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Metal-free synthesis of imidazo[1,5-*a*]pyridines *via* elemental sulfur mediated sequential dual oxidative Csp^3-H amination

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Supporting Information

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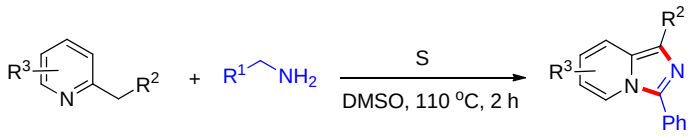
1. General information

^{1}H NMR and ^{13}C NMR were recorded in $CDCl_3$ at room temperature on the Bruker spectrometer (500 MHz ^{1}H). The chemical-shifts scale is based on internal TMS. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; qui, quintet; sxt, sextet. The coupling constants, *J* are reported in Hertz (Hz). If not stated otherwise, all melting points are uncorrected. Mass spectroscopy data were collected on an HRMS-ESI instrument. Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Glassware was dried for 4 h at 140 ^{o}C. All solvents were purified and dried according to standard methods prior to use. Products were purified by flash column chromatography on 200-300 mesh silica gel, SiO_2.

2. General procedure for elemental sulfur mediated sequential dual oxidative Csp^3-H amination.

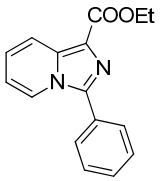


1 **2** **3**

2-pyridyl acetate **1** (0.2 mmol), amine **2** (0.24 mmol), elemental sulfur (0.6 mmol), and anhydrous DMSO (1 mL) were added in a sealed pressure vessel (25 mL) containing a magnetic stirring bar and then capped and stirred at 110 °C for 2 h under air atmosphere. After the reaction was completed (TLC), the cooled mixture was diluted with ethyl acetate and filtered with a short column on silica gel. The combined organic layer was washed with brine and dried over sodium sulfate. Concentration in vacuo followed by silica gel column purification with petroleum ether/ethyl acetate eluent to afford product **3**.

3. Characterization data of products.

Ethyl 3-phenylimidazo[1,5-*a*]pyridine-1-carboxylate (3a)



Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/2) as a white solid in 88% yield.

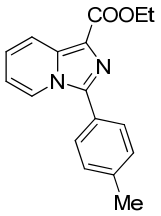
M.p. = 129-130 ^{o}C;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.28 (d, J = 7.2 Hz, 1H), 8.22 (d, J = 9.2 Hz, 1H), 7.79-7.73 (m, 2H), 7.53-7.44 (m, 3H), 7.12-7.08 (m, 1H), 6.78-6.72 (m, 1H), 4.47 (q, J = 7.1 Hz, 2H), 1.44 (t, J = 7.1 Hz, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 163.52, 139.06, 135.33, 129.45, 128.99, 128.89, 128.69, 124.14, 122.42, 121.67, 119.96, 114.32, 60.31, 14.58;

HRMS (ESI) calcd for $C_{16}H_{15}N_2O_2$: $[M+H]^+$ 267.1128, found: 267.1123.

Ethyl 3-(*p*-tolyl)imidazo[1,5-*a*]pyridine-1-carboxylate (3b)



Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/2) as a yellow solid in 90% yield.

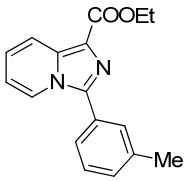
M.p. = 113-114 ^{o}C;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.23 (d, J = 7.2 Hz, 1H), 8.18 (d, J = 9.2 Hz, 1H), 7.63 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 7.9 Hz, 2H), 7.06 (dd, J = 8.8, 6.7 Hz, 1H), 6.71 (t, J = 6.6 Hz, 1H), 4.46 (q, J = 7.1 Hz, 2H), 2.38 (s, 3H), 1.42 (t, J = 7.1 Hz, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 163.59, 139.54, 139.27, 135.29, 129.56, 128.61, 126.12, 124.01, 122.51, 121.53, 119.95, 114.17, 60.28, 21.39, 14.61;

HRMS (ESI) calcd for $C_{17}H_{17}N_2O_2$: $[M+H]^+$ 281.1285, found: 281.1289.

Ethyl 3-(*m*-tolyl)imidazo[1,5-*a*]pyridine-1-carboxylate (3c)



Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/2) as a yellow solid in 85% yield.

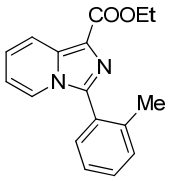
M.p. = 86-87 ^{o}C;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.26 (d, J = 7.2 Hz, 1H), 8.18 (d, J = 9.2 Hz, 1H), 7.59 (s, 1H), 7.50 (d, J = 7.6 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.23 (d, J = 7.6 Hz, 1H), 7.10-7.01 (m, 1H), 6.71 (t, J = 6.8 Hz, 1H), 4.45 (q, J = 7.1 Hz, 2H), 2.37 (s, 3H), 1.42 (t, J = 7.1 Hz, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 163.45, 139.16, 138.72, 135.22, 130.12, 129.51, 128.78, 128.55, 125.27, 124.00, 122.46, 121.50, 119.81, 114.15, 60.17, 21.23, 14.53;

HRMS (ESI) calcd for $C_{17}H_{17}N_2O_2$: $[M+H]^+$ 281.1285, found: 281.1286.

Ethyl 3-(*o*-tolyl)imidazo[1,5-*a*]pyridine-1-carboxylate (3d)



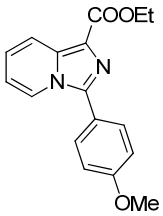
Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/2) as a yellow oil in 82% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.25 (d, J = 9.2 Hz, 1H), 7.67 (d, J = 7.1 Hz, 1H), 7.48-7.38 (m, 2H), 7.37-7.28 (m, 2H), 7.16-7.10 (m, 1H), 6.76-6.70 (m, 1H), 4.49 (q, J = 7.1 Hz, 2H), 2.16 (s, 3H), 1.46 (t, J = 7.1 Hz, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 163.69, 138.77, 138.55, 134.60, 130.87, 130.60, 130.07, 128.27, 126.05, 124.06, 122.51, 121.20, 119.84, 114.11, 60.33, 19.60, 14.65;

HRMS (ESI) calcd for $C_{17}H_{17}N_2O_2$: $[M+H]^+$ 281.1285, found: 281.1285.

Ethyl 3-(4-methoxyphenyl)imidazo[1,5-*a*]pyridine-1-carboxylate (3e)



Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/2) as a yellow solid in 83% yield.

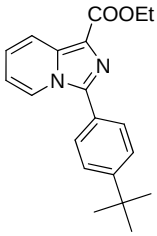
M.p. = 127-128 ^{o}C;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.27-8.17 (m, 2H), 7.70 (d, J = 8.8 Hz, 2H), 7.12-7.06 (m, 1H), 7.03 (d, J = 8.8 Hz, 2H), 6.77-6.72 (m, 1H), 4.48 (q, J = 7.1 Hz, 2H), 3.87 (s, 3H), 1.45 (t, J = 7.1 Hz, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 163.63, 160.44, 139.14, 135.23, 130.23, 123.94, 121.44, 121.42, 119.99, 114.32, 114.15, 60.30, 55.35, 14.64 (one signal was overlapped by other ones);

HRMS (ESI) calcd for $C_{17}H_{17}N_2O_3$: $[M+H]^+$ 297.1234, found: 297.1236.

Ethyl 3-(4-(tert-butyl)phenyl)imidazo[1,5-*a*]pyridine-1-carboxylate (3f)



Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/2) as a white solid in 80% yield.

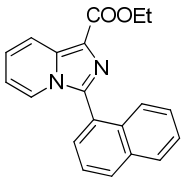
M.p. = 153-154 ^{o}C;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.30 (d, J = 7.2 Hz, 1H), 8.22 (d, J = 9.2 Hz, 1H), 7.74-7.67 (m, 2H), 7.56-7.49 (m, 2H), 7.11-7.07 (m, 1H), 6.77-6.68 (m, 1H), 4.48 (q, J = 7.1 Hz, 2H), 1.45 (t, J = 7.1 Hz, 3H), 1.35 (s, 9H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 163.59, 152.73, 139.28, 135.30, 128.41, 126.11, 125.84, 124.01, 122.60, 121.59, 119.97, 114.13, 60.27, 34.80, 31.16, 14.60;

HRMS (ESI) calcd for $C_{20}H_{23}N_2O_2$: $[M+H]^+$ 323.1754, found: 323.1757.

Ethyl 3-(naphthalen-1-yl)imidazo[1,5-*a*]pyridine-1-carboxylate (3g)



Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/2) as a yellow solid in 84% yield.

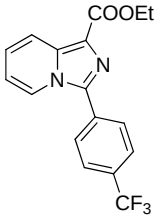
M.p. = 137-138 ^{o}C;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.30 (d, J = 9.2 Hz, 1H), 8.00 (d, J = 8.3 Hz, 1H), 7.93 (d, J = 8.2 Hz, 1H), 7.74 (dd, J = 7.0, 1.0 Hz, 1H), 7.63 (d, J = 7.1 Hz, 1H), 7.58 (dd, J = 8.2, 7.2 Hz, 1H), 7.53-7.47 (m, 2H), 7.45-7.39 (m, 1H), 7.15-7.12 (m, 1H), 6.69-6.62 (m, 1H), 4.51 (q, J = 7.1 Hz, 2H), 1.46 (t, J = 7.1 Hz, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 163.62, 137.80, 134.97, 133.61, 131.73, 130.47, 129.45, 128.57, 127.15, 126.36, 126.10, 125.23, 125.06, 124.24, 122.83, 121.63, 119.78, 114.03, 60.31, 14.62;

HRMS (ESI) calcd for $C_{20}H_{17}N_2O_2$: $[M+H]^+$ 317.1285, found: 317.1282.

Ethyl 3-(4-(trifluoromethyl)phenyl)imidazo[1,5-*a*]pyridine-1-carboxylate (3h)



Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/2) as a yellow solid in 75% yield.

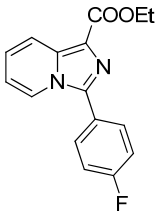
M.p. = 144-145 ^{o}C;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.28 (d, J = 7.2 Hz, 1H), 8.22 (d, J = 9.2 Hz, 1H), 7.90 (d, J = 8.1 Hz, 2H), 7.73 (d, J = 8.2 Hz, 2H), 7.14-7.11 (m, 1H), 6.84-6.77 (m, 1H), 4.45 (q, J = 7.1 Hz, 2H), 1.42 (t, J = 7.1 Hz, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 163.21, 137.30, 135.53, 132.51, 131.00 (q, $J_{C\text{-}F}$ = 32.5 Hz), 128.75, 125.81 (q, $J_{C\text{-}F}$ = 3.7 Hz), 124.46, 123.69 (q, $J_{C\text{-}F}$ = 270 Hz), 122.27, 122.08, 120.08, 114.88, 60.40, 14.48;

HRMS (ESI) calcd for $C_{17}H_{14}F_3N_2O_2$: $[M+H]^+$ 335.1002, found: 335.1003.

Ethyl 3-(4-fluorophenyl)imidazo[1,5-*a*]pyridine-1-carboxylate (3i)



Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/2) as a yellow solid in 82% yield.

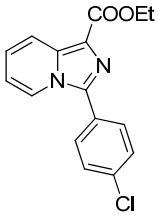
M.p. = 124-125 ^{o}C;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.24 (dd, J = 14.3, 8.2 Hz, 2H), 7.82-7.73 (m, 2H), 7.22 (dd, J = 12.0, 5.3 Hz, 2H), 7.15-7.12 (m, 1H), 6.83-6.76 (m, 1H), 4.49 (q, J = 7.1 Hz, 2H), 1.46 (t, J = 7.1 Hz, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 163.53, 163.31 (d, $J_{C\text{-}F}$ = 248.8 Hz), 138.14, 135.36, 130.83 (d, $J_{C\text{-}F}$ = 8.8 Hz), 125.25, 124.20, 122.22, 121.79, 120.14, 116.19 (d, $J_{C\text{-}F}$ = 22.5 Hz), 114.57, 60.46, 14.64;

HRMS (ESI) calcd for $C_{16}H_{14}FN_2O_2$: $[M+H]^+$ 285.1034, found: 285.1034.

Ethyl 3-(4-chlorophenyl)imidazo[1,5-*a*]pyridine-1-carboxylate (3j)



Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/2) as a white solid in 86% yield.

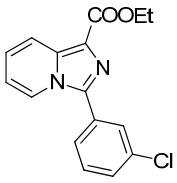
M.p. = 138-139 ^{o}C;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.23 (d, J = 8.7 Hz, 2H), 7.76-7.66 (m, 2H), 7.53-7.44 (m, 2H), 7.16-7.08 (m, 1H), 6.80-6.77 (m, 1H), 4.48 (q, J = 7.1 Hz, 2H), 1.44 (t, J = 7.1 Hz, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 163.40, 137.86, 135.45, 135.43, 129.93, 129.22, 127.52, 124.25, 122.19, 121.95, 120.11, 114.65, 60.42, 14.59;

HRMS (ESI) calcd for $C_{16}H_{14}ClN_2O_2$: $[M+H]^+$ 301.0738, found: 301.0741.

Ethyl 3-(3-chlorophenyl)imidazo[1,5-*a*]pyridine-1-carboxylate (3k)



Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/2) as a white solid in 85% yield.

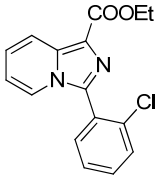
M.p. = 117-118 ^{o}C;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.29 (d, J = 7.2 Hz, 1H), 8.25 (d, J = 9.2 Hz, 1H), 7.80 (s, 1H), 7.71-7.64 (m, 1H), 7.49-7.41 (m, 2H), 7.14 (dd, J = 8.8, 6.9 Hz, 1H), 6.82 (dd, J = 10.0, 3.7 Hz, 1H), 4.48 (q, J = 7.1 Hz, 2H), 1.45 (t, J = 7.1 Hz, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 163.35, 137.46, 135.47, 134.96, 130.75, 130.16, 129.50, 128.74, 126.53, 124.35, 122.20, 122.04, 120.09, 114.75, 60.42, 14.58;

HRMS (ESI) calcd for $C_{16}H_{14}ClN_2O_2$: $[M+H]^+$ 301.0738, found: 301.0739.

Ethyl 3-(2-chlorophenyl)imidazo[1,5-*a*]pyridine-1-carboxylate (3l)



Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/2) as a white solid in 84% yield.

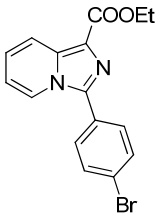
M.p. = 102-103 ^{o}C;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.26 (d, J = 9.2 Hz, 1H), 7.68 (d, J = 7.1 Hz, 1H), 7.63 (dd, J = 7.5, 1.6 Hz, 1H), 7.51 (dd, J = 8.0, 1.1 Hz, 1H), 7.48-7.44 (m, 1H), 7.42-7.39 (m, 1H), 7.19-7.12 (m, 1H), 6.81-6.75 (m, 1H), 4.47 (q, J = 7.1 Hz, 2H), 1.44 (t, J = 7.1 Hz, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 163.45, 136.57, 134.91, 134.36, 133.54, 131.37, 129.72, 128.29, 127.16, 124.34, 123.16, 121.47, 119.70, 114.03, 60.34, 14.60;

HRMS (ESI) calcd for $C_{16}H_{14}ClN_2O_2$: $[M+H]^+$ 301.0738, found: 301.0738.

Ethyl 3-(4-bromophenyl)imidazo[1,5-*a*]pyridine-1-carboxylate (3m)



Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/2) as a yellow solid in 86% yield.

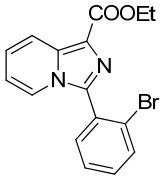
M.p. = 142-143 ^{o}C;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.31-8.15 (m, 2H), 7.72-7.59 (m, 4H), 7.13 (dd, J = 8.9, 6.8 Hz, 1H), 6.79 (t, J = 6.8 Hz, 1H), 4.47 (q, J = 7.1 Hz, 2H), 1.44 (t, J = 7.1 Hz, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 163.31, 137.82, 135.38, 132.10, 130.05, 127.91, 124.24, 123.61, 122.15, 121.92, 120.03, 114.64, 60.36, 14.55;

HRMS (ESI) calcd for $C_{16}H_{14}BrN_2O_2$: $[M+H]^+$ 345.0233, found: 345.0235.

Ethyl 3-(2-bromophenyl)imidazo[1,5-*a*]pyridine-1-carboxylate (3n)



Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/2) as a yellow solid in 82% yield.

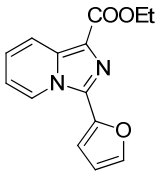
M.p. = 145-146 ^{o}C;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.24 (d, J = 9.2 Hz, 1H), 7.70-7.62 (m, 2H), 7.57 (dd, J = 7.6, 1.6 Hz, 1H), 7.45-7.42 (m, 1H), 7.39-7.35 (m, 1H), 7.16-7.13 (m, 1H), 6.80-6.74 (m, 1H), 4.46 (q, J = 7.1 Hz, 2H), 1.43 (t, J = 7.1 Hz, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 163.43, 137.65, 134.69, 133.69, 132.85, 131.53, 130.34, 127.64, 124.34, 124.11, 123.14, 121.21, 119.64, 113.98, 60.30, 14.57;

HRMS (ESI) calcd for $C_{16}H_{14}BrN_2O_2$: $[M+H]^+$ 345.0233, found: 345.0236.

Ethyl 3-(furan-2-yl)imidazo[1,5-*a*]pyridine-1-carboxylate (3o)



Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/2) as a yellow solid in 75% yield.

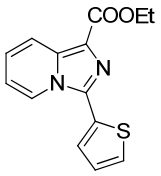
M.p. = 105-106 ^{o}C;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.79 (d, J = 7.2 Hz, 1H), 8.21 (d, J = 9.2 Hz, 1H), 7.57 (d, J = 1.0 Hz, 1H), 7.20-7.14 (m, 1H), 7.13-7.10 (m, 1H), 6.90-6.75 (m, 1H), 6.58 (dd, J = 3.5, 1.8 Hz, 1H), 4.47 (q, J = 7.1 Hz, 2H), 1.45 (t, J = 7.1 Hz, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 163.25, 145.23, 142.57, 134.89, 131.05, 124.34, 124.00, 121.82, 119.76, 114.78, 111.82, 110.43, 60.46, 14.54;

HRMS (ESI) calcd for $C_{14}H_{13}N_2O_3$: $[M+H]^+$ 257.0921, found: 257.0926.

Ethyl 3-(thiophen-2-yl)imidazo[1,5-*a*]pyridine-1-carboxylate (3p)



Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/2) as a white solid in 72% yield.

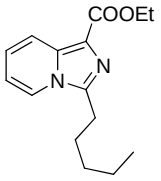
M.p. = 131-132 ^{o}C;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.40 (d, J = 7.1 Hz, 1H), 8.22 (d, J = 9.2 Hz, 1H), 7.60-7.52 (m, 1H), 7.46 (dd, J = 5.1, 0.5 Hz, 1H), 7.17 (dd, J = 5.0, 3.7 Hz, 1H), 7.12 (dd, J = 9.0, 6.5 Hz, 1H), 6.89-6.78 (m, 1H), 4.47 (q, J = 7.1 Hz, 2H), 1.44 (t, J = 7.1 Hz, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 163.27, 135.32, 133.57, 130.43, 127.51, 127.23, 127.05, 124.19, 122.62, 121.78, 119.95, 114.79, 60.41, 14.52;

HRMS (ESI) calcd for $C_{14}H_{13}N_2O_2S$: $[M+H]^+$ 273.0692, found: 273.0690.

Ethyl 3-pentylimidazo[1,5-*a*]pyridine-1-carboxylate (3q)



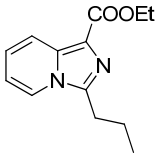
Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/3) as a yellow oil in 67% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.16 (d, J = 9.2 Hz, 1H), 7.87 (d, J = 7.1 Hz, 1H), 7.08-7.05 (m, 1H), 6.81-6.72 (m, 1H), 4.46 (q, J = 7.1 Hz, 2H), 3.07-2.96 (m, 2H), 1.83 (dt, J = 15.7, 7.8 Hz, 2H), 1.46-1.35 (m, 7H), 0.90 (t, J = 7.1 Hz, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 163.62, 140.27, 134.74, 123.32, 121.65, 120.14, 120.02, 113.73, 60.20, 31.66, 26.78, 26.76, 22.35, 14.68, 13.94;

HRMS (ESI) calcd for $C_{15}H_{21}N_2O_2$: $[M+H]^+$ 261.1598, found: 261.1597.

Ethyl 3-propylimidazo[1,5-*a*]pyridine-1-carboxylate (3r)



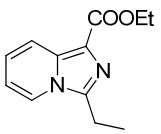
Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/3) as a yellow oil in 63% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.16 (d, J = 9.2 Hz, 1H), 7.87 (d, J = 7.1 Hz, 1H), 7.07-7.04 (m, 1H), 6.80-6.74 (m, 1H), 4.45 (q, J = 7.1 Hz, 2H), 3.04-2.97 (m, 2H), 1.86 (dd, J = 15.3, 7.6 Hz, 2H), 1.44 (t, J = 7.1 Hz, 3H), 1.02 (t, J = 7.4 Hz, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 163.60, 140.09, 134.73, 123.33, 121.66, 120.14, 120.00, 113.72, 60.19, 28.62, 20.54, 14.66, 13.98;

HRMS (ESI) calcd for $C_{13}H_{17}N_2O_2$: $[M+H]^+$ 233.1285, found: 233.1283.

Ethyl 3-ethylimidazo[1,5-*a*]pyridine-1-carboxylate (3s)



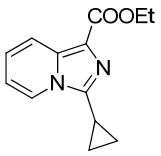
Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/3) as a yellow oil in 70% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.16 (d, J = 9.2 Hz, 1H), 7.87 (d, J = 7.1 Hz, 1H), 7.11-7.04 (m, 1H), 6.82-6.75 (m, 1H), 4.46 (q, J = 7.1 Hz, 2H), 3.06 (q, J = 7.6 Hz, 2H), 1.46-1.41 (m, 6H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 163.59, 141.02, 134.81, 123.43, 121.56, 120.04, 113.79, 60.24, 20.11, 14.65, 11.20 (one signal was overlapped by other ones);

HRMS (ESI) calcd for $C_{12}H_{15}N_2O_2$: $[M+H]^+$ 219.1128, found: 219.1131.

Ethyl 3-cyclopropylimidazo[1,5-*a*]pyridine-1-carboxylate (3t)



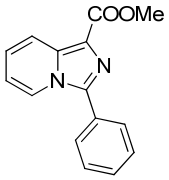
Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/3) as a yellow oil in 65% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.14 (d, J = 8.5 Hz, 2H), 7.09 (dd, J = 9.8, 6.6 Hz, 1H), 6.82-6.79 (m, 1H), 4.44 (q, J = 7.1 Hz, 2H), 2.05-2.00 (m, 1H), 1.43 (t, J = 7.1 Hz, 3H), 1.17-1.13 (m, 2H), 1.13-1.07 (m, 2H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 163.58, 140.84, 134.95, 123.80, 121.81, 119.91, 119.66, 113.70, 60.24, 14.62, 6.68, 6.16;

HRMS (ESI) calcd for $C_{13}H_{15}N_2O_2$: $[M+H]^+$ 231.1128, found: 231.1126.

Methyl 3-phenylimidazo[1,5-*a*]pyridine-1-carboxylate (3u)



Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/2) as a yellow solid in 92% yield.

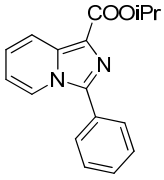
M.p. = 132-133 ^{o}C;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.27 (d, J = 7.2 Hz, 1H), 8.22 (d, J = 9.2 Hz, 1H), 7.79-7.71 (m, 2H), 7.52-7.42 (m, 3H), 7.11-7.08 (m, 1H), 6.78-6.72 (m, 1H), 3.97 (s, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 163.84, 139.03, 135.45, 129.45, 128.90, 128.87, 128.61, 124.26, 122.42, 121.31, 119.81, 114.37, 51.47;

HRMS (ESI) calcd for $C_{15}H_{13}N_2O_2$: $[M+H]^+$ 253.0972, found: 253.0970.

Isopropyl 3-phenylimidazo[1,5-*a*]pyridine-1-carboxylate (3v)



Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/2) as a yellow solid in 86% yield.

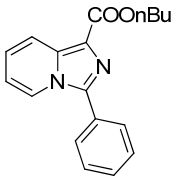
M.p. = 144-145 ^{o}C;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.26 (d, J = 7.2 Hz, 1H), 8.19 (d, J = 9.2 Hz, 1H), 7.75 (d, J = 7.1 Hz, 2H), 7.49 (t, J = 7.3 Hz, 2H), 7.45 (d, J = 7.2 Hz, 1H), 7.09 (dd, J = 8.9, 6.7 Hz, 1H), 6.74 (t, J = 6.6 Hz, 1H), 5.36 (hept, J = 6.2 Hz, 1H), 1.43 (d, J = 6.3 Hz, 6H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 163.12, 139.05, 135.06, 129.38, 129.06, 128.86, 128.71, 123.96, 122.36, 122.05, 120.02, 114.19, 67.62, 22.09;

HRMS (ESI) calcd for $C_{17}H_{17}N_2O_2$: $[M+H]^+$ 281.1285, found: 281.1288.

Butyl 3-phenylimidazo[1,5-*a*]pyridine-1-carboxylate (3w)



Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/2) as a yellow solid in 84% yield.

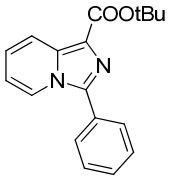
M.p. = 130-131 ^{o}C;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.27 (d, J = 7.2 Hz, 1H), 8.19 (d, J = 9.2 Hz, 1H), 7.81-7.70 (m, 2H), 7.50 (dd, J = 11.4, 4.4 Hz, 2H), 7.47-7.42 (m, 1H), 7.12-7.06 (m, 1H), 6.78-6.71 (m, 1H), 4.41 (t, J = 6.9 Hz, 2H), 1.88-1.74 (m, 2H), 1.53-1.40 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 163.59, 139.09, 135.20, 129.42, 128.99, 128.86, 128.67, 124.10, 122.40, 121.71, 119.92, 114.25, 64.18, 30.94, 19.19, 13.74;

HRMS (ESI) calcd for $C_{18}H_{19}N_2O_2$: $[M+H]^+$ 295.1441, found: 295.1437.

Tert-butyl 3-phenylimidazo[1,5-*a*]pyridine-1-carboxylate (3x)



Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/2) as a yellow solid in 82% yield.

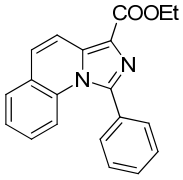
M.p. = 136-137 ^oC;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.27 (d, J = 7.2 Hz, 1H), 8.15 (d, J = 9.2 Hz, 1H), 7.83-7.73 (m, 2H), 7.52-7.47 (m, 2H), 7.47-7.41 (m, 1H), 7.08-7.04 (m, 1H), 6.76-6.69 (m, 1H), 1.67 (s, 9H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 162.84, 138.86, 134.62, 129.29, 129.25, 128.86, 128.60, 123.62, 123.12, 122.34, 120.14, 114.06, 80.78, 28.47;

HRMS (ESI) calcd for $C_{18}H_{19}N_2O_2$: $[M+H]^+$ 295.1441, found: 295.1438.

Ethyl 1-phenylimidazo[1,5-*a*]quinoline-3-carboxylate (3y)



Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/2) as a yellow solid in 90% yield.

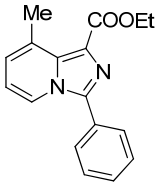
M.p. = 162-163 ^oC;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.14 (d, J = 9.5 Hz, 1H), 7.67 (dd, J = 7.8, 1.1 Hz, 1H), 7.60 (dd, J = 7.8, 1.6 Hz, 2H), 7.55-7.47 (m, 3H), 7.44 (d, J = 8.6 Hz, 1H), 7.37-7.31 (m, 2H), 7.23-7.17 (m, 1H), 4.47 (q, J = 7.1 Hz, 2H), 1.43 (t, J = 7.1 Hz, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 163.47, 142.30, 134.36, 132.82, 131.88, 129.77, 129.72, 128.80, 128.71, 128.20, 126.16, 125.67, 125.19, 123.16, 117.43, 117.36, 60.41, 14.51;

HRMS (ESI) calcd for $C_{20}H_{17}N_2O_2$: $[M+H]^+$ 317.1285, found: 317.1288.

Ethyl 8-methyl-3-phenylimidazo[1,5-*a*]pyridine-1-carboxylate (3z)



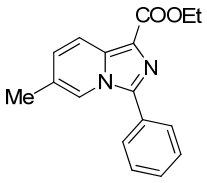
Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/2) as a yellow oil in 85% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.10 (d, J = 7.0 Hz, 1H), 7.73 (d, J = 7.1 Hz, 2H), 7.52-7.45 (m, 3H), 6.84 (d, J = 6.6 Hz, 1H), 6.64 (t, J = 6.9 Hz, 1H), 4.45 (q, J = 7.1 Hz, 2H), 2.81 (s, 3H), 1.44 (t, J = 7.1 Hz, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 163.72, 138.82, 134.73, 130.49, 129.46, 129.37, 129.10, 128.91, 124.47, 123.21, 120.29, 114.13, 60.63, 21.94, 14.53;

HRMS (ESI) calcd for $C_{17}H_{17}N_2O_2$: $[M+H]^+$ 281.1285, found: 281.1287.

Ethyl 6-methyl-3-phenylimidazo[1,5-*a*]pyridine-1-carboxylate (3aa)



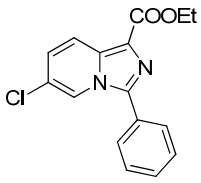
Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/2) as a yellow oil in 88% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12 (d, J = 9.3 Hz, 1H), 8.04 (d, J = 1.0 Hz, 1H), 7.79-7.73 (m, 2H), 7.52-7.49 (m, 2H), 7.47-7.42 (m, 1H), 6.96 (dd, J = 9.3, 0.9 Hz, 1H), 4.46 (q, J = 7.1 Hz, 2H), 2.26 (s, 3H), 1.44 (t, J = 7.1 Hz, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 163.53, 138.55, 134.48, 129.27, 128.82, 128.70, 127.55, 124.13, 121.47, 119.58, 119.15, 60.18, 18.30, 14.56;

HRMS (ESI) calcd for $C_{17}H_{17}N_2O_2$: $[M+H]^+$ 281.1285, found: 281.1284.

Ethyl 6-chloro-3-phenylimidazo[1,5-*a*]pyridine-1-carboxylate (3ab)



Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/2) as a yellow oil in 80% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.30 (s, 1H), 8.20 (d, J = 9.6 Hz, 1H), 7.79 -7.73 (m, 2H), 7.56-7.48 (m, 3H), 7.06 (dd, J = 9.6, 1.5 Hz, 1H), 4.49 (q, J = 7.1 Hz, 2H), 1.45 (t, J = 7.1 Hz, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 163.19, 139.19, 133.43, 129.86, 129.11, 128.72, 128.52, 125.49, 123.09, 122.89, 120.53, 120.06, 60.61, 14.58;

HRMS (ESI) calcd for $C_{16}H_{14}ClN_2O_2$: $[M+H]^+$ 301.0738, found: 301.0740.

N-benzyl-3-phenylimidazo[1,5-*a*]pyridine-1-carboxamide (3ac)

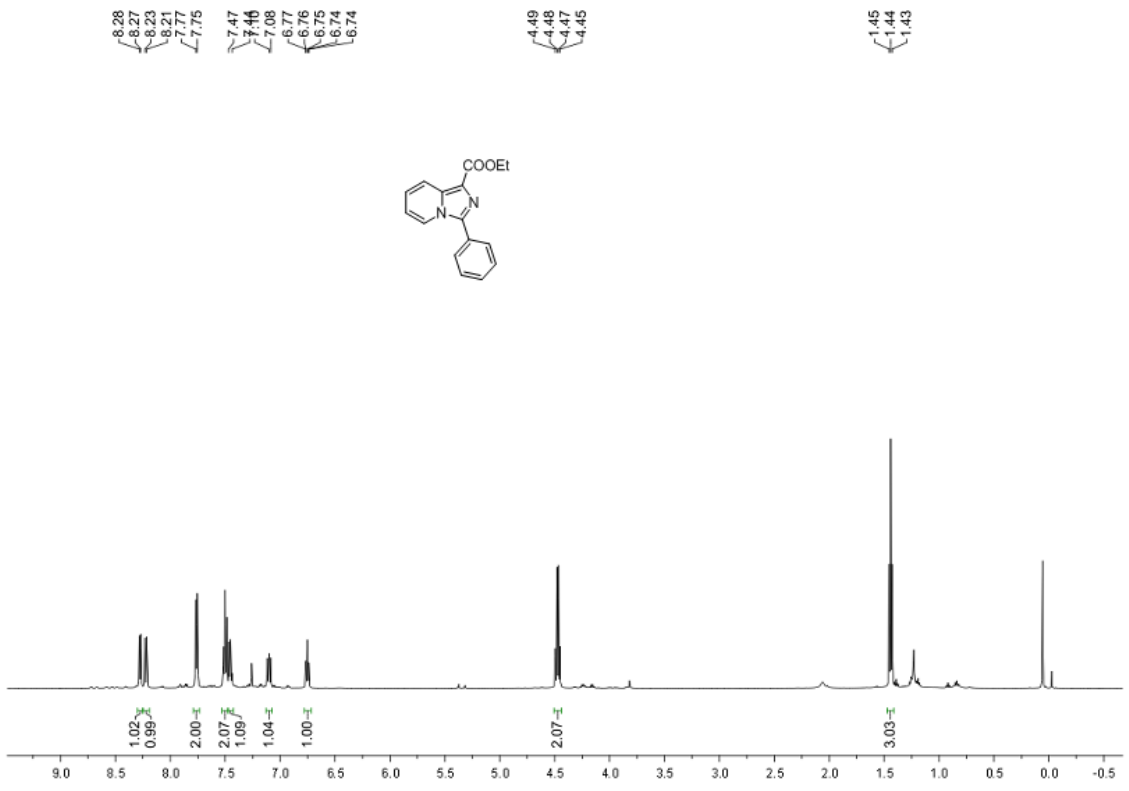
Following the general procedure the title compound was isolated by flash chromatography (eluent: ethyl acetate/petrol ether =1/2) as a yellow solid in 83% yield.

M.p. = 125-126 ^{o}C;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.42-8.40 (m, 1H), 8.25-8.23 (m, 1H), 7.75-7.73 (m, 2H), 7.64 (t, J = 5.6 Hz, 1H), 7.55-7.50 (m, 2H), 7.49-7.45 (m, 1H), 7.43-7.37 (m, 2H), 7.33 (dd, J = 10.2, 4.8 Hz, 2H), 7.27-7.24 (m, 1H), 7.05-7.01 (m, 1H), 6.75-6.69 (m, 1H), 4.69 (d, J = 6.1 Hz, 2H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 163.42, 138.86, 137.42, 133.01, 129.35, 129.33, 129.11, 128.54, 128.32, 127.83, 127.18, 124.41, 122.97, 121.90, 120.55, 114.27, 42.81;

HRMS (ESI) calcd for $C_{21}H_{18}N_3O$: $[M+H]^+$ 328.1444, found: 328.1446.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8.27
8.23
8.21
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7.75
7.47
7.08
6.77
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6.75
6.74
6.74
4.49
4.48
4.47
4.45
1.45
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1.09
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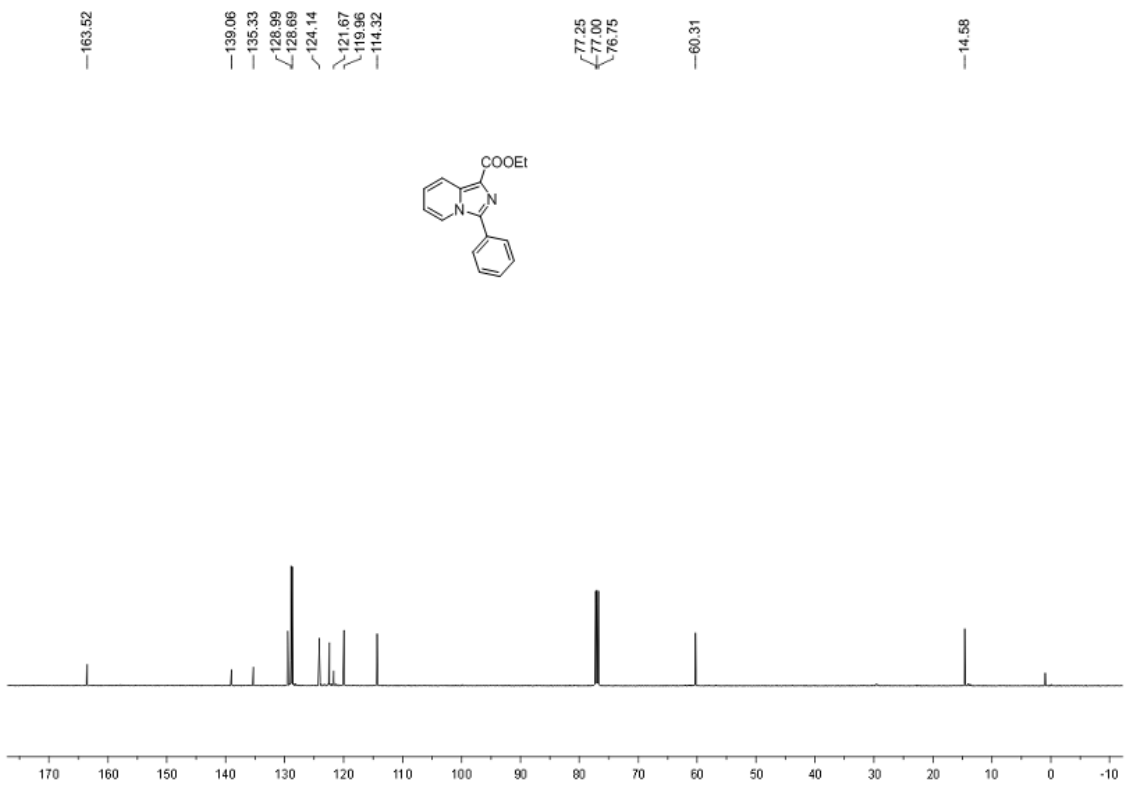
1.00
2.07
3.03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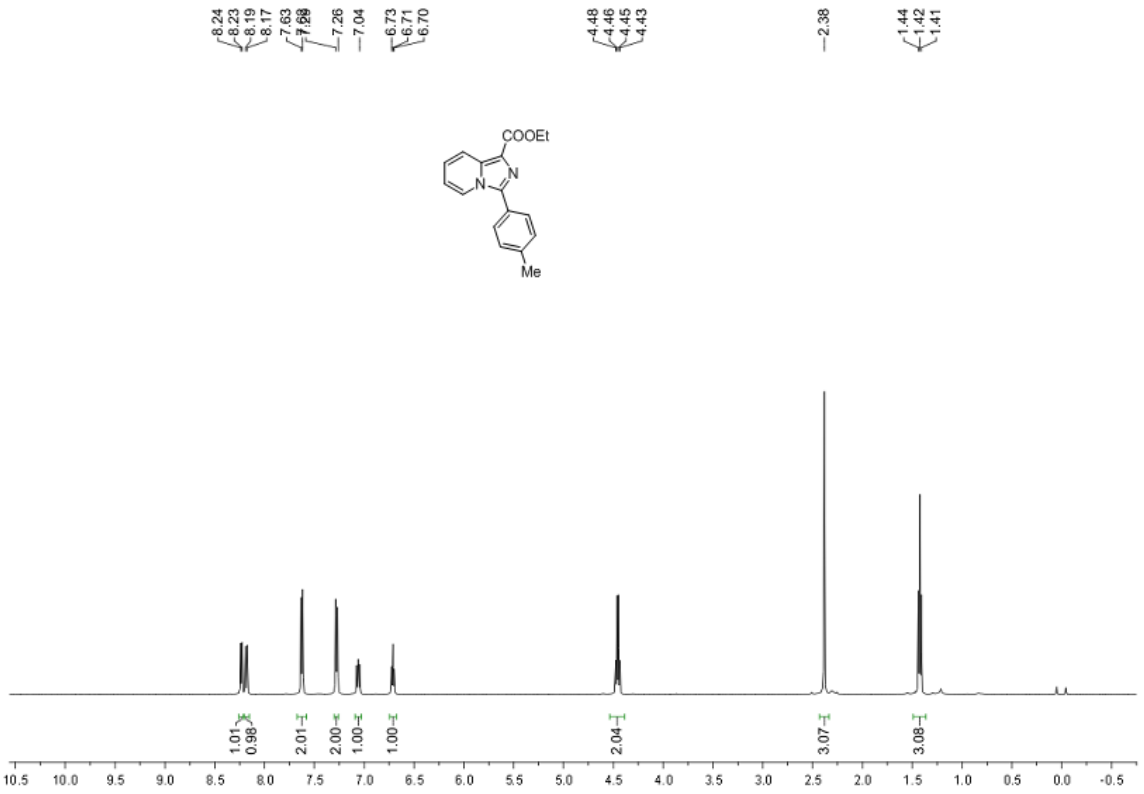
COOEt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1.44
1.42
1.41
COOEt
N
Me
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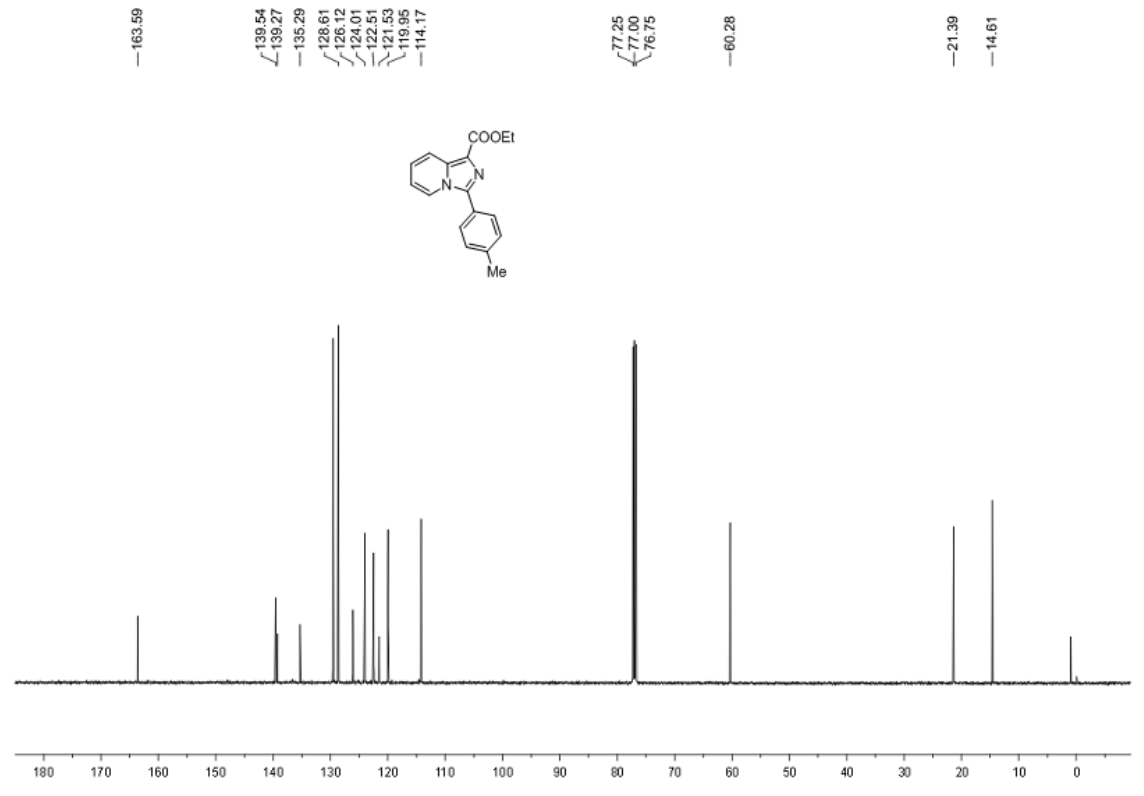
2.01
2.00
1.00
1.00
2.04
3.07
3.08
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5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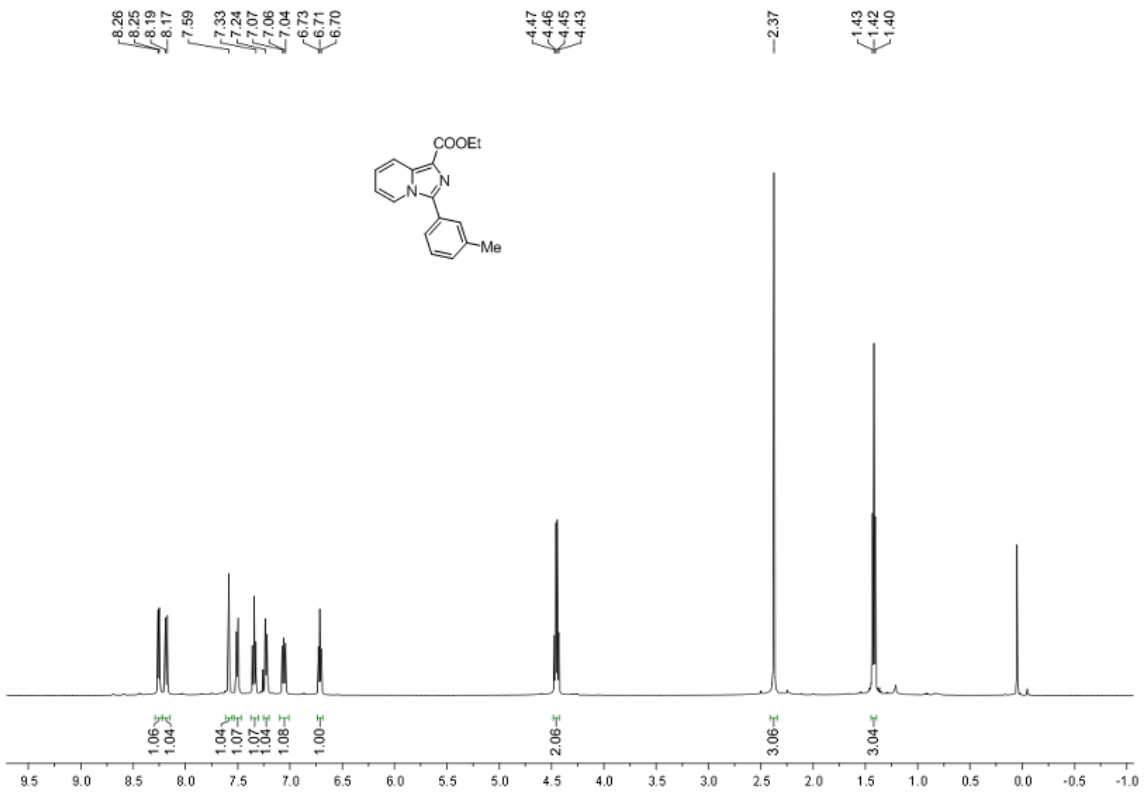
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1.04
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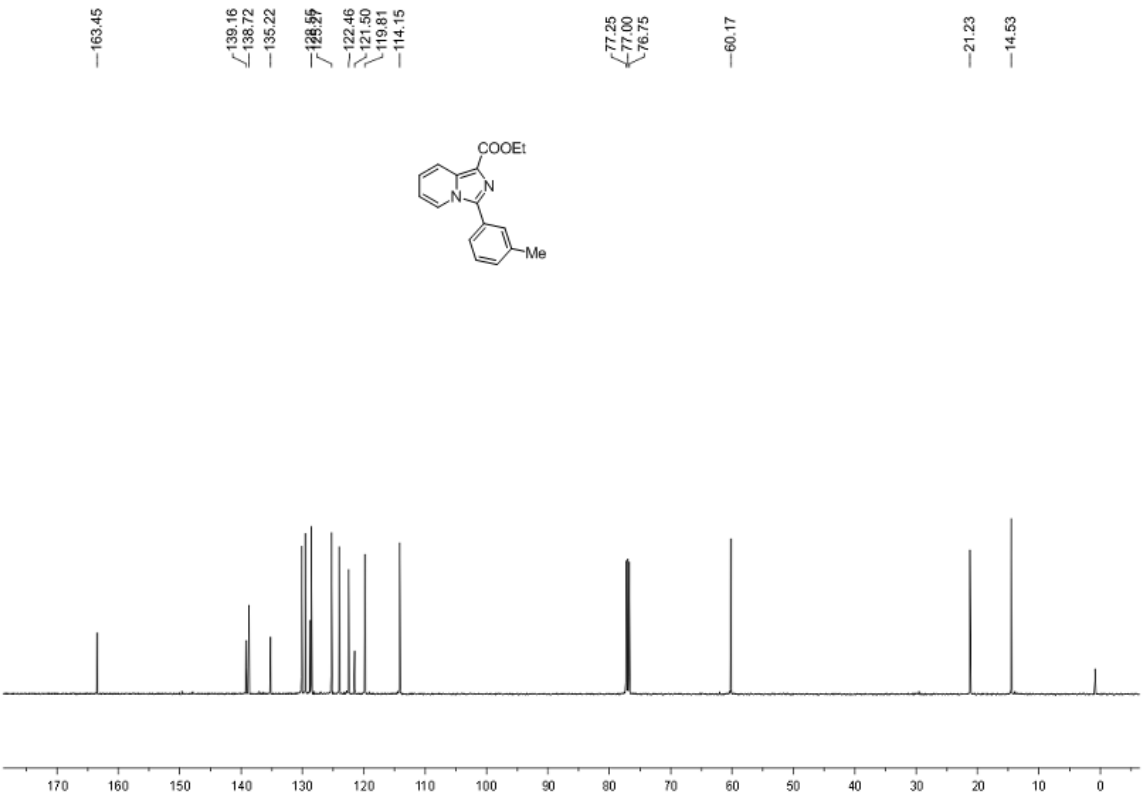
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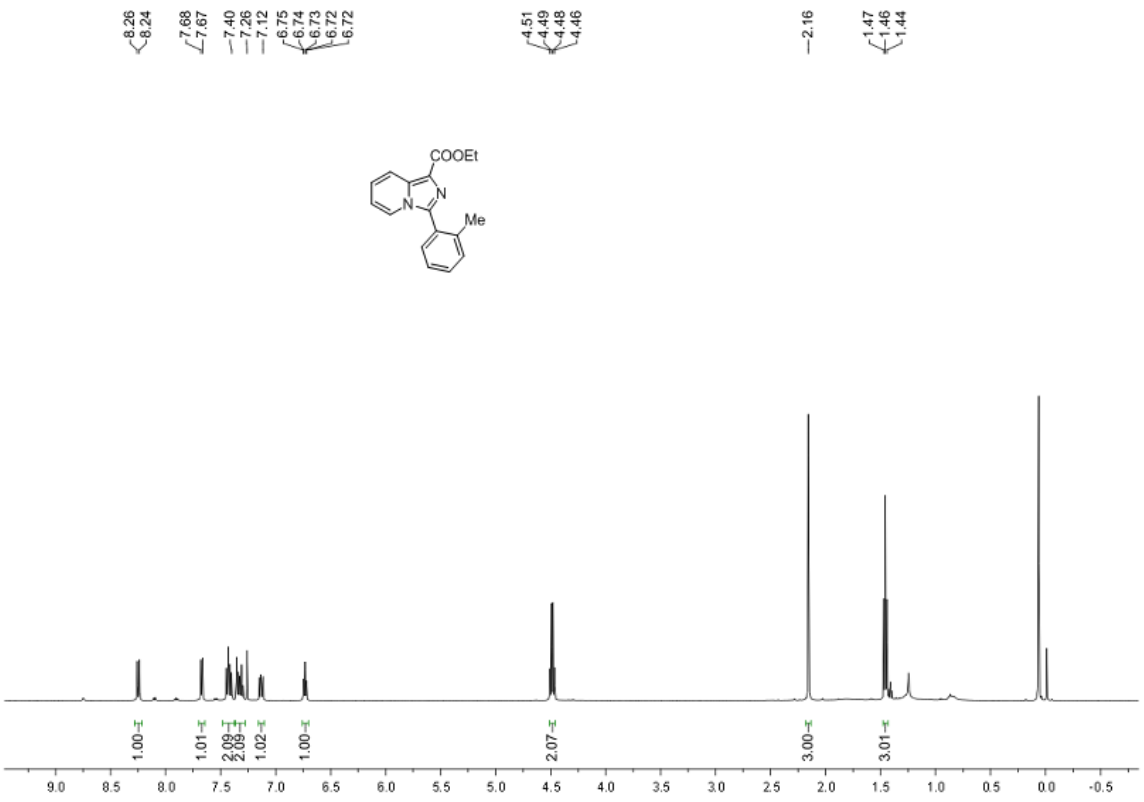
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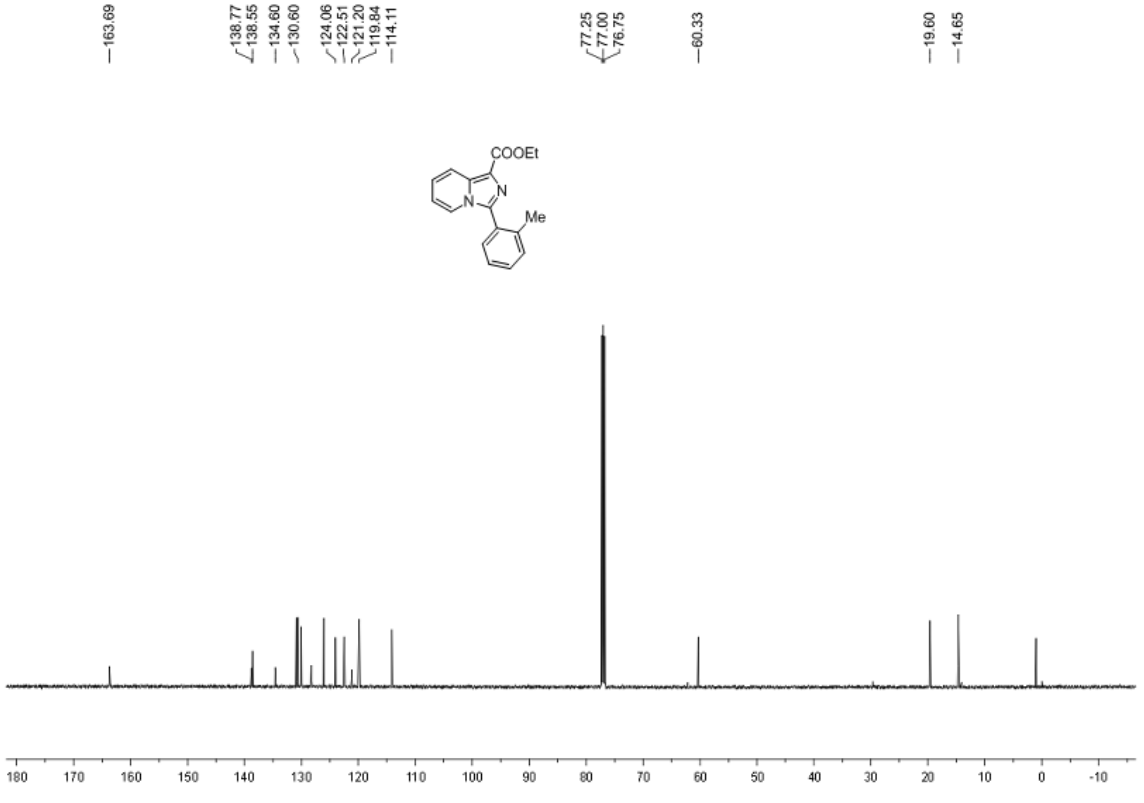
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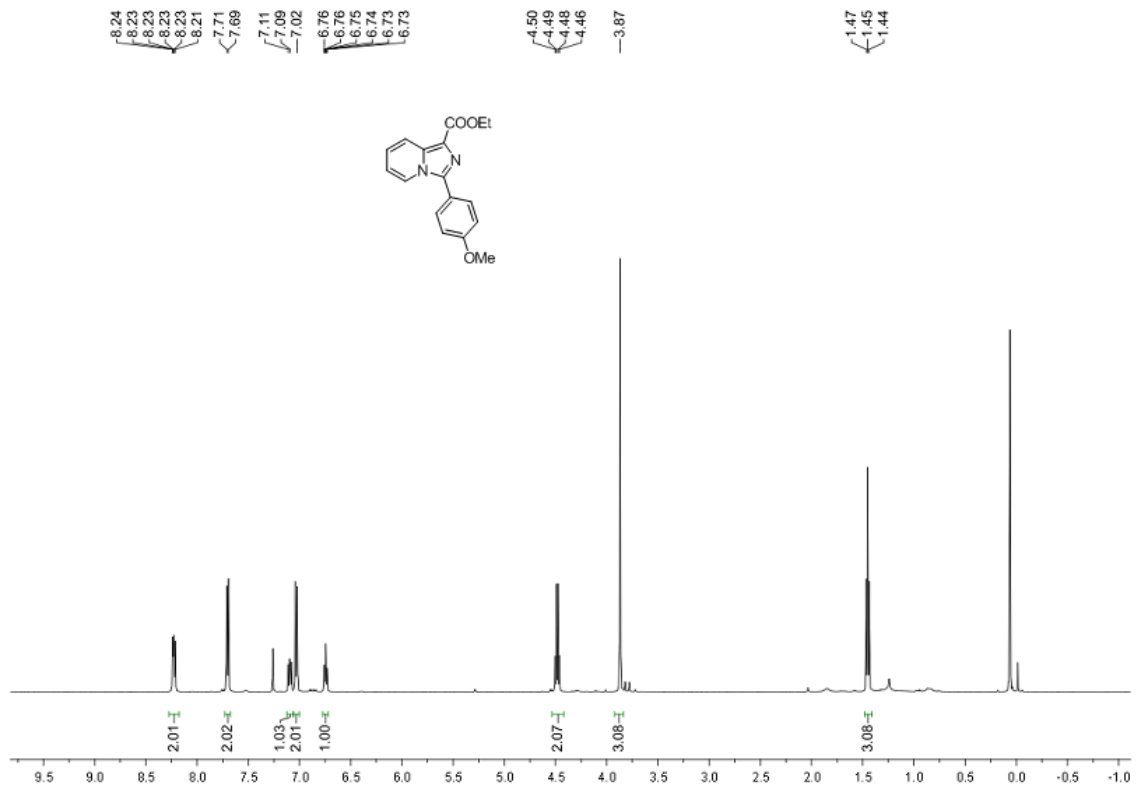
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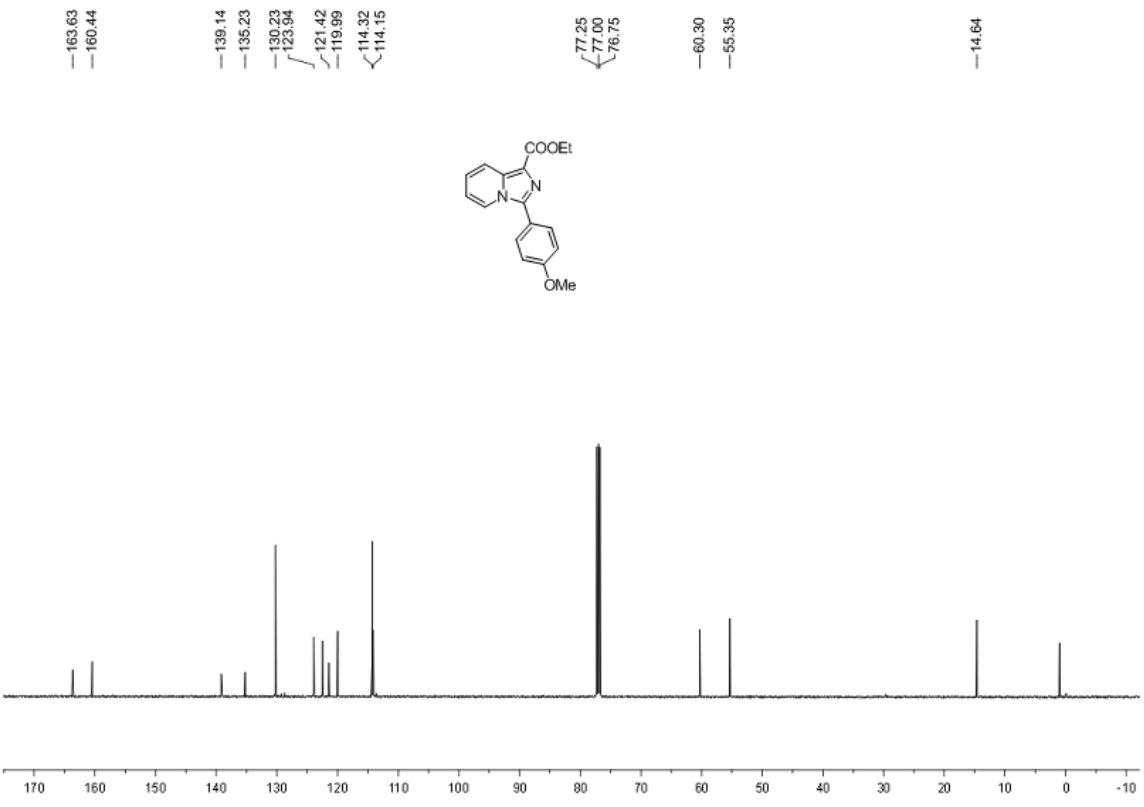
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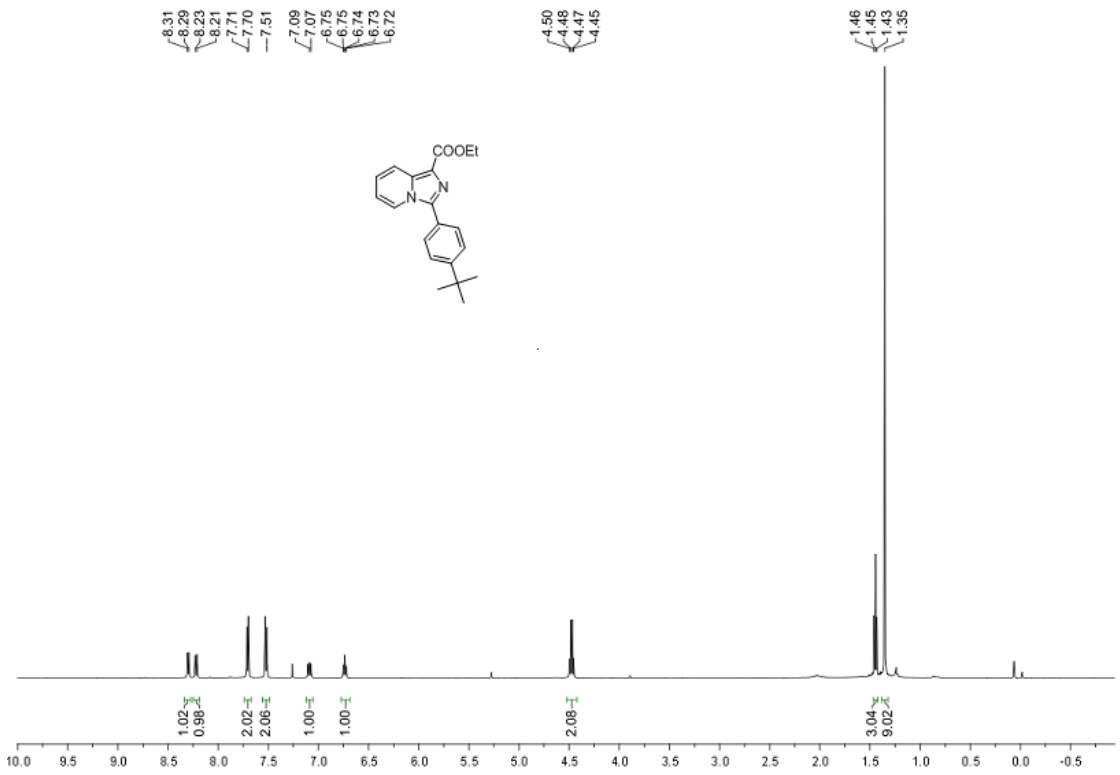
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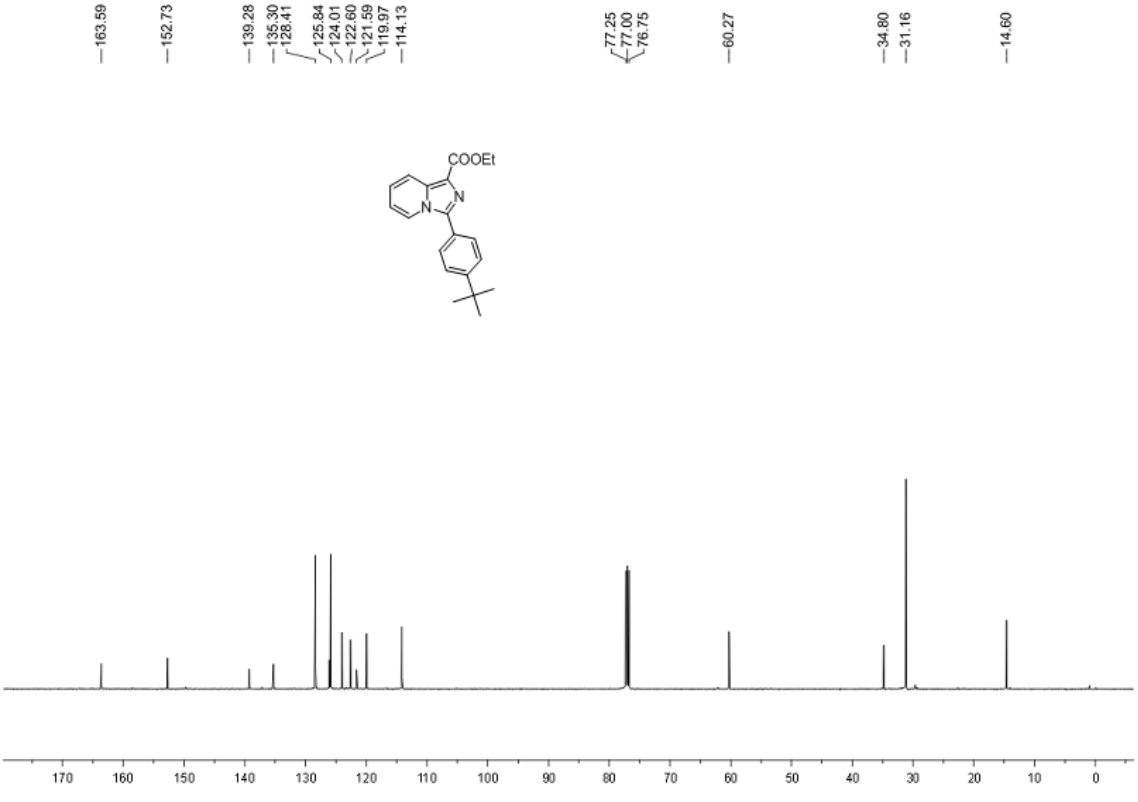
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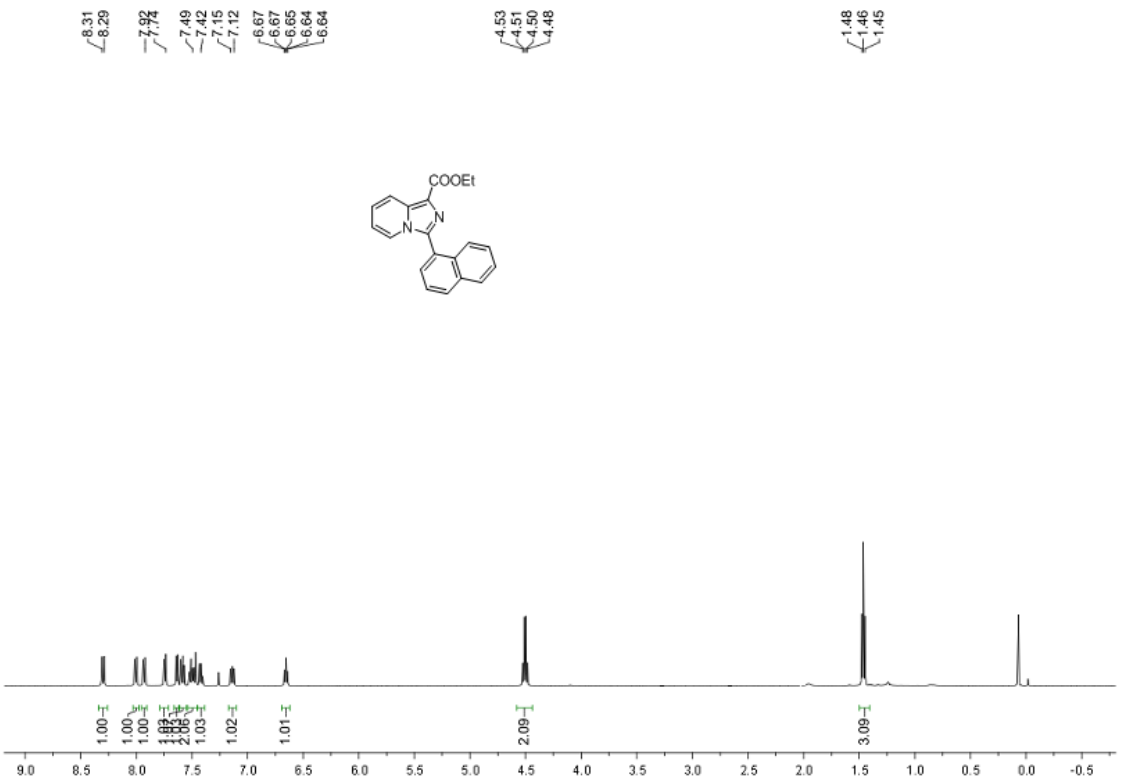
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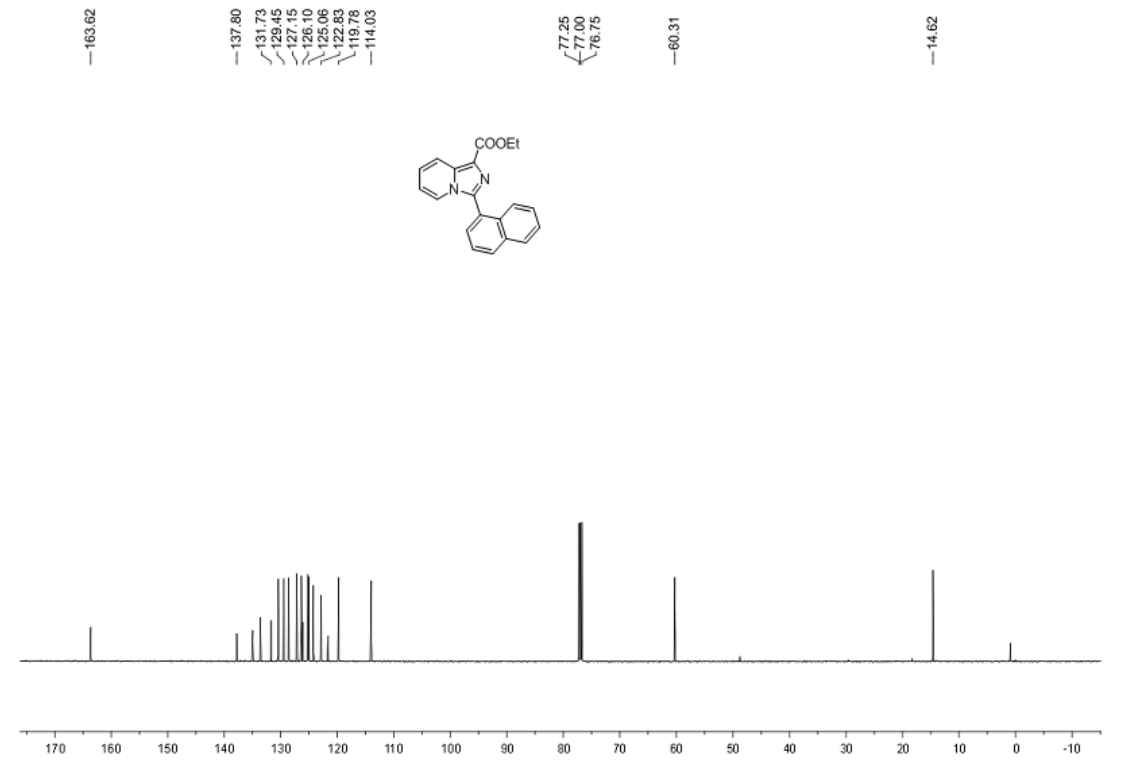
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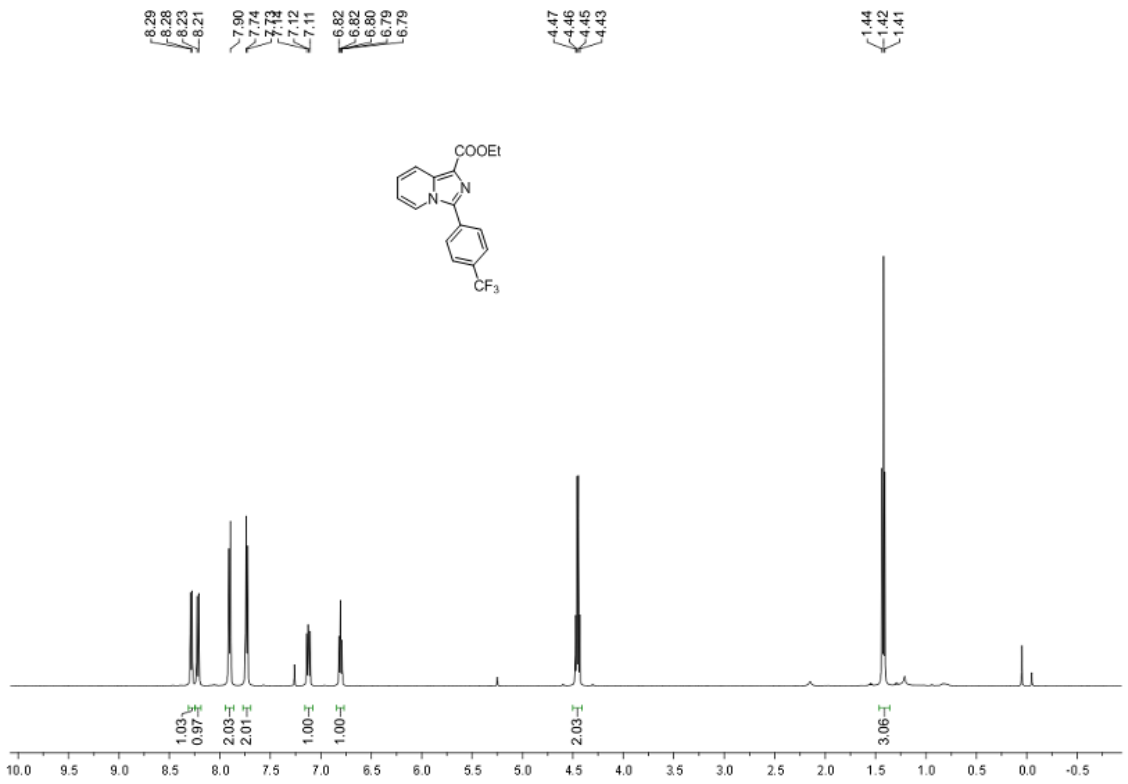
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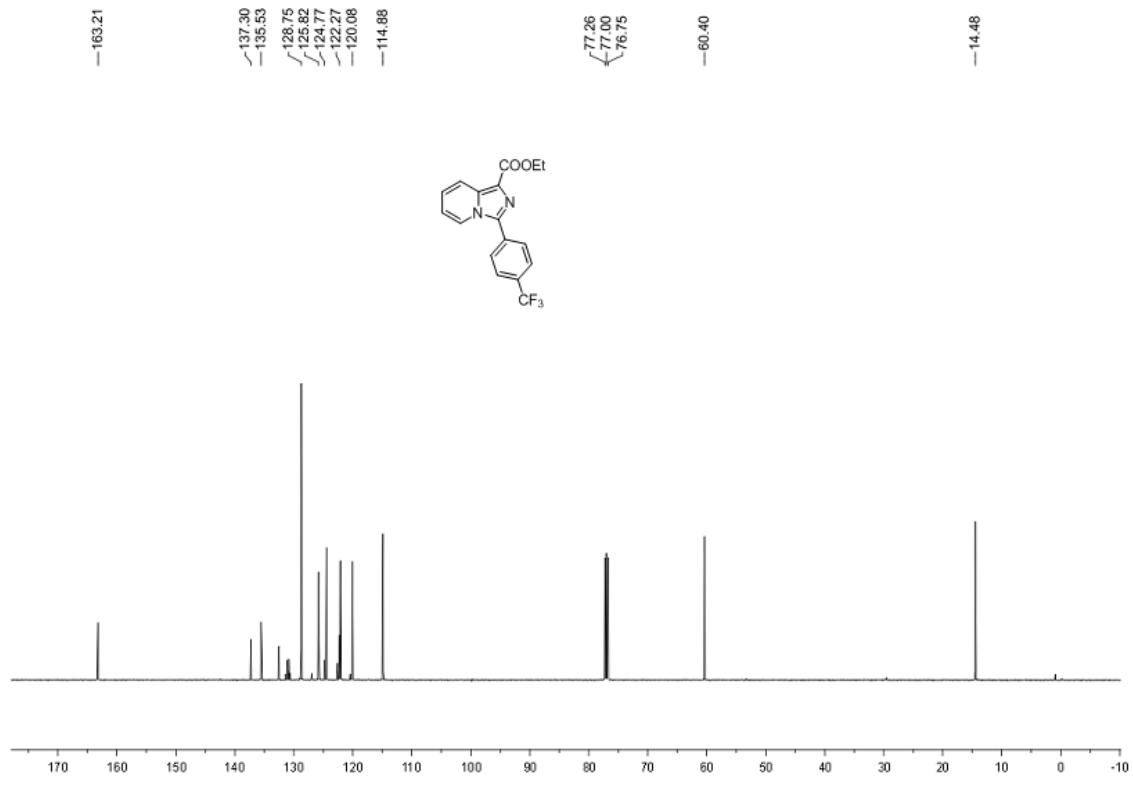
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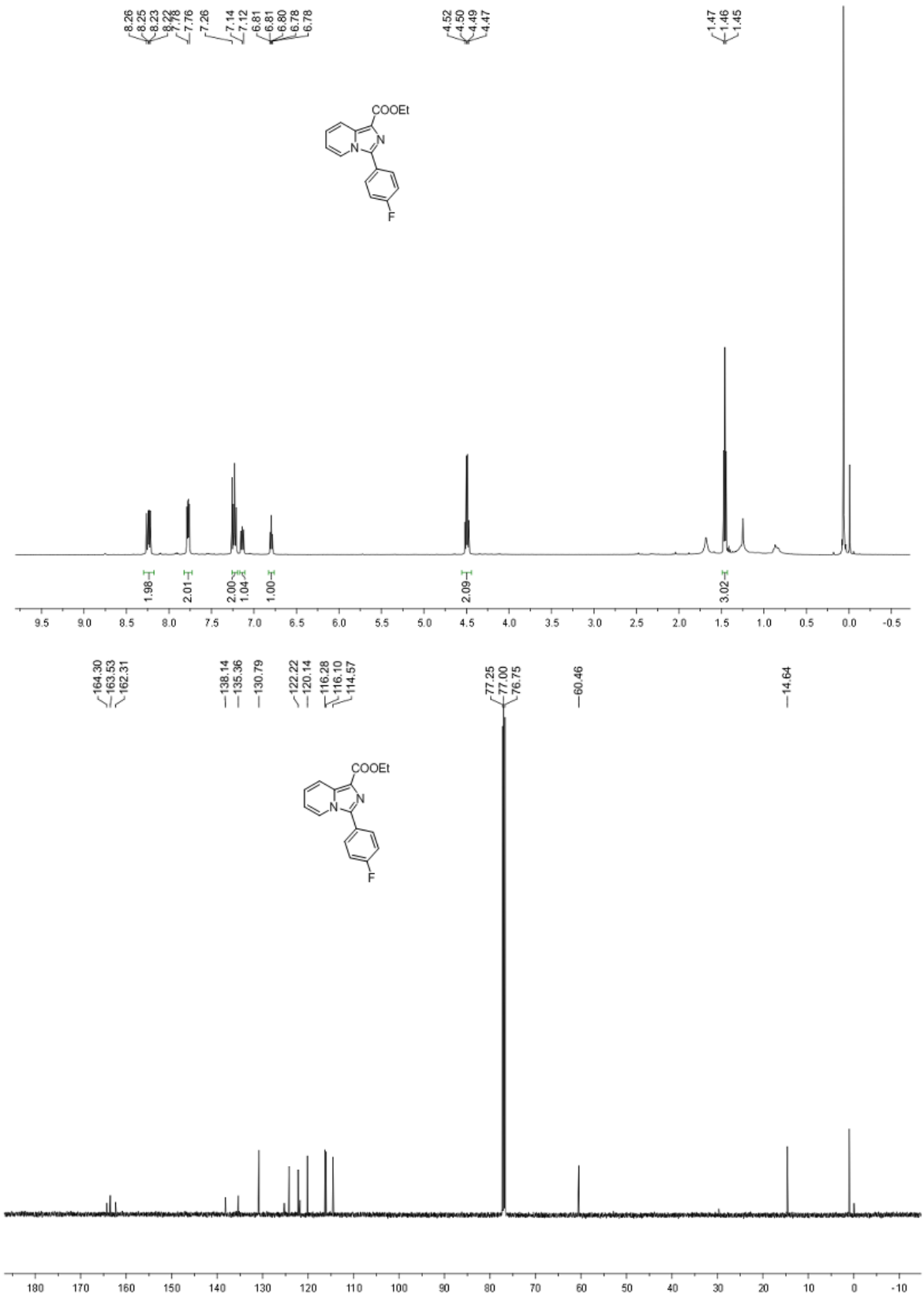
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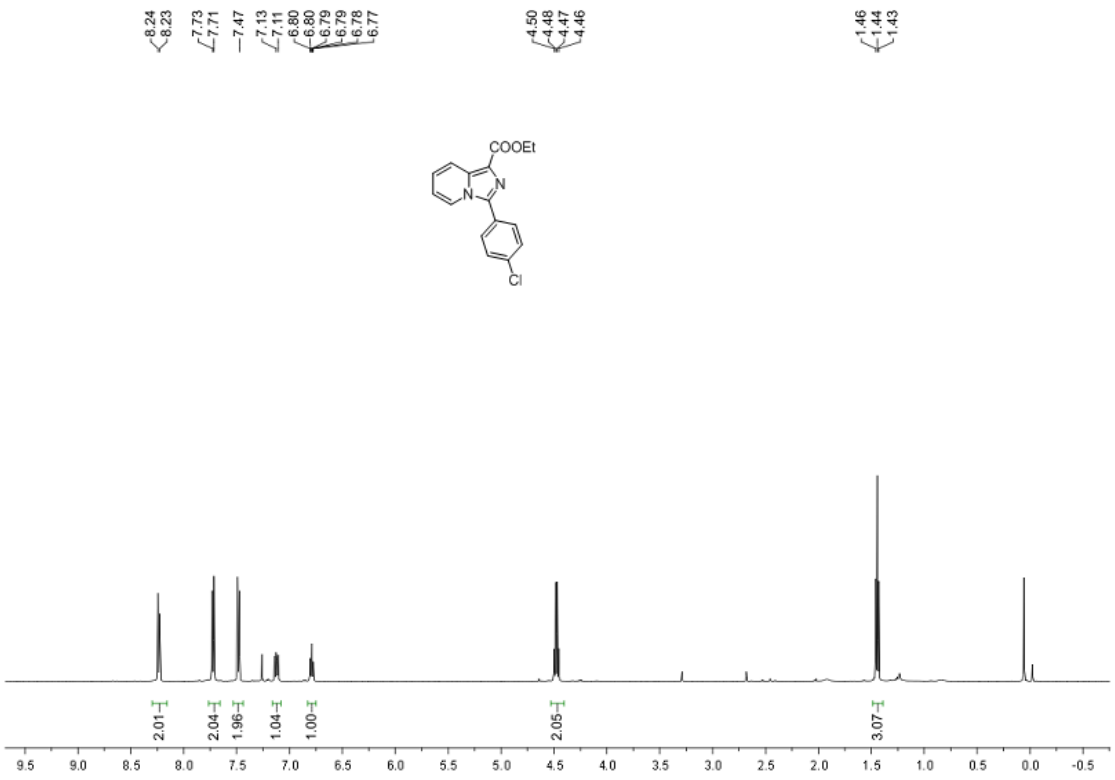
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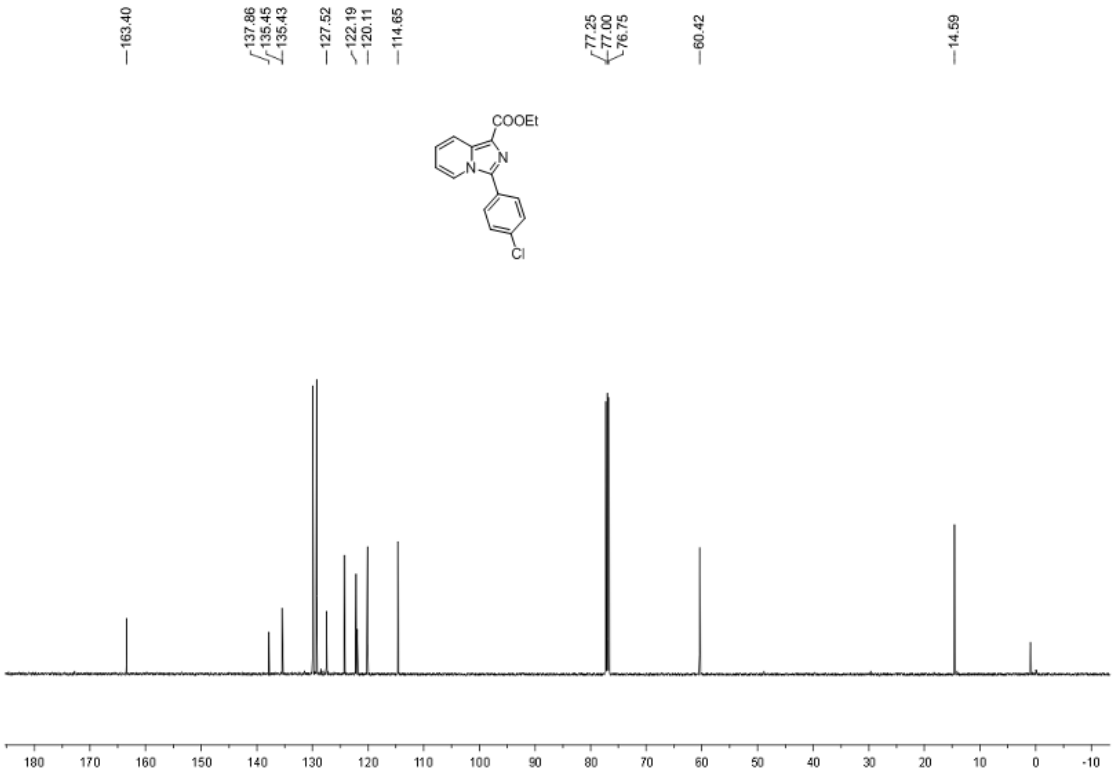
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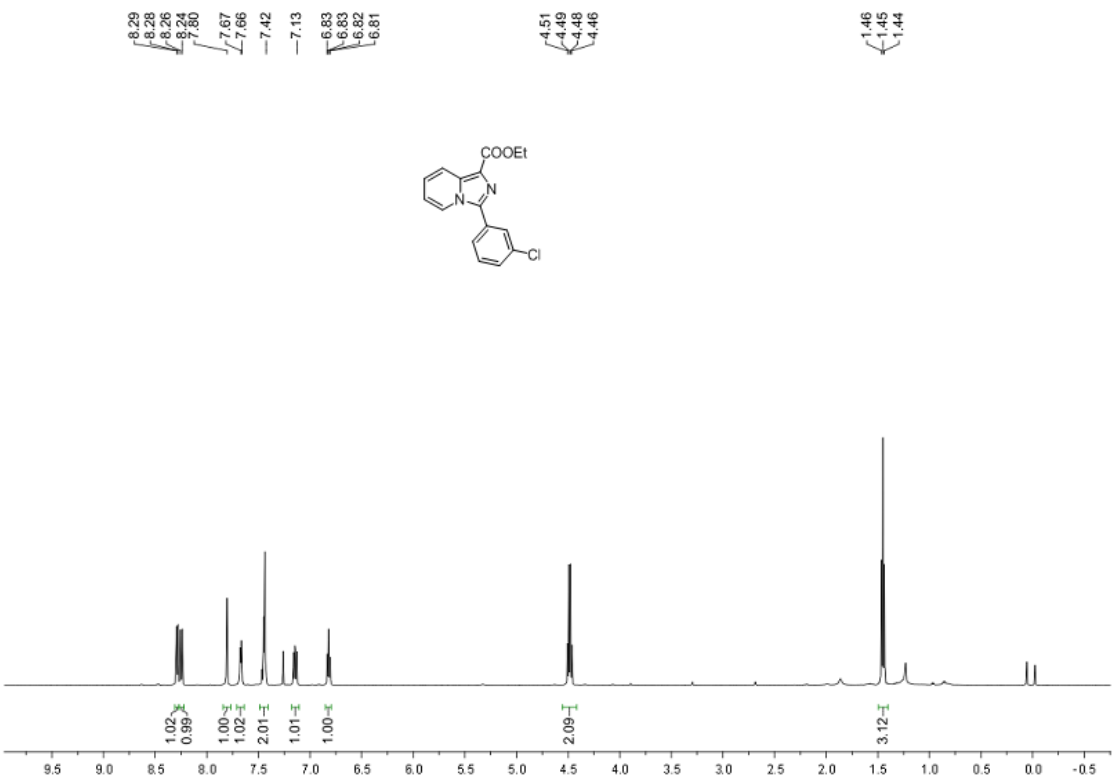
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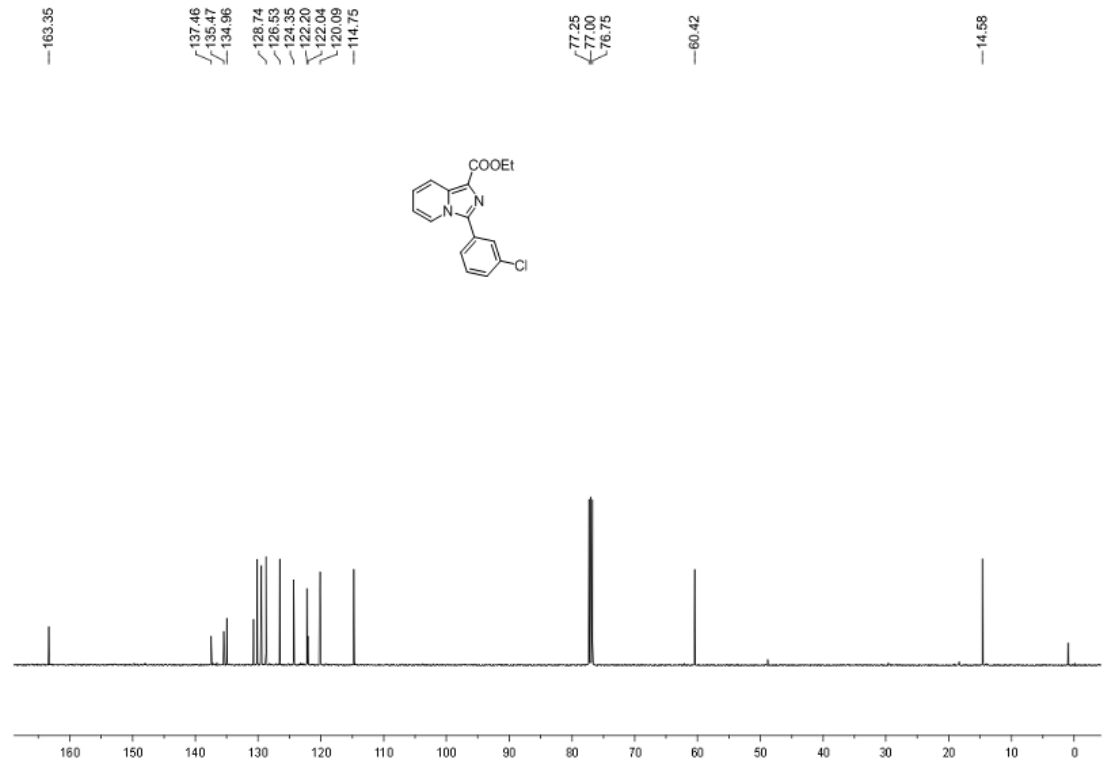
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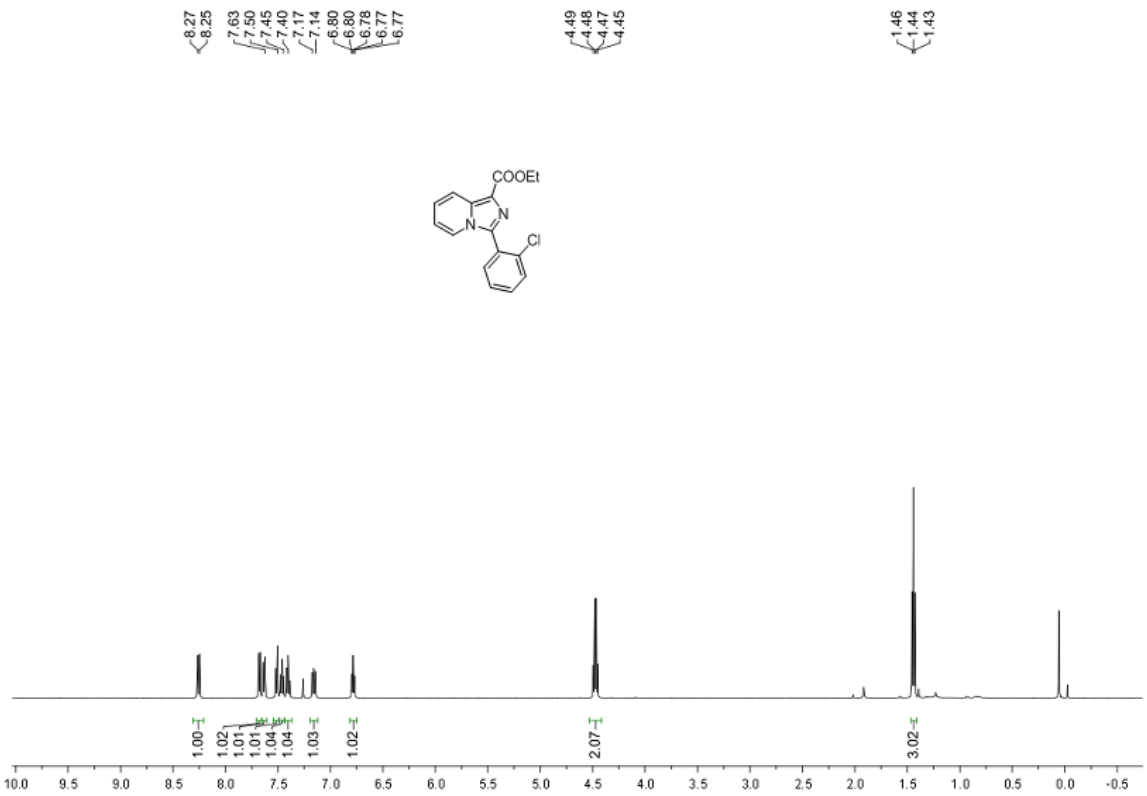
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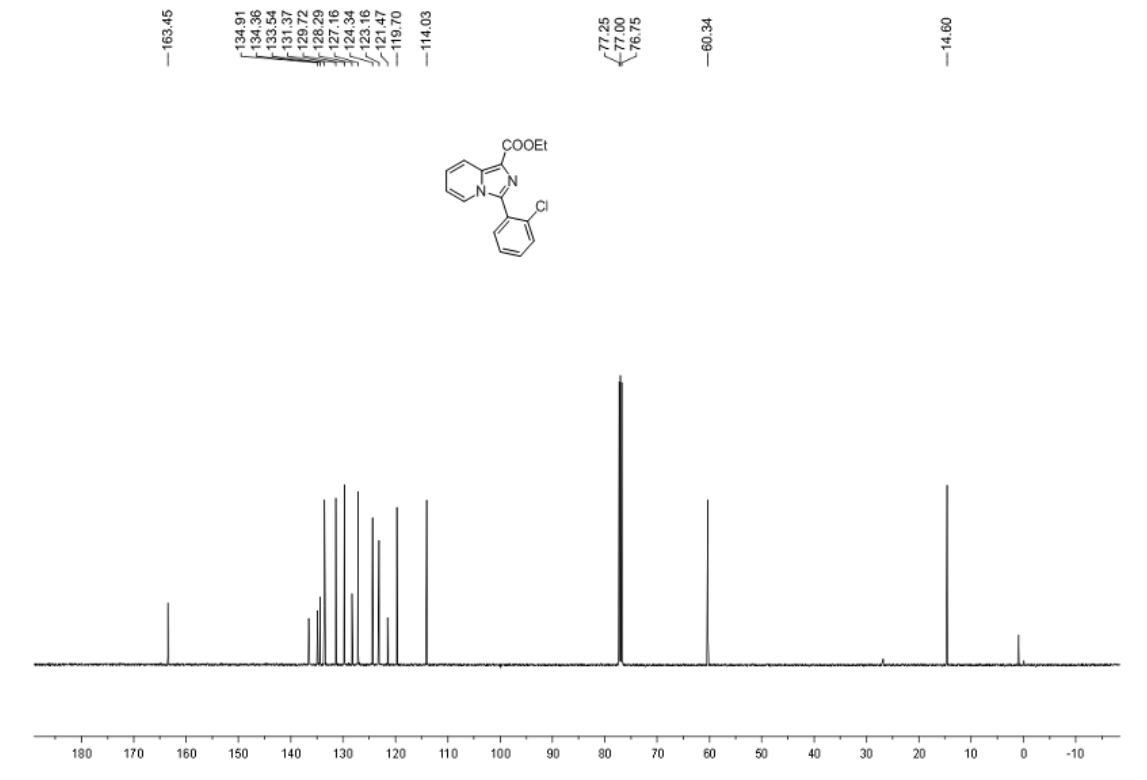
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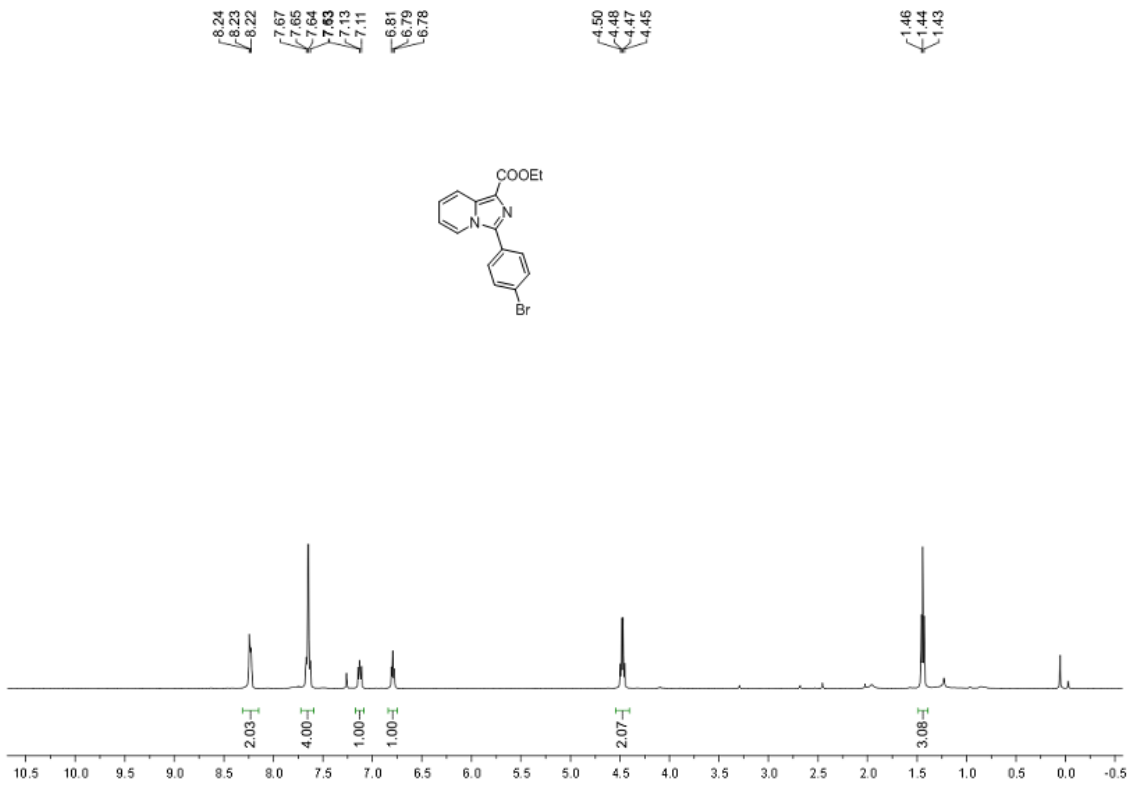
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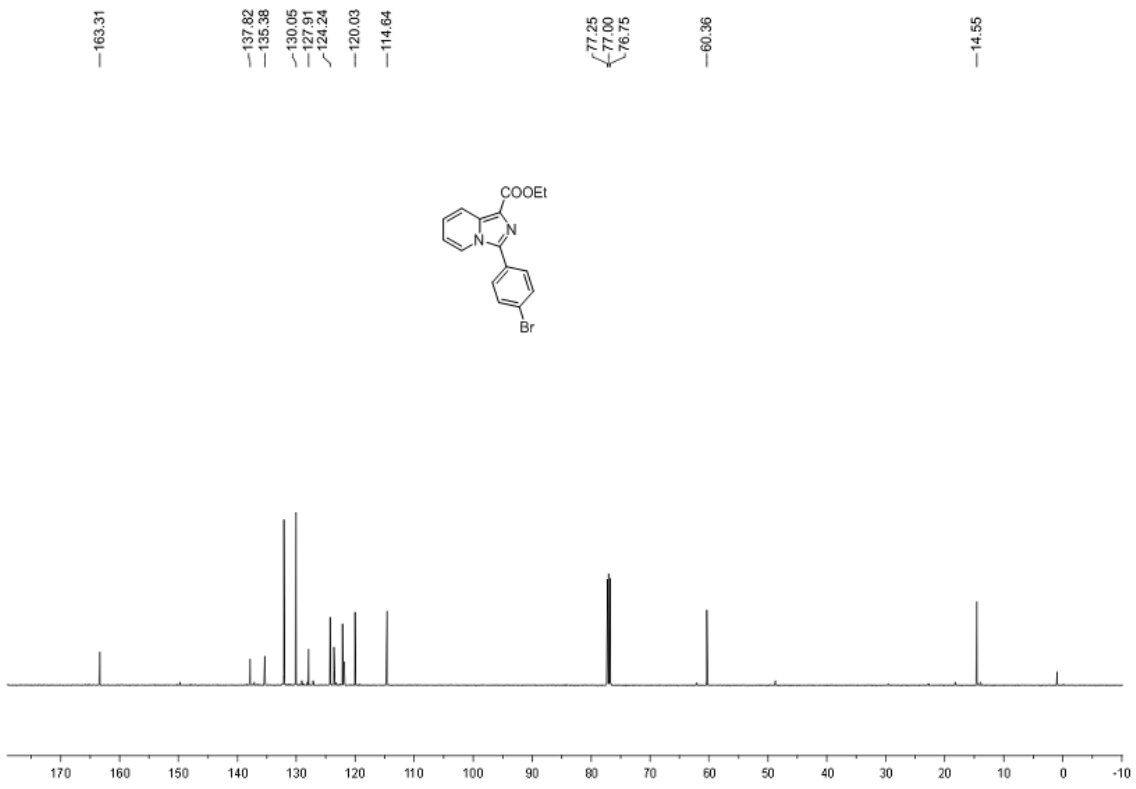
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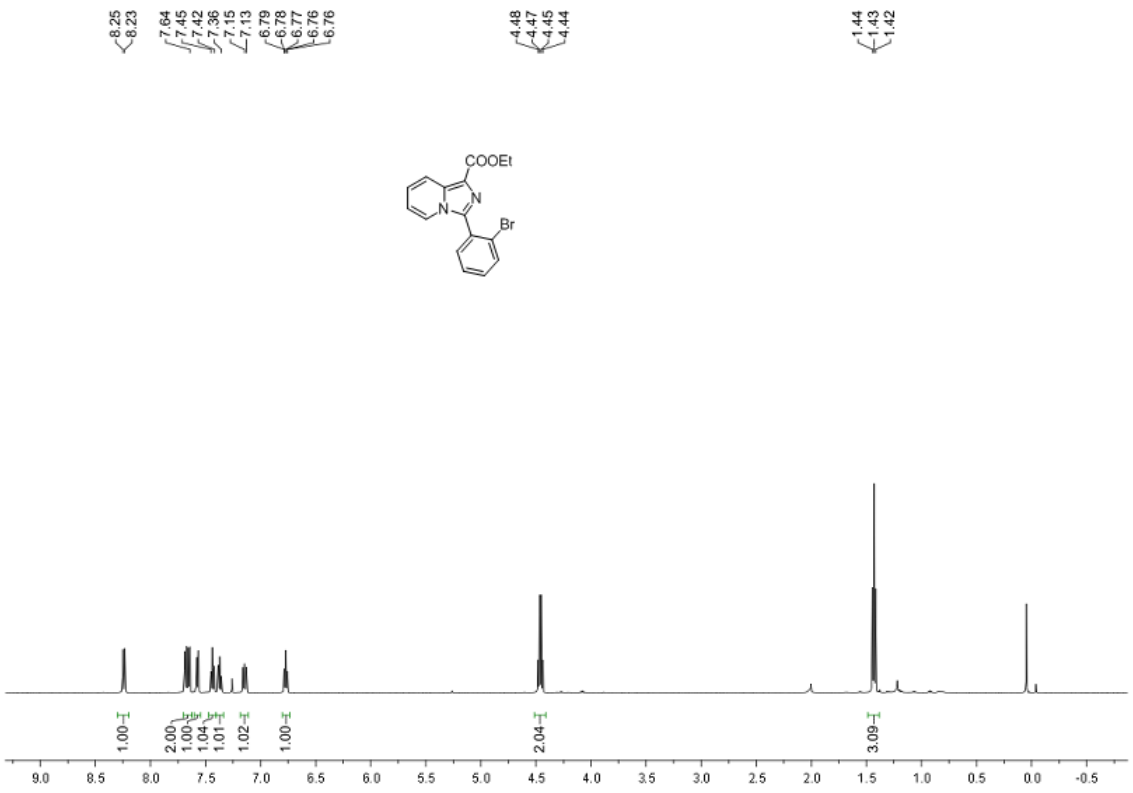
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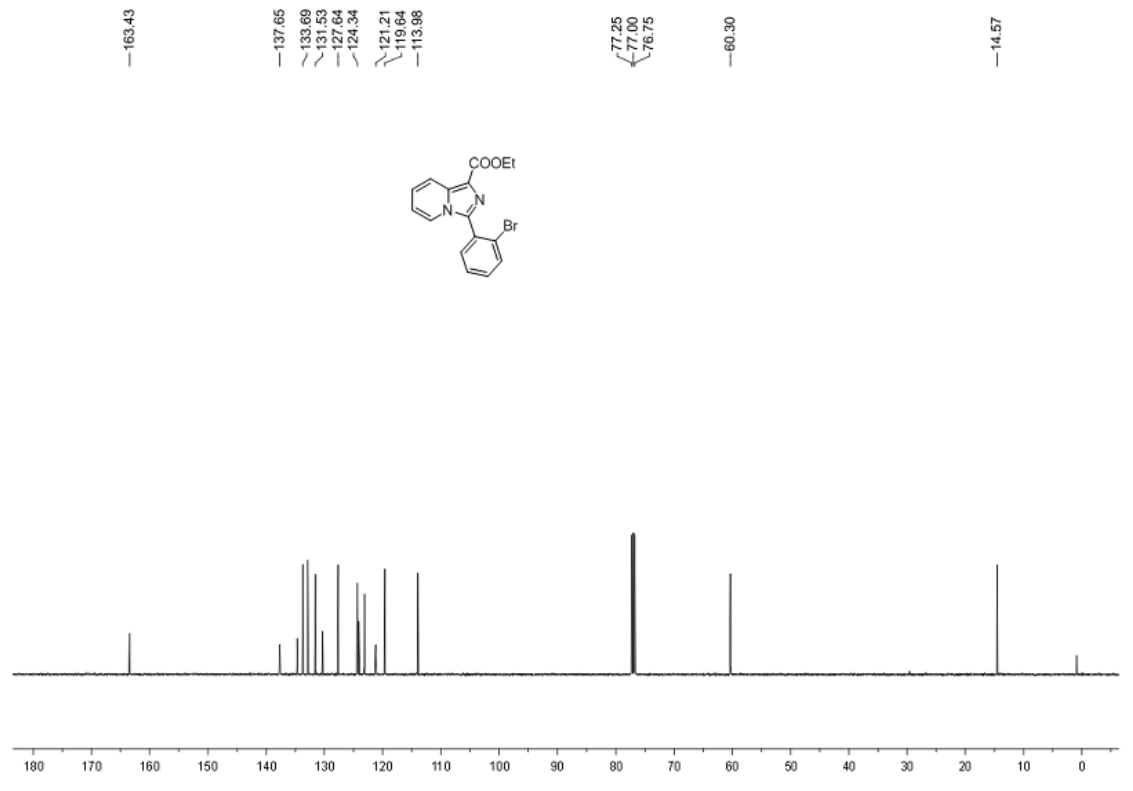
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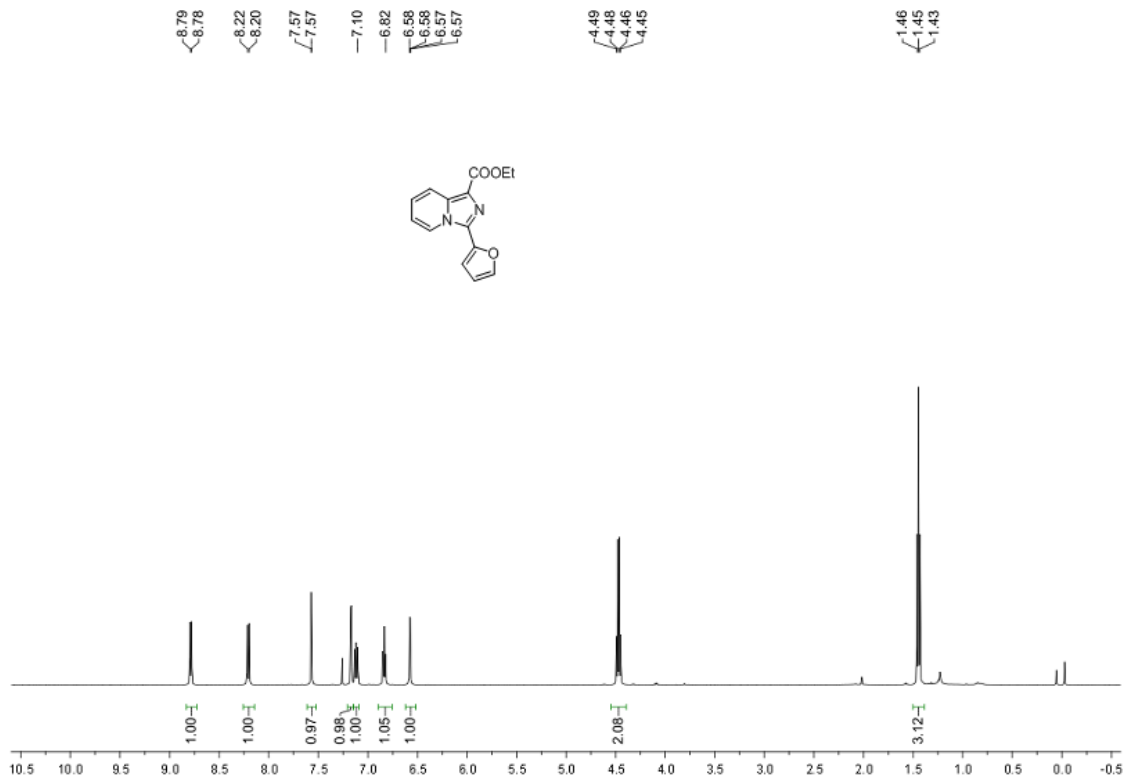
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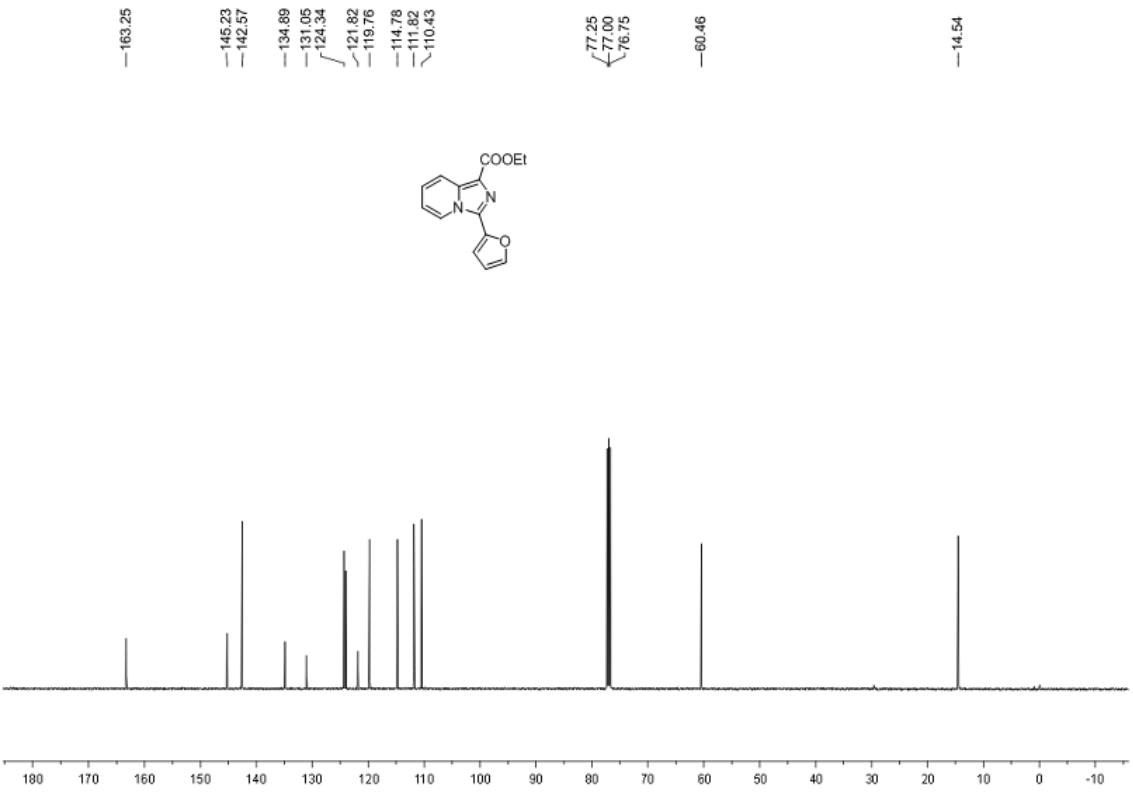
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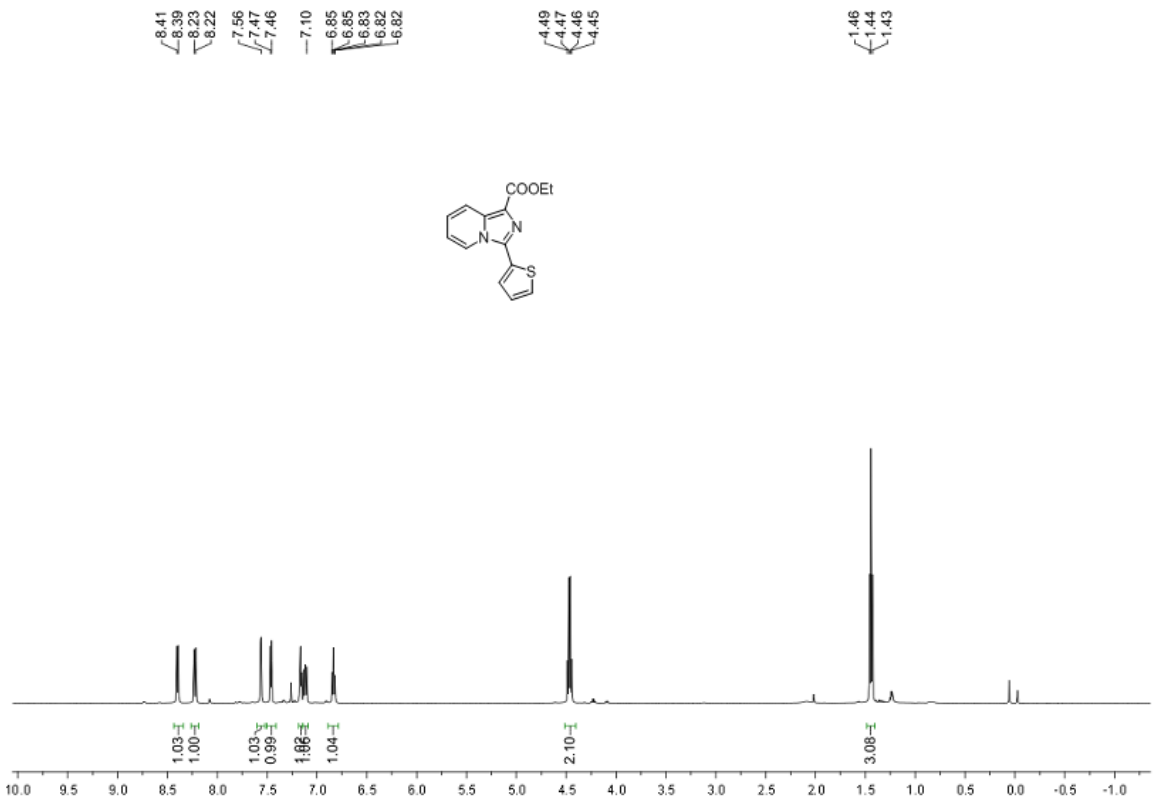
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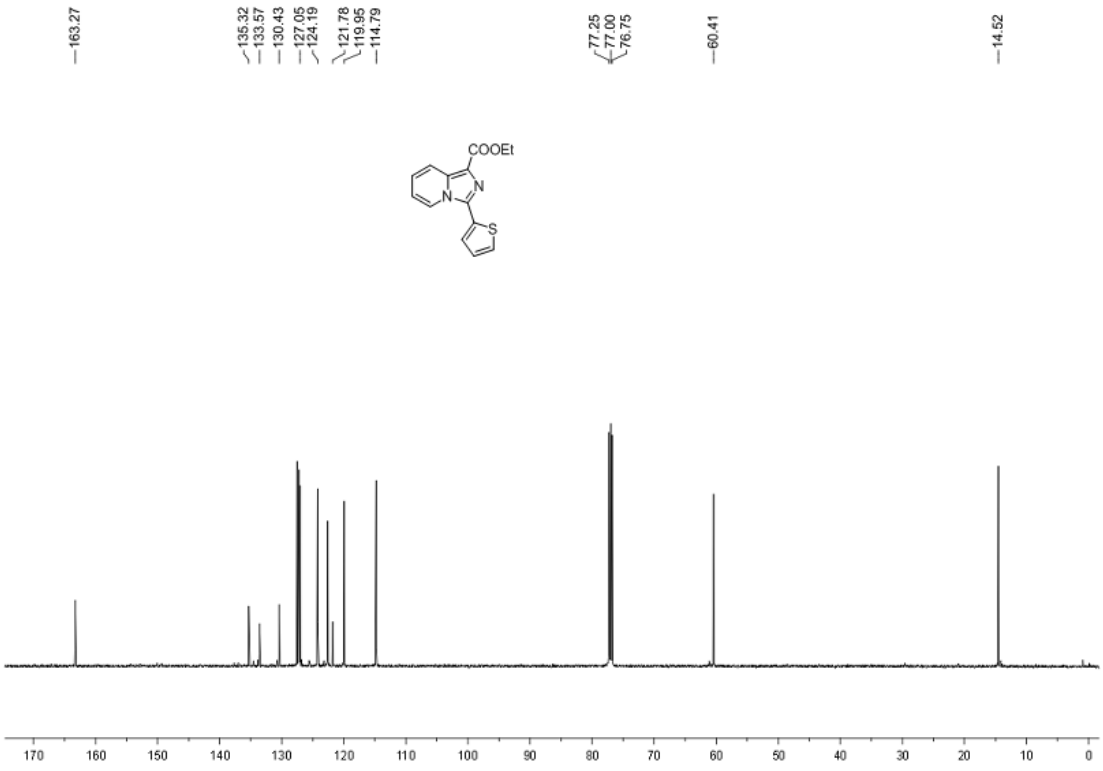
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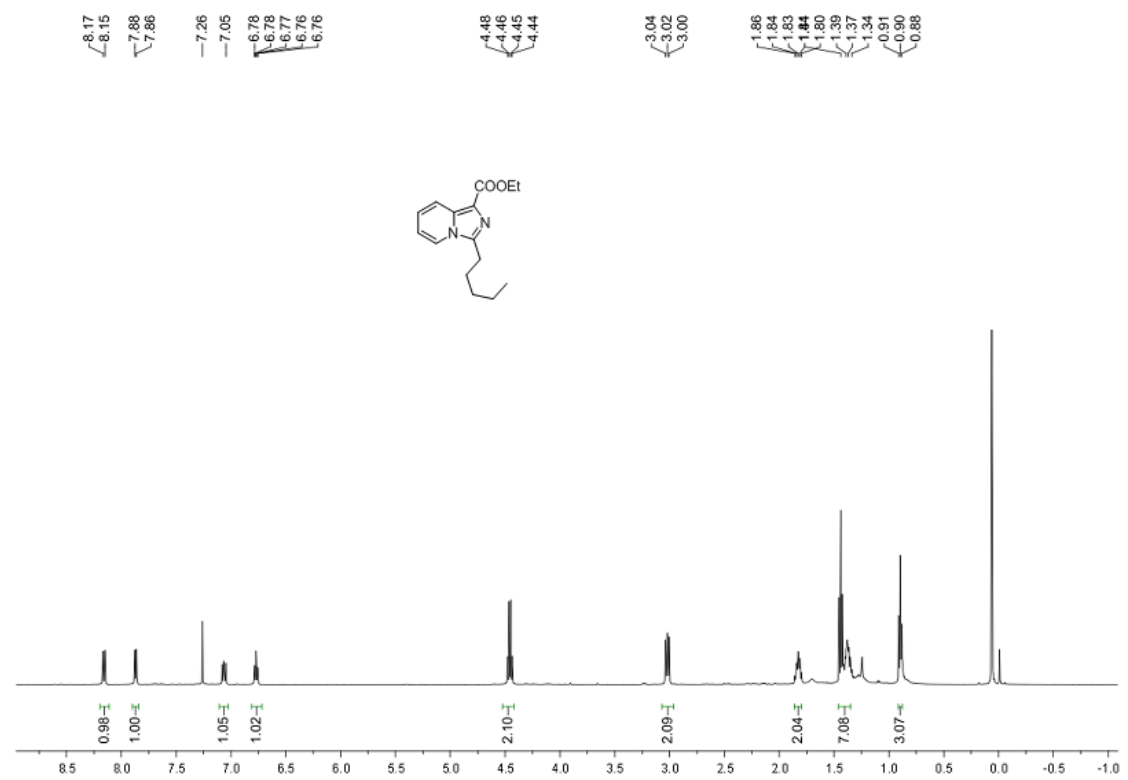
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4.44
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2.04
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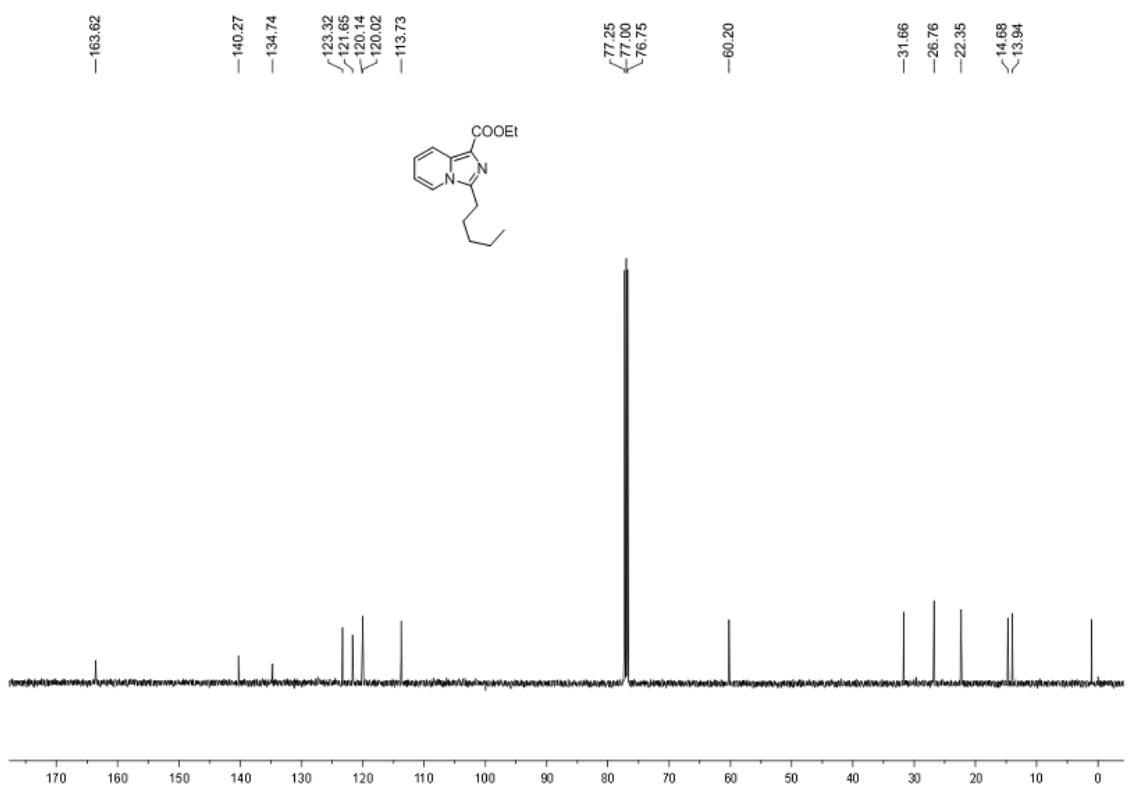
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13.94
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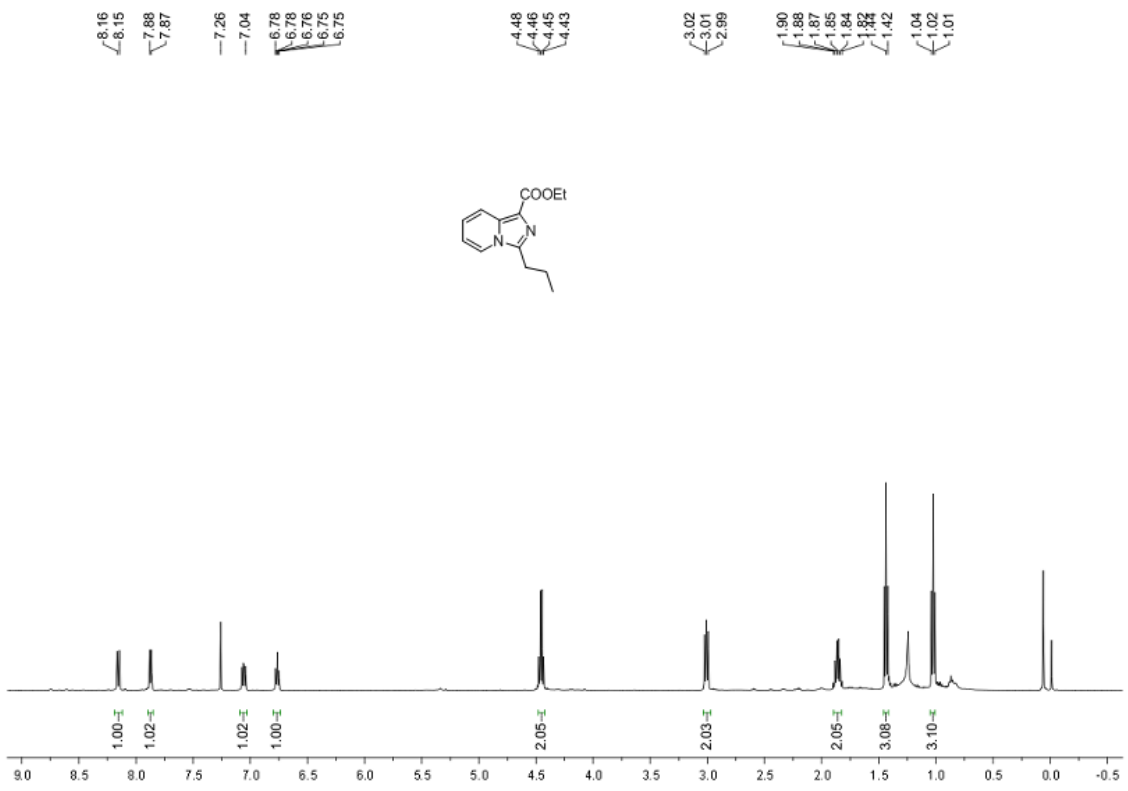
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1.04
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2.05
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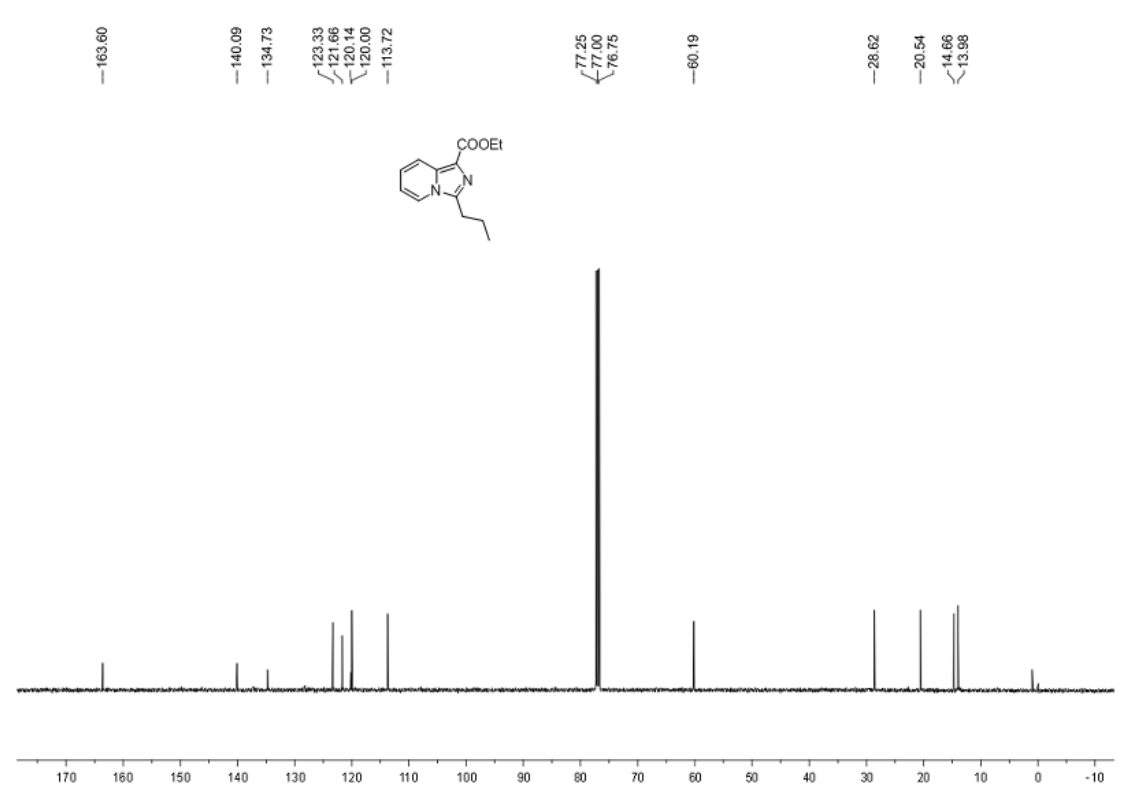
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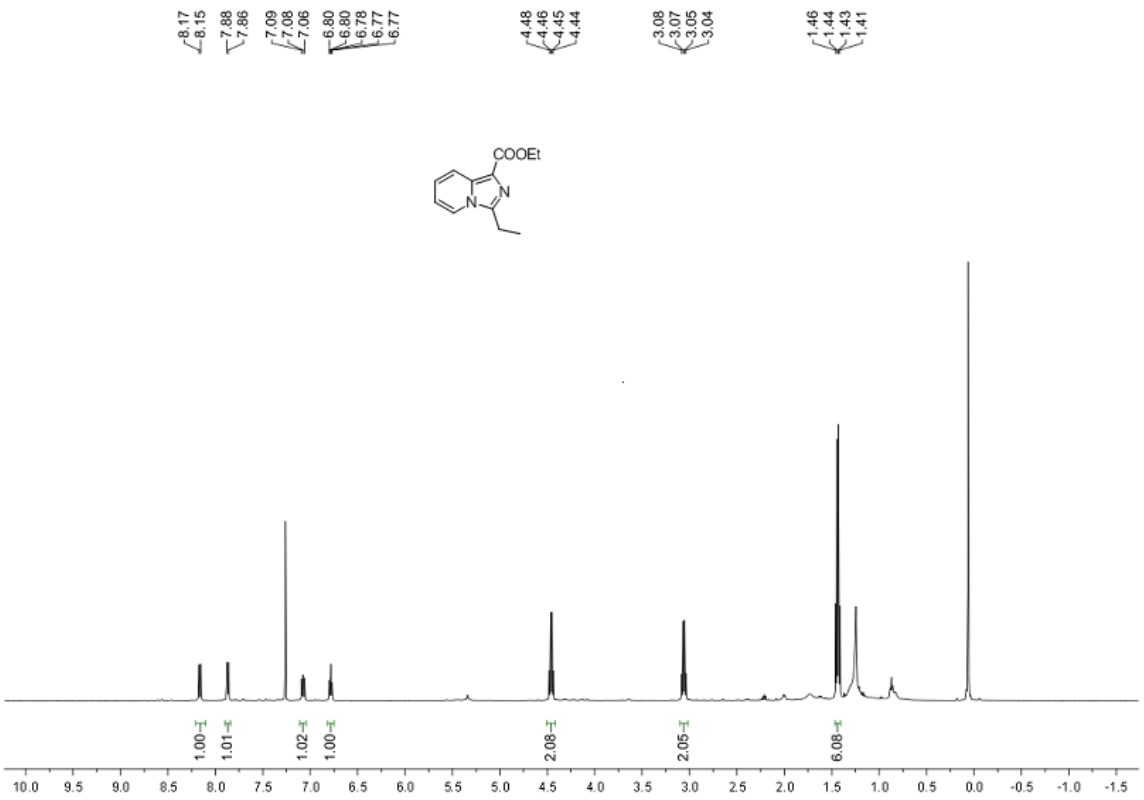
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4.45
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3.08
3.07
3.05
3.04
1.46
1.44
1.43
1.41
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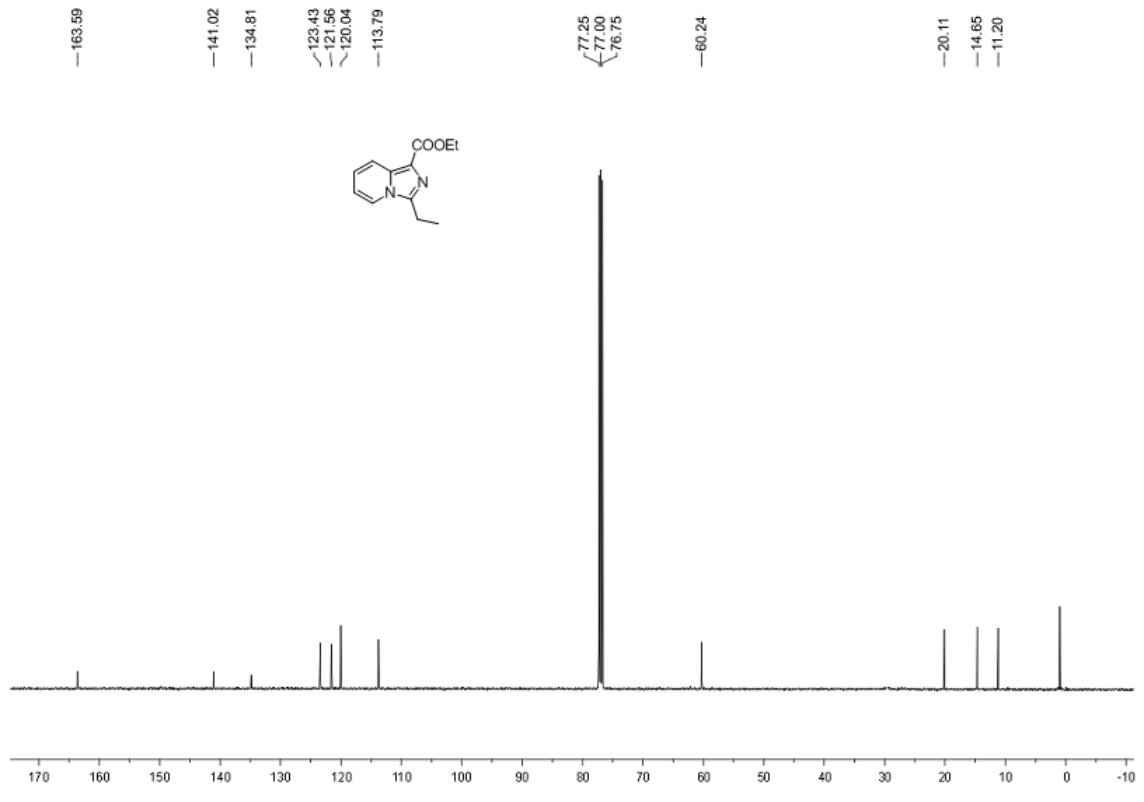
1.00
1.01
1.02
1.00
2.08
2.05
6.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5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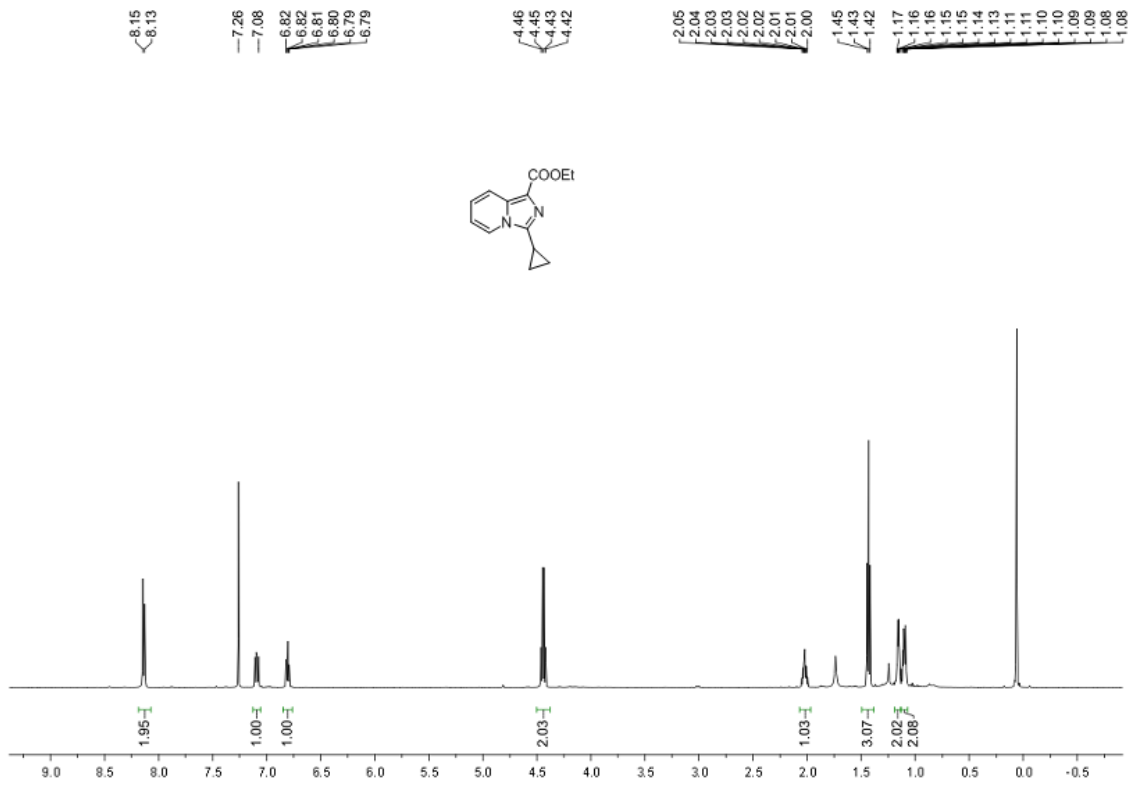
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2.05
2.04
2.03
2.03
2.02
2.02
2.01
2.01
2.00
1.45
1.43
1.42
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1.09
1.08
1.08
COOEt
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1.00
2.03
1.03
3.07
2.02
2.08
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8.0
7.5
7.0
6.5
6.0
5.5
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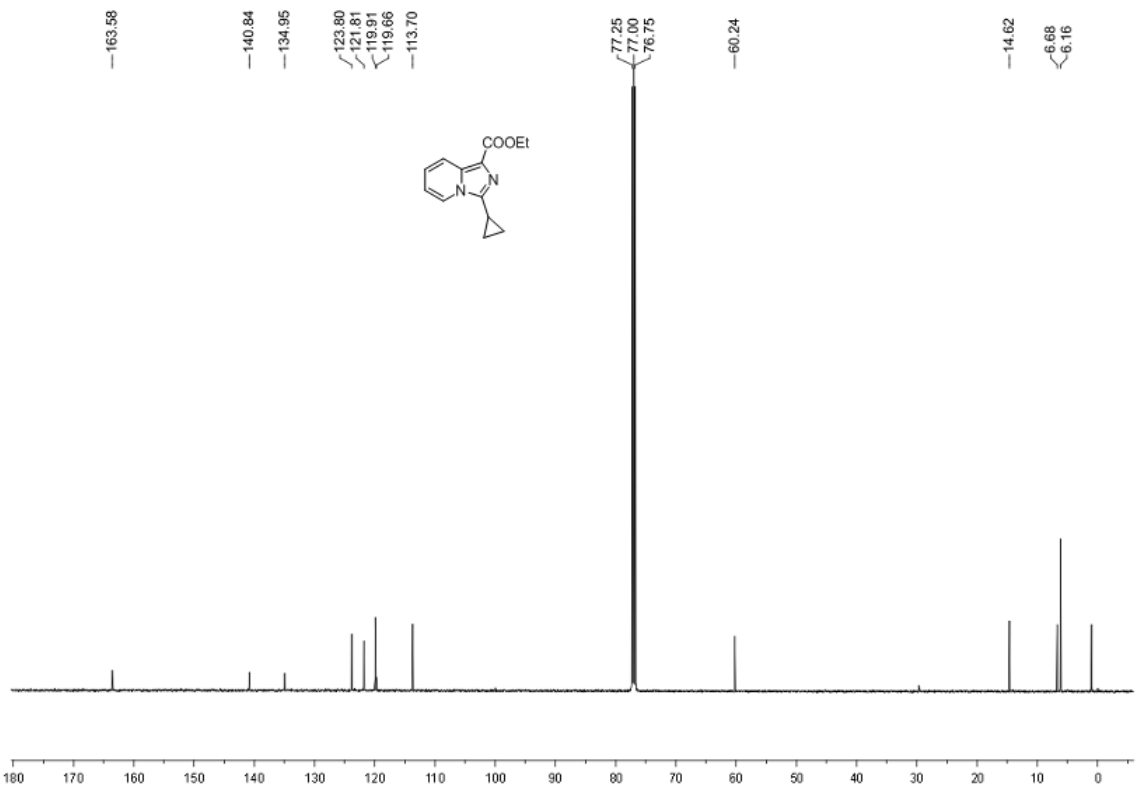
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76.75
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6.16
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140
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100
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10
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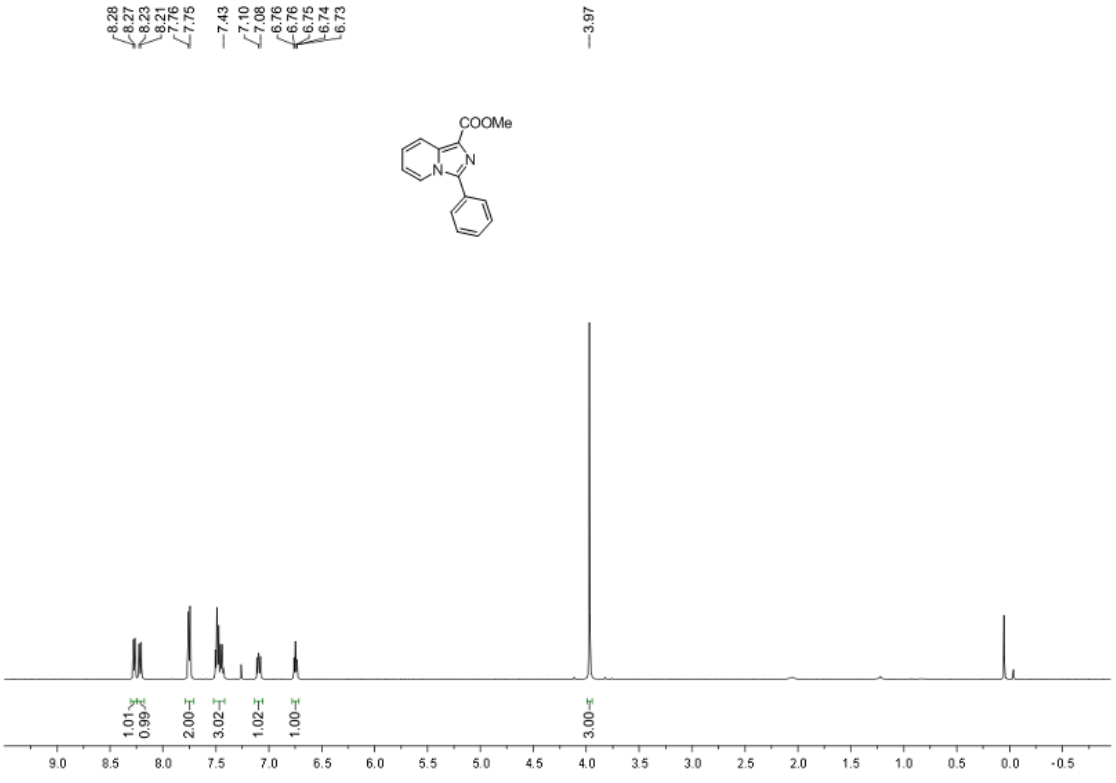
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6.76
6.75
6.74
6.73
3.97
COOMe
N
N
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0.99
2.00
3.02
1.02
1.00
3.00
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8.0
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7.0
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2.0
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0.0
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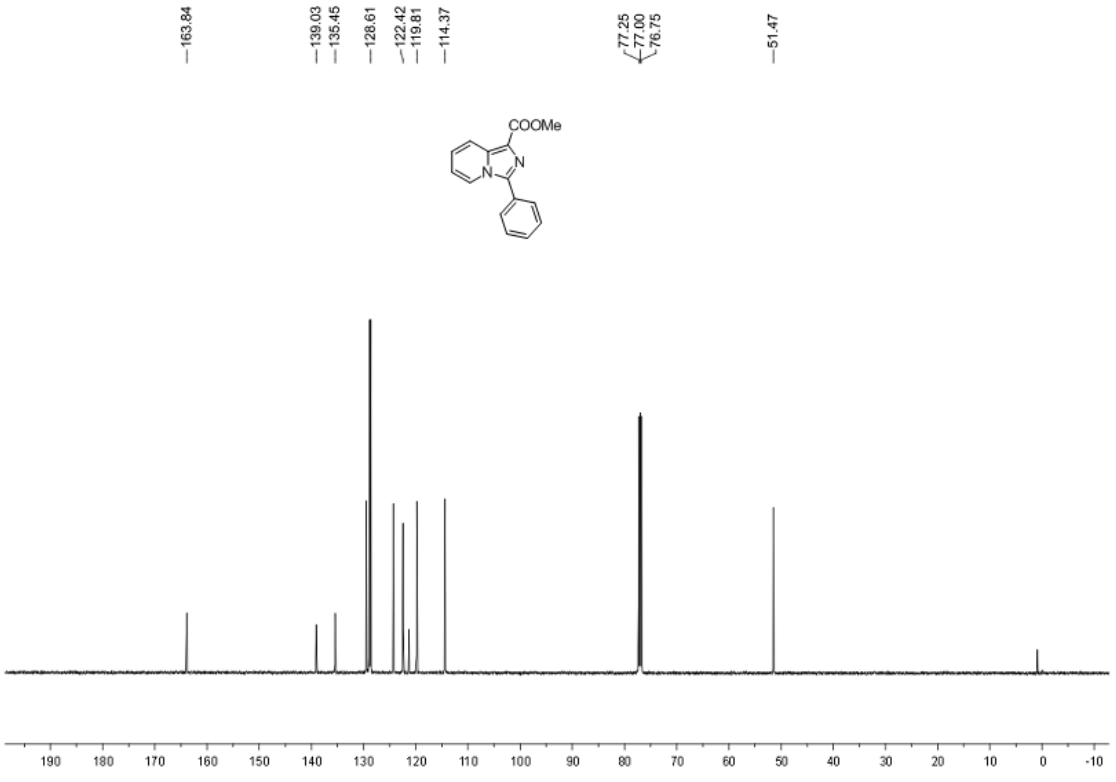
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51.47
COOMe
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N
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130
120
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100
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80
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60
50
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30
20
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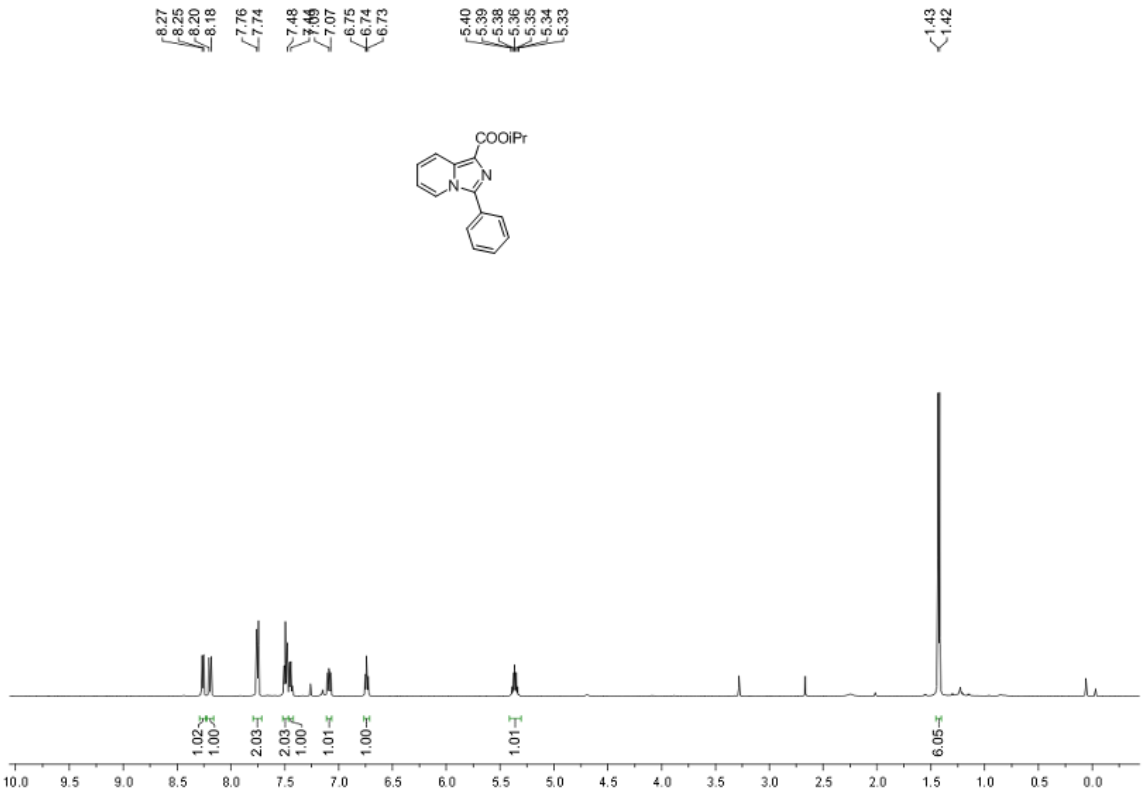
0
-10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5.39
5.38
5.36
5.35
5.34
5.33
1.43
1.42
COOiPr
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1.00
2.03
2.03
1.00
1.01
1.00
1.01
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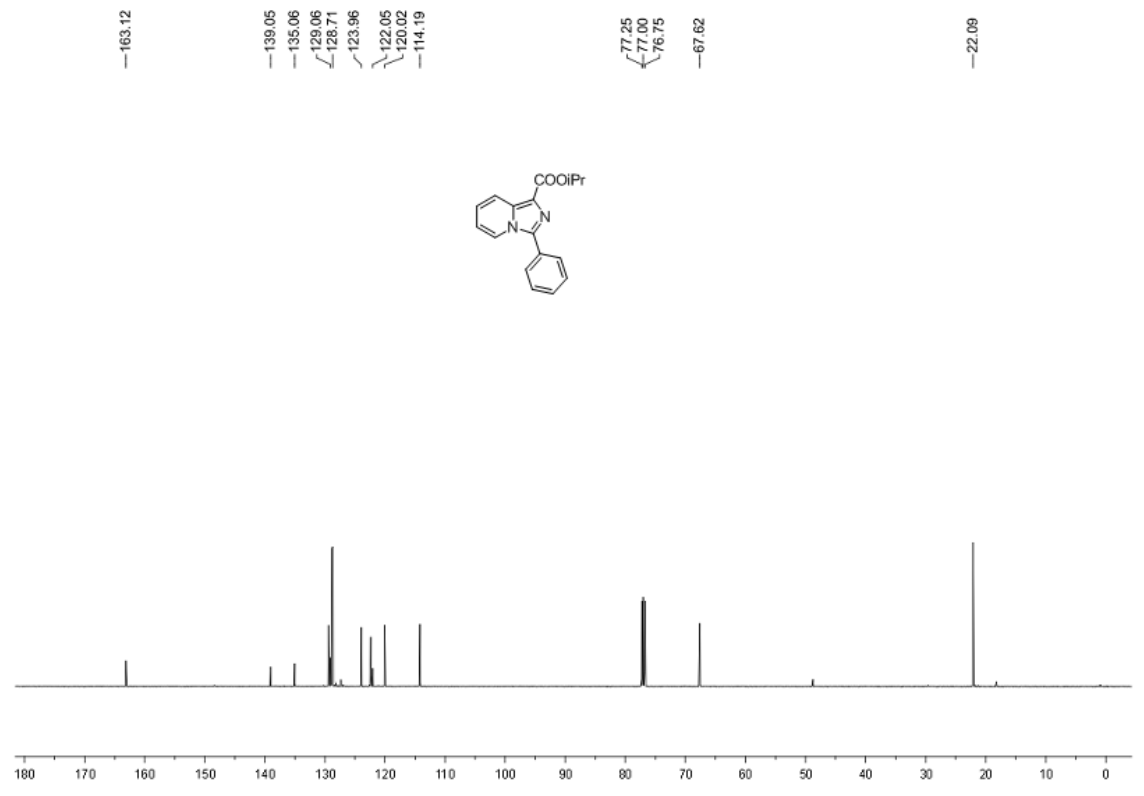
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22.09
COOiPr
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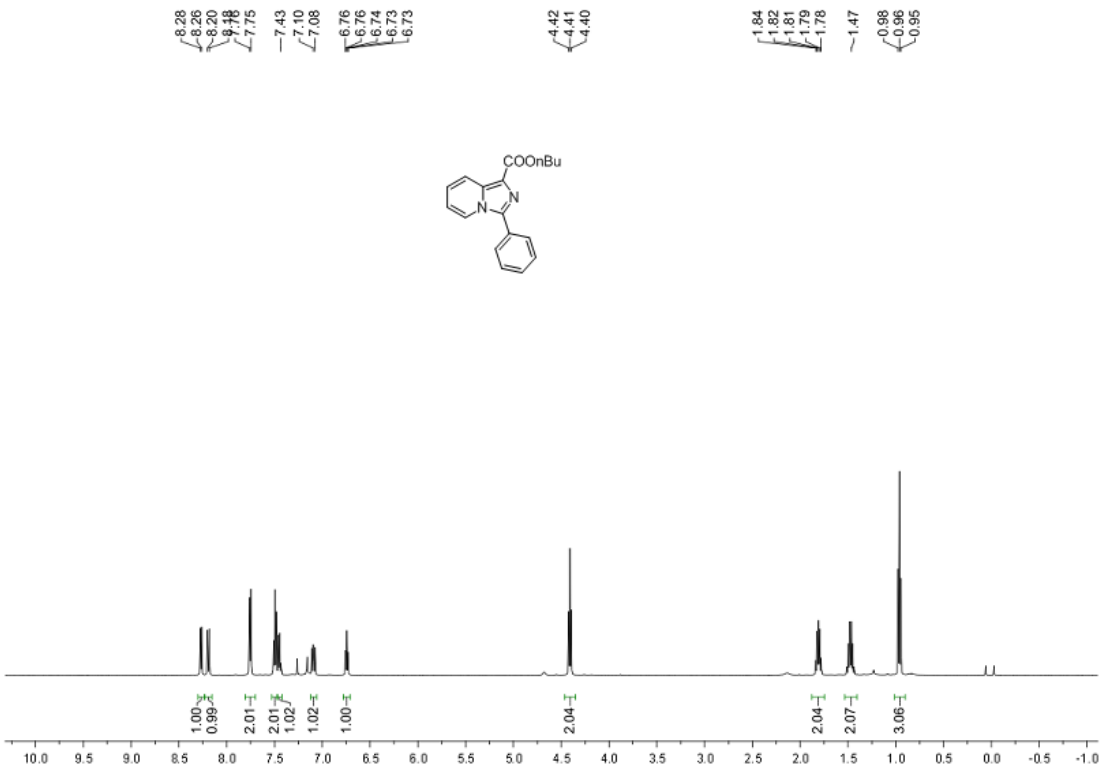
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1.81
1.79
1.78
1.47
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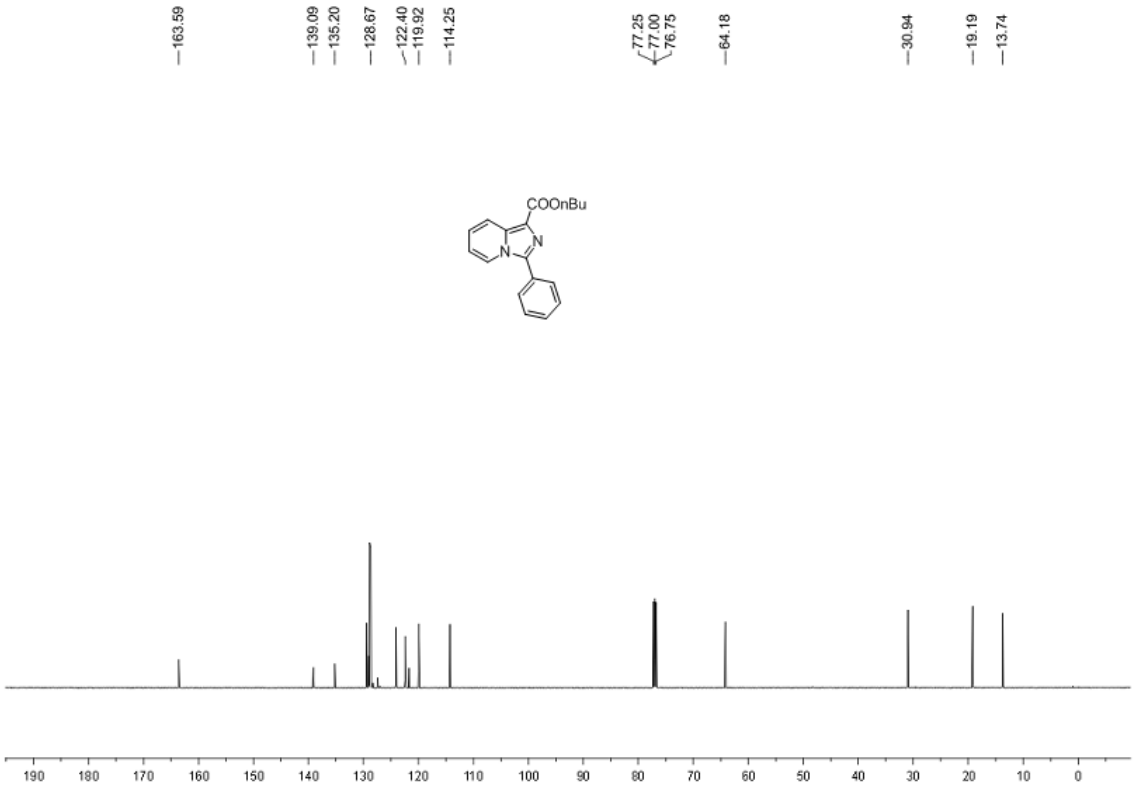
0.96
0.95
COOnBu
1.00
0.99
2.01
2.01
1.02
1.02
1.00
2.04
2.04
2.07
3.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0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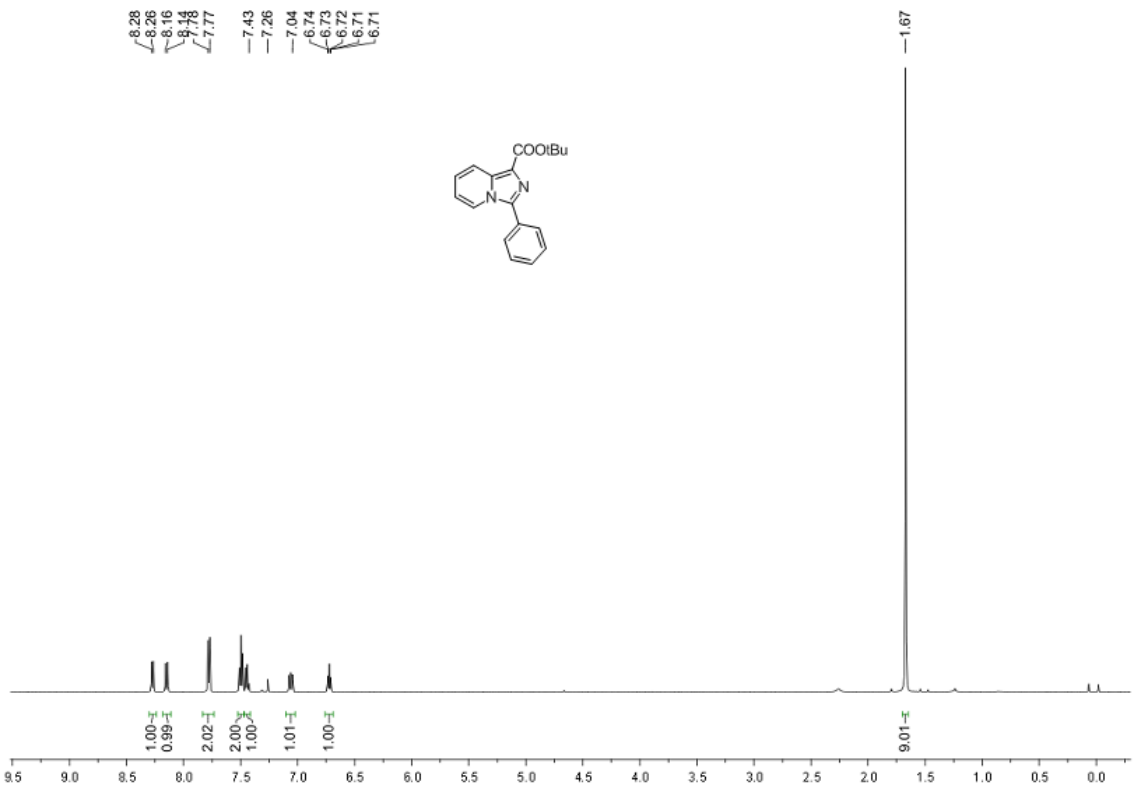
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2.00
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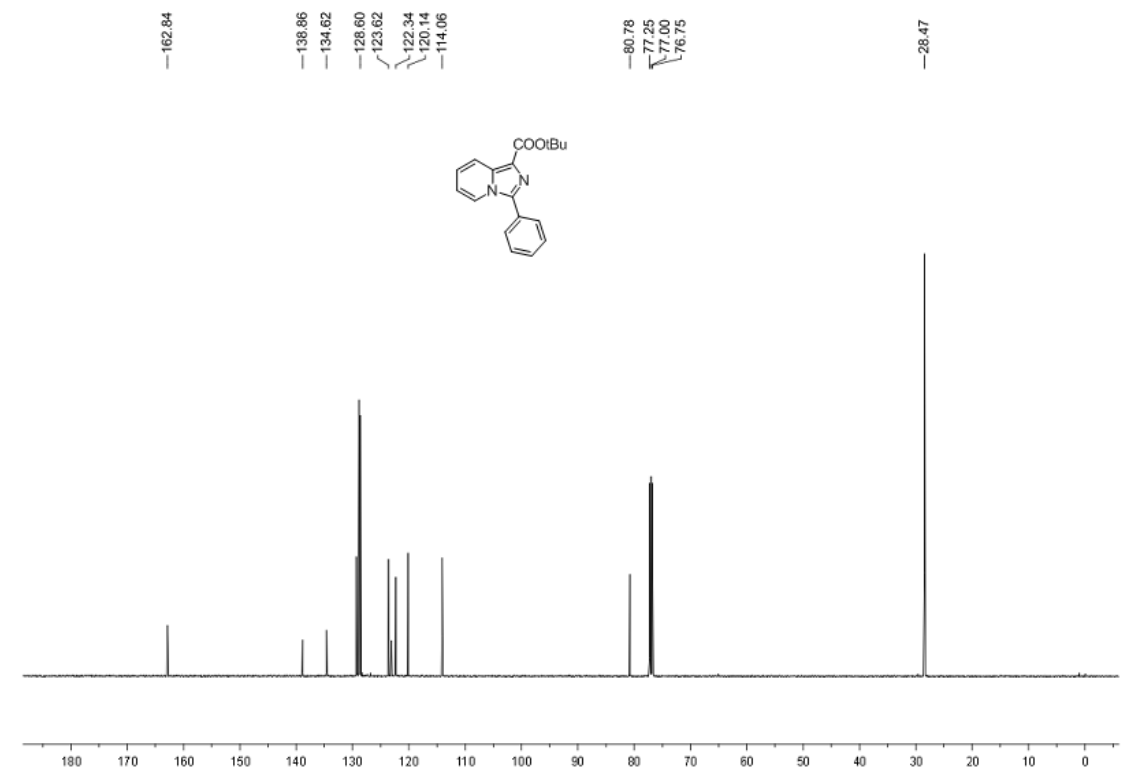
9.01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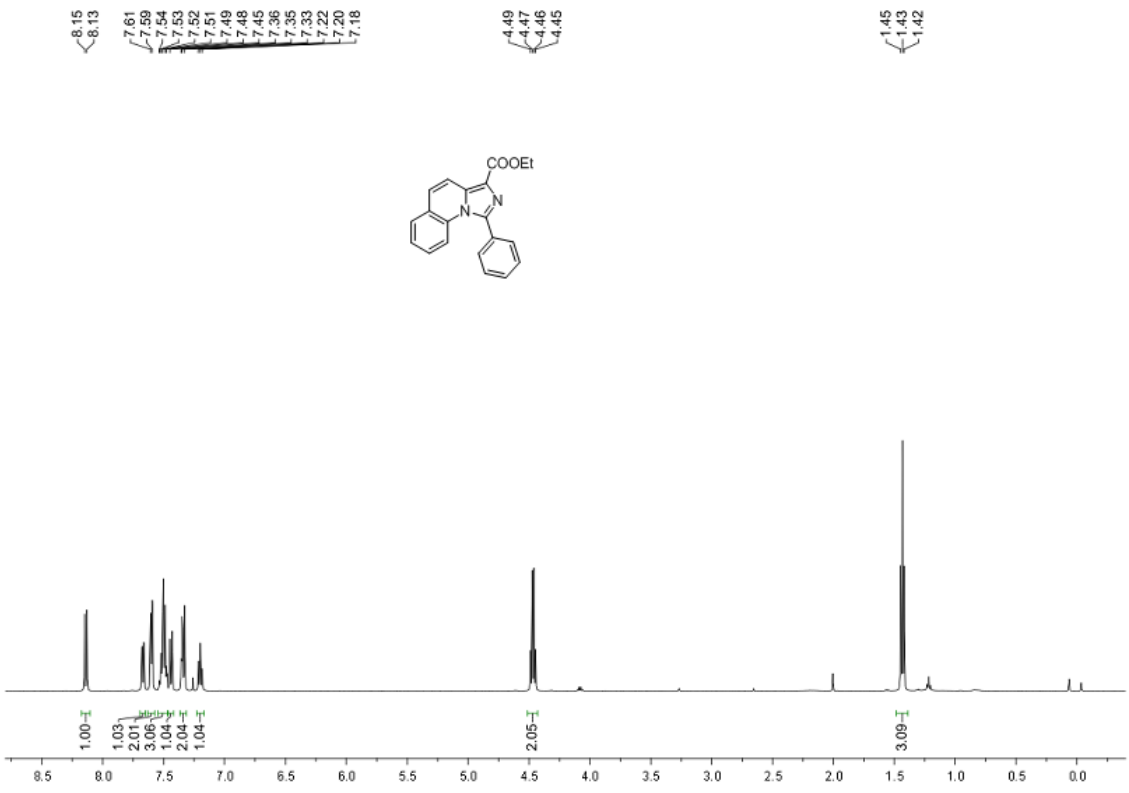
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4.46
4.45
1.45
1.43
1.42
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1.03
2.01
3.06
1.04
2.04
1.04
2.05
3.09
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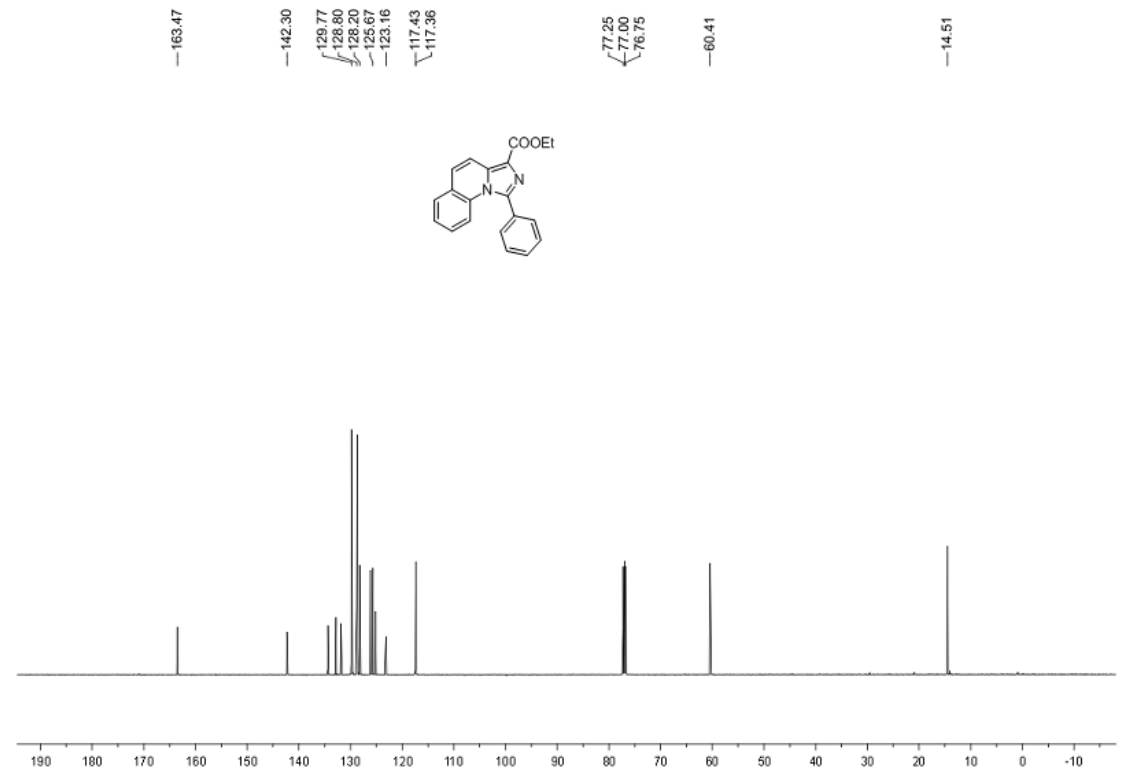
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60.41
14.51
COOEt
N
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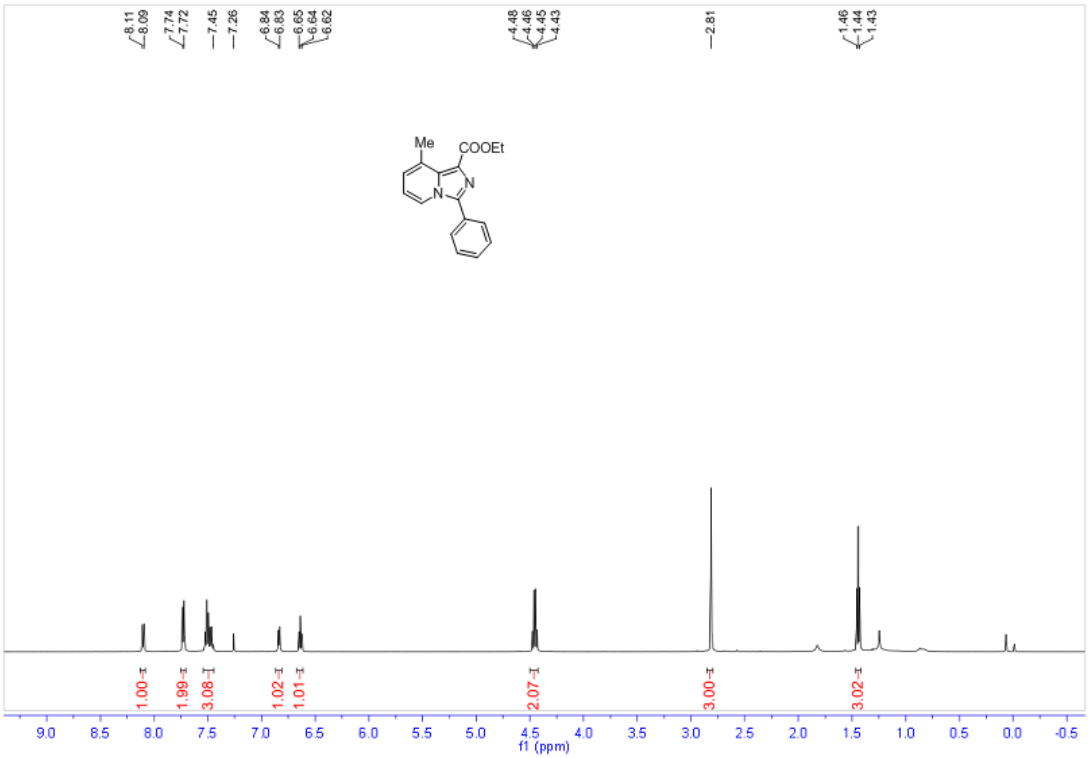
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4.46
4.45
4.43
2.81
1.46
1.44
1.43
Me
COOEt
N
N
1.00
1.99
3.08
1.02
1.01
2.07
3.00
3.02
9.0
8.5
8.0
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7.0
6.5
6.0
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5.0
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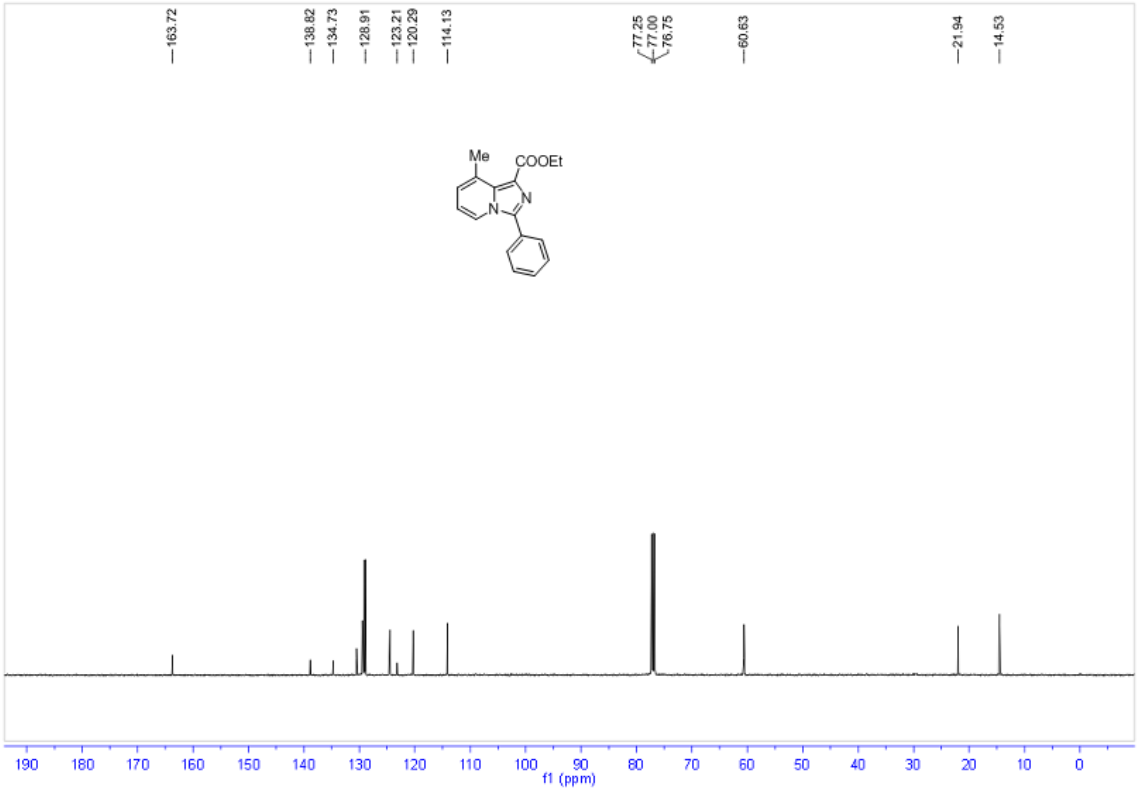
-0.5
f1 (ppm)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14.53
Me
COOEt
N
N
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180
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110
100
90
80
70
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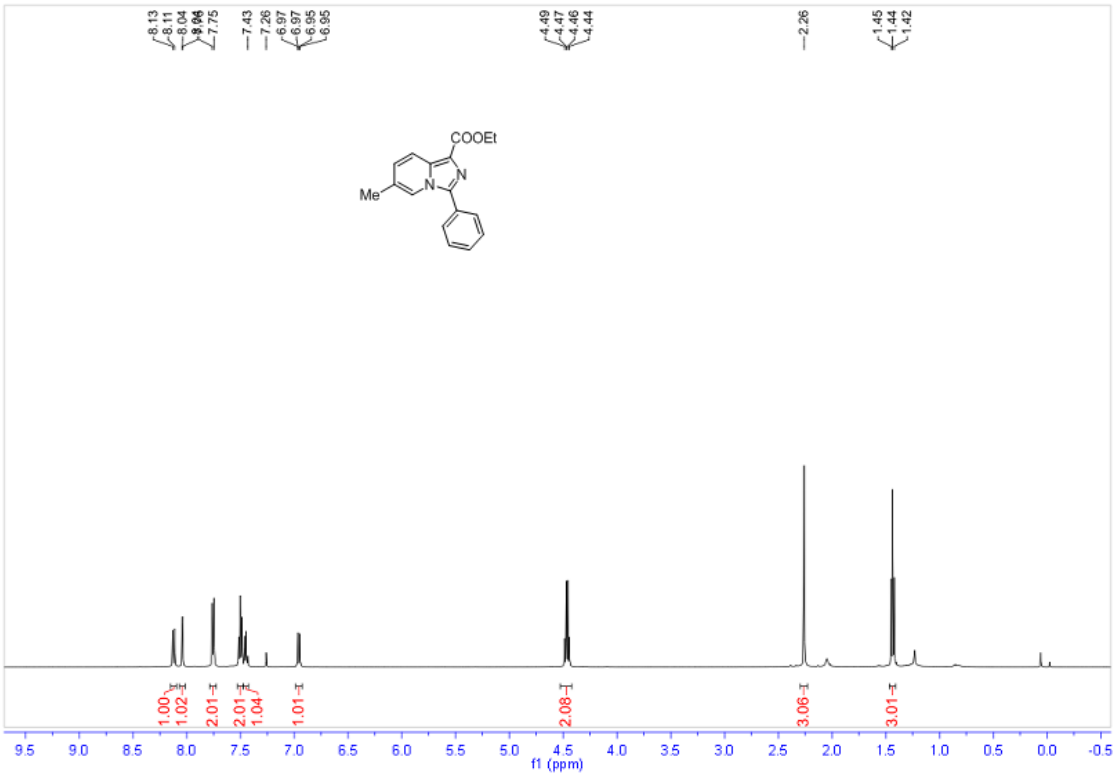
50
40
30
20
10
0
f1 (ppm)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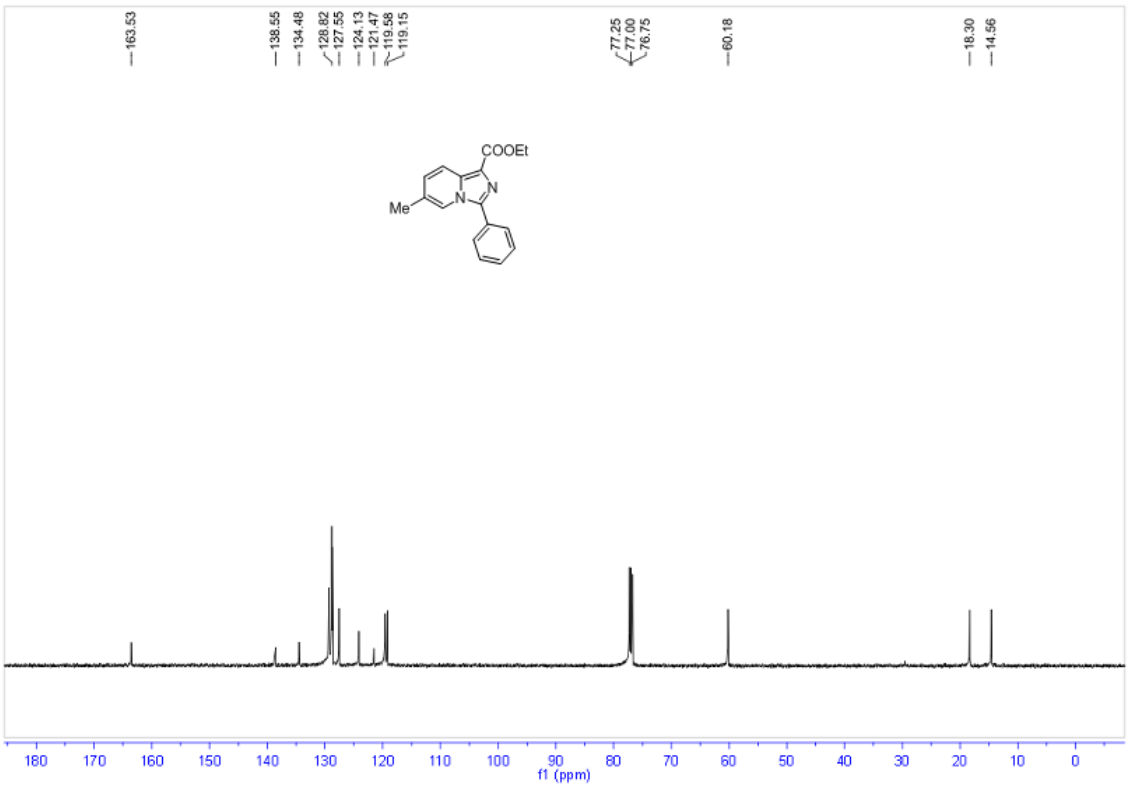
4.44
2.26
1.45
1.44
1.42
COOEt
Me
N
1.00
1.02
2.01
2.01
1.04
1.01
2.08
3.06
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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77.00
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N
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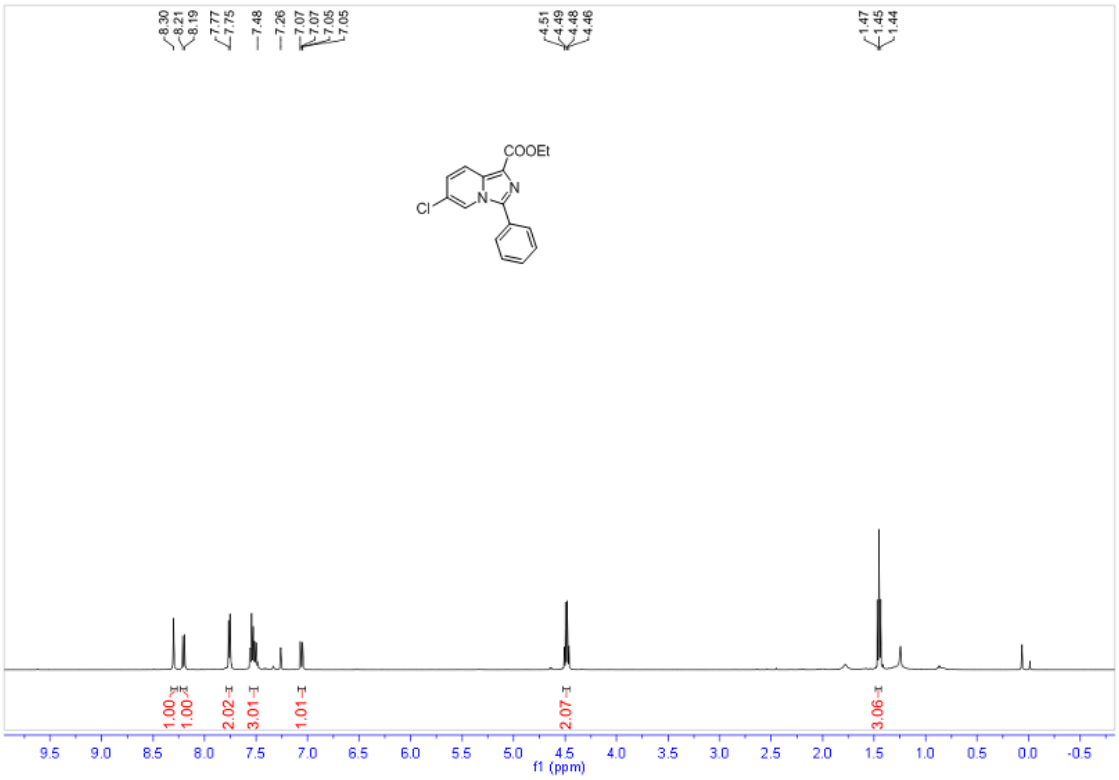
f1 (ppm)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4.48
4.46
1.47
1.45
1.44
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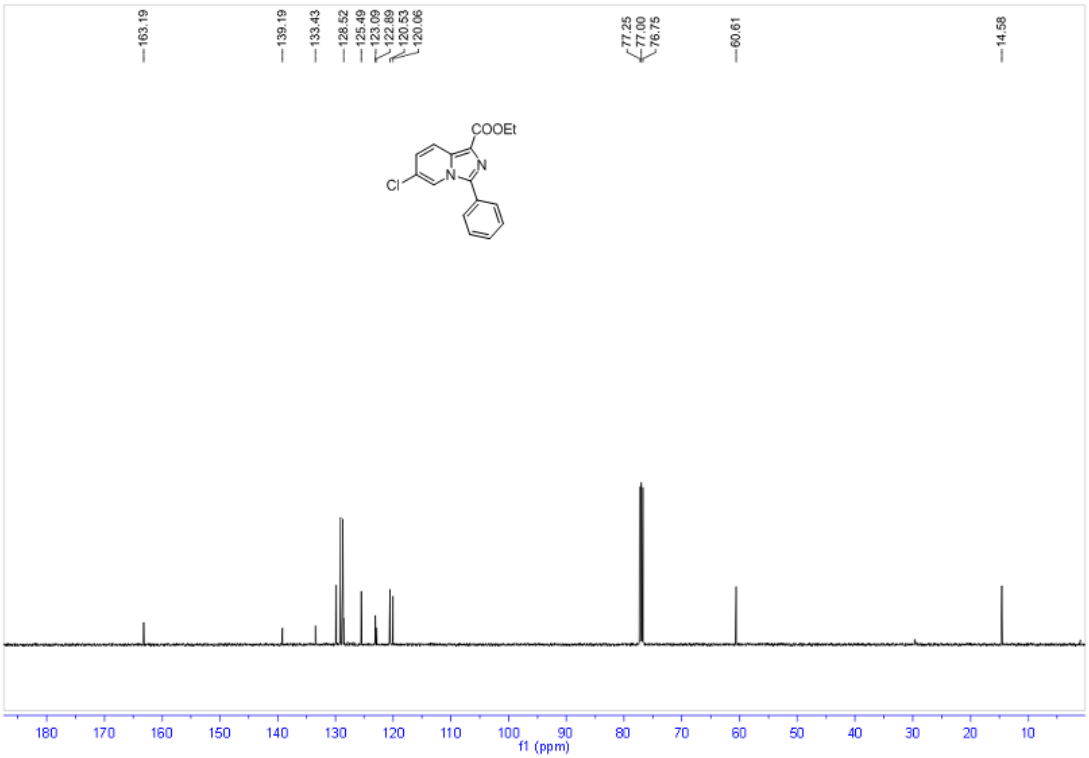
Cl
N
N
1.00
1.00
2.02
3.01
1.01
2.07
3.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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COOEt
Cl
N
N
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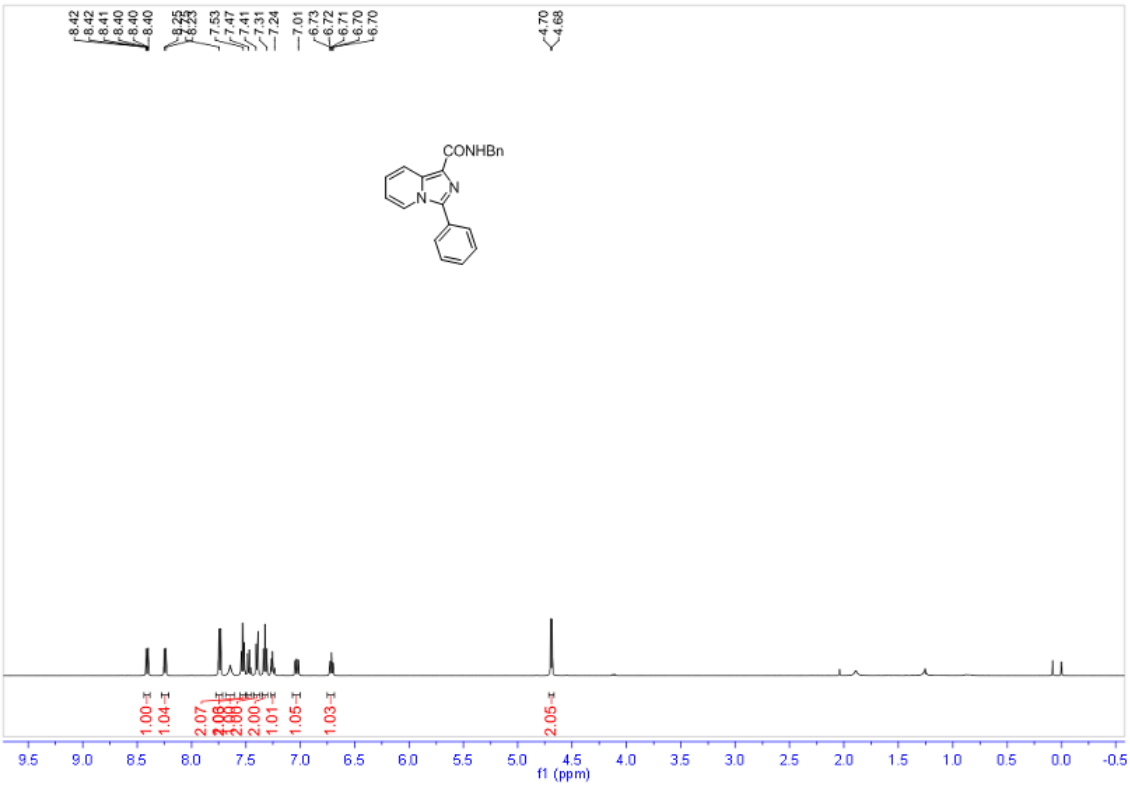
f1 (ppm)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6.72
6.71
6.70
6.70
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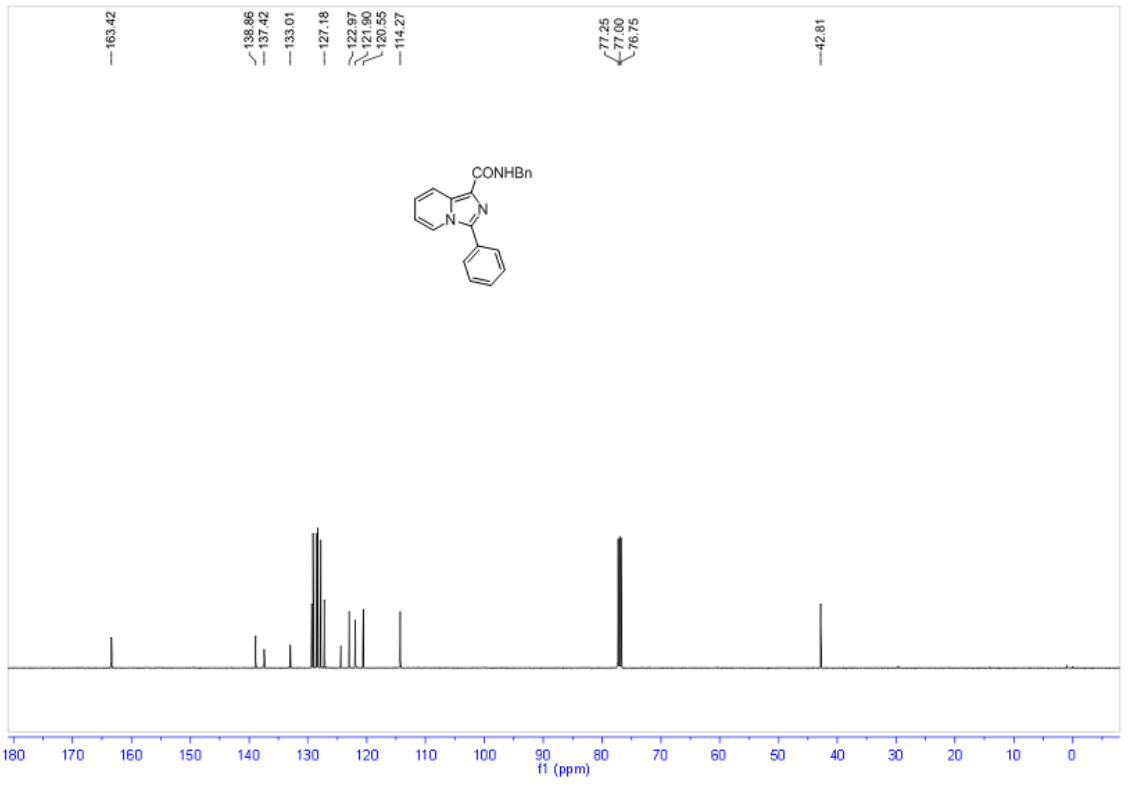
1.04
2.07
2.00
1.01
1.05
1.03
2.05
f1 (ppm)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77.00
76.75
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CONHBn
f1 (ppm)