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Supporting Information

Phosphine-Catalyzed (3+2)/(2+3) Sequential Annulation by Triple Nucleophilic Addition Reaction of γ-Vinyl Allenoates

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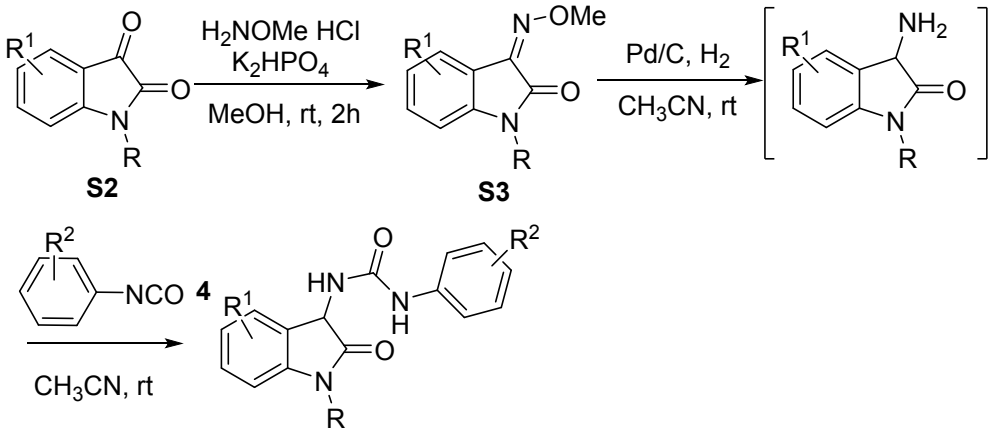
General information

All the starting materials were obtained from commercial sources and used without further purification unless otherwise stated. Yields refer to isolated compounds through flash column chromatography performed using 300-400 mesh silica gel. All compounds were fully characterized. ^{1}H and ^{13}C NMR spectra were recorded on Varian Brucker ARX 400 spectrometer in $CDCl_3$ or DMSO-d_6 as solvent. Chemical shifts (δ) are given in ppm. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm and DMSO-d_6: δ_H = 2.50 ppm, δ_C = 39.50 ppm). Multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) , dd (doublet of doublet) and brs (broad singlet). Coupling constants J are reported in Hz. Flash column chromatography was carried out using silica gel eluting with ethyl acetate and petroleum ether. High resolution mass spectrometry (HRMS) were obtained on an IonSpec FT-ICR mass spectrometer with ESI or MALDI resource. Melting points were measured on a RY-I apparatus and are reported uncorrected.

Preparation of starting materials

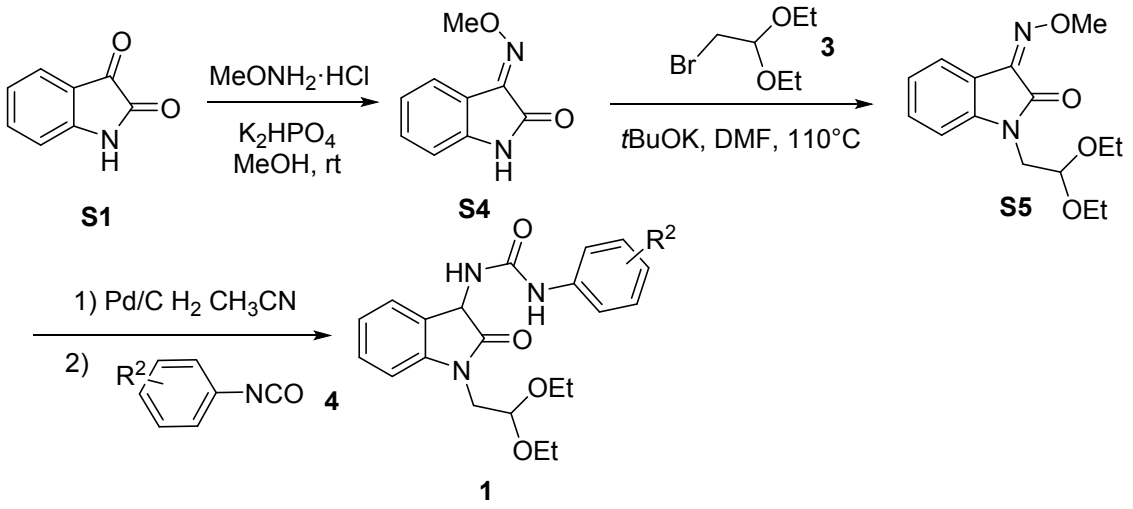
1. General procedure for preparation of urea **1a-1l**, **1s-1v**[1]



Step 1: **(Z)-3-(methoxyimino)-1-alkylindolin-2-one (S3)** To a suspension of N-alkylated isatin derivatives (30 mmol) in methanol (50mL) were add O-methylhydroxylamine hydrochloride (31.5 mmol) and dipotassium hydrogenphosphate (30 mmol). After the mixture was stirred for 2h at ambient temperature, the solvent was removed in vacuo.Water (50 mL) was added to the mixture to give yellow solids. The solids was collected and then dried under reduced pressure to give the title compound **S3** as yellow crystals (4g, 70% yield).

Step 2: **1-(1-alkyl-2-oxoindolin-3-yl)-3-phenylurea 1** To a suspension of **S3** (10.5 mmol) in acetonitrile (50 mL) were added 5% palladium on carbon (0.2 g). The mixture was stirred under hydrogen under atmospheric pressure at ambient temperature for 6h. Substituted phenyl isocyanates **4** (10.5 mmol) was added to the suspension after the palladium carbon was removed by filtration. The mixture was stirred for 1h and a solid was generated at the same time. Then the solid was collected through celite and washed with acetonitrile and then dried under reduced pressure to give the compound **1** as white crystals (2.2g, 71% yield).

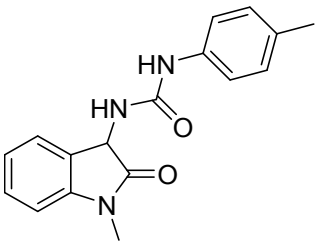
2. General procedure for preparation of urea **1m-1r**[1]



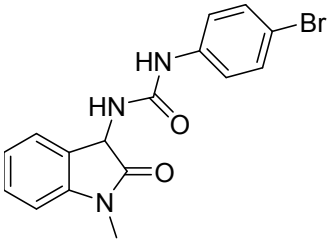
Step 1: **(E)-3-(methoxyimino)indolin-2-one (S4)** To a suspension of isatin derivatives (20 mmol) in methanol (30mL) were add O-methylhydroxylamine hydrochloride (31.5 mmol) and dipotassium hydrogenphosphate (30 mmol). After the mixture was stirred for 2h at ambient temperature, the solvent was removed in vacuo.Water (30 mL) was added to the mixture to give yellow solids. The solids was collected and then dried under reduced pressure to give the title compound **S4** as yellow crystals (2.5g, 71% yield).

Step 2: **(Z)-1-(2,2-diethoxyethyl)-3-(methoxyimino)indolin-2-one (S5)** To a stirred solution of **S4** (11.3 mmol) in DMF (20 mL) was added potassium *tert*-butoxide (13.6 mmol) and bromoacetaldehyde (14.2 mmol). The resulting mixture was stirred at 110℃ for 4h. After the mixture was cooled to ambient temperature, aqueous ammonium chloride (10 mL) was added to quench the reaction, and the resulting mixture was extracted with ethyl acetate several times (3 x 15 mL). The combined organic phases were washed with brine, dried over anhydrous Mg_2SO_4, filtered and concentrated in *vacuum*. The crude residue was then purified by column chromatography on silica fel with ethyl acetate-hexane (10/90) to provide compounds **S5** (1.8g, 54% yield).

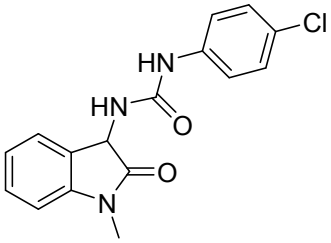
Step 3: **1-(1-alkyl-2-oxoindolin-3-yl)-3-phenylurea 1** To a suspension of **S5** (10.5 mmol) in acetonitrile (50 mL) were added 5% palladium on carbon (0.2 g). The mixture was stirred under hydrogen under atmospheric pressure at ambient temperature for 6h. Substituted phenyl isocyanates **4** (10.5 mmol) was added to the suspension after the palladium carbon was removed by filtration. The mixture was stirred for 1h and a solid was generated at the same time. Then the solid was collected through celite and washed with acetonitrile and then dried under reduced pressure to give the compound **1** as white crystals (2.2g, 71% yield).



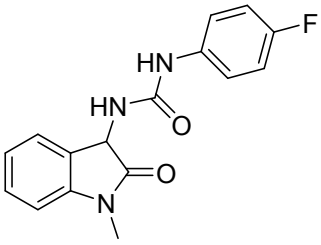
1-(1-methyl-2-oxoindolin-3-yl)-3-(p-tolyl)urea (1a): A white solid. ^{1}H NMR (400 MHz, DMSO) δ 8.71 (s, 1H), 7.34 – 7.22 (m, 4H), 7.02 (dd, *J* = 8.7, 4.8 Hz, 4H), 6.95 (d, *J* = 7.8 Hz, 1H), 5.04 (d, *J* = 7.7 Hz, 1H), 3.14 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 174.77, 154.60, 143.83, 137.50, 130.13, 129.04, 128.31, 128.11, 123.20, 121.97, 117.93, 108.24, 52.66, 26.14, 20.30. HRMS (ESI) m/z calcd for $C_{17}H_{18}N_3O_2$ $[M+H]^+$ = 296.1394, found = 296.1393.



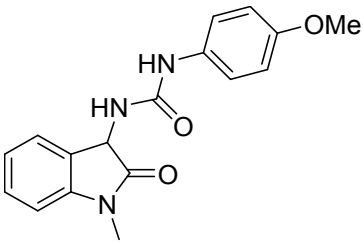
1-(4-bromophenyl)-3-(1-methyl-2-oxoindolin-3-yl)urea (1b): A white solid. ^{1}H NMR (400 MHz, DMSO) δ 9.02 (s, 1H), 7.42 – 7.33 (m, 4H), 7.32 – 7.21 (m, 2H), 7.09 (d, *J* = 7.8 Hz, 1H), 7.00 (dd, *J* = 16.6, 7.7 Hz, 2H), 5.04 (d, *J* = 7.7 Hz, 1H), 3.14 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 174.63, 154.39, 143.87, 139.53, 131.36, 128.37, 127.92, 123.20, 122.00, 119.80, 112.74, 108.27, 52.68, 26.16. HRMS (ESI) m/z calcd for $C_{16}H_{15}BrN_3O_2$ $[M+H]^+$ = 360.0342, found = 360.0340.



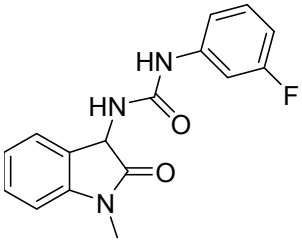
1-(4-chlorophenyl)-3-(1-methyl-2-oxoindolin-3-yl)urea (1c): A white solid. ^{1}H NMR (400 MHz, DMSO) δ 9.01 (s, 1H), 7.47 – 7.37 (m, 2H), 7.34 – 7.20 (m, 4H), 7.08 (d, *J* = 7.6 Hz, 1H), 7.01 (dd, *J* = 16.5, 8.0 Hz, 2H), 5.04 (d, *J* = 7.6 Hz, 1H), 3.13 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 174.64, 154.43, 143.87, 139.10, 128.47, 128.37, 127.94, 124.88, 123.20, 122.00, 119.38, 108.27, 52.68, 26.16. HRMS (ESI) m/z calcd for $C_{16}H_{15}ClN_3O_2$ $[M+H]^+$ = 316.0847, found = 316.0846.



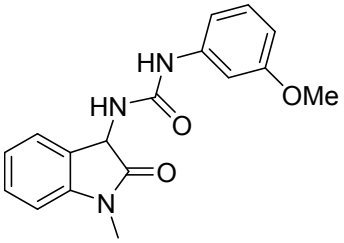
1-(4-fluorophenyl)-3-(1-methyl-2-oxoindolin-3-yl)urea (1d): A white solid. ^{1}H NMR (400 MHz, DMSO) δ 8.91 (d, *J* = 6.1 Hz, 1H), 7.49 – 7.35 (m, 2H), 7.34 – 7.20 (m, 2H), 7.13 – 6.87 (m, 5H), 5.07 (d, *J* = 6.6 Hz, 1H), 3.13 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 174.78, 158.33, 155.95, 154.73, 143.88, 136.49, 128.39, 128.07, 123.25, 122.03, 119.61, 119.55, 115.25, 115.03, 108.29, 52.73, 26.17. HRMS (ESI) m/z calcd for $C_{16}H_{15}FlN_3O_2$ $[M+H]^+$ = 300.1143, found = 300.1145.



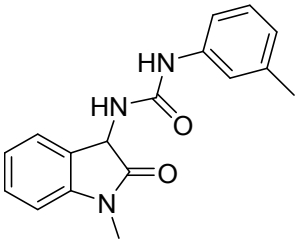
1-(4-methoxyphenyl)-3-(1-methyl-2-oxoindolin-3-yl)urea (1e): A white solid. ^{1}H NMR (400 MHz, DMSO) δ 8.61 (s, 1H), 7.33 – 7.18 (m, 4H), 6.98 (dt, *J* = 26.1, 10.2 Hz, 2H), 6.88 (t, *J* = 10.3 Hz, 1H), 6.85 – 6.76 (m, 2H), 5.04 (d, *J* = 7.8 Hz, 1H), 3.68 (s, 3H), 3.13 (d, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 174.83, 154.80, 154.16, 143.83, 133.18, 128.32, 128.18, 123.22, 121.98, 119.64, 113.85, 108.24, 55.13, 52.69, 26.14. HRMS (ESI) m/z calcd for $C_{17}H_{18}N_3O_3$ $[M+H]^+$ = 312.1343, found = 312.1343.



1-(3-fluorophenyl)-3-(1-methyl-2-oxoindolin-3-yl)urea (1f): A white solid. ^{1}H NMR (400 MHz, DMSO) δ 9.11 (s, 1H), 7.43 – 7.36 (m, 1H), 7.33 – 7.20 (m, 3H), 7.11 (d, *J* = 7.8 Hz, 1H), 7.09 – 7.03 (m, 1H), 7.03 – 6.95 (m, 2H), 6.71 (d, *J* = 2.3 Hz, 1H), 5.06 (d, *J* = 7.8 Hz, 1H), 3.14 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 174.59, 163.58, 161.19, 154.42, 143.86, 142.05, 141.94, 130.22, 130.12, 128.41, 127.88, 123.21, 122.03, 113.56, 108.30, 107.82, 107.61, 104.64, 104.38, 52.66, 26.17. HRMS (ESI) m/z calcd for $C_{16}H_{15}FlN_3O_2$ $[M+H]^+$ = 300.1143, found = 300.1144.

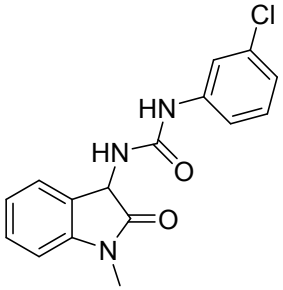


1-(3-methoxyphenyl)-3-(1-methyl-2-oxoindolin-3-yl)urea (1g): A white solid. ^{1}H NMR (400 MHz, DMSO) δ 8.84 (s, 1H), 7.36 – 7.21 (m, 2H), 7.15 – 7.05 (m, 2H), 7.05 – 6.94 (m, 3H), 6.89 (d, *J* = 7.9 Hz, 1H), 6.49 (d, *J* = 7.9 Hz, 1H), 5.06 (d, *J* = 7.7 Hz, 1H), 3.69 (s, 3H), 3.13 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 174.67, 159.63, 154.50, 143.82, 141.30, 129.40, 128.35, 128.00, 123.21, 122.00, 110.21, 108.28, 106.92, 103.55, 54.89, 52.63, 26.15. HRMS (ESI) m/z calcd for $C_{17}H_{18}N_3O_3$ $[M+H]^+$ = 312.1343, found = 312.1347.

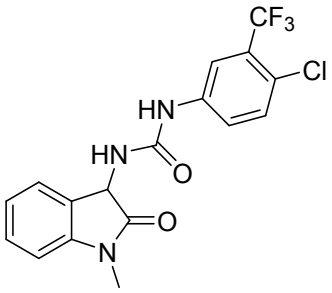


1-(1-methyl-2-oxoindolin-3-yl)-3-(m-tolyl)urea (1h): A white solid. ^{1}H NMR (400 MHz, DMSO) δ 8.75 (s, 1H), 7.32 – 7.22 (m, 3H), 7.15 – 7.06 (m, 2H), 7.01 (dd, *J* = 15.5, 7.7 Hz, 3H), 6.72 (d, *J* = 6.9 Hz, 1H), 5.02 (d, *J* = 7.7 Hz, 1H), 3.13 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 174.74, 154.52, 143.84, 139.99, 137.81, 128.50, 128.33, 128.10, 123.17,

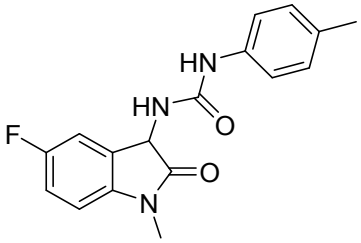
122.16, 121.99, 118.33, 115.01, 108.27, 52.71, 26.16, 21.22. HRMS (ESI) m/z calcd for $C_{17}H_{18}N_3O_2$ $[M+H]^+$ = 296.1394, found = 296.1395.



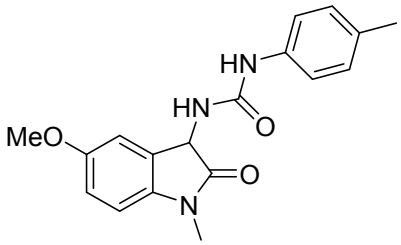
1-(3-chlorophenyl)-3-(1-methyl-2-oxoindolin-3-yl)urea (1i): A white solid. ^{1}H NMR (400 MHz, DMSO) δ 9.09 (s, 1H), 7.63 (d, *J* = 1.9 Hz, 1H), 7.38 – 7.17 (m, 4H), 7.13 (d, *J* = 7.8 Hz, 1H), 7.06 – 6.87 (m, 3H), 5.04 (d, *J* = 7.7 Hz, 1H), 3.14 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 174.55, 154.35, 143.85, 141.63, 133.09, 130.26, 128.38, 127.85, 123.17, 122.00, 121.01, 117.17, 116.23, 108.28, 52.68, 26.16. HRMS (ESI) m/z calcd for $C_{16}H_{15}ClN_3O_2$ $[M+H]^+$ = 316.0847, found = 316.0849.



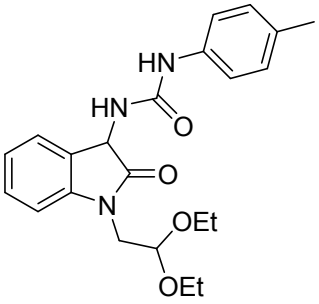
1-(4-chloro-3-(trifluoromethyl)phenyl)-3-(1-methyl-2-oxoindolin-3-yl)urea (1j): A white solid. ^{1}H NMR (400 MHz, DMSO) δ 9.42 (s, 1H), 8.02 (s, 1H), 7.58 (dd, *J* = 30.0, 8.8 Hz, 2H), 7.41 – 7.19 (m, 3H), 7.02 (dd, *J* = 14.6, 7.5 Hz, 2H), 5.07 (d, *J* = 7.7 Hz, 1H), 3.15 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 174.48, 154.32, 143.87, 139.76, 131.89, 128.44, 127.74, 126.75, 126.44, 124.21, 123.18, 122.62, 122.04, 121.82, 121.50, 116.33, 108.33, 52.70, 26.19. HRMS (ESI) m/z calcd for $C_{17}H_{14}ClF_3N_3O_2$ $[M+H]^+$ = 384.0721, found = 384.0720.



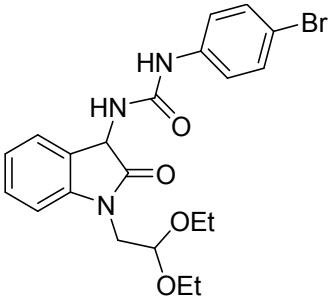
1-(5-fluoro-1-methyl-2-oxoindolin-3-yl)-3-(p-tolyl)urea (1k): A white solid. ^{1}H NMR (400 MHz, DMSO) δ 8.76 (s, 1H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.15 – 7.07 (m, 2H), 7.02 (d, *J* = 4.5 Hz, 1H), 7.01 – 6.95 (m, 3H), 5.02 (d, *J* = 7.5 Hz, 1H), 3.12 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 174.64, 159.61, 157.25, 154.51, 140.05, 137.40, 130.21, 129.03, 117.96, 114.31, 114.08, 111.22, 110.97, 108.97, 108.89, 53.05, 26.29, 20.29. HRMS (ESI) m/z calcd for $C_{17}H_{17}FN_3O_2$ $[M+H]^+$ = 314.1299, found = 314.1301.



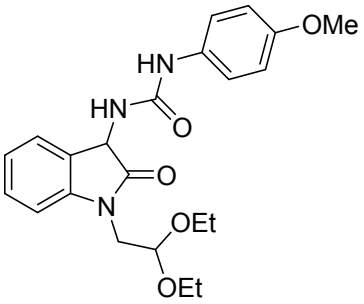
1-(5-methoxy-1-methyl-2-oxoindolin-3-yl)-3-(p-tolyl)urea (1l): A white solid. ^{1}H NMR (400 MHz, DMSO) δ 8.72 (d, *J* = 4.7 Hz, 1H), 7.28 (t, *J* = 6.4 Hz, 2H), 7.02 (d, *J* = 8.2 Hz, 2H), 6.94 (d, *J* = 7.2 Hz, 1H), 6.87 (dd, *J* = 10.0, 7.5 Hz, 3H), 5.01 (d, *J* = 7.3 Hz, 1H), 3.71 (s, 3H), 3.10 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 174.37, 155.32, 154.59, 137.47, 137.22, 130.11, 129.37, 129.01, 117.88, 112.53, 110.48, 108.58, 55.45, 52.98, 26.16, 20.26. HRMS (ESI) m/z calcd for $C_{18}H_{18}N_3O_3$ $[M-H]^-$ = 324.1354, found = 324.1347.



1-(1-(2,2-diethoxyethyl)-2-oxoindolin-3-yl)-3-(p-tolyl)urea (1m): A white solid. ^{1}H NMR (400 MHz, DMSO) δ 8.71 (s, 1H), 7.25 (dd, *J* = 10.5, 5.6 Hz, 4H), 7.08 (d, *J* = 7.8 Hz, 1H), 7.01 (d, *J* = 8.9 Hz, 3H), 6.99 – 6.92 (m, 1H), 5.07 (d, *J* = 7.7 Hz, 1H), 4.70 (t, *J* = 5.3 Hz, 1H), 3.84 (dd, *J* = 14.2, 5.5 Hz, 1H), 3.69 – 3.60 (m, 3H), 3.48 (dd, *J* = 9.5, 7.0 Hz, 2H), 2.20 (s, 3H), 1.06 (td, *J* = 7.0, 3.8 Hz, 6H). ^{13}C NMR (101 MHz, DMSO) δ 175.51, 155.06, 143.78, 137.96, 130.61, 129.51, 128.54, 128.26, 123.66, 122.39, 118.33, 109.76, 100.15, 62.96, 62.66, 52.94, 43.52, 20.75, 15.69. HRMS (ESI) m/z calcd for $C_{22}H_{27}N_3O_4Na$ $[M+Na]^+$ = 420.1894, found = 420.1891.

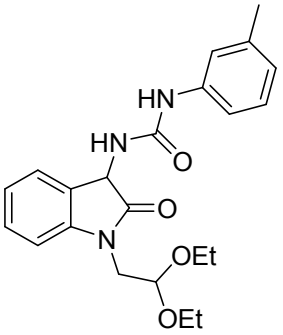


1-(4-bromophenyl)-3-(1-(2,2-diethoxyethyl)-2-oxoindolin-3-yl)urea (1n): A white solid. ^{1}H NMR (400 MHz, DMSO) δ 8.98 (s, 1H), 7.46 – 7.30 (m, 4H), 7.25 (dd, *J* = 14.5, 7.3 Hz, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 7.00 (t, *J* = 7.4 Hz, 1H), 5.06 (d, *J* = 7.6 Hz, 1H), 4.70 (t, *J* = 5.3 Hz, 1H), 3.84 (dd, *J* = 14.2, 5.4 Hz, 1H), 3.71 – 3.59 (m, 3H), 3.48 (dq, *J* = 14.3, 7.1 Hz, 2H), 1.06 (td, *J* = 7.0, 3.2 Hz, 6H). ^{13}C NMR (101 MHz, DMSO) δ 174.85, 154.36, 143.34, 139.48, 131.35, 128.11, 127.57, 123.18, 121.93, 119.74, 112.73, 109.30, 99.68, 62.49, 62.17, 52.47, 43.07, 15.22. HRMS (ESI) m/z calcd for $C_{21}H_{24}BrN_3O_4Na$ $[M+Na]^+$ = 484.0842, found = 484.0837.

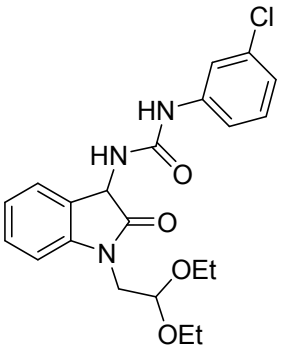


1-(1-(2,2-diethoxyethyl)-2-oxoindolin-3-yl)-3-(4-methoxyphenyl)urea (1o): A white solid. ^{1}H NMR (400 MHz, DMSO) δ 8.59 (s, 1H), 7.25 (dd, *J* = 14.4, 7.8 Hz, 4H), 7.07 (d, *J* = 7.8 Hz, 1H), 7.00 (t, *J* = 7.4 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 6.80 (d, *J* = 8.9 Hz, 2H), 5.05 (d, *J* = 7.7 Hz, 1H), 4.70 (t, *J* = 5.2 Hz, 1H), 3.83 (dd, *J* = 14.2, 5.5 Hz, 1H), 3.72 – 3.59 (m, 6H), 3.54 – 3.38 (m, 2H), 1.06 (td, *J* = 7.0, 4.3 Hz, 6H). ^{13}C NMR (101 MHz, DMSO) δ 175.06, 154.73, 154.13, 143.30,

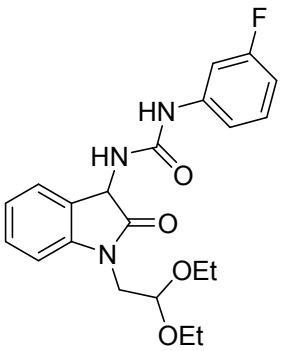
133.15, 128.05, 127.84, 123.20, 121.91, 119.52, 113.85, 109.28, 99.68, 62.48, 62.19, 55.12, 52.48, 43.06, 15.23. HRMS (ESI) m/z calcd for $C_{22}H_{27}N_3O_5Na$ $[M+Na]^+$ = 436.1843, found = 436.1844.



1-(1-(2,2-diethoxyethyl)-2-oxoindolin-3-yl)-3-(m-tolyl)urea (1p): A white solid. ^{1}H NMR (400 MHz, DMSO) δ 8.75 (s, 1H), 7.25 (t, *J* = 9.6 Hz, 3H), 7.17 – 7.05 (m, 3H), 7.00 (t, *J* = 7.5 Hz, 2H), 6.72 (d, *J* = 6.7 Hz, 1H), 5.05 (d, *J* = 7.4 Hz, 1H), 4.71 (t, *J* = 4.8 Hz, 1H), 3.85 (dd, *J* = 14.1, 5.2 Hz, 1H), 3.71 – 3.59 (m, 3H), 3.55 – 3.43 (m, 2H), 2.22 (s, 3H), 1.06 (dd, *J* = 7.9, 5.0 Hz, 6H). ^{13}C NMR (101 MHz, DMSO) δ 175.03, 154.52, 143.35, 139.99, 137.81, 128.51, 128.09, 127.80, 123.18, 122.16, 121.94, 118.31, 114.96, 109.31, 99.69, 62.52, 62.20, 52.54, 43.08, 21.22, 15.26. HRMS (ESI) m/z calcd for $C_{22}H_{27}N_3O_4Na$ $[M+Na]^+$ = 420.1894, found = 420.1891.

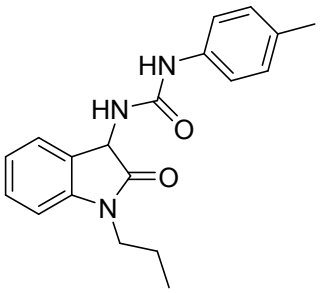


1-(3-chlorophenyl)-3-(1-(2,2-diethoxyethyl)-2-oxoindolin-3-yl)urea (1q): A white solid. ^{1}H NMR (400 MHz, DMSO) δ 9.10 (s, 1H), 7.65 (s, 1H), 7.32 – 7.22 (m, 3H), 7.18 (dd, *J* = 15.4, 8.2 Hz, 2H), 7.10 (d, *J* = 7.8 Hz, 1H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.96 (d, *J* = 7.8 Hz, 1H), 5.06 (d, *J* = 7.6 Hz, 1H), 4.72 (t, *J* = 5.3 Hz, 1H), 3.85 (dd, *J* = 14.2, 5.5 Hz, 1H), 3.73 – 3.61 (m, 3H), 3.55 – 3.45 (m, 2H), 1.08 (td, *J* = 7.0, 4.5 Hz, 6H). ^{13}C NMR (101 MHz, DMSO) δ 174.76, 154.39, 143.44, 141.61, 132.99, 130.26, 128.12, 127.53, 123.11, 121.94, 121.01, 117.13, 116.17, 109.23, 99.67, 62.48, 62.21, 52.80, 43.46, 15.23. HRMS (ESI) m/z calcd for $C_{21}H_{24}ClN_3O_4Na$ $[M+Na]^+$ = 440.1348, found = 440.1345.

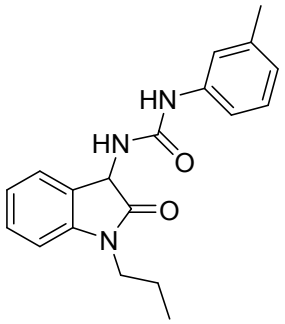


1-(1-(2,2-diethoxyethyl)-2-oxoindolin-3-yl)-3-(3-fluorophenyl)urea (1r): A white solid. ^{1}H NMR (400 MHz, DMSO) δ 9.11 (s, 1H), 7.41 (d, *J* = 12.1 Hz, 1H), 7.34 – 7.20 (m, 3H), 7.18 – 6.97 (m, 4H), 6.73 (td, *J* = 8.5, 2.2 Hz, 1H), 5.08 (d, *J* = 7.6 Hz, 1H), 4.72 (t, *J* = 5.3 Hz, 1H), 3.85 (dd, *J* = 14.2, 5.5 Hz, 1H), 3.67 (dq, *J* = 9.8, 6.8 Hz, 3H), 3.50 (dq, *J* = 14.3, 7.0 Hz, 2H), 1.07 (dd, *J* = 12.0, 6.9 Hz, 6H). ^{13}C NMR (101 MHz, DMSO) δ 174.82, 163.55, 154.35, 143.34, 142.00, 130.11,

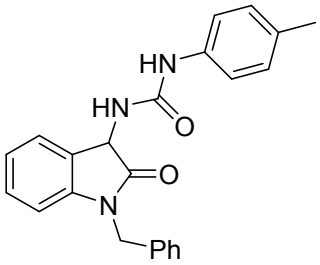
128.13, 127.53, 123.17, 121.94, 113.48, 109.33, 107.80, 107.59, 104.57, 104.30, 99.68, 62.47, 62.22, 52.47, 43.09, 15.22. HRMS (ESI) m/z calcd for $C_{21}H_{24}FN_3O_4Na$ $[M+Na]^+$ = 424.1643, found = 424.1640.



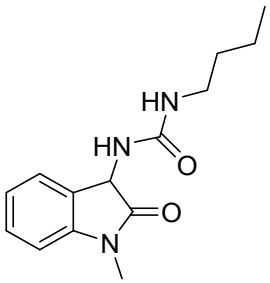
1-(2-oxo-1-propylindolin-3-yl)-3-(p-tolyl)urea (1s): A white solid. ^{1}H NMR (400 MHz, DMSO) δ 8.66 (s, 1H), 7.26 (dd, *J* = 13.6, 8.1 Hz, 4H), 7.04 – 6.99 (m, 4H), 6.98 – 6.93 (m, 1H), 5.02 (d, *J* = 7.7 Hz, 1H), 3.62 (tq, *J* = 13.8, 7.0 Hz, 2H), 2.20 (s, 3H), 1.71 – 1.55 (m, 2H), 0.97 – 0.82 (m, 3H). ^{13}C NMR (101 MHz, DMSO) δ 174.73, 154.58, 143.18, 137.50, 130.12, 129.05, 128.28, 128.18, 123.37, 121.79, 117.91, 108.46, 52.64, 20.33, 11.23. HRMS (ESI) m/z calcd for $C_{19}H_{22}N_3O_2$ $[M+H]^+$ = 324.1707, found = 324.1709.



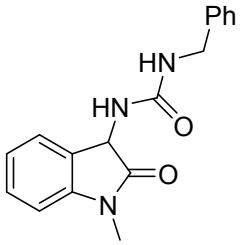
1-(2-oxo-1-propylindolin-3-yl)-3-(m-tolyl)urea (1t): A white solid. ^{1}H NMR (400 MHz, DMSO) δ 8.70 (s, 1H), 7.32 – 7.19 (m, 3H), 7.16 – 7.05 (m, 2H), 7.05 – 6.97 (m, 3H), 6.72 (d, *J* = 7.1 Hz, 1H), 5.02 (d, *J* = 7.6 Hz, 1H), 3.63 (ddq, *J* = 20.8, 13.9, 7.0 Hz, 2H), 2.22 (s, 3H), 1.75 – 1.50 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 174.70, 154.51, 143.17, 139.98, 137.79, 128.50, 128.29, 128.15, 123.35, 122.15, 121.80, 118.32, 115.01, 108.47, 52.67, 21.23, 20.36, 11.24. HRMS (ESI) m/z calcd for $C_{19}H_{22}N_3O_2$ $[M+H]^+$ = 324.1707, found = 324.1708.



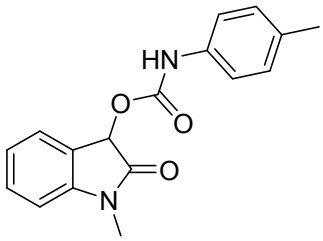
1-(1-benzyl-2-oxoindolin-3-yl)-3-(p-tolyl)urea (1u): A white solid. ^{1}H NMR (400 MHz, DMSO) δ 8.71 (s, 1H), 7.42 (d, *J* = 7.2 Hz, 2H), 7.36 – 7.23 (m, 6H), 7.16 (dd, *J* = 17.3, 9.7 Hz, 1H), 7.08 (d, *J* = 7.7 Hz, 1H), 7.06 – 6.95 (m, 3H), 6.79 (d, *J* = 7.8 Hz, 1H), 5.15 (d, *J* = 7.5 Hz, 1H), 4.99 – 4.81 (m, 2H), 2.21 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 174.96, 154.59, 142.73, 137.49, 136.41, 130.19, 129.06, 128.48, 128.19, 128.14, 127.25, 123.34, 122.09, 117.98, 108.87, 52.83, 42.81, 20.31. HRMS (ESI) m/z calcd for $C_{23}H_{22}N_3O_2$ $[M+H]^+$ = 372.1707, found = 372.1712.



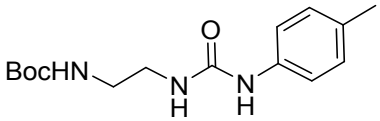
1-butyl-3-(1-methyl-2-oxoindolin-3-yl)urea (1v): A white solid. ^{1}H NMR (400 MHz, DMSO) δ 7.27 (t, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 7.1 Hz, 1H), 7.07 – 6.89 (m, 2H), 6.63 (d, *J* = 7.8 Hz, 1H), 6.14 (t, *J* = 5.2 Hz, 1H), 4.96 (d, *J* = 7.9 Hz, 1H), 3.09 (s, 3H), 2.97 (d, *J* = 6.2 Hz, 2H), 1.40 – 1.30 (m, 2H), 1.25 (dt, *J* = 14.2, 7.2 Hz, 2H), 0.86 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 175.07, 157.42, 143.74, 128.61, 128.23, 123.23, 121.95, 108.17, 52.69, 32.07, 26.07, 19.57, 13.74. HRMS (ESI) m/z calcd for $C_{14}H_{20}N_3O_2$ $[M+H]^+$ = 262.1550, found = 262.1554.



1-benzyl-3-(1-methyl-2-oxoindolin-3-yl)urea (1w): A white solid. ^{1}H NMR (400 MHz, DMSO) δ 7.34 – 7.26 (m, 3H), 7.26 – 7.16 (m, 4H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 7.7 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.69 (t, *J* = 6.0 Hz, 1H), 5.00 (d, *J* = 7.9 Hz, 1H), 4.20 (d, *J* = 6.0 Hz, 2H), 3.10 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 174.99, 157.50, 143.78, 140.62, 128.50, 128.30, 128.24, 127.05, 126.64, 123.25, 121.99, 108.22, 52.79, 43.04, 26.10. HRMS (ESI) m/z calcd for $C_{17}H_{18}N_3O_2$ $[M+H]^+$ = 296.1394, found = 296.1397.

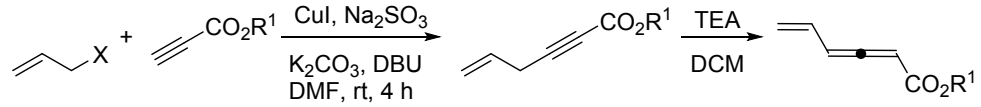


methyl-2-oxoindolin-3-yl p-tolylcarbamate (1x): A white solid. ^{1}H NMR (400 MHz, DMSO) δ 9.95 (s, 1H), 7.45 – 7.26 (m, 4H), 7.13 – 7.00 (m, 4H), 5.96 (s, 1H), 3.15 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 172.20, 152.38, 144.28, 129.98, 129.25, 129.17, 124.85, 124.58, 122.54, 118.33, 118.21, 108.91, 69.90, 26.10, 20.35. HRMS (ESI) m/z calcd for $C_{17}H_{18}N_3O_2$ $[M+H]^+$ = 297.1234, found = 297.1238.



tert-butyl (2-(3-(p-tolyl)ureido)ethyl)carbamate (1y): A white solid. ^{1}H NMR (400 MHz, DMSO) δ 8.39 (s, 1H), 7.26 (d, *J* = 8.3 Hz, 2H), 7.01 (d, *J* = 8.1 Hz, 2H), 6.86 (s, 1H), 6.09 (s, 1H), 3.16 – 3.05 (m, 2H), 2.99 (d, *J* = 5.6 Hz, 2H), 2.20 (s, 3H), 1.37 (s, 9H). ^{13}C NMR (101 MHz, DMSO) δ 155.71, 155.35, 137.96, 129.68, 129.02, 117.76, 77.62, 40.51, 39.01, 28.25, 20.30. HRMS (ESI) m/z calcd for $C_{17}H_{18}N_3O_2$ $[M+H]^+$ = 294.1812, found = 294.1816.

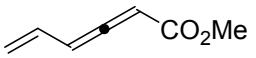
3. General procedure for preparation of vinyl allenoates**.**



S2-1 **S2-2** **S2-3** **2**

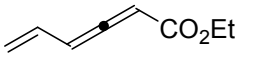
Compound **S2-3** was prepared following the synthetic method describes previously[2], and directly used for the following reaction.

To a stirred solution of compound **S2-3** (2.3g, 18.6 mmol) in anhydrous CH_2Cl_2 (70 mL) was added triethylamine (5.2 mL, 37.2 mmol). The mixture was stirred at room temperature for 6 h under argon atmosphere. The reaction was quenched by saturated $NaHCO_3$ solution. The aqueous phase was extracted by ethyl acetate, and the combined organic layers were washed with water and brine, and dried by Mg_2SO_4. The desired product was obtained after filtered and concentrated under reduced pressure.



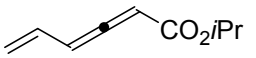
methyl hexa-2,3,5-trienoate (**2a**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.32 – 6.23 (m, 1H), 6.23 – 6.11 (m, 1H), 5.85 – 5.77 (m, 1H), 5.41 – 5.27 (m, 1H), 5.18 (d, *J* = 9.6 Hz, 1H), 3.75 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 216.12, 165.58, 129.01, 119.37, 98.40, 89.48, 52.22. **HRMS(EI)** m/z calcd for $C_7H_8O_2$ M^+: 124.0524; found: 124.0519.



ethyl hexa-2,3,5-trienoate (**2b**)

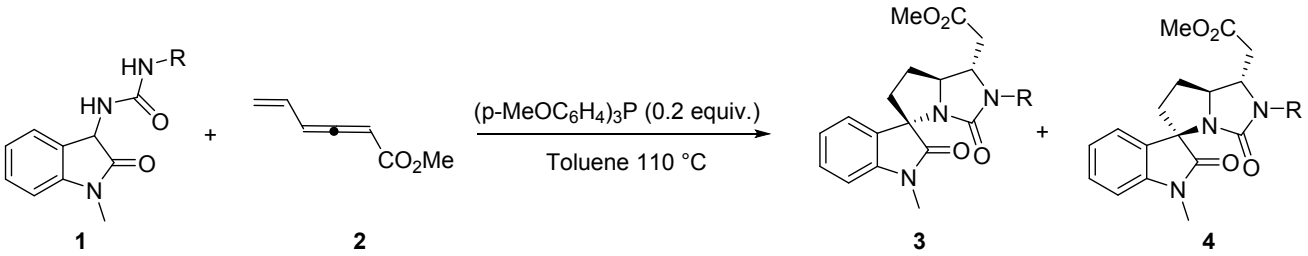
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.27 (dt, *J* = 14.8, 7.4 Hz, 1H), 6.22 – 6.14 (m, 1H), 5.85 – 5.75 (m, 1H), 5.39 – 5.30 (m, 1H), 5.23 – 5.10 (m, 1H), 4.25 – 4.15 (m, 2H), 1.30 – 1.25 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 215.79, 164.82, 128.98, 118.95, 98.16, 89.60, 60.83, 14.03. **HRMS(EI)** m/z calcd for $C_8H_{10}O_2$ M^+: 138.0681; found: 138.0675.



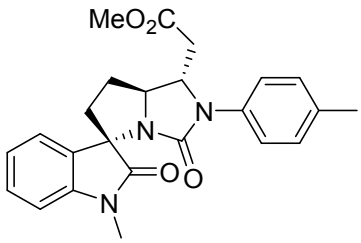
isopropyl hexa-2,3,5-trienoate (**2c**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.27 (dt, *J* = 9.2, 3.5 Hz, 1H), 6.22 – 6.14 (m, 1H), 5.81 – 5.73 (m, 1H), 5.38 – 5.29 (m, 1H), 5.14 (dd, *J* = 8.8, 7.8 Hz, 1H), 5.09 – 5.01 (m, 1H), 1.27 (d, *J* = 1.8 Hz, 3H), 1.25 (d, *J* = 1.6 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 214.85, 163.57, 128.23, 117.92, 97.30, 89.16, 67.43, 20.76. **HRMS(EI)** m/z calcd for $C_9H_{12}O_2$ M^+: 152.0837; found: 152.0831.

General procedures of the catalytic reactions for 2 with urea:

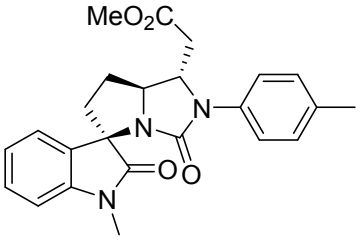


A round bottom flask equipped with a magnetic stirrer bar was charged with the corresponding substituted urea **1** (0.2 mmol) in toluene (2 mL). (p-$MeOC_6H_4)_3P$ (0.04 mmol) and allenoates **2** (0.6 mmol) was added and then the reaction was stirred at 110℃ for 10 min. The mixture concentrated *in vacuo* and the crude was purified by column chromatography (ethyl aceate : hexane = 2:1) to give the product **3** and **4** specifically.



methyl 2-((1'S,3R,7a'S)-1-methyl-2,3'-dioxo-2'-(p-tolyl)-1',2',3',6',7',7a'-hexahydrospiro[indoline-3,5'-pyrrolo[1,2-c]imidazol]-1'-yl)acetate (3aa):

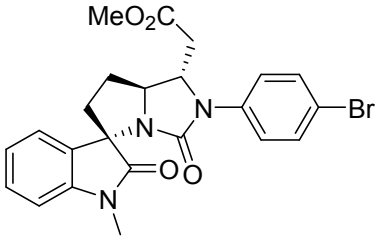
White solid 39 mg. 46% yield. **m.p.** = 195-198℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 12.5, 5.3 Hz, 2H), 7.16 – 7.04 (m, 5H), 6.81 (d, *J* = 7.7 Hz, 1H), 4.74 – 4.63 (m, 1H), 4.11 (dt, *J* = 10.6, 5.4 Hz, 1H), 3.69 (s, 3H), 3.17 (s, 3H), 2.98 (dd, *J* = 16.5, 3.4 Hz, 1H), 2.62 – 2.48 (m, 2H), 2.44 – 2.29 (m, 3H), 2.27 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.47, 171.20, 158.25, 143.68, 134.75, 134.55, 130.65, 129.63, 129.24, 123.04, 122.96, 122.69, 108.48, 66.85, 64.25, 58.97, 51.96, 40.22, 38.30, 31.45, 26.46, 20.93. **HRMS** (ESI) m/z calcd for $C_{24}H_{26}N_3O_4$ $[M+H]^+$ = 420.1918, found = 420.1922.



methyl 2-((1'S,3S,7a'S)-1-methyl-2,3'-dioxo-2'-(p-tolyl)-1',2',3',6',7',7a'-hexahydrospiro[indoline-3,5'-pyrrolo[1,2-c]imidazol]-1'-yl)acetate (4aa)

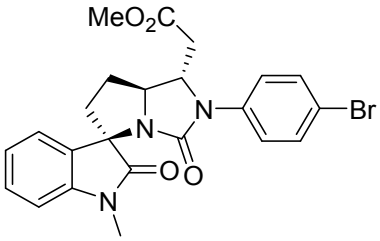
White solid 42 mg. 50% yield. **m.p.** = 67-70 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 (dd, *J* = 14.3, 6.6 Hz, 1H), 7.13 – 7.04 (m, 5H), 6.99 (t, *J* = 7.4 Hz, 1H), 6.85 (dd, *J* = 20.9, 7.8 Hz, 1H), 4.70 – 4.58 (m, 1H), 4.25 – 4.12 (m, 1H), 3.70 (s, 3H), 3.24 (s, 3H), 2.99 (dd, *J* = 16.9, 3.2 Hz, 1H), 2.55 (ddd, *J* = 23.8, 11.3, 5.7 Hz, 3H), 2.30 – 2.25 (m, 3H), 2.19 (d, *J* = 8.2 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.99, 171.38, 155.65, 143.14, 134.78, 134.47, 129.69, 129.52, 129.23, 123.10, 122.40,

122.34, 108.64, 66.29, 64.58, 58.29, 52.05, 40.22, 38.04, 32.45, 26.79, 20.94. **HRMS** (ESI) m/z calcd for $C_{24}H_{26}N_3O_4$ $[M+H]^+$ = 420.1918, found = 420.1923.



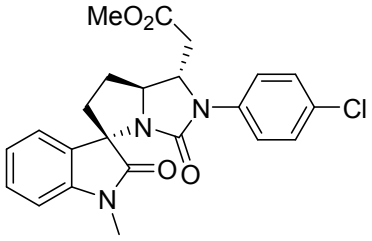
methyl 2-((1'S,3R,7a'S)-2'-(4-bromophenyl)-1-methyl-2,3'-dioxo-1',2',3',6',7',7a'-hexahydrospiro[indoline-3,5'-pyrrolo[1,2-c]imidazol]-1'-yl)acetate (3ba)

White solid 40 mg. 41% yield. **m.p.** = > 240 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.7 Hz, 2H), 7.30 (dd, *J* = 16.2, 8.5 Hz, 2H), 7.12 (dd, *J* = 16.4, 8.1 Hz, 3H), 6.83 (d, *J* = 7.7 Hz, 1H), 4.76 – 4.64 (m, 1H), 4.12 (dt, *J* = 10.4, 5.3 Hz, 1H), 3.72 (s, 3H), 3.19 (s, 3H), 2.99 (dd, *J* = 16.6, 3.2 Hz, 1H), 2.61 – 2.47 (m, 2H), 2.46 – 2.24 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.31, 170.99, 157.74, 143.65, 136.54, 132.09, 130.37, 129.44, 123.69, 123.20, 122.99, 117.57, 108.64, 66.88, 64.30, 58.39, 52.14, 40.19, 38.05, 31.47, 26.54. **HRMS** (ESI) m/z calcd for $C_{23}H_{23}BrN_3O_4$ $[M+H]^+$ = 484.0866, found = 484.0860.



methyl 2-((1'S,3S,7a'S)-2'-(4-bromophenyl)-1-methyl-2,3'-dioxo-1',2',3',6',7',7a'-hexahydrospiro[indoline-3,5'-pyrrolo[1,2-c]imidazol]-1'-yl)acetate (4ba)

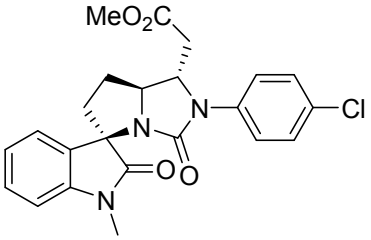
White solid 50 mg. 52% yield. **m.p.** = 88-91 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 12.1, 9.1 Hz, 1H), 7.29 (d, *J* = 7.5 Hz, 2H), 7.09 (d, *J* = 8.8 Hz, 3H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 4.69 – 4.58 (m, 1H), 4.20 (dt, *J* = 10.6, 5.5 Hz, 1H), 3.72 (s, 3H), 3.25 (s, 3H), 2.98 (dd, *J* = 16.9, 3.2 Hz, 1H), 2.58 (tdd, *J* = 16.8, 11.4, 5.4 Hz, 3H), 2.28 – 2.10 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.73, 171.08, 155.00, 143.12, 132.07, 131.99, 129.37, 129.14, 123.39, 123.12, 122.35, 121.69, 117.37, 108.71, 66.11, 64.57, 57.72, 52.14, 40.12, 37.76, 32.43, 26.77. **HRMS** (ESI) m/z calcd for $C_{23}H_{23}BrN_3O_4$ $[M+H]^+$ = 484.0866, found = 484.0863.



methyl 2-((1'S,3R,7a'S)-2'-(4-chlorophenyl)-1-methyl-2,3'-dioxo-1',2',3',6',7',7a'-hexahydrospiro[indoline-3,5'-pyrrolo[1,2-c]imidazol]-1'-yl)acetate (3ca)

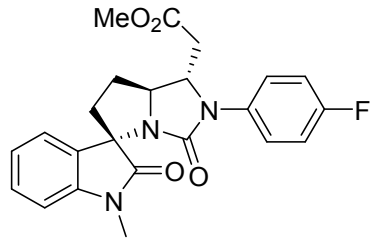
Yellow solid 43 mg. 48% yield. **m.p.** = 239-242 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.23 (m, 4H), 7.23 – 7.16 (m, 2H), 7.10 (dd, *J* = 11.0, 4.0 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 4.70 (ddd, *J* = 10.2, 5.4, 3.4 Hz, 1H), 4.12 (dt, *J* = 10.4, 5.3 Hz, 1H), 3.72 (s, 3H), 3.19 (s, 3H), 2.98 (dd, *J* = 16.5, 3.3 Hz, 1H), 2.61 – 2.48 (m, 2H), 2.46 – 2.24 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.33, 170.99, 157.82, 143.65, 136.02, 130.39, 129.88, 129.42, 129.14, 123.43, 123.18, 122.99, 108.62, 66.88,

64.29, 58.51, 52.12, 40.20, 38.08, 31.46, 26.54. **HRMS** (ESI) m/z calcd for $C_{23}H_{23}ClN_3O_4$ $[M+H]^+$ = 440.1372, found = 440.1372.



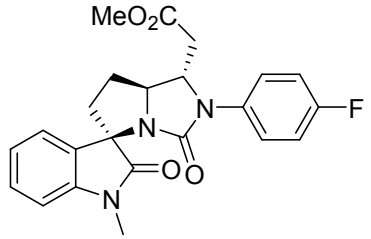
methyl 2-((1'S,3S,7a'S)-2'-(4-chlorophenyl)-1-methyl-2,3'-dioxo-1',2',3',6',7',7a'-hexahydrospiro[indoline-3,5'-pyrrolo[1,2-c]imidazol]-1'-yl)acetate (4ca)

White solid 43 mg. 48% yield. **m.p.** = 169-172 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.20 (m, 3H), 7.17 – 7.06 (m, 3H), 7.00 (t, *J* = 7.4 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 4.71 – 4.55 (m, 1H), 4.21 (dd, *J* = 10.4, 5.5 Hz, 1H), 3.72 (s, 3H), 3.25 (s, 3H), 2.98 (dd, *J* = 16.9, 3.3 Hz, 1H), 2.67 – 2.47 (m, 3H), 2.20 (ddd, *J* = 16.9, 11.4, 6.9 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.77, 171.12, 155.13, 143.13, 136.00, 129.77, 129.40, 129.16, 123.15, 122.35, 108.74, 66.14, 64.59, 57.88, 52.16, 40.15, 37.81, 32.44, 26.80. **HRMS** (ESI) m/z calcd for $C_{23}H_{23}ClN_3O_4$ $[M+H]^+$ = 440.1372, found = 440.1378.



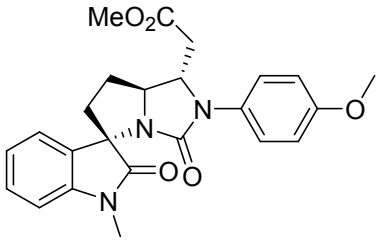
methyl 2-((1'S,3R,7a'S)-2'-(4-fluorophenyl)-1-methyl-2,3'-dioxo-1',2',3',6',7',7a'-hexahydrospiro[indoline-3,5'-pyrrolo[1,2-c]imidazol]-1'-yl)acetate (3da)

White solid 37 mg. 44% yield. **m.p.** = 166-169 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (ddd, *J* = 9.5, 7.6, 5.5 Hz, 2H), 7.24 – 7.17 (m, 2H), 7.09 (t, *J* = 7.5 Hz, 1H), 7.00 (t, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 8.1 Hz, 1H), 4.71 – 4.58 (m, 1H), 4.12 (dt, *J* = 10.5, 5.4 Hz, 1H), 3.70 (s, 3H), 3.19 (s, 3H), 2.93 (dd, *J* = 16.5, 3.5 Hz, 1H), 2.63 – 2.48 (m, 2H), 2.45 – 2.21 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.45, 170.98, 161.19, 158.28, 143.65, 133.44, 130.47, 129.34, 124.70, 124.62, 123.13, 122.97, 116.00, 115.77, 108.56, 66.92, 64.26, 59.34, 52.03, 40.25, 38.26, 31.41. **HRMS** (ESI) m/z calcd for $C_{23}H_{23}FN_3O_4$ $[M+H]^+$ = 424.1667, found = 424.1662.



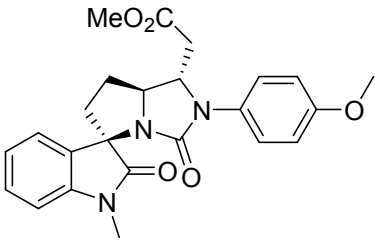
methyl 2-((1'S,3S,7a'S)-2'-(4-fluorophenyl)-1-methyl-2,3'-dioxo-1',2',3',6',7',7a'-hexahydrospiro[indoline-3,5'-pyrrolo[1,2-c]imidazol]-1'-yl)acetate (4da)

White solid 40 mg. 47% yield. **m.p.** = 71-74 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 – 7.22 (m, 1H), 7.18 – 7.08 (m, 3H), 7.04 – 6.93 (m, 3H), 6.84 (d, *J* = 7.8 Hz, 1H), 4.68 – 4.55 (m, 1H), 4.26 – 4.14 (m, 1H), 3.70 (s, 3H), 3.25 (s, 3H), 2.94 (dd, *J* = 16.8, 3.5 Hz, 1H), 2.66 – 2.49 (m, 3H), 2.28 – 2.09 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.84, 171.16, 155.53, 143.15, 133.32, 129.37, 124.26, 124.18, 123.13, 122.32, 116.04, 115.82, 108.72, 66.15, 64.58, 58.52, 52.13, 40.21, 37.97, 32.41, 26.80. **HRMS** (ESI) m/z calcd for $C_{23}H_{23}FN_3O_4$ $[M+H]^+$ = 424.1667, found = 424.1671.



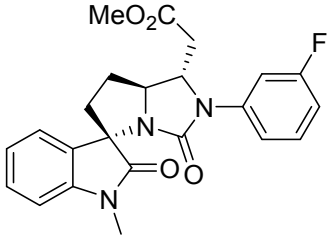
methyl 2-((1'S,3R,7a'S)-2'-(4-methoxyphenyl)-1-methyl-2,3'-dioxo-1',2',3',6',7',7a'-hexahydrospiro[indoline-3,5'-pyrrolo[1,2-c]imidazol]-1'-yl)acetate (3ea)

White solid 43 mg. 49% yield. **m.p.** = 182-185 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.4 Hz, 2H), 7.15 (d, *J* = 9.0 Hz, 2H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.82 (dd, *J* = 11.6, 8.3 Hz, 3H), 4.66 – 4.57 (m, 1H), 4.11 (dt, *J* = 10.6, 5.4 Hz, 1H), 3.75 (s, 3H), 3.68 (s, 3H), 3.18 (s, 3H), 2.92 (dd, *J* = 16.4, 3.6 Hz, 1H), 2.62 – 2.48 (m, 2H), 2.34 (dddd, *J* = 31.9, 25.9, 12.8, 5.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.56, 171.13, 158.67, 157.19, 143.65, 130.65, 130.33, 129.21, 124.99, 123.03, 122.94, 114.44, 108.46, 66.92, 64.22, 59.80, 55.54, 51.93, 40.25, 38.45, 31.39, 26.45. **HRMS** (ESI) m/z calcd for $C_{24}H_{26}N_3O_5$ $[M+H]^+$ = 436.1867, found = 436.1875.



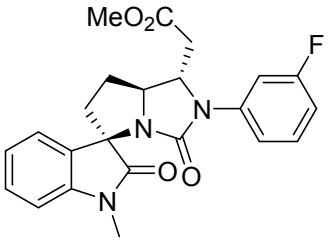
methyl 2-((1'S,3S,7a'S)-2'-(4-methoxyphenyl)-1-methyl-2,3'-dioxo-1',2',3',6',7',7a'-hexahydrospiro[indoline-3,5'-pyrrolo[1,2-c]imidazol]-1'-yl)acetate (4ea)

Yellow solid 34 mg. 39% yield. **m.p.** = 61-64 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.22 (m, 1H), 7.15 – 7.05 (m, 3H), 7.00 (t, *J* = 7.2 Hz, 1H), 6.86 – 6.78 (m, 3H), 4.59 (ddd, *J* = 10.0, 6.2, 3.6 Hz, 1H), 4.25 – 4.14 (m, 1H), 3.74 (s, 3H), 3.69 (s, 3H), 3.24 (s, 3H), 2.93 (dd, *J* = 16.8, 3.6 Hz, 1H), 2.66 – 2.48 (m, 3H), 2.31 – 2.12 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.98, 171.34, 157.02, 155.98, 143.13, 130.19, 129.55, 129.23, 124.48, 123.09, 122.33, 114.48, 108.64, 66.27, 64.55, 58.91, 55.59, 52.05, 40.24, 38.15, 32.39, 26.78. **HRMS** (ESI) m/z calcd for $C_{24}H_{26}N_3O_5$ $[M+H]^+$ = 436.1867, found = 436.1871.



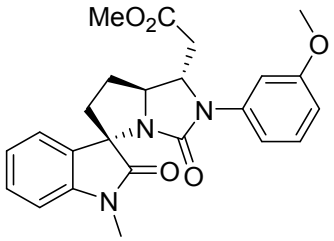
methyl 2-((1'S,3R,7a'S)-2'-(3-fluorophenyl)-1-methyl-2,3'-dioxo-1',2',3',6',7',7a'-hexahydrospiro[indoline-3,5'-pyrrolo[1,2-c]imidazol]-1'-yl)acetate (3fa)

Yellow solid 38 mg. 45% yield. **m.p.** = 228-231 ℃.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.20 (m, 3H), 7.13 – 7.05 (m, 2H), 6.99 (dd, *J* = 8.2, 1.3 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 6.80 – 6.71 (m, 1H), 4.71 (ddd, *J* = 10.3, 5.2, 3.3 Hz, 1H), 4.11 (dt, *J* = 10.4, 5.3 Hz, 1H), 3.73 (s, 3H), 3.19 (s, 3H), 3.05 (dd, *J* = 16.6, 3.2 Hz, 1H), 2.66 – 2.46 (m, 2H), 2.46 – 2.21 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.25, 170.99, 164.37, 161.93, 157.57, 143.65, 139.12, 139.02, 130.37, 130.14, 130.05, 129.43, 123.18, 122.99, 116.81, 111.36, 111.14, 109.59, 109.34, 108.62, 66.86, 64.29, 58.18, 52.10, 40.17, 38.05, 31.47, 26.53. **HRMS** (ESI) m/z calcd for $C_{23}H_{23}FN_3O_4$ $[M+H]^+$ = 424.1667, found = 424.1669.



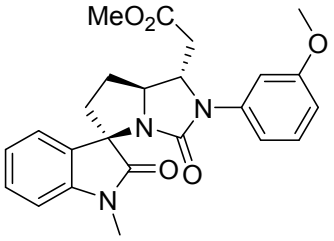
methyl 2-((1'S,3S,7a'S)-2'-(3-fluorophenyl)-1-methyl-2,3'-dioxo-1',2',3',6',7',7a'-hexahydrospiro[indoline-3,5'-pyrrolo[1,2-c]imidazol]-1'-yl)acetate (4fa)

Yellow solid 42 mg. 49% yield. **m.p.** = 81-84 ℃.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 (dt, *J* = 15.0, 8.4 Hz, 2H), 7.07 (d, *J* = 7.2 Hz, 1H), 6.96 (dt, *J* = 15.9, 9.4 Hz, 3H), 6.82 (d, *J* = 7.8 Hz, 1H), 6.73 (dd, *J* = 8.2, 6.7 Hz, 1H), 4.70 – 4.57 (m, 1H), 4.25 – 4.11 (m, 1H), 3.70 (s, 3H), 3.23 (s, 3H), 3.01 (dd, *J* = 16.9, 3.0 Hz, 1H), 2.68 – 2.47 (m, 3H), 2.17 (ddd, *J* = 17.1, 11.1, 7.0 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.74, 171.10, 164.34, 161.90, 154.96, 143.12, 139.03, 130.16, 130.07, 129.40, 129.12, 123.13, 122.36, 116.75, 111.32, 111.11, 109.43, 109.18, 108.73, 66.16, 64.55, 57.68, 52.13, 40.09, 37.78, 32.44, 29.78, 26.78. **HRMS** (ESI) m/z calcd for $C_{23}H_{23}FN_3O_4$ $[M+H]^+$ = 424.1667, found = 424.1668.



methyl 2-((1'S,3R,7a'S)-2'-(3-methoxyphenyl)-1-methyl-2,3'-dioxo-1',2',3',6',7',7a'-hexahydrospiro[indoline-3,5'-pyrrolo[1,2-c]imidazol]-1'-yl)acetate (3ga)

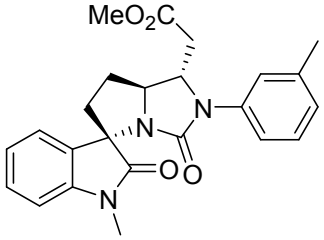
White solid 42 mg. 39% yield. **m.p.** = 114-117 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.24 (m, 2H), 7.19 (t, *J* = 8.2 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 6.89 (t, *J* = 2.1 Hz, 1H), 6.81 (dd, *J* = 14.4, 5.0 Hz, 2H), 6.64 (dd, *J* = 8.2, 2.1 Hz, 1H), 4.72 (ddd, *J* = 10.3, 5.2, 3.4 Hz, 1H), 4.10 (dt, *J* = 10.4, 5.3 Hz, 1H), 3.74 (s, 3H), 3.71 (s, 3H), 3.21 (d, *J* = 13.1 Hz, 3H), 3.05 (dd, *J* = 16.6, 3.3 Hz, 1H), 2.54 (ddd, *J* = 22.9, 11.4, 5.0 Hz, 2H), 2.45 – 2.20 (m, 3H). **^{13}C NM**R (101 MHz, $CDCl_3$) δ 176.38, 171.24, 160.28, 157.94, 143.67, 138.61, 130.63, 129.69, 129.35, 123.15, 123.00, 114.11, 110.80, 108.61, 108.28, 77.48, 77.16, 76.84, 66.94, 64.32, 58.55, 55.44, 52.04, 40.34, 38.26, 31.50, 26.55. **HRMS** (ESI) m/z calcd for $C_{24}H_{26}N_3O_5$ $[M+H]^+$ = 436.1867, found = 436.1868.



methyl 2-((1'S,3S,7a'S)-2'-(3-methoxyphenyl)-1-methyl-2,3'-dioxo-1',2',3',6',7',7a'-hexahydrospiro[indoline-3,5'-pyrrolo[1,2-c]imidazol]-1'-yl)acetate (4ga)

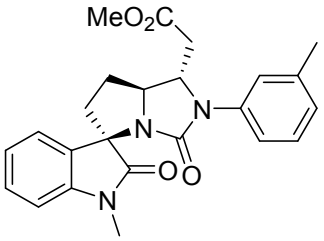
White solid 41 mg. 38% yield. **m.p.** = 178-181 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 (dt, *J* = 7.7, 1.8 Hz, 1H), 7.18 (t, *J* = 8.2 Hz, 1H), 7.13 – 7.05 (m, 1H), 6.99 (t, *J* = 7.4 Hz, 1H), 6.83 (t, *J* = 4.9 Hz, 2H), 6.75 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.62 (dd, *J* = 8.2, 2.3 Hz, 1H), 4.72 – 4.61 (m, 1H), 4.25 – 4.15 (m, 1H), 3.73 – 3.72 (m, 3H), 3.71 (s, 3H), 3.24 (s, 3H), 3.04 (dd, *J* = 17.0, 3.3 Hz, 1H), 2.66 – 2.48 (m, 3H), 2.28 – 2.10 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.92, 171.30, 160.25, 155.41, 143.01,

138.56, 129.70, 129.37, 129.28, 123.15, 122.32, 113.93, 110.50, 108.73, 108.37, 66.33, 64.57, 58.15, 55.37, 52.04, 40.32, 37.93, 32.40, 26.79. **HRMS** (ESI) m/z calcd for $C_{24}H_{26}N_3O_5$ $[M+H]^+$ = 436.1867, found = 436.1868.



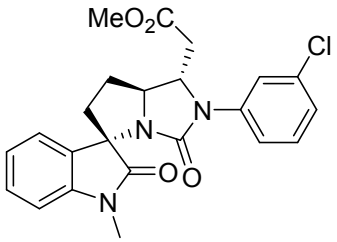
methyl 2-((1'S,3R,7a'S)-1-methyl-2,3'-dioxo-2'-(m-tolyl)-1',2',3',6',7',7a'-hexahydrospiro[indoline-3,5'-pyrrolo[1,2-c]imidazol]-1'-yl)acetate (3ha)

White solid 40 mg. 47% yield. **m.p.** = 152-155 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 13.4, 6.2 Hz, 2H), 7.21 – 7.06 (m, 3H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.89 (d, *J* = 7.5 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 4.74 (ddd, *J* = 10.3, 5.4, 3.4 Hz, 1H), 4.18 – 4.04 (m, 1H), 3.71 (s, 3H), 3.18 (s, 3H), 3.02 (dd, *J* = 16.6, 3.4 Hz, 1H), 2.62 – 2.49 (m, 2H), 2.46 – 2.31 (m, 3H), 2.28 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.40, 171.25, 158.01, 143.65, 138.93, 137.17, 130.60, 129.26, 128.78, 125.53, 123.36, 123.07, 122.95, 119.01, 108.51, 66.81, 64.25, 58.52, 52.00, 40.21, 38.25, 31.48, 26.49, 21.53. **HRMS** (ESI) m/z calcd for $C_{24}H_{26}N_3O_4$ $[M+H]^+$ = 420.1918, found = 420.1918.



methyl 2-((1'S,3S,7a'S)-1-methyl-2,3'-dioxo-2'-(m-tolyl)-1',2',3',6',7',7a'-hexahydrospiro[indoline-3,5'-pyrrolo[1,2-c]imidazol]-1'-yl)acetate (4ha)

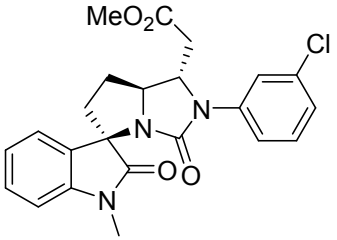
White solid 42 mg. 50% yield. **m.p.** = 73-76 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 – 7.22 (m, 1H), 7.14 (d, *J* = 24.5 Hz, 2H), 7.07 (s, 1H), 7.03 – 6.91 (m, 2H), 6.86 (dd, *J* = 19.4, 7.5 Hz, 2H), 4.72 – 4.67 (m, 1H), 4.66 (d, *J* = 3.4 Hz, 1H), 4.26 – 4.15 (m, 1H), 3.71 (s, 3H), 3.25 (s, 3H), 3.01 (dd, *J* = 16.9, 3.3 Hz, 1H), 2.57 (tdd, *J* = 17.1, 11.5, 5.3 Hz, 3H), 2.27 (s, 3H), 2.25 – 2.13 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.96, 171.41, 155.49, 143.10, 139.05, 137.23, 129.26, 128.83, 125.53, 123.33, 123.13, 122.38, 118.79, 108.65, 66.23, 64.55, 58.07, 52.06, 40.21, 38.02, 32.47, 26.79, 21.56. **HRMS** (ESI) m/z calcd for $C_{24}H_{26}N_3O_4$ $[M+H]^+$ = 420.1918, found = 420.1917.



methyl 2-((1'S,3R,7a'S)-2'-(3-chlorophenyl)-1-methyl-2,3'-dioxo-1',2',3',6',7',7a'-hexahydrospiro[indoline-3,5'-pyrrolo[1,2-c]imidazol]-1'-yl)acetate (3ia)

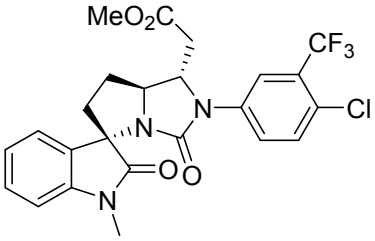
White solid 40 mg. 46% yield. **m.p.** = 215-218 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 3H), 7.23 (dd, *J* = 17.3, 9.2 Hz, 1H), 7.13 – 7.00 (m, 3H), 6.83 (d, *J* = 7.7 Hz, 1H), 4.77 – 4.65 (m, 1H), 4.12 (dt, *J* = 10.4, 5.3 Hz, 1H), 3.72 (s, 3H), 3.19 (s, 3H), 3.02 (dd, *J* = 16.6, 3.3 Hz, 1H), 2.62 – 2.47 (m, 2H), 2.45 – 2.21 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.23,

170.93, 157.55, 143.61, 138.63, 134.75, 130.31, 129.94, 129.42, 124.55, 123.17, 122.97, 122.27, 119.61, 108.61, 66.83, 64.27, 58.19, 52.09, 40.16, 38.02, 31.44, 26.51. **HRMS** (ESI) m/z calcd for $C_{23}H_{23}ClN_3O_4$ $[M+H]^+$ = 440.1372, found = 440.1373.



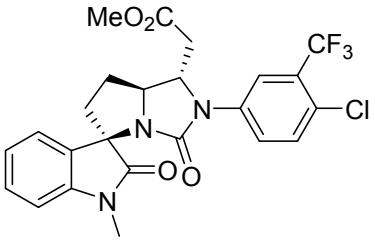
methyl 2-((1'S,3S,7a'S)-2'-(3-chlorophenyl)-1-methyl-2,3'-dioxo-1',2',3',6',7',7a'-hexahydrospiro[indoline-3,5'-pyrrolo[1,2-c]imidazol]-1'-yl)acetate (4ia)

White solid 42 mg. 48% yield. **m.p.** = 197-200 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 2H), 7.20 (t, *J* = 8.1 Hz, 1H), 7.14 – 6.96 (m, 4H), 6.85 (d, *J* = 7.8 Hz, 1H), 4.66 (ddd, *J* = 9.6, 6.0, 3.3 Hz, 1H), 4.21 (dt, *J* = 10.3, 5.3 Hz, 1H), 3.73 (s, 3H), 3.26 (s, 3H), 3.02 (dd, *J* = 17.0, 3.3 Hz, 1H), 2.76 – 2.43 (m, 3H), 2.31 – 2.04 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.73, 171.13, 154.92, 143.17, 138.74, 134.84, 130.01, 129.45, 129.14, 124.53, 123.17, 122.41, 122.04, 119.63, 108.75, 66.12, 64.60, 57.69, 52.19, 40.12, 37.83, 32.50, 26.82. **HRMS** (ESI) m/z calcd for $C_{23}H_{23}ClN_3O_4$ $[M+H]^+$ = 440.1372, found = 440.1367.



methyl 2-((1'S,3R,7a'S)-2'-(4-chloro-3-(trifluoromethyl)phenyl)-1-methyl-2,3'-dioxo-1',2',3',6',7',7a'-hexahydrospiro[indoline-3,5'-pyrrolo[1,2-c]imidazol]-1'-yl)acetate (3ja)

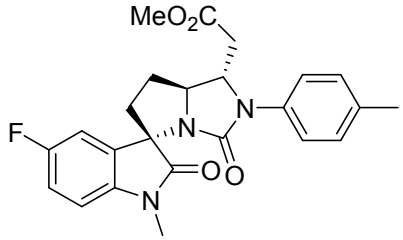
White solid 34 mg. 33% yield. **m.p.** = > 240 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 2.1 Hz, 1H), 7.43 (d, *J* = 8.7 Hz, 1H), 7.37 – 7.28 (m, 3H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 7.7 Hz, 1H), 4.78 – 4.71 (m, 1H), 4.15 (dt, *J* = 10.4, 5.3 Hz, 1H), 3.73 (s, 3H), 3.20 (s, 3H), 2.95 (dd, *J* = 16.5, 3.3 Hz, 1H), 2.55 (ddd, *J* = 17.0, 14.1, 8.2 Hz, 2H), 2.47 – 2.24 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.08, 170.55, 157.36, 143.49, 136.34, 131.89, 130.00, 129.47, 127.27, 125.39, 123.21, 122.90, 121.02, 120.96, 120.92, 108.66, 66.87, 64.27, 58.12, 52.10, 40.18, 37.84, 31.28, 26.47. **HRMS** (ESI) m/z calcd for $C_{24}H_{22}ClF_3N_3O_4$ $[M+H]^+$ = 508.1245, found = 508.1245.



methyl 2-((1'S,3S,7a'S)-2'-(4-chloro-3-(trifluoromethyl)phenyl)-1-methyl-2,3'-dioxo-1',2',3',6',7',7a'-hexahydrospiro[indoline-3,5'-pyrrolo[1,2-c]imidazol]-1'-yl)acetate (4ja)

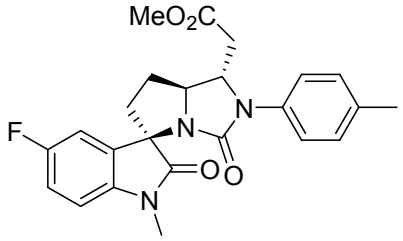
White solid 30 mg. 30% yield. **m.p.** = 229-232 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 2.3 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.31 (dd, *J* = 11.9, 5.5 Hz, 2H), 7.10 (d, *J* = 7.4 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.87 (t, *J* = 9.7 Hz, 1H), 4.68 (ddd, *J* = 9.8, 6.0, 3.4 Hz, 1H), 4.27 – 4.18 (m, 1H), 3.73 (s, 3H), 3.26 (s, 3H), 2.96 (dd, *J* = 16.9, 3.3 Hz, 1H), 2.68 – 2.51 (m, 3H), 2.32 – 2.11 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.55, 170.83, 154.65, 143.13, 136.42, 132.03, 129.58, 128.86, 127.27,

125.64, 123.22, 122.34, 120.72, 120.68, 120.62, 108.87, 66.00, 64.70, 57.59, 52.29, 40.22, 37.69, 32.42, 26.84. **HRMS** (ESI) m/z calcd for $C_{24}H_{22}ClF_3N_3O_4$ $[M+H]^+$ = 508.1245, found = 508.1245.



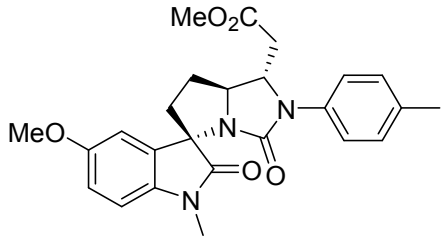
methyl 2-((1'S,3R,7a'S)-5-fluoro-1-methyl-2,3'-dioxo-2'-(p-tolyl)-1',2',3',6',7',7a'-hexahydrospiro[indoline-3,5'-pyrrolo[1,2-c]imidazol]-1'-yl)acetate (3ka)

White solid 28.5 mg. 33% yield. **m.p.** = 217-220 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16 – 7.08 (m, 4H), 7.05 (d, *J* = 2.4 Hz, 1H), 6.99 (td, *J* = 9.0, 2.5 Hz, 1H), 6.73 (dd, *J* = 8.5, 4.0 Hz, 1H), 4.71 – 4.64 (m, 1H), 4.10 (dt, *J* = 10.6, 5.5 Hz, 1H), 3.70 (s, 3H), 3.16 (s, 3H), 2.98 (dd, *J* = 16.5, 3.4 Hz, 1H), 2.56 (ddd, *J* = 16.6, 11.9, 5.5 Hz, 2H), 2.46 – 2.33 (m, 2H), 2.31 – 2.19 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.38, 171.17, 158.38, 134.87, 134.67, 129.74, 122.93, 115.57, 115.34, 111.39, 111.14, 109.10, 109.02, 67.16, 64.26, 59.27, 52.00, 40.31, 38.33, 31.45, 26.65, 20.98. **HRMS** (ESI) m/z calcd for $C_{24}H_{25}FN_3O_4$ $[M+H]^+$ = 438.1824, found = 438.1831.



methyl 2-((1'S,3S,7a'S)-5-fluoro-1-methyl-2,3'-dioxo-2'-(p-tolyl)-1',2',3',6',7',7a'-hexahydrospiro[indoline-3,5'-pyrrolo[1,2-c]imidazol]-1'-yl)acetate (4ka)

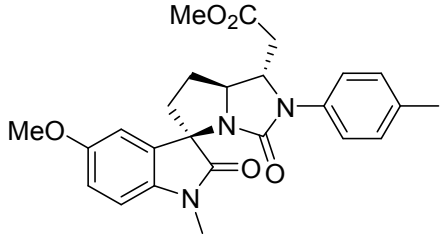
White solid 41 mg. 47% yield. **m.p.** = 125-128 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14 – 7.04 (m, 4H), 6.94 (tt, *J* = 6.7, 3.3 Hz, 1H), 6.86 (dd, *J* = 7.6, 2.5 Hz, 1H), 6.79 – 6.71 (m, 1H), 4.69 – 4.57 (m, 1H), 4.28 – 4.12 (m, 1H), 3.70 (s, 3H), 3.23 (s, 3H), 2.99 (dd, *J* = 16.9, 3.4 Hz, 1H), 2.68 – 2.49 (m, 3H), 2.30 – 2.25 (m, 3H), 2.24 – 2.07 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.68, 171.24, 160.59, 158.20, 155.54, 139.09, 134.74, 134.49, 131.09, 131.02, 129.74, 129.67, 122.45, 121.89, 115.55, 115.31, 110.83, 110.58, 109.14, 109.06, 66.27, 64.50, 58.39, 52.03, 40.16, 37.97, 32.45, 26.89, 20.92. **HRMS** (ESI) m/z calcd for $C_{24}H_{25}FN_3O_4$ $[M+H]^+$ = 438.1824, found = 438.1830.



methyl 2-((1'S,3S,7a'S)-5-methoxy-1-methyl-2,3'-dioxo-2'-(p-tolyl)-1',2',3',6',7',7a'-hexahydrospiro[indoline-3,5'-pyrrolo[1,2-c]imidazol]-1'-yl)acetate (3la)

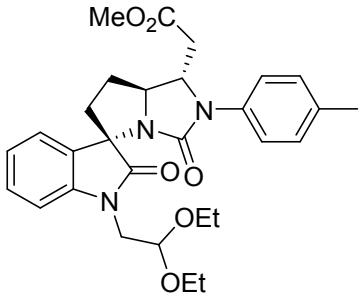
Yellow oil. 38 mg. 42% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.12 (q, *J* = 8.7 Hz, 4H), 6.91 (d, *J* = 2.5 Hz, 1H), 6.81 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.72 (d, *J* = 8.5 Hz, 1H), 4.73 – 4.64 (m, 1H), 4.11 (dt, *J* = 10.6, 5.5 Hz, 1H), 3.79 (s, 3H), 3.70 (s, 3H), 3.15 (s, 3H), 2.99 (dd, *J* = 16.5, 3.4 Hz, 1H), 2.61 – 2.49 (m, 2H), 2.44 – 2.32 (m, 2H), 2.32 – 2.25 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.25, 171.23, 158.32, 156.46, 137.11, 134.73, 134.58, 131.85, 129.65, 122.70, 113.70, 110.32, 108.91, 67.26,

64.28, 59.02, 55.93, 51.99, 40.42, 38.32, 31.44, 26.56, 20.95. **HRMS** (ESI) m/z calcd for $C_{25}H_{27}N_3O_5Na$ $[M+Na]^+$ = 472.1843, found = 472.1846.



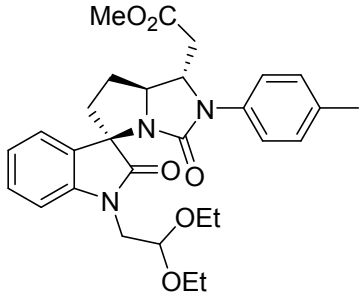
methyl 2-((1'S,3R,7a'S)-5-methoxy-1-methyl-2,3'-dioxo-2'-(p-tolyl)-1',2',3',6',7',7a'-hexahydrospiro[indoline-3,5'-pyrrolo[1,2-c]imidazol]-1'-yl)acetate (4la)

Yellow oil. 36 mg. 40% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.12 – 7.03 (m, 4H), 6.78 – 6.71 (m, 3H), 4.63 (ddd, *J* = 10.1, 6.3, 3.4 Hz, 1H), 4.25 – 4.15 (m, 1H), 3.71 (s, 3H), 3.70 (s, 3H), 3.22 (s, 3H), 2.98 (dd, *J* = 16.9, 3.4 Hz, 1H), 2.66 – 2.49 (m, 3H), 2.27 (s, 3H), 2.17 (dt, *J* = 11.9, 6.2 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.54, 171.32, 156.11, 155.64, 136.69, 134.65, 134.57, 131.05, 129.69, 122.47, 112.01, 110.91, 108.71, 66.45, 64.54, 58.56, 55.69, 52.03, 40.29, 38.03, 32.35, 26.87, 20.93. **HRMS** (ESI) m/z calcd for $C_{25}H_{27}N_3O_5Na$ $[M+Na]^+$ = 472.1843, found = 472.1846.



methyl 2-((1'S,3R,7a'S)-1-(2,2-diethoxyethyl)-2,3'-dioxo-2'-(p-tolyl)-1',2',3',6',7',7a'-hexahydrospiro[indoline-3,5'-pyrrolo[1,2-c]imidazol]-1'-yl)acetate (3ma)

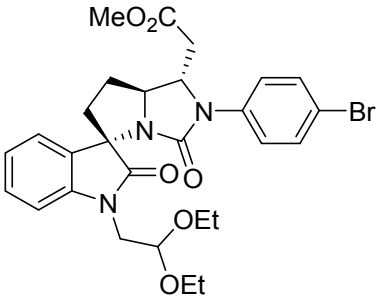
Yellow oil 49 mg. 47% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.22 (m, 2H), 7.16 – 7.09 (m, 4H), 7.06 (t, *J* = 7.8 Hz, 2H), 4.72 – 4.61 (m, 2H), 4.15 – 4.06 (m, 1H), 3.93 (dd, *J* = 14.3, 5.9 Hz, 1H), 3.76 – 3.62 (m, 6H), 3.51 (ddd, *J* = 16.3, 9.2, 7.1 Hz, 2H), 2.98 (dd, *J* = 16.5, 3.4 Hz, 1H), 2.54 (dd, *J* = 16.5, 10.5 Hz, 2H), 2.38 (d, *J* = 6.2 Hz, 3H), 2.28 (s, 3H), 1.12 (dd, *J* = 14.7, 7.2 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.92, 171.24, 158.22, 143.24, 134.88, 134.59, 130.44, 129.63, 128.92, 122.93, 122.87, 122.75, 110.14, 100.78, 66.77, 64.30, 63.49, 59.05, 51.97, 43.79, 40.57, 38.34, 31.43, 20.96, 15.39, 15.32. **HRMS** (ESI) m/z calcd for $C_{29}H_{35}N_3O_6Na$ $[M+Na]^+$ = 544.2418, found = 544.2412.



methyl 2-((1'S,3S,7a'S)-1-(2,2-diethoxyethyl)-2,3'-dioxo-2'-(p-tolyl)-1',2',3',6',7',7a'-hexahydrospiro[indoline-3,5'-pyrrolo[1,2-c]imidazol]-1'-yl)acetate (4ma)

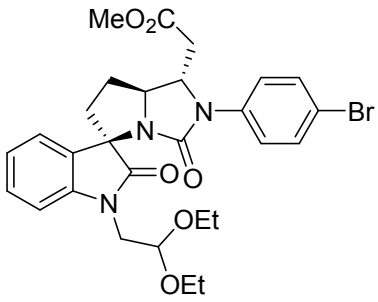
Yellow oil 46 mg. 44% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 – 7.19 (m, 1H), 7.06 (q, *J* = 7.7 Hz, 6H), 6.97 (t, *J* = 7.5 Hz, 1H), 4.73 (t, *J* = 5.4 Hz, 1H), 4.67 – 4.58 (m, 1H), 4.19 (dt, *J* = 5.8, 3.8 Hz, 1H), 3.94 (dt, *J* = 14.9, 7.4 Hz, 1H), 3.80 – 3.67 (m, 6H), 3.58 – 3.46 (m, 2H), 2.98 (dd, *J* = 16.8, 3.4 Hz, 1H), 2.64 – 2.49 (m, 3H), 2.26 (s, 3H), 2.20 (dt, *J* = 11.0, 6.6 Hz,

2H), 1.17 – 1.10 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.43, 171.32, 155.57, 142.66, 134.76, 134.52, 129.68, 129.35, 128.89, 122.91, 122.52, 122.16, 110.14, 100.58, 66.16, 64.61, 63.89, 63.68, 58.44, 51.99, 44.17, 40.58, 38.05, 32.27, 20.91, 15.39, 15.34. **HRMS** (ESI) m/z calcd for $C_{29}H_{35}N_3O_6Na$ $[M+Na]^+$ = 544.2418, found = 544.2411.



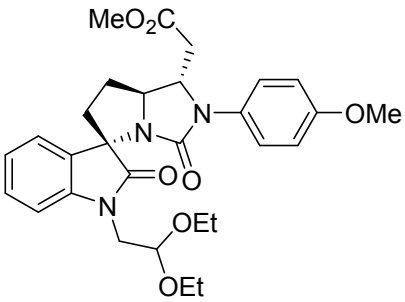
methyl 2-((1'S,3R,7a'S)-2'-(4-bromophenyl)-1-(2,2-diethoxyethyl)-2,3'-dioxo-1',2',3',6',7',7a'-hexahydrospiro[indoline-3,5'-pyrrolo[1,2-c]imidazol]-1'-yl)acetate (3na)

Yellow oil 22 mg. 38% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.8 Hz, 2H), 7.31 – 7.22 (m, 2H), 7.14 (d, *J* = 8.8 Hz, 2H), 7.11 – 7.01 (m, 2H), 4.67 (dd, *J* = 10.7, 5.6 Hz, 2H), 4.11 (dt, *J* = 5.2, 3.4 Hz, 1H), 3.91 (dd, *J* = 14.3, 5.9 Hz, 1H), 3.75 – 3.63 (m, 6H), 3.57 – 3.42 (m, 2H), 2.98 (dd, *J* = 16.6, 3.2 Hz, 1H), 2.52 (ddd, *J* = 22.1, 13.9, 8.3 Hz, 2H), 2.45 – 2.24 (m, 3H), 1.11 (dd, *J* = 15.3, 7.1 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.78, 170.99, 157.77, 143.26, 136.67, 132.09, 130.16, 129.12, 123.85, 123.06, 122.78, 117.66, 110.31, 100.77, 66.85, 64.35, 63.55, 63.52, 58.51, 52.13, 43.82, 40.53, 38.11, 31.46, 15.41, 15.35. **HRMS** (ESI) m/z calcd for $C_{28}H_{32}BrN_3O_6Na$ $[M+Na]^+$ = 608.1367, found = 608.1364.



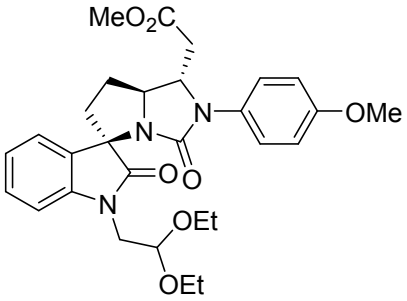
methyl 2-((1'S,3S,7a'S)-2'-(4-bromophenyl)-1-(2,2-diethoxyethyl)-2,3'-dioxo-1',2',3',6',7',7a'-hexahydrospiro[indoline-3,5'-pyrrolo[1,2-c]imidazol]-1'-yl)acetate (4na)

White oil 22 mg. 38% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.33 (m, 2H), 7.31 – 7.19 (m, 1H), 7.12 – 7.02 (m, 4H), 7.02 – 6.93 (m, 1H), 4.77 – 4.68 (m, 1H), 4.68 – 4.59 (m, 1H), 4.24 – 4.15 (m, 1H), 3.98 – 3.88 (m, 1H), 3.82 – 3.68 (m, 6H), 3.59 – 3.47 (m, 2H), 2.99 (dd, *J* = 16.9, 3.3 Hz, 1H), 2.60 (dddd, *J* = 19.6, 16.9, 11.9, 6.7 Hz, 3H), 2.30 – 2.08 (m, 2H), 1.14 (q, *J* = 7.0 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.25, 171.15, 154.94, 142.71, 136.59, 132.13, 129.11, 129.00, 123.50, 123.01, 122.16, 121.87, 117.43, 110.27, 100.55, 66.04, 64.66, 63.95, 63.75, 57.81, 52.18, 44.17, 40.49, 37.81, 32.34, 15.43, 15.39. **HRMS** (ESI) m/z calcd for $C_{28}H_{32}BrN_3O_6Na$ $[M+Na]^+$ = 608.1367, found = 608.1363.



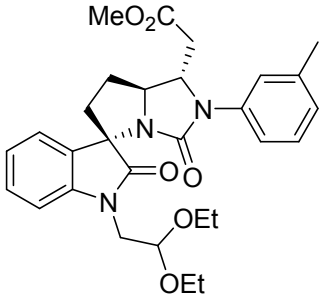
methyl 2-((1'S,3R,7a'S)-1-(2,2-diethoxyethyl)-2'-(4-methoxyphenyl)-2,3'-dioxo-1',2',3',6',7',7a'-hexahydrospiro[indoline-3,5'-pyrrolo[1,2-c]imidazol]-1'-yl)acetate (3oa)

Yellow oil 22 mg. 41% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 (dt, *J* = 7.8, 3.6 Hz, 2H), 7.19 – 7.12 (m, 2H), 7.09 – 7.01 (m, 2H), 6.87 – 6.79 (m, 2H), 4.67 (t, *J* = 5.3 Hz, 1H), 4.63 – 4.52 (m, 1H), 4.11 (dt, *J* = 11.0, 4.0 Hz, 1H), 3.93 (dd, *J* = 14.3, 5.9 Hz, 1H), 3.76 (s, 3H), 3.73 – 3.62 (m, 6H), 3.50 (ddq, *J* = 12.0, 9.3, 7.0 Hz, 2H), 2.91 (dd, *J* = 16.4, 3.6 Hz, 1H), 2.53 (ddd, *J* = 15.3, 13.6, 7.8 Hz, 2H), 2.44 – 2.24 (m, 3H), 1.11 (dt, *J* = 11.0, 7.0 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.07, 171.20, 158.76, 157.33, 143.28, 130.51, 128.93, 125.35, 122.96, 122.77, 114.48, 110.19, 100.85, 66.93, 64.34, 63.53, 63.50, 60.07, 55.58, 51.98, 43.86, 40.69, 38.59, 31.42, 15.41, 15.35. **HRMS** (ESI) m/z calcd for $C_{29}H_{35}N_3O_7Na$ $[M+Na]^+$ = 560.2367, found = 560.2363.



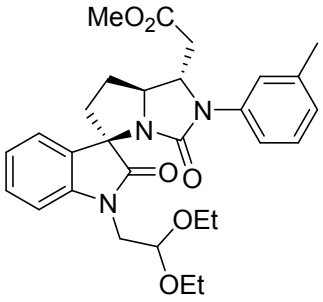
methyl 2-((1'S,3S,7a'S)-1-(2,2-diethoxyethyl)-2'-(4-methoxyphenyl)-2,3'-dioxo-1',2',3',6',7',7a'-hexahydrospiro[indoline-3,5'-pyrrolo[1,2-c]imidazol]-1'-yl)acetate (4oa)

Yellow oil 20 mg. 37% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 – 7.18 (m, 1H), 7.07 (dt, *J* = 16.6, 6.5 Hz, 4H), 6.99 (d, *J* = 7.5 Hz, 1H), 6.86 – 6.79 (m, 2H), 4.71 (q, *J* = 5.7 Hz, 1H), 4.57 (ddd, *J* = 10.1, 6.3, 3.6 Hz, 1H), 4.25 – 4.16 (m, 1H), 3.94 (dd, *J* = 14.2, 5.8 Hz, 1H), 3.83 – 3.70 (m, 6H), 3.69 (s, 3H), 3.58 – 3.44 (m, 2H), 2.92 (dd, *J* = 16.8, 3.6 Hz, 1H), 2.65 – 2.47 (m, 3H), 2.25 – 2.13 (m, 2H), 1.14 (dt, *J* = 8.7, 7.0 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.47, 171.34, 157.13, 155.92, 142.74, 130.32, 129.45, 128.94, 124.75, 122.93, 122.15, 114.54, 100.68, 66.18, 64.65, 63.95, 63.77, 59.15, 55.61, 52.04, 44.24, 40.66, 38.25, 32.26, 15.44, 15.38. **HRMS** (ESI) m/z calcd for $C_{29}H_{35}N_3O_7Na$ $[M+Na]^+$ = 560.2367, found = 560.2370.



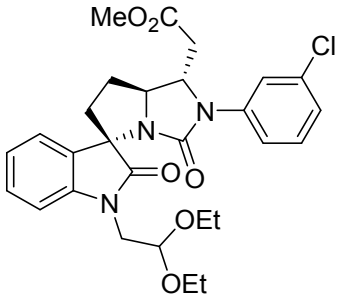
methyl 2-((1'S,3R,7a'S)-1-(2,2-diethoxyethyl)-2,3'-dioxo-2'-(m-tolyl)-1',2',3',6',7',7a'-hexahydrospiro[indoline-3,5'-pyrrolo[1,2-c]imidazol]-1'-yl)acetate (3pa)

Yellow solid 38 mg. 45% yield. **m.p.** = 132-135 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 – 7.21 (m, 2H), 7.18 (t, *J* = 7.8 Hz, 1H), 7.12 (s, 1H), 7.10 – 6.96 (m, 3H), 6.90 (d, *J* = 7.5 Hz, 1H), 4.70 (dt, *J* = 10.7, 4.4 Hz, 2H), 4.10 (dt, *J* = 10.6, 5.3 Hz, 1H), 3.96 (dd, *J* = 14.3, 5.7 Hz, 1H), 3.76 – 3.61 (m, 6H), 3.58 – 3.42 (m, 2H), 3.01 (dd, *J* = 16.6, 3.4 Hz, 1H), 2.54 (dd, *J* = 16.6, 10.6 Hz, 2H), 2.39 (t, *J* = 6.2 Hz, 3H), 2.29 (s, 3H), 1.12 (t, *J* = 7.0 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.88, 171.25, 158.01, 143.25, 138.91, 137.35, 130.43, 128.95, 128.79, 125.60, 123.52, 122.94, 122.76, 119.36, 110.11, 100.68, 100.07, 66.77, 64.30, 63.49, 63.30, 58.72, 51.98, 43.75, 40.57, 38.33, 31.44, 21.52, 15.39, 15.31. **HRMS** (ESI) m/z calcd for $C_{29}H_{35}N_3O_6Na$ $[M+Na]^+$ = 544.2418, found = 544.2420.



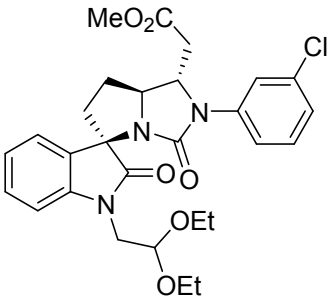
methyl 2-((1'S,3S,7a'S)-1-(2,2-diethoxyethyl)-2,3'-dioxo-2'-(m-tolyl)-1',2',3',6',7',7a'-hexahydrospiro[indoline-3,5'-pyrrolo[1,2-c]imidazol]-1'-yl)acetate (4pa)

Yellow oil 40 mg. 48% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 – 7.14 (m, 2H), 7.13 – 7.07 (m, 1H), 7.06 – 7.02 (m, 2H), 7.00 – 6.92 (m, 2H), 6.88 (d, *J* = 7.5 Hz, 1H), 4.73 (t, *J* = 5.4 Hz, 1H), 4.67 (ddd, *J* = 9.9, 6.1, 3.4 Hz, 1H), 4.25 – 4.16 (m, 1H), 3.97 (dd, *J* = 14.2, 5.7 Hz, 1H), 3.80 – 3.68 (m, 6H), 3.58 – 3.47 (m, 2H), 3.01 (dd, *J* = 16.9, 3.4 Hz, 1H), 2.56 (ddd, *J* = 16.9, 12.5, 8.4 Hz, 3H), 2.27 (s, 3H), 2.25 – 2.13 (m, 2H), 1.14 (td, *J* = 7.0, 1.6 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.41, 171.38, 155.40, 142.62, 139.01, 137.23, 129.28, 128.94, 128.84, 125.56, 123.35, 122.95, 122.15, 119.01, 110.13, 100.52, 66.13, 64.59, 63.93, 63.60, 58.15, 52.04, 44.13, 40.55, 38.02, 32.31, 21.55, 15.40, 15.35. **HRMS** (ESI) m/z calcd for $C_{29}H_{35}N_3O_6Na$ $[M+Na]^+$ = 544.2418, found = 544.2420.



methyl 2-((1'S,3R,7a'S)-2'-(3-chlorophenyl)-1-(2,2-diethoxyethyl)-2,3'-dioxo-1',2',3',6',7',7a'-hexahydrospiro[indoline-3,5'-pyrrolo[1,2-c]imidazol]-1'-yl)acetate (3qa)

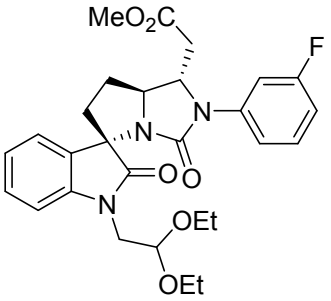
Yellow oil 18 mg. 33% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (t, *J* = 1.9 Hz, 1H), 7.31 – 7.19 (m, 3H), 7.09 (ddd, *J* = 17.1, 8.1, 1.5 Hz, 4H), 4.74 – 4.62 (m, 2H), 4.11 (dt, *J* = 10.5, 5.3 Hz, 1H), 3.93 (dd, *J* = 14.3, 5.8 Hz, 1H), 3.76 – 3.63 (m, 6H), 3.58 – 3.42 (m, 2H), 3.02 (dd, *J* = 16.6, 3.3 Hz, 1H), 2.62 – 2.45 (m, 2H), 2.45 – 2.23 (m, 3H), 1.12 (td, *J* = 7.0, 3.5 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.72, 171.00, 157.57, 143.27, 138.82, 134.78, 130.15, 129.96, 129.13, 124.59, 123.07, 122.79, 122.35, 119.79, 110.28, 100.70, 66.83, 64.34, 63.51, 63.46, 58.29, 52.14, 43.80, 40.50, 38.12, 31.46, 15.41, 15.34. **HRMS** (ESI) m/z calcd for $C_{28}H_{36}ClN_4O_6$ $[M+NH_4]^+$ = 559.2318, found = 559.2315.



methyl 2-((1'S,3S,7a'S)-2'-(3-chlorophenyl)-1-(2,2-diethoxyethyl)-2,3'-dioxo-1',2',3',6',7',7a'-hexahydrospiro[indoline-3,5'-pyrrolo[1,2-c]imidazol]-1'-yl)acetate (4qa)

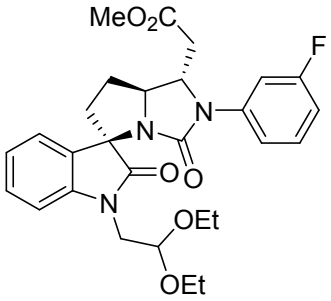
Yellow oil 18 mg. 33% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 – 7.17 (m, 3H), 7.15 – 6.96 (m, 5H), 4.74 (t, *J* = 5.4 Hz, 1H), 4.66 (dd, *J* = 8.5, 4.6 Hz, 1H), 4.21 (dd, *J* = 10.4, 5.4 Hz, 1H), 3.96 (dd, *J* = 14.2, 5.8 Hz, 1H), 3.83 – 3.69 (m, 6H), 3.61

– 3.47 (m, 2H), 3.02 (dd, *J* = 17.0, 3.3 Hz, 1H), 2.68 – 2.50 (m, 3H), 2.29 – 2.11 (m, 2H), 1.14 (tt, *J* = 7.0, 3.5 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.21, 171.13, 154.83, 142.70, 138.74, 134.79, 130.03, 129.15, 128.95, 124.53, 123.02, 122.16, 122.05, 119.76, 110.25, 100.51, 66.01, 64.63, 63.96, 63.71, 57.73, 52.18, 44.15, 40.45, 37.82, 32.37, 15.42, 15.38. **HRMS** (ESI) m/z calcd for $C_{28}H_{36}ClN_4O_6$ $[M+NH_4]^+$ = 559.2318, found = 559.2314.



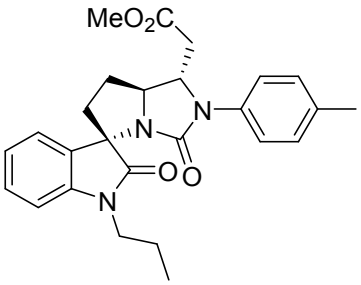
methyl 2-((1'S,3R,7a'S)-1-(2,2-diethoxyethyl)-2'-(3-fluorophenyl)-2,3'-dioxo-1',2',3',6',7',7a'-hexahydrospiro[indoline-3,5'-pyrrolo[1,2-c]imidazol]-1'-yl)acetate (3ra)

Yellow solid 24 mg. 46% yield. **m.p.** = 107-110 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 – 7.19 (m, 3H), 7.15 – 7.04 (m, 3H), 6.99 (dd, *J* = 8.2, 1.4 Hz, 1H), 6.78 (td, *J* = 8.3, 1.9 Hz, 1H), 4.76 – 4.63 (m, 2H), 4.10 (dt, *J* = 10.4, 5.2 Hz, 1H), 3.93 (dd, *J* = 14.3, 5.9 Hz, 1H), 3.77 – 3.65 (m, 6H), 3.59 – 3.44 (m, 2H), 3.05 (dd, *J* = 16.7, 3.2 Hz, 1H), 2.63 – 2.45 (m, 2H), 2.44 – 2.24 (m, 3H), 1.12 (dd, *J* = 13.0, 7.0 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.69, 171.06, 164.34, 161.92, 157.51, 143.24, 139.25, 139.14, 130.16, 130.11, 130.02, 129.12, 123.05, 122.78, 116.77, 111.30, 111.09, 110.28, 109.55, 109.30, 100.72, 66.78, 64.31, 63.53, 63.52, 58.09, 52.14, 43.77, 40.44, 38.07, 31.48, 15.41, 15.33. **HRMS** (ESI) m/z calcd for $C_{28}H_{36}FN_4O_6$ $[M+NH_4]^+$ = 543.2613, found = 543.2609.



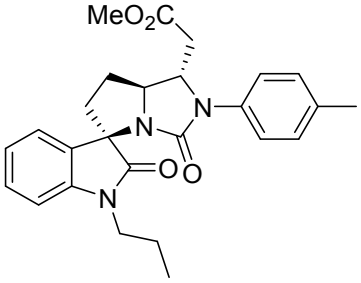
methyl 2-((1'S,3S,7a'S)-1-(2,2-diethoxyethyl)-2'-(3-fluorophenyl)-2,3'-dioxo-1',2',3',6',7',7a'-hexahydrospiro[indoline-3,5'-pyrrolo[1,2-c]imidazol]-1'-yl)acetate (4ra)

Yellow oil 20 mg. 38% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 – 7.19 (m, 2H), 7.04 (dddd, *J* = 27.7, 24.2, 16.0, 8.3 Hz, 5H), 6.75 (tt, *J* = 8.9, 4.5 Hz, 1H), 4.74 (t, *J* = 5.4 Hz, 1H), 4.69 – 4.59 (m, 1H), 4.20 (dt, *J* = 10.6, 5.5 Hz, 1H), 4.01 – 3.89 (m, 1H), 3.84 – 3.67 (m, 6H), 3.59 – 3.46 (m, 2H), 3.05 (dd, *J* = 16.9, 3.1 Hz, 1H), 2.69 – 2.50 (m, 3H), 2.28 – 2.11 (m, 2H), 1.15 (q, *J* = 6.9 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.25, 171.16, 154.84, 142.74, 139.22, 130.19, 130.10, 129.13, 128.99, 123.01, 122.19, 116.80, 111.33, 111.12, 110.25, 109.51, 109.27, 100.55, 77.48, 77.16, 76.84, 66.06, 64.64, 63.95, 63.76, 57.71, 52.15, 44.19, 40.44, 37.84, 32.37, 15.42, 15.38. **HRMS** (ESI) m/z calcd for $C_{28}H_{32}FN_3O_6Na$ $[M+Na]^+$ = 548.2167, found = 548.2161.



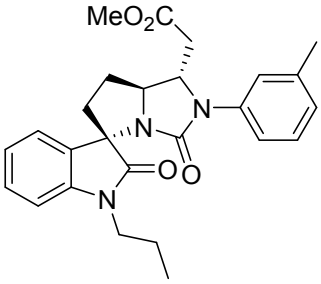
methyl 2-((1'S,3R,7a'S)-2,3'-dioxo-1-propyl-2'-(p-tolyl)-1',2',3',6',7',7a'-hexahydrospiro[indoline-3,5'-pyrrolo[1,2-c]imidazol]-1'-yl)acetate (3sa)

White solid 35 mg. 39% yield. **m.p.** = 161-164 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.22 (m, 2H), 7.17 – 7.03 (m, 5H), 6.82 (d, *J* = 7.8 Hz, 1H), 4.72 – 4.60 (m, 1H), 4.11 (dt, *J* = 10.6, 5.4 Hz, 1H), 3.75 – 3.64 (m, 4H), 3.56 (dt, *J* = 14.0, 7.0 Hz, 1H), 2.97 (dd, *J* = 16.5, 3.4 Hz, 1H), 2.61 – 2.48 (m, 2H), 2.36 (ddd, *J* = 16.4, 11.3, 5.7 Hz, 2H), 2.29 – 2.24 (m, 3H), 1.76 – 1.59 (m, 3H), 0.93 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.60, 171.26, 158.25, 143.14, 134.91, 134.66, 130.90, 129.68, 129.12, 123.14, 123.03, 122.83, 108.80, 66.88, 64.34, 59.23, 51.98, 41.92, 40.65, 38.40, 31.44, 20.98, 20.81, 11.51. **HRMS** (ESI) m/z calcd for $C_{26}H_{30}N_3O_4$ $[M+H]^+$ = 448.2231, found = 448.2233.



methyl 2-((1'S,3S,7a'S)-2,3'-dioxo-1-propyl-2'-(p-tolyl)-1',2',3',6',7',7a'-hexahydrospiro[indoline-3,5'-pyrrolo[1,2-c]imidazol]-1'-yl)acetate (4sa)

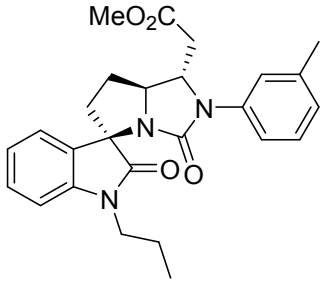
White solid 28 mg. 31% yield. **m.p.** = 133-136 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21 (dd, *J* = 15.2, 7.5 Hz, 1H), 7.11 – 7.01 (m, 5H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 4.66 – 4.55 (m, 1H), 4.18 (dd, *J* = 13.3, 7.4 Hz, 1H), 3.73 – 3.64 (m, 5H), 2.96 (dd, *J* = 16.8, 3.4 Hz, 1H), 2.66 – 2.45 (m, 3H), 2.24 (s, 3H), 2.22 – 2.11 (m, 2H), 1.71 (dt, *J* = 12.7, 7.1 Hz, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.04, 171.39, 155.71, 142.62, 134.84, 134.53, 129.84, 129.70, 129.08, 122.80, 122.56, 122.48, 108.97, 66.32, 64.56, 58.68, 52.03, 42.00, 40.35, 38.12, 32.38, 20.95, 20.76, 11.38. **HRMS** (ESI) m/z calcd for $C_{26}H_{30}N_3O_4$ $[M+H]^+$ = 448.2231, found = 448.2235.



methyl 2-((1'S,3R,7a'S)-2,3'-dioxo-1-propyl-2'-(m-tolyl)-1',2',3',6',7',7a'-hexahydrospiro[indoline-3,5'-pyrrolo[1,2-c]imidazol]-1'-yl)acetate (3ta)

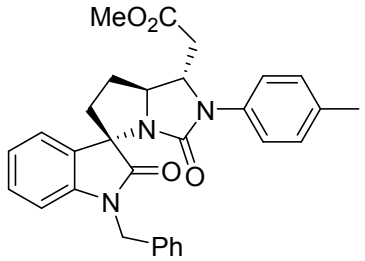
White solid 30 mg. 34% yield. **m.p.** = 101-104 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 – 7.23 (m, 2H), 7.18 (t, *J* = 7.8 Hz, 1H), 7.11 (s, 1H), 7.06 (dd, *J* = 11.0, 4.0 Hz, 1H), 6.99 (d, *J* = 7.9 Hz, 1H), 6.86 (dd, *J* = 27.5, 7.7 Hz, 2H), 4.71 (ddd, *J* = 10.3, 5.5, 3.4 Hz, 1H), 4.10 (dt, *J* = 10.6, 5.4 Hz, 1H), 3.70 (s, 3H), 3.55 (dt, *J* = 13.9, 6.9 Hz, 1H), 3.01 (dd, *J* = 16.6, 3.4 Hz, 1H),

2.62 – 2.49 (m, 2H), 2.44 – 2.30 (m, 3H), 2.28 (s, 3H), 1.76 – 1.64 (m, 3H), 0.93 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.51, 171.26, 157.98, 143.08, 138.92, 137.30, 130.84, 129.12, 128.79, 125.63, 123.62, 123.11, 122.82, 119.42, 108.79, 66.82, 64.31, 58.77, 51.98, 41.88, 40.62, 38.33, 31.42, 21.52, 20.79, 11.48. **HRMS** (ESI) m/z calcd for $C_{26}H_{29}N_3O_4$ $[M+H]^+$ = 448.2231, found = 448.2236. HRMS (ESI) m/z calcd for $C_{26}H_{30}N_3O_4$ $[M+H]^+$ = 448.2231, found = 448.2236.



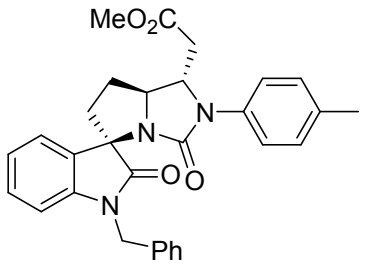
methyl 2-((1'S,3S,7a'S)-2,3'-dioxo-1-propyl-2'-(m-tolyl)-1',2',3',6',7',7a'-hexahydrospiro[indoline-3,5'-pyrrolo[1,2-c]imidazol]-1'-yl)acetate (4ta)

White solid 29 mg. 32% yield. **m.p.** = 128-131 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 (td, *J* = 7.8, 1.0 Hz, 1H), 7.19 – 7.10 (m, 2H), 7.05 (s, 1H), 6.96 (dd, *J* = 14.0, 7.1 Hz, 2H), 6.86 (dd, *J* = 16.4, 7.5 Hz, 2H), 4.71 – 4.62 (m, 1H), 4.20 (dd, *J* = 13.5, 7.5 Hz, 1H), 3.71 (s, 4H), 3.01 (dd, *J* = 16.9, 3.4 Hz, 1H), 2.65 – 2.49 (m, 3H), 2.27 (s, 3H), 2.24 – 2.14 (m, 2H), 1.80 – 1.65 (m, 3H), 0.96 (td, *J* = 7.4, 4.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.01, 171.39, 155.53, 142.51, 139.02, 137.27, 129.74, 129.09, 128.83, 125.57, 123.41, 122.81, 122.43, 119.06, 108.97, 100.07, 66.27, 64.51, 58.40, 52.03, 41.96, 40.33, 38.05, 32.37, 21.55, 20.72, 11.36. **HRMS** (ESI) m/z calcd for $C_{26}H_{30}N_3O_4$ $[M+H]^+$ = 448.2231, found = 448.2235.



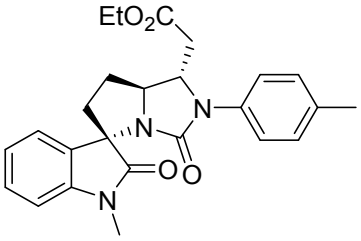
methyl 2-((1'S,3R,7a'S)-1-benzyl-2,3'-dioxo-2'-(p-tolyl)-1',2',3',6',7',7a'-hexahydrospiro[indoline-3,5'-pyrrolo[1,2-c]imidazol]-1'-yl)acetate (3ua)

White solid 23 mg. 23% yield. **m.p.** = 237-240 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.25 (m, 5H), 7.23 (d, *J* = 7.0 Hz, 1H), 7.19 – 7.09 (m, 5H), 7.04 (t, *J* = 7.4 Hz, 1H), 6.63 (d, *J* = 7.8 Hz, 1H), 4.89 (dd, *J* = 90.4, 15.9 Hz, 2H), 4.73 – 4.63 (m, 1H), 4.14 (dt, *J* = 10.8, 5.4 Hz, 1H), 3.70 (s, 3H), 3.00 (dd, *J* = 16.5, 3.4 Hz, 1H), 2.66 – 2.51 (m, 2H), 2.50 – 2.31 (m, 3H), 2.29 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.73, 171.27, 158.31, 142.71, 135.96, 134.93, 134.71, 130.78, 129.72, 129.12, 128.88, 127.53, 127.38, 123.14, 123.07, 123.00, 109.68, 67.02, 64.42, 59.18, 52.01, 44.18, 40.83, 38.43, 31.51, 21.01. **HRMS** (ESI) m/z calcd for $C_{30}H_{30}N_3O_4$ $[M+H]^+$ = 496.2231, found = 496.2232.



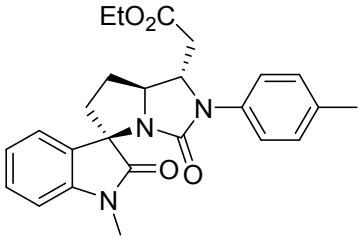
methyl 2-((1'S,3S,7a'S)-1-benzyl-2,3'-dioxo-2'-(p-tolyl)-1',2',3',6',7',7a'-hexahydrospiro[indoline-3,5'-pyrrolo[1,2-c]imidazol]-1'-yl)acetate (4ua)

White solid 41 mg. 41% yield. **m.p.** = 235-238 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 4.4 Hz, 4H), 7.25 – 7.19 (m, 1H), 7.15 – 7.06 (m, 6H), 6.94 (dd, *J* = 11.0, 4.1 Hz, 1H), 6.64 (d, *J* = 7.7 Hz, 1H), 5.05 – 4.89 (m, 2H), 4.65 (ddd, *J* = 10.1, 6.3, 3.4 Hz, 1H), 4.24 (dt, *J* = 10.2, 5.8 Hz, 1H), 3.70 (s, 3H), 3.00 (dd, *J* = 16.8, 3.4 Hz, 1H), 2.77 – 2.48 (m, 3H), 2.32 – 2.17 (m, 5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.23, 171.37, 155.79, 142.19, 135.45, 134.76, 134.64, 129.74, 129.68, 129.09, 128.93, 127.52, 126.97, 123.10, 122.62, 122.35, 109.81, 66.42, 64.59, 58.76, 52.05, 44.07, 40.50, 38.12, 32.39, 20.96. **HRMS** (ESI) m/z calcd for $C_{30}H_{30}N_3O_4$ $[M+H]^+$ = 496.2231, found = 496.2238.



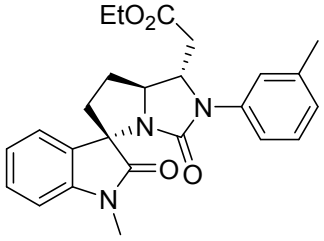
ethyl 2-((1'S,3R,7a'S)-1-methyl-2,3'-dioxo-2'-(p-tolyl)-1',2',3',6',7',7a'-hexahydrospiro[indoline-3,5'-pyrrolo[1,2-c]imidazol]-1'-yl)acetate (3ab)

White solid 40 mg. 46% yield. **m.p.** = 162-165 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 12.7, 5.0 Hz, 2H), 7.16 – 7.03 (m, 5H), 6.81 (d, *J* = 7.6 Hz, 1H), 4.74 – 4.62 (m, 1H), 4.20 – 4.07 (m, 3H), 3.17 (s, 3H), 2.96 (dd, *J* = 16.5, 3.4 Hz, 1H), 2.63 – 2.47 (m, 2H), 2.45 – 2.29 (m, 3H), 2.27 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.50, 170.74, 158.29, 143.66, 134.74, 134.57, 130.65, 129.62, 129.23, 123.04, 122.95, 122.77, 108.49, 66.85, 64.22, 60.99, 59.03, 40.22, 38.55, 31.47, 26.46, 20.93, 14.25. **HRMS** (ESI) m/z calcd for $C_{25}H_{28}N_3O_4$ $[M+H]^+$ = 434.2074, found = 434.2076.



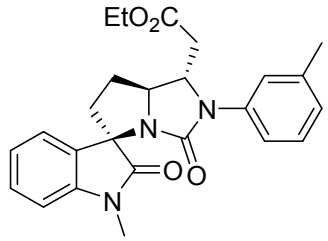
ethyl 2-((1'S,3S,7a'S)-1-methyl-2,3'-dioxo-2'-(p-tolyl)-1',2',3',6',7',7a'-hexahydrospiro[indoline-3,5'-pyrrolo[1,2-c]imidazol]-1'-yl)acetate (4ab)

White solid 40 mg. 46% yield. **m.p.** = 75-78 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.19 (m, 1H), 7.13 – 7.04 (m, 5H), 7.03 – 6.92 (m, 1H), 6.87 – 6.79 (m, 1H), 4.75 – 4.54 (m, 1H), 4.25 – 4.11 (m, 3H), 3.23 (s, 3H), 2.96 (dd, *J* = 16.9, 3.4 Hz, 1H), 2.69 – 2.47 (m, 3H), 2.26 (s, 3H), 2.24 – 2.14 (m, 2H), 1.31 – 1.22 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.99, 170.89, 155.75, 143.07, 134.52, 129.66, 129.50, 129.22, 123.09, 122.46, 122.31, 108.66, 66.31, 64.54, 61.07, 58.38, 40.21, 38.25, 32.45, 26.76, 20.91, 14.25. **HRMS** (ESI) m/z calcd for $C_{25}H_{28}N_3O_4$ $[M+H]^+$ = 434.2074, found = 434.2082.



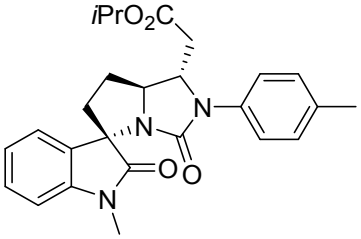
ethyl 2-((1'S,3R,7a'S)-1-methyl-2,3'-dioxo-2'-(m-tolyl)-1',2',3',6',7',7a'-hexahydrospiro[indoline-3,5'-pyrrolo[1,2-c]imidazol]-1'-yl)acetate (3hb)

White solid 41 mg. 47% yield. **m.p.** = 75-78 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 2H), 7.24 – 7.07 (m, 3H), 7.02 (d, *J* = 8.0 Hz, 1H), 6.92 (d, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 7.7 Hz, 1H), 4.76 (ddd, *J* = 10.2, 5.4, 3.4 Hz, 1H), 4.25 – 4.10 (m, 3H), 3.21 (s, 3H), 3.02 (dd, *J* = 16.5, 3.4 Hz, 1H), 2.67 – 2.51 (m, 2H), 2.48 – 2.26 (m, 6H), 1.29 (dd, *J* = 9.8, 4.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.43, 170.76, 158.07, 143.63, 138.91, 137.18, 130.61, 129.24, 128.77, 125.58, 123.51, 123.05, 122.95, 119.18, 108.50, 66.82, 64.21, 61.00, 58.66, 40.21, 38.51, 31.48, 26.47, 21.49, 14.25. **HRMS** (ESI) m/z calcd for $C_{25}H_{28}N_3O_4$ $[M+H]^+$ = 434.2074, found = 434.2080.



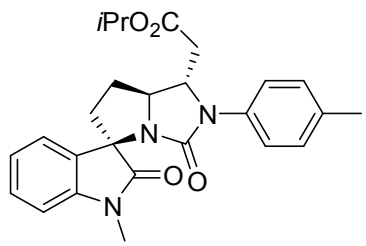
ethyl 2-((1'S,3S,7a'S)-1-methyl-2,3'-dioxo-2'-(m-tolyl)-1',2',3',6',7',7a'-hexahydrospiro[indoline-3,5'-pyrrolo[1,2-c]imidazol]-1'-yl)acetate (4hb)

White solid 42 mg. 48% yield. **m.p.** = 71-74 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 (dd, *J* = 7.8, 0.8 Hz, 1H), 7.20 – 7.10 (m, 2H), 7.06 (s, 1H), 7.02 – 6.91 (m, 2H), 6.85 (dd, *J* = 20.7, 7.6 Hz, 2H), 4.75 – 4.59 (m, 1H), 4.26 – 4.07 (m, 3H), 3.24 (s, 3H), 2.98 (dd, *J* = 16.9, 3.4 Hz, 1H), 2.69 – 2.47 (m, 3H), 2.29 – 2.15 (m, 5H), 1.31 – 1.20 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.95, 170.89, 155.56, 143.05, 139.00, 137.20, 129.45, 129.23, 128.80, 125.55, 123.40, 123.09, 122.30, 122.01, 118.92, 108.65, 66.26, 64.51, 61.07, 58.16, 40.18, 38.24, 32.46, 26.75, 21.51, 14.25. **HRMS** (ESI) m/z calcd for $C_{25}H_{28}N_3O_4$ $[M+H]^+$ = 434.2074, found = 434.2077.



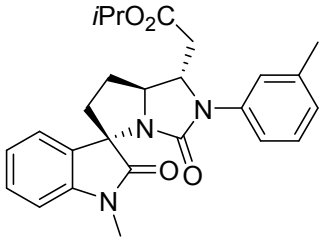
isopropyl 2-((1'S,3R,7a'S)-1-methyl-2,3'-dioxo-2'-(p-tolyl)-1',2',3',6',7',7a'-hexahydrospiro[indoline-3,5'-pyrrolo[1,2-c]imidazol]-1'-yl)acetate (3ac)

White solid 33 mg. 37% yield. **m.p.** = 108-111 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 13.2, 5.3 Hz, 2H), 7.16 – 7.04 (m, 5H), 6.81 (d, *J* = 7.7 Hz, 1H), 5.03 (dt, *J* = 12.5, 6.3 Hz, 1H), 4.73 – 4.62 (m, 1H), 4.18 – 4.07 (m, 1H), 3.18 (s, 3H), 2.93 (dd, *J* = 16.3, 3.4 Hz, 1H), 2.54 (ddd, *J* = 26.7, 14.5, 8.5 Hz, 2H), 2.45 – 2.29 (m, 3H), 2.28 (s, 3H), 1.24 (dd, *J* = 9.0, 6.3 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.54, 170.27, 158.35, 143.71, 134.79, 134.61, 130.71, 129.65, 129.25, 123.06, 123.00, 122.89, 108.51, 68.65, 66.90, 64.19, 59.15, 40.26, 38.89, 31.54, 26.49, 21.97, 21.92, 20.96. **HRMS** (ESI) m/z calcd for $C_{26}H_{30}N_3O_4$ $[M+H]^+$ = 448.2231, found = 448.2234.



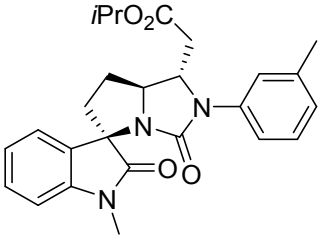
isopropyl 2-((1'S,3S,7a'S)-1-methyl-2,3'-dioxo-2'-(p-tolyl)-1',2',3',6',7',7a'-hexahydrospiro[indoline-3,5'-pyrrolo[1,2-c]imidazol]-1'-yl)acetate (4ac)

White solid 46 mg. 51% yield. **m.p.** = 78-81 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 (dd, *J* = 11.6, 8.2 Hz, 1H), 7.14 – 6.93 (m, 6H), 6.85 (dd, *J* = 21.1, 7.8 Hz, 1H), 5.09 – 4.97 (m, 1H), 4.70 – 4.58 (m, 1H), 4.28 – 4.10 (m, 1H), 3.24 (s, 3H), 2.90 (td, *J* = 16.8, 3.5 Hz, 1H), 2.69 – 2.44 (m, 3H), 2.26 (s, 3H), 2.19 (dt, *J* = 14.3, 7.1 Hz, 2H), 1.33 – 1.18 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.01, 170.43, 155.75, 143.08, 134.72, 134.50, 129.67, 129.55, 129.20, 123.08, 122.51, 122.33, 108.64, 68.73, 66.32, 64.50, 58.39, 40.21, 38.57, 32.50, 26.77, 21.97, 21.87, 20.92. **HRMS** (ESI) m/z calcd for $C_{26}H_{30}N_3O_4$ $[M+H]^+$ = 448.2231, found = 448.2235.



isopropyl 2-((1'S,3R,7a'S)-1-methyl-2,3'-dioxo-2'-(m-tolyl)-1',2',3',6',7',7a'-hexahydrospiro[indoline-3,5'-pyrrolo[1,2-c]imidazol]-1'-yl)acetate (3hc)

White solid 37 mg. 41% yield. **m.p.** = 141-144 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 14.0, 5.9 Hz, 2H), 7.18 (t, *J* = 7.8 Hz, 1H), 7.09 (dd, *J* = 15.4, 7.8 Hz, 2H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.90 (d, *J* = 7.5 Hz, 1H), 6.82 (d, *J* = 7.7 Hz, 1H), 5.04 (dt, *J* = 12.5, 6.3 Hz, 1H), 4.77 – 4.66 (m, 1H), 4.18 – 4.07 (m, 1H), 3.18 (s, 3H), 2.95 (dd, *J* = 16.4, 3.3 Hz, 1H), 2.63 – 2.46 (m, 2H), 2.46 – 2.30 (m, 3H), 2.28 (s, 3H), 1.25 (dd, *J* = 8.4, 6.3 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.49, 170.29, 158.12, 143.68, 138.93, 137.23, 130.67, 129.27, 128.80, 125.63, 123.67, 123.08, 123.00, 119.29, 108.52, 68.67, 66.87, 64.18, 58.81, 40.26, 38.85, 31.54, 26.50, 21.97, 21.92, 21.52. **HRMS** (ESI) m/z calcd for $C_{26}H_{30}N_3O_4$ $[M+H]^+$ = 448.2231, found = 448.2237.

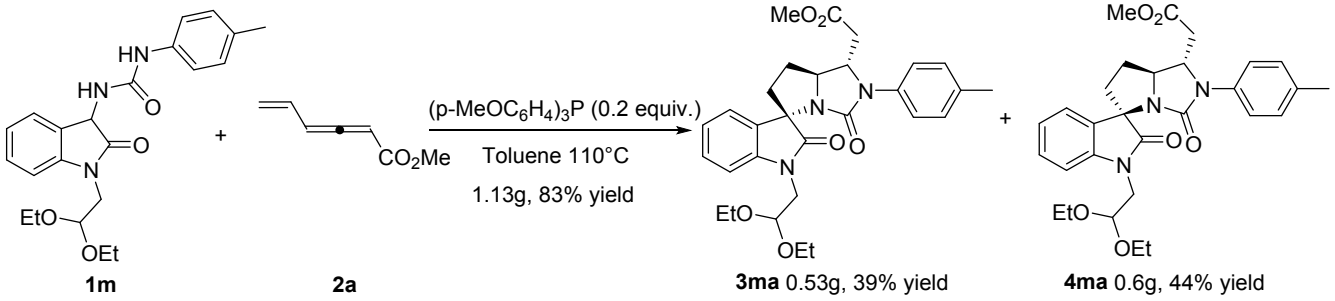


isopropyl 2-((1'S,3S,7a'S)-1-methyl-2,3'-dioxo-2'-(m-tolyl)-1',2',3',6',7',7a'-hexahydrospiro[indoline-3,5'-pyrrolo[1,2-c]imidazol]-1'-yl)acetate (4hc)

White solid 33 mg. 37% yield. **m.p.** = 72-75 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 – 7.22 (m, 1H), 7.20 – 7.05 (m, 3H), 7.02 – 6.92 (m, 2H), 6.85 (dd, *J* = 19.9, 7.6 Hz, 2H), 5.03 (dt, *J* = 12.5, 6.3 Hz, 1H), 4.74 – 4.58 (m, 1H), 4.33 – 4.12 (m, 1H), 3.24 (s, 3H), 2.95 (dd, *J* = 16.8, 3.4 Hz, 1H), 2.74 – 2.41 (m, 3H), 2.30 – 2.14 (m, 5H), 1.25 (dd, *J* = 12.6, 6.2 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.99, 170.47, 155.58, 143.09, 139.03, 137.25, 129.52, 129.24, 128.82, 125.56, 123.51, 123.12, 122.34, 118.97, 108.65, 68.77, 66.29, 64.49, 58.20, 40.21, 38.58, 32.54, 26.78, 21.99, 21.89, 21.54. **HRMS** (ESI) m/z calcd for $C_{26}H_{30}N_3O_4$ $[M+H]^+$ = 448.2231, found = 448.2231.

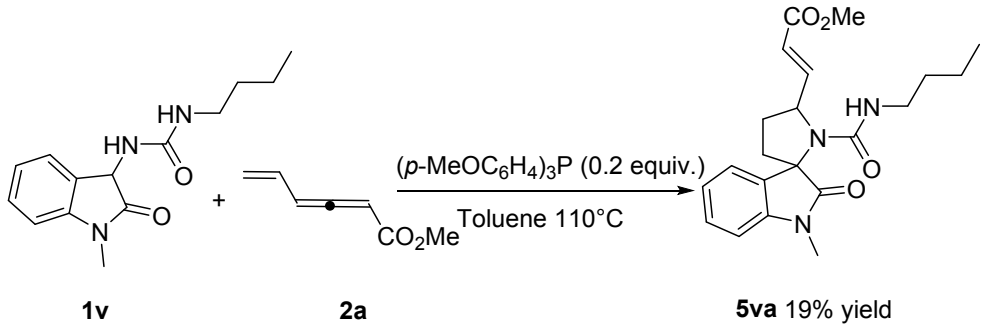
Gram-scale experiments and mechanistic investigations

1, Gram-scale experiment



A round bottom flask equipped with a magnetic stirrer bar was charged with the corresponding substituted urea **1m** (2.6 mmol) in toluene (26 mL). (p-MeOPh)$_3$P (0.52 mmol) and allenoates **2a** (7.8 mmol) was added and then the reaction was stirred at 110℃ for 10 min. The mixture concentrated *in vacuo* and the crude was purified by column chromatography (ethyl aceate : hexane = 2:1) to give the product **3ma** and **4ma** specifically.

2, The reaction intermediate trapping of mechanistic investigations

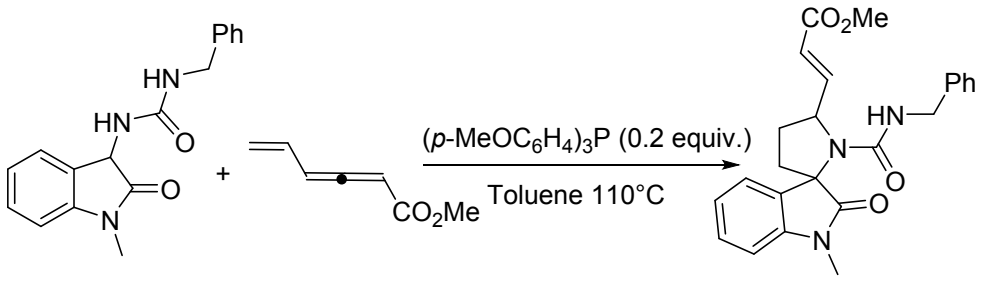


A round bottom flask equipped with a magnetic stirrer bar was charged with the corresponding substituted urea **1v** (0.2 mmol) in toluene (2 mL). (*p*-MeOC$_6$H$_4$)$_3$P (0.04 mmol) and allenoates **2a** (0.6 mmol) was added and then the reaction was stirred at 110℃ for 10 min. The mixture concentrated *in vacuo* and the crude was purified by column chromatography (ethyl aceate : hexane = 2:1) to give the reaction intermediate **5va**.

methyl (E)-3-(1'-(butylcarbamoyl)-1-methyl-2-oxospiro[indoline-3,2'-pyrrolidin]-5'-yl)acrylate (5va)

White solid. 19% yield. **m.p.** = 147-150 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 6.5 Hz, 1H), 7.19 (d, *J* = 7.1 Hz, 1H), 7.10 – 6.98 (m, 2H), 6.85 (d, *J* = 7.8 Hz, 1H), 6.77 (s, 1H), 4.72 – 4.59 (m, 1H), 4.06 (s, 1H), 3.78 (s, 3H), 3.28 (s, 3H), 3.03 (dtd, *J* = 18.9, 13.1, 6.0 Hz, 2H), 2.77 – 2.59 (m, 1H), 2.39 (td, *J* = 12.8, 6.5 Hz, 1H), 2.17 – 2.02 (m, 1H), 1.88 (dd, *J* = 12.4,

6.1 Hz, 1H), 1.30 (d, J = 7.2 Hz, 2H), 1.17 (d, J = 7.6 Hz, 2H), 0.82 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.96, 166.82, 154.25, 146.36, 142.84, 139.10, 128.80, 123.26, 122.52, 121.22, 108.40, 68.40, 58.36, 51.81, 40.36, 35.38, 32.04, 30.61, 26.62, 19.96, 13.72. **HRMS** (ESI) m/z calcd for $C_{21}H_{28}N_3O_4$ $[M+H]^+$ = 386.2074, found = 386.2079.



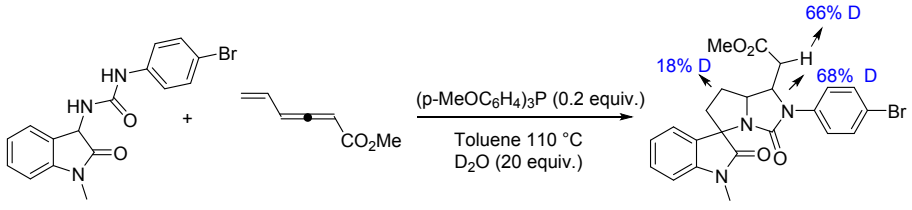
1w **2a** **5wa** 20% yield

A round bottom flask equipped with a magnetic stirrer bar was charged with the corresponding substituted urea **1w** (0.2 mmol) in toluene (2 mL). (p-$MeOC_6H_4)_3P$ (0.04 mmol) and allenoates **2a** (0.6 mmol) was added and then the reaction was stirred at 110℃ for 10 min. The mixture concentrated *in vacuo* and the crude was purified by column chromatography (ethyl aceate : hexane = 2:1) to give the reaction intermediate **5wa** .

methyl (E)-3-(1'-(benzylcarbamoyl)-1-methyl-2-oxospiro[indoline-3,2'-pyrrolidin]-5'-yl)acrylate (5wa)

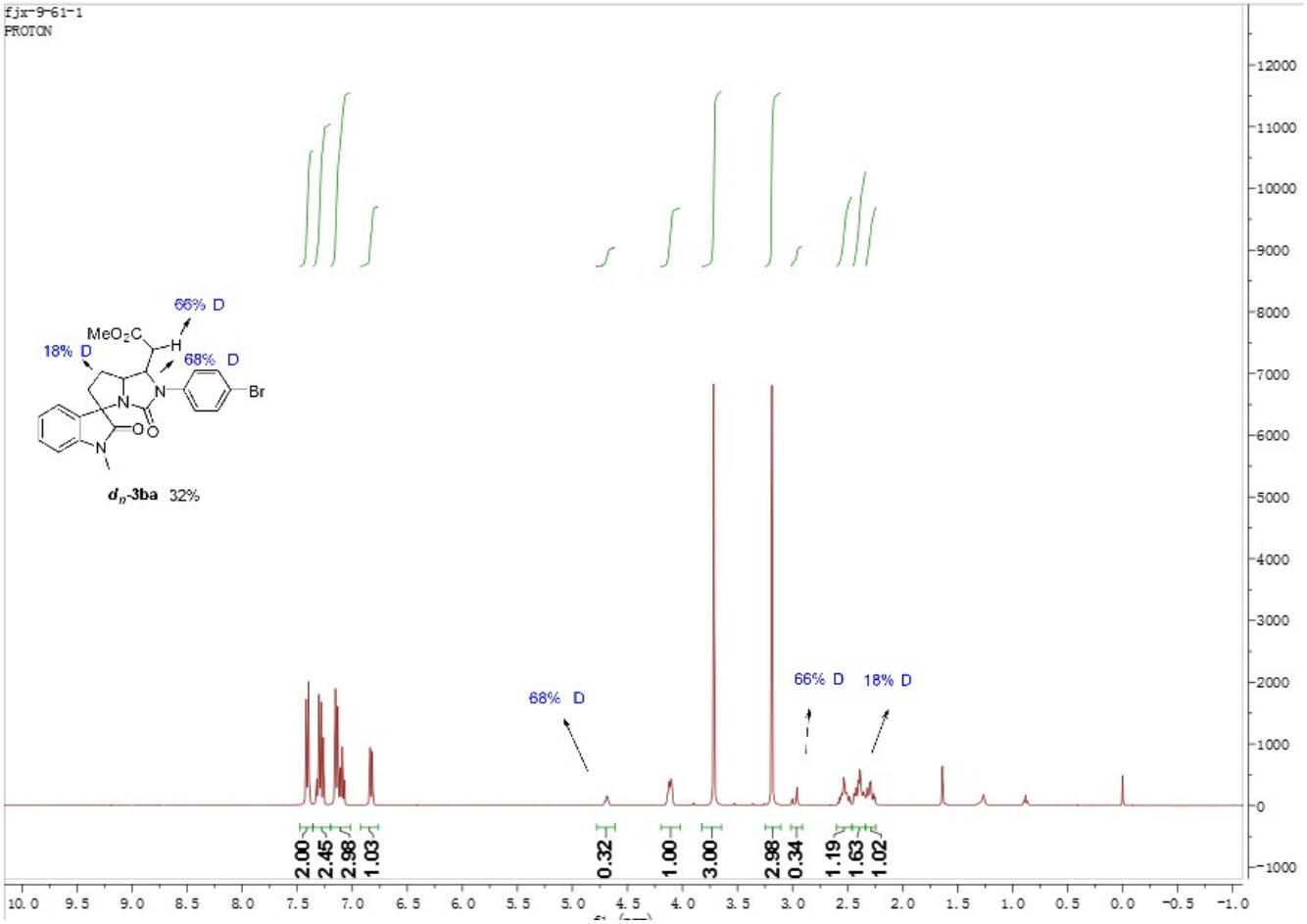
White solid 17 mg. 20% yield. **m.p.** = 186-189 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.19 (m, 5H), 7.04 (ddd, J = 15.6, 14.2, 6.0 Hz, 4H), 6.86 (d, J = 7.8 Hz, 1H), 6.75 (d, J = 15.6 Hz, 1H), 4.73 – 4.65 (m, 1H), 4.40 (s, 1H), 4.33 – 4.15 (m, 2H), 3.76 (s, 3H), 3.27 (s, 3H), 2.77 – 2.60 (m, 1H), 2.42 (td, J = 12.8, 6.4 Hz, 1H), 2.16 – 2.02 (m, 1H), 1.90 (dd, J = 12.5, 5.2 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.01, 166.79, 154.27, 146.32, 142.98, 138.85, 131.99, 129.03, 128.64, 127.53, 127.33, 123.44, 122.70, 121.40, 108.58, 68.59, 58.50, 51.85, 44.69, 35.53, 30.67, 26.72. **HRMS** (ESI) m/z calcd for $C_{21}H_{28}N_3O_4$ $[M+H]^+$ = 420.1918, found = 420.1920.

3, The Deuterium-labeling reaction

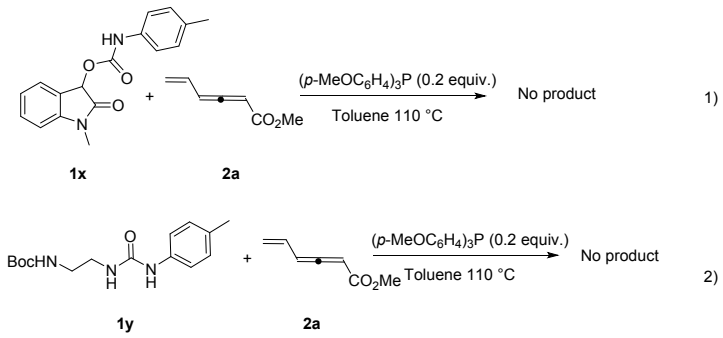


1b **2a** ***d_n*-3ba** 32%

A mixture of compound **1b** (0.2 mmol), allenoates **2a** (0.6 mmol), D_2O (20 equiv) and (p-$MeOC_6H_4)_3P$ (0.04 mmol) in Toluene (2 mL) was heated at 110℃ for 10 min. The mixture concentrated *in vacuo* and the crude was purified by column chromatography (ethyl aceate : hexane = 2:1) to give the reaction intermediate ***d_n*-3ba**. The result showed that α and β positions can be deuterated in almost 66% ratio, whereas the ratios at δ position were less than 20%, which suggests that α and β positions in the intermediate may displayed stronger nucleophilicity. Deuterium incorporation at the other position is still unclear.

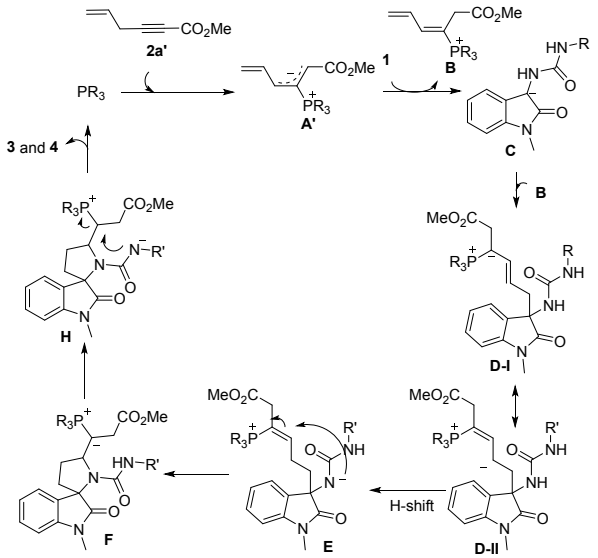


Further Mechanistic studies



Scheme S1 Further mechanistic studies

Proposed reaction mechanism of 2a’



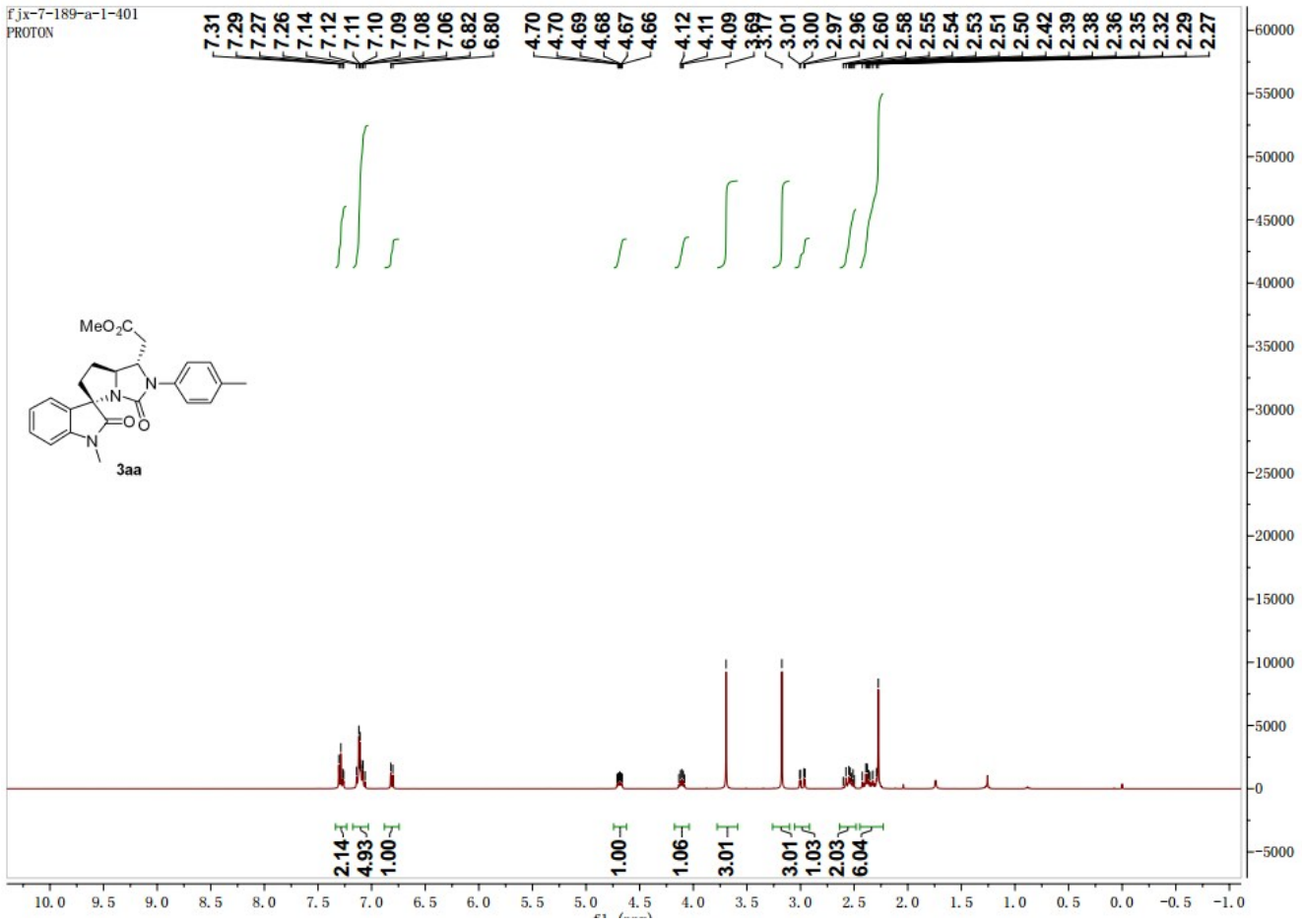
Scheme S2 Proposed reaction mechanism of 2a’

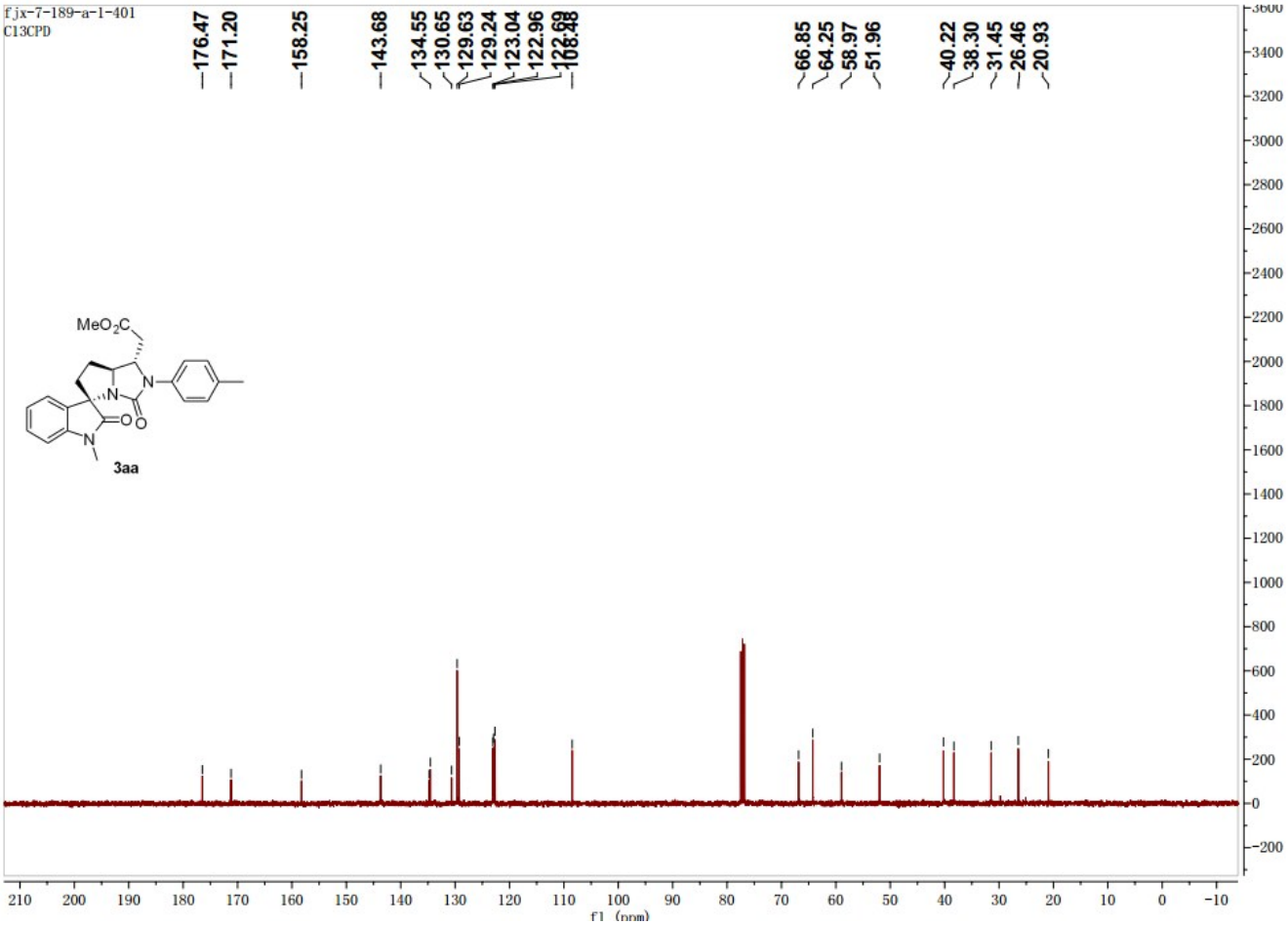
References

[1] Emura, T.; Esaki, T.; Tachibana, K.; Shimizu, M. *J. Org. Chem.* **2006**, *71*, 8559.

[2] (a) X.-F. Wei, T. Wakaki, T. Itoh, H.-L. Li, T. Yoshimura, A. Miyazaki, K. Oisaki, M. Hatanaka, Y. Shimizu and M. Kanai, *Chem*, 2019, **5**, 585-599. (b) L. W. Bieber and M. F. da Silva, *Tetrahedron Lett.*, 2007, **48**, 7088-7090.

NMR spectra of products

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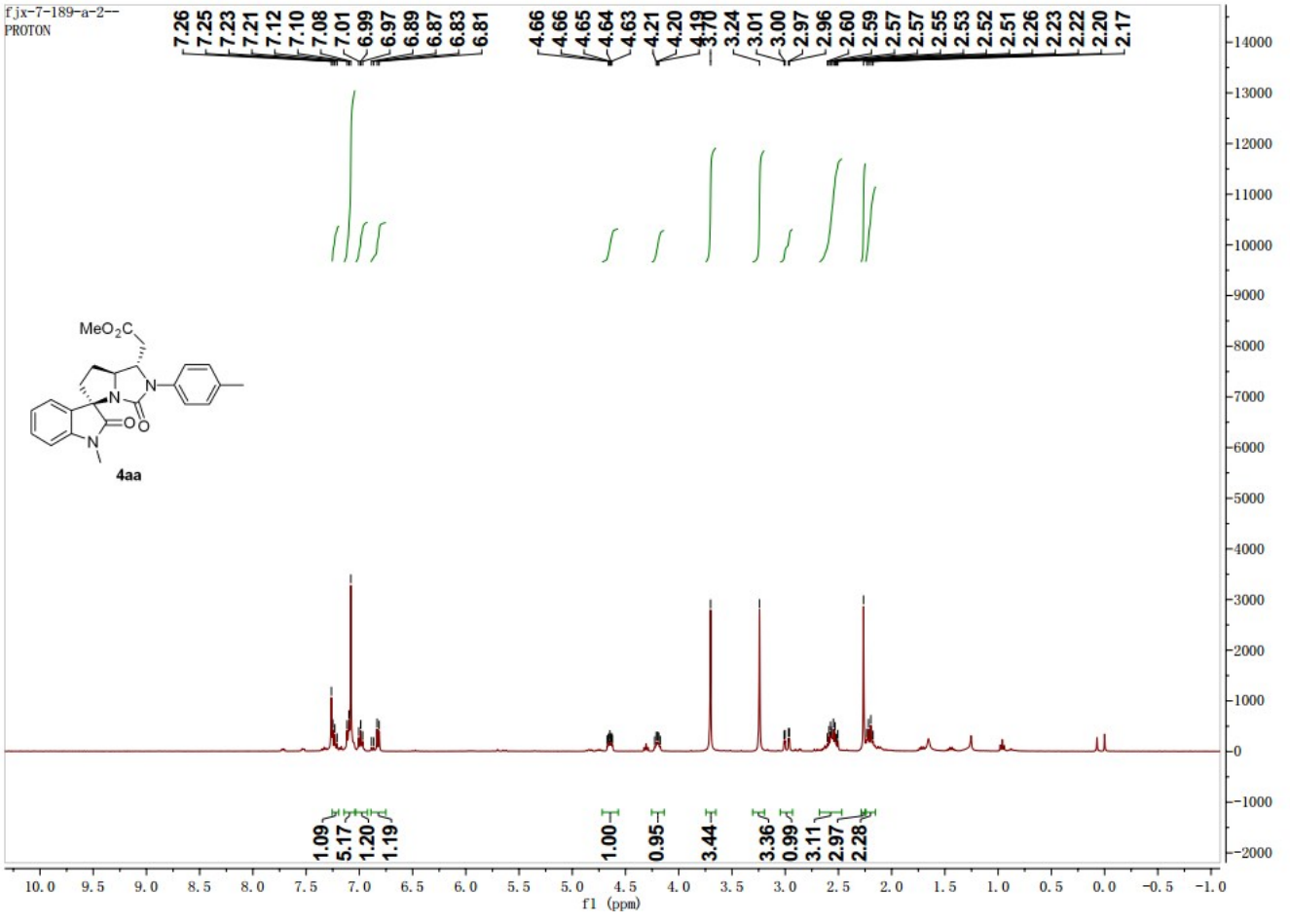
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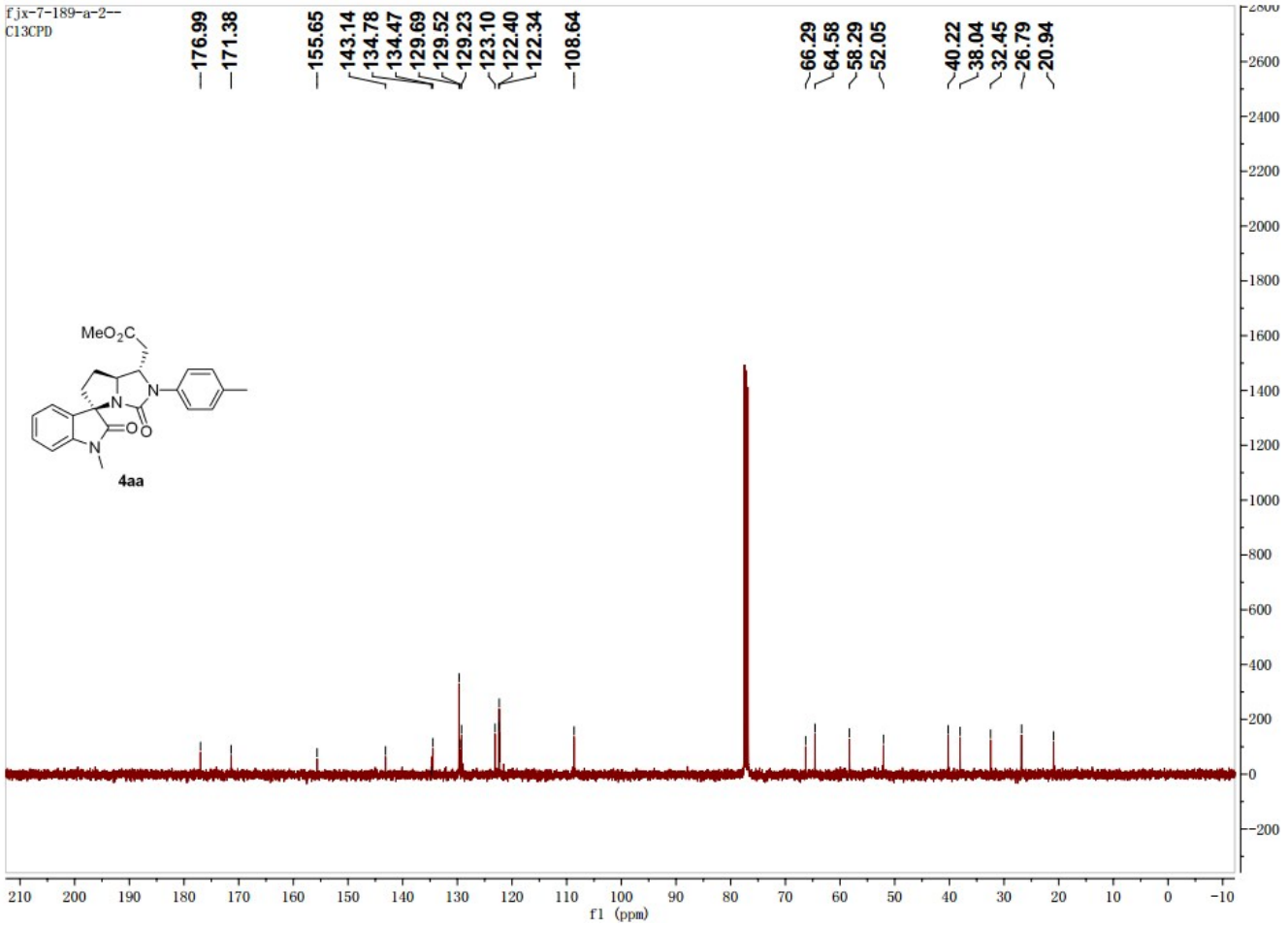
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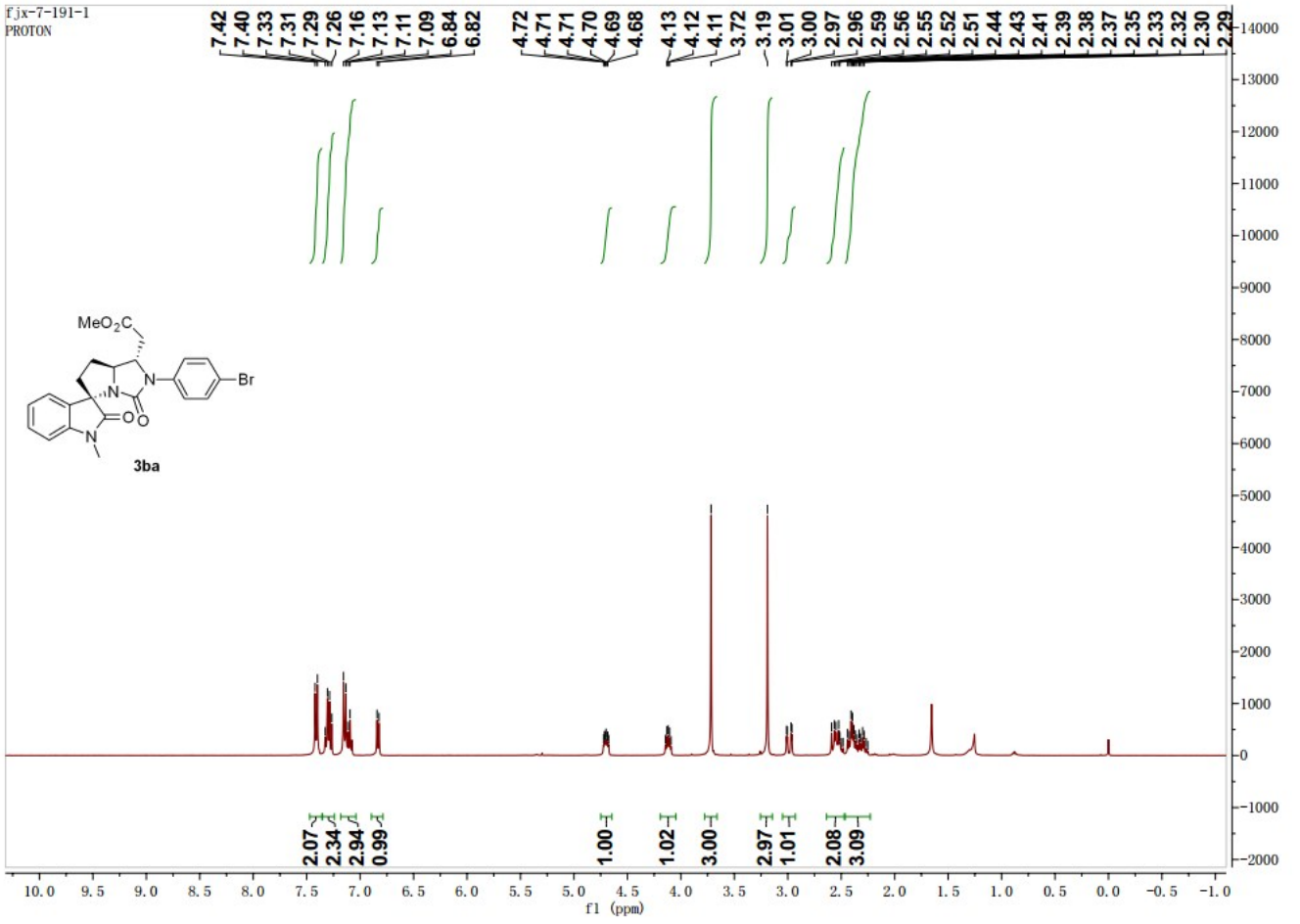
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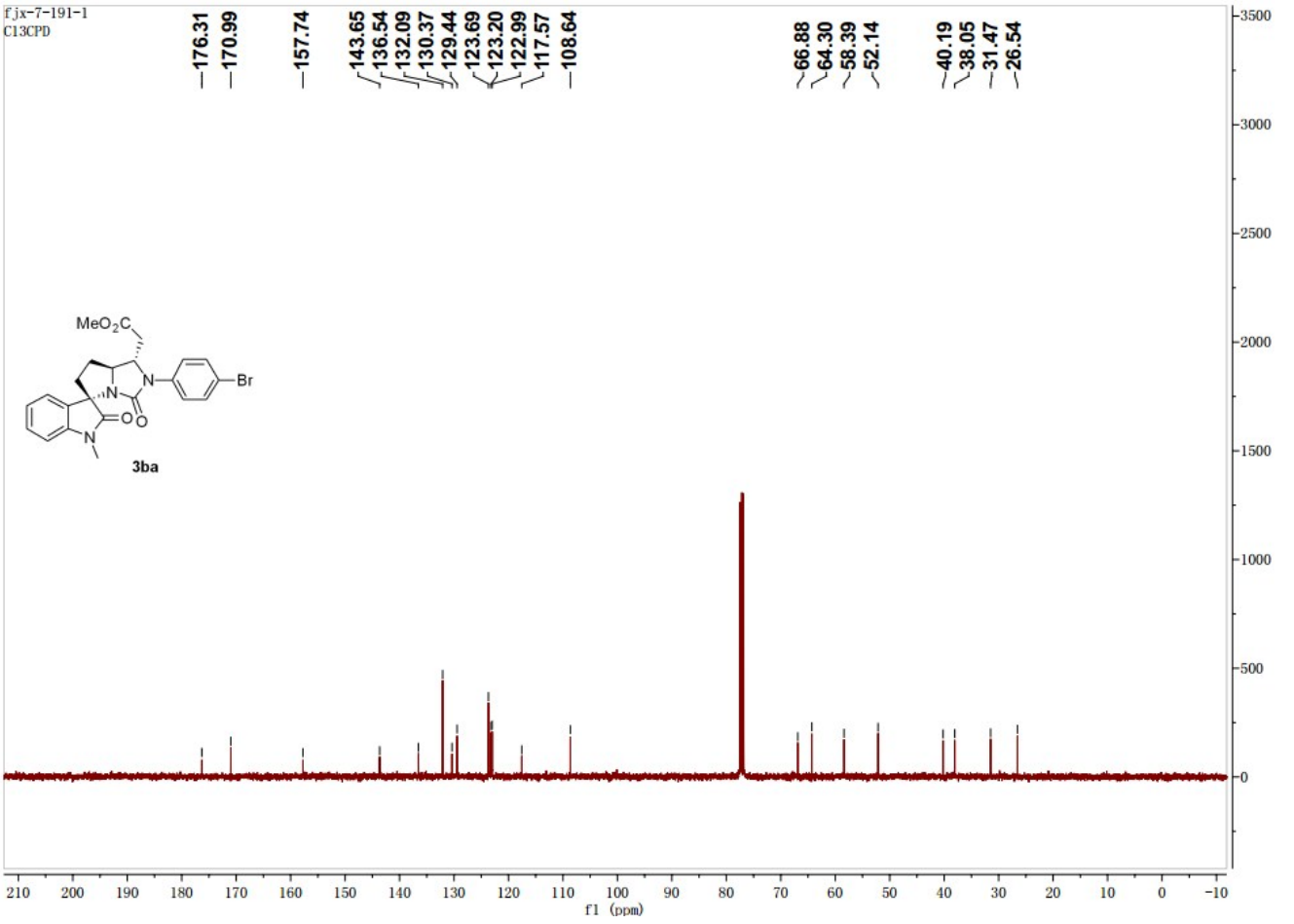
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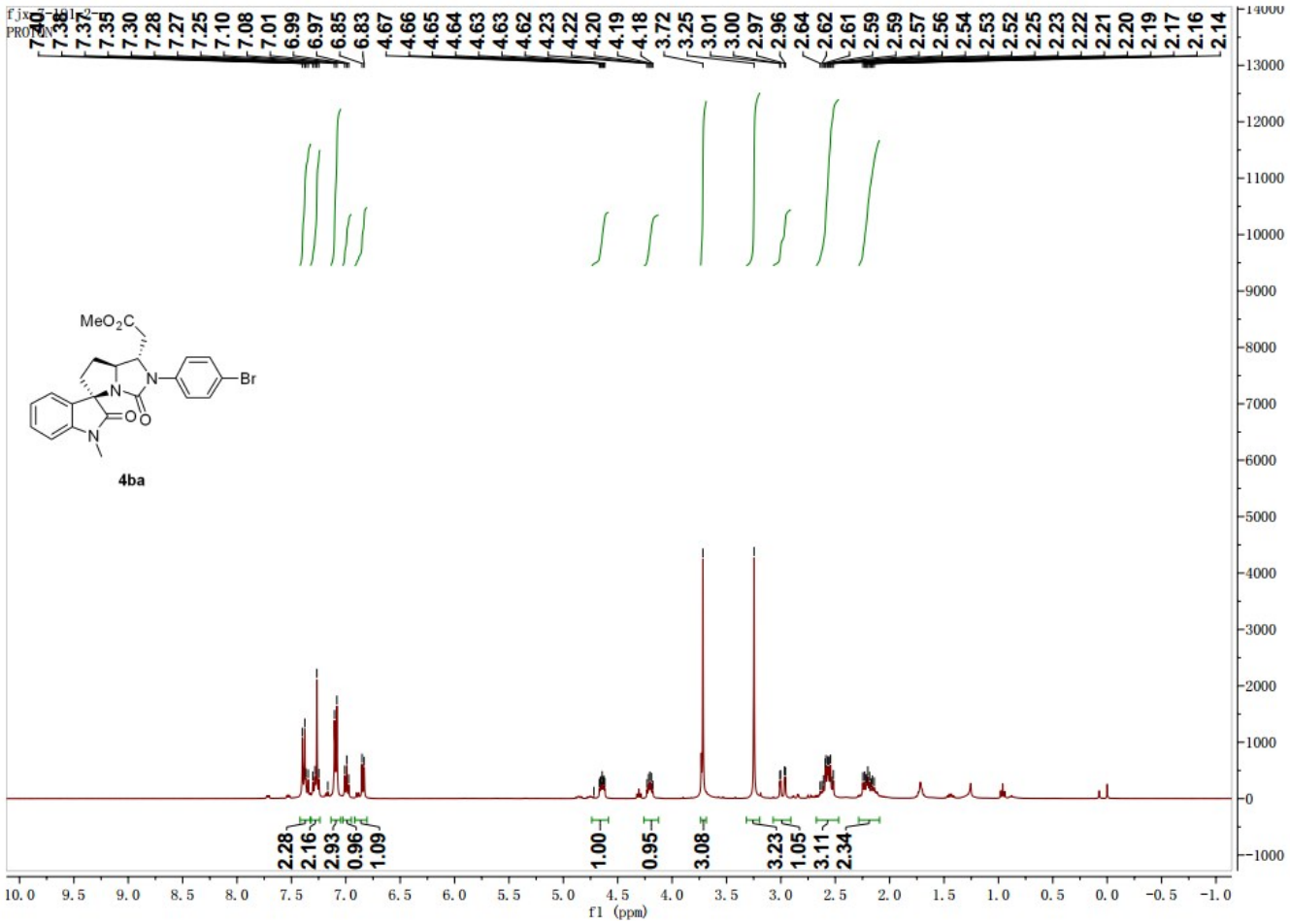
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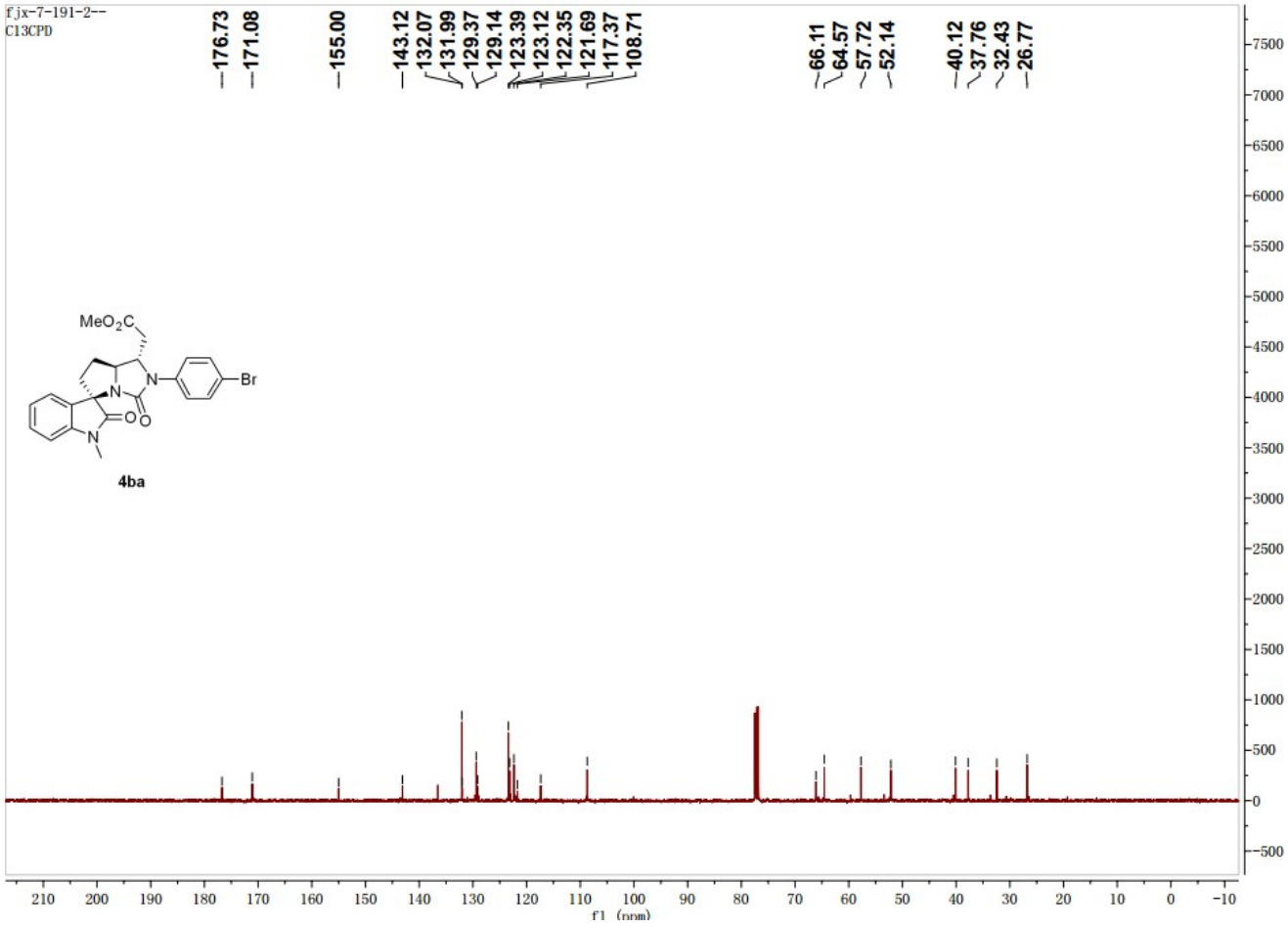
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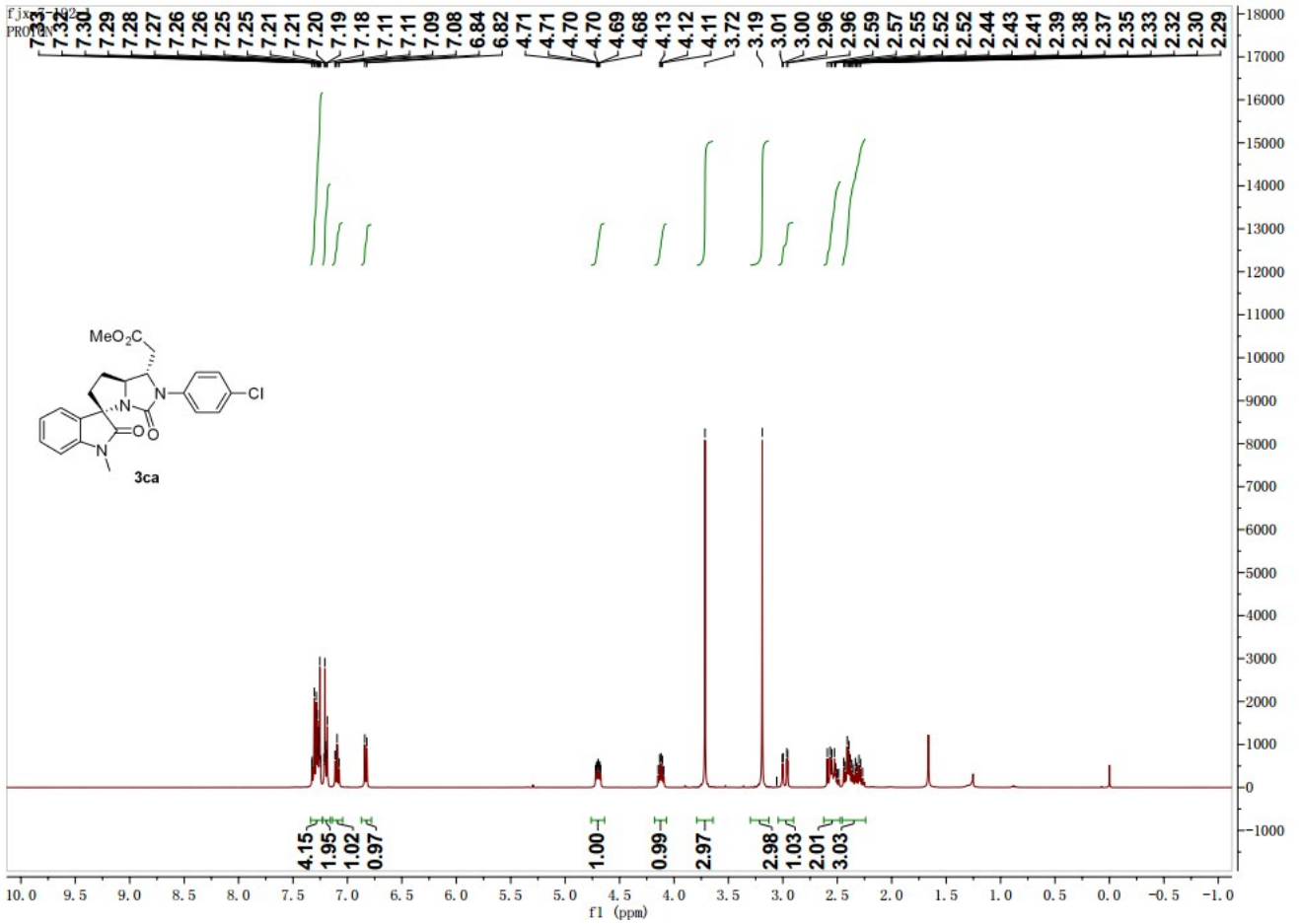
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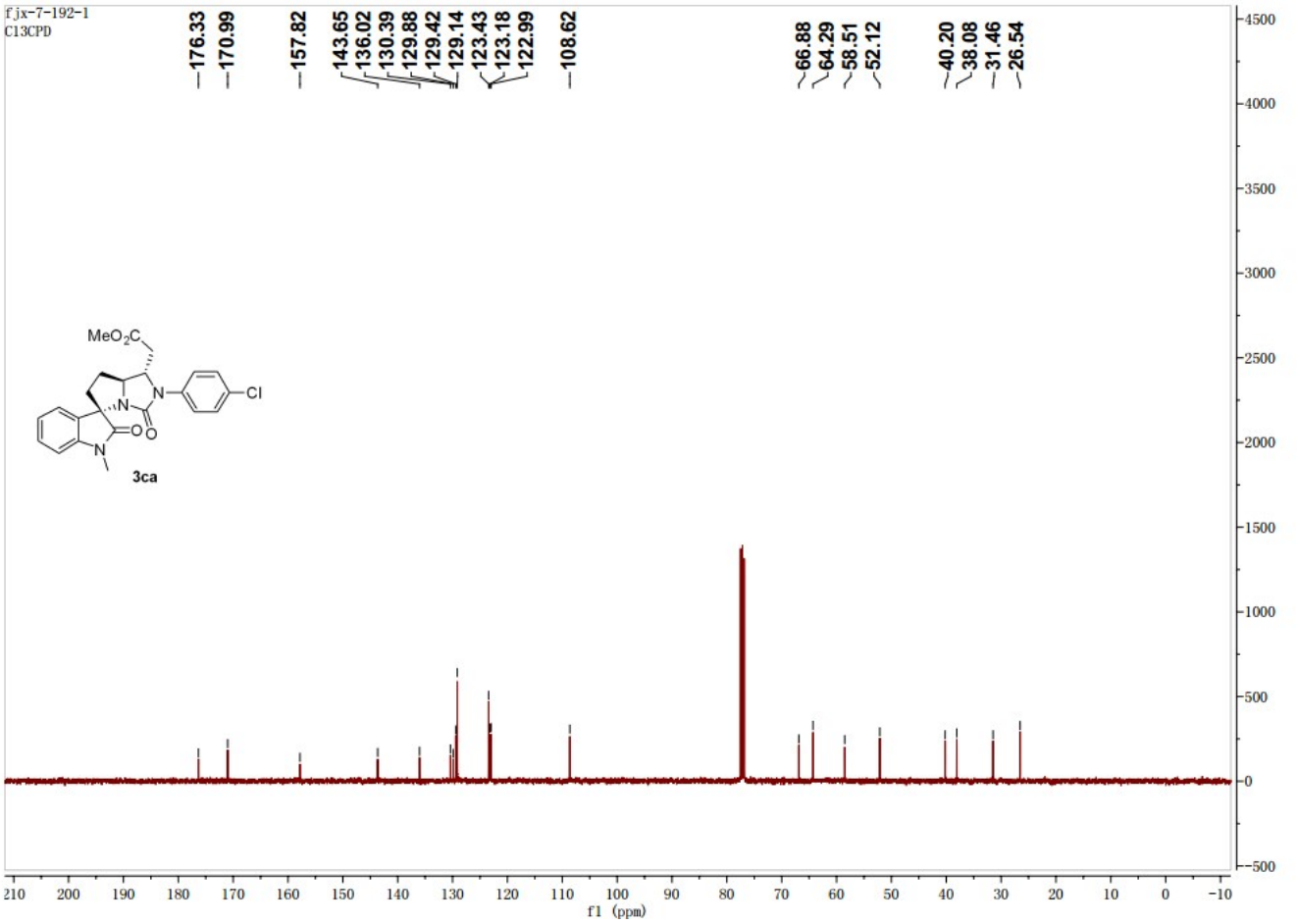
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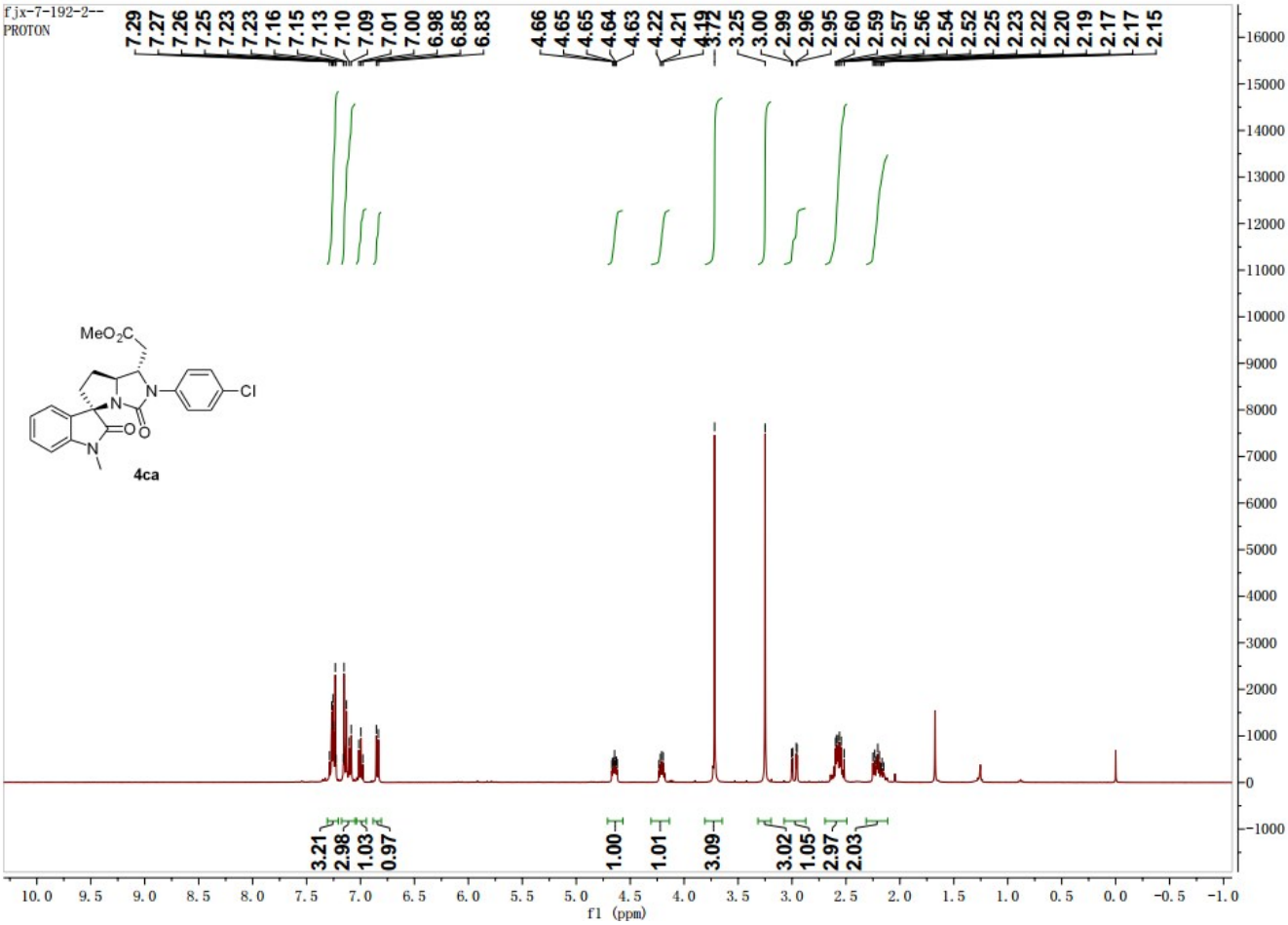
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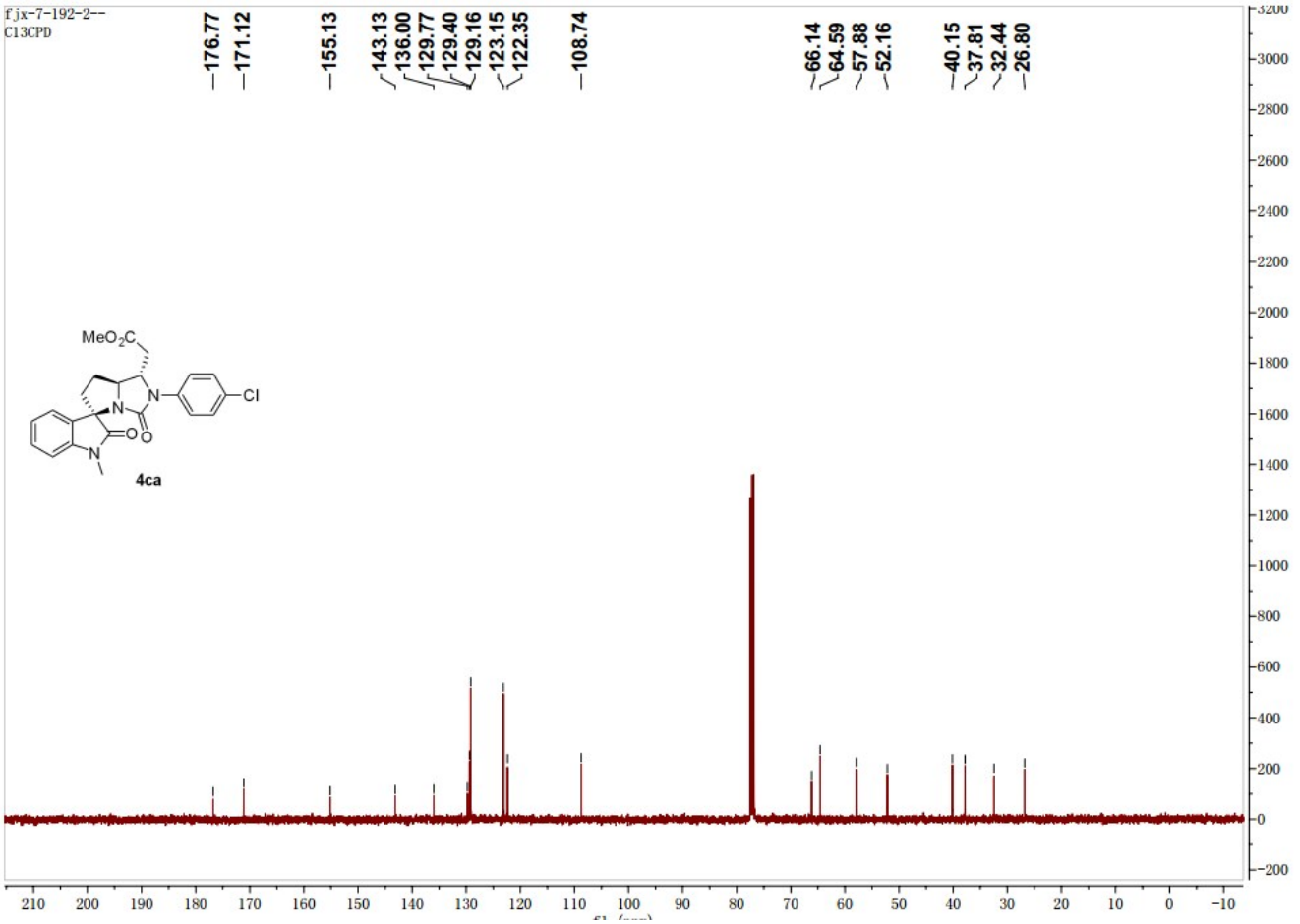
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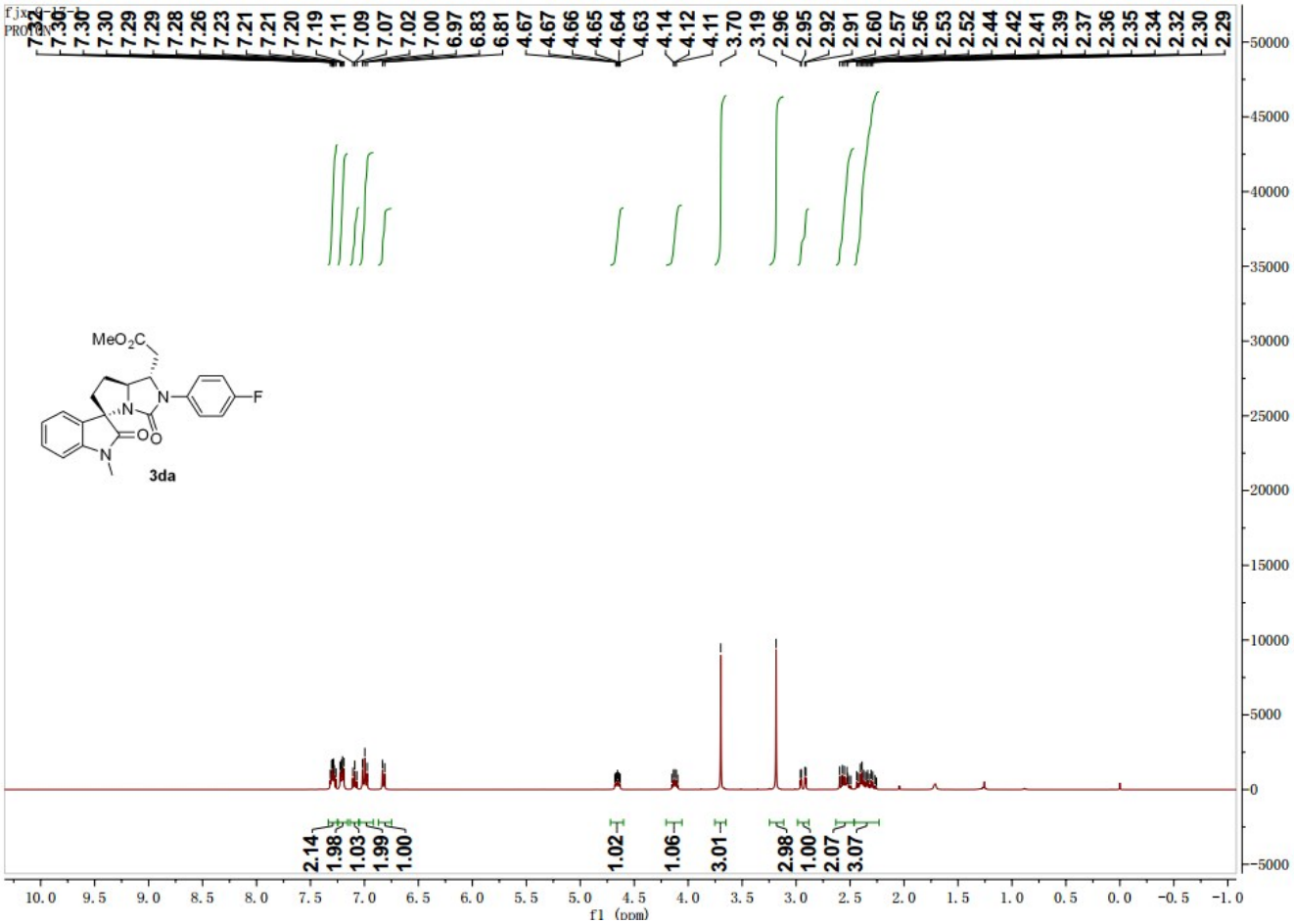
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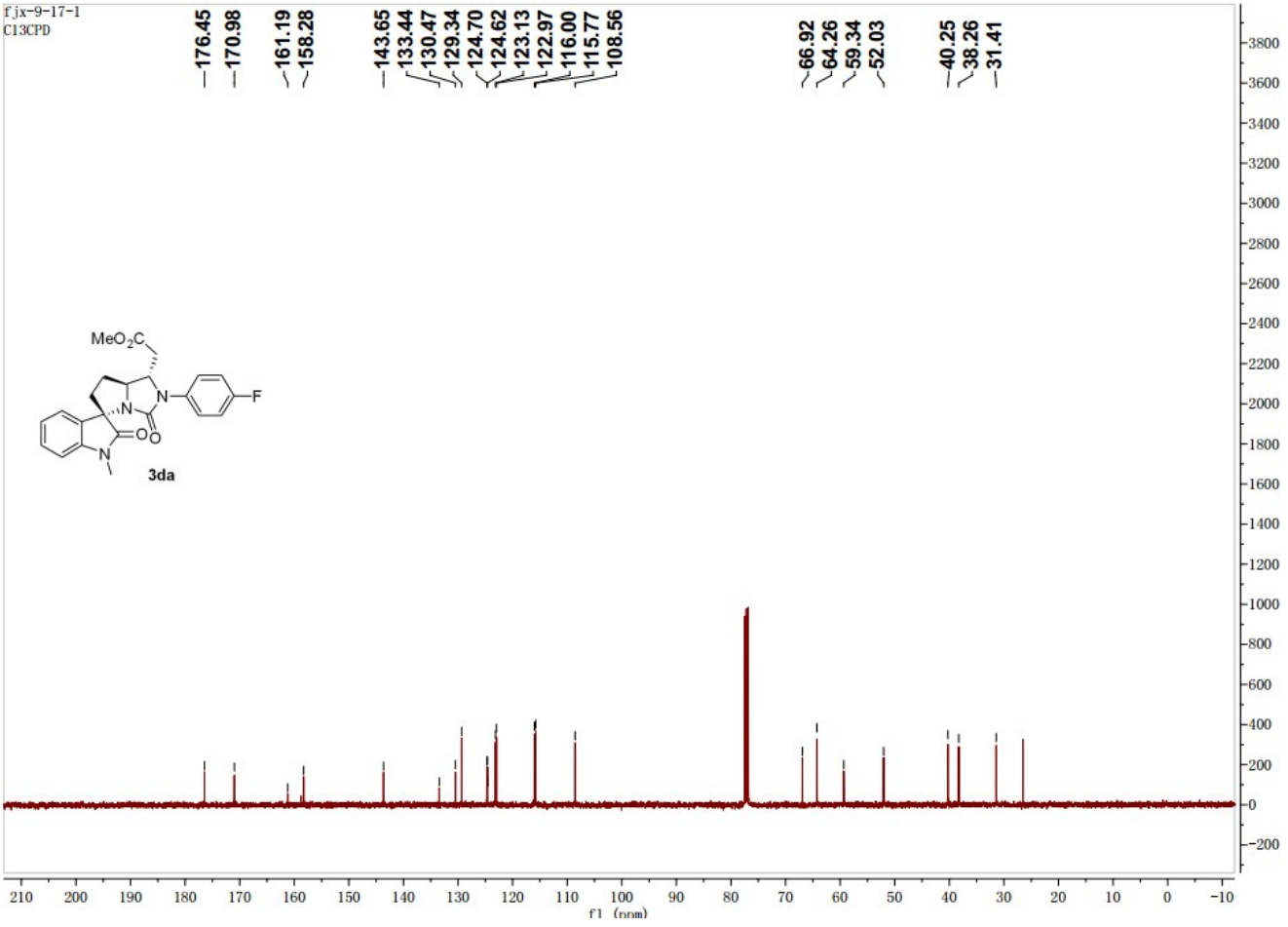
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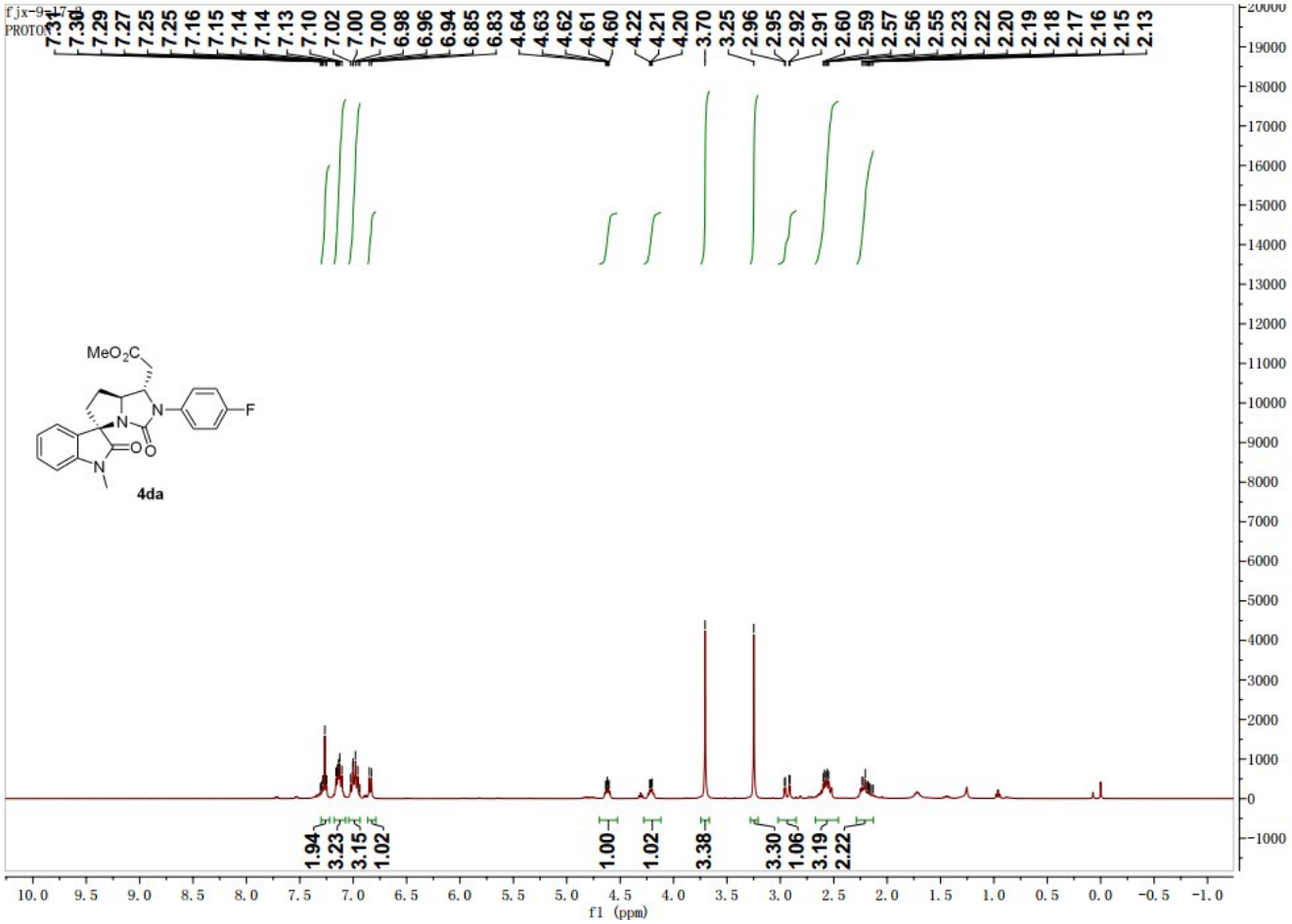
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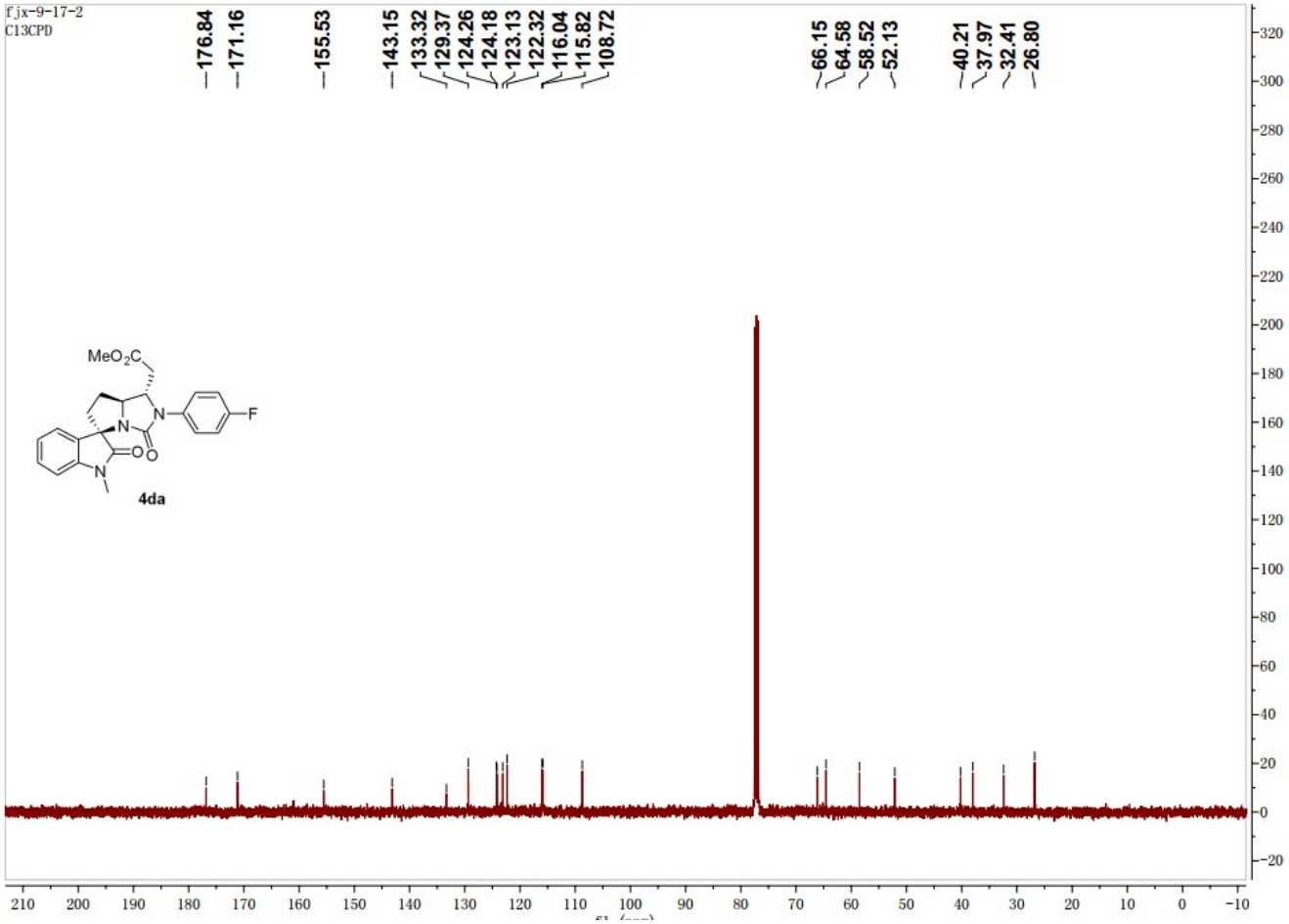
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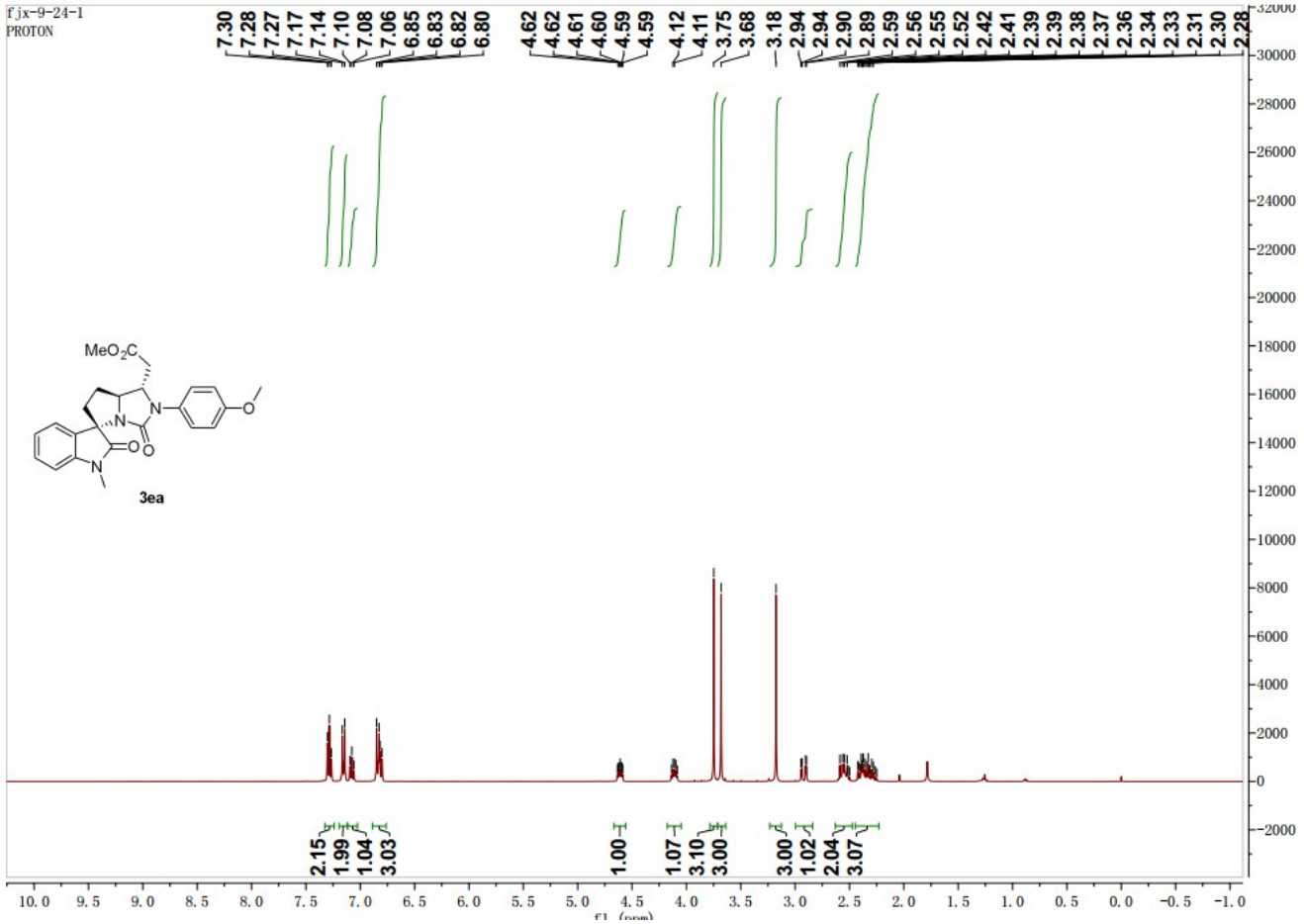
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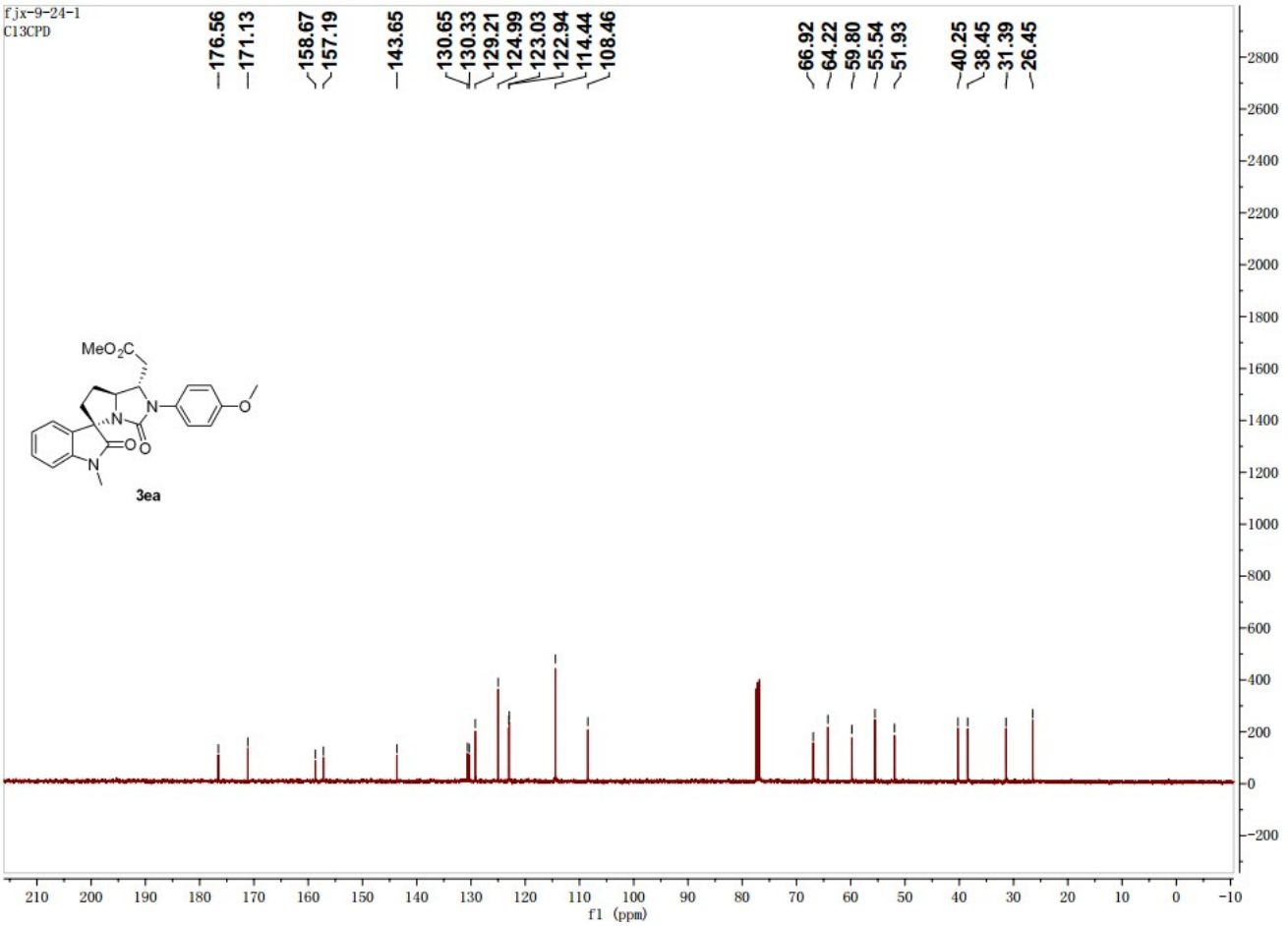
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129.21
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123.03
122.94
114.44
108.46
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55.54
51.93
40.25
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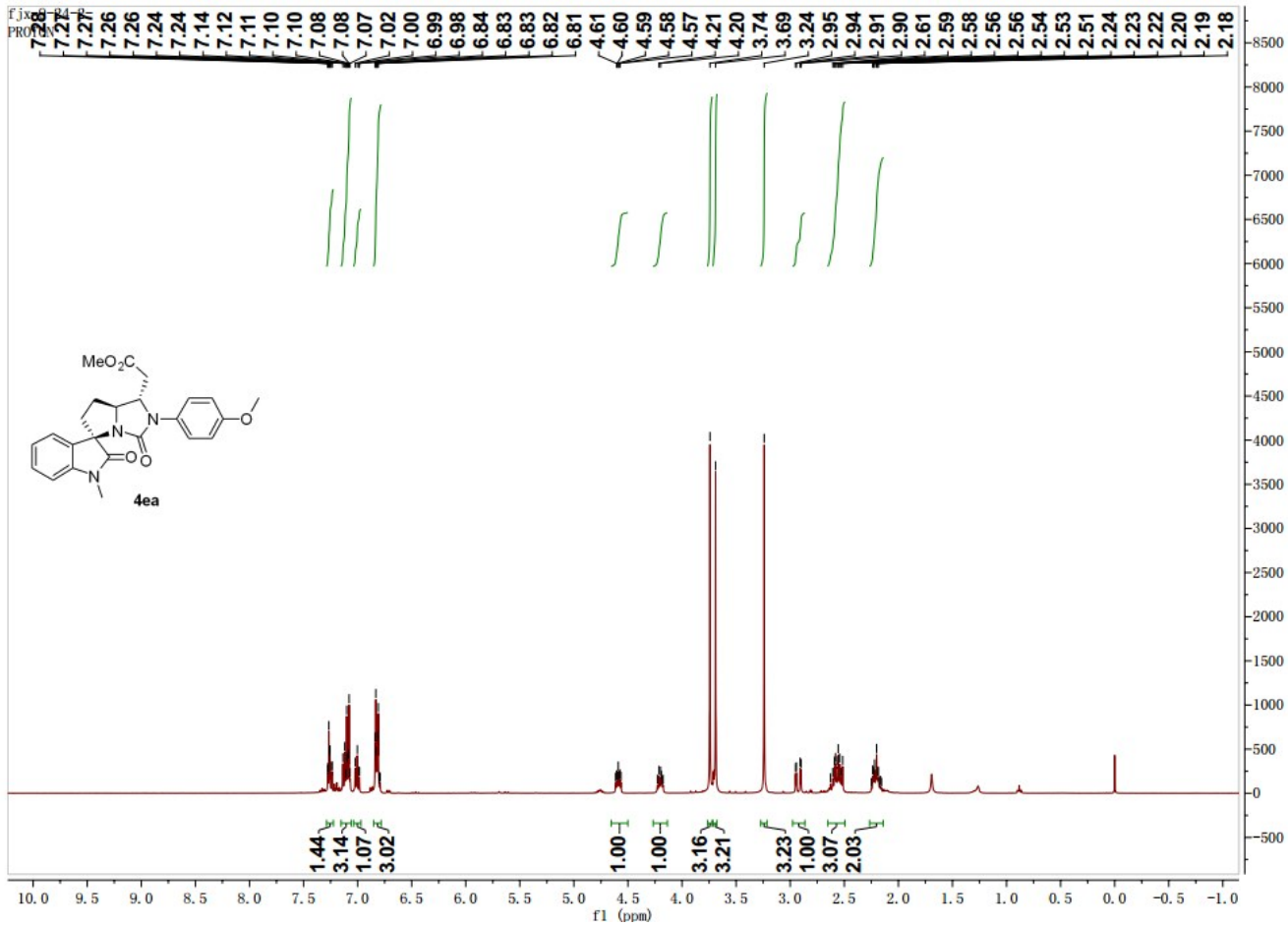
31.39
26.45
MeO2C
3ea
f1 (ppm)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4ea
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1.00
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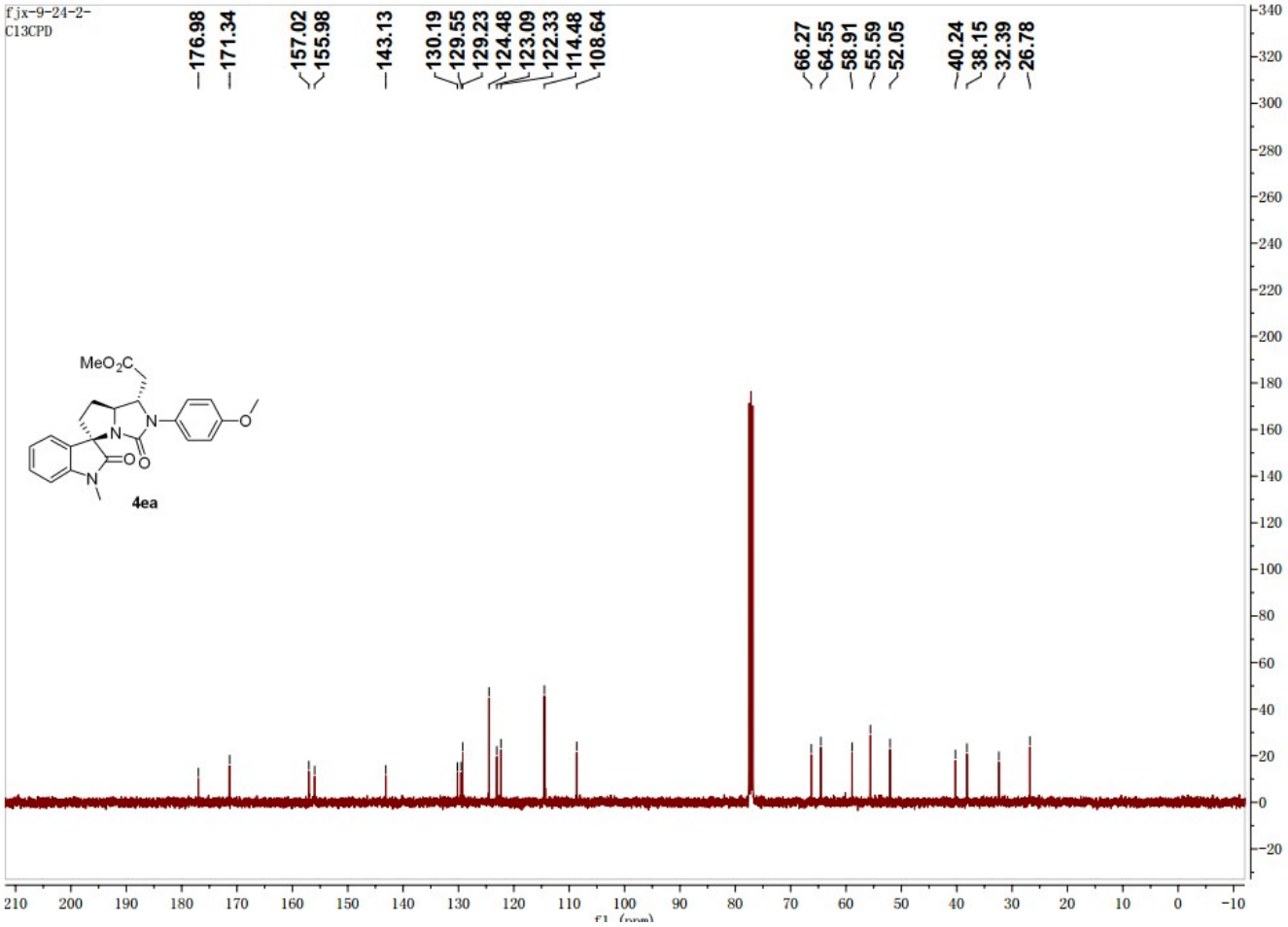
3.21
3.23
1.00
3.07
2.03
f1 (ppm)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129.23
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123.09
122.33
114.48
108.64
66.27
64.55
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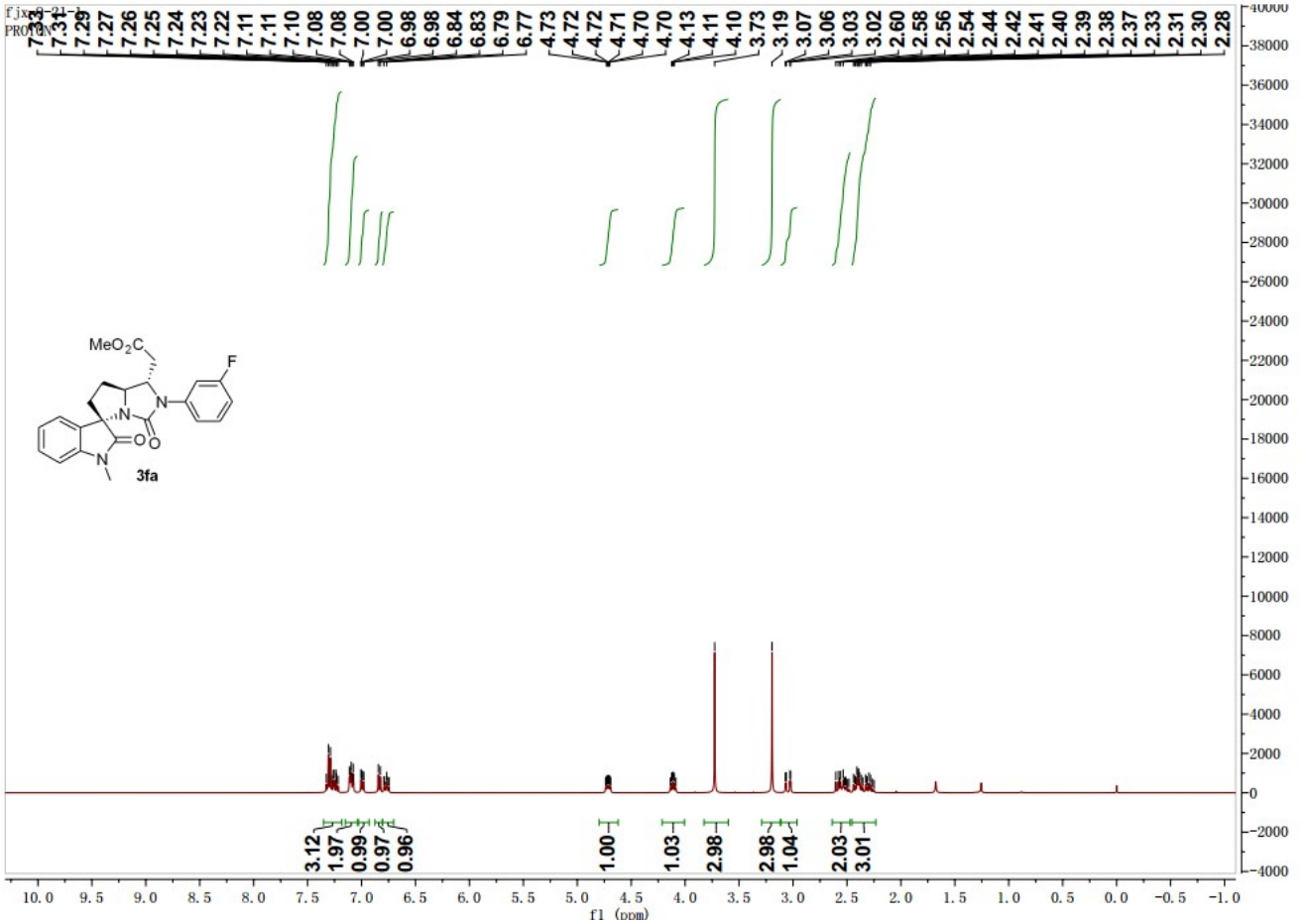
40.24
38.15
32.39
26.78
MeO2C
O
N
O
N
O
4ea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O
O
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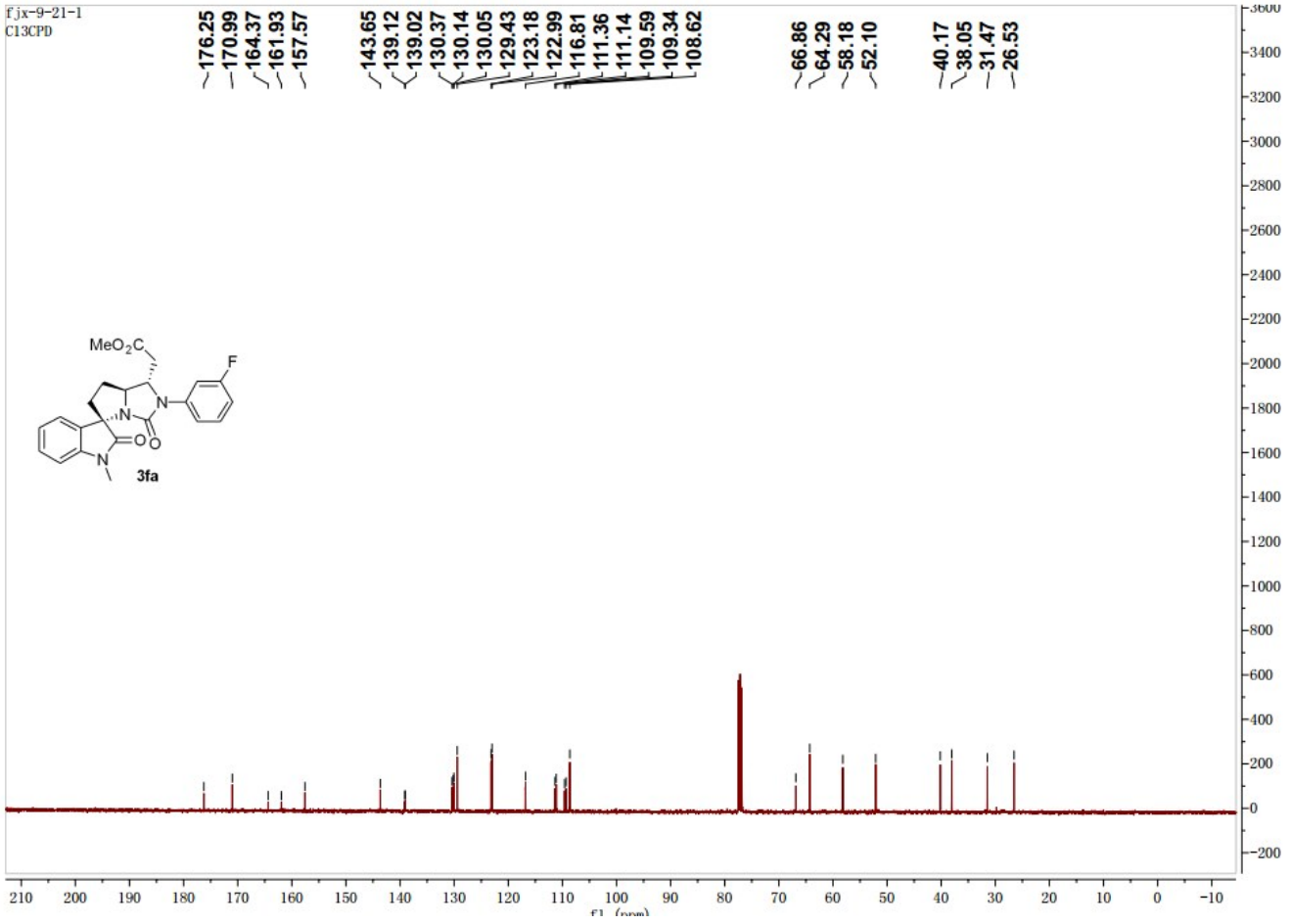
1.03
2.98
2.98
1.04
2.03
3.01
f1 (ppm)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129.43
123.18
122.99
116.81
111.36
111.14
109.59
109.34
108.62
66.86
64.29
58.18
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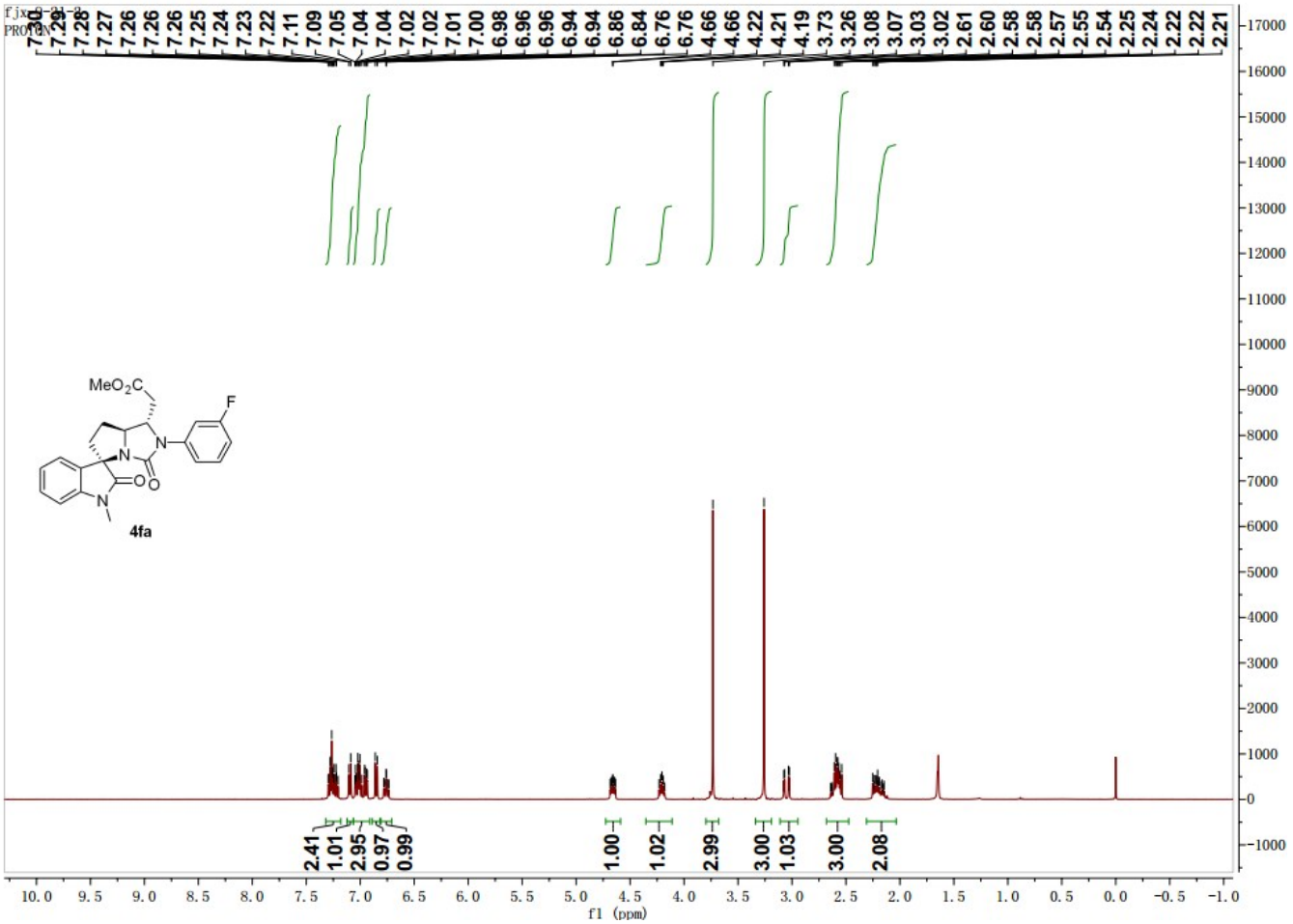
38.05
31.47
26.53
MeO2C
F
O
O
N
N
N
3fa
f1 (ppm)


PROTON
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7.24
7.23
7.22
7.11
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7.04
7.04
7.02
7.02
7.01
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6.96
6.94
6.94
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4.19
3.73
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3.03
3.02
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2.60
2.58
2.58
2.57
2.55
2.54
2.25
2.24
2.22
2.22
2.21
MeO2C
F
O
O
N
N
N
4fa
2.41
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1.02
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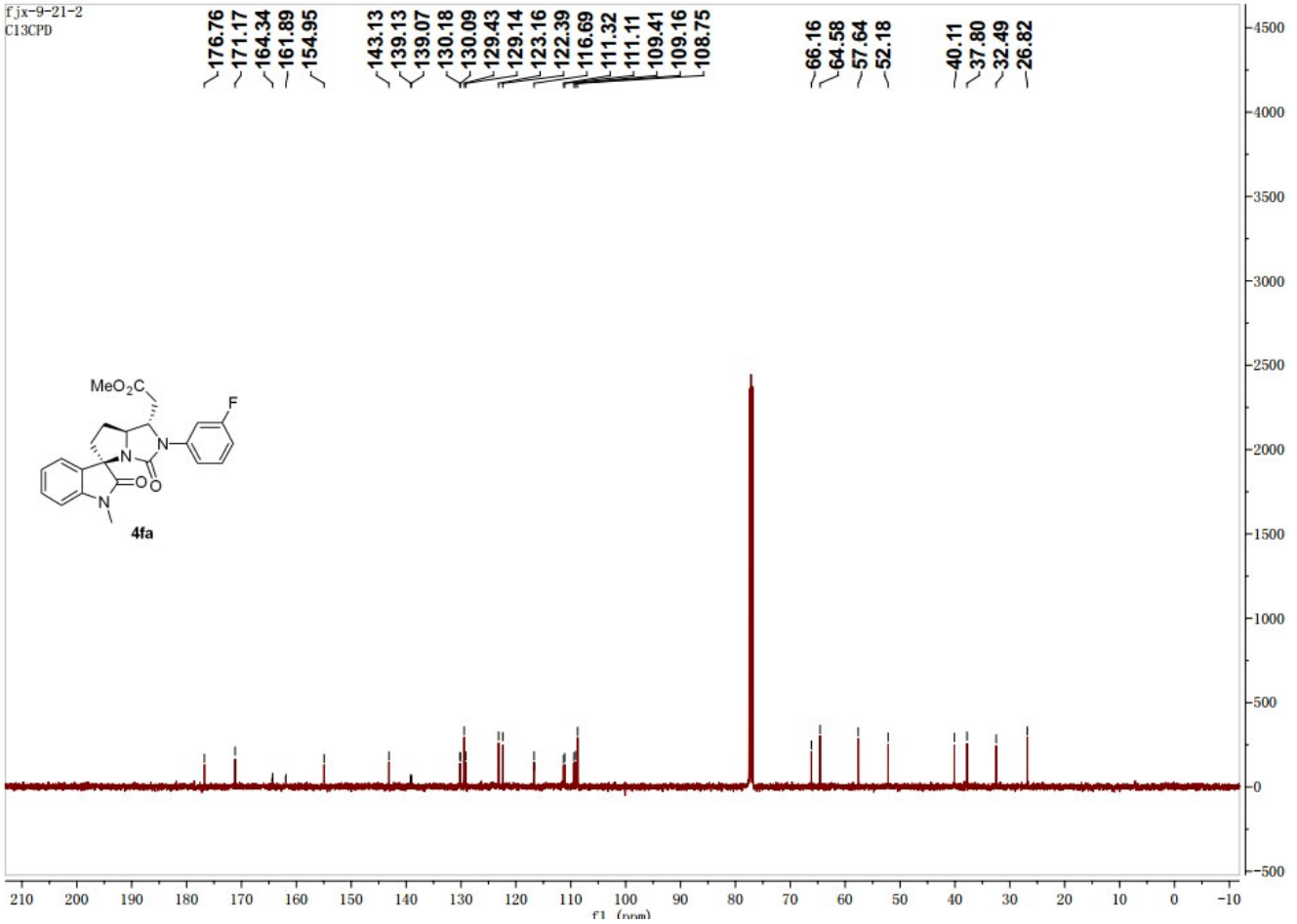
1.03
3.00
2.08
f1 (ppm)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129.43
129.14
123.16
122.39
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111.32
111.11
109.41
109.16
108.75
66.16
64.58
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37.80
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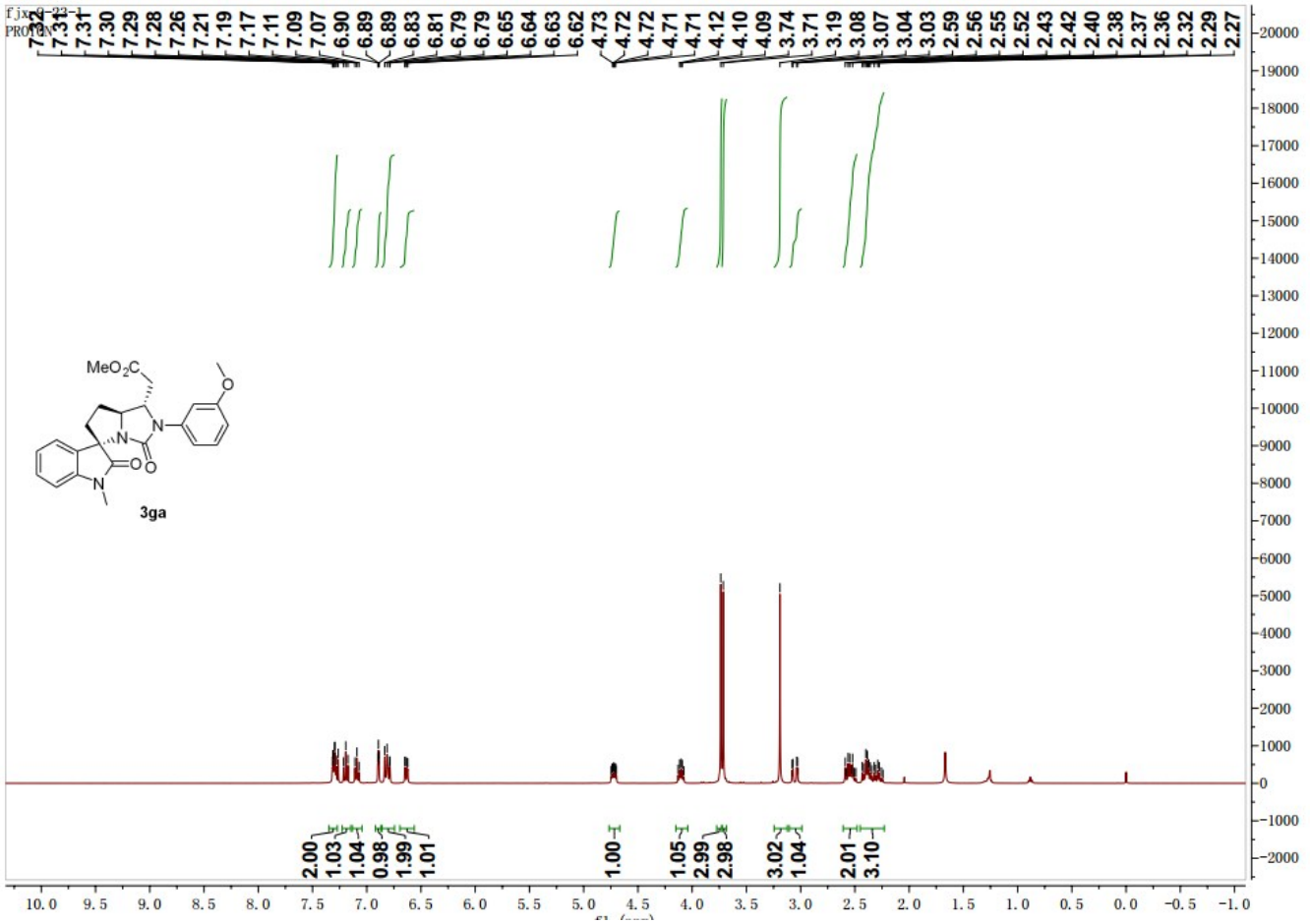
26.82
MeO2C
F
N
O
O
N
4fa
f1 (ppm)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6.81
6.79
6.79
6.65
6.64
6.63
6.62
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4.72
4.72
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4.71
4.12
4.10
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3.71
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3.08
3.07
3.04
3.03
2.59
2.56
2.55
2.52
2.43
2.42
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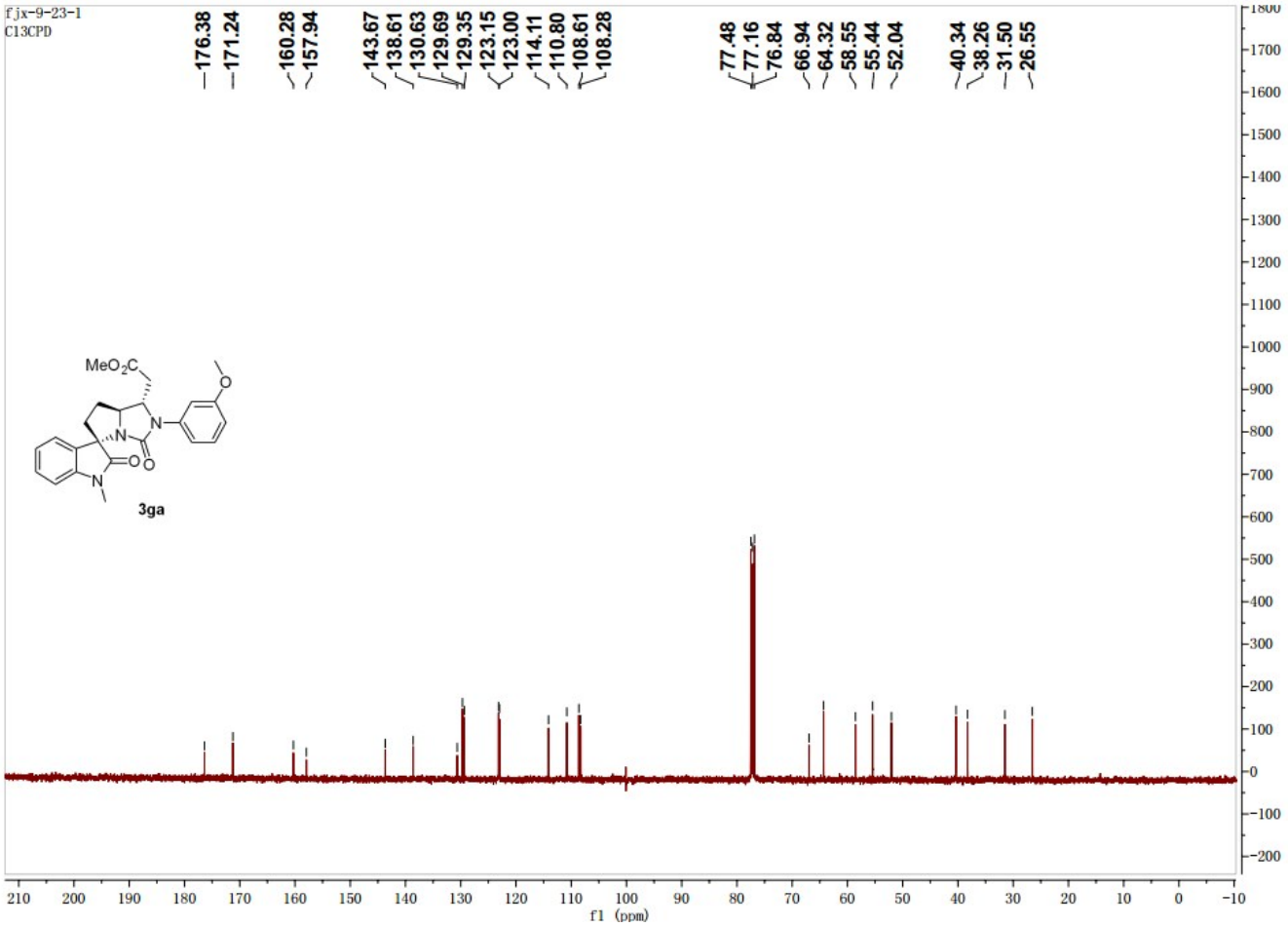
2.37
2.36
2.32
2.29
2.27
MeO2C
O
N
N
O
O
N
3ga
2.00
1.03
1.04
0.98
1.99
1.01
1.00
1.05
2.99
2.98
3.02
1.04
2.01
3.10
f1 (ppm)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129.69
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123.00
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110.80
108.61
108.28
77.48
77.16
76.84
66.94
64.32
58.55
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52.04
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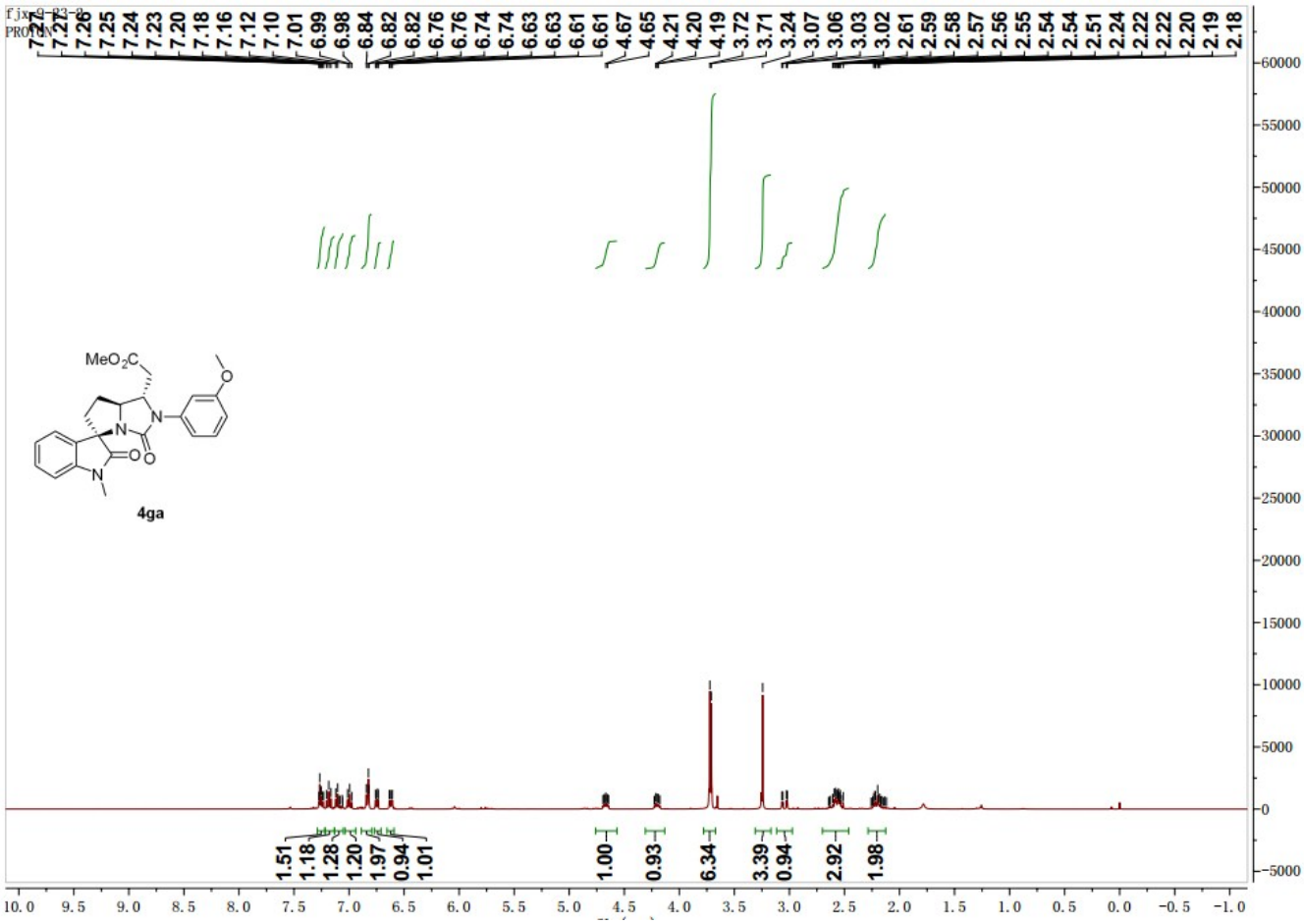
38.26
31.50
26.55
MeO2C
O
N
O
O
N
3ga
f1 (ppm)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7.10
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6.82
6.76
6.76
6.74
6.74
6.63
6.63
6.61
6.61
4.67
4.65
4.21
4.20
4.19
3.72
3.71
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3.07
3.06
3.03
3.02
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2.59
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2.57
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2.55
2.54
2.54
2.51
2.24
2.22
2.22
2.20
2.19
2.18
MeO2C
O
N
O
O
N
4ga
1.51
1.18
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1.00
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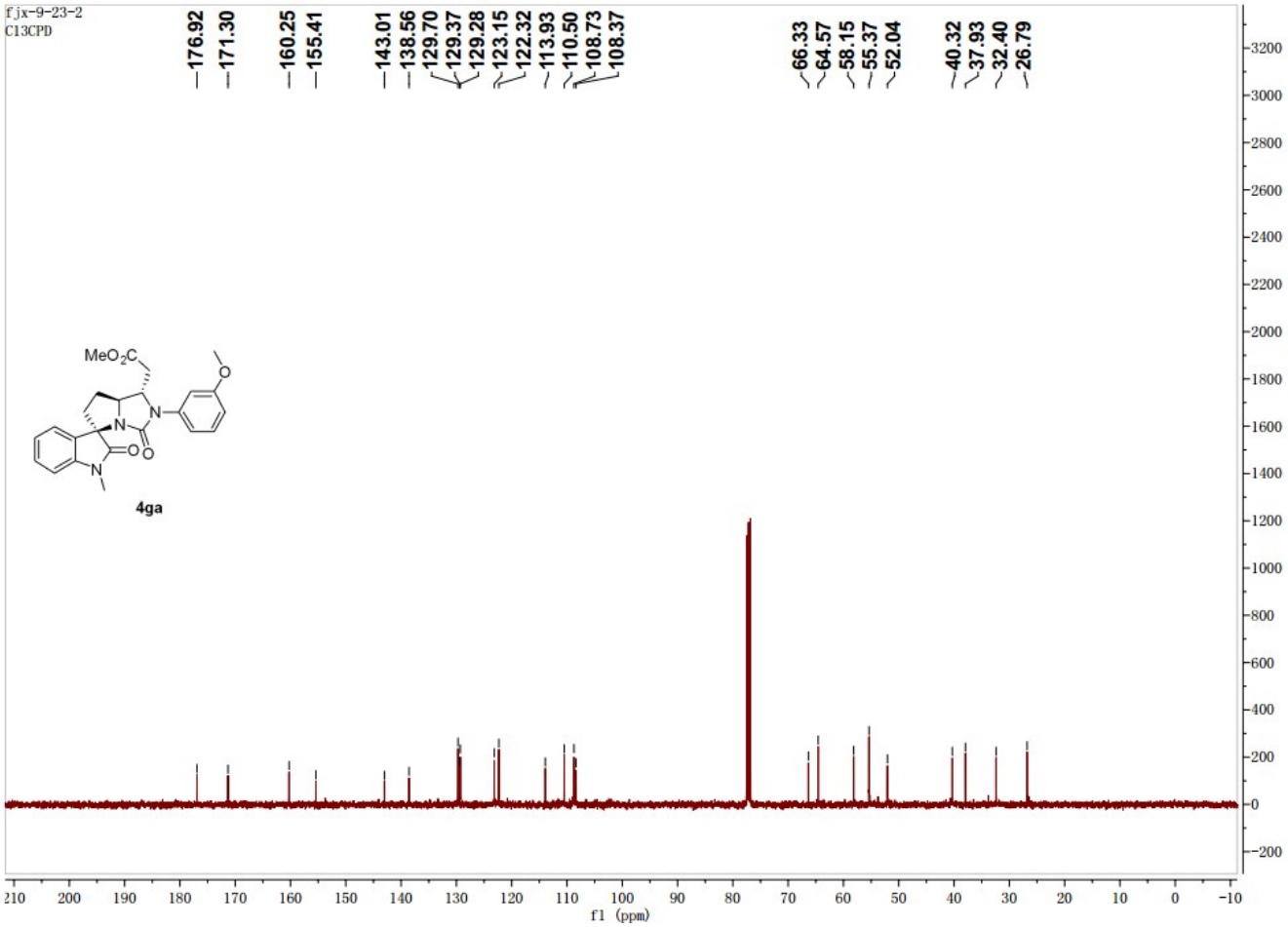
2.92
1.98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122.32
113.93
110.50
108.73
108.37
66.33
64.57
58.15
55.37
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37.93
32.40
26.79
MeO2C
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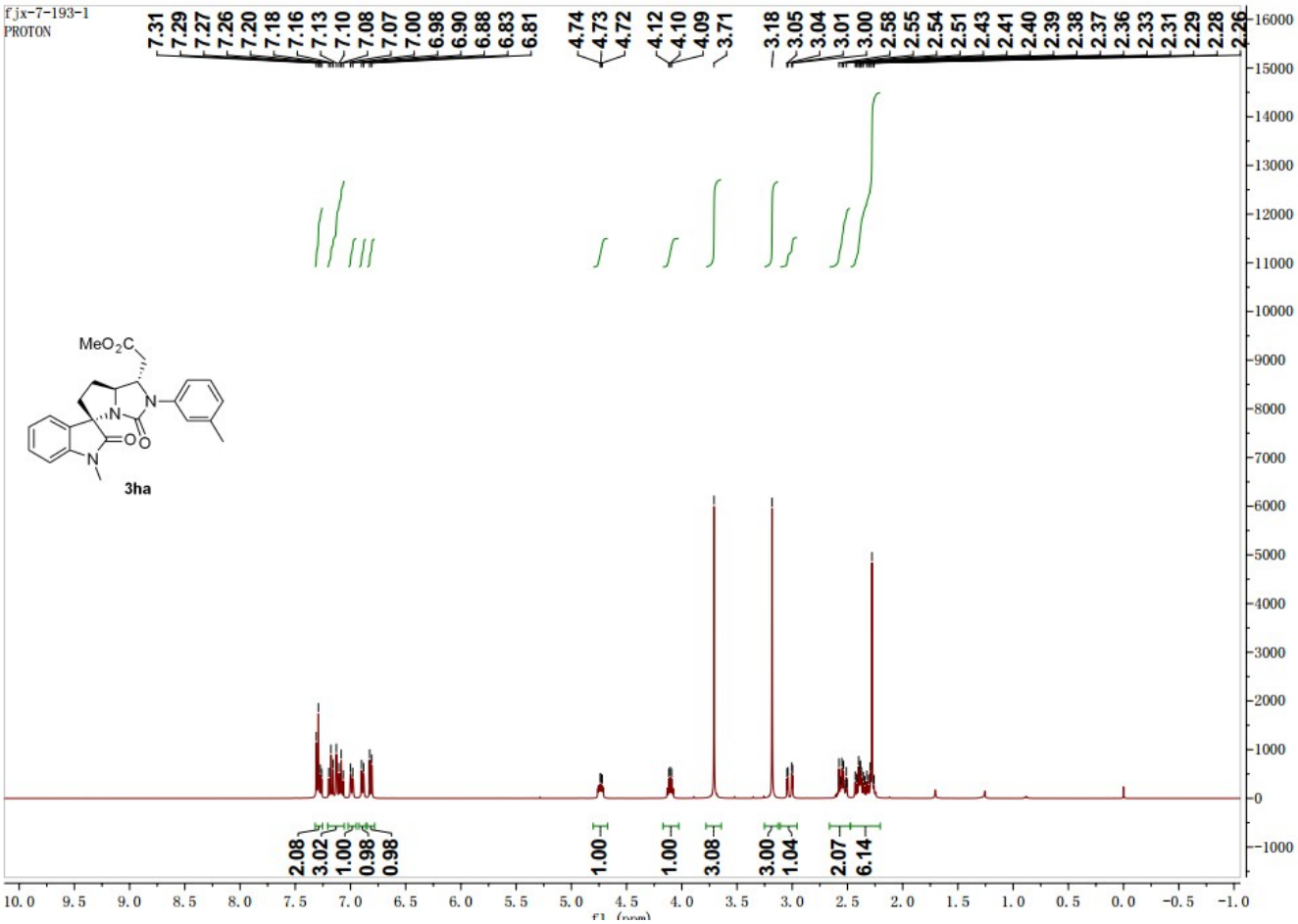
N
N
O
O
N
4ga
f1 (ppm)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7.10
7.08
7.07
7.00
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6.90
6.88
6.83
6.81
4.74
4.73
4.72
4.12
4.10
4.09
3.71
3.18
3.05
3.04
3.01
3.00
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2.55
2.54
2.51
2.43
2.41
2.40
2.39
2.38
2.37
2.36
2.33
2.31
2.29
2.28
2.26
MeO2C
O
N
N
O
O
N
3ha
2.08
3.02
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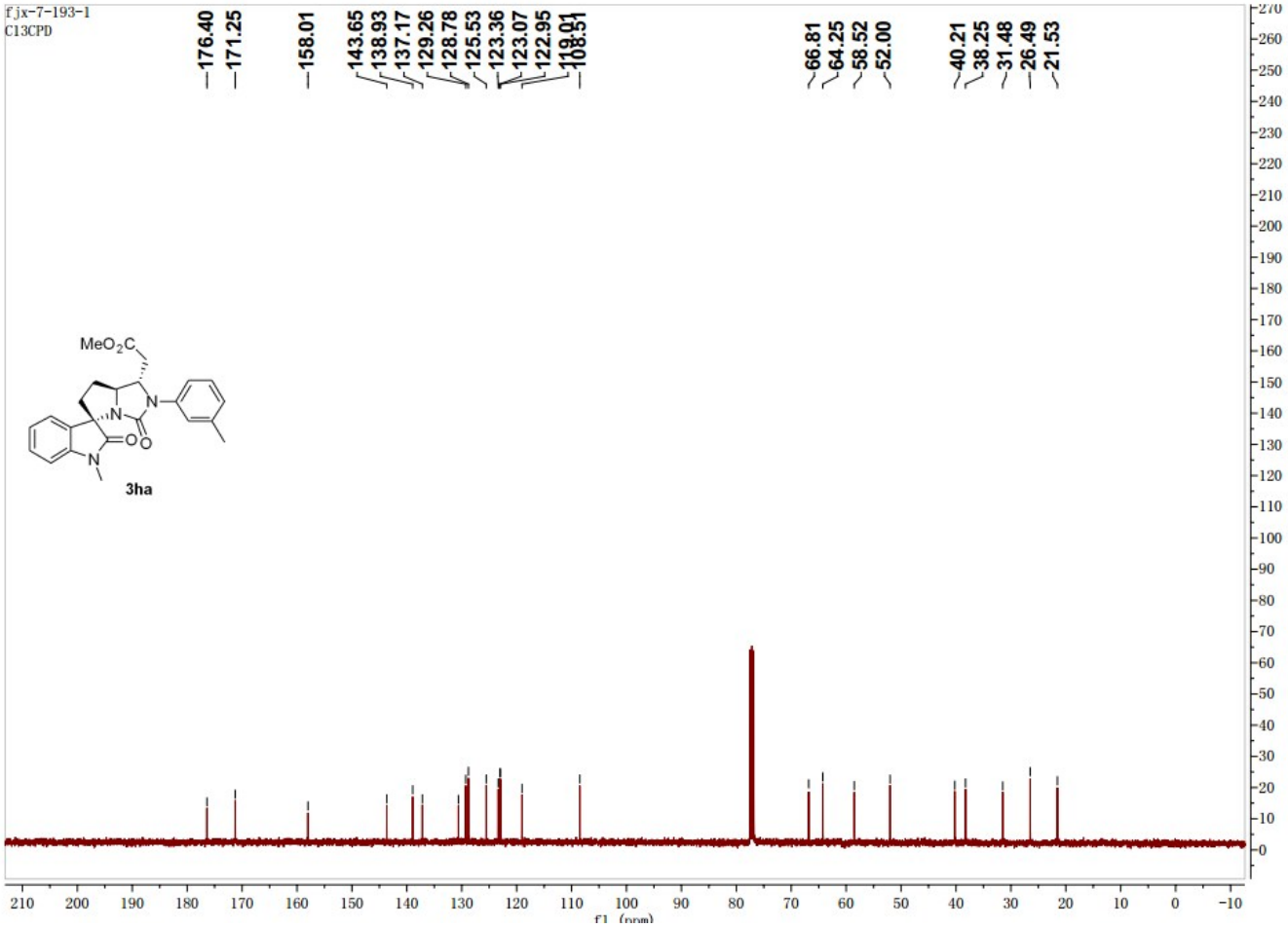
0.98
1.00
1.00
3.08
3.00
1.04
2.07
6.14
f1 (ppm)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137.17
129.26
128.78
125.53
123.36
123.07
122.95
119.01
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58.52
52.00
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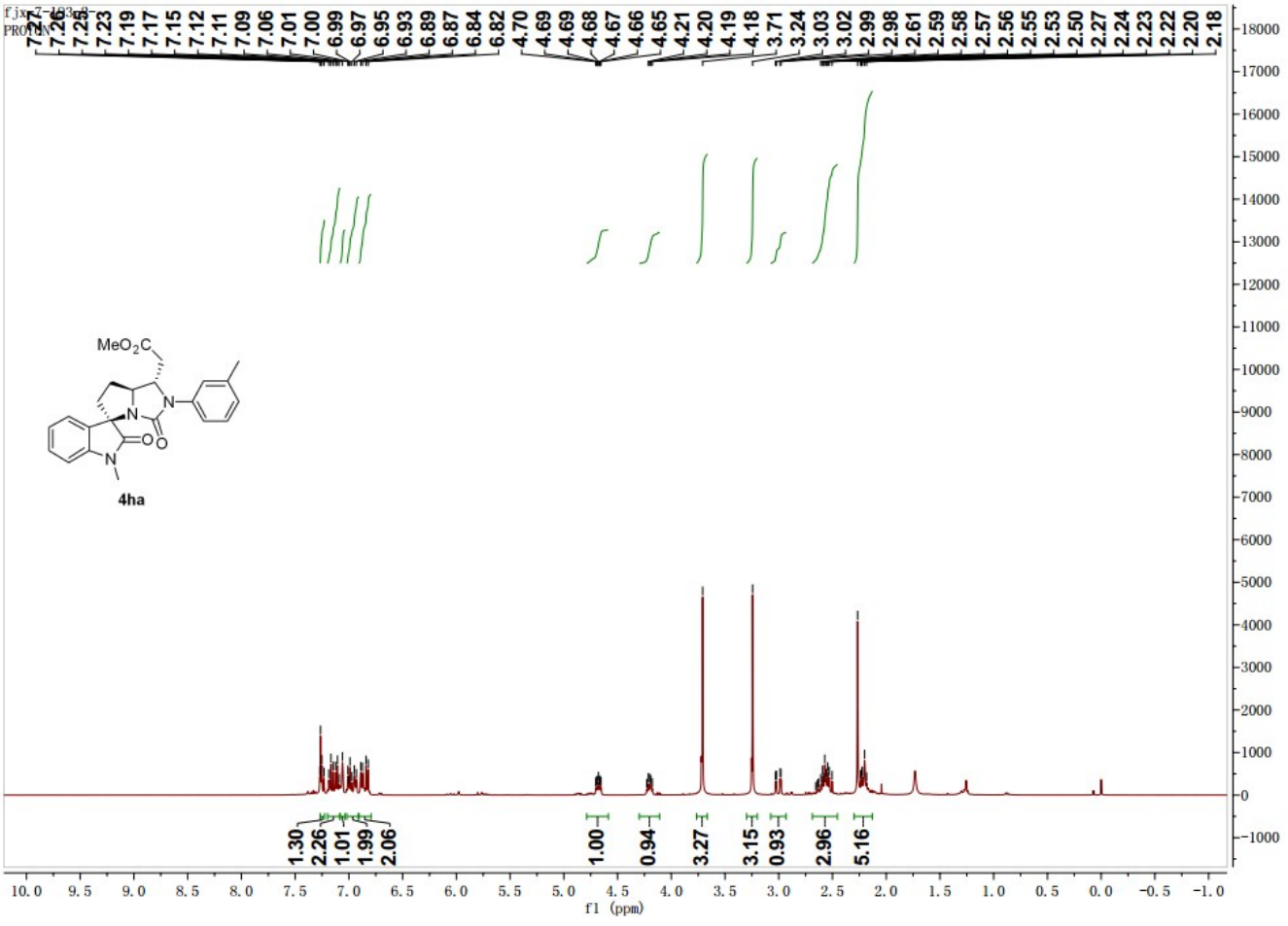
31.48
26.49
21.53
MeO2C
3ha


MeO2C
4ha
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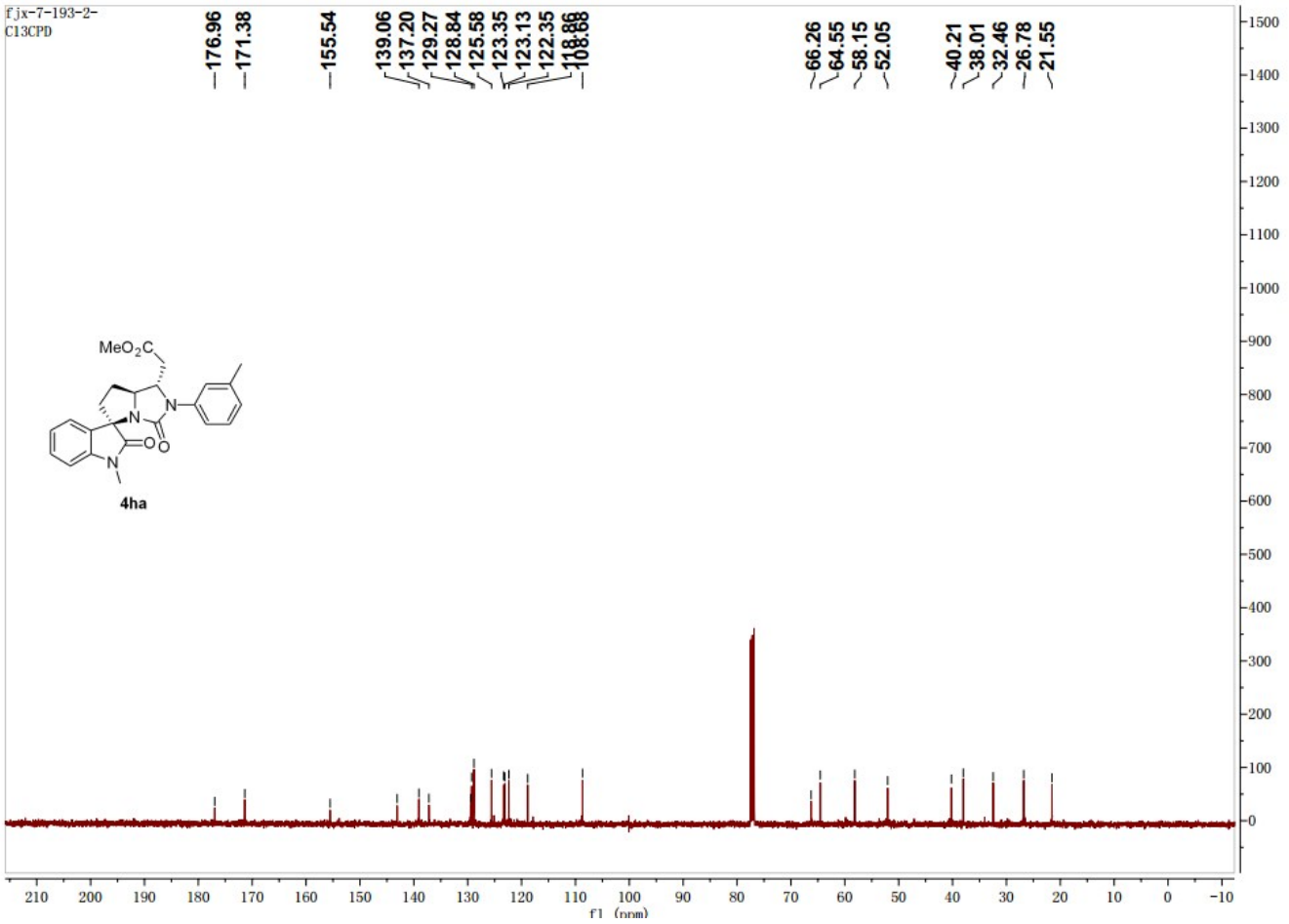
1.00
0.94
3.27
3.15
0.93
2.96
5.16
f1 (ppm)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128.84
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123.35
123.13
122.35
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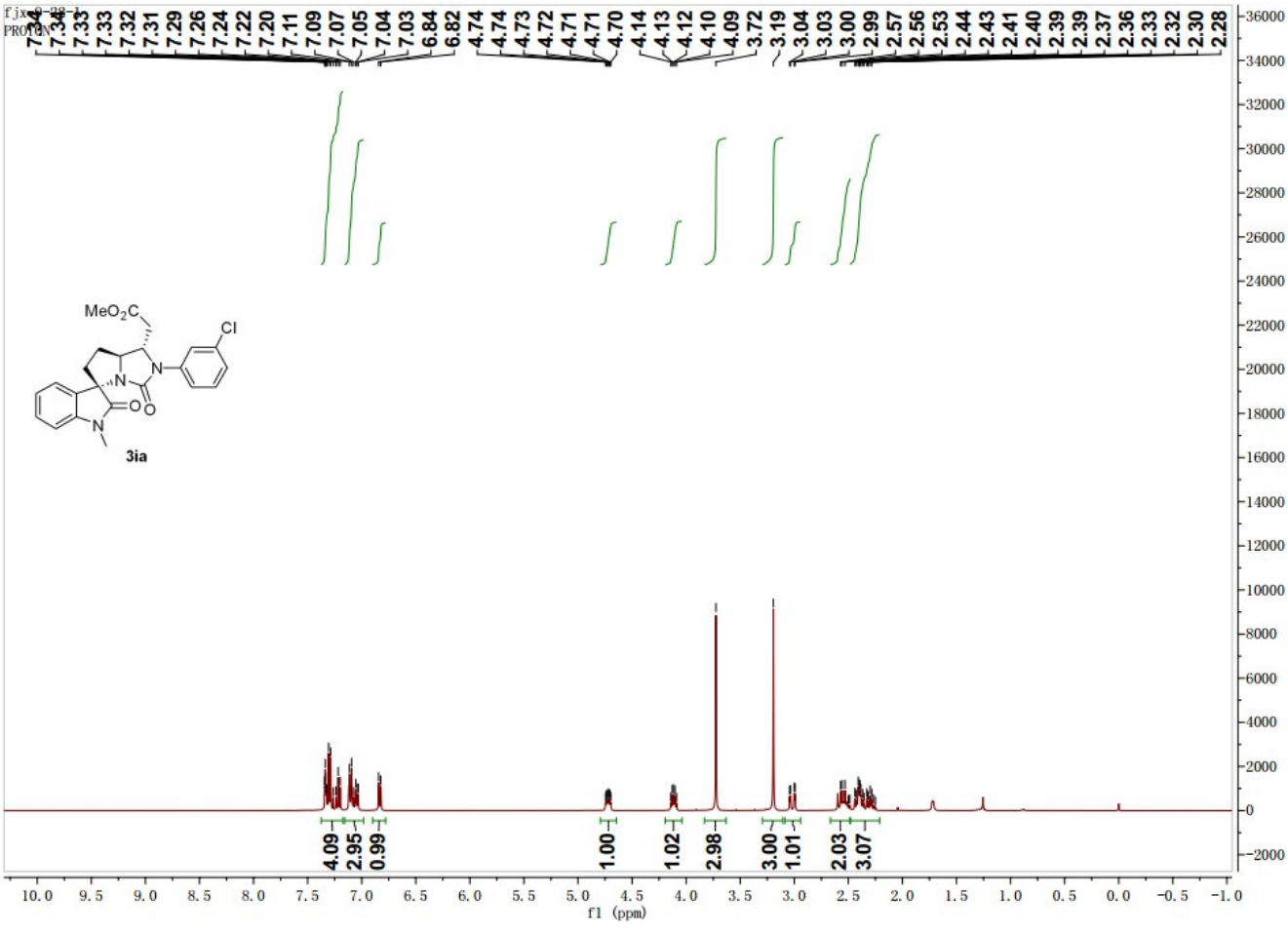
52.05
40.21
38.01
32.46
26.78
21.55
MeO2C
4ha
f1 (ppm)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7.20
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7.09
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7.05
7.04
7.03
6.84
6.82
4.74
4.73
4.72
4.71
4.70
4.14
4.12
4.10
4.09
3.72
3.19
3.04
3.03
3.00
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2.56
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2.43
2.41
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2.39
2.37
2.36
2.33
2.32
2.30
2.28
MeO2C
Cl
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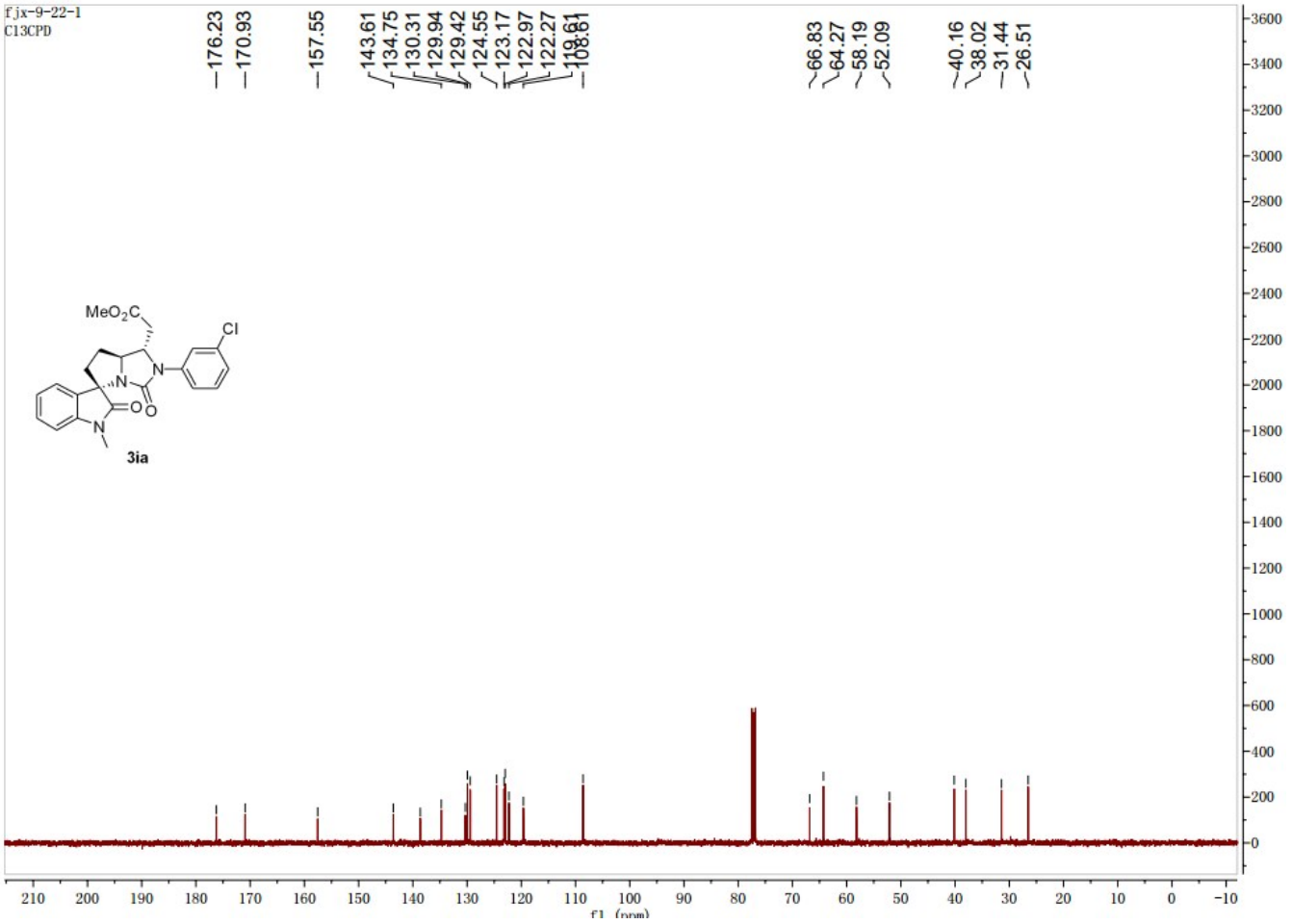
1.00
1.02
2.98
3.00
1.01
2.03
3.07
f1 (ppm)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123.17
122.97
122.27
119.61
108.81
66.83
64.27
58.19
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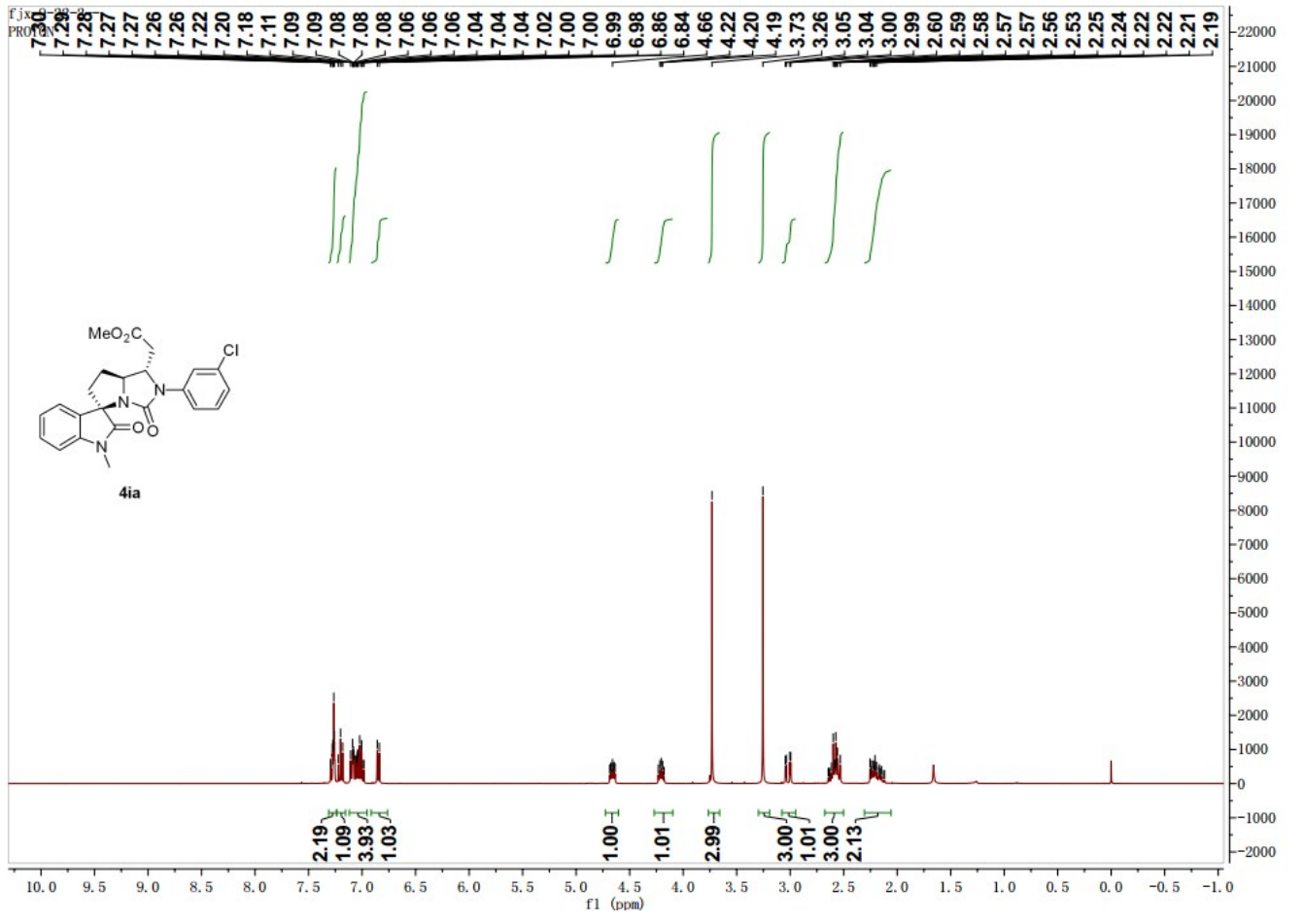
40.16
38.02
31.44
26.51
MeO2C
Cl
O
O
N
N
N
3ia
f1 (ppm)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O
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N
N
4ia
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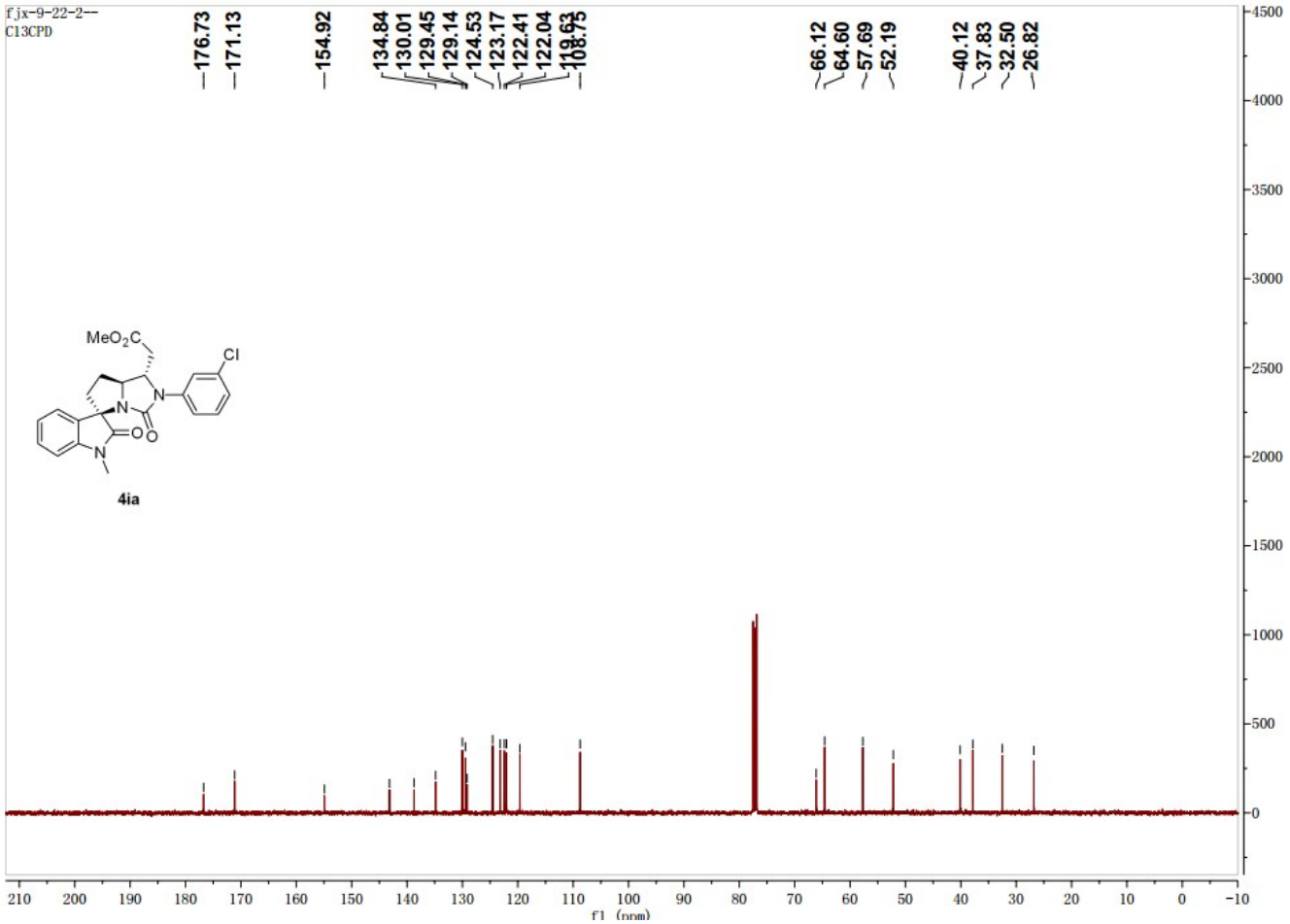
1.09
3.93
1.03
1.00
1.01
2.99
3.00
1.01
3.00
2.13
f1 (ppm)


fjx-9-22-2--
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123.17
122.41
122.04
119.63
108.75
66.12
64.60
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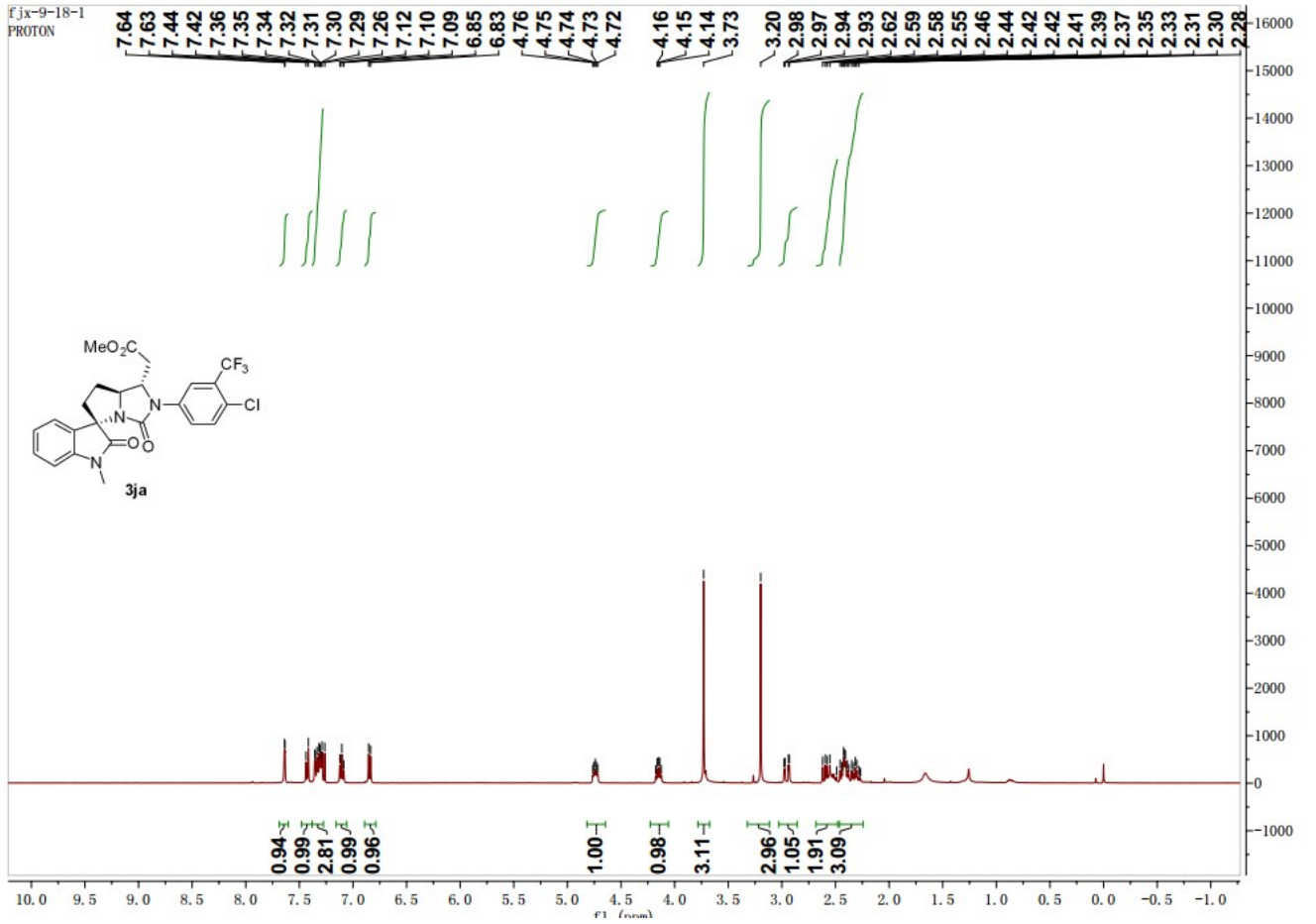
37.83
32.50
26.82
MeO2C
Cl
N
O
O
N
4ia
f1 (ppm)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7.12
7.10
7.09
6.85
6.83
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4.16
4.15
4.14
3.73
3.20
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2.94
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2.59
2.58
2.55
2.46
2.44
2.42
2.42
2.41
2.39
2.37
2.35
2.33
2.31
2.30
2.28
MeO2C
CF3
Cl
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O
O
N
3ja
0.94
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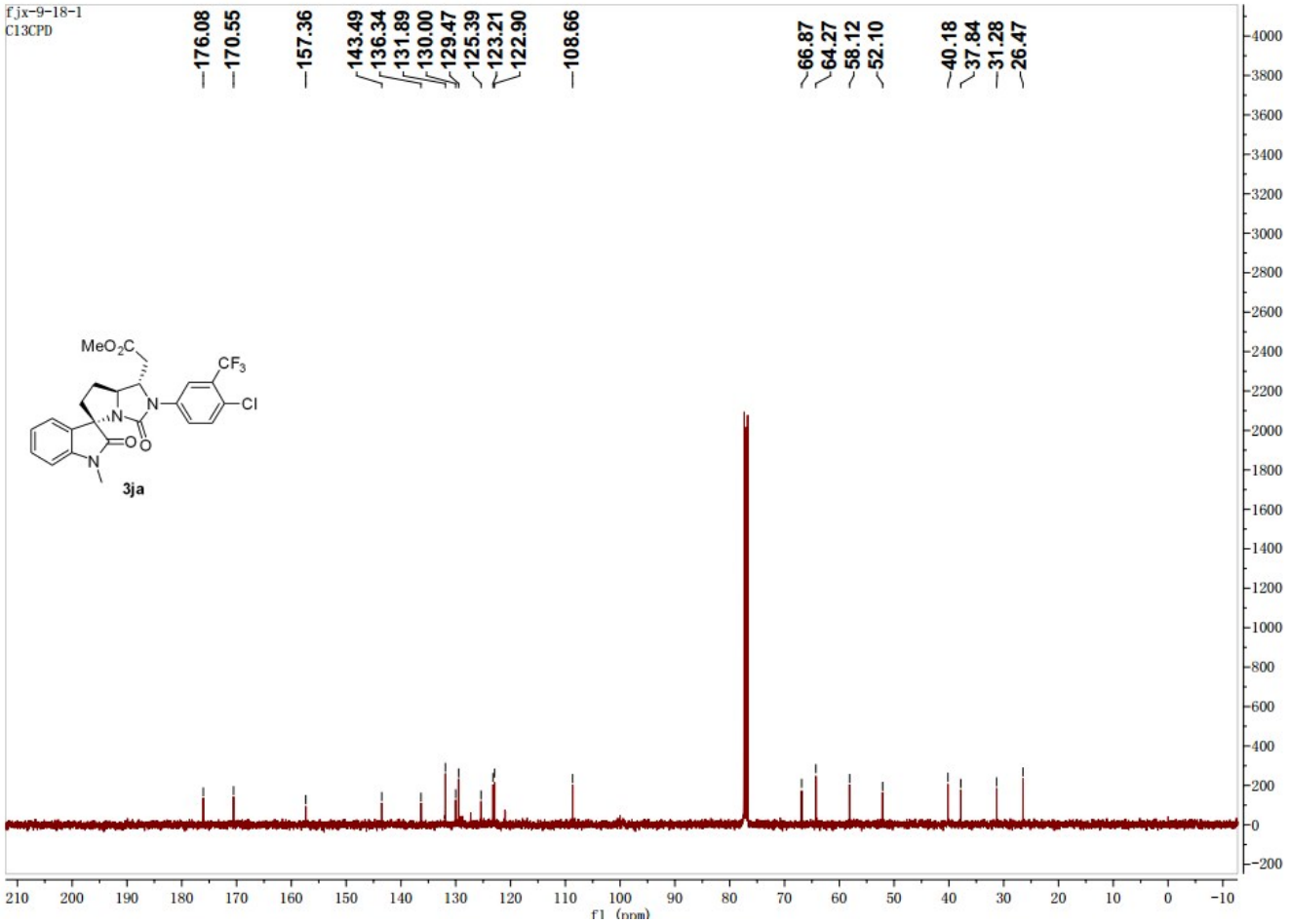
0.96
1.00
0.98
3.11
2.96
1.05
1.91
3.09
f1 (ppm)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108.66
66.87
64.27
58.12
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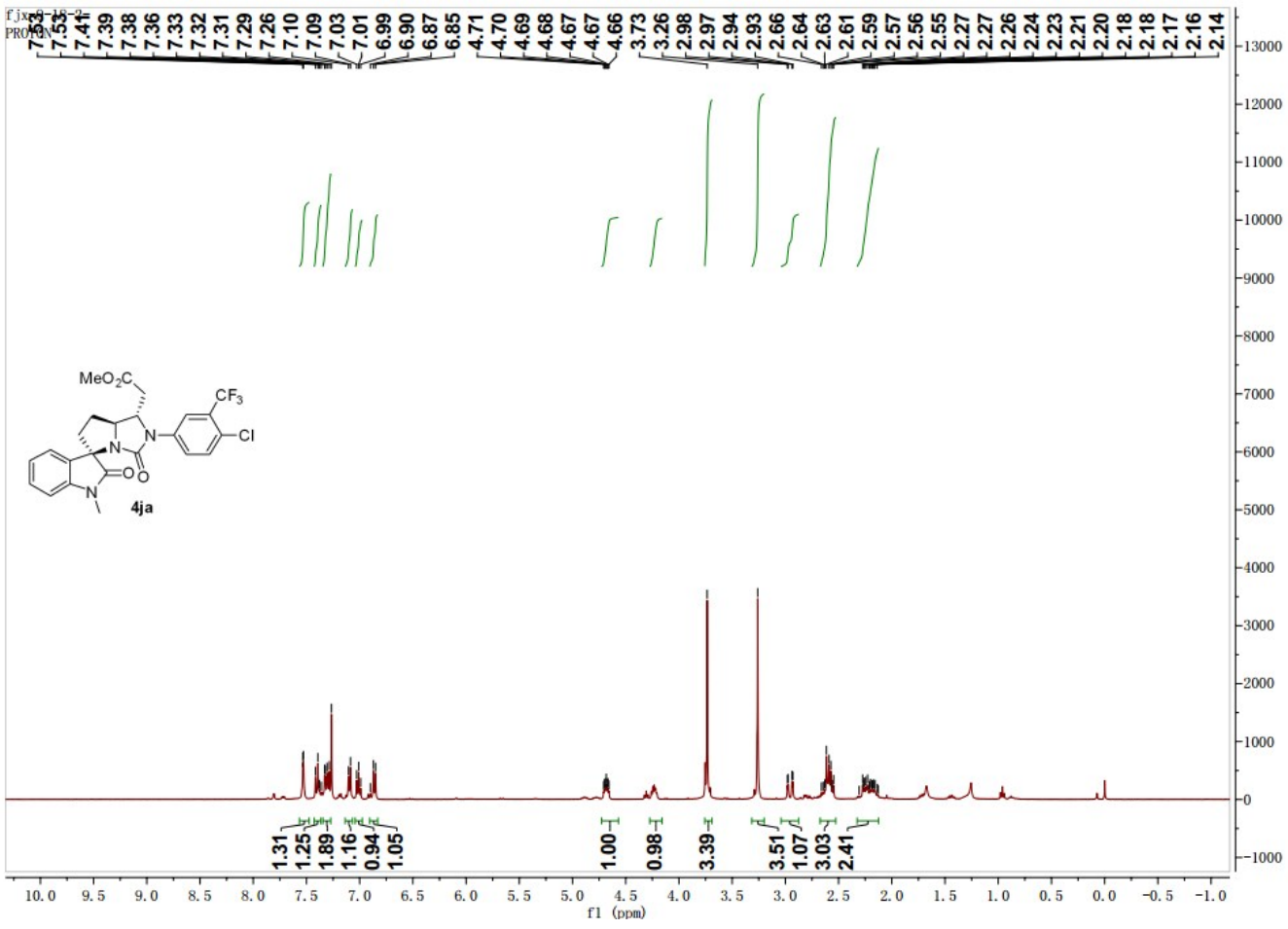
31.28
26.47
MeO2C
CF3
Cl
N
O
O
N
3ja
f1 (ppm)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7.03
7.01
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3.73
3.26
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2.97
2.94
2.93
2.66
2.64
2.63
2.61
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2.57
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2.26
2.24
2.23
2.21
2.20
2.18
2.18
2.17
2.16
2.14
MeO2C
CF3
Cl
N
O
O
N
4ja
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1.25
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3.39
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1.07
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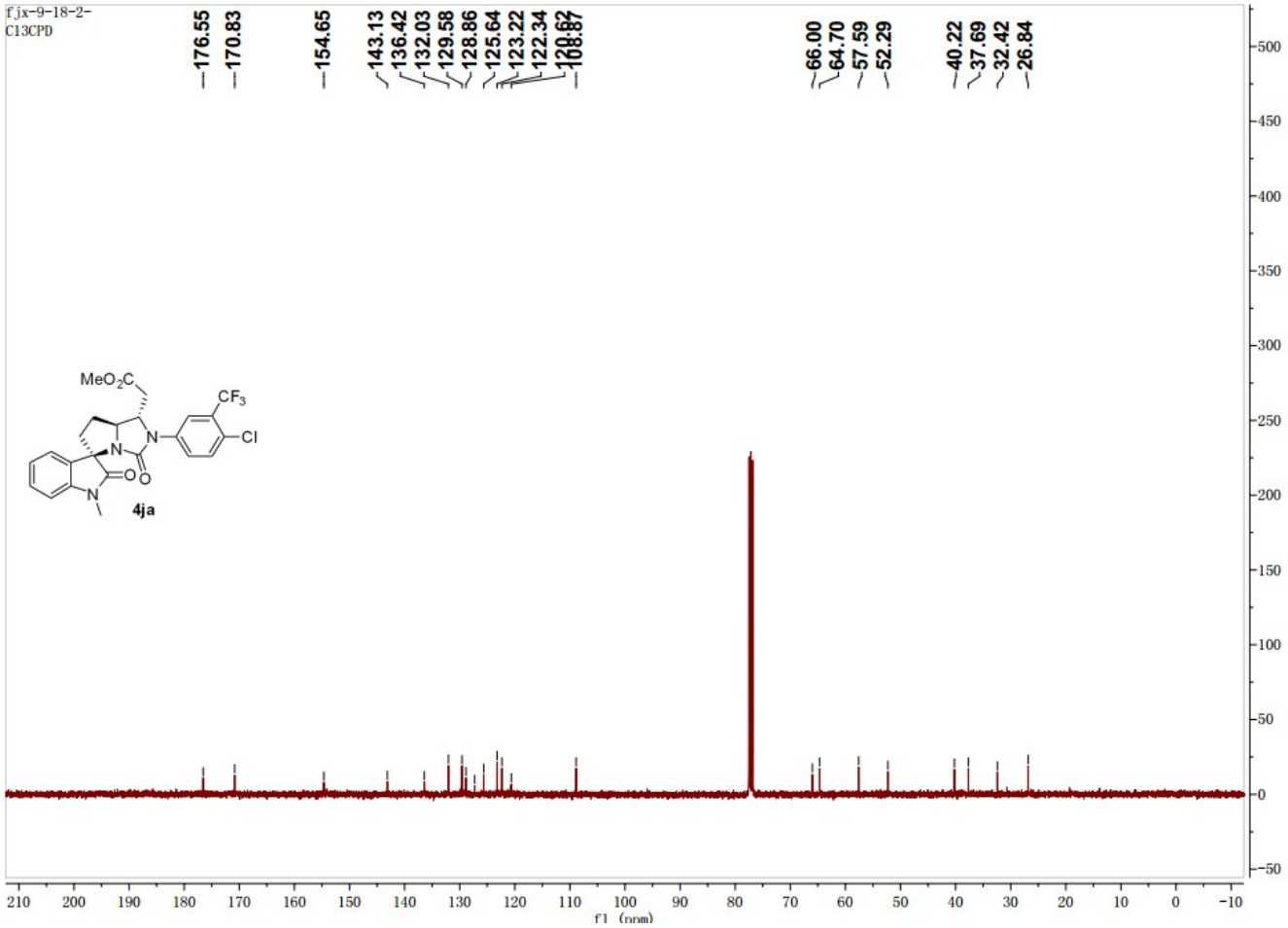
2.41
f1 (ppm)


fjx-9-18-2-
C13CPD
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143.13
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132.03
129.58
128.86
125.64
123.22
122.34
120.62
108.87
66.00
64.70
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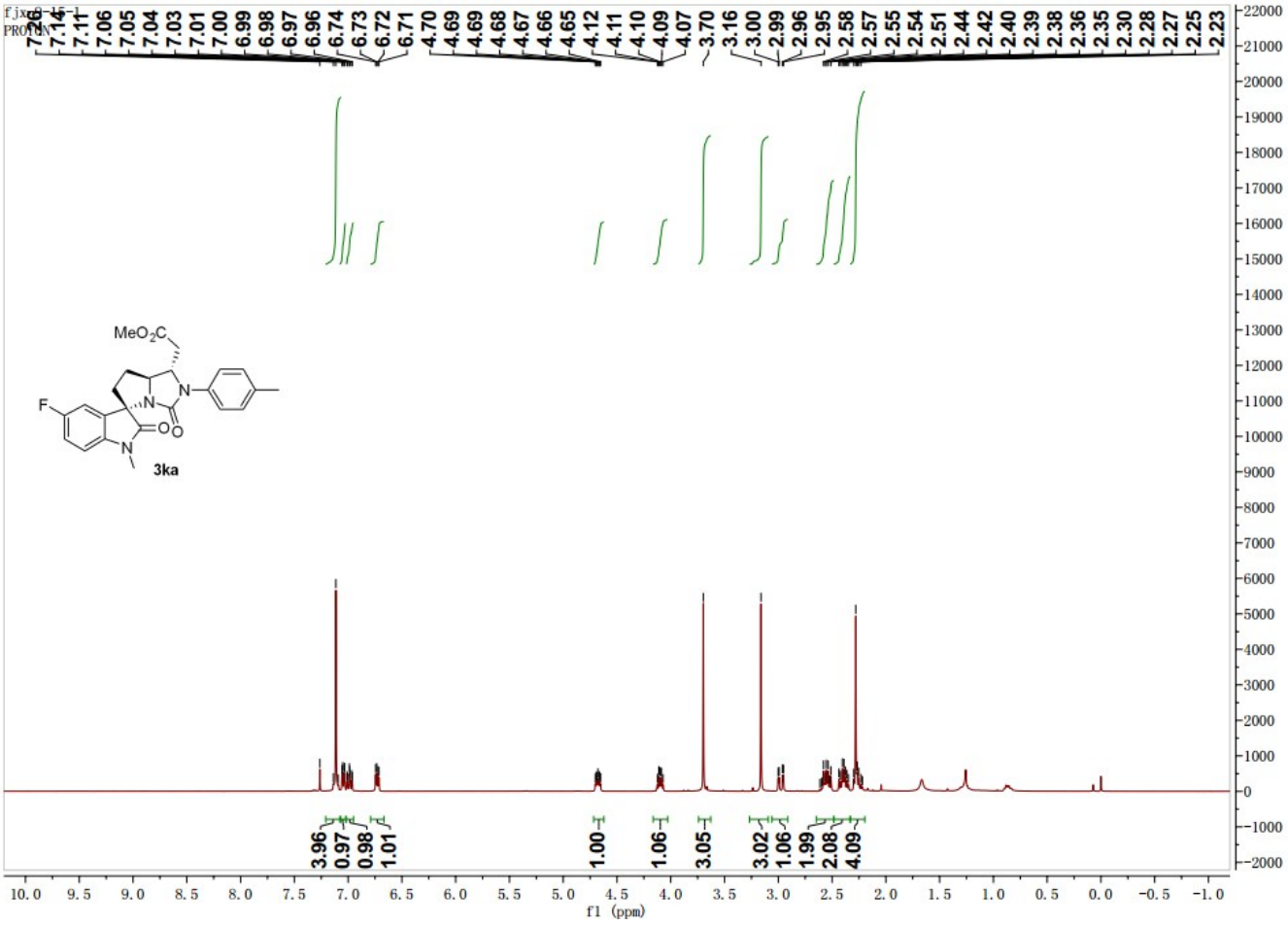
40.22
37.69
32.42
26.84
MeO2C
CF3
Cl
N
O
4ja
f1 (ppm)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4.12
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4.07
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2.54
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2.23
MeO2C
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0.98
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1.00
1.06
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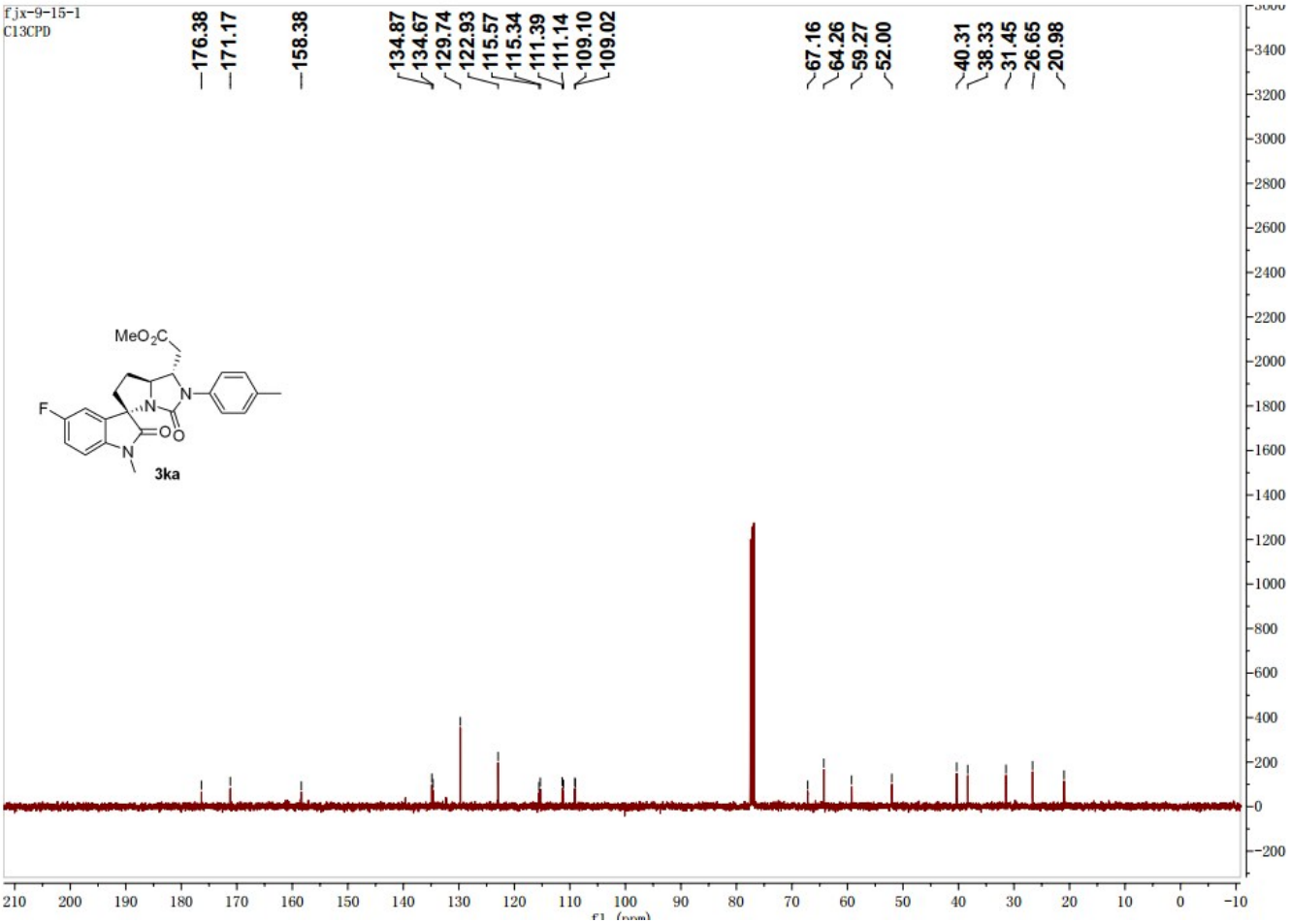
2.08
4.09
f1 (ppm)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111.39
111.14
109.10
109.02
67.16
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MeO2C
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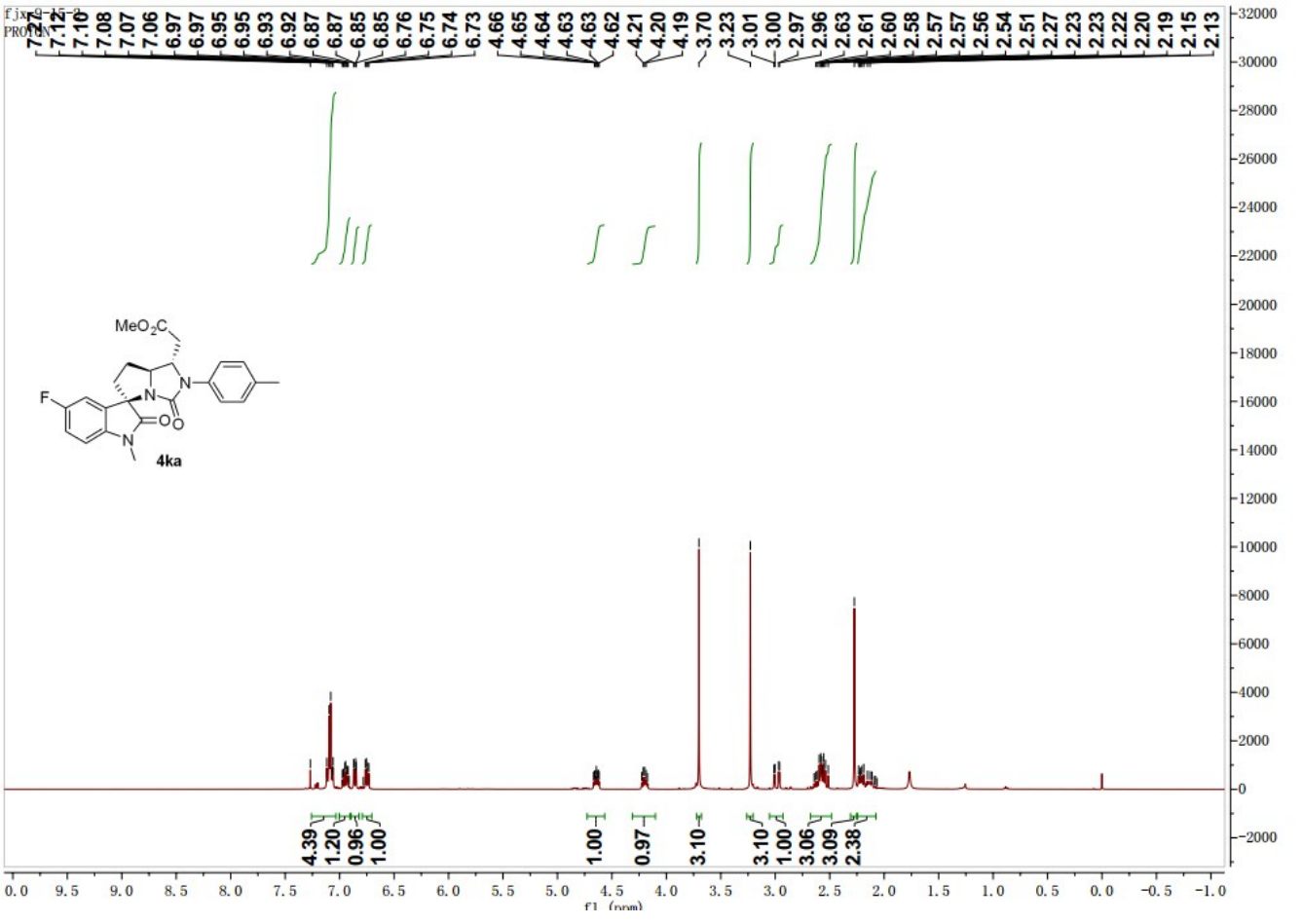
O
N
N
3ka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6.85
6.76
6.75
6.74
6.73
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4.65
4.64
4.63
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4.62
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3.23
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3.00
2.97
2.96
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2.61
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2.57
2.57
2.56
2.54
2.51
2.27
2.23
2.23
2.22
2.20
2.19
2.15
2.13
MeO2C
F
O
O
N
N
4ka
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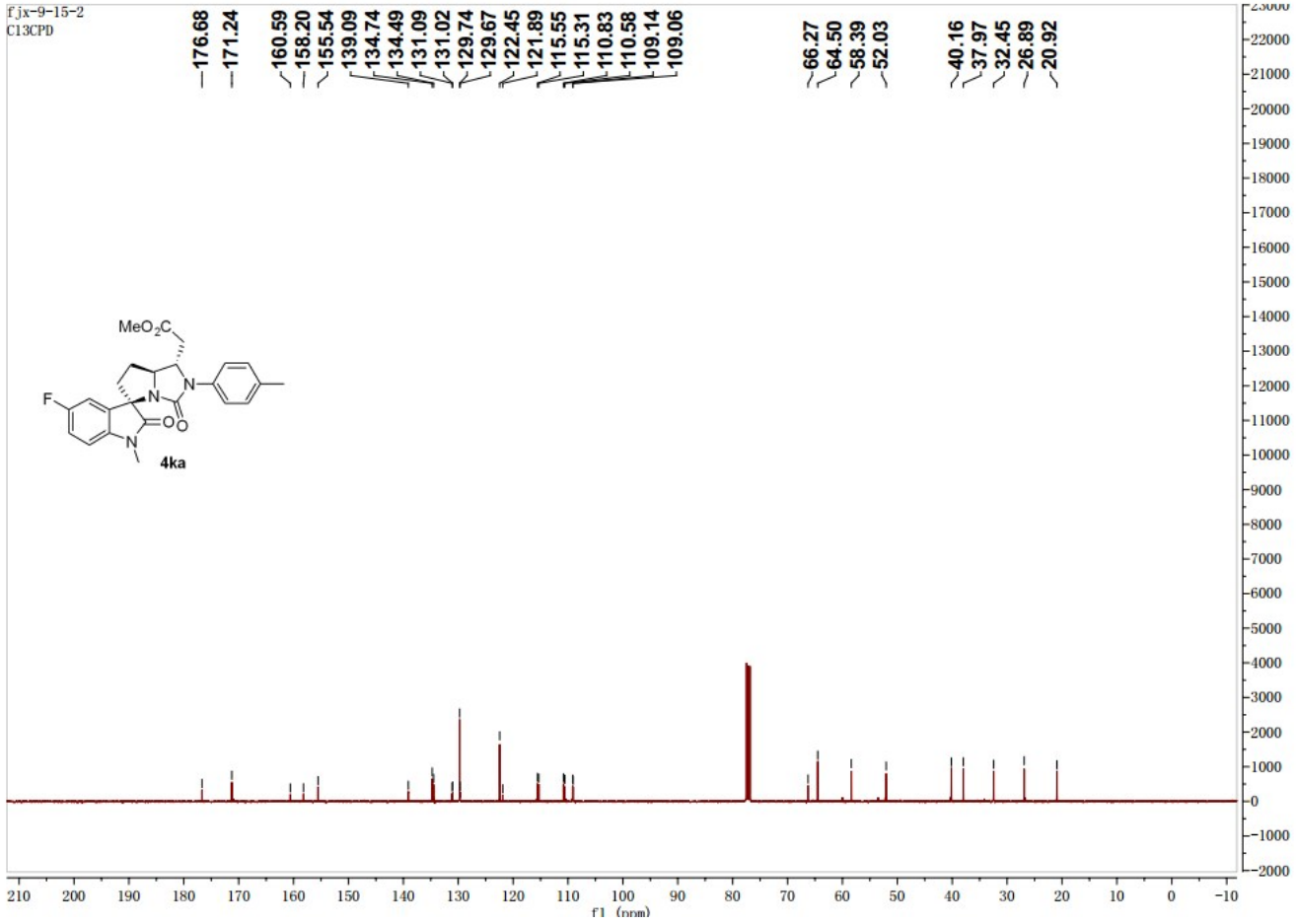
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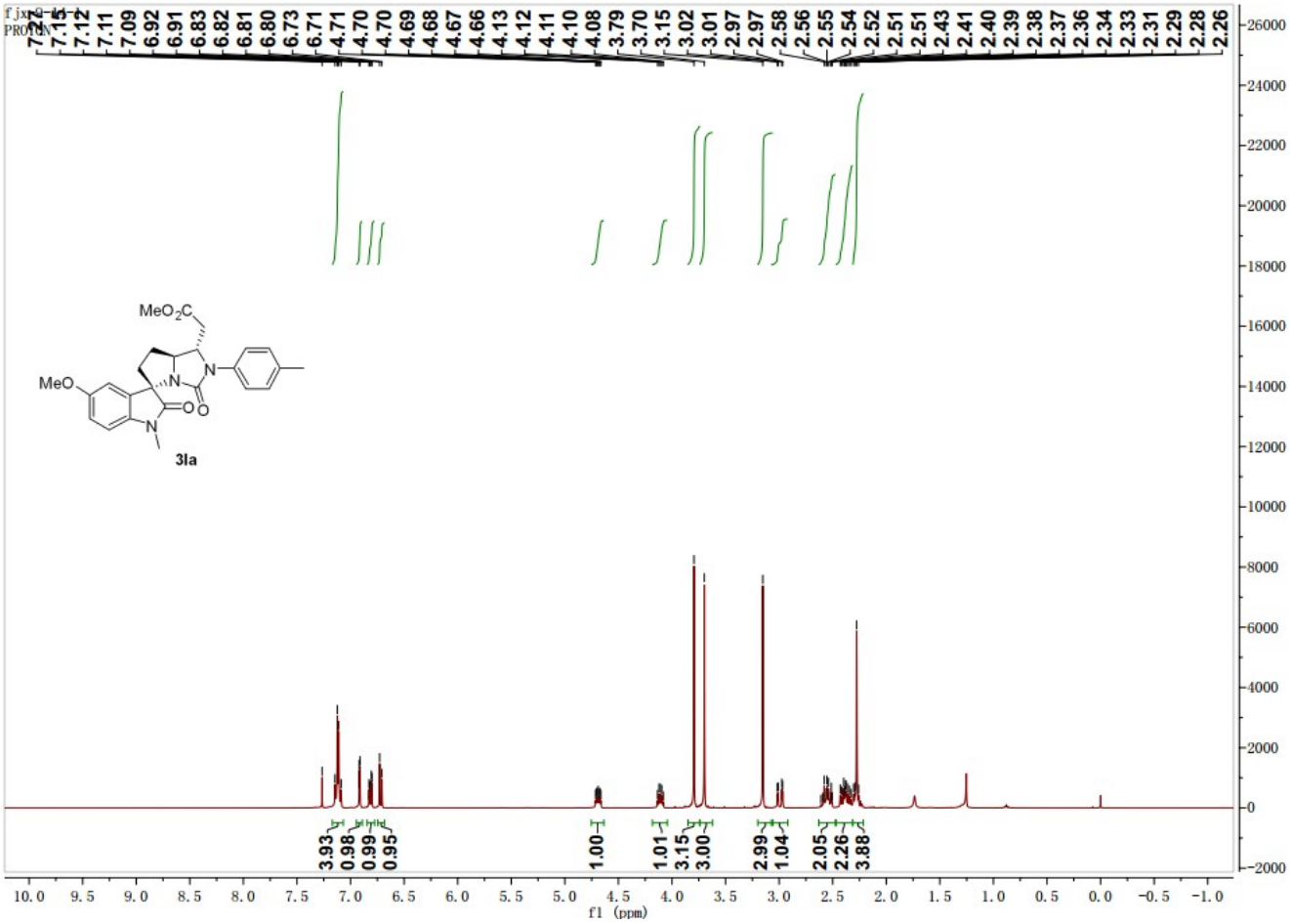
26.89
20.92
MeO2C
F
O
O
4ka
f1 (ppm)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4.68
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2.51
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2.37
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MeO
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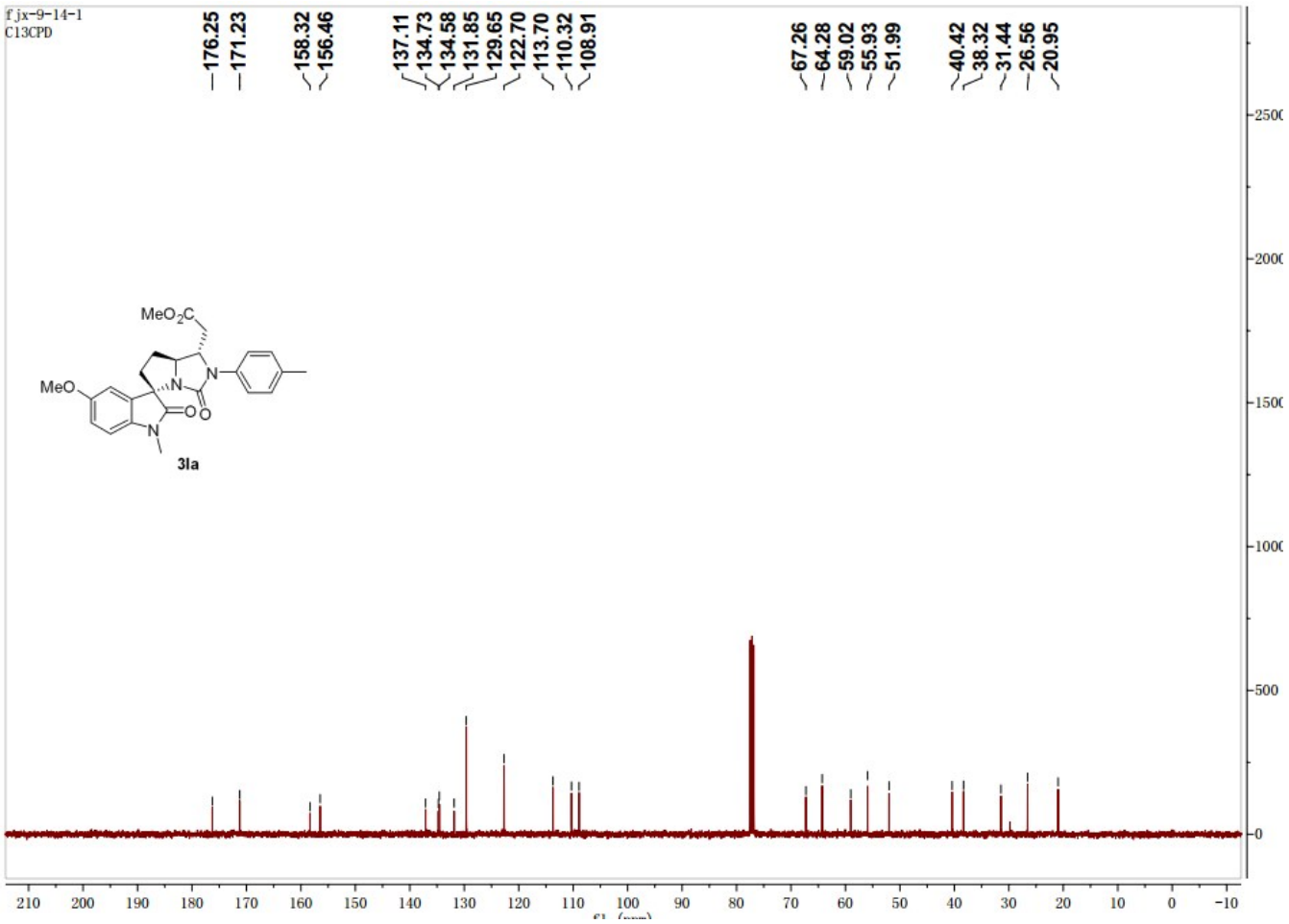
f1 (ppm)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108.91
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59.02
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N
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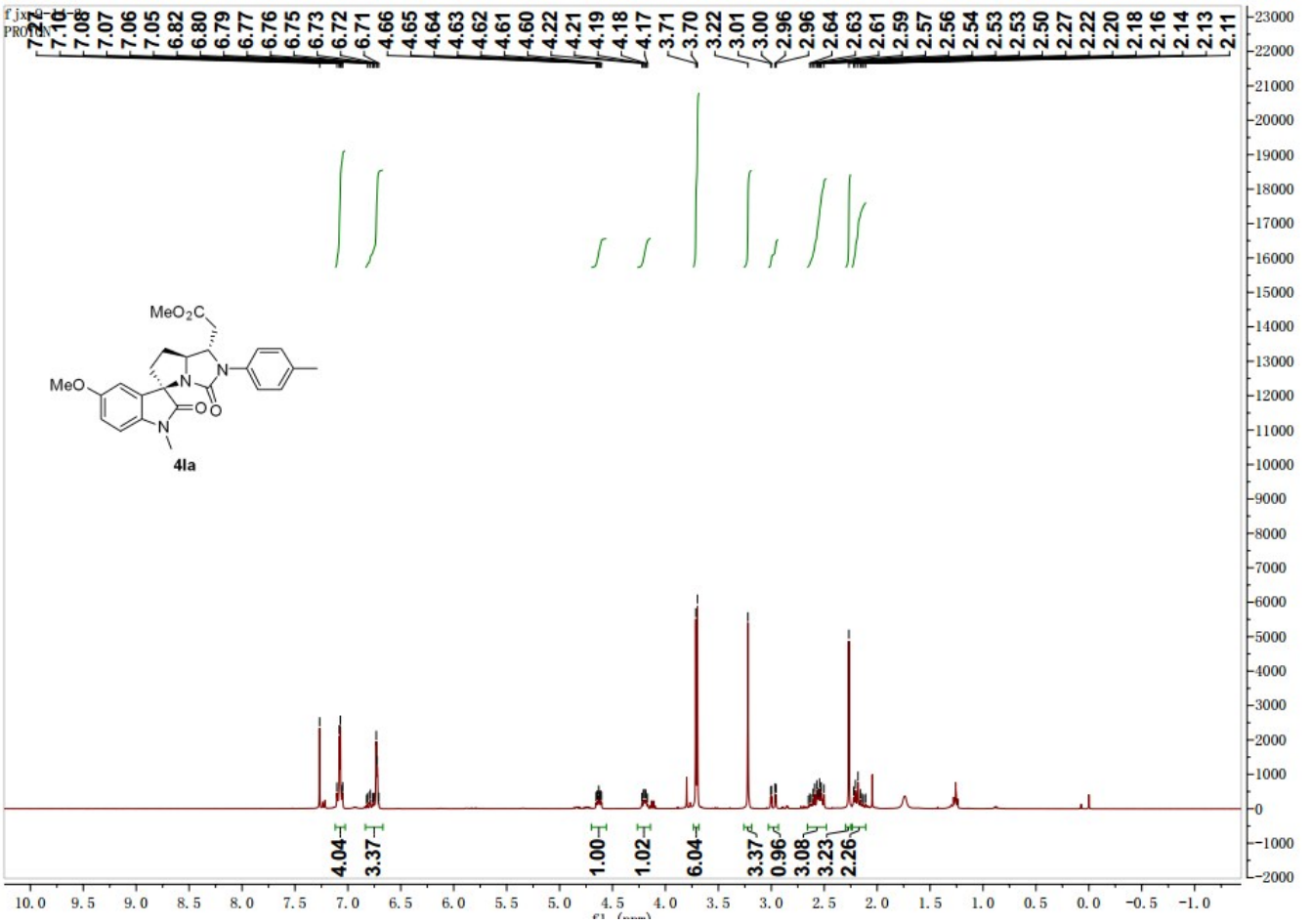
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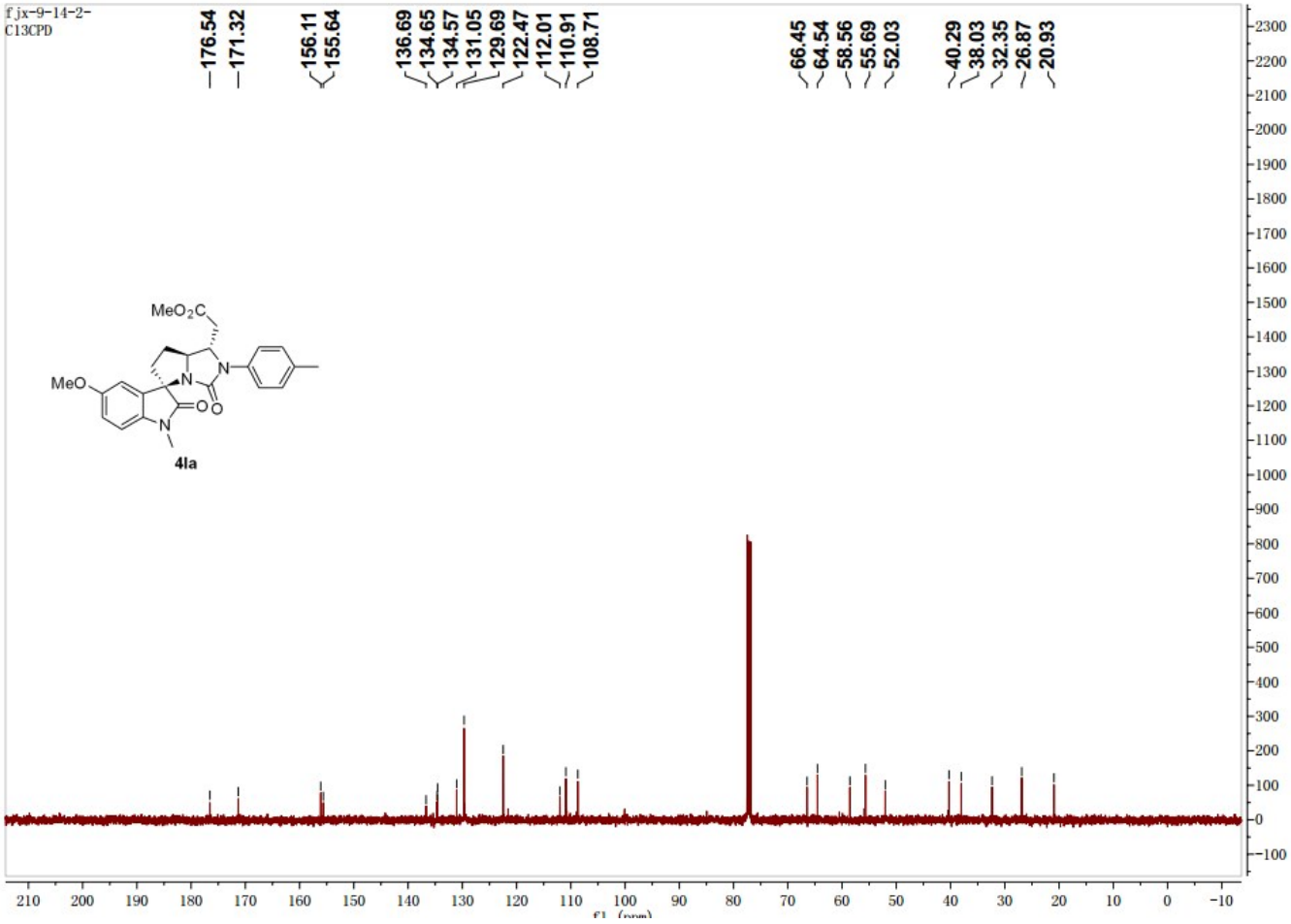
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66.45
64.54
58.56
55.69
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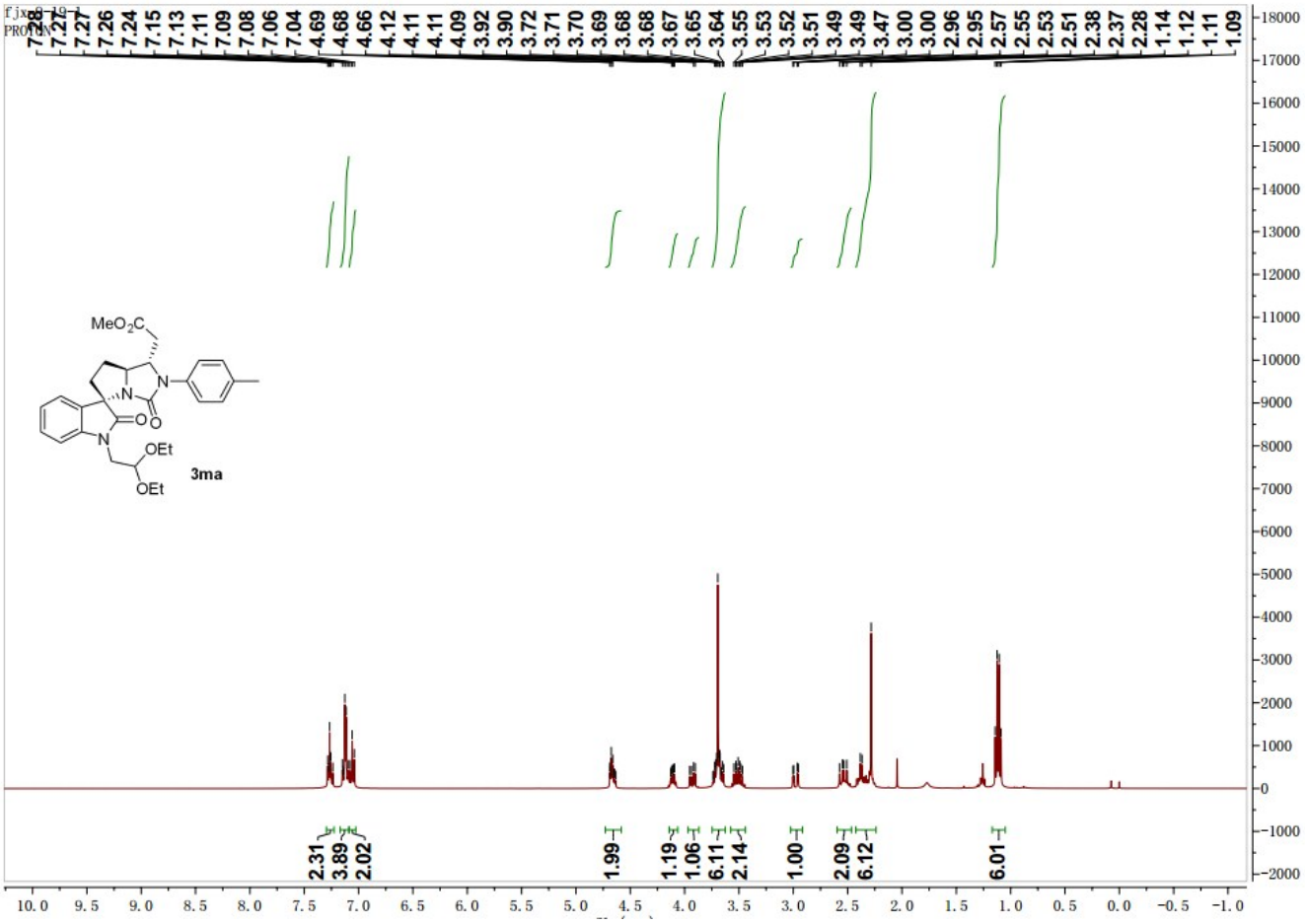
26.87
20.93
MeO2C
MeO
N
O
O
N
4la
f1 (ppm)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7.13
7.11
7.09
7.08
7.06
7.04
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4.68
4.66
4.12
4.11
4.11
4.09
3.92
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3.70
3.69
3.68
3.68
3.67
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3.53
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3.51
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2.95
2.57
2.55
2.53
2.51
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1.14
1.12
1.11
1.09
MeO2C
O
O
OEt
OEt
3ma
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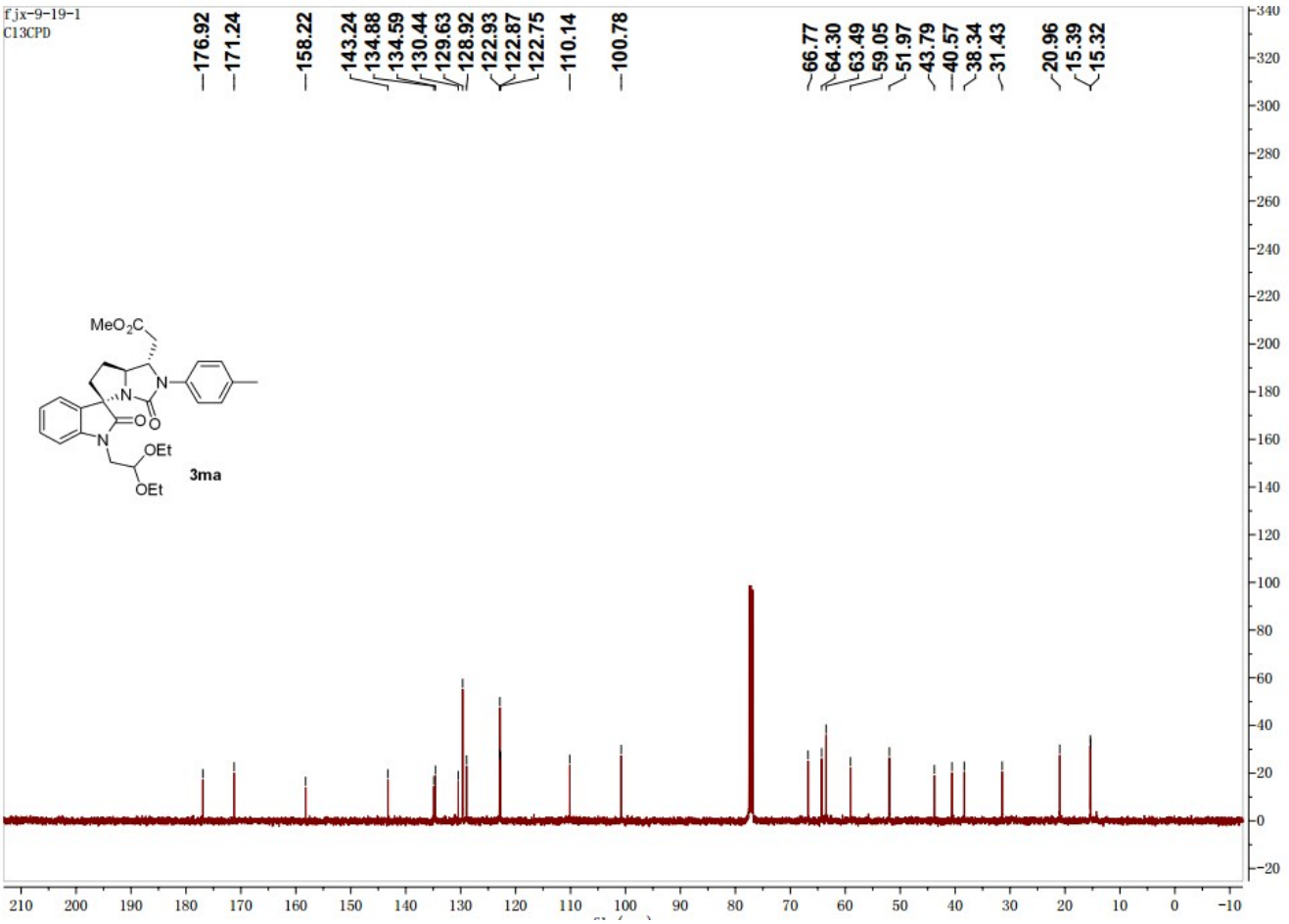
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MeO2C
O
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OEt
OEt
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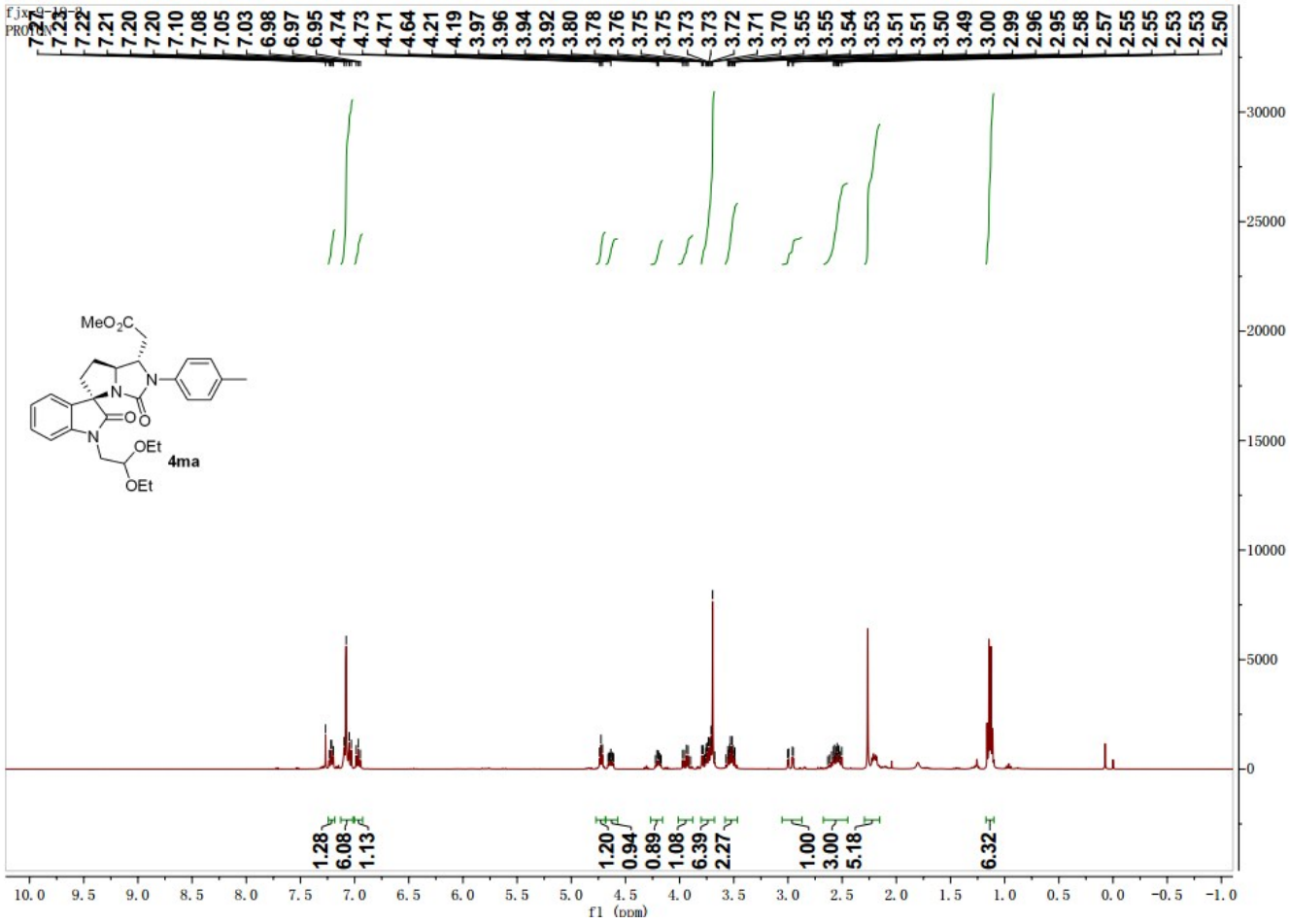
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2.50
MeO2C
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OEt
4ma
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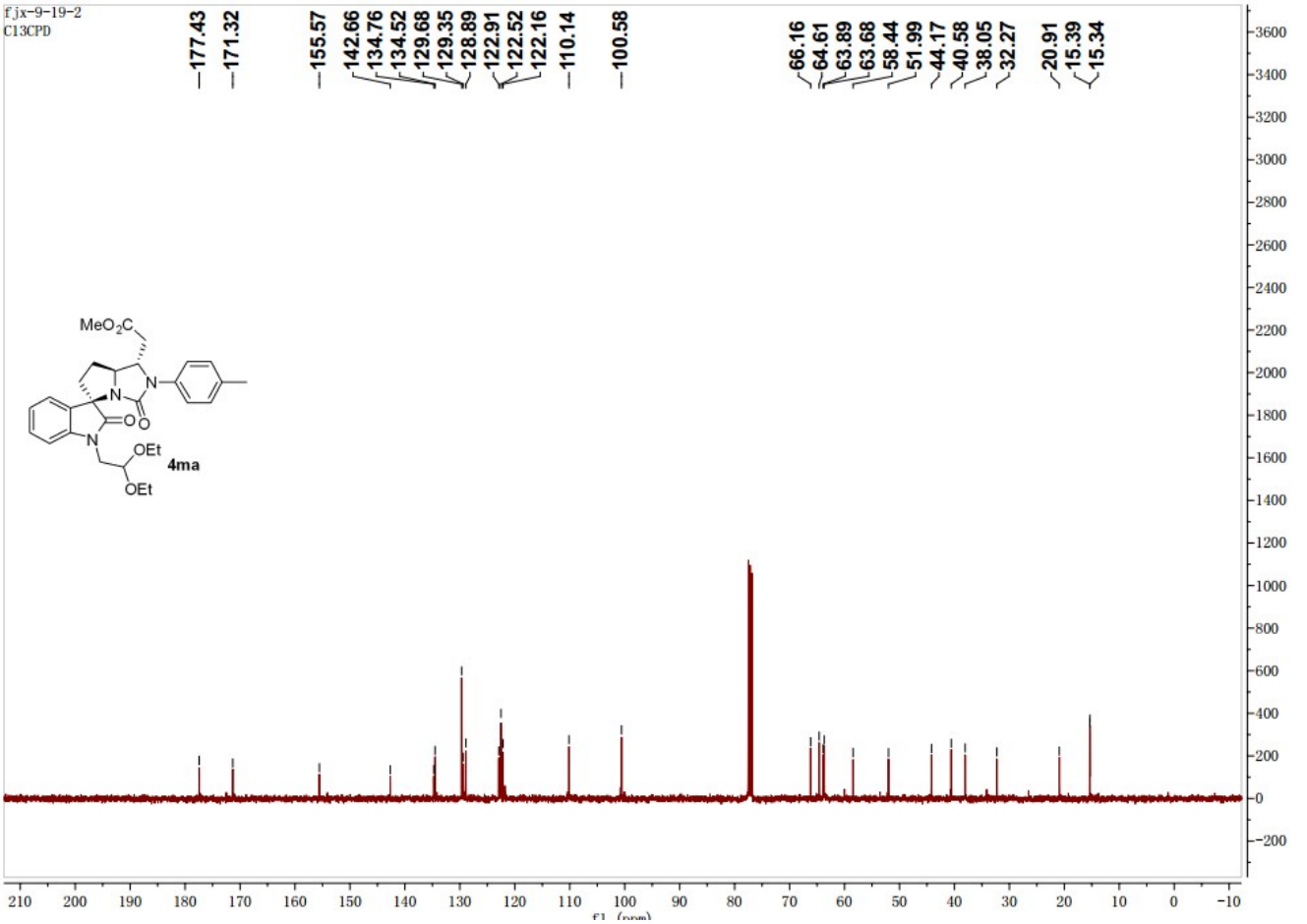
f1 (ppm)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63.68
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51.99
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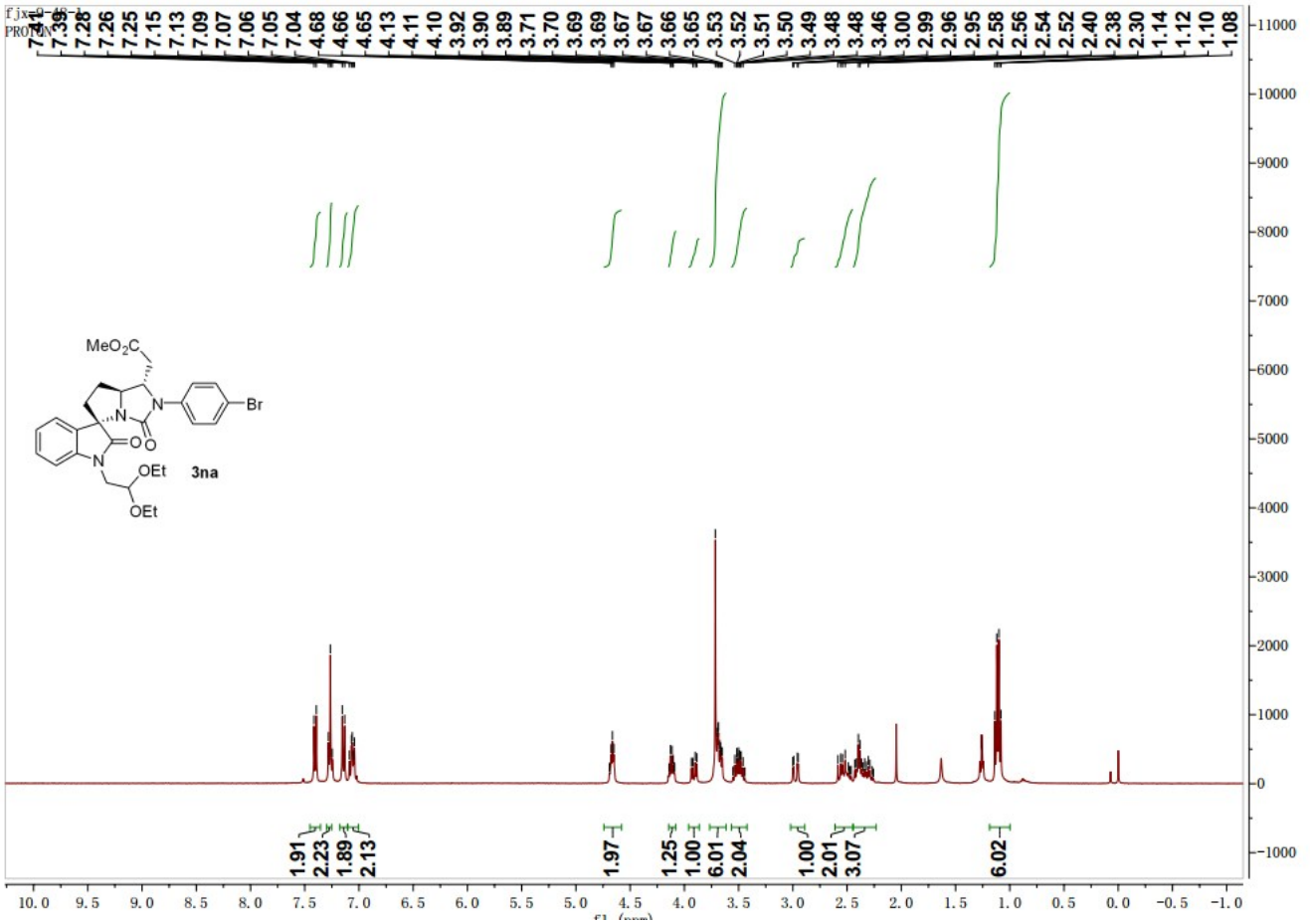
15.34
MeO2C
OEt
OEt
4ma
f1 (ppm)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MeO2C
Br
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O
N
OEt
OEt
3na
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2.01
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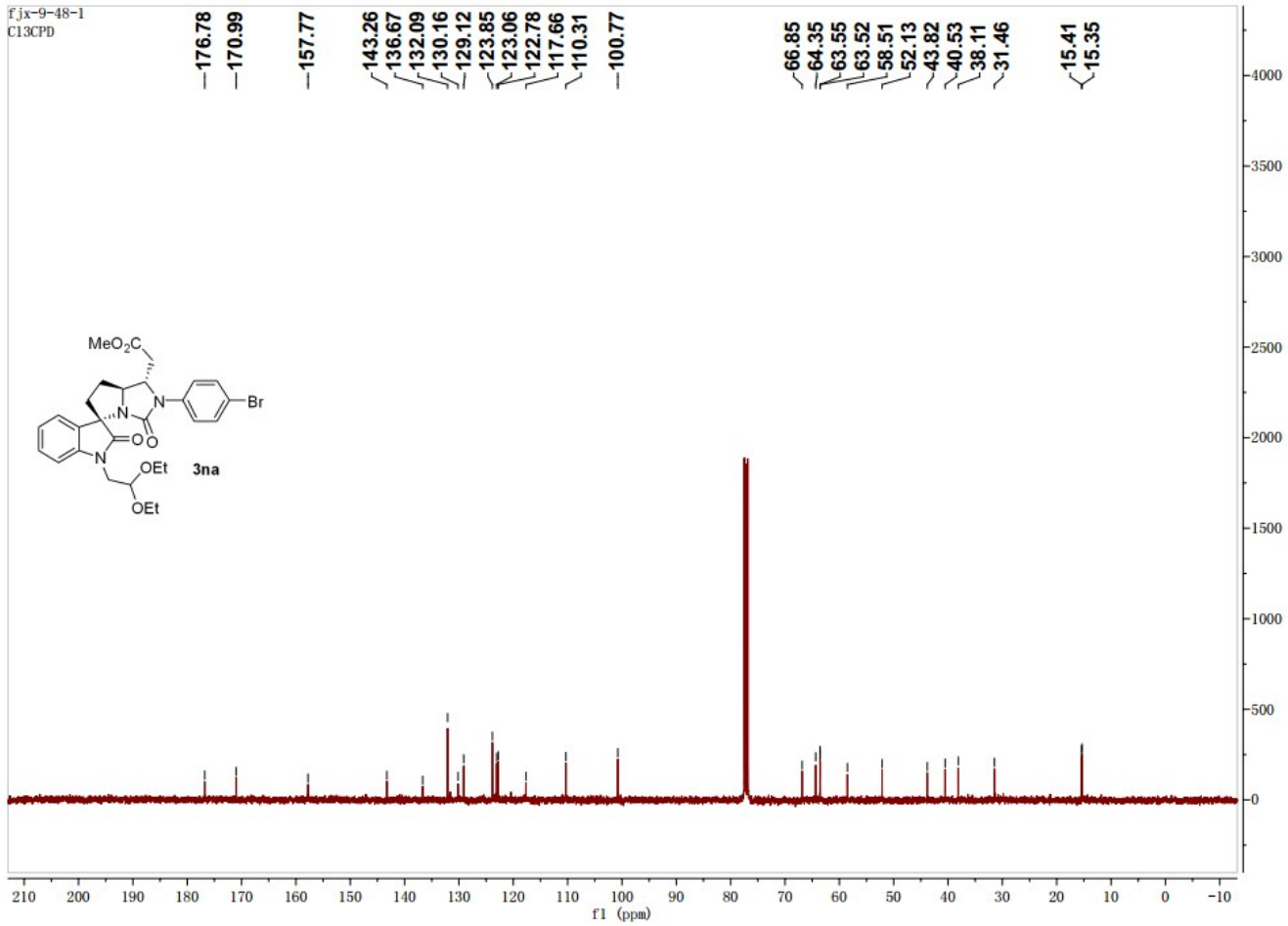
6.02
f1 (ppm)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63.52
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52.13
43.82
40.53
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15.35
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Br
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O
N
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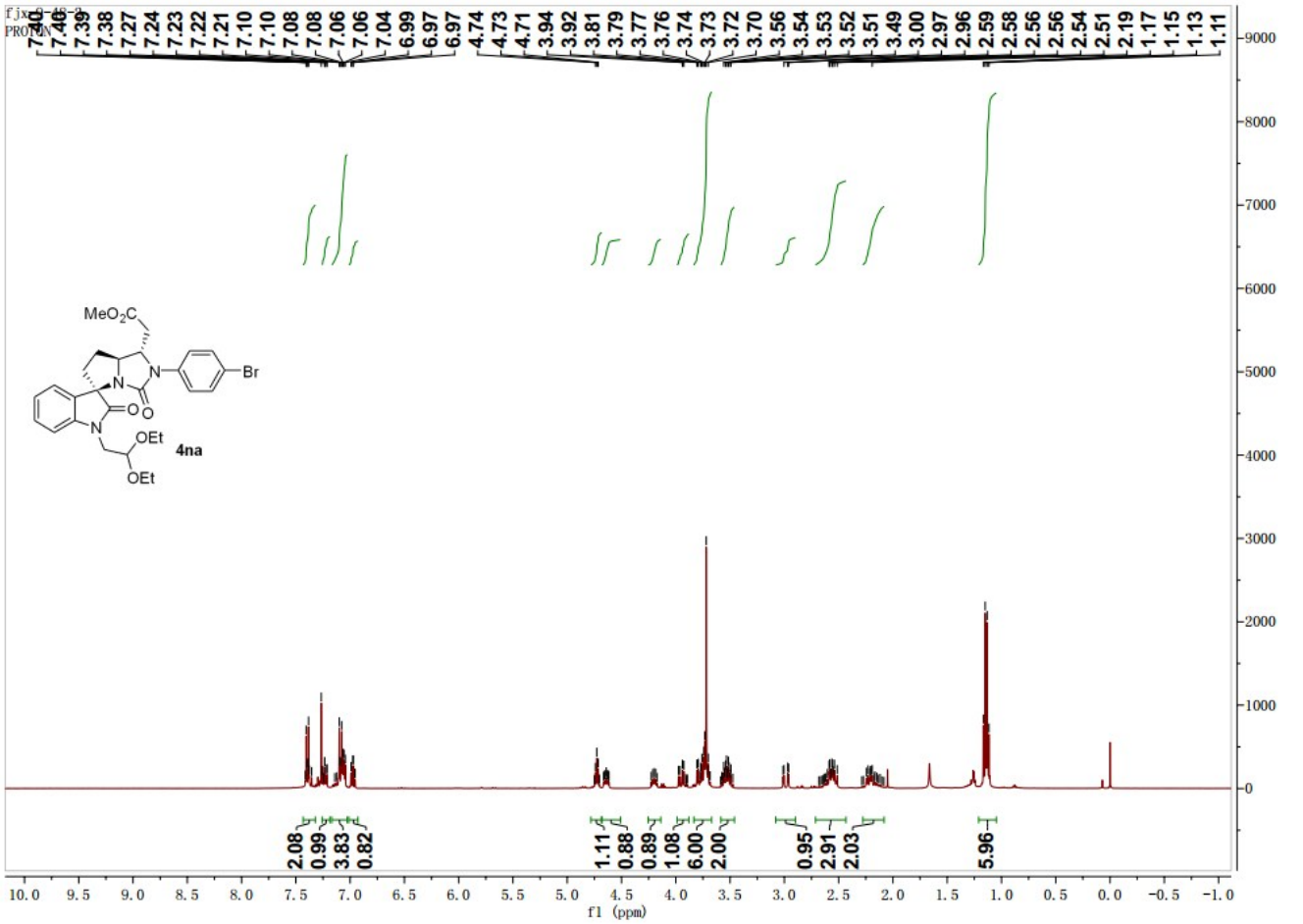
OEt
3na
f1 (ppm)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2.19
1.17
1.15
1.13
1.11
MeO2C
Br
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O
N
N
N
OEt
OEt
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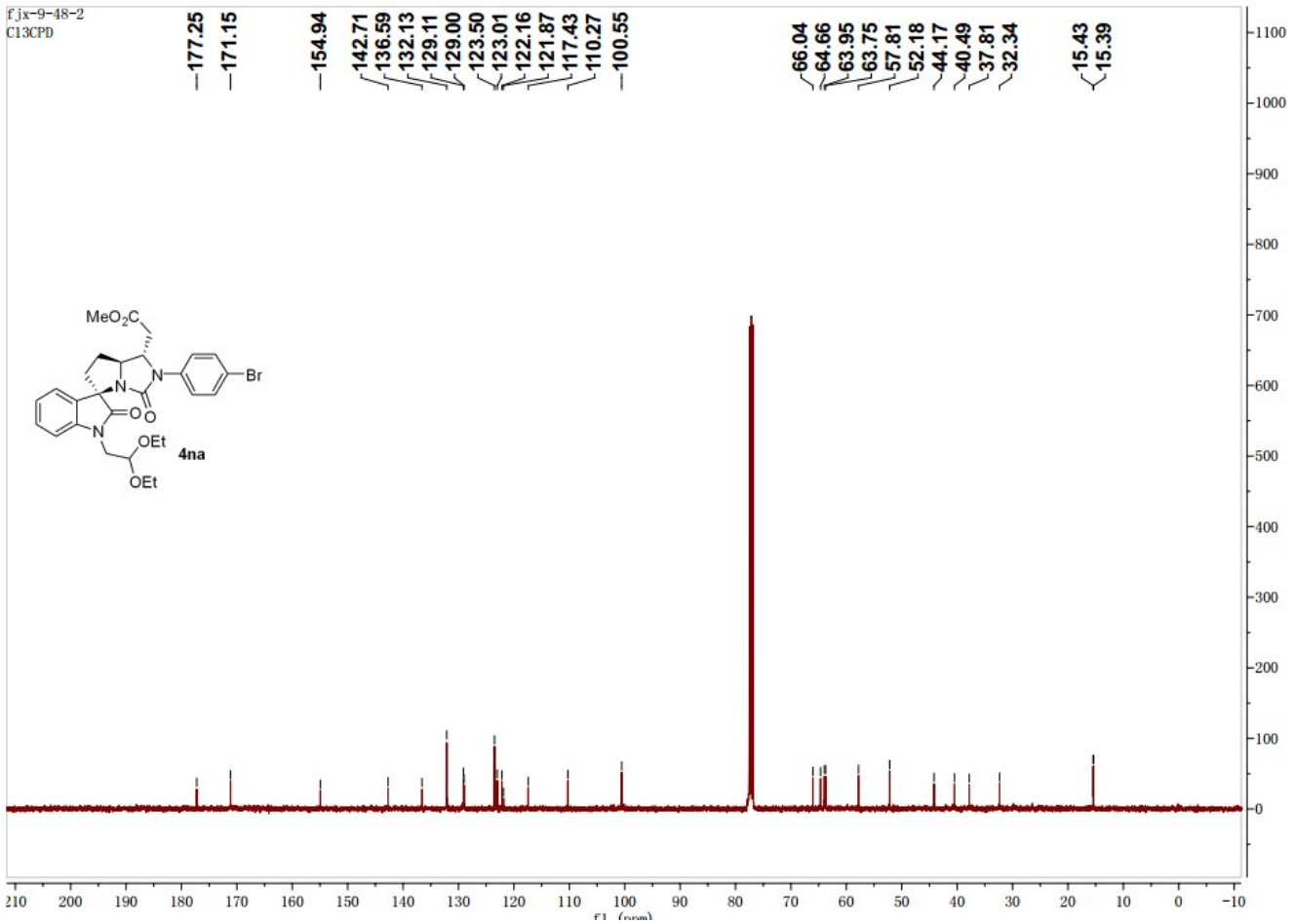
5.96
f1 (ppm)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123.01
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100.55
66.04
64.66
63.95
63.75
57.81
52.18
44.17
40.49
37.81
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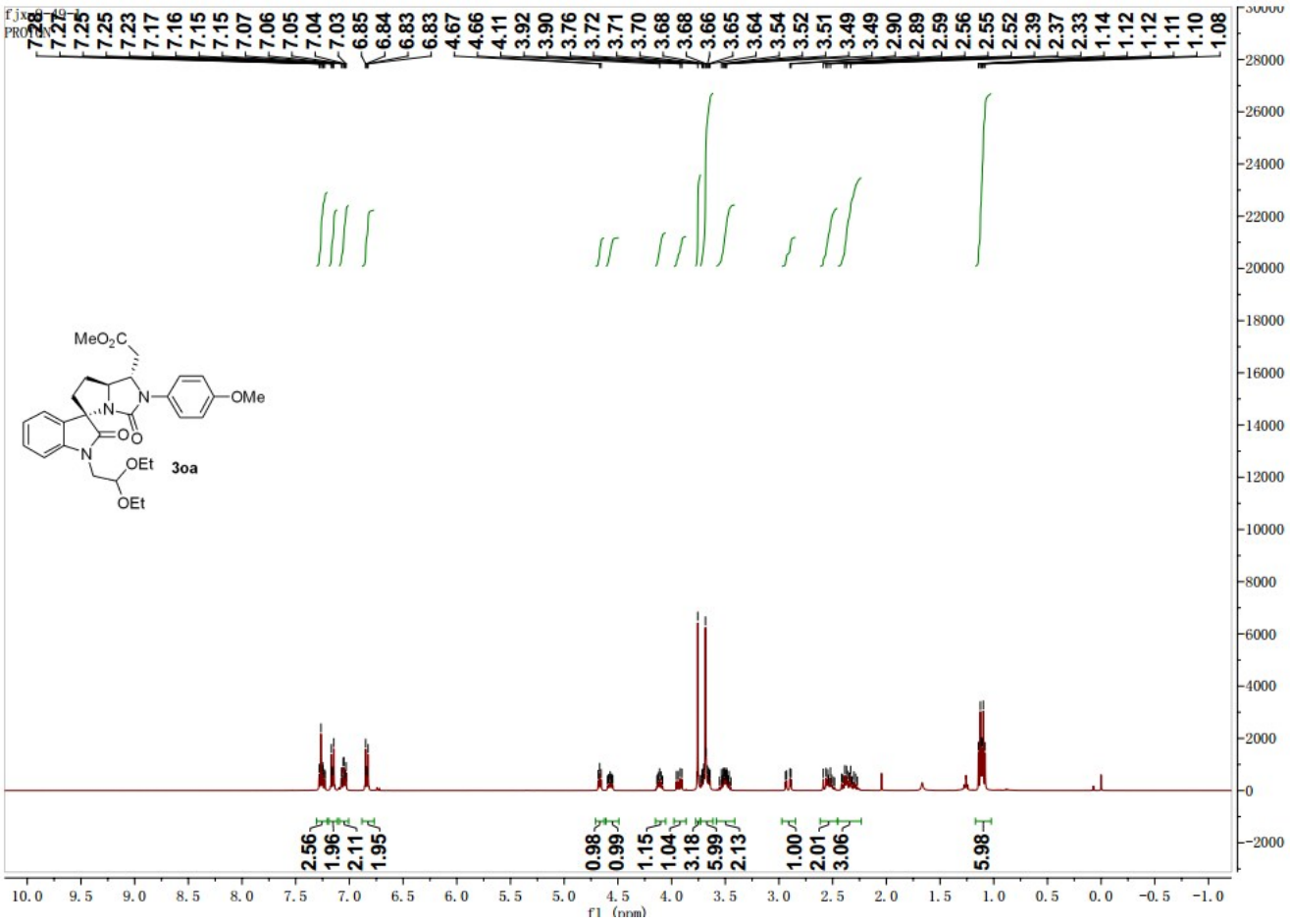
15.39
MeO2C
Br
O
O
N
N
N
OEt
OEt
4na
f1 (ppm)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MeO2C
OMe
OEt
OEt
3oa
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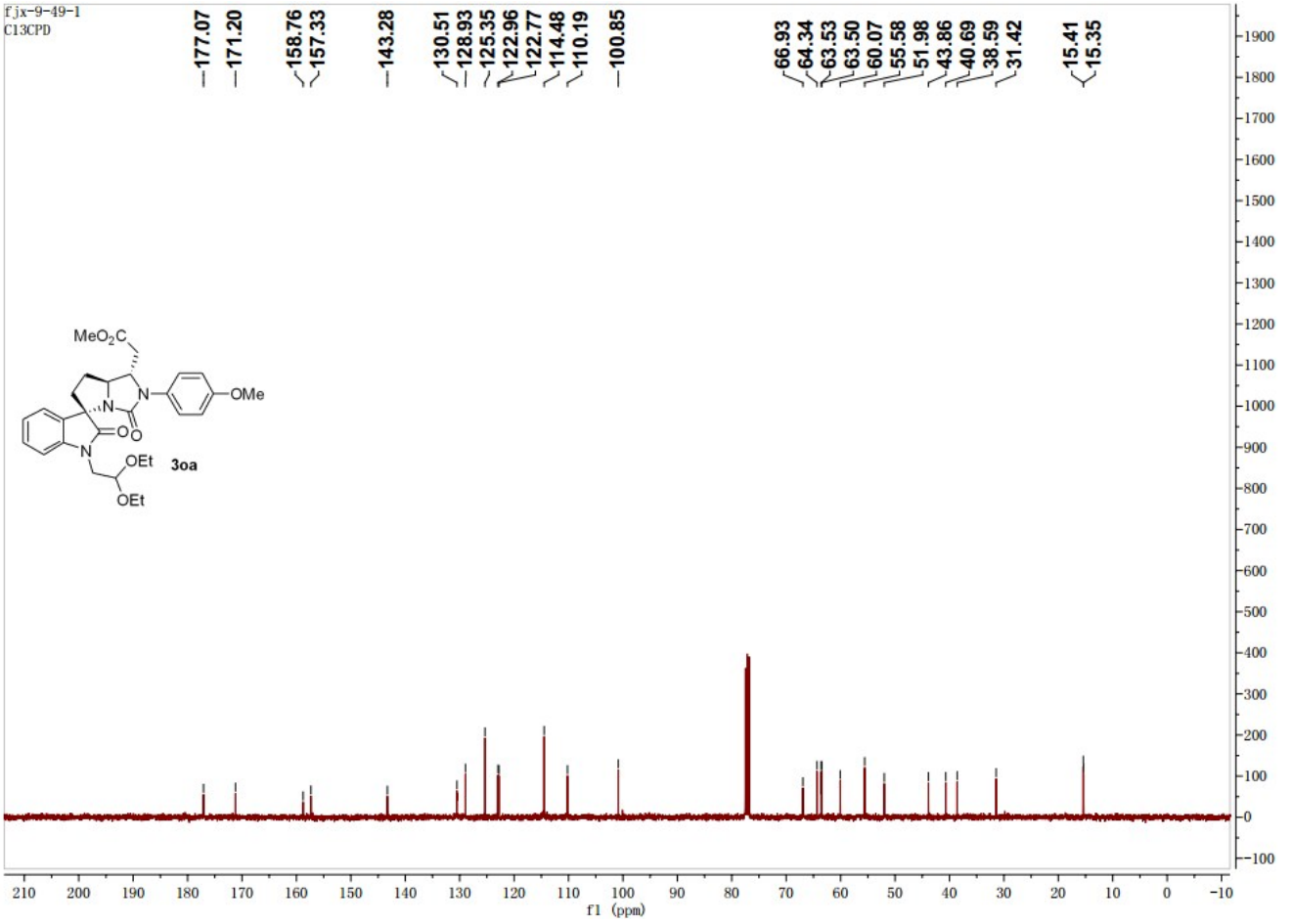
f1 (ppm)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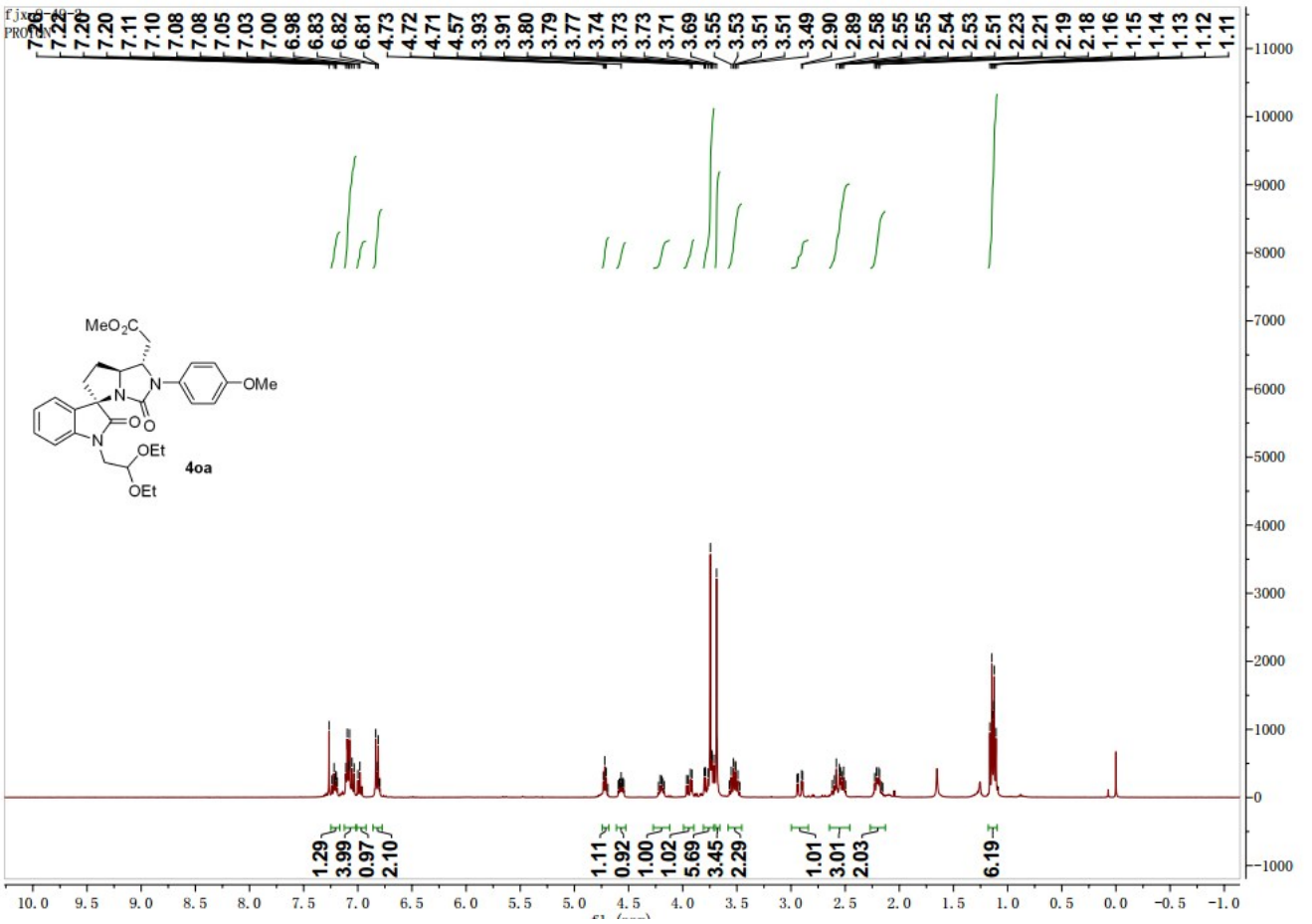
MeO2C
OMe
OEt
OEt
3oa
f1 (ppm)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OMe
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OEt
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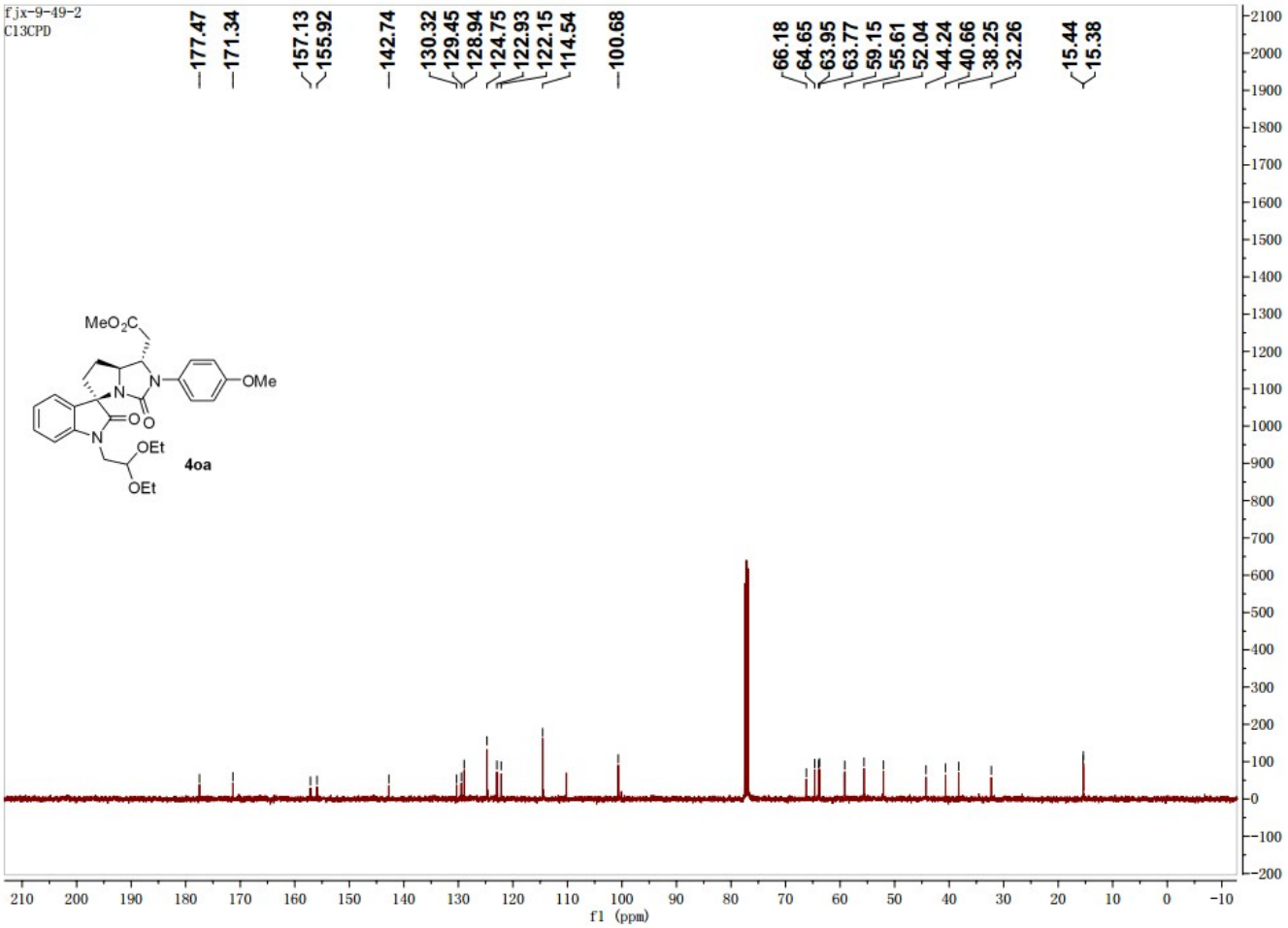
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55.61
52.04
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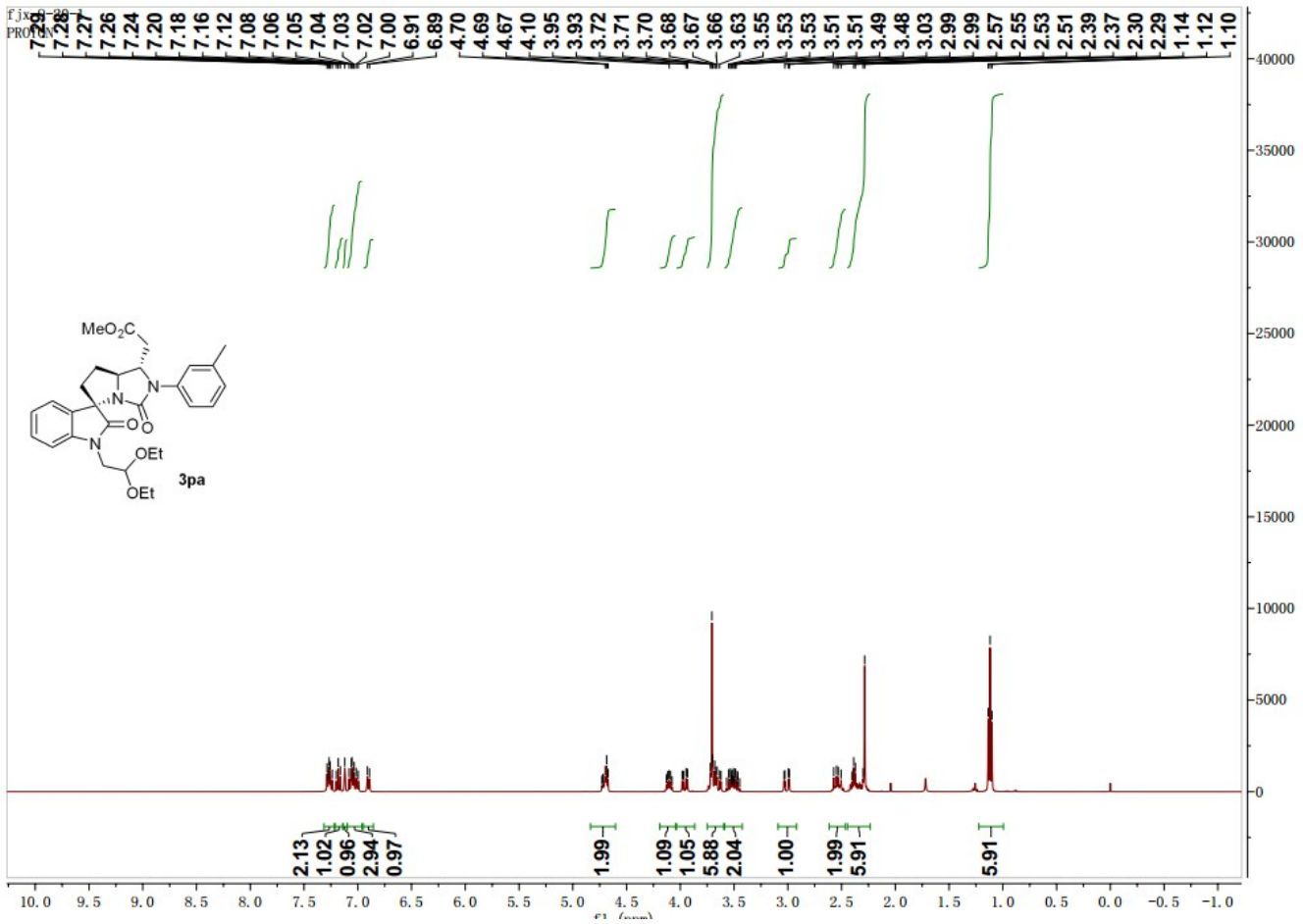
15.38
MeO2C
OMe
OEt
OEt
4oa
f1 (ppm)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7.08
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1.14
1.12
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OEt
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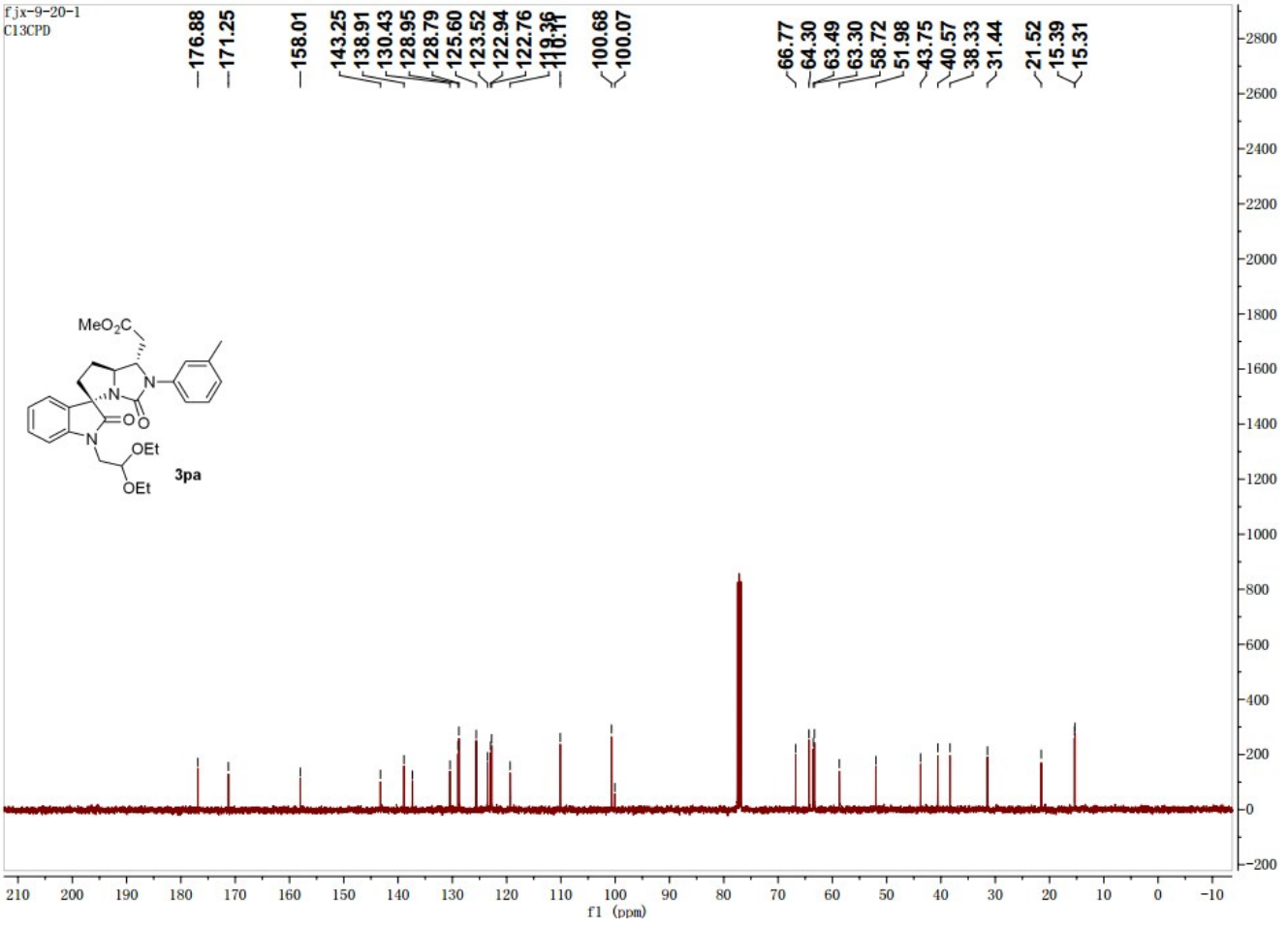
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MeO2C
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OEt
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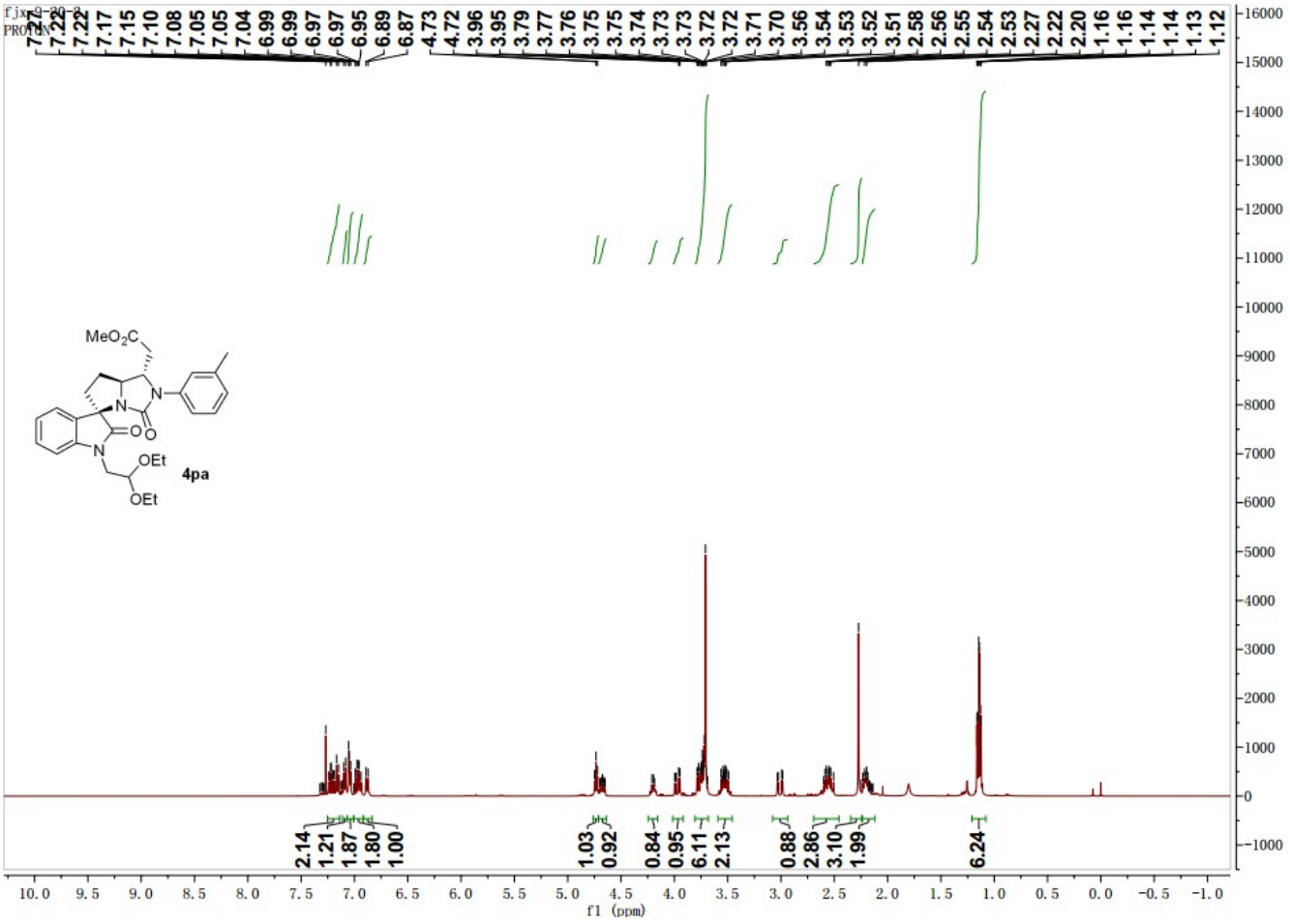
f1 (ppm)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3.73
3.72
3.72
3.71
3.70
3.56
3.54
3.53
3.52
3.51
2.58
2.56
2.55
2.54
2.53
2.27
2.22
2.20
1.16
1.16
1.14
1.14
1.13
1.12
MeO2C
OEt
OEt
4pa
2.14
1.21
1.87
1.80
1.00
1.03
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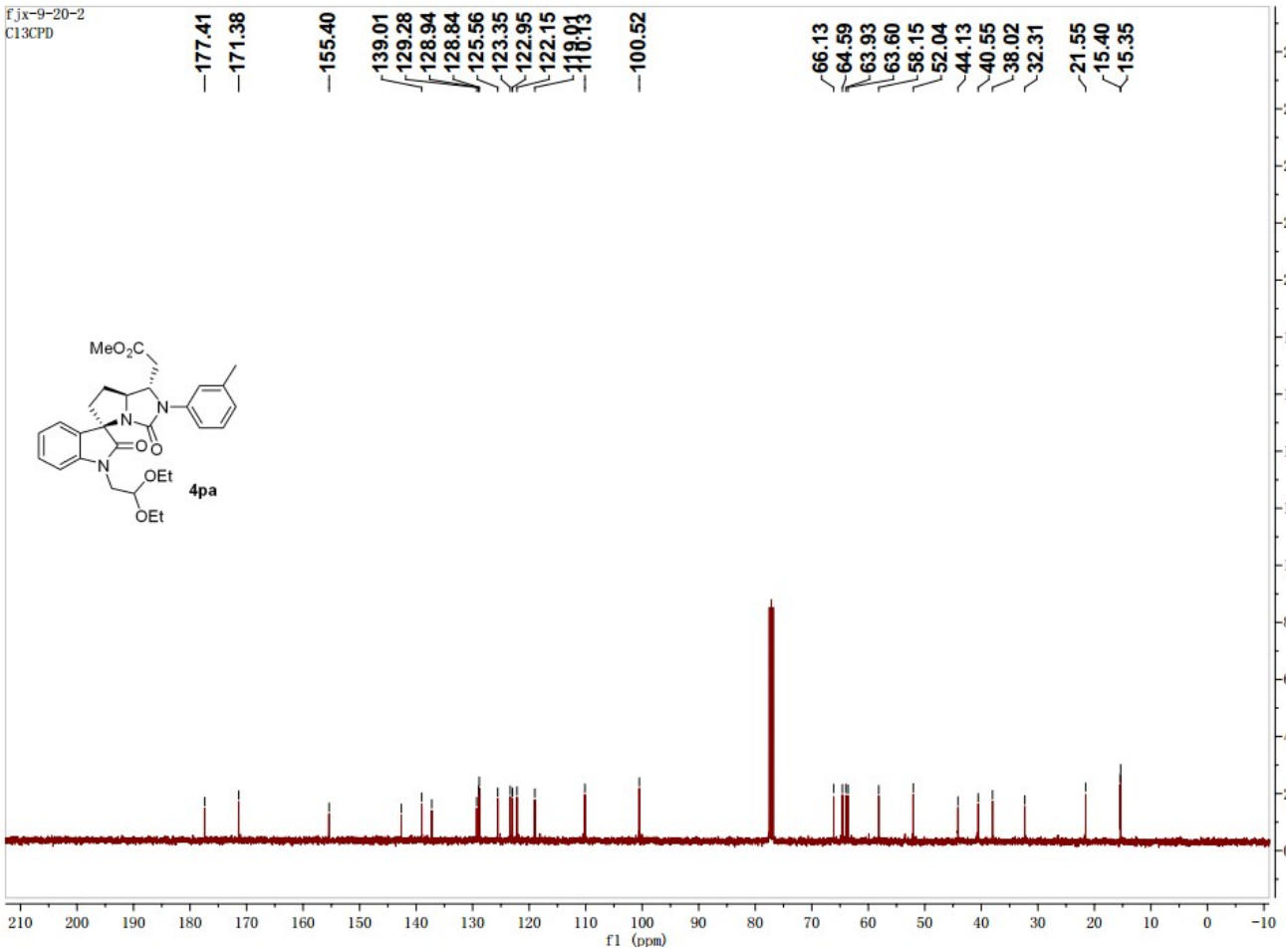
0.95
6.11
2.13
0.88
2.86
3.10
1.99
6.24
f1 (ppm)


fjx-9-20-2
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122.95
122.15
110.01
110.13
100.52
66.13
64.59
63.93
63.60
58.15
52.04
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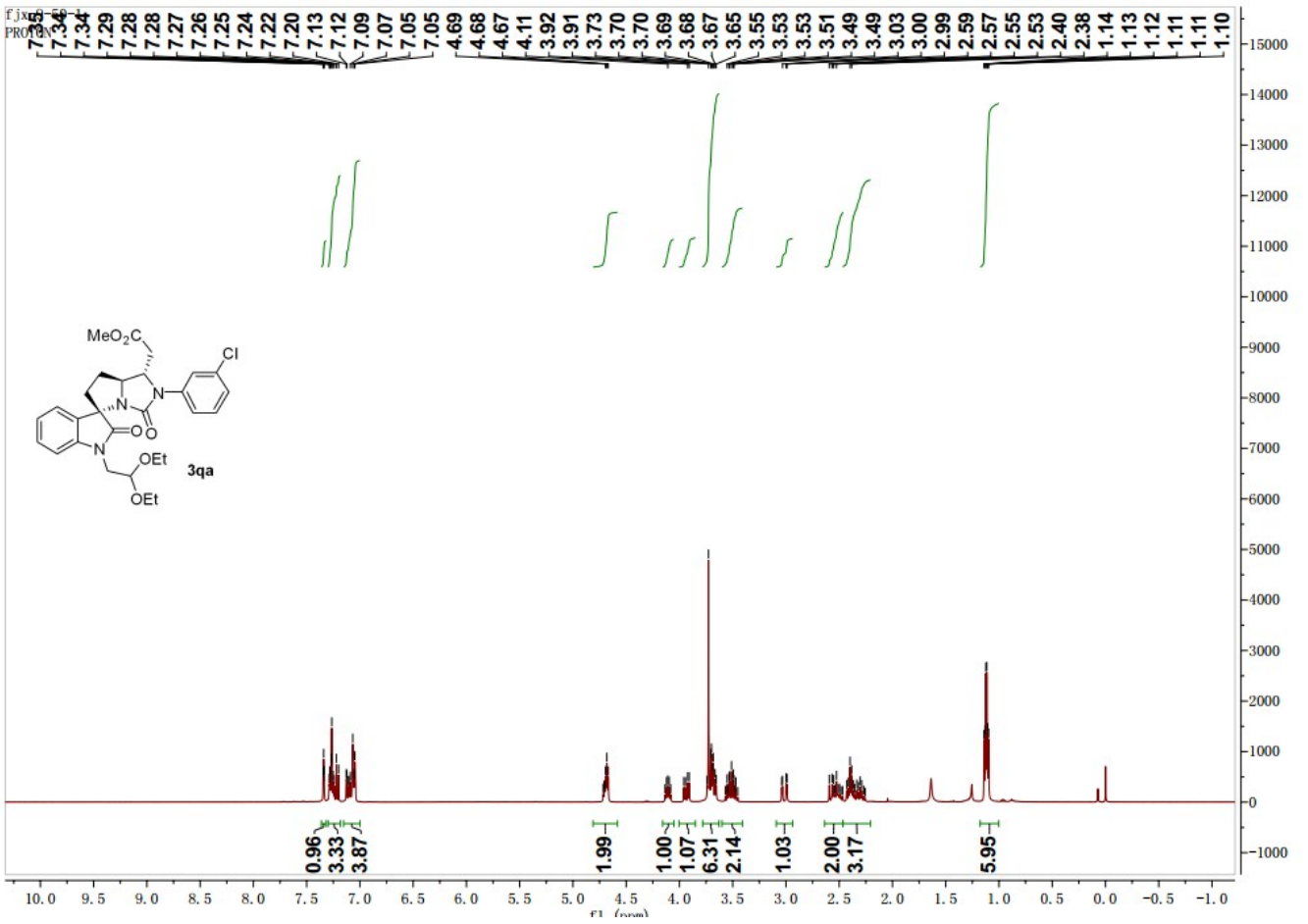
38.02
32.31
21.55
15.40
15.35
MeO2C
OEt
OEt
4pa
f1 (ppm)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7.05
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3.70
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3.55
3.53
3.53
3.51
3.49
3.49
3.03
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2.53
2.40
2.38
1.14
1.13
1.12
1.11
1.11
1.10
MeO2C
Cl
N
O
O
N
OEt
OEt
3qa
0.96
3.33
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1.00
1.07
6.31
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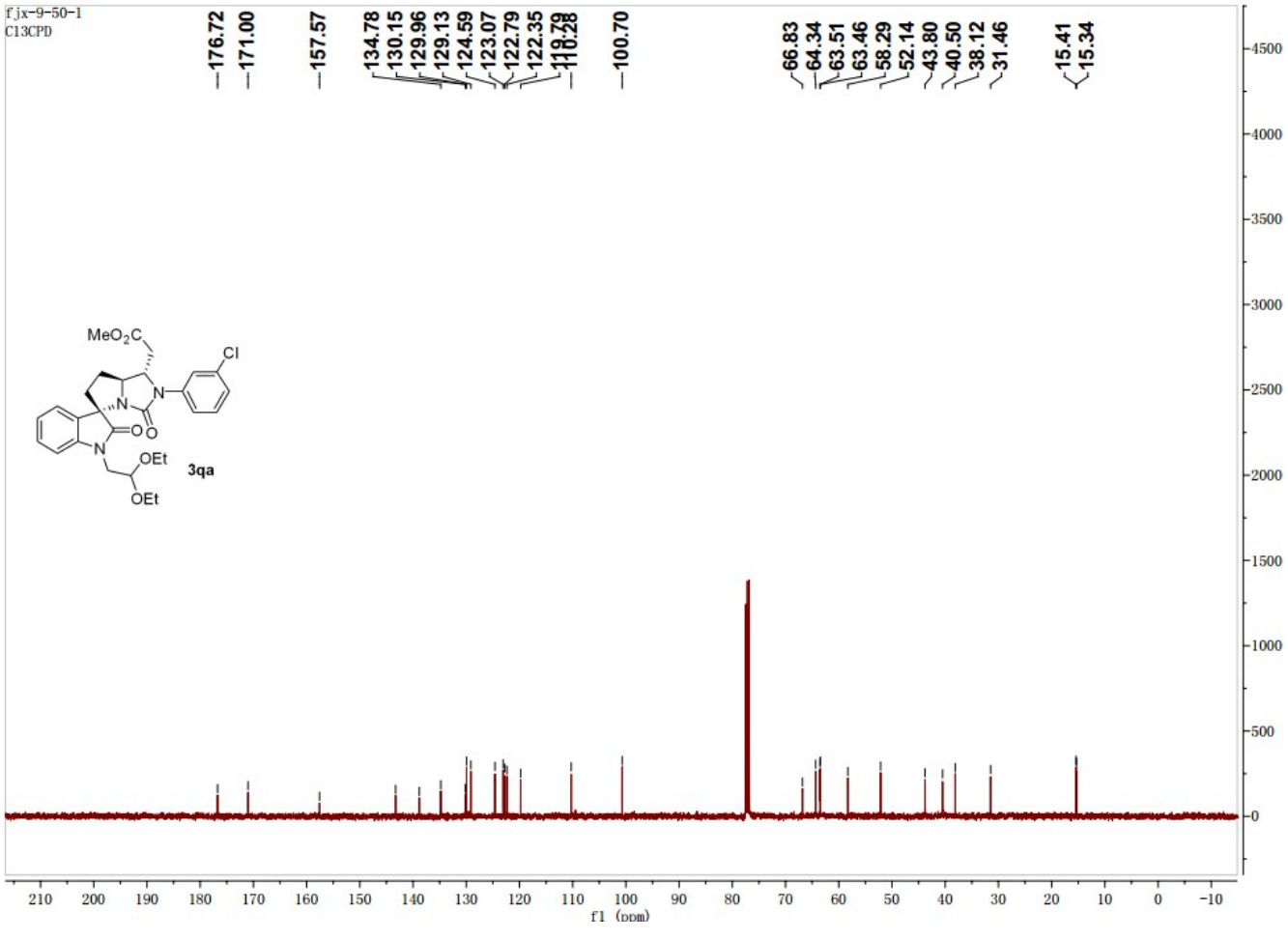
1.03
2.00
3.17
5.95
f1 (ppm)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122.35
100.70
66.83
64.34
63.51
63.46
58.29
52.14
43.80
40.50
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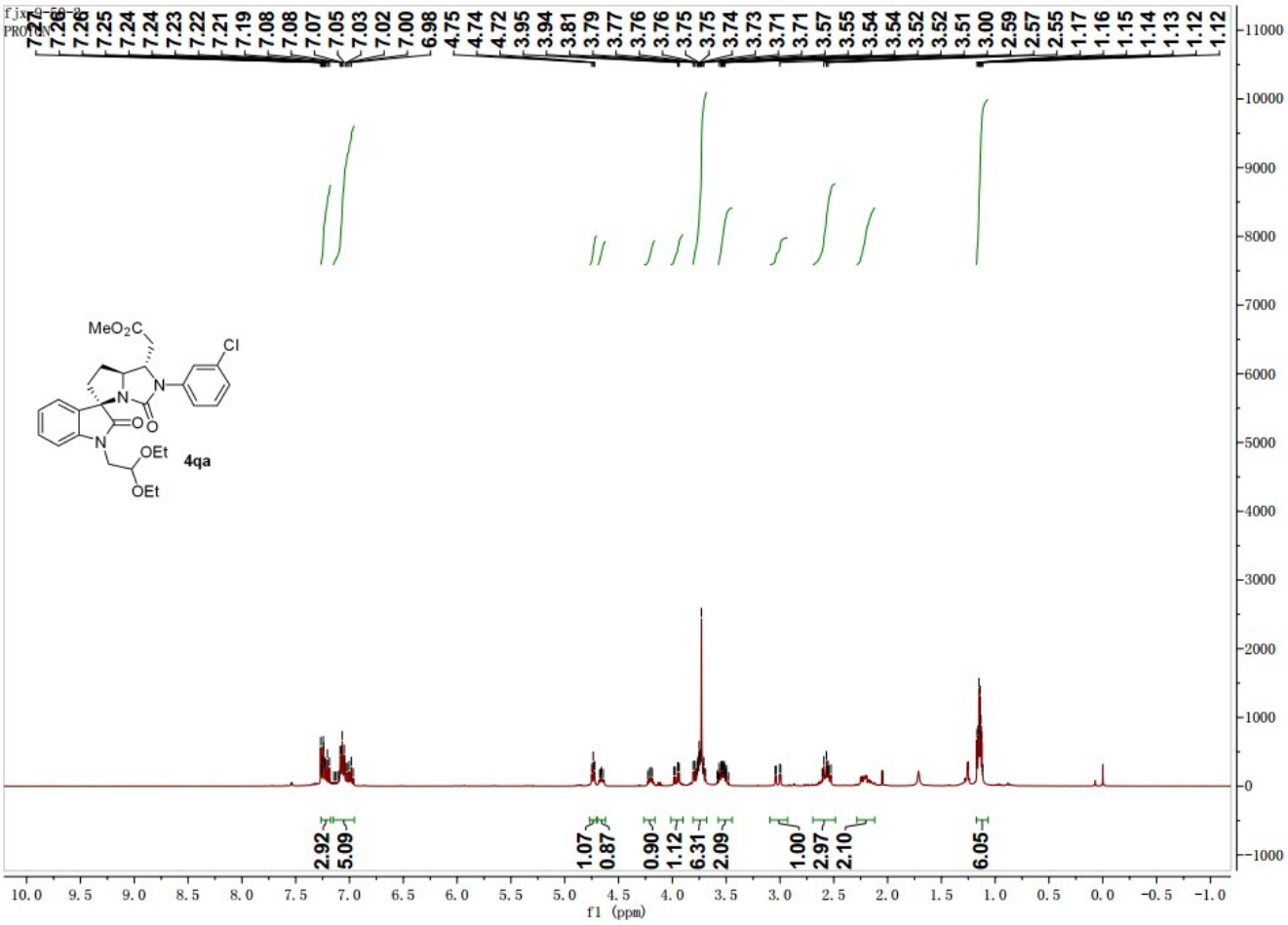
15.41
15.34
MeO2C
Cl
N
O
O
N
OEt
OEt
3qa
f1 (ppm)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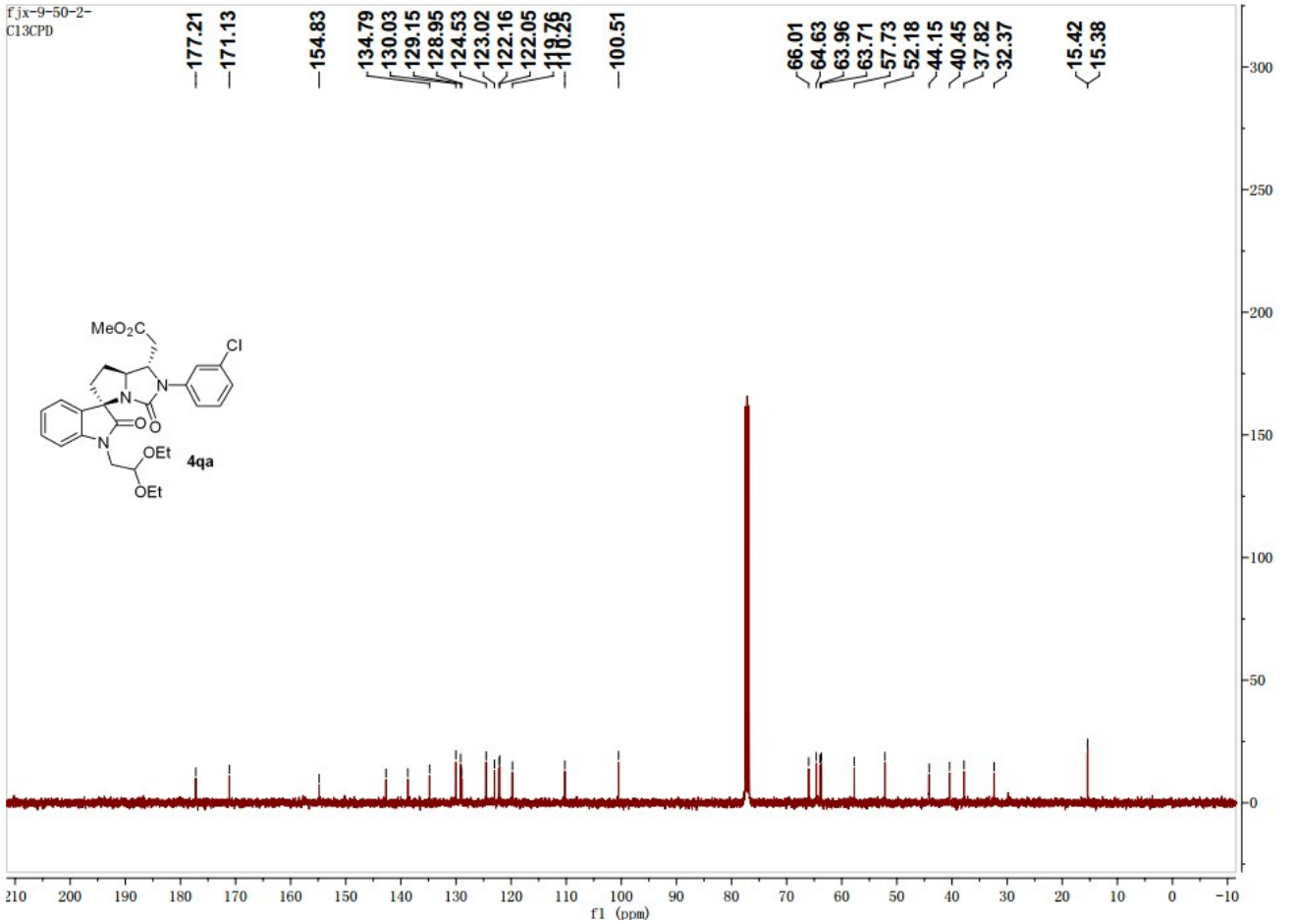
4.75 4.74 4.72 3.95 3.94 3.81 3.79 3.77 3.76 3.76 3.75 3.75 3.74 3.73 3.71 3.57 3.55 3.54 3.54 3.52 3.52 3.51 3.00 2.59 2.57 2.55 1.17 1.16 1.15 1.14 1.13 1.12 1.12
MeO2C
Cl
N
O
O
N
OEt
OEt
4qa
2.92 5.09 1.07 0.87 0.90 1.12 6.31 2.09 1.00 2.97 2.10 6.05
f1 (ppm)


fjx-9-50-2-
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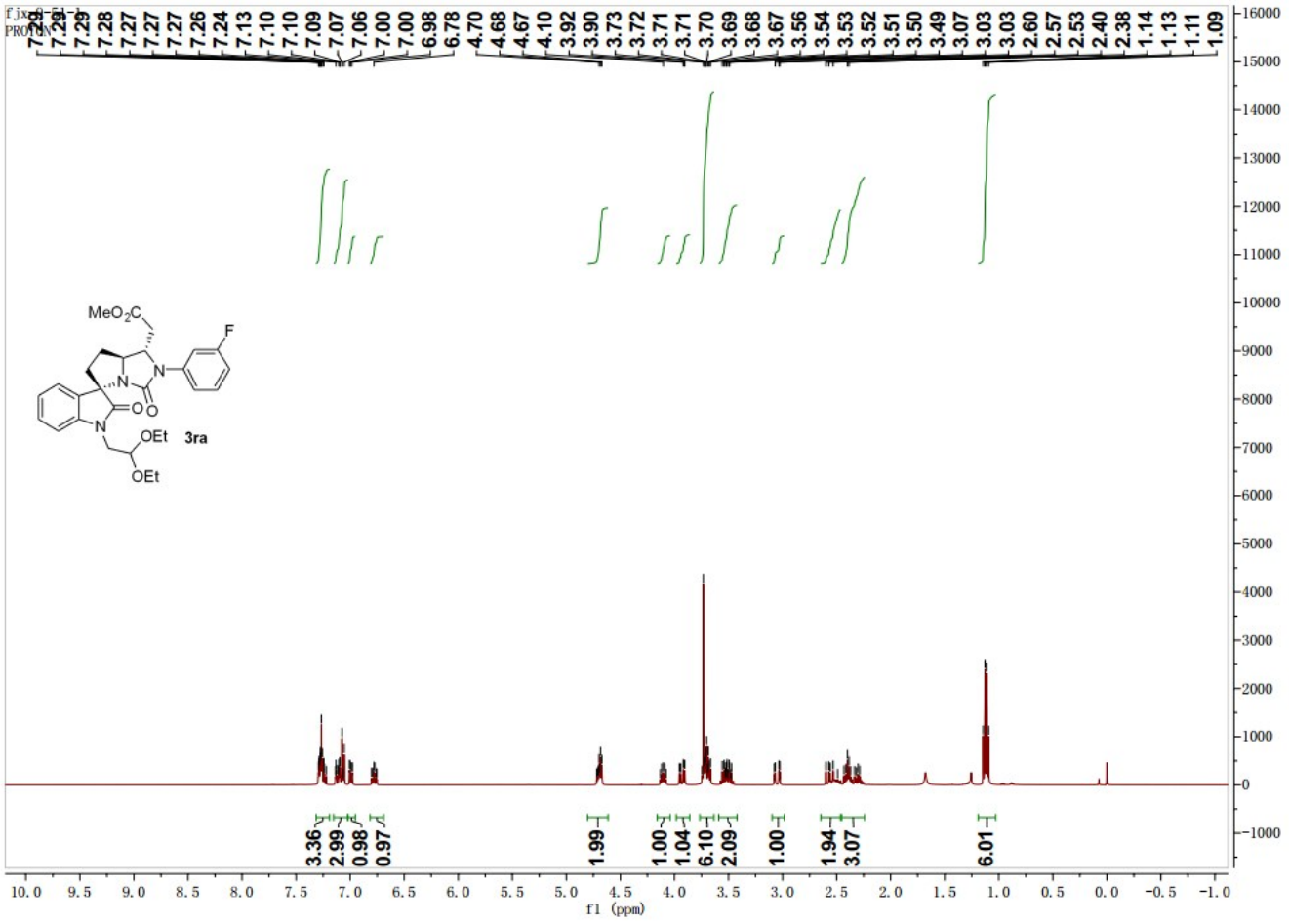
177.21 171.13 154.83 134.79 130.03 129.15 128.95 124.53 123.02 122.16 122.05 119.76 110.25 100.51
66.01 64.63 63.96 63.71 57.73 52.18 44.15 40.45 37.82 32.37 15.42 15.38
MeO2C
Cl
N
O
O
N
OEt
OEt
4qa
f1 (ppm)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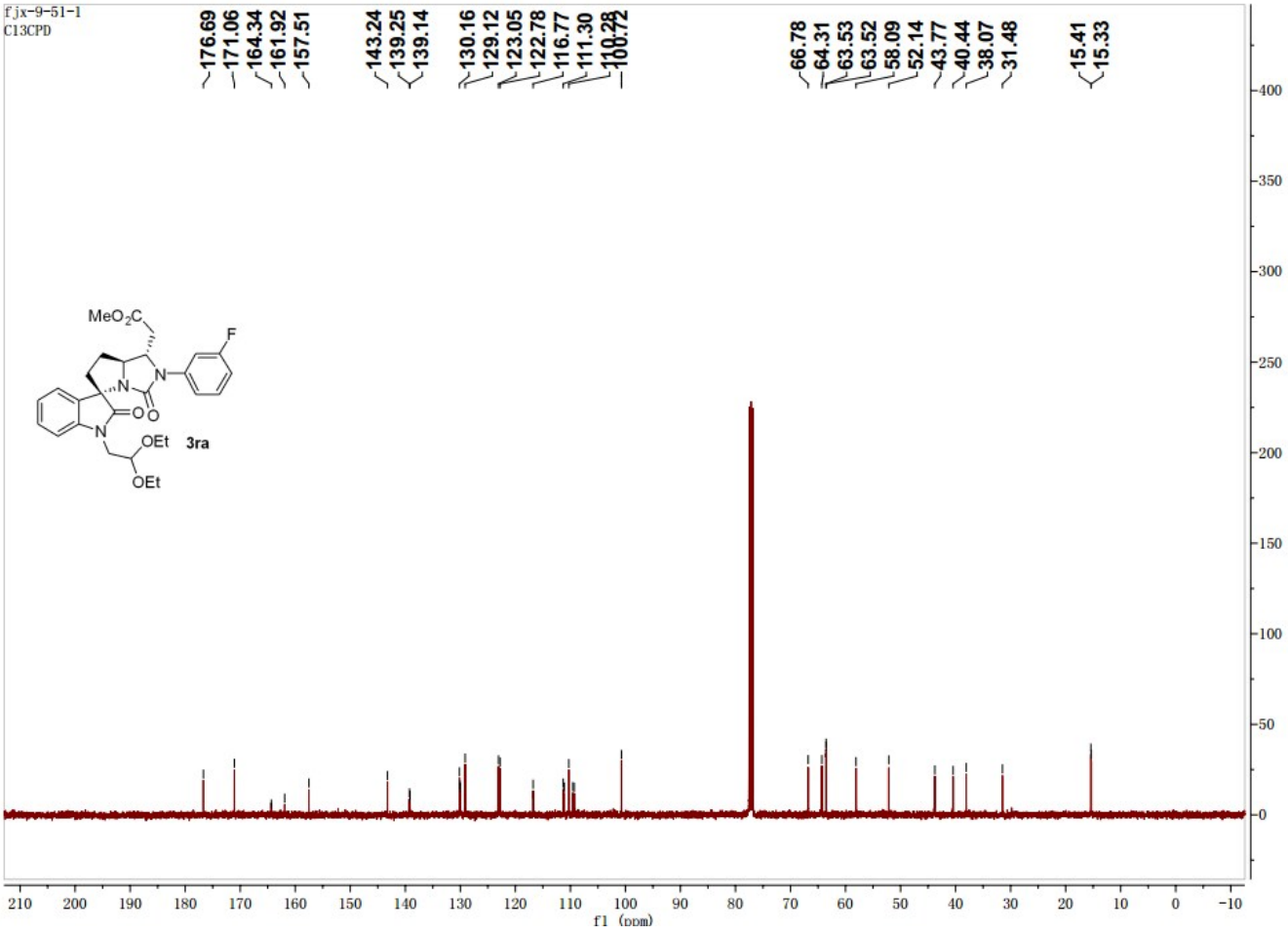
4.70 4.68 4.67 4.10 3.92 3.90 3.73 3.72 3.71 3.71 3.70 3.69 3.68 3.67 3.56 3.54 3.53 3.52 3.51 3.50 3.49 3.07 3.03 3.03 2.60 2.57 2.53 2.40 2.38 1.14 1.13 1.11 1.09
MeO2C
F
OEt
OEt
3ra
3.36 2.99 0.98 0.97 1.99 1.00 1.04 6.10 2.09 1.00 1.94 3.07 6.01
f1 (ppm)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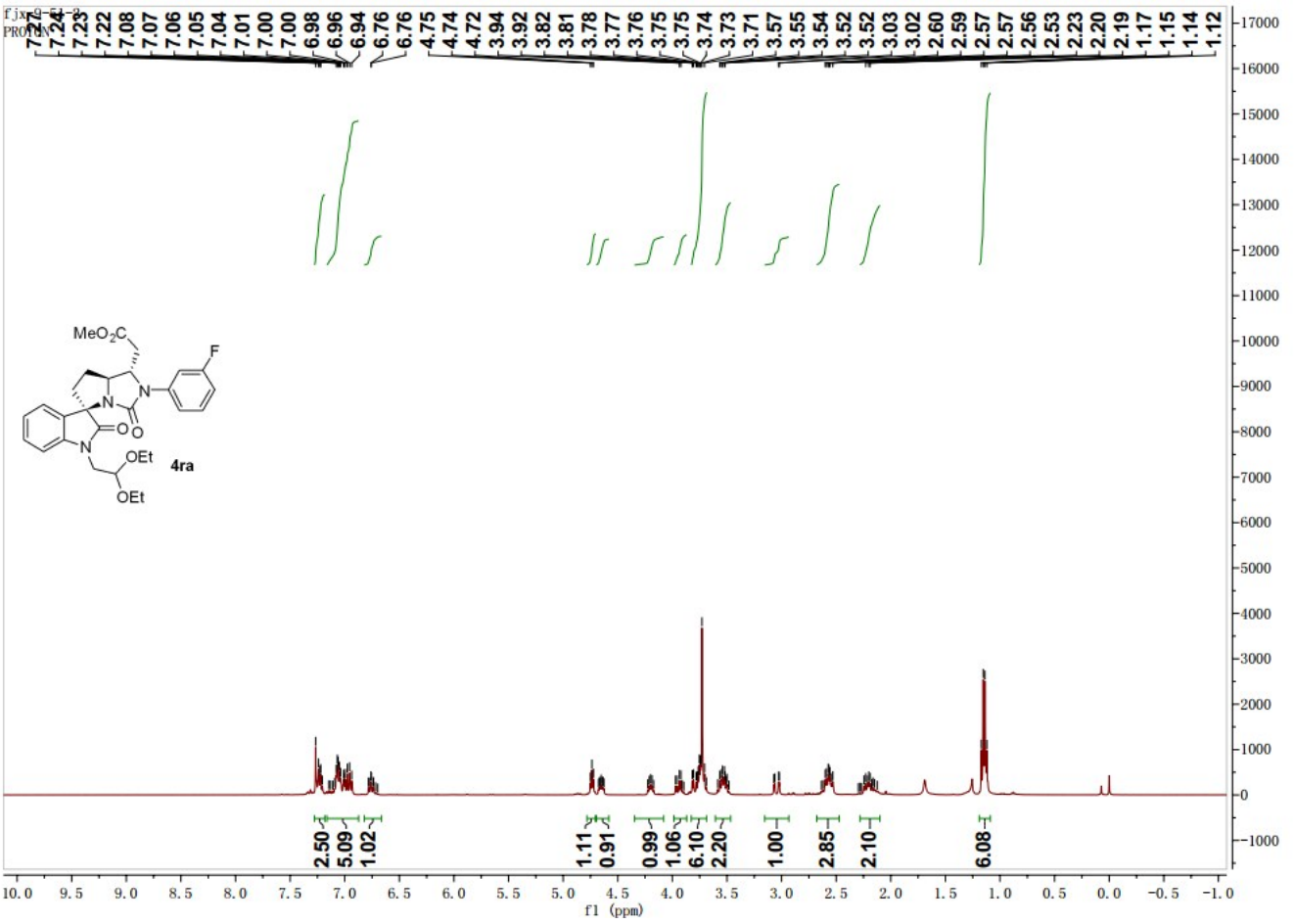
MeO2C
F
OEt
OEt
3ra
f1 (ppm)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7.07
7.06
7.05
7.04
7.01
7.00
7.00
6.98
6.96
6.94
6.76
6.76
4.75
4.74
4.72
3.94
3.92
3.82
3.81
3.78
3.77
3.76
3.75
3.75
3.74
3.73
3.71
3.57
3.55
3.54
3.52
3.52
3.03
3.02
2.60
2.59
2.57
2.57
2.56
2.53
2.23
2.20
2.19
1.17
1.15
1.14
1.12
MeO2C
F
N
N
O
O
N
OEt
OEt
4ra
2.50
5.09
1.02
1.11
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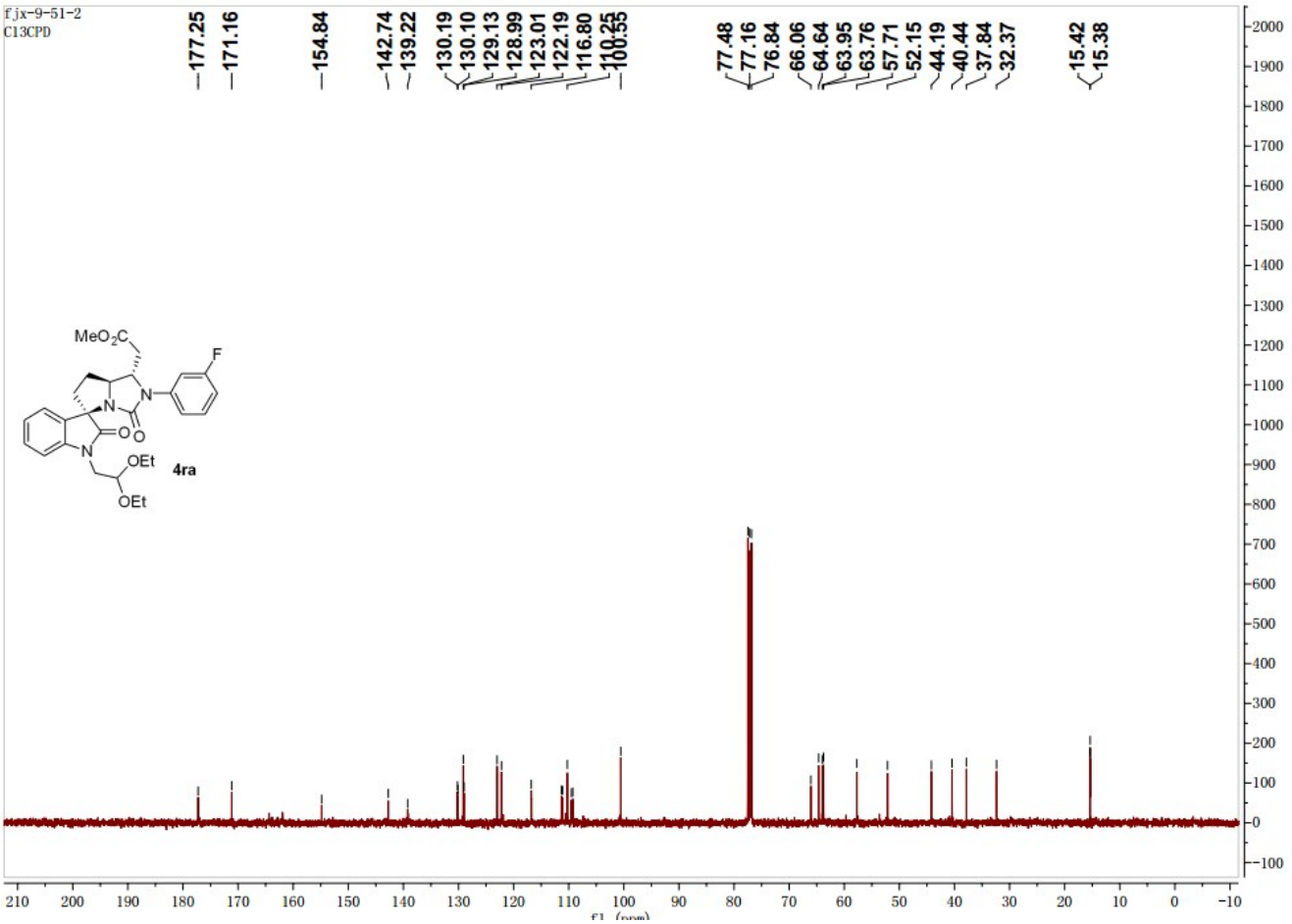
0.99
1.06
6.10
2.20
1.00
2.85
2.10
6.08
f1 (ppm)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66.06
64.64
63.95
63.76
57.71
52.15
44.19
40.44
37.84
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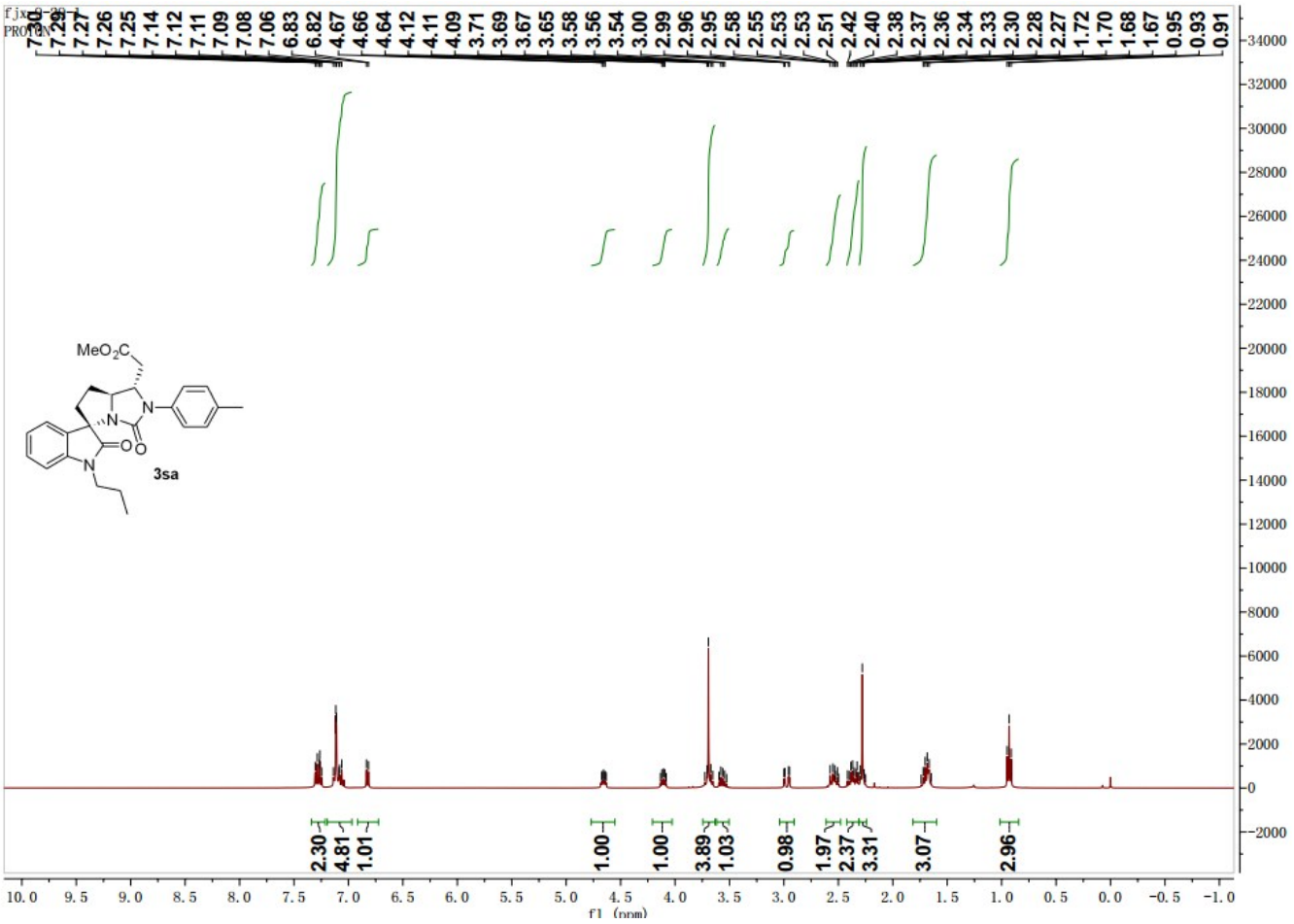
15.38
MeO2C
F
N
N
O
O
N
OEt
OEt
4ra
f1 (ppm)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2.27
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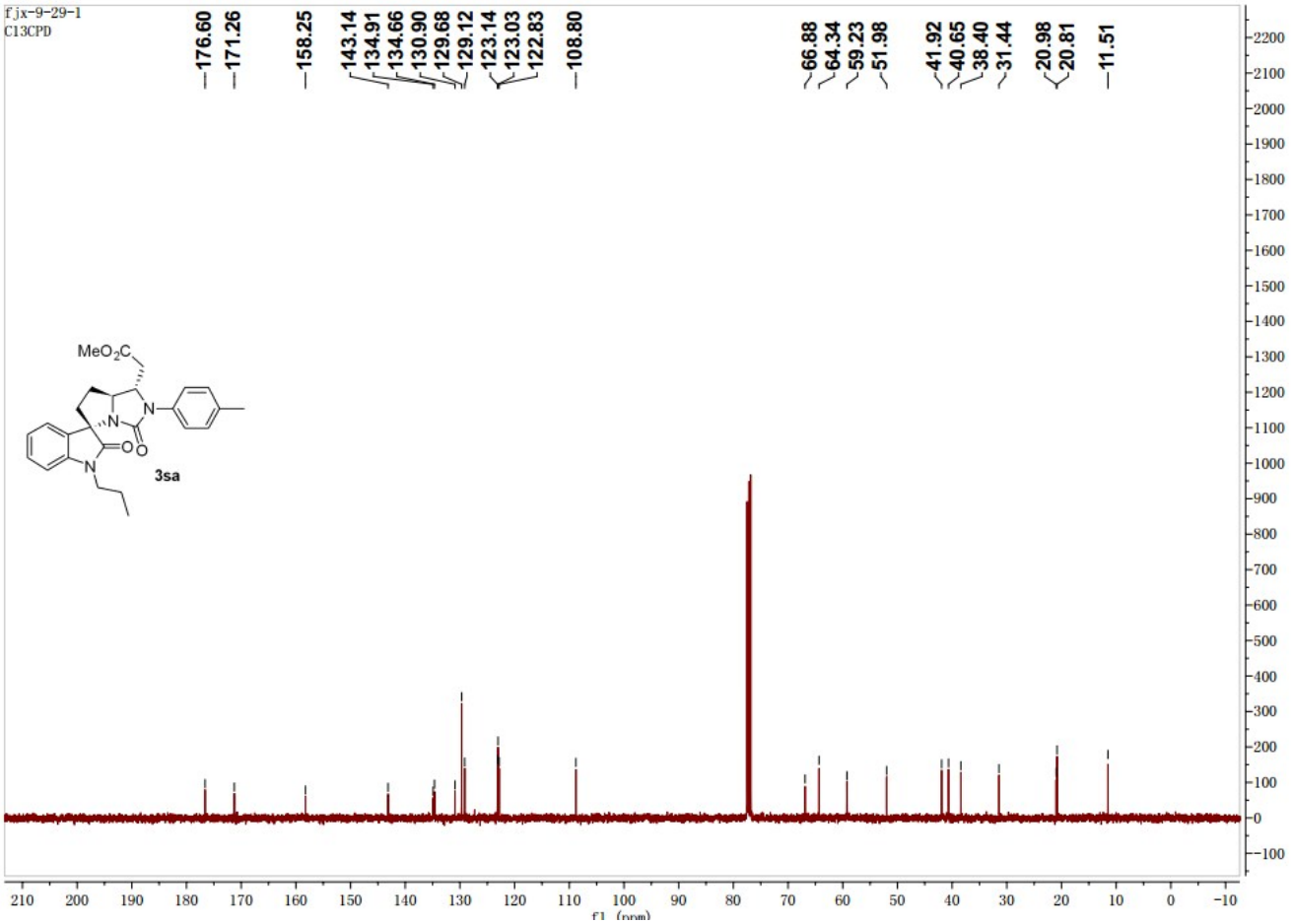
1.70
1.68
1.67
0.95
0.93
0.91
MeO2C
3sa
2.30
4.81
1.01
1.00
1.00
3.89
1.03
0.98
1.97
2.37
3.31
3.07
2.96
f1 (ppm)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130.90
129.68
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123.14
123.03
122.83
108.80
66.88
64.34
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51.98
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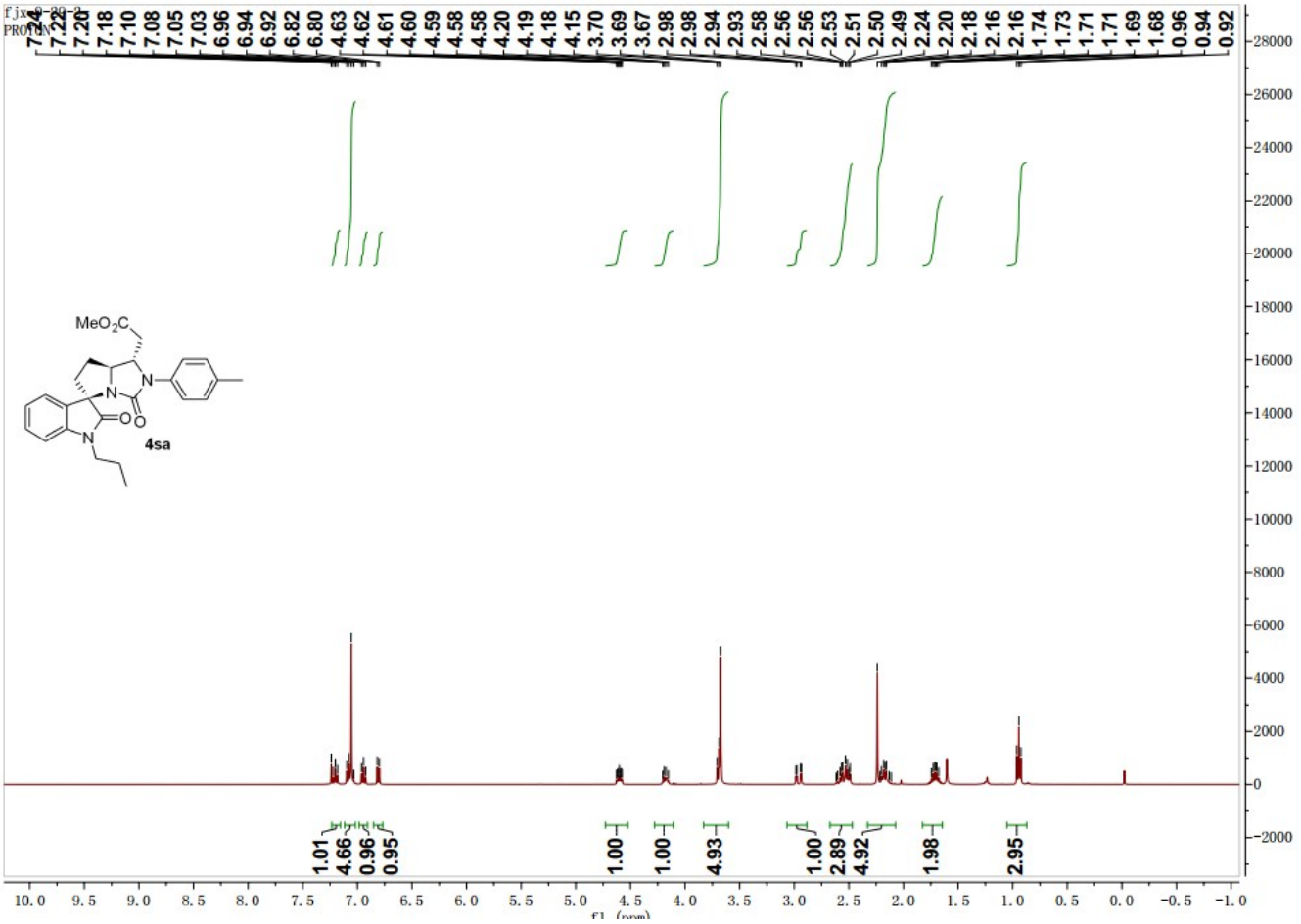
40.65
38.40
31.44
20.98
20.81
11.51
MeO2C
3sa
f1 (ppm)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6.92
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6.80
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4.62
4.61
4.60
4.59
4.58
4.58
4.20
4.19
4.18
4.15
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3.67
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1.71
1.71
1.69
1.68
0.96
0.94
0.92
MeO2C
4sa
1.01
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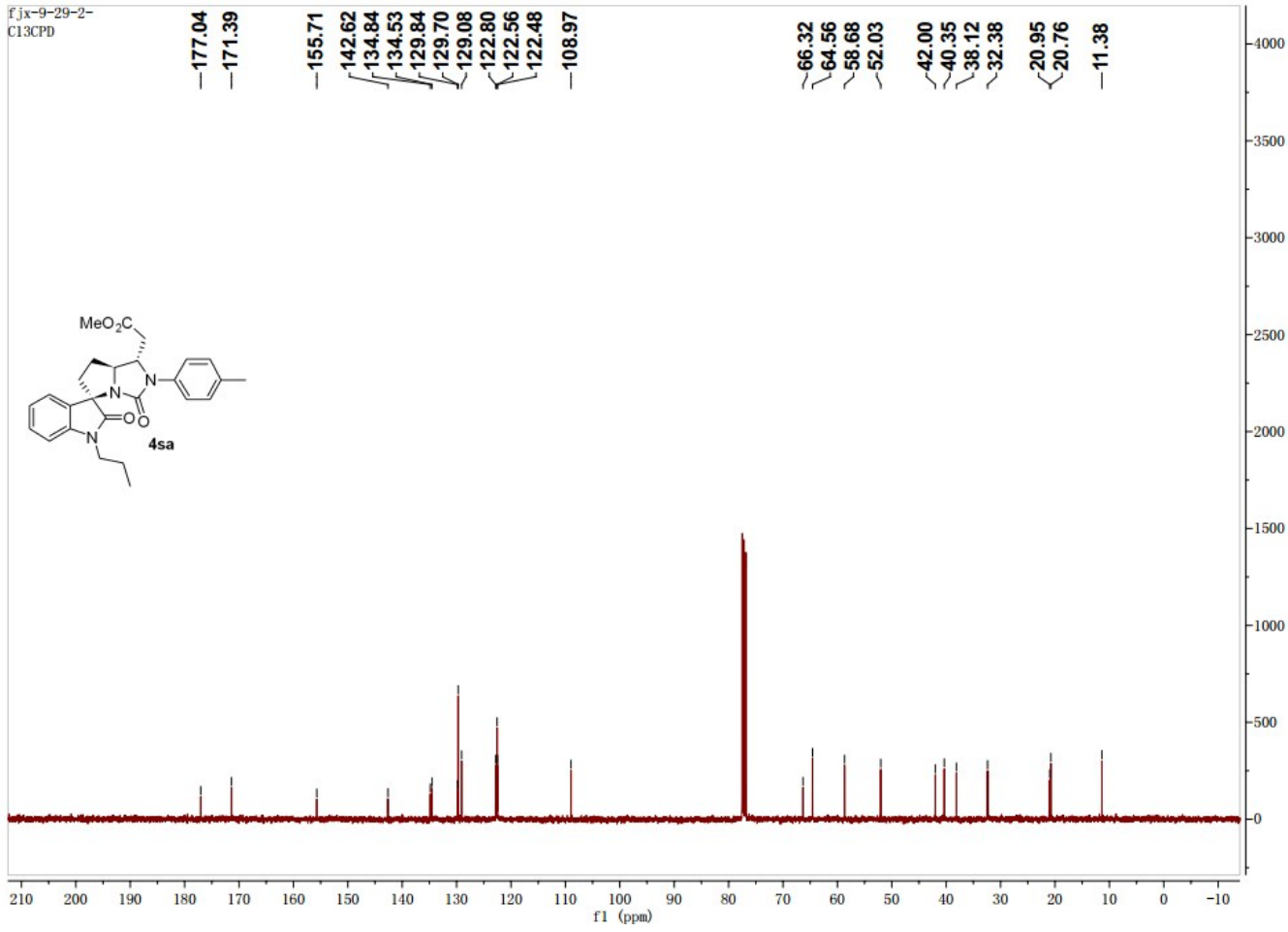
1.00
4.93
1.00
2.89
4.92
1.98
2.95
f1 (ppm)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129.84
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122.48
108.97
66.32
64.56
58.68
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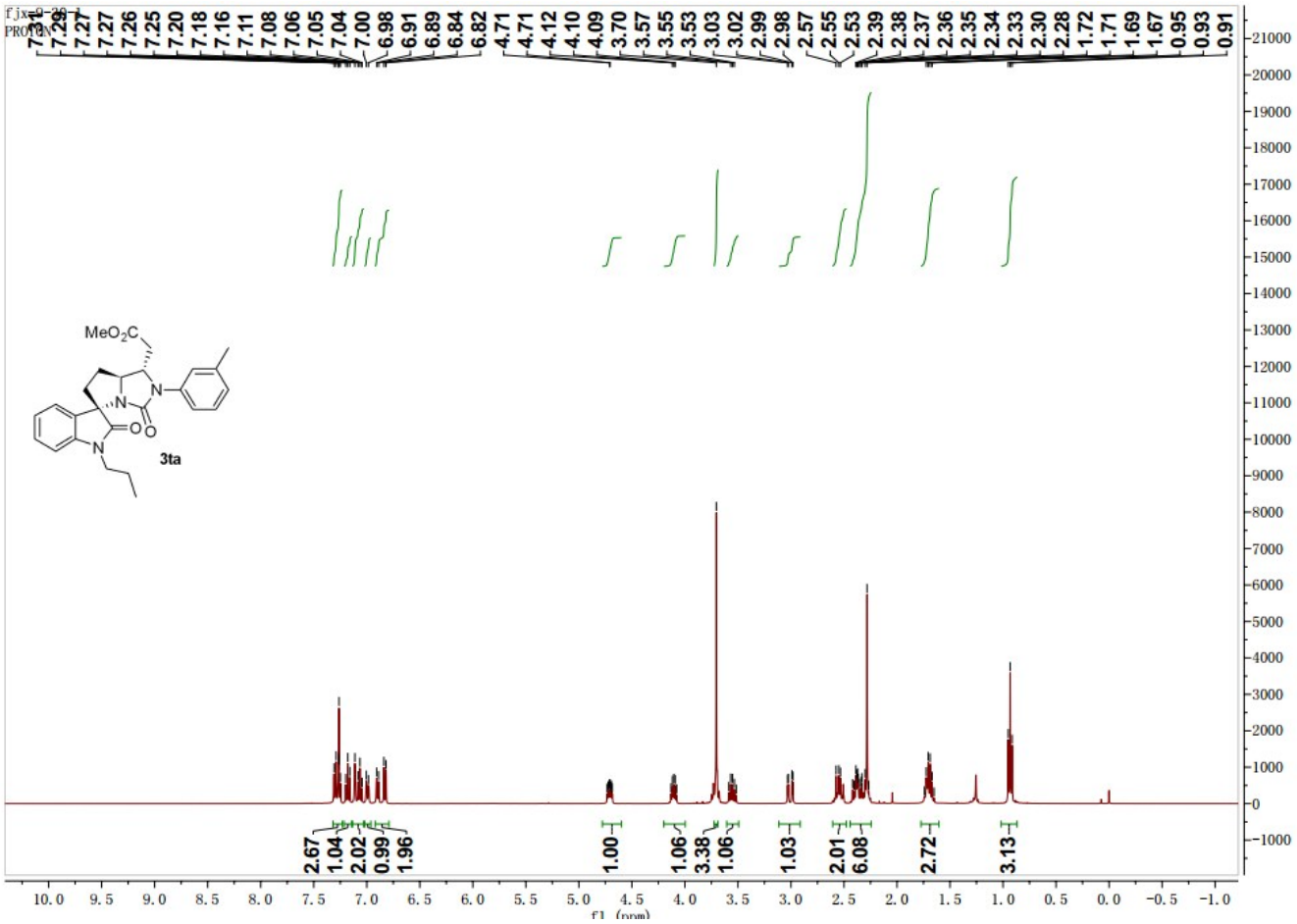
40.35
38.12
32.38
20.95
20.76
11.38
MeO2C
4sa
f1 (ppm)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7.20
7.18
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7.06
7.05
7.04
7.00
6.98
6.91
6.89
6.84
6.82
4.71
4.71
4.12
4.10
4.09
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3.55
3.53
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2.30
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1.72
1.71
1.69
1.67
0.95
0.93
0.91
MeO2C
3ta
2.67
1.04
2.02
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1.06
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1.06
1.03
2.01
6.08
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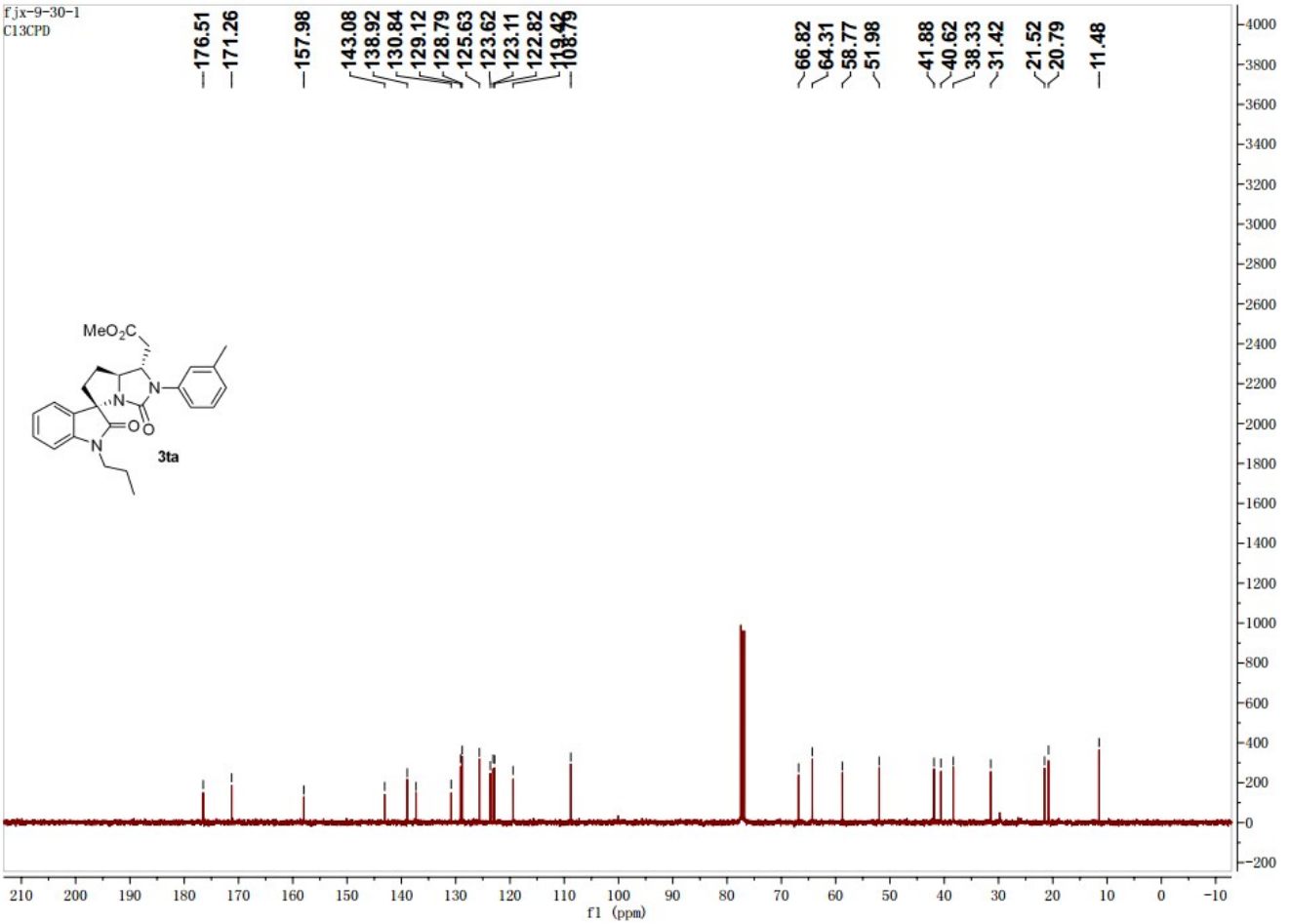
3.13
f1 (ppm)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123.62
123.11
122.82
66.82
64.31
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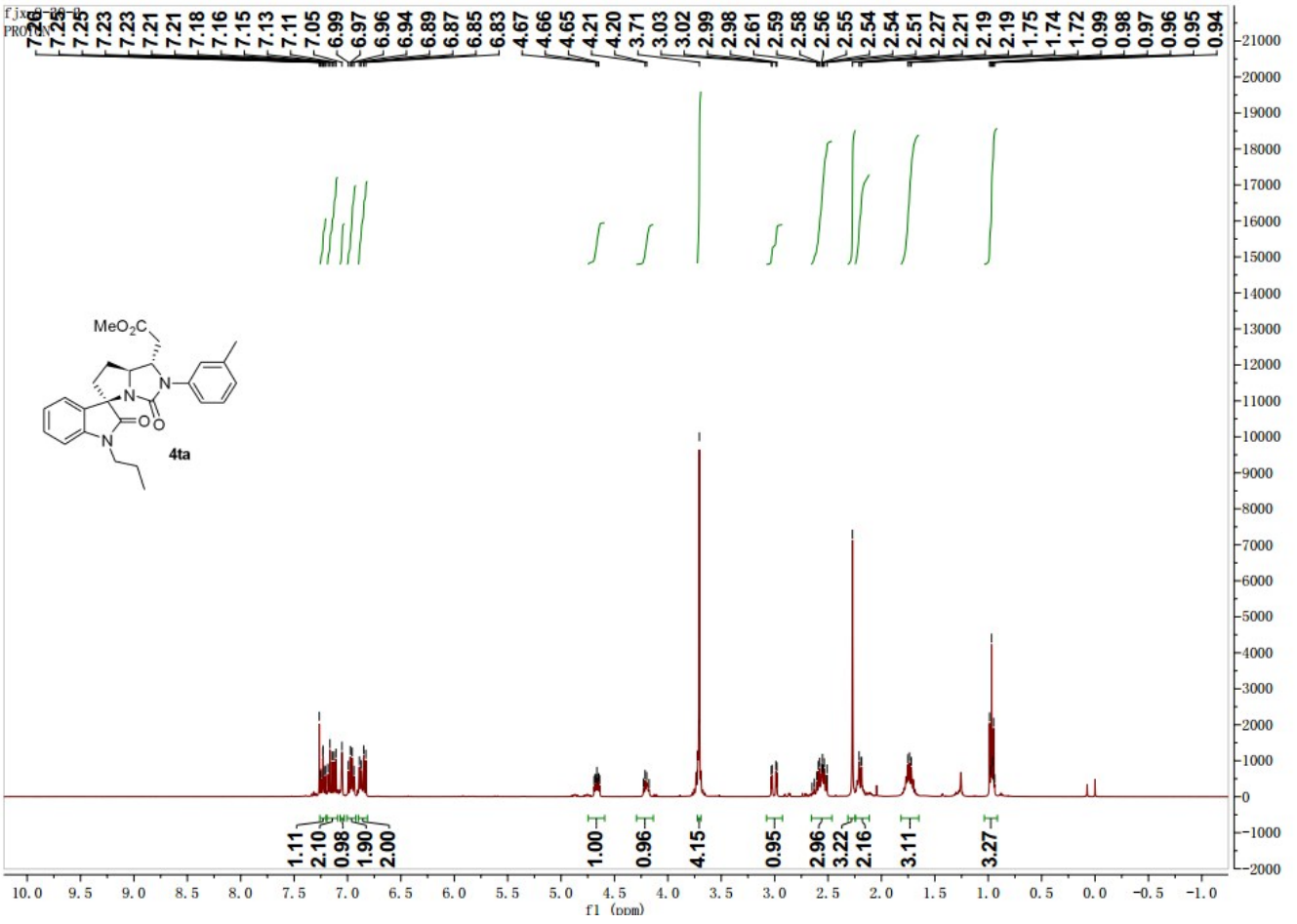
40.62
38.33
31.42
21.52
20.79
11.48
MeO2C
3ta
f1 (ppm)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7.11
7.05
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3.03
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0.95
0.94
MeO2C
4ta
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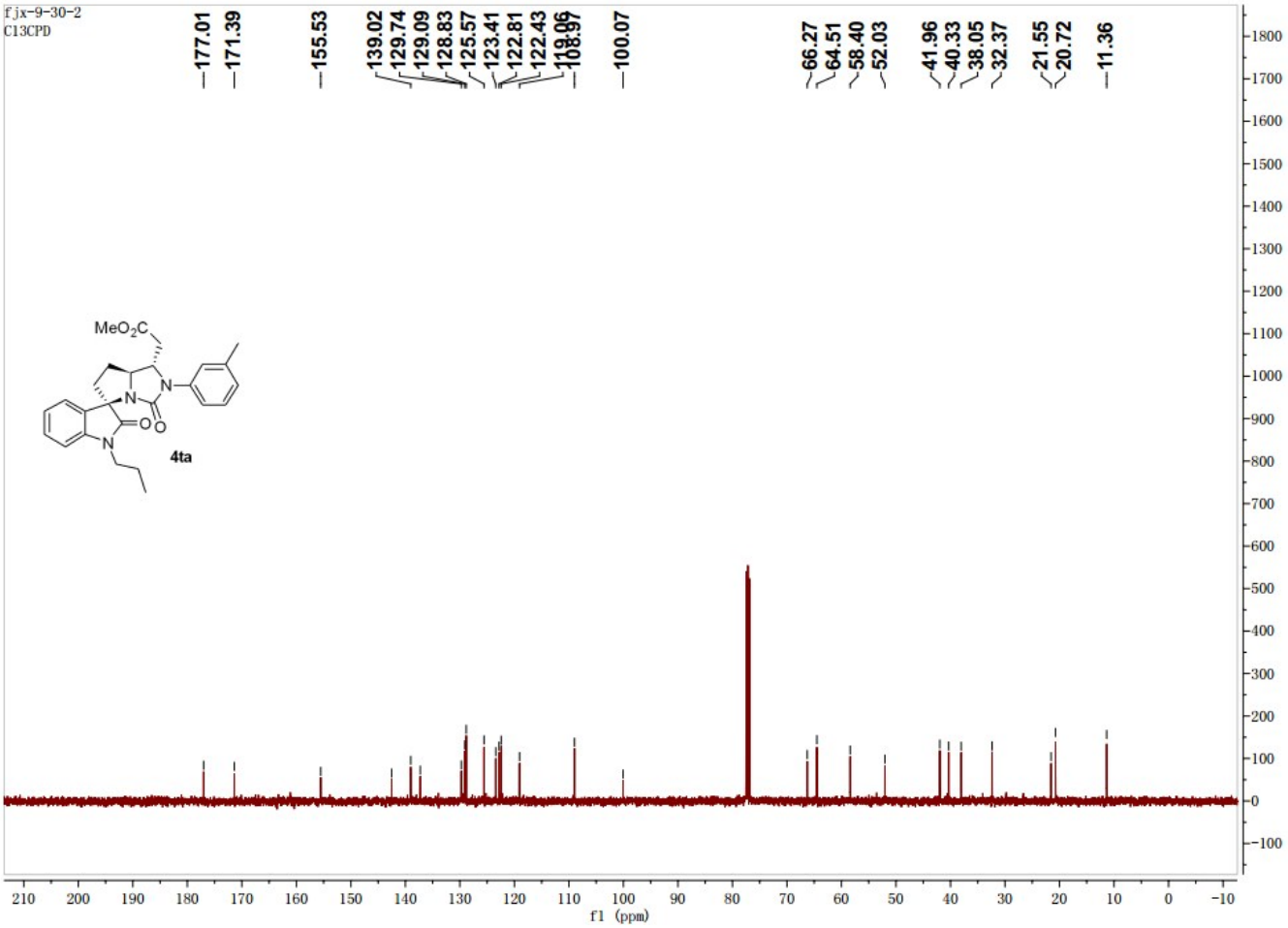
3.22
2.16
3.11
3.27
f1 (ppm)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64.51
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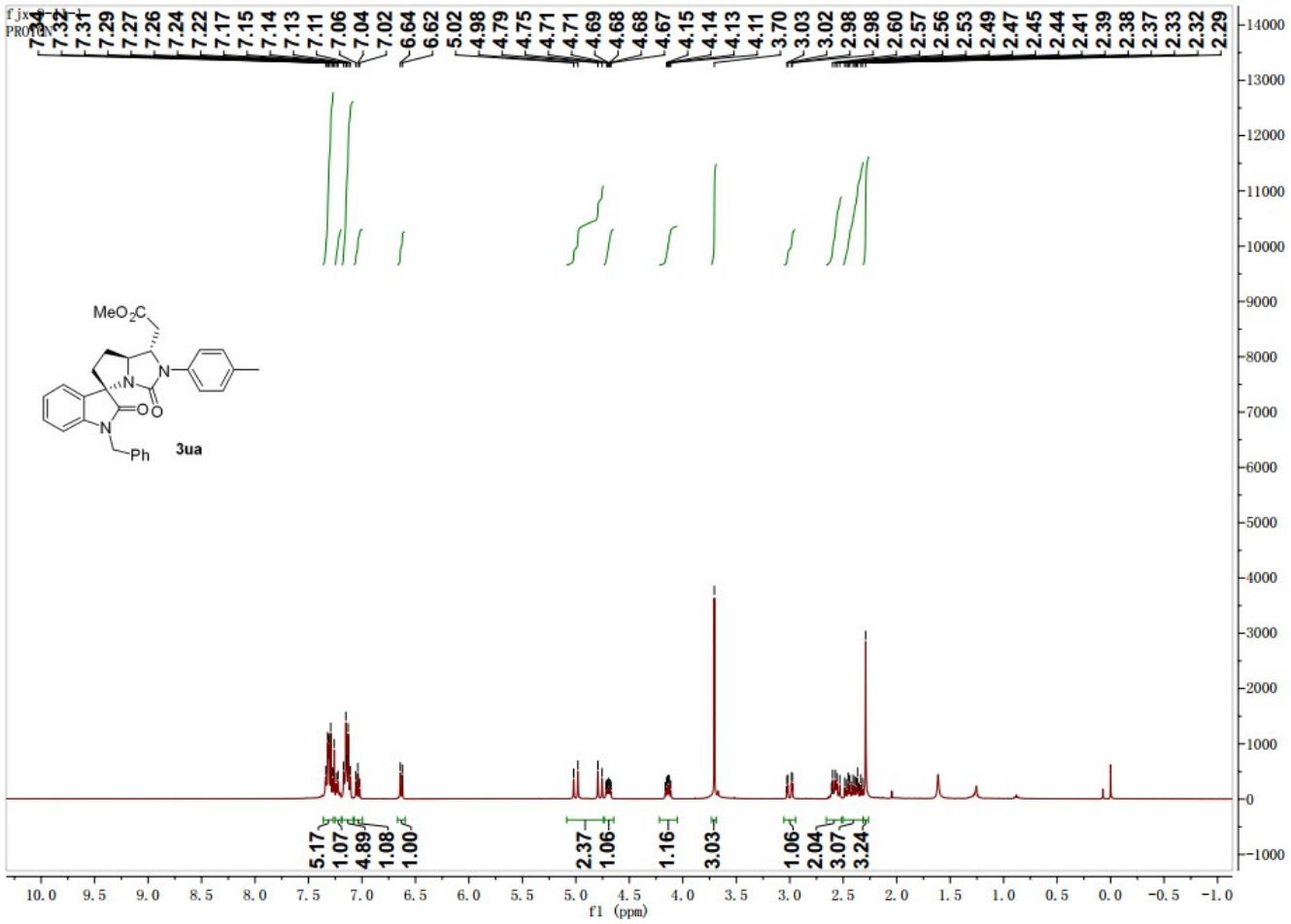
38.05
32.37
21.55
20.72
11.36
MeO2C
4ta
f1 (ppm)


f jx-9-11-1
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7.15
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2.38
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2.29
MeO2C
N
N
O
O
N
Ph
3ua
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1.06
1.16
3.03
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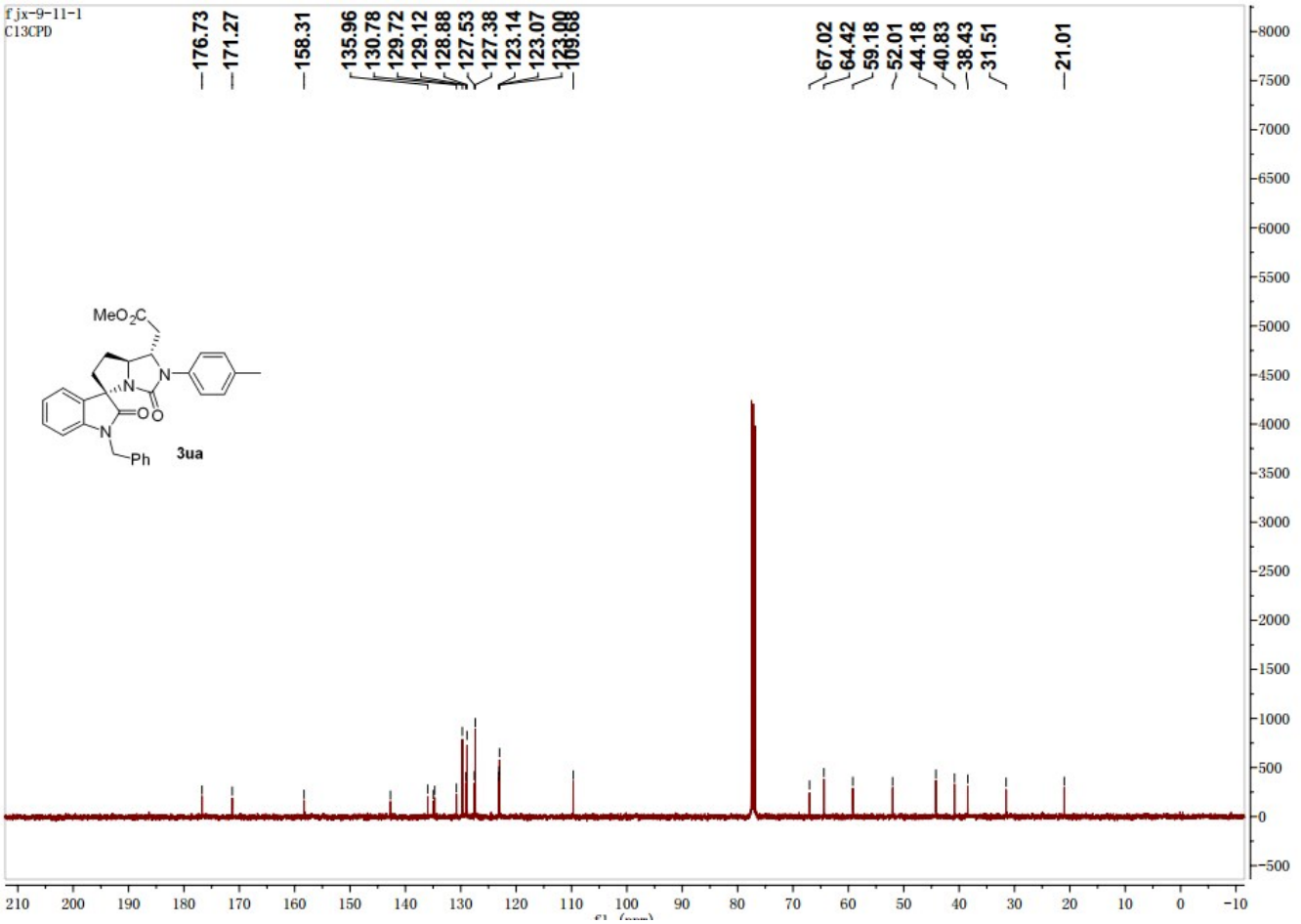
2.04
3.07
3.24
f1 (ppm)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129.12
128.88
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127.38
123.14
123.07
67.02
64.42
59.18
52.01
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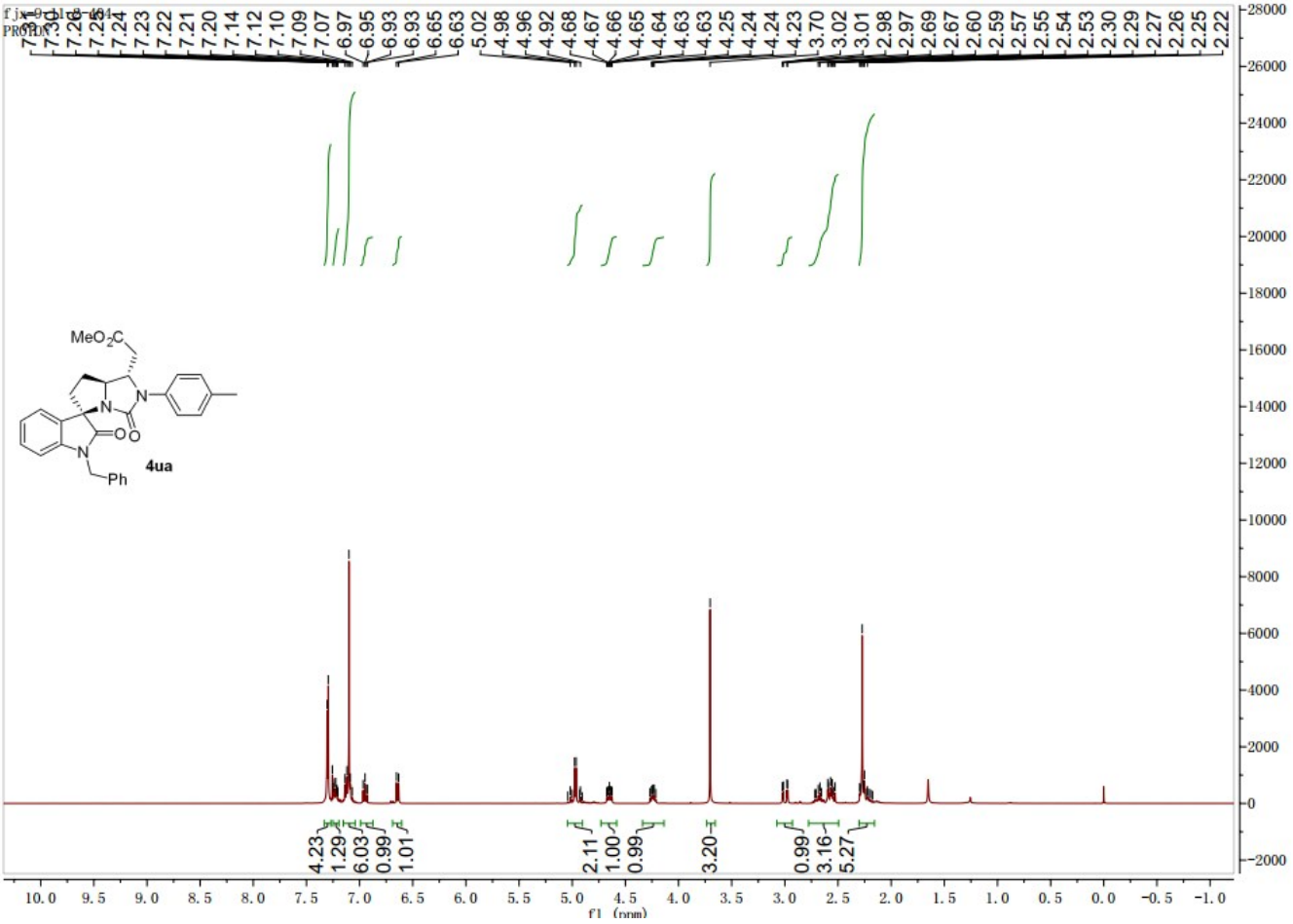
40.83
38.43
31.51
21.01
MeO2C
N
N
O
O
N
Ph
3ua
f1 (ppm)


MeO2C
4ua
Ph
4.23
1.29
6.03
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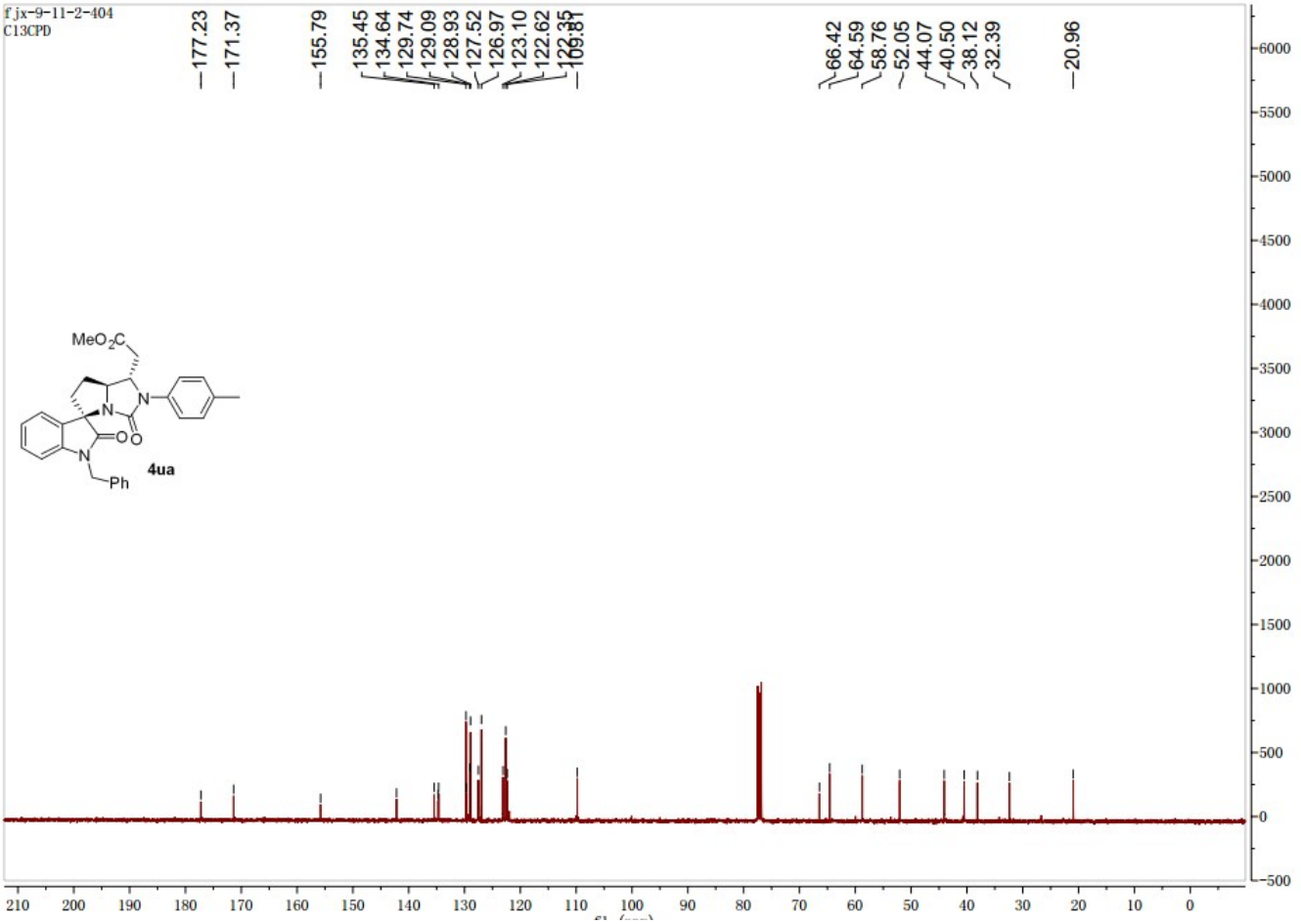
1.01
2.11
1.00
0.99
3.20
0.99
3.16
5.27
f1 (ppm)


f jx-9-11-2-404
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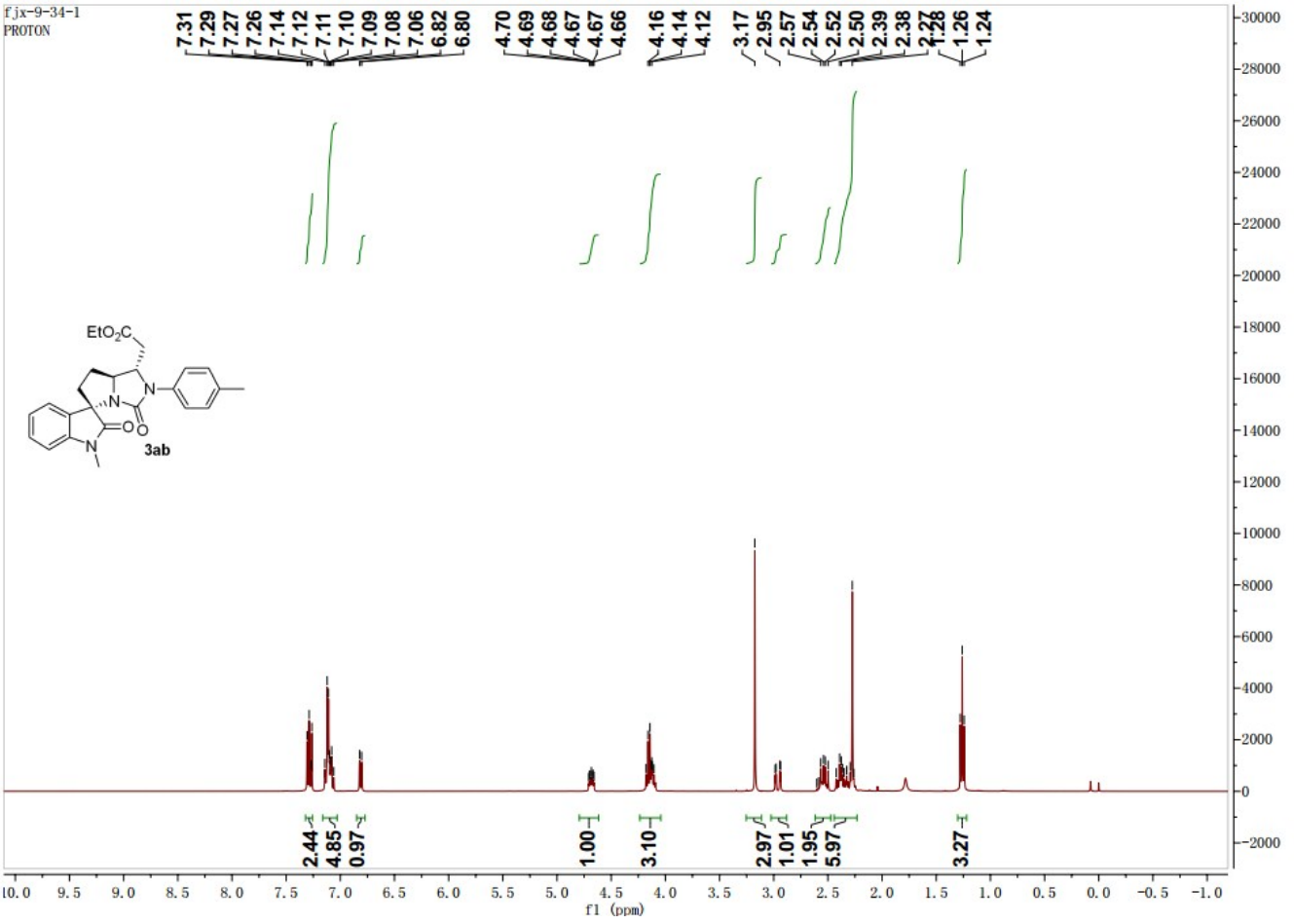
32.39
20.96
MeO2C
4ua
Ph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EtO2C
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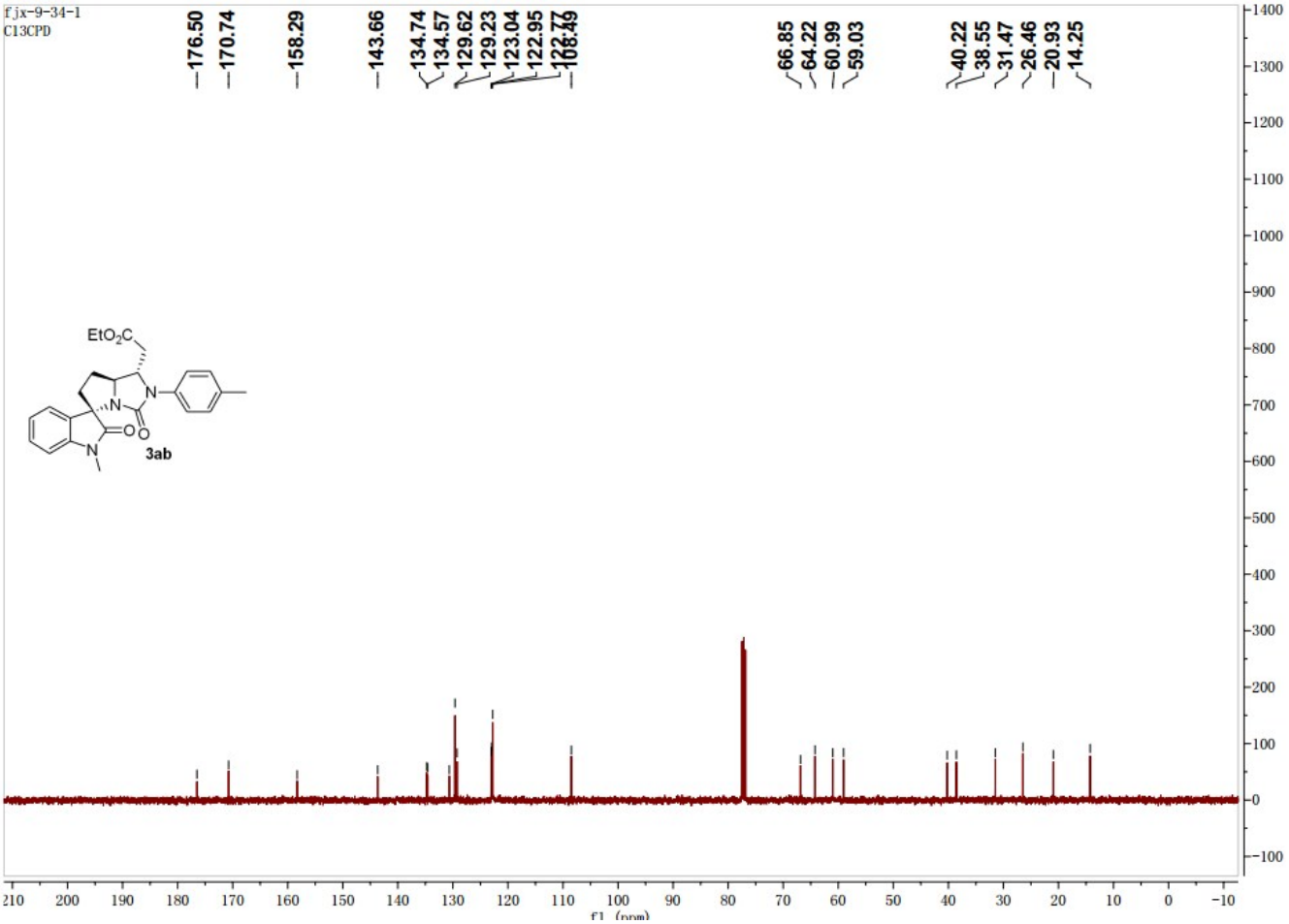
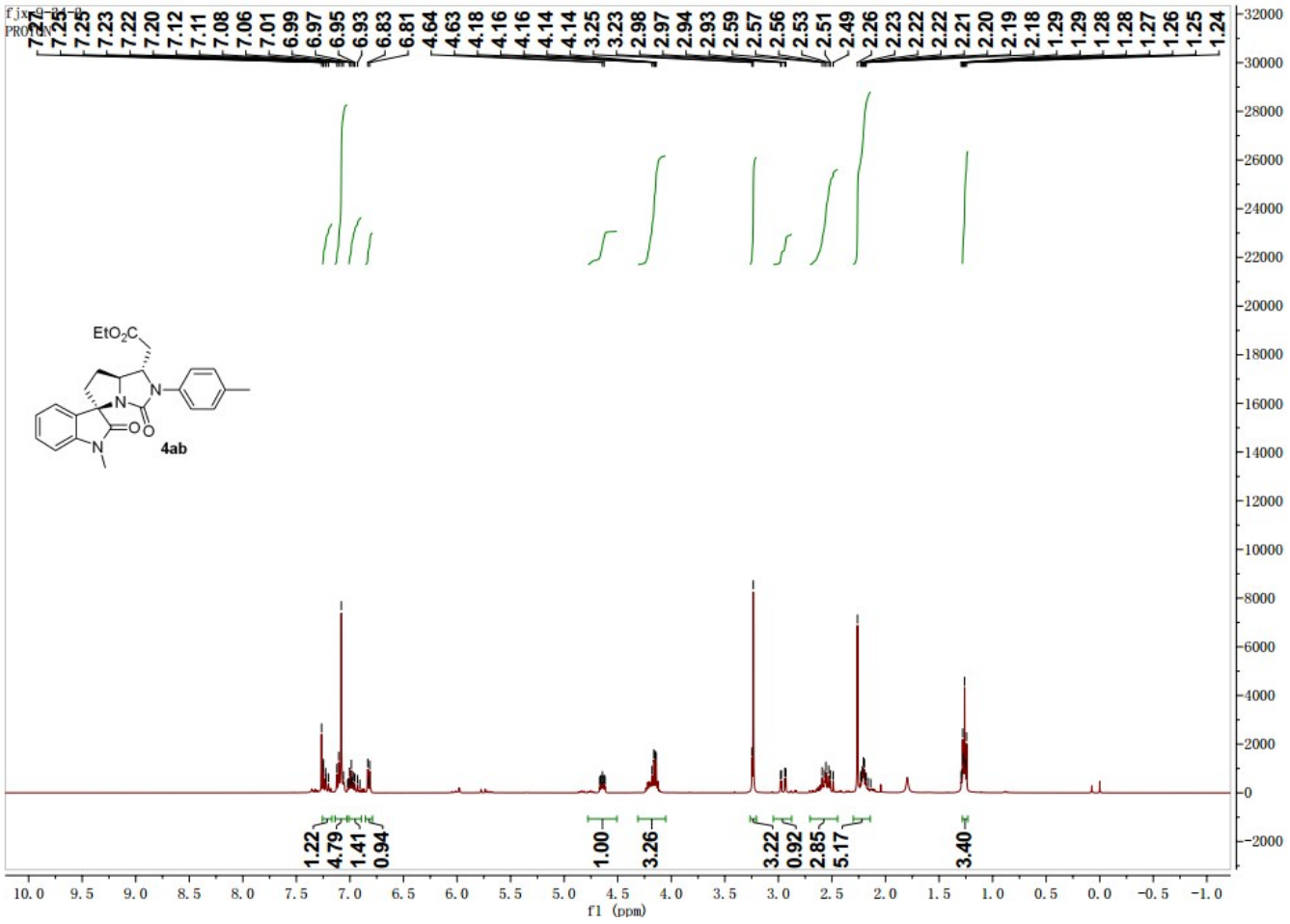
3.10
2.97
1.01
1.95
5.97
3.27
f1 (ppm)


fjx-9-34-1
C13CPD
176.50
170.74
158.29
143.66
134.74
134.57
129.62
129.23
123.04
122.95
66.85
64.22
60.99
59.03
40.22
38.55
31.47
26.46
20.93
14.25
EtO2C
3ab
f1 (ppm)


fjx-9-34-2
PROTON
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7.23
7.22
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7.11
7.08
7.06
7.01
6.99
6.97
6.95
6.93
6.83
6.81
4.64
4.63
4.18
4.16
4.16
4.14
4.14
3.25
3.23
2.98
2.97
2.94
2.93
2.59
2.57
2.56
2.53
2.51
2.49
2.26
2.23
2.22
2.22
2.21
2.20
2.19
2.18
1.29
1.29
1.28
1.28
1.27
1.26
1.25
1.24
EtO2C
4ab
1.22
4.79
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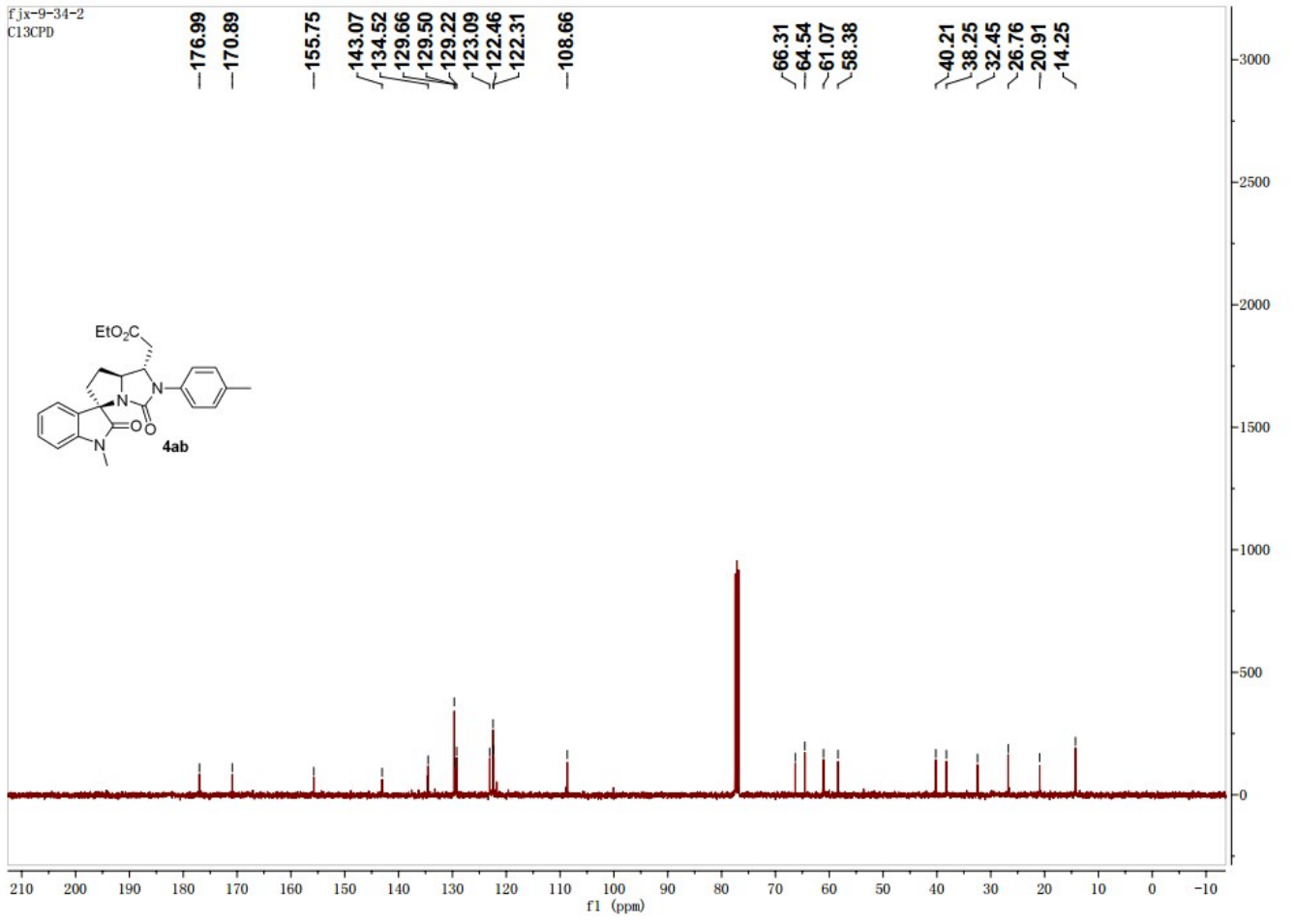
0.94
1.00
3.26
3.22
0.92
2.85
5.17
3.40
f1 (ppm)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129.50
129.22
123.09
122.46
122.31
108.66
66.31
64.54
61.07
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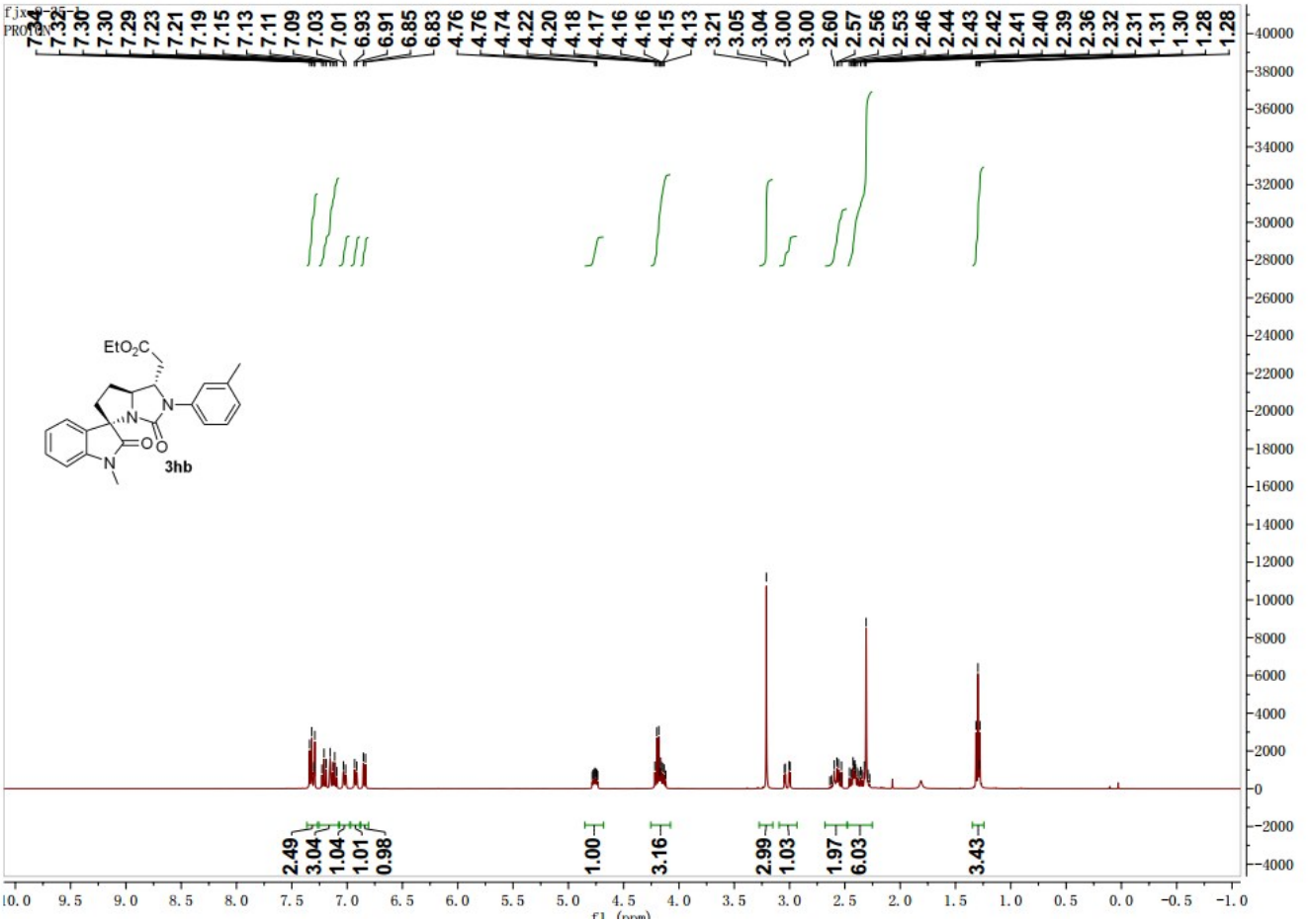
40.21
38.25
32.45
26.76
20.91
14.25
EtO2C
4ab
f1 (ppm)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7.29
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7.21
7.19
7.15
7.13
7.11
7.09
7.03
7.01
6.93
6.91
6.85
6.83
4.76
4.76
4.74
4.22
4.20
4.18
4.17
4.16
4.16
4.15
4.13
3.21
3.05
3.04
3.00
3.00
2.60
2.57
2.56
2.53
2.46
2.44
2.43
2.42
2.41
2.40
2.39
2.36
2.32
2.31
1.31
1.30
1.28
1.28
EtO2C
N
N
O
O
N
3hb
2.49
3.04
1.04
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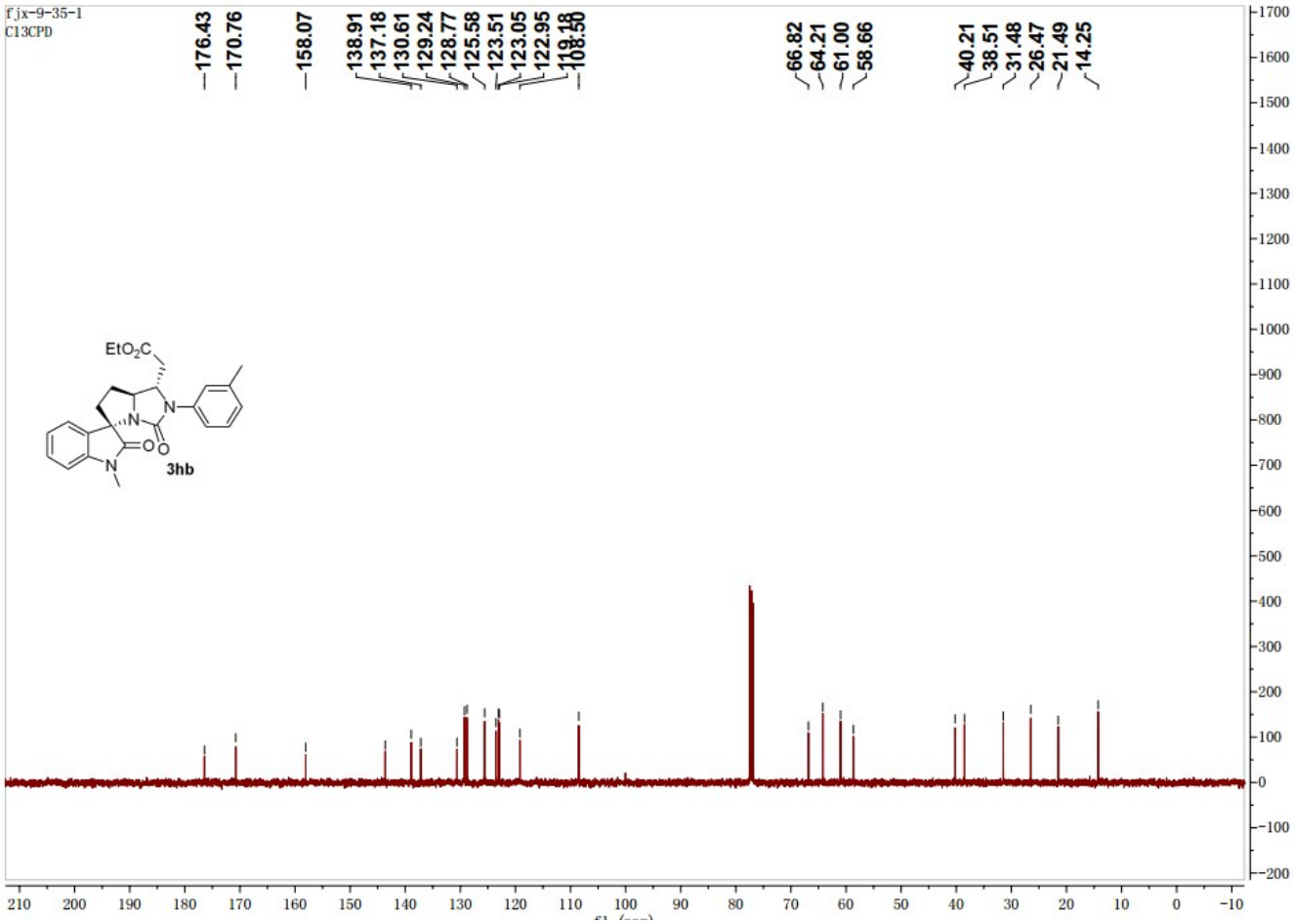
0.98
1.00
3.16
2.99
1.03
1.97
6.03
3.43
f1 (ppm)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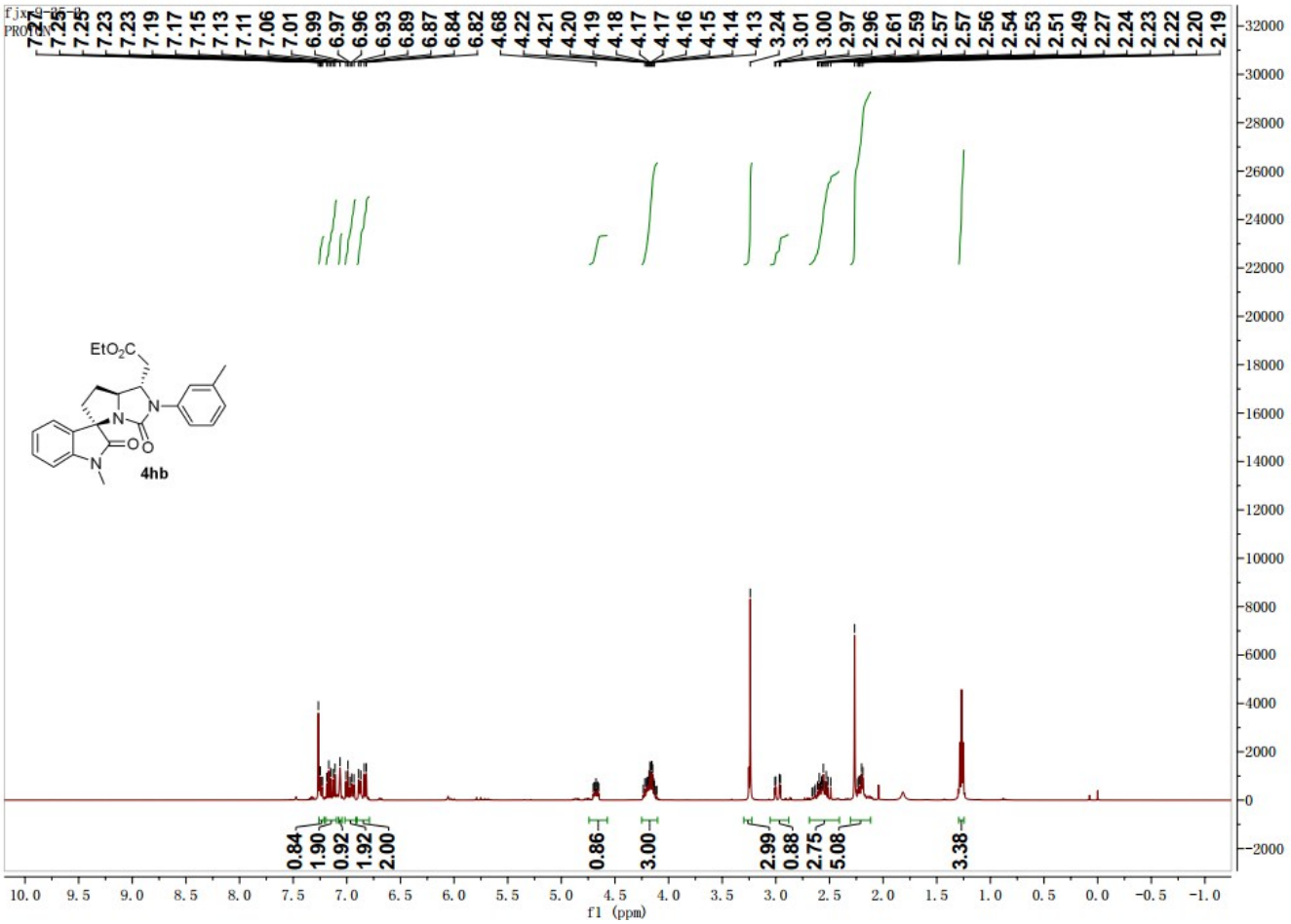
130.61
129.24
128.77
125.58
123.51
123.05
122.95
66.82
64.21
61.00
58.66
40.21
38.51
31.48
26.47
21.49
14.25
EtO2C
N
N
O
O
N
3hb
f1 (ppm)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7.15
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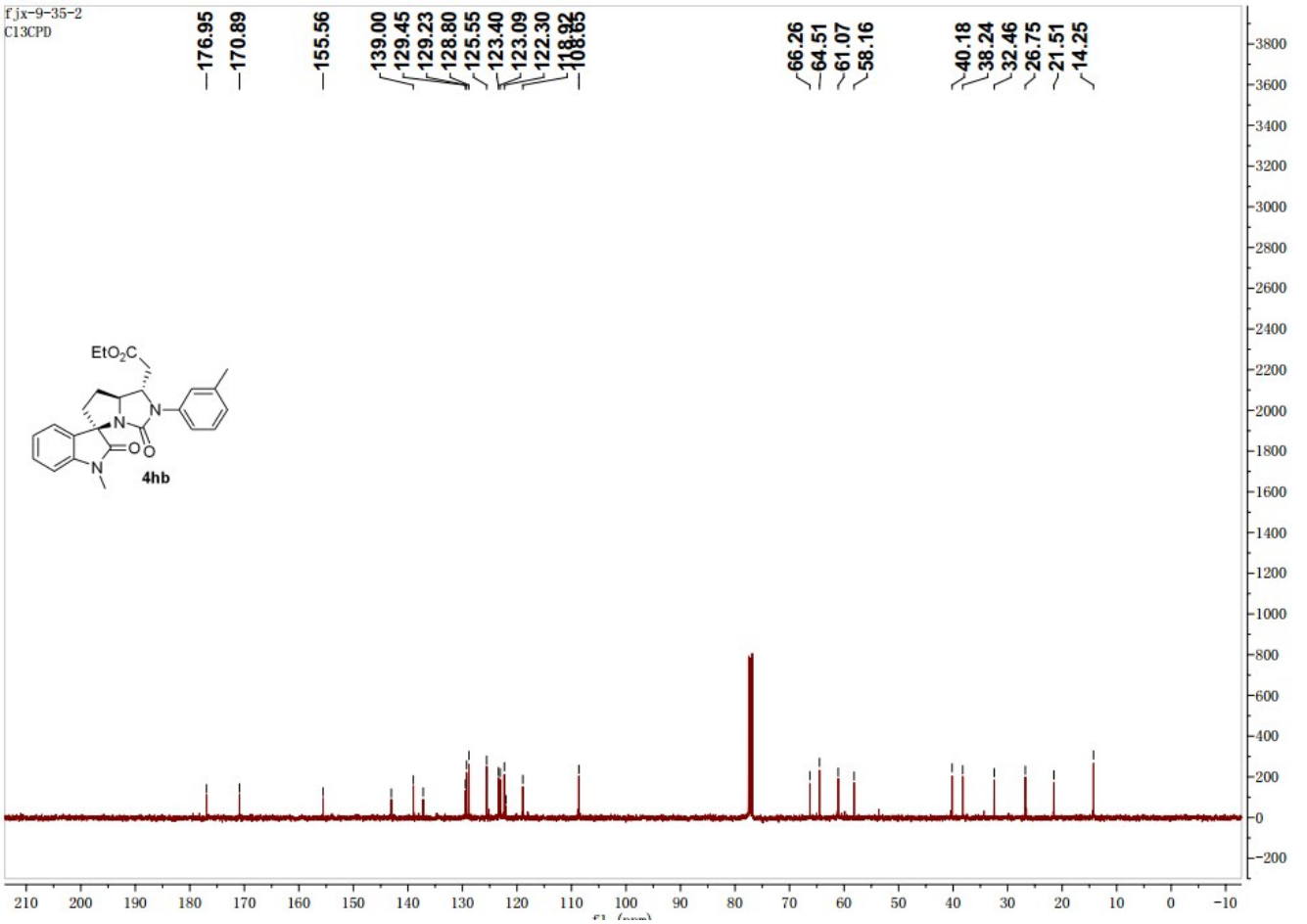
7.11
7.06
7.01
6.99
6.97
6.96
6.93
6.89
6.87
6.84
6.82
4.68
4.22
4.21
4.20
4.19
4.18
4.17
4.16
4.15
4.14
4.13
3.24
3.01
3.00
2.97
2.96
2.61
2.59
2.57
2.56
2.54
2.53
2.51
2.49
2.27
2.24
2.23
2.22
2.20
2.19
EtO2C
4hb
0.84
1.90
0.92
1.92
2.00
0.86
3.00
2.99
0.88
2.75
5.08
3.38
f1 (ppm)


fjx-9-35-2
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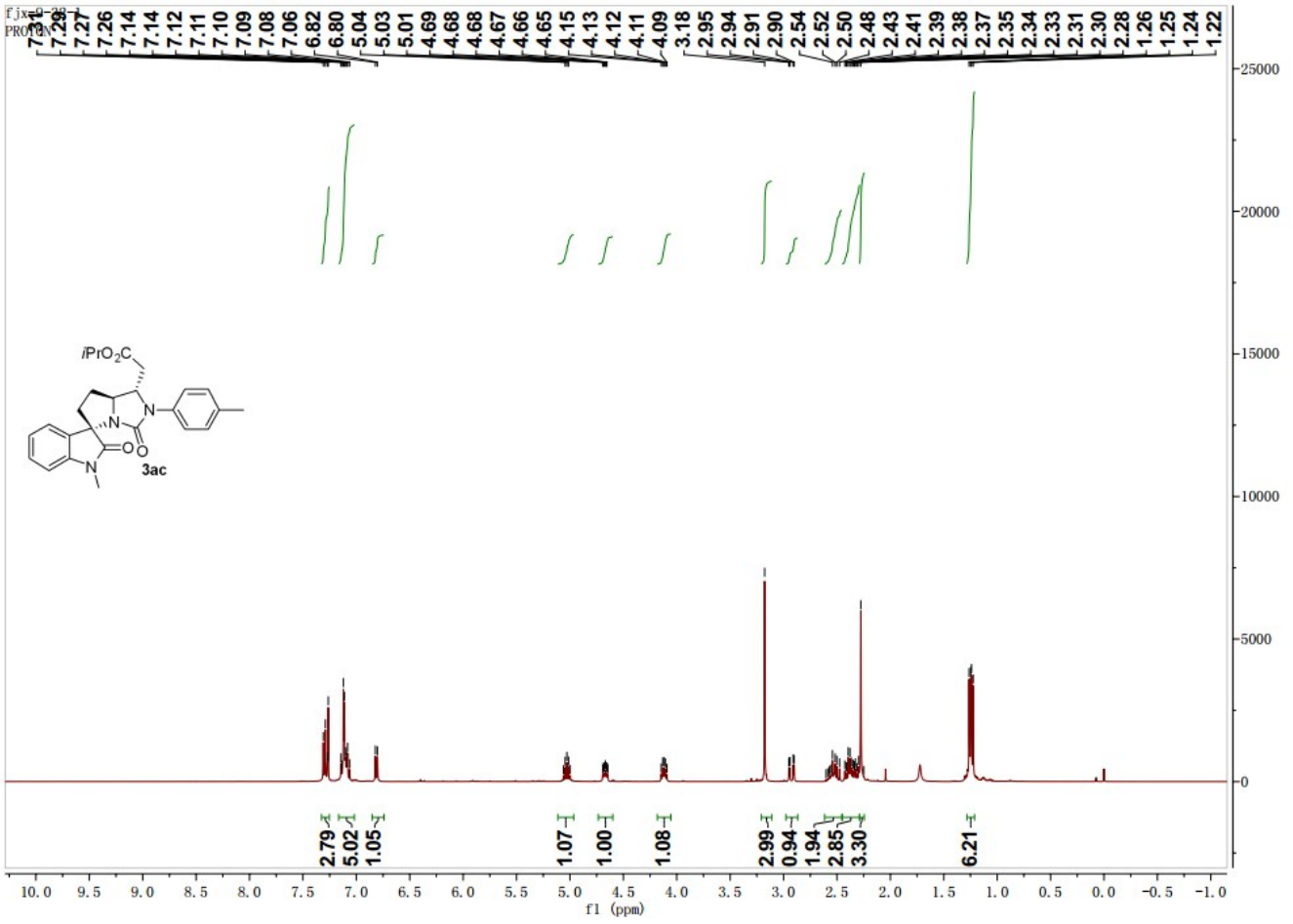
129.23
128.80
125.55
123.40
123.09
122.30
118.92
108.65
66.26
64.51
61.07
58.16
40.18
38.24
32.46
26.75
21.51
14.25
EtO2C
4hb
f1 (ppm)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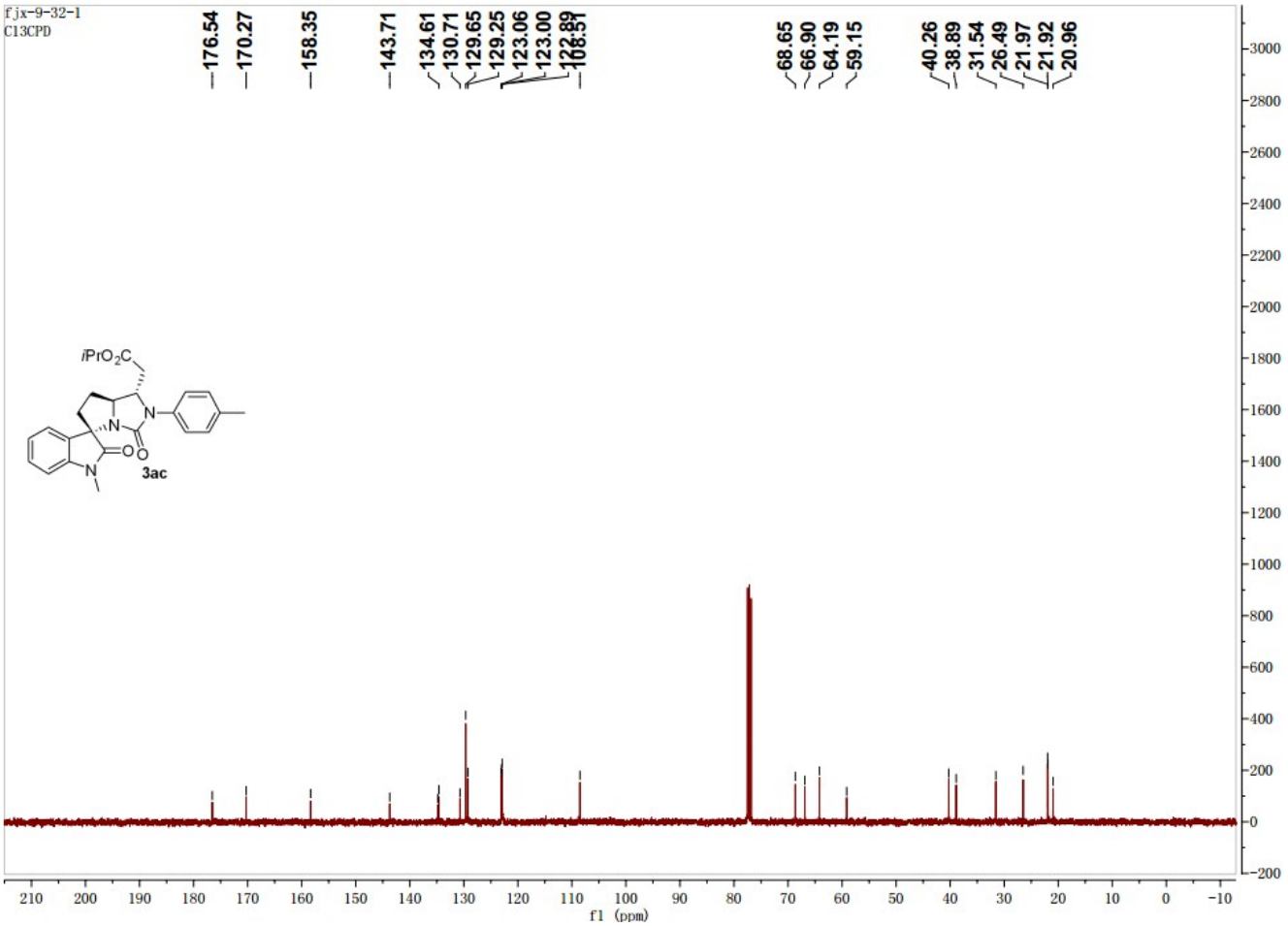
7.26
7.14
7.14
7.12
7.11
7.10
7.09
7.08
7.06
6.82
6.80
5.04
5.03
5.01
4.69
4.68
4.68
4.67
4.66
4.65
4.15
4.13
4.12
4.11
4.09
3.18
2.95
2.94
2.91
2.90
2.54
2.52
2.50
2.48
2.43
2.41
2.39
2.38
2.37
2.35
2.34
2.33
2.31
2.30
2.28
1.26
1.25
1.24
1.22
iPrO2C
3ac
2.79
5.02
1.05
1.07
1.00
1.08
2.99
0.94
1.94
2.85
3.30
6.21
f1 (ppm)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C13CPD
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123.00
122.89
108.51
68.65
66.90
64.19
59.15
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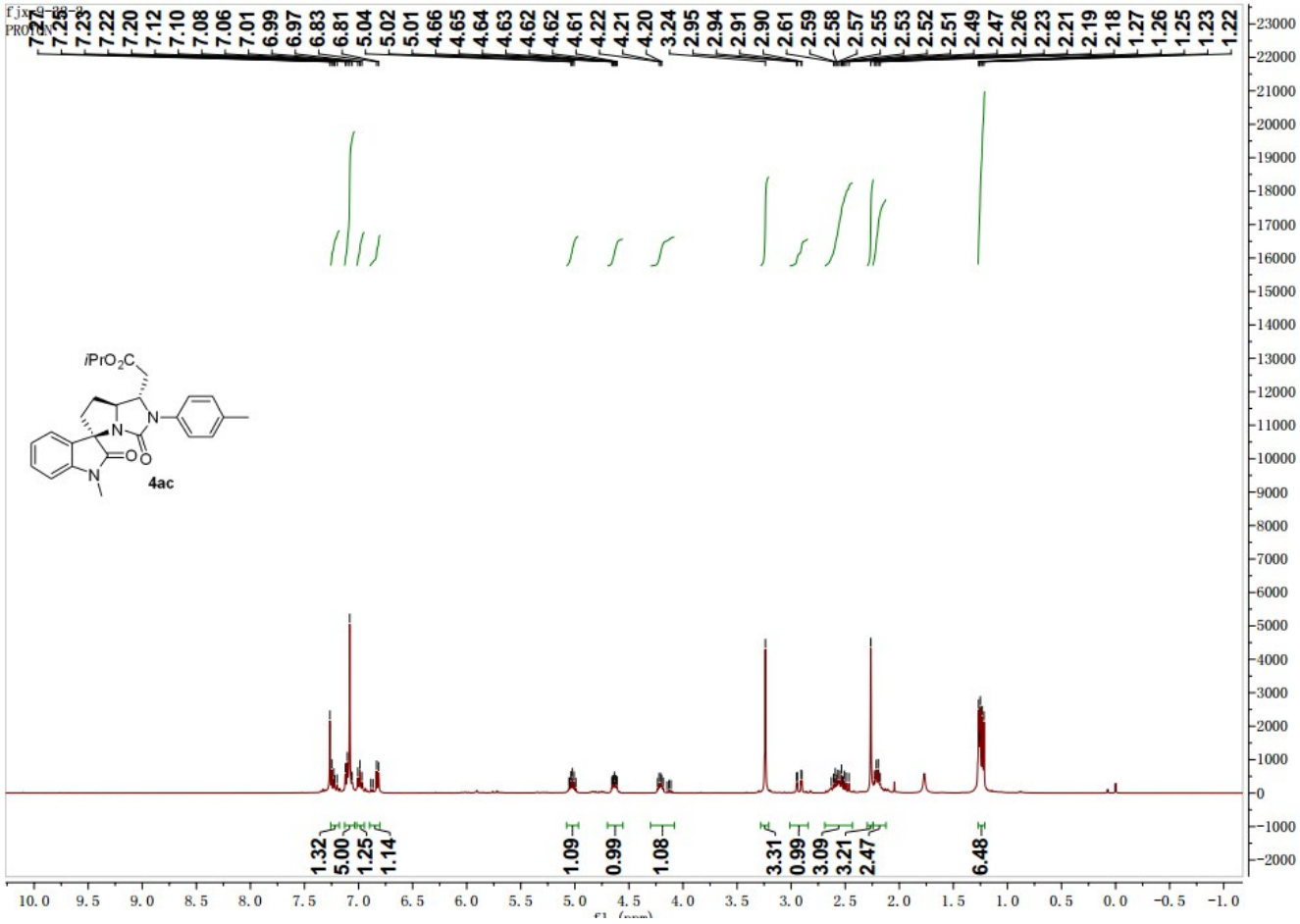
38.89
31.54
26.49
21.97
21.92
20.96
iPrO2C
3ac
f1 (ppm)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PROTON
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7.20
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7.08
7.06
7.01
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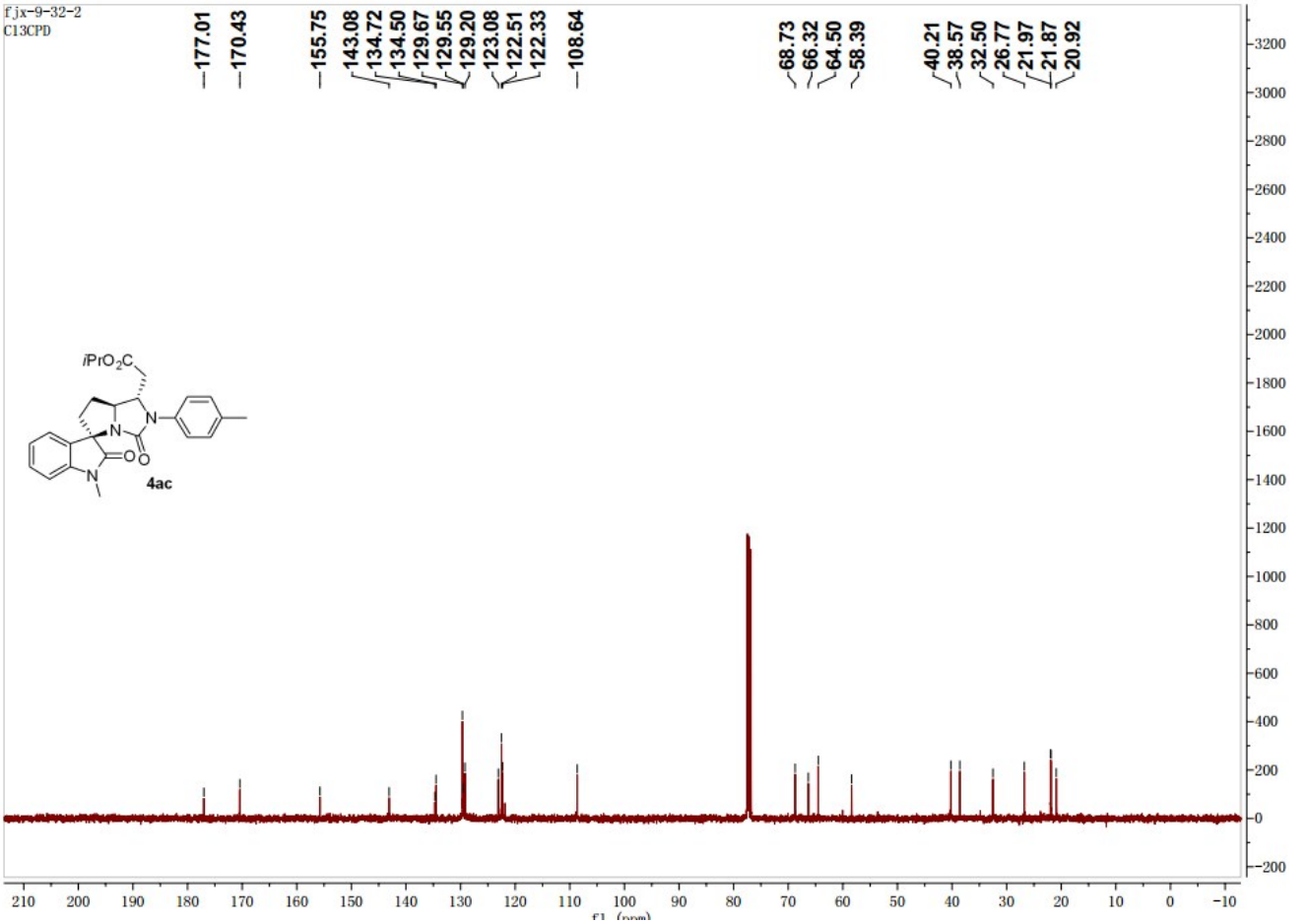
5.04
5.02
5.01
4.66
4.65
4.64
4.63
4.62
4.62
4.61
4.22
4.21
4.20
3.24
2.95
2.94
2.91
2.90
2.61
2.59
2.58
2.57
2.55
2.53
2.52
2.51
2.49
2.47
2.26
2.23
2.21
2.19
2.18
1.27
1.26
1.25
1.23
1.22
iPrO2C
4ac
1.32
5.00
1.25
1.14
1.09
0.99
1.08
3.31
0.99
3.09
3.21
2.47
6.48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C13CPD
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134.72
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129.67
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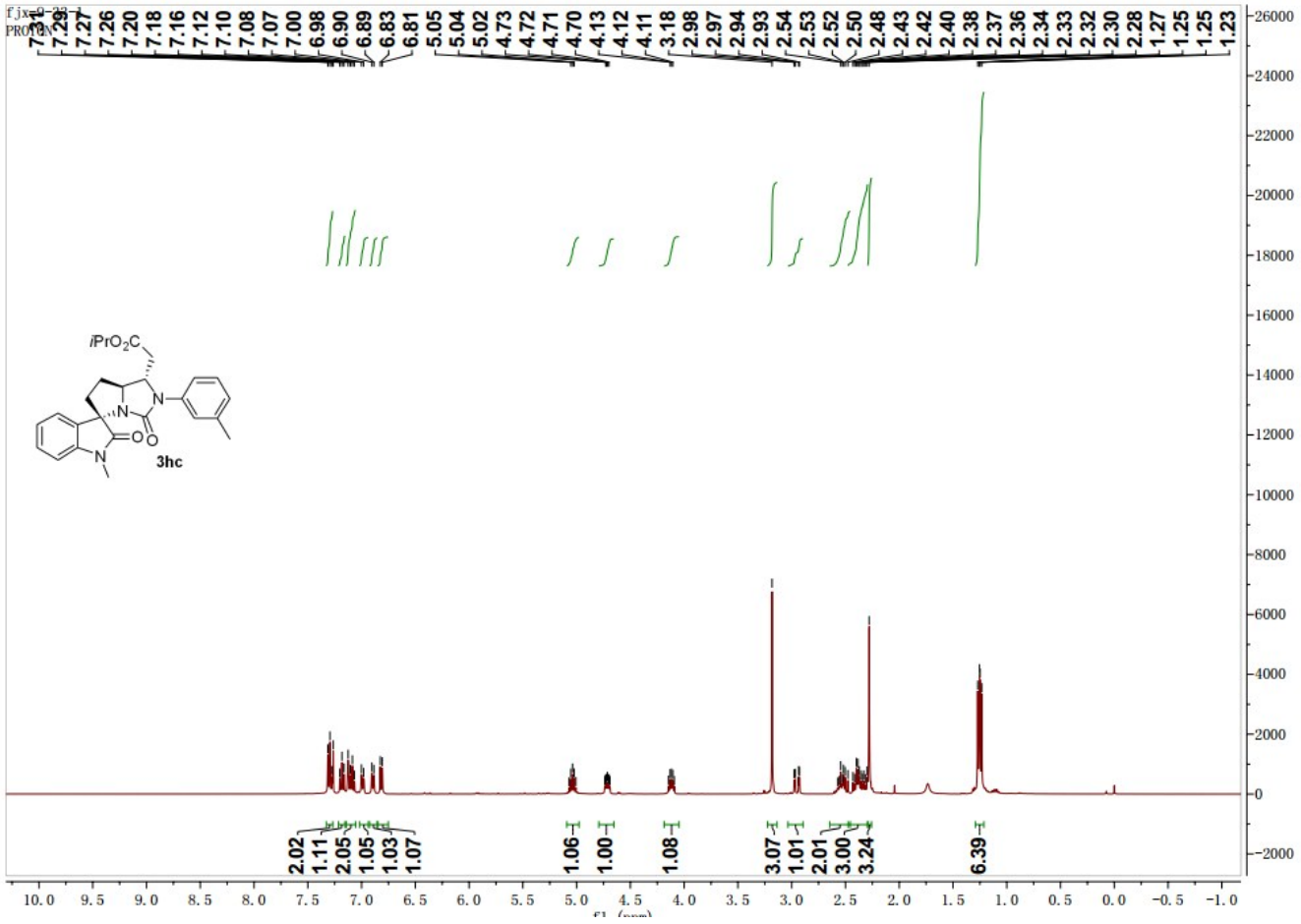
123.08
122.51
122.33
108.64
68.73
66.32
64.50
58.39
40.21
38.57
32.50
26.77
21.97
21.87
20.92
iPrO2C
4ac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7.12
7.10
7.08
7.07
7.00
6.98
6.90
6.89
6.83
6.81
5.05
5.04
5.02
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4.72
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4.13
4.12
4.11
3.18
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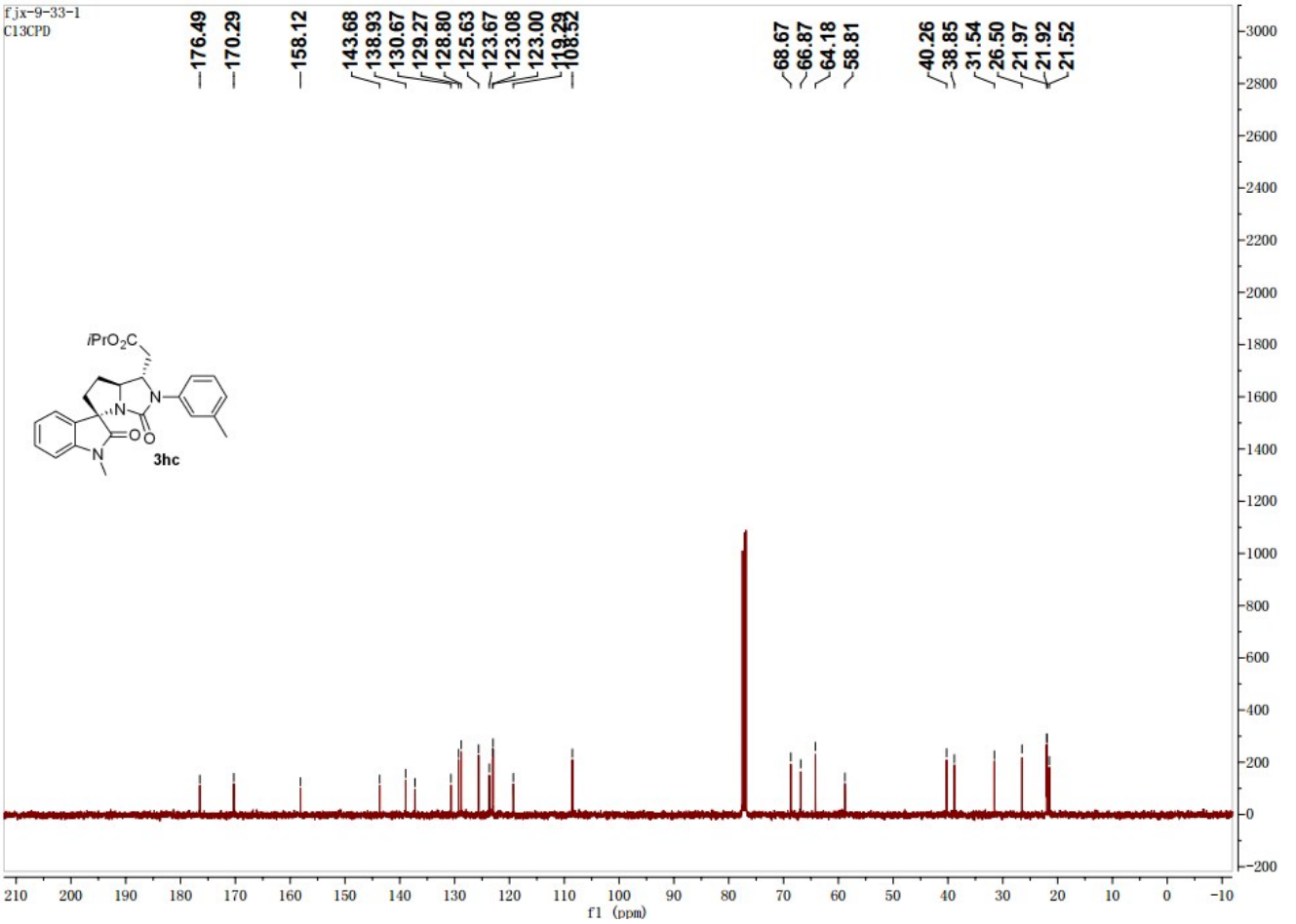
2.97
2.94
2.93
2.54
2.53
2.52
2.50
2.48
2.43
2.42
2.40
2.38
2.37
2.36
2.34
2.33
2.32
2.30
2.28
1.27
1.25
1.25
1.23
iPrO2C
3hc
2.02
1.11
2.05
1.05
1.03
1.07
1.06
1.00
1.08
3.07
1.01
2.01
3.00
3.24
6.39
f1 (ppm)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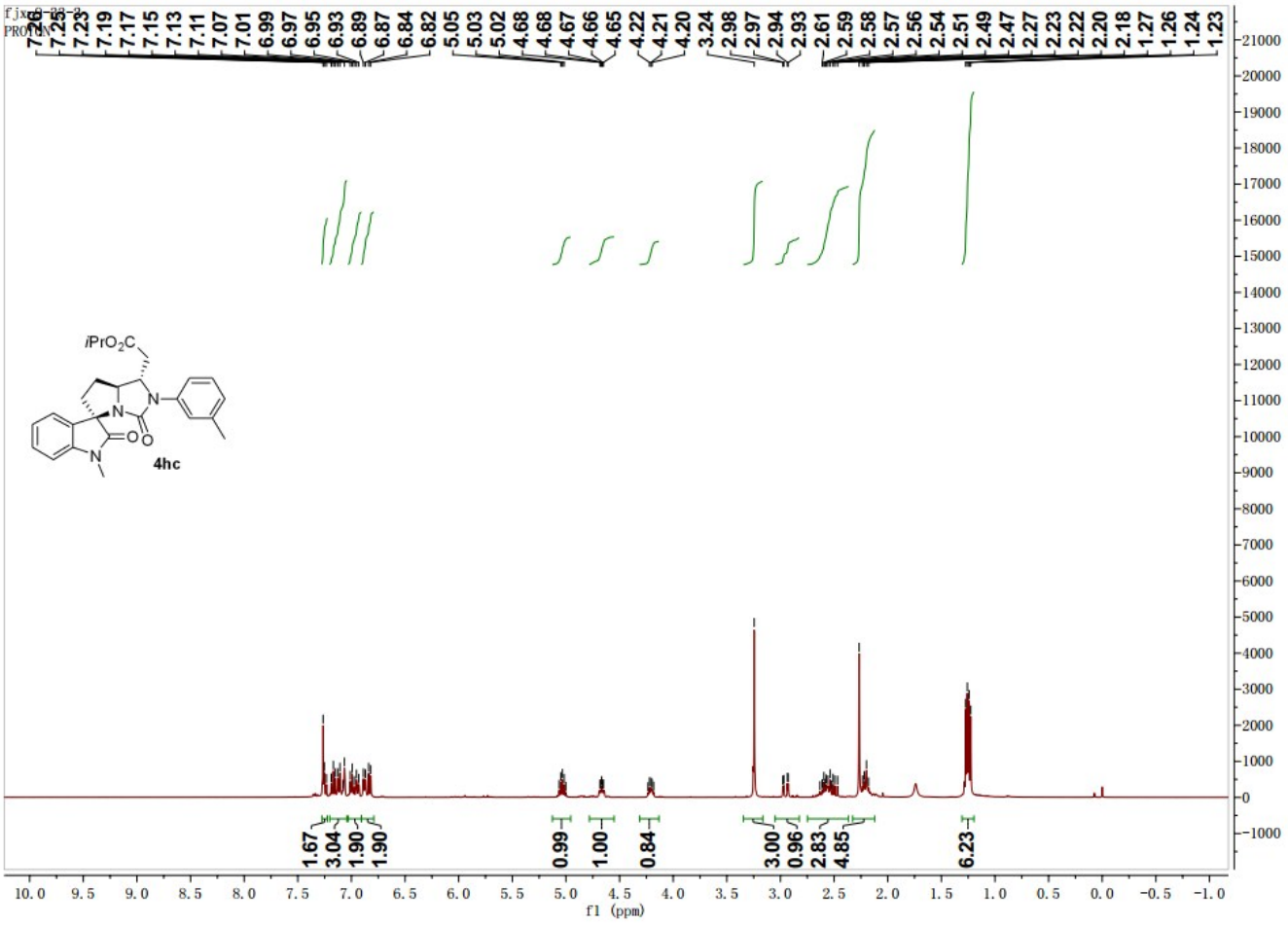
130.67
129.27
128.80
125.63
123.67
123.08
123.00
68.67
66.87
64.18
58.81
40.26
38.85
31.54
26.50
21.97
21.92
21.52
iPrO2C
3hc
f1 (ppm)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6.84
6.82
5.05
5.03
5.02
4.68
4.68
4.67
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4.21
4.20
3.24
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2.94
2.93
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2.47
2.27
2.23
2.22
2.20
2.18
1.27
1.26
1.24
1.23
iPrO2C
4hc
1.67
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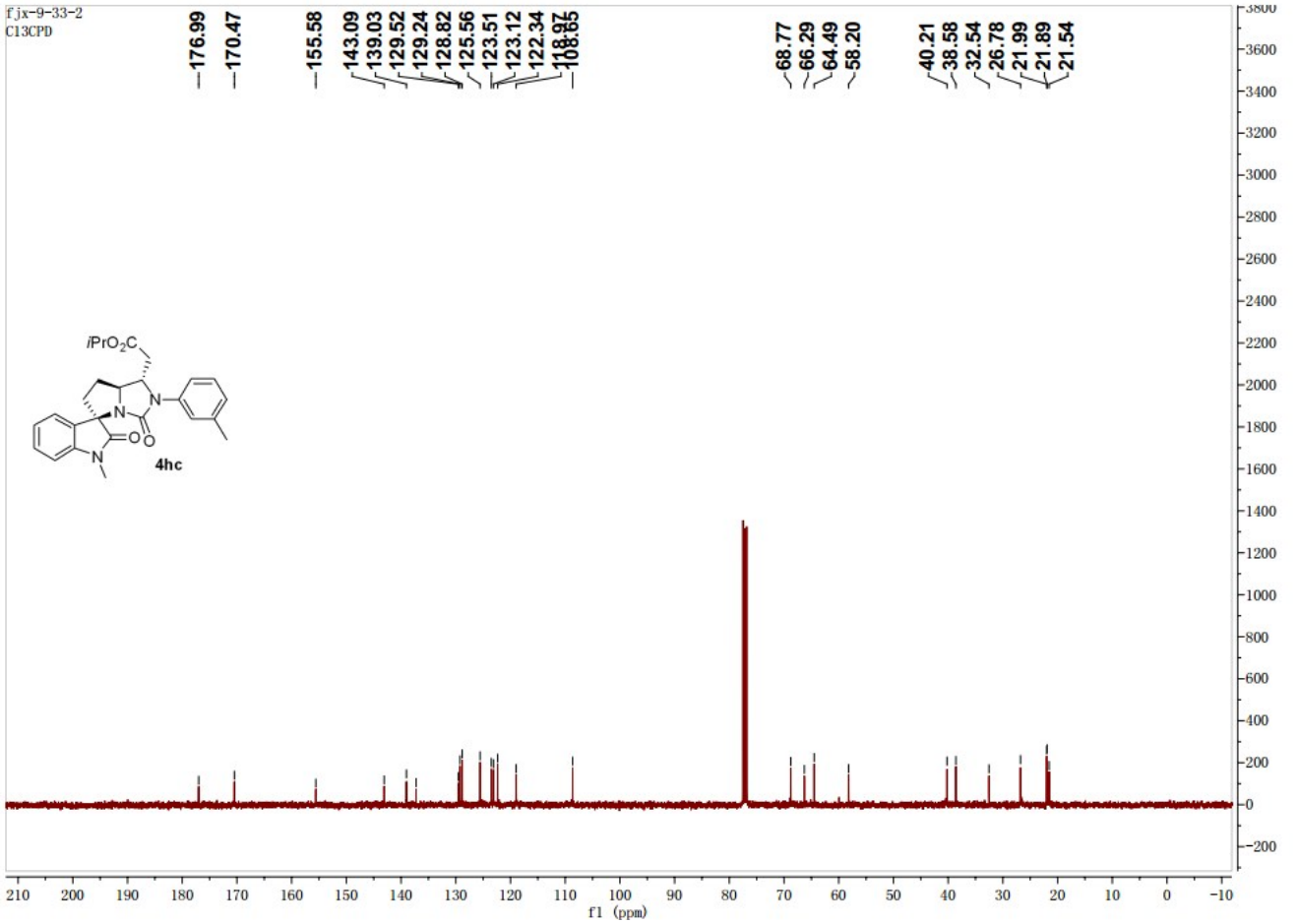
1.00
0.84
3.00
0.96
2.83
4.85
6.23
f1 (ppm)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C13CPD
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139.03
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129.24
128.82
125.56
123.51
123.12
122.34
118.97
108.85
68.77
66.29
64.49
58.20
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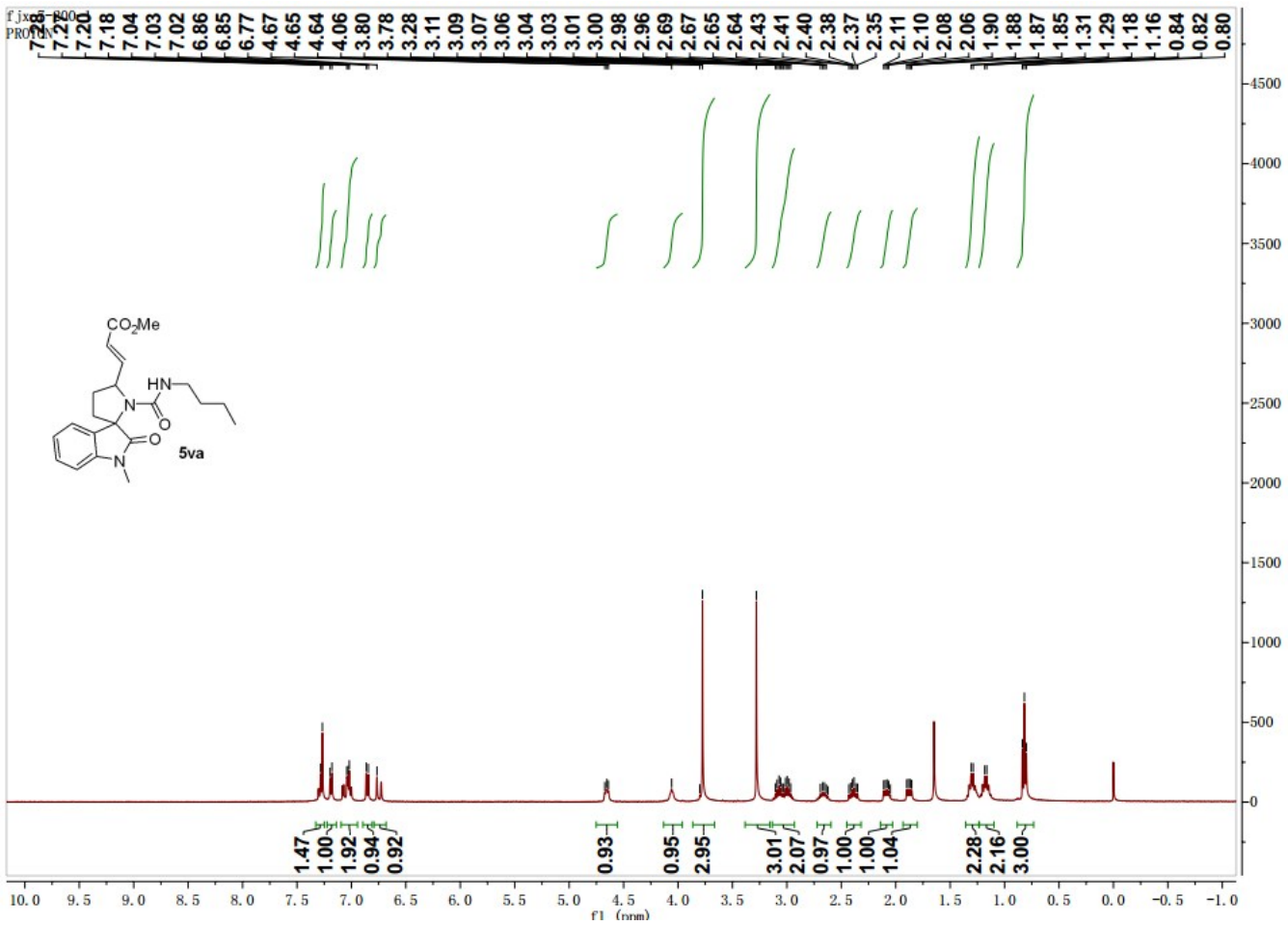
38.58
32.54
26.78
21.99
21.89
21.54
iPrO2C
4hc
f1 (ppm)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4.64
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3.78
3.28
3.11
3.09
3.07
3.06
3.04
3.03
3.01
3.00
2.98
2.96
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2.67
2.65
2.64
2.43
2.41
2.40
2.38
2.37
2.35
2.11
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2.08
2.06
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1.88
1.87
1.85
1.31
1.29
1.18
1.16
0.84
0.82
0.80
CO2Me
HN
N
O
O
N
5va
1.47
1.00
1.92
0.94
0.92
0.93
0.95
2.95
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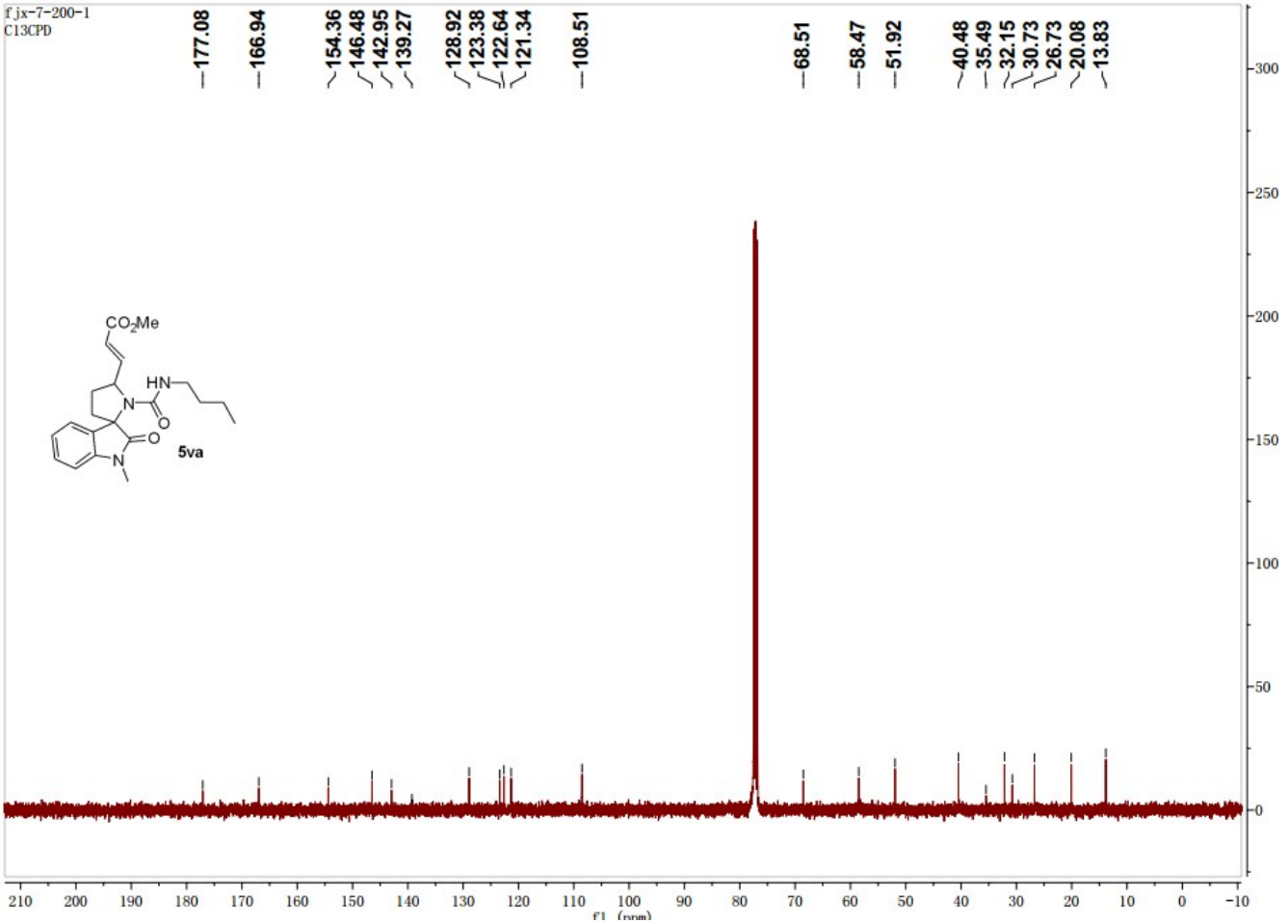
2.07
0.97
1.00
1.00
1.04
2.28
2.16
3.00
f1 (ppm)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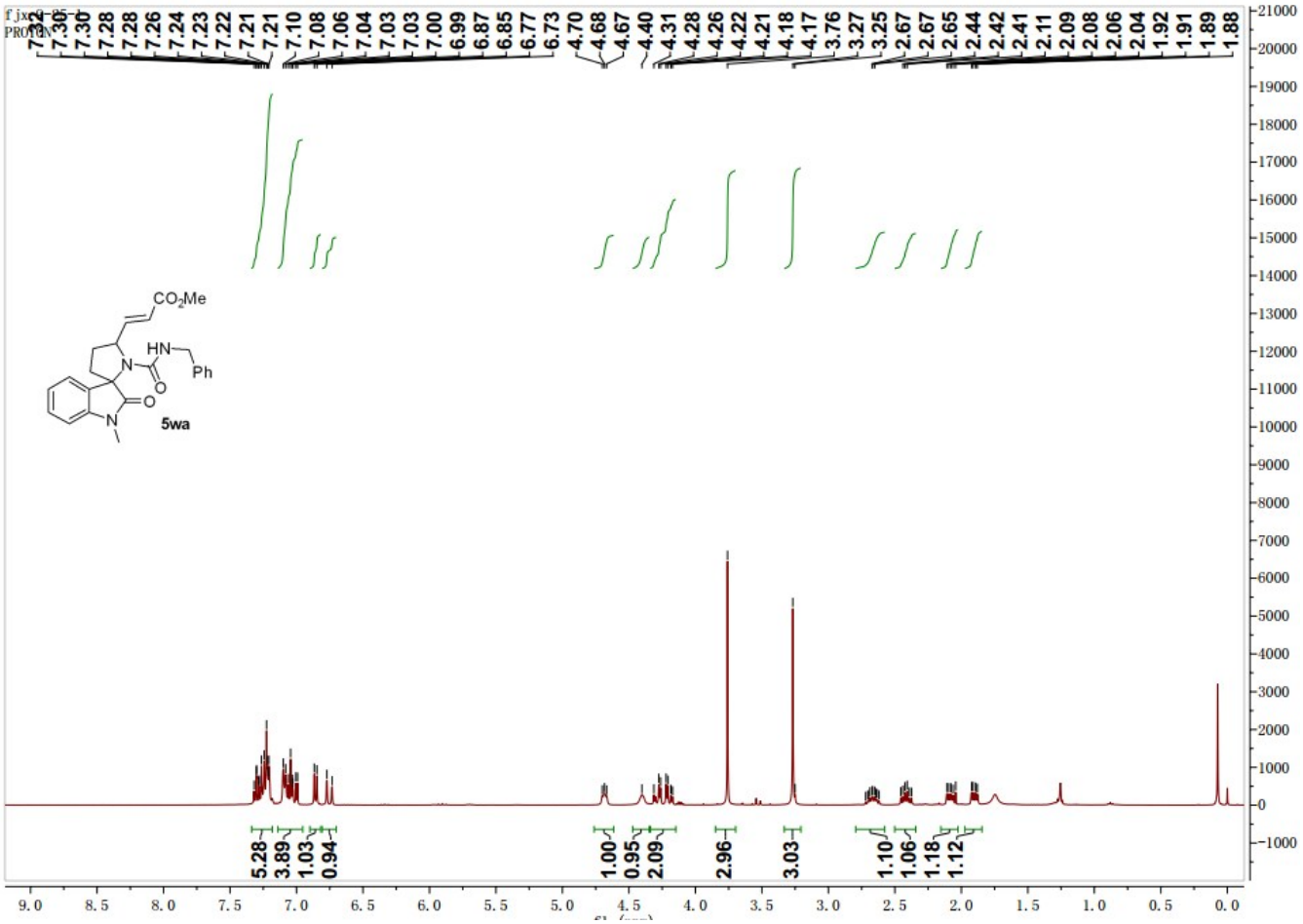
128.92
123.38
122.64
121.34
108.51
68.51
58.47
51.92
40.48
35.49
32.15
30.73
26.73
20.08
13.83
CO2Me
HN
N
O
O
N
5va
f1 (ppm)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7.23
7.22
7.21
7.21
7.10
7.08
7.06
7.04
7.03
7.03
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6.87
6.85
6.77
6.73
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4.67
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4.28
4.26
4.22
4.21
4.18
4.17
3.76
3.27
3.25
2.67
2.67
2.65
2.44
2.42
2.41
2.11
2.09
2.08
2.06
2.04
1.92
1.91
1.89
1.88
CO2Me
HN
Ph
O
O
N
N
5wa
5.28
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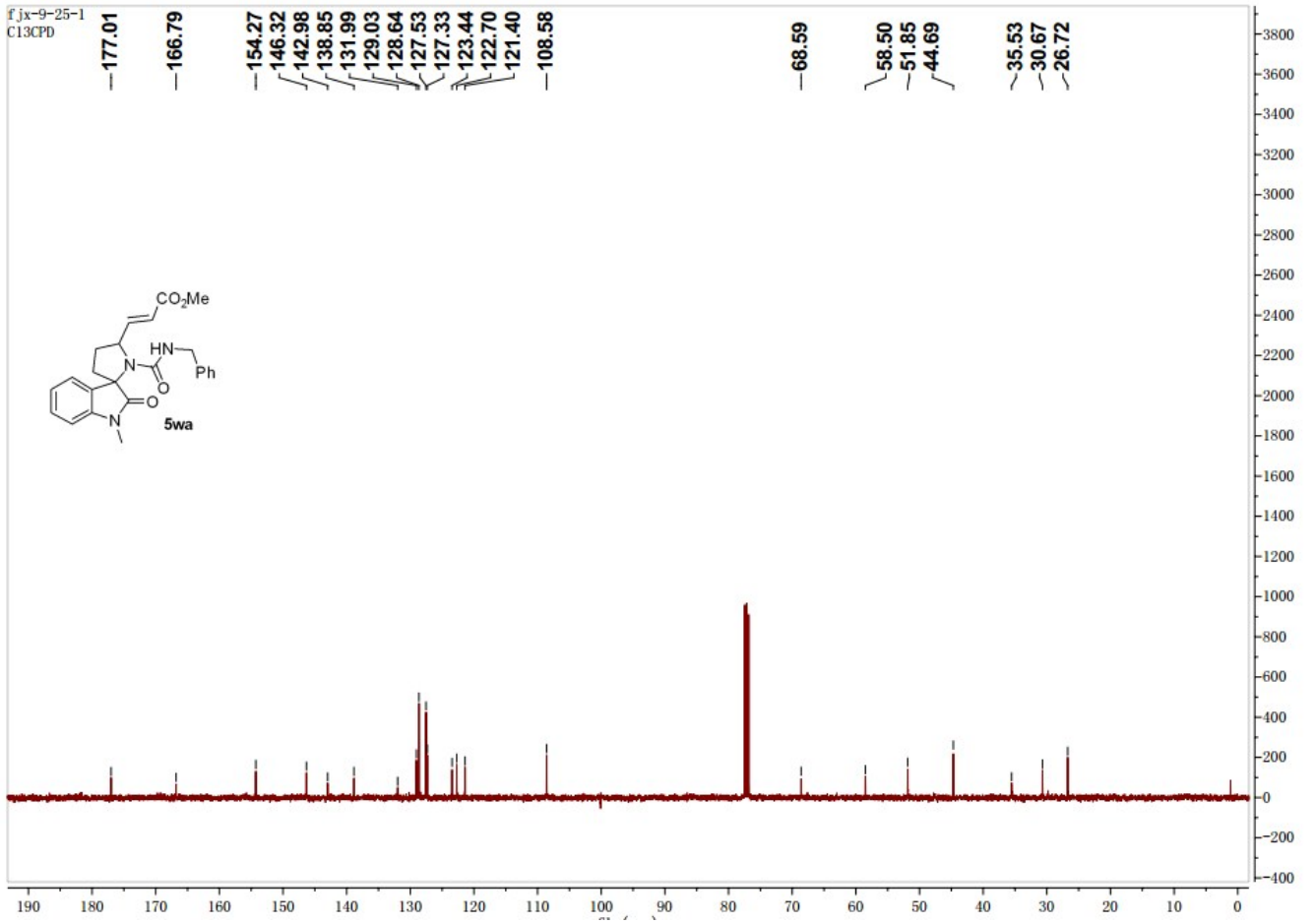
1.00
0.95
2.09
2.96
3.03
1.10
1.06
1.18
1.12


fjx-9-25-1
C13CPD
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146.32
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131.99
129.03
128.64
127.53
127.33
123.44
122.70
121.40
108.58
68.59
58.50
51.85
44.69
35.53
30.67
26.72
CO2Me
HN
Ph
O
O
N
N
5wa