Supporting information

Lewis Acid-Catalyzed [4 + 2] Cycloaddition of Donor–Acceptor Cyclobutanes with Iminooxindoles: Access to Spiro[piperidine-3,2'-oxindoles]

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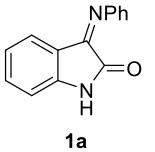
General information.

^{1}H NMR spectra, ^{13}C NMR spectra were recorded on a Bruker 400 MHz spectrometer in chloroform-d_3 or dmso-d_6. All signals are reported in ppm with the internal TMS signal at 0 ppm as a standard. The data is being reported as (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad signal, coupling constant(s) in Hz, integration). All reactions were carried out under an atmosphere of nitrogen in flame-dried glassware with magnetic stirring. All solvents were freshly distilled from CaH_2 prior to use. Lewis-acid purchased from Accela ChemBio Co. Ltd or J&K or Energy Chemical Company were used directly. 4 Å molecular sieves purchased from Sinopharm Chemical Reagent Co.,Ltd were powdered and dried at 300 ºC in muffle furnace for 8-10 hours prior to use. Bisoxazoline ligand (bis(S)-4-isopropyl-4,5-dihydrooxazol-2-yl)methane) was purchased from Energy Chemical Company and used directly.

Synthesis of substrates.

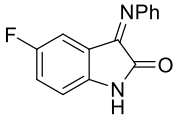
Cyclobutanes **2** were synthesized according to our previous method.[1] Iminooxindoles **1** were synthesized according to the literature, and the spectral data refer to the literature.[2] Chiral cyclobutane **2a** (ee = 85%) was synthesized according to the literature by using bis(S)-4-isopropyl-4,5-dihydrooxazol-2-yl)methane as ligand.[3]

Iminooxindoles **1**:



1a

E:Z=5:1
86%



1b

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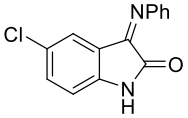
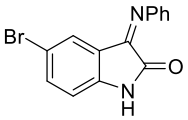


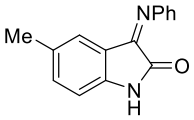
1c

E:Z=9:2
56%



1d

E:Z=9:2
74%



1e

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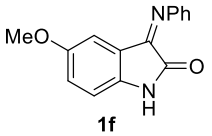
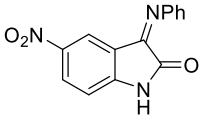


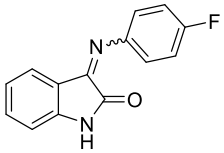
1f

E:Z=5:1
73%



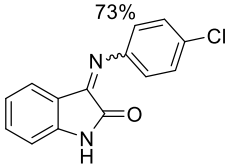
1g

E:Z=5:1
81%



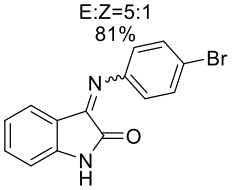
1h

E:Z=9:2
81%



1i

E:Z=4:1
88%



1j

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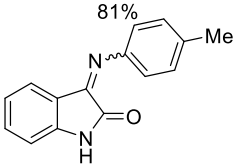
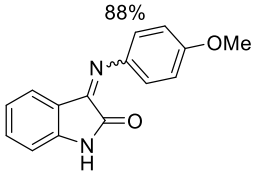


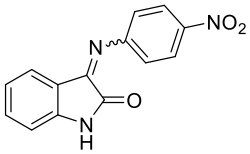
1k

E:Z=6:1
87%



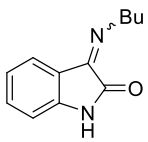
1l

E:Z=5:1
90%



1m

E:Z=2:1
62%



1n

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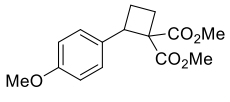
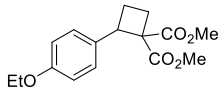
91%

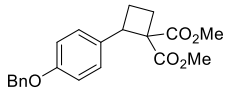
Cyclobutanes **2**:



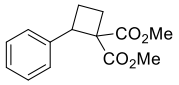
2a



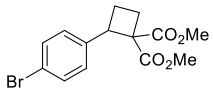
2b



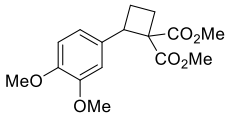
2c



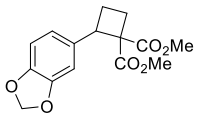
2d



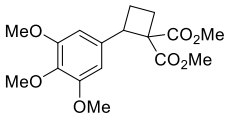
2e



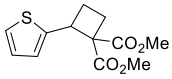
2f



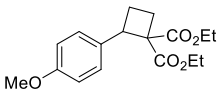
2g



2h



2i



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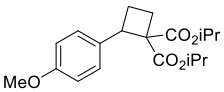


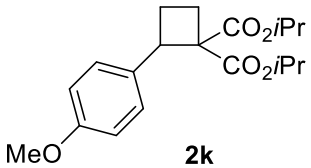
2k

Reference

1. H. Luo, J. Yan, Z. Chen, Y. Wei, B. Chen and Y. Liu, *ChemistrySelect*. 2020, **5**, 4074-4077.

2. A. A. Akaev, S. I. Bezzubov, V. G. Desyatkin, N. S. Vorobyeva, A. G. Majouga, M. Y. Melnikov and E. M. Budynina, *J. Org. Chem.*, 2019, **84**, 3340-3356.

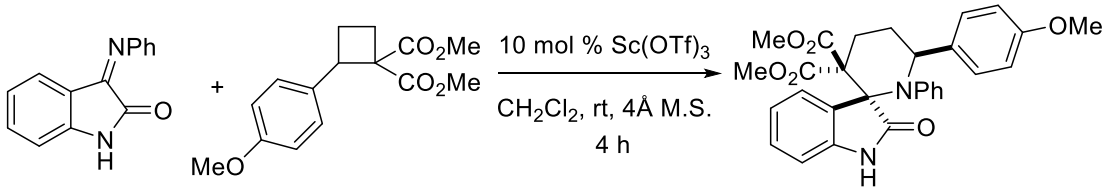
3. J. Hu, L. Feng, L. Wang, Z. Xie, Y. Tang and X. Li, *J. Am. Chem. Soc.*, 2016, **138**, 13151-13154.



2k

Cyclobutane **2k**, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.8 Hz, 2 H), 6.81 (d, *J* = 8.8 Hz, 2 H), 5.15-5.05 (m, 1 H), 4.66-4.60 (m, 1 H), 4.29 (t, *J* = 9.6 Hz, 1 H), 3.77 (s, 3 H), 2.67-2.48 (m, 2 H), 2.17-2.09 (m, 2 H), 1.25 (d, *J* = 6.4 Hz, 3 H), 1.23 (d, *J* = 6.4 Hz, 3 H), 0.99 (d, *J* = 6.4 Hz, 3 H), 0.58 (d, *J* = 6.4 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 169.1, 158.5, 131.5, 129.0, 113.3, 68.4, 59.5, 55.3, 44.1, 25.4, 21.7, 21.6, 21.5, 21.4, 20.8, 20.7 ; HRMS-ESI: $[M+Na]^+$ calcd for $C_{19}H_{26}O_5Na$: 357.1678, found: 357.1678.

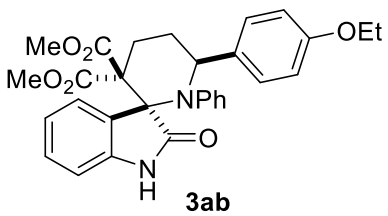
1. Typical procedure for $Sc(OTf)_3$ catalyzed [4+2] cycloaddition reaction.



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

A flame-dried schlenk tube (25 mL) was evacuated and recharged with N_2 for 3 times. Under N_2, the tube was charged with 10 mol % $Sc(OTf)_3$, 60 mg of activated 4Å molecular sieves powder (M S), iminooxindole **1a** (0.22 mmol, 49 mg), cyclobutane **2a** (0.2 mmol, 56 mg), dry CH_2Cl_2 (1.5 mL) at room temperature (rt). The reaction mixture was stirred at rt for 4 hours until the reaction was complete (monitored by TLC, hexanes:AcOEt = 5:1). The reaction mixture was passed over a plug of silica gel with 10 mL of CH_2Cl_2. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography, eluting with (hexanes:AcOEt = 4:1) to afford 82 mg (82%) of **3aa**, white solid, m.p. 228-230 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.6 Hz, 1 H), 7.34 (s, 1H), 7.25-7.10 (m, 2 H), 6.99-6.83 (m, 3 H), 6.76-6.55 (m, 5 H), 6.38 (d, *J* = 7.6 Hz, 1 H), 5.20 (dd, *J* = 12.0 Hz, 4.0 Hz, 1 H), 3.85 (s, 3 H), 3.64 (s, 3 H), 3.53 (s, 3 H), 3.35 (td, *J* = 14.0 Hz, 4.4 Hz, 1 H), 2.63-2.48 (m, 1 H), 2.42-2.33 (m, 1 H), 2.02-1.91 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.1, 170.0, 169.0, 157.8, 145.8, 140.9, 136.3, 129.3, 129.0, 128.8, 127.5, 126.9, 125.0, 121.4, 113.0, 108.8, 68.9, 58.9, 58.8, 54.9, 52.5, 52.1, 31.4, 26.5; HRMS-TOF-ES$^+$: $[M+H]^+$ calcd for $C_{29}H_{28}N_2O_6H$: 501.2025, found: 501.2026.

1. Synthesis of 3ab

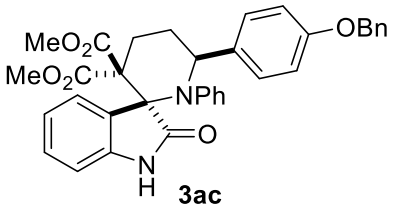


3ab

The reaction of iminooxindole **1a** (0.22 mmol, 49 mg), cyclobutane **2b** (0.2 mmol, 58 mg) and 60 mg of 4Å M.S. and 10 mol % $Sc(OTf)_3$ in dry CH_2Cl_2 (2.0 mL) was carried out at rt for 6 h, eluting with (hexanes:AcOEt = 4:1) to afford 74 mg (72%) of

3ab, white solid, m.p. 233-235 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.6 Hz, 1 H), 7.33 (s, 1 H), 7.25-7.10 (m, 2 H), 7.00-6.83 (m, 3 H), 6.75-6.53 (m, 5 H), 6.37 (d, *J* = 7.6 Hz, 1 H), 5.19 (dd, *J* = 12.0 Hz, 4.0 Hz, 1 H), 3.89-3.80 (m, 5 H), 3.53 (s, 3 H), 3.35 (td, *J* = 14.0 Hz, 4.4 Hz, 1 H), 2.62-2.48 (m, 1 H), 2.44-2.33 (m, 1 H), 2.00-1.91 (m, 1 H), 1.29 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.1, 170.0, 169.0, 157.2, 145.8, 140.9, 136.1, 129.3, 129.0, 128.8, 127.4, 126.9, 125.0, 121.4, 113.5, 108.8, 68.9, 63.0, 58.9, 52.5, 52.1, 31.4, 26.6, 14.8; HRMS-TOF-ES$^+$: $[M+H]^+$ calcd for $C_{30}H_{30}N_2O_6H$: 515.2182, found: 515.2179.

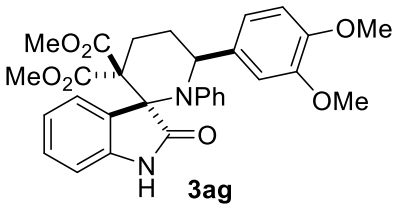
2. Synthesis of 3ac



3ac

The reaction of iminooxindole **1a** (0.22 mmol, 49 mg), cyclobutane **2c** (0.2 mmol, 71 mg) and 60 mg of 4Å M.S. and 10 mol % $Sc(OTf)_3$ in dry CH_2Cl_2 (2.0 mL) was carried out at rt for 6 h, eluting with (hexanes:AcOEt = 4:1) to afford 77 mg (67%) of **3ac**, white solid, m.p. 232-234 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.6 Hz, 1 H), 7.35-7.16 (m, 8 H), 7.00-6.83 (m, 3 H), 6.75-6.61 (m, 5 H), 6.37 (d, *J* = 7.6 Hz, 1 H), 5.20 (dd, *J* = 12.0 Hz, 4.0 Hz, 1 H), 4.87 (s, 2 H), 3.85 (s, 3 H), 3.53 (s, 3 H), 3.35 (td, *J* = 14.0 Hz, 4.4 Hz, 1 H), 2.62-2.48 (m, 1 H), 2.42-2.33 (m, 1 H), 2.02-1.92 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.1, 170.0, 169.0, 157.1, 145.8, 140.9, 137.1, 136.6, 129.4, 128.8, 128.4, 127.8, 127.5, 127.4, 126.9, 125.1, 121.4, 113.9, 108.8, 69.8, 68.9, 58.9, 52.5, 52.1, 31.4, 26.5; HRMS-TOF-ES$^+$: $[M+H]^+$ calcd for $C_{35}H_{32}N_2O_6H$: 577.2339, found: 577.2340.

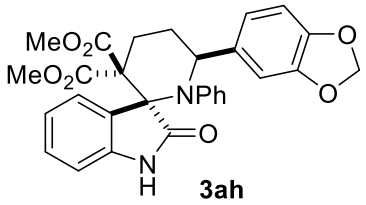
3. Synthesis of 3ag



3ag

The reaction of iminooxindole **1a** (0.22 mmol, 49 mg), cyclobutane **2g** (0.2 mmol, 62 mg) and 60 mg of 4Å M.S. and 10 mol % $Sc(OTf)_3$ in dry CH_2Cl_2 (2.0 mL) was carried out at rt for 4 h, eluting with (CH_2Cl_2:MeOH = 80:1) to afford 92 mg (86%) of **3ag**, white solid, m.p. 211-213 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.6 Hz, 1 H), 7.33 (s, 1 H), 7.02-6.85 (m, 4 H), 6.81-6.61 (m, 4 H), 6.52 (d, *J* = 7.6 Hz, 1 H), 6.37 (d, *J* = 7.6 Hz, 1 H), 5.20 (dd, *J* = 12.0 Hz, 4.0 Hz, 1 H), 3.84 (s, 3 H), 3.81 (s, 3 H), 3.71 (s, 3 H), 3.53 (s, 3 H), 3.35 (td, *J* = 14.0 Hz, 4.4 Hz, 1 H), 2.62-2.48 (m, 1 H), 2.42-2.33 (m, 1 H), 2.04-1.94 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.0, 170.0, 168.9, 148.1, 147.1, 145.7, 140.9, 136.8, 129.0, 128.8, 127.4, 126.9, 125.1, 121.4, 120.4, 111.5, 110.0, 108.8, 68.9, 59.1, 58.9, 55.5, 52.5, 52.1, 31.4, 26.5; HRMS-TOF-ES$^+$: $[M+H]^+$ calcd for $C_{30}H_{30}N_2O_7H$: 531.2133, found: 531.2130.

4. Synthesis of 3ah

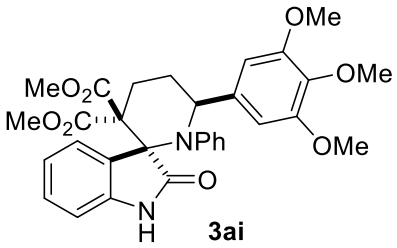


3ah

The reaction of iminooxindole **1a** (0.22 mmol, 49 mg), cyclobutane **2h** (0.2 mmol, 58.4 mg) and 60 mg of 4Å M.S. and 20 mol % $Sc(OTf)_3$ in dry CH_2Cl_2 (2.0 mL) was carried out at rt for 19 h, eluting with (CH_2Cl_2:MeOH = 80:1) to afford 72 mg (70%) of **3ah**, white solid, m.p. 212-214 °C.. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.6 Hz, 1 H), 7.23 (s, 1 H), 6.99-6.85 (m, 4 H), 6.77-6.61 (m, 4 H), 6.45 (d, *J* = 8.0 Hz, 1 H), 6.36 (dd, *J* = 7.6 Hz, 0.8 Hz, 1 H), 5.78 (s, 2 H), 5.17 (dd, *J* = 12.0 Hz, 4.0 Hz, 1 H), 3.85 (s, 3 H), 3.52 (s, 3 H), 3.34 (td, *J* = 14.0 Hz, 4.4 Hz, 1 H), 2.62-2.45 (m, 1 H), 2.42-2.33 (m, 1 H), 2.02-1.93 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.0, 170.0, 168.9, 145.7, 145.6, 140.9, 138.3, 129.0, 128.8, 127.5, 126.9, 125.1, 121.6, 121.5,

108.7, 100.5, 68.9, 59.3, 58.9, 52.5, 52.1, 31.5, 26.5; HRMS-TOF-ES$^+$: $[M+H]^+$ calcd for $C_{29}H_{26}N_2O_7H$: 515.1818, found: 515.1815.

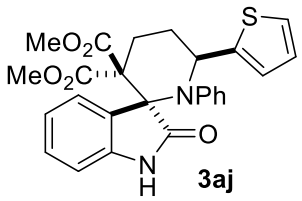
5. Synthesis of 3ai



3ai

The reaction of iminooxindole **1a** (0.22 mmol, 49 mg), cyclobutane **2i** (0.2 mmol, 68 mg) and 60 mg of 4Å M.S. and 30 mol % $Sc(OTf)_3$ in dry CH_2Cl_2 (2.0 mL) was carried out at rt for 13 h, eluting with (CH_2Cl_2:MeOH = 80:1) to afford 75 mg (67%) of **3ai**, white solid, m.p. 213-215 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.6 Hz, 1 H), 7.33 (s, 1 H), 7.02-6.85 (m, 4 H), 6.75-6.55 (m, 5 H), 6.38 (d, *J* = 7.6 Hz, 1 H), 5.20 (dd, *J* = 12.0 Hz, 4.0 Hz, 1 H), 3.84 (s, 3 H), 3.74 (s, 6 H), 3.68 (s, 3 H), 3.52 (s, 3 H), 3.34 (td, *J* = 14.0 Hz, 4.4 Hz, 1 H), 2.56-2.45 (m, 1 H), 2.42-2.33 (m, 1 H), 2.04-1.97 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.0, 170.0, 168.9, 152.4, 145.6, 141.0, 139.9, 136.2, 129.0, 128.9, 127.5, 126.9, 125.2, 121.5, 108.9, 105.6, 69.0, 60.7, 59.8, 58.9, 56.0, 52.6, 52.1, 31.4, 26.6; HRMS-TOF-ES$^+$: $[M+H]^+$ calcd for $C_{31}H_{32}N_2O_8H$: 561.2237, found: 561.2234.

6. Synthesis of 3aj

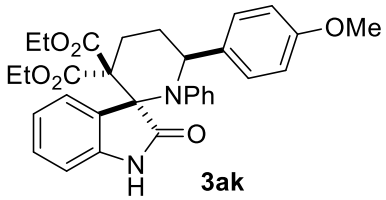


3aj

The reaction of iminooxindole **1a** (0.22 mmol, 49 mg), cyclobutane **2j** (0.2 mmol, 51 mg) and 60 mg of 4Å M.S. and 20 mol % $Sc(OTf)_3$ in dry CH_2Cl_2 (2.0 mL) was carried out at rt for 5.5 h, eluting with (hexanes:AcOEt:DCM = 4:1:1) to afford 44 mg (46%) of **3aj**, white solid, m.p. 240-242 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.0 Hz, 1 H), 7.14 (s, 1 H), 7.00-6.92 (m, 2 H), 6.90-6.65 (m, 5 H), 6.64 (dd, *J* = 3.6

Hz, 1.2 Hz, 1 H), 6.60-6.54 (m, 1 H), 6.38 (d, *J* = 7.6 Hz, 1 H), 5.59 (dd, *J* = 12.0 Hz, 4.0 Hz, 1 H), 3.87 (s, 3 H), 3.54 (s, 3 H), 3.32 (td, *J* = 14.0 Hz, 4.4 Hz, 1 H), 2.81-2.67 (m, 1 H), 2.45-2.37 (m, 1 H), 2.19-2.11 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.1, 169.9, 168.9, 148.1, 145.5, 140.9, 128.8, 128.7, 127.7, 126.9, 125.6, 125.4, 125.3, 124.1, 121.5, 108.8, 68.9, 58.8, 55.1, 52.6, 52.2, 32.3, 26.5; HRMS-TOF-ES$^+$: $[M+H]^+$ calcd for $C_{26}H_{24}N_2O_5SH$: 477.1484, found: 477.1485.

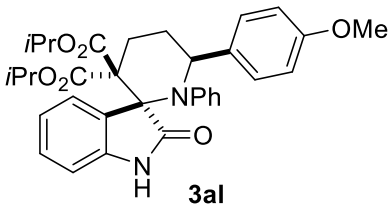
7. Synthesis of 3ak



3ak

The reaction of iminooxindole **1a** (0.22 mmol, 49 mg), cyclobutane **2k** (0.2 mmol, 61 mg) and 60 mg of 4Å M.S. and 10 mol % $Sc(OTf)_3$ in dry CH_2Cl_2 (2.0 mL) was carried out at rt for 13 h, eluting with (hexanes:AcOEt = 4:1) to afford 61 mg (58%) of **3ak**, white solid, m.p. 220-222 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.6 Hz, 1 H), 7.35 (s, 1 H), 7.25-7.10 (m, 2 H), 6.99-6.81 (m, 3 H), 6.78-6.55 (m, 5 H), 6.36 (d, *J* = 7.6 Hz, 1 H), 5.22 (dd, *J* = 11.6 Hz, 3.6 Hz, 1 H), 4.40-4.23 (m, 2 H), 4.02-3.88 (m, 2 H), 3.64 (s, 3 H), 3.40 (td, *J* = 14.0 Hz, 4.4 Hz, 1 H), 2.48-2.32 (m, 2 H), 2.01-1.91 (m, 1 H), 1.30 (t, *J* = 7.2 Hz, 3 H), 0.96 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.1, 169.4, 168.6, 157.8, 146.0, 140.9, 136.4, 129.3, 129.2, 128.6, 128.1, 126.9, 125.0, 121.4, 113.0, 108.7, 69.1, 61.3, 61.0, 58.9, 54.9, 31.6, 26.4, 14.0, 13.4; HRMS-TOF-ES$^+$: $[M+H]^+$ calcd for $C_{31}H_{32}N_2O_6H$: 529.2339, found: 529.2337.

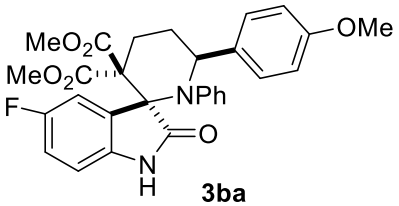
8. Synthesis of 3al



3al

The reaction of iminooxindole **1a** (0.22 mmol, 49 mg), cyclobutane **2l** (0.2 mmol, 67 mg) and 60 mg of 4Å M.S. and 10 mol % $Sc(OTf)_3$ in dry CH_2Cl_2 (2.0 mL) was carried out at rt for 13 h, eluting with (hexanes:AcOEt = 4:1) to afford 79 mg (70%) of **3al**, white solid, m.p. 231-233 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.6 Hz, 1 H), 7.32-7.14 (m, 3 H), 6.99-6.82 (m, 3 H), 6.78-6.55 (m, 5 H), 6.33 (d, *J* = 7.6 Hz, 1 H), 5.28-5.20 (m, 2 H), 4.85-4.75 (m, 1 H), 3.64 (s, 3 H), 3.46 (td, *J* = 14.0 Hz, 4.4 Hz, 1 H), 2.37-2.23 (m, 2 H), 2.01-1.94 (m, 1 H), 1.32 (d, *J* = 6.0 Hz, 3 H), 1.25 (d, *J* = 6.0 Hz, 3 H), 1.01 (d, *J* = 6.0 Hz, 3 H), 0.82 (d, *J* = 6.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 168.7, 168.0, 157.8, 146.1, 140.7, 136.5, 129.3, 129.2, 128.9, 128.5, 126.9, 125.0, 121.1, 113.0, 108.6, 69.3, 68.8, 68.7, 59.0, 58.9, 54.9, 31.8, 26.4, 21.7, 21.6, 21.2, 20.7; HRMS-TOF-ES$^+$: $[M+H]^+$ calcd for $C_{33}H_{36}N_2O_6H$: 557.2654, found: 557.2653.

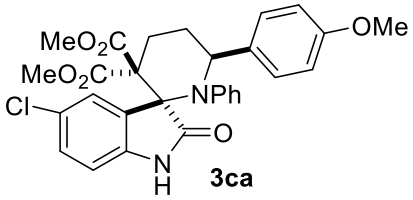
9. Synthesis of 3ba



3ba

The reaction of iminooxindole **1b** (0.22 mmol, 53 mg), cyclobutane **2a** (0.2 mmol, 56 mg) and 60 mg of 4Å M.S. and 10 mol % $Sc(OTf)_3$ in dry CH_2Cl_2 (2.0 mL) was carried out at rt for 4 h, eluting with (hexanes:AcOEt = 4:1) to afford 79 mg (76%) of **3ba**, white solid, m.p. 240-242 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 1 H), 7.33-7.15 (m, 3 H), 7.00-6.55 (m, 7 H), 6.31 (dd, *J* = 8.4, 4.0 Hz, 1 H), 5.17 (dd, *J* = 12.0 Hz, 4.0 Hz, 1 H), 3.86 (s, 3 H), 3.64 (s, 3 H), 3.53 (s, 3 H), 3.38 (td, *J* = 14.0 Hz, 4.4 Hz, 1 H), 2.53-2.31 (m, 2 H), 2.02-1.92 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.2, 169.9, 168.7, 158.3 (d, *J* = 237 Hz), 157.9, 145.7, 136.8, 135.9, 130.7 (d, *J* = 8.2 Hz), 129.3, 127.2, 125.3, 115.8 (d, *J* = 25.7 Hz), 115.1 (d, *J* = 23.5 Hz), 113.0, 109.0 (d, *J* = 8.0 Hz), 69.4, 59.0, 54.9, 52.6, 52.3, 31.4, 26.4; ^{19}F NMR (300 MHz, $CDCl_3$) δ -121.1; HRMS-TOF-ES$^+$: $[M+H]^+$ calcd for $C_{29}H_{27}FN_2O_6H$: 519.1931, found: 519.1927.

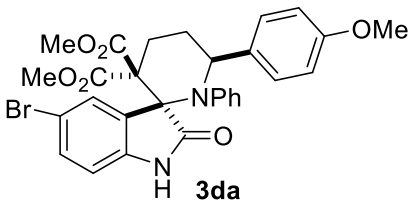
10. Synthesis of 3ca



3ca

The reaction of iminooxindole **1c** (0.22 mmol, 57 mg), cyclobutane **2a** (0.2 mmol, 56 mg) and 60 mg of 4Å M.S. and 10 mol % $Sc(OTf)_3$ in dry CH_2Cl_2 (2.0 mL) was carried out at rt for 4 h, eluting with (hexanes:AcOEt = 4:1) to afford 77 mg (72%) of **3ca**, white solid, 243-245 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (s, 1 H), 7.42 (d, *J* = 2.0 Hz, 1 H), 7.25-7.10 (m, 2 H), 6.95 (dd, *J* = 8.4, 2.0 Hz, 1 H), 6.78-6.55 (m, 6 H), 6.31 (d, *J* = 8.4 Hz, 1 H), 5.14 (dd, *J* = 12.0 Hz, 4.0 Hz, 1 H), 3.87 (s, 3 H), 3.64 (s, 3 H), 3.55 (s, 3 H), 3.30 (td, *J* = 14.0 Hz, 4.4 Hz, 1 H), 2.65-2.51 (m, 1 H), 2.45-2.35 (m, 1 H), 2.02-1.92 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.0, 170.0, 168.7, 157.9, 145.5, 139.6, 135.9, 130.8, 129.3, 128.6, 127.9, 127.1, 126.8, 125.3, 113.0, 109.7, 69.0, 58.9, 58.8, 54.9, 52.6, 52.2, 31.2, 26.5; HRMS-TOF-ES$^+$: $[M+H]^+$ calcd for $C_{29}H_{27}ClN_2O_6H$: 535.1636, found: 535.1633.

11. Synthesis of 3da

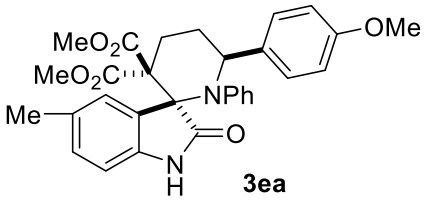


3da

The reaction of iminooxindole **1d** (0.22 mmol, 66 mg), cyclobutane **2a** (0.2 mmol, 56 mg) and 60 mg of 4Å M.S. and 10 mol % $Sc(OTf)_3$ in dry CH_2Cl_2 (2.0 mL) was carried out at rt for 4 h, eluting with (hexanes:AcOEt = 4:1) to afford 77 mg (67%) of **3da**, white solid, 250-252 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 1 H), 7.52 (d, *J* = 2.0 Hz, 1 H), 7.25-7.10 (m, 2 H), 7.09 (dd, *J* = 8.4, 2.0 Hz, 1 H), 6.90-6.55 (m, 6 H), 6.27 (d, *J* = 8.4 Hz, 1 H), 5.14 (dd, *J* = 12.0 Hz, 3.6 Hz, 1 H), 3.87 (s, 3 H), 3.64 (s, 3

H), 3.56 (s, 3 H), 3.28 (td, *J* = 14.0 Hz, 4.4 Hz, 1 H), 2.69-2.55 (m, 1 H), 2.45-2.35 (m, 1 H), 2.00-1.90 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 170.0, 168.7, 157.9, 145.5, 140.1, 135.9, 131.4, 131.1, 130.6, 129.3, 127.1, 125.3, 114.0, 113.0, 110.2, 68.9, 58.9, 58.7, 54.9, 52.6, 52.2, 31.2, 26.5; HRMS-TOF-ES$^+$: $[M+H]^+$ calcd for $C_{29}H_{27}{}^{79}BrN_2O_6H$: 579.1131, found: 579.1130.

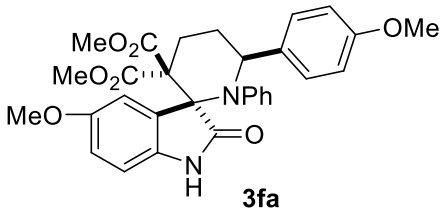
12. Synthesis of 3ea



3ea

The reaction of iminooxindole **1e** (0.22 mmol, 52 mg), cyclobutane **2a** (0.2 mmol, 56 mg) and 60 mg of 4Å M.S. and 10 mol % $Sc(OTf)_3$ in dry CH_2Cl_2 (2.0 mL) was carried out at rt for 2.5 h, eluting with (hexanes:AcOEt = 4:1) to afford 69 mg (67%) of **3ea**, white solid, m.p. 245-247 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.15 (m, 4 H), 6.87-6.54 (m, 7 H), 6.25 (d, *J* = 8.0 Hz, 1 H), 5.19 (dd, *J* = 12.0 Hz, 3.6 Hz, 1 H), 3.85 (s, 3 H), 3.64 (s, 3 H), 3.55 (s, 3 H), 3.30 (td, *J* = 14.0 Hz, 4.4 Hz, 1 H), 2.68-2.60 (m, 1 H), 2.45-2.35 (m, 1 H), 2.27 (s, 3 H), 2.00-1.91 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.2, 170.1, 169.1, 157.8, 145.8, 138.6, 136.4, 130.5, 139.3, 129.0 (2C), 128.0, 126.8, 125.0, 68.9, 58.8, 58.7, 54.9, 52.5, 52.0, 31.4, 26.6, 21.3; HRMS-TOF-ES$^+$: $[M+H]^+$ calcd for $C_{30}H_{30}N_2O_6H$: 515.2182, found: 515.2180.

13. Synthesis of 3fa

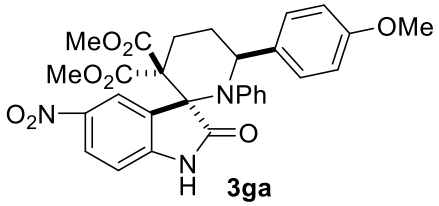


3fa

The reaction of iminooxindole **1f** (0.22 mmol, 55.4 mg), cyclobutane **2a** (0.2 mmol, 56 mg) and 60 mg of 4Å M.S. and 10 mol % $Sc(OTf)_3$ in dry CH_2Cl_2 (2.0 mL) was carried out at rt for 13 h, eluting with (hexanes:AcOEt = 4:1) to afford 71 mg (67%)

of **3fa**, white solid, 214-216 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.12 (m, 4 H), 7.00-6.88 (m, 1 H), 6.77-6.69 (m, 2 H), 6.66-6.61 (m, 1 H), 6.58-6.55 (m, 2 H), 6.53-6.48 (m, 1 H), 6.26 (d, *J* = 8.4 Hz, 1 H), 5.19 (dd, *J* = 12.0 Hz, 3.6 Hz, 1 H), 3.86 (s, 3 H), 3.75 (s, 3 H), 3.64 (s, 3 H), 3.53 (s, 3 H), 3.38 (td, *J* = 14.0 Hz, 4.4 Hz, 1 H), 2.55-2.30 (m, 2 H), 2.01-1.91 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.2, 170.0, 168.9, 157.9, 155.0, 145.9, 136.3, 134.5, 130.4, 129.4, 127.0, 125.1, 69.4, 59.0, 55.0, 52.5, 52.2, 31.5, 26.6; HRMS-TOF-ES^{+}: $[M+H]^{+}$ calcd for $C_{30}H_{30}N_2O_7H$: 531.2131, found: 531.2132.

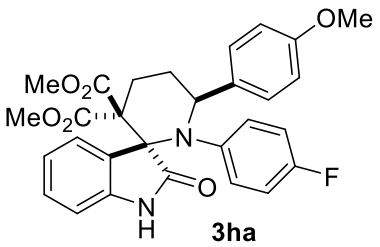
14. Synthesis of 3ga



3ga

The reaction of iminooxindole **1g** (0.22 mmol, 59 mg), cyclobutane **2a** (0.2 mmol, 56 mg) and 60 mg of 4Å M.S. and 10 mol % $Sc(OTf)_3$ in dry CH_2Cl_2 (2.0 mL) was carried out at rt for 13 h, eluting with (hexanes:AcOEt = 4:1) to afford 80 mg (73%) of **3ga**, white solid, m.p. 262-264 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 2.4 Hz, 1 H), 7.98-7.92 (m, 1 H), 7.77-7.70 (m, 1 H), 7.25-7.12 (m, 2 H), 6.82-6.55 (m, 6 H), 6.48 (d, *J* = 8.4 Hz, 1 H), 5.11 (dd, *J* = 12.0 Hz, 3.6 Hz, 1 H), 3.92 (s, 3 H), 3.64 (s, 3 H), 3.58 (s, 3 H), 3.23 (td, *J* = 14.0 Hz, 4.4 Hz, 1 H), 2.78-2.66 (m, 1 H), 2.52-2.47 (m, 1 H), 2.01-1.94 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.2, 170.2, 168.5, 158.0, 147.0, 129.4, 127.4, 125.8, 125.7, 123.4, 113.1, 108.6, 68.6, 59.0, 58.8, 55.0, 52.8, 52.6, 31.0, 26.5; HRMS-TOF-ES^{+}: $[M+H]^{+}$ calcd for $C_{29}H_{27}N_3O_8H$: 546.1876, found: 546.1880.

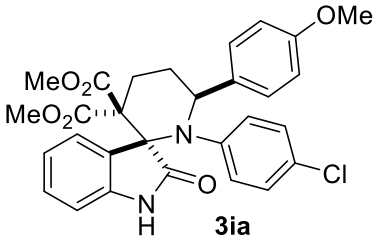
15. Synthesis of 3ha



3ha

The reaction of iminooxindole **1h** (0.22 mmol, 53 mg), cyclobutane **2a** (0.2 mmol, 56 mg) and 60 mg of 4Å M.S. and 10 mol % $Sc(OTf)_3$ in dry CH_2Cl_2 (2.0 mL) was carried out at rt for 4.5 h, eluting with (hexanes:AcOEt = 4:1) to afford 70 mg (68%) of **3ha**, white solid, m.p. 240-242 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 1 H), 7.41 (d, *J* = 7.6 Hz, 1 H), 7.25-7.10 (m, 2 H), 7.02-6.84 (m, 3 H), 6.63-6.24 (m, 5 H), 5.12 (dd, *J* = 12.0 Hz, 4.0 Hz, 1 H), 3.84 (s, 3 H), 3.66 (s, 3 H), 3.52 (s, 3 H), 3.33 (td, *J* = 14.0 Hz, 4.4 Hz, 1 H), 2.61-2.45 (m, 1 H), 2.42-2.33 (m, 1 H), 2.01-1.91 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.1, 170.0, 168.9, 159.6 (d, *J* = 242 Hz), 157.9, 141.7, 140.9, 136.0, 129.3, 128.9, 128.8, 127.3, 121.5, 113.6 (d, *J* = 21.7 Hz), 113.1, 109.0, 68.9, 59.1, 58.8, 55.0, 52.6, 52.2, 31.3, 26.5; ^{19}F NMR (300 MHz, $CDCl_3$) δ -116.8; HRMS-TOF-ES$^+$: $[M+H]^+$ calcd for $C_{29}H_{27}FN_2O_6H$: 519.1931, found: 519.1931.

16. Synthesis of 3ia

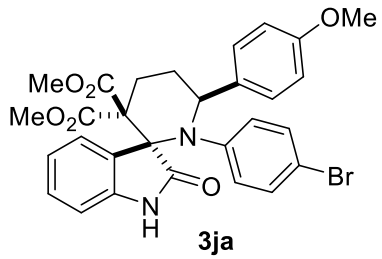


3ia

The reaction of iminooxindole **1i** (0.22 mmol, 57 mg), cyclobutane **2a** (0.2 mmol, 56 mg) and 60 mg of 4Å M.S. and 10 mol % $Sc(OTf)_3$ in dry CH_2Cl_2 (2.0 mL) was carried out at rt for 3.5 h, eluting with (hexanes:AcOEt = 4:1) to afford 78 mg (73%) of **3ia**, white solid, 244-246 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (s, 1 H), 7.40 (d, *J* = 3.6 Hz, 1 H), 7.25-7.10 (m, 2 H), 7.04-6.75 (m, 3 H), 6.70-6.56 (m, 4 H), 6.42 (d, *J* = 7.2 Hz, 1 H), 5.14 (dd, *J* = 12.0 Hz, 4.0 Hz, 1 H), 3.84 (s, 3 H), 3.67 (s, 3 H), 3.52

(s, 3 H), 3.32 (td, *J* = 14.0 Hz, 4.4 Hz, 1 H), 2.60-2.45 (m, 1 H), 2.41-2.32 (m, 1 H), 2.01-1.91 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 170.0, 168.9, 158.0, 144.6, 140.9, 135.8, 130.4, 129.2, 129.1, 128.7, 127.3, 127.1, 121.6, 113.2, 109.1, 68.9, 58.9, 58.8, 55.0, 52.6, 52.2, 31.3, 26.5; HRMS-TOF-ES$^+$: $[M+H]^+$ calcd for $C_{29}H_{27}ClN_2O_6H$: 535.1636, found: 535.1636.

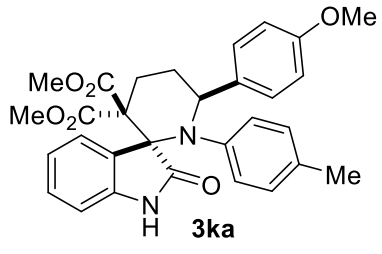
17. Synthesis of 3ja



3ja

The reaction of iminooxindole **1j** (0.22 mmol, 66 mg), cyclobutane **2a** (0.2 mmol, 56 mg) and 60 mg of 4Å M.S. and 10 mol % $Sc(OTf)_3$ in dry CH_2Cl_2 (2.0 mL) was carried out at rt for 8 h, eluting with (hexanes:AcOEt = 4:1) to afford 80 mg (69%) of **3ja**, white solid, 254-256 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.38 (m, 2 H), 7.25-7.10 (m, 2 H), 7.04-6.70 (m, 5 H), 6.63-6.57 (m, 2 H), 6.42 (d, *J* = 8.0 Hz, 1 H), 5.14 (dd, *J* = 11.6 Hz, 3.6 Hz, 1 H), 3.84 (s, 3 H), 3.67 (s, 3 H), 3.52 (s, 3 H), 3.32 (td, *J* = 14.0 Hz, 4.4 Hz, 1 H), 2.59-2.32 (m, 2 H), 2.01-1.91 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 170.0, 168.9, 158.0, 145.1, 140.9, 135.8, 130.0, 129.2, 129.1, 128.7, 127.3, 121.6, 118.6, 113.2, 109.1, 68.8, 58.8, 58.7, 55.0, 52.6, 52.2, 31.4, 26.5; HRMS-TOF-ES$^+$: $[M+H]^+$ calcd for $C_{29}H_{27}{}^{79}BrN_2O_6H$: 579.1131, found: 579.1128.

18. Synthesis of 3ka

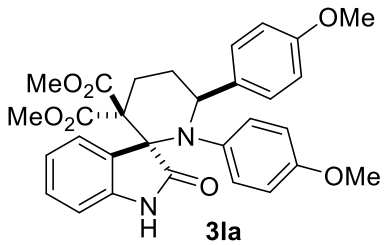


3ka

The reaction of iminooxindole **1k** (0.22 mmol, 52 mg), cyclobutane **2a** (0.2 mmol, 56

mg) and 60 mg of 4Å M.S. and 10 mol % $Sc(OTf)_3$ in dry CH_2Cl_2 (2.0 mL) was carried out at rt for 8 h, eluting with (hexanes:AcOEt = 4:1) to afford 72 mg (70%) of **3ka**, white solid, m.p. 255-257 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.6 Hz, 1 H), 7.25-7.10 (m, 3 H), 7.02-6.70 (m, 3 H), 6.63-6.43 (m, 4 H), 6.38 (d, *J* = 7.6 Hz, 1 H), 5.17 (dd, *J* = 12.0 Hz, 4.0 Hz, 1 H), 3.84 (s, 3 H), 3.65 (s, 3 H), 3.52 (s, 3 H), 3.34 (td, *J* = 14.0 Hz, 4.4 Hz, 1 H), 2.60-2.43 (m, 1 H), 2.40-2.31 (m, 1 H), 2.01-1.90 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.2, 170.0, 169.0, 157.7, 143.1, 140.9, 136.6, 134.2, 129.2, 129.1, 128.7, 127.6, 127.5, 121.3, 113.0, 108.8, 69.0, 59.0, 58.9, 55.0, 52.5, 52.1, 31.6, 26.5, 20.7; HRMS-TOF-ES$^+$: $[M+H]^+$ calcd for $C_{30}H_{30}N_2O_6H$: 515.2182, found: 515.2183.

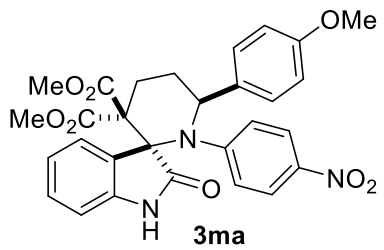
19. Synthesis of 3la



3la

The reaction of iminooxindole **1l** (0.22 mmol, 55.4 mg), cyclobutane **2a** (0.2 mmol, 56 mg) and 60 mg of 4Å M.S. and 10 mol % $Sc(OTf)_3$ in dry CH_2Cl_2 (2.0 mL) was carried out at rt for 3.5 h, eluting with (hexanes:AcOEt = 4:1) to afford 69 mg (65%) of **3la**, white solid, m.p. 214-216 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.6 Hz, 1 H), 7.38 (s, 1 H), 7.25-7.10 (m, 2 H), 7.00-6.57 (m, 5 H), 6.39 (d, *J* = 7.6 Hz, 1 H), 6.30-6.08 (m, 2 H), 5.14 (dd, *J* = 12.0 Hz, 4.0 Hz, 1 H), 3.83 (s, 3 H), 3.65 (s, 3 H), 3.51 (s, 3 H), 3.49 (s, 3 H), 3.33 (td, *J* = 14.0 Hz, 4.4 Hz, 1 H), 2.57-2.42 (m, 1 H), 2.40-2.31 (m, 1 H), 2.00-1.90 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.4, 170.0, 169.0, 157.7, 126.2, 140.9, 138.6, 136.5, 129.2, 129.1, 128.7, 127.3, 121.4, 113.0, 112.0, 108.9, 69.1, 59.1, 59.0, 54.9, 54.8, 52.5, 52.1, 31.5, 26.5; HRMS-TOF-ES$^+$: $[M+H]^+$ calcd for $C_{30}H_{30}N_2O_7H$: 531.2131, found: 531.2126.

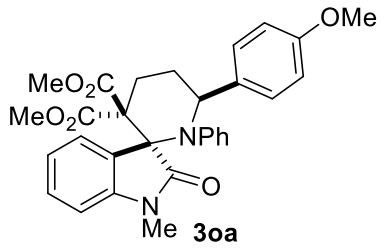
20. Synthesis of 3ma



3ma

The reaction of iminooxindole **1m** (0.22 mmol, 59 mg), cyclobutane **2a** (0.2 mmol, 56 mg) and 60 mg of 4Å M.S. and 10 mol % $Sc(OTf)_3$ in dry CH_2Cl_2 (2.0 mL) was carried out at rt for 14 h, eluting with (hexanes:AcOEt = 4:1) to afford 47 mg (43%) of **3ma**, white solid, m.p. 260-262 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.56 (m, 2 H), 7.46 (d, *J* = 8.0 Hz, 1 H), 7.33 (s, 1 H), 7.17-6.88 (m, 5 H), 6.62-6.56 (m, 2 H), 6.40 (d, *J* = 8.0 Hz, 1 H), 5.21 (dd, *J* = 12.0 Hz, 3.6 Hz, 1 H), 3.86 (s, 3 H), 3.65 (s, 3 H), 3.54 (s, 3 H), 3.34 (td, *J* = 14.0 Hz, 4.4 Hz, 1 H), 2.60-2.50 (m, 1 H), 2.44-2.36 (m, 1 H), 2.03-1.96 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.0, 169.8, 168.8, 158.3, 153.1, 144.6, 140.8, 138.6, 135.0, 129.6, 129.3, 128.1, 127.4, 125.9, 124.0, 122.3, 122.0, 68.9, 58.8, 58.7, 55.0, 52.7, 52.3, 31.2, 26.5; HRMS-TOF-ES$^+$: $[M+H]^+$ calcd for $C_{29}H_{27}N_3O_8H$: 546.1876, found: 546.1880.

21. Synthesis of 3oa

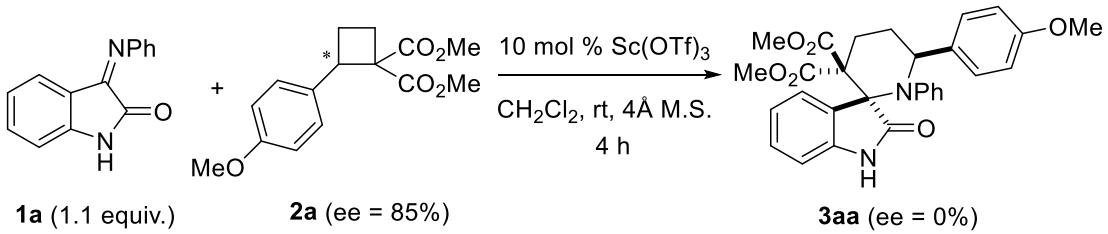


3oa

The reaction of iminooxindole **1o** (0.22 mmol, 52 mg), cyclobutane **2a** (0.2 mmol, 56 mg) and 60 mg of 4Å M.S. and 10 mol % $Sc(OTf)_3$ in dry CH_2Cl_2 (2.0 mL) was carried out at rt for 14 h, eluting with (hexanes:AcOEt = 4:1) to afford 36 mg (35%) of **3oa**, white solid, m.p. 183-185 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.0 Hz, 1 H), 7.27-7.14 (m, 2 H), 7.07-6.98 (m, 1 H), 6.92-6.54 (m, 8 H), 6.31 (d, *J* = 8.0

Hz, 1 H), 5.18 (dd, *J* = 12.0 Hz, 3.6 Hz, 1 H), 3.84 (s, 3 H), 3.64 (s, 3 H), 3.51 (s, 3 H), 3.37 (td, *J* = 14.0 Hz, 4.4 Hz, 1 H), 2.94 (s, 3 H), 2.69-2.53 (m, 1 H), 2.44-2.34 (m, 1 H), 2.03-1.91 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 170.0, 169.2, 157.8, 145.8, 144.0, 136.4, 129.3, 128.8, 126.7, 126.6, 125.0, 121.4, 113.0, 107.2, 68.6, 58.8, 58.6, 54.9, 52.4, 52.0, 31.4, 26.7, 25.4; HRMS-TOF-ES$^+$: $[M+Na]^+$ calcd for $C_{30}H_{30}N_2O_6Na$: 537.2002, found: 537.1996.

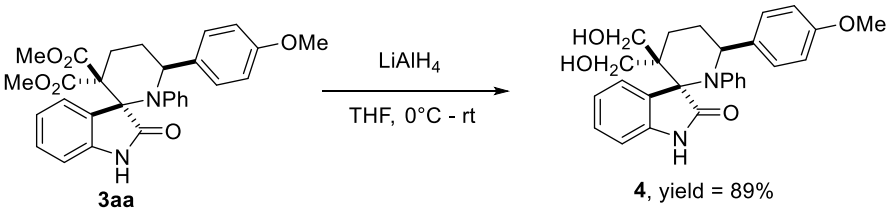
The [4+2] cycloaddition reaction of enantioenriched cyclobutane 2a and 1a.



1a (1.1 equiv.) **2a** (ee = 85%) **3aa** (ee = 0%)

3aa, determined by HPLC, chiralcel ADH, *i*-PrOH/hexane =20/80, 1.0 mL/min, 240 nm; t_r = 9.34 min, t'_r = 17.8 min).

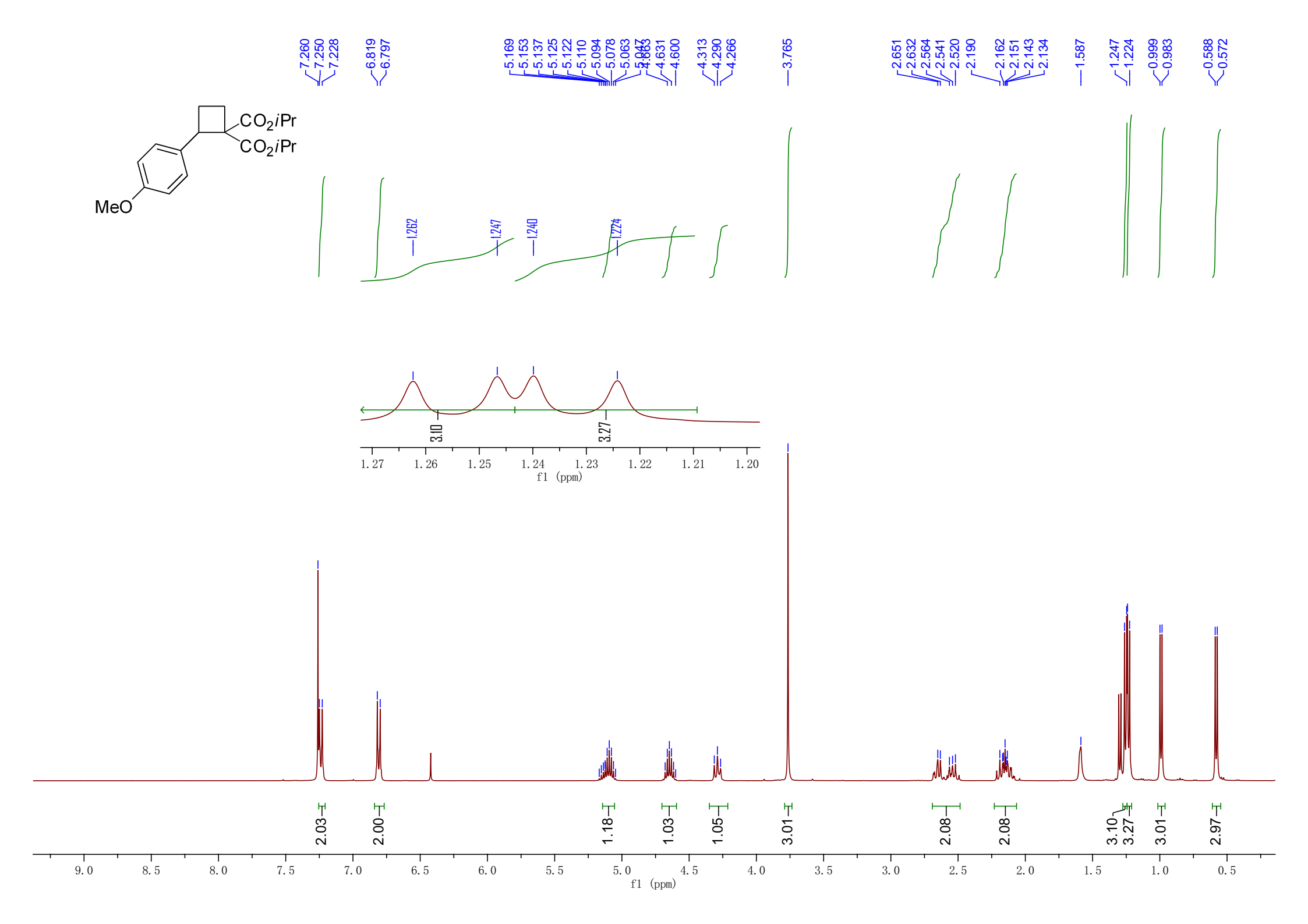
The transformations of cycloadduct 3aa.



3aa **4**, yield = 89%

Under N_2, the cycloadduct **3aa** (0.2 mmol, 100.0 mg) was dissolved in THF, and cooled at 0°C, $LiAlH_4$ (2.35 mmol, 39 mg) was added into the reaction mixture. The reaction mixture was stirred at room temperature. When the cycloadduct **3aa** disappeared (monitored by TLC), the reaction mixture was quenched with H_2O (1.2 mL), 15% NaOH (1.2 mL), H_2O (3.6 mL), and then passed over a plug of celite with 30 mL of MeOH. The filtrate was removed under reduced pressure and the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate, v/v= 2:1) to give the desired product in 89% yield (79 mg), white solid. m.p. 230-232 °C. ^{1}H NMR (400MHz, DMSO-D_6) δ 10.11 (s, 1 H), 7.41 (d, *J* = 7.6 Hz, 1 H), 7.15 (d, *J* = 7.6 Hz, 2 H), 7.05-6.85 (m, 3 H), 6.78-6.68 (m, 3 H), 6.64-6.55 (m, 3 H), 6.35 (d, *J* = 7.6 Hz, 1 H), 5.30 (dd, *J* = 11.6 Hz, 3.6 Hz, 1 H), 4.78 (dd, *J* = 10.4 Hz, 6.8 Hz, 1 H), 4.45-4.38 (m, 2 H), 3.88-3.81 (m, 1 H), 3.58 (s, 3 H), 3.20-3.01 (m, 2 H), 2.64-2.54 (m, 2 H), 2.09-1.87 (m, 2 H), 1.79-1.70 (m, 1 H), ^{13}C NMR (100MHz, DMSO-D_6) δ 178.9, 157.4, 147.4, 142.1, 137.0, 128.8, 128.2, 128.0, 127.0, 124.8,

119.8, 113.0, 108.5, 99.6, 71.3, 65.8, 61.8, 59.6, 54.7, 43.6, 31.9, 21.0; HRMS-TOF-ES$^+$:[M+H]$^+$ cacld for $C_{27}H_{28}N_2O_4H$: 445.2127, found: 445.2129.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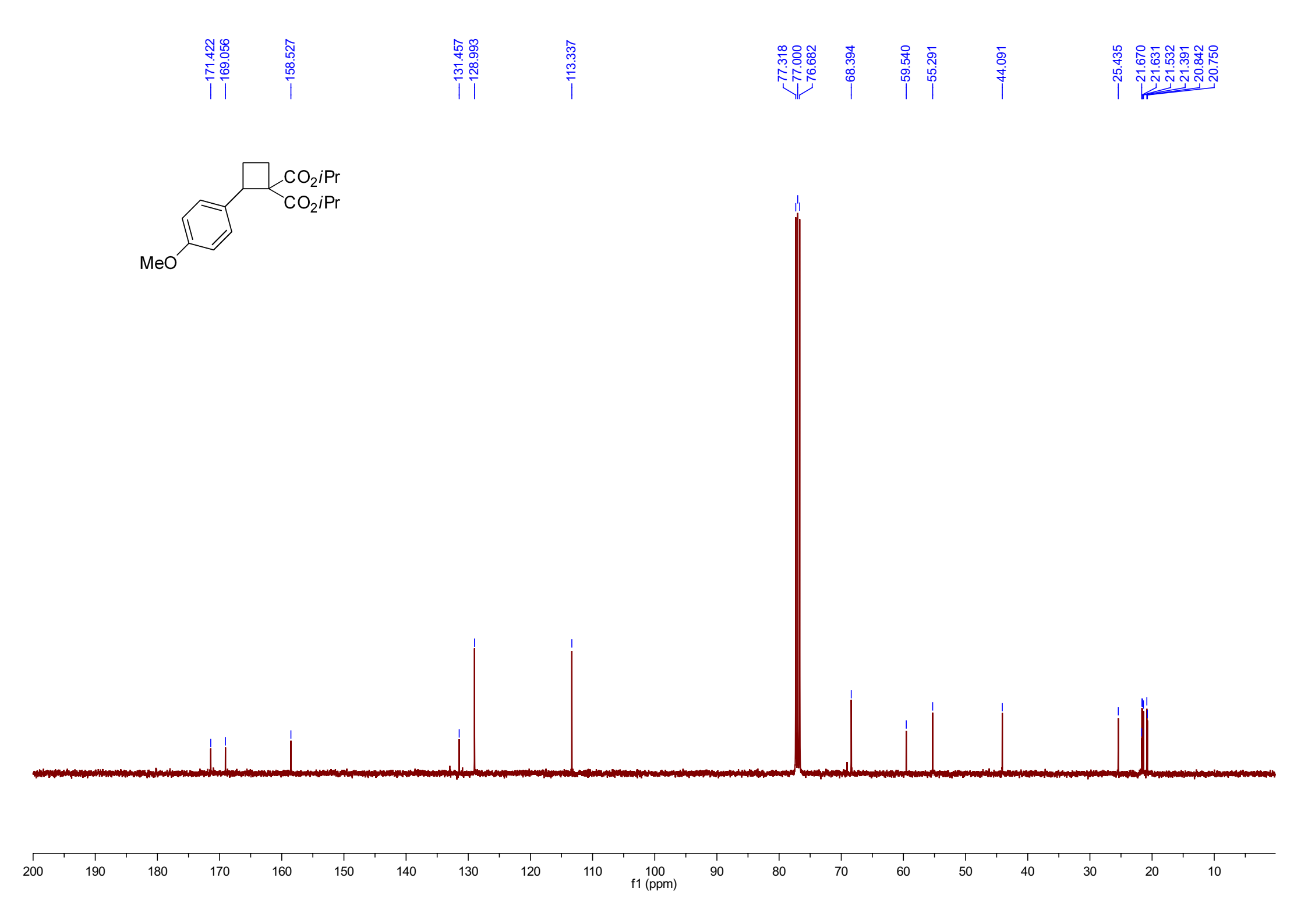
5.169
5.153
5.137
5.125
5.122
5.110
5.094
5.078
5.063
4.631
4.600
4.313
4.290
4.266
3.765
2.651
2.632
2.564
2.541
2.520
2.190
2.162
2.151
2.143
2.134
1.587
1.247
1.224
0.999
0.983
0.588
0.572
CO2iPr
CO2iPr
MeO
1.262
1.247
1.240
1.224
3.10
3.27
1.27
1.26
1.25
1.24
1.23
1.22
1.21
1.20
f1 (ppm)
2.03
2.00
1.18
1.03
1.05
3.01
2.08
2.08
3.10
3.27
3.01
2.97
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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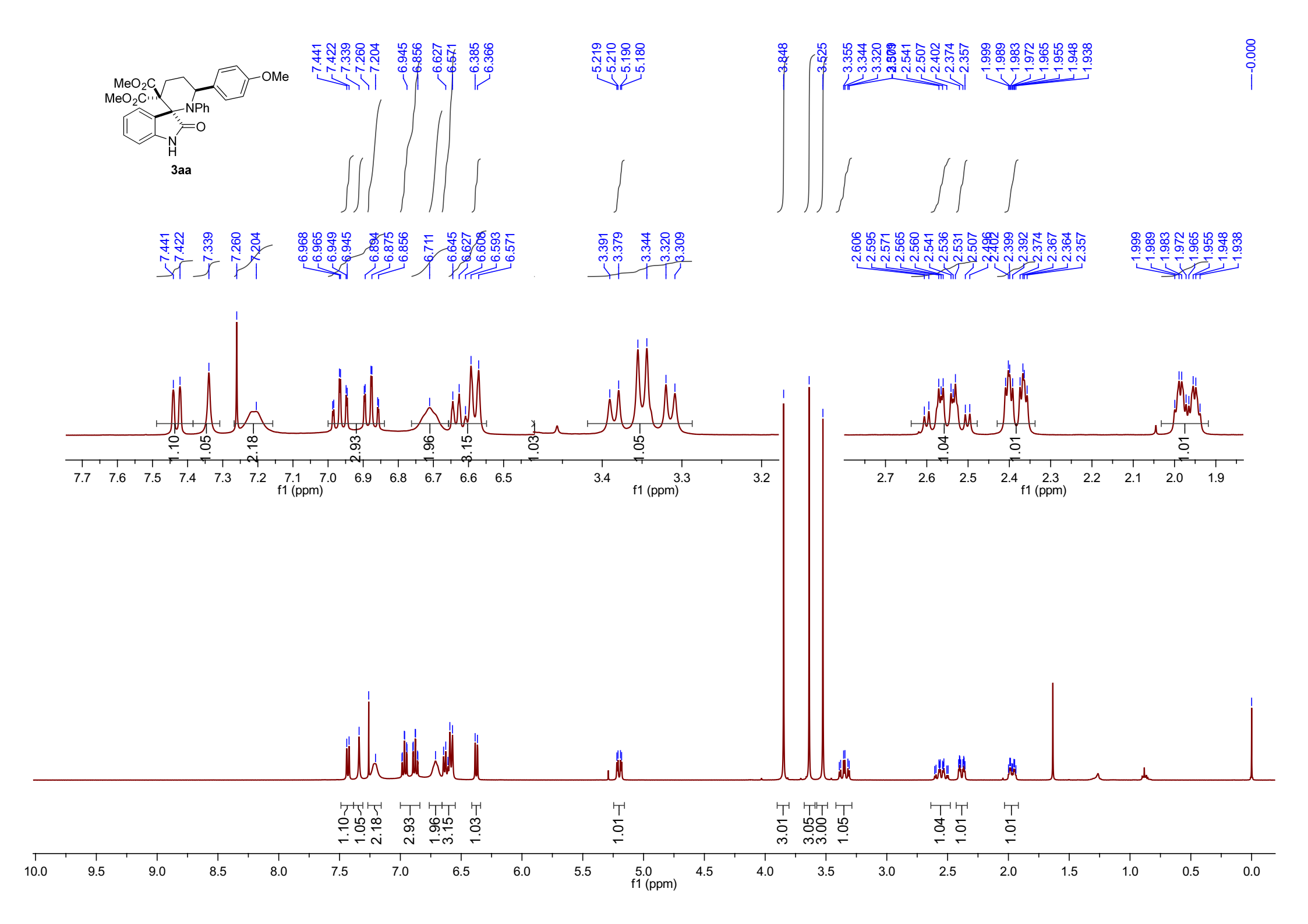
158.527
131.457
128.993
113.337
77.318
77.000
76.682
68.394
59.540
55.291
44.091
25.435
21.670
21.631
21.532
21.391
20.842
20.750
CO2iPr
CO2iPr
MeO
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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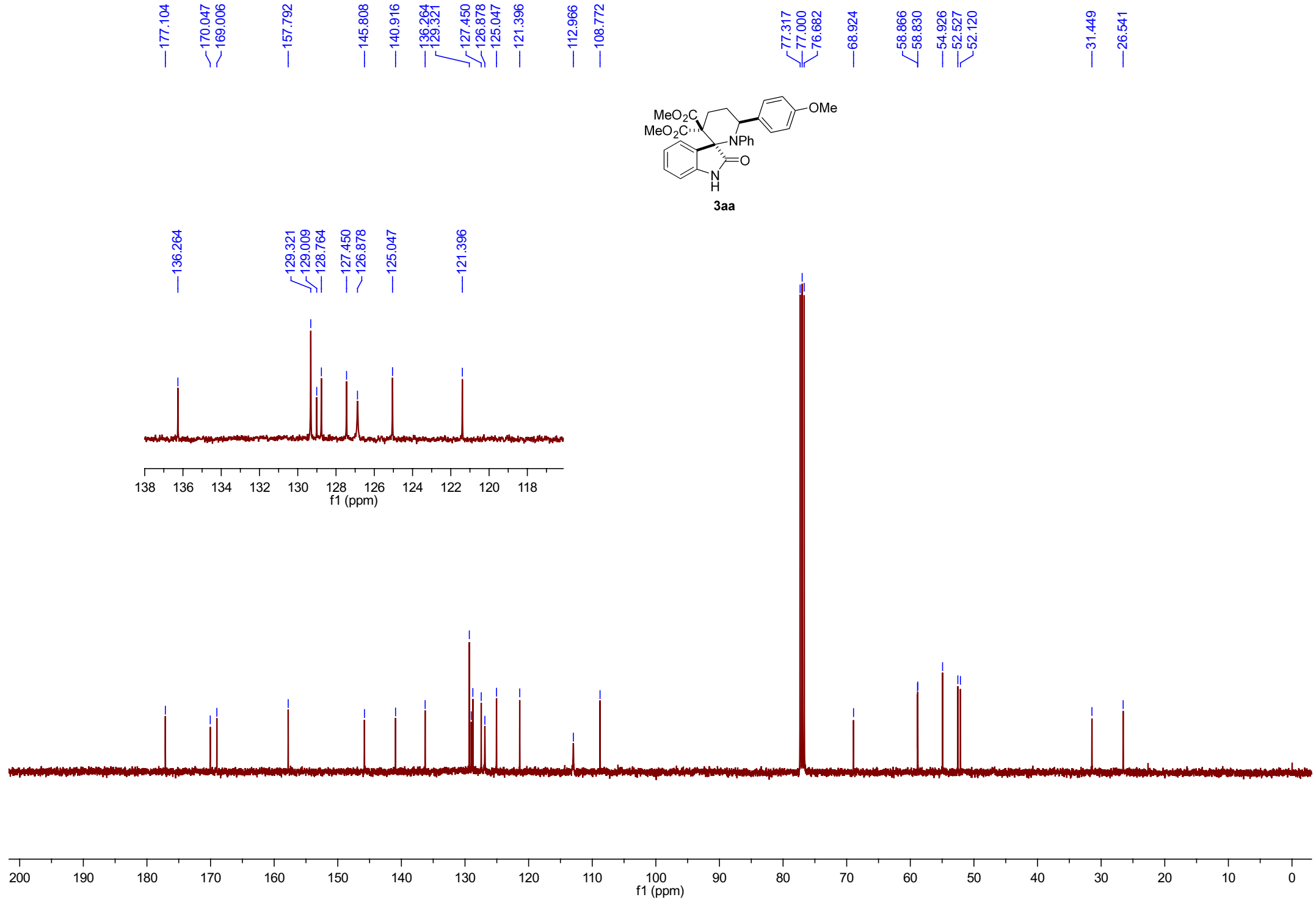
MeO2C
NPh
O
N
H
OMe
3aa
f1 (ppm)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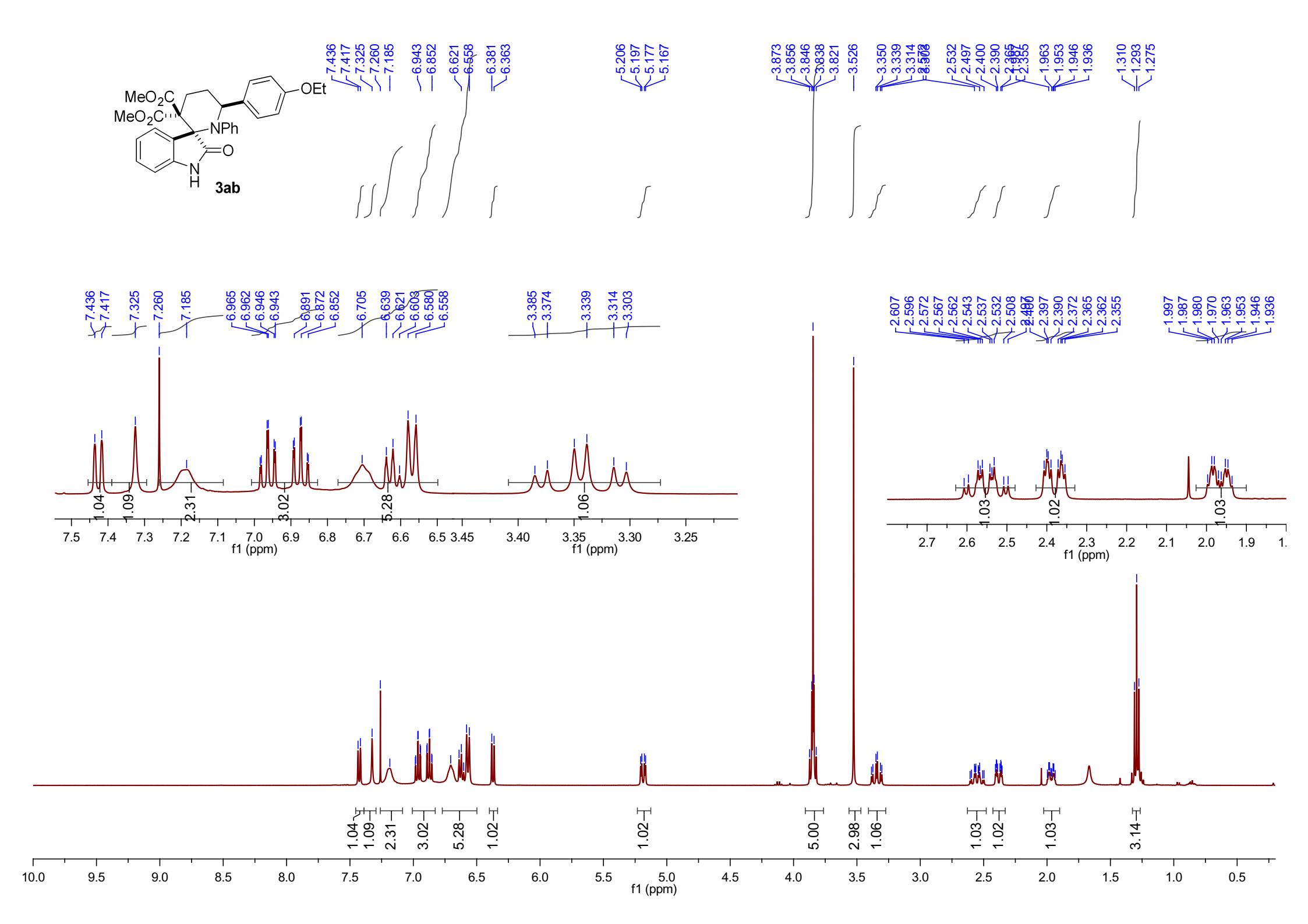
140.916
136.264
129.321
127.450
126.878
125.047
121.396
112.966
108.772
77.317
77.000
76.682
68.924
58.866
58.830
54.926
52.527
52.120
31.449
26.541
MeO2C
MeO2C
NPh
O
N
H
OMe
3aa
136.264
129.321
129.009
128.764
127.450
126.878
125.047
121.396
138 136 134 132 130 128 126 124 122 120 118
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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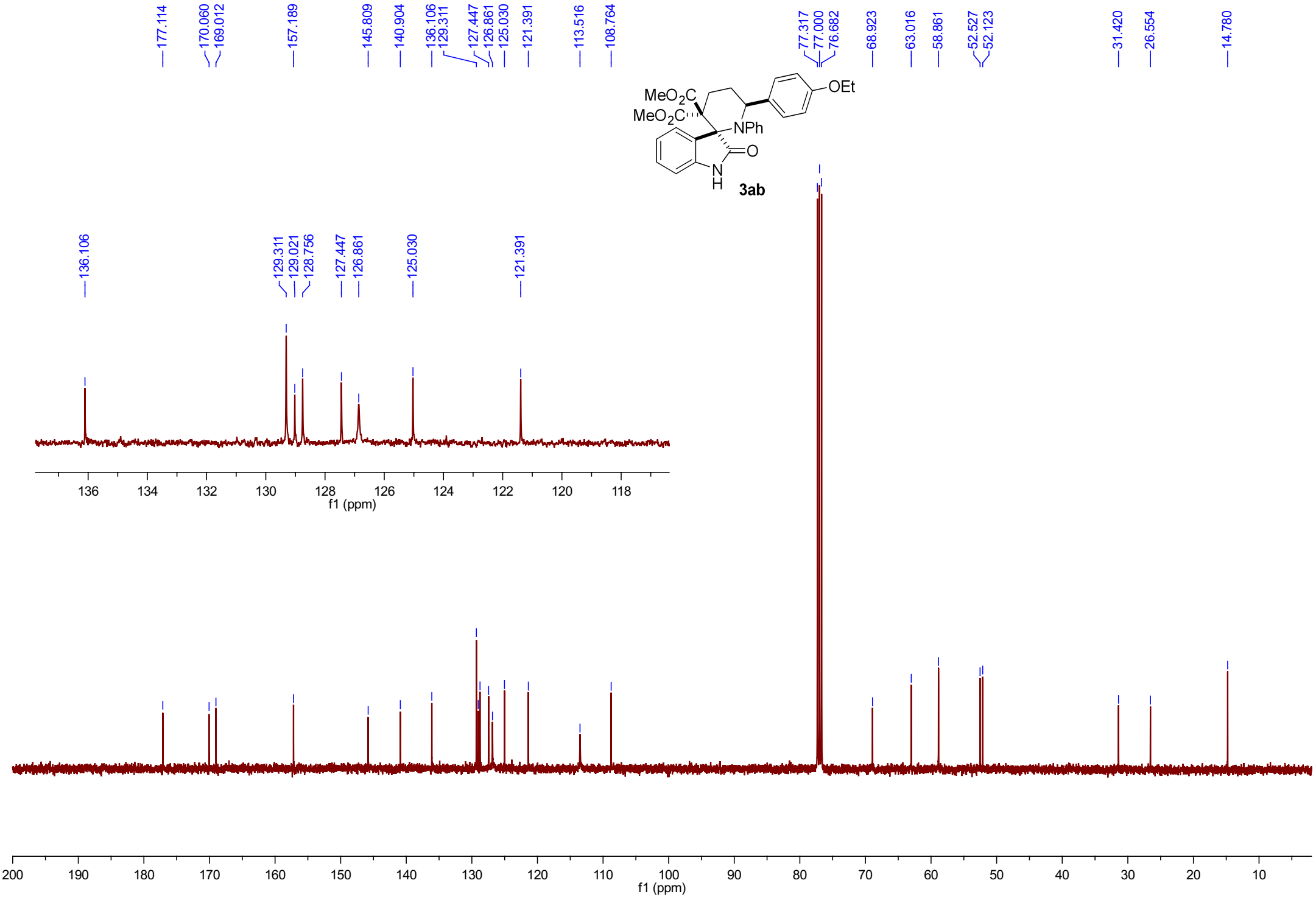
MeO2C
NPh
O
N
H
OEt
3ab
f1 (ppm)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140.904
136.106
129.311
127.447
126.861
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121.391
113.516
108.764
77.317
77.000
76.682
68.923
63.016
58.861
52.527
52.123
31.420
26.554
14.780
MeO2C
MeO2C
NPh
O
N
H
OEt
3ab
136.106
129.311
129.021
128.756
127.447
126.861
125.030
121.391
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f1 (ppm)
200
190
180
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150
140
130
120
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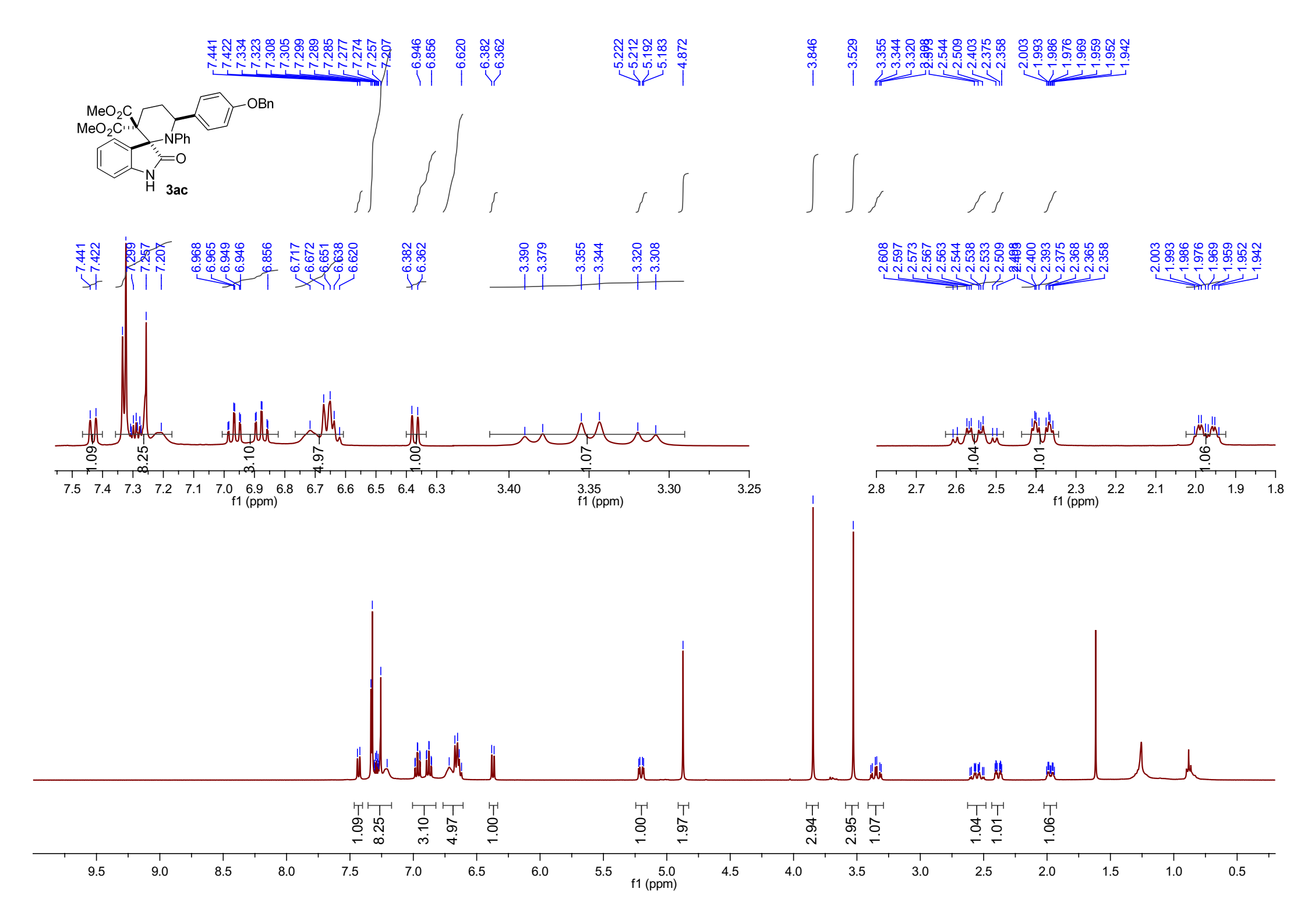
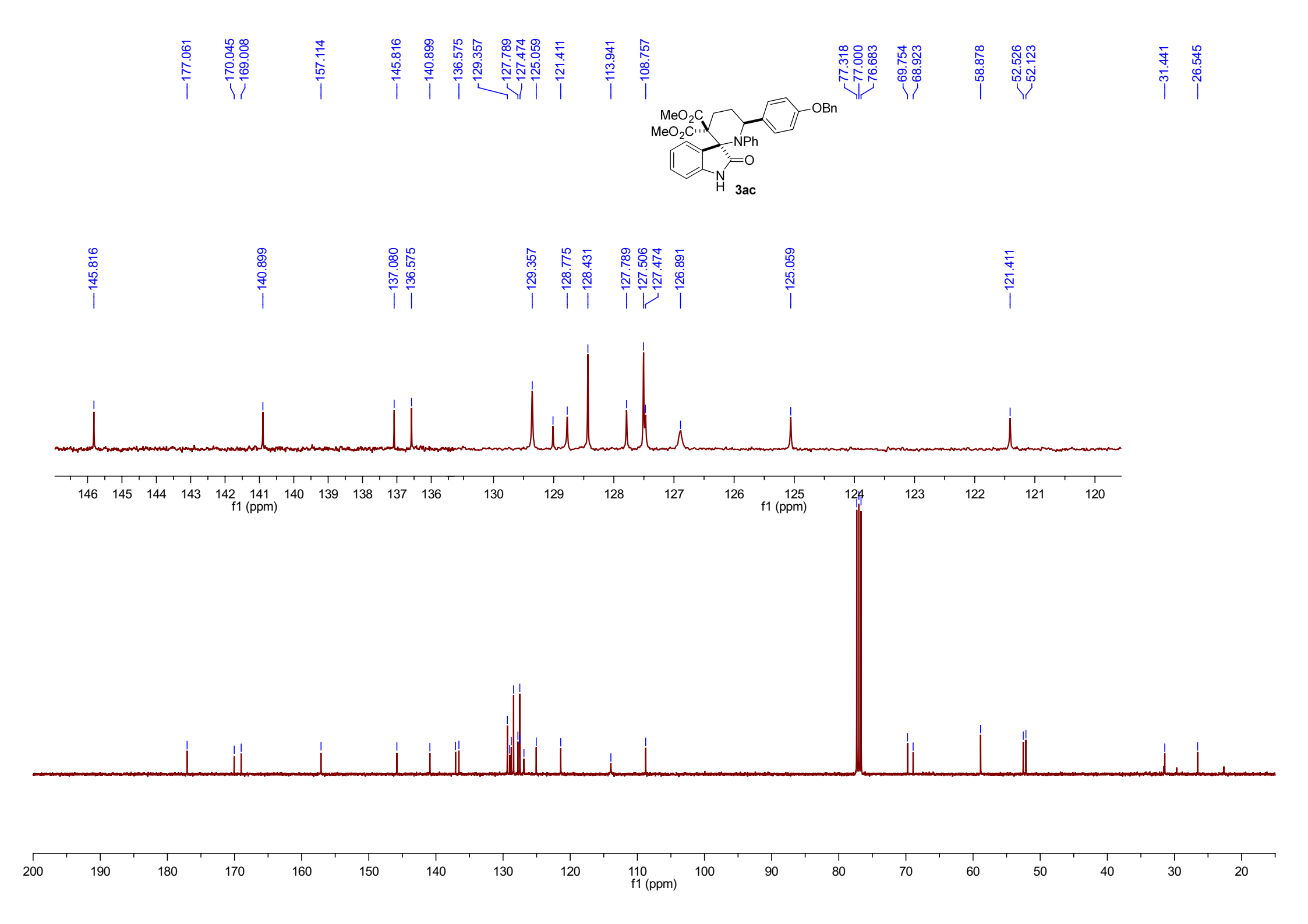
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


MeO2C
MeO2C
NPh
O
N
H
OBn
3ac
f1 (ppm)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157.114
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140.899
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129.357
127.789
127.474
125.059
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113.941
108.757
77.318
77.000
76.683
69.754
68.923
58.878
52.526
52.123
31.441
26.545
MeO2C
MeO2C
NPh
O
N
H
OBn
3ac
145.816
140.899
137.080
136.575
129.357
128.775
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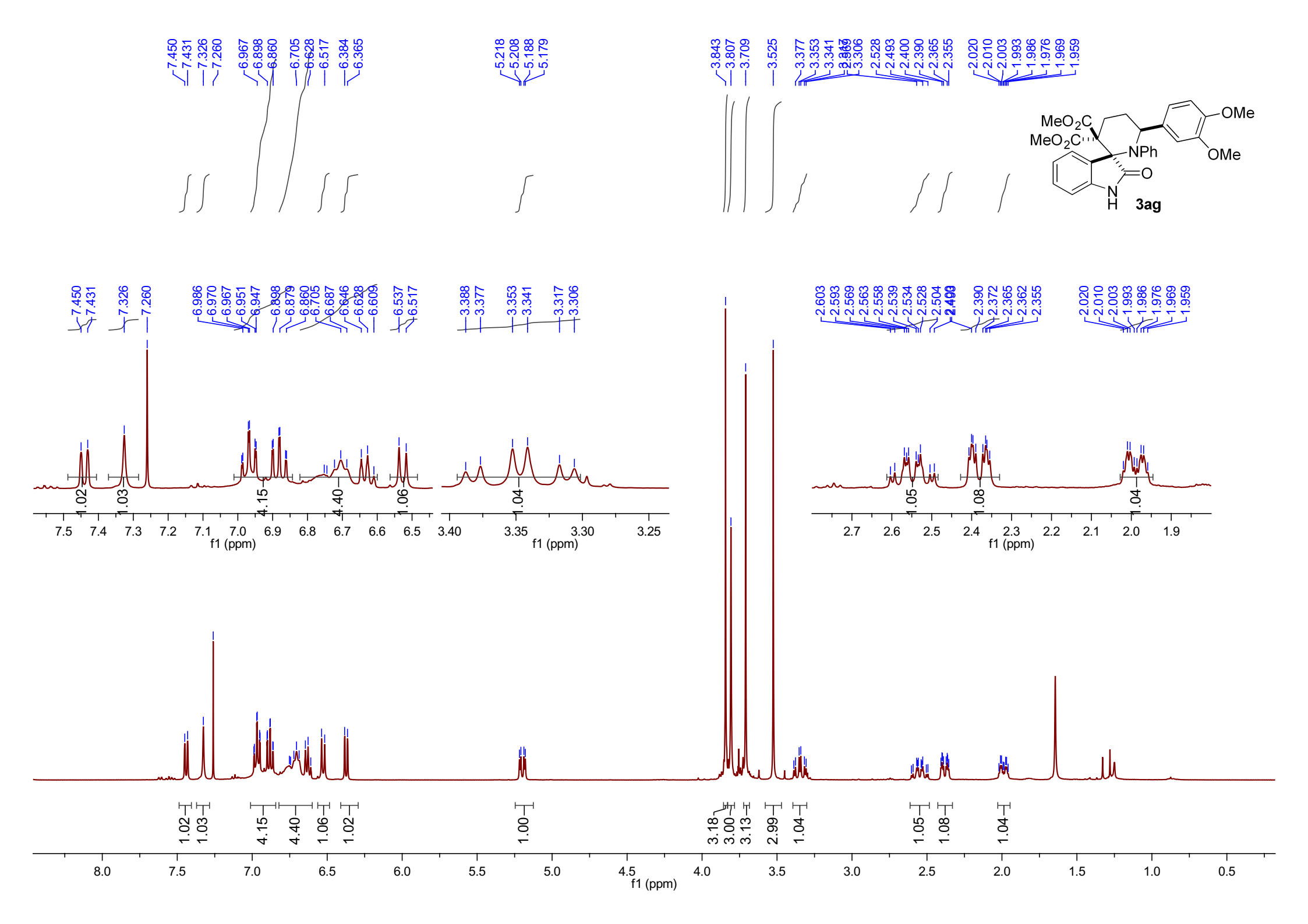
126.891
125.059
121.411
f1 (ppm)
f1 (ppm)
f1 (ppm)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6.705
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6.365
5.218
5.208
5.188
5.179
3.843
3.807
3.709
3.525
3.377
3.353
3.341
3.306
2.528
2.493
2.400
2.390
2.365
2.355
2.020
2.010
2.003
1.993
1.986
1.976
1.969
1.959
MeO2C
MeO2C
NPh
O
N
H
OMe
OMe
3ag
f1 (ppm)
1.02
1.03
4.15
4.40
1.06
1.02
1.00
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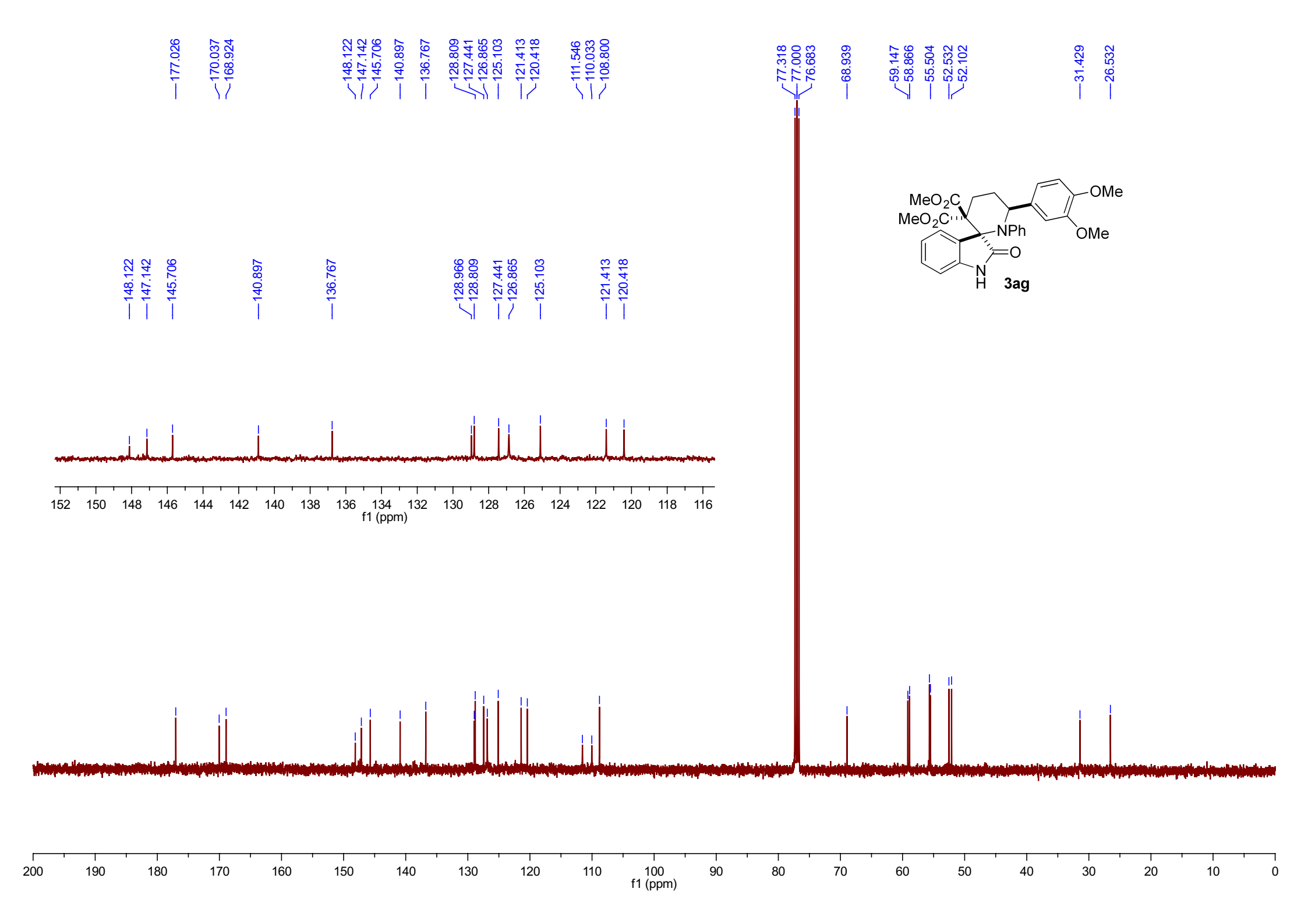
3.13
2.99
1.04
1.05
1.08
1.04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147.142
145.706
140.897
136.767
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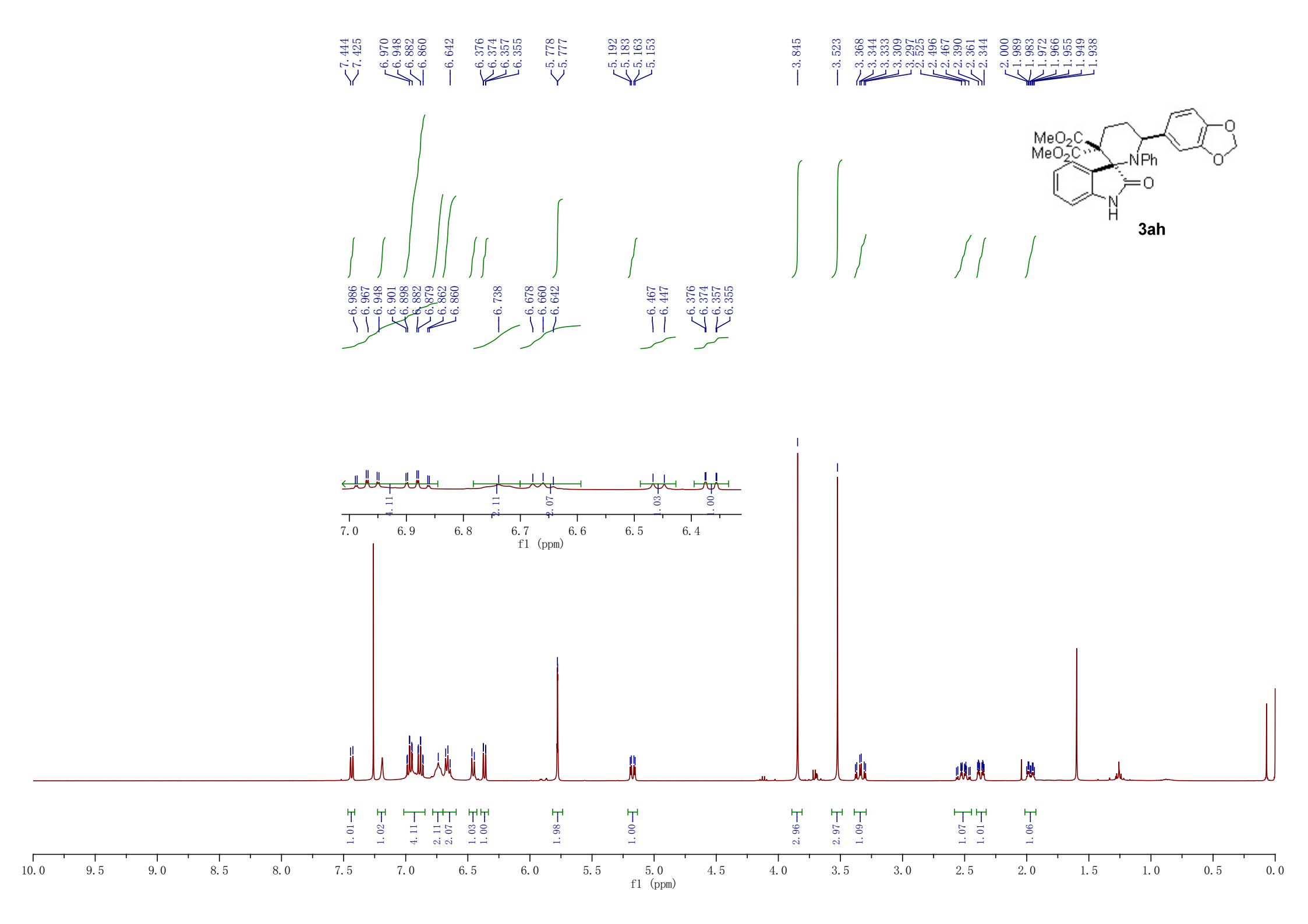
127.441
126.865
125.103
121.413
120.418
111.546
110.033
108.800
77.318
77.000
76.683
68.939
59.147
58.866
55.504
52.532
52.102
31.429
26.532
MeO2C
MeO2C
NPh
OMe
OMe
O
N
H
3ag
f1 (ppm)
f1 (ppm)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6.860
6.642
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6.374
6.357
6.355
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6.860
6.738
6.678
6.660
6.642
6.467
6.447
6.376
6.374
6.357
6.355
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MeO2C
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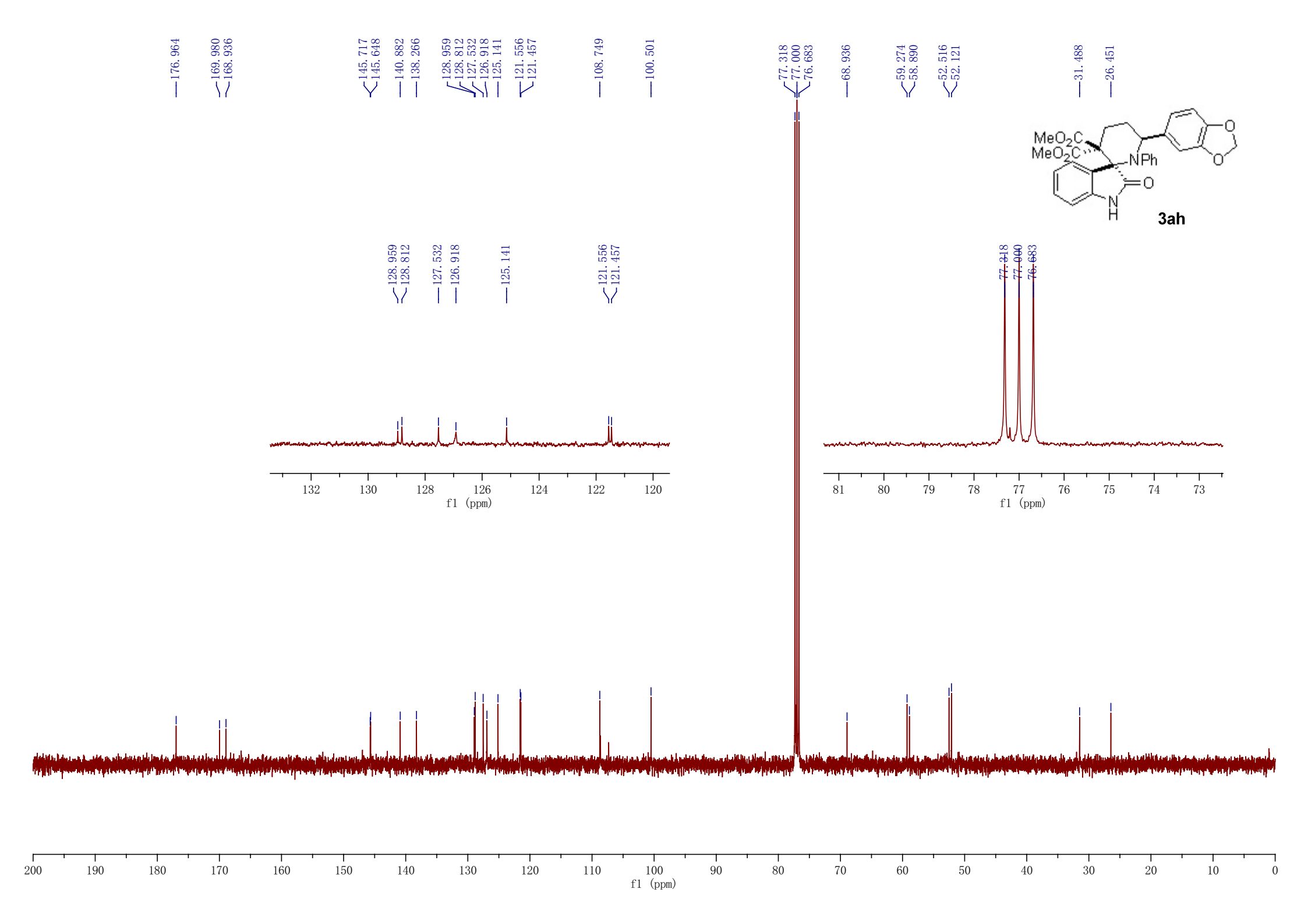
O
N
H
O
O
3ah
4.11
2.11
2.07
1.03
1.00
7.0
6.9
6.8
6.7
6.6
6.5
6.4
f1 (ppm)
1.01
1.02
4.11
2.11
2.07
1.03
1.00
1.98
1.00
2.96
2.97
1.09
1.07
1.01
1.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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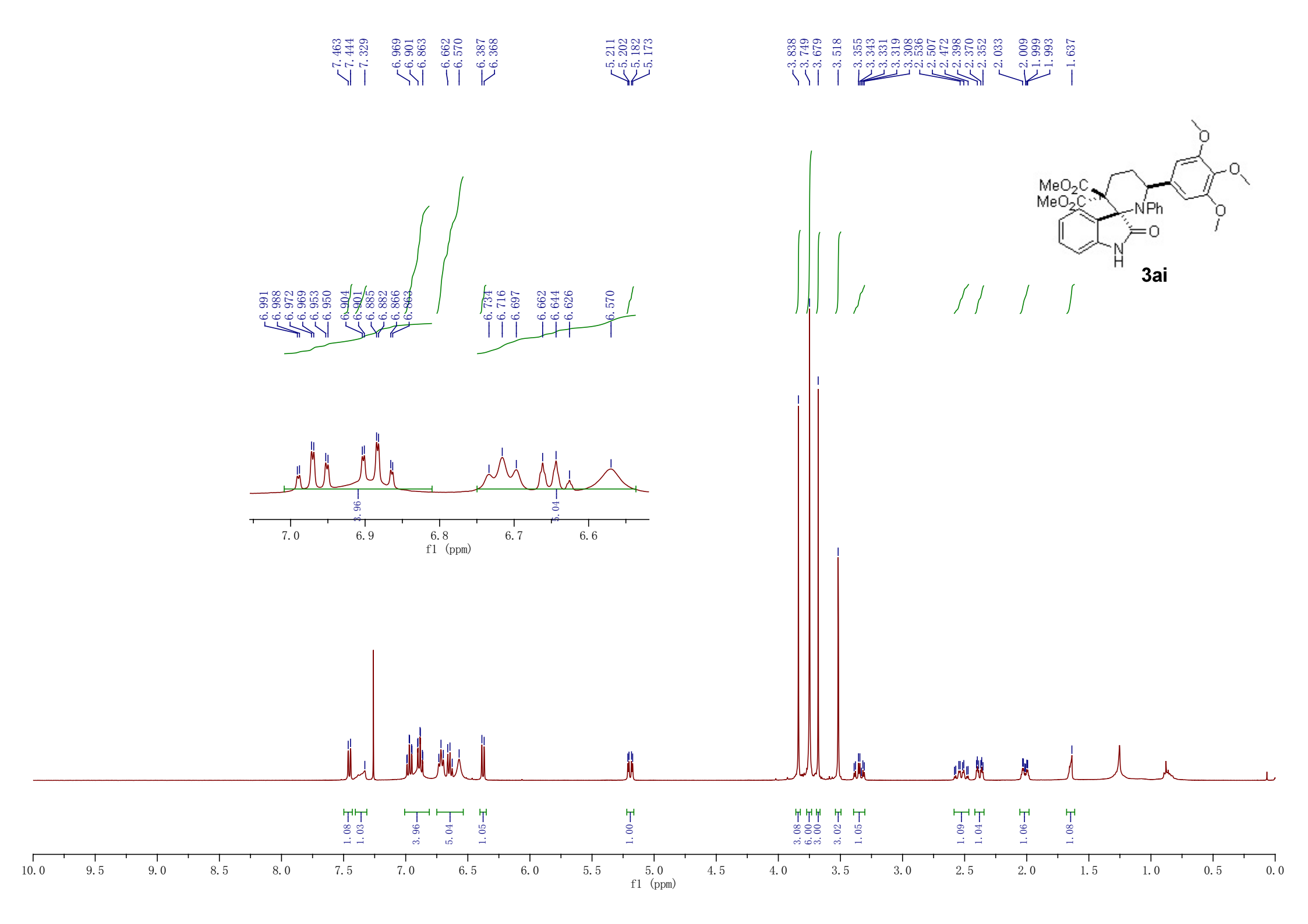
169.980
168.936
145.717
145.648
140.882
138.266
128.959
128.812
127.532
126.918
125.141
121.556
121.457
108.749
100.501
77.318
77.000
76.683
68.936
59.274
58.890
52.516
52.121
31.488
26.451
MeO2C
MeO2C
NPh
O
O
O
N
H
3ah
f1 (ppm)
f1 (ppm)
f1 (ppm)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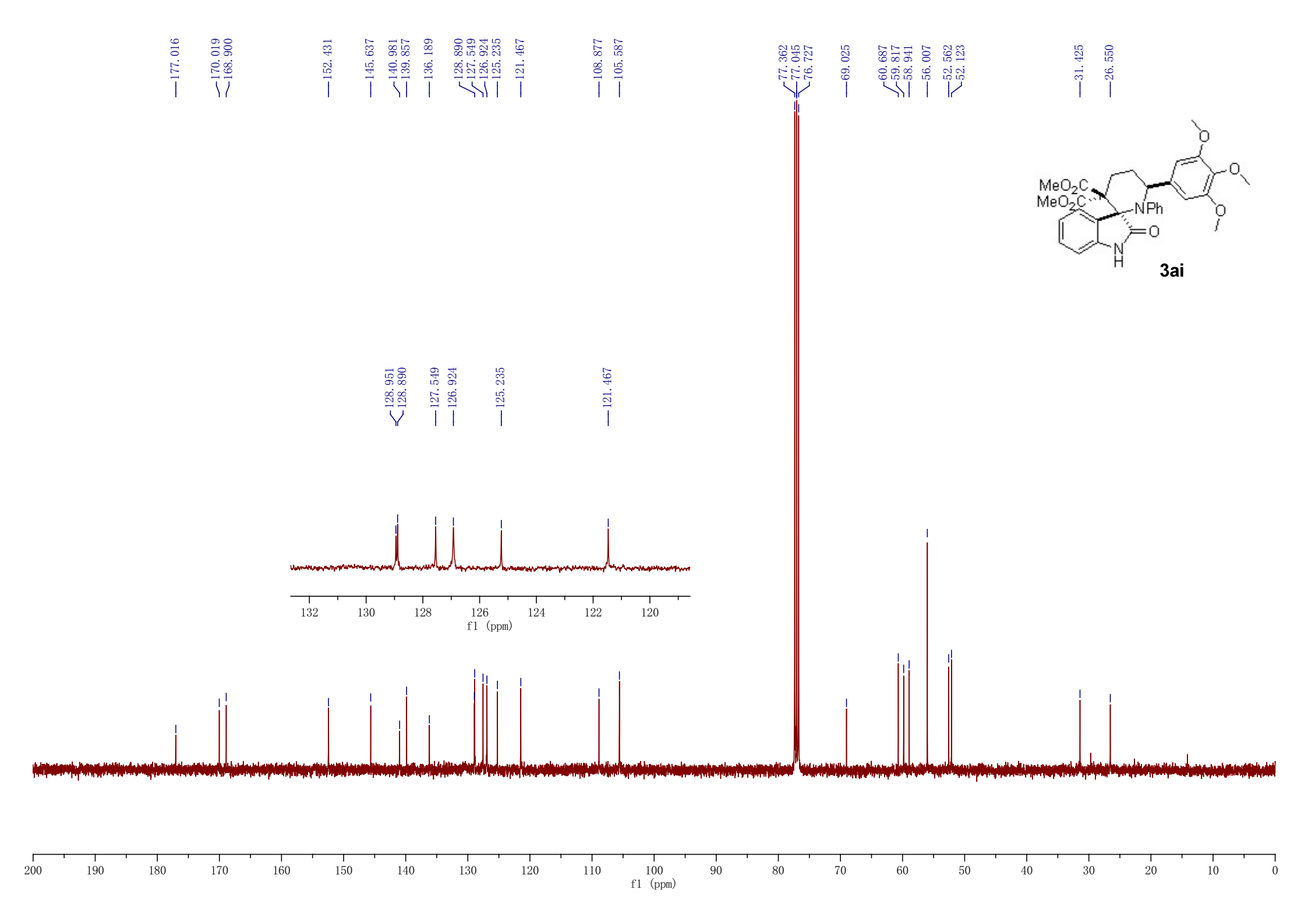
7.444
7.329
6.969
6.901
6.863
6.662
6.570
6.387
6.368
5.211
5.202
5.182
5.173
3.838
3.749
3.679
3.518
3.355
3.343
3.331
3.319
3.308
2.536
2.507
2.472
2.398
2.370
2.352
2.033
2.009
1.999
1.993
1.637
6.991
6.988
6.972
6.969
6.953
6.950
6.904
6.901
6.885
6.882
6.866
6.863
6.734
6.716
6.697
6.662
6.644
6.626
6.570
3.96
5.04
7.0
6.9
6.8
6.7
6.6
f1 (ppm)
1.08
1.03
3.96
5.04
1.05
1.00
3.08
6.00
3.00
3.02
1.05
1.09
1.04
1.06
1.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
MeO2C
MeO2C
NPh
O
N
H
O
O
O
3ai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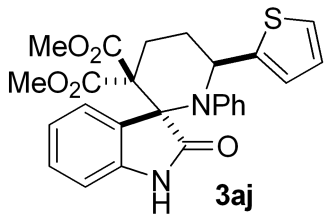
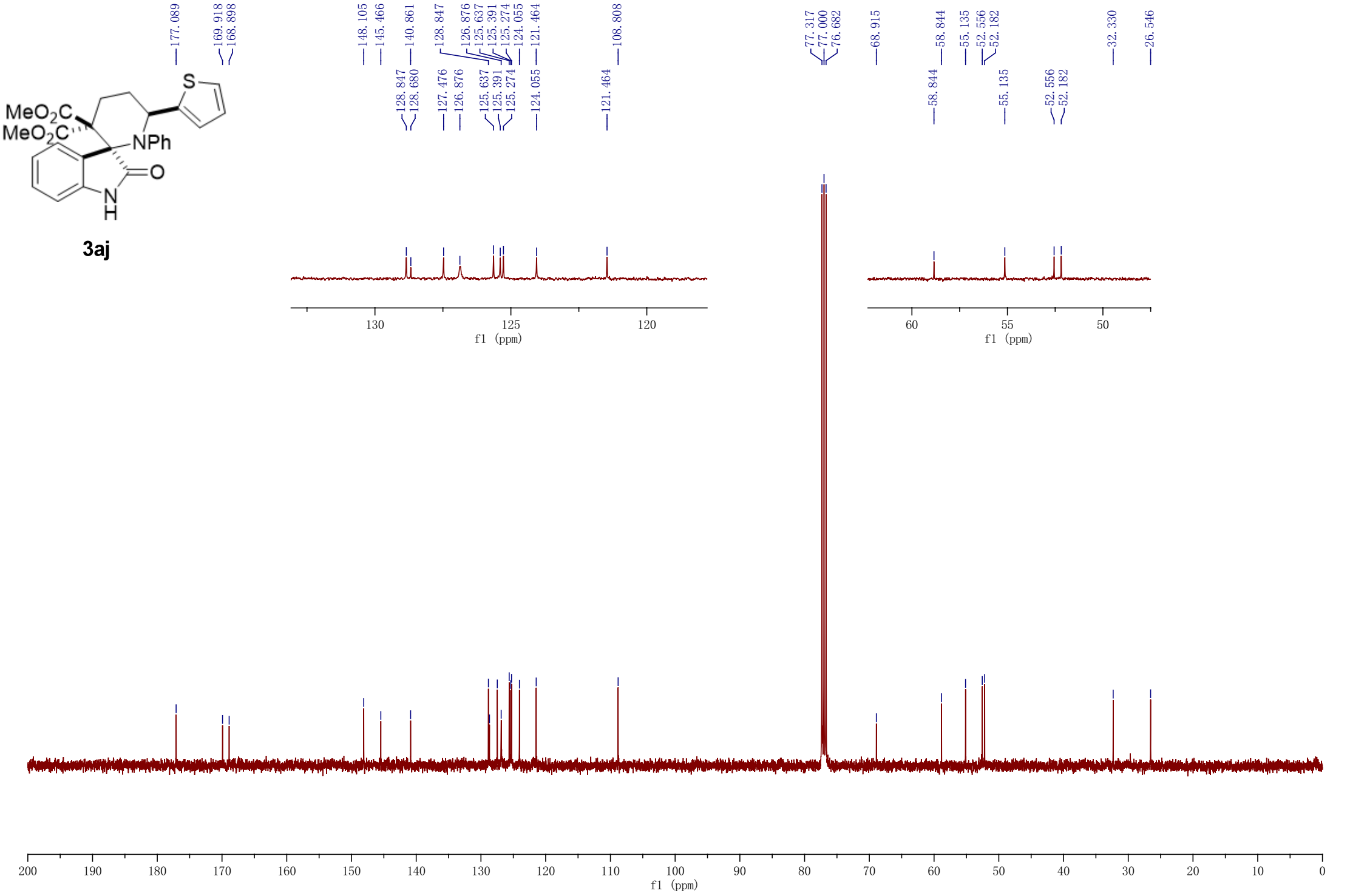
170.019
168.900
152.431
145.637
140.981
139.857
136.189
128.890
127.549
126.924
125.235
121.467
108.877
105.587
77.362
77.045
76.727
69.025
60.687
59.817
58.941
56.007
52.562
52.123
31.425
26.550
MeO2C
MeO2C
NPh
O
N
H
O
O
O
3ai
128.951
128.890
127.549
126.924
125.235
121.467
132
130
128
126
124
122
120
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


MeO2C
MeO2C
NPh
O
N
H
S

3aj

7.374
7.354
7.260
7.141
6.944
6.841
6.642
6.566
6.389
6.370
5.609
5.599
5.579
5.570
3.867
3.543
3.360
3.325
2.758
2.734
2.724
2.689
2.425
2.390
2.180
2.170
2.164
2.153
2.146
2.136
2.129
1.10
1.08
2.27
4.97
1.06
1.14
1.09
1.10
3.11
3.08
1.19
1.20
1.13
1.15
f1 (ppm)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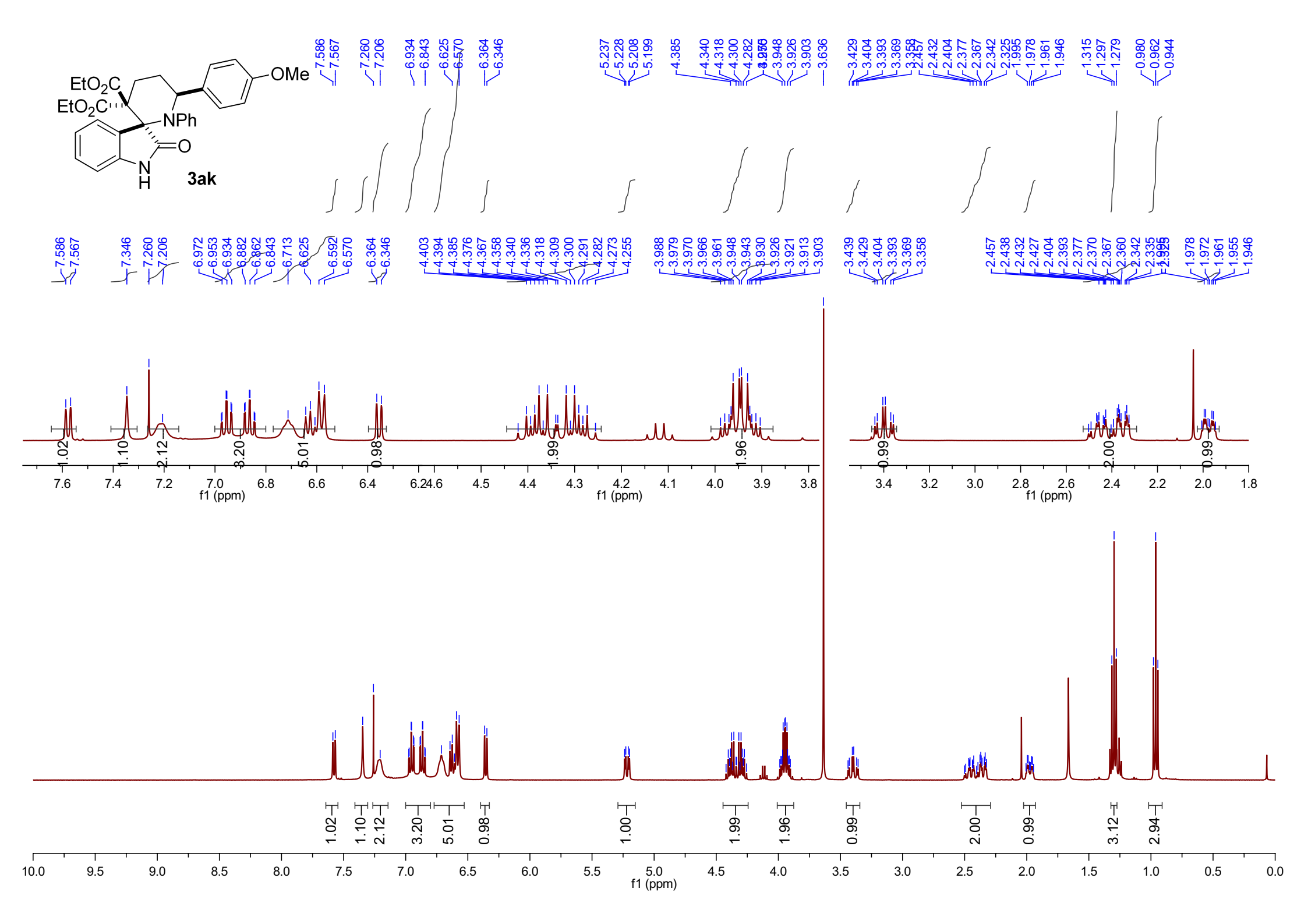
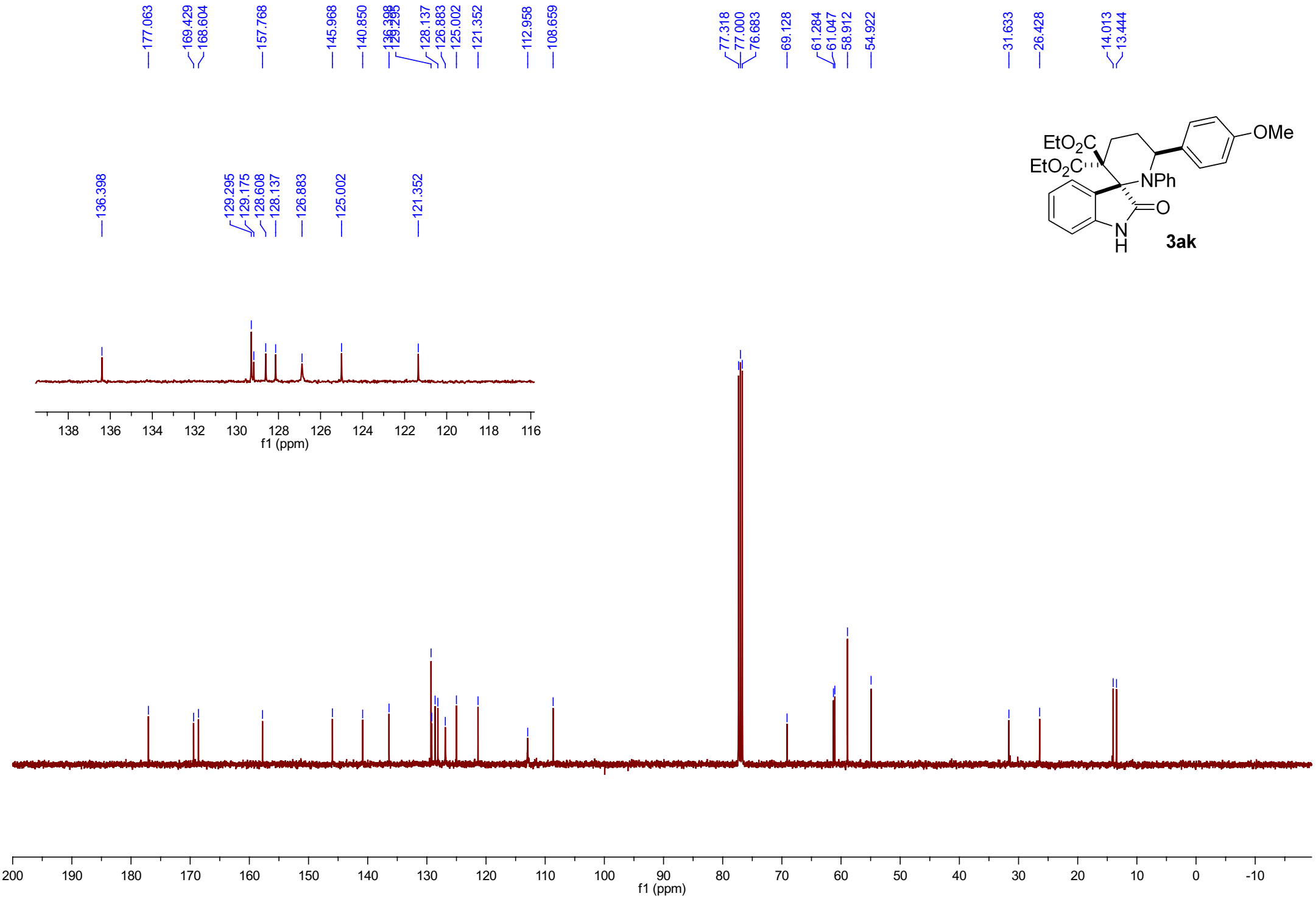
169.918
168.898
148.105
145.466
140.861
128.847
126.876
125.637
125.391
125.274
124.055
121.464
108.808
77.317
77.000
76.682
68.915
58.844
55.135
52.556
52.182
32.330
26.546
MeO2C
MeO2C
NPh
O
N
H
S
3aj
f1 (ppm)
f1 (ppm)
f1 (ppm)


EtO2C
EtO2C
NPh
O
N
H
OMe
3ak
f1 (ppm)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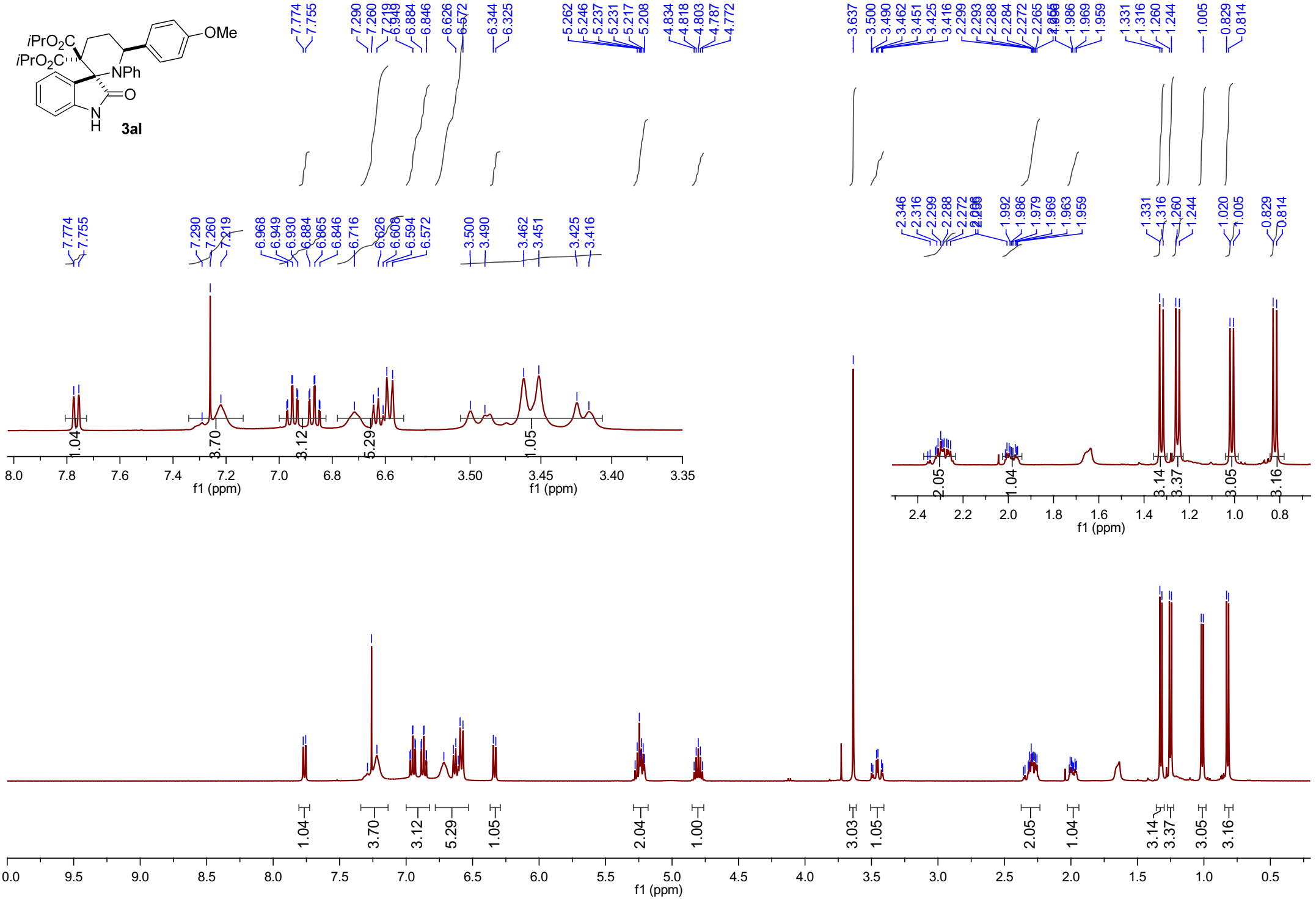
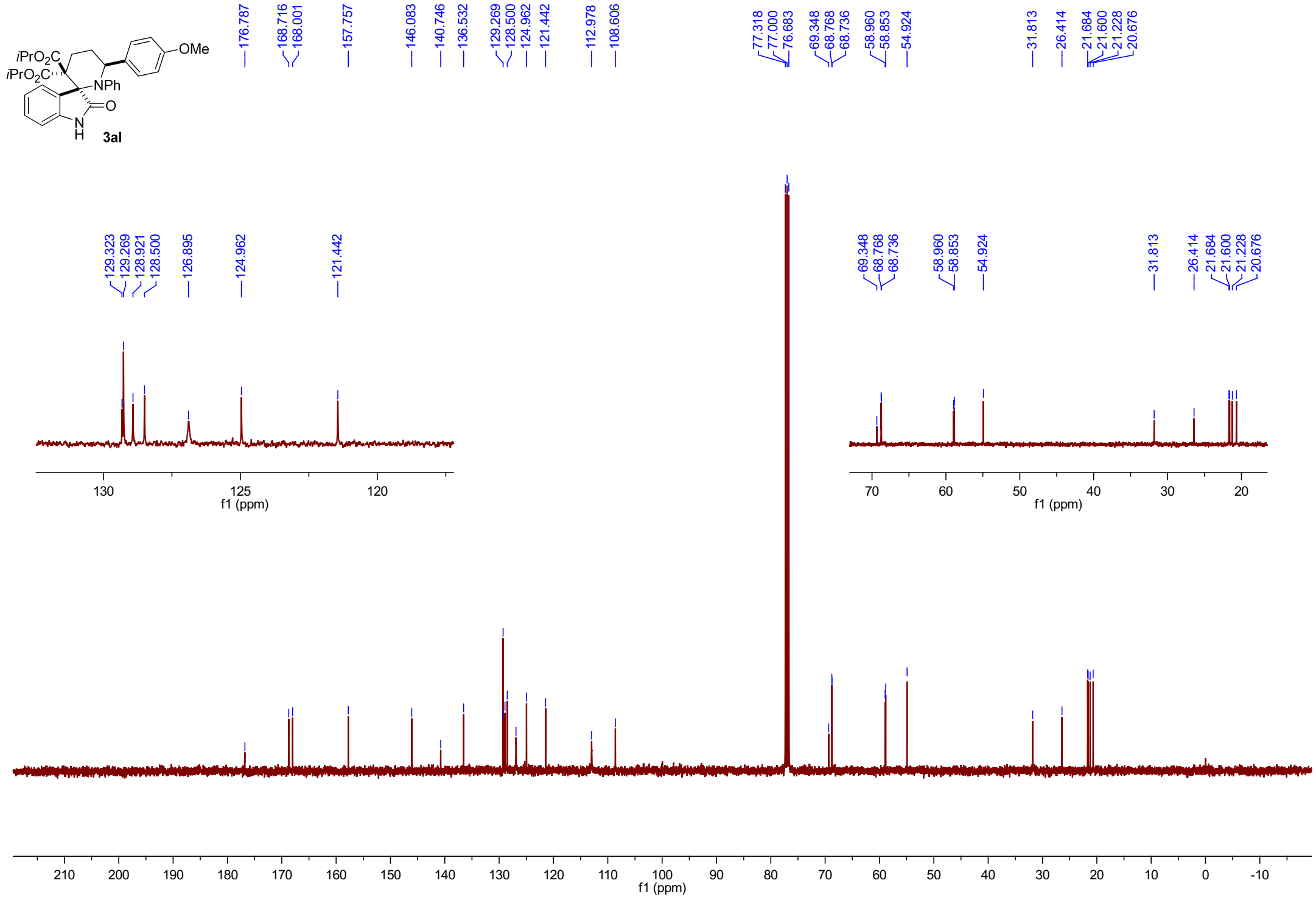
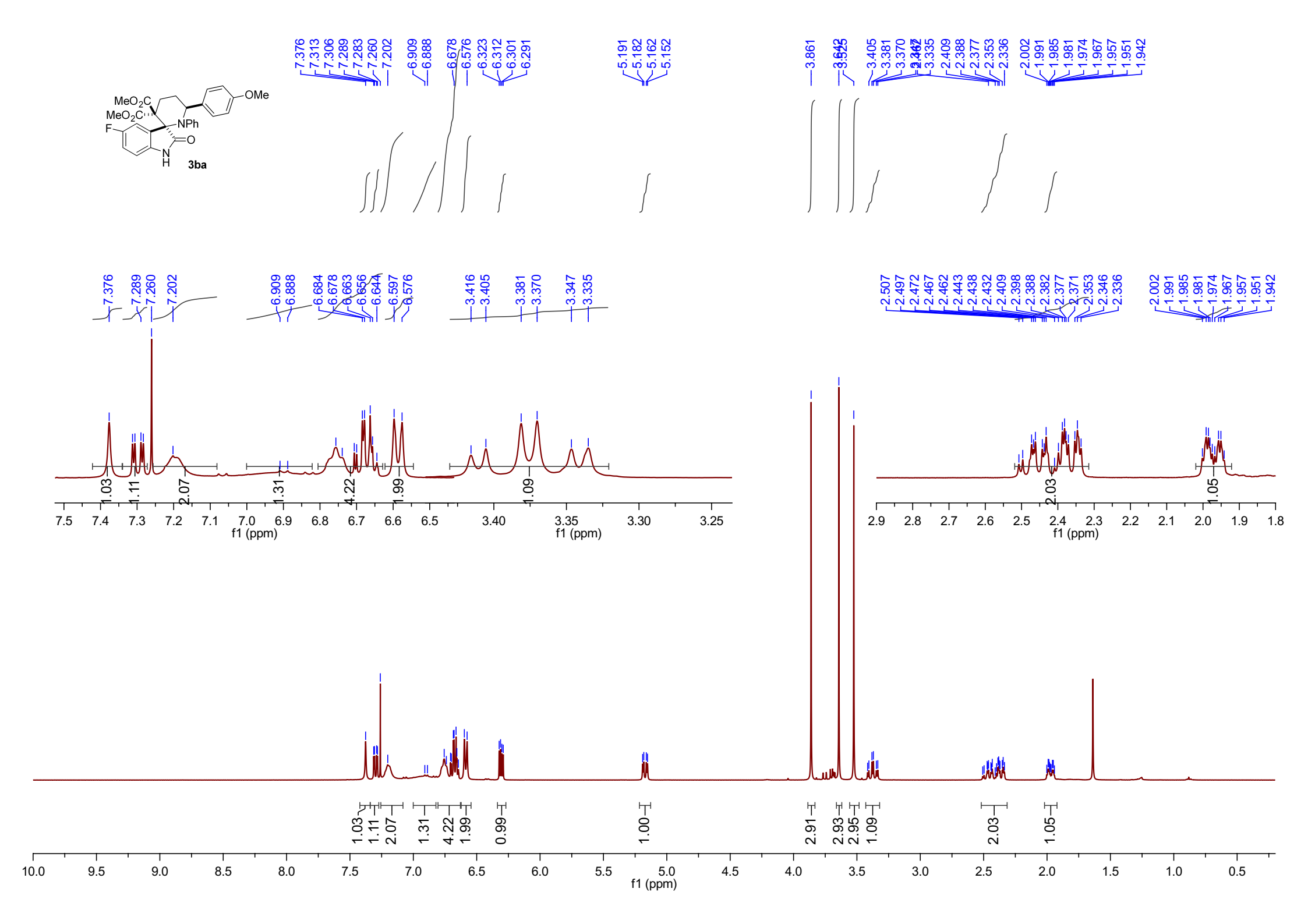
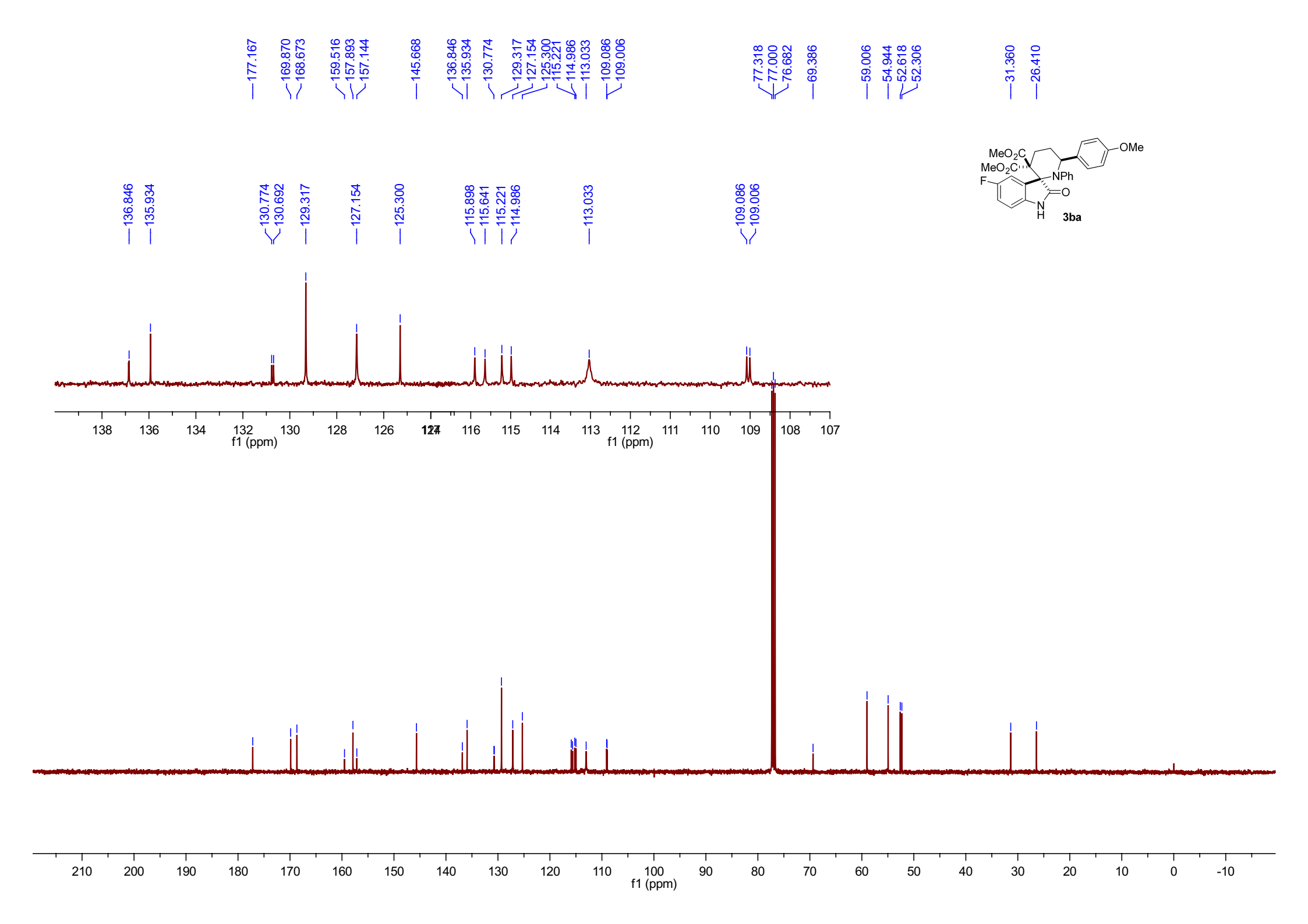
169.429
168.604
157.768
145.968
140.850
136.398
129.295
129.175
128.608
128.137
126.883
125.002
121.352
112.958
108.659
77.318
77.000
76.683
69.128
61.284
61.047
58.912
54.922
31.633
26.428
14.013
13.444
EtO2C
EtO2C
NPh
O
N
H
OMe
3ak
f1 (ppm)


iPrO2C
iPrO2C
NPh
O
N
H
OMe
3al
f1 (ppm)


iPrO2C
iPrO2C
NPh
O
N
H
OMe
3al
176.787
168.716
168.001
157.757
146.083
140.746
136.532
129.269
128.500
124.962
121.442
112.978
108.606
77.318
77.000
76.683
69.348
68.768
68.736
58.960
58.853
54.924
31.813
26.414
21.684
21.600
21.228
20.676
f1 (ppm)


MeO2C
MeO2C
F
NPh
O
N
H
OMe
3ba
7.376
7.313
7.306
7.289
7.283
7.260
7.202
6.909
6.888
6.678
6.576
6.323
6.312
6.301
6.291
5.191
5.182
5.162
5.152
3.861
3.405
3.381
3.370
3.335
2.409
2.388
2.377
2.353
2.336
2.002
1.991
1.985
1.981
1.974
1.967
1.957
1.951
1.942
1.03
1.11
2.07
1.31
4.22
1.99
1.09
2.03
1.05
0.99
1.00
2.91
2.93
2.95
f1 (ppm)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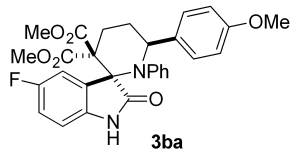
168.673
159.516
157.893
157.144
145.668
136.846
135.934
130.774
129.317
127.154
125.300
115.221
114.986
113.033
109.086
109.006
77.318
77.000
76.682
69.386
59.006
54.944
52.618
52.306
31.360
26.410
MeO2C
MeO2C
NPh
F
O
N
H
OMe
3ba
f1 (ppm)
f1 (ppm)
f1 (ppm)

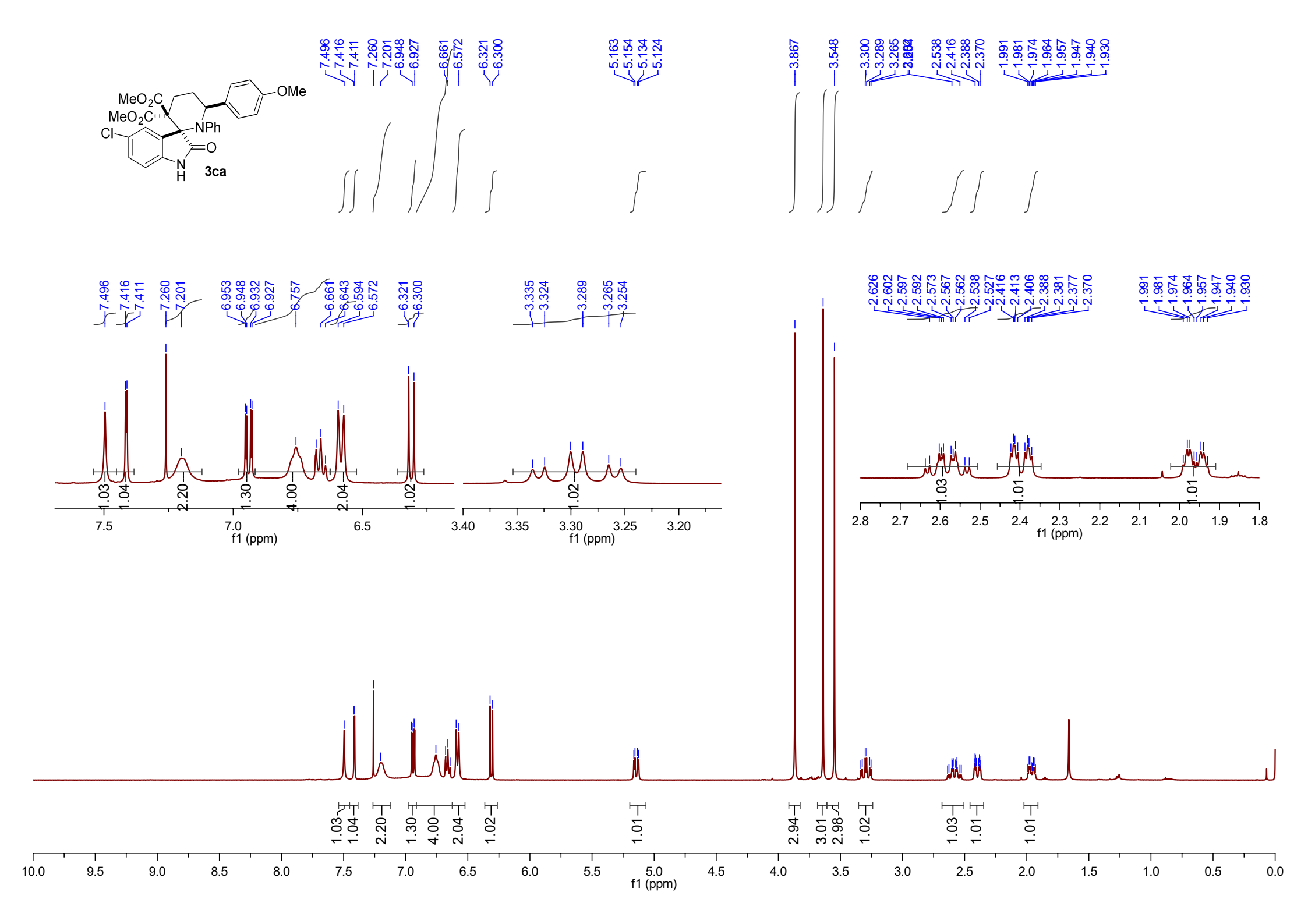


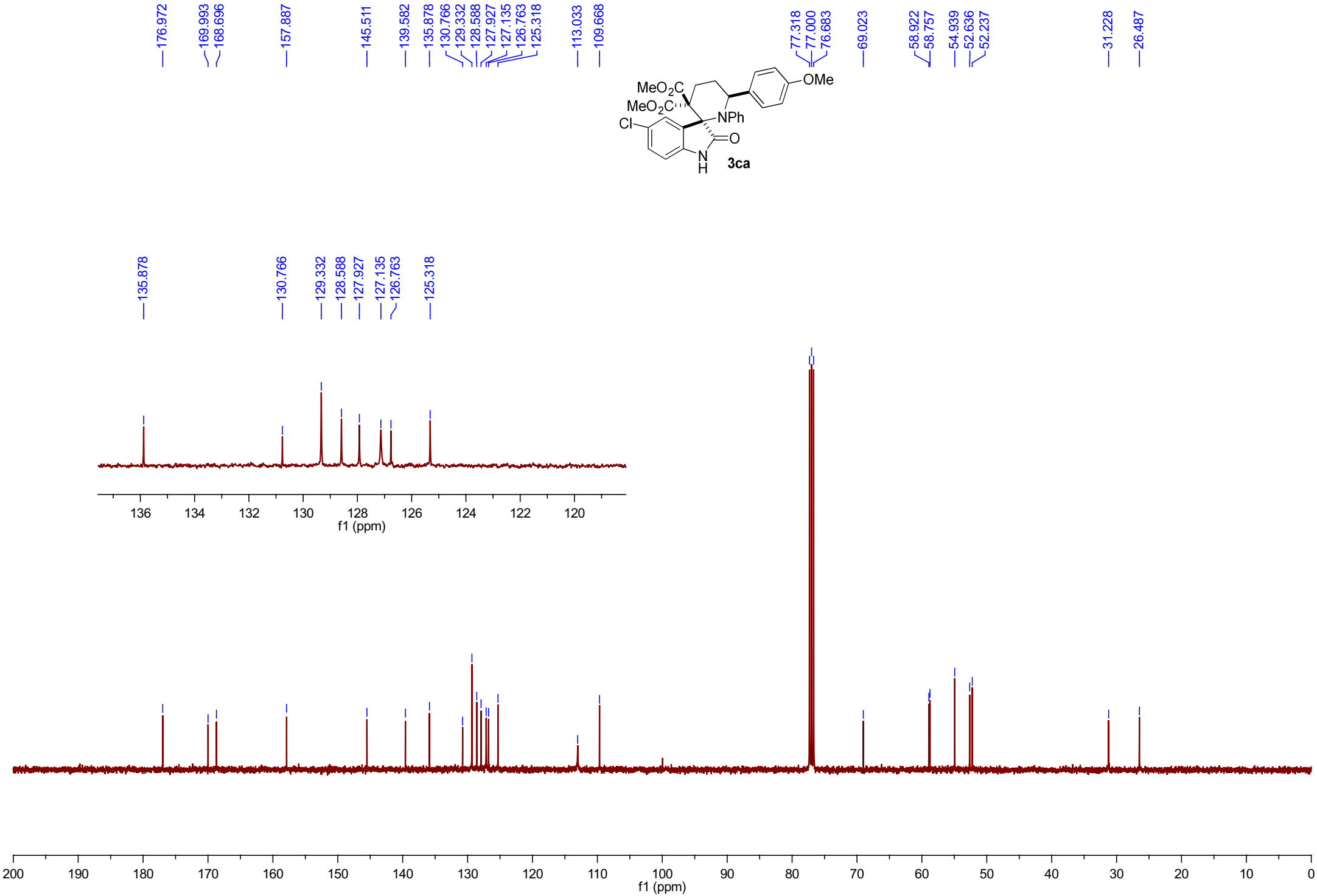
3ba

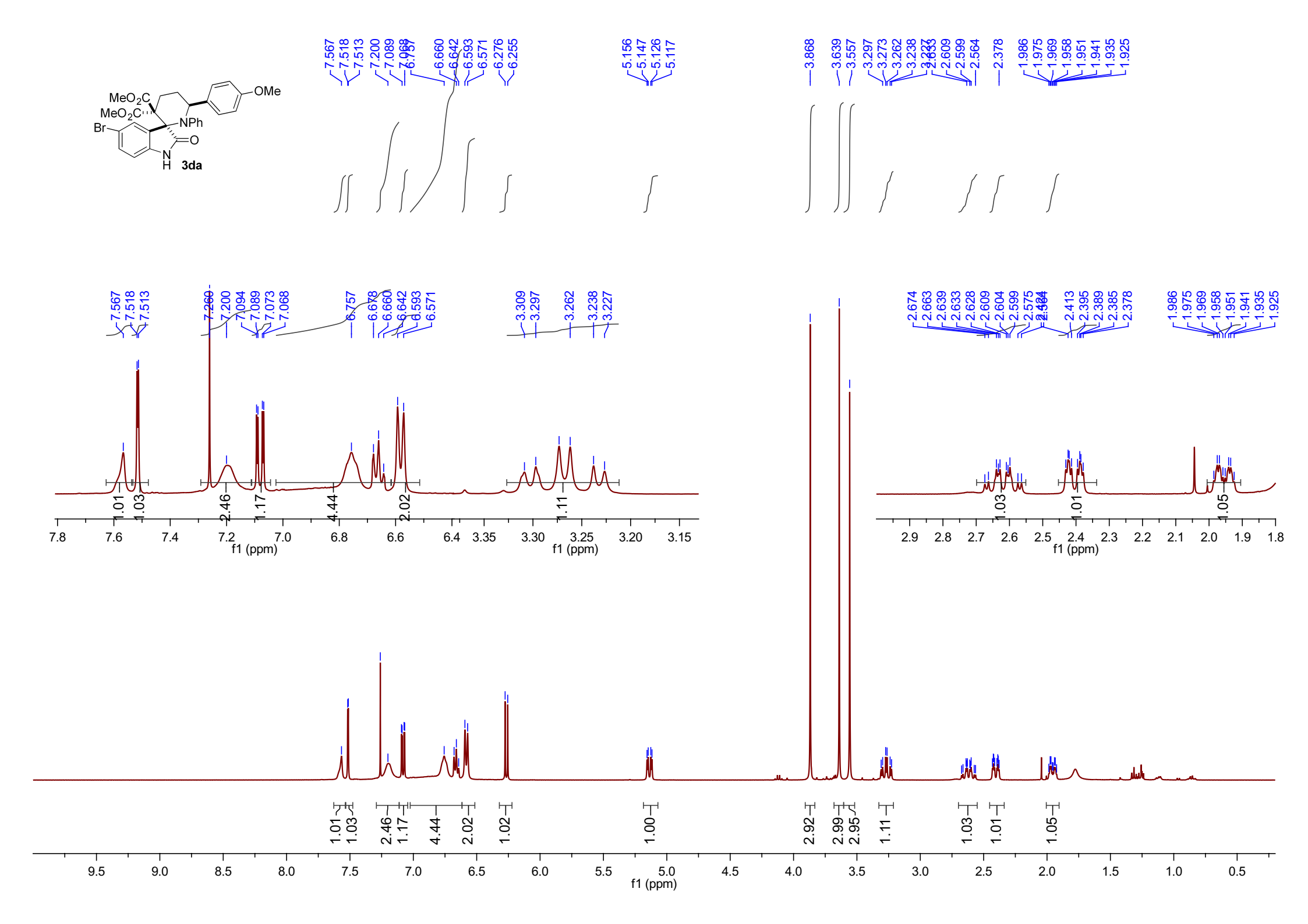
-121.052

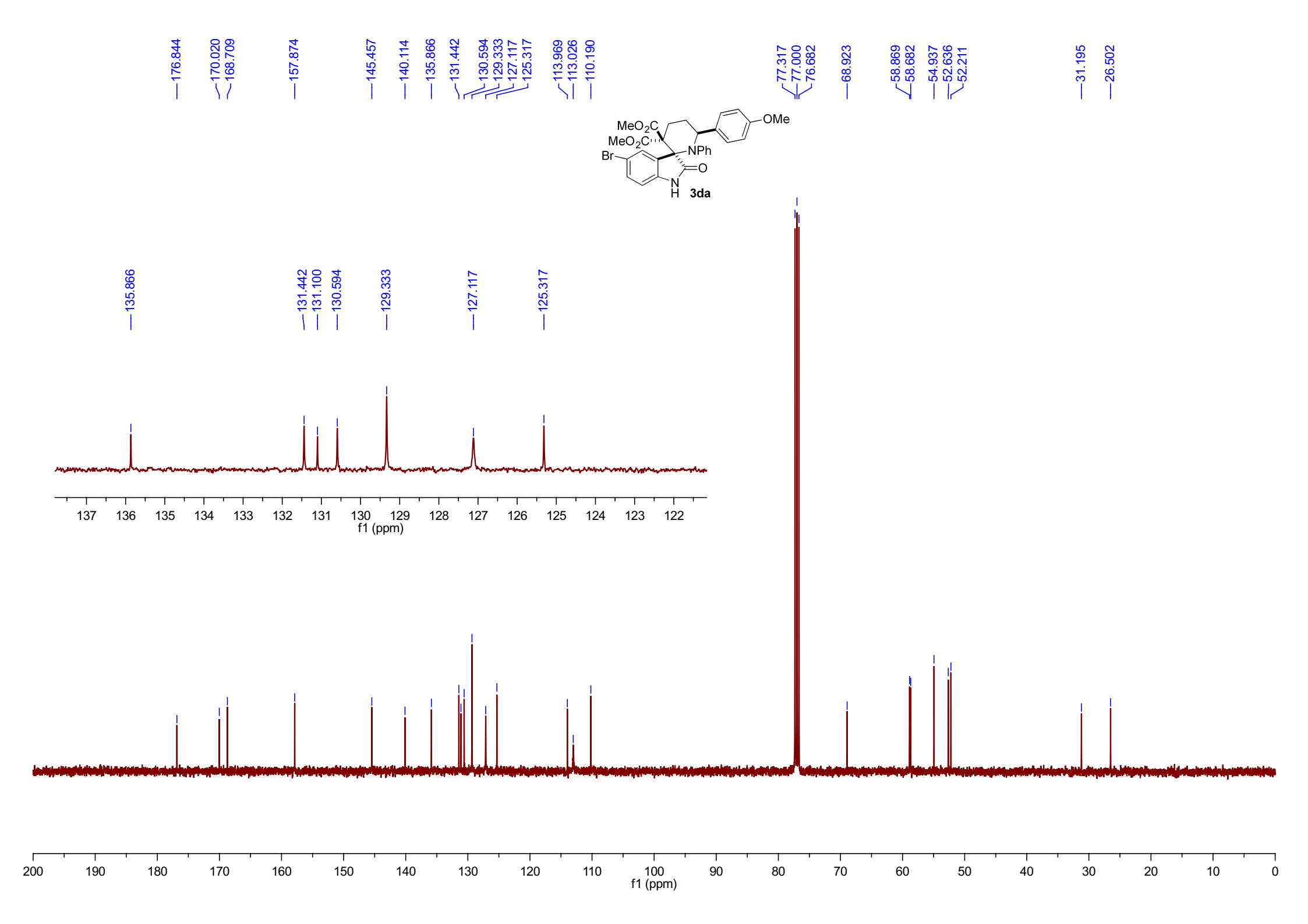
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

f1 (ppm)


MeO2C
MeO2C
Cl
NPh
O
N
H
OMe
3ca
7.496
7.416
7.411
7.260
7.201
6.948
6.927
6.661
6.572
6.321
6.300
5.163
5.154
5.134
5.124
3.867
3.548
3.300
3.289
3.265
2.538
2.416
2.388
2.370
1.991
1.981
1.974
1.964
1.957
1.947
1.940
1.930
f1 (ppm)


176.972
169.993
168.696
157.887
145.511
139.582
135.878
130.766
129.332
128.588
127.927
127.135
126.763
125.318
113.033
109.668
77.318
77.000
76.683
69.023
58.922
58.757
54.939
52.636
52.237
31.228
26.487
MeO2C
MeO2C
Cl
NPh
O
N
H
OMe
3ca
f1 (ppm)
f1 (ppm)


MeO2C
MeO2C
Br
NPh
O
N
H
OMe
3da
7.567
7.518
7.513
7.200
7.089
6.757
6.660
6.642
6.593
6.571
6.276
6.255
5.156
5.147
5.126
5.117
3.868
3.639
3.557
3.297
3.273
3.262
3.238
2.609
2.599
2.564
2.378
1.986
1.975
1.969
1.958
1.951
1.941
1.935
1.925
f1 (ppm)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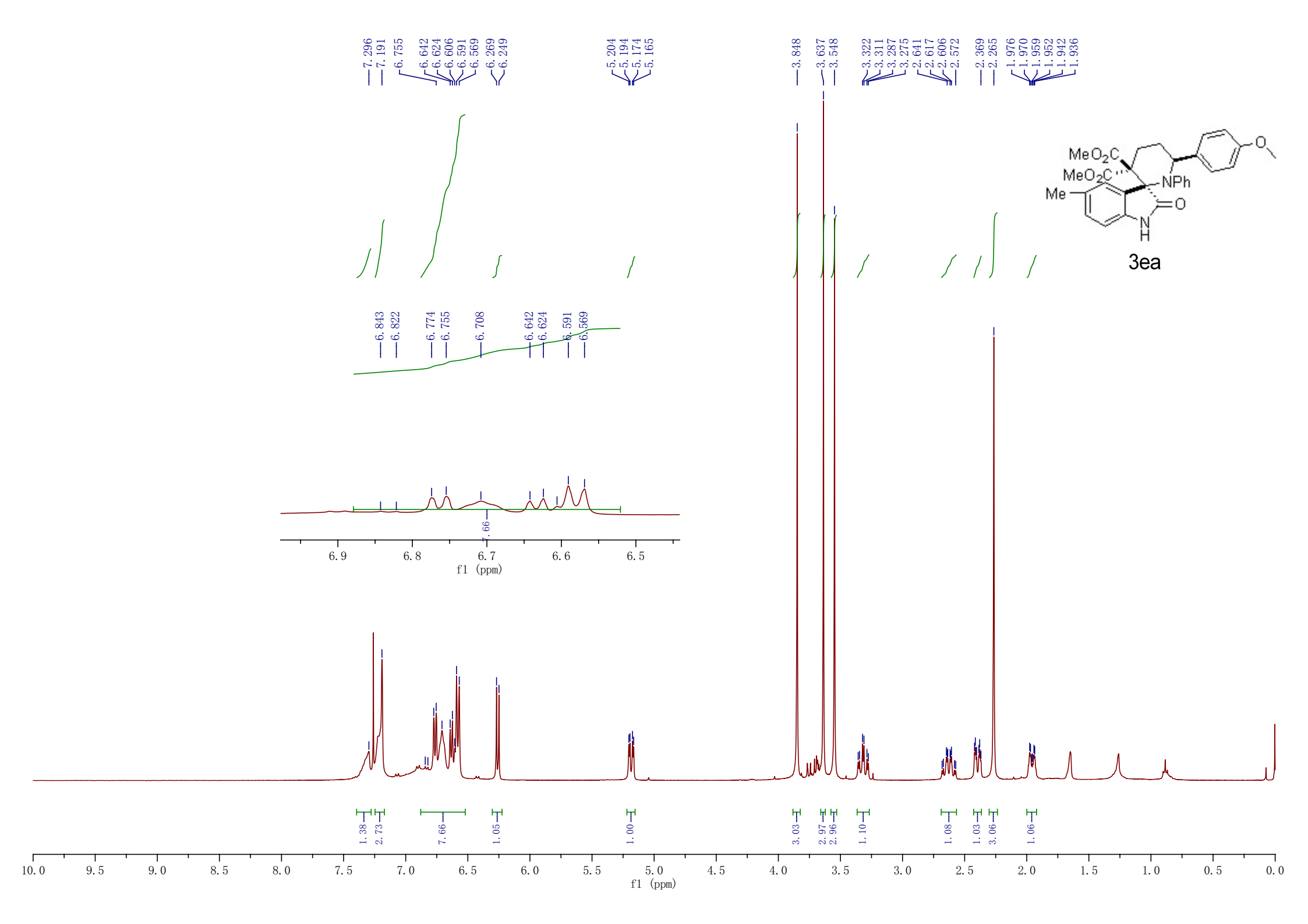
170.020
168.709
157.874
145.457
140.114
135.866
131.442
130.594
129.333
127.117
125.317
113.969
113.026
110.190
77.317
77.000
76.682
68.923
58.869
58.682
54.937
52.636
52.211
31.195
26.502
MeO2C
MeO2C
Br
NPh
O
N
H
OMe
3da
f1 (ppm)
f1 (ppm)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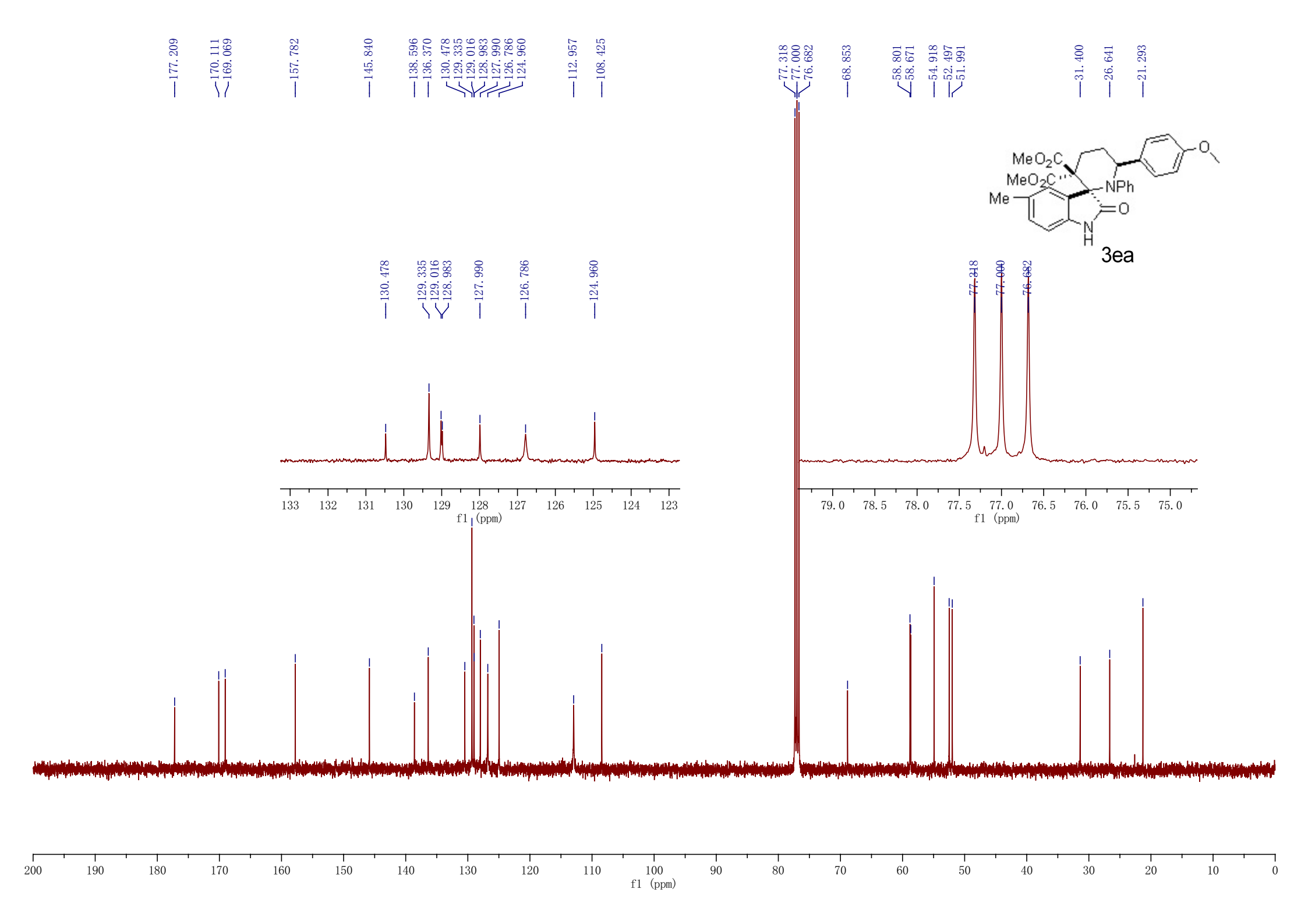
6.591
6.569
6.269
6.249
5.204
5.194
5.174
5.165
3.848
3.637
3.548
3.322
3.311
3.287
3.275
2.641
2.617
2.606
2.572
2.369
2.265
1.976
1.970
1.959
1.952
1.942
1.936
6.843
6.822
6.774
6.755
6.708
6.642
6.624
6.591
6.569
7.66
6.9
6.8
6.7
6.6
6.5
f1 (ppm)
Me O2C
MeO2C
NPh
Me
O
N
H
O
3ea
1.38
2.73
7.66
1.05
1.00
3.03
2.97
2.96
1.10
1.08
1.03
3.06
1.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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169.069
157.782
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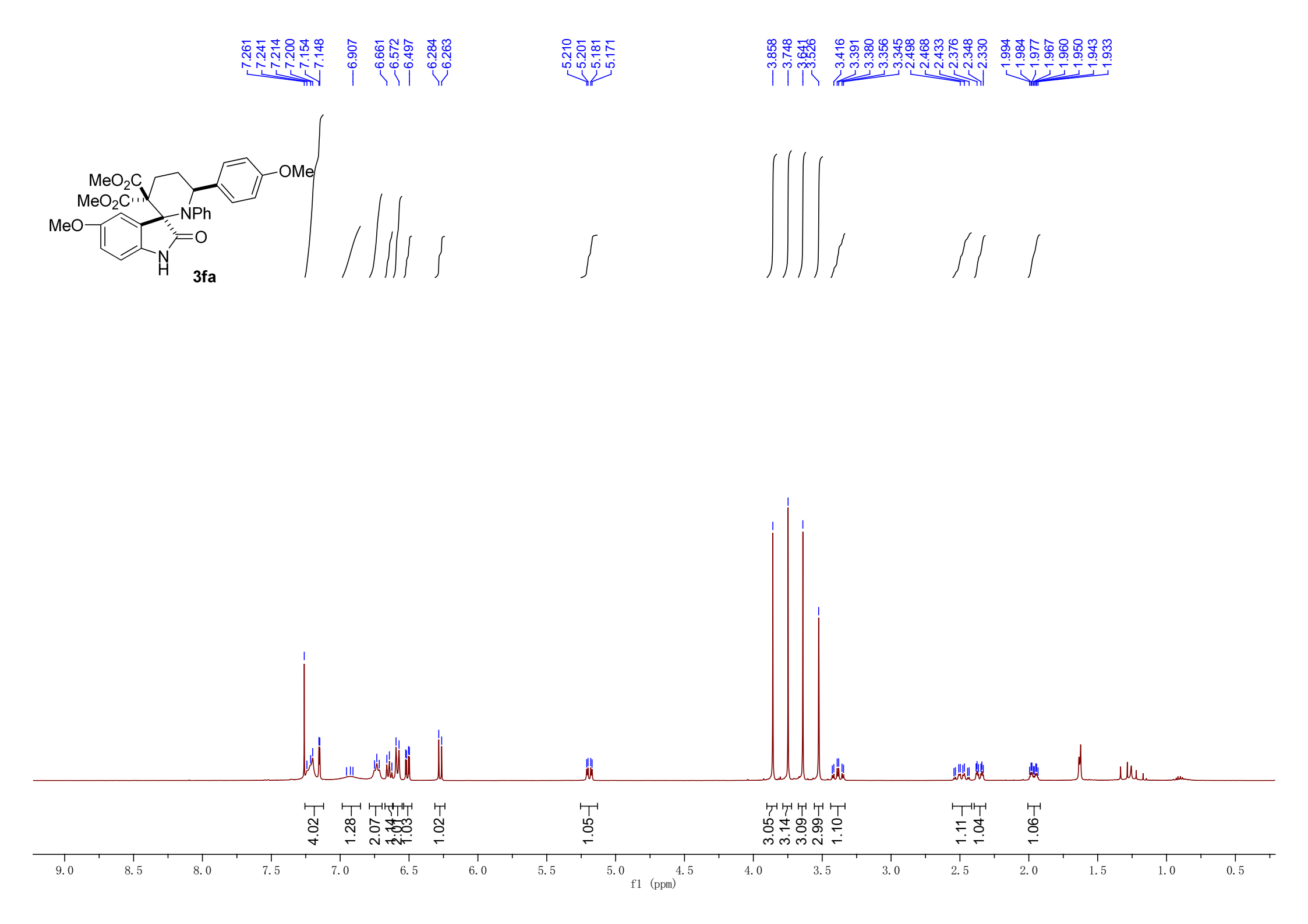
138.596
136.370
130.478
129.335
129.016
128.983
127.990
126.786
124.960
112.957
108.425
77.318
77.000
76.682
68.853
58.801
58.671
54.918
52.497
51.991
31.400
26.641
21.293
MeO2C
MeO2C
NPh
Me
O
O
N
H
3ea
f1 (ppm)
f1 (ppm)
f1 (ppm)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7.214
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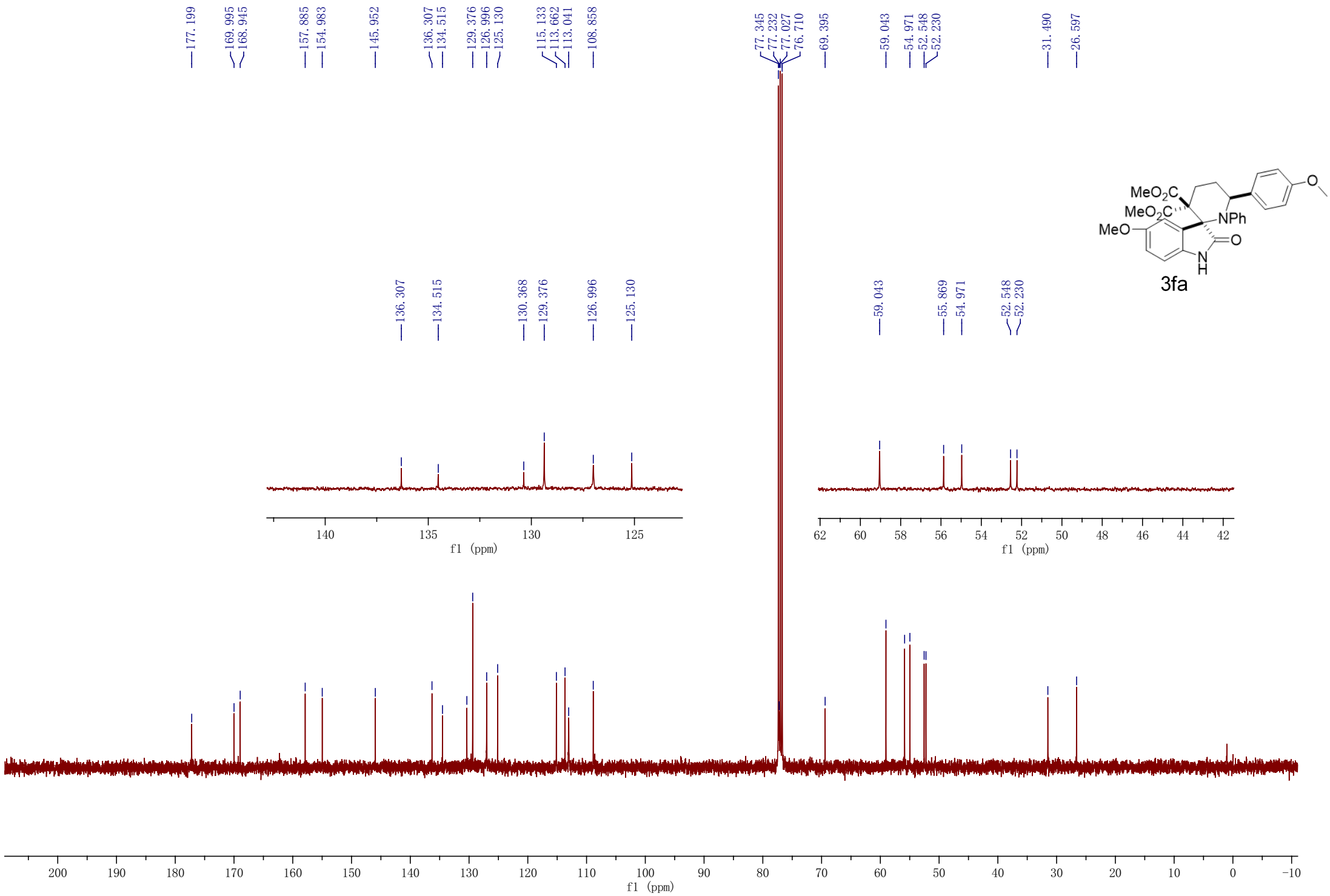
7.154
7.148
6.907
6.661
6.572
6.497
6.284
6.263
5.210
5.201
5.181
5.171
3.858
3.748
3.641
3.526
3.416
3.391
3.380
3.356
3.345
2.498
2.468
2.433
2.376
2.348
2.330
1.994
1.984
1.977
1.967
1.960
1.950
1.943
1.933
MeO2C
MeO2C
NPh
OMe
MeO
O
N
H
3fa
4.02
1.28
2.07
2.14
2.03
1.03
1.02
1.05
3.05
3.14
3.09
2.99
1.10
1.11
1.04
1.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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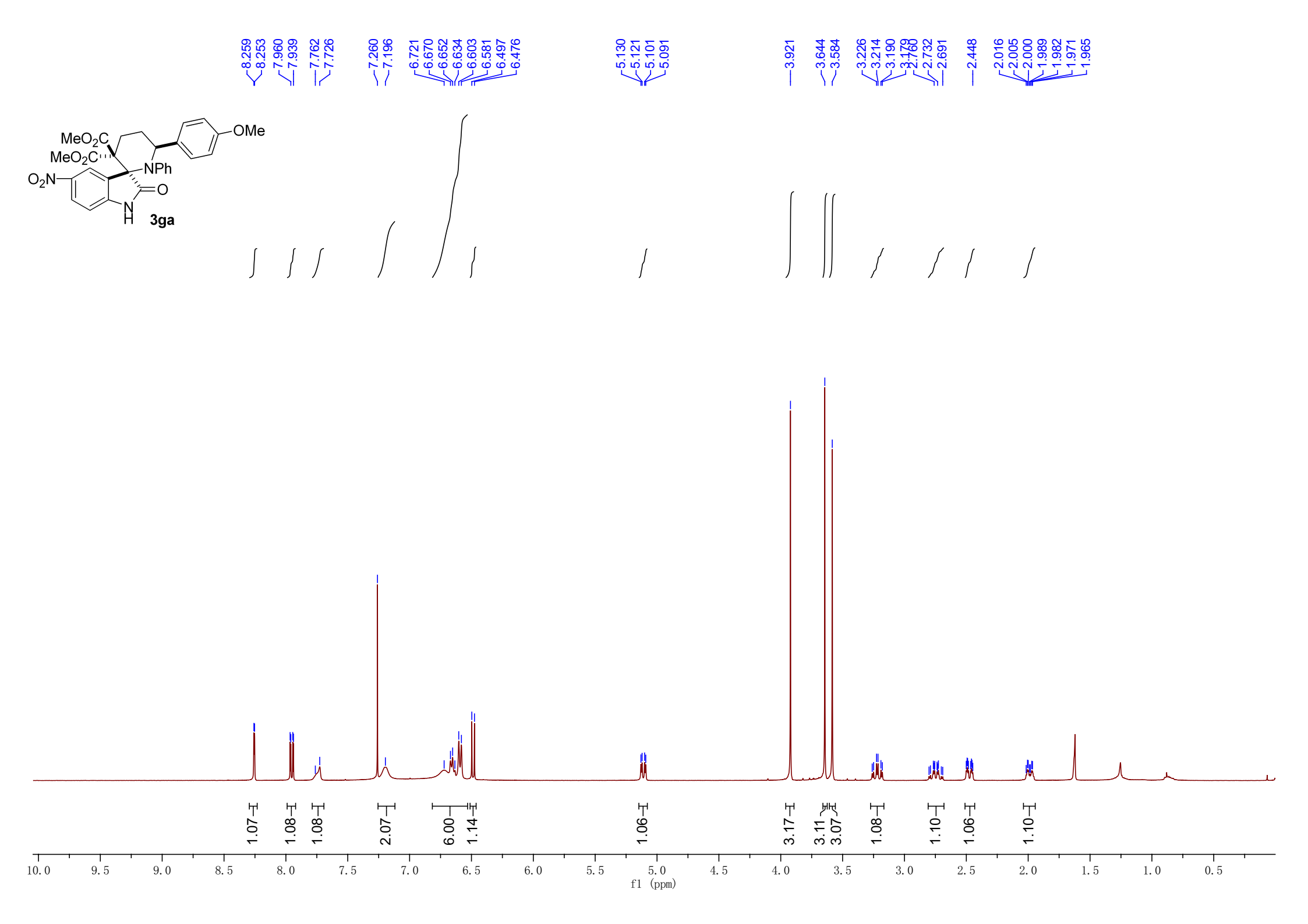
168.945
157.885
154.983
145.952
136.307
134.515
129.376
126.996
125.130
115.133
113.662
113.041
108.858
77.345
77.232
77.027
76.710
69.395
59.043
54.971
52.548
52.230
31.490
26.597
MeO2C
MeO2C
NPh
MeO
O
N
H
O
3fa
f1 (ppm)
f1 (ppm)
f1 (ppm)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7.939
7.762
7.726
7.260
7.196
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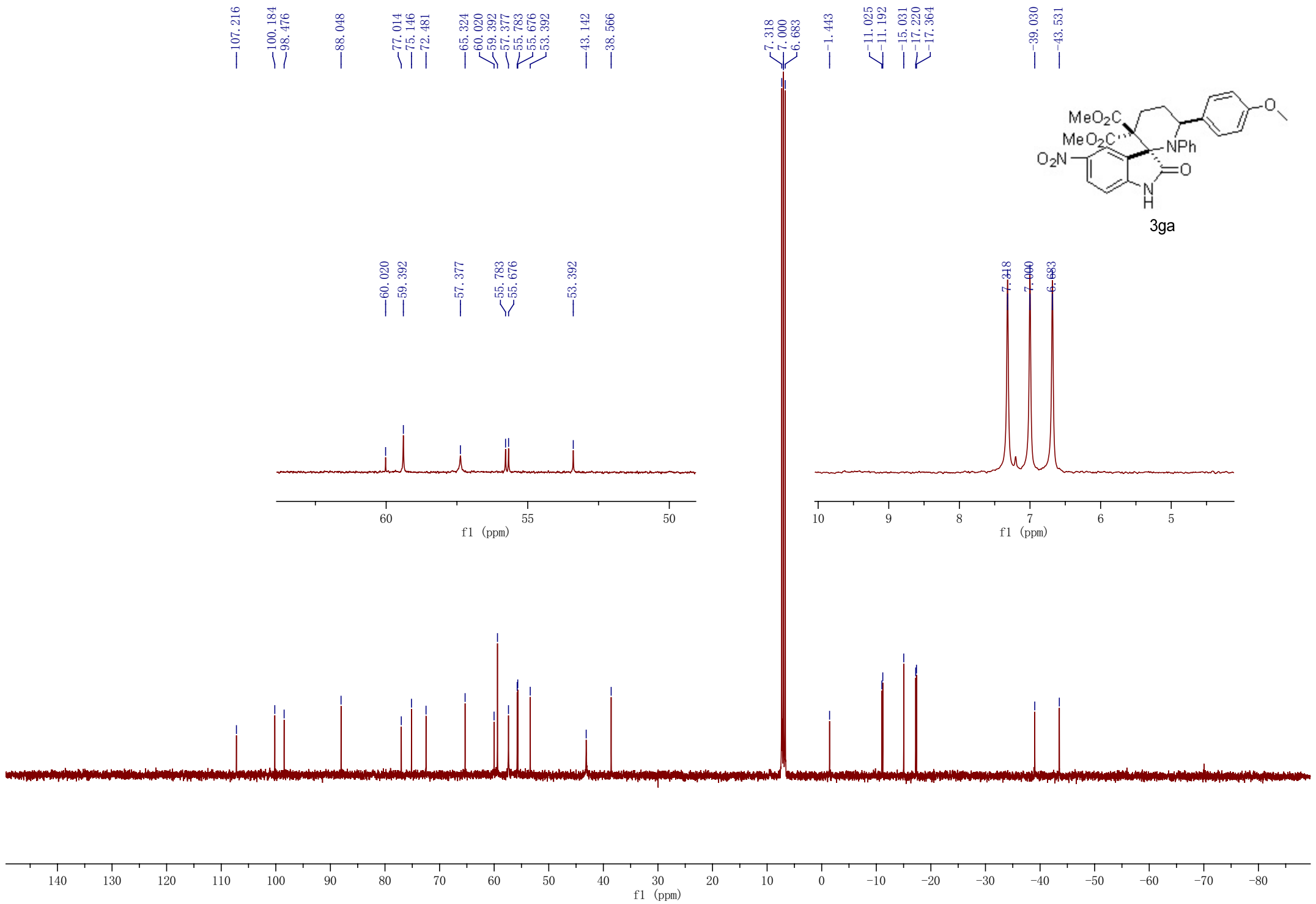
6.670
6.652
6.634
6.603
6.581
6.497
6.476
5.130
5.121
5.101
5.091
3.921
3.644
3.584
3.226
3.214
3.190
3.178
3.160
2.732
2.691
2.448
2.016
2.005
2.000
1.989
1.982
1.971
1.965
MeO2C
MeO2C
O2N
NPh
O
N
H
OMe
3ga
1.07
1.08
1.08
2.07
6.00
1.14
1.06
3.17
3.11
3.07
1.08
1.10
1.06
1.10
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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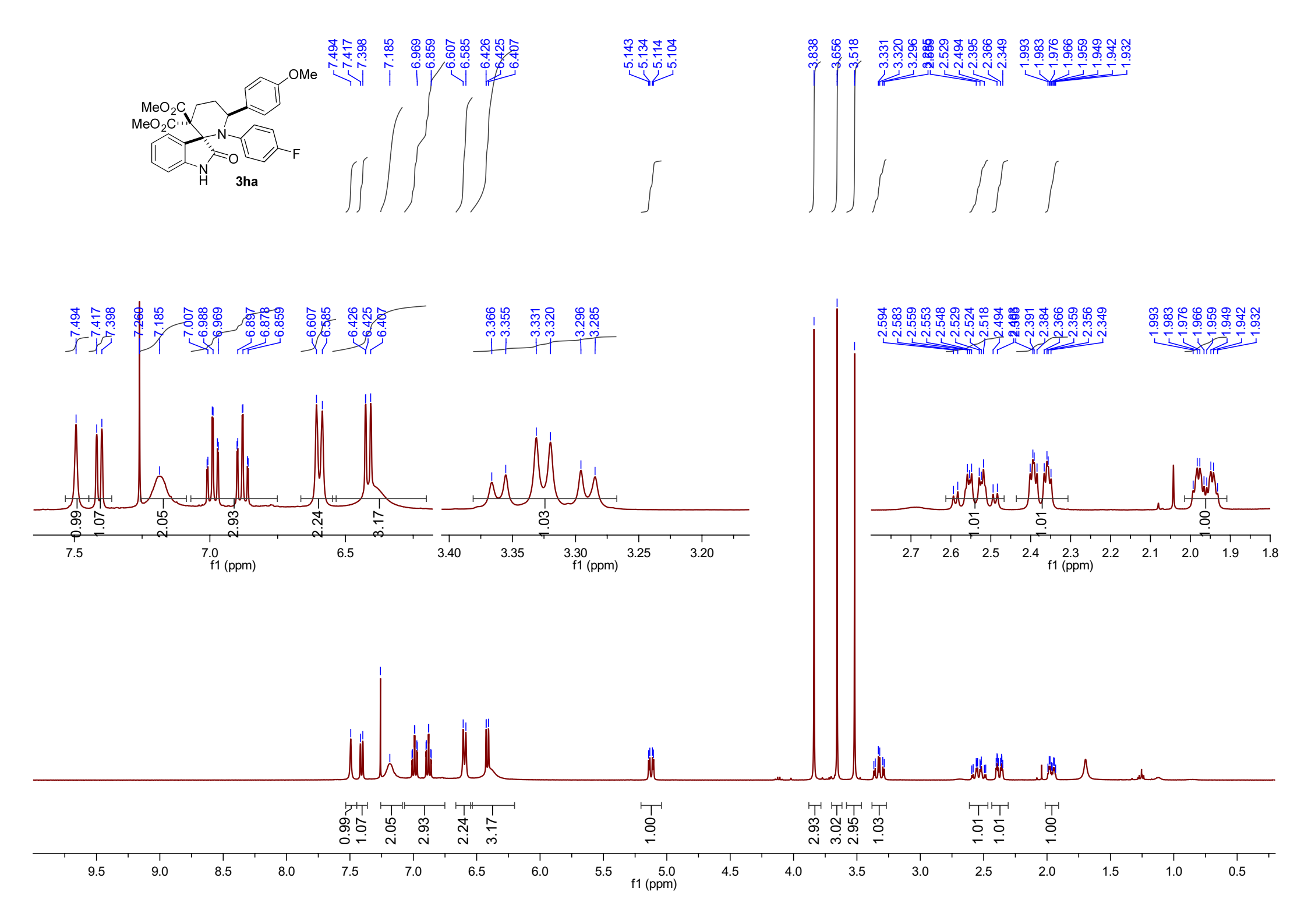
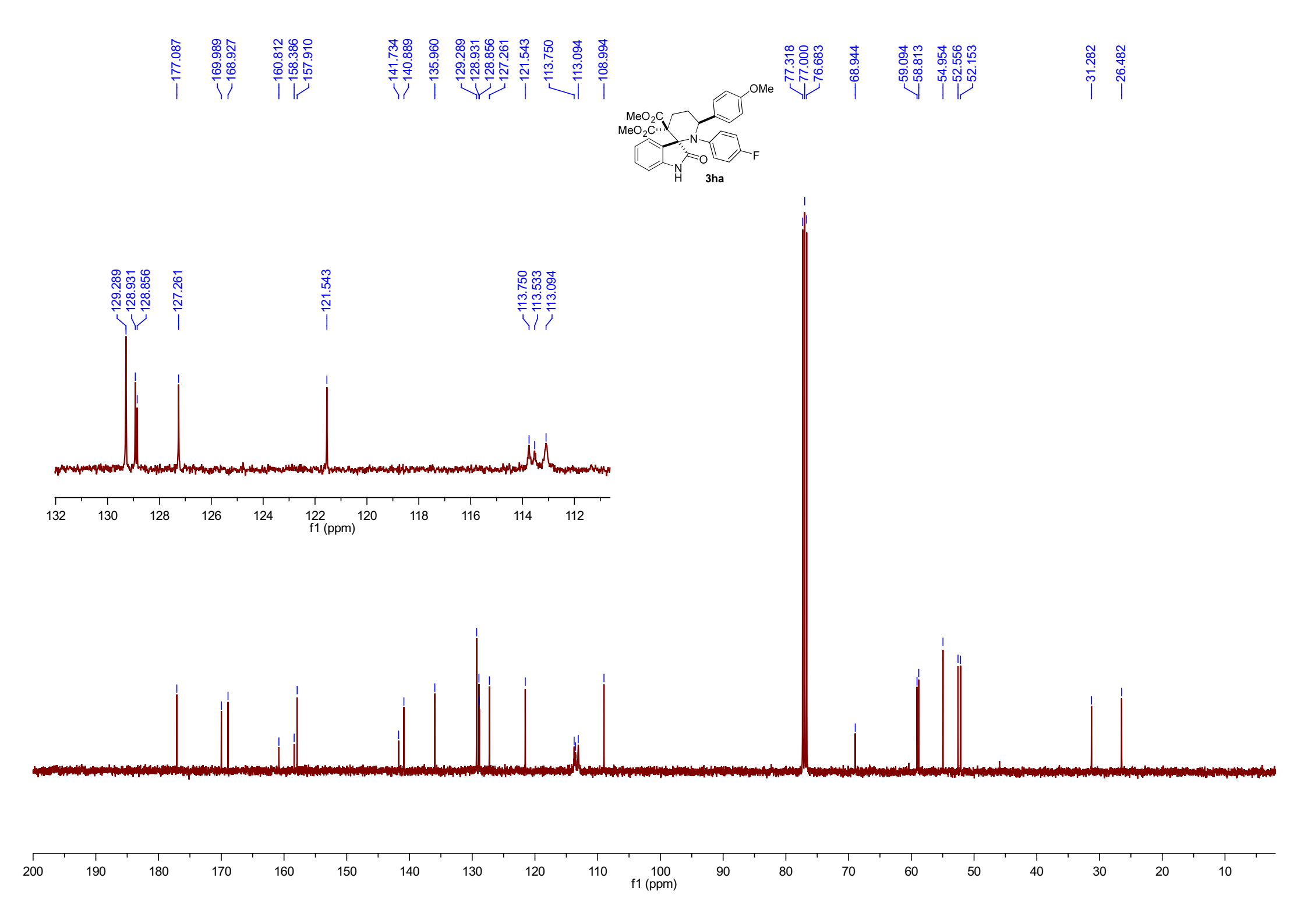
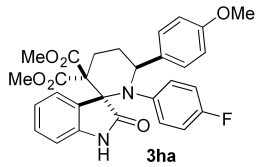
98.476
88.048
77.014
75.146
72.481
65.324
60.020
59.392
57.377
55.783
55.676
53.392
43.142
38.566
7.318
7.000
6.683
1.443
-11.025
-11.192
-15.031
-17.220
-17.364
-39.030
-43.531
MeO2C
MeO2C
NPh
O2N
O
O
N
H
3ga
f1 (ppm)
f1 (ppm)
f1 (ppm)


OMe
MeO2C
MeO2C
N
O
F
N
H
3ha
7.494
7.417
7.398
7.185
6.969
6.859
6.607
6.585
6.426
6.425
6.407
5.143
5.134
5.114
5.104
3.838
3.656
3.518
3.331
3.320
3.296
2.529
2.494
2.395
2.366
2.349
1.993
1.983
1.976
1.966
1.959
1.949
1.942
1.932
0.99
1.07
2.05
2.93
2.24
3.17
1.03
1.01
1.01
1.00
2.93
3.02
2.95
1.03
1.01
1.01
1.00
f1 (ppm)


177.087
169.989
168.927
160.812
158.386
157.910
141.734
140.889
135.960
129.289
128.931
128.856
127.261
121.543
113.750
113.094
108.994
77.318
77.000
76.683
68.944
59.094
58.813
54.954
52.556
52.153
31.282
26.482
OMe
MeO2C
MeO2C
N
O
N
H
F
3ha
129.289
128.931
128.856
127.261
121.543
113.750
113.533
113.094
132
130
128
126
124
122
120
118
116
114
112
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

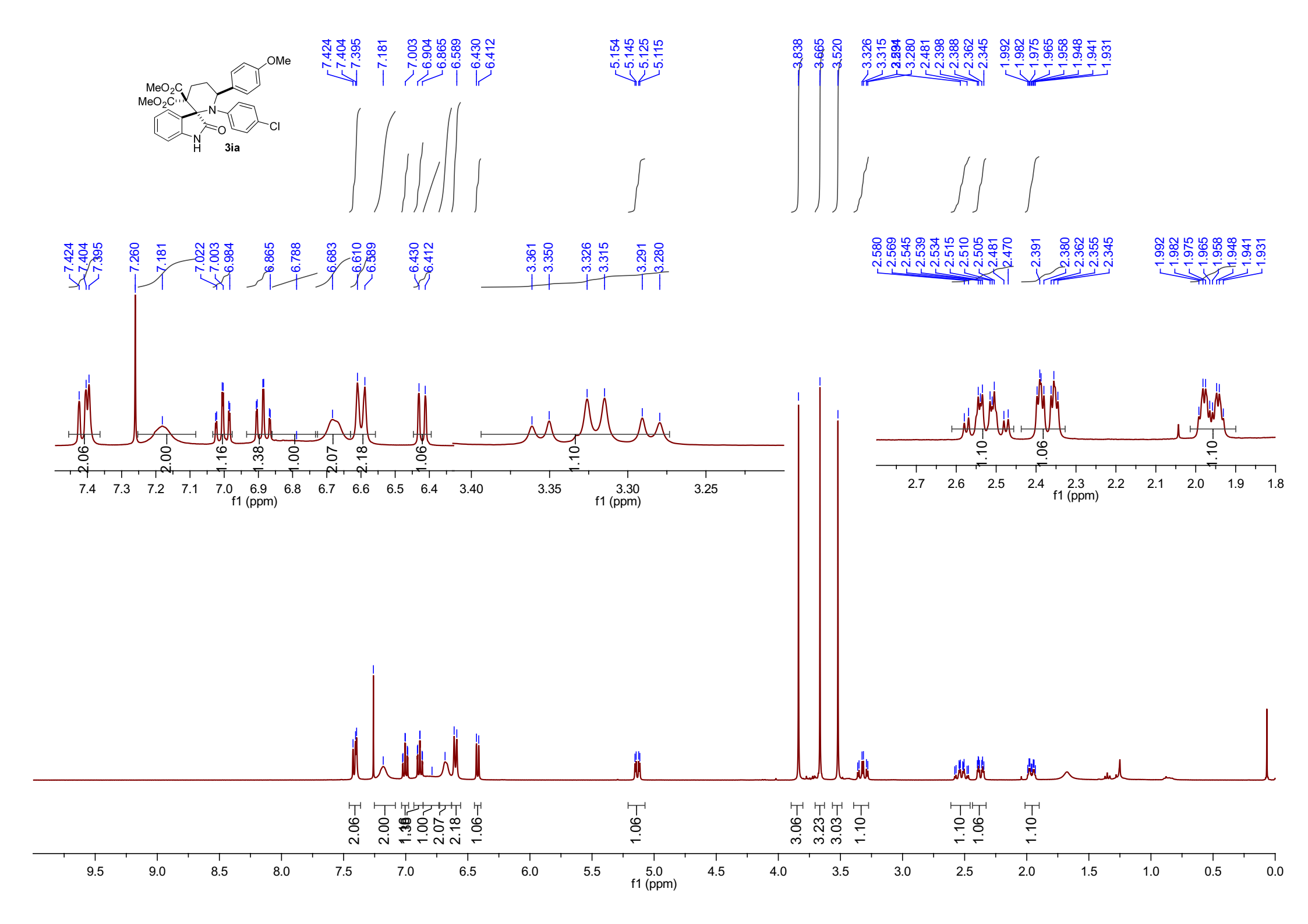


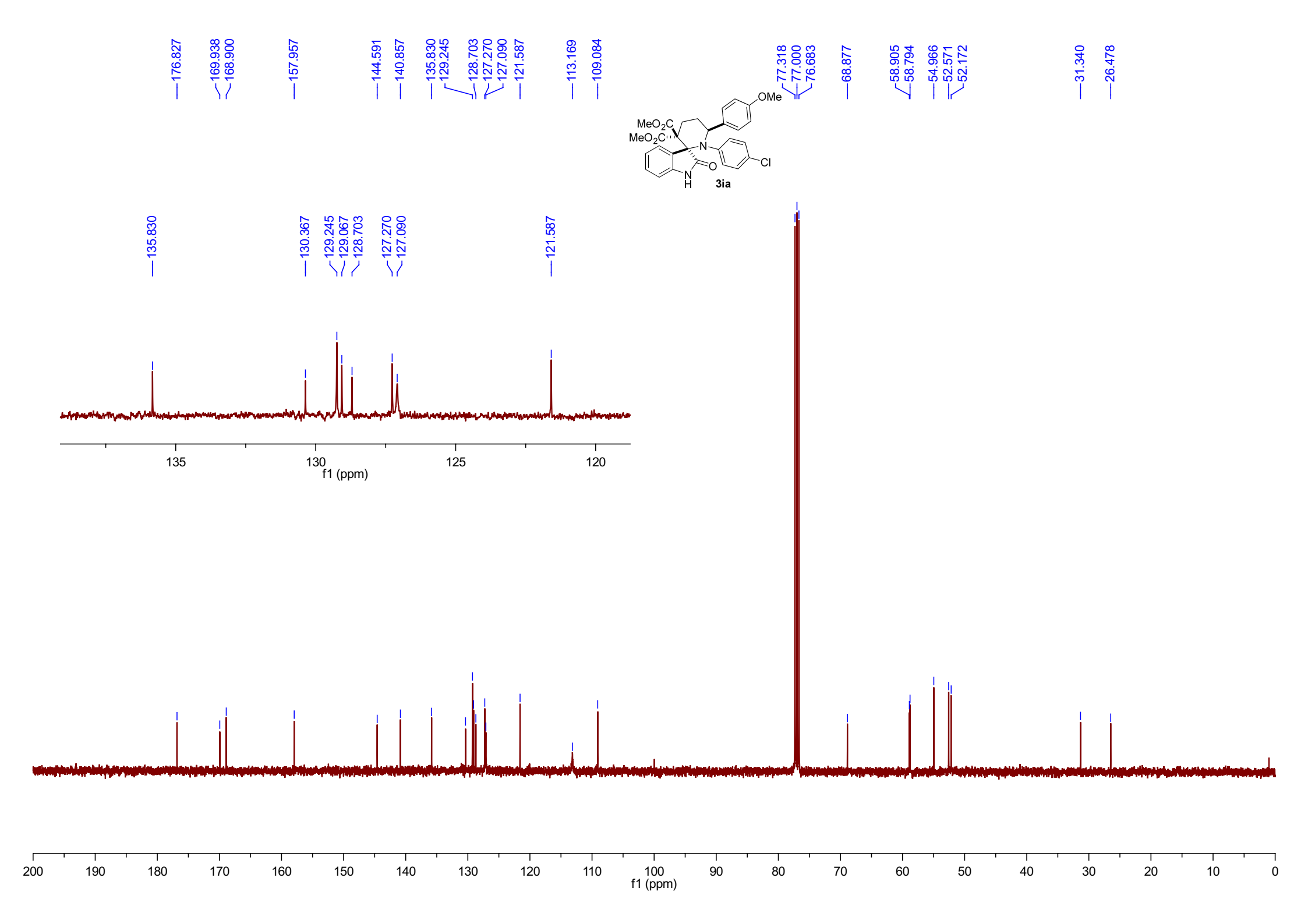
3ha

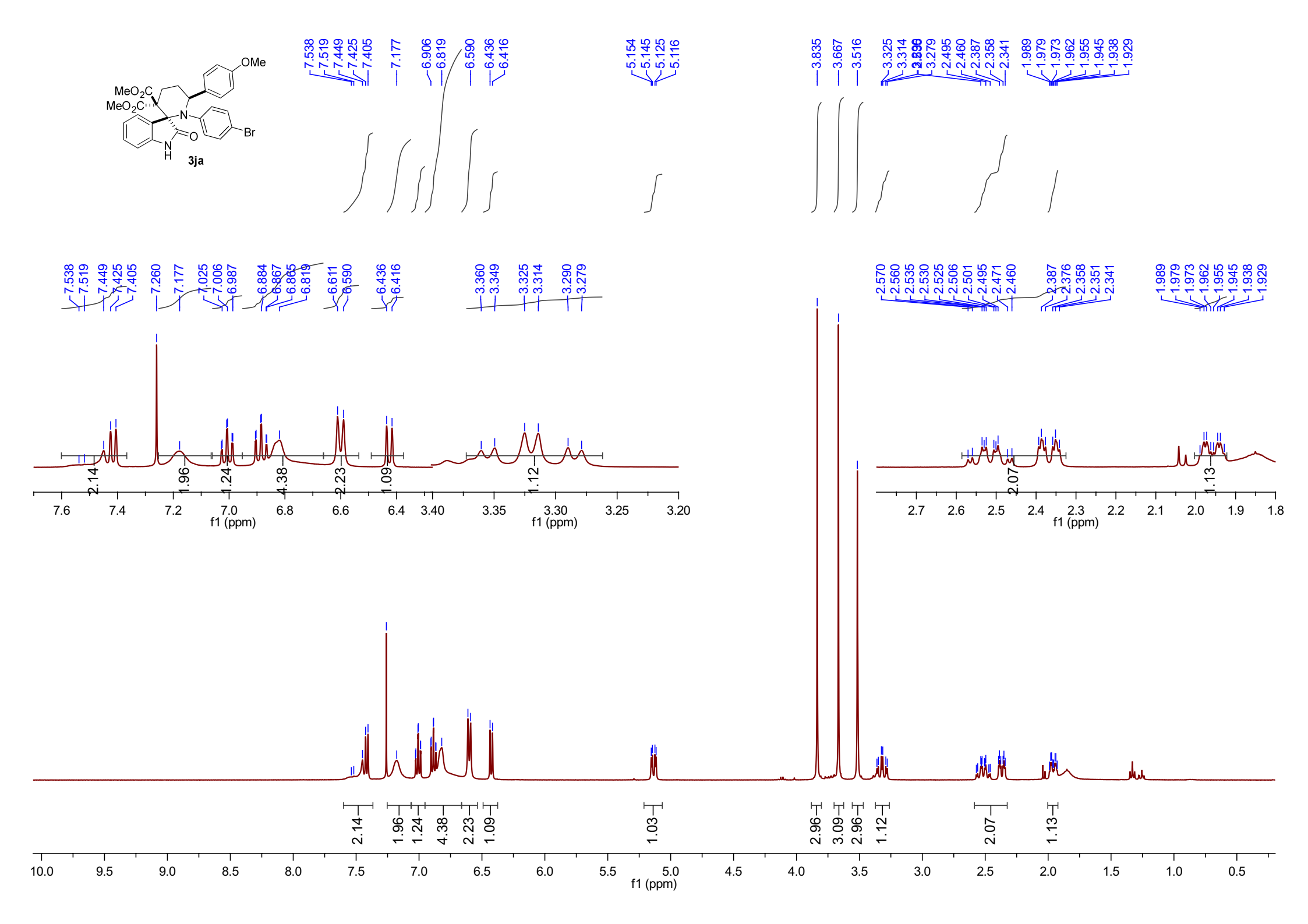
-116.798

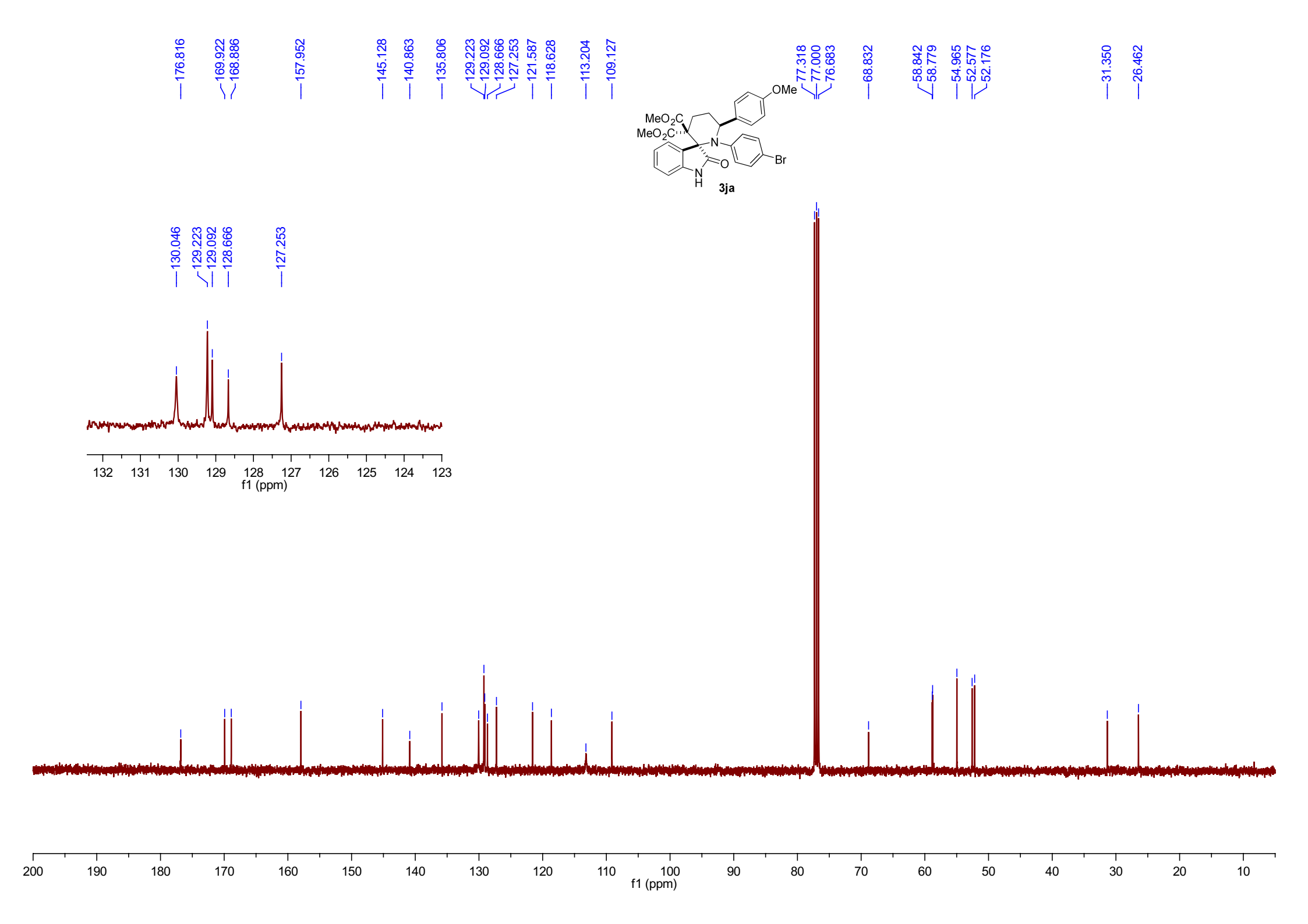
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

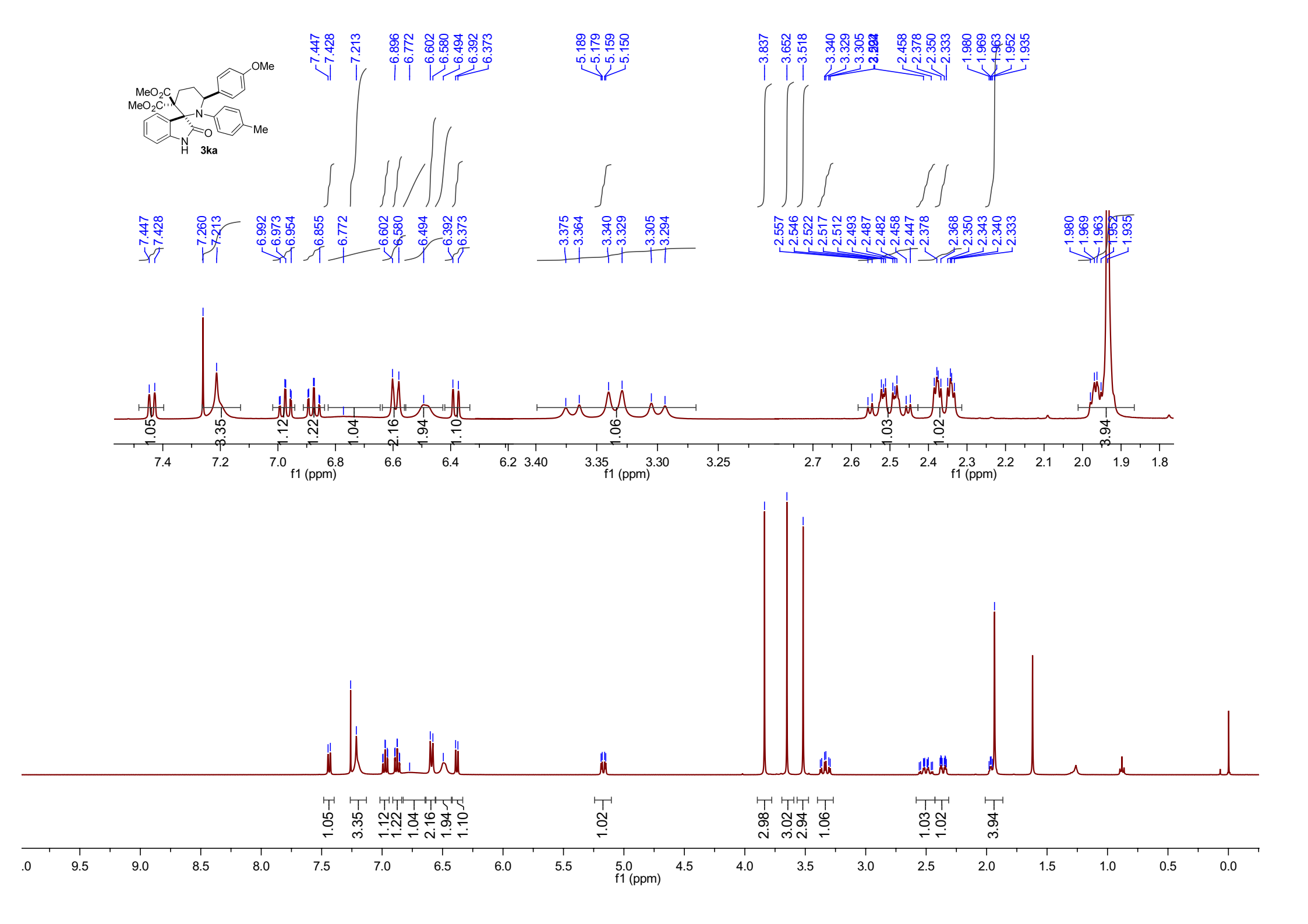
f1 (ppm)

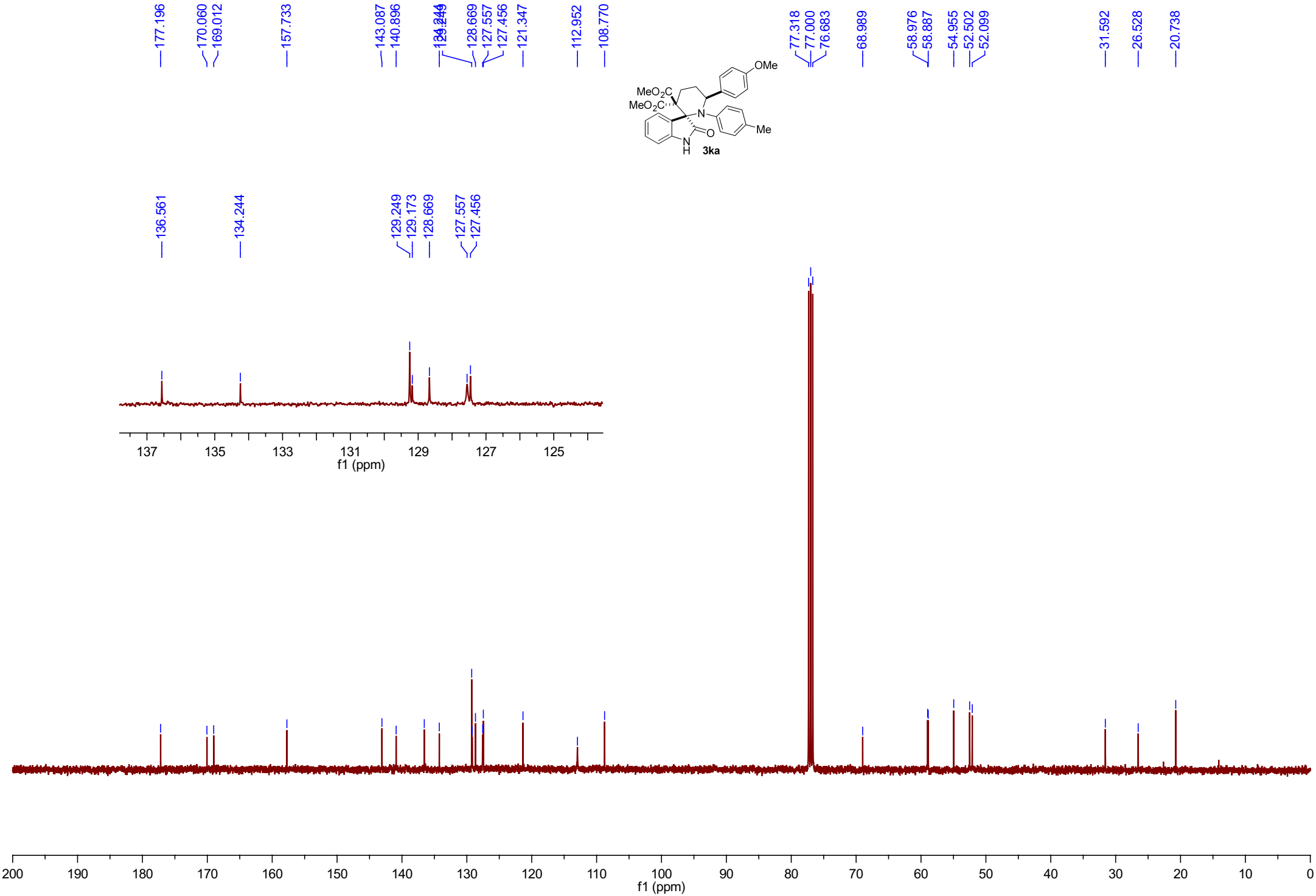

OMe
MeO2C
MeO2C
N
O
Cl
N
H
3ia
7.424
7.404
7.395
7.181
7.003
6.904
6.865
6.589
6.430
6.412
5.154
5.145
5.125
5.115
3.838
3.665
3.520
3.326
3.315
3.280
2.481
2.398
2.388
2.362
2.345
1.992
1.982
1.975
1.965
1.958
1.948
1.941
1.931
2.06
2.00
1.16
1.38
1.00
2.07
2.18
1.06
1.10
f1 (ppm)
1.10
1.06
1.10
f1 (ppm)
2.06
2.00
1.00
2.07
2.18
1.06
1.06
3.06
3.23
3.03
1.10
1.10
1.06
1.10
f1 (ppm)

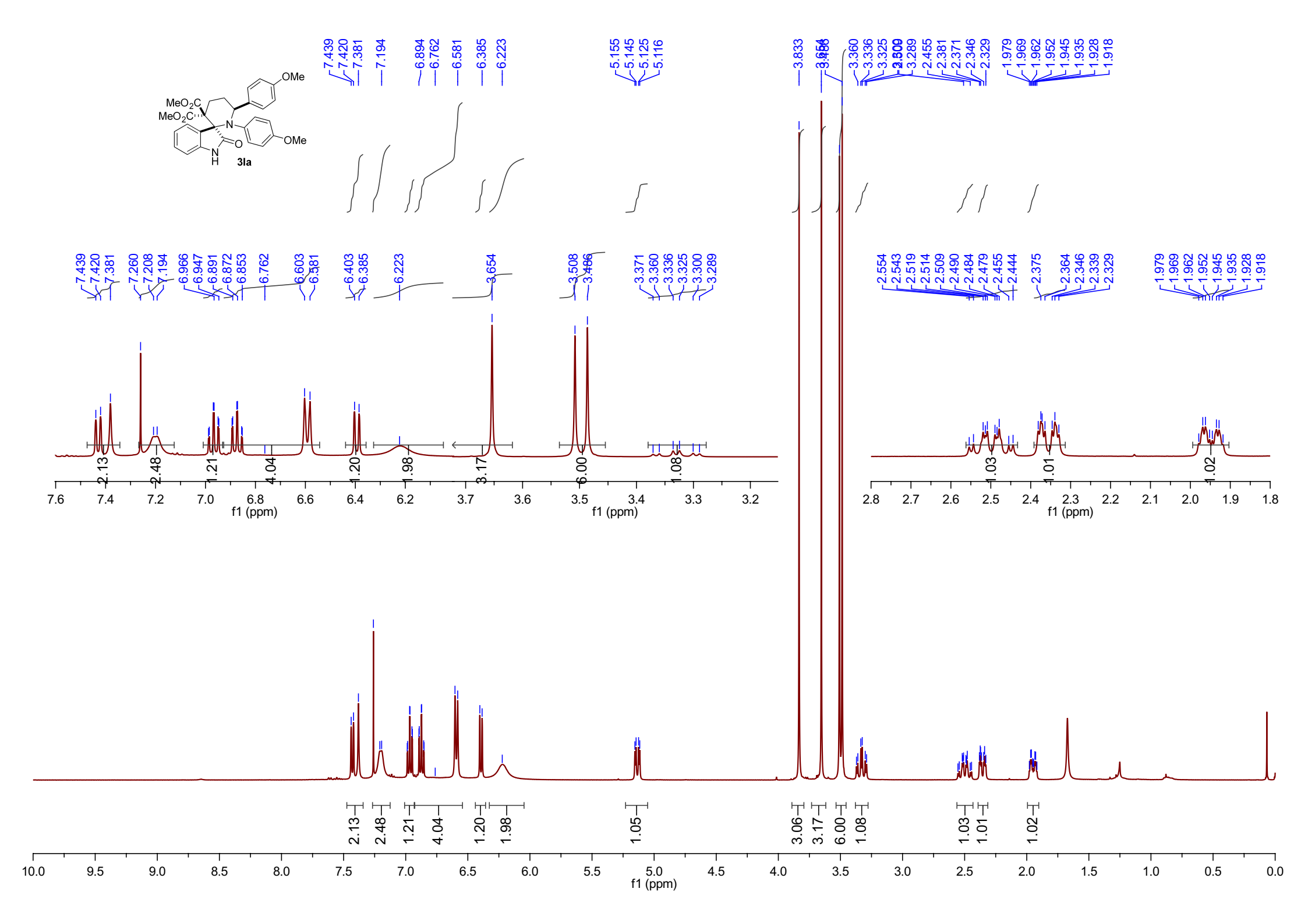

176.827
169.938
168.900
157.957
144.591
140.857
135.830
129.245
128.703
127.270
127.090
121.587
113.169
109.084
77.318
77.000
76.683
68.877
58.905
58.794
54.966
52.571
52.172
31.340
26.478
OMe
MeO2C
MeO2C
N
Cl
O
N
H
3ia
135.830
130.367
129.245
129.067
128.703
127.270
127.090
121.587
135
130
125
120
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

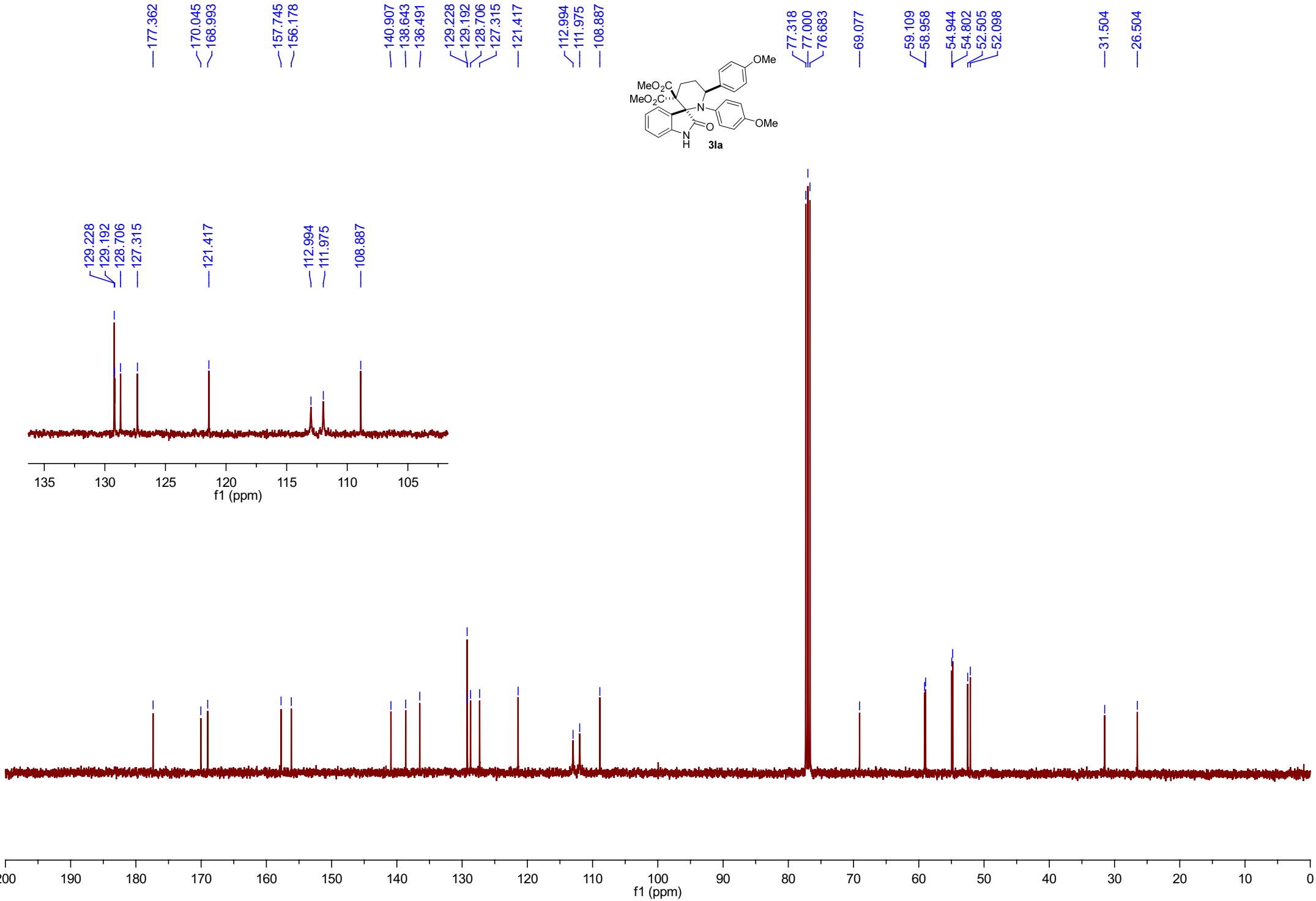

OMe
MeO2C
MeO2C
N
Br
O
N
H
3ja
7.538
7.519
7.449
7.425
7.405
7.177
6.906
6.819
6.590
6.436
6.416
5.154
5.145
5.125
5.116
3.835
3.667
3.516
3.325
3.314
3.279
2.495
2.460
2.387
2.358
2.341
1.989
1.979
1.973
1.962
1.955
1.945
1.938
1.929
7.260
7.025
7.006
6.987
6.884
6.867
6.865
6.819
6.611
6.590
6.436
6.416
3.360
3.349
3.325
3.314
3.290
3.279
2.570
2.560
2.535
2.530
2.525
2.506
2.501
2.495
2.471
2.460
2.387
2.376
2.358
2.351
2.341
1.989
1.979
1.973
1.962
1.955
1.945
1.938
1.929
2.14
1.96
1.24
4.38
2.23
1.09
1.12
2.07
1.13
1.03
2.96
3.09
2.96
1.12
2.07
1.13
f1 (ppm)

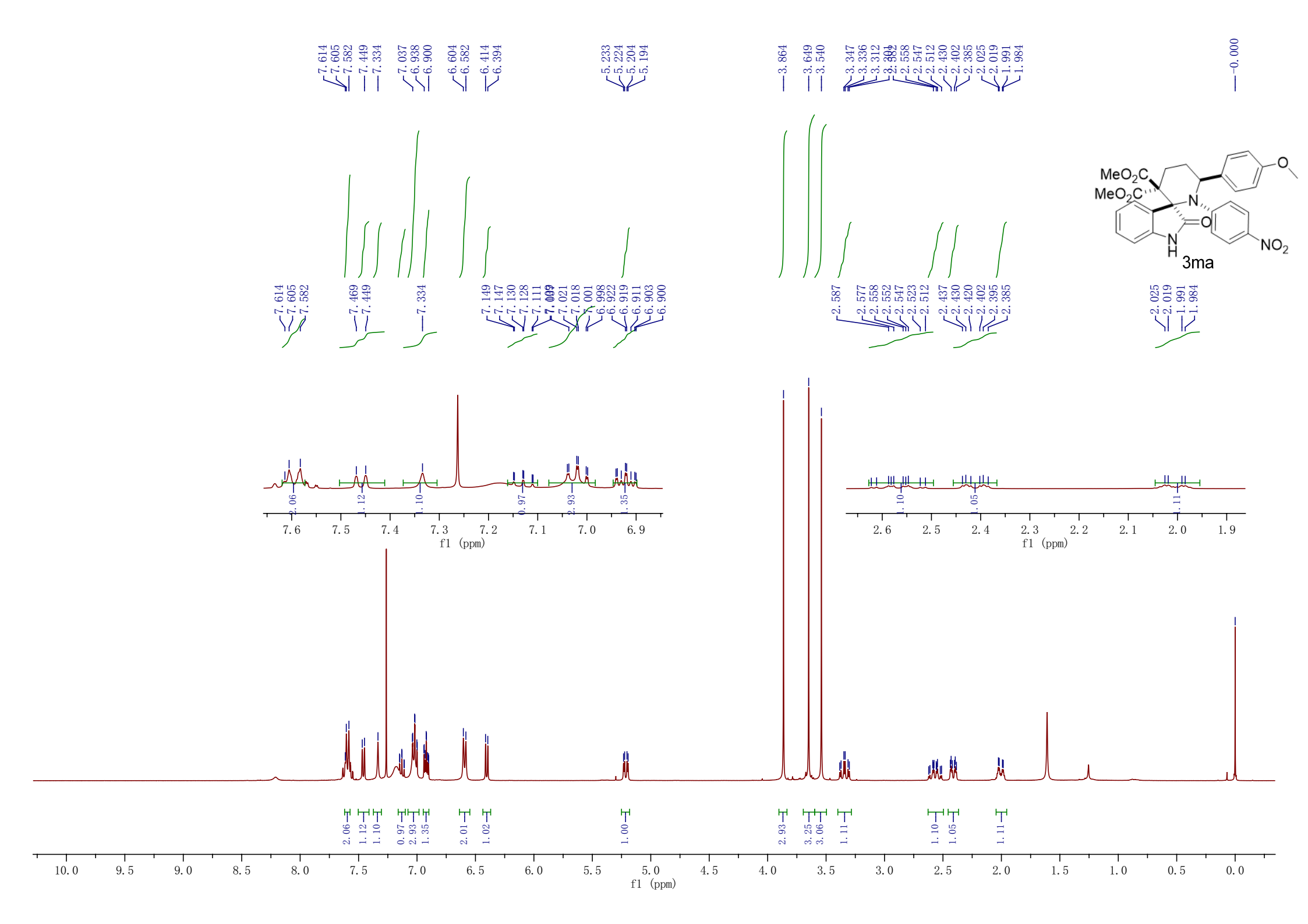

176.816
169.922
168.886
157.952
145.128
140.863
135.806
129.223
129.092
128.666
127.253
121.587
118.628
113.204
109.127
77.318
77.000
76.683
68.832
58.842
58.779
54.965
52.577
52.176
31.350
26.462
OMe
MeO2C
MeO2C
N
O
N
H
Br
3ja
130.046
129.223
129.092
128.666
127.253
132 131 130 129 128 127 126 125 124 123
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

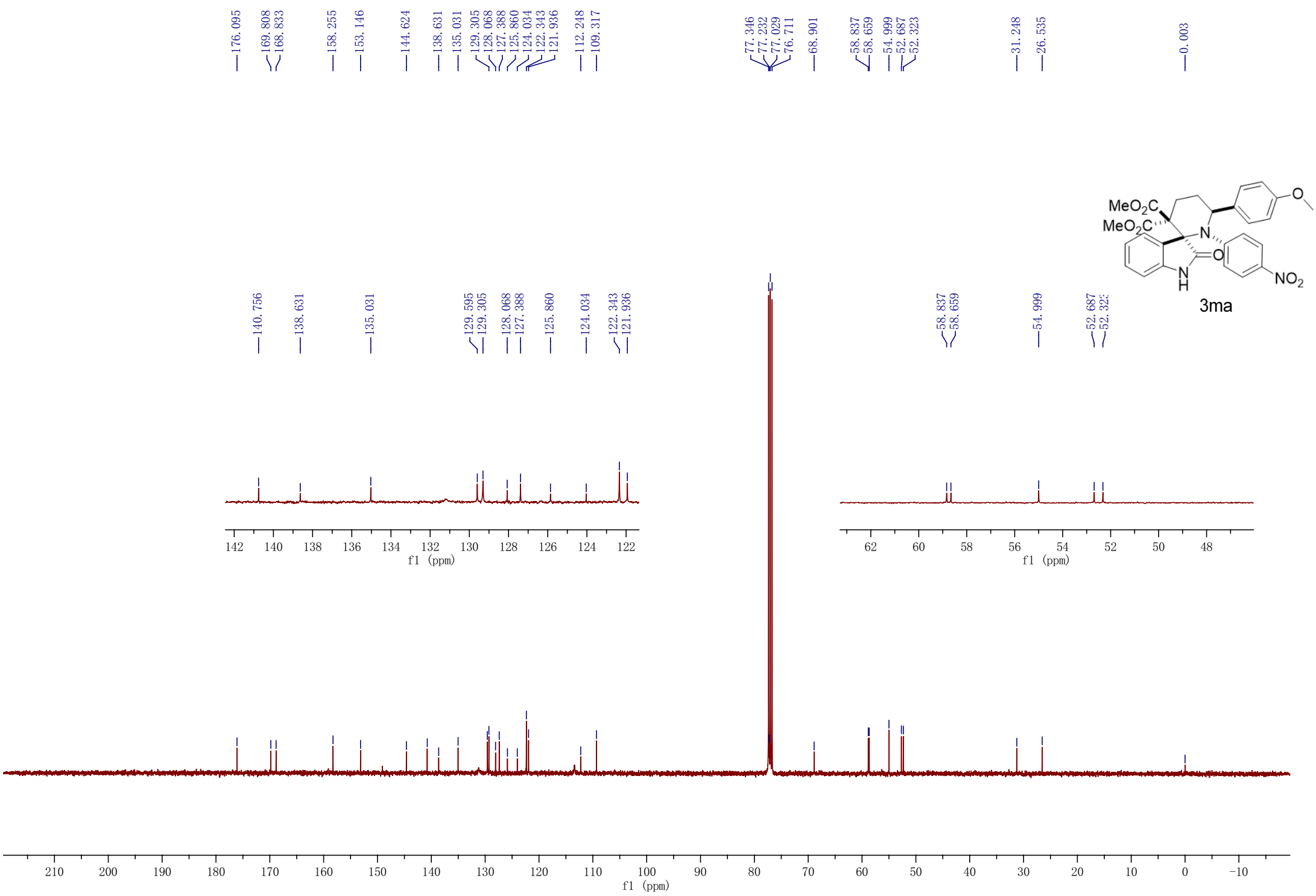

OMe
MeO2C
MeO2C
N
Me
O
N
H
3ka
7.447
7.428
7.213
6.896
6.772
6.602
6.580
6.494
6.392
6.373
5.189
5.179
5.159
5.150
3.837
3.652
3.518
3.340
3.329
3.305
2.458
2.378
2.350
2.333
1.980
1.969
1.963
1.952
1.935
7.260
6.992
6.973
6.954
6.855
3.375
3.364
3.294
2.557
2.546
2.522
2.517
2.512
2.493
2.487
2.482
2.447
2.368
2.343
2.340
1.05
3.35
1.12
1.22
1.04
2.16
1.94
1.10
1.06
1.03
1.02
3.94
f1 (ppm)
2.98
3.02
2.94

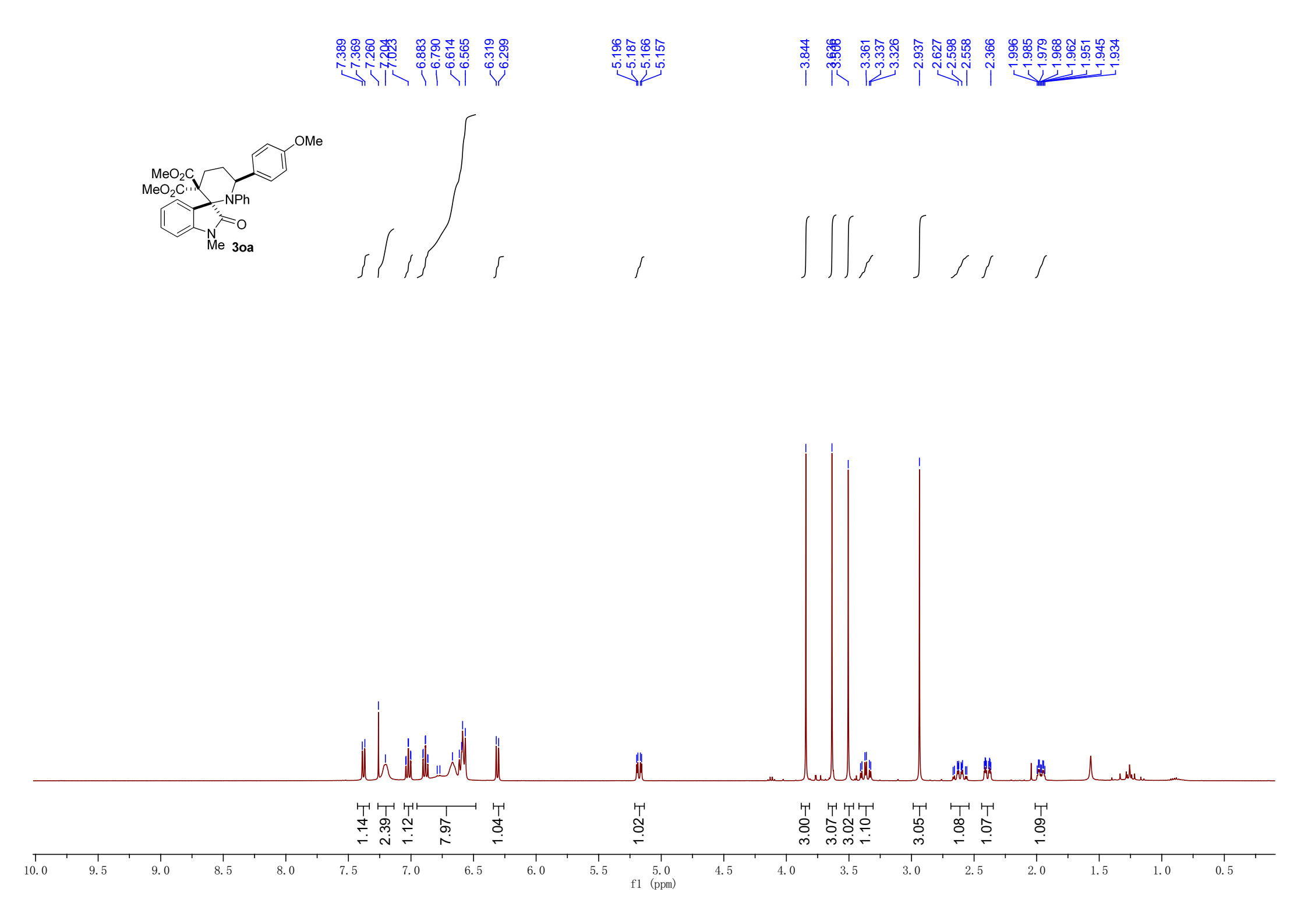

177.196
170.060
169.012
157.733
143.087
140.896
128.669
127.557
127.456
121.347
112.952
108.770
77.318
77.000
76.683
68.989
58.976
58.887
54.955
52.502
52.099
31.592
26.528
20.738
OMe
MeO2C
MeO2C
N
Me
O
N
H
3ka
136.561
134.244
129.249
129.173
128.669
127.557
127.456
137
135
133
131
129
127
125
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

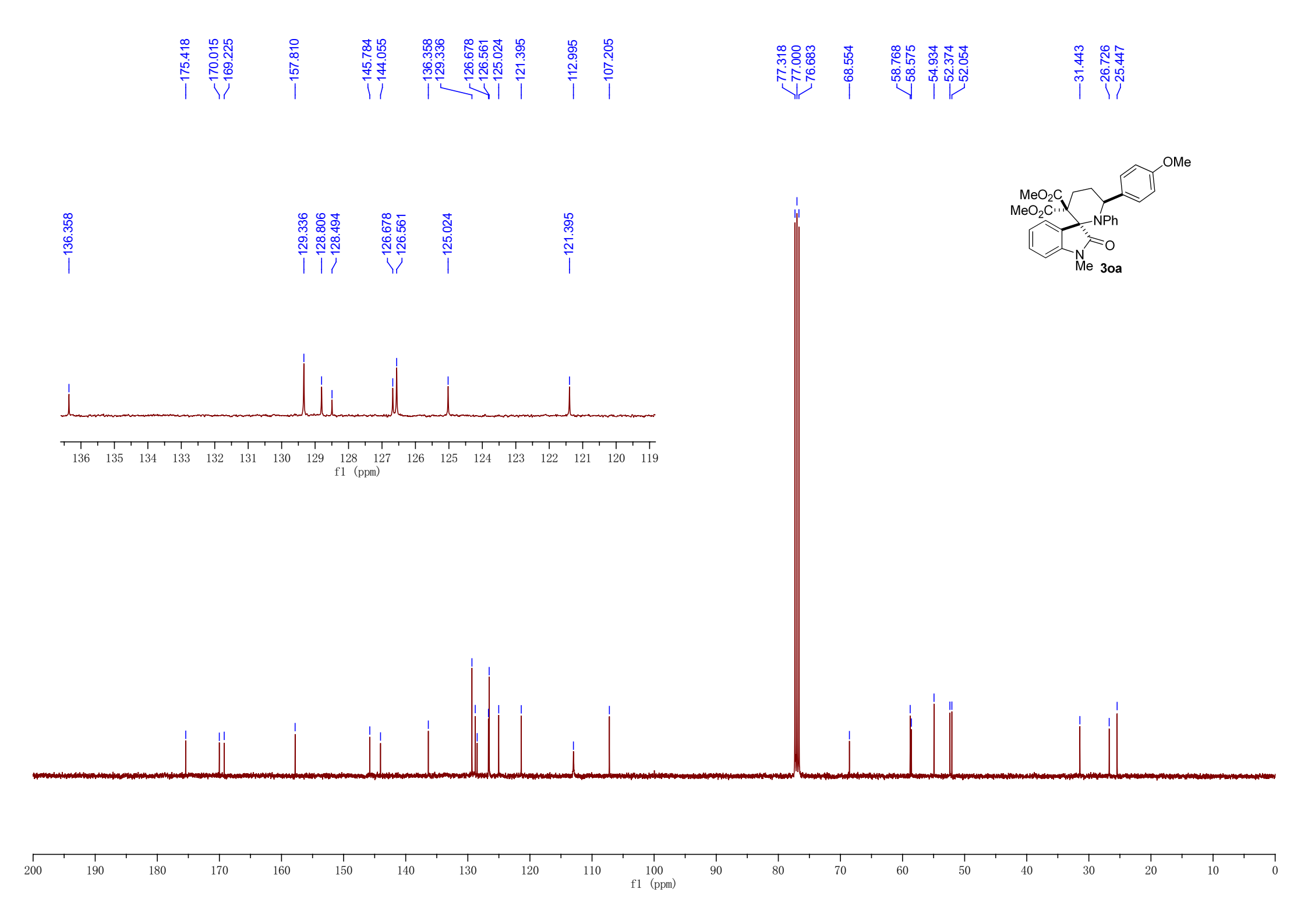

MeO2C
MeO2C
OMe
OMe
N
O
N
H
3la
7.439 7.420 7.381 7.194 6.894 6.762 6.581 6.385 6.223 5.155 5.145 5.125 5.116 3.833 3.654 3.360 3.336 3.325 3.289 2.455 2.381 2.371 2.346 2.329 1.979 1.969 1.962 1.952 1.945 1.935 1.928 1.918
2.13 2.48 1.21 4.04 1.20 1.98 3.17 6.00 1.08
f1 (ppm)
1.03 1.01 1.02
f1 (ppm)
2.13 2.48 1.21 4.04 1.20 1.98 1.05 3.06 3.17 6.00 1.08 1.03 1.01 1.02
f1 (ppm)


177.362
170.045
168.993
157.745
156.178
140.907
138.643
136.491
129.228
129.192
128.706
127.315
121.417
112.994
111.975
108.887
77.318
77.000
76.683
69.077
59.109
58.958
54.944
54.802
52.505
52.098
31.504
26.504
MeO2C
MeO2C
OMe
OMe
N
O
N
H
3la
f1 (ppm)
f1 (ppm)


7.614
7.605
7.582
7.449
7.334
7.037
6.938
6.900
6.604
6.582
6.414
6.394
5.233
5.224
5.204
5.194
3.864
3.649
3.540
3.347
3.336
3.312
2.558
2.547
2.512
2.430
2.402
2.385
2.025
2.019
1.991
1.984
0.000
MeO2C
MeO2C
N
O
N
H
O
NO2
3ma
f1 (ppm)
f1 (ppm)
f1 (ppm)


176.095
169.808
168.833
158.255
153.146
144.624
138.631
135.031
129.305
128.068
127.388
125.860
124.034
122.343
121.936
112.248
109.317
77.346
77.232
77.029
76.711
68.901
58.837
58.659
54.999
52.687
52.323
31.248
26.535
0.003
MeO2C
MeO2C
N
O
N
H
O
NO2
3ma
140.756
138.631
135.031
129.595
129.305
128.068
127.388
125.860
124.034
122.343
121.936
58.837
58.659
54.999
52.687
52.323
f1 (ppm)
f1 (ppm)
f1 (ppm)


7.389
7.369
7.260
7.204
7.023
6.883
6.790
6.614
6.565
6.319
6.299
5.196
5.187
5.166
5.157
3.844
3.636
3.606
3.361
3.337
3.326
2.937
2.627
2.598
2.558
2.366
1.996
1.985
1.979
1.968
1.962
1.951
1.945
1.934
OMe
MeO2C
MeO2C
NPh
O
N
Me
3oa
1.14
2.39
1.12
7.97
1.04
1.02
3.00
3.07
3.02
1.10
3.05
1.08
1.07
1.09
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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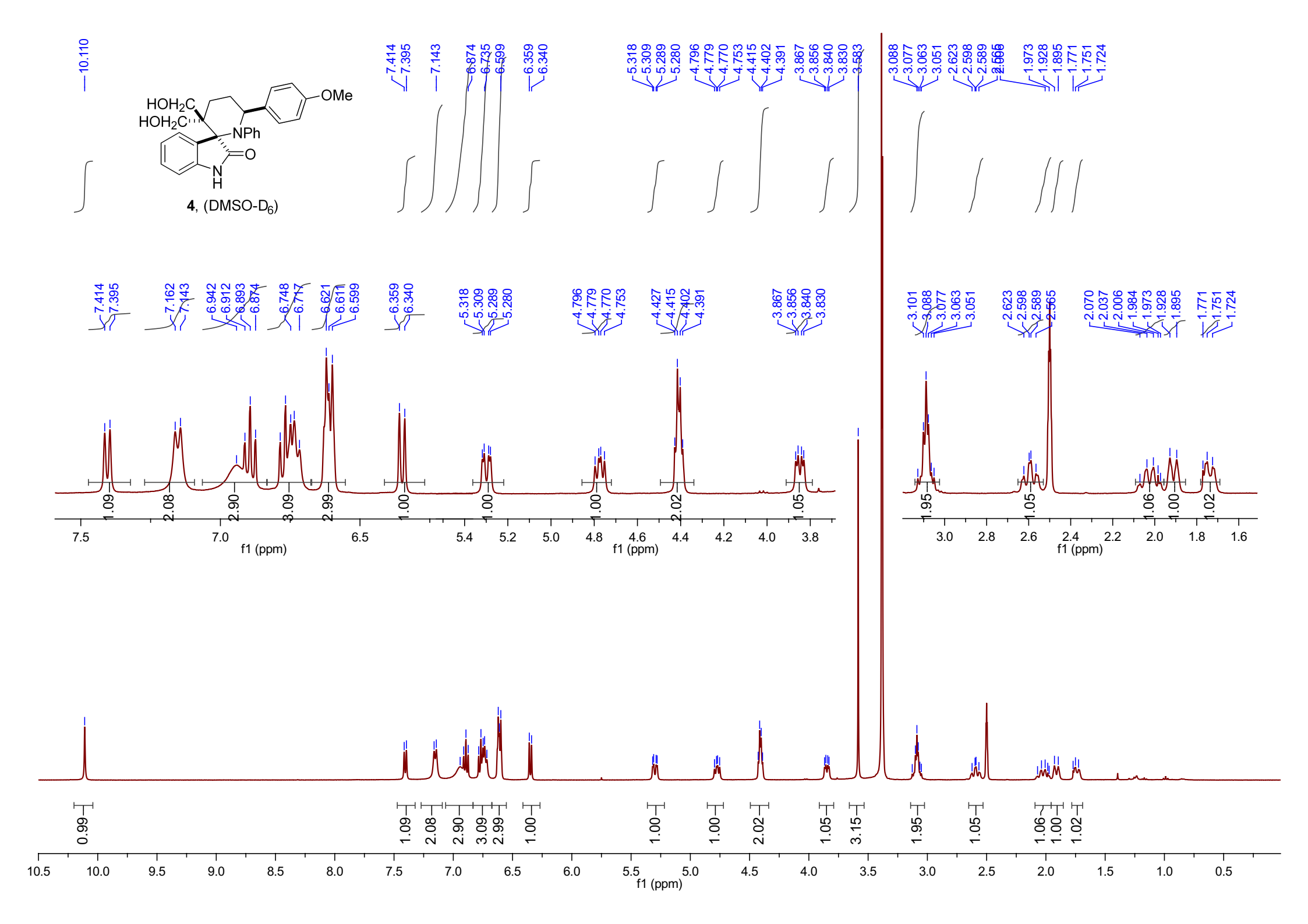
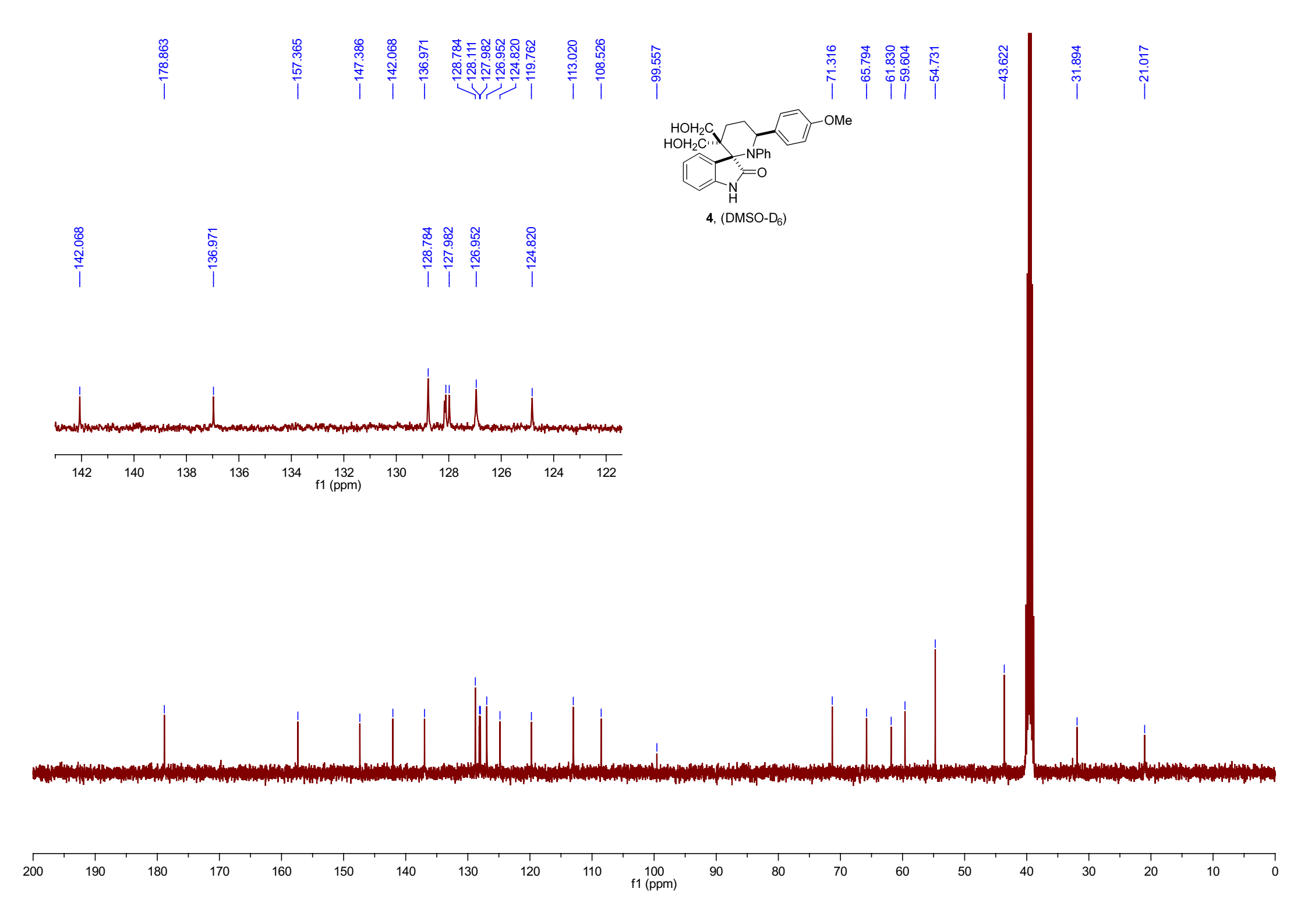
157.810
145.784
144.055
136.358
129.336
126.678
126.561
125.024
121.395
112.995
107.205
77.318
77.000
76.683
68.554
58.768
58.575
54.934
52.374
52.054
31.443
26.726
25.447
OMe
MeO2C
MeO2C
NPh
O
N
Me
3oa
f1 (ppm)


10.110
7.414
7.395
7.143
6.874
6.735
6.599
6.359
6.340
5.318
5.309
5.289
5.280
4.796
4.779
4.770
4.753
4.415
4.402
4.391
3.867
3.856
3.840
3.830
3.583
3.088
3.077
3.063
3.051
2.623
2.598
2.589
1.973
1.928
1.895
1.771
1.751
1.724
HOH2C
HOH2C
NPh
OMe
O
N
H
4, (DMSO-D6)
f1 (ppm)


178.863
157.365
147.386
142.068
136.971
128.784
128.111
127.982
126.952
124.820
119.762
113.020
108.526
99.557
71.316
65.794
61.830
59.604
54.731
43.622
31.894
21.017
HOH2C
HOH2C
NPh
O
N
H
OMe
4, (DMSO-D6)
142.068
136.971
128.784
127.982
126.952
124.820
142
140
138
136
134
132
130
128
126
124
122
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Data File E:\赵老师课题组\LC\数据\zmh\RFC-1 2021-11-01 11-10-36\002-P1-A1-RFC-rac.D
Sample Name: RFC-rac

```
==========================================================================
Acq. Operator   : SYSTEM                          Seq. Line :   2
Sample Operator : SYSTEM
Acq. Instrument : 1260                           Location :   P1-A-01
Injection Date  : 11/1/2021 11:42:26 AM               Inj :   1
                                                 Inj Volume : 1.000 µl
Acq. Method     : E:\赵老师课题组\LC\数据\zmh\RFC-1 2021-11-01 11-10-36\ZMH-ADH-98-2 -0.6-30
                  min_LC.M
Last changed    : 11/1/2021 11:11:18 AM by SYSTEM
Analysis Method : E:\赵老师课题组\LC\数据\zmh\RFC-1 2021-11-01 11-10-36\ZMH-ADH-98-2 -0.6-30
                  min_LC.M (Sequence Method)
Last changed    : 11/1/2021 12:31:36 PM by SYSTEM
Additional Info : Peak(s) manually integrated
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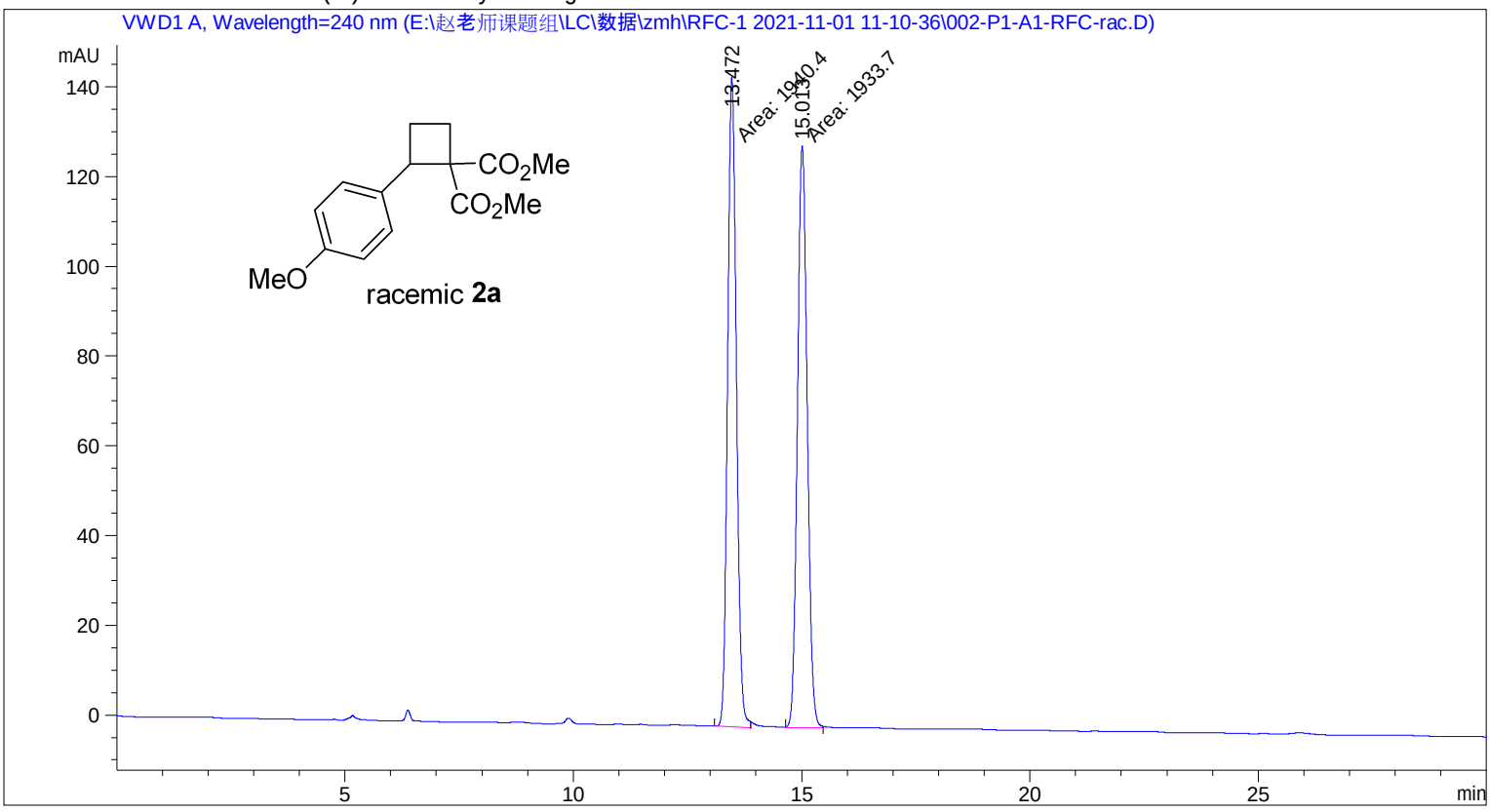


```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=240 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  13.472 MM    0.2236 1940.40222  144.63777  50.0865
   2  15.013 MM    0.2485 1933.69824  129.68158  49.9135

Totals :                  3874.10046  274.31935
```

Data File E:\赵老师课题组\LC\数据\zmh\HMF-3-121 2021-11-11 09-59-16\002-P1-A1-HMF-3-121.D
Sample Name: HMF-3-121

```
==========================================================================
Acq. Operator   : SYSTEM                        Seq. Line :   2
Sample Operator : SYSTEM
Acq. Instrument : 1260                          Location :   P1-A-01
Injection Date  : 11/11/2021 10:04:05 AM             Inj :   1
                                               Inj Volume : 1.000 µl
Acq. Method     : E:\赵老师课题组\LC\数据\zmh\HMF-3-121 2021-11-11 09-59-16\ZMH-ADH-98-2 -0.6
                  -30 min_LC.M
Last changed    : 11/11/2021 10:06:25 AM by SYSTEM
                  (modified after loading)
Analysis Method : E:\赵老师课题组\LC\数据\zmh\HMF-3-121 2021-11-11 09-59-16\ZMH-ADH-98-2 -0.6
                  -30 min_LC.M (Sequence Method)
Last changed    : 11/11/2021 10:32:43 AM by SYSTEM
Additional Info : Peak(s) manually integrated
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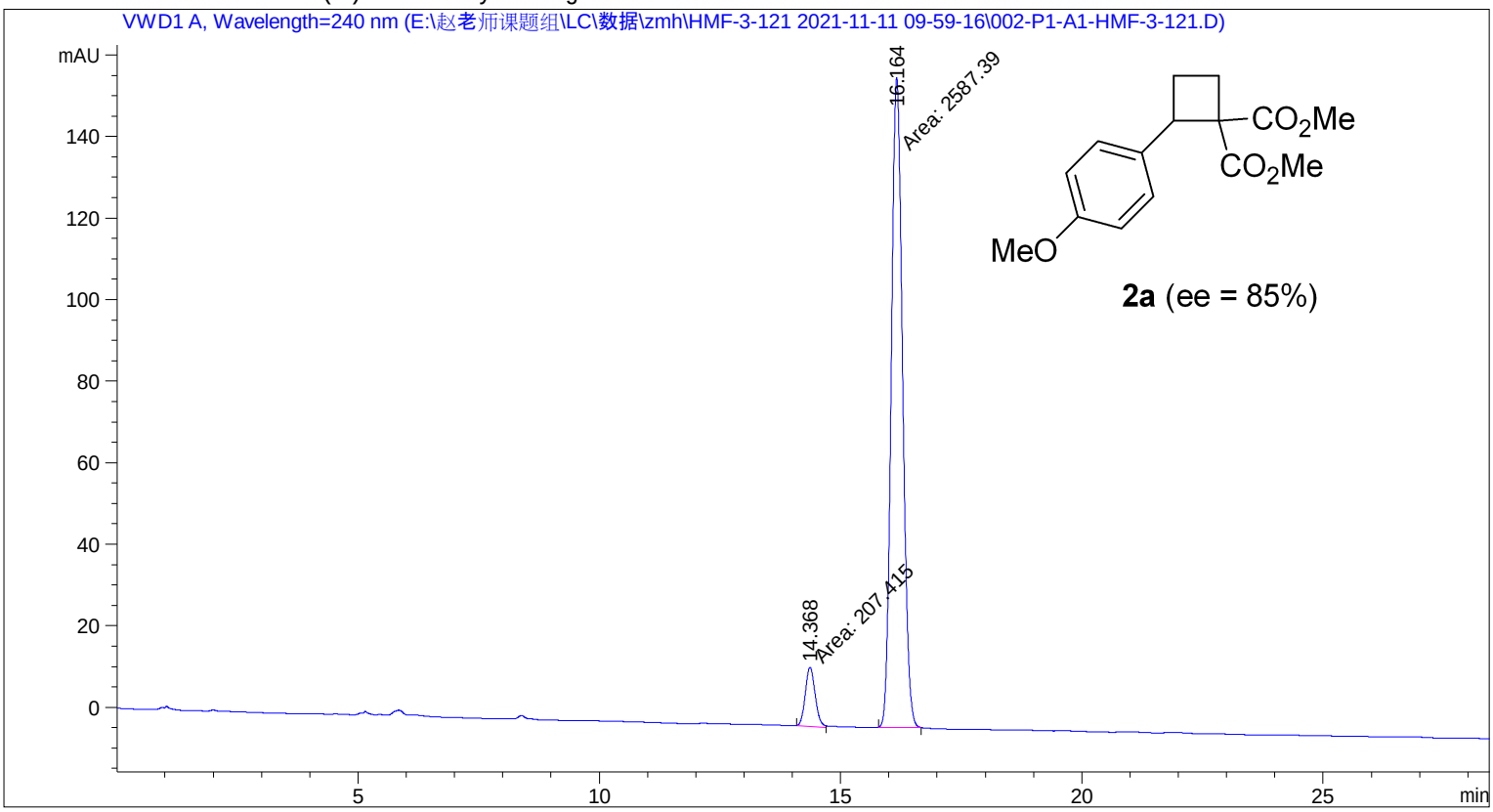
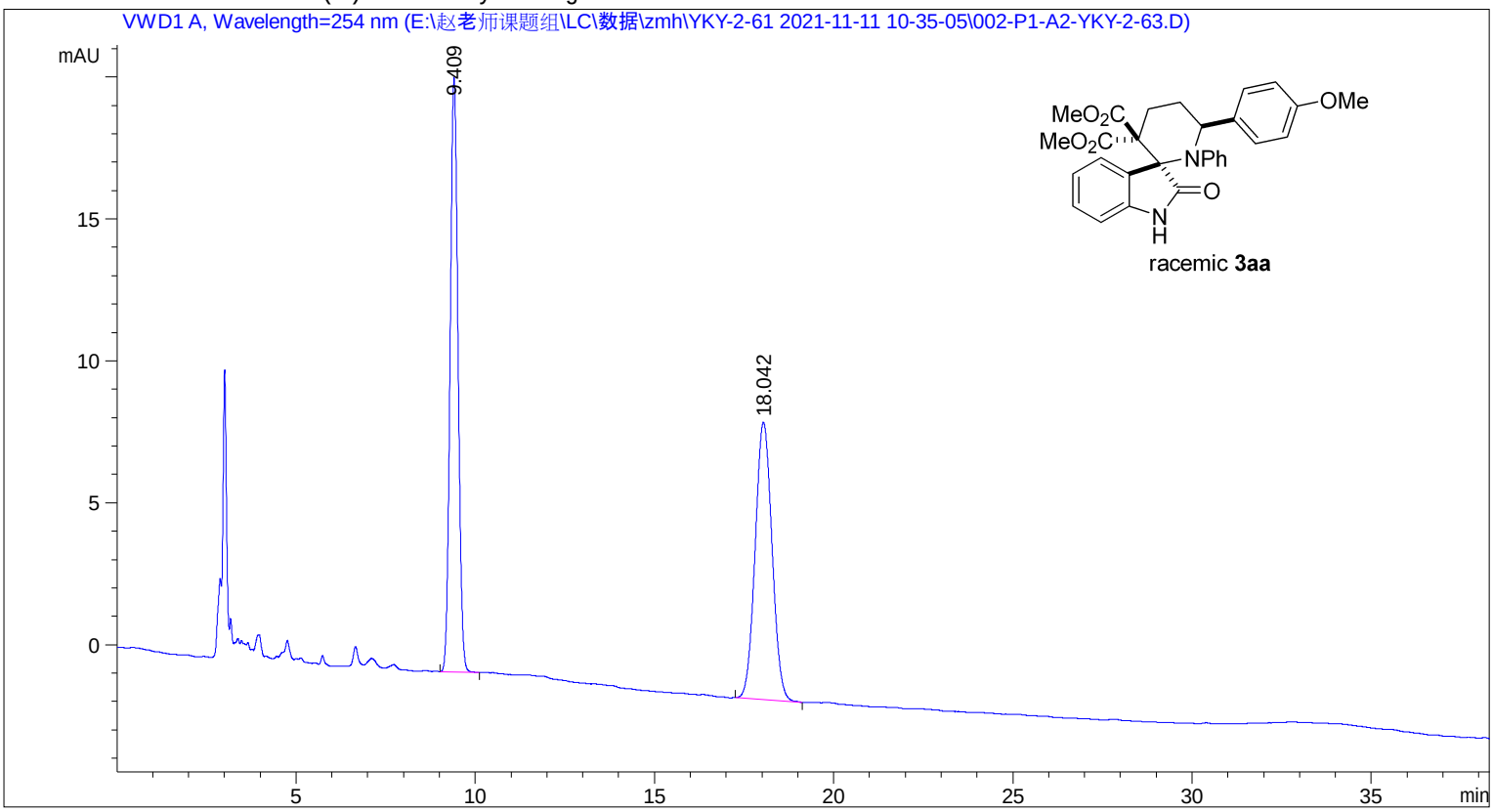



```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=240 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  14.368 MM    0.2374  207.41479   14.56042   7.4215
   2  16.164 MM    0.2705 2587.38501  159.41397  92.5785

Totals :                  2794.79980  173.97439
```

Data File E:\赵老师课题组\LC\数据\zmh\YKY-2-61 2021-11-11 10-35-05\002-P1-A2-YKY-2-63.D
Sample Name: YKY-2-63

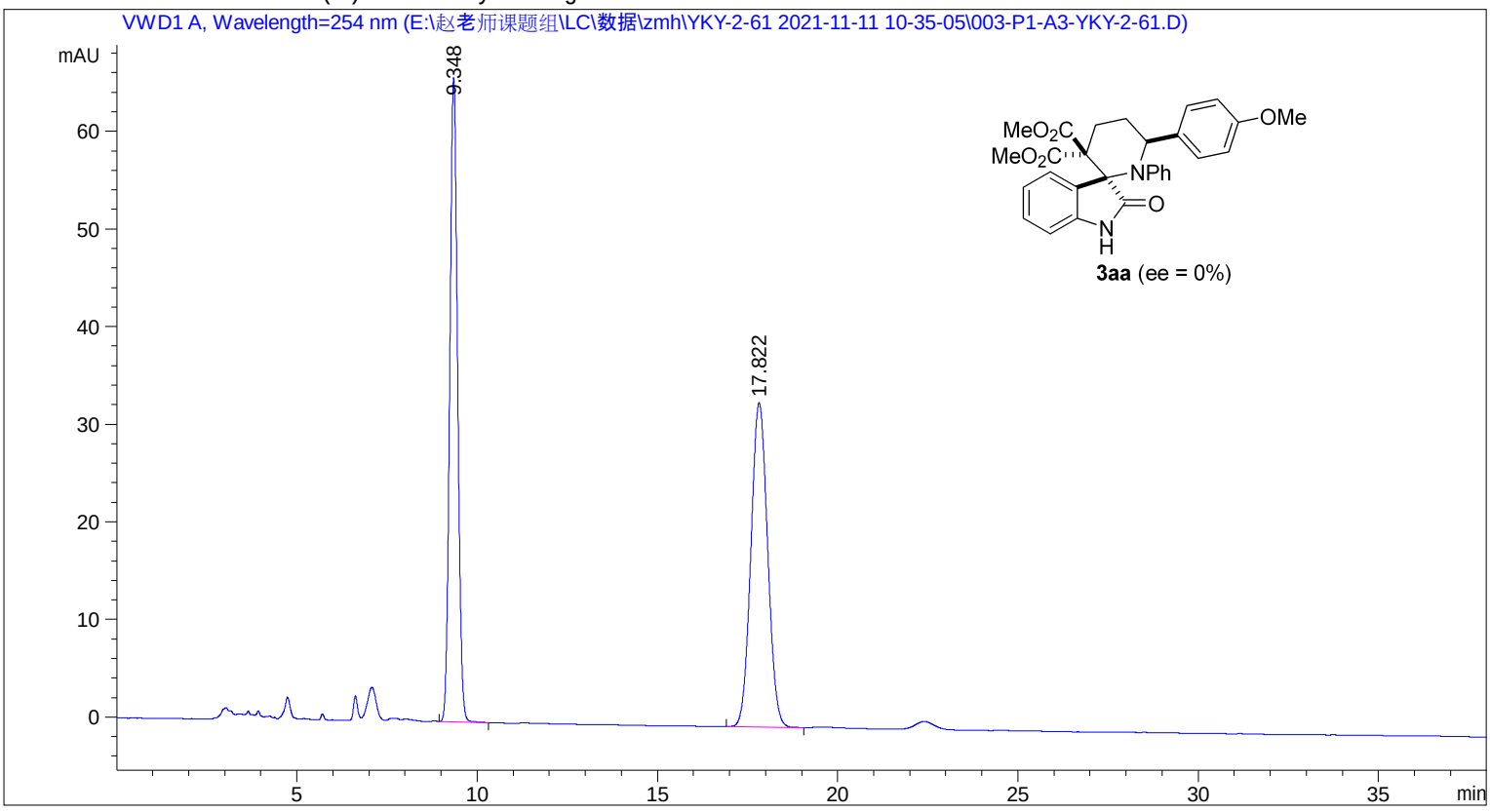
```
==========================================================================
Acq. Operator   : SYSTEM                          Seq. Line :   2
Sample Operator : SYSTEM
Acq. Instrument : 1260                           Location :   P1-A-02
Injection Date  : 11/11/2021 10:44:17 AM              Inj :   1
                                                 Inj Volume : 1.000 µl
Acq. Method     : E:\赵老师课题组\LC\数据\zmh\YKY-2-61 2021-11-11 10-35-05\ADH-80-20-1.0-
                  30min-240nm.M
Last changed    : 11/11/2021 11:22:36 AM by SYSTEM
                  (modified after loading)
Analysis Method : E:\赵老师课题组\LC\数据\zmh\YKY-2-61 2021-11-11 10-35-05\ADH-80-20-1.0-
                  30min-240nm.M (Sequence Method)
Last changed    : 11/11/2021 11:22:39 AM by SYSTEM
Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.409 BB    0.2372  319.91473   20.94012  50.0676
   2  18.042 BB    0.5078  319.05035    9.77391  49.9324

Totals :                   638.96509   30.71403
```

Data File E:\赵老师课题组\LC\数据\zmh\YKY-2-61 2021-11-11 10-35-05\003-P1-A3-YKY-2-61.D
Sample Name: YKY-2-61

```
==================================================================
Acq. Operator   : SYSTEM                        Seq. Line :   3
Sample Operator : SYSTEM
Acq. Instrument : 1260                           Location :   P1-A-03
Injection Date  : 11/11/2021 11:23:15 AM              Inj :   1
                                                Inj Volume : 3.000 µl
Acq. Method     : E:\赵老师课题组\LC\数据\zmh\YKY-2-61 2021-11-11 10-35-05\ADH-80-20-1.0-
                  30min-240nm.M
Last changed    : 11/11/2021 11:22:36 AM by SYSTEM
Analysis Method : E:\赵老师课题组\LC\数据\zmh\YKY-2-61 2021-11-11 10-35-05\ADH-80-20-1.0-
                  30min-240nm.M (Sequence Method)
Last changed    : 11/11/2021 11:22:39 AM by SYSTEM
Additional Info : Peak(s) manually integrated
```




```
==================================================================
                        Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.348 BB    0.2331  990.16406   65.97707  48.0589
   2  17.822 BB    0.5019 1070.14856   33.21149  51.9411

Totals :                  2060.31262   99.18855
```