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Supporting Information

Pd(II)-catalyzed C8−H alkoxycarbonylmethylation of 1-naphthylamides with α-chloroalkyl esters

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Table of Contents

1. **General Information** S2
2. **Preparation of Substrates** S2
3. **Optimization of Reaction Conditions** S2
4. **Typical Procedure for the Reaction** S3
5. **Characterization Data of the Products** S5
6. **References** S12
7. **The Single Crystal X-ray Diffraction Study of 3aa** S12
8. **Copies of ^{1}H and ^{13}C NMR Spectra for the Products** S13

1. General Information

^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrometer with $CDCl_3$ as the solvent and TMS as an internal standard. Melting points were measured using a WC-1 microscopic apparatus and are uncorrected. High resolution mass spectra were ensured on a MALDI-FTMS. All solvents were used directly without further purification. Dichloromethane, ethyl acetate, and petroleum ether were used for column chromatography. Chemical shift multiplicities are represented as follows: (s = singlet, d = doublet, m = multiplet, dd = double doublet). The commercials were obtained from commercial sources and used as-received without further purification unless otherwise noted.

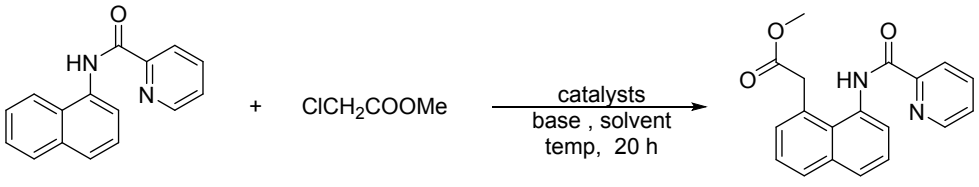
2. Preparation of Substrates 1 [1]

All of N-(naphthalen-1-yl)picolinamides as substrates were prepared from the corresponding carboxylic acids and 1-naphthylamines according to the reported procedure.[1]

3. Optimization of Reaction Conditions

A 25 mL schlenk tube was equipped with a magnetic stir bar and charged with N-(naphthalen-1-yl)picolinamide **1a** (24.8 mg, 0.1 mmol), methyl chloroacetate **2a** (20.0 μL, 0.2 mmol, 2.0 equiv), catalyst, base (0.2 mmol, 2.0 equiv), additive (0.2 mmol) in solvent (1.0 mL). The resulting mixture was reacted at 130 °C under air atmosphere for 20 h, and cooled to room temperature. Upon completion, the mixture was added into CH_2Cl_2 (25 mL) and the resulting mixture was filtered through a pad of celite. After evaporation of the solvent under vacuum, the residue was purified by column chromatography on silica gel (100–200 mesh) using petroleum ether/ethyl acetate as an eluent (3:1, V/V) to afford the pure product **3aa**.

Table S1 Screening of Reaction Conditions[a,b]



1a **2a** **3aa**

Entry	Catalyst	Base	Additive	Solvent	Temp(°C)	Yield(%)
1	$Co(OAc)_2$	NaOAc	NaI	1,4-dioxane	130	NR
2	$FeCl_3$	NaOAc	NaI	1,4-dioxane	130	NR
3	$NiBr_2$	NaOAc	NaI	1,4-dioxane	130	NR
4	$Cu(OAc)_2.H_2O$	NaOAc	NaI	1,4-dioxane	130	NR
5	Ag_2O	NaOAc	NaI	1,4-dioxane	130	NR
6	$Pd(OAc)_2$	NaOAc	NaI	1,4-dioxane	130	59
7	$Pd(OAc)_2$	NaOAc	NaI	acetone	130	NR

8	$Pd(OAc)_2$	NaOAc	NaI	CH_3CN	130	8
9	$Pd(OAc)_2$	NaOAc	NaI	EtOH	130	NR
10	$Pd(OAc)_2$	NaOAc	NaI	hexane	130	NR
11	$Pd(OAc)_2$	NaOAc	NaI	NMP	130	NR
12	$Pd(OAc)_2$	NaOAc	NaI	DMSO	130	NR
13	$Pd(OAc)_2$	NaOAc	NaI	DMF	130	NR
14	$Pd(OAc)_2$	NaOAc	NaI	DCE	130	20
15	$Pd_2(dba)_3$	NaOAc	NaI	1,4-dioxane	130	35
16	$Pd(CH_3CN)_2Cl_2$	NaOAc	NaI	1,4-dioxane	130	55
17	$PdCl_2$	NaOAc	NaI	1,4-dioxane	130	50
18	$Pd(TFA)_2$	NaOAc	NaI	1,4-dioxane	130	92
19	$Pd(PPh)_4$	NaOAc	NaI	1,4-dioxane	130	45
20[c]	$Pd(TFA)_2$	NaOAc	NaI	1,4-dioxane	130	30
21	$Pd(TFA)_2$	NaOAc	NaI	1,4-dioxane	100	60
22	$Pd(TFA)_2$	NaOAc	NaI	1,4-dioxane	80	30
23	$Pd(TFA)_2$	NaOAc	NaI	1,4-dioxane	60	NR
24	$Pd(TFA)_2$	NaOAc	-	1,4-dioxane	130	NR
25[d]	$Pd(TFA)_2$	NaOAc	NaI	1,4-dioxane	130	70
26[e]	$Pd(TFA)_2$	NaOAc	NaI	1,4-dioxane	130	91
27[f]	$Pd(TFA)_2$	NaOAc	NaI	1,4-dioxane	130	60
28[g]	-	NaOAc	NaI	1,4-dioxane	130	NR

[a] Reaction conditions: substrate **1a** (0.1 mmol), **2a** (0.2 mmol), catalyst (15 mol%), base (2.0 equiv) and an additive (2.0 equiv) in solvent (1.0 mL) at 130 °C in air for 20 h. [b]Isolated yield based on **1a**. [c] With the addition of NaI (0.03 mmol). [d] Catalyst (10 mol%). [e] For 24 h. [f] For 12 h. [g] Without Pd catalyst.

4. Typical Procedure for the Reaction.

(**a**) **Procedure for the synthesis of 3**:

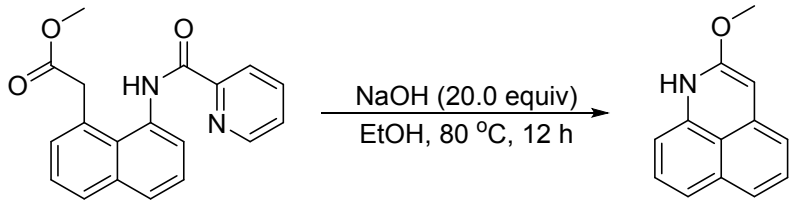
A 25 mL schlenk tube was equipped with a magnetic stir bar and charged with **1** (0.1 mmol), **2** (0.2 mmol, 2.0 equiv), $Pd(TFA)_2$ (0.015 mmol, 15 mol%), NaOAc (0.2 mmol, 2.0 equiv), NaI (0.2 mmol) in solvent (1.0 mL). The resulting mixture was reacted at 130 °C under air atmosphere for 20 h, and cooled to room temperature. Upon completion, the mixture was added into CH_2Cl_2 (25 mL) and the resulting mixture was filtered through a pad of celite. After evaporation of the solvent under vacuum, the residue was purified by column chromatography on silica gel (100–200 mesh) using petroleum ether/ethyl acetate as an eluent to afford pure products **3**.

(**b**) **Procedure for the gram-scale reaction**:

A oven-dried, 100 mL round-bottom flask was equipped with a magnetic stir bar and charged with N-(naphthalen-1-yl)picolinamide **1a** (0.500g, 2.0 mmol), methyl chloroacetate **2a** (400 μl, 4.0 mmol,), $Pd(TFA)_2$ (90 mg), NaOAc (320 mg), and NaI (600 mg) in dioxane (20 mL). The resulting mixture was stirred at 130 °C under air for 20 h. Upon completion, the mixture was added into H_2O (50 mL) and extracted with ethyl acetate (40 mL) six times. The combined organic layer was dried

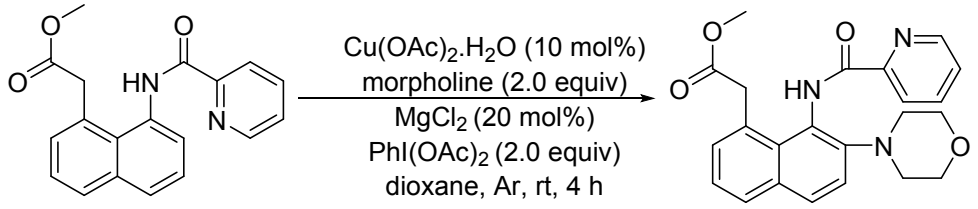
over anhydrous Na_2SO_4 and filtered. After evaporation of the solvent under vacuum, the residue was purified by column chromatography on silica gel (100−200 mesh) using petroleum ether/ethyl acetate as an eluent (4:1, V/V) to afford the desired yellow product **3aa** in 70% yield (0.446 g).

(**c**) **Synthesis of 4a and 4b.**



3aa **4a** 81%

A mixture of **3aa** (65.2 mg, 0.2 mmol, 1.0 equiv) and NaOH (240 mg, 6 mmol, 30 equiv) were heated in ethanol (3.0 mL) for 12 h at 80 °C. After completion, the mixture was cooled to room temperature and diluted with water (3.0 mL); HCl (18%) was added until it was acidic. Then saturated $NaHCO_3$ was added until the pH was about 7. The mixture was extracted with CH_2Cl_2, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography to give the desired product **4a**. Yellow solid (32 mg, 81%); mp 266-267 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.18 (s, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 7.92-7.84 (m, 2H), 7.76-7.72 (m, 3H), 7.32-7.30 (m, 1H), 3.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.6, 135.5, 131.8, 131.1, 130.9, 129.6, 129.0, 127.8, 127.2, 126.1, 120.7, 110.2, 23.9; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{13}H_{12}NO$ 198.0913, found: 198.0925.

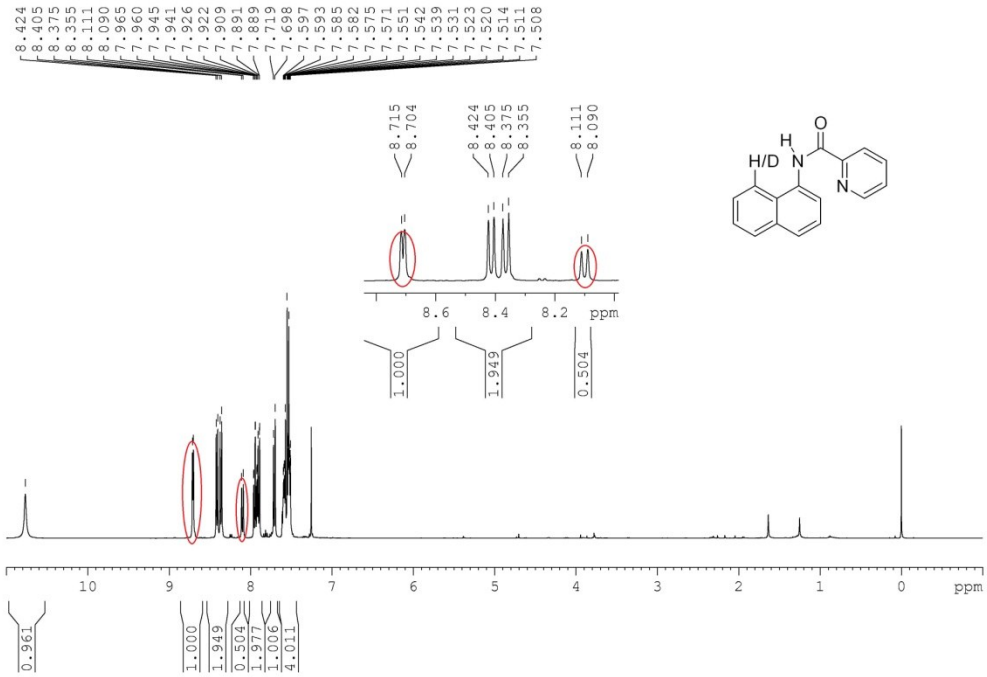


3aa **4b** 55%

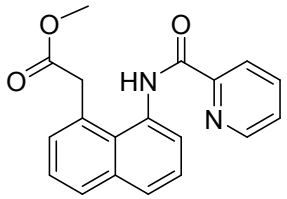
A mixture of **3aa** (65.2 mg, 0.2 mmol, 1.0 equiv), $Cu(OAc)_2 \cdot H_2O$ (4.0 mg, 0.02 mmol, 0.1 equiv) and $PhI(OAc)_2$ (129 mg, 0.4 mmol, 2.0 equiv), and morpholine (35 μl, 0.4 mmol, 2.0 equiv) in 1,4-dioxane (2.0 mL) was stirred at room temperature under argon for 4 hours. The reaction mixture was concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography to give the amination product **4b**. Yellow solid (45 mg, 55%); mp 115-117 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.95 (s, 1H), 8.696-8.68 (m, 1H), 8.31-8.29 (m, 1H), 7.94 (td, *J* = 7.7 Hz, 1.7 Hz, 1H), 7.88-7.86 (m, 1H), 7.80-7.77 (m, 1H), 7.54-7.51 (1H), 7.46-7.44 (m, 1H), 7.36-7.32 (m, 1H), 7.28-7.27 (m, 1H), 4.57 (d, *J* = 17.3 Hz, 1H), 3.74 (d, *J* = 17.3 Hz, 1H), 3.60-3.56 (m, 4H), 3.50 (s, 3H), 2.93 (t, *J* = 4.5 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.3, 165.7, 150.2, 148.2, 147.4, 137.6, 133.1, 132.0, 131.1, 130.1, 129.3, 129.2, 127.5, 126.5, 124.6, 122.6, 119.9, 67.5, 52.4, 51.7, 41.7; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{23}H_{24}N_3O_4$ 406.1761, found: 406.1770.

(**d**) **Kinetic isotope effect measurements:**

A Schlenk tube was equipped with a magnetic stir bar and charged with N-(naphthalen-1-yl)picolinamide **1a** (0.05 mmol), **1a**-d_1 (0.05 mmol), **2a** (2.0 equiv), NaI (2.0 equiv), $Pd(TFA)_2$ (15 mol%), NaOAc (2.0 equiv) in dioxane (1.0 mL). The resulting mixture was sealed and heated at 130 ^oC for 120 min, and cooled to room temperature. Upon completion, CH_2Cl_2 (20 mL) was added to the reaction system, and the resulting mixture was filtered through a pad of Celite. After evaporation of the solvent under vacuum, the residue was purified by column chromatography on silica gel (100–200 mesh) using petroleum ether-EtOAc as an eluent (3:1, V/V) to afford the pure product 1a/1a-d_1 and analyzed by ^1H NMR spectrum. The KIE value (k_H/k_D) was calculated as 1.0.



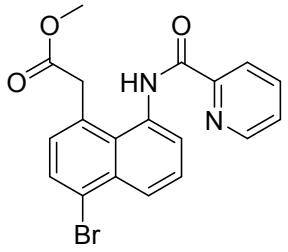
5. Characterization Data of the Products



3aa

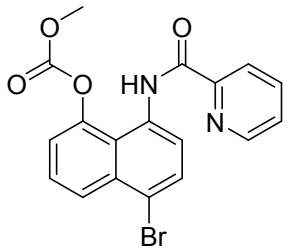
methyl 2-(8-(picolinamido)naphthalen-1-yl)acetate **(3aa):** white solid (29.4 mg, 92%); mp 133-134 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ: 10.51 (s, 1H), 8.63-8.62 (m, 1H), 8.35-8.33 (m, 1H), 7.93 (td, J = 1.6 Hz, J = 7.7 Hz, 1H), 7.85-7.82 (m, 2H), 7.78-7.76 (m, 1H), 7.55-7.48 (m, 2H), 7.42-7.38 (m, 1H), 7.31-7.30 (m, 1H), 4.27 (s, 2H), 3.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.2, 163.7, 150.2, 148.1, 137.6, 136.1, 132.3, 131.3, 129.5, 128.9, 128.8, 128.5, 126.9, 126.5, 125.5, 125.3,

122.9, 52.2, 41.8; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{16}N_2O_3$ 321.1234, found: 321.1235.



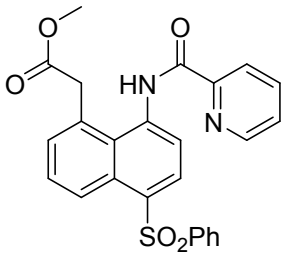
3ba

methyl 2-(4-bromo-8-(picolinamido)naphthalen-1-yl)acetate **(3ba):** white solid (32 mg, 80%); mp 163-165 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.43 (s, 1H), 8.62-8.61 (m, 1H), 8.36-8.32 (m, 2H), 7.93 (td, *J* = 1.7 Hz, 7.7 Hz, 1H), 7.84-7.82 (m, 1H), 7.75 (d, *J* = 7.7 Hz, 1H), 7.66-7.62 (m, 1H), 7.52-7.49 (m, 1H), 7.13 (d, *J* = 7.7 Hz, 1H), 4.28 (s, 2H), 3.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.7, 163.7, 150.0, 148.1, 137.7, 134.0, 132.8, 131.3, 130.3, 129.8, 129.3, 127.8, 127.7, 126.9, 126.6, 123.9, 122.9, 52.3, 41.8; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{16}N_2O_3Br$ 399.0339, found: 399.0393.



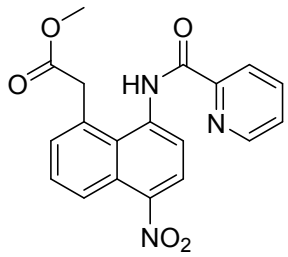
3ca

methyl 2-(5-bromo-8-(picolinamido)naphthalen-1-yl)acetate **(3ca):** yellow solid (33 mg, 85%); mp 152-155 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.46 (s, 1H), 8.62 (d, *J* = 4.2 Hz, 1H), 8.36-8.31 (m, 2H), 7.93 (td, *J* = 7.7 Hz, 1.6 Hz, 1H), 7.86 (d, *J* = 8.1 Hz), 7.65 (d, *J* = 8.1 Hz), 7.53-7.49 (m, 2H), 7.38-7.36 (m, 1H), 4.28 (s, 3H), 3.68 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.9, 163.5, 149.9, 148.2, 137.7, 134.0, 132.4, 132.3, 130.3, 130.0, 129.6, 128.8, 126.9, 126.7, 126.6, 122.9, 122.4, 52.3, 41.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $c_{19}H_{16}N_2O_3Br$ 399.0339, found: 399.0399.



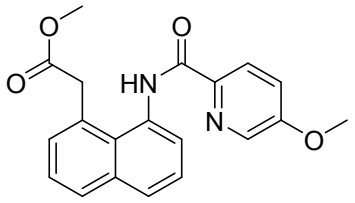
3da

methyl 2-(5-(phenylsulfonyl)-8-(picolinamido)naphthalen-1-yl)acetate **(3da):** white solid (20 mg, mp 148-150 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.74 (s, 1H), 8.70 (d, *J* = 8.0 Hz, 1H), 8.64-8.61 (m, 2H), 8.35 (d, *J* = 8.0 Hz, 1H), 8.15-8.13 (m, 1H), 7.97-7.95 (m, 3H), 7.56-7.46 (m, 5H), 7.36-7.35 (m, 1H), 4.31 (s, 2H), 3.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.6, 163.2, 149.6, 148.2, 141.7, 138.9, 137.9, 134.2, 133.1, 132.2, 131.4, 130.2, 129.5, 129.1, 127.5, 127.4, 126.9, 125.2, 123.6, 123.1, 52.4, 42.2; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{25}H_{20}N_2O_5S$ 461.1166, found: 461.1168.



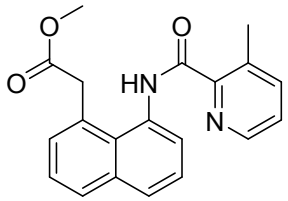
3ea

methyl 2-(5-nitro-8-(picolinamido)naphthalen-1-yl)acetate **(3ea):** yellow solid (13mg 36%); mp 148-150 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.76 (s, 1H), 8.64-8.63 (m, 1H), 8.44-8.42 (m, 1H), 8.36-8.34 (m, 1H), 8.17-8.15 (m, 1H), 8.08-8.05, (m, 1H), 7.97 (td, J = 7.8 Hz, 1.5 Hz, 1H), 7.64-7.60 (m, 1H), 7.57-7.54 (m, 1H), 7.47-7.45 (m, 1H), 4.37 (s, 2H), 3.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.5, 163.2, 149.6, 148.2, 146.1, 137.9, 137.8, 132.7, 129.9, 128.9, 128.3, 127.8, 127.0, 123.6, 123.5, 123.3, 123.0, 52.4, 42.1; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{19}H_{16}N_3O_5$ 366.1084, found: 366.1087.



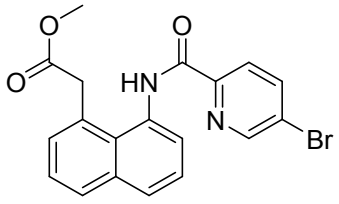
3fa

methyl 2-(8-(5-methoxypicolinamido)naphthalen-1-yl)acetate **(3fa):** white solid (30.9 mg, 90%); mp 142-145 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.31 (s, 1H), 8.30-8.26 (m, 2H), 7.84-7.80 (m, 2H), 7.76 (d, J = 7.2 Hz, 1H), 7.54-7.50 (m, 1H), 7.40-7.34 (m, 2H), 7.30-7.28 (m, 1H), 4.26 (s, 2H), 3.94 (s, 3H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.2, 136.6, 158.1, 142.8, 136.6, 136.1, 132.5, 131.2, 129.5, 129.1, 129.0, 128.4, 126.9, 125.5, 125.3, 124.1, 120.3, 55.6, 52.3, 41.8; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{20}H_{19}N_2O_4$ 351.1339, found: 351.1342.



3ga

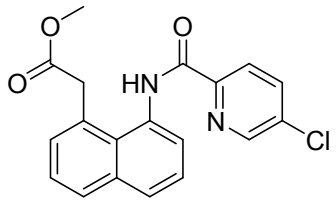
methyl 2-(8-(3-methylpicolinamido)naphthalen-1-yl)acetate **(3ga)**: white solid (29.7 mg, 86%); mp 130-132 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.56 (s, 1H), 8.45 (dd, J = 4.5 Hz, 1.0 Hz, 1H), 7.85-7.80 (m, 2H), 7.76-7.75 (m, 1H), 7.67 (d, J = 7.8 Hz, 1H), 7.53 (t, J = 7.8 Hz, 1H), 7.41-7.36 (m, 2H), 7.30-7.29 (m, 1H), 4.31 (s, 2H), 3.65 (s, 3H), 2.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.3, 165.3, 147.5, 145.5, 141.1, 136.2, 136.1, 132.6, 131.2, 129.5, 129.2, 129.1, 128.4, 126.9, 125.9, 125.5, 125.2, 52.1, 41.9, 20.7; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{20}H_{19}N_2O_3$ 335.1390, found: 335.1392.



3ha

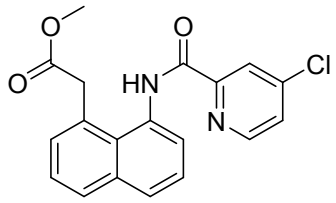
methyl 2-(8-(5-bromopicolinamido)naphthalen-1-yl)acetate **(3ha):** yellow solid (28.1 mg, 73%);

mp 166-168 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.44 (s, 1H), 8.68-8.67 (m, 1H), 8.25 (d, *J* = 8.2 Hz, 1H), 8.05 (dd, *J* = 8.3 Hz, 2.3 Hz 1H), 7.85-7.82 (m, 2H), 7.76 (d, *J* = 7.4 Hz, 4H), 7.55-7.51 (m, 1H), 7.42-7.38 (m, 1H), 7.32-7.30 (m, 1H), 4.25 (s, 2H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ:173.2, 162.9, 149.4, 148.8, 140.3, 136.1, 132.0, 131.4, 129.6, 128.7, 126.9, 125.5, 125.4, 124.3, 52.3, 41.8; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{16}N_2O_3Br$ 399.0339, found: 399.0342.



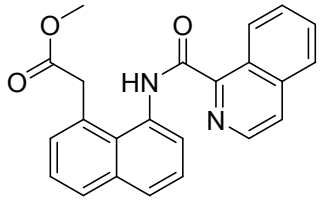
3ia

methyl 2-(8-(5-chloropicolinamido)naphthalen-1-yl)acetate **(3ia)**: yellow solid (24.6 mg, 71%); mp 153-155 °C; ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 10.43 (s, 1H), 8.57-8.56 (m, 1H), 8.30-8.28 (m, 1H), 7.91-7.88 (m, 1H), 7.85-7.82 (m, 2H), 7.74 (d, *J* = 7.3Hz, 1H), 7.55-7.51 (m, 1H), 7.42-7.38 (m, 1H), 7.32-7.30 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 173.2, 162.8, 148.4, 147.2, 137.4, 136.1, 135.4, 132.0, 131.4, 129.6, 128.8, 128.7, 128.7, 126.9, 125.5, 125.4, 123.9, 52.3, 41.8; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{19}H_{16}N_2O_3Cl$ 355.0844, found: 355.0846.



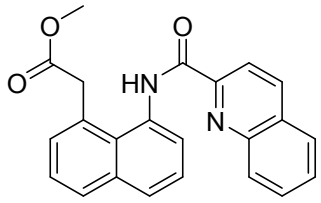
3ja

methyl 2-(8-(4-chloropicolinamido)naphthalen-1-yl)acetate **(3ja)**: yellow solid (27 mg, 76%); mp 142-144 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.47 (s, 1H), 8.51 (d, *J* = 5.2 Hz, 1H), 8.34-8.33 (m, 1H), 7.85-7.82 (m, 2H), 7.75 (d, *J* = 7.4 Hz, 1H), 7.55-7.49 (m, 2H), 7.41-7.37 (m, 1H), 7.32-7.30 (m, 1H), 4.24 (s, 2H), 3.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.1, 162.5, 151.8, 149.0, 146.2, 136.1, 131.9, 131.4, 129.6, 128.3, 128.8, 128.7, 126.9, 126.7, 125.5, 125.4, 123.5, 52.2, 41.8; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{16}N_2O_3Cl$ 355.0844, found: 355.0847.



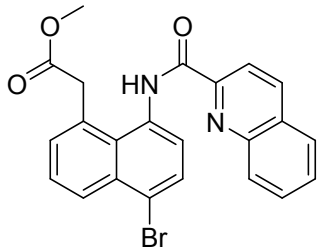
3ka

methyl 2-(8-(isoquinoline-1-carboxamido)naphthalen-1-yl)acetate **(3ka):** yellow solid (19 mg, 51%); mp 160-161 °C; ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 10.80 (s, 1H), 8.45-8.38 (m, 2H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.87-7.78 (m, 4H), 7.68-7.64 (m, 1H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.43-7.39 (m, 1H), 7.35-7.33 (m, 1H), 4.35 (s, 2H), 3.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 173.1, 164.1, 150.2, 146.6, 137.7, 136.2, 132.4, 131.3, 130.3, 139.7, 129.6, 129.5, 129.1, 129.0, 128.7, 128.2, 127.9, 127.1, 125.6, 125.3, 119.3, 52.2, 41.8; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{23}H_{19}N_2O_3$ 371.1390, found: 371.1393.



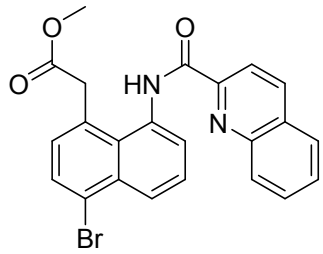
3la

methyl 2-(8-(quinoline-2-carboxamido)naphthalen-1-yl)acetate **(3la):** white solid (22 mg, 60%); mp 162-163 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ:10.74 (s, 1H), 9.66-9.64 (m, 1H), 8.53 (d, *J* = 5.6 Hz, 1H), 7.92-7.84 (m, 5H), 7.79-7.70 (m, 2H), 7.59-7.56 (m, 1H), 7.43-7.39 (m, 1H), 7.34-7.32 (m, 1H), 4.38 (s, 2H), 3.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.5, 165.2, 148.5, 140.2, 137.5, 136.2, 132.5, 131.3, 130.7, 129.5, 129.1, 129.0, 128.9, 128.5, 127.8, 127.3, 127.0, 125.5, 125.3, 124.7, 52.2, 41.8; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{23}H_{19}N_2O_3$ 371.1390, found: 371.1393.



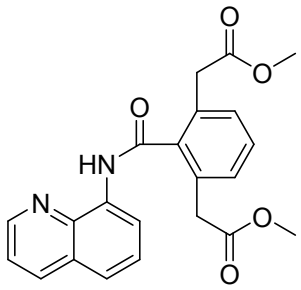
3ma

methyl 2-(5-bromo-8-(quinoline-2-carboxamido)naphthalen-1-yl)acetate **(3ma):** yellow solid (22 mg, 43%); mp 184-186 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.76 (s, 1H), 8.43-8.37 (m, 3H), 8.14 (d, *J* = 8.5 Hz, 3H), 7.94 (m, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.84-7.79 (m, 1H), 7.70-7.65 (m, 2H), 7.55-7.51 (m, 1H), 7.42-7.40 (m, 1H), 4.37 (s, 2H), 3.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.8, 164.0, 149.9, 146.6, 137.8, 134.0, 132.5, 132.3, 130.4, 130.3, 130.0, 129.7, 129.5, 128.9, 128.3, 127.9, 127.2, 126.7, 122.6, 119.2, 52.3, 41.8; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{23}H_{18}N_2O_3Br$ 449.0495, found: 449.0497.



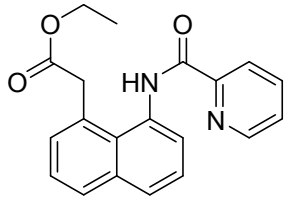
3na

methyl 2-(4-bromo-8-(quinoline-2-carboxamido)naphthalen-1-yl)acetate **(3na)**: yellow solid (24 mg, 46%); mp 184-186 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.71 (s, 1H), 8.43-8.36 (m, 3H), 8.15-8.13 (m, 1H), 7.94-7.92 (m, 1H), 7.86 (d, *J* = 7.4 Hz, 1H), 7.83-7.80 (m, 1H), 7.74 (d, *J* = 7.5 Hz, 1H), 7.68-7.64 (m, 2H), 7.17 (d, *J* = 7.7 Hz, 1H), 4.29 (s, 2H), 3.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.6, 164.1, 149.9, 146.6, 137.8, 134.0, 132.9, 131.3, 130.4, 130.3, 129.8, 129.7, 129.5, 129.3, 128.3, 128.1, 127.9, 127.9, 126.9, 124.0, 119.2, 52.3, 41.8; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{23}H_{18}N_2O_3Br$ 449.0495, found: 449.0497.



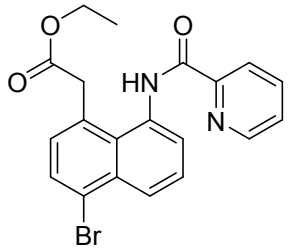
3oa

dimethyl 2,2'-(2-(quinolin-8-ylcarbamoyl)-1,3-phenylene)diacetate **(3oa):** white solid (30 mg, 77%); mp 107-109 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.12 (s, 1H), 8.95 (dd, *J* = 6.8 Hz, 2.1 Hz, 1H), 8.76 (dd, *J* = 4.2 Hz, 1.7 Hz, 1H), 8.18 (dd, *J* = 8.3 Hz, 1.6 Hz, 1H), 7.62-7.56 (m, 2H), 7.46-7.39 (m, 2H), 7.33-7.31 (m, 2H), 3.80 (s, 4H), 3.52 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.4, 167.3, 148.3, 138.6, 138.4, 136.3, 134.2, 131.5, 129.6, 128.0, 127.4, 122.4, 121.7, 117.2, 52.2, 38.4; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{22}H_{21}N_2O_5$ 393.1455, found: 393.1448.



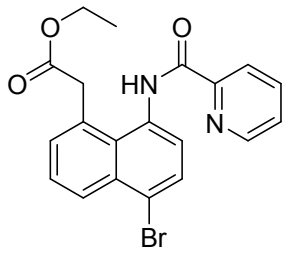
3ab

ethyl 2-(8-(picolinamido)naphthalen-1-yl)acetate **(3ab)**: white solid (30 mg, 90%,); mp 128-130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.58 (s, 1H), 8.62-8.60 (m, 1H), 8.35-8.33 (m, 1H), 7.93 (td, *J* = 7.7 Hz, 1.7 Hz, 1H), 7.84-7.77 (m, 3H), 7.55-7.48 (m, 2H), 7.41-7.37 (m, 1H), 7.32-7.30 (m, 1H), 4.26 (s, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 1.15, (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.8, 163.7, 150.3, 148.1, 137.6, 136.1, 132.3, 131.2, 129.5, 129.2, 129.0, 128.5, 126.8, 126.4, 125.5, 125.3, 122.9, 61.2, 42.0, 14.0; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{19}N_2O_3$ 335.1390, found: 335.1392.



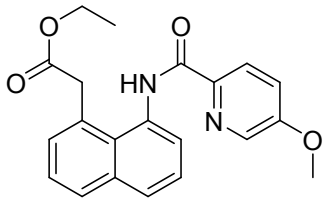
3bb

ethyl 2-(4-bromo-8-(picolinamido)naphthalen-1-yl)acetate **(3bb):** yellow solid (34 mg, 83%,); mp 137-139 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.50 (s, 1H), 8.61-8.60 (m, 1H), 8.36-8.33 (m, 2H), 7.93 (td, *J* = 7.8 Hz, 1.7 Hz, 1H), 7.84-7.82 (m, 1H), 7.73 (d, *J* = 7.7 Hz, 1H), 7.66-7.62 (m, 1H), 7.53-7.49 (m, 1H), 7.15 (d, *J* = 7.7 Hz, 1H), 4.22 (s, 2H), 4.14 (q, *J* = 7.2 Hz, 2H), 1.14 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.3, 163.7, 150.1, 148.1, 137.6, 134.0, 132.8, 131.2, 130.3, 129.7, 129.4, 127.8, 127.7, 126.8, 126.6, 123.8, 122.9, 61.3, 42.0, 14.0; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{18}N_2O_3Br$ 413.0495, found: 413.0498.



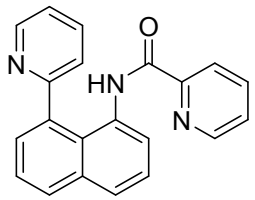
3cb

ethyl 2-(5-bromo-8-(picolinamido)naphthalen-1-yl)acetate **(3cb):** yellow solid (31.3 mg, 77%); mp 140-142 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.53 (s,1H), 8.60-8.59 (m, 1H), 8.36-8.31 (m, 2H), 7.92 (td, *J* = 7.7 Hz, 1.6 Hz, 1H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.53-7.49 (m, 2H), 7.38-7.37 (m, 1H), 4.28 (s, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 1.14 (t, *J* = 7.1Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.5, 163.6, 150.1, 148.2, 137.6, 134.0, 132.5, 132.2, 130.3, 130.0, 129.8, 128.7, 126.8, 126.7, 126.6, 122.9, 122.4, 61.3, 42.0, 14.0; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{18}N_2O_3Br$ 413.0495, found: 413.0493.



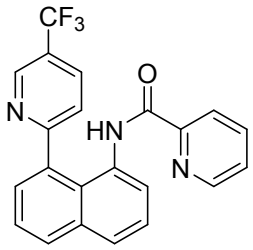
3db

ethyl 2-(8-(5-methoxypicolinamido)naphthalen-1-yl)acetate **(3db):** white solid (32 mg, 90%); mp 142-144 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.40 (s, 1H), 8.30-8.25 (m, 2H), 7.82 (t, *J* = 7.9 Hz, 2H), 7.77-7.75 (m, 1H), 7.54-7.50 (m, 1H), 7.40-7.34 (m, 2H), 7.30-7.29 (m, 1H), 4.26 (s, 2H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.94 (s, 3H), 1.17 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.8, 163.6, 158.1, 14.03, 136.6, 136.1, 132.5, 131.1, 129.4, 129.2, 129.0, 128.4, 126.9, 125.5, 125.2, 124.1, 120.3, 61.2, 55.8, 42.0, 14.0; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{21}N_2O_4$ 365.1496, found: 365.1500.



3ad

N-(8-(pyridin-2-yl)naphthalen-1-yl)picolinamide **(3ad)**: yellow solid (14.6 mg, 45%); mp 102-104 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.59 (s, 1H), 8.66-8.65 (m, 1H), 8.30-8.29 (m, 1H), 8.07 (m, 1H), 8.00-7.94 (m, 2H), 7.87-7.85 (m, 1H), 7.46 (td, *J* = 7.7 Hz, 1.7 Hz, 1H), 7.59 (t, *J* = 7.8 Hz, 1H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.43-7.33 (m, 4H), 6.95-6.91 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.4, 161.7, 149.7, 149.4, 147.3, 137.1, 136.8, 136.1, 135.6, 132.4, 130.7, 129.8, 127.2, 126.1, 126.0, 126.1, 124.9, 124.8, 124.4, 122.1, 121.1; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{16}N_3O$ 369.1288, found: 369.1291.



3ae

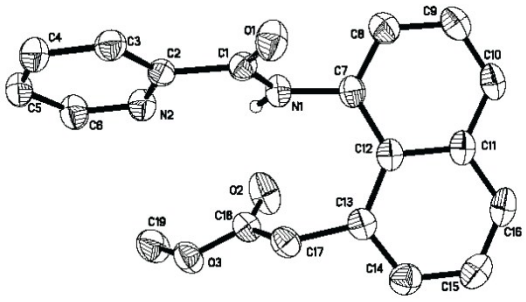
N-(8-(5-(trifluoromethyl)pyridin-2-yl)naphthalen-1-yl)picolinamide **(3ae):** yellow solid (18.2 mg, 47%); mp 104-106 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.39 (s, 1H), 8.89-8.88 (m, 1H), 8.30-8.29 (m, 1H), 8.06 (d, *J* = 7.8 Hz, 1H), 8.02-7.99 (m, 1H), 7.91-7.88 (m, 2H), 7.78 (td, *J* = 7.7 Hz, 1.7 Hz, 1H), 7.63−7.59 (m, 2H), 7.57-7.53 (m, 1H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.43-7.41 (m, 1H), 7.39-7.35 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.2, 162.3, 149.2, 147.5, 146.1 (q, *J* = 4.8 Hz), 137.3, 135.6, 135.5, 132.8 (q, *J* = 3.4 Hz), 132.0, 130.7, 130.5, 127.6, 126.5, 126.4, 126.3, 125.8, 125.3 (q, *J* = 271 Hz) 125.0, 124.1, 124.0 (q, *J* = 33.4 Hz), 122.0; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{22}H_{15}N_3F_3O$ 394.1162, found: 394.1164.

6. References

[1]. R. Shang, L. Ilies, E. Nakamura, *J. Am. Chem. Soc*. 2015, **137**, 7660.

7. The Single Crystal X-ray Diffraction Study

The Single Crystal X-ray Diffraction Study of 3aa

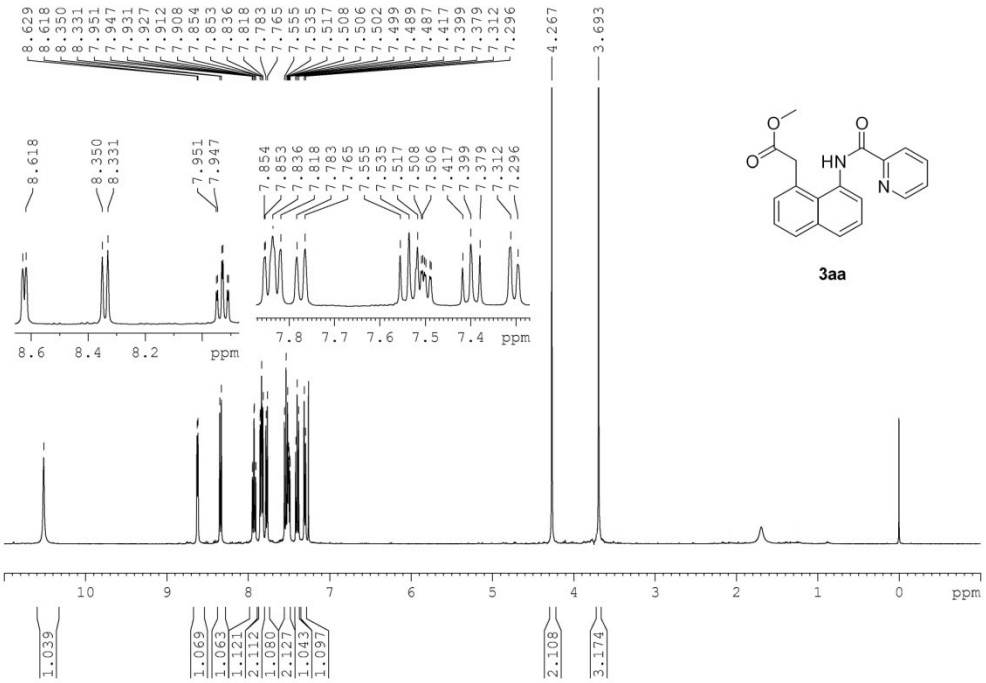


CCDC 1901462 (**3aa**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Table 1 Crystal data and structure refinement for 3aa.

Identification code	1901462
Empirical formula	$C_{19}H_{16}N_2O_3$
Formula weight	320.34
Temperature/K	293(2)
Crystal system	trigonal
Space group	$P3_1$
a/Å	7.6372(6)
b/Å	7.6372(6)
c/Å	23.721(2)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	1198.2(2)
Z	3
ρ_{calc}g/cm^3	1.332
μ/mm^{-1}	0.745
F(000)	504.0
Crystal size/mm^3	0.22 × 0.17 × 0.14
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	11.19 to 141.988
Index ranges	$-7 \le h \le 9$, $-9 \le k \le 8$, $-27 \le l \le 28$
Reflections collected	8281
Independent reflections	2965 [R_{int} = 0.0285, R_{sigma} = 0.0316]
Data/restraints/parameters	2965/1/223
Goodness-of-fit on F^2	1.058
Final R indexes [I>=2σ (I)]	R_1 = 0.0411, wR_2 = 0.1040
Final R indexes [all data]	R_1 = 0.0477, wR_2 = 0.1119
Largest diff. peak/hole / e Å^{-3}	0.22/-0.15
Flack parameter	-0.09(18)

8 Copies of ^{1}H and ^{13}C NMR Spectra for the Products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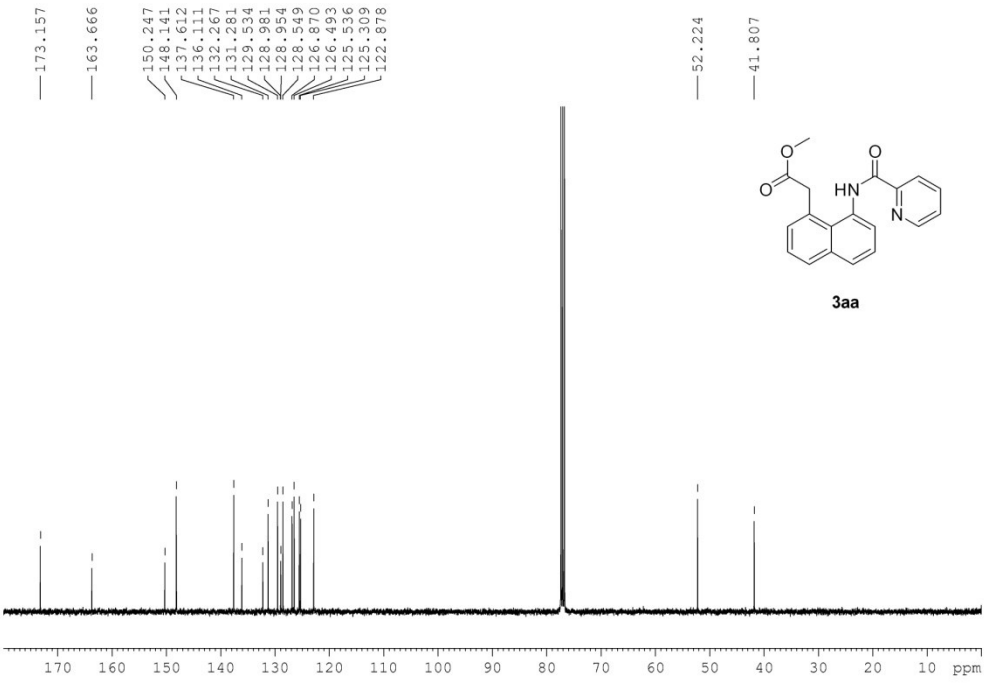
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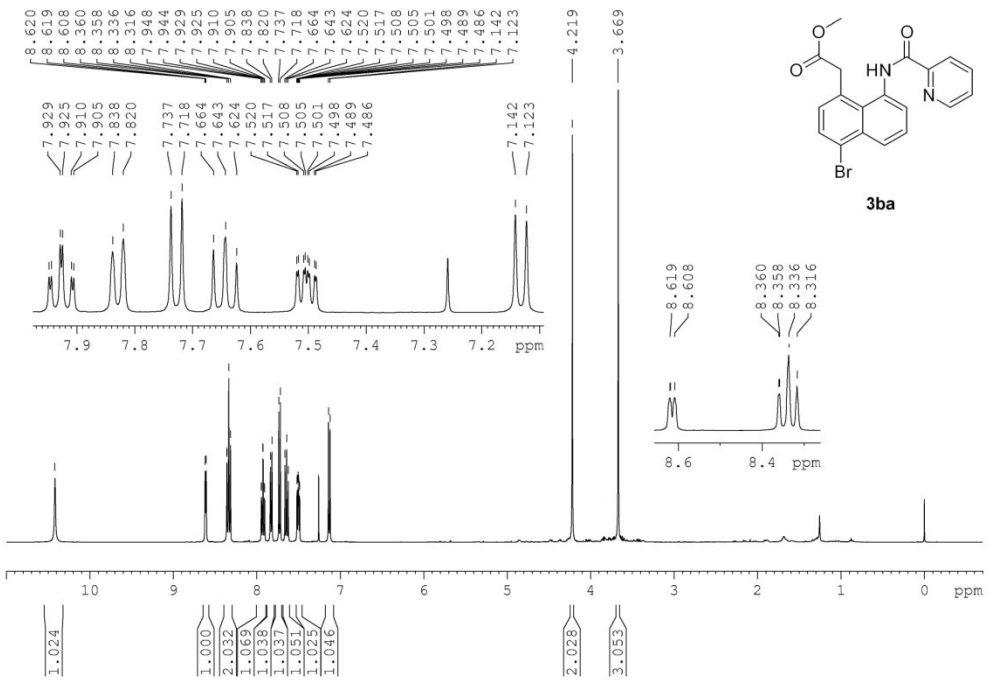
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7.624
7.520
7.517
7.508
7.505
7.501
7.498
7.489
7.486
7.142
7.123
4.219
3.669
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1.038
1.037
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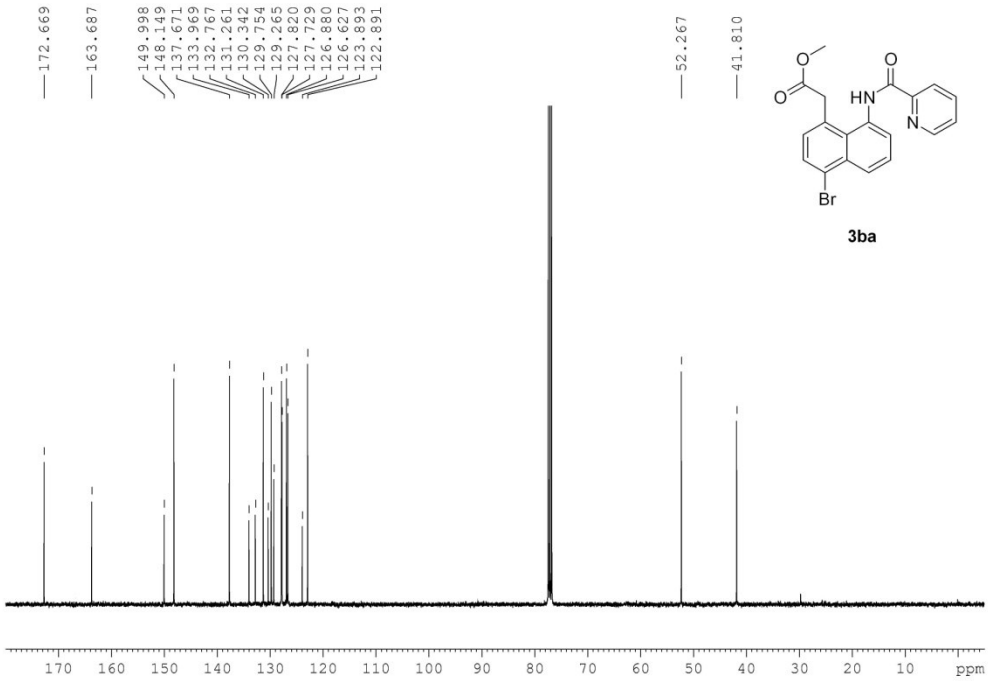
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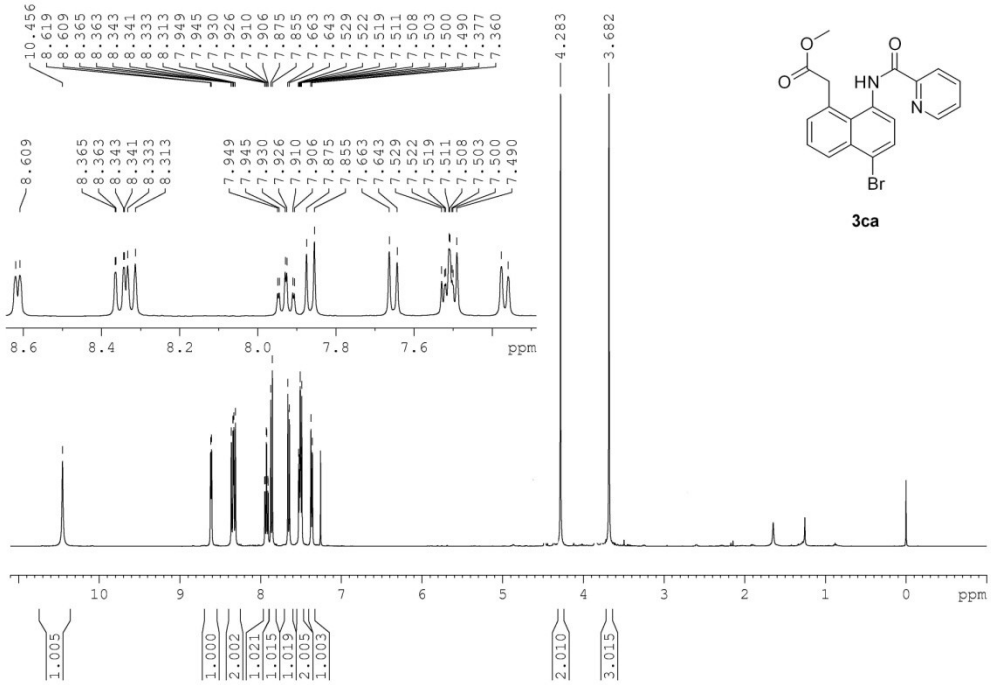
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7.926
7.910
7.906
7.875
7.855
7.663
7.643
7.529
7.522
7.519
7.511
7.508
7.503
7.500
7.490
7.377
7.360
4.283
3.682
8.6
8.4
8.2
8.0
7.8
7.6
ppm
10
9
8
7
6
5
4
3
2
1
0
ppm
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1.000
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1.019
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3.015
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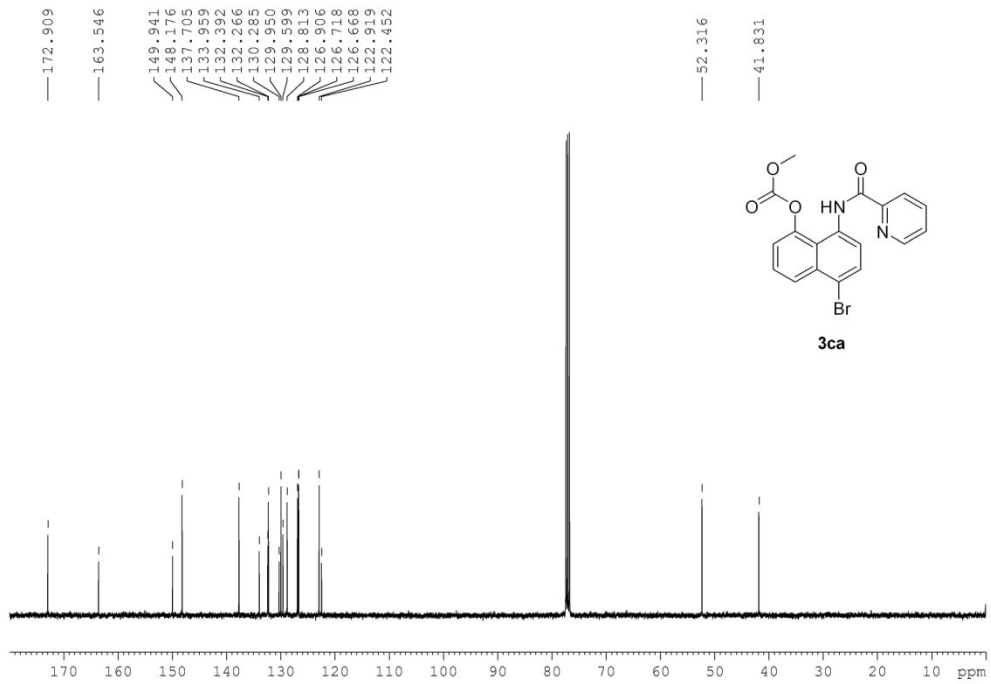
HN
N
Br
3ca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126.718
126.668
122.919
122.452
52.316
41.831
170
160
150
140
130
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70
60
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ppm
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Br
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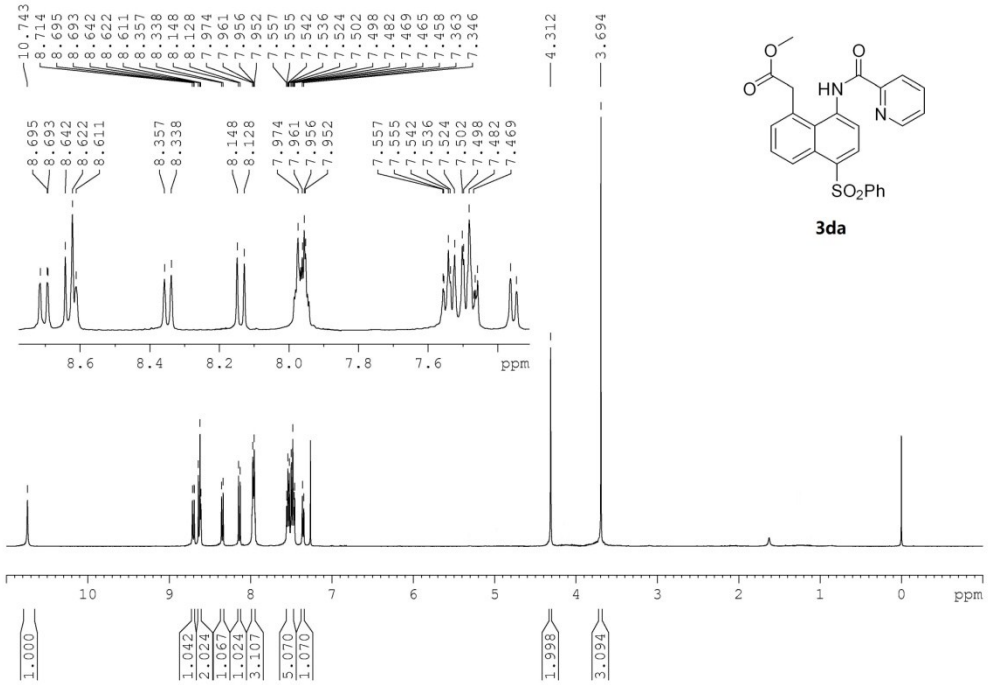
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7.961
7.956
7.952
7.557
7.555
7.542
7.536
7.524
7.502
7.498
7.482
7.469
7.465
7.458
7.363
7.346
4.312
3.694
HN
N
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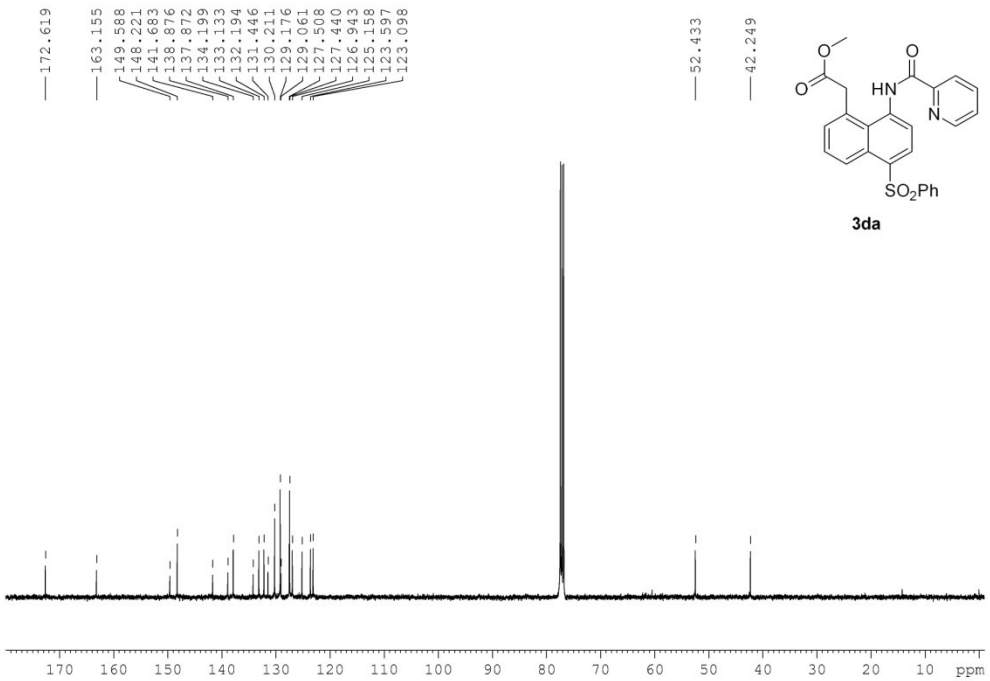
3.094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125.158
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42.249
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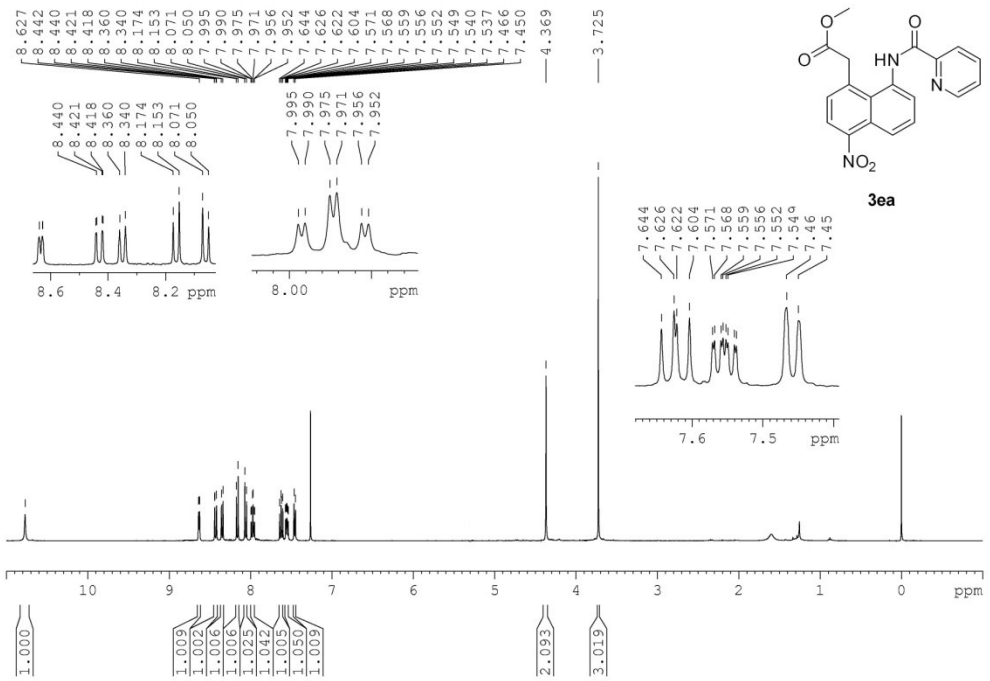
SO2Ph
3da
ppm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8.440
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8.340
8.174
8.153
8.071
8.050
7.995
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7.975
7.971
7.956
7.952
7.644
7.626
7.622
7.604
7.571
7.568
7.559
7.556
7.552
7.549
7.540
7.537
7.466
7.450
4.369
3.725
8.6
8.4
8.2 ppm
8.00
ppm
7.6
7.5
ppm
10
9
8
7
6
5
4
3
2
1
0
ppm
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1.009
1.002
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N
NO2
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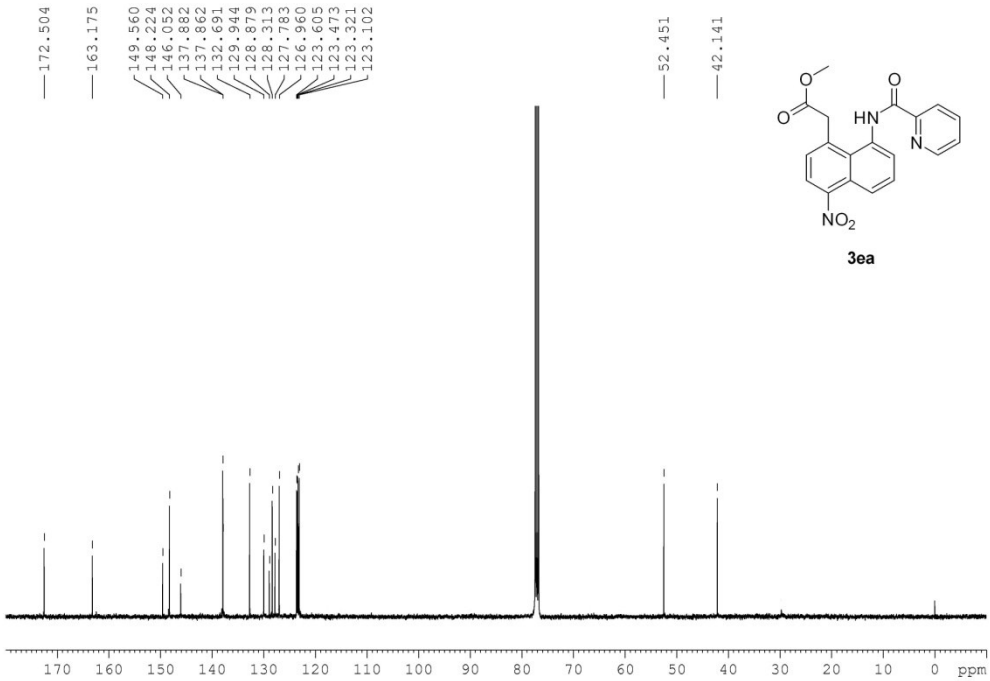
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123.605
123.473
123.321
123.102
52.451
42.141
170
160
150
140
130
120
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80
70
60
50
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30
20
10
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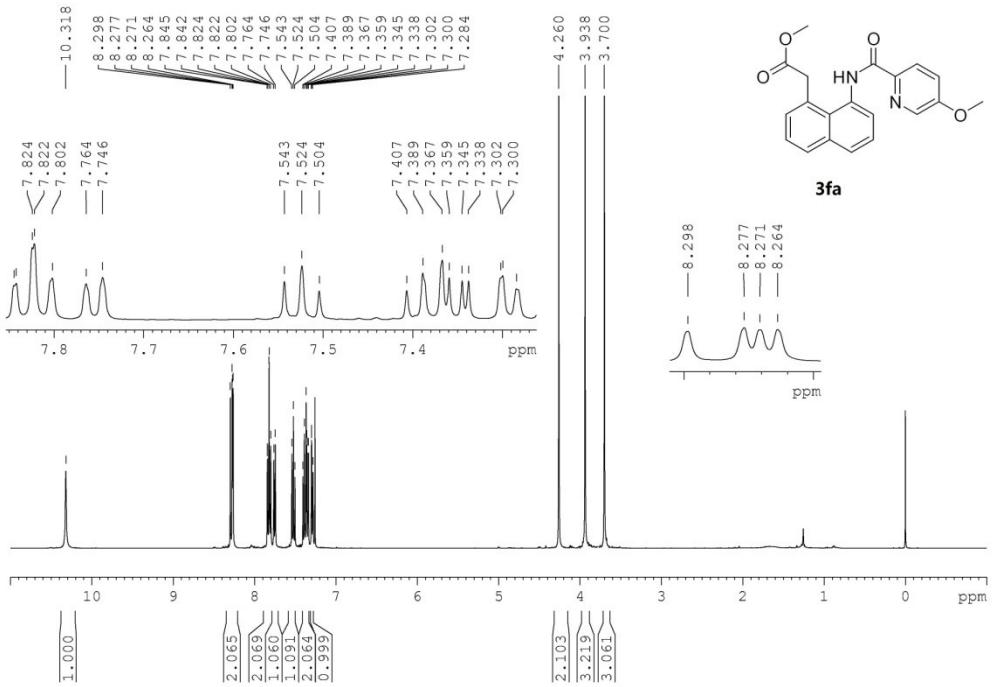
ppm
HN
N
NO2
3ea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7.842
7.824
7.822
7.802
7.764
7.746
7.543
7.524
7.504
7.407
7.389
7.367
7.359
7.345
7.338
7.302
7.300
7.284
4.260
3.938
3.700
HN
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O
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1.060
1.091
2.064
0.999
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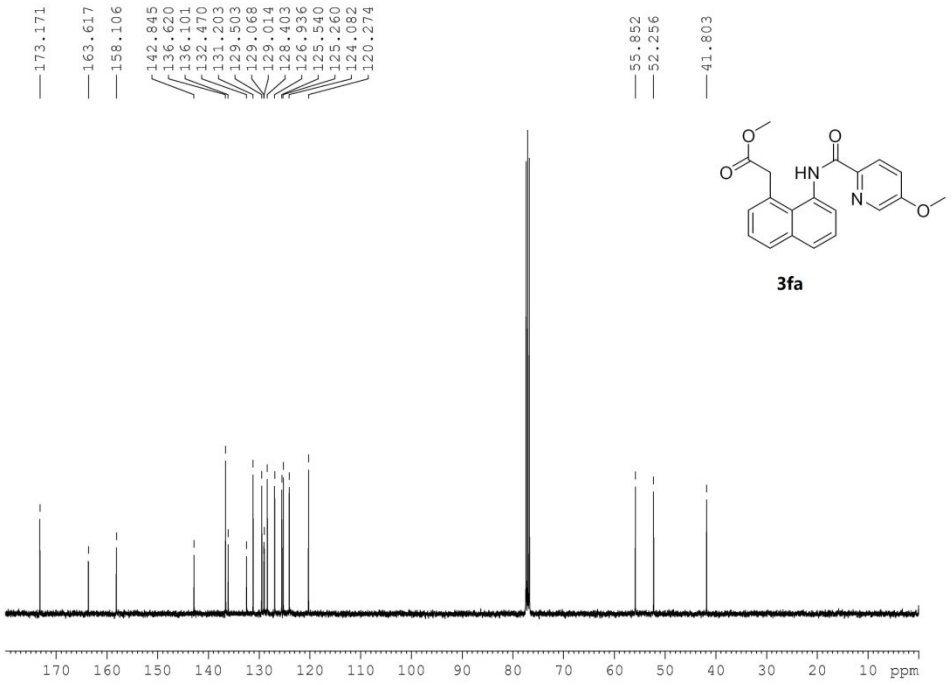
3.219
3.061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129.068
129.014
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125.260
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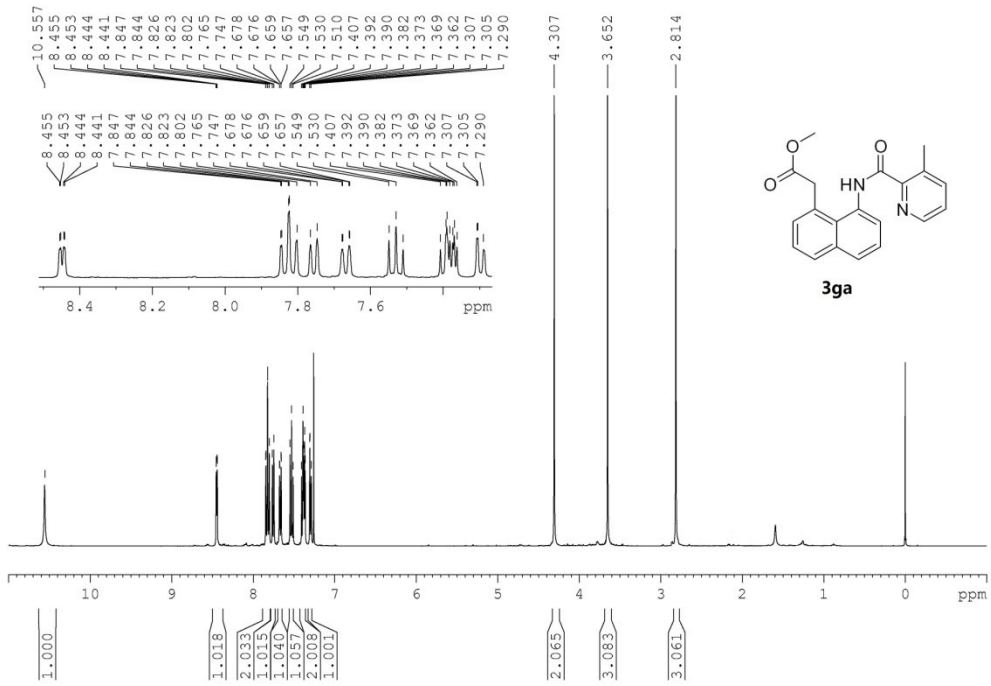
41.803
HN
N
O
3fa
ppm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7.847
7.844
7.826
7.823
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7.765
7.747
7.678
7.676
7.659
7.657
7.549
7.530
7.510
7.407
7.392
7.390
7.382
7.373
7.369
7.362
7.307
7.305
7.290
4.307
3.652
2.814
8.4
8.2
8.0
7.8
7.6
ppm
3ga
10
9
8
7
6
5
4
3
2
1
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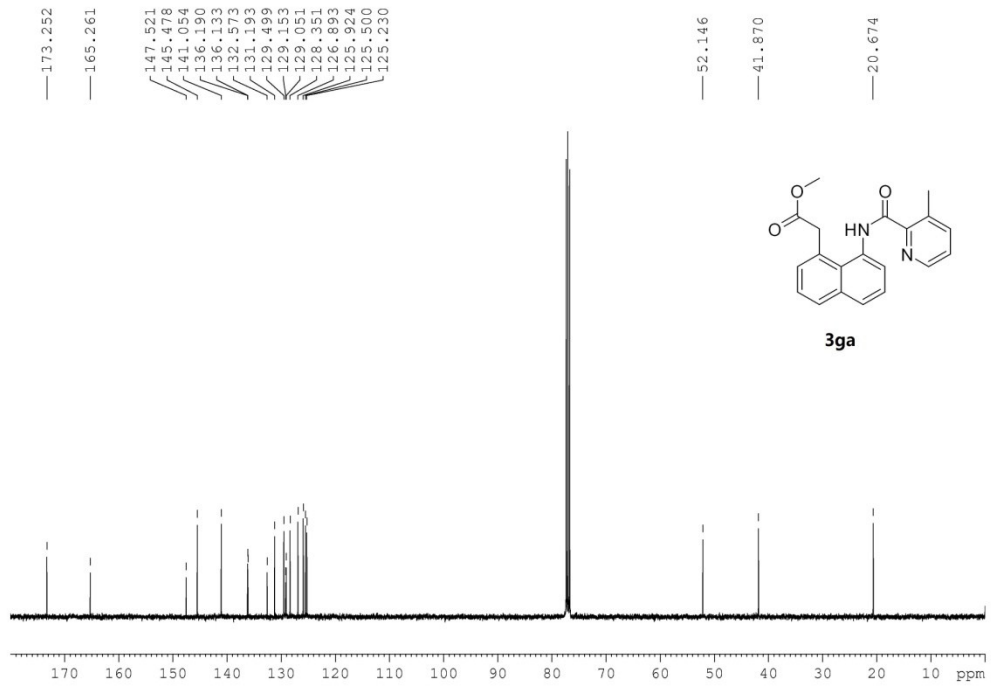
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129.153
129.051
128.351
126.893
125.924
125.500
125.230
52.146
41.870
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150
140
130
120
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90
80
70
60
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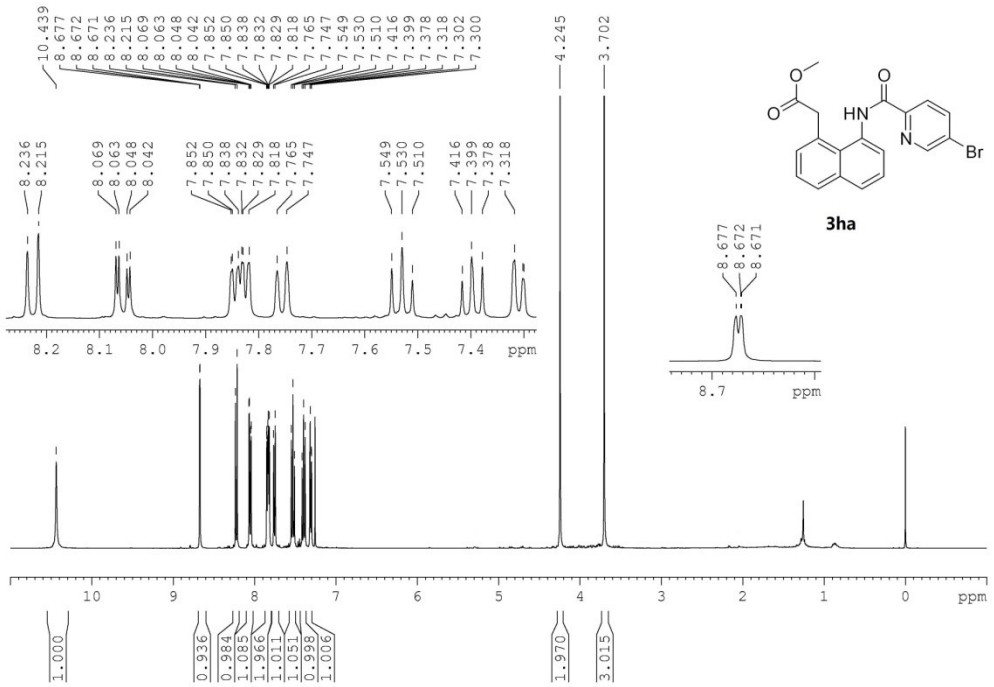
40
30
20
10
ppm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8.671
8.236
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8.063
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8.042
7.852
7.850
7.838
7.832
7.829
7.818
7.765
7.747
7.549
7.530
7.510
7.416
7.399
7.378
7.318
7.302
7.300
4.245
3.702
1.000
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1.966
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1.006
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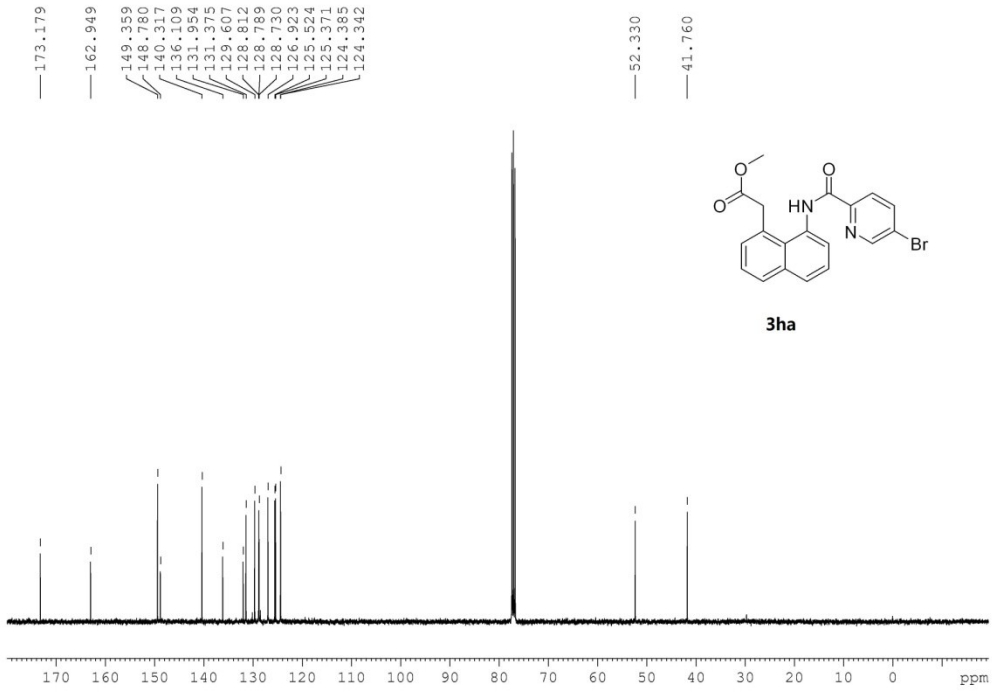
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131.375
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124.342
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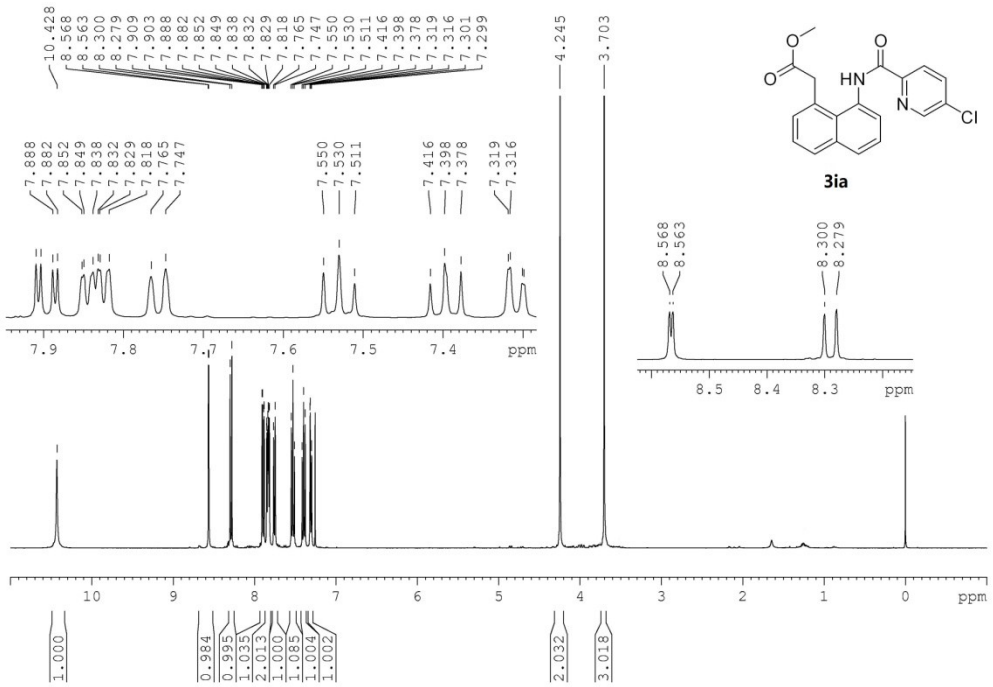
ppm
3ha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7.849
7.838
7.832
7.829
7.818
7.765
7.747
7.550
7.530
7.511
7.416
7.398
7.378
7.319
7.316
7.301
7.299
4.245
3.703
7.888
7.882
7.852
7.849
7.838
7.832
7.829
7.818
7.765
7.747
7.550
7.530
7.511
7.416
7.398
7.378
7.319
7.316
8.568
8.563
8.300
8.279
7.9
7.8
7.7
7.6
7.5
7.4
8.5
8.4
8.3
ppm
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9
8
7
6
5
4
3
2
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0
1.000
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0.995
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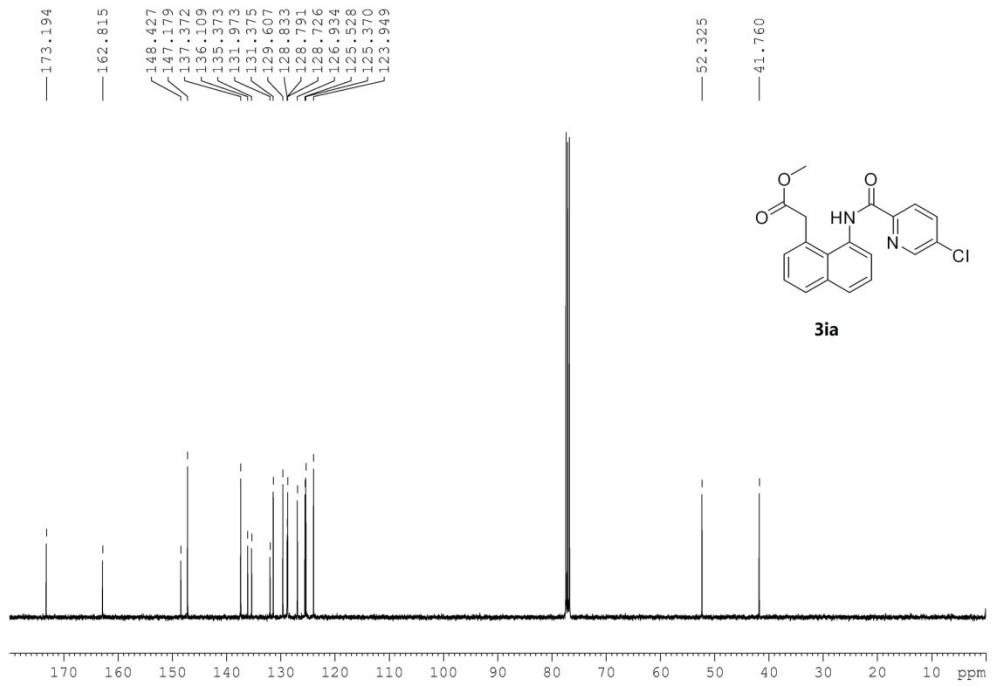
N
Cl
3ia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128.791
128.726
126.934
125.528
125.370
123.949
52.325
41.760
170
160
150
140
130
120
110
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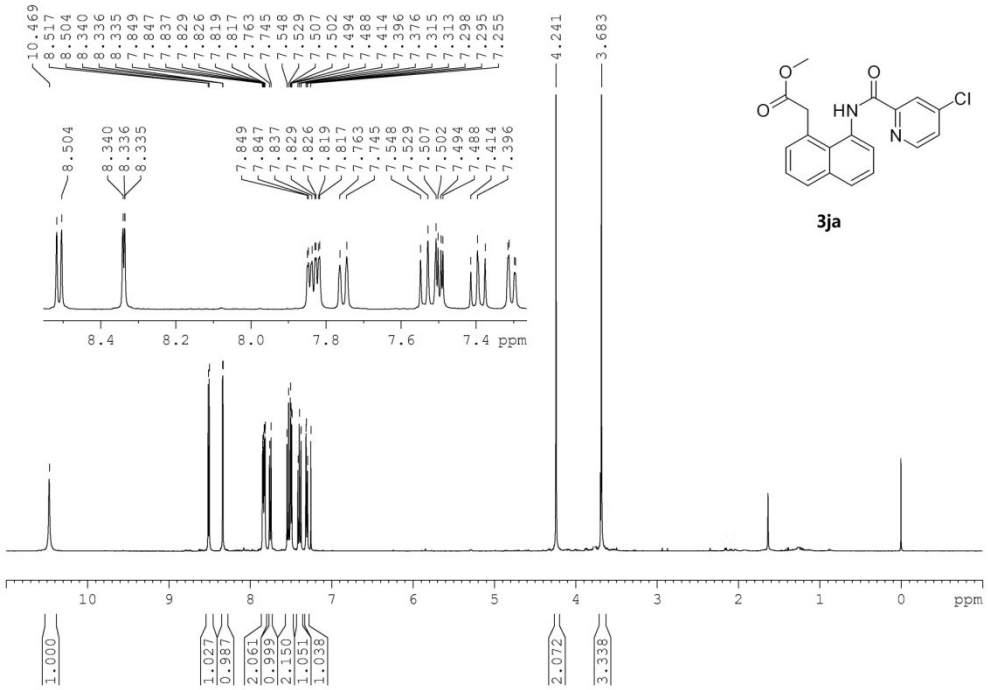
90
80
70
60
50
40
30
20
10
ppm
O
O
HN
N
Cl
3ia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7.829
7.826
7.819
7.817
7.763
7.745
7.548
7.529
7.507
7.502
7.494
7.488
7.414
7.396
7.376
7.315
7.313
7.298
7.295
7.255
4.241
3.683
8.4
8.2
8.0
7.8
7.6
7.4 ppm
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9
8
7
6
5
4
3
2
1
0
ppm
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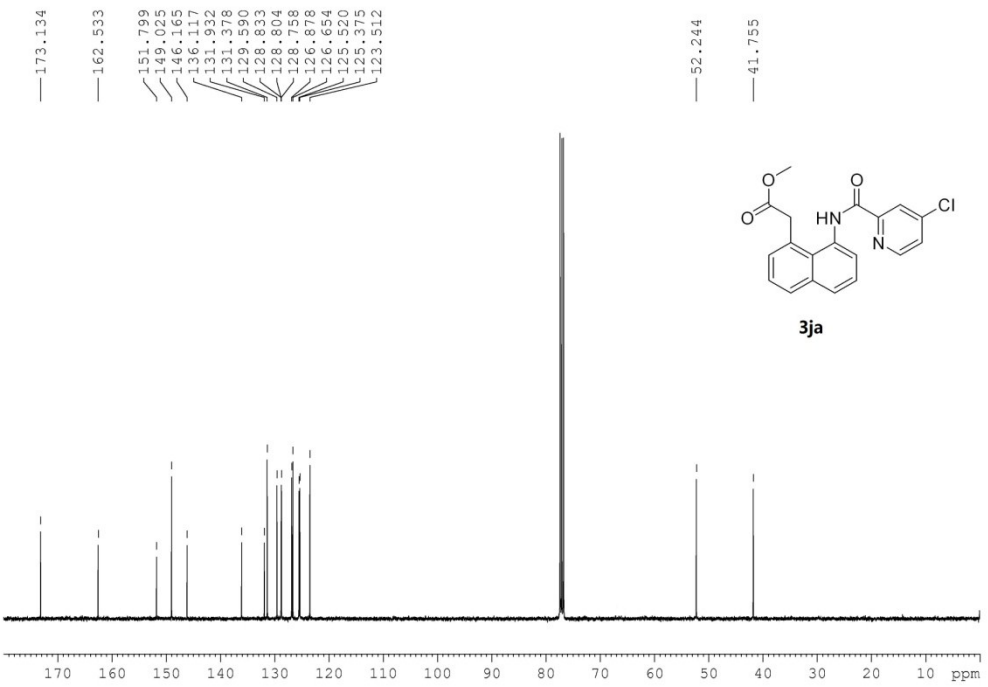
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126.654
125.520
125.375
123.512
52.244
41.755
170
160
150
140
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ppm
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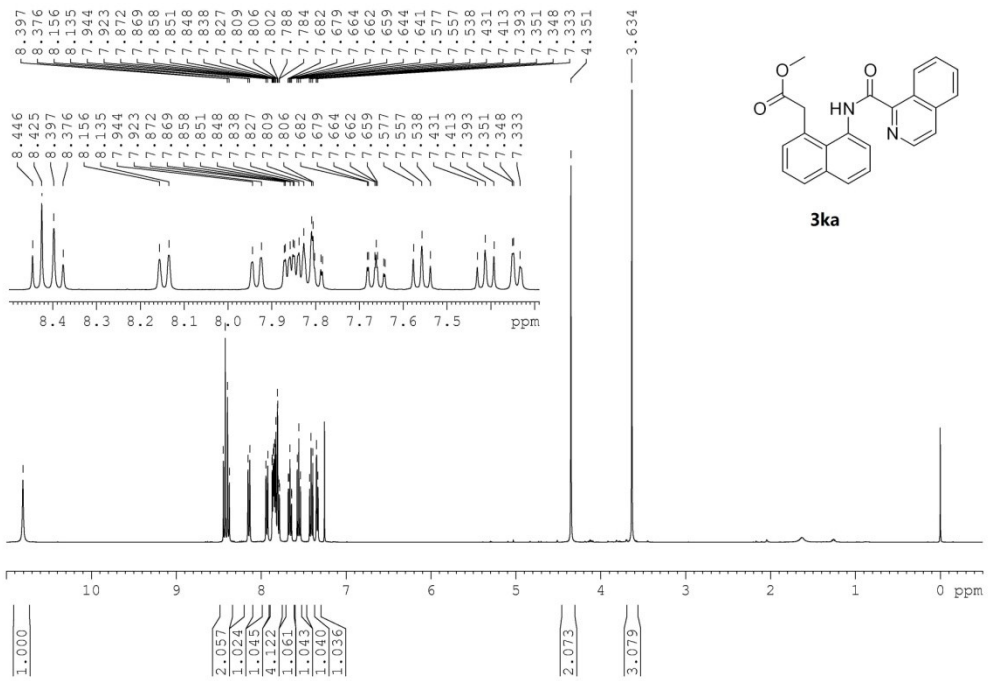
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7.802
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7.784
7.682
7.679
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7.662
7.659
7.644
7.641
7.577
7.557
7.538
7.431
7.413
7.393
7.351
7.348
7.333
4.351
3.634
8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 ppm
10 9 8 7 6 5 4 3 2 1 0 ppm
1.000
2.057
1.024
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1.043
1.040
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O
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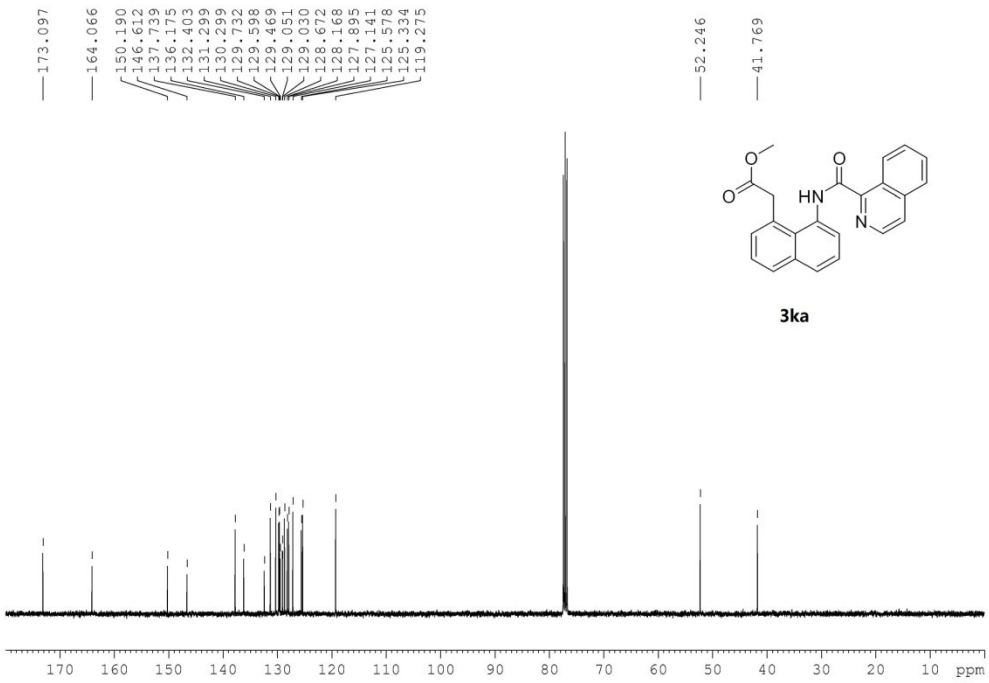
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129.598
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129.051
129.030
128.672
128.168
127.895
127.141
125.578
125.334
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52.246
41.769
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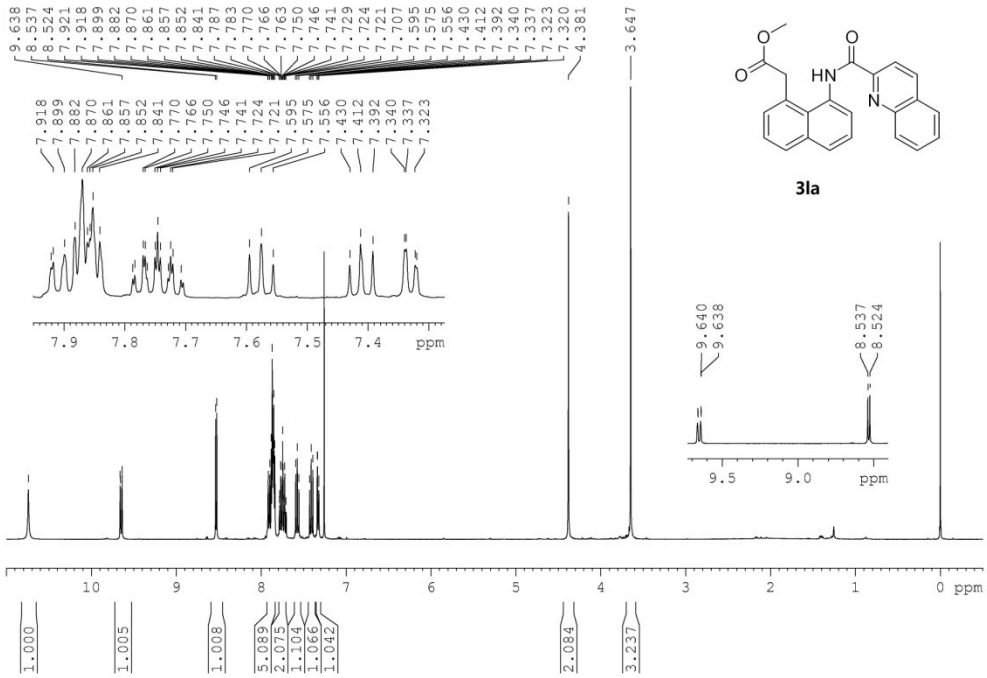
O
O
HN
O
N
3ka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7.861
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7.841
7.787
7.783
7.770
7.766
7.763
7.750
7.746
7.741
7.729
7.724
7.721
7.707
7.595
7.575
7.556
7.430
7.412
7.392
7.340
7.337
7.323
7.320
4.381
3.647
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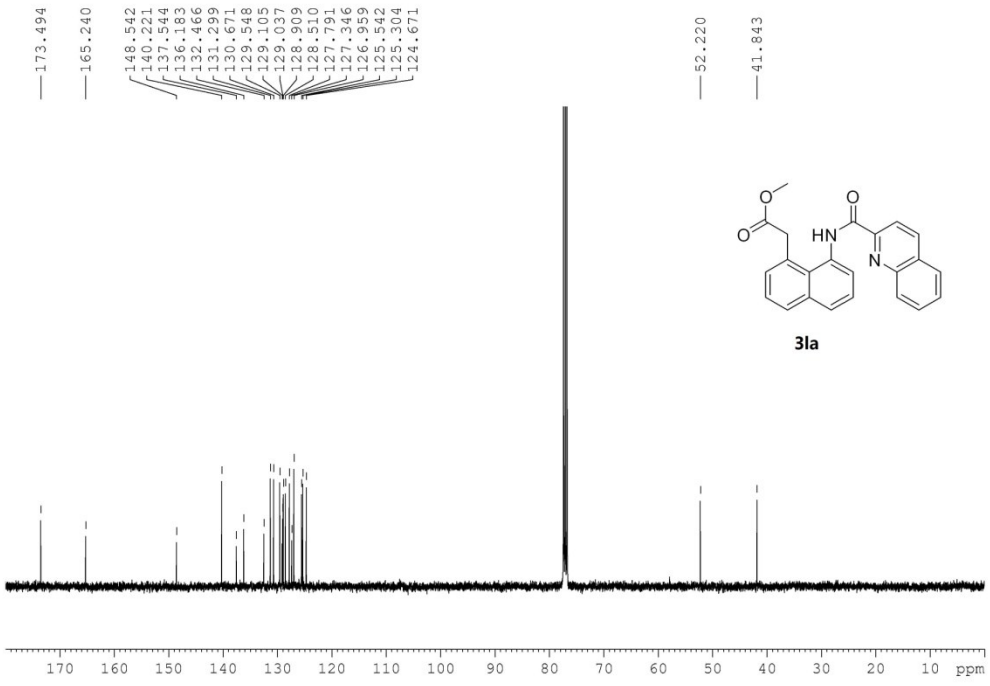
3.237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130.671
129.548
129.105
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127.346
126.959
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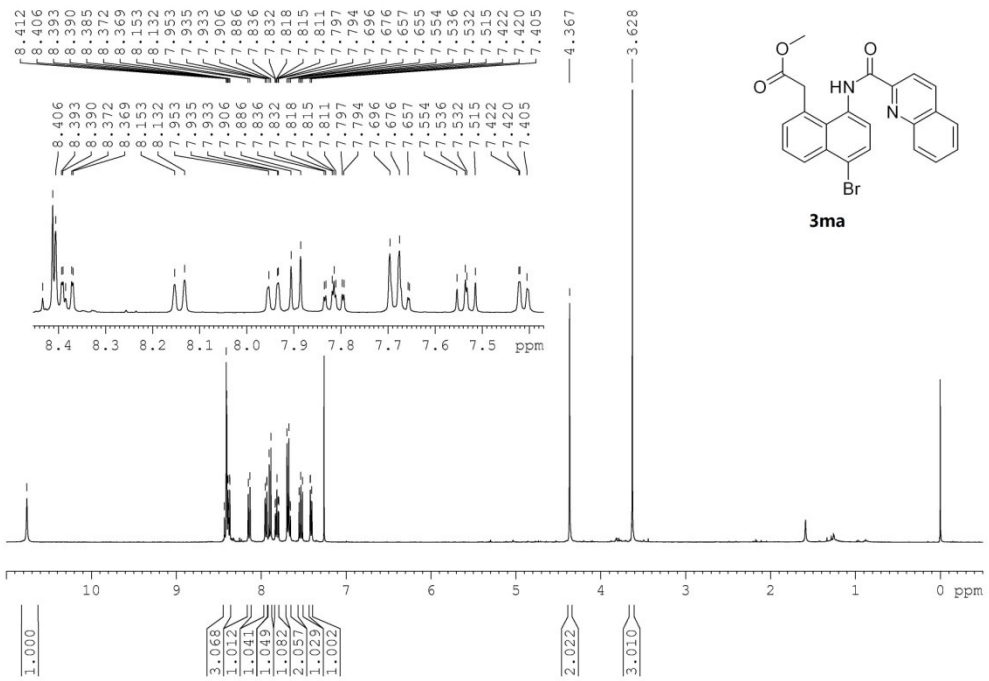
3la
ppm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8.132
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7.935
7.933
7.906
7.886
7.836
7.832
7.818
7.815
7.811
7.797
7.794
7.696
7.676
7.657
7.655
7.554
7.536
7.532
7.515
7.422
7.420
7.405
4.367
3.628
8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 ppm
10 9 8 7 6 5 4 3 2 1 0 ppm
1.000
3.068
1.012
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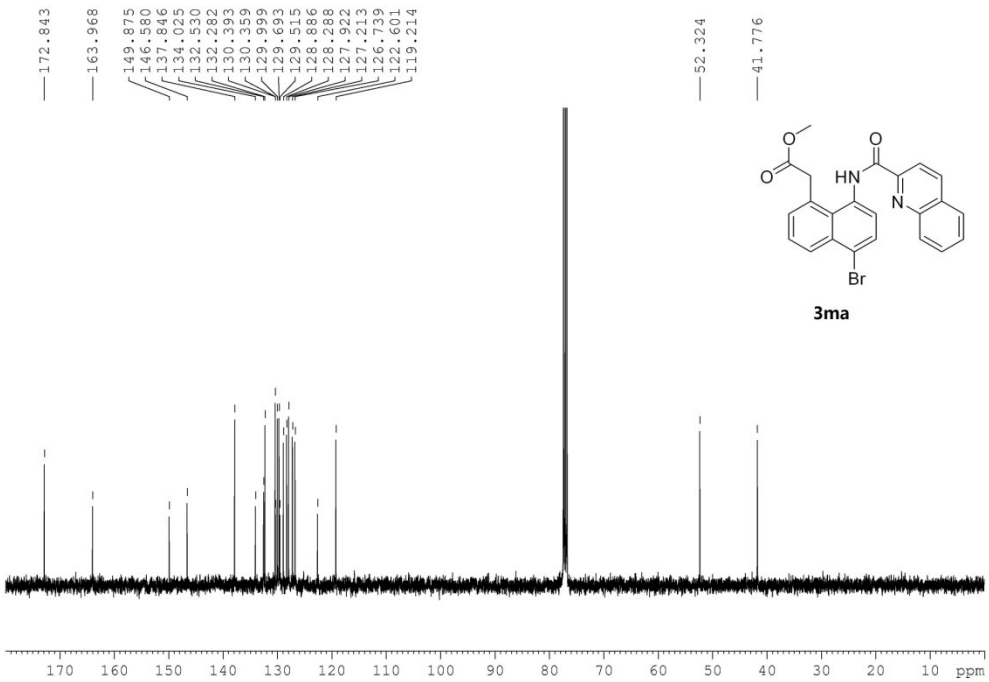
1.082
2.057
1.029
1.002
2.022
3.010
O
O
HN
N
Br
3ma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129.515
128.886
128.288
127.922
127.213
126.739
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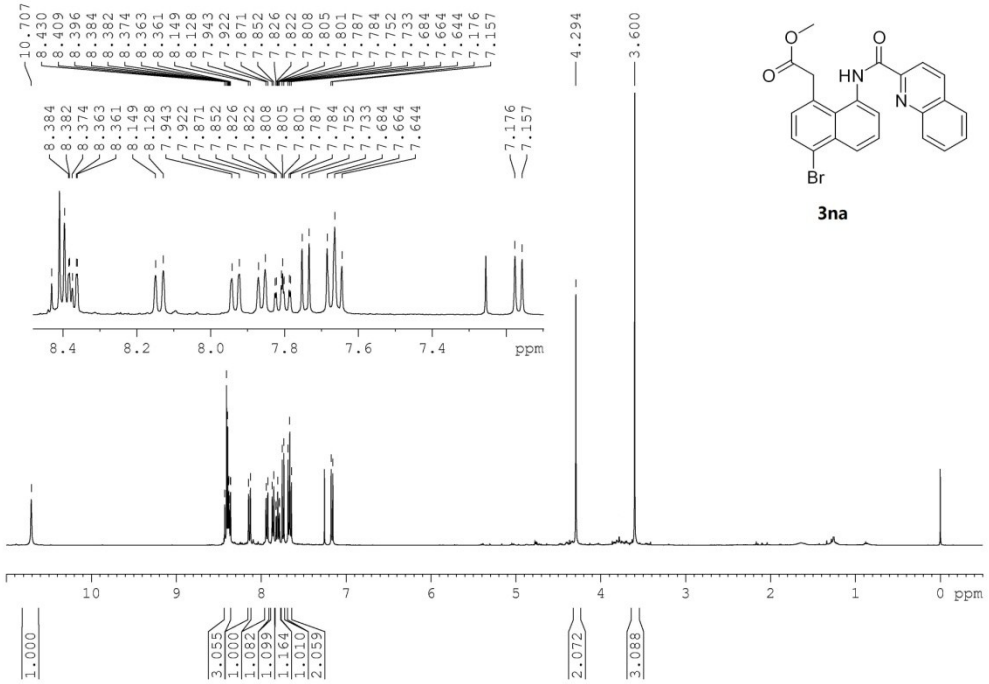
119.214
52.324
41.776
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
O
O
HN
N
Br
3ma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8.396
8.384
8.382
8.374
8.363
8.361
8.149
8.128
7.943
7.922
7.871
7.852
7.826
7.822
7.808
7.805
7.801
7.787
7.784
7.752
7.733
7.684
7.664
7.644
7.176
7.157
4.294
3.600
ppm
1.000
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1.164
1.010
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2.072
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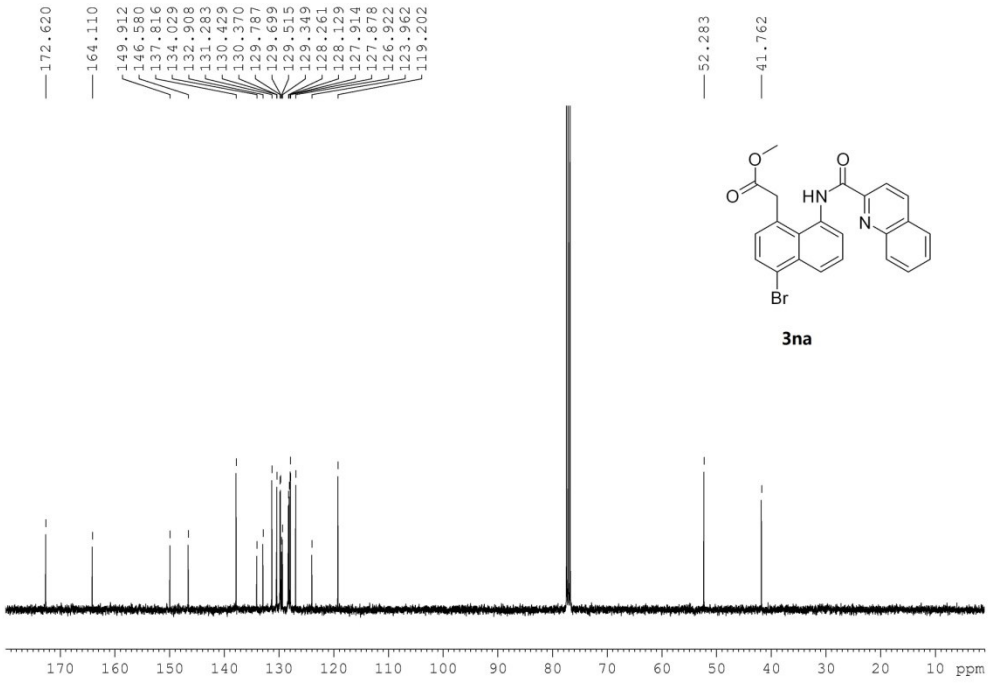
HN
N
O
Br
3na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149.912
146.580
137.816
134.029
132.908
131.283
130.429
130.370
129.787
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129.515
129.349
128.261
128.129
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127.878
126.922
123.962
119.202
52.283
41.762
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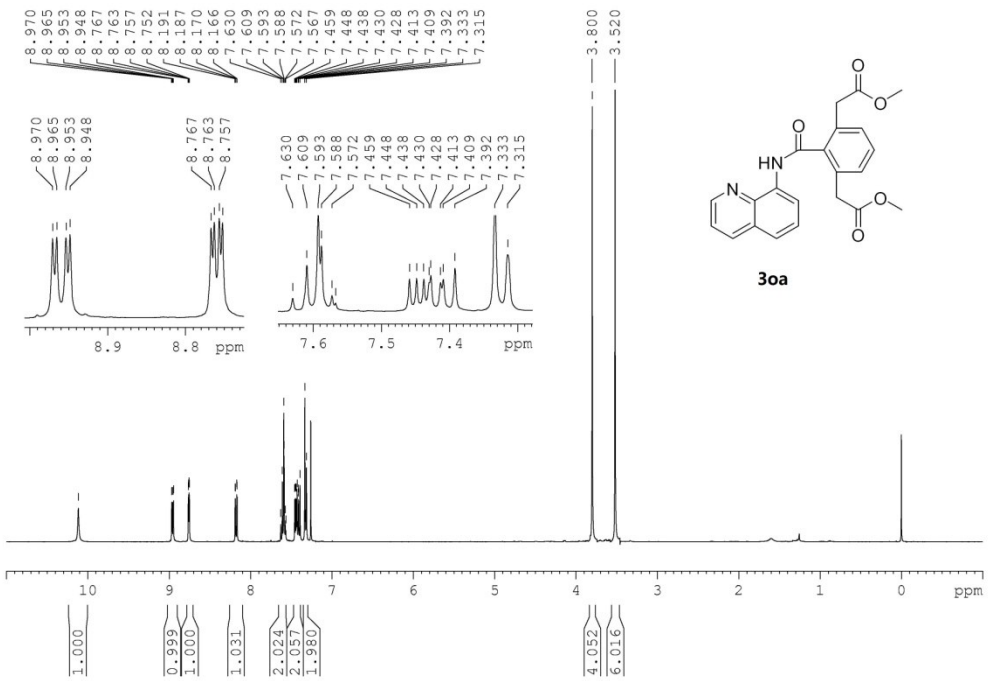
O
Br
3na
ppm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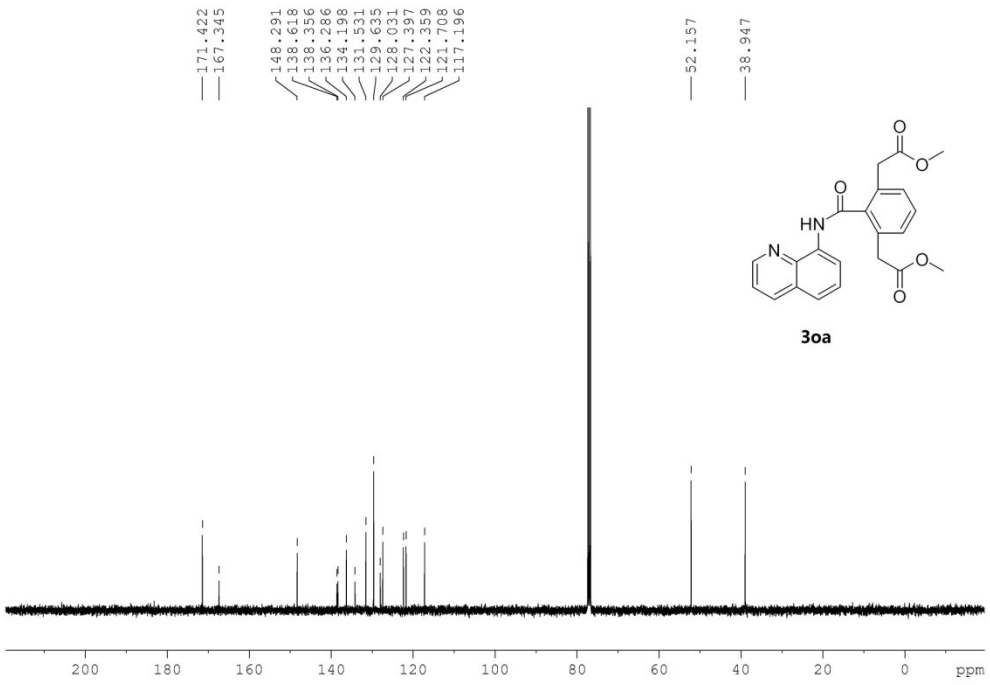
8.965
8.953
8.948
8.767
8.763
8.757
8.752
8.191
8.187
8.170
8.166
7.630
7.609
7.593
7.588
7.572
7.567
7.459
7.448
7.438
7.430
7.428
7.413
7.409
7.392
7.333
7.315
3.800
3.520
8.9
8.8
ppm
7.6
7.5
7.4
ppm
HN
N
O
O
O
O
O
3oa
10
9
8
7
6
5
4
3
2
1
0
ppm
1.000
0.999
1.000
1.031
2.024
2.057
1.980
4.052
6.016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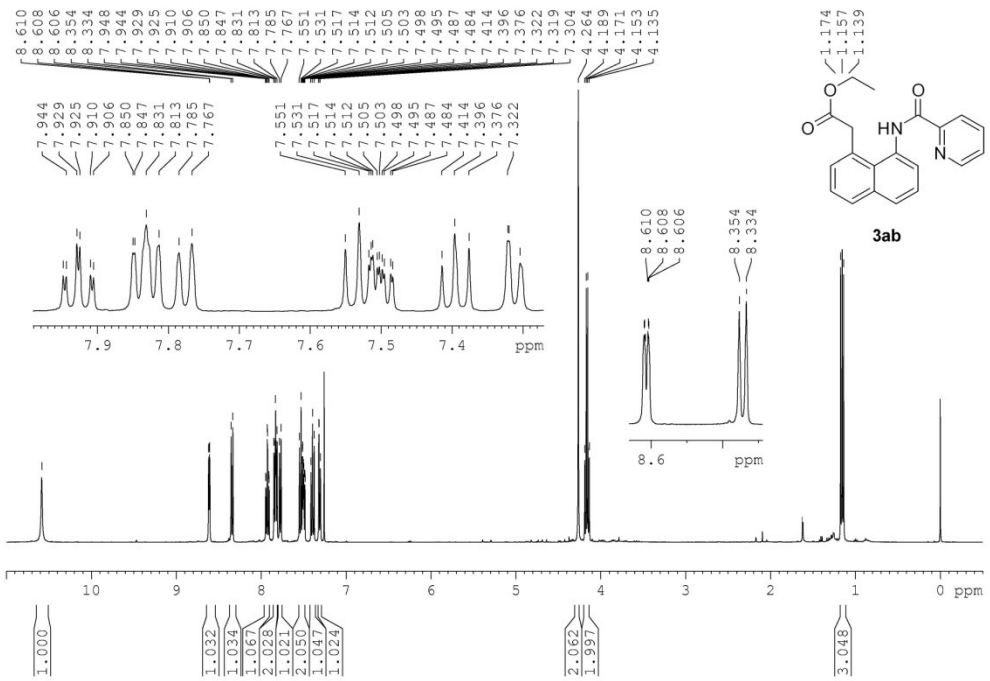
167.345
148.291
138.618
138.356
136.286
134.198
131.531
129.635
128.031
127.397
122.359
121.708
117.196
52.157
38.947
HN
N
O
O
O
O
O
3oa
200
180
160
140
120
100
80
60
40
20
0
ppm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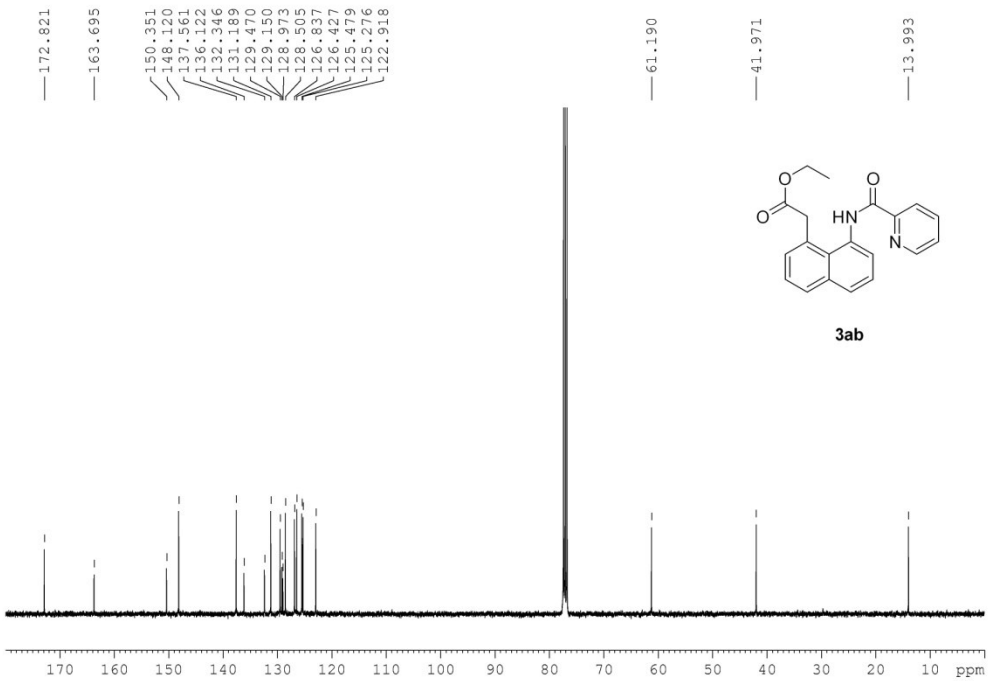
8.608
8.606
8.354
8.334
7.948
7.944
7.929
7.925
7.910
7.906
7.850
7.847
7.831
7.813
7.785
7.767
7.551
7.531
7.517
7.514
7.512
7.505
7.503
7.498
7.495
7.487
7.484
7.414
7.396
7.376
7.322
7.319
7.304
4.264
4.189
4.171
4.153
4.135
1.174
1.157
1.139
O
O
HN
N
3ab
ppm
10 9 8 7 6 5 4 3 2 1 0 ppm
1.000
1.032
1.034
1.067
2.028
2.021
2.050
1.047
1.024
2.062
1.997
3.048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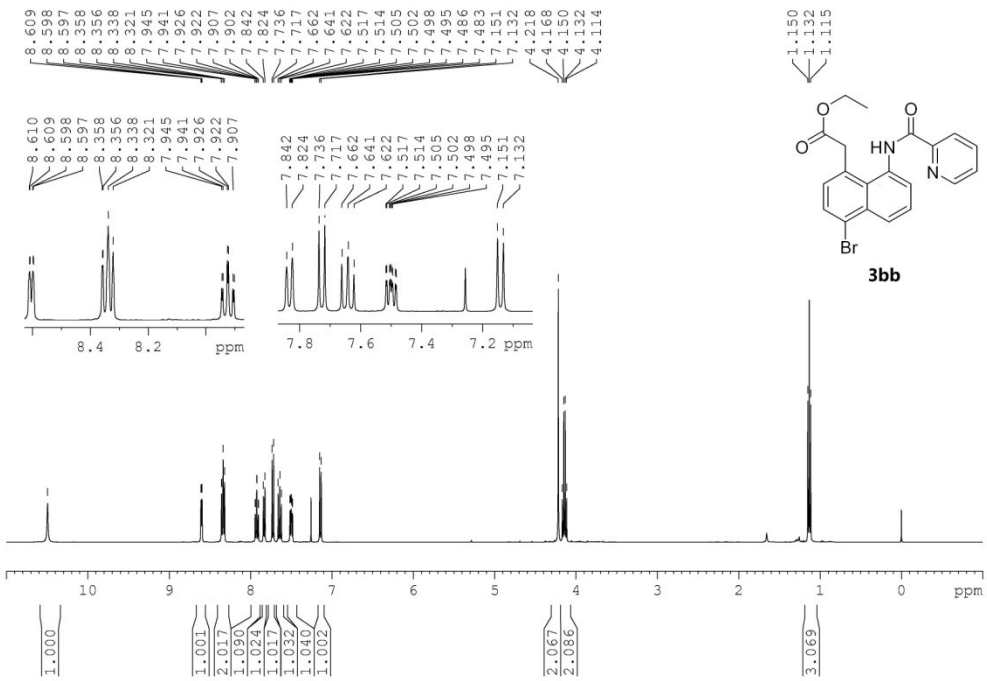
150.351
148.120
137.561
136.122
132.346
131.189
129.470
129.150
128.973
128.505
126.837
126.427
125.479
125.276
122.918
61.190
41.971
13.993
O
O
HN
N
3ab
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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8.597
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8.356
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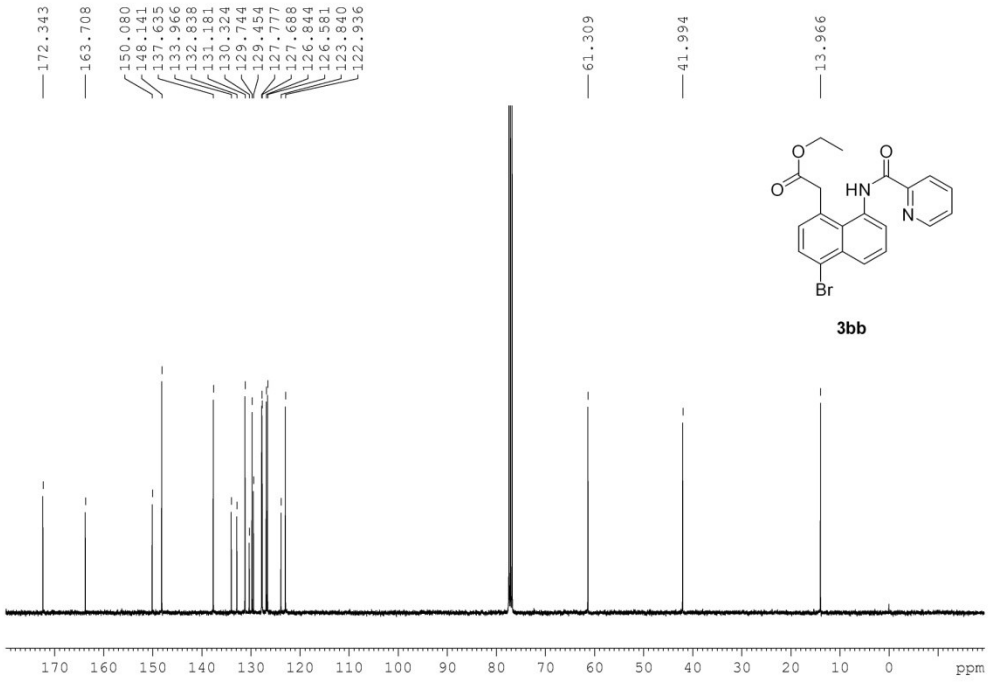
8.321
7.945
7.941
7.926
7.922
7.907
7.902
7.842
7.824
7.736
7.717
7.662
7.641
7.622
7.517
7.514
7.505
7.502
7.498
7.495
7.486
7.483
7.151
7.132
4.218
4.168
4.150
4.132
4.114
1.150
1.132
1.115
8.4
8.2
ppm
7.8
7.6
7.4
7.2 ppm
10
9
8
7
6
5
4
3
2
1
0
ppm
1.000
1.001
2.017
1.090
1.024
1.017
1.032
1.040
1.002
2.067
2.086
3.069
HN
N
O
Br
3bb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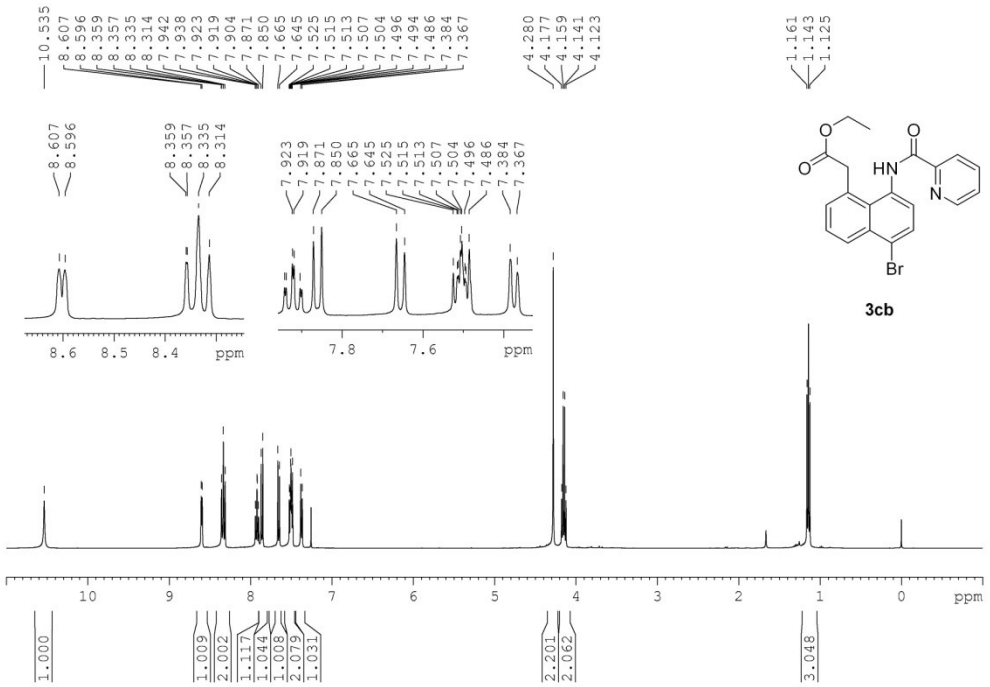
150.080
148.141
137.635
133.966
132.838
131.181
130.324
129.744
129.454
127.777
127.688
126.844
126.581
123.840
122.936
61.309
41.994
13.966
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
HN
N
O
Br
3bb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8.607
8.596
8.359
8.357
8.335
8.314
7.942
7.938
7.923
7.919
7.904
7.871
7.850
7.665
7.645
7.525
7.515
7.513
7.507
7.504
7.496
7.494
7.486
7.384
7.367
4.280
4.177
4.159
4.141
4.123
1.161
1.143
1.125
HN
O
N
Br
3cb
ppm
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2.002
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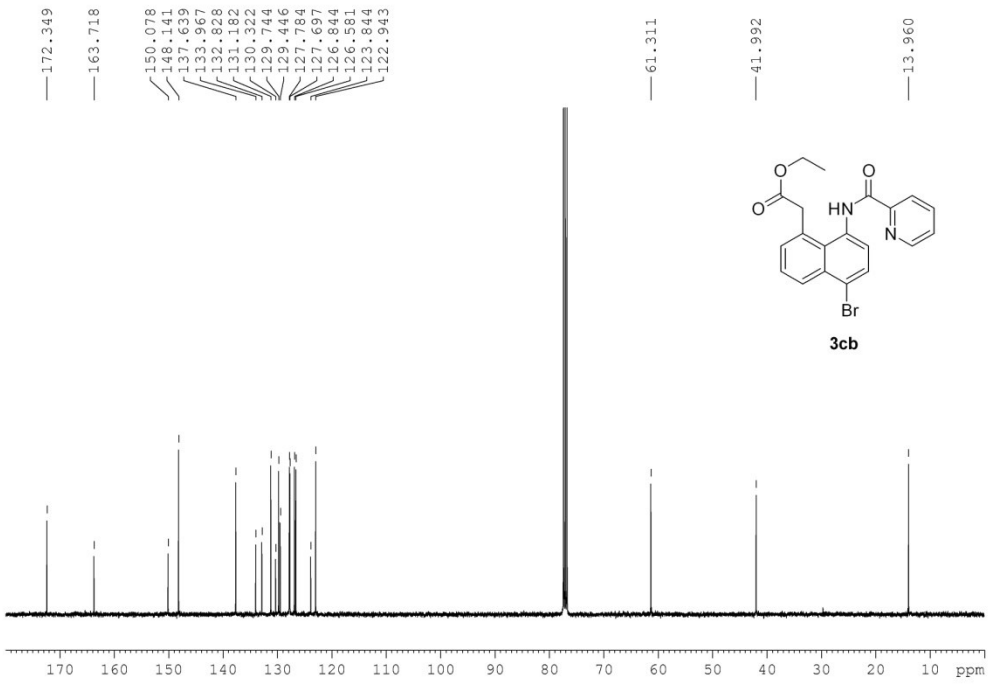
1.008
2.079
1.031
2.201
2.062
3.048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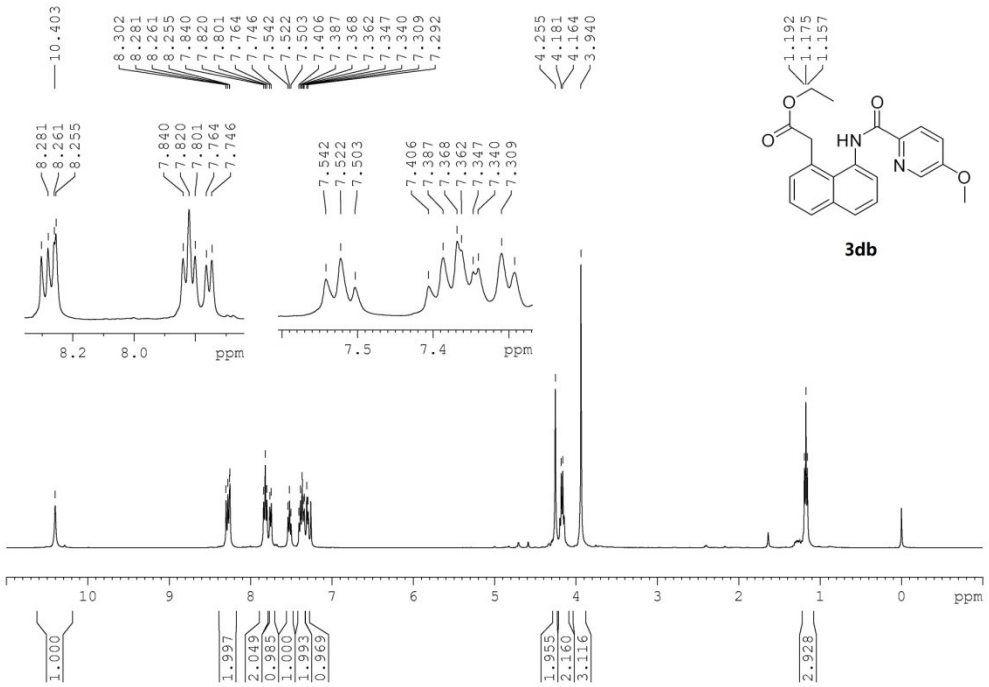
133.967
132.828
131.182
130.322
129.744
129.446
127.784
127.697
126.844
126.581
123.844
122.943
61.311
41.992
13.960
HN
O
N
Br
3cb
ppm


10.403
8.302
8.281
8.261
8.255
7.840
7.820
7.801
7.764
7.746
7.542
7.522
7.503
7.406
7.387
7.368
7.362
7.347
7.340
7.309
7.292
4.255
4.181
4.164
3.940
1.192
1.175
1.157
HN
N
O
3db
ppm
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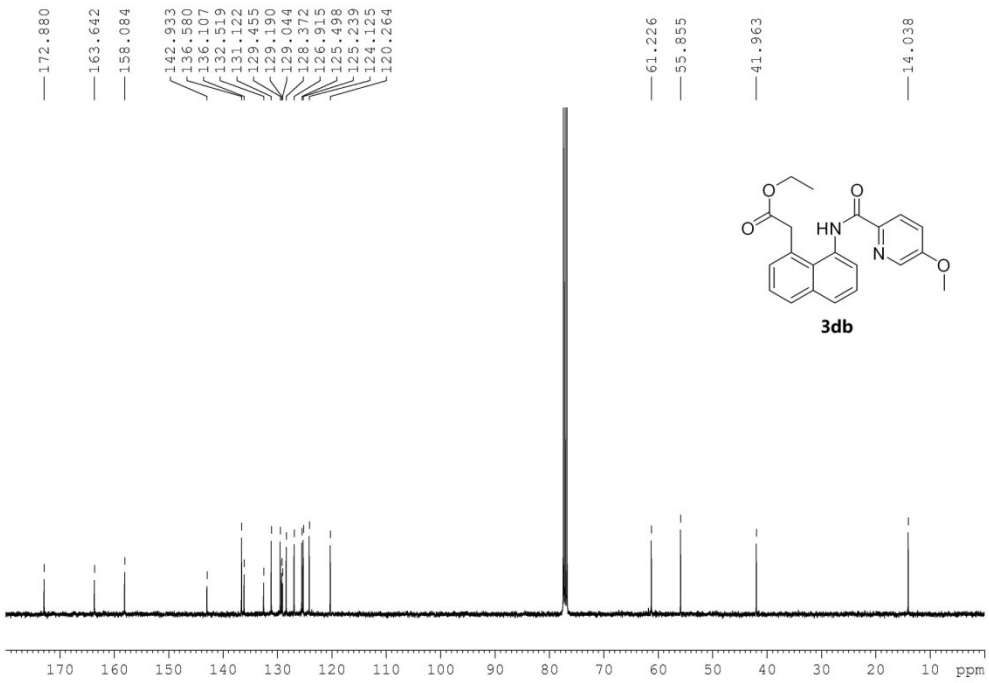
2.049
0.985
1.000
1.993
0.969
1.955
2.160
3.116
2.928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142.933
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132.519
131.122
129.455
129.190
129.044
128.372
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124.125
120.264
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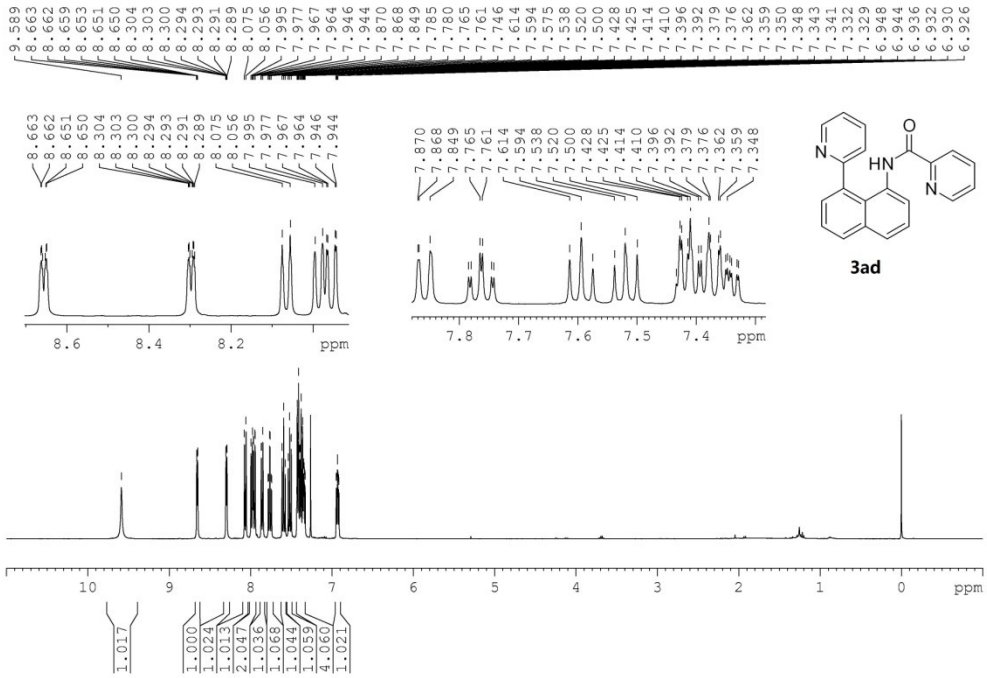
55.855
41.963
14.038
HN
N
O
3db
ppm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8.663
8.662
8.659
8.653
8.651
8.650
8.304
8.303
8.300
8.294
8.293
8.291
8.289
8.075
8.056
7.995
7.977
7.967
7.964
7.946
7.944
7.870
7.868
7.849
7.785
7.780
7.765
7.761
7.746
7.614
7.594
7.575
7.538
7.520
7.500
7.428
7.425
7.414
7.410
7.396
7.392
7.379
7.376
7.362
7.359
7.350
7.348
7.343
7.341
7.332
7.329
6.948
6.944
6.936
6.932
6.930
6.926
8.6
8.4
8.2
ppm
7.8
7.7
7.6
7.5
7.4
ppm
3ad
10
9
8
7
6
5
4
3
2
1
0
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1.000
1.024
1.013
2.047
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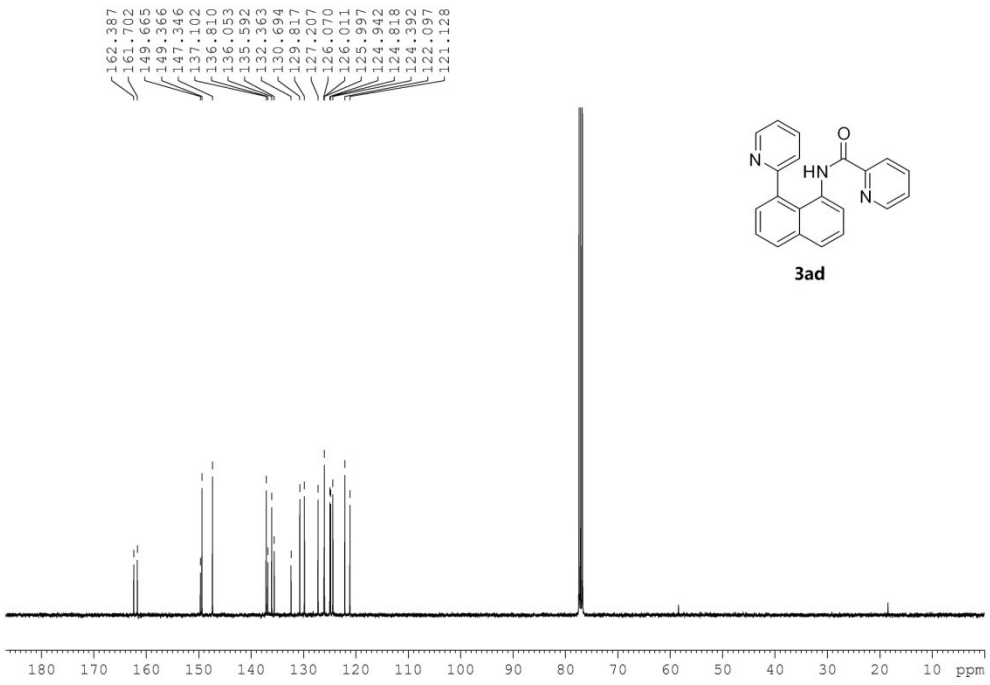
1.068
1.044
1.059
4.060
1.021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149.366
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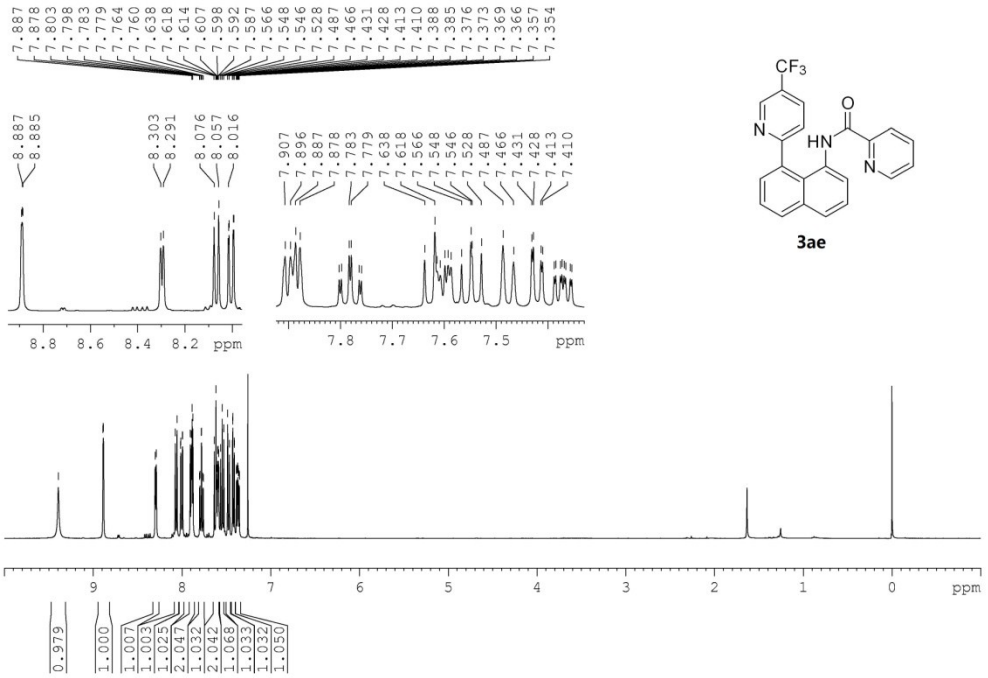
136.053
135.592
132.363
130.694
129.817
127.207
126.070
126.011
125.997
124.942
124.818
124.392
122.097
121.128
3ad
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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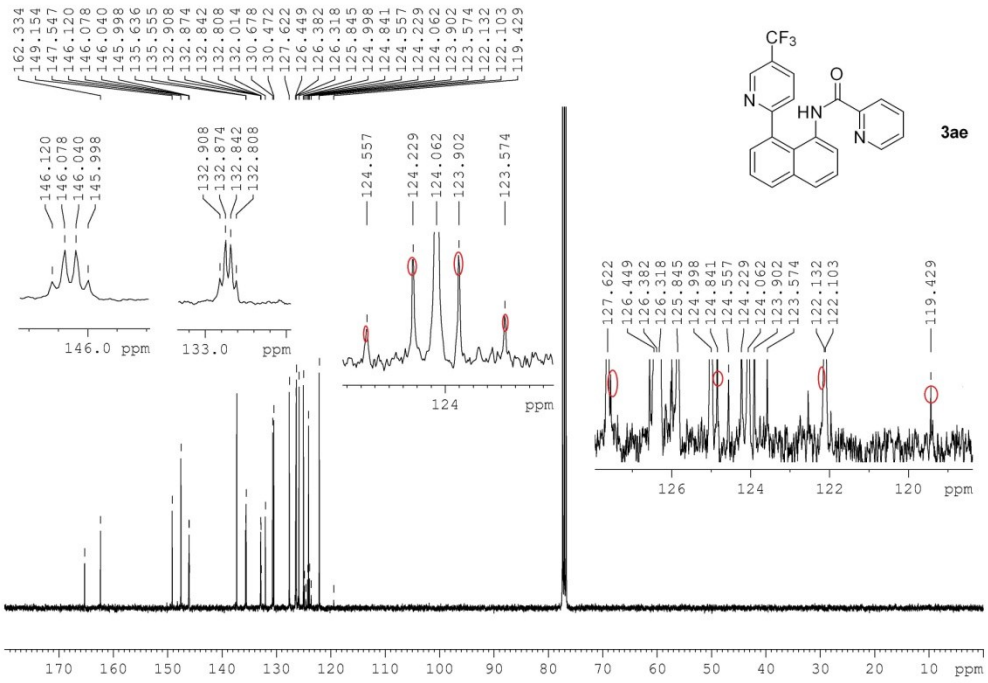
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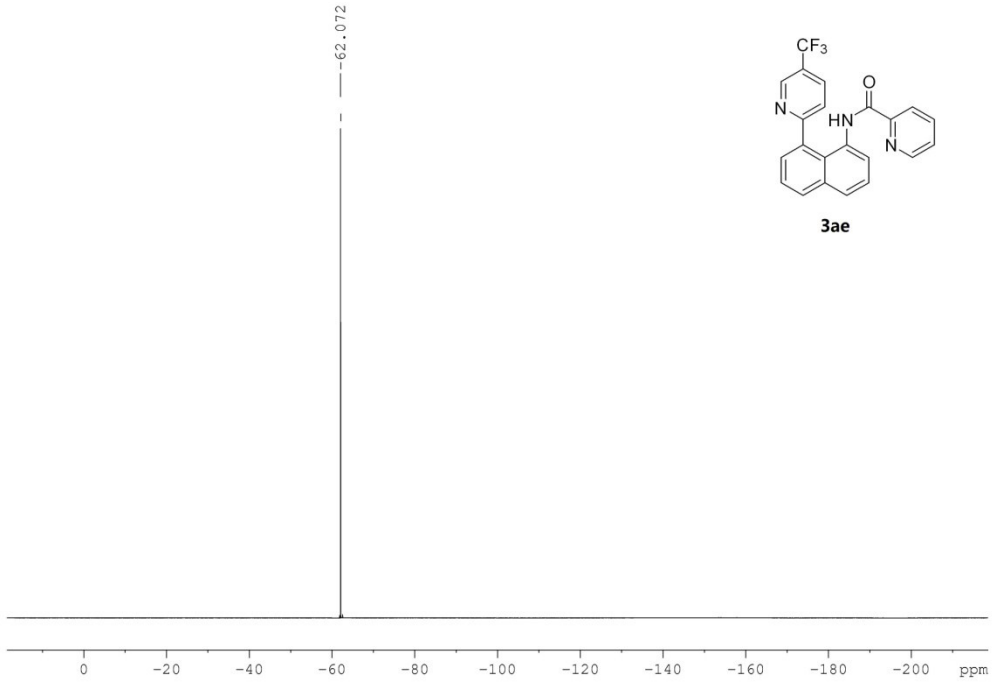
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CF3
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O
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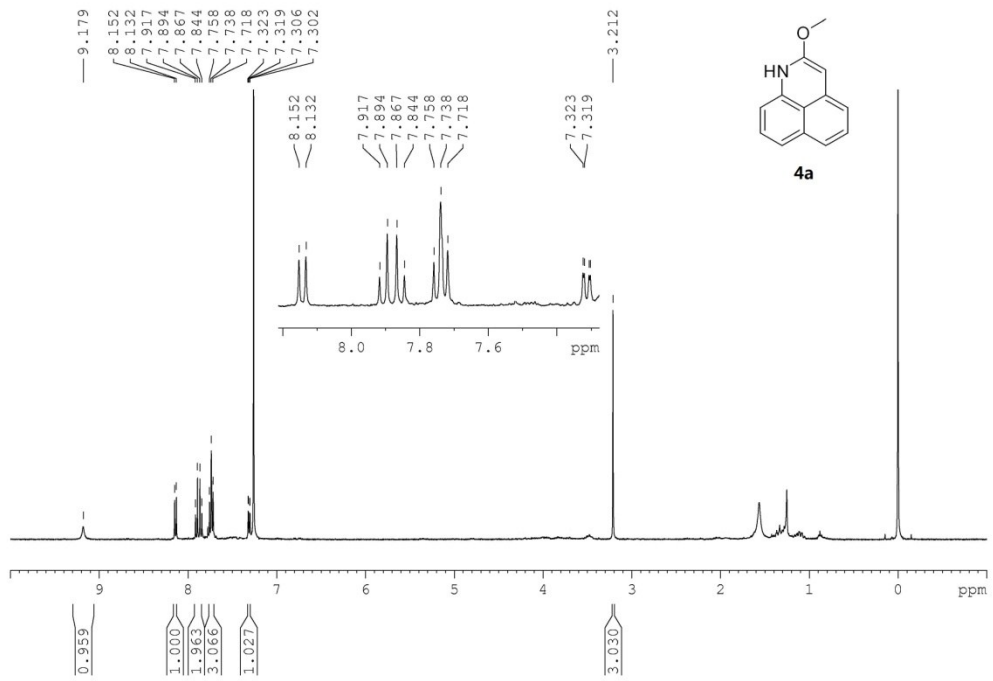
-60
-80
-100
-120
-140
-160
-180
-200
ppm

3ae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7.758
7.738
7.718
7.323
7.319
7.306
7.302
3.212
HN
O
8.0
7.8
7.6
ppm
9
8
7
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3
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1
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ppm
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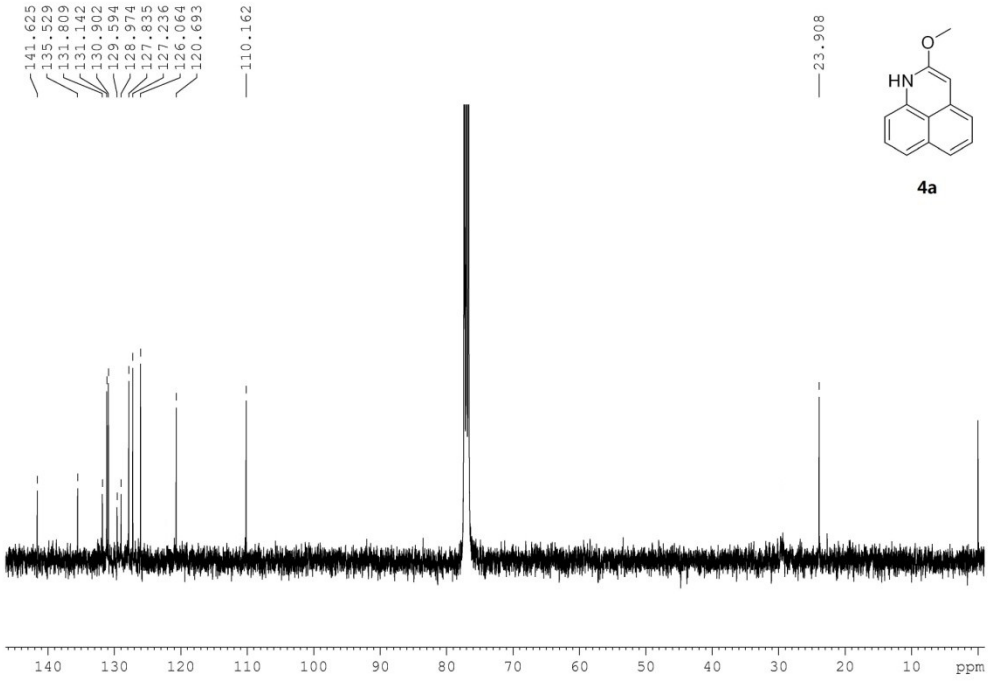
1.963
3.066
1.027
3.030

4a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127.835
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126.064
120.693
110.162
23.908
O
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4a
140
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120
110
100
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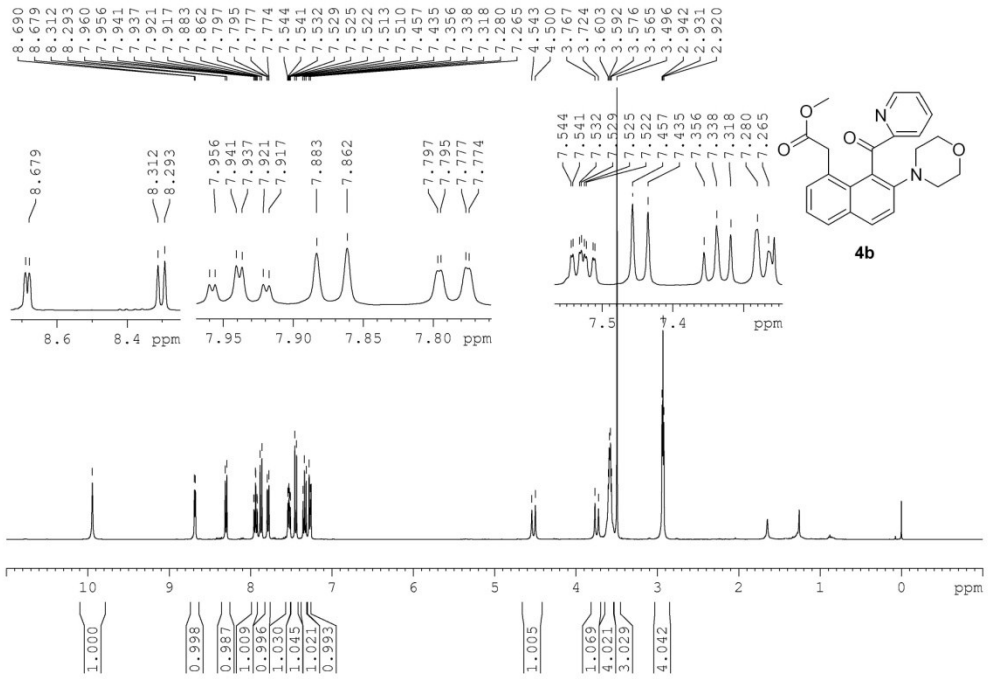
80
70
60
50
40
30
20
10
ppm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7.937
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7.917
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7.862
7.797
7.795
7.777
7.774
7.544
7.541
7.532
7.529
7.525
7.522
7.513
7.510
7.457
7.435
7.356
7.338
7.318
7.280
7.265
4.543
4.500
3.767
3.724
3.603
3.592
3.576
3.565
3.496
2.942
2.931
2.920
O
O
N
O
N
4b
8.6
8.4 ppm
7.95
7.90
7.85
7.80 ppm
7.5
7.4
ppm
10
9
8
7
6
5
4
3
2
1
0
ppm
1.000
0.998
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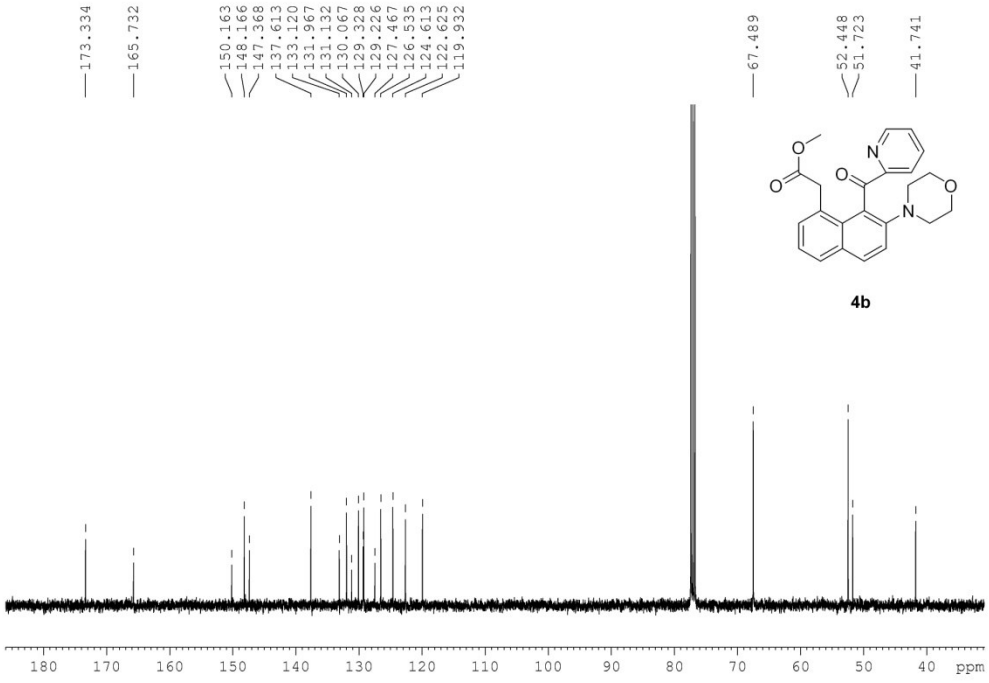
4.042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150.163
148.166
147.368
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131.967
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130.067
129.328
129.226
127.467
126.535
124.613
122.625
119.932
67.489
52.448
51.723
41.741
O
O
N
O
N
4b
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm