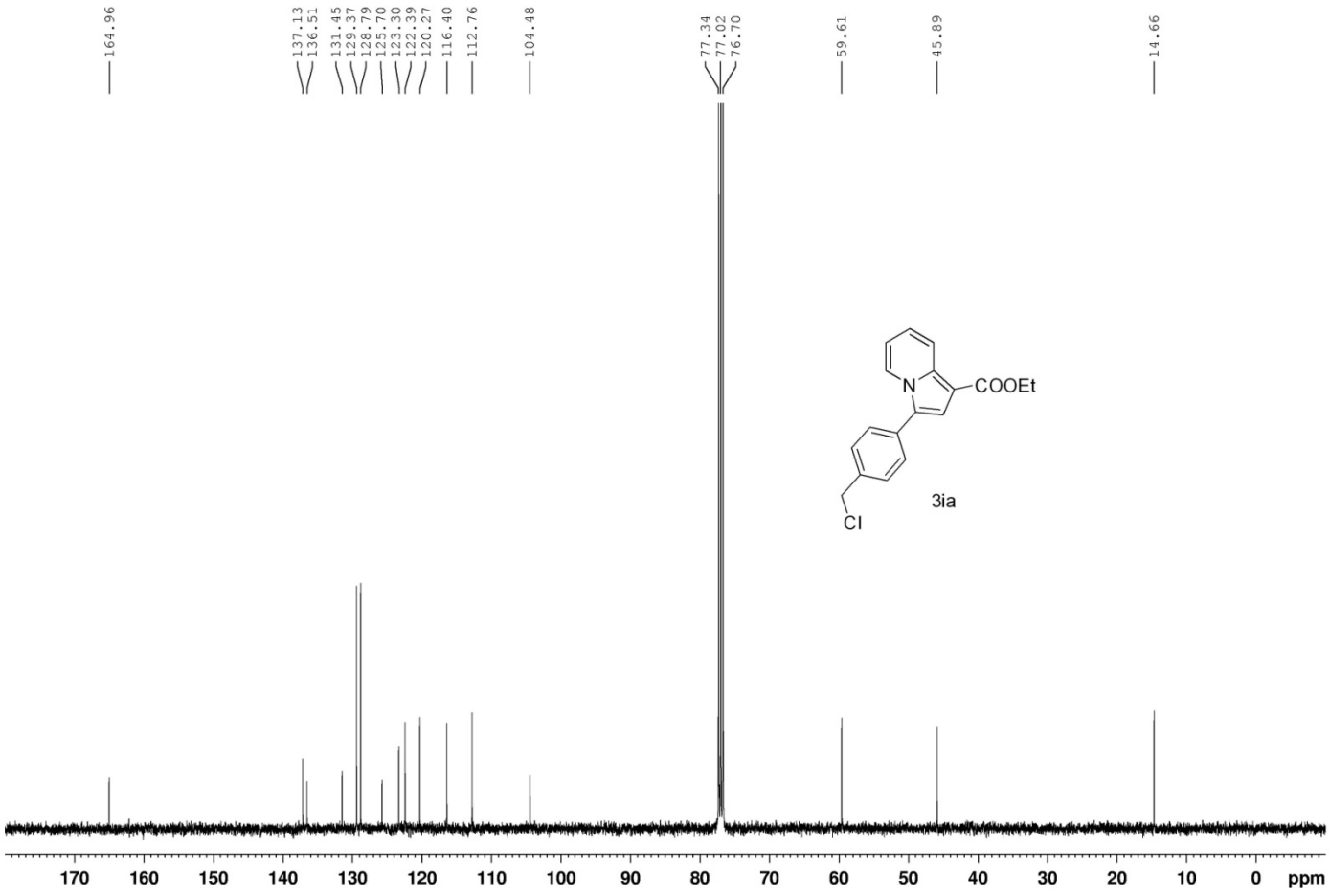

8.192
8.189
8.186
8.169
8.166
8.164
7.320
7.317
7.315
7.302
7.300
7.297
7.187
7.075
7.005
7.002
6.988
6.985
6.982
6.979
6.965
6.963
6.935
6.575
6.572
6.558
6.555
6.541
6.538
4.352
4.334
4.317
4.299
2.292
1.881
1.375
1.358
1.340
0.000
N
COOEt
3ga
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
0.96
0.98
0.91
2.97
0.99
2.00
2.96
5.92
3.02

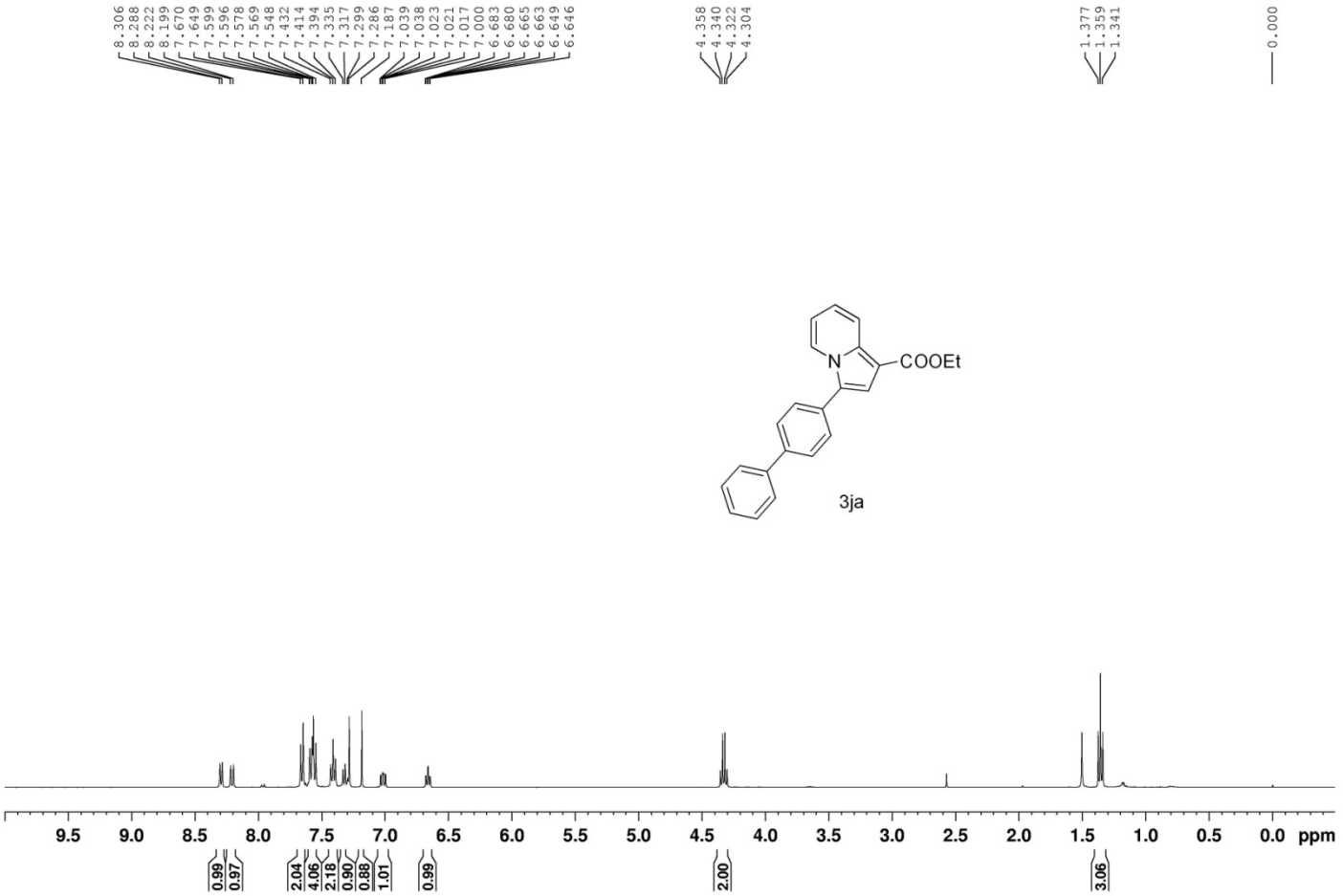

165.33
139.41
138.95
135.41
128.48
126.79
124.04
123.30
121.73
119.92
116.18
112.30
103.57
77.33
77.01
76.69
59.51
21.19
19.77
14.68
N
COOEt
3ga
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

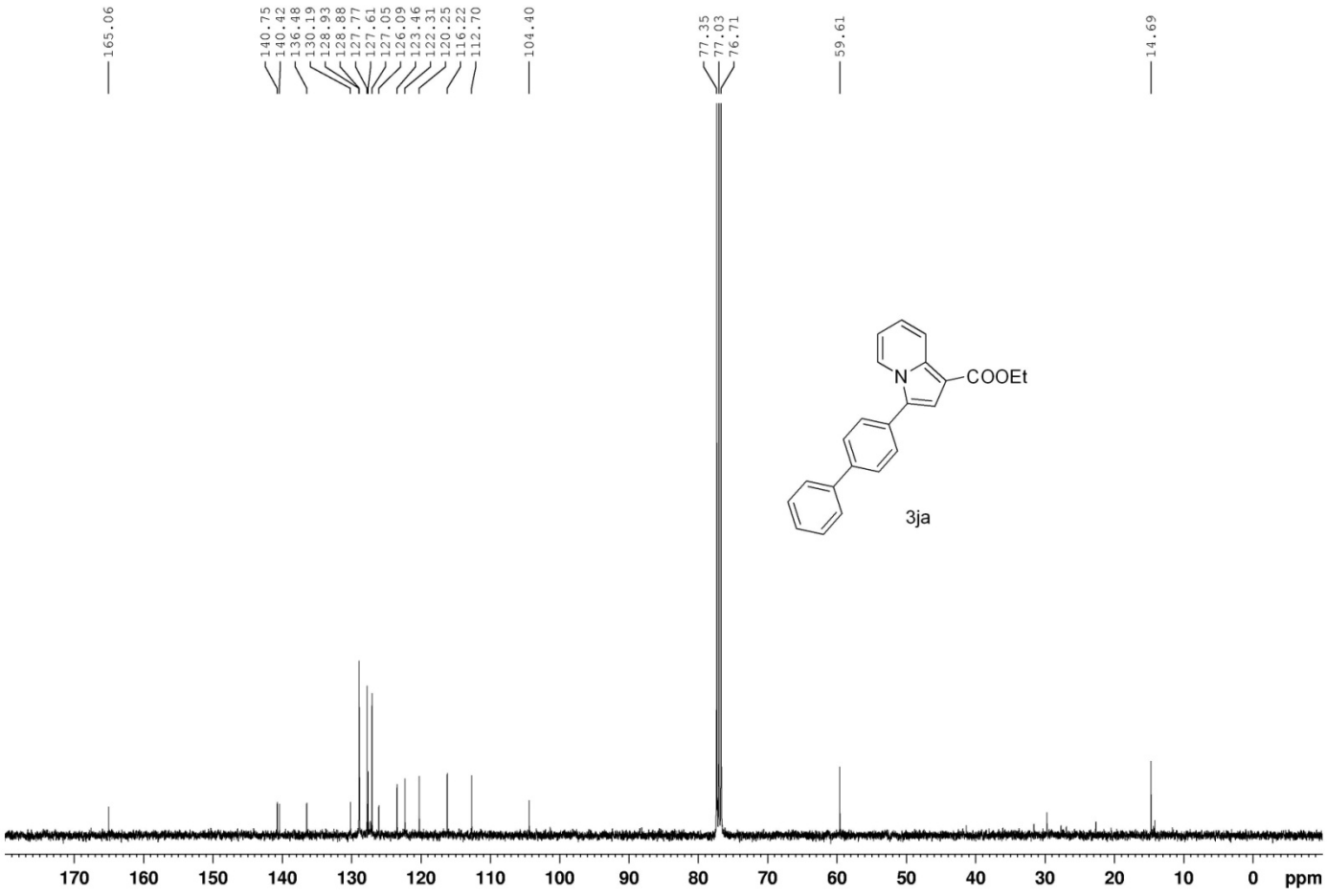

8.184
8.161
8.136
8.118
7.388
7.366
7.187
7.166
6.995
6.979
6.976
6.973
6.965
6.960
6.957
6.948
6.943
6.626
6.623
6.609
6.592
6.589
4.340
4.323
4.305
4.287
3.803
1.361
1.344
1.326
-0.000
N
COOEt
MeO
3ha
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.97
2.02
1.40
3.03
1.00
2.03
3.05
3.07

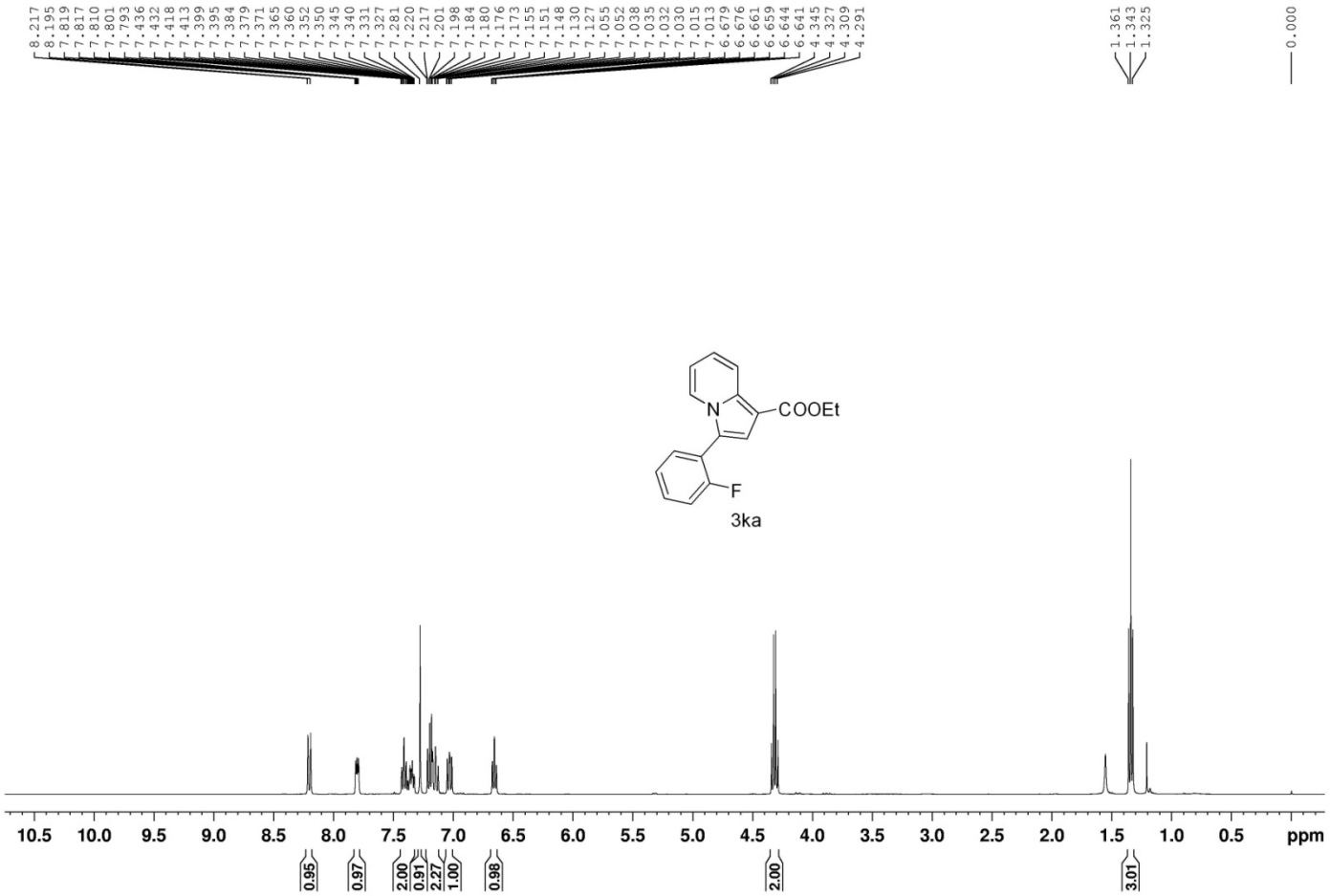

165.11
159.48
136.05
130.17
126.24
123.60
123.33
121.95
120.12
115.61
114.53
112.42
103.99
77.33
77.01
76.70
59.50
55.39
14.67
N
COOEt
MeO
3ha
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

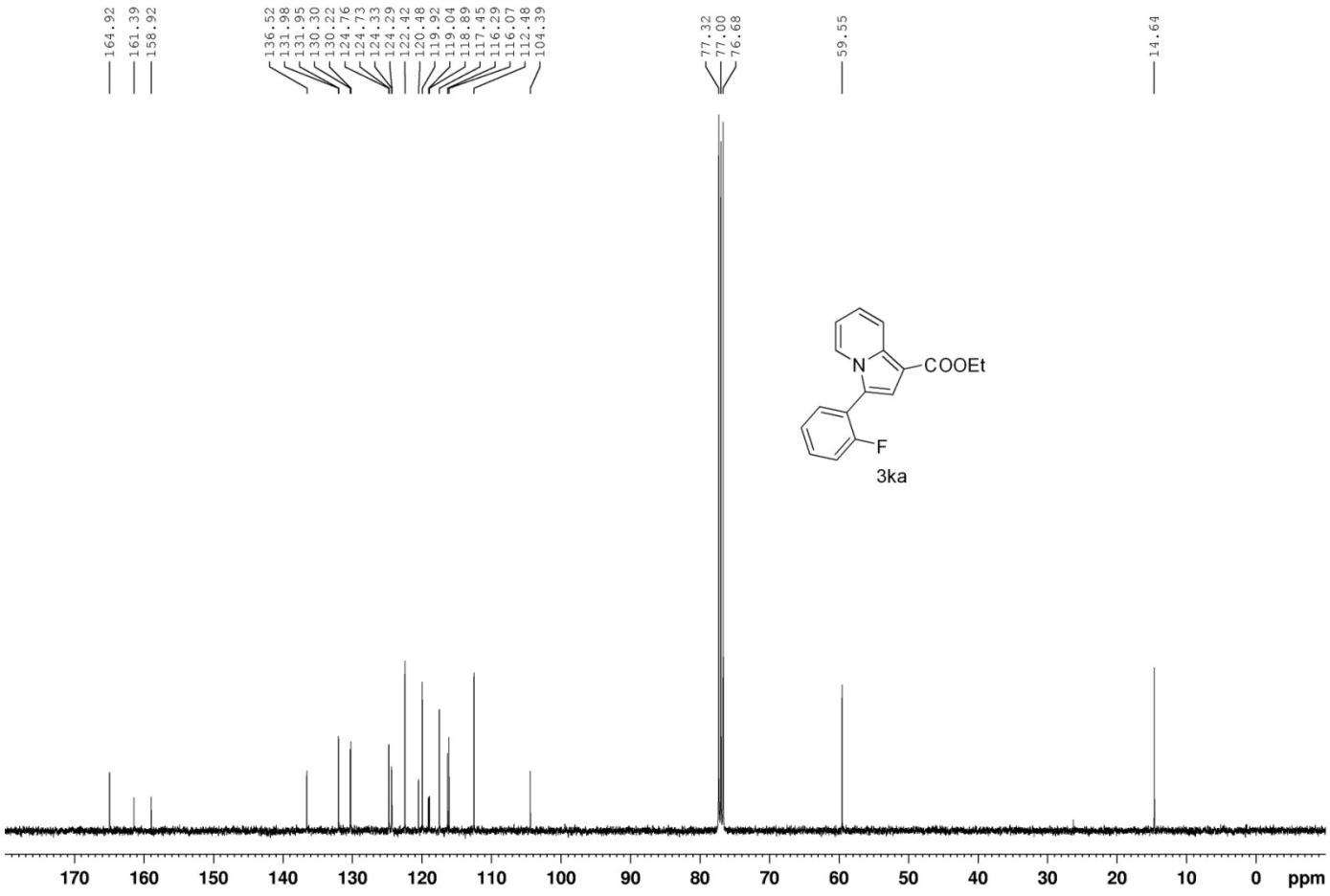

8.230
8.213
8.211
8.208
8.188
8.185
7.493
7.472
7.456
7.435
7.242
7.188
7.031
7.028
7.014
7.011
7.008
7.006
6.992
6.989
6.665
6.662
6.648
6.645
6.631
6.628
4.585
4.346
4.328
4.310
4.293
1.366
1.348
1.331
0.000
N
COOEt
Cl
3ia
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.94
3.96
0.92
1.00
0.98
1.96
2.00
3.03

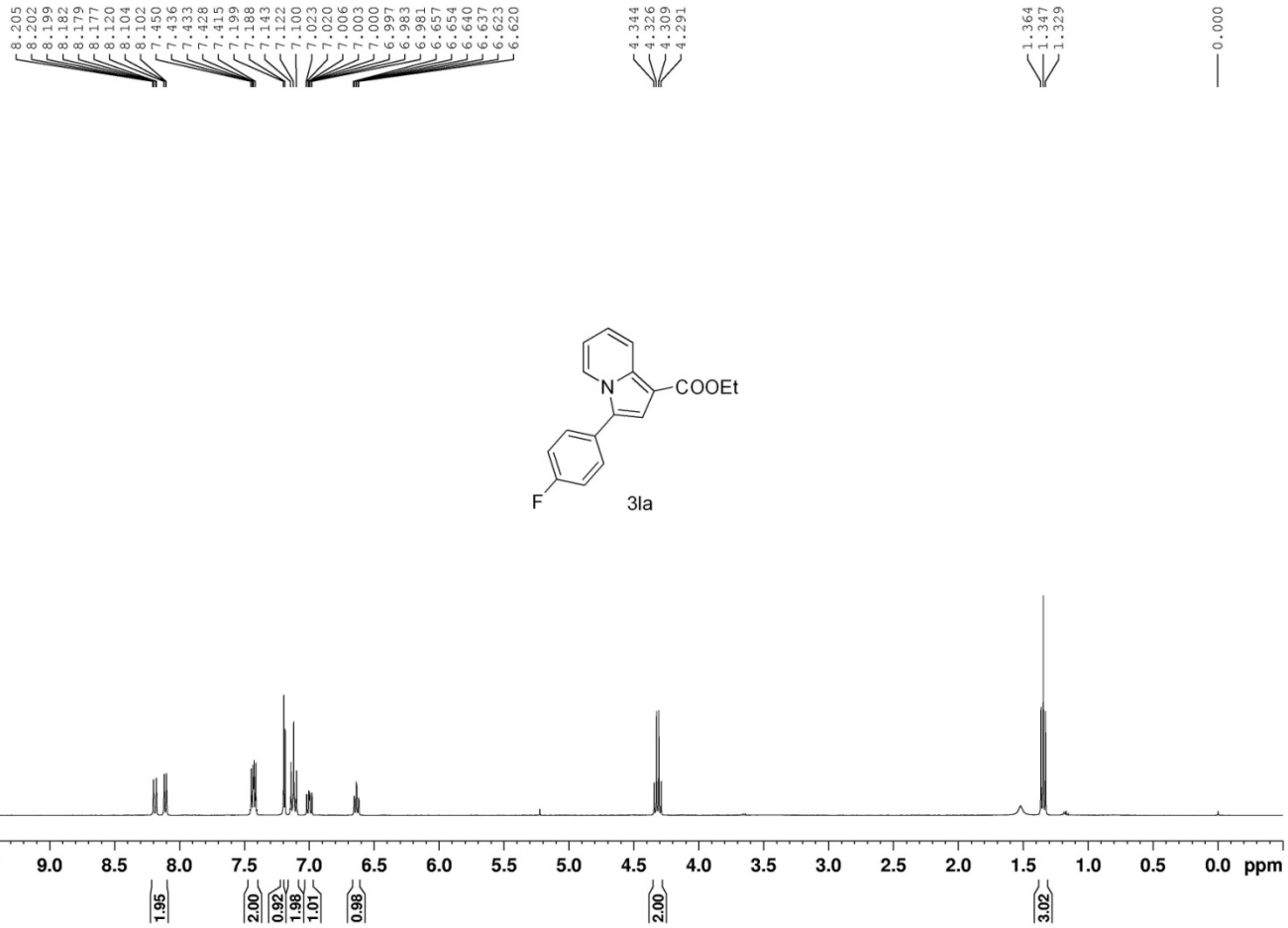

164.96
137.13
136.51
131.45
129.37
128.79
125.70
123.30
122.39
120.27
116.40
112.76
104.48
77.34
77.02
76.70
59.61
45.89
14.66
N
COOEt
Cl
3ia
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

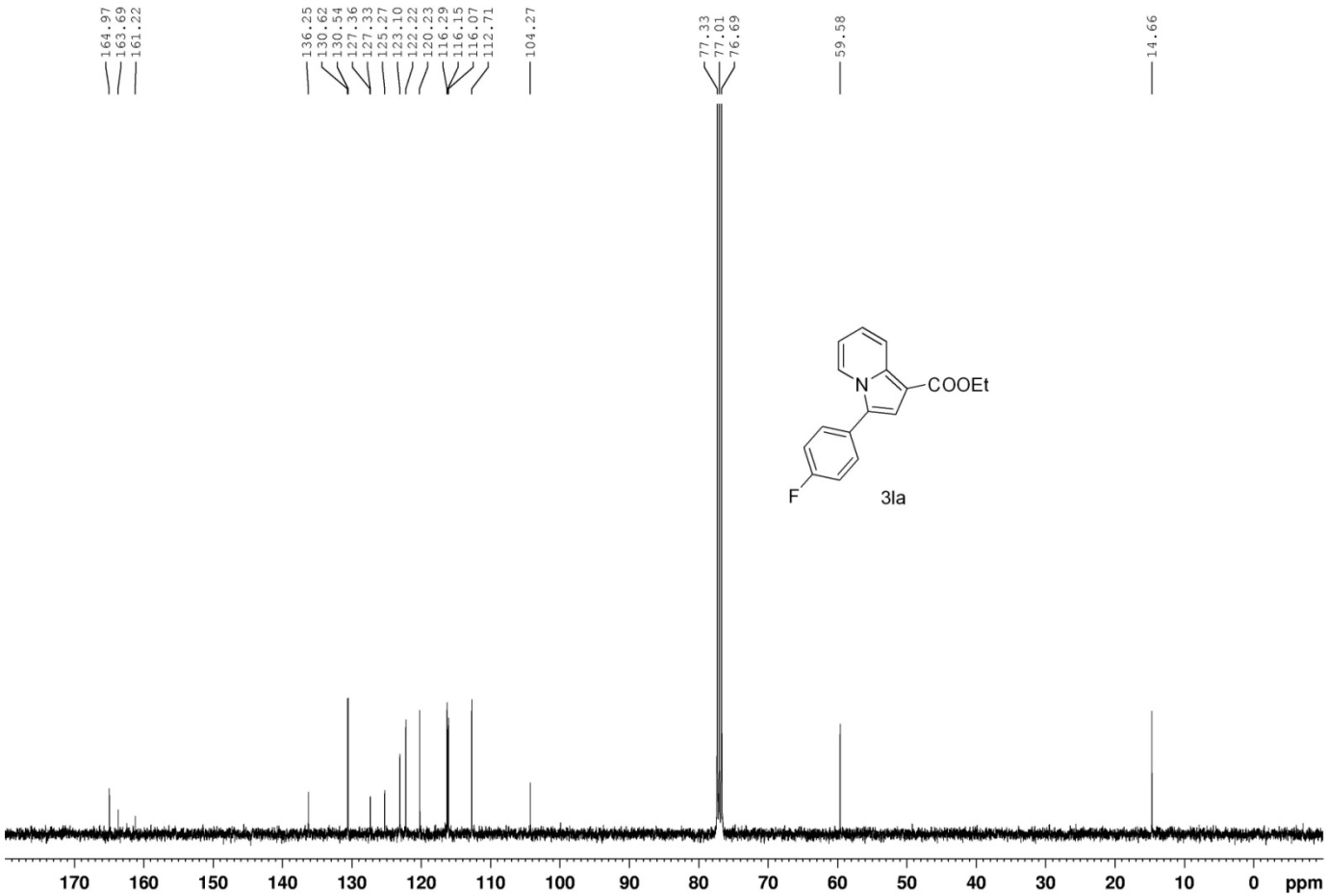

8.306
8.288
8.222
8.199
7.670
7.649
7.599
7.596
7.578
7.569
7.548
7.432
7.414
7.394
7.335
7.317
7.299
7.286
7.187
7.039
7.038
7.023
7.021
7.017
7.000
6.683
6.680
6.665
6.663
6.649
6.646
4.358
4.340
4.322
4.304
1.377
1.359
1.341
0.000
N
COOEt
3ja
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
0.99
0.97
2.04
4.06
2.18
0.90
0.88
1.01
0.99
2.00
3.06

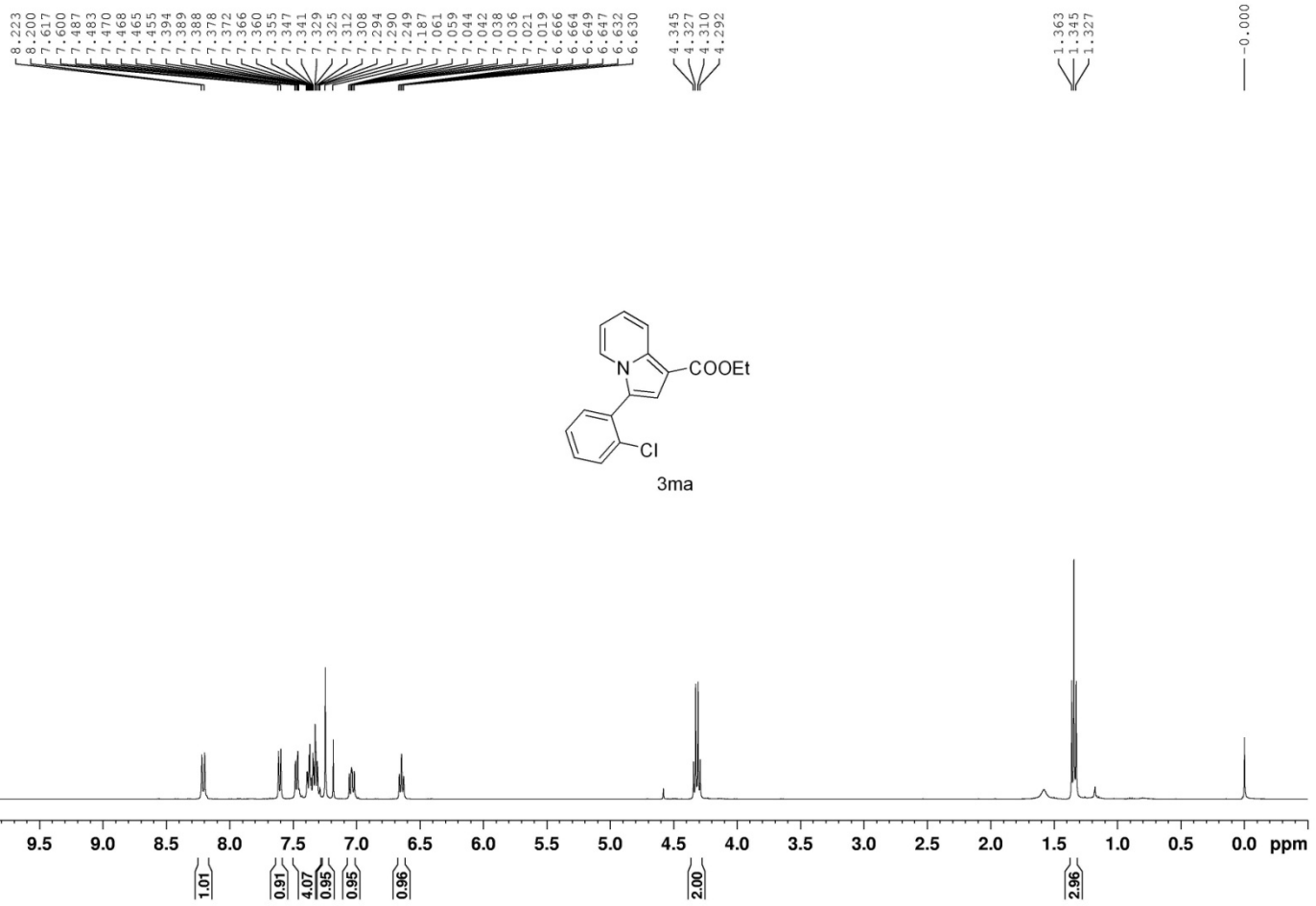

165.06
140.75
140.42
136.48
130.19
128.93
128.88
127.77
127.61
127.05
126.09
123.46
122.31
120.25
116.22
112.70
104.40
77.35
77.03
76.71
59.61
14.69
N
COOEt
3ja
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

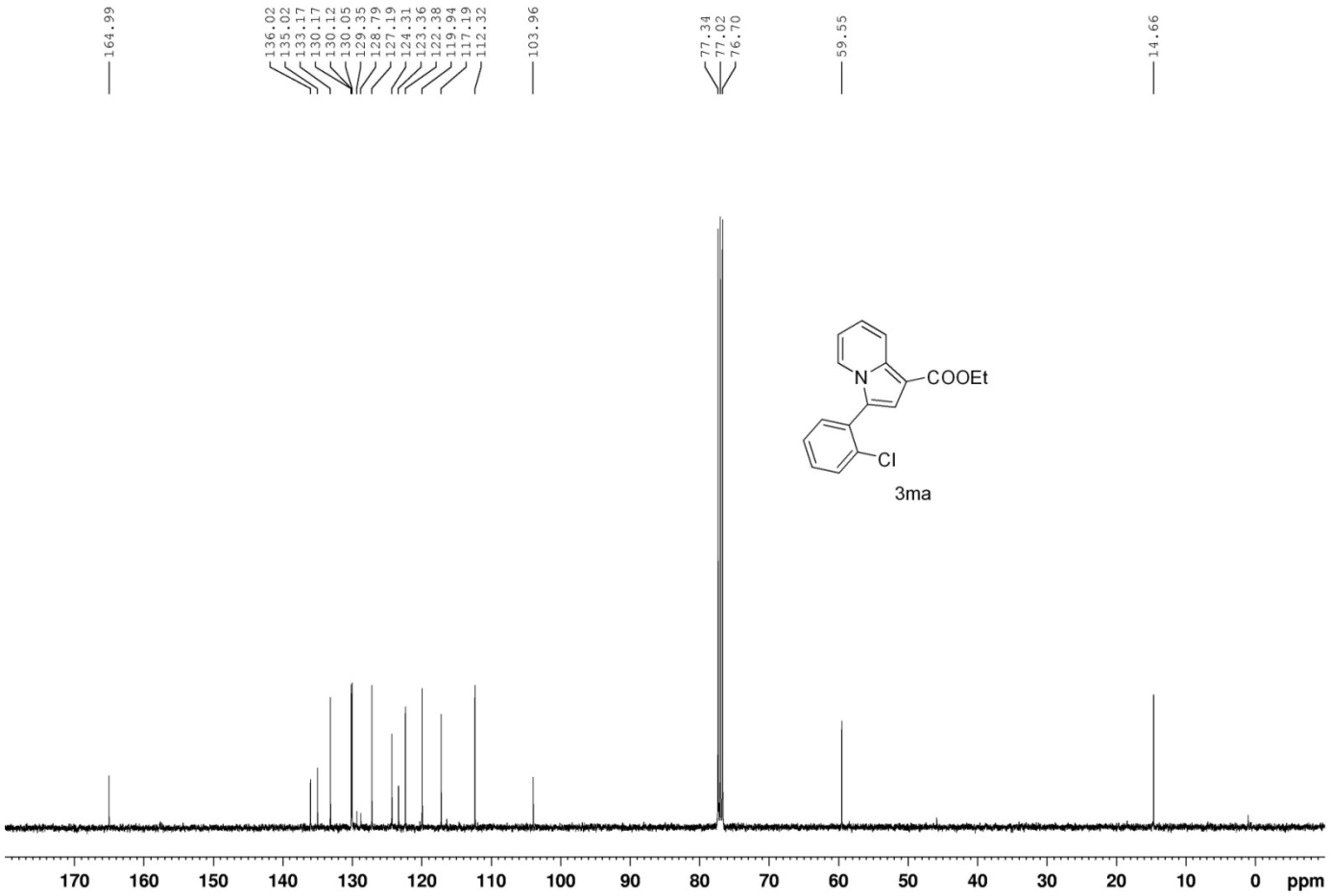

8.217
8.195
7.819
7.817
7.810
7.801
7.793
7.436
7.432
7.418
7.413
7.399
7.395
7.384
7.379
7.371
7.365
7.360
7.352
7.350
7.345
7.340
7.331
7.327
7.281
7.220
7.217
7.201
7.198
7.184
7.180
7.176
7.173
7.155
7.151
7.148
7.130
7.127
7.055
7.052
7.038
7.035
7.032
7.030
7.015
7.013
6.679
6.676
6.661
6.659
6.644
6.641
4.345
4.327
4.309
4.291
1.361
1.343
1.325
0.000
N
COOEt
F
3ka
10.5
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
ppm
0.95
0.97
2.00
0.91
2.27
1.00
0.98
2.00
3.01

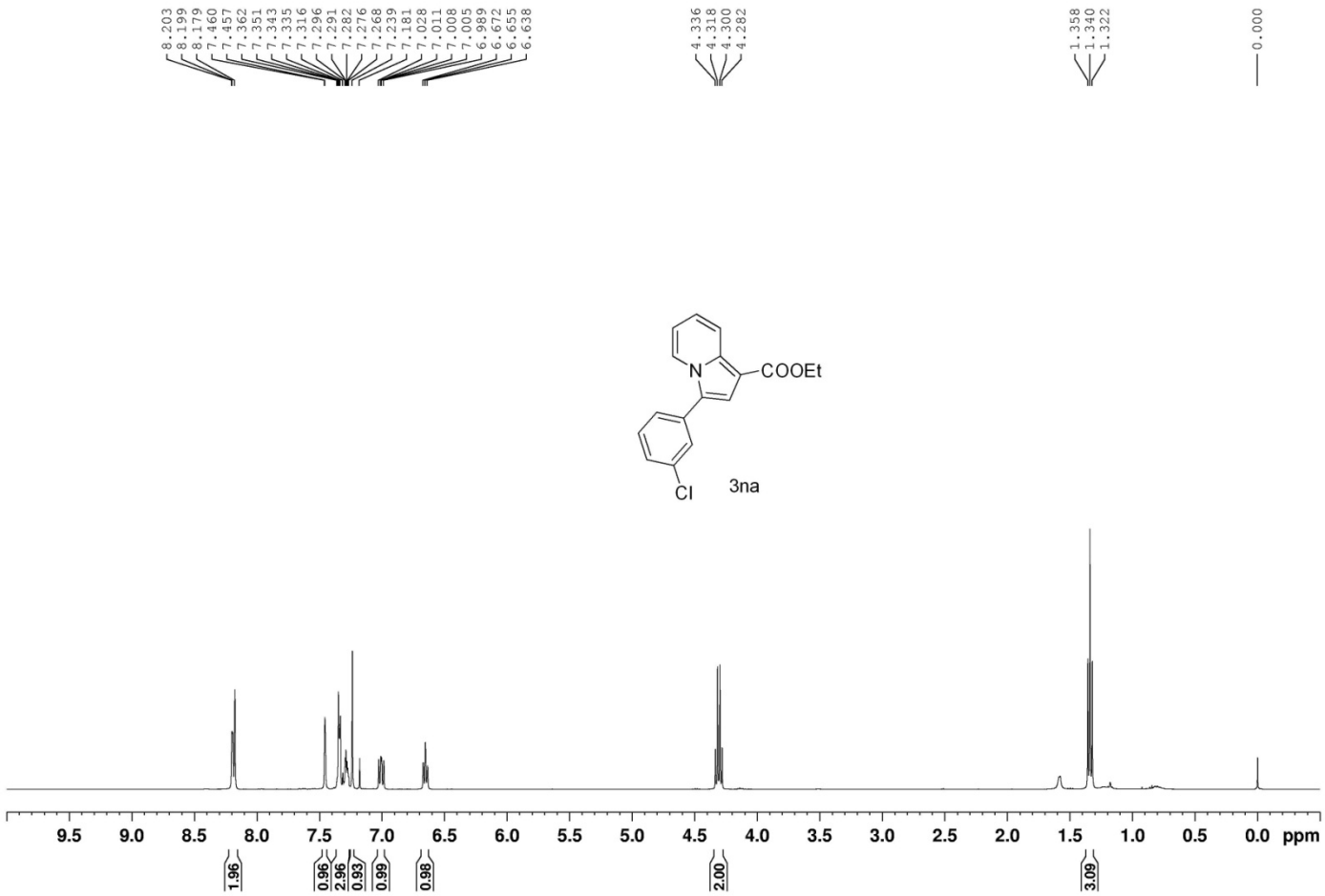

164.92
161.39
158.92
136.52
131.98
131.95
130.30
130.22
124.76
124.73
124.33
124.29
122.42
120.48
119.92
119.04
118.89
117.45
116.29
116.07
112.48
104.39
77.32
77.00
76.68
59.55
14.64
N
COOEt
F
3ka
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

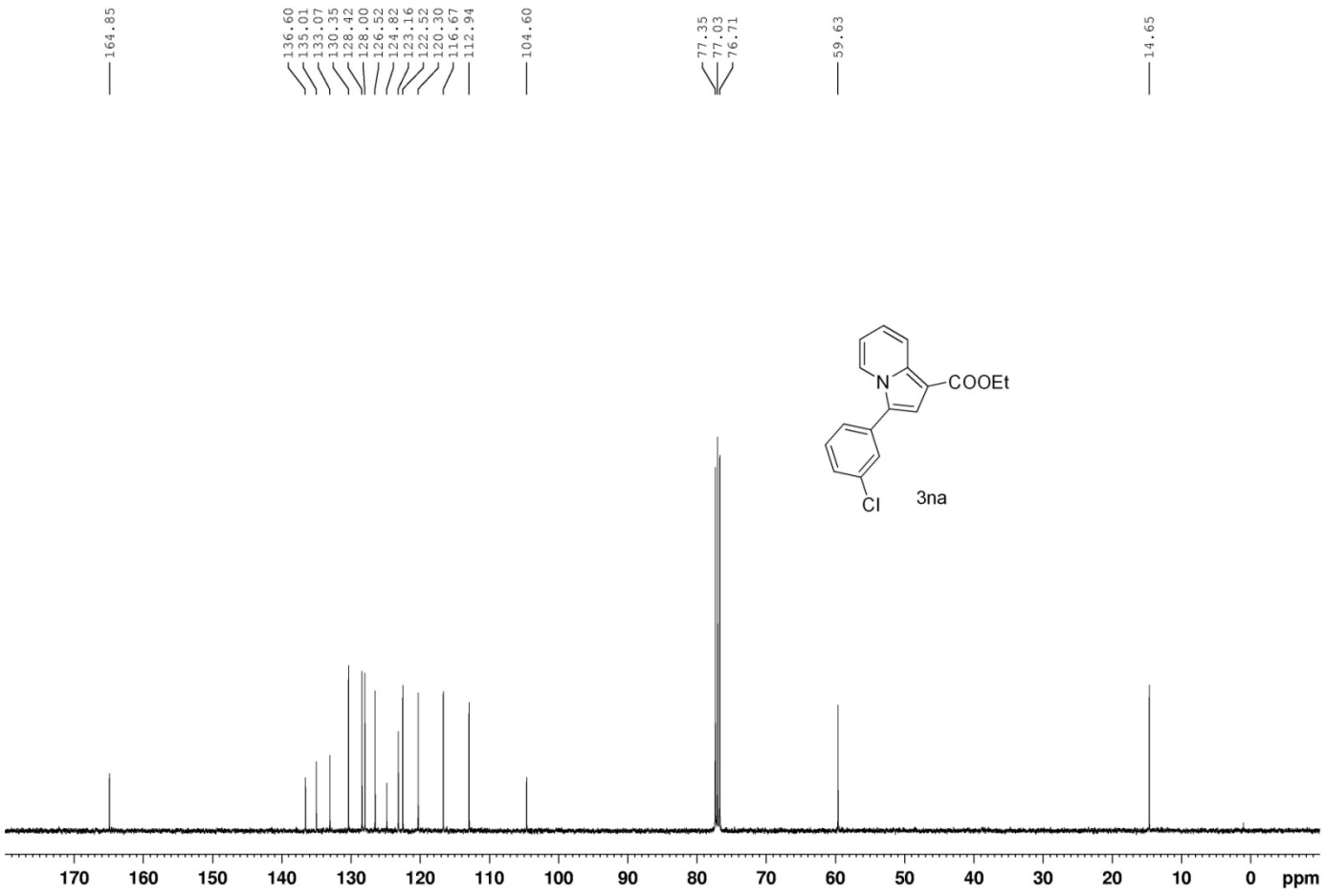

8.205
8.202
8.199
8.182
8.179
8.177
8.120
8.104
8.102
7.450
7.436
7.433
7.428
7.415
7.199
7.188
7.143
7.122
7.100
7.023
7.020
7.006
7.003
7.000
6.997
6.983
6.981
6.657
6.654
6.640
6.637
6.623
6.620
4.344
4.326
4.309
4.291
1.364
1.347
1.329
0.000
N
COOEt
F
3la
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.95
2.00
0.92
1.98
1.01
0.98
2.00
3.02

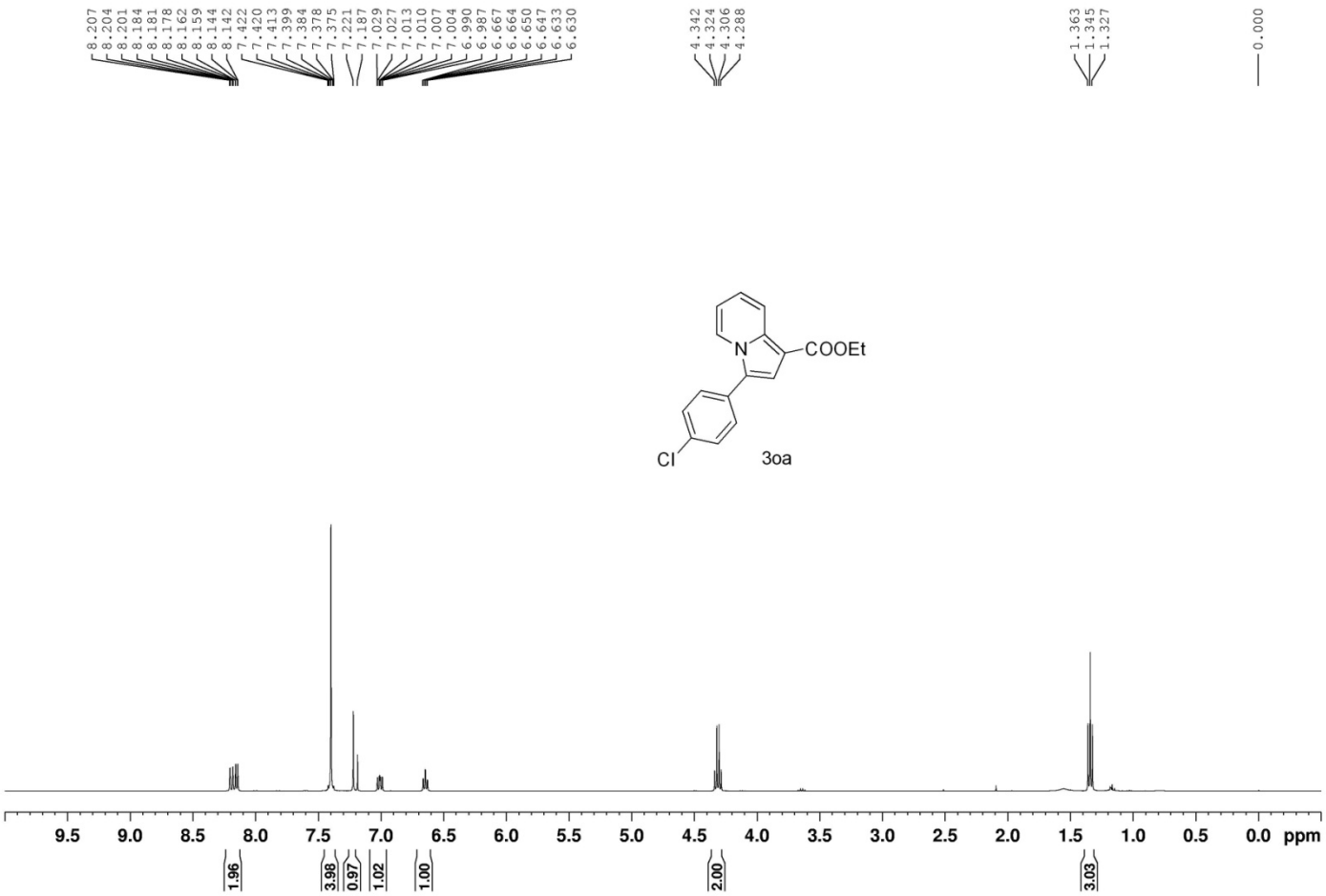

164.97
163.69
161.22
136.25
130.62
130.54
127.36
127.33
125.27
123.10
122.22
120.23
116.29
116.15
116.07
112.71
104.27
77.33
77.01
76.69
59.58
14.66
N
COOEt
F
3la
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

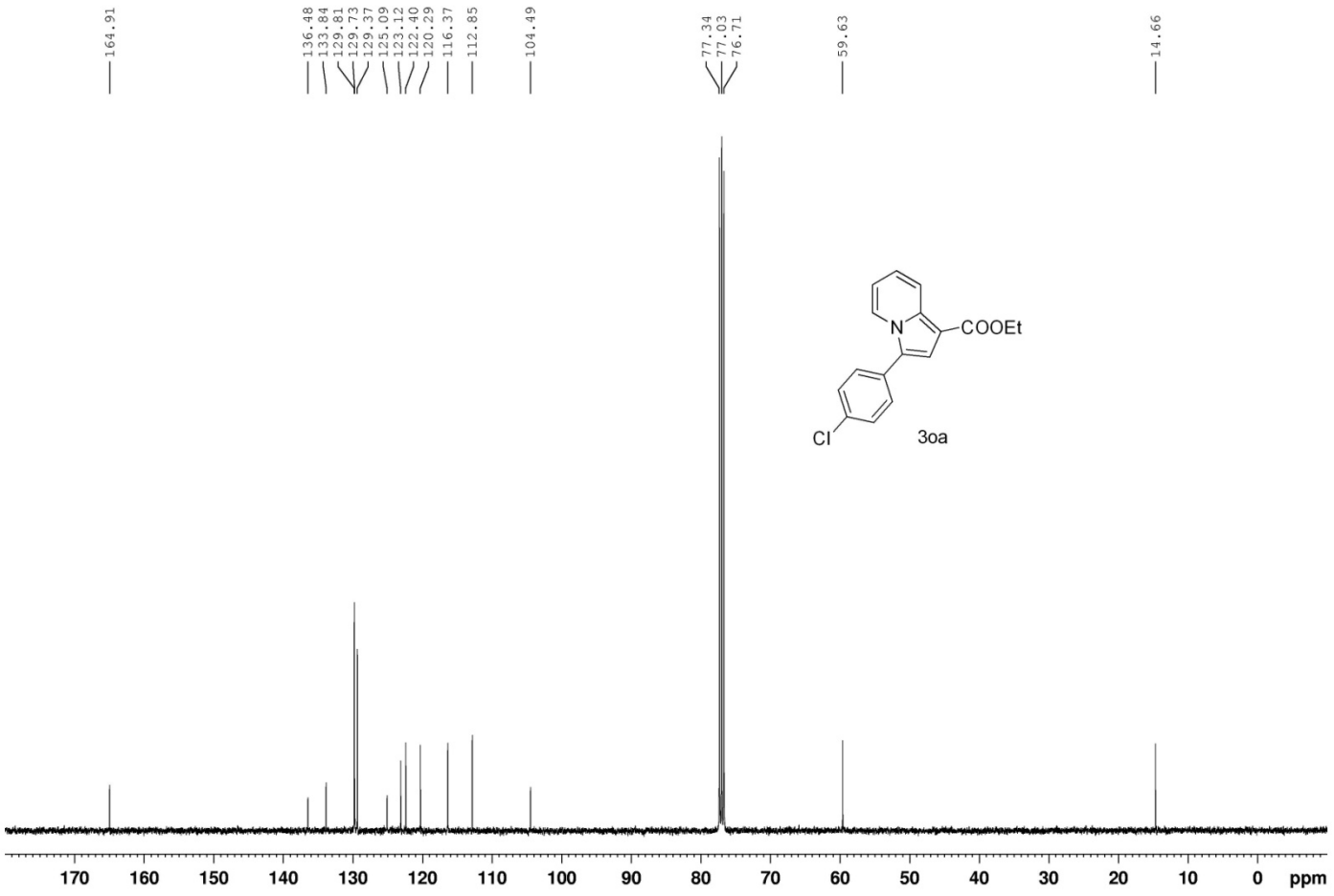

8.223
8.200
7.617
7.600
7.487
7.483
7.470
7.468
7.465
7.455
7.394
7.389
7.388
7.378
7.372
7.366
7.360
7.355
7.347
7.341
7.329
7.325
7.312
7.308
7.294
7.290
7.249
7.187
7.061
7.059
7.044
7.042
7.038
7.036
7.021
7.019
6.666
6.664
6.649
6.647
6.632
6.630
4.345
4.327
4.310
4.292
1.363
1.345
1.327
0.000
N
COOEt
Cl
3ma
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
1.01
0.91
4.07
0.95
0.95
0.96
2.00
2.96

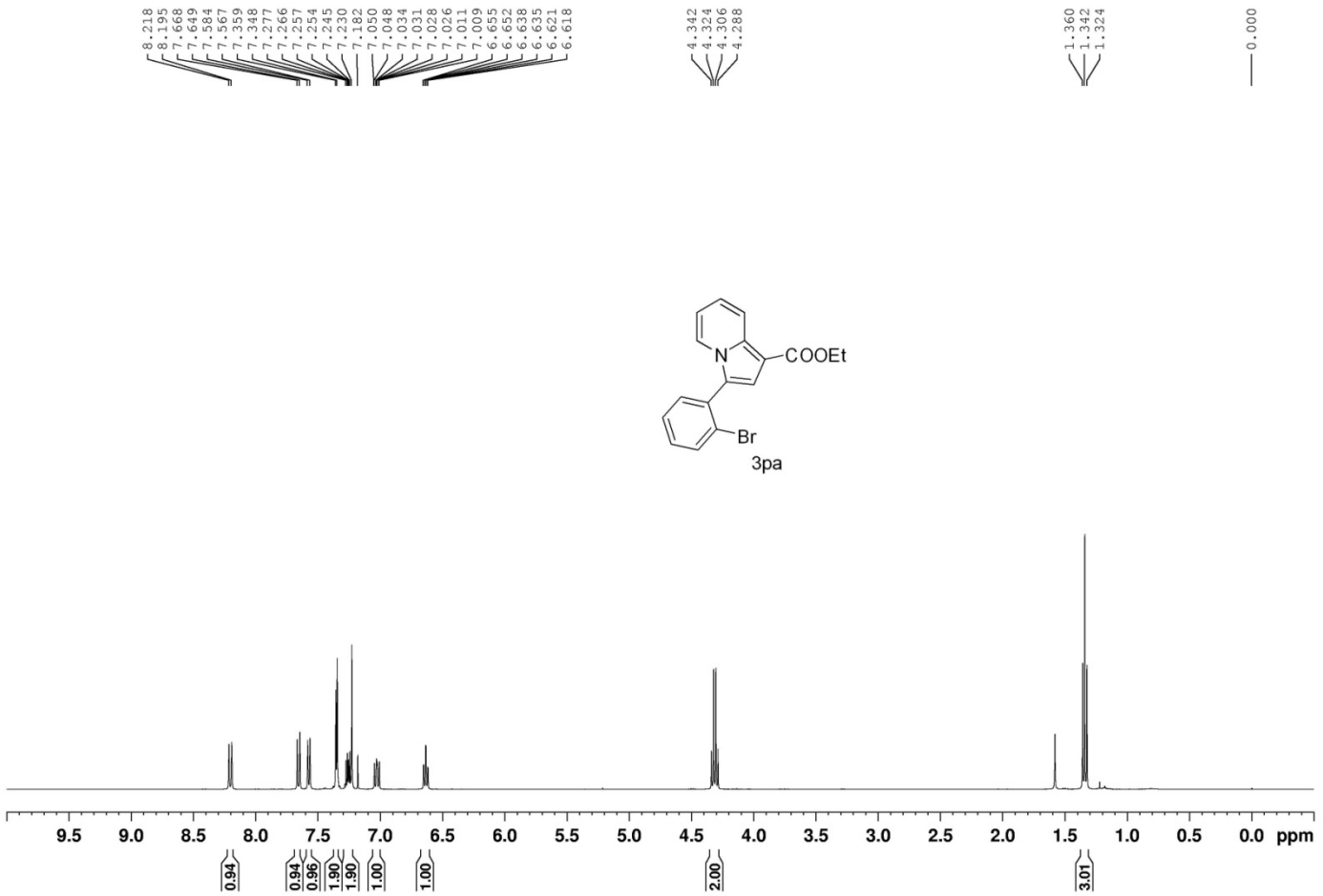

164.99
136.02
135.02
133.17
130.17
130.12
130.05
129.35
128.79
127.19
124.31
123.36
122.38
119.94
117.19
112.32
103.96
77.34
77.02
76.70
59.55
14.66
COOEt
N
Cl
3ma
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

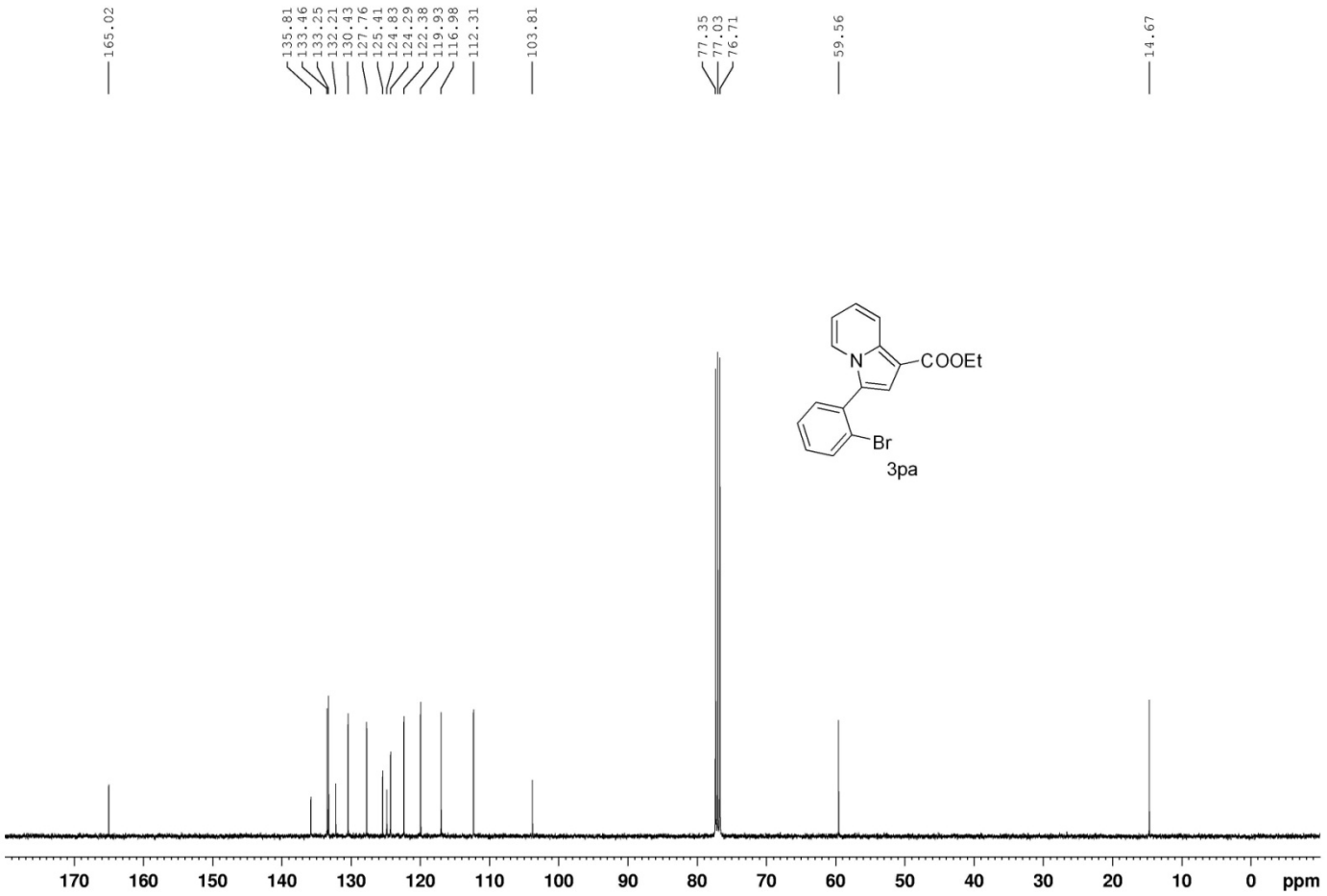

8.203
8.199
8.179
7.460
7.457
7.362
7.351
7.343
7.335
7.316
7.296
7.291
7.282
7.276
7.268
7.239
7.181
7.028
7.011
7.008
7.005
6.989
6.672
6.655
6.638
4.336
4.318
4.300
4.282
1.358
1.340
1.322
0.000
N
COOEt
Cl
3na
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.96
0.96
2.96
0.93
0.99
0.98
2.00
3.09

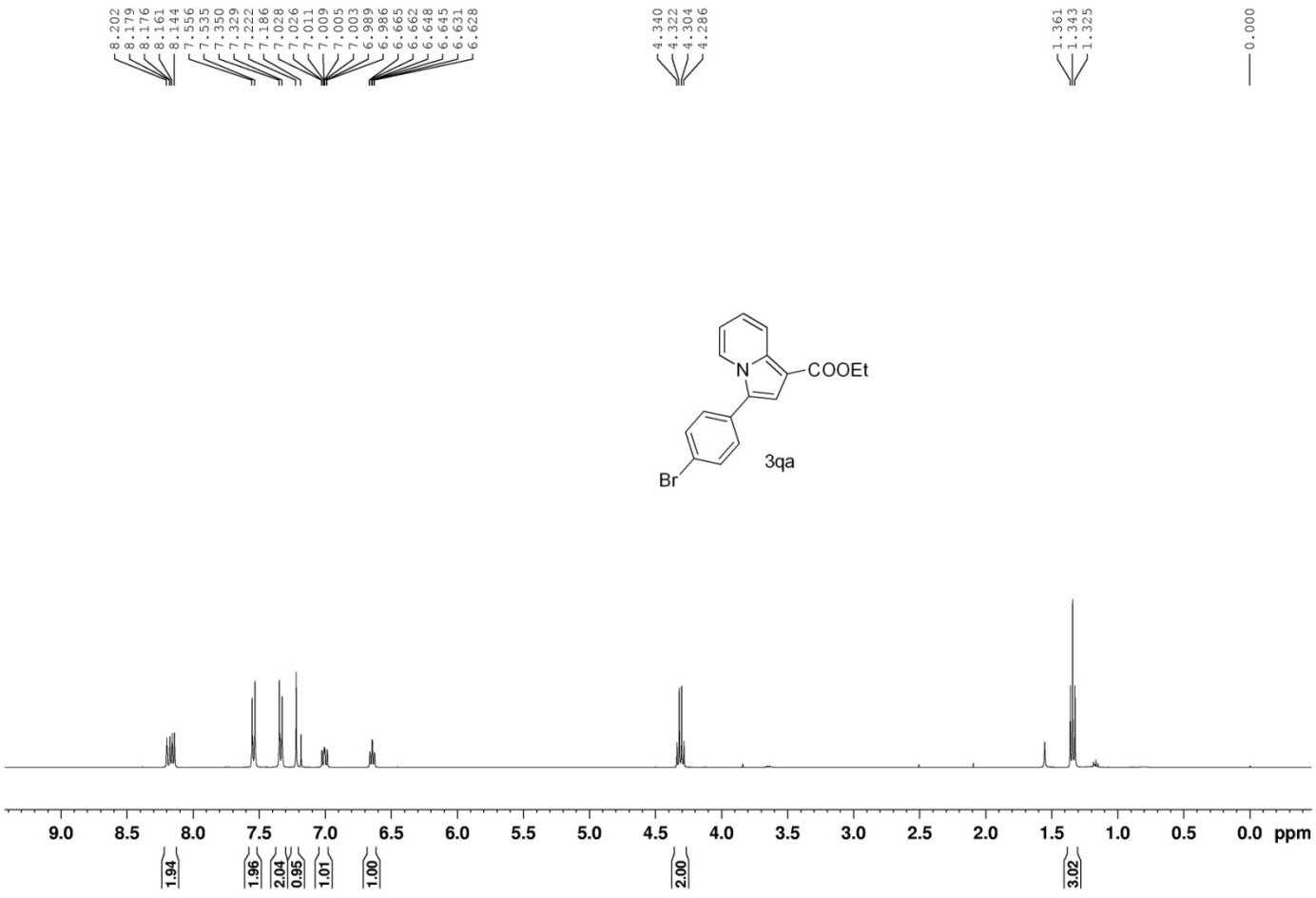

164.85
136.60
135.01
133.07
130.35
128.42
128.00
126.52
124.82
123.16
122.52
120.30
116.67
112.94
104.60
77.35
77.03
76.71
59.63
14.65
COOEt
N
Cl
3na
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

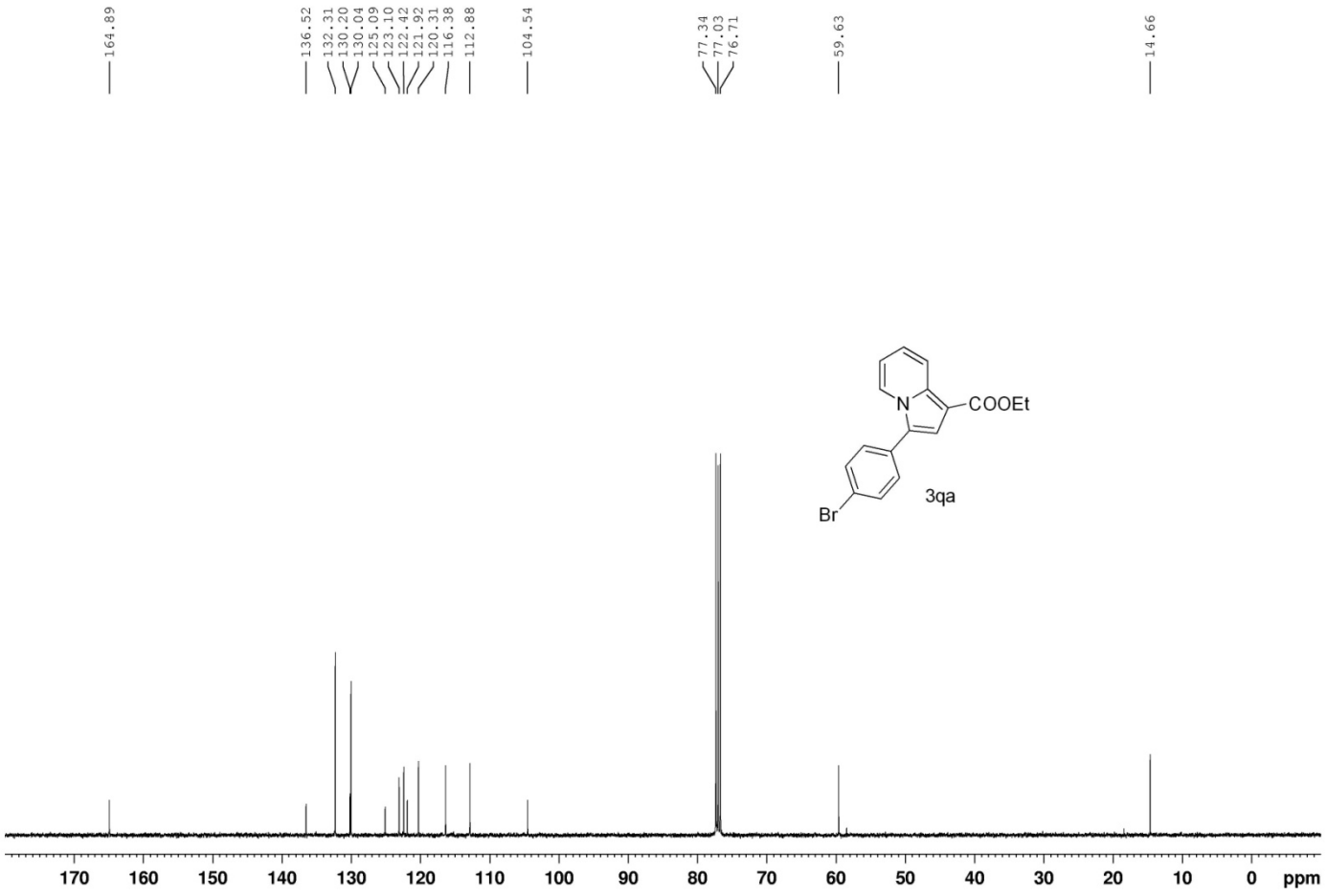

8.207
8.204
8.201
8.184
8.181
8.178
8.162
8.159
8.144
8.142
7.422
7.420
7.413
7.399
7.384
7.378
7.375
7.221
7.187
7.029
7.027
7.013
7.010
7.007
7.004
6.990
6.987
6.667
6.664
6.650
6.647
6.633
6.630
4.342
4.324
4.306
4.288
1.363
1.345
1.327
0.000
COOEt
N
Cl
3oa
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.96
3.98
0.97
1.02
1.00
2.00
3.03

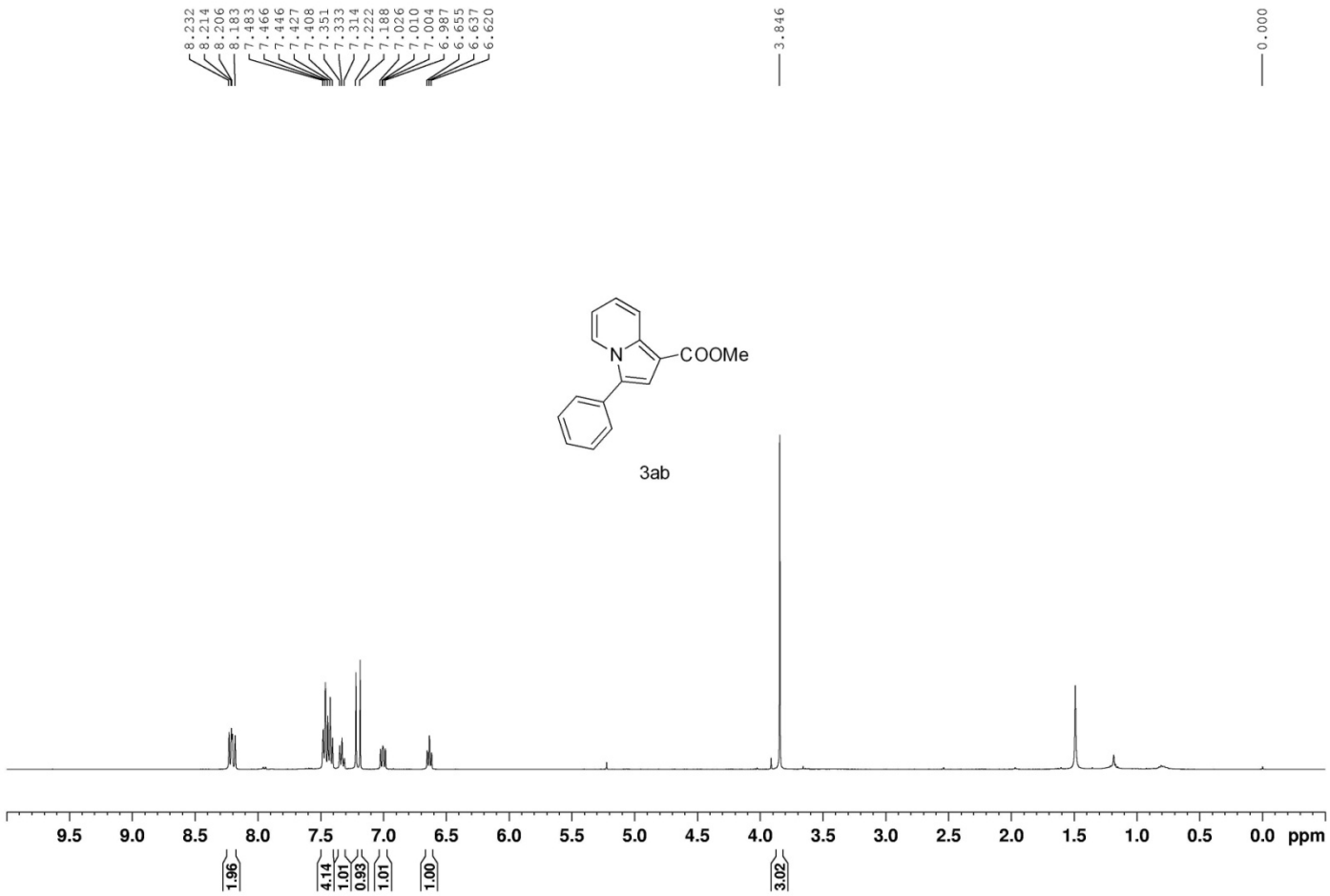

164.91
136.48
133.84
129.81
129.73
129.37
125.09
123.12
122.40
120.29
116.37
112.85
104.49
77.34
77.03
76.71
59.63
14.66
COOEt
N
Cl
3oa
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

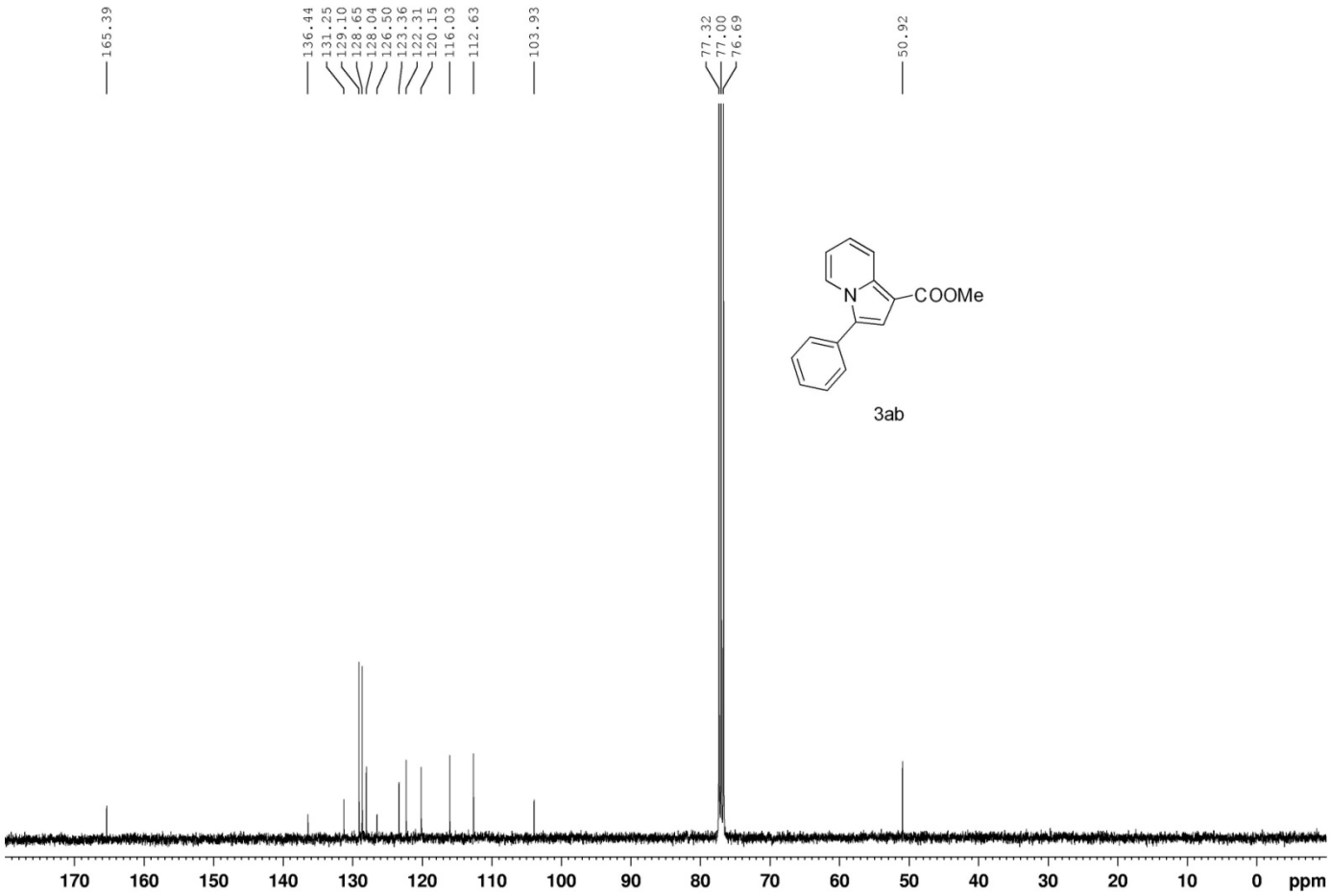

8.218
8.195
7.668
7.649
7.584
7.567
7.359
7.348
7.277
7.266
7.257
7.254
7.245
7.230
7.182
7.050
7.048
7.034
7.031
7.028
7.026
7.011
7.009
6.655
6.652
6.638
6.635
6.621
6.618
4.342
4.324
4.306
4.288
1.360
1.342
1.324
0.000
N
COOEt
Br
3pa
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
0.94
0.94
0.96
1.90
1.90
1.00
1.00
2.00
3.01

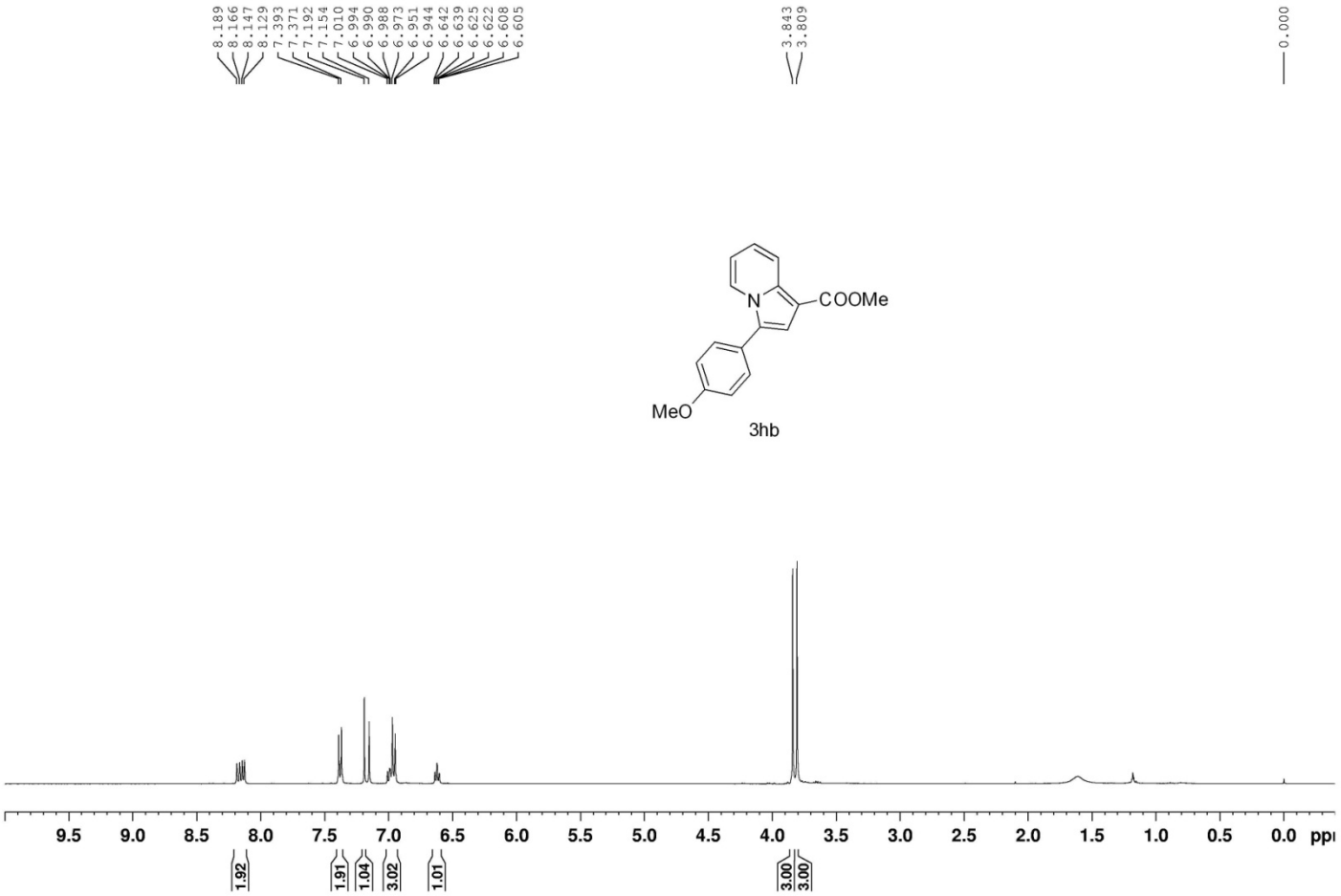

165.02
135.81
133.46
133.25
132.21
130.43
127.76
125.41
124.83
124.29
122.38
119.93
116.98
112.31
103.81
77.35
77.03
76.71
59.56
14.67
COOEt
N
Br
3pa
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

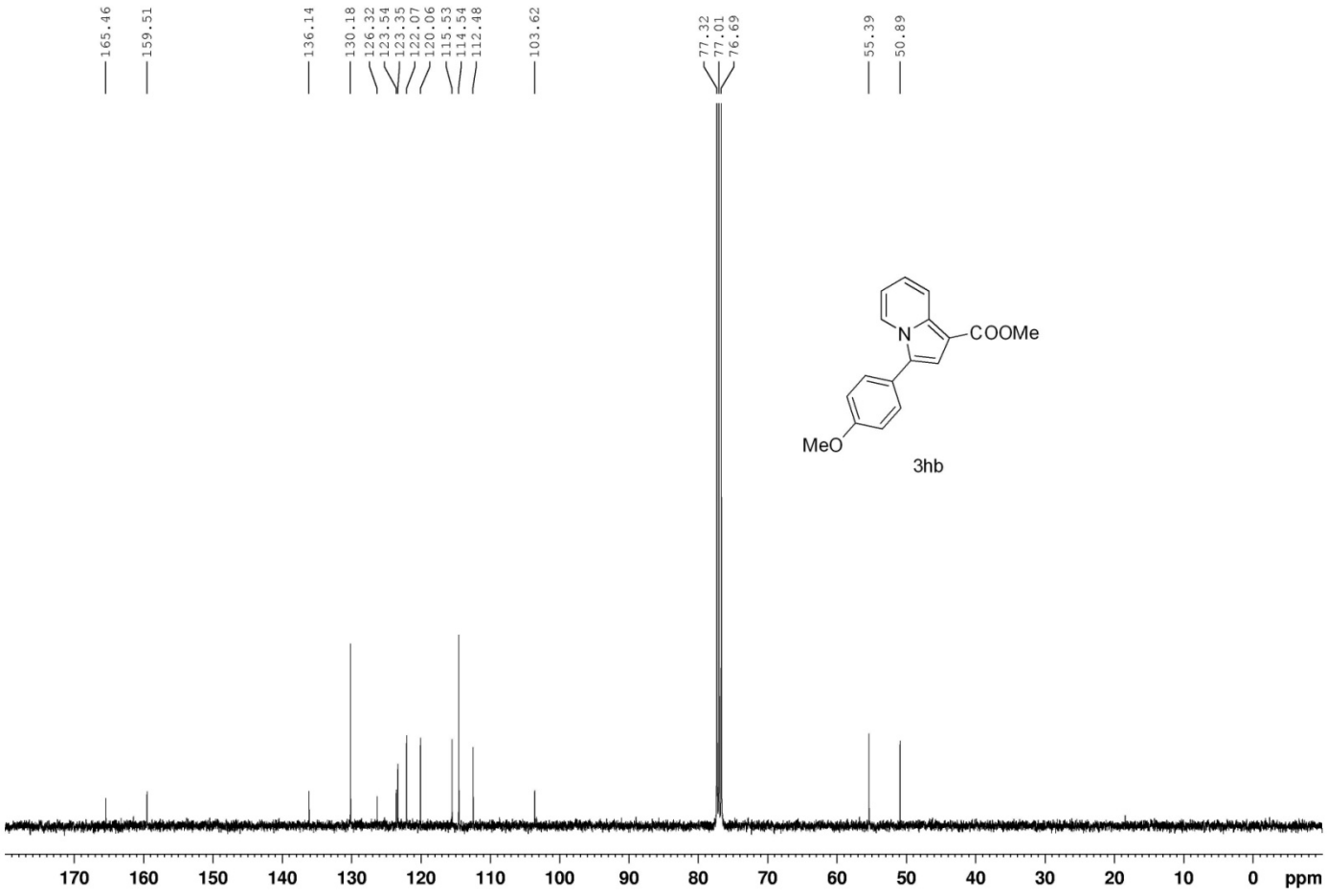

8.202
8.179
8.176
8.161
8.144
7.556
7.535
7.350
7.329
7.222
7.186
7.028
7.026
7.011
7.009
7.005
7.003
6.989
6.986
6.665
6.662
6.648
6.645
6.631
6.628
4.340
4.322
4.304
4.286
1.361
1.343
1.325
0.000
COOEt
N
Br
3qa
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.94
1.96
2.04
0.95
1.01
1.00
2.00
3.02

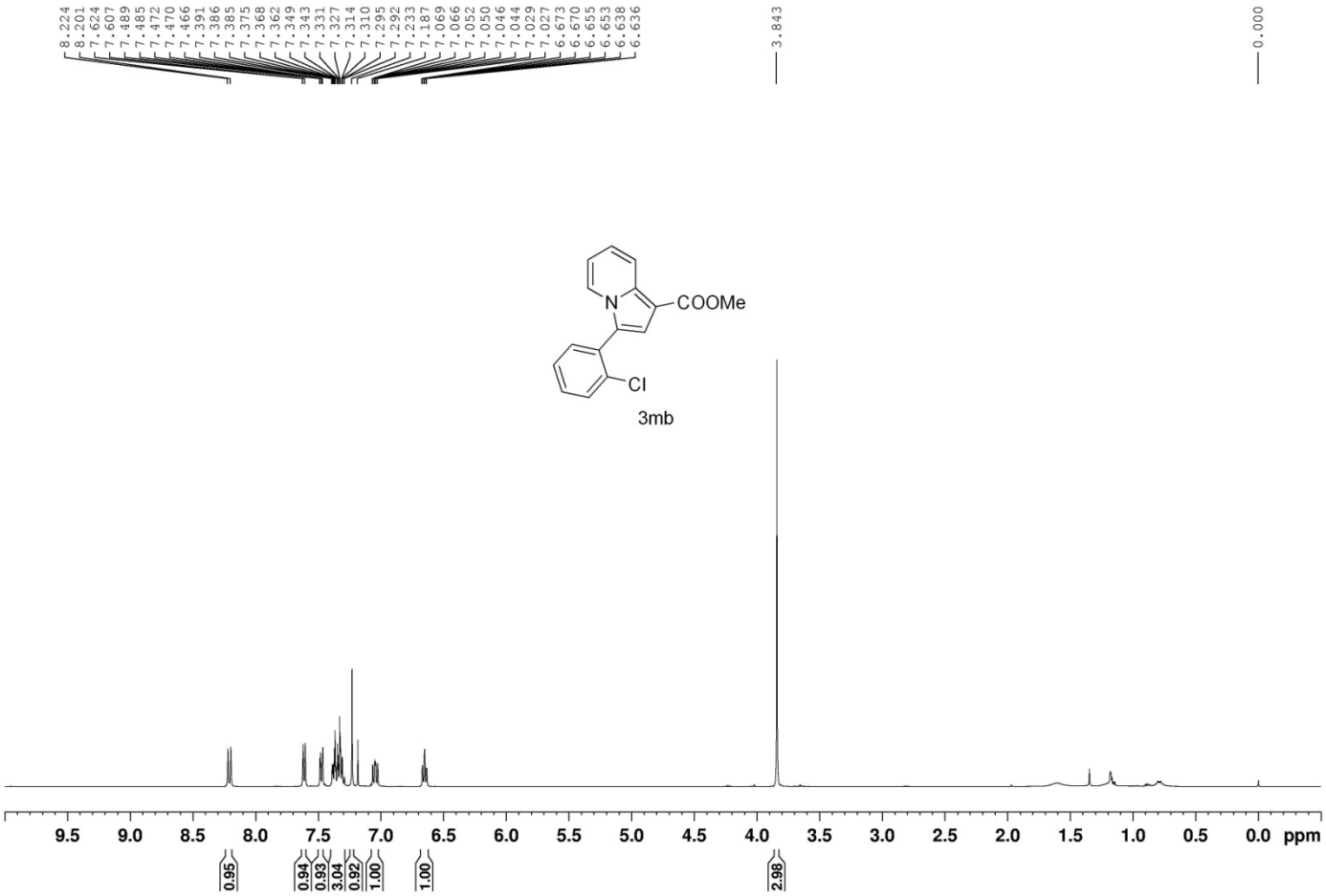

164.89
136.52
132.31
130.20
130.04
125.09
123.10
122.42
121.92
120.31
116.38
112.88
104.54
77.34
77.03
76.71
59.63
14.66
N
COOEt
Br
3qa
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

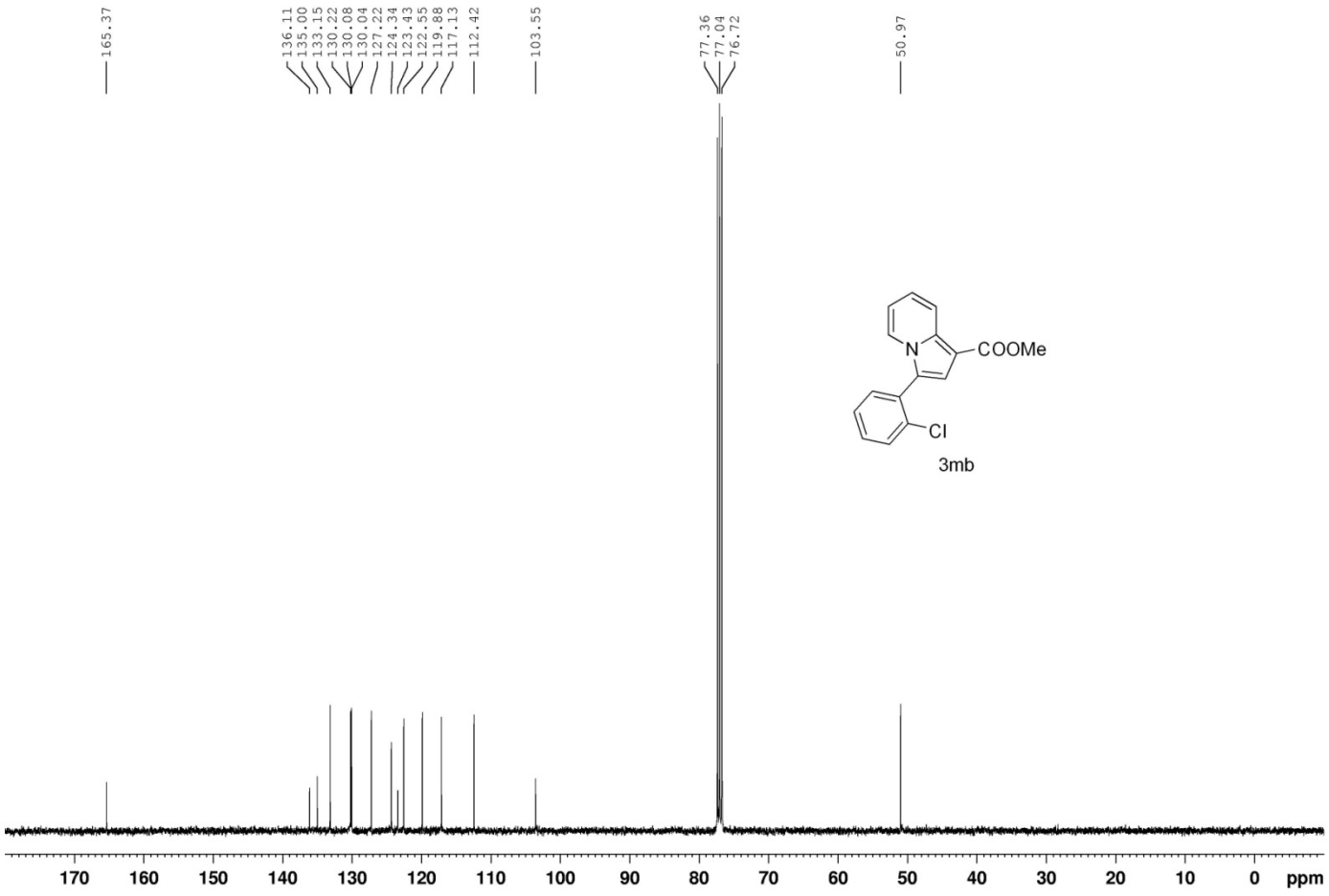

8.232
8.214
8.206
8.183
7.483
7.466
7.446
7.427
7.408
7.351
7.333
7.314
7.222
7.188
7.026
7.010
7.004
6.987
6.655
6.637
6.620
3.846
0.000
N
COOMe
3ab
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.96
4.14
1.01
0.93
1.01
1.00
3.02

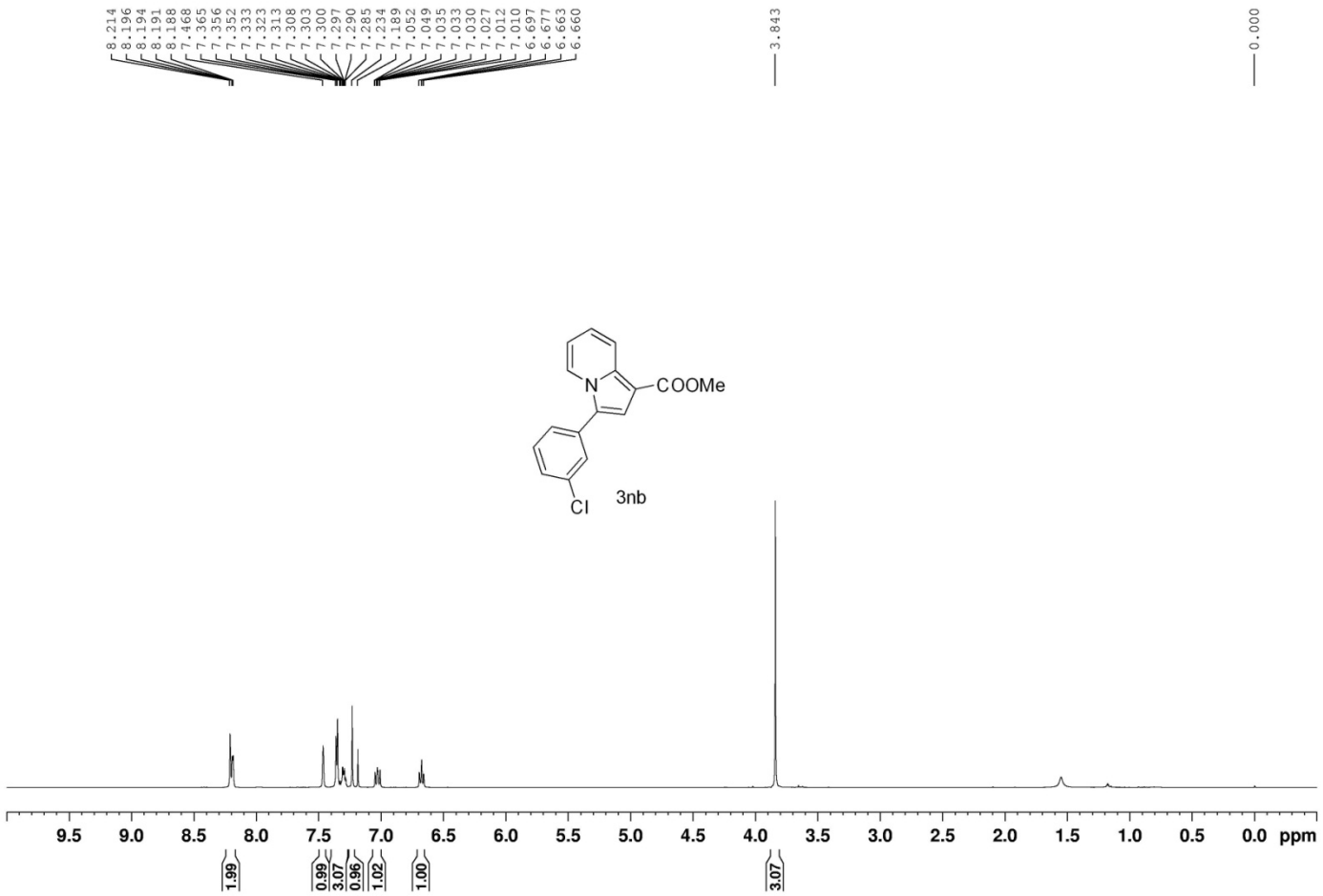

165.39
136.44
131.25
129.10
128.65
128.04
126.50
123.36
122.31
120.15
116.03
112.63
103.93
77.32
77.00
76.69
50.92
N
COOMe
3ab
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

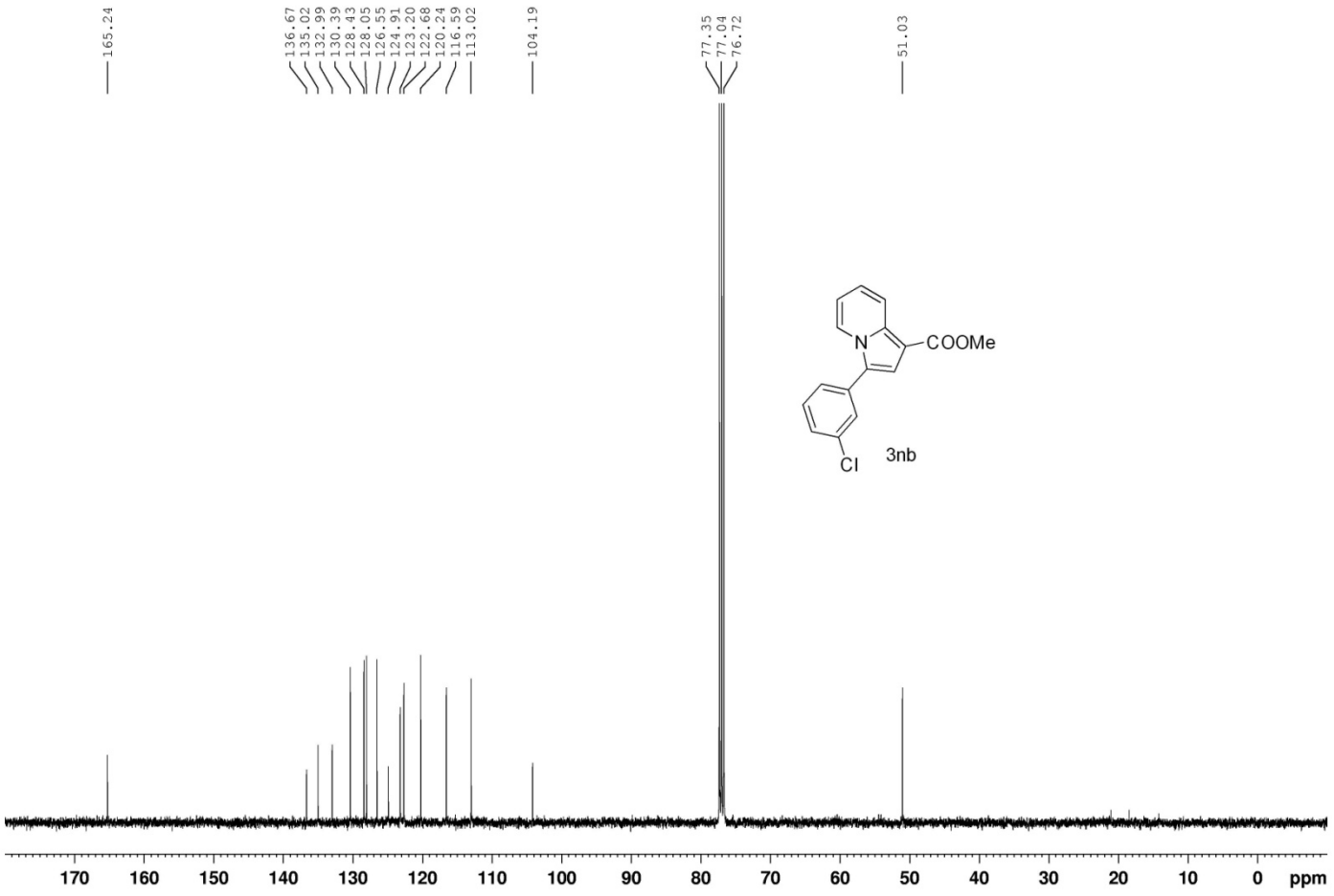

8.189
8.166
8.147
8.129
7.393
7.371
7.192
7.154
7.010
6.994
6.990
6.988
6.973
6.951
6.944
6.642
6.639
6.625
6.622
6.608
6.605
3.843
3.809
0.000
N
COOMe
MeO
3hb
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.92
1.91
1.04
3.02
1.01
3.00
3.00

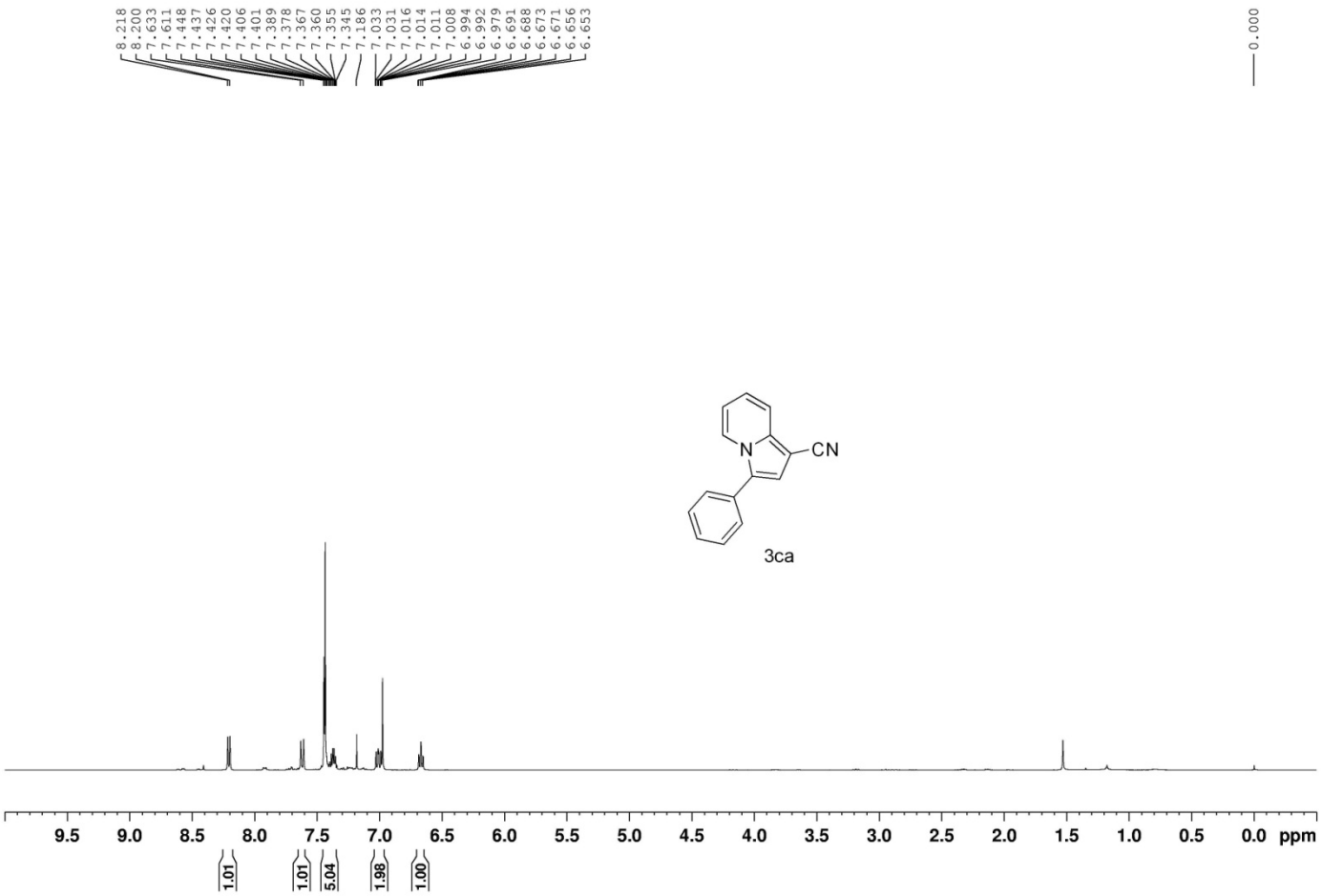

165.46
159.51
136.14
130.18
126.32
123.54
123.35
122.07
120.06
115.53
114.54
112.48
103.62
77.32
77.01
76.69
55.39
50.89
N
COOMe
MeO
3hb
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

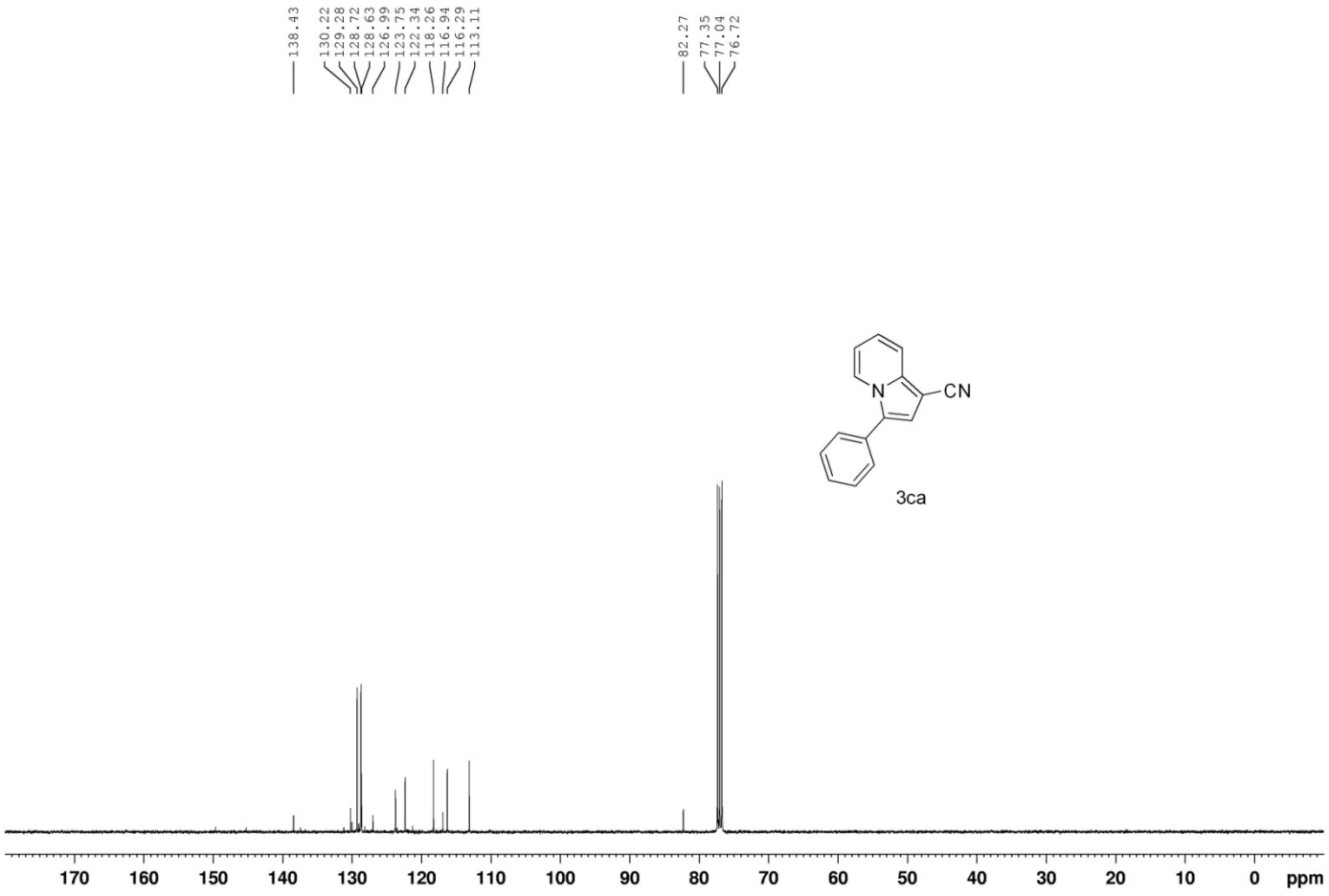

8.224
8.201
7.624
7.607
7.489
7.485
7.472
7.470
7.466
7.391
7.386
7.385
7.375
7.368
7.362
7.349
7.343
7.331
7.327
7.314
7.310
7.295
7.292
7.233
7.187
7.069
7.066
7.052
7.050
7.046
7.044
7.029
7.027
6.673
6.670
6.655
6.653
6.638
6.636
3.843
0.000
N
COOMe
Cl
3mb
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
0.95
0.94
0.93
3.04
0.92
1.00
1.00
2.98

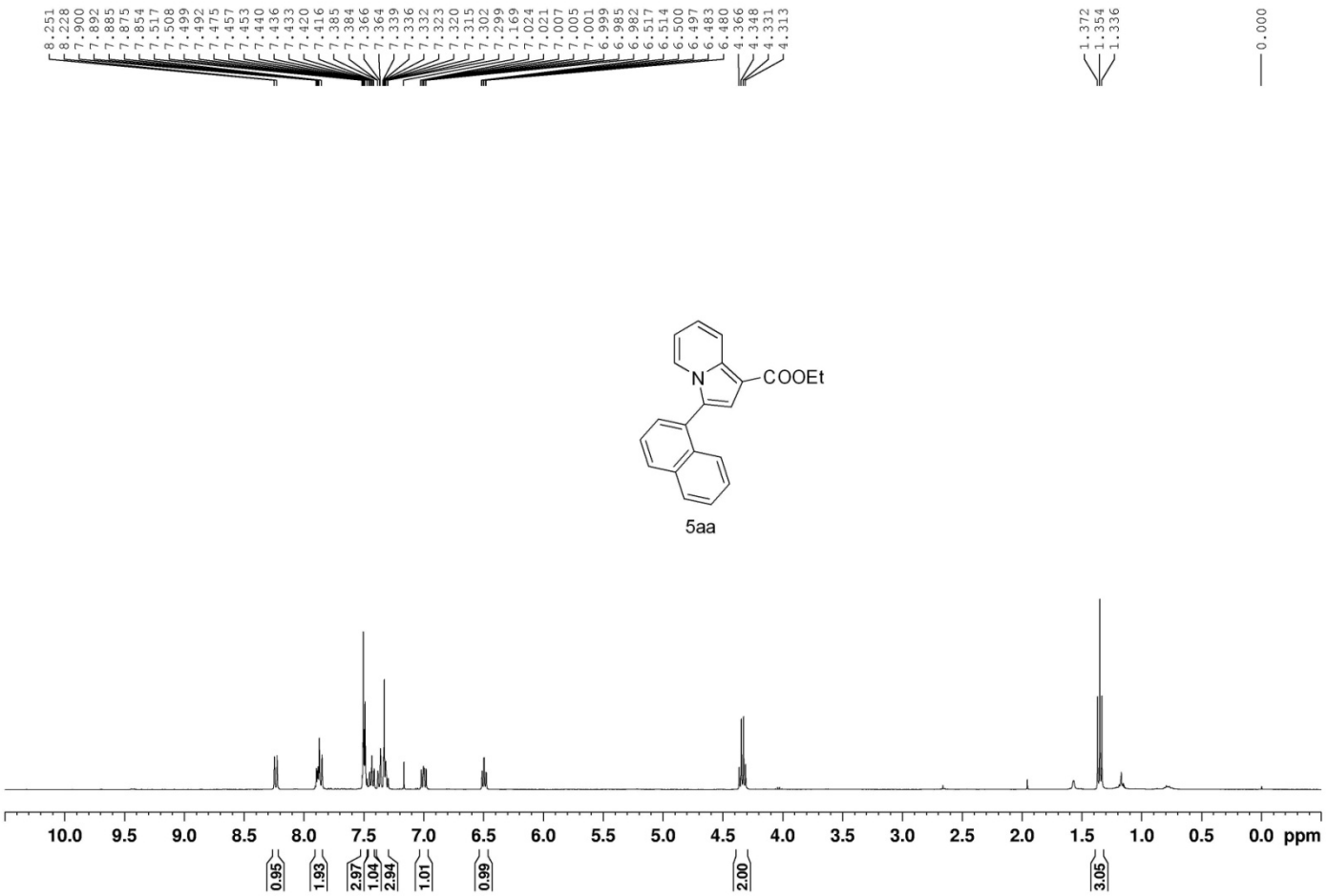

165.37
136.11
135.00
133.15
130.22
130.08
130.04
127.22
124.34
123.43
122.55
119.88
117.13
112.42
103.55
77.36
77.04
76.72
50.97
COOMe
N
Cl
3mb
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

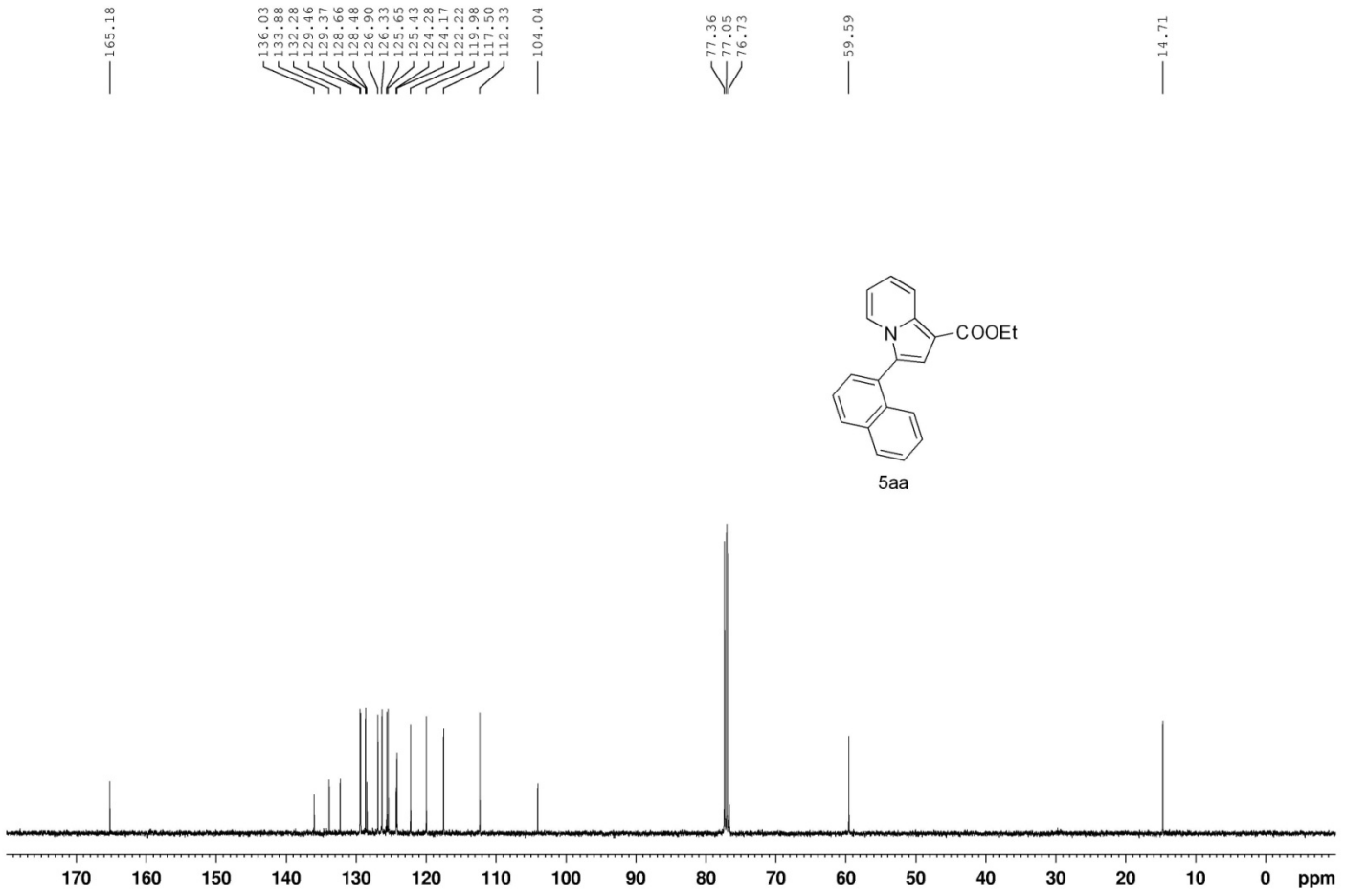

8.214
8.196
8.194
8.191
8.188
7.468
7.365
7.356
7.352
7.333
7.323
7.313
7.308
7.303
7.300
7.297
7.290
7.285
7.234
7.189
7.052
7.049
7.035
7.033
7.030
7.027
7.012
7.010
6.697
6.677
6.663
6.660
3.843
0.000
N
COOMe
Cl
3nb
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.99
0.99
3.07
0.96
1.02
1.00
3.07

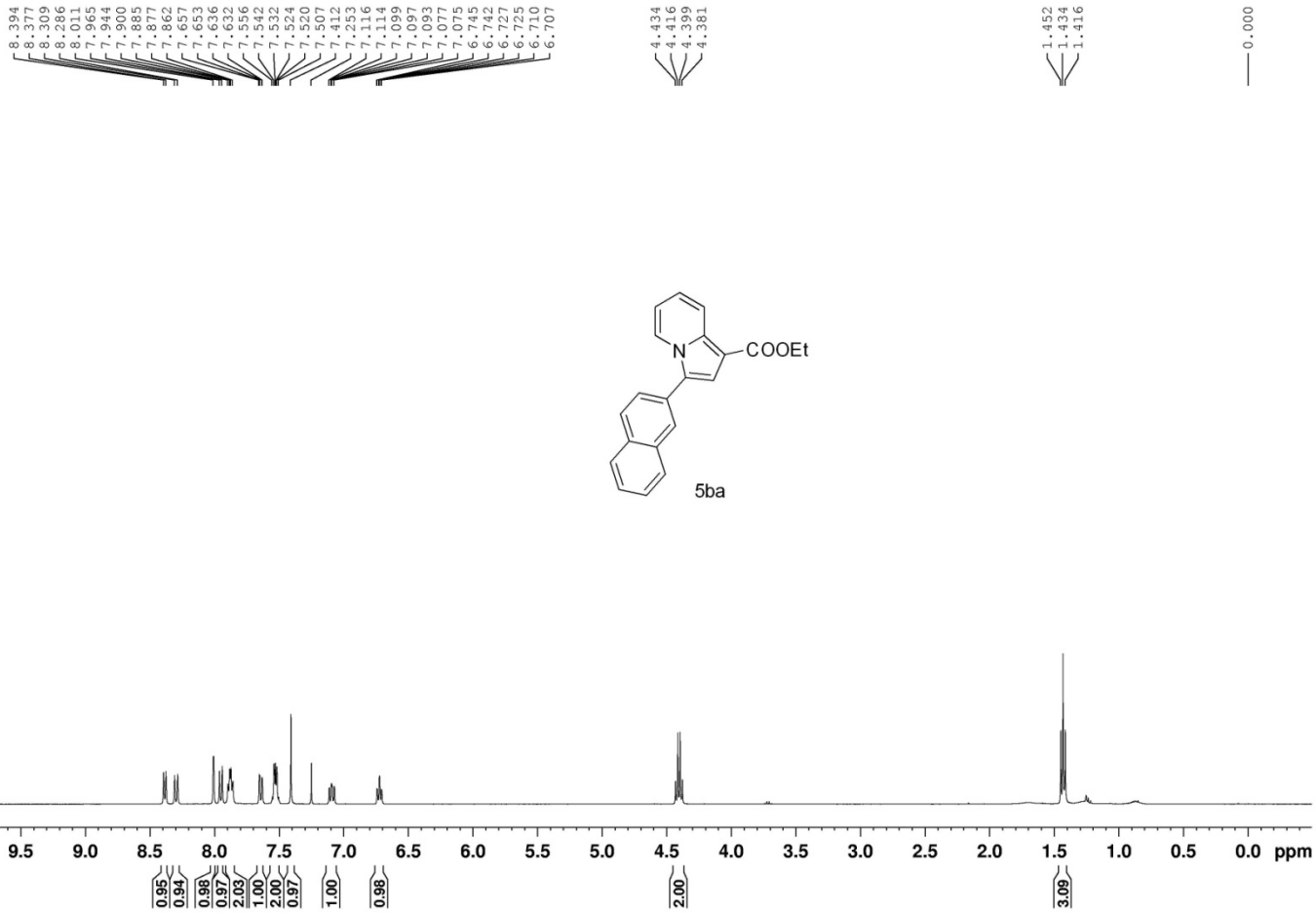

165.24
136.67
135.02
132.99
130.39
128.43
128.05
126.55
124.91
123.20
122.68
120.24
116.59
113.02
104.19
77.35
77.04
76.72
51.03
N
COOMe
Cl
3nb
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

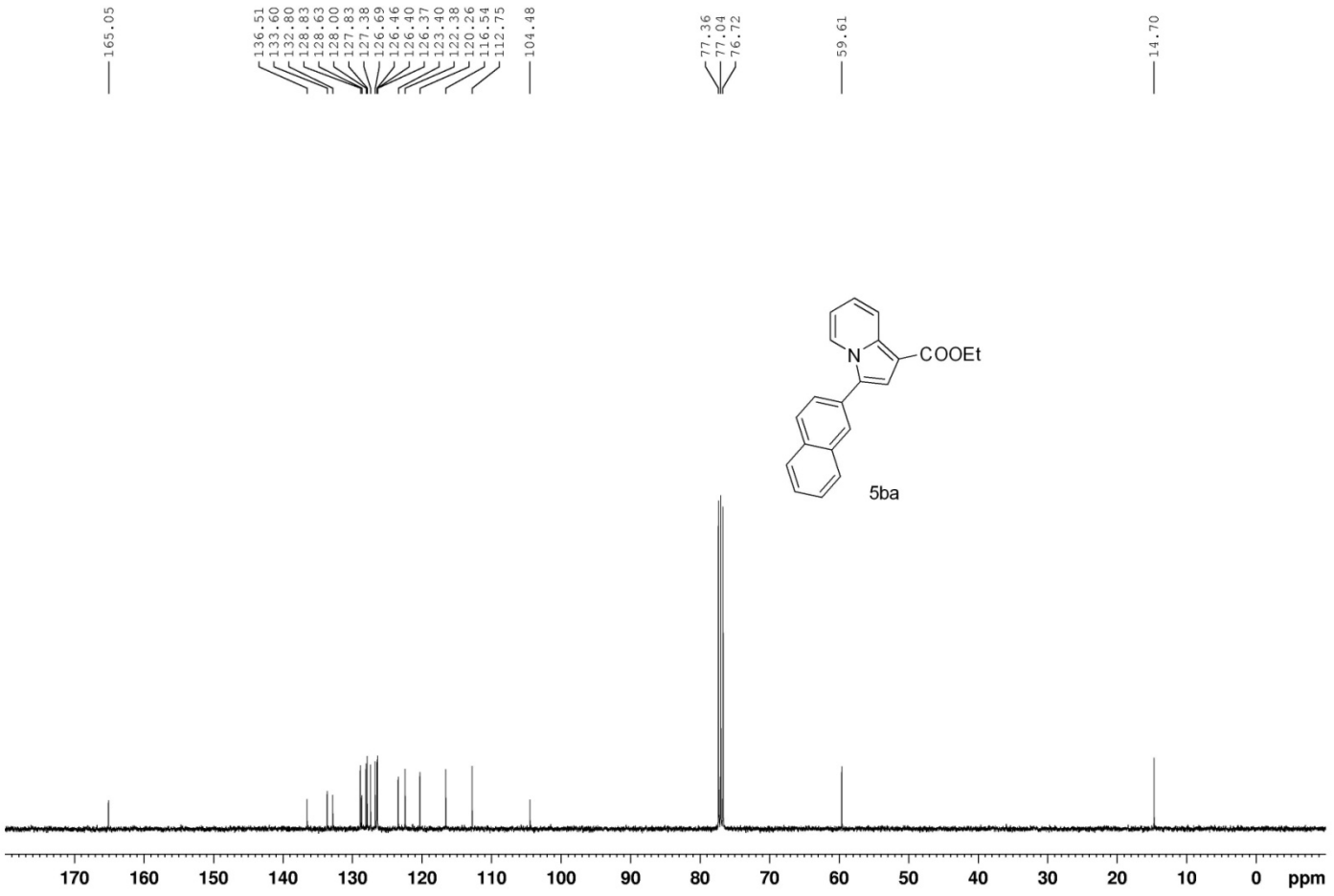

8.218
8.200
7.633
7.611
7.448
7.437
7.426
7.420
7.406
7.401
7.389
7.378
7.367
7.360
7.355
7.345
7.186
7.033
7.031
7.016
7.014
7.011
7.008
6.994
6.992
6.979
6.691
6.688
6.673
6.671
6.656
6.653
0.000
N
CN
3ca
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.01
1.01
5.04
1.98
1.00

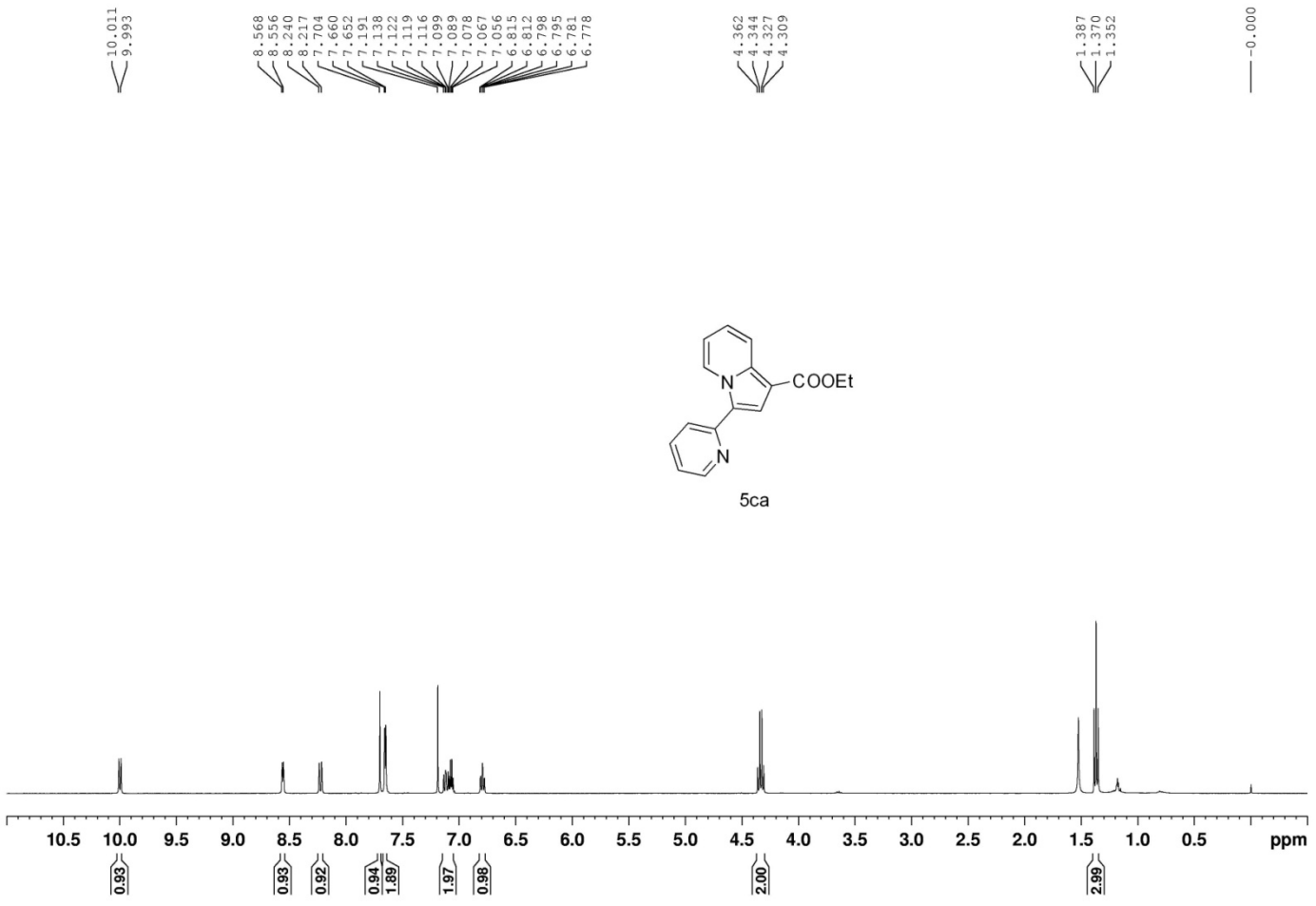

138.43
130.22
129.28
128.72
128.63
126.99
123.75
122.34
118.26
116.94
116.29
113.11
82.27
77.35
77.04
76.72
N
CN
3ca
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

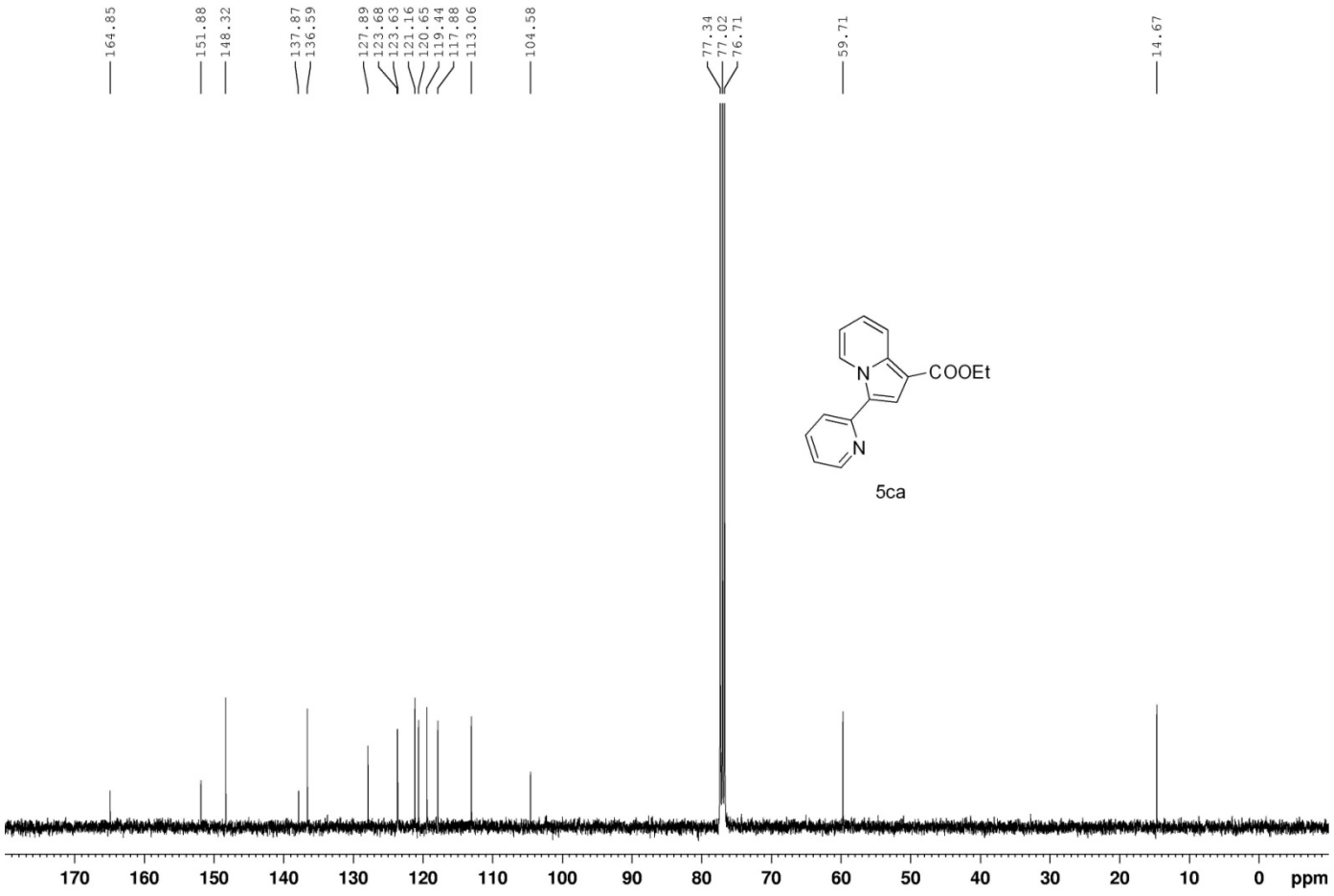

8.251
8.228
7.900
7.892
7.885
7.875
7.854
7.517
7.508
7.499
7.492
7.475
7.457
7.453
7.440
7.436
7.433
7.420
7.416
7.385
7.384
7.366
7.364
7.339
7.336
7.332
7.323
7.320
7.315
7.302
7.299
7.169
7.024
7.021
7.007
7.005
7.001
6.999
6.985
6.982
6.517
6.514
6.500
6.497
6.483
6.480
4.366
4.348
4.331
4.313
1.372
1.354
1.336
0.000
N
COOEt
5aa
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
0.95
1.93
2.97
1.04
2.94
1.01
0.99
2.00
3.05

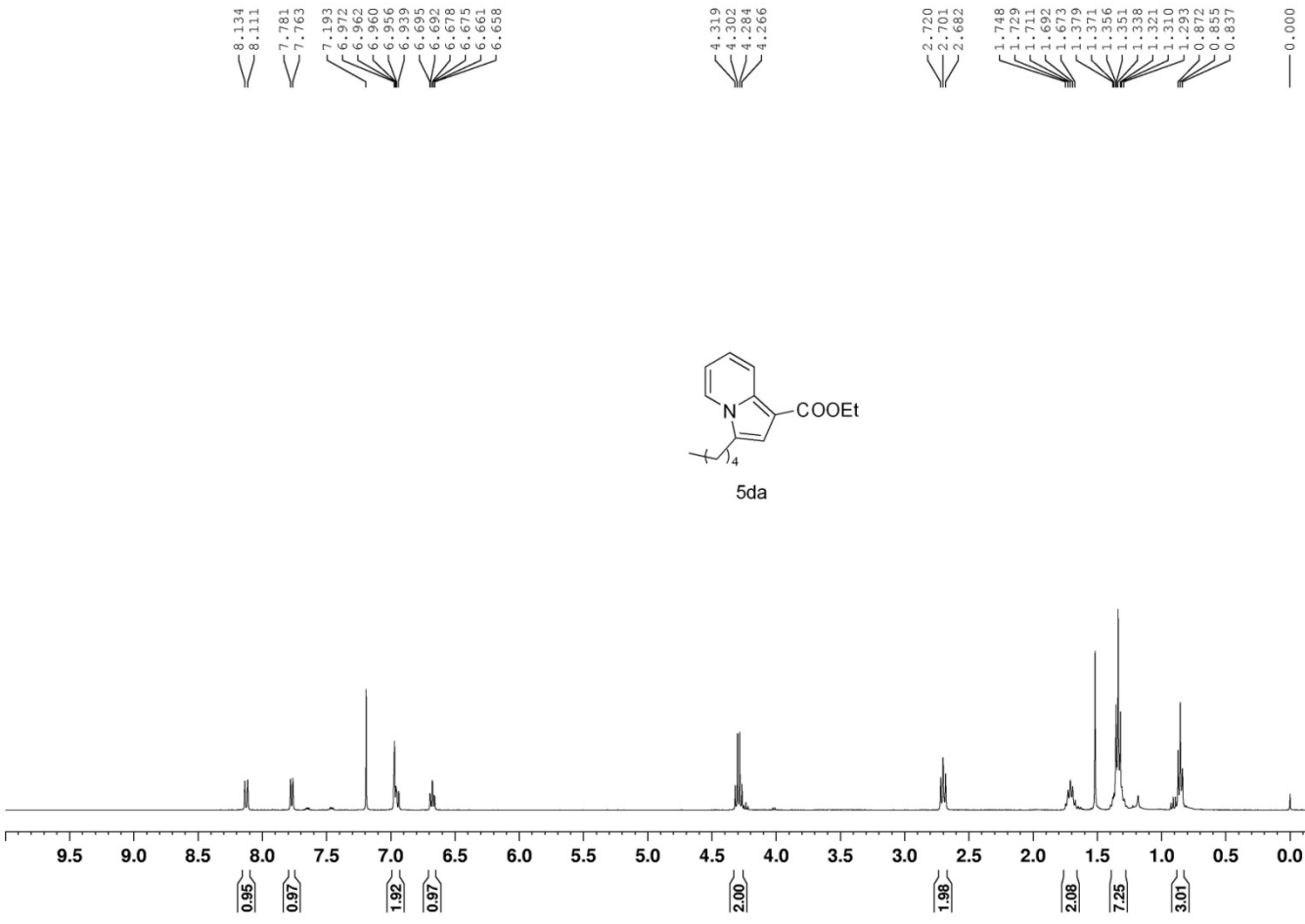

165.18
136.03
133.88
132.28
129.46
129.37
128.66
128.48
126.90
126.33
125.65
125.43
124.28
124.17
122.22
119.98
117.50
112.33
104.04
77.36
77.05
76.73
59.59
14.71
N
COOEt
5aa
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

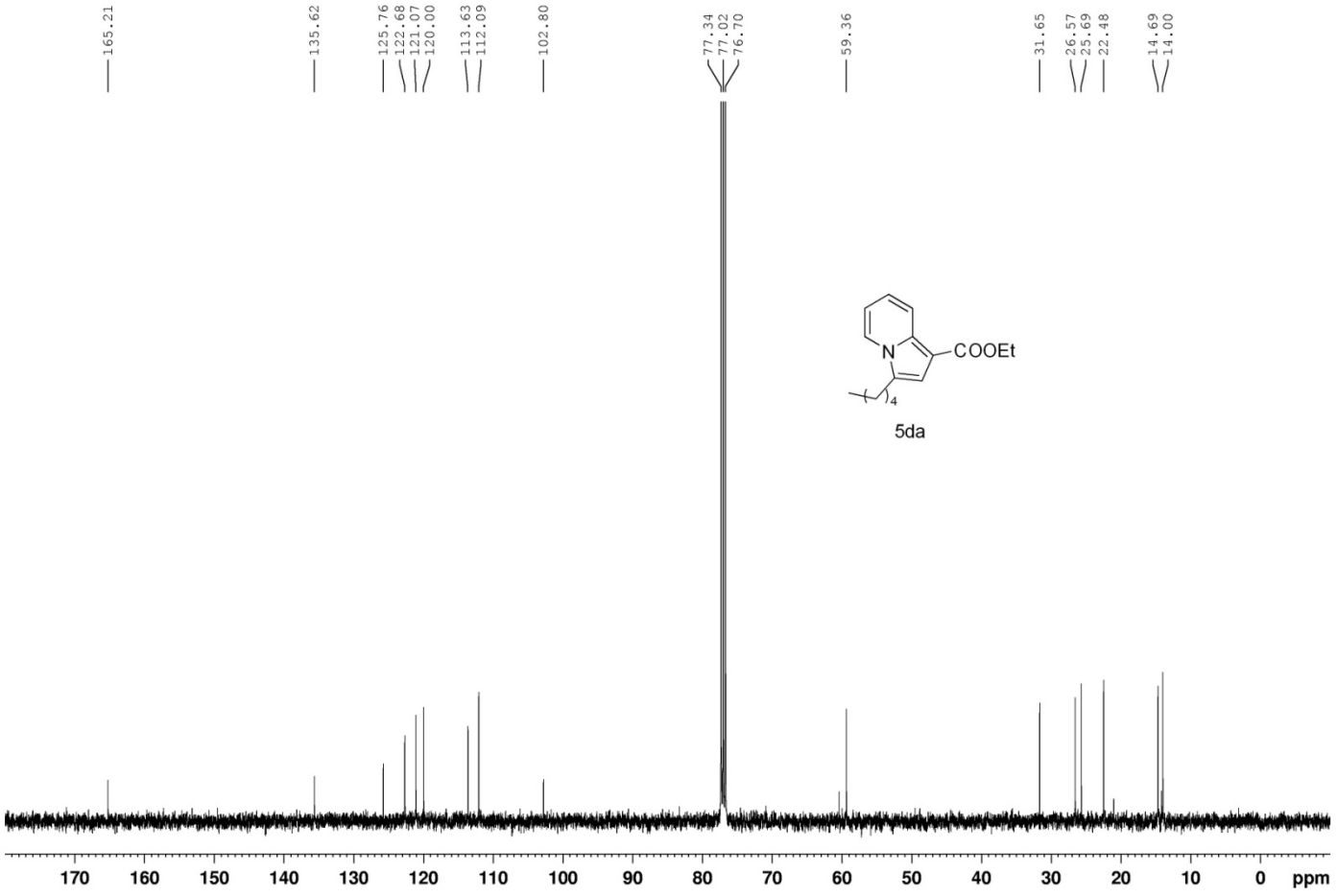

8.394
8.377
8.309
8.286
8.011
7.965
7.944
7.900
7.885
7.877
7.862
7.657
7.653
7.636
7.632
7.556
7.542
7.532
7.524
7.520
7.507
7.412
7.253
7.116
7.114
7.099
7.097
7.093
7.077
7.075
6.745
6.742
6.727
6.725
6.710
6.707
4.434
4.416
4.399
4.381
1.452
1.434
1.416
0.000
N
COOEt
5ba
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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
0.95
0.94
0.98
0.97
2.03
1.00
2.00
0.97
1.00
0.98
2.00
3.09

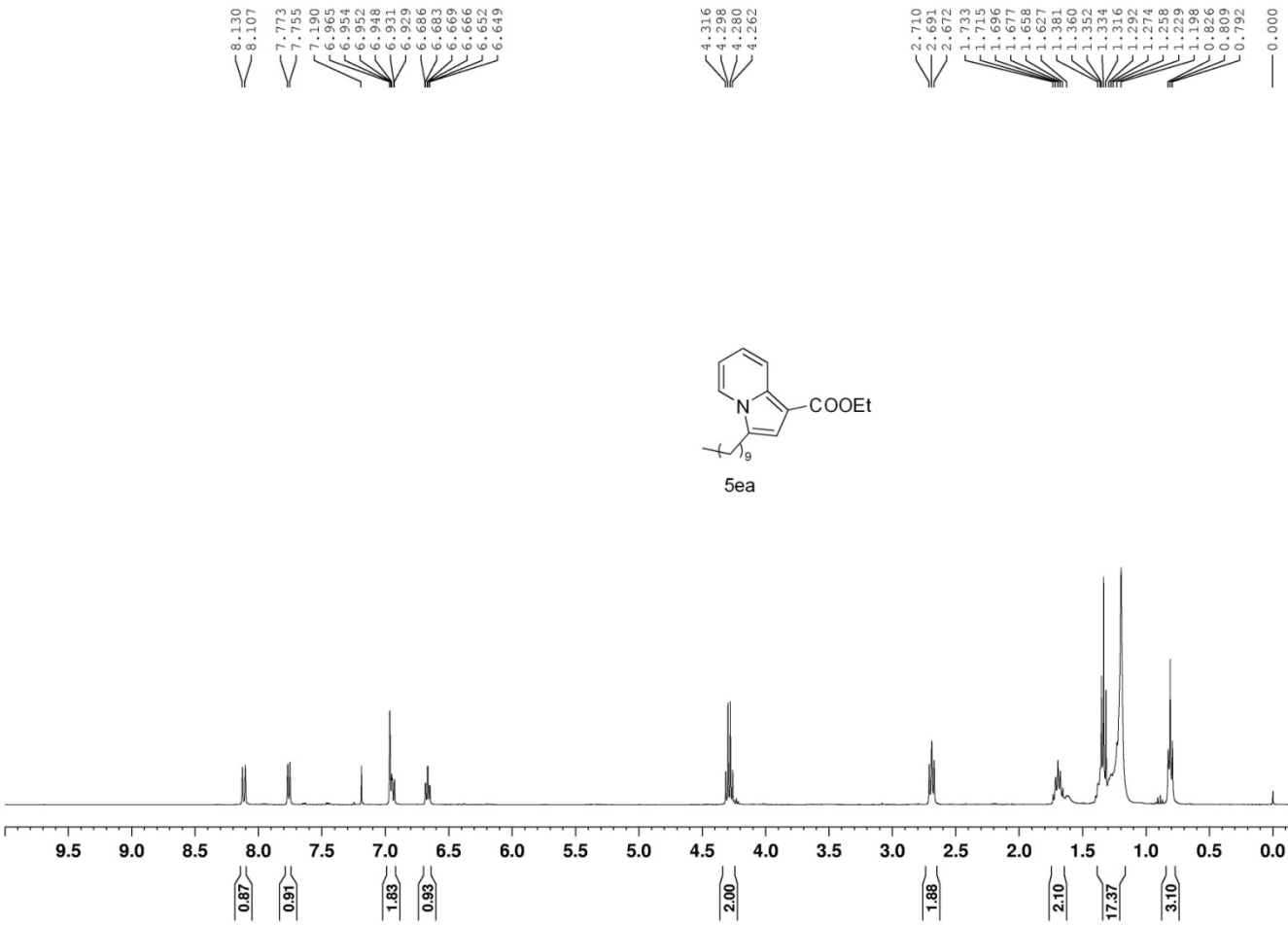

165.05
136.51
133.60
132.80
128.83
128.63
128.00
127.83
127.38
126.69
126.46
126.40
126.37
123.40
122.38
120.26
116.54
112.75
104.48
77.36
77.04
76.72
59.61
14.70
N
COOEt
5ba
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

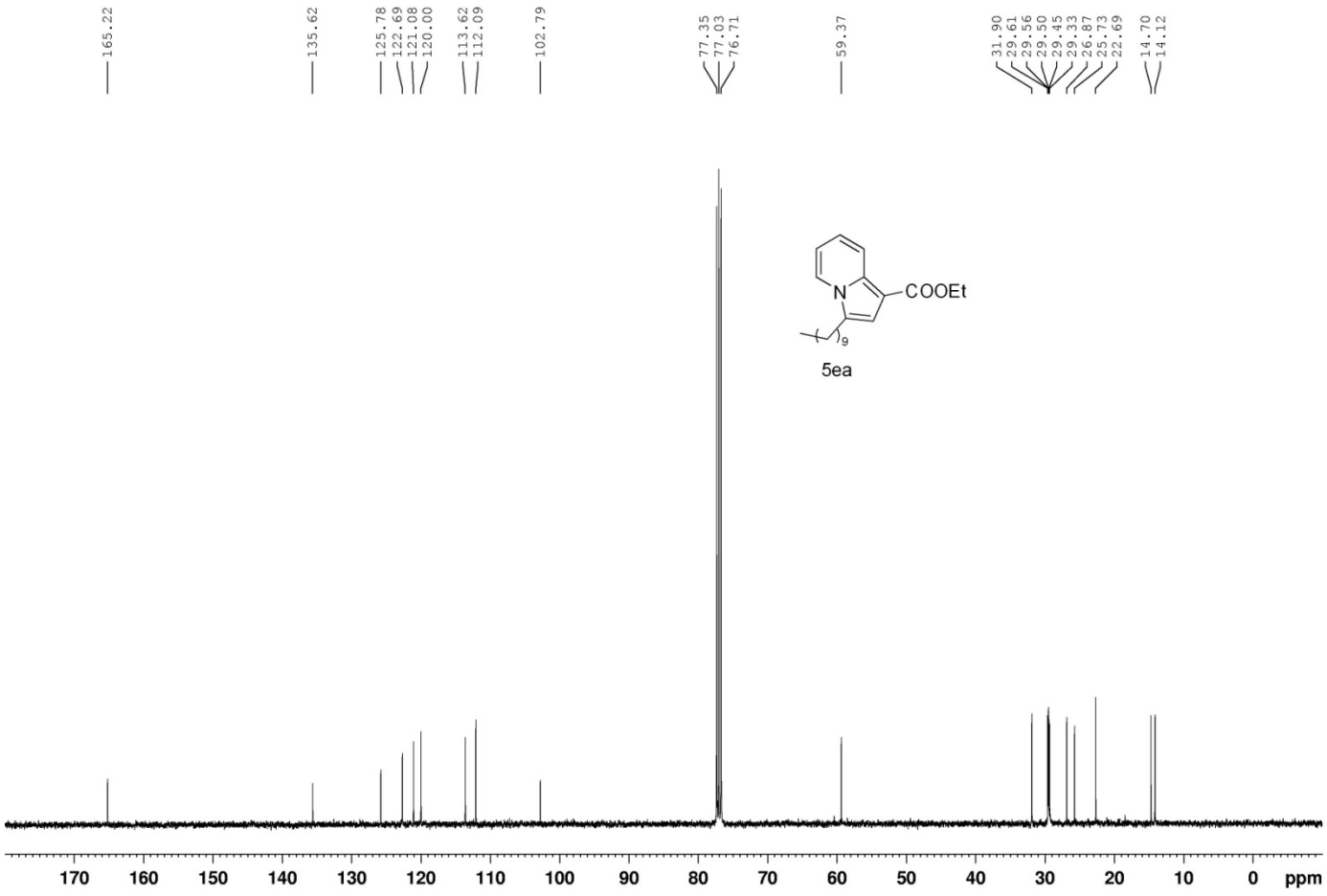

10.011
9.993
8.568
8.556
8.240
8.217
7.704
7.660
7.652
7.191
7.138
7.122
7.119
7.116
7.099
7.089
7.078
7.067
7.056
6.815
6.812
6.798
6.795
6.781
6.778
4.362
4.344
4.327
4.309
1.387
1.370
1.352
0.000
COOEt
N
N
5ca
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.93
0.93
0.92
0.94
1.89
1.97
0.98
2.00
2.99

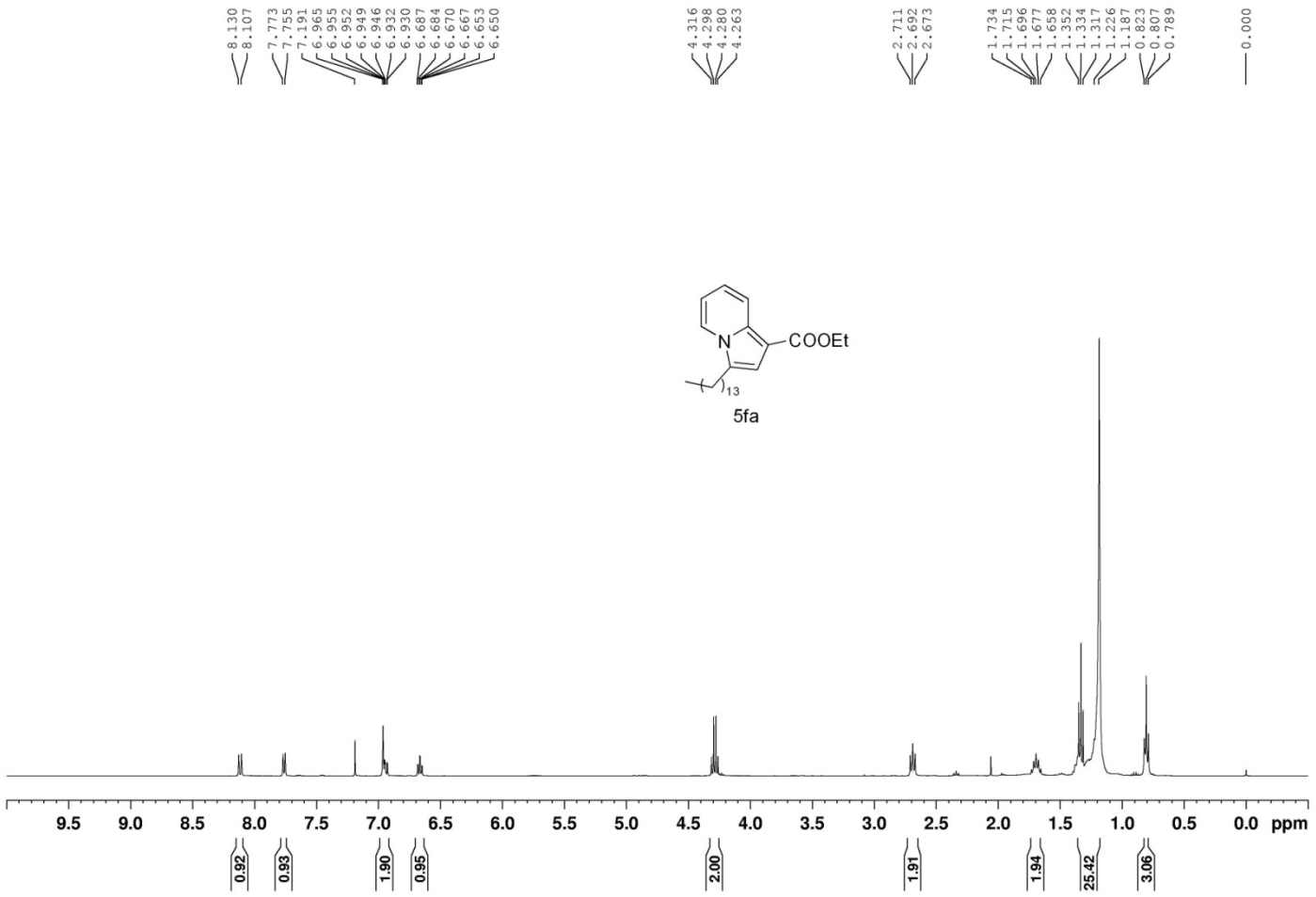

164.85
151.88
148.32
137.87
136.59
127.89
123.68
123.63
121.16
120.65
119.44
117.88
113.06
104.58
77.34
77.02
76.71
59.71
14.67
COOEt
N
N
5ca
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

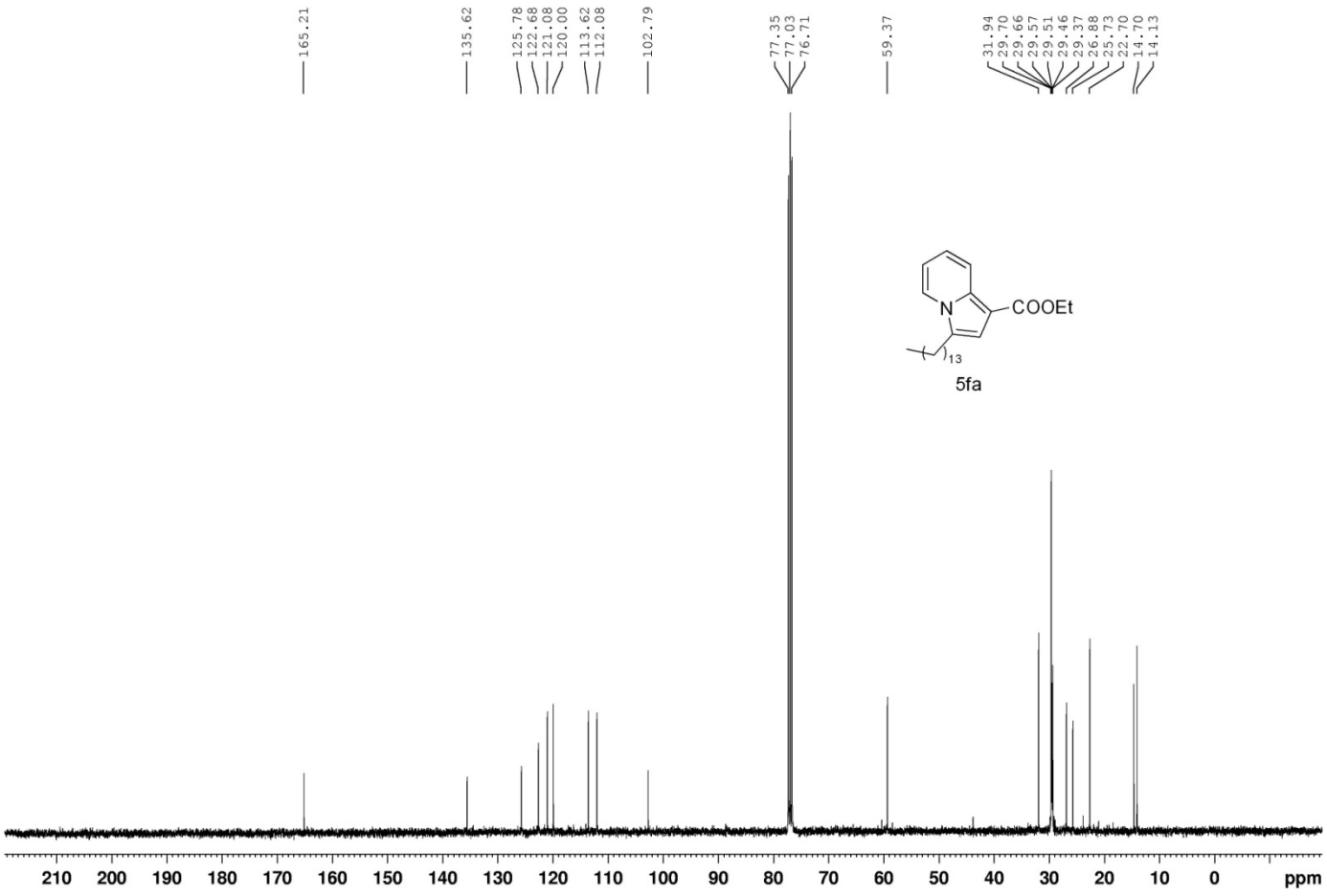

8.134
8.111
7.781
7.763
7.193
6.972
6.962
6.960
6.956
6.939
6.695
6.692
6.678
6.675
6.661
6.658
4.319
4.302
4.284
4.266
2.720
2.701
2.682
1.748
1.729
1.711
1.692
1.673
1.379
1.371
1.356
1.351
1.338
1.321
1.310
1.293
0.872
0.855
0.837
0.000
N
COOEt
4
5da
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
0.95
0.97
1.92
0.97
2.00
1.98
2.08
7.25
3.01

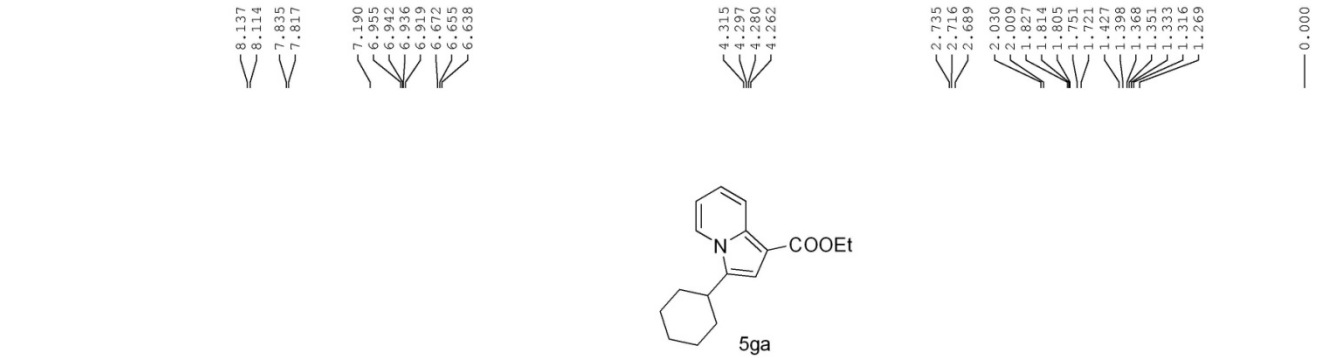

165.21
135.62
125.76
122.68
121.07
120.00
113.63
112.09
102.80
77.34
77.02
76.70
59.36
31.65
26.57
25.69
22.48
14.69
14.00
N
COOEt
4
5da
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

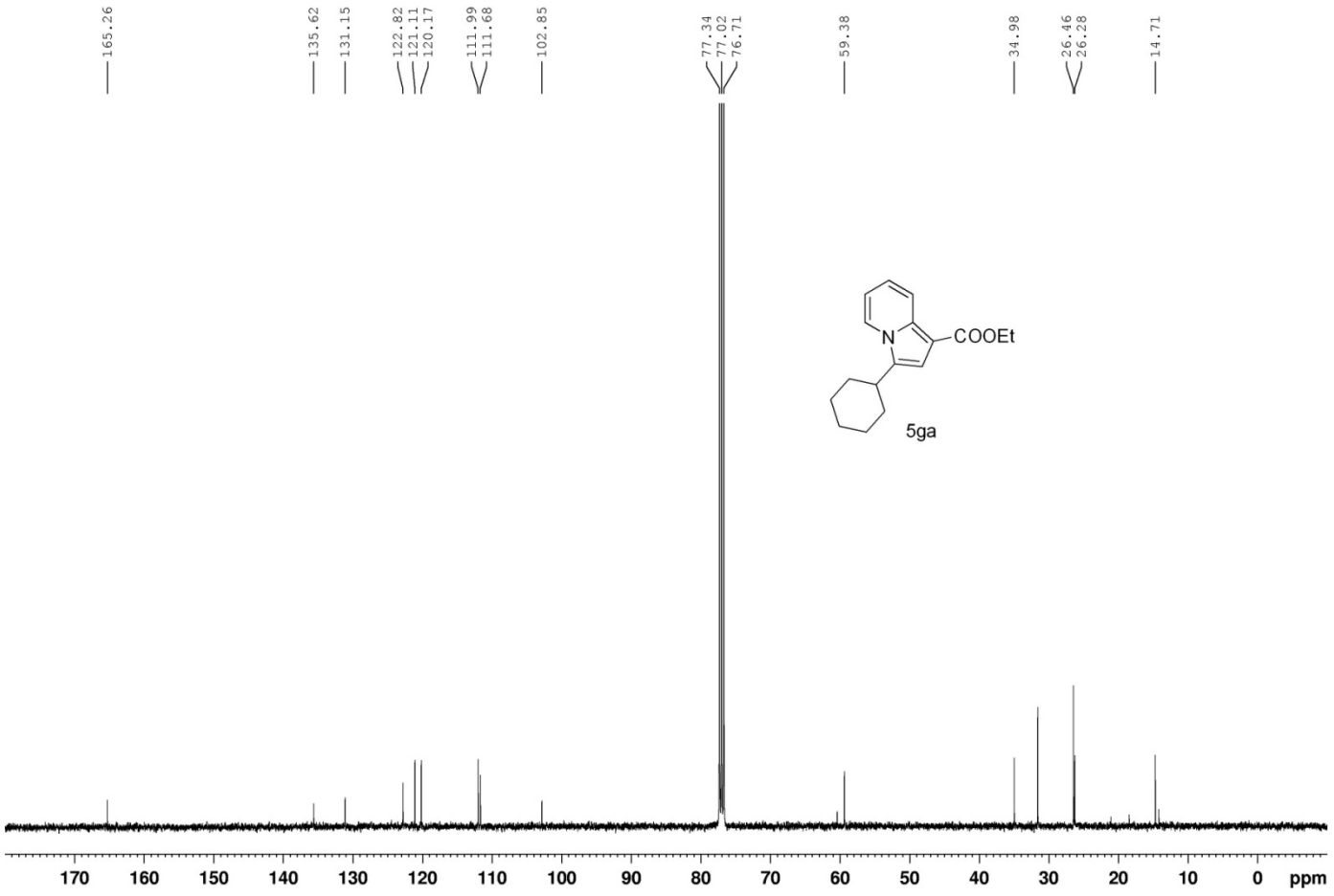

8.130
8.107
7.773
7.755
7.190
6.965
6.954
6.952
6.948
6.931
6.929
6.686
6.683
6.669
6.666
6.652
6.649
4.316
4.298
4.280
4.262
2.710
2.691
2.672
1.733
1.715
1.696
1.677
1.658
1.627
1.381
1.360
1.352
1.334
1.316
1.292
1.274
1.258
1.229
1.198
0.826
0.809
0.792
0.000
N
COOEt
9
5ea
9.5
9.0
8.5
8.0
7.5
7.0
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
0.87
0.91
1.83
0.93
2.00
1.88
2.10
17.37
3.10

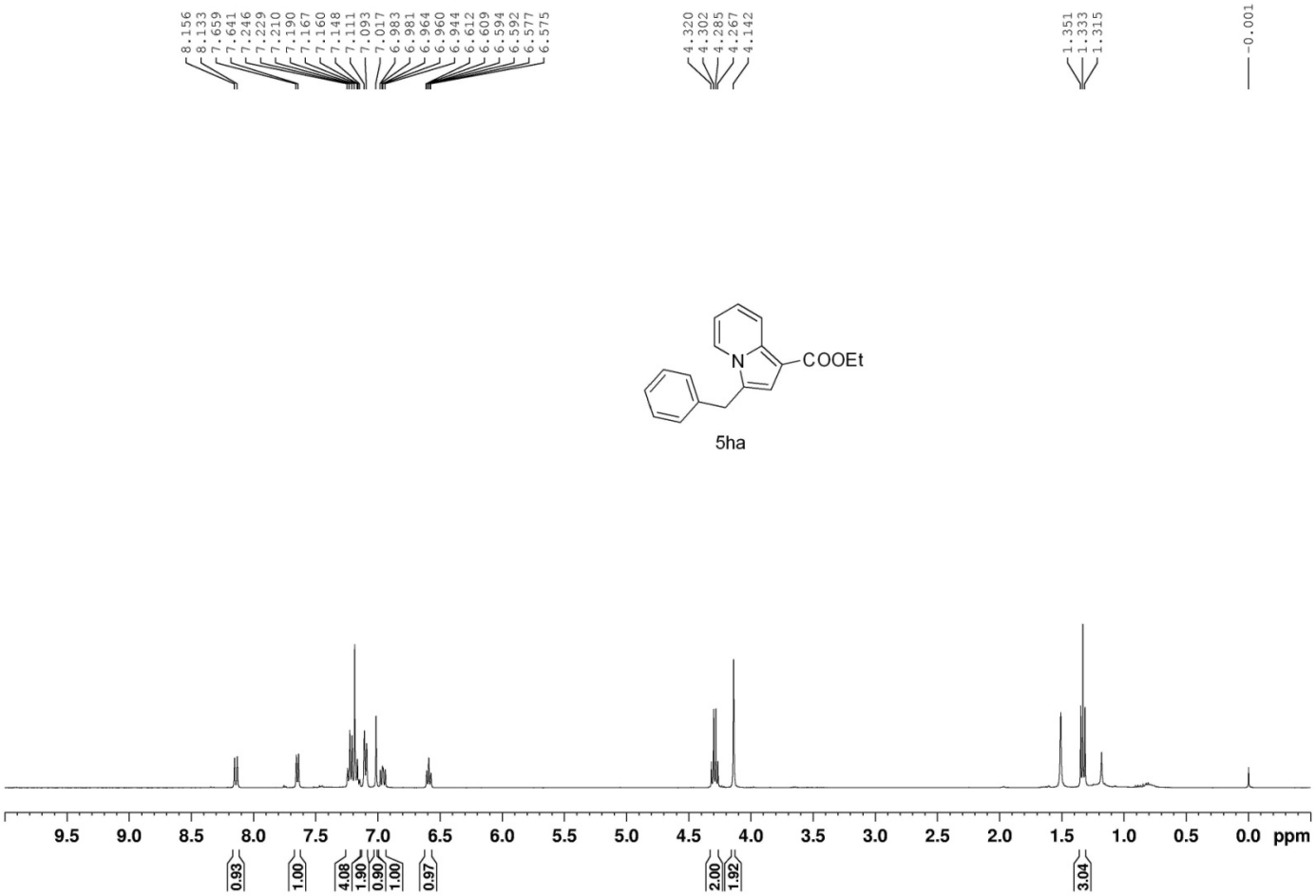

165.22
135.62
125.78
122.69
121.08
120.00
113.62
112.09
102.79
77.35
77.03
76.71
59.37
31.90
29.61
29.56
29.50
29.45
29.33
26.87
25.73
22.69
14.70
14.12
COOEt
N
9
5ea
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

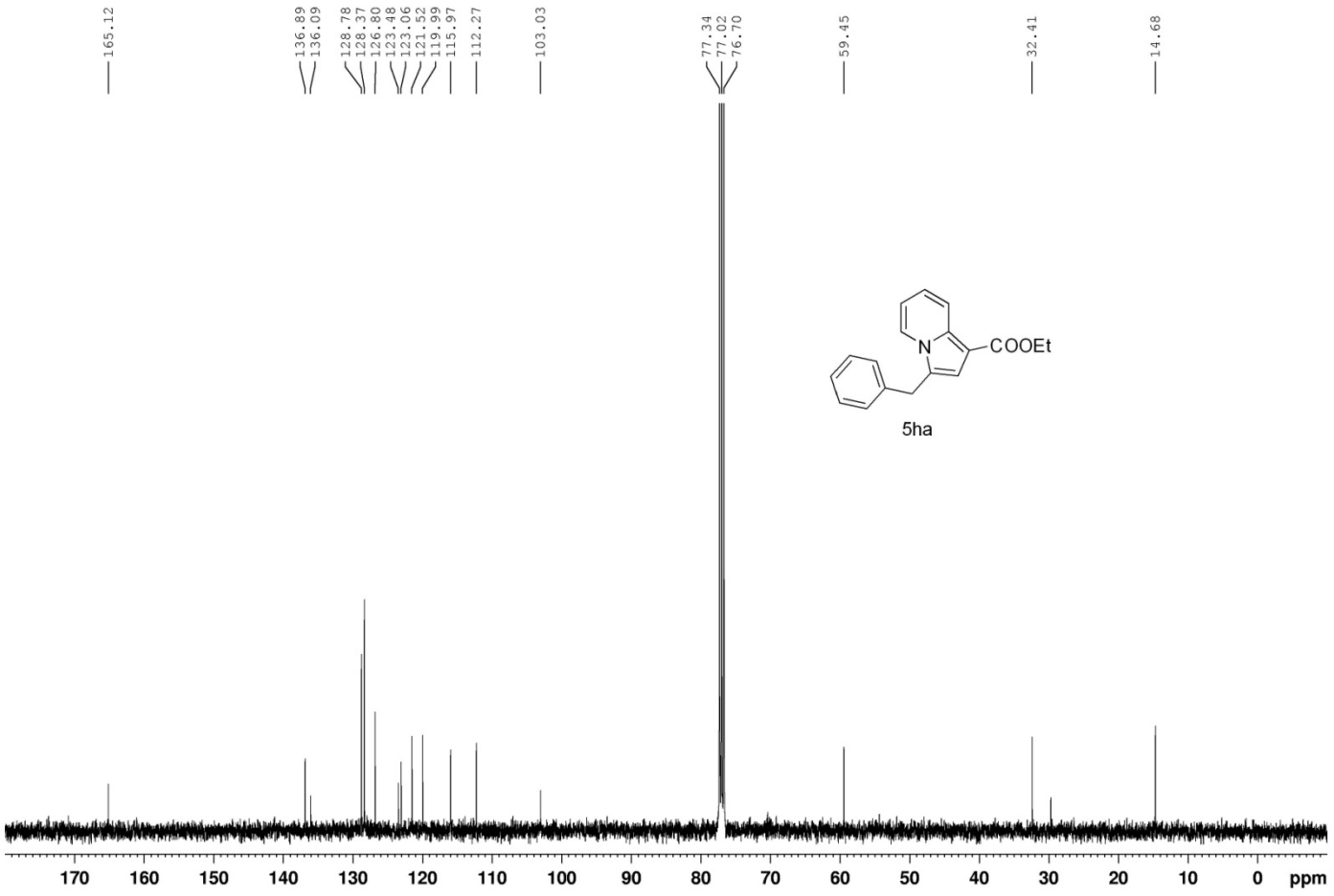

8.130
8.107
7.773
7.755
7.191
6.965
6.955
6.952
6.949
6.946
6.932
6.930
6.687
6.684
6.670
6.667
6.653
6.650
4.316
4.298
4.280
4.263
2.711
2.692
2.673
1.734
1.715
1.696
1.677
1.658
1.352
1.334
1.317
1.226
1.187
0.823
0.807
0.789
0.000
COOEt
N
13
5fa
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
0.92
0.93
1.90
0.95
2.00
1.91
1.94
25.42
3.06

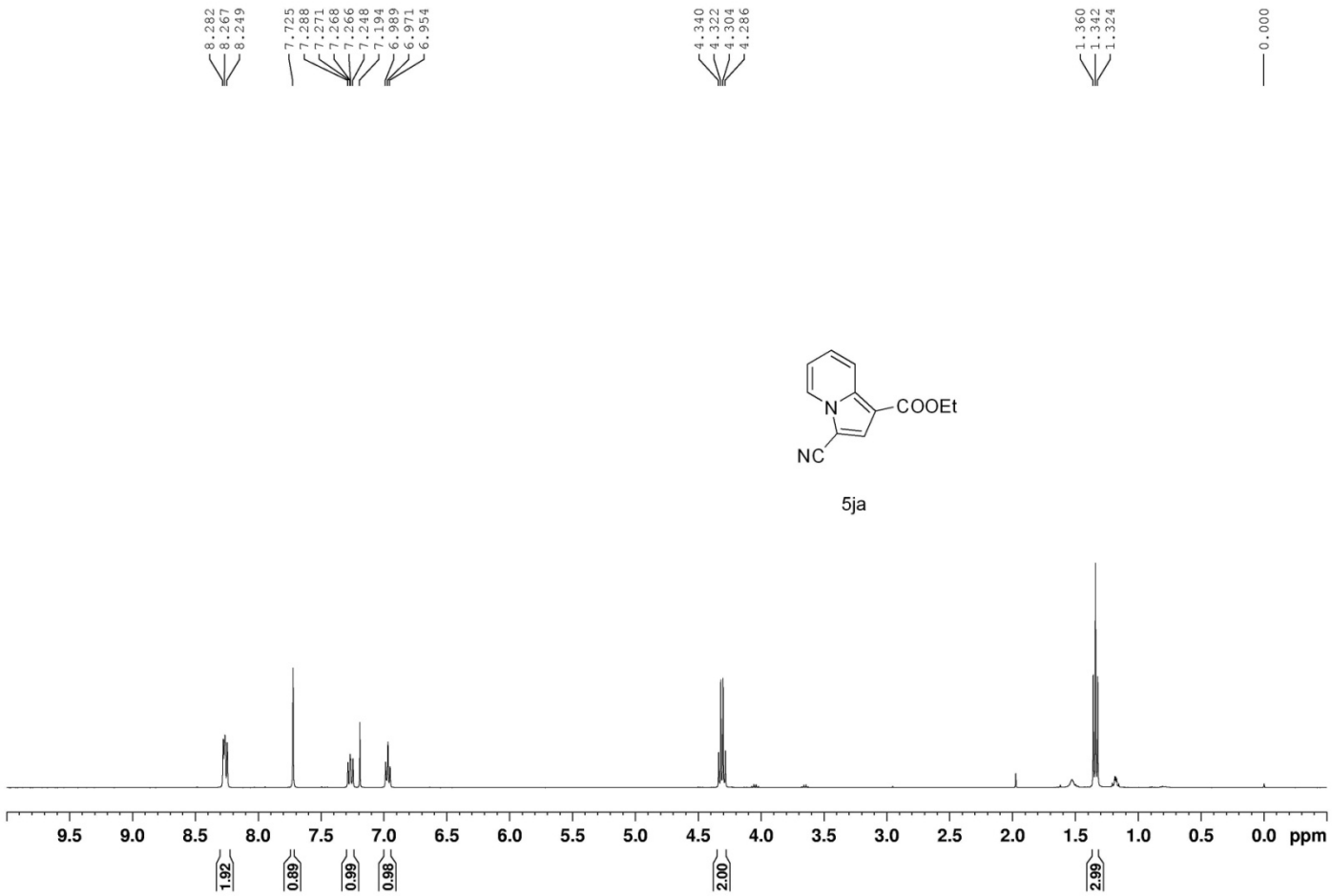

165.21
135.62
125.78
122.68
121.08
120.00
113.62
112.08
102.79
77.35
77.03
76.71
59.37
31.94
29.70
29.66
29.57
29.51
29.46
29.37
26.88
25.73
22.70
14.70
14.13
N
COOEt
13
5fa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

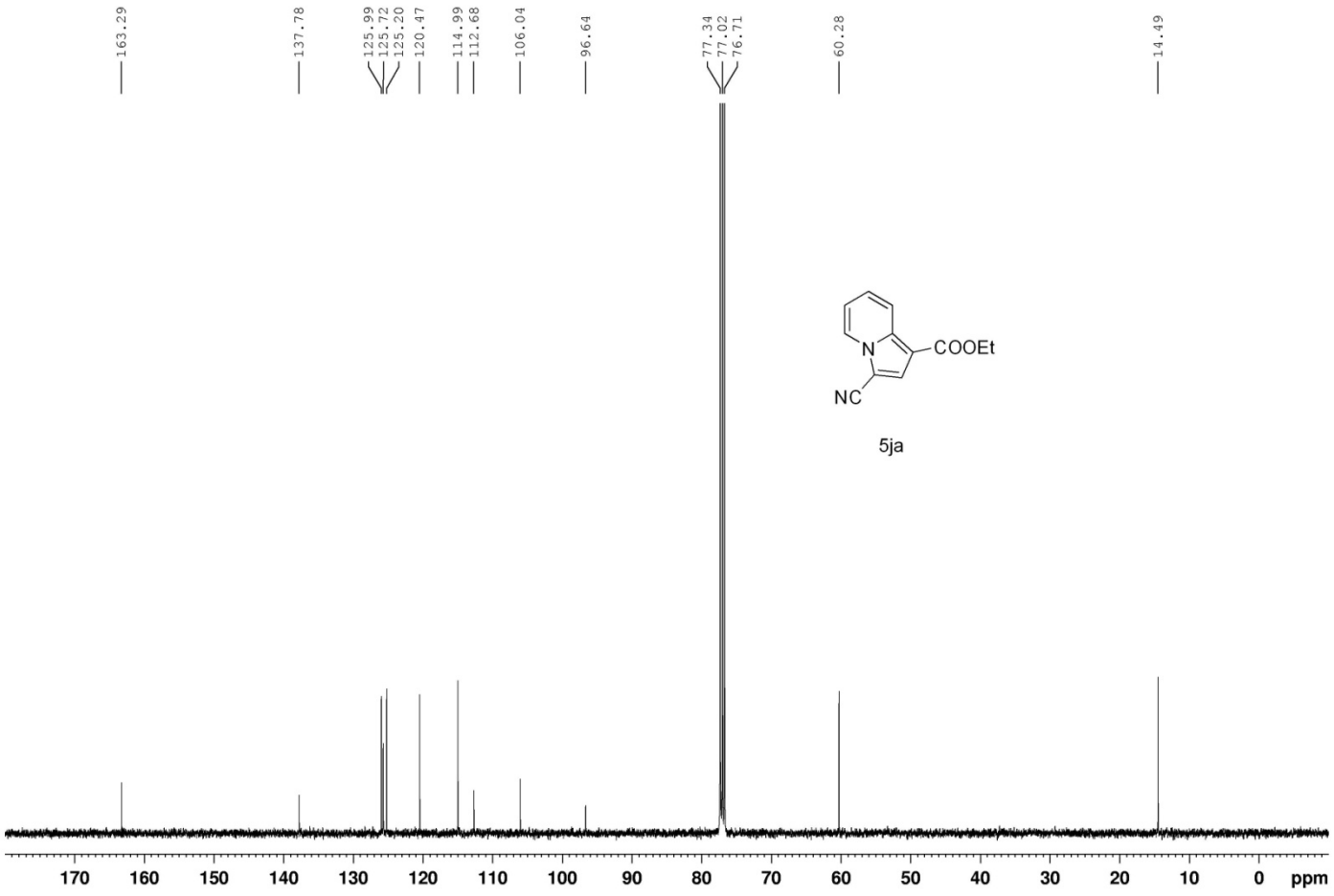

8.137
8.114
7.835
7.817
7.190
6.955
6.942
6.936
6.919
6.672
6.655
6.638
4.315
4.297
4.280
4.262
2.735
2.716
2.689
2.030
2.009
1.827
1.814
1.805
1.751
1.721
1.427
1.398
1.368
1.351
1.333
1.316
1.269
0.000
N
COOEt
5ga
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
0.95
0.98
1.95
0.97
2.00
1.04
2.04
3.09
8.32

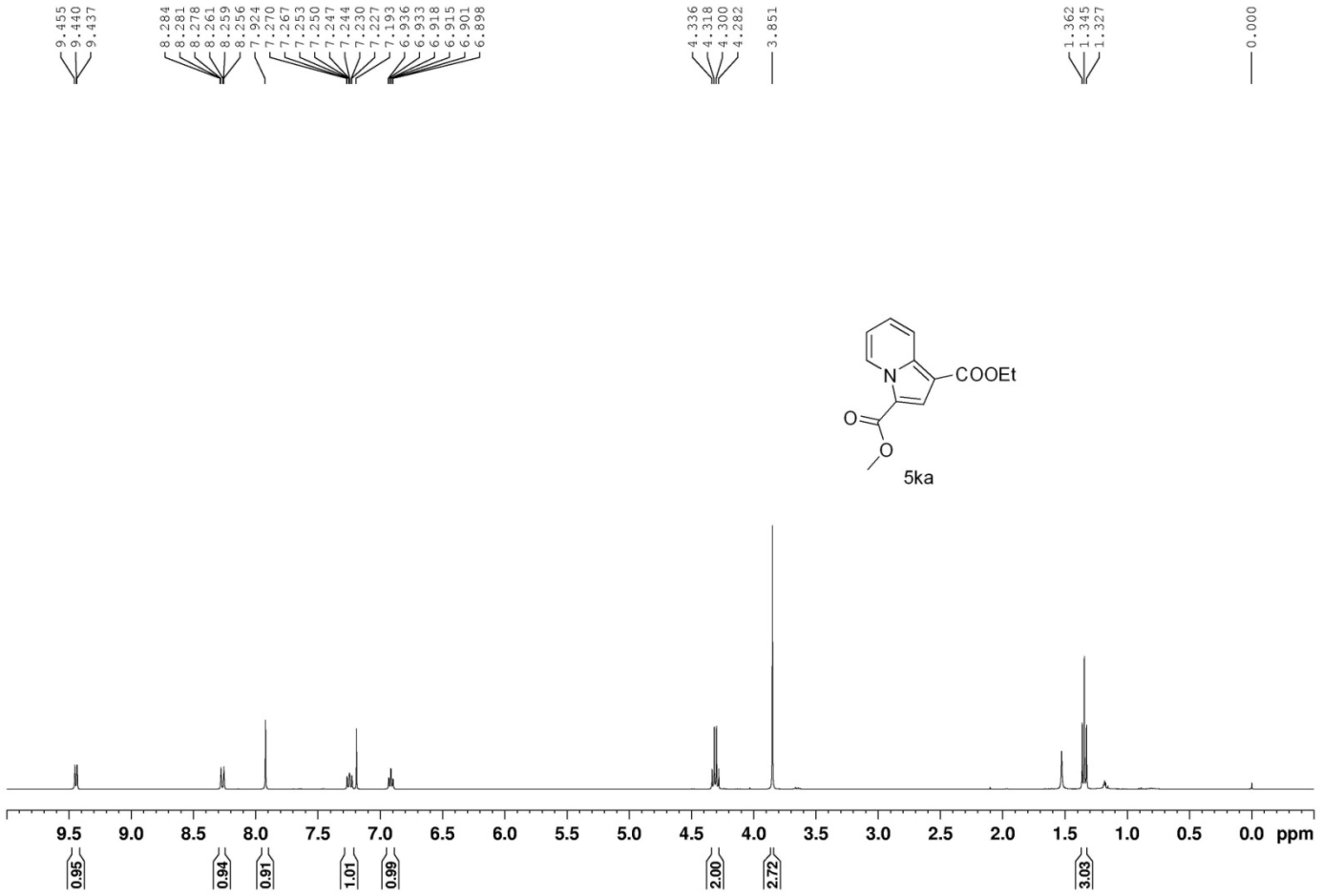

165.26
135.62
131.15
122.82
121.11
120.17
111.99
111.68
102.85
77.34
77.02
76.71
59.38
34.98
26.46
26.28
14.71
N
COOEt
5ga
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

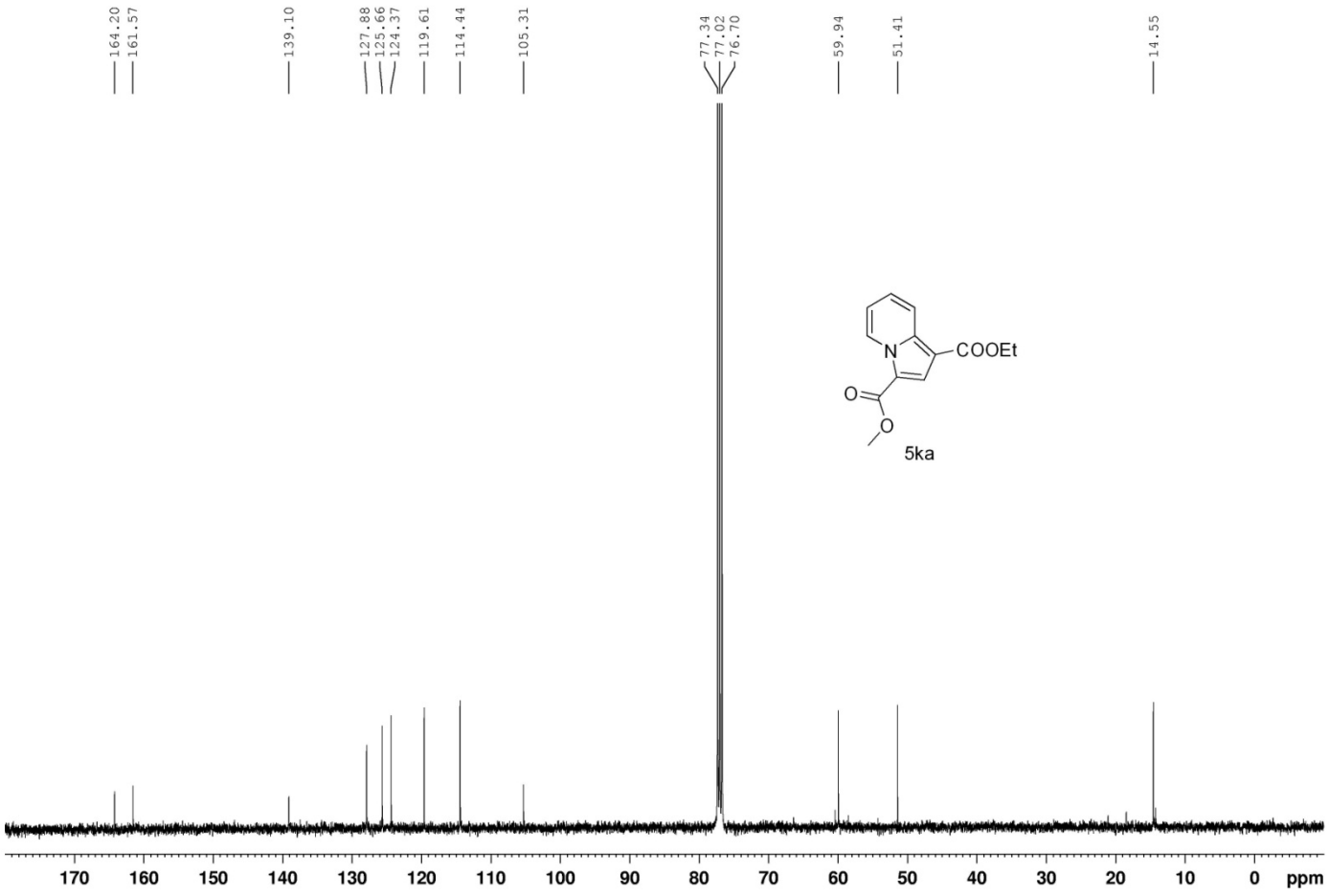

8.156
8.133
7.659
7.641
7.246
7.229
7.210
7.190
7.167
7.160
7.148
7.111
7.093
7.017
6.983
6.981
6.964
6.960
6.944
6.612
6.609
6.594
6.592
6.577
6.575
4.320
4.302
4.285
4.267
4.142
1.351
1.333
1.315
-0.001
N
COOEt
5ha
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.93
1.00
4.08
1.90
0.90
1.00
0.97
2.00
1.92
3.04

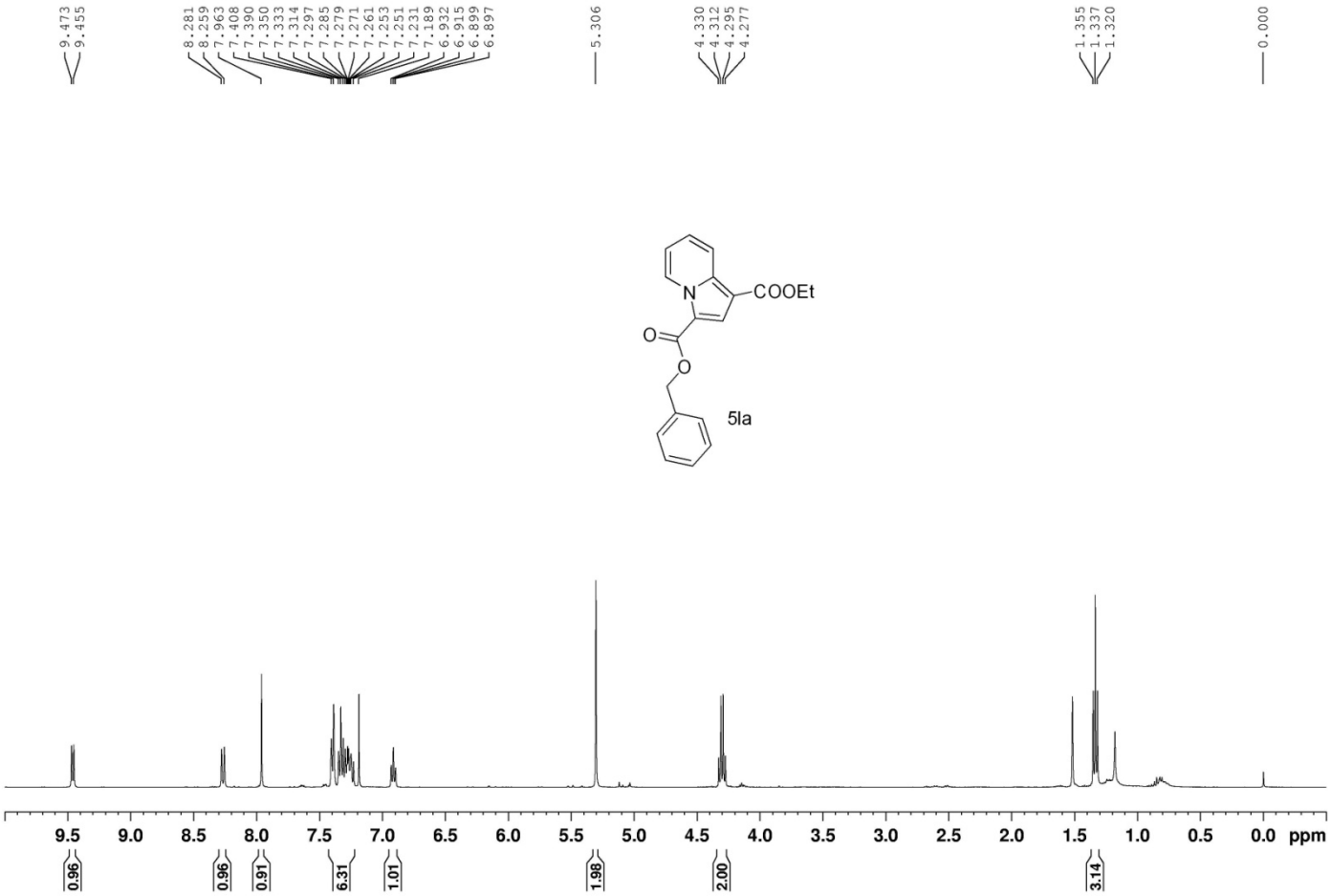

165.12
136.89
136.09
128.78
128.37
126.80
123.48
123.06
121.52
119.99
115.97
112.27
103.03
77.34
77.02
76.70
59.45
32.41
14.68
N
COOEt
5ha
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

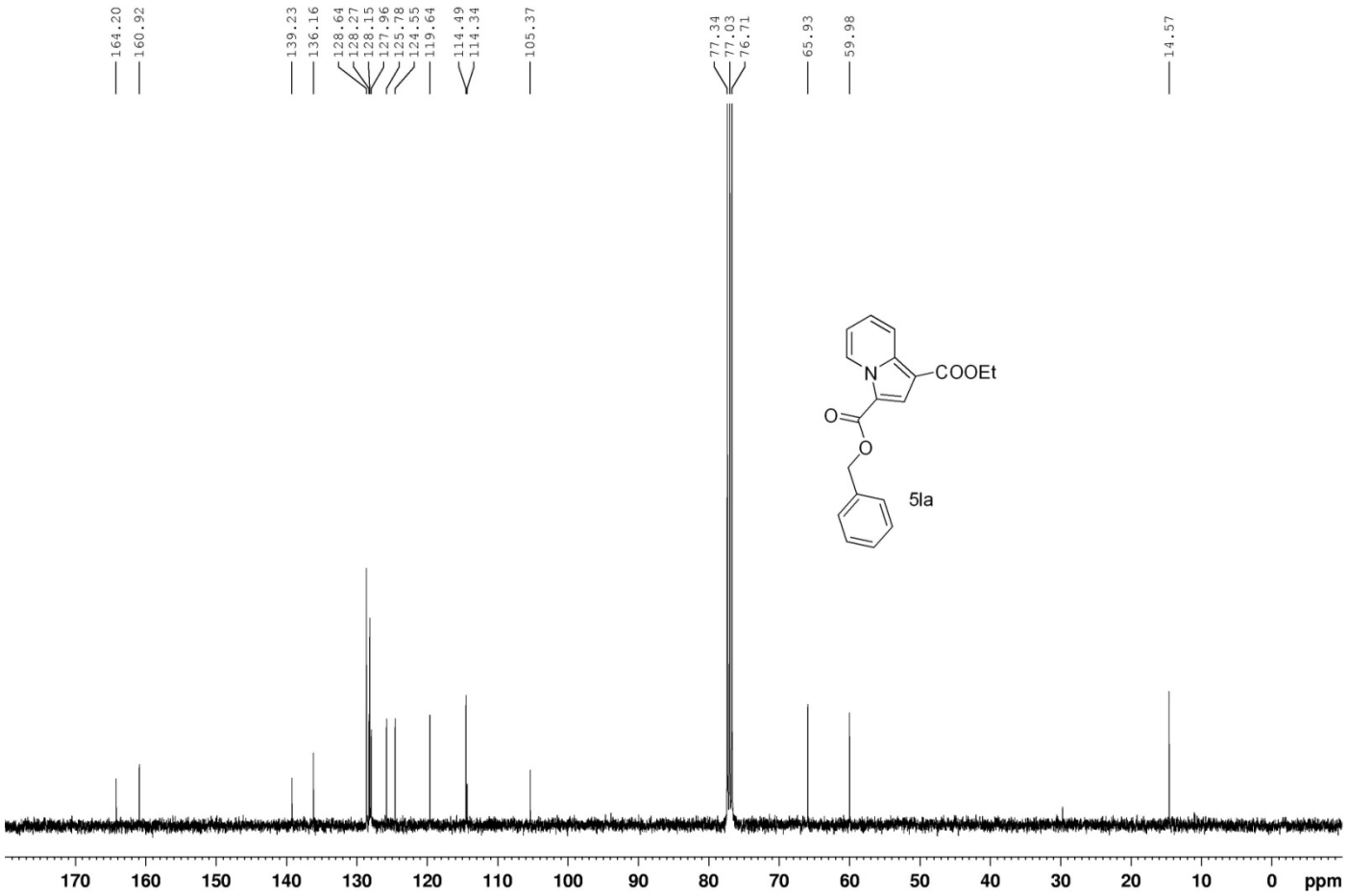

8.282
8.267
8.249
7.725
7.288
7.271
7.268
7.266
7.248
7.194
6.989
6.971
6.954
4.340
4.322
4.304
4.286
1.360
1.342
1.324
0.000
N
COOEt
NC
5ja
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.92
0.89
0.99
0.98
2.00
2.99

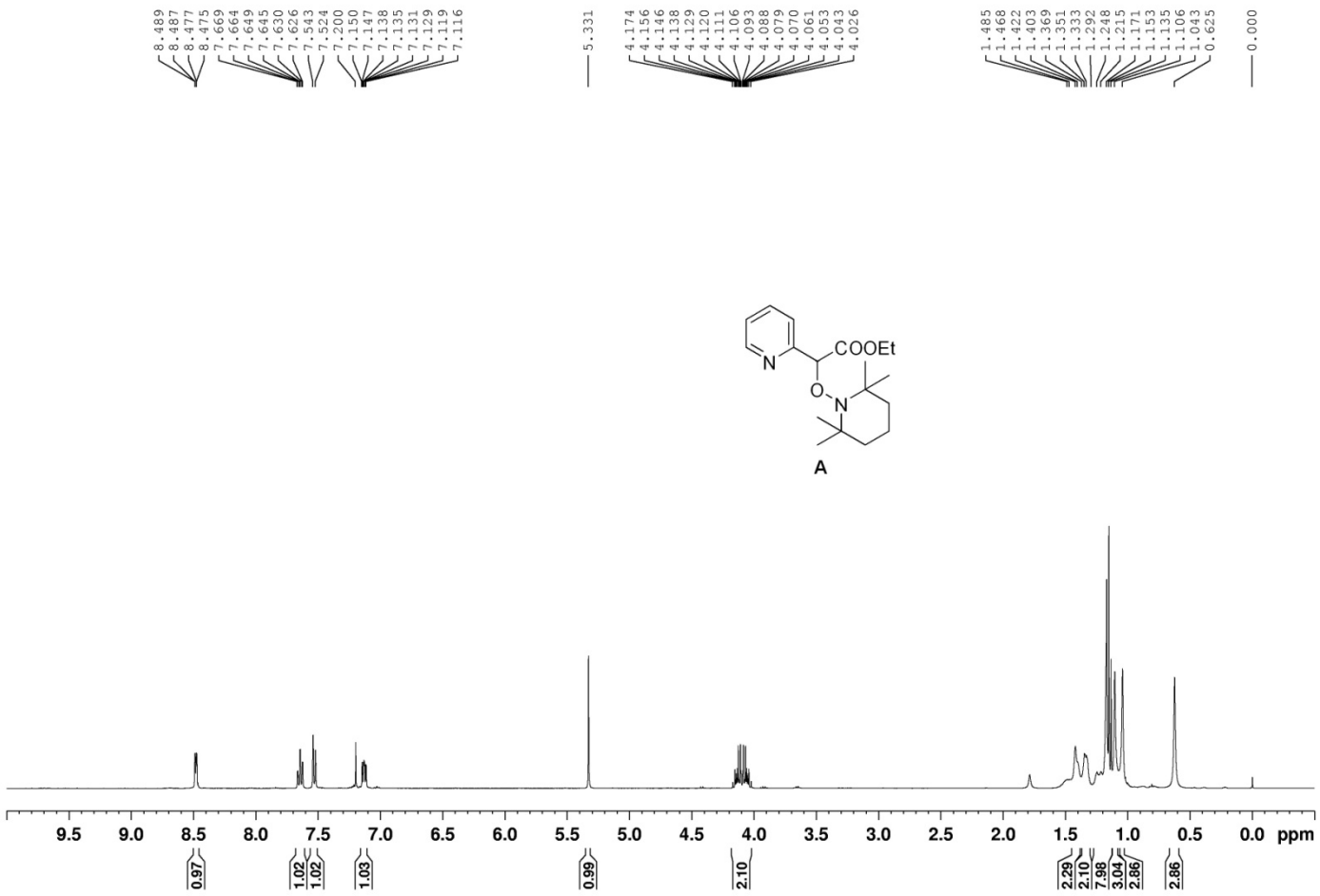

163.29
137.78
125.99
125.72
125.20
120.47
114.99
112.68
106.04
96.64
77.34
77.02
76.71
60.28
14.49
COOEt
N
NC
5ja
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

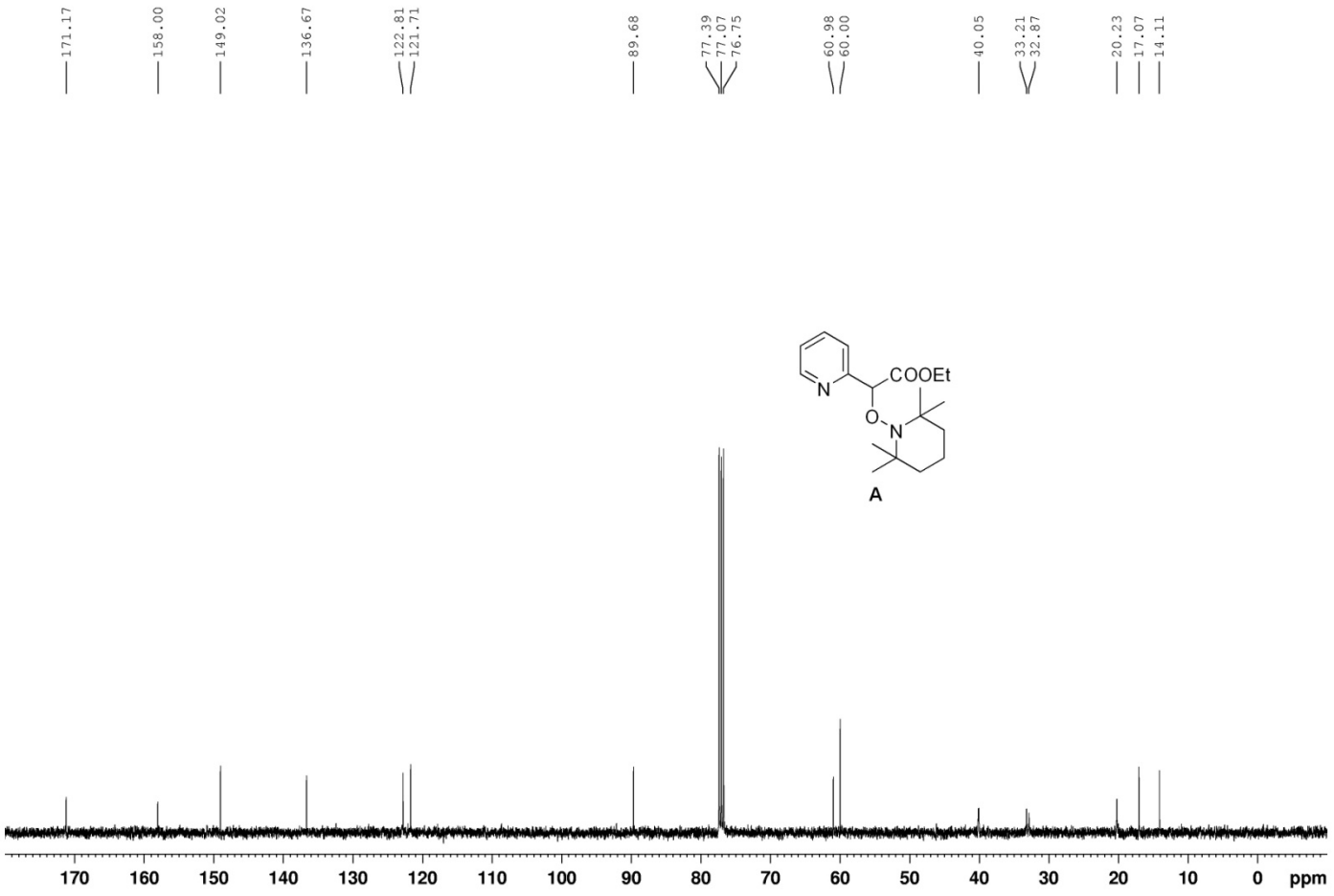

9.455
9.440
9.437
8.284
8.281
8.278
8.261
8.259
8.256
7.924
7.270
7.267
7.253
7.250
7.247
7.244
7.230
7.227
7.193
6.936
6.933
6.918
6.915
6.901
6.898
4.336
4.318
4.300
4.282
3.851
1.362
1.345
1.327
0.000
COOEt
N
O
O
5ka
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
0.95
0.94
0.91
1.01
0.99
2.00
2.72
3.03


164.20
161.57
139.10
127.88
125.66
124.37
119.61
114.44
105.31
77.34
77.02
76.70
59.94
51.41
14.55
COOEt
N
O
O
5ka
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


9.473
9.455
8.281
8.259
7.963
7.408
7.390
7.350
7.333
7.314
7.297
7.285
7.279
7.271
7.261
7.253
7.251
7.231
7.189
6.932
6.915
6.899
6.897
5.306
4.330
4.312
4.295
4.277
1.355
1.337
1.320
0.000
COOEt
N
O
O
5la
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
0.96
0.96
0.91
6.31
1.01
1.98
2.00
3.14


164.20
160.92
139.23
136.16
128.64
128.27
128.15
127.96
125.78
124.55
119.64
114.49
114.34
105.37
77.34
77.03
76.71
65.93
59.98
14.57
COOEt
N
O
O
5la
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


8.489
8.487
8.477
8.475
7.669
7.664
7.649
7.645
7.630
7.626
7.543
7.524
7.200
7.150
7.147
7.138
7.135
7.131
7.129
7.119
7.116
5.331
4.174
4.156
4.146
4.138
4.129
4.120
4.111
4.106
4.093
4.088
4.079
4.070
4.061
4.053
4.043
4.026
1.485
1.468
1.422
1.403
1.369
1.351
1.333
1.292
1.248
1.215
1.171
1.153
1.135
1.106
1.043
0.625
0.000
COOEt
N
O
N
A
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
0.97
1.02
1.02
1.03
0.99
2.10
2.29
2.10
7.98
3.04
2.86
2.86


171.17
158.00
149.02
136.67
122.81
121.71
89.68
77.39
77.07
76.75
60.98
60.00
40.05
33.21
32.87
20.23
17.07
14.11
COOEt
N
O
N
A
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm