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Organocatalytic asymmetric conjugate addition of *t*-butyl nitroacetate to *o*-quinone methides: Synthesis of optically active α-nitro-β,β-diaryl-propionates

Ri-long Liu, Xiang-zheng Tang, Xue-jing Zhang, Ming Yan*, Albert S. C. Chan

Institute of Drug Synthesis and Pharmaceutical Process, School of Pharmaceutical Sciences, Sun Yat-sen University, Guangzhou 510006, China. E-mail: yanming@mail.sysu.edu.cn

Supporting Information

I. General information

^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer. Chemical shifts of protons are reported in parts per million downfield from tetramethylsilane. Chemical shifts of carbon are referenced to the carbon resonances of the solvent (CDCl3: d 77.0). Peaks are labeled as single (s), broad singlet (br), doublet (d), triplet (t), double doublet (dd), multiplet (m). Melting points were determined with a commercially available melting point apparatus. The IR spectra were recorded as thin films with KBr and reported in wavenumbers (cm^{-1}). High-resolution mass spectra (HRMS) were acquired using an electron spray ionization time-offflight (ESI-TOF) mass spectrometer in positive mode. All reagents were used without further purification as received from commercial suppliers unless otherwise noted. All solvents were dried and distilled prior to use according to the standard protocols. 2-Tosylmethylphenols **2a**-**2m** were prepared according to the reported procedure.[1]

II. Synthetic procedures of products 3-6

(1) General procedure for the addition of *t*-butyl nitroacetate to *o*-QMs: To a solution of 2-tosylmethylphenol **2** (0.20 mmol) and catalyst **1a** (0.02 mmol) in $CHCl_3$ (2.5 mL) was added *t*-butyl nitroacetate (0.40 mmol) and 5% aqueous $NaHCO_3$ (16.8 mL). The reaction mixture was stirred at rt for 72 h and then was extracted with CH_2Cl_2 (15 mL × 3). The combined organic layers were washed with brine (50 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate =10:1) to give the product **3**.

(2) General synthetic procedure of 5:[2] To a stirred solution of **3** (1.58 mmol) in CH_2Cl_2 (30 mL) was added trifluoroacetic acid (4.8 mL). The reaction mixture was refluxed for 3 h. The solvent was evaporated under the reduced pressure. The residue was purified by flash chromatography over silica gel (petroleum ether/ethylacetate = 20:1) to give **5**.

(3) General synthetic procedure of 4:[3] To a 10 mL round flask was added a solution of NaOH (30.0 mg, 0.75 mmol) in water (10 mL). A solution of **5** (0.15 mmol) in 1 mL THF was added at 0℃. The resulting orange solution was stirred at 0℃ for 45 min. The solution was acidified to pH = 4.0 by adding aqueous 1.5 M H_2SO_4. The solution was saturated with NaCl and extracted with ethyl acetate (10 mL × 2). The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was purified by column chromatography over silica gel (petroleum ether/ethyl acetate = 10:1) to give **4**.

(4) General synthetic procedure of 6: To a solution of **4** (0.2 mmol) in MeOH/CH_2Cl_2 (1:1, 20 mL) was added 10 wt% Pd/C (28 mg). The mixture was stirred with a hydrogen balloon for 3 h at room temperature. After the filtration over celite, the filtrate was concentrated under vacuum to afford the amine intermediate as a colorless oil. The oil was dissolved in CH_2Cl_2 (10 mL) under an ice bath. After triethylamine (22.3 mg, 0.22 mmol) was added in a portion, a solution of $(Boc)_2O$ (48 mg, 0.22 mmol) in CH_2Cl_2 (5 mL) was added dropwise. The reaction mixture was stirred under the ice bath for 20 min, and then at room temperature for 12 h. The mixture was diluted with CH_2Cl_2 (10 mL) and washed with water (20 mL × 2). The combined organic layer was dried

over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was purified by column chromatography over silica gel (petroleum ether/ethylacetate = 10:1) to afford **6**.

III. Characterization data of products 3-6

(3S)-tert-butyl 3-(2-hydroxyphenyl)-2-nitro-3-phenylpropanoate (3a)

White solid, mp 144.8 – 146.5℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (m, 4H), 7.33 – 7.16 (m, 8H), 7.11 – 7.01 (m, 2H), 6.88 (t, *J* = 7.5, 1H), 6.87 (t, *J* = 7.5, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 6.66 (d, *J* = 8.0 Hz, 1H), 6.21 (dd, *J* = 12.0, 1H), 6.21 (dd, *J* = 12.0, 1H), 5.58 (s, 2H), 5.26 (d, *J* = 12.0 Hz, 2H), 1.22 (s, 9H), 1.21 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.8, 162.8, 153.4, 153.2, 138.5, 137.5, 129.9, 129.0, 128.9, 128.8, 128.7, 128.6, 128.1, 127.7, 127.6, 127.5, 125.6, 125.0, 121.3, 121.2, 116.7, 116.6, 91.1, 90.8, 84.8, 84.7, 47.6, 47.3, 27.3, 27.3. HRMS (ESI) calcd for $C_{19}H_{21}NO_5$ $(M + Na)^+$: 366.1317, found: 366.1312; $[\alpha]^{20}_D$ = +67.2 (*c* = 1.0, CH_2Cl_2); The enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (hexane/2-PrOH = 90:10, λ= 204 nm, 0.5 mL/min), t_R (major enantiomer) = 17.0 min, t_R (minor enantiomer)= 19.0 min, 97% ee; t_R (minor enantiomer) = 19.8 min, t_R (major enantiomer) = 24.5 min, 98% ee.

(3S)-tert-butyl 3-(2-hydroxy-5-methylphenyl)-2-nitro-3-phenylpropanoate (3b)

White solid, mp 130.5 – 132.7℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.5 Hz, 2H), 7.40 (d, *J* = 7.5 Hz, 2H),7.33 – 7.14 (m, 6H), 7.05 (s, 1H), 7.02 (s, 1H), 6.92 – 6.80 (m, 2H), 6.60 (d, *J* = 8.1 Hz, 1H), 6.56 (d, *J* = 8.1 Hz, 1H), 6.22 (d, *J* = 11.6 Hz, 1H), 6.19 (d, *J* = 11.6 Hz, 1H), 5.41 (s, 1H), 5.26 (s, 1H), 5.20 (d, *J* = 12.0, 1H), 5.18 (d, *J* = 12.0, 1H), 2.23 (s, 3H), 2.23 (s, 3H),1.23 (s, 9H), 1.21 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.9, 162.9, 151.1, 150.8, 138.6, 137.6, 130.5, 130.4, 130.4, 129.4, 129.2, 128.9, 128.8, 128.7, 128.7, 127.7, 127.6, 127.4, 125.2, 124.6, 116.6, 116.5, 91.0, 90.7, 84.7, 84.6, 47.9, 47.5, 27.3, 27.3, 20.7, 20.5. HRMS (ESI) calcd for $C_{20}H_{23}NO_5$ $(M + Na)^+$: 380.1474, found: 380.1468; $[\alpha]^{20}_D$ = +90.8 (*c* = 1.0, CH_2Cl_2); The enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexane/2-PrOH = 90:10, λ= 204 nm, 0.3 mL/min), t_R (major enantiomer) = 17.2 min, t_R (minor enantiomer) = 19.1 min, 97% ee; t_R (major enantiomer) = 18.3 min, t_R (minor enantiomer) = 28.8 min, 98% ee.

(3S)-tert-butyl 3-(5-tert-butyl-2-hydroxyphenyl)-2-nitro-3-phenylpropanoate (3c)

White solid, mp 138.2 – 140.2℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.43 (m, 4H), 7.35 (d, *J* = 2.2 Hz, 1H), 7.33 – 7.20 (m, 7H), 7.14 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.11 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.67 (d, *J* = 8.4 Hz, 1H), 6.63 (d, *J* = 8.4 Hz, 1H), 6.32 (d, *J* = 12.0 Hz, 1H), 6.28 (d, *J* = 12.1 Hz, 1H), 5.58 (s, 1H), 5.43 (s, 1H), 5.26 (d, *J* = 12.1 Hz, 1H), 5.22 (d, *J* = 12.0 Hz, 1H), 1.31 (s, 9H), 1.30 (s, 9H), 1.26 (s, 9H), 1.24 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.9, 162.8, 151.2, 150.8, 143.9, 138.6, 137.7, 129.0, 128.7, 128.6, 127.7, 127.5, 127.4, 126.9, 125.8, 125.5, 125.1, 124.6, 124.0, 116.2, 116.0, 91.0, 90.9, 84.6, 84.5, 48.5, 48.3, 34.2, 34.1, 31.5, 31.5, 27.4, 27.3. HRMS (ESI) calcd for $C_{23}H_{29}NO_5$ $(M + Na)^+$: 422.1943, found: 422.1938; $[\alpha]^{20}_D$ = -45.5 (*c* = 1.0, CH_2Cl_2); The enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (hexane/2-PrOH = 90:10, λ= 204 nm, 0.5 mL/min), t_R (major enantiomer) = 20.1 min, t_R (minor enantiomer) = 22.5 min, 96% ee; t_R (major enantiomer)= 21.8 min, t_R (minor enantiomer) = 24.2 min, 92% ee.

(3S)-tert-butyl 3-(2-hydroxy-5-methoxyphenyl)-2-nitro-3-phenylpropanoate (3d)

Yellow viscous solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 –7.42 (m, 4H), 7.33 – 7.19 (m, 6H), 6.89 (d, *J* = 1.9 Hz, 1H), 6.81 (d, *J* = 2.6 Hz, 1H), 6.71 – 6.68 (m, 2H), 6.67 – 6.62 (m, 2H), 6.23 (d, *J* = 8.0 Hz, 1H), 6.20 (d, *J* = 7.9 Hz, 1H), 5.65 (s, 1H), 5.53 (s, 1H), 5.25 (d, *J* = 7.6 Hz, 1H), 5.22 (d, *J* = 7.7 Hz, 1H), 3.75 (s, 3H), 3.74 (s, 3H), 1.28 (s, 9H), 1.24 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.8, 162.7, 153.8, 147.4, 147.2, 138.3, 137.4, 128.9, 128.8, 128.7, 127.7, 127.6, 127.5, 126.6, 126.0, 117.6, 117.4, 115.7, 114.3, 113.7, 113.3, 91.1, 90.7, 84.8, 84.6, 55.8, 55.8, 48.0, 47.4, 27.3. HRMS (ESI) calcd for $C_{20}H_{23}NO_6$ $(M + Na)^+$: 396.1423, found: 396.1418; $[\alpha]^{20}_D$ = +27.1 (*c* = 1.0, CH_2Cl_2); The enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (hexane/2-PrOH = 90:10, λ= 204 nm, 0.5 mL/min), t_R (minor enantiomer) = 24.6 min, t_R (major enantiomer)= 26.0 min, 97% ee; t_R (minor enantiomer) = 35.3 min, t_R (major enantiomer) = 42.2 min, 97% ee.

(3S)-tert-butyl 3-(2-hydroxy-4-methoxyphenyl)-2-nitro-3-phenylpropanoate (3e)

Yellow viscous solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.33 (m, 4H), 7.28 – 7.21 (m, 4H), 7.21 – 7.14 (m, 3H), 7.11 (d, *J* = 8.5 Hz, 1H), 6.45 – 6.41 (m, 1H), 6.41 – 6.37 (m, 1H), 6.28 (d, *J* = 2.5 Hz, 1H), 6.24 (d, *J* = 2.5 Hz, 1H), 6.19 (d, *J* = 12.0 Hz, 1H), 6.18 (d, *J* = 12.0Hz, 1H), 5.18 (d, *J* = 11.9 Hz, 1H), 5.17 (d, *J* = 12.0 Hz, 1H), 3.66 (s, 3H), 3.64 (s, 3H), 1.25 (s, 9H), 1.20 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.1, 163.0, 160.2, 159.8, 154.6, 154.4, 138.9, 138.0, 130.6, 128.9, 128.8, 128.7, 128.6, 127.6, 127.5, 127.3, 118.1, 117.3, 106.4, 106.3, 102.8, 102.6, 91.1, 91.0, 84.9, 84.7, 55.3, 55.2, 47.5, 47.0, 27.3. HRMS (ESI) calcd for $C_{20}H_{23}NO_6$ $(M + Na)^+$: 396.1423, found: 396.1418; $[\alpha]^{20}_D$ = -6.4 (*c* = 1.0, CH_2Cl_2); The enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexane/2-PrOH = 90:10, λ= 220 nm, 0.9 mL/min), t_R (major enantiomer)= 14.8 min, t_R (minor enantiomer) = 16.9 min, 98% ee; t_R (major enantiomer)= 23.6 min, t_R (minor enantiomer) = 25.2 min, 98% ee.

(3S)-tert-butyl 3-(2-hydroxy-3-methoxyphenyl)-2-nitro-3-phenylpropanoate (3f)

White solid，mp 143.5 – 145.5℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (m, 4H), 7.32 – 7.19 (m, 6H), 6.95 (dd, *J* = 7.9, 1.1 Hz, 1H), 6.89 (dd, *J* = 7.7, 1.6 Hz, 1H), 6.84 (dd, *J* = 8.0, 2.1 Hz, 1H), 6.82 (dd, *J* = 7.8, 2.0 Hz, 1H), 6.79 – 6.73 (m, 2H), 6.26 (d, *J* = 7.5 Hz, 1H), 6.23 (d, *J* = 7.6 Hz, 1H), 5.98 – 5.95 (m, 2H), 5.26 (d, *J* = 12.0 Hz, 1H), 5.25 (d, *J* = 12.2 Hz, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 1.25 (s, 9H), 1.24 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.6, 162.3, 146.8, 143.5, 143.3, 138.6, 137.6, 128.9, 128.7, 128.6, 127.8, 127.5, 127.4, 124.7, 124.1, 121.5, 120.1, 119.9, 119.9, 109.8, 109.7, 90.9, 90.5, 84.3, 84.1, 56.1, 56.0, 47.8, 47.56, 27.3, 27.3. HRMS (ESI) calcd for $C_{20}H_{23}NO_6$ $(M + Na)^+$: 396.1423, found: 396.1418;; $[\alpha]^{20}_D$ = +73.7 (*c* = 1.0, CH_2Cl_2); The enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexane/2-PrOH = 90:10, λ= 204 nm, 0.3 mL/min), t_R (major enantiomer)= 35.3 min, t_R (minor enantiomer) = 53.5 min, 96% ee; t_R (major enantiomer)= 38.8 min, t_R (minor enantiomer) = 41.7 min, 98% ee.

(3S)-tert-butyl 3-(6-hydroxybenzo[d][1,3]dioxol-5-yl)-2-nitro-3-phenylpropanoate (3g)

Yellow viscous solid. **^{1}H NMR** δ 7.40 – 7.21 (m, 10H), 6.75 (s, 1H), 6.61 (s, 1H), 6.35 (s, 1H), 6.27 (s, 1H), 6.07 (d, *J* = 11.9 Hz, 1H), 6.01 (t, *J* = 10.0 Hz, 1H), 5.88 – 5.80 (m, 4H), 5.61 (s, 1H), 5.30 (d, *J* = 10.3 Hz, 1H), 5.25 – 5.20 (m, 1H), 5.16 (t, *J* = 9.9 Hz, 1H), 1.30 (s, 9H), 1.22 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.0, 162.6, 148.0, 147.9, 147.5, 147.3, 142.0, 138.6, 137.8, 128.9, 128.7, 128.6, 127.6, 127.5, 127.4, 117.5, 116.9, 108.6, 107.4, 101.3, 99.6, 99.3, 91.0, 91.0,

85.1, 84.7, 47.1, 46.1, 27.4, 27.3. HRMS (ESI) calcd for $C_{20}H_{21}NO_7$ (M - H)$^-$: 386.1245, found: 386.1237; $[\alpha]^{21}_D$ = +7.6 (*c* = 1.7, CH_2Cl_2); The enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexane/2-PrOH = 85:15, λ= 220 nm, 0.9 mL/min), t_R (major enantiomer)= 14.2 min, t_R (minor enantiomer) = 11.0 min, 99% ee; t_R (major enantiomer)= 20.9 min, t_R (minor enantiomer) = 15.4 min, 99% ee.

(3S)-tert-butyl 3-(2-hydroxy-3-methylphenyl)-2-nitro-3-phenylpropanoate (3h)

White solid, mp 154.0 – 155.8℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.40 (m, 4H), 7.33 – 7.28 (m, 4H), 7.27 – 7.20 (m, 3H), 7.13 – 7.10 (m, 1H), 7.06 – 7.00 (m, 2H), 6.87 – 6.82 (m, 2H), 6.17 (d, *J* = 10.5 Hz, 1H), 6.14 (d, *J* = 10.6 Hz, 1H), 5.36 (d, *J* = 7.9 Hz, 1H), 5.33 (d, *J* = 7.8 Hz, 1H), 5.18 (s, 1H), 5.00 (s, 1H), 2.22 (s, 3H), 2.20 (s, 3H), 1.25 (s, 9H), 1.25 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.8, 162.7, 151.7, 151.5, 138.5, 137.5, 130.2, 130.1, 123.0, 128.8, 128.6, 127.7, 127.6, 127.5, 127.4, 125.4, 125.2, 124.9, 124.4, 123.9, 121.0, 91.2, 90.9, 84.6, 84.5, 47.0, 46.9, 27.3, 27.3, 15.9, 15.8. HRMS (ESI) calcd for $C_{20}H_{23}NO_5$ (M + Na)$^+$: 380.1474, found: 380.1468; $[\alpha]^{20}_D$ = -41.7 (*c* = 1.0, CH_2Cl_2); The enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexane/2-PrOH = 90:10, λ= 204 nm, 0.3 mL/min), t_R (minor enantiomer)= 21.2 min, t_R (major enantiomer) = 20.2 min, 97% ee; t_R (major enantiomer) = 22.3 min, t_R (minor enantiomer)= 27.8 min, 95% ee.

(3S)-tert-butyl 3-(3-fluoro-2-hydroxyphenyl)-2-nitro-3-phenylpropanoate (3i)

White solid, mp 148.2 – 150.0℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.37 (m, 2H), 7.31 – 7.20 (m, 3H), 7.10 (d, *J* = 7.9 Hz, 1H), 7.06 – 6.99 (m, 0.27H), 6.95 (m, 1H), 6.81 (m, 1H), 6.18 (d, *J* = 12.1 Hz, 0.2H), 6.14 (d, *J* = 12.1 Hz, 1H), 5.62 (s, 1H), 5.28 (d, *J* = 12.1 Hz, 1H), 1.24 (s, 1.5H), 1.21 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.4, 152.6, 150.2, 141.6, 141.5, 136.9, 128.9, 128.8, 128.7, 127.8, 127.7, 127.7, 123.0, 122.9, 120.6, 120.6, 114.7, 114.5, 90.4, 84.6, 47.3, 47.3, 27.3. HRMS (ESI) calcd for $C_{19}H_{20}FNO_5$ (M + Na)$^+$: 384.1223, found: 384.1218; $[\alpha]^{20}_D$ = +61.5 (*c* = 1.0, CH_2Cl_2); The enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (hexane/2-PrOH = 90:10, λ= 204 nm, 0.5 mL/min), t_R (minor enantiomer) = 17.7 min, t_R (major enantiomer) = 20.3 min, 97% ee; t_R (minor enantiomer) = 22.1 min, t_R (major enantiomer) = 46.8 min, 97% ee.

(3S)-tert-butyl 3-(2-hydroxy-4-methoxyphenyl)-2-nitro-3-o-tolylpropanoate (3j)

White solid, mp. 107.0 – 108.5℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19 – 7.09 (m, 8H), 7.00 (t, *J* = 8.0 Hz, 1H), 6.43 (d, *J* = 2.4 Hz, 1H), 6.41 (d, *J* = 2.4 Hz, 1H), 6.28 (d, *J* = 2.5 Hz, 1H), 6.23 (d, *J* = 2.4 Hz, 1H), 6.16 (d, *J* = 1.0 Hz, 1H), 6.13 (d, *J* = 1.1 Hz, 1H), 6.02 (s, 1H), 5.83 (s, 1H), 5.16 (d, *J* = 6.2 Hz, 1H), 5.13 (d, *J* = 6.2 Hz, 1H), 3.67 (s, 3H), 3.65 (s, 3H), 2.27 (s, 3H), 2.27 (s, 3H), 1.25 (s, 9H), 1.22 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.2, 162.9, 160.1, 159.8, 154.5, 154.3, 138.8, 138.4, 138.2, 137.8, 130.5, 129.5, 128.8, 128.6, 128.6, 128.5, 128.2, 128.2, 125.7, 124.4, 118.1, 117.4, 106.6, 106.4, 102.8, 102.7, 91.1, 91.0, 84.9, 84.6, 55.3, 55.2, 47.1, 46.6, 27.3, 21.5, 21.4. HRMS (ESI) calcd for $C_{21}H_{25}NO_6$ (M + Na)$^+$: 410.1580, found: 410.1574; $[\alpha]^{20}_D$ = -2.6 (*c* = 1.0, CH_2Cl_2); The enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (hexane/2-PrOH = 90:10, λ= 204 nm, 0.5 mL/min), t_R (major enantiomer)= 19.6 min, t_R (minor enantiomer) = 27.6 min, 99% ee; t_R (major enantiomer)= 32.6 min, t_R (minor enantiomer) = 36.7 min, 99% ee.

(3R)-tert-butyl 3-(2-hydroxy-4-methoxyphenyl)-3-(2-methoxyphenyl)-2-nitropropanoate (3k)

Yellow viscous solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.33 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.24 – 7.15 (m, 3H), 7.12 (d, *J* = 8.5 Hz, 1H), 6.95 – 6.89 (m, 2H), 6.86 (d, *J* = 8.3, 1H), 6.86 (d, *J* = 8.3, 1H), 6.55 (s, 1H), 6.43 (d, *J* = 2.4 Hz, 1H), 6.41 (d, *J* = 2.1 Hz, 1H), 6.39 (d, *J* = 2.5 Hz, 1H), 6.33 (d, *J* = 2.6 Hz, 1H), 6.29 (s, 1H), 6.22 (d, *J* = 12.0 Hz, 1H), 6.16 (d, *J* = 12.2 Hz, 1H), 5.48 (d, *J* = 12.0 Hz, 1H), 5.47 (d, *J* = 12.0 Hz, 1H), 3.90 (s, 3H), 3.90 (s, 3H), 3.69 (s, 3H), 3.68 (s, 3H), 1.26 (s, 9H), 1.19 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.6, 162.5, 160.1, 159.9, 156.1, 156.0, 155.0, 154.8, 129.5, 129.3, 128.8, 128.6, 127.7, 127.0, 126.8, 126.0, 121.6, 121.3, 117.1, 116.3, 111.6, 111.3, 107.0, 106.8, 102.8, 102.7, 90.5, 90.4, 84.7, 84.3, 56.1, 55.8, 55.3, 55.2, 39.5, 39.0, 27.3, 27.2. HRMS (ESI) calcd for $C_{21}H_{25}NO_7$ $(M + Na)^+$: 426.1529, found: 426.1523; $[\alpha]^{20}_D$ = +3.6 (*c* = 1.0, CH_2Cl_2); The enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexane/2-PrOH = 90:10, λ= 204 nm, 0.3 mL/min), t_R (major enantiomer)= 28.3 min, t_R (minor enantiomer) = 34.5 min, 97% ee; t_R (major enantiomer)= 30.9 min, t_R (minor enantiomer) = 38.7 min, 97% ee.

(3S)-tert-butyl 3-(2-hydroxy-4-methoxyphenyl)-2-nitro-3-p-tolylpropanoate (3l)

Yellow viscous solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 2.7 Hz, 2H), 7.26 (d, *J* = 2.7 Hz, 2H), 7.16 (d, *J* = 8.5 Hz, 1H), 7.12 – 7.03 (m, 5H), 6.42 (t, *J* = 2.4 Hz, 1H), 6.40 (t, *J* = 2.4 Hz, 1H), 6.28 (d, *J* = 2.5 Hz, 1H), 6.23 (d, *J* = 2.4 Hz, 1H), 6.15 (d, *J* = 12.0 Hz, 1H), 6.15 (d, *J* = 12.0 Hz, 1H), 6.06 (s, 1H), 5.14 (d, *J* = 12.0 Hz, 1H), 5.13 (d, *J* = 12.0 Hz, 1H), 3.66 (s, 3H), 3.65 (s, 3H), 2.26 (s, 3H), 2.24 (s, 3H), 1.25 (s, 9H), 1.23 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.2, 162.9, 160.1, 159.8, 154.6, 154.3, 137.1, 137.0, 135.9, 134.9, 130.5, 129.5, 129.3, 128.8, 128.6, 127.5, 118.3, 117.5, 106.4, 106.3, 102.8, 102.7, 91.2, 91.0, 84.8, 84.6, 55.3, 55.2, 47.0, 46.6, 27.4, 27.3, 21.0, 21.0. HRMS (ESI) calcd for $C_{21}H_{25}NO_6$ $(M + Na)^+$: 410.1580, found: 410.1574; $[\alpha]^{20}_D$ = -10.0 (*c* = 1.0, CH_2Cl_2); The enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexane/2-PrOH = 90:10, λ= 204 nm, 0.3 mL/min), t_R (major enantiomer)= 18.9 min, t_R (minor enantiomer) = 22.4 min, 96% ee; t_R (major enantiomer)= 29.0 min, t_R (minor enantiomer) = 34.8 min, 98% ee.

(3S)-tert-butyl 3-(2-hydroxy-4-methoxyphenyl)-3-(4-methoxyphenyl)-2- nitropropanoate (3m)

Yellow viscous solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 4.8 Hz, 2H), 7.30 (d, *J* = 4.8 Hz, 2H), 7.16 (d, *J* = 8.5 Hz, 1H), 7.10 (d, *J* = 8.5 Hz, 1H), 6.82 – 6.76 (m, 4H), 6.42 (t, *J* = 2.7 Hz, 1H), 6.40 (t, *J* = 2.8 Hz, 1H), 6.29 (s, 1H), 6.29 (d, *J* = 2.5 Hz, 1H), 6.24 (d, *J* = 2.4 Hz, 1H), 6.15 (s, 1H),6.15 (d, *J* = 12.0 Hz, 1H), 6.13 (d, *J* = 11.9 Hz, 1H), 5.12 (d, *J* = 11.9 Hz, 1H), 5.12 (d, *J* = 11.9 Hz, 1H), 3.73 (s, 3H), 3.72 (s, 3H), 3.67 (s, 3H), 3.65 (s, 3H), 1.25 (s, 9H), 1.24 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.1, 163.0, 160.1, 159.8, 158.8, 158.6, 154.5, 154.3, 131.0, 130.4, 130.0, 129.9, 128.8, 118.3, 117.6, 114.2, 114.0, 112.2, 106.3, 106.3, 102.8, 102.7, 91.5, 91.0, 84.8, 84.6, 55.1, 55.2, 46.7, 46.4, 27.4, 27.3. HRMS (ESI) calcd for $C_{21}H_{25}NO_7$ $(M + Na)^+$: 426.1529, found: 426.1523; $[\alpha]^{20}_D$ = +7.6 (*c* = 1.0, CH_2Cl_2); The enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexane/2-PrOH = 90:10, λ= 204 nm, 0.3 mL/min), t_R (major enantiomer)= 24.8min, t_R (minor enantiomer) = 27.3 min, 99% ee; t_R (major enantiomer)= 34.0 min, t_R (minor enantiomer) = 38.5 min, 99% ee.

(3S)-tert-butyl 3-(2-hydroxy-4-methoxyphenyl)-2-nitrobutanoate (3n)

White solid, mp 111.3 – 113.6℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.04 (d, *J* = 8.5 Hz, 1.5H), 7.03 (d, *J* = 8.5 Hz, 1H), 6.49 – 6.40 (m, 2.6H), 6.35 (d, *J* = 19.0 Hz, 1.5H), 6.34 (d, *J* = 18.9 Hz, 1H), 6.11 (s, 1.5H), 5.83 (s, 1H), 5.57 (d, *J* = 9.4 Hz, 1H), 5.48 (d, *J* = 10.1 Hz, 1.5H), 3.74 (s, 4.5H), 3.73 (s, 3H), 1.50 (s, 9H), 1.29 (s, 13.5H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.6, 163.3, 160.1, 159.9, 154.8, 154.4, 130.0, 118.6, 118.1, 106.7, 106.3, 102.8, 102.7, 92.9, 92.1, 84.8, 84.7, 55.3, 55.3, 36.6, 36.1, 27.7, 27.4. HRMS (ESI) calcd for $C_{15}H_{21}NO_6$ $(M + Na)^+$: 334.1267, found: 334.1262; $[\alpha]^{20}_D$ = -3.5 (*c* = 1.0, CH_2Cl_2); The enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (hexane/2-PrOH = 90:10, λ= 204 nm, 0.5 mL/min), t_R (major enantiomer)= 12.8 min, t_R (minor enantiomer) = 14.3 min, 83% ee; t_R (minor enantiomer) = 15.9 min, t_R (major enantiomer)= 17.2 min, 86% ee.

(S)-5-methoxy-2-(2-nitro-1-phenylethyl)phenol (4e)

White viscous solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 (m, 5H), 6.96 (d, *J* = 8.5 Hz, 1H), 6.42 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.27 (t, *J* = 5.6 Hz, 1H), 5.45 (s, 1H), 5.13-5.02 (m, 2H), 4.94 (dd, *J* = 12.5, 8.4 Hz, 1H), 3.69 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.94, 154.13, 139.06, 129.51, 128.87, 128.87, 127.84, 127.84, 127.40, 118.34, 106.25, 102.65, 78.16, 55.35, 43.25. HRMS (ESI) calcd for $C_{15}H_{15}NO_4$ $(M + H)^+$: 274.1074, found: 274.1064; $[\alpha]^{25}_D$ = -29.7 (*c* = 0.5, CH_2Cl_2); The enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (hexane/2-PrOH = 85:15, λ= 230 nm, 0.8 mL/min), t_R (minor enantiomer)= 16.5 min, t_R (major enantiomer) = 18.2 min, 98% ee.

(S)-6-(2-nitro-1-phenylethyl)benzo[d][1,3]dioxol-5-ol (4g)

White viscous solid . **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 (m, 5H), 6.57 (s, 1H), 6.38 (s, 1H), 5.90 (s, 2H), 5.18 (t, *J* = 8.1 Hz, 1H), 5.06 – 4.95 (m, 2H), 4.81 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.7, 147.3, 142.1, 138.8, 129.0, 127.7, 127.6, 117.9, 108.0, 101.4, 99.0, 78.0, 43.2. HRMS (ESI) calcd for $C_{15}H_{13}NO_5$ $(M - H)^-$: 286.0721, found: 286.0709; $[\alpha]^{23}_D$ = -15.0 (*c* = 1.0, CH_2Cl_2); The enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (hexane/2-PrOH = 80:20, λ= 220 nm, 0.5 mL/min), t_R (minor enantiomer)= 20.2 min, t_R (major enantiomer) = 23.4 min, 99% ee.

(7R,8S)-7-nitro-8-phenyl-7,8-dihydro-6H-[1,3]dioxolo[4,5-g]chromen-6-one (5g):

White viscous solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.36 (m, 3H), 7.22 – 7.19 (m, 2H), 6.70 (s, 1H), 6.26 (s, 1H), 5.98 (s, 2H), 5.56 (d, *J* = 10.0 Hz, 1H), 4.95 (d, *J* = 9.9 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.9, 148.7, 145.6, 144.6, 134.5, 129.7, 129.2, 128.3, 113.7, 107.6, 102.2, 99.2, 87.3, 45.9. HRMS (ESI) calcd for $C_{16}H_{11}NO_6$ $(M - H)^-$: 312.0514, found: 312.0528; $[\alpha]^{22}_D$ = +77.9 (*c* = 1.1, CH_2Cl_2).

(3R,4S)-7-methoxy-3-nitro-4-phenylchroman-2-one (5e)

White viscous solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.34 (m, 3H), 7.21 (dd, *J* = 7.7, 1.7 Hz, 2H), 6.77 – 6.71 (m, 2H), 6.68 (dd, *J* = 8.6, 2.5 Hz, 1H), 5.61 (d, *J* = 10.3 Hz, 1H), 5.00 (d, *J* = 10.4 Hz, 1H), 3.81 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.9, 159.1, 150.7, 134.7, 129.6, 129.6, 129.1, 128.4, 113.3, 112.1, 102.6, 87.6, 55.7, 45.6. HRMS (ESI) calcd for $C_{16}H_{13}NO_5$ $(M + Na)^+$: 322.0691, found: 322.0686; $[\alpha]^{20}_D$ = +77.9 (*c* = 1.0, CH_2Cl_2).

(S)-tert-butyl (2-(2-hydroxy-4-methoxyphenyl)-2-phenylethyl)carbamate (6e)

White viscous solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39-7.33 (m, 2H), 7.29 (m, 4H), 6.79 (d, *J* = 6.7 Hz, 1H), 6.49 (s, 1H), 6.39 (dd, *J* = 8.5, 2.4 Hz, 1H), 4.85 (s, 1H), 4.53-4.38 (m, 1H), 3.75 (s, 3H), 1.46 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.41, 156.89, 155.48, 141.20, 128.95, 128.63, 126.71, 120.78, 105.63, 102.31, 80.10, 60.49, 55.19, 44.45, 28.39. HRMS (ESI) calcd for $C_{20}H_{25}NO_4$ $(M-H)^-$: 342.1711, found: 342.1695; $[\alpha]^{25}_D$ = -36.3 (*c* = 0.5, CH_2Cl_2); The enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (hexane/2-PrOH = 85:15, λ= 220 nm, 0.8 mL/min), t_R (major enantiomer) = 13.8 min, t_R (minor enantiomer)= 21.7 min, 98% ee.

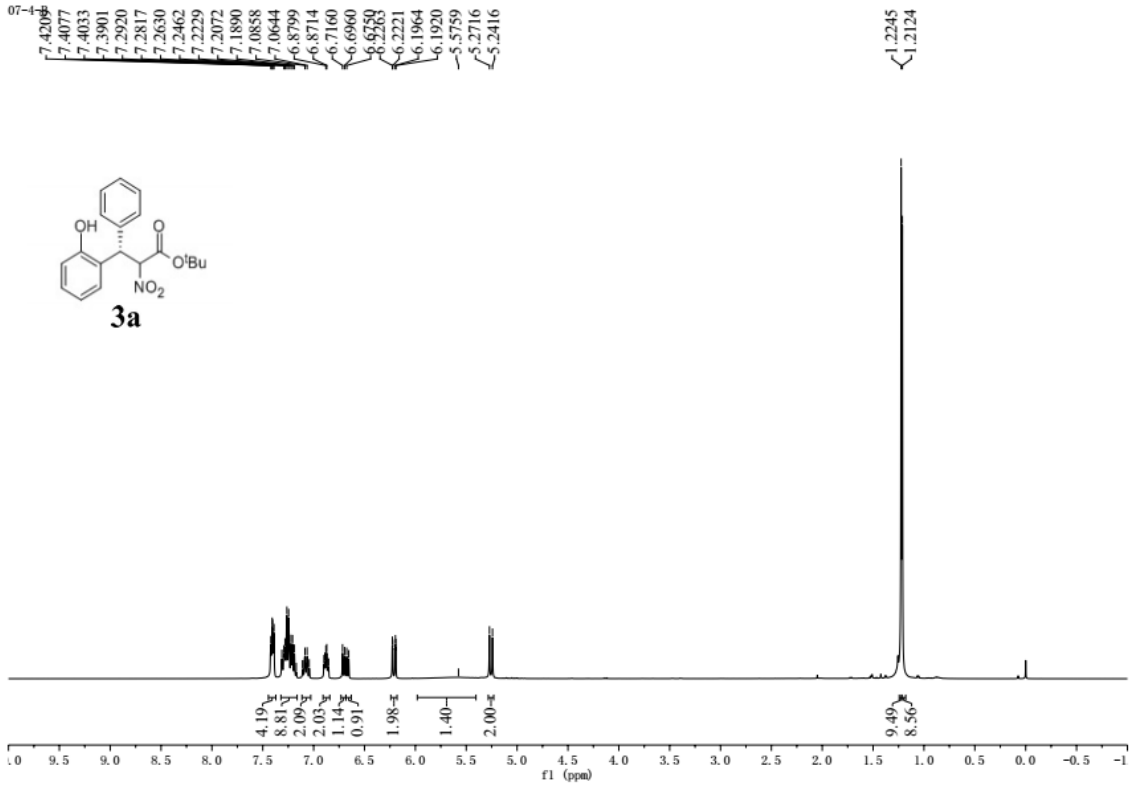
(S)-tert-butyl (2-(6-hydroxybenzo[d][1,3]dioxol-5-yl)-2-phenylethyl)carbamate (6g)

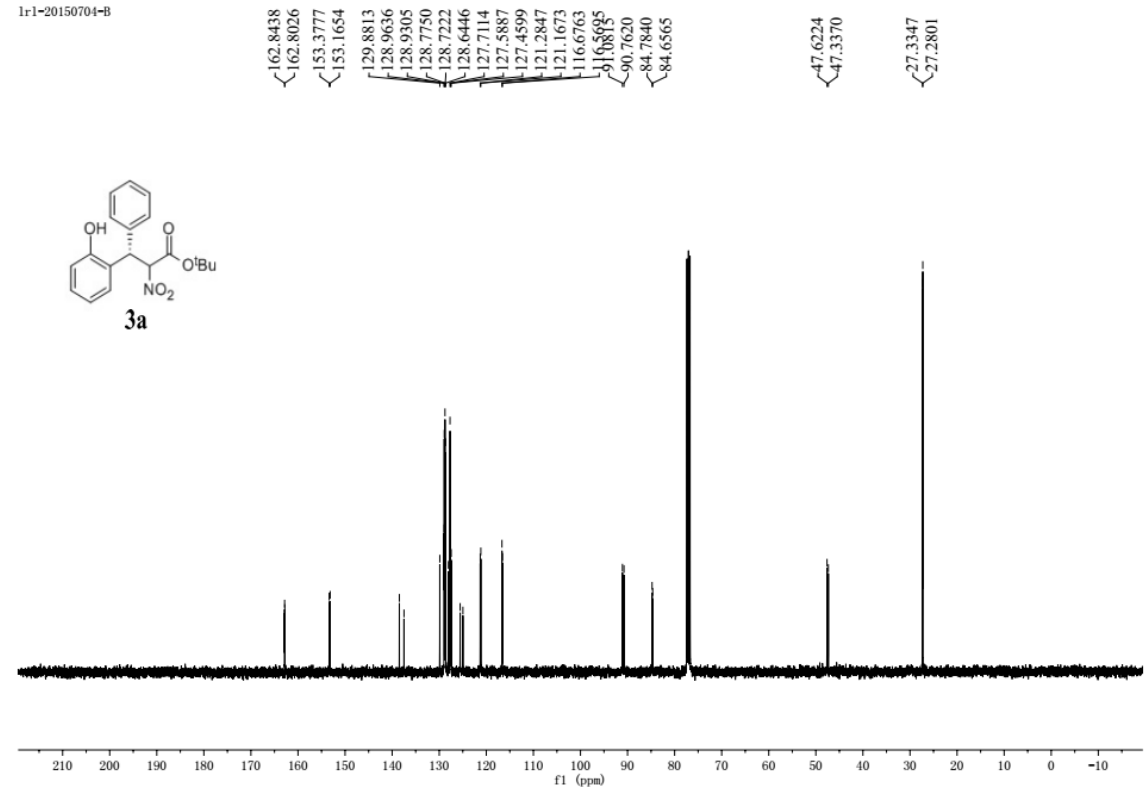
White viscous solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.27 (m, 6H), 6.50 (s, 1H), 6.35 (s, 1H), 5.86 (s, 2H), 4.84 (s, 1H), 4.51 – 4.41 (m, 1H), 3.73 – 3.56 (m, 2H), 1.46 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.2, 146.6, 141.1, 128.8, 128.7, 128.6, 128.1, 126.9, 120.1, 107.6, 100.9, 99.1, 80.3, 44.8, 29.7, 28.3. HRMS (ESI) calcd for $C_{20}H_{23}NO_5$ $(M-H)^-$: 356.1503, found: 356.1503; $[\alpha]^{23}_D$ = +11.3 (*c* = 0.8, CH_2Cl_2); The enantiomeric excess was determined by HPLC with a Chiralpak OD-H column (hexane/2-PrOH = 95:5, λ= 220 nm, 0.6mL/min), t_R (major enantiomer) = 24.9 min, t_R (minor enantiomer)= 27.3 min, 99% ee.

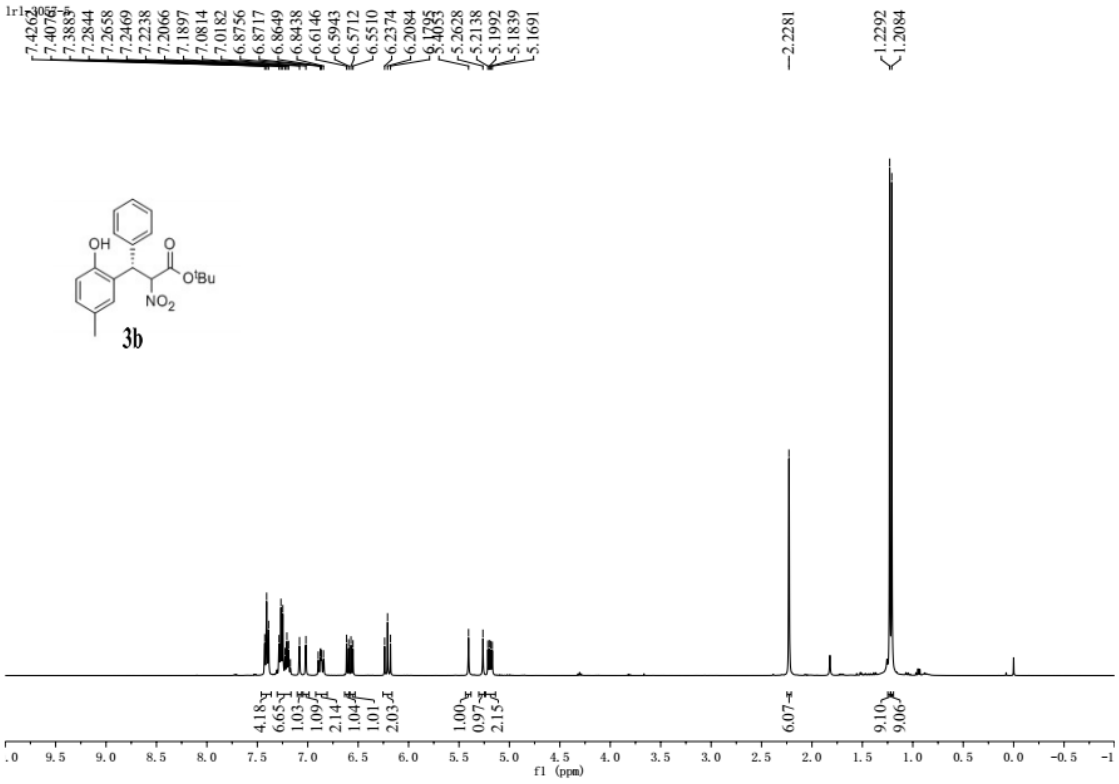
IV. References

1. M.-W. Chen, L.-L. Cao, Z.-S. Ye, G.-F. Jiang and Y.-G. Zhou, *Chem. Commun.,* 2013, **49**, 1660.
2. J. H. Chaplin, K. Jackson, J. M. White and B. L. Flynn, *J. Org. Chem.,* 2014, **79**, 3659.
3. D. Lanari, R. Ballini, A. Palmieri, F. Pizzo and L. Vaccaro, *Eur. J. Org. Chem.,* 2011, 2874.

V. Copies of NMR spectra



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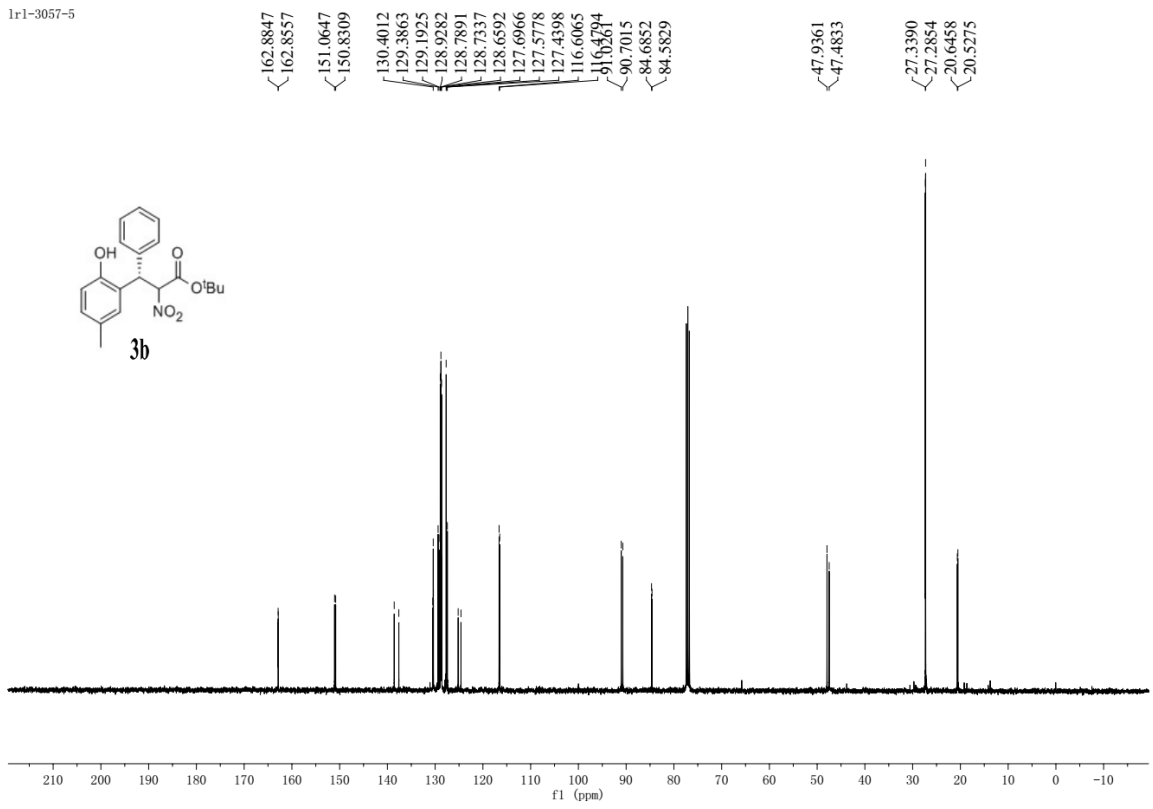
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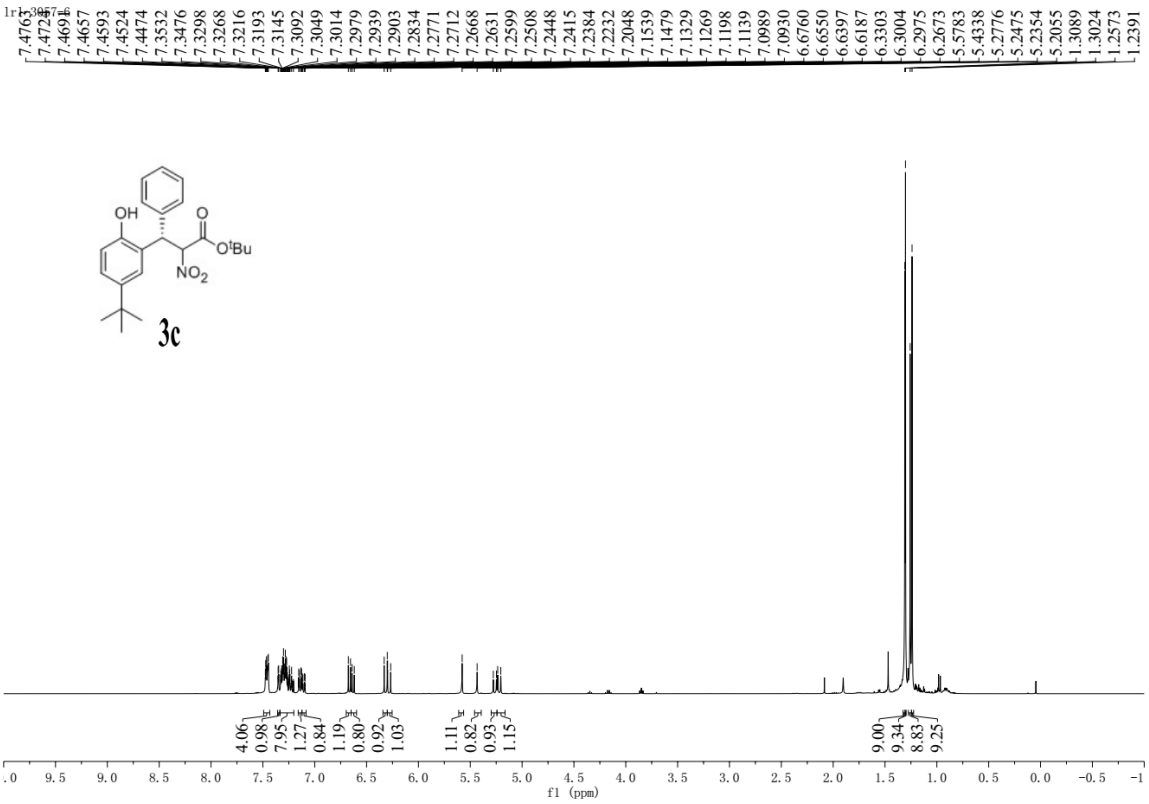
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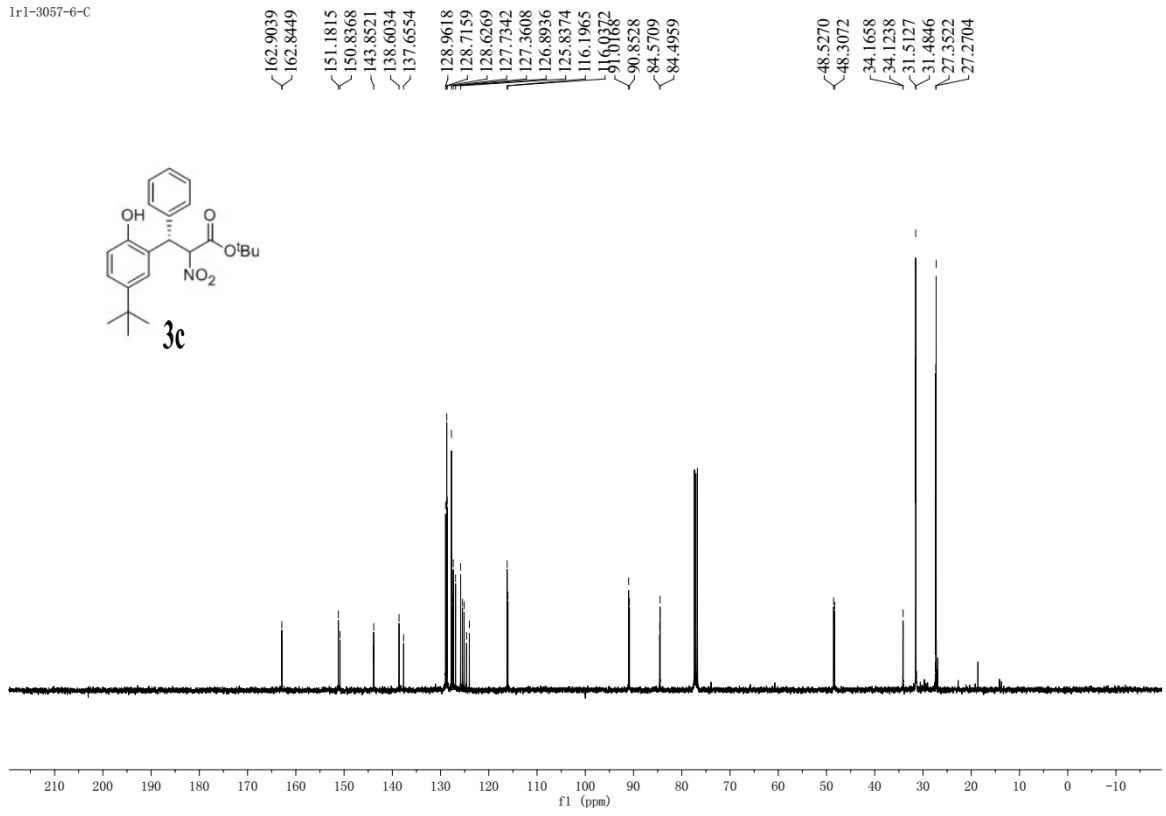
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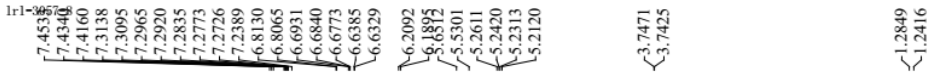

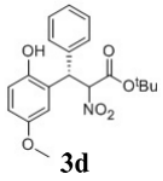

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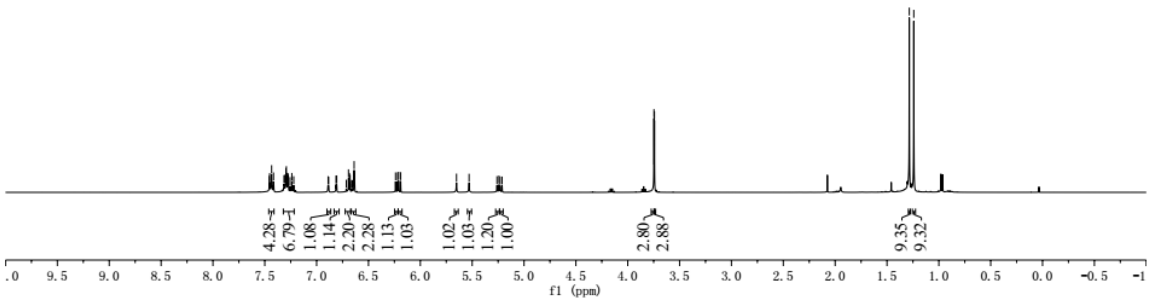

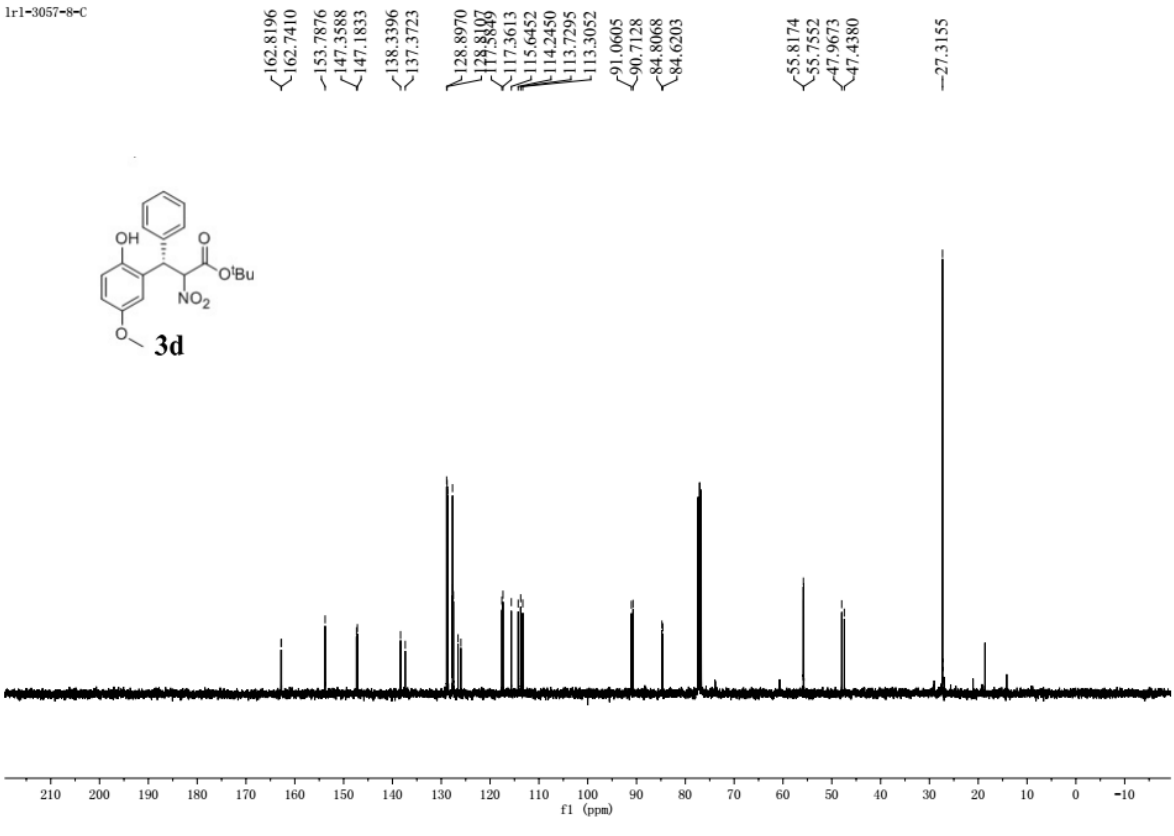

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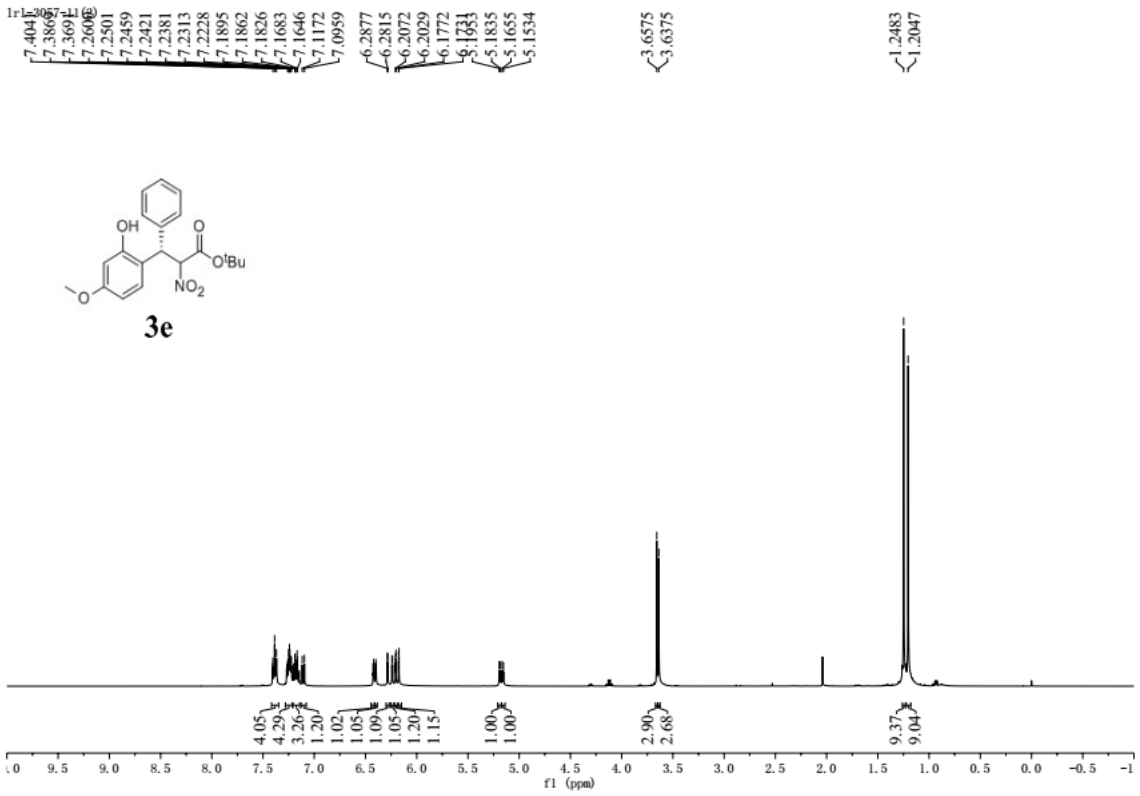
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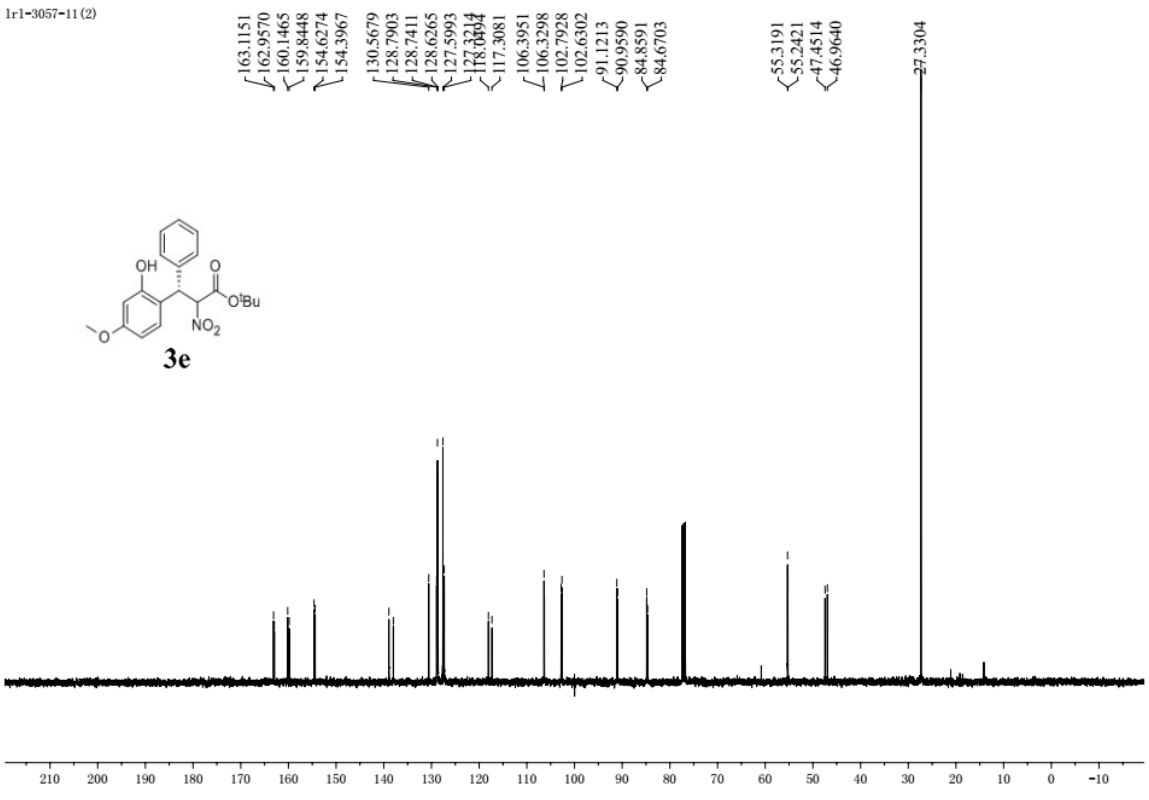
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118.0494
117.3081
106.3951
106.3298
102.7928
102.6302
91.1213
90.9590
84.8591
84.6703
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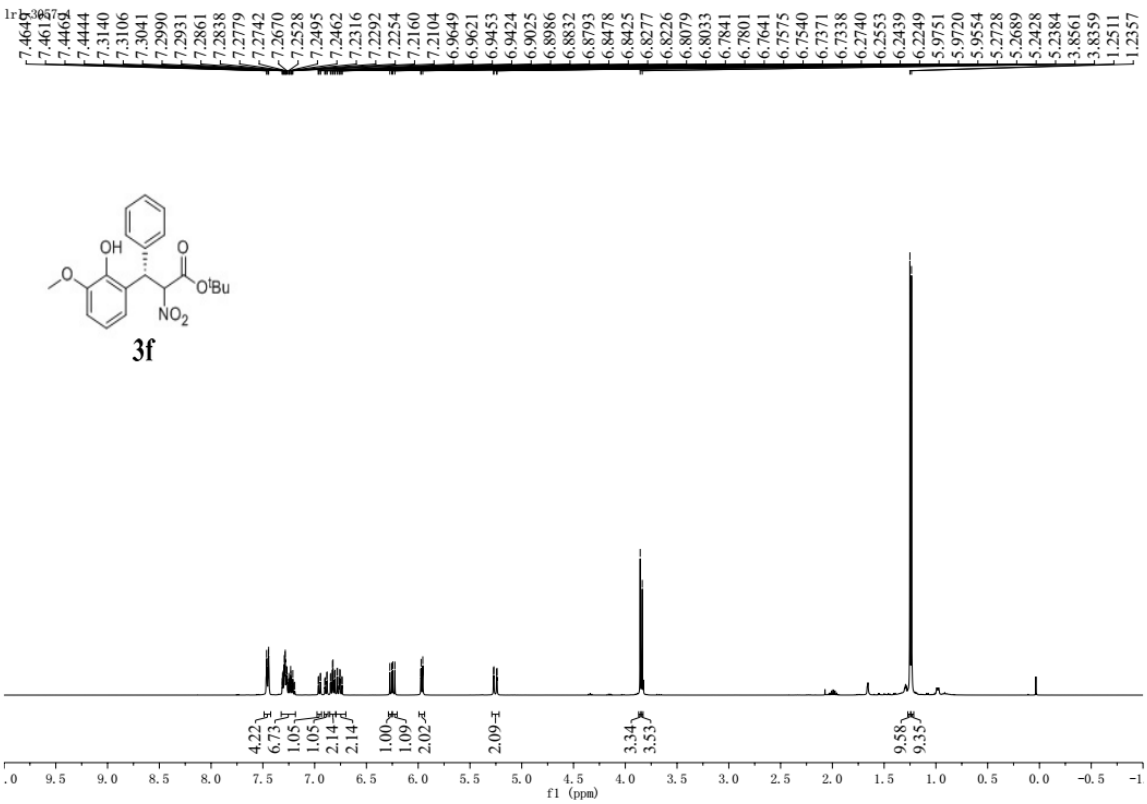
55.2421
47.4514
46.9640
27.3304
OH
O
O^{t}Bu
NO$_2$
O
3e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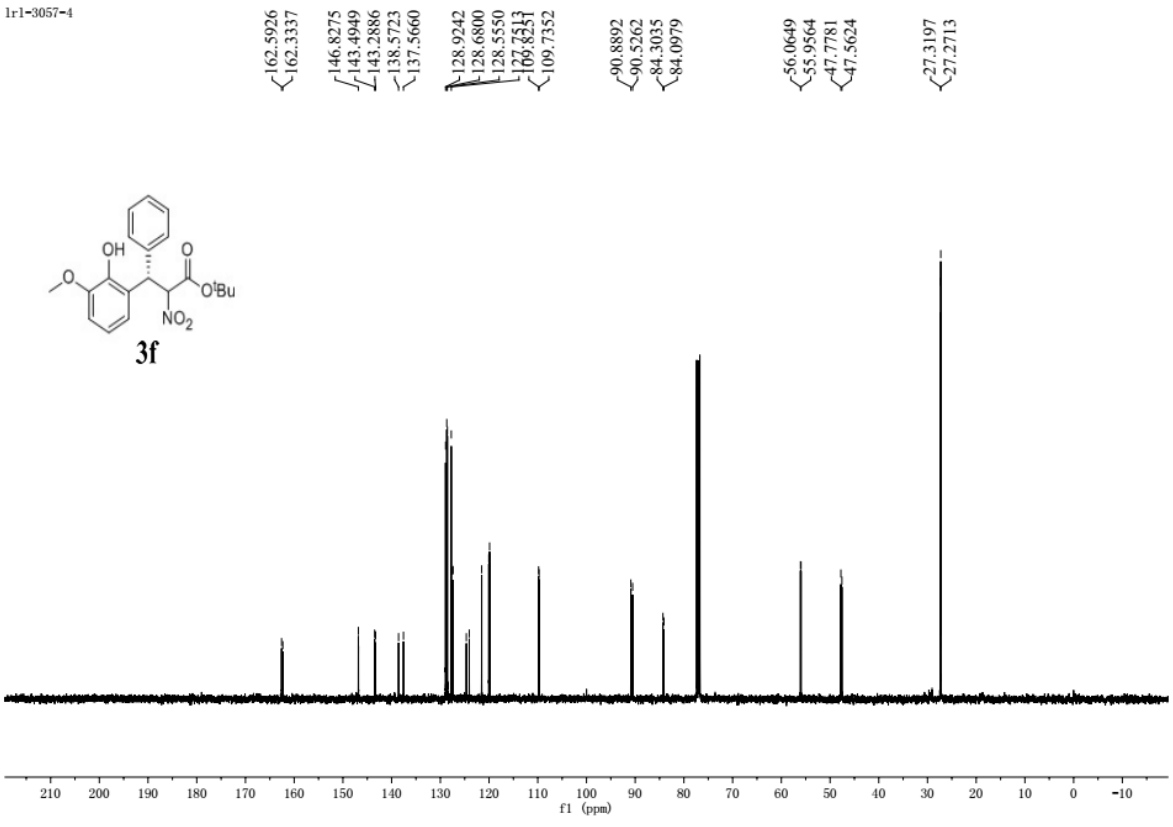
7.3041
7.2990
7.2931
7.2861
7.2838
7.2779
7.2742
7.2670
7.2528
7.2495
7.2462
7.2316
7.2292
7.2254
7.2160
7.2104
6.9649
6.9621
6.9453
6.9424
6.9025
6.8986
6.8832
6.8793
6.8478
6.8425
6.8277
6.8226
6.8079
6.8033
6.7841
6.7801
6.7641
6.7575
6.7540
6.7371
6.7338
6.2740
6.2553
6.2439
6.2249
5.9751
5.9720
5.9554
5.2728
5.2689
5.2428
5.2384
3.8561
3.8359
1.2511
1.2357
OH
O
O
tBu
NO2
3f
4.22
6.73
1.05
1.05
2.14
2.14
1.00
1.09
2.02
2.09
3.34
3.53
9.58
9.35
f1 (ppm)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143.4949
143.2886
138.5723
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128.9242
128.6800
128.5550
127.7513
109.8251
109.7352
90.8892
90.5262
84.3035
84.0979
56.0649
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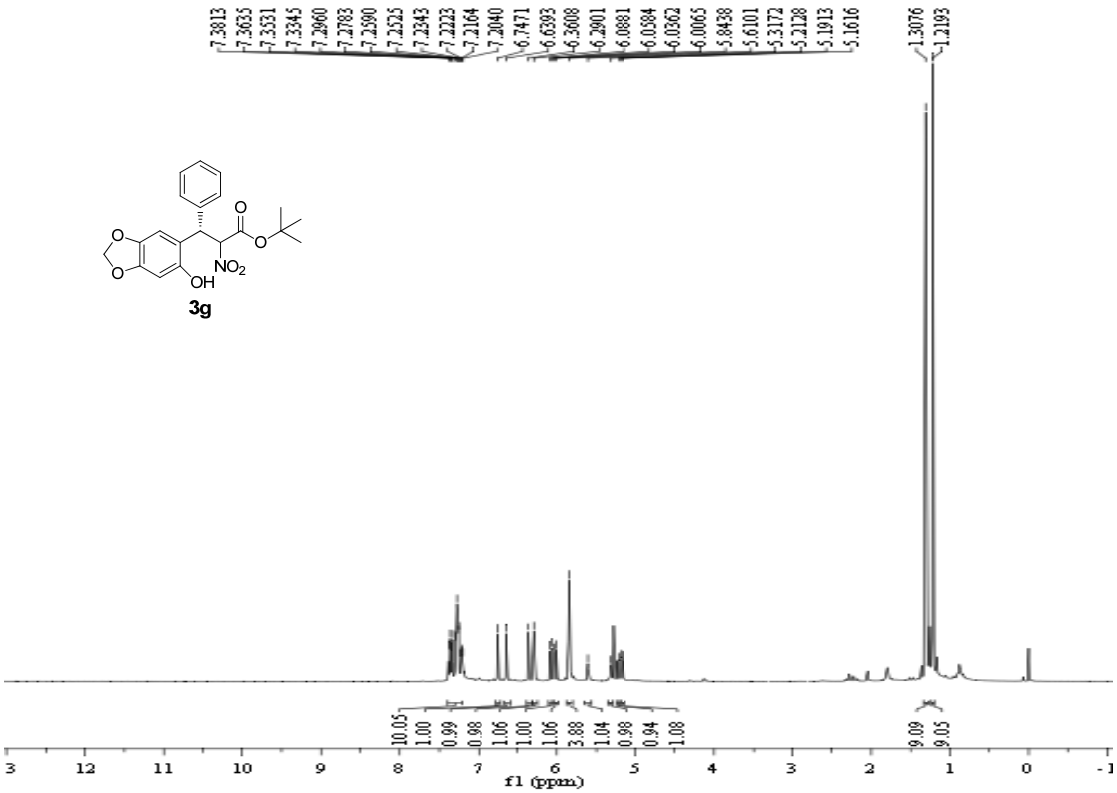
47.7781
47.5624
27.3197
27.2713
OH
O
O
tBu
NO2
3f
f1 (ppm)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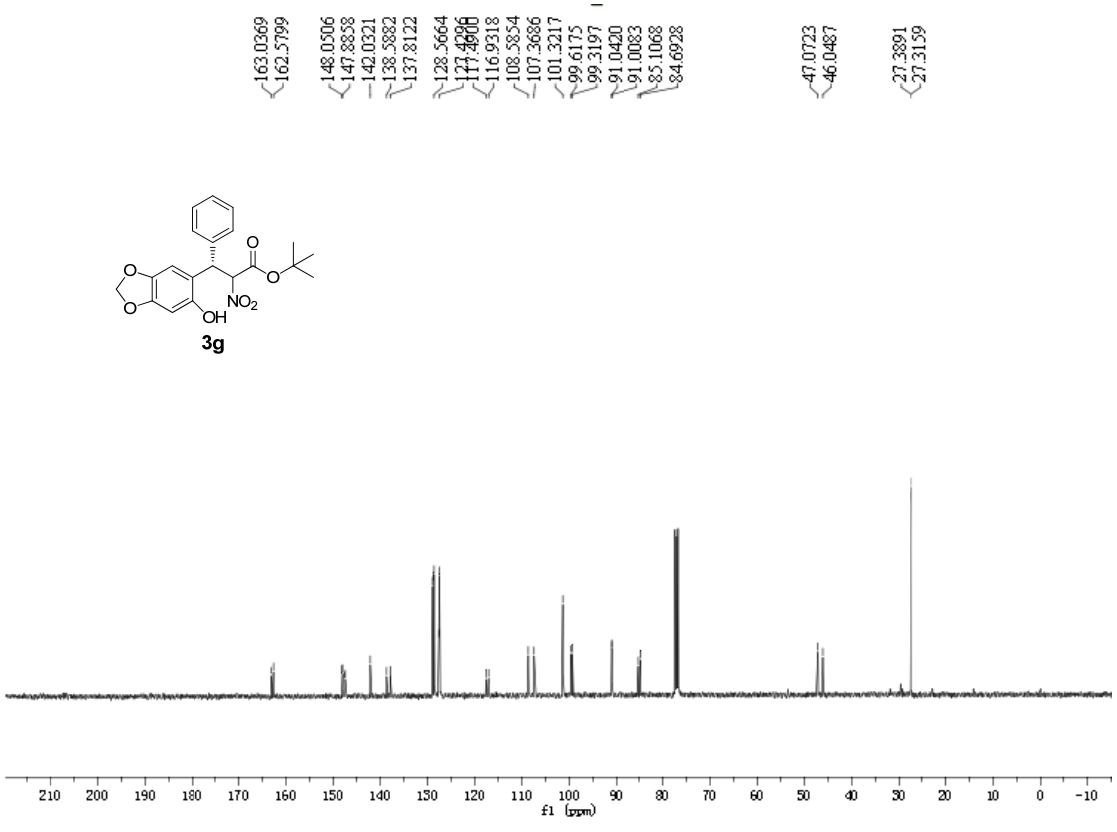
7.3531
7.3345
7.2960
7.2783
7.2590
7.2525
7.2343
7.2223
7.2164
7.2040
6.7471
6.6393
6.3608
6.2901
6.0881
6.0384
6.0362
6.0065
5.8438
5.6101
5.3172
5.2128
5.1913
5.1616
1.3076
1.2193
10.05
1.00
0.99
0.98
1.06
1.00
1.06
3.88
1.04
0.98
0.94
1.08
9.09
9.05
f1 (ppm)

O
O
O
O
NO2
OH

3g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148.0506
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142.0321
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137.8122
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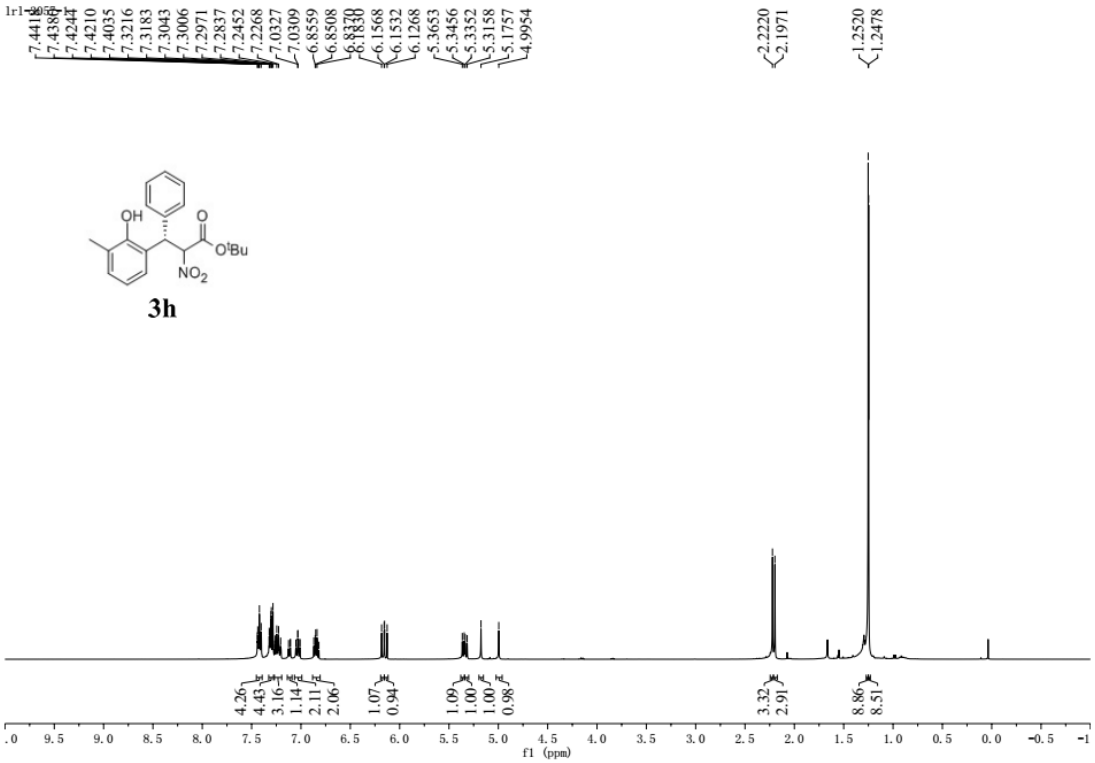
116.9318
108.5854
107.3686
101.3217
99.6175
99.3197
91.0420
91.0083
85.1068
84.6928
47.0723
46.0487
27.3891
27.3159
f1 (ppm)

O
O
O
O
NO2
OH

3g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7.4035
7.3216
7.3183
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7.3006
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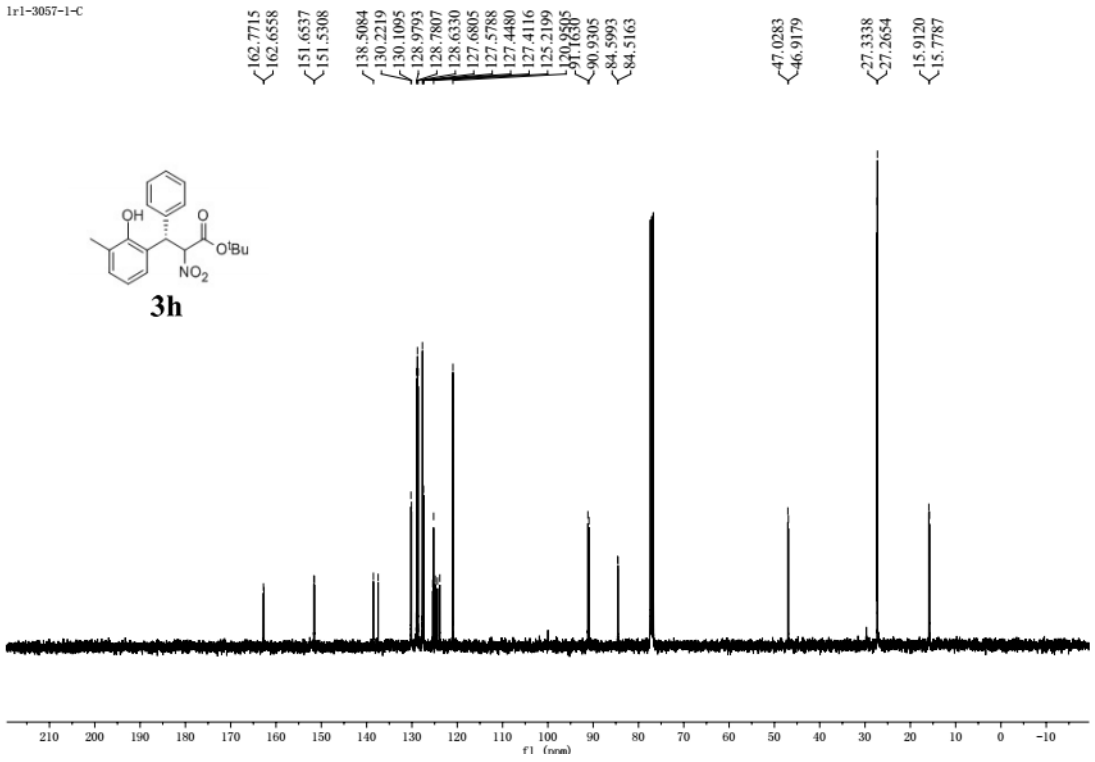
7.2837
7.2452
7.2268
7.0327
7.0309
6.8559
6.8508
6.8370
6.8330
6.1568
6.1532
6.1268
5.3653
5.3456
5.3352
5.3158
5.1757
4.9954
2.2220
2.1971
1.2520
1.2478
OH
O
O'Bu
NO2
4.26
4.43
3.16
1.14
2.11
2.06
1.07
0.94
1.09
1.00
1.00
0.98
3.32
2.91
8.86
8.51
f1 (ppm)

3h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162.6558
151.6537
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138.5084
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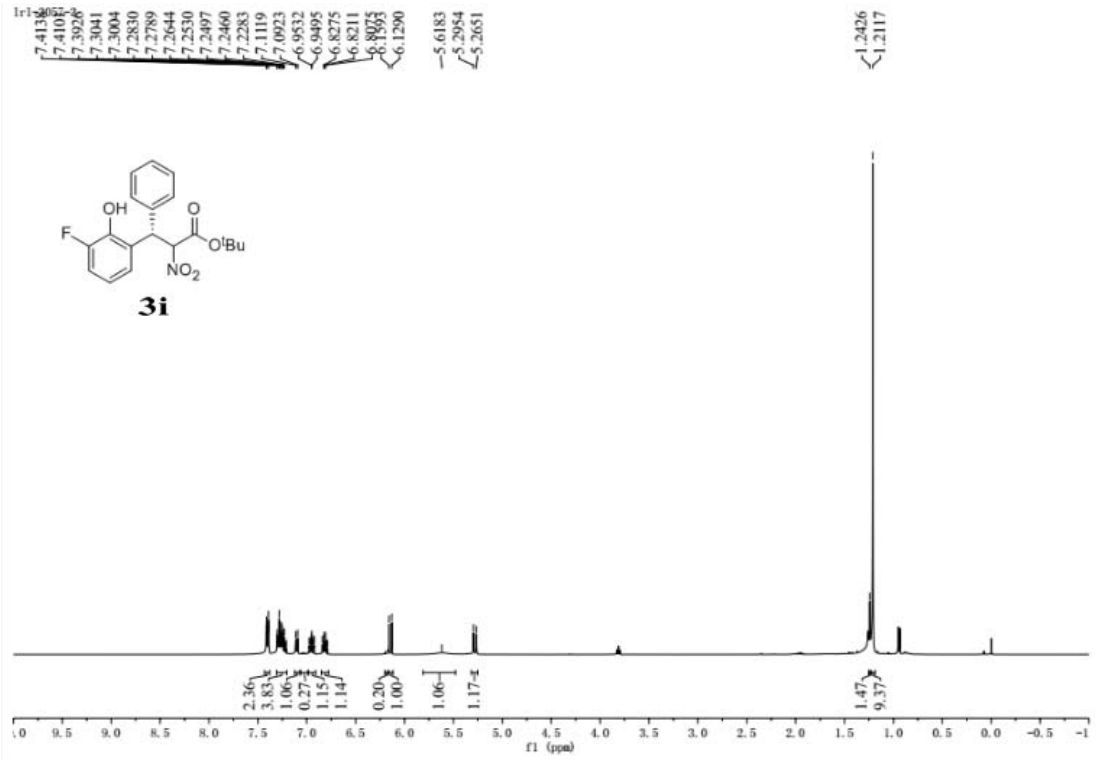
130.1095
128.9793
128.7807
128.6330
127.6805
127.5788
127.4480
127.4116
125.2199
120.9505
91.1630
90.9305
84.5993
84.5163
47.0283
46.9179
27.3338
27.2654
15.9120
15.7787
OH
O
O'Bu
NO2
f1 (ppm)

3h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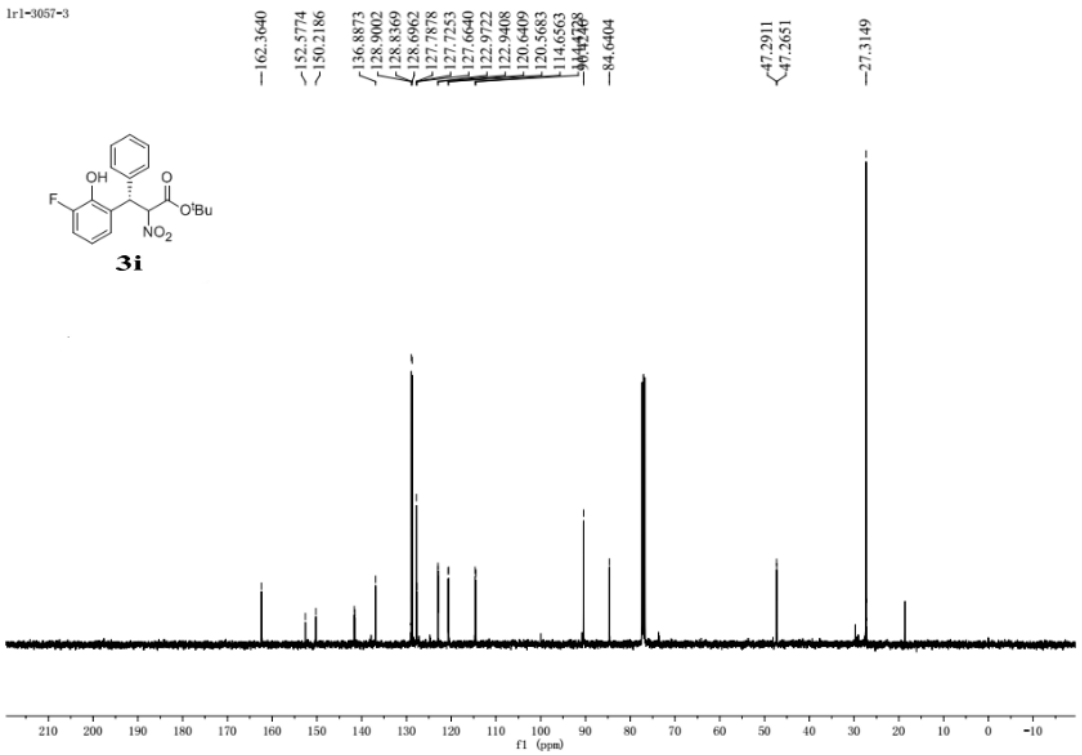
7.3041
7.3004
7.2830
7.2789
7.2644
7.2530
7.2497
7.2460
7.2283
7.1119
7.0923
6.9532
6.9495
6.8275
6.8211
6.8075
6.8033
6.1593
6.1290
5.6183
5.2954
5.2651
1.2426
1.2117
OH
O
F
O'Bu
NO2
3i
2.36
3.83
1.06
0.27
1.15
1.14
0.20
1.00
1.06
1.17
1.47
9.37
f1 (ppm)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127.7878
127.7253
127.6640
122.9722
122.9408
120.6409
120.5683
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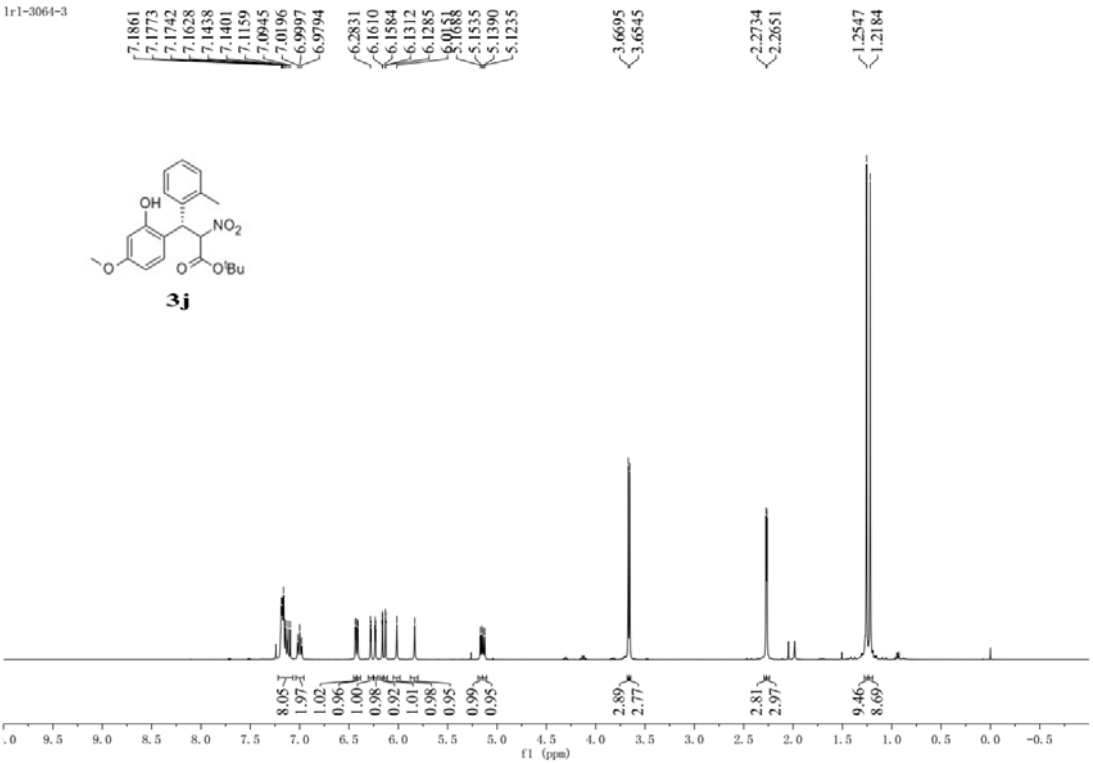
47.2911
47.2651
27.3149
OH
O
F
O'Bu
NO2
3i
f1 (ppm)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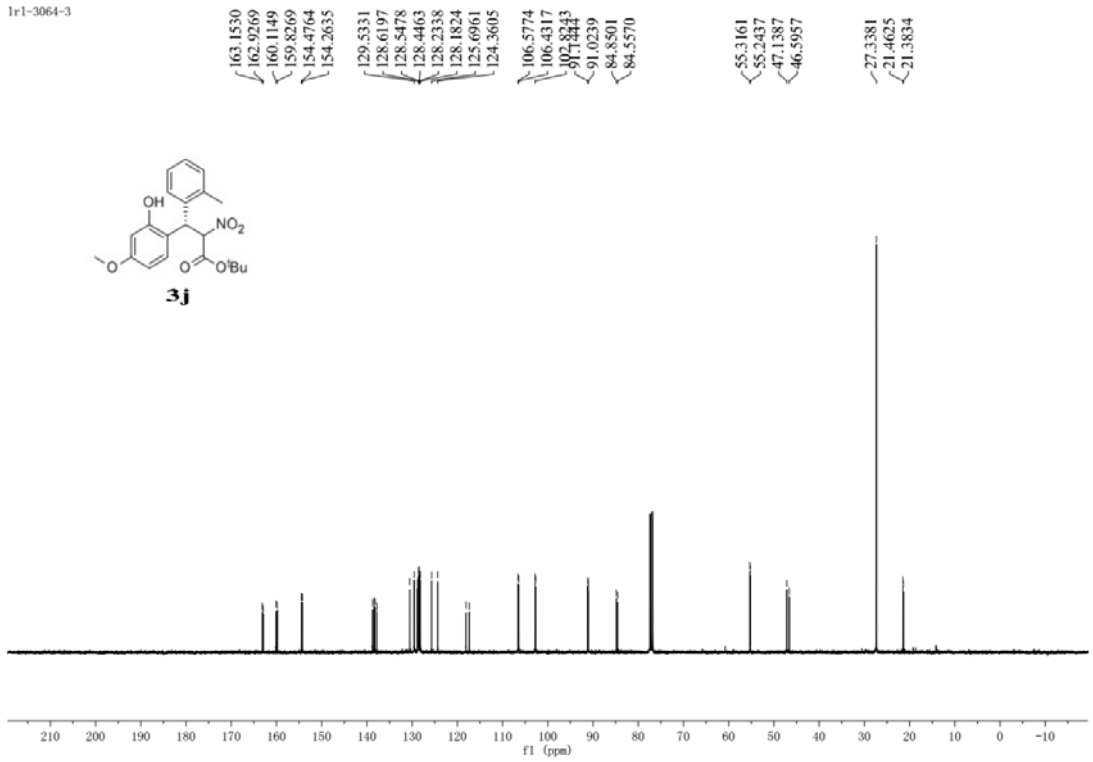
7.1628
7.1438
7.1401
7.1159
7.0945
7.0196
6.9997
6.9794
6.2831
6.1610
6.1584
6.1312
6.1285
6.0151
5.1688
5.1535
5.1390
5.1235
3.6695
3.6545
2.2734
2.2651
1.2547
1.2184
OH
NO2
O
O
tBu
3j
8.05
1.97
1.02
0.96
1.00
0.98
0.92
1.01
0.98
0.95
0.99
0.95
2.89
2.77
2.81
2.97
9.46
8.69
f1 (ppm)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128.5478
128.4463
128.2338
128.1824
125.6961
124.3605
106.5774
106.4317
102.8243
97.1444
91.0239
84.8501
84.5570
55.3161
55.2437
47.1387
46.5957
27.3381
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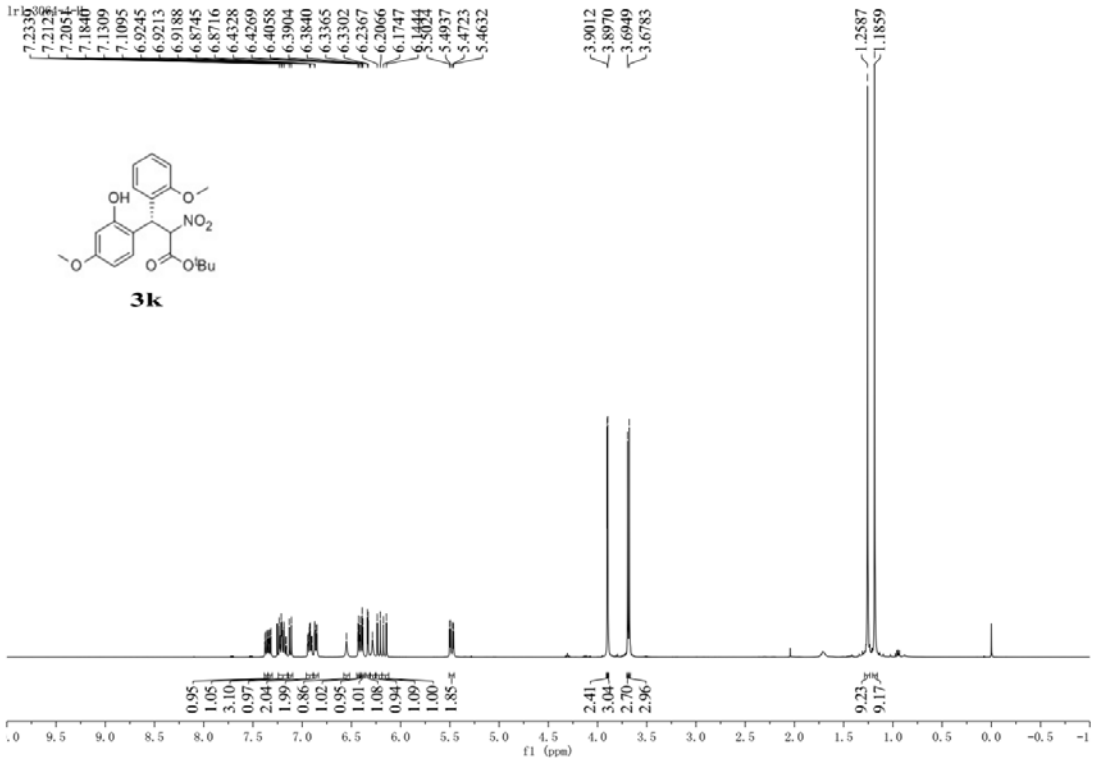
21.3834
OH
NO2
O
O
tBu
3j
f1 (ppm)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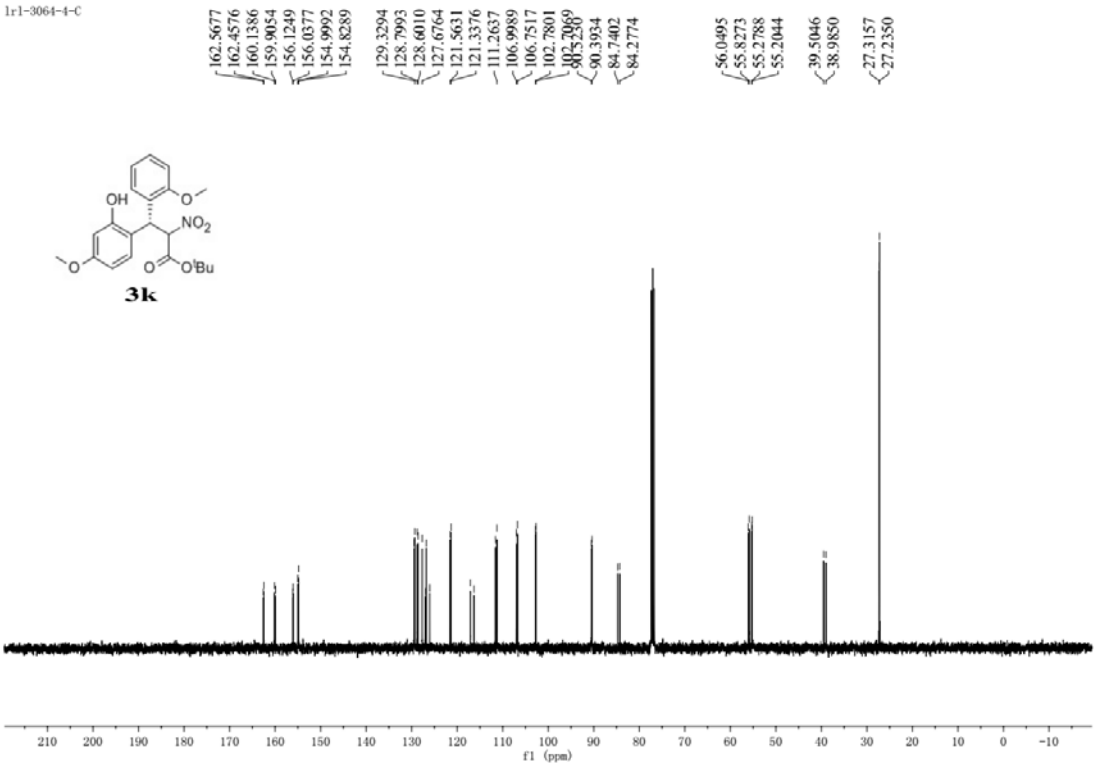
7.1309
7.1095
6.9245
6.9213
6.9188
6.8745
6.8716
6.4328
6.4269
6.4058
6.3904
6.3840
6.3365
6.3302
6.2367
6.2066
6.1747
5.4937
5.4723
5.4632
3.9012
3.8970
3.6949
3.6783
1.2587
1.1859
OH
NO2
O
O
tBu
3k
0.95
1.05
3.10
0.97
2.04
1.99
0.86
1.02
0.95
1.01
1.08
0.94
1.09
1.00
1.85
2.41
3.04
2.70
2.96
9.23
9.17
f1 (ppm)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154.8289
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128.7993
128.6010
127.6764
121.5631
121.3376
111.2637
106.9989
106.7517
102.7801
90.3934
84.7402
84.2774
56.0495
55.8273
55.2788
55.2044
39.5046
38.9850
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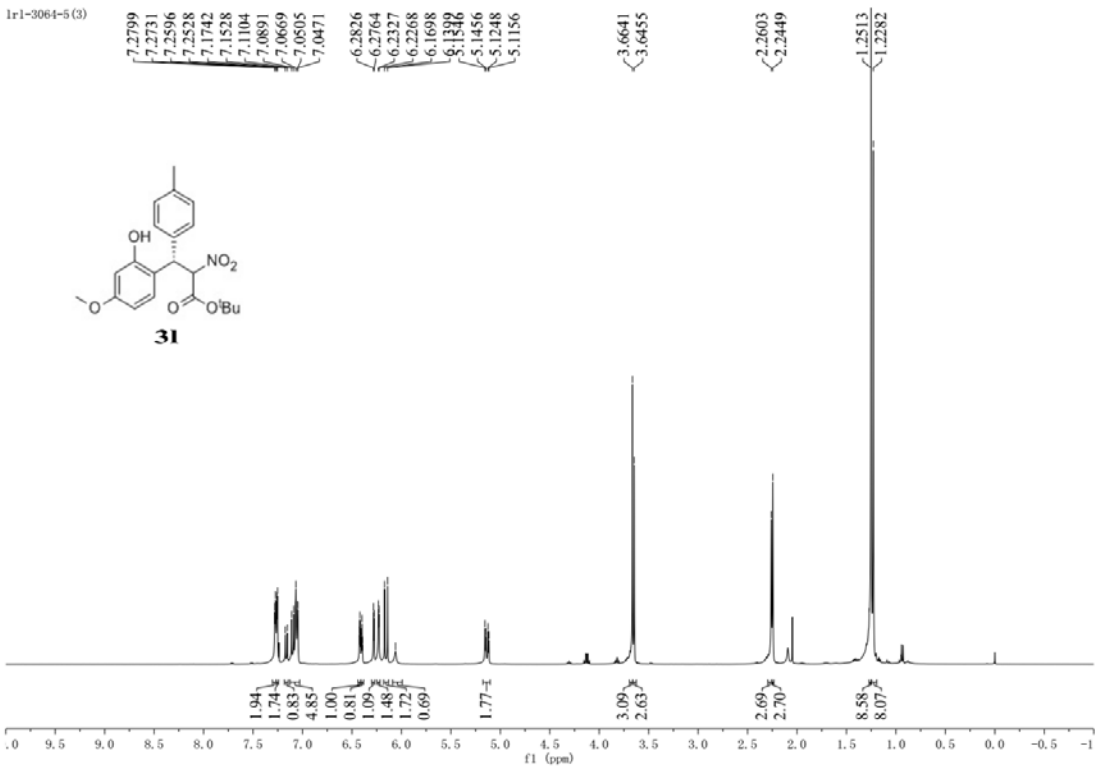
27.2350
OH
NO2
O
O
tBu
3k
f1 (ppm)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7.2528
7.1742
7.1528
7.1104
7.0891
7.0669
7.0505
7.0471
6.2826
6.2764
6.2327
6.2268
6.1698
6.1390
5.1546
5.1456
5.1248
5.1156
3.6641
3.6455
2.2603
2.2449
1.2513
1.2282
OH
NO2
O
OtBu
31
1.94
1.74
0.83
4.85
1.00
0.81
1.09
1.48
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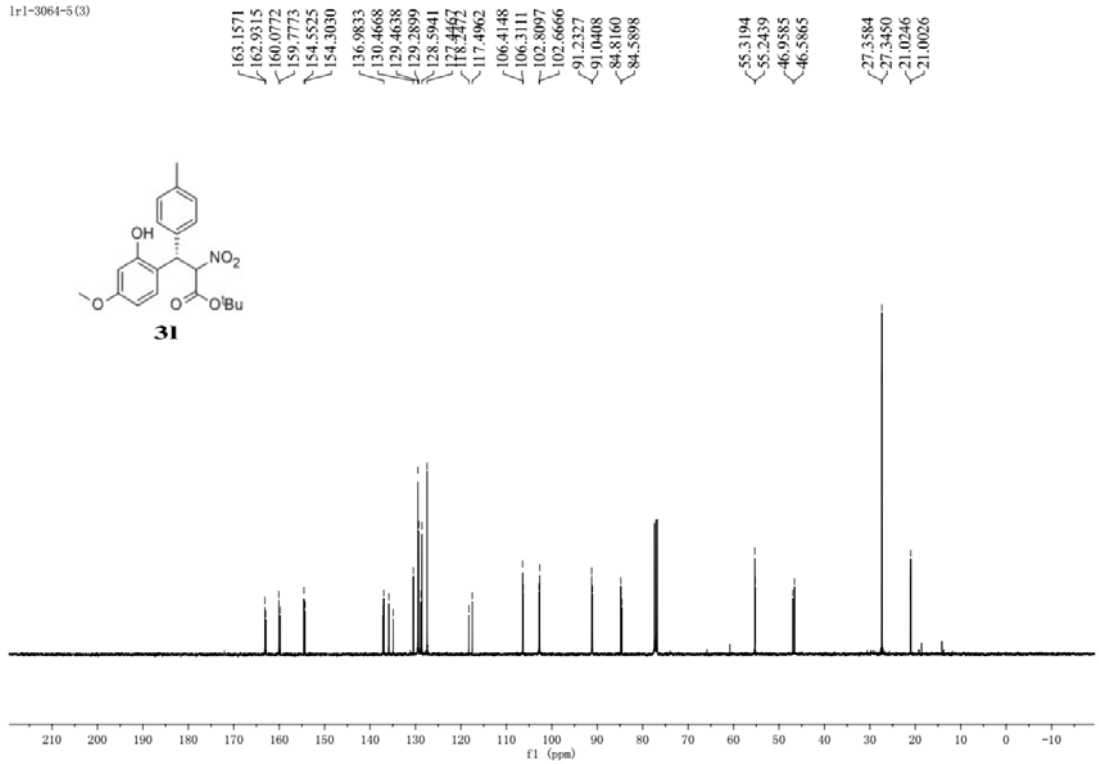
0.69
1.77
3.09
2.63
2.69
2.70
8.58
8.07
f1 (ppm)


lrl-3064-5(3)
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136.9833
130.4668
129.4638
129.2899
128.5941
127.4467
118.2472
117.4962
106.4148
106.3111
102.8097
102.6666
91.2327
91.0408
84.8160
84.5898
55.3194
55.2439
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27.3584
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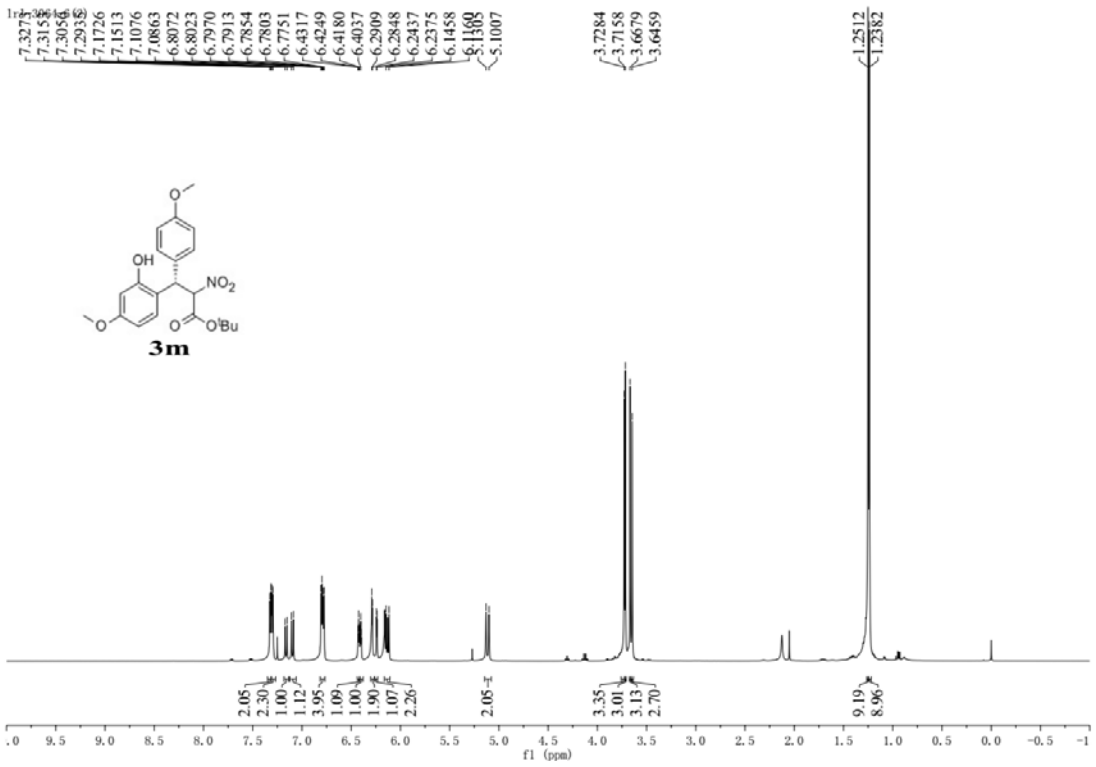
21.0026
OH
NO2
O
OtBu
31
f1 (ppm)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7.1076
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6.7970
6.7913
6.7854
6.7803
6.7751
6.4317
6.4249
6.4180
6.4037
6.2909
6.2848
6.2437
6.2375
6.1458
6.1160
6.1108
5.1007
3.7284
3.7158
3.6679
3.6459
1.2512
1.2382
OH
NO2
O
OtBu
3m
2.05
2.30
1.00
1.12
3.95
1.09
1.00
1.90
1.07
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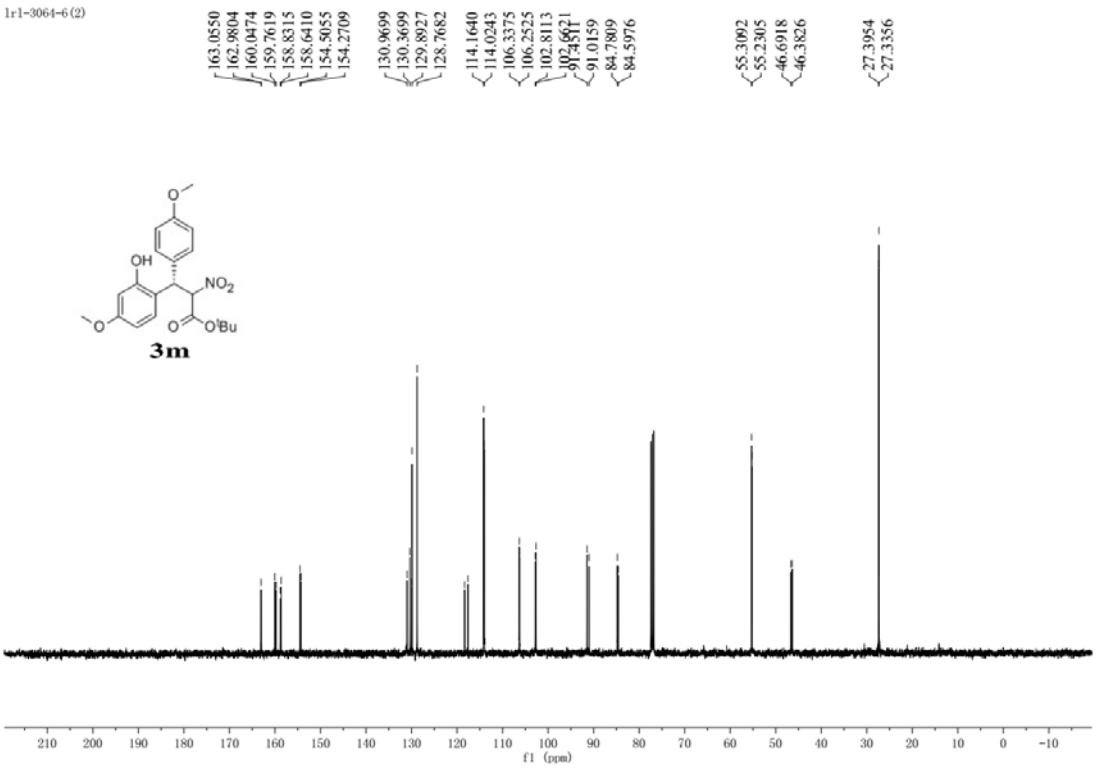
3.13
2.70
9.19
8.96
f1 (ppm)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114.0243
106.3375
106.2525
102.8113
102.6621
97.4511
91.0159
84.7809
84.5976
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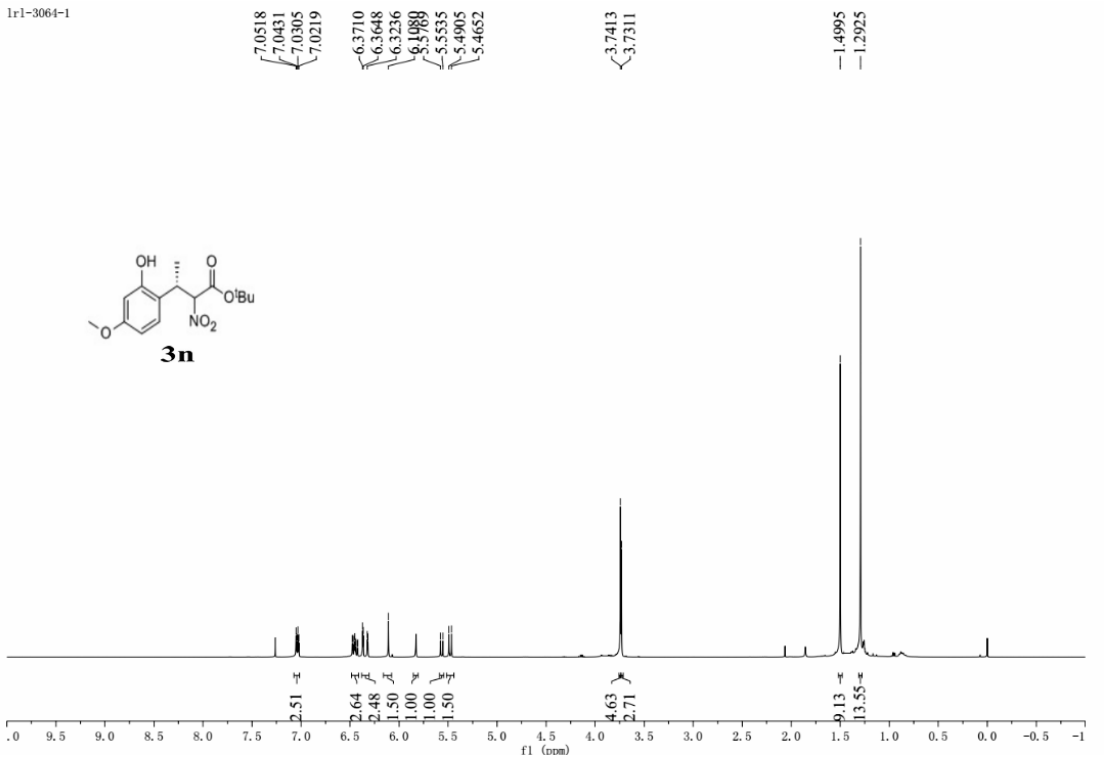
46.6918
46.3826
27.3954
27.3356
OH
NO2
O
OtBu
3m
f1 (ppm)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5.4905
5.4652
3.7413
3.7311
1.4995
1.2925
OH
O
O'Bu
NO2
O
3n
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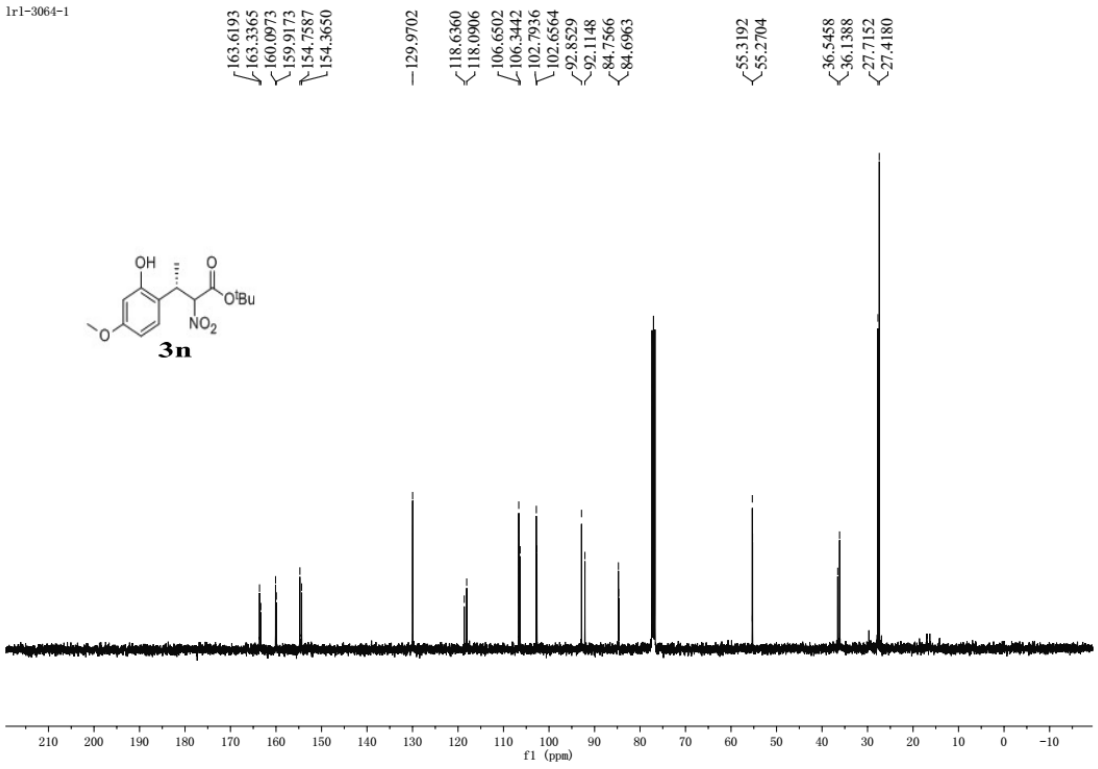
1.00
1.00
1.50
4.63
2.71
9.13
13.55
f1 (ppm)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129.9702
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106.6502
106.3442
102.7936
102.6564
92.8529
92.1148
84.7566
84.6963
55.3192
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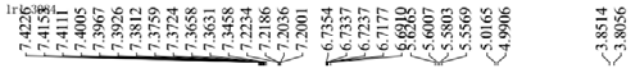
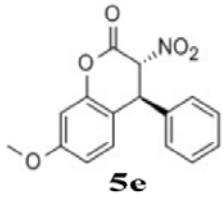
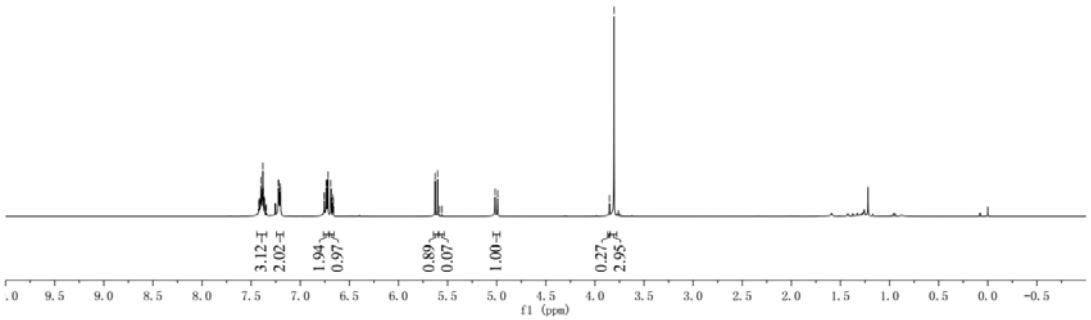
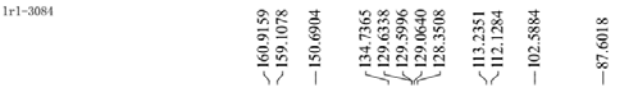
OH
O
O'Bu
NO2
O
3n
f1 (ppm)

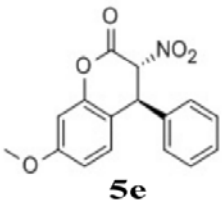




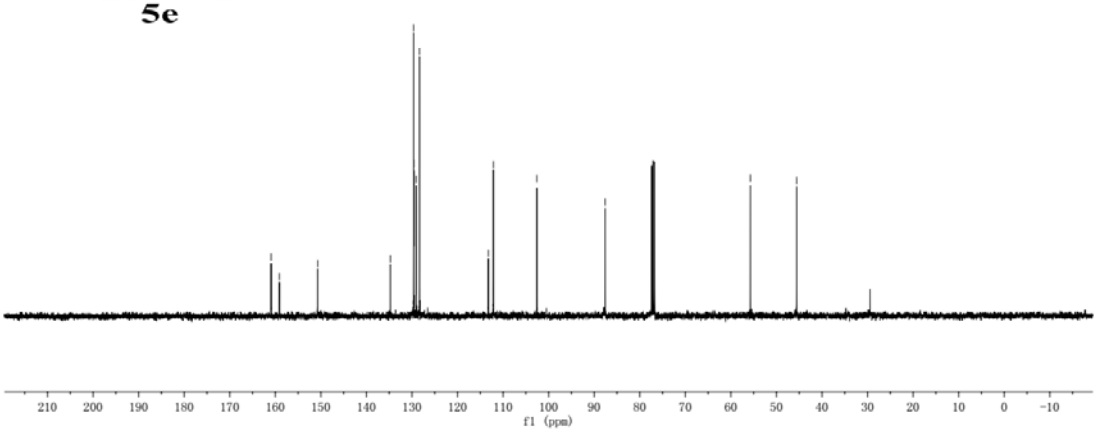
5e

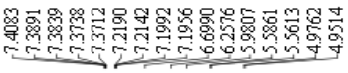






5e

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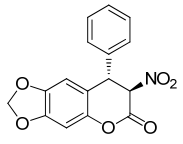
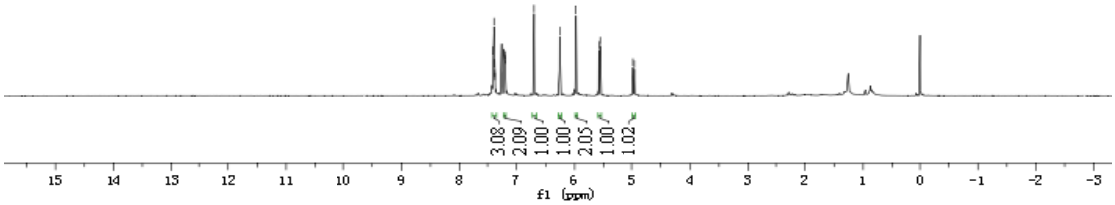
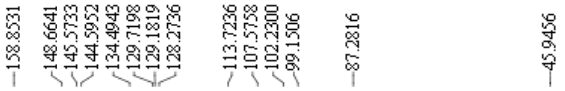
4.9762
4.9514


NO2
O
O
O
O

5g


3.08
2.09
1.00
1.00
2.05
1.00
1.02
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)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134.4943
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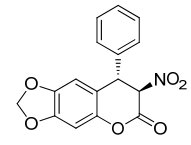
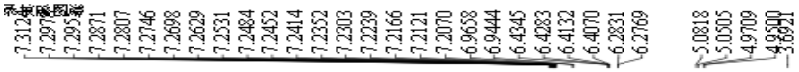
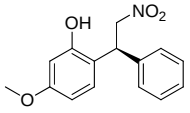
129.1819
128.2736
113.7236
107.5758
102.2300
99.1506
87.2816
45.9456


NO2
O
O
O
O

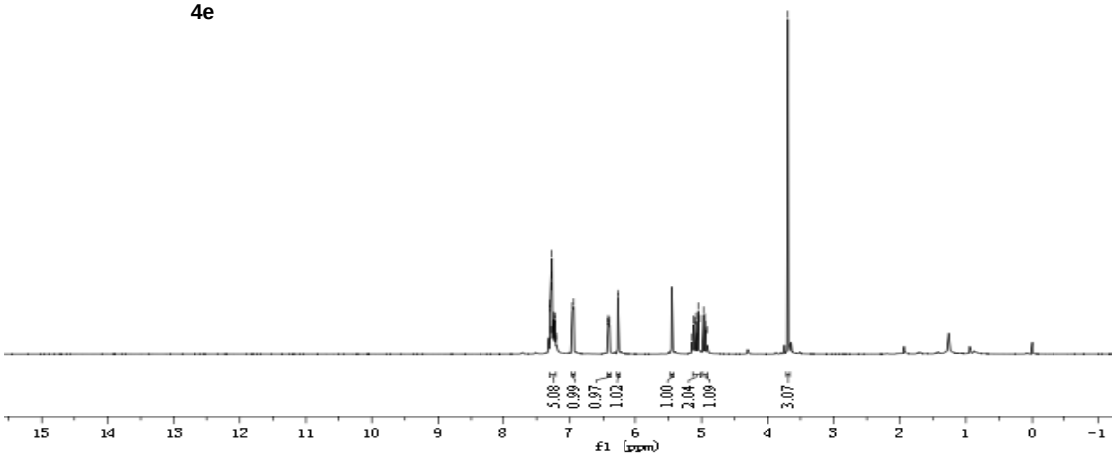
5g

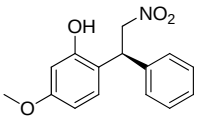
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



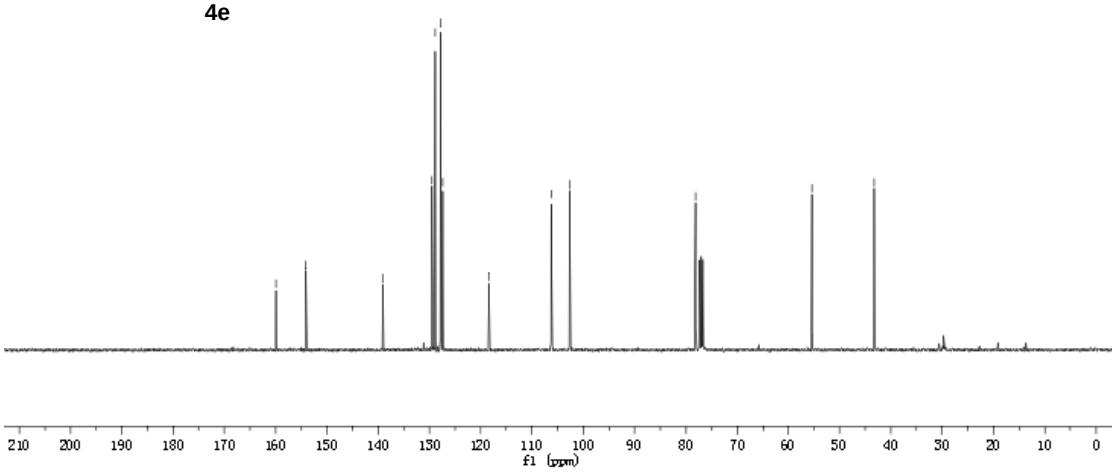


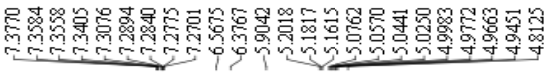
4e





4e

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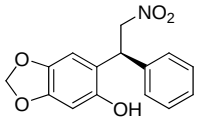
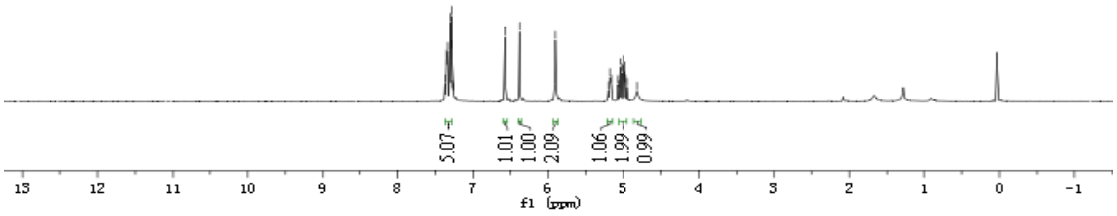
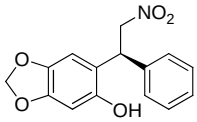
7.3558
7.3405
7.3076
7.2894
7.2840
7.2775
7.2701
6.5675
6.3767
5.9042
5.2018
5.1817
5.1615
5.0762
5.0570
5.0441
5.0250
4.9983
4.9772
4.9663
4.9451
4.8125


NO2
O
O
OH

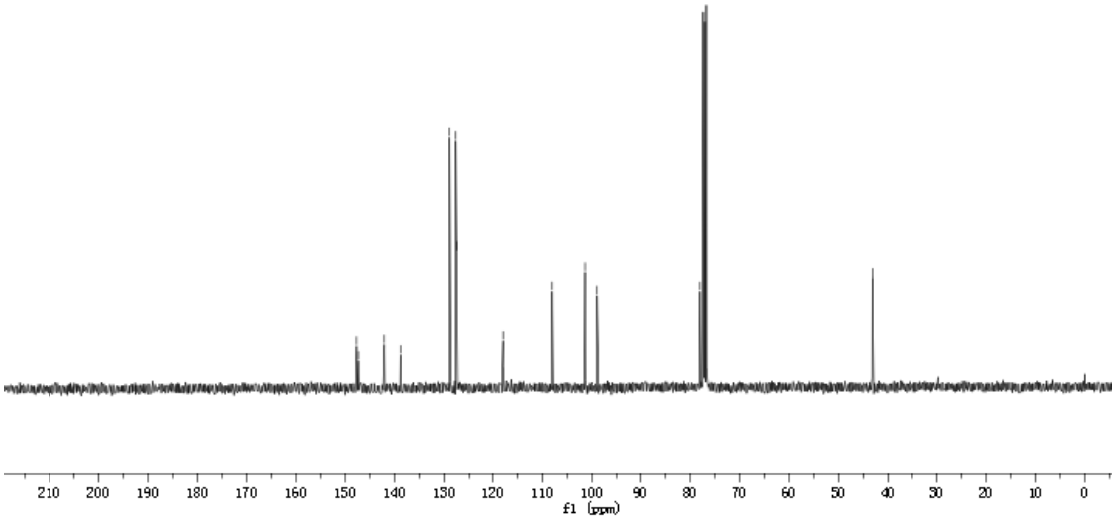
4g

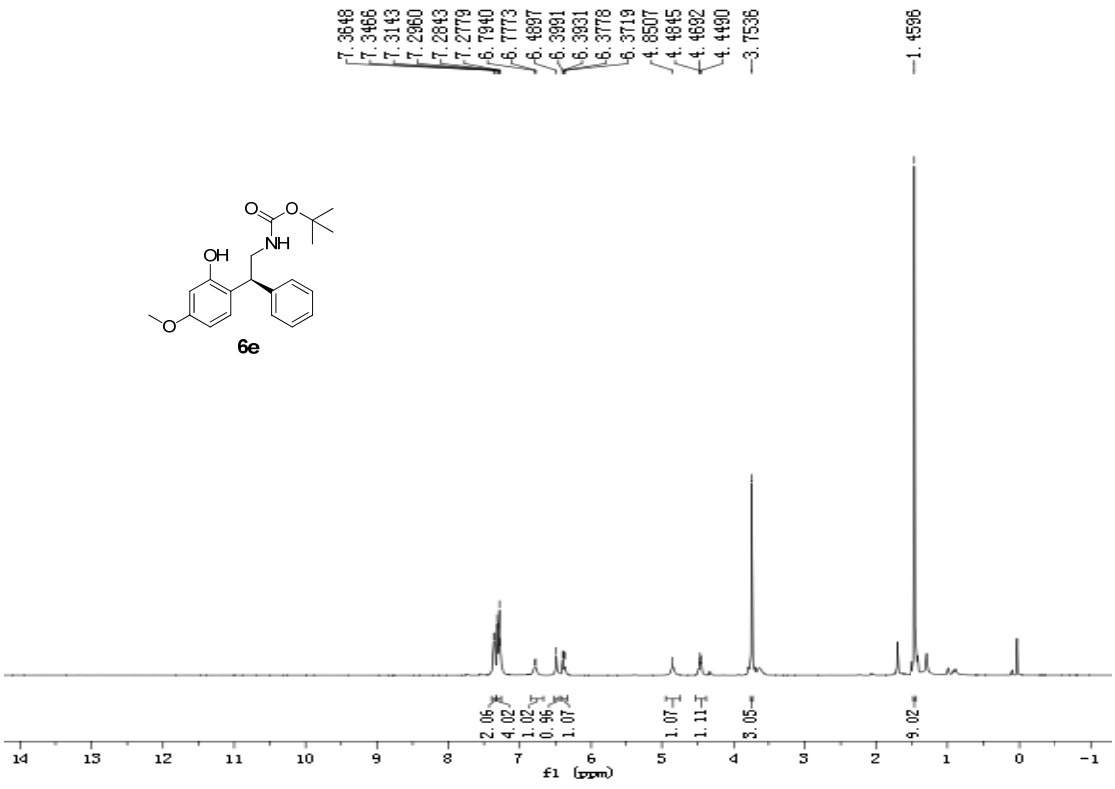

5.07
1.01
1.00
2.09
1.06
1.99
0.99
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)


147.6829
147.3251
142.0817
138.8112
128.9822
127.7155
127.5424
117.9022
108.0214
101.3792
98.9639
77.9860
43.1515


NO2
O
O
OH

4g


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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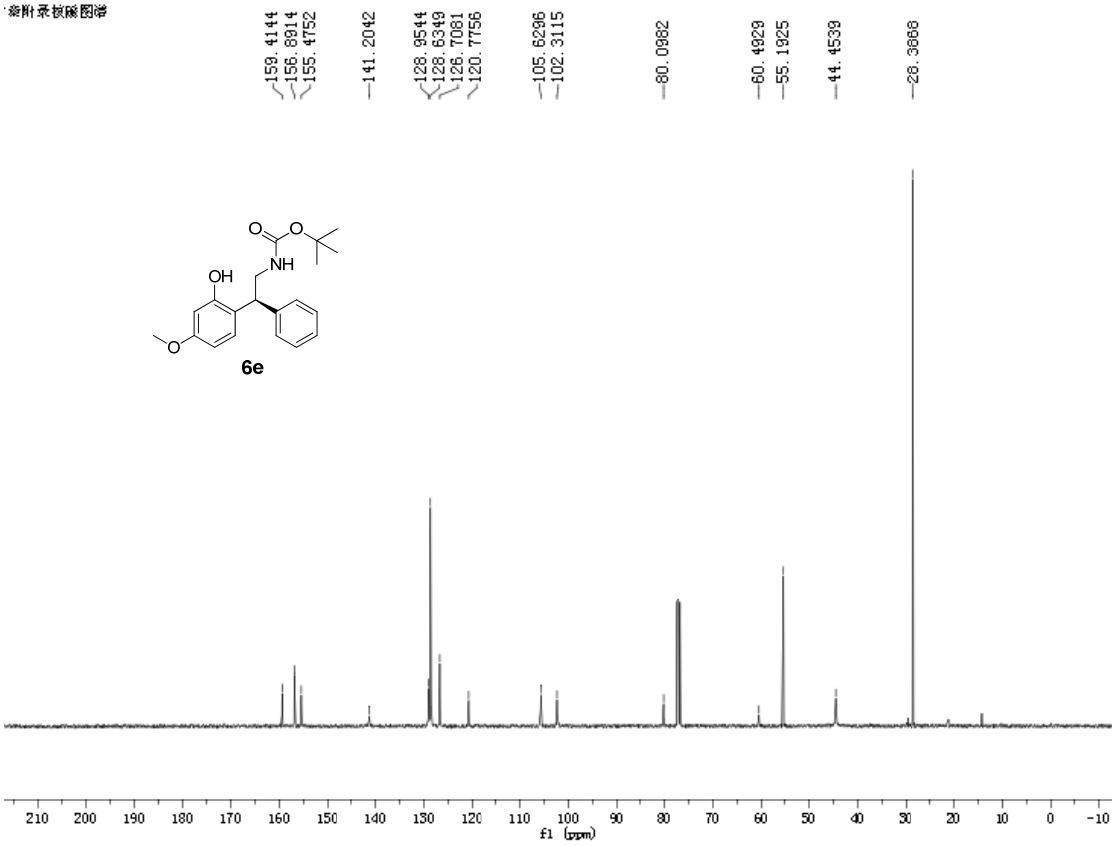
7.3466
7.3143
7.2960
7.2843
7.2779
6.7940
6.7773
6.4897
6.3991
6.3831
6.3778
6.3719
4.8507
4.4845
4.4682
4.4490
3.7536
1.4596
OH
NH
O
O
O
6e
2.06
4.02
1.02
0.96
1.07
1.07
1.11
3.05
9.02
f1 (ppm)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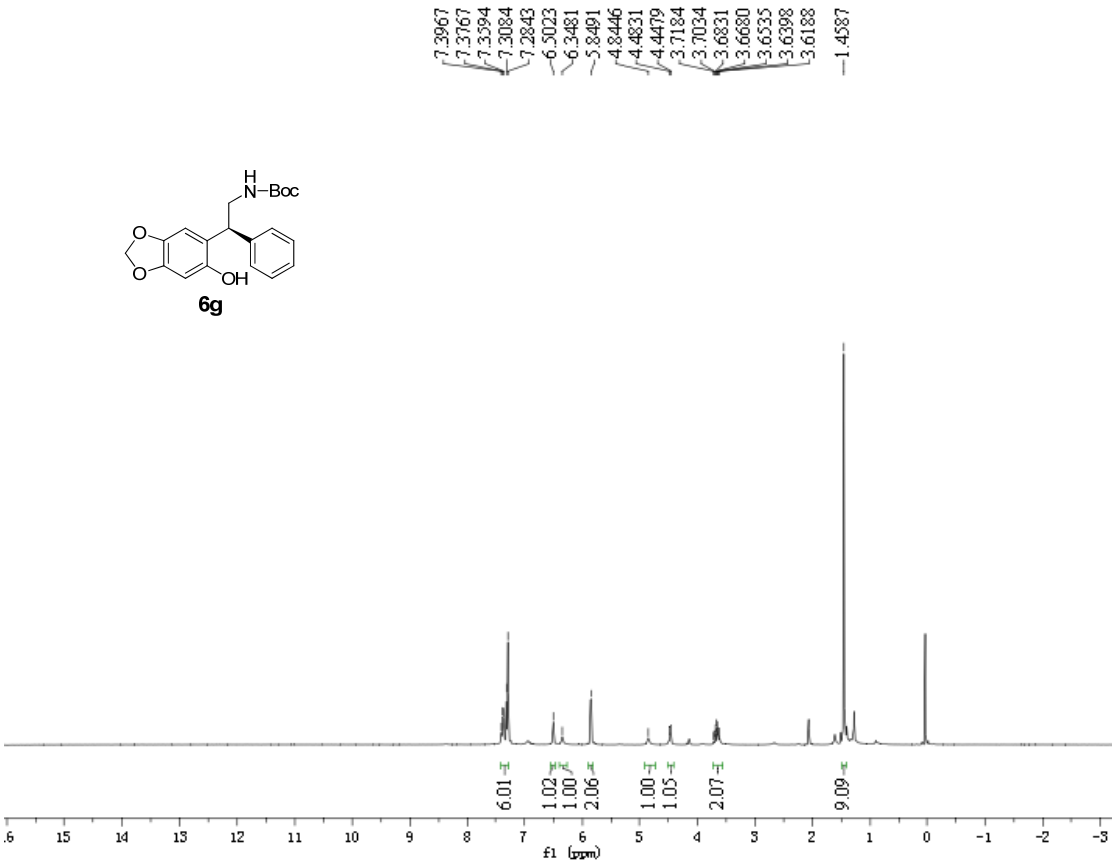
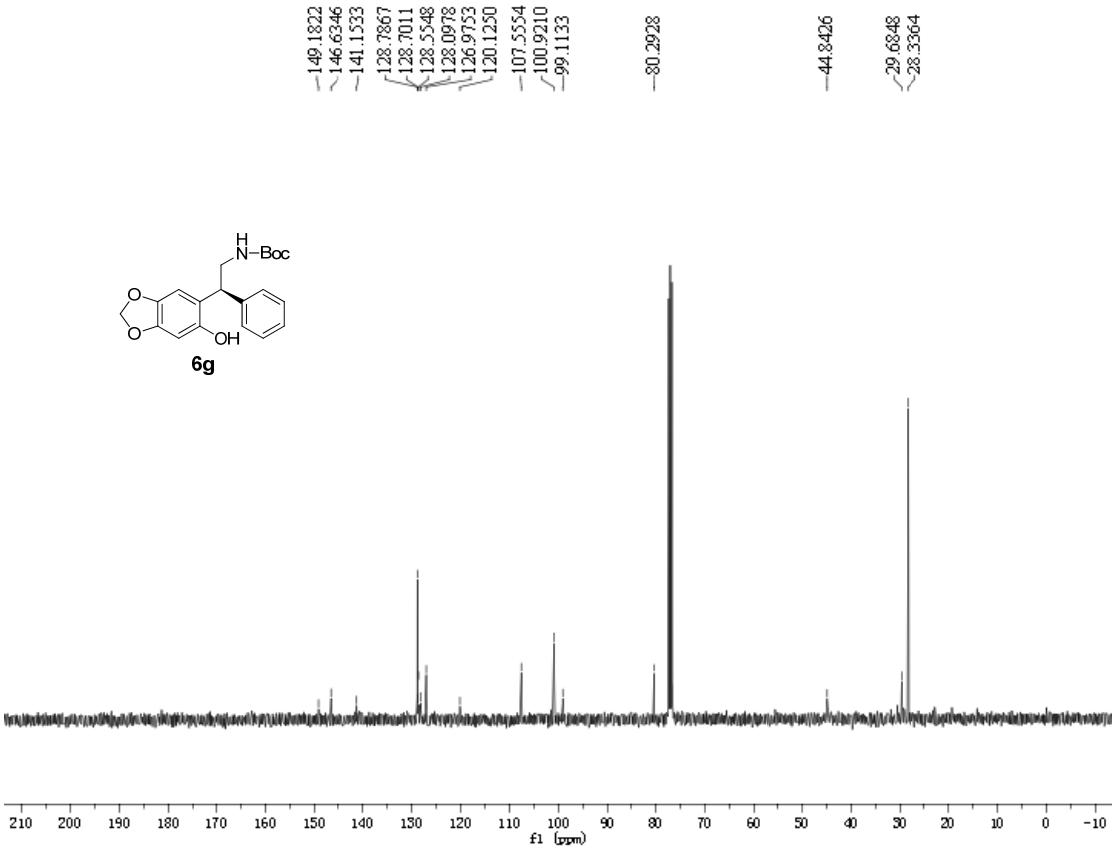
156.8914
155.4752
141.2042
128.9544
128.6349
126.7081
120.7756
105.6296
102.3115
80.0982
60.4929
55.1925
44.4539
28.3868
OH
NH
O
O
O
6e
f1 (ppm)


7.3967
7.3767
7.3594
7.3084
7.2843
6.5023
6.3481
5.8491
4.8446
4.4831
4.4479
3.7184
3.7034
3.6831
3.6680
3.6535
3.6398
3.6188
1.4587
H
N–Boc
O
O
OH
6g
6.01
1.02
1.00
2.06
1.00
1.05
2.07
9.09
f1 (ppm)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141.1533
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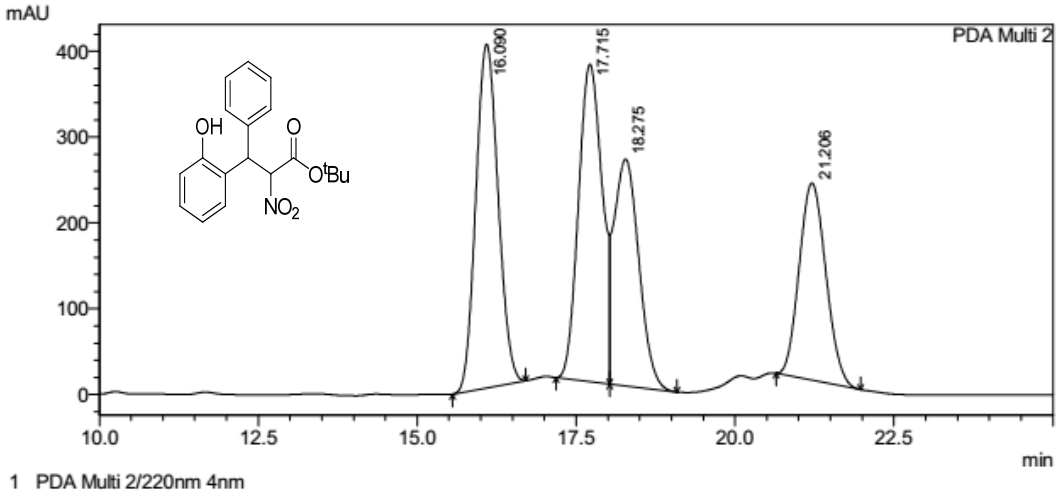
128.7011
128.5548
128.0978
126.9753
120.1250
107.5554
100.9210
99.1133
80.2928
44.8426
29.6848
28.3364
H
N–Boc
O
O
OH
6g
f1 (ppm)

VI. Copies of chiral HPLC chromatograms

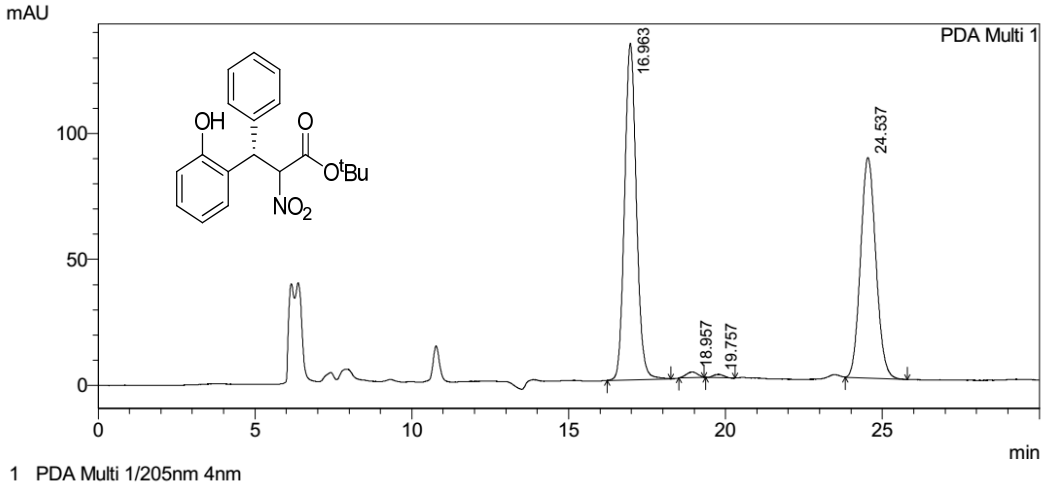


1 PDA Multi 2/220nm 4nm

PeakTable

PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.090	9739399	400158	29.316	31.673
2	17.715	9559998	369611	28.776	29.255
3	18.275	7226726	264104	21.752	20.904
4	21.206	6696460	229540	20.156	18.168
Total		33222582	1263413	100.000	100.000

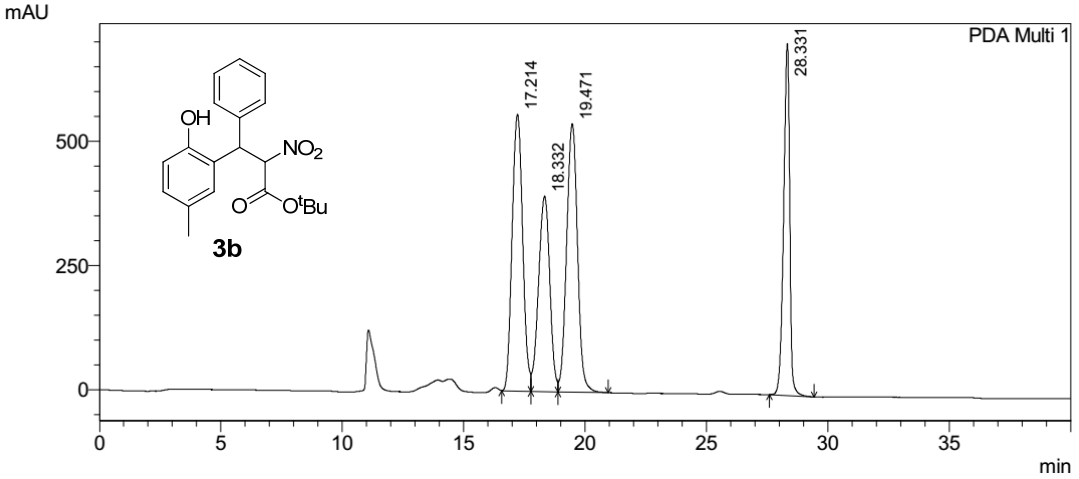


1 PDA Multi 1/205nm 4nm

PeakTable

PDA Ch1 205nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.963	3484044	133512	53.207	59.433
2	18.957	56351	2242	0.861	0.998
3	19.757	29508	1308	0.451	0.582
4	24.537	2978131	87583	45.481	38.987
Total		6548034	224644	100.000	100.000

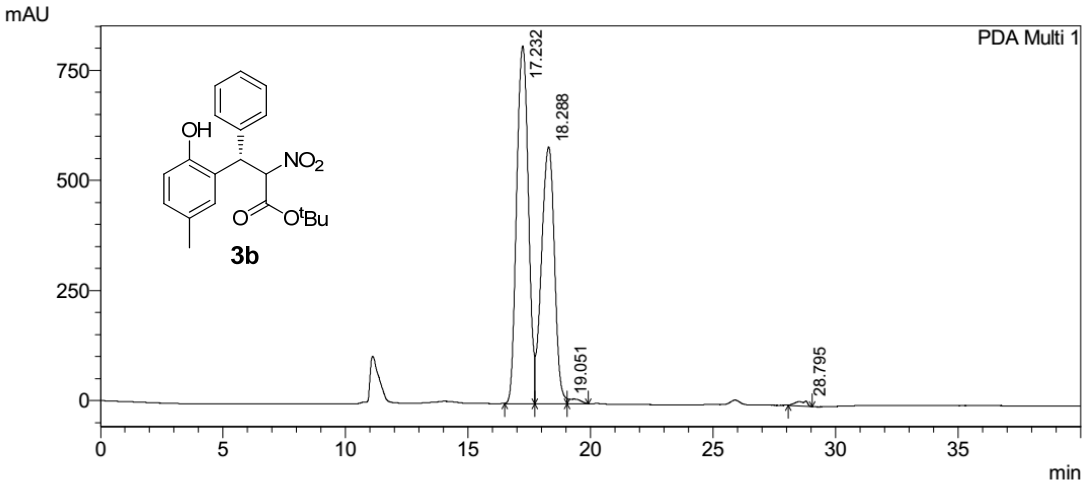


1 PDA Multi 1/205nm 4nm

PeakTable

PDA Ch1 205nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.214	16842011	556642	28.644	25.329
2	18.332	12704663	393021	21.608	17.884
3	19.471	16881725	539999	28.712	24.571
4	28.331	12368306	708005	21.036	32.216
Total		58796705	2197668	100.000	100.000

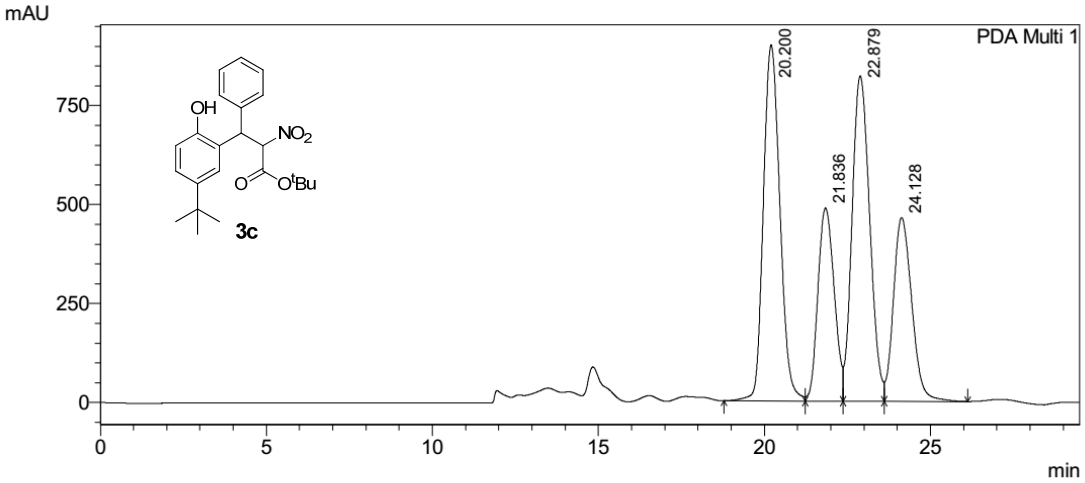


1 PDA Multi 1/205nm 4nm

PeakTable

PDA Ch1 205nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.232	27128458	812220	54.806	57.203
2	18.288	21599187	583945	43.635	41.126
3	19.051	412617	12035	0.834	0.848
4	28.795	358941	11699	0.725	0.824
Total		49499203	1419899	100.000	100.000

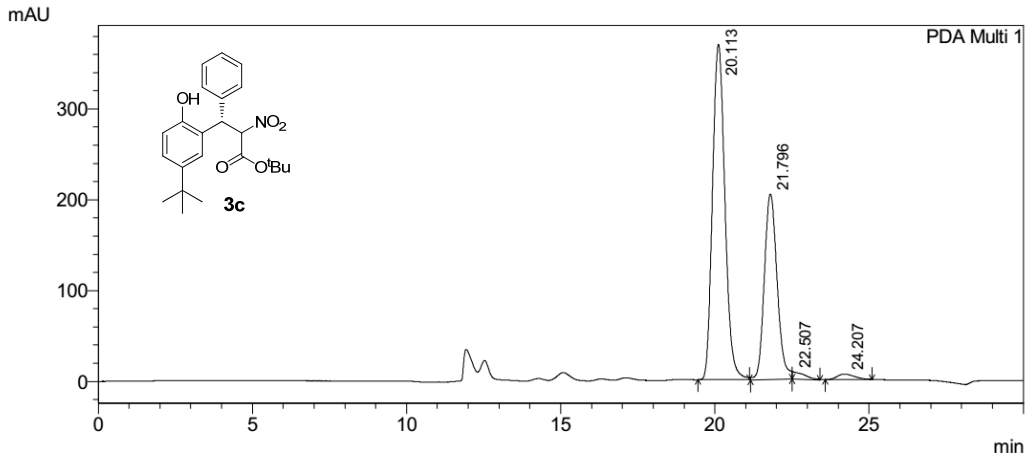


1 PDA Multi 1/205nm 4nm

PeakTable

PDA Ch1 205nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.200	31265518	899212	32.489	33.626
2	21.836	16679859	488166	17.332	18.255
3	22.879	30391367	822268	31.580	30.749
4	24.128	17898851	464488	18.599	17.370
Total		96235594	2674135	100.000	100.000

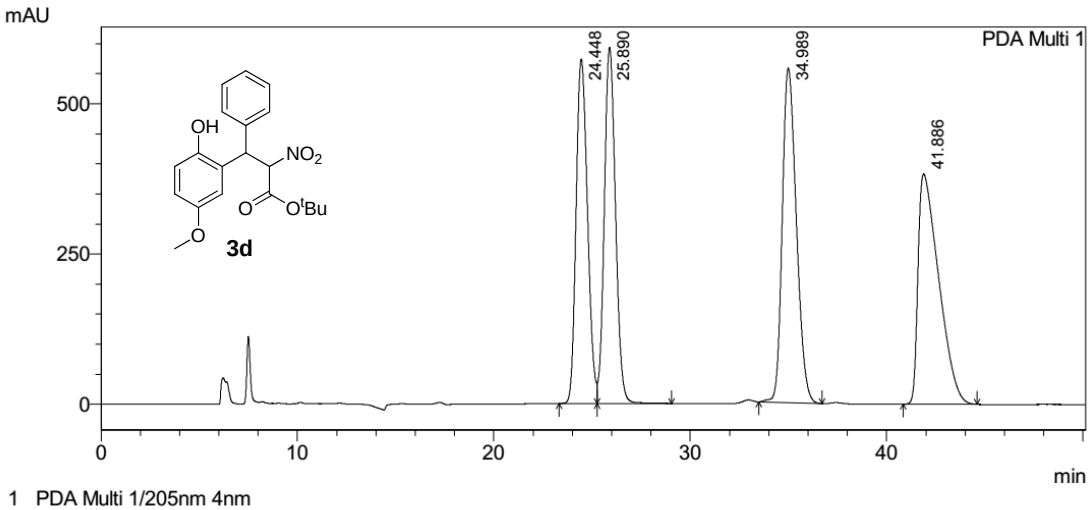


1 PDA Multi 1/205nm 4nm

PeakTable

PDA Ch1 205nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.113	10350187	368869	61.849	62.731
2	21.796	5911664	204581	35.326	34.791
3	22.507	233930	8517	1.398	1.448
4	24.207	238869	6053	1.427	1.029
Total		16734649	588020	100.000	100.000

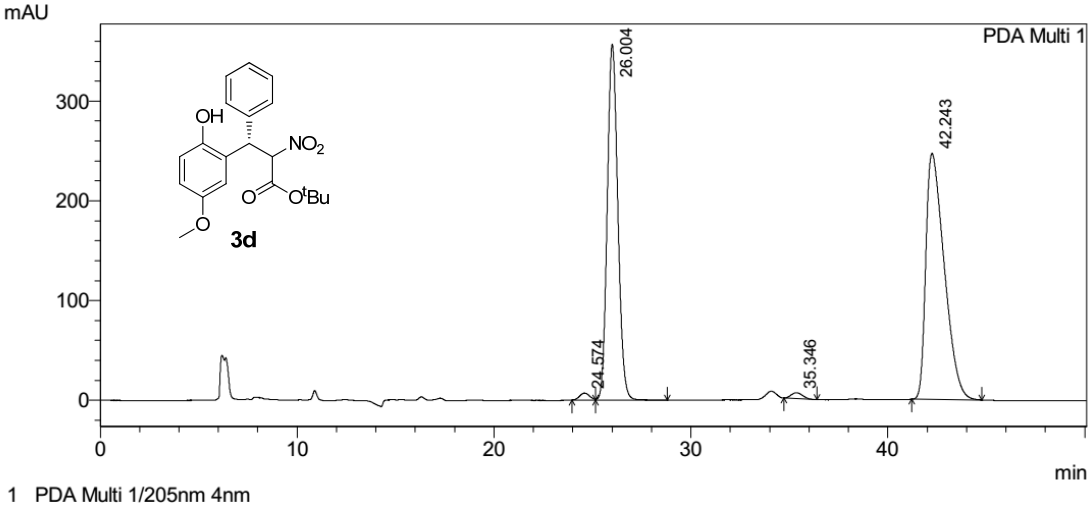


1 PDA Multi 1/205nm 4nm

PeakTable

PDA Ch1 205nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.448	23131351	572678	22.585	27.217
2	25.890	23478626	592039	22.924	28.138
3	34.989	27788252	556435	27.132	26.445
4	41.886	28021720	382941	27.360	18.200
Total		102419949	2104094	100.000	100.000

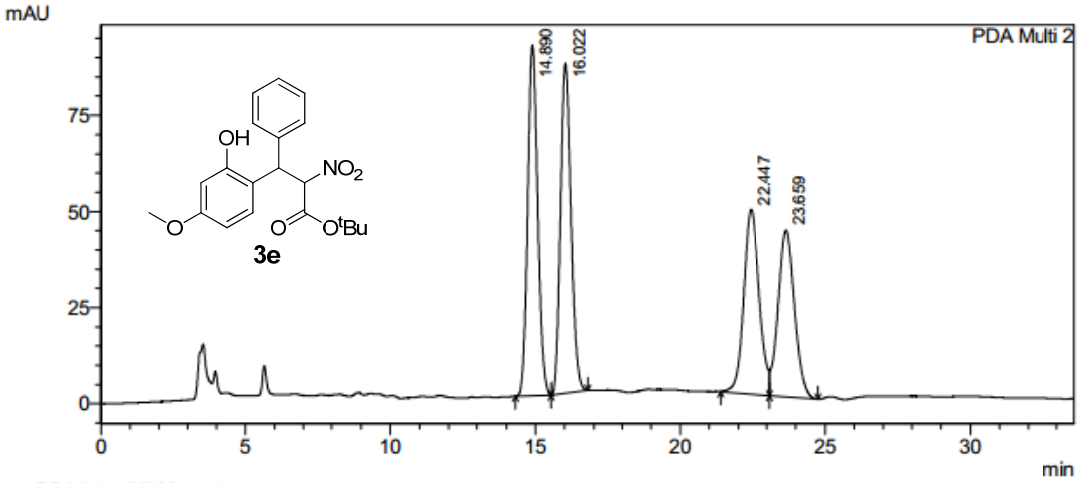


1 PDA Multi 1/205nm 4nm

PeakTable

PDA Ch1 205nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.574	236570	6840	0.793	1.110
2	26.004	13292289	356442	44.581	57.858
3	35.346	245606	6037	0.824	0.980
4	42.243	16041520	246739	53.802	40.051
Total		29815985	616058	100.000	100.000

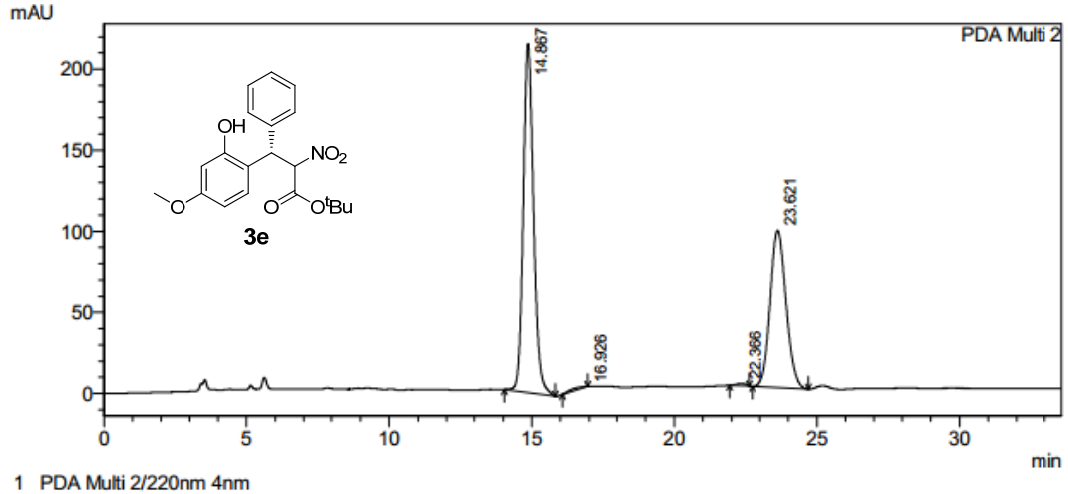


1 PDA Multi 2/220nm 4nm

PeakTable

PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.890	2167978	91199	27.626	33.984
2	16.022	2165347	85764	27.593	31.958
3	22.447	1819470	48083	23.185	17.917
4	23.659	1694673	43314	21.595	16.140
Total		7847467	268360	100.000	100.000

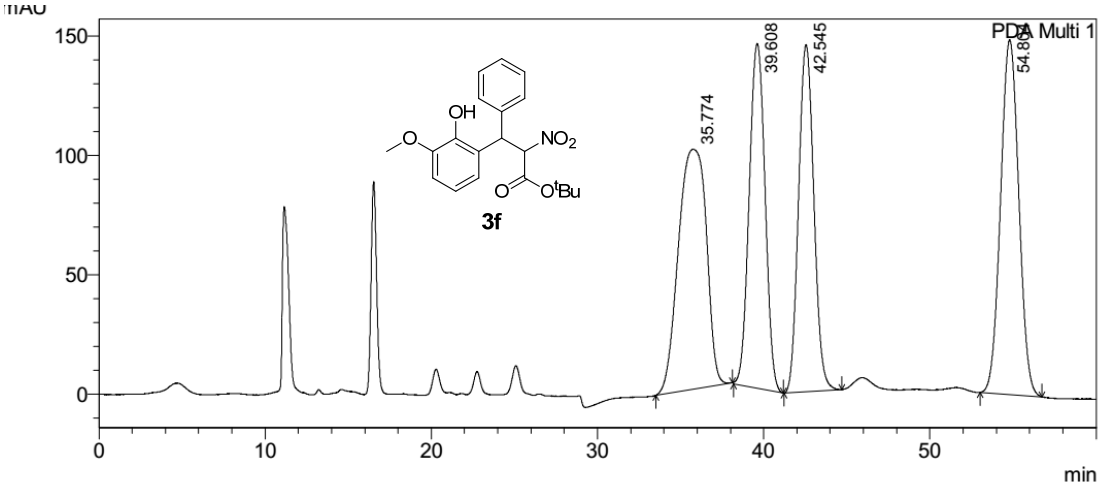


1 PDA Multi 2/220nm 4nm

PeakTable

PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.867	5370231	215143	58.403	68.617
2	16.926	43768	126	0.476	0.040
3	22.366	28134	1301	0.306	0.415
4	23.621	3752992	96973	40.815	30.928
Total		9195124	313543	100.000	100.000

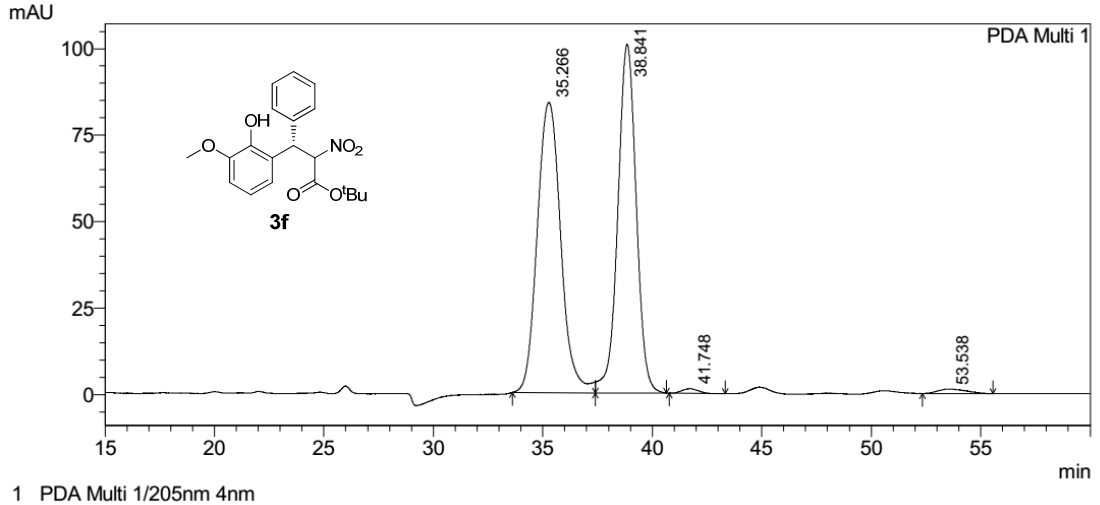


1 PDA Multi 1/205nm 4nm

PeakTable

PDA Ch1 205nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	35.774	11766742	100475	28.006	18.639
2	39.608	9609263	144540	22.871	26.813
3	42.545	9325391	145407	22.196	26.974
4	54.804	11313137	148642	26.927	27.574
Total		42014533	539064	100.000	100.000

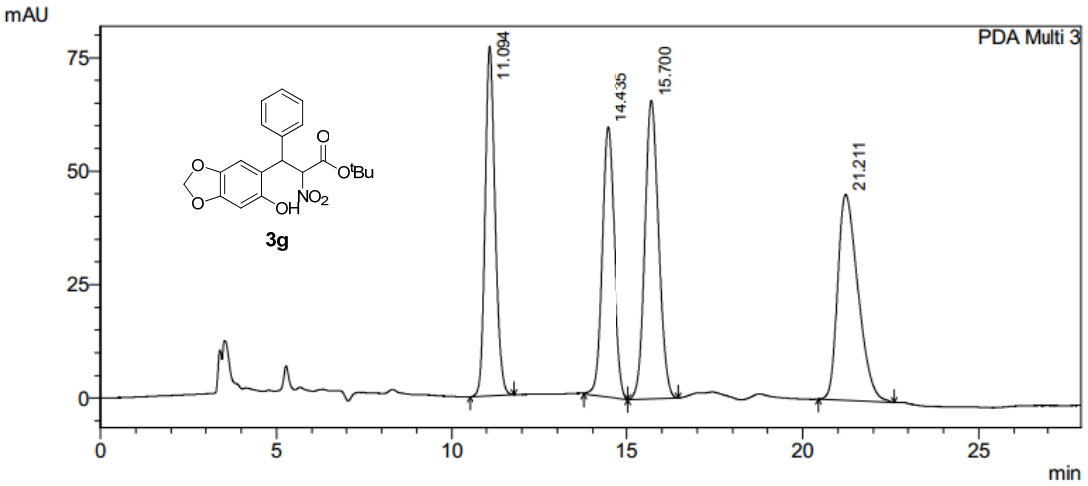


1 PDA Multi 1/205nm 4nm

PeakTable

PDA Ch1 205nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	35.266	6277805	83956	50.739	44.779
2	38.841	5905602	100809	47.731	53.768
3	41.748	72846	1389	0.589	0.741
4	53.538	116417	1336	0.941	0.712
Total		12372670	187491	100.000	100.000

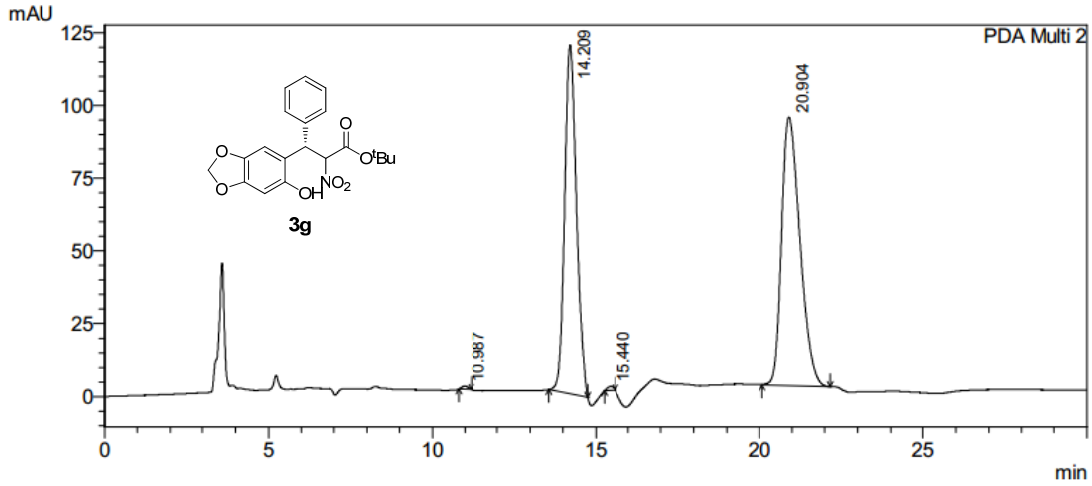


1 PDA Multi 3/230nm 4nm

PeakTable

PDA Ch3 230nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.094	1509124	76958	22.911	31.076
2	14.435	1469242	59511	22.305	24.031
3	15.700	1786874	65797	27.127	26.569
4	21.211	1821801	45377	27.657	18.324
Total		6587040	247643	100.000	100.000

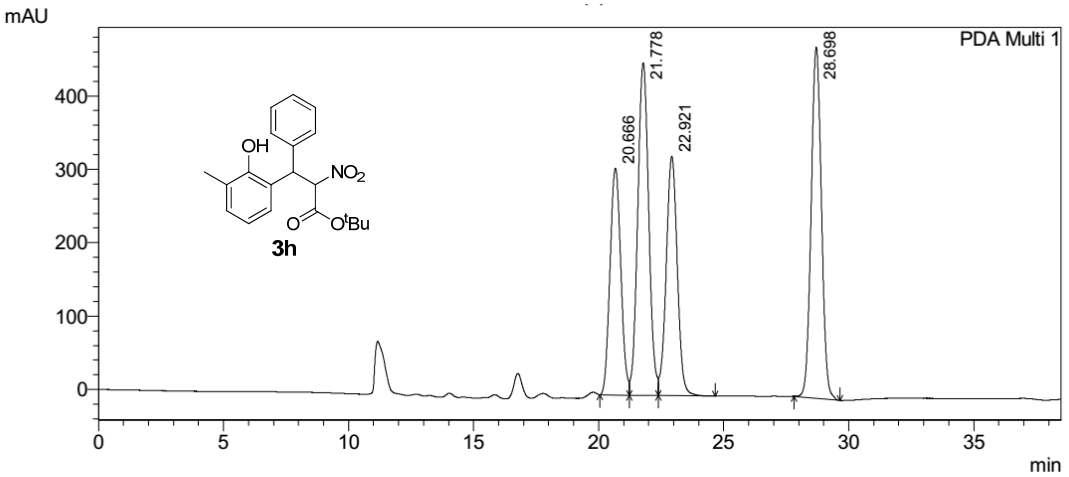


1 PDA Multi 2/220nm 4nm

PeakTable

PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.987	14422	1079	0.219	0.503
2	14.209	2972262	119800	45.058	55.844
3	15.440	18236	1396	0.276	0.651
4	20.904	3591650	92252	54.447	43.002
Total		6596569	214528	100.000	100.000

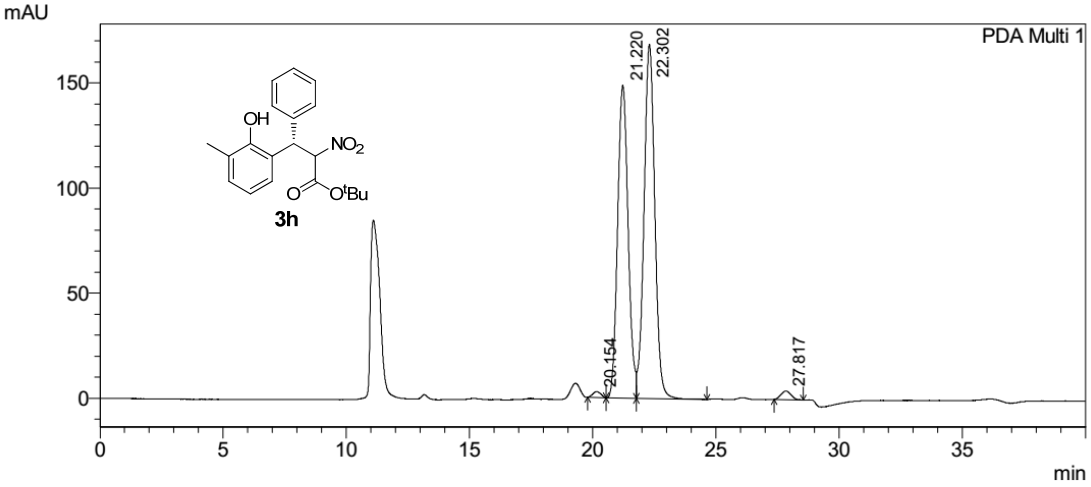


1 PDA Multi 1/205nm 4nm

PeakTable

PDA Ch1 205nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.666	9299115	309230	19.808	19.734
2	21.778	13898110	453099	29.604	28.916
3	22.921	10055922	326404	21.420	20.830
4	28.698	13692811	478219	29.167	30.519
Total		46945958	1566951	100.000	100.000

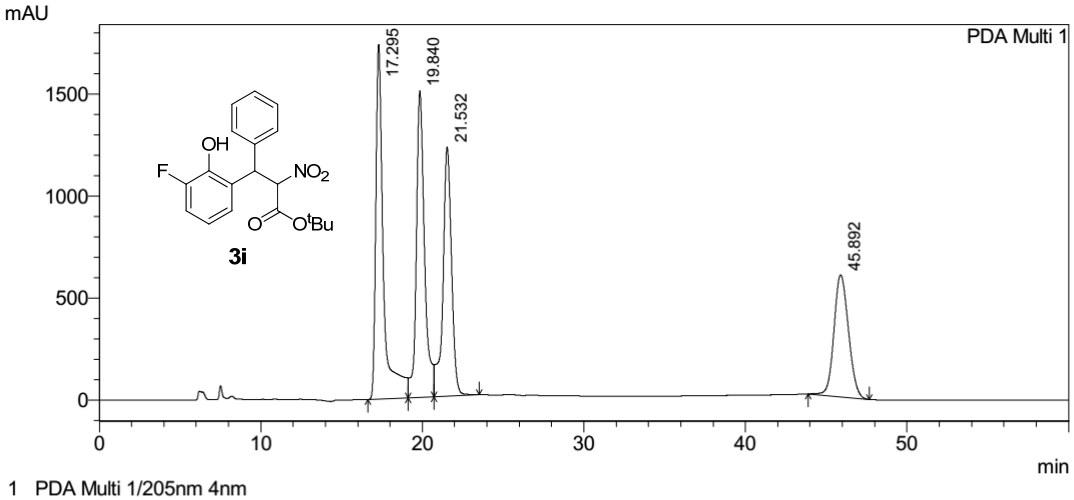


1 PDA Multi 1/205nm 4nm

PeakTable

PDA Ch1 205nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.154	67441	2874	0.693	0.886
2	21.220	4423449	148922	45.477	45.901
3	22.302	5119989	168547	52.637	51.949
4	27.817	116008	4101	1.193	1.264
Total		9726888	324445	100.000	100.000

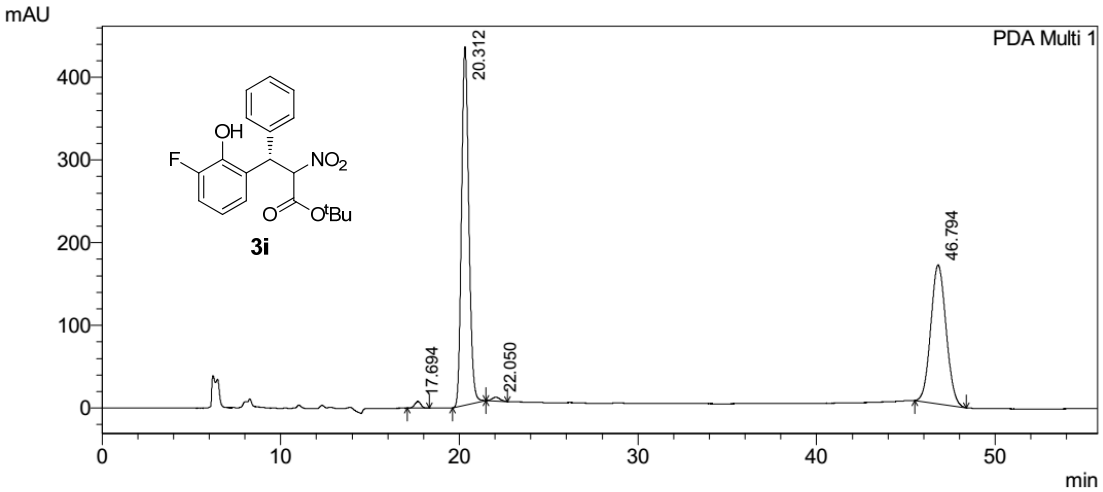


1 PDA Multi 1/205nm 4nm

PeakTable

PDA Ch1 205nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.295	57101310	1738704	29.605	34.332
2	19.840	52713038	1503676	27.330	29.691
3	21.532	45544984	1223046	23.614	24.150
4	45.892	37516785	598954	19.451	11.827
Total		192876117	5064381	100.000	100.000

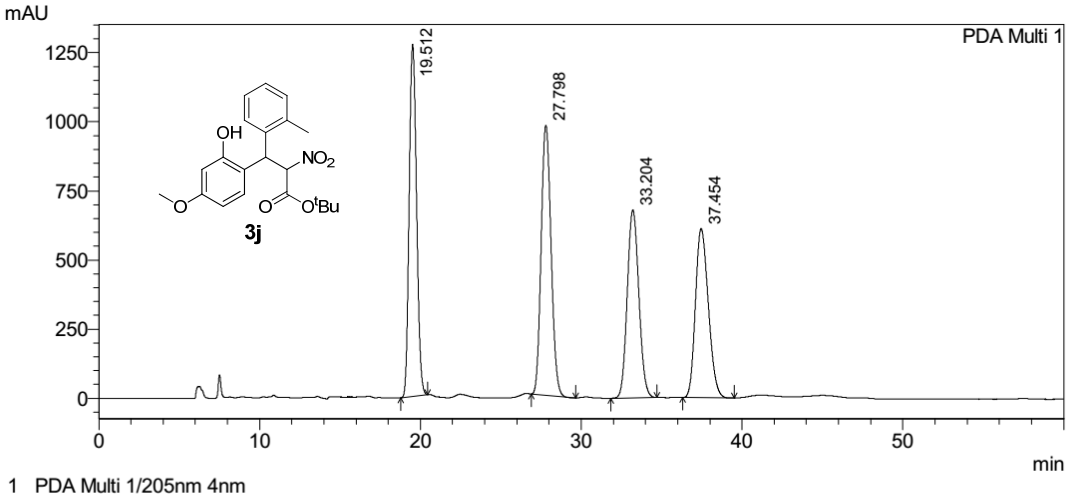


1 PDA Multi 1/205nm 4nm

PeakTable

PDA Ch1 205nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.694	196298	8125	0.867	1.323
2	20.312	12284462	433235	54.244	70.569
3	22.050	143141	4644	0.632	0.757
4	46.794	10022951	167910	44.258	27.351
Total		22646854	613914	100.000	100.000

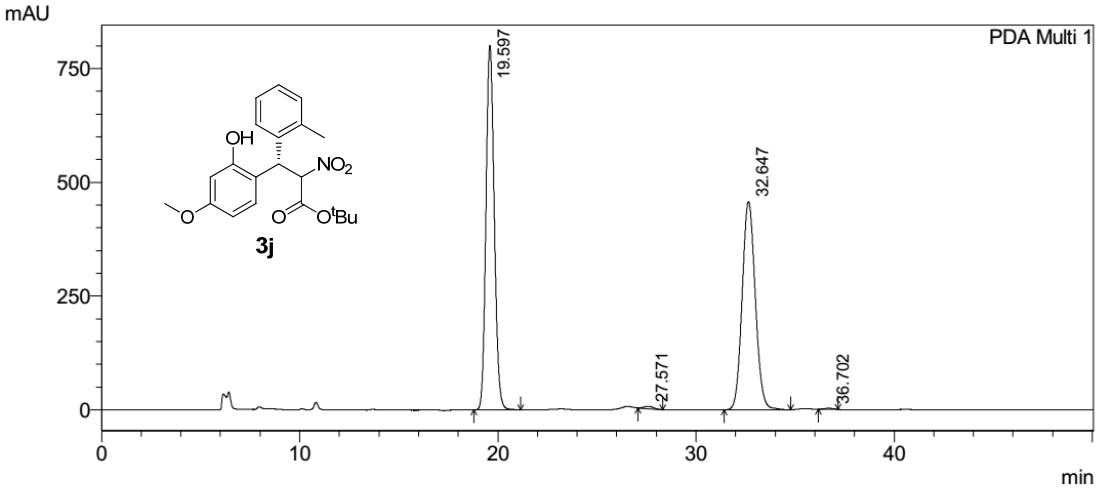


1 PDA Multi 1/205nm 4nm

PeakTable

PDA Ch1 205nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.512	40755081	1273598	27.016	35.948
2	27.798	41867674	977537	27.754	27.591
3	33.204	34079007	680363	22.591	19.203
4	37.454	34153176	611414	22.640	17.257
Total		150854938	3542912	100.000	100.000

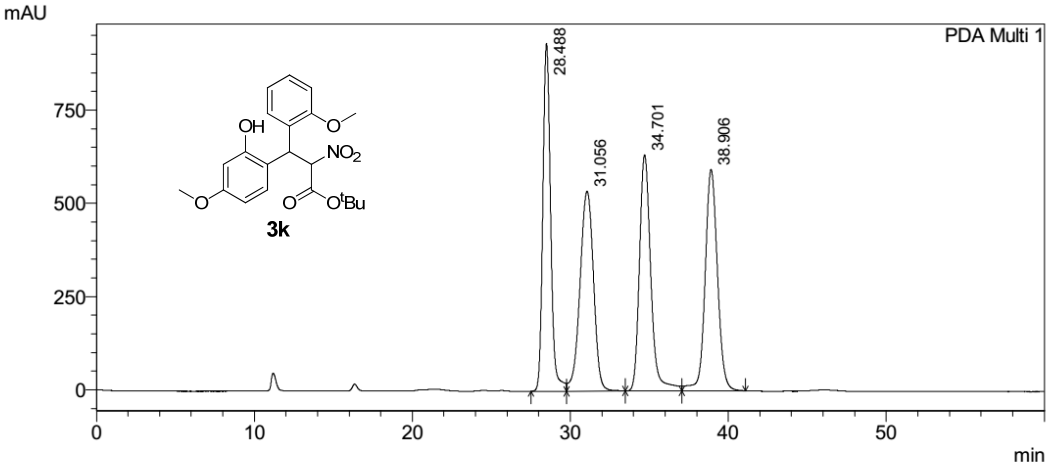


1 PDA Multi 1/205nm 4nm

PeakTable

PDA Ch1 205nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.597	23245137	800360	52.089	63.243
2	27.571	169079	4917	0.379	0.389
3	32.647	21129079	457848	47.347	36.178
4	36.702	82857	2404	0.186	0.190
Total		44626152	1265530	100.000	100.000

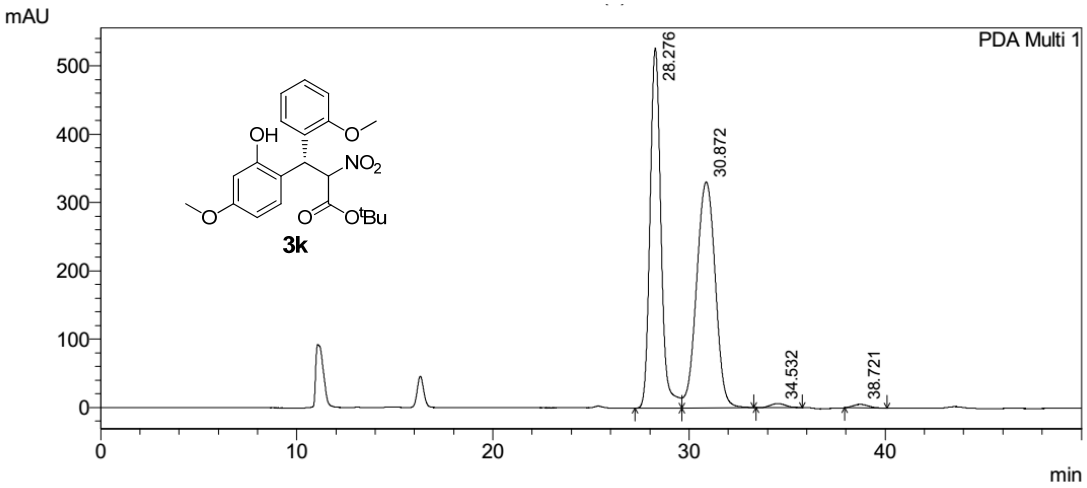


1 PDA Multi 1/205nm 4nm

PeakTable

PDA Ch1 205nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.488	31907627	931949	24.918	34.580
2	31.056	31987664	536064	24.981	19.890
3	34.701	31708166	633417	24.763	23.503
4	38.906	32445515	593661	25.338	22.027
Total		128048973	2695092	100.000	100.000

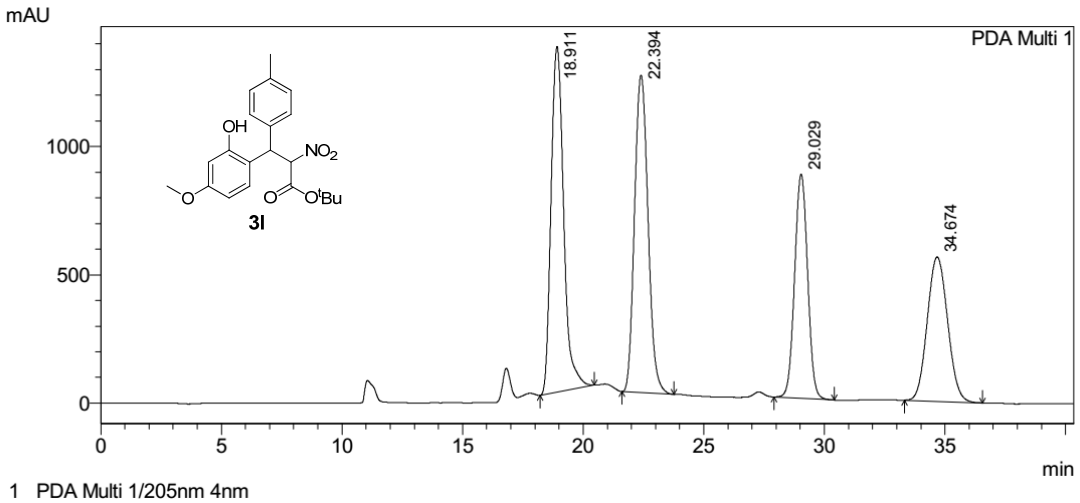


1 PDA Multi 1/205nm 4nm

PeakTable

PDA Ch1 205nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.276	20345138	526867	47.436	60.647
2	30.872	21951276	330769	51.181	38.075
3	34.532	305864	5873	0.713	0.676
4	38.721	287403	5230	0.670	0.602
Total		42889681	868739	100.000	100.000

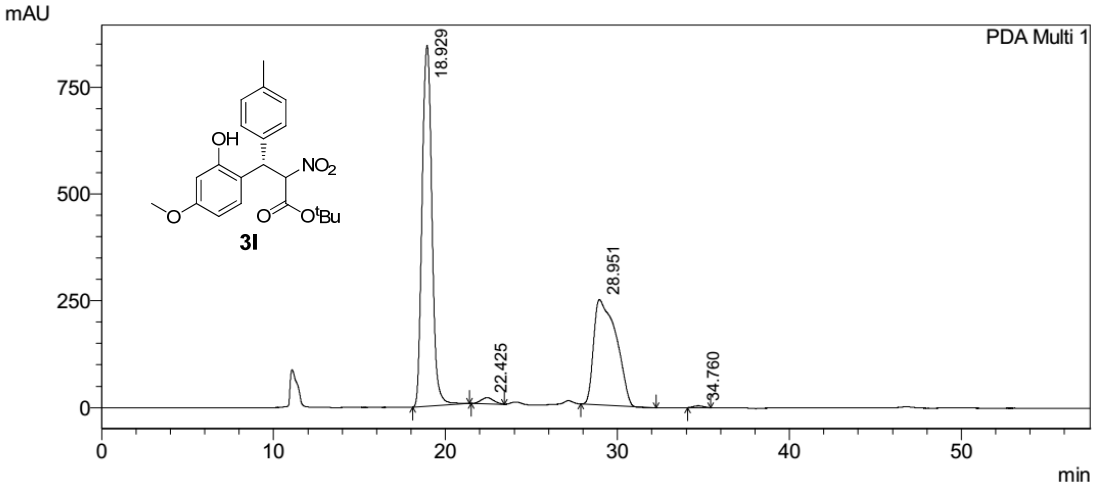


1 PDA Multi 1/205nm 4nm

PeakTable

PDA Ch1 205nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.911	48977723	1345960	30.061	33.481
2	22.394	48170295	1237770	29.566	30.790
3	29.029	32735306	873568	20.092	21.730
4	34.674	33041800	562745	20.280	13.998
Total		162925124	4020043	100.000	100.000

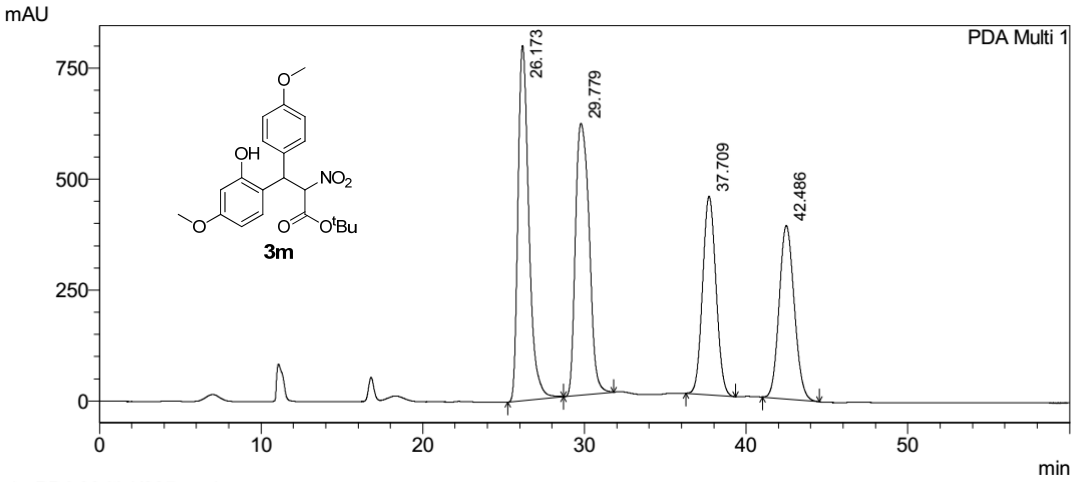


1 PDA Multi 1/205nm 4nm

PeakTable

PDA Ch1 205nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.929	33526703	844281	58.960	76.073
2	22.425	741597	14335	1.304	1.292
3	28.951	22410733	246771	39.411	22.235
4	34.760	184841	4436	0.325	0.400
Total		56863874	1109824	100.000	100.000

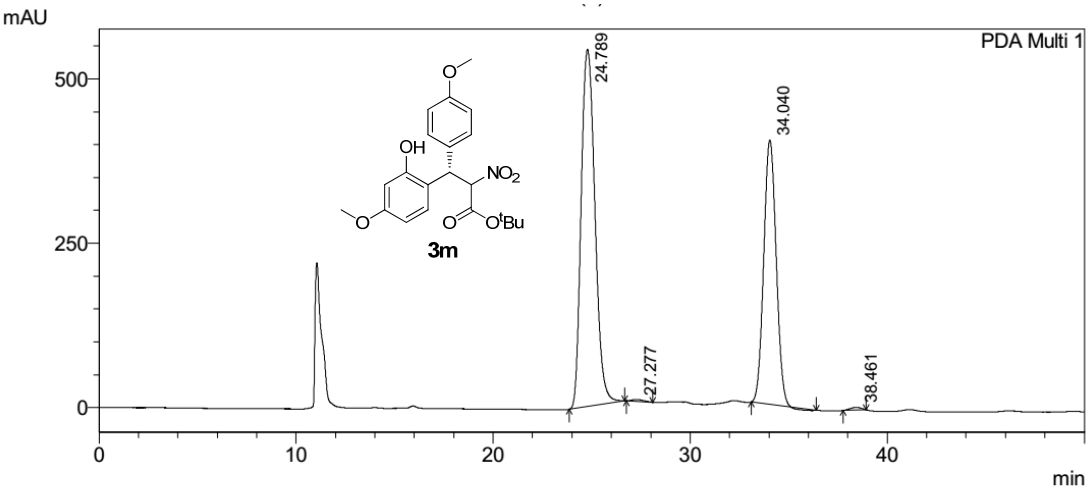


1 PDA Multi 1/205nm 4nm

PeakTable

PDA Ch1 205nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.173	37341926	800202	29.960	35.533
2	29.779	36129196	613029	28.987	27.221
3	37.709	25761592	447705	20.669	19.880
4	42.486	25406944	391071	20.384	17.365
Total		124639658	2252006	100.000	100.000

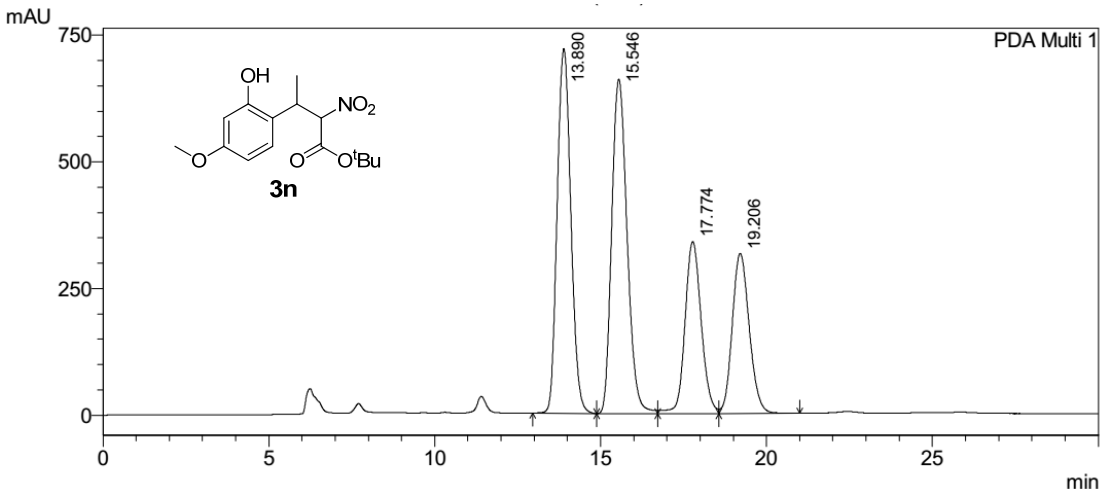


1 PDA Multi 1/205nm 4nm

PeakTable

PDA Ch1 205nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.789	26422543	543127	59.671	56.999
2	27.277	118743	2986	0.268	0.313
3	34.040	17575176	402573	39.691	42.248
4	38.461	164025	4193	0.370	0.440
Total		44280488	952879	100.000	100.000

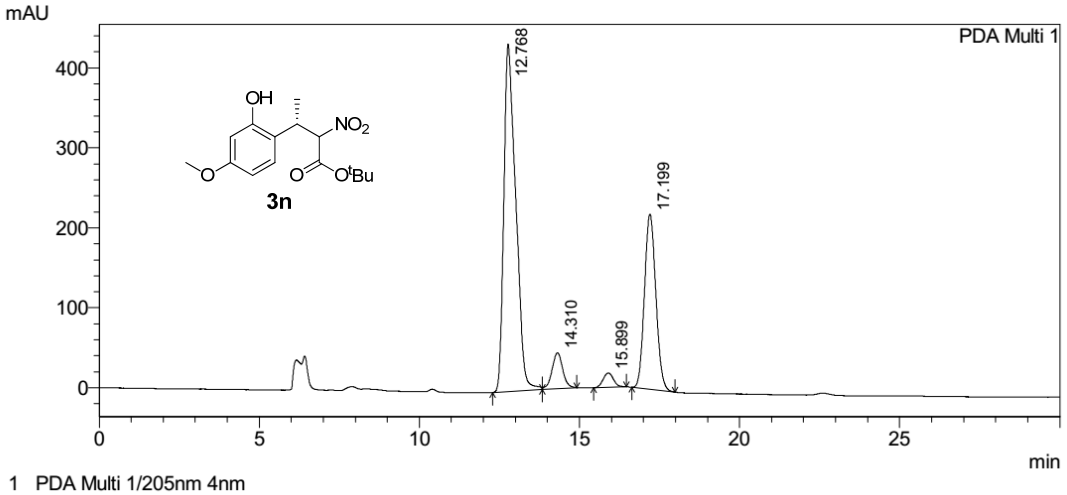


1 PDA Multi 1/205nm 4nm

PeakTable

PDA Ch1 205nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.890	20672446	719620	31.922	35.344
2	15.546	21275998	660638	32.854	32.447
3	17.774	11545697	339557	17.829	16.677
4	19.206	11264731	316207	17.395	15.531
Total		64758872	2036021	100.000	100.000

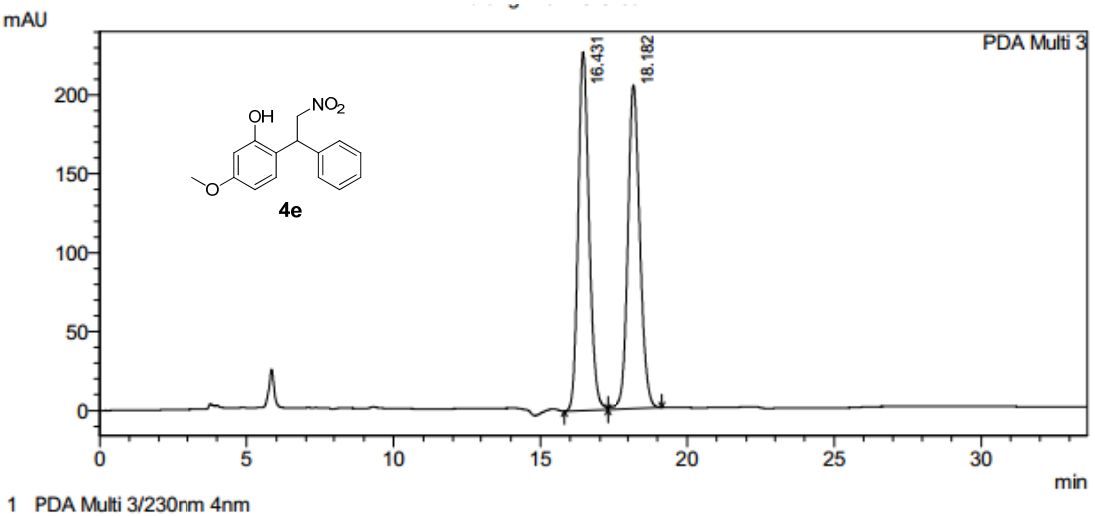


1 PDA Multi 1/205nm 4nm

PeakTable

PDA Ch1 205nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.768	11214428	434179	62.039	60.620
2	14.310	1042189	44826	5.765	6.259
3	15.899	401370	18098	2.220	2.527
4	17.199	5418370	219129	29.975	30.595
Total		18076357	716232	100.000	100.000

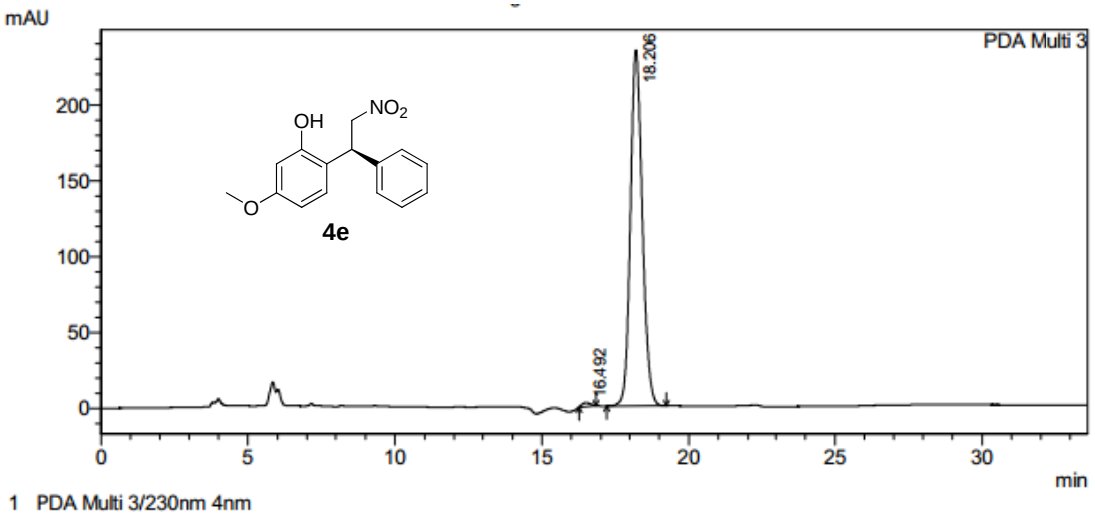


1 PDA Multi 3/230nm 4nm

PeakTable

PDA Ch3 230nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.431	5799211	227410	49.991	52.577
2	18.182	5801220	205119	50.009	47.423
Total		11600432	432529	100.000	100.000

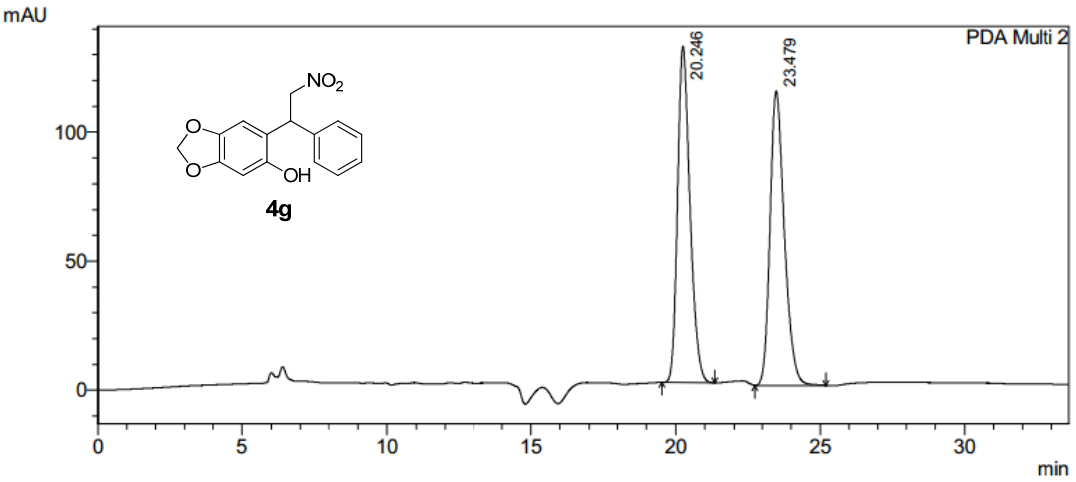


1 PDA Multi 3/230nm 4nm

PeakTable

PDA Ch3 230nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.492	47839	2505	0.724	1.058
2	18.206	6557410	234367	99.276	98.942
Total		6605249	236872	100.000	100.000

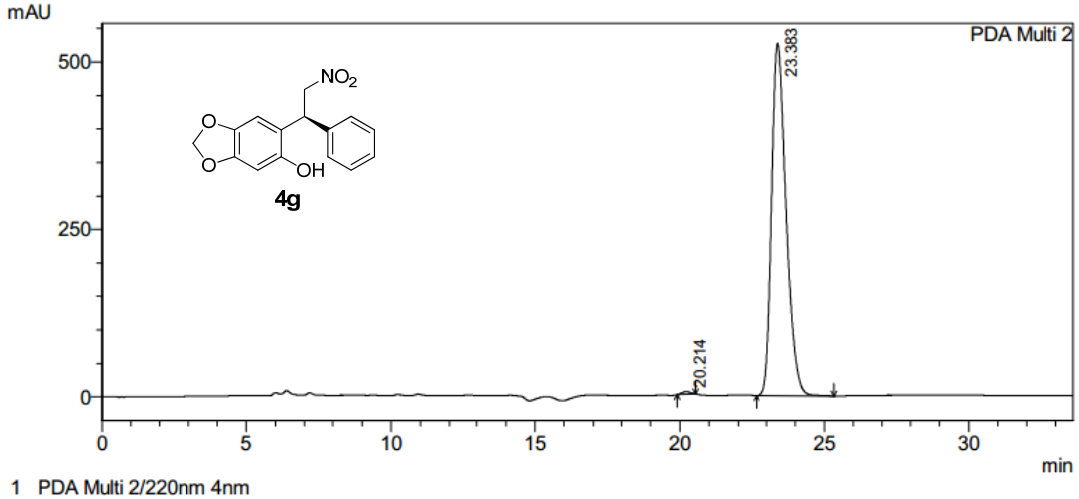


1 PDA Multi 2/220nm 4nm

PeakTable

PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.246	3866825	130233	49.610	53.297
2	23.479	3927547	114119	50.390	46.703
Total		7794372	244352	100.000	100.000

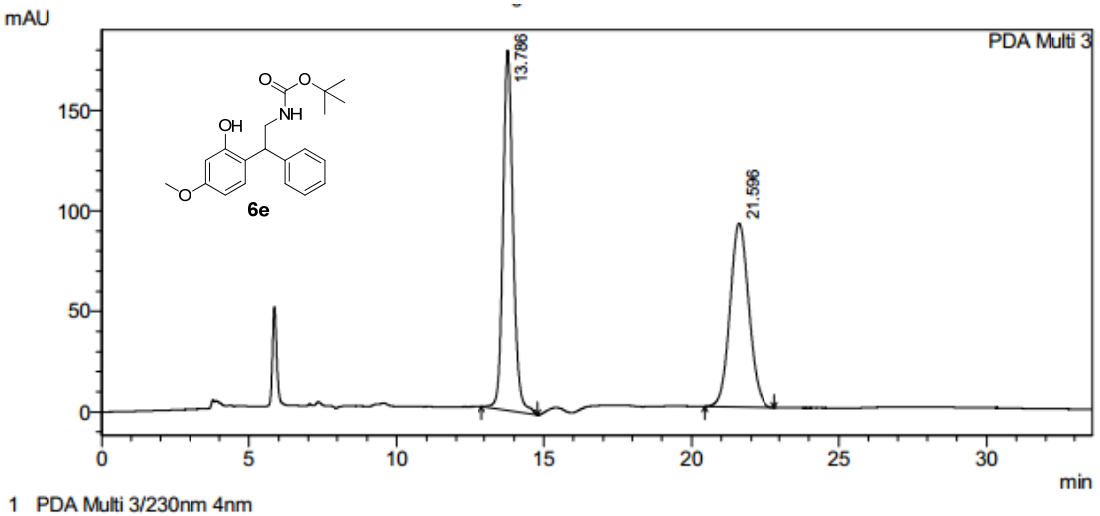


1 PDA Multi 2/220nm 4nm

PeakTable

PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.214	83574	3929	0.453	0.742
2	23.383	18347124	525779	99.547	99.258
Total		18430698	529708	100.000	100.000

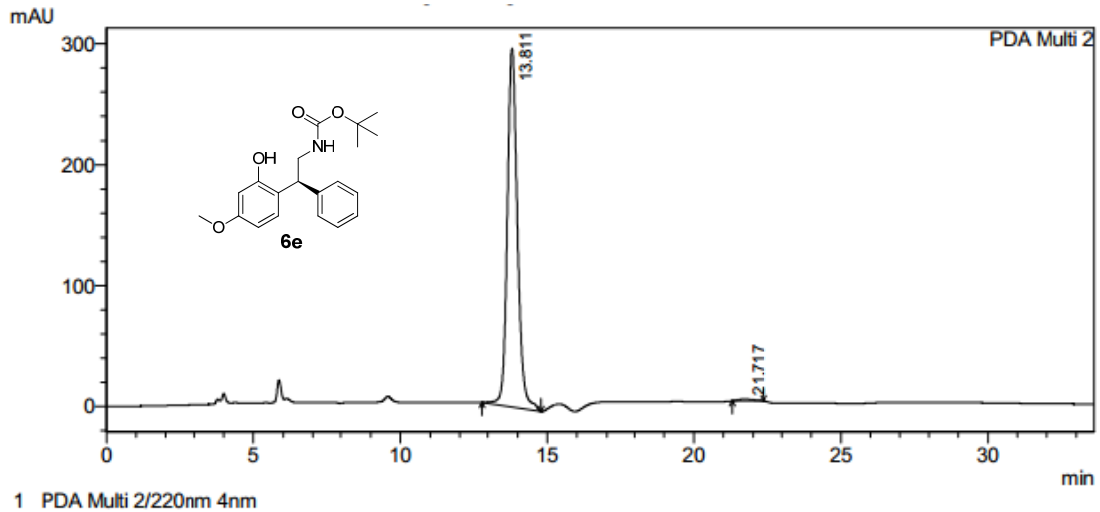


1 PDA Multi 3/230nm 4nm

PeakTable

PDA Ch3 230nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.786	4225608	179099	51.043	66.187
2	21.596	4052921	91497	48.957	33.813
Total		8278529	270596	100.000	100.000

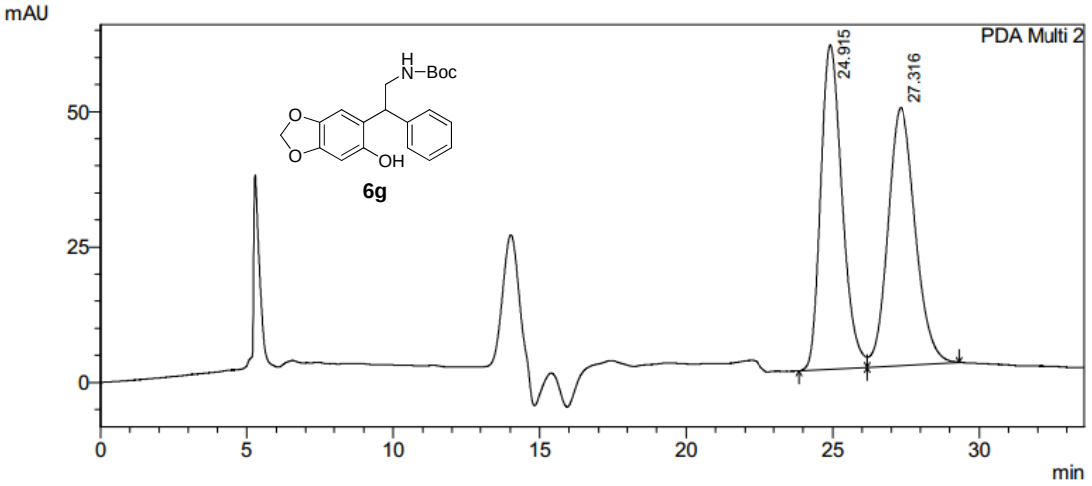


1 PDA Multi 2/220nm 4nm

PeakTable

PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.811	7016479	296588	99.300	99.533
2	21.717	49471	1391	0.700	0.467
Total		7065950	297979	100.000	100.000

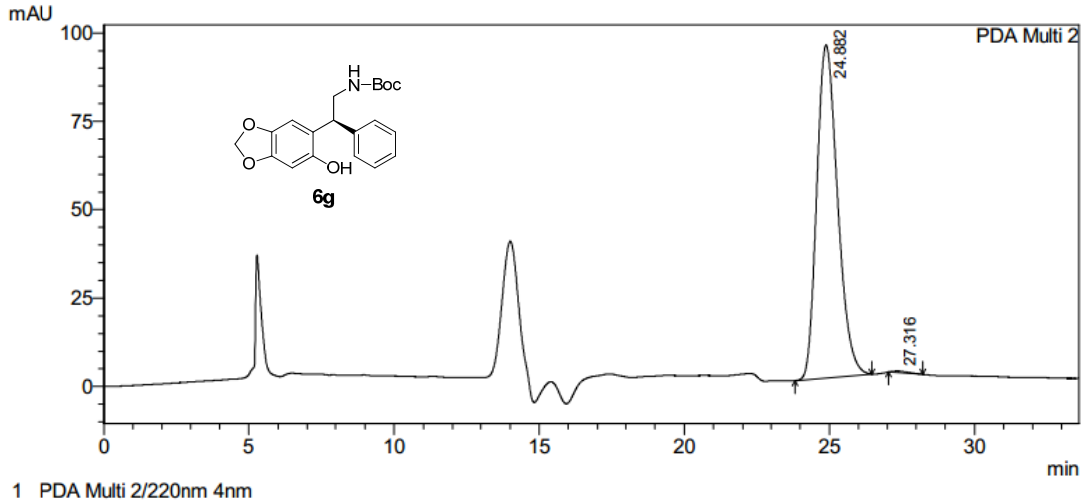


1 PDA Multi 2/220nm 4nm

PeakTable

PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.915	3018527	59889	49.241	55.698
2	27.316	3111568	47635	50.759	44.302
Total		6130094	107524	100.000	100.000



1 PDA Multi 2/220nm 4nm

PeakTable

PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.882	4679690	94156	99.621	99.555
2	27.316	17797	420	0.379	0.445
Total		4697487	94577	100.000	100.000