Supplementary Information (SI) for Organic Chemistry Frontiers.

Cyclizative Dearomative Rearrangement of Pyridines with Isocyanates

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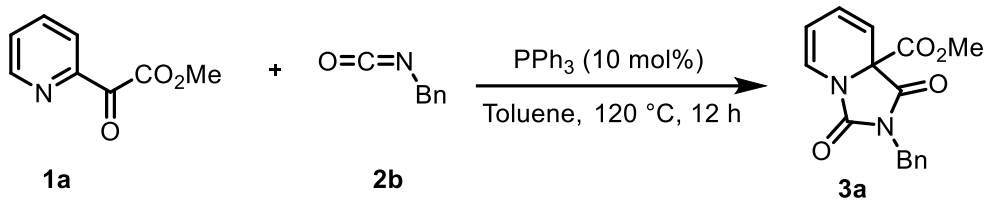
1. General information

NMR spectra were recorded on Bruker AV 400 MHz spectrometer. Chemical shifts are given in ppm. The spectra are calibrated to the residual ^{1}H and ^{13}C signals of the solvents. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), doublet-doublet (dd), quintet (quint), sextet (sext), septet (sept), multiplet (m), and broad (b), doublet of triplets (dt), triplet of doublets (td). Mass spectrometry analysis was carried out using an electrospray spectrometer Waters Micromass Q-TOF Premier Mass Spectrometer. Melting points were measured with SGW X-4 micro melting point apparatus. Optical rotations were measured on a Rudolph Research Analytical Autopol VI automatic polarimeter using a 50 mm path-length cell at 589 nm.

Materials and Methods: Unless otherwise stated, starting materials were purchased from commercial sources (Adamas-Beta®, Shanghai Haohong Scientific Co., Ltd., Shanghai Bide pharmatech Co., Ltd. J&K®, Aladdin® and Energy chemical), and used without further purification. Sensitive compounds were stored in a desiccator or in a glove box if required. Solvents were purchased in HPLC quality, degassed by purging thoroughly with nitrogen and dried over activated molecular sieves of appropriate size. Alternatively, they were purged with argon and passed through alumina columns in a solvent purification system (Innovative Technology). The $CDCl_3$ was supplied by Shanghai Haohong Scientific Co. Reactions were monitored by thin layer chromatography (TLC) using Xinnuo TLC silica gel 60 F254. Compounds were visualized by UV-light at 254 nm and by dipping the plates in an ethanolic vanillin/ sulfuric acid solution or an aqueous potassium permanganate solution followed by heating. Flash column chromatography was performed over silica gel (300-400 mesh). The $CDCl_3$ used in the NMR experiments was stored over anhydrous K_2CO_3 before use.

2. Survey of reaction conditions

Table S1. Temperature effect[a]

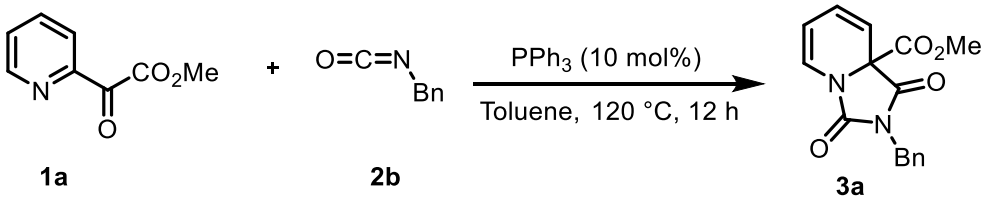


1a **2b** **3a**

60 °C	**80 °C**	**100 °C**	**120 °C**
20% yield	34% yield	58% yield	67% yield

[a]**1a** (0.10 mmol), **2a** (0.15 mmol), toluene (*c* 0.1 M), sealed tube, argon, 12 h.

Table S2. Additives effect[a]

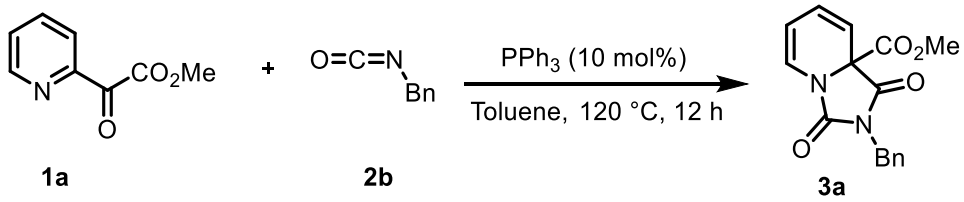


1a **2b** **3a**

$Zn(OTf)_2$	**$Cu(OTf)_2$**	**$Ni(OTf)_2$**	**$Sc(OTf)_3$**
25% yield	43% yield	51% yield	35% yield

[a]**1a** (0.10 mmol), **2a** (0.15 mmol), toluene (*c* 0.1 M), sealed tube, argon, 12 h.

Table S3. Additives effect[a]

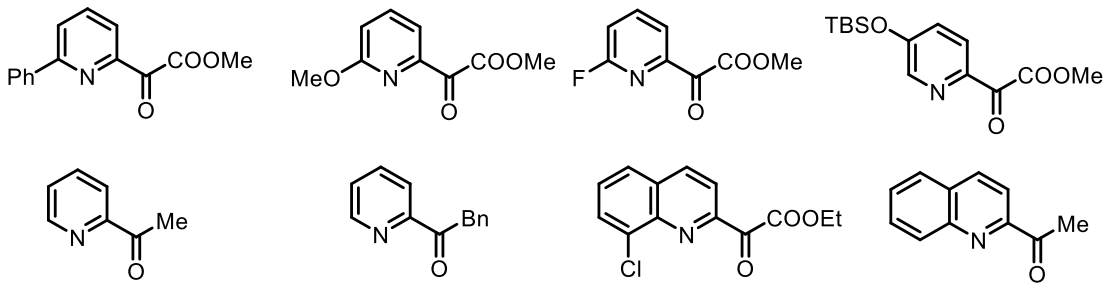


1a **2b** **3a**

NO M.S.	**3 Å M.S.**	**4 Å M.S.**	**5 Å M.S.**
54% yield	51% yield	62% yield	60% yield

[a]**1a** (0.10 mmol), **2a** (0.15 mmol), M.S. (30 mg), toluene (*c* 0.1 M), sealed tube, argon, 12 h.

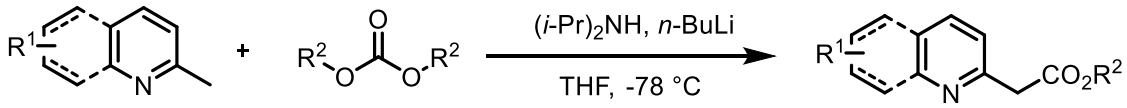
Table S4. Failed Substrates



3. Synthesis and characterization data of compounds 1

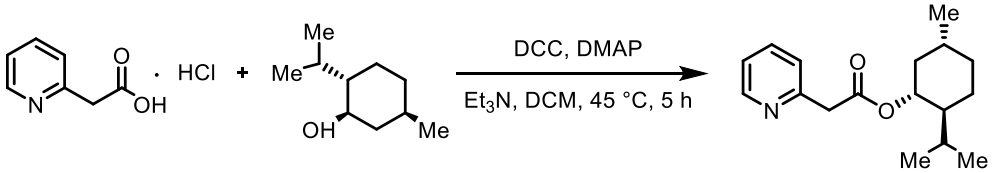
The compounds **1a-1b**, **1f-1t**, **1v-1ad** were prepared according to the reported method.[1-2] The compound **1c** was prepared according to the reported method.[2-3] The compounds **1d-1e** were prepared according to the reported method. [2, 4]The compound **1af** were prepared according to the reported method.[5] And the characterization data for unknown compounds were shown below:

General procedure A



To a solution of diisopropylamine (3.0 equiv) in dry THF was added *n*-butyllithium (3.0 equiv) dropwisely at -78 °C under nitrogen atmosphere. The solution was stirred at the same temperature for 30 mins, and a solution of 2-methyl substituted pyridine/quinoline compound (1.0 equiv) in dry THF was added dropwisely. After stirring 30 mins, carbonate ester (3.7 equiv) was added dropwisely and stirred at -78 °C for another 2 h. After completion of the reaction (monitored by TLC), the reaction was quenched by water, The layers were separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4. the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel eluting with petroleum ether/ethyl acetate = 30:1 to afford ester.

General procedure B



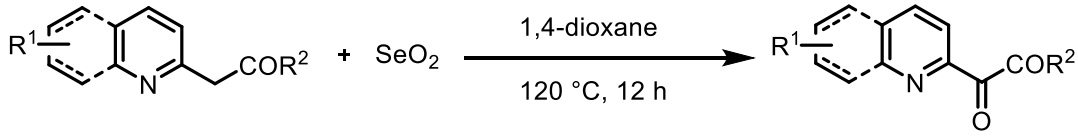
To a solution of 2-pyridine acetic acid hydrochloride (1.0 equiv) in DCM was added, L-menthol (1.5 equiv), *N,N*'-dicyclohexylcarbamate (DCC) (1.0 equiv), 4-dimethylaminopyridine (DMAP) (0.05 equiv), triethylamine (2.0 equiv) at room temperature and the mixture was warmed to 45 °C and stirred for 5 h. After completion of the reaction (monitored by TLC), the reaction mixture was diluted with DCM and

washed with water. The organic layers were dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel eluting with petroleum ether/ethyl acetate = 30:1 to afford ester.

General procedure C

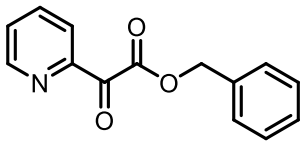
To a solution of 2-pyridine acetic acid hydrochloride (1.0 equiv) in DCM was added, substituted amines hydrochloride (1.0 equiv), 1-hydroxybenzotriazole (HOBT) (1.0 equiv), *N,N*-diisopropylethylamine (DIPEA) (3.0 equiv) and the mixture was cooled to 0 °C. 1-ethyl-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDCI) (1.0 equiv) was added and then the mixture was warmed to room temperature and stirred for 5 h. After completion of the reaction (monitored by TLC), the reaction mixture was diluted with DCM and washed with water. The organic layers were dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel eluting with petroleum ether/ethyl acetate = 10:1 to afford acidamide.

General procedure D



Selenium dioxide (1.2 equiv) was added to the 1,4-dioxane and stirred at 80 ℃ for 30 mins. 1,4-dioxane solution of ester/acidamide was added to the selenium dioxide solution, and then warmed up to 120 ℃ and stirred for 12 h. After completion of the reaction (monitored by TLC), the reaction mixture was filtered through Celite and concentrated. The residue was purified by column chromatography on silica gel eluting with petroleum ether/ethyl acetate = 30:1 to afford the compound **1**.

benzyl 2-oxo-2-(pyridin-2-yl)acetate (1b)



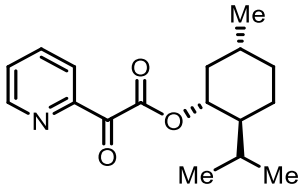
56% yield, yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.77 – 8.73 (m, 1H), 8.10 (d, *J* = 7.9 Hz, 1H), 7.90 (t, *J* = 7.9 Hz, 1H), 7.58 – 7.52 (m, 1H), 7.48 – 7.43 (m, 2H), 7.42 – 7.32 (m, 3H), 5.46 (s, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 187.5, 165.3, 150.3, 149.9, 137.4, 134.7, 128.7, 128.6, 128.5, 123.5, 67.7.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{11}NNaO_3^+$ 264.0631; Found 264.0636.

(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 2-oxo-2-(pyridin-2-yl)acetate (1c)



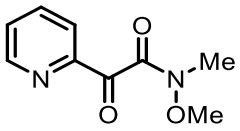
55% yield, white solid, m.p = 82 – 84 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.74 – 8.70 (m, 1H), 8.11 – 8.07 (m, 1H), 7.89 (t, *J* = 7.8 Hz, 1H), 7.55 – 7.50 (m, 1H), 5.04 (td, *J* = 11.0, 4.4 Hz, 1H), 2.28 – 2.20 (m, 1H), 2.12 – 2.02 (m, 1H), 1.75 – 1.66 (m, 2H), 1.62 – 1.51 (m, 1H), 1.51 – 1.41 (m, 1H), 1.20 – 1.06 (m, 2H), 0.95 (d, *J* = 6.5 Hz, 3H), 0.92 – 0.85 (m, 7H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 188.1, 165.5, 150.6, 149.9, 137.2, 128.2, 123.4, 77.0, 47.1, 40.8, 34.3, 31.7, 26.1, 23.5, 22.1, 20.9, 16.3.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{23}NNaO_3^+$ 312.1570; Found 312.1570.

***N*-methoxy-*N*-methyl-2-oxo-2-(pyridin-2-yl)acetamide (1d)**



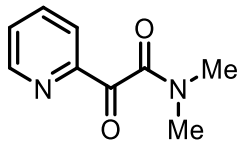
67% yield, yellow solid, m.p = 60 – 62 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.77 – 8.74 (m, 1H), 8.13 – 8.08 (m, 1H), 7.90 (td, *J* = 7.7, 1.7 Hz, 1H), 7.55 – 7.50 (m, 1H), 3.63 (s, 3H), 3.38 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.3, 168.1, 150.8, 149.9, 137.2, 128.0, 122.7, 61.9, 31.5.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_9H_{10}N_2NaO_3^+$ 217.0584; Found 217.0583.

***N*,*N*-dimethyl-2-oxo-2-(pyridin-2-yl)acetamide (1e)**



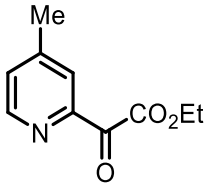
53% yield, yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.75 (d, *J* = 4.8 Hz, 1H), 8.12 (d, *J* = 7.8 Hz, 1H), 7.91 (td, *J* = 7.7, 1.6 Hz, 1H), 7.55 – 7.51 (m, 1H), 3.14 (s, 3H), 2.96 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 192.2, 168.0, 151.3, 150.1, 137.4, 128.2, 123.4, 37.0, 34.0.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_9H_{10}N_2NaO_2^+$ 201.0634; Found 201.0636.

ethyl 2-(4-methylpyridin-2-yl)acetate (1f)



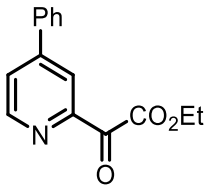
55% yield, brown oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.59 (d, *J* = 4.9 Hz, 1H), 7.92 (s, 1H), 7.35 (d, *J* = 4.9 Hz, 1H), 4.47 (q, *J* = 7.2 Hz, 2H), 2.45 (s, 3H), 1.41 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 188.1, 165.6, 150.4, 149.8, 148.9, 129.2, 124.3, 62.3, 21.2, 14.2.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{10}H_{11}NNaO_3^+$ 216.0631; Found 216.0630.

ethyl 2-oxo-2-(4-phenylpyridin-2-yl)acetate (1g)



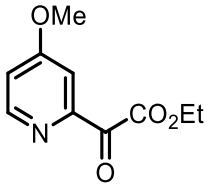
84% yield, colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.79 (d, *J* = 5.1 Hz, 1H), 8.34 (s, 1H), 7.76 (d, *J* = 5.2 Hz, 1H), 7.72 – 7.65 (m, 2H), 7.57 – 7.44 (m, 3H), 4.51 (q, *J* = 7.1 Hz, 2H), 1.44 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 188.0, 165.5, 151.1, 150.5, 150.0, 137.0, 130.0, 129.5, 127.2, 126.0, 121.3, 62.4, 14.3.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{13}NNaO_3^+$ 278.0788; Found 278.0792.

ethyl 2-(3-methoxyphenyl)-2-oxoacetate (1h)



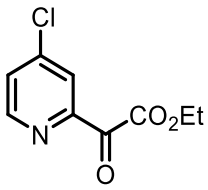
59% yield, yellow solid, m.p = 41 – 43 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.53 (d, *J* = 5.5 Hz, 1H), 7.60 (d, *J* = 2.7 Hz, 1H), 7.02 (dd, *J* = 5.6, 2.2 Hz, 1H), 4.47 (q, *J* = 7.3 Hz, 2H), 3.91 (s, 3H), 1.40 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 187.9, 166.7, 165.4, 152.2, 151.1, 115.0, 108.7, 62.4, 55.8, 14.2.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{10}H_{11}NNaO_4^+$ 232.0580; Found 232.0579.

ethyl 2-(4-chloropyridin-2-yl)-2-oxoacetate (1i)



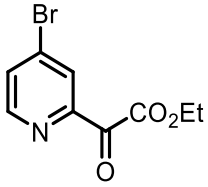
60% yield, yellow solid, m.p = 40 – 42 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.65 – 8.62 (m, 1H), 8.08 – 8.06 (m, 1H), 7.54 (dd, *J* = 5.2, 2.1 Hz, 1H), 4.47 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 186.6, 164.7, 151.6, 150.8, 145.9, 128.4, 123.8, 62.5, 14.2.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_9H_8ClNNaO_3^+$ 236.0085; Found 236.0084.

ethyl 2-(4-bromopyridin-2-yl)-2-oxoacetate (1j)



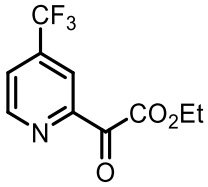
85% yield, yellow solid, m.p = 49 – 51 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.56 – 8.53 (m, 1H), 8.25 – 8.21 (m, 1H), 7.72 – 7.68 (m, 1H), 4.48 (q, *J* = 7.2 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 186.5, 164.7, 151.4, 150.6, 134.3, 131.4, 126.9, 62.5, 14.2.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_9H_8BrNNaO_3^+$ 279.9580; Found 279.9582.

ethyl 2-(4-(trifluoromethyl)pyridin-2-yl)acetate (1k)



39% yield, yellow oil.

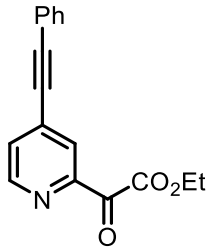
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.95 (d, *J* = 5.0 Hz, 1H), 8.31 (s, 1H), 7.78 (d, *J* = 5.3 Hz, 1H), 4.49 (q, *J* = 7.2 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 186.4, 164.5, 151.6, 151.0, 140.1 (q, *J* = 35.3 Hz), 123.8 (q, *J* = 3.4 Hz), 122.3 (q, *J* = 274.6 Hz), 119.3 (q, *J* = 3.6 Hz). 62.7, 14.2.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.9

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{10}H_8F_3NNaO_3^+$ 270.0348; Found 270.0350.

ethyl 2-oxo-2-(4-(phenylethynyl)pyridin-2-yl)acetate (1l)



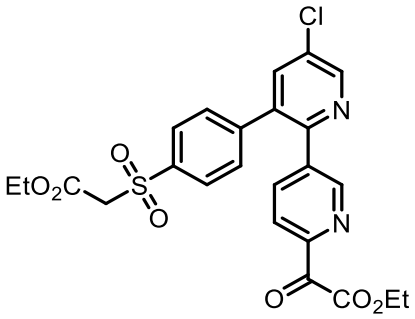
44% yield, brown solid, m.p = 57 – 59 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.72 (d, *J* = 5.1 Hz, 1H), 8.17 (s, 1H), 7.61 – 7.54 (m, 3H), 7.44 – 7.36 (m, 3H), 4.49 (q, *J* = 7.2 Hz, 2H), 1.42 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 187.3, 165.1, 150.5, 149.9, 133.3, 132.2, 129.8, 129.7, 128.7, 125.4, 121.7, 96.1, 85.8, 62.4, 14.2.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{13}NNaO_3^+$ 302.0788; Found 302.0787.

ethyl 2-(5-chloro-3-(4-((2-ethoxy-2-oxoethyl)sulfonyl)phenyl)-[2,3'-bipyridin]-6'-yl)-2-oxoacetate (1m)



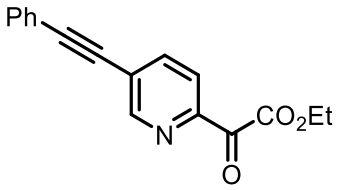
24% yield, yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.77 – 8.71 (m, 2H), 7.98 (d, *J* = 8.1 Hz, 1H), 7.93 (d, *J* = 8.1 Hz, 2H), 7.82 – 7.80 (m, 1H), 7.78 – 7.74 (m, 1H), 7.40 (d, *J* = 8.3 Hz, 2H), 4.44 (q, *J* = 7.1 Hz, 2H), 4.17 (q, *J* = 7.2 Hz, 2H), 4.13 (s, 2H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 187.2, 165.1, 162.3, 150.8, 150.7, 149.5, 149.0, 143.6, 138.9, 138.5, 138.4, 138.3, 136.0, 132.4, 130.3, 129.6, 122.9, 62.7, 62.4, 61.0, 14.2, 14.1.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{21}ClN_2NaO_7S^+$ 539.0650; Found 539.0649.

ethyl 2-oxo-2-(5-(phenylethynyl)pyridin-2-yl)acetate (1n)



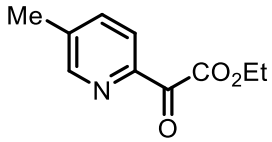
40% yield, yellow solid, m.p = 78 – 80 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.83 (s, 1H), 8.11 – 8.06 (m, 1H), 8.00 – 7.96 (m, 1H), 7.60 – 7.55 (m, 2H), 7.44 – 7.36 (m, 3H), 4.49 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 187.1, 165.2, 152.1, 148.4, 139.5, 132.1, 129.7, 128.7, 125.5, 122.9, 121.9, 97.1, 85.6, 62.4, 14.2.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{13}NNaO_3^+$ 302.0788; Found 302.0786.

ethyl 2-(5-methylpyridin-2-yl)-2-oxoacetate (1o)



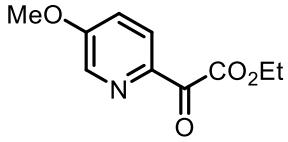
57% yield, white solid, m.p = 74 – 76 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.56 (s, 1H), 8.01 (d, *J* = 7.9 Hz, 1H), 7.69 (d, *J* = 7.9 Hz, 1H), 4.47 (q, *J* = 7.1 Hz, 2H), 2.44 (s, 3H), 1.40 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 187.7, 165.6, 150.6, 148.2, 139.3, 137.6, 123.3, 62.2, 19.1, 14.2.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{10}H_{11}NNaO_3^+$ 216.0631; Found 216.0627.

ethyl 2-(5-methoxypyridin-2-yl)-2-oxoacetate (1p)



35% yield, white solid, m.p = 52 – 54 ℃.

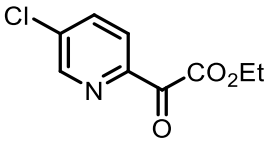
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.38 (d, *J* = 2.9 Hz, 1H), 8.11 (d, *J* = 8.7 Hz, 1H),

7.31 (dd, *J* = 8.7, 2.8 Hz, 1H), 4.46 (q, *J* = 7.2 Hz, 2H), 3.94 (s, 3H), 1.40 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 186.7, 165.8, 159.4, 143.2, 138.5, 125.5, 120.1, 62.2, 56.1, 14.2.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{10}H_{11}NNaO_4^+$ 232.0580; Found 232.0577.

ethyl 2-(5-chloropyridin-2-yl)-2-oxoacetate (1q)



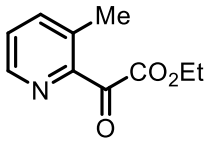
63% yield, yellow solid, m.p = 38 – 40 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.69 (dd, *J* = 2.3, 0.8 Hz, 1H), 8.07 (dd, *J* = 8.3, 0.8 Hz, 1H), 7.89 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.48 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 186.6, 164.9, 149.1, 148.4, 137.5, 137.2, 124.3, 62.5, 14.2.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_9H_8ClNNaO_3^+$ 236.0085; Found 236.0080.

ethyl 2-(3-methylpyridin-2-yl)-2-oxoacetate (1s)



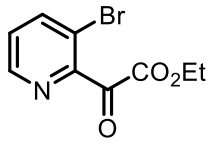
68% yield, pink solid, m.p = 71 – 73 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.57 (d, *J* = 4.0 Hz, 1H), 7.64 (d, *J* = 8.3 Hz, 1H), 7.39 (dd, *J* = 7.8, 4.6 Hz, 1H), 4.45 (q, *J* = 7.2 Hz, 2H), 2.66 (s, 3H), 1.40 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 189.5, 166.3, 147.8, 147.1, 140.3, 137.6, 127.3, 62.0, 19.5, 14.2.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{10}H_{11}NNaO_3^+$ 216.0631; Found 216.0627.

ethyl 2-(3-bromopyridin-2-yl)-2-oxoacetate (1t)



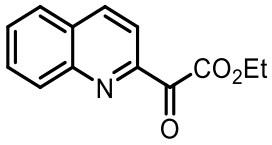
56% yield, yellow solid, m.p = 41 – 43 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.66 (dd, *J* = 4.6, 1.3 Hz, 1H), 8.05 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.37 (dd, *J* = 8.2, 4.5 Hz, 1H), 4.45 (q, *J* = 7.2 Hz, 2H), 1.40 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 185.6, 164.1, 148.4, 147.9, 142.9, 127.9, 120.3, 62.5, 14.2.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_9H_8BrNNaO_3^+$ 279.9580; Found 279.9579.

ethyl 2-oxo-2-(quinolin-2-yl)acetate (1v)



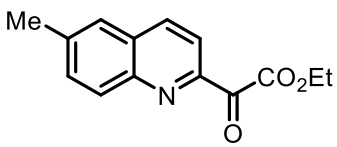
46% yield, yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.34 (d, *J* = 8.5 Hz, 1H), 8.19 (d, *J* = 8.5 Hz, 1H), 8.13 (d, *J* = 8.5 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.80 (t, *J* = 7.7 Hz, 1H), 7.70 (t, *J* = 7.2 Hz, 1H), 4.56 (q, *J* = 7.1 Hz, 2H), 1.47 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 188.3, 165.8, 150.0, 147.5, 137.6, 131.0, 130.6, 130.1, 129.7, 127.9, 118.6, 62.2, 14.3.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{11}NNaO_3^+$ 252.0631; Found 252.0639.

ethyl 2-(6-methylquinolin-2-yl)-2-oxoacetate (1w)



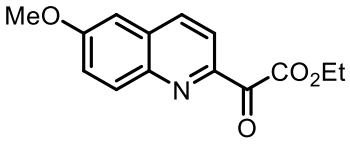
72% yield, pink solid, m.p = 101 – 103 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21 (d, *J* = 8.4 Hz, 1H), 8.10 – 8.05 (m, 2H), 7.65 – 7.58 (m, 2H), 4.54 (q, *J* = 7.0 Hz, 2H), 2.57 (s, 3H), 1.47 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 188.2, 165.7, 149.1, 146.1, 140.1, 136.5, 132.8, 130.6, 130.0, 126.5, 118.6, 62.0, 21.9, 14.2.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{13}NNaO_3^+$ 266.0788; Found 266.0791.

ethyl 2-(6-methoxyquinolin-2-yl)-2-oxoacetate (1x)



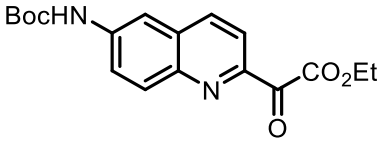
54% yield, white solid, m.p = 114 – 116 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.20 – 8.16 (m, 1H), 8.10 – 8.05 (m, 2H), 7.43 (dd, *J* = 9.3 Hz, 2.8Hz, 1H), 7.11 (d, *J* = 2.8 Hz, 1H), 4.54 (q, *J* = 7.2 Hz, 2H), 3.97 (s, 3H), 1.47 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 188.2, 166.0, 160.5, 147.8, 143.8, 135.8, 132.7, 131.8, 123.9, 119.3, 105.0, 62.1, 55.9, 14.3.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{13}NNaO_4^+$ 282.0737; Found 282.0741.

ethyl 2-(6-((tert-butoxycarbonyl)amino)quinolin-2-yl)-2-oxoacetate (1y)



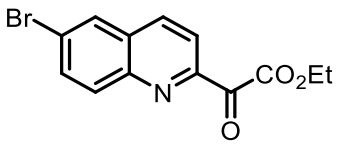
67% yield, yellow solid, m.p = 131 – 133 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.22 – 8.16 (m, 2H), 8.07 (dd, *J* = 8.9, 5.6 Hz, 2H), 7.53 (d, *J* = 9.2 Hz, 1H), 6.88 (s, 1H), 4.54 (q, *J* = 7.2 Hz, 2H), 1.56 (s, 9H), 1.46 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 188.1, 166.0, 152.5, 148.5, 144.2, 139.3, 136.6, 132.0, 131.3, 123.4, 119.3, 113.0, 81.7, 62.2, 28.4, 14.3.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{20}N_2NaO_5^+$ 367.1264; Found 367.1265.

ethyl 2-(6-bromoquinolin-2-yl)-2-oxoacetate (1z)



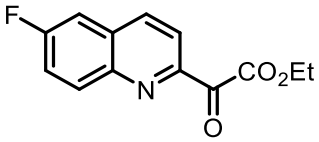
23% yield, pink solid, m.p = 75 – 77 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.27 – 8.23 (m, 1H), 8.16 – 8.12 (m, 1H), 8.08 – 8.03 (m, 2H), 7.89 – 7.84 (m, 1H), 4.54 (q, *J* = 7.1 Hz, 2H), 1.47 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 187.9, 165.5, 150.3, 146.1, 136.6, 134.3, 132.6, 131.0, 130.0, 124.3, 119.6, 62.4, 14.3.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{10}BrNNaO_3^+$ 329.9736; Found 329.9729.

ethyl 2-(6-fluoroquinolin-2-yl)-2-oxoacetate (1aa)



79% yield, yellow solid, m.p = 54 – 56 ℃.

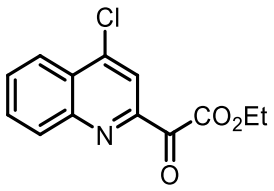
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.30 – 8.26 (m, 1H), 8.22 – 8.16 (m, 1H), 8.16 – 8.12 (m, 1H), 7.60 – 7.53 (m, 1H), 7.53 – 7.48 (m, 1H), 4.55 (q, *J* = 7.4 Hz, 2H), 1.47 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 187.9, 165.6, 162.4 (d, *J* = 254.7Hz), 149.5 (d, *J* = 3.0 Hz), 144.6, 137.0 (d, *J* = 5.7 Hz), 133.8 (d, *J* = 9.7 Hz), 131.1 (d, *J* = 10.7 Hz), 121.2 (d, *J* = 26.2 Hz), 119.4, 111.1 (d, *J* = 22.2 Hz), 62.3, 14.3.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -107.7.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{10}FNNaO_3^+$ 270.0537; Found 270.0541.

ethyl 2-(4-chloroquinolin-2-yl)-2-oxoacetate (1ab)



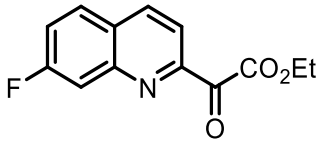
35% yield, yellow solid, m.p = 125 – 127 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.32 – 8.29 (m, 1H), 8.24 – 8.20 (m, 1H), 8.20 (s, 1H), 7.89 – 7.84 (m, 1H), 7.83 – 7.78 (m, 1H), 4.55 (q, *J* = 7.1 Hz, 2H), 1.47 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 187.3, 165.1, 149.8, 148.3, 144.4, 131.47, 131.45, 130.8, 128.2, 124.5, 118.8, 62.4, 14.3.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{10}ClNNaO_3^+$ 286.0241; Found 286.0243.

ethyl 2-(7-fluoroquinolin-2-yl)-2-oxoacetate (1ac)



26% yield, yellow solid, m.p = 47 – 49 ℃.

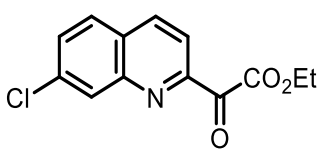
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.34 (d, *J* = 8.5 Hz, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 7.90 (dd, *J* = 9.1, 5.9 Hz, 1H), 7.80 (dd, *J* = 9.6, 2.5 Hz, 1H), 7.51 – 7.44 (m, 1H), 4.55 (q, *J* = 7.2 Hz, 2H), 1.47 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 188.0, 165.5, 163.5 (d, *J* = 253.6 Hz), 150.8, 148.5 (d, *J* = 12.9 Hz), 137.6 (d, *J* = 1.2 Hz), 130.0 (d, *J* = 9.9 Hz), 127.1, 120.4 (d, *J* = 25.9 Hz), 118.0 (d, *J* = 2.5 Hz), 114.3 (d, *J* = 20.5 Hz), 62.3, 14.3.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -107.4

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{10}FNO_3Na^+$ 270.0537; Found 270.0540.

ethyl 2-(7-chloroquinolin-2-yl)-2-oxoacetate (1ad)



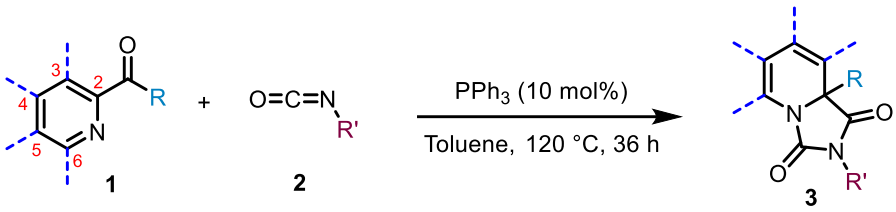
57% yield, white solid, m.p = 102 – 104 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.35 – 8.30 (m, 1H), 8.21 – 8.17 (m, 1H), 8.14 – 8.09 (m, 1H), 7.87 – 7.81 (m, 1H), 7.66 – 7.60 (m, 1H), 4.55 (q, *J* = 7.1 Hz, 2H), 1.47 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 187.9, 165.4, 150.8, 147.8, 137.6, 136.7, 130.7, 129.8, 129.1, 128.4, 118.8, 62.4, 14.3.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{10}ClNNaO_3^+$ 286.0241; Found 286.0243.

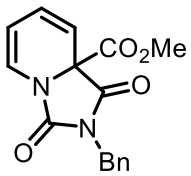
4. General procedure for the synthesis of 3



A suspension of **1** (0.1 mmol, 1.0 equiv), **2** (0.15 mmol, 1.5 equiv), PPh_3 (0.01 mmol, 0.1 equiv) in toluene (1.0 mL) was stirred in a dry sealed tube under argon at 120 ℃ for 36 h. After completion of the reaction (monitored by TLC), the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel eluting with petroleum ether/ethyl acetate = 8/1 to afford the products **3**.

5. Characterization data of 3

methyl 2-benzyl-1,3-dioxo-2,3-dihydroimidazo[1,5-a]pyridine-8a(1H)-carboxylate (3a)



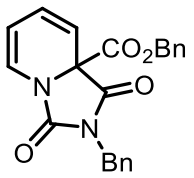
120 ℃, 36 h, 26.2 mg, 88% yield, yellow solid, m.p = 46 – 48 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.28 (m, 5H), 6.88 (d, *J* = 7.3 Hz, 1H), 6.21 – 6.17 (m, 1H), 6.01 (d, *J* = 9.3 Hz, 1H), 5.63 (t, *J* = 6.6 Hz, 1H), 4.74 – 4.66 (m, 2H), 3.75 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.5, 166.9, 154.2, 135.1, 128.9, 128.5, 128.3, 125.0, 122.4, 115.8, 109.8, 67.3, 54.1, 43.1.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{14}N_2NaO_4^+$ 321.0846; Found 321.0835.

benzyl 2-benzyl-1,3-dioxo-2,3-dihydroimidazo[1,5-a]pyridine-8a(1H)-carboxylate (3b)



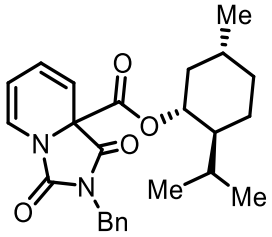
120 ℃, 36 h, 30.8 mg, 82% yield, white solid, m.p = 53 – 55 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.20 (m, 10H), 6.87 (d, *J* = 7.2 Hz, 1H), 6.18 (dd, *J* = 9.4, 5.6 Hz, 1H), 6.02 (d, *J* = 9.3 Hz, 1H), 5.62 (t, *J* = 6.5 Hz, 1H), 5.15 (s, 2H), 4.68 (s, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.3, 166.3, 154.1, 135.0, 134.6, 128.8, 128.7, 128.6, 128.4, 128.2, 127.9, 125.0, 122.3, 115.8, 109.9, 68.7, 67.4, 43.0.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{18}N_2NaO_4^+$ 397.1159; Found 397.1167.

(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 2-benzyl-1,3-dioxo-2,3-dihydroimidazo[1,5-a]pyridine-8a(1H)-carboxylate (3c)



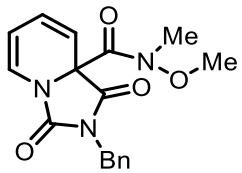
120 ℃, 36 h, 31.6 mg, 75% yield, 1/1 *d.r.*, colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.27 (m, 5H), 6.87 (t, *J* = 7.1 Hz, 1H), 6.23 – 6.13 (m, 1H), 6.05 – 5.97 (m, 1H), 5.68 – 5.57 (m, 1H), 4.74 – 4.57 (m, 3H), 1.85 – 1.62 (m, 3H), 1.48 – 1.24 (m, 2H), 1.06 – 0.90 (m, 2H), 0.89 – 0.69 (m, 8H), 0.68 – 0.59 (m, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.6, 167.5, 166.0, 165.9, 154.2, 154.1, 135.3, 135.2, 128.9, 128.6, 128.5, 128.22, 128.21, 124.8, 124.6, 122.3, 121.9, 116.14, 116.10, 109.8, 109.7, 78.0, 77.9, 67.5, 67.3, 46.9, 46.8, 42.9, 42.8, 40.2, 40.0, 34.1, 31.5, 31.4, 26.3, 26.2, 23.4, 23.3, 22.0, 20.7, 16.2, 16.1.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{30}N_2NaO_4^+$ 445.2098; Found 445.2097.

2-benzyl-*N*-methoxy-*N*-methyl-1,3-dioxo-2,3-dihydroimidazo[1,5-a]pyridine-8a(1H)-carboxamide (3d)



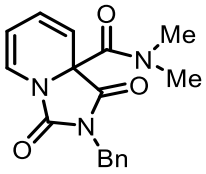
130 ℃, 36 h, 26.5 mg, 81% yield, colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.39 (m, 2H), 7.36 – 7.27 (m, 3H), 6.84 (d, *J* = 7.1 Hz, 1H), 6.21 (dd, *J* = 9.3, 5.5 Hz, 1H), 5.97 – 5.92 (m, 1H), 5.73 – 5.66 (m, 1H), 4.74 – 4.62 (m, 2H), 3.39 (s, 3H), 3.15 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.2, 165.6, 154.9, 135.3, 129.1, 128.8, 128.3, 124.3, 122.4, 117.5, 111.6, 67.6, 61.1, 43.0, 33.8.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{17}N_3NaO_4^+$ 350.1111; Found 350.1105.

2-benzyl-*N*,*N*-dimethyl-1,3-dioxo-2,3-dihydroimidazo[1,5-a]pyridine-8a(1H)-carboxamide (3e)



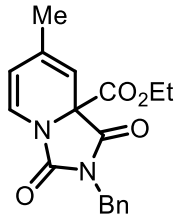
130 ℃, 36 h, 22.7 mg, 73% yield, colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.26 (m, 5H), 7.03 (d, *J* = 7.1 Hz, 1H), 6.16 – 6.10 (m, 1H), 6.04 – 5.98 (m, 1H), 5.59 (t, *J* = 6.3 Hz, 1H), 4.67 (s, 2H), 3.30 (s, 3H), 2.94 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.7, 164.1, 153.2, 135.2, 128.9, 128.5, 128.2, 125.0, 123.4, 113.8, 108.6, 69.4, 42.9, 38.3, 37.8.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{17}N_3NaO_3^+$ 334.1162; Found 334.1161.

ethyl 2-benzyl-7-methyl-1,3-dioxo-2,3-dihydroimidazo[1,5-a]pyridine-8a(1H)-carboxylate (3f)



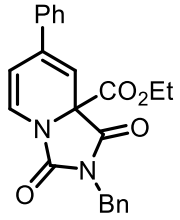
120 ℃, 36 h, 28.5 mg, 87% yield, yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.27 (m, 5H), 6.83 (d, *J* = 7.3 Hz, 1H), 5.72 (s, 1H), 5.48 (d, *J* = 7.3 Hz, 1H), 4.75 – 4.63 (m, 2H), 4.20 – 4.14 (m, 2H), 1.86 (s, 3H), 1.18 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.9, 166.7, 154.2, 135.3, 133.9, 128.8, 128.5, 128.2, 121.6, 113.6, 111.1, 67.8, 63.3, 42.9, 20.7, 14.0.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{18}N_2NaO_4^+$ 349.1159; Found 349.1154.

ethyl 2-benzyl-1,3-dioxo-7-phenyl-2,3-dihydroimidazo[1,5-a]pyridine-8a(1H)-carboxylate (3g)



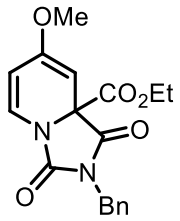
120 ℃, 36 h, 34.5 mg, 89% yield, yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.27 (m, 10H), 7.04 (dd, *J* = 7.4, 1.1 Hz, 1H), 6.20 (t, *J* = 1.4 Hz, 1H), 5.99 (dd, *J* = 7.4, 1.5 Hz, 1H), 4.78 – 4.70 (m, 2H), 4.28 – 4.17 (m, 2H), 1.22 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.6, 166.5, 154.0, 137.6, 137.1, 135.2, 128.9, 128.8, 128.5, 128.2, 126.3, 122.8, 111.4, 111.2, 67.9, 63.5, 43.0, 14.0.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{20}N_2NaO_4^+$ 411.1315; Found 411.1315.

ethyl 2-benzyl-7-methoxy-1,3-dioxo-2,3-dihydroimidazo[1,5-a]pyridine-8a(1H)-carboxylate (3h)



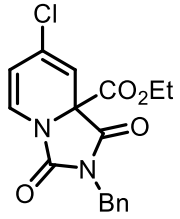
120 ℃, 36 h, 29.3 mg, 86% yield, yellow solid, m.p = 96 – 98 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.27 (m, 5H), 6.86 (d, *J* = 7.5 Hz, 1H), 5.48 (dd, *J* = 7.6, 2.1 Hz, 1H), 5.00 (d, *J* = 2.1 Hz, 1H), 4.70 (s, 2H), 4.24 – 4.11 (m, 2H), 3.63 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.4, 167.2, 154.7, 154.0, 135.2, 128.8, 128.5, 128.2, 123.7, 109.3, 85.6, 68.1, 63.3, 55.4, 43.0, 14.0.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{18}N_2NaO_5^+$ 365.1108; Found 365.1114.

ethyl 2-benzyl-7-chloro-1,3-dioxo-2,3-dihydroimidazo[1,5-a]pyridine-8a(1H)-carboxylate (3i)



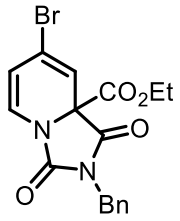
120 ℃, 36 h, 29.1 mg, 84% yield, yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.27 (m, 5H), 6.95 – 6.90 (m, 1H), 6.04 (s, 1H), 5.61 – 5.54 (m, 1H), 4.70 (s, 2H), 4.21 (q, *J* = 7.5 Hz, 2H), 1.20 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.5, 165.7, 153.7, 134.9, 130.9, 128.9, 128.6, 128.4, 123.8, 111.8, 111.7, 68.3, 63.9, 43.2, 14.0.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{15}ClN_2NaO_4^+$ 369.0613; Found 369.0599.

ethyl 2-benzyl-7-bromo-1,3-dioxo-2,3-dihydroimidazo[1,5-a]pyridine-8a(1H)-carboxylate (3j)



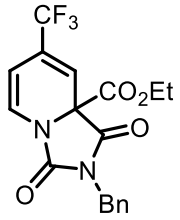
120 ℃, 36 h, 32.4 mg, 83% yield, yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.28 (m, 5H), 6.86 (d, *J* = 7.4 Hz, 1H), 6.24 (s, 1H), 5.68 (dd, *J* = 7.4, 1.6 Hz, 1H), 4.70 (s, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 1.20 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.2, 165.5, 153.7, 134.8, 128.9, 128.5, 128.4, 123.4, 118.6, 115.2, 113.6, 68.8, 63.8, 43.2, 14.0.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{15}BrN_2NaO_4^+$ 413.0107; Found 413.0105.

ethyl 2-benzyl-1,3-dioxo-7-(trifluoromethyl)-2,3-dihydroimidazo[1,5-a]pyridine-8a(1H)-carboxylate (3k)



120 ℃, 36 h, 30.7 mg, 81% yield, colorless oil.

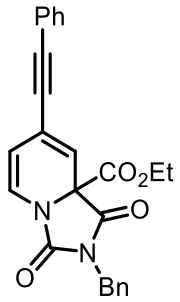
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.27 (m, 5H), 7.06 (d, *J* = 7.4 Hz, 1H), 6.47 (s, 1H), 5.73 (d, *J* = 7.4 Hz, 1H), 4.72 (s, 2H), 4.29 – 4.16 (m, 2H), 1.20 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.2, 165.2, 153.5, 134.8, 129.0, 128.8 (q, *J* = 33.7 Hz), 128.6, 128.5, 124.7, 122.1 (q, *J* = 273.6 Hz), 116.1 (q, *J* = 5.8 Hz), 104.7 (q, *J* = 2.4 Hz), 66.8, 64.1, 43.3, 13.9.

^{19}F NMR (377 MHz, Chloroform-*d*) δ -67.9.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{15}F_3N_2NaO_4^+$ 403.0876; Found 403.0879.

ethyl 2-benzyl-1,3-dioxo-7-(phenylethynyl)-2,3-dihydroimidazo[1,5-a]pyridine-8a(1H)-carboxylate (3l)



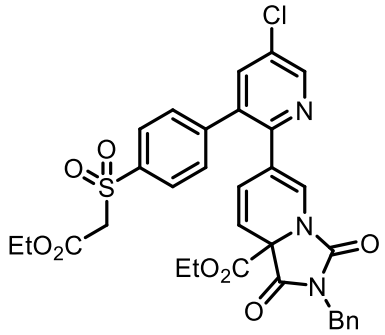
120 ℃, 36 h, 35.2 mg, 85% yield, yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.42 (m, 2H), 7.39 – 7.27 (m, 8H), 6.95 (dd, *J* = 7.3, 1.2 Hz, 1H), 6.30 (t, *J* = 1.3 Hz, 1H), 5.71 (dd, *J* = 7.3, 1.3 Hz, 1H), 4.75 – 4.68 (m, 2H), 4.22 (q, *J* = 7.1 Hz, 2H), 1.22 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.8, 165.9, 153.8, 135.0, 131.9, 129.1, 128.9, 128.6, 128.5, 128.3, 122.4, 122.3, 120.7, 118.9, 111.9, 91.6, 86.3, 67.7, 63.8, 43.1, 14.0.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{20}N_2NaO_4^+$ 435.1315; Found 435.1314.

ethyl 2-benzyl-6-(5-chloro-3-(4-((2-ethoxy-2-oxoethyl)sulfinyl)phenyl)pyridin-2-yl)-1,3-dioxo-2,3-dihydroimidazo[1,5-a]pyridine-8a(1H)-carboxylate (3m)



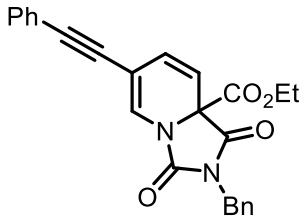
130 ℃, 36 h, 48.9 mg, 81% yield, colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.58 (d, *J* = 2.2 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 2.3 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.36 – 7.27 (m, 5H), 6.98 (s, 1H), 6.23 (d, *J* = 9.5 Hz, 1H), 5.90 (d, *J* = 9.4 Hz, 1H), 4.66 (s, 2H), 4.27 – 4.12 (m, 6H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.16 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.9, 166.1, 162.3, 153.6, 150.8, 148.1, 144.2, 138.5, 137.7, 134.8, 134.6, 130.8, 130.0, 129.3, 128.8, 128.4, 128.3, 126.8, 124.7, 121.0, 114.8, 66.8, 63.8, 62.6, 61.0, 43.0, 14.1, 14.0.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{28}ClN_3NaO_8S^+$ 672.1178; Found 672.1171.

ethyl 2-benzyl-1,3-dioxo-6-(phenylethynyl)-2,3-dihydroimidazo[1,5-a]pyridine-8a(1H)-carboxylate (3n)



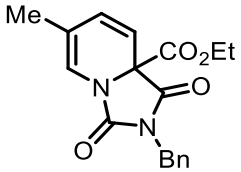
130 ℃, 3 days, 35.6 mg, 86% yield, white solid, m.p = 98 – 100 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.40 (m, 2H), 7.39 – 7.28 (m, 8H), 7.25 (s, 1H), 6.29 (d, *J* = 9.4 Hz, 1H), 6.10 (d, *J* = 9.4 Hz, 1H), 4.73 (s, 2H), 4.27 – 4.13 (m, 2H), 1.21 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.9, 165.9, 153.4, 135.0, 131.6, 128.9, 128.6, 128.50, 128.48, 128.3, 127.3, 125.9, 122.8, 115.7, 106.3, 90.7, 85.5, 66.8, 63.8, 43.2, 13.9.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{20}N_2NaO_4^+$ 435.1315; Found 435.1316.

ethyl 2-benzyl-6-methyl-1,3-dioxo-2,3-dihydroimidazo[1,5-a]pyridine-8a(1H)-carboxylate (3o)



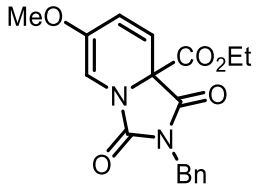
130 ℃, 3 days, 28.6 mg, 88% yield, yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.26 (m, 5H), 6.64 – 6.60 (m, 1H), 6.07 (d, *J* = 9.3 Hz, 1H), 6.01 (d, *J* = 9.4 Hz, 1H), 4.69 (s, 2H), 4.24 – 4.12 (m, 2H), 1.82 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.7, 166.6, 154.4, 135.3, 129.0, 128.8, 128.4, 128.1, 119.5, 117.6, 116.3, 67.3, 63.4, 42.9, 17.6, 13.9.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{18}N_2NaO_4^+$ 349.1159; Found 349.1153.

ethyl 2-benzyl-6-methoxy-1,3-dioxo-2,3-dihydroimidazo[1,5-a]pyridine-8a(1H)-carboxylate (3p)



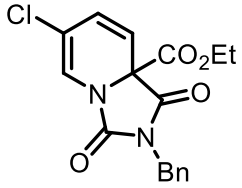
130 ℃, 3 days, 28.6 mg, 84% yield, colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.26 (m, 5H), 6.19 (s, 1H), 6.11 (d, *J* = 1.3 Hz, 2H), 4.70 (s, 2H), 4.26 – 4.13 (m, 2H), 3.60 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.2, 166.1, 155.1, 147.6, 135.3, 128.8, 128.4, 128.2, 125.0, 119.4, 97.6, 67.7, 63.5, 55.5, 43.0, 14.0.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{18}N_2NaO_5^+$ 365.1108; Found 365.1113.

ethyl 2-benzyl-6-chloro-1,3-dioxo-2,3-dihydroimidazo[1,5-a]pyridine-8a(1H)-carboxylate (3q)



130 ℃, 7 days, 27.7 mg, 80% yield, white solid, m.p = 81 – 83 ℃.

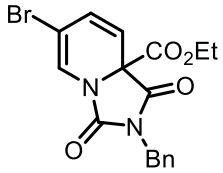
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.26 (m, 5H), 6.97 (t, *J* = 1.1 Hz, 1H), 6.16 (dd, *J* = 9.6, 1.3 Hz, 1H), 6.07 (dd, *J* = 9.6, 1.1 Hz, 1H), 4.70 (s, 2H), 4.27 – 4.14 (m, 2H), 1.20 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.7, 165.7, 153.7, 134.9, 128.9, 128.5, 128.4, 127.5, 119.4, 117.9, 117.5, 66.8, 63.9, 43.2, 13.9.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{15}ClN_2NaO_4^+$ 369.0613; Found 369.0612.

ethyl 2-benzyl-6-bromo-1,3-dioxo-2,3-dihydroimidazo[1,5-a]pyridine-8a(1H)-

carboxylate (3r)



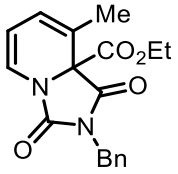
130 ℃, 7 days, 29.6 mg, 76% yield, yellow solid, m.p = 99 – 101 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.27 (m, 5H), 7.10 (s, 1H), 6.23 (d, *J* = 9.6 Hz, 1H), 6.01 (d, *J* = 9.6 Hz, 1H), 4.70 (s, 2H), 4.27 – 4.15 (m, 2H), 1.21 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.8, 165.8, 153.5, 134.9, 129.0, 128.9, 128.5, 128.4, 121.9, 117.5, 104.5, 66.6, 63.9, 43.2, 14.0.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{15}BrN_2NaO_4^+$ 413.0107; Found 413.0119.

ethyl 2-benzyl-8-methyl-1,3-dioxo-2,3-dihydroimidazo[1,5-a]pyridine-8a(1H)-carboxylate (3s)



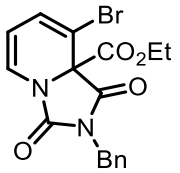
130 ℃, 3 days, 20.1 mg, 62% yield, yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.27 (m, 5H), 6.76 (d, *J* = 7.1 Hz, 1H), 5.93 – 5.88 (m, 1H), 5.60 – 5.52 (m, 1H), 4.77 – 4.65 (m, 2H), 4.22 – 4.11 (m, 2H), 2.15 (s, 3H), 1.16 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.7, 166.2, 153.7, 135.3, 128.8, 128.5, 128.2, 126.7, 121.6, 119.8, 110.4, 69.1, 63.3, 42.9, 18.8, 13.9.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{18}N_2NaO_4^+$ 349.1159; Found 349.1155.

ethyl 2-benzyl-8-bromo-1,3-dioxo-2,3-dihydroimidazo[1,5-a]pyridine-8a(1H)-carboxylate (3t)



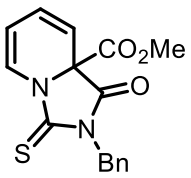
130 ℃, 3 days, 28.5 mg, 73% yield, yellow solid, m.p = 66 – 68 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.36 (m, 2H), 7.36 – 7.27 (m, 3H), 6.91 (d, *J* = 7.0 Hz, 1H), 6.60 (d, *J* = 6.1 Hz, 1H), 5.59 – 5.52 (m, 1H), 4.73 (s, 2H), 4.27 – 4.11 (m, 2H), 1.16 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.0, 164.6, 153.3, 134.9, 128.9, 128.7, 128.6, 128.3, 121.3, 110.2, 107.3, 67.9, 63.9, 43.3, 13.9.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{15}BrN_2NaO_4^+$ 413.0107; Found 413.0115.

methyl 2-benzyl-1-oxo-3-thioxo-2,3-dihydroimidazo[1,5-a]pyridine-8a(1H)-carboxylate (3u)



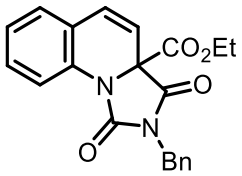
130 ℃, 5 days, 23.4 mg, 75% yield, yellow solid, m.p = 56 – 58 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.37 (m, 2H), 7.35 – 7.27 (m, 4H), 6.27 – 6.23 (m, 1H), 6.15 – 6.08 (m, 1H), 5.80 – 5.72 (m, 1H), 5.11 (d, *J* = 14.7 Hz, 1H), 5.02 (d, *J* = 14.7 Hz, 1H), 3.75 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 180.9, 168.1, 165.7, 135.1, 128.7, 128.5, 128.1, 125.4, 124.5, 117.2, 111.6, 69.1, 54.3, 45.1.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{14}N_2NaO_3S^+$ 337.0617; Found 337.0614.

ethyl 2-benzyl-1,3-dioxo-2,3-dihydroimidazo[1,5-a]quinoline-3a(1H)-carboxylate (3v)



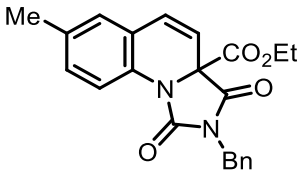
120 ℃, 12 h, 34.5 mg, 95% yield, white solid, m.p = 98 – 100 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 8.0 Hz, 1H), 7.44 – 7.27 (m, 6H), 7.21 – 7.13 (m, 2H), 6.68 (d, *J* = 9.5 Hz, 1H), 6.27 (d, *J* = 9.5 Hz, 1H), 4.76 (s, 2H), 4.21 – 4.09 (m, 2H), 1.17 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.0, 165.8, 154.4, 135.3, 131.9, 129.7, 128.9, 128.6, 128.24, 128.18, 127.9, 125.6, 125.0, 121.9, 119.9, 68.3, 63.5, 43.3, 14.0.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{18}N_2NaO_4^+$ 385.1159; Found 385.1150.

ethyl 2-benzyl-7-methyl-1,3-dioxo-2,3-dihydroimidazo[1,5-a]quinoline-3a(1H)-carboxylate (3w)



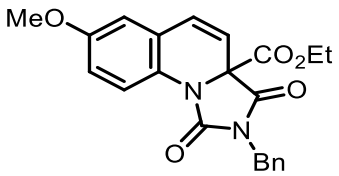
120 ℃, 12 h, 35.5 mg, 94% yield, yellow solid, m.p = 92 – 94 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.1 Hz, 1H), 7.43 – 7.37 (m, 2H), 7.35 – 7.27 (m, 3H), 7.17 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.00 (d, *J* = 1.9 Hz, 1H), 6.64 (d, *J* = 9.6 Hz, 1H), 6.25 (d, *J* = 9.5 Hz, 1H), 4.76 (s, 2H), 4.21 – 4.10 (m, 2H), 2.32 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.1, 165.9, 154.4, 135.34, 135.32, 130.2, 129.4, 128.8, 128.5, 128.32, 128.25, 128.2, 124.9, 121.7, 119.8, 68.3, 63.4, 43.2, 21.0, 13.9.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{20}N_2NaO_4^+$ 399.1315; Found 399.1316.

ethyl 2-benzyl-7-methoxy-1,3-dioxo-2,3-dihydroimidazo[1,5-a]quinoline-3a(1H)-carboxylate (3x)



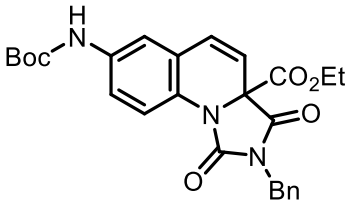
120 ℃, 12 h, 35.5 mg, 91% yield, white solid, m.p = 119 – 121 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.8 Hz, 1H), 7.41 – 7.37 (m, 2H), 7.35 – 7.27 (m, 3H), 6.89 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.72 (d, *J* = 2.8 Hz, 1H), 6.64 (d, *J* = 9.5 Hz, 1H), 6.28 (d, *J* = 9.5 Hz, 1H), 4.75 (s, 2H), 4.21 – 4.10 (m, 2H), 3.79 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 166.6, 165.6, 156.8, 154.0, 135.7, 128.7, 127.79, 127.75, 127.2, 126.0, 124.3, 122.5, 120.6, 114.8, 112.9, 67.8, 63.2, 55.4, 42.2, 13.7.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{20}N_2NaO_5^+$ 415.1264; Found 415.1265.

ethyl 2-benzyl-7-((tert-butoxycarbonyl)amino)-1,3-dioxo-2,3-dihydroimidazo[1,5-a]quinoline-3a(1H)-carboxylate (3y)



120 ℃, 12 h, 43.5 mg, 91% yield, yellow solid, m.p = 162 – 164 ℃.

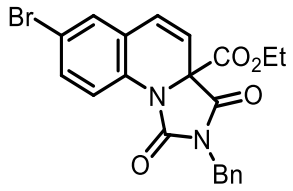
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.6 Hz, 1H), 7.47 (s, 1H), 7.42 – 7.37 (m, 2H), 7.35 – 7.27 (m, 3H), 7.13 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.64 (d, *J* = 9.6 Hz, 1H), 6.59 (s, 1H), 6.27 (d, *J* = 9.5 Hz, 1H), 4.75 (s, 2H), 4.20 – 4.09 (m, 2H), 1.50 (s, 9H), 1.17 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.9, 165.8, 154.4, 152.8, 136.0, 135.3, 128.8, 128.5, 128.19, 128.17, 127.0, 125.7, 122.4, 120.5, 119.4, 117.8, 80.9, 68.3, 63.5, 43.2, 28.4, 13.9.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{27}N_3NaO_6^+$ 500.1792; Found 500.1792.

ethyl 2-benzyl-7-bromo-1,3-dioxo-2,3-dihydroimidazo[1,5-a]quinoline-3a(1H)-

carboxylate (3z)



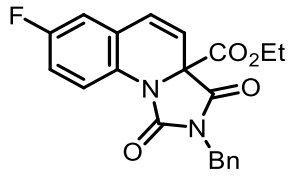
120 ℃, 12 h, 41.5 mg, 94% yield, yellow solid, m.p = 111 – 113 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 8.6 Hz, 1H), 7.46 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.40 – 7.36 (m, 2H), 7.36 – 7.27 (m, 4H), 6.61 (d, *J* = 9.5 Hz, 1H), 6.31 (d, *J* = 9.5 Hz, 1H), 4.75 (s, 2H), 4.22 – 4.11 (m, 2H), 1.18 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.6, 165.4, 154.1, 135.1, 132.4, 130.8, 130.4, 128.9, 128.5, 128.3, 127.0, 126.7, 123.4, 121.2, 118.5, 68.1, 63.7, 43.3, 13.9.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{17}BrN_2NaO_4^+$ 463.0264; Found 463.0268.

ethyl 2-benzyl-7-fluoro-1,3-dioxo-2,3-dihydroimidazo[1,5-a]quinoline-3a(1H)-carboxylate (3aa)



120 ℃, 12 h, 36.5 mg, 96% yield, yellow solid, m.p = 101 – 103 ℃.

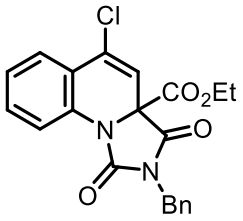
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (dd, *J* = 8.9, 4.9 Hz, 1H), 7.43 – 7.37 (m, 2H), 7.36 – 7.27 (m, 3H), 7.05 (td, *J* = 8.6, 2.9 Hz, 1H), 6.91 (dd, *J* = 8.4, 2.9 Hz, 1H), 6.63 (d, *J* = 9.5 Hz, 1H), 6.33 (d, *J* = 9.6 Hz, 1H), 4.76 (s, 2H), 4.23 – 4.12 (m, 2H), 1.19 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.7, 165.5, 160.1 (d, *J* = 245.7 Hz), 154.4, 135.2, 128.9, 128.5, 128.3, 127.8 (d, *J* = 2.8 Hz), 127.4 (d, *J* = 2.2 Hz), 126.6 (d, *J* = 8.6 Hz), 123.5 (d, *J* = 8.4 Hz), 121.5, 116.2 (d, *J* = 23.1 Hz), 114.3 (d, *J* = 23.8 Hz), 68.3, 63.6, 43.3, 13.9.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -116.4.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{17}FN_2NaO_4^+$ 403.1065; Found 403.1060.

ethyl 2-benzyl-5-chloro-1,3-dioxo-2,3-dihydroimidazo[1,5-a]quinoline-3a(1H)-carboxylate (3ab)



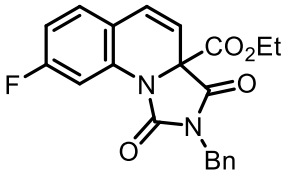
120 ℃, 12 h, 37.5 mg, 95% yield, yellow solid, m.p = 86 – 88 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.68 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.48 – 7.38 (m, 3H), 7.37 – 7.29 (m, 3H), 7.28 – 7.23 (m, 1H), 6.44 (s, 1H), 4.77 (s, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 1.19 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.1, 165.1, 153.9, 135.0, 132.3, 132.0, 130.9, 128.9, 128.6, 128.3, 126.0, 125.7, 123.6, 121.9, 117.3, 68.6, 63.8, 43.4, 13.9.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{17}ClN_2NaO_4^+$ 419.0769; Found 419.0762.

ethyl 2-benzyl-8-fluoro-1,3-dioxo-2,3-dihydroimidazo[1,5-a]quinoline-3a(1H)-carboxylate (3ac)



120 ℃, 12 h, 32.7 mg, 86% yield, yellow solid, m.p = 140 – 142 ℃.

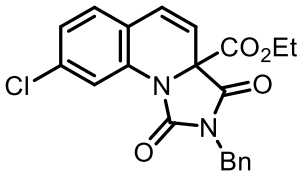
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (dd, *J* = 9.7, 2.6 Hz, 1H), 7.42 – 7.37 (m, 2H), 7.37 – 7.27 (m, 3H), 7.15 (dd, *J* = 8.5, 5.9 Hz, 1H), 6.86 (td, *J* = 8.4, 2.6 Hz, 1H), 6.65 (d, *J* = 9.6 Hz, 1H), 6.22 (d, *J* = 9.5 Hz, 1H), 4.76 (s, 2H), 4.22 – 4.13 (m, 2H), 1.18 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.6, 165.6, 163.0 (d, *J* = 250.2 Hz), 154.1, 135.1, 133.2 (d, *J* = 11.7 Hz), 129.1 (d, *J* = 9.6 Hz), 128.9, 128.6, 128.3, 127.3 (d, *J* = 1.4 Hz), 121.1 (d, *J* = 3.3 Hz), 118.6 (d, *J* = 2.6 Hz), 112.6 (d, *J* = 22.3 Hz), 109.7 (d, *J* = 26.9 Hz), 68.0, 63.6, 43.3, 13.9.

^{19}F NMR (377 MHz, Chloroform-*d*) δ -108.94.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{17}FN_2NaO_4^+$ 403.1065; Found 403.1063.

ethyl 2-benzyl-8-chloro-1,3-dioxo-2,3-dihydroimidazo[1,5-a]quinoline-3a(1H)-carboxylate (3ad)



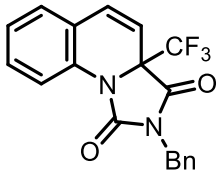
120 ℃, 12 h, 36.7 mg, 93% yield, yellow solid, m.p = 135 – 137 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (s, 1H), 7.44 – 7.27 (m, 5H), 7.18 – 7.04 (m, 2H), 6.65 (d, *J* = 9.5 Hz, 1H), 6.27 (d, *J* = 9.5 Hz, 1H), 4.76 (s, 2H), 4.23 – 4.11 (m, 2H), 1.18 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.6, 165.5, 154.1, 135.2, 135.1, 132.7, 128.9, 128.7, 128.6, 128.3, 127.3, 125.7, 123.3, 122.0, 119.9, 68.1, 63.7, 43.3, 13.9.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{17}ClN_2NaO_4^+$ 419.0769; Found 419.0768.

2-benzyl-3a-(trifluoromethyl)imidazo[1,5-a]quinoline-1,3(2H,3aH)-dione (3ae)



130 ℃, 7 days, 17.2 mg, 48% yield, yellow solid, m.p = 91 – 93 ℃.

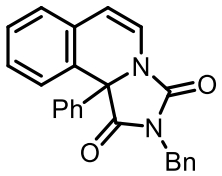
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 – 7.75 (m, 1H), 7.44 – 7.28 (m, 6H), 7.24 – 7.16 (m, 2H), 6.87 (d, *J* = 9.6 Hz, 1H), 6.06 (d, *J* = 9.6 Hz, 1H), 4.83 – 4.71 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.7, 154.8, 134.8, 132.4, 132.2, 130.3, 129.0, 128.6, 128.5, 128.3, 126.0, 124.3, 122.37, 122.35 (d, *J* = 290.3 Hz), 114.8, 65.7 (d, *J* = 30.9 Hz), 43.5.

^{19}F NMR (376 MHz, Chloroform-d) δ -79.1.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{13}F_3N_2NaO_2^+$ 381.0821; Found 381.0823.

2-benzyl-10b-phenylimidazo[5,1-a]isoquinoline-1,3(2H,10bH)-dione (3af)



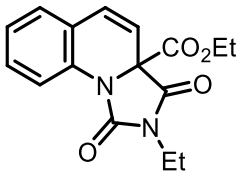
130 ℃, 7 days, 22.5 mg, 61% yield, yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21 (d, *J* = 7.6 Hz, 1H), 7.42 – 7.23 (m, 10H), 7.22 – 7.17 (m, 2H), 7.15 (d, *J* = 7.4 Hz, 1H), 6.99 (d, *J* = 7.3 Hz, 1H), 6.10 (d, *J* = 7.3 Hz, 1H), 4.76 (d, *J* = 14.5 Hz, 1H), 4.71 (d, *J* = 15.4 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.4, 153.3, 137.6, 135.6, 130.7, 128.92, 128.86, 128.81, 128.77, 128.6, 128.2, 127.8, 126.6, 125.8, 125.0, 120.8, 114.2, 66.4, 42.9.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{18}N_2NaO_2^+$ 389.1260; Found 389.1259.

ethyl 2-ethyl-1,3-dioxo-2,3-dihydroimidazo[1,5-a]quinoline-3a(1H)-carboxylate (3ag)



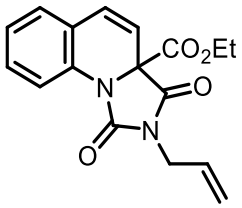
120 ℃, 12 h, 27.3 mg, 91% yield, yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 8.3 Hz, 1H), 7.39 – 7.33 (m, 1H), 7.21 – 7.12 (m, 2H), 6.68 (d, *J* = 9.5 Hz, 1H), 6.27 (d, *J* = 9.5 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.72 – 3.60 (m, 2H), 1.31 – 1.19 (m, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.0, 165.9, 154.5, 131.9, 129.7, 128.0, 127.8, 125.5, 125.0, 121.9, 120.0, 68.1, 63.4, 34.8, 14.0, 13.3.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{16}N_2NaO_4^+$ 323.1002; Found 323.1000.

ethyl 2-allyl-1,3-dioxo-2,3-dihydroimidazo[1,5-a]quinoline-3a(1H)-carboxylate (3ah)



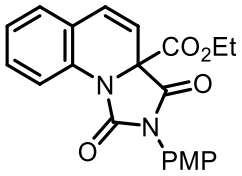
120 ℃, 12 h, 28.8 mg, 92% yield, yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 8.0 Hz, 1H), 7.37 (td, *J* = 8.0, 7.6, 2.0 Hz, 1H), 7.22 – 7.12 (m, 2H), 6.70 (d, *J* = 9.5 Hz, 1H), 6.28 (d, *J* = 9.5 Hz, 1H), 5.91 – 5.78 (m, 1H), 5.32 – 5.19 (m, 2H), 4.23 – 4.15 (m, 4H), 1.23 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.8, 165.9, 154.2, 131.8, 130.4, 129.7, 128.1, 127.8, 125.6, 125.0, 121.9, 119.9, 118.4, 68.2, 63.5, 41.6, 14.0.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{16}N_2NaO_4^+$ 335.1002; Found 335.1002.

ethyl 2-(4-methoxyphenyl)-1,3-dioxo-2,3-dihydroimidazo[1,5-a]quinoline-3a(1H)-carboxylate (3ai)



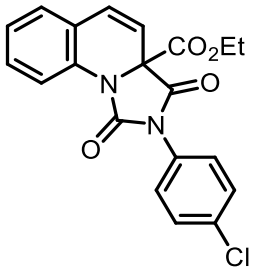
130 ℃, 36 h, 23.6 mg, 62% yield, yellow solid, m.p = 160 – 162 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 8.0 Hz, 1H), 7.41 – 7.37 (m, 1H), 7.36 – 7.30 (m, 2H), 7.25 – 7.17 (m, 2H), 7.02 – 6.95 (m, 2H), 6.76 (d, *J* = 9.5 Hz, 1H), 6.36 (d, *J* = 9.5 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.4, 165.9, 159.8, 153.8, 131.9, 129.8, 128.2, 127.9, 127.8, 125.7, 125.1, 123.7, 122.1, 120.1, 114.6, 68.1, 63.6, 55.6, 14.1.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{18}N_2NaO_5^+$ 401.1108; Found 401.1105.

ethyl 2-(4-chlorophenyl)-1,3-dioxo-2,3-dihydroimidazo[1,5-a]quinoline-3a(1H)-carboxylate (3aj)



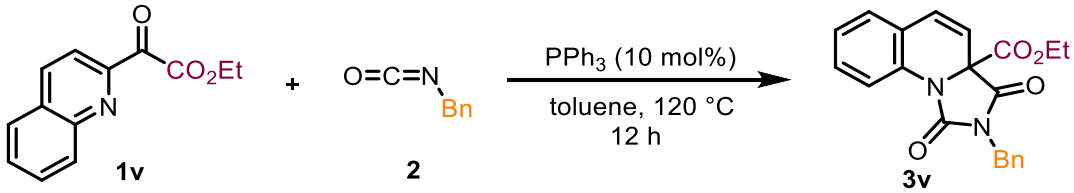
130 ℃, 36 h, 17.5 mg, 46% yield, yellow solid, m.p = 121 – 123 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 8.0 Hz, 1H), 7.50 – 7.37 (m, 5H), 7.26 – 7.16 (m, 2H), 6.77 (d, *J* = 9.4 Hz, 1H), 6.36 (d, *J* = 9.5 Hz, 1H), 4.27 – 4.21 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.0, 165.7, 153.2, 134.6, 131.7, 129.9, 129.7, 129.6, 128.4, 128.0, 127.5, 125.9, 125.1, 122.1, 119.9, 68.1, 63.8, 14.1.

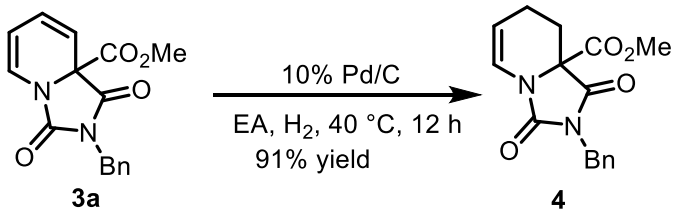
HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{15}ClN_2NaO_4^+$ 405.0613; Found 405.0609.

6. Gram-scale reaction

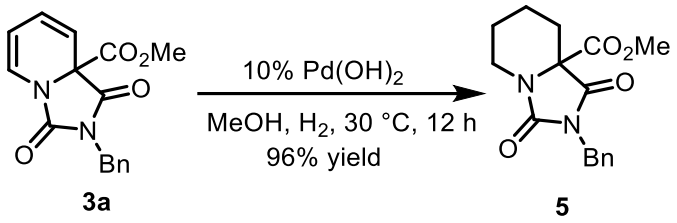


A suspension of **1v** (7.0 mmol, 1.0 equiv), **2** (10.5 mmol, 1.5 equiv), PPh_3 (0.7 mmol, 0.1 equiv) in toluene (50.0 mL) was stirred in a dry sealed tube under argon at 120 ℃ for 12 h. After completion of the reaction (monitored by TLC), the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel eluting with petroleum ether/ethyl acetate = 8/1 to afford the products **3v** in 94% yield (2.38 g) as a white solid.

7. Synthetic transformations

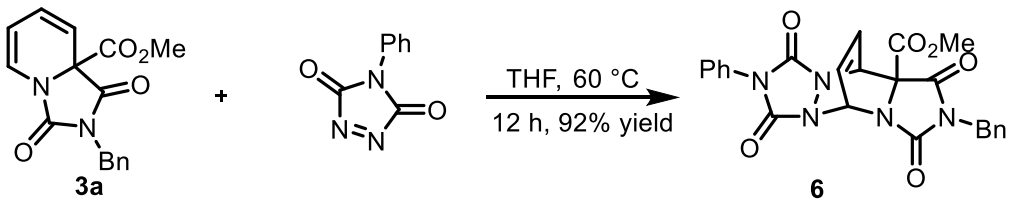


To a solution of **3a** (0.1 mmol, 1.0 equiv) in ethyl acetate was added palladium on activated charcoal (10% Pd, 3.0 mg). The reaction mixture was stirred at 40 ℃ under H_2 atmosphere for 12 h. After completion of the reaction (monitored by TLC), the reaction mixture was filtered through Celite and concentrated. The residue was purified by column chromatography on silica gel eluting with petroleum ether/ethyl acetate = 4/1 to afford the products **4** in 91% yield (27.2 mg) as a colorless oil.



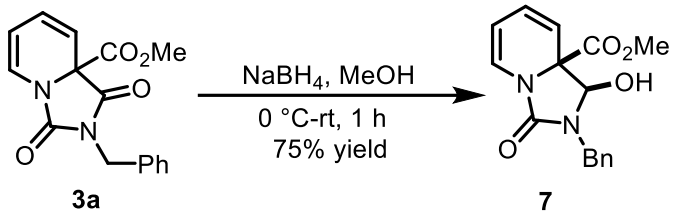
3a **5**

To a solution of **3a** (0.1 mmol, 1.0 equiv) in MeOH was added palladium hydroxide on activated charcoal (20% $Pd(OH)_2$, 3.0 mg). The reaction mixture was stirred at 30 ℃ under H_2 atmosphere for 12 h. After completion of the reaction (monitored by TLC), the reaction mixture was filtered through Celite and concentrated. The residue was purified by column chromatography on silica gel eluting with petroleum ether/ethyl acetate = 4/1 to afford the products **5** in 91% yield (27.2 mg) as a colorless oil.



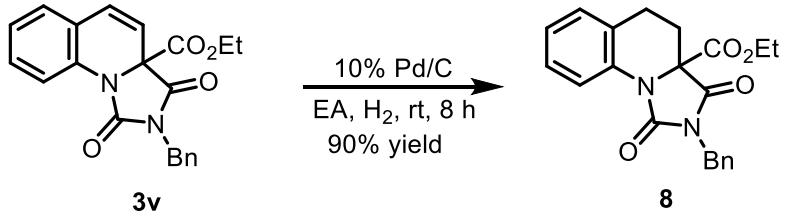
3a **6**

A suspension of **3a** (0.1 mmol, 1.0 equiv), 4-phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione (0.1 mmol, 1.0 equiv) in THF (1.0 mL) was stirred in a dry sealed tube under argon at 60 ℃ for 12 h. After completion of the reaction (monitored by TLC), the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel eluting with petroleum ether/ethyl acetate = 4/1 to afford the products **6** in 92% yield (43.5 mg) as a colorless oil.



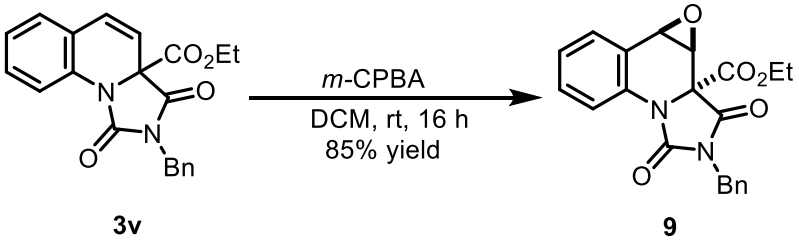
3a **7**

$NaBH_4$ (0.15 mmol, 1.5 equiv) was added to a solution of **3a** (0.1 mmol. 1.0 equiv) in MeOH (1.0 mL) at 0 ℃. The mixture was allowed to room temperature and stirred for 1 h. After completion of the reaction (monitored by TLC), the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel, eluting with petroleum ether/ethyl acetate = 2/1 to give the compound **7** in 75% yield (22.4 mg) as a white solid.



3v **8**

To a solution of **3v** (0.1 mmol, 1.0 equiv) in ethyl acetate was added palladium on activated charcoal (10% Pd, 3.6 mg). The reaction mixture was stirred at rt under H_2 atmosphere for 8 h. After completion of the reaction (monitored by TLC), the reaction mixture was filtered through Celite and concentrated. The residue was purified by column chromatography on silica gel eluting with petroleum ether/ethyl acetate = 4/1 to afford the products **8** in 90% yield (32.8 mg) as a colorless oil.

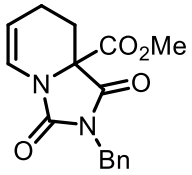


3v **9**

m-CPBA (0.15 mmol, 1.5 equiv) was added to a solution of **3v** (0.1 mmol. 1.0 equiv) in DCM (1.0 mL). The mixture was stirred at room temperature for 16 h. After

completion of the reaction (monitored by TLC), the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel, eluting with petroleum ether/ethyl acetate = 4/1 to give the compound **9** in 85% yield (32.0 mg) as a colorless oil.

methyl 2-benzyl-1,3-dioxo-2,3,7,8-tetrahydroimidazo[1,5-a]pyridine-8a(1H)-carboxylate (4)



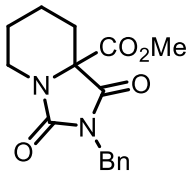
40 ℃, 12 h, 27.2 mg, 91% yield, white solid, m.p = 95 – 97 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.26 (m, 5H), 6.76 (dd, *J* = 8.1, 2.1 Hz, 1H), 5.17 – 5.11 (m, 1H), 4.69 (s, 2H), 3.75 (s, 3H), 2.86 – 2.75 (m, 1H), 2.31 – 2.15 (m, 2H), 1.69 – 1.59 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.4, 166.4, 153.0, 135.4, 128.8, 128.4, 128.2, 120.0, 109.4, 66.4, 53.9, 42.9, 25.3, 19.7.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{16}N_2NaO_4^+$ 323.1002; Found 323.1001.

methyl 2-benzyl-1,3-dioxohexahydroimidazo[1,5-a]pyridine-8a(1H)-carboxylate (5)



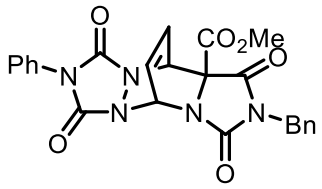
30 ℃, 12 h, 28.9 mg, 96% yield, colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.23 (m, 5H), 4.66 (s, 2H), 4.15 (dd, *J* = 13.5, 4.6 Hz, 1H), 3.79 (s, 3H), 2.87 (td, *J* = 13.1, 3.5 Hz, 1H), 2.74 – 2.64 (m, 1H), 1.93 – 1.83 (m, 1H), 1.72 – 1.64 (m, 1H), 1.54 – 1.34 (m, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.4, 166.6, 154.3, 135.9, 128.8, 128.3, 128.0, 67.4, 53.7, 42.8, 38.4, 30.3, 24.6, 20.9.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{18}N_2NaO_4^+$ 325.1159; Found 325.1151.

methyl 2-benzyl-1,3,7,9-tetraoxo-8-phenyl-2,3,8,9-tetrahydro-1H,5H,7H-5,11-ethenoimidazo[1,5-d][1,2,4]triazolo[1,2-a][1,2,4]triazine-11a(11H)-carboxylate (6)



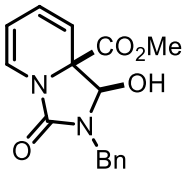
60 ℃, 12 h, 43.5 mg, 92% yield, white solid, m.p = 181 – 183 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 – 7.26 (m, 10H), 6.75 – 6.67 (m, 2H), 6.44 (dd, *J* = 4.7, 2.2 Hz, 1H), 5.79 (dd, *J* = 4.8, 2.4 Hz, 1H), 4.83 – 4.71 (m, 2H), 3.74 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.2, 164.9, 159.6, 156.3, 154.6, 134.5, 130.6, 129.4, 129.2, 129.0, 128.8, 128.38, 128.35, 128.0, 125.5, 70.9, 63.5, 54.2, 53.2, 43.8.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{19}N_5NaO_6^+$ 496.1228; Found 496.1232.

methyl (1R,8aR)-2-benzyl-1-hydroxy-3-oxo-2,3-dihydroimidazo[1,5-a]pyridine-8a(1H)-carboxylate (7)



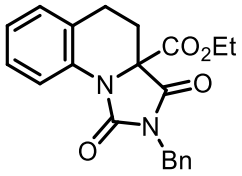
0 ℃ to rt, 1 h, 22.4 mg, 75% yield, white solid. m.p = 166 – 168 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.27 (m, 5H), 6.91 (d, *J* = 7.3 Hz, 1H), 6.17 – 6.08 (m, 1H), 5.63 (dd, *J* = 9.3, 1.1 Hz, 1H), 5.49 – 5.45 (m, 1H), 5.03 (d, *J* = 8.0 Hz, 1H), 4.75 (d, *J* = 15.1 Hz, 1H), 4.27 (d, *J* = 15.1 Hz, 1H), 3.75 (s, 1H), 3.73 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.4, 154.6, 135.8, 128.9, 128.6, 127.9, 124.9, 123.5, 115.3, 106.0, 86.4, 65.4, 53.0, 44.4.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{16}N_2NaO_4^+$ 323.1002; Found 323.0993.

ethyl 2-benzyl-1,3-dioxo-2,3,4,5-tetrahydroimidazo[1,5-a]quinoline-3a(1H)-carboxylate (8)



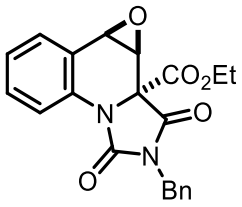
RT, 12 h, 32.8 mg, 90% yield, white solid, m.p = 123 – 125 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 (d, *J* = 8.3 Hz, 1H), 7.44 – 7.37 (m, 2H), 7.36 – 7.27 (m, 3H), 7.26 – 7.22 (m, 1H), 7.15 – 7.10 (m, 1H), 7.09 – 7.04 (m, 1H), 4.76 (s, 2H), 4.27 – 4.06 (m, 2H), 3.11 – 2.99 (m, 1H), 2.98 – 2.87 (m, 2H), 1.92 – 1.82 (m, 1H), 1.13 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.2, 165.6, 153.2, 135.5, 133.2, 129.3, 128.8, 128.5, 128.2, 127.3, 124.6, 124.5, 120.7, 67.6, 63.2, 43.0, 26.1, 23.9, 13.9.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{20}N_2NaO_4^+$ 387.1315; Found 387.1319.

ethyl (1aS,1bS,9bR)-3-benzyl-2,4-dioxo-1a,3,4,9b-tetrahydroimidazo[1,5-a]oxireno[2,3-c]quinoline-1b(2H)-carboxylate (9)



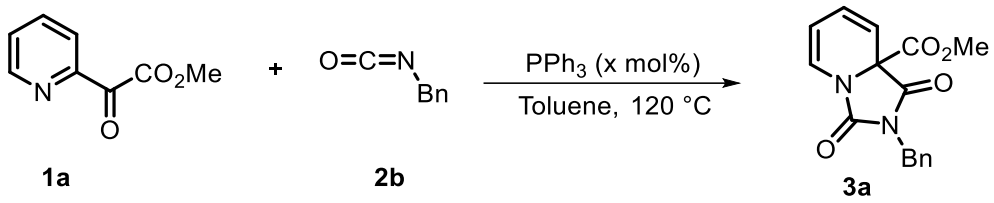
RT, 16 h, 32.0 mg, 85% yield, white solid, m.p = 106 – 108 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 8.0 Hz, 1H), 7.51 – 7.41 (m, 2H), 7.40 – 7.27 (m, 5H), 7.25 – 7.20 (m, 1H), 4.88 – 4.72 (m, 2H), 4.61 (d, *J* = 4.1 Hz, 1H), 4.26 – 4.12 (m, 2H), 4.10 (d, *J* = 4.1 Hz, 1H), 1.15 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.5, 164.2, 154.8, 135.1, 131.8, 130.41, 130.35, 128.9, 128.2, 128.0, 126.1, 123.7, 67.1, 63.6, 59.6, 51.5, 43.2, 13.9.

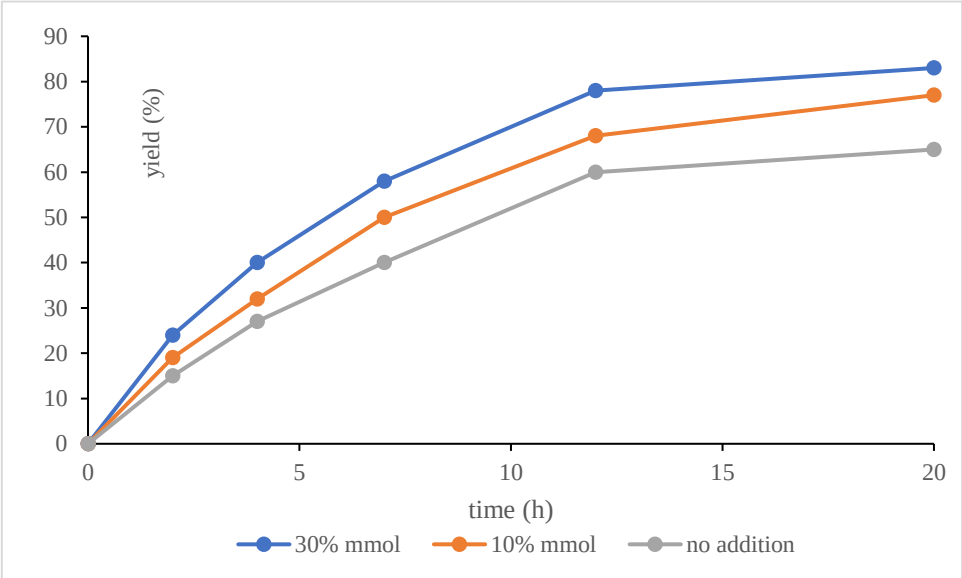
HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{18}N_2NaO_5^+$ 401.1108; Found 401.1104

8. Control experiments



1a **2b** **3a**

A suspension of **1a** (0.1 mmol, 1.0 equiv), **2b** (0.15 mmol, 1.5 equiv), PPh_3 (x mmol) in toluene (1.0 mL) was stirred in a dry sealed tube under argon at 120 ℃ for corresponding time, then the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel eluting with petroleum ether/ethyl acetate = 8/1 to afford the products **3a**.



9. References

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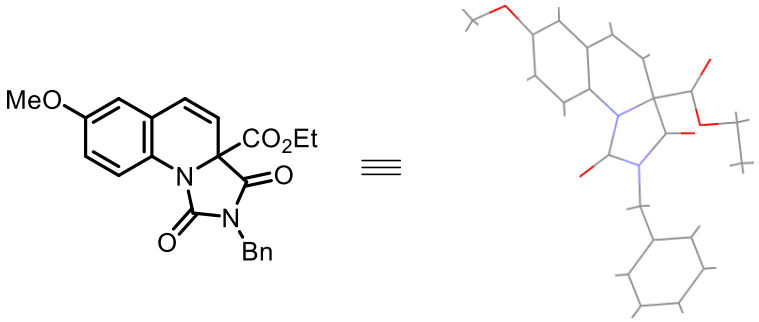
5. W. Ali, A. Behera, S. Guin, B. K. Patel, *J. Org. Chem.* **2015**, *80*, 5625-5632.

10. Crystallographic data for 3X (CCDC 2328306)



Bond precision:	C-C =0.0018 A	Wavelength=1.54178	
Cell:	a=27.3021(9)	b=8.3073(3)	c=17.6695(6)
	alpha=90	beta=103.709(1)	gamma=90
Temperature:	173 K		
	Calculated	Reported	
Volume	3893.4(2)	3893.4(2)	
Space group	C 2/c	C 2/c	
Hall group	-C 2yc	-C 2yc	
Moiety formula	C22 H20 N2 O5	C22 H20 N2 O5	
Sum formula	C22 H20 N2 O5	C22 H20 N2 O5	
Mr	392.40	392.40	
Dx,g cm-3	1.339	1.339	
Z	8	8	
Mu (mm-1)	0.793	0.793	
F000	1648.0	1648.0	
F000’	1653.40		
h,k,lmax	32,10,21	32,10,21	
Nref	3564	3528	
Tmin,Tmax	0.840,0.867	0.644,0.753	
Tmin’	0.840		

Correction method= # Reported T Limits: Tmin=0.644 Tmax=0.753

AbsCorr = MULTI-SCAN

Data completeness= 0.990		Theta(max)= 68.391
		wR2(reflections)=
R(reflections)= 0.0363(3164)		0.1397(3528)
S = 1.223	Npar= 264	

Table 1. Crystal data and structure refinement for t_a.

Identification code	t_a	
Empirical formula	C22 H20 N2 O5	
Formula weight	392.40	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 27.3021(9) Å	a= 90°.
	b = 8.3073(3) Å	b= 103.7090(10)°.
	c = 17.6695(6) Å	g = 90°.
Volume	3893.4(2) $Å^3$	
Z	8	
Density (calculated)	1.339 Mg/m^3	
Absorption coefficient	0.793 mm^{-1}	
F(000)	1648	
Crystal size	0.220 x 0.200 x 0.180 mm^3	
Theta range for data collection	5.435 to 68.391°.	
Index ranges	-32<=h<=32, -9<=k<=10, -21<=l<=21	
Reflections collected	26425	
Independent reflections	3528 [R(int) = 0.0348]	
Completeness to theta = 67.679°	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7531 and 0.6439	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3528 / 0 / 264	
Goodness-of-fit on F^2	1.223	
Final R indices [I>2sigma(I)]	R1 = 0.0363, wR2 = 0.1345	
R indices (all data)	R1 = 0.0401, wR2 = 0.1397	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.264 and -0.219 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for t_a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(2)	5694(1)	9435(1)	4658(1)	42(1)
O(1)	8244(1)	11590(1)	6330(1)	51(1)
O(3)	5708(1)	7710(1)	5646(1)	31(1)
O(4)	5764(1)	5221(1)	4166(1)	43(1)
O(5)	7071(1)	4820(1)	6323(1)	34(1)
N(1)	6710(1)	7045(1)	5606(1)	24(1)
N(2)	6379(1)	4611(1)	5273(1)	29(1)
C(1)	7097(1)	8212(1)	5835(1)	24(1)
C(2)	7380(1)	8340(2)	6596(1)	30(1)
C(3)	7768(1)	9466(2)	6787(1)	36(1)
C(4)	7867(1)	10472(2)	6212(1)	35(1)
C(5)	7577(1)	10360(1)	5452(1)	31(1)
C(6)	7195(1)	9223(1)	5250(1)	25(1)
C(7)	6916(1)	8988(2)	4443(1)	29(1)
C(8)	6512(1)	8047(2)	4262(1)	30(1)
C(9)	6313(1)	7295(1)	4899(1)	26(1)
C(10)	6109(1)	5588(2)	4708(1)	29(1)
C(11)	6758(1)	5446(1)	5802(1)	25(1)
C(12)	5869(1)	8302(1)	5051(1)	26(1)
C(13)	5263(1)	8519(2)	5796(1)	32(1)
C(14)	5136(1)	7709(2)	6484(1)	42(1)
C(15)	8613(1)	11531(3)	7051(1)	64(1)
C(16)	6298(1)	2879(2)	5334(1)	36(1)
C(17)	6080(1)	2489(1)	6024(1)	30(1)
C(18)	5627(1)	3184(2)	6087(1)	34(1)
C(19)	5422(1)	2805(2)	6712(1)	38(1)
C(20)	5664(1)	1740(2)	7276(1)	39(1)
C(21)	6117(1)	1048(2)	7218(1)	40(1)
C(22)	6323(1)	1431(2)	6595(1)	36(1)

Table 3. Bond lengths [Å] and angles [°] for t_a.

O(2)-C(12)	1.1991(15)
O(1)-C(4)	1.3639(15)
O(1)-C(15)	1.426(2)
O(3)-C(12)	1.3267(14)
O(3)-C(13)	1.4661(14)
O(4)-C(10)	1.2108(14)
O(5)-C(11)	1.2134(14)
N(1)-C(11)	1.3713(15)
N(1)-C(1)	1.4222(14)
N(1)-C(9)	1.4611(14)
N(2)-C(10)	1.3613(16)
N(2)-C(11)	1.4023(15)
N(2)-C(16)	1.4636(16)
C(1)-C(2)	1.3863(16)
C(1)-C(6)	1.4063(16)
C(2)-C(3)	1.3931(18)
C(3)-C(4)	1.392(2)
C(4)-C(5)	1.3905(19)
C(5)-C(6)	1.3893(17)
C(6)-C(7)	1.4609(16)
C(7)-C(8)	1.3275(17)
C(8)-C(9)	1.4991(16)
C(9)-C(10)	1.5319(16)
C(9)-C(12)	1.5470(15)
C(13)-C(14)	1.4999(18)
C(16)-C(17)	1.5147(17)
C(17)-C(22)	1.3835(18)
C(17)-C(18)	1.3926(17)
C(18)-C(19)	1.3879(18)
C(19)-C(20)	1.379(2)
C(20)-C(21)	1.389(2)
C(21)-C(22)	1.386(2)
C(4)-O(1)-C(15)	117.46(13)
C(12)-O(3)-C(13)	114.77(9)
C(11)-N(1)-C(1)	124.54(9)

C(11)-N(1)-C(9)	111.20(9)
C(1)-N(1)-C(9)	119.86(9)
C(10)-N(2)-C(11)	112.39(10)
C(10)-N(2)-C(16)	125.05(11)
C(11)-N(2)-C(16)	122.55(11)
C(2)-C(1)-C(6)	120.60(11)
C(2)-C(1)-N(1)	122.31(10)
C(6)-C(1)-N(1)	117.07(10)
C(1)-C(2)-C(3)	120.21(11)
C(4)-C(3)-C(2)	119.63(11)
O(1)-C(4)-C(5)	115.51(12)
O(1)-C(4)-C(3)	124.53(12)
C(5)-C(4)-C(3)	119.96(11)
C(6)-C(5)-C(4)	121.08(11)
C(5)-C(6)-C(1)	118.49(11)
C(5)-C(6)-C(7)	121.85(11)
C(1)-C(6)-C(7)	119.55(10)
C(8)-C(7)-C(6)	121.62(11)
C(7)-C(8)-C(9)	119.56(10)
N(1)-C(9)-C(8)	111.94(9)
N(1)-C(9)-C(10)	102.39(9)
C(8)-C(9)-C(10)	113.42(10)
N(1)-C(9)-C(12)	112.41(9)
C(8)-C(9)-C(12)	110.13(9)
C(10)-C(9)-C(12)	106.25(9)
O(4)-C(10)-N(2)	127.91(12)
O(4)-C(10)-C(9)	125.58(11)
N(2)-C(10)-C(9)	106.48(9)
O(5)-C(11)-N(1)	128.00(11)
O(5)-C(11)-N(2)	124.62(11)
N(1)-C(11)-N(2)	107.36(9)
O(2)-C(12)-O(3)	126.03(11)
O(2)-C(12)-C(9)	122.99(11)
O(3)-C(12)-C(9)	110.95(9)
O(3)-C(13)-C(14)	107.60(10)
N(2)-C(16)-C(17)	111.36(10)
C(22)-C(17)-C(18)	119.12(12)
C(22)-C(17)-C(16)	120.69(11)

C(18)-C(17)-C(16)	120.19(12)
C(19)-C(18)-C(17)	120.22(12)
C(20)-C(19)-C(18)	120.35(12)
C(19)-C(20)-C(21)	119.68(13)
C(22)-C(21)-C(20)	119.96(13)
C(17)-C(22)-C(21)	120.66(12)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for t_a. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(2)	35(1)	41(1)	51(1)	13(1)	16(1)	15(1)
O(1)	38(1)	47(1)	71(1)	-20(1)	16(1)	-18(1)
O(3)	25(1)	32(1)	39(1)	3(1)	13(1)	7(1)
O(4)	32(1)	44(1)	47(1)	-12(1)	0(1)	-4(1)
O(5)	34(1)	34(1)	36(1)	9(1)	10(1)	5(1)
N(1)	20(1)	25(1)	27(1)	1(1)	5(1)	1(1)
N(2)	27(1)	24(1)	37(1)	-3(1)	12(1)	-2(1)
C(1)	19(1)	24(1)	29(1)	-4(1)	9(1)	2(1)
C(2)	27(1)	35(1)	28(1)	-4(1)	9(1)	2(1)
C(3)	29(1)	43(1)	34(1)	-13(1)	6(1)	-1(1)
C(4)	27(1)	32(1)	49(1)	-15(1)	14(1)	-5(1)
C(5)	28(1)	26(1)	45(1)	-1(1)	17(1)	2(1)
C(6)	22(1)	23(1)	32(1)	0(1)	11(1)	5(1)
C(7)	26(1)	32(1)	31(1)	7(1)	13(1)	7(1)
C(8)	27(1)	35(1)	25(1)	2(1)	4(1)	6(1)
C(9)	20(1)	28(1)	27(1)	-1(1)	4(1)	2(1)
C(10)	23(1)	31(1)	35(1)	-6(1)	9(1)	0(1)
C(11)	24(1)	27(1)	28(1)	2(1)	12(1)	3(1)
C(12)	21(1)	26(1)	32(1)	-1(1)	5(1)	1(1)
C(13)	22(1)	34(1)	39(1)	-6(1)	10(1)	6(1)
C(14)	34(1)	48(1)	48(1)	1(1)	20(1)	2(1)
C(15)	41(1)	84(1)	70(1)	-43(1)	15(1)	-27(1)
C(16)	40(1)	23(1)	51(1)	-5(1)	23(1)	-2(1)
C(17)	30(1)	22(1)	41(1)	-7(1)	13(1)	-4(1)

C(18)	33(1)	29(1)	44(1)	0(1)	12(1)	0(1)
C(19)	33(1)	38(1)	47(1)	-7(1)	18(1)	0(1)
C(20)	44(1)	41(1)	36(1)	-6(1)	16(1)	-8(1)
C(21)	45(1)	36(1)	37(1)	-1(1)	3(1)	1(1)
C(22)	33(1)	30(1)	44(1)	-7(1)	9(1)	2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for t_a.

	x	y	z	U(eq)
H(2)	7309	7658	6988	35
H(3)	7964	9547	7308	43
H(5)	7640	11073	5066	38
H(7)	7027	9522	4038	35
H(8)	6351	7851	3732	35
H(13A)	4976	8433	5335	38
H(13B)	5336	9673	5909	38
H(14A)	4840	8230	6601	62
H(14B)	5422	7798	6936	62
H(14C)	5061	6570	6364	62
H(15A)	8890	12265	7030	97
H(15B)	8744	10431	7143	97
H(15C)	8459	11854	7475	97
H(16A)	6623	2308	5390	43
H(16B)	6065	2495	4850	43
H(18)	5458	3921	5702	41
H(19)	5112	3281	6752	46
H(20)	5523	1481	7703	47
H(21)	6286	313	7605	49
H(22)	6634	962	6559	43

Table 6. Torsion angles [°] for t_a.

C(11)-N(1)-C(1)-C(2)	-47.28(15)
C(9)-N(1)-C(1)-C(2)	158.39(10)
C(11)-N(1)-C(1)-C(6)	131.05(11)
C(9)-N(1)-C(1)-C(6)	-23.28(14)
C(6)-C(1)-C(2)-C(3)	-0.51(17)
N(1)-C(1)-C(2)-C(3)	177.76(10)
C(1)-C(2)-C(3)-C(4)	0.54(18)
C(15)-O(1)-C(4)-C(5)	-167.57(12)
C(15)-O(1)-C(4)-C(3)	11.66(19)
C(2)-C(3)-C(4)-O(1)	-178.54(11)
C(2)-C(3)-C(4)-C(5)	0.65(18)
O(1)-C(4)-C(5)-C(6)	177.36(11)
C(3)-C(4)-C(5)-C(6)	-1.90(18)
C(4)-C(5)-C(6)-C(1)	1.90(16)
C(4)-C(5)-C(6)-C(7)	-174.32(10)
C(2)-C(1)-C(6)-C(5)	-0.70(16)
N(1)-C(1)-C(6)-C(5)	-179.06(9)
C(2)-C(1)-C(6)-C(7)	175.61(10)
N(1)-C(1)-C(6)-C(7)	-2.75(14)
C(5)-C(6)-C(7)-C(8)	-171.57(11)
C(1)-C(6)-C(7)-C(8)	12.25(16)
C(6)-C(7)-C(8)-C(9)	4.46(17)
C(11)-N(1)-C(9)-C(8)	-119.58(10)
C(1)-N(1)-C(9)-C(8)	37.92(13)
C(11)-N(1)-C(9)-C(10)	2.23(11)
C(1)-N(1)-C(9)-C(10)	159.73(9)
C(11)-N(1)-C(9)-C(12)	115.85(10)
C(1)-N(1)-C(9)-C(12)	-86.65(12)
C(7)-C(8)-C(9)-N(1)	-28.10(15)
C(7)-C(8)-C(9)-C(10)	-143.34(11)
C(7)-C(8)-C(9)-C(12)	97.73(13)
C(11)-N(2)-C(10)-O(4)	178.88(12)
C(16)-N(2)-C(10)-O(4)	-0.35(19)
C(11)-N(2)-C(10)-C(9)	-2.93(12)
C(16)-N(2)-C(10)-C(9)	177.84(10)
N(1)-C(9)-C(10)-O(4)	178.67(11)

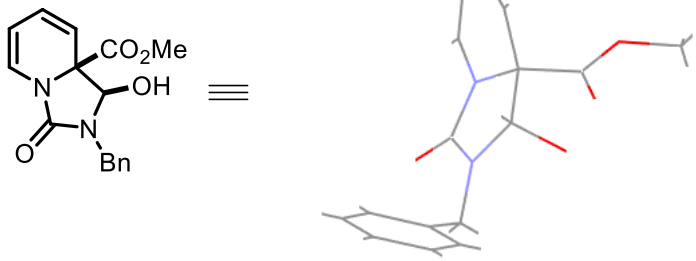
C(8)-C(9)-C(10)-O(4)	-60.54(16)
C(12)-C(9)-C(10)-O(4)	60.59(15)
N(1)-C(9)-C(10)-N(2)	0.43(12)
C(8)-C(9)-C(10)-N(2)	121.23(10)
C(12)-C(9)-C(10)-N(2)	-117.64(10)
C(1)-N(1)-C(11)-O(5)	18.65(18)
C(9)-N(1)-C(11)-O(5)	174.90(11)
C(1)-N(1)-C(11)-N(2)	-160.26(9)
C(9)-N(1)-C(11)-N(2)	-4.01(12)
C(10)-N(2)-C(11)-O(5)	-174.56(11)
C(16)-N(2)-C(11)-O(5)	4.70(17)
C(10)-N(2)-C(11)-N(1)	4.40(12)
C(16)-N(2)-C(11)-N(1)	-176.35(9)
C(13)-O(3)-C(12)-O(2)	2.30(17)
C(13)-O(3)-C(12)-C(9)	-175.77(9)
N(1)-C(9)-C(12)-O(2)	131.25(12)
C(8)-C(9)-C(12)-O(2)	5.69(16)
C(10)-C(9)-C(12)-O(2)	-117.52(13)
N(1)-C(9)-C(12)-O(3)	-50.61(12)
C(8)-C(9)-C(12)-O(3)	-176.17(9)
C(10)-C(9)-C(12)-O(3)	60.61(12)
C(12)-O(3)-C(13)-C(14)	-179.66(10)
C(10)-N(2)-C(16)-C(17)	-109.98(13)
C(11)-N(2)-C(16)-C(17)	70.87(14)
N(2)-C(16)-C(17)-C(22)	-123.09(13)
N(2)-C(16)-C(17)-C(18)	57.49(16)
C(22)-C(17)-C(18)-C(19)	-0.62(18)
C(16)-C(17)-C(18)-C(19)	178.81(11)
C(17)-C(18)-C(19)-C(20)	0.2(2)
C(18)-C(19)-C(20)-C(21)	0.1(2)
C(19)-C(20)-C(21)-C(22)	0.1(2)
C(18)-C(17)-C(22)-C(21)	0.80(19)
C(16)-C(17)-C(22)-C(21)	-178.62(12)
C(20)-C(21)-C(22)-C(17)	-0.5(2)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for t_a [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

11. Crystallographic data for 7 (CCDC 2333917)



Bond precision:	C-C =0.0025 A	Wavelength=1.54178	
Cell:	a=13.0389(3)	b=6.6376(2)	c=17.0474(4)
	alpha=90	beta=91.103(1)	gamma=90
Temperature:	173 K		
	Calculated	Reported	
Volume	1475.13(7)	1475.13(7)	
Space group	P 21/n	P 21/n	
Hall group	-P 2yn	-P 2yn	
Moiety formula	C16 H16 N2 O4	C16 H16 N2 O4	
Sum formula	C16 H16 N2 O4	C16 H16 N2 O4	
Mr	300.31	300.31	
Dx,g cm-3	1.352	1.352	
Z	4	4	
Mu (mm-1)	0.816	0.816	
F000	632.0	632.0	
F000’	634.09		
h,k,lmax	15,8,20	15,7,20	
Nref	2697	2676	
Tmin,Tmax	0.878,0.907	0.612,0.753	
Tmin’	0.878		

Correction method= # Reported T Limits: Tmin=0.612 Tmax=0.753

AbsCorr = MULTI-SCAN

Data completeness= 0.992	Theta(max)= 68.340	
R(reflections)= 0.0359(2195)	wR2(reflections)= 0.1083(2676)	
S = 1.024	Npar= 204	

Table 1. Crystal data and structure refinement for t_a.

Identification code	t_a	
Empirical formula	C16 H16 N2 O4	
Formula weight	300.31	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 13.0389(3) Å	a= 90°.
	b = 6.6376(2) Å	b= 91.1030(10)°.
	c = 17.0474(4) Å	g = 90°.
Volume	1475.13(7) $Å^3$	
Z	4	
Density (calculated)	1.352 Mg/m^3	
Absorption coefficient	0.816 mm^{-1}	
F(000)	632	
Crystal size	0.160 x 0.140 x 0.120 mm^3	
Theta range for data collection	4.230 to 68.340°.	
Index ranges	-15<=h<=15, -7<=k<=7, -19<=l<=20	
Reflections collected	14811	
Independent reflections	2676 [R(int) = 0.0561]	
Completeness to theta = 67.679°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7531 and 0.6123	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2676 / 0 / 204	
Goodness-of-fit on F^2	1.024	
Final R indices [I>2sigma(I)]	R1 = 0.0359, wR2 = 0.1010	
R indices (all data)	R1 = 0.0591, wR2 = 0.1083	
Extinction coefficient	0.0034(4)	
Largest diff. peak and hole	0.265 and -0.188 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for t_a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(2)	5258(1)	8849(2)	6035(1)	36(1)
O(3)	3881(1)	5903(2)	6968(1)	39(1)
O(4)	4443(1)	8643(2)	7623(1)	33(1)
O(1)	6181(1)	2385(1)	5849(1)	34(1)
N(1)	6136(1)	5845(2)	5793(1)	28(1)
N(2)	5852(1)	4389(2)	6927(1)	27(1)
C(1)	5883(1)	2977(2)	7528(1)	34(1)
C(2)	6145(1)	3587(2)	8249(1)	40(1)
C(3)	6503(1)	5638(2)	8366(1)	37(1)
C(4)	6357(1)	7046(2)	7819(1)	31(1)
C(5)	5710(1)	6515(2)	7102(1)	24(1)
C(6)	6019(1)	7551(2)	6319(1)	25(1)
C(7)	6063(1)	4046(2)	6154(1)	25(1)
C(8)	4559(1)	6942(2)	7222(1)	26(1)
C(9)	3396(1)	9340(3)	7704(1)	46(1)
C(10)	6266(1)	6091(2)	4952(1)	31(1)
C(11)	7236(1)	7187(2)	4754(1)	30(1)
C(12)	7186(2)	9165(2)	4495(1)	42(1)
C(13)	8066(2)	10175(3)	4289(1)	64(1)
C(14)	8995(2)	9243(5)	4343(1)	76(1)
C(15)	9063(2)	7303(5)	4605(1)	72(1)
C(16)	8180(1)	6245(3)	4815(1)	48(1)

Table 3. Bond lengths [Å] and angles [°] for t_a.

O(2)-C(6)	1.3941(16)
O(3)-C(8)	1.1955(17)
O(4)-C(8)	1.3299(16)
O(4)-C(9)	1.4502(18)
O(1)-C(7)	1.2298(16)
N(1)-C(7)	1.3476(17)
N(1)-C(6)	1.4535(17)
N(1)-C(10)	1.4573(18)

N(2)-C(7)	1.3706(18)
N(2)-C(1)	1.3886(17)
N(2)-C(5)	1.4549(16)
C(1)-C(2)	1.332(2)
C(2)-C(3)	1.452(2)
C(3)-C(4)	1.331(2)
C(4)-C(5)	1.5132(18)
C(5)-C(8)	1.5445(18)
C(5)-C(6)	1.5621(19)
C(10)-C(11)	1.504(2)
C(11)-C(16)	1.382(2)
C(11)-C(12)	1.387(2)
C(12)-C(13)	1.380(3)
C(13)-C(14)	1.362(4)
C(14)-C(15)	1.365(4)
C(15)-C(16)	1.400(3)

C(8)-O(4)-C(9)	115.89(12)
C(7)-N(1)-C(6)	113.58(11)
C(7)-N(1)-C(10)	124.00(11)
C(6)-N(1)-C(10)	122.35(11)
C(7)-N(2)-C(1)	126.41(11)
C(7)-N(2)-C(5)	112.76(10)
C(1)-N(2)-C(5)	120.38(12)
C(2)-C(1)-N(2)	118.60(14)
C(1)-C(2)-C(3)	119.25(14)
C(4)-C(3)-C(2)	121.33(14)
C(3)-C(4)-C(5)	118.23(13)
N(2)-C(5)-C(4)	108.68(11)
N(2)-C(5)-C(8)	109.42(11)
C(4)-C(5)-C(8)	112.21(11)
N(2)-C(5)-C(6)	102.47(10)
C(4)-C(5)-C(6)	116.04(11)
C(8)-C(5)-C(6)	107.48(10)
O(2)-C(6)-N(1)	110.49(11)
O(2)-C(6)-C(5)	111.97(11)
N(1)-C(6)-C(5)	102.45(10)
O(1)-C(7)-N(1)	126.22(13)

O(1)-C(7)-N(2)	125.77(12)
N(1)-C(7)-N(2)	108.00(11)
O(3)-C(8)-O(4)	125.78(13)
O(3)-C(8)-C(5)	124.03(12)
O(4)-C(8)-C(5)	110.16(11)
N(1)-C(10)-C(11)	112.92(11)
C(16)-C(11)-C(12)	119.30(16)
C(16)-C(11)-C(10)	121.06(15)
C(12)-C(11)-C(10)	119.63(14)
C(13)-C(12)-C(11)	120.40(19)
C(14)-C(13)-C(12)	120.3(2)
C(13)-C(14)-C(15)	120.16(19)
C(14)-C(15)-C(16)	120.5(2)
C(11)-C(16)-C(15)	119.3(2)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for t_a. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(2)	34(1)	26(1)	47(1)	11(1)	7(1)	5(1)
O(3)	26(1)	44(1)	49(1)	-4(1)	4(1)	-7(1)
O(4)	29(1)	33(1)	38(1)	-6(1)	6(1)	8(1)
O(1)	42(1)	21(1)	38(1)	-4(1)	6(1)	3(1)
N(1)	35(1)	22(1)	27(1)	2(1)	8(1)	-3(1)
N(2)	31(1)	19(1)	31(1)	2(1)	7(1)	2(1)
C(1)	38(1)	27(1)	38(1)	10(1)	13(1)	7(1)
C(2)	38(1)	47(1)	34(1)	14(1)	12(1)	15(1)
C(3)	27(1)	52(1)	32(1)	-2(1)	3(1)	11(1)
C(4)	24(1)	35(1)	35(1)	-6(1)	3(1)	1(1)
C(5)	23(1)	19(1)	30(1)	0(1)	5(1)	-1(1)
C(6)	23(1)	20(1)	32(1)	2(1)	5(1)	-1(1)
C(7)	22(1)	22(1)	31(1)	2(1)	4(1)	0(1)
C(8)	25(1)	26(1)	28(1)	2(1)	6(1)	0(1)
C(9)	37(1)	59(1)	42(1)	-4(1)	6(1)	24(1)
C(10)	33(1)	33(1)	26(1)	1(1)	3(1)	-4(1)

C(11)	29(1)	40(1)	20(1)	-4(1)	4(1)	-4(1)
C(12)	54(1)	41(1)	31(1)	1(1)	8(1)	-12(1)
C(13)	89(2)	68(1)	37(1)	-4(1)	15(1)	-45(1)
C(14)	62(2)	129(2)	38(1)	-17(1)	15(1)	-56(2)
C(15)	30(1)	139(2)	48(1)	-23(1)	5(1)	-1(1)
C(16)	36(1)	73(1)	35(1)	-9(1)	1(1)	10(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for t_a.

	x	y	z	U(eq)
H(5)	5548(16)	10030(30)	5975(11)	53
H(1)	5721	1604	7427	41
H(2)	6099	2691	8681	48
H(3)	6848	5983	8843	44
H(4)	6651	8348	7877	38
H(6)	6685	8285	6388	30
H(9A)	3396	10619	7991	69
H(9B)	3003	8335	7993	69
H(9C)	3082	9536	7183	69
H(10A)	5672	6845	4731	37
H(10B)	6273	4745	4701	37
H(12)	6541	9829	4458	50
H(13)	8023	11528	4109	77
H(14)	9598	9945	4199	91
H(15)	9714	6665	4644	87
H(16)	8229	4896	4997	58

Table 6. Torsion angles [°] for t_a.

C(7)-N(2)-C(1)-C(2)	148.17(15)
C(5)-N(2)-C(1)-C(2)	-23.5(2)
N(2)-C(1)-C(2)-C(3)	-7.1(2)
C(1)-C(2)-C(3)-C(4)	15.6(2)
C(2)-C(3)-C(4)-C(5)	6.2(2)

C(7)-N(2)-C(5)-C(4)	-130.90(12)
C(1)-N(2)-C(5)-C(4)	41.82(17)
C(7)-N(2)-C(5)-C(8)	106.26(12)
C(1)-N(2)-C(5)-C(8)	-81.01(15)
C(7)-N(2)-C(5)-C(6)	-7.57(14)
C(1)-N(2)-C(5)-C(6)	165.15(12)
C(3)-C(4)-C(5)-N(2)	-32.31(18)
C(3)-C(4)-C(5)-C(8)	88.83(16)
C(3)-C(4)-C(5)-C(6)	-147.08(13)
C(7)-N(1)-C(6)-O(2)	-126.42(12)
C(10)-N(1)-C(6)-O(2)	50.63(16)
C(7)-N(1)-C(6)-C(5)	-6.98(14)
C(10)-N(1)-C(6)-C(5)	170.07(11)
N(2)-C(5)-C(6)-O(2)	126.59(11)
C(4)-C(5)-C(6)-O(2)	-115.17(13)
C(8)-C(5)-C(6)-O(2)	11.34(14)
N(2)-C(5)-C(6)-N(1)	8.20(13)
C(4)-C(5)-C(6)-N(1)	126.43(12)
C(8)-C(5)-C(6)-N(1)	-107.06(11)
C(6)-N(1)-C(7)-O(1)	-176.39(13)
C(10)-N(1)-C(7)-O(1)	6.6(2)
C(6)-N(1)-C(7)-N(2)	2.57(15)
C(10)-N(1)-C(7)-N(2)	-174.43(12)
C(1)-N(2)-C(7)-O(1)	10.4(2)
C(5)-N(2)-C(7)-O(1)	-177.42(13)
C(1)-N(2)-C(7)-N(1)	-168.59(13)
C(5)-N(2)-C(7)-N(1)	3.61(15)
C(9)-O(4)-C(8)-O(3)	-4.5(2)
C(9)-O(4)-C(8)-C(5)	173.55(12)
N(2)-C(5)-C(8)-O(3)	-22.16(18)
C(4)-C(5)-C(8)-O(3)	-142.87(14)
C(6)-C(5)-C(8)-O(3)	88.39(15)
N(2)-C(5)-C(8)-O(4)	159.74(11)
C(4)-C(5)-C(8)-O(4)	39.03(15)
C(6)-C(5)-C(8)-O(4)	-89.71(12)
C(7)-N(1)-C(10)-C(11)	-119.88(14)
C(6)-N(1)-C(10)-C(11)	63.37(17)
N(1)-C(10)-C(11)-C(16)	74.91(17)

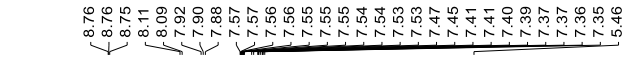
N(1)-C(10)-C(11)-C(12)	-106.05(15)
C(16)-C(11)-C(12)-C(13)	0.9(2)
C(10)-C(11)-C(12)-C(13)	-178.14(14)
C(11)-C(12)-C(13)-C(14)	-0.4(3)
C(12)-C(13)-C(14)-C(15)	-0.3(3)
C(13)-C(14)-C(15)-C(16)	0.4(3)
C(12)-C(11)-C(16)-C(15)	-0.7(2)
C(10)-C(11)-C(16)-C(15)	178.30(15)
C(14)-C(15)-C(16)-C(11)	0.1(3)

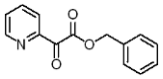
Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for t_a [Å and °].

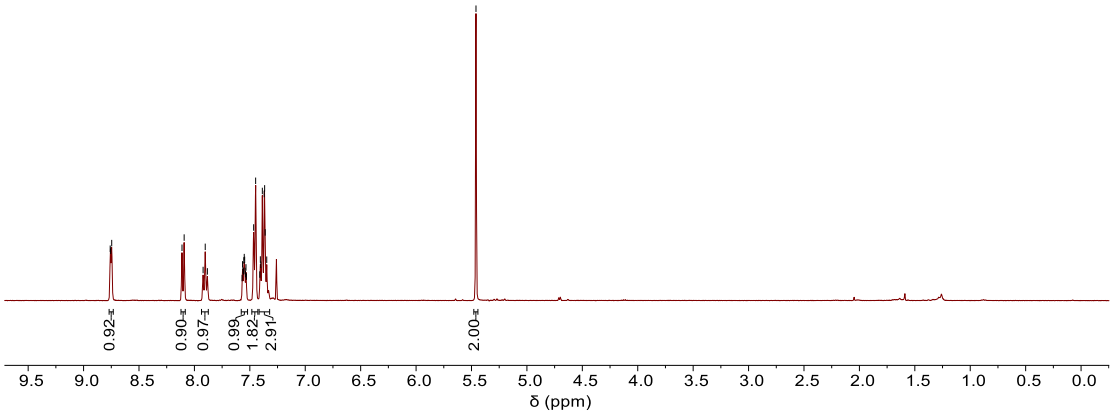
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

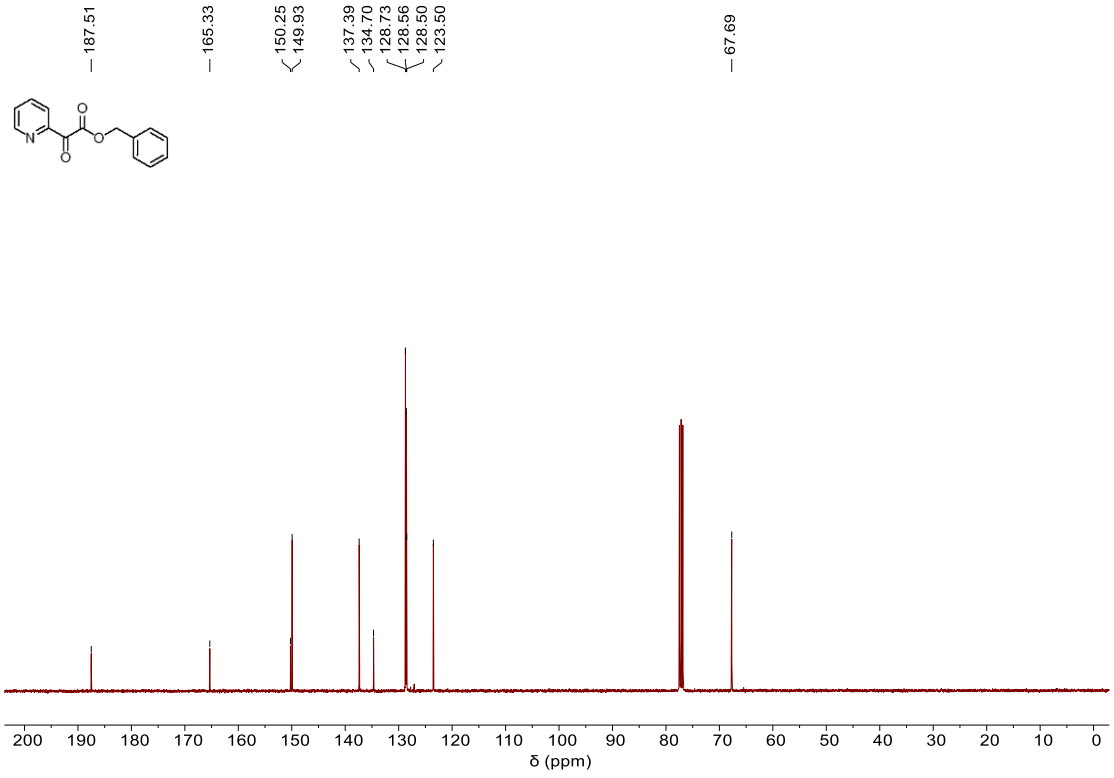
12. Copies of NMR spectra

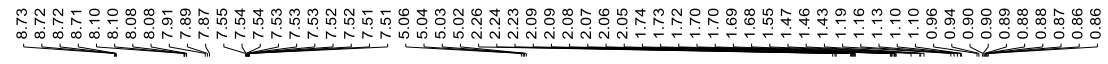




1b



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8.08
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7.54
7.53
7.53
7.52
7.52
7.51
7.51
5.06
5.04
5.03
5.02
2.26
2.24
2.23
2.09
2.09
2.08
2.07
2.06
2.05
1.74
1.73
1.72
1.70
1.70
1.69
1.68
1.55
1.47
1.46
1.43
1.19
1.16
1.13
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0.96
0.94
0.90
0.90
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0.88
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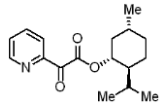
0.87
0.86
0.86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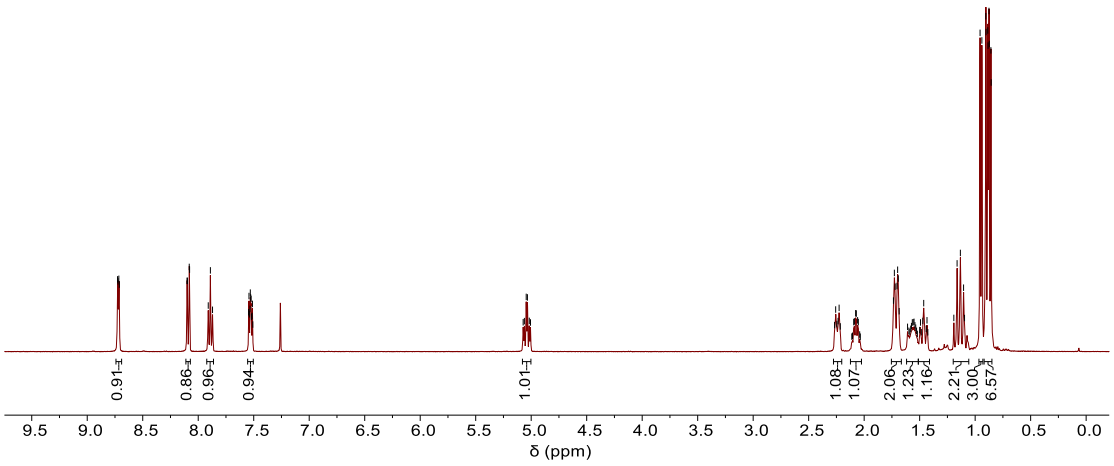
N
O
Me
Me

1c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2.06
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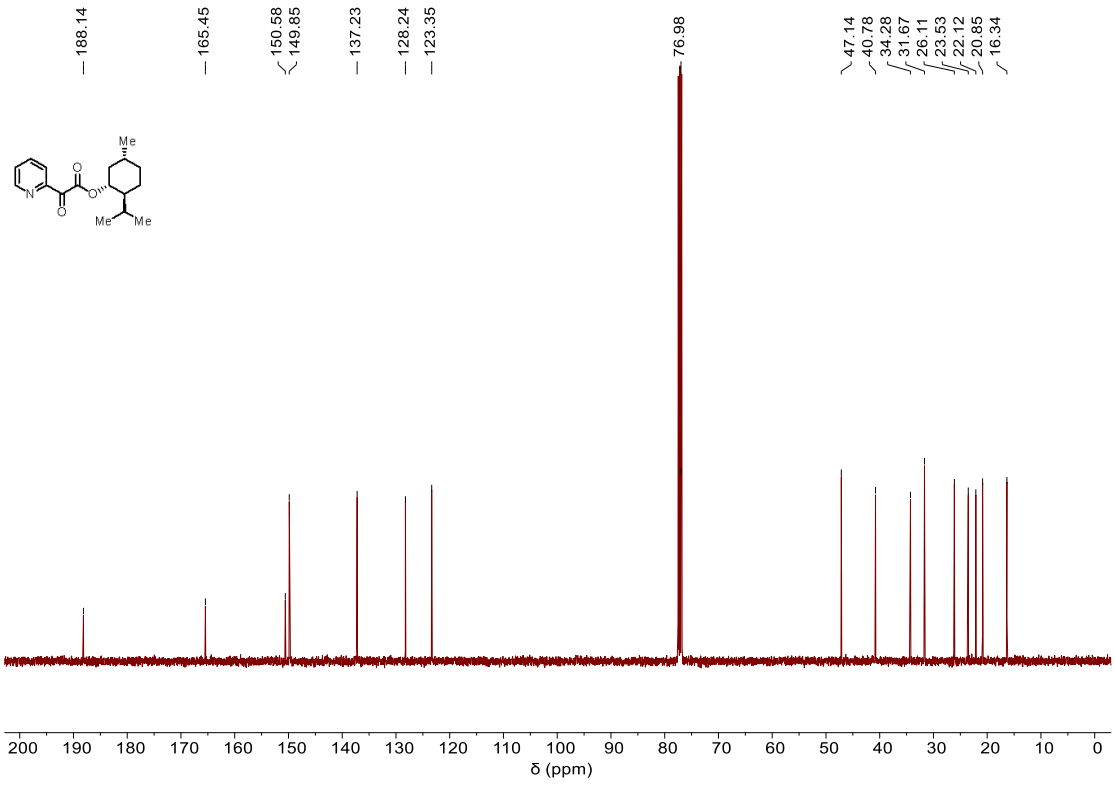
1.16
2.21
3.00
6.57
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)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26.11
23.53
22.12
20.85
16.34
Me
O
O
N
O
Me
Me
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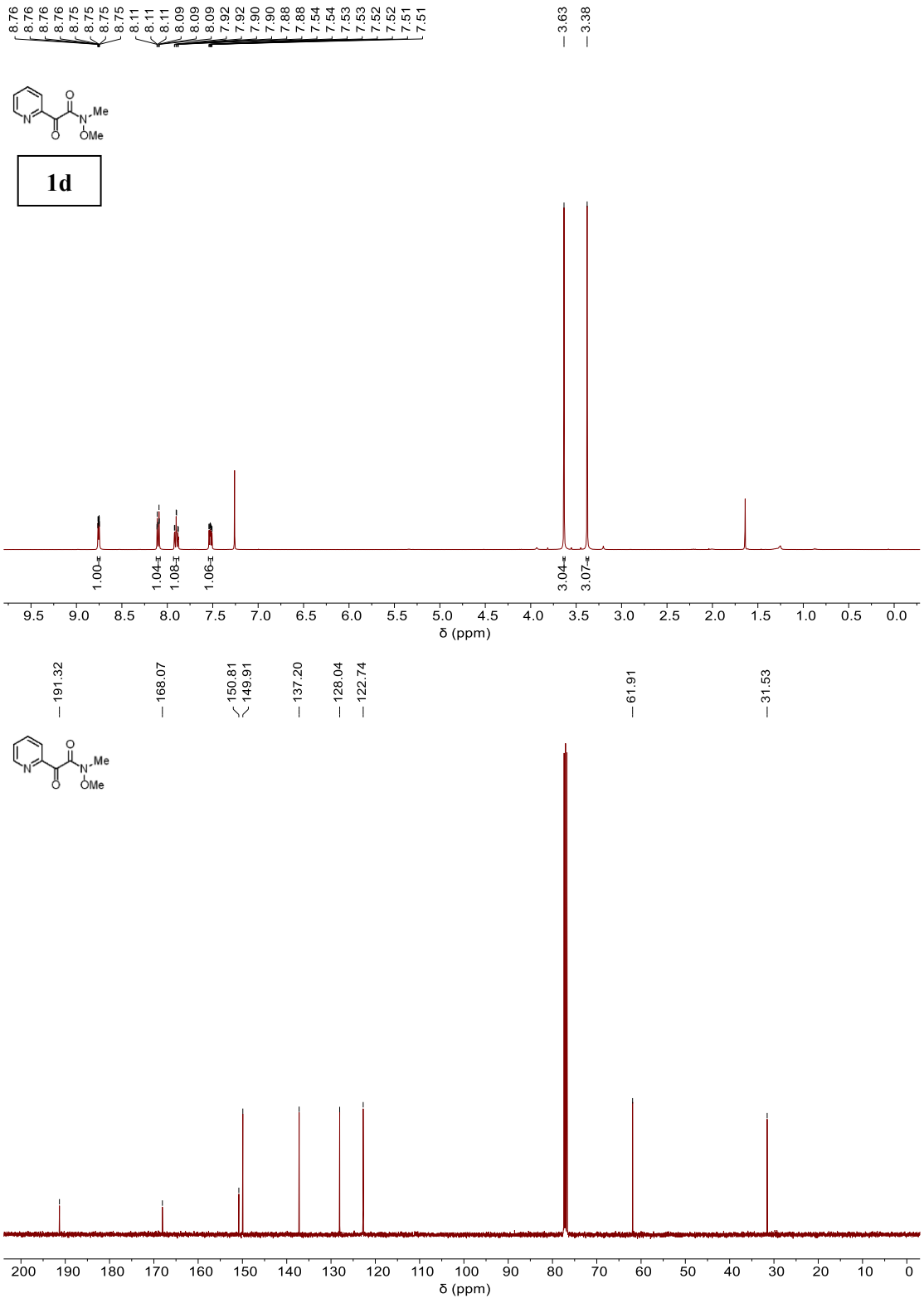
δ (ppm)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7.90
7.90
7.88
7.88
7.54
7.54
7.53
7.53
7.52
7.52
7.51
7.51
3.63
3.38
Me
OMe
1d
1.00
1.04
1.08
1.06
3.04
3.07
δ (ppm)
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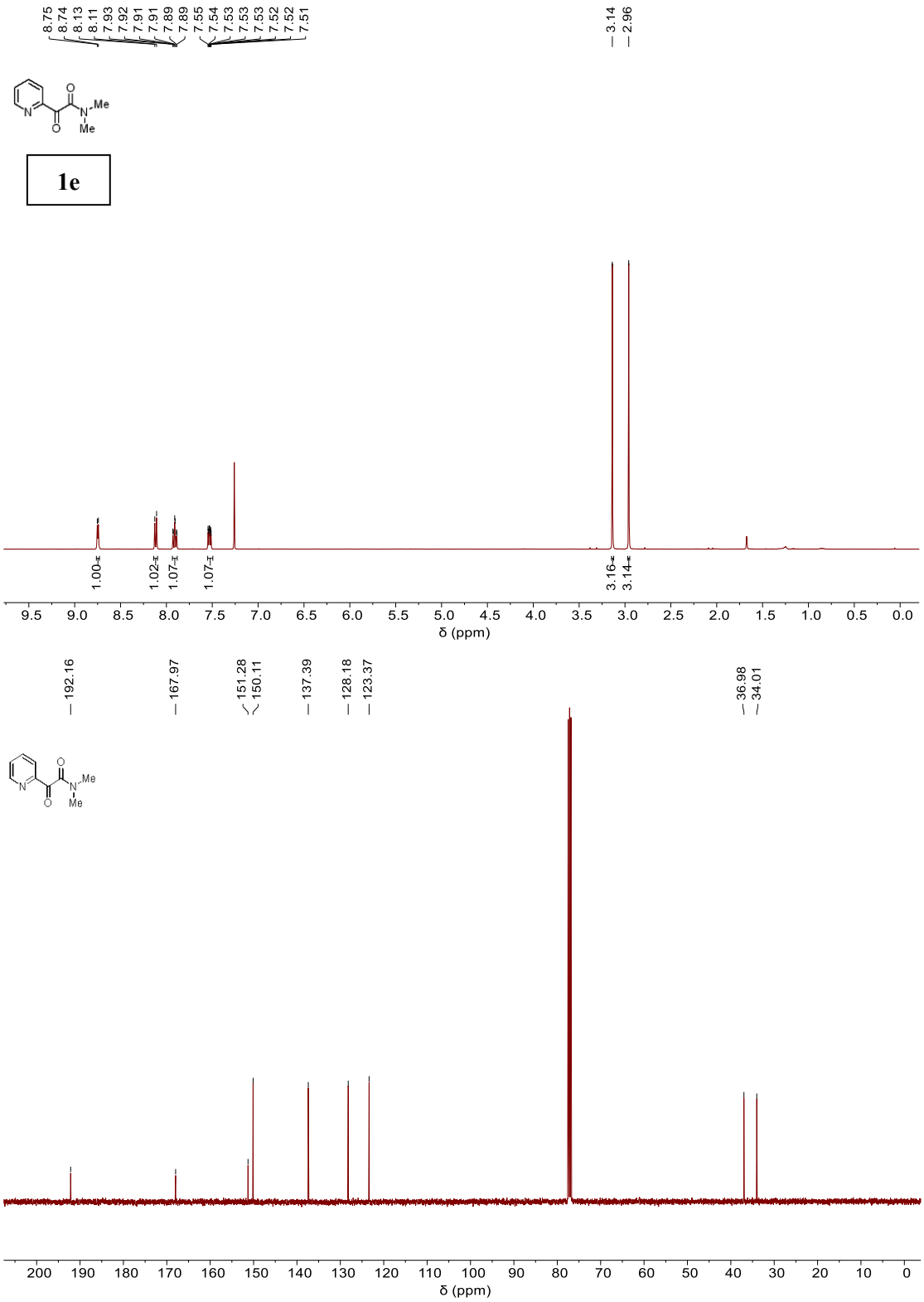
168.07
150.81
149.91
137.20
128.04
122.74
61.91
31.53
δ (ppm)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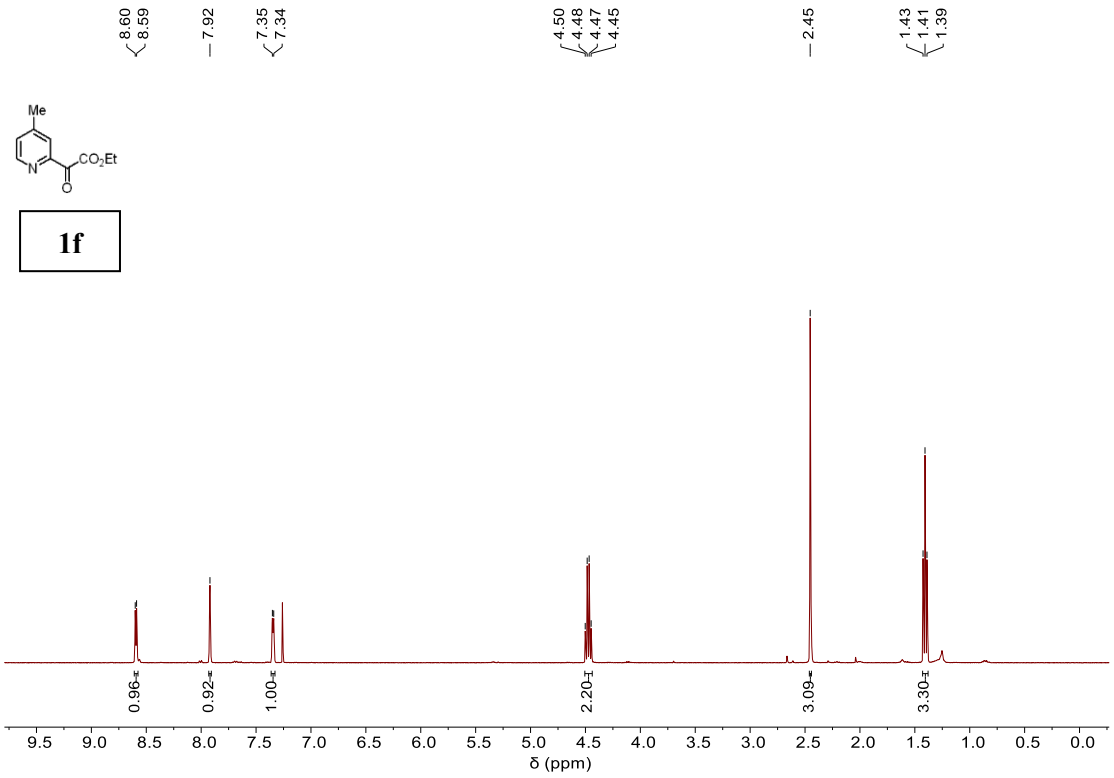
7.91
7.91
7.89
7.89
7.55
7.54
7.53
7.53
7.53
7.52
7.52
7.51
3.14
2.96
Me
Me
1e
1.00
1.02
1.07
1.07
3.16
3.14
δ (ppm)
192.16
167.97
151.28
150.11
137.39
128.18
123.37
36.98
34.01
δ (ppm)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4.48
4.47
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2.45
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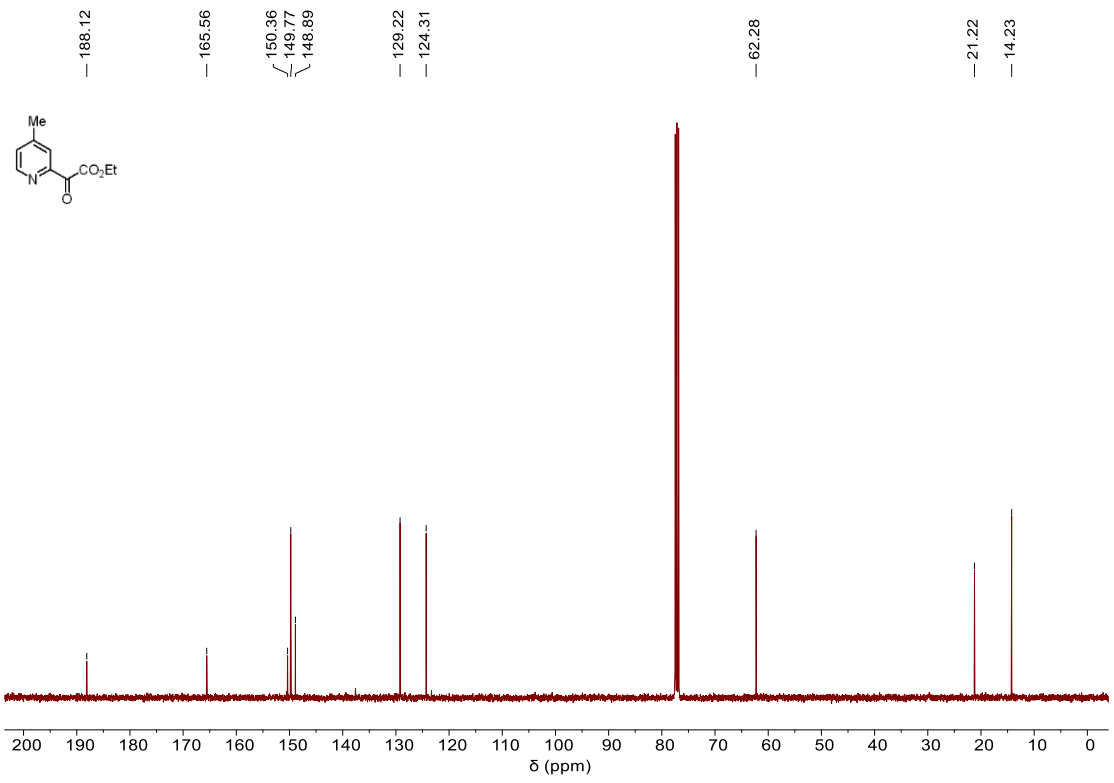
1.41
1.39
Me
CO2Et
O
N
1f
0.96
0.92
1.00
2.20
3.09
3.30
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)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21.22
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O
N
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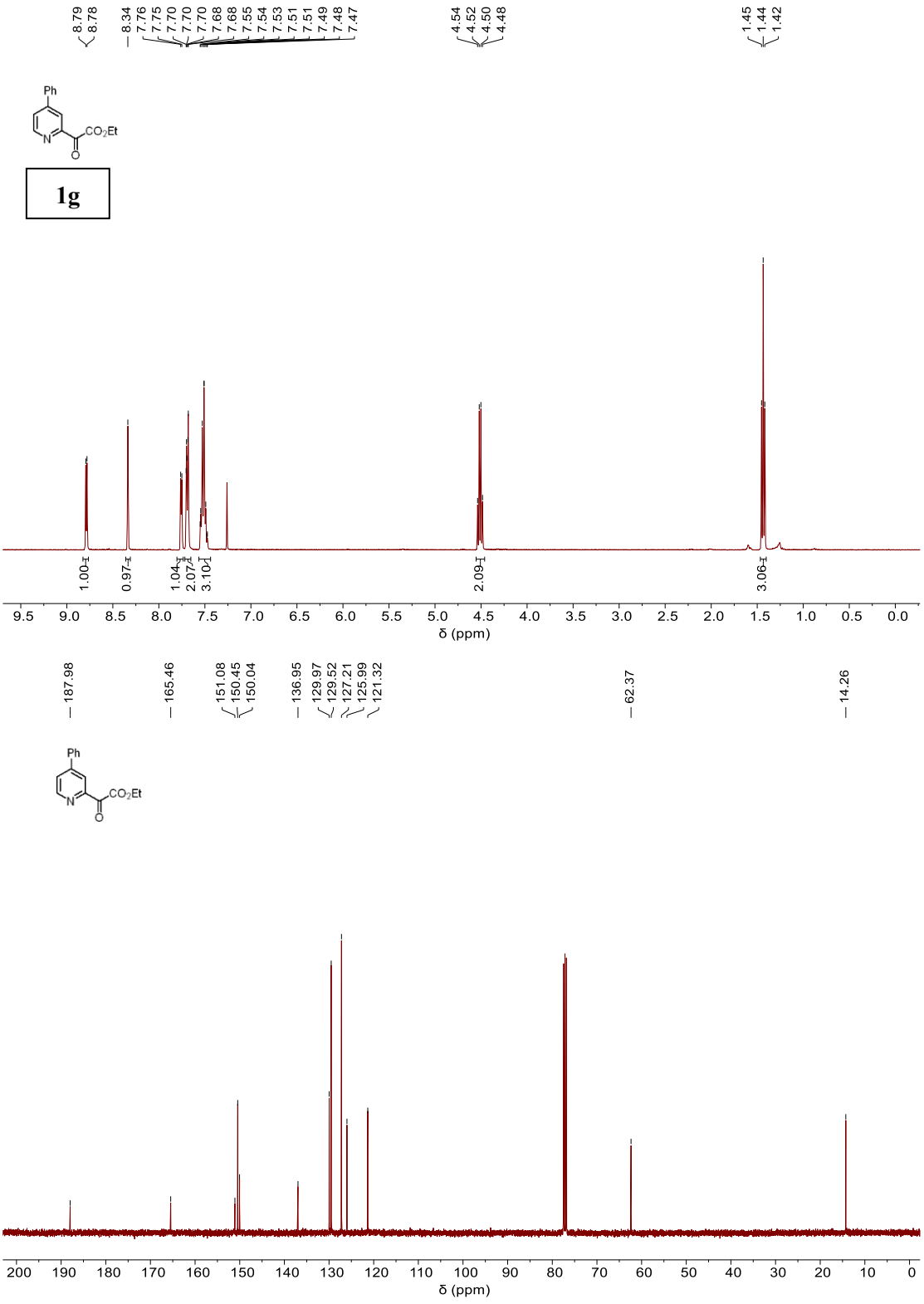
δ (ppm)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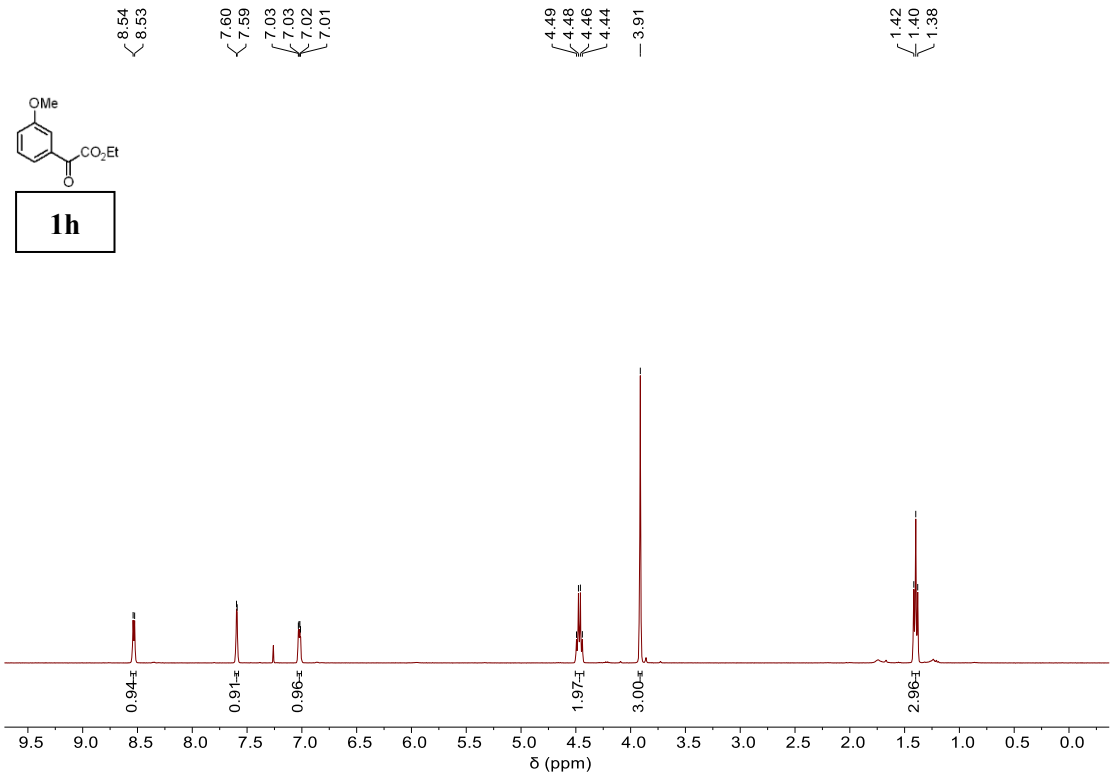
7.53
7.51
7.51
7.49
7.48
7.47
4.54
4.52
4.50
4.48
1.45
1.44
1.42
Ph
CO2Et
O
N
1g
1.00
0.97
1.04
2.07
3.10
2.09
3.06
δ (ppm)
187.98
165.46
151.08
150.45
150.04
136.95
129.97
129.52
127.21
125.99
121.32
62.37
14.26
δ (ppm)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7.03
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7.01
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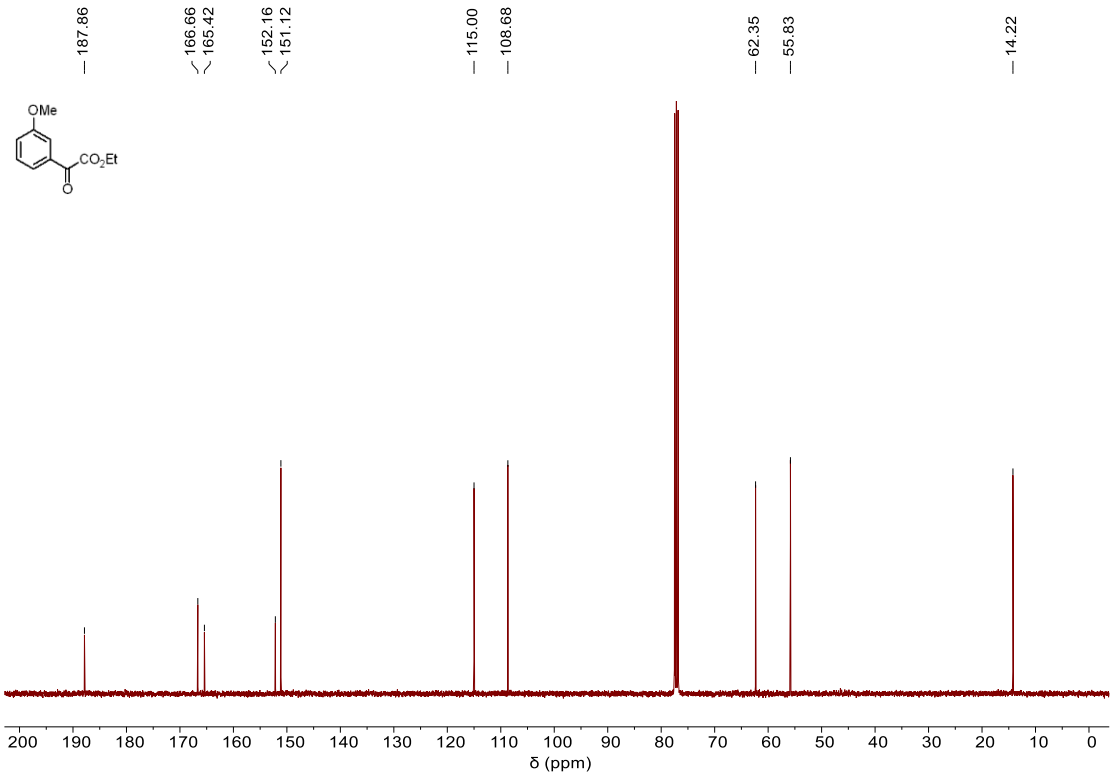
3.91
1.42
1.40
1.38
OMe
CO2Et
O
1h
0.94
0.91
0.96
1.97
3.00
2.96
δ (ppm)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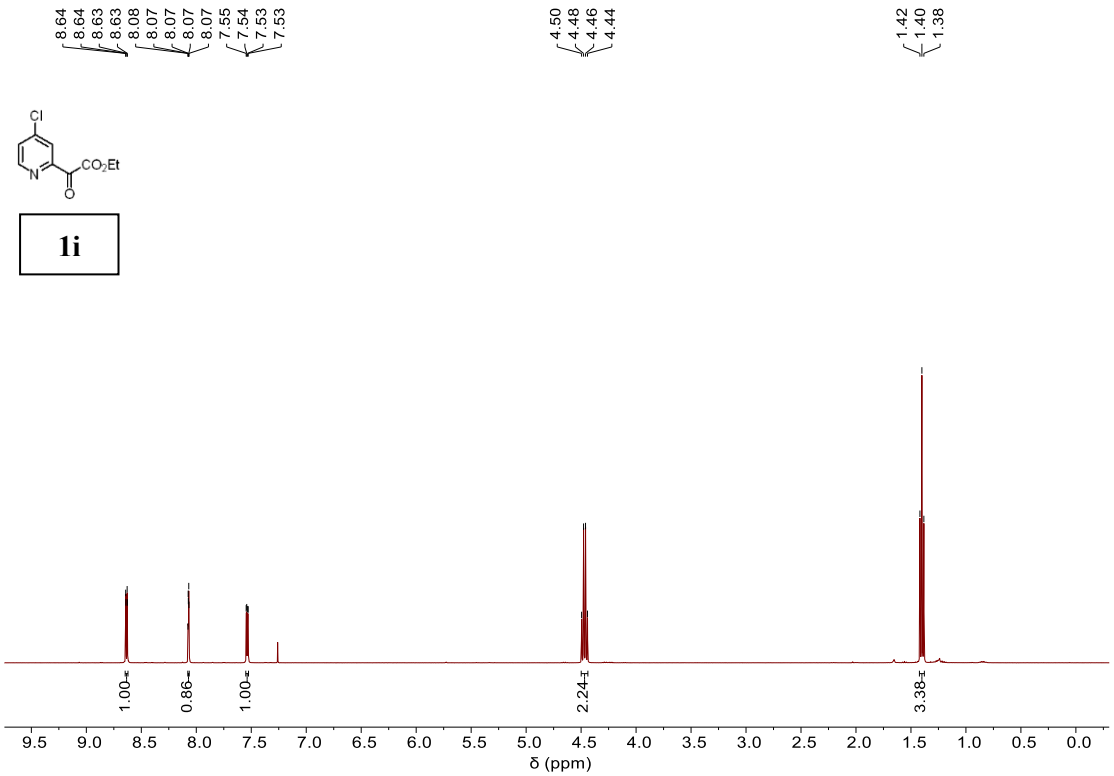
CO2Et
O
δ (ppm)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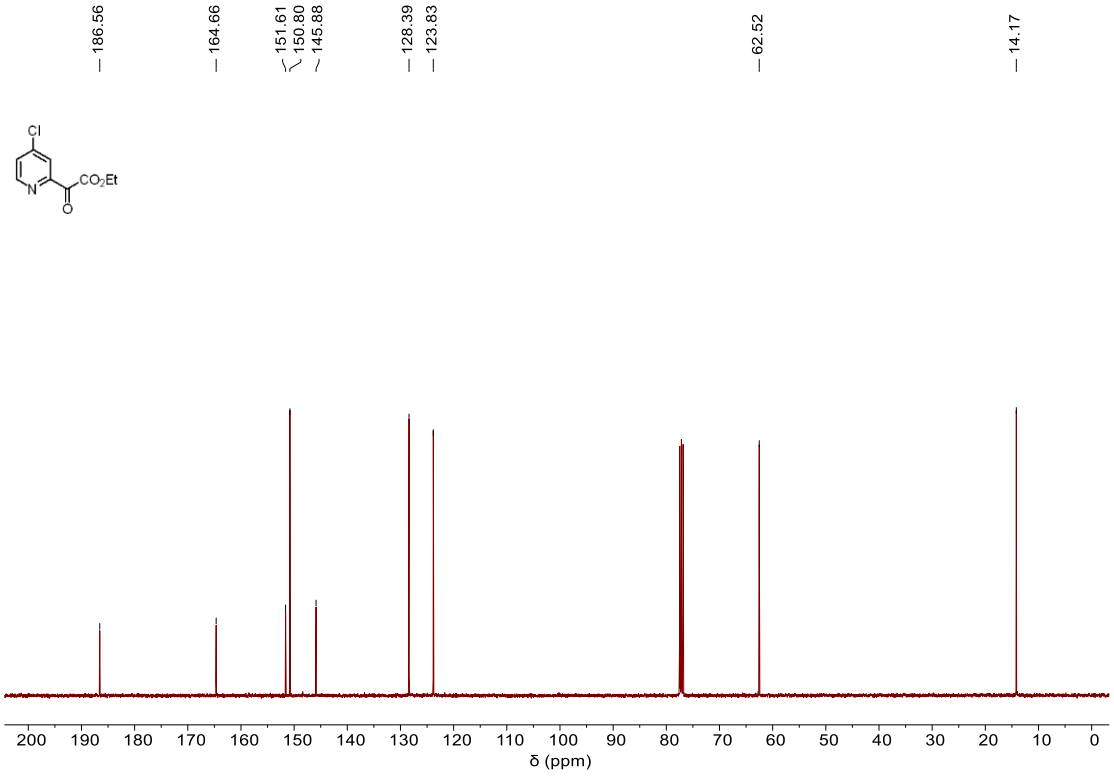
7.53
4.50
4.48
4.46
4.44
1.42
1.40
1.38
Cl
N
CO2Et
O
1i
1.00
0.86
1.00
2.24
3.38
δ (ppm)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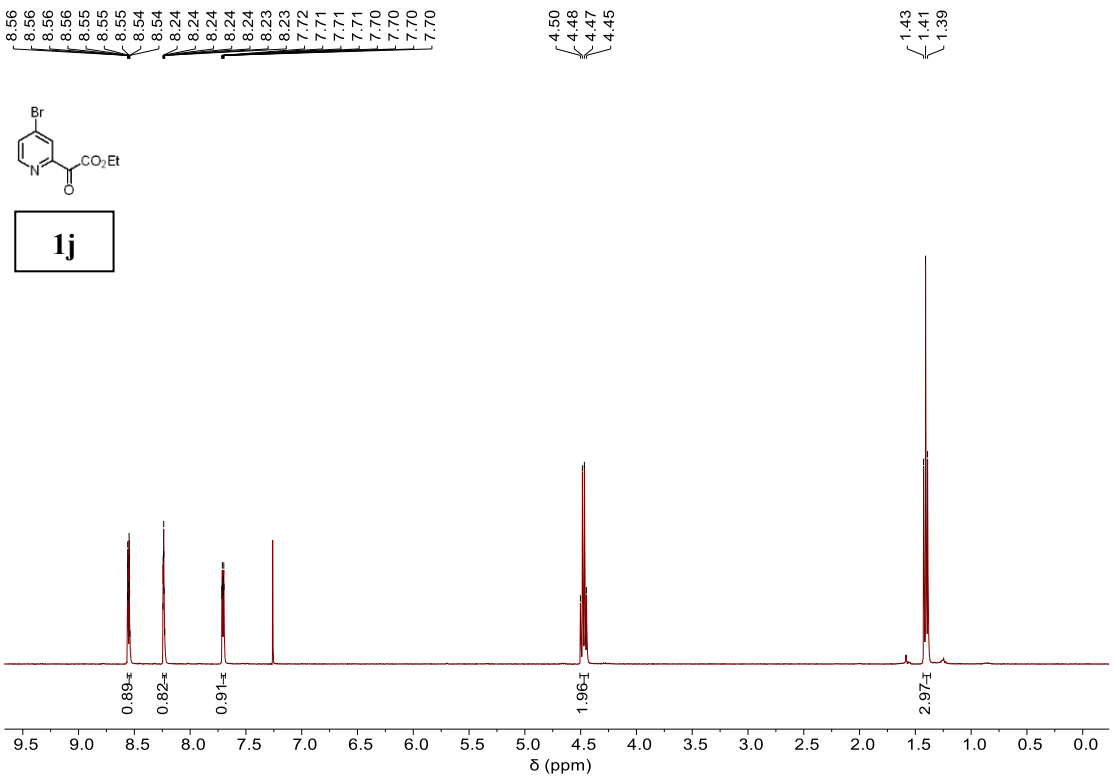
N
CO2Et
O
δ (ppm)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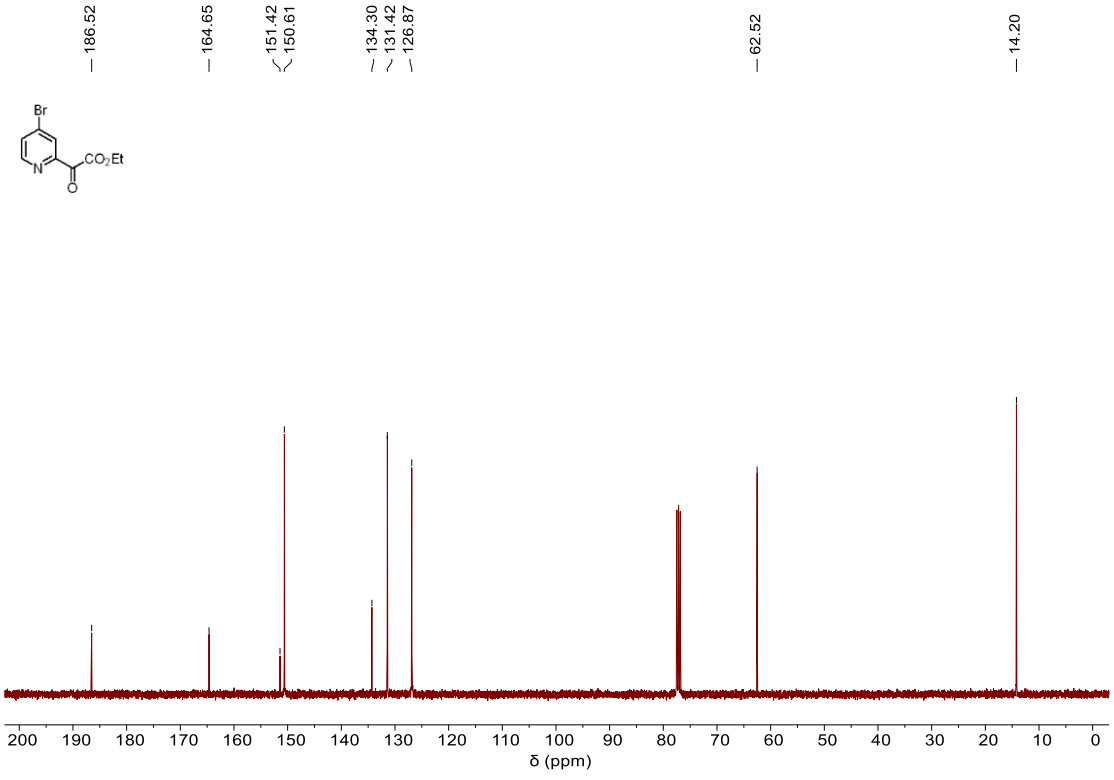
7.72
7.71
7.71
7.71
7.70
7.70
7.70
7.70
4.50
4.48
4.47
4.45
1.43
1.41
1.39
Br
CO2Et
O
N
1j
0.89
0.82
0.91
1.96
2.97
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)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14.20
Br
CO2Et
O
N
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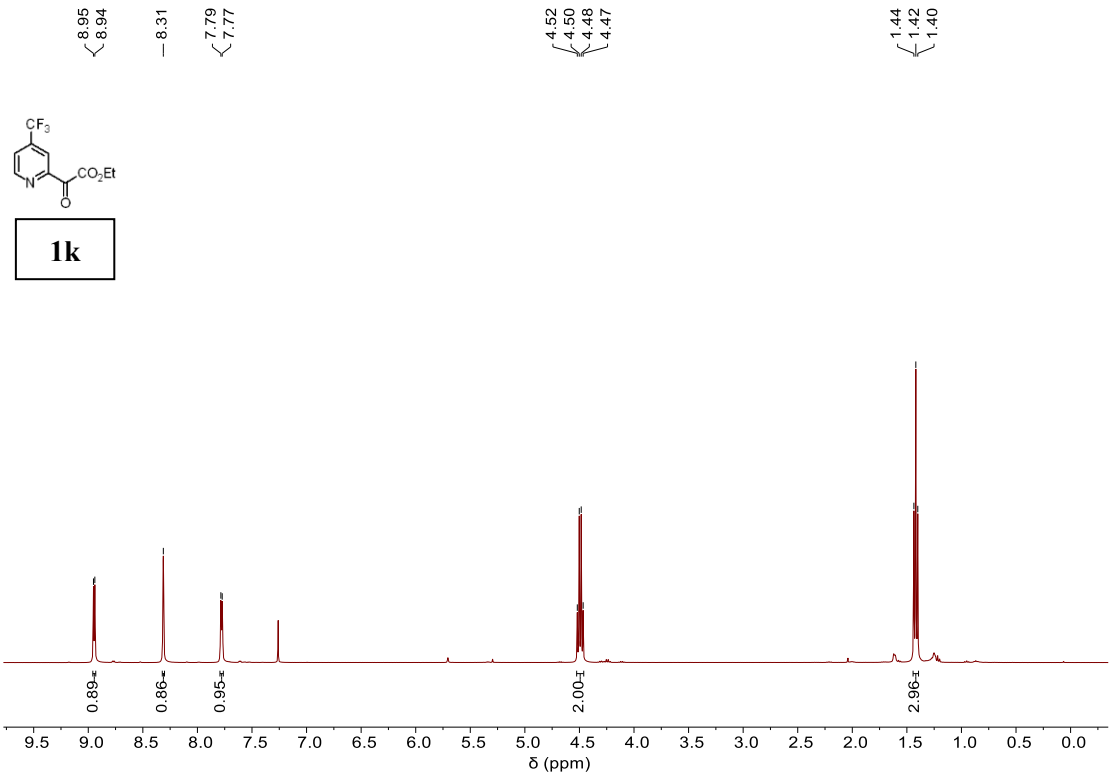
δ (ppm)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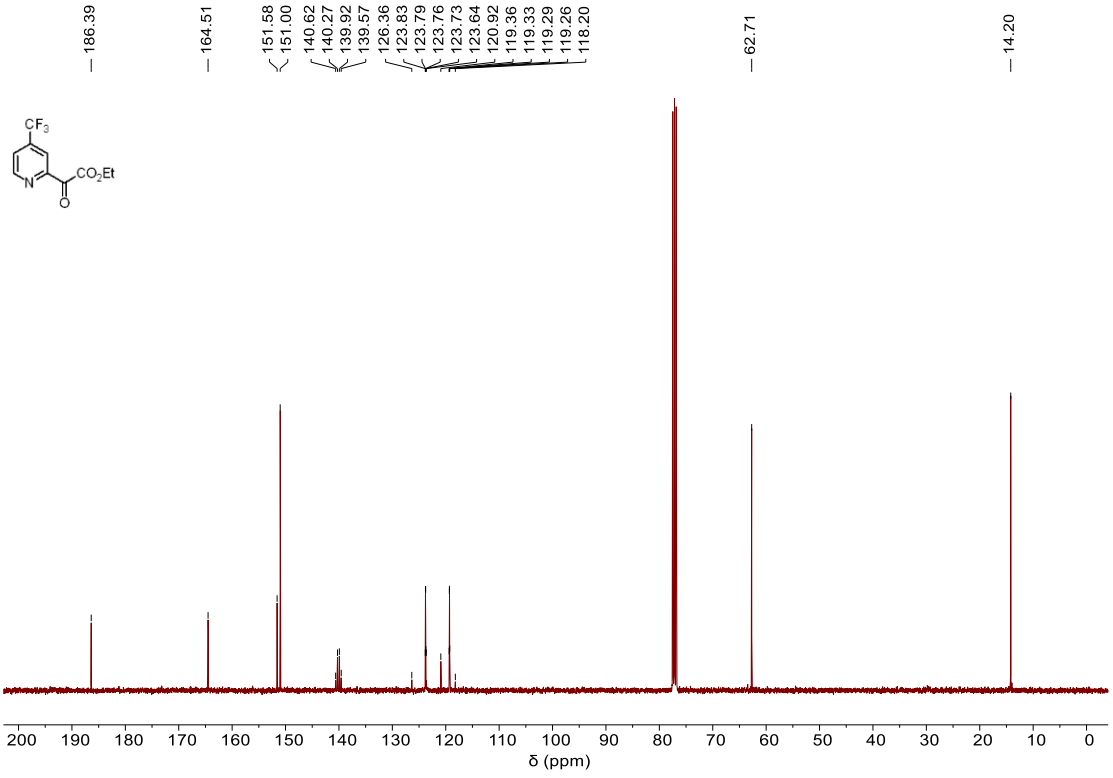
CF3
CO2Et
O
N
1k
0.89
0.86
0.95
2.00
2.96
δ (ppm)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123.64
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119.29
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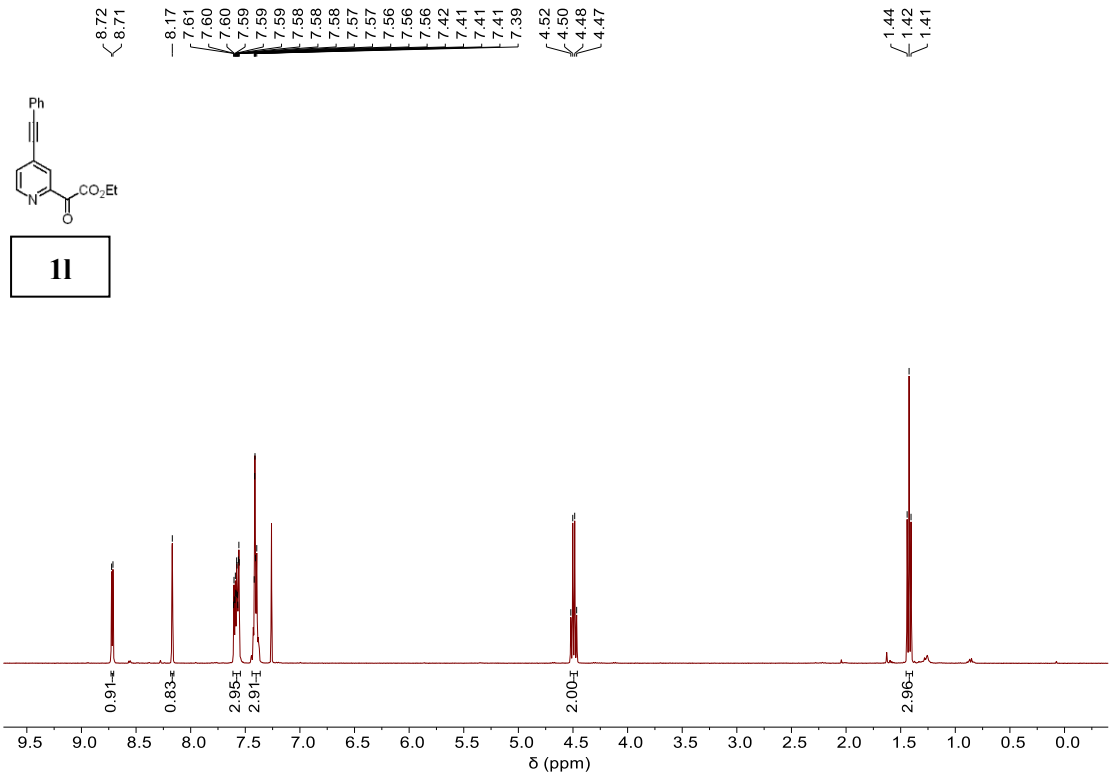
118.20
62.71
14.20
CF3
CO2Et
O
N
δ (ppm)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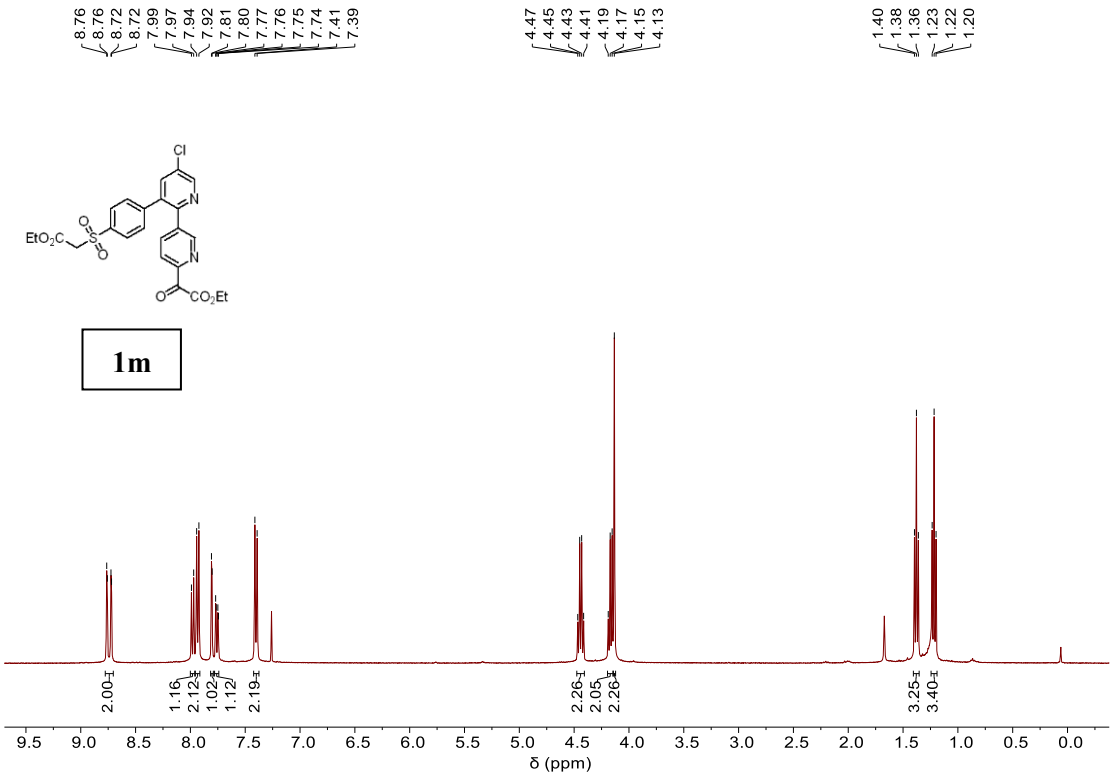
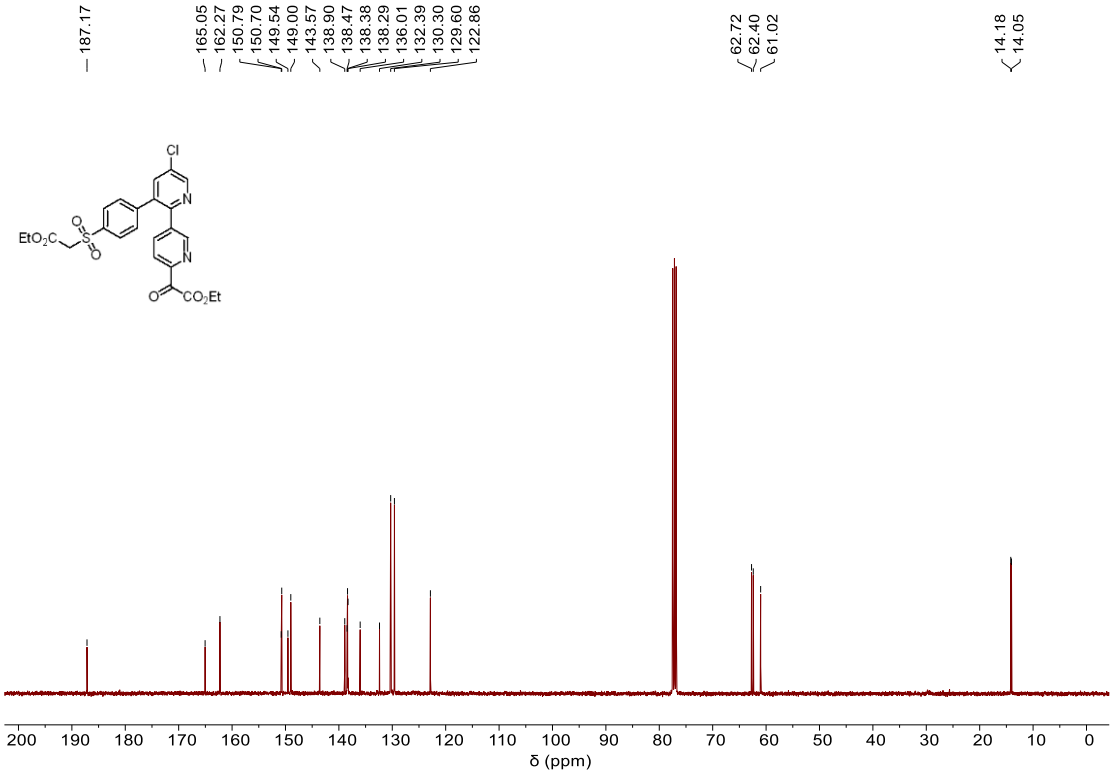
7.42
7.41
7.41
7.41
7.39
4.52
4.50
4.48
4.47
1.44
1.42
1.41
Ph
CO2Et
O
N
1l
0.91
0.83
2.95
2.91
2.00
2.96
δ (ppm)
187.34
165.12
150.53
149.92
133.32
132.15
129.80
129.73
128.72
125.35
121.65
96.10
85.75
62.42
14.22
δ (ppm)


8.76
8.76
8.72
8.72
7.99
7.97
7.94
7.92
7.81
7.80
7.77
7.76
7.75
7.74
7.41
7.39
4.47
4.45
4.43
4.41
4.19
4.17
4.15
4.13
1.40
1.38
1.36
1.23
1.22
1.20
Cl
N
N
O
S
O
O
EtO2C
O
CO2Et
1m
2.00
1.16
2.12
1.02
1.12
2.19
2.26
2.05
2.26
3.25
3.40
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
δ (ppm)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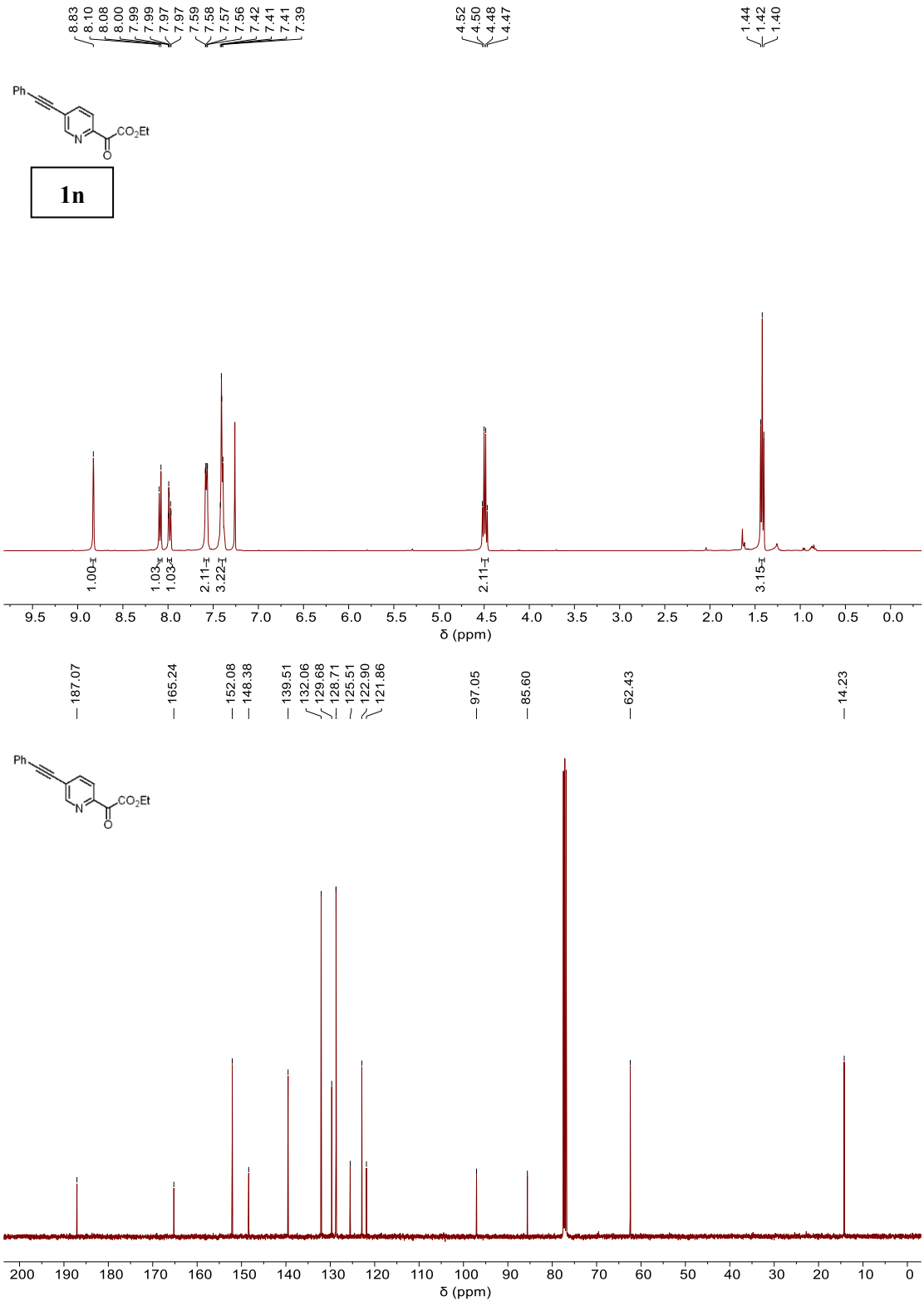
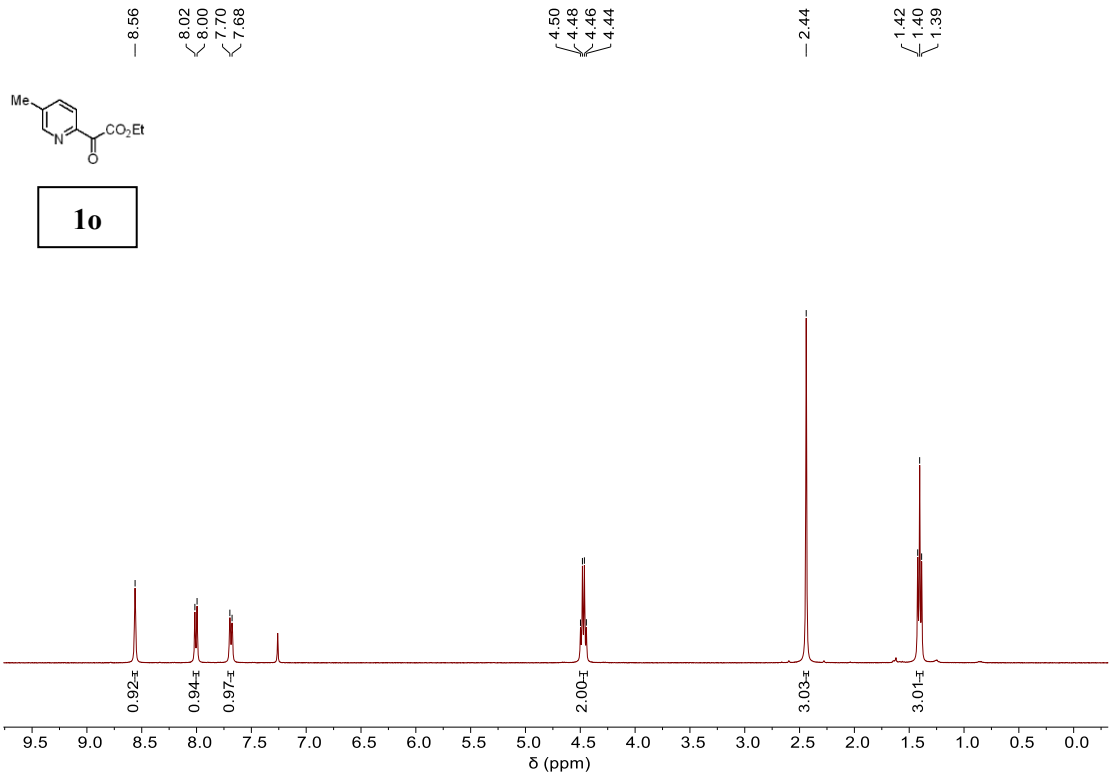
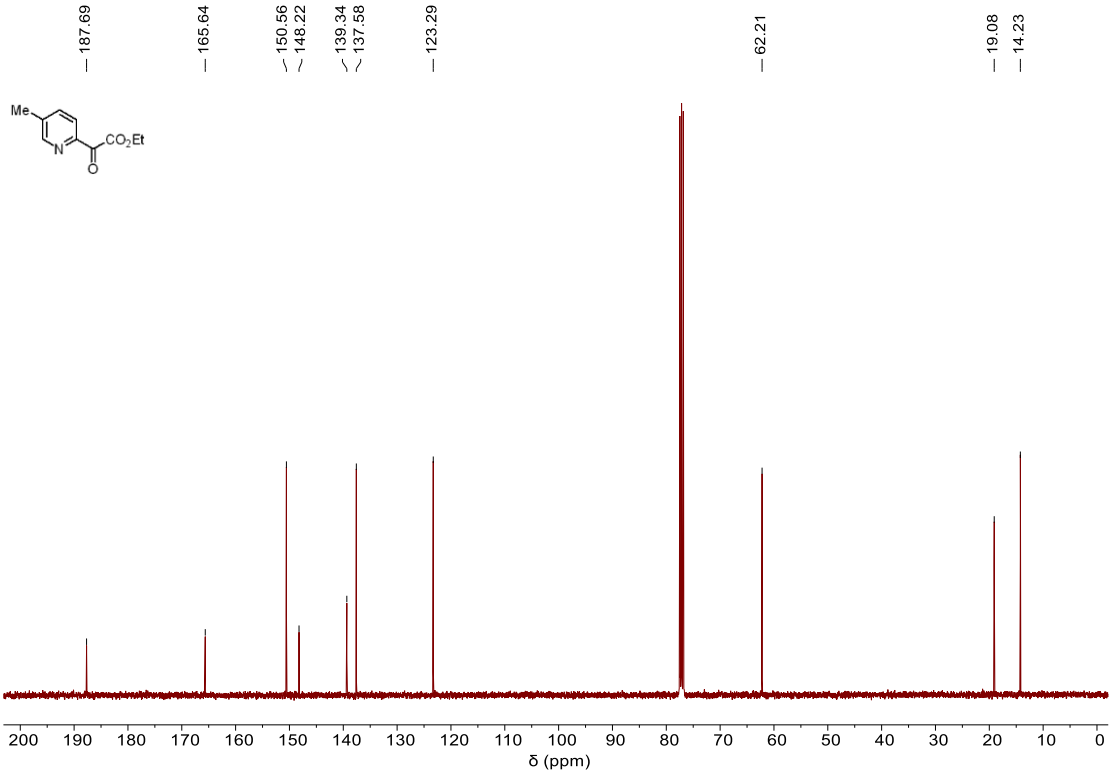
165.05
162.27
150.79
150.70
149.54
149.00
143.57
138.90
138.47
138.38
138.29
136.01
132.39
130.30
129.60
122.86
62.72
62.40
61.02
14.18
14.05
Cl
N
N
O
S
O
O
EtO2C
O
CO2Et
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)


8.83
8.10
8.08
8.00
7.99
7.99
7.97
7.97
7.59
7.58
7.57
7.56
7.42
7.41
7.41
7.39
4.52
4.50
4.48
4.47
1.44
1.42
1.40
Ph
CO2Et
N
O
1n
1.00
1.03
1.03
2.11
3.22
2.11
3.15
δ (ppm)
187.07
165.24
152.08
148.38
139.51
132.06
129.68
128.71
125.51
122.90
121.86
97.05
85.60
62.43
14.23
δ (ppm)


8.56
8.02
8.00
7.70
7.68
4.50
4.48
4.46
4.44
2.44
1.42
1.40
1.39
Me
N
CO2Et
O
1o
0.92
0.94
0.97
2.00
3.03
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
δ (ppm)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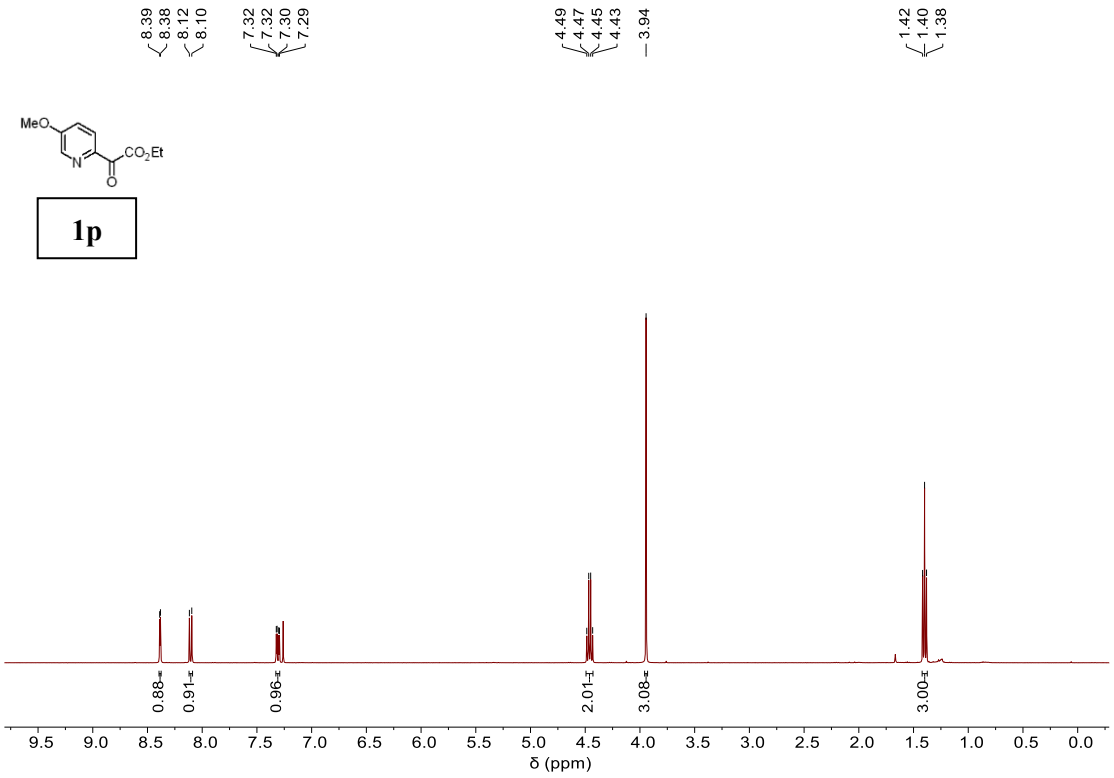
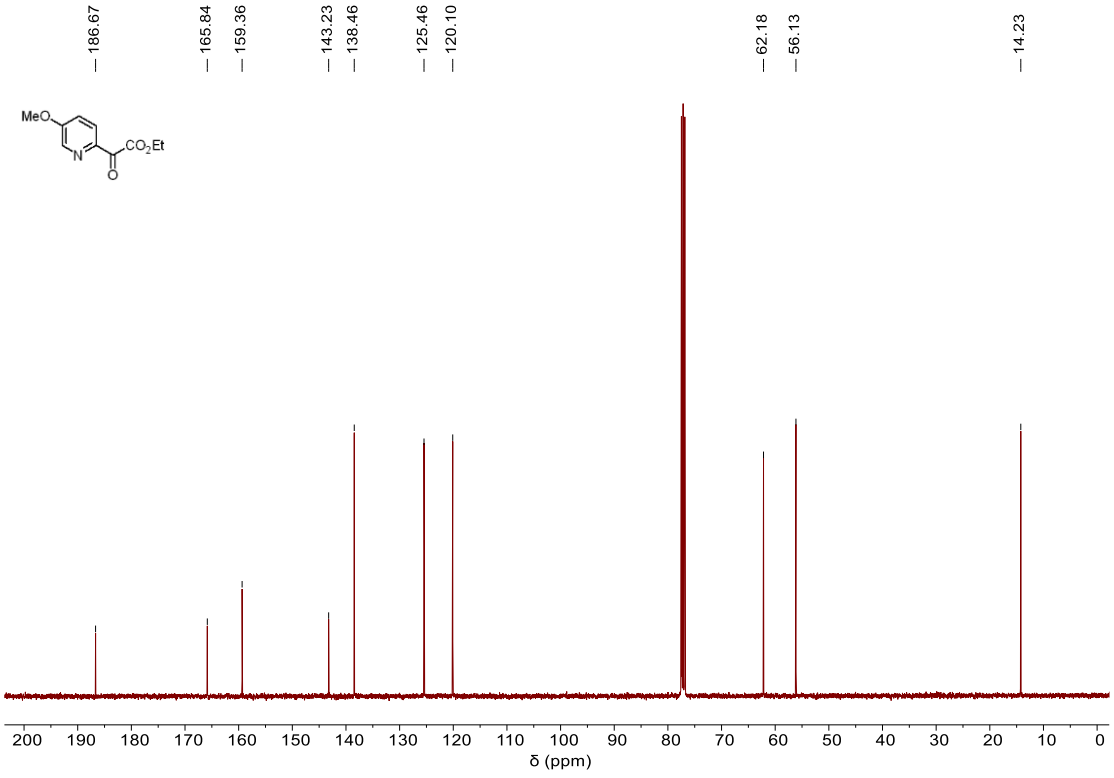
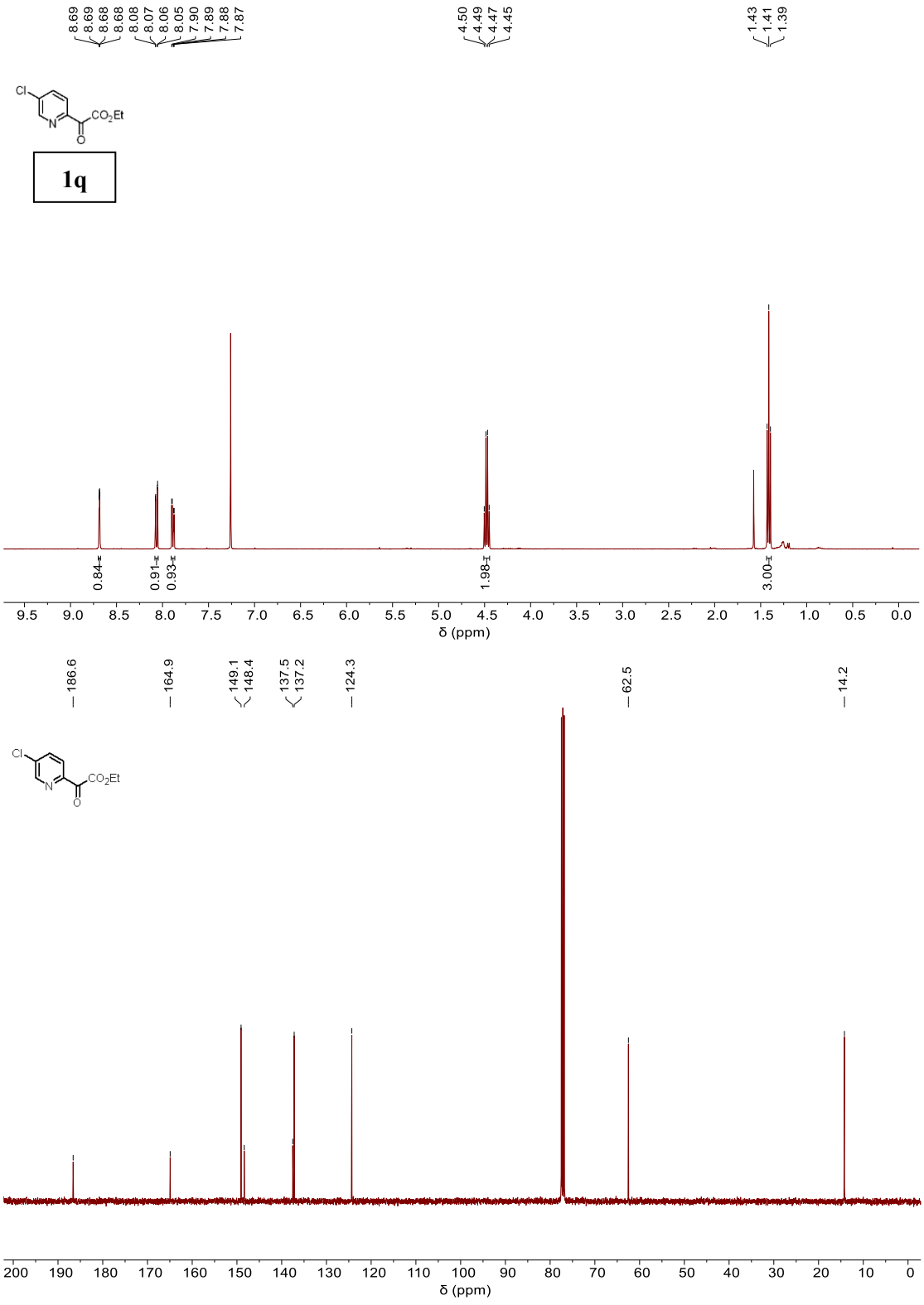
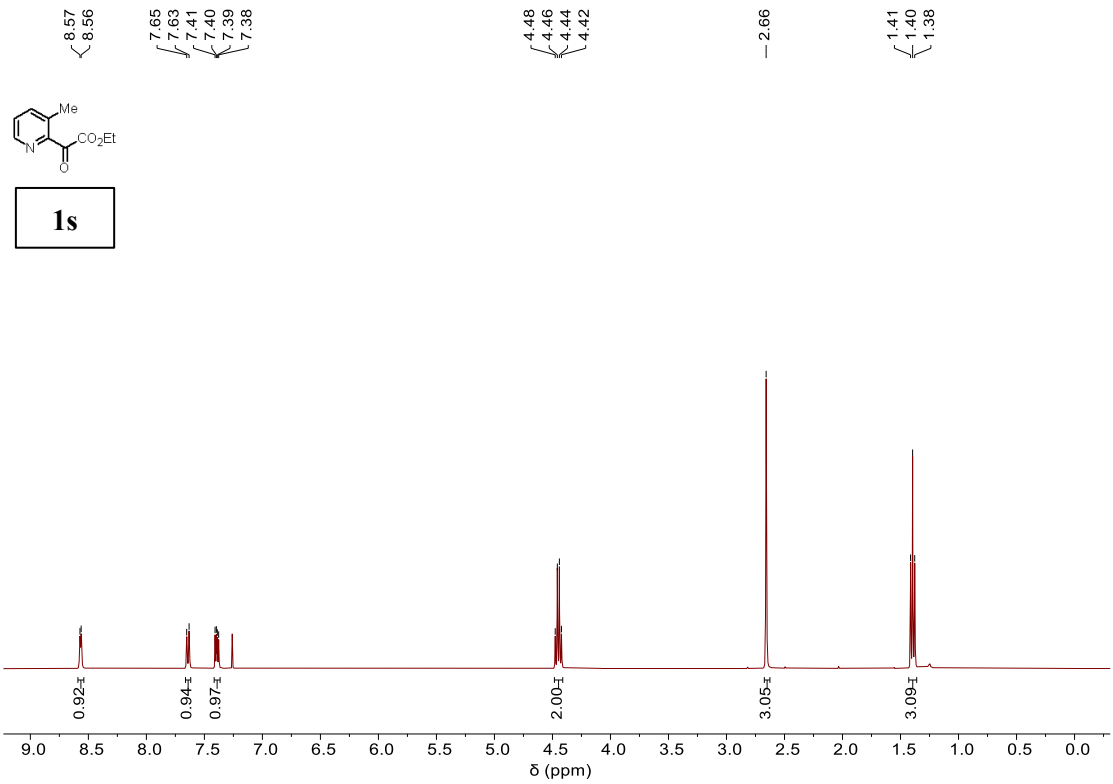
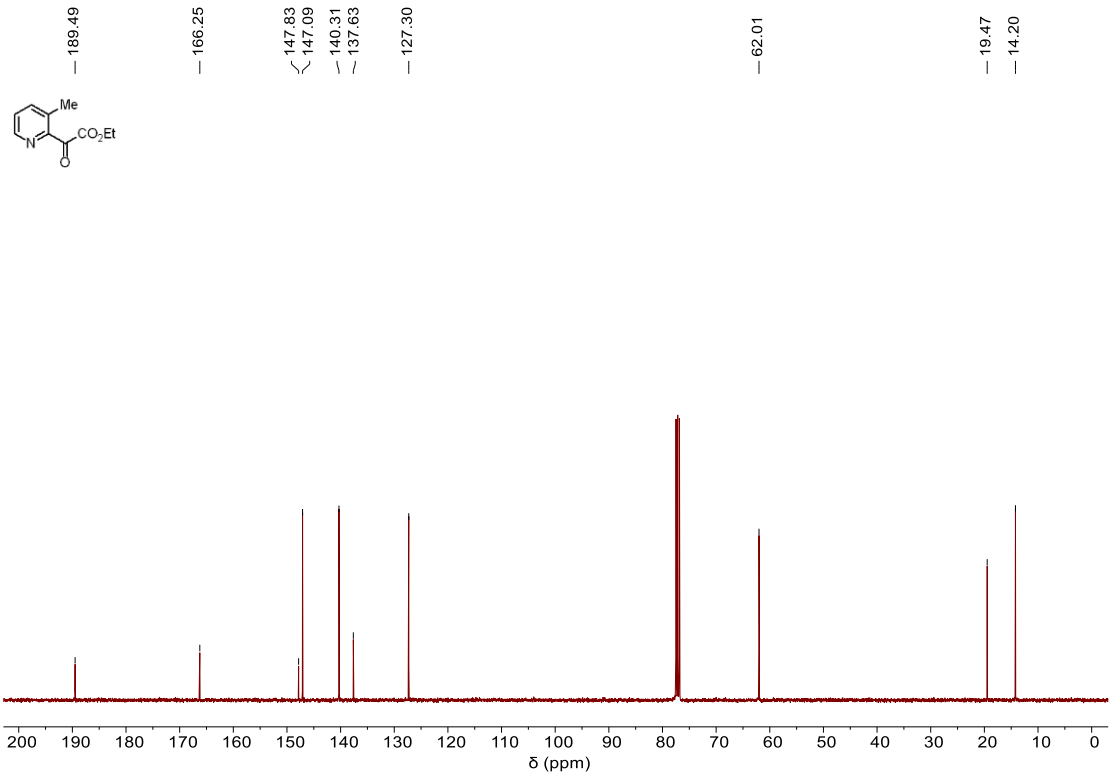
165.64
150.56
148.22
139.34
137.58
123.29
62.21
19.08
14.23
Me
N
CO2Et
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

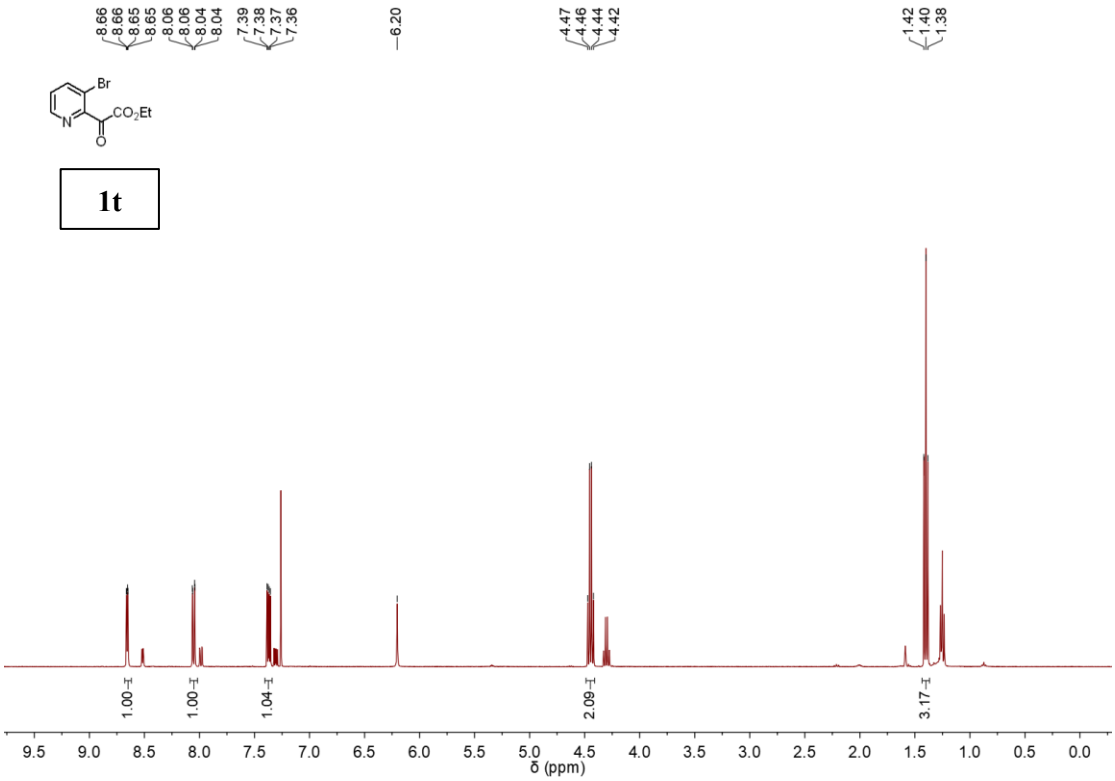

8.39
8.38
8.12
8.10
7.32
7.32
7.30
7.29
4.49
4.47
4.45
4.43
3.94
1.42
1.40
1.38
MeO
N
CO2Et
O
1p
0.88
0.91
0.96
2.01
3.08
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)

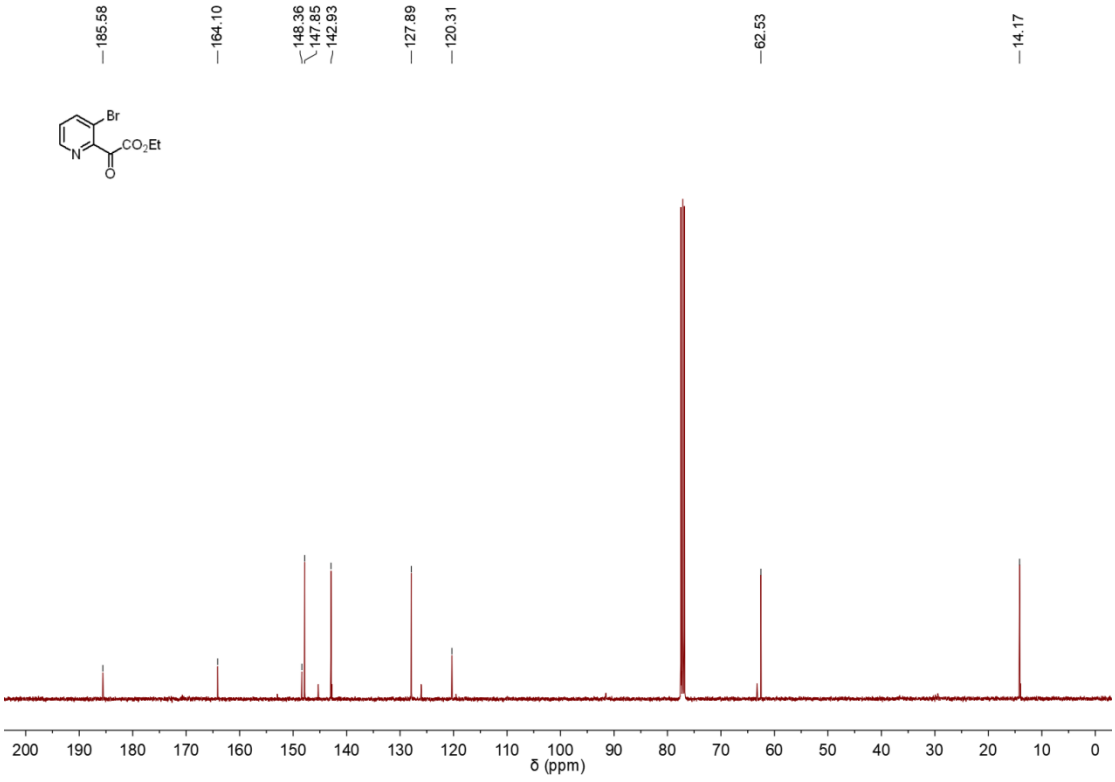

186.67
165.84
159.36
143.23
138.46
125.46
120.10
62.18
56.13
14.23
MeO
N
CO2Et
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

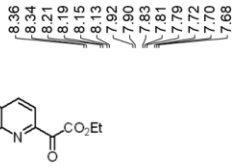

8.69
8.69
8.68
8.68
8.08
8.07
8.06
8.05
7.90
7.89
7.88
7.87
4.50
4.49
4.47
4.45
1.43
1.41
1.39
Cl
N
CO2Et
O
1q
0.84
0.91
0.93
1.98
3.00
δ (ppm)
186.6
164.9
149.1
148.4
137.5
137.2
124.3
62.5
14.2
δ (ppm)


8.57
8.56
7.65
7.63
7.41
7.40
7.39
7.38
4.48
4.46
4.44
4.42
2.66
1.41
1.40
1.38
Me
CO2Et
O
N
1s
0.92
0.94
0.97
2.00
3.05
3.09
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
δ (ppm)

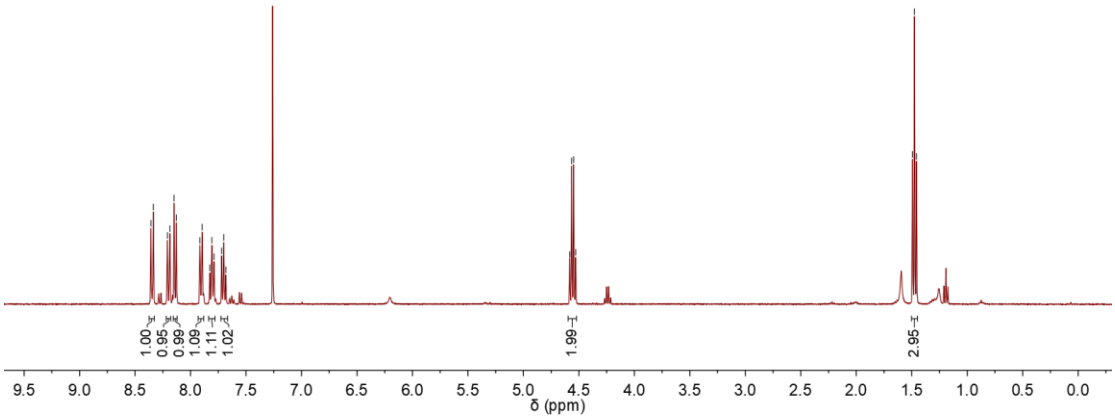

189.49
166.25
147.83
147.09
140.31
137.63
127.30
62.01
19.47
14.20
Me
CO2Et
O
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

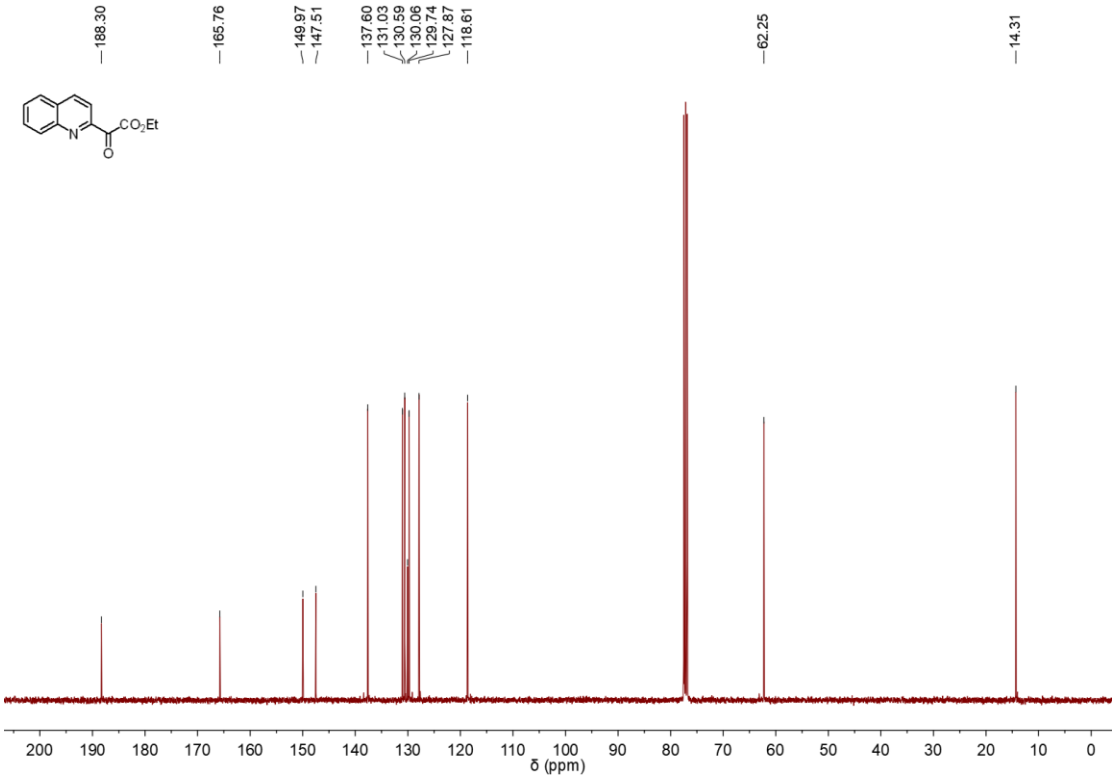

8.66
8.66
8.65
8.65
8.06
8.06
8.04
8.04
7.39
7.38
7.37
7.36
6.20
4.47
4.46
4.44
4.42
1.42
1.40
1.38
Br
CO2Et
O
N
1t
1.00
1.00
1.04
2.09
3.17
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)

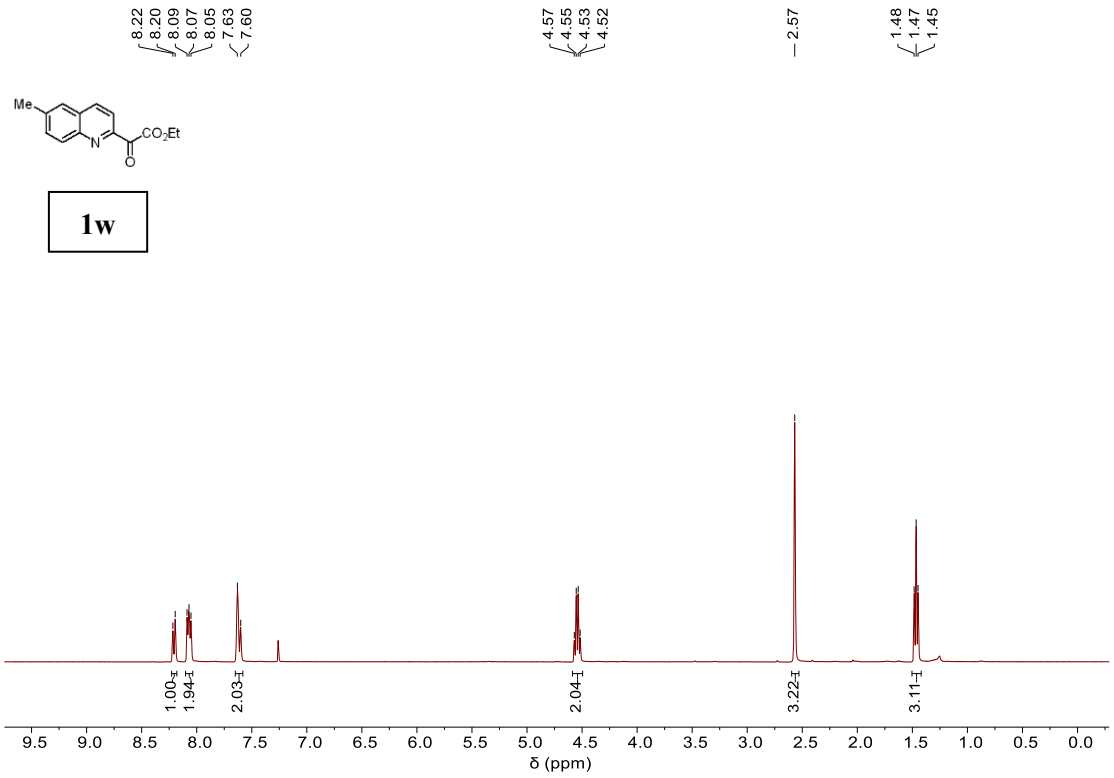

185.58
164.10
148.36
147.85
142.93
127.89
120.31
62.53
14.17
Br
CO2Et
O
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

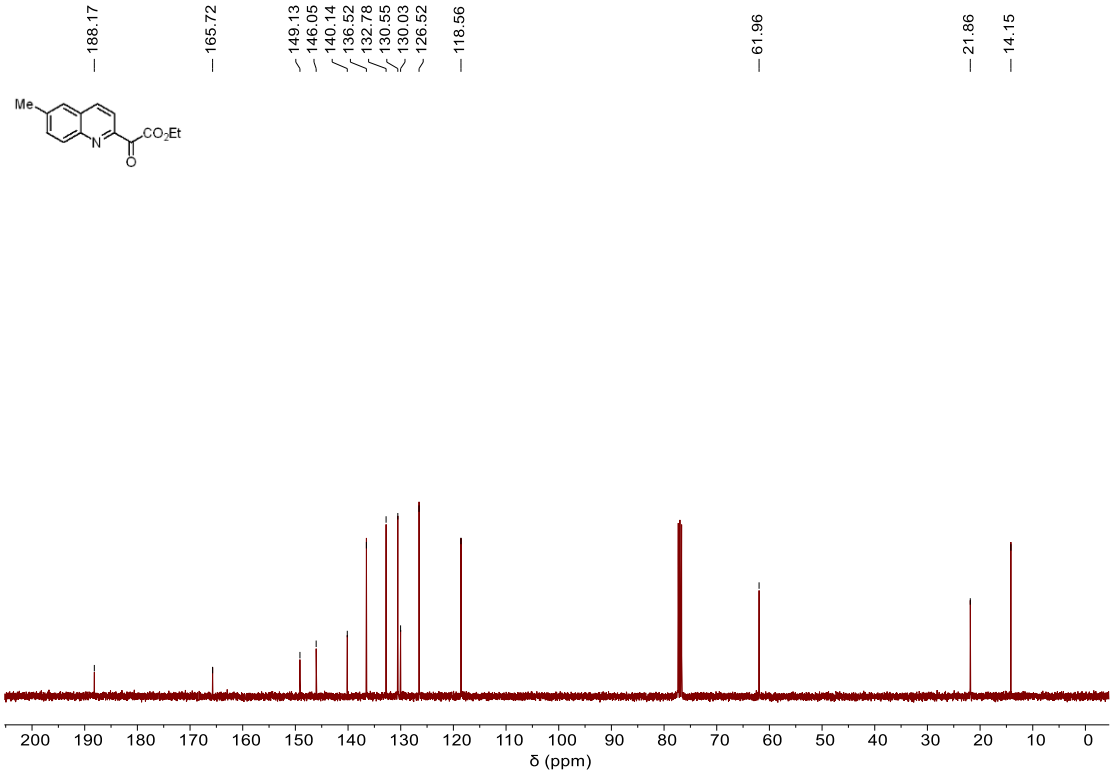

8.36
8.34
8.21
8.19
8.15
8.13
7.92
7.90
7.83
7.81
7.79
7.72
7.70
7.68
4.58
4.56
4.55
4.53
1.49
1.48
1.46
CO2Et
O
N

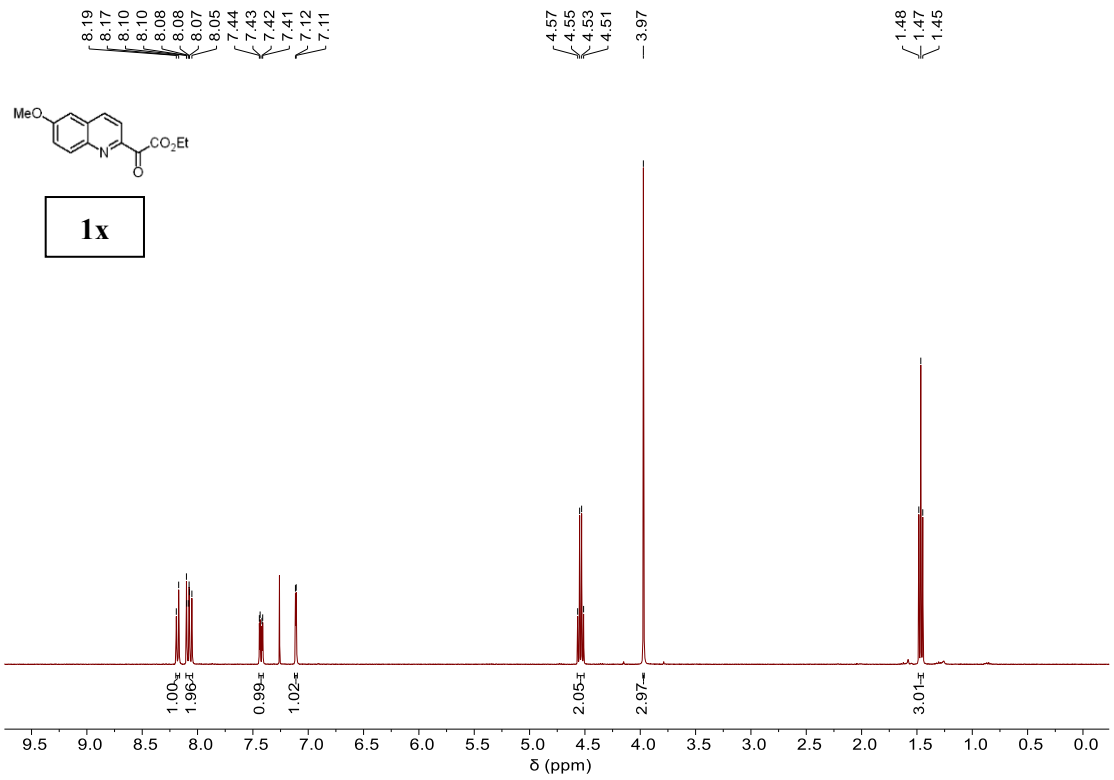
1v

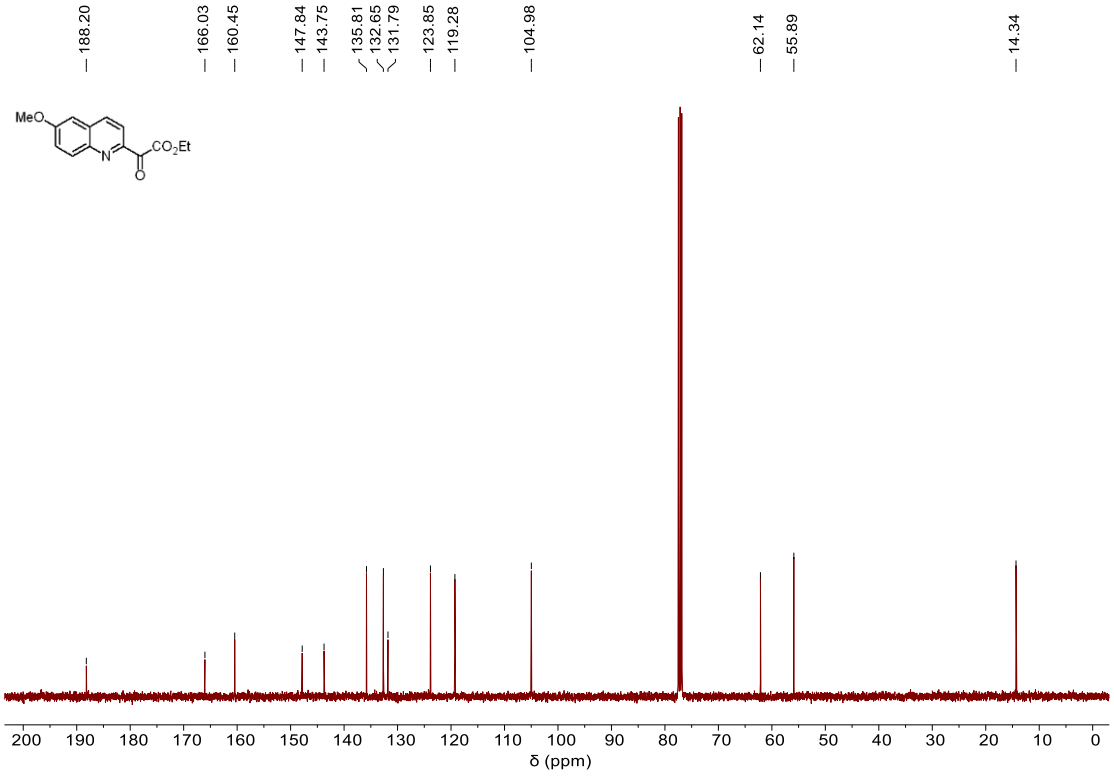

1.00
0.95
0.99
1.09
1.11
1.02
1.99
2.95
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)

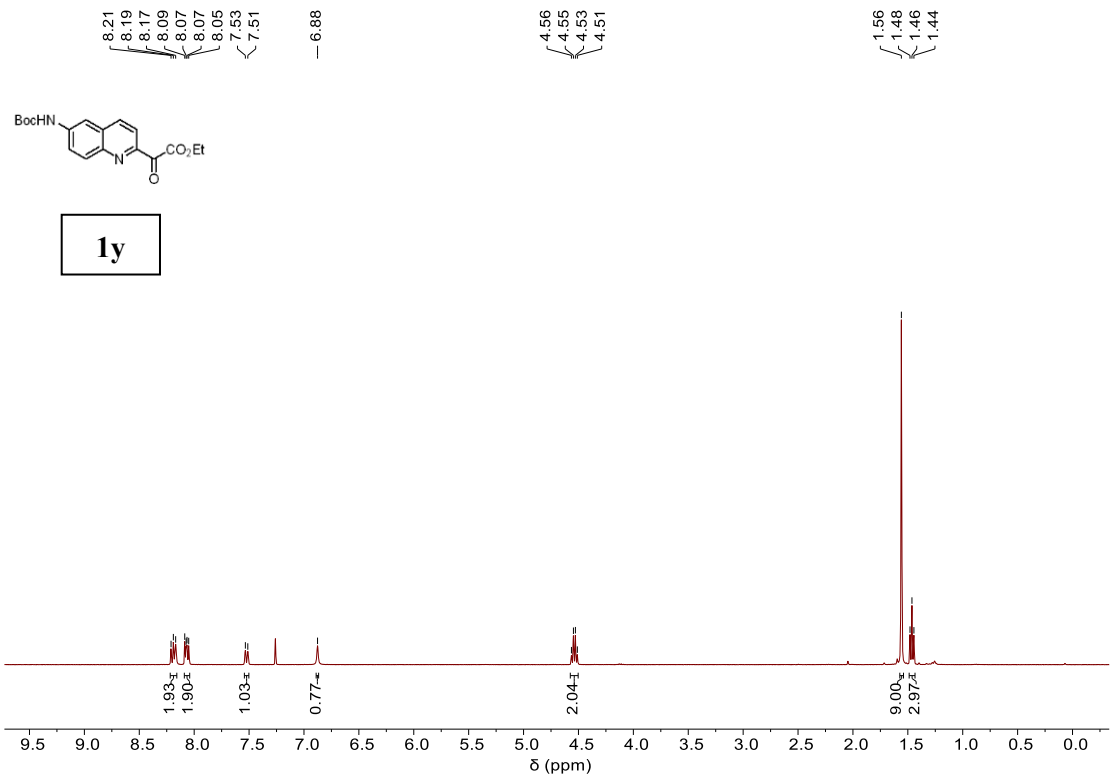

188.30
165.76
149.97
147.51
137.60
131.03
130.59
130.06
129.74
127.87
118.61
62.25
14.31
CO2Et
O
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)


8.22
8.20
8.09
8.07
8.05
7.63
7.60
4.57
4.55
4.53
4.52
2.57
1.48
1.47
1.45
Me
CO2Et
O
N
1w
1.00
1.94
2.03
2.04
3.22
3.11
δ (ppm)


188.17
165.72
149.13
146.05
140.14
136.52
132.78
130.55
130.03
126.52
118.56
61.96
21.86
14.15
Me
CO2Et
O
N
δ (ppm)


8.19
8.17
8.10
8.10
8.08
8.08
8.07
8.05
7.44
7.43
7.42
7.41
7.12
7.11
4.57
4.55
4.53
4.51
3.97
1.48
1.47
1.45
MeO
CO2Et
O
N
1x
1.00
1.96
0.99
1.02
2.05
2.97
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
δ (ppm)


188.20
166.03
160.45
147.84
143.75
135.81
132.65
131.79
123.85
119.28
104.98
62.14
55.89
14.34
MeO
CO2Et
O
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)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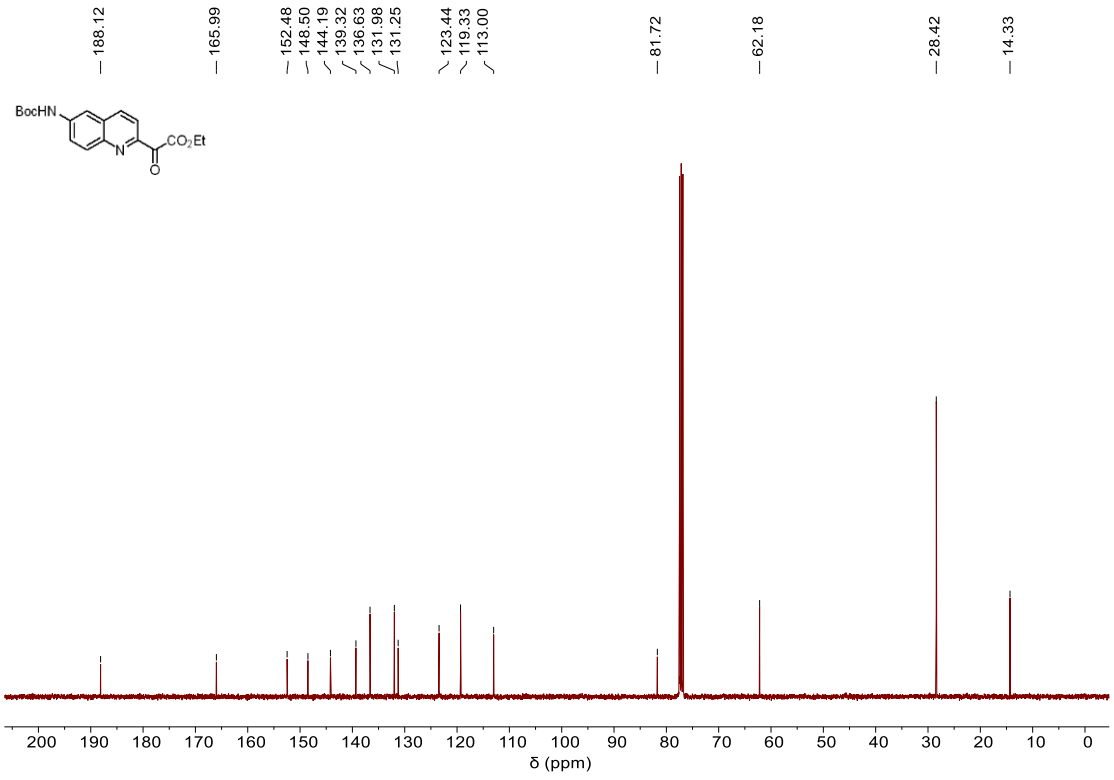
8.19
8.17
8.09
8.07
8.07
8.05
7.53
7.51
6.88
4.56
4.55
4.53
4.51
1.56
1.48
1.46
1.44
BocHN
CO2Et
O
N
1y
1.93
1.90
1.03
0.77
2.04
9.00
2.97
δ (ppm)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152.48
148.50
144.19
139.32
136.63
131.98
131.25
123.44
119.33
113.00
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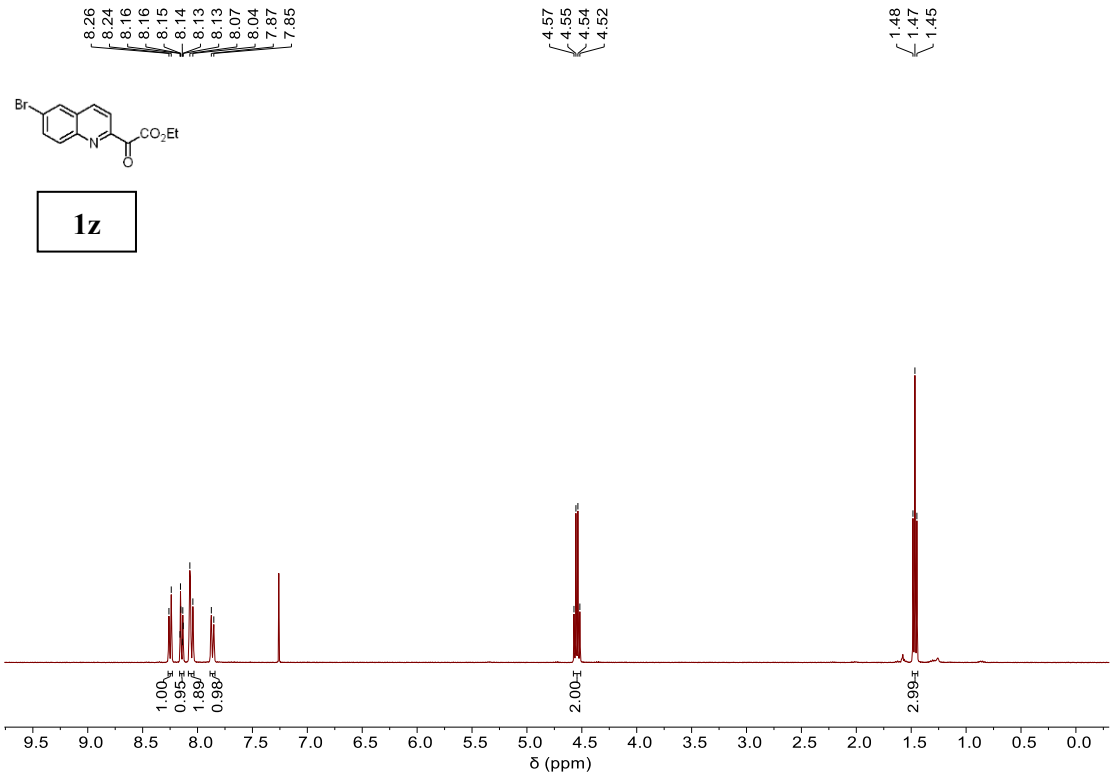
62.18
28.42
14.33
BocHN
CO2Et
O
N
δ (ppm)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8.24
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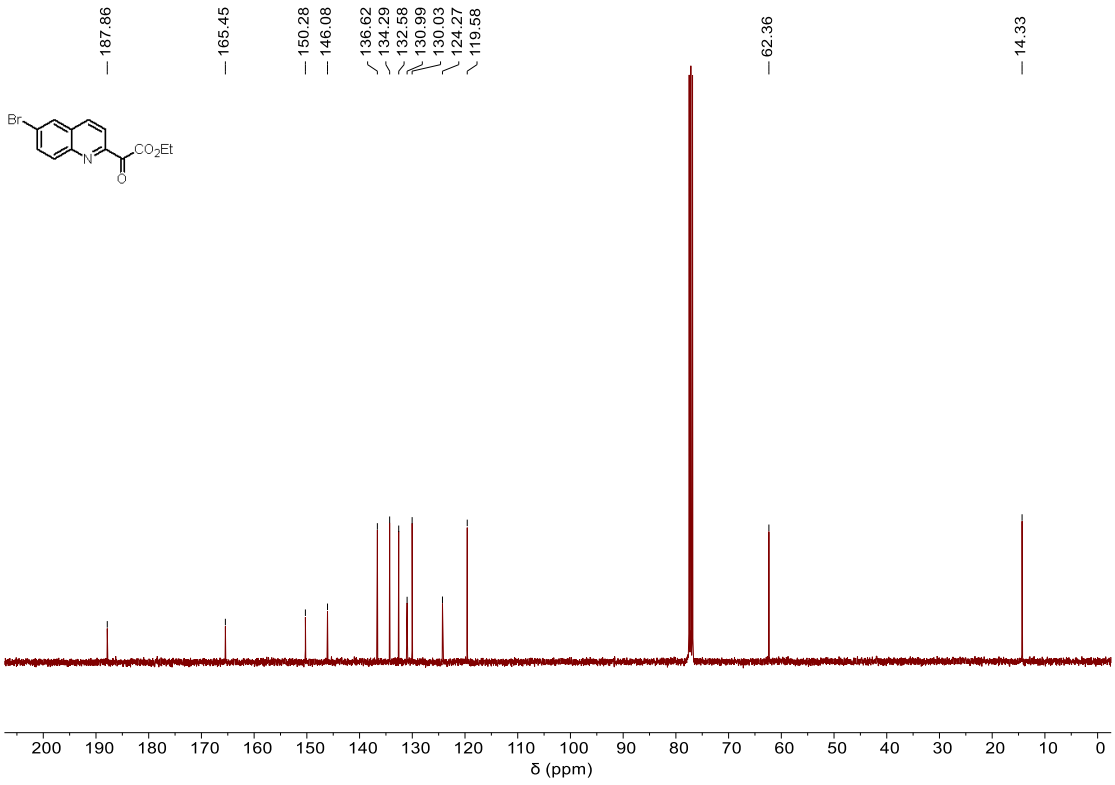
8.16
8.15
8.14
8.13
8.13
8.07
8.04
7.87
7.85
4.57
4.55
4.54
4.52
1.48
1.47
1.45
Br
N
CO2Et
O
1z
1.00
0.95
1.89
0.98
2.00
2.99
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)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146.08
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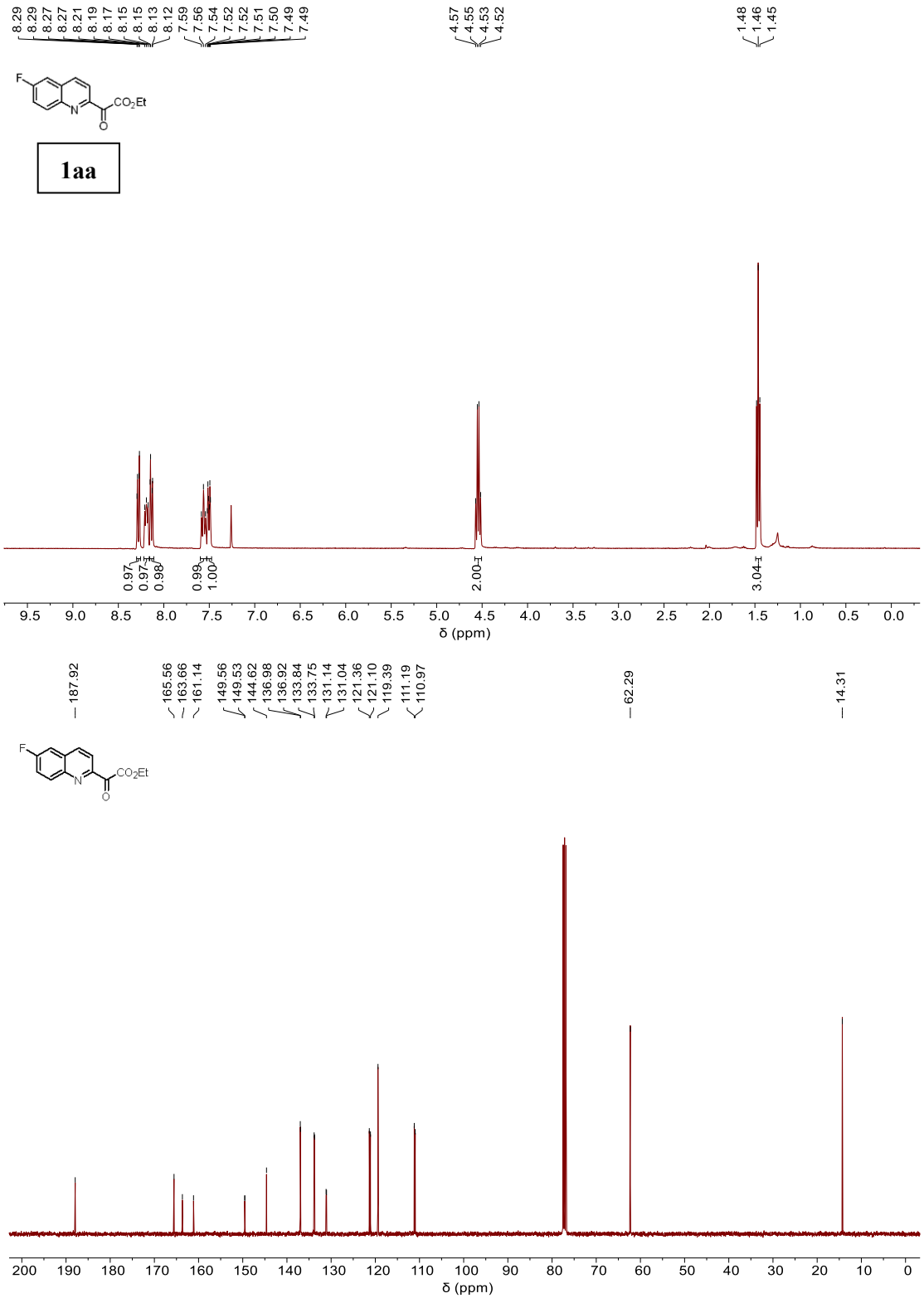
134.29
132.58
130.99
130.03
124.27
119.58
62.36
14.33
Br
N
CO2Et
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)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8.19
8.17
8.15
8.15
8.13
8.12
7.59
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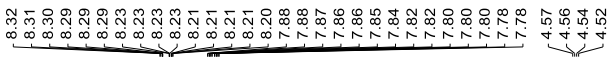
7.54
7.52
7.52
7.51
7.50
7.49
7.49
4.57
4.55
4.53
4.52
1.48
1.46
1.45
F
N
CO2Et
O
1aa
0.97
0.97
0.98
0.99
1.00
2.00
3.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)
187.92
165.56
163.66
161.14
149.56
149.53
144.62
136.98
136.92
133.84
133.75
131.14
131.04
121.36
121.10
119.39
111.19
110.97
62.29
14.31
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)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8.31
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8.29
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8.29
8.23
8.23
8.23
8.23
8.21
8.21
8.21
8.21
8.20
7.88
7.88
7.87
7.86
7.86
7.85
7.84
7.82
7.82
7.80
7.80
7.80
7.78
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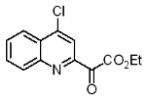
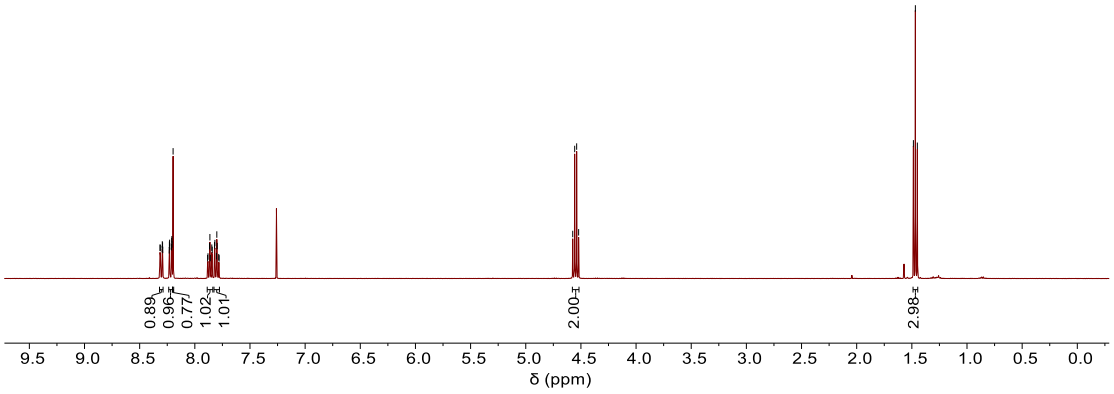
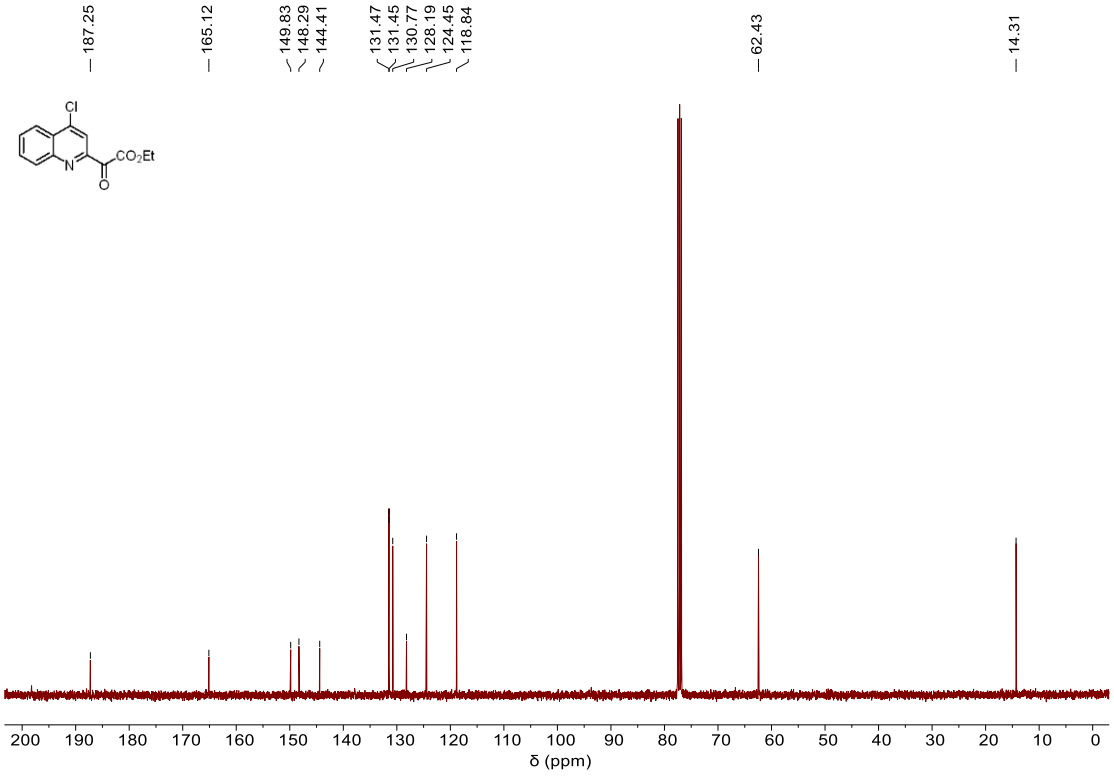
4.56
4.54
4.52
1.49
1.47
1.45


Cl
N
CO2Et
O

1ab


0.89
0.96
0.77
1.02
1.01
2.00
2.98
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
δ (ppm)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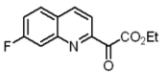
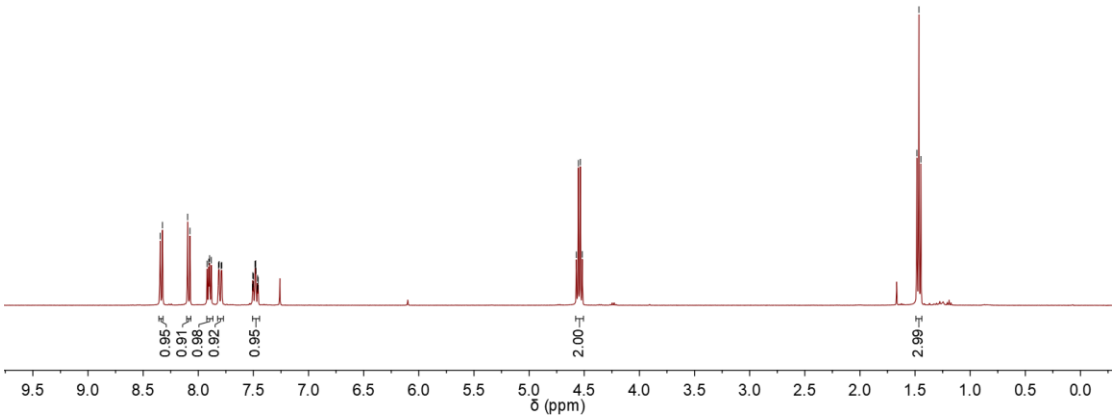
165.12
149.83
148.29
144.41
131.47
131.45
130.77
128.19
124.45
118.84
62.43
14.31
Cl
N
CO2Et
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)


8.35
8.33
8.10
8.08
7.92
7.91
7.90
7.88
7.82
7.81
7.79
7.79
7.51
7.51
7.50
7.50
7.49
7.48
7.48
7.48
7.47
7.46
7.46
7.46
4.57
4.55
4.54
4.52
1.48
1.47
1.45


F
N
CO2Et
O

1ac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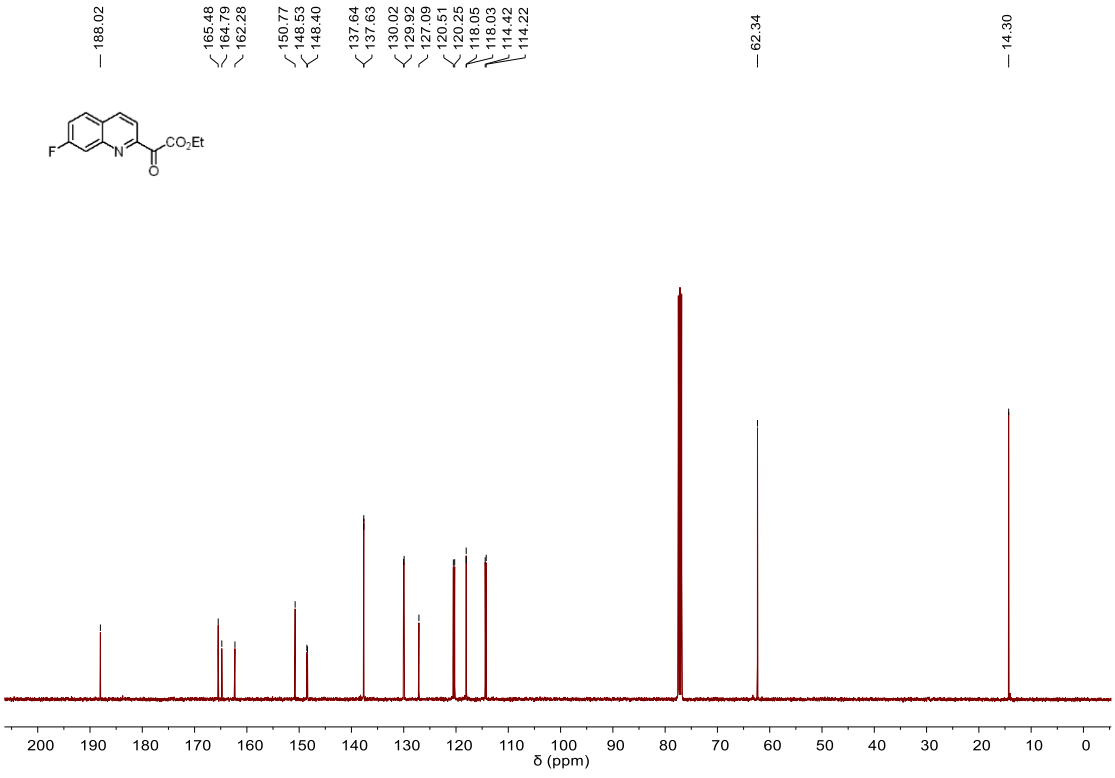
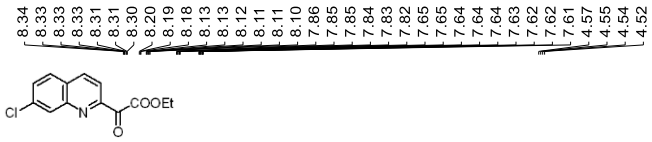
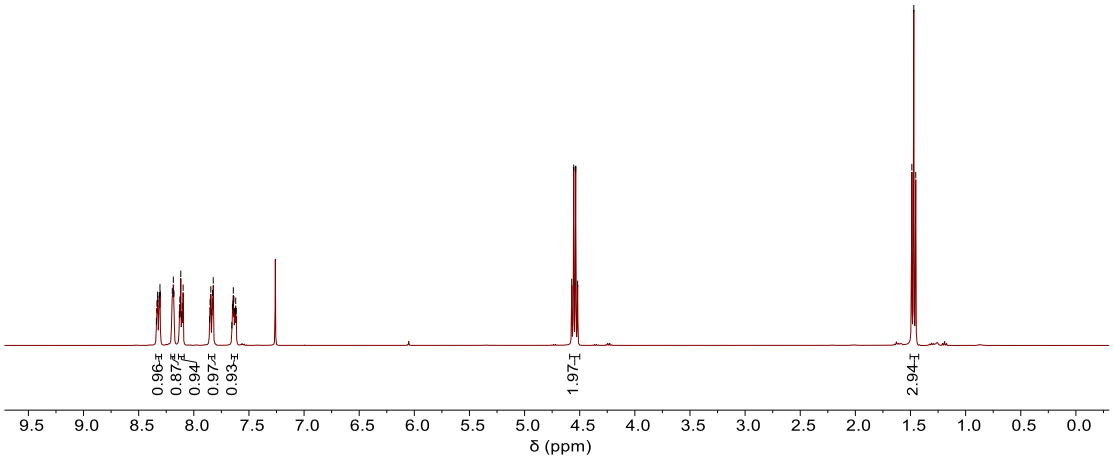
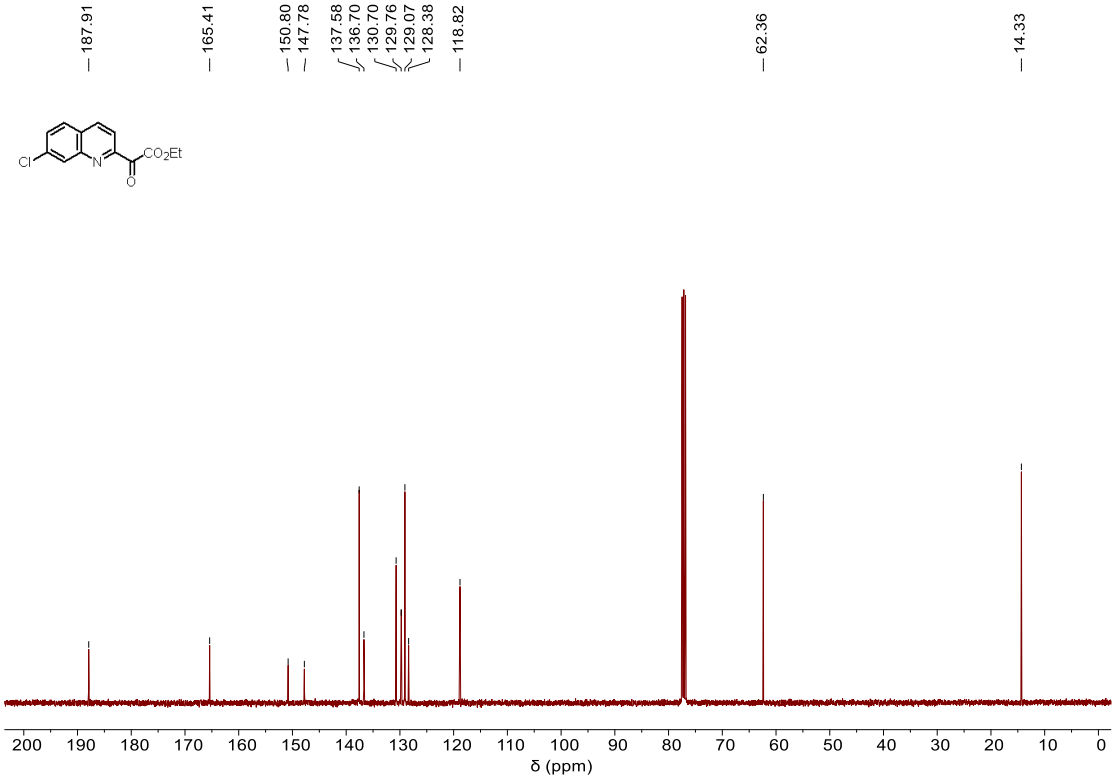
0.91
0.98
0.92
0.95
2.00
2.99
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

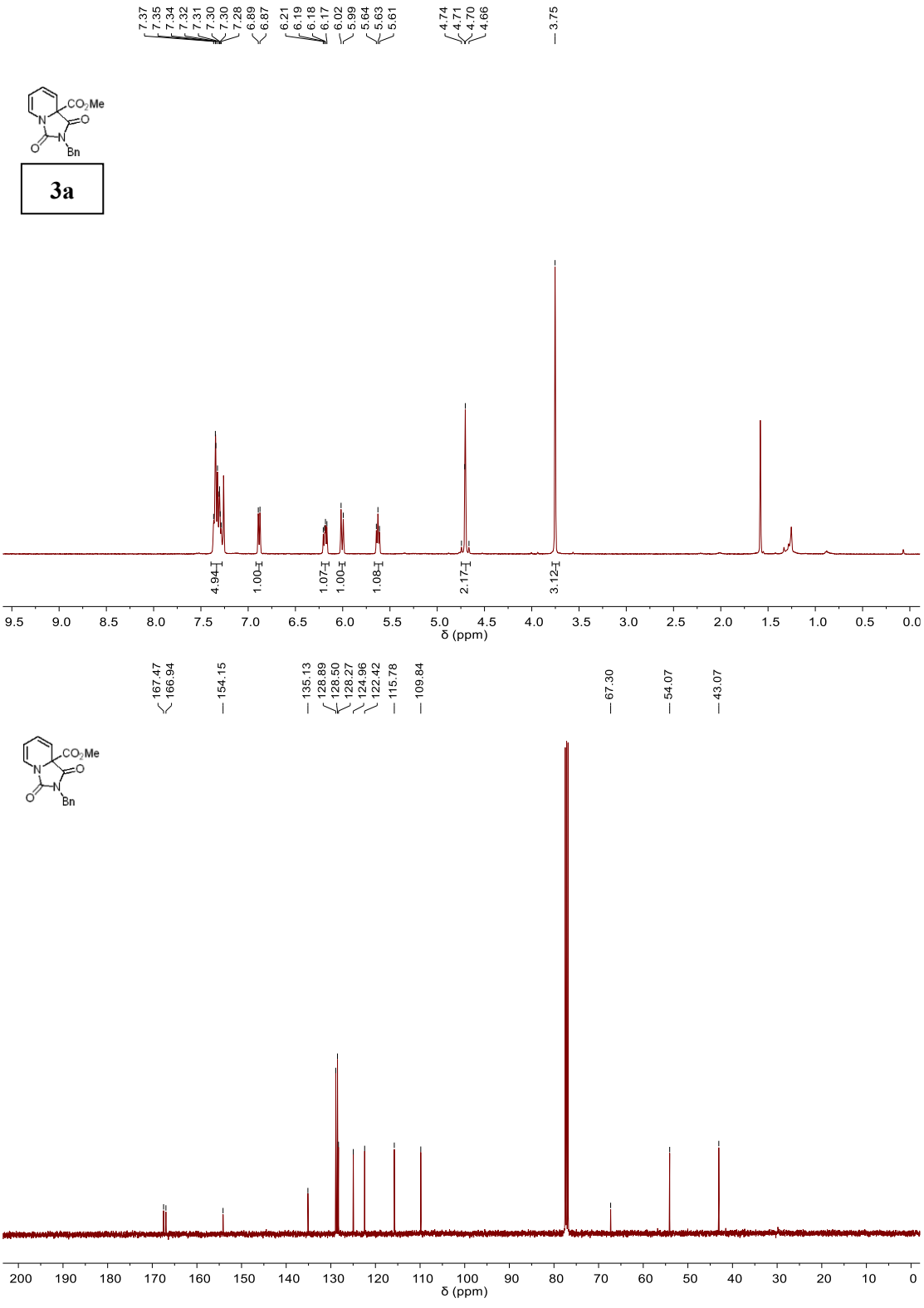

188.02
165.48
164.79
162.28
150.77
148.53
148.40
137.64
137.63
130.02
129.92
127.09
120.51
120.25
118.05
118.03
114.42
114.22
62.34
14.30
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

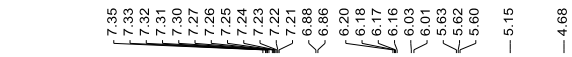

8.34
8.33
8.33
8.33
8.31
8.31
8.30
8.20
8.19
8.18
8.13
8.13
8.12
8.11
8.11
8.10
7.86
7.85
7.85
7.84
7.83
7.82
7.65
7.65
7.64
7.64
7.64
7.63
7.62
7.62
7.61
4.57
4.55
4.54
4.52
1.49
1.47
1.45
Cl
N
COOEt
O

1ad


0.96
0.87
0.94
0.97
0.93
1.97
2.94
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
δ (ppm)


187.91
165.41
150.80
147.78
137.58
136.70
130.70
129.76
129.07
128.38
118.82
62.36
14.33
Cl
N
CO2Et
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)


7.37
7.35
7.34
7.32
7.31
7.30
7.30
7.28
6.89
6.87
6.21
6.19
6.18
6.17
6.02
5.99
5.64
5.63
5.61
4.74
4.71
4.70
4.66
3.75
CO2Me
O
N
O
N
Bn
3a
4.94
1.00
1.07
1.00
1.08
2.17
3.12
δ (ppm)
167.47
166.94
154.15
135.13
128.89
128.50
128.27
124.96
122.42
115.78
109.84
67.30
54.07
43.07
δ (ppm)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7.33
7.32
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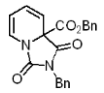
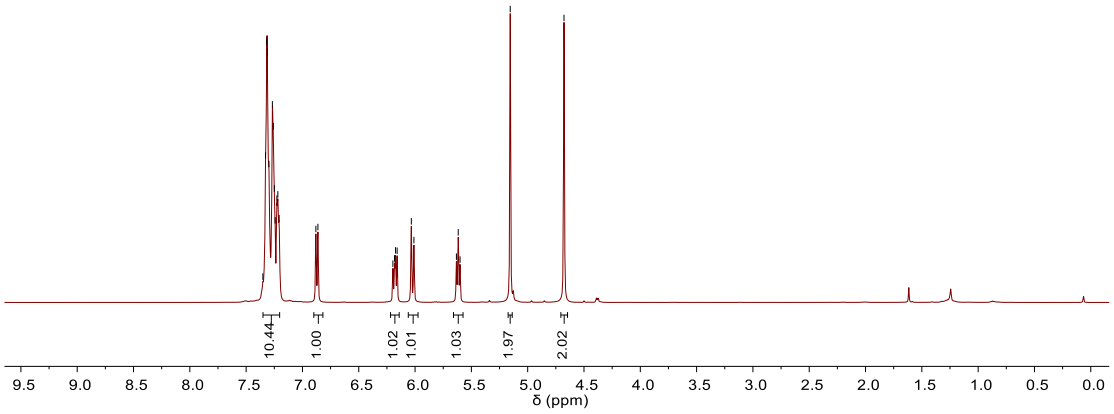
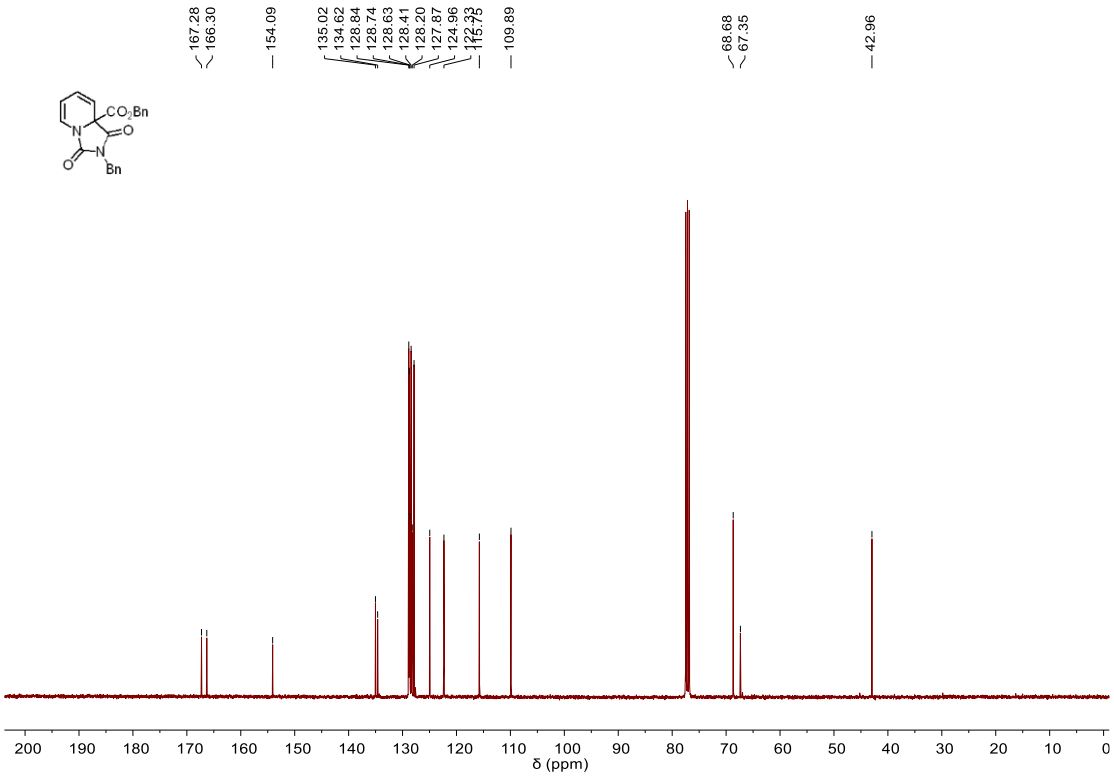
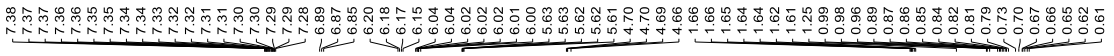
7.27
7.26
7.25
7.24
7.23
7.22
7.21
6.88
6.86
6.20
6.18
6.17
6.16
6.03
6.01
5.63
5.62
5.60
5.15
4.68

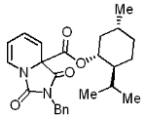

CO2Bn
O
N
N
O
Bn

3b

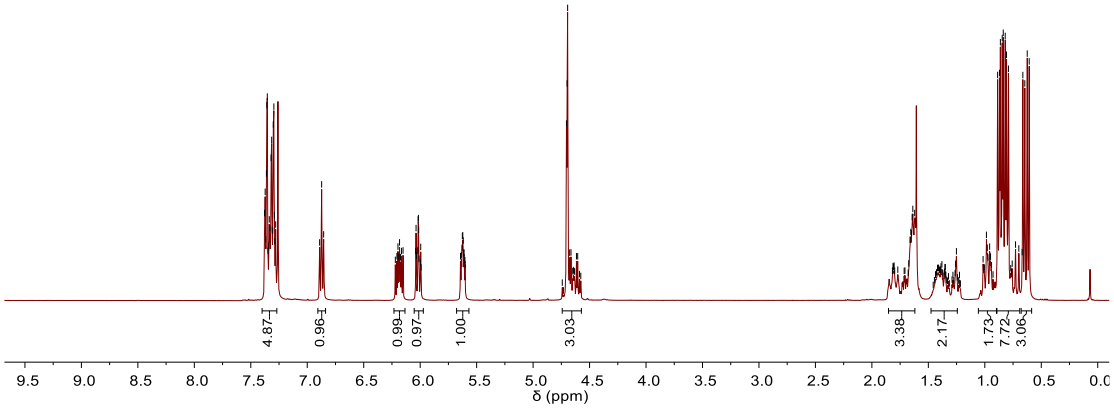

10.44
1.00
1.02
1.01
1.03
1.97
2.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)

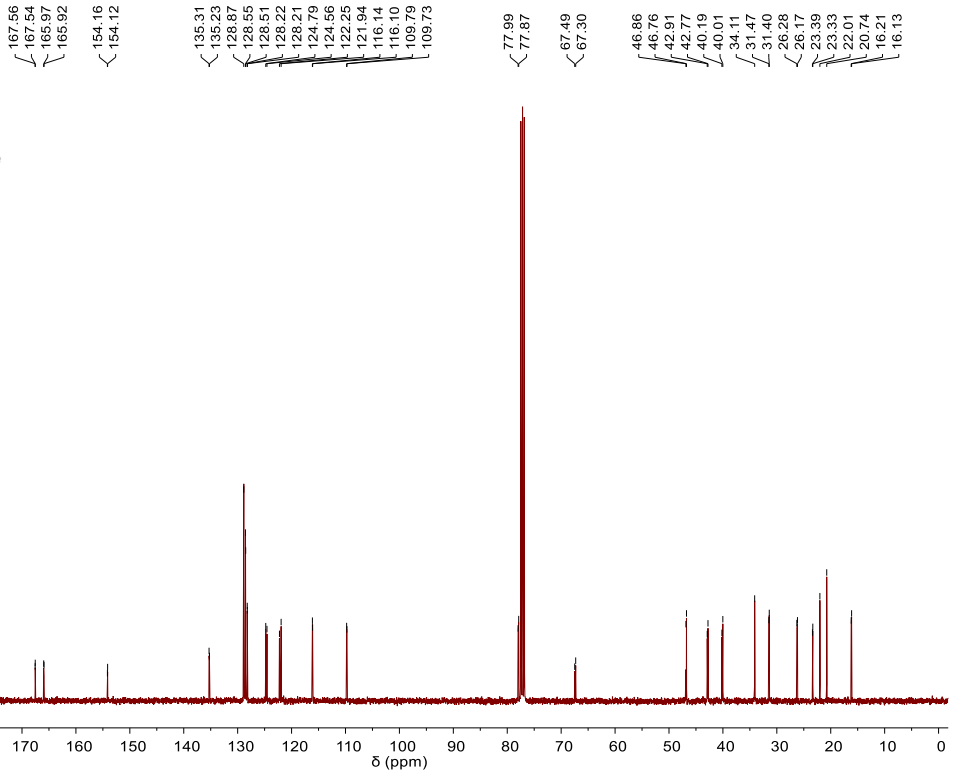

167.28
166.30
154.09
135.02
134.62
128.84
128.74
128.63
128.41
128.20
127.87
124.96
115.75
109.89
68.68
67.35
42.96
CO2Bn
O
N
N
O
Bn
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

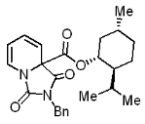

7.38 7.37 7.37 7.36 7.36 7.35 7.35 7.34 7.34 7.33 7.32 7.32 7.31 7.31 7.30 7.30 7.29 7.29 7.28 6.89 6.87 6.85 6.20 6.18 6.17 6.15 6.04 6.04 6.02 6.02 6.02 6.01 6.00 5.63 5.63 5.62 5.62 5.61 4.70 4.69 4.66 1.66 1.66 1.65 1.64 1.64 1.62 1.61 1.25 0.99 0.98 0.96 0.89 0.87 0.86 0.85 0.84 0.82 0.81 0.79 0.73 0.70 0.67 0.66 0.65 0.62 0.61

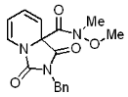

Me
O
O
O
N
O
N
Bn
Me
Me

3c


4.87
0.96
0.99
0.97
1.00
3.03
3.38
2.17
1.73
7.72
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
δ (ppm)

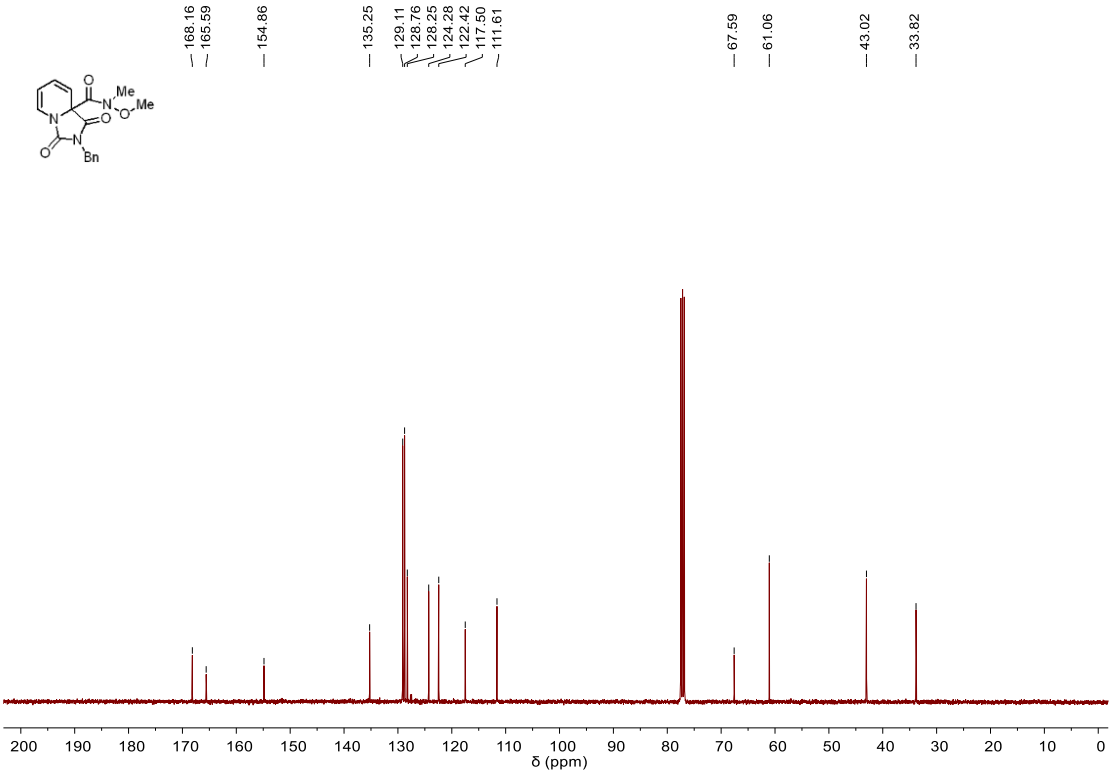

167.56 167.54 165.97 165.92 154.16 154.12 135.31 135.23 128.87 128.55 128.51 128.22 128.21 124.79 124.56 122.25 121.94 116.14 116.10 109.79 109.73 77.99 77.87 67.49 67.30 46.86 46.76 42.91 42.77 40.19 40.01 34.11 31.47 31.40 26.28 26.17 23.39 23.33 22.01 20.74 16.21 16.13
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

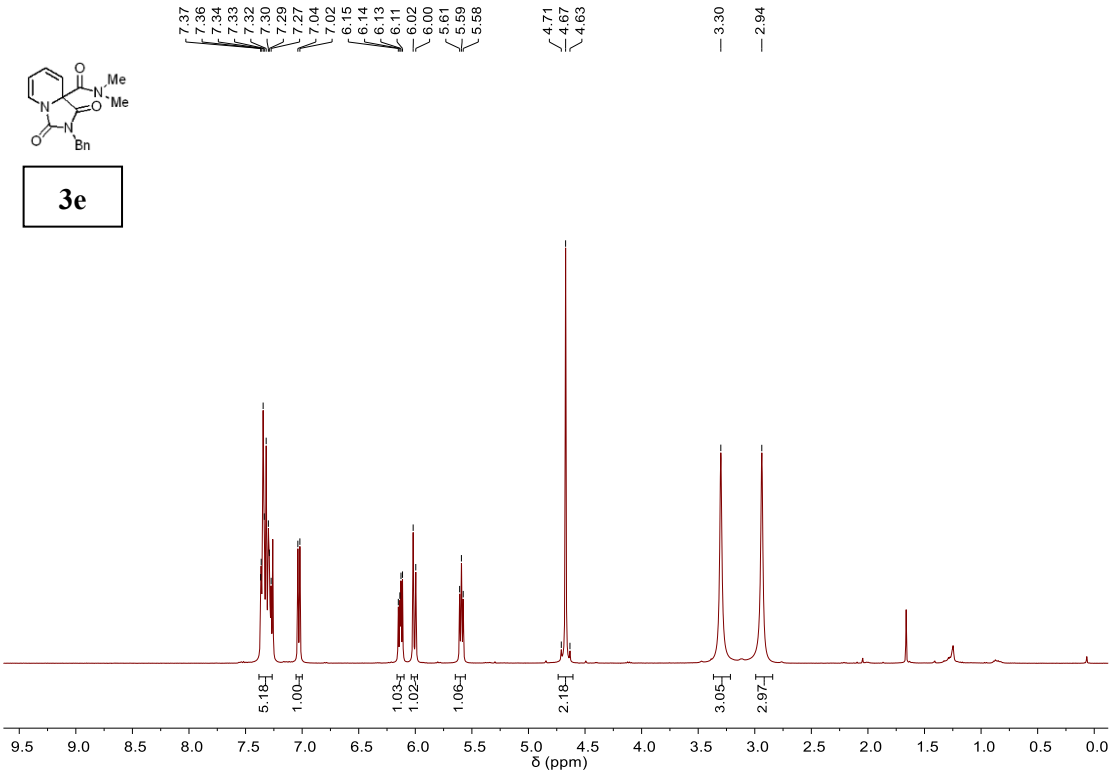

Me
O
O
O
N
O
N
Bn
Me
Me



3d

7.42
7.42
7.41
7.40
7.34
7.33
7.32
7.30
7.28
6.85
6.83
6.23
6.22
6.21
6.20
5.96
5.96
5.96
5.94
5.72
5.71
5.70
5.68
5.68
4.72
4.69
4.68
4.64
3.39
3.15
2.00
3.16
1.00
1.11
1.02
1.09
2.28
3.20
3.15
δ (ppm)


168.16
165.59
154.86
135.25
129.11
128.76
128.25
124.28
122.42
117.50
111.61
67.59
61.06
43.02
33.82
δ (ppm)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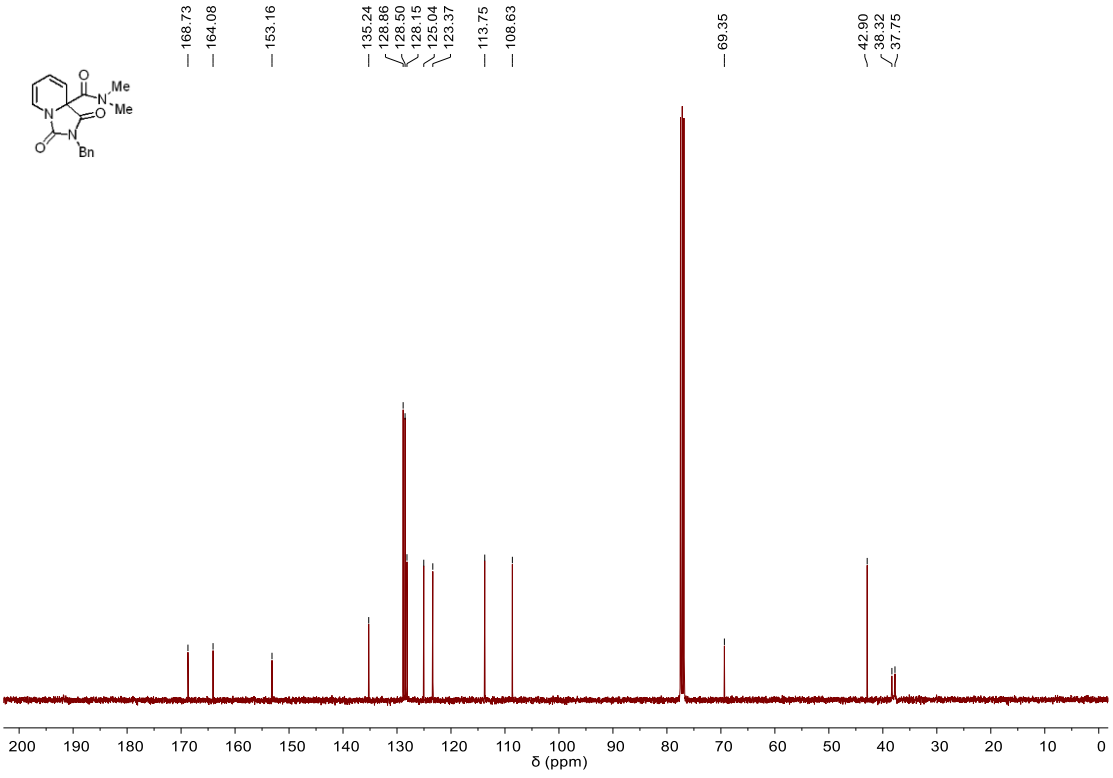
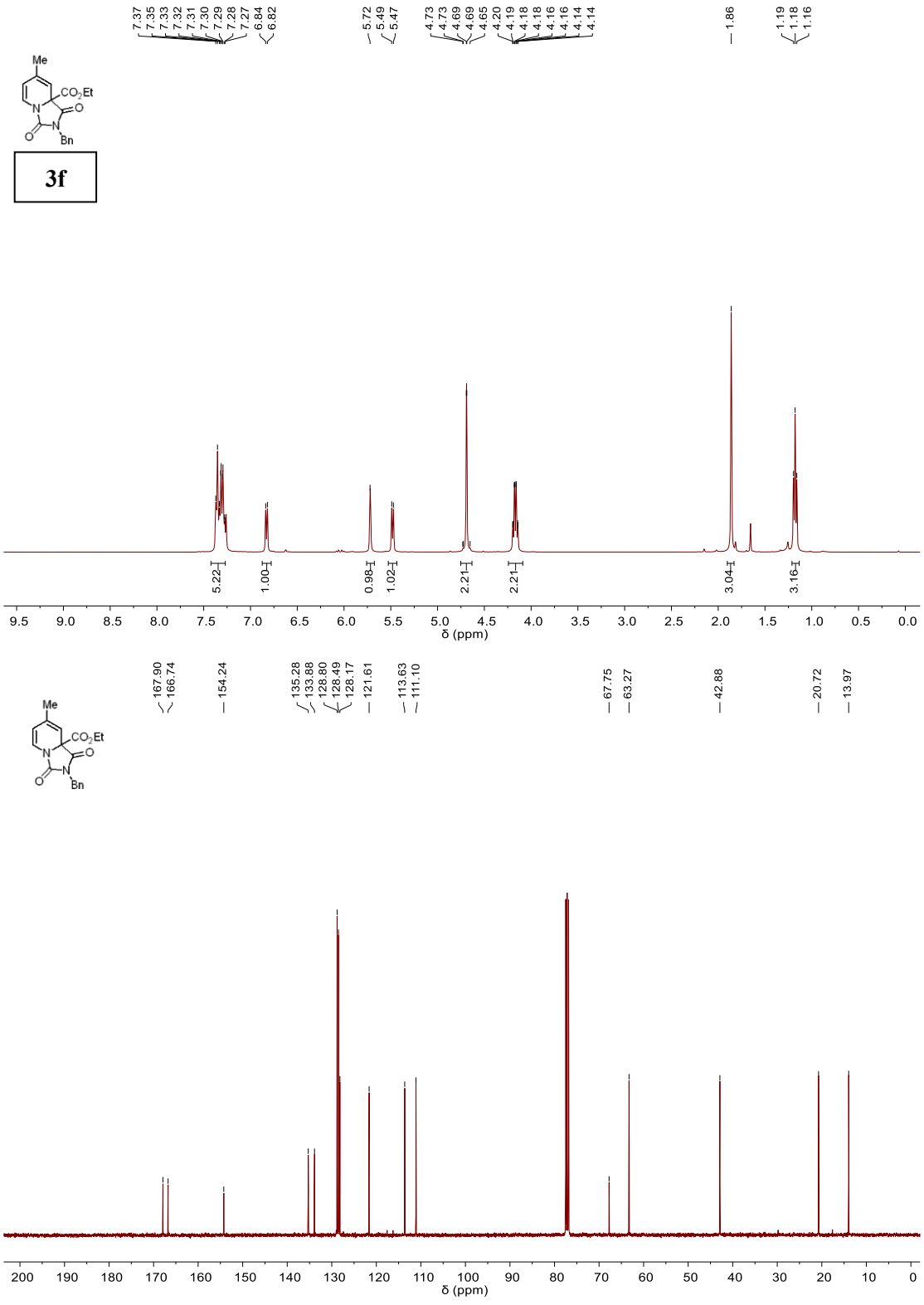
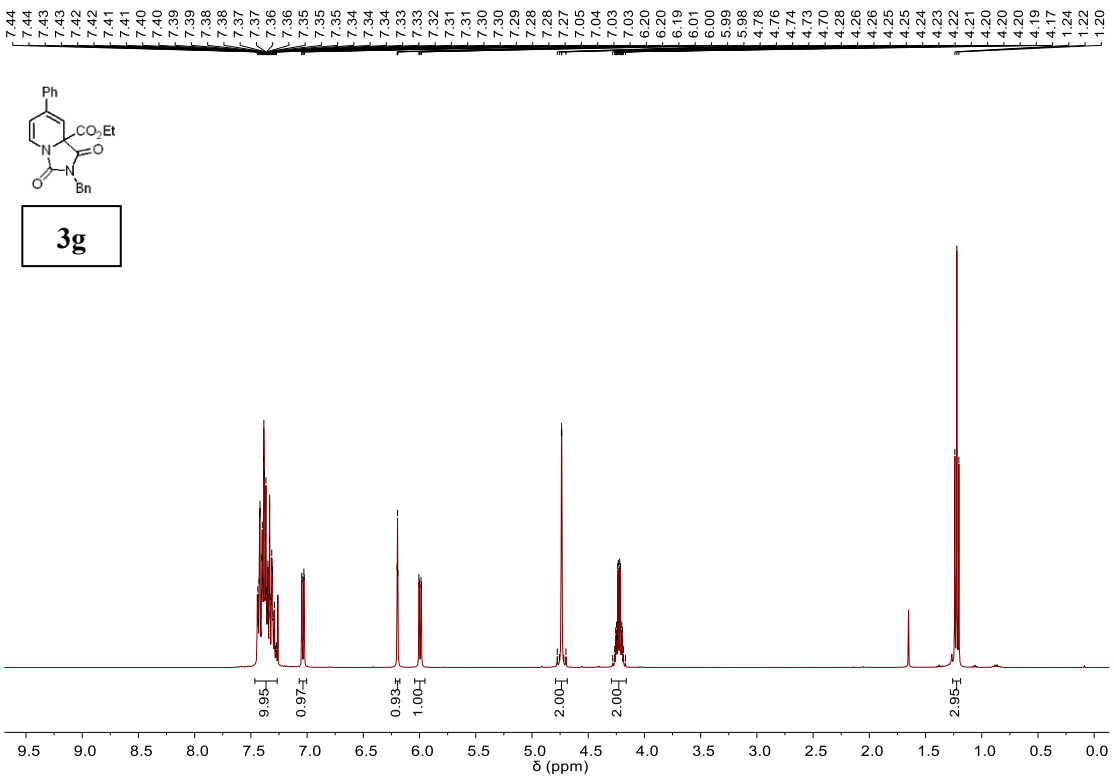
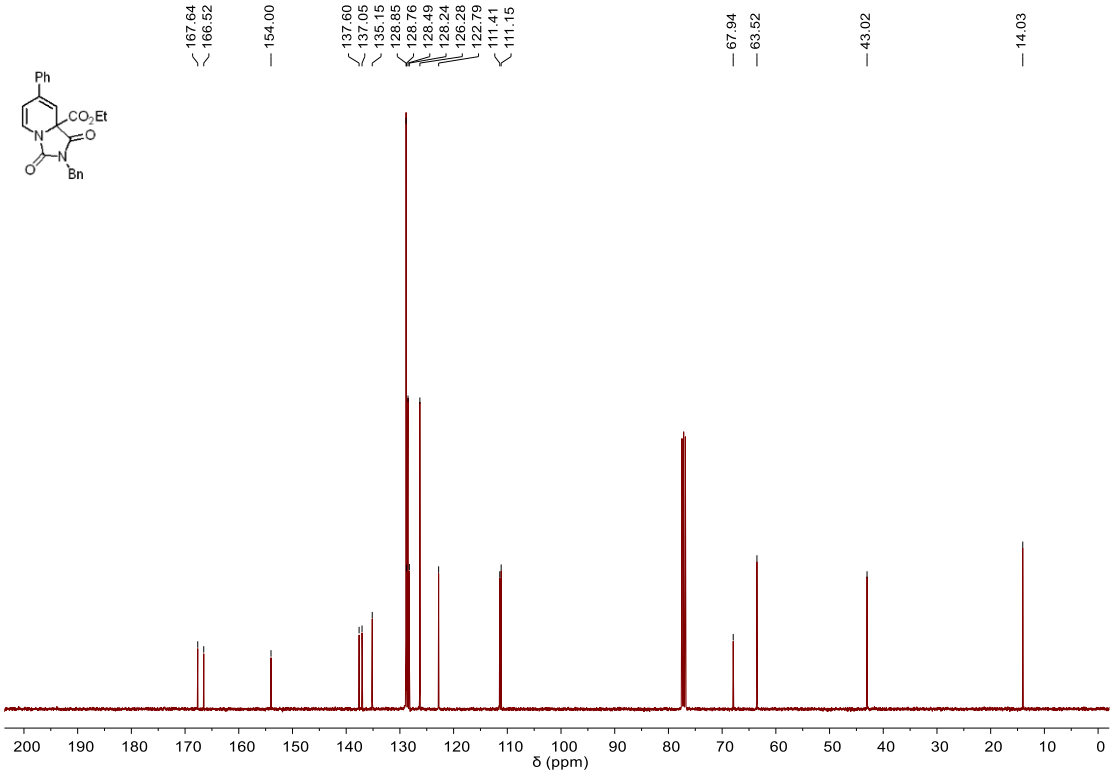
7.36
7.34
7.33
7.32
7.30
7.29
7.27
7.04
7.02
6.15
6.14
6.13
6.11
6.02
6.00
5.61
5.59
5.58
4.71
4.67
4.63
3.30
2.94
Me
Me
Bn
3e
5.18
1.00
1.03
1.02
1.06
2.18
3.05
2.97
δ (ppm)


168.73
164.08
153.16
135.24
128.86
128.50
128.15
125.04
123.37
113.75
108.63
69.35
42.90
38.32
37.75
Me
Me
Bn
δ (ppm)


7.37
7.35
7.33
7.32
7.31
7.30
7.29
7.28
7.27
6.84
6.82
5.72
5.49
5.47
4.73
4.73
4.69
4.69
4.65
4.20
4.19
4.18
4.18
4.16
4.16
4.14
4.14
1.86
1.19
1.18
1.16
Me
CO2Et
O
N
N
O
Bn
3f
5.22
1.00
0.98
1.02
2.21
2.21
3.04
3.16
δ (ppm)
167.90
166.74
154.24
135.28
133.88
128.80
128.49
128.17
121.61
113.63
111.10
67.75
63.27
42.88
20.72
13.97
δ (ppm)


7.44 7.44 7.43 7.43 7.42 7.42 7.41 7.41 7.40 7.40 7.39 7.38 7.38 7.37 7.37 7.36 7.36 7.35 7.35 7.35 7.34 7.34 7.34 7.33 7.33 7.32 7.31 7.31 7.30 7.30 7.29 7.28 7.28 7.27 7.05 7.04 7.03 7.03 6.20 6.20 6.19 6.01 6.00 5.99 5.98 4.78 4.76 4.74 4.73 4.70 4.28 4.26 4.26 4.25 4.25 4.24 4.23 4.22 4.21 4.20 4.20 4.20 4.19 4.17 1.24 1.22 1.20
Ph
CO2Et
O
N
O
N
Bn
3g
9.95
0.97
0.93
1.00
2.00
2.00
2.95
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
δ (ppm)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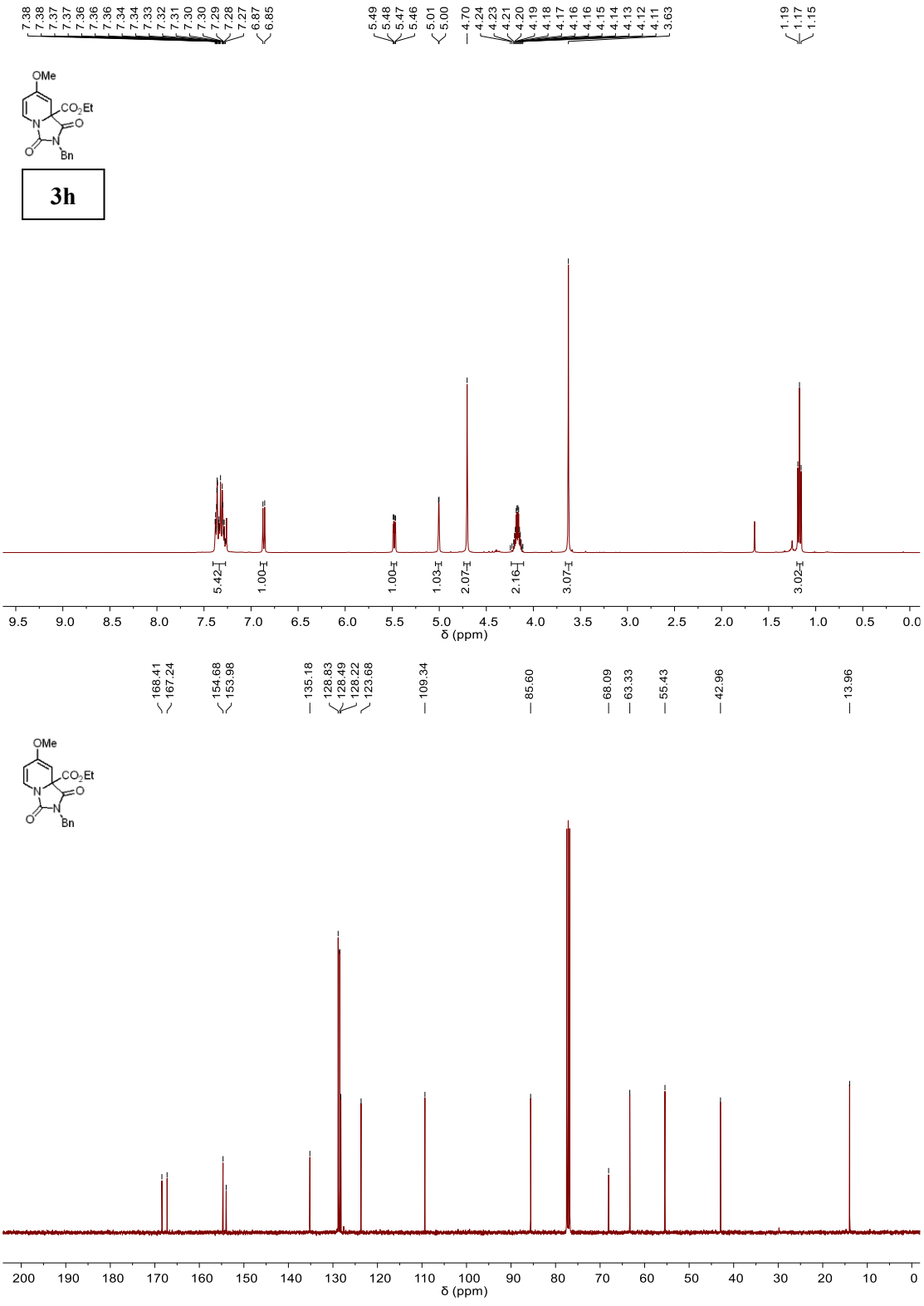
137.05
135.15
128.85
128.76
128.49
128.24
126.28
122.79
111.41
111.15
67.94
63.52
43.02
14.03
Ph
CO2Et
O
N
O
N
Bn
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)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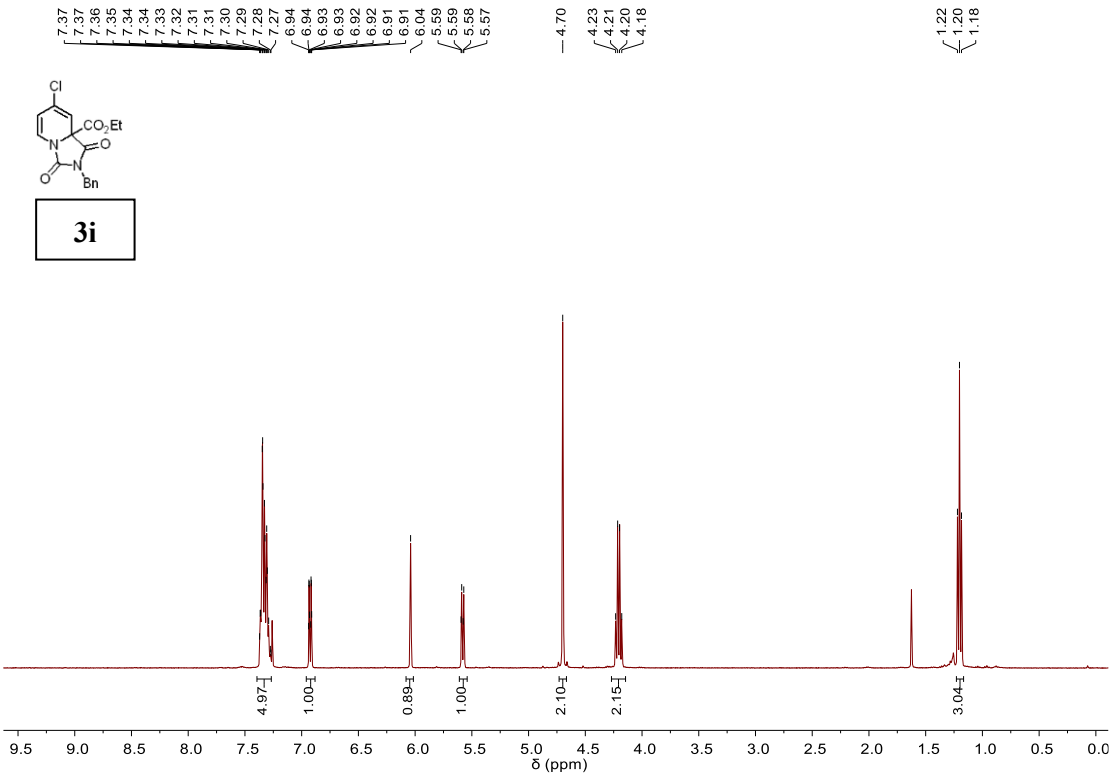
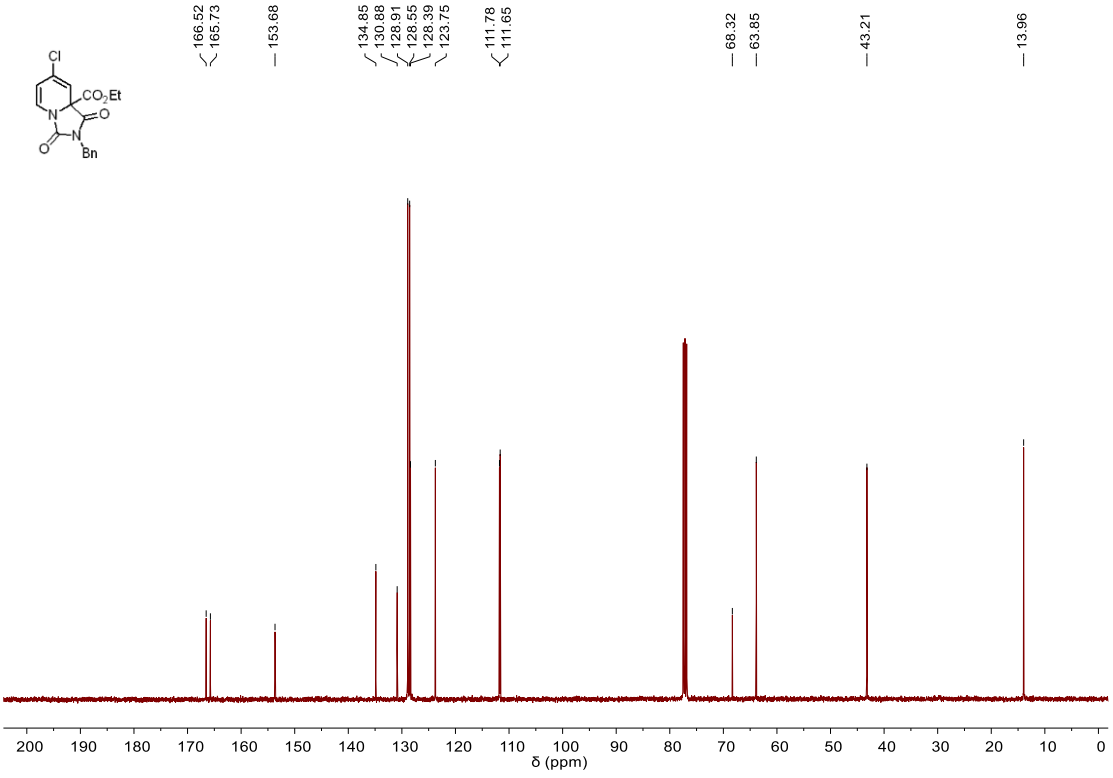
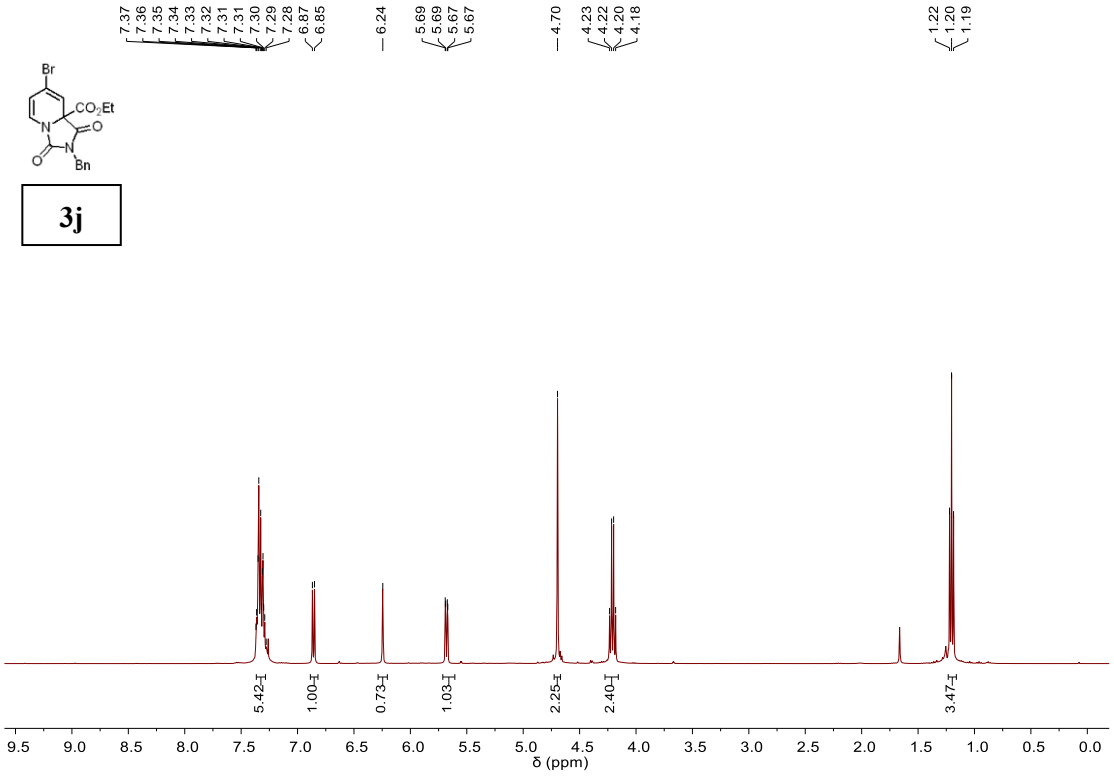
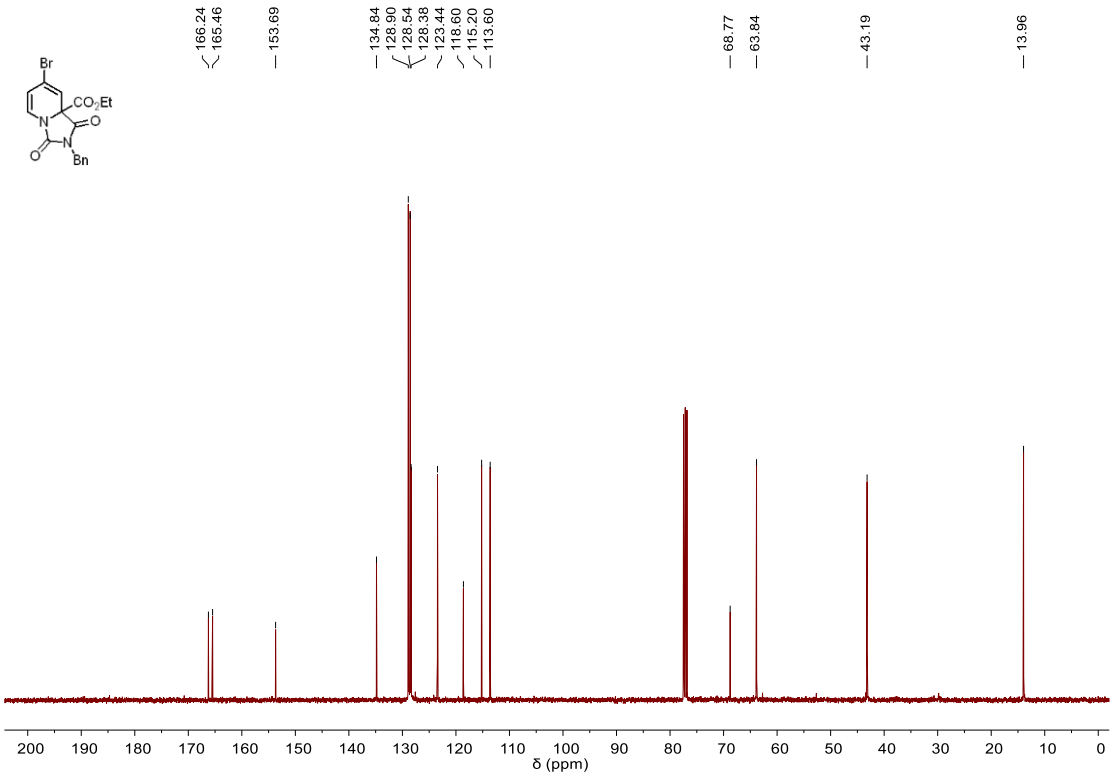
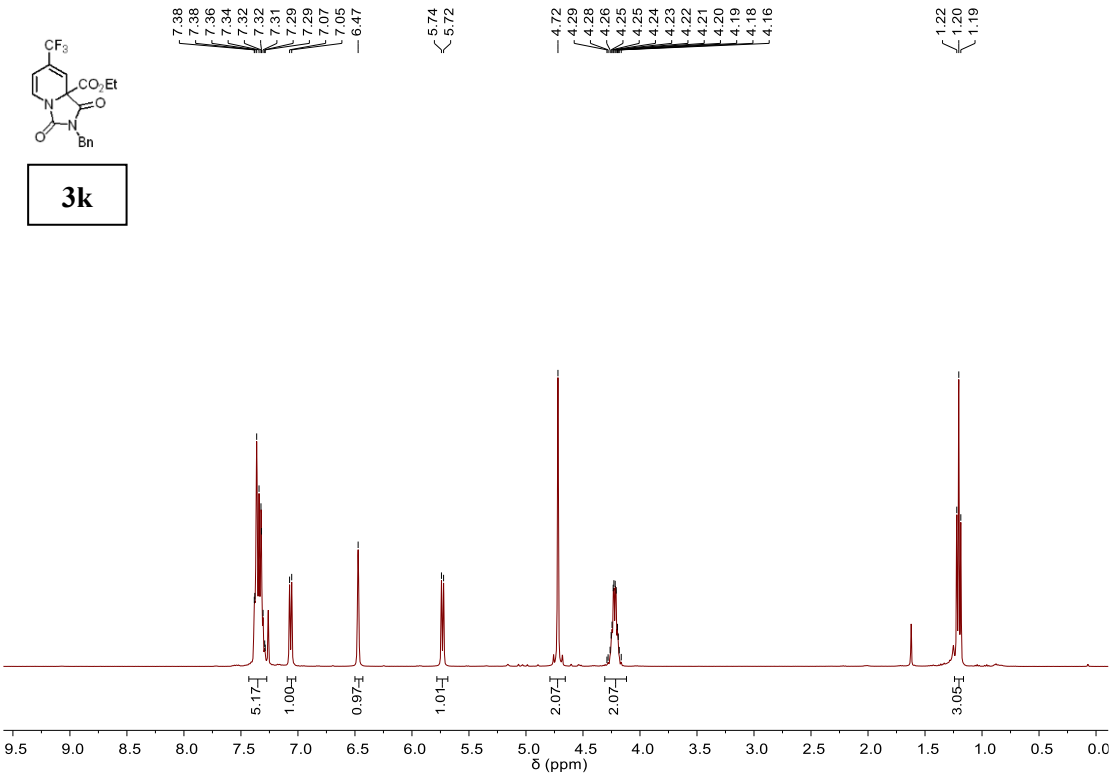
7.36
7.36
7.36
7.34
7.34
7.33
7.32
7.31
7.30
7.30
7.29
7.28
7.27
6.87
6.85
5.49
5.48
5.47
5.46
5.01
5.00
4.70
4.24
4.23
4.21
4.20
4.19
4.18
4.17
4.16
4.16
4.15
4.14
4.13
4.12
4.11
3.63
1.19
1.17
1.15
OMe
CO2Et
O
N
O
N
Bn
3h
5.42
1.00
1.00
1.03
2.07
2.16
3.07
3.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)
168.41
167.24
154.68
153.98
135.18
128.83
128.49
128.22
123.68
109.34
85.60
68.09
63.33
55.43
42.96
13.96
OMe
CO2Et
O
N
O
N
Bn
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)


7.37
7.37
7.36
7.35
7.34
7.34
7.33
7.32
7.31
7.31
7.30
7.29
7.28
7.27
6.94
6.94
6.93
6.93
6.92
6.92
6.91
6.91
6.04
5.59
5.59
5.58
5.57
4.70
4.23
4.21
4.20
4.18
1.22
1.20
1.18
Cl
CO2Et
O
N
O
N
Bn
3i
4.97
1.00
0.89
1.00
2.10
2.15
3.04
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
δ (ppm)

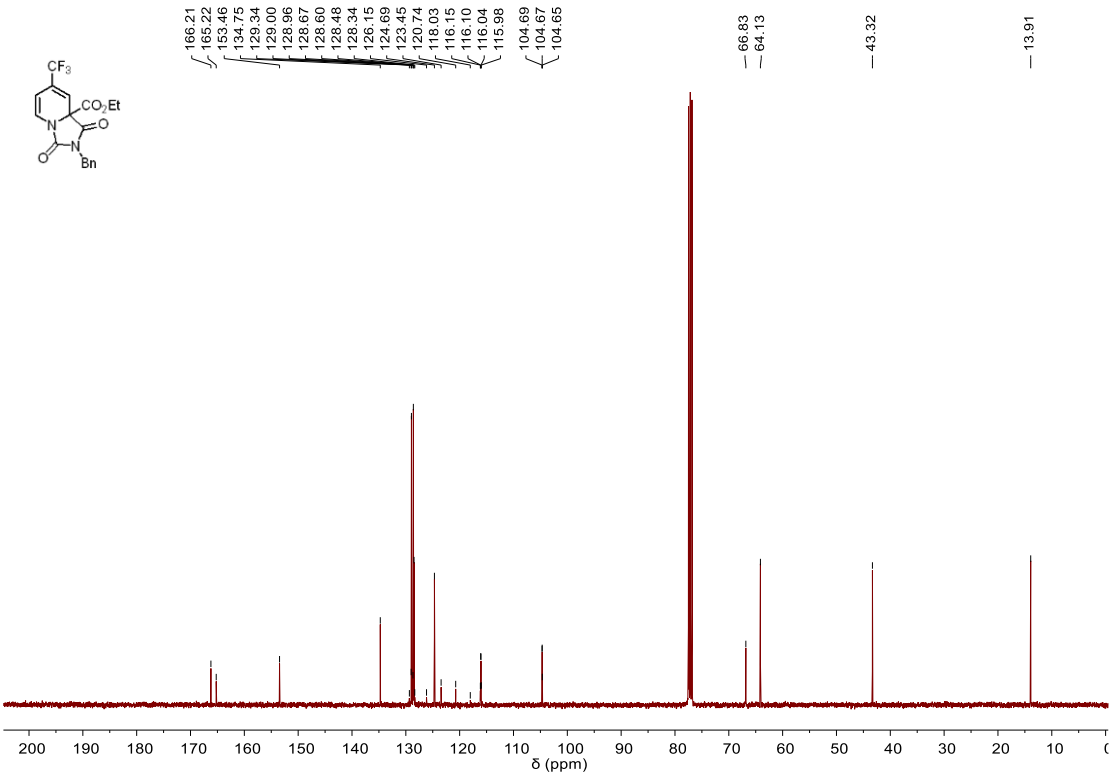

166.52
165.73
153.68
134.85
130.88
128.91
128.55
128.39
123.75
111.78
111.65
68.32
63.85
43.21
13.96
Cl
CO2Et
O
N
O
N
Bn
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)


7.37
7.36
7.35
7.34
7.33
7.32
7.31
7.31
7.30
7.29
7.28
6.87
6.85
6.24
5.69
5.69
5.67
5.67
4.70
4.23
4.22
4.20
4.18
1.22
1.20
1.19
Br
CO2Et
O
N
N
O
Bn
3j
5.42
1.00
0.73
1.03
2.25
2.40
3.47
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
δ (ppm)


166.24
165.46
153.69
134.84
128.90
128.54
128.38
123.44
118.60
115.20
113.60
68.77
63.84
43.19
13.96
Br
CO2Et
O
N
N
O
Bn
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)


7.38
7.38
7.36
7.34
7.32
7.32
7.31
7.29
7.29
7.07
7.05
6.47
5.74
5.72
4.72
4.29
4.28
4.26
4.25
4.25
4.24
4.23
4.22
4.21
4.20
4.19
4.18
4.16
1.22
1.20
1.19
CF3
CO2Et
O
N
O
N
Bn
5.17
1.00
0.97
1.01
2.07
2.07
3.05
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
δ (ppm)

3k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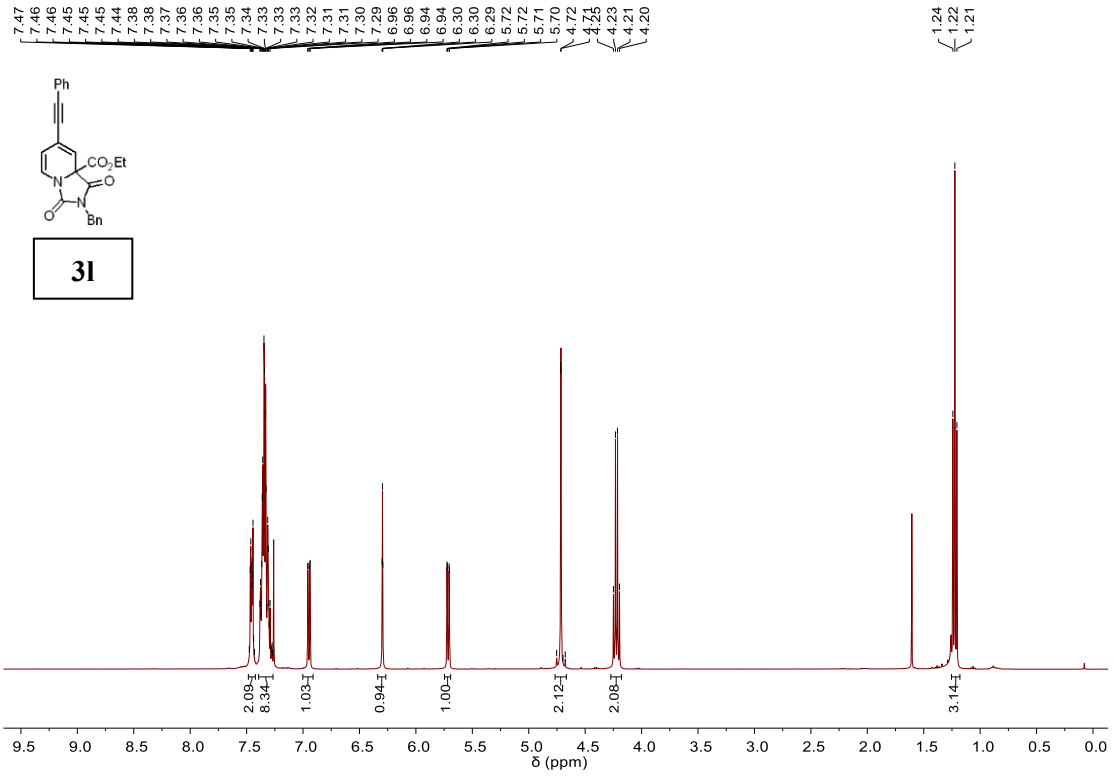
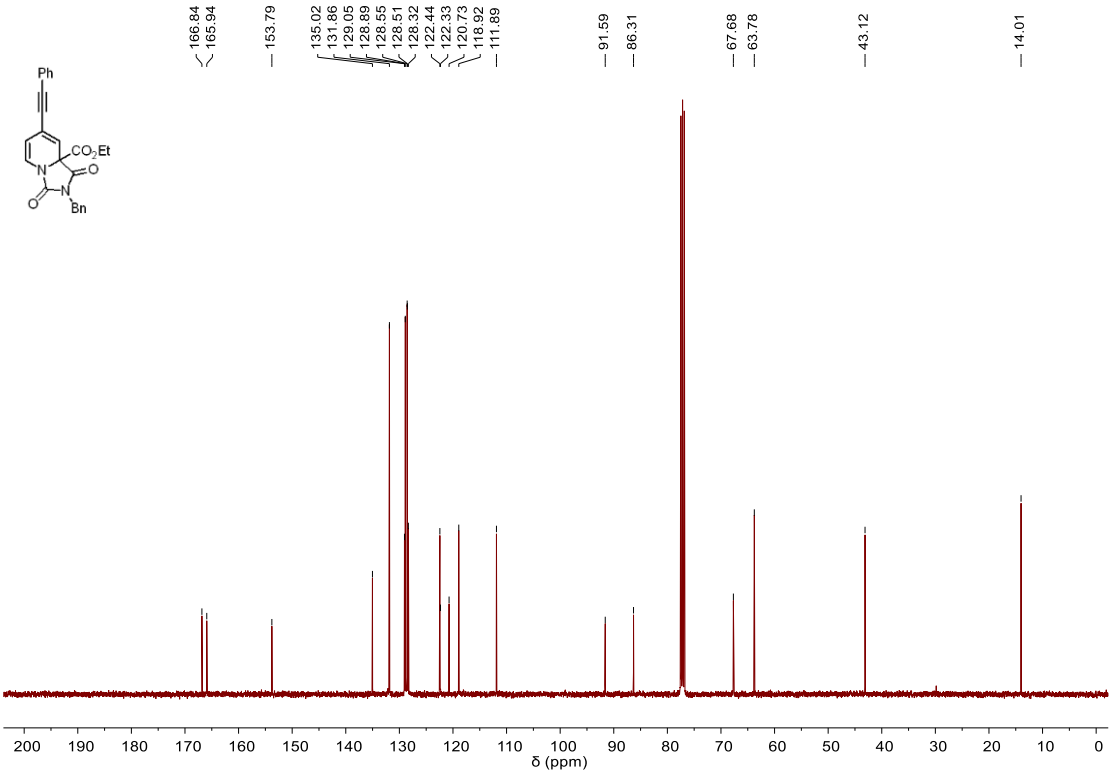
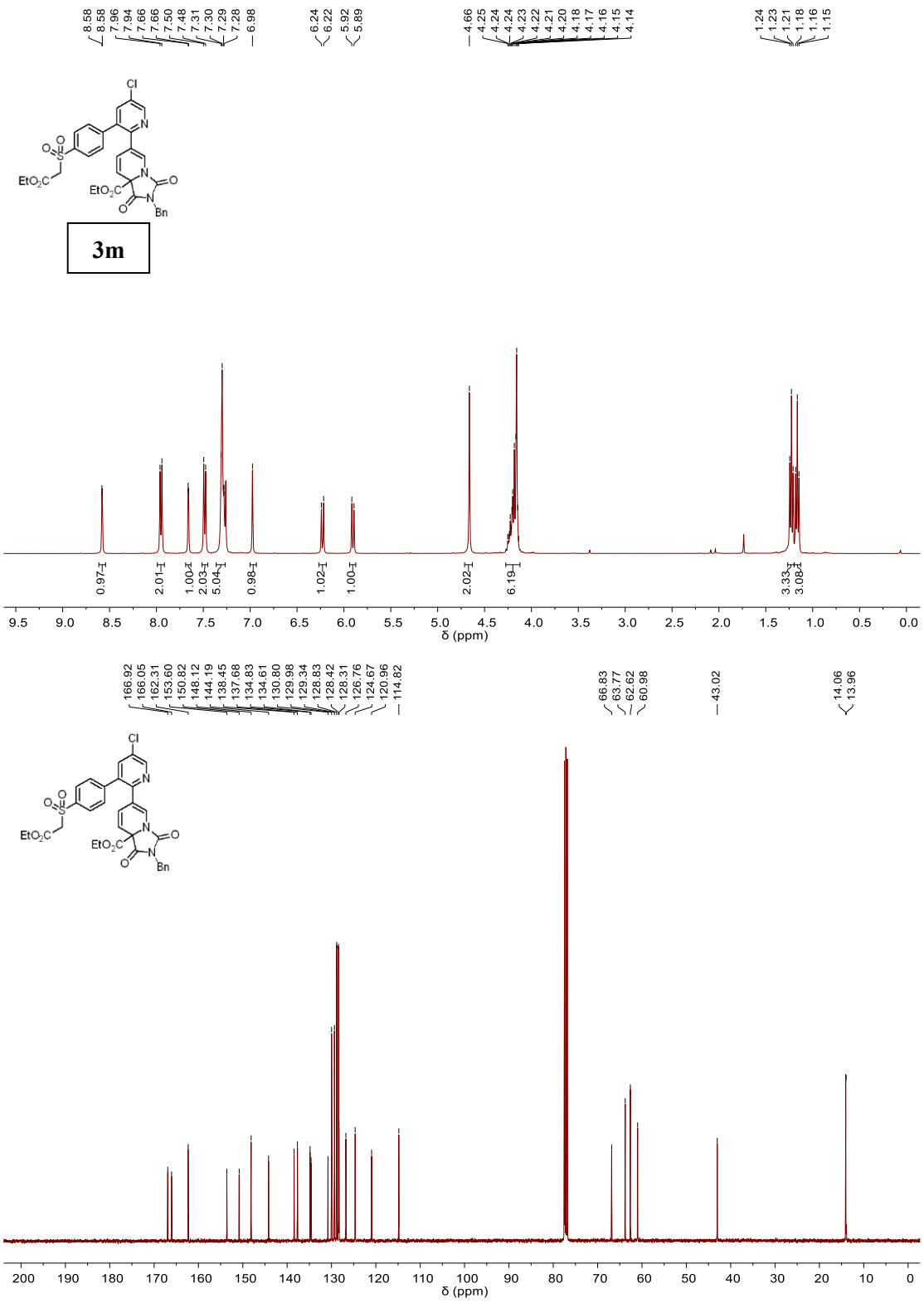
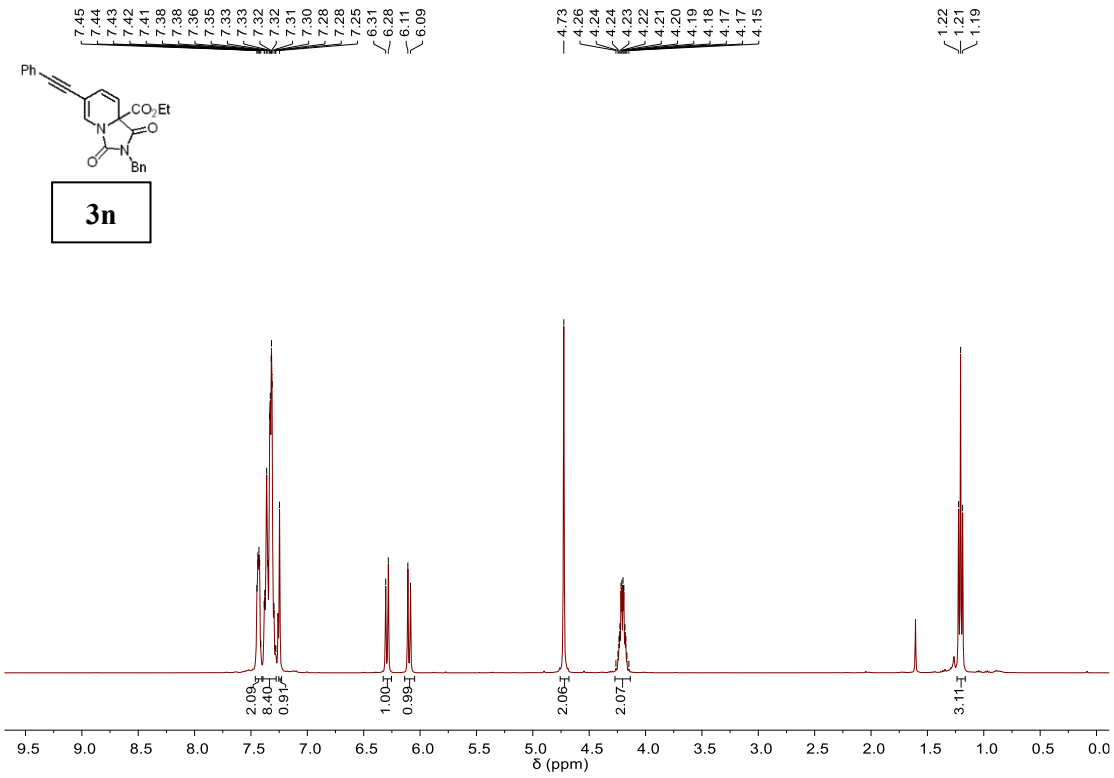
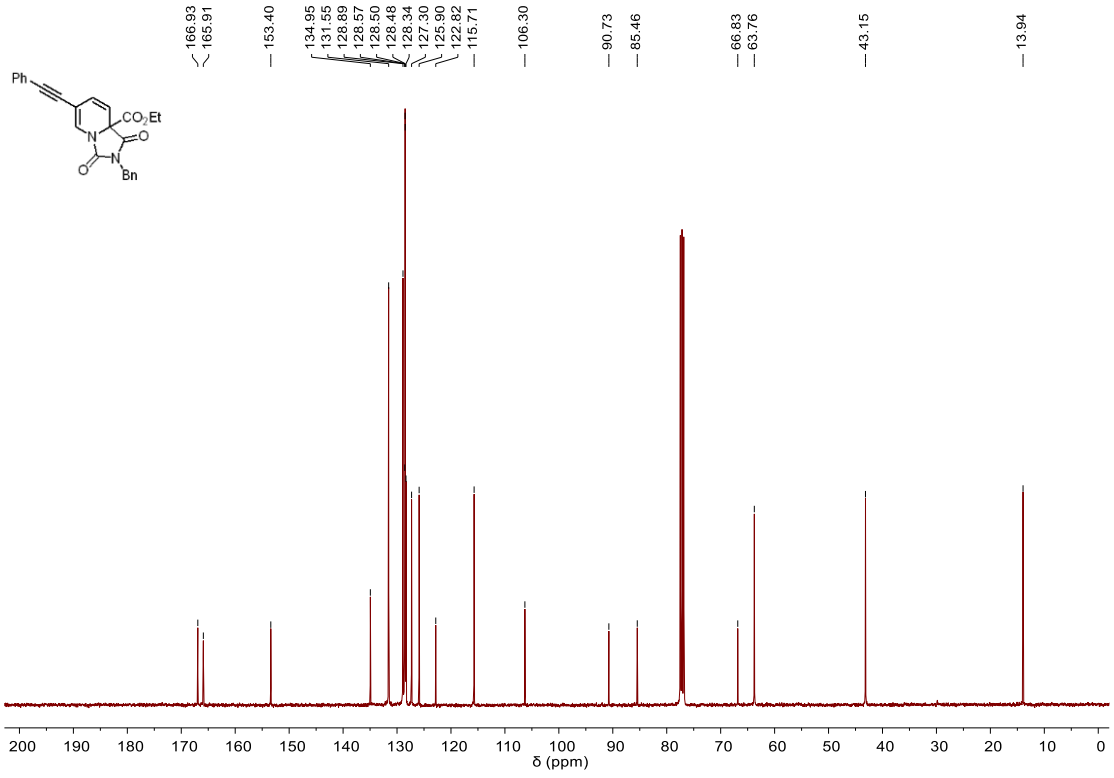
165.22
153.46
134.75
129.34
129.00
128.96
128.67
128.60
128.48
128.34
126.15
124.69
123.45
120.74
118.03
116.15
116.10
116.04
115.98
104.69
104.67
104.65
66.83
64.13
43.32
13.91
CF3
CO2Et
O
N
O
N
Bn
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
δ (ppm)

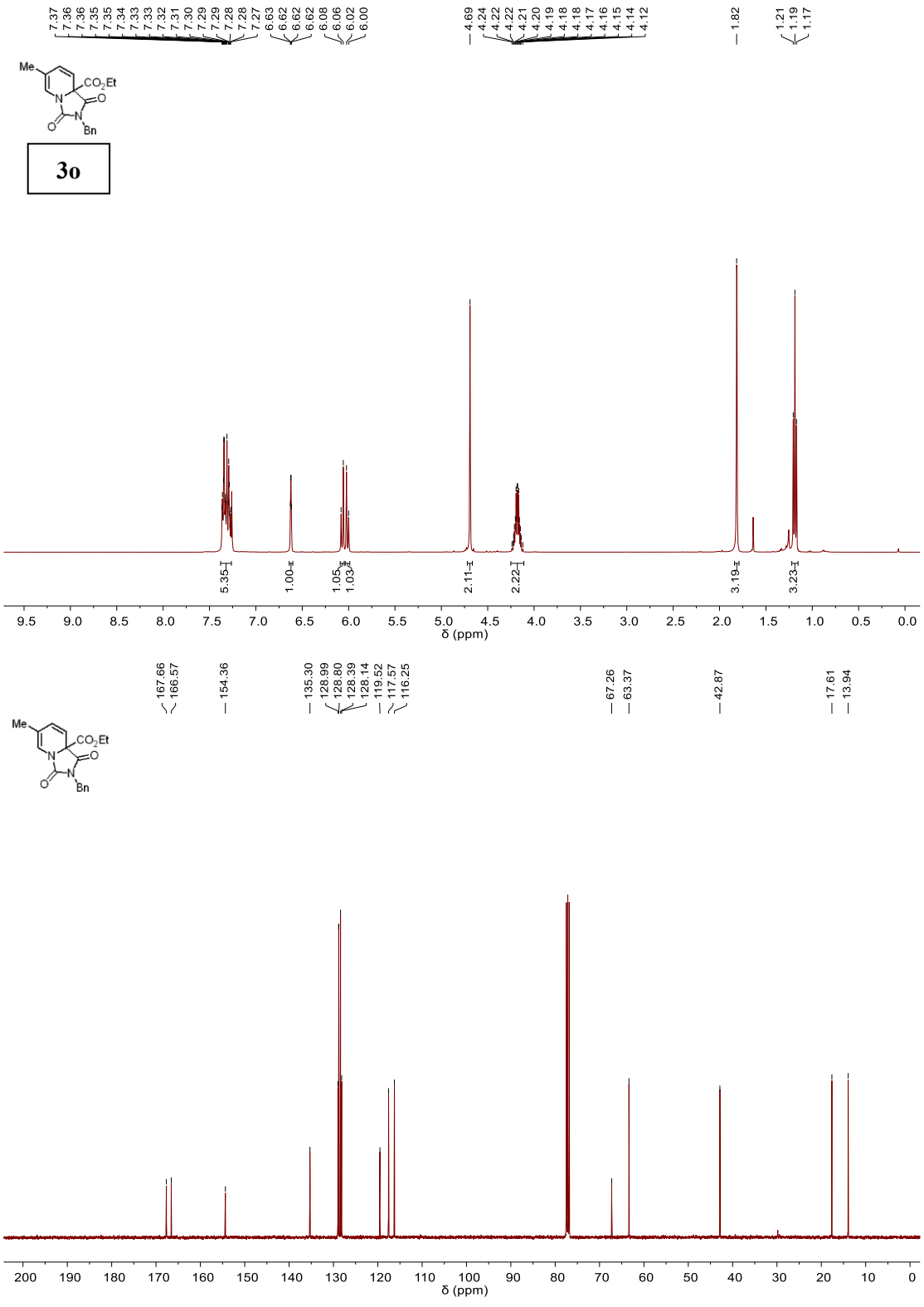

7.47 7.46 7.46 7.45 7.45 7.45 7.44 7.38 7.38 7.37 7.36 7.36 7.35 7.35 7.34 7.33 7.33 7.33 7.32 7.31 7.31 7.30 7.29 6.96 6.96 6.94 6.94 6.30 6.30 6.29 5.72 5.72 5.71 5.70 4.72 4.71 4.25 4.23 4.21 4.20
1.24 1.22 1.21
Ph
CO2Et
O
N
O
N
Bn
3l
2.09 8.34 1.03 0.94 1.00 2.12 2.08 3.14
9.5 9.0 8.5 8.0 7.5 7.0 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
δ (ppm)

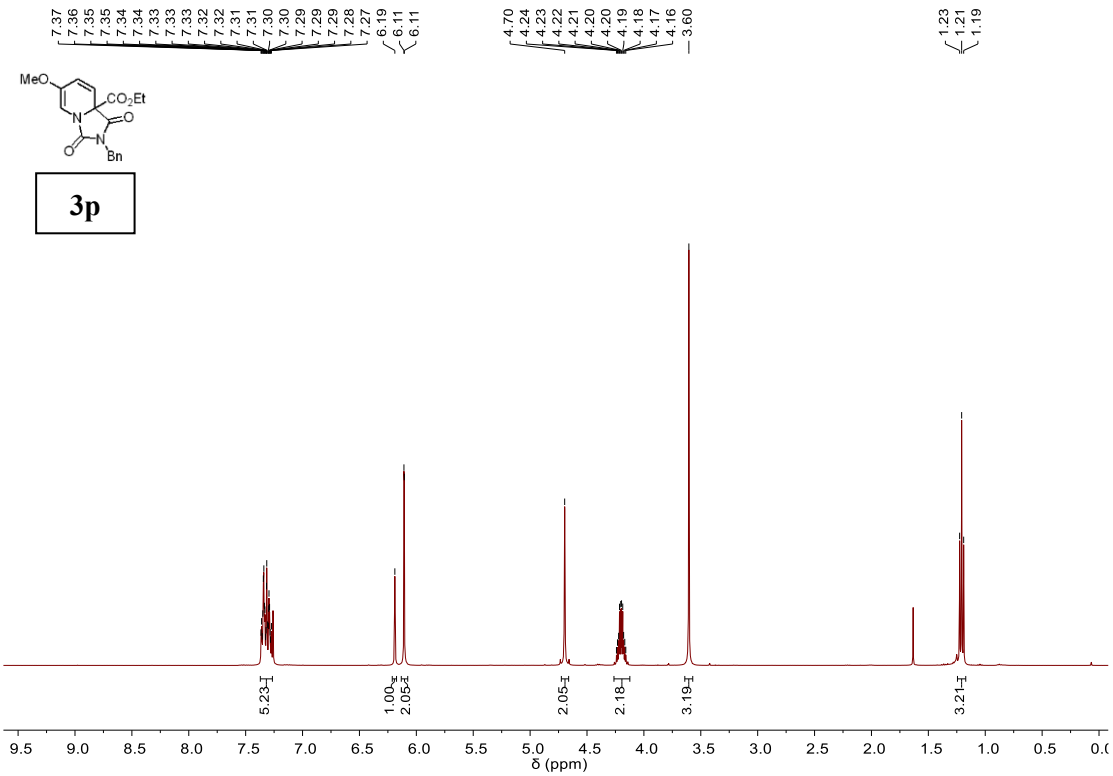

166.84 165.94 153.79 135.02 131.86 129.05 128.89 128.55 128.51 128.32 122.44 122.33 120.73 118.92 111.89 91.59 86.31 67.68 63.78 43.12 14.01
Ph
CO2Et
O
N
O
N
Bn
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)


8.58
8.58
7.96
7.94
7.66
7.66
7.50
7.48
7.31
7.30
7.29
7.28
6.98
6.24
6.22
5.92
5.89
4.66
4.25
4.24
4.24
4.23
4.22
4.21
4.20
4.18
4.17
4.16
4.15
4.14
1.24
1.23
1.21
1.18
1.16
1.15
Cl
N
O
S
O
EtO2C
EtO2C
N
O
O
N
Bn
3m
0.97
2.01
1.00
2.03
5.04
0.98
1.02
1.00
2.02
6.19
3.33
3.08
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
δ (ppm)
166.92
166.05
162.31
153.60
150.82
148.12
144.19
138.45
137.68
134.83
134.61
130.80
129.98
129.34
128.83
128.42
128.31
126.76
124.67
120.96
114.82
66.83
63.77
62.62
60.98
43.02
14.06
13.96
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)


7.45
7.44
7.43
7.42
7.41
7.38
7.38
7.36
7.35
7.33
7.33
7.32
7.32
7.31
7.30
7.28
7.28
7.25
6.31
6.28
6.11
6.09
4.73
4.26
4.24
4.24
4.23
4.22
4.21
4.20
4.19
4.18
4.17
4.17
4.15
1.22
1.21
1.19
Ph
CO2Et
O
N
O
N
Bn
3n
2.09
8.40
0.91
1.00
0.99
2.06
2.07
3.11
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
δ (ppm)


166.93
165.91
153.40
134.95
131.55
128.89
128.57
128.50
128.48
128.34
127.30
125.90
122.82
115.71
106.30
90.73
85.46
66.83
63.76
43.15
13.94
Ph
CO2Et
O
N
O
N
Bn
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)


7.37
7.36
7.36
7.35
7.35
7.34
7.33
7.33
7.32
7.31
7.30
7.29
7.29
7.28
7.28
7.27
6.63
6.62
6.62
6.62
6.08
6.06
6.02
6.00
4.69
4.24
4.22
4.22
4.21
4.20
4.19
4.18
4.18
4.17
4.16
4.15
4.14
4.12
1.82
1.21
1.19
1.17
Me
CO2Et
N
O
O
N
Bn
3o
5.35
1.00
1.05
1.03
2.11
2.22
3.19
3.23
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
δ (ppm)
167.66
166.57
154.36
135.30
128.99
128.80
128.39
128.14
119.52
117.57
116.25
67.26
63.37
42.87
17.61
13.94
Me
CO2Et
N
O
O
N
Bn
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)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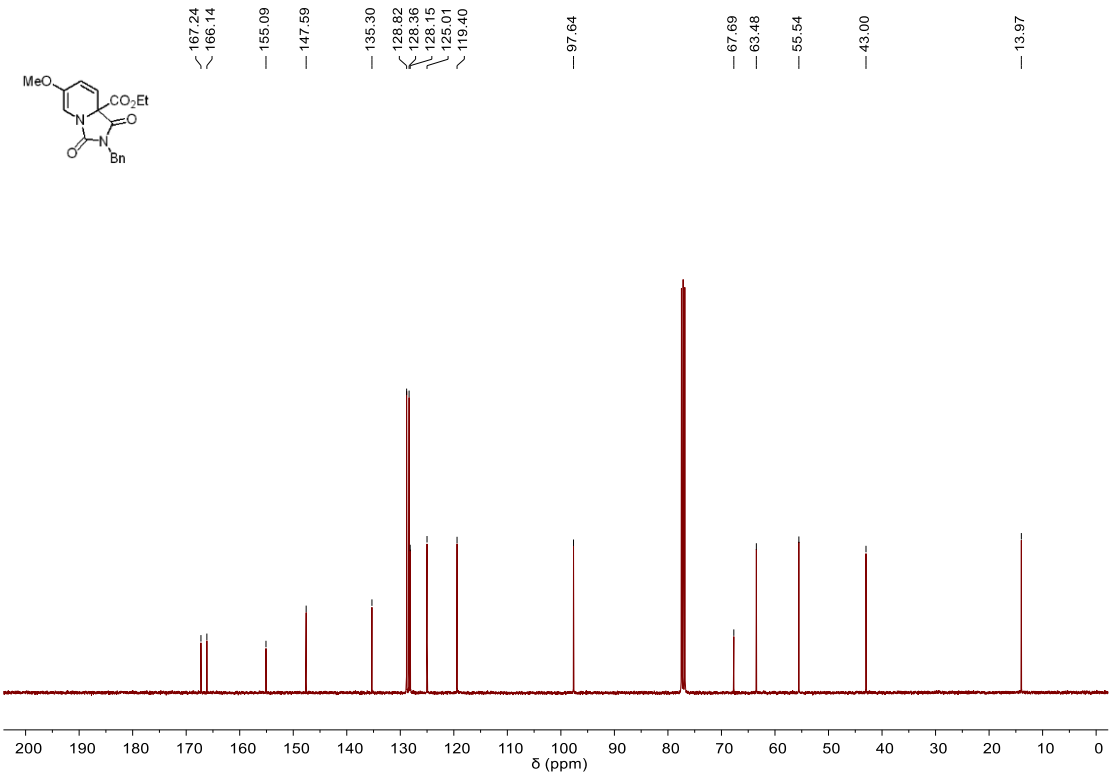
7.36
7.35
7.35
7.34
7.34
7.33
7.33
7.33
7.32
7.32
7.31
7.31
7.30
7.30
7.29
7.29
7.29
7.28
7.27
6.19
6.11
6.11
4.70
4.24
4.23
4.22
4.21
4.20
4.20
4.19
4.18
4.17
4.16
3.60
1.23
1.21
1.19
MeO
CO2Et
O
N
O
N
Bn
3p
5.23
1.00
2.05
2.05
2.18
3.19
3.21
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
δ (ppm)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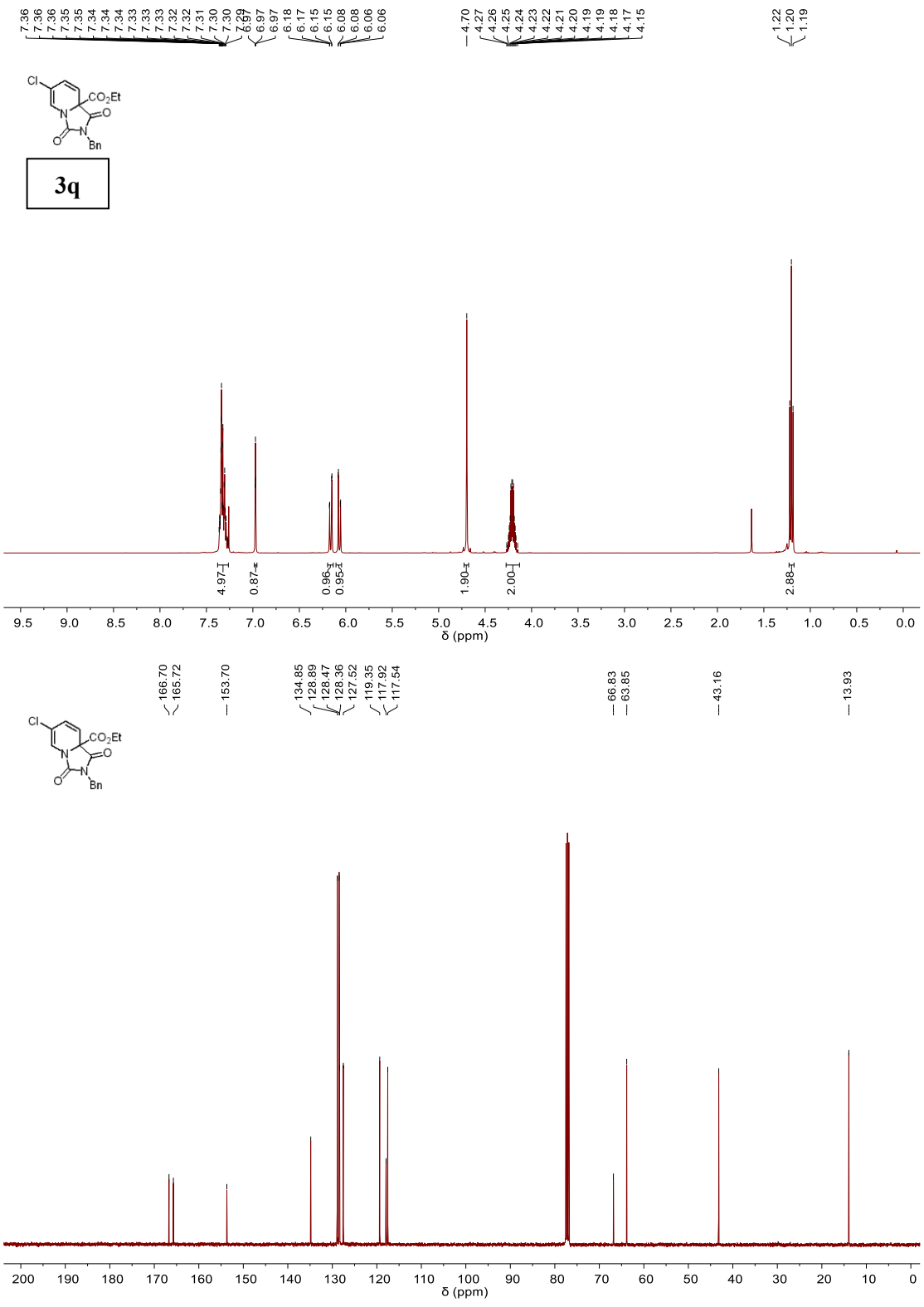
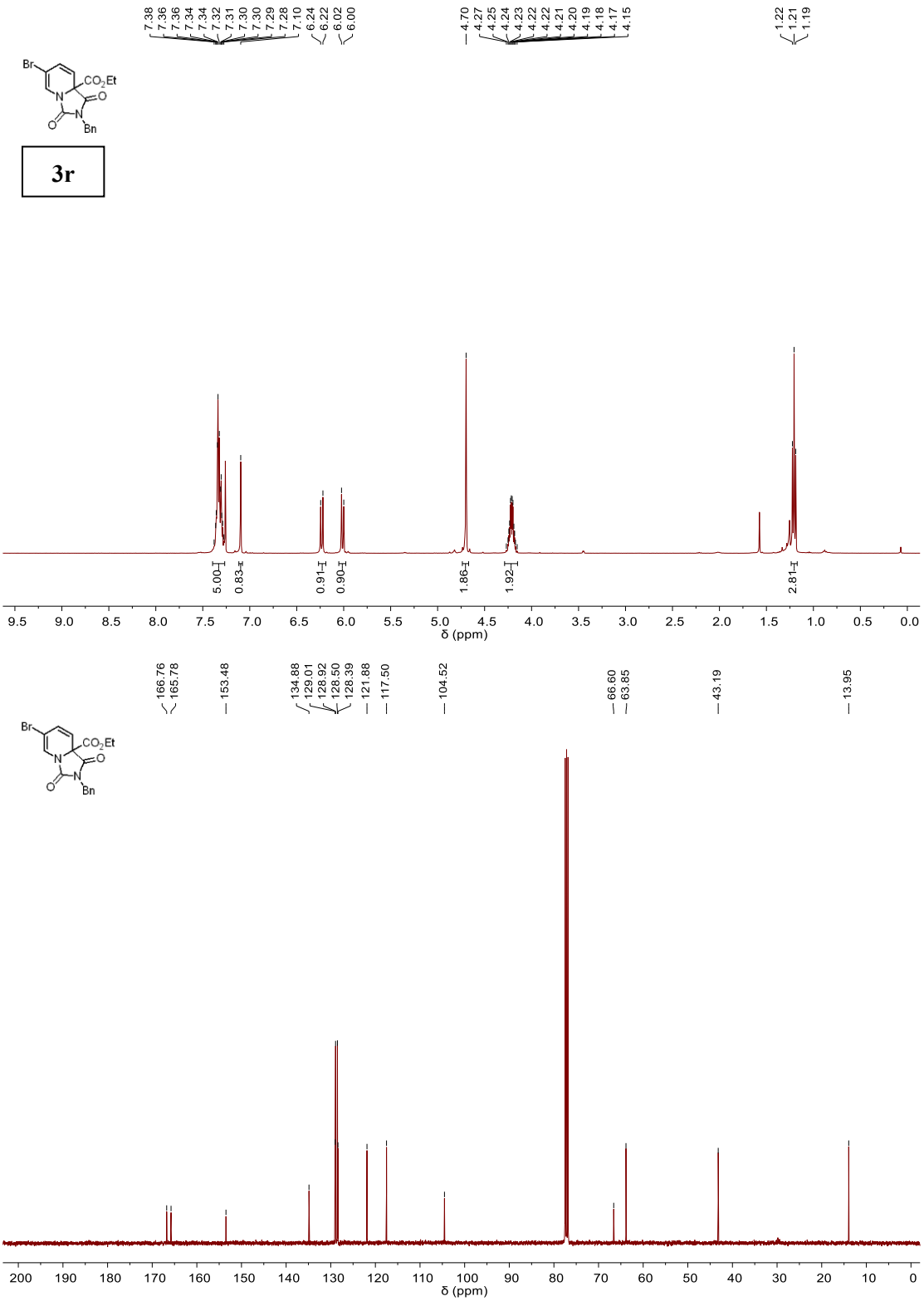
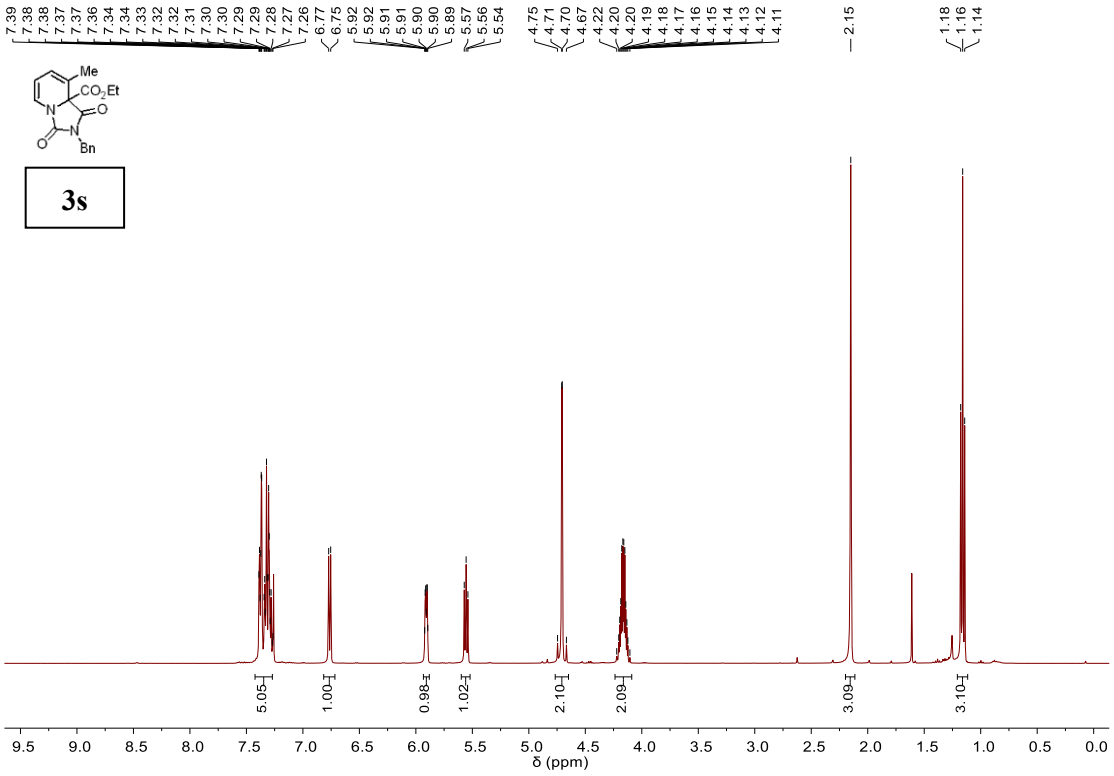
166.14
155.09
147.59
135.30
128.82
128.36
128.15
125.01
119.40
97.64
67.69
63.48
55.54
43.00
13.97
MeO
CO2Et
O
N
O
N
Bn
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)


7.36
7.36
7.36
7.35
7.35
7.34
7.34
7.34
7.33
7.33
7.33
7.32
7.32
7.31
7.30
7.30
7.29
6.97
6.97
6.18
6.17
6.15
6.15
6.08
6.08
6.06
6.06
4.70
4.27
4.26
4.25
4.24
4.23
4.22
4.21
4.20
4.19
4.19
4.18
4.17
4.15
1.22
1.20
1.19
Cl
CO2Et
O
N
O
N
Bn
3q
4.97
0.87
0.96
0.95
1.90
2.00
2.88
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
δ (ppm)
166.70
165.72
153.70
134.85
128.89
128.47
128.36
127.52
119.35
117.92
117.54
66.83
63.85
43.16
13.93
Cl
CO2Et
O
N
O
N
Bn
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)


7.38
7.36
7.36
7.34
7.34
7.32
7.31
7.30
7.30
7.29
7.28
7.10
6.24
6.22
6.02
6.00
4.70
4.27
4.25
4.24
4.23
4.22
4.22
4.21
4.20
4.19
4.18
4.17
4.15
1.22
1.21
1.19
Br
CO2Et
O
N
O
N
Bn
3r
5.00
0.83
0.91
0.90
1.86
1.92
2.81
δ (ppm)
166.76
165.78
153.48
134.88
129.01
128.92
128.50
128.39
121.88
117.50
104.52
66.60
63.85
43.19
13.95
δ (ppm)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7.38
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7.37
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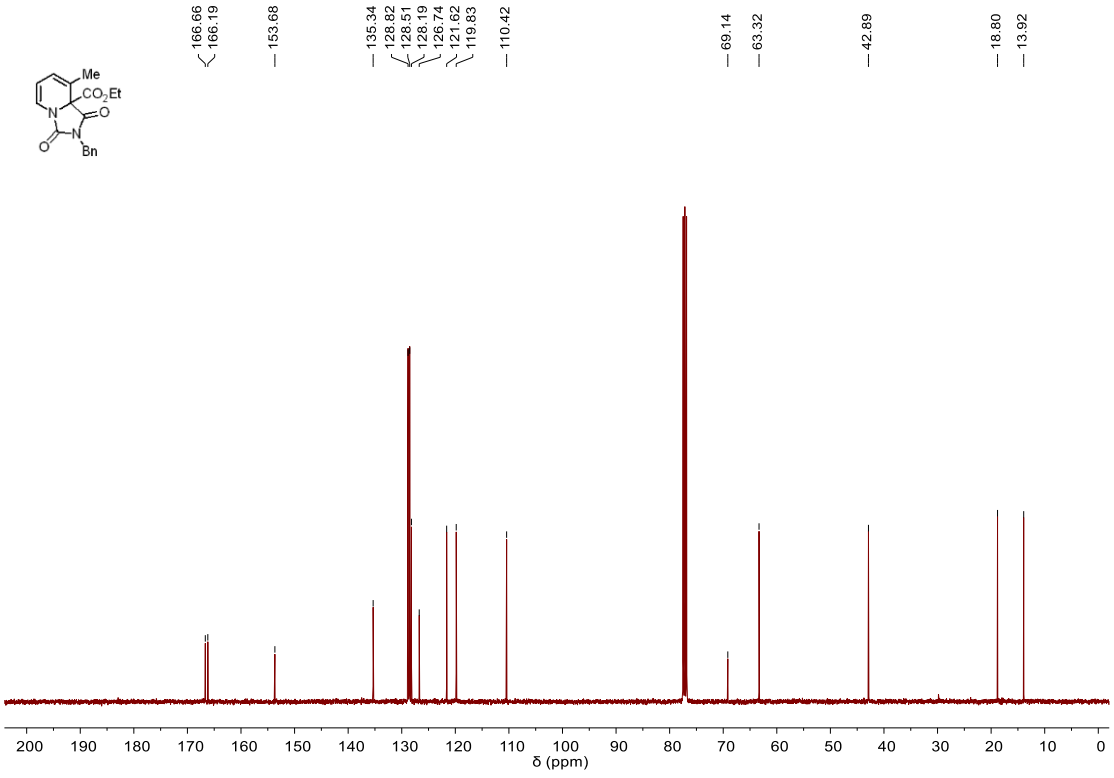
7.36
7.34
7.34
7.33
7.32
7.32
7.31
7.30
7.30
7.29
7.29
7.28
7.27
7.26
6.77
6.75
5.92
5.92
5.91
5.91
5.90
5.90
5.89
5.57
5.56
5.54
4.75
4.71
4.70
4.67
4.22
4.20
4.20
4.19
4.18
4.17
4.16
4.15
4.14
4.13
4.12
4.11
2.15
1.18
1.16
1.14
Me
CO2Et
O
N
O
N
Bn
3s
5.05
1.00
0.98
1.02
2.10
2.09
3.09
3.10
δ (ppm)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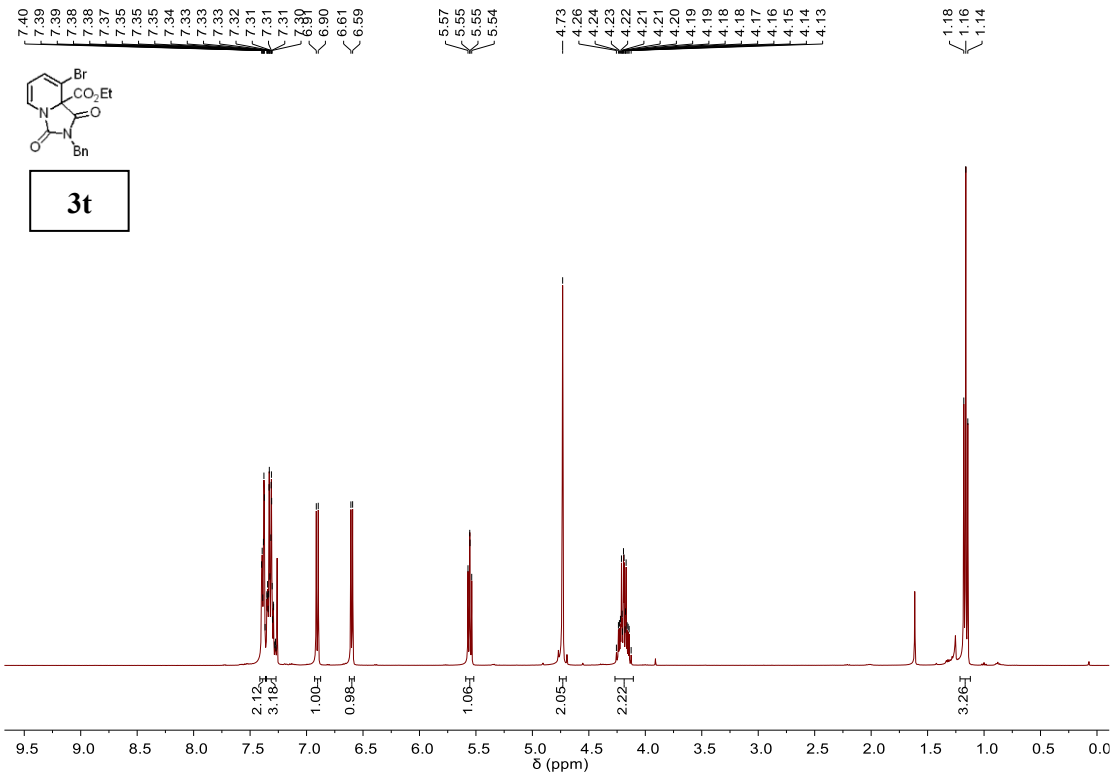
166.19
153.68
135.34
128.82
128.51
128.19
126.74
121.62
119.83
110.42
69.14
63.32
42.89
18.80
13.92
Me
CO2Et
O
N
O
N
Bn
δ (ppm)


7.40
7.39
7.39
7.38
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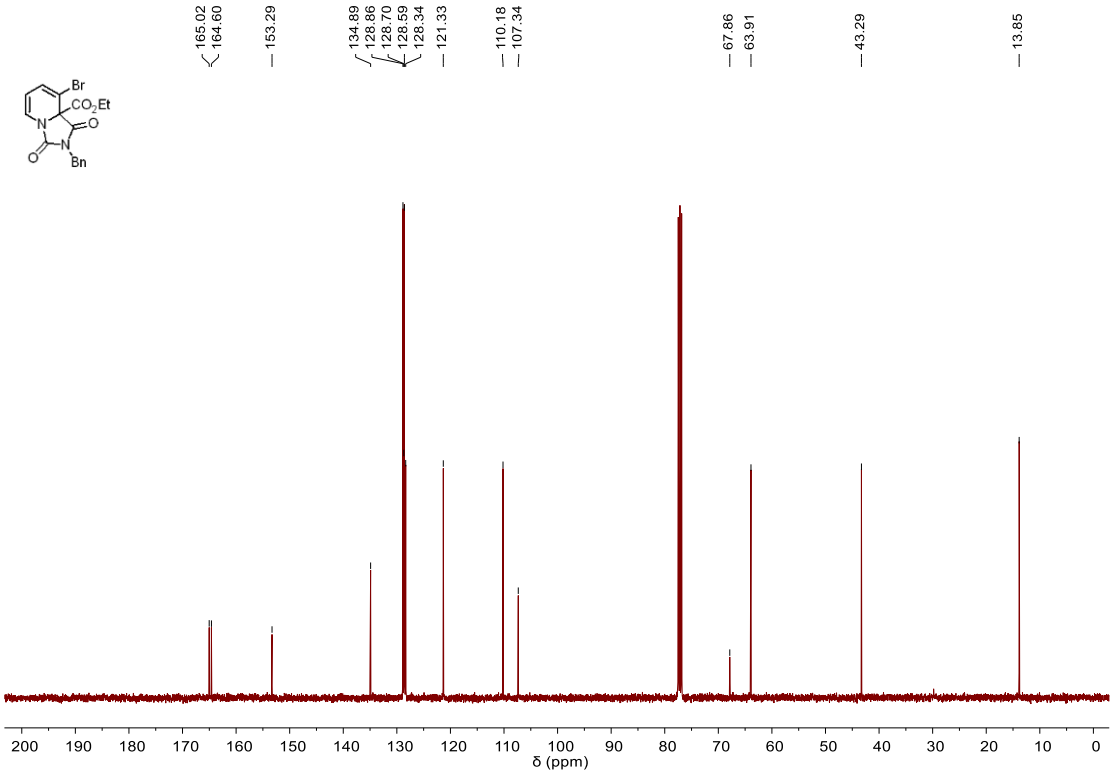
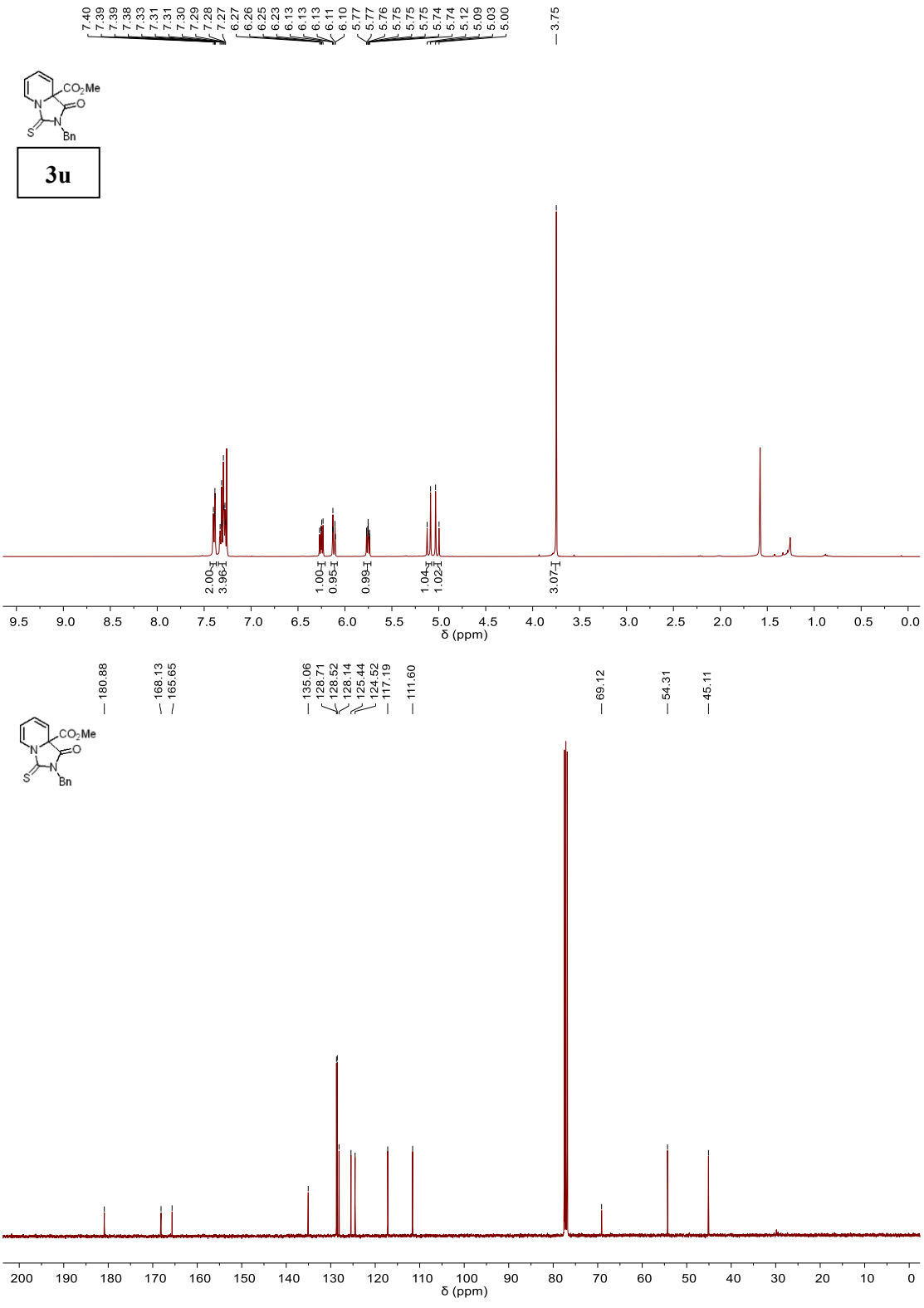
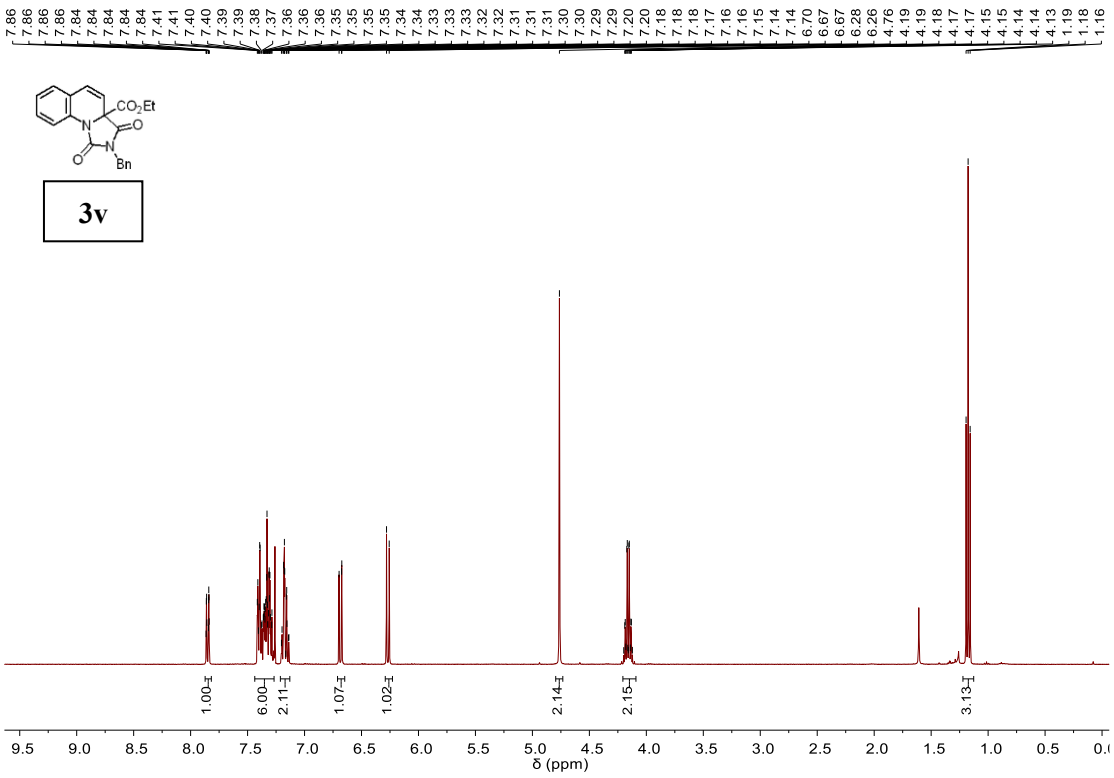
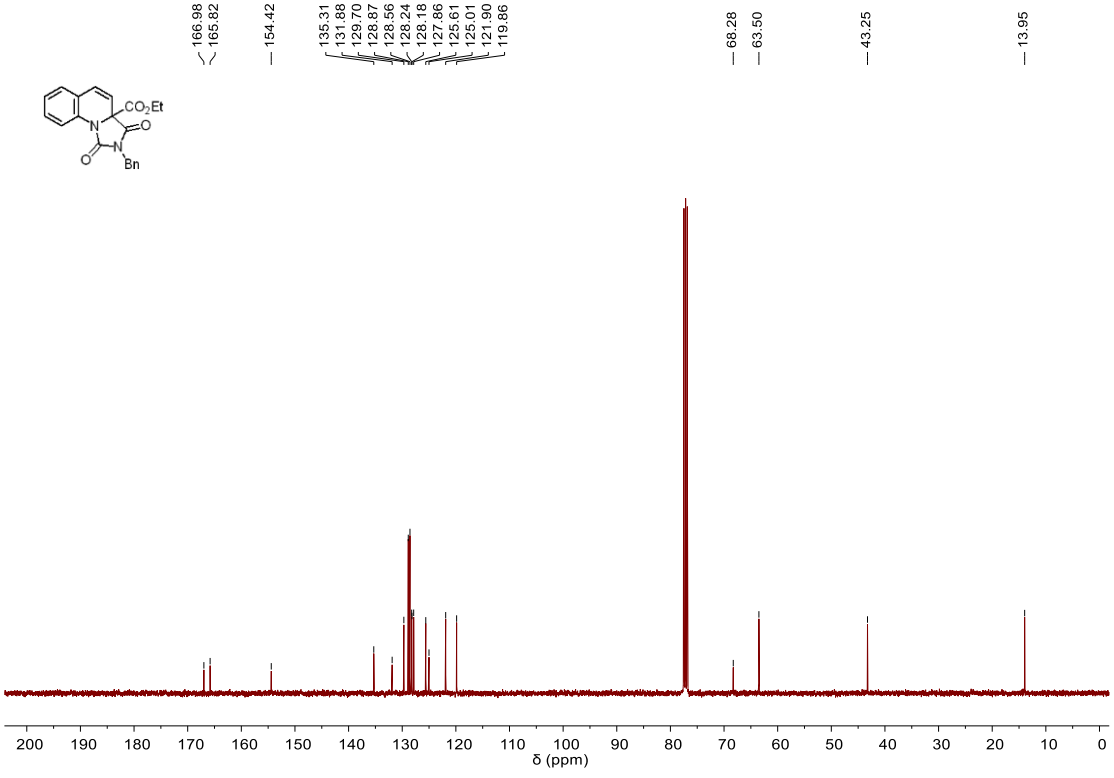
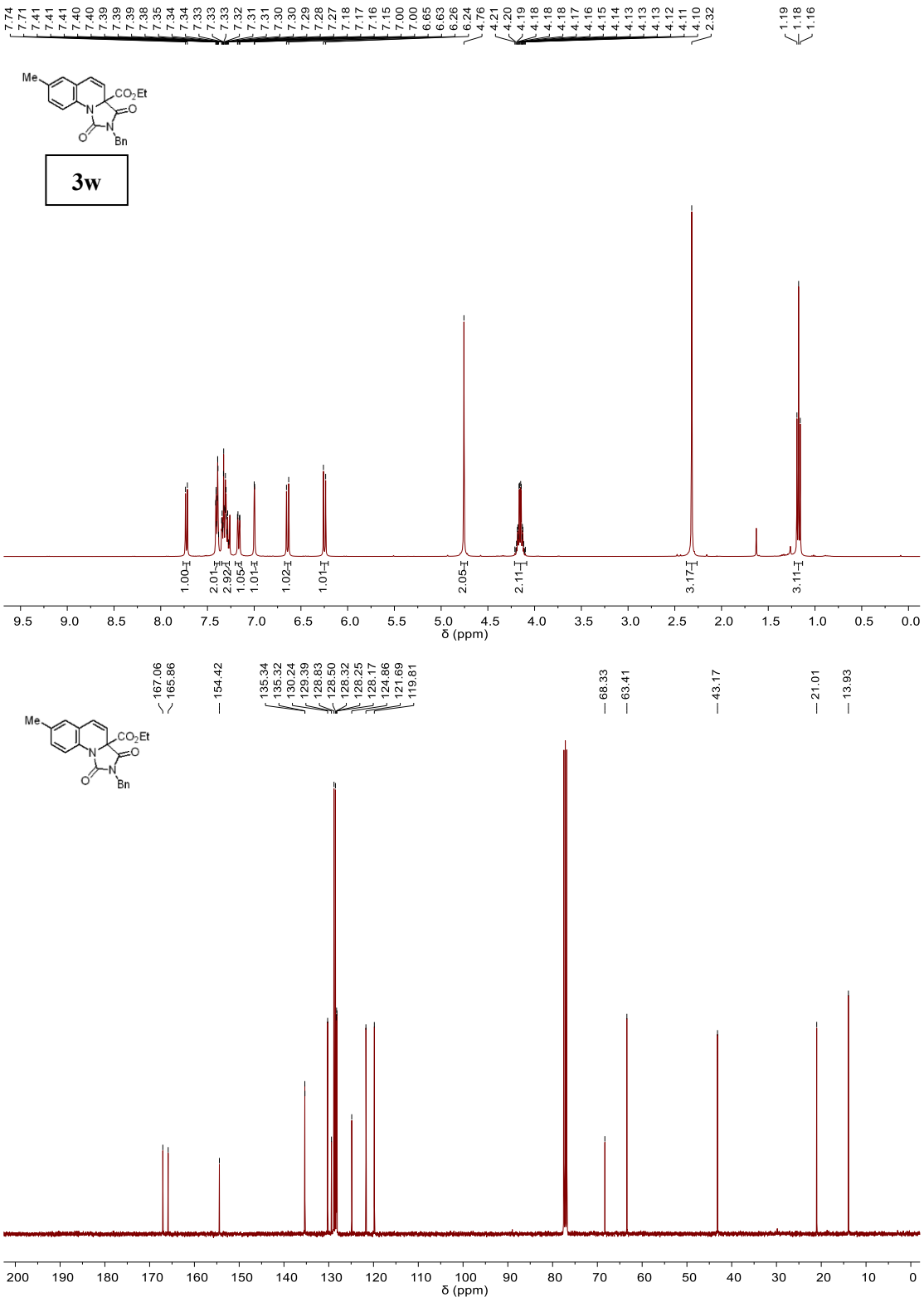
7.37
7.35
7.35
7.35
7.34
7.33
7.33
7.33
7.32
7.31
7.31
7.31
6.90
6.61
6.59
5.57
5.55
5.55
5.54
4.73
4.26
4.24
4.23
4.22
4.21
4.21
4.20
4.19
4.19
4.18
4.18
4.17
4.16
4.15
4.14
4.13
1.18
1.16
1.14
Br
CO2Et
O
N
N
O
Bn
3t
2.12
3.18
1.00
0.98
1.06
2.05
2.22
3.26
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

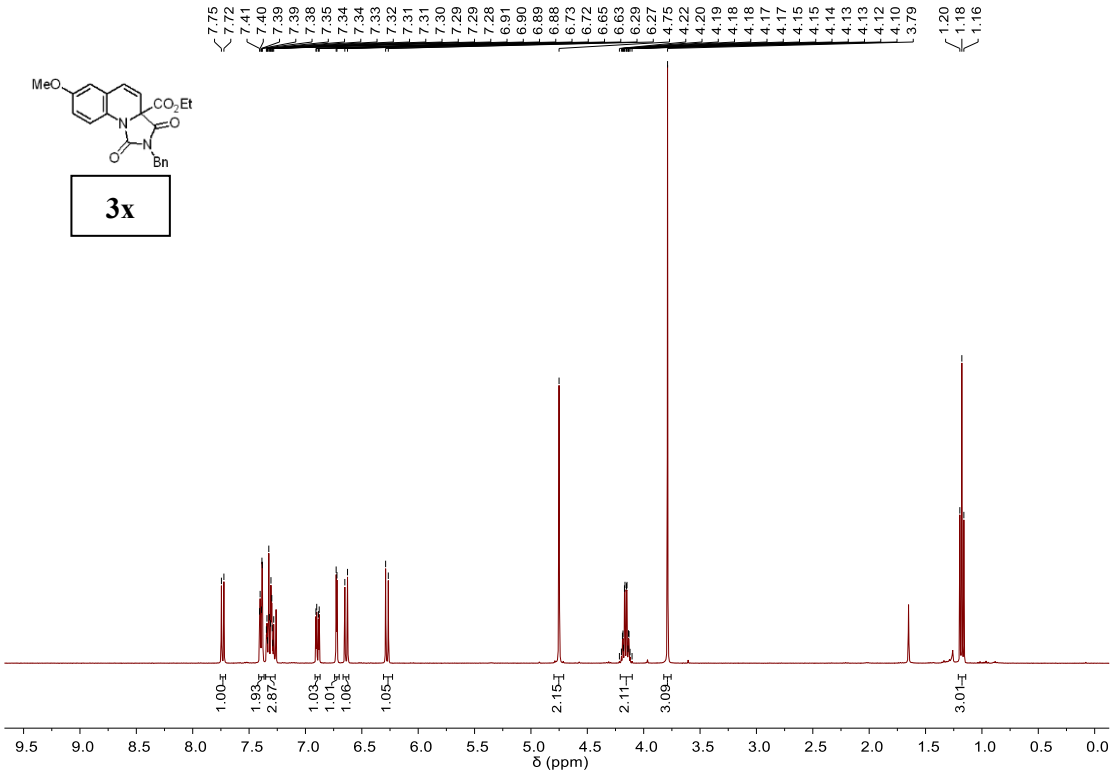

165.02
164.60
153.29
134.89
128.86
128.70
128.59
128.34
121.33
110.18
107.34
67.86
63.91
43.29
13.85
Br
CO2Et
O
N
N
O
Bn
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)


7.40
7.39
7.39
7.38
7.33
7.31
7.31
7.30
7.29
7.28
7.27
6.27
6.26
6.25
6.23
6.13
6.13
6.13
6.11
6.10
5.77
5.77
5.76
5.75
5.75
5.75
5.74
5.74
5.12
5.09
5.03
5.00
3.75
CO2Me
O
N
S
N
Bn
3u
2.00
3.96
1.00
0.95
0.99
1.04
1.02
3.07
δ (ppm)
180.88
168.13
165.65
135.06
128.71
128.52
128.14
125.44
124.52
117.19
111.60
69.12
54.31
45.11
δ (ppm)


7.86 7.86 7.86 7.86 7.84 7.84 7.84 7.84 7.84 7.41 7.41 7.40 7.40 7.39 7.39 7.38 7.37 7.36 7.36 7.36 7.35 7.35 7.35 7.35 7.34 7.34 7.33 7.33 7.32 7.32 7.31 7.31 7.31 7.30 7.30 7.29 7.29 7.20 7.20 7.18 7.18 7.17 7.16 7.16 7.15 7.14 7.14 6.70 6.67 6.67 6.28 6.26 4.76 4.19 4.19 4.18 4.17 4.17 4.15 4.15 4.14 4.14 4.13 1.19 1.18 1.16
CO2Et
O
N
O
N
Bn
3v
1.00 6.00 2.11 1.07 1.02 2.14 2.15 3.13
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
δ (ppm)


166.98 165.82 154.42 135.31 131.88 129.70 128.87 128.56 128.24 128.18 127.86 125.61 125.01 121.90 119.86 68.28 63.50 43.25 13.95
CO2Et
O
N
O
N
Bn
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)


7.74 7.71 7.41 7.41 7.41 7.40 7.40 7.39 7.39 7.39 7.38 7.35 7.34 7.34 7.33 7.33 7.33 7.32 7.31 7.31 7.30 7.30 7.29 7.28 7.27 7.18 7.17 7.16 7.15 7.00 6.65 6.63 6.26 6.24 4.76 4.21 4.20 4.19 4.18 4.18 4.18 4.17 4.16 4.15 4.14 4.13 4.13 4.12 4.11 4.10 2.32 1.19 1.18 1.16
Me
CO2Et
O
N
O
N
Bn
3w
1.00 2.01 2.92 1.05 1.01 1.02 1.01 2.05 2.11 3.17 3.11
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
δ (ppm)
167.06 165.86 154.42 135.34 135.32 130.24 129.39 128.83 128.50 128.32 128.25 128.17 124.86 121.69 119.81 68.33 63.41 43.17 21.01 13.93
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)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7.39
7.38
7.35
7.34
7.34
7.33
7.32
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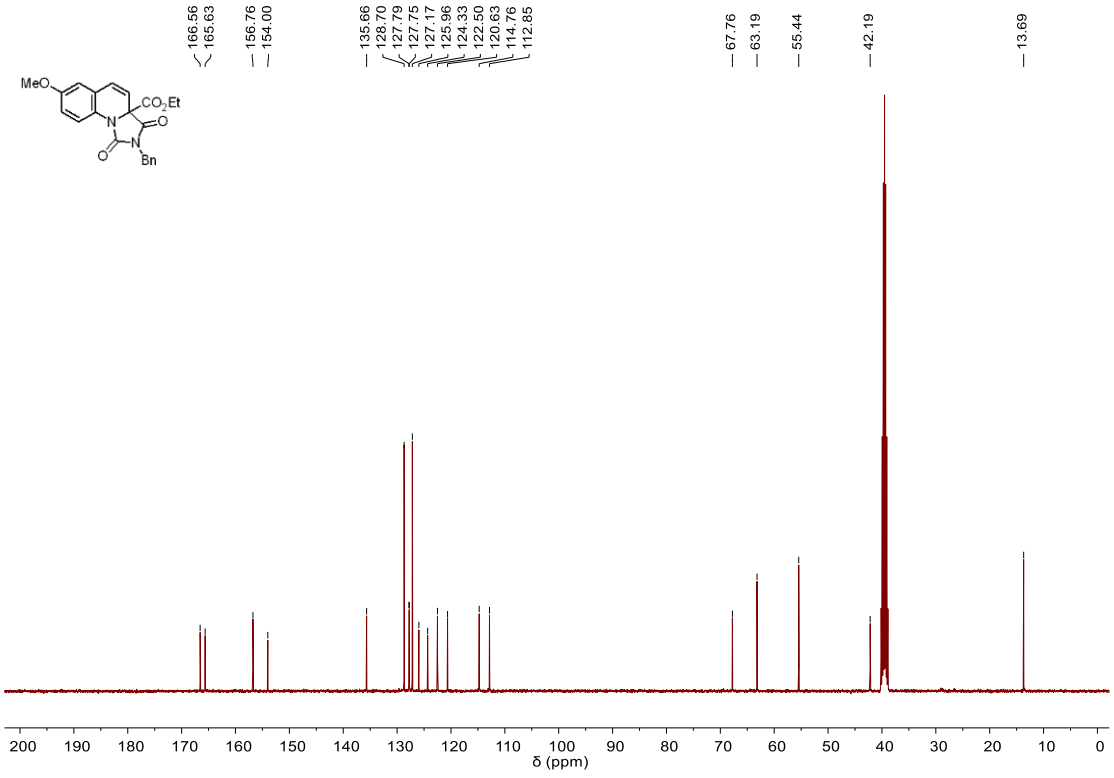
7.31
7.30
7.29
7.29
7.28
6.91
6.90
6.89
6.88
6.73
6.72
6.65
6.63
6.29
6.27
4.75
4.22
4.20
4.19
4.18
4.18
4.17
4.17
4.15
4.15
4.14
4.13
4.12
4.10
3.79
1.20
1.18
1.16
MeO
CO2Et
O
N
O
N
Bn
3x
1.00
1.93
2.87
1.03
1.01
1.06
1.05
2.15
2.11
3.09
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)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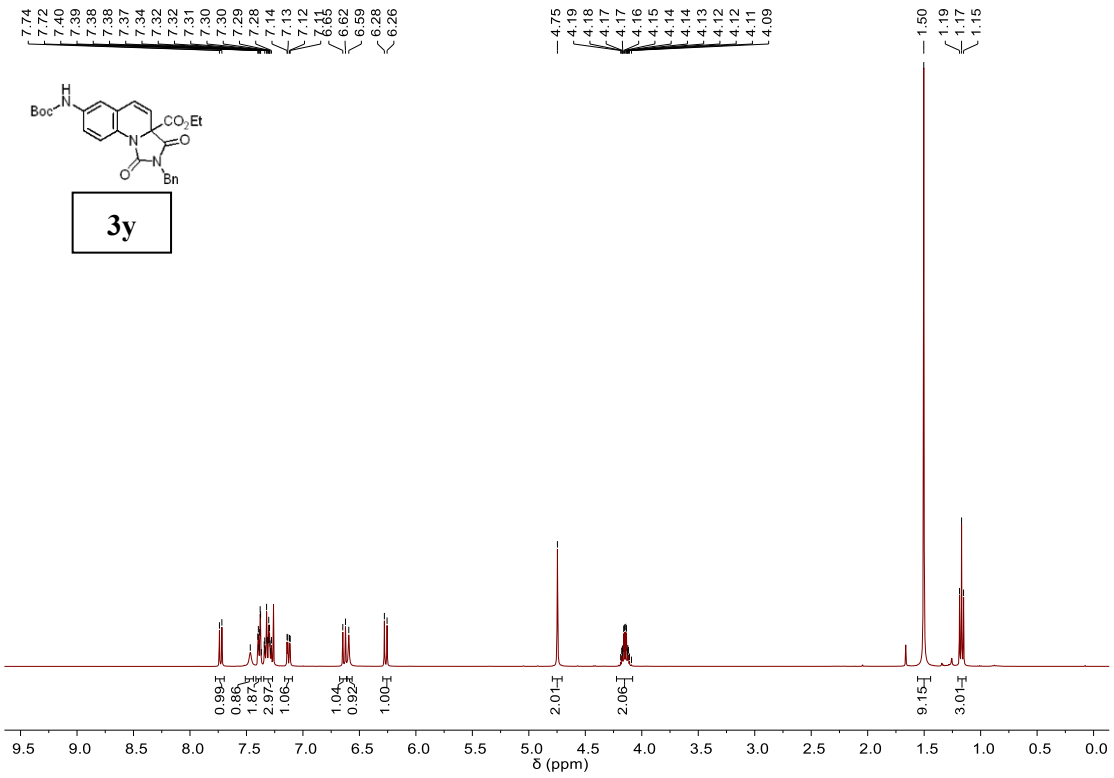
127.79
127.75
127.17
125.96
124.33
122.50
120.63
114.76
112.85
67.76
63.19
55.44
42.19
13.69
MeO
CO2Et
O
N
O
N
Bn
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)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7.72
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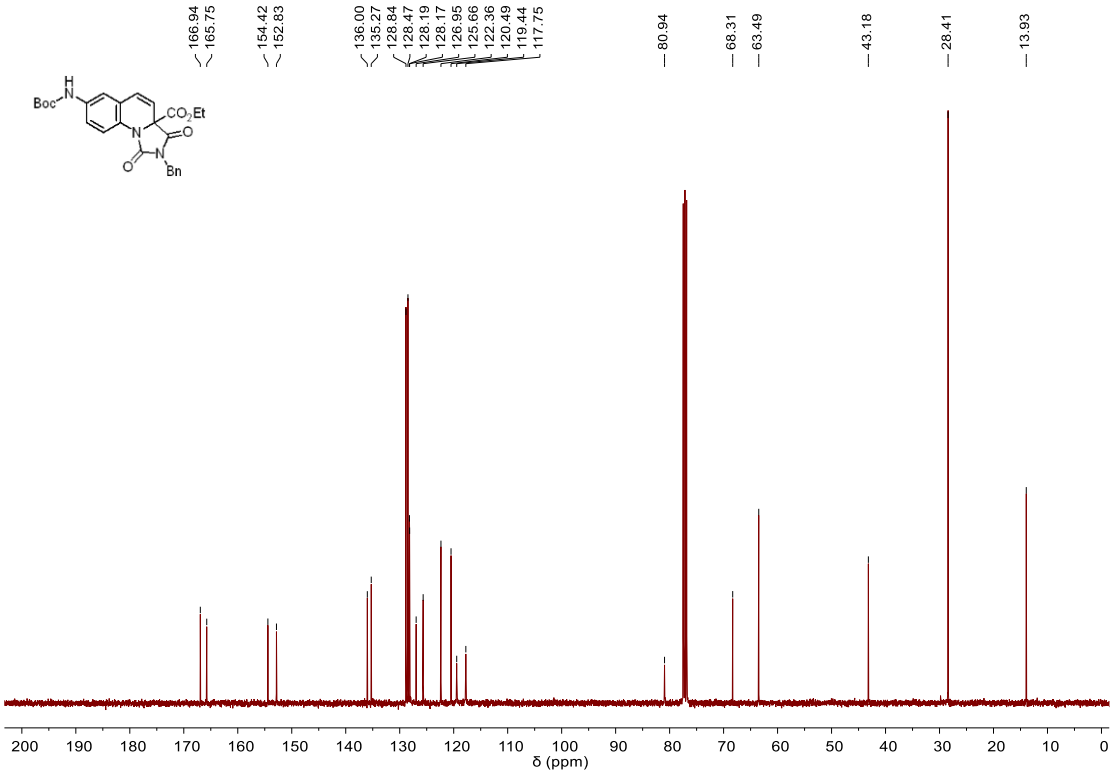
7.39
7.38
7.38
7.37
7.34
7.32
7.32
7.31
7.30
7.30
7.29
7.28
7.14
7.13
7.12
7.11
6.65
6.62
6.59
6.28
6.26
4.75
4.19
4.18
4.17
4.17
4.16
4.15
4.14
4.14
4.13
4.12
4.12
4.11
4.09
1.50
1.19
1.17
1.15
Boc
H
N
CO2Et
O
N
O
N
Bn
3y
0.99
0.86
1.87
2.97
1.06
1.04
0.92
1.00
2.01
2.06
9.15
3.01
δ (ppm)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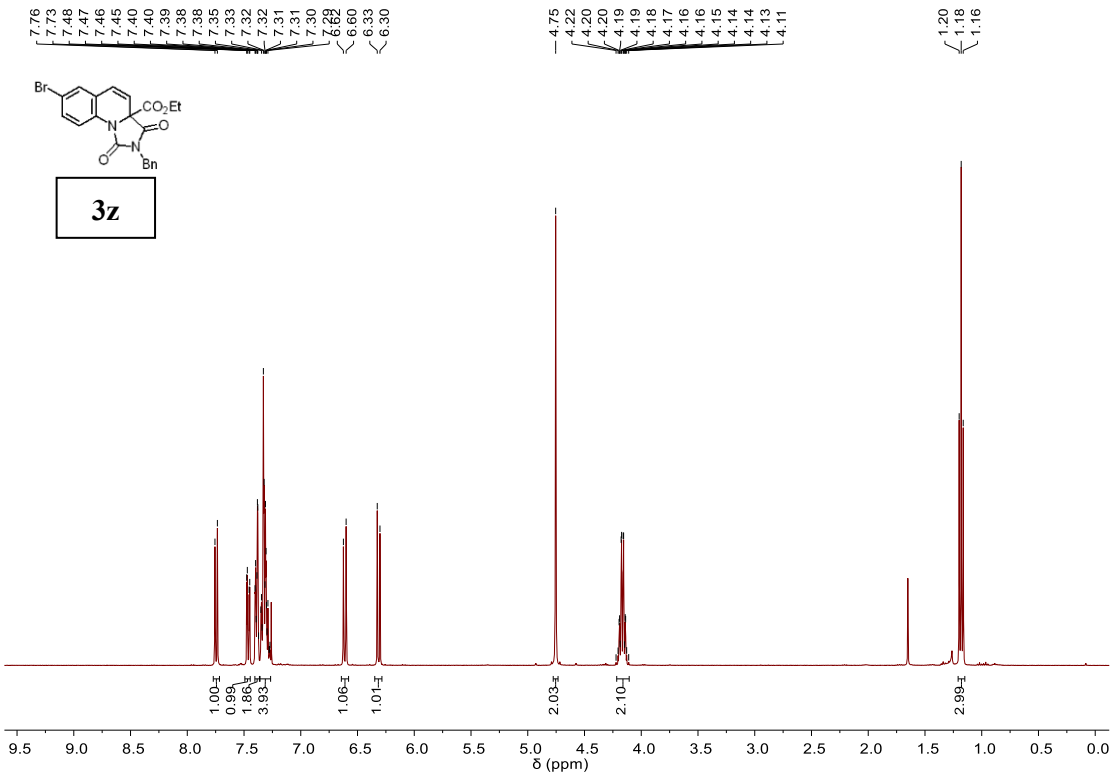
128.47
128.19
128.17
126.95
125.66
122.36
120.49
119.44
117.75
80.94
68.31
63.49
43.18
28.41
13.93
Boc
H
N
CO2Et
O
N
O
N
Bn
δ (ppm)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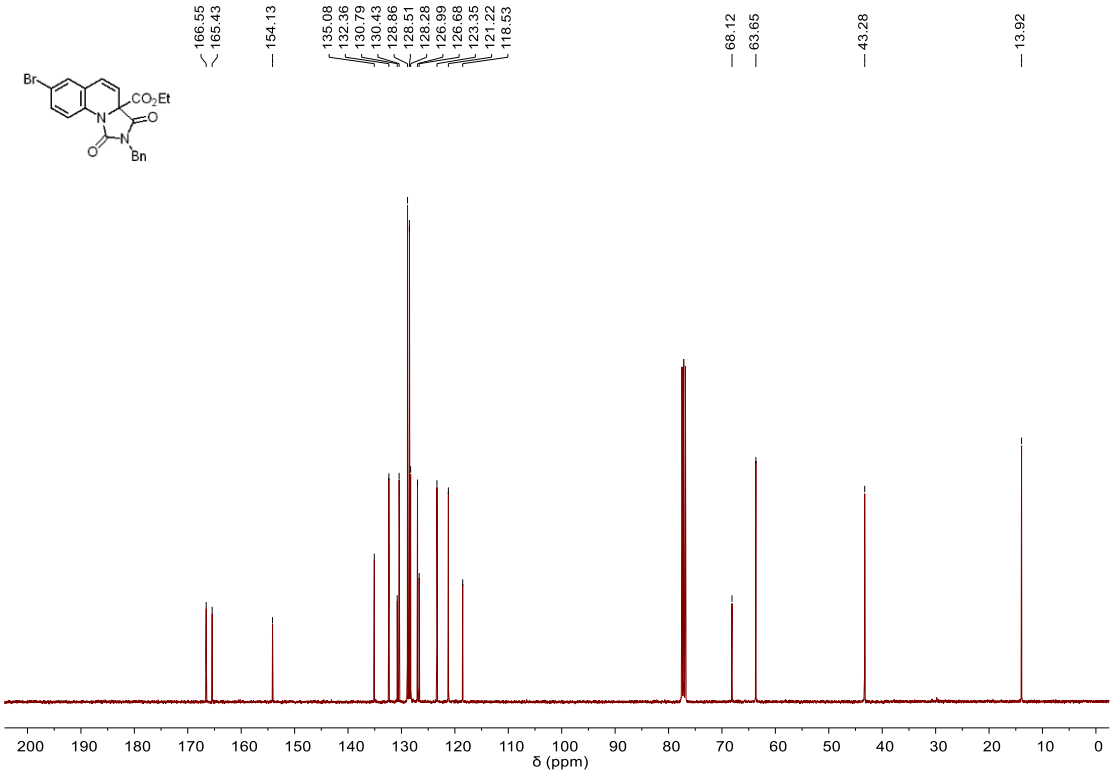
7.40
7.39
7.38
7.38
7.35
7.33
7.32
7.32
7.31
7.31
7.30
6.62
6.60
6.33
6.30
4.75
4.22
4.20
4.20
4.19
4.19
4.18
4.17
4.16
4.16
4.15
4.14
4.14
4.13
4.11
1.20
1.18
1.16
Br
CO2Et
O
N
O
N
Bn
3z
1.00
0.99
1.86
3.93
1.06
1.01
2.03
2.10
2.99
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)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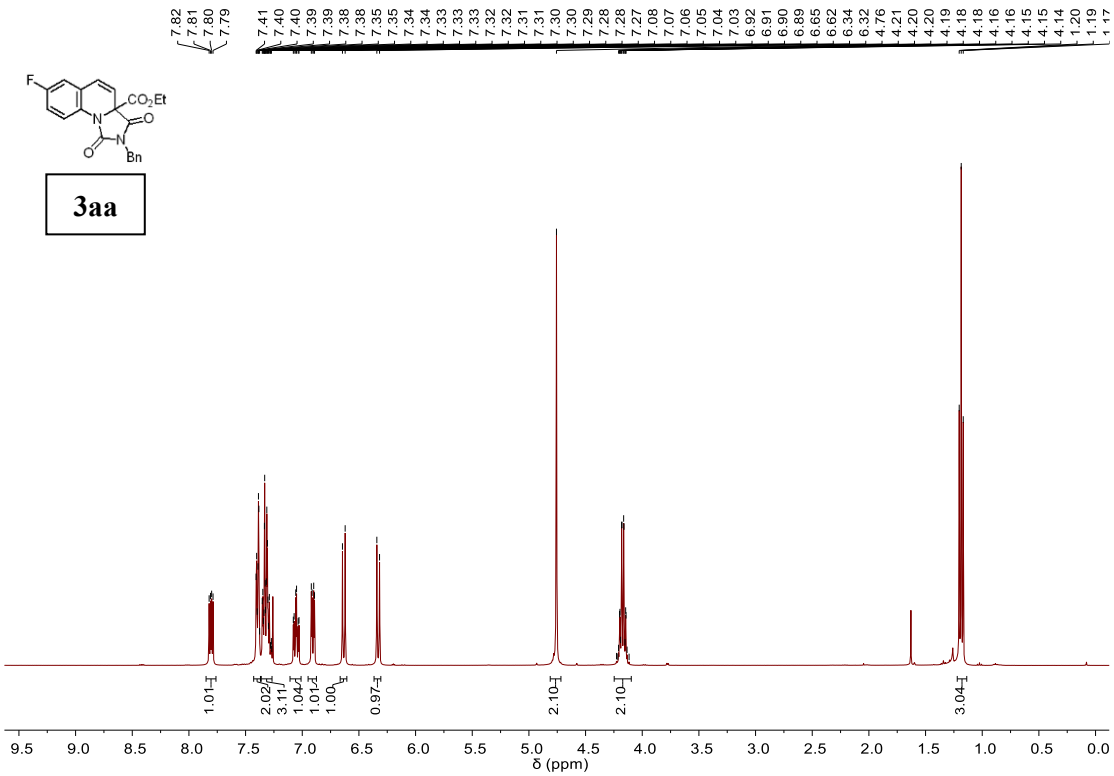
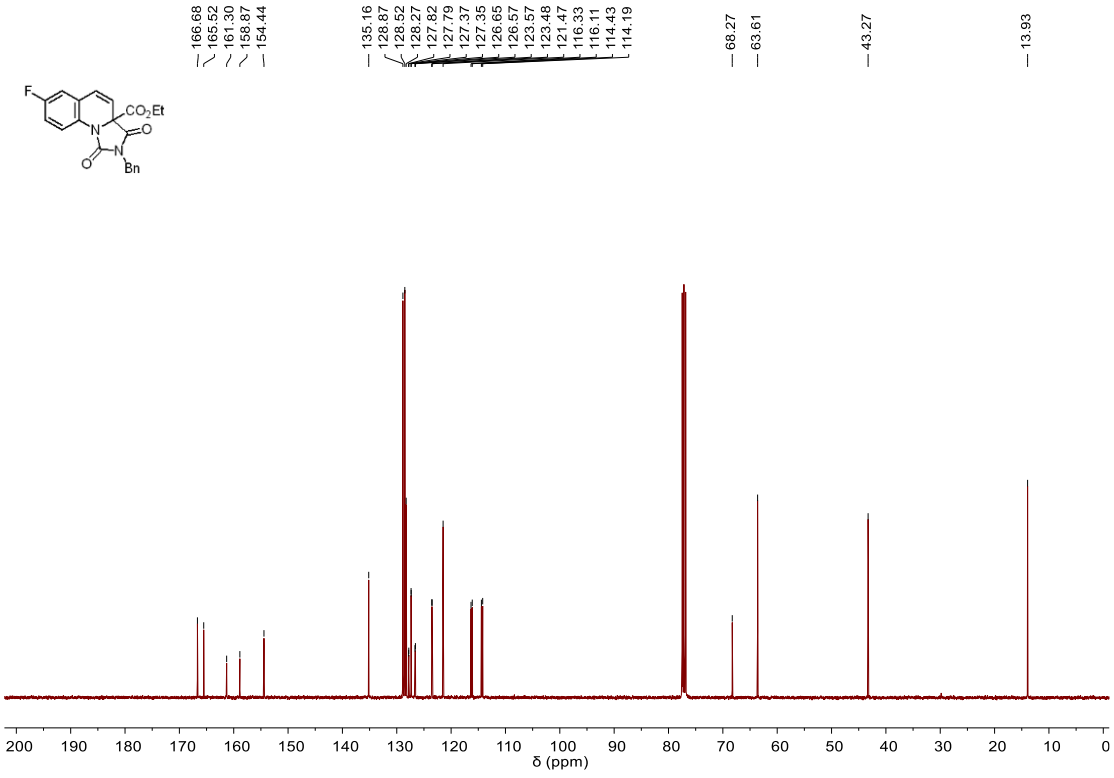
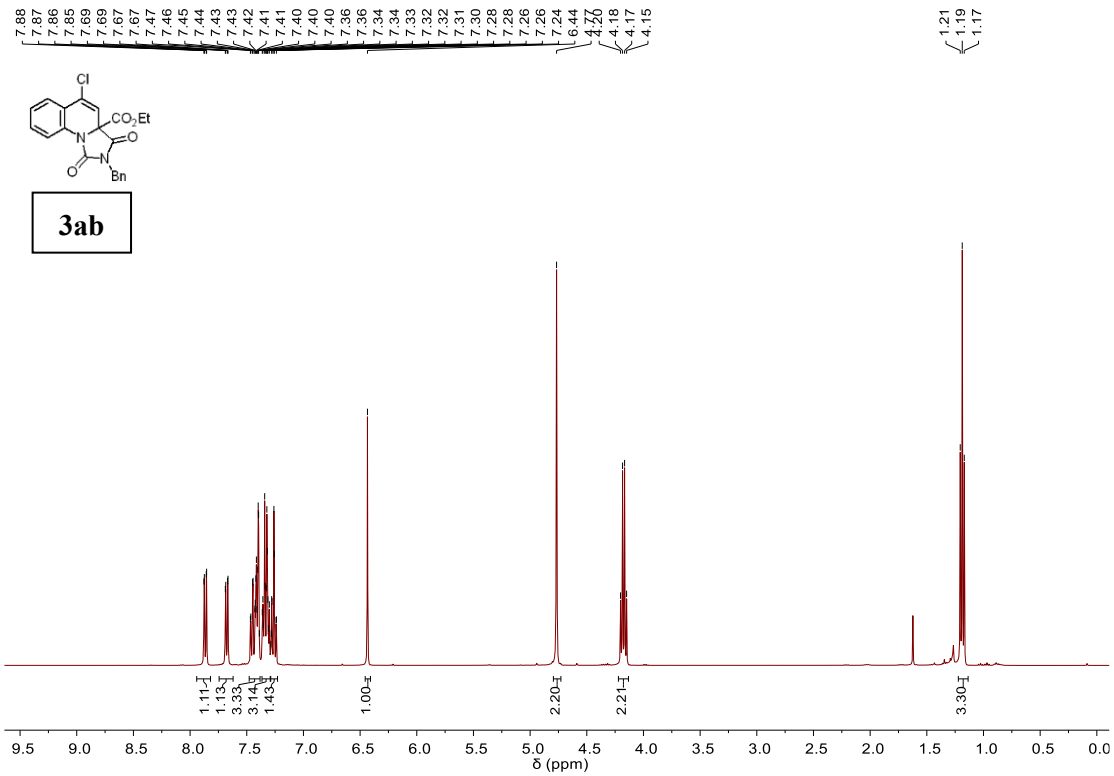
165.43
154.13
135.08
132.36
130.79
130.43
128.86
128.51
128.28
126.99
126.68
123.35
121.22
118.53
68.12
63.65
43.28
13.92
Br
CO2Et
O
N
O
N
Bn
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)


7.82 7.81 7.80 7.79 7.41 7.40 7.40 7.39 7.39 7.38 7.38 7.35 7.35 7.34 7.34 7.33 7.33 7.33 7.32 7.32 7.31 7.31 7.30 7.30 7.29 7.28 7.28 7.27 7.08 7.07 7.06 7.05 7.04 7.03 6.92 6.91 6.90 6.89 6.65 6.62 6.34 6.32 4.76 4.21 4.20 4.20 4.19 4.18 4.18 4.16 4.16 4.15 4.15 4.14 1.20 1.19 1.17
F
CO2Et
O
N
O
N
Bn
3aa
1.01 2.02 3.11 1.04 1.01 1.00 0.97 2.10 2.10 3.04
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
δ (ppm)


166.68 165.52 161.30 158.87 154.44 135.16 128.87 128.52 128.27 127.82 127.79 127.37 127.35 126.65 126.57 123.57 123.48 121.47 116.33 116.11 114.43 114.19 68.27 63.61 43.27 13.93
F
CO2Et
O
N
O
N
Bn
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)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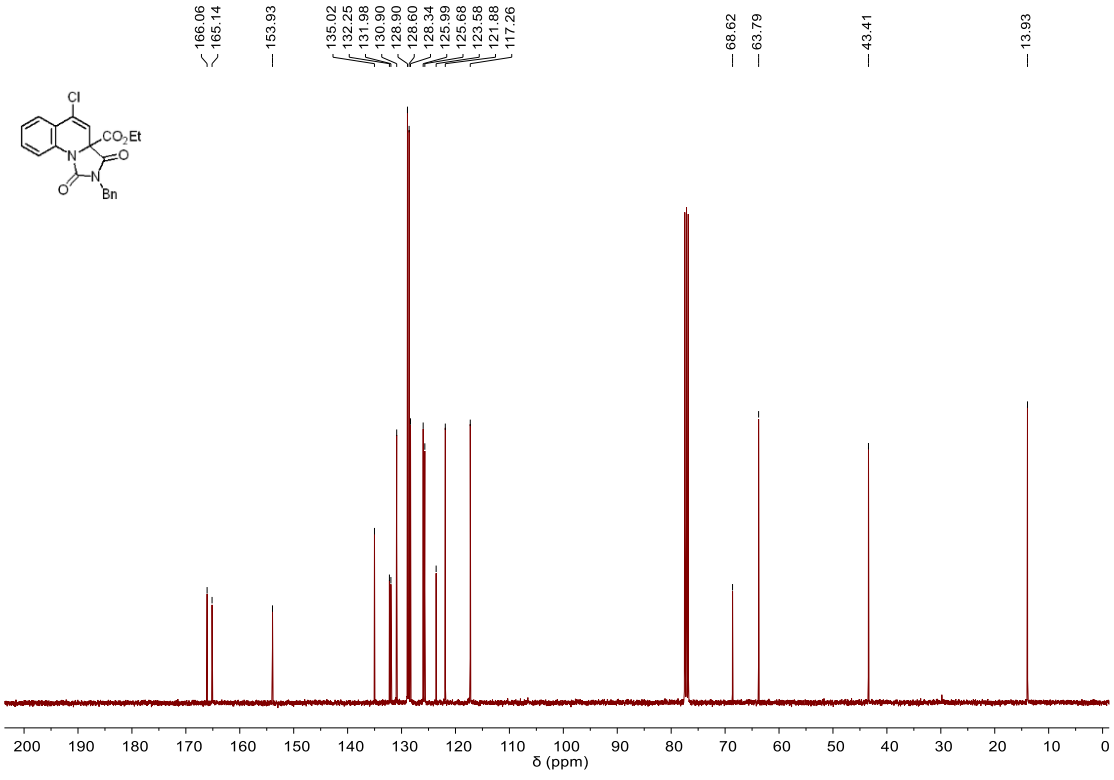
7.45
7.44
7.43
7.43
7.42
7.41
7.41
7.40
7.40
7.40
7.36
7.36
7.34
7.34
7.33
7.32
7.32
7.31
7.30
7.28
7.28
7.26
7.26
7.24
6.44
4.20
4.18
4.17
4.15
1.21
1.19
1.17
Cl
CO2Et
O
N
O
N
Bn
3ab
1.11
1.13
3.33
3.14
1.43
1.00
2.20
2.21
3.30
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)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128.34
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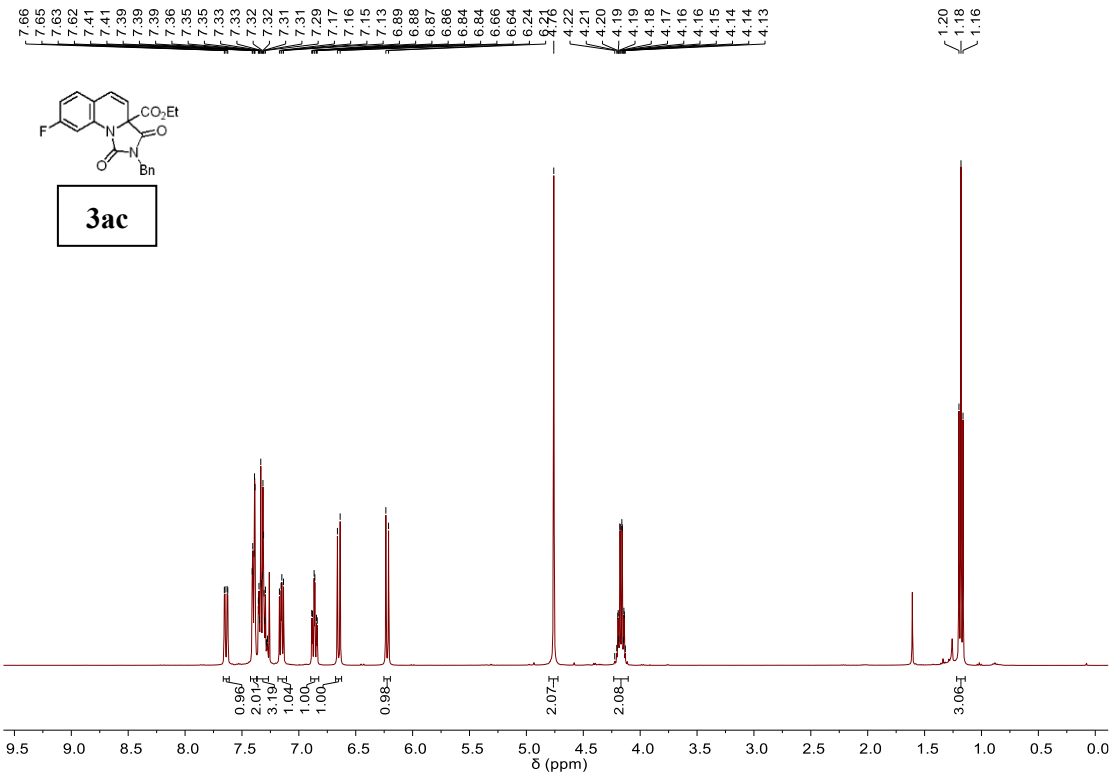
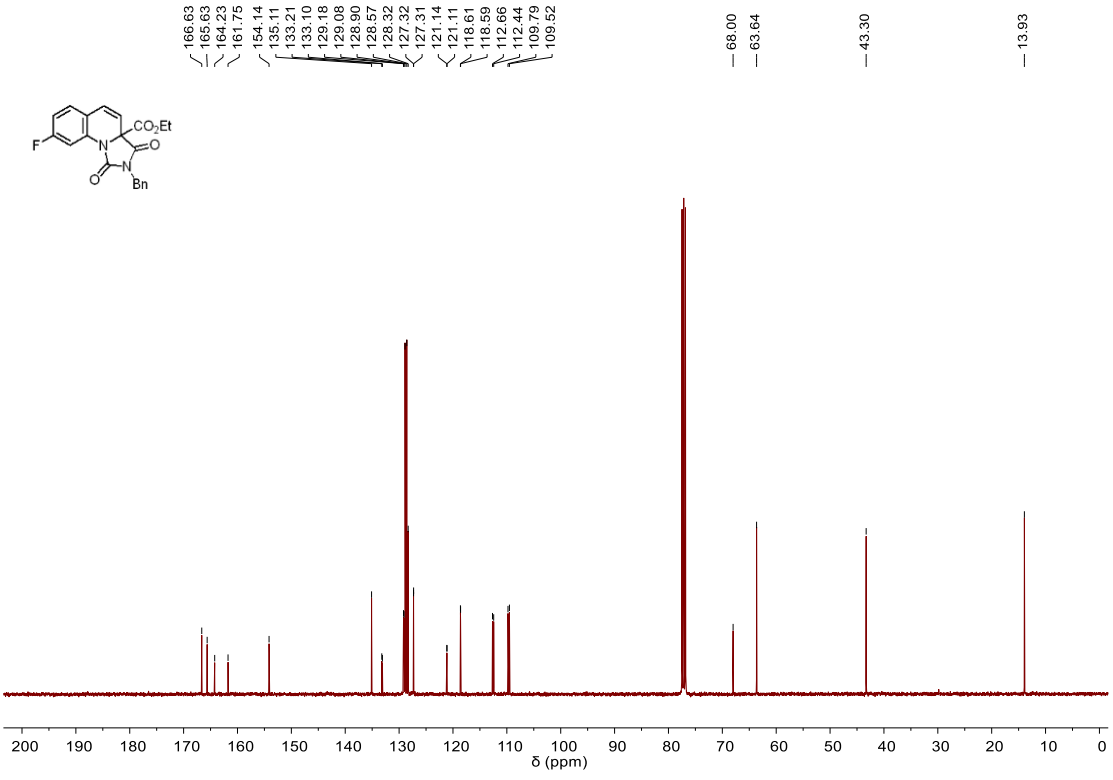
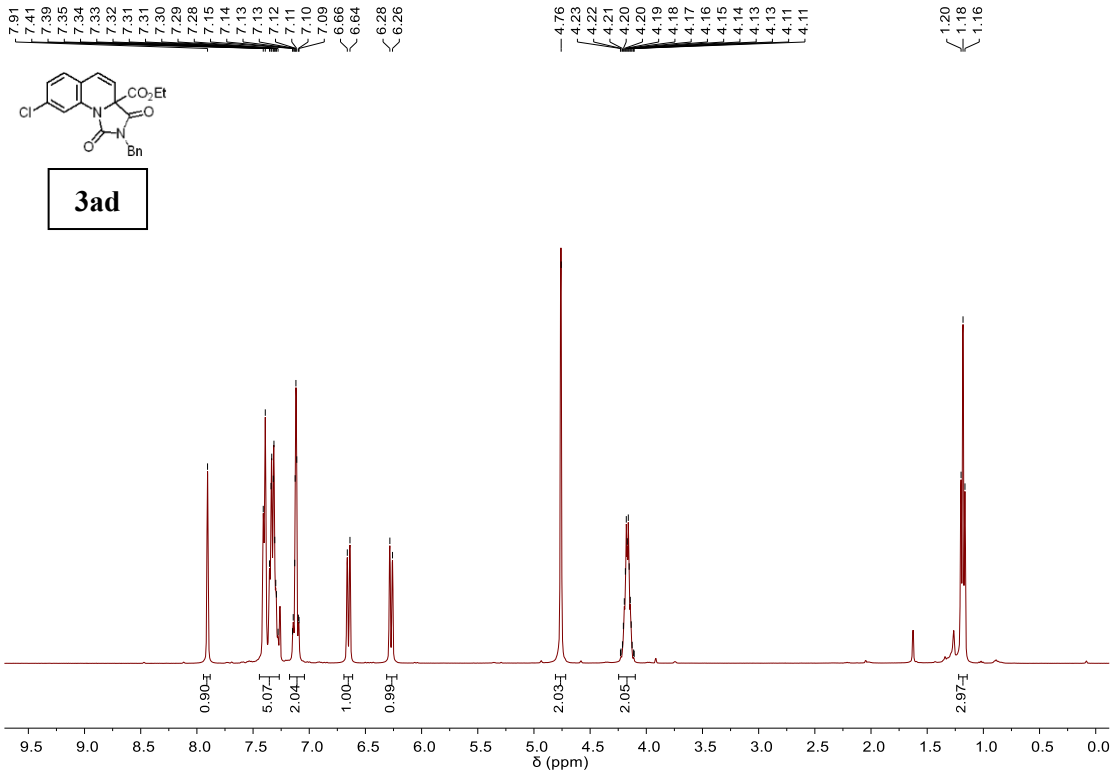
121.88
117.26
68.62
63.79
43.41
13.93
Cl
CO2Et
O
N
O
N
Bn
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)


7.66 7.65 7.63 7.62 7.41 7.41 7.39 7.39 7.39 7.36 7.35 7.35 7.33 7.33 7.32 7.32 7.31 7.31 7.29 7.17 7.16 7.15 7.13 6.89 6.88 6.87 6.86 6.84 6.84 6.66 6.64 6.24 6.21 4.76 4.22 4.21 4.20 4.19 4.19 4.18 4.17 4.16 4.16 4.15 4.14 4.14 4.13 1.20 1.18 1.16
CO2Et
F
O
N
O
N
Bn
3ac
0.96 2.01 3.19 1.04 1.00 1.00 0.98 2.07 2.08 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
δ (ppm)


166.63 165.63 164.23 161.75 154.14 135.11 133.21 133.10 129.18 129.08 128.90 128.57 128.32 127.32 127.31 121.14 121.11 118.61 118.59 112.66 112.44 109.79 109.52 68.00 63.64 43.30 13.93
CO2Et
F
O
N
O
N
Bn
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)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7.29
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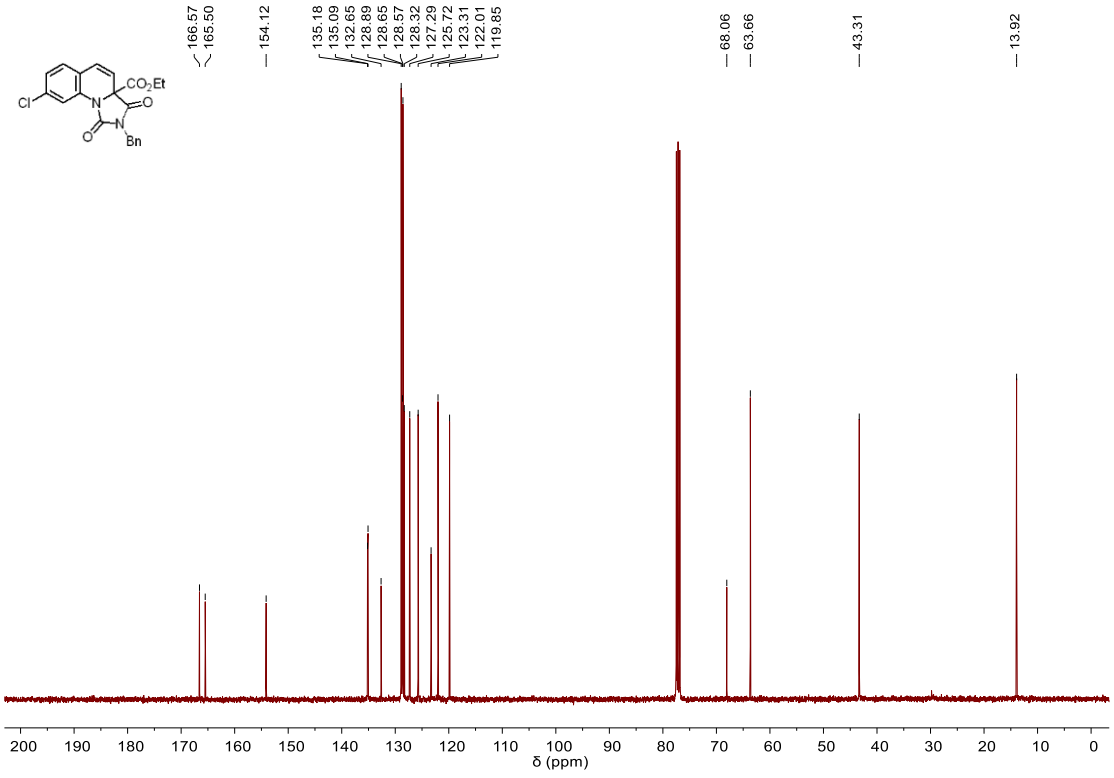
7.15
7.14
7.13
7.12
7.11
7.10
7.09
6.66
6.64
6.28
6.26
4.76
4.23
4.22
4.21
4.20
4.20
4.19
4.18
4.17
4.16
4.15
4.14
4.13
4.13
4.11
4.11
1.20
1.18
1.16
CO2Et
Cl
N
O
O
N
Bn
0.90
5.07
2.04
1.00
0.99
2.03
2.05
2.97
δ (ppm)

3ad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128.65
128.57
128.32
127.29
125.72
123.31
122.01
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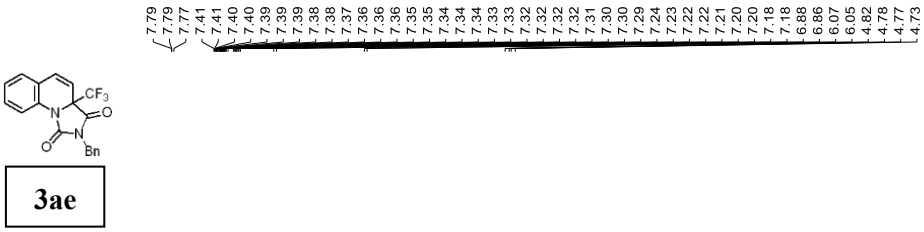
68.06
63.66
43.31
13.92
CO2Et
Cl
N
O
O
N
Bn
δ (ppm)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7.39
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7.38
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7.34
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7.32
7.32
7.31
7.30
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7.29
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7.23
7.22
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7.21
7.20
7.20
7.18
7.18
6.88
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6.05
4.82
4.78
4.77
4.73

CF3
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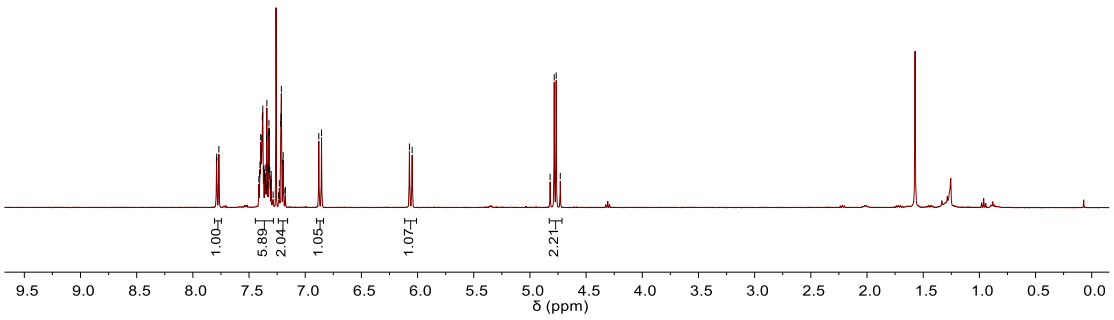
N
N
O
Bn

3ae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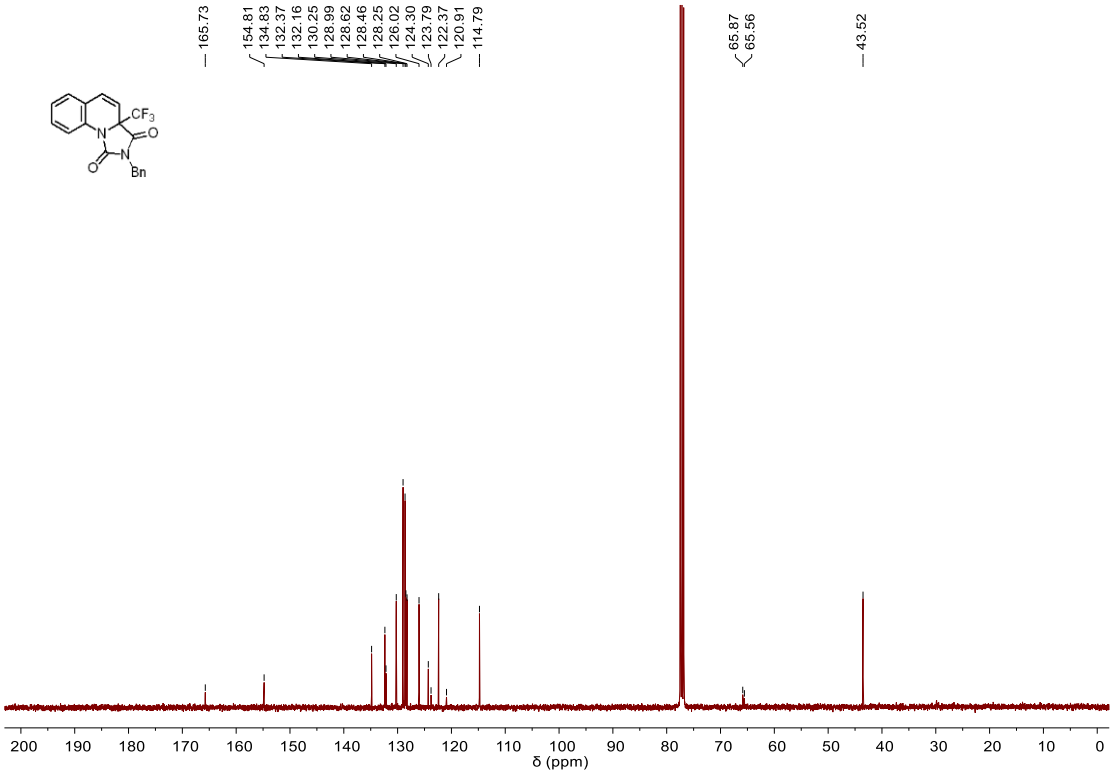
2.04
1.05
1.07
2.21
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)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132.16
130.25
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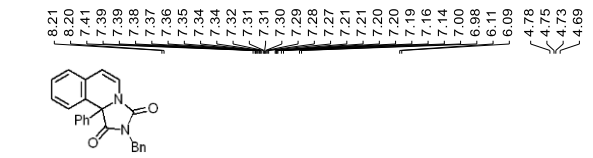
128.62
128.46
128.25
126.02
124.30
123.79
122.37
120.91
114.79
65.87
65.56
43.52
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

CF3
O
N
N
O
Bn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7.31
7.31
7.30
7.29
7.28
7.27
7.21
7.21
7.20
7.20
7.19
7.16
7.14
7.00
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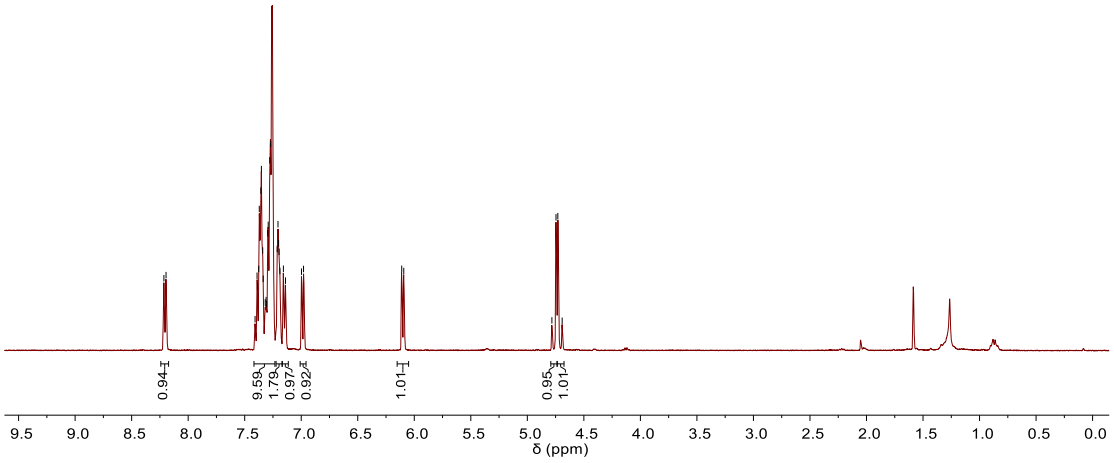
6.09
4.78
4.75
4.73
4.69
Ph
N
O
O
N
Bn

3af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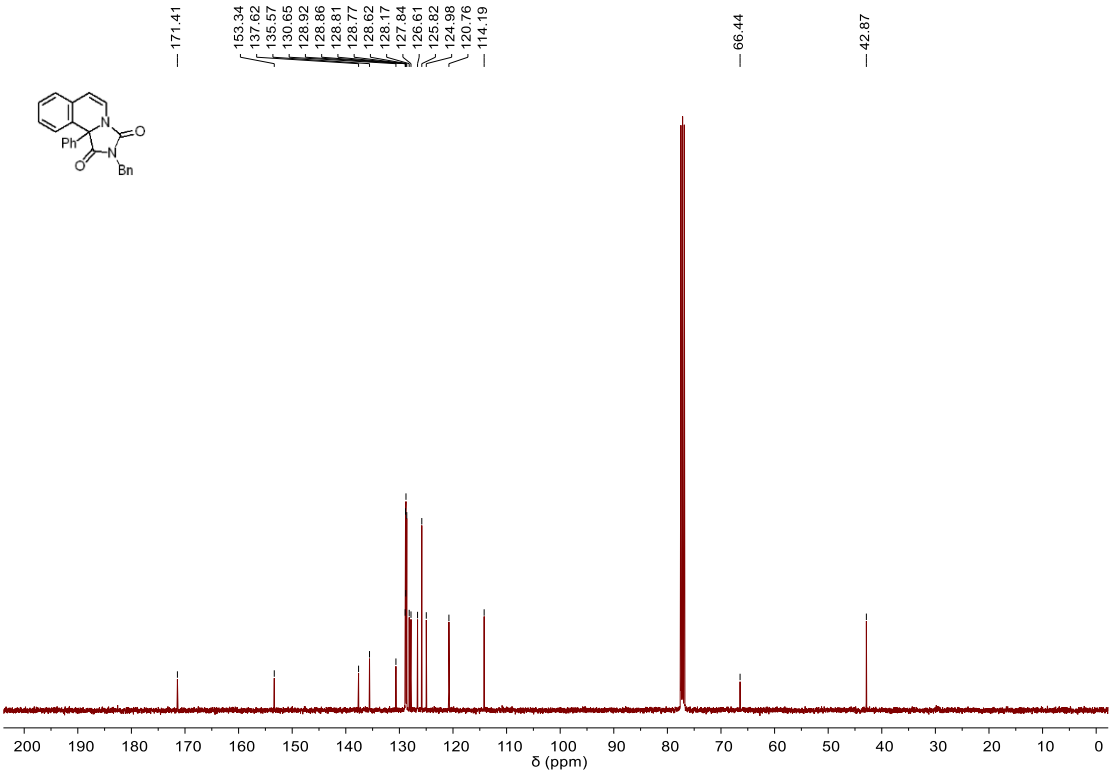
9.59
1.79
0.97
0.92
1.01
0.95
1.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)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135.57
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128.92
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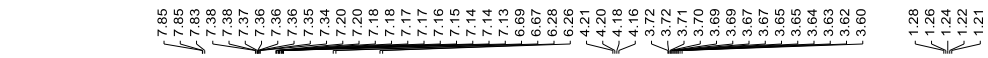
128.81
128.77
128.62
128.17
127.84
126.61
125.82
124.98
120.76
114.19
66.44
42.87
Ph
N
O
O
N
Bn
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)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7.85
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7.36
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7.34
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7.20
7.18
7.18
7.17
7.17
7.16
7.15
7.14
7.14
7.13
6.69
6.67
6.28
6.26
4.21
4.20
4.18
4.16
3.72
3.72
3.71
3.70
3.69
3.69
3.67
3.67
3.65
3.65
3.64
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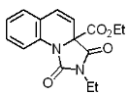
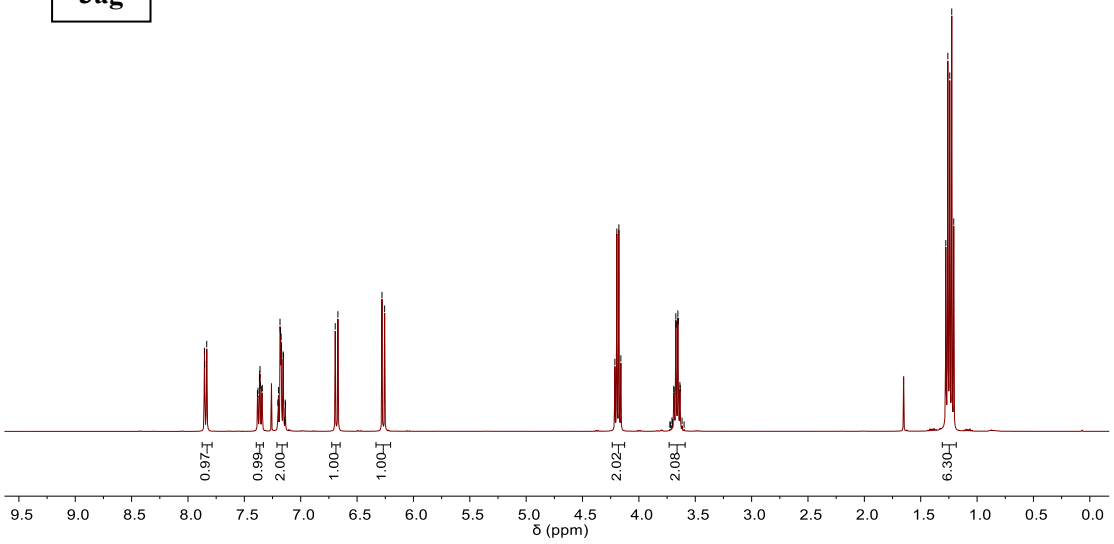
3.60
1.28
1.26
1.24
1.22
1.21


CO2Et
O
N
O
N
Et

3ag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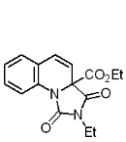
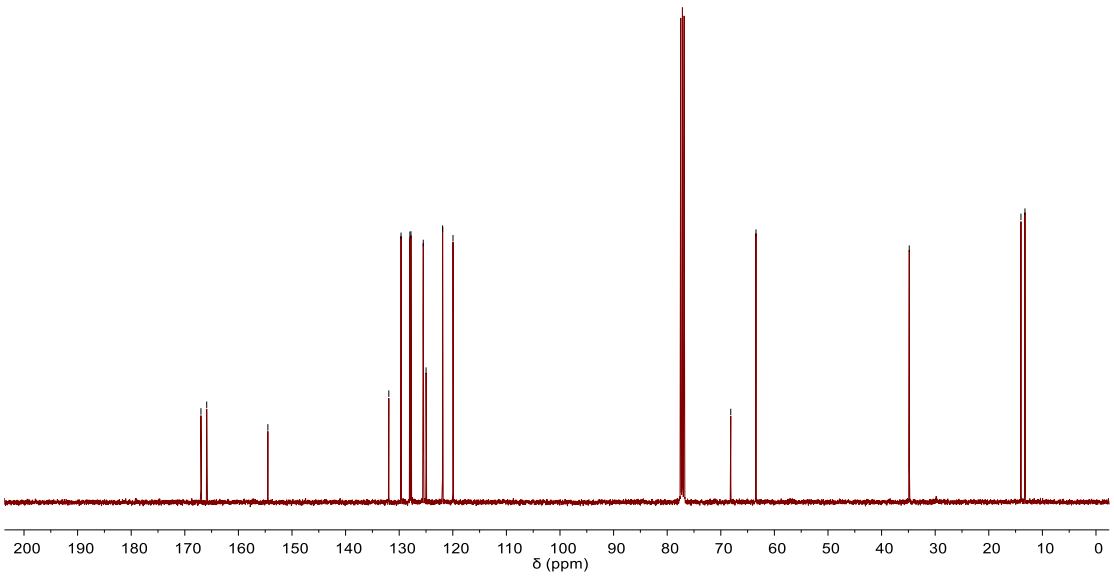
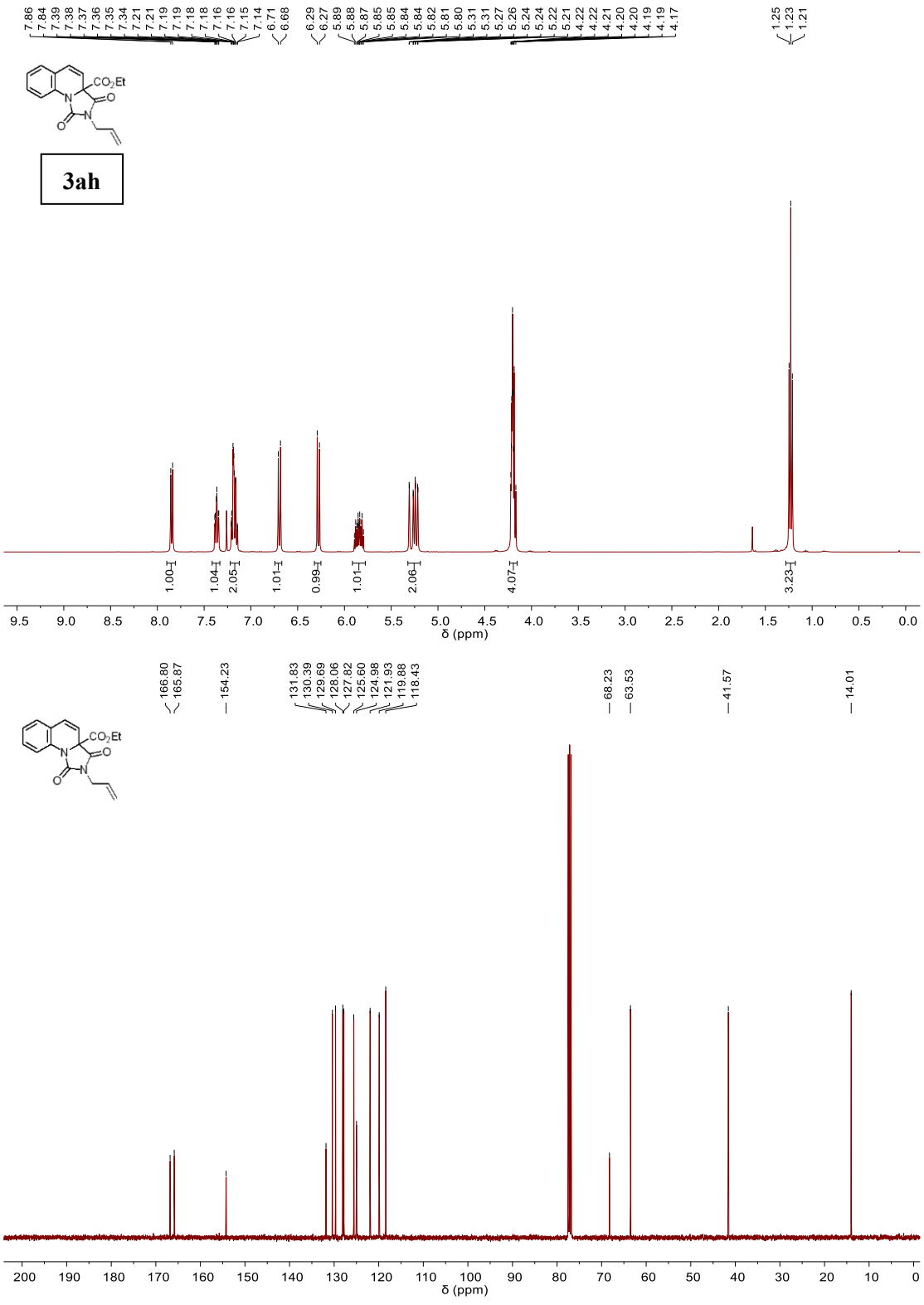
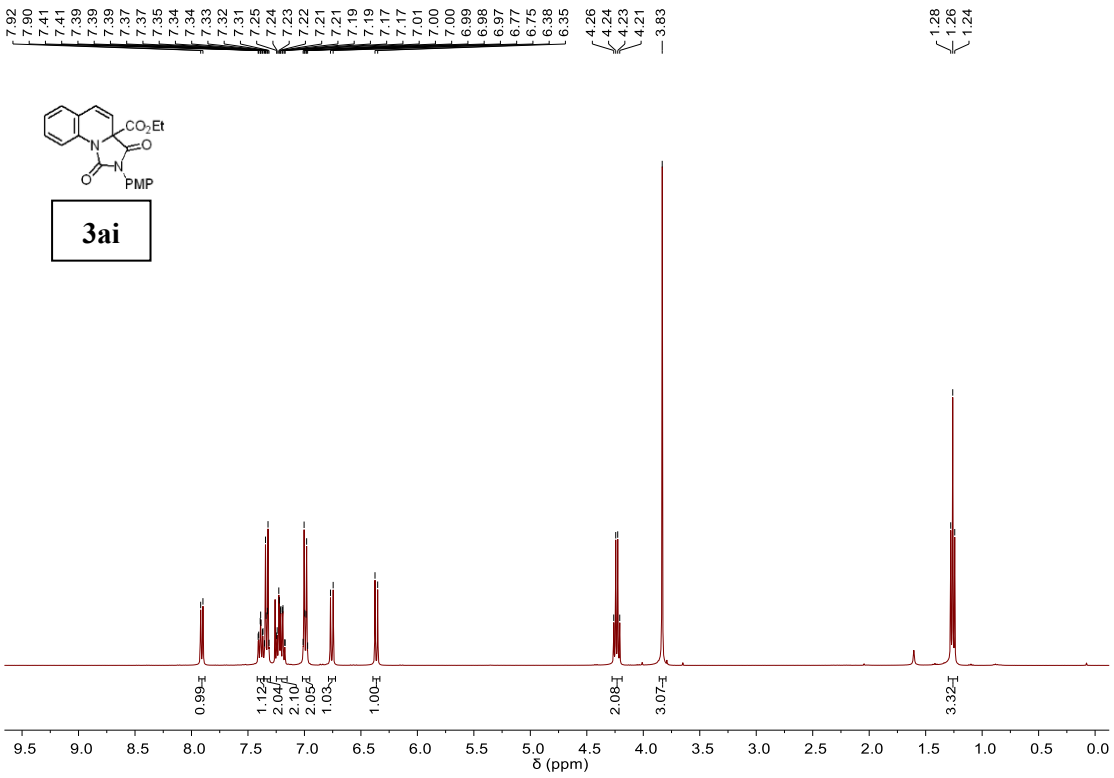
0.99
2.00
1.00
1.00
2.02
2.08
6.30
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)

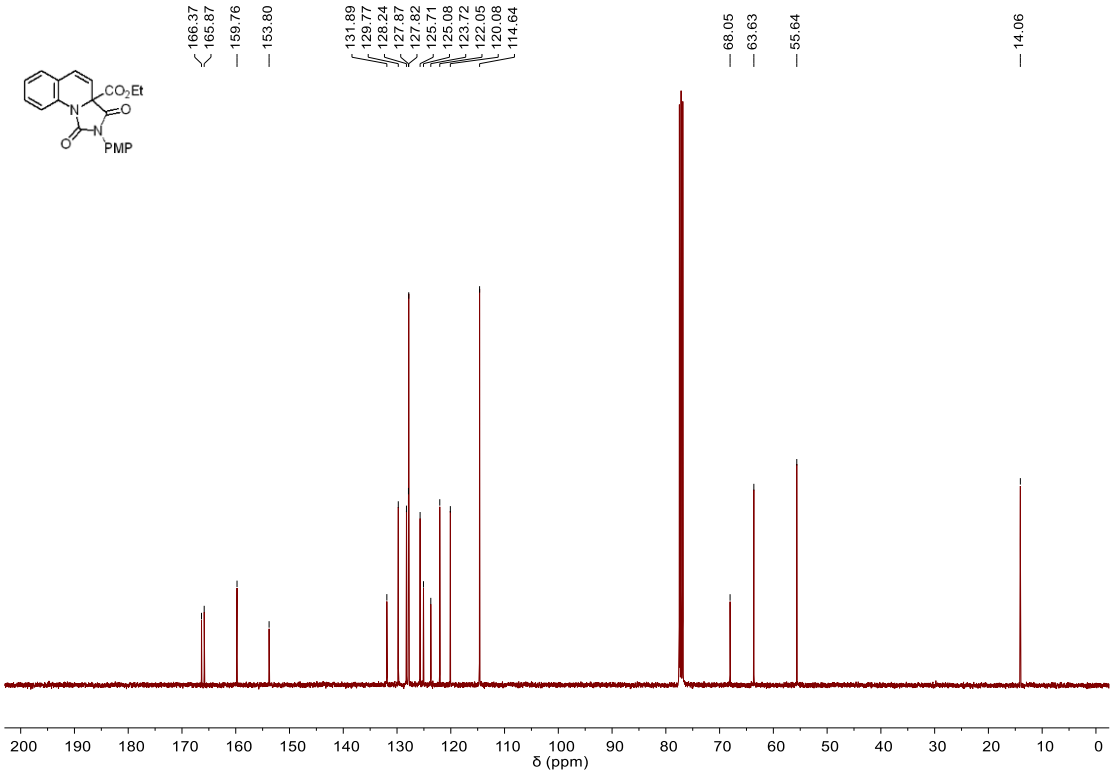

CO2Et
O
N
O
N
Et

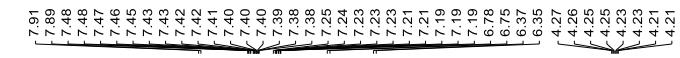

166.99
165.91
154.50
131.94
129.66
128.00
127.81
125.51
124.99
121.90
119.96
68.14
63.44
34.84
14.00
13.25

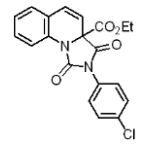

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)


7.86
7.84
7.39
7.38
7.37
7.36
7.35
7.34
7.21
7.21
7.19
7.19
7.18
7.18
7.16
7.16
7.15
7.14
6.71
6.68
6.29
6.27
5.89
5.88
5.87
5.85
5.85
5.84
5.84
5.82
5.81
5.80
5.31
5.31
5.27
5.26
5.24
5.24
5.22
5.21
4.22
4.22
4.21
4.20
4.20
4.19
4.19
4.17
1.25
1.23
1.21
CO2Et
O
N
O
N
3ah
1.00
1.04
2.05
1.01
0.99
1.01
2.06
4.07
3.23
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
δ (ppm)
166.80
165.87
154.23
131.83
130.39
129.69
128.06
127.82
125.60
124.98
121.93
119.88
118.43
68.23
63.53
41.57
14.01
CO2Et
O
N
O
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

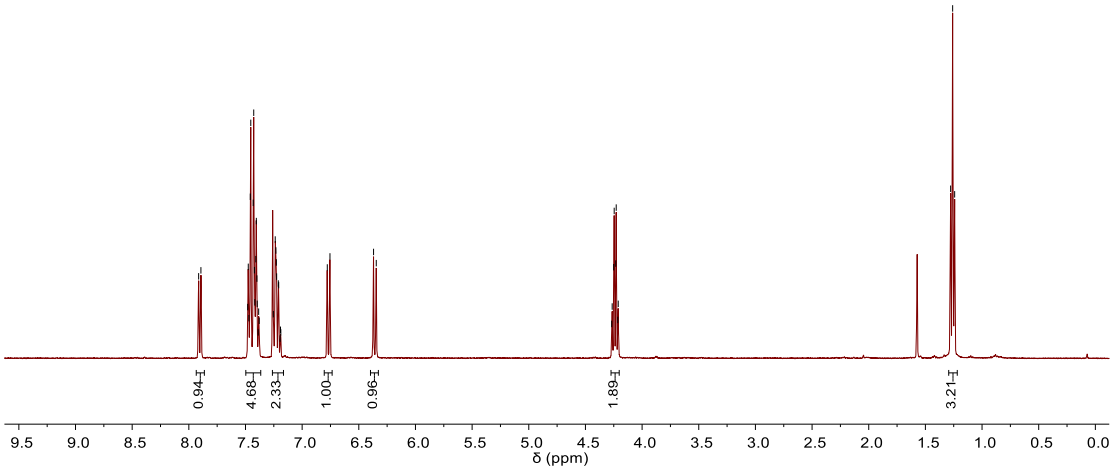

7.92
7.90
7.41
7.41
7.39
7.39
7.39
7.37
7.37
7.35
7.34
7.34
7.33
7.32
7.31
7.25
7.24
7.23
7.22
7.21
7.21
7.19
7.19
7.17
7.17
7.01
7.00
7.00
6.99
6.98
6.97
6.77
6.75
6.38
6.35
4.26
4.24
4.23
4.21
3.83
1.28
1.26
1.24
CO2Et
O
N
O
N
PMP
3ai
0.99
1.12
2.04
2.10
2.05
1.03
1.00
2.08
3.07
3.32
9.5 9.0 8.5 8.0 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
δ (ppm)

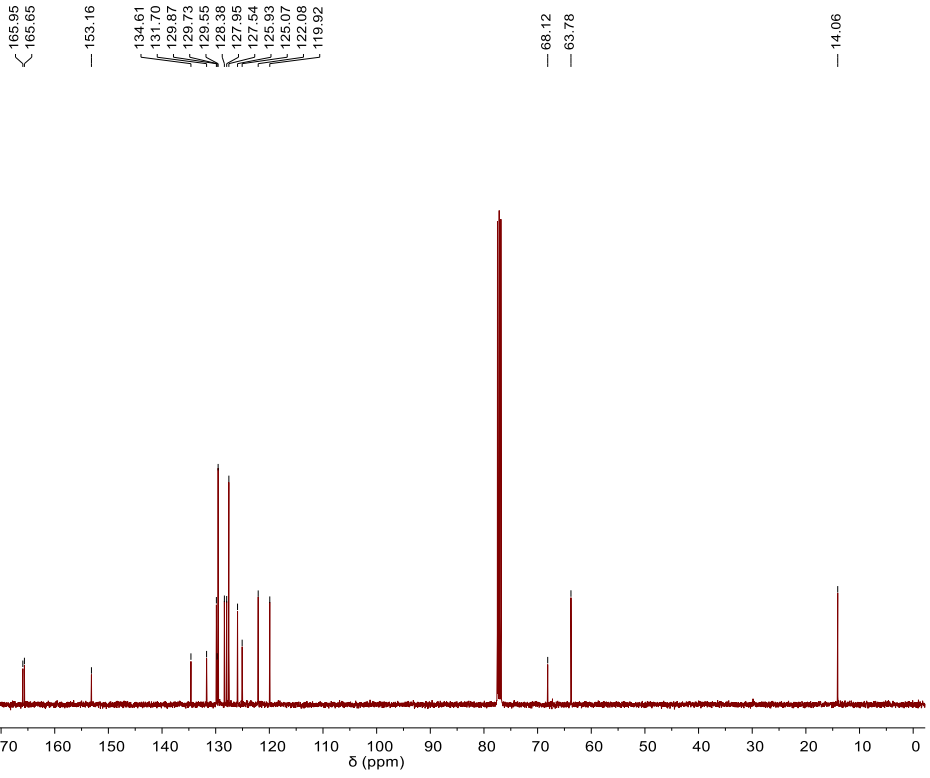

166.37
165.87
159.76
153.80
131.89
129.77
128.24
127.87
127.82
125.71
125.08
123.72
122.05
120.08
114.64
68.05
63.63
55.64
14.06
CO2Et
O
N
O
N
PMP
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

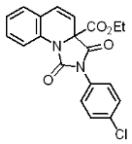

7.91
7.89
7.48
7.48
7.47
7.46
7.45
7.43
7.43
7.42
7.42
7.41
7.40
7.40
7.40
7.39
7.38
7.38
7.25
7.24
7.23
7.23
7.23
7.21
7.21
7.19
7.19
7.19
6.78
6.75
6.37
6.35
4.27
4.26
4.25
4.25
4.23
4.23
4.21
4.21
1.28
1.26
1.24

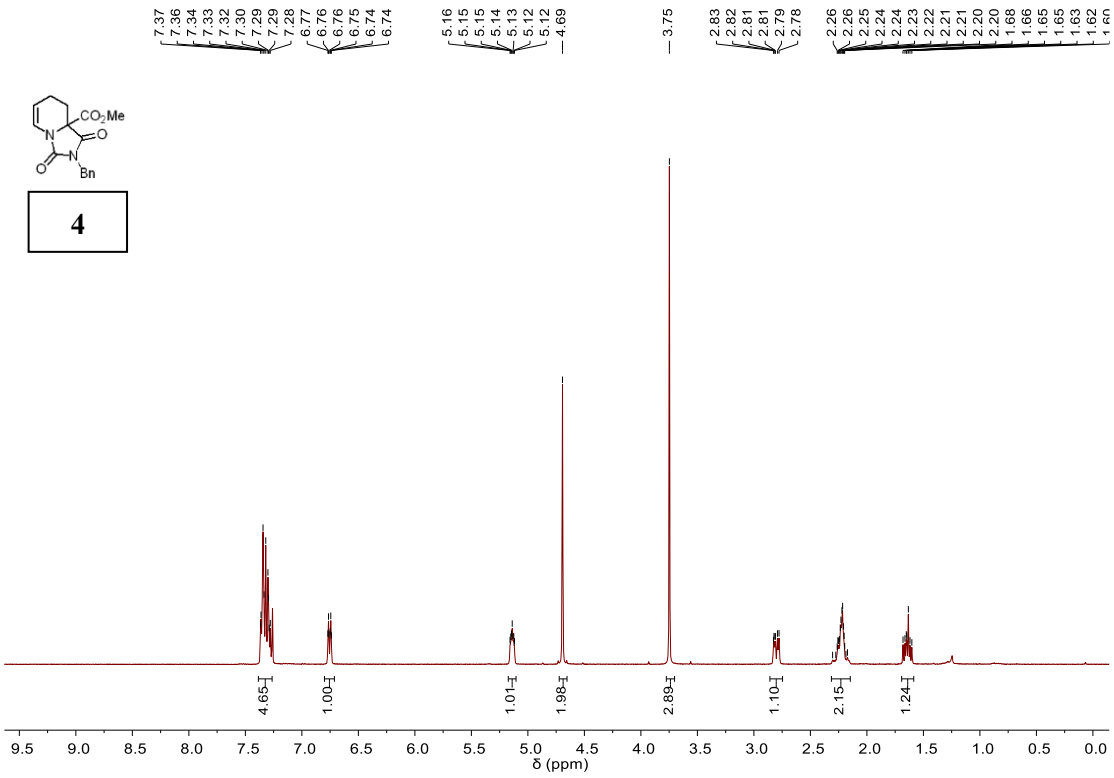

CO2Et
O
N
O
N
Cl

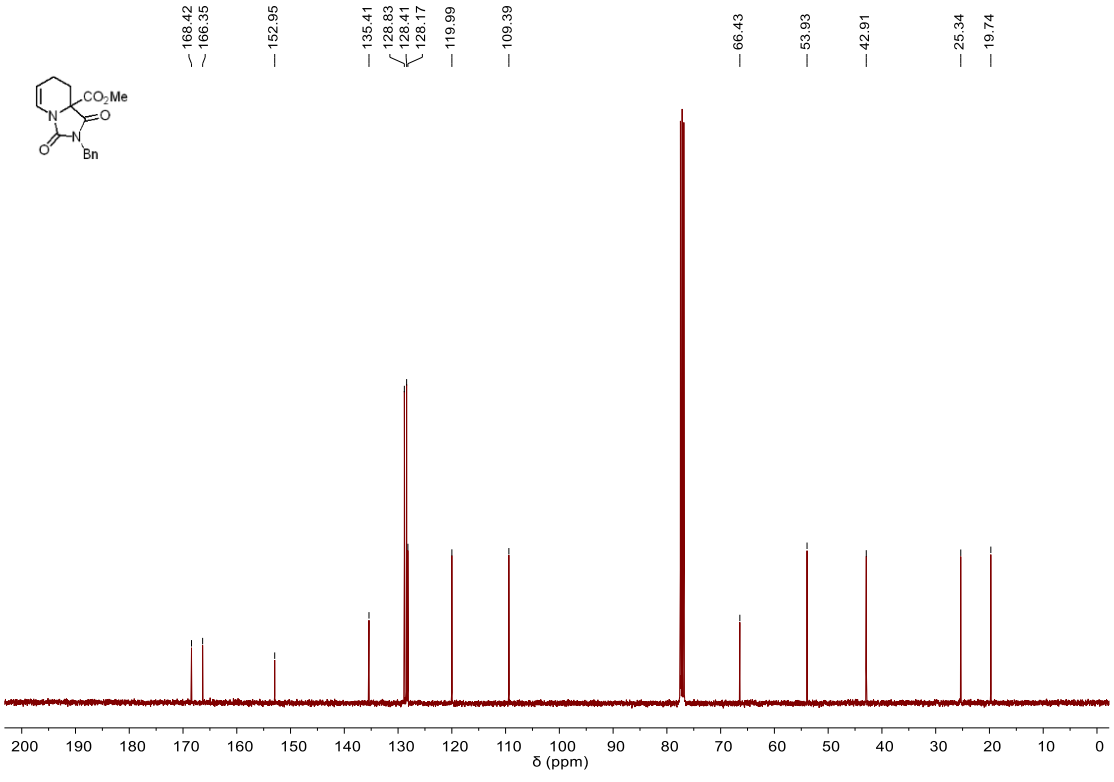
3aj

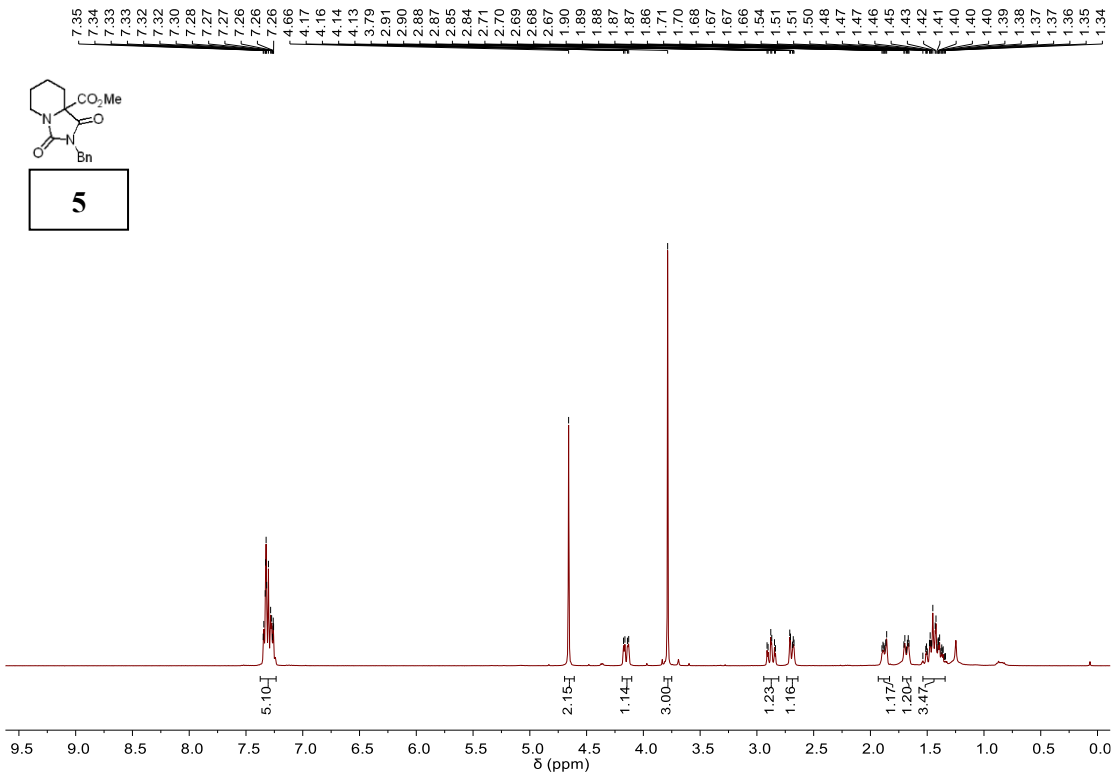

0.94
4.68
2.33
1.00
0.96
1.89
3.21
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

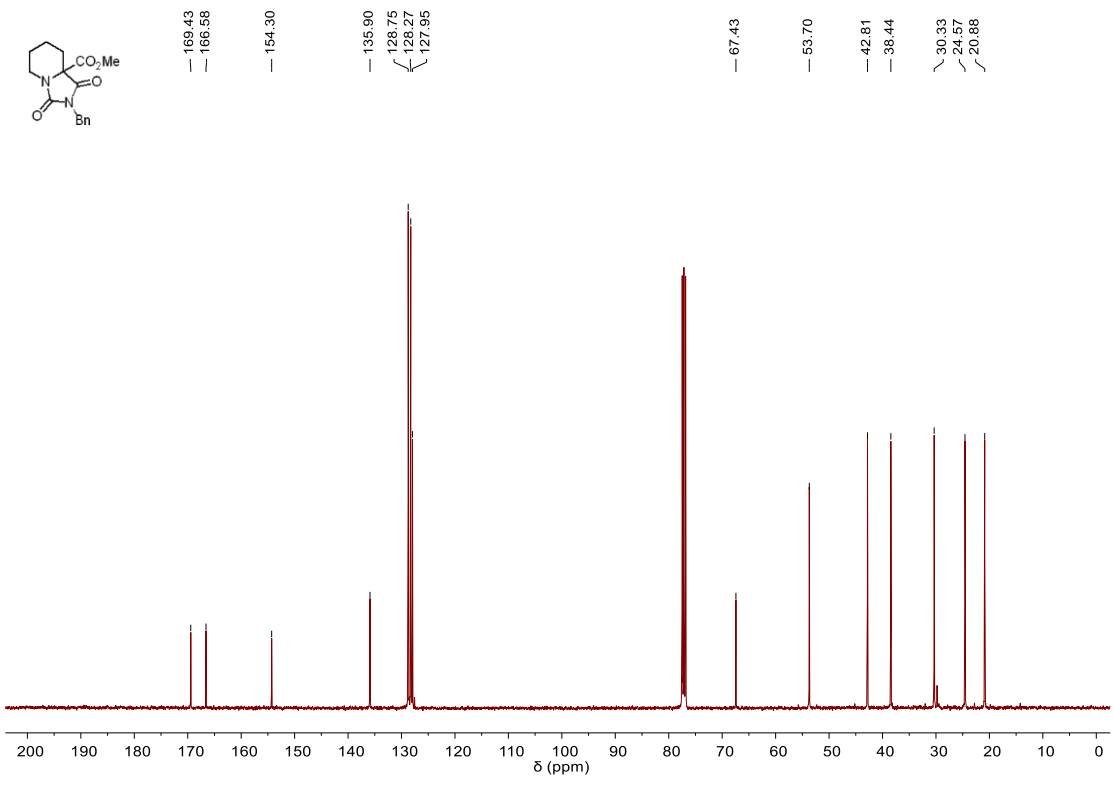

165.95
165.65
153.16
134.61
131.70
129.87
129.73
129.55
128.38
127.95
127.54
125.93
125.07
122.08
119.92
68.12
63.78
14.06
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

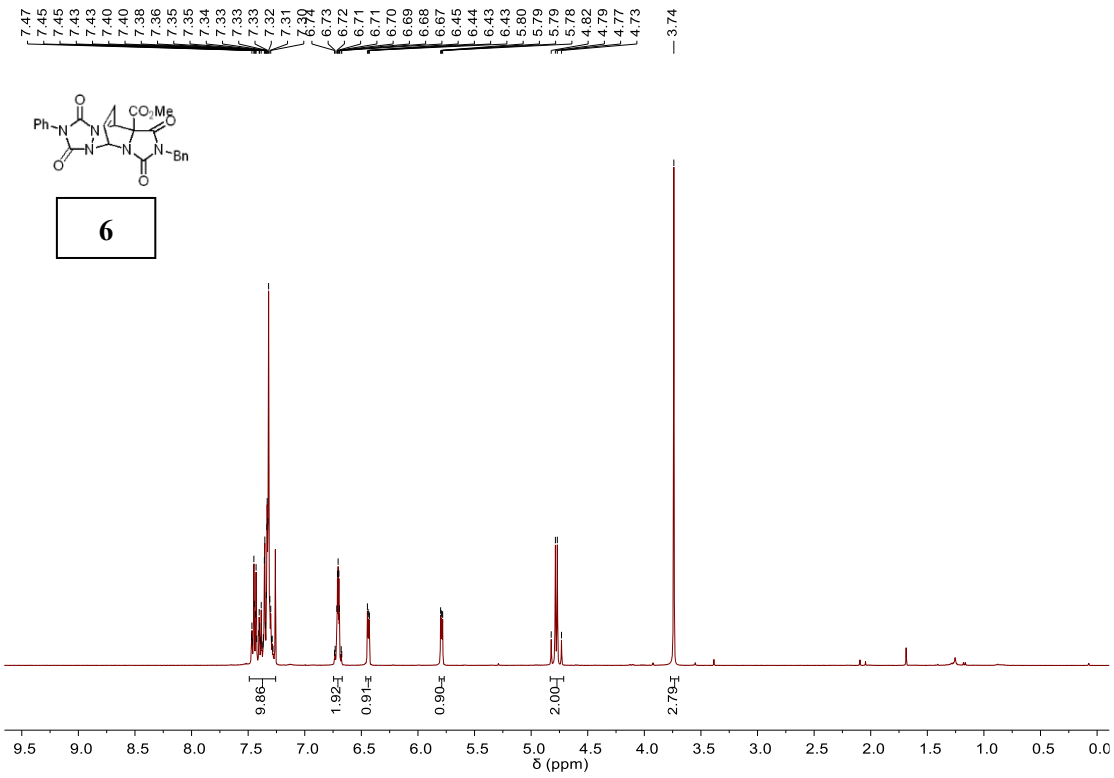

CO2Et
O
N
O
N
Cl

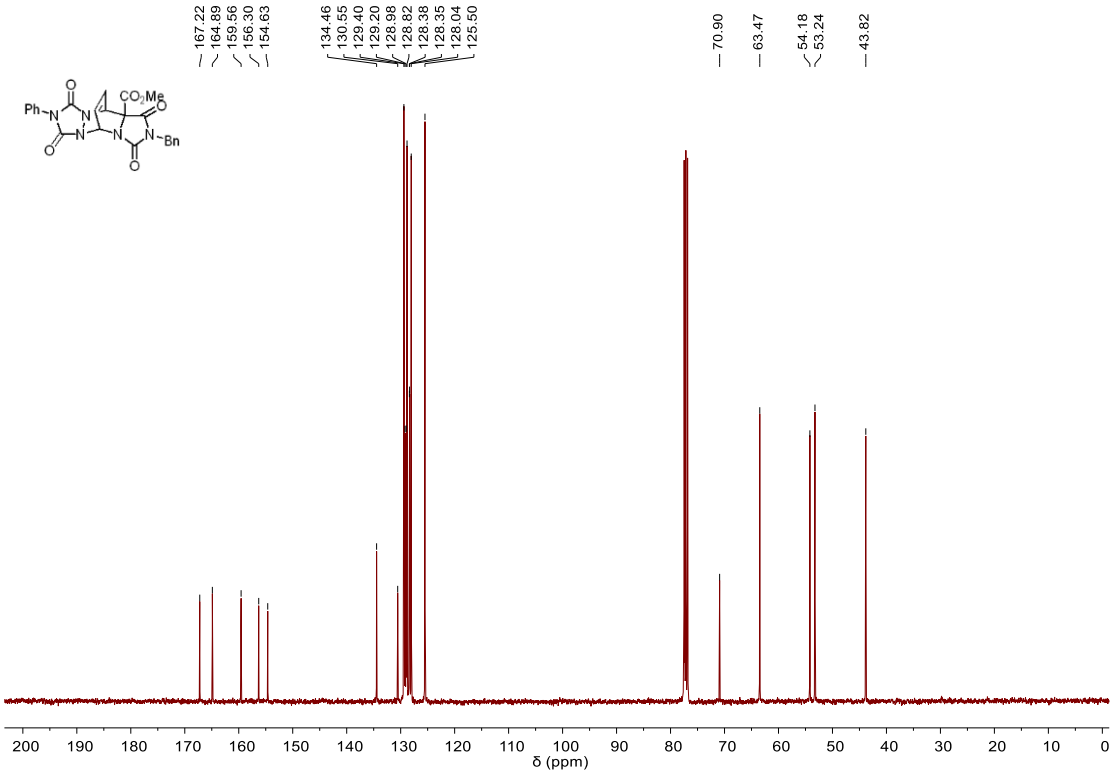

7.37
7.36
7.34
7.33
7.32
7.30
7.29
7.29
7.28
6.77
6.76
6.76
6.75
6.74
6.74
5.16
5.15
5.15
5.14
5.13
5.12
5.12
4.69
3.75
2.83
2.82
2.81
2.81
2.79
2.78
2.26
2.26
2.25
2.24
2.24
2.23
2.22
2.21
2.21
2.20
2.20
1.68
1.66
1.65
1.65
1.63
1.62
CO2Me
O
N
O
N
Bn
4
4.65
1.00
1.01
1.98
2.89
1.10
2.15
1.24
9.5 9.0 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
δ (ppm)

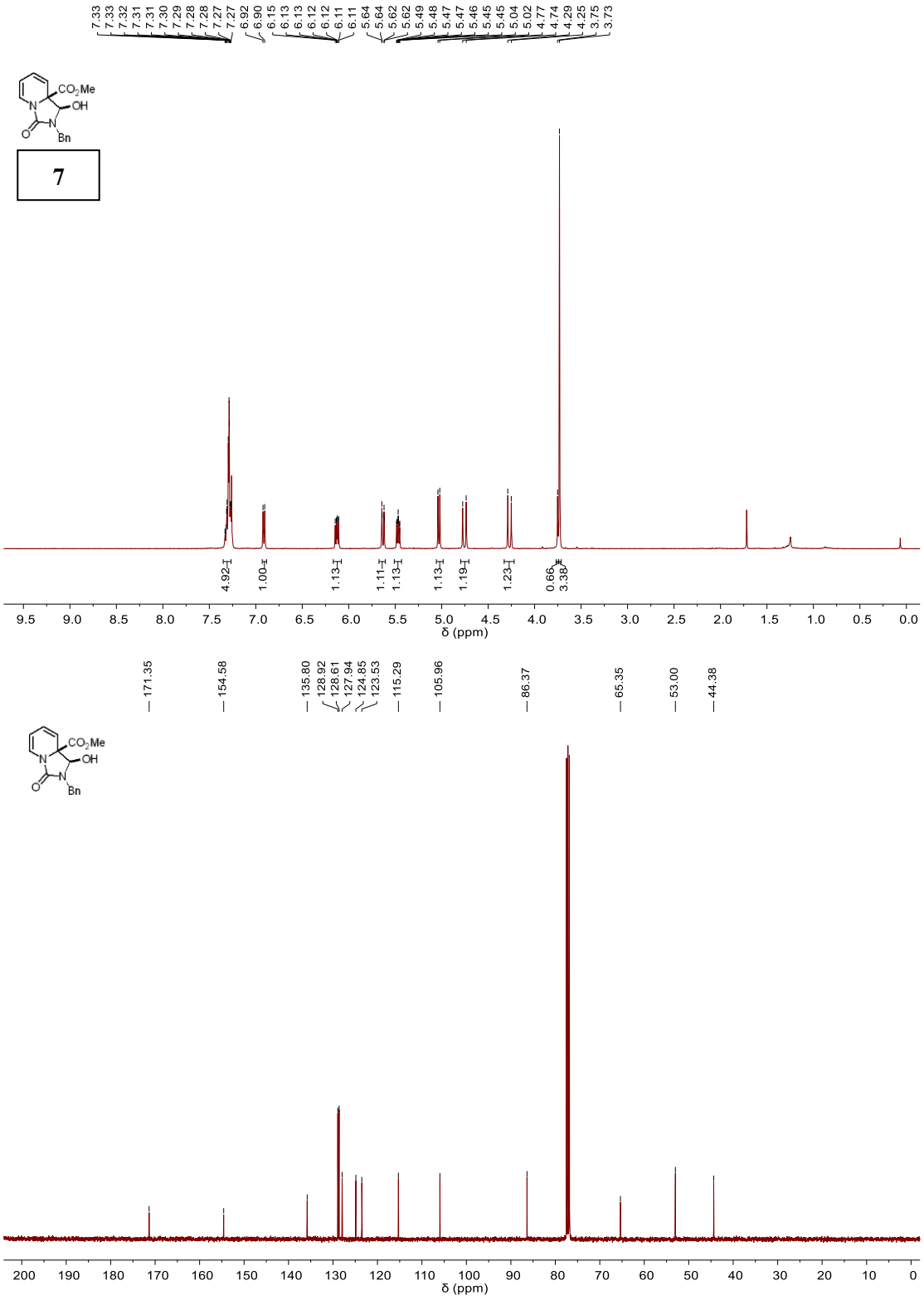

168.42
166.35
152.95
135.41
128.83
128.41
128.17
119.99
109.39
66.43
53.93
42.91
25.34
19.74
CO2Me
O
N
O
N
Bn
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)


7.35 7.34 7.33 7.33 7.32 7.32 7.30 7.28 7.27 7.27 7.26 7.26 7.26
4.66 4.17 4.16 4.14 4.13 3.79 2.91 2.90 2.88 2.87 2.85 2.84 2.71 2.70 2.69 2.68 2.67 1.90 1.89 1.88 1.87 1.87 1.86 1.71 1.70 1.68 1.67 1.66 1.54 1.51 1.51 1.50 1.48 1.47 1.47 1.46 1.45 1.43 1.42 1.41 1.40 1.40 1.39 1.38 1.37 1.37 1.36 1.35 1.34
CO2Me
Bn
5
5.10
2.15
1.14
3.00
1.23
1.16
1.17
1.20
3.47
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
δ (ppm)


169.43
166.58
154.30
135.90
128.75
128.27
127.95
67.43
53.70
42.81
38.44
30.33
24.57
20.88
CO2Me
Bn
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)


7.47
7.45
7.45
7.43
7.43
7.40
7.40
7.38
7.36
7.35
7.35
7.34
7.33
7.33
7.33
7.32
7.31
6.73
6.72
6.71
6.71
6.70
6.69
6.68
6.67
6.45
6.44
6.43
6.43
5.80
5.79
5.79
5.78
4.82
4.79
4.77
4.73
3.74
Ph
CO2Me
Bn
6
9.86
1.92
0.91
0.90
2.00
2.79
δ (ppm)


167.22
164.89
159.56
156.30
154.63
134.46
130.55
129.40
129.20
128.98
128.82
128.38
128.35
128.04
125.50
70.90
63.47
54.18
53.24
43.82
Ph
CO2Me
Bn
δ (ppm)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7.32
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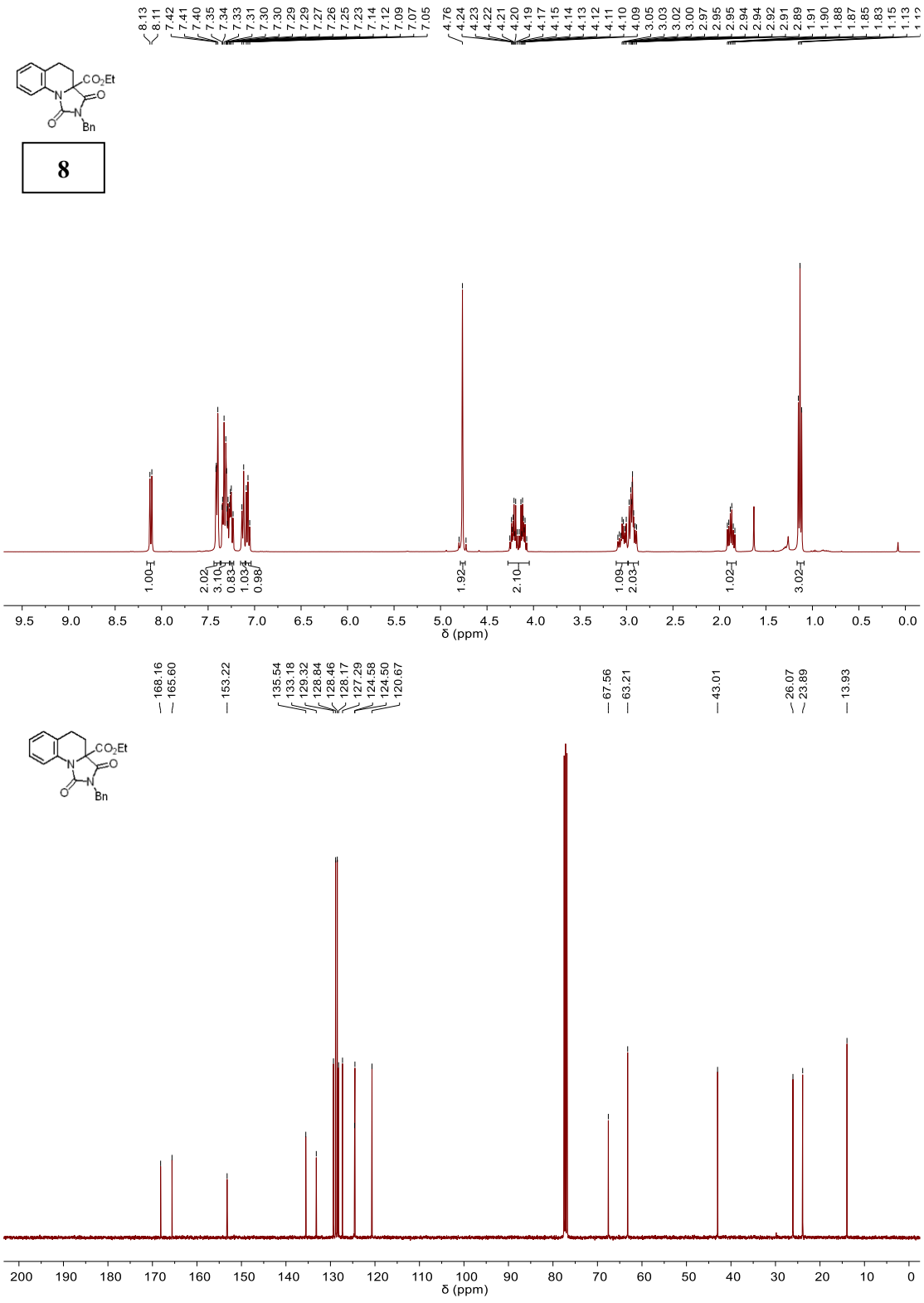
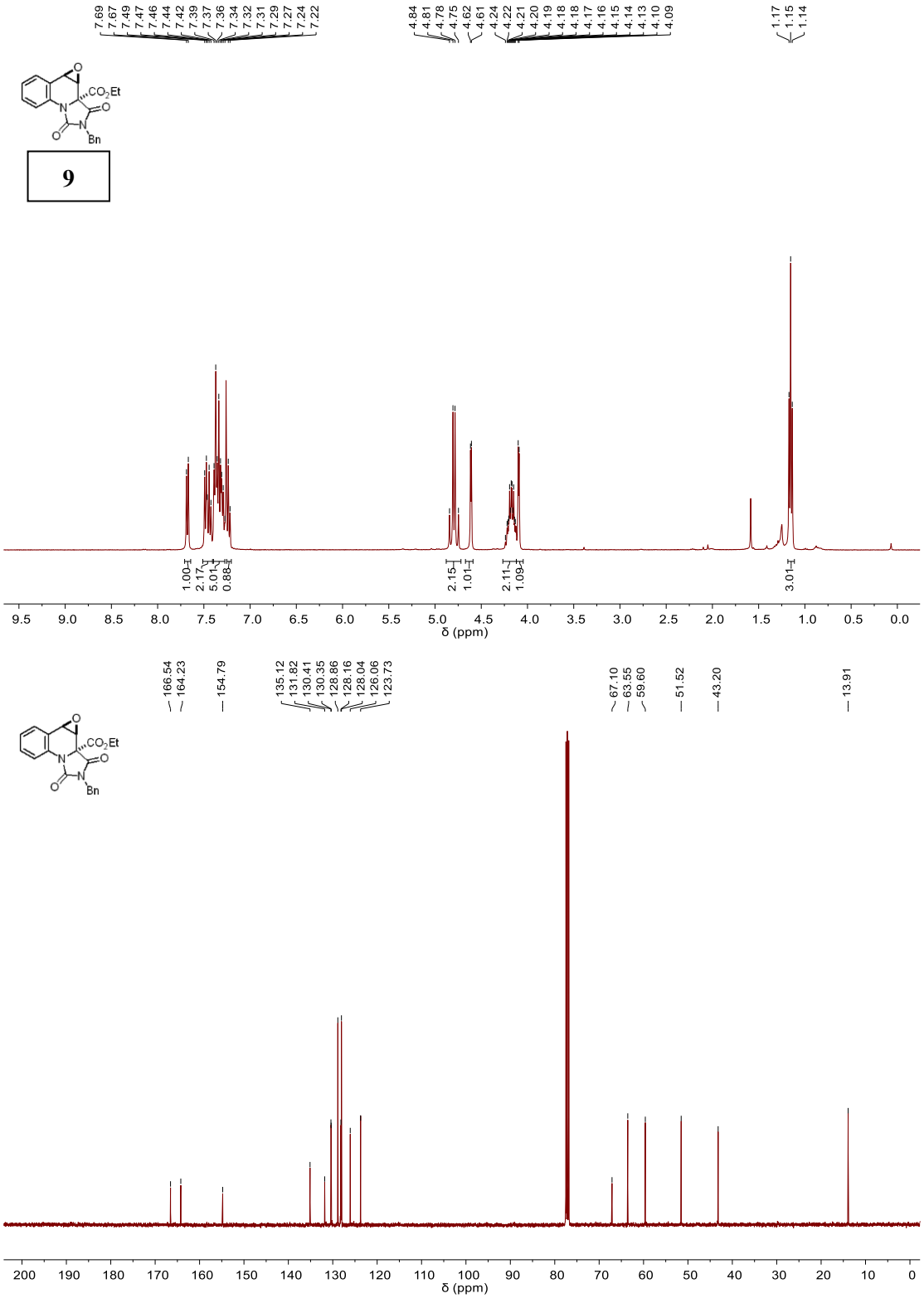
7.31
7.30
7.29
7.28
7.28
7.27
7.27
6.92
6.90
6.15
6.13
6.13
6.12
6.12
6.11
6.11
5.64
5.64
5.62
5.62
5.49
5.48
5.47
5.47
5.46
5.45
5.45
5.04
5.02
4.77
4.74
4.29
4.25
3.75
3.73
CO2Me
OH
N
N
O
Bn
7
4.92
1.00
1.13
1.11
1.13
1.13
1.19
1.23
0.66
3.38
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)
171.35
154.58
135.80
128.92
128.61
127.94
124.85
123.53
115.29
105.96
86.37
65.35
53.00
44.38
CO2Me
OH
N
N
O
Bn
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)


8.13
8.11
7.42
7.41
7.40
7.35
7.34
7.33
7.31
7.30
7.30
7.29
7.29
7.27
7.26
7.25
7.23
7.14
7.12
7.09
7.07
7.05
4.76
4.24
4.23
4.22
4.21
4.20
4.19
4.17
4.15
4.14
4.13
4.12
4.11
4.10
4.09
3.05
3.03
3.02
3.00
2.97
2.95
2.95
2.94
2.94
2.92
2.91
2.89
1.91
1.90
1.88
1.87
1.85
1.83
1.15
1.13
CO2Et
O
N
O
N
Bn
8
1.00
2.02
3.10
0.83
1.03
0.98
1.92
2.10
1.09
2.03
1.02
3.02
δ (ppm)
168.16
165.60
153.22
135.54
133.18
129.32
128.84
128.46
128.17
127.29
124.58
124.50
120.67
67.56
63.21
43.01
26.07
23.89
13.93
δ (ppm)


7.69
7.67
7.49
7.47
7.46
7.44
7.42
7.39
7.37
7.36
7.34
7.32
7.31
7.29
7.27
7.24
7.22
4.84
4.81
4.78
4.75
4.62
4.61
4.24
4.22
4.21
4.20
4.19
4.18
4.18
4.17
4.16
4.15
4.14
4.13
4.10
4.09
1.17
1.15
1.14
CO2Et
O
N
O
N
Bn
9
1.00
2.17
5.01
0.88
2.15
1.01
2.11
1.09
3.01
δ (ppm)
166.54
164.23
154.79
135.12
131.82
130.41
130.35
128.86
128.16
128.04
126.06
123.73
67.10
63.55
59.60
51.52
43.20
13.91
δ (ppm)