Asymmetric allylic alkylations of 3-alkylidene oxindoles

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1. General Information

Commercial reagents were used as received, unless otherwise stated. ^{1}H and ^{13}C NMR were recorded on 400 MHz spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard. The following abbreviations were used to designate chemical shift mutiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m). Mass spectra were obtained using electrospray ionization (ESI) or electron impact ionization (EI) mass spectrometer. In each case, enantiomeric ratio was determined by chiral HPLC analysis on Chiralcel column in comparison with authentic racemates. 3-Alkylidene oxindoles and isopropylidene benzofuran-2-one were synthesized according to the literature procedure.[1] MBH carbonates were synthesized by the reported method.[2]

References:

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(2) (*a*) M. Kamlar, S. Hybelbauerová, I. Císařovác and J. Veselý, *Org. Biomol. Chem*., 2014, **12**, 5071. (*b*) D. J. V. C. van Steenis, T. Marcelli, M. Lutz, A. L. Spek, J. H. van Maarseveen, and H. Hiemstra, *Adv. Synth. Catal.*, 2007, **349**, 281. (*c*) N.-J. Zhong, F. Wei, Q.-Q. Xuan, L. Liu, D. Wang and Y.-J. Chen, *Chem. Coummun*., 2013, **49**, 11071.

2. General experimental reaction procedure

To a stirred solution of (E)-*tert*-butyl 2-oxo-3-(1-phenylethylidene)indoline-1-carboxylate (1.5 equiv) and MBH carbonates (0.1 mmol) in dry $PhCF_3$ was added biscinchona alkaloid catalyst (0.1 equiv) at 50 ºC. After the reaction was complete, the reaction solution was concentrated in *vacuo*, the crude was purified by flash chromatography to afford the product.

(E)-tert-butyl-3-(4-(methoxycarbonyl)-1,3-diphenylpent-4-en-1-ylidene)-2-oxoindoline-1-carboxylate(3a)

Light yellow oil. Yield 63%, ee 97%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 1H), 7.43 (s, 3H), 7.23 – 7.16 (m, 4H), 7.12 (dd, *J* = 14.1, 5.9 Hz, 2H), 7.04 (s, 1H), 6.90 (s, 1H), 6.65 (t, *J* = 7.7 Hz, 1H), 6.31 (s, 1H), 5.96 (d, *J* = 7.9 Hz, 1H), 5.86 (s, 1H), 4.14 (dd, *J* = 17.2, 10.8 Hz, 1H), 4.00 – 3.89 (m, 2H), 3.61 (s, 3H), 1.68 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 166.1, 158.6, 149.3, 142.5, 141.7, 139.7, 138.1, 129.2, 128.7, 128.5, 128.3, 126.9, 126.6, 125.9, 123.3, 123.0, 123.0, 114.2, 84.2, 51.8, 44.3, 38.0, 28.2; HRMS (ESI^+) calcd for $[C_{32}H_{31}NO_5+Na]^+$ 532.2094, found: 532.2094. $[\alpha]^{20}D$ -15.9° (c = 2.0, $CHCl_3$); The enantiomeric excess was determined by HPLC with an IC column at 210 nm (2-propanol: hexane=2:98), 1.0 mL/min; t_R= 20.2 min (minor), 21.6 min (major).

(E)-tert-butyl-3-(4-(methoxycarbonyl)-1-(4-methoxyphenyl)-3-phenylpent-4-en-1-ylidene)-2-oxoindoline-1-carboxylate(3b)

Light yellow oil. Yield 54%, ee >99%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.1 Hz, 1H), 7.32 (s, 1H), 7.28 (d, *J* = 12.7 Hz, 3H), 7.23 – 7.15 (m, 2H), 7.01 (s, 3H), 6.93 (d, *J* = 8.5 Hz, 1H), 6.76 (t, *J* = 7.7 Hz, 1H), 6.37 (s, 1H), 6.21 (d, *J* = 7.9 Hz, 1H), 5.91 (s, 1H), 4.14 (td, *J* = 11.3, 7.4 Hz, 1H), 4.08 – 3.99 (m, 2H), 3.95 (s, 3H), 3.67 (s, 3H), 1.75 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 166.3, 160.0, 159.0, 149.4, 142.7, 141.8, 138.1, 131.9, 128.6, 128.4, 128.3, 126.7, 126.0, 123.9, 123.4, 123.4, 123.0, 114.6, 114.3, 84.3, 55.4, 51.9, 44.7, 38.1, 28.3; HRMS (ESI^+) calcd for $[C_{33}H_{33}NO_6+Na]^+$ 562.2200, found: 562.2195; $[\alpha]^{20}D$ -24.3° (c = 0.6, $CHCl_3$); The enantiomeric excess was determined by HPLC with an AS-H column at 210 nm (2-propanol: hexane=2:98), 1.0 mL/min; t_R= 8.2 min (major).

(E)-tert-butyl-3-(4-(methoxycarbonyl)-3-phenyl-1-(p-tolyl)pent-4-en-1-ylidene)-2-oxoindoline-1-carboxylate(3c)

Light yellow oil. Yield 61%, ee >99%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.2 Hz, 1H), 7.33 – 7.25 (m, 6H), 7.19 (dt, *J* = 15.6, 5.5 Hz, 2H), 7.00 (d, *J* = 6.4 Hz, 1H), 6.88 (dd, *J* = 16.5, 7.0 Hz, 1H), 6.73 (t, *J* = 7.7 Hz, 1H), 6.37 (s, 1H), 6.12 (d, *J* = 7.9 Hz, 1H), 5.92 (s, 1H), 4.18 (dd, *J* = 17.0, 11.1 Hz, 1H), 4.06 – 3.93 (m, 2H), 3.66 (s, 3H), 2.50 (s, 3H), 1.74 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 166.3, 159.2, 149.4, 142.7, 141.8, 138.7, 138.1, 136.7, 129.9, 128.6, 128.5, 128.3, 126.9, 126.7, 126.0, 123.8, 123.3, 123.3, 123.1, 114.2, 84.3, 51.8, 44.5, 38.1, 28.3; $[\alpha]^{20}D$ -29.0° (c = 0.8, $CHCl_3$); HRMS (ESI^+) calcd for $[C_{33}H_{33}NO_5+Na]^+$ 546.2251, found: 546.2250. The enantiomeric excess was determined by HPLC with an AS-H column at 210 nm (2-propanol: hexane=2:98), 1.0 mL/min; t_R= 5.1 min (major).

(E)-tert-butyl-3-(1-(4-chlorophenyl)-4-(methoxycarbonyl)-3-phenylpent-4-en-1-ylidene)-2-oxoindoline-1-carboxylate(3d)

Light yellow oil. Yield 44%, ee 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 1H), 7.47 – 7.35 (m, 2H), 7.25 – 7.11 (m, 6H), 7.00 (t, *J* = 9.9 Hz, 1H), 6.83 (d, *J* = 8.1 Hz, 1H), 6.71 (t, *J* = 7.7 Hz, 1H), 6.31 (s, 1H), 6.05 (d, *J* = 7.9 Hz, 1H), 5.80 (s, 1H), 4.02 (d, *J* = 8.1 Hz, 2H), 3.93 (t, *J* = 8.0 Hz, 1H), 3.63 (s, 3H), 1.69 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 166.0, 156.9, 149.3, 142.7, 141.4, 138.4, 138.2, 134.8, 129.5, 128.9, 128.6, 128.4, 126.8, 126.1, 124.3, 123.5, 123.0, 122.8, 114.4, 84.4, 77.5, 77.2, 76.8, 51.9, 44.5, 37.9, 28.3; HRMS (ESI^+) calcd for $[C_{32}H_{30}ClNO_5+Na]^+$ 566.1705, found: 566.1700; $[\alpha]^{20}$D -15.0° (c = 0.9, $CHCl_3$); The enantiomeric excess was determined by HPLC with an AD-H column at 210 nm (2-propanol: hexane=2:98), 1.0 mL/min; t_R= 7.6 min (minor), 6.9 min (major).

(E)-tert-butyl-3-(1-(3-chlorophenyl)-4-(methoxycarbonyl)-3-phenylpent-4-en-1-ylidene)-2-oxoindoline-1-carboxylate(3e)

Light yellow oil. Yield 42%, ee 97%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.2 Hz, 1H), 7.38 (dt, *J* = 14.7, 7.7 Hz, 2H), 7.25 – 7.11 (m, 6H), 6.94 (t, *J* = 10.3 Hz, 1H), 6.83 (d, *J* = 9.3 Hz, 1H), 6.71 (t, *J* = 7.7 Hz, 1H), 6.33 (d, *J* = 7.0 Hz, 1H), 6.01 (t, *J* = 7.6 Hz, 1H), 5.83 (s, 1H), 4.18 – 4.02 (m, 1H), 3.90 (ddd, *J* = 22.4, 16.1, 8.4 Hz, 2H), 3.64 (d, *J* = 8.1 Hz, 3H), 1.69 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 165.9, 156.2, 149.2, 142.5, 141.6, 141.3, 138.3, 135.1, 130.6, 128.9, 128.8, 128.5, 128.4, 128.3, 127.2, 127.1, 126.8, 125.9, 125.8, 125.2, 124.3, 123.5, 122.9, 122.6, 114.4, 84.4, 51.9, 44.3, 38.1, 37.7; HRMS (ESI^+) calcd for $[C_{32}H_{30}ClNO_5+Na]^+$ 566.1705, found: 566.1702; $[\alpha]^{20}$D -29.0° (c = 0.8, $CHCl_3$); The enantiomeric excess was determined by HPLC with an IC column at 210 nm (2-propanol: hexane=2:98), 1.0 mL/min; t_R= 16.1 min (minor), 17.2 min (major).

(E)-tert-butyl-3-(1-(3-bromophenyl)-4-(methoxycarbonyl)-3-phenylpent-4-en-1-ylidene)-2-oxoindoline-1-carboxylate(3f)

Light yellow oil. Yield 53%, ee >99%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (t, *J* = 8.6 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.35 – 7.28 (m, 1H), 7.26 – 7.04 (m, 7H), 6.98 (d, *J* = 6.1 Hz, 1H), 6.72 (t, *J* = 7.7 Hz, 1H), 6.33 (d, *J* = 10.7 Hz, 1H), 6.01 (t, *J* = 7.8 Hz, 1H), 5.83 (d, *J* = 7.6 Hz, 1H), 4.18 – 3.76 (m, 3H), 3.64 (d, *J* = 10.5 Hz, 3H), 1.69 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 165.9, 156.1, 149.2, 142.5, 141.9, 141.6, 141.3, 141.2, 138.3, 131.7, 130.8, 130.0, 129.9, 128.9, 128.5, 128.5, 128.4, 128.3, 126.9, 126.8, 126.0, 125.8, 125.6, 125.5, 123.5, 123.0, 122.5, 114.4, 84.4, 52.0, 51.9, 44.3, 38.2, 37.7, 28.2; HRMS (ESI^+) calcd for $[C_{32}H_{30}BrNO_5+Na]^+$ 610.1200, found: 610.1198; $[\alpha]^{20}$D -25.0° (c = 1.3, $CHCl_3$); The enantiomeric excess was determined by HPLC with an IA column at 210 nm (2-propanol: hexane=2:98), 1.0 mL/min; t_R= 7.5 min (major).

(E)-tert-butyl-5-chloro-3-(4-(methoxycarbonyl)-1,3-diphenylpent-4-en-1-ylidene)-2-oxoindoline-1-carboxylate(3g)

Light yellow oil. Yield 46%, ee 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.7 Hz, 1H), 7.50 – 7.42 (m, 3H), 7.25 – 7.13 (m, 5H), 7.08 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.03 (d, *J* = 4.4 Hz, 1H), 6.88 (d, *J* = 6.9 Hz, 1H), 6.31 (s, 1H), 5.83 (s, 2H), 4.11 (dd, *J* = 17.3, 10.6 Hz, 1H), 3.98 (q, *J* = 8.2 Hz, 2H), 3.61 (s, 3H), 1.68 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 165.6, 160.7, 149.3, 142.7, 141.6, 139.2, 136.7, 129.5, 129.2, 128.9, 128.6, 128.4, 128.3, 126.8, 126.0, 124.6, 123.2, 123.2, 115.4, 84.7, 51.9, 44.5, 38.2, 28.3; HRMS (ESI^+) calcd for $[C_{32}H_{30}ClNO_5+ Na]^+$ 566.1705, found: 566.1700; $[\alpha]^{20}$D -32.1°

(c = 0.6, $CHCl_3$); The enantiomeric excess was determined by HPLC with an IA column at 210 nm (2-propanol: hexane=2:98), 1.0 mL/min; t_R= 7.7 min (minor), 6.7 min (major).

(E)-tert-butyl-3-(3-(4-fluorophenyl)-4-(methoxycarbonyl)-1-phenylpent-4-en-1-ylidene)-2-oxoindoline-1-carboxylate(3h)

White solid. Yield 46%, ee 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 1H), 7.44 (s, 3H), 7.19 – 7.09 (m, 3H), 7.06 (s, 1H), 6.89 (t, *J* = 8.5 Hz, 3H), 6.66 (t, *J* = 7.7 Hz, 1H), 6.30 (s, 1H), 5.98 (d, *J* = 7.9 Hz, 1H), 5.82 (s, 1H), 4.10 – 3.89 (m, 3H), 3.61 (s, 3H), 1.68 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 166.1, 162.9, 160.4, 158.1, 142.6, 139.6, 138.1, 137.2, 137.2, 130.1, 123.0, 129.3, 128.8, 128.6, 127.0, 126.8, 125.7, 123.9, 123.3, 123.0, 122.9, 115.1, 114.9, 114.20, 84.3, 51.8, 43.7, 37.9, 28.2; HRMS (ESI^+) calcd for $[C_{32}H_{30}FNO_5+Na]^+$ 550.2000, found: 550.2000; $[\alpha]^{20}D$ -32.2° (c = 1.6, $CHCl_3$); The enantiomeric excess was determined by HPLC with an AD-H column at 210 nm (2-propanol: hexane=2:98), 1.0 mL/min; t_R= 7.9 min (major), 9.6 min (minor).

(E)-tert-butyl-3-(3-(4-chlorophenyl)-4-(methoxycarbonyl)-1-phenylpent-4-en-1-ylidene)-2-oxoindoline-1-carboxylate(3i)

Light yellow oil. Yield 76%, ee 94%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 4.2 Hz, 1H), 7.44 (s, 3H), 7.16 (d, *J* = 9.2 Hz, 5H), 7.06 (s, 1H), 6.91 (s, 1H), 6.66 (s, 1H), 6.31 (s, 1H), 5.98 (s, 1H), 5.83 (s, 1H), 4.13 – 4.03 (m, 1H), 3.95 (d, *J* = 15.5 Hz, 2H), 3.61 (s, 3H), 1.68 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 166.3, 158.0, 149.4, 142.5, 140.2, 139.7, 138.3, 132.5, 130.1, 129.2, 129.0, 128.8, 128.5, 126.9, 126.0, 124.2, 123.4, 123.1, 123.0, 114.4, 84.4, 52.0, 44.0, 37.8, 28.4; HRMS (ESI^+) calcd for $[C_{32}H_{30}ClNO_5+ Na]^+$ 566.1705, found: 566.1702; $[\alpha]^{20}D$ -27.6° (c = 1.0, $CHCl_3$); The enantiomeric excess was determined by HPLC with an AD-H column at 210 nm (2-propanol: hexane=3:97), 1.0 mL/min; t_R= 8.7 min (minor), 6.8 min (major).

(E)-tert-butyl-3-(4-(methoxycarbonyl)-3-(4-nitrophenyl)-1-phenylpent-4-en-1-ylidene)-2-oxoindoline-1-carboxylate(3j)

Light yellow oil. Yield 51%, ee 91%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 7.9 Hz, 1H), 7.50 – 7.31 (m, 5H), 7.12 (dd, *J* = 17.8, 9.6 Hz, 2H), 6.94 (s, 1H), 6.67 (t, *J* = 7.6 Hz, 1H), 6.38 (s, 1H), 6.02 (d, *J* = 7.8 Hz, 1H), 5.91 (s, 1H), 4.19 – 3.94 (m, 3H), 3.61 (s, 3H), 1.68 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 166.3, 156.8, 149.6, 149.3, 147.0, 141.6, 139.5, 138.4, 129.6, 129.2, 129.0, 127.2, 126.7, 124.5, 123.6, 123.1, 122.8, 114.4, 84.6, 52.1, 44.5, 37.64, 28.3; HRMS (ESI^+) calcd for $[C_{32}H_{30}N_2O_7+Na]^+$ 577.1945, found: 577.1946; $[\alpha]^{20}D$ -53.5° (c = 1.2, $CHCl_3$); The enantiomeric excess was determined by HPLC with an AD-H column at 210 nm (2-propanol: hexane=2:98), 1.0 mL/min; t_R= 32.6 min (minor), 19.1 min (major).

(E)-tert-butyl-3-(4-(methoxycarbonyl)-1-phenyl-3-(m-tolyl)pent-4-en-1-ylidene)-2-oxoindoline-1-carboxylate(3k)

Light yellow oil. Yield 40%, ee 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 1H), 7.43 (s, 3H), 7.15 – 6.99 (m, 6H), 6.92 (d, *J* = 6.6 Hz, 1H), 6.65 (t, *J* = 7.7 Hz, 1H), 6.29 (s, 1H), 5.95 (d, *J* = 7.9 Hz, 1H), 5.85 (s, 1H), 4.11 (dd, *J* = 13.8, 7.2 Hz, 1H), 3.99 – 3.87 (m, 2H), 3.60 (s, 3H), 2.28 (s, 3H), 1.69 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 166.2, 158.9, 149.5, 142.9, 139.8, 138.8, 138.2, 136.2, 129.2, 129.1, 128.8, 128.6, 128.5, 127.0, 125.9, 123.9, 123.4, 123.2, 123.1, 114.3, 84.3, 51.9, 44.1, 38.1, 28.4, 21.2; HRMS (ESI^+) calcd for $[C_{33}H_{33}NO_5+Na]^+$ 546.2251, found: 546.2250;

$[\alpha]^{20}D$ -31.3° (c = 0.9, CHCl3); The enantiomeric excess was determined by HPLC with an AD-H column at 210 nm (2-propanol: hexane=2:98), 1.0 mL/min; t_R= 9.4 min (minor), 7.7 min (major).

(E)-tert-butyl-3-(3-(3-chlorophenyl)-4-(methoxycarbonyl)-1-phenylpent-4-en-1-ylidene)-2-oxoindoline-1-carboxylate(3l)

Light yellow oil. Yield 53%, ee 88%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 1H), 7.44 (d, *J* = 3.9 Hz, 3H), 7.18 – 7.08 (m, 5H), 7.05 (s, 1H), 6.96 (s, 1H), 6.67 (t, *J* = 7.7 Hz, 1H), 6.35 (s, 1H), 6.00 (d, *J* = 7.9 Hz, 1H), 5.90 (s, 1H), 4.16 (dd, *J* = 13.7, 7.3 Hz, 1H), 3.97 – 3.82 (m, 2H), 3.61 (s, 3H), 1.69 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 166.0, 157.7, 149.3, 143.8, 141.8, 139.5, 138.2, 134.0, 129.5, 129.2, 128.8, 128.6, 126.9, 126.8, 126.6, 126.3, 124.0, 123.3, 123.0, 122.9, 114.2, 84.3, 51.8, 44.1, 37.9, 28.2; HRMS (ESI^+) calcd for $[C_{32}H_{30}ClNO_5+Na]^+$ 566.1705, found: 566.1704; $[\alpha]^{20}D$ -35.8° (c = 1.0, $CHCl_3$); The enantiomeric excess was determined by HPLC with an OD-H column at 210 nm (2-propanol: hexane=1:99), 1.0 mL/min; t_R= 10.7 min (minor), 8.9 min (major).

(E)-tert-butyl-3-(3-(3-bromophenyl)-4-(methoxycarbonyl)-1-phenylpent-4-en-1-ylidene)-2-oxoindoline-1-carboxylate(3m)

Light yellow oil. Yield 85%, ee 91%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 1H), 7.44 (d, *J* = 4.3 Hz, 3H), 7.30 (d, *J* = 7.5 Hz, 2H), 7.17 – 7.01 (m, 4H), 6.96 (s, 1H), 6.67 (t, *J* = 7.7 Hz, 1H), 6.35 (s, 1H), 6.00 (d, *J* = 7.9 Hz, 1H), 5.90 (s, 1H), 4.15 (dd, *J* = 13.5, 7.2 Hz, 1H), 3.95 – 3.81 (m, 2H), 3.61 (s, 3H), 1.69 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 166.2, 157.8, 149.4, 144.2, 141.9, 139.6, 138.3, 131.7, 129.9, 129.9, 129.3, 129.0, 128.8, 127.2, 127.0, 126.4, 124.2, 123.4, 123.1, 123.0, 122.4, 114.4, 84.4, 52.0, 44.3, 38.0, 28.3; HRMS (ESI^+) calcd for $[C_{32}H_{30}BrNO_5+Na]^+$ 610.1200, found: 610.1195; $[\alpha]^{20}D$ -28.1° (c = 0.7, $CHCl_3$); The enantiomeric excess was determined by HPLC with an AD-H column at 210 nm (2-propanol: hexane=2:98), 1.0 mL/min; t_R= 7.0 min (minor), 8.0 min (major).

(E)-tert-butyl-3-(4-(methoxycarbonyl)-3-(3-nitrophenyl)-1-phenylpent-4-en-1-ylidene)-2-oxoindoline-1-carboxylate(3n)

Light yellow oil. Yield 79%, ee 89%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.5 Hz, 2H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.48 – 7.35 (m, 4H), 7.13 (t, *J* = 7.8 Hz, 1H), 7.09 – 6.94 (m, 2H), 6.67 (t, *J* = 7.7 Hz, 1H), 6.39 (s, 1H), 6.04 (d, *J* = 7.9 Hz, 1H), 5.95 (s, 1H), 4.13 – 3.97 (m, 3H), 3.60 (s, 3H), 1.68 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 166.1, 156.9, 149.3, 148.23, 144.0, 141.6, 139.6, 138.4, 134.9, 129.4, 129.2, 129.0, 127.1, 126.7, 124.4, 123.7, 123.5, 123.1, 122.8, 121.9, 114.4, 84.5, 52.1, 44.4, 37.9, 28.3; HRMS (ESI^+) calcd for $[C_{32}H_{30}N_2O_7+Na]^+$ 577.1945, found: 577.1945; $[\alpha]^{20}D$ -47.7° (c = 1.2, $CHCl_3$); The enantiomeric excess was determined by HPLC with an AD-H column at 210 nm (2-propanol: hexane=2:98), 1.0 mL/min; t_R= 28.2 min (minor), 16.1 min (major).

(E)-tert-butyl-3-(3-(2-bromophenyl)-4-(methoxycarbonyl)-1-phenylpent-4-en-1-ylidene)-2-oxoindoline-1-carboxylate(3o)

Light yellow oil. Yield 92%, ee 94%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.2 Hz, 1H), 7.48 – 7.37 (m, 5H), 7.24 (dd, *J* = 13.8, 6.3 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 2H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.83 (d, *J* = 7.1 Hz, 1H), 6.67 (t, *J* = 7.7 Hz, 1H), 6.40 (s, 1H), 5.97 (d, *J* = 7.9 Hz, 1H), 5.73 (s, 1H), 4.35 (t, *J* = 8.0 Hz, 1H), 4.16 (dd, *J* = 15.5, 8.1 Hz, 1H), 3.87 (dd, *J* = 15.6, 8.0 Hz, 1H), 3.63 (s, 3H), 1.69 (s,

9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 166.4, 158.7, 149.4, 141.4, 140.8, 138.9, 138.2, 133.1, 129.6, 129.4, 129.2, 128.8, 128.6, 128.3, 127.6, 127.3, 126.8, 125.3, 123.9, 123.5, 123.1, 114.3, 84.4, 52.0, 43.6, 36.9, 28.3; HRMS (ESI^+) calcd for $[C_{32}H_{30}BrNO_5+Na]^+$ 610.1200, found: 610.1196; $[\alpha]^{20}D$ 21.8° (c = 1.2, $CHCl_3$); The enantiomeric excess was determined by HPLC with an AD-H column at 210 nm (2-propanol: hexane=2:98), 1.0 mL/min; t_R= 6.1 min (minor), 7.2 min (major).

(E)-tert-butyl-3-(3-(3,4-dichlorophenyl)-4-(methoxycarbonyl)-1-phenylpent-4-en-1-ylidene)-2-oxo indoline-1-carboxylate(3p)

Light yellow oil. Yield 85%, ee 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 1H), 7.41 (dd, *J* = 18.9, 7.3 Hz, 4H), 7.29 (s, 1H), 7.14 (dd, *J* = 15.2, 7.8 Hz, 3H), 6.83 (d, *J* = 7.0 Hz, 1H), 6.67 (t, *J* = 7.7 Hz, 1H), 6.38 (s, 1H), 5.99 (d, *J* = 7.9 Hz, 1H), 5.72 (s, 1H), 4.33 (t, *J* = 8.0 Hz, 1H), 4.10 (dd, *J* = 15.3, 7.8 Hz, 1H), 3.89 (dd, *J* = 15.3, 8.3 Hz, 1H), 3.64 (s, 3H), 1.69 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 166.4, 158.1, 149.4, 141.1, 138.9, 138.3, 138.0, 135.0, 133.1, 130.4, 129.5, 129.0, 128.8, 127.4, 127.3, 124.1, 123.5, 123.2, 123.0, 114.4, 84.5, 52.1, 40.6, 36.7, 28.3; HRMS (ESI^+) calcd for $[C_{32}H_{29}Cl_2NO_5+Na]^+$ 600.1315, found: 600.1314; $[\alpha]^{20}D$ -0.4° (c = 1.1, $CHCl_3$); The enantiomeric excess was determined by HPLC with an OD-H column at 210 nm (2-propanol: hexane=1:99), 1.0 mL/min; t_R= 11.5 min (minor), 9.8 min (major).

(E)-tert-butyl-3-(3-(2,4-dichlorophenyl)-4-(methoxycarbonyl)-1-phenylpent-4-en-1-ylidene)-2-oxoindoline-1-carboxylate(3q)

Light yellow oil. Yield 88%, ee 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 1H), 7.45 (d, *J* = 5.3 Hz, 3H), 7.27 (d, *J* = 8.3 Hz, 2H), 7.14 (t, *J* = 7.9 Hz, 1H), 7.07 (d, *J* = 8.2 Hz, 2H), 6.96 (s, 1H), 6.67 (t, *J* = 7.7 Hz, 1H), 6.34 (s, 1H), 6.02 (d, *J* = 7.9 Hz, 1H), 5.88 (s, 1H), 4.07 – 3.87 (m, 3H), 3.61 (s, 3H), 1.68 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 166.1, 157.2, 149.2, 142.0, 141.7, 139.5, 138.3, 132.1, 130.6, 130.5, 130.1, 129.2, 129.0, 128.8, 127.9, 126.9, 126.2, 124.2, 123.3, 123.0, 122.8, 114.3, 84.3, 51.9, 43.7, 37.7, 28.2. HRMS (ESI^+) calcd for $[C_{32}H_{29}Cl_2NO_5+Na]^+$ 600.1315, found: 600.1313. $[\alpha]^{20}D$ -45.0° (c = 1.1, $CHCl_3$); The enantiomeric excess was determined by HPLC with an AD-H column at 210 nm (2-propanol: hexane=3:97), 1.0 mL/min; t_R= 7.7 min (minor), 6.0 min (major).

(E)-tert-butyl-3-(3-(2-bromophenyl)-1-(3-chlorophenyl)-4-(methoxycarbonyl)pent-4-en-1-ylidene) -2-oxoindoline-1-carboxylate(3r)

Light yellow oil. Yield 92%, ee 87%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.2 Hz, 1H), 7.49 (dd, *J* = 12.5, 8.0 Hz, 1H), 7.37 (dd, *J* = 22.0, 9.8 Hz, 3H), 7.25 – 7.12 (m, 2H), 7.09 – 6.99 (m, 2H), 6.81 – 6.67 (m, 2H), 6.40 (d, *J* = 14.9 Hz, 1H), 6.08 – 6.00 (m, 1H), 5.71 (s, 1H), 4.34 (dt, *J* = 24.8, 8.0 Hz, 1H), 4.12 (td, *J* = 14.8, 7.8 Hz, 1H), 3.82 (ddd, *J* = 37.1, 15.5, 8.3 Hz, 1H), 3.66 (d, *J* = 13.7 Hz, 3H), 1.69 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 166.1, 156.1, 155.9, 149.2, 141.2, 141.0, 140.7, 140.4, 140.3, 138.2, 135.2, 135.0, 133.1, 133.0, 130.7, 130.5, 129.4, 129.3, 128.9, 128.8, 128.3, 127.5, 127.3, 127.1, 126.9, 125.2, 125.1, 124.9, 124.3, 124.2, 123.5, 123.0, 122.5, 114.4, 84.4, 52.0, 51.9, 43.4, 43.2, 36.9, 36.6, 28.2; HRMS (ESI^+) calcd for $[C_{32}H_{29}BrClNO_5+NH_4]^+$ 639.1256, found: 641.1243; $[\alpha]^{20}D$ +7.0° (c = 1.2, $CHCl_3$); The enantiomeric excess was determined by HPLC with an OD-H column at 210 nm (2-propanol: hexane=2:98), 1.0 mL/min; t_R= 12.3 min (minor), 16.0 min (major).

(E)-tert-butyl-3-(3-(2-bromophenyl)-1-(3-bromophenyl)-4-(methoxycarbonyl)pent-4-en-1-ylidene

)-2-oxoindoline-1-carboxylate(3s)

Light yellow oil. Yield 87%, ee 88%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.2 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.49 (dd, *J* = 15.0, 7.9 Hz, 1H), 7.34 (ddd, *J* = 24.3, 14.7, 7.6 Hz, 2H), 7.20 (dd, *J* = 19.0, 9.5 Hz, 2H), 7.15 – 7.01 (m, 2H), 6.94 – 6.79 (m, 1H), 6.73 (t, *J* = 7.7 Hz, 1H), 6.45 – 6.36 (m, 1H), 6.05 (t, *J* = 7.2 Hz, 1H), 5.71 (d, *J* = 9.3 Hz, 1H), 4.33 (dt, *J* = 32.5, 7.9 Hz, 1H), 4.20 – 4.05 (m, 1H), 3.94 – 3.69 (m, 1H), 3.66 (d, *J* = 16.6 Hz, 3H), 1.68 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 166.1, 156.1, 155.8, 149.2, 141.2, 141.1, 140.7, 140.3, 138.2, 133.1, 131.8, 130.7, 129.9, 129.3, 128.9, 128.3, 127.3, 125.4, 123.6, 123.0, 114.4, 84.5, 52.0, 43.4, 36.6, 28.2; HRMS (ESI^+) calcd for $[C_{32}H_{29}Br_2NO_5+NH_4]^+$ 683.0751, found: 683.0717; $[\alpha]^{20}D$ +3.69° (c = 1.3, $CHCl_3$); The enantiomeric excess was determined by HPLC with an OD-H column at 210 nm (2-propanol: hexane=2:98), 1.0 mL/min; t_R= 11.5 min (minor), 14.9 min (major).

(E)-tert-butyl-3-(3-(4-chlorophenyl)-4-(ethoxycarbonyl)-1-phenylpent-4-en-1-ylidene)-2-oxoindoline-1-carboxylate(3t)

Light yellow oil. Yield 41%, ee 94%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 1H), 7.44 (s, 3H), 7.22 – 7.09 (m, 5H), 7.07 (s, 1H), 6.90 (d, *J* = 6.5 Hz, 1H), 6.66 (t, *J* = 7.7 Hz, 1H), 6.31 (s, 1H), 5.98 (d, *J* = 7.9 Hz, 1H), 5.80 (s, 1H), 4.13 – 4.02 (m, 3H), 4.02 – 3.87 (m, 2H), 1.68 (s, 9H), 1.17 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 166.1, 158.0, 149.2, 142.6, 140.2, 139.5, 138.2, 132.3, 123.0, 129.3, 128.8, 128.6, 128.3, 126.8, 125.7, 124.0, 123.3, 123.0, 122.9, 120.8, 114.2, 84.3, 60.7, 43.8, 37.7, 28.2, 14.1; HRMS (ESI^+) calcd for $[C_{33}H_{32}ClNO_5+Na]^+$ 580.1861, found: 580.1861; $[\alpha]^{20}D$ -68.9° (c = 0.7, $CHCl_3$); The enantiomeric excess was determined by HPLC with an AD-H column at 210 nm (2-propanol: hexane=2:98), 1.0 mL/min; t_R= 9.7 min (minor), 7.4 min (major).

(Z)-tert-butyl-3-(4-(3-chlorophenyl)-5-(methoxycarbonyl)hex-5-en-2-ylidene)-2-oxoindoline-1-carboxylate(3u)

Light yellow oil. Yield 56%, ee 94%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.2 Hz, 1H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 7.7 Hz, 2H), 7.20 – 7.08 (m, 4H), 6.38 (s, 1H), 5.87 (s, 1H), 4.32 (t, *J* = 7.9 Hz, 1H), 3.89 (dd, *J* = 12.6, 6.9 Hz, 1H), 3.65 (s, 3H), 3.41 (dd, *J* = 12.5, 9.1 Hz, 1H), 2.15 (s, 3H), 1.66 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 165.5, 157.3, 149.3, 144.1, 141.9, 138.1, 134.1, 129.6, 128.2, 126.9, 126.5, 125.7, 123.8, 123.7, 123.4, 114.5, 84.2, 52.0, 44.9, 40.2, 28.2, 24.1; HRMS (ESI^+) calcd for $[C_{27}H_{28}ClNO_5+H]^+$ 482.1729, found: 482.1734; $[\alpha]^{20}D$ -37.8° (c = 0.33, $CHCl_3$); The enantiomeric excess was determined by HPLC with an AD-H column at 210 nm (2-propanol: hexane=3:97), 1.0 mL/min; t_R= 7.4 min (minor), 8.1 min (major).

Dimethyl-5-(1-(tert-butoxycarbonyl)-2-oxoindolin-3-ylidene)-2,8-dimethylene-3,7-diphenylnonanedioate(3v)

Light yellow oil. Yield 60%, ee 89%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.2 Hz, 1H), 7.35 – 7.27 (m, 2H), 7.25 – 7.18 (m, 5H), 7.05 (ddd, *J* = 22.7, 15.5, 7.4 Hz, 6H), 6.32 (s, 1H), 6.25 (s, 1H), 5.41 (s, 2H), 4.06 (dd, *J* = 13.8, 9.4 Hz, 2H), 3.84 – 3.68 (m, 2H), 3.66 – 3.59 (m, 1H), 3.57 (d, *J* = 11.4 Hz, 6H), 2.92 (dd, *J* = 13.1, 4.4 Hz, 1H), 1.68 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 166.5, 165.3, 162.1, 149.3, 142.5, 142.3, 142.3, 140.9, 138.4, 128.6, 128.4, 128.3, 128.1, 128.0, 127.1, 126.6, 124.3, 124.2, 124.0, 123.9, 123.3, 122.8, 114.7, 84.3, 52.0, 51.7, 45.5, 44.2, 41.2, 39.8, 28.2; HRMS (ESI^+) calcd for $[C_{38}H_{39}NO_7+Na]^+$ 644.2619, found: 644.2612; $[\alpha]^{20}D$ -271.1° (c = 0.4, $CHCl_3$); The enantiomeric excess was determined by HPLC with an AD-H column at 210 nm (2-propanol:

hexane=1:19), 1.0 mL/min; t_R= 11.2 min (minor), 4.6 min (major).

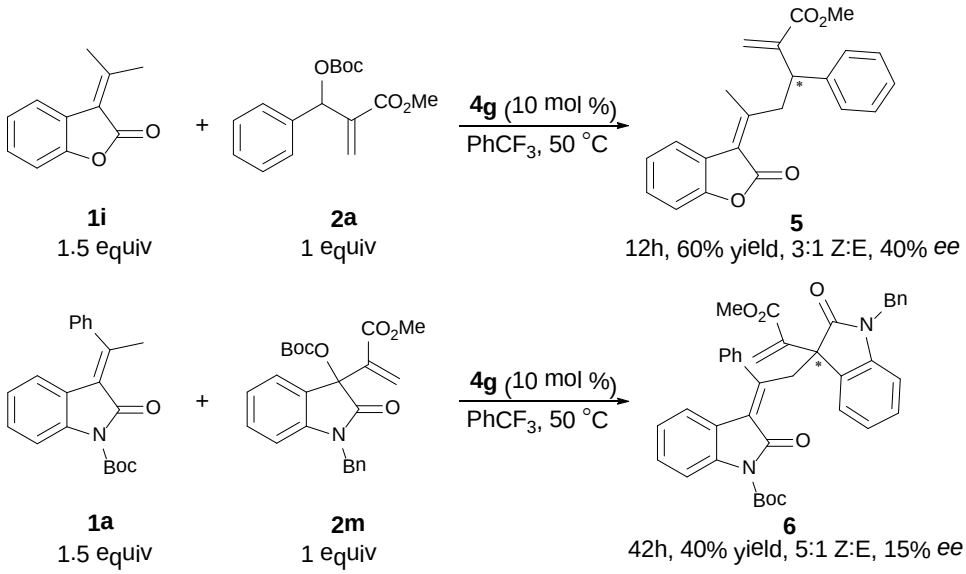
(Z)-methyl 2-methylene-5-(2-oxobenzofuran-3(2H)-ylidene)-3-phenylhexanoate(5)

Light yellow oil. Yield 60%, ee 40%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.7 Hz, 1H), 7.33 – 7.26 (m, 3H), 7.25 – 7.14 (m, 3H), 7.14 – 7.06 (m, 2H), 6.35 (s, 1H), 5.81 (s, 1H), 4.41 – 4.33 (m, 1H), 3.72 (dd, *J* = 12.8, 6.8 Hz, 1H), 3.66 (s, 3H), 3.53 (dd, *J* = 12.8, 9.3 Hz, 1H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 166.7, 160.7, 152.5, 142.5, 141.2, 128.9, 128.7, 128.4, 128.1, 127.8, 126.9, 125.3, 124.3, 123.7, 123.5, 119.7, 110.6, 51.9, 44.9, 39.8, 22.9; HRMS (ESI^+) calcd for $[C_{27}H_{22}O_4+H]^+$ 349.1434, found: 349.1429. $[\alpha]^{20}D$ -12.9° (c = 0.5, $CHCl_3$); The enantiomeric excess was determined by HPLC with an OD-H column at 210 nm (2-propanol: hexane=2:98), 1.0 mL/min; t_R= 20.8 min (minor), 30.7 min (major).

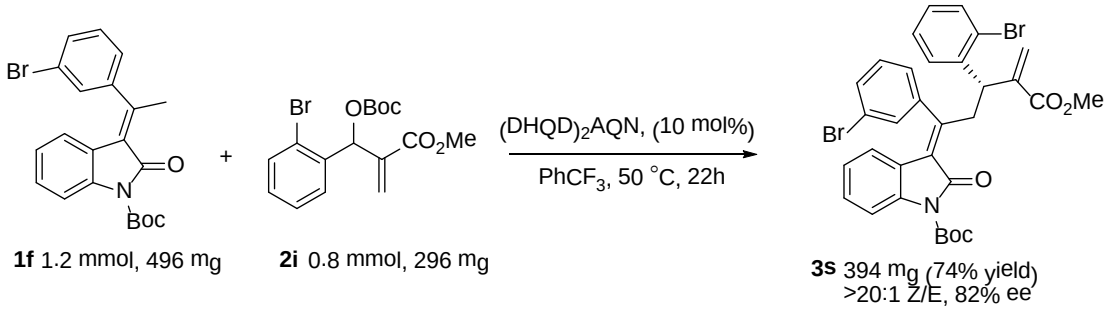
(Z)-methyl 2-methylene-5-(2-oxobenzofuran-3(2H)-ylidene)-3-phenylhexanoate(6)

Orange powder. Yield 40%, ee 15%.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.2 Hz, 1H), 7.51 (s, 1H), 7.44 – 7.34 (m, 2H), 7.29 (d, *J* = 9.1 Hz, 2H), 7.25 – 7.13 (m, 5H), 7.06 (t, *J* = 7.2 Hz, 2H), 6.86 (t, *J* = 7.5 Hz, 1H), 6.58 (t, *J* = 7.7 Hz, 1H), 6.51 (d, *J* = 7.8 Hz, 1H), 6.40 (s, 2H), 6.18 (s, 1H), 5.91 (d, *J* = 7.9 Hz, 1H), 5.50 (d, *J* = 13.4 Hz, 1H), 4.58 (d, *J* = 15.7 Hz, 1H), 3.62 (d, *J* = 15.8 Hz, 1H), 3.49 (d, *J* = 13.4 Hz, 1H), 3.27 (s, 3H), 1.66 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 166.2, 166.0, 155.4, 149.2, 143.4, 140.3, 138.2, 135.9, 130.7, 129.4, 129.2, 128.7, 128.5, 128.3, 127.8, 127.8, 127.3, 125.3, 124.5, 123.1, 123.0, 122.9, 122.2, 114.1, 108.7, 84.2, 54.7, 51.6, 44.0, 37.4, 28.2; HRMS (ESI^+) calcd for $[C_{40}H_{36}N_2O_6+Na]^+$ 641.2652, found: 641.2639; $[\alpha]^{20}D$ +10.8° (c = 0.3, $CHCl_3$); The enantiomeric excess was determined by HPLC with an IA column at 210 nm (2-propanol: hexane=1:4), 1.0 mL/min; t_R= 19.1 min (minor), 13.1 min (major).

3. Results for other examples and large scale.



Scheme S1



Scheme S2

4. X-ray crystallography data of 3h.

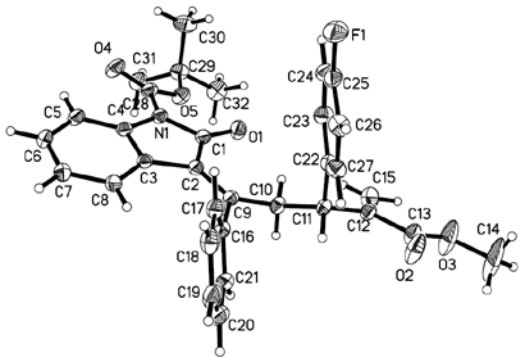
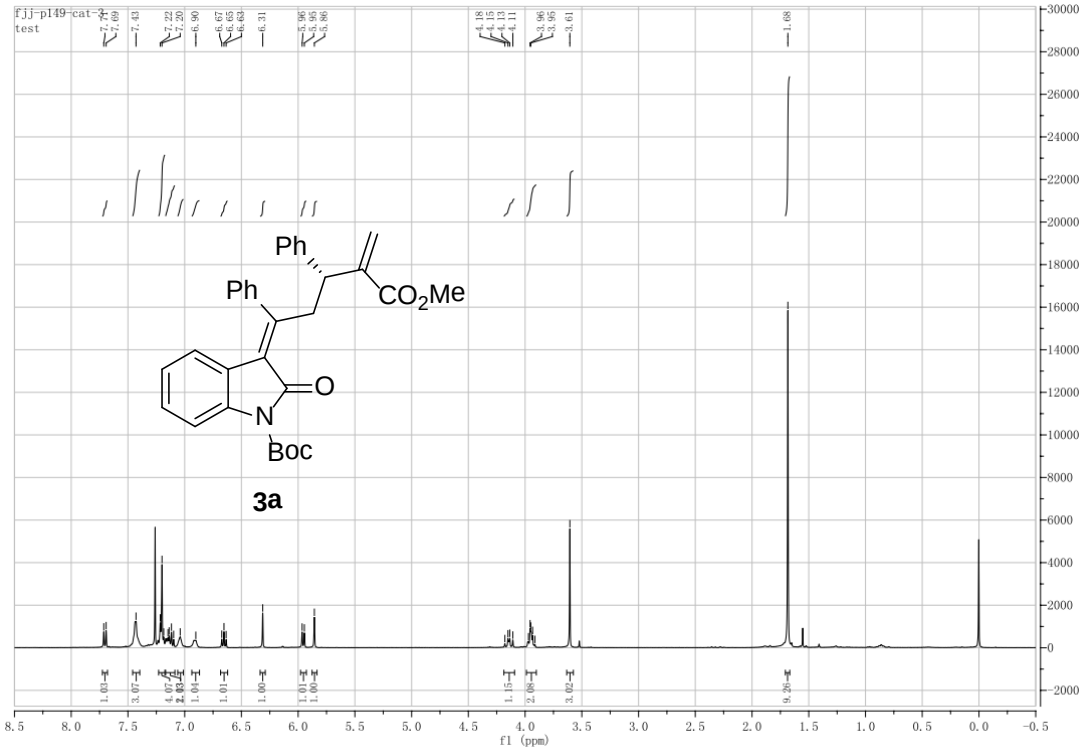


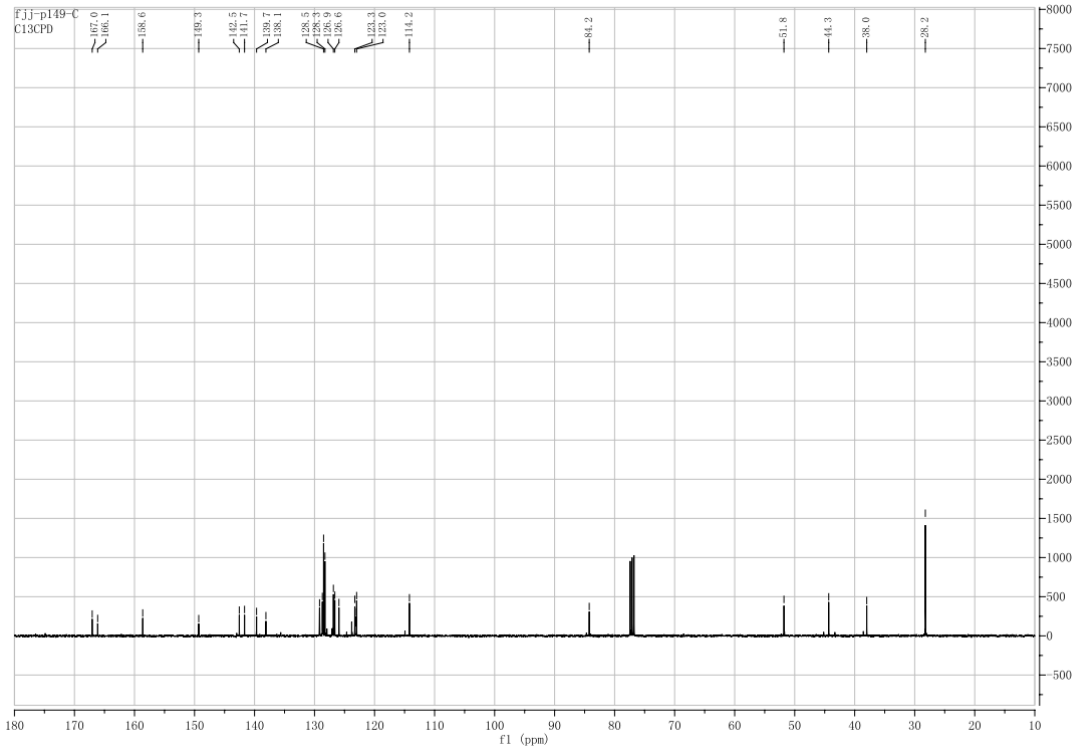
Figure S1 ORTEP diagram showing of compound **3h**.

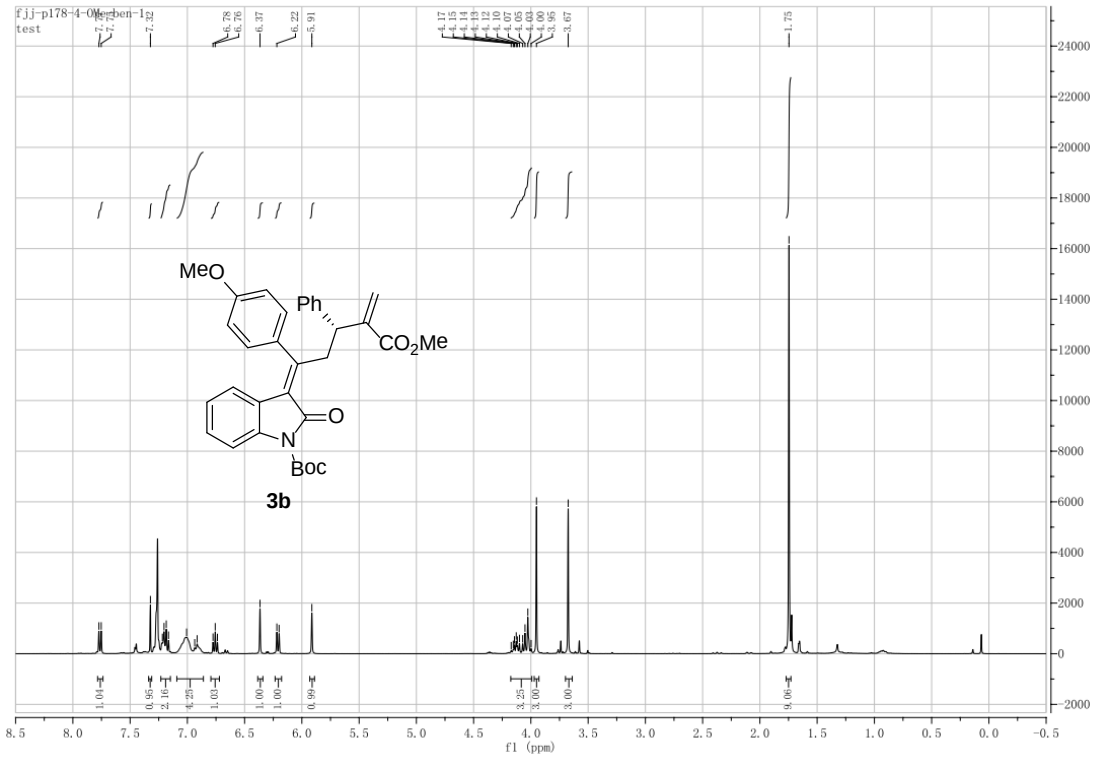
Table 1. Crystal data and structure refinement for shelxl.

Identification code	shelxl
Empirical formula	C32 H30 F N O5
Formula weight	527.57
Temperature	173(2) K
Wavelength	1.54187 A
Crystal system, space group	Monoclinic, P2(1)
Unit cell dimensions	a = 11.665(2) A alpha = 90 deg. b = 18.047(3) A beta = 106.488(5) deg. c = 13.710(3) A gamma = 90 deg.
Volume	2767.5(9) A^3
Z, Calculated density	4, 1.266 Mg/m^3
Absorption coefficient	0.735 mm^-1
F(000)	1112
Crystal size	0.220 x 0.200 x 0.120 mm
Theta range for data collection	6.302 to 79.251 deg.
Limiting indices	-13<=h<=10, -22<=k<=22, -17<=l<=17
Reflections collected / unique	46860 / 11424 [R(int) = 0.0298]
Completeness to theta = 67.687	98.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.915 and 0.677
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11424 / 1 / 712
Goodness-of-fit on F^2	1.083
Final R indices [I>2sigma(I)]	R1 = 0.0357, wR2 = 0.1020
R indices (all data)	R1 = 0.0375, wR2 = 0.1029
Absolute structure parameter	0.10(6)
Extinction coefficient	0.0016(3)
Largest diff. peak and hole	0.218 and -0.163 e.A^-3

5. NMR Spectra (^{1}H NMR, ^{13}C NMR)



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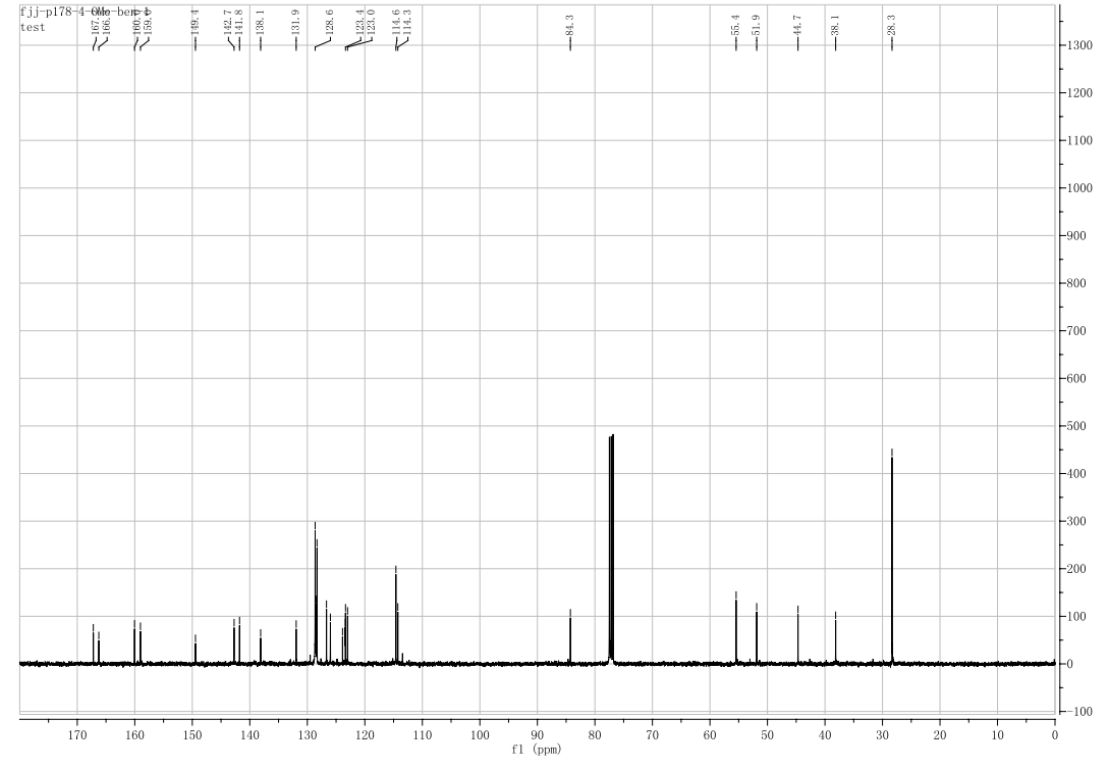
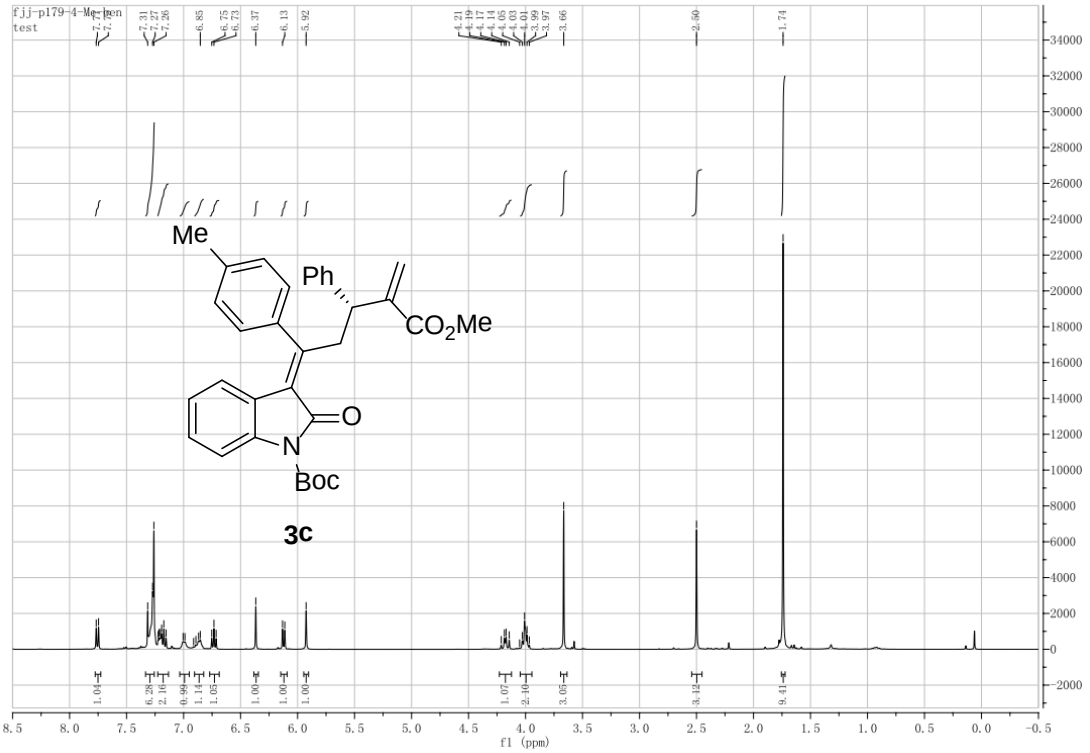
Ph
CO2Me
O
N
Boc
3b
f1 (ppm)


fjj-p178-4-OMe-ben-1
test
f1 (ppm)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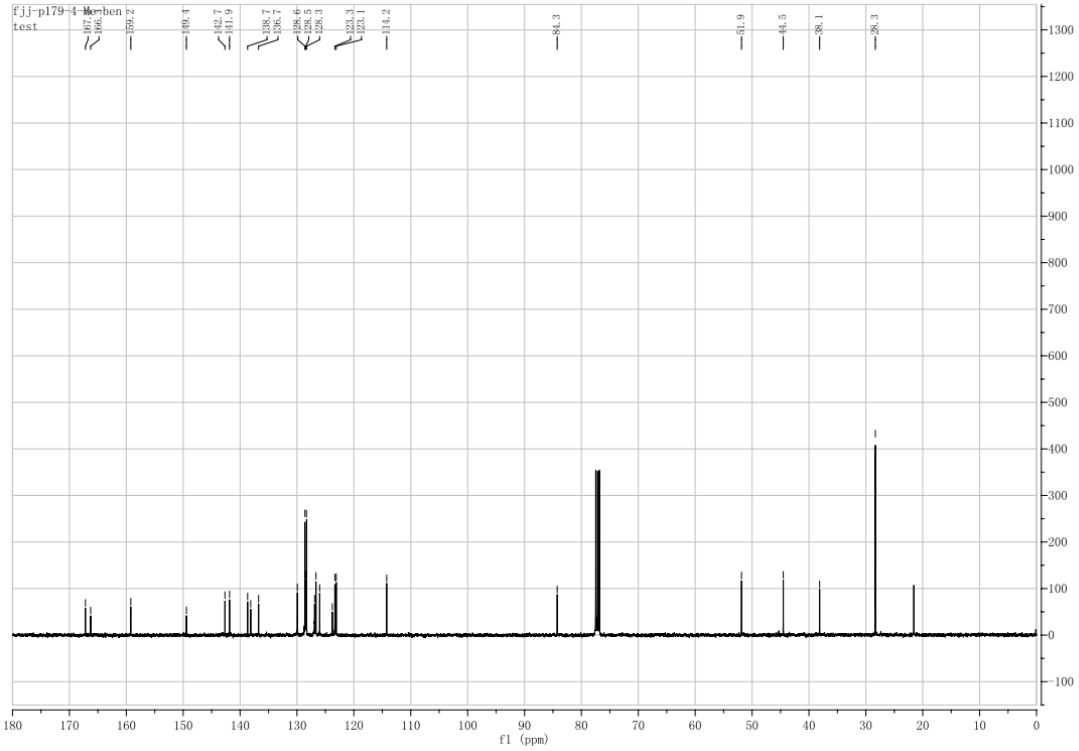
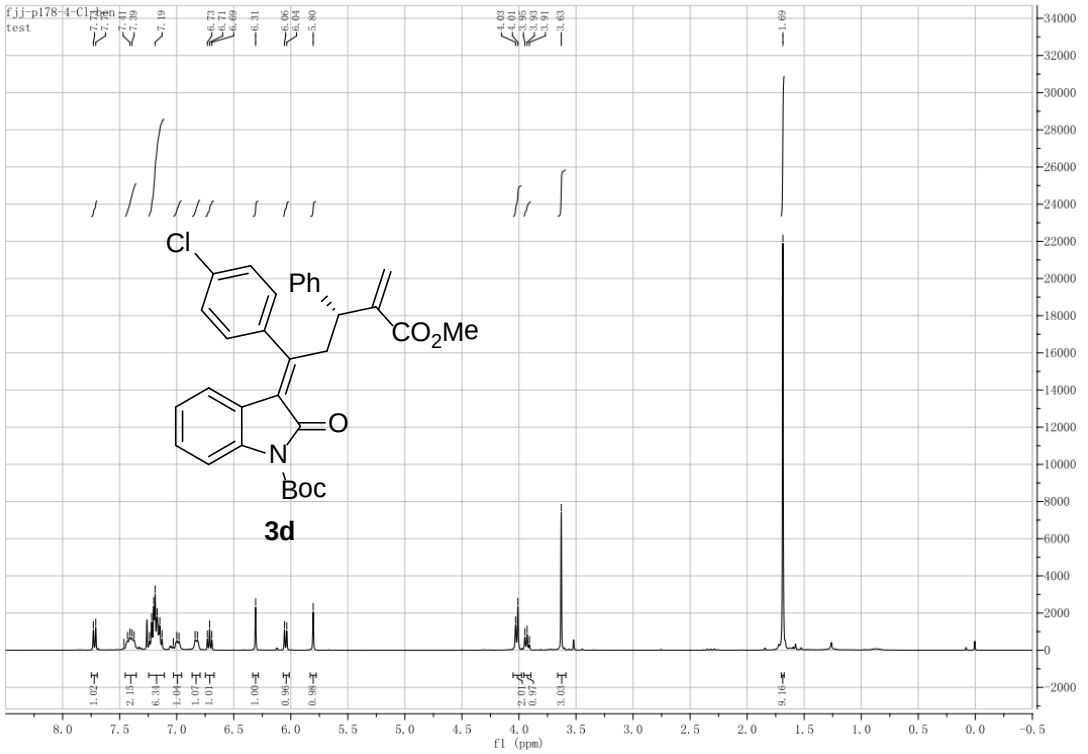
test
Me
Ph
CO2Me
O
N
Boc
3c
f1 (ppm)


fjj-p179-4-Me-ben
test
f1 (ppm)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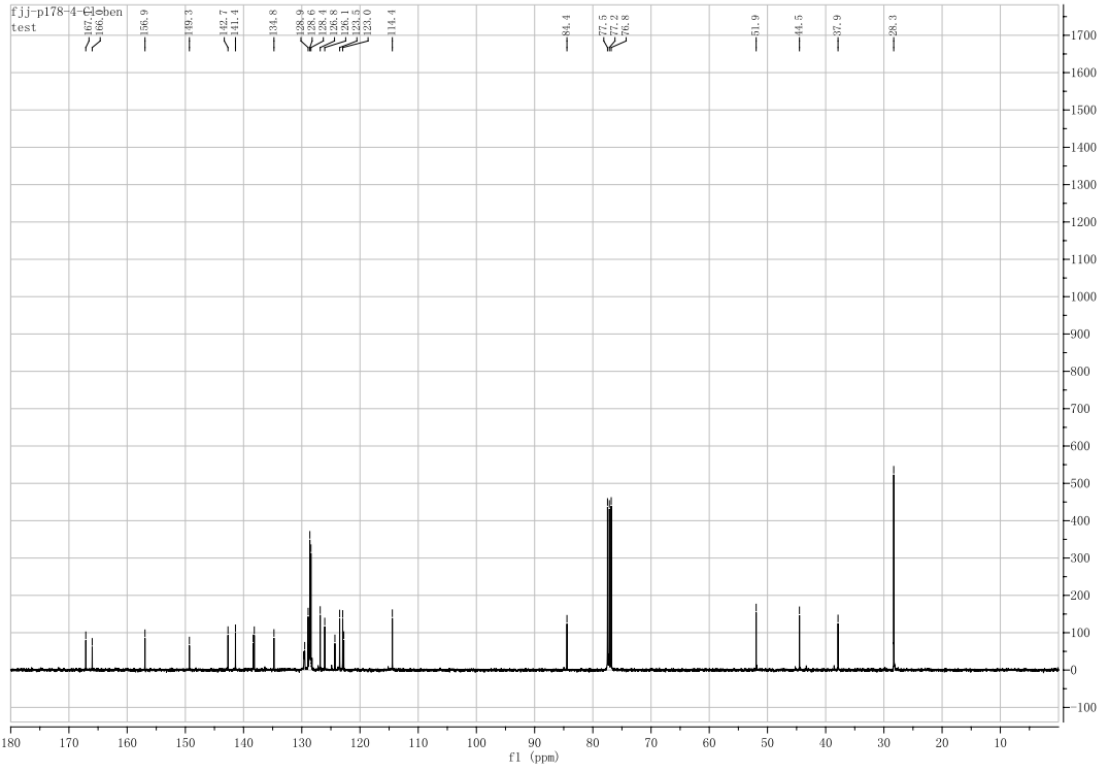
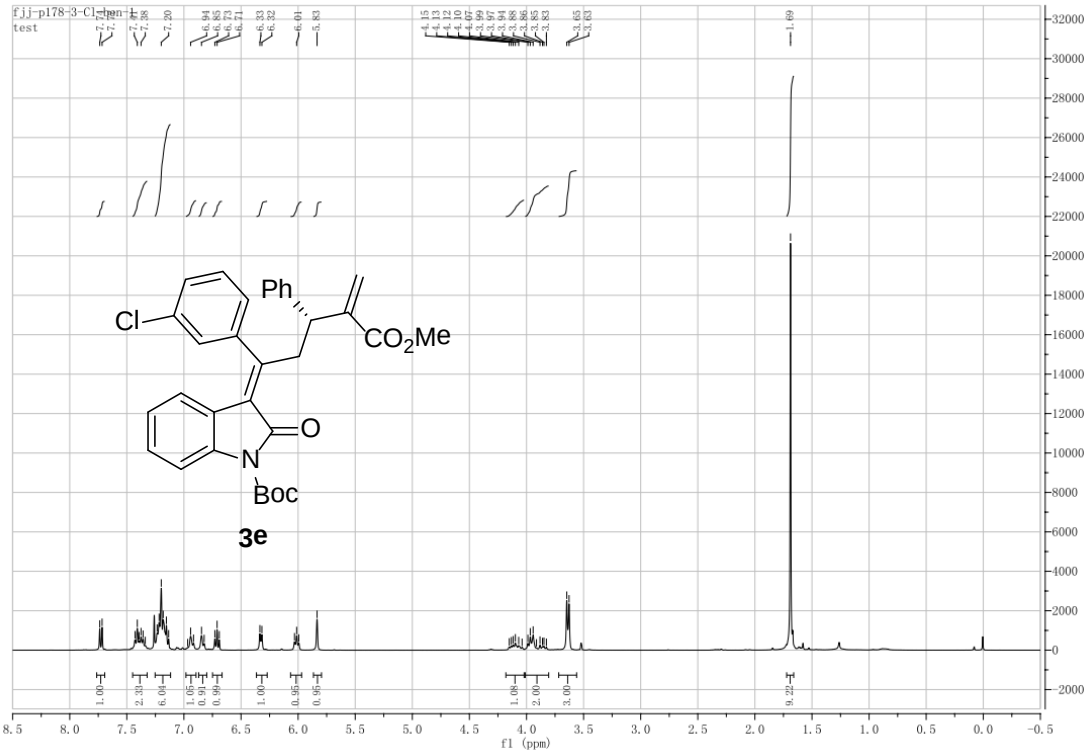
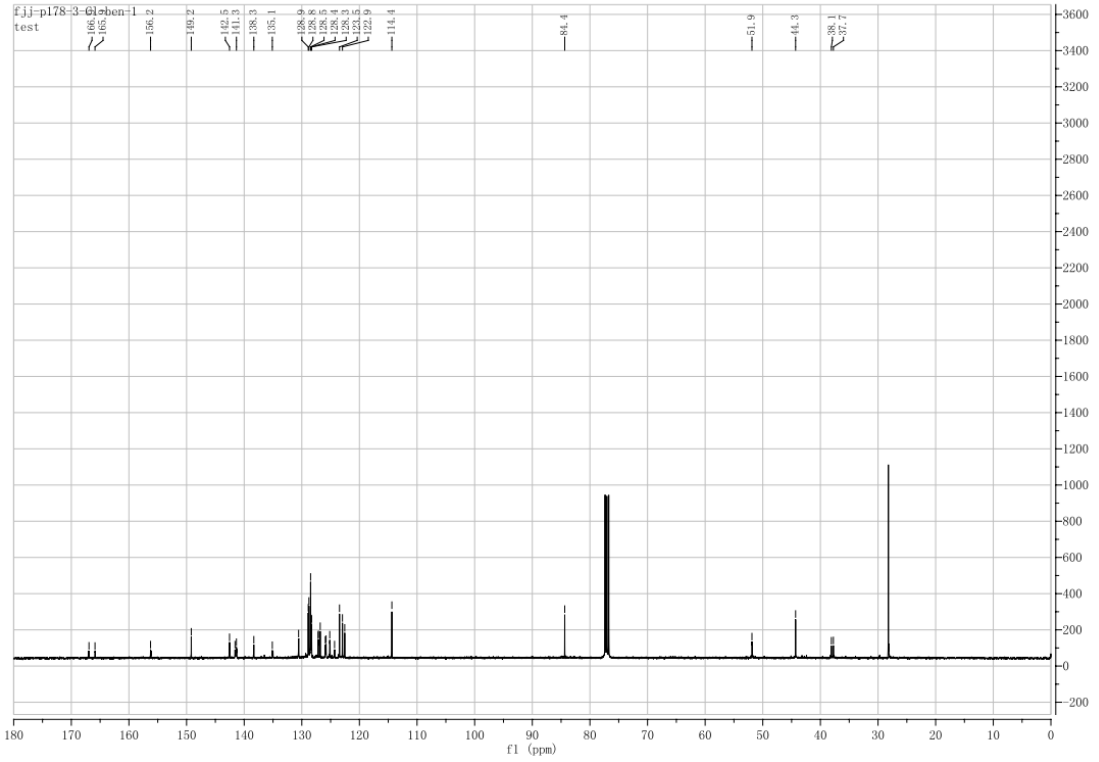
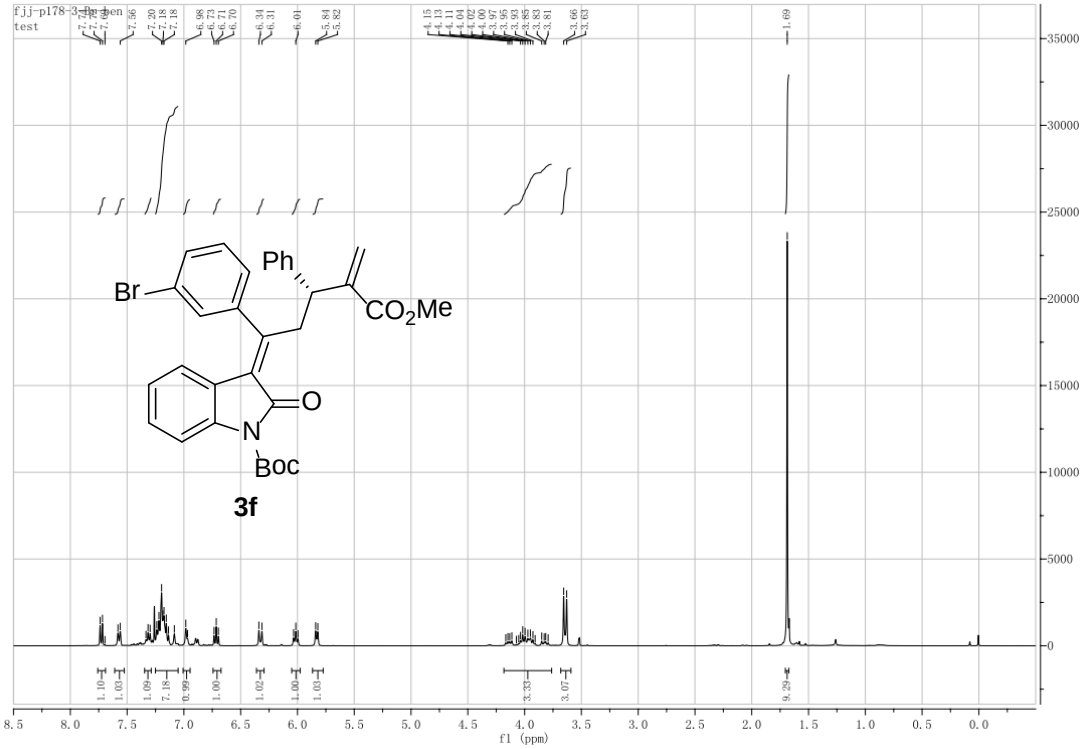
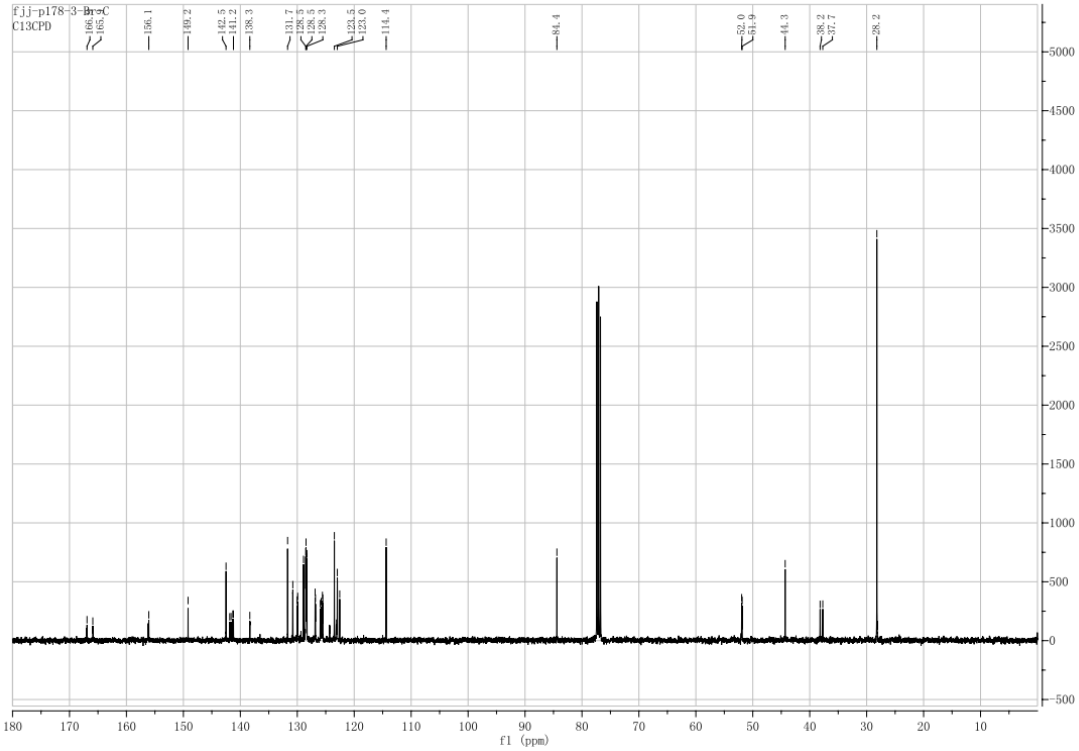
test
Cl
Ph
CO2Me
O
N
Boc
3d
f1 (ppm)

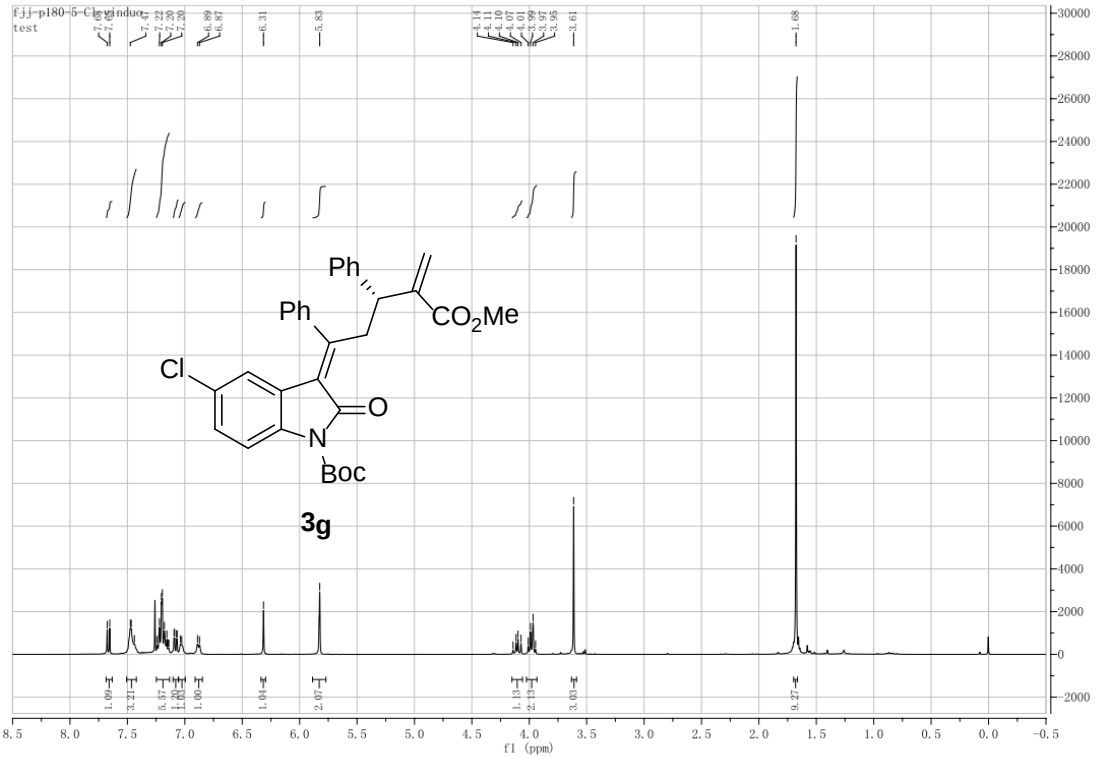

fjj-p178-4-Clphen
test
f1 (ppm)

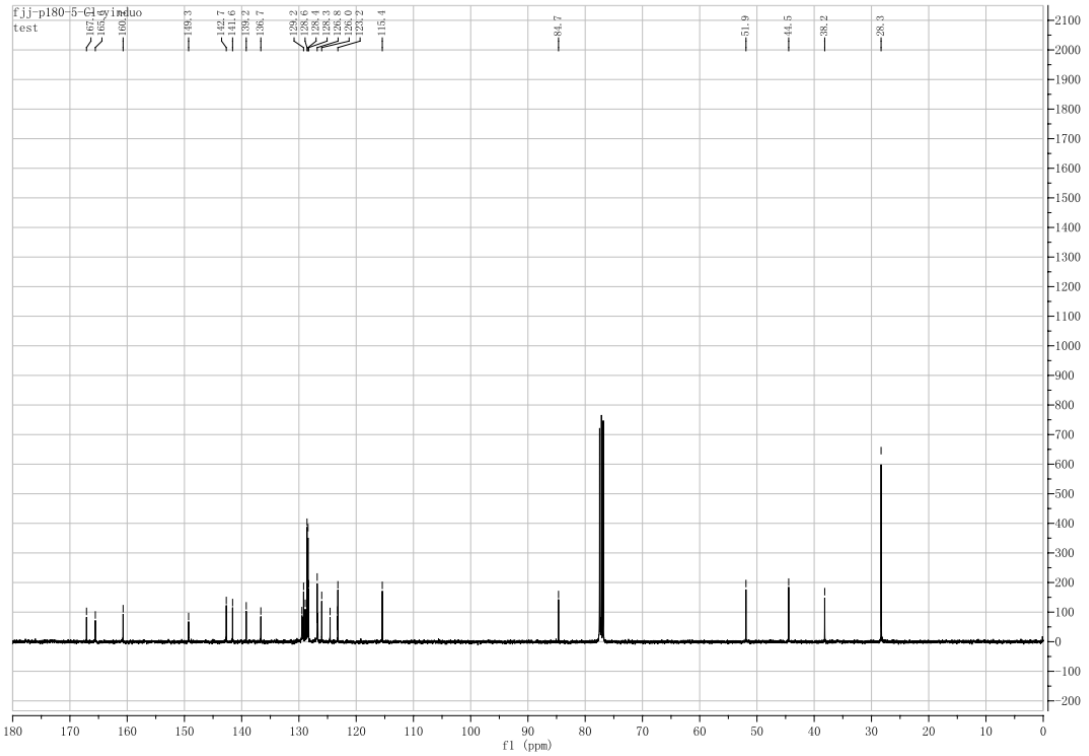

fjj-p178-3-Cl-ben-1
test
Cl
Ph
CO2Me
O
N
Boc
3e
f1 (ppm)

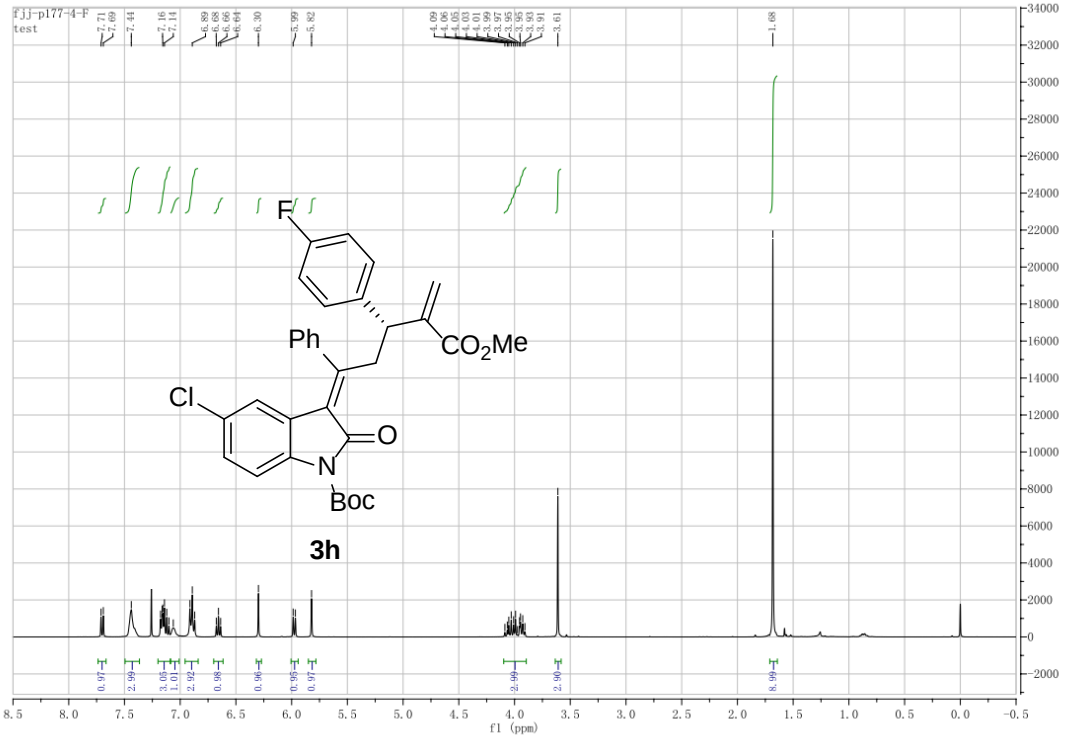

fjj-p178-3-Cl-ben-1
test
f1 (ppm)

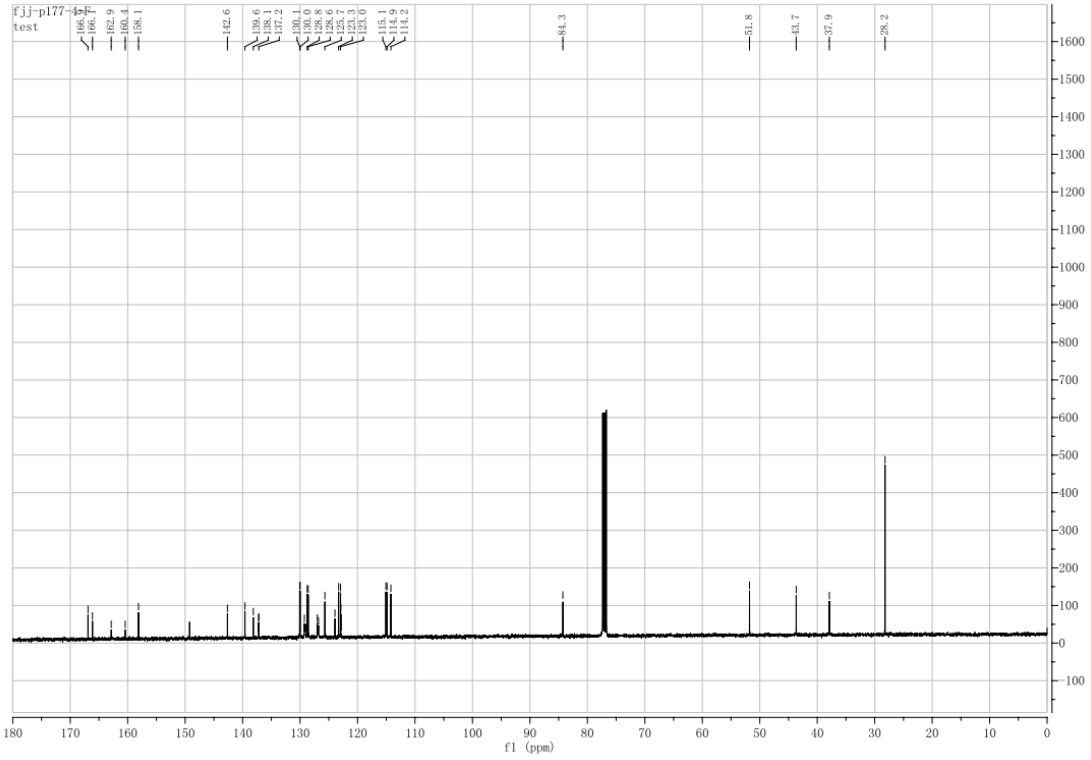

Br
Ph
CO2Me
O
N
Boc
3f
f1 (ppm)

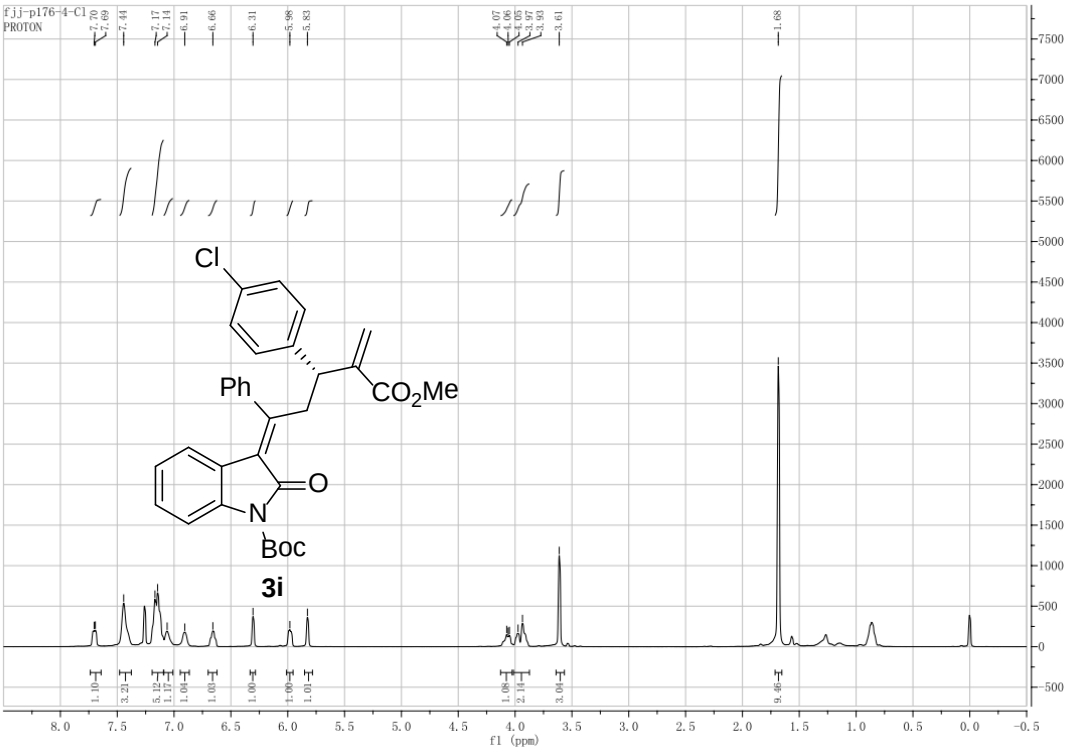

f1 (ppm)

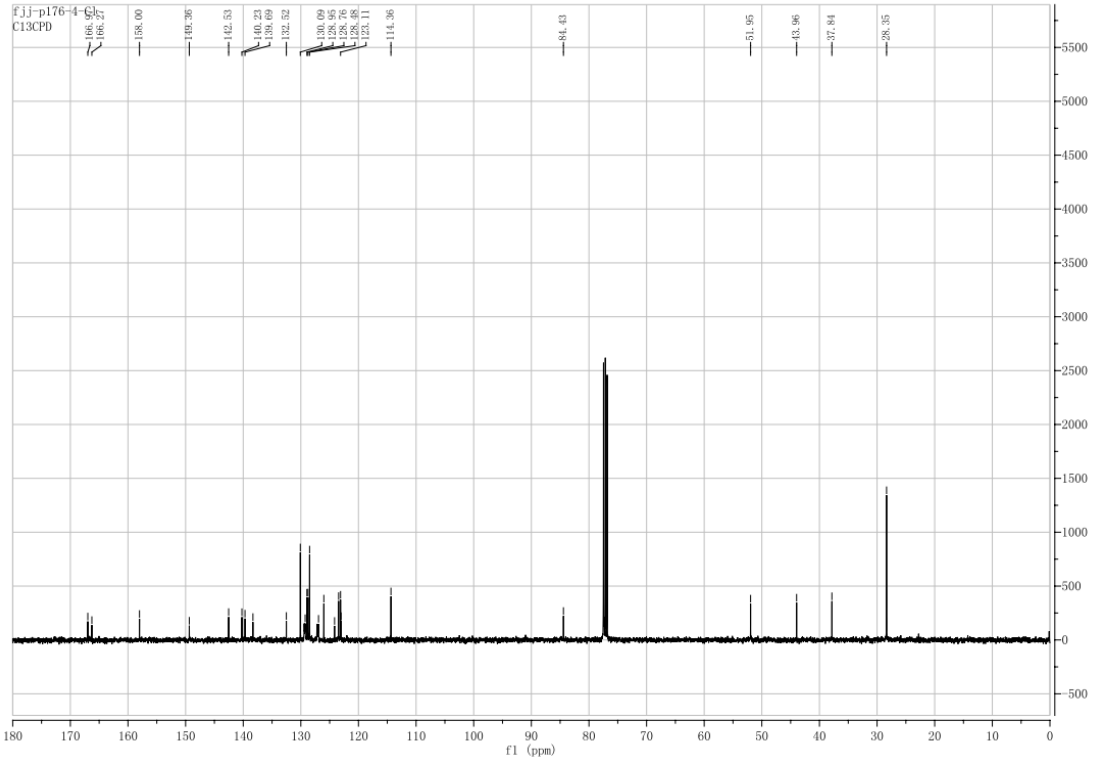

Ph
Ph
CO2Me
Cl
O
N
Boc
3g
f1 (ppm)

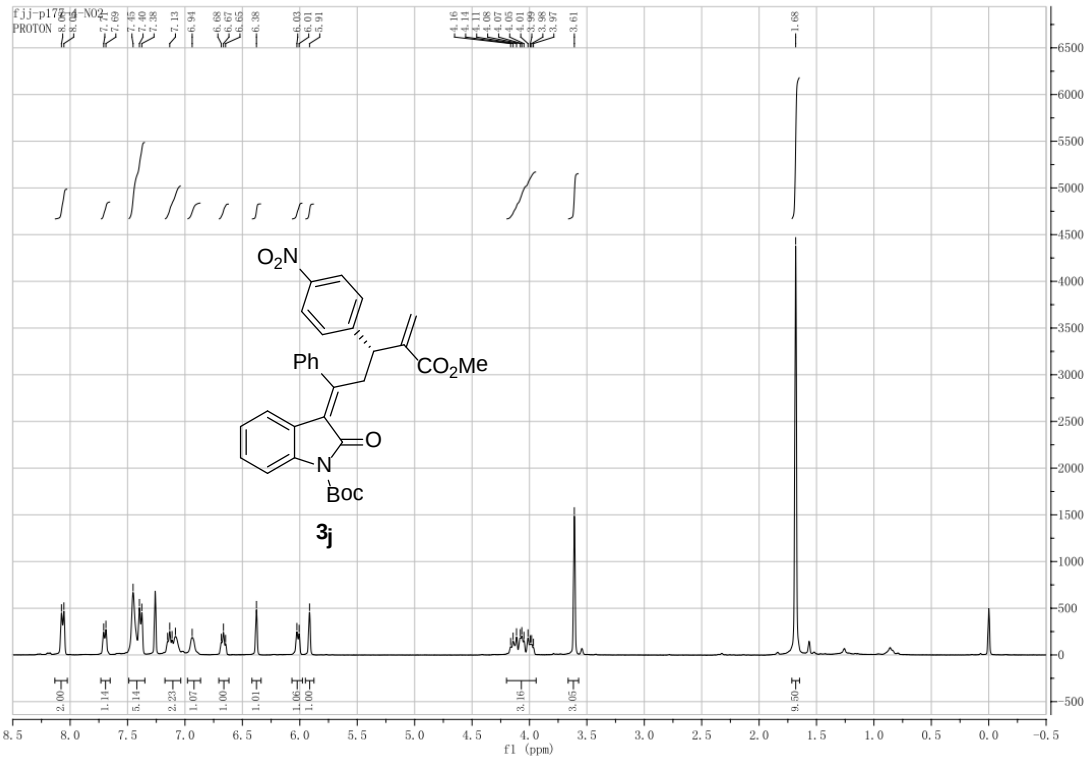

f1 (ppm)

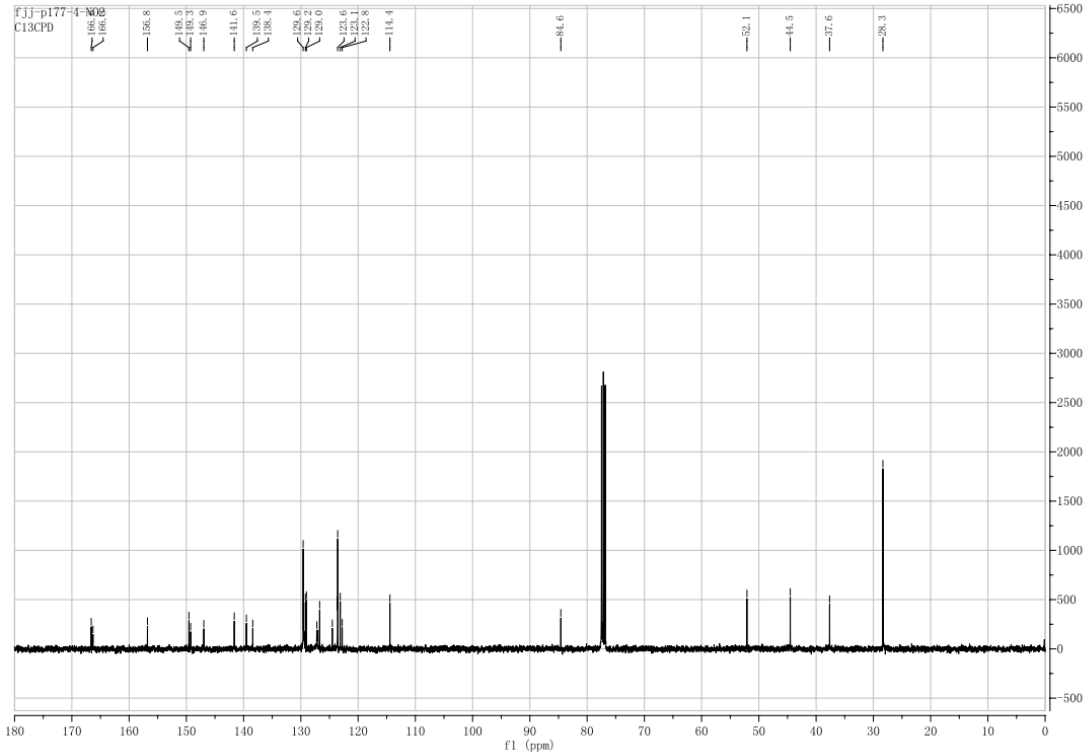

fjj-p177-4-F
test
F
Ph
CO2Me
Cl
O
N
Boc
3h
f1 (ppm)

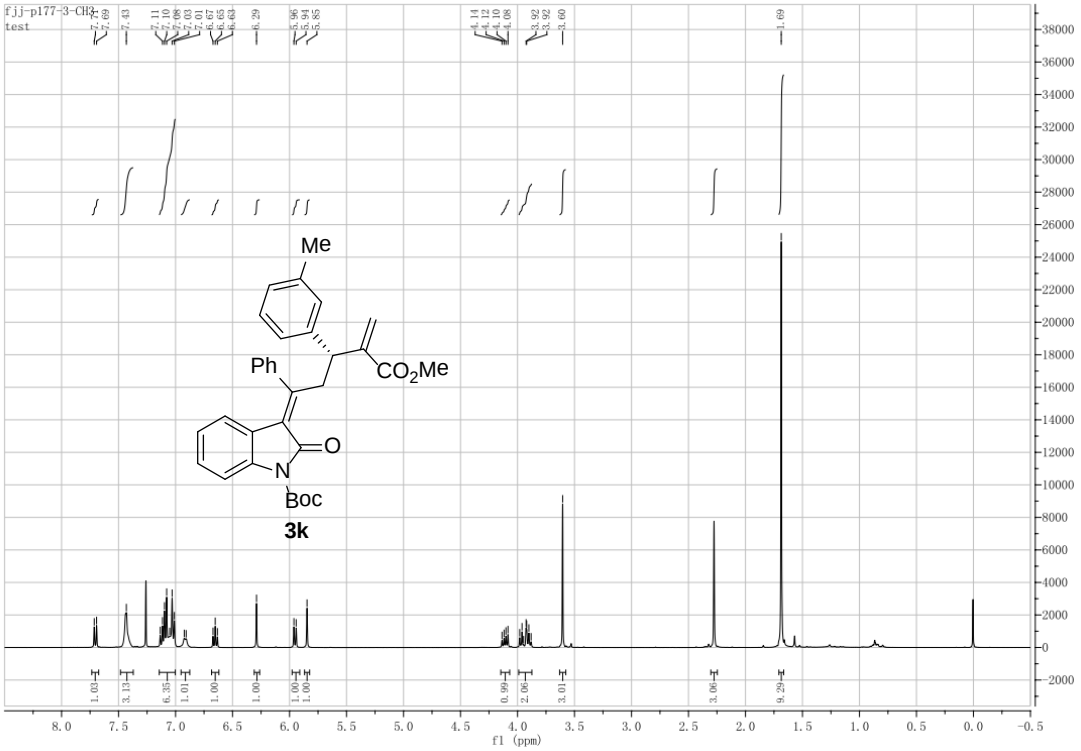

fjj-p177-4-F
test
f1 (ppm)

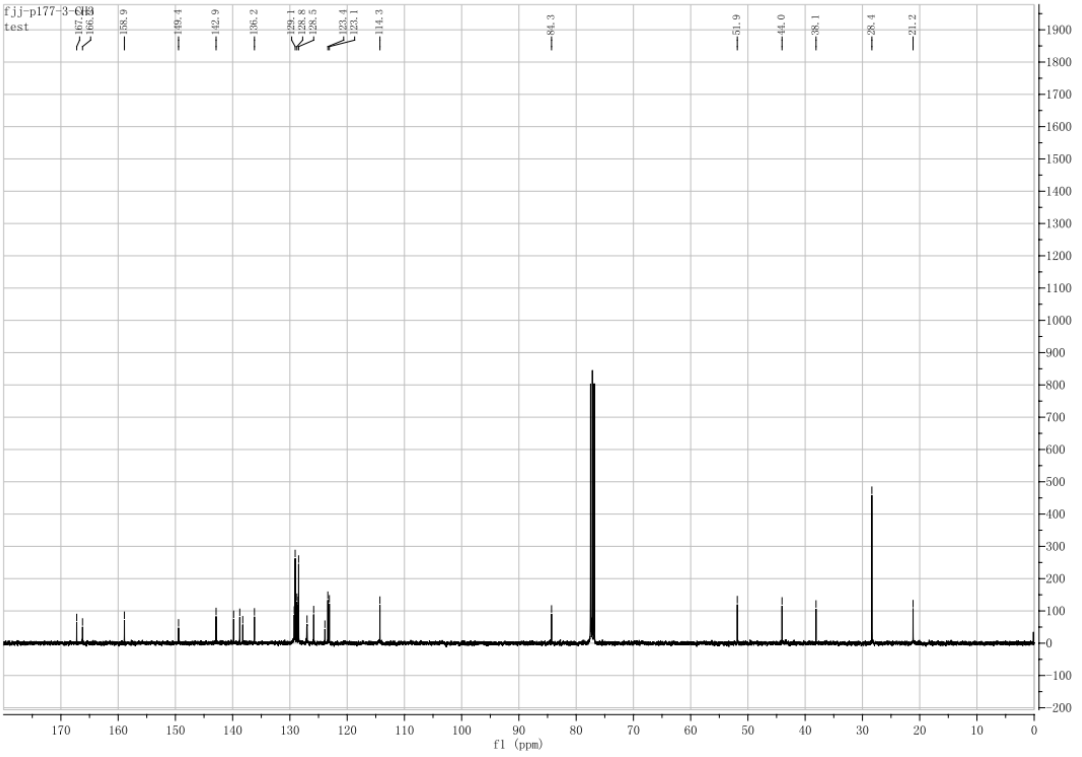

fjj-p176-4-Cl
PROTON
Cl
Ph
CO2Me
O
N
Boc
3i
f1 (ppm)

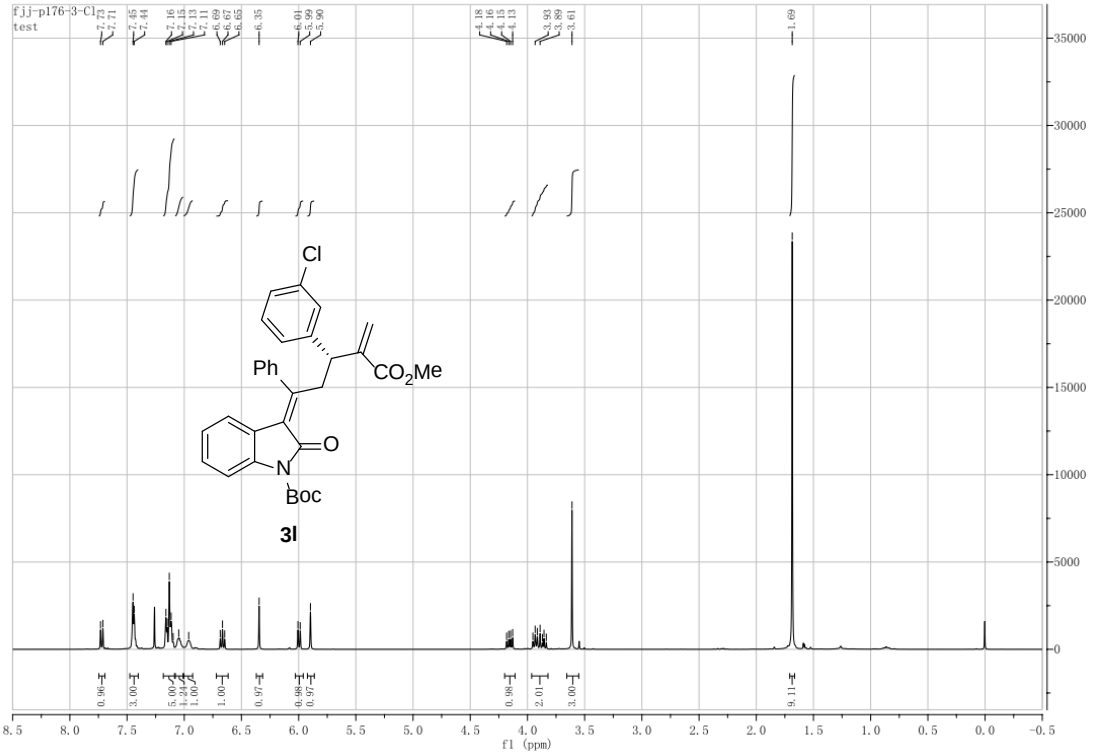

fjj-p176-4-Cl
C13CPD
f1 (ppm)

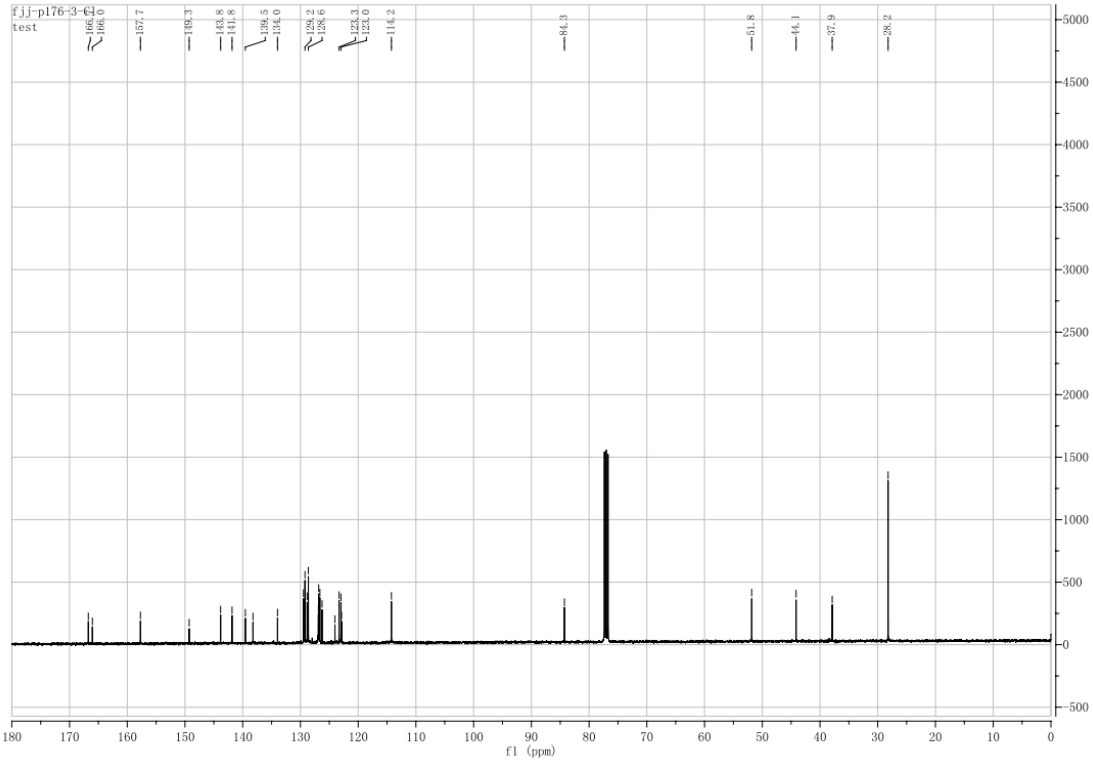

fjj-p177-4-NO2
PROTON
O2N
Ph
CO2Me
O
N
Boc
3j
f1 (ppm)

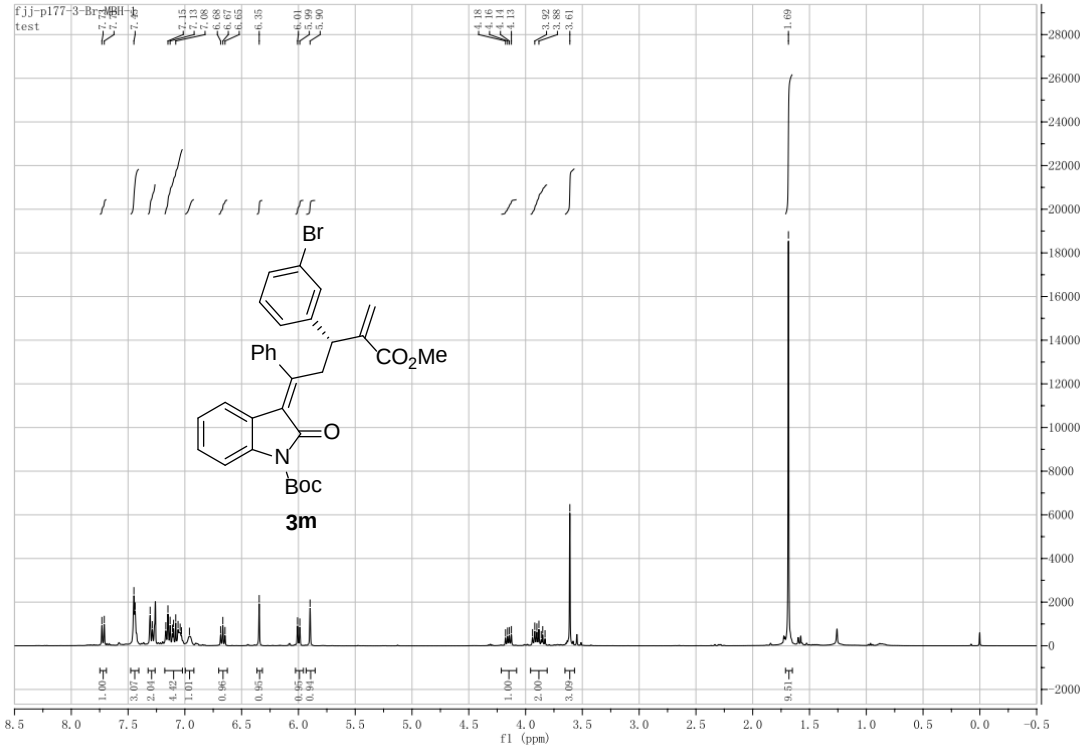

fjj-p177-4-NO2
C13CPD
f1 (ppm)

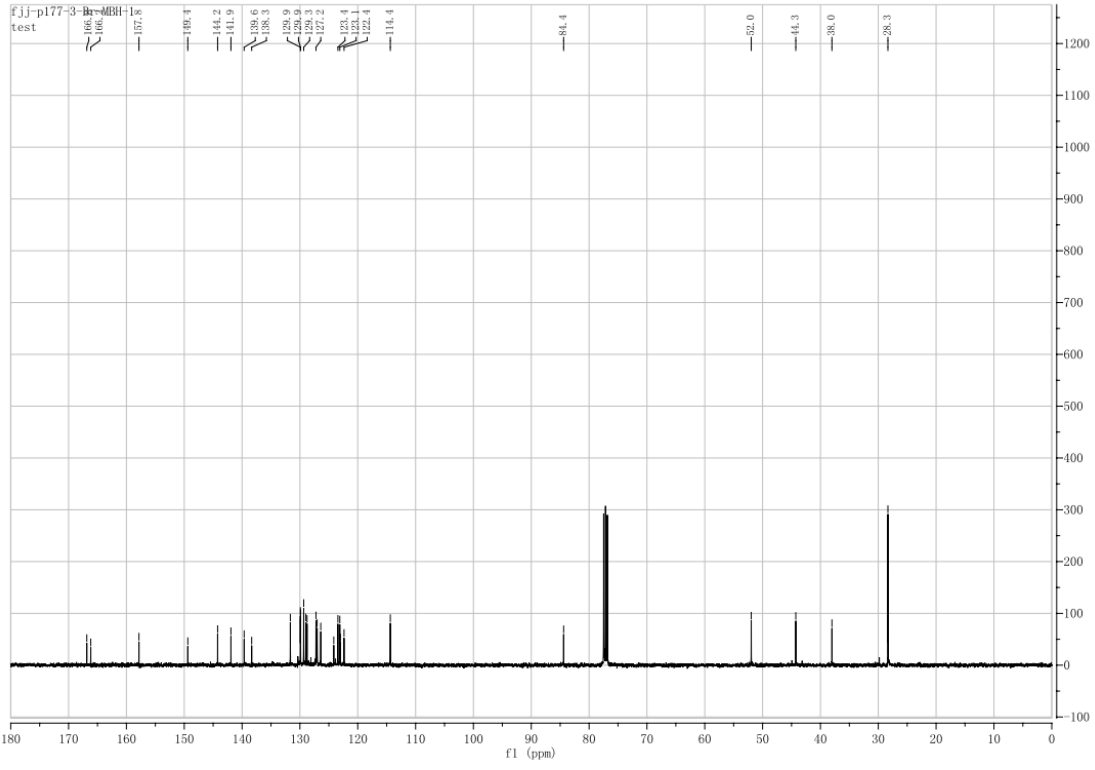

Me
Ph
CO2Me
O
N
Boc
3k
f1 (ppm)

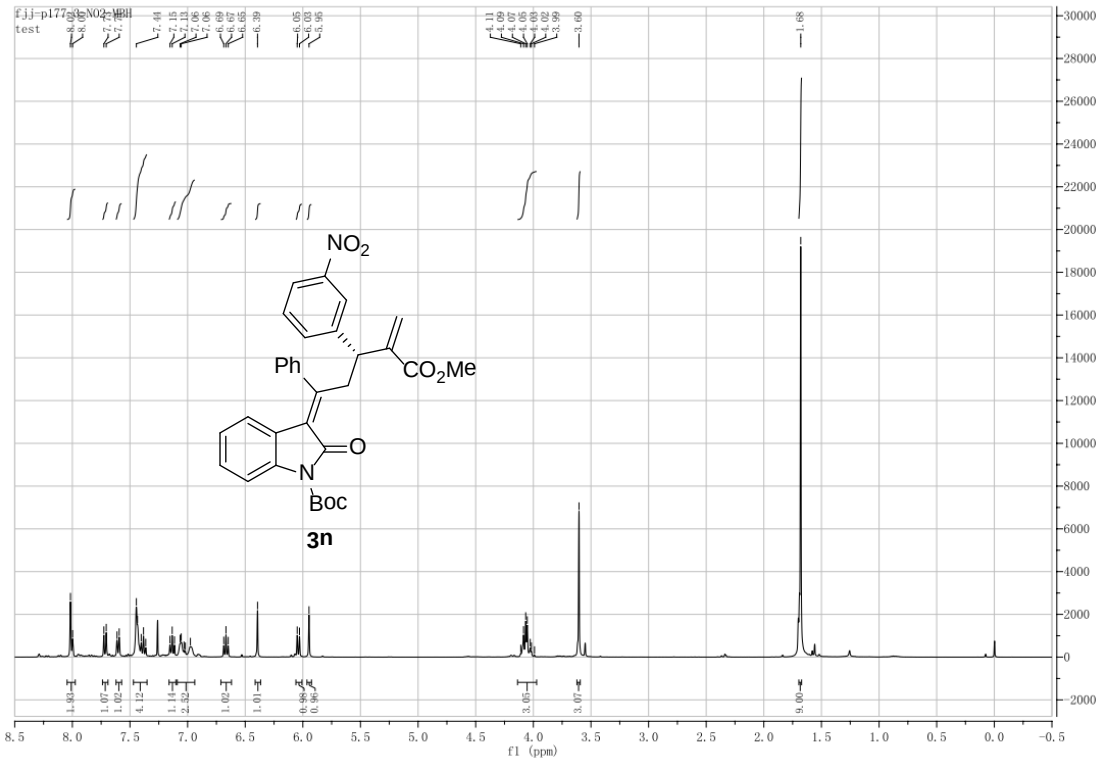

f1 (ppm)

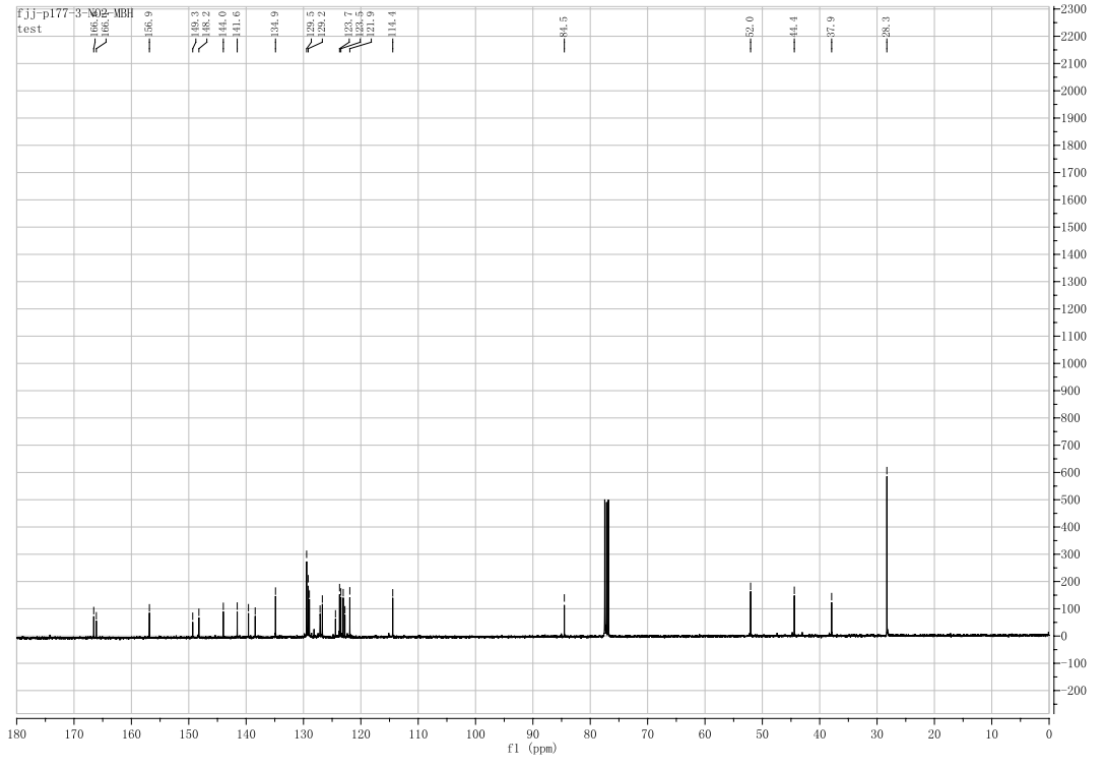

fjj-p176-3-Cl
test
Cl
Ph
CO2Me
O
N
Boc
3l
f1 (ppm)

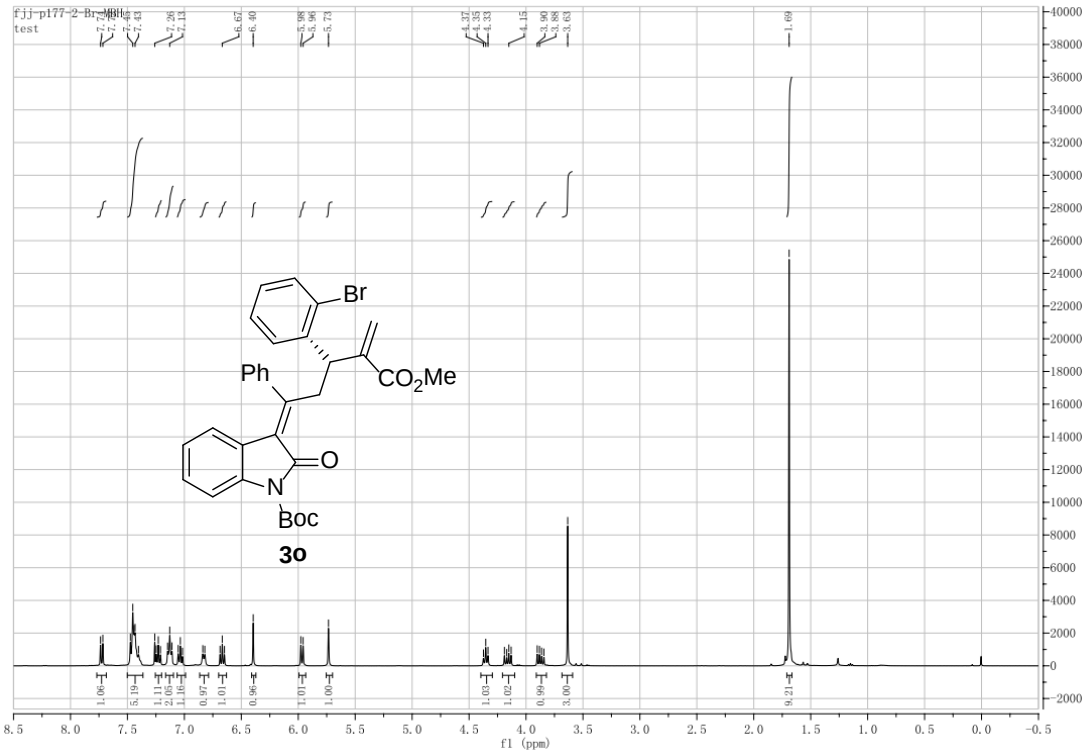

fjj-p176-3-Cl
test
f1 (ppm)

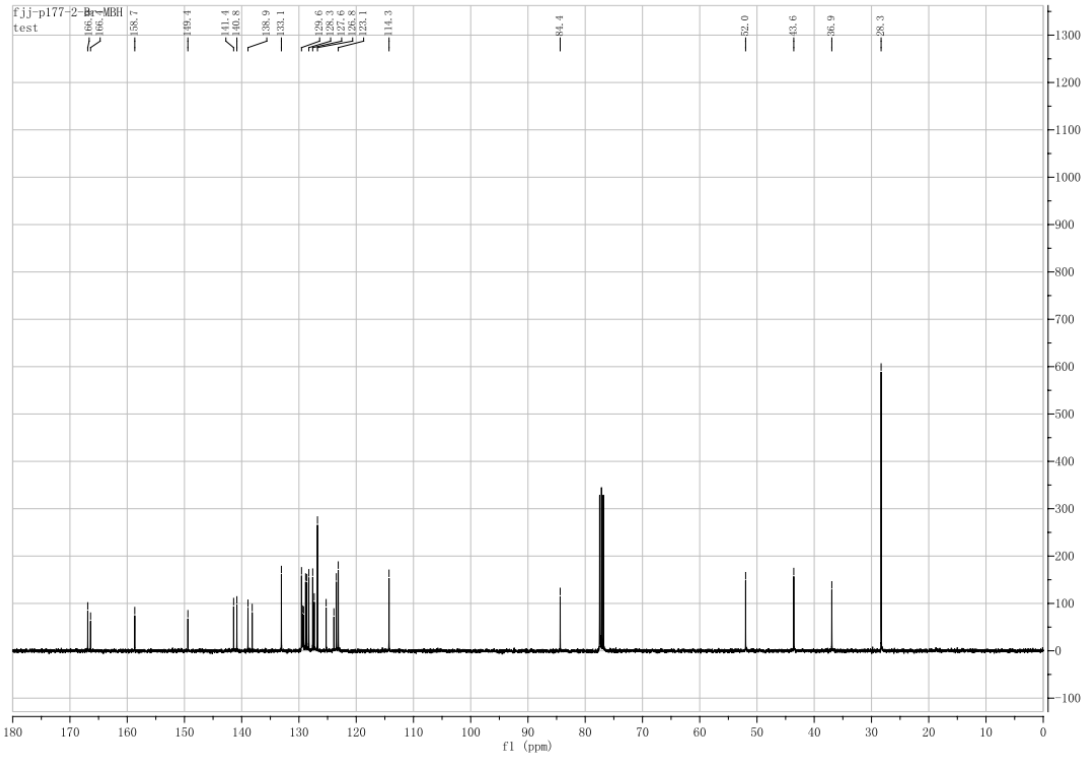

Br
Ph
CO2Me
O
N
Boc
3m
f1 (ppm)

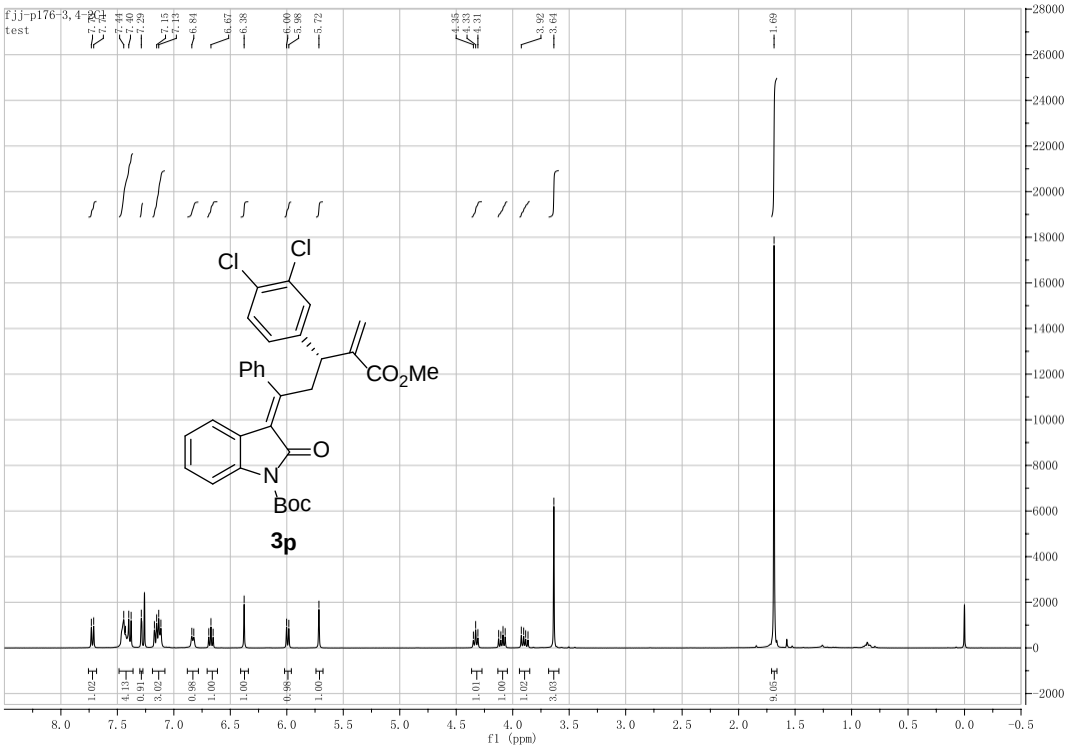

f1 (ppm)

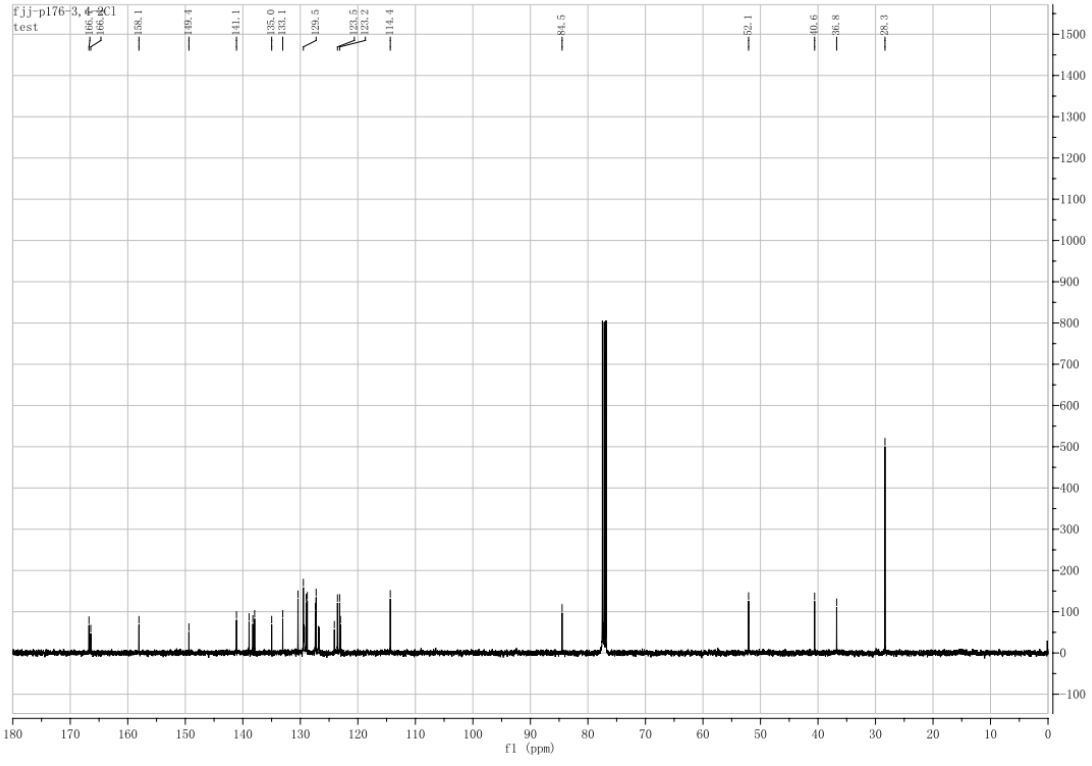

NO2
Ph
CO2Me
O
N
Boc
3n
f1 (ppm)

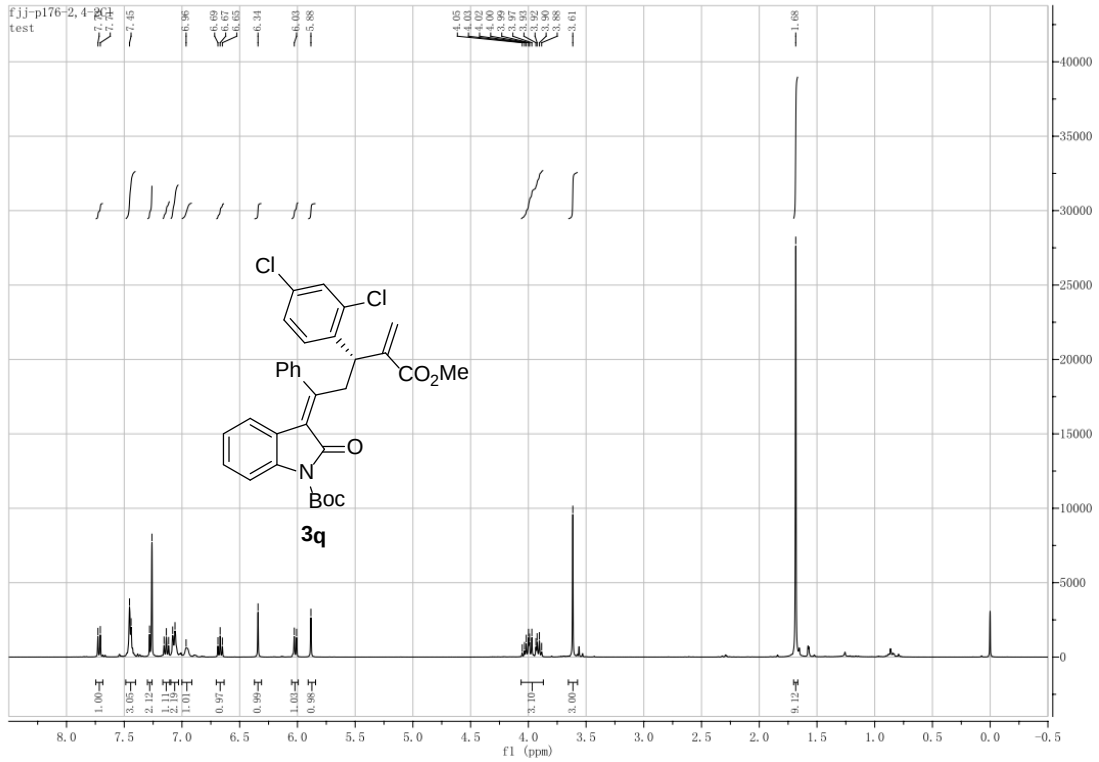

f1 (ppm)

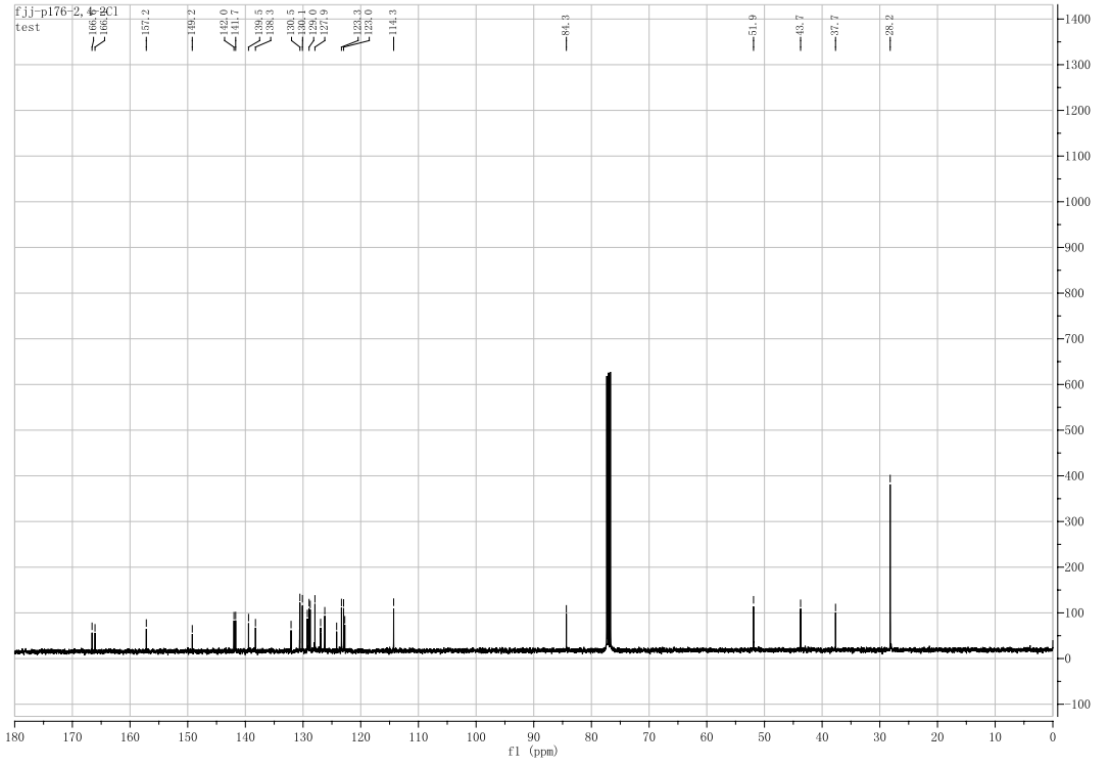

Br
Ph
CO2Me
O
N
Boc
3o
f1 (ppm)

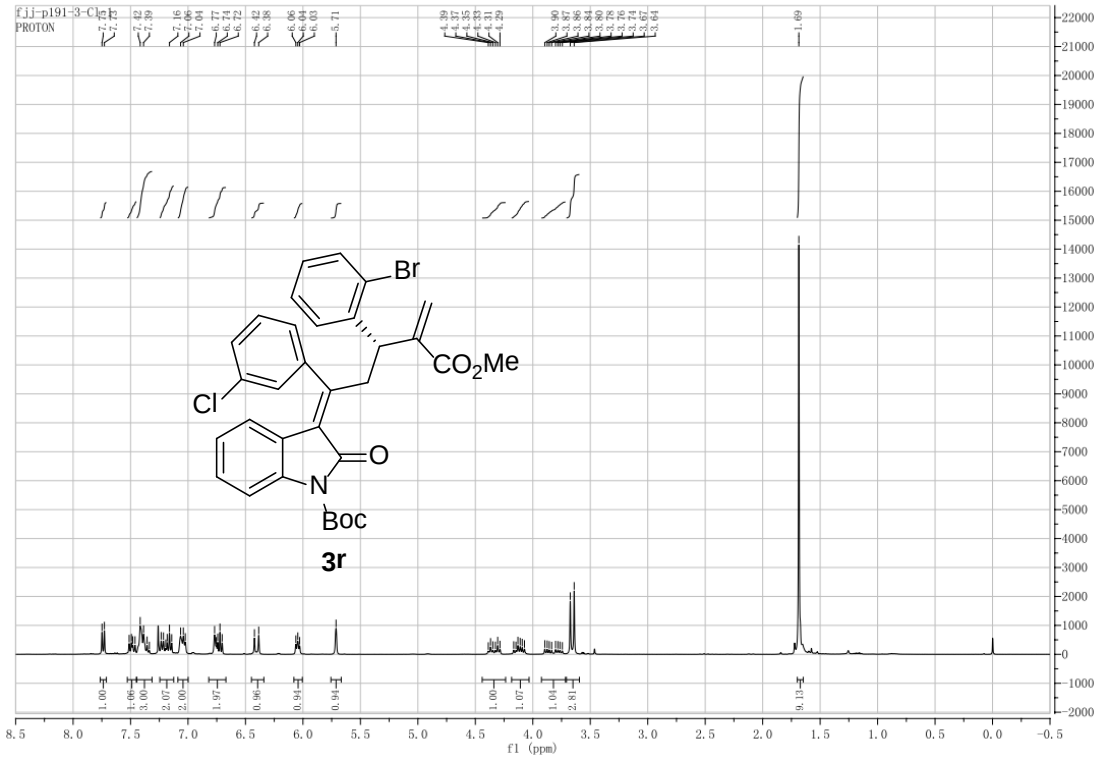

f1 (ppm)

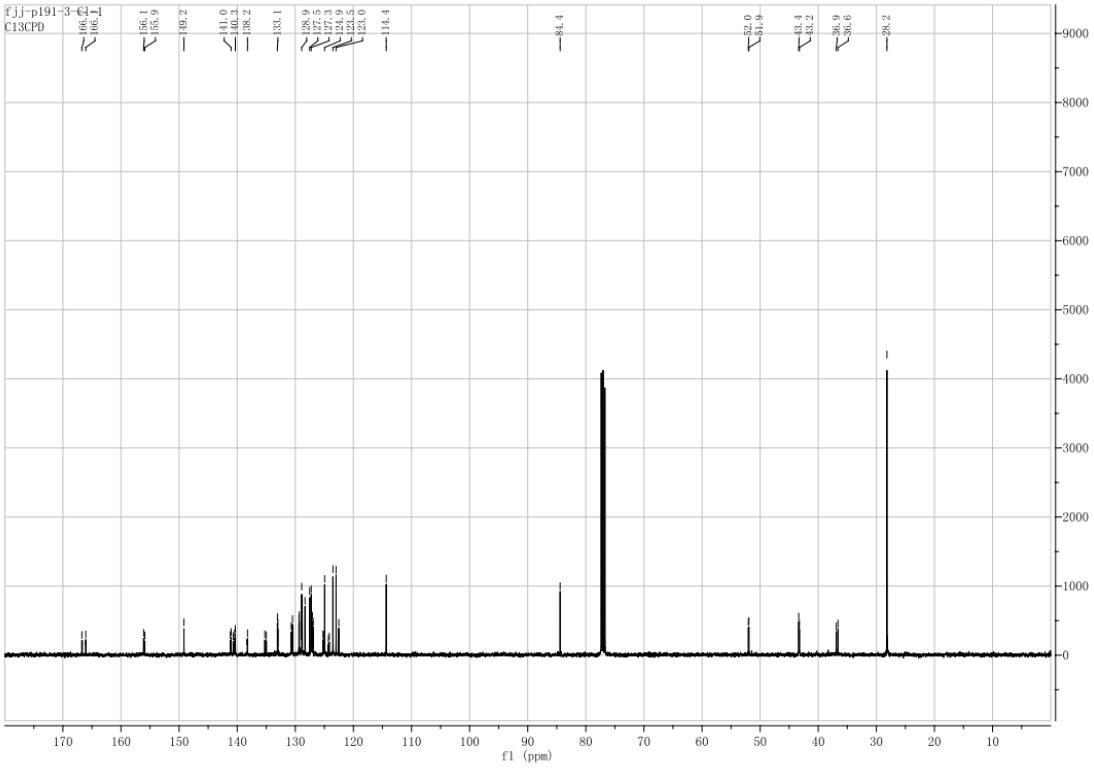

fjj-p176-3,4-2Cl
test
Cl
Cl
Ph
CO2Me
O
N
Boc
3p
f1 (ppm)

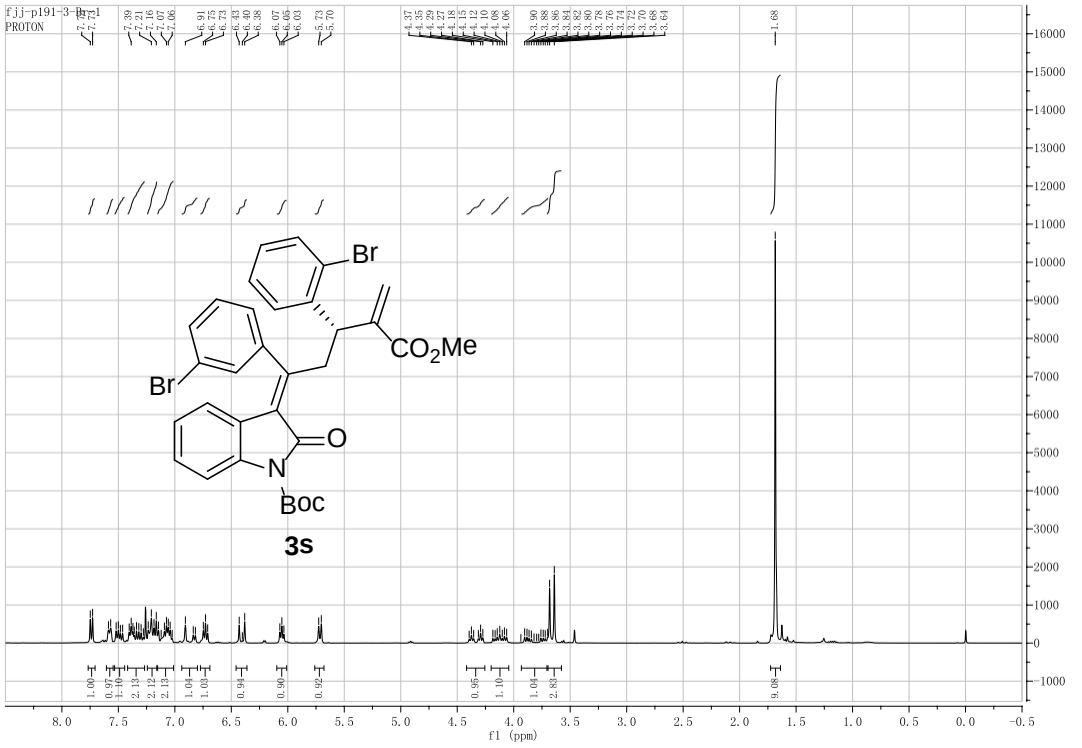

fjj-p176-3,4-2Cl
test
f1 (ppm)

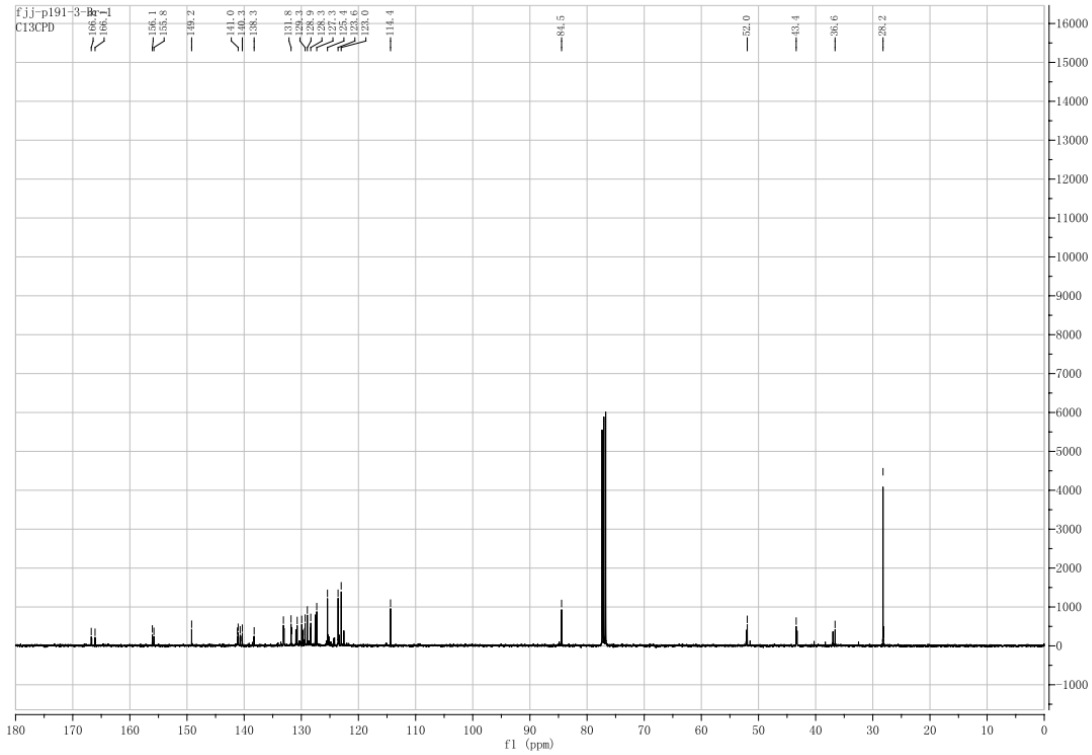

Cl
Cl
Ph
CO2Me
O
N
Boc
3q
f1 (ppm)

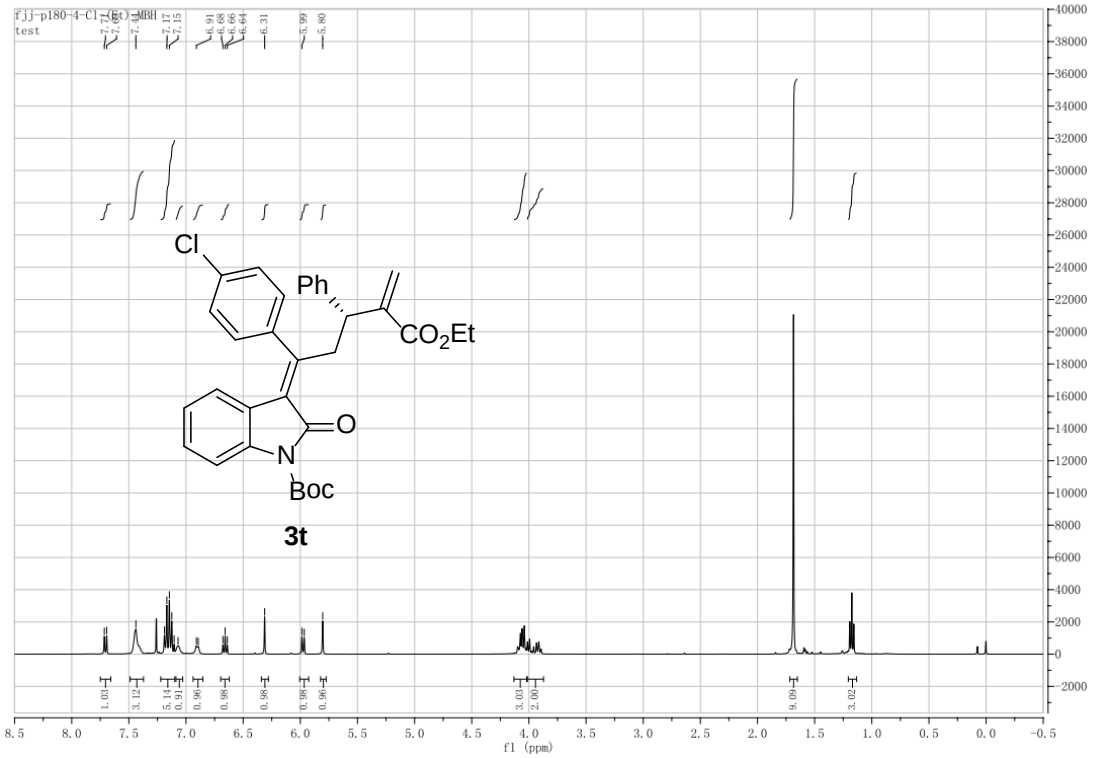

f1 (ppm)

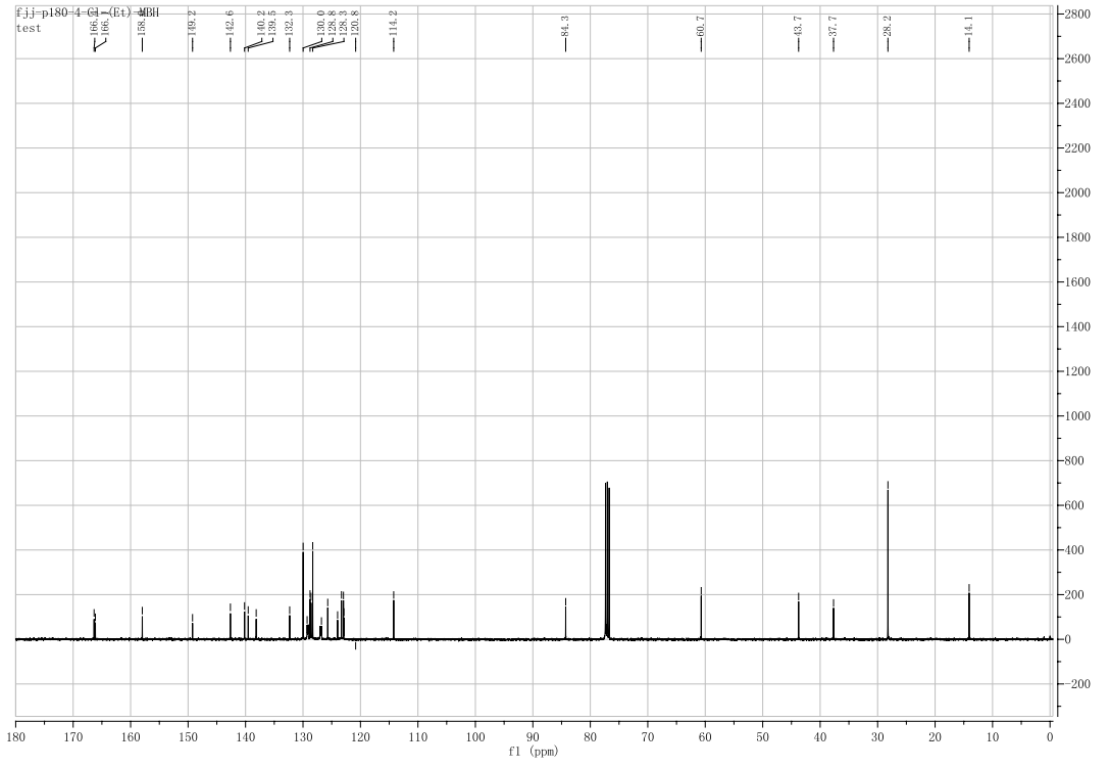

fjj-p191-3-Cl-1
PROTON
Br
CO2Me
Cl
O
N
Boc
3r
f1 (ppm)

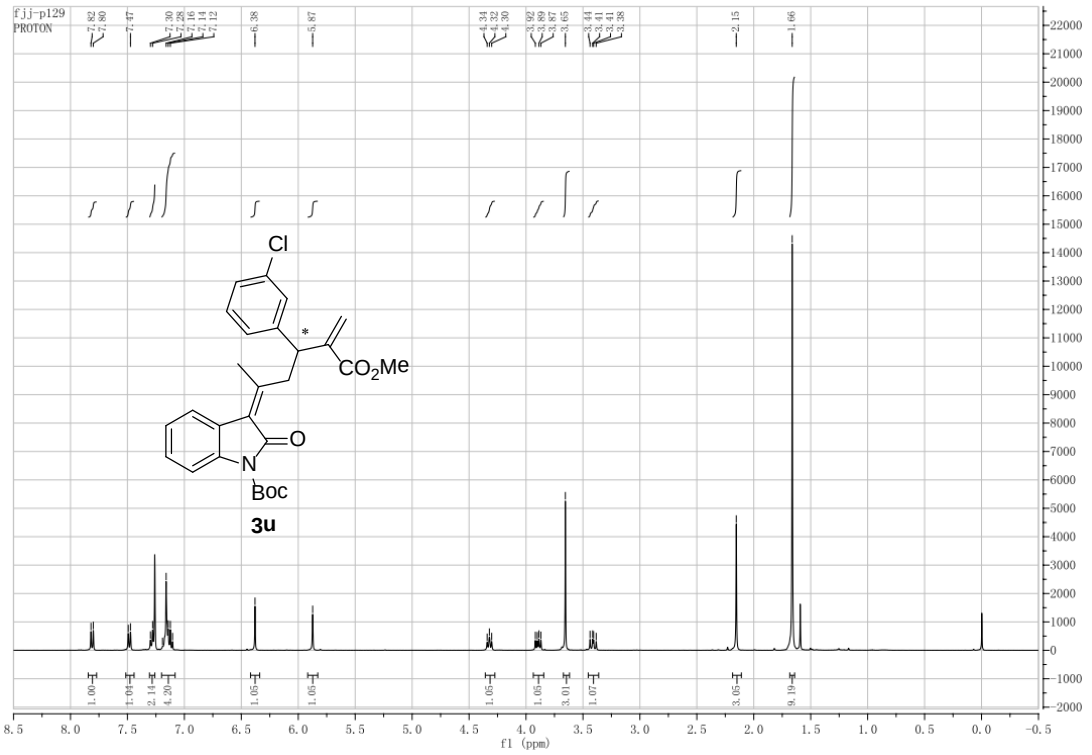

fjj-p191-3-Cl-1
C13CPD
f1 (ppm)

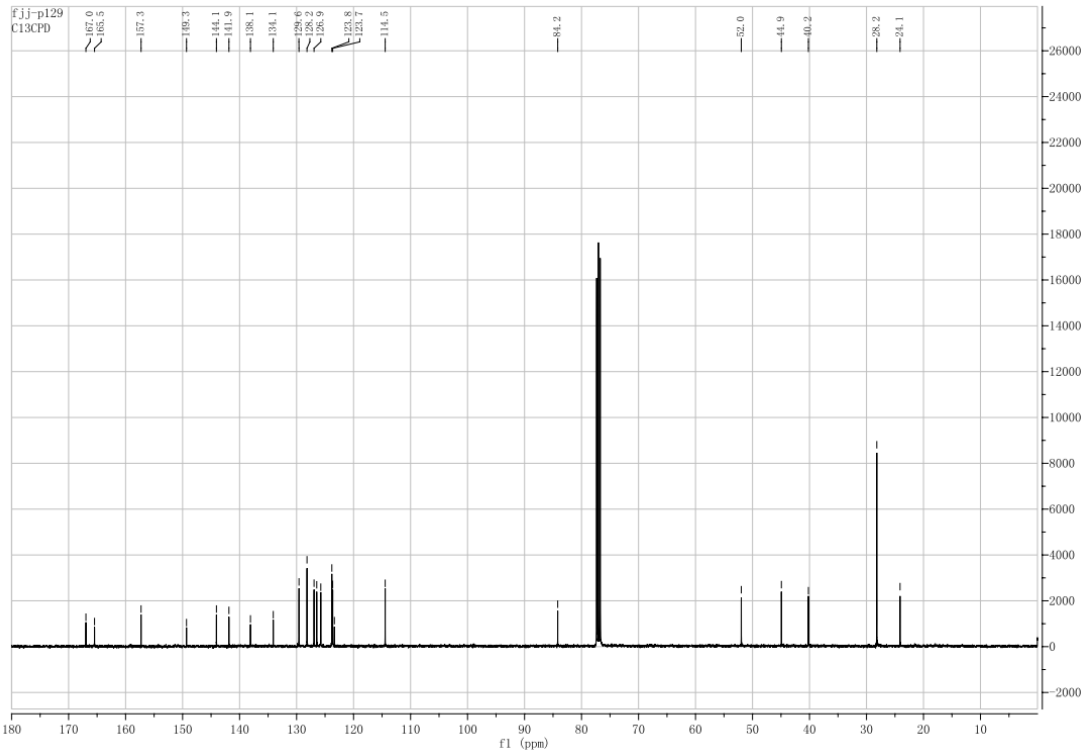

fjj-p191-3-Br-1
PROTON
Br
CO2Me
Br
O
N
Boc
3s
f1 (ppm)

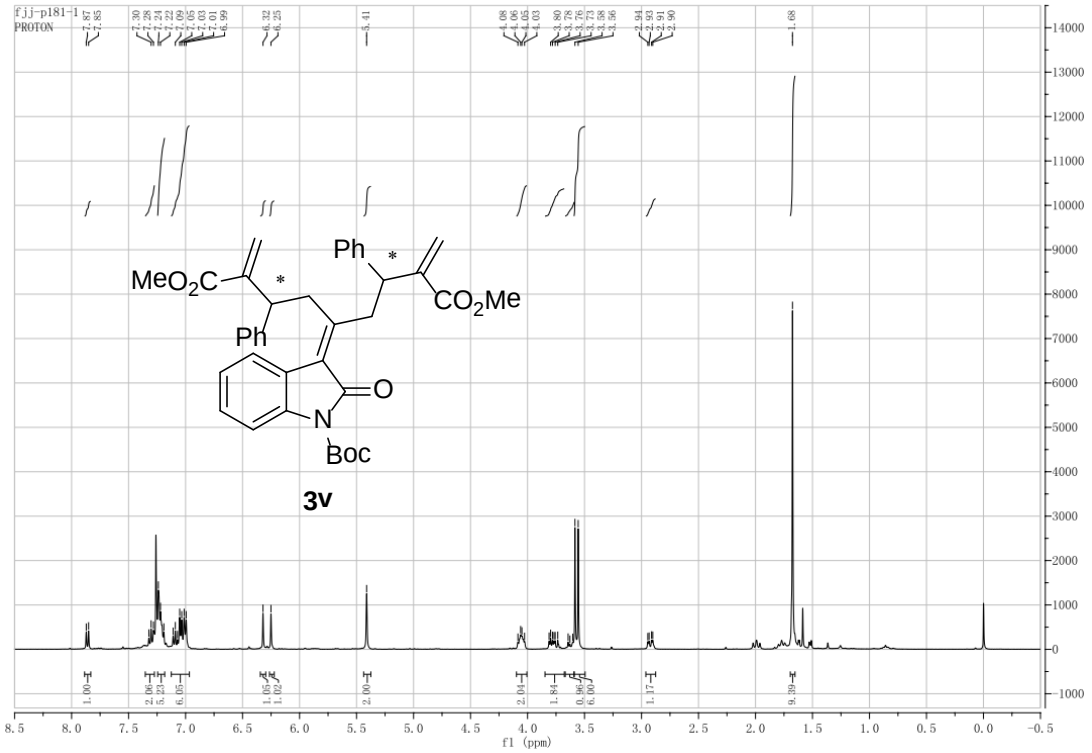

fjj-p191-3-Br-1
C13CPD
f1 (ppm)

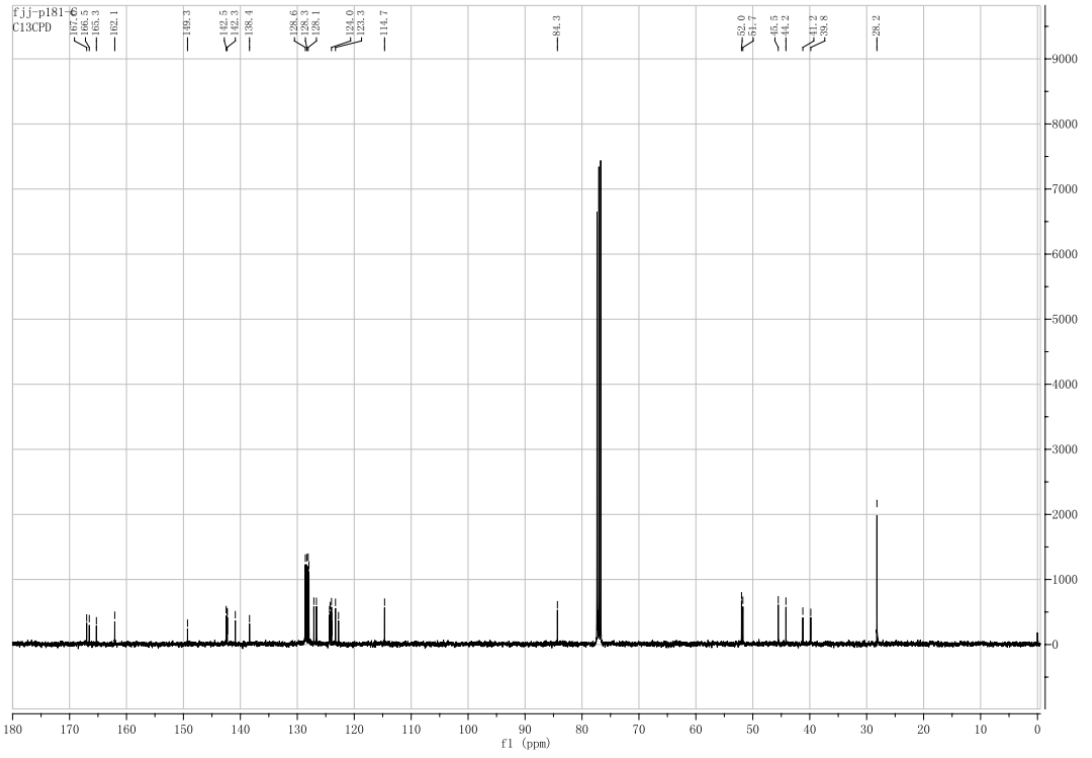

Cl
Ph
CO2Et
O
N
Boc
3t
f1 (ppm)

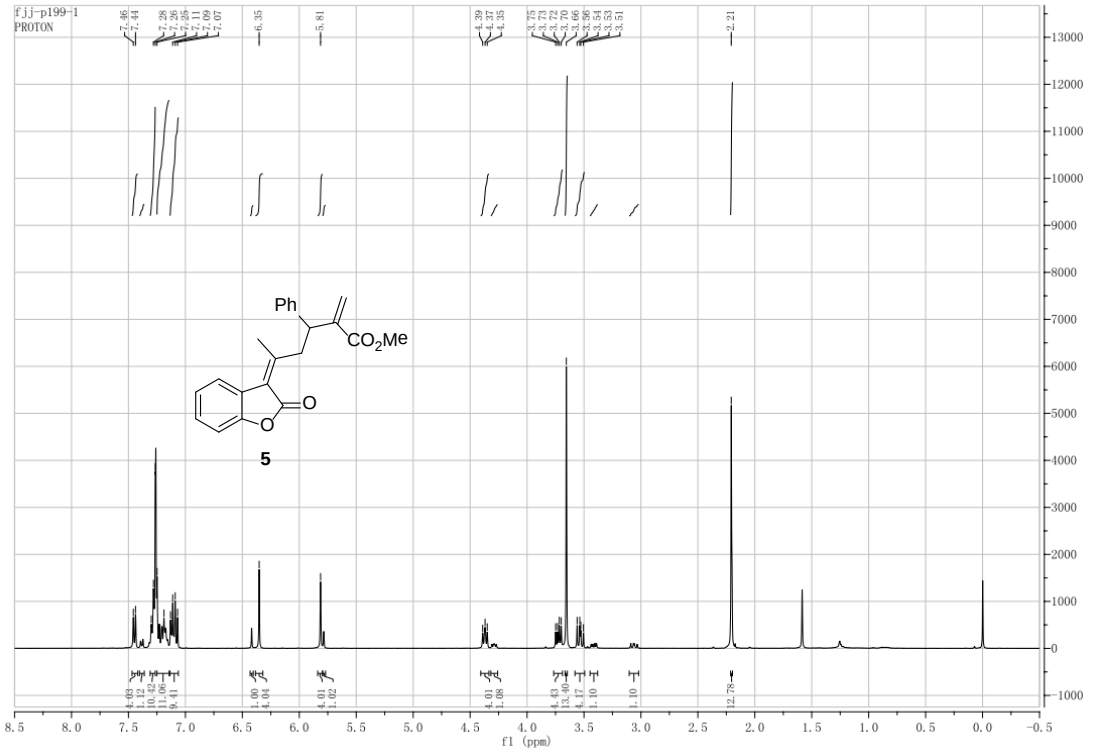

f1 (ppm)

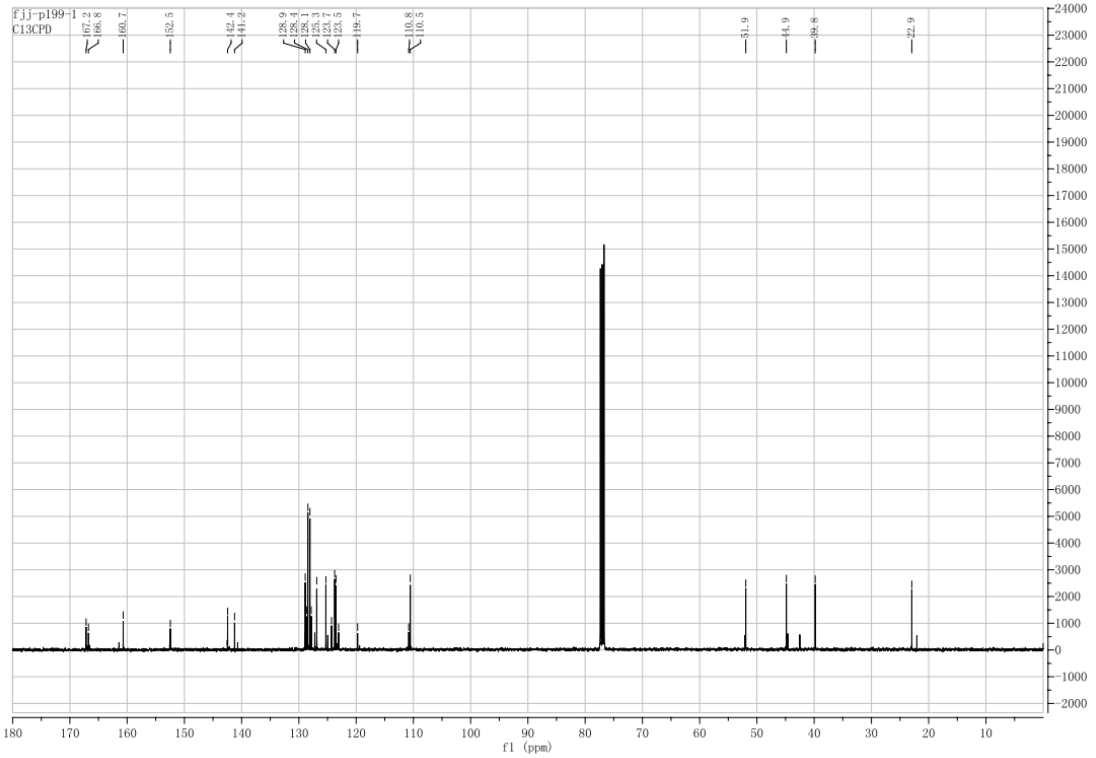

fjj-p129
PROTON
Cl
CO2Me
O
N
Boc
3u
f1 (ppm)

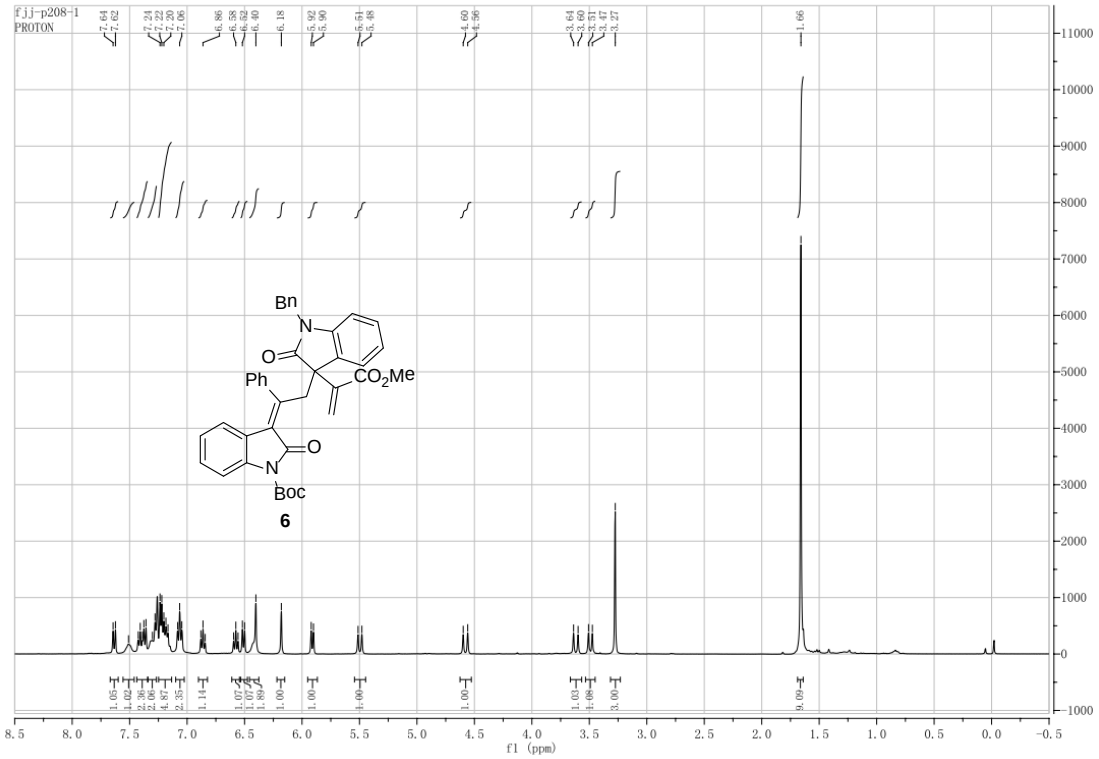

fjj-p129
C13CPD
f1 (ppm)

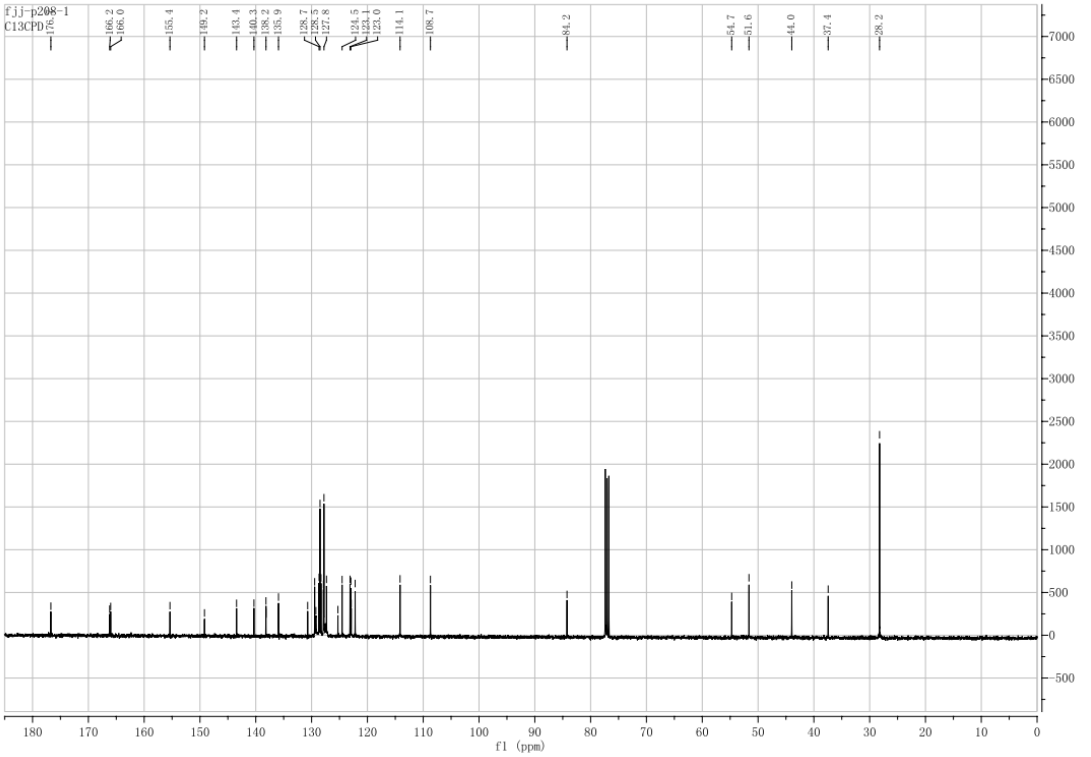

fjj-p181-1
PROTON
MeO2C
CO2Me
Ph
Ph
O
N
Boc
3v
f1 (ppm)


fjj-p181-6
C13CPD
f1 (ppm)

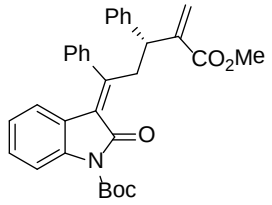

fjj-p199-1
PROTON
Ph
CO2Me
O
O
5
f1 (ppm)


fjj-p199-1
C13CPD
f1 (ppm)

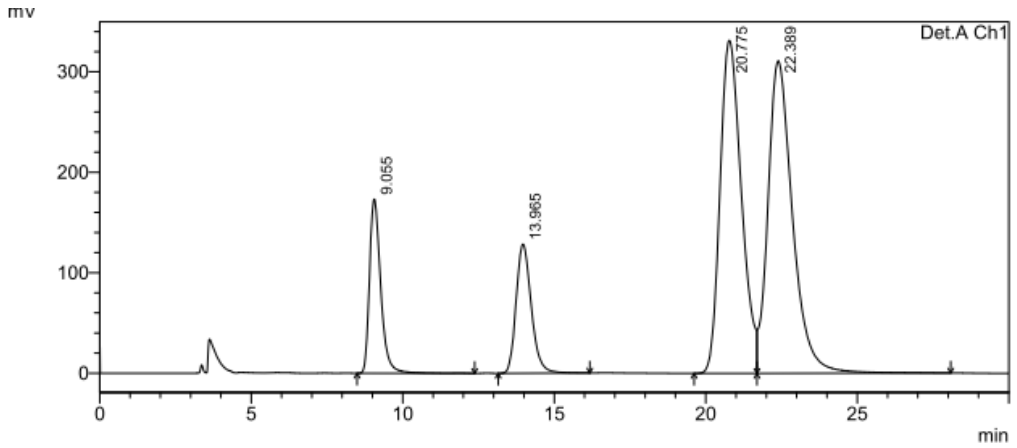

fjj-p208-1
PROTON
Bn
N
O
Ph
CO2Me
O
N
Boc
6
f1 (ppm)


fjj-p208-1
C13CPD
f1 (ppm)

6. Chiral HPLC Chromatography



3a

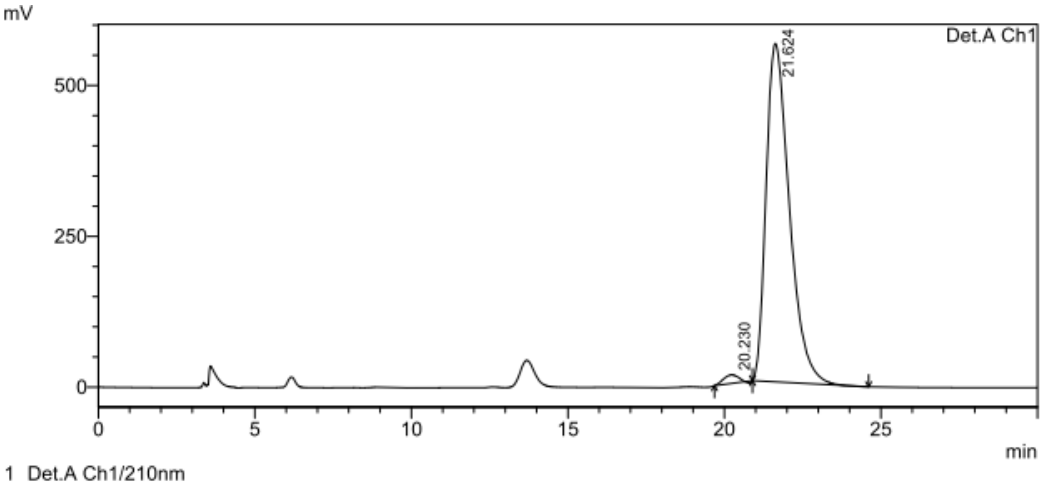


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.055	4482124	173388	10.498	18.365
2	13.965	4468621	128461	10.466	13.607
3	20.775	16201393	331378	37.947	35.099
4	22.389	17542731	310888	41.089	32.929
Total		42694869	944116	100.000	100.000

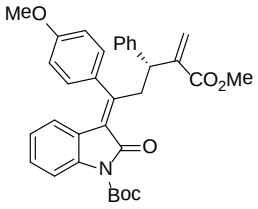


1 Det.A Ch1/210nm

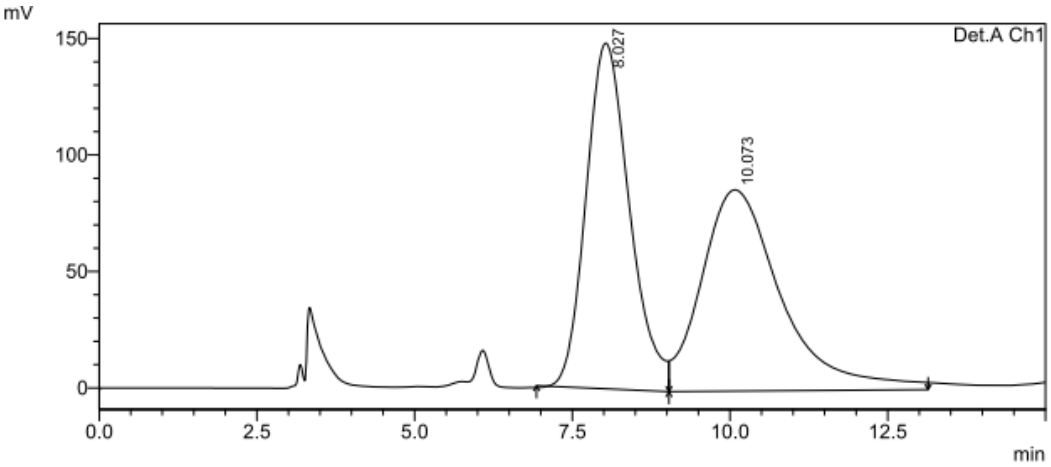
PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.230	439477	14102	1.496	2.453
2	21.624	28945297	560710	98.504	97.547
Total		29384773	574811	100.000	100.000



3b

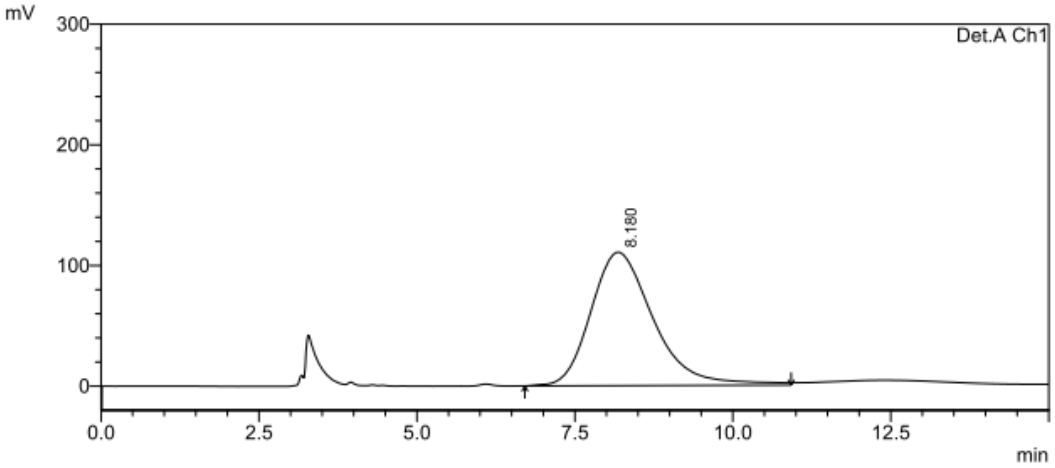


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.027	7105115	148386	48.374	63.205
2	10.073	7582761	86381	51.626	36.795
Total		14687876	234767	100.000	100.000

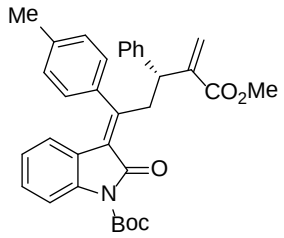


1 Det.A Ch1/210nm

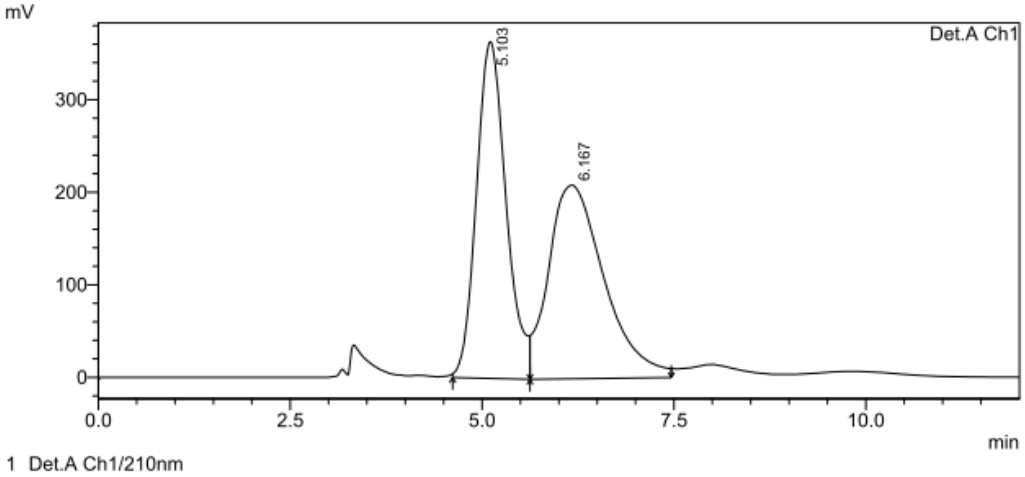
PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.180	7620185	110650	100.000	100.000
Total		7620185	110650	100.000	100.000



3c

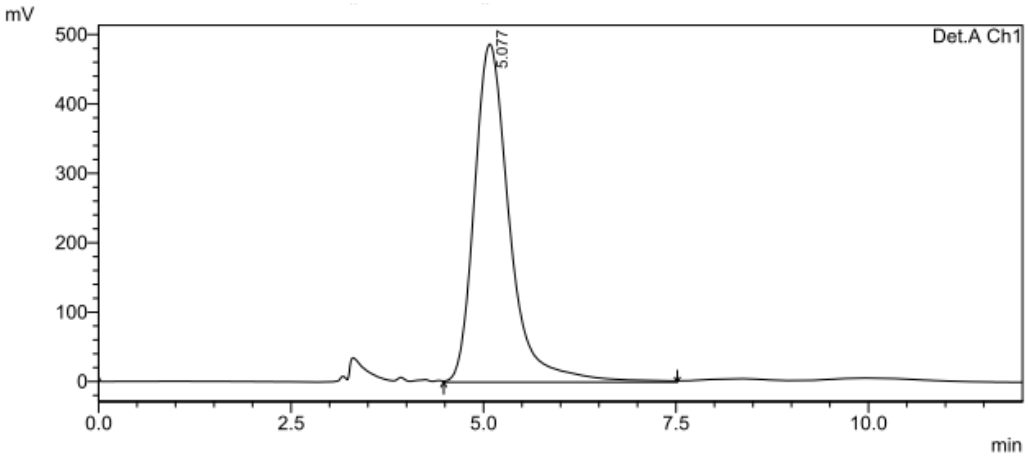


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.103	9796815	363718	48.149	63.479
2	6.167	10549918	209257	51.851	36.521
Total		20346733	572975	100.000	100.000

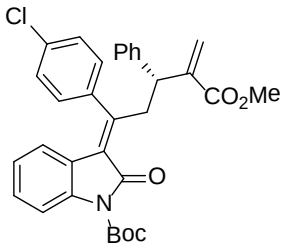


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.077	15494336	487100	100.000	100.000
Total		15494336	487100	100.000	100.000



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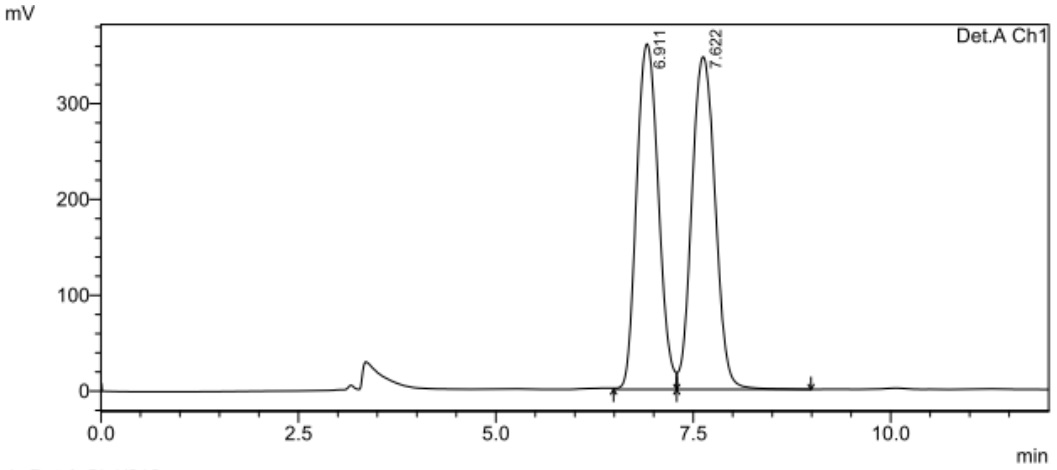
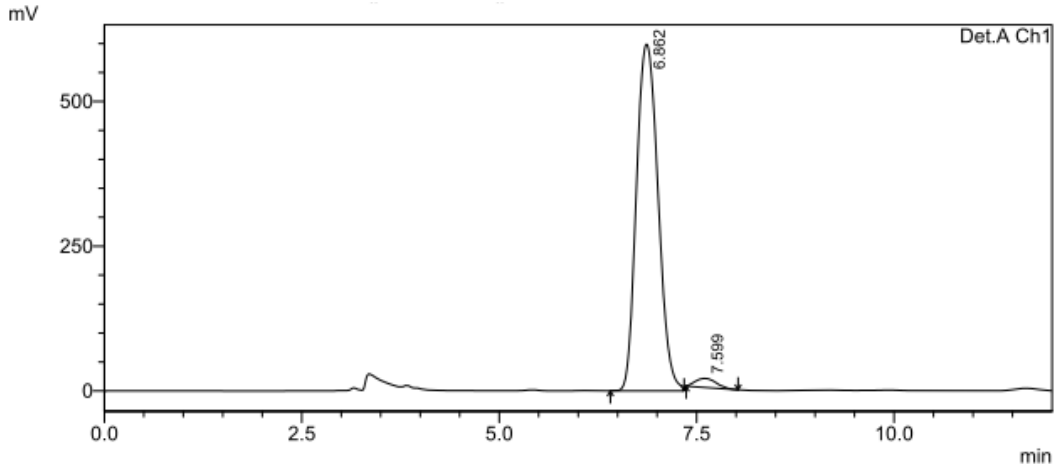


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.911	6931941	360498	49.157	50.953
2	7.622	7169833	347014	50.843	49.047
Total		14101774	707512	100.000	100.000

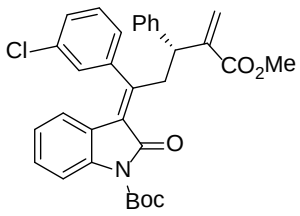


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.862	11442031	598841	97.556	97.468
2	7.599	286604	15559	2.444	2.532
Total		11728635	614400	100.000	100.000



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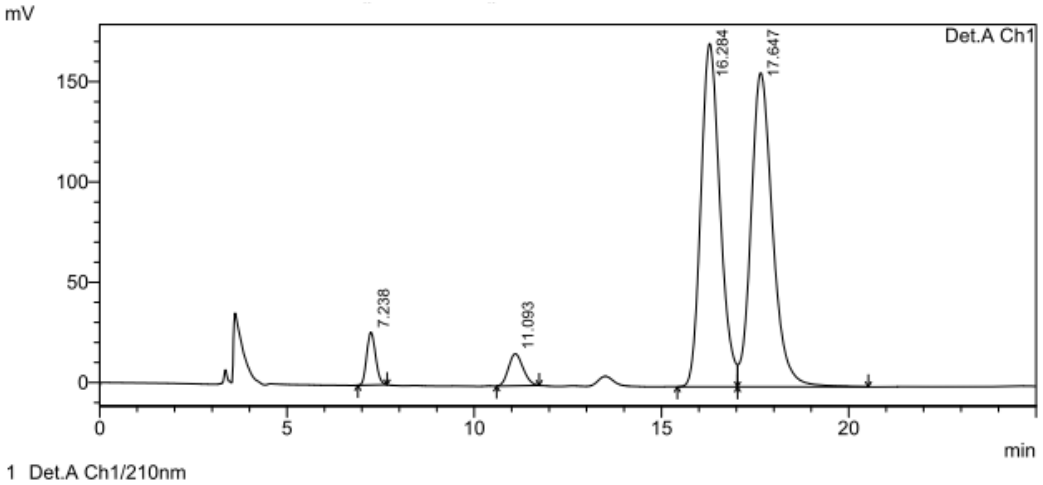
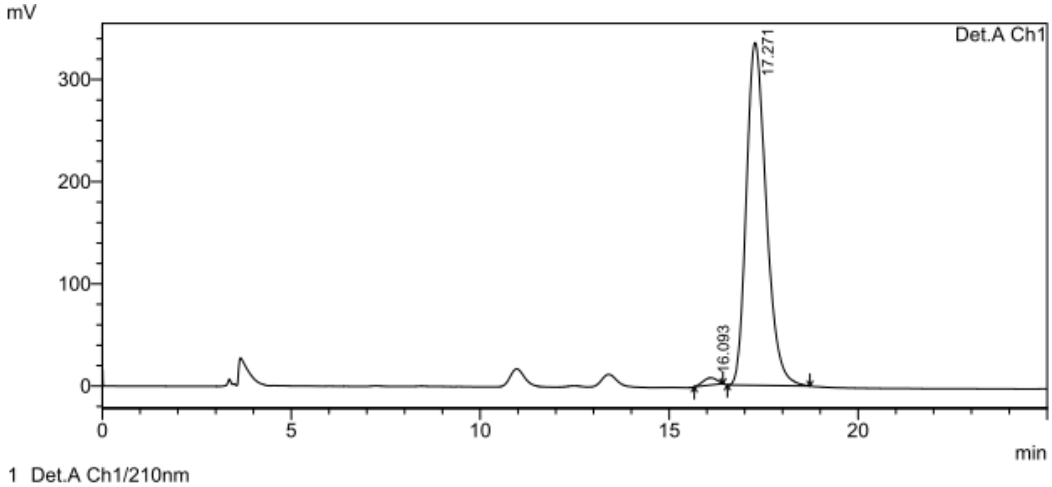


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.238	435993	26248	3.307	7.097
2	11.093	432243	15924	3.278	4.306
3	16.284	6066313	171055	46.009	46.253
4	17.647	6250538	156599	47.406	42.344
Total		13185087	369826	100.000	100.000

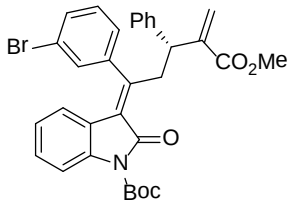


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.093	176893	7018	1.424	2.050
2	17.271	12249262	335375	98.576	97.950
Total		12426155	342394	100.000	100.000



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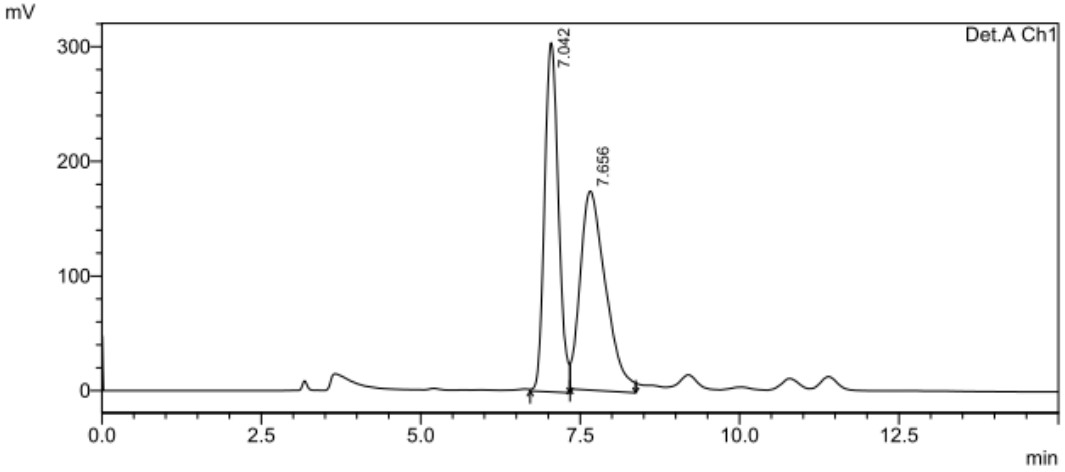
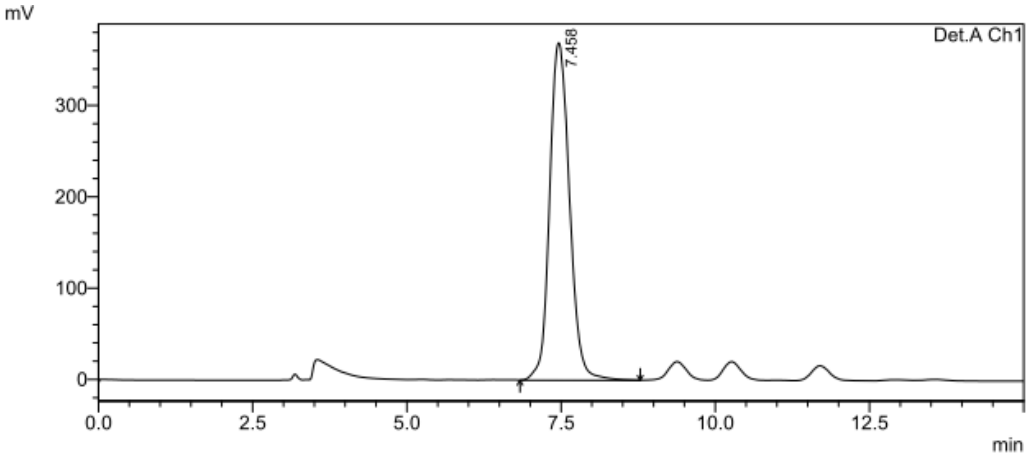


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.042	4616848	304441	48.889	63.701
2	7.656	4826695	173484	51.111	36.299
Total		9443543	477925	100.000	100.000

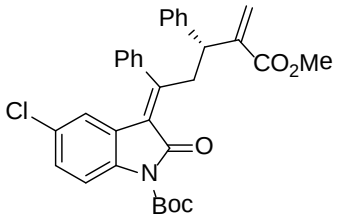


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.458	8329989	369396	100.000	100.000
Total		8329989	369396	100.000	100.000



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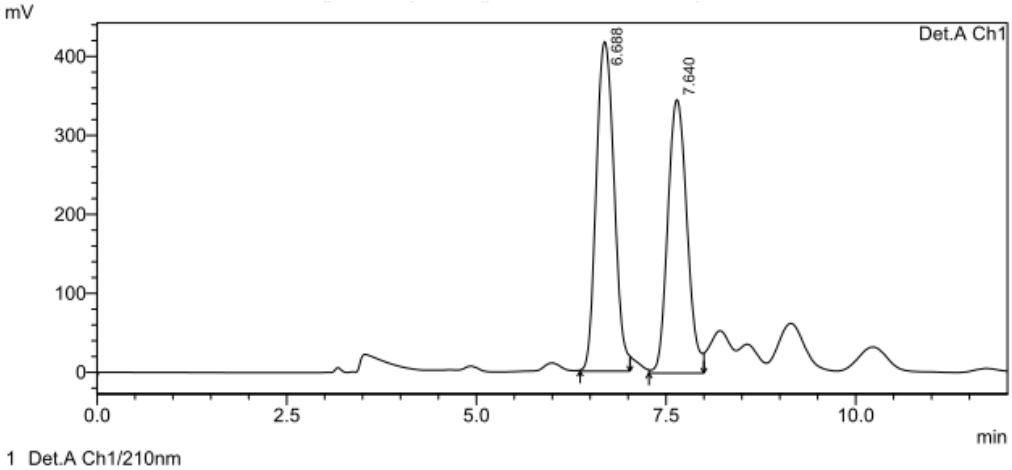
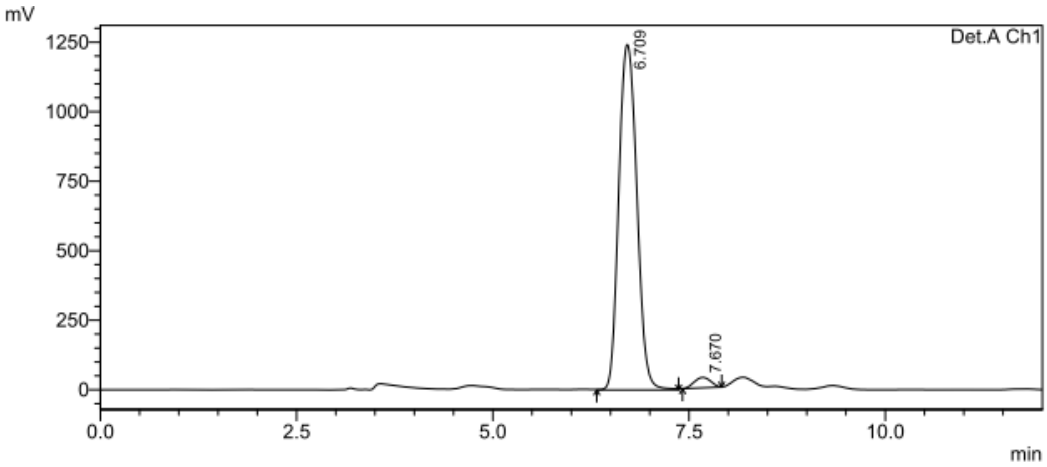


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.688	6839656	417438	52.792	54.668
2	7.640	6116083	346146	47.208	45.332
Total		12955739	763584	100.000	100.000

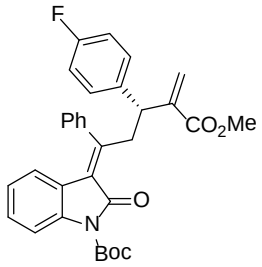


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.709	19907245	1241363	97.317	97.067
2	7.670	548900	37509	2.683	2.933
Total		20456145	1278872	100.000	100.000



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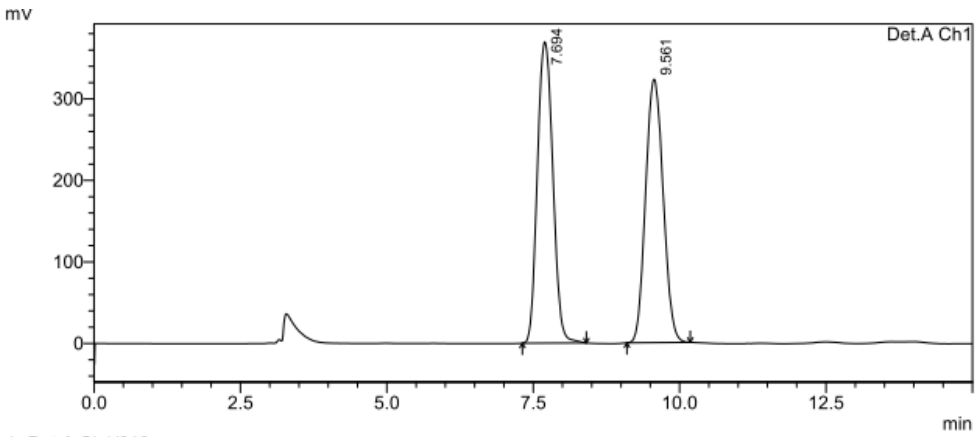
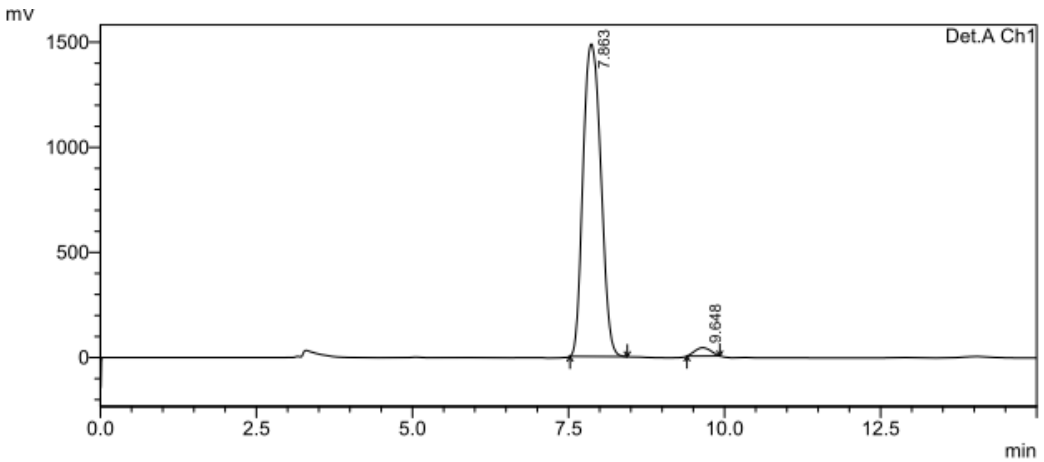


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.694	6806827	369507	50.193	53.349
2	9.561	6754446	323117	49.807	46.651
Total		13561273	692623	100.000	100.000

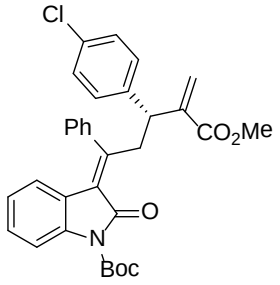


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.863	29589551	1486063	97.688	97.419
2	9.648	700157	39366	2.312	2.581
Total		30289708	1525429	100.000	100.000



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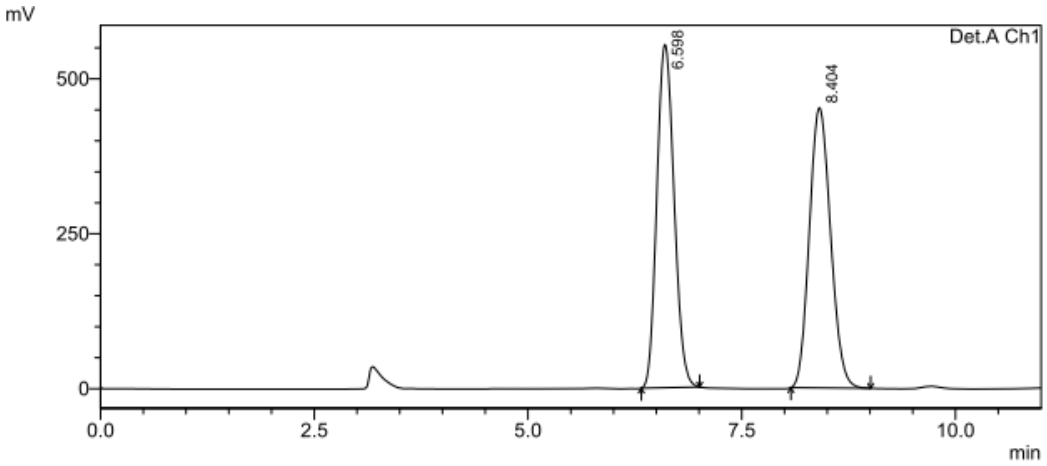
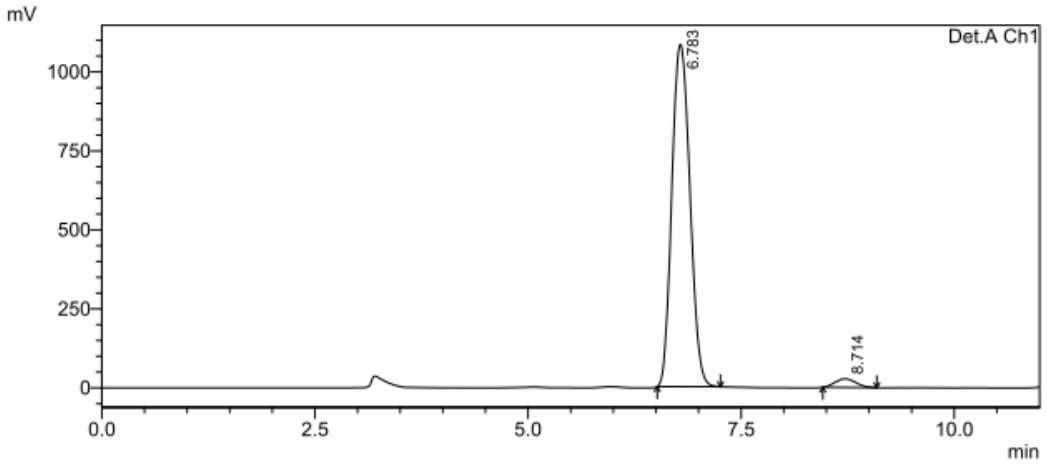


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.598	7770422	553819	49.829	55.054
2	8.404	7823610	452133	50.171	44.946
Total		15594032	1005952	100.000	100.000

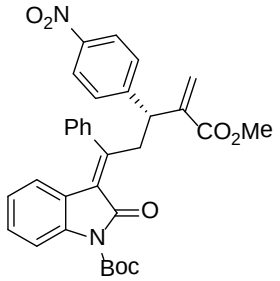


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.783	15994906	1083159	97.180	97.537
2	8.714	464208	27353	2.820	2.463
Total		16459114	1110511	100.000	100.000



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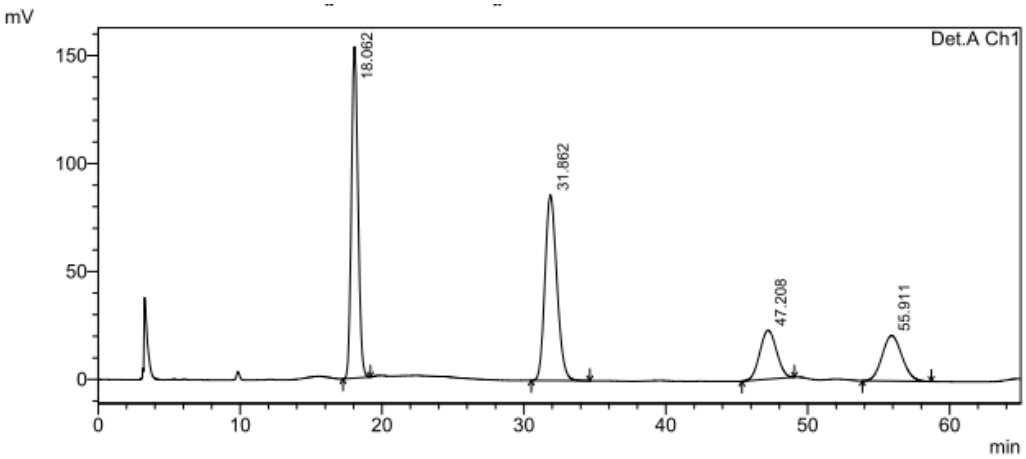
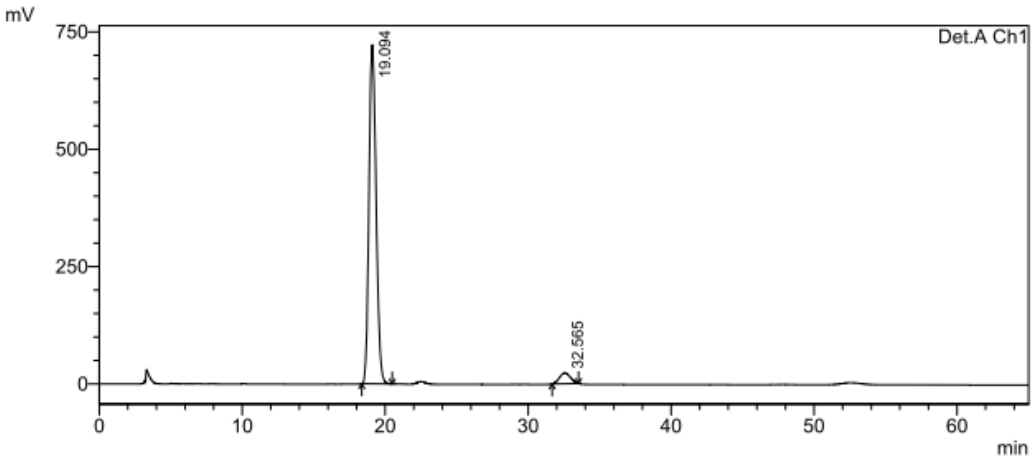


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.062	4971744	153559	35.820	54.218
2	31.862	5003519	85976	36.049	30.356
3	47.208	1856957	22631	13.379	7.990
4	55.911	2047716	21060	14.753	7.436
Total		13879935	283226	100.000	100.000

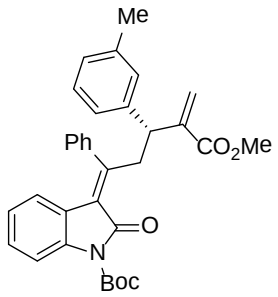


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.094	24893729	722394	95.301	96.927
2	32.565	1227382	22905	4.699	3.073
Total		26121111	745298	100.000	100.000



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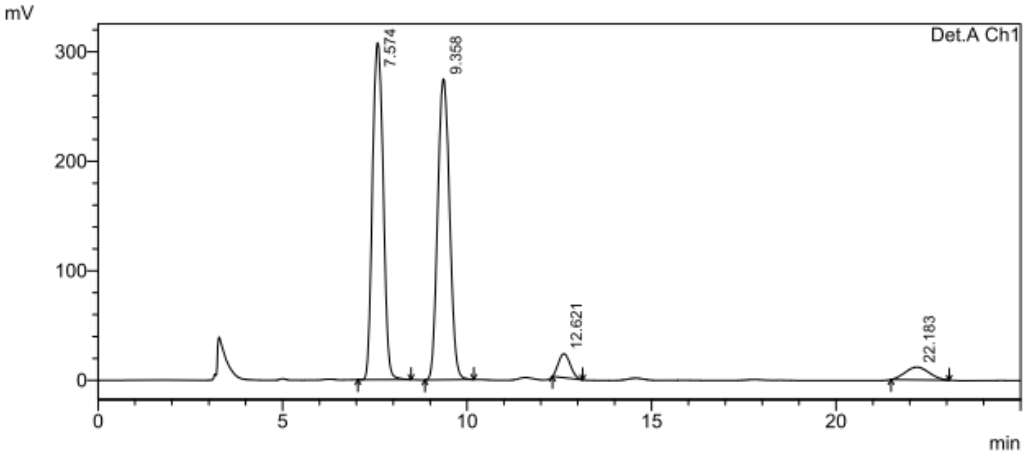
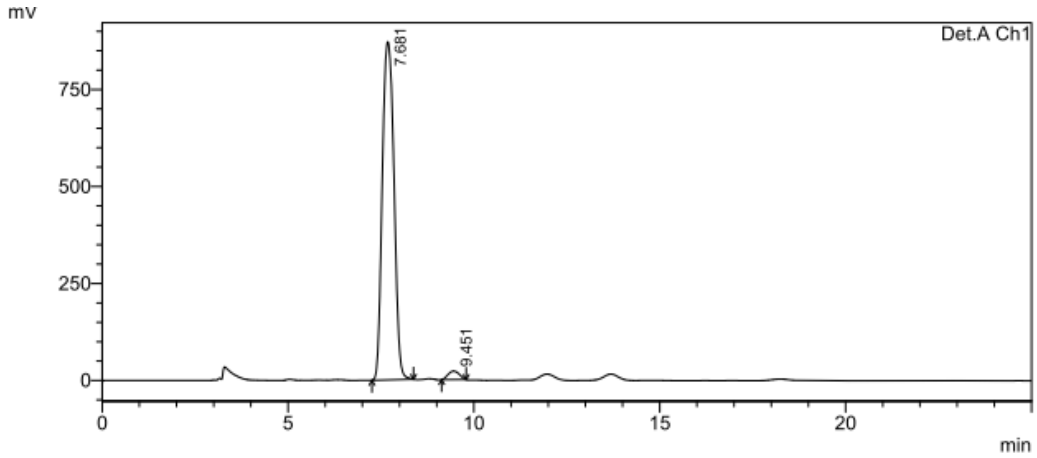


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.574	6227556	307633	46.488	49.964
2	9.358	6162144	274610	46.000	44.601
3	12.621	485535	21882	3.624	3.554
4	22.183	520787	11581	3.888	1.881
Total		13396021	615706	100.000	100.000

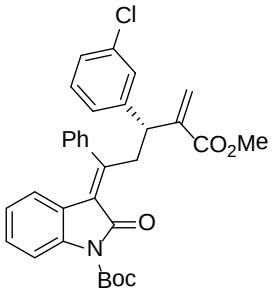


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.681	19032818	871538	97.634	97.556
2	9.451	461249	21836	2.366	2.444
Total		19494068	893374	100.000	100.000



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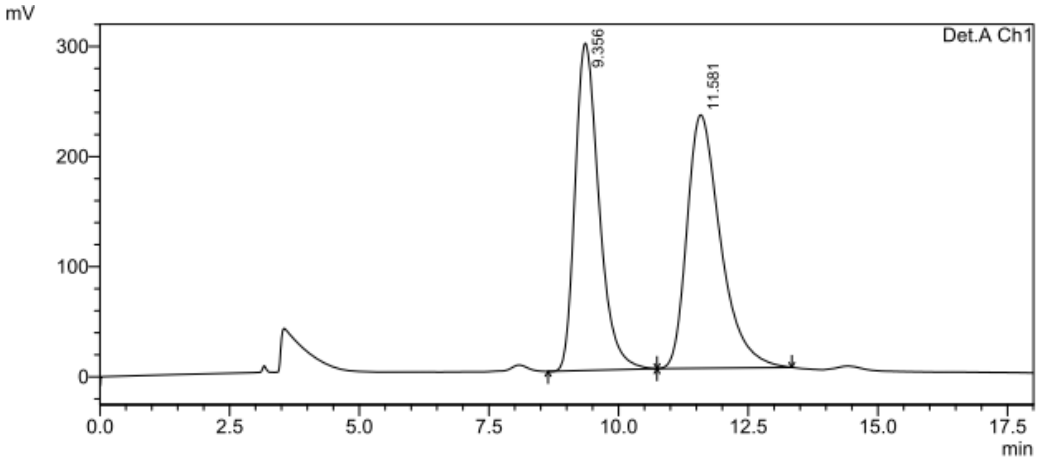
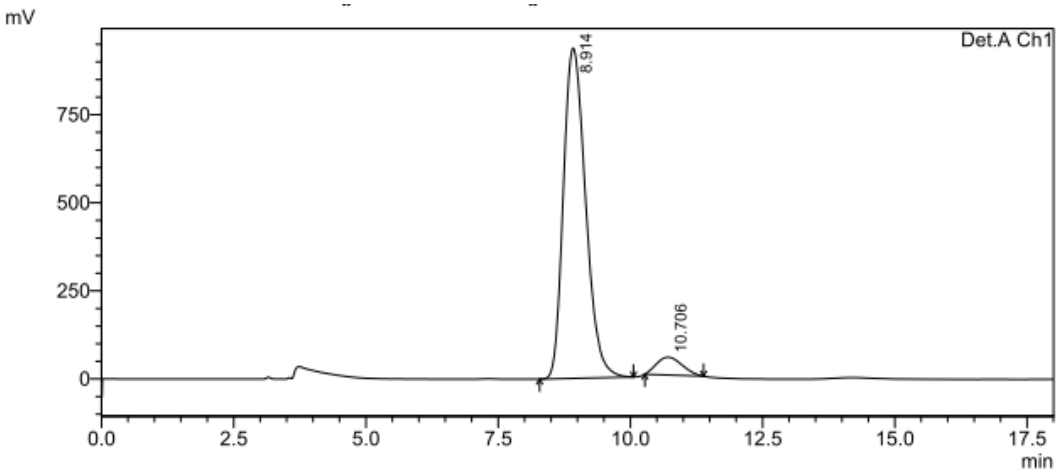


1 Det.A Ch1/210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.356	9530093	297173	47.892	56.362
2	11.581	10369080	230085	52.108	43.638
Total		19899173	527257	100.000	100.000

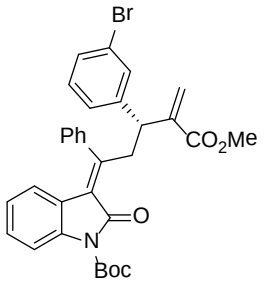


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.914	27391790	937829	94.121	94.873
2	10.706	1711007	50685	5.879	5.127
Total		29102797	988514	100.000	100.000



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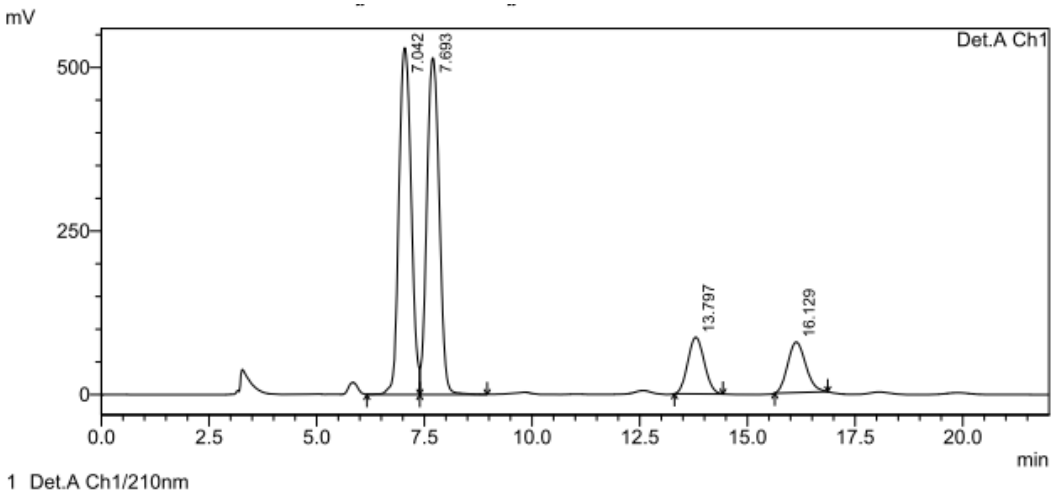
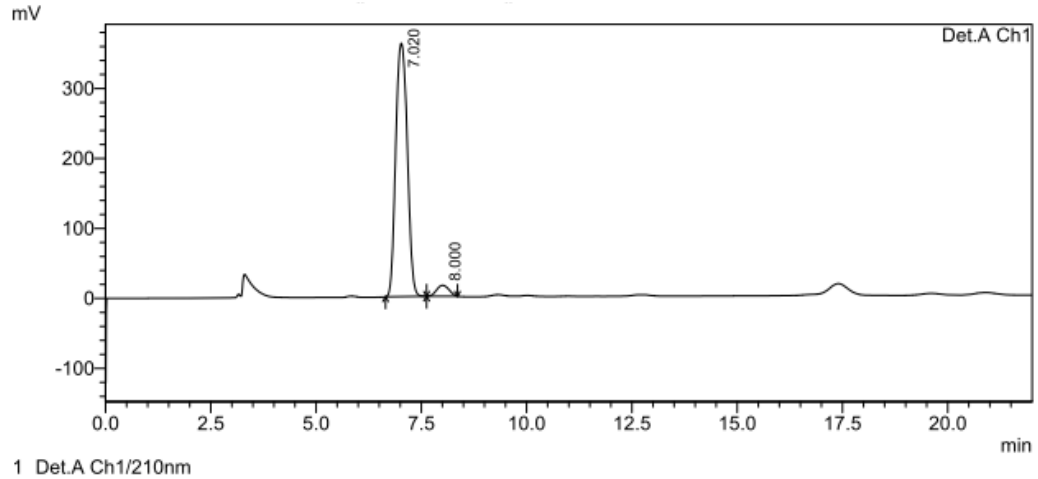


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.042	10519576	529804	41.388	43.855
2	7.693	10338682	514557	40.676	42.593
3	13.797	2306563	86484	9.075	7.159
4	16.129	2252292	77239	8.861	6.394
Total		25417112	1208084	100.000	100.000

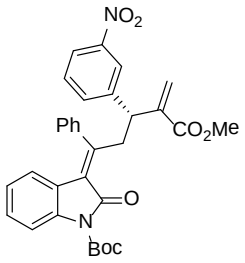


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.020	6922112	362042	95.640	95.876
2	8.000	315576	15573	4.360	4.124
Total		7237688	377615	100.000	100.000



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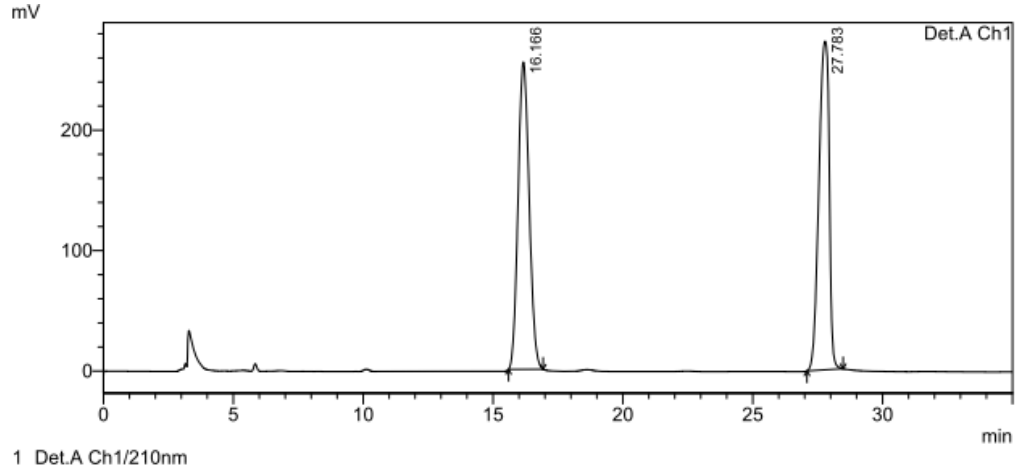
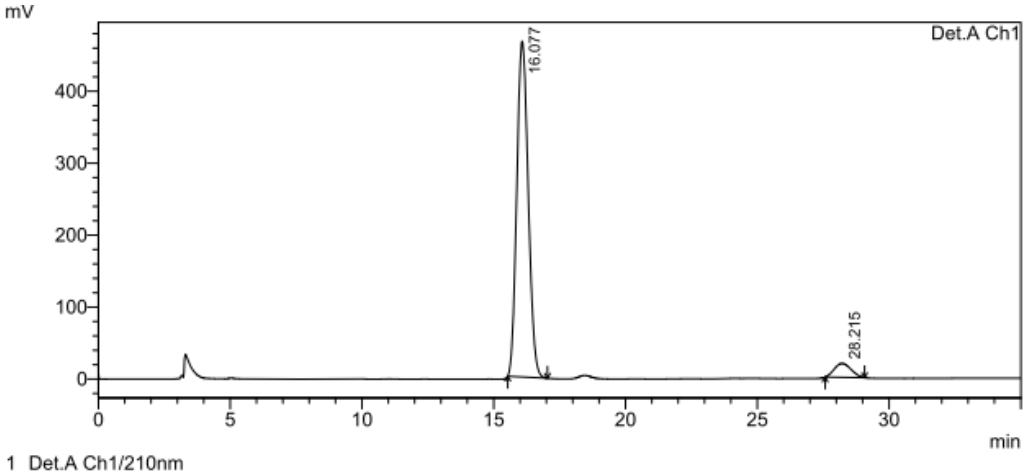


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.166	7557934	255072	50.072	48.322
2	27.783	7536052	272782	49.928	51.678
Total		15093985	527855	100.000	100.000

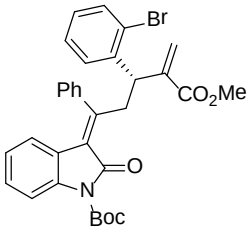


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.077	14075324	466774	94.285	96.029
2	28.215	853172	19301	5.715	3.971
Total		14928496	486075	100.000	100.000



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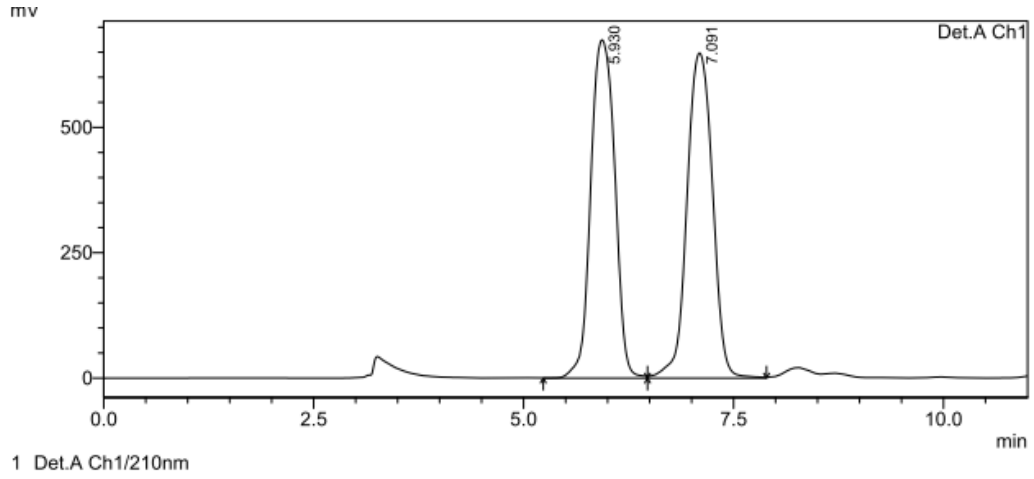
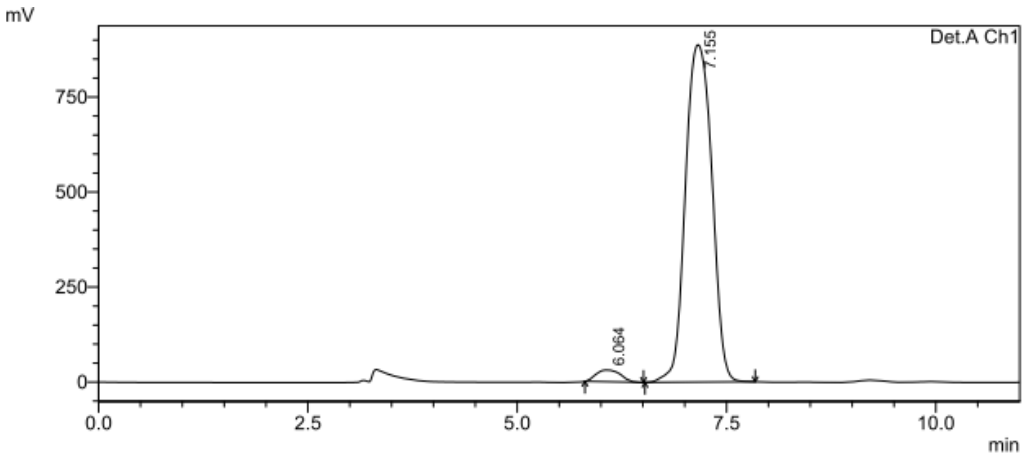


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.930	13491322	674632	49.499	50.992
2	7.091	13764401	648383	50.501	49.008
Total		27255723	1323014	100.000	100.000

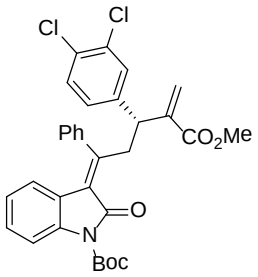


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.064	621920	30785	3.085	3.352
2	7.155	19539102	887532	96.915	96.648
Total		20161022	918317	100.000	100.000



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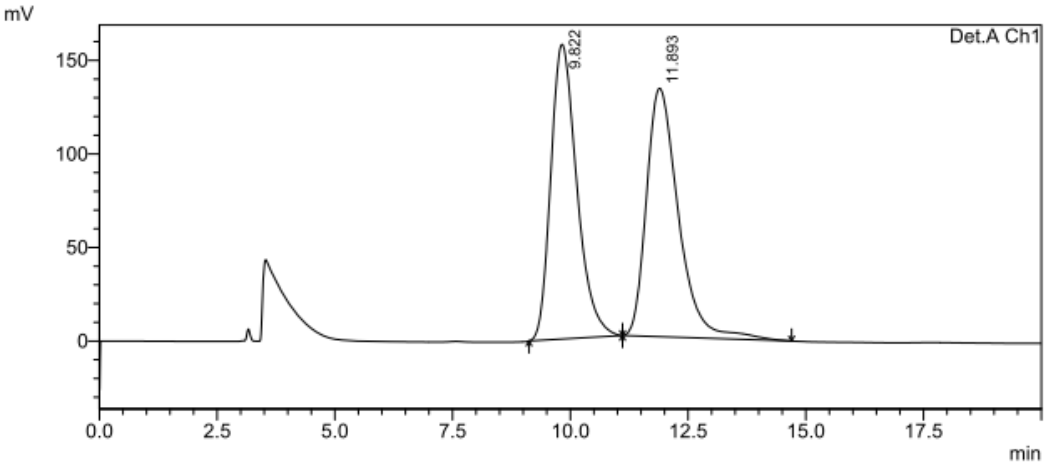
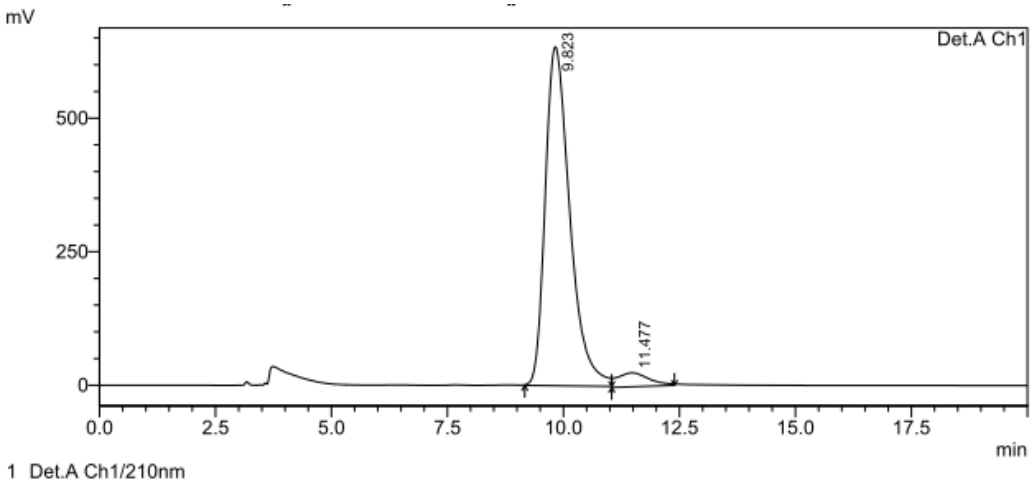


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.822	6066815	157558	49.159	54.263
2	11.893	6274329	132802	50.841	45.737
Total		12341144	290360	100.000	100.000

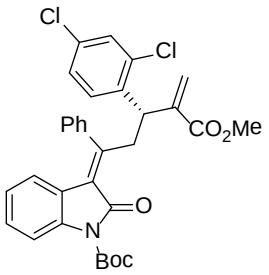


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.823	23385158	634284	94.950	96.038
2	11.477	1243653	26169	5.050	3.962
Total		24628811	660452	100.000	100.000



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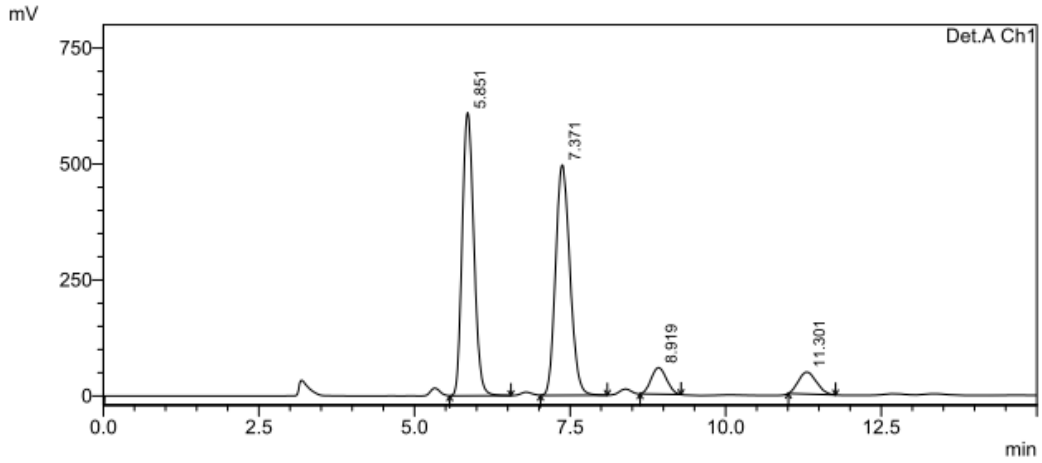
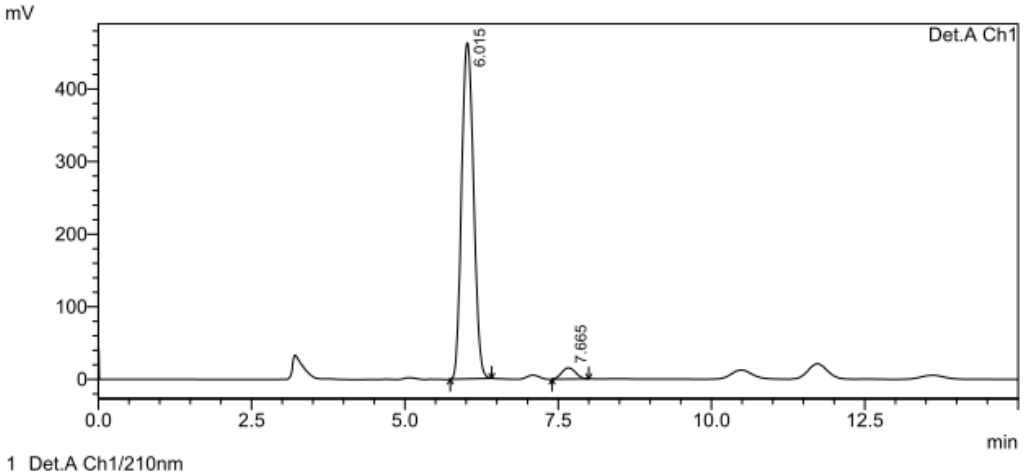


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.851	7951542	609672	44.503	50.352
2	7.371	7982670	496751	44.677	41.026
3	8.919	984299	57179	5.509	4.722
4	11.301	948855	47208	5.311	3.899
Total		17867366	1210809	100.000	100.000

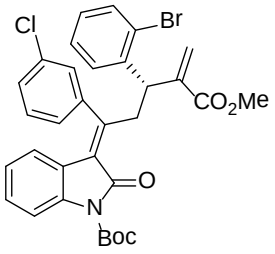


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.015	6267218	463102	96.292	96.771
2	7.665	241310	15455	3.708	3.229
Total		6508528	478557	100.000	100.000



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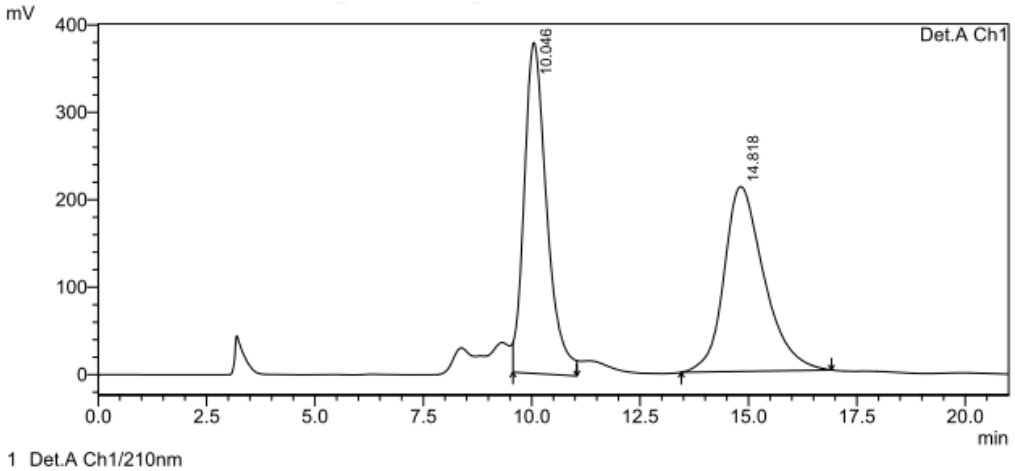
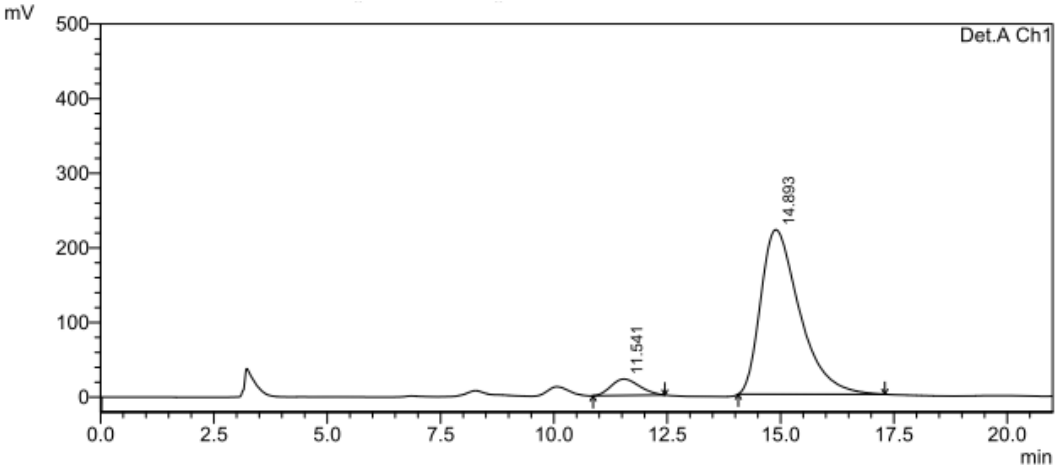


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.046	13678526	378467	50.175	64.141
2	14.818	13582922	211586	49.825	35.859
Total		27261448	590054	100.000	100.000

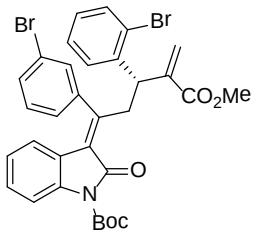


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.541	952011	21966	6.729	9.061
2	14.893	13196155	220465	93.271	90.939
Total		14148166	242432	100.000	100.000



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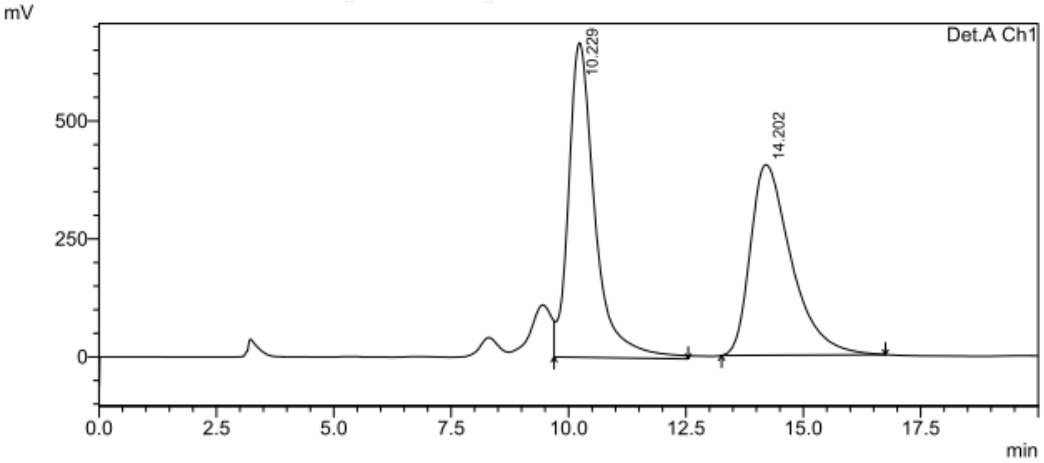
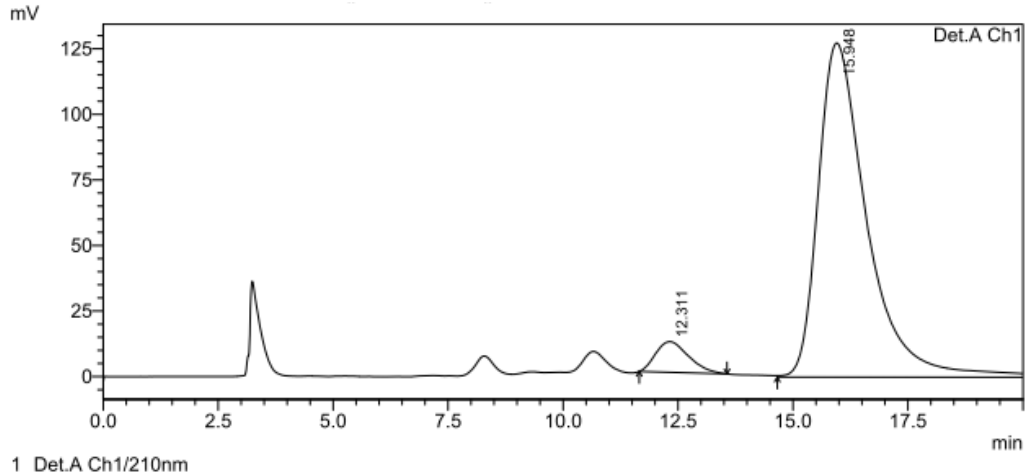


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.229	26119580	666677	51.549	62.243
2	14.202	24549843	404415	48.451	37.757
Total		50669422	1071092	100.000	100.000

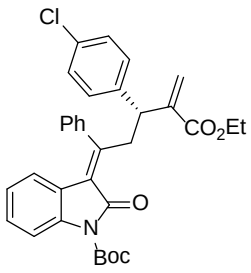


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.311	584173	11705	5.857	8.415
2	15.948	9389861	127392	94.143	91.585
Total		9974034	139097	100.000	100.000



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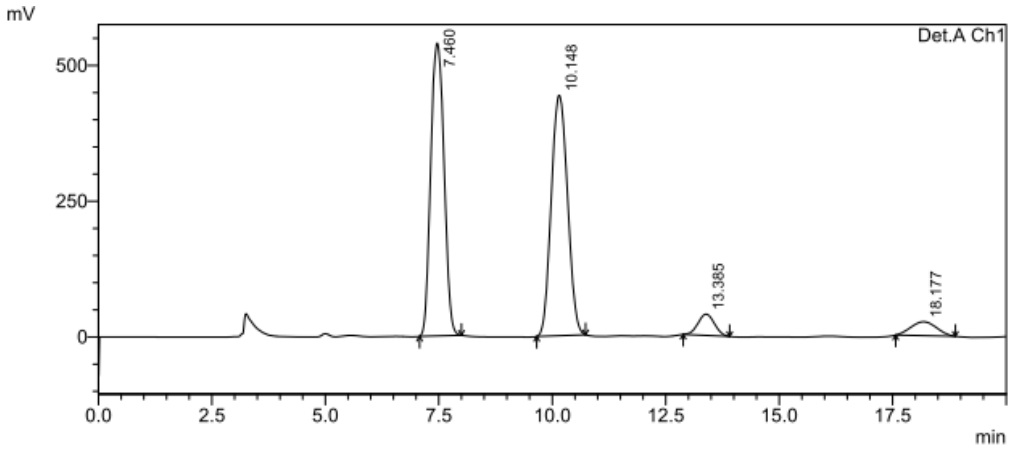
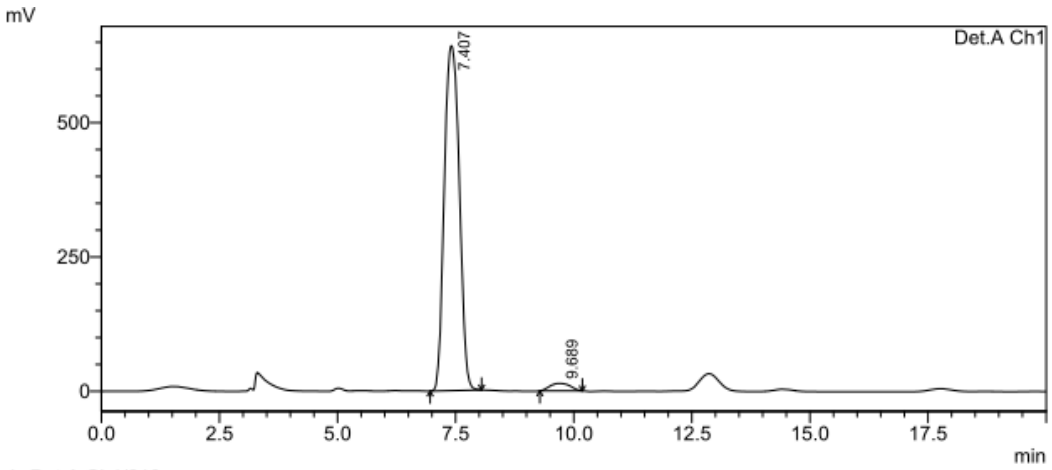


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.460	11024759	539070	45.761	51.500
2	10.148	11067000	442733	45.936	42.297
3	13.385	990225	39299	4.110	3.754
4	18.177	1010045	25626	4.192	2.448
Total		24092028	1046728	100.000	100.000

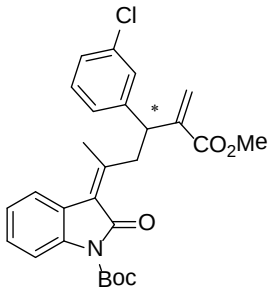


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.407	14208086	642209	97.105	97.874
2	9.689	423513	13951	2.895	2.126
Total		14631599	656160	100.000	100.000



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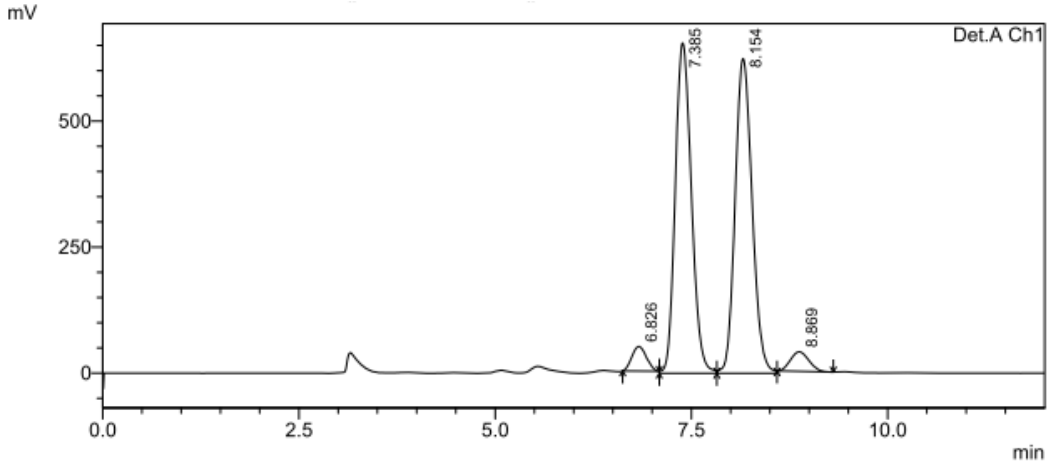
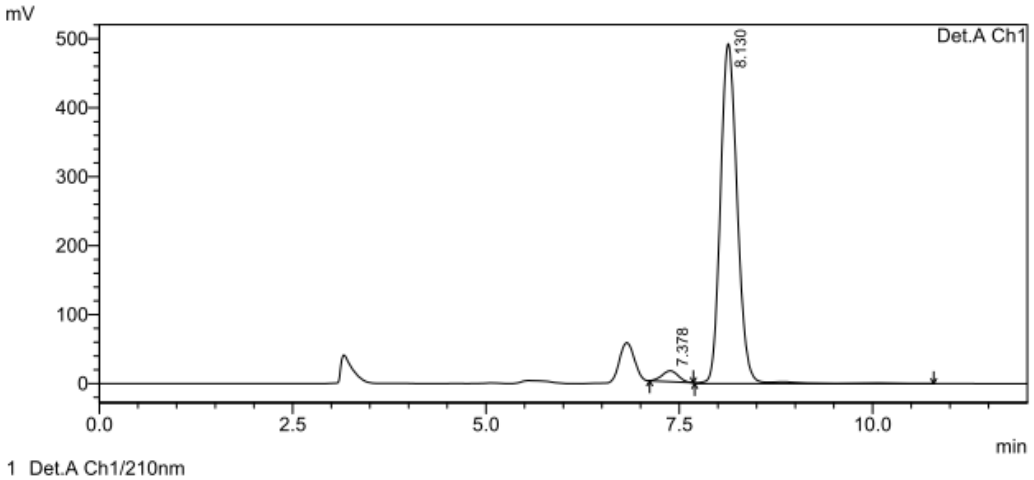


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.826	623038	48511	3.113	3.551
2	7.385	9380798	654988	46.871	47.945
3	8.154	9380089	623966	46.868	45.674
4	8.869	630092	38657	3.148	2.830
Total		20014017	1366121	100.000	100.000

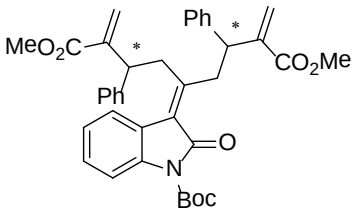


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.378	229158	15775	2.981	3.100
2	8.130	7457421	493100	97.019	96.900
Total		7686579	508875	100.000	100.000



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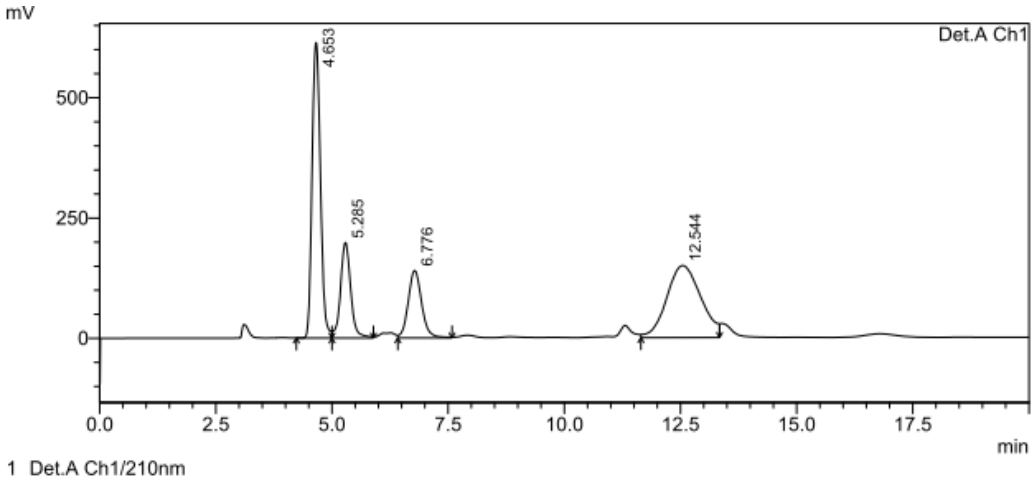
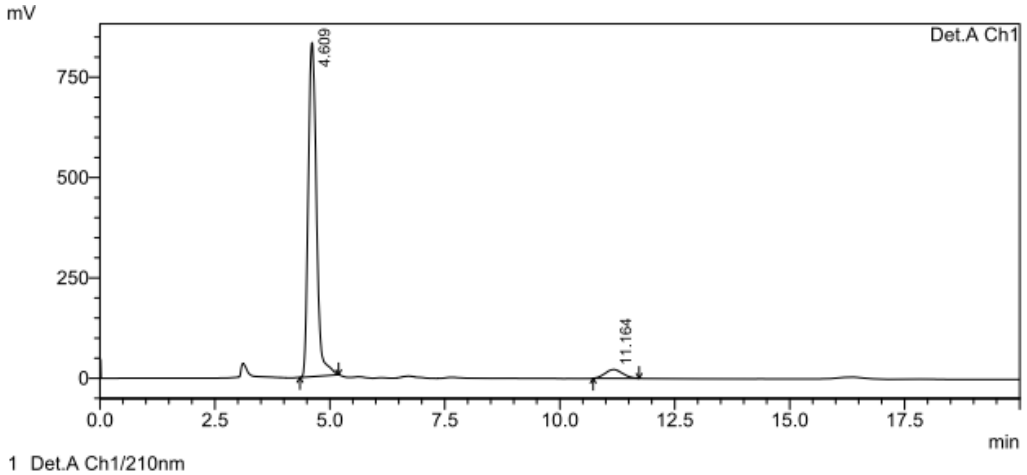


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.653	7688442	614390	36.304	55.721
2	5.285	3034077	198317	14.327	17.986
3	6.776	2816944	140034	13.301	12.700
4	12.544	7638508	149884	36.068	13.593
Total		21177972	1102625	100.000	100.000

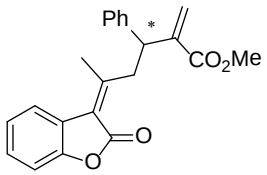


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.609	10362528	832227	94.741	97.438
2	11.164	575211	21885	5.259	2.562
Total		10937738	854112	100.000	100.000



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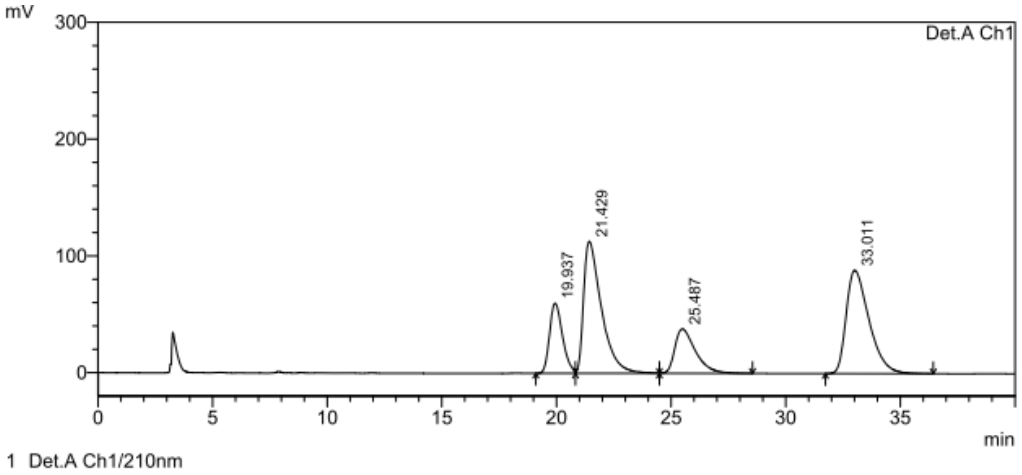
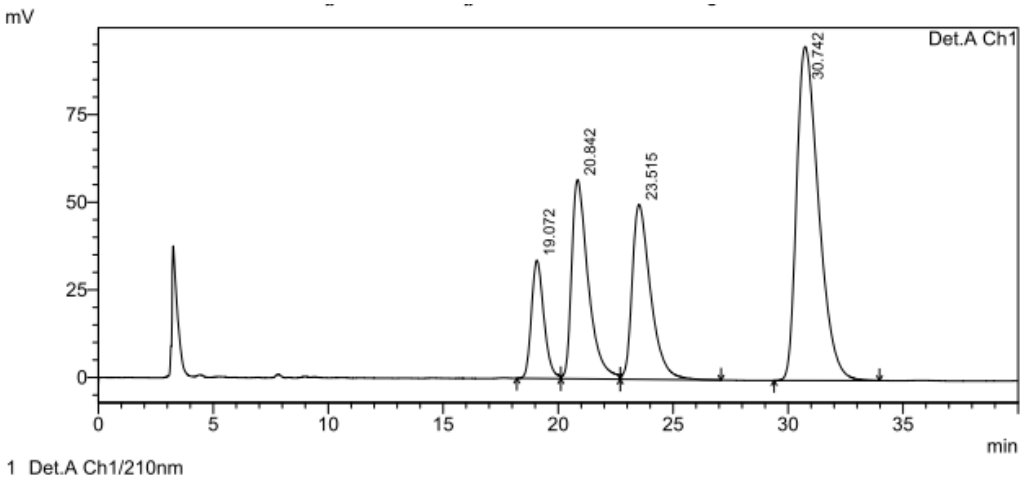


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.937	2361322	60161	13.899	20.074
2	21.429	6118592	113027	36.016	37.713
3	25.487	2384480	38067	14.036	12.702
4	33.011	6124376	88449	36.050	29.512
Total		16988770	299705	100.000	100.000

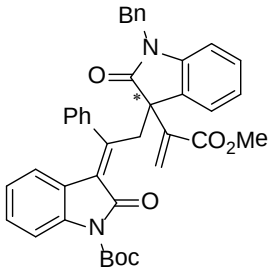


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.072	1267453	33712	9.581	14.303
2	20.842	2838193	56791	21.454	24.095
3	23.515	2783518	49903	21.041	21.172
4	30.742	6339857	95294	47.924	40.430
Total		13229021	235700	100.000	100.000



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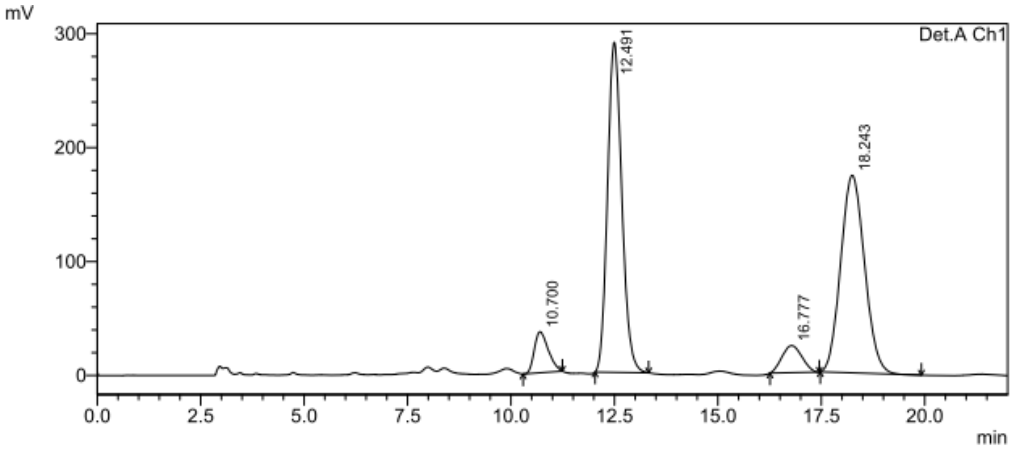
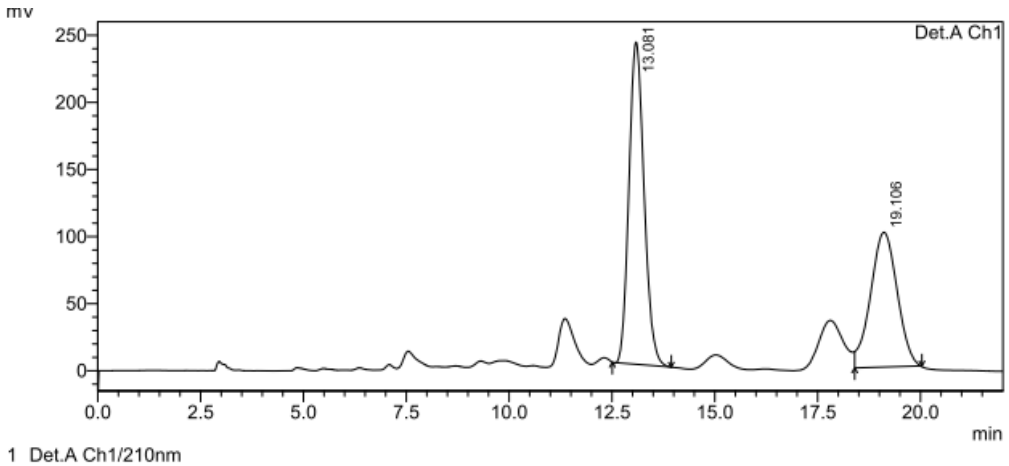


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.700	841683	36049	5.414	6.893
2	12.491	6969400	289753	44.830	55.406
3	16.777	794997	23748	5.114	4.541
4	18.243	6940352	173415	44.643	33.160
Total		15546432	522965	100.000	100.000



1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.081	6141509	240003	57.675	70.500
2	19.106	4506884	100426	42.325	29.500
Total		10648394	340429	100.000	100.000