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PyBroP-mediated nucleophilic addition of oxindoles with pyridine *N*-oxides to access 3-pyridyl-3,3-disubstituted oxindoles

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Supporting Information

A. General Information

All reactions were carried out under air. Oxindoles **1** [1] and pyridine *N*-oxides **2** [2] were synthesized according to reported procedures. Commercial reagent (PyBroP) were used without further purification. Flash chromatography was performed on silica gel 60 (40-63μm, 60Å). Thin layer chromatography (TLC) was performed on glass plates coated with silica gel 60 with F254 indicator. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker 600 MHz spectrometer. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CDCl_3$ = δ 7.26, DMSO = δ 2.54). Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker 150 MHz spectrometer. Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent ($CDCl_3$ = δ 77.16, DMSO = δ 39.50). Data are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz), integration. Electrospray ionization high-resolution mass spectra (ESI-HRMS) were recorded on a Bruke P-SIMS-Gly FT-ICR mass spectrometer.

General procedure for the nucleophilic addition of oxindoles with pyridine *N*-oxides.

An Ar-filled 25 mL Schlenk tube was charged with oxindoles **1** (0.5 mmol), pyridine *N*-oxides **2** (0.75 mmol), Et_3N (1.5 mmol), PyBroP (0.65 mmol) and 1,4-dioxane (3 mL). The mixture was stirred at 25 ^{o}C for 12 h, after concentration under reduced pressure, the resulting residue was purified by column chromatography (SiO_2; hexanes/EtOAc, 10:1-4:1) to afford the desired product **3**.

Tert-butyl 3-benzyl-2-oxo-3-(pyridin-2-yl)indoline-1-carboxylate (3aa). White solid, 95% yield, m.p. = 83.6-84.4 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.72 (d, *J* = 4.2 Hz, 1H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.58 (d, *J* = 8.1 Hz, 1H), 7.43 (d, *J* = 7.3 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.22 (td, *J* = 7.9, 1.4 Hz, 1H), 7.17-7.14 (m, 1H), 7.08 (dd, *J* = 8.4, 6.2 Hz, 1H), 7.03 (t, *J* = 7.4 Hz, 2H), 6.86 (d, *J* = 7.2 Hz, 2H), 3.84 (dd, *J* = 30.5, 13.0 Hz, 2H), 1.55 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.8, 158.4, 149.3, 148.7, 139.7, 137.1, 135.1, 130.2, 130.1, 128.5, 127.6, 126.7, 125.1, 124.3, 122.6, 122.1, 114.8, 84.1, 61.2, 44.1, 28.0. HRMS (ESI) *m*/*z*: $[M+H]^+$ calcd. for $C_{25}H_{25}N_2O_3$, 401.1865, found: 401.1845.

Tert-butyl 3-(4-methylbenzyl)-2-oxo-3-(pyridin-2-yl)indoline-1-carboxylate (3ba). Yellow oil, 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (dd, *J* = 4.8, 0.9 Hz, 1H), 7.64-7.59 (m, 2H), 7.34 (dd, *J* = 7.4, 1.1 Hz, 1H), 7.26-7.23 (m, 1H), 7.23-7.18 (m, 2H), 7.15 (dt, *J* = 7.5, 3.8 Hz, 1H), 6.83 (d, *J* = 7.9 Hz, 2H),

6.73 (d, *J* = 8.0 Hz, 2H), 3.73 (t, *J* = 9.9 Hz, 2H), 2.19 (s, 3H), 1.55 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.0, 158.7, 149.5, 148.8, 139.8, 136.7, 136.2, 132.0, 130.5, 129.9, 128.4, 128.3, 125.0, 124.2, 122.5, 121.9, 114.8, 83.9, 61.3, 43.7, 28.0, 21.0. HRMS (ESI) *m*/*z*: $[M+H]^+$ calcd. for $C_{26}H_{27}N_2O_3$, 415.2022, found: 415.2007.

Tert-butyl 3-(4-methoxybenzyl)-2-oxo-3-(pyridin-2-yl)indoline-1-carboxylate (3ca). Yellow oil, 93% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.69 (d, *J* = 4.0 Hz, 1H), 7.66-7.63 (m, 1H), 7.60 (d, *J* = 8.1 Hz, 1H), 7.38 (d, *J* = 7.4 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.24-7.21 (m, 2H), 7.15 (td, *J* = 7.5, 0.9 Hz, 1H), 6.77 (d, *J* = 8.7 Hz, 2H), 6.58-6.56 (m, 2H), 3.75 (s, 2H), 3.68 (s, 3H), 1.56 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.1, 158.6, 158.4, 149.5, 148.8, 139.8, 136.8, 131.1, 130.4, 128.4, 127.2, 125.0, 124.20, 122.5, 121.9, 114.9, 113.1, 84.0, 61.4, 55.1, 43.4, 28.0. HRMS (ESI) *m*/*z*: $[M+H]^+$ calcd. for $C_{26}H_{27}N_2O_4$, 431.1971, found: 431.1955.

Tert-butyl 3-(4-bromobenzyl)-2-oxo-3-(pyridin-2-yl)indoline-1-carboxylate (3da). Yellow oil, 90% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.68 (dd, *J* = 4.4, 1.4 Hz, 1H), 7.64-7.59 (m, 2H), 7.36 (dd, *J* = 7.5, 0.8 Hz, 1H), 7.25-7.20 (m, 3H), 7.16 (dq, *J* = 4.9, 2.8 Hz, 3H), 6.72 (d, *J* = 8.4 Hz, 2H), 3.76 (t, *J* = 9.2 Hz, 2H), 1.57 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.6, 158.0, 149.3, 148.5, 139.6, 137.2, 134.2, 131.8, 130.8, 129.8, 128.7, 125.0, 124.4, 122.7, 122.1, 121.0, 115.0, 84.4, 61.0, 43.4, 28.0. HRMS (ESI) *m*/*z*: $[M+H]^+$ calcd. for $C_{25}H_{24}BrN_2O_3$, 479.0970, found: 479.0953.

Tert-butyl 3-(4-chlorobenzyl)-2-oxo-3-(pyridin-2-yl)indoline-1-carboxylate (3ea). Yellow oil, 89% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.71 (d, *J* = 4.3 Hz, 1H), 7.67 (t, *J* = 7.2 Hz, 1H), 7.60 (d, *J* = 8.1 Hz, 1H), 7.42 (d, *J* = 7.4 Hz, 1H), 7.26-7.23 (m, 2H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.00 (dd, *J* = 8.7, 2.1 Hz, 2H), 6.79 (d, *J* = 8.4 Hz, 2H), 3.80 (dd, *J* = 28.9, 13.0 Hz, 2H), 1.57 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.7, 158.2, 149.4, 148.6, 139.7, 137.0, 133.7, 132.7, 131.4, 129.9, 128.6, 127.8, 125.0, 124.4, 122.7, 121.9, 114.9, 84.3, 61.1, 43.3, 28.0. HRMS (ESI) *m*/*z*: $[M+H]^+$ calcd. for $C_{25}H_{24}ClN_2O_3$, 435.1475, found: 435.1463.

Tert-butyl 3-(3-methylbenzyl)-2-oxo-3-(pyridin-2-yl)indoline-1-carboxylate (3fa). Yellow oil, 90% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.70 (d, *J* = 4.2 Hz, 1H), 7.65 (d, *J* = 1.1 Hz, 1H), 7.59 (d, *J* = 8.1 Hz, 1H), 7.38 (d, *J* = 7.3 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.22 (ddd, *J* = 9.1, 6.5, 1.6 Hz, 2H), 7.16 (d, *J* = 7.5 Hz, 1H), 6.92-6.87 (m, 2H), 6.67 (s, 1H), 6.63 (d, *J* = 7.3 Hz, 1H), 3.77 (s, 2H), 2.13 (s, 3H), 1.55 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.8, 158.5, 149.3, 148.8, 139.8, 137.1, 137.0, 134.9, 130.8, 130.3, 128.4,

127.5, 127.4, 127.1, 125.1, 124.2, 122.6, 122.1, 114.7, 84.0, 61.2, 44.1, 28.0, 21.2. HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{26}H_{27}N_2O_3$, 415.2022, found: 415.2004.

Tert-butyl 3-(3-bromobenzyl)-2-oxo-3-(pyridin-2-yl)indoline-1-carboxylate (3ga). Yellow oil, 83% yield. ^{1}H NMR (600 MHz, DMSO) δ 8.54 (d, *J* = 3.4 Hz, 1H), 7.85 (t, *J* = 7.4 Hz, 1H), 7.50 (dd, *J* = 13.7, 8.1 Hz, 2H), 7.35 (d, *J* = 6.5 Hz, 2H), 7.29-7.23 (m, 2H), 7.16 (t, *J* = 7.3 Hz, 1H), 7.02-6.97 (m, 2H), 6.77 (d, *J* = 7.4 Hz, 1H), 3.83 (d, *J* = 12.8 Hz, 1H), 3.66 (d, *J* = 12.8 Hz, 1H), 1.51 (s, 9H). ^{13}C NMR (151 MHz, DMSO) δ 175.6, 159.5, 149.7, 148.6, 139.7, 138.4, 137.9, 132.8, 130.9, 130.1, 130.0, 129.3, 128.9, 125.2, 124.9, 123.4, 121.9, 121.3, 114.6, 84.2, 61.5, 41.4, 28.0. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{25}H_{23}BrN_2NaO_3$, 501.0790, found: 501.0774.

Tert-butyl 3-(3-fluorobenzyl)-2-oxo-3-(pyridin-2-yl)indoline-1-carboxylate (3ha). Yellow oil, 78% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.69 (dd, *J* = 2.9, 1.8 Hz, 1H), 7.65-7.61 (m, 2H), 7.38-7.35 (m, 1H), 7.23 (ddd, *J* = 6.4, 5.9, 1.0 Hz, 3H), 7.16 (td, *J* = 7.5, 1.0 Hz, 1H), 6.98 (td, *J* = 7.9, 6.1 Hz, 1H), 6.79-6.76 (m, 1H), 6.63-6.58 (m, 2H), 3.82-3.76 (m, 2H), 1.56 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.6, 163.0, 161.3, 158.1, 149.4, 148.7, 139.7, 137.8, 137.7, 137.0, 129.9, 129.0, 129.0, 128.7, 125.9, 125.9, 124.9, 124.4, 122.7, 122.0, 117.0, 116.8, 114.8, 113.7, 113.6, 84.3, 61.0, 43.6, 28.0. HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{25}H_{24}FN_2O_3$, 419.1771, found: 419.1765.

Tert-butyl 3-(3-cyanobenzyl)-2-oxo-3-(pyridin-2-yl)indoline-1-carboxylate (3ia). Yellow oil, 84% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.68 (ddd, *J* = 4.8, 1.7, 0.8 Hz, 1H), 7.64-7.59 (m, 2H), 7.38 (ddd, *J* = 7.5, 3.7, 1.1 Hz, 2H), 7.26-7.21 (m, 2H), 7.19-7.16 (m, 2H), 7.14 (dd, *J* = 10.0, 4.9 Hz, 2H), 7.10 (dd, *J* = 5.3, 3.9 Hz, 1H), 3.83 (dd, *J* = 30.7, 13.1 Hz, 2H), 1.57 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.3, 157.7, 149.5, 148.6, 139.5, 137.1, 136.9, 134.7, 133.5, 130.6, 129.4, 129.0, 128.5, 124.9, 124.7, 122.8, 122.0, 118.6, 114.9, 111.8, 84.6, 60.9, 43.4, 28.0. HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{26}H_{24}N_3O_3$, 426.1818, found: 426.1812.

Tert-butyl 3-(2-bromobenzyl)-2-oxo-3-(pyridin-2-yl)indoline-1-carboxylate (3ja). Yellow oil, 90% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.74 (d, *J* = 4.0 Hz, 1H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.64 (td, *J* = 7.8, 1.8 Hz, 1H), 7.35 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.26-7.22 (m, 3H), 7.07 (td, *J* = 7.6, 0.9 Hz, 1H), 7.04 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.01 (td, *J* = 7.5, 1.2 Hz, 1H), 6.95 (td, *J* = 7.6, 1.8 Hz, 1H), 4.28 (d, *J* = 13.8 Hz, 1H), 3.98 (d, *J* = 13.8 Hz, 1H), 1.61 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.7, 157.9, 149.2, 149.0, 139.5, 137.2, 135.5, 132.8, 130.9, 129.2, 128.7, 128.4, 126.8, 126.3, 126.2, 124.1,

122.7, 122.3, 114.5, 84.3, 60.4, 41.9, 28.1. HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{25}H_{24}BrN_2O_3$, 479.0970, found: 479.0958.

Tert-butyl 2-oxo-3-(pyridin-2-yl)-3-(thiophen-2-ylmethyl) indoline-1-carboxylate (3ka). Yellow oil, 90% yield. ^{1}H NMR (600 MHz, DMSO) δ 8.55 (d, *J* = 4.1 Hz, 1H), 7.83 (dd, *J* = 11.0, 4.4 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.34 (dd, *J* = 7.1, 5.0 Hz, 1H), 7.31-7.28 (m, 2H), 7.19-7.14 (m, 2H), 6.78-6.75 (m, 1H), 6.59 (d, *J* = 2.8 Hz, 1H), 4.08 (d, *J* = 14.2 Hz, 1H), 3.91 (d, *J* = 14.3 Hz, 1H), 1.52 (s, 9H). ^{13}C NMR (151 MHz, DMSO) δ 175.5, 159.2, 149.7, 148.7, 140.1, 138.0, 137.3, 131.1, 129.1, 127.9, 126.7, 125.8, 125.1, 125.0, 123.4, 121.8, 114.9, 84.2, 61.2, 36.3, 28.1. HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{23}H_{23}N_2O_3S$, 407.1429, found: 407.1416.

Tert-butyl 3-methyl-2-oxo-3-(pyridin-2-yl)indoline-1-carboxylate (3la). Yellow oil, 91% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.59 (d, *J* = 4.0 Hz, 1H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.64 (td, *J* = 7.8, 1.7 Hz, 1H), 7.33-7.30 (m, 1H), 7.23 (d, *J* = 7.2 Hz, 1H), 7.18 (dd, *J* = 7.1, 5.1 Hz, 1H), 7.14 (td, *J* = 7.5, 0.9 Hz, 1H), 1.93 (s, 3H), 1.66 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.2, 159.5, 149.5, 149.4, 139.1, 136.9, 133.4, 128.3, 124.7, 124.0, 122.4, 121.0, 115.2, 84.4, 55.3, 28.1, 23.7. HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{19}H_{21}N_2O_3$, 325.1552, found: 325.1537.

3-Benzyl-3-(pyridin-2-yl)indolin-2-one (3ma). White solid, 52% yield, m.p. = 191.5-192.5 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.71 (d, *J* = 4.1 Hz, 1H), 7.88 (s, 1H), 7.66 (t, *J* = 7.1 Hz, 1H), 7.46 (d, *J* = 7.3 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 7.0 Hz, 1H), 7.16-7.13 (m, 1H), 7.07-7.04 (m, 2H), 7.04-7.01 (m, 2H), 6.94-6.93 (m, 2H), 6.68 (d, *J* = 7.7 Hz, 1H), 3.87 (d, *J* = 13.1 Hz, 1H), 3.74 (d, *J* = 13.1 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.3, 158.7, 149.5, 140.6, 136.9, 135.8, 131.9, 130.2, 128.2, 127.6, 126.5, 125.6, 122.4, 121.5, 109.7, 61.3, 42.7. HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{20}H_{17}N_2O$, 301.1341, found: 301.1323.

3-benzyl-1-methyl-3-(pyridin-2-yl)indolin-2-one (3na). White solid, 78% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.71 (d, *J* = 3.4 Hz, 1H), 7.65 (s, 1H), 7.50 (s, 1H), 7.33 (d, *J* = 7.9 Hz, 1H), 7.23 (s, 1H), 7.19 (td, *J* = 7.7, 1.2 Hz, 1H), 7.07-7.03 (m, 2H), 7.02-6.99 (m, 2H), 6.87 (d, *J* = 6.9 Hz, 2H), 6.58 (d, *J* = 7.7 Hz, 1H), 3.85 (d, *J* = 12.5 Hz, 1H), 3.71 (d, *J* = 12.9 Hz, 1H), 2.97 (s, 3H). ^{13}C NMR (151 MHz, DMSO) δ 176.9, 159.7, 149.6, 143.9, 137.7, 136.3, 131.8, 130.2, 128.5, 127.8, 126.9, 125.1, 123.0, 122.5, 121.8, 108.7, 61.0, 41.7, 39.6, 26.3. HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{21}H_{19}N_2O$, 315.1497, found: 315.1481.

1,3-dibenzyl-3-(pyridin-2-yl)indolin-2-one (3oa). White solid, 70% yield. m.p. = 141.7-142.5 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.70 (d, *J* = 4.1 Hz, 1H), 7.66 (t, *J* = 7.3 Hz, 1H), 7.58 (d, *J* = 5.9 Hz, 1H), 7.33 (d, *J* = 7.9 Hz, 1H), 7.24-7.21 (m, 1H), 7.15 (ddt, *J* = 12.4, 7.1, 4.0 Hz, 4H), 7.06 (ddd, *J* = 6.8, 3.7, 1.5 Hz, 4H), 6.97-6.95 (m, 2H), 6.67 (d, *J* = 6.8 Hz, 2H), 6.41 – 6.39 (m, 1H), 4.96 (d, *J* = 16.0 Hz, 1H), 4.59 (d, *J* = 16.0 Hz, 1H), 3.94 (d, *J* = 13.0 Hz, 1H), 3.81 (d, *J* = 13.0 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.9, 159.2, 149.4, 142.7, 137.1, 135.9, 135.2, 131.3, 130.5, 128.6, 128.2, 127.8, 127.1, 126.7, 126.6, 125.3, 122.5, 122.4, 121.4, 109.3, 61.0, 43.7, 42.8. HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{27}H_{23}N_2O$, 391.1810, found: 391.1792.

Tert-butyl 3-benzyl-5-bromo-2-oxo-3-(pyridin-2-yl)indoline-1-carboxylate (3pa). Yellow oil, 90% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.70 (d, *J* = 4.1 Hz, 1H), 7.68 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.55 (d, *J* = 2.0 Hz, 1H), 7.48 (d, *J* = 8.7 Hz, 1H), 7.34 (dd, *J* = 8.7, 2.0 Hz, 2H), 7.27 (d, *J* = 5.4 Hz, 1H), 7.08 (dt, *J* = 14.5, 7.0 Hz, 3H), 6.86 (d, *J* = 7.0 Hz, 2H), 3.77 (d, *J* = 3.4 Hz, 2H), 1.54 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.0, 157.7, 149.5, 148.5, 138.7, 137.3, 134.6, 132.3, 131.4, 130.0, 128.1, 127.8, 127.0, 122.9, 121.9, 117.2, 116.4, 84.4, 61.1, 44.5, 28.0. HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{25}H_{24}BrN_2O_3$, 479.0970, found: 479.0955.

Tert-butyl 3-benzyl-5-chloro-2-oxo-3-(pyridin-2-yl)indoline-1-carboxylate (3qa). Yellow oil, 88% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.68 (dd, *J* = 4.8, 0.9 Hz, 1H), 7.67 (td, *J* = 7.8, 1.8 Hz, 1H), 7.53 (d, *J* = 8.7 Hz, 1H), 7.40 (d, *J* = 2.2 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.24 (ddd, *J* = 7.5, 4.9, 0.8 Hz, 1H), 7.18 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.09 (dd, *J* = 4.9, 3.6 Hz, 1H), 7.08-7.05 (m, 2H), 6.88-6.85 (m, 2H), 3.76 (s, 2H), 1.54 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.2, 157.8, 149.6, 148.5, 138.2, 137.1, 134.7, 132.1, 130.0, 129.7, 128.4, 127.8, 127.0, 125.3, 122.8, 121.8, 116.0, 84.4, 61.2, 44.5, 28.0. HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{25}H_{24}ClN_2O_3$, 435.1475, found: 435.1459.

Tert-butyl 3-benzyl-6-chloro-2-oxo-3-(pyridin-2-yl)indoline-1-carboxylate (3ra). Yellow oil, 86% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.65 (d, *J* = 4.0 Hz, 1H), 7.65 (ddd, *J* = 9.3, 8.1, 1.6 Hz, 2H), 7.31 (dd, *J* = 8.0, 4.4 Hz, 2H), 7.21 (dd, *J* = 7.0, 5.1 Hz, 1H), 7.14-7.08 (m, 2H), 7.06 (t, *J* = 7.3 Hz, 2H), 6.86 (d, *J* = 7.2 Hz, 2H), 3.78-3.73 (m, 2H), 1.55 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.4, 158.0, 149.6, 148.44, 140.5, 137.0, 134.8, 134.1, 130.0, 128.6, 127.80, 126.9, 126.1, 124.3, 122.7, 121.7, 115.5, 84.5, 60.9, 44.2, 28.0. HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{25}H_{24}ClN_2O_3$, 435.1475, found: 435.1460.

1-(tert-butyl)-6-methyl 3-benzyl-2-oxo-3-(pyridin-2-yl)indoline-1,6-dicarboxylate (3sa) Yellow oil, 85% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.68 (d, *J* = 3.9 Hz, 1H), 8.25 (d, *J* = 1.3 Hz, 1H), 7.88 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.68 (t, *J* = 7.1 Hz, 1H), 7.51 (d, *J* = 7.9 Hz, 1H), 7.34 (d, *J* = 7.9 Hz, 1H), 7.26-7.24 (m, 1H), 7.08 (t, *J* = 7.3 Hz, 1H), 7.03 (t, *J* = 7.4 Hz, 2H), 6.85 (d, *J* = 7.1 Hz, 2H), 3.89 (s, 3H), 3.81 (t, *J* = 9.4 Hz, 2H), 1.58 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.4, 166.6, 157.7, 149.5, 148.3, 139.8, 137.3, 135.2, 134.6, 130.4, 130.0, 127.8, 127.0, 125.9, 125.2, 122.9, 122.0, 115.9, 84.6, 61.4, 52.3, 44.2, 28.0. HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{27}H_{27}N_2O_5$, 459.1920, found: 459.1904.

Tert-butyl 3-benzyl-3-(4-methylpyridin-2-yl)-2-oxoindoline-1-carboxylate (3ab). Yellow oil, 92% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.54 (d, *J* = 4.8 Hz, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.40 (d, *J* = 6.4 Hz, 1H), 7.21 (td, *J* = 7.9, 1.4 Hz, 1H), 7.15 (td, *J* = 7.5, 1.0 Hz, 1H), 7.08-7.05 (m, 3H), 7.04-7.01 (m, 2H), 6.86-6.84 (m, 2H), 3.80 (t, *J* = 14.9 Hz, 2H), 2.31 (s, 3H), 1.55 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.1, 158.3, 149.0, 148.7, 139.6, 135.2, 130.4, 130.1, 128.3, 127.6, 126.7, 125.0, 124.3, 123.6, 122.8, 114.8, 84.0, 61.1, 44.1, 28.0, 21.2. HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{26}H_{27}N_2O_3$, 415.2022, found: 415.1999.

Tert-butyl 3-benzyl-3-(4-methoxypyridin-2-yl)-2-oxoindoline-1-carboxylate (3ac). Yellow oil, 90% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.43 (s, 1H), 7.22 (td, *J* = 7.9, 1.4 Hz, 1H), 7.16 (t, *J* = 7.2 Hz, 1H), 7.08-7.06 (m, 1H), 7.04-7.01 (m, 2H), 6.86-6.82 (m, 3H), 6.78 (s, 1H), 3.82 (s, 3H), 3.77 (d, *J* = 12.7 Hz, 1H), 1.55 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.8, 166.3, 160.1, 150.7, 148.7, 139.7, 135.1, 130.2, 130.1, 128.4, 127.6, 126.7, 125.1, 124.2, 114.8, 108.5, 108.4, 84.0, 61.2, 55.3, 44.1, 28.0. HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{26}H_{27}N_2O_4$, 431.1971, found: 431.1958.

Tert-butyl 3-benzyl-3-(4-(methoxycarbonyl)pyridin-2-yl)-2-oxoindoline-1-carboxylate (3ad). White solid, 72% yield. m.p. = 161.9-162.6 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.84 (dd, *J* = 5.0, 0.5 Hz, 1H), 7.85 (s, 1H), 7.81 (dd, *J* = 5.1, 1.4 Hz, 1H), 7.59 (d, *J* = 8.1 Hz, 1H), 7.34 (dd, *J* = 7.5, 0.9 Hz, 1H), 7.25-7.22 (m, 1H), 7.16 (td, *J* = 7.5, 0.9 Hz, 1H), 7.09 (dd, *J* = 8.3, 6.3 Hz, 1H), 7.03 (dd, *J* = 10.1, 4.7 Hz, 2H), 6.87-6.82 (m, 2H), 3.93 (s, 3H), 3.85-3.80 (m, 2H), 1.55 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.6, 165.4, 159.9, 150.2, 148.6, 139.8, 138.4, 134.8, 130.1, 129.9, 128.6, 127.7, 126.8, 124.9, 124.4, 121.8, 121.2, 114.9, 84.1, 61.3, 52.8, 44.2, 28.0. HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{27}H_{27}N_2O_5$, 459.1920, found: 459.1903.

Tert-butyl 3-benzyl-3-(4-cyanopyridin-2-yl)-2-oxoindoline-1-carboxylate (3ae). Yellow oil, 52% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.87 (dd, *J* = 5.0, 0.6 Hz, 1H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.56 (s, 1H), 7.46 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.37 (dd, *J* = 7.5, 0.9 Hz, 1H), 7.29-7.26 (m, 1H), 7.20-7.17 (m, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 7.04 (t, *J* = 7.4 Hz, 2H), 6.83 (d, *J* = 7.2 Hz, 2H), 3.75 (q, *J* = 13.0 Hz, 2H), 1.56 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.0, 160.2, 150.5, 148.5, 139.8, 134.4, 130.0, 129.0, 128.9, 127.8, 127.0, 125.1, 124.5, 123.9, 123.7, 121.2, 116.3, 115.0, 84.5, 61.1, 44.5, 28.0. HRMS (ESI) *m*/*z*: $[M+Na]^+$ calcd. for $C_{26}H_{23}N_3NaO_3$, 448.1637, found: 448.1620.

Tert-butyl 3-benzyl-3-(6-bromopyridin-2-yl)-2-oxoindoline-1-carboxylate (3af). White solid, 62% yield. m.p. = 157.5-158.4 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.37 (d, *J* = 5.3 Hz, 1H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.60 (s, 1H), 7.43 (dd, *J* = 5.3, 1.2 Hz, 1H), 7.33-7.30 (m, 1H), 7.25-7.23 (m, 1H), 7.16-7.10 (m, 2H), 7.05 (t, *J* = 7.5 Hz, 2H), 6.80 (d, *J* = 7.3 Hz, 2H), 3.69 (d, *J* = 12.9 Hz, 1H), 3.40 (d, *J* = 12.9 Hz, 1H), 1.56 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6, 151.1, 150.3, 148.4, 142.9, 140.0, 133.8, 130.0, 129.3, 127.9, 127.6, 127.3, 127.0, 125.3, 124.5, 121.9, 115.4, 84.7, 58.0, 44.7, 28.0. HRMS (ESI) *m*/*z*: $[M+H]^+$ calcd. for $C_{25}H_{24}BrN_2O_3$, 479.0970, found: 479.0952.

Tert-butyl 3-benzyl-3-(isoquinolin-1-yl)-2-oxoindoline-1-carboxylate (3ag). White solid, 71% yield. m.p. = 173.3-173.8 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.67 (d, *J* = 5.7 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.71 (d, *J* = 5.6 Hz, 1H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.32 – 7.29 (m, 1H), 7.24 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.20 (d, *J* = 8.6 Hz, 1H), 7.12-7.06 (m, 2H), 7.04-6.99 (m, 3H), 6.76 -6.70 (m, 2H), 4.04 (dd, *J* = 28.7, 12.8 Hz, 2H), 1.54 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.3, 156.5, 148.6, 140.8, 139.3, 137.2, 134.8, 131.9, 130.1, 129.7, 128.6, 127.9, 127.4, 126.7, 126.4, 124.8, 124.3, 123.5, 121.6, 115.2, 84.0, 61.3, 46.1, 28.0. HRMS (ESI) *m*/*z*: $[M+H]^+$ calcd. for $C_{29}H_{27}N_2O_3$, 451.2022, found: 451.2004.

General procedure for the synthetic transformation of 3.

To the solution of 3-Pyridyl-3,3-disubstituted oxindoles **3** (0.05 mmol, 1.0 equiv.) in CH_2Cl_2 (1.5 mL) was slowly added CF_3CO_2H (0.1 mL) at 0 ℃. The resulting mixture was stirred at 0 ℃ for 1 h, followd by warming to rt. The progress of the reaction was monitored by TLC. Upon completion, the reaction was concentrated at rt., and the residue was dissolved in CH_2Cl_2 (5.0 mL). Then the mixture was adjusted to pH 10 with saturated aqueous solution of $NaHCO_3$ and extracted with CH_2Cl_2 (3 × 5mL). The combined organic extracts were dried over anhydrous sodium sulfate, filtered, and concentrated under

reduced pressure. The residue was purified by column chromatography (SiO_2; hexanes/EtOAc, 1:1) to give product **3ma**, **4** or **5**.

3-benzyl-3-(4-methylpyridin-2-yl)indolin-2-one (4). White solid, 93% yield, m.p. = 208.9-209.6 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.53 (d, *J* = 5.0 Hz, 1H), 7.42 (d, *J* = 7.4 Hz, 1H), 7.13 (td, *J* = 7.7, 1.2 Hz, 1H), 7.04 (ddd, *J* = 13.7, 7.8, 5.5 Hz, 4H), 6.98 (t, *J* = 7.5 Hz, 2H), 6.94-6.91 (m, 2H), 6.70 (d, *J* = 7.7 Hz, 1H), 3.85 (d, *J* = 13.1 Hz, 1H), 3.72 (d, *J* = 13.1 Hz, 1H), 2.26 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.6, 158.5, 149.2, 148.2, 140.7, 135.9, 132.1, 130.2, 128.2, 127.6, 126.5, 125.5, 123.4, 122.4, 122.3, 109.7, 61.3, 42.7, 21.16. HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{21}H_{19}N_2O$, 315.1497, found: 315.1489.

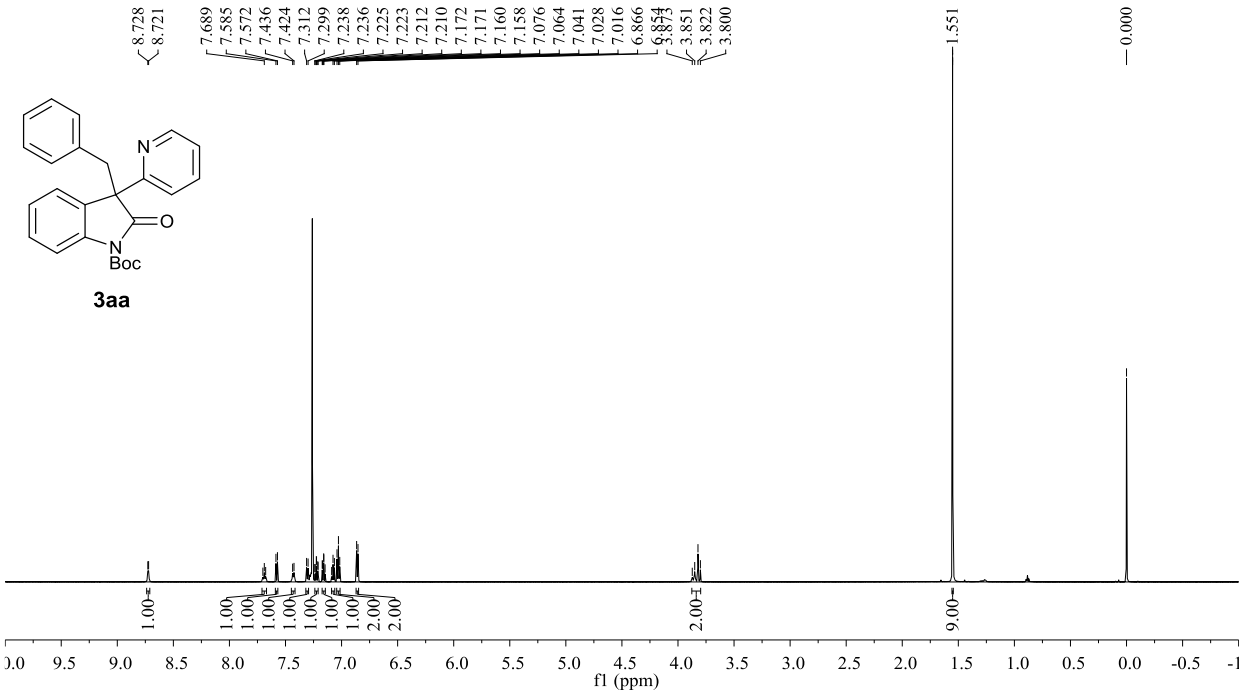
3-benzyl-5-chloro-3-(pyridin-2-yl)indolin-2-one (5). White solid, 91% yield, m.p. = 229.2-229.8 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.68 (d, *J* = 4.0 Hz, 1H), 8.44 (s, 1H), 7.66 (td, *J* = 7.8, 1.6 Hz, 1H), 7.44 (d, *J* = 2.0 Hz, 1H), 7.33 (d, *J* = 7.9 Hz, 1H), 7.25 (dd, *J* = 7.4, 5.3 Hz, 1H), 7.11 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.07 (dd, *J* = 8.4, 6.0 Hz, 1H), 7.04 (t, *J* = 7.2 Hz, 2H), 6.94-6.92 (m, 2H), 6.62 (d, *J* = 8.3 Hz, 1H), 3.80 (d, *J* = 13.1 Hz, 1H), 3.70 (d, *J* = 13.1 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.9, 157.9, 149.6, 139.2, 137.3, 135.3, 133.5, 130.2, 128.3, 127.8, 126.8, 126.0, 122.7. 121.5, 110.7, 61.5, 43.1. HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{20}H_{16}ClN_2O$, 335.0951, found: 335.0939.

References

[1] Wei D. Q.; Liu Z. T.; Wang X. M.; Hou C. J.; Hu X. P. *J. Org. Chem.* **2011**, *76*, 6401-6406.

[2] Londregan, A. T.; Farley, K. A.; Limberakis, C.; Mullins, P. B.; Piotrowski, D. W. *Org. Lett.*, **2012**, *14*, 2890-2893.

NMR Spectra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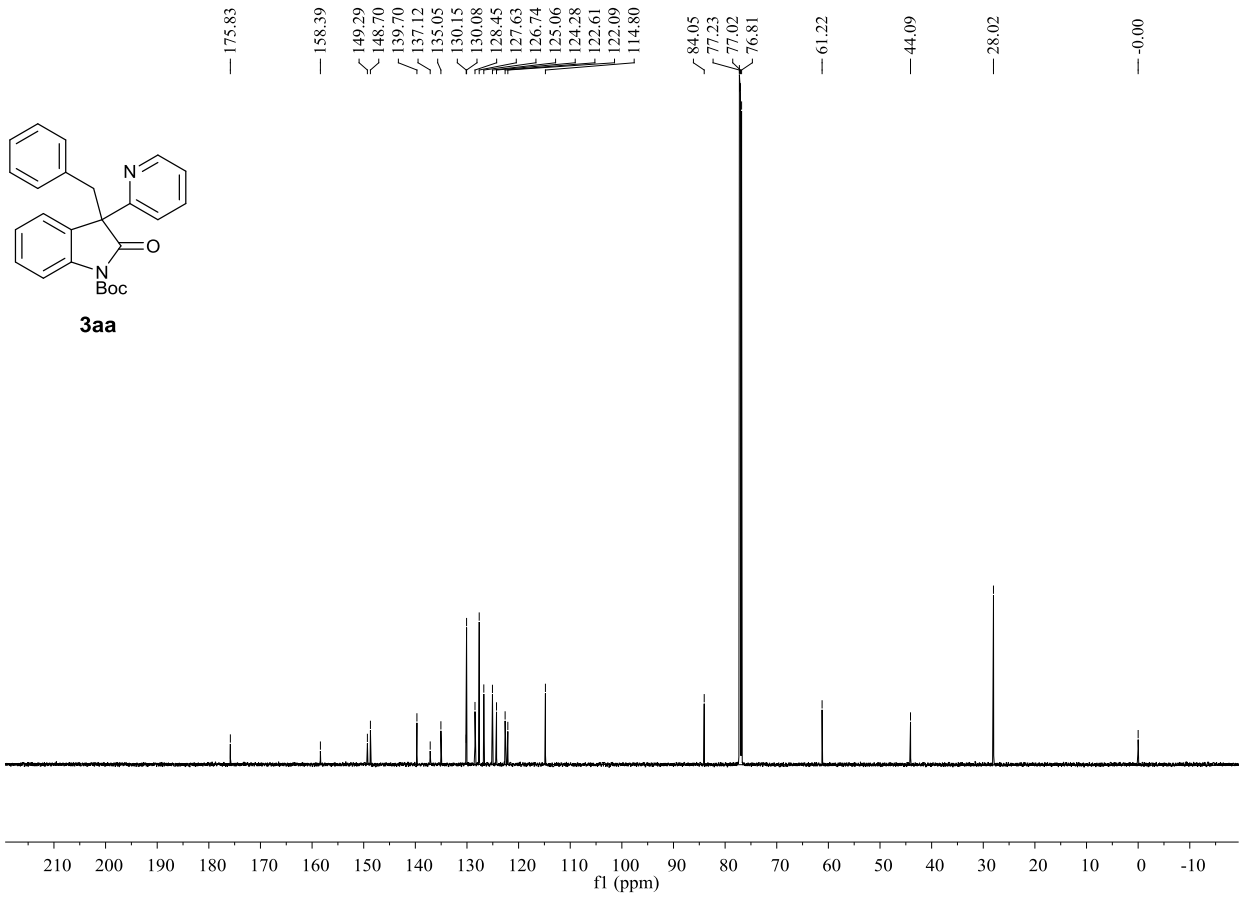
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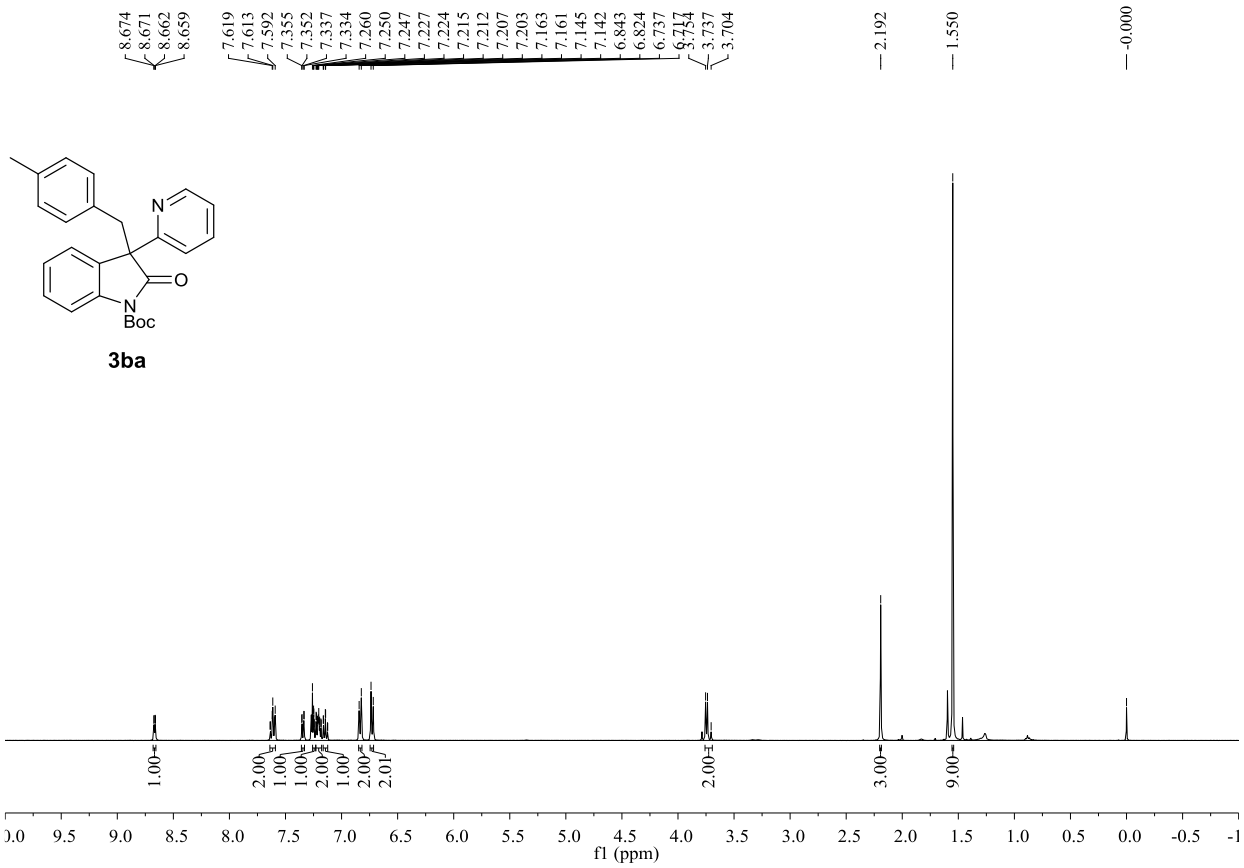
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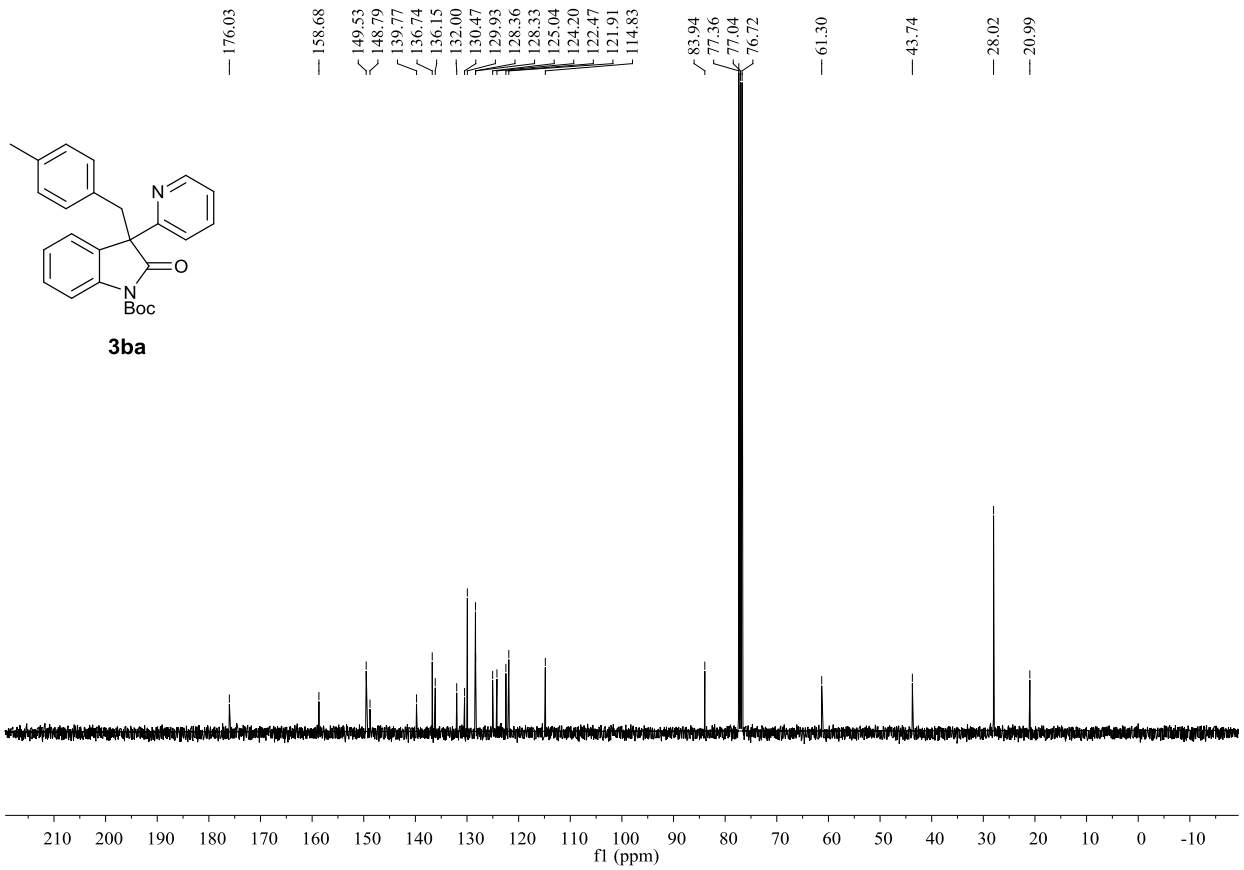
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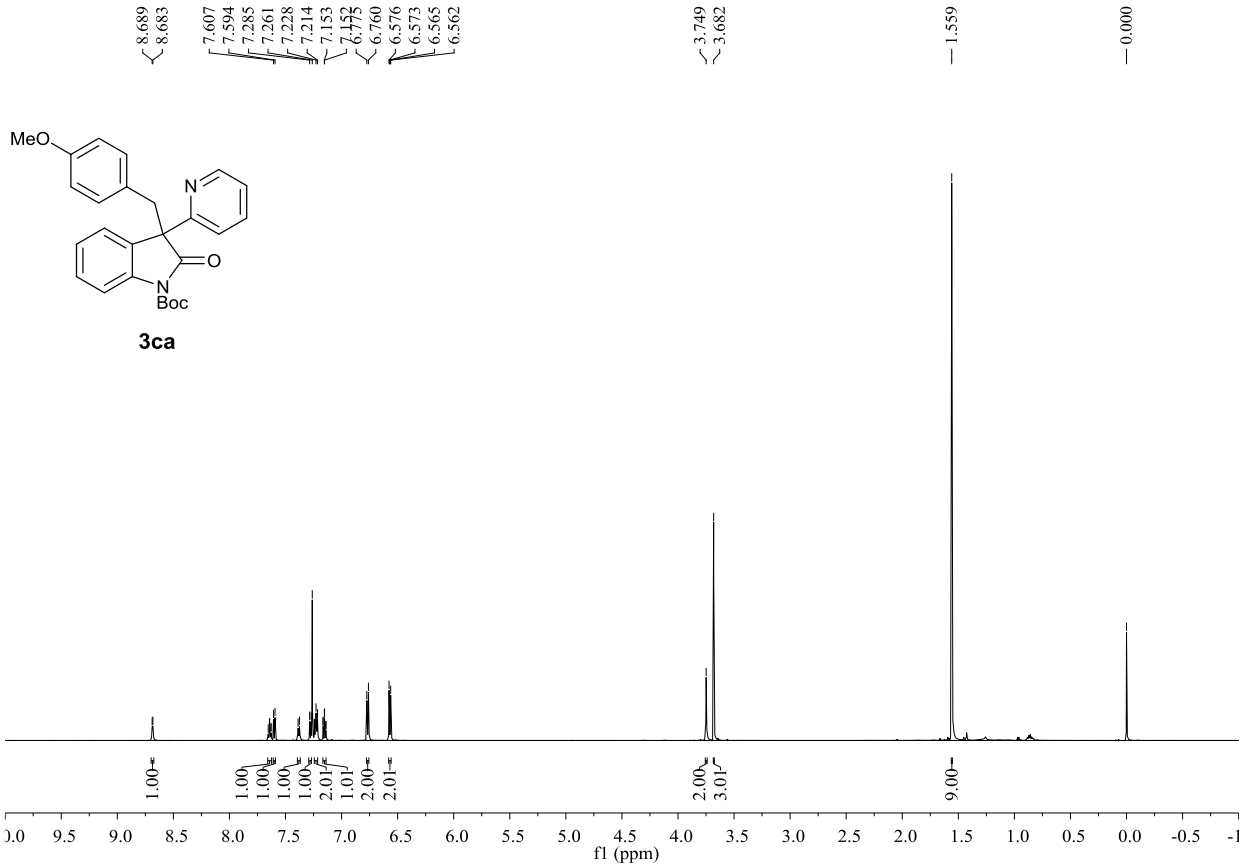
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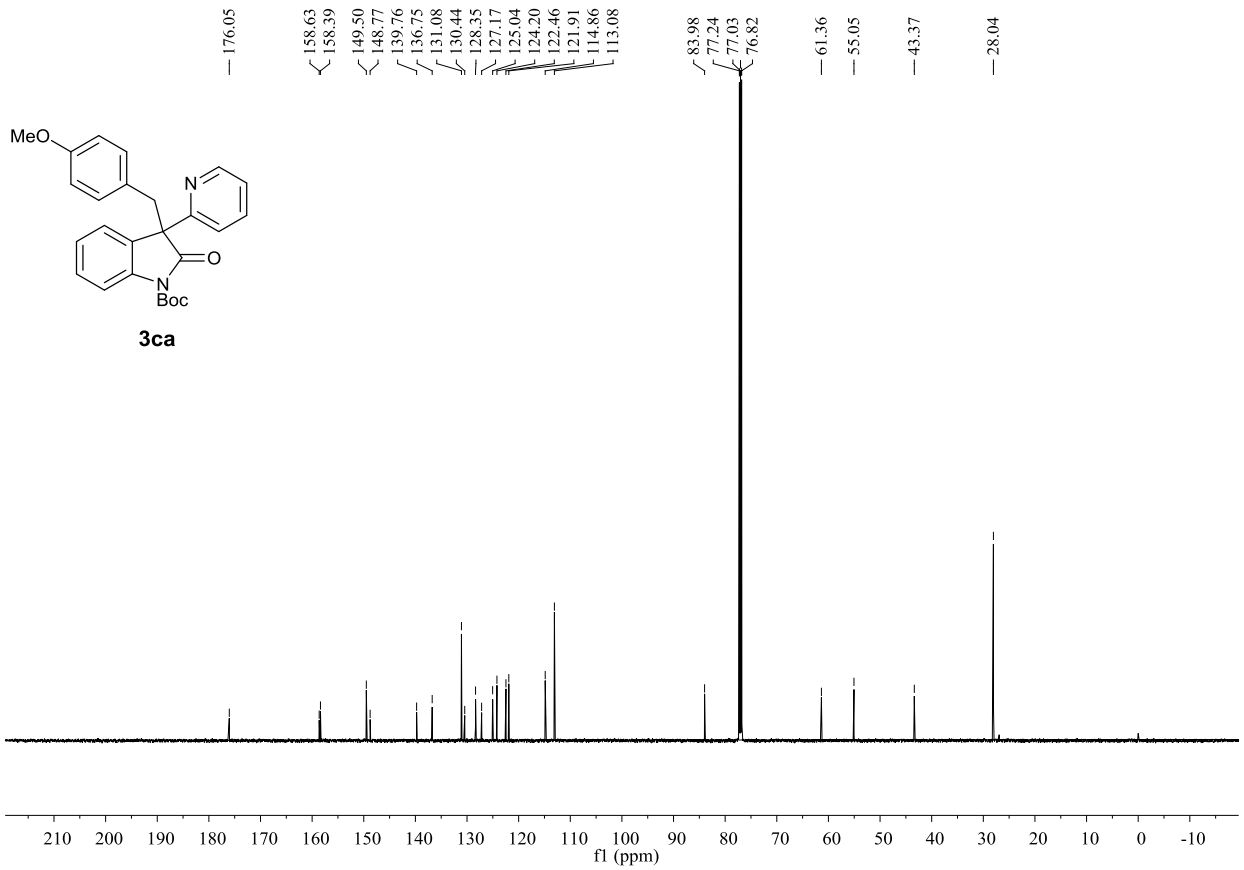
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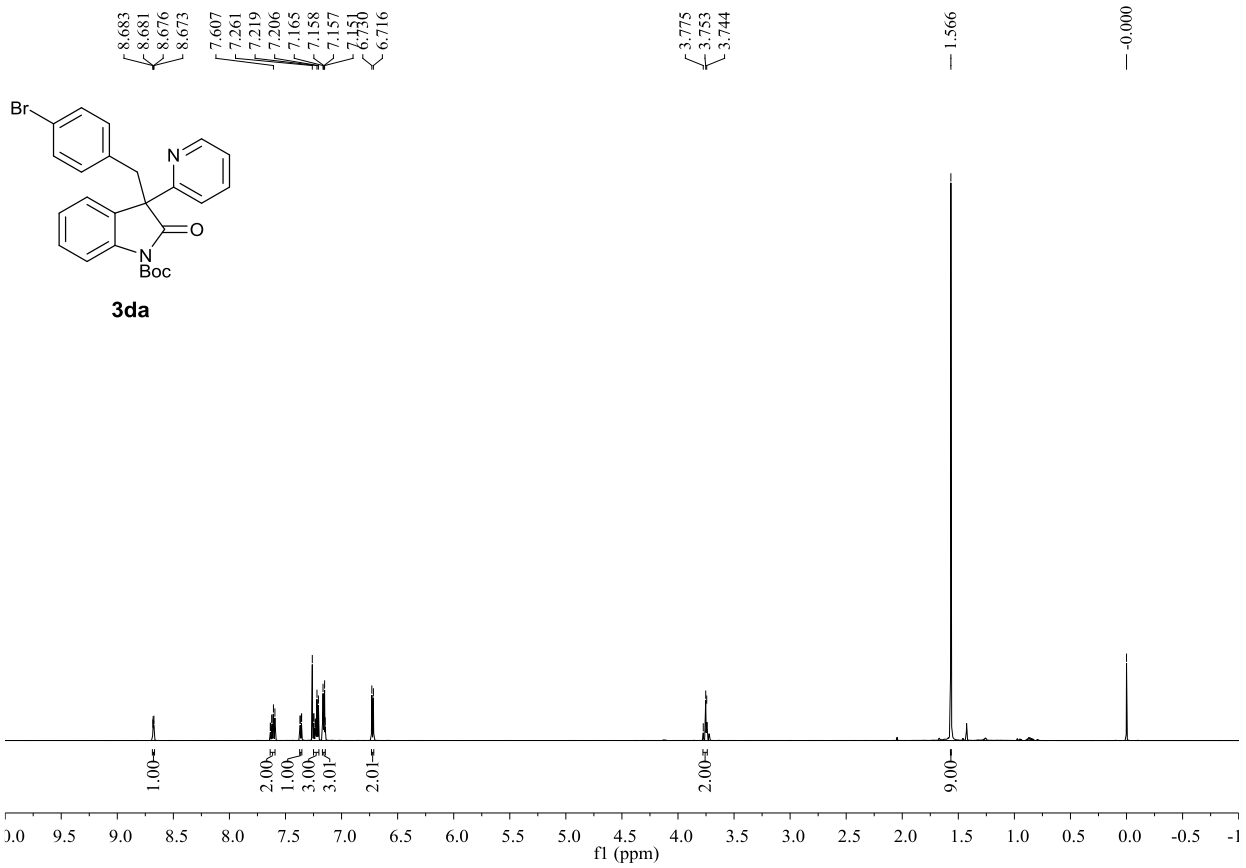
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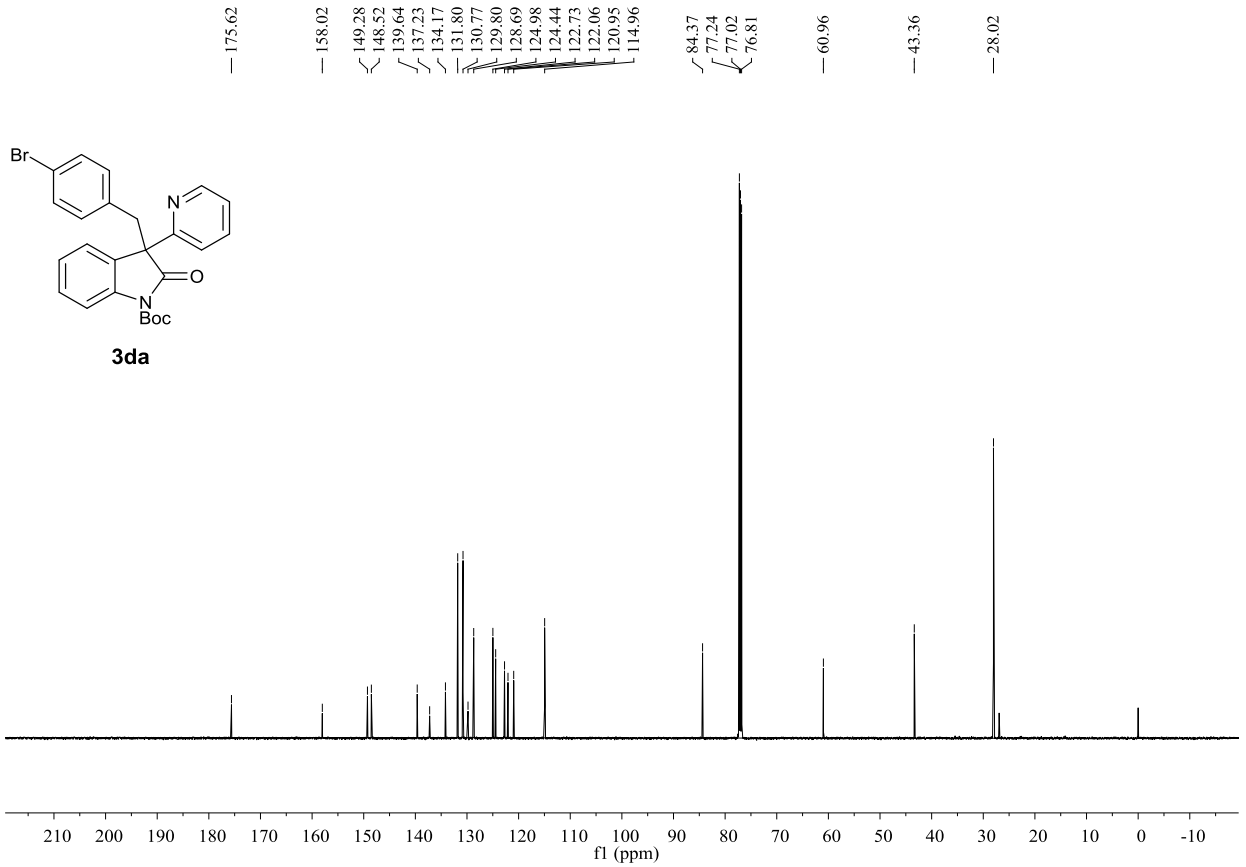
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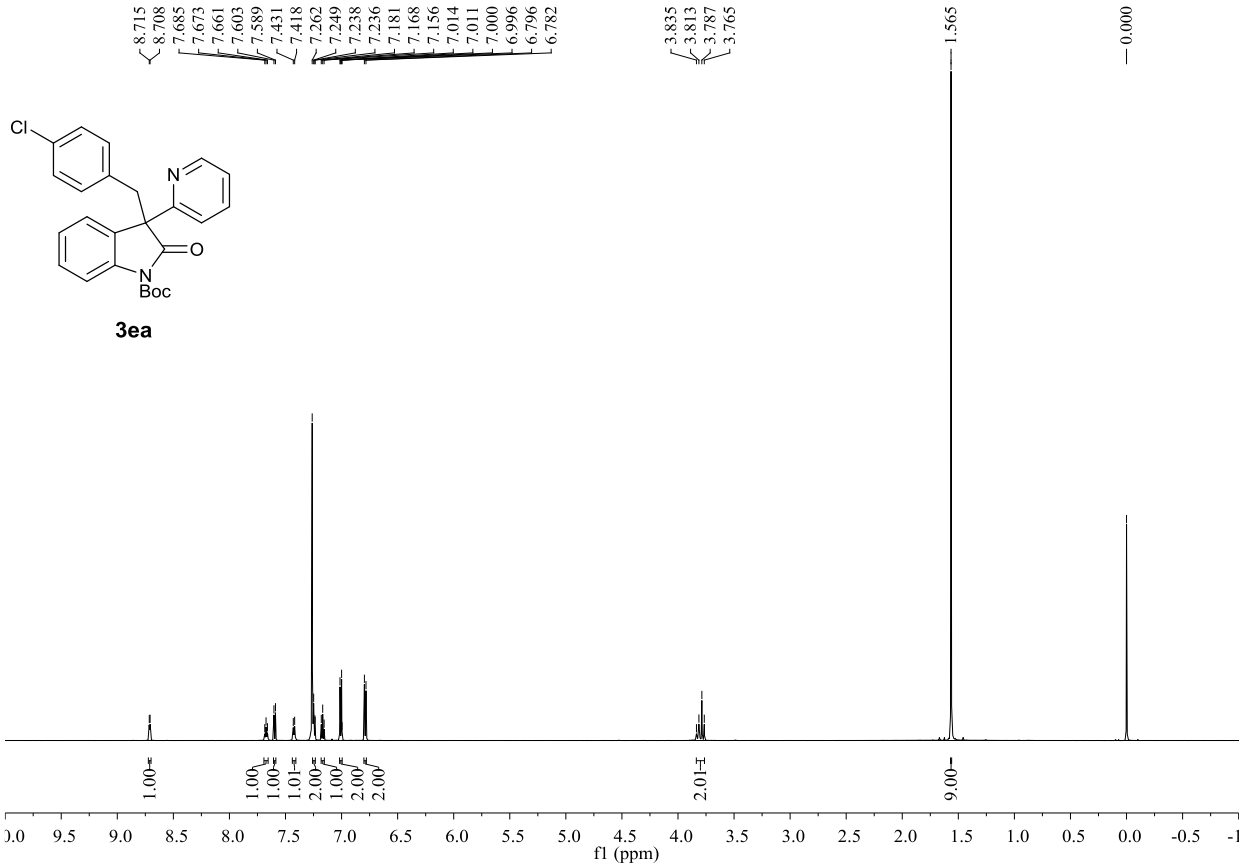
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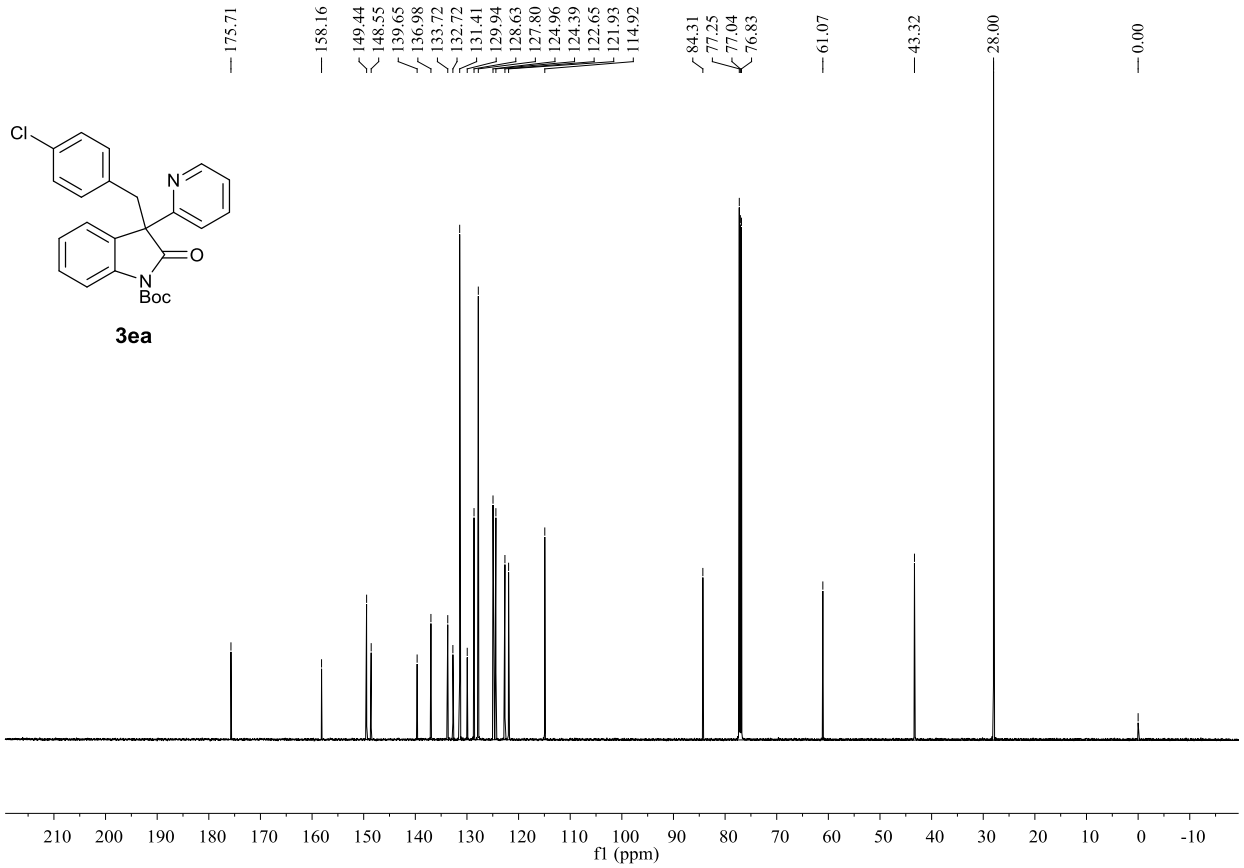
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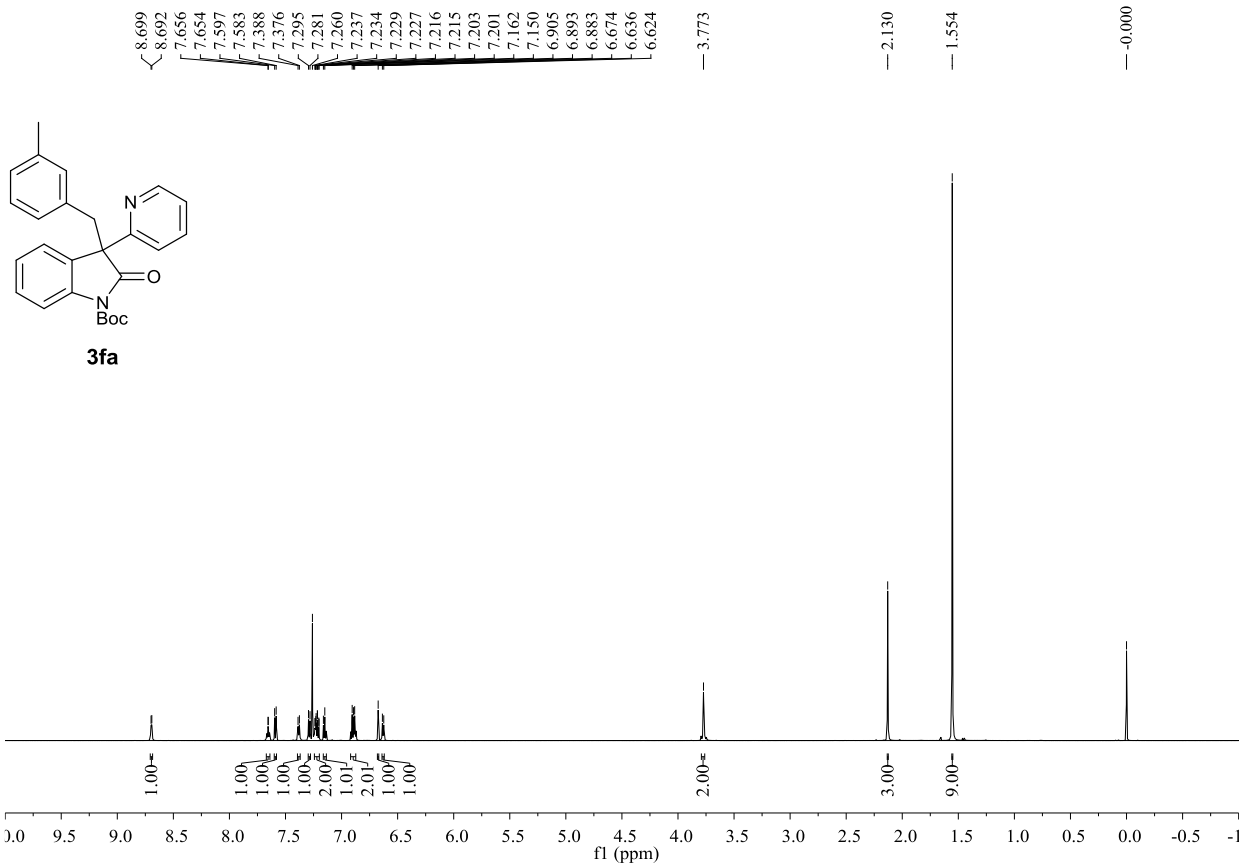
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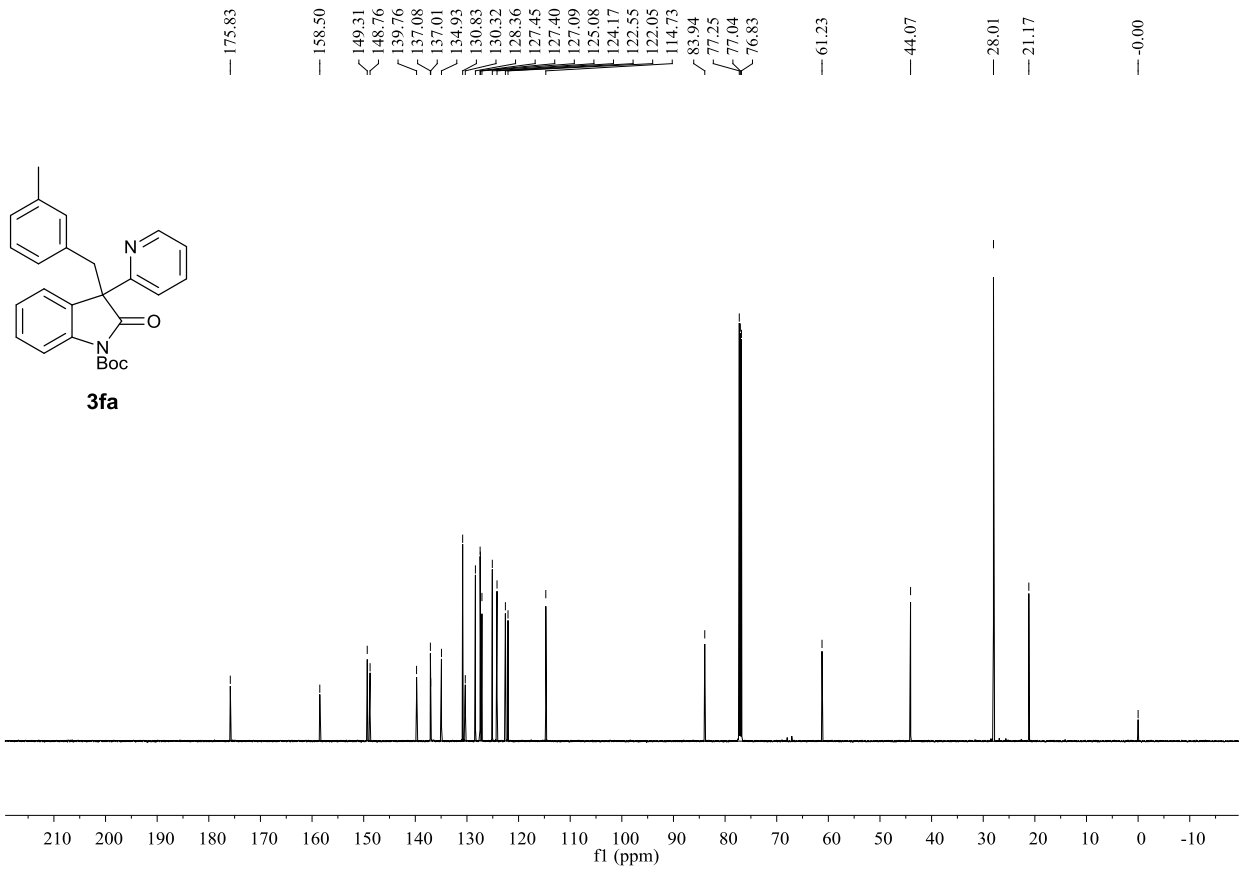
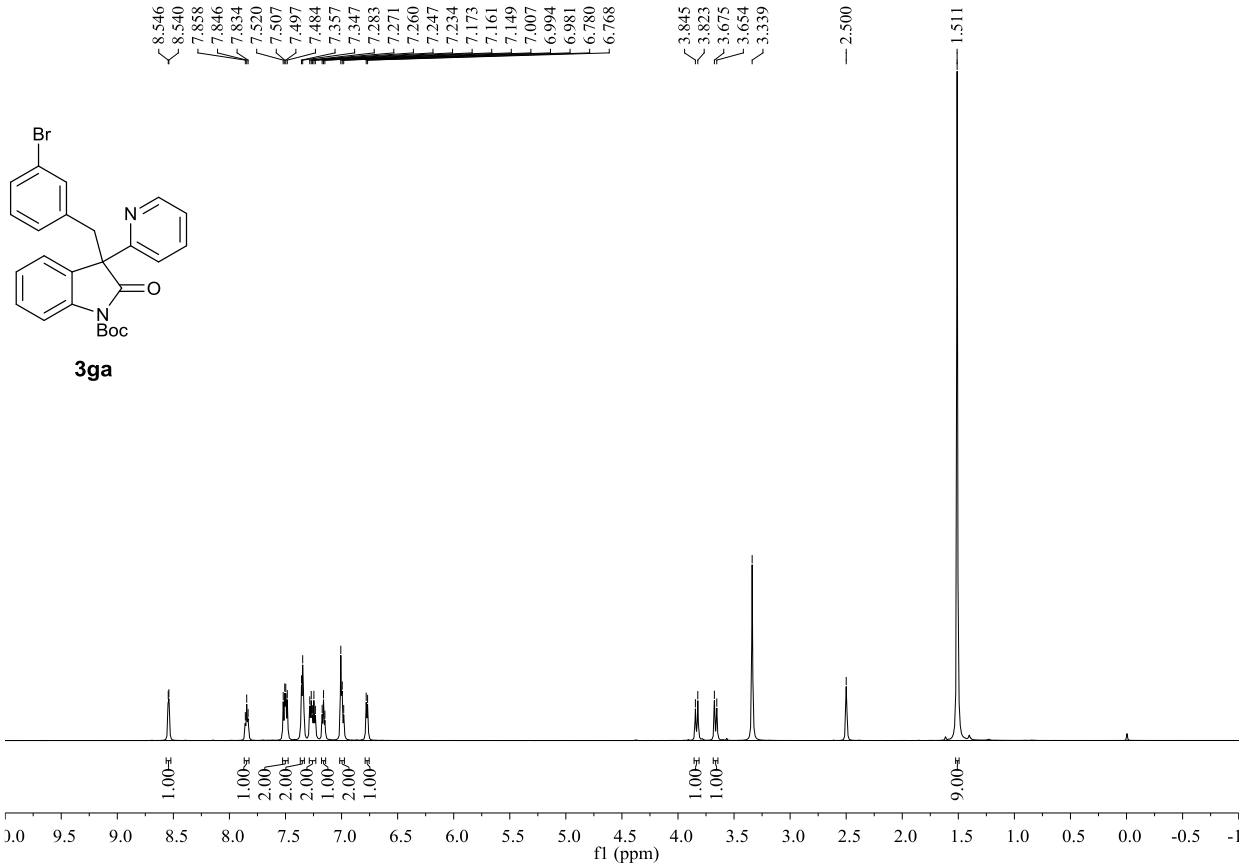
7.227
7.216
7.215
7.203
7.201
7.162
7.150
6.905
6.893
6.883
6.674
6.636
6.624
3.773
2.130
1.554
-0.000
N
O
N
Boc
1.00
1.00
1.00
1.00
2.00
1.01
2.01
1.00
1.00
2.00
3.00
9.00
f1 (ppm)

3fa


175.83
158.50
149.31
148.76
139.76
137.08
137.01
134.93
130.83
130.32
128.36
127.45
127.40
127.09
125.08
124.17
122.55
122.05
114.73
83.94
77.25
77.04
76.83
61.23
44.07
28.01
21.17
-0.00
N
O
N
Boc
f1 (ppm)

3fa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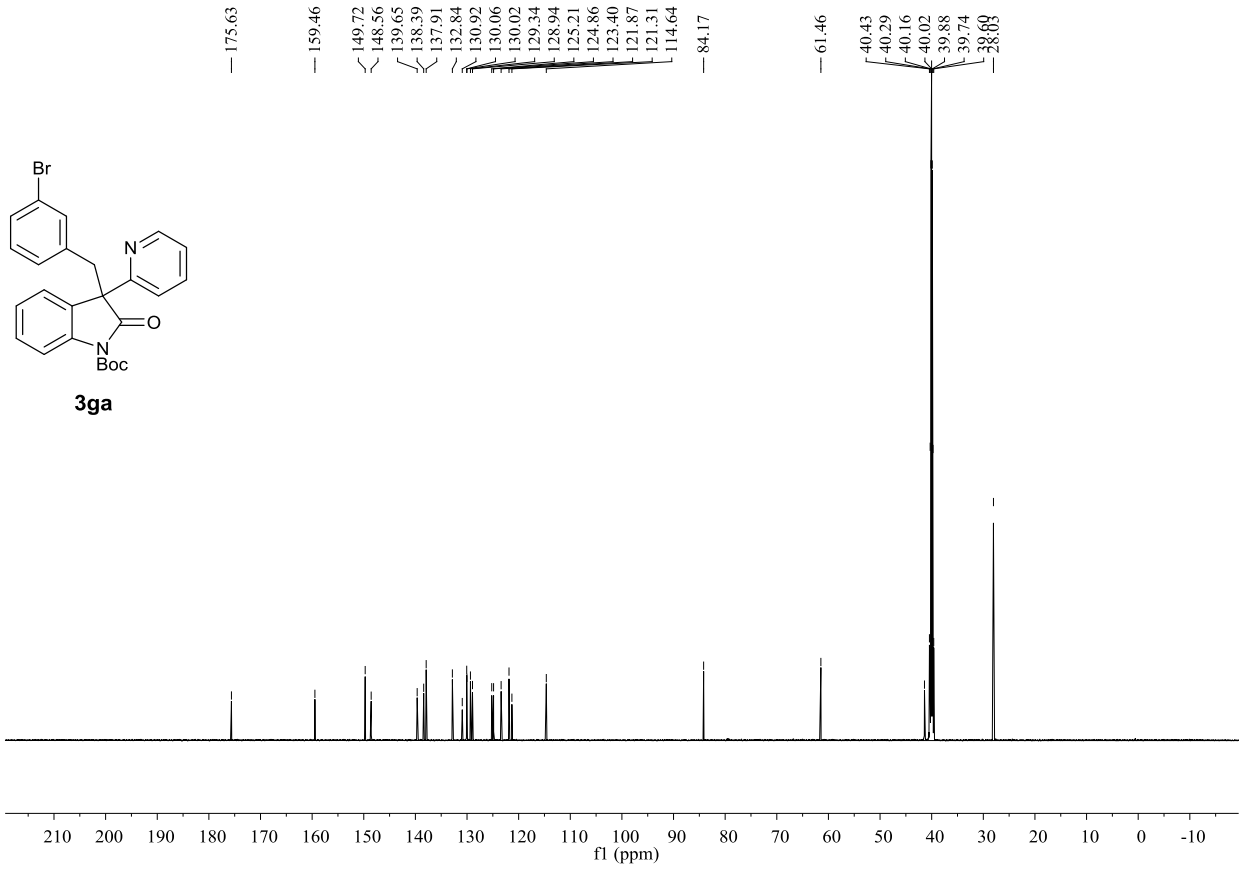
7.846
7.834
7.520
7.507
7.497
7.484
7.357
7.347
7.283
7.271
7.260
7.247
7.234
7.173
7.161
7.149
7.007
6.994
6.981
6.780
6.768
3.845
3.823
3.675
3.654
3.339
2.500
1.511
Br
N
O
N
Boc
1.00
1.00
2.00
2.00
1.00
2.00
1.00
1.00
1.00
9.00
f1 (ppm)

3ga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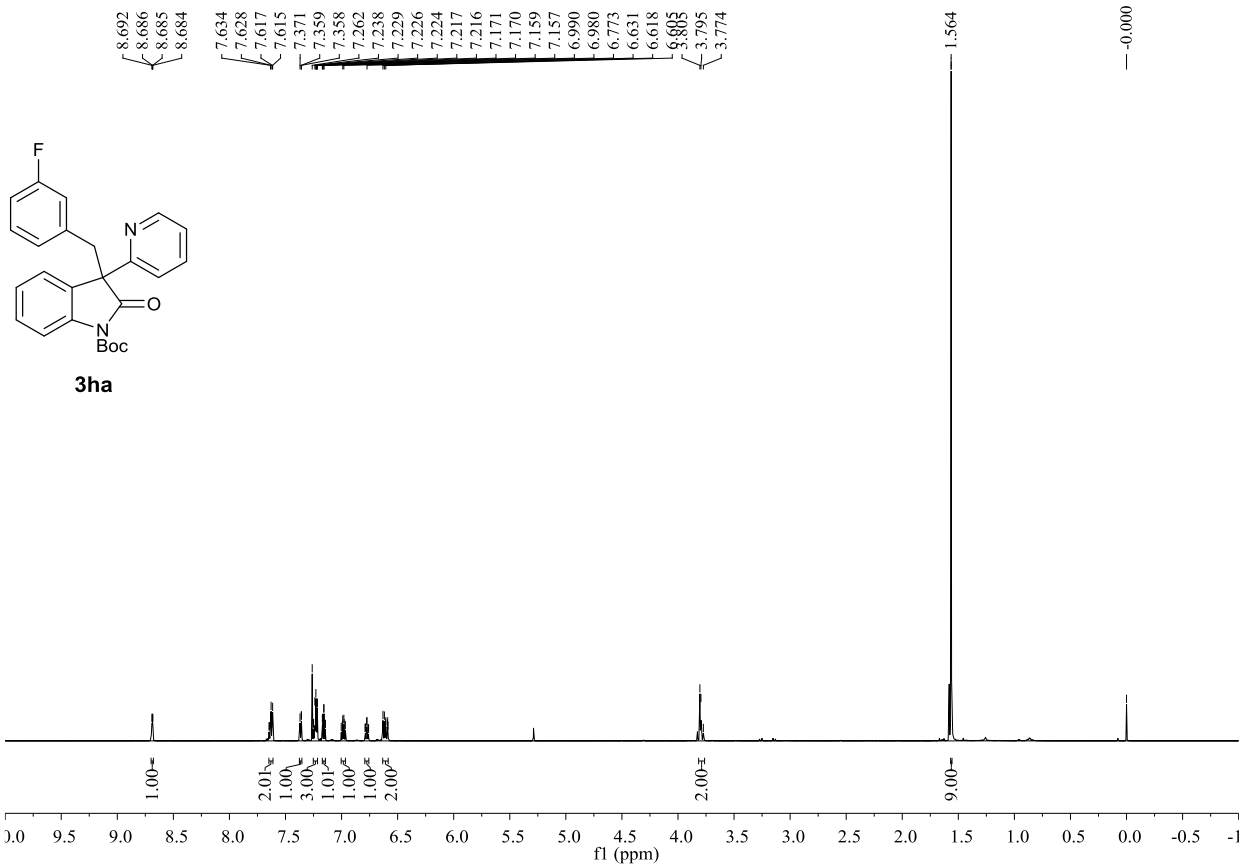
159.46
149.72
148.56
139.65
138.39
137.91
132.84
130.92
130.06
130.02
129.34
128.94
125.21
124.86
123.40
121.87
121.31
114.64
84.17
61.46
40.43
40.29
40.16
40.02
39.88
39.74
39.60
28.03
Br
N
O
N
Boc
f1 (ppm)

3ga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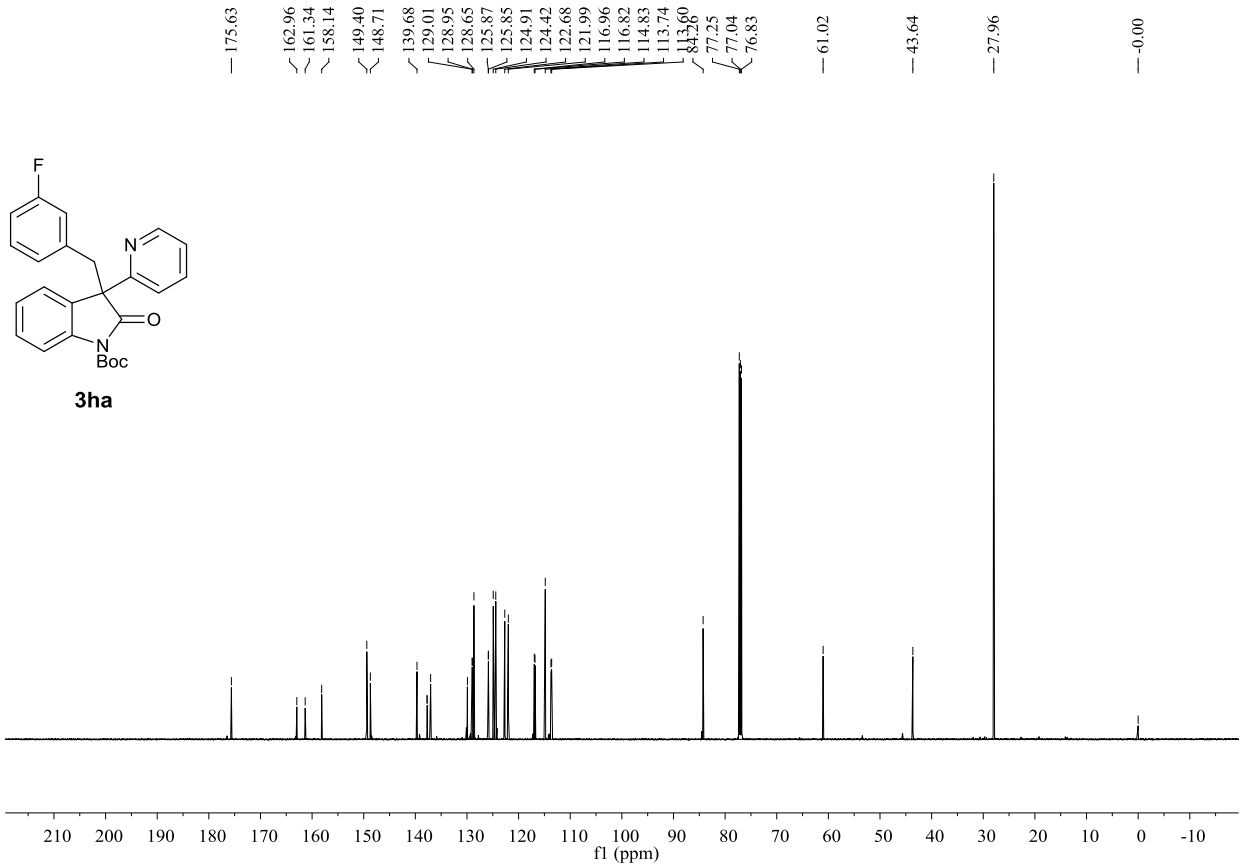
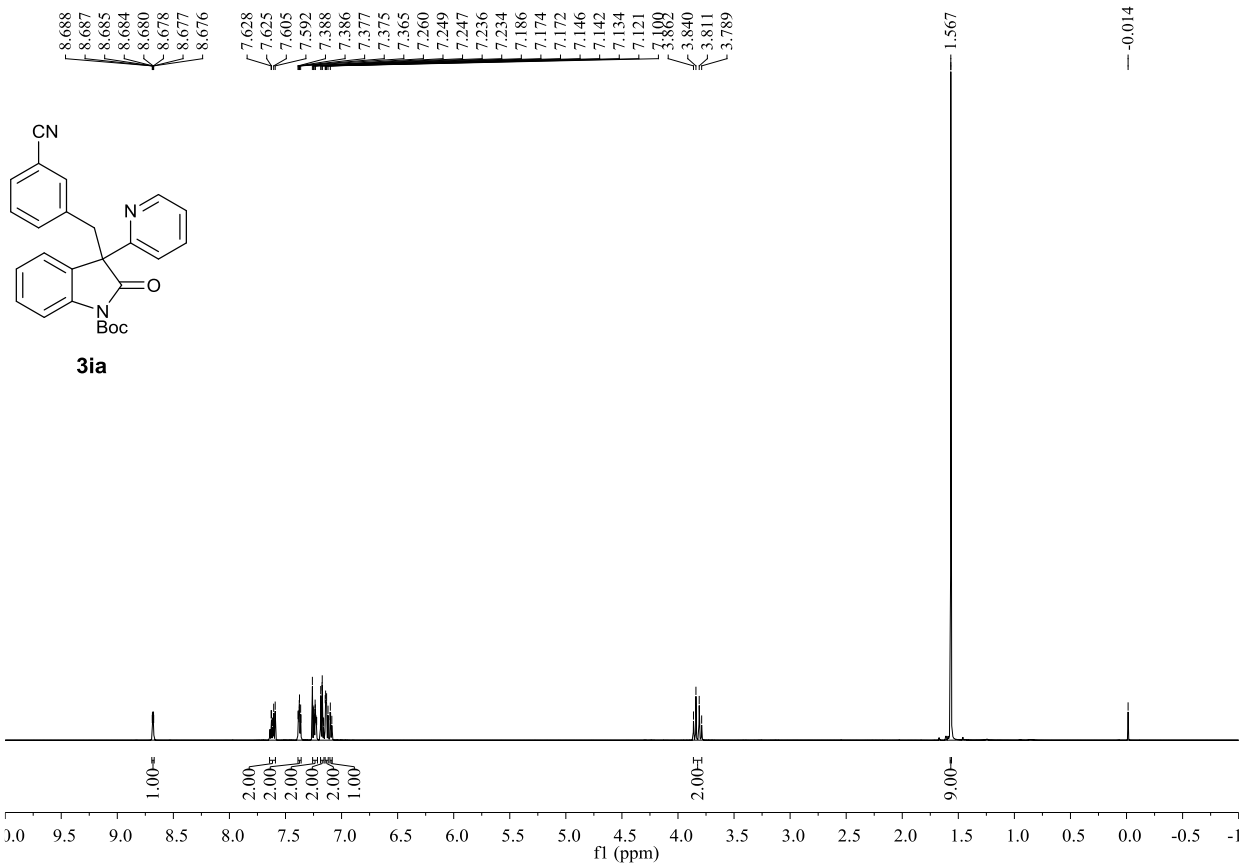
8.685
8.684
7.634
7.628
7.617
7.615
7.371
7.359
7.358
7.262
7.238
7.229
7.226
7.224
7.217
7.216
7.171
7.170
7.159
7.157
6.990
6.980
6.773
6.631
6.618
3.805
3.795
3.774
1.564
-0.000
F
N
O
N
Boc
1.00
2.01
1.00
3.00
1.01
1.00
1.00
2.00
2.00
9.00
f1 (ppm)

3ha


175.63
162.96
161.34
158.14
149.40
148.71
139.68
129.01
128.95
128.65
125.87
125.85
124.91
124.42
122.68
121.99
116.96
116.82
114.83
113.74
113.60
84.26
77.25
77.04
76.83
61.02
43.64
27.96
-0.00
F
N
O
N
Boc
f1 (ppm)

3ha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8.684
8.680
8.678
8.677
8.676
7.628
7.625
7.605
7.592
7.388
7.386
7.377
7.375
7.365
7.260
7.249
7.247
7.236
7.234
7.186
7.174
7.172
7.146
7.142
7.134
7.121
7.100
3.862
3.840
3.811
3.789
1.567
-0.014
CN
N
O
N
Boc
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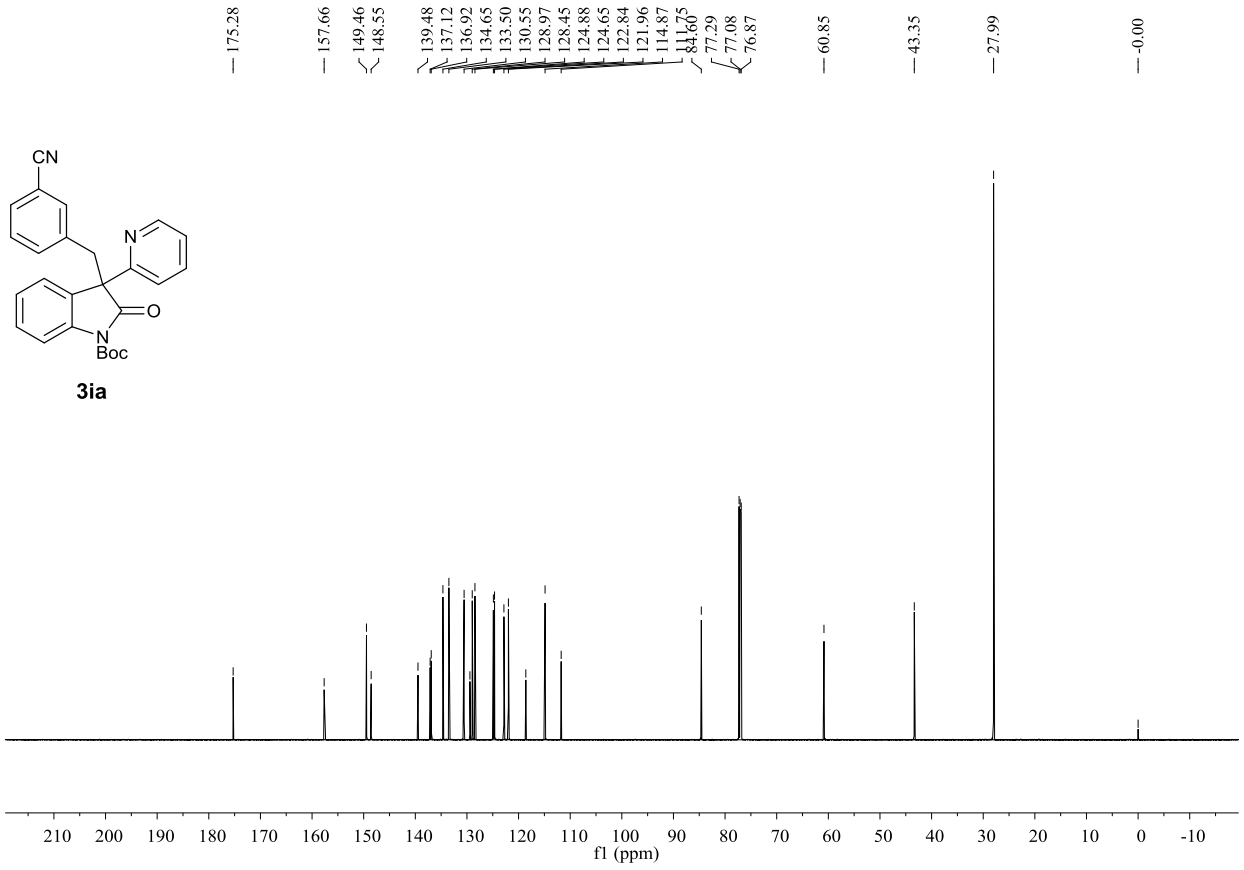
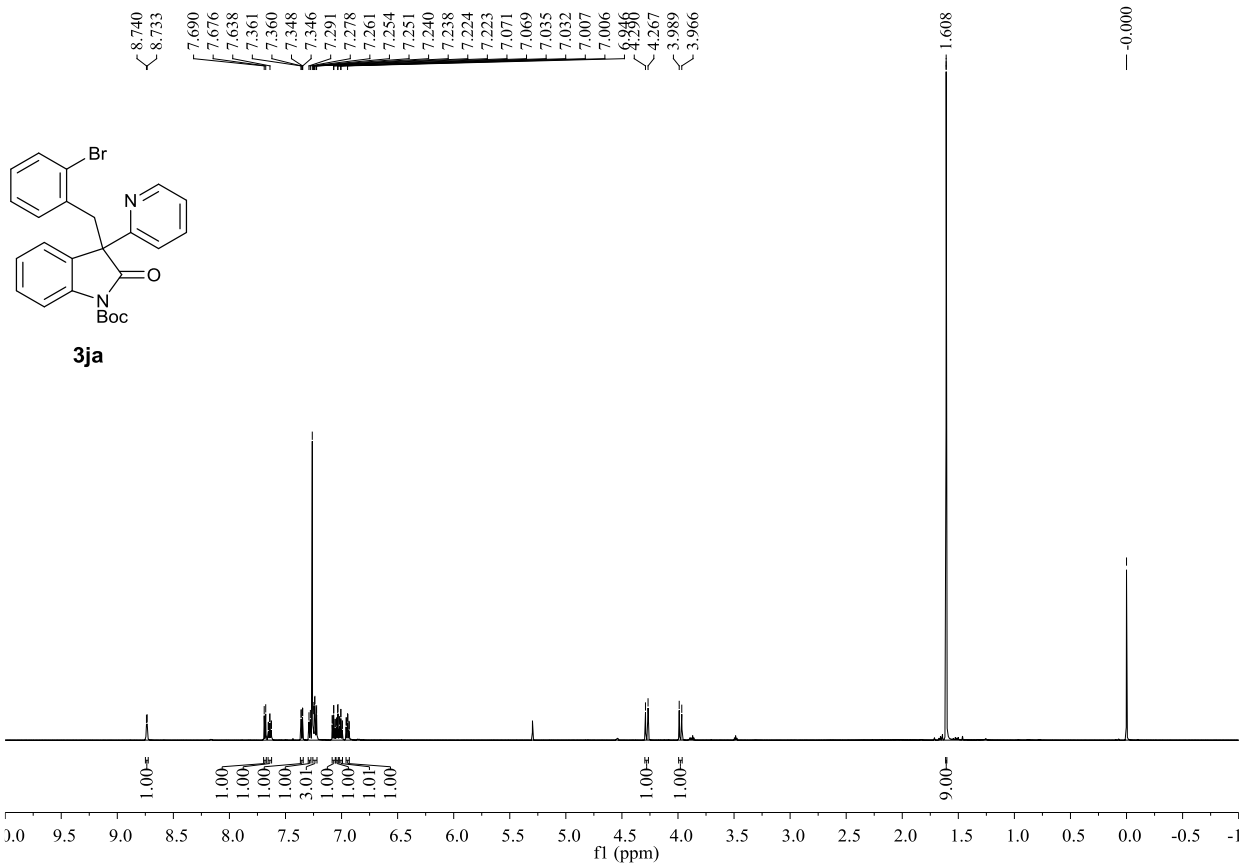
2.00
2.00
2.00
2.00
1.00
2.00
9.00
f1 (ppm)

3ia


175.28
157.66
149.46
148.55
139.48
137.12
136.92
134.65
133.50
130.55
128.97
128.45
124.88
124.65
122.84
121.96
114.87
111.75
84.60
77.29
77.08
76.87
60.85
43.35
27.99
-0.00
CN
N
O
N
Boc
f1 (ppm)

3ia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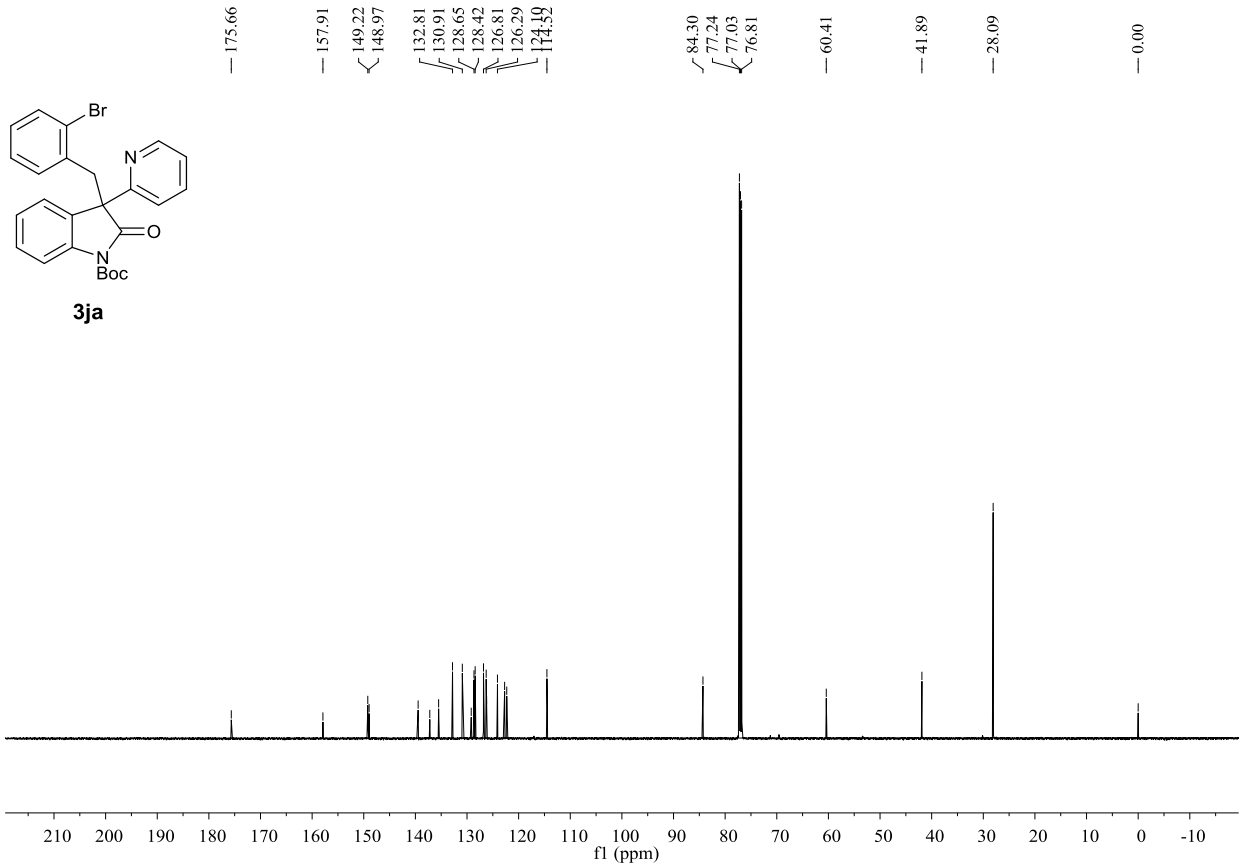
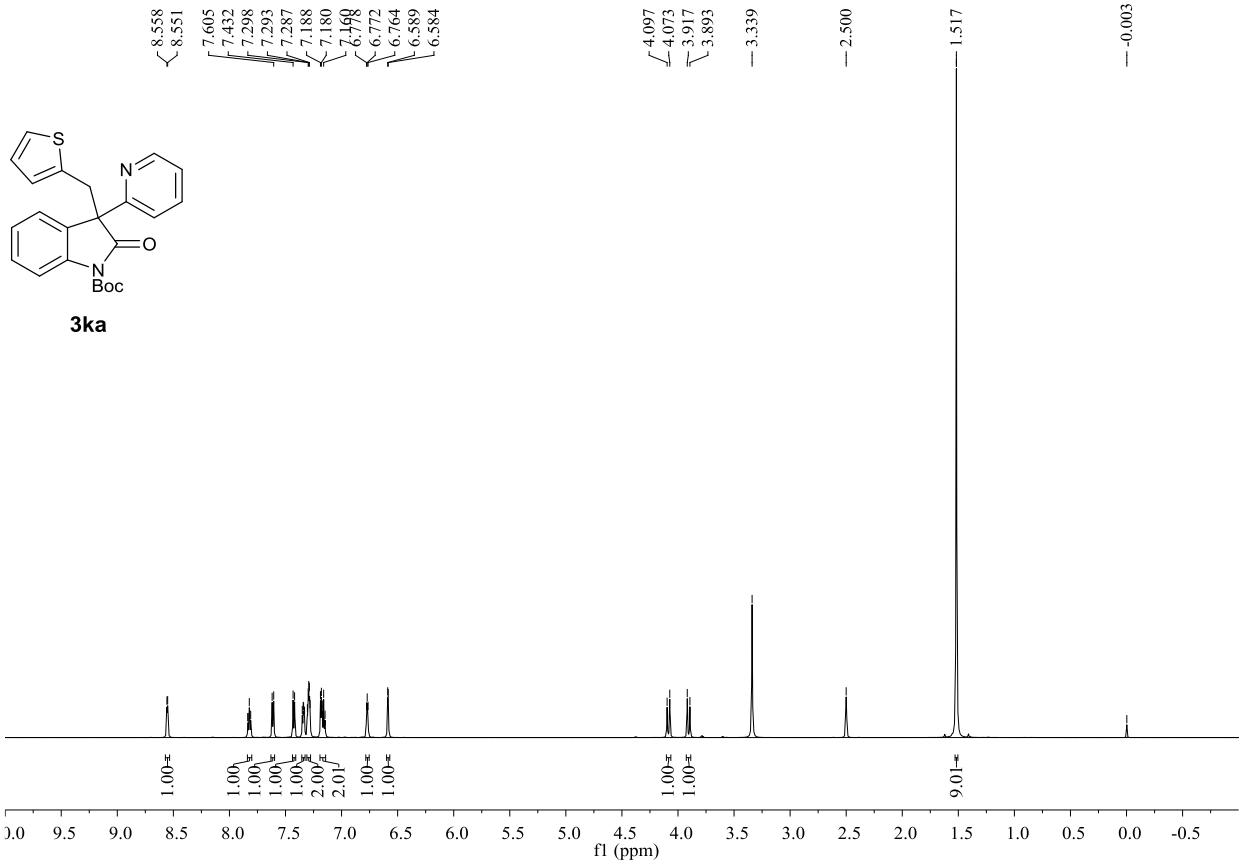
7.690
7.676
7.638
7.361
7.360
7.348
7.346
7.291
7.278
7.261
7.254
7.251
7.240
7.238
7.224
7.223
7.071
7.069
7.035
7.032
7.007
7.006
6.946
6.940
4.290
4.267
3.989
3.966
1.608
-0.000
Br
N
O
N
Boc
1.00
1.00
1.00
1.00
3.01
1.00
1.01
1.00
1.00
1.00
9.00
f1 (ppm)

3ja


175.66
157.91
149.22
148.97
132.81
130.91
128.65
128.42
126.81
126.29
124.19
114.52
84.30
77.24
77.03
76.81
60.41
41.89
28.09
0.00
Br
N
O
N
Boc
f1 (ppm)

3ja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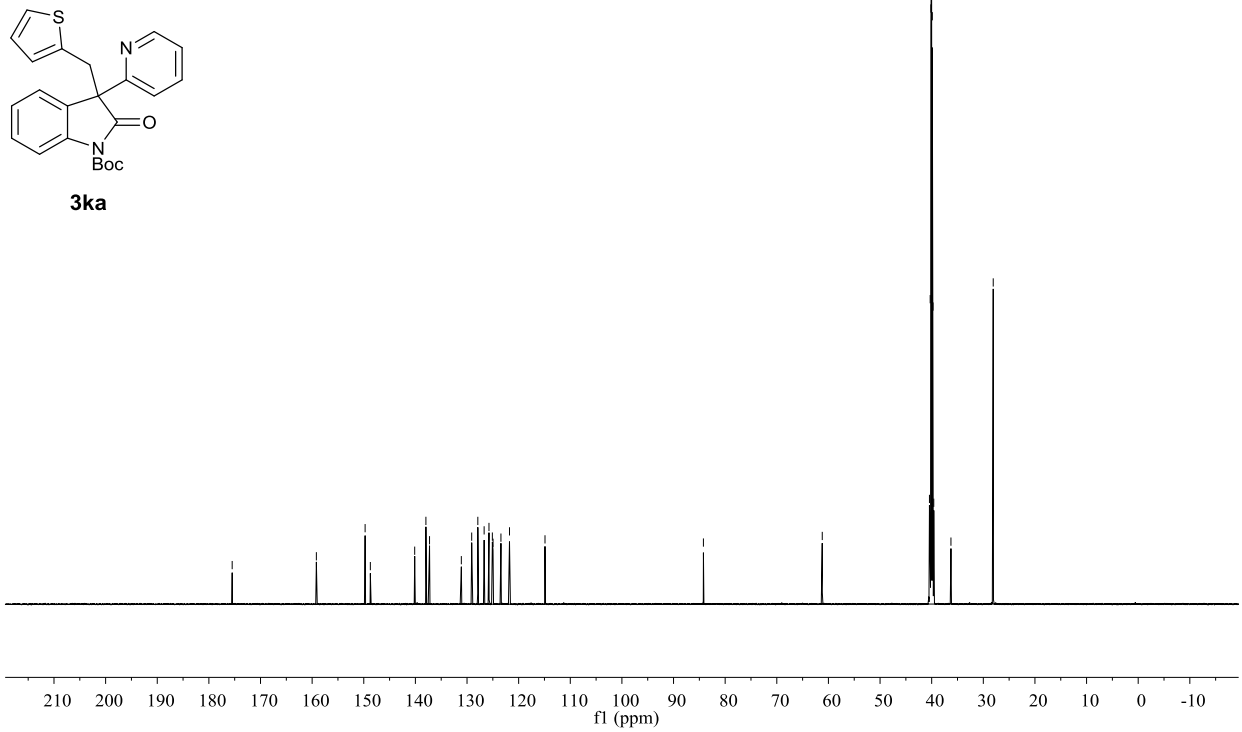
8.551
7.605
7.432
7.298
7.293
7.287
7.188
7.180
7.160
6.778
6.772
6.764
6.589
6.584
4.097
4.073
3.917
3.893
3.339
2.500
1.517
-0.003
1.00
1.00
1.00
1.00
1.00
2.00
2.01
1.00
1.00
1.00
1.00
9.01
f1 (ppm)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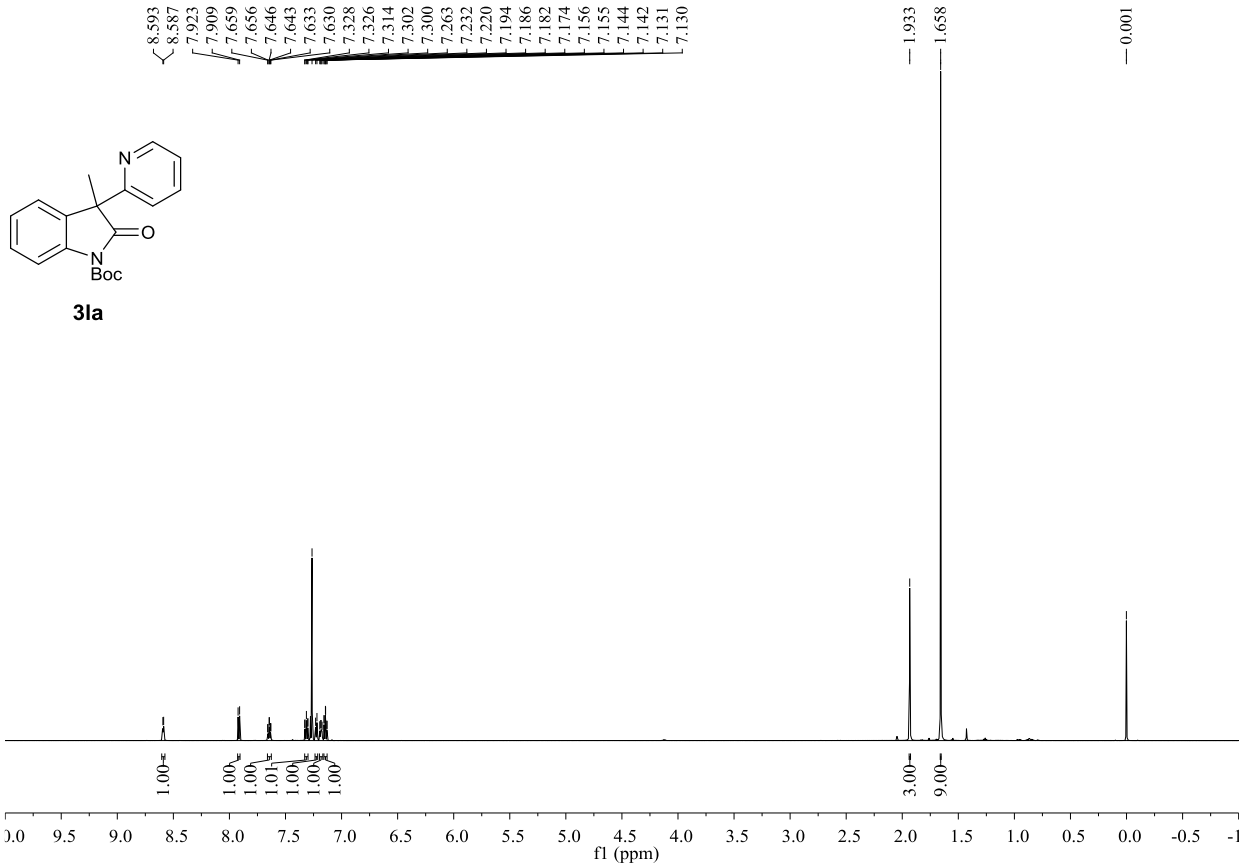
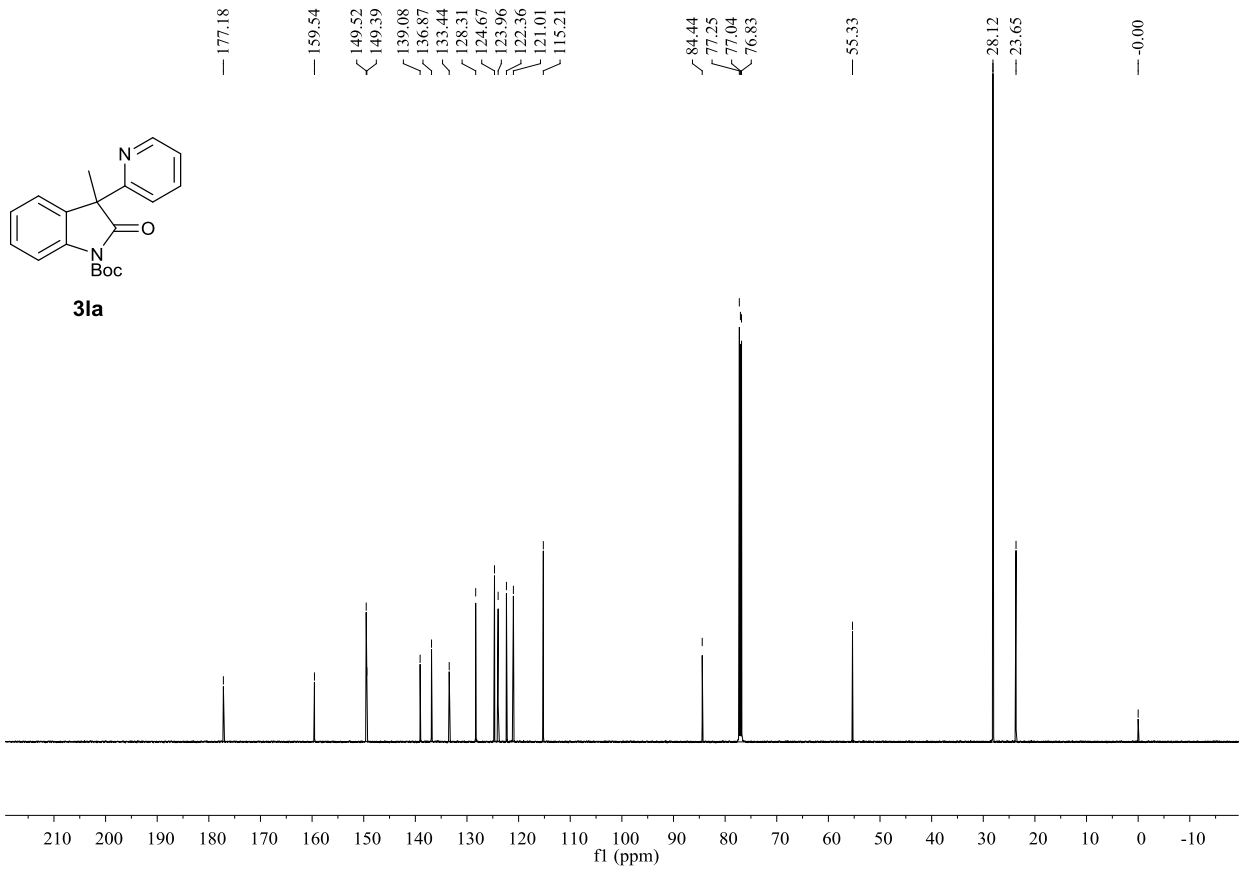
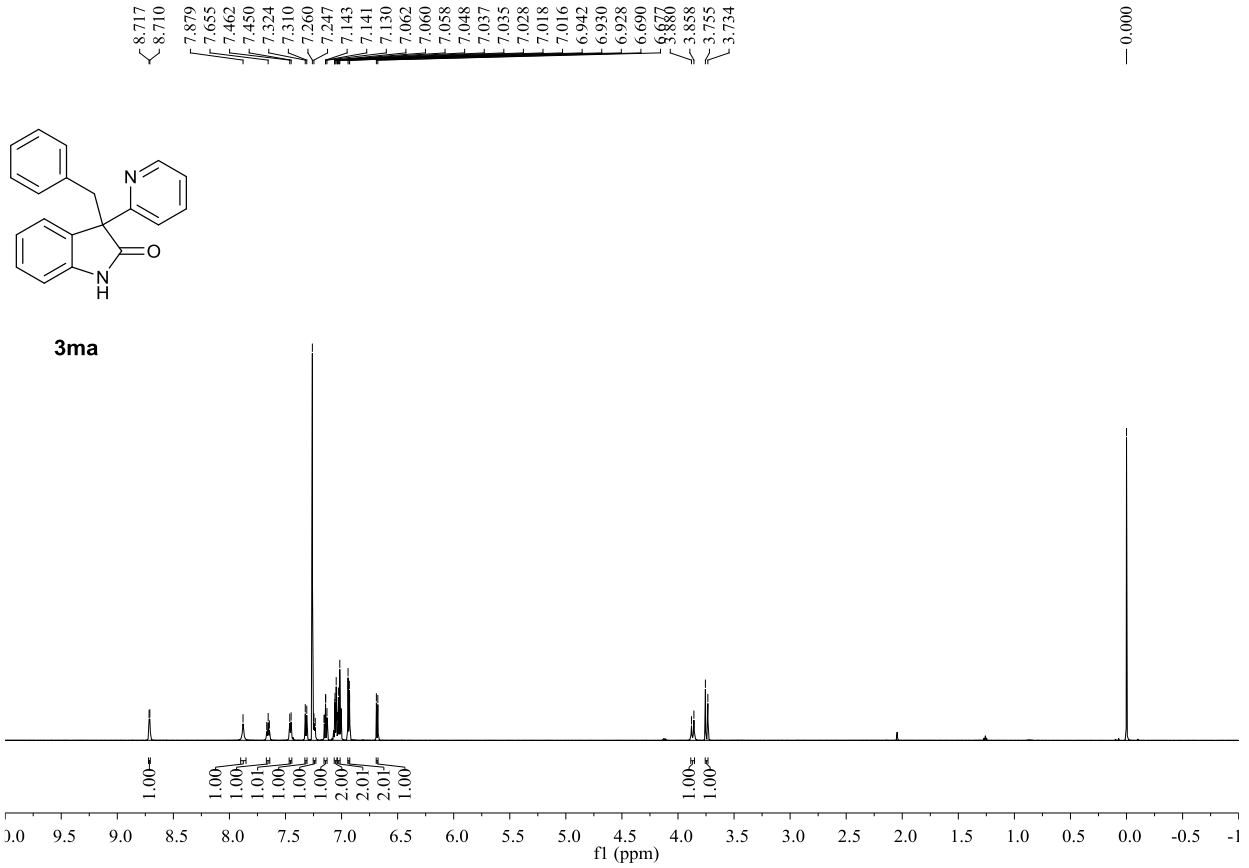
159.18
149.74
148.73
140.14
137.96
137.26
131.10
129.09
127.91
126.69
125.75
125.09
124.96
123.43
121.77
114.90
84.21
61.20
40.43
40.29
40.15
40.01
39.87
39.73
39.60
28.08
f1 (ppm)

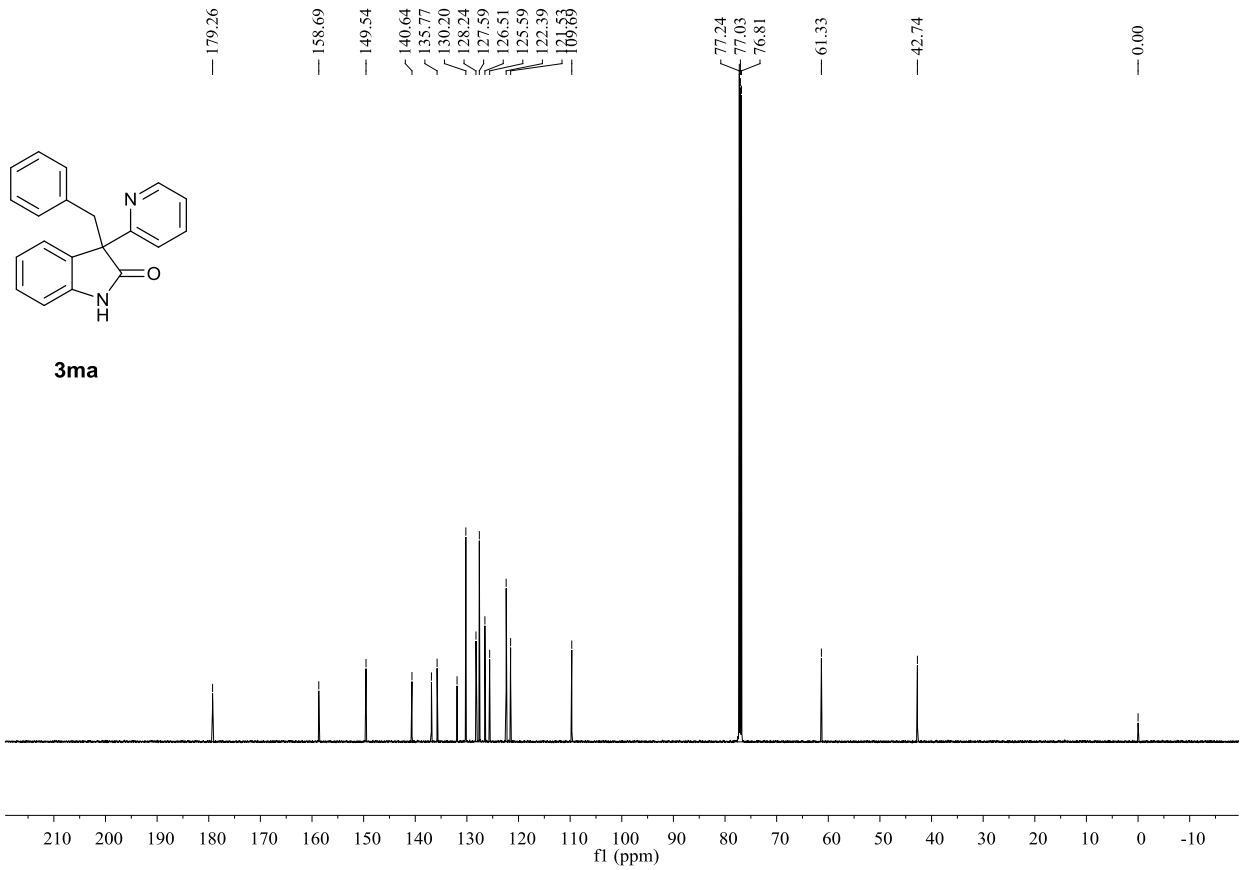

8.593
8.587
7.923
7.909
7.659
7.656
7.646
7.643
7.633
7.630
7.328
7.326
7.314
7.302
7.300
7.263
7.232
7.220
7.194
7.186
7.182
7.174
7.156
7.155
7.144
7.142
7.131
7.130
1.933
1.658
0.001
N
O
N
Boc
1.00
1.00
1.00
1.01
1.00
1.00
1.00
3.00
9.00
f1 (ppm)

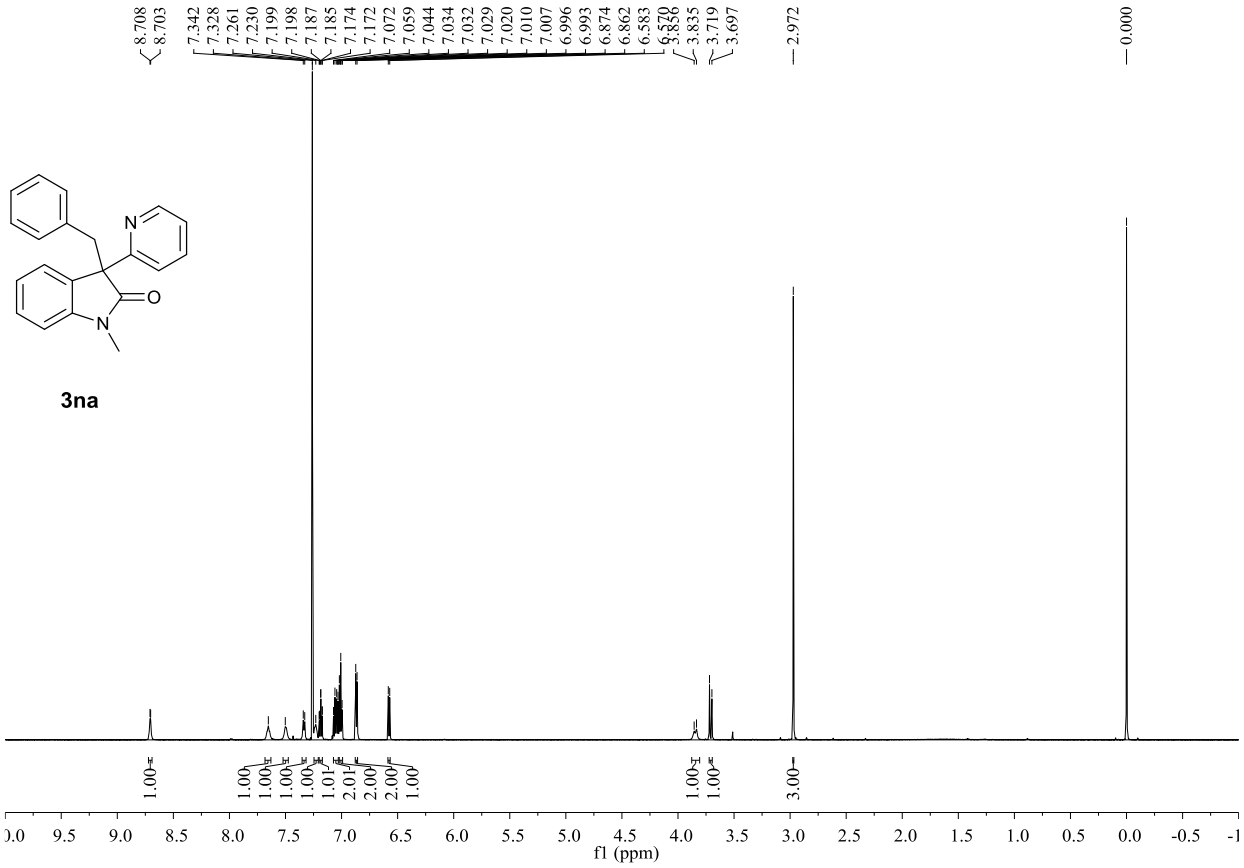
3la


177.18
159.54
149.52
149.39
139.08
136.87
133.44
128.31
124.67
123.96
122.36
121.01
115.21
84.44
77.25
77.04
76.83
55.33
28.12
23.65
-0.00
N
O
N
Boc
f1 (ppm)

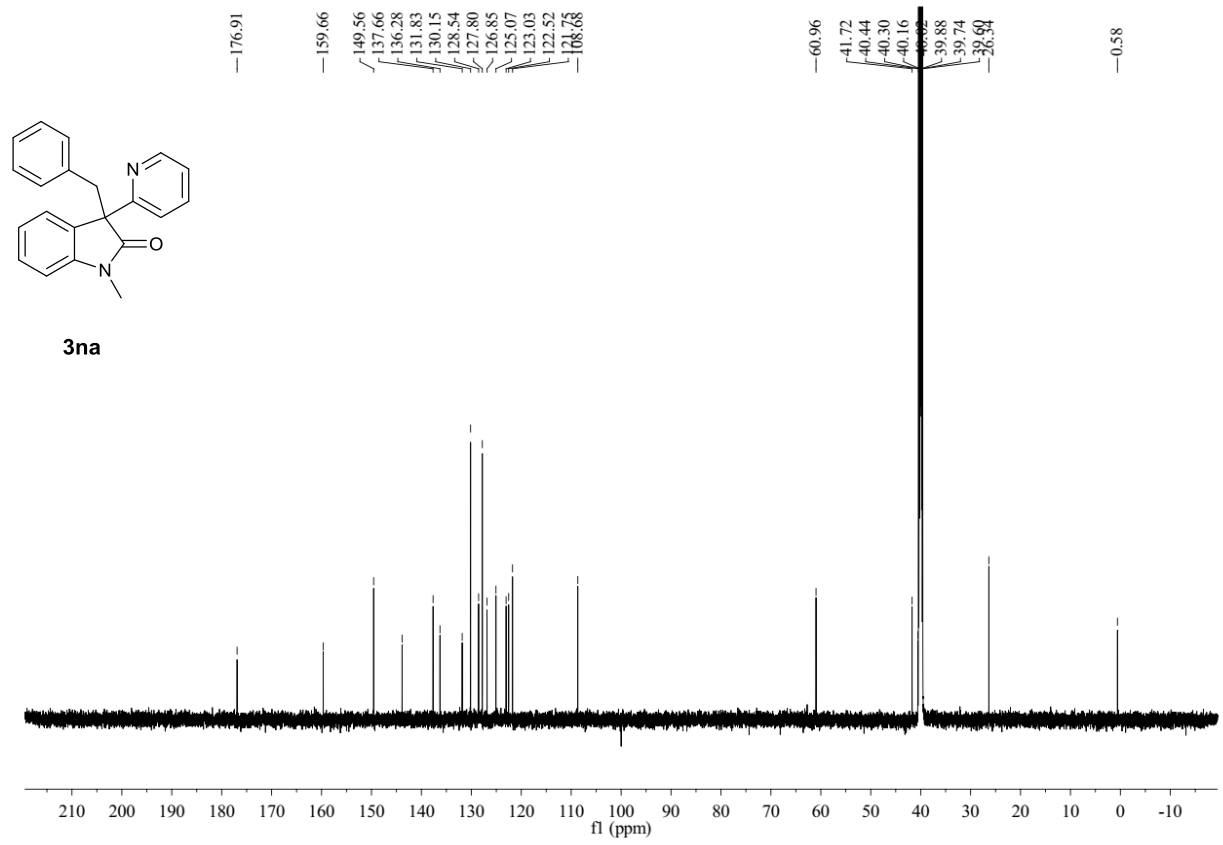
3la


8.717
8.710
7.879
7.655
7.462
7.450
7.324
7.310
7.260
7.247
7.143
7.141
7.130
7.062
7.060
7.058
7.048
7.037
7.035
7.028
7.018
7.016
6.942
6.930
6.928
6.690
6.677
3.880
3.858
3.755
3.734
0.000
N
O
N
H
3ma
1.00
1.00
1.00
1.01
1.00
1.00
1.00
2.00
2.01
2.01
1.00
1.00
1.00
f1 (ppm)

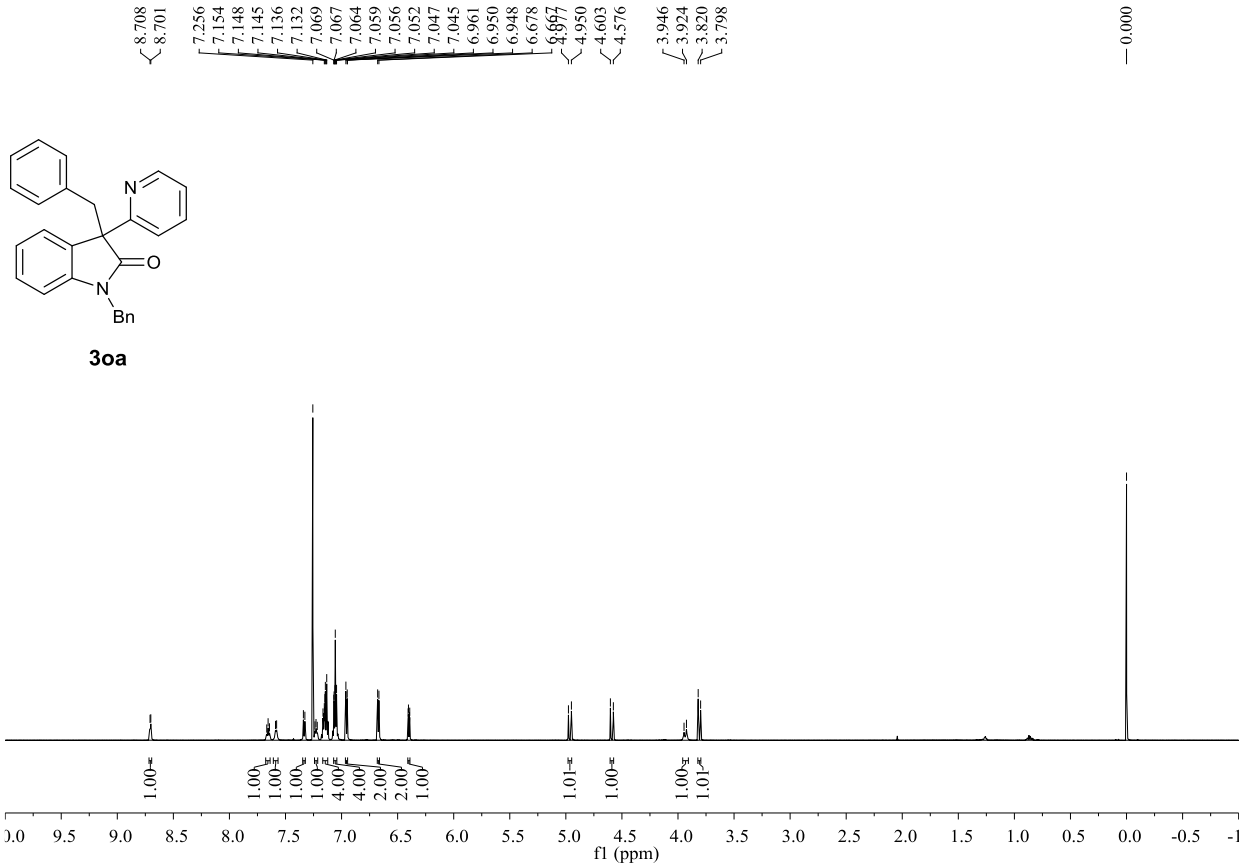

179.26
158.69
149.54
140.64
135.77
130.20
128.24
127.59
126.51
125.59
122.39
121.53
109.68
77.24
77.03
76.81
61.33
42.74
0.00
N
O
N
H
3ma
f1 (ppm)


8.708
8.703
7.342
7.328
7.261
7.230
7.199
7.198
7.187
7.185
7.174
7.172
7.072
7.059
7.044
7.034
7.032
7.029
7.020
7.010
7.007
6.996
6.993
6.874
6.862
6.583
6.570
3.835
3.719
3.697
2.972
0.000
1.00
1.00
1.00
1.00
1.01
2.01
2.00
2.00
1.00
1.00
1.00
3.00
f1 (ppm)

3na


176.91
159.66
149.56
137.66
136.28
131.83
130.15
128.54
127.80
126.85
125.07
123.03
122.52
60.96
41.72
40.44
40.30
40.16
39.88
39.74
39.60
26.34
0.58
f1 (ppm)

3na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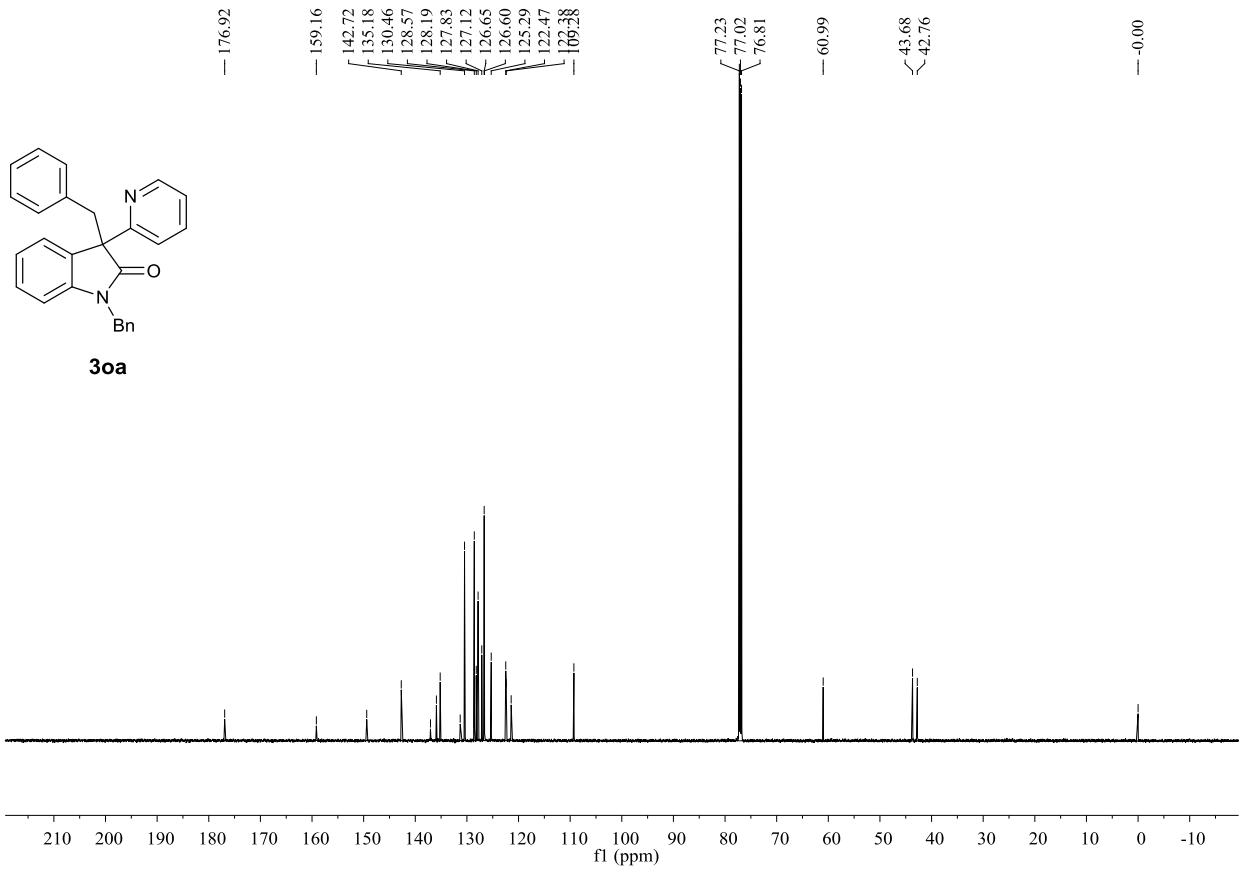
8.701
7.256
7.154
7.148
7.145
7.136
7.132
7.069
7.067
7.064
7.059
7.056
7.052
7.047
7.045
6.961
6.950
6.948
6.678
6.667
4.950
4.603
4.576
3.946
3.924
3.820
3.798
0.000
N
O
N
Bn
1.00
1.00
1.00
1.00
4.00
4.00
2.00
2.00
1.00
1.01
1.00
1.00
1.01
f1 (ppm)

3oa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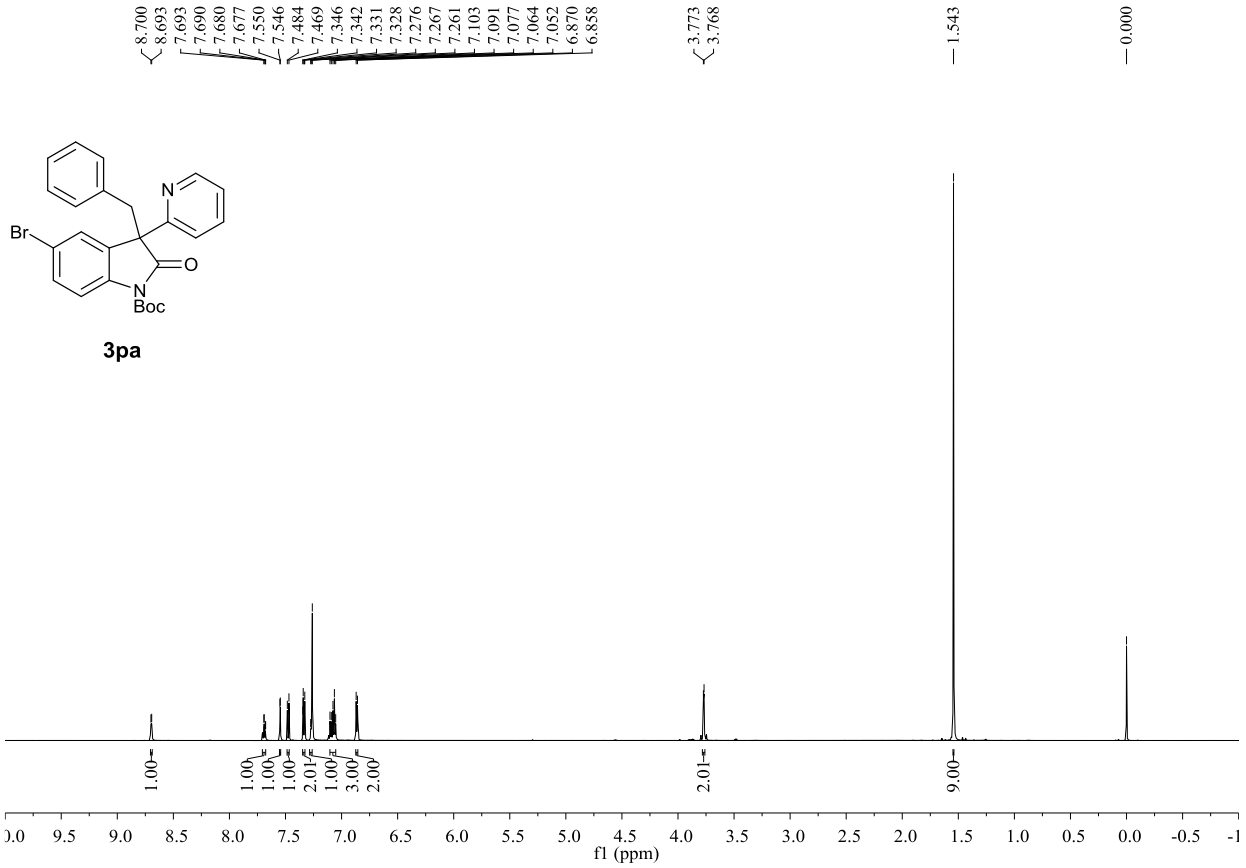
159.16
142.72
135.18
130.46
128.57
128.19
127.83
127.12
126.65
126.60
125.29
122.47
77.23
77.02
76.81
60.99
43.68
42.76
-0.00
N
O
N
Bn
f1 (ppm)

3oa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7.677
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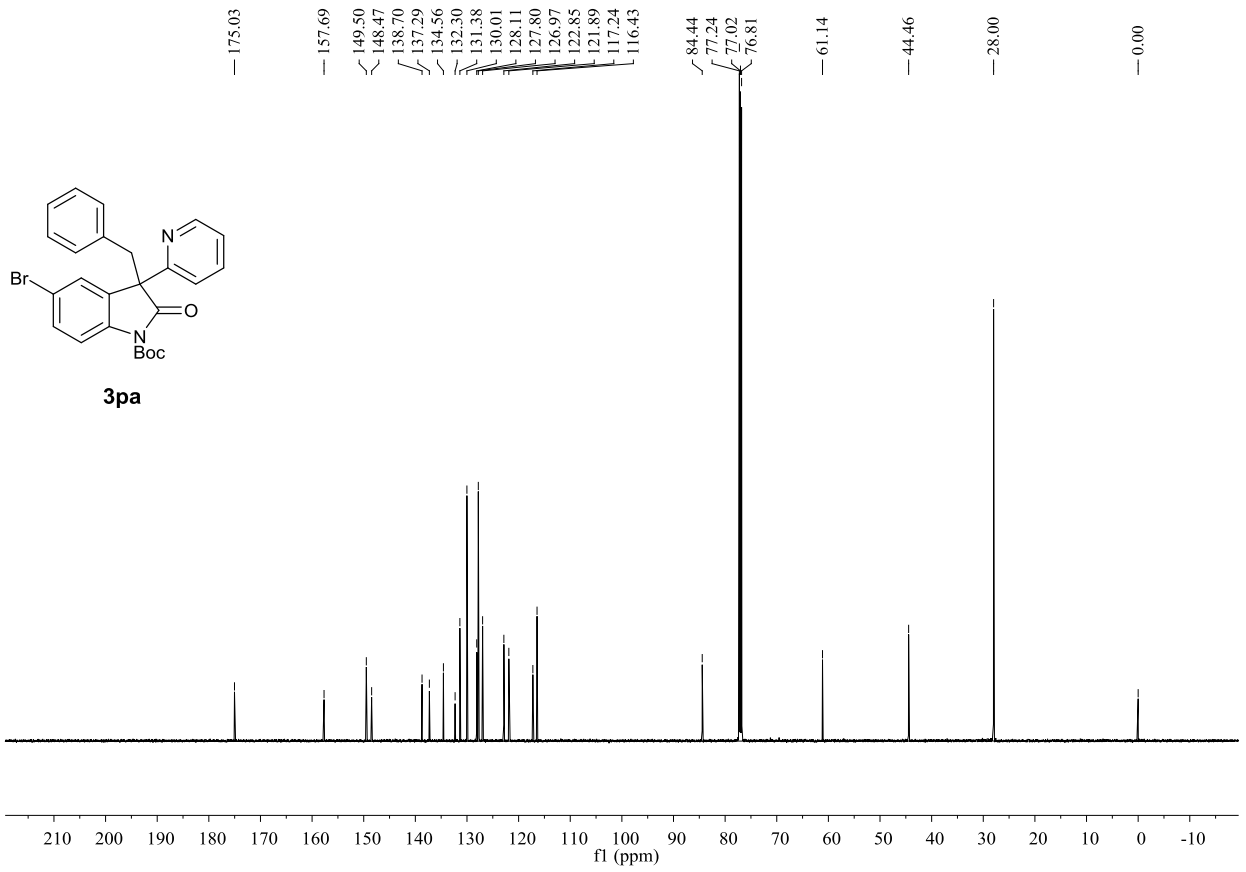
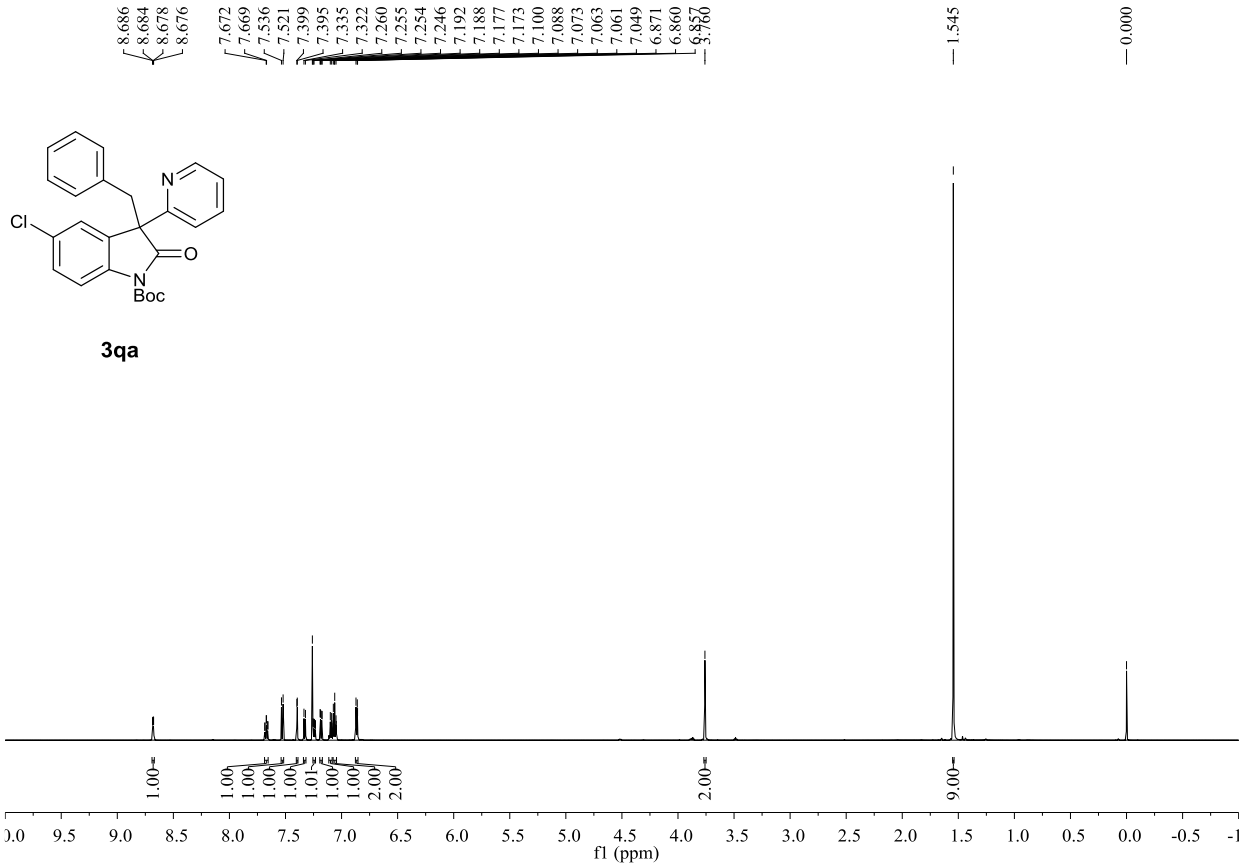
7.546
7.484
7.469
7.346
7.342
7.331
7.328
7.276
7.267
7.261
7.103
7.091
7.077
7.064
7.052
6.870
6.858
3.773
3.768
1.543
0.000
Br
N
O
N
Boc
1.00
1.00
1.00
1.00
2.01
1.00
3.00
2.00
2.01
9.00
f1 (ppm)

3pa


175.03
157.69
149.50
148.47
138.70
137.29
134.56
132.30
131.38
130.01
128.11
127.80
126.97
122.85
121.89
117.24
116.43
84.44
77.24
77.02
76.81
61.14
44.46
28.00
0.00
Br
N
O
N
Boc
f1 (ppm)

3pa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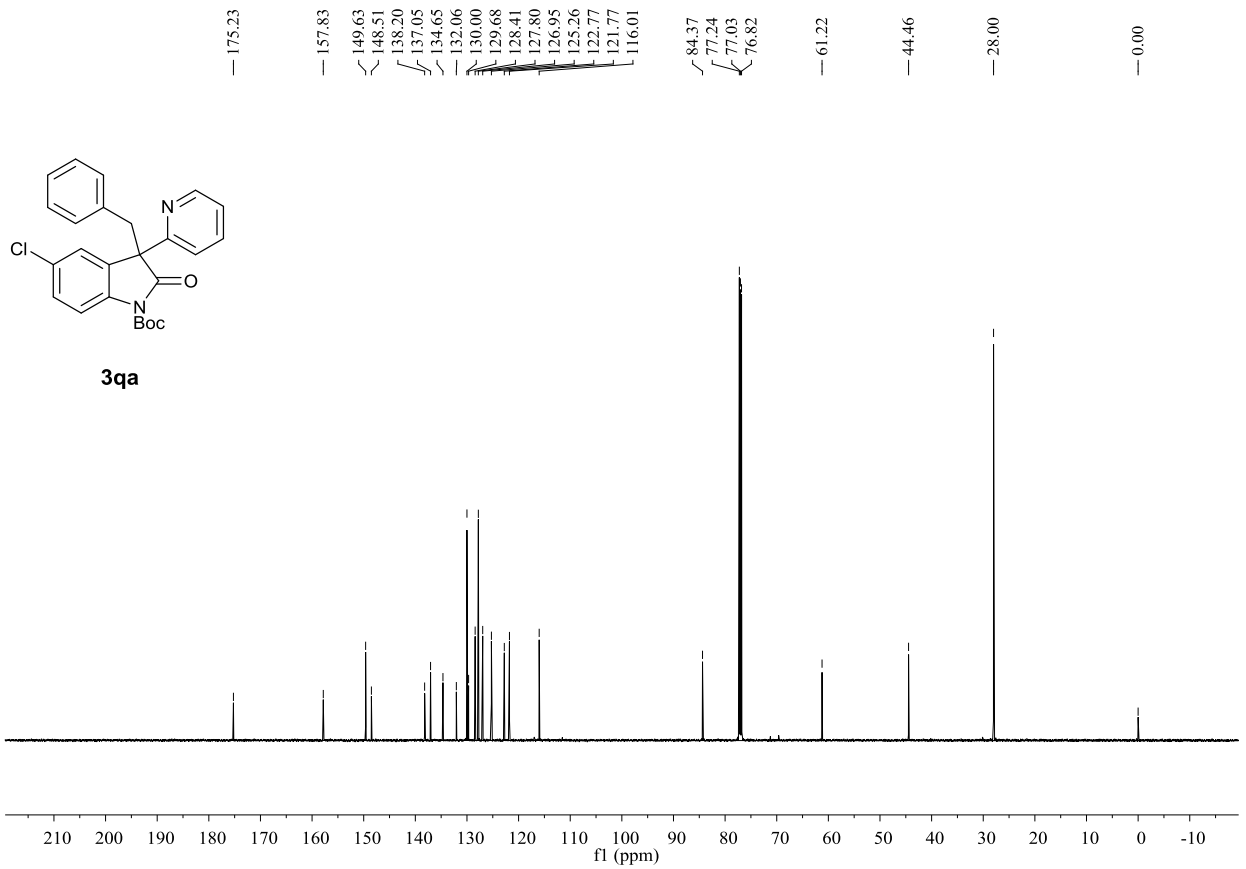
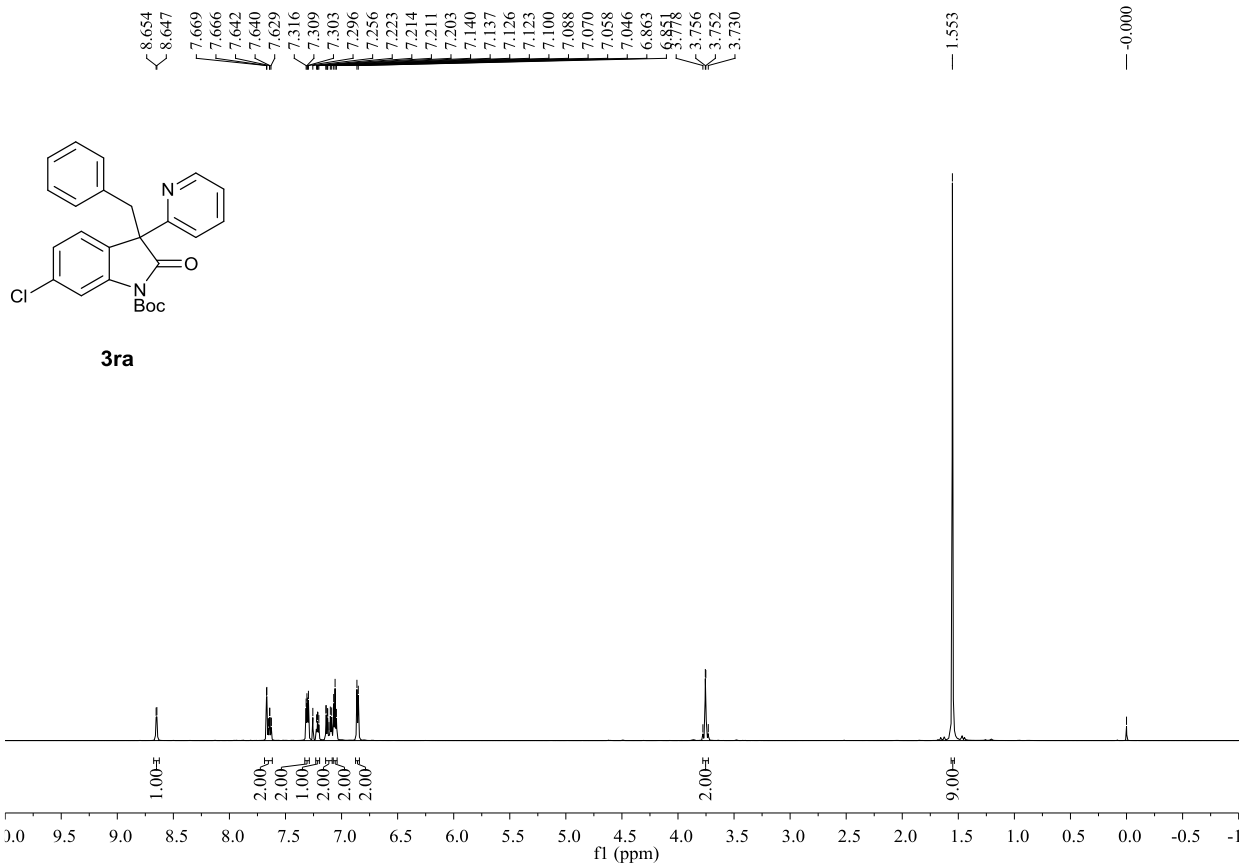
8.684
8.678
8.676
7.672
7.669
7.536
7.521
7.399
7.395
7.335
7.322
7.260
7.255
7.254
7.246
7.192
7.188
7.177
7.173
7.100
7.088
7.073
7.063
7.061
7.049
6.871
6.860
6.857
3.760
1.545
0.000
Cl
N
O
N
Boc
1.00
1.00
1.00
1.00
1.01
1.00
1.00
2.00
2.00
2.00
9.00
f1 (ppm)

3qa


175.23
157.83
149.63
148.51
138.20
137.05
134.65
132.06
130.00
129.68
128.41
127.80
126.95
125.26
122.77
121.77
116.01
84.37
77.24
77.03
76.82
61.22
44.46
28.00
0.00
Cl
N
O
N
Boc
f1 (ppm)

3qa


8.654
8.647
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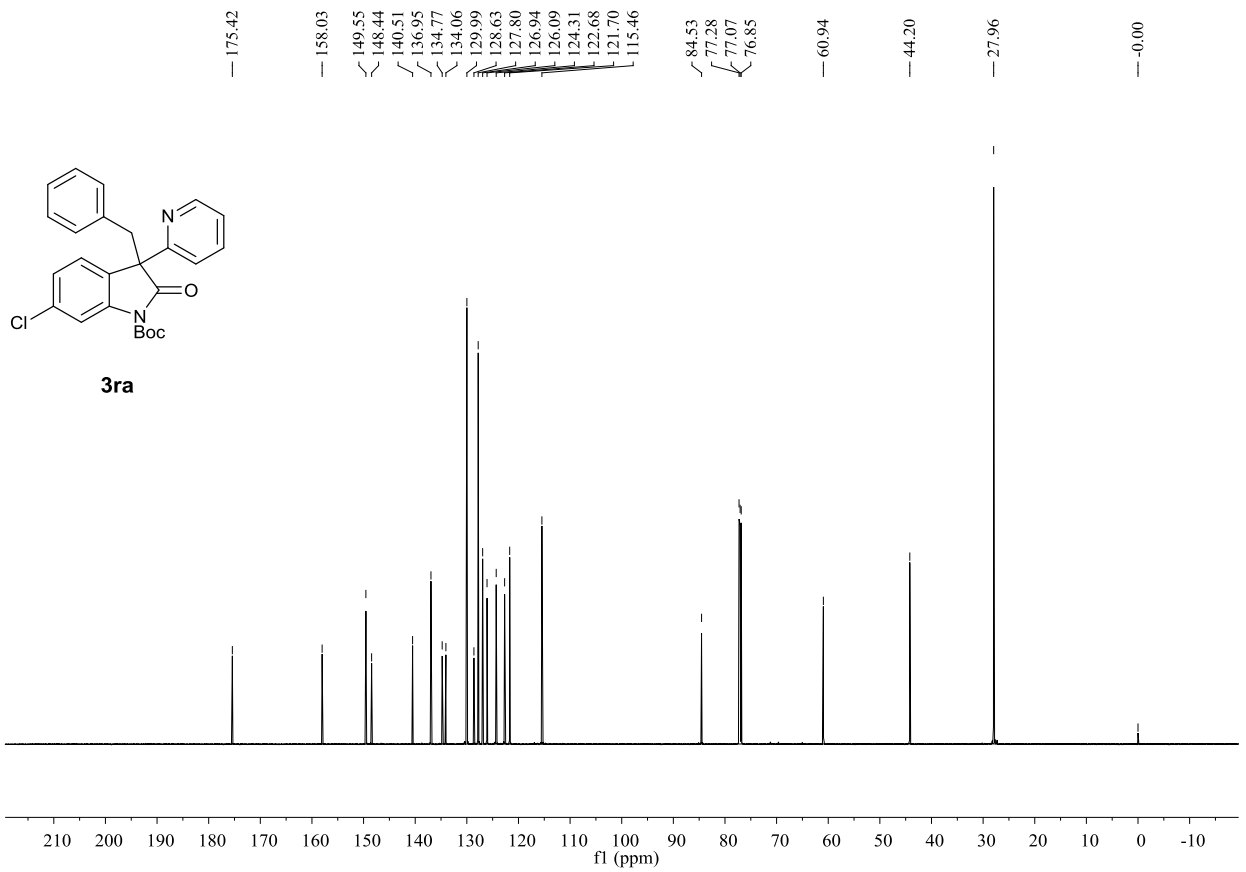
7.666
7.642
7.640
7.629
7.316
7.309
7.303
7.296
7.256
7.223
7.214
7.211
7.203
7.140
7.137
7.126
7.123
7.100
7.088
7.070
7.058
7.046
6.863
3.778
3.756
3.752
3.730
1.553
-0.000
N
O
N
Boc
Cl
1.00
2.00
2.00
1.00
2.00
2.00
2.00
9.00
f1 (ppm)

3ra


175.42
158.03
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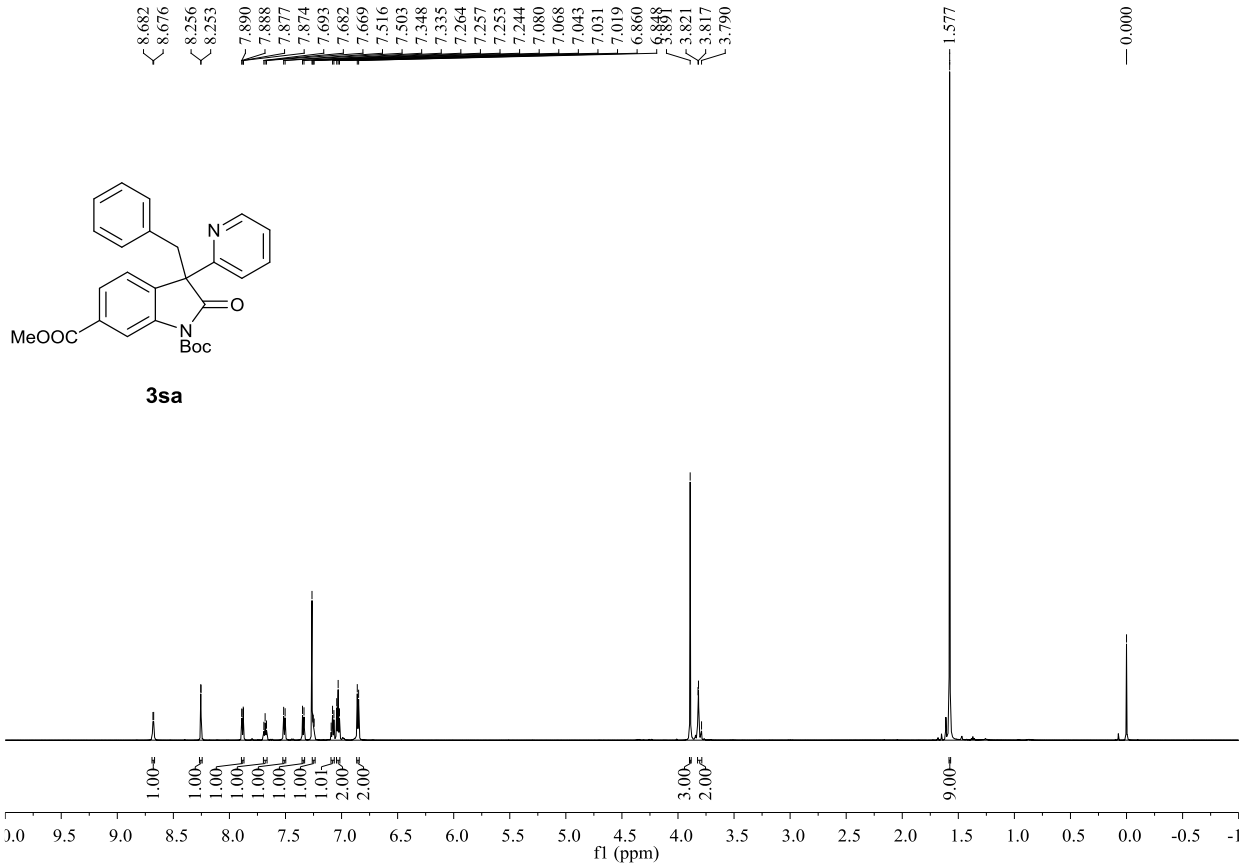
148.44
140.51
136.95
134.77
134.06
129.99
128.63
127.80
126.94
126.09
124.31
122.68
121.70
115.46
84.53
77.28
77.07
76.85
60.94
44.20
27.96
-0.00
N
O
N
Boc
Cl
f1 (ppm)

3ra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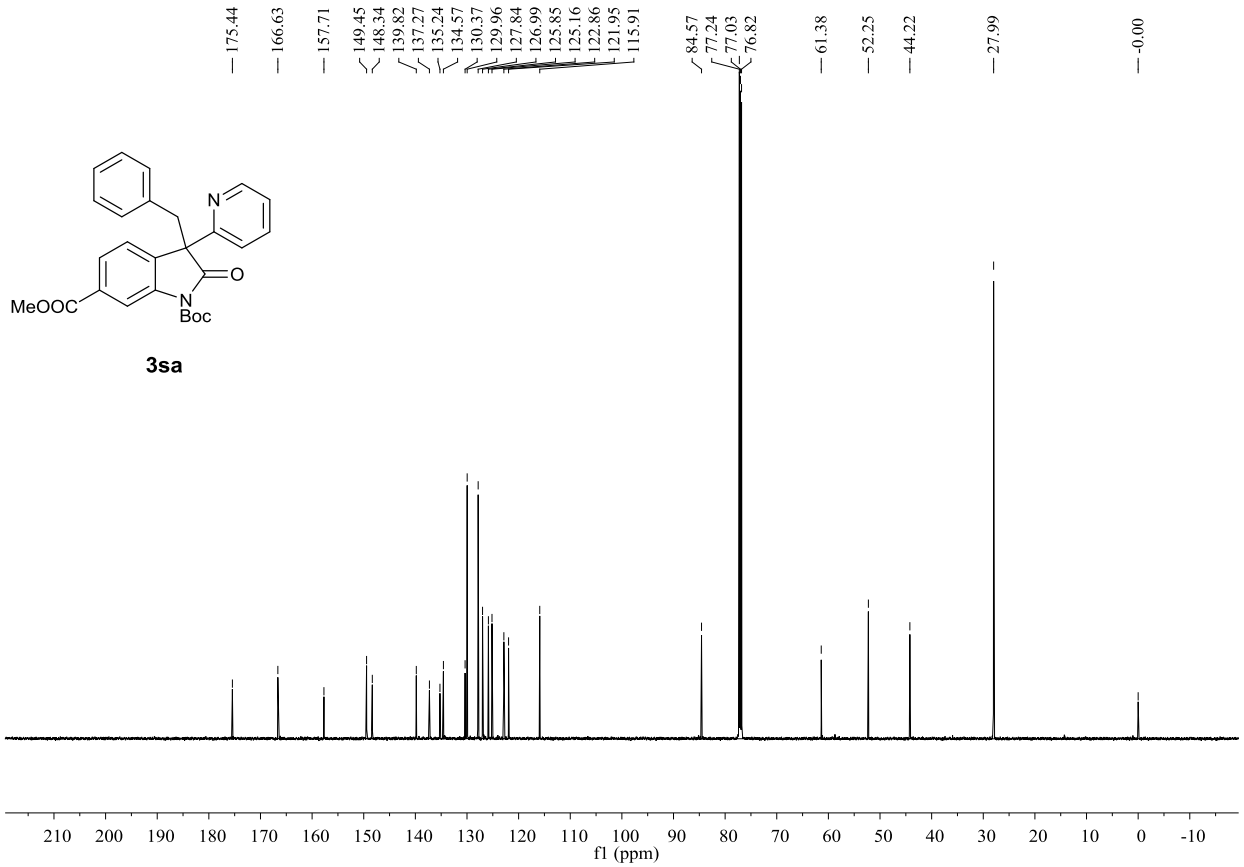
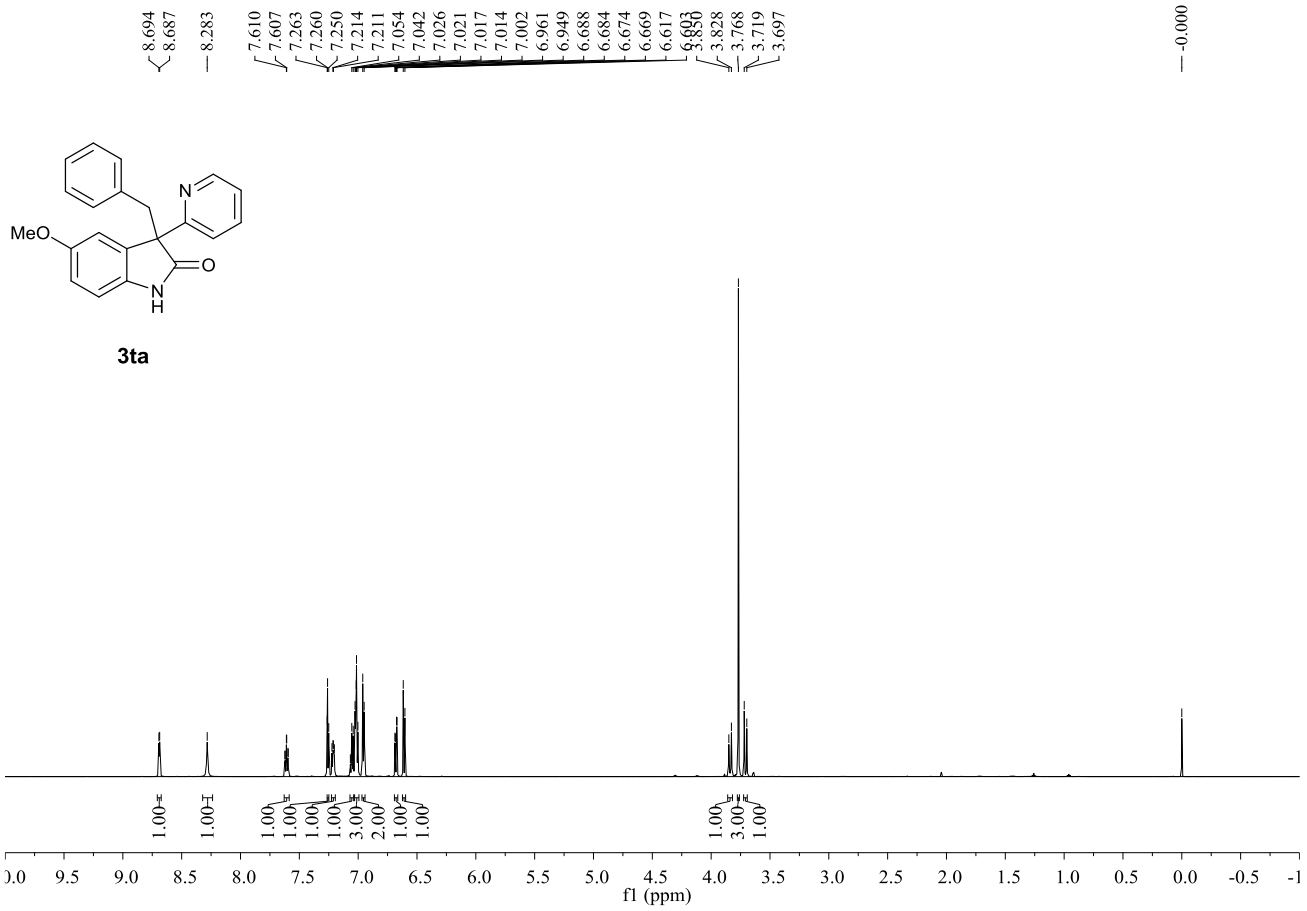
8.676
8.256
8.253
7.890
7.888
7.877
7.874
7.693
7.682
7.669
7.516
7.503
7.348
7.335
7.264
7.257
7.253
7.244
7.080
7.068
7.043
7.031
7.019
6.860
6.848
3.891
3.821
3.817
3.790
1.577
0.000
N
O
MeOOC
N
Boc
1.00
1.00
1.00
1.00
1.00
1.00
1.01
2.00
2.00
3.00
2.00
9.00
f1 (ppm)

3sa


175.44
166.63
157.71
149.45
148.34
139.82
137.27
135.24
134.57
130.37
129.96
127.84
126.99
125.85
125.16
122.86
121.95
115.91
84.57
77.24
77.03
76.82
61.38
52.25
44.22
27.99
-0.00
N
O
MeOOC
N
Boc
f1 (ppm)

3sa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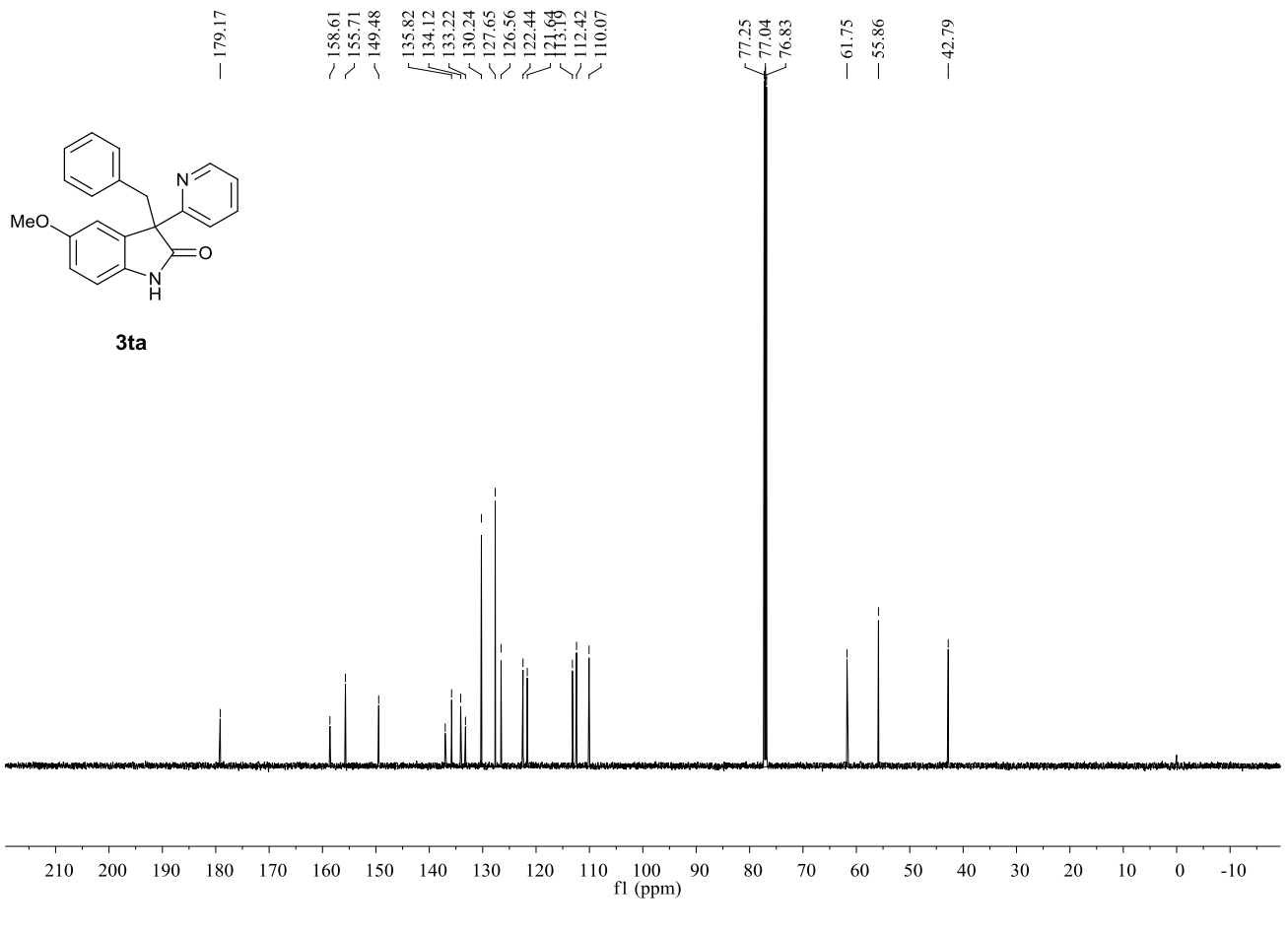
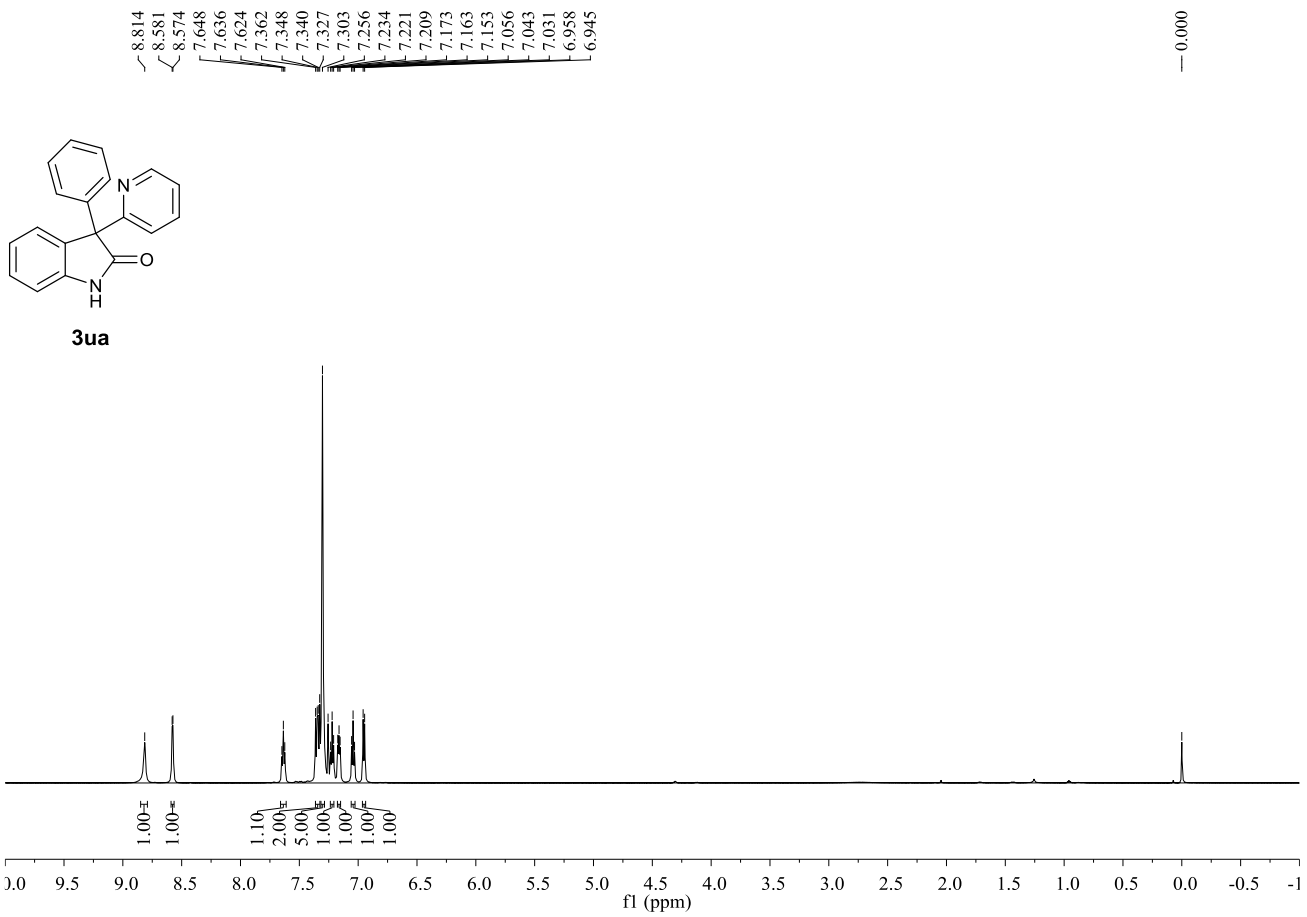
8.687
8.283
7.610
7.607
7.263
7.260
7.250
7.214
7.211
7.054
7.042
7.026
7.021
7.017
7.014
7.002
6.961
6.949
6.688
6.684
6.674
6.669
6.617
6.603
3.850
3.828
3.768
3.719
3.697
-0.000
MeO
N
O
N
H
1.00
1.00
1.00
1.00
1.00
3.00
2.00
1.00
1.00
1.00
3.00
1.00
f1 (ppm)

3ta


179.17
158.61
155.71
149.48
135.82
134.12
133.22
130.24
127.65
126.56
122.44
121.64
113.19
112.42
110.07
77.25
77.04
76.83
61.75
55.86
42.79
MeO
N
O
N
H
f1 (ppm)

3ta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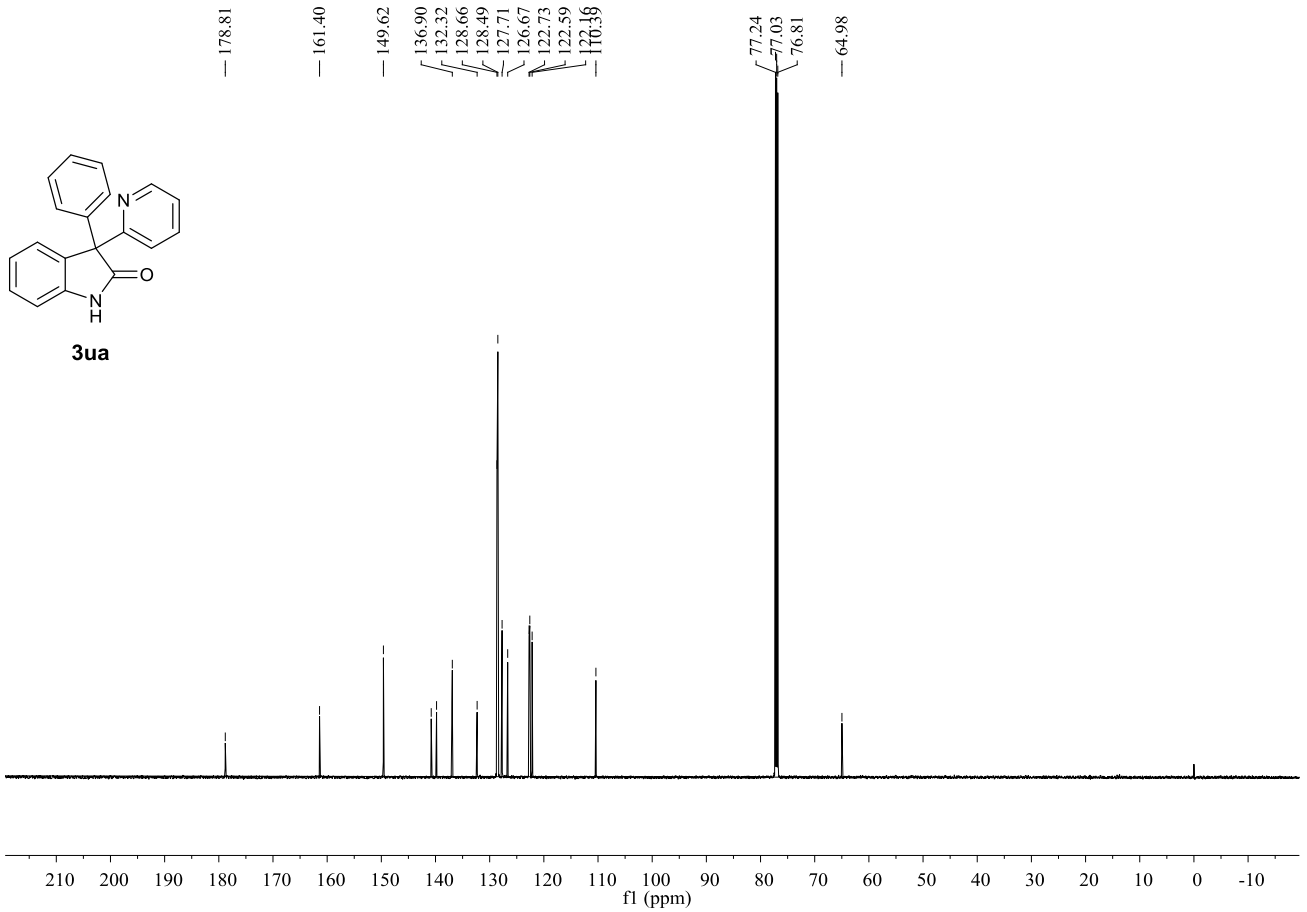
8.581
8.574
7.648
7.636
7.624
7.362
7.348
7.340
7.327
7.303
7.256
7.234
7.221
7.209
7.173
7.163
7.153
7.056
7.043
7.031
6.958
6.945
0.000
N
O
N
H
3ua
1.00
1.00
1.10
2.00
5.00
1.00
1.00
1.00
f1 (ppm)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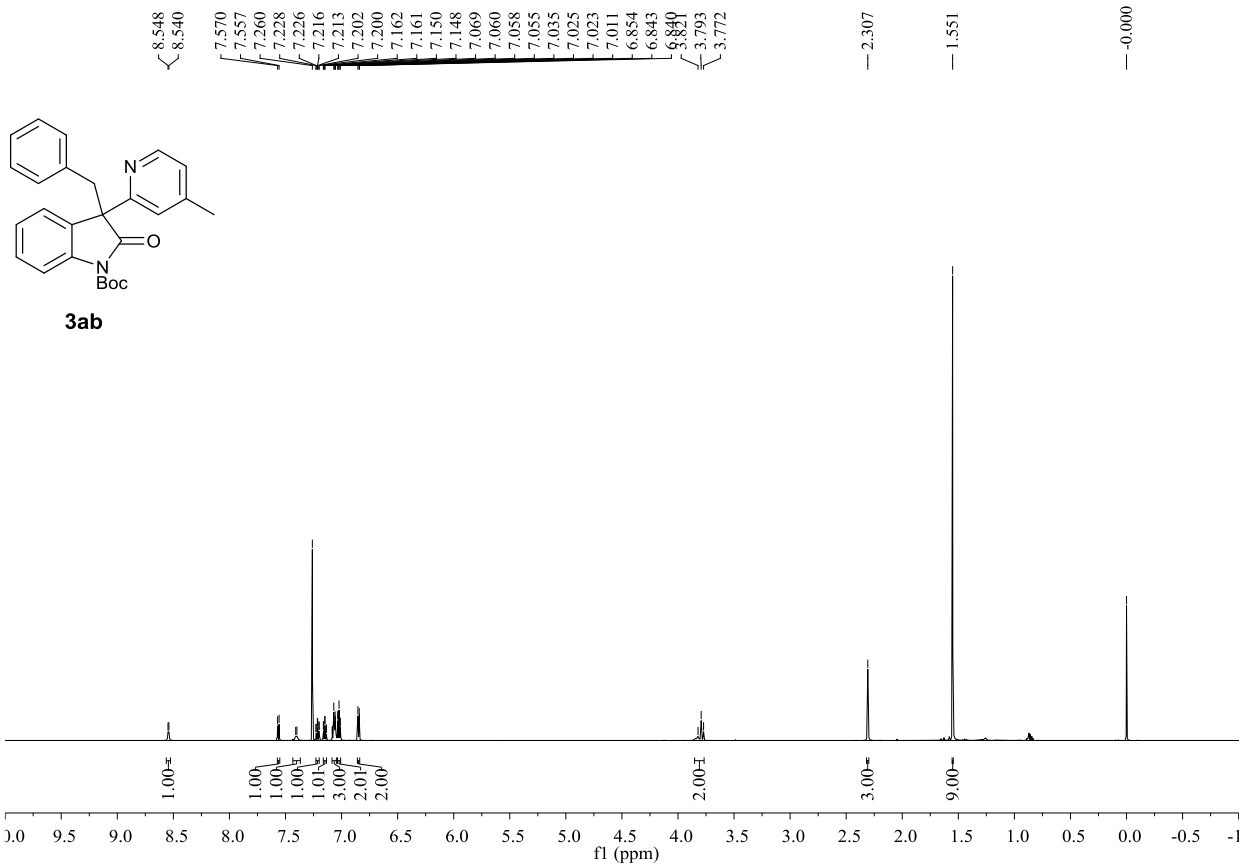
161.40
149.62
136.90
132.32
128.66
128.49
127.71
126.67
122.73
122.59
122.16
110.39
77.24
77.03
76.81
64.98
N
O
N
H
3ua
f1 (ppm)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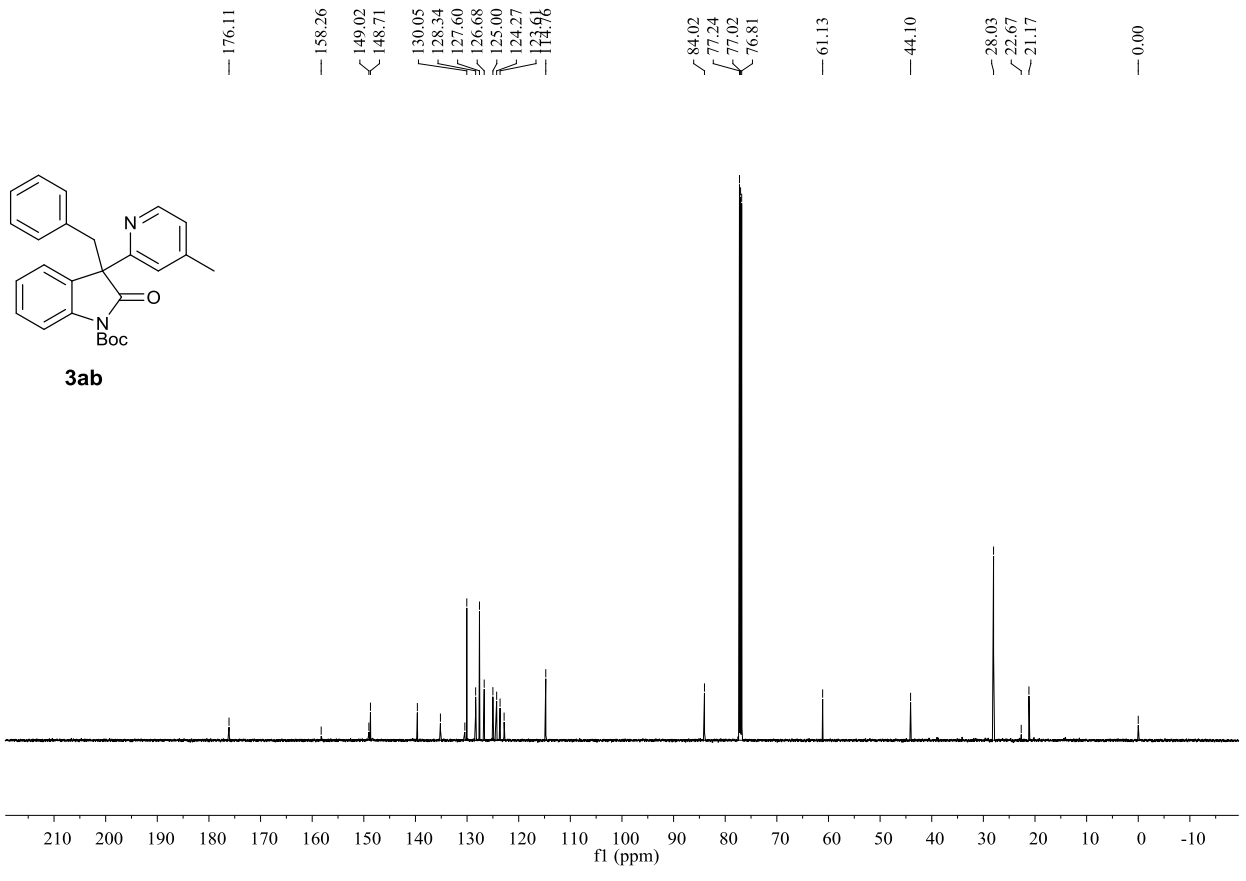
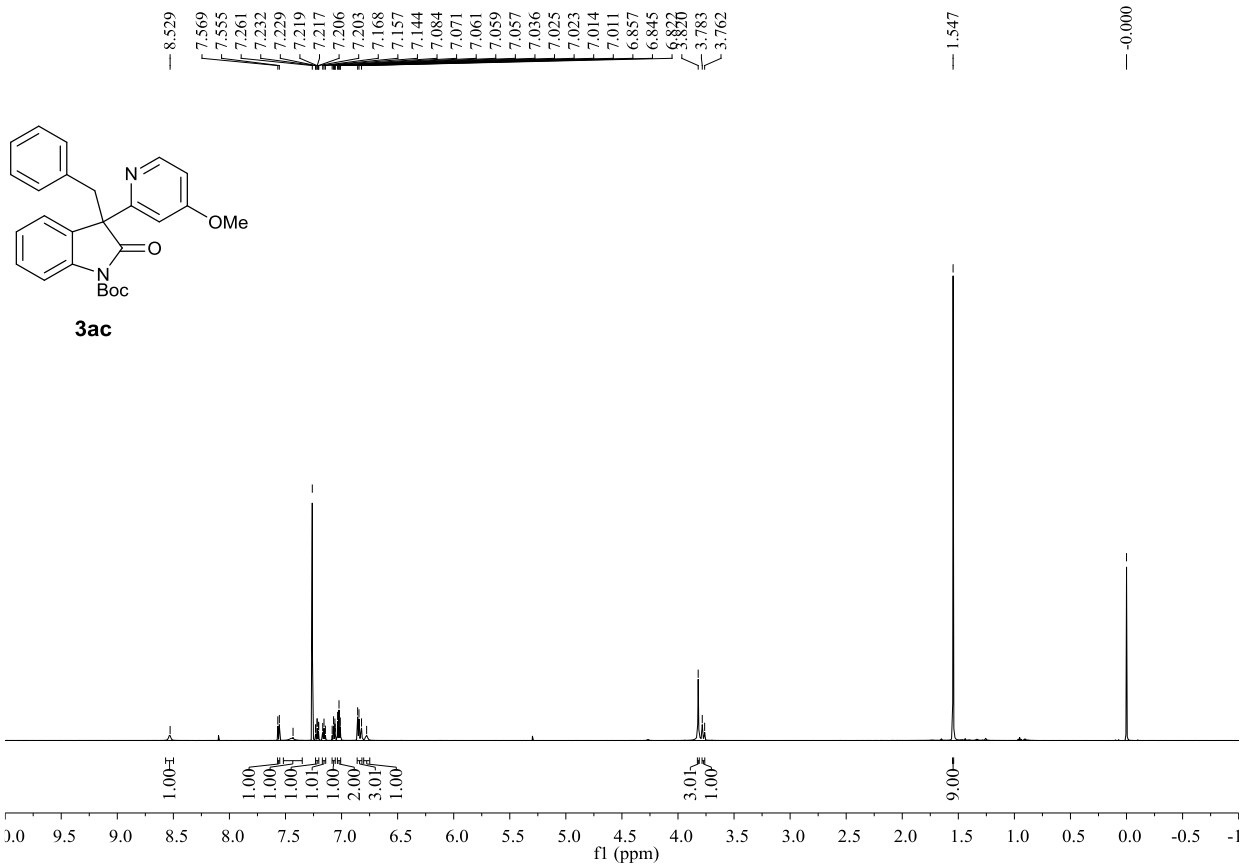
8.540
7.570
7.557
7.260
7.228
7.226
7.216
7.213
7.202
7.200
7.162
7.161
7.150
7.148
7.069
7.060
7.058
7.055
7.035
7.025
7.023
7.011
6.854
6.843
6.840
3.821
3.793
3.772
2.307
1.551
-0.000
N
O
N
Boc
1.00
1.00
1.00
1.01
3.00
2.01
2.00
2.00
3.00
9.00
f1 (ppm)

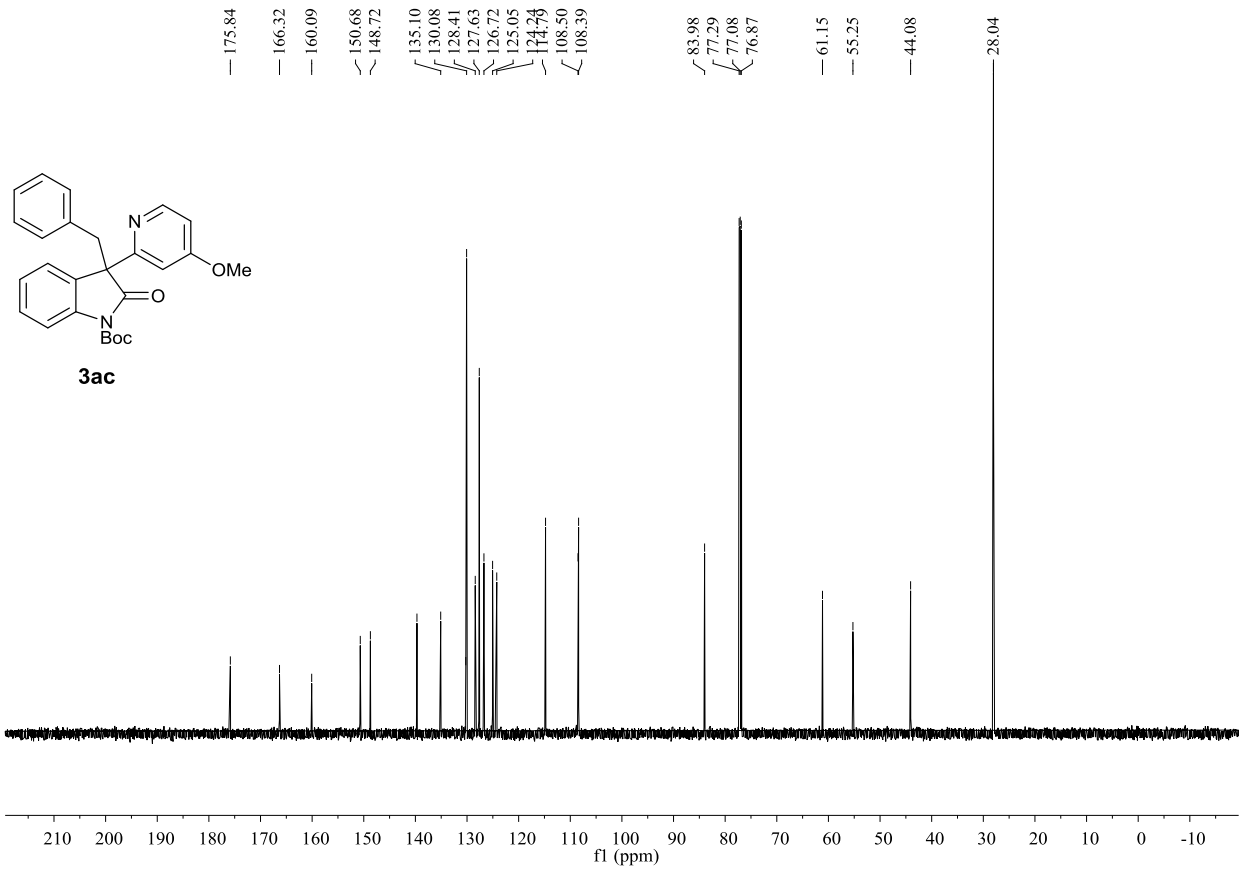
3ab


176.11
158.26
149.02
148.71
130.05
128.34
127.60
126.68
125.00
124.27
123.61
114.76
84.02
77.24
77.02
76.81
61.13
44.10
28.03
22.67
21.17
0.00
N
O
N
Boc
f1 (ppm)

3ab


8.529
7.569
7.555
7.261
7.232
7.229
7.219
7.217
7.206
7.203
7.168
7.157
7.144
7.084
7.071
7.061
7.059
7.057
7.036
7.025
7.023
7.014
7.011
6.857
6.845
6.822
3.826
3.783
3.762
1.547
-0.000
N
OMe
O
N
Boc
1.00
1.00
1.00
1.01
1.00
2.00
3.01
1.00
3.01
1.00
9.00
f1 (ppm)

3ac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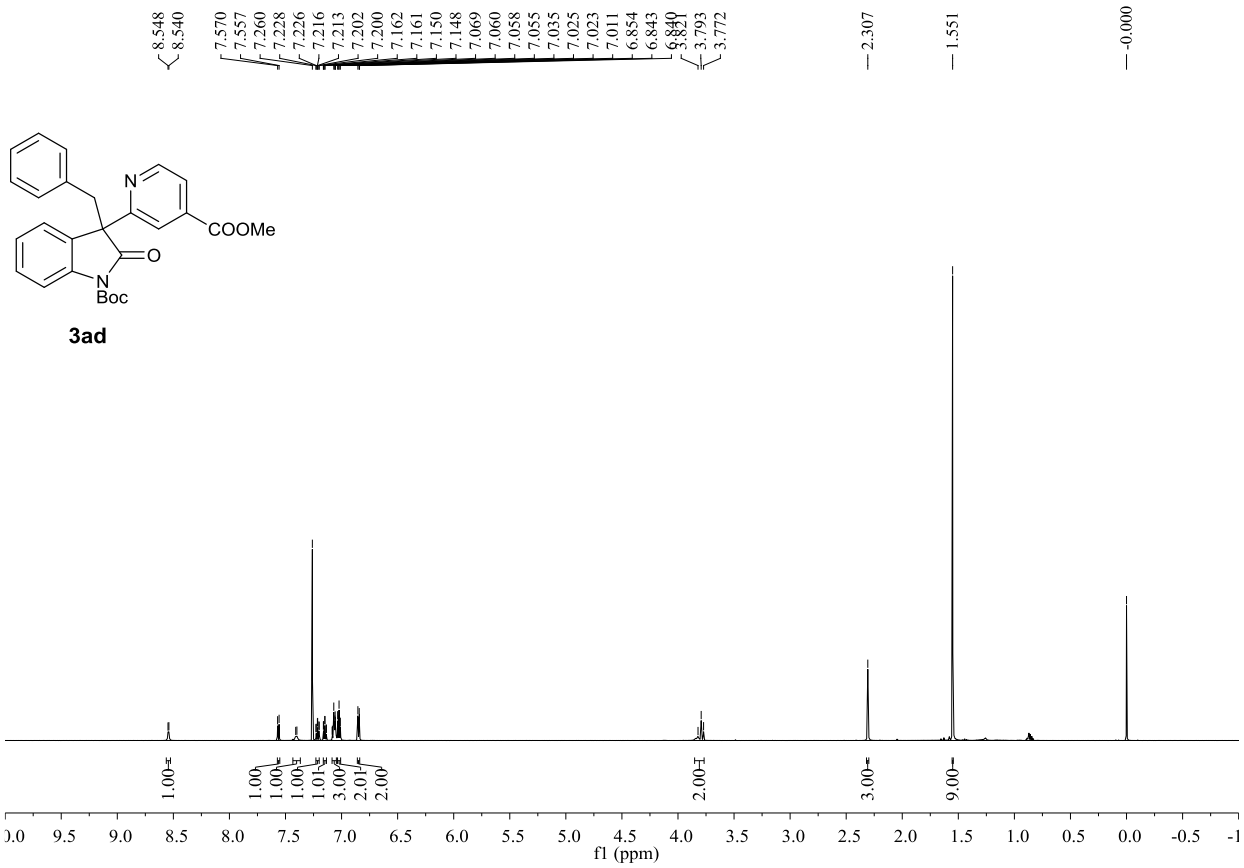
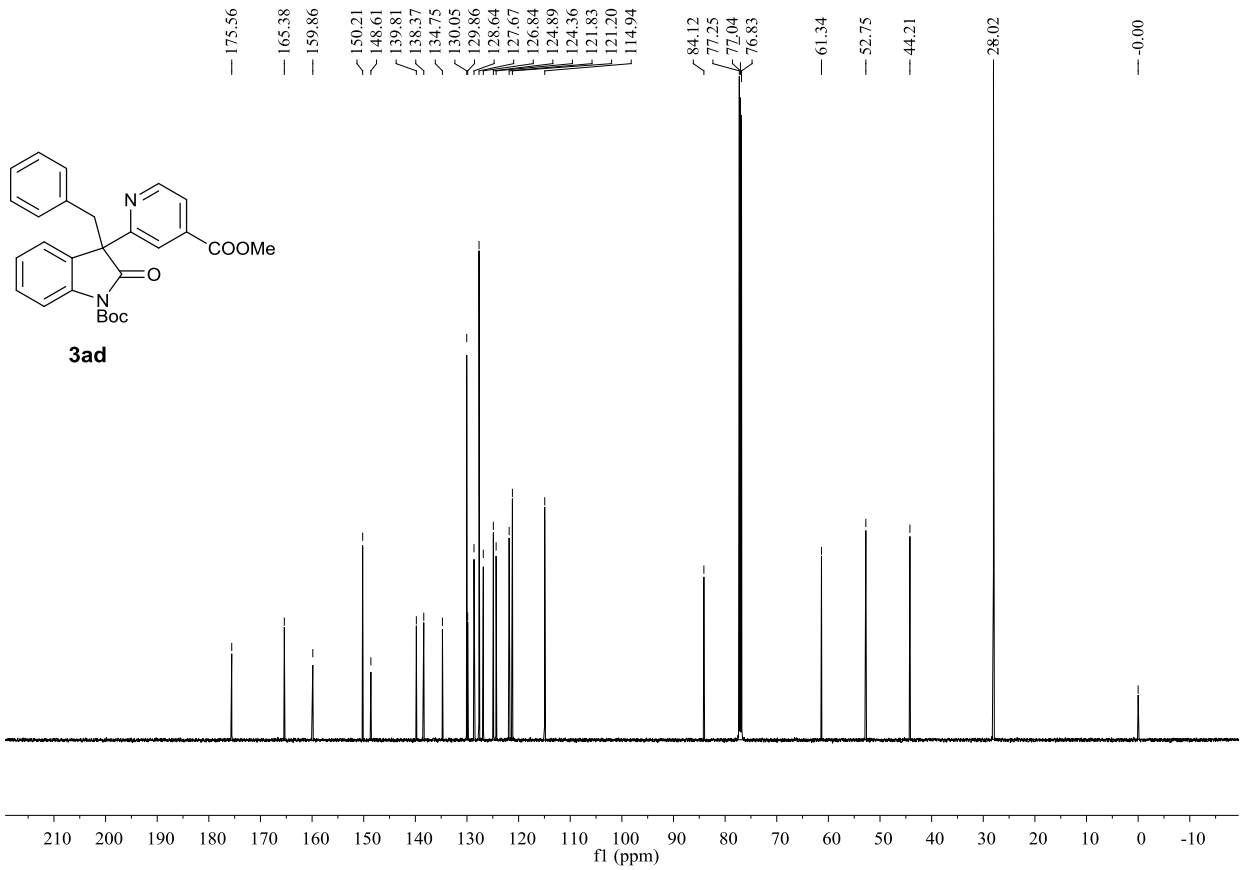
166.32
160.09
150.68
148.72
135.10
130.08
128.41
127.63
126.72
125.05
124.24
114.78
108.50
108.39
83.98
77.29
77.08
76.87
61.15
55.25
44.08
28.04
N
OMe
O
N
Boc
f1 (ppm)

3ac


8.548
8.540
7.570
7.557
7.260
7.228
7.226
7.216
7.213
7.202
7.200
7.162
7.161
7.150
7.148
7.069
7.060
7.058
7.055
7.035
7.025
7.023
7.011
6.854
6.843
6.840
3.821
3.793
3.772
2.307
1.551
-0.000
N
COOMe
O
N
Boc
3ad
1.00
1.00
1.00
1.01
3.00
2.01
2.00
2.00
3.00
9.00
f1 (ppm)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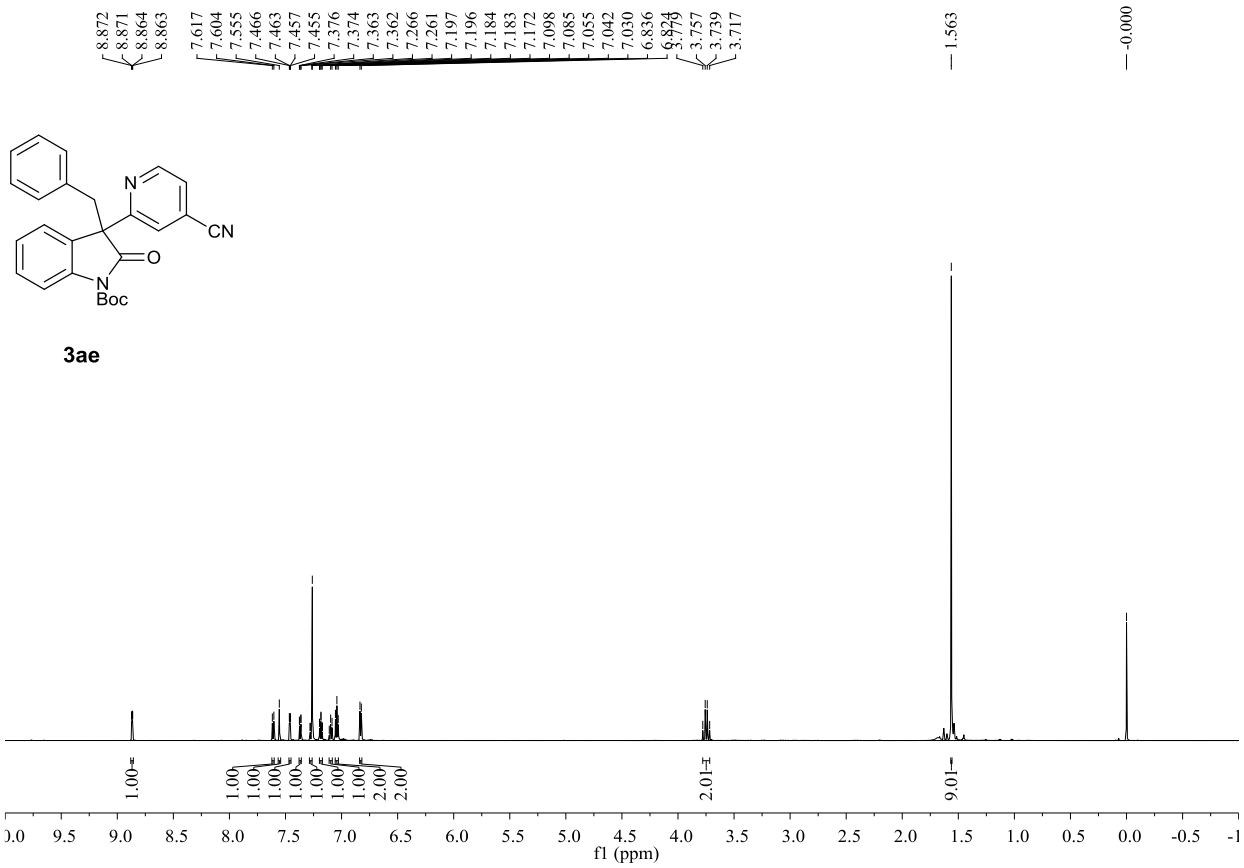
165.38
159.86
150.21
148.61
139.81
138.37
134.75
130.05
129.86
128.64
127.67
126.84
124.89
124.36
121.83
121.20
114.94
84.12
77.25
77.04
76.83
61.34
52.75
44.21
28.02
-0.00
N
COOMe
O
N
Boc
3ad
f1 (ppm)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8.863
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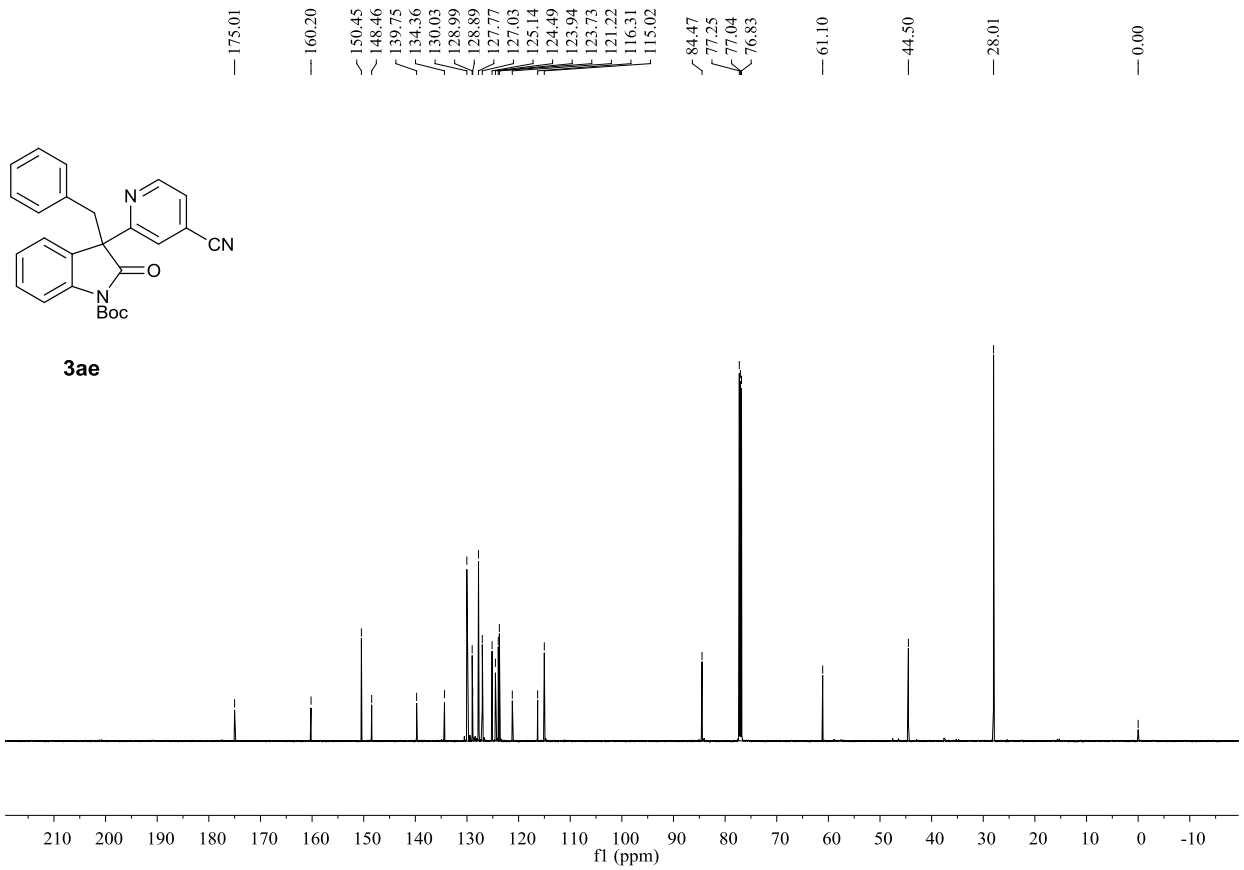
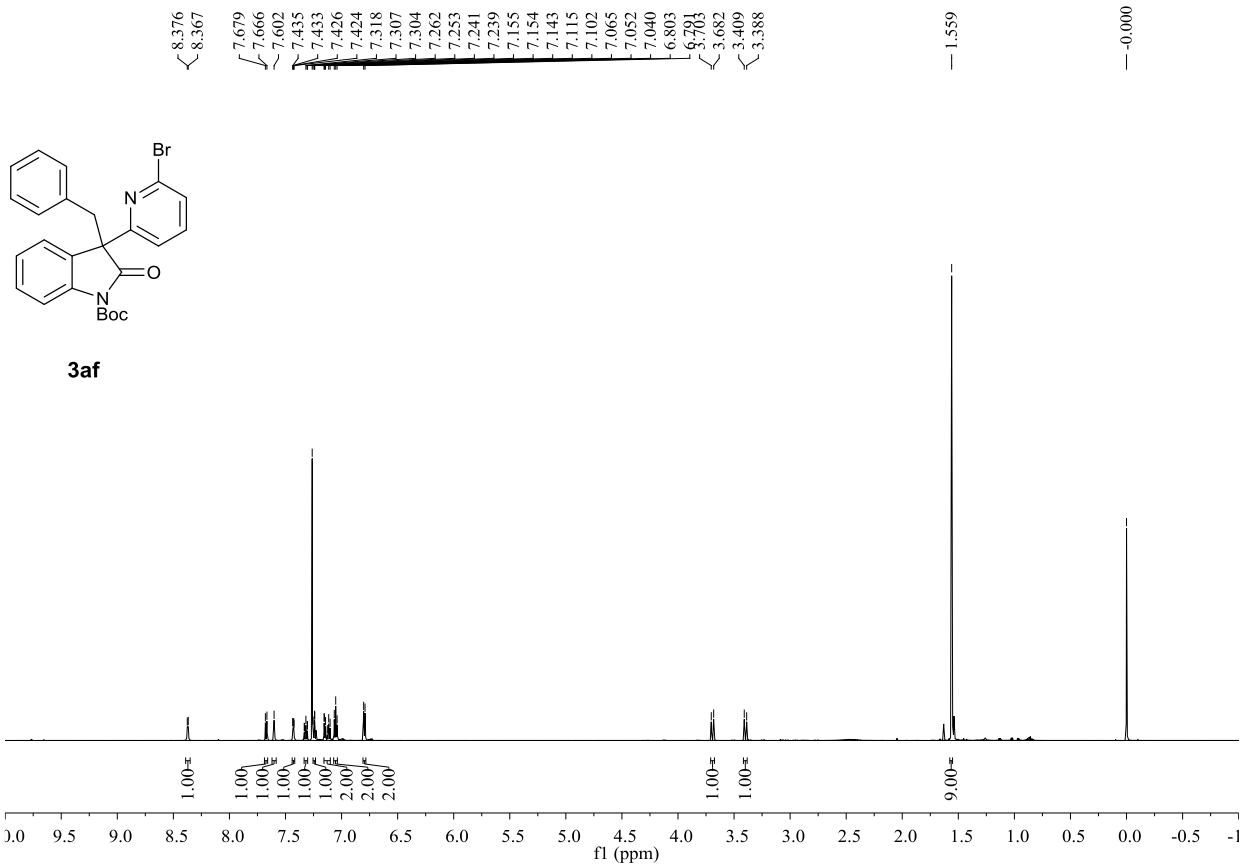
7.604
7.555
7.466
7.463
7.457
7.455
7.376
7.374
7.363
7.362
7.266
7.261
7.197
7.196
7.184
7.183
7.172
7.098
7.085
7.055
7.042
7.030
6.836
3.757
3.739
3.717
1.563
-0.000
N
CN
O
N
Boc
1.00
1.00
1.00
1.00
1.00
1.00
1.00
2.00
2.00
2.01
9.01
f1 (ppm)

3ae


175.01
160.20
150.45
148.46
139.75
134.36
130.03
128.99
128.89
127.77
127.03
125.14
124.49
123.94
123.73
121.22
116.31
115.02
84.47
77.25
77.04
76.83
61.10
44.50
28.01
0.00
N
CN
O
N
Boc
f1 (ppm)

3ae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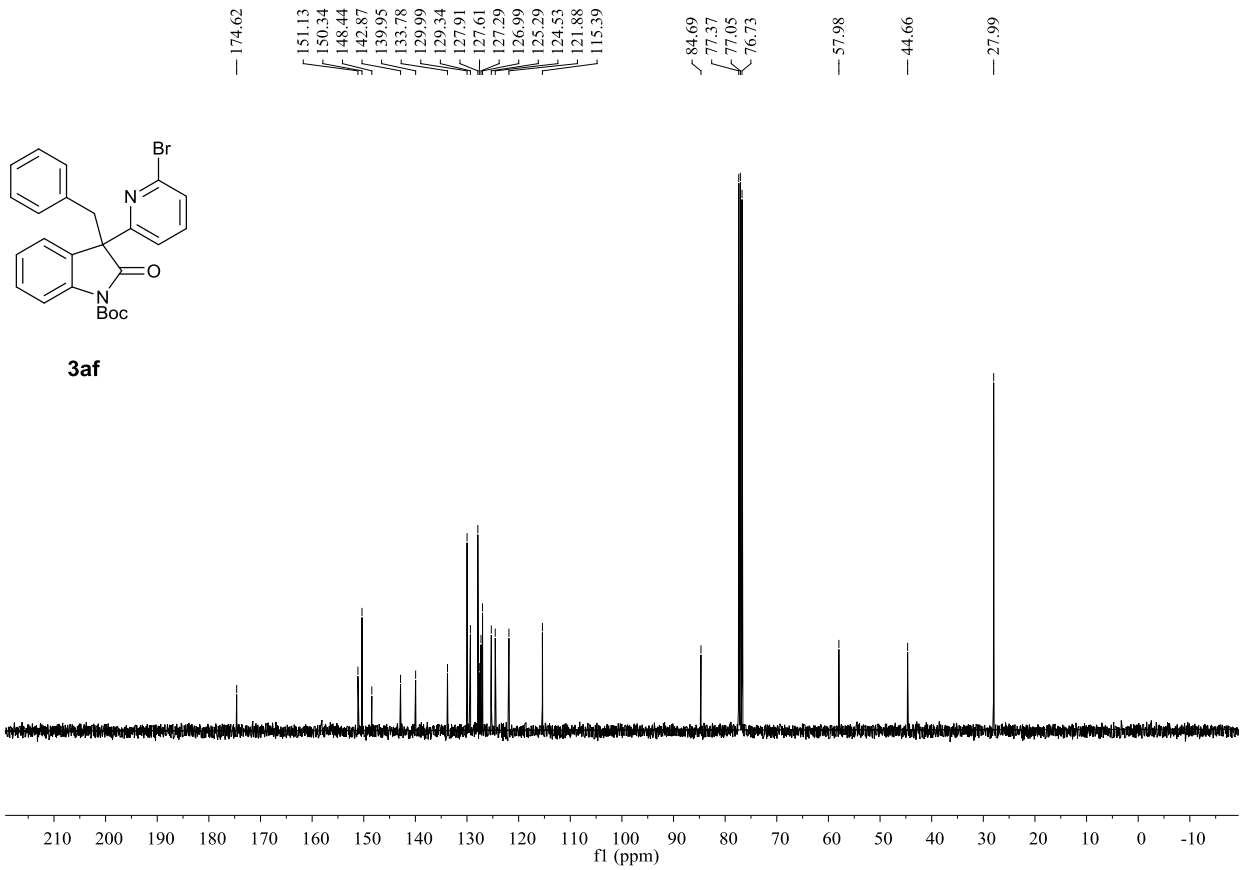
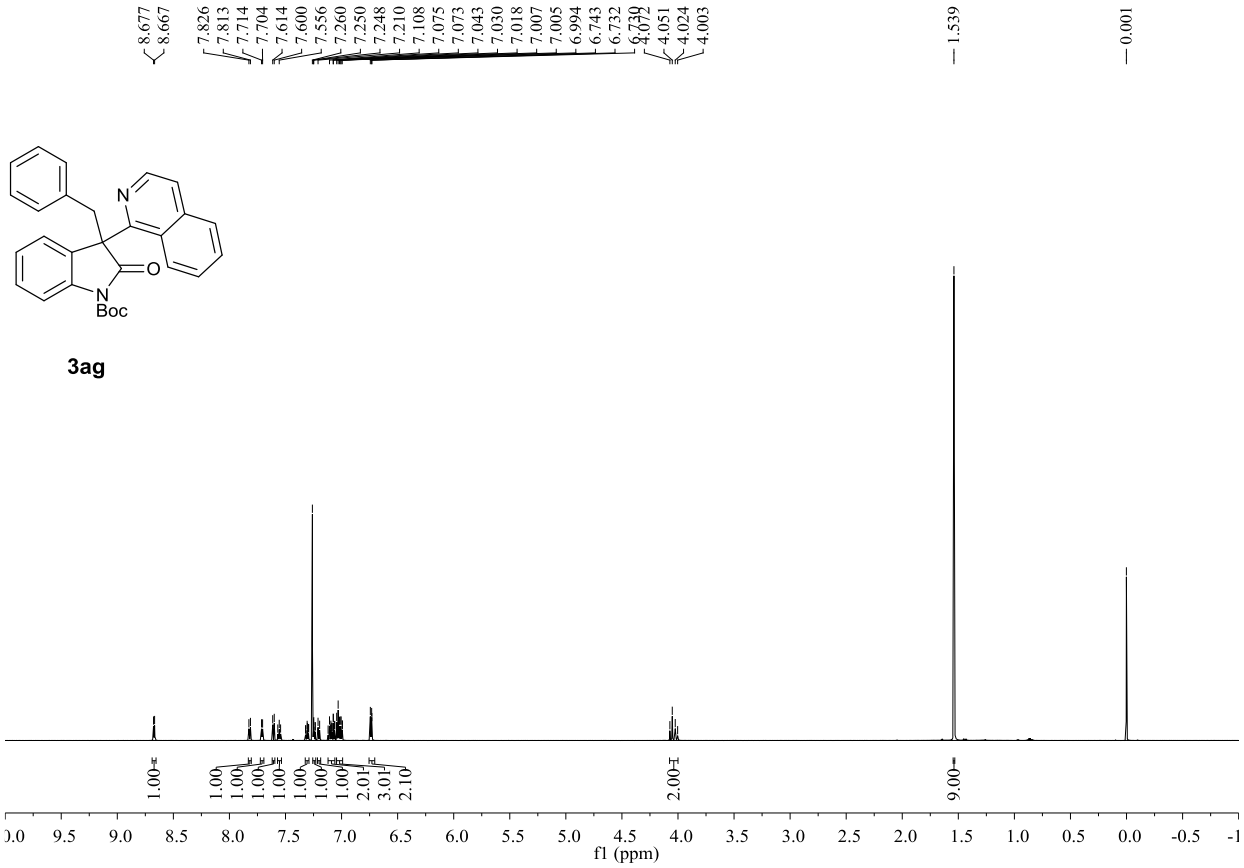
7.679
7.666
7.602
7.435
7.433
7.426
7.424
7.318
7.307
7.304
7.262
7.253
7.241
7.239
7.155
7.154
7.143
7.115
7.102
7.065
7.052
7.040
6.803
6.791
6.783
3.682
3.409
3.388
1.559
-0.000
Br
N
O
N
Boc
1.00
1.00
1.00
1.00
1.00
2.00
2.00
1.00
1.00
9.00
f1 (ppm)

3af


174.62
151.13
150.34
148.44
142.87
139.95
133.78
129.99
129.34
127.91
127.61
127.29
126.99
125.29
124.53
121.88
115.39
84.69
77.37
77.05
76.73
57.98
44.66
27.99
Br
N
O
N
Boc
f1 (ppm)

3af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8.667
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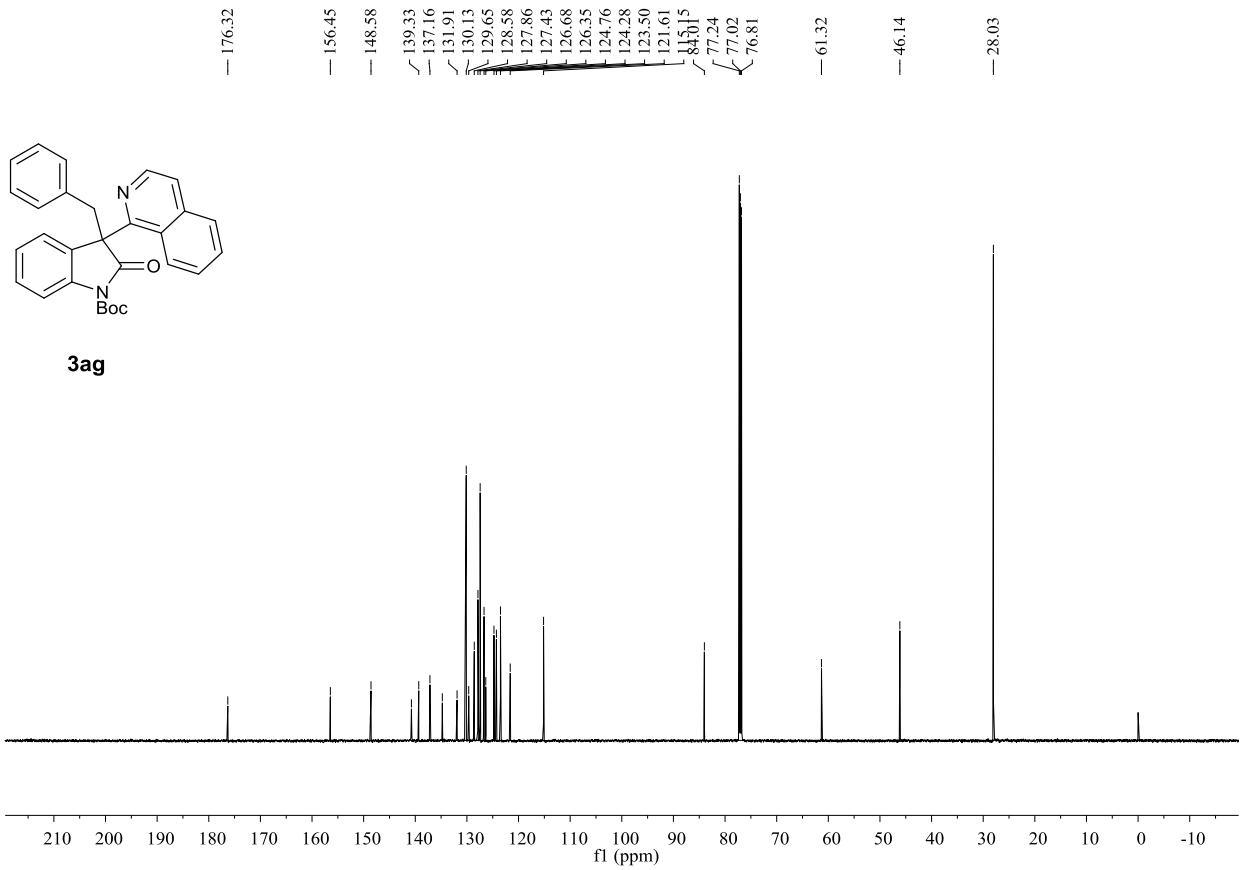
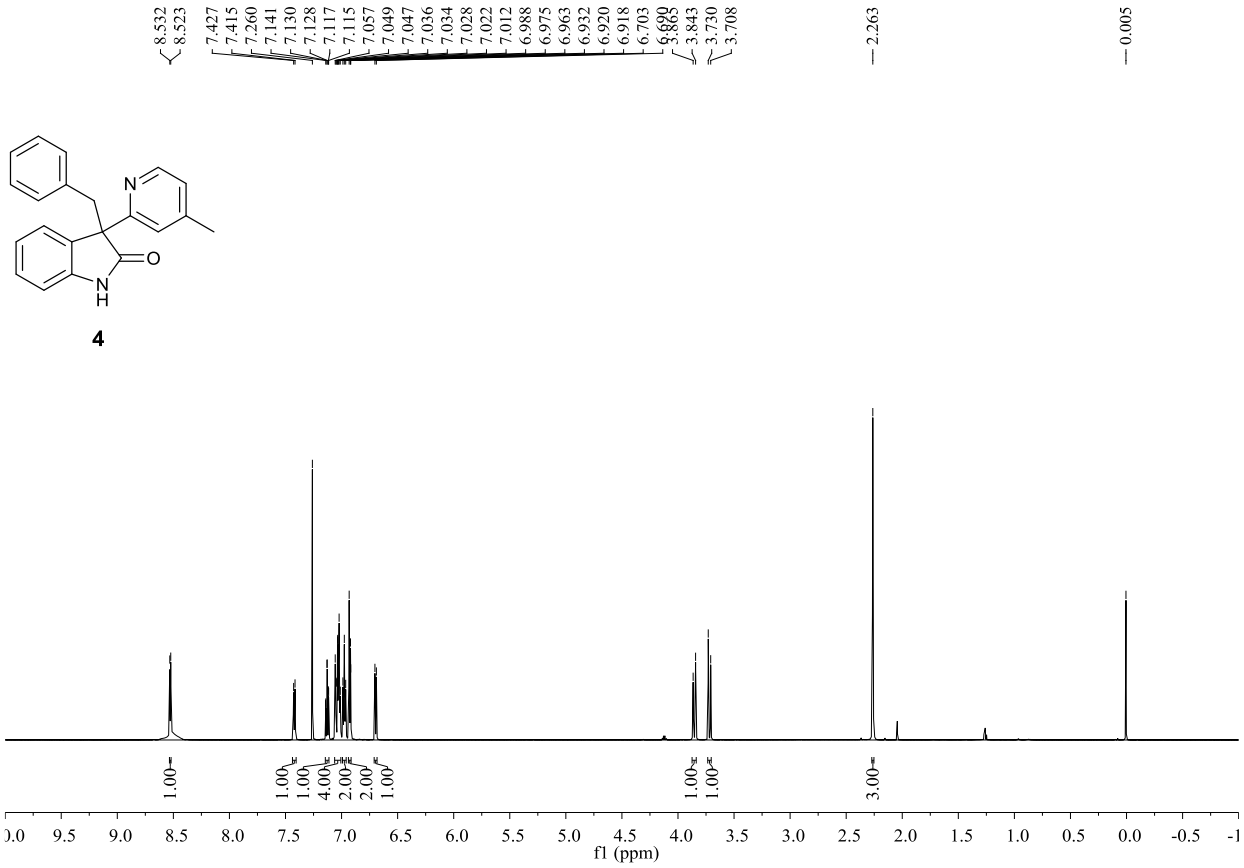
7.813
7.714
7.704
7.614
7.600
7.556
7.260
7.250
7.248
7.210
7.108
7.075
7.073
7.043
7.030
7.018
7.007
7.005
6.994
6.743
6.732
4.051
4.024
4.003
1.539
0.001
N
O
N
Boc
1.00
1.00
1.00
1.00
1.00
1.00
2.01
3.01
2.10
2.00
9.00
f1 (ppm)

3ag


176.32
156.45
148.58
139.33
137.16
131.91
130.13
129.65
128.58
127.86
127.43
126.68
126.35
124.76
124.28
123.50
121.61
115.15
84.01
77.24
77.02
76.81
61.32
46.14
28.03
N
O
N
Boc
f1 (ppm)

3ag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7.141
7.130
7.128
7.117
7.115
7.057
7.049
7.047
7.036
7.034
7.028
7.022
7.012
6.988
6.975
6.963
6.932
6.920
6.918
6.703
3.843
3.730
3.708
2.263
0.005
1.00
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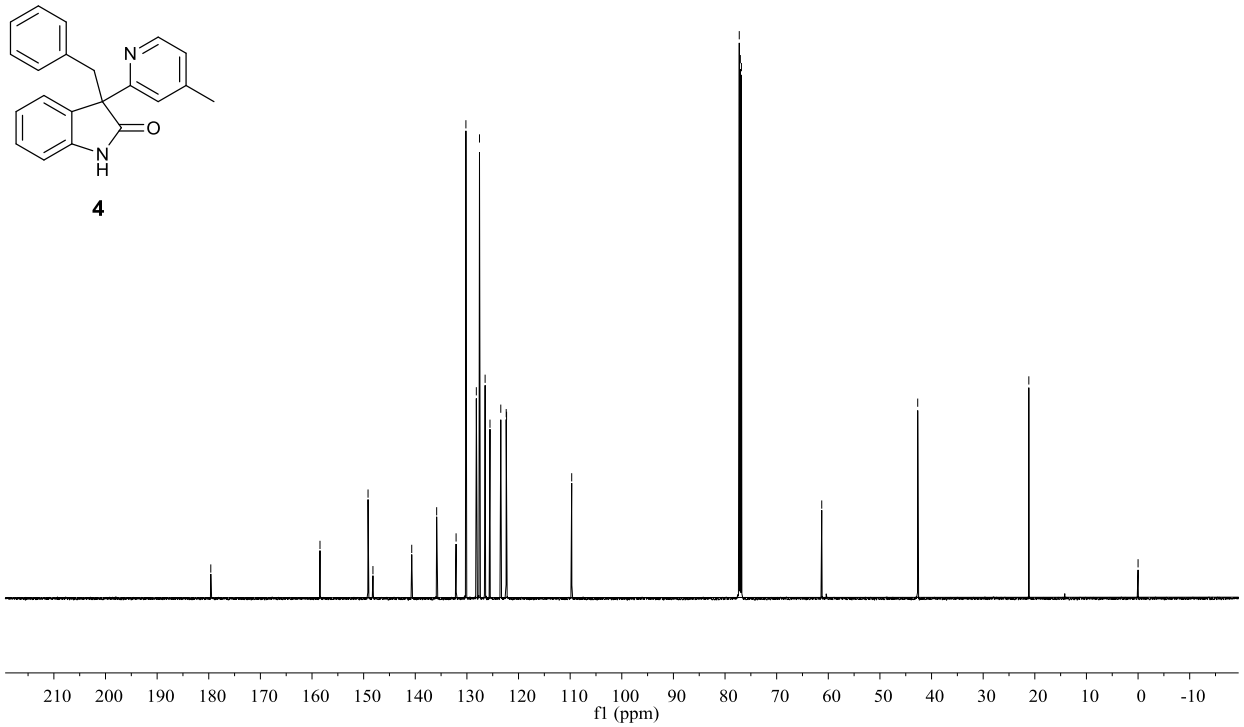
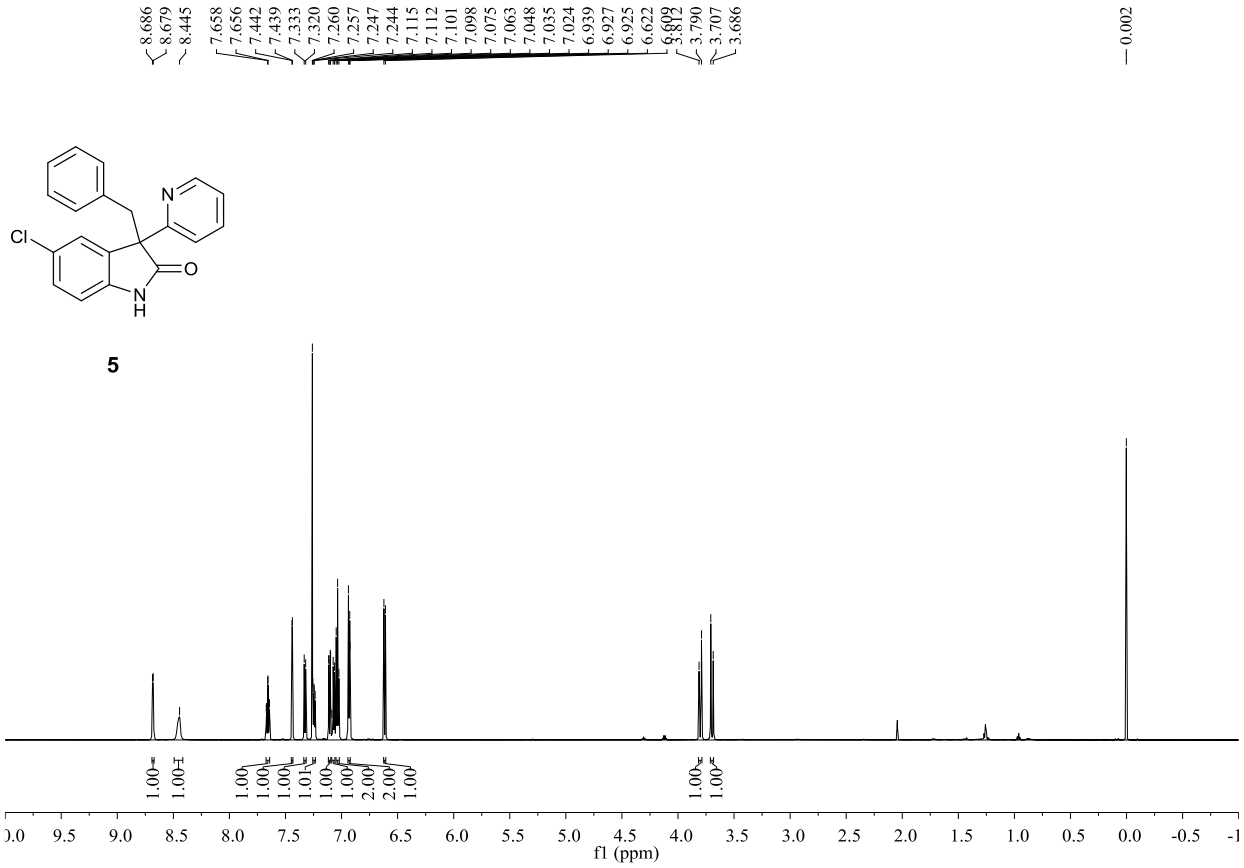
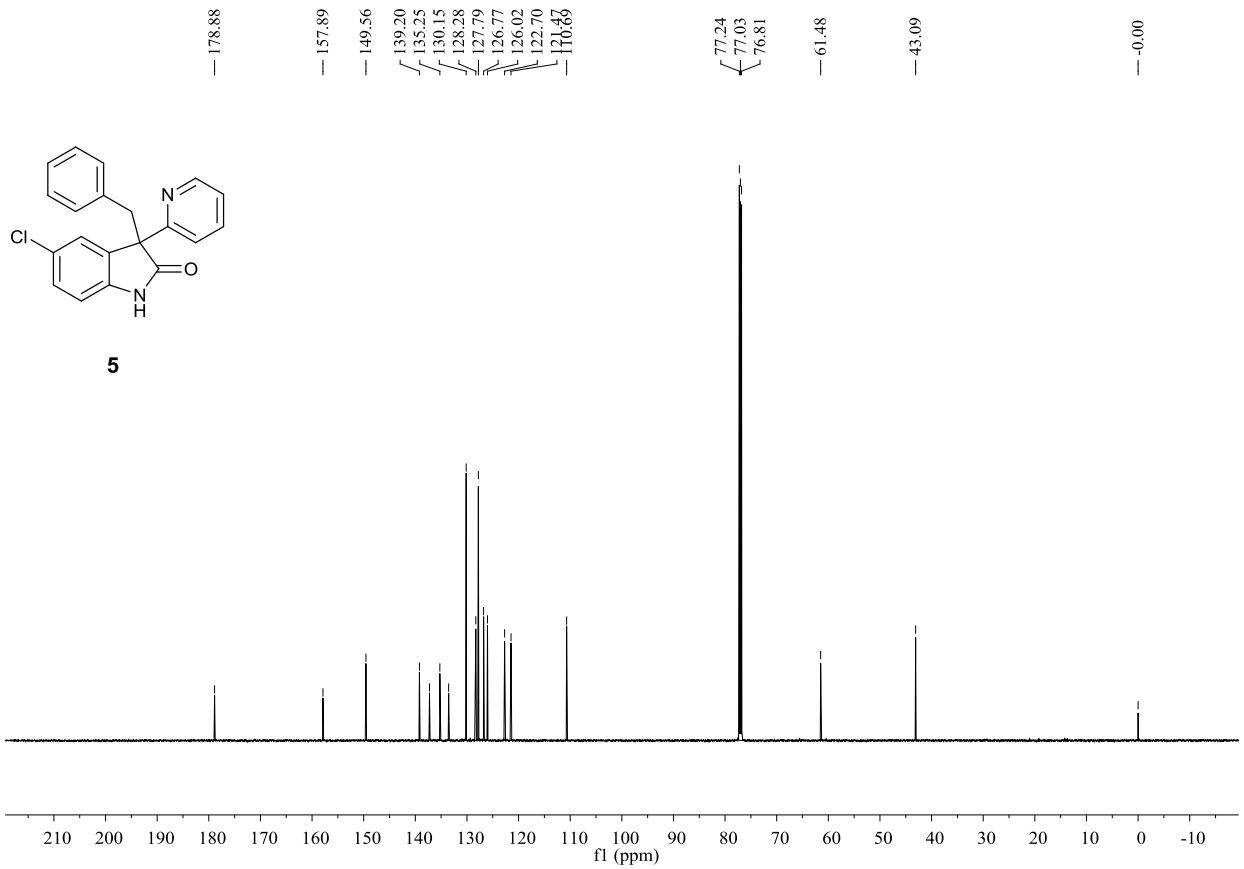
1.00
4.00
2.00
2.00
1.00
1.00
1.00
3.00
f1 (ppm)


179.61
158.46
149.15
135.85
132.09
130.19
128.17
127.56
126.47
125.53
123.44
122.39
122.32
109.70
77.25
77.04
76.82
61.27
42.68
21.16
-0.00
f1 (ppm)


8.686
8.679
8.445
7.658
7.656
7.442
7.439
7.333
7.320
7.260
7.257
7.247
7.244
7.115
7.112
7.101
7.098
7.075
7.063
7.048
7.035
7.024
6.939
6.927
6.925
6.622
6.609
3.812
3.790
3.707
3.686
0.002
Cl
N
O
N
H
1.00
1.00
1.00
1.00
1.01
1.00
1.00
2.00
2.00
1.00
1.00
1.00
f1 (ppm)

5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157.89
149.56
139.20
135.25
130.15
128.28
127.79
126.77
126.02
122.70
121.47
110.69
77.24
77.03
76.81
61.48
43.09
-0.00
Cl
N
O
N
H
f1 (ppm)

5