Amphiphillic Methyleneamino Synthon through Organic Dye Catalyzed-Decarboxylative Aminoalkylation

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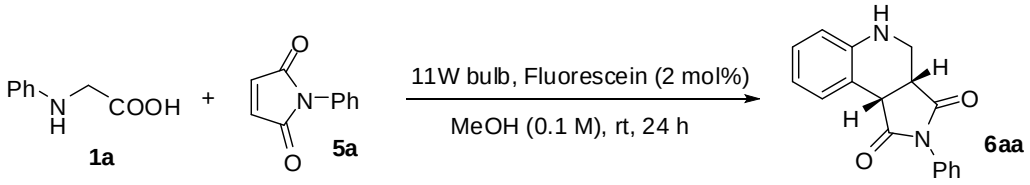
Supporting Information

General procedures and methods

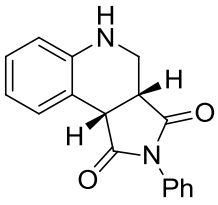
^{1}H and ^{13}C NMR spectra were recorded on a Bruker ACF300 (300MHz), Bruker DPX300 (300MHz) DRX500 (500MHz) or AMX500 (500MHz) spectrometer. Chemical shifts are reported in parts per million (ppm). The residual solvent peak was used as an internal reference. Low resolution mass spectra were obtained on a Finnigan/MAT LCQ spectrometer in ESI mode and a Finnigan/MAT 95XL-T mass spectrometer in FAB mode. All high resolution mass spectra were obtained on a Finnigan/MAT 95XL-T spectrometer. Analytical thin layer chromatography (TLC) was performed with Merck pre-coated TLC plates, silica gel 60F-254, layer thickness 0.25 mm. Flash chromatography separations were performed on Merck 60 (0.040 - 0.063mm) mesh silica gel. Reagents and solvents were commercial grade and were used as supplied without further purification, unless otherwise stated. Irradiation was performed using 11 W house hold bulbs.

Representative procedure for decarboxylative annulations between *N*-aryl-glycine (1a) and *N*-phenyl maleimide (5a) catalyzed by fluorescein



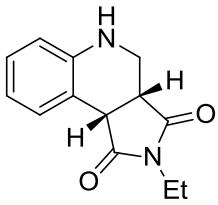
Maleimide **5a** (17.3 mg, 0.10 mmol, 1.0 equiv.) and Fluorescein (0.66 mg, 0.002 mmol, 2 mol%) were dissolved in MeOH (0.5 mL) at a 5 mL rbf equipped with a stir bar. Modified amino acid **1a** (18.12 mg, 0.12 mmol, 1.2 equiv. dissolved in 0.5 mL MeOH) was slowly added into the reaction mixture described above by syringe pump over 10 hours under a 11 W house hold bulb irradiation at room temperature. After addition, the reaction mixture was stirred under same irradiation for another 14 hours. Upon reactiion completion assessed by TLC, the reaction solvent was removed under reduced pressure. The resulting crude mixture syrup was directly loaded onto a short pad of silica gel, and then purified by flash chromatography using gradient elution of hexane/EtOAc mixtures (10/1 - 2/1 ratio) to afford the expected product **6aa** (20.9 mg) as pale yellow solid in 89% yield.

2-phenyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione (6aa)



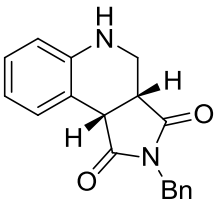
Pale yellow solid, ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.57 (d, *J* = 7.6 Hz, 1H), 7.48 – 7.42 (m, 2H), 7.42 – 7.35 (m, 1H), 7.32 – 7.26 (m, 2H), 7.20 – 7.08 (m, 1H), 6.96 – 6.85 (m, 1H), 6.64 (d, *J* = 7.8 Hz, 1H), 4.16 (d, *J* = 9.3 Hz, 1H), 3.89 (br, 1H), 3.74 (dd, *J* = 11.3, 3.1 Hz, 1H), 3.59 – 3.45 (m, 1H), 3.30 (dd, *J* = 11.3, 4.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.6, 175.9, 146.2, 132.1, 130.6, 129.1, 128.6, 128.5, 126.5, 120.1, 116.9, 115.8, 43.4, 41.7, 41.6. LRMS (ESI) m/z 279.0 (M + H^+). HRMS (ESI) m/z 279.1138 (M + H^+), Cal. $C_{17}H_{15}N_2O_2$, 279.1134.

2-ethyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione (6ab)



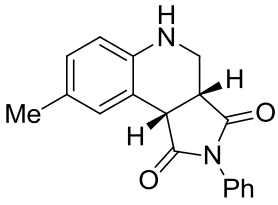
Pale yellow solid, ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.49 (d, *J* = 7.6 Hz, 1H), 7.14 – 7.03 (m, 1H), 6.89 – 6.80 (m, 1H), 6.59 (d, *J* = 7.9 Hz, 1H), 3.97 (d, *J* = 9.2 Hz, 1H), 3.73 (br, 1H), 3.65 (dd, *J* = 11.2, 3.0 Hz, 1H), 3.61 – 3.48 (m, 2H), 3.38 – 3.29 (m, 1H), 3.29 – 3.20 (m, 1H), 1.13 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.4, 176.7, 146.2, 130.7, 128.5, 120.3, 117.3, 115.8, 43.4, 41.8, 41.6, 34.4, 13.2. LRMS (ESI) m/z 231.1 (M + H^+). HRMS (ESI) m/z 231.1130 (M + H^+), Cal. $C_{13}H_{15}N_2O_2$, 231.1134.

2-benzyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione (6ac)



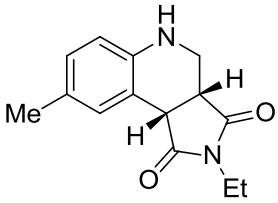
Pale yellow solid, ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.49 (d, *J* = 7.7 Hz, 1H), 7.33 – 7.23 (m, 6H), 7.11 – 7.06 (m, 1H), 6.85 (t, *J* = 7.5 Hz, 1H), 6.59 (d, *J* = 8.1 Hz, 1H), 4.65 (q, *J* = 14.3 Hz, 2H), 3.99 (d, *J* = 9.1 Hz, 1H), 3.75 (br, 1H), 3.64 (dd, *J* = 11.2, 3.2 Hz, 1H), 3.43 – 3.31 (m, 1H), 3.25 (dd, *J* = 11.2, 4.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.3, 176.6, 146.2, 135.8, 130.7, 128.8, 128.6, 128.5, 128.0, 120.3, 117.1, 115.8, 43.5, 43.0, 41.8, 41.6. LRMS (ESI) m/z 293.1 (M + H^+). HRMS (ESI) m/z 293.1291 (M + H^+), Cal. $C_{18}H_{17}N_2O_2$, 293.1290.

8-methyl-2-phenyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione (6ba)



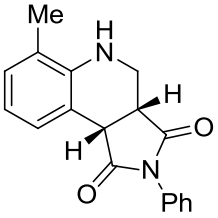
Pale yellow solid, ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.45 – 7.39 (m, 2H), 7.39 – 7.33 (m, 2H), 7.30 – 7.24 (m, 2H), 6.93 (d, *J* = 7.5 Hz, 1H), 6.59 (d, *J* = 8.1 Hz, 1H), 4.12 (d, *J* = 9.4 Hz, 1H), 3.75 (dd, *J* = 11.3, 3.2 Hz, 1H), 3.58 – 3.48 (m, 1H), 3.28 (dd, *J* = 11.3, 4.4 Hz, 1H), 2.29 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.6, 176.0, 143.1, 132.2, 131.0, 130.2, 129.4, 129.2, 128.7, 126.6, 117.2, 116.2, 43.2, 42.1, 41.6, 20.8. LRMS (ESI) m/z 293.1 (M + H^+). HRMS (ESI) m/z 293.1295 (M + H^+), Cal. $C_{18}H_{17}N_2O_2$, 293.1290.

2-ethyl-8-methyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione (6bb)



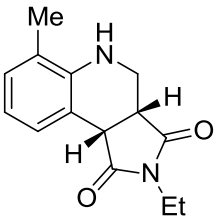
Pale yellow solid, ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.34 (s, 1H), 6.92 (d, *J* = 7.7 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 1H), 3.94 (d, *J* = 9.2 Hz, 1H), 3.64 (dd, *J* = 11.4, 3.5 Hz, 1H), 3.59 – 3.48 (m, 2H), 3.40 – 3.32 (m, 1H), 3.24 (dd, *J* = 11.3, 4.7 Hz, 1H), 2.29 (s, 3H), 1.14 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.2, 176.6, 130.9, 129.2, 117.9, 116.5, 42.8, 42.1, 41.4, 34.5, 20.9, 13.1. LRMS (ESI) m/z 245.1 (M + H^+). HRMS (ESI) m/z 245.1293 (M + H^+), Cal. $C_{14}H_{17}N_2O_2$, 245.1290.

6-methyl-2-phenyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione (6ca)



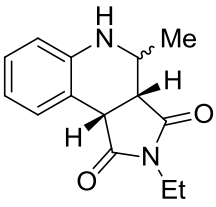
Pale yellow solid, ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.45 – 7.38 (m, 3H), 7.38 – 7.31 (m, 1H), 7.28 – 7.20 (m, 2H), 7.01 (d, *J* = 7.3 Hz, 1H), 6.78 (t, *J* = 7.6 Hz, 1H), 4.16 (d, *J* = 9.3 Hz, 1H), 3.92 – 3.73 (m, 2H), 3.60 – 3.44 (m, 1H), 3.30 (dd, *J* = 11.3, 4.4 Hz, 1H), 2.13 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.5, 175.8, 144.2, 132.0, 129.5, 128.9, 128.4, 128.3, 126.3, 122.5, 119.2, 116.0, 43.3, 41.7, 41.5, 16.8. LRMS (ESI) m/z 293.1 (M + H^+). HRMS (ESI) m/z 293.1284 (M + H^+), Cal. $C_{18}H_{17}N_2O_2$, 293.1290.

2-ethyl-6-methyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione (6cb)



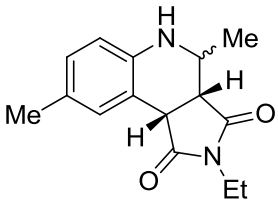
Pale yellow solid, ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.38 (d, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 7.3 Hz, 1H), 6.78 (t, *J* = 7.6 Hz, 1H), 3.99 (d, *J* = 9.2 Hz, 1H), 3.76 (br, 1H), 3.73 – 3.66 (m, 1H), 3.59 – 3.46 (m, 2H), 3.38 – 3.31 (m, 1H), 3.23 (dd, *J* = 11.3, 4.4 Hz, 1H), 2.11 (s, 3H), 1.14 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.4, 176.6, 144.2, 129.4, 128.3, 122.5, 119.2, 116.4, 43.3, 41.6, 41.6, 34.2, 16.8, 13.0. LRMS (ESI) m/z 245.1 (M + H^+). HRMS (ESI) m/z 245.1285 (M + H^+), Cal. $C_{14}H_{17}N_2O_2$, 245.1290.

2-ethyl-4-methyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione (6db)



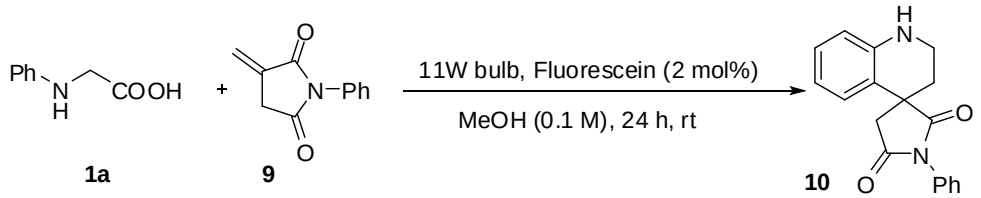
Pale yellow solid, mixture of the two diastereoisomers: ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.59 (d, *J* = 7.9 Hz, 0.4H, minor isomer), 7.50 (d, *J* = 7.6 Hz, 0.6H, major isomer), 7.08 (dd, *J* = 11.0, 4.2 Hz, 1H), 6.90 – 6.80 (m, 1H), 6.58 (d, *J* = 7.9 Hz, 1H), 3.98 (d, *J* = 9.0 Hz, 0.6H, major isomer), 3.90 (d, *J* = 8.7 Hz, 0.4H, minor isomer), 3.73 – 3.42 (m, 4H), 3.32 – 3.24 (m, 0.6H, major isomer), 3.02 – 2.93 (m, 0.4H, minor isomer), 1.56 (d, *J* = 6.9 Hz, 1.9H, major isomer), 1.38 (d, *J* = 6.4 Hz, 1H, minor isomer), 1.16 – 1.07 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.3, 176.6, 176.6, 176.4, 146.1, 143.6, 130.2, 128.3, 128.2, 120.0, 119.5, 117.3, 116.0, 116.0, 115.6, 49.1, 47.6, 47.2, 46.9, 42.8, 40.3, 34.0, 33.9, 20.1, 18.1, 13.0, 12.9. LRMS (ESI) m/z 245.1 (M + H^+). HRMS (ESI) m/z 245.1285 (M + H^+), Cal. $C_{14}H_{17}N_2O_2$, 245.1290.

4,8-dimethyl-2-phenyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione (6eb)



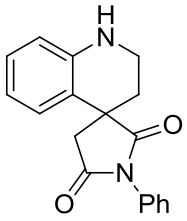
Pale yellow solid, mixture of the two diastereoisomers: ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.41-7.31 (m, 1H), 6.89 (dd, *J* = 4.9, 2.8 Hz, 1H), 6.49 (d, *J* = 8.0 Hz, 1H), 3.94 (d, *J* = 9.0 Hz, 0.5H), 3.86 (d, *J* = 8.7 Hz, 0.5H), 3.65 – 3.38 (m, 4H), 3.25 (dd, *J* = 9.0, 4.0 Hz, 0.6H, major isomer), 2.95 (dd, *J* = 8.6, 6.1 Hz, 0.4H, minor isomer), 2.33 – 2.24 (m, 3H), 1.55 (d, *J* = 6.7 Hz, 1.8H, major isomer), 1.37 (d, *J* = 6.4 Hz, 1.5H, minor isomer), 1.17 – 1.08 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.4, 176.7, 176.6, 176.4, 143.8, 141.2, 130.5, 130.4, 129.3, 129.0, 128.9, 117.2, 115.9, 115.6, 115.5, 49.4, 47.7, 47.4, 47.0, 42.9, 40.4, 34.0, 33.9, 20.6, 20.1, 18.1, 13.0, 12.90. LRMS (ESI) m/z 259.1 (M + H^+). HRMS (ESI) m/z 259.1444 (M + H^+), Cal. $C_{15}H_{19}N_2O_2$, 259.1447.

Procedure for decarboxylative annulations between *N*-aryl-glycine (1a) and (9) catalyzed by fluorescein and visible light



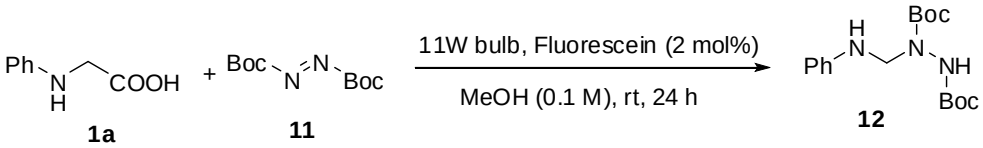
Compound **9** (37.4 mg, 0.2 mmol, 1.0 equiv.) and Fluorescein (1.33 mg, 0.004 mmol, 2 mol%) were dissolved in MeOH (1.0 mL) at a 5 mL rbf equipped with a stir bar. Modified amino acid **1a** (36.1 mg, 0.24 mmol, 1.2 equiv. dissolved in 1.0 mL MeOH) was slowly added into the reaction mixture described above by syringe pump over 10 hours under a 11 W house hold bulb irradiation at room temperature. After addition, the reaction mixture was stirred under same irradiation for another 14 hours. Upon reactiion completion assessed by TLC, the reaction solvent was removed under reduced pressure. The resulting crude mixture syrup was directly loaded onto a short pad of silica gel, and then purified by flash chromatography using gradient elution of hexane/EtOAc mixtures (4/1 - 2/1 ratio) to afford the expected product **10** (44.2 mg) as pale yellow solid in 85% yield.

1-phenyl-2',3'-dihydro-1'H-spiro[pyrrolidine-3,4'-quinoline]-2,5-dione (10)



White solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 – 7.45 (m, 2H), 7.44 – 7.38 (m, 1H), 7.38 – 7.33 (m, 2H), 7.12 – 7.02 (m, 1H), 6.94 (dd, *J* = 7.8, 1.3 Hz, 1H), 6.69 (td, *J* = 7.8, 1.2 Hz, 1H), 6.57 (dd, *J* = 8.1, 1.0 Hz, 1H), 4.10 (s, 1H), 3.77 – 3.65 (m, 1H), 3.32 (ddd, *J* = 11.9, 8.9, 3.3 Hz, 1H), 3.19 (d, *J* = 18.4 Hz, 1H), 2.95 (d, *J* = 18.5 Hz, 1H), 2.45 (ddd, *J* = 12.8, 8.9, 3.6 Hz, 1H), 2.09 – 2.01 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.20, 174.68, 144.31, 131.94, 129.19, 128.77, 128.68, 126.45, 126.38, 120.53, 118.09, 115.39, 77.25, 77.00, 76.75, 46.33, 45.45, 38.14, 32.54. LRMS (ESI) m/z 293.2 ($M + H^+$). HRMS (ESI) m/z 293.1289 ($M + H^+$), Cal. $C_{18}H_{17}N_2O_2$, 293.1285.

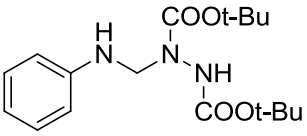
Procedure for decarboxylative coupling reaction between *N*-aryl-glycine 1a and 11 catalyzed by fluorescein



Diazodicarboxylate ester **11** (92.0 mg, 0.4 mmol, 2.0 equiv.) and Fluorescein (1.33 mg, 0.004 mmol, 2 mol%) were dissolved in MeOH (1.0 mL) at a 5 mL rbf equipped with a stir bar. Modified amino acid **1a** (30.2 mg, 0.2 mmol, 1 equiv., dissolved in 1.0 mL MeOH) was

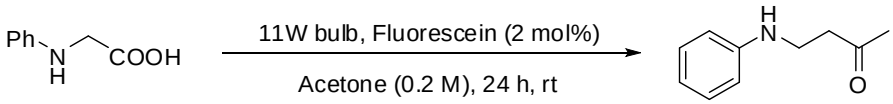
slowly added into the reaction mixture described above by syringe pump over 10 hours under a 11 W house hold bulb irradiation at room temperature. After addition, the reaction mixture was stirred under same irradiation for another 14 hours. Upon reactiion completion assessed by TLC, the reaction solvent was removed under reduced pressure. The resulting crude mixture syrup was directly loaded onto a short pad of silica gel, and then purified by flash chromatography using gradient elution of hexane/EtOAc mixtures (6/1 ratio) to afford the expected product **12** (55.6 mg) as pale yellow solid in 82% yield.

di-tert-butyl 1-((phenylamino)methyl)hydrazine-1,2-dicarboxylate (12)



Brown liquid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (dd, *J* = 8.5, 7.4 Hz, 2H), 6.77 – 6.72 (m, 3H), 6.34 (s, 1H), 4.90 (s, 2H), 4.59 (s, 1H), 1.47 (s, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.22, 145.72, 129.25, 118.50, 113.59, 81.45, 77.25, 77.00, 76.75, 58.49, 28.11. LRMS (ESI) m/z 337.9 ($M + H^+$). HRMS (ESI) m/z 338.2066, ($M + H^+$), Cal. $C_{17}H_{28}N_3O_4$, 338.2074.

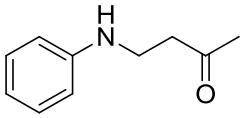
Representative procedure for decarboxylative coupling reaction between *N*-aryl-glycine (1a) and acetone catalyzed by fluorescein and L-proline



1a **13**

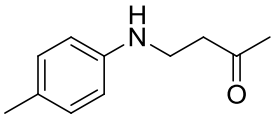
L-proline (3.4 mg, 0.03 mmol, 0.3 equiv.) and Fluorescein (0.6 mg, 0.002 mmol, 2 mol%) were dissolved in acetone (0.5 mL) at a 5 mL rbf equipped with a stir bar. Modified amino acid **1a** (15.1 mg, 0.10 mmol, 1.0 equiv. dissolved in 0.5 mL acetone) was slowly added into the reaction mixture described above by syringe pump over 10 hours under a 11 W house hold bulb irradiation at room temperature. After addition, the reaction mixture was stirred under same irradiation for another 14 hours. Upon reactiion completion assessed by TLC, the reaction solvent was removed under reduced pressure. The resulting crude mixture syrup was directly loaded onto a short pad of silica gel, and then purified by flash chromatography using gradient elution of hexane/EtOAc mixtures (6/1 ratio) to afford the expected product **13** (15.0 mg) as pale yellow solid in 85% yield.

4-(phenylamino)butan-2-one (13a)



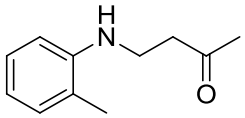
Pale yellow solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 – 7.15 (m, 2H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.64 (dd, *J* = 8.5, 0.9 Hz, 2H), 3.87 (s, 1H), 3.42 (t, *J* = 6.2 Hz, 2H), 2.76 (t, *J* = 6.2 Hz, 2H), 2.16 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.95, 147.27, 129.28, 117.94, 113.26, 77.25, 77.00, 76.75, 42.44, 38.58, 30.22. LRMS (ESI) m/z 164.0 ($M + H^+$). HRMS (ESI) m/z 164.1074 ($M + H^+$), Cal. $C_{10}H_{14}NO$, 164.1070.

4-(p-tolylamino)butan-2-one (13b)



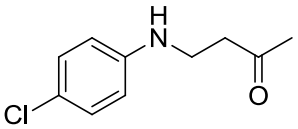
Pale yellow solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.99 (d, *J* = 8.3 Hz, 2H), 6.54 (d, *J* = 8.4 Hz, 2H), 3.83 (s, 1H), 3.39 (t, *J* = 6.1 Hz, 2H), 2.73 (t, *J* = 6.1 Hz, 2H), 2.24 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.13, 145.35, 129.77, 126.91, 113.26, 77.25, 77.00, 76.75, 42.61, 38.76, 30.25, 20.33. LRMS (ESI) m/z 178.0 (M + H^+). HRMS (ESI) m/z 178.1236, (M + H^+), Cal. $C_{11}H_{16}NO$, 178.1226.

4-(o-tolylamino)butan-2-one (13c)



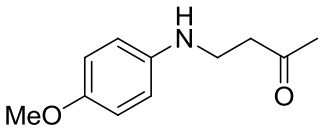
Pale yellow liquid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13 (t, *J* = 7.7 Hz, 1H), 7.05 (d, *J* = 7.3 Hz, 1H), 6.67 (t, *J* = 7.4 Hz, 1H), 6.62 (d, *J* = 8.0 Hz, 1H), 3.90 (s, 1H), 3.47 (t, *J* = 6.1 Hz, 2H), 2.79 (t, *J* = 6.1 Hz, 2H), 2.17 (s, 3H), 2.11 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.16, 145.61, 130.25, 127.06, 122.53, 117.15, 109.58, 77.25, 77.00, 76.75, 42.57, 38.29, 30.29, 17.40. LRMS (ESI) m/z 178.0 (M + H^+). HRMS (ESI) m/z 178.1235, (M + H^+), Cal. $C_{11}H_{16}NO$, 178.1226.

4-((4-chlorophenyl)amino)butan-2-one (13d)



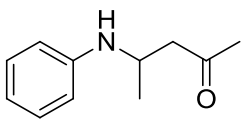
Pale yellow solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 – 7.07 (m, 2H), 6.57 – 6.47 (m, 2H), 4.01 (s, 1H), 3.37 (t, *J* = 6.1 Hz, 2H), 2.73 (t, *J* = 6.0 Hz, 2H), 2.16 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.88, 146.25, 129.10, 122.17, 114.07, 77.25, 77.00, 76.75, 42.33, 38.45, 30.29. LRMS (ESI) m/z 198.0 (M + H^+). HRMS (ESI) m/z 198.0680 (M + H^+), Cal. $C_{10}H_{13}ClNO$, 198.0680.

4-((4-methoxyphenyl)amino)butan-2-one (13e)



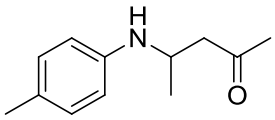
Brown solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.78 (d, *J* = 8.9 Hz, 2H), 6.58 (d, *J* = 8.9 Hz, 2H), 3.74 (s, 4H), 3.36 (t, *J* = 6.1 Hz, 2H), 2.72 (t, *J* = 6.1 Hz, 2H), 2.16 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.16, 152.33, 141.84, 114.89, 114.55, 77.25, 77.00, 76.75, 55.74, 42.63, 39.49, 30.25. LRMS (ESI) m/z 194.0 (M + H^+). HRMS (ESI) m/z 194.1181 (M + H^+), Cal. $C_{11}H_{16}NO_2$, 194.1176.

4-(phenylamino)pentan-2-one (13f)



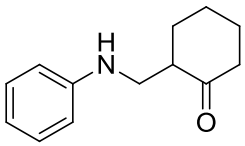
white solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 – 7.13 (m, 2H), 6.76 – 6.67 (m, 1H), 6.60 (dd, *J* = 8.6, 0.9 Hz, 2H), 4.02 – 3.89 (m, 1H), 3.67 (s, 1H), 2.76 (dd, *J* = 16.4, 4.8 Hz, 1H), 2.55 (dd, *J* = 16.4, 7.1 Hz, 1H), 2.16 (s, 3H), 1.25 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.90, 146.78, 129.35, 117.65, 113.53, 77.25, 77.00, 76.75, 49.63, 45.26, 30.77, 20.78. LRMS (ESI) m/z 178.0 (M + H^+). HRMS (ESI) m/z 178.1231 (M + H^+), Cal. $C_{11}H_{16}NO$, 178.1126.

4-(p-tolylamino)pentan-2-one (13g)



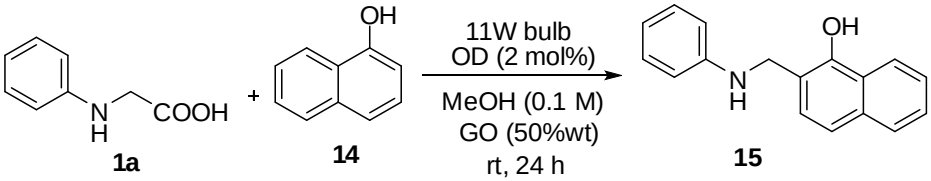
White solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.99 (d, *J* = 8.3 Hz, 2H), 6.54 (d, *J* = 8.4 Hz, 2H), 3.83 (s, 1H), 3.39 (t, *J* = 6.1 Hz, 2H), 2.73 (t, *J* = 6.1 Hz, 2H), 2.24 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.13, 145.35, 129.77, 126.91, 113.26, 77.25, 77.00, 76.75, 42.61, 38.76, 30.25, 20.33. LRMS (ESI) m/z 192.0 ($M + H^+$). HRMS (ESI) m/z 214.1205 ($M + Na^+$), Cal. $C_{12}H_{17}NONa$, 214.1202.

2-((phenylamino)methyl)cyclohexanone (S1)



White solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 – 7.15 (m, 2H), 6.73 (t, *J* = 7.3 Hz, 1H), 6.68 – 6.63 (m, 2H), 3.43 (dd, *J* = 13.5, 7.8 Hz, 1H), 3.12 (dd, *J* = 13.5, 4.6 Hz, 1H), 2.67 (dq, *J* = 7.8, 4.6 Hz, 1H), 2.44 – 2.37 (m, 1H), 2.31 (ddd, *J* = 18.8, 9.6, 3.5 Hz, 1H), 2.16 (ddd, *J* = 12.2, 5.7, 2.7 Hz, 1H), 2.09 (ddd, *J* = 8.9, 5.9, 2.8 Hz, 1H), 1.95 – 1.84 (m, 1H), 1.75 – 1.59 (m, 2H), 1.48 (qd, *J* = 12.7, 3.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 213.17, 147.28, 129.29, 117.99, 113.47, 77.25, 77.00, 76.75, 49.57, 44.37, 42.19, 32.01, 27.71, 24.81. LRMS (ESI) m/z 204.0 ($M + H^+$). HRMS (ESI) m/z 204.1391 ($M + H^+$), Cal. $C_{13}H_{18}NO$, 204.1383.

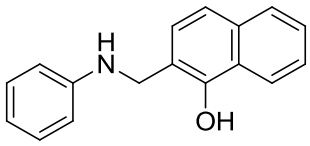
Procedure for decarboxylative friedel-crafts reaction between *N*-aryl-glycine (1a) and (15) catalyzed by fluorescein



1a **14** **15**

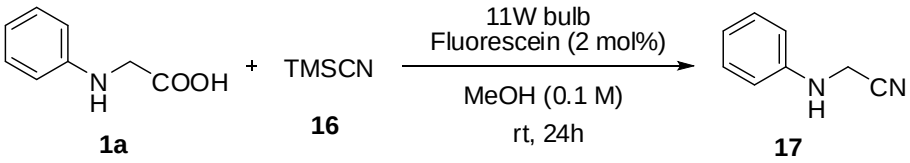
Modified amino acid **1a** (30.2 mg, 0.2 mmol, 2.0 equiv. dissolved in 0.5 mL MeOH) was slowly added into a mixture of **14** (14.4 mg, 0.1 mmol, 1.0 equiv.), GO (grapheme oxide powder, 50%wt of **14**) and Rose bengal (2.0 mg, 0.002 mmol, 2 mol%) in MeOH (0.5 mL) under 11 W house hold bulb irradiation at room temperature over 10 hours. After addition, the reaction was stirred at same irradiation for another 14 hours. After then, the reaction solvent was removed under reduced pressure. The resulting crude mixture was directly loaded onto a short pad of silica gel and then was purified by flash chromatography using gradient elution with hexane/EtOAc mixtures (20/1 to 12/1 ratio) to afford the expected product **15** (12.0 mg) as pale yellow solid in 46% yield.

2-((phenylamino)methyl)naphthalen-1-ol (15)



^{1}H NMR (500 MHz, $CDCl_3$) δ 9.54 (s, 1H), 8.36 – 8.15 (m, 1H), 7.80 (dd, *J* = 5.2, 3.8 Hz, 1H), 7.58 – 7.36 (m, 3H), 7.36 – 7.16 (m, 3H), 7.02 – 6.79 (m, 3H), 4.59 (s, 2H), 4.13 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.74, 147.16, 134.10, 129.42, 127.38, 126.28, 126.22, 125.22, 125.16, 122.01, 121.22, 119.36, 116.26, 115.22, 77.31, 77.05, 76.80, 49.56. LRMS (ESI) m/z 249.9 (M + H^+). HRMS (ESI) m/z 250.1231 (M + H^+), Cal. $C_{17}H_{15}NO$, 250.1226.

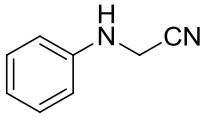
Procedure for decarboxylative coupling reaction between *N*-aryl-glycine (1a) and (16) catalyzed by Fluorescein



1a **16** **17**

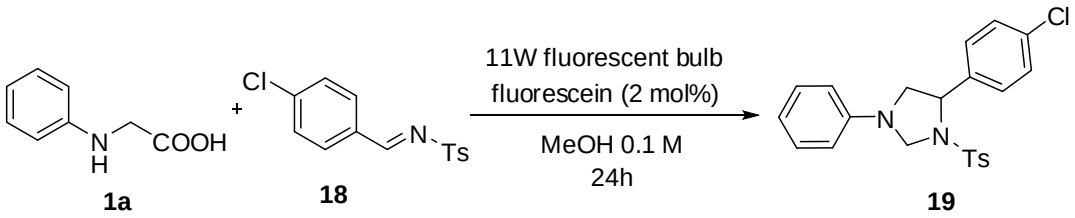
TMSCN (39.6 mg, 0.40 mmol, 2.0 equiv.) and Fluorescein (0.6 mg, 0.002 mmol, 2 mol%) were dissolved in MeOH (0.5 mL) at a 5 mL rbf equipped with a stir bar. Modified amino acid **1a** (30.2 mg, 0.2 mmol, 1.0 equiv. dissolved in 0.5 mL MeOH) was slowly added into the reaction mixture described above by syringe pump over 10 hours under a 11 W house hold bulb irradiation at room temperature. After addition, the reaction mixture was stirred under same irradiation for another 14 hours. Upon reactiion completion assessed by TLC, the reaction solvent was removed under reduced pressure. The resulting crude mixture syrup was directly loaded onto a short pad of silica gel, and then purified by flash chromatography using gradient elution of hexane/EtOAc mixtures (6/1 ratio) to afford the expected product **17** (23.2 mg) as pale yellow solid in 87% yield.

2-(phenylamino)acetonitrile (17)



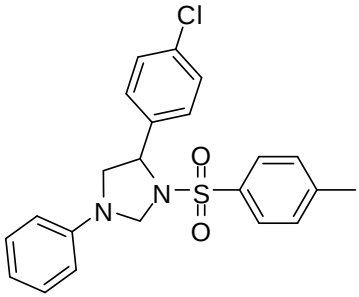
Pale yellow liquid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.26 (m, 2H), 6.96 – 6.82 (m, 1H), 6.72 (dd, *J* = 8.5, 0.9 Hz, 2H), 4.11 (d, *J* = 7.0 Hz, 2H), 3.96 (s, 1H).^{13}C NMR (126 MHz, $CDCl_3$) δ 144.95, 129.56, 120.10, 116.88, 113.62, 77.25, 77.00, 76.75, 32.65. (M + H^+). HRMS (ESI) m/z 133.0762 (M + H^+), Cal. $C_8H_9N_2$, 133.0760.

Procedure for decarboxylative annulations between *N*-phenyl-glycine (1a) and (18) catalyzed by fluorescein



1a **18** **19**

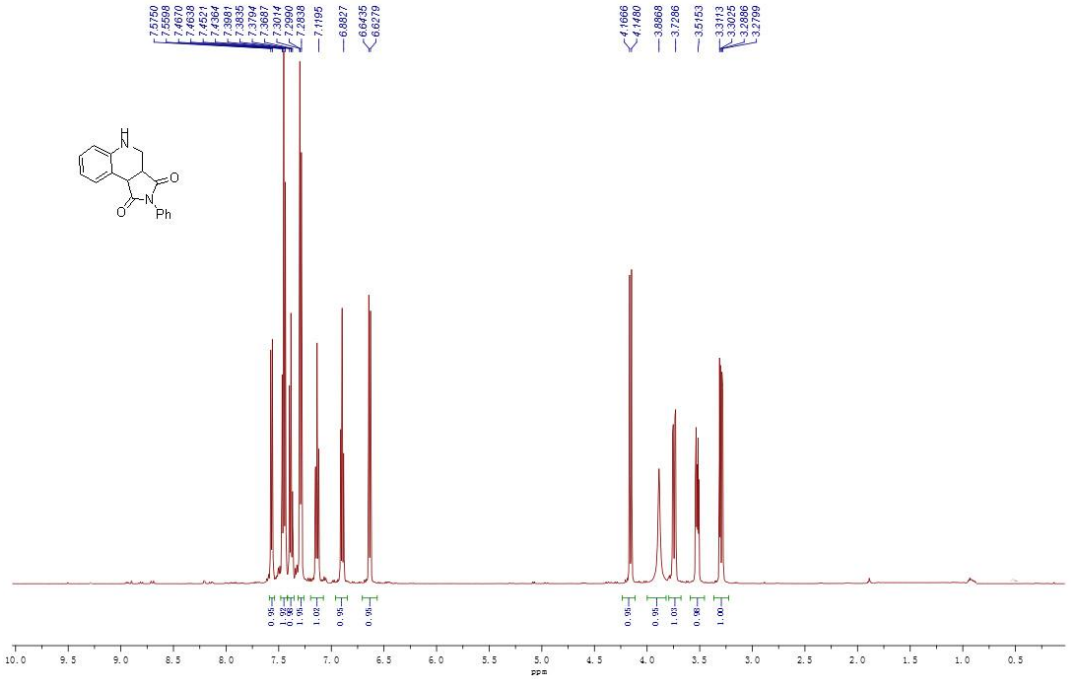
N-Tosyl imine **18** (29.3 mg, 0.1 mmol, 1 equiv.) and Fluorescein (0.6 mg, 0.002 mmol, 2 mol%) were dissolved in MeOH (0.5 mL) at a 5 mL rbf equipped with a stir bar. Modified amino acid **1a** (15.1 mg, 0.1 mmol, 1 equiv. dissolved in 0.5 mL MeOH) was slowly added into the reaction mixture described above by syringe pump over 10 hours under a 11 W house hold bulb irradiation at room temperature. After addition, the reaction mixture was stirred under same irradiation for another 14 hours. Upon reactiion completion assessed by TLC, the reaction solvent was removed under reduced pressure. The resulting crude mixture syrup was directly loaded onto a short pad of silica gel, and then purified by flash chromatography using gradient elution of hexane/EtOAc mixtures (6/1 ratio) to afford the expected product **19** (18.3 mg) as pale yellow solid in 89% yield.



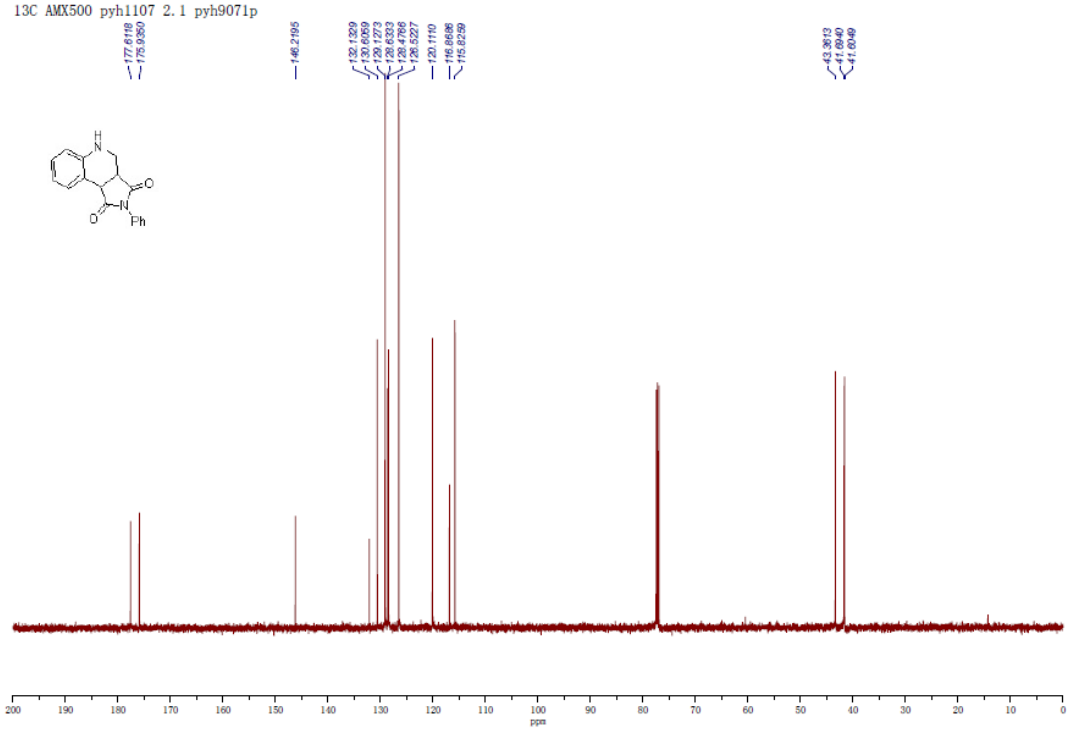
4-(4-chlorophenyl)-1-phenyl-3-tosylimidazolidine (19)
Pale yellow solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.33 – 7.21 (m, 9H), 6.85 (t, *J* = 7.4 Hz, 1H), 6.56 (d, *J* = 7.8 Hz, 2H), 4.97 (dd, *J* = 7.2, 4.4 Hz, 1H), 4.88 (d, *J* = 6.2 Hz, 1H), 4.81 (d, *J* = 6.2 Hz, 1H), 3.52 (dd, *J* = 9.2, 7.3 Hz, 1H), 3.37 (dd, *J* = 9.3, 4.4 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.19, 144.24, 138.31, 134.23, 133.89, 129.81, 129.42, 128.80, 128.10, 127.58, 119.28, 113.51, 65.57, 61.46, 54.87, 21.52. LRMS (ESI) m/z 413.0 ($M + H^+$). HRMS (ESI) m/z 413.1089 ($M + H^+$), Cal. $C_{22}H_{22}ClN_2O_2S$, 413.1085.

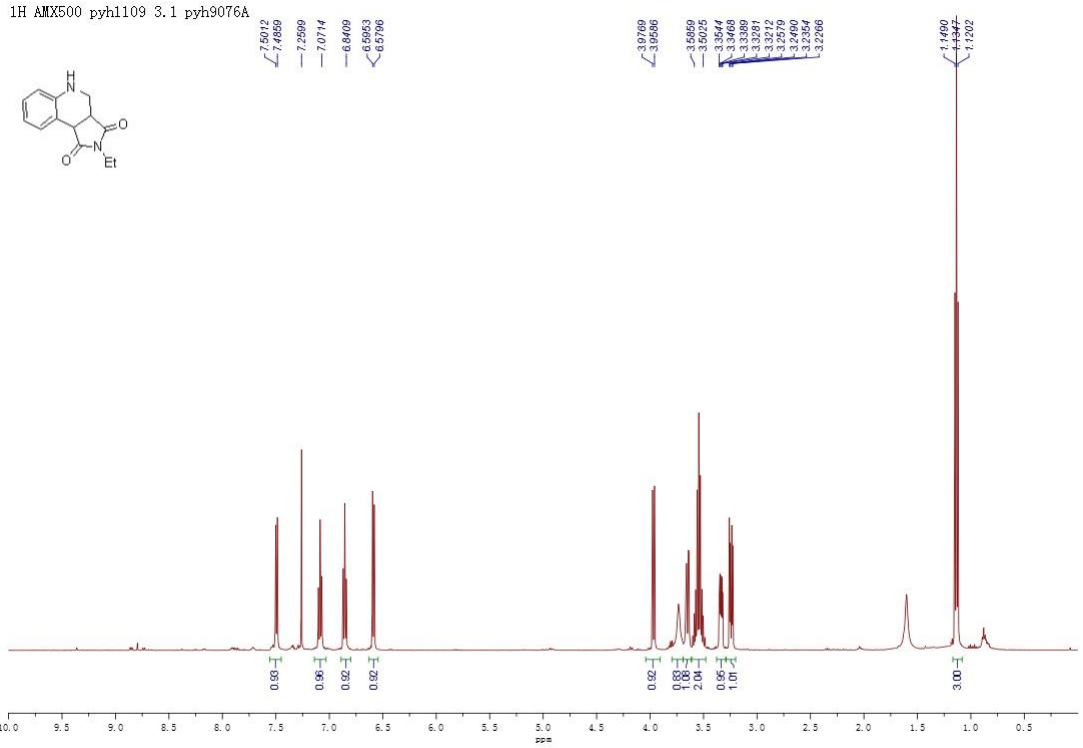
NMR Spectra of New Compounds

1H AMX500 pyh1108 1.1 pyh9071p



13C AMX500 pyh1107 2.1 pyh9071p

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3.5859
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3.3544
3.3468
3.3389
3.3281
3.3212
3.2959
3.2490
3.2354
3.2266
1.1490
1.1347
1.1202
0.93
0.96
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0.92
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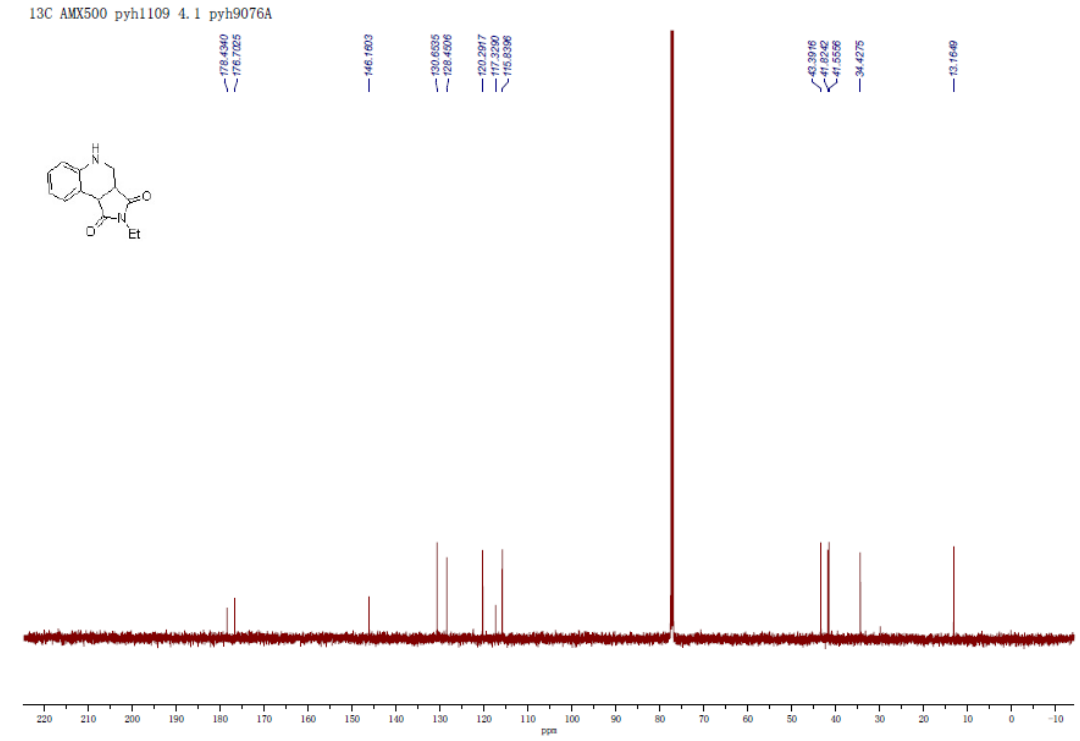
1.01
3.00
H
O
O
N
Et


13C AMX500 pyh1109 4.1 pyh9076A
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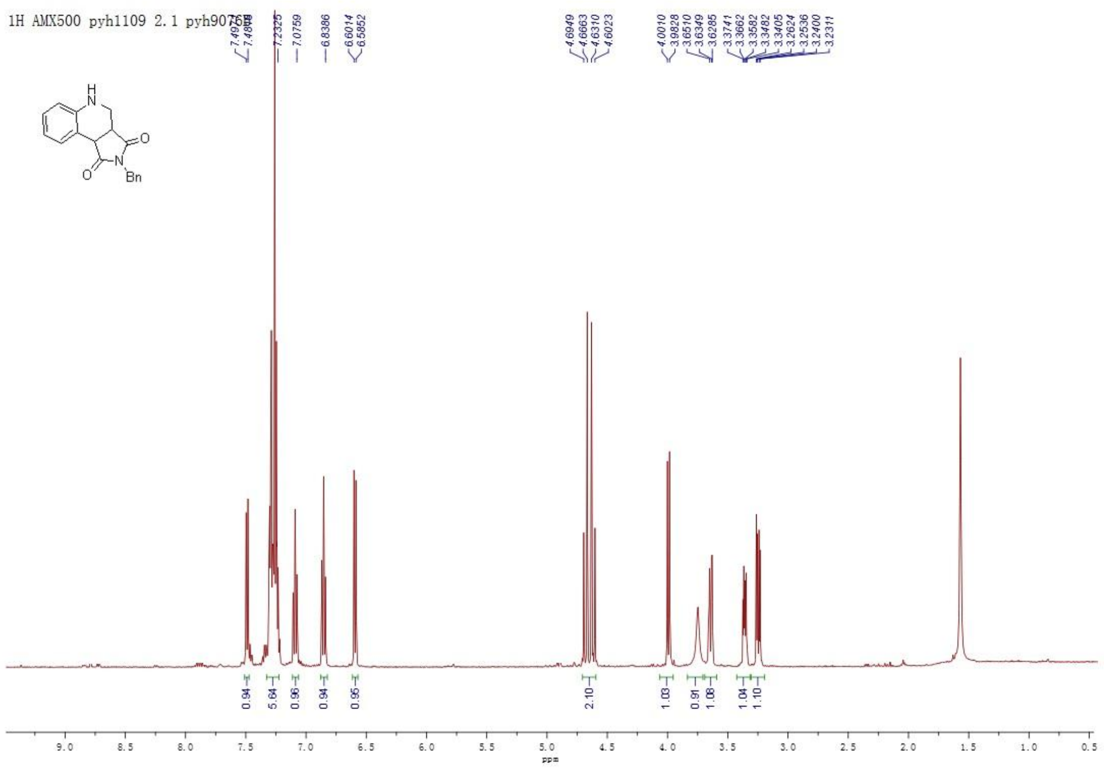
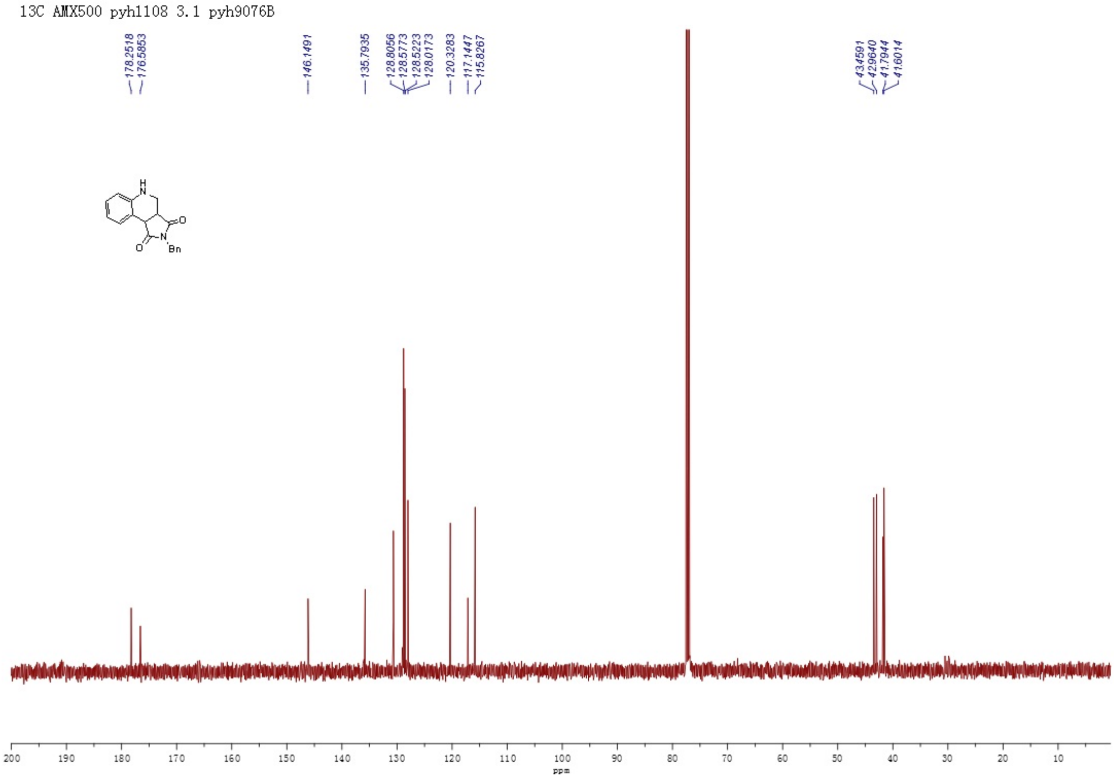
Et





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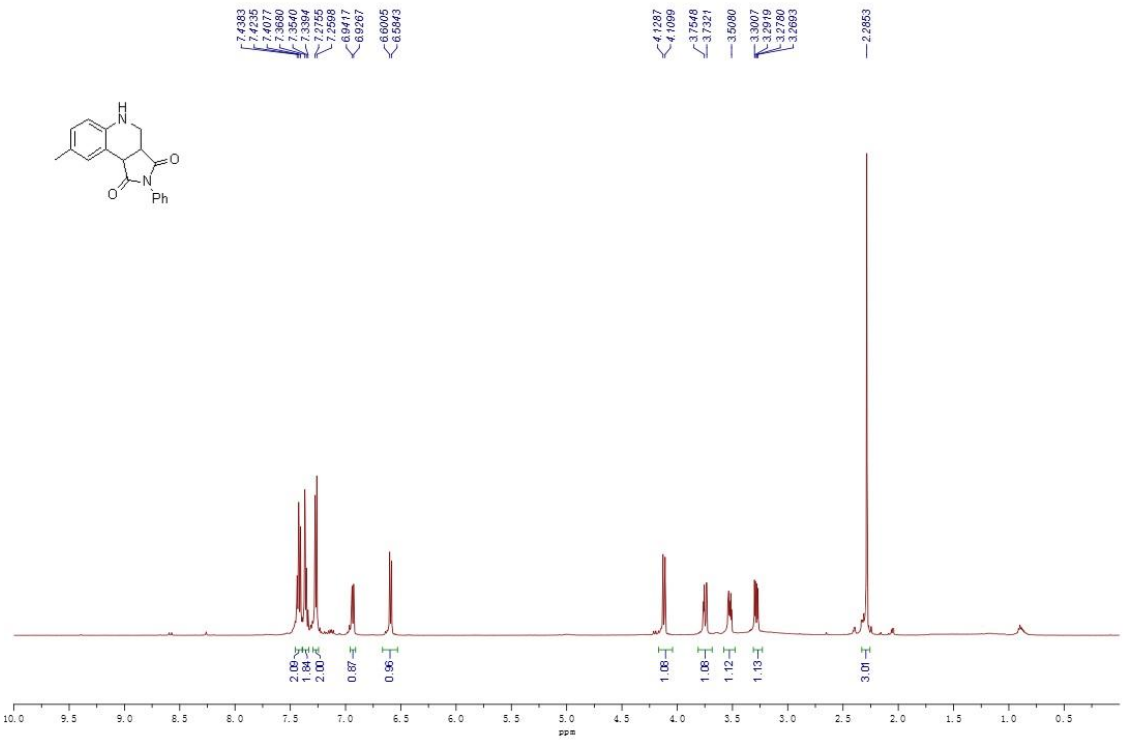
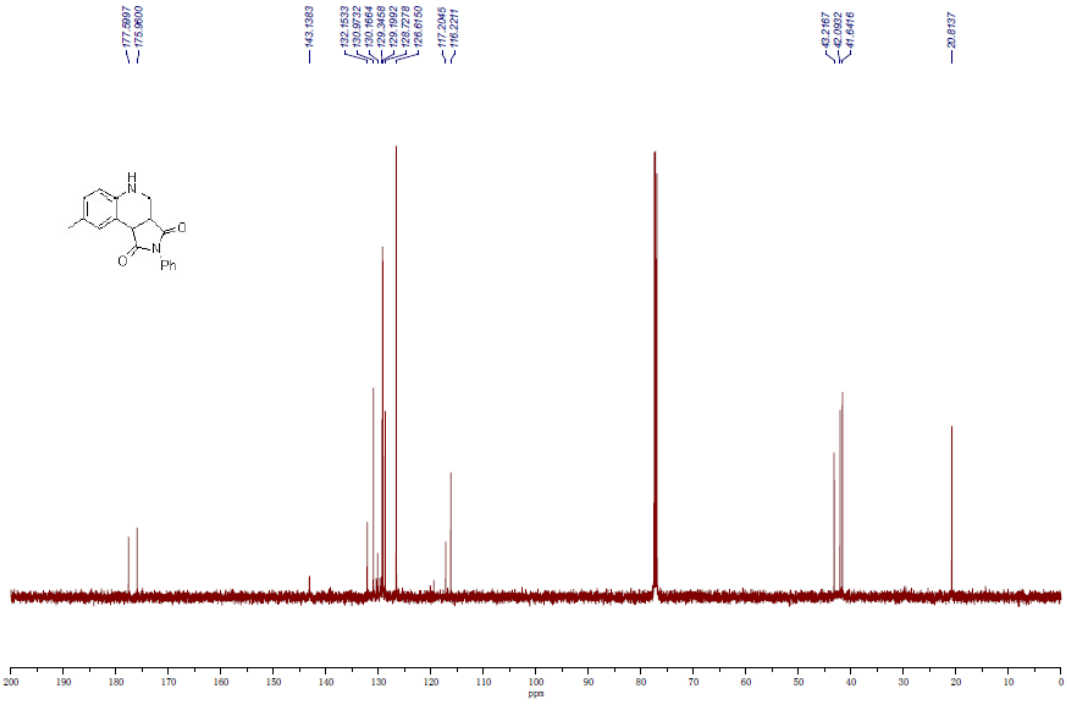
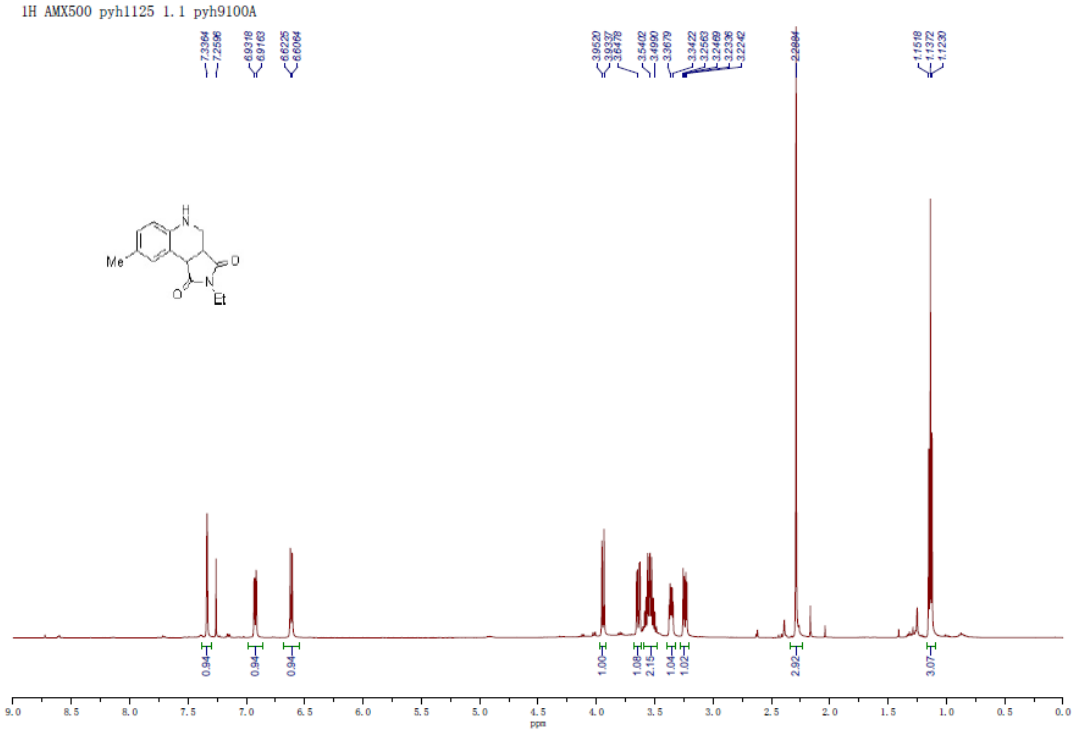


13C AMX500 pyh1121 6.1 pyh9093

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Me
O
N
O
Et
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0.94
1.00
1.08
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1.04
1.02
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8.5
8.0
7.5
7.0
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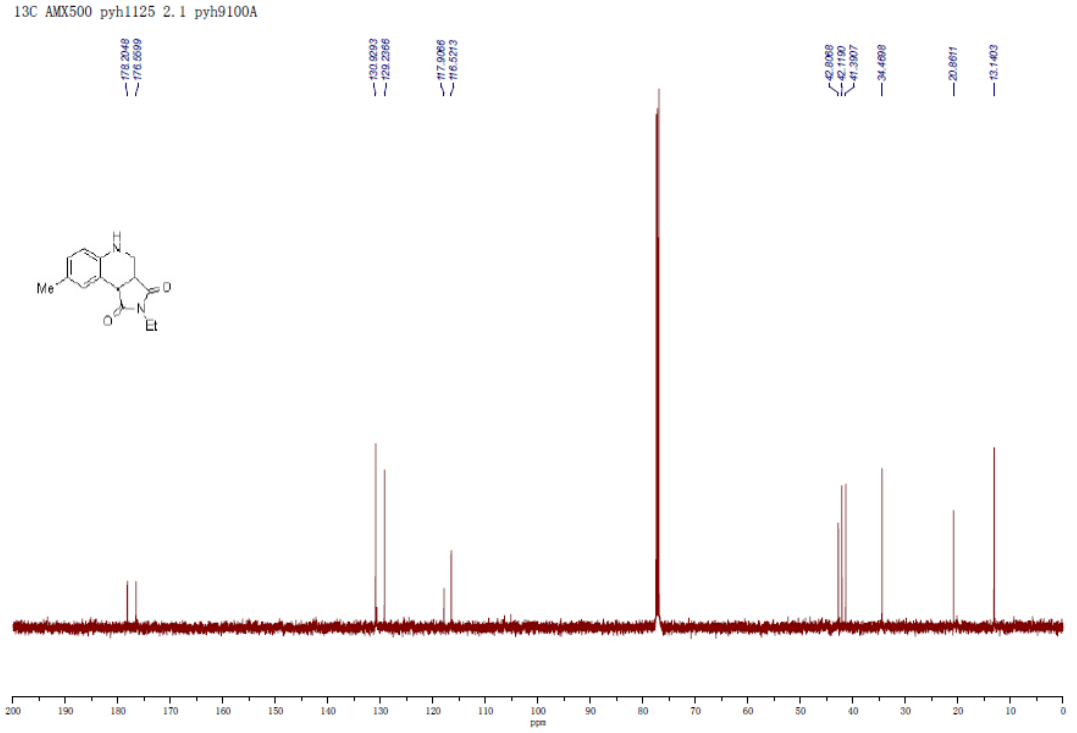
ppm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41.3907
34.4698
20.8611
13.1403
Me
O
N
O
Et
200
190
180
170
160
150
140
130
120
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80
70
60
50
40
30
20
10
0
ppm

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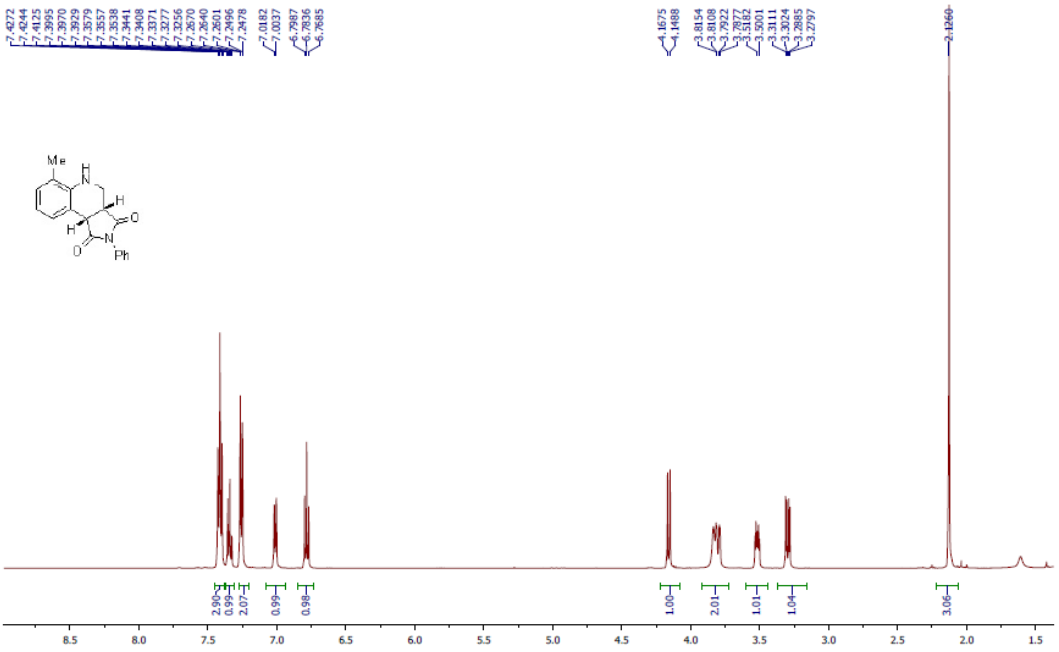

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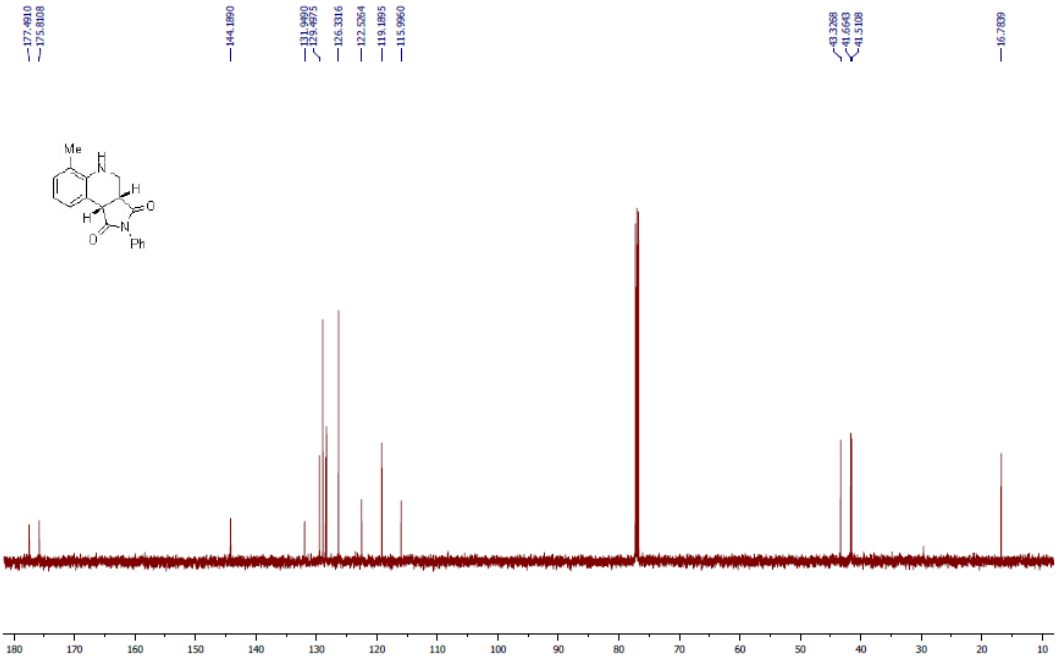

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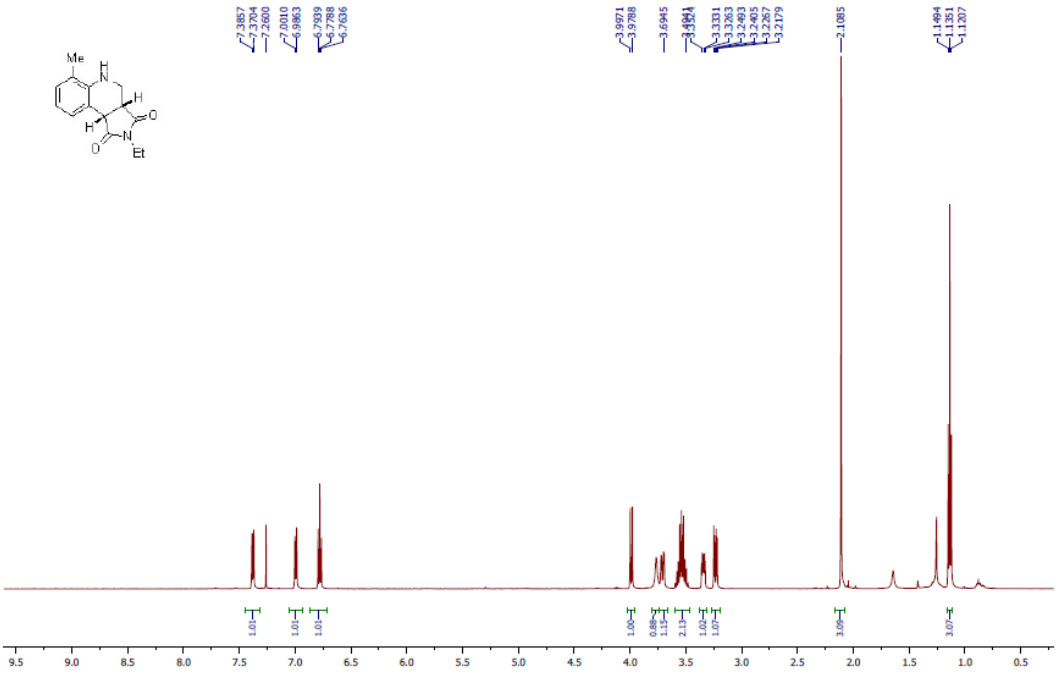

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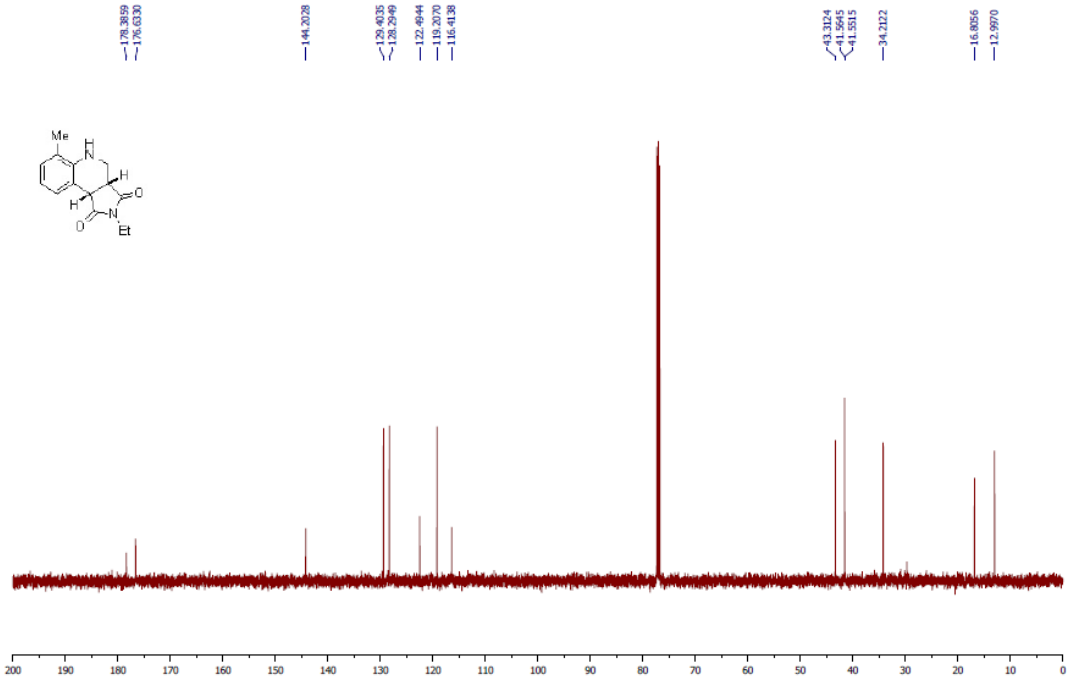

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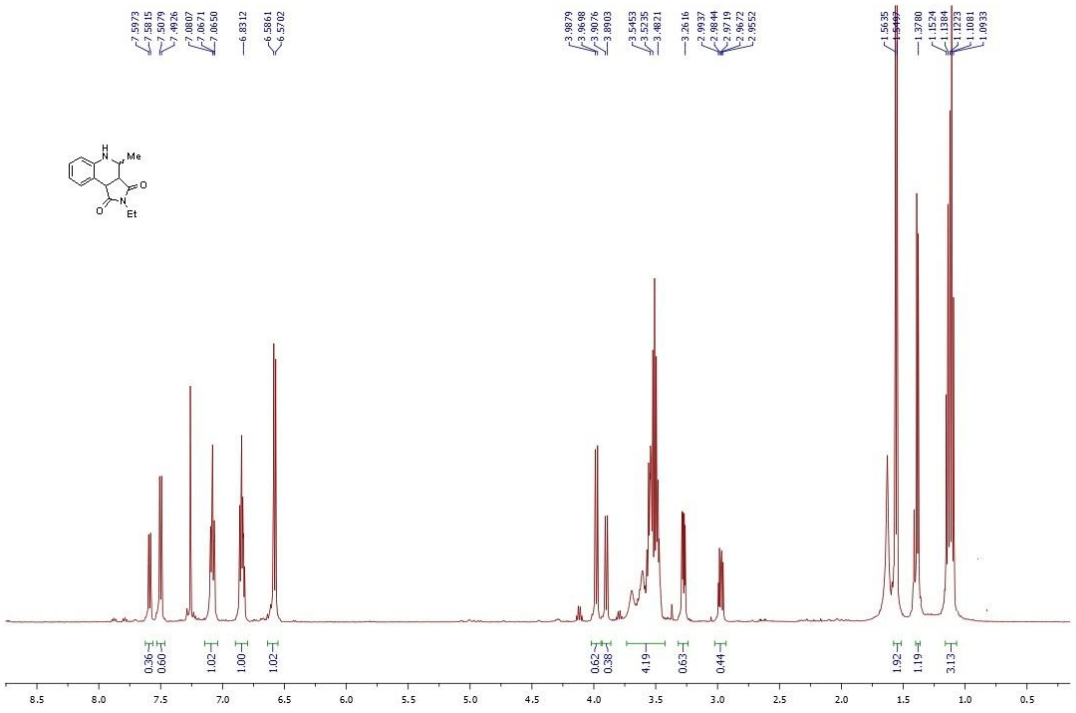

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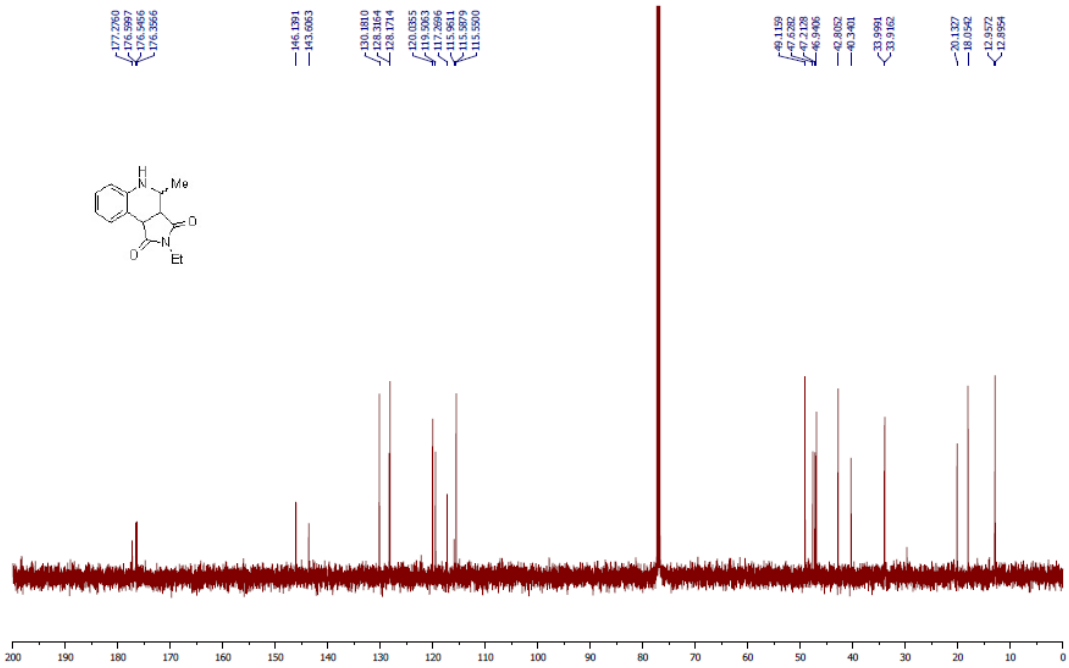

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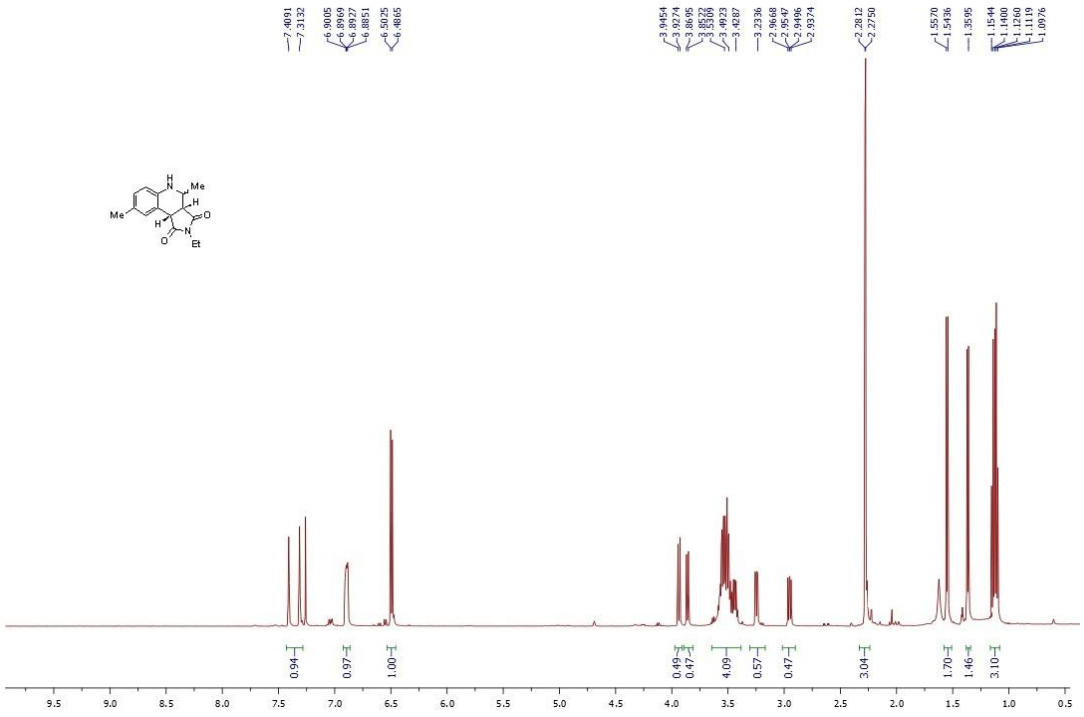

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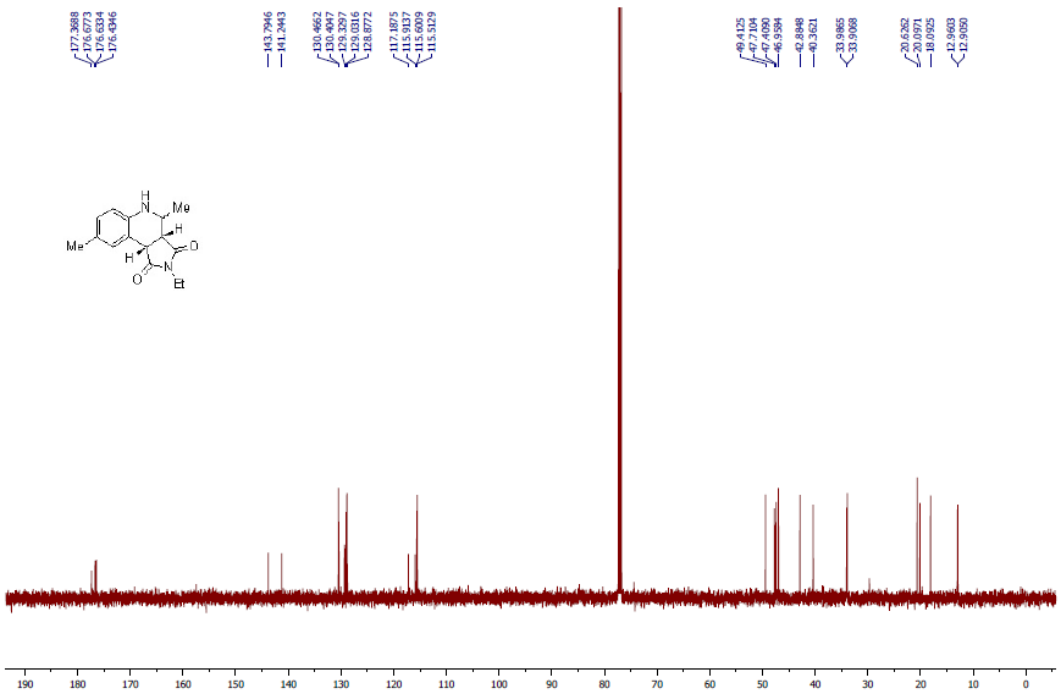

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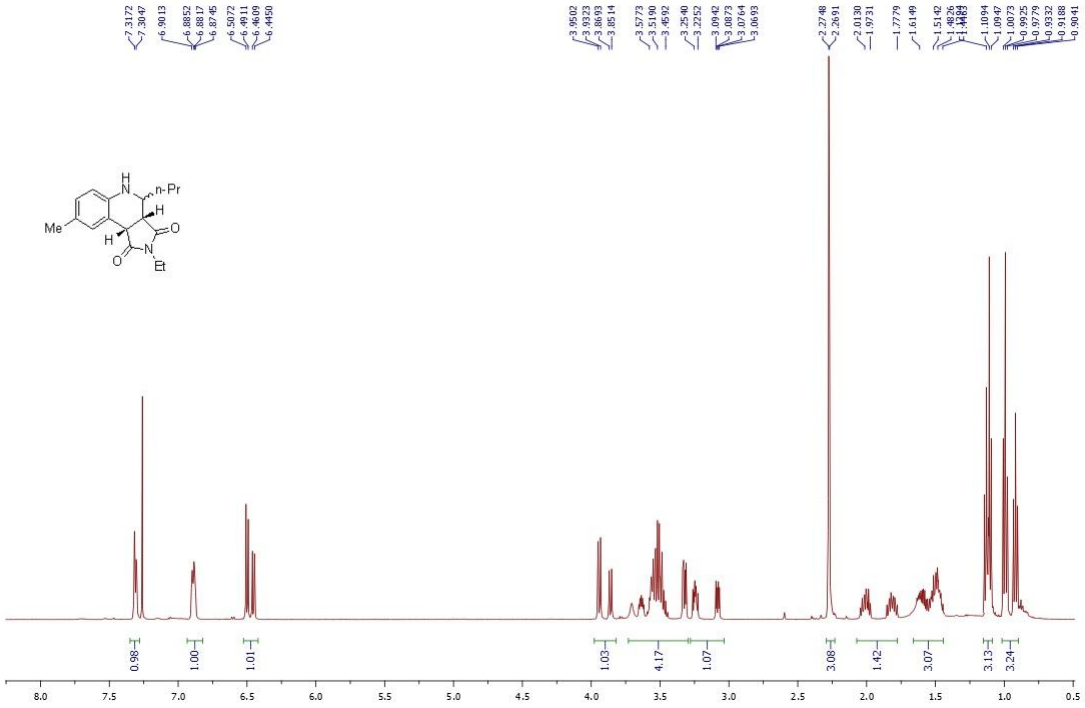

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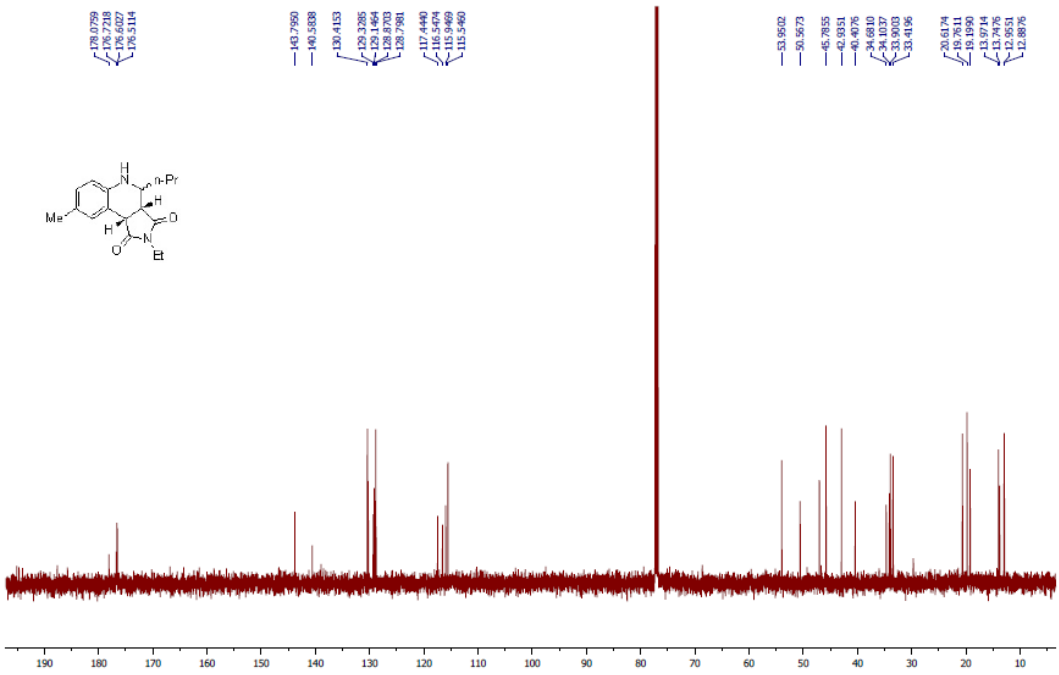

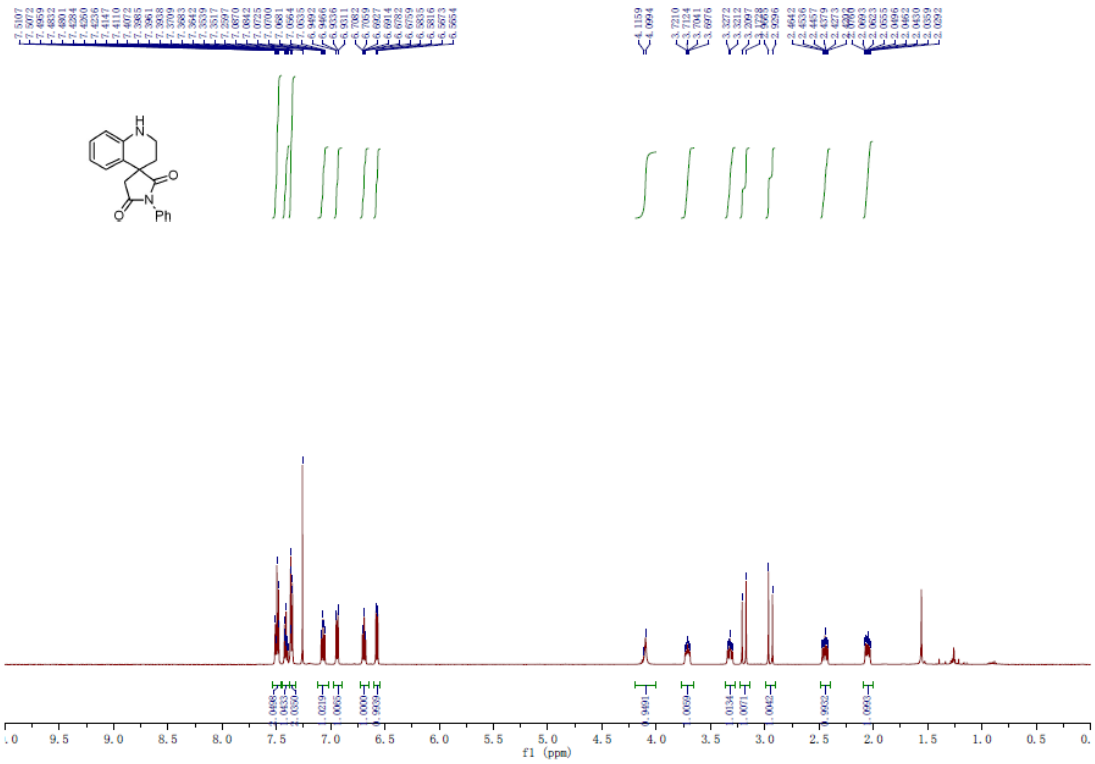
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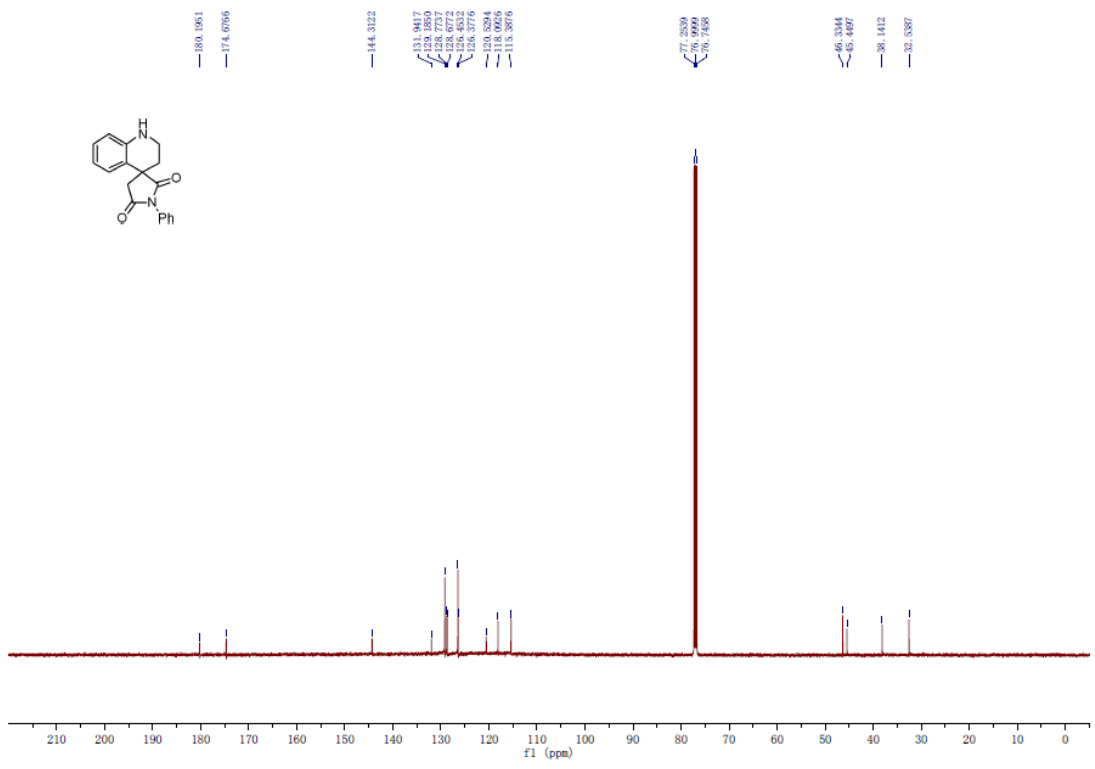
f1 (ppm)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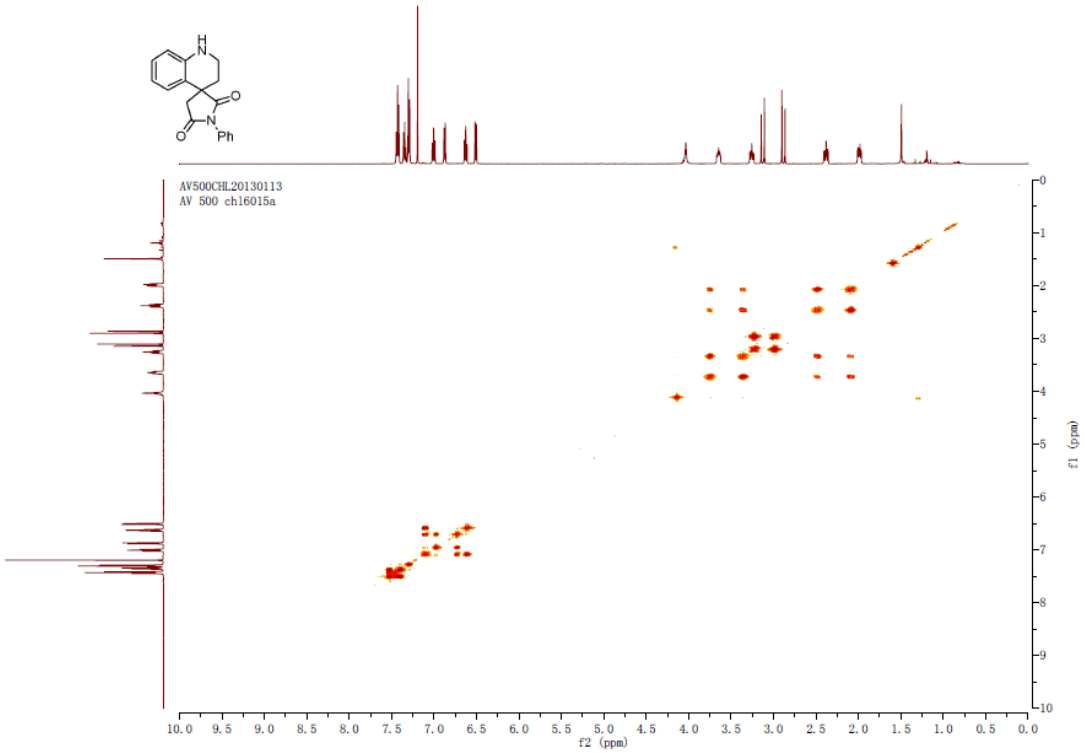
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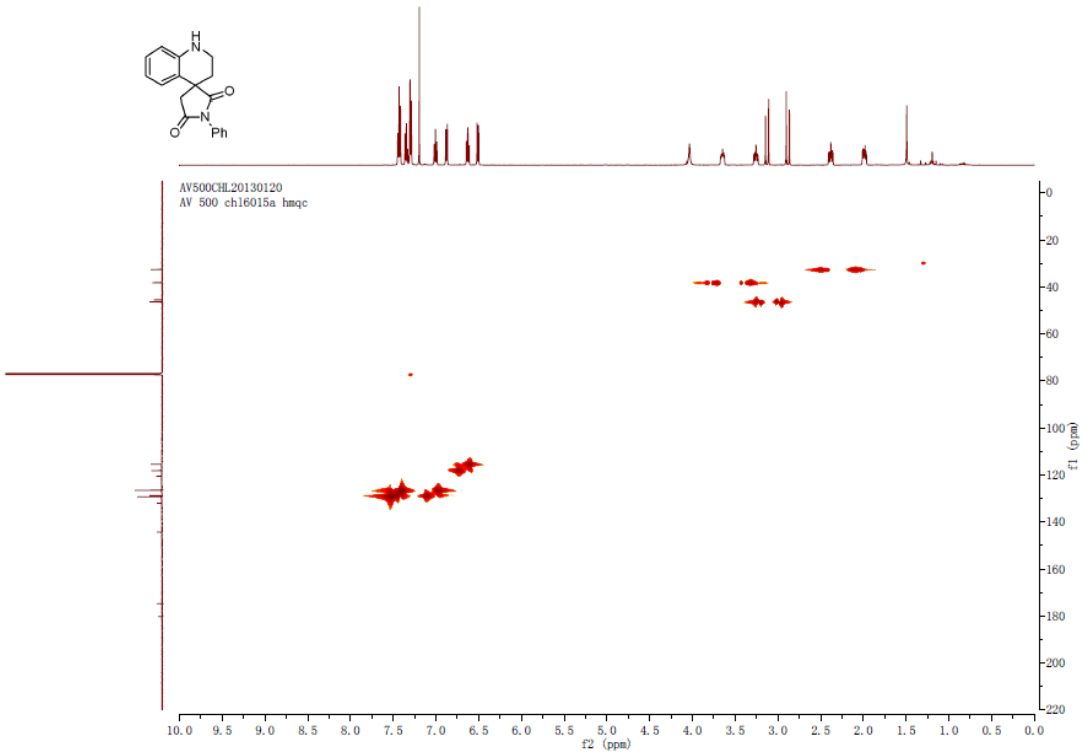
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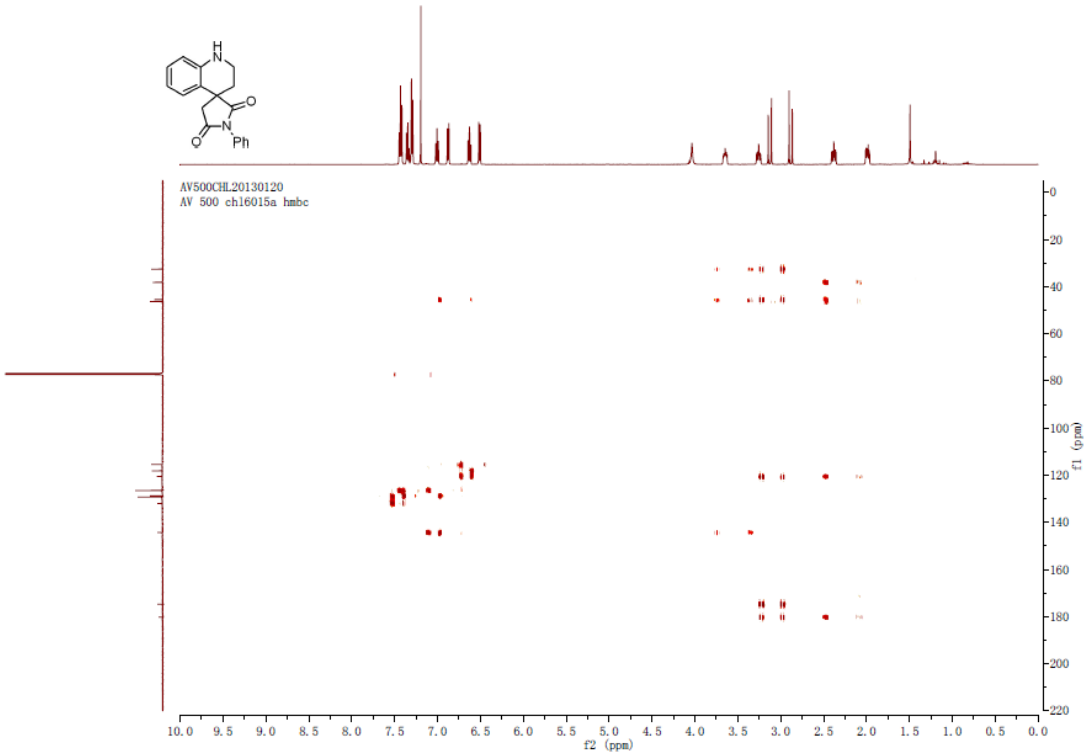
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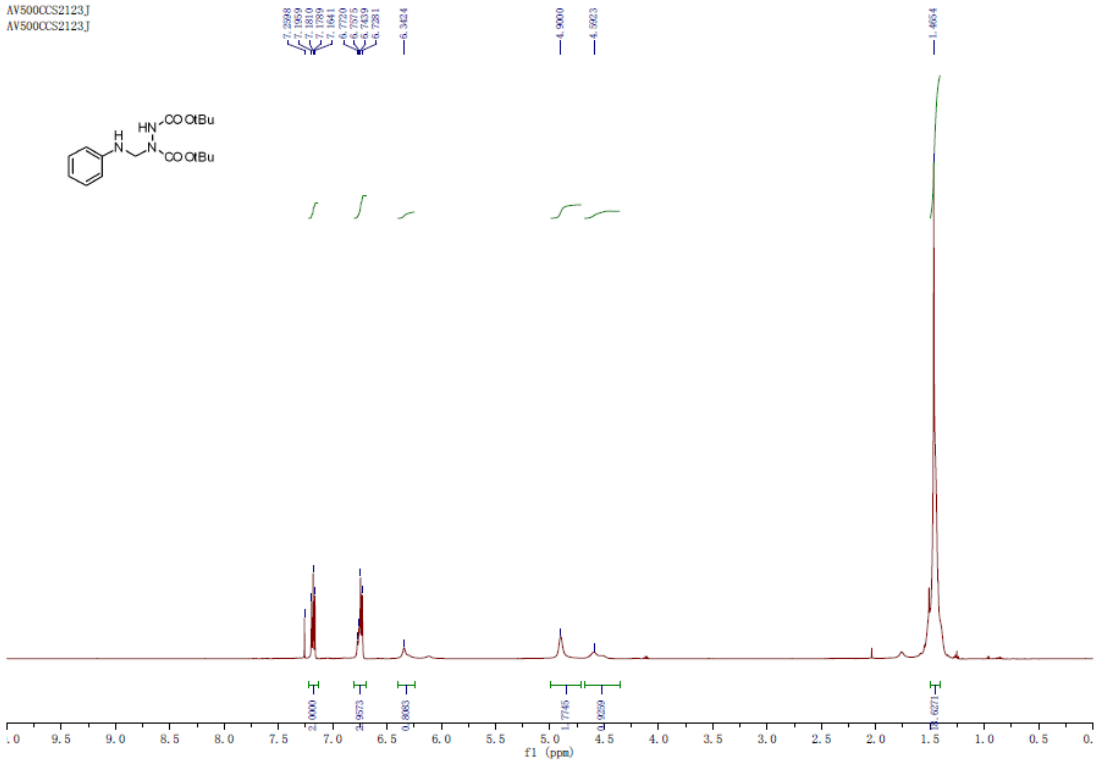
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6.7439
6.7281
5.3424
4.9000
4.6923
1.4654
HN
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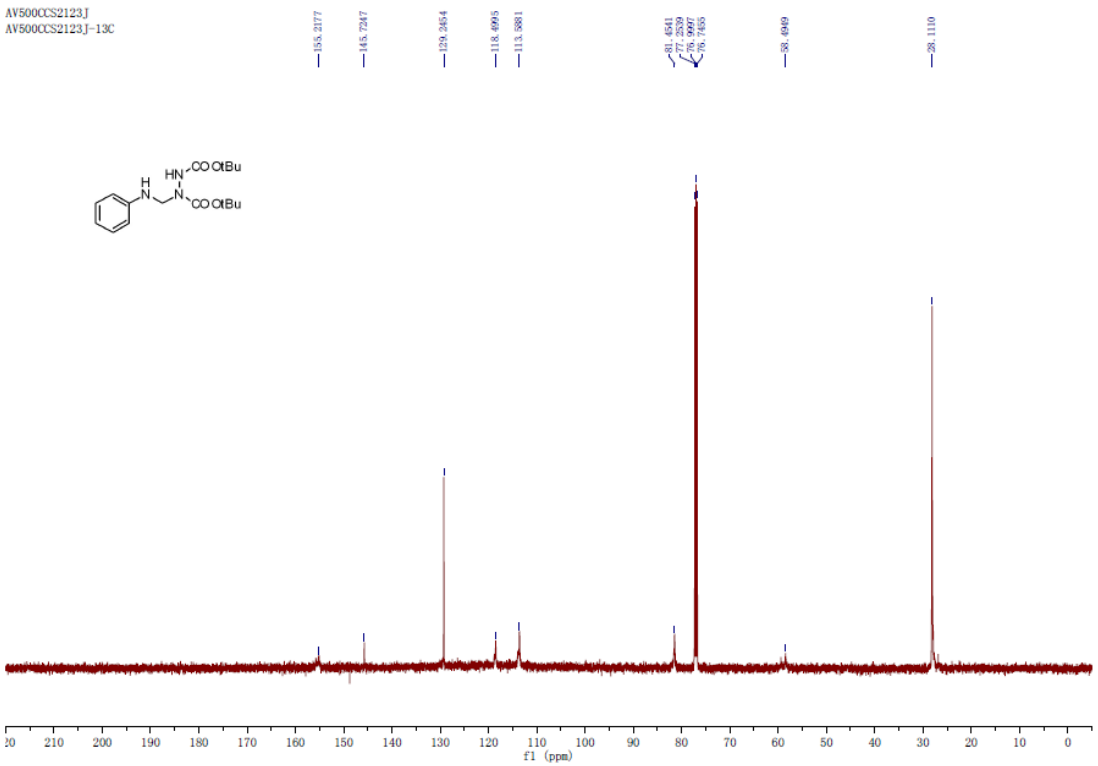
9.6271
f1 (ppm)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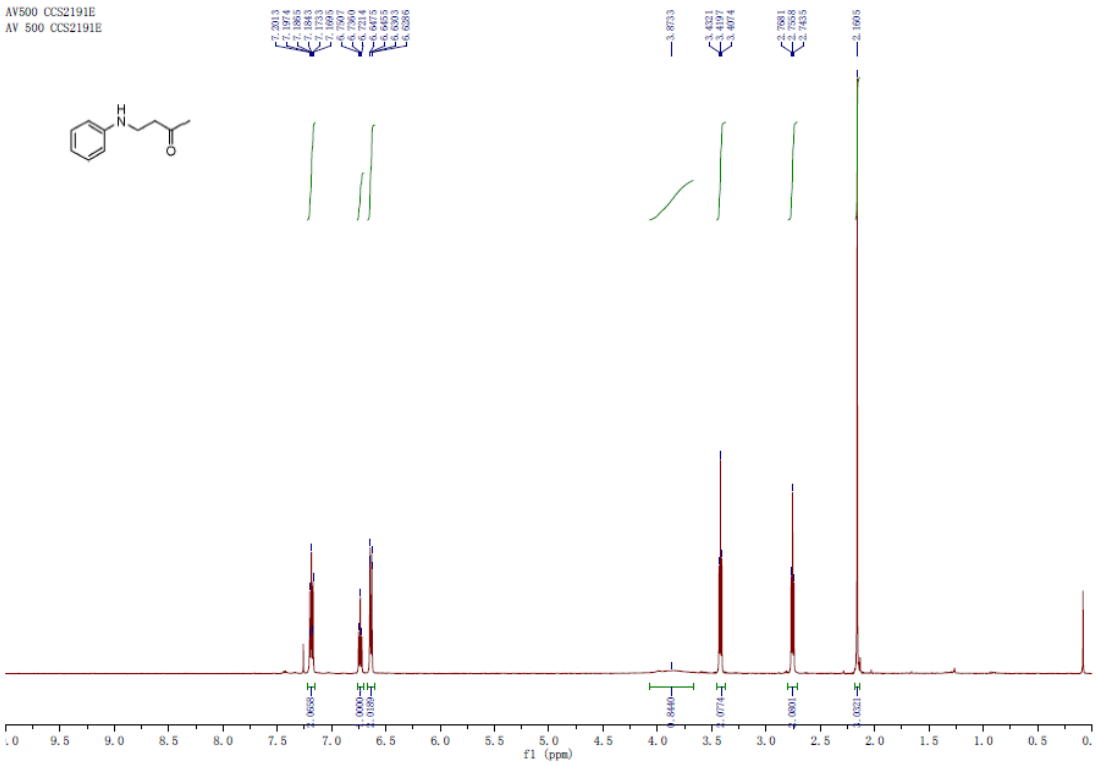
N
CO2tBu
f1 (ppm)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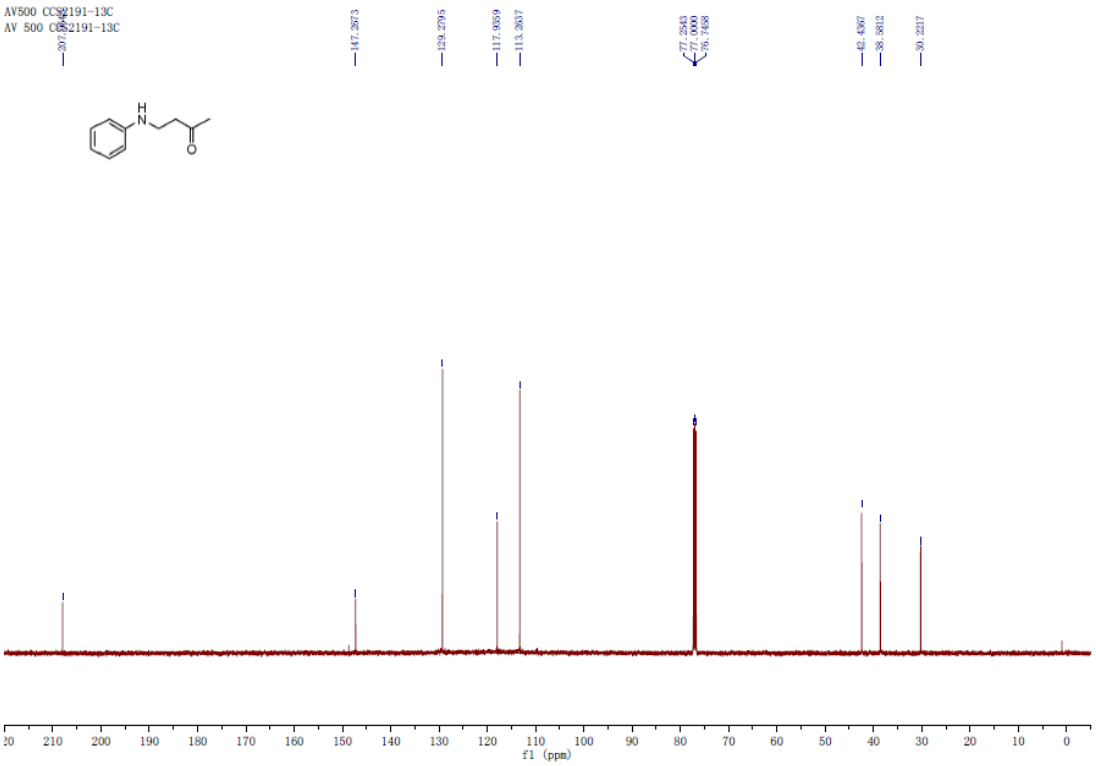
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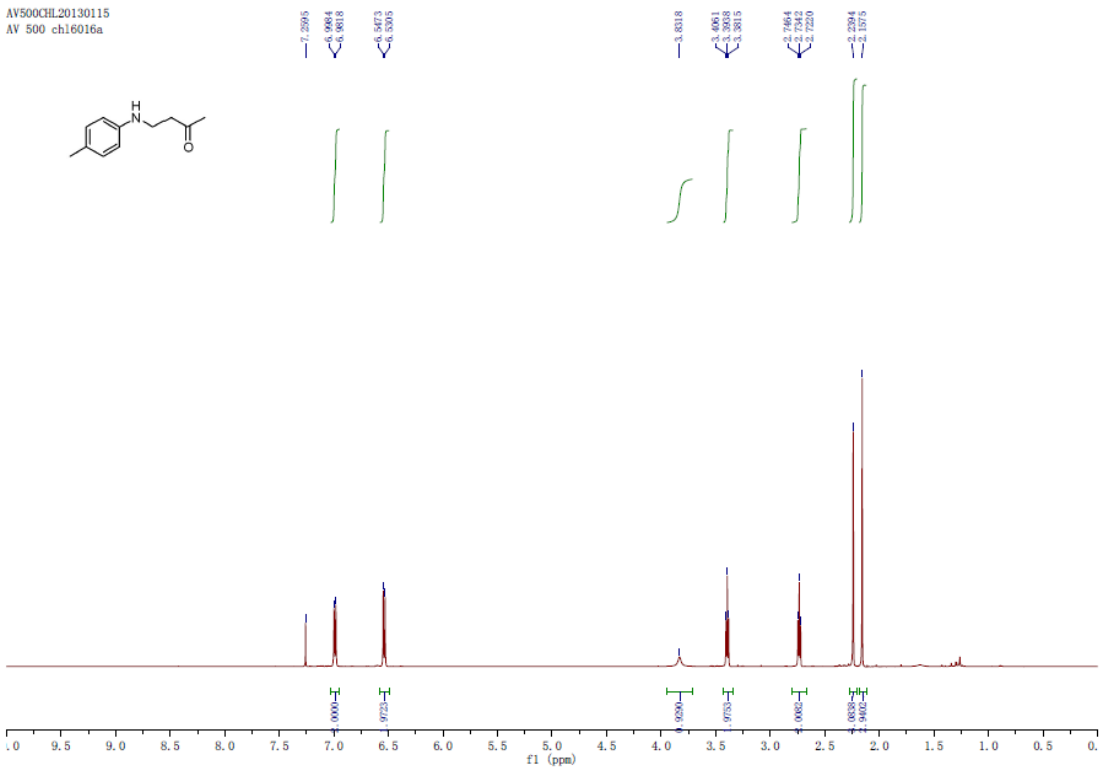

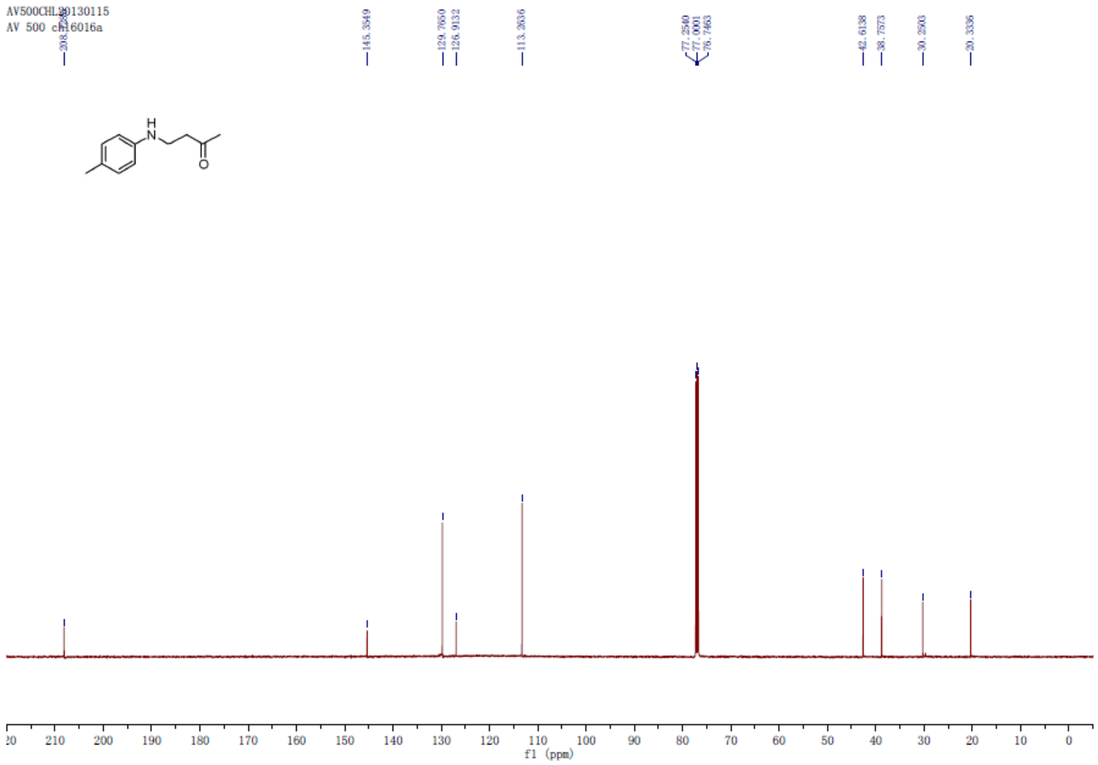

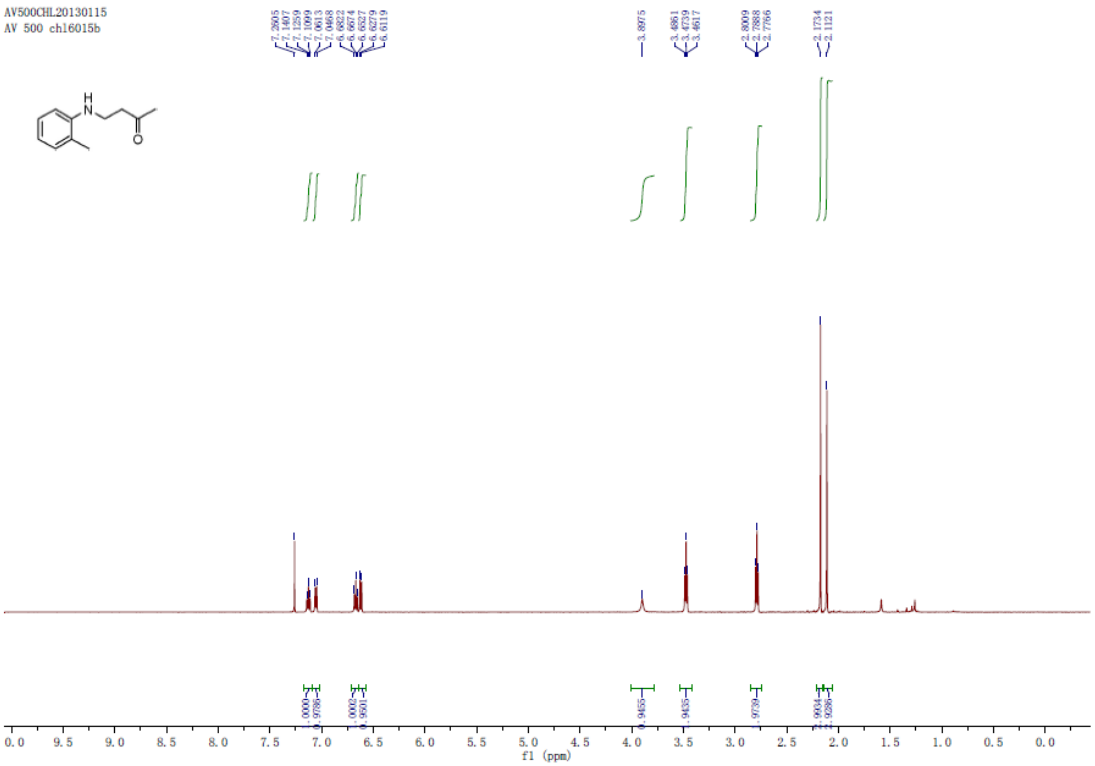
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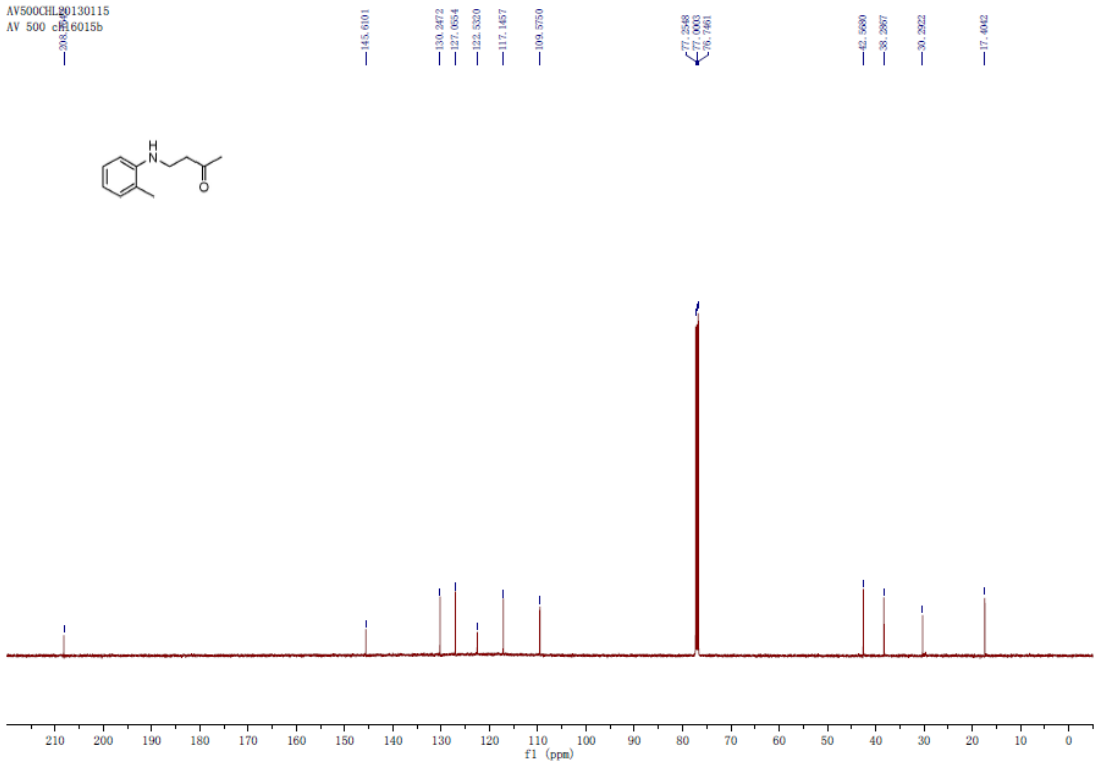
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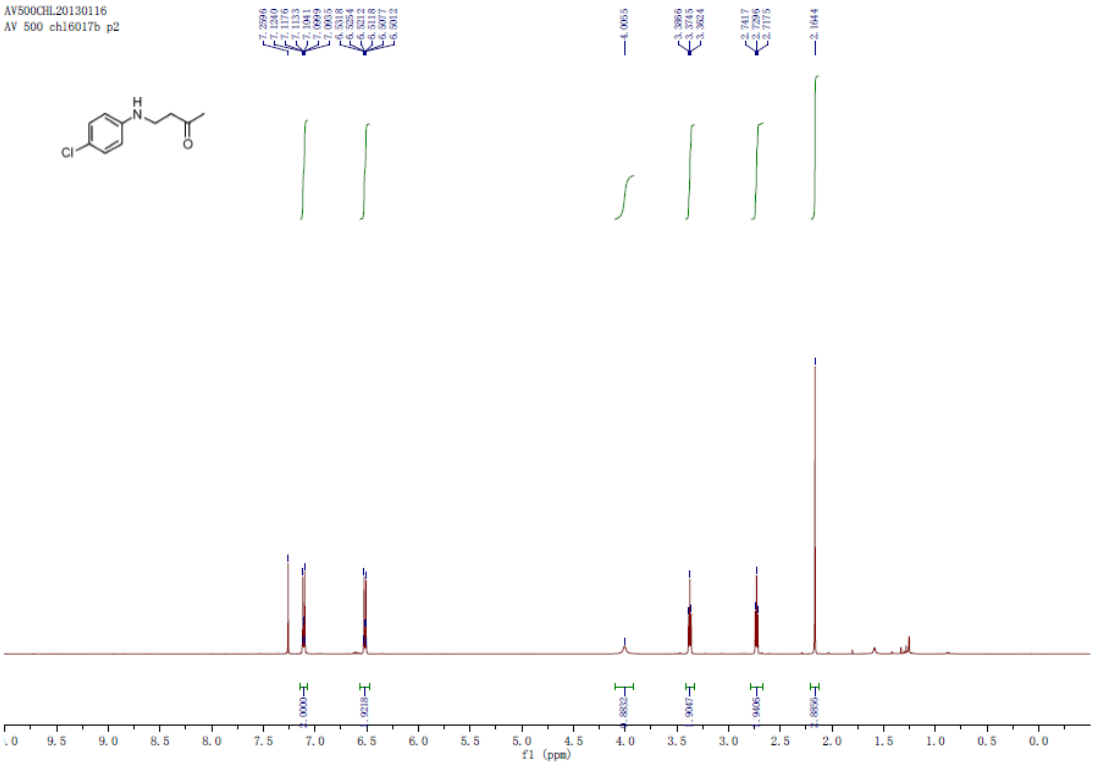
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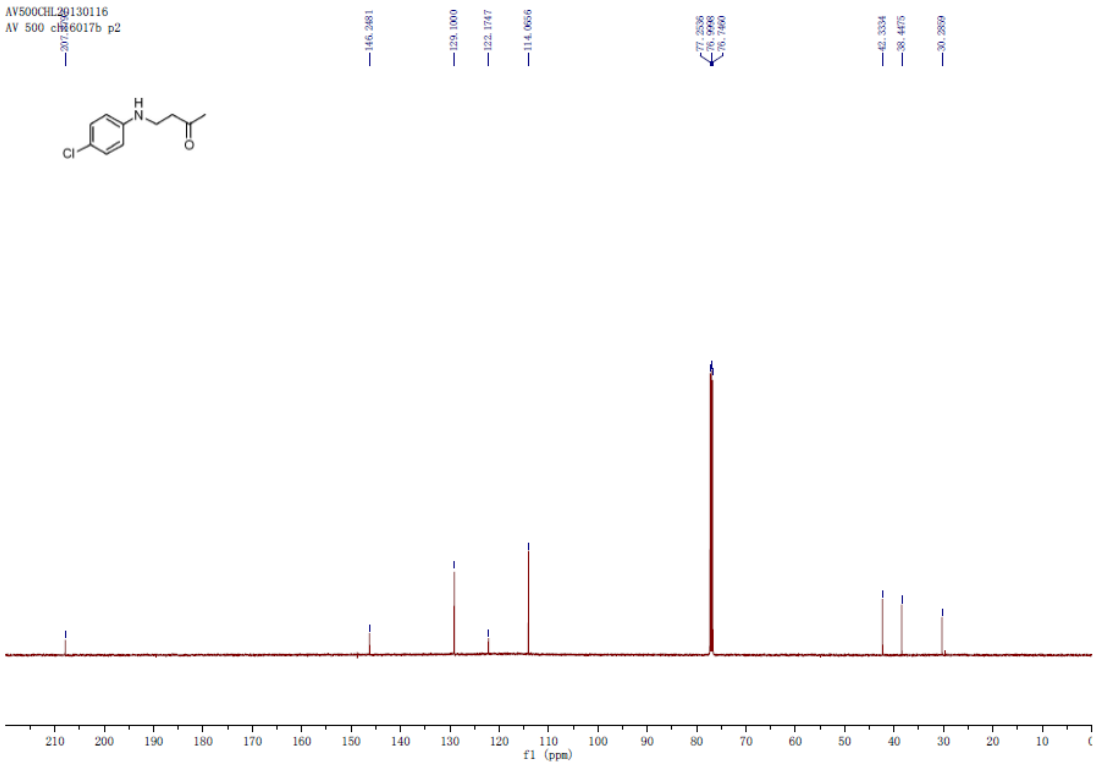
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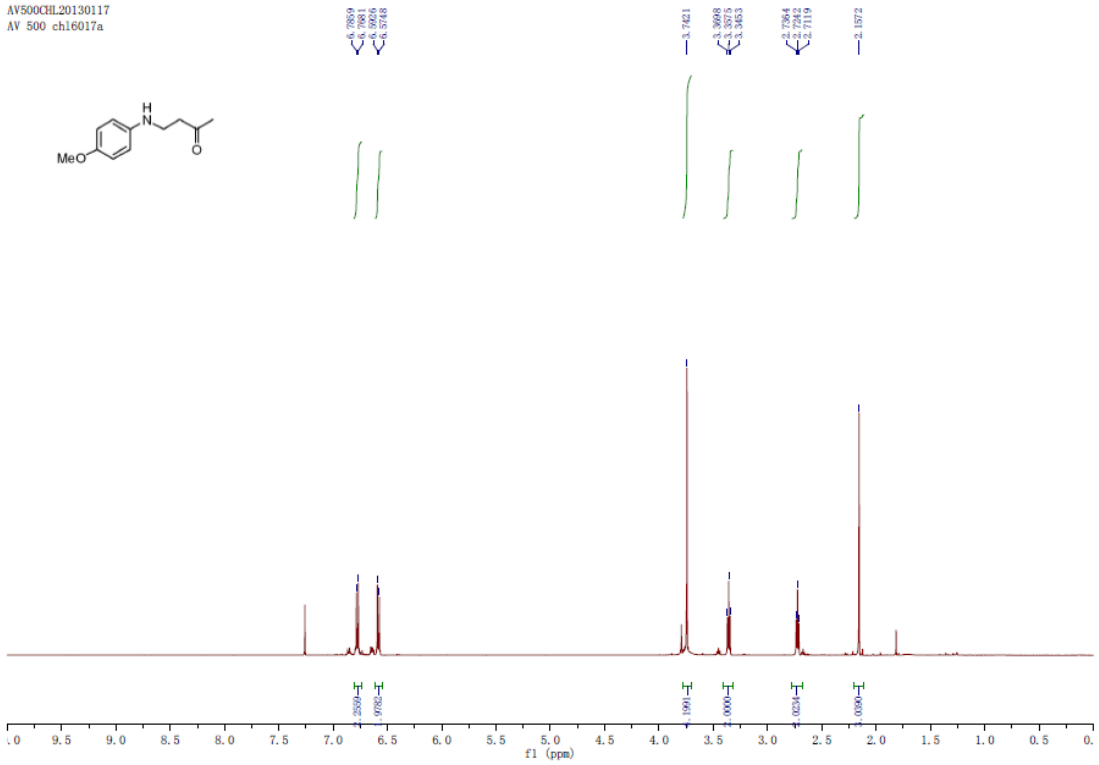
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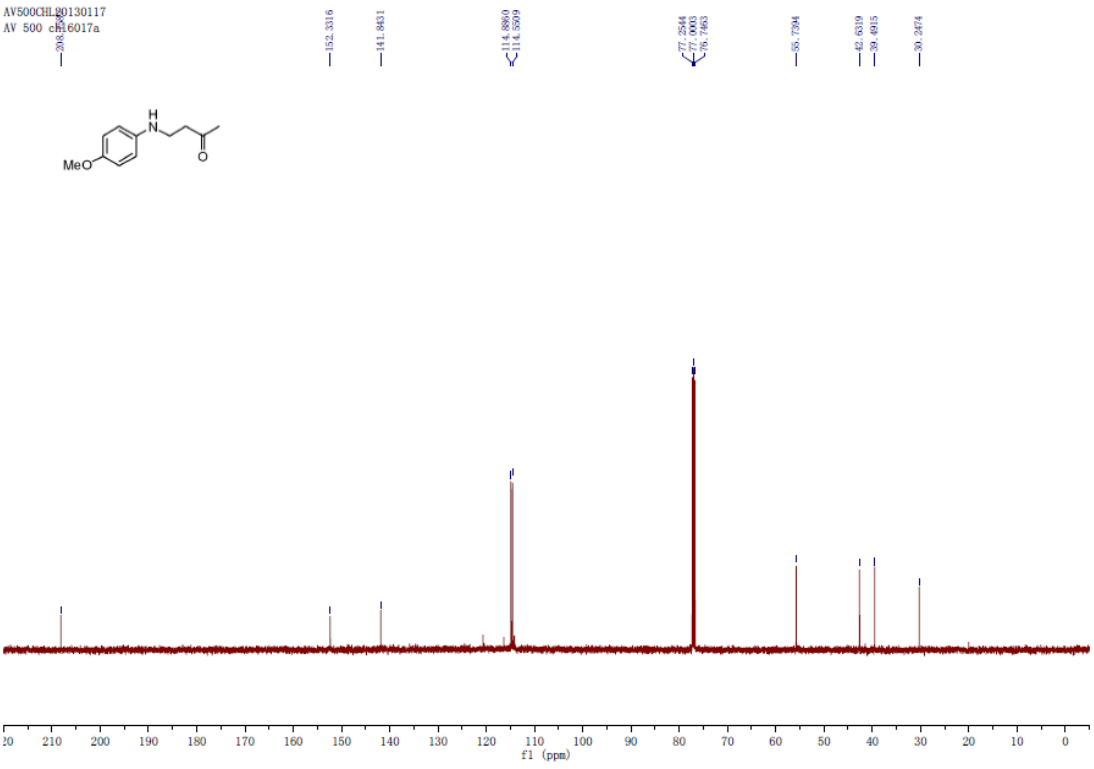
f1 (ppm)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N
O
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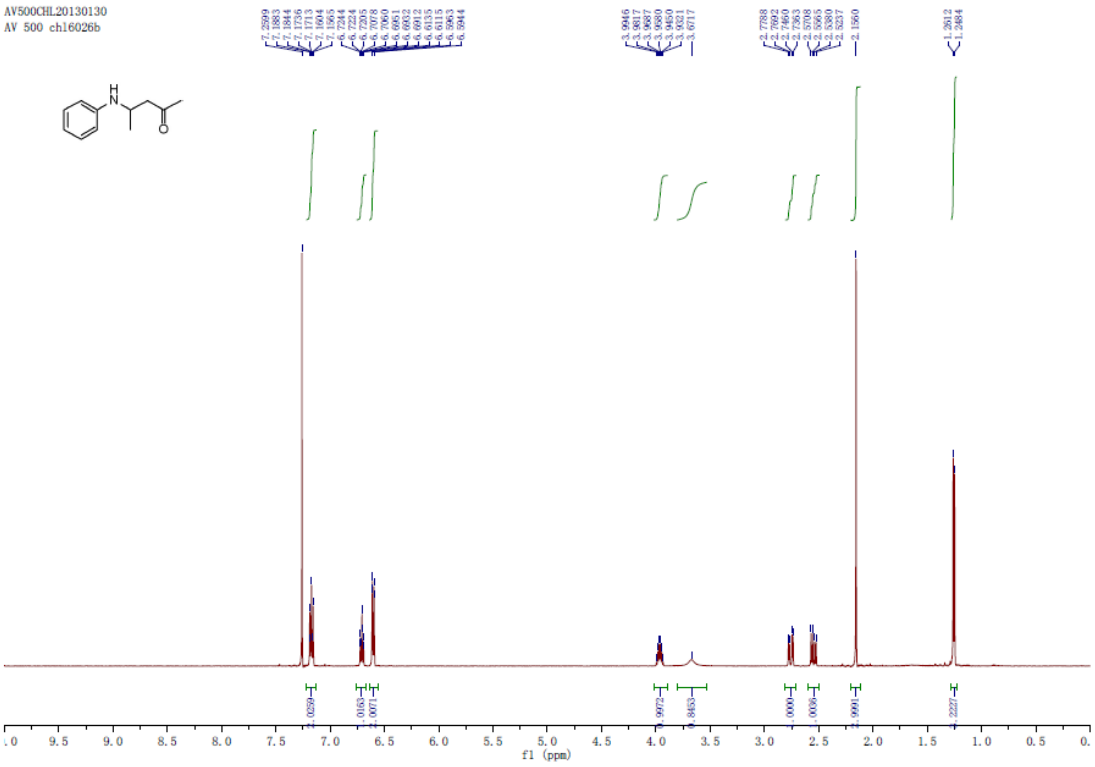
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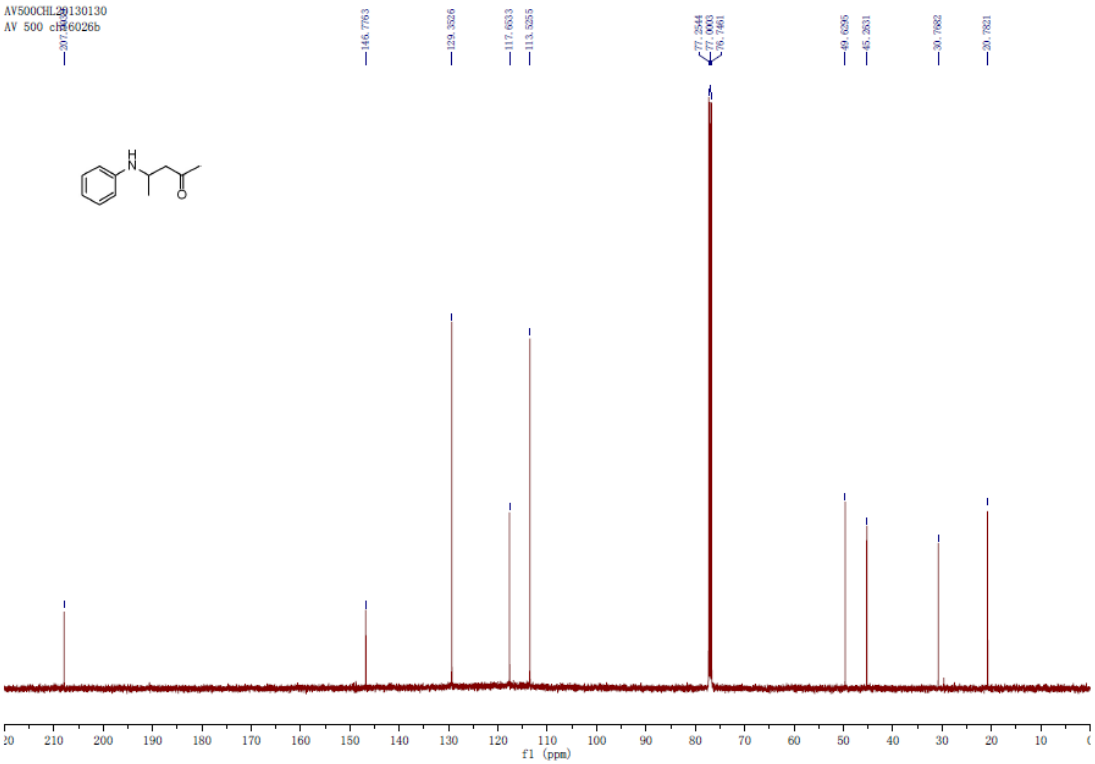
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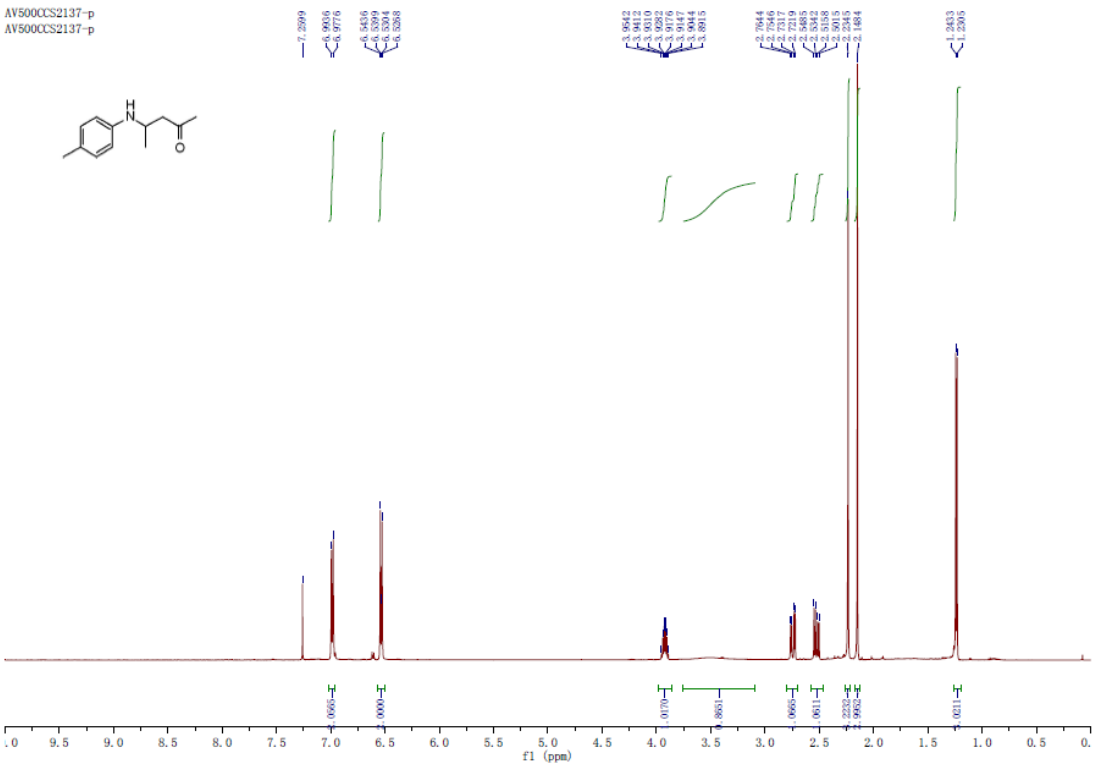
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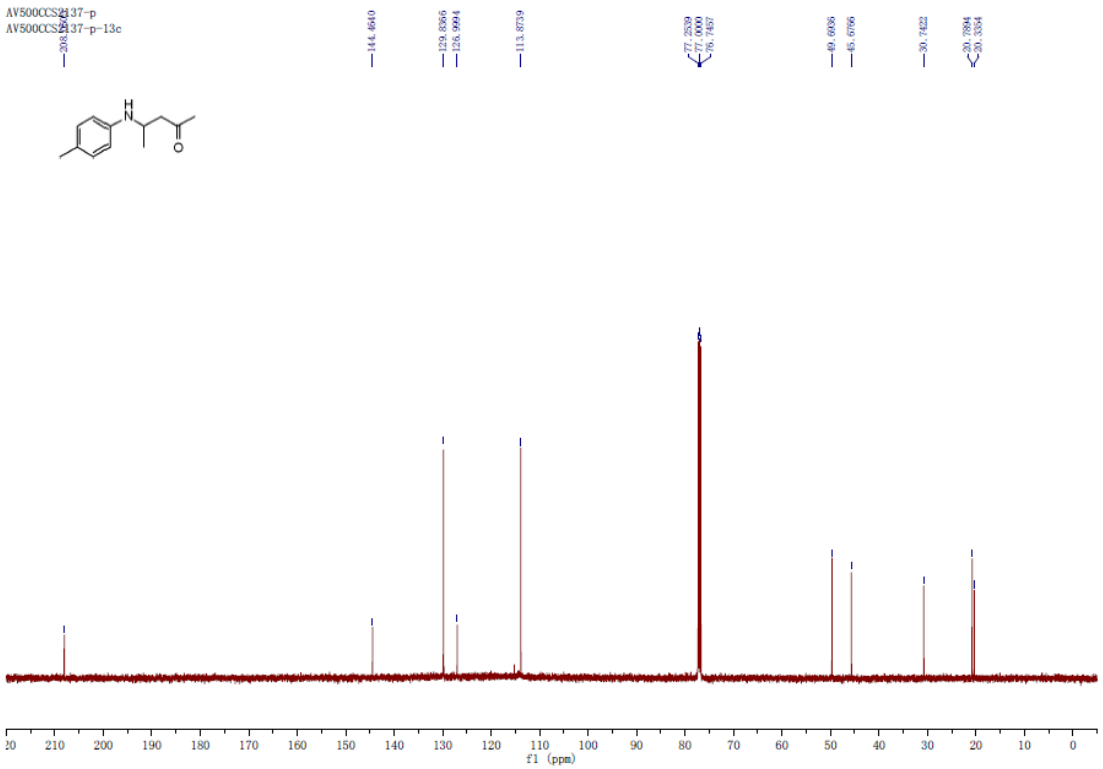
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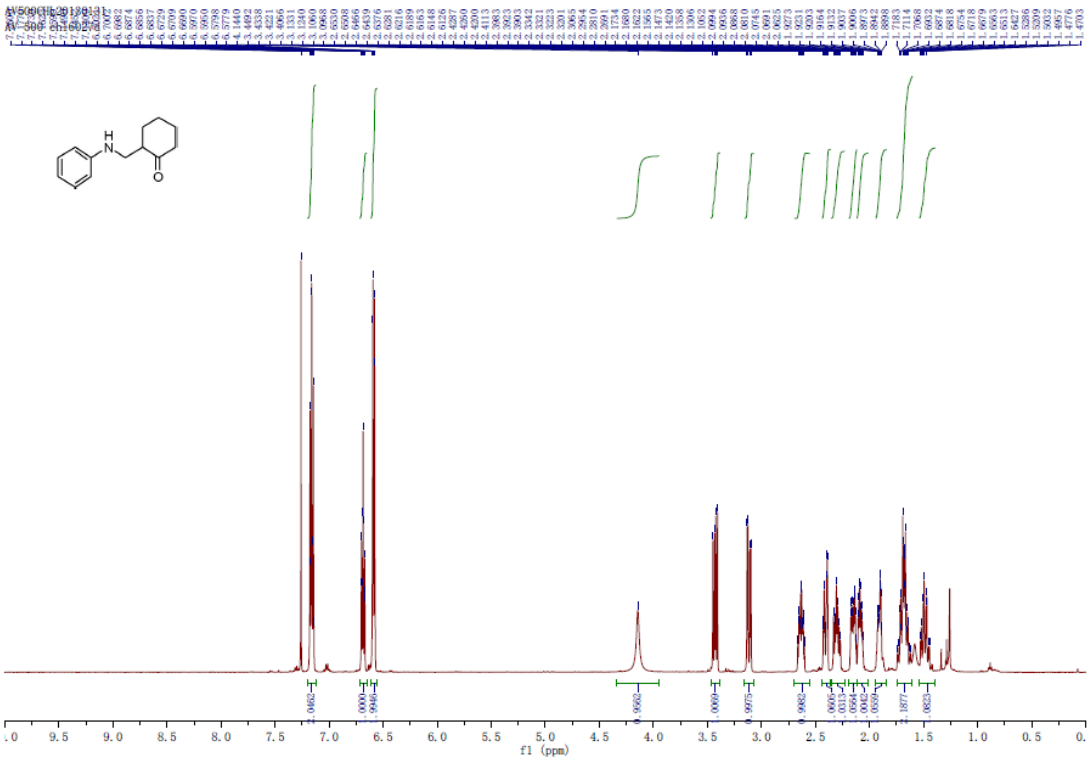
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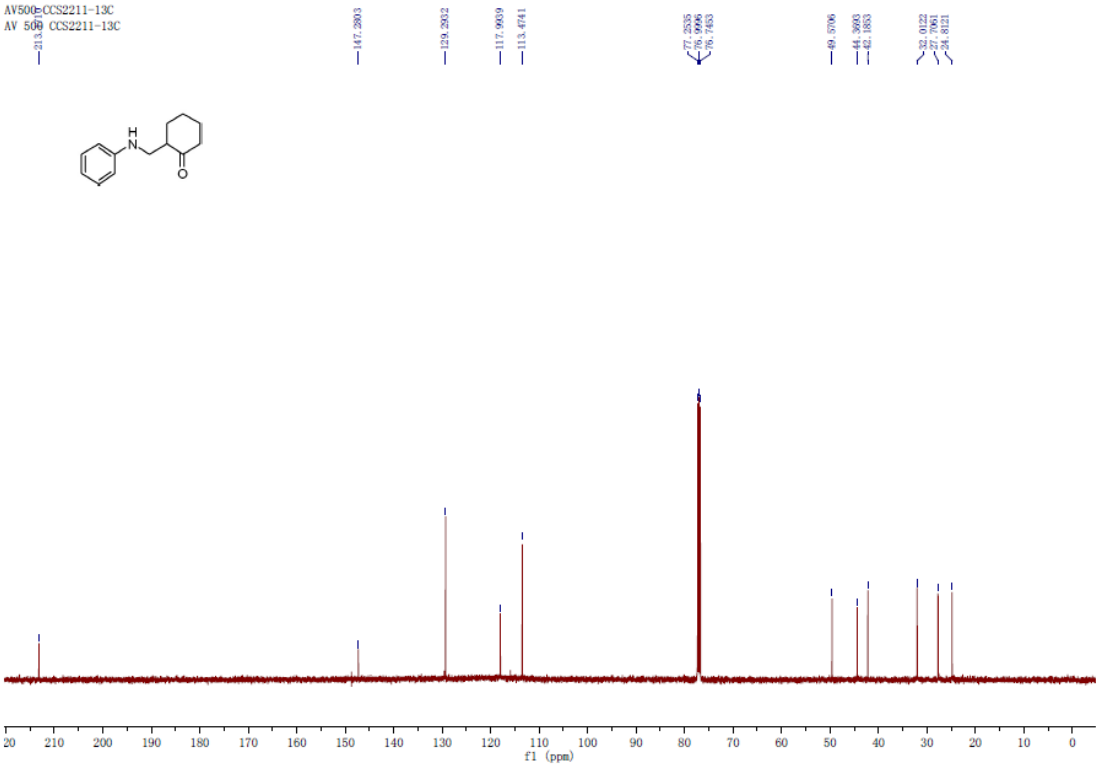
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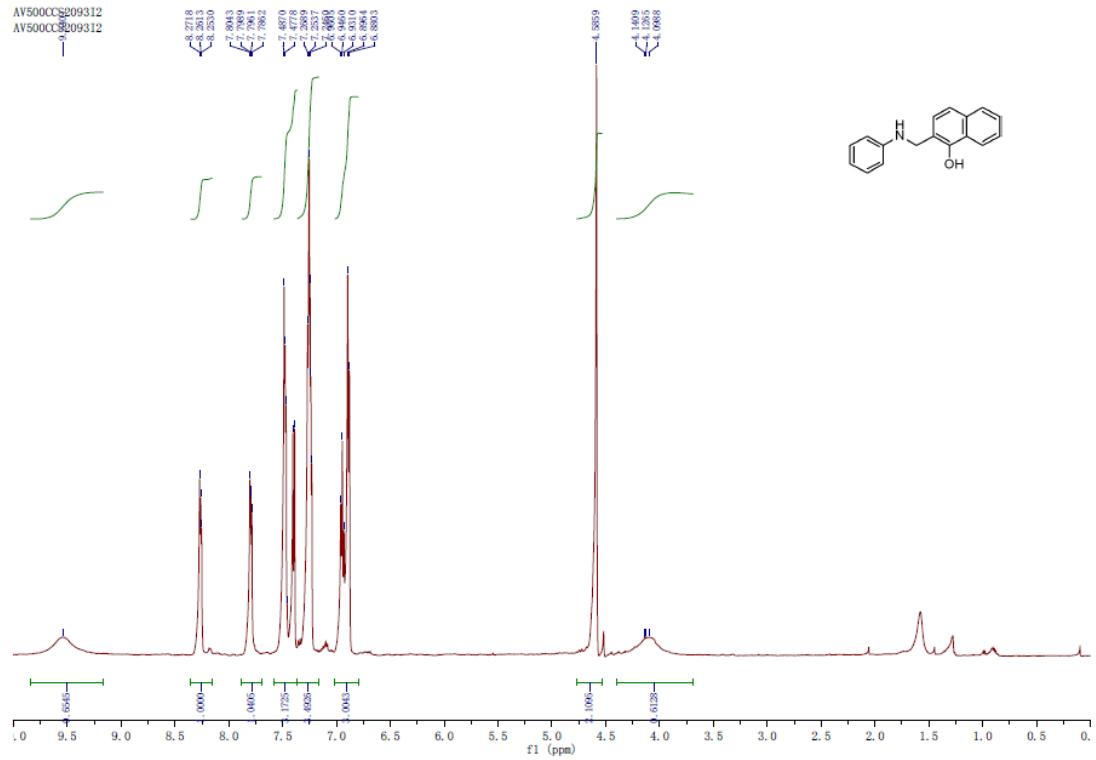
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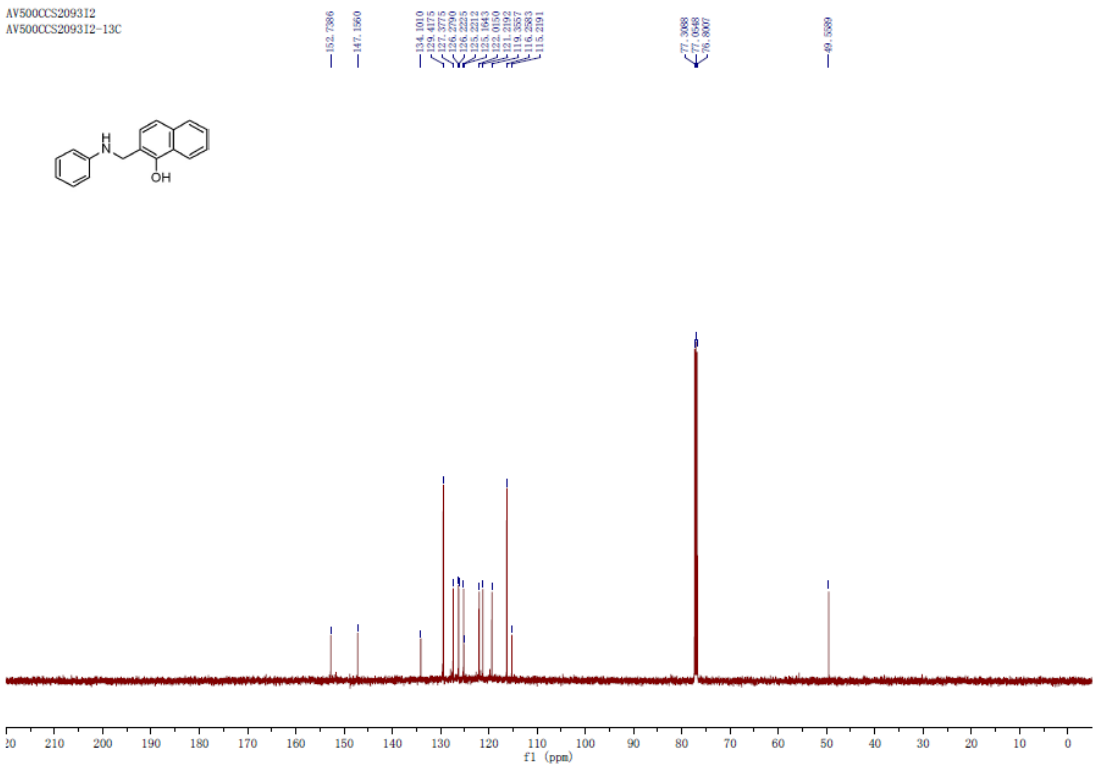
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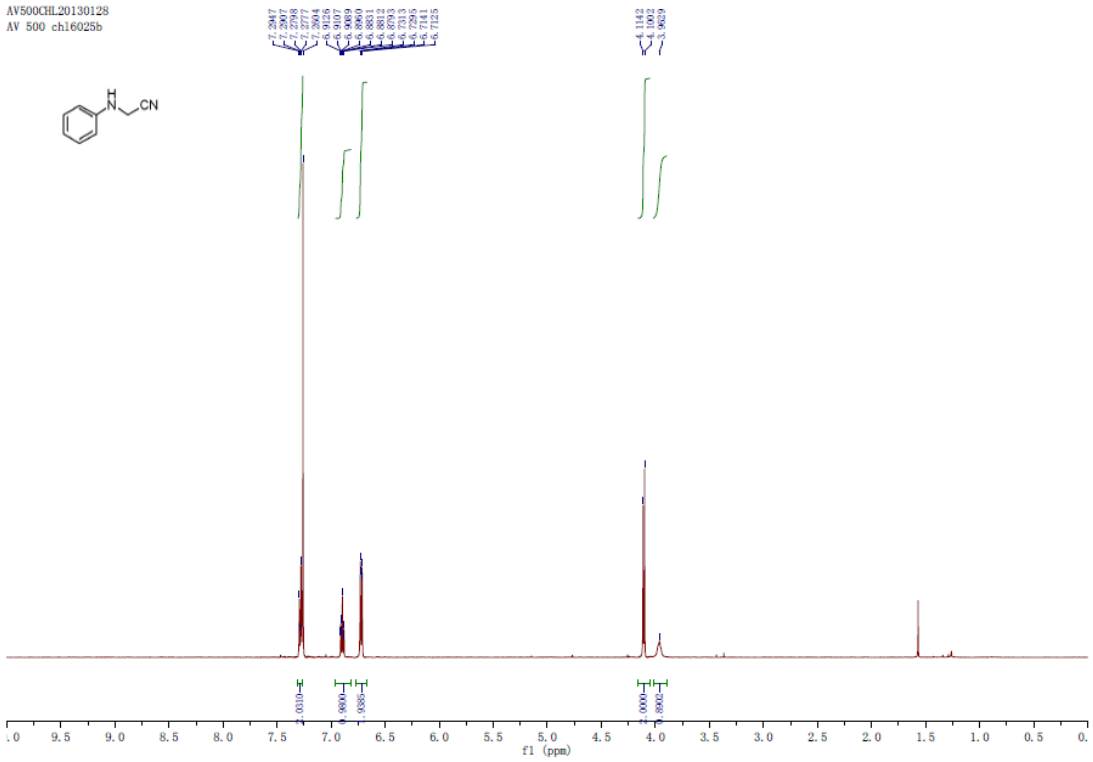
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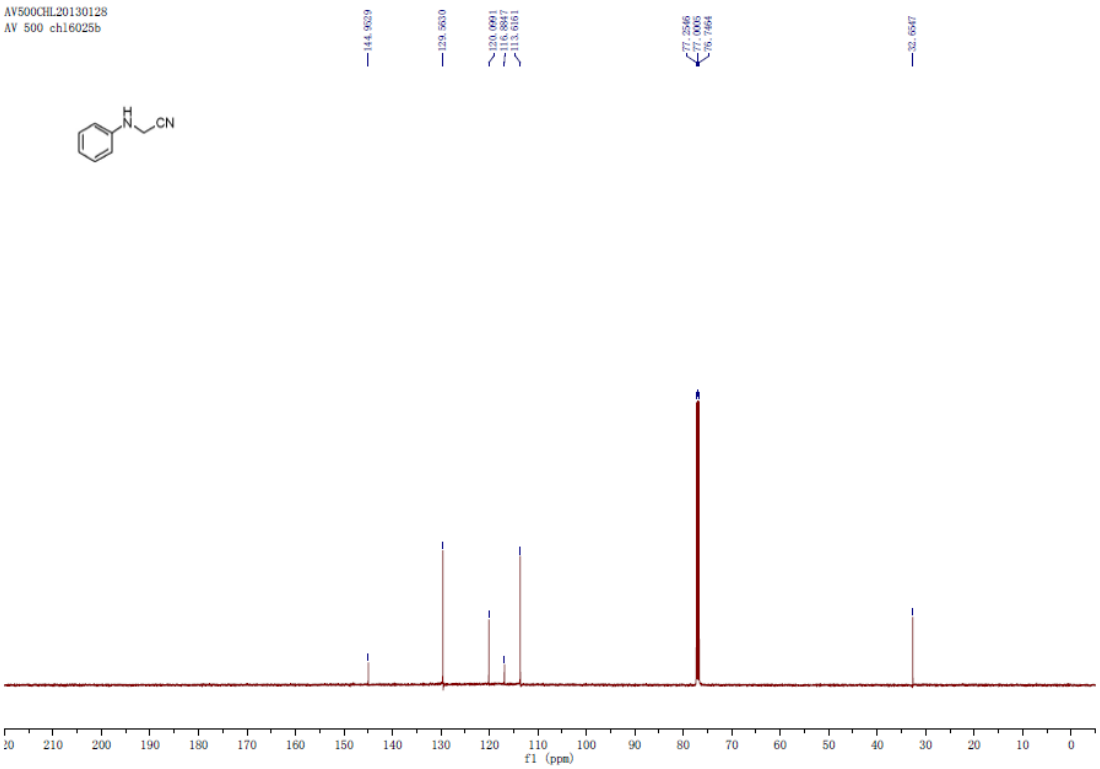
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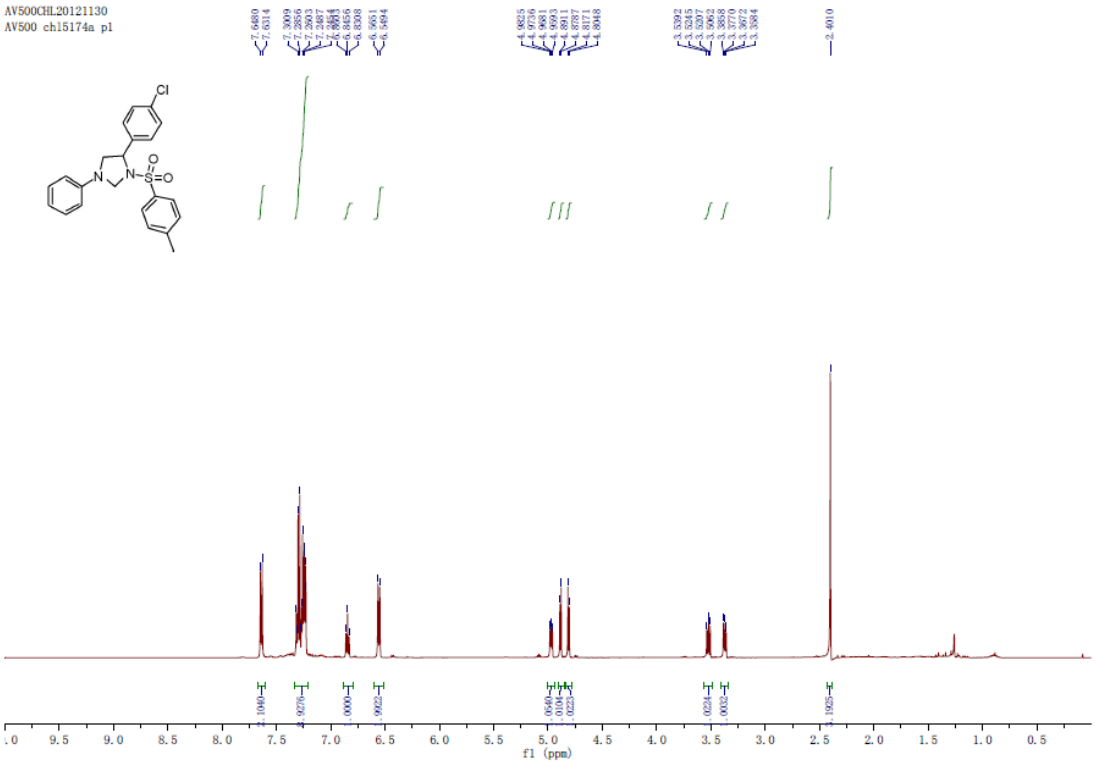
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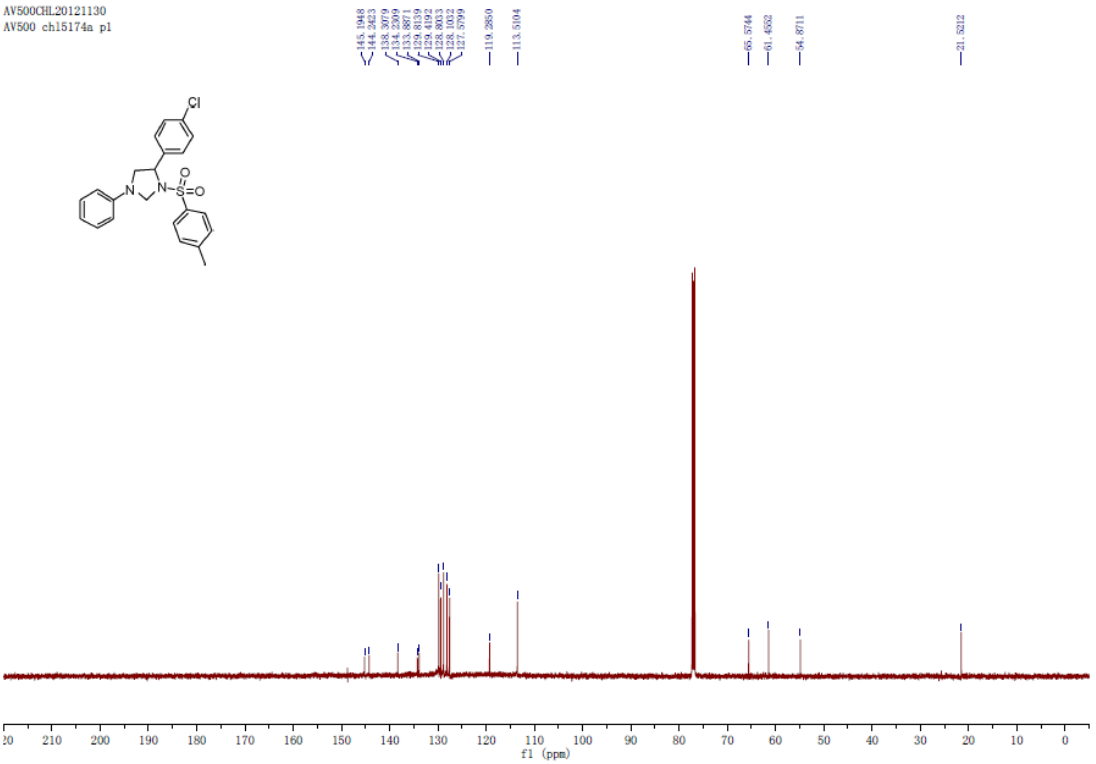
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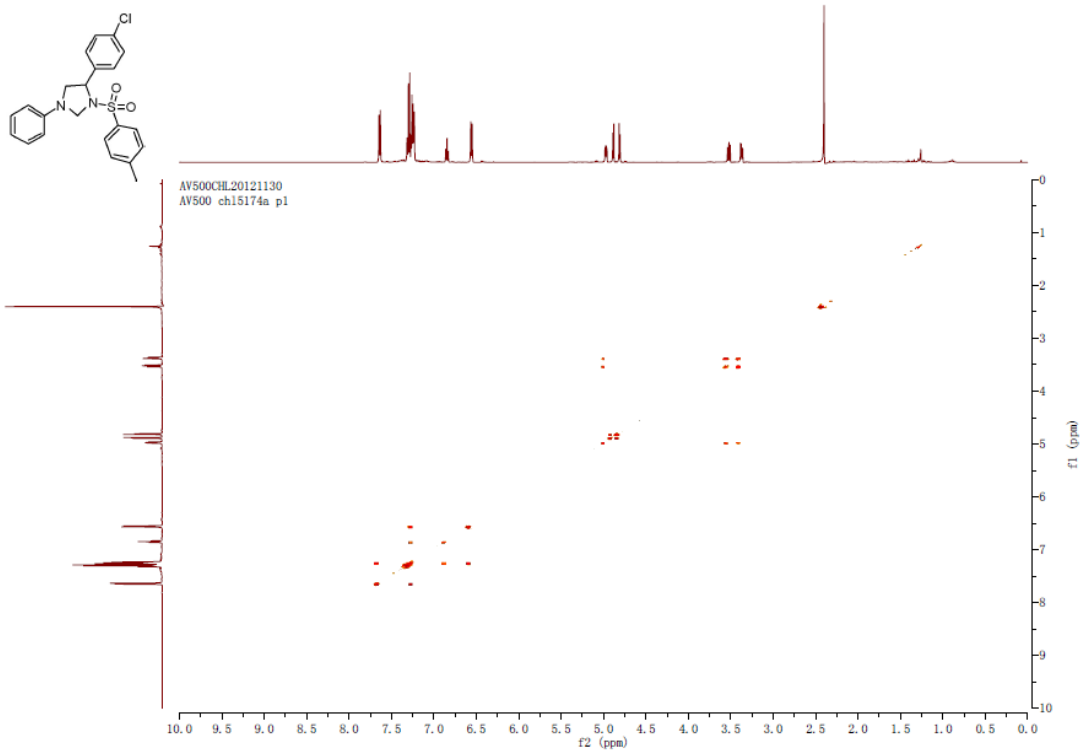
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f1 (ppm)