Supporting Information for

Rhodium/Chiral Urea Relay Catalysis Enables an Enantioselective Semipinacol Rearrangement/Michael Addition Cascade

Dian-Feng Chen, Pei-Yu Wu and Liu-Zhu Gong*

Hefei National Laboratory for Physical Sciences at Microscale and Department of Chemistry, University of Science and Technology of China, Hefei, 230026, China; E-mail: gonglz@ustc.edu.cn

General data: NMR spectra were recorded on a Brucker-400 MHz spectrometer. ESIMS spectra were recorded on BioTOF Q. Infrared spectra were recorded on a Nicolet MX-1E FT-IR spectrometer. Optical rotations were determined at 589 nm (sodium D line) by using a Perkin-Elmer-343 polarimeter. HPLC analysis was performed on Waters-Breeze (2487 Dual λ Absorbance Detector and 1525 Binary HPLC Pump, UV detection monitored at 254 or 220 nm). All chiral columns were purchased from Daicel Chemical Industries, LTD. Toluene, diethyl ether and tetrahydrofuran were dried over Na and distilled prior to use. Dichloromethane and dichloroethane were dried over CaH_2 and distilled prior to use.

Materials: All starting materials were purchased from Alfa and Aldrich and used directly. nitroalkenes **2** were prepared following the known procedure[1] and diazoalcohols **1** were synthesized according to the literatures.[2]

***General procedure for semipinacol rearrangement/Michael addition cascade*:**

To a solution of $Rh_2(OAc)_4$ (0.5 mg, 0.001 mmol), quinine-based squaramide **4e** (2.6 mg, 0.004 mmol), and (*E*)-nitroalkenes **2** (0.2 mmol) in CH_2Cl_2 (0.5 mL) was added a solution of diazoalcohols **1** (0.3 mmol) in CH_2Cl_2 (0.5 mL) in one portion under argon. After the resulting mixture was allowed to be stirred at 25 °C for the indicated time, the solution was directly subjected to a flash column chromatography on silica gel (ethyl acetate/petroleum ether) to afford product **3**.

Note: Compounds **3aa**, **3ba**, **3ia**, **3ib**, **3ic**, **3if** and **3ii** have been reported,[3] the analytical data of which was mached with those reported in the literatures and the absolute configuration of all the products was assigned either by comparison of the retention time of HPLC with the literature data

or by analogy.

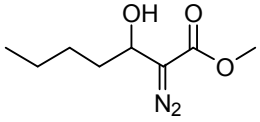
The synthesis of 3,4-disubstitutedy-lactam 6:

A solution of **3ea** (30.3 mg, 0.10 mmol) and p-TSA•H_2O (8.5 mg, 0.050 mmol) in 2mL toluene was stirred vigorously at 90°C for 12 hours. The mixture was then cooled to room temperature, and washed with 10% $NaHCO_3$ (5ml × 3), dried (anhydrous Na_2SO_4), concentrated in vacuo to afford crude **5** (yellowish oil, as a 1.5:1 mixture. **^{1}H-NMR**($CDCl_3$, 400 MHz) δ (ppm) ***major***： 7.34 – 7.22 (m, 4H), 7.16 – 7.12 (m, 1H), 6.24 (d, *J* = 3.1 Hz, 1H), 5.97 – 5.95 (m, 1H), 4.97 (dd, *J* = 13.3, 9.7 Hz, 1H), 4.62 – 4.52 (m, 1H), 4.06 (d, *J* = 10.6 Hz, 1H), 3.69 (s, 1H), 2.31 (d, *J* = 0.7 Hz, 1H); ***minor***: 7.35 – 7.21 (m, 4H), 7.16 – 7.12 (m, 1H), 5.98 (d, *J* = 3.1 Hz, 1H), 5.81 – 5.79 (m, 1H), 4.80 (dd, *J* = 13.3, 4.7 Hz, 1H), 4.63 – 4.50 (m, 1H), 4.28 – 4.17 (m, 1H), 4.10 (d, *J* = 8.0 Hz, 1H), 3.49 (s, 1H), 2.20 (d, *J* = 0.7 Hz, 1H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ (ppm) ***major***: 170.5, 152.9, 146.3, 137.1, 128.9, 128.2, 127.9, 110.2, 106.9, 78.3, 76.71, 52.4, 49.0, 45.6, 45.23, 13.6; ***minor***: 169.7, 152.4, 146.4, 136.8, 128.7, 128.0, 127.8, 109.7, 106.40, 78.3, 52.5, 49.0, 45.2, 13.5.)

To a stirred solution of crude **5** and $NiCl_2$•$6H_2O$ (23.8mg, 0.10 mmol) in 1mL EtOH at 0°C, $NaBH_4$ was added in portions. The reaction was quenched carefully by saturated aqueous NH_4Cl anfter stirring at 0°C for 2 hours, and extracted with CH_2Cl_2 (5ml × 3), dried (anhydrous Na_2SO_4), concentrated in vacuo. The residue was purified by column chromatography on silica gel to afford **6** and the enantiomeric excess was determined by HPLC analysis.

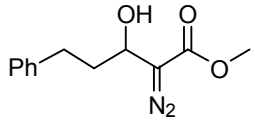
Characterization of diazoalcohols:

methyl 2-diazo-3-hydroxyheptanoate (1c)



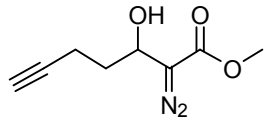
(Yellow oil) **^{1}H-NMR**($CDCl_3$, 400 MHz) δ (ppm) 4.66 (td, *J* = 7.1, 4.2 Hz, 1H), 3.8 (s, 3H), 2.68 (brs, 1H), 1.78 – 1.67 (m,1H), 1.64 – 1.55 (m, 1H), 1.49 – 1.28 (m, 4H), 0.91 (t, *J* = 7.1 Hz, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ (ppm) 167.0, 129.0, 66.7, 52.0, 33.7, 27.7, 22.3, 13.9; **IR(KBr)**: γ 3464, 2957, 2097, 1698, 1438, 1294 cm^{-1}; **ESI HRMS** exact mass calcd for $(C_8H_{14}N_2O_3Na)^+$ requires m/z 209.05891, found m/z 205.08923.

methyl 2-diazo-3-hydroxy-5-phenylpentanoate (1d)



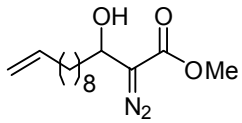
(Yellow oil) **^{1}H-NMR**($CDCl_3$, 400 MHz) δ (ppm) 7.32 – 7.24 (m, 2H), 7.22 - 7.16 (m, 3H), 7.37 - 7.27 (m, 2H), 4.67 (m, 1H), 3.77 (s, 3H), 2.80 - 2.60 (m, 2H), 2.13 – 1.84 (m, 2H), 1.73 (brs, 1H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ (ppm) 166.9, 140.9, 128.5, 128.4, 126.2, 166.0, 52.0, 35.7, 31.9; **IR(KBr)**: γ 3455, 2097, 1694, 1438, 1298, 1118, 747, 700 cm^{-1}; **ESI HRMS** exact mass calcd for $(C_{12}H_{14}N_2O_3Na)^+$ requires m/z 257.09021, found m/z 257.08932.

methyl 2-diazo-3-hydroxyhept-6-ynoate (1e)



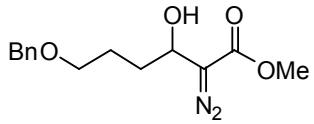
(Yellow oil) **^{1}H-NMR**($CDCl_3$, 400 MHz) δ (ppm) 4.87 – 4.77 (m, 1H), 3.79 (s, 3H), 2.82 (brs, 1H), 2.42 – 2.35 (m, 2H), 2.00 (t, *J* = 2.6 Hz, 1H), 1.98 – 1.79 (m, 2H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ (ppm) 166.1, 82.8, 69.4, 65.6, 52.1, 32.9, 15.0; **IR(KBr)**: γ 3455, 3294, 2955, 2099, 1685, 1438, 1298, 1120, 1052, 640 cm^{-1}; **ESI HRMS** exact mass calcd for $(C_8H_{10}N_2O_3Na)^+$ requires m/z 205.05891, found m/z 205.05812.

methyl 2-diazo-3-hydroxytridec-12-enoate (1f)



(Yellow oil) **^{1}H-NMR**($CDCl_3$, 400 MHz) δ (ppm) 5.81 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.02 – 4.90 (m, 2H), 4.67 (ddd, *J* = 7.6, 6.4, 4.2 Hz, 1H), 3.79 (s, 3H), 2.47 (brs, 1H), 2.03 (dt, *J* = 6.8, 4.0 Hz, 2H), 1.78 – 1.67 (m, 1H), 1.60 – 1.54 (m, 1H), 1.51 – 1.42 (m, 1H), 1.40 – 1.23 (m, 11H).; **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ (ppm) 167.0, 139.2, 114.1, 77.2, 66.7, 52.0, 34.0, 33.8, 29.4, 29.3, 29.2, 29.1, 28.9, 25.6.; **IR(KBr)**: γ 3462, 2926, 2855, 2096, 1697, 1438, 1296, 1115, 909 cm^{-1}; **ESI HRMS** exact mass calcd for $(C_{14}H_{24}N_2O_3Na)^+$ requires m/z 291.16846, found m/z 291.16734.

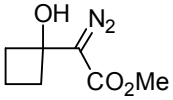
methyl 6-(benzyloxy)-2-diazo-3-hydroxyhexanoate (1g)



(Yellow oil) **^{1}H-NMR**($CDCl_3$, 400 MHz) δ (ppm) 7.37 – 7.27 (m, 5H), 4.71 – 4.65 (m, 1H), 4.52 (s, 2H), 3.77 (s, 3H), 3.55 – 3.48 (m, 2H), 3.14 (brs, 1H), 1.84 – 1.71 (m, 4H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ (ppm) 166.8, 138.0, 128.5, 128.4, 127.7, 73.11, 69.8, 66.3, 51.9, 39.8, 31.9, 26.1; **IR(KBr)**: γ 3434, 2952, 2859, 2097, 1693, 1438, 1297, 1101, 741, 698 cm^{-1}; **ESI HRMS** exact mass calcd for

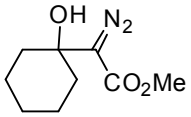
$(C_{14}H_{18}N_2O_3Na)^+$ requires m/z 301.11643, found m/z 301.11526.

methyl 2-diazo-2-(1-hydroxycyclobutyl)acetate(1i)



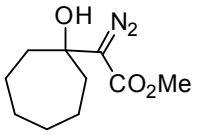
(Yellow oil) **^{1}H-NMR**($CDCl_3$, 400 MHz) δ (ppm) 3.80 (s, 3H), 3.27 (brs, 1H), 2.40 – 2.24 (m, 4H), 2.01 – 1.89 (m, 1H), 1.75 – 1.63 (m, 1H).; **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ (ppm) 166.9, 77.2, 72.2, 51.9, 35.4, 13.1; **IR(KBr)**: γ 3476, 2954, 2094, 1728, 1427, 1316, 1119 cm^{-1}; **ESI HRMS** exact mass calcd for $(C_7H_{10}N_2O_3Na)^+$ requires m/z 193.05891, found m/z 193.05788.

methyl 2-diazo-2-(1-hydroxycyclohexyl)acetate(1k)



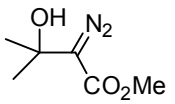
(Yellow oil) **^{1}H-NMR**($CDCl_3$, 400 MHz) δ (ppm) 3.77 (s, 3H), 3.39 (brs, 1H), 1.90 – 1.83 (m, 2H), 1.75 – 1.65 (m, 2H), 1.58 – 1.50 (m, 1H), 1.48 – 1.38 (m, 2H), 1.38 – 1.28 (m, 1H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ (ppm) 167.6, 70.2, 51.7, 36.4, 25.3, 22.0; **IR(KBr)**: γ 3465, 2935, 2858, 2091, 1694, 14371308, 745 cm^{-1}; **ESI HRMS** exact mass calcd for $(C_9H_{14}N_2O_3Na)^+$ requires m/z 221.09021, found m/z 221.08922.

methyl 2-diazo-2-(1-hydroxycycloheptyl)acetate(1l)



(Yellow oil) **^{1}H-NMR**($CDCl_3$, 400 MHz) δ (ppm) 3.71 (s, 3H), 3.62 (brs, 1H), 1.97 (ddd, J = 14.4, 9.0, 1.5 Hz, 2H), 1.83 (ddd, J = 14.5, 9.6, 1.7 Hz, 2H), 1.69 – 1.53 (m, 4H), 1.53 – 1.41 (m, 2H), 1.41 – 1.29 (m, 2H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ (ppm) 167.9, 77.0, 74.0, 51.8, 40.2, 29.0, 21.8; **IR(KBr)**: γ 3485, 2927, 2090, 1694, 1437, 1311, 1103, 747 cm^{-1}; **ESI HRMS** exact mass calcd for $(C_{10}H_{16}N_2O_3Na)^+$ requires m/z 235.10586, found m/z 235.10507.

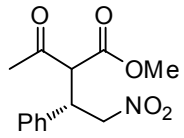
methyl 2-diazo-3-hydroxy-3-methylbutanoate(1m)



(Yellow oil) **^{1}H-NMR**($CDCl_3$, 400 MHz) δ (ppm) 3.79 (s, 3H), 3.71 (brs, 1H), 1.53 (s, 6H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ (ppm) 167.5, 77.2, 68.6, 51.8, 28.6; **IR(KBr)**: γ 3454, 2981, 2097, 1697, 1437, 1306, 1084, 969, 845, 746 cm^{-1}; **ESI HRMS** exact mass calcd for $(C_6H_{10}N_2O_3Na)^+$ requires m/z 181.05891, found m/z 181.05794.

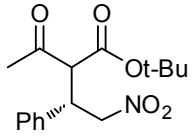
Characterization of the rearrangement/Michael addition Products:

(3S)-methyl 2-acetyl-4-nitro-3-phenylbutanoate (3aa)



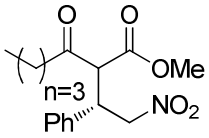
(White solid, 1:1 mixture of diastereomers) **^{1}H-NMR**($CDCl_3$, 400 MHz) δ (ppm) 7.34 – 7.25 (m, 6H), 7.23 – 7.18 (m, 4H), 4.88 – 4.80 (m, 2H), 4.77 (d, *J* = 6.4 Hz, 2H), 4.27 – 4.17 (m, 2H), 4.14 (d, *J* = 9.6 Hz, 1H), 4.05 (d, *J* = 9.8 Hz, 1H), 3.77 (s, 3H), 3.52 (s, 3H), 2.29 (s, 3H), 2.04 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ (ppm) 201.2, 200.3, 168.0, 167.4, 136.4, 136.3, 129.2, 129.0, 128.4, 128.3, 127.9, 127.8, 77.8, 77.7, 61.8, 61.4, 53.0, 52.8, 42.6, 42.3, 30.4, 30.3; Enantiomeric excess determined by HPLC (Chiracel-AD-H, hexane / isopropanol = 95/5, flow rate 1.0 mL/min, T = 30 ^{o}C, 220 nm): ***major:*** t_R = 17.34 min (major), t_R = 23.40 min, 99% ee; ***minor:*** t_R = 22.25 min, t_R = 27.16 min (major), 99% ee.

(3S)-tert-butyl 2-acetyl-4-nitro-3-phenylbutanoate (3ba)



(White solid, 3:1 mixture of diastereomers) **^{1}H-NMR**($CDCl_3$, 400 MHz) δ (ppm) ***major:*** 7.34 – 7.26 (m, 3H), 7.22 – 7.17 (m, 2H), 4.76 – 4.65 (m, 2H), 4.23 – 4.09 (m, 1H), 4.02 (d, *J* = 10.3 Hz, 1H), 2.30 (s, 3H), 1.17 (s, 9H).; ***minor:*** 7.33 – 7.27 (m, 3H), 7.23 – 7.15 (m, 2H), 4.88 – 4.78 (m, 2H), 4.23 – 4.09 (m, 1H), 3.92 (d, *J* = 9.6 Hz, 1H), 2.06 (s, 3H), 1.46 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ (ppm) ***major:*** 201.4, 165.9, 136.6, 128.8, 128.3, 128.0, 83.0, 78.4, 63.1, 42.4, 29.7, 27.4; ***minor:*** 200.7, 166.7, 136.6, 129.1, 128.2, 128.0, 83.5, 77.9, 62.7, 42.5, 30.1, 27.8; Enantiomeric excess determined by HPLC (Chiracel-AD-H, hexane / isopropanol = 95/5, flow rate 1.0 mL/min, T = 30 ^{o}C, 220 nm): ***major:*** t_R = 11.53 min (major), t_R = 17.40 min, 97% ee; ***minor:*** t_R = 18.74 min, t_R = 24.20 min (major), 99% ee.

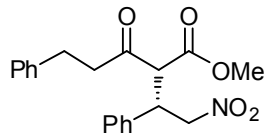
methyl 2-((S)-2-nitro-1-phenylethyl)-3-oxoheptanoate (3ca)



(Colourless oil, 1.7:1 mixture of diastereomers)**^{1}H-NMR**($CDCl_3$, 400 MHz) δ (ppm) ***major:*** 7.33 – 7.23 (m, 3H), 7.19 (dd, *J* = 5.2, 3.1 Hz, 2H), 5.80 (m, 1H), 5.02 – 4.95 (m, 1H), 4.95 – 4.90 (m, 1H), 4.88 – 4.82 (m, 1H), 4.81 – 4.76 (m, 1H), 4.23 (ddd, *J* = 12.2, 8.6, 4.2 Hz, 1H), 4.12 (d, *J* = 9.4 Hz, 1H), 4.03 (d, *J* = 10.0 Hz, 1H), 3.75 (s, 1H), 2.43 (ddd, *J* = 17.7, 14.7, 7.3 Hz, 1H), 2.13 (dt, *J* = 17.7, 7.1 Hz, 1H), 2.06 – 1.97 (m, 2H), 1.58 – 1.49 (m, 1H), 1.40 – 1.06 (m, 9H), 1.05 – 0.93 (m, 2H).; ***minor:*** 7.33 – 7.23 (m, 3H), 7.19 (dd, *J* = 5.2, 3.1 Hz, 2H), 5.80 (dqd, *J* = 20.2, 6.7, 3.2 Hz, 1H), 5.02 – 4.95 (m, 1H), 4.95 – 4.90 (m, 1H), 4.88 – 4.82 (m, 1H), 4.81 – 4.76 (m, 1H), 4.23 (ddd, *J* = 12.2, 8.6, 4.2 Hz, 1H), 4.12 (d, *J* = 9.4

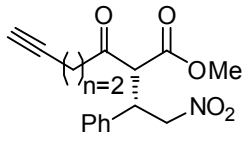
Hz, 1H), 3.52 (s, 1H), 2.60 (dt, *J* = 17.7, 7.4 Hz, 1H), 2.43 (ddd, *J* = 17.7, 14.7, 7.3 Hz, 1H), 2.04 – 2.00 (m, 2H), 1.40 – 1.06 (m, 12H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ (ppm) ***major:*** 202.6, 168.0, 136.4, 129.1, 128.4, 128.0, 77.8, 60.9, 52.9, 43.4, 42.8, 25.0, 21.7, 13.6; ***minor:*** 203.6, 167.6, 136.6, 129.0, 128.3, 127.8, 77.6, 61.3, 52.7, 43.0, 42.4, 25.3, 22.0, 13.7; **IR(KBr)**: γ 2958, 1744, 1556, 1435, 1378, 1272, 1170, 700 cm^{-1}; **ESI HRMS** exact mass calcd for $(C_{16}H_{21}NO_5Na)^+$ requires m/z 330.13174, found m/z 330.13052; Enantiomeric excess determined by HPLC (Chiracel-IC-H, hexane / isopropanol = 80/20, flow rate 1.0 mL/min, T = 30 ^oC, 220 nm): ***major:*** t_R = 8.43 min (major), t_R = 9.73 min, 98% ee; ***minor:*** t_R = 7.01 min (major), t_R = 9.12 min, 94% ee.

(S)-methyl 2-((S)-2-nitro-1-phenylethyl)-3-oxo-5-phenylpentanoate (3da)



(White solid, 4.5:1 mixture of diastereomers) **^{1}H-NMR**($CDCl_3$, 400 MHz) δ (ppm) ***major:*** 7.35 - 7.10 (m, 8H), 6.96 (d, *J* = 6.9 Hz, 2H), 4.88 – 4.74 (m, 1H), 4.66 (d, J = 6.5 Hz, 1H), 4.27 – 4.15 (m, 1H), 4.01 (d, *J* = 10.0 Hz, 1H), 3.67 (s, 1H), 2.84 – 2.73 (m, 1H), 2.72 – 2.55 (m, 2H), 2.42 (ddd, *J* = 17.5, 8.4, 6.0 Hz, 1H); ***minor:*** 7.35 - 7.10 (m, 10H), 4.88 – 4.74 (m, 1H), 4.66 (d, J = 6.5 Hz, 1H), 4.25 – 4.20 (m, 1H), 4.06 (d, *J* = 9.4 Hz, 1H), 3.44 (s, 1H), 3.02 – 2.87 (m, 3H), 2.84 – 2.70 (m, 1H).**^{13}C-NMR** ($CDCl_3$, 100 MHz) δ (ppm) ***major:*** 201.6, 167.8, 140.2, 136.3, 129.2, 128.5, 128.4, 128.2, 128.0, 126.2, 77.4, 61.0, 52.9, 45.2, 42.7, 29.0; ***minor:*** 202.7, 167.2, 140.2, 136.5, 129.0, 128.6, 128.4, 128.3, 127.8, 126.4, 77.8, 61.5, 52.8, 44.7, 42.4, 29.4; **IR(KBr)**: γ 3063, 3029, 2953, 1739, 1556, 1496, 1455, 1376, 1079, 751, 700, 552 cm^{-1}; **ESI HRMS** exact mass calcd for $(C_{20}H_{21}NO_5Na)^+$ requires m/z 378.13174, found m/z 378.13052; Enantiomeric excess determined by HPLC (Chiracel-IC-H, hexane / isopropanol = 80/20, flow rate 1.0 mL/min, T = 30 ^oC, 220 nm): ***major:*** t_R = 9.80 min (major), t_R = 12.32 min, 98% ee; ***minor:*** t_R = 8.57 min (major), t_R = 11.02 min, 96% ee.

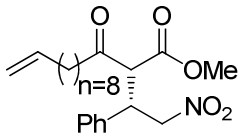
(S)-methyl 2-((S)-2-nitro-1-phenylethyl)-3-oxohex-5-ynoate (3ea)



(Colourless oil, 1.5:1 mixture of diastereomers) **^{1}H-NMR**($CDCl_3$, 400 MHz) δ (ppm) ***major***: 7.34 – 7.25 (m, 3H), 7.19 (dd, *J* = 6.4, 1.5 Hz, 2H), 4.90 – 4.76 (m, 2H), 4.29 – 4.21 (m, 1H), 4.07 (d, *J* = 9.9 Hz, 1H), 3.77 (s, 1H), 2.79 – 2.65 (m, 1H), 2.47 (td, *J* = 7.0, 2.6 Hz, 1H), 2.37 (ddd, *J* = 18.0, 7.7, 6.5 Hz, 1H), 2.31 – 2.14 (m, 1H), 1.86 (t, J = 2.6 Hz, 1H); ***minor***: 7.35 – 7.25 (m, 3H), 7.21 (dd, *J* = 6.4, 1.5 Hz, 1H), 4.90 – 4.75 (m, 2H), 4.30 – 4.20 (m, 1H), 4.15 (d, *J* = 9.3 Hz, 1H), 3.54 (s, 1H), 2.90 (dt, *J* = 18.1, 7.0 Hz, 1H),

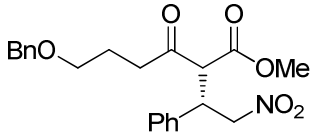
2.75 – 2.65 (m, 1H), 2.47 (td, *J* = 7.0, 2.6 Hz, 1H), 2.33 – 2.15 (m, 1H), 1.96 (t, J = 2.6 Hz, 1H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ (ppm) ***major***: 200.4, 167.7, 136.4, 129.2, 128.5, 127.9, 82.1, 77.7, 68.9, 60.7, 53.0, 42.6, 42.3, 12.6; ***minor***: 201.5, 167.1, 136.2, 129.1, 128.4, 127.8, 82.2, 77.5, 69.2, 61.2, 52.9, 42.4, 41.9, 12.9; **IR(KBr)**: γ 3292, 3034, 2955, 2097, 1716, 1552, 1434, 1376, 1074, 769, 700, 644 cm^{-1}; **ESI HRMS** exact mass calcd for $(C_{16}H_{17}NO_5Na)^+$ requires m/z 326.10044, found m/z 326.09921; Enantiomeric excess determined by HPLC (Chiracel-IC-H, hexane / isopropanol = 80/20, flow rate 1.0 mL/min, T = 30 ^oC, 220 nm): ***major:*** t_R = 9.41 min (major), t_R = 10.79 min, 98% ee; ***minor:*** t_R = 8.48 min (major), t_R = 12.02 min, 98% ee.

(S)-methyl 2-((S)-2-nitro-1-phenylethyl)-3-oxohex-5-enoate (3fa)



(Colourless oil, 2.5:1 mixture of diastereomers) **^{1}H-NMR**($CDCl_3$, 400 MHz) δ (ppm) ***major:*** 7.35 - 7.10 (m, 8H), 6.96 (d, *J* = 6.9 Hz, 2H), 4.88 – 4.74 (m, 1H), 4.66 (d, J = 6.5 Hz, 1H), 4.27 – 4.15 (m, 1H), 4.01 (d, *J* = 10.0 Hz, 1H), 3.67 (s, 1H), 2.84 – 2.73 (m, 1H), 2.72 – 2.55 (m, 2H), 2.42 (ddd, *J* = 17.5, 8.4, 6.0 Hz, 1H); ***minor:*** 7.35 - 7.10 (m, 10H), 4.88 – 4.74 (m, 1H), 4.66 (d, J = 6.5 Hz, 1H), 4.25 – 4.20 (m, 1H), 4.06 (d, *J* = 9.4 Hz, 1H), 3.44 (s, 1H), 3.02 – 2.87 (m, 3H), 2.84 – 2.70 (m, 1H).**^{13}C-NMR** ($CDCl_3$, 100 MHz) δ (ppm) ***major:*** 202.6, 168.0, 139.1, 136.4, 129.1, 128.4, 128.0, 114.2, 77.8, 60.9, 52.9, 43.7, 42.8, 33.8, 29.2, 29.1, 29.03, 29.0, 28.9, 28.6, 22.9; ***minor:*** 203.6, 167.5, 139.1, 136.6, 129.0, 128.3, 127.8, 114.2, 77.6, 61.3, 52.7, 43.3, 42.4, 33.8, 29.2, 29.0, 28.9, 28.8, 28.6, 23.3; **IR(KBr)**: γ 2929, 2855, 1743, 1556, 1433, 1375, 1170, 911, 701 cm^{-1}; **ESI HRMS** exact mass calcd for $(C_{22}H_{31}NO_5Na)^+$ requires m/z 412.20999, found m/z 412.20862; Enantiomeric excess determined by HPLC (Chiracel-IC-H, hexane / isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ^oC, 220 nm): ***major:*** t_R = 6.05 min (major), t_R = 6.95 min, 99% ee; ***minor:*** t_R = 5.47 min (major), t_R = 6.46 min, 99% ee.

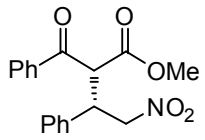
(S)-methyl 6-(benzyloxy)-2-((S)-2-nitro-1-phenylethyl)-3-oxohexanoate (3ga)



(While solid, 1.2:1 mixture of diastereomers) **^{1}H-NMR**($CDCl_3$, 400 MHz) δ (ppm) ***major:*** 7.38 – 7.21 (m, 8H), 7.16 (d, *J* = 7.8 Hz, 2H), 4.88 – 4.77 (m, 2H), 4.36 (s, 2H), 4.22 (ddd, *J* = 16.4, 8.5, 4.9 Hz, 1H), 4.03 (d, *J* = 9.7 Hz, 1H), 3.72 (s, 3H), 3.28 (dt, *J* = 9.4, 6.1 Hz, 1H), 3.20 (dt, *J* = 9.4, 6.1 Hz, 1H), 2.59 (m, 1H), 2.27 (dt, *J* = 18.2, 7.0 Hz, 1H), 2.00 – 1.83 (m, 1H), 1.67 (m, 1H).; ***minor:*** 7.35 –

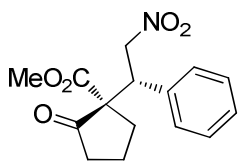
7.23 (m, 8H), 7.16 (d, *J* = 7.8 Hz, 2H), 4.68 (dd, *J* = 12.8, 4.5 Hz, 1H), 4.60 (dd, *J* = 12.8, 8.6 Hz, 1H), 4.45 (s, 2H), 4.22 (ddd, *J* = 16.4, 8.5, 4.9 Hz, 1H), 4.09 (d, *J* = 9.6 Hz, 1H), 3.47 (s, 3H), 3.49 – 3.43 (m, 2H), 2.77 – 2.65 (m, 1H), 2.59 (dtd, *J* = 17.8, 6.9, 3.0 Hz, 1H), 1.98 – 1.85 (m, 1H), 1.67 (p, *J* = 6.6 Hz, 1H);**^{13}C-NMR** ($CDCl_3$, 100 MHz) δ (ppm) ***major:*** 202.3, 168.0, 138.3, 136.4, 129.1, 128.4, 128.3, 128.0, 127.8, 127.6, 77.7, 72.8, 68.7, 60.9, 52.9, 42.7, 40.4, 40.02, 23.3; ***minor:*** 203.1, 167.5, 138.2, 136.5, 129.0, 128.5, 128.3, 127.9, 127.8, 127.6, 77.5, 73.0, 69.0, 61.30, 52.7, 42.4, 40.0, 23.7; **IR(KBr)**: γ 3031, 2953, 2860, 1744, 1556, 1455, 1377, 1267, 1169, 1097, 740, 701 cm^{-1}; **ESI HRMS** exact mass calcd for $(C_{22}H_{25}NO_6Na)^+$ requires m/z 422.15796, found m/z 422.15668; Enantiomeric excess determined by HPLC (Chiracel-OD-H, hexane / isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 ^oC, 220 nm): ***major:*** t_R = 30.00 min, t_R = 56.57 min(major), 99% ee; ***minor:*** t_R = 26.76 min (major), t_R = 33.02 min, 99% ee.

(2S,3S)-methyl 2-benzoyl-4-nitro-3-phenylbutanoate (3ha)



(White solid, 1.7:1 mixture of diastereomers) **^{1}H-NMR**($CDCl_3$, 400 MHz) δ (ppm) ***major***: 7.86 – 7.82 (m, 2H), 7.57 – 7.53 (m, 1H), 7.44 – 7.39 (m, 2H), 7.35 – 7.26 (m, 2H), 7.24 – 7.15 (m, 3H), 4.98 – 4.92 (m, 2H), 4.86 – 4.75 (m, 1H), 4.43 (ddd, *J* = 9.3, 7.9, 5.7 Hz, 1H), 3.72 (s, 3H); ***minor***: 8.05 – 7.99 (m, 2H), 7.64 – 7.59 (m, 1H), 7.51 – 7.46 (m, 2H), 7.32 – 7.27 (m, 2H), 7.22 – 7.16 (m, 3H), 4.99 – 4.90 (m, 2H), 4.90 – 4.75 (m, 1H), 4.52 – 4.47 (m, 1H), 3.43 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ (ppm) ***major***: 192.6, 168.2, 136.6, 136.0, 133.9, 129.0, 128.9, 128.8, 128.2, 128.1, 78.0, 56.0, 53.1, 43.2; ***minor***: 192.8, 167.5, 136.3, 135.8, 134.3, 129.0, 128.9, 128.6, 128.4, 128.0, 77.7, 56.9, 52.8, 43.2; **IR(KBr)**: γ 3060, 3029, 2950, 1739, 1551, 1496, 1455, 1377, 1079, 751, 700, 551 cm^{-1}; **ESI HRMS** exact mass calcd for $(C_{18}H_{18}NO_5)^+$ requires m/z 328.11850, found m/z 328.11713; Enantiomeric excess determined by HPLC (Chiracel-AS-H, hexane / isopropanol = 97/3, flow rate 1.0 mL/min, T = 30 ^oC, 254 nm): ***major:*** t_R = 28.25 min(major), t_R = 49.76 min, 96% ee; ***minor:*** t_R = 34.25 min (major), t_R = 42.74 min, 99% ee.

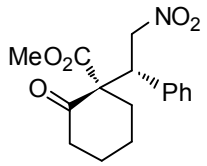
(S)-methyl 1-((R)-2-nitro-1-phenylethyl)-2-oxocyclopentanecarboxylate (3ia)



(White solid, 20:1dr) **^{1}H-NMR**($CDCl_3$, 400 MHz) δ (ppm) 7.34 – 7.21 (m, 5H), 5.17 (dd, *J* = 13.6, 3.9 Hz, 1H), 5.01 (dd, *J* = 13.6, 10.8 Hz, 1H), 4.07

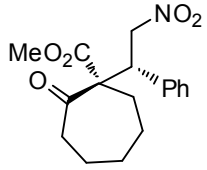
(dd, *J* = 10.8, 3.9 Hz, 1H), 3.76 (s, 3H), 2.43 – 2.30 (m, 2H), 2.08 – 1.76 (m, 4H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ (ppm) 212.2, 169.8, 135.3, 129.3, 128.9, 128.4, 77.7, 62.5, 53.0, 46.2, 37.9, 31.2, 19.3; Enantiomeric excess determined by HPLC (Chiracel-OD-H, hexane / isopropanol = 80/20, flow rate 1.0 mL/min, T = 30 ^{o}C, 220 nm): t_R = 8.61 min (major), t_R = 12.77 min, 91% ee.

(S)-methyl 1-((R)-2-nitro-1-phenylethyl)-2-oxocyclohexanecarboxylate (3ja)



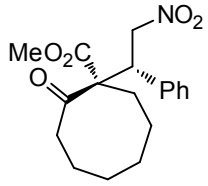
(White solid, 50:1dr) **^{1}H-NMR**($CDCl_3$, 400 MHz) δ (ppm) 7.31 – 7.24 (m, 3H), 7.16 – 7.11 (m, 2H), 5.05 (dd, *J* = 13.5, 3.3 Hz, 1H), 4.78 (dd, *J* = 13.5, 11.2 Hz, 1H), 4.01 (dd, *J* = 11.2, 3.3 Hz, 1H), 3.74 (s, 3H), 2.57 – 2.50 (m, 1H), 2.44 (td, *J* = 12.8, 5.8 Hz, 1H), 2.11 (ddd, *J* = 13.3, 6.0, 3.3 Hz, 1H), 2.05 – 1.98 (m, 1H), 1.76 – 1.57 (m, 3H), 1.53 – 1.44 (m, 1H).;**^{13}C-NMR** ($CDCl_3$, 100 MHz) δ (ppm) 206.9, 170.2, 135.3, 129.4, 128.5, 128.3, 63.1, 52., 47.4, 41.4, 37.0, 27.9, 22.3 ; **IR(KBr)**: γ 3420, 3050, 2927, 2855, 1706, 1551, 1380, 1216, 703 cm^{-1}; **ESI HRMS** exact mass calcd for $(C_{16}H_{20}NO_5)^+$ requires m/z 306.13415, found m/z 306.13329; $[\alpha]_D^{20}$ = -76.1 (*c* 0.45, EtOAc); Enantiomeric excess determined by HPLC (Chiracel-IC-H, hexane / isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 ^{o}C, 220 nm): **major**: t_R = 18.06 min(major), t_R = 22.12 min, 98% ee.

(S)-methyl 1-((R)-2-nitro-1-phenylethyl)-2-oxocycloheptanecarboxylate (3ka)



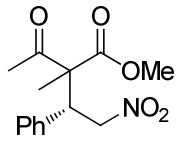
(Colourless oil, 12:1dr) **^{1}H-NMR**($CDCl_3$, 400 MHz) δ (ppm) 7.31 – 7.26 (m, 3H), 7.16 – 7.12 (m, 2H), 4.94 (dd, *J* = 7.1, 5.7 Hz, 2H), 4.06 (dd, *J* = 9.8, 4.4 Hz, 1H), 3.77 (s, 3H), 2.61 (ddd, *J* = 12.4, 8.3, 4.1 Hz, 1H), 2.52 (ddd, *J* = 12.8, 8.9, 4.2 Hz, 1H), 1.93 – 1.85 (m, 1H), 1.80 – 1.50 (m, 6H), 1.47 – 1.36 (m, 1H);**^{13}C-NMR** ($CDCl_3$, 100 MHz) δ (ppm) 208.2, 171.3, 135.6, 129.4, 128.7, 128.3, 77.9, 65.6, 52.5, 48.6, 41.4, 33.0, 29.0, 25.1, 24.6; **IR(KBr)**: γ 3420, 3050, 2923, 2850, 1688, 1591, 1460, 1430, 1260, 1184, 1117, 811, 696 cm^{-1}; **ESI HRMS** exact mass calcd for $(C_{17}H_{22}NO_5)^+$ requires m/z 320.14980, found m/z 320.15011; $[\alpha]_D^{20}$ = -27.6 (*c* 1.03, EtOAc); Enantiomeric excess determined by HPLC (Chiracel-IC-H, hexane / isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 ^{o}C, 210 nm): **major**: t_R = 9.37 min(major), t_R = 18.89 min, 91% ee.

(S)-methyl 1-((R)-2-nitro-1-phenylethyl)-2-oxocyclooctanecarboxylate (3la)



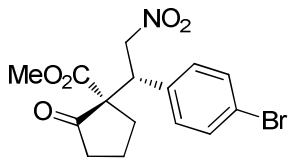
(Colourless oil, 6:1 mixture of diastereomers) **^{1}H-NMR**($CDCl_3$, 400 MHz) δ (ppm) 7.30 – 7.25 (m, 3H), 7.10 – 7.06 (m, 2H), 5.07 (dd, *J* = 13.4, 3.2 Hz, 1H), 4.72 (dd, *J* = 13.4, 11.3 Hz, 1H), 4.21 (dd, *J* = 11.2, 3.1 Hz, 1H), 3.81 (s, 3H), 2.62 (ddd, *J* = 13.4, 10.4, 4.2 Hz, 1H), 2.40 (ddd, *J* = 13.3, 6.6, 4.1 Hz, 1H), 2.20 – 2.10 (m, 1H), 1.90 – 1.76 (m, 2H), 1.72 – 1.59 (m, 4H), 1.48 – 1.33 (m, 2H), 1.23 – 1.11 (m, 1H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ (ppm) 210.7, 171.1, 135.8, 129.0, 128.7, 128.3, 78.4, 64.6, 52.6, 46.3, 40.0, 27.1, 26.4, 24.8, 22.5; **IR(KBr)**: γ 2927, 2854, 1706, 1552, 1379, 1216, 703 cm^{-1}; **ESI HRMS** exact mass calcd for $(C_{18}H_{24}NO_5)^+$ requires m/z 334.16545, found m/z 334.16461; Enantiomeric excess determined by HPLC (Chiracel-OD-H, hexane / isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 ^oC, 210 nm): ***major:*** t_R = 7.83 min(major), t_R = 8.36 min, 88% ee; ***minor:*** t_R = 10.53 min(major), t_R = 14.36 min, 68% ee

(3R)-methyl 2-acetyl-2-methyl-4-nitro-3-phenylbutanoate (3ma)



(White solid, 3:1 mixture of diastereomers) **^{1}H-NMR**($CDCl_3$, 400 MHz) δ (ppm) ***major*** : δ 7.33 – 7.27 (m, 3H), , 7.13 – 7.09 (m, 2H), 5.00 – 4.92 (m, 1H), 4.88 (dd, *J* = 13.5, 3.5 Hz, 1H), 4.13 (dd, *J* = 10.9, 3.5 Hz, 1H), 3.80 (s, 3H), 2.16 (s, 3H); ***minor***: δ 7.30 – 7.25 (m, 3H), 7.22 – 7.18 (m, 2H), 5.05 – 4.95 (m, 2H), 4.24 (dd, *J* = 8.5, 6.2 Hz, 1H), 3.63 (s, 3H), 2.11 (s, 3H).;**^{13}C-NMR** ($CDCl_3$, 100 MHz) δ (ppm) ***major***:204.2, 171.8, 135.3, 128.9, 128.8, 128.4, 62.6,52.8, 47.8, 26.5, 20.1; ***minor***: 205.2, 171.3, 135.4, 129.2, 128.8, 128.4, 62.0, 52.8, 47.3, 27.3, 18.0; **IR(KBr)**: γ 3425, 3050, 2923, 2847, 1688, 1591, 1459, 1431, 1260, 1184, 1117, 811, 697 cm^{-1}; **EI HRMS** exact mass calcd for $(C_{14}H_{17}NO_5)^+$ requires m/z 279.1107, found m/z 279.1113; Enantiomeric excess determined by HPLC (Chiracel-IC-H, hexane / isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 ^oC, 220 nm): ***major:*** t_R = 15.69 min(major), t_R = 42.00 min, 99% ee; ***minor:*** t_R = 16.55 min(major), t_R = 28.30 min, 97% ee.

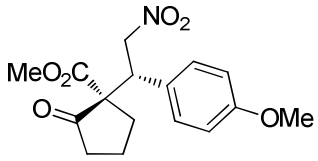
(S)-methyl 1-((R)-1-(4-bromophenyl)-2-nitroethyl)-2-oxocyclopentanecarboxylate (3ib)



(White solid, 30:1dr) **^{1}H-NMR**($CDCl_3$, 400 MHz) δ (ppm) 7.46 – 7.41 (m, 2H), 7.17 – 7.13 (m, 2H), 5.15 (dd, *J* = 13.7, 3.8 Hz, 1H), 4.97 (dd, *J* = 13.7, 11.0 Hz, 1H), 4.02 (dd, *J* = 11.0, 3.8 Hz, 1H), 3.75 (s, 3H), 2.44 – 2.28 (m, 2H), 2.15 – 2.00 (m, 1H), 1.99 – 1.80 (m, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ (ppm) 212.0, 169.7, 134.4, 132.0, 131.1, 122.6, 77.8, 62.2, 53.1, 45.7, 37.9,

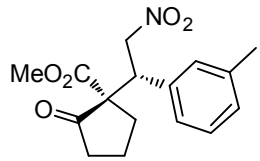
31.4, 19.3; Enantiomeric excess determined by HPLC (Chiracel-OD-H, hexane / isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 ^{o}C, 220 nm): t_R = 12.92 min(major), t_R = 20.15 min, 92% ee.

(S)-methyl 1-((R)-1-(4-methoxyphenyl)-2-nitroethyl)-2-oxocyclopentanecarboxylate (3ic)



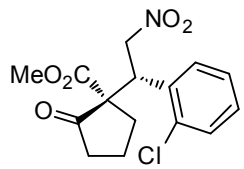
(White solid, 20:1dr) **^{1}H-NMR**($CDCl_3$, 400 MHz) δ (ppm) 7.16 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 5.11 (dd, *J* = 13.4, 4.0 Hz, 1H), 4.96 (dd, *J* = 13.4, 11.0 Hz, 1H), 4.05 (dd, *J* = 11.0, 4.0 Hz, 1H), 3.77 (s, 3H), 3.75 (s, 3H), 2.44 – 2.27 (m, 2H), 2.08 – 1.75 (m, 4H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ (ppm) 212.3, 169.9, 159.4, 130.4, 127.0, 114.2, 77.7, 62.7, 55.2, 53.0, 45.5, 38.0, 31.0, 19.4; Enantiomeric excess determined by HPLC (Chiracel-OD-H, hexane / isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 ^{o}C, 220 nm): t_R = 13.69 min(major), t_R = 19.21 min, 90% ee.

(S)-methyl 1-((R)-2-nitro-1-(m-tolyl)ethyl)-2-oxocyclopentanecarboxylate (3id)



(Corlourless oil, 50:1dr) **^{1}H-NMR**($CDCl_3$, 400 MHz) δ (ppm) 7.18 (t, *J* = 7.8 Hz, 1H), 7.07 (d, *J* = 7.7 Hz, 1H), 7.05 – 6.96 (m, 2H), 5.15 (dd, *J* = 13.6, 3.9 Hz, 1H), 4.99 (dd, *J* = 13.6, 10.8 Hz, 1H), 4.02 (dd, *J* = 10.8, 3.9 Hz, 1H), 3.74 (s, 3H), 2.36 (ddt, *J* = 8.5, 6.6, 4.9 Hz, 2H), 2.31 (s, 3H), 2.09 – 1.77 (m, 4H).; **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ (ppm) 212.2, 169.8, 138.5, 135.2, 130.1, 129.1, 128.7, 126.1, 76.5, 62.5, 53.0, 46.2, 37.9, 31.2, 21.5, 19.3; **IR(KBr)**: γ 2957, 1727, 1553, 1434, 1378, 1231, 1148, 727 cm^{-1}; **ESI HRMS** exact mass calcd for $(C_{16}H_{19}NO_5Na)^{+}$ requires m/z 328.11609, found m/z 328.11499; $[\alpha]_D^{20}$ = +37.7 (*c* 1.14, EtOAc); Enantiomeric excess determined by HPLC (Chiracel-OD-H, hexane / isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 ^{o}C, 220 nm): t_R = 9.51 min(major), t_R = 13.26 min, 98% ee.

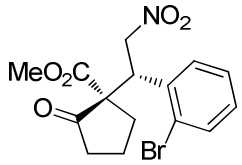
(S)-methyl 1-((S)-1-(2-chlorophenyl)-2-nitroethyl)-2-oxocyclopentanecarboxylate (3ie)



(White solid, 25:1dr) **^{1}H-NMR**($CDCl_3$, 400 MHz) δ (ppm) 7.52 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.39 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.29 – 7.19 (m, 2H), 5.48 (dd, *J* = 14.0, 3.5 Hz, 1H), 5.09 (dd, *J* = 13.9, 10.6 Hz, 1H), 4.53 (dd, *J* = 10.6, 3.4 Hz, 1H), 3.75 (s, 3H), 2.49 (t, *J* = 7.4 Hz, 2H), 2.35 – 2.21 (m, 2H), 2.18 – 1.83 (m, 4H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ (ppm) 212.5, 169.8, 135.6, 134.7, 130.2, 129.4, 128.9, 127.7, 62.2, 54.6, 52.9, 37.8, 32.9, 27.2, 19.3; **IR(KBr)**: γ 2956, 1729, 1553, 1435, 1377, 1232, 1160, 1037,

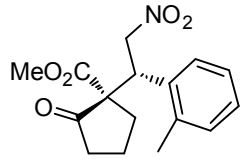
761 cm^{-1}; **ESI HRMS** exact mass calcd for $(C_{15}H_{16}NO_5ClNa)^+$ requires m/z 348.06147, found m/z 348.06052; $[\alpha]_D^{20}$ = -20.0 (*c* 1.07, EtOAc); Enantiomeric excess determined by HPLC (Chiracel-OD-H, hexane / isopropanol = 99/1, flow rate 0.5 mL/min, T = 30 °C, 220 nm): t_R = 22.63 min(major), t_R = 23.68 min, 97% ee.

(S)-methyl 1-((S)-1-(2-bromophenyl)-2-nitroethyl)-2-oxocyclopentanecarboxylate (3if)



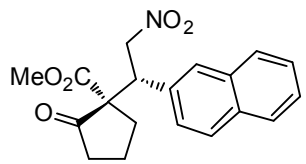
(White solid, 50:1dr) **^{1}H-NMR**($CDCl_3$, 400 MHz) δ (ppm) 7.58 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.52 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.33 – 7.28 (m, 1H), 7.14 (ddd, *J* = 9.0, 7.7, 1.6 Hz, 1H), 5.48 (dd, *J* = 13.8, 3.5 Hz, 1H), 5.06 (dd, *J* = 13.8, 10.6 Hz, 1H), 4.51 (dd, *J* = 10.6, 3.5 Hz, 1H), 3.75 (s, 3H), 2.50 (m, 2H), 2.28 – 2.17 (m, 1H), 2.16 – 2.05 (m, 1H), 2.02 – 1.87 (m, 2H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ (ppm) 212.5, 169.9, 136.5, 133.6, 129.7, 128.9, 128.3, 126.8, 77.7, 62.2, 52.9, 43.9, 37.8, 33.0, 19.34; Enantiomeric excess determined by HPLC (Chiracel-OD-H, hexane / isopropanol = 95/5, flow rate 1.0 mL/min, T = 30 °C, 220 nm): t_R = 8.69 min (major), t_R = 10.49 min, 99% ee.

(S)-methyl 1-((R)-2-nitro-1-(o-tolyl)ethyl)-2-oxocyclopentanecarboxylate (3ig)



(Corlourless oil, 25:1dr) **^{1}H-NMR**($CDCl_3$, 400 MHz) δ (ppm) 7.29 (m, 1H), 7.19 – 7.11 (m, 3H), 5.26 (dd, *J* = 13.5, 3.9 Hz, 1H), 4.94 (dd, *J* = 13.4, 10.8 Hz, 1H), 4.37 (dd, *J* = 10.8, 3.9 Hz, 1H), 3.74 (s, 3H), 2.41 (s, 3H), 2.44 – 2.33 (m, 2H), 2.21 – 2.09 (m, 1H), 2.03 – 1.88 (m, 3H).; **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ (ppm) 212.2, 170.1, 138.0, 134.7, 131.3, 128.0, 126.9, 126.6, 76.7, 62.6, 53.0, 40.6, 37.9, 31.9, 20.1, 19.4; **IR(KBr)**: γ 2957, 1727, 1553, 1434, 1378, 1231, 1145 cm^{-1}; **ESI HRMS** exact mass calcd for $(C_{16}H_{19}NO_5Na)^+$ requires m/z 328.11609, found m/z 328.11508; $[\alpha]_D^{20}$ = +1.48 (*c* 1.02, EtOAc); Enantiomeric excess determined by HPLC (Chiracel-AD-H, hexane / isopropanol = 95/5, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 7.52 min(major), t_R = 8.25 min, 98% ee.

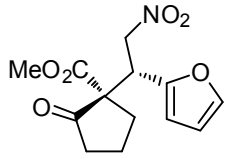
(S)-methyl 1-((R)-1-(naphthalen-2-yl)-2-nitroethyl)-2-oxocyclopentanecarboxylate (3ih)



(White solid, 20:1dr) **^{1}H-NMR**($CDCl_3$, 400 MHz) δ (ppm) 7.82 – 7.78 (m, 3H), 7.72 (d, *J* = 1.5 Hz, 1H), 7.51 – 7.46 (m, 2H), 7.38 (dd, *J* = 8.6, 1.9 Hz, 1H), 5.25 (dd, *J* = 13.7, 4.0 Hz, 1H), 5.15 (dd, *J* = 13.7, 10.7 Hz, 1H), 4.25 (dd, *J* = 10.7, 4.0 Hz, 1H), 3.78 (s, 3H), 2.44 – 2.31 (m, 2H), 2.10 – 1.99 (m, 2H), 1.98 –

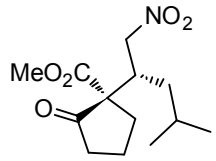
1.77 (m, 2H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ (ppm) 212.2, 169.9, 133.2, 133.0, 132.8, 128.9, 128.7, 128.07, 127.6, 126.6, 126.6, 126.5, 76.5, 62.6, 53.1, 46.4, 37.9, 31.4, 19.4; **IR(KBr)**: γ 3065, 3030, 2953, 1739, 1556, 1500, 1456, 1376, 1079, 751, 700, 550 cm^{-1}; **EI HRMS** exact mass calcd for $(C_{19}H_{19}NO_5)^+$ requires m/z 341.1263, found m/z 341.1267; $[\alpha]_D^{20}$ = +35.2 (*c* 1.17, EtOAc); Enantiomeric excess determined by HPLC (Chiracel-OD-H, hexane / isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ^oC, 254 nm): t_R = 13.26 min, t_R = 37.64 min (major), 93% ee.

(S)-methyl 1-((R)-1-(furan-2-yl)-2-nitroethyl)-2-oxocyclopentanecarboxylate (3ii)



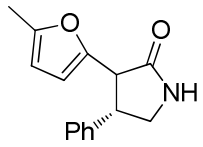
(Corlourless oil, 25:1dr) **^{1}H-NMR**($CDCl_3$, 400 MHz) δ (ppm) 7.34 (dd, *J* = 1.8, 0.6 Hz, 1H), 6.32 – 6.28 (m, 1H), 6.19 (d, *J* = 3.3 Hz, 1H), 4.98 – 4.85 (m, 2H), 4.43 (dd, *J* = 9.7, 4.8 Hz, 1H), 3.76 (s, 3H), 2.53 – 2.44 (m, 1H), 2.40 – 2.30 (m, 1H), 2.18 – 2.08 (m, 1H), 2.05 – 1.92 (m, 2H), 1.80 – 1.69 (m, 1H).; **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ (ppm) 211.9, 169.4, 149.1, 142.7, 110.9, 110.1, 77.5, 61.9, 53.2, 40.4, 37.9, 30.3, 19.4; Enantiomeric excess determined by HPLC (Chiracel-OD-H, hexane / isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 ^oC, 220 nm): t_R = 8.22 min(major), t_R = 12.80 min, 94% ee.

(S)-methyl 1-((R)-4-methyl-1-nitropentan-2-yl)-2-oxocyclopentanecarboxylate (3ij)



(Corlourless oil, 99:1dr) **^{1}H-NMR**($CDCl_3$, 400 MHz) δ (ppm) 4.88 (dd, *J* = 14.2, 5.6 Hz, 1H), 4.32 (dd, *J* = 14.2, 4.5 Hz, 1H), 3.69 (s, 3H), 2.95 – 2.86 (m, 1H), 2.64 – 2.55 (m, 1H), 2.48 – 2.37 (m, 1H), 2.36 – 2.25 (m, 1H), 2.08 – 1.88 (m, 3H), 1.60 – 1.50 (m, 1H), 1.44 (ddd, *J* = 14.2, 8.2, 3.7 Hz, 1H), 1.03 – 0.95 (m, 1H), 0.91 (s, 3H), 0.89 (s, 3H).; **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ (ppm) 213.2, 169.9, 76.6, 63.0, 52.7, 39.5, 38.4, 38.3, 31.1, 25.7, 23.7, 21.1, 19.4; **IR(KBr)**: γ 2958, 17241553, 1432, 1380, 1231, 1164 cm^{-1}; **ESI HRMS** exact mass calcd for $(C_{13}H_{21}NO_5Na)^+$ requires m/z 294.13174, found m/z 294.13043; $[\alpha]_D^{20}$ = -59.9 (*c* 1.10, EtOAc); Enantiomeric excess determined by HPLC (Chiracel-OD-H, hexane / isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 ^oC, 220 nm): t_R = 5.99 min(major), t_R = 8.05 min, 99% ee.

(4S)-3-(5-methylfuran-2-yl)-4-phenylpyrrolidin-2-one (6)



(Corlourless oil, 3:1mixture of diastereomers) **^{1}H-NMR**($CDCl_3$, 400 MHz) δ (ppm) ***major:*** 7.36 – 7.30 (m, 2H), 7.29 – 7.22 (m, 3H), 6.43 (s, 1H), 6.11 (d, *J* =

3.0 Hz, 1H), 5.91 – 5.86 (m, 1H), 4.01 – 3.85 (m, 1H), 3.85 – 3.72 (m, 2H), 3.53 – 3.46 (m, 1H), 2.26 (s, 3H); ***minor:*** 7.30 – 7.20 (m, 1H), 7.20 – 7.15 (m, 2H), 7.05 – 7.00 (m, 1H), 6.40 (s, 1H), 5.81 (d, *J* = 3.0 Hz, 1H), 5.71 – 5.68 (m, 1H), 4.01 – 3.85 (m, 2H), 3.82 – 3.72 (m, 2H), 2.11 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ (ppm) ***major:*** 175.2, 152.1, 148.3, 140.3, 128.9, 127.3, 127.1, 109.3, 106.4, 49.0, 47.3, 46.3, 13.7; ***minor:*** 175.1, 151.5, 147.1, 138.2, 128.1, 127.9, 127.0, 109.9, 106.1, 47.5, 46.4, 45.7, 13.5 ; **IR(KBr)**: γ 2924, 2853, 1695, 1462, 1376, 1260, 1021, 793, 700 cm^{-1}; **ESI HRMS** exact mass calcd for $(C_{15}H_{15}NO_2Na)^+$ requires m/z 264.10005, found m/z 264.09900; Enantiomeric excess determined by HPLC (Chiracel-IC-H, hexane / isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ^oC, 220 nm): ***major:*** t_R = 15.31 min, t_R = 32.39 min(major), 99% ee; ***minor:*** t_R = 19.57 min(major), t_R = 47.56 min, 99% ee.

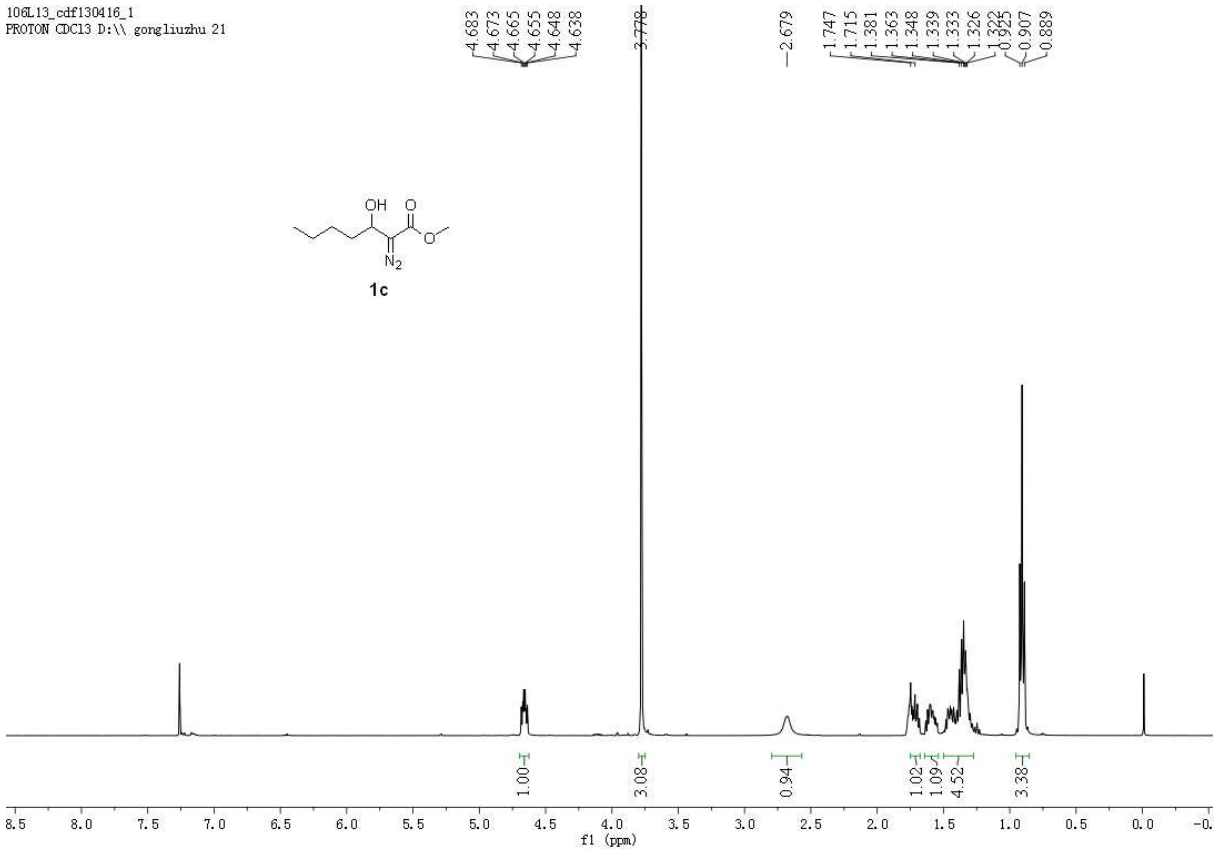
References:

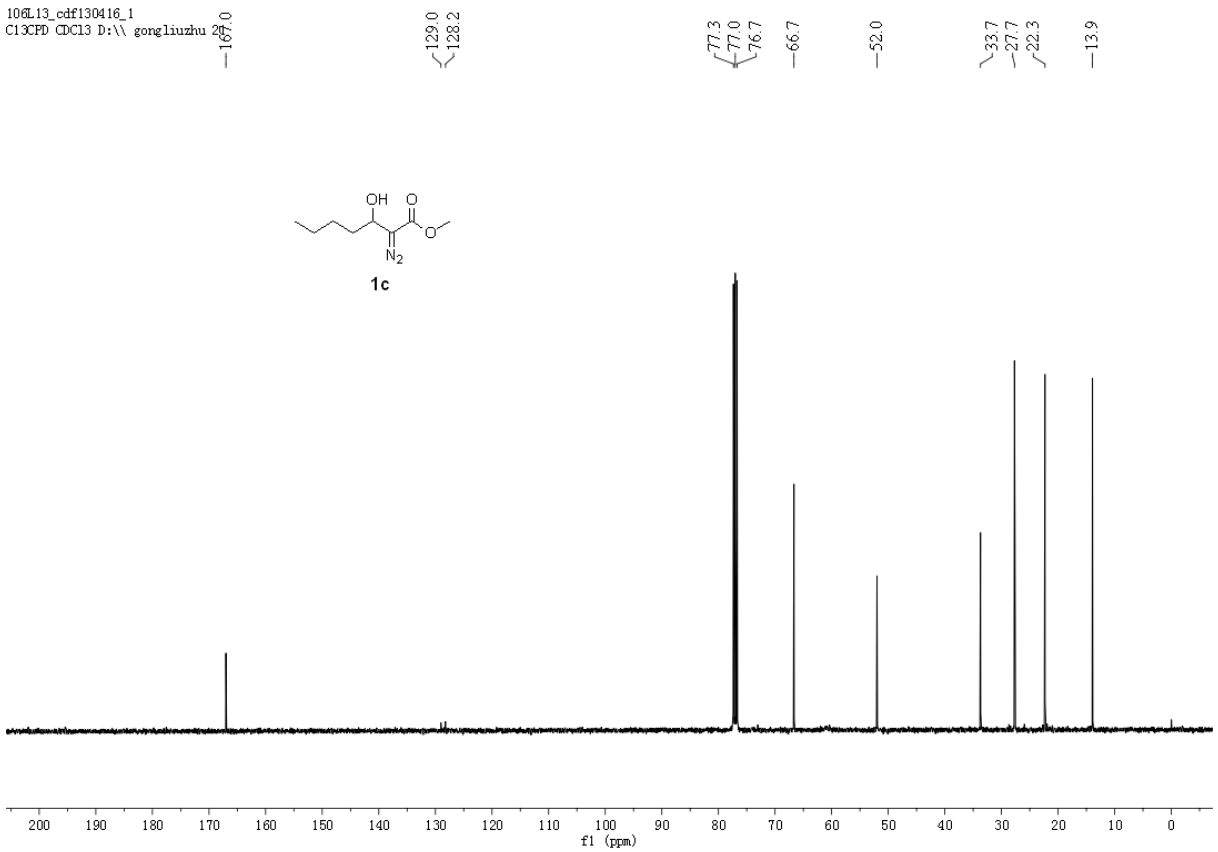
(1) (a) Denmark, S. E.; Marcin, L. R. *J. Org. Chem.* **1993**, *58*, 3850-3856; (b) Bulbule, V. J.; Jnaneshwara, G. K.; Deshmukh, R. R.; Borate, H. B.; Deshpande, V. H. *Synthetic Commun.* **2001**, *31*, 3623-3626.

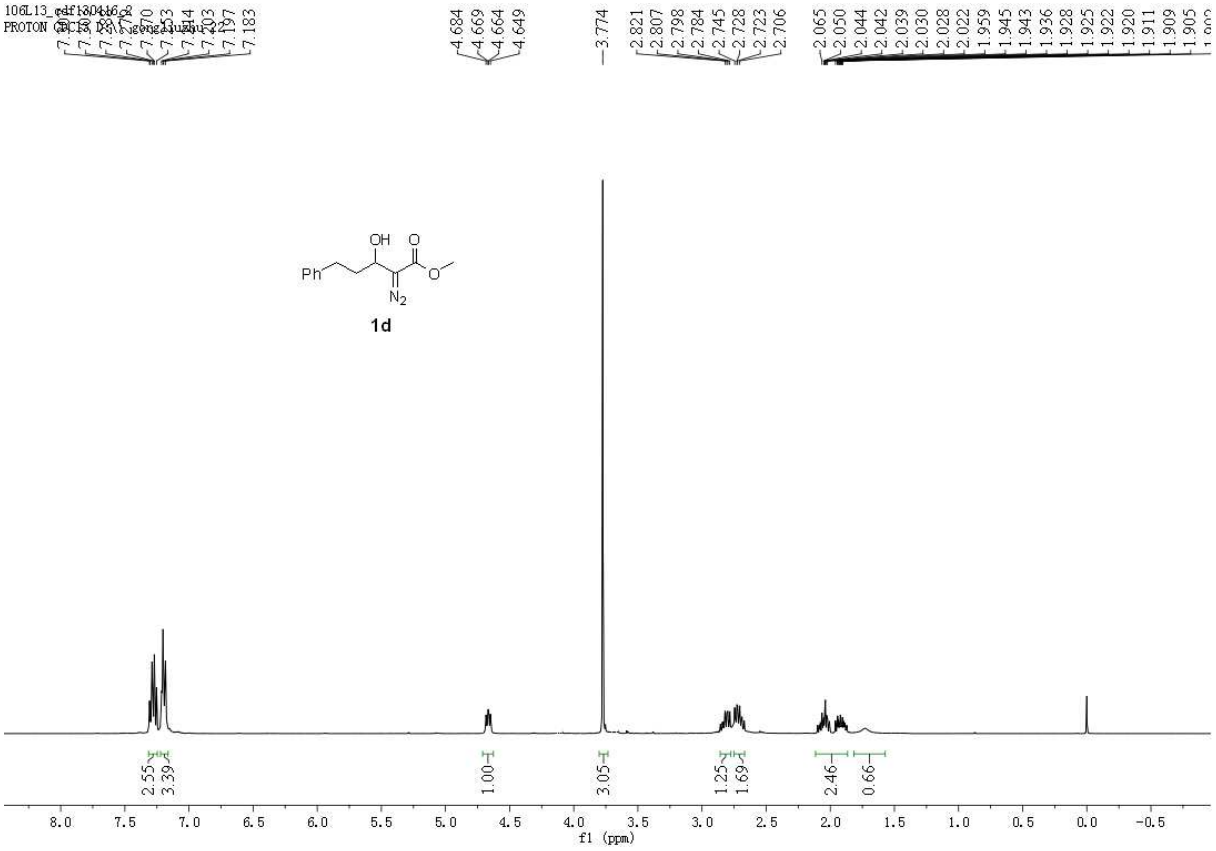
(2) (a) Schwartz, B. D.; Denton, J. R.; Lian, Y.-J.; Davies, H. M. L.; Williams, C. M. *J. Am. Chem. Soc.* **2009**, *131*, 8329-8332; (b) Xiao, F.-P.; Liu, Y.; Wang, J.-B. *Tetrahedron Lett.* **2007**, *48*, 1147-1149; (c) Pallicciari, R.; Natalini, B.; Sadeghpour, B. M.; Marinozzi, M.; Snyder, J. P.; Williamson, B. L.; Kuethe, J. T.; Padwa, A. *J. Am. Chem. Soc.* **1996**, *118*, 1-12.

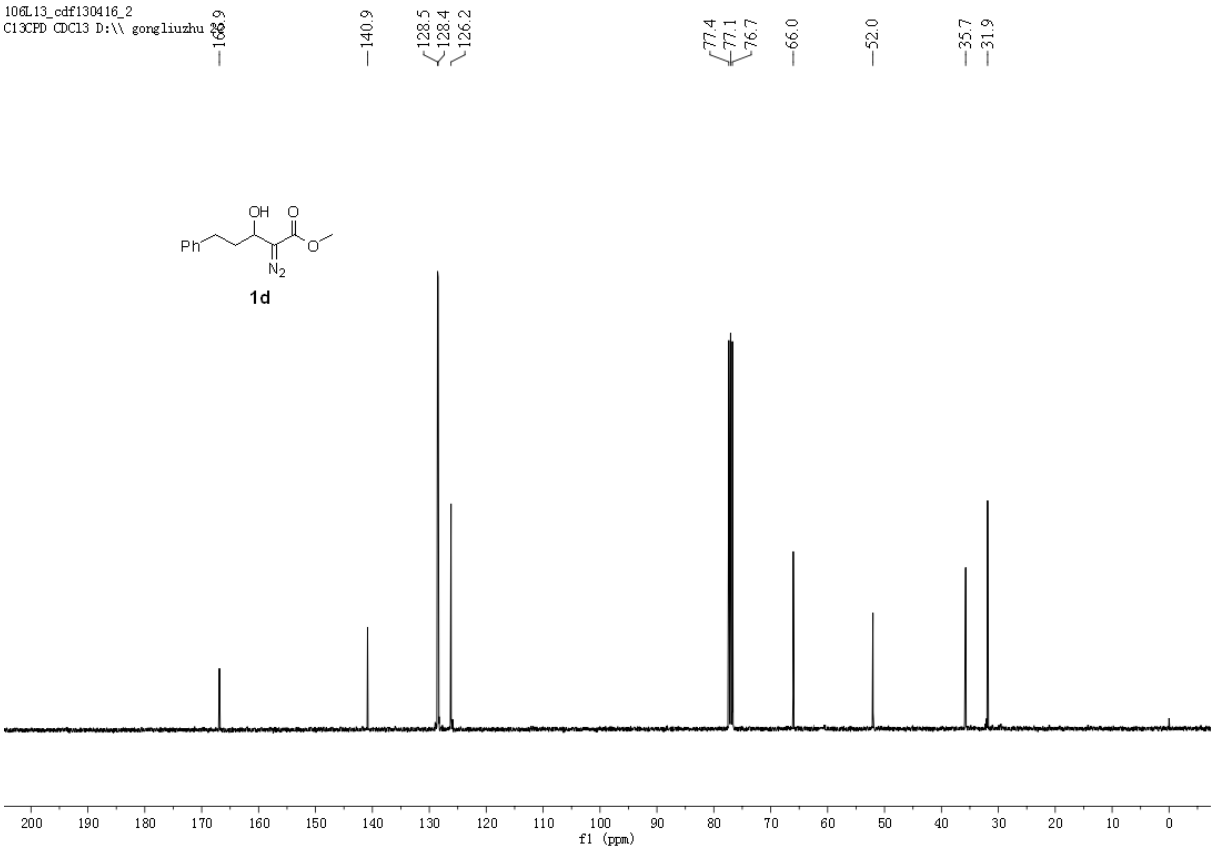
(3) (a) Han, Y. B.; Surajit, S.; Joong, S. O.; Yong, S. L.; Choong, E. S. *Chem. Commun.* **2011**, *47*, 9621-9623; (b) Furutachi, M.; Chen, Z.-H.; Matsunaga, S.; Shibasaki, M. *Molecules* **2010**, *15*, 532-544.

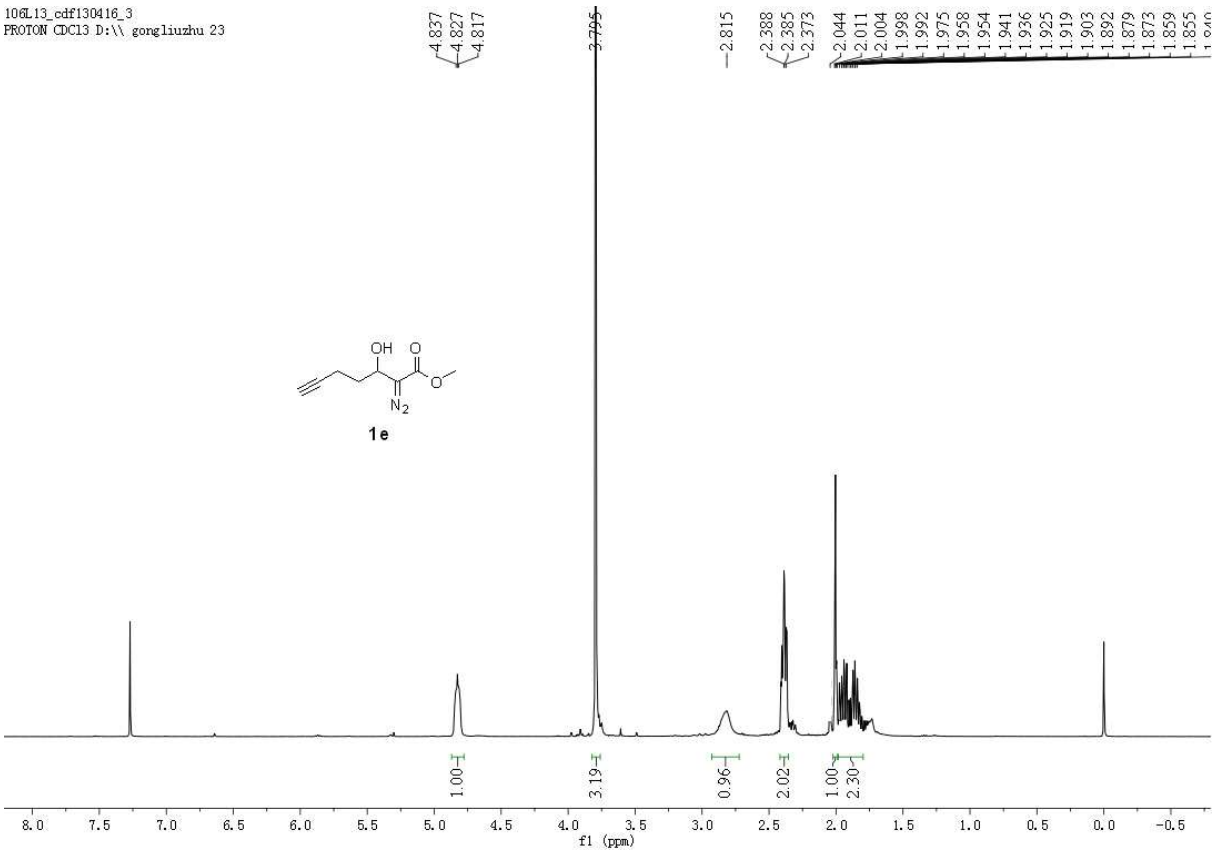
Selected NMR and HPLC Spectra

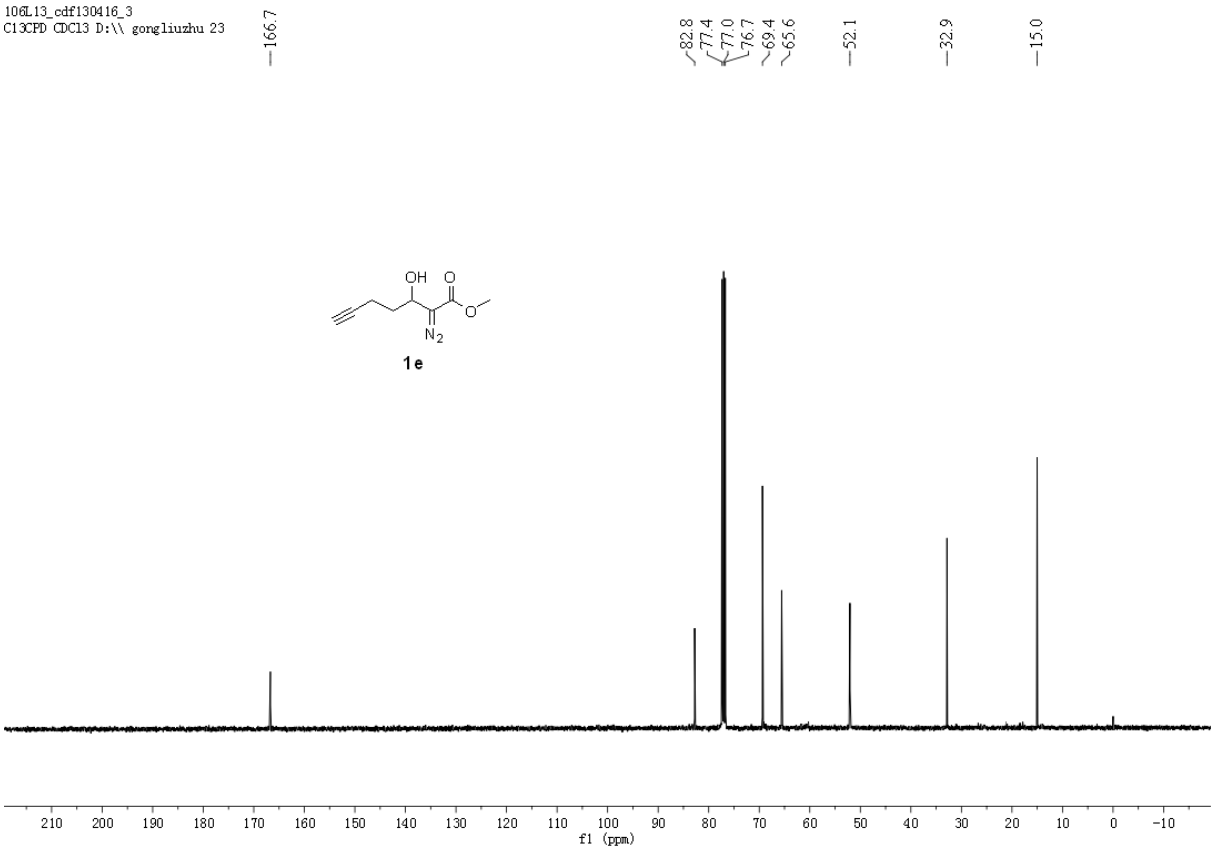


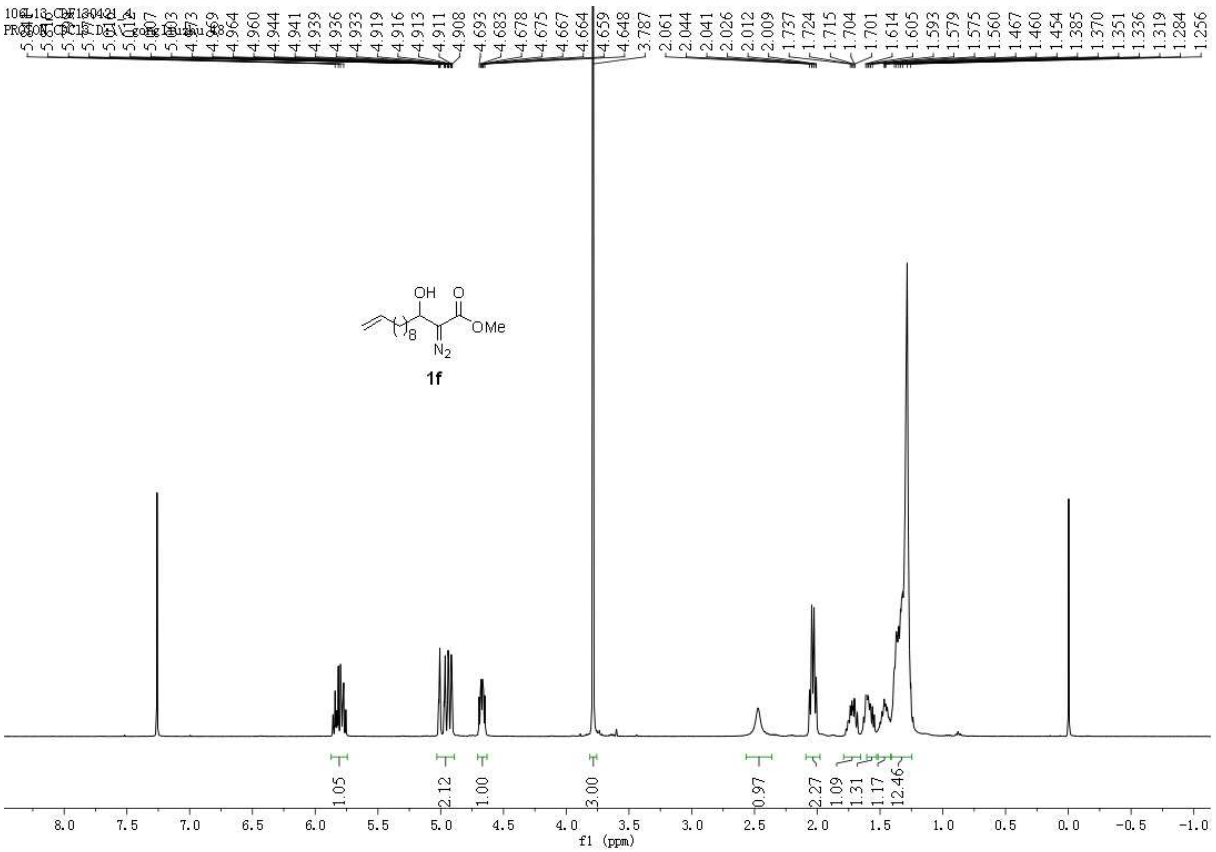


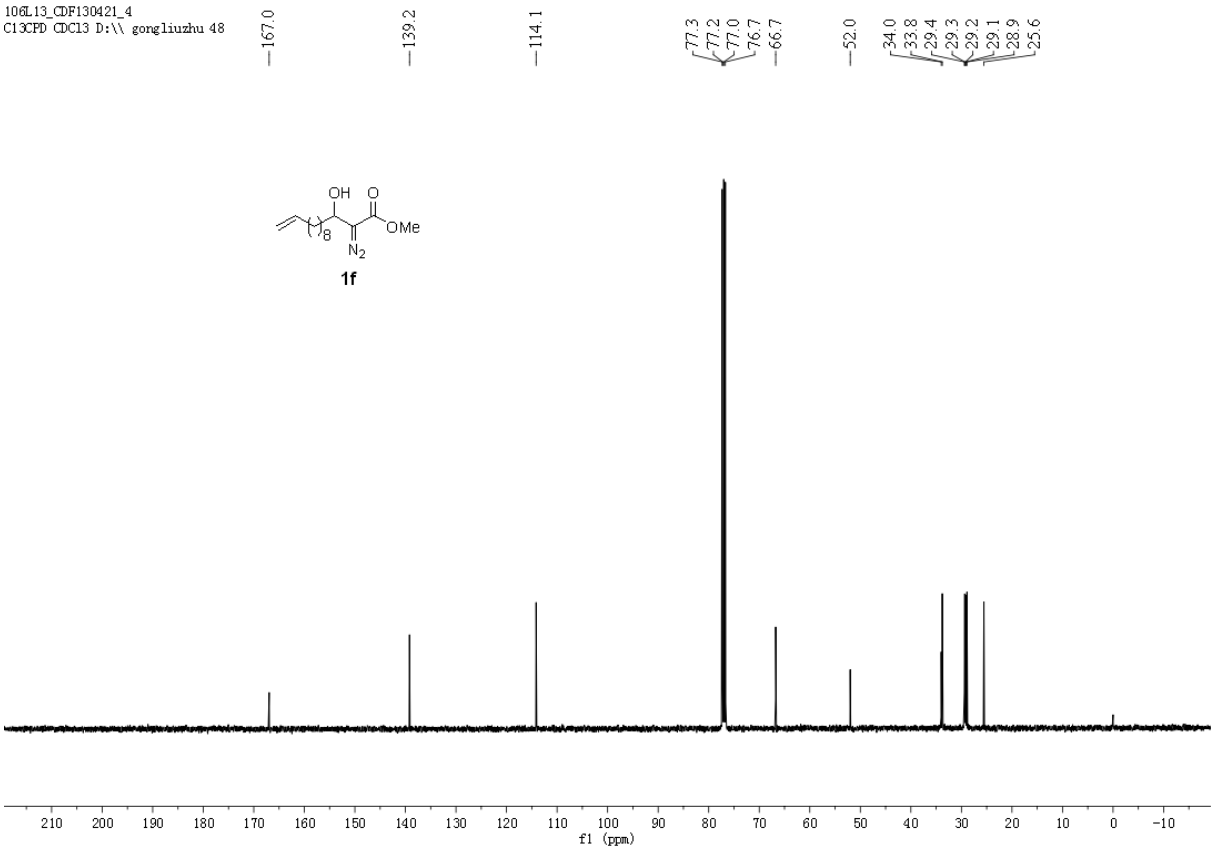

106L13_cdf130416_2
PROTON CDCl3 D:\\ gongliuzhu 42
7.270
7.213
7.204
7.197
7.183
4.684
4.669
4.664
4.649
3.774
2.821
2.807
2.798
2.784
2.745
2.728
2.723
2.706
2.065
2.050
2.044
2.042
2.039
2.030
2.028
2.022
1.959
1.945
1.943
1.936
1.928
1.925
1.922
1.920
1.911
1.909
1.905
OH
O
Ph
O
N2
1d
2.55
3.39
1.00
3.05
1.25
1.69
2.46
0.66
f1 (ppm)

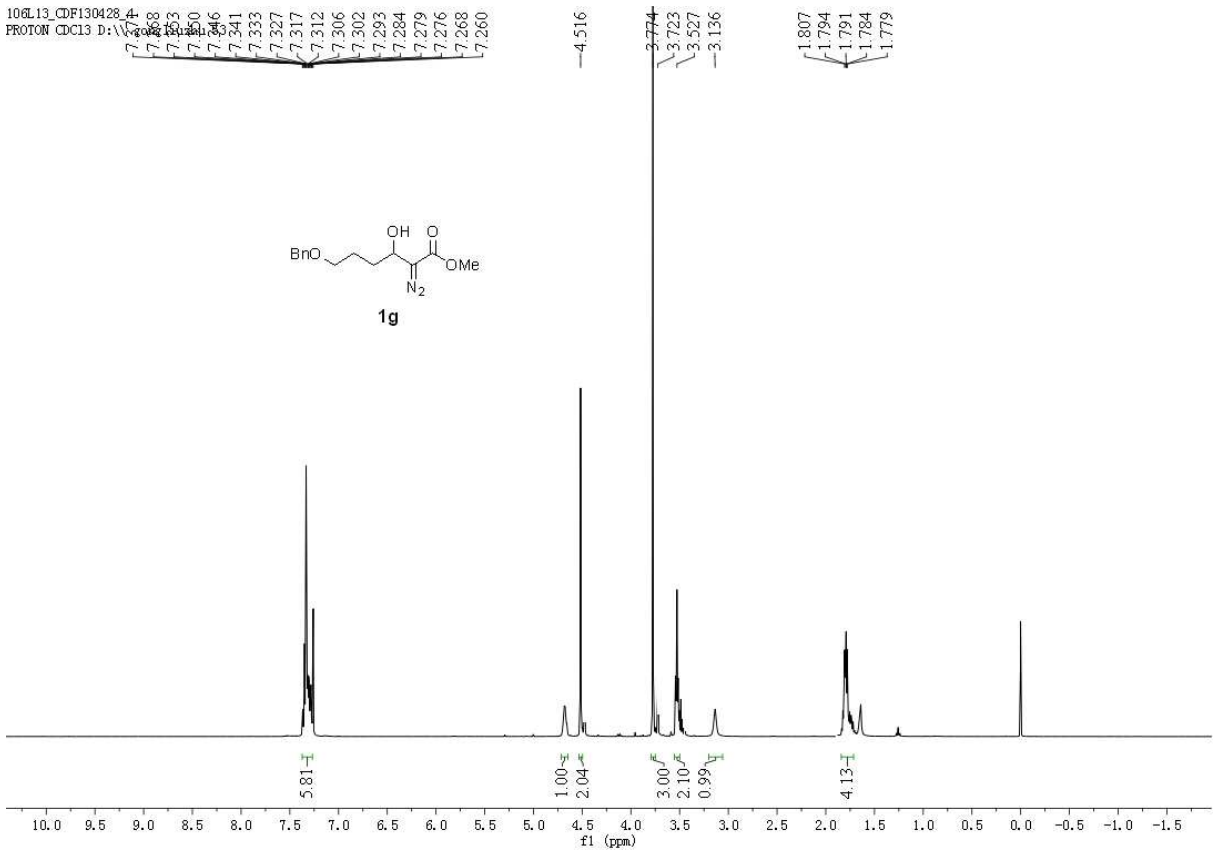

106L13_cdf130416_2
C13CPD CDCl3 D:\\ gongliuzhu 42
169.9
140.9
128.5
128.4
126.2
77.4
77.1
76.7
66.0
52.0
35.7
31.9
OH
O
Ph
O
N2
1d
f1 (ppm)

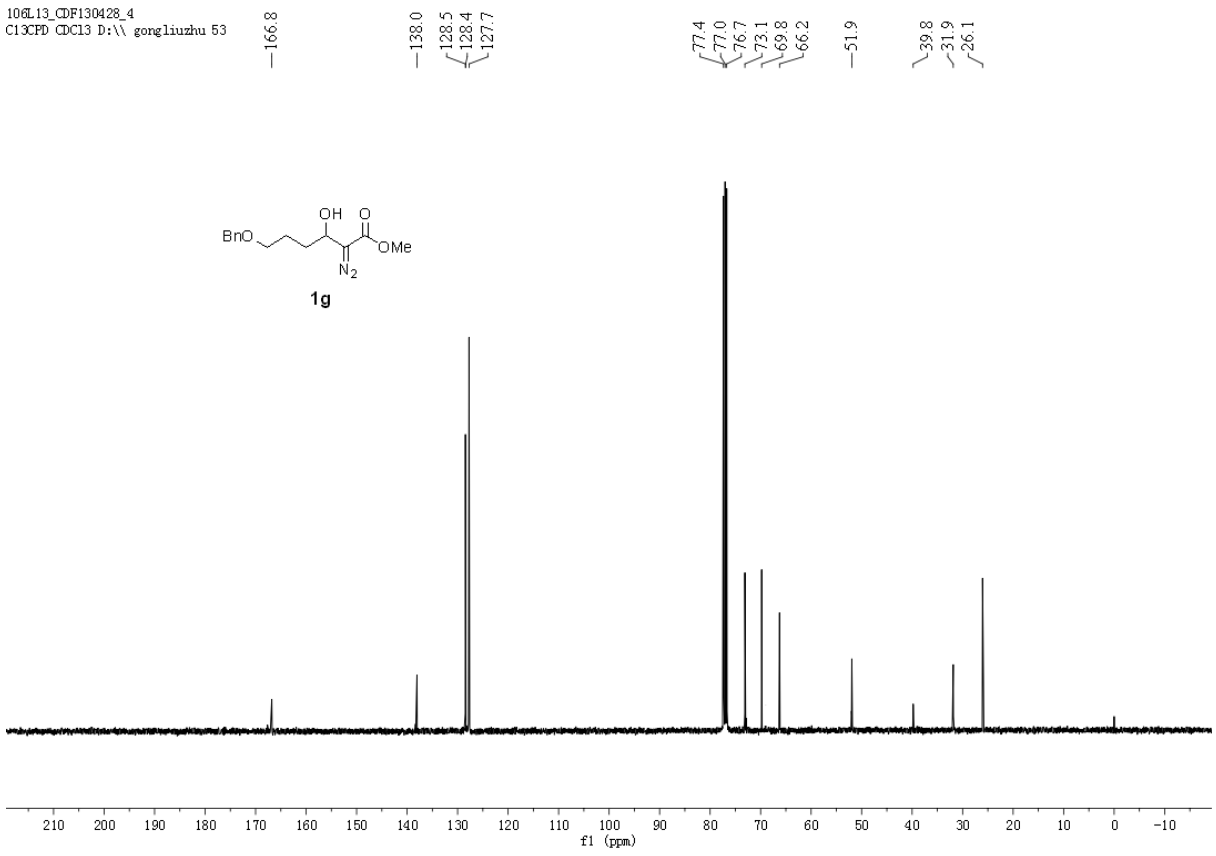

106L13_cdf130416_3
PROTON CDCl3 D:\\ gongliuzhu 23
4.837
4.827
4.817
3.795
2.815
2.388
2.385
2.373
2.044
2.011
2.004
1.998
1.992
1.975
1.958
1.954
1.941
1.936
1.925
1.919
1.903
1.892
1.879
1.873
1.859
1.855
OH
O
O
N2
1e
1.00
3.19
0.96
2.02
1.00
2.30
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

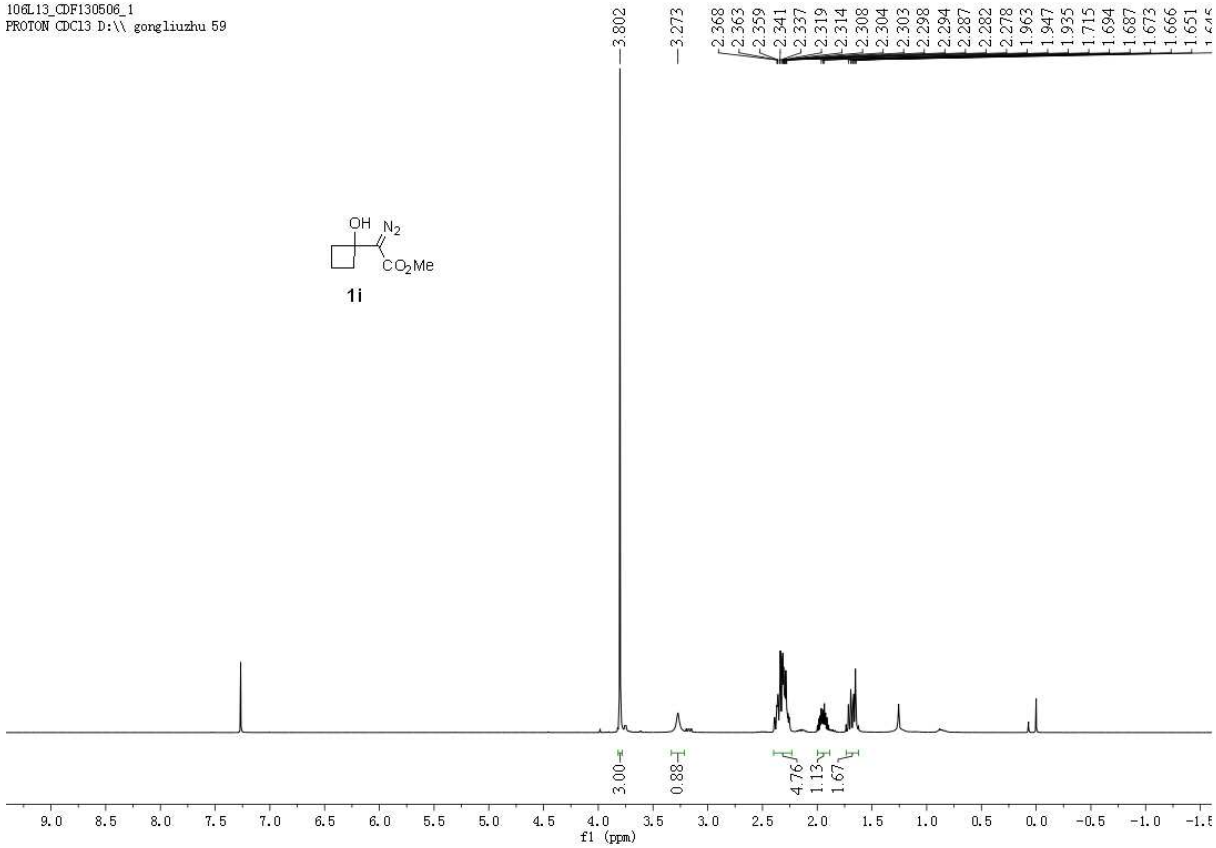

106L13_cdf130416_3
C13CPD CDCl3 D:\\ gongliuzhu 23
166.7
82.8
77.4
77.0
76.7
69.4
65.6
52.1
32.9
15.0
OH
O
O
N2
1e
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

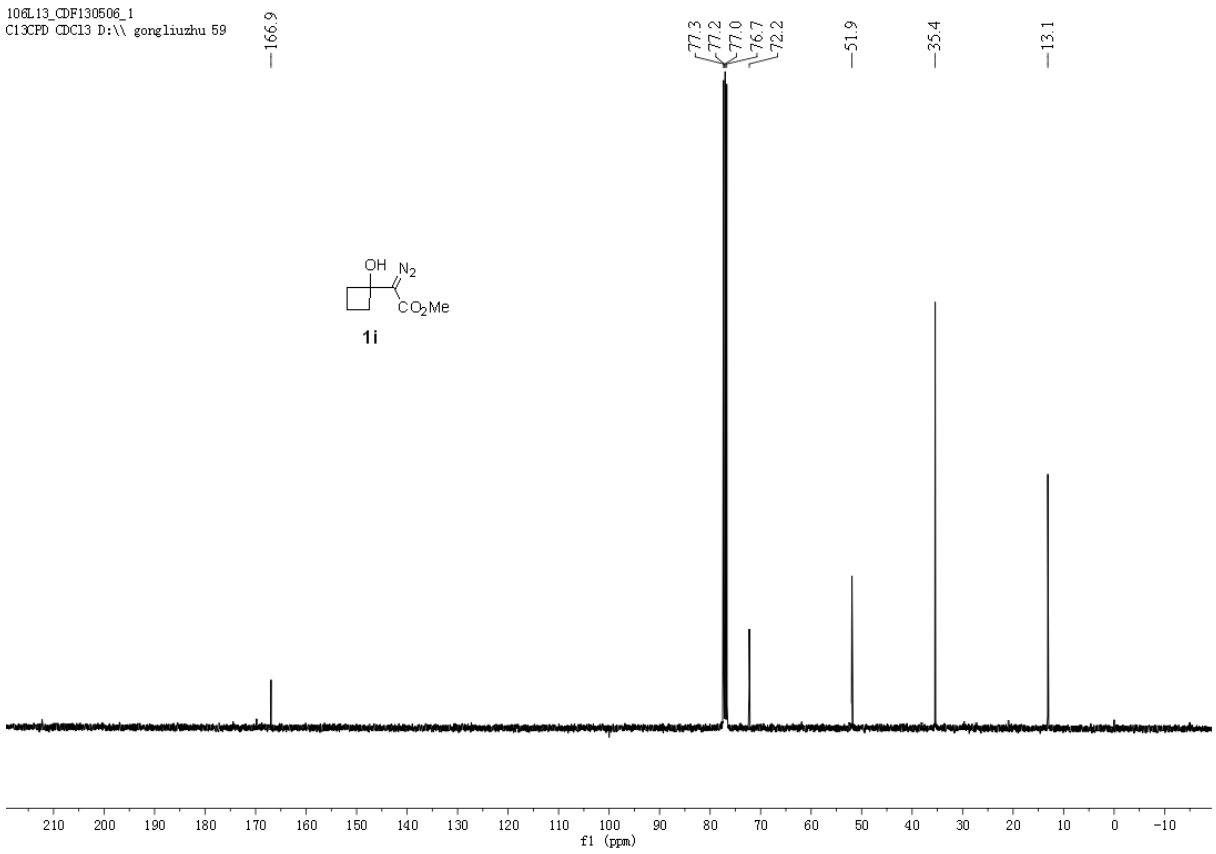

OH
O
OMe
8
N2
1f
1.05
2.12
1.00
3.00
0.97
2.27
1.09
1.31
1.17
12.46
f1 (ppm)

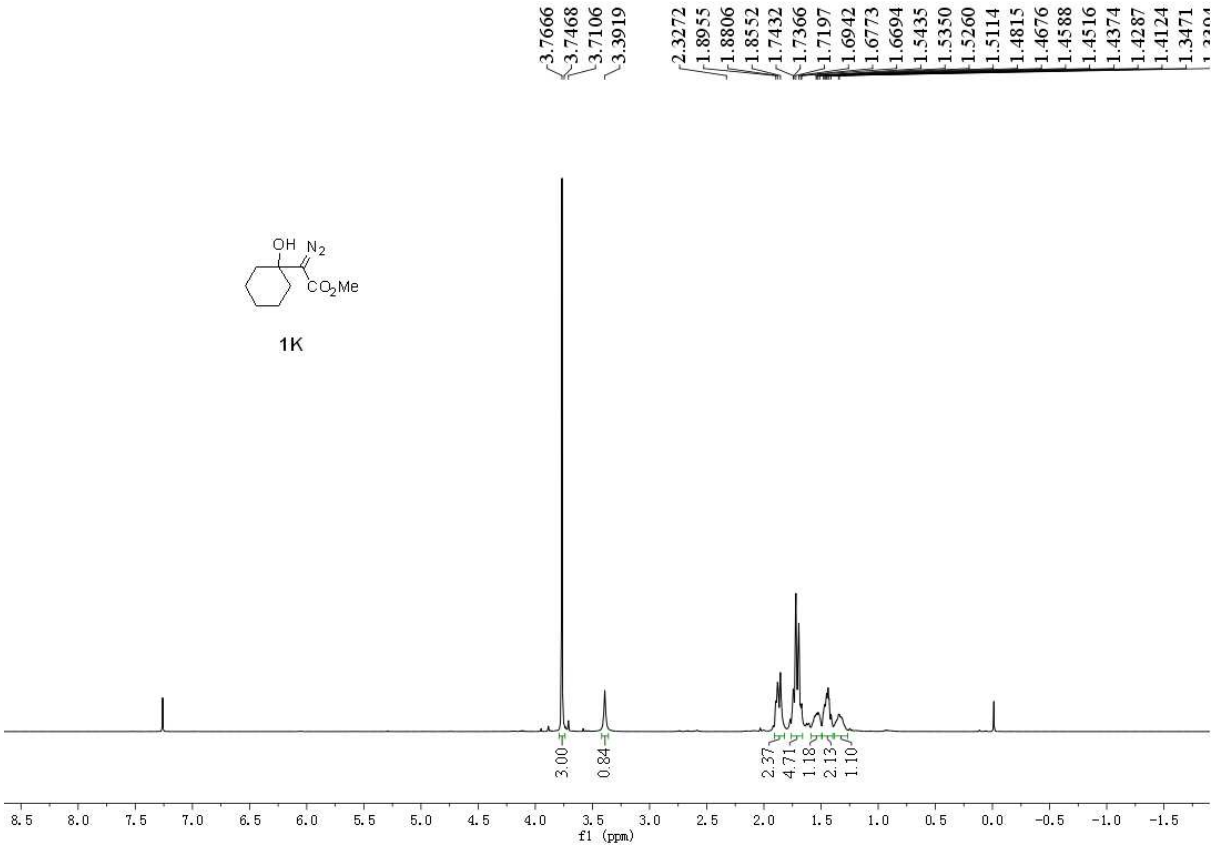

106L13_CDF130421_4
C13CPD CDCl3 D:\\ gongliuzhu 48
167.0
139.2
114.1
77.3
77.2
77.0
76.7
66.7
52.0
34.0
33.8
29.4
29.3
29.2
29.1
28.9
25.6
OH
O
OMe
8
N2
1f
f1 (ppm)

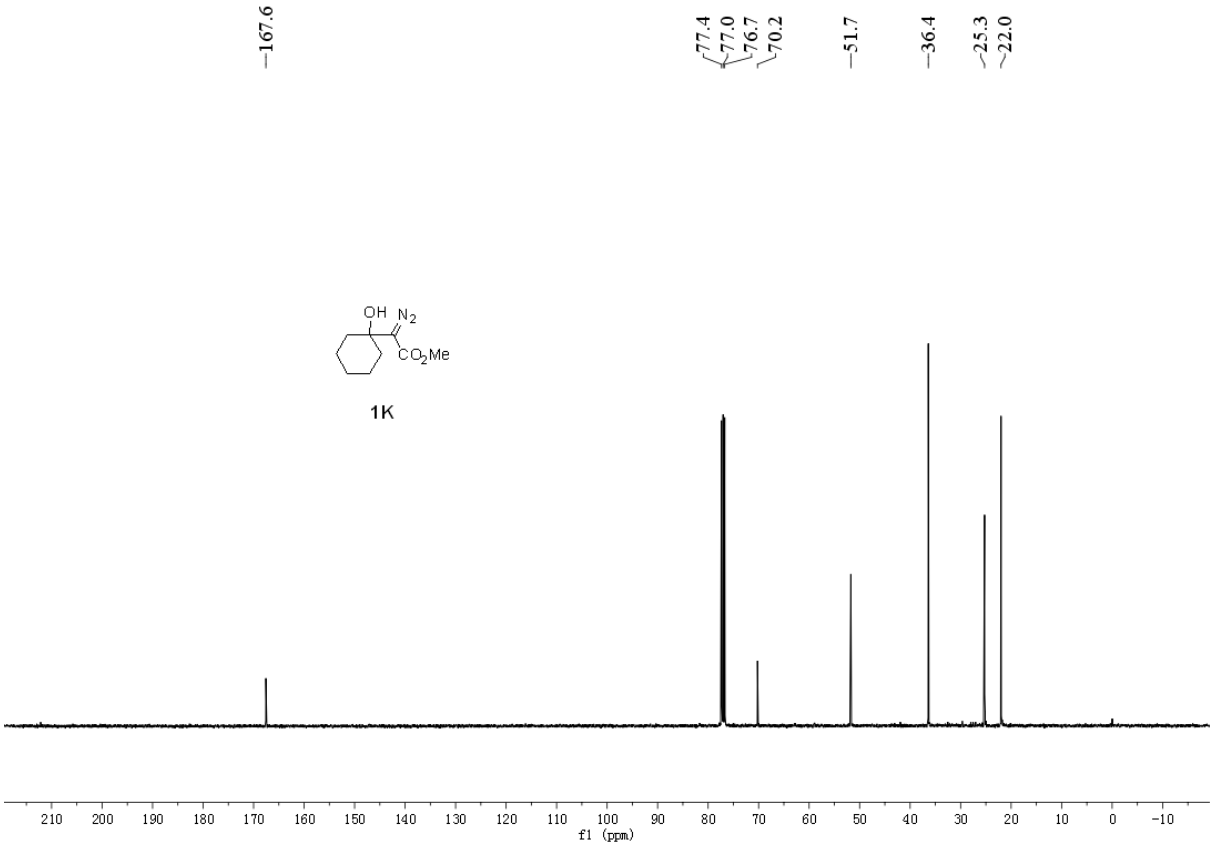

106L13_CDF130428_4
PROTON CDCl3 D:\\ gongliuzhu 53
7.688
7.683
7.680
7.666
7.341
7.333
7.327
7.317
7.312
7.306
7.302
7.293
7.284
7.279
7.276
7.268
7.260
4.516
3.774
3.723
3.527
3.136
1.807
1.794
1.791
1.784
1.779
OH
O
BnO
OMe
N2
1g
5.81
1.00
2.04
3.00
2.10
0.99
4.13
f1 (ppm)

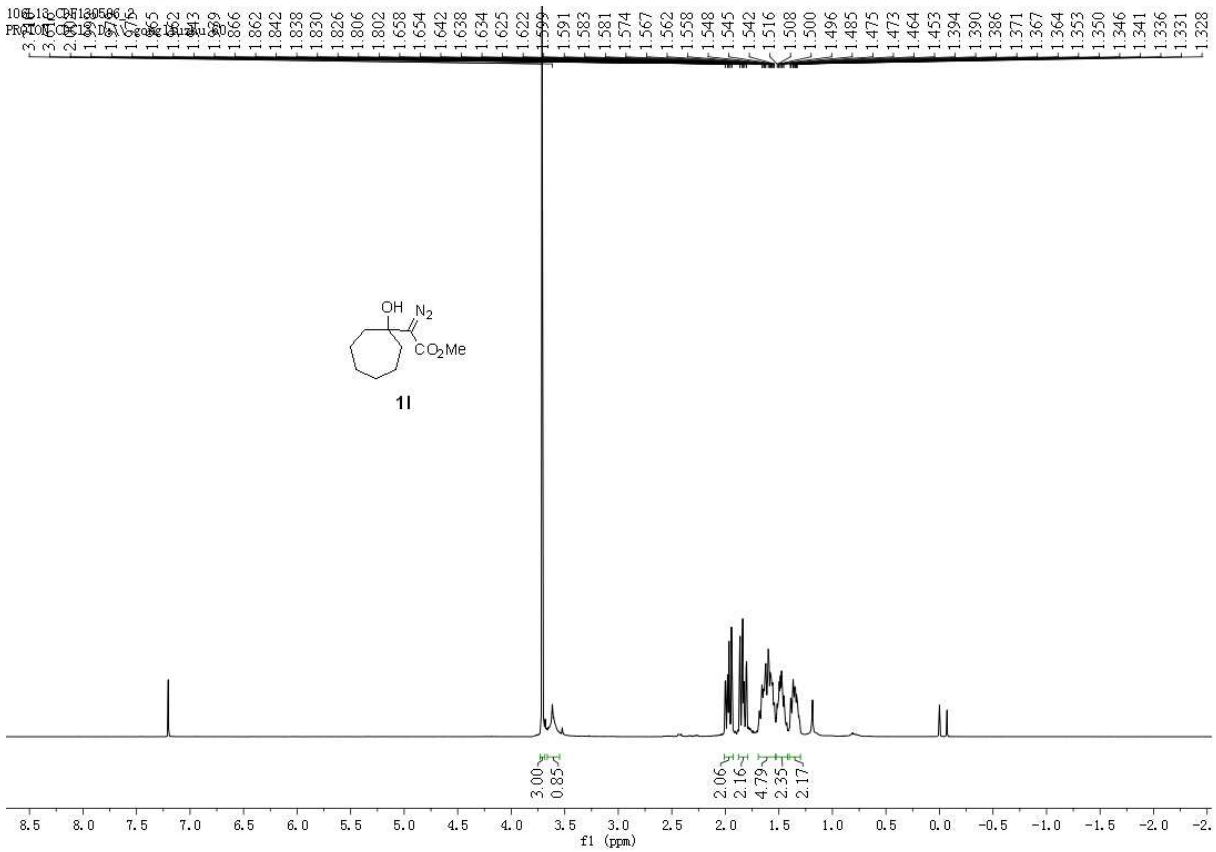

106L13_CDF130428_4
C13CPD CDCl3 D:\\ gongliuzhu 53
166.8
138.0
128.5
128.4
127.7
77.4
77.0
76.7
73.1
69.8
66.2
51.9
39.8
31.9
26.1
OH
O
BnO
OMe
N2
1g
f1 (ppm)

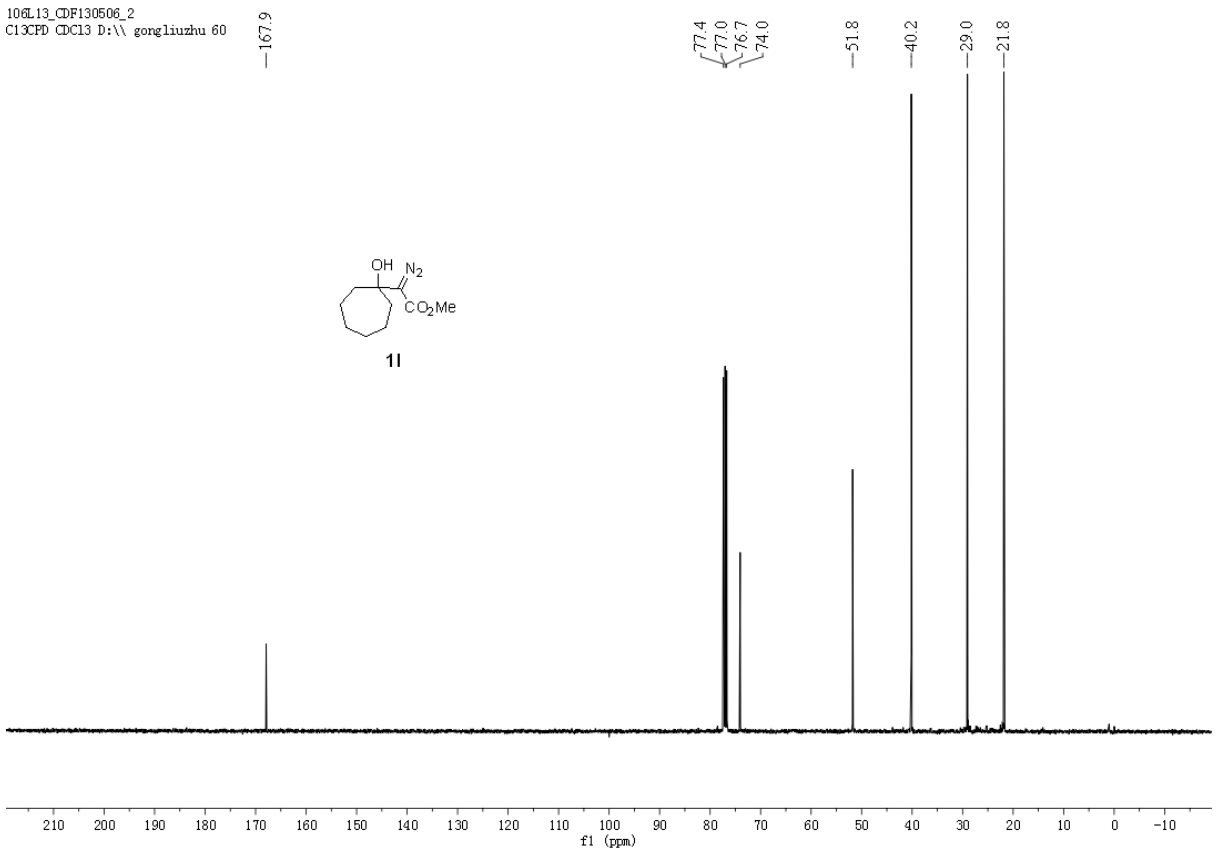

106L13_CDF130506_1
PROTON CDCl3 D:\\ gongliuzhu 59
3.802
3.273
2.368
2.363
2.359
2.341
2.337
2.319
2.314
2.308
2.304
2.303
2.298
2.294
2.287
2.282
2.278
1.963
1.947
1.935
1.715
1.694
1.687
1.673
1.666
1.651
OH
N2
CO2Me
1i
3.00
0.88
4.76
1.13
1.67
f1 (ppm)

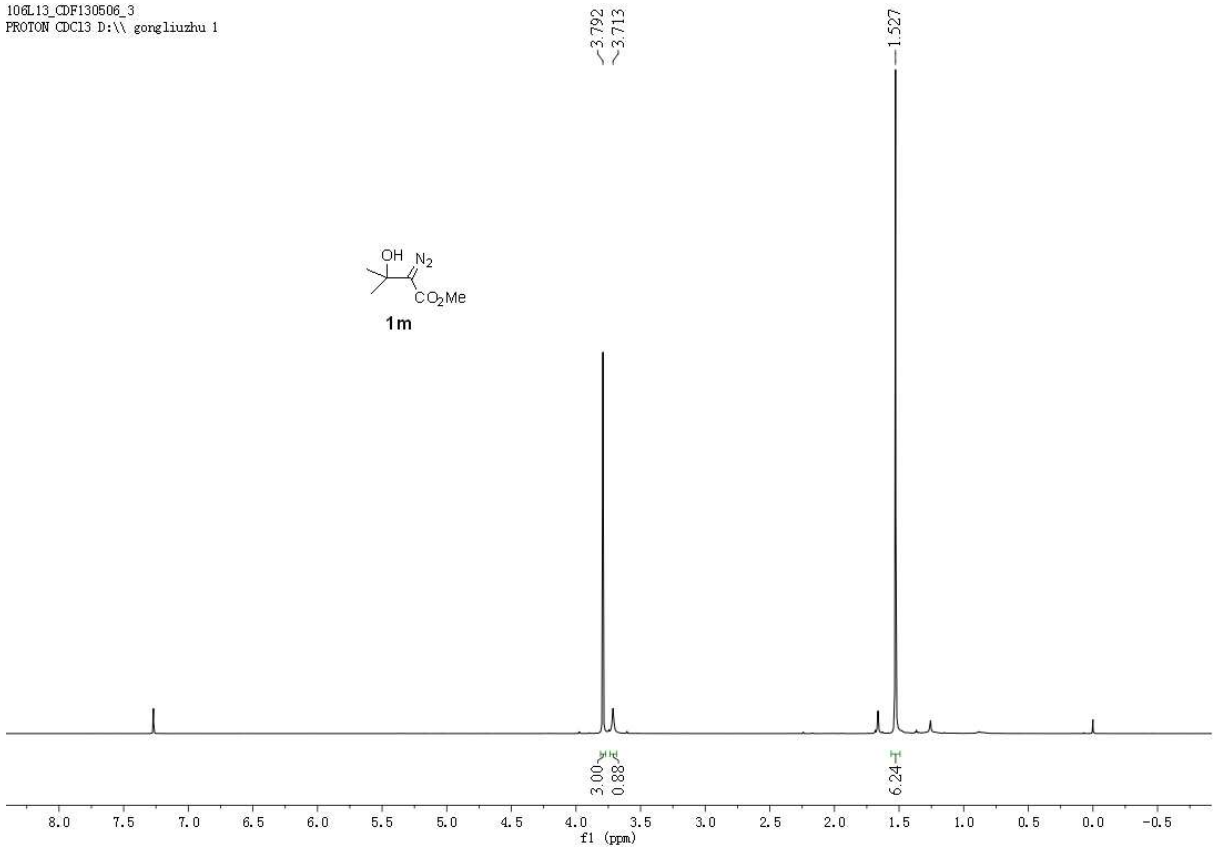

106L13_CDF130506_1
C13CPD CDCl3 D:\\ gongliuzhu 59
166.9
77.3
77.2
77.0
76.7
72.2
51.9
35.4
13.1
OH
N2
CO2Me
1i
f1 (ppm)

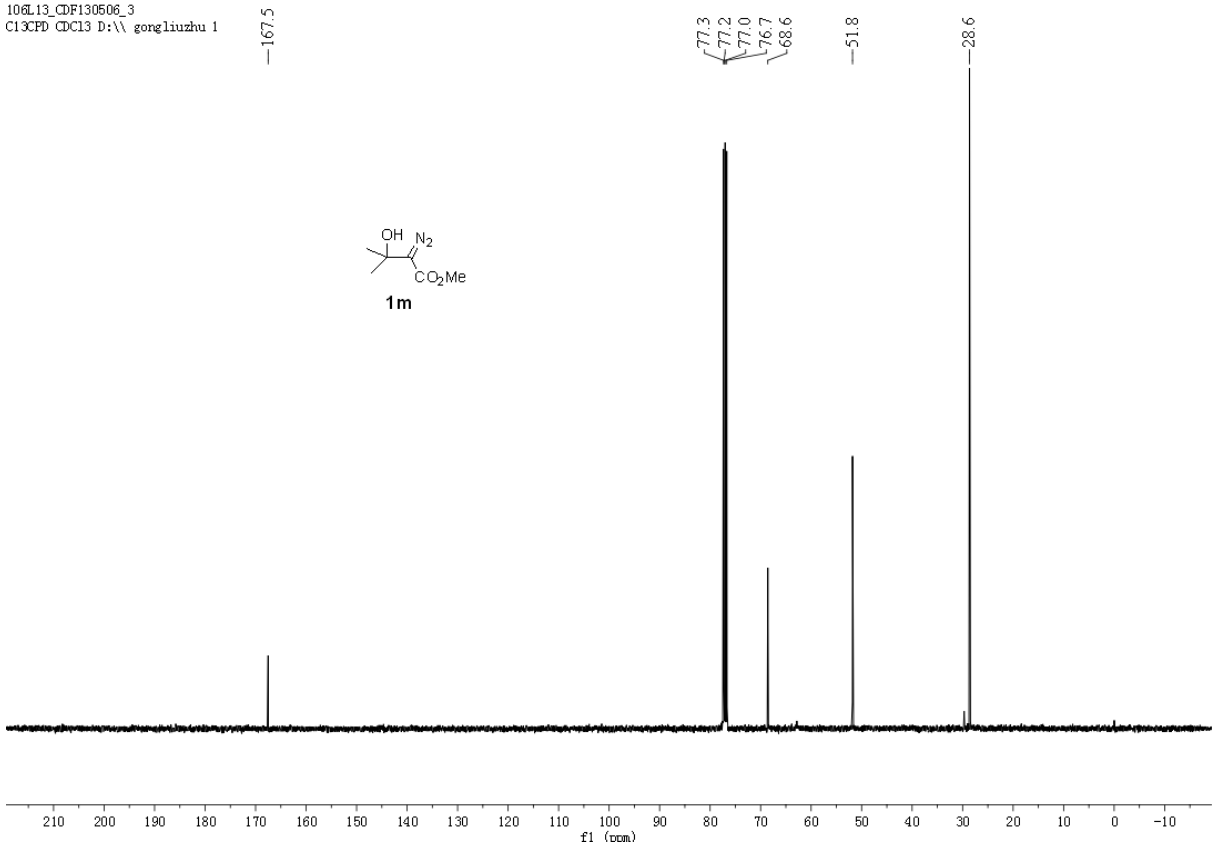

3.7666
3.7468
3.7106
3.3919
2.3272
1.8955
1.8806
1.8552
1.7432
1.7366
1.7197
1.6942
1.6773
1.6694
1.5435
1.5350
1.5260
1.5114
1.4815
1.4676
1.4588
1.4516
1.4374
1.4287
1.4124
1.3471
OH N2
CO2Me
1K
3.00
0.84
2.37
4.71
1.18
2.13
1.10
f1 (ppm)

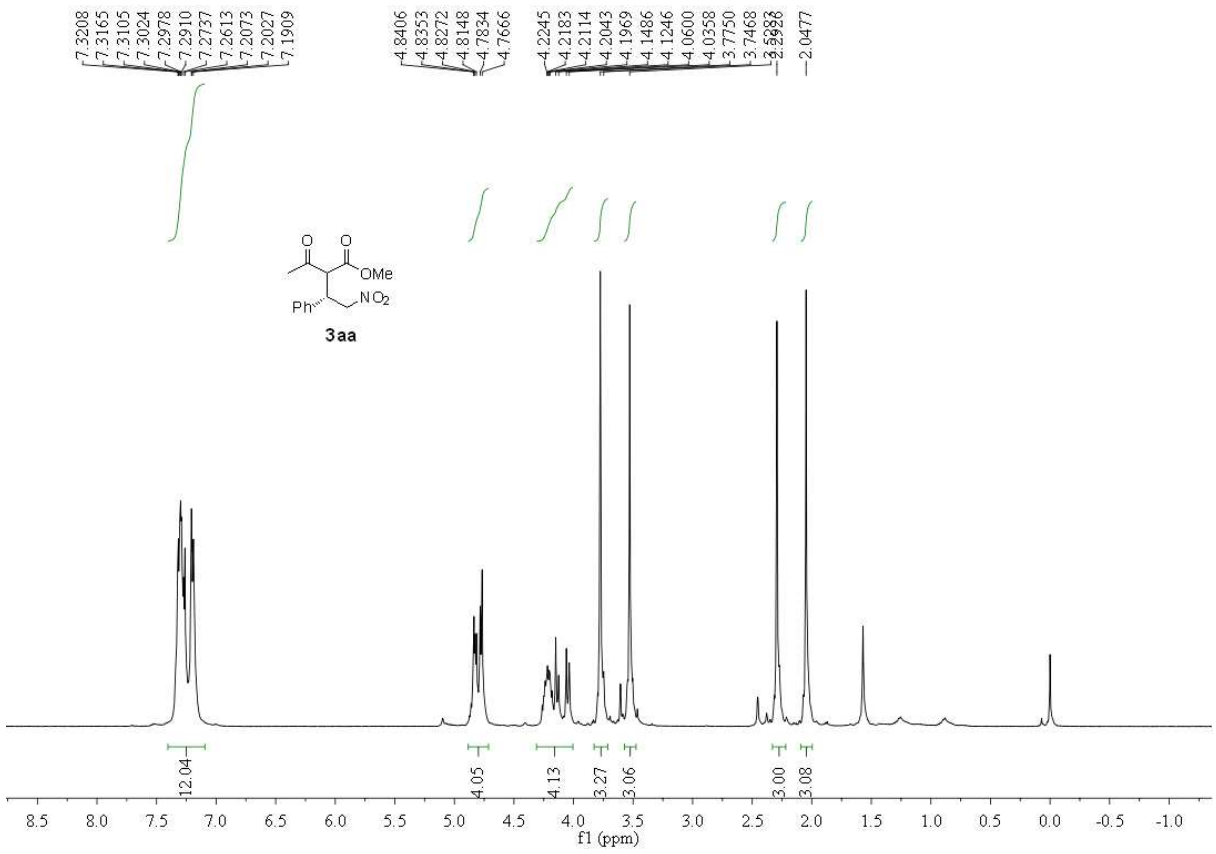

167.6
77.4
77.0
76.7
70.2
51.7
36.4
25.3
22.0
OH N2
CO2Me
1K
f1 (ppm)

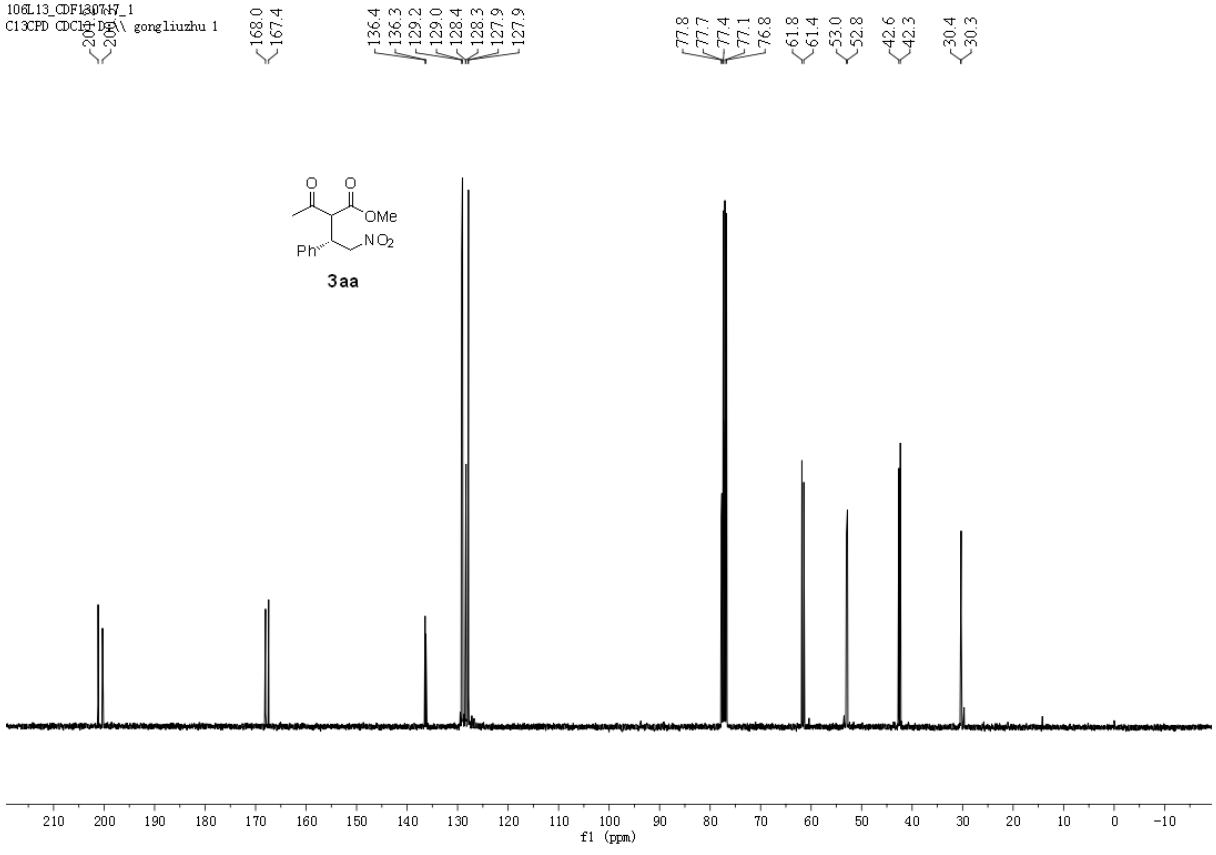

OH
N2
CO2Me
1l
3.00
0.85
2.06
2.16
4.79
2.35
2.17
f1 (ppm)

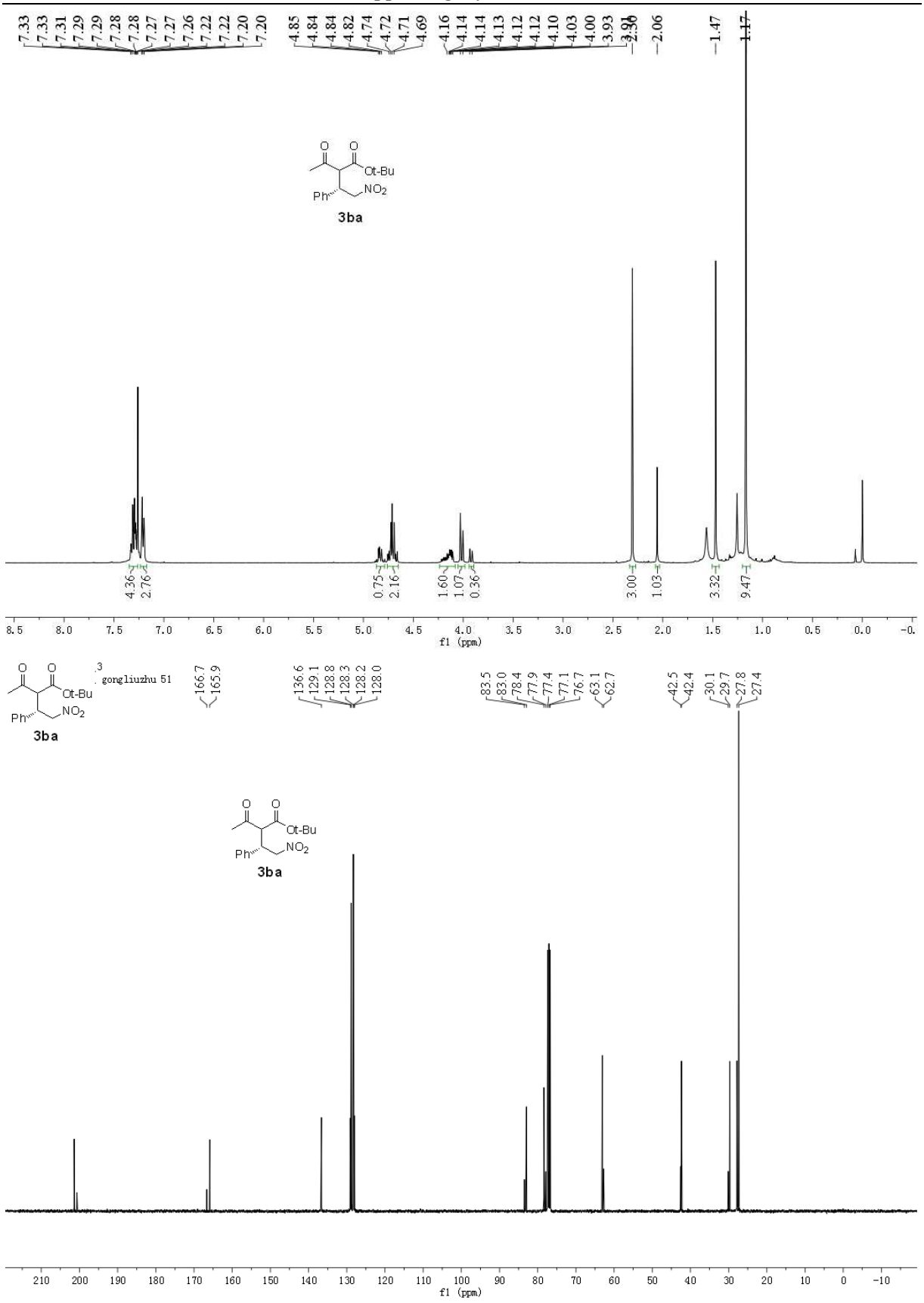

106L13_CDF130506_2
C13CPD CDCl3 D:\\ gongliuzhu 60
167.9
77.4
77.0
76.7
74.0
51.8
40.2
29.0
21.8
OH
N2
CO2Me
1l
f1 (ppm)

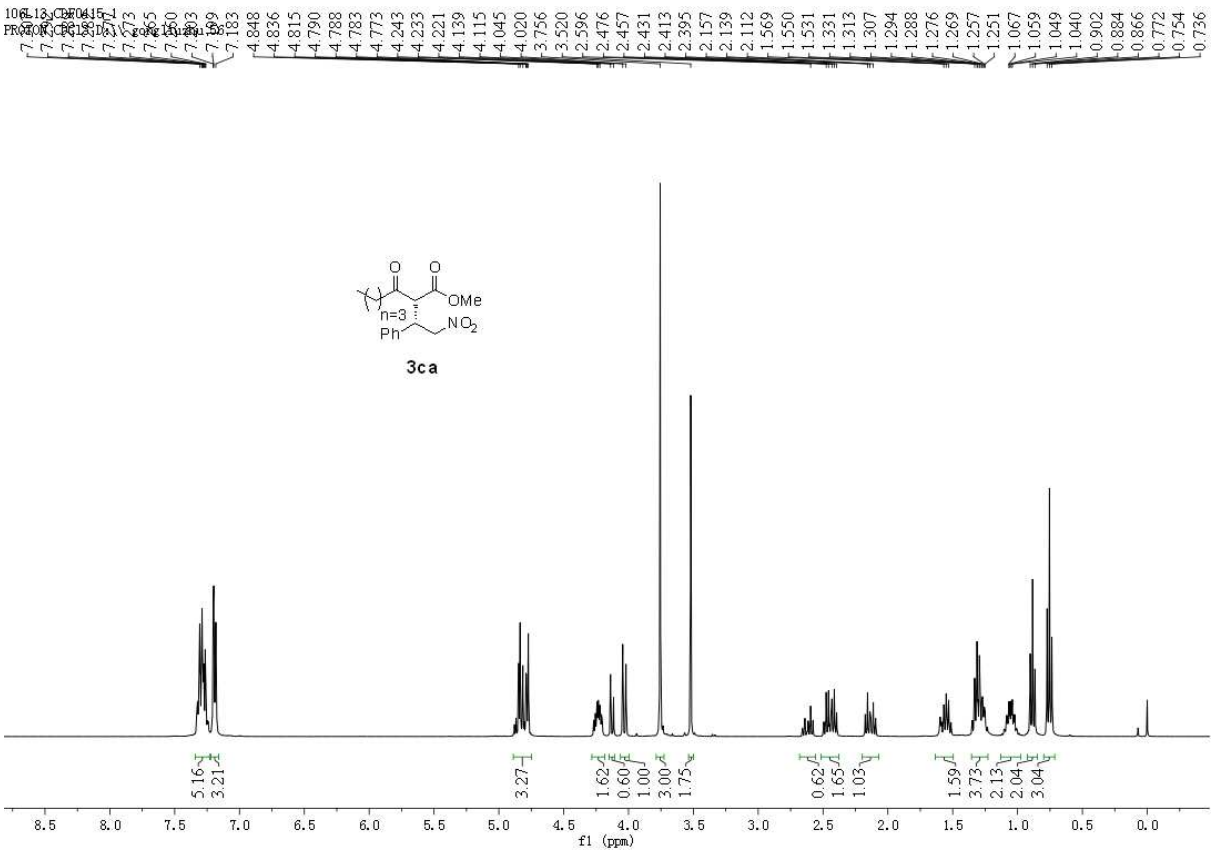

106L13_CDF130506_3
PROTON CDCl3 D:\\ gongliuzhu 1
3.792
3.713
1.527
OH
N2
CO2Me
1m
3.00
0.88
6.24
f1 (ppm)

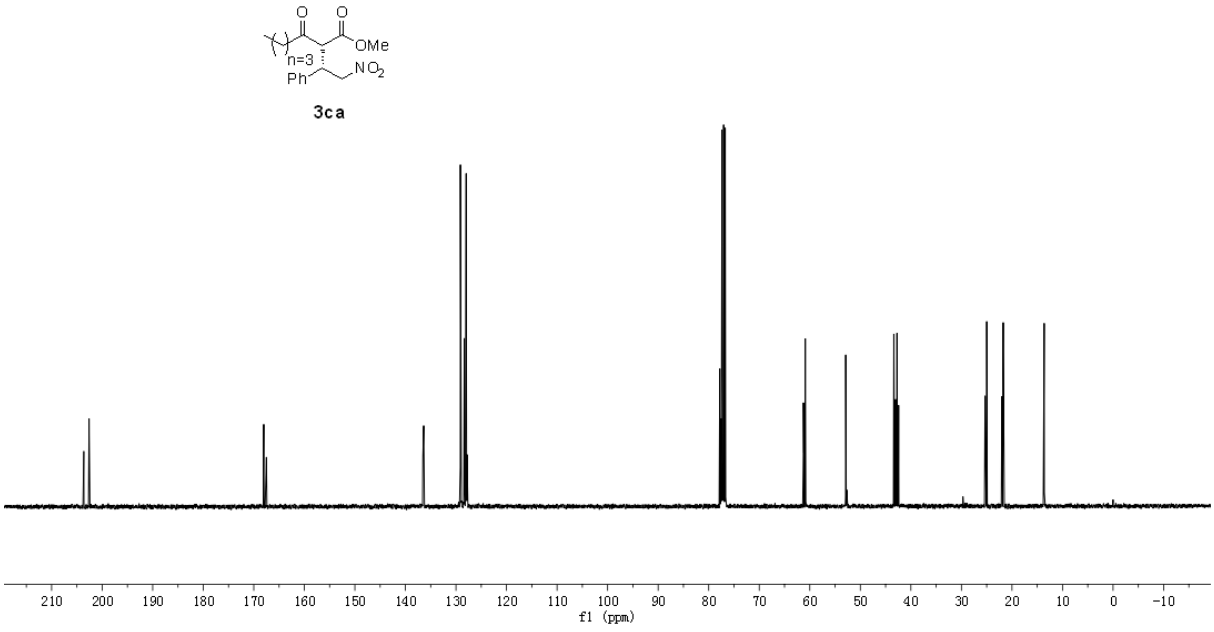

106L13_CDF130506_3
C13CPD CDCl3 D:\\ gongliuzhu 1
167.5
77.3
77.2
77.0
76.7
68.6
51.8
28.6
OH
N2
CO2Me
1m
f1 (ppm)

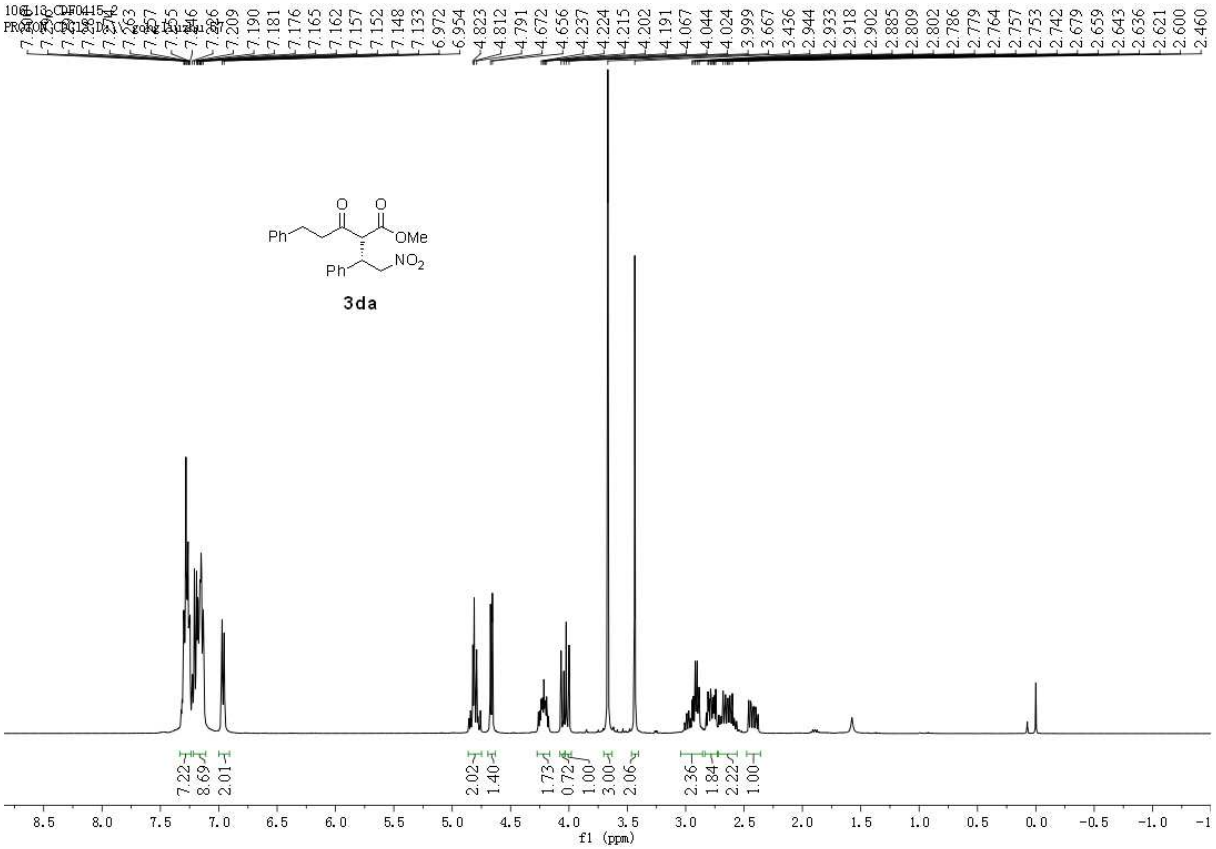

7.3208
7.3165
7.3105
7.3024
7.2978
7.2910
7.2737
7.2613
7.2073
7.2027
7.1909
4.8406
4.8353
4.8272
4.8148
4.7834
4.7666
4.2245
4.2183
4.2114
4.2043
4.1969
4.1486
4.1246
4.0600
4.0358
3.7750
3.7468
2.5683
2.2928
2.0477
OMe
NO2
Ph
3aa
12.04
4.05
4.13
3.27
3.06
3.00
3.08
f1 (ppm)

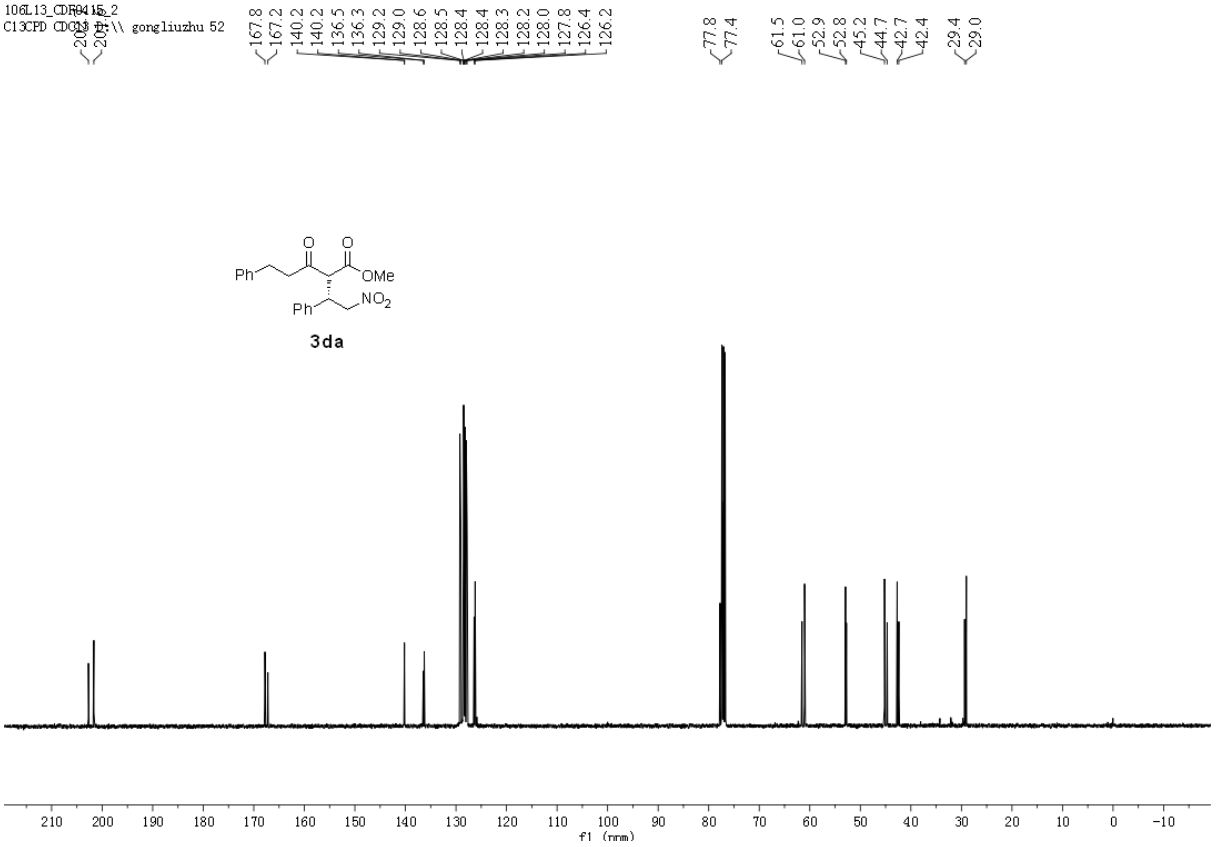

168.0
167.4
136.4
136.3
129.2
129.0
128.4
128.3
127.9
127.9
77.8
77.7
77.4
77.1
76.8
61.8
61.4
53.0
52.8
42.6
42.3
30.4
30.3
OMe
NO2
Ph
3aa
f1 (ppm)

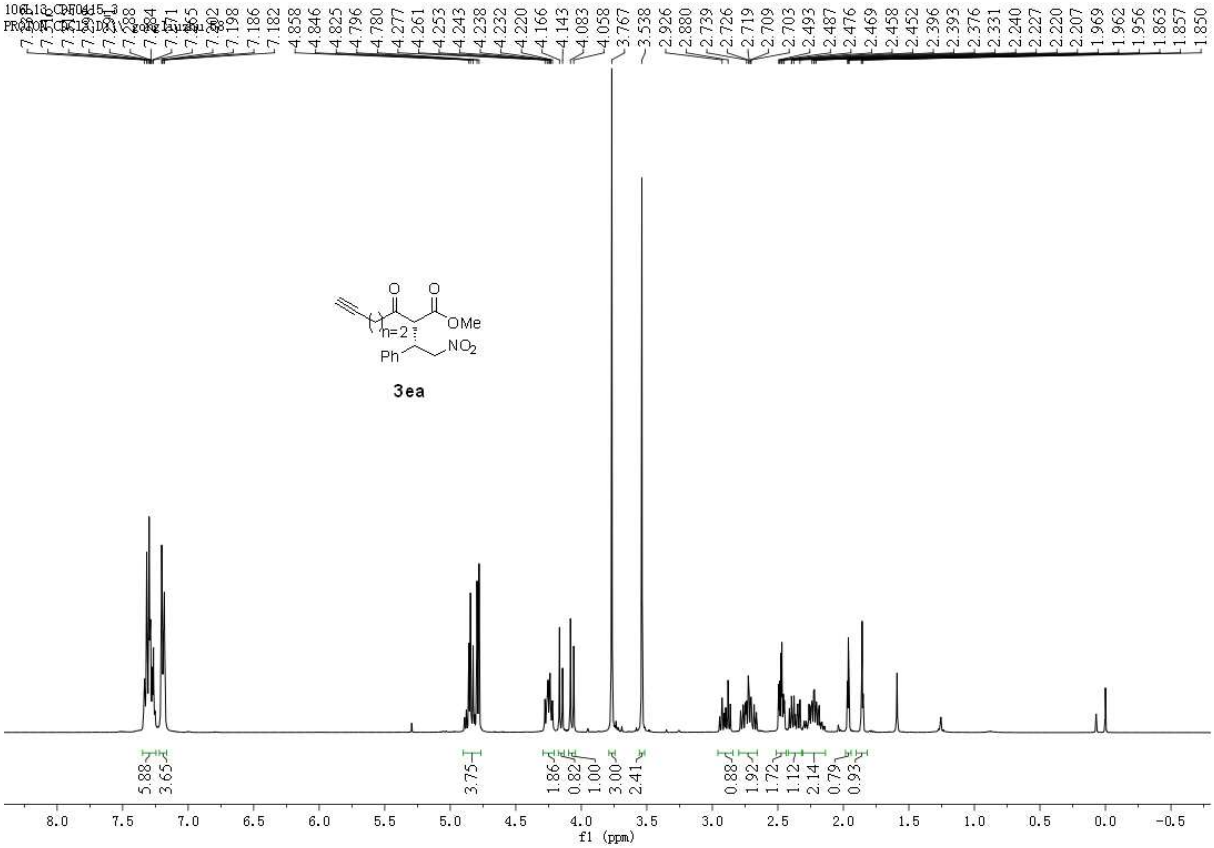

7.33
7.33
7.31
7.29
7.29
7.28
7.28
7.27
7.27
7.26
7.22
7.22
7.20
7.20
4.85
4.84
4.84
4.82
4.74
4.72
4.71
4.69
4.16
4.14
4.14
4.13
4.12
4.12
4.10
4.03
4.00
3.93
2.06
1.47
1.17
Ot-Bu
NO2
Ph
3ba
4.36
2.76
0.75
2.16
1.60
1.07
0.36
3.00
1.03
3.32
9.47
f1 (ppm)
gongliuzhu 51
166.7
165.9
136.6
129.1
128.8
128.3
128.2
128.0
83.5
83.0
78.4
77.9
77.4
77.1
76.7
63.1
62.7
42.5
42.4
30.1
29.7
27.8
27.4
f1 (ppm)

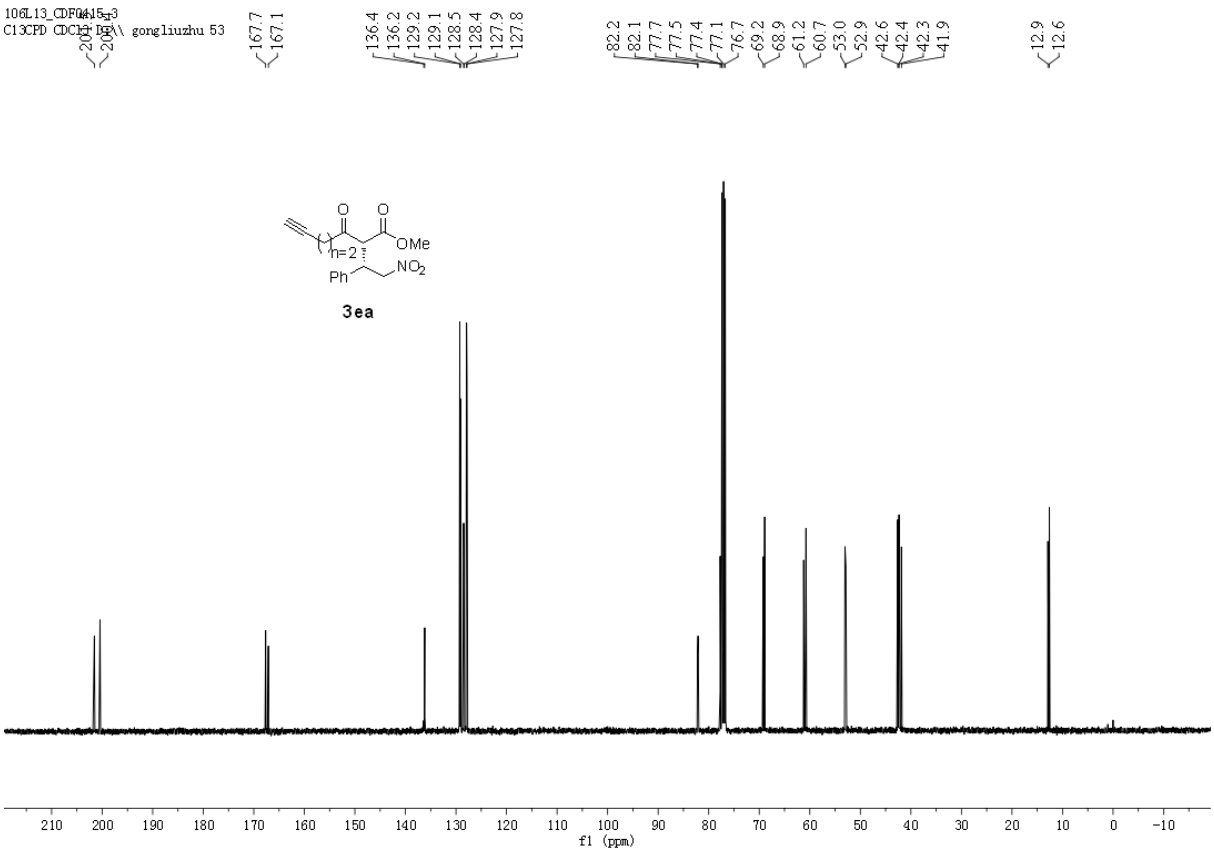

3ca
f1 (ppm)

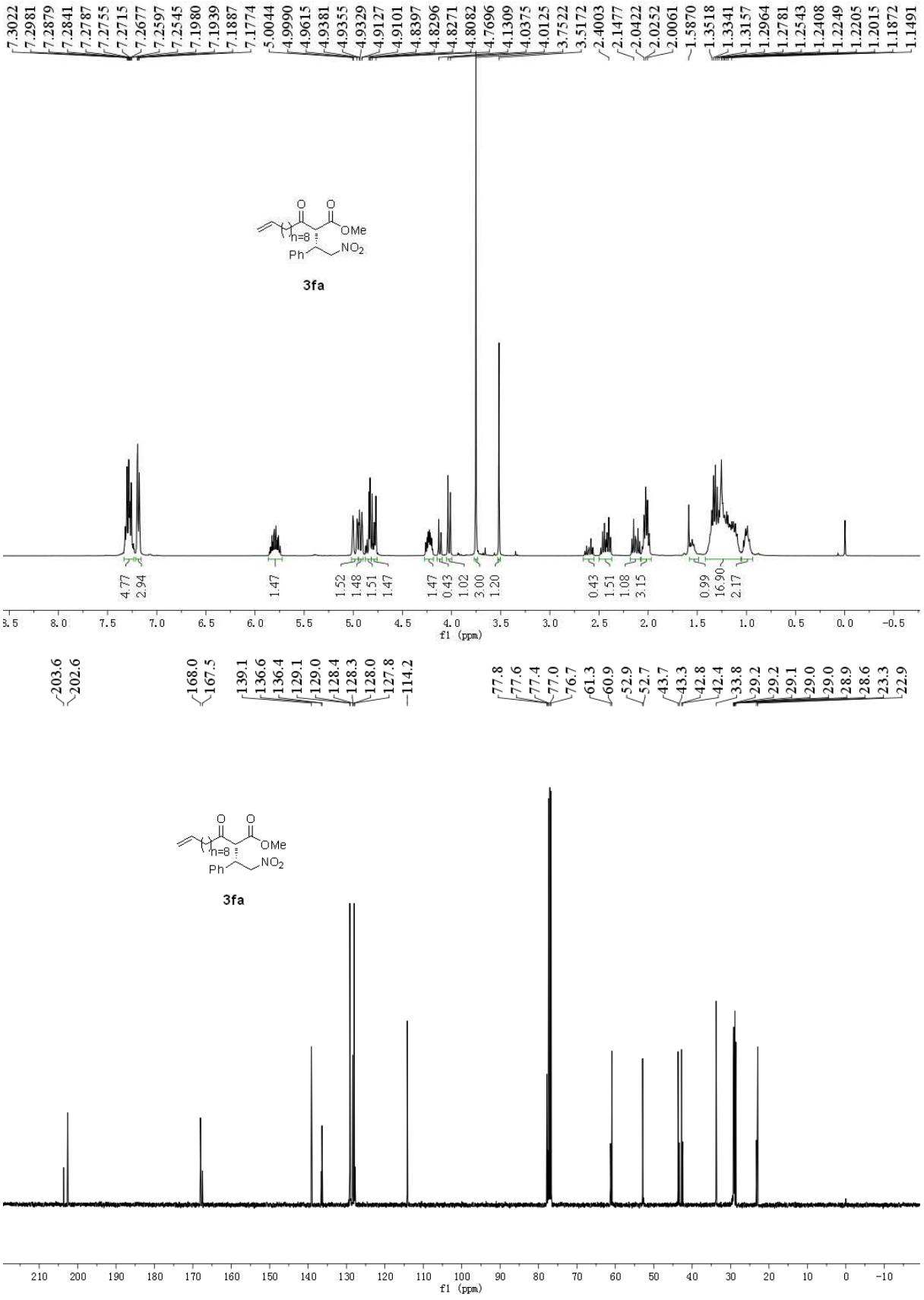

3ca
f1 (ppm)

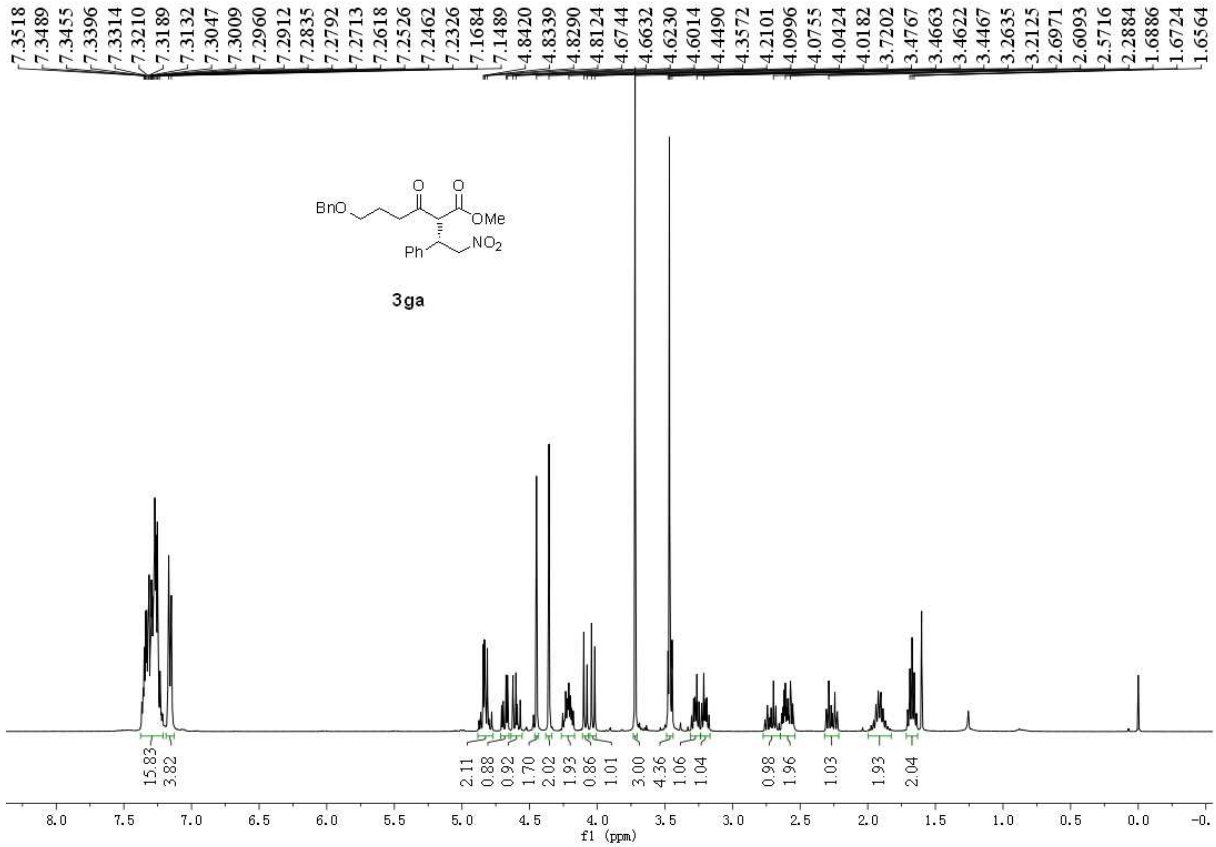

3da
f1 (ppm)

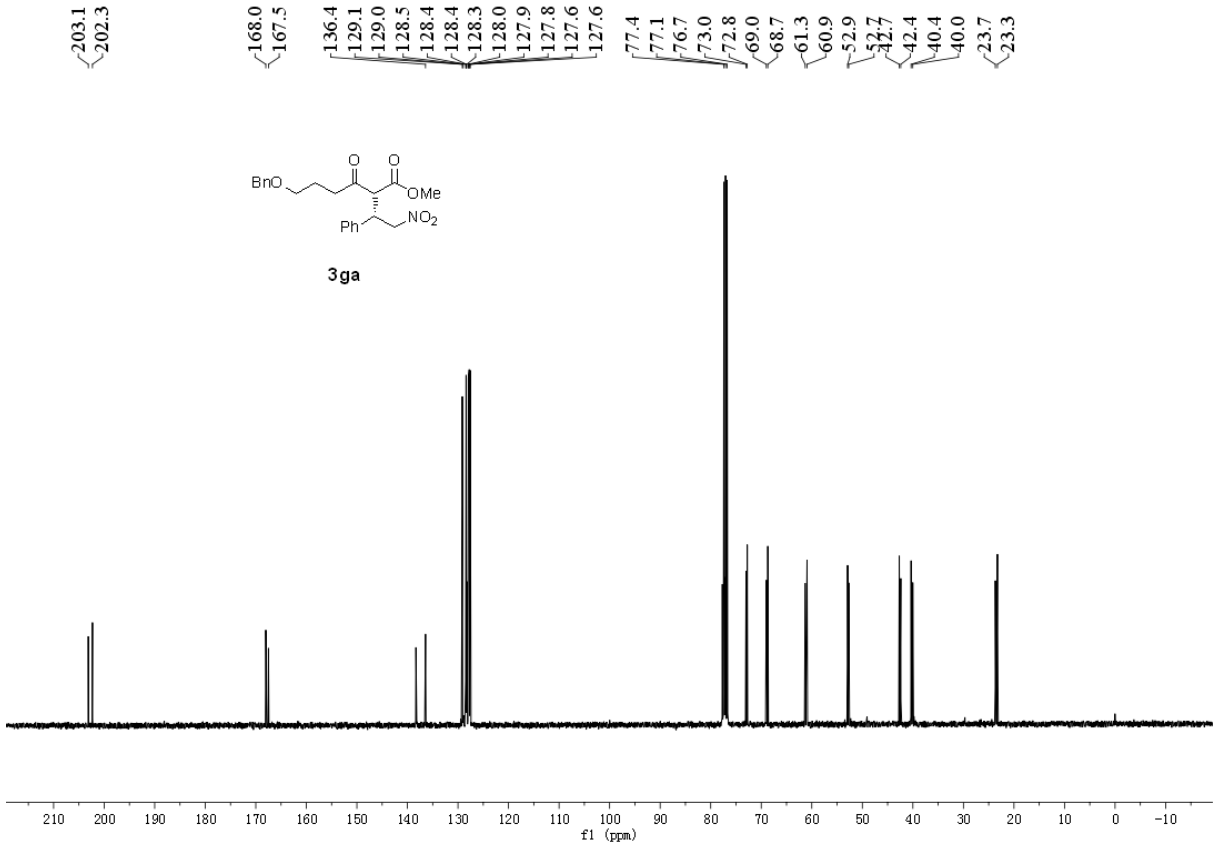

3da
f1 (ppm)

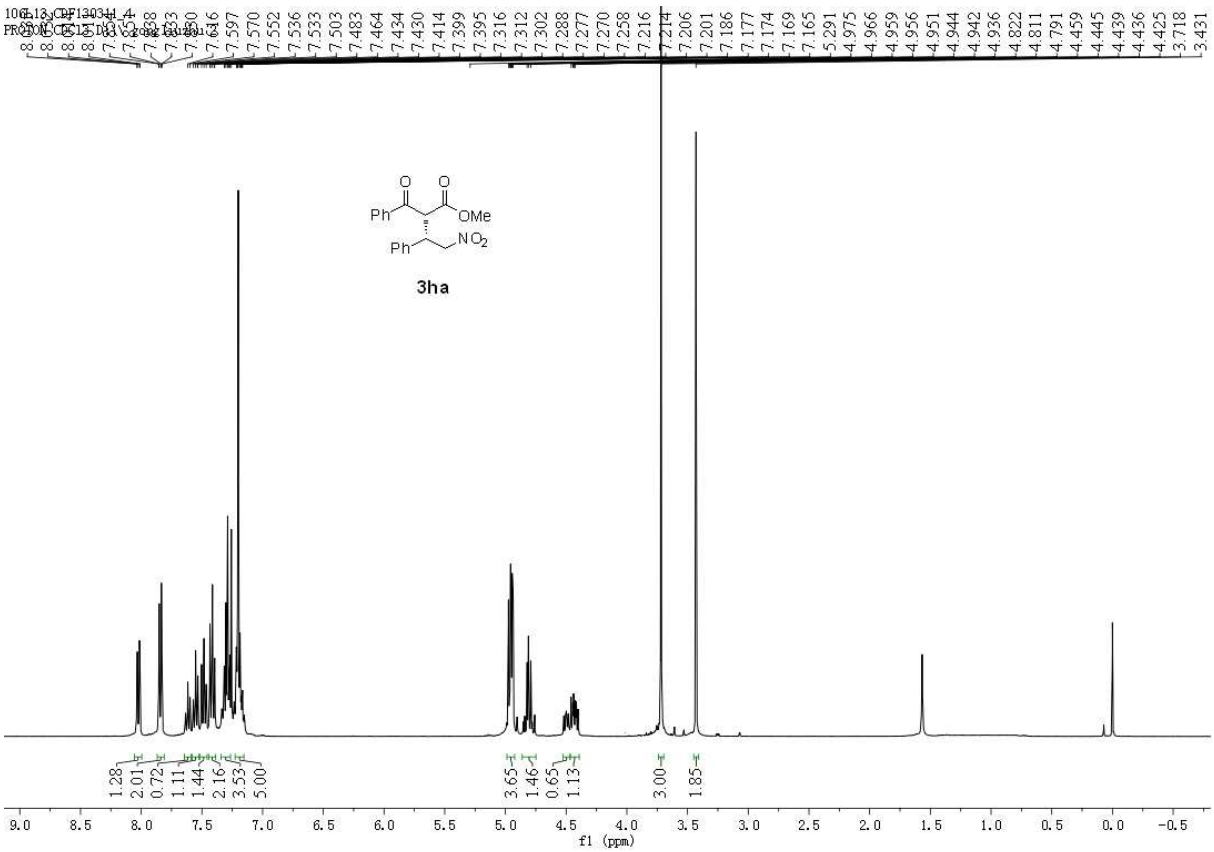

3ea
f1 (ppm)

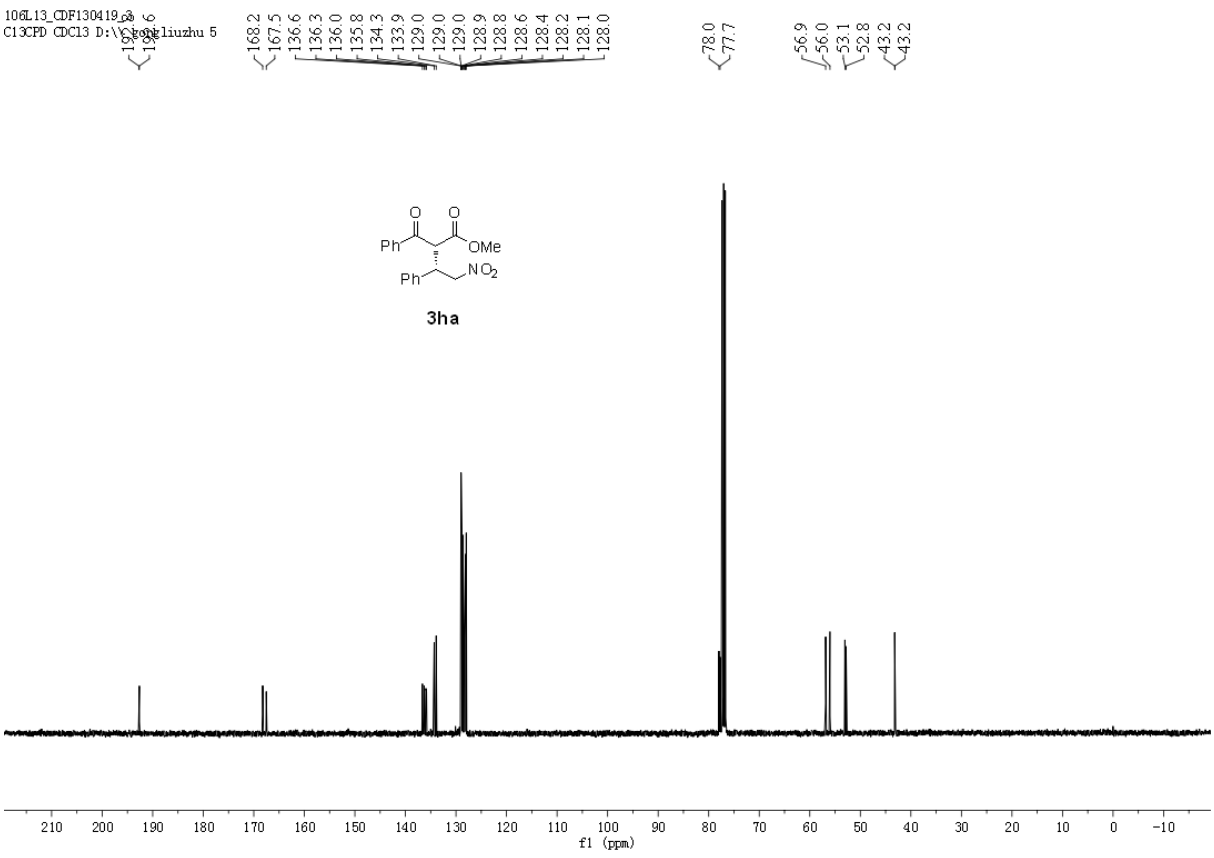

3ea
f1 (ppm)

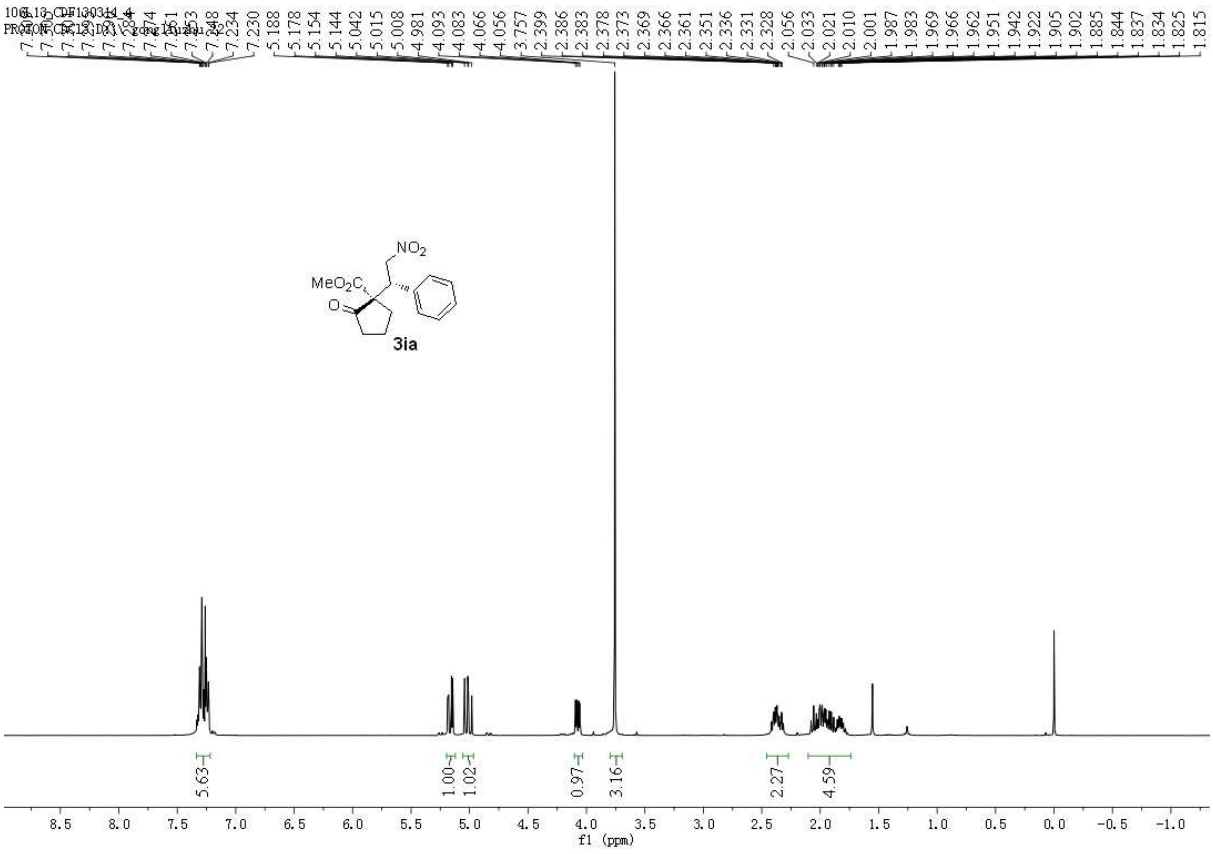

7.3022
7.2981
7.2879
7.2841
7.2787
7.2755
7.2715
7.2677
7.2597
7.2545
7.1980
7.1939
7.1887
7.1774
5.0044
4.9990
4.9615
4.9381
4.9355
4.9329
4.9127
4.9101
4.8397
4.8296
4.8271
4.8082
4.7696
4.1309
4.0375
4.0125
3.7522
3.5172
2.4003
2.1477
2.0422
2.0252
2.0061
1.5870
1.3518
1.3341
1.3157
1.2964
1.2781
1.2543
1.2408
1.2249
1.2205
1.2015
1.1872
1.1491
n=8
OMe
NO2
Ph
3fa
4.77
2.94
1.47
1.52
1.48
1.51
1.47
1.47
0.43
1.02
3.00
1.20
0.43
1.51
1.08
3.15
0.99
16.90
2.17
f1 (ppm)
203.6
202.6
168.0
167.5
139.1
136.6
136.4
129.1
129.0
128.4
128.3
128.0
127.8
114.2
77.8
77.6
77.4
77.0
76.7
61.3
60.9
52.9
52.7
43.7
43.3
42.8
42.4
33.8
29.2
29.2
29.1
29.0
29.0
28.9
28.6
23.3
22.9
n=8
OMe
NO2
Ph
3fa
f1 (ppm)

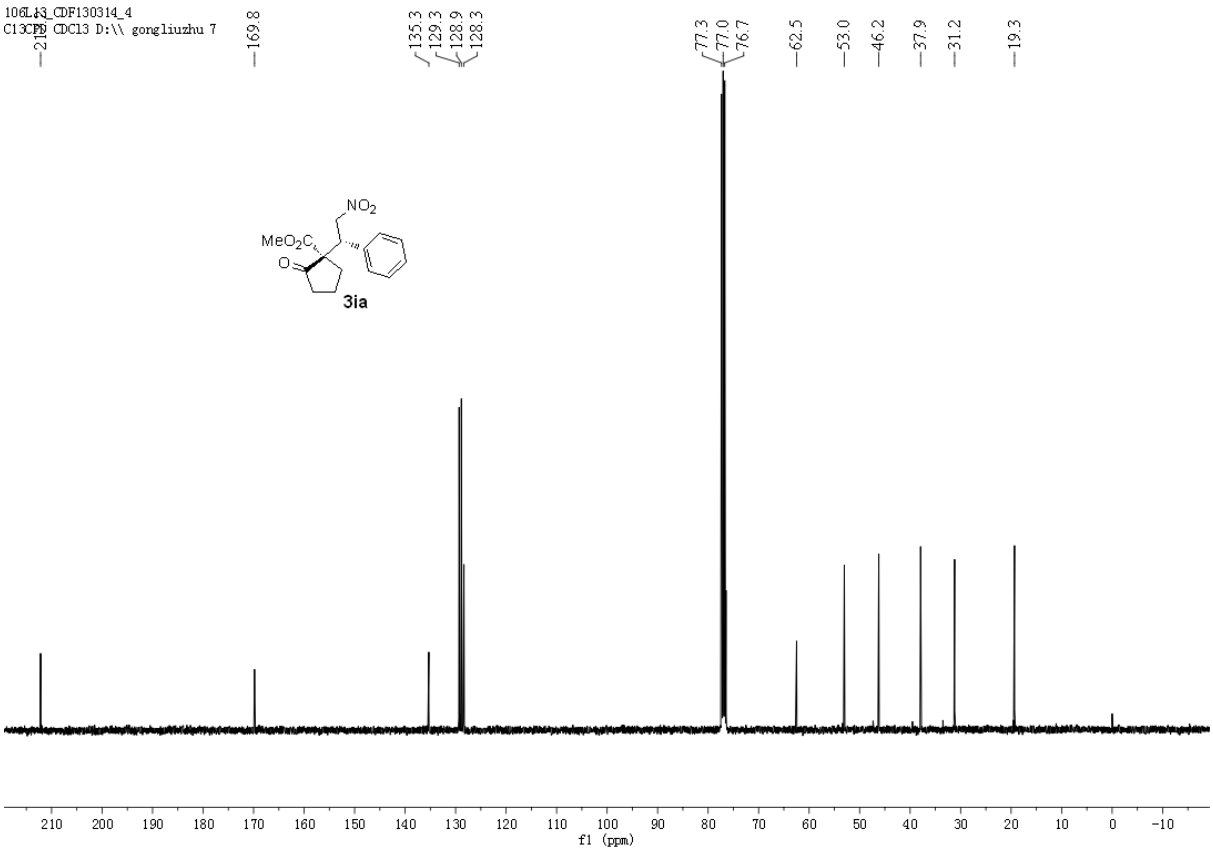

7.3518
7.3489
7.3455
7.3396
7.3314
7.3210
7.3189
7.3132
7.3047
7.3009
7.2960
7.2912
7.2835
7.2792
7.2713
7.2618
7.2526
7.2462
7.2326
7.1684
7.1489
4.8420
4.8339
4.8290
4.8124
4.6744
4.6632
4.6230
4.6014
4.4490
4.3572
4.2101
4.0996
4.0755
4.0424
4.0182
3.7202
3.4767
3.4663
3.4622
3.4467
3.2635
3.2125
2.6971
2.6093
2.5716
2.2884
1.6886
1.6724
1.6564
BnO
O
O
OMe
Ph
NO2
3ga
15.83
3.82
2.11
0.88
0.92
1.70
2.02
1.93
0.86
1.01
3.00
4.36
1.06
1.04
0.98
1.96
1.03
1.93
2.04
f1 (ppm)

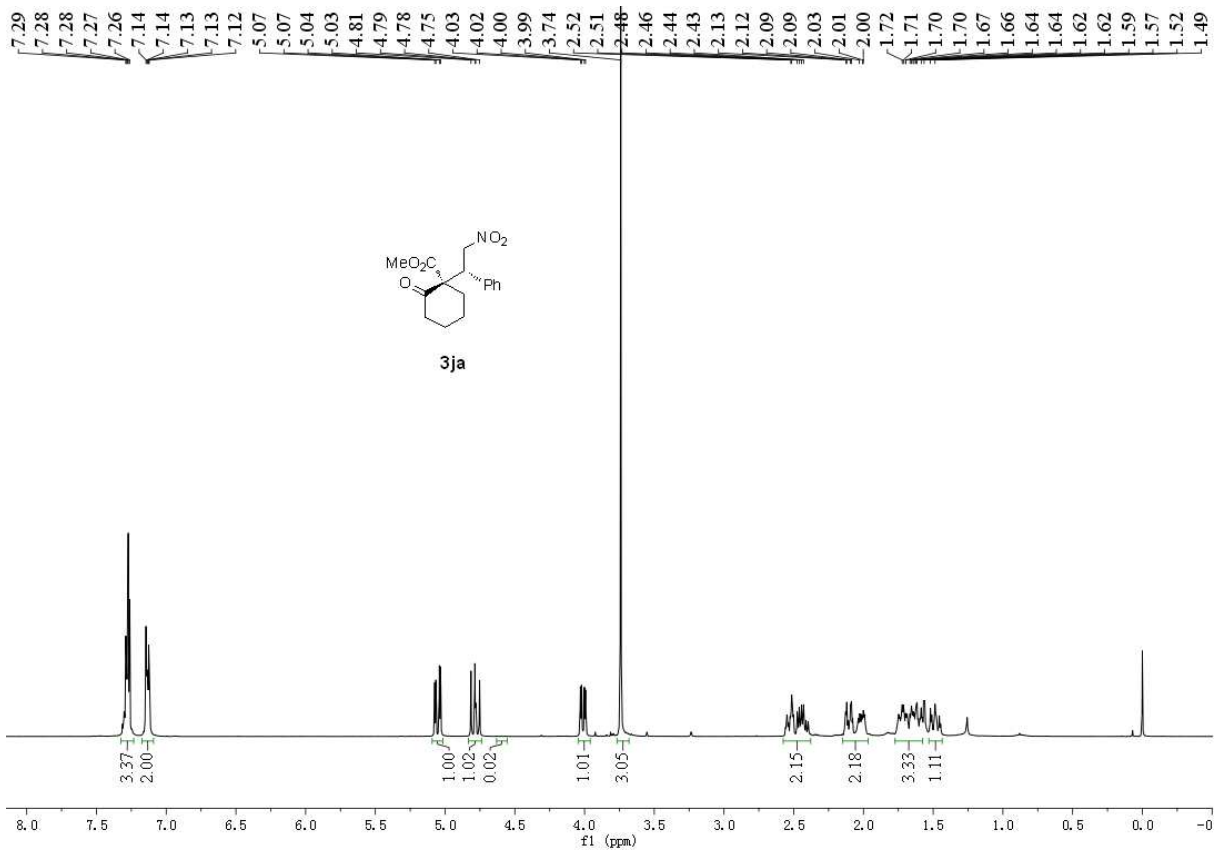

203.1
202.3
168.0
167.5
136.4
129.1
129.0
128.5
128.4
128.4
128.3
128.0
127.9
127.8
127.6
127.6
77.4
77.1
76.7
73.0
72.8
69.0
68.7
61.3
60.9
52.9
52.7
42.7
42.4
40.4
40.0
23.7
23.3
BnO
O
O
OMe
Ph
NO2
3ga
f1 (ppm)

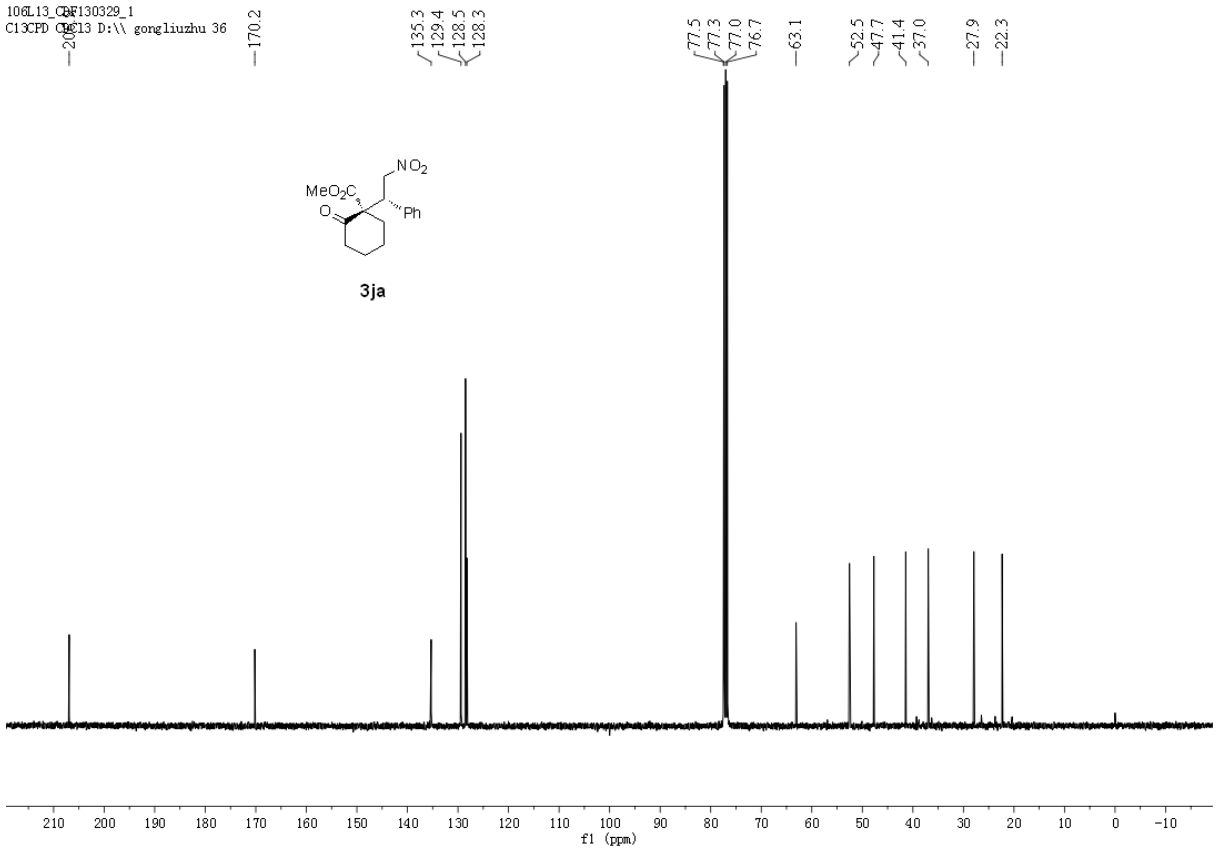

3ha
f1 (ppm)

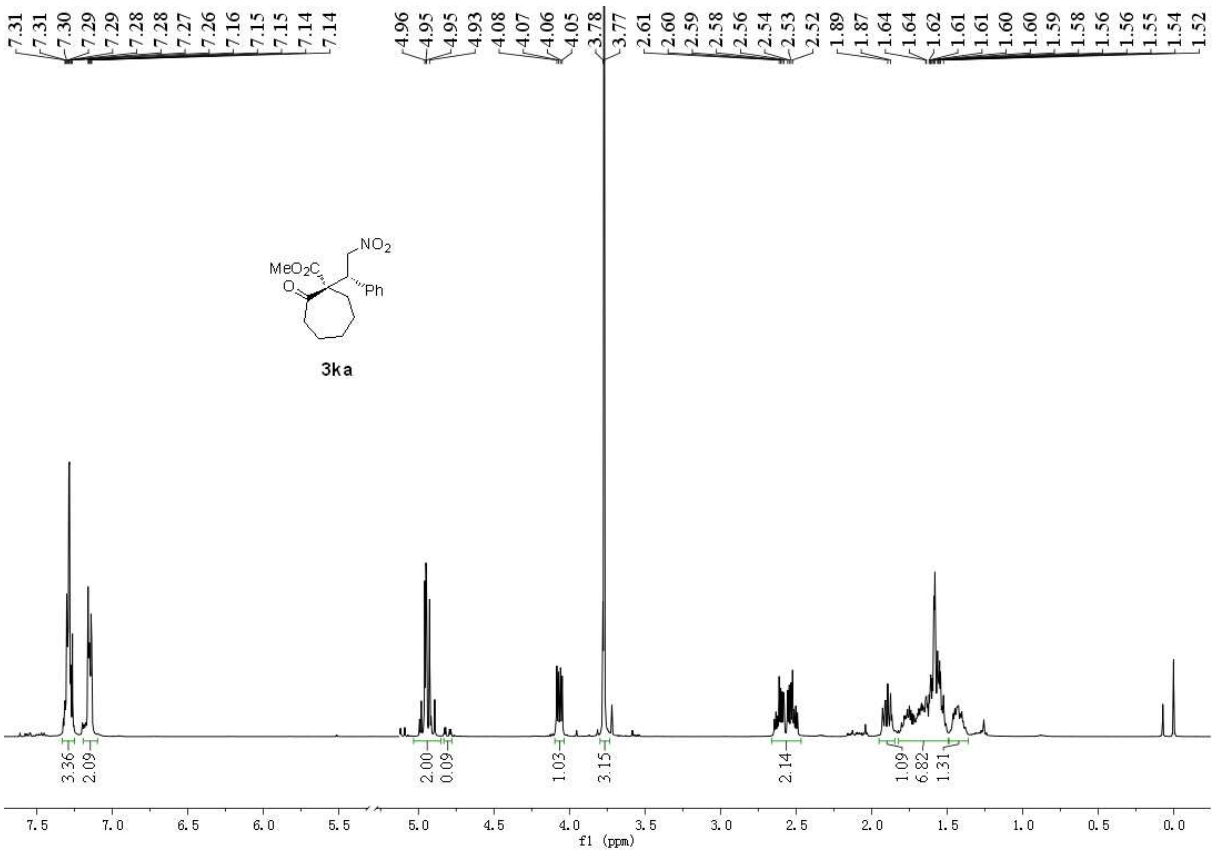

3ha
f1 (ppm)


NO2
MeO2C
O
3ia
5.63
1.00
1.02
0.97
3.16
2.27
4.59
f1 (ppm)

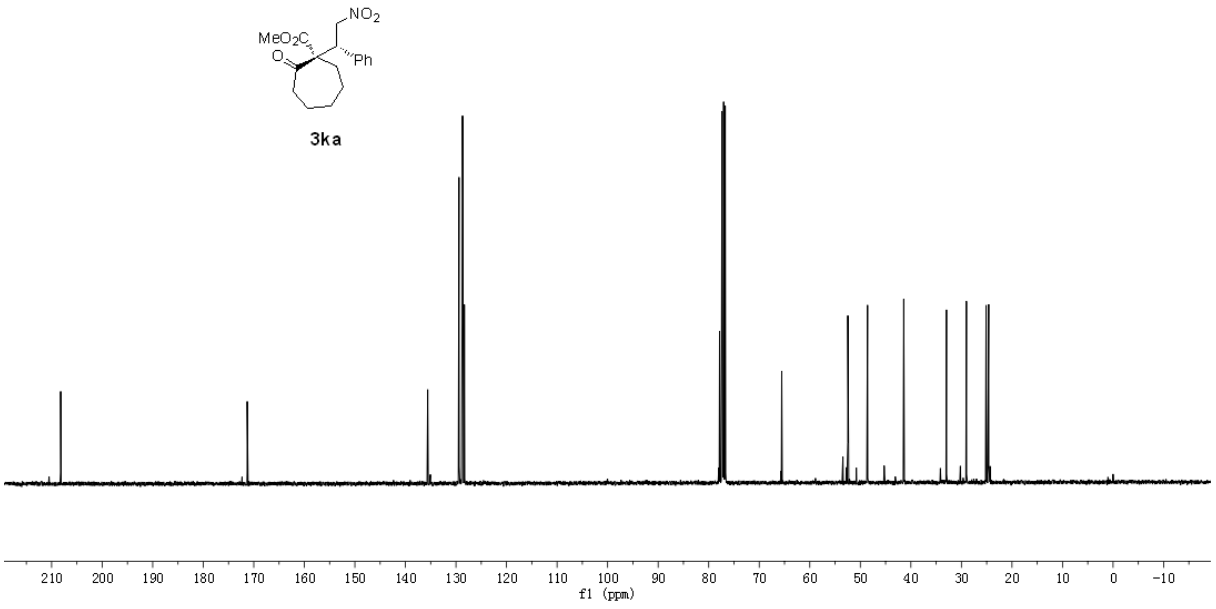

106L43_CDF130314_4
C13CPD CDCl3 D:\\ gongliuzhu 7
169.8
135.3
129.3
128.9
128.3
77.3
77.0
76.7
62.5
53.0
46.2
37.9
31.2
19.3
NO2
MeO2C
O
3ia
f1 (ppm)

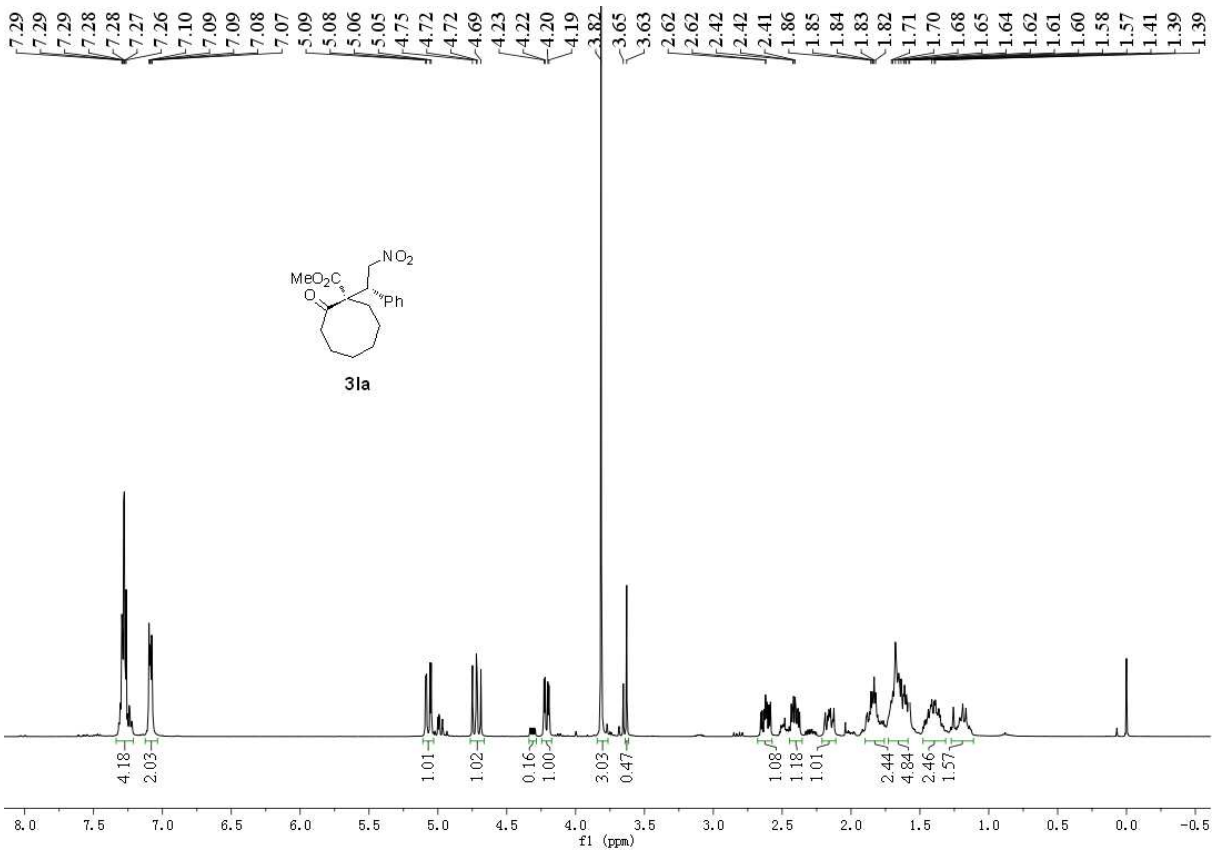

7.29 7.28 7.28 7.27 7.26 7.14 7.14 7.13 7.13 7.12 5.07 5.07 5.04 5.03 4.81 4.79 4.78 4.75 4.03 4.02 4.00 3.99 3.74 2.52 2.51 2.48 2.46 2.44 2.43 2.13 2.12 2.09 2.09 2.03 2.01 2.00 1.72 1.71 1.70 1.70 1.67 1.66 1.64 1.64 1.62 1.62 1.59 1.57 1.52 1.49
NO2
MeO2C
O
Ph
3ja
3.37 2.00 1.00 1.02 0.02 1.01 3.05 2.15 2.18 3.33 1.11
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

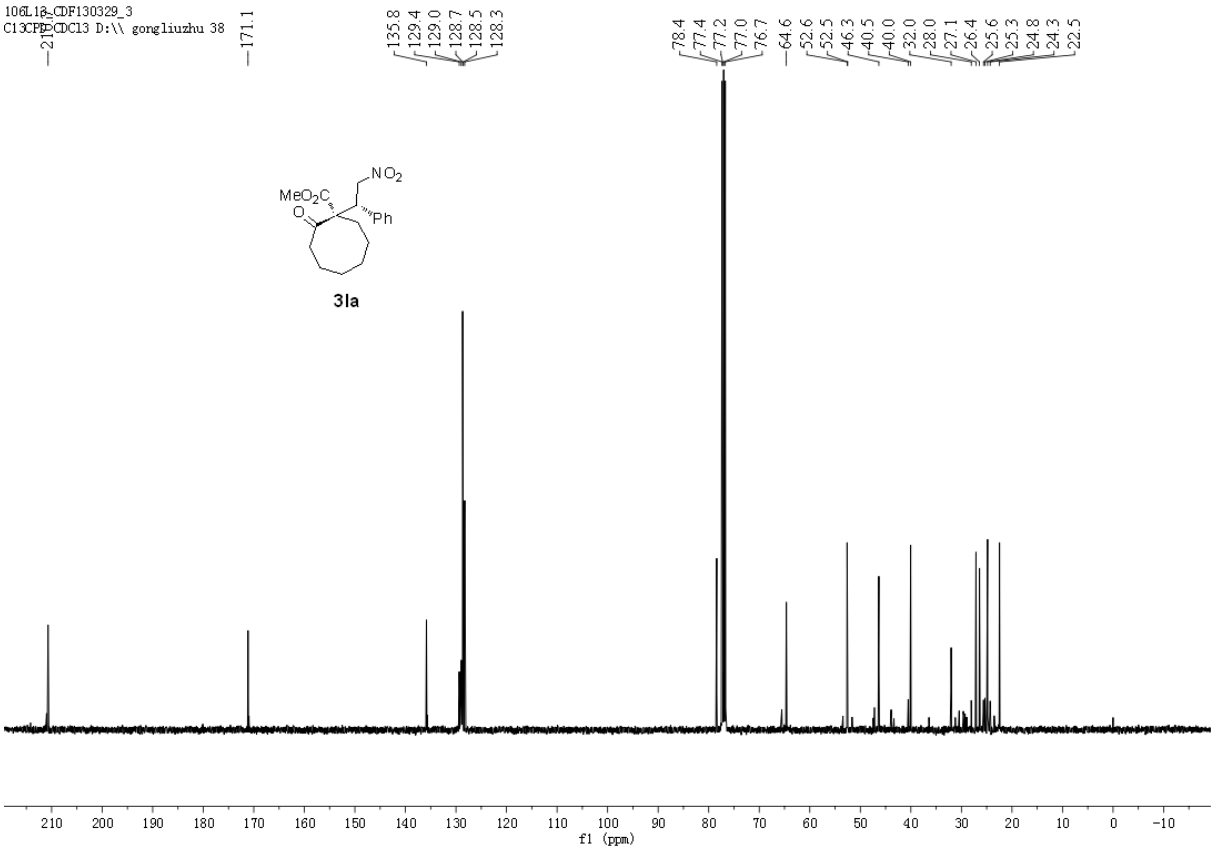

106L13_CDF130329_1
C13CPD CDCl3 D:\\ gongliuzhu 36
170.2
135.3 129.4 128.5 128.3
77.5 77.3 77.0 76.7
63.1
52.5 47.7 41.4 37.0
27.9 22.3
NO2
MeO2C
O
Ph
3ja
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

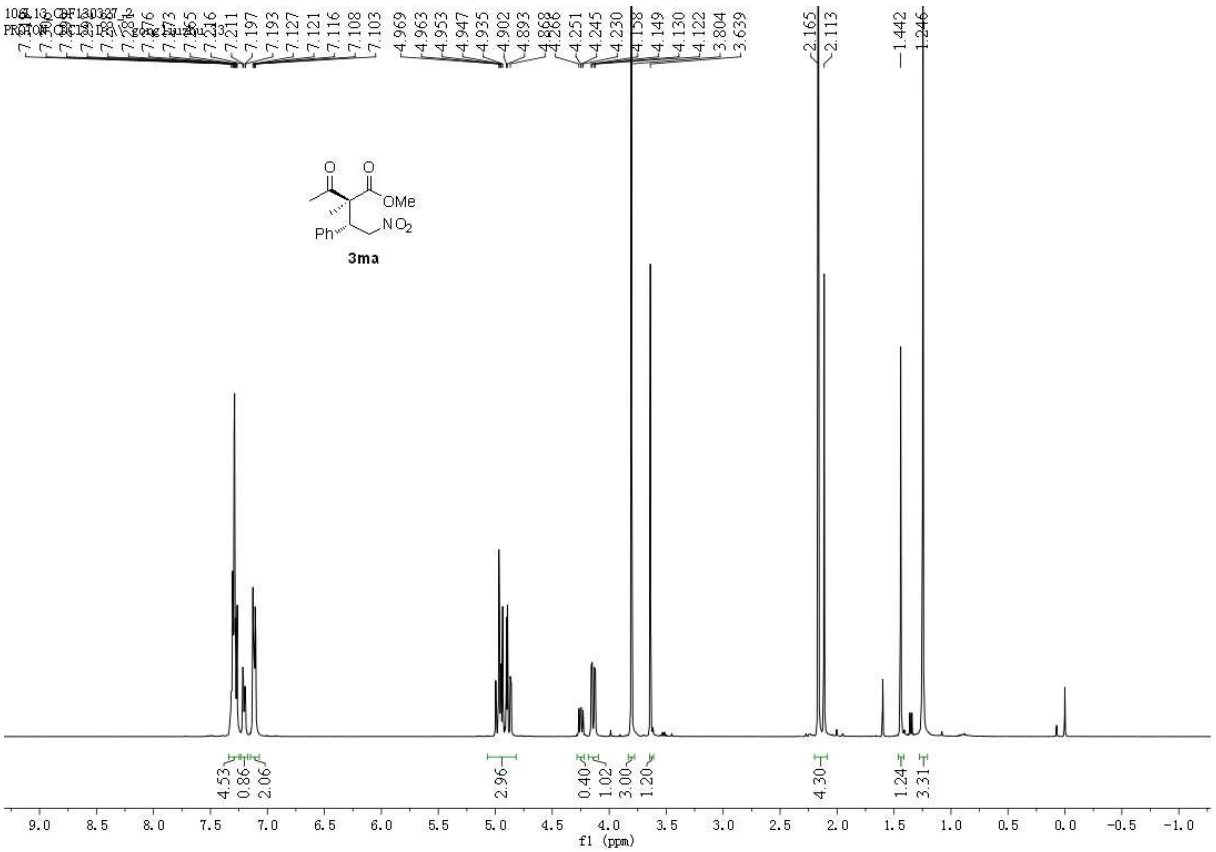

7.31 7.31 7.30 7.29 7.29 7.28 7.28 7.27 7.26 7.16 7.15 7.15 7.14 7.14
4.96 4.95 4.95 4.93 4.08 4.07 4.06 4.05 3.78 3.77 2.61 2.60 2.59 2.58 2.56 2.54 2.53 2.52 1.89 1.87 1.64 1.64 1.62 1.61 1.61 1.60 1.60 1.59 1.58 1.56 1.56 1.55 1.54 1.52
NO2
MeO2C
O
Ph
3ka
3.36 2.09 2.00 0.09 1.03 3.15 2.14 1.09 6.82 1.31
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

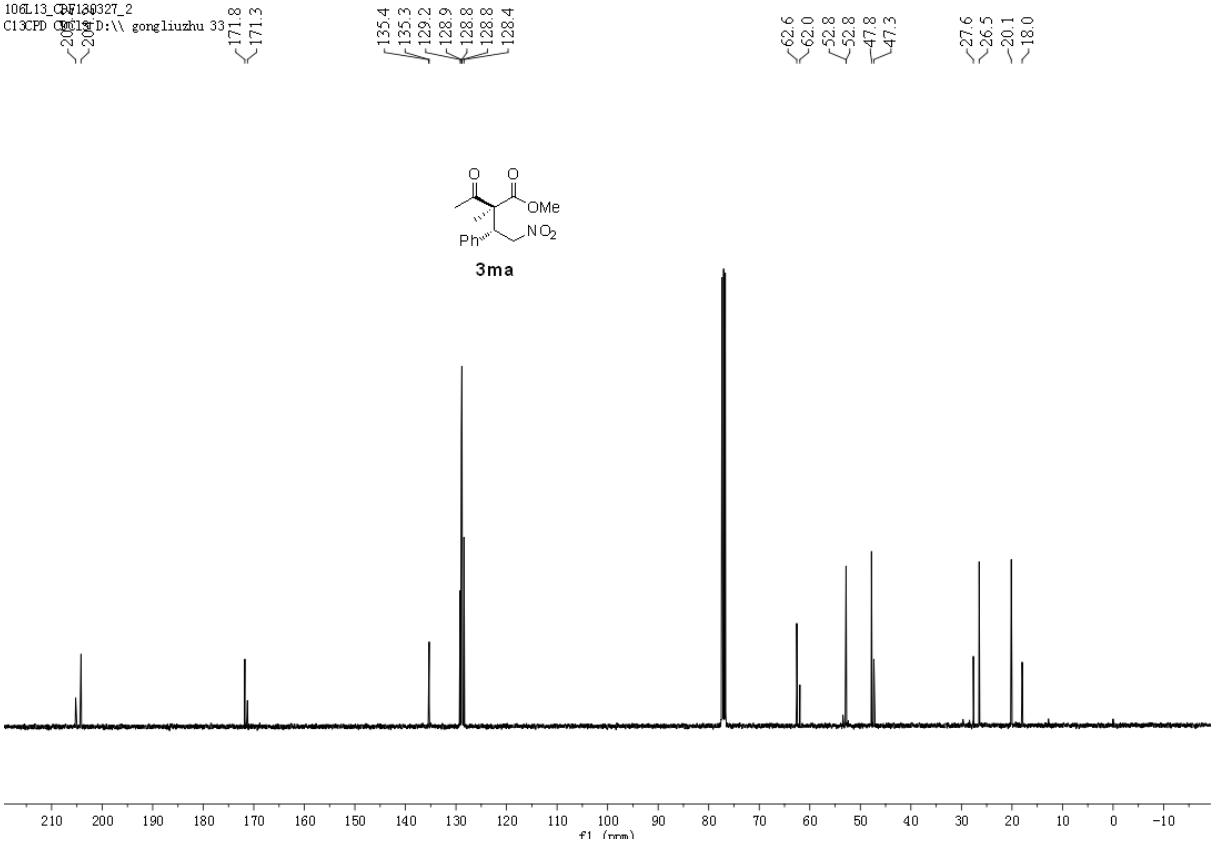

106L13_60F130329_2
C13CPD 200C13 D:\\ gongliuzhu 37
171.3
135.6 129.4 128.7 128.3
77.9 77.4 77.0 76.7
65.6
52.5 48.6 41.4
33.0 29.0 25.1 24.6

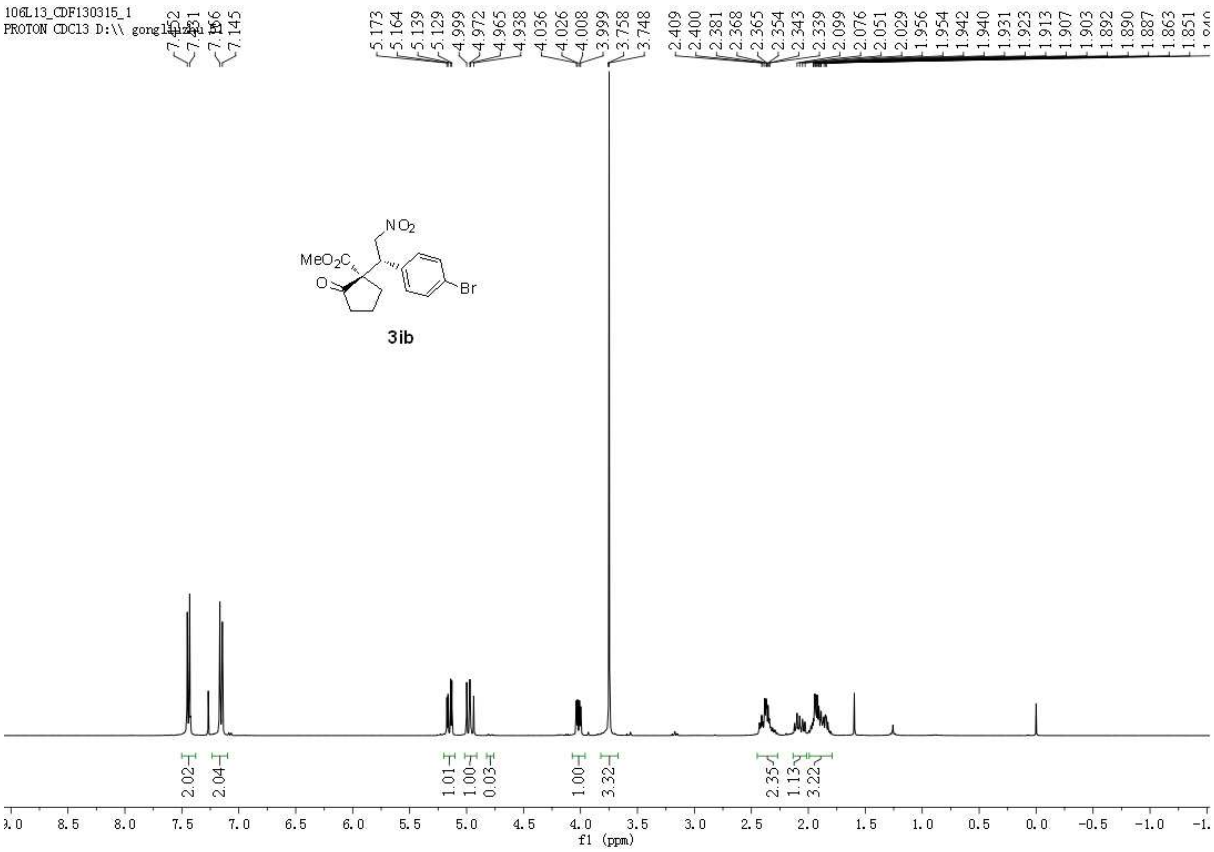

NO2
MeO2C
O
Ph
3ka
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

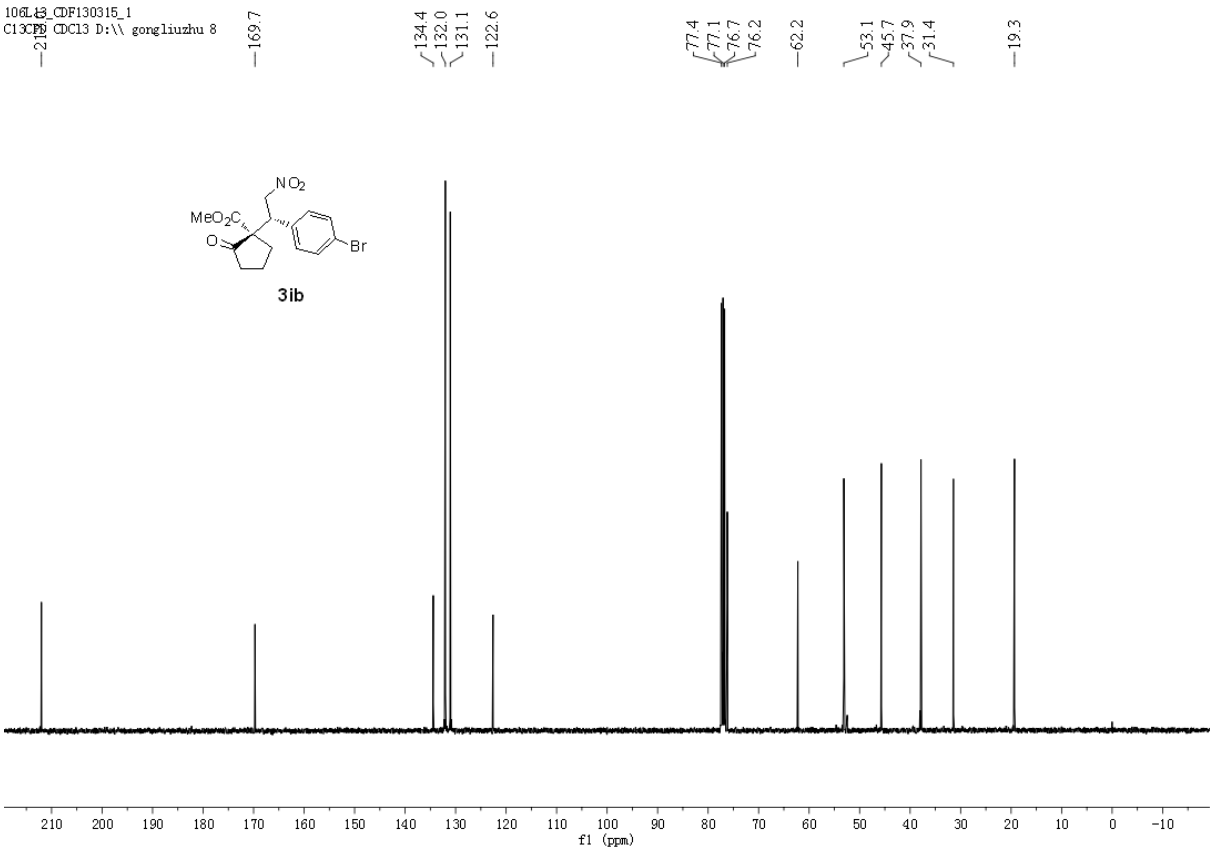

7.29 7.29 7.29 7.28 7.28 7.27 7.26 7.10 7.09 7.09 7.08 7.07 5.09 5.08 5.06 5.05 4.75 4.72 4.72 4.69 4.23 4.22 4.20 4.19 3.82 3.65 3.63 2.62 2.62 2.42 2.42 2.41 1.86 1.85 1.84 1.83 1.82 1.71 1.70 1.68 1.65 1.64 1.62 1.61 1.60 1.58 1.57 1.41 1.39 1.39
NO2
MeO2C
O
Ph
3la
4.18 2.03 1.01 1.02 0.16 1.00 3.03 0.47 1.08 1.18 1.01 2.44 4.84 2.46 1.57
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

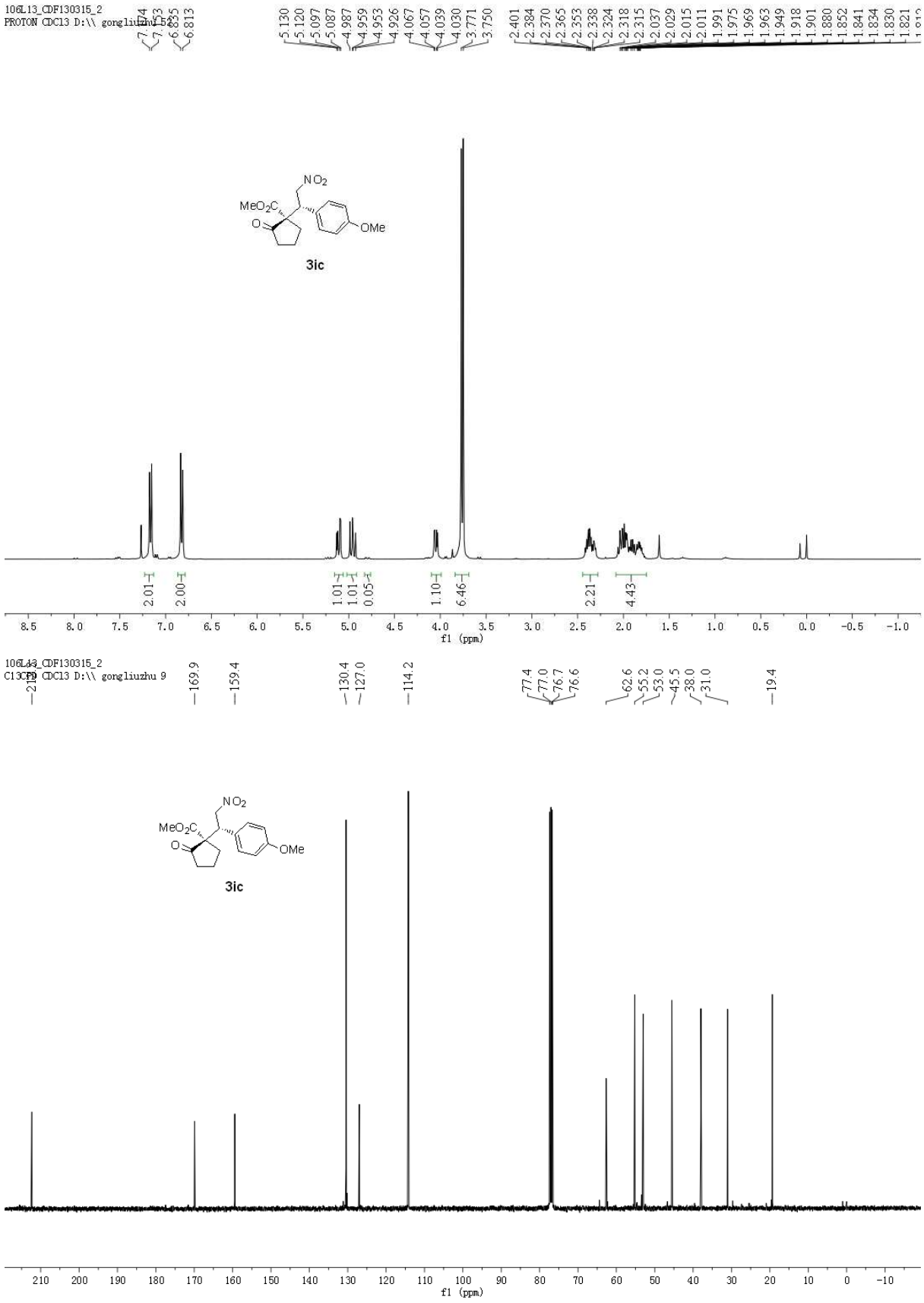

106L1a-CDF130329_3
C13CPD CDCl3 D:\\ gongliuzhu 38
171.1
135.8 129.4 129.0 128.7 128.5 128.3
78.4 77.4 77.2 77.0 76.7
64.6
52.6 52.5 46.3 40.5 40.0 32.0 28.0 27.1 26.4 25.6 25.3 24.8 24.3 22.5
NO2
MeO2C
O
Ph
3la
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

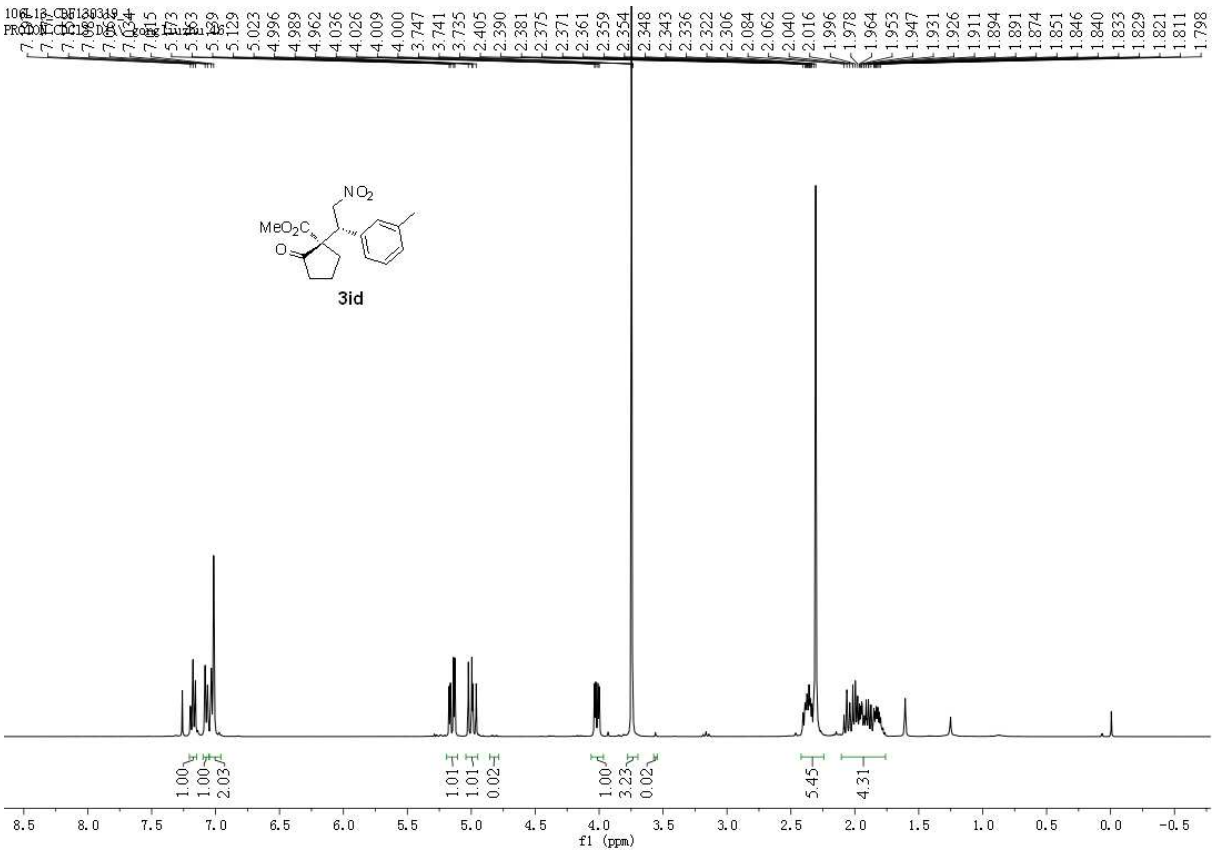

3ma
f1 (ppm)

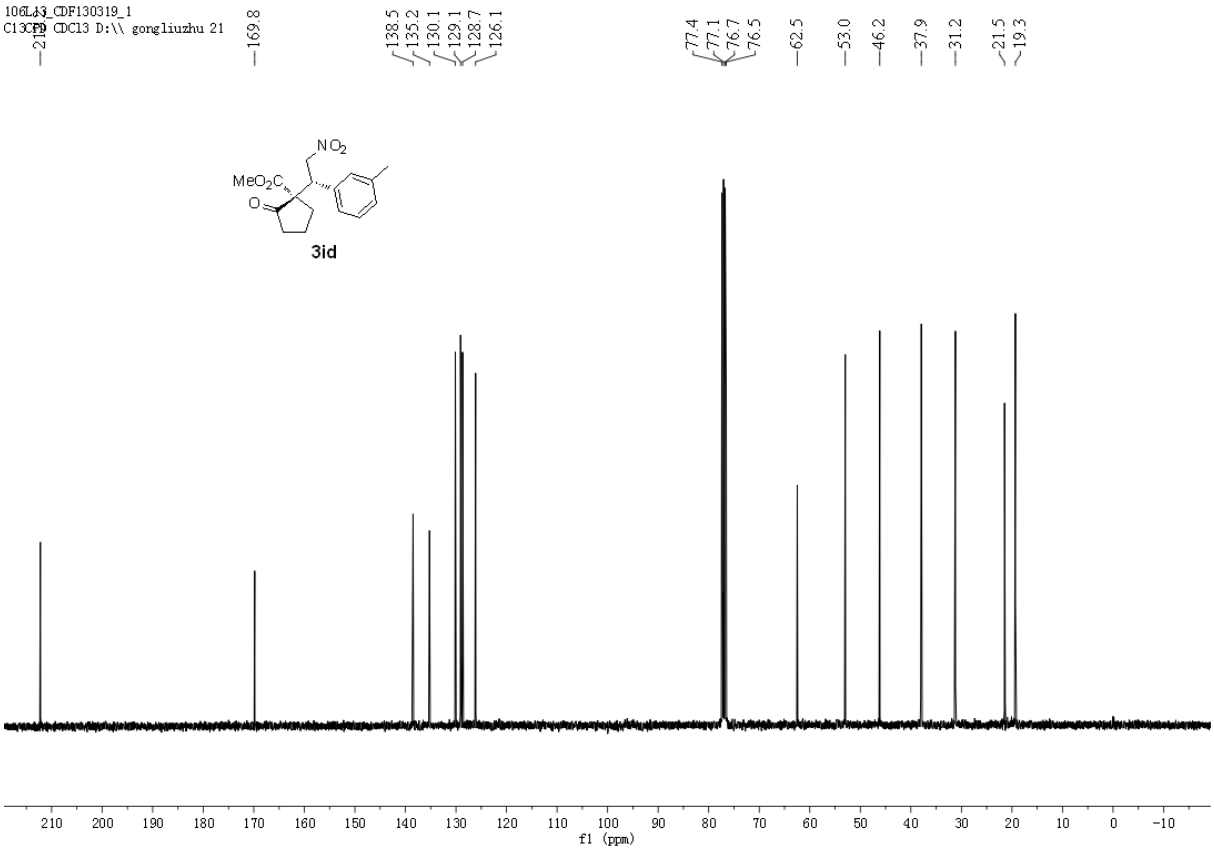

3ma
f1 (ppm)

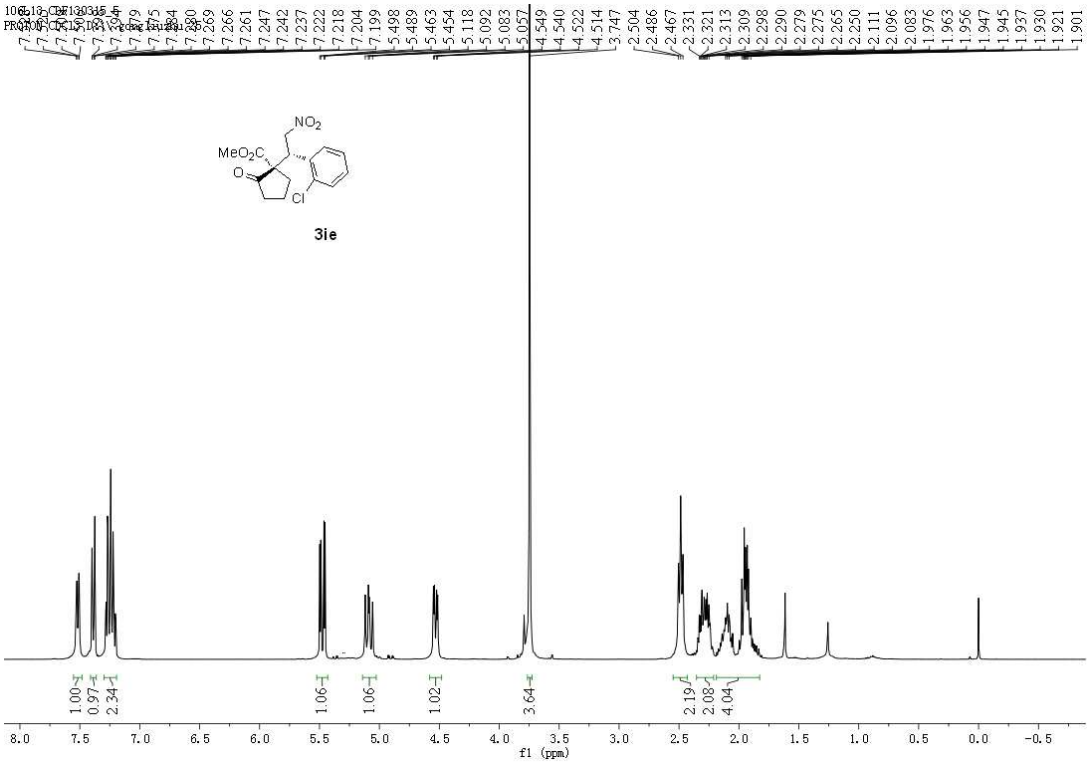

106L13_CDF130315_1
PROTON CDCl3 D:\\ gongliuzhu 8
NO2
MeO2C
O
Br
3ib
f1 (ppm)

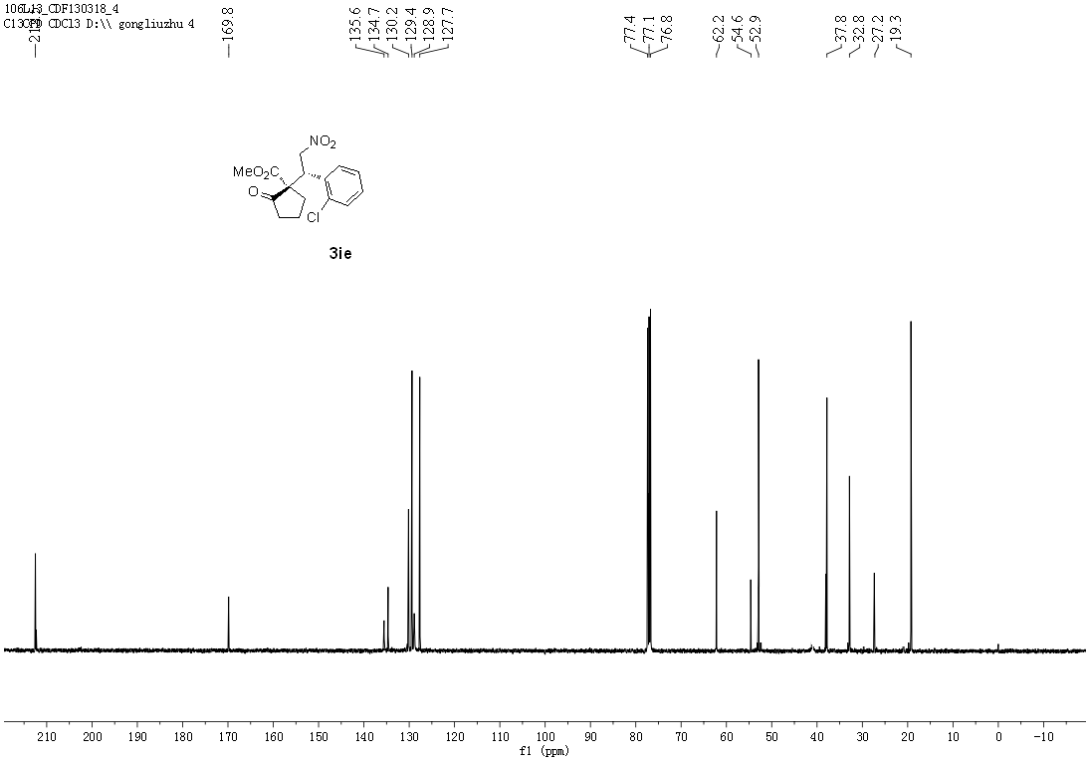

106L13_CDF130315_1
C13CPD CDCl3 D:\\ gongliuzhu 8
NO2
MeO2C
O
Br
3ib
f1 (ppm)

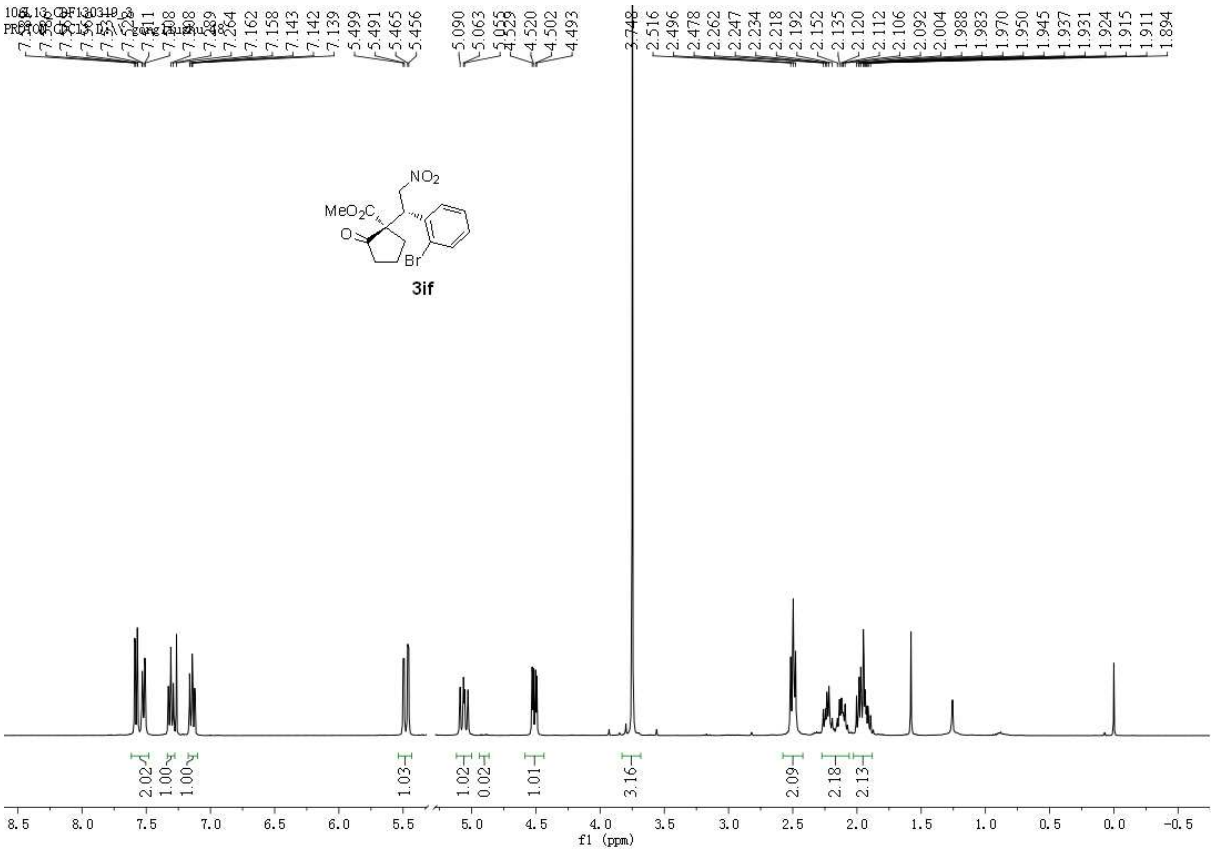

106L13_CDF130315_2
PROTON CDCl3 D:\\ gongliuzhu 9
7.314
7.293
6.835
6.813
5.130
5.120
5.097
5.087
4.987
4.959
4.953
4.926
4.067
4.057
4.039
4.030
3.771
3.750
2.401
2.384
2.370
2.365
2.353
2.338
2.324
2.318
2.315
2.037
2.029
2.015
2.011
1.991
1.975
1.969
1.963
1.949
1.918
1.901
1.880
1.852
1.841
1.834
1.830
1.821
NO2
MeO2C
O
OMe
3ic
2.01
2.00
1.01
1.01
0.05
1.10
6.46
2.21
4.43
f1 (ppm)
106L13_CDF130315_2
C13CPD CDCl3 D:\\ gongliuzhu 9
169.9
159.4
130.4
127.0
114.2
77.4
77.0
76.7
76.6
62.6
55.2
53.0
45.5
38.0
31.0
19.4
NO2
MeO2C
O
OMe
3ic
f1 (ppm)

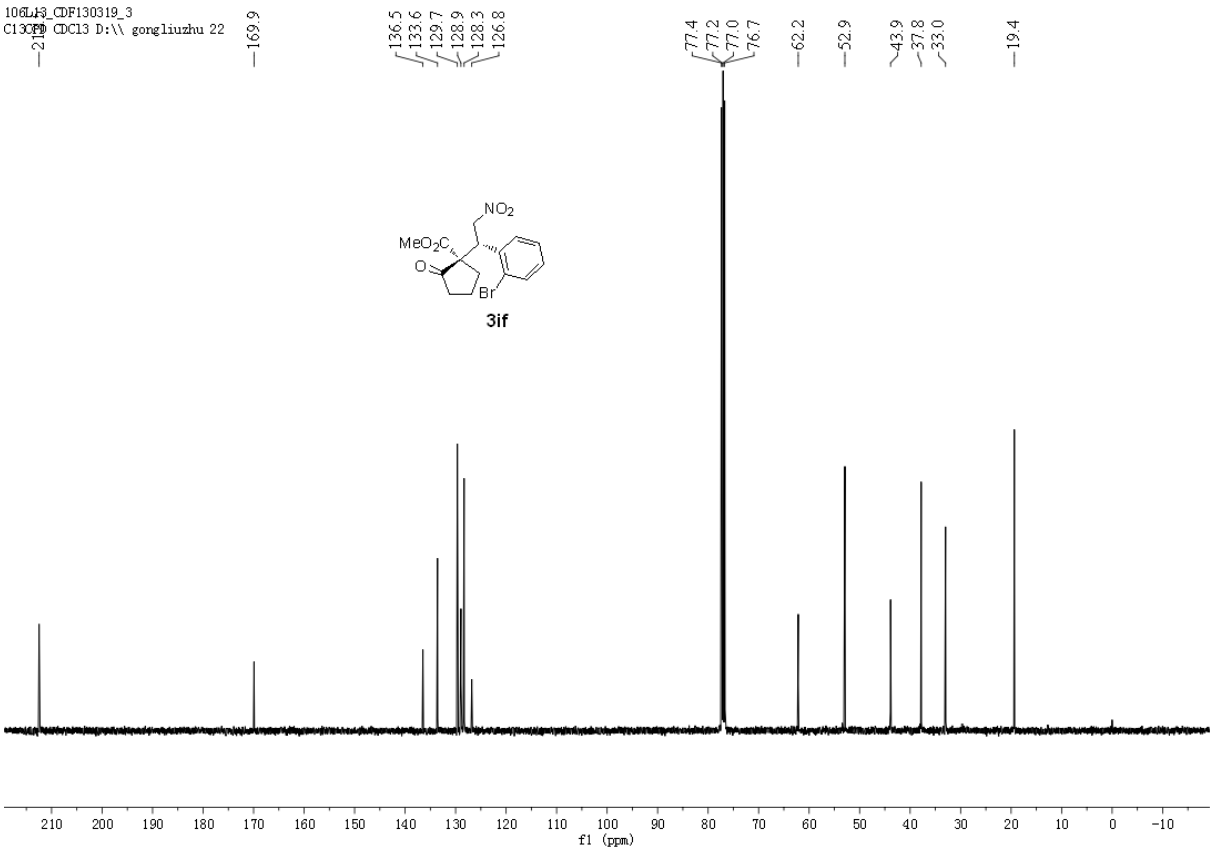

3id
f1 (ppm)

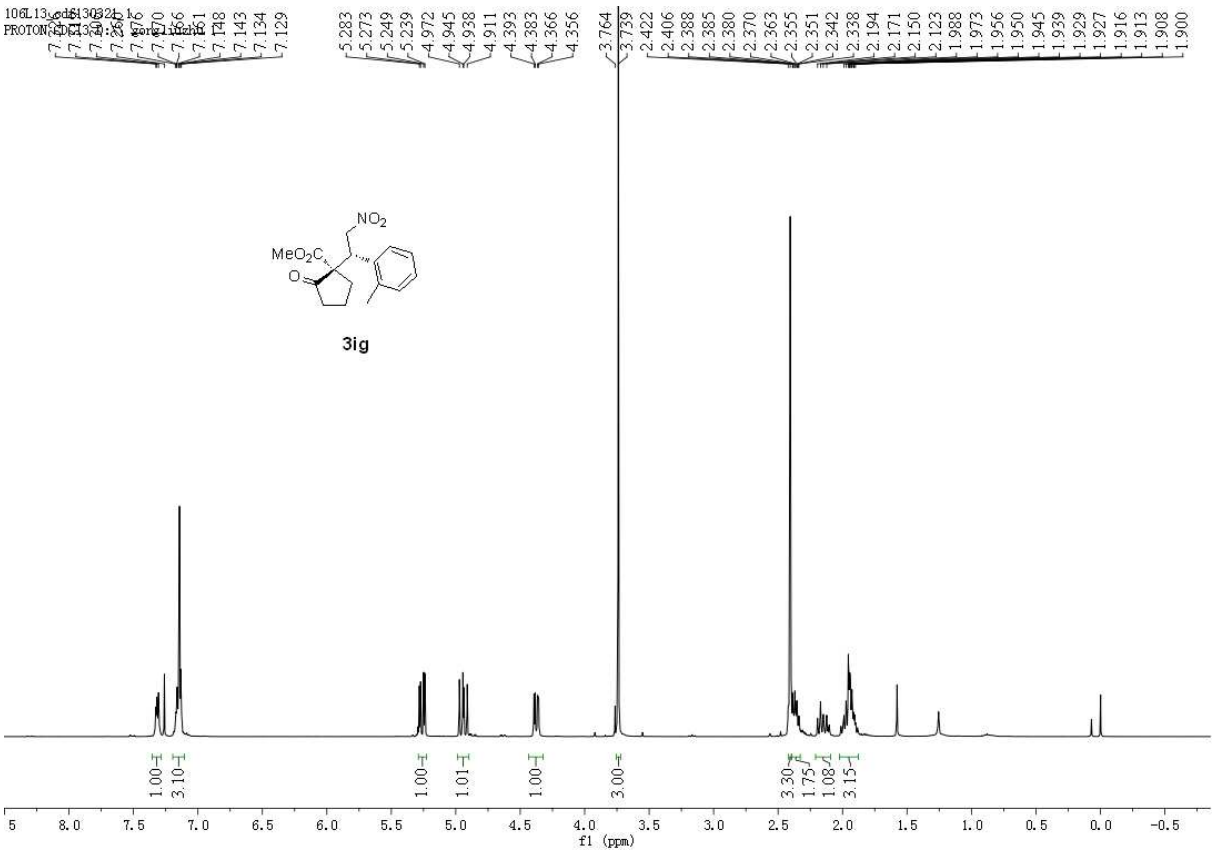

3id
f1 (ppm)


3ie
f1 (ppm)

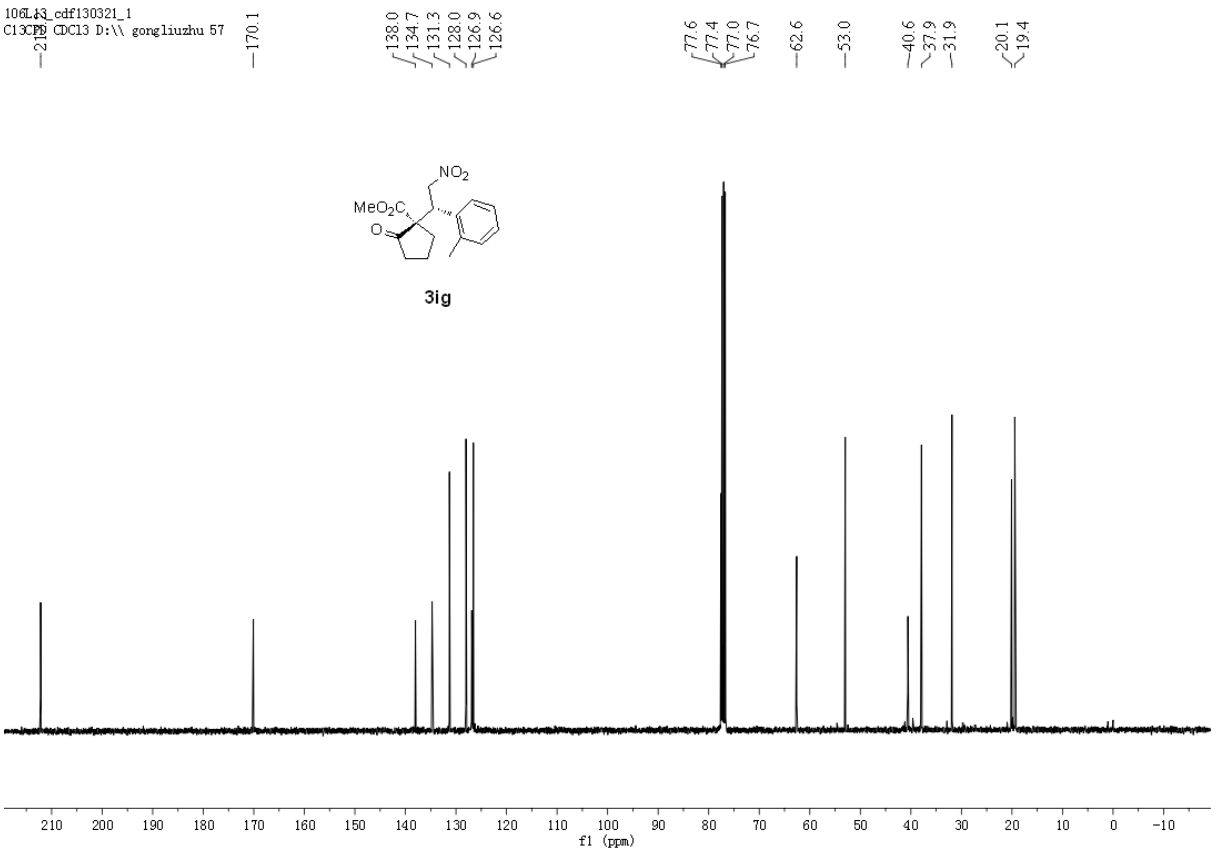

3ie
f1 (ppm)


3if
f1 (ppm)

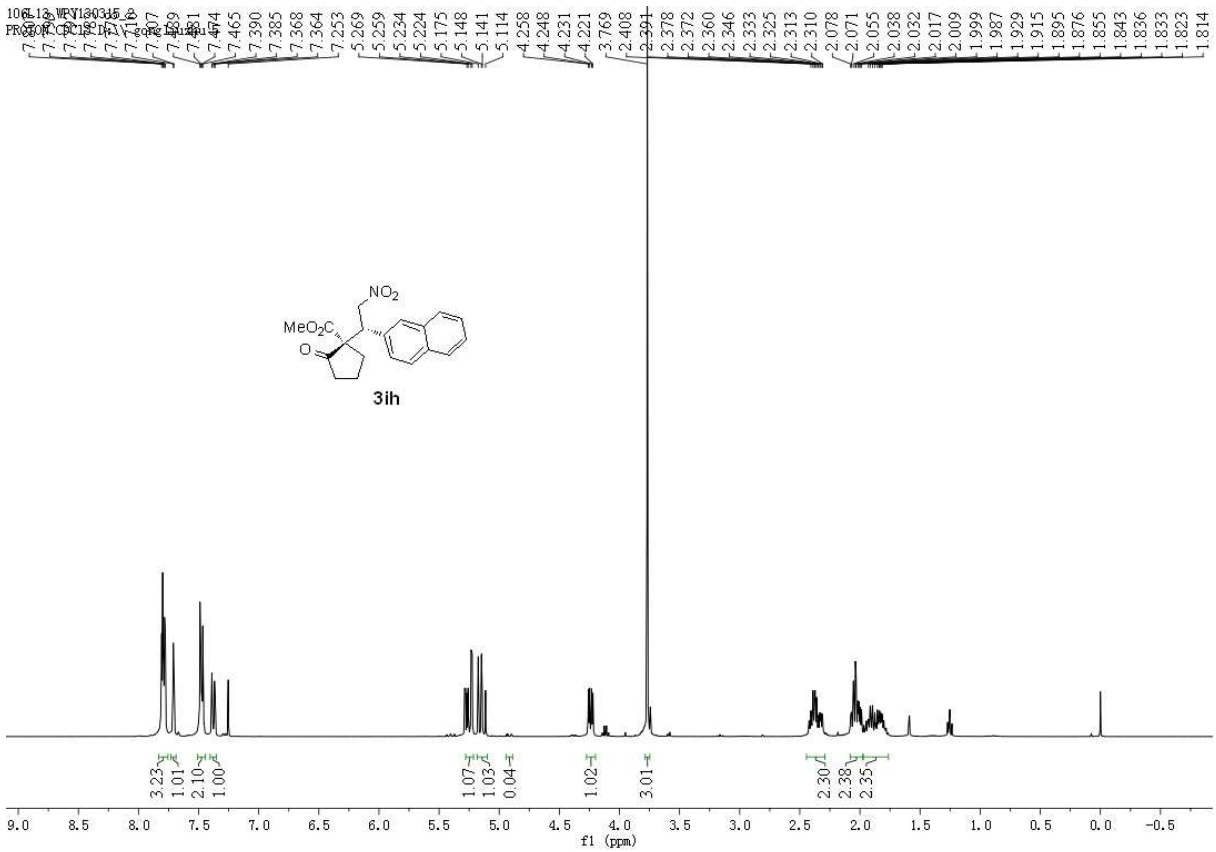

3if
f1 (ppm)

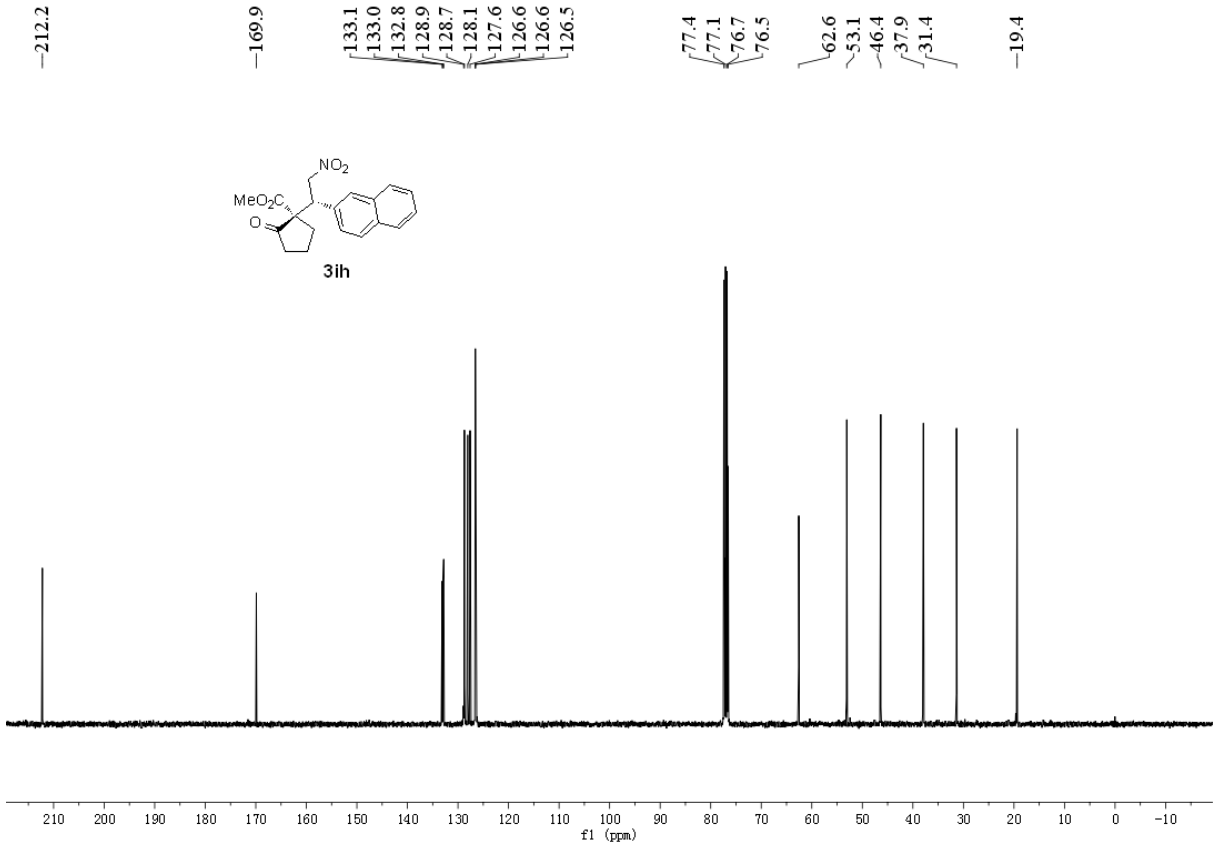


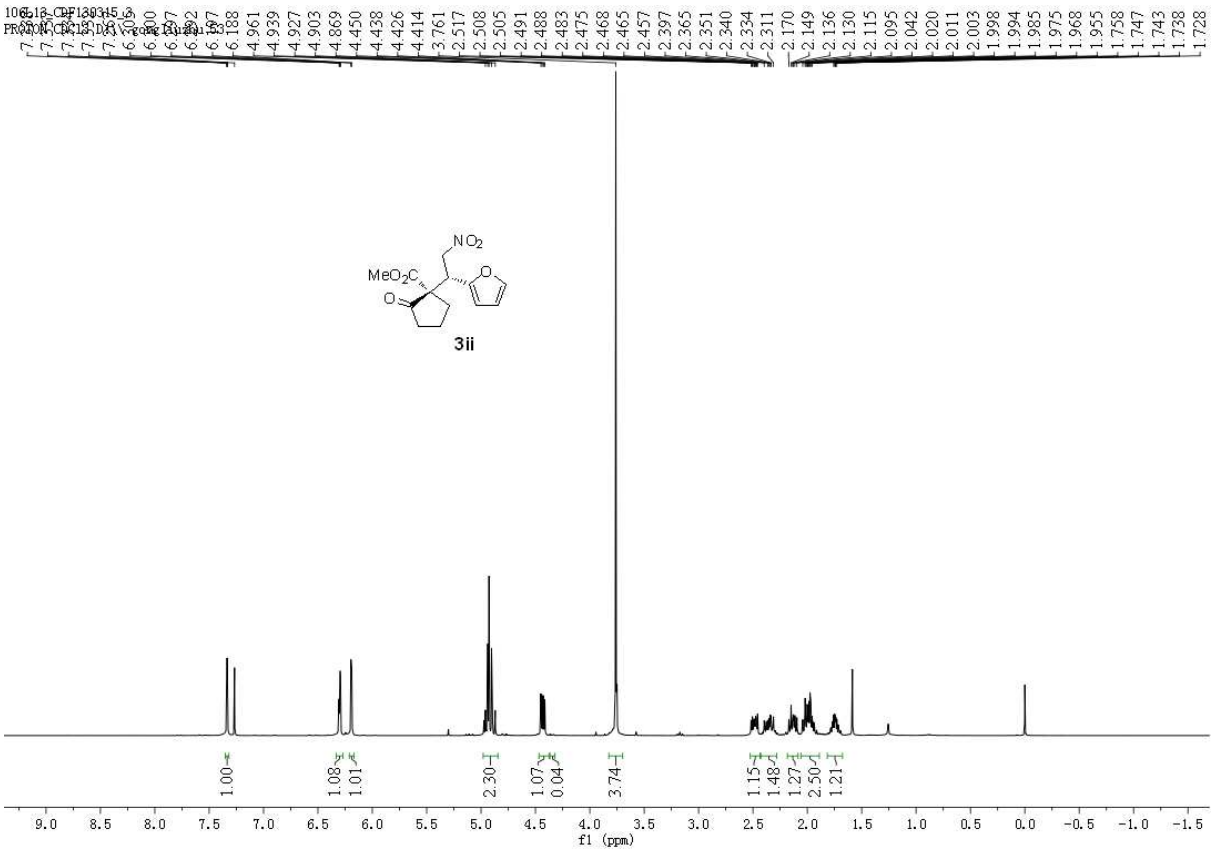
3ig

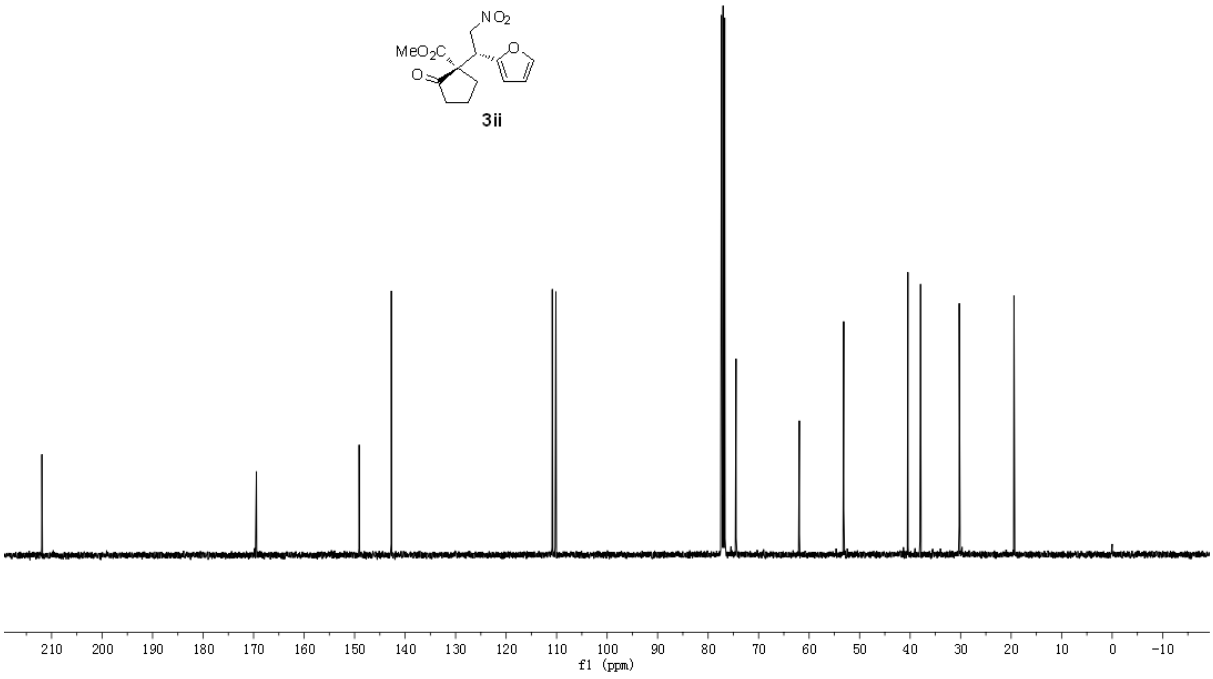


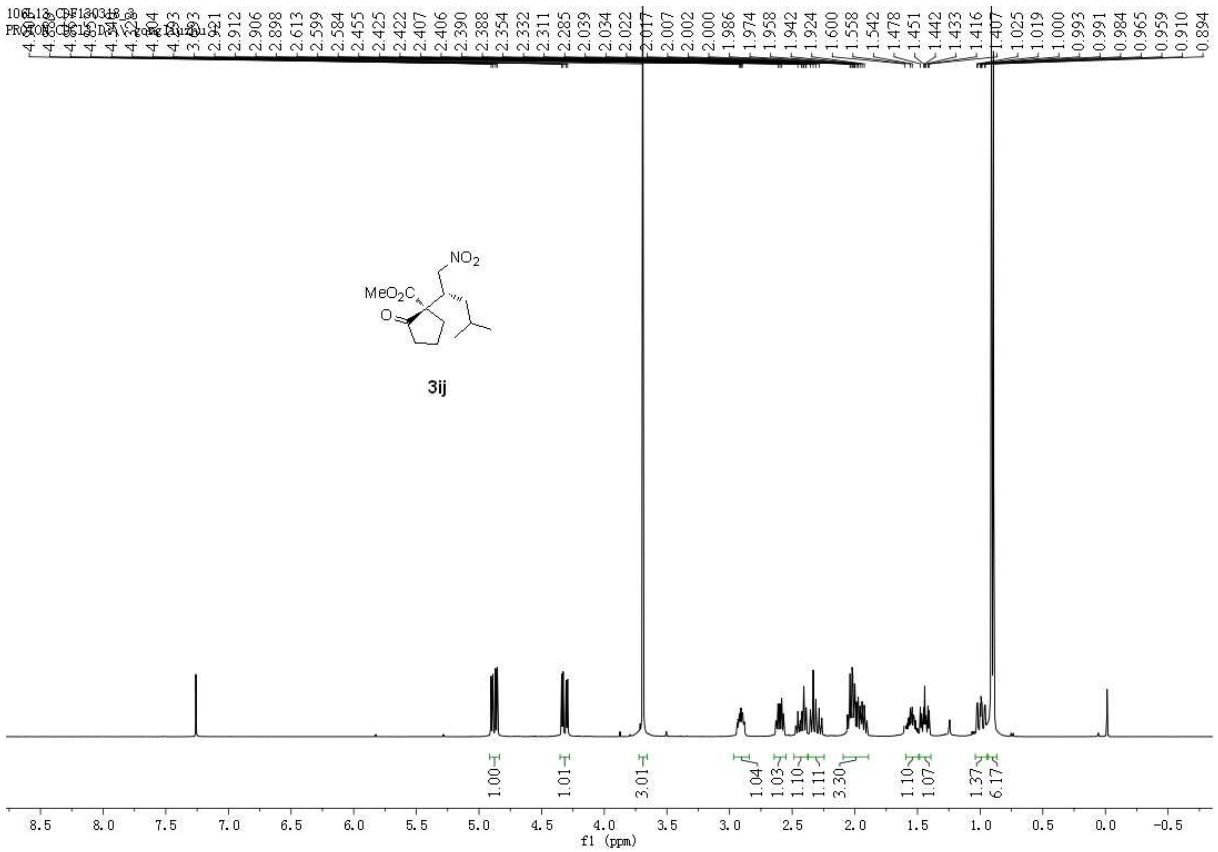
3ig

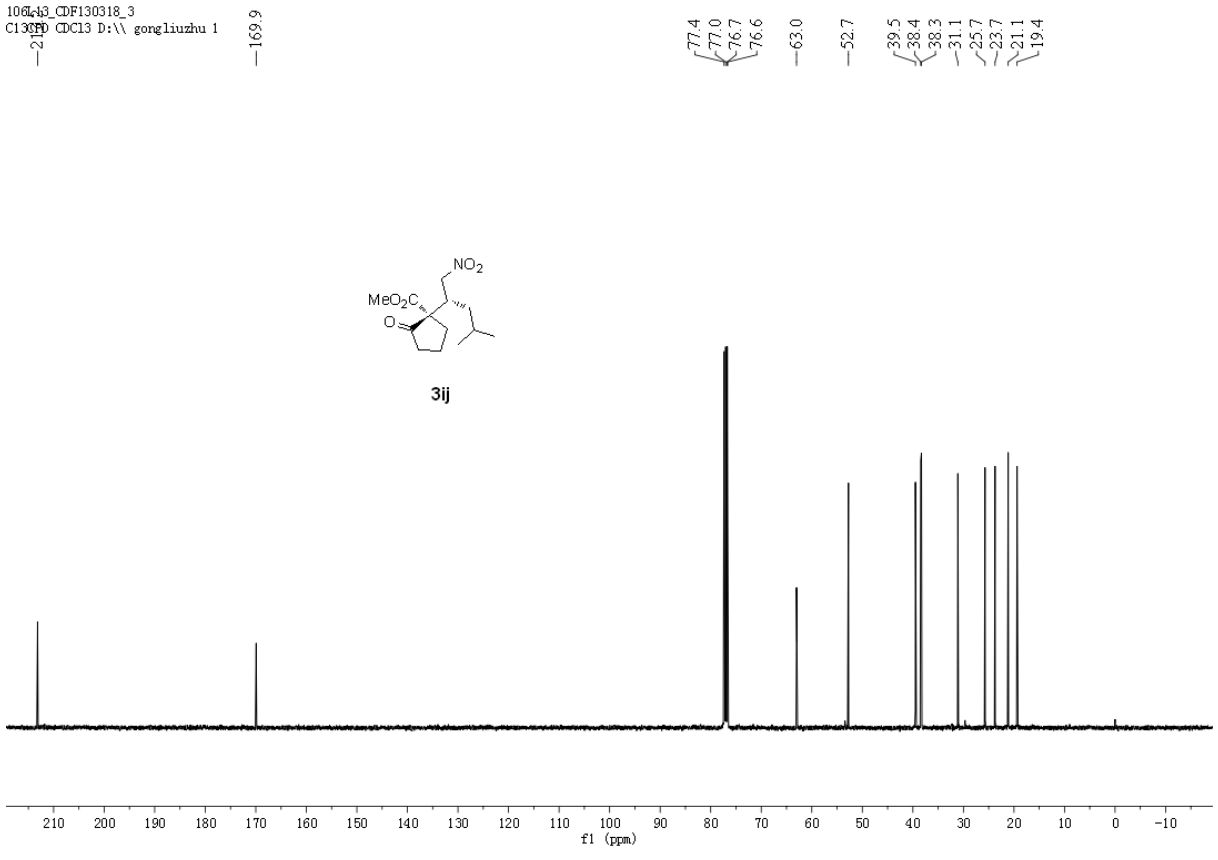

NO2
MeO2C
O
3ih
f1 (ppm)

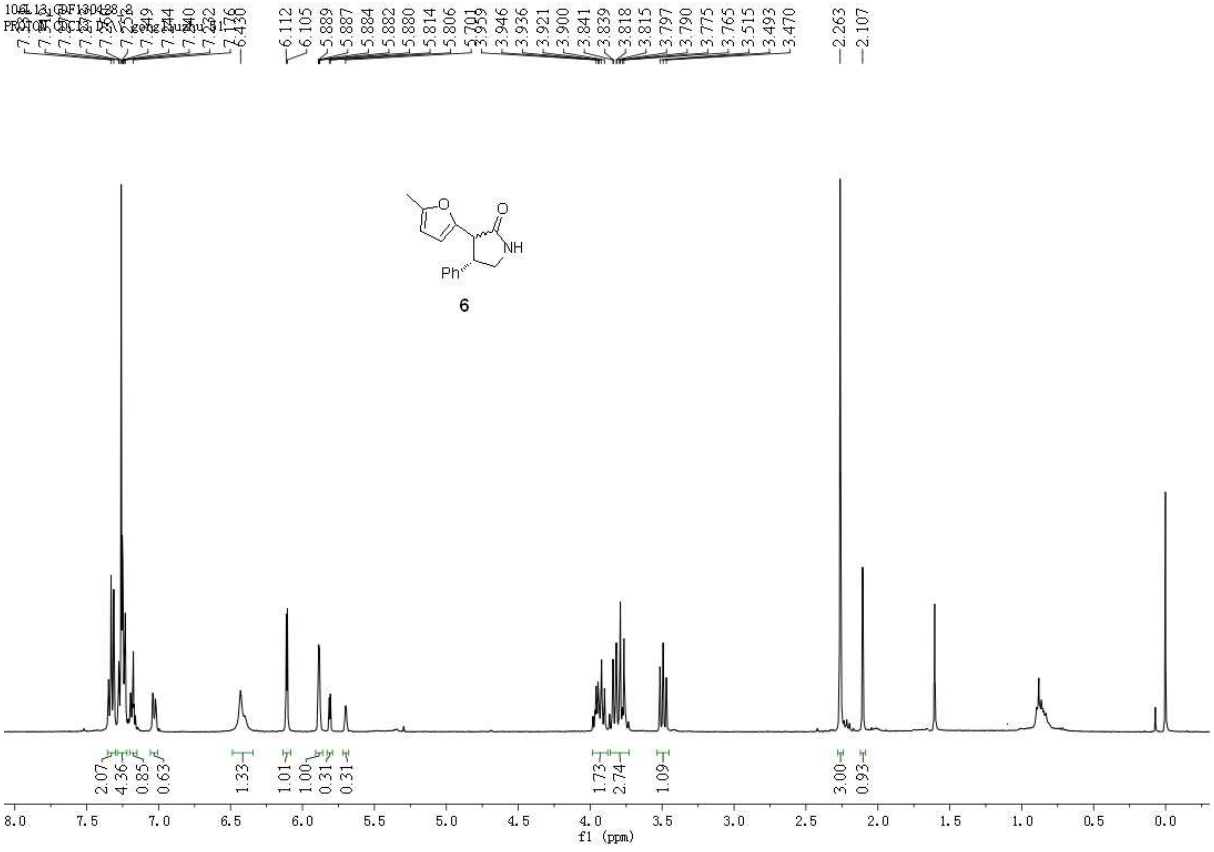

212.2
169.9
133.1
133.0
132.8
128.9
128.7
128.1
127.6
126.6
126.6
126.5
77.4
77.1
76.7
76.5
62.6
53.1
46.4
37.9
31.4
19.4
NO2
MeO2C
O
3ih
f1 (ppm)

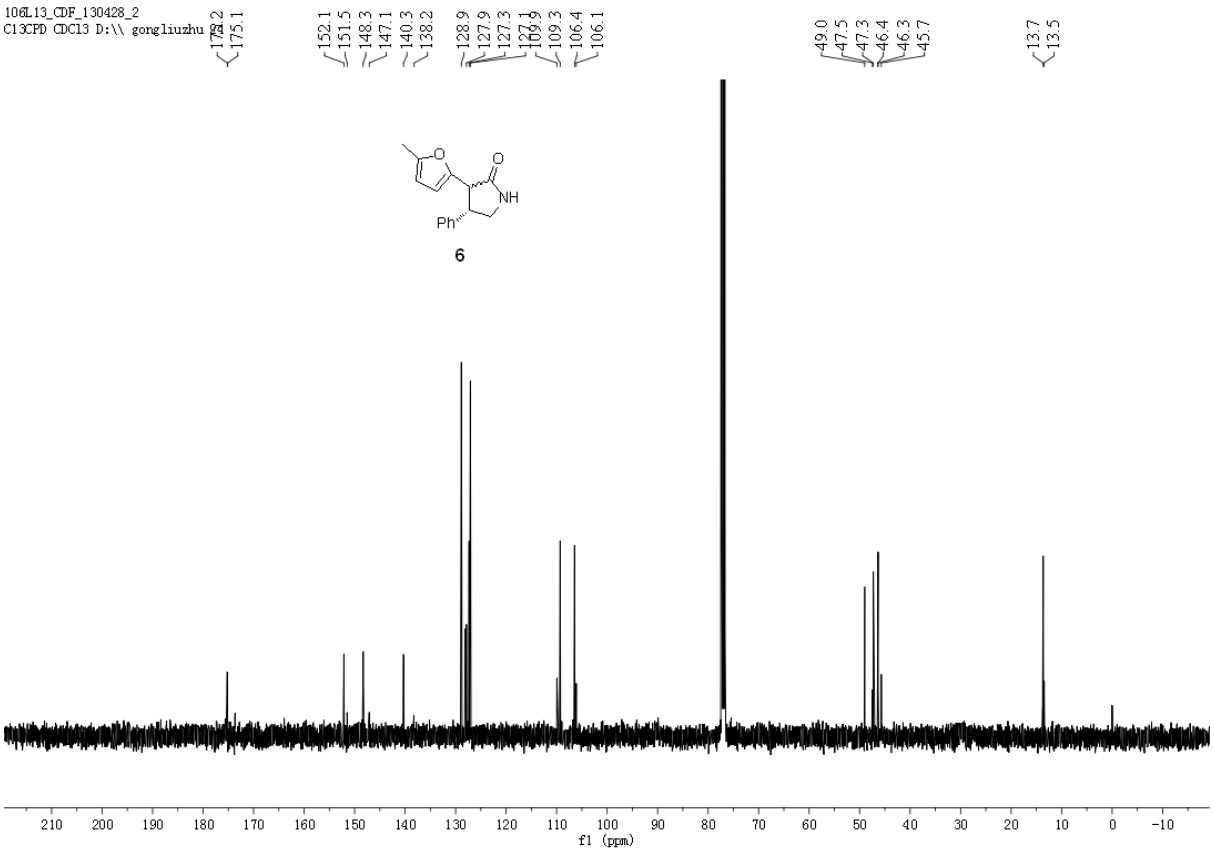

3ii
f1 (ppm)

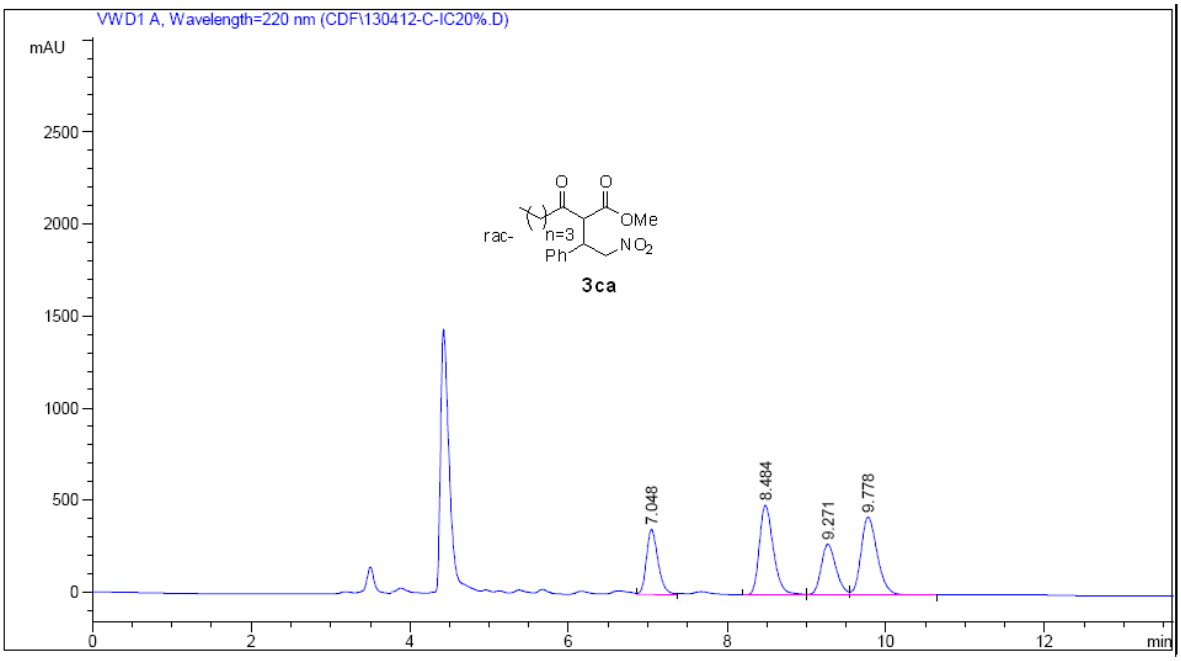

3ii
f1 (ppm)


NO2
MeO2C
O
3ij
f1 (ppm)

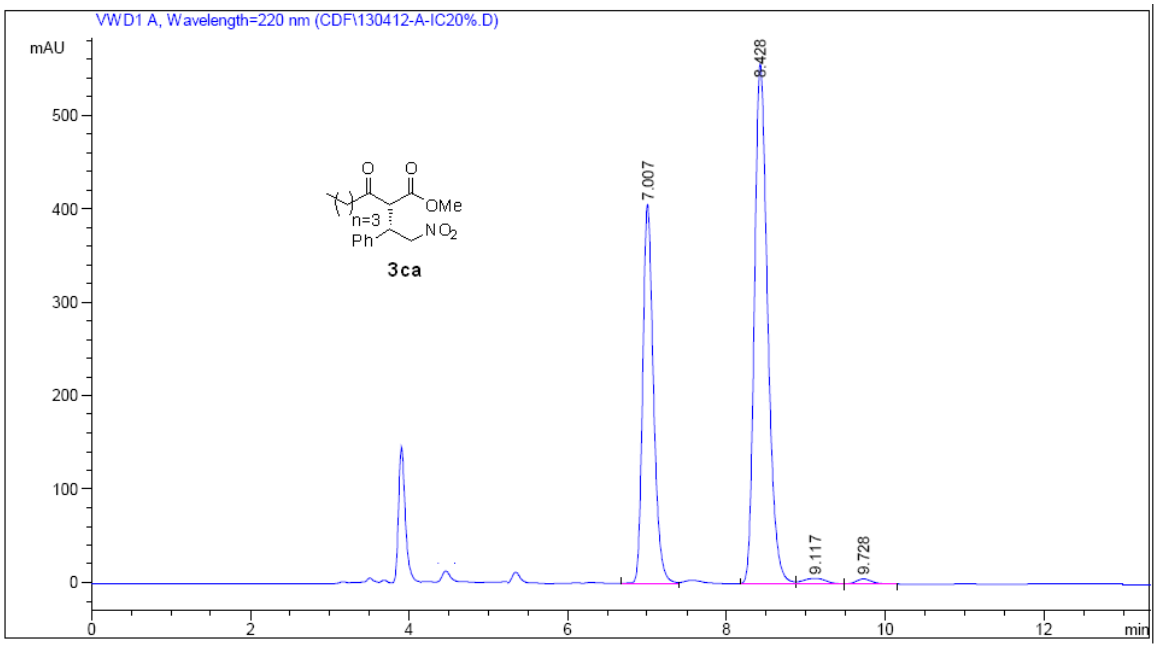

NO2
MeO2C
O
3ij
f1 (ppm)


6.112
6.105
5.889
5.887
5.884
5.882
5.880
5.814
5.806
3.946
3.936
3.921
3.900
3.841
3.839
3.818
3.815
3.797
3.790
3.775
3.765
3.515
3.493
3.470
2.263
2.107
O
NH
Ph
6
2.07
4.36
0.85
0.63
1.33
1.01
1.00
0.31
0.31
1.73
2.74
1.09
3.00
0.93
f1 (ppm)

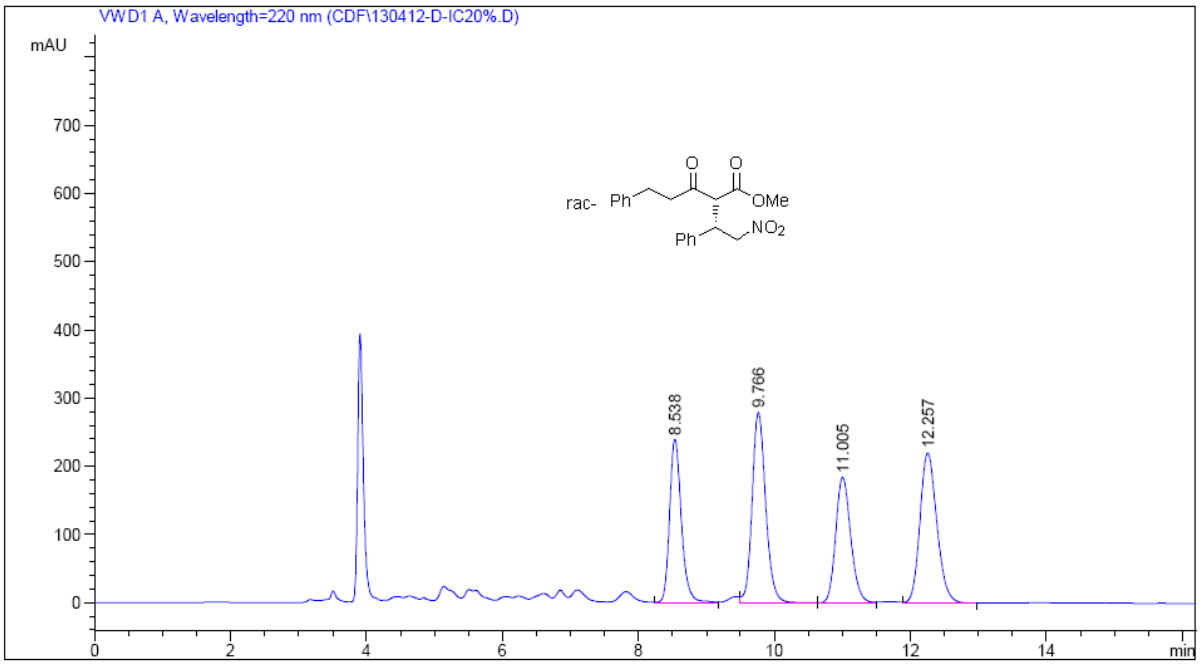

106L13_CDF_130428_2
C13CPD CDCl3 D:\\ gongliuzhu
175.1
152.1
151.5
148.3
147.1
140.3
138.2
128.9
127.9
127.3
109.9
109.3
106.4
106.1
49.0
47.5
47.3
46.4
46.3
45.7
13.7
13.5
O
NH
Ph
6
f1 (ppm)



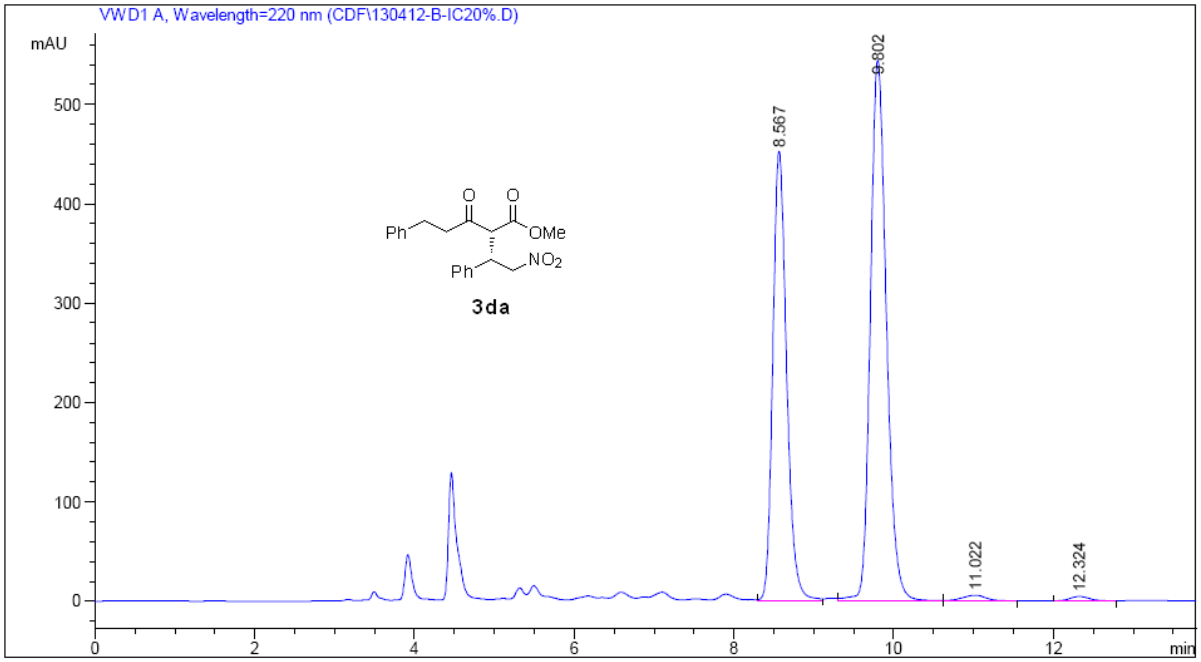
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.048	VV	0.1551	3606.75122	354.38651	18.7784
2	8.484	VV	0.1885	5980.94141	486.73535	31.1395
3	9.271	VV	0.2015	3589.26245	275.51825	18.6873
4	9.778	VB	0.2183	6029.96436	424.06894	31.3948



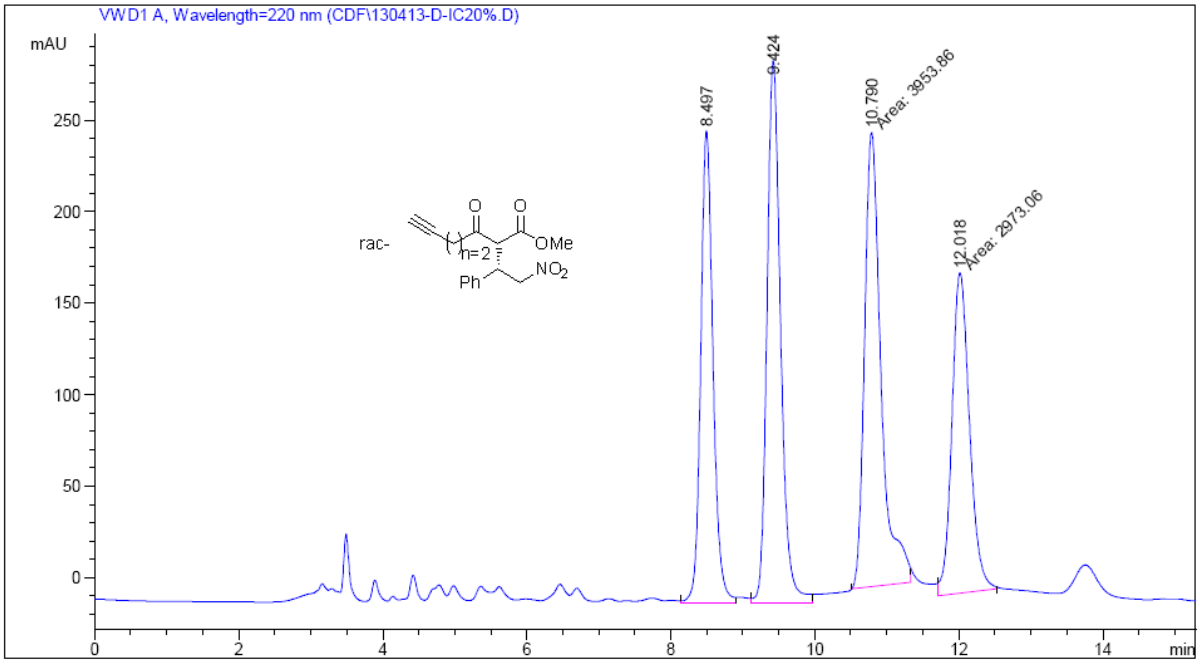
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.007	BV	0.1450	3835.78857	406.43787	36.6204
2	8.428	BV	0.1787	6441.97607	556.81561	61.5018
3	9.117	VV	0.3206	121.30968	5.95600	1.1581
4	9.728	VB	0.2103	75.38403	5.46998	0.7197



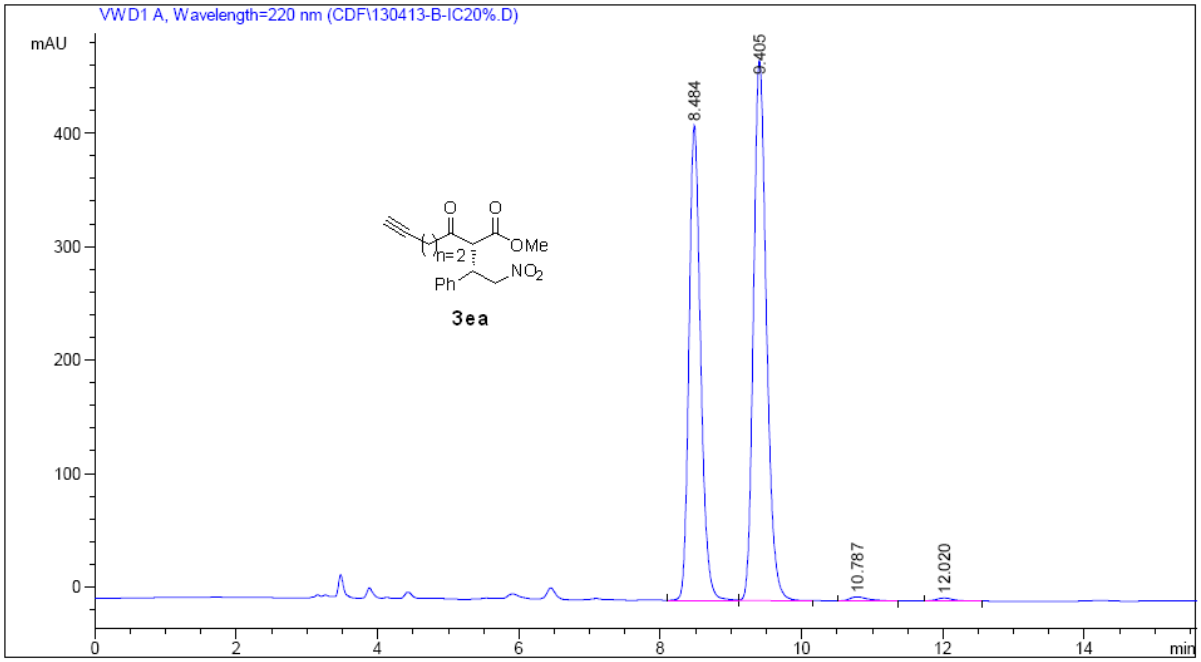
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.538	VV	0.1868	2917.03906	240.25330	21.6580
2	9.766	VV	0.2132	3889.95874	279.67722	28.8816
3	11.005	VV	0.2383	2845.64795	184.38074	21.1280
4	12.257	VB	0.2693	3815.99561	220.02940	28.3324



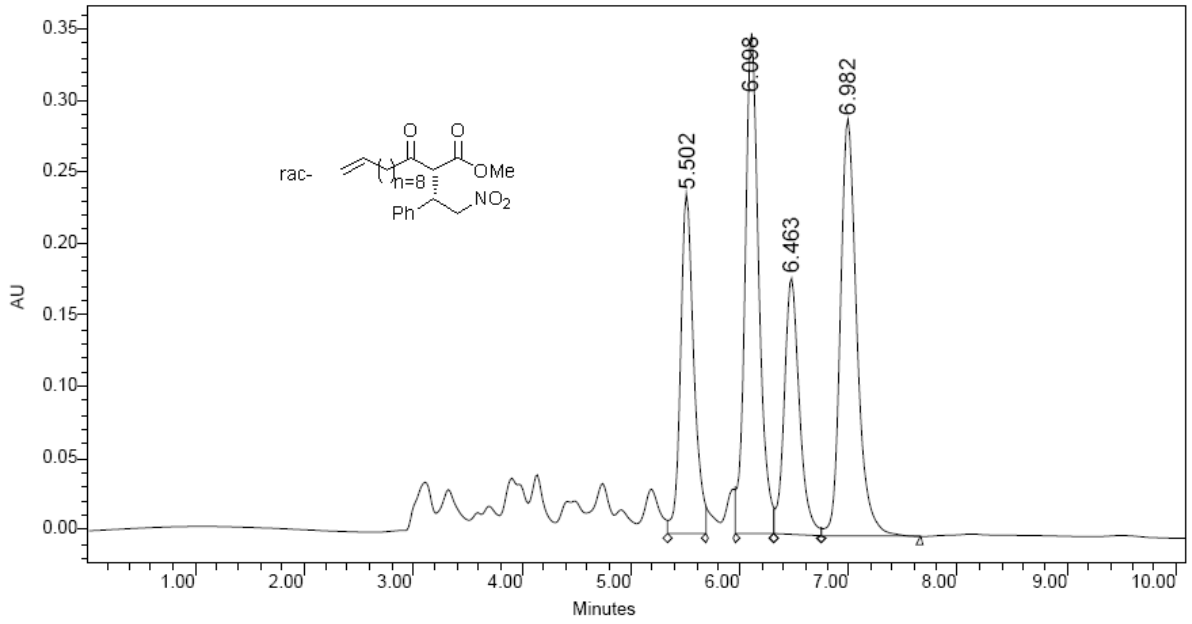
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.567	BV	0.1852	5432.83984	452.62158	41.1291
2	9.802	VB	0.2151	7583.46680	543.96185	57.4104
3	11.022	BB	0.3133	116.68601	5.72870	0.8834
4	12.324	BB	0.2624	76.23893	4.48418	0.5772



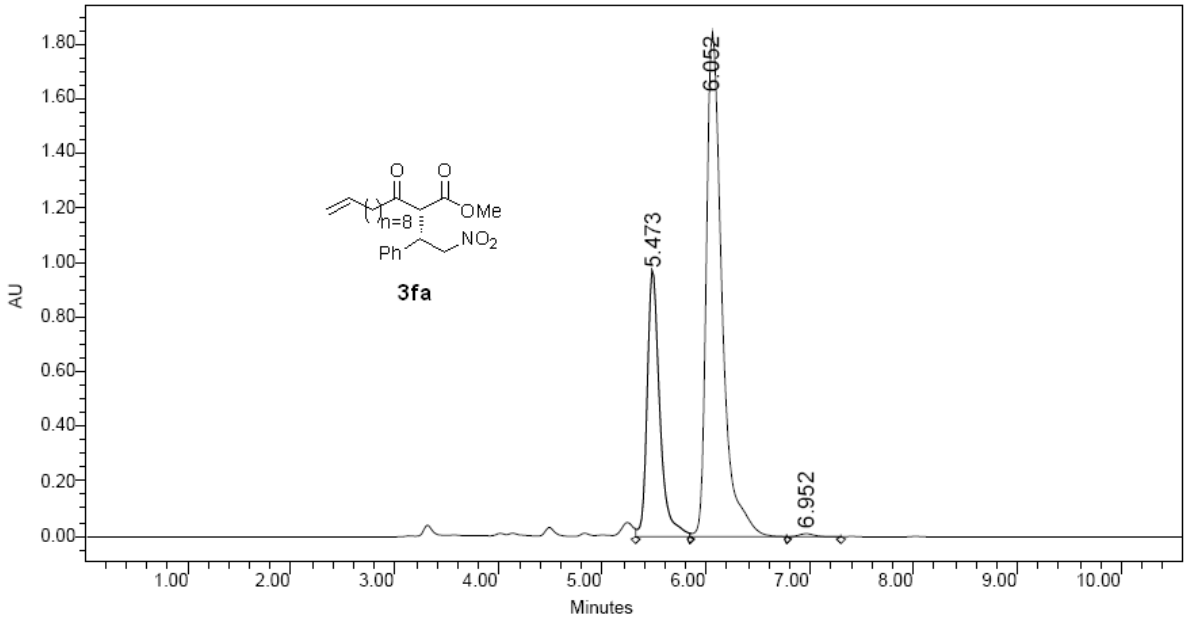
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.497	VV	0.1801	3039.29761	257.26315	21.9464
2	9.424	VV	0.2012	3882.50854	295.73712	28.0351
3	10.790	MM T	0.2655	3953.85742	248.18892	28.5503
4	12.018	MM T	0.2832	2973.05981	174.95692	21.4681



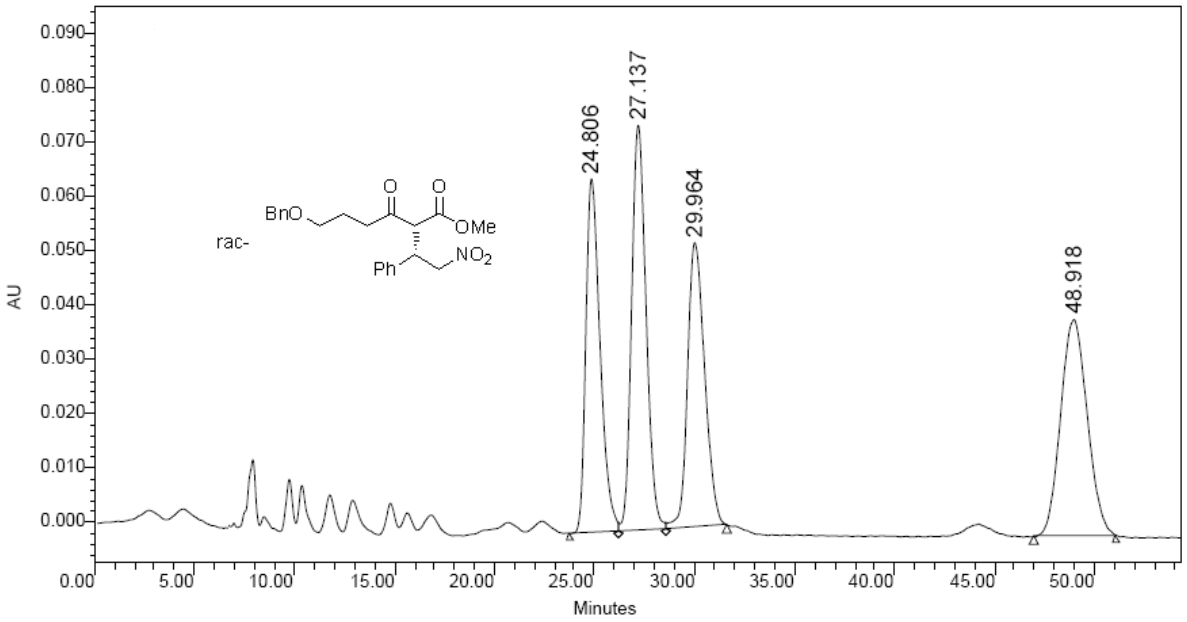
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.484	VV	0.1760	4803.72461	419.06570	43.7562
2	9.405	VB	0.1966	6064.91992	476.22531	55.2442
3	10.787	BB	0.2580	65.00278	3.68815	0.5921
4	12.020	BB	0.2612	44.73731	2.58984	0.4075



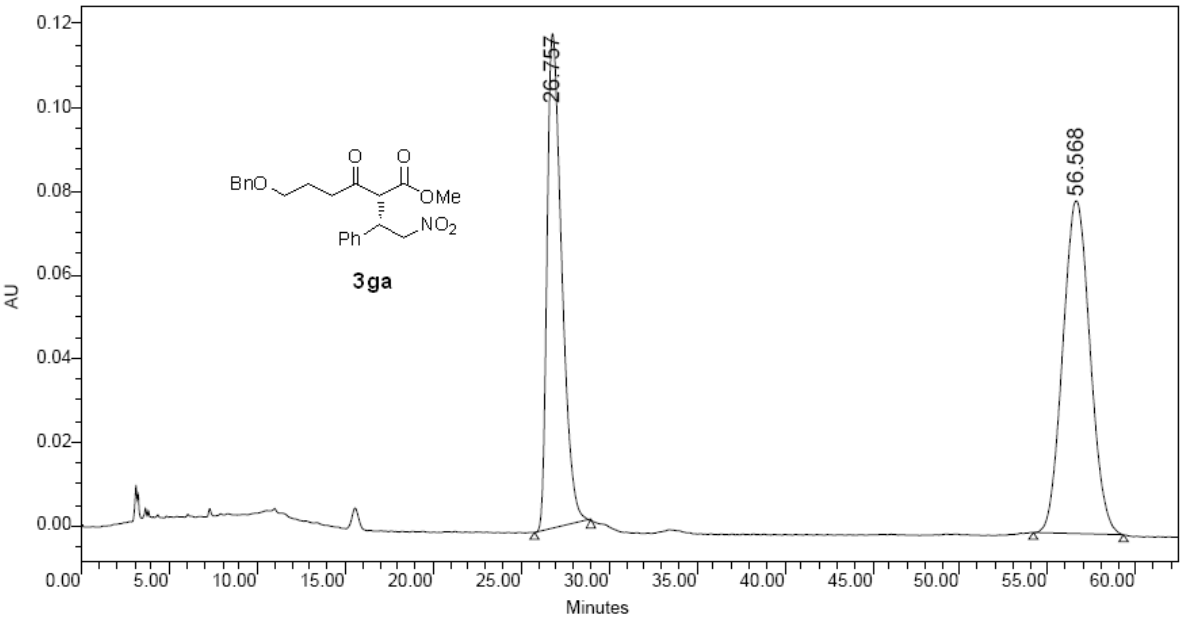
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	5.502	2027535	20.38	238027	22.46
2	6.098	3097266	31.13	350607	33.08
3	6.463	1744940	17.54	179969	16.98
4	6.982	3079104	30.95	291244	27.48



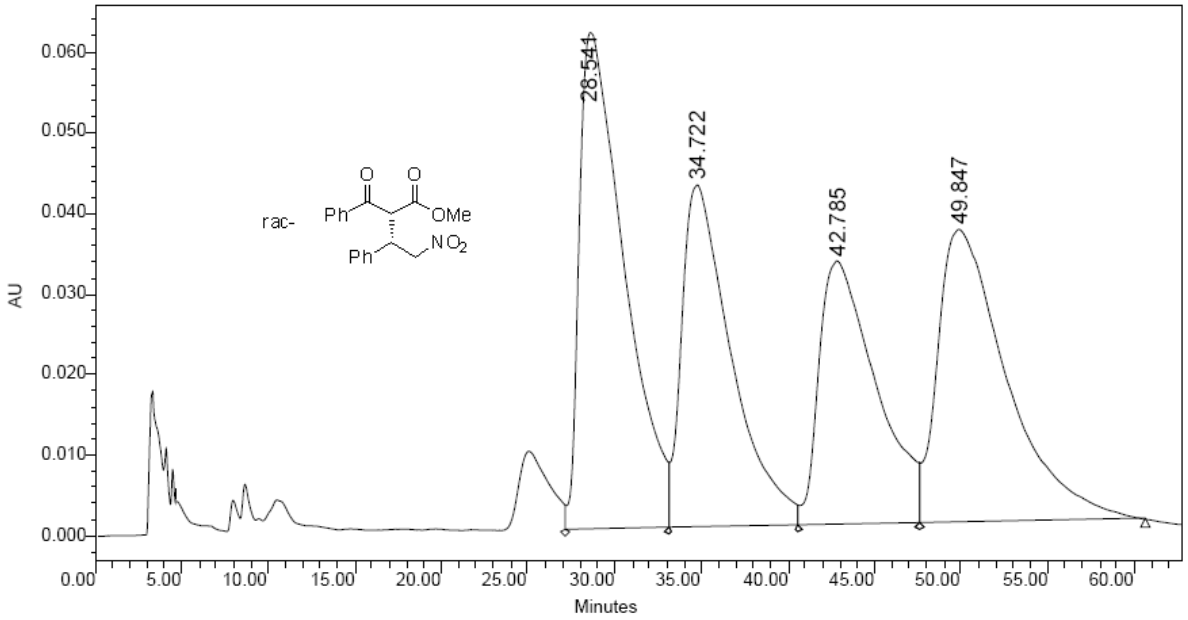
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	5.473	8287067	29.65	979085	34.50
2	6.052	19509004	69.80	1846354	65.06
3	6.952	154641	0.55	12609	0.44



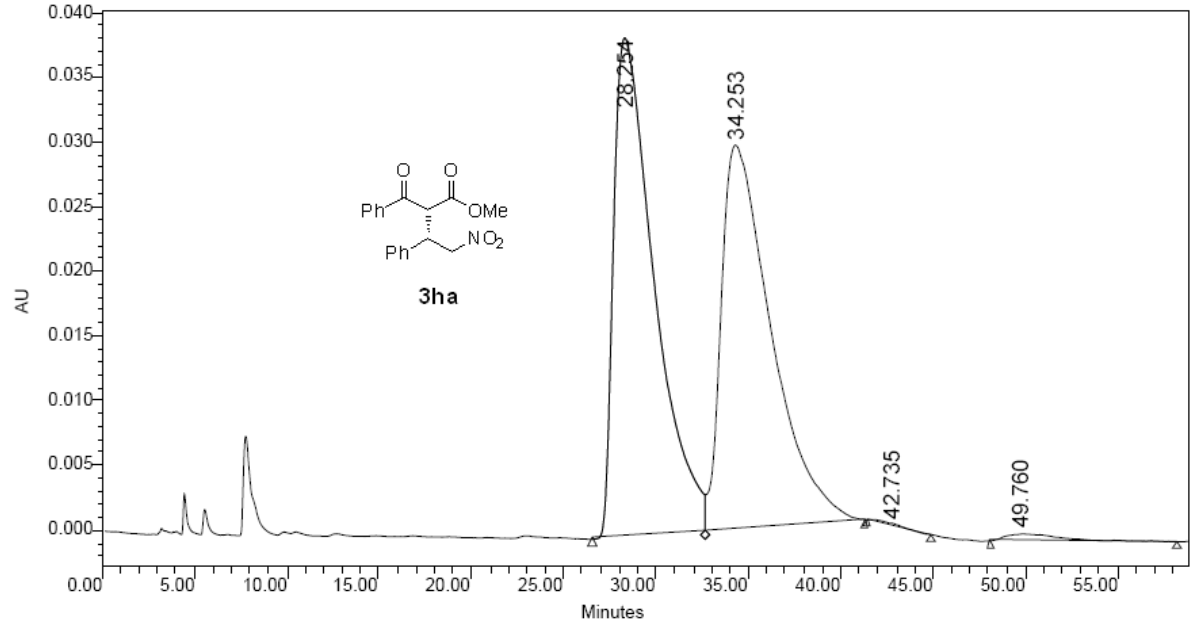
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	24.806	3237939	23.40	65184	28.08
2	27.137	3752765	27.13	74569	32.12
3	29.964	3136007	22.67	52472	22.60
4	48.918	3707900	26.80	39908	17.19



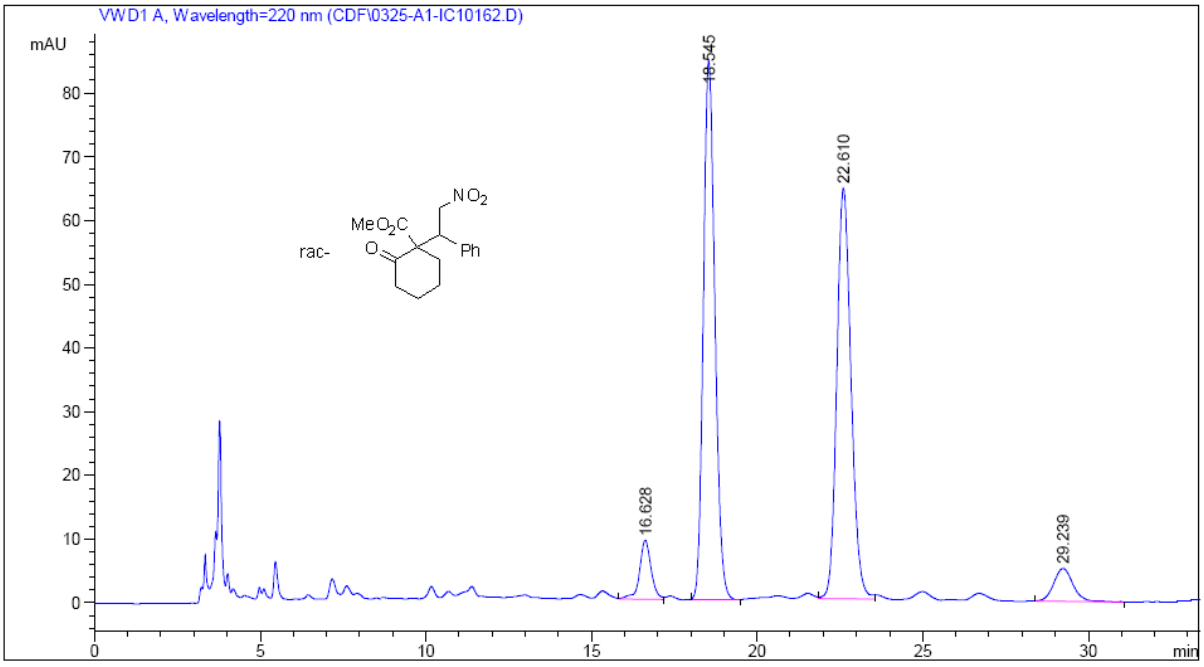
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	26.757	6905375	44.49	118462	59.81
2	56.568	8614149	55.51	79591	40.19



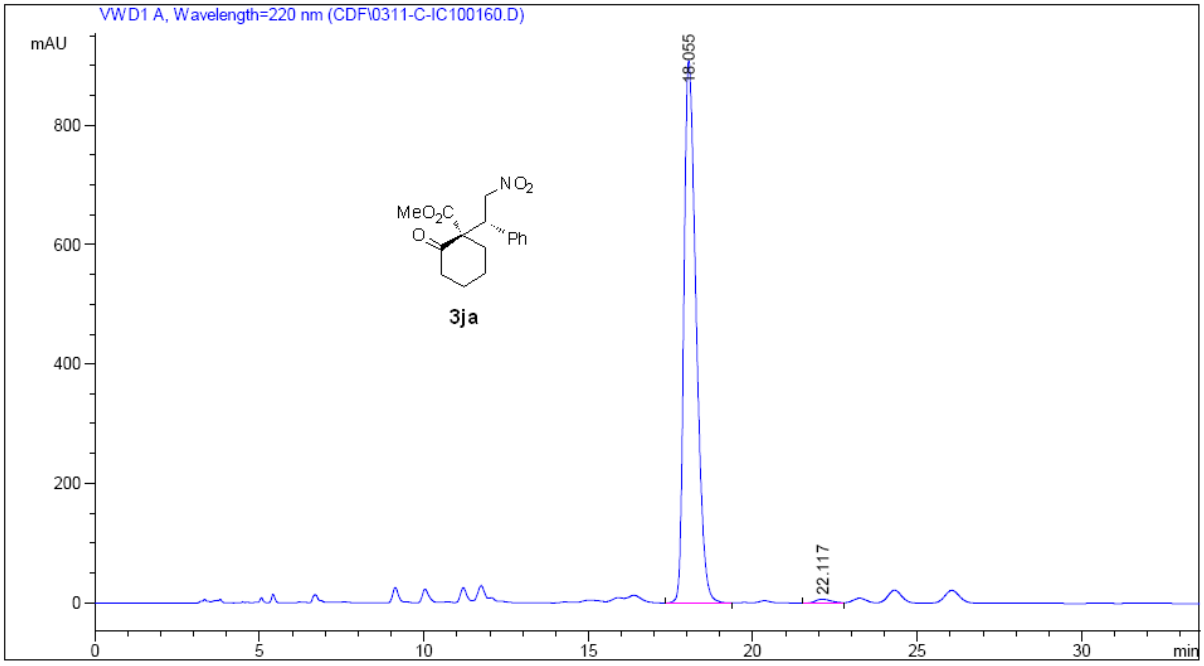
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	28.541	11134856	29.87	61635	35.57
2	34.722	8481578	22.76	42479	24.51
3	42.785	7512601	20.16	32757	18.90
4	49.847	10143734	27.21	36423	21.02



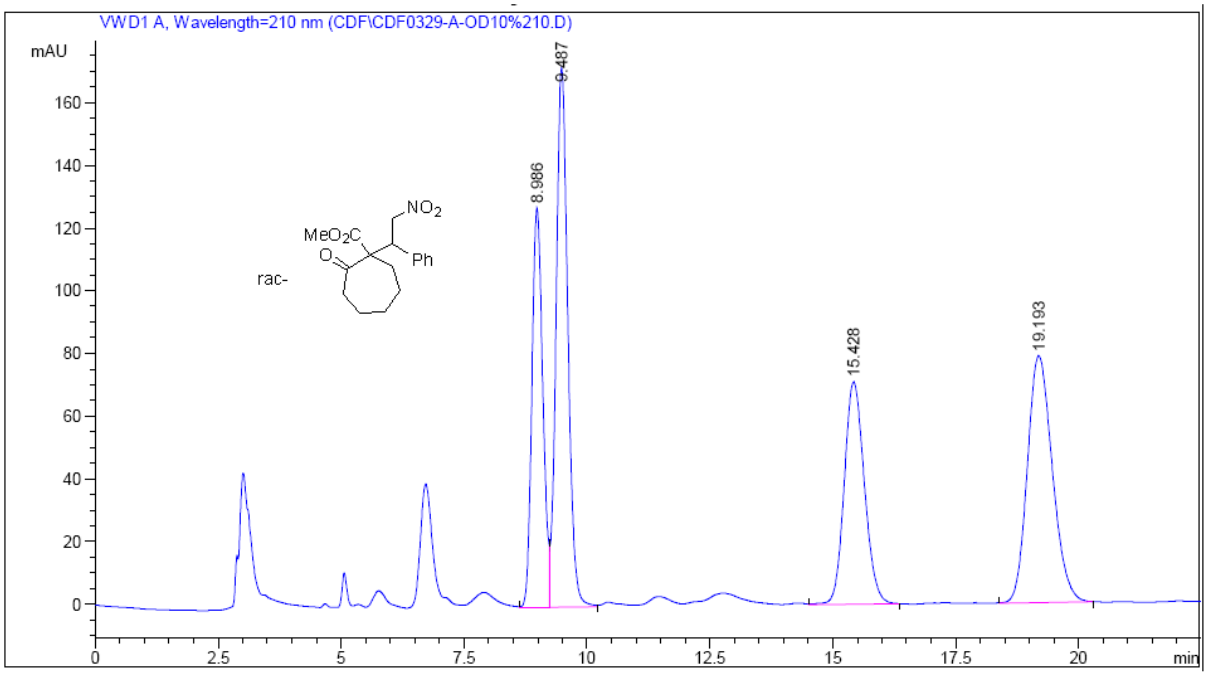
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	28.254	5891578	50.73	38570	55.93
2	34.253	5587268	48.11	29682	43.04
3	42.735	17312	0.15	174	0.25
4	49.760	118443	1.02	539	0.78



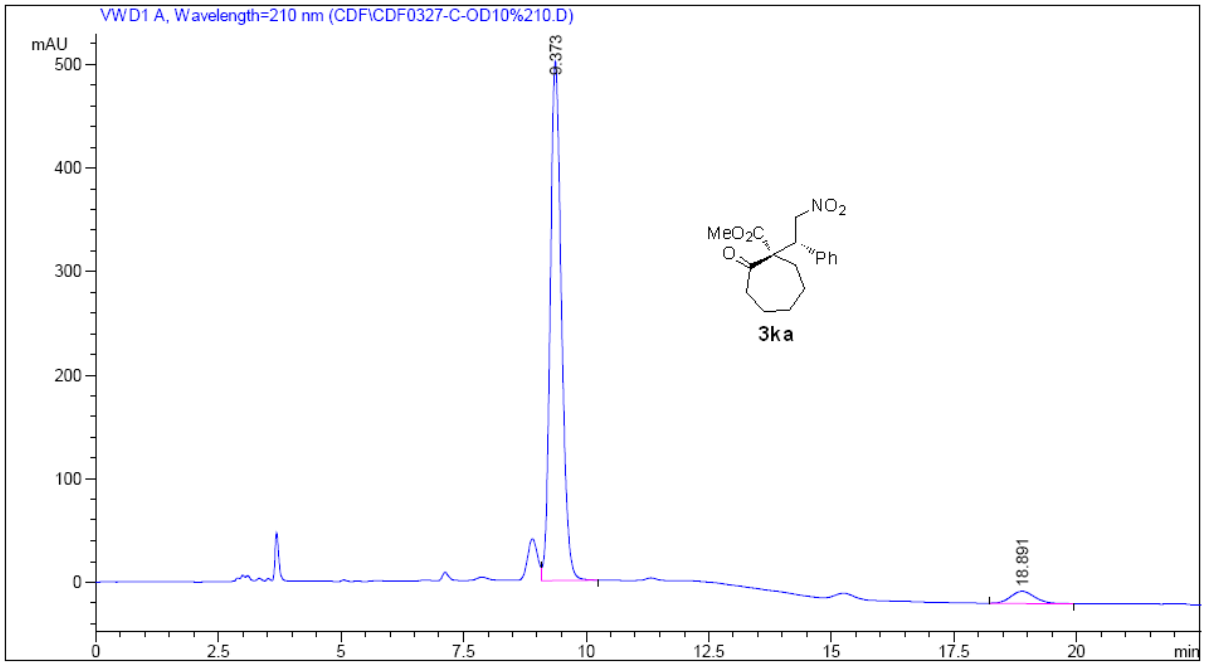
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.628	VV	0.3696	226.38724	9.26372	5.1418
2	18.545	BB	0.3749	2040.78577	84.51760	46.3512
3	22.610	VB	0.4623	1925.69019	64.42747	43.7371
4	29.239	BB	0.6256	210.01315	5.16715	4.7699



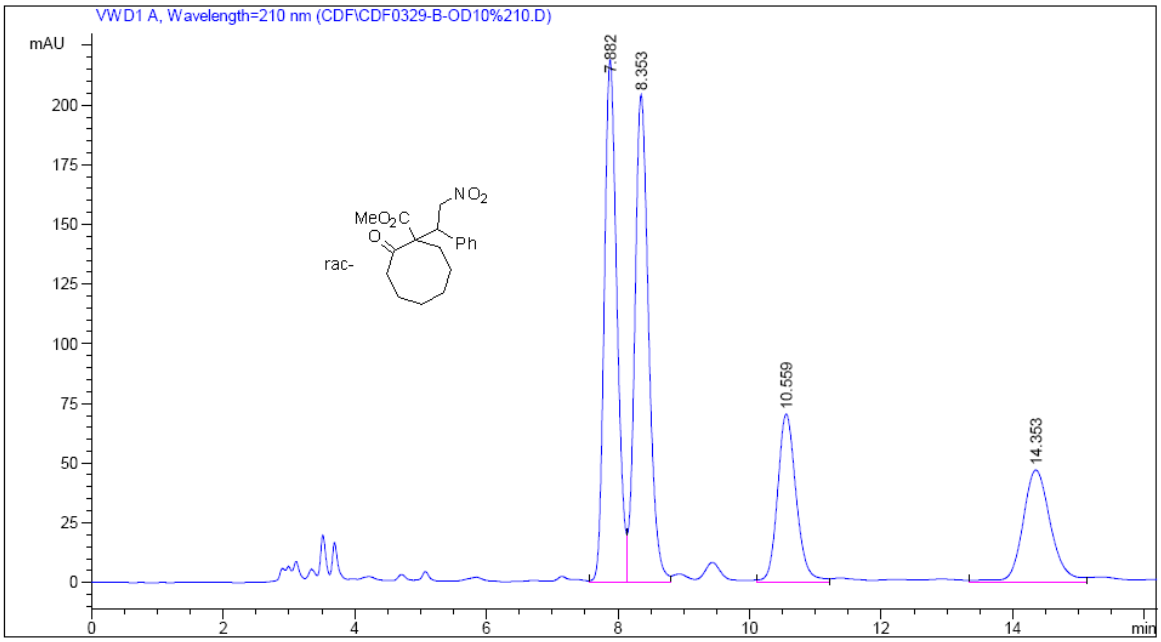
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.055	VB	0.4018	2.34851e4	909.29431	98.9810
2	22.117	VV	0.5140	241.77689	7.04420	1.0190



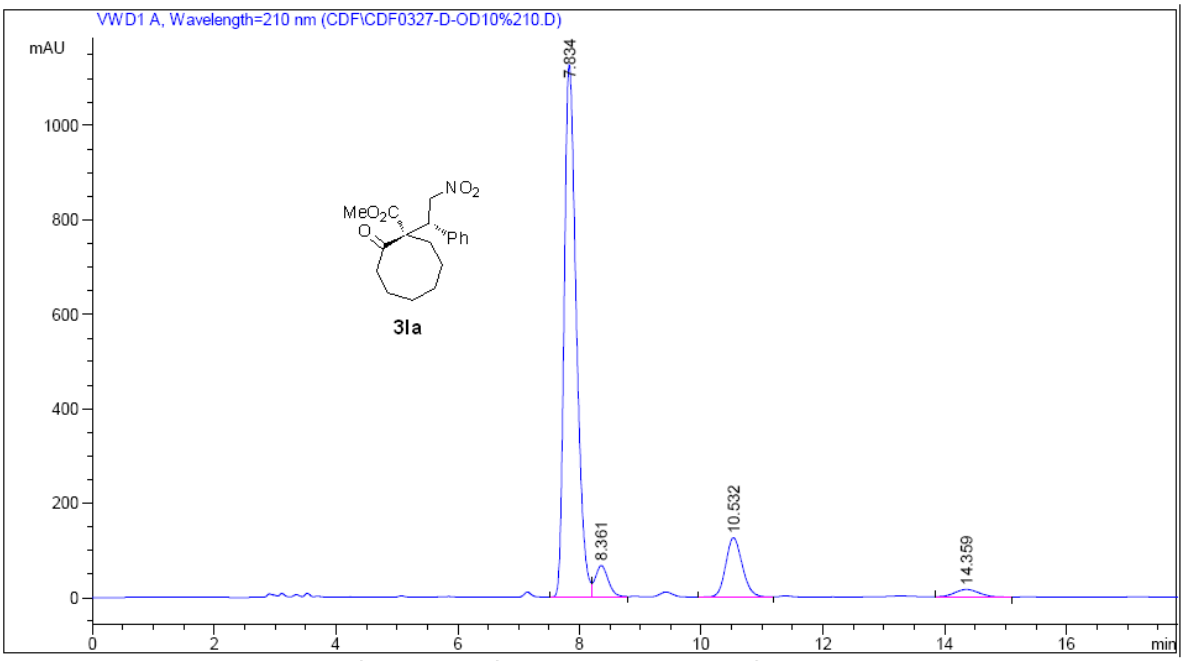
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.986	VV	0.2388	1958.20764	127.52129	20.3487
2	9.487	VV	0.2565	2856.60547	171.90135	29.6844
3	15.428	VB	0.4443	2028.56689	70.93903	21.0798
4	19.193	BB	0.5472	2779.87549	78.75198	28.8871



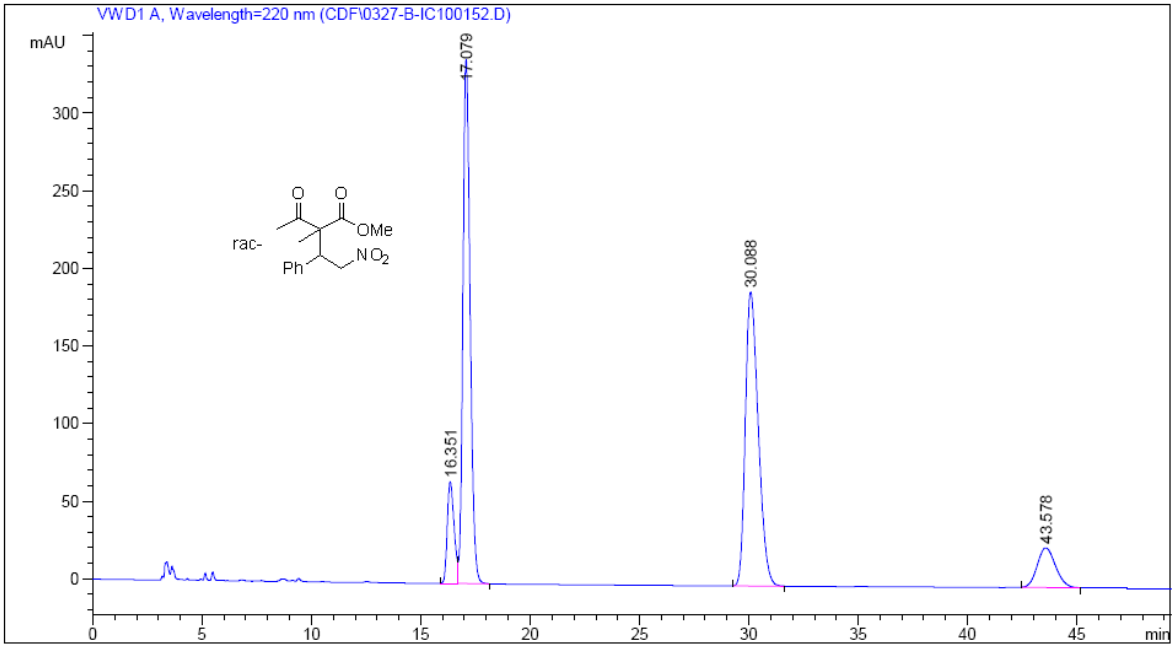
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.373	VB	0.2447	7951.53564	501.32217	95.2189
2	18.891	BB	0.5196	399.26181	11.68188	4.7811



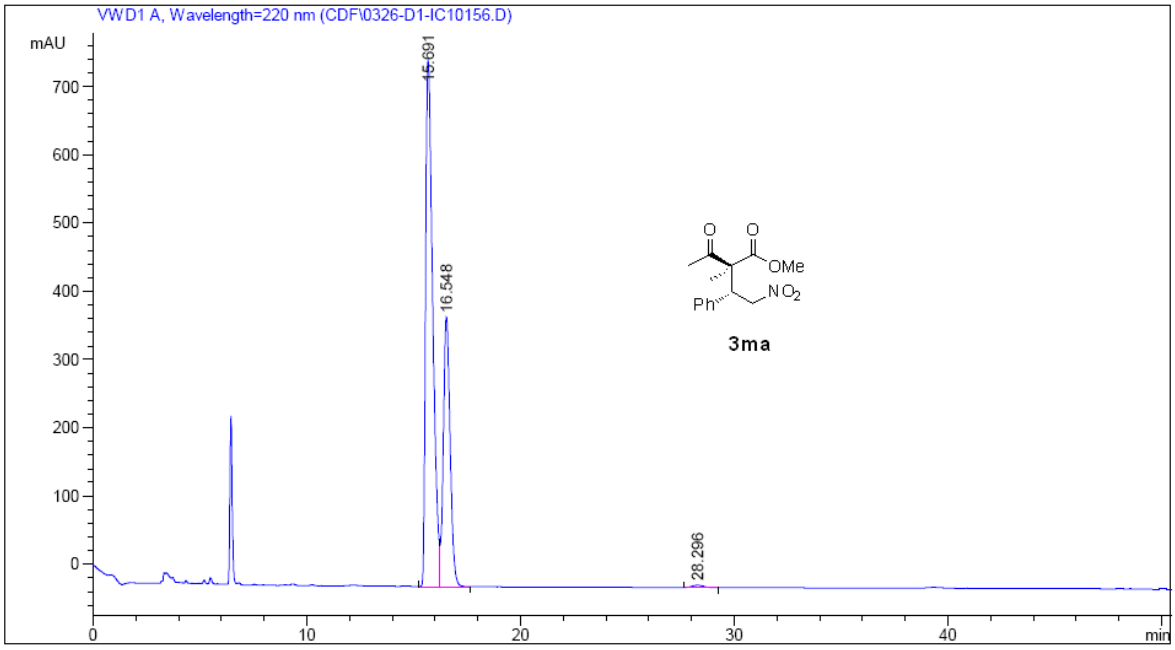
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.882	BV	0.2071	2930.05835	219.00027	33.5950
2	8.353	VV	0.2232	2991.99390	204.44043	34.3052
3	10.559	BV	0.3044	1400.41943	70.55777	16.0567
4	14.353	VB	0.4524	1399.22925	47.16156	16.0431



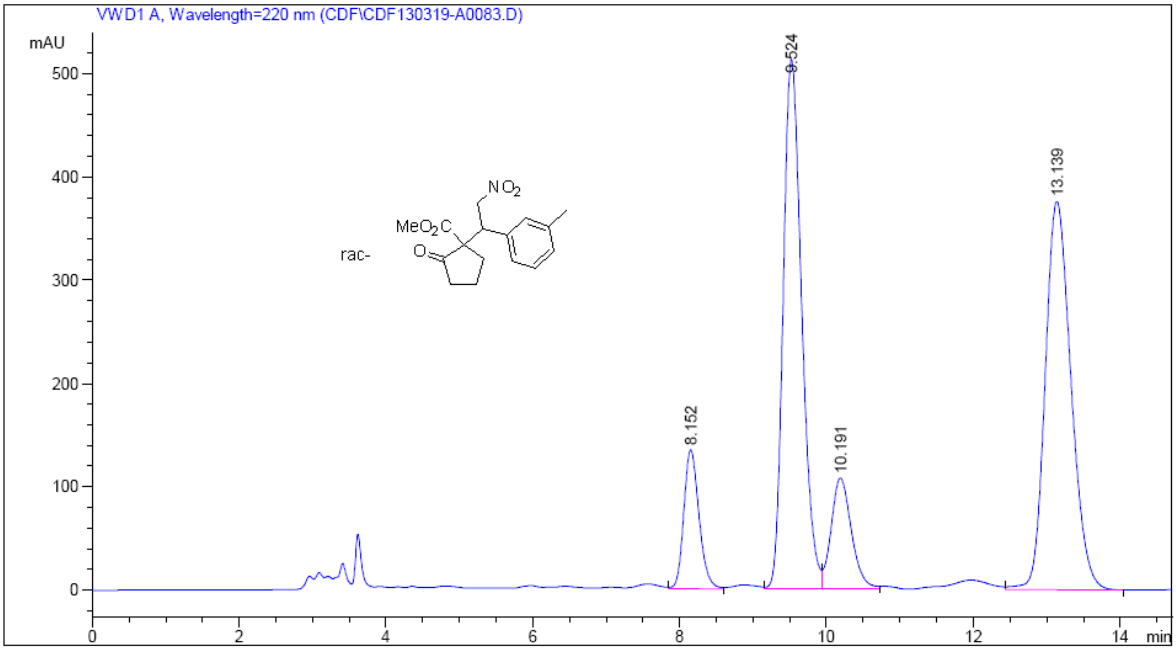
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.834	VV	0.2119	1.55688e4	1128.78845	79.9573
2	8.361	VV	0.2275	1021.52307	67.49862	5.2463
3	10.532	VV	0.2945	2411.64526	126.10632	12.3855
4	14.359	VV	0.4455	469.43552	16.28344	2.4109



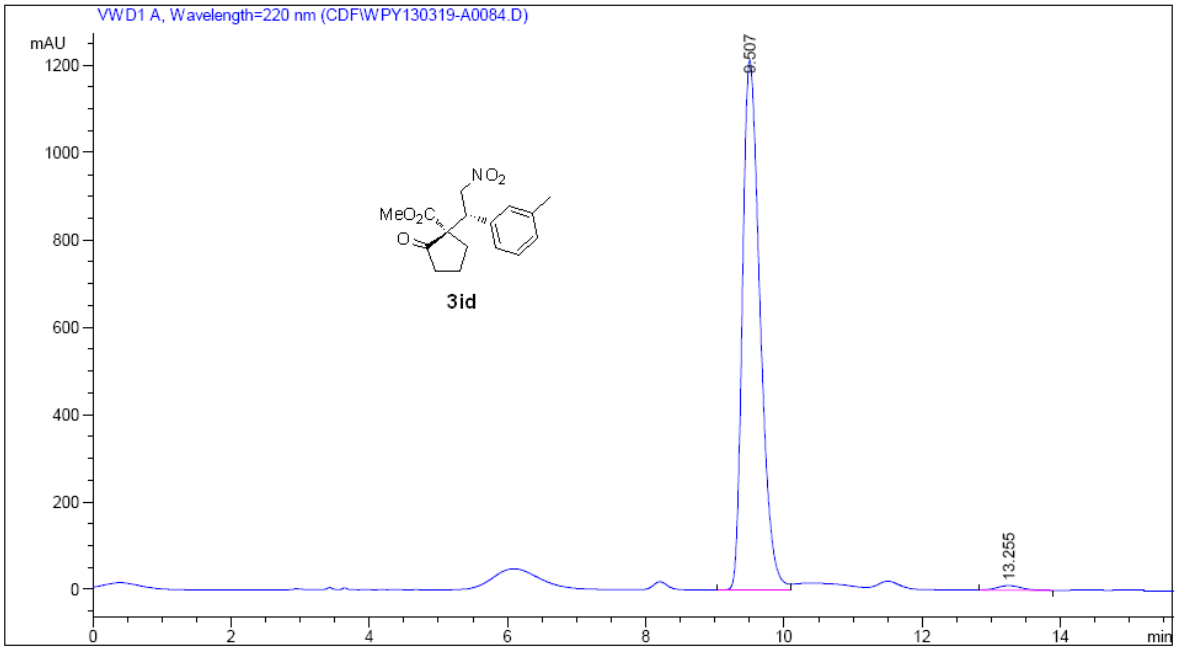
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.351	BV	0.3368	1421.27014	65.32420	7.7302
2	17.079	VB	0.3505	7695.88232	337.52994	41.8573
3	30.088	BB	0.6366	7775.92432	189.26443	42.2927
4	43.578	BB	0.9077	1492.90833	25.59149	8.1198



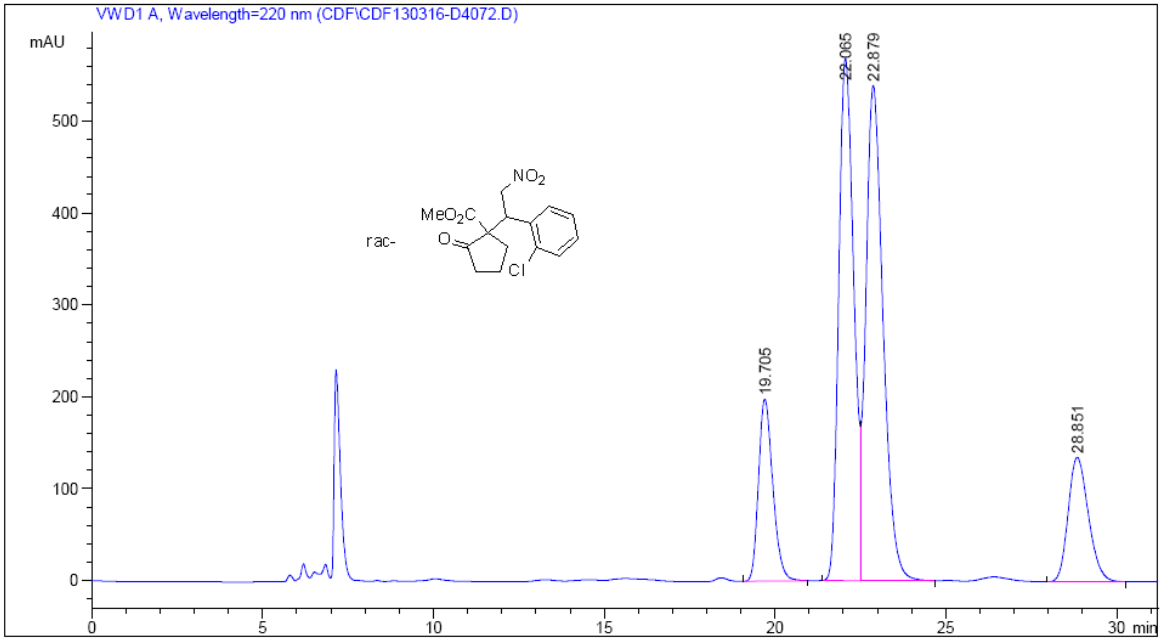
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.691	VV	0.3558	1.79523e4	771.73865	66.9509
2	16.548	VB	0.3397	8740.97852	394.97717	32.5985
3	28.296	BB	0.5461	120.83073	3.39606	0.4506



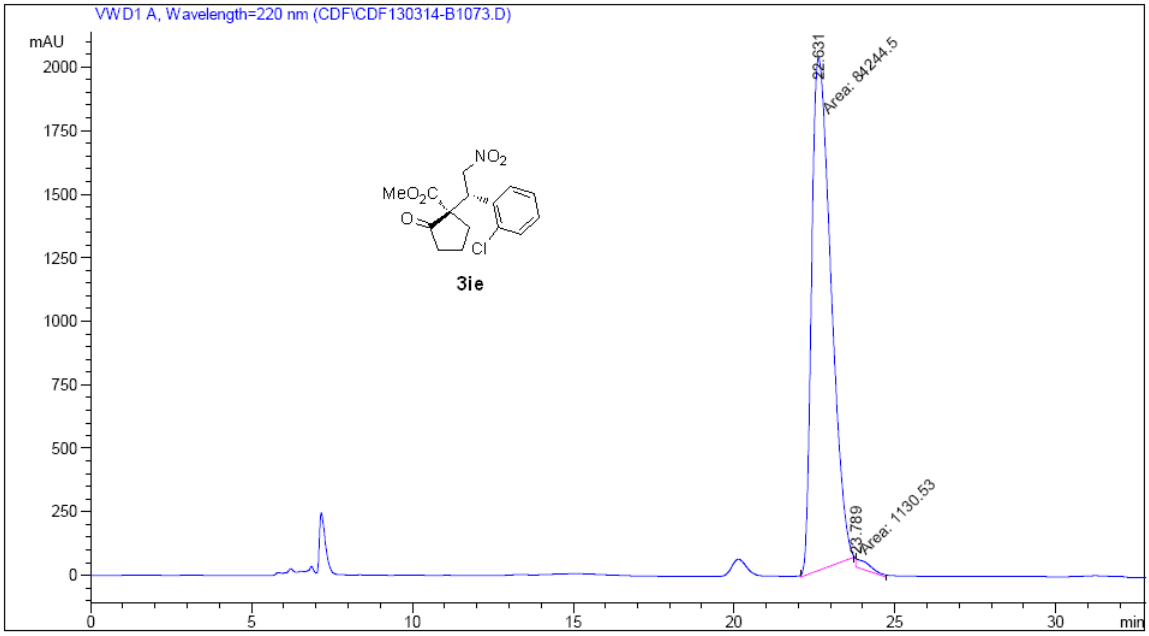
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.152	VV	0.2218	1937.34900	134.59714	8.7446
2	9.524	VV	0.2709	8966.56543	512.97906	40.4721
3	10.191	VV	0.2949	2076.04517	107.66341	9.3706
4	13.139	VB	0.3791	9174.95703	376.23843	41.4127



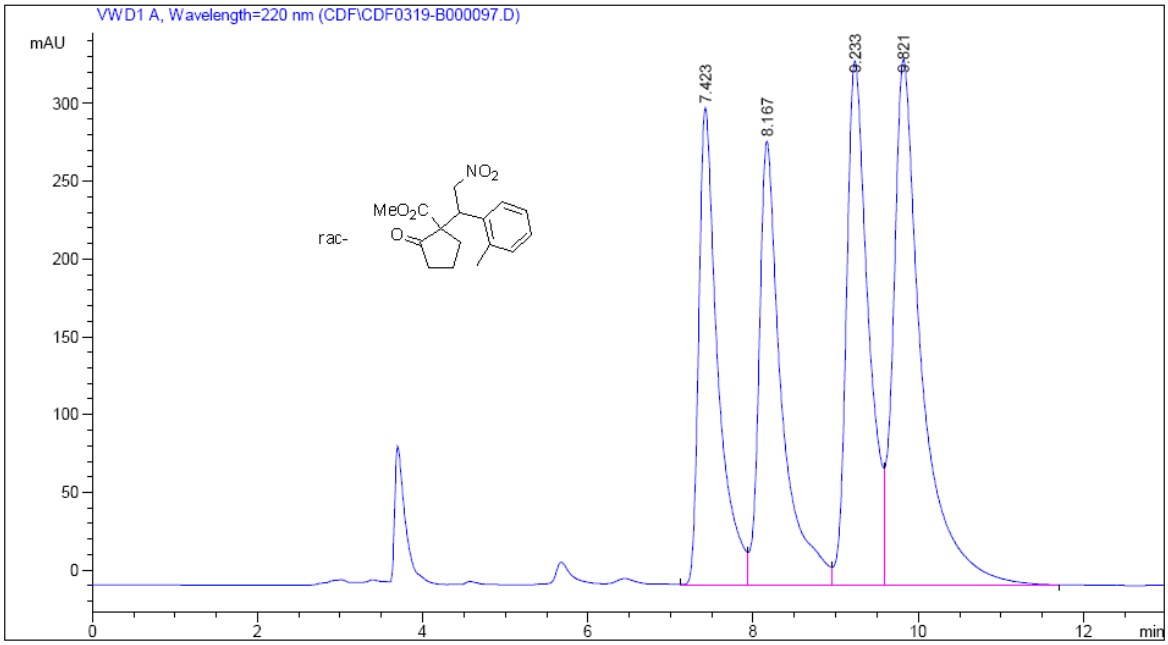
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.507	BV	0.2734	2.14785e4	1213.70715	98.8944
2	13.255	BB	0.3631	240.11440	10.26907	1.1056



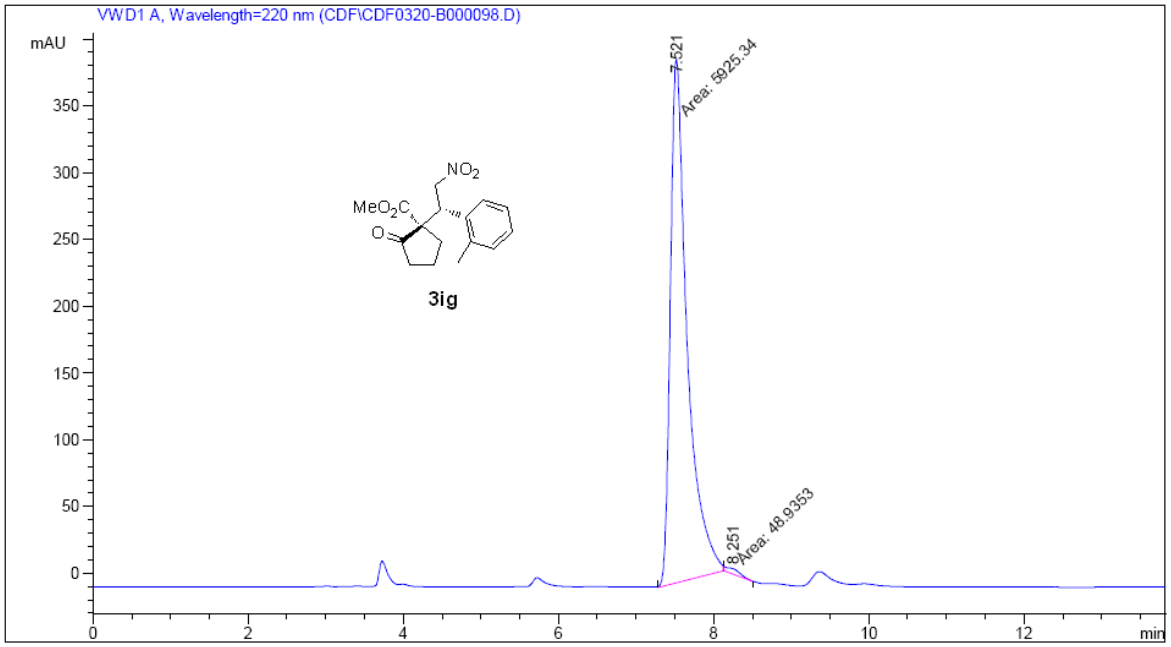
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.705	BB	0.4495	5772.01123	197.89561	12.1391
2	22.065	BV	0.4730	1.72260e4	568.27582	36.2280
3	22.879	VB	0.5298	1.89606e4	538.99890	39.8762
4	28.851	BB	0.6411	5590.13818	135.61095	11.7566



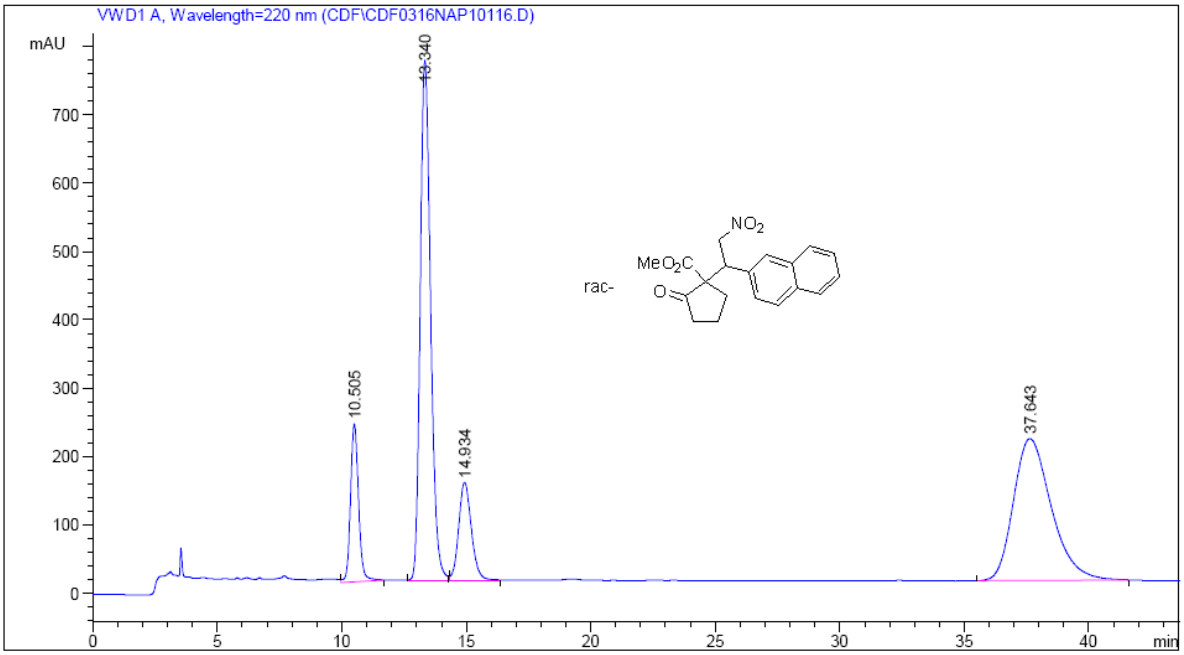
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	22.631	MM T	0.6964	8.42445e4	2016.26257	98.6758
2	23.789	MM T	0.4247	1130.53357	34.07327	1.3242



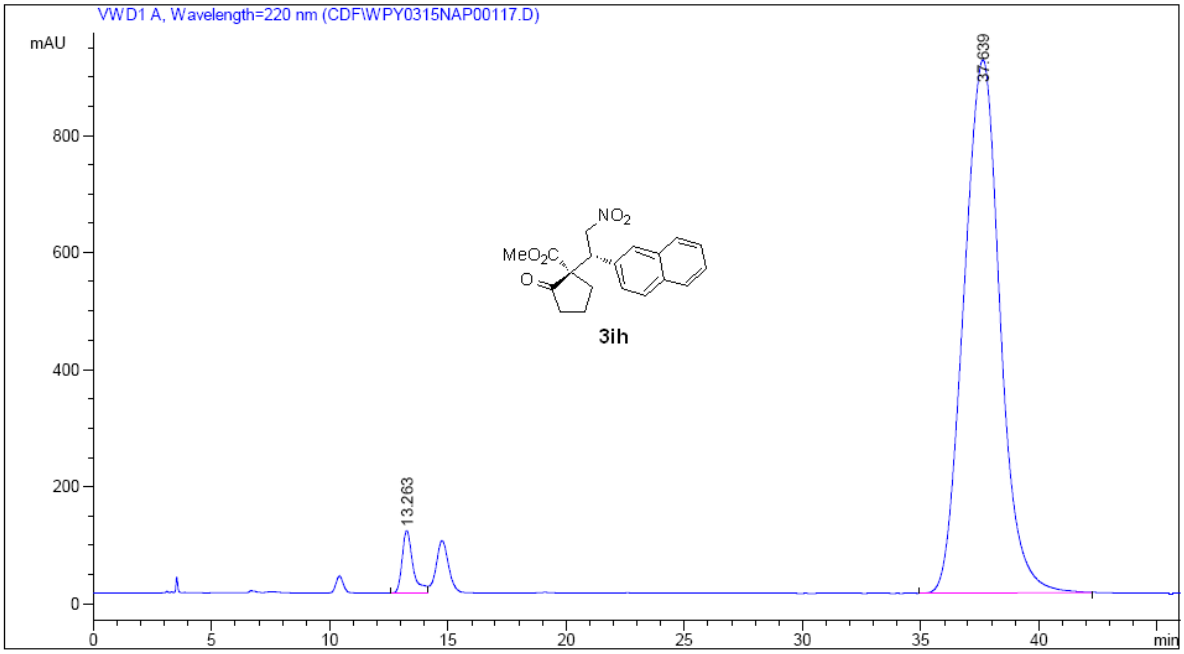
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.423	VV	0.2330	4943.23438	306.92804	20.1608
2	8.167	VV	0.2685	5389.02002	285.18512	21.9789
3	9.233	VV	0.2689	6170.64795	337.04190	25.1668
4	9.821	VB	0.3365	8016.12061	337.89905	32.6935



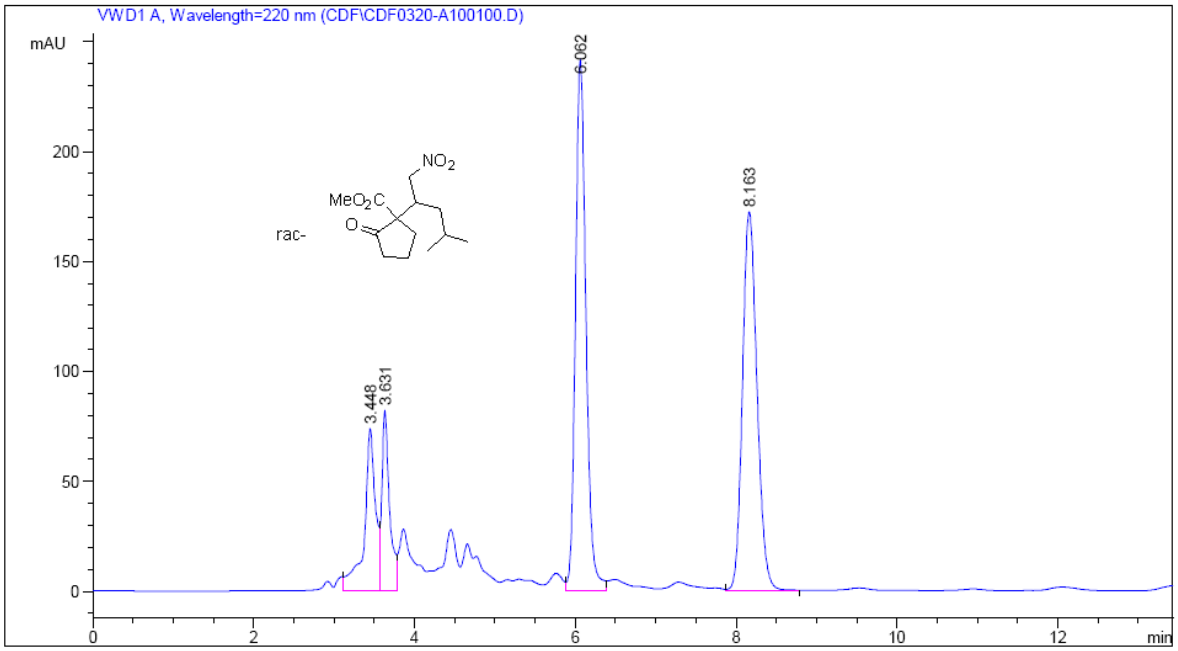
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.521	MM T	0.2520	5925.34082	391.82938	99.1809
2	8.251	MM T	0.1976	48.93531	4.06988	0.8191



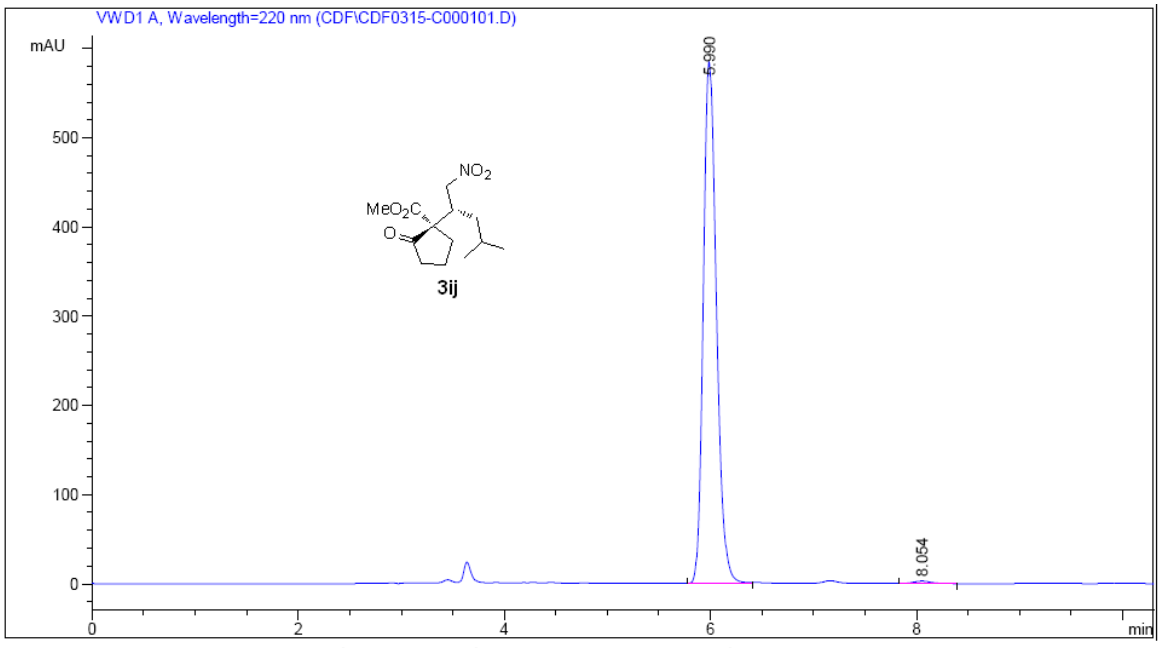
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.505	VB	0.3454	5206.53516	231.45364	9.6221
2	13.340	BV	0.4459	2.19354e4	760.04700	40.5385
3	14.934	VB	0.5413	5028.62012	143.01169	9.2933
4	37.643	BB	1.6208	2.19395e4	207.51237	40.5461



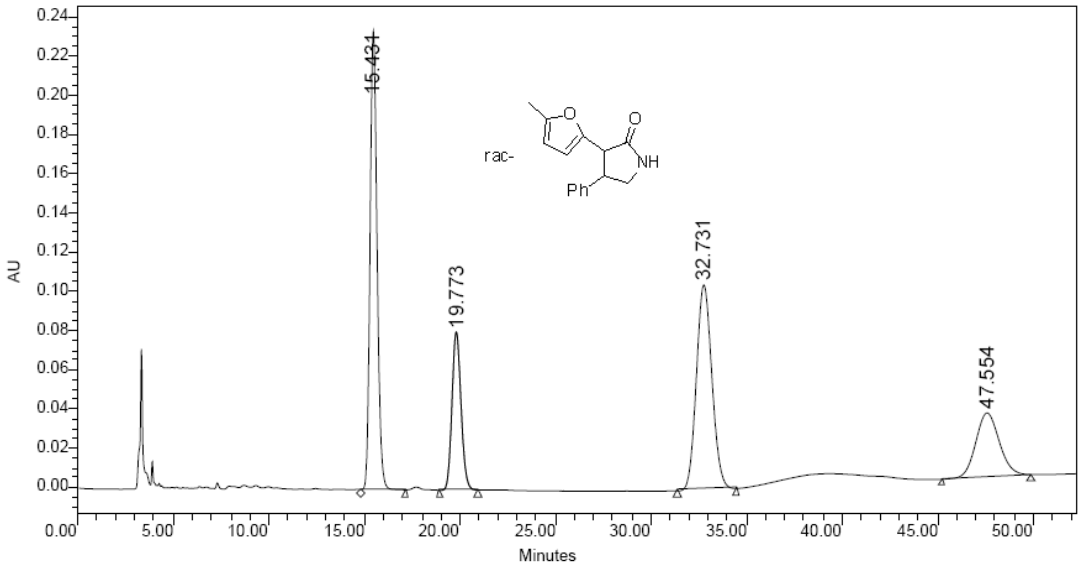
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.263	BV	0.4810	3424.77441	107.04883	3.4062
2	37.639	BB	1.6589	9.71220e4	910.89758	96.5938



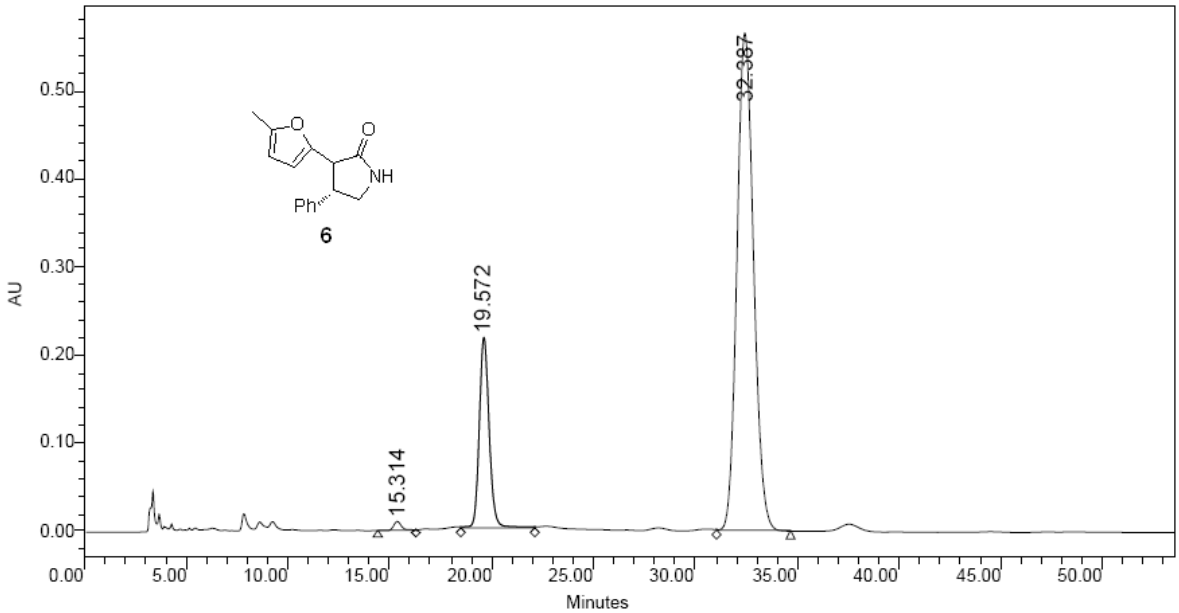
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	3.448	VV	0.1327	702.05115	73.86320	12.5302
2	3.631	VV	0.0954	549.05493	82.15633	9.7995
3	6.062	VV	0.1398	2197.02612	241.18153	39.2124
4	8.163	VB	0.1940	2154.75415	172.22391	38.4579



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.990	BB	0.1368	5176.01807	584.23676	99.3777
2	8.054	BB	0.1862	32.41217	2.70929	0.6223



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	15.431	5959078	34.38	233958	51.78
2	19.773	2665973	15.38	80743	17.87
3	32.731	5912929	34.11	104534	23.13
4	47.554	2797417	16.14	32610	7.22



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	15.314	300921	0.75	10448	1.32
2	19.572	7786422	19.35	218120	27.48
3	32.387	32156432	79.90	565270	71.21