Organocatalyzed Aza-Michael-Michael Cascade Reactions to Construct Spirooxindole Tetrahydroquinolines with All-carbon Chiral Centers

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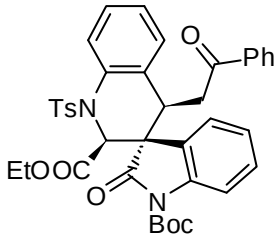
1. General Information

The ^{1}H NMR spectra were recorded on a Bruker NMR Spectrometer (400 MHz). All chemical shifts (δ) were given in ppm. Data were reported as follows: chemical shift, integration, multiplicity (s = single, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet) and coupling constants (Hz). ^{13}C NMR spectra were recorded on a DPX-400 (400 MHz). Flash column chromatography was performed using H silica gel. For thin-layer chromatography (TLC), silica gel plates (HSGF 254) were used and compounds were visualized by irradiation with UV light. Analytical high performance liquid chromatography (HPLC) was carried out on Waters or Shimadzu using chiral columns. Melting points were determined on a SGW X-4 and were uncorrected. Optical rotations were measured on a *J*ASCO P-1010 Polarimeter at λ = 589 nm. IR spectra were recorded on a Perkin-Elmer 983G instrument. Mass spectra analysis was performed on API 200 LC/MS system (Applied Biosystems Co. Ltd.). All bifunctional thiourea catalysts were prepared according to procedures reported previously.[1] All methyleneindolinones were synthesized using reported procedures from corresponding isatins.[2] All ortho- (*p*-methylbenzenesulfonamide)- α, β- unsaturated ketones was prepared following reported procedures.[3] All solvents were used after redistillation according to standard procedures. All reactions were carried out employing oven-dried glassware.

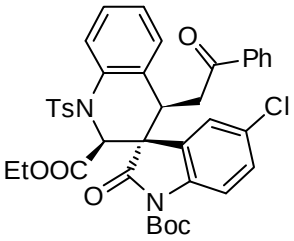
2. General procedure for the enantioselective aza-Michael-Michael reaction

Methyleneindolinone (0.12 mmol, 1.2 equiv) was added to thiourea (0.01 mmol, 0.1 equiv) in toluene (2 mL). After 10 min, ortho-(*p*-methylbenzenesulfonamide)-α,β-unsaturated ketone (0.1 mmol, 1.0 equiv) and 40 mg 4Å MS was added and the resulting solution was stirred at room temperature for 24 h. The crude mixture was purified by flash column chromatography to afford the corresponding product (with hexanes/ethyl acetate = 5/1).

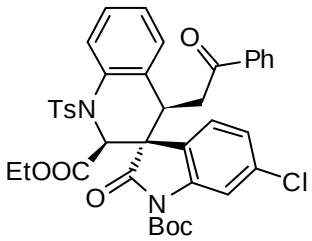
3. Spectral data of the products



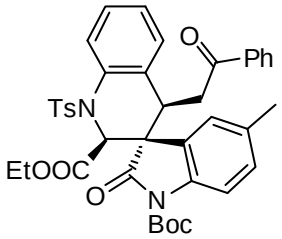
3a, 97% yield, White solid; m.p. = 91-93 °C; $[\alpha]_D^{30}$ = -6.6 (*c* = 1.7 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ = 0.75 (t, *J* = 6.8 Hz, 3H), 1.66 (s, 9H), 2.37(s, 3H), 2.53 (dd, *J* = 2.4 Hz, *J* = 16.0 Hz, 1H), 2.64 (dd, *J* = 10.8 Hz, *J* = 16.0 Hz, 1H), 2.94 (d, *J* = 10.8 Hz, 1H), 3.48-3.53 (m, 1H), 3.69-3.74 (m, 1H), 5.26 (d, *J* = 7.6 Hz, 1H), 5.57 (s, 1H), 6.56 (d, *J* = 7.6 Hz, 2H), 6.70 (t, *J* = 7.6 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H) 7.26-7.28 (m, 2H), 7.34-7.42(m, 3H), 7.54(t, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 7.6 Hz, 2H), 7.80 (*J* = 8.0 Hz, 1H), 8.05(d, *J* = 7.6 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.24, 21.66, 28.07, 34.79, 39.21, 60.07, 61.37, 66.05, 85.31, 111.14, 114.53, 124.32, 124.41, 124.83, 126.27, 126.92, 126.97, 127.91, 128.31, 128.57, 128.64, 129.39, 129.99, 133.21, 133.37, 135.06, 136.02, 136.45, 140.15, 144.42, 148.72, 167.70, 174,92, 195.23 ppm; IR (neat): *v* 2981, 2927, 1791, 1763, 1690, 1599, 1479, 1463, 1360, 1301, 1241, 1168, 1098, 1020, 956, 755, 662 cm^{-1}; MALDI/DHB (m/z): 617.2 (M-Boc+Na^+); MALDI/DHB Calcd. For $C_{39}H_{38}N_2O_8SNa^+$ 717.2241, Found: 717.2250; HPLC-separation conditions: Chiralcel AD, 25 °C, 254 nm, 80 : 20 hexane/*i*-PrOH, 0.7 mL/min; t_{major} = 17.4 min, t_{minor} = 9.5 min; 90 % ee.



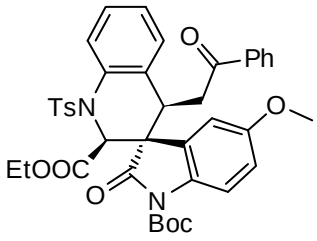
3b, 99% yield, Yellow solid, m.p. = 108-110 °C, $[\alpha]_D^{30}$ = 39.7 (*c* = 0.93 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ = 0.81 (t, *J* = 7.2 Hz, 3H), 1.65 (s, 9H), 2.38(s, 3H), 2.49 (dd, *J* = 2.0 Hz, *J* = 16.8 Hz, 1H), 2.66 (dd, *J* = 10.8 Hz, *J* = 16.8 Hz, 1H), 2.95 (d, *J* = 10.0 Hz, 1H), 3.62-3.66 (m, 1H), 3.77-3.81 (m, 1H), 5.11 (d, *J* = 2.0 Hz, 1H), 5.56 (s, 1H), 6.57 (d, *J* = 8.0 Hz, 2H), 7.15-7.22 (m, 2H), 7.26-7.29 (m, 2H), 7.41 (t, *J* = 7.6 Hz, 2H) 7.48 (t, *J* = 7.6 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 7.6 Hz, 2H), 7.79 (d, *J* = 8.0 Hz, 1H), 8.04 (d, *J* = 7.6 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.33, 21.66, 28.04, 34.62, 39.22, 60.16, 61.61, 66.03, 85.70,111.14, 115.78, 124.65, 126.30, 126.63, 129.96, 127.08, 127.90, 128.60, 128.70, 129.42, 129.77, 130.04, 132.85, 133.49, 134.96, 135.93, 136.31, 138.76, 144.54, 148.56, 167.51, 174.08, 194.92 ppm; IR (neat): *v* 2982, 2928, 1793, 1765, 1738, 1689, 1598, 1471, 1363, 1334, 1298, 1240, 1150, 1103, 1019, 811, 754, 662 cm^{-1}; MALDI/DHB (m/z): 651.1 (M-Boc+Na^+); MALDI/DHB Calcd. For $C_{39}H_{37}N_2O_8SClNa^+$ 751.1851, Found: 751.1856; HPLC-separation conditions: Chiralcel AD, 25 °C, 254 nm, 19 : 1 hexane/*i*-PrOH, 0.6 mL/min; t_{major} = 45.3 min, t_{minor} = 40.8 min; 88 % ee.



3c, 98% yield, Yellow solid, m.p. = 179-181 °C, $[\alpha]_D^{30}$ = 1.58 (*c* = 0.50 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.83 (t, *J* = 7.2 Hz, 3H), 1.66 (s, 9H), 2.38(s, 3H), 2.49 (dd, *J* = 2.0 Hz, *J* = 16.8 Hz, 1H), 2.66 (dd, *J* = 8.8 Hz, *J* = 16.8 Hz, 1H), 2.93 (d, *J* = 10.0 Hz, 1H), 3.58-3.62 (m, 1H), 3.75-3.79 (m, 1H), 5.15 (d, *J* = 8.0 Hz, 1H), 5.55 (s, 1H), 6.54 (d, *J* = 7.6 Hz, 1H), 6.70 (dd, *J* = 2.0 Hz, *J* = 8.0 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.26-7.29 (m, 2H), 7.40-7.47 (m, 3H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.71 (t, *J* = 8.0 Hz, 2H), 7.90 (d, *J* = 1.6 Hz, 1H), 8.04 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.35, 21.66, 28.01, 34.63, 39.14, 59.82, 61.58, 65.99, 85.90, 115.35, 123.24, 124.38, 125.23, 126.20, 126.93, 127.04, 127.90, 128.48, 128.57, 128.70, 130.05, 132.92, 133.51, 134.91, 135.37, 135.89, 136.38, 141. 11, 144.56, 148.47, 136.38, 167.58, 174.35, 194.92 ppm; IR (neat): *v* 2962, 2926, 1765, 1737, 1691, 1601, 1483, 1461, 1367, 1346, 1283, 1241, 1168, 1149, 1103, 1019, 808, 770, 661 cm^{-1}; MALDI/DHB (m/z): 651.1 (M-Boc+Na^+); MALDI/DHB Calcd. For $C_{39}H_{37}N_2O_8SClNa^+$ 751.1851, Found: 751.1856; HPLC-separation conditions: Chiralcel OD, 25 °C, 254 nm, 90 : 10 hexane/*i*-PrOH, 0.7 mL/min; t_{major} = 9.7 min, t_{minor} = 21.9 min; 92 % ee.

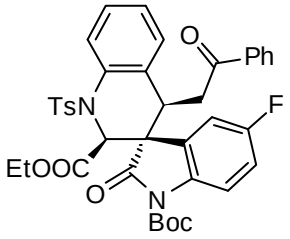


3d, 94% yield, Yellow solid, m.p. = 145-146 °C, $[\alpha]_D^{29}$ = 9.5 (*c* = 1.32 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.75 (t, *J* = 6.8 Hz, 3H), 1.65 (s, 9H), 1.92(s, 3H), 2.37(s, 3H), 2.53 (dd, *J* = 2.4 Hz, *J* = 17.2 Hz, 1H), 2.63 (dd, *J* = 10.0 Hz, *J* = 17.2 Hz 1H), 2.91 (d, *J* = 8.8 Hz, 1H), 3.52-3.57 (m, 1H), 3.70-3.76 (m, 1H), 4.97 (s, 1H), 5.56 (s, 1H), 6.56 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 10.0 Hz, 1H) 7.38-7.47 (m, 3H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.62 (t, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 2H), 8.05(d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.22, 20.90, 21.64, 28.06, 34.79, 39.21, 60.10, 61.33, 60.00, 85.12, 114.28, 124.68, 125.08, 126.37, 126.74, 126.96, 127.90, 128.17, 128.63, 129.75, 129.99, 133.36, 133.38, 133.82, 135.04, 136.01, 136.49, 137.70, 142.02, 144.40, 148.75, 167.67, 172.81, 175.06, 195.32 ppm; IR (neat): *v* 2927, 1764, 1736, 1368, 1339, 1280, 1244, 1219, 1186, 1168, 1102, 772, 675, cm^{-1}; MALDI/DHB (m/z): 631.2 (M-Boc+Na^+); MALDI/DHB Calcd. For $C_{40}H_{40}N_2O_8SNa^+$ 731.2398, Found: 731.2387; HPLC-separation conditions: Chiralcel OD, 25 °C, 254 nm, 90 : 10 hexane/*i*-PrOH, 0.7 mL/min; t_{major} = 10.4 min, t_{minor} = 13.4 min; 94 % ee.

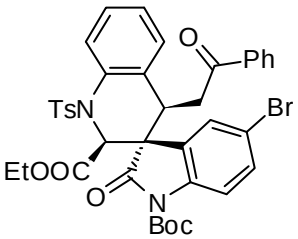


3e, 96% yield, Yellow solid, m.p. = 165-166 °C, $[\alpha]_D^{29}$ = 12.8 (*c* = 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.71 (t, *J* = 7.2 Hz, 3H), 1.57 (s, 9H), 2.29 (s, 3H), 2.46 (dd, *J* = 2.0 Hz, *J* = 16.8 Hz, 1H), 2.59 (dd, *J* = 10.8 Hz, *J* =

16.8 Hz, 1H), 3.22 (s, 3H), 3.48-3.52 (m, 1H), 3.66-3.70 (m, 1H), 4.72 (d, *J* = 2.4 Hz, 1H), 5.48 (s, 1H), 6.52 (d, *J* = 7.2 Hz, 1H), 6.67 (dd, *J* = 2.8 Hz, *J* = 9.2 Hz,1H), 6.07 (t, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 7.30-7.38 (m, 3H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.62-7.65 (m, 3H) 7.98 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.33, 21.67, 28.11, 34.83, 39.30, 55.05, 60.28, 61.42, 66.07, 85.11, 109.36, 115.58, 115.62, 125.84, 126.59, 126.93, 126.01, 127.95, 128.25, 128.70, 130.07, 133.39, 133.44, 133.50, 135.10, 136.07, 136.71, 144.49, 148.82, 156.11, 167.65, 174.93, 195.29 ppm; IR (neat): *v* 2958, 2926, 1789, 1763, 1732, 1691, 1598, 1486, 1456, 1366, 1300, 1250, 1168, 1099, 1021, 812, 756, 662 cm^{-1}; MALDI/DHB (m/z): 647.2 (M-Boc+Na$^+$); MALDI/DHB Calcd. For $C_{40}H_{40}N_2O_9SNa^+$ 747.2347 Found: 747.2353; HPLC-separation conditions: Chiralcel AD, 25 °C, 254 nm, 90 : 10 hexane/*i*-PrOH, 0.7 mL/min; t_{major} = 29.7 min, t_{minor} = 23.2 min; 88 % ee.

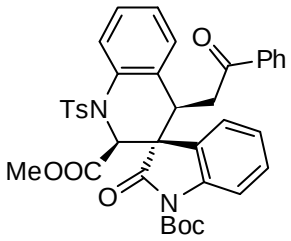


3f, 79% yield, Yellow solid, m.p. = 105-108 °C, $[\alpha]_D^{30}$ = -9.9 (*c* = 0.93 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.81 (t, *J* = 7.2 Hz, 3H), 1.65 (s, 9H), 2.38(s, 3H), 2.50 (dd, *J* = 2.0 Hz, *J* = 16.8 Hz, 1H), 2.66 (dd, *J* = 11.2 Hz, *J* = 16.8 Hz, 1H), 2.95 (d, *J* = 10.0 Hz, 1H), 3.59-3.64 (m, 1H), 3.74-3.80 (m, 1H), 4.43 (dd, *J* = 2.8 Hz, *J* = 8.0 Hz, 1H), 5.57 (s, 1H), 6.57 (d, *J* = 8.0 Hz, 1H), 6.93 (dt, *J* = 2.4 Hz, *J* = 8.8 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 8.8 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 2H), 7.47 (t, *J* = 8.0 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.83 (dd, *J* = 4.4 Hz, *J* = 8.4 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.30, 21.66, 28.04, 34.66, 39.15, 60.22, 65.97, 85.57, 112.01, 115.83, 115.91, 116.12, 126.29, 126.71, 126.94, 127.14, 127.89, 128.60, 128.64, 128.70, 133.49, 134.90, 135.92, 136.20, 136.27, 144.56, 148.66, 157.80, 174.41, 194.96 ppm; IR (neat): *v* 2959, 2925, 1792, 1764, 1737, 1670, 1598, 1484, 1449, 1365, 1299, 1248,, 1149, 1096, 1019, 770, 662 cm^{-1}; MALDI/DHB (m/z): 635.2 (M-Boc+Na$^+$); MALDI/DHB Calcd. For $C_{39}H_{37}N_2O_8SFNa^+$ 735.2147, Found: 735.2148; HPLC-separation conditions: Chiralcel AD, 25 °C, 254 nm, 90 : 10 hexane/*i*-PrOH, 0.7 mL/min; t_{major} = 27.5 min, t_{minor} = 14.6 min; 90 % ee.

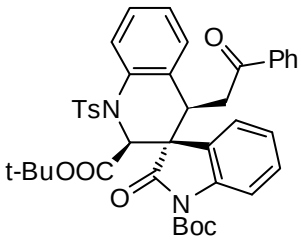


3g, 99% yield, Yellow solid, m.p. = 132-135 °C, $[\alpha]_D^{30}$ = 43.0 (*c* = 2.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.81 (t, *J* = 7.2 Hz, 3H), 1.72 (s, 9H), 2.48 (s, 3H), 2.50 (dd, *J* = 2.0 Hz, *J* = 17.2 Hz, 1H), 2.66 (dd, *J* = 11.2 Hz, *J* = 17.2 Hz, 1H), 2.95 (d, *J* = 10.0 Hz, 1H), 3.63-3.67 (m, 1H), 3.76-3.81 (m, 1H), 5.24 (d, *J* = 2.0 Hz, 1H), 5.56 (s, 1H), 6.58 (d, *J* = 7.6 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 7.6 Hz, 1H), 7.35-7.43 (m, 3H), 7.49 (t, *J* = 8.0 Hz, 1H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.70-7.75

(m, 3H), 8.04 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.68, 28.06, 34.63, 39.30, 60.19, 61.10, 85.74, 116.20, 117.35, 126.37, 127.00, 127.08, 127.55, 127.95, 128.62, 128.74, 130.07, 132.38, 132.93, 133.52, 135.05, 135.99, 136.38, 139.32, 144.56, 144.56, 148.58, 167.56, 173.97, 194.96 ppm; IR (neat): *v* 2982, 2928, 1794, 1764, 1736, 1690, 1598, 1469, 1364, 1332, 1297, 1186, 1168, 1101, 1019, 956, 810, 755, 662 cm^{-1}; MALDI/DHB (m/z): 695.1 (M-Boc+Na+); MALDI/DHB Calcd. For $C_{39}H_{37}N_2O_8SBrNa$+ 795.1346, Found: 795.1353; HPLC-separation conditions: Chiralcel AD, 25 °C, 254 nm, 19 : 1, hexane/*i*-PrOH, 0.7 mL/min; t_{major} = 45.4 min, t_{minor} = 49.7 min; 88 % ee.

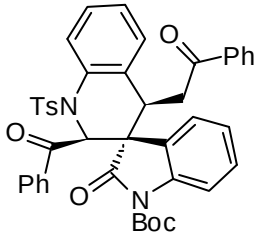


3h, 99% yield, Yellow solid, m.p. = 85-90 °C, $[\alpha]_D^{30}$ = -0.88 (*c* = 2.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.66 (s, 9H), 2.37(s, 3H), 2.53 (dd, *J* = 2.4 Hz, *J* = 16.8 Hz, 1H), 2.66 (dd, *J* = 10.8 Hz, *J* = 16.8 Hz, 1H), 2.94 (d, *J* = 9.6 Hz, 1H), 3.45 (s, 3H), 5.26 (dd, *J* = 7.2 Hz, 1H), 5.59 (s, 1H), 6.58 (d, *J* = 8.0 Hz, 1H), 6.71 (t, *J* = 7.6 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.21-7.28 (m, 3H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 7.2 Hz, 2H), 7.80 (d, *J* = 8.4 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.66, 28.06, 34.84, 39.07, 52.02, 60.16, 66.35, 85.35, 114.61, 124.22, 124.29, 124.76, 126.29, 126.96, 127.90, 128.32, 128.51, 128.66, 129.42, 130.02, 133.16, 133.40, 134.94, 135.98, 136.39, 140.03, 144.49, 148.68, 168.36, 174.85, 195.24 ppm; IR (neat): *v* 3027, 2953, 2927, 1790, 1765, 1738, 1690, 1479, 1463, 1360, 1301, 1241, 1168, 1150, 1196, 1002, 755, 662 cm^{-1}; MALDI/DHB (m/z): 603.2 (M-Boc+Na^+); MALDI/DHB Calcd. For $C_{38}H_{36}N_2O_8SNa^+$ 703.2085, Found: 703.2070; HPLC-separation conditions: Chiralcel AD, 25 °C, 254 nm, 90 : 10 hexane/*i*-PrOH, 0.7 mL/min; t_{major} = 16.7 min, t_{minor} = 13.9 min; 92 % ee.

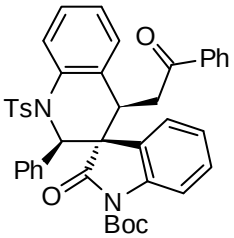


3i, 90% yield, Yellow solid, m.p. = 170-173 °C, $[\alpha]_D^{30}$ = -12.7 (*c* = 2.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.95 (s, 9H), 1.65 (s, 9H), 2.36(s, 3H), 2.53 (dd, *J* = 2.8 Hz, *J* = 17.6 Hz, 1H), 2.63 (dd, *J* = 10.8 Hz, *J* = 17.6 Hz, 1H), 2.93 (d, *J* = 8.4 Hz, 1H), 5.27 (d, *J* = 7.6 Hz, 1H), 5.50 (s, 1H), 6.54 (d, *J* = 7.6 Hz, 1H), 6.71 (t, *J* = 7.6 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.22-7.27 (m, 3H) 7.38-7.45 (m, 3H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 7.6 Hz, 2H), 7.86 (d, *J* = 8.0 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.63, 27.02, 28.05, 34.66, 39.42, 59.91, 66.03, 82.52, 85.29, 114.54, 124.41, 124.61, 125.23, 126.26, 126.82, 126.92, 127.91, 128.30, 128.48, 128.64, 128.68, 129.33, 129.93, 133.28, 133.37, 135.26, 136.01, 136.49, 140.25, 144.28, 148.81, 166.38, 175.01, 196.29 ppm; IR (neat): *v* 2979, 1791, 1759, 1737, 1690, 1599, 1479, 1463, 1360, 1302, 1286, 1243, 1153, 1097, 754, 660

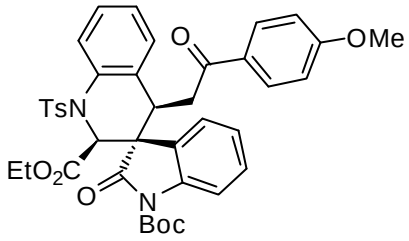
cm^{-1}; MALDI/DHB (m/z): 645.2 (M-Boc+Na^+); MALDI/DHB Calcd. For $C_{41}H_{42}N_2O_8SNa^+$ 745.2554, Found: 745.2543; HPLC-separation conditions: Chiralcel AD, 25 °C, 254 nm, 90 : 10 hexane/*i*-PrOH, 0.7 mL/min; t_{major} = 10.1 min, t_{minor} = 8.1 min; 90 % ee.



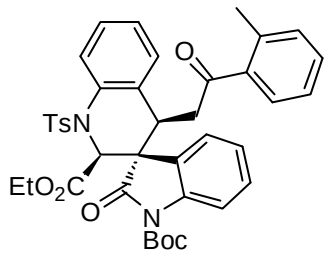
3j, 97% yield, Yellow solid, m.p. = 118-120 °C, $[\alpha]_D^{29}$ = -4.3 (*c* = 2.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.57 (s, 9H), 2.38-2.41 (m, 4H), 2.59 (dd, *J* = 11.2 Hz, *J* = 17.2 Hz, 1H), 2.61 (d, *J* = 10.0Hz, 1H), 5.28 (d, *J* = 8.0 Hz, 1H), 6.51 (s, 1H), 6.57 (d, *J* = 8.0 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 7.08 (t, *J* = 8.0 Hz, 1H), 7.12-7.21 (m, 5H), 7.30 (d, *J* = 8.0 Hz, 3H), 7.36 (t, *J* = 7.6 Hz, 3H), 7.50 (q, *J* = 7.6 Hz, 2H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 2H), 8.17 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.69, 28.06, 34.79, 39.73, 60.41, 68.99, 85.13, 114.12, 124.19, 125.65, 126.12, 126.83, 127.08, 127.72, 127.96, 128.26, 128.39, 128.66, 128.99, 129.23, 130.05, 132.72, 133.30, 133.36, 135.80, 136.08, 137.14, 139.45, 144.32, 147.81, 175.64, 195.25, 195.92 ppm; IR (neat): *v* 2925, 2854, 1788, 1753, 1708, 1691, 1598, 1479, 1448, 1356, 1238, 1166, 1149, 1093, 970, 754, 694, 664 cm^{-1}; MALDI/DHB (m/z): 649.2 (M-Boc+Na^+); MALDI/DHB Calcd. For $C_{43}H_{38}N_2O_7SNa^+$ 749.2292, Found: 749.2301; HPLC-separation conditions: Chiralcel AD, 25 °C, 254 nm, 90 : 10 hexane/*i*-PrOH, 0.7 mL/min; t_{major} = 12.1 min, t_{minor} = 17.2 min; 90 % ee.



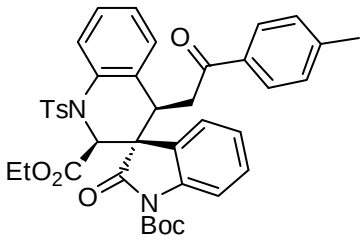
3k, 74% yield, Yellow solid, m.p. = 96-98 °C, $[\alpha]_D^{30}$ = -20.2 (*c* = 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.57 (s, 9H), 2.32(s, 3H), 2.46 (dd, *J* = 2.0 Hz, *J* = 16.8 Hz, 1H), 2.58 (dd, *J* = 10.8 Hz, *J* = 16.8 Hz, 1H), 2.99 (d, *J* = 9.6 Hz, 1H), 5.05 (d, *J* = 7.6 Hz, 1H), 5.92 (s, 1H), 6.47 (t, *J* = 7.6 Hz, 1H), 6.58 (d, *J* = 8.0 Hz, 1H), 6.88-6.94 (m, 4H), 6.98 (d, *J* = 7.2 Hz, 2H), 7.11 (t, *J* = 7.2 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.32 (t, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.41-7.48 (m, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 7.2 Hz, 2H), 8.03 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.70, 28.11, 35.99, 63.06, 69.05, 85.09, 114.13, 123.75, 125.11, 125.25, 126.05, 126.05, 126.82, 126.86, 127.23, 127.27, 127.80, 128.01, 128.25, 128.64, 129.94, 133.30, 134.41, 134.47, 136.18, 138.02, 139.35, 139.42, 144.49, 148.52, 175.98, 195.62 ppm; IR (neat): *v* 2959, 2926, 1787, 1753, 1690, 1599, 1479, 1455, 1360, 1303, 1254, 1150, 1084, 1069, 1019, 809, 754, 659 cm^{-1}; MALDI/DHB (m/z): 621.2 (M-Boc+Na^+); MALDI/DHB Calcd. For $C_{42}H_{38}N_2O_8SNa^+$, Found: 721.2343; HPLC-separation conditions: Chiralcel AD, 25 °C, 254 nm, 90 : 10 hexane/*i*-PrOH, 0.7 mL/min; t_{major} = 8.7 min, t_{minor} = 10.3 min; 86 % ee.



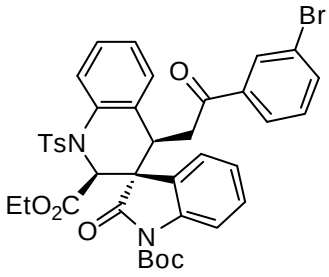
3l, 99% yield, Yellow solid, m.p. = 100-102 °C, $[\alpha]_D^{30}$ = 8.5 (*c* = 0.94 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.67 (t, *J* = 6.8 Hz, 3H), 1.59 (s, 9H), 2.28 (s, 3H), 2.41 (dd, *J* = 2.0 Hz, *J* = 16.8 Hz, 1H), 2.51 (dd, *J* = 10.4 Hz, *J* = 16.8 Hz, 1H), 2.85 (d, *J* = 9.2 Hz, 1H), 3.40-3.45 (m, 1H), 3.61-3.66 (m, 1H), 3.77 (s, 3H), 5.18 (d, *J* = 7.6 Hz, 1H), 5.50 (s, 1H), 6.53 (d, *J* = 7.6 Hz, 1H), 6.63 (t, *J* = 7.6 Hz, 1H), 6.79 (d, *J* = 8.8 Hz, 2H), 7.05 (t, *J* = 7.6 Hz, 1H), 7.13-7.19 (m, 3H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.27, 21.63, 28.10, 34.52, 39.39, 55.50, 60.16, 61.38, 66.10, 85.30, 113.80, 114.53, 124.34, 124.45, 124.94, 126.44, 126.97, 127.01, 128.29, 128.50, 129.13, 129.38, 130.00, 130.28, 133.41, 135.14, 136.47, 140.20, 144.43, 148.77, 163.68, 167.76, 175.00, 193.79 ppm; IR (neat): *v* 2927, 1762, 1681, 1601, 1480, 1463, 1348, 1241, 1220, 1168, 1098, 772, 662cm^{-1}; MALDI/DHB (m/z): 647.2 (M-Boc+Na^+); MALDI/DHB Calcd. For $C_{40}H_{40}N_2O_9SNa^+$ 747.2347, Found: 747.2332; HPLC-separation conditions: Chiralcel OD, 25 °C, 254 nm, 80 : 20 hexane/*i*-PrOH, 0.7 mL/min; t_{major} = 9.8 min, t_{minor} = 13.8 min; 93 % ee.



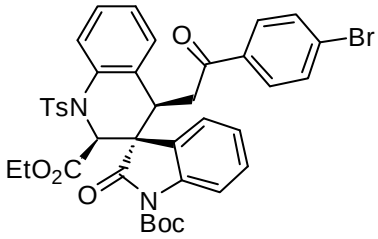
3m, 96% yield, Yellow solid, m.p. = 112-115 °C, $[\alpha]_D^{30}$ = -14.4 (*c* = 2.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.66 (t, *J* = 6.8 Hz, 3H), 1.59 (s, 9H), 2.25 (s, 3H), 2.31 (s, 3H), 2.36-2.53 (m, 2H), 2.80 (d, *J* = 9.6 Hz, 1H), 3.40-3.44 (m, 1H), 3.60-3.65 (m, 1H), 5.16 (d, *J* = 7.2 Hz, 1H), 5.49 (s, 1H), 6.47 (d, *J* = 7.6 Hz, 1H), 6.61 (t, *J* = 7.6 Hz, 1H), 7.05-7.09 (m, 4H), 7.13 (d, *J* =6.8 Hz, 2H), 7.19-7.29 (m, 5H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.26, 21.16, 21.68, 28.11, 37.22, 39.63, 60.06, 61.37, 66.10, 85.34, 114.55, 124.30, 124.94, 125.74, 126.18, 126.93, 127.02, 128.21, 128.32, 128.70, 129.38, 130.09, 131.72, 132.21, 133.55, 135.09, 136.63, 136.80, 138.52, 144.38, 148.68, 167.73, 174.97, 198.48 ppm; IR (neat): *v* 3024, 2961, 2927, 1790, 1750, 1738, 1690, 1602, 1479, 1463, 1360, 1300, 1241, 1168, 1097, 1020, 956, 811, 757, 662 cm^{-1}; MALDI/DHB (m/z): 631.2 (M-Boc+Na^+); MALDI/DHB Calcd. For $C_{40}H_{40}N_2O_8SNa^+$ 731.2398, Found: 731.2399; HPLC-separation conditions: Chiralcel AD, 25 oC, 254 nm, 90 : 10 hexane/i-PrOH, 0.7 mL/min; tmajor = 37.4 min, tminor = 14.9 min; 88 % ee.



3n, 99% yield, Yellow solid, m.p. = 93-96 °C, $[\alpha]_D^{29}$ = 0.54 (*c* = 1.32 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.67 (t, *J* = 6.8 Hz, 3H), 1.58 (s, 9H), 2.29 (s, 3H), 2.30 (s, 3H), 2.42 (dd, *J* = 2.4 Hz, *J* = 17.2 Hz, 1H), 2.55 (dd, *J* = 11.2 Hz, *J* = 17.2 Hz, 1H), 3.40-3.46 (m, 1H), 3.59-3.65 (m, 1H), 5.18 (d, *J* = 7.6 Hz, 1H), 5.50 (s, 1H), 6.49 (d, *J* = 7.6 Hz, 1H), 6.62 (t, *J* = 7.6 Hz, 1H),7.04 (t, *J* =7.6 Hz, 1H), 7.10-7.20 (m, 5H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 4H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.28, 21.66, 28.11, 34.67, 39.28, 60.12, 61.39, 66.10, 85.31, 114.56, 124.34, 124.45, 124.94, 126.38, 126.96, 127.02, 128.07, 128.29, 128.55, 129.35, 129.41, 130.03, 133.37, 133.65, 135.12, 136.49, 140.21, 144.26, 144..46, 148.77, 167.76, 174.97, 194.85 ppm; IR (neat): *ν* 2956, 2925, 1793, 1763, 1736, 1686, 1606, 1479, 1463, 1360, 1301, 1285, 1168, 1151, 1097, 772, 661 cm^{-1}; MALDI/DHB (m/z): 631.2 (M-Boc+Na^+); MALDI/DHB Calcd. For $C_{40}H_{40}N_2O_8SNa^+$ 731.2398, Found: 731.2386; HPLC-separation conditions: Chiralcel OD, 25 °C, 254 nm, 80 : 20 hexane/*i*-PrOH, 0.7 mL/min; t_{major} = 7.4 min, t_{minor} = 9.9 min; 92 % ee.

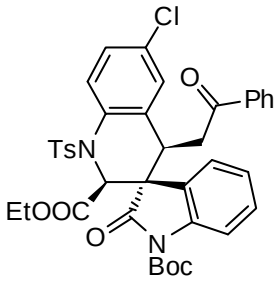


3o, 75% yield, Yellow solid, m.p. = 116-119 °C, $[\alpha]_D^{30}$ = 0.52 (*c* = 0.89 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.75 (t, *J* = 7.2 Hz, 3H), 1.67 (s, 9H), 2.37 (s, 3H), 2.47-2.63 (m, 2H), 2.92 (d, *J* = 8.4 Hz, 1H), 3.48-3.52 (m, 1H), 3.70-3.74 (m, 1H), 5.25 (d, *J* = 7.6 Hz, 1H), 5.56 (s, 1H), 6.54 (d, *J* = 7.2 Hz, 1H), 6.71 (t, *J* = 7.6 Hz, 1H), 7.13-7.31 (m, 5H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.80-7.83 (m, 2H), 8.06 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.27, 21.67, 28.12, 34.97, 39.28, 60.11, 61.43, 66.12, 85.42, 114.62, 123.10, 124.40, 124.49, 124.69, 126.14, 126.56, 127.01, 128.47, 128.68, 128.76, 129.13, 129.65, 130.00, 130.27, 130.99, 132.96, 135.20, 136.29, 136.57, 137.76, 140.23, 144.41, 148.72, 167.65, 174.89, 194.04 ppm; IR (neat): *ν* 2956, 2925, 2853, 1790, 1762, 1694, 1488, 1463, 1359, 1285, 1241, 1187, 1169, 1150, 1098, 759, 661 cm^{-1}; IR (neat): ν 2956, 2924, 2953, 1792, 1762, 1734, 1698, 1458, 1362, 1301, 1285, 1241, 1168, 1150, 1096, 763 cm^{-1}; MALDI/DHB (m/z): 695.1 (M-Boc+Na^+); MALDI/DHB Calcd. For $C_{39}H_{37}N_2O_8SBrNa^+$ 795.1346, Found: 795.1345; HPLC-separation conditions: Chiralcel AD, 25 °C, 254 nm, 80 : 20 hexane/*i*-PrOH, 0.7 mL/min; t_{major} = 10.8 min, t_{minor} = 14.1 min; 89 % ee.

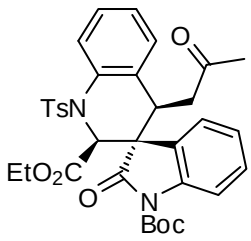


3p, 73% yield, Yellow solid, m.p. = 102-105 °C, $[\alpha]_D^{30}$ = 8.1 (*c* = 1.00 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.75 (t, 3H), 1.66 (s, 9H), 2.36 (s, 3H), 2.51-2.58 (m, 2H), 2.92 (d, *J* = 8.4 Hz, 1H), 3.51-3.52 (m, 1H),

3.69-3.71 (m, 1H), 5.25 (d, *J* = 7.2 Hz, 1H), 5.56 (s, 1H), 6.56 (d, *J* = 7.6 Hz, 1H), 6.73 (t, *J* = 8.0 Hz, 1H), 7.14-7.24 (m, 4H), 7.45 (t, *J* = 7.2 Hz, 3H), 7.55-7.61 (m, 6H), 7.80 (d, *J* = 8.0 Hz, 1H), 8.05 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.26, 21,63, 28.11, 34.91, 39,35, 60.16, 61.41, 66.12, 85.38, 114.53, 124.37, 124.50, 124.75, 126.19, 126.91, 127.03, 128.44, 128.62, 128.64, 129.46, 129.53, 129.95, 132.01, 133.01, 134.75, 135.28, 136.59, 140.25, 144.39, 148.73, 167.65, 174.90, 194.44 ppm; IR (neat): *v* 2954, 2922, 2853, 1763, 1736, 1686, 1561, 1478, 1466, 1459, 1364, 1301, 1284, 1241, 1275, 1150, 1097, 1072, 772, 660 cm^{-1}; MALDI/DHB (m/z): 695.1 (M-Boc+Na$^+$); MALDI/DHB Calcd. For $C_{39}H_{37}N_2O_8SBrNa^+$ 795.1346, Found: 795.1346; HPLC-separation conditions: Chiralcel OD, 25 °C, 254 nm, 80 : 20 hexane/*i*-PrOH, 0.7 mL/min; t_{major} = 7.4 min, t_{minor} = 9.9 min; 92 % ee.

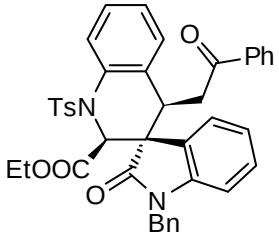


3q, 72% yield, Yellow solid, m.p. = 125-127 °C, $[\alpha]_D^{30}$ = 30.0 (*c* = 1.00 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.57 (s, 9H), 2.38-2.41 (m, 4H), 2.59 (dd, *J* = 11.2 Hz, *J* = 17.2 Hz, 1H), 3.13 (d, *J* = 10.0 Hz, 1H), 2.28 (d, *J* = 8.0 Hz, 1H), 6.51 (s, 1H), 6.57 (d, *J* = 8.0 Hz, 1H), 6.71 (t, *J* = 8.0 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 7.12-7.21 (m, 5H), 7.30 (d, *J* = 8.0 Hz, 3H), 7.50 (q, *J* = 7.6 Hz, 2H), 7.65 (d, *J* = 7.6 Hz, 2H), 7.74 (d, *J* = 7.6 Hz, 2H), 8.17 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.26, 21.67, 28.10, 34.70, 39.20, 59.91, 61.52, 66.01, 85.47, 114.75, 124.27, 124.57, 126.61, 127.02, 127.95, 128.50, 128.74, 129.65, 129.68, 130.18, 132.74, 133.53, 134.95, 135.31, 135.94, 140.21, 144.71, 148.66, 167.52, 194.87 ppm; IR (neat): *v* 2926, 2854, 1791, 1764, 1738, 1690, 1598, 1479, 1465, 1367, 1285, 1243, 1169, 1150, 1093, 1020, 760, 665 cm^{-1}; MALDI/DHB (m/z): 651.1 (M-Boc+Na$^+$); MALDI/DHB Calcd. For $C_{39}H_{37}N_2O_8SClNa^+$ 751.1851, Found: 751.1851; HPLC-separation conditions: Chiralcel OD, 25 °C, 254 nm, 19 : 1 hexane/*i*-PrOH, 0.7 mL/min; t_{major} = 12.8 min, t_{minor} = 16.6 min; 90 % ee.

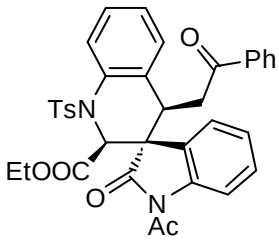


3r, 95% yield, Yellow solid, m.p. = 74-75 °C, $[\alpha]_D^{30}$ = -30.7 (*c* = 1.00 in $CHCl_3$);^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.73 (t, *J* = 7.2 Hz, 3H), 1.68 (s, 9H), 1.81 (s, 3H), 2.01-2.04 (m, 2H), 2.39 (s, 3H), 2.65 (t, *J* = 6.8 Hz, 1H), 3.46-3.52 (m, 1H), 3.66-3.74 (m, 1H), 5.19 (d, *J* = 7.6 Hz, 1H), 5.53 (s, 1H), 6.54 (d, *J* = 7.6 Hz, 1H), 6.67 (t, *J* = 7.6 Hz, 1H), 7.19 (q, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 7.6 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 1H), 8.04 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ =

13.32, 21.55, 28.11, 28.95, 60.03, 61.40, 65.99, 85.45, 114.54, 124.28, 124.32, 124.56, 125.93, 127.10, 127.14, 128.59, 128.85, 129.42, 130.01, 133.00, 136.48, 140.17, 144.38, 148.57, 167.58, 174.99 ppm; IR (neat): *v* 2977, 2927, 1762, 1738, 1368, 1301, 1285, 1241, 1169, 1151, 1097, 1048, 661 cm^{-1}; ESI-MS (m/z): 655.2 ($M+Na^+$); HRMS Calcd. For $C_{34}H_{36}N_2O_8SNa^+$ 655.2066, Found: 655.2058; HPLC-separation conditions: Chiralcel AD-H, 25 °C, 254 nm, 9 : 1 hexane/*i*-PrOH, 0.7 mL/min; t_{major} = 22.0 min, t_{minor} = 15.9 min; 74 % ee.



3s, 90% yield, Yellow solid, m.p. = 113-116 °C, $[\alpha]_D^{30}$ = -3.6 (*c* = 2.0 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ = 0.43 (t, *J* = 6.8 Hz, 3H), 2.23(s, 3H), 2.53 (dd, *J* = 2.4 Hz, *J* = 16.0 Hz, 1H), 2.64 (dd, *J* = 10.8 Hz, *J* = 16.0 Hz 1H), 2.94 (d, *J* = 10.8 Hz, 1H), 3.48-3.53 (m, 1H), 3.69-3.74 (m, 1H), 5.26 (d, *J* = 7.6 Hz, 1H), 5.57 (s, 1H), 6.56 (d, *J* = 7.6 Hz, 2H), 6.70 (t, *J* = 7.6 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H) 7.26-7.28 (m, 2H), 7.34-7.42(m, 3H), 7.54(t, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 7.6 Hz, 2H), 7.80 (*J* = 8.0 Hz, 1H), 8.05(d, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.25, 21.70, 34.64, 38.60, 44.46, 59.58, 61.22, 65.43, 108.89, 122.65, 124.98, 125.91, 126.09, 126.84, 127.02, 127.33, 128.08, 128.15, 128.57, 128.62, 128.74, 128.95, 129.19, 129.75, 130.01, 133.34, 133.93, 135.42, 135.72, 136.09, 136.53, 143.35, 144.39, 168.11, 176.01, 195.47 ppm; IR (neat): *v* 3028, 2958, 2854, 1758, 1716, 1691, 1610, 1486, 1357, 1239, 1187, 1167, 1099, 1018, 754, 662 cm^{-1}; MALDI/DHB (m/z): 707.2 ($M+Na^+$); MALDI/DHB Calcd. For $C_{41}H_{36}N_2O_6SNa^+$ 707.2186, Found: 707.2179; HPLC-separation conditions: Chiralcel OD, 25 °C, 254 nm, 80 : 20 hexane/*i*-PrOH, 0.7 mL/min; t_{major} = 20.4 min, t_{minor} = 17.5 min; 82 % ee.



3t, 78% yield, Yellow solid, m.p. = 206-210 °C, $[\alpha]_D^{30}$ = -0.96 (*c* = 1.00 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ = 0.71 (t, *J* = 7.2 Hz, 3H), 2.42 (s, 3H), 2.71 (s, 3H), 2.99 (d, *J* = 10.8 Hz, 1H), 3.53-3.58 (m, 1H), 3.68-3.72 (m, 1H), 5.29 (d, *J* = 8.0 Hz, 1H), 5.55 (s, 1H), 6.54 (d, *J* = 7.6 Hz, 1H), 6.75 (t, *J* = 7.6 Hz, 1H), 7.13-7.27 (m, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 8.0 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 7.6 Hz, 2H), 8.06 (d, *J* = 7.6 Hz, 1H), 8.21 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.30, 21.71, 26.79, 34.75, 39.25, 60.19, 61.59, 66.26, 116.11, 124.24, 125.03, 125.07, 126.22, 127.02, 129.93, 128.50, 128.55, 128.69, 128.78, 129.64, 129.76, 130.04, 133.03, 133.59, 135.09, 135.91, 136.52, 140.55, 144.64, 167.70, 170.65, 177.30, 194.99 ppm; MALDI/DHB (m/z): 659.2 ($M+Na^+$); MALDI/DHB Calcd. For $C_{36}H_{32}N_2O_7SNa^+$ 659.1823, Found:

659.1828; HPLC-separation conditions: Chiralcel AD, 25 ^{o}C, 254 nm, 90 : 10 hexane/*i*-PrOH, 1.0 mL/min; t_{major} = 19.7 min, t_{minor} = 16.6 min; 58 % ee.

4. References:

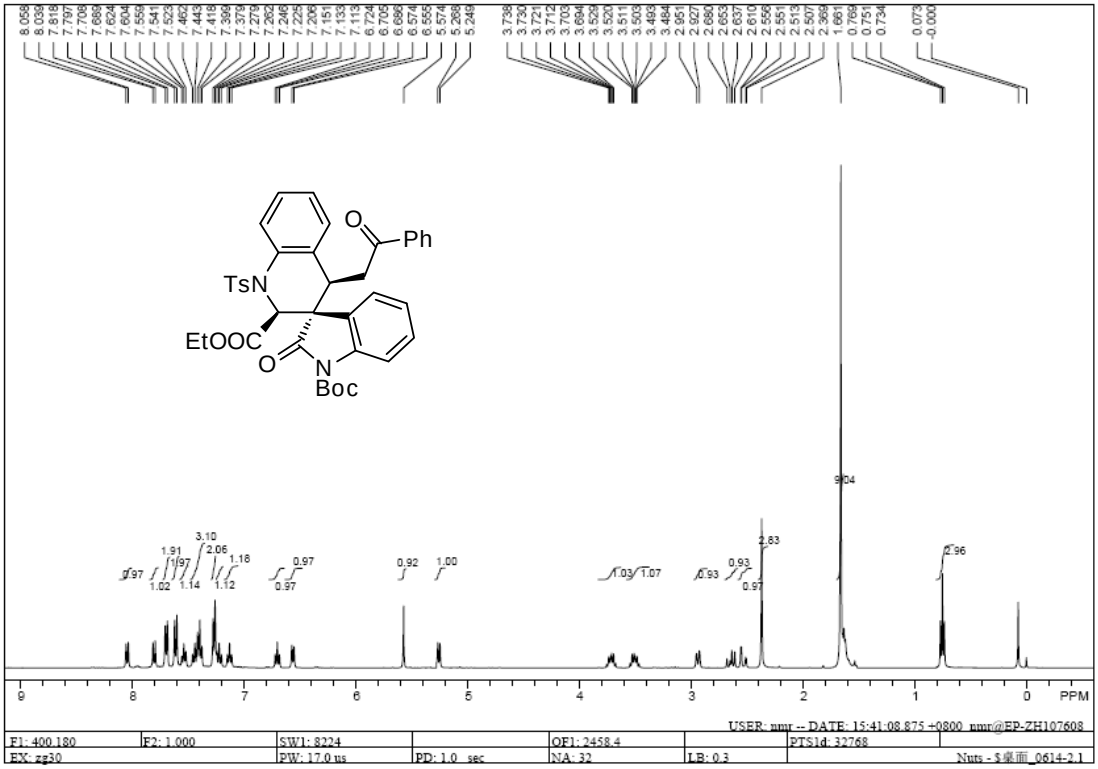
[1] (a) P. Li, Z. chai, S.-L. Zhao, Y.-Q. Yang, H.-F. Wang, C.-W. Zheng, Y.-P. Cai, G. Zhao; S.-Z. Zhu, *Chem Commun*. 2009, **47**, 7369-7371. (b) J. M. Andres, R. Manzano, R. Pedrosa, *Chem. Eur. J*. 2008, **14**, 5116-5119. (c) Y. -J. Gao, Q. Ren, L. Wang, J. Wang, Chem. Eur. J. 2010, 16, 13068-13071. (d) V. Benedek, V. Szilard, C. Antal, S. Tibor, *Org. Lett*. 2005, **7**, 1967-1969.

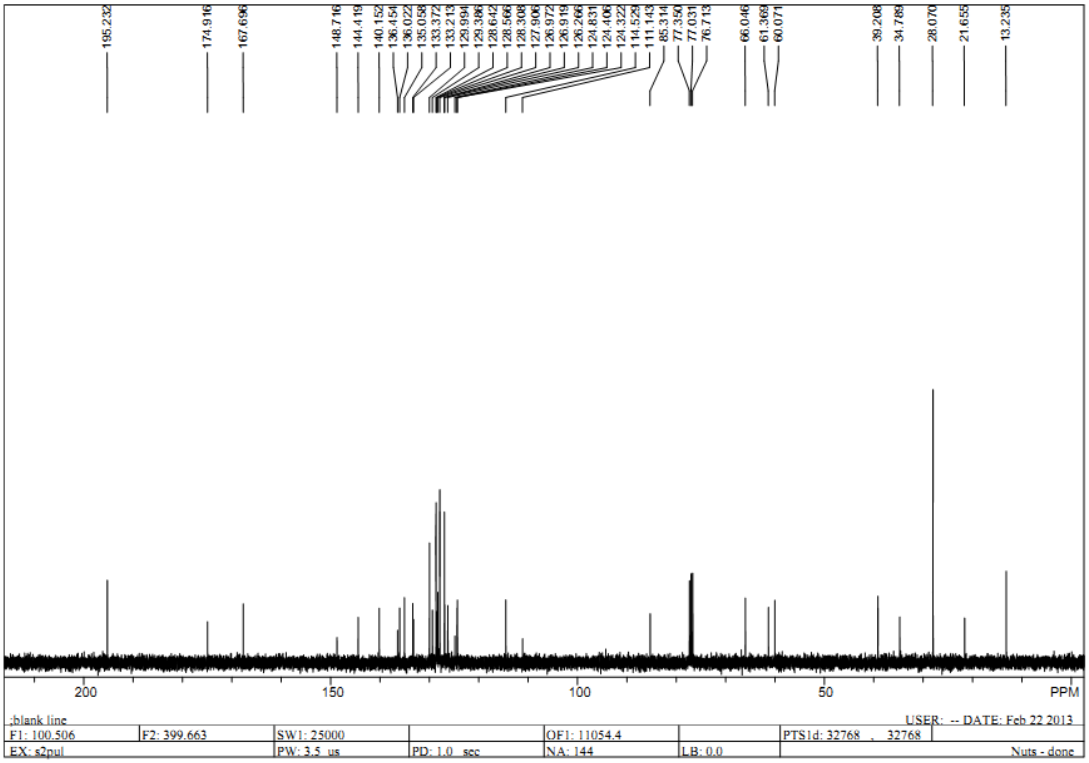
[2] (a) S.-H. Cao, X.-C. Zhang, W. Yin, M. Shi, *Eur. J. Org. Chem*. 2011, **14**, 2668-2672; (b) Y.-M. Cao, X.-X. Jiang, L.-P. Liu, F.-F Shen, F. Zhang, R. Wang, *Angew. Chem, Int. Ed.* 2011, **50**, 9124-9127. (c) K. S. Halskov, T. K. Johansen, R. L. Davis, M. Steurer, F. Jensen, K. A. Jorgensen, *J. Am. Chem. Soc*. 2012, **134**, 12943-12946. (d) G. Wang, X.-H Liu, T.-Y Huang, Y.-L. Kuang, L.-L Lin, X.-M. Feng, *Org. Lett.* 2013, **15**, 76-79.

[3] (a) Z.-X. Jia, Y.-C. Luo, P.-F. Xu, *Org. Lett.* 2011, **13**, 832-835. (b) Y.-T. Lee, Y.-J. Jang, S.-E. Syu, S.-C. Chou, C.-J. Lee, W.-W. Lin, *Chem. Commun.* 2012, **48**, 8135–8137.

5. Copies of NMR spectra and HPLC traces

3a





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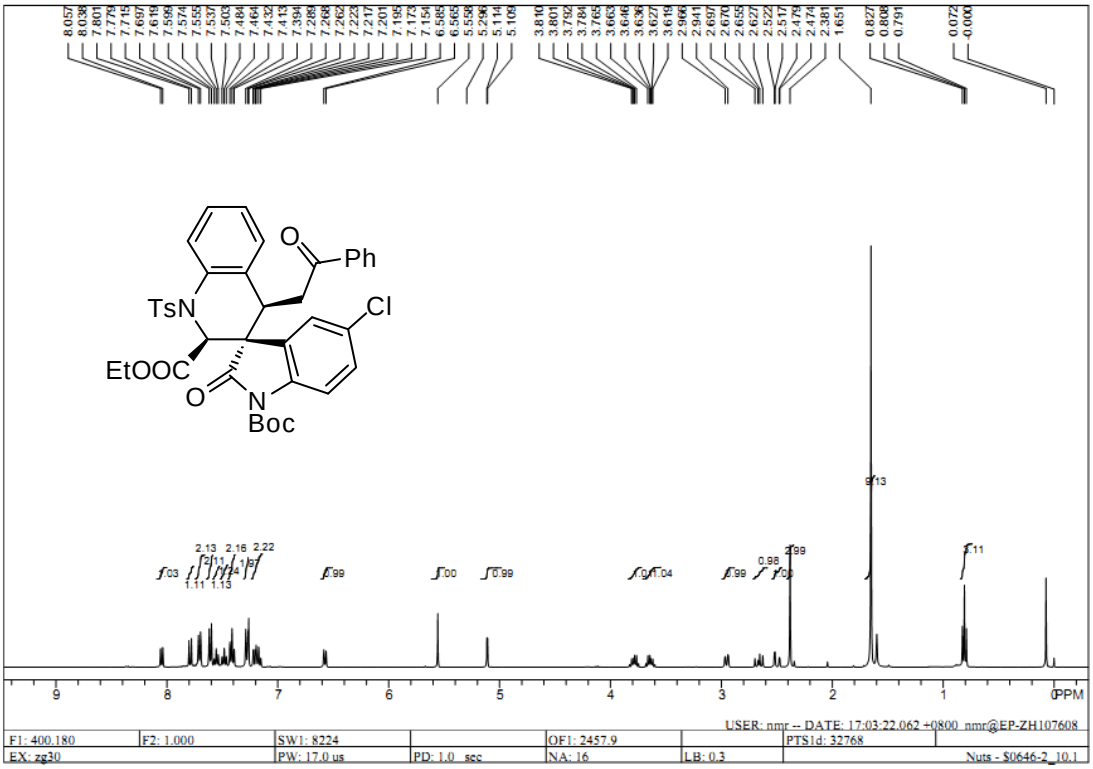
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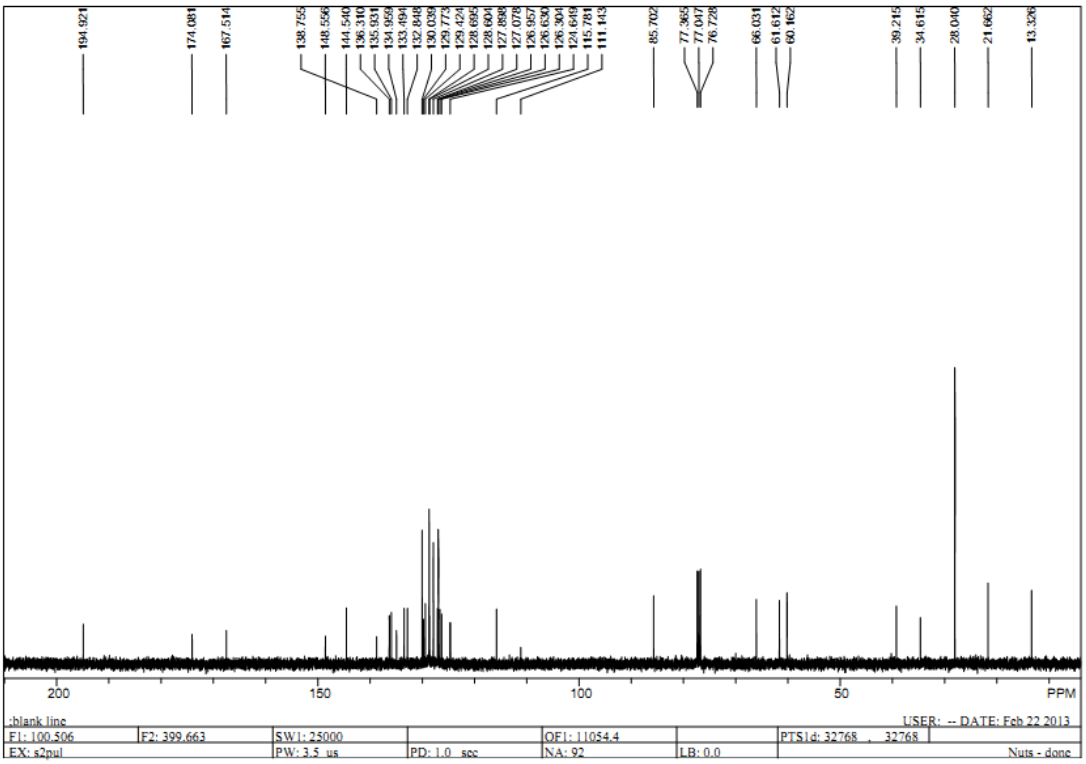
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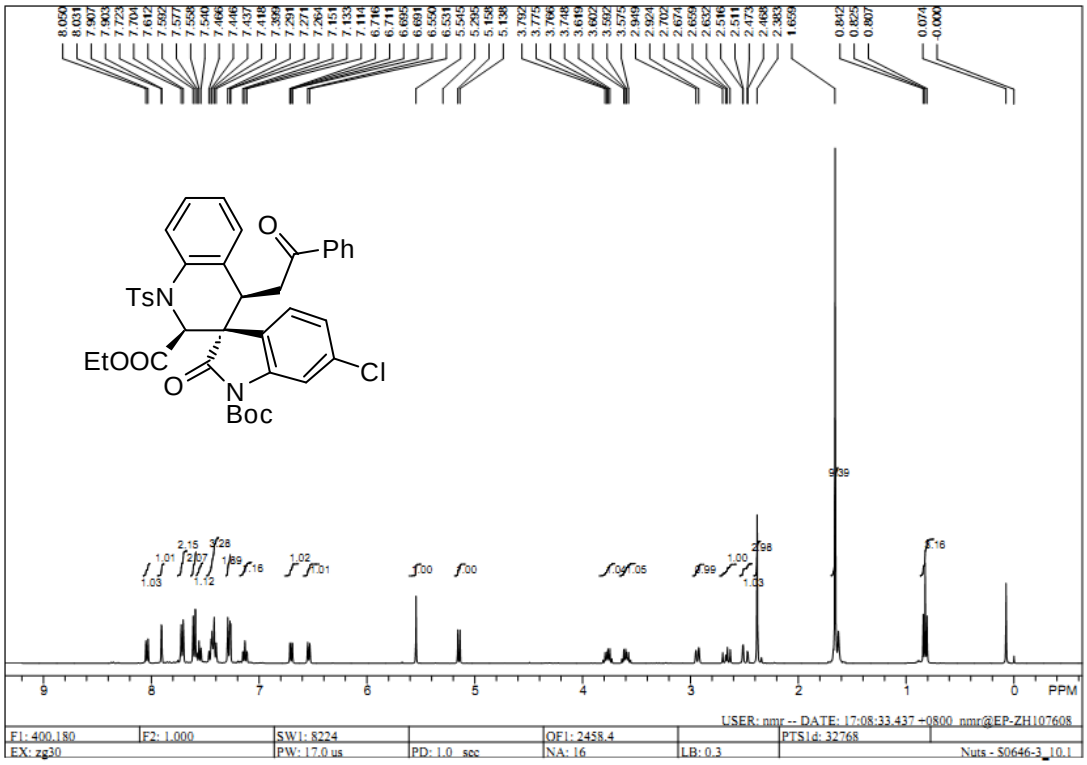
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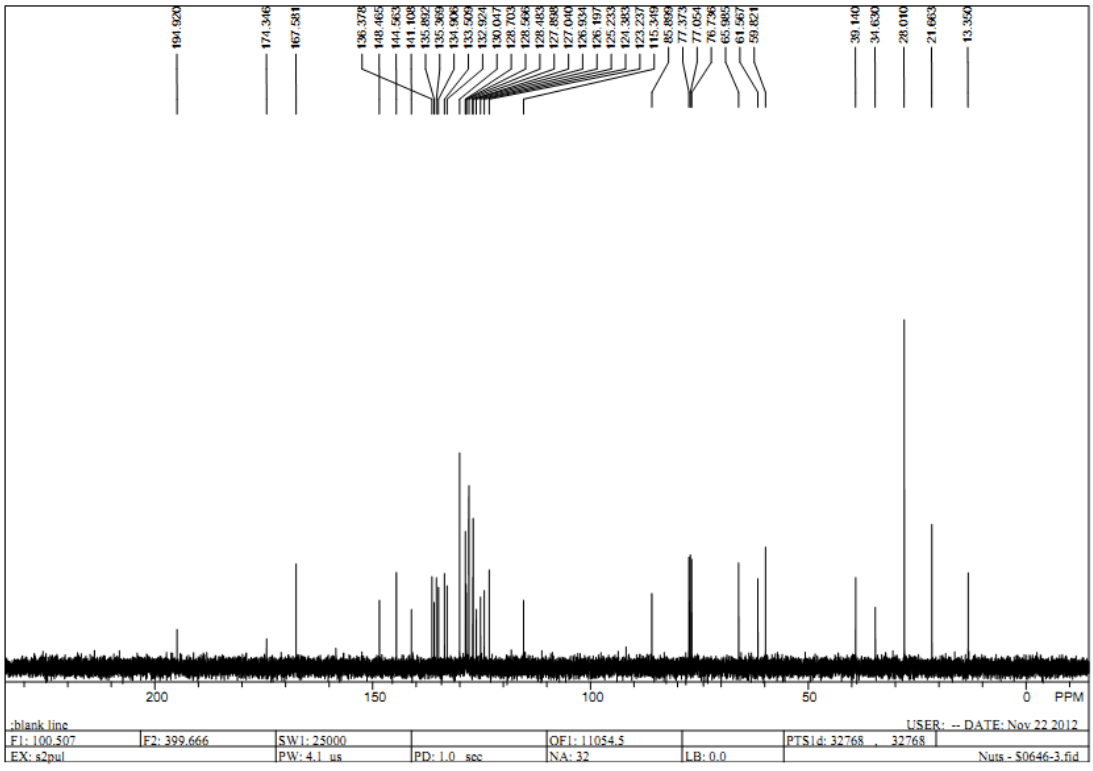
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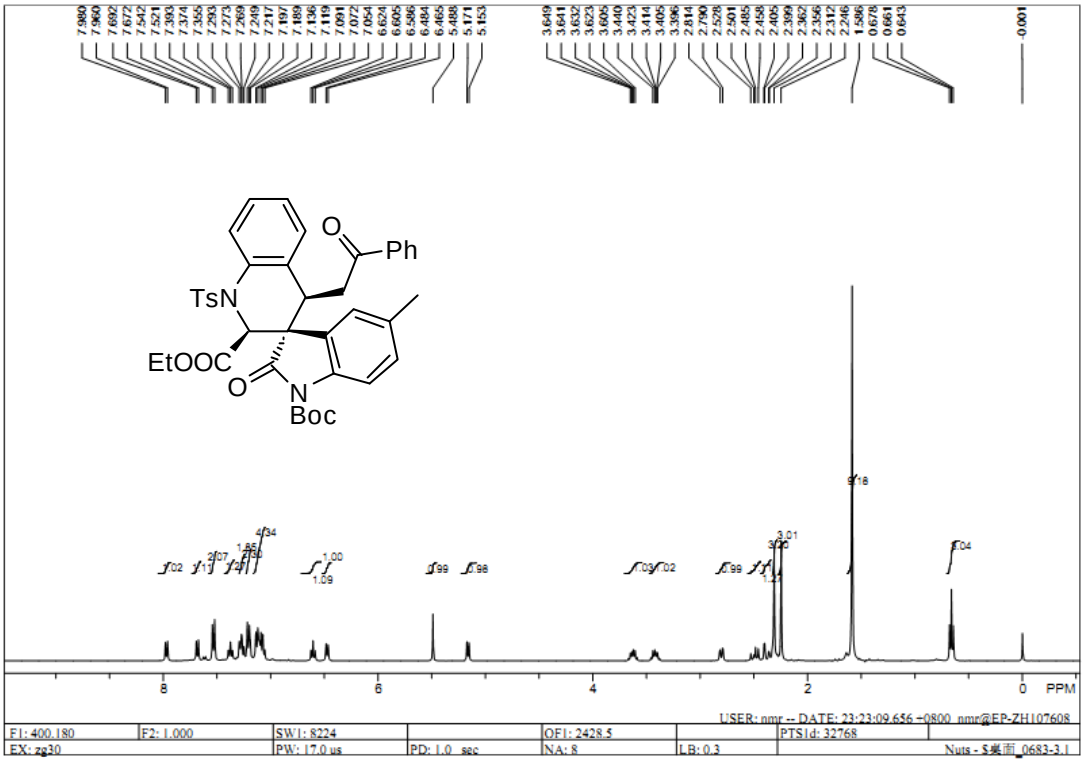
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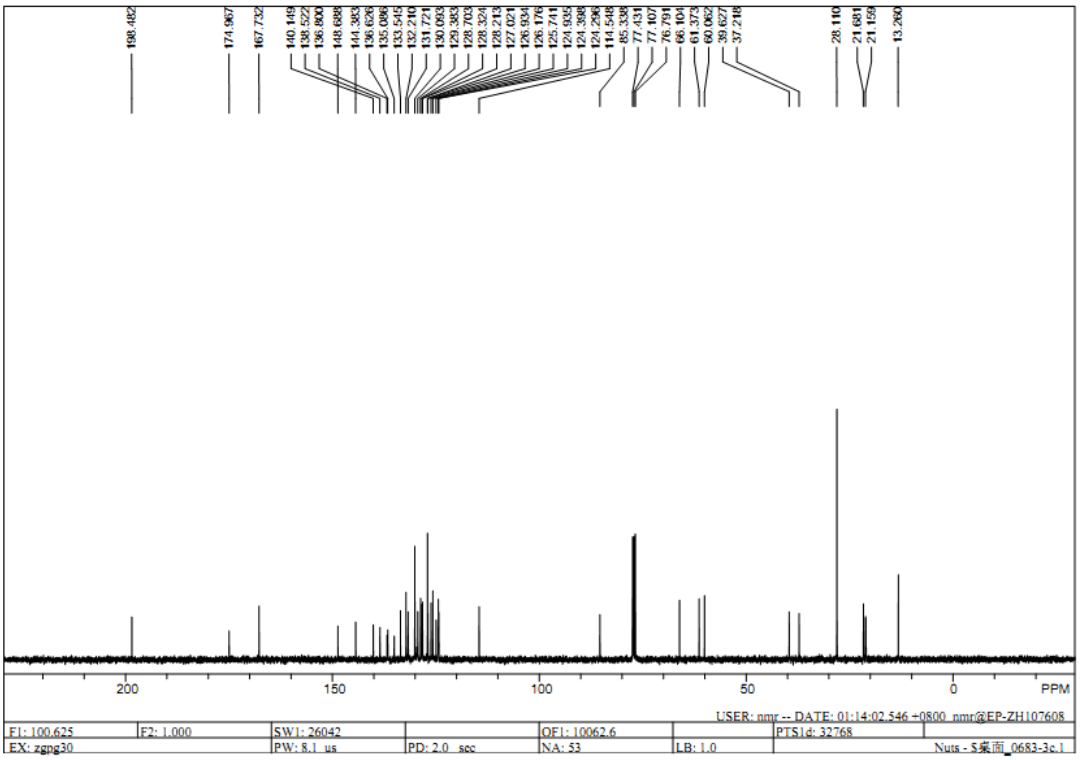
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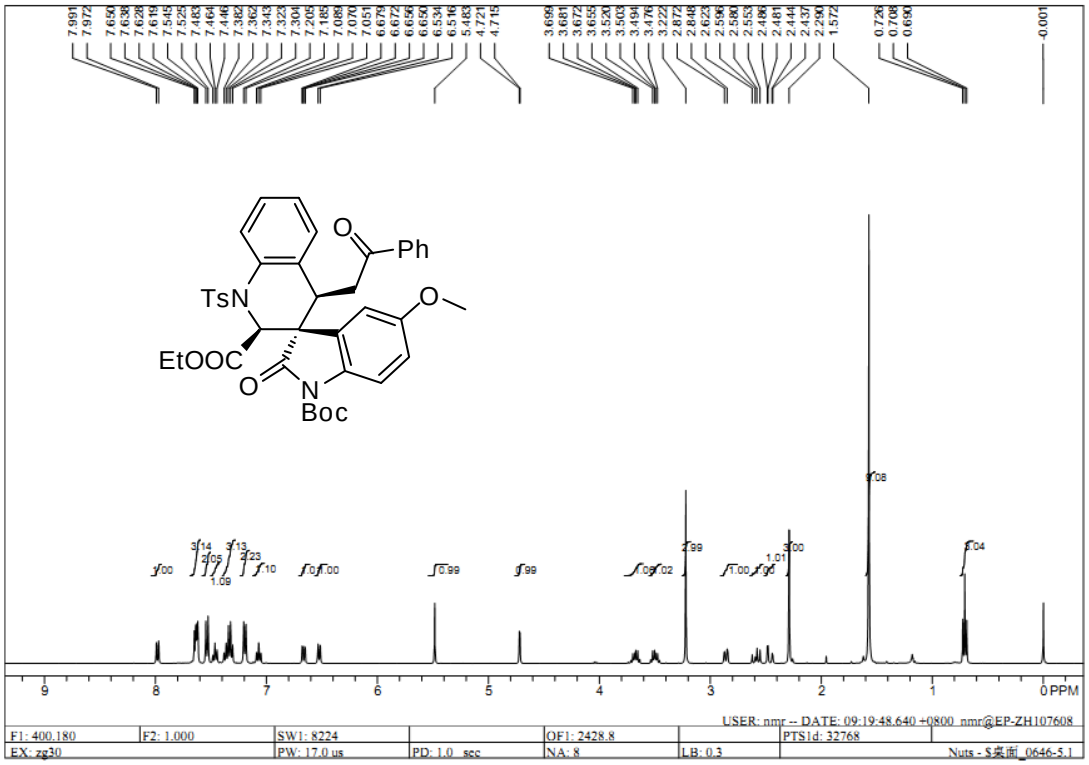
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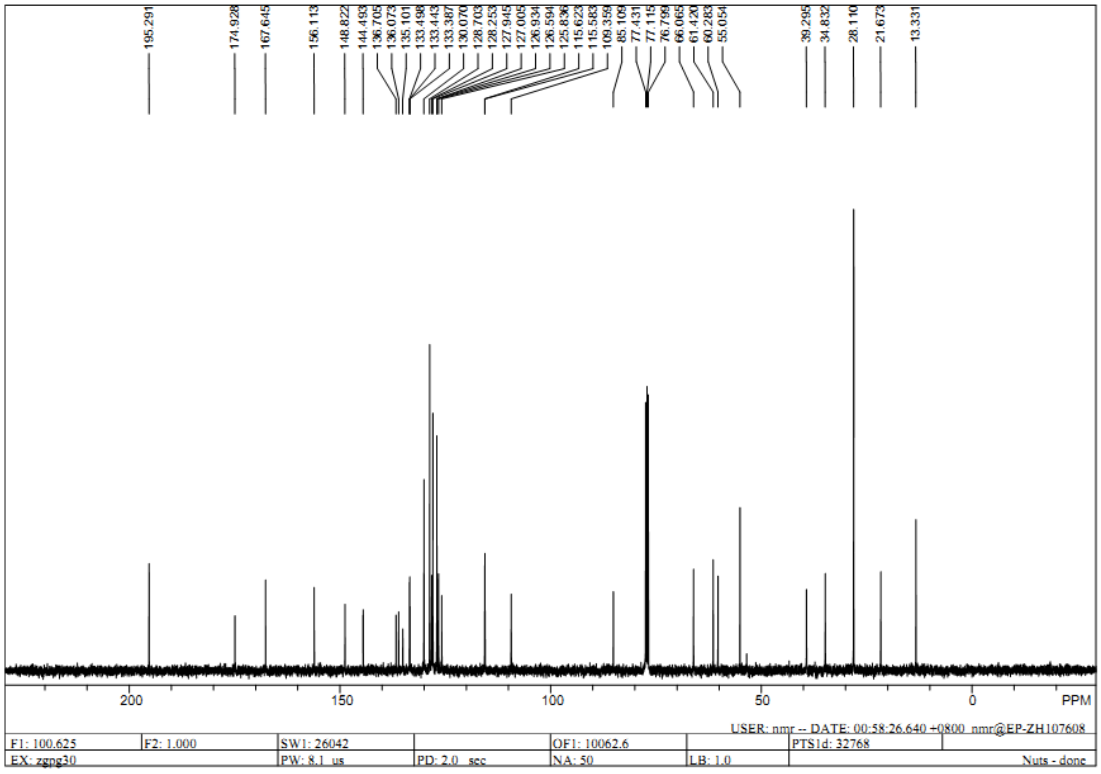
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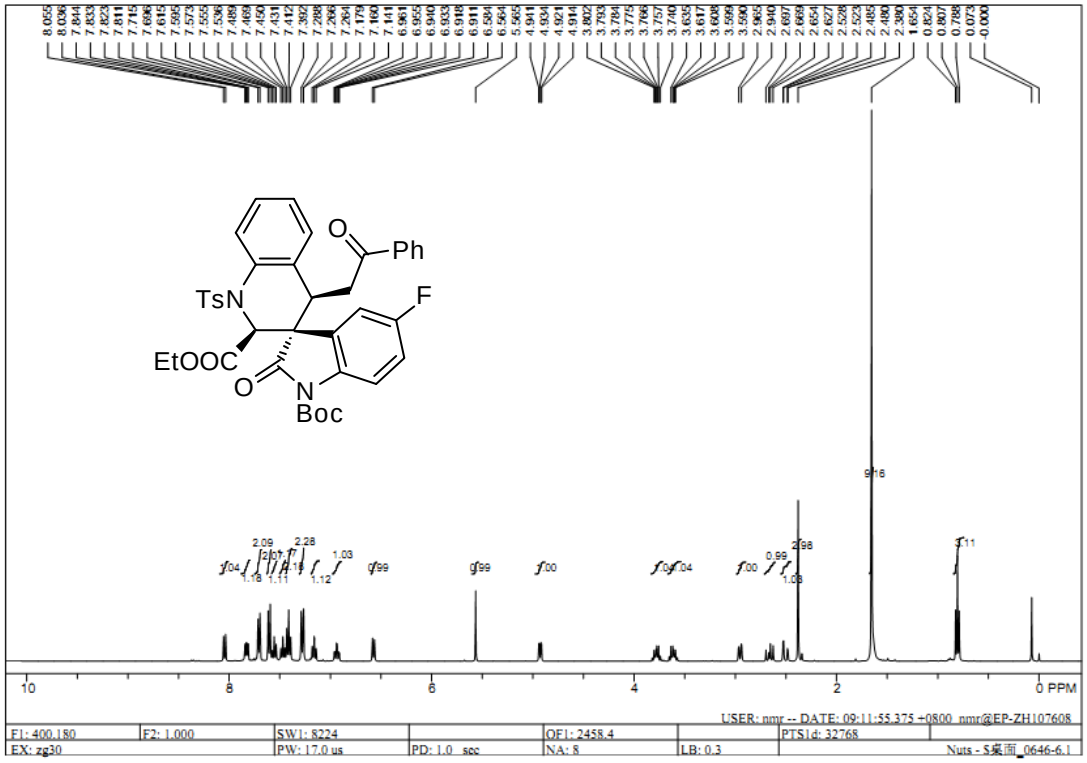

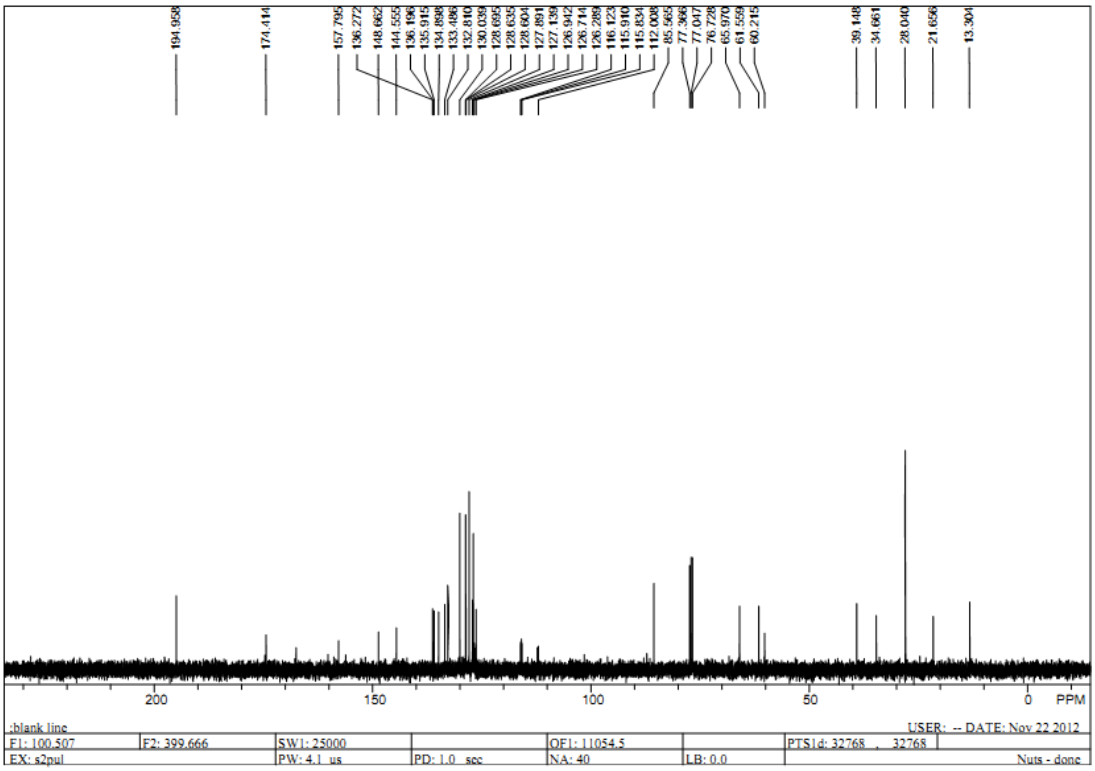

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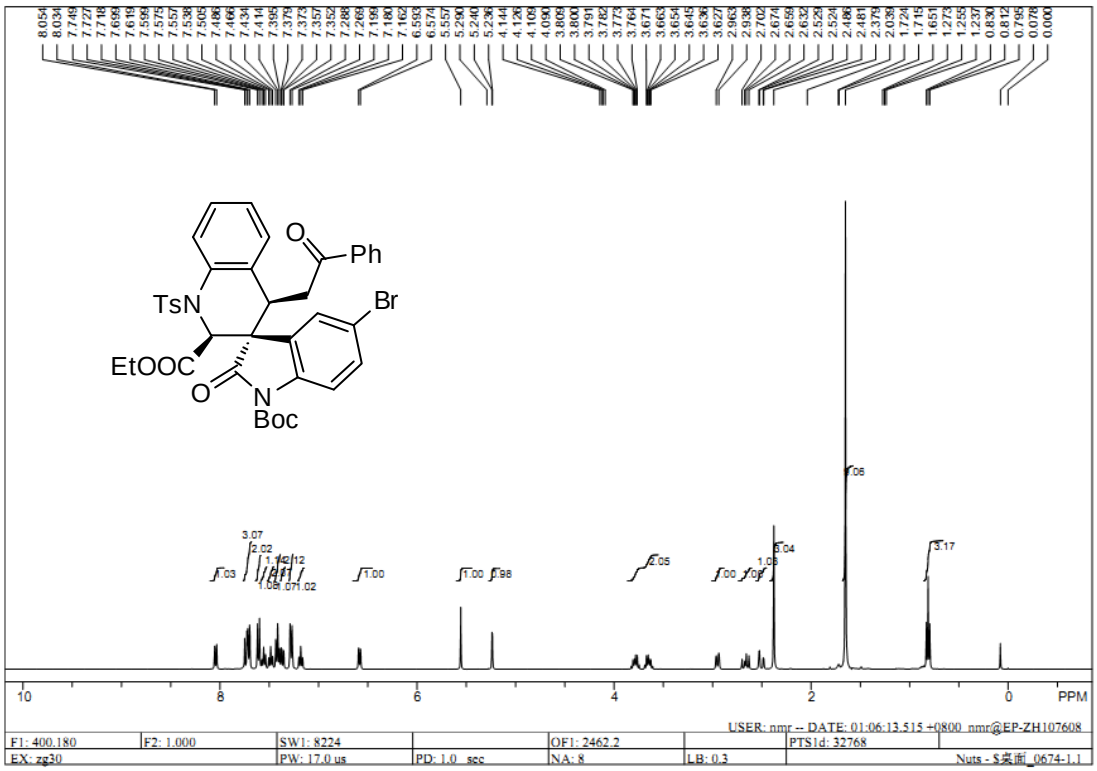
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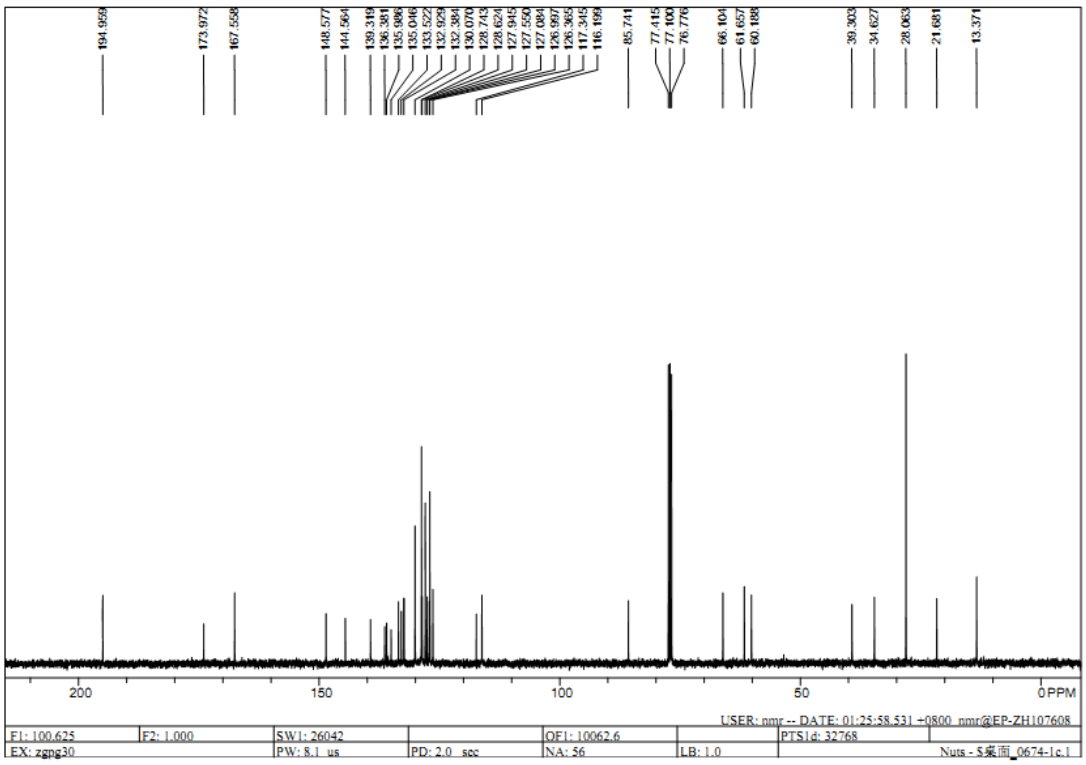
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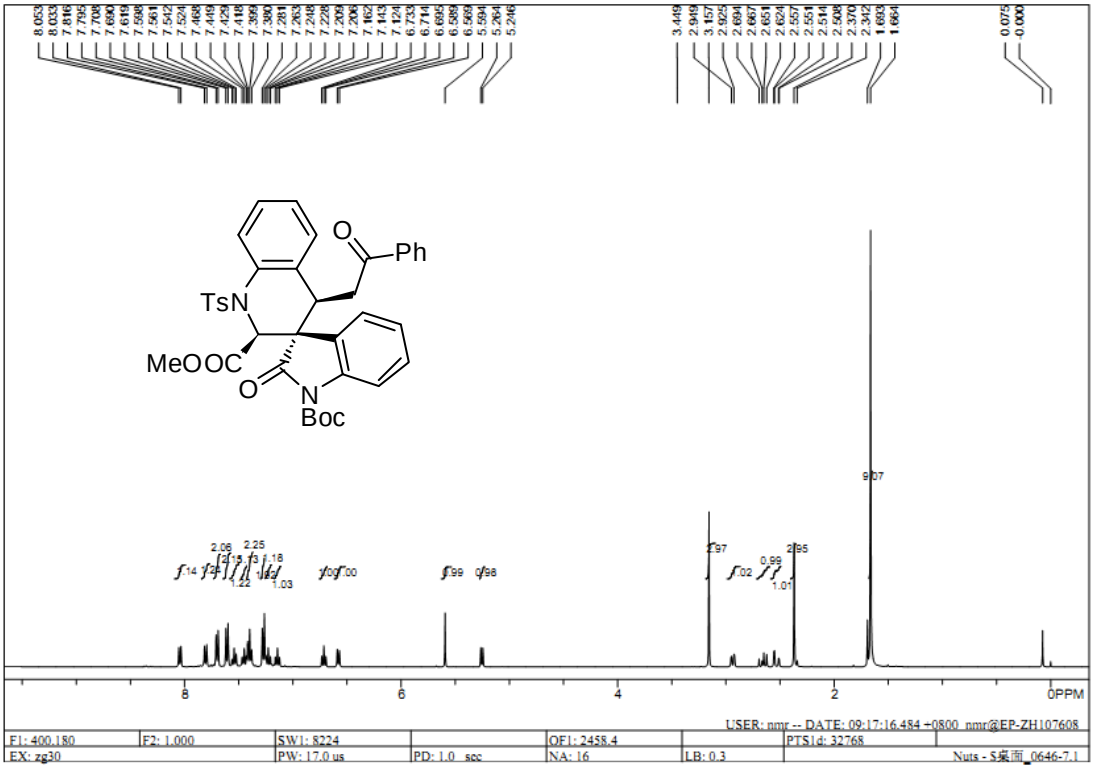
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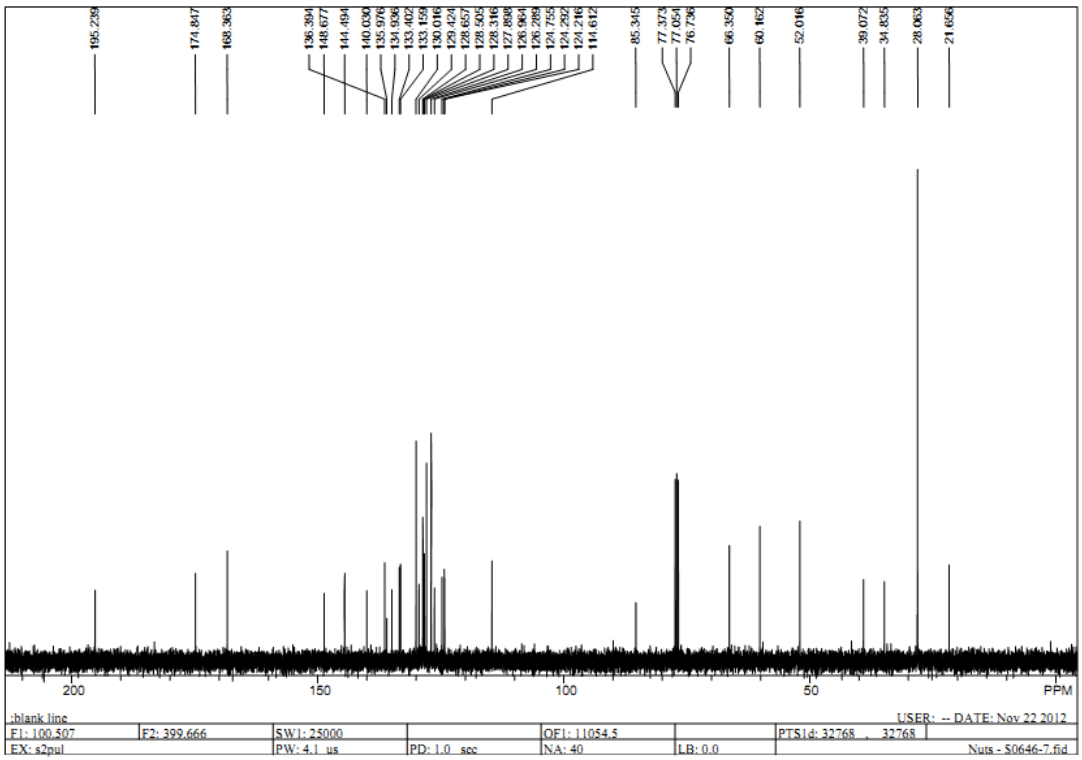
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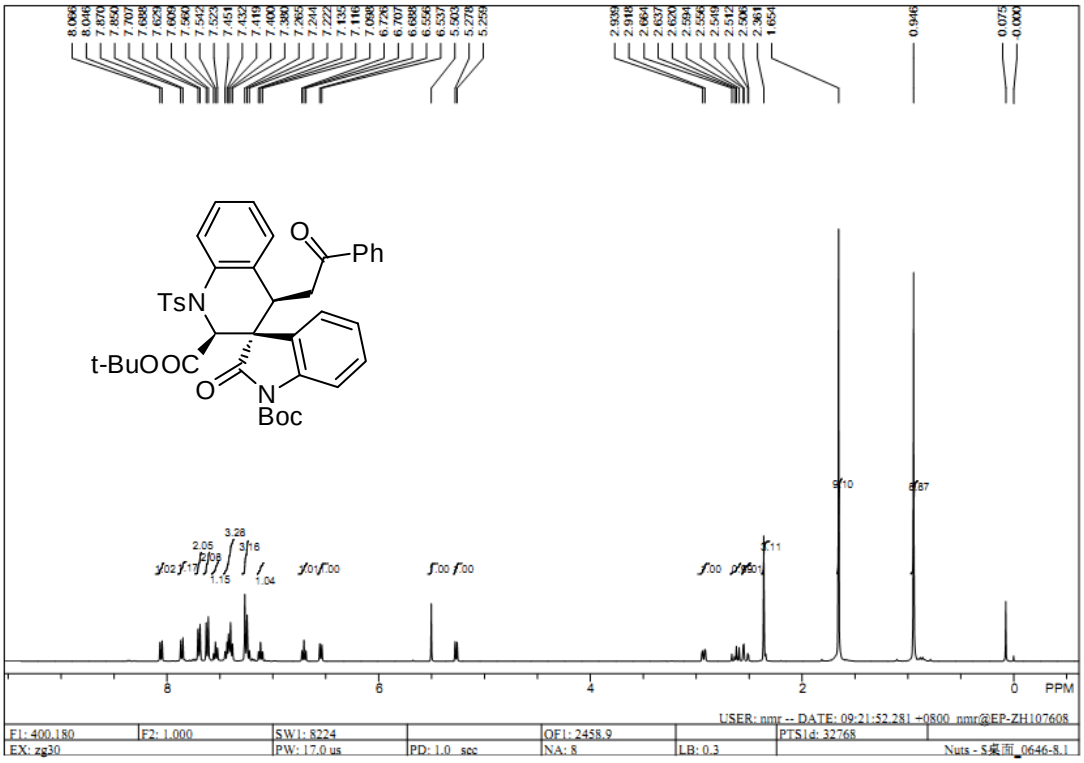
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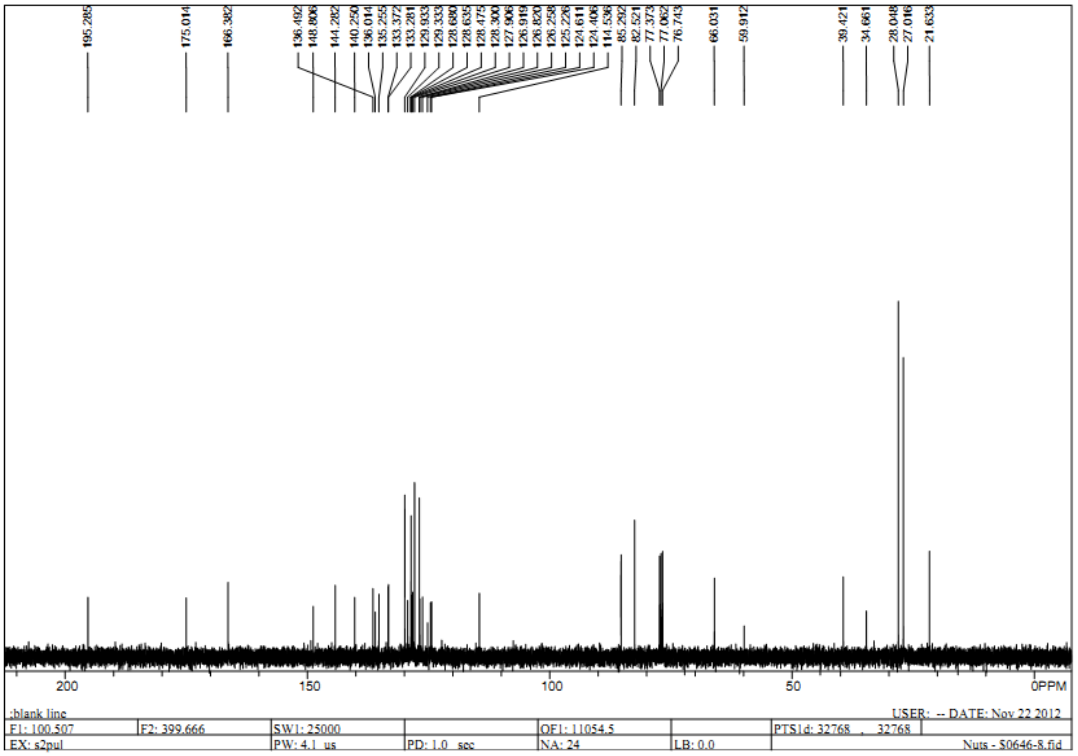
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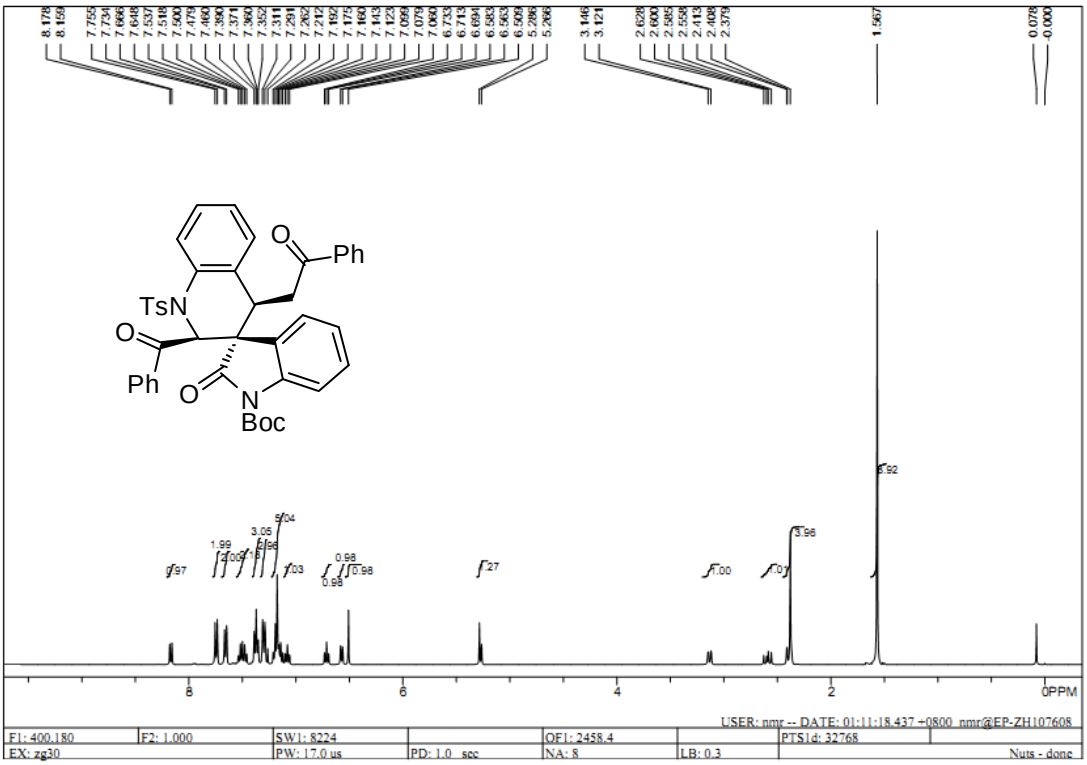
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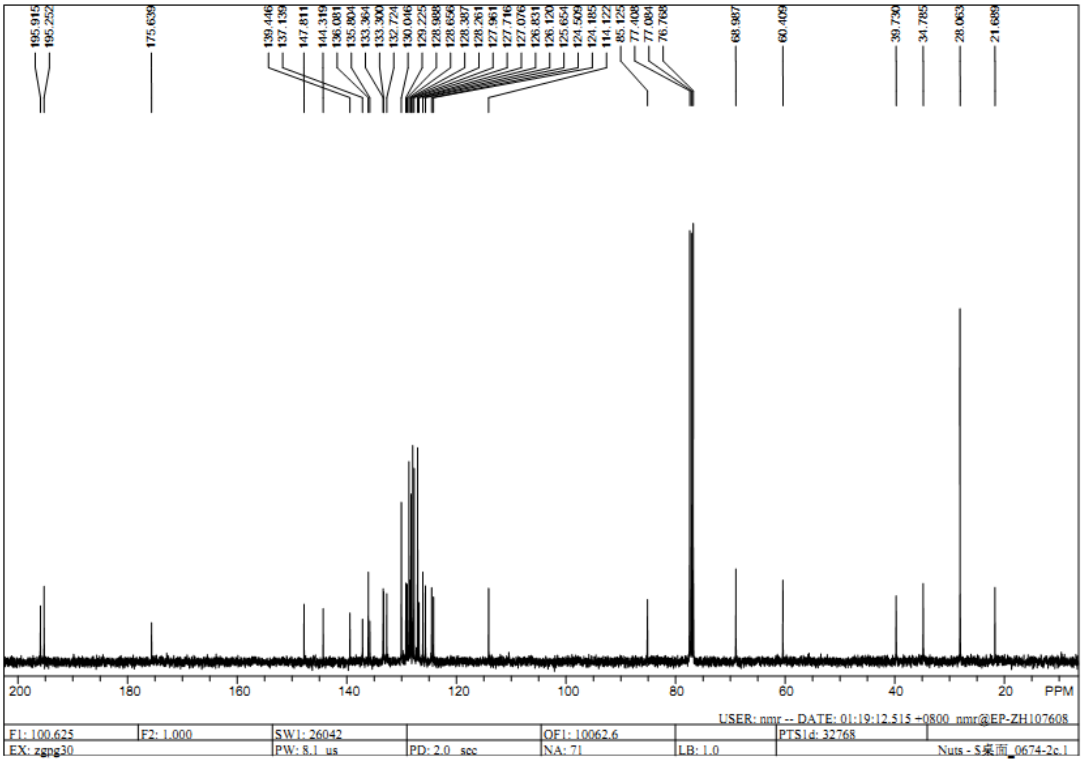
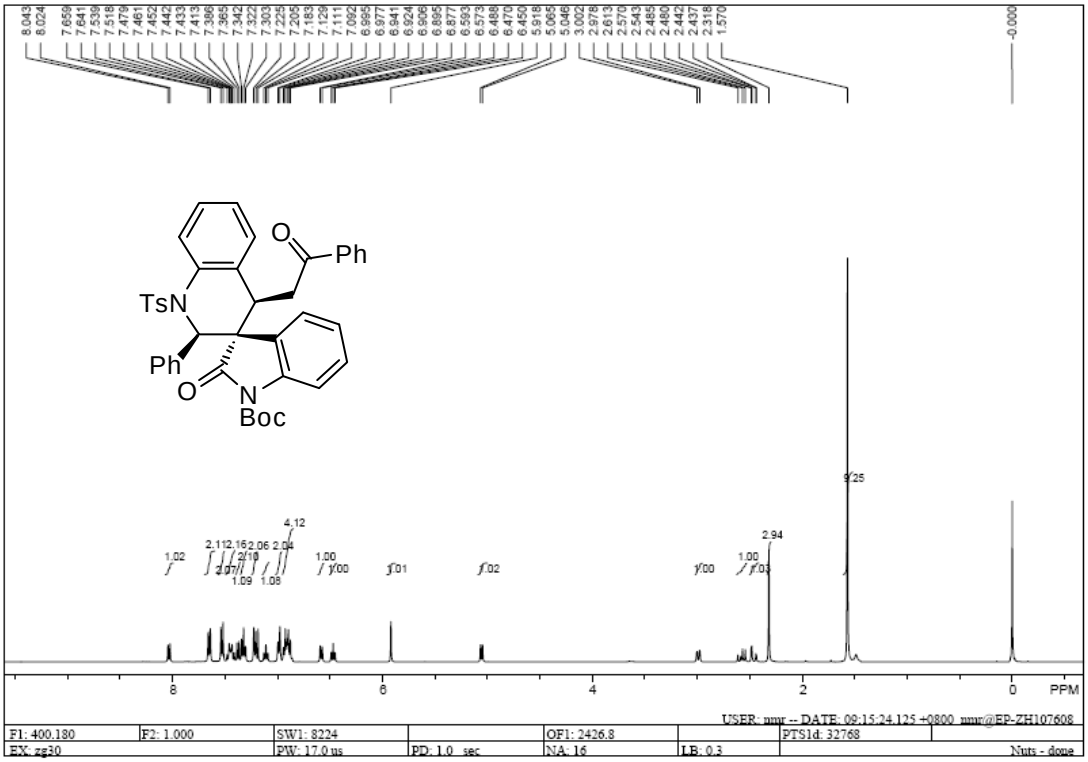
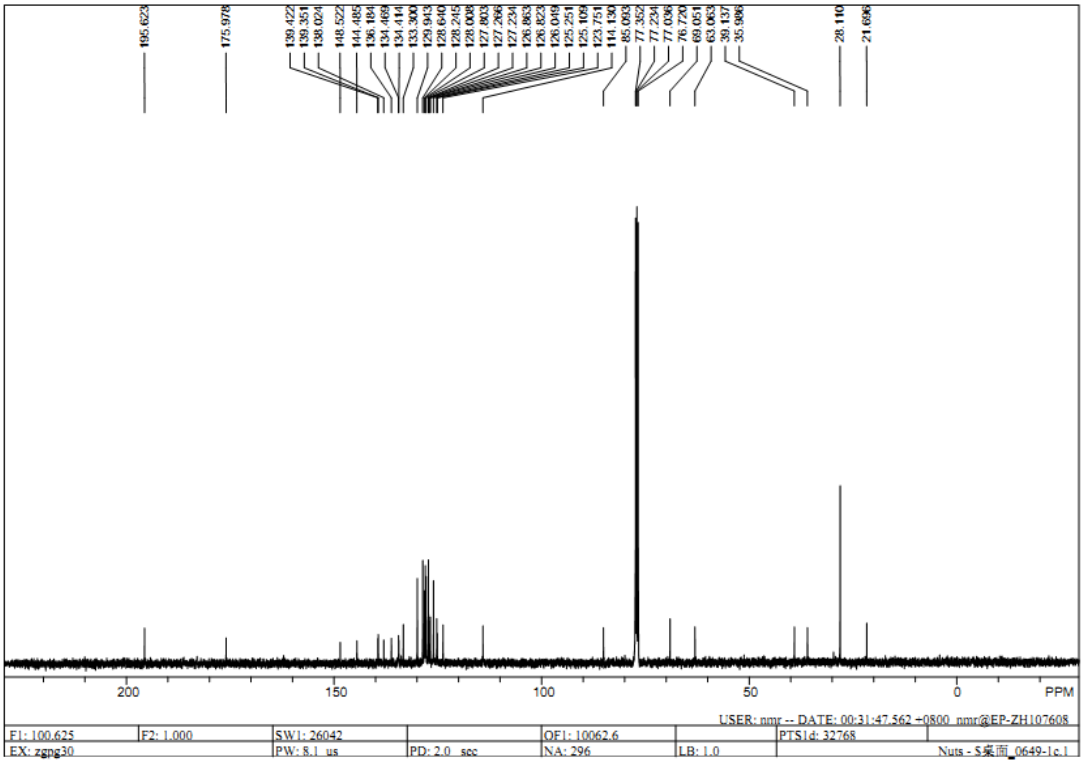
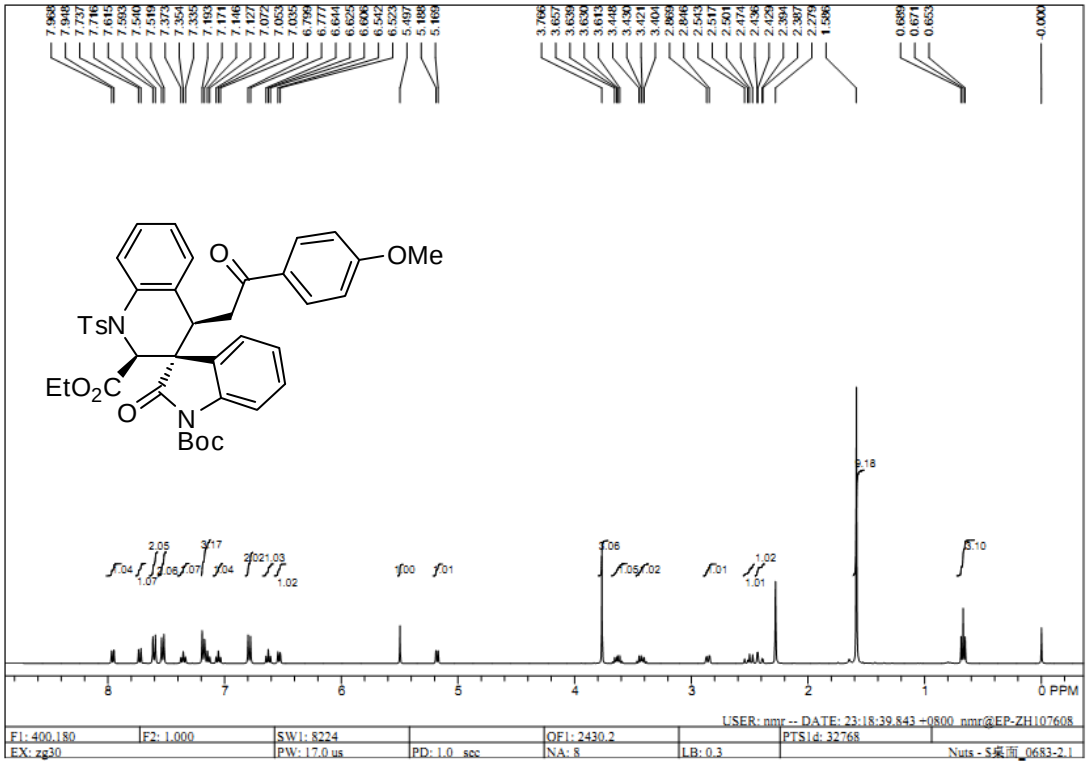

USER: nmr -- DATE: 01:19:12.515 +0800 nmr@EP-ZH107608
F1: 100.625 F2: 1.000 SW1: 26042 OF1: 10062.6 PTS1d: 32768
EX: zgpg30 PW: 8.1 us PD: 2.0 scc NA: 71 LB: 1.0 Nuts - S桌面_0674-2c.1

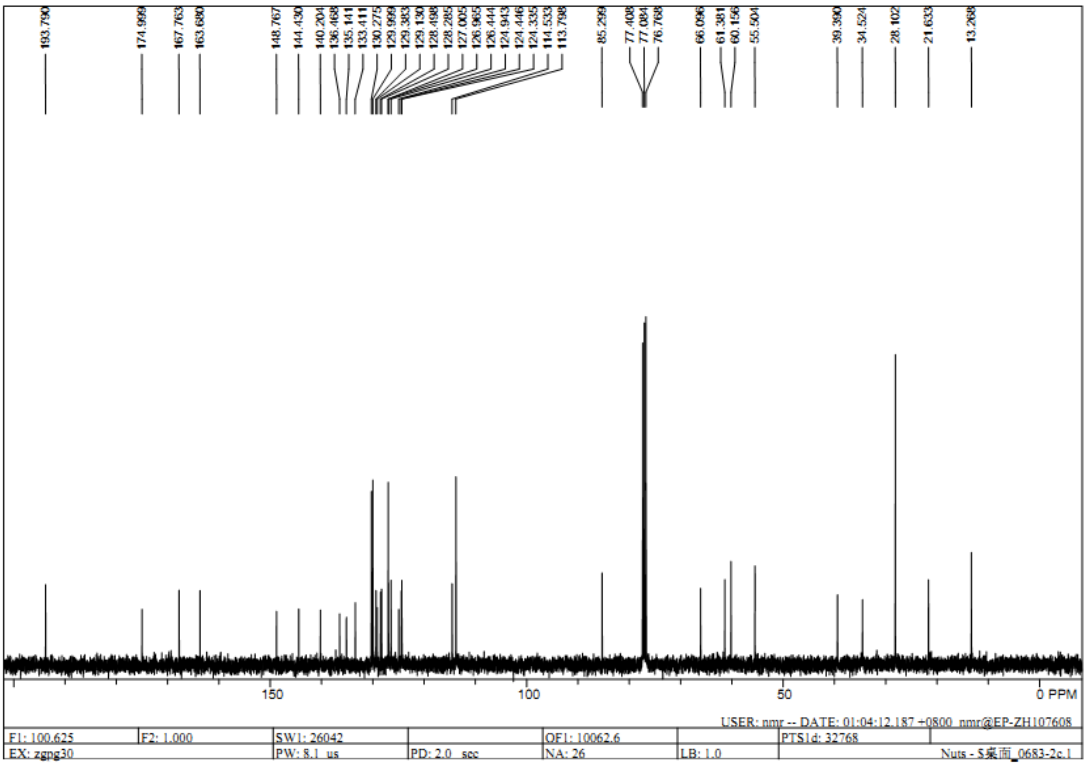
3k


TsN
Ph
O
Ph
O
N
Boc
PPM
F1: 400.180
F2: 1.000
SW1: 8224
OF1: 2426.8
PTS1d: 32768
EX: zg30
PW: 17.0 us
PD: 1.0 sec
NA: 16
LB: 0.3
Nuts - done

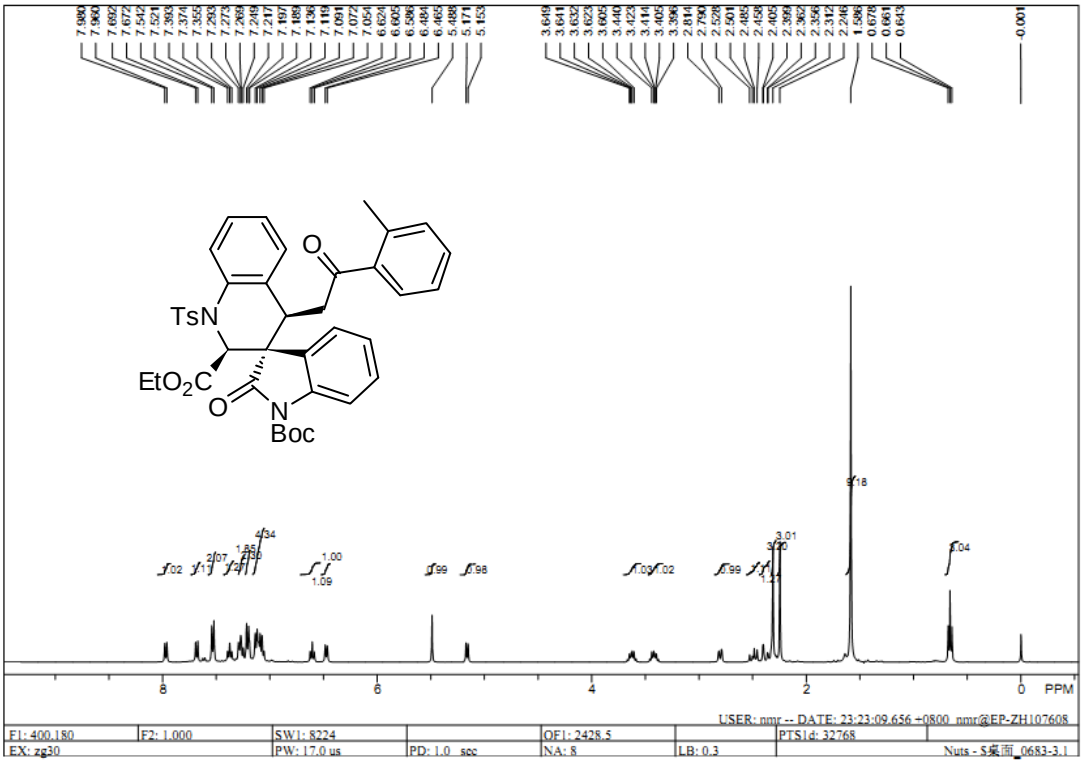

PPM
F1: 100.625
F2: 1.000
SW1: 26042
OF1: 10062.6
PTS1d: 32768
EX: zgpg30
PW: 8.1 us
PD: 2.0 scc
NA: 296
LB: 1.0

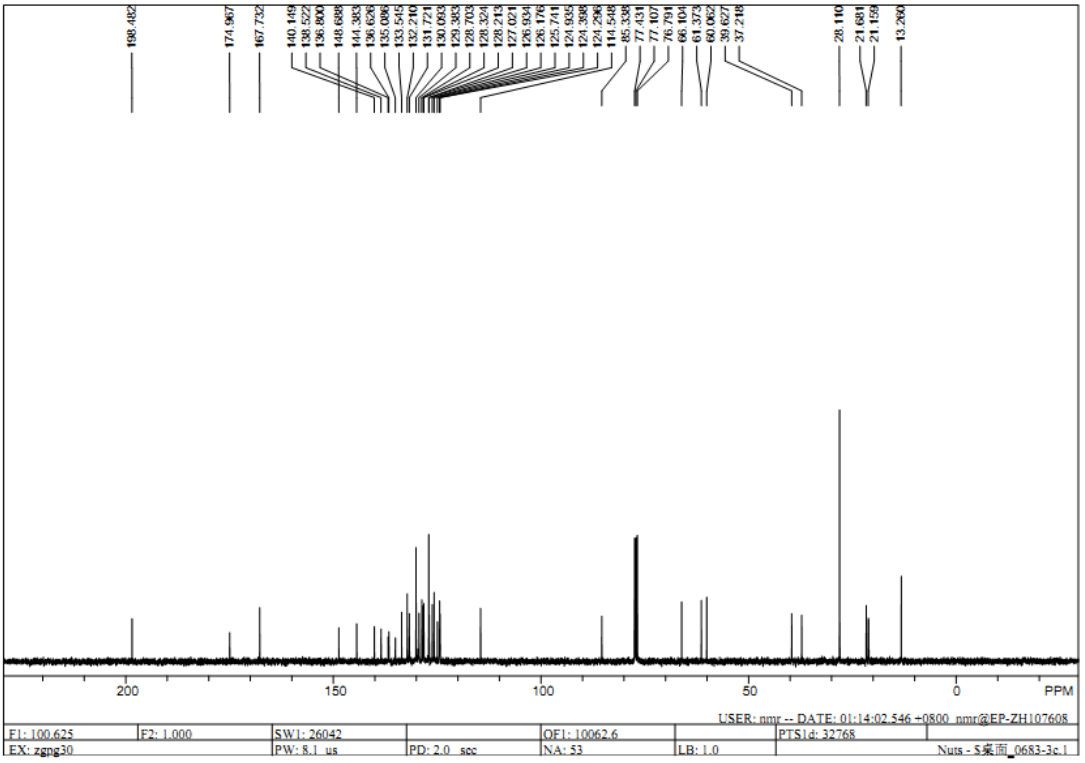
3l


OMe
O
TsN
EtO2C
O
N
Boc
PPM
USER: nmr -- DATE: 23:18:39.843 +0800 nmr@EP-ZH107608
F1: 400.180
F2: 1.000
SW1: 8224
OF1: 2430.2
PTS1d: 32768
EX: zg30
PW: 17.0 us
PD: 1.0 sec
NA: 8
LB: 0.3
Nuts - S桌面_0683-2.1

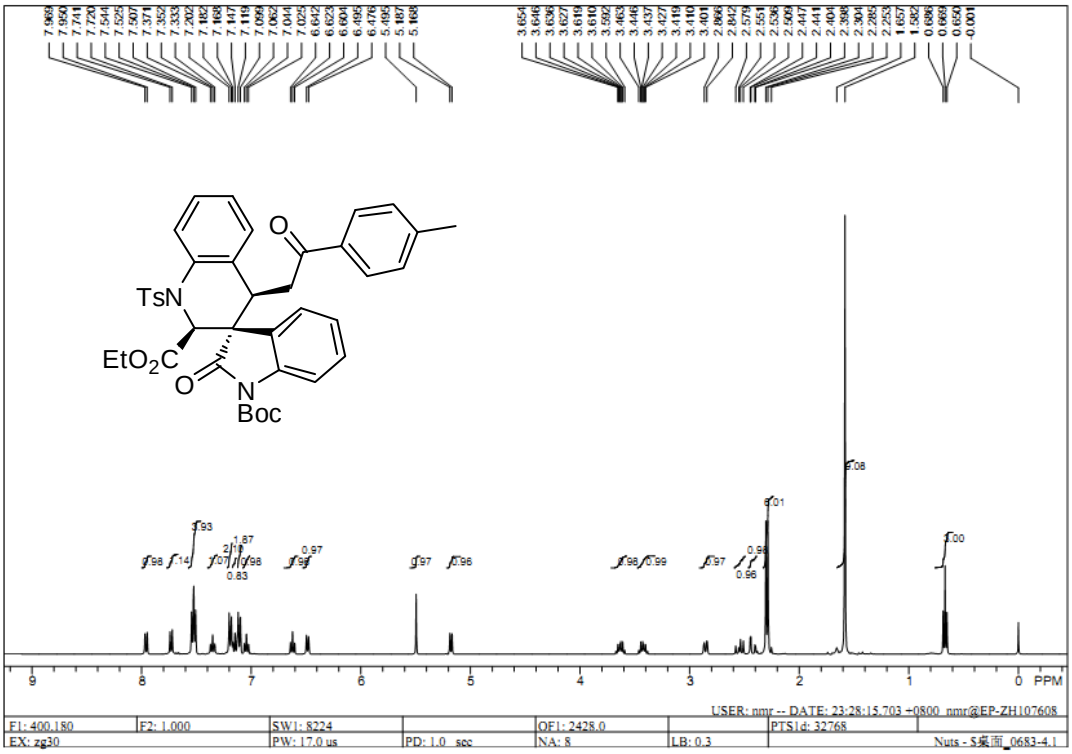

PPM
USER: nmr -- DATE: 01:04:12.187 +0800 nmr@EP-ZH107608
F1: 100.625
F2: 1.000
SW1: 26042
OF1: 10062.6
PTS1d: 32768
EX: zgpg30
PW: 8.1 us
PD: 2.0 sec
NA: 26
LB: 1.0
Nuts - S桌面_0683-2c.1

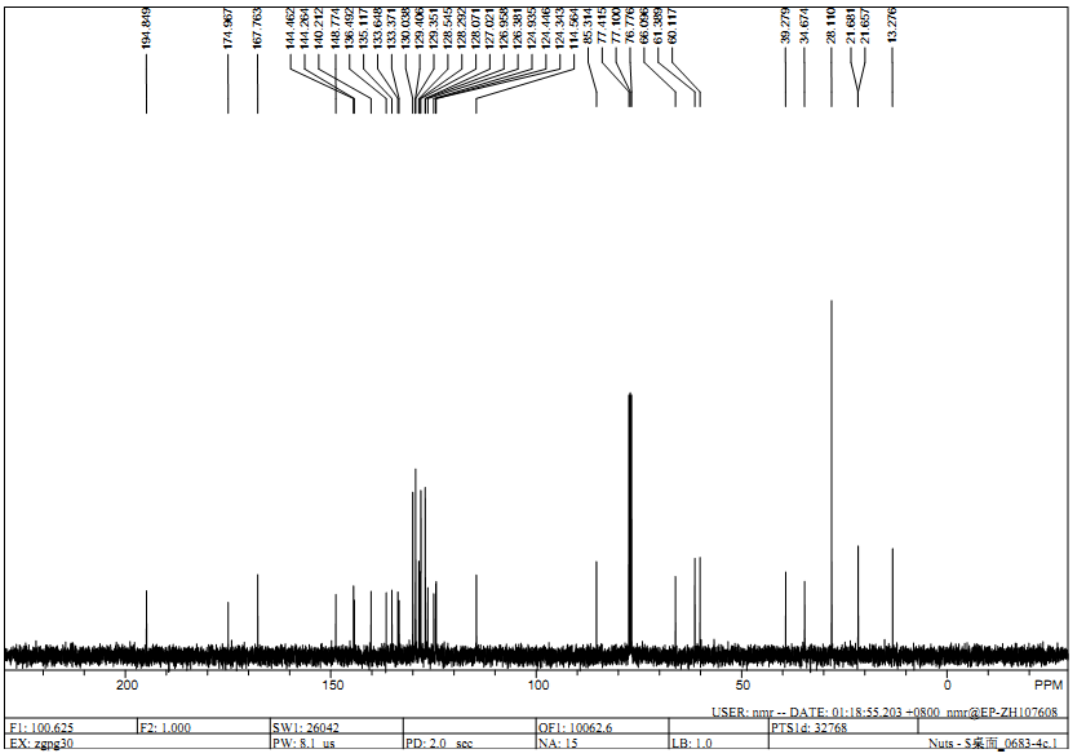
3m


TsN
EtO2C
O
N
Boc
PPM
USER: nmr -- DATE: 23:23:09.656 +0800 nmr@EP-ZH107608
F1: 400.180 F2: 1.000 SW1: 8224 OF1: 2428.5 PTS1d: 32768
EX: zg30 PW: 17.0 us PD: 1.0 sec NA: 8 LB: 0.3
Nuts - S桌面_0683-3.1

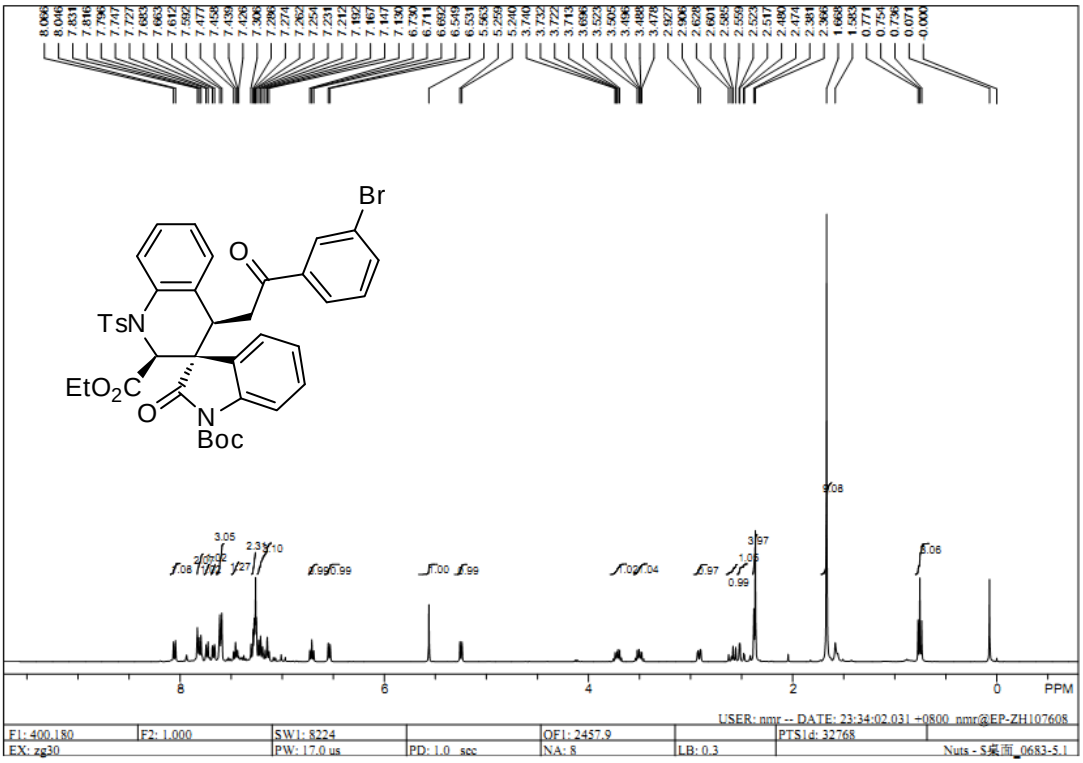

PPM
USER: nmr -- DATE: 01:14:02.546 +0800 nmr@EP-ZH107608
F1: 100.625 F2: 1.000 SW1: 26042 OF1: 10062.6 PTS1d: 32768
EX: zgpg30 PW: 8.1 us PD: 2.0 sec NA: 53 LB: 1.0
Nuts - S桌面_0683-3c.1

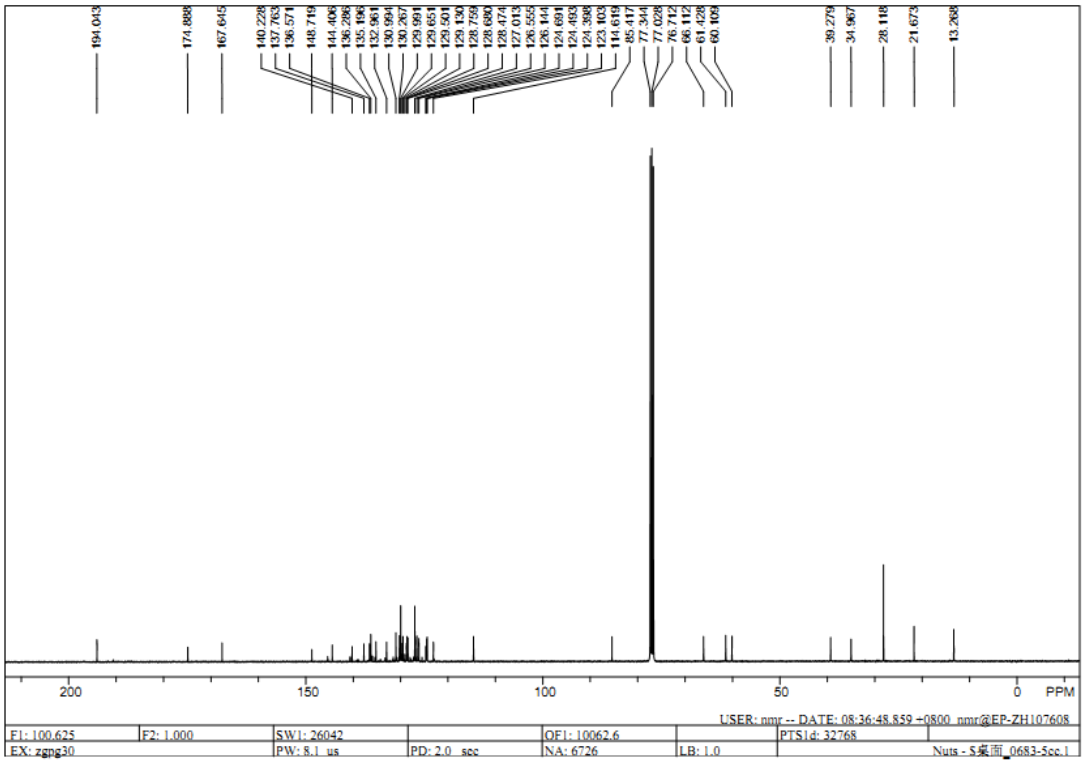
3n


TsN
EtO2C
O
N
Boc
PPM
USER: nmr -- DATE: 23:28:15.703 +0800 nmr@EP-ZH107608
F1: 400.180 F2: 1.000 SW1: 8224 OF1: 2428.0 PTS1d: 32768
EX: zg30 PW: 17.0 us PD: 1.0 scc NA: 8 LB: 0.3
Nuts - S桌面_0683-4.1

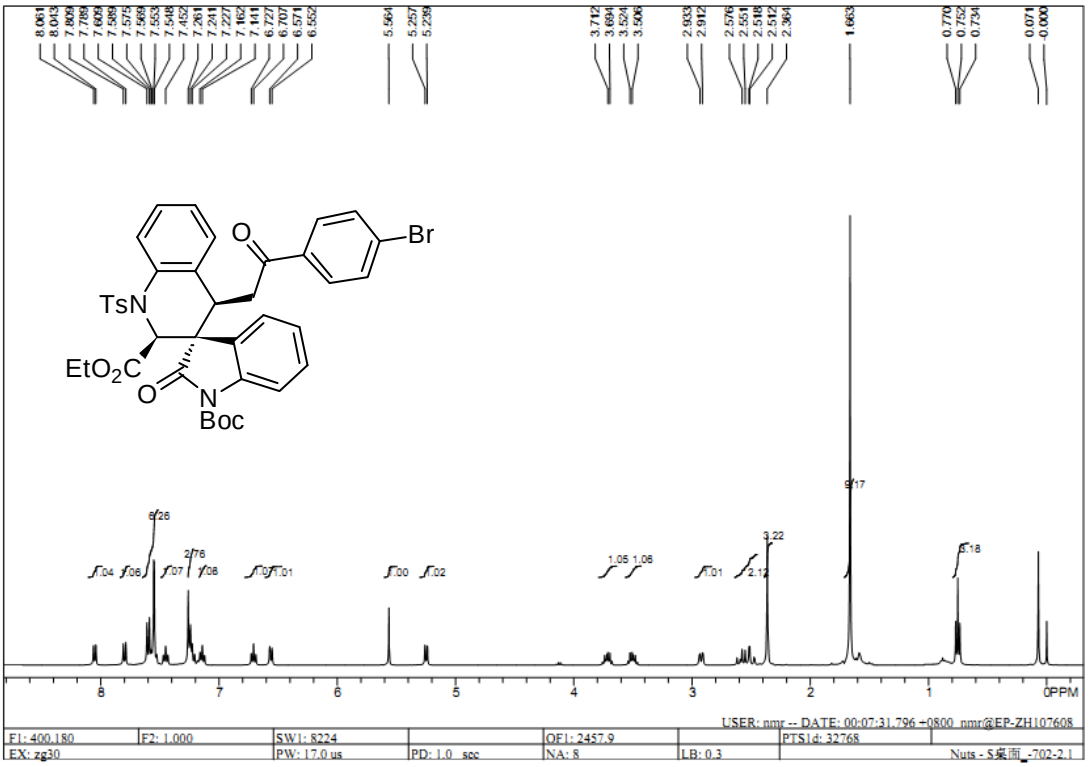

PPM
USER: nmr -- DATE: 01:18:55.203 +0800 nmr@EP-ZH107608
F1: 100.625 F2: 1.000 SW1: 26042 OF1: 10062.6 PTS1d: 32768
EX: zgpg30 PW: 8.1 us PD: 2.0 scc NA: 15 LB: 1.0
Nuts - S桌面_0683-4c.1

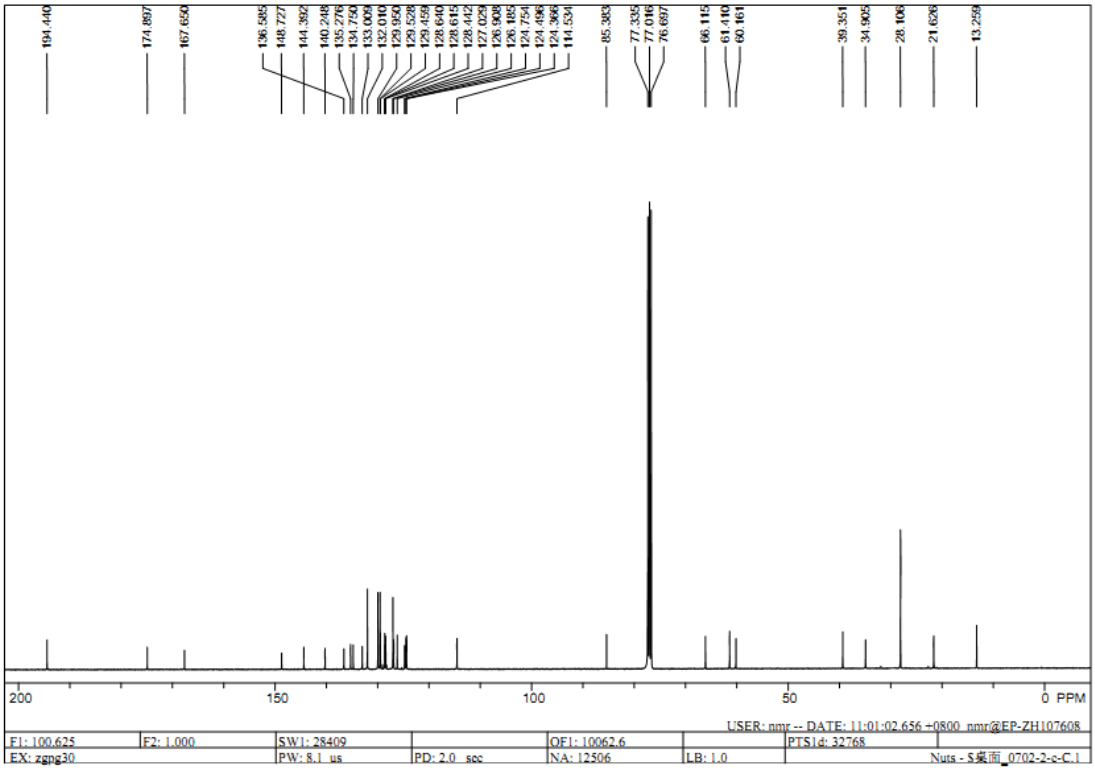
3o


Br
O
TsN
EtO2C
O
N
Boc
PPM
USER: nmr -- DATE: 23:34:02.031 +0800 nmr@EP-ZH107608
F1: 400.180 F2: 1.000 SW1: 8224 OF1: 2457.9 PTS1d: 32768
EX: zg30 PW: 17.0 us PD: 1.0 sec NA: 8 LB: 0.3 Nuts - S桌面_0683-5.1

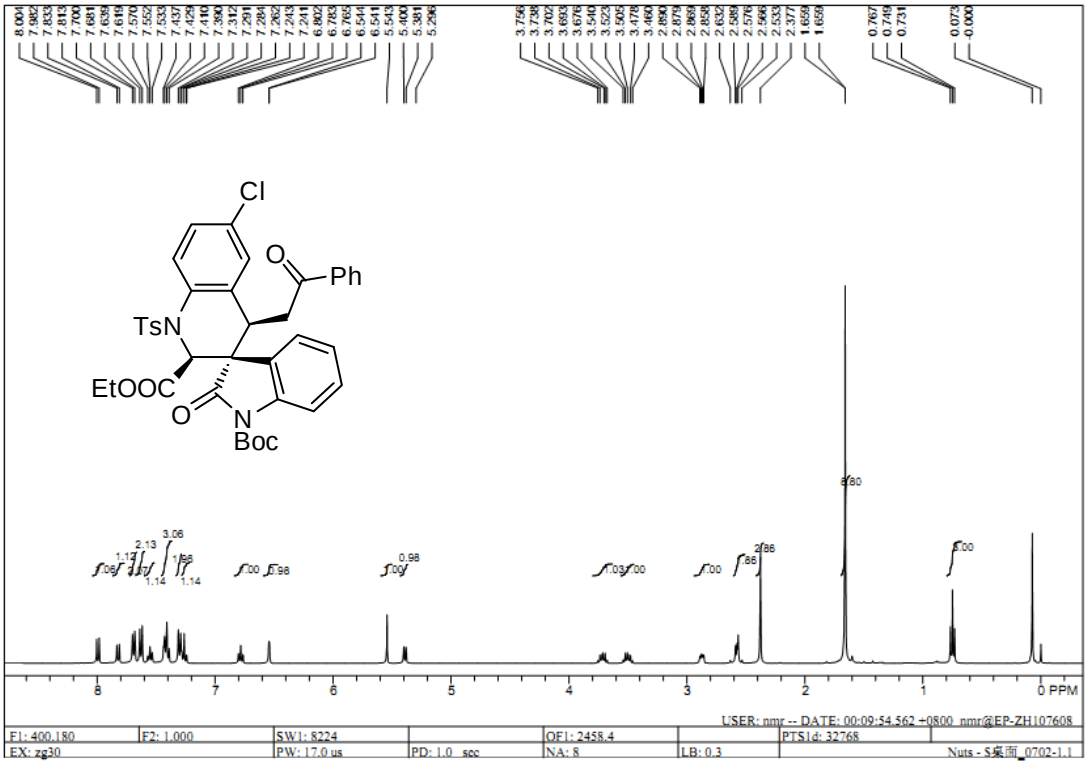

PPM
USER: nmr -- DATE: 08:36:48.859 +0800 nmr@EP-ZH107608
F1: 100.625 F2: 1.000 SW1: 26042 OF1: 10062.6 PTS1d: 32768
EX: zgpg30 PW: 8.1 us PD: 2.0 sec NA: 6726 LB: 1.0 Nuts - S桌面_0683-5cc.1

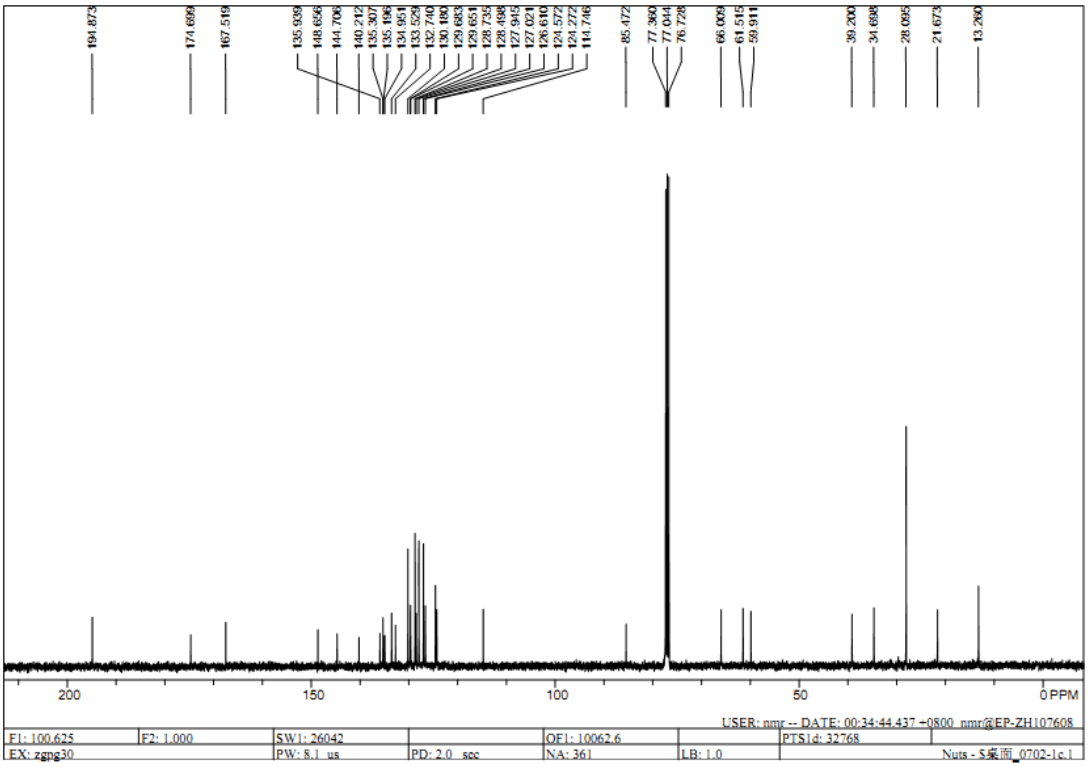
3p


O
Br
TsN
EtO2C
O
N
Boc
8.061
8.043
7.809
7.789
7.609
7.589
7.575
7.569
7.553
7.548
7.452
7.261
7.241
7.227
7.162
7.141
6.727
6.707
6.571
6.552
5.564
5.257
5.239
3.712
3.694
3.524
3.506
2.933
2.912
2.576
2.551
2.518
2.512
2.364
1.663
0.770
0.752
0.734
0.071
0.000
8.26
2.76
9.17
3.22
6.18
1.05
1.06
2.12
8
7
6
5
4
3
2
1
0PPM
USER: nmr -- DATE: 00:07:31.796 +0800 nmr@EP-ZH107608
F1: 400.180
F2: 1.000
SW1: 8224
OF1: 2457.9
PTS1d: 32768
EX: zg30
PW: 17.0 us
PD: 1.0 scc
NA: 8
LB: 0.3
Nuts - S桌面_-702-2.1

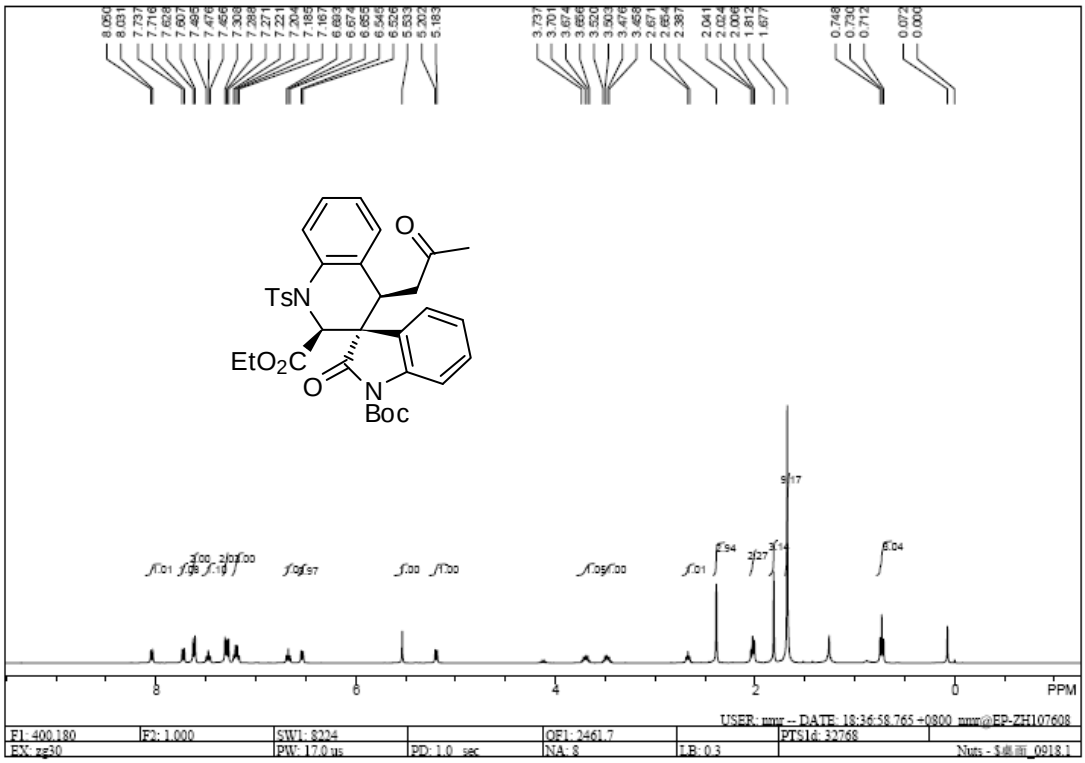

194.440
174.897
167.650
136.585
148.727
144.392
140.248
135.276
134.750
133.009
132.010
129.950
129.528
129.459
128.640
128.615
128.442
127.029
126.908
126.185
124.754
124.496
124.366
114.534
85.383
77.335
77.016
76.697
66.115
61.410
60.161
39.351
34.905
28.106
21.626
13.259
200
150
100
50
0 PPM
USER: nmr -- DATE: 11:01:02.656 +0800 nmr@EP-ZH107608
F1: 100.625
F2: 1.000
SW1: 28409
OF1: 10062.6
PTS1d: 32768
EX: zgpg30
PW: 8.1 us
PD: 2.0 scc
NA: 12506
LB: 1.0
Nuts - S桌面_0702-2-c-C.1

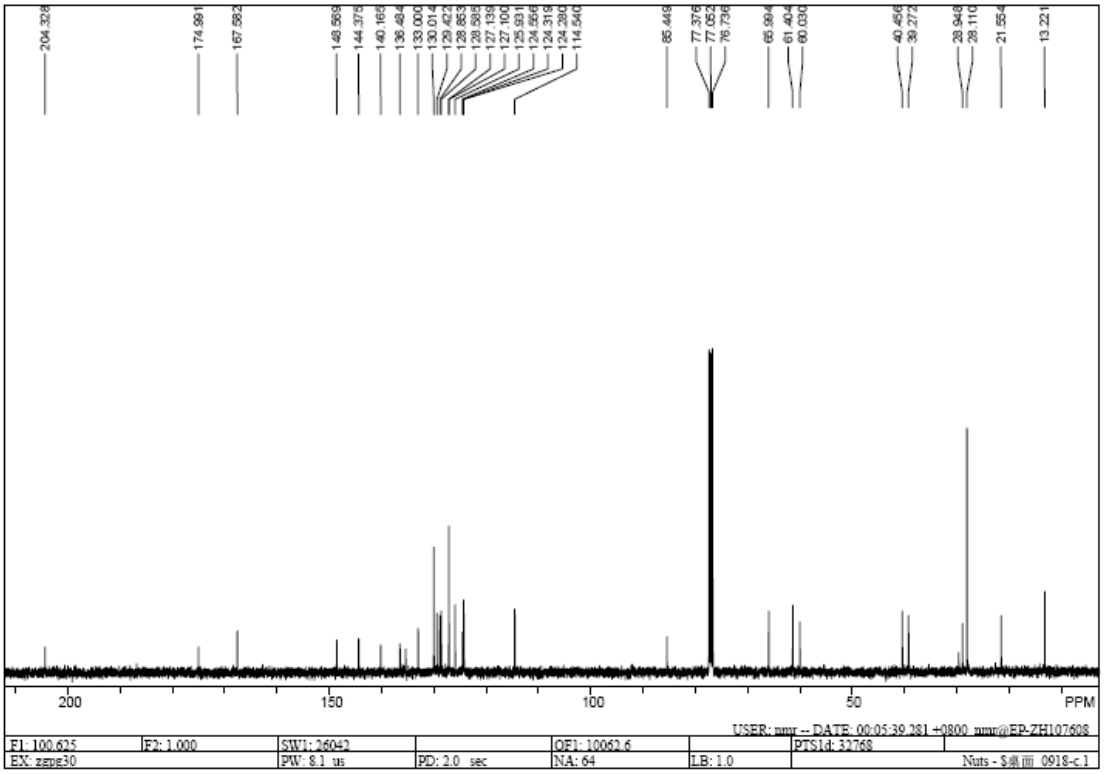
3q


Cl
O
Ph
TsN
EtOOC
O
N
Boc
0 PPM
F1: 400.180
F2: 1.000
SW1: 8224
OF1: 2458.4
PTS1d: 32768
EX: zg30
PW: 17.0 us
PD: 1.0 sec
NA: 8
LB: 0.3
Nuts - S紫雨_0702-1.1

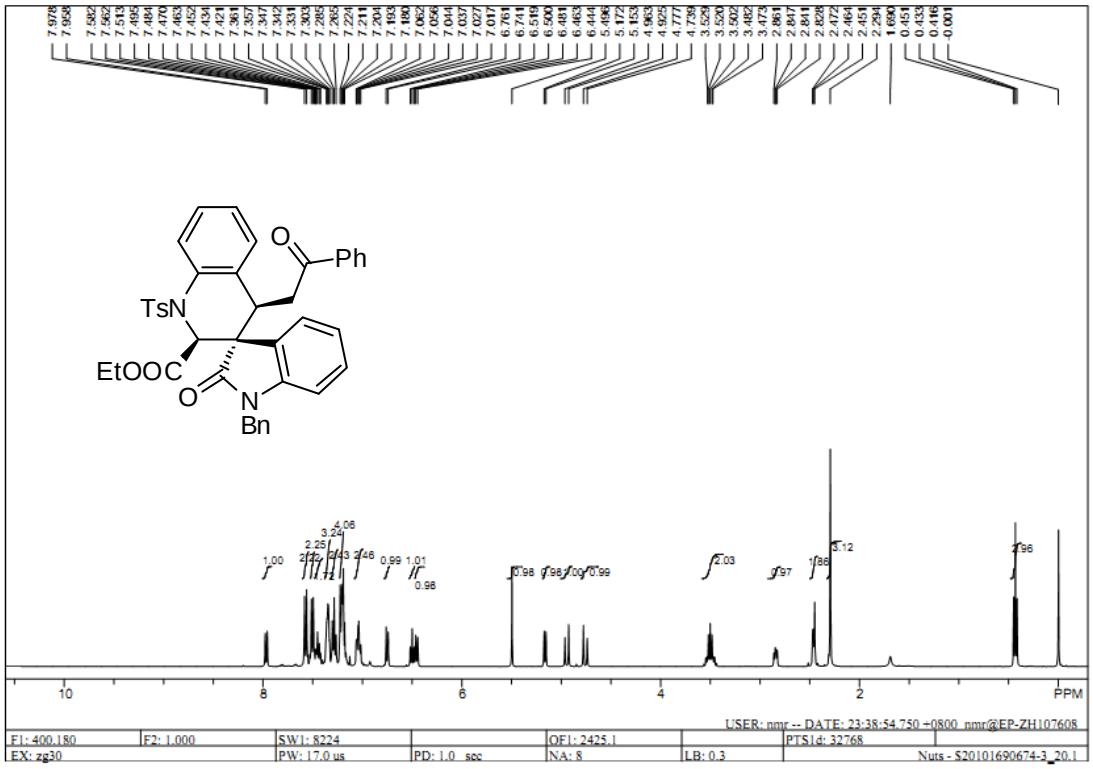

0 PPM
F1: 100.625
F2: 1.000
SW1: 26042
OF1: 10062.6
PTS1d: 32768
EX: zgpg30
PW: 8.1 us
PD: 2.0 sec
NA: 361
LB: 1.0
Nuts - S紫雨_0702-1c.1

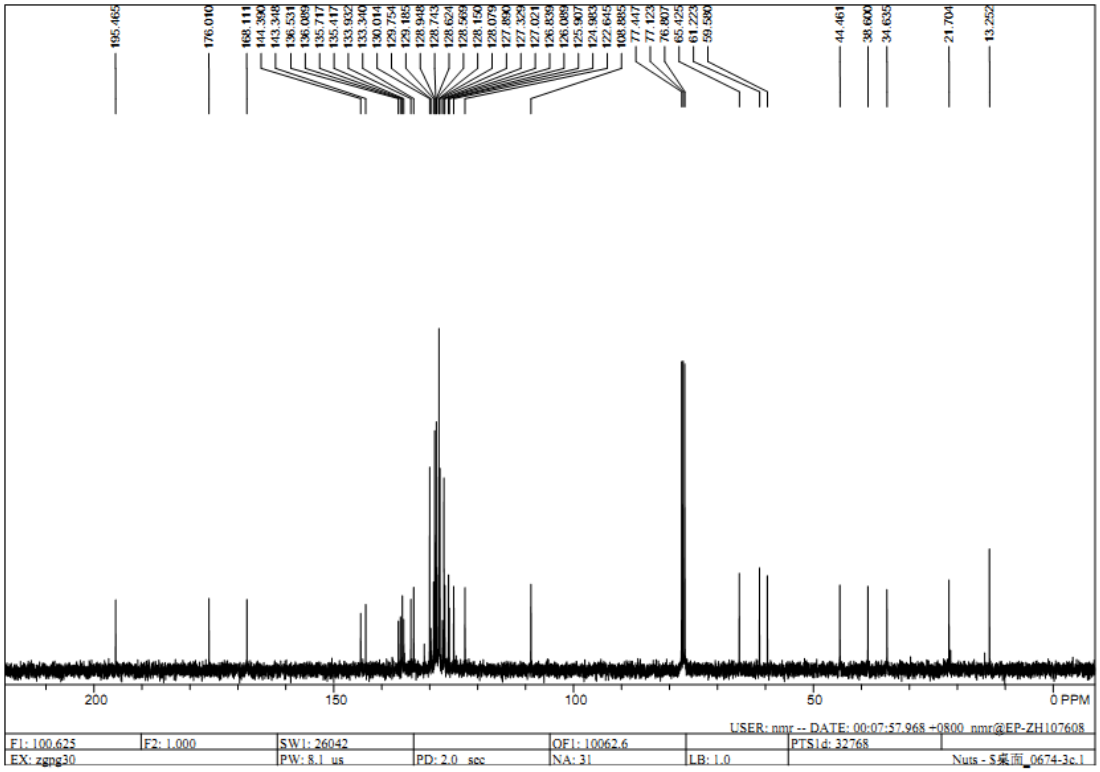
3r


TsN
EtO2C
O
N
Boc
PPM
USER: nmr -- DATE: 18:36:58.765 +0800 nmr@EP-ZH107608
F1: 400.180 F2: 1.000 SW1: 8224 OF1: 2461.7 PTS1d: 32768
EX: zg30 PW: 17.0 us PD: 1.0 sec NA: 8 LB: 0.3
Nuts - $桌面_0918.1

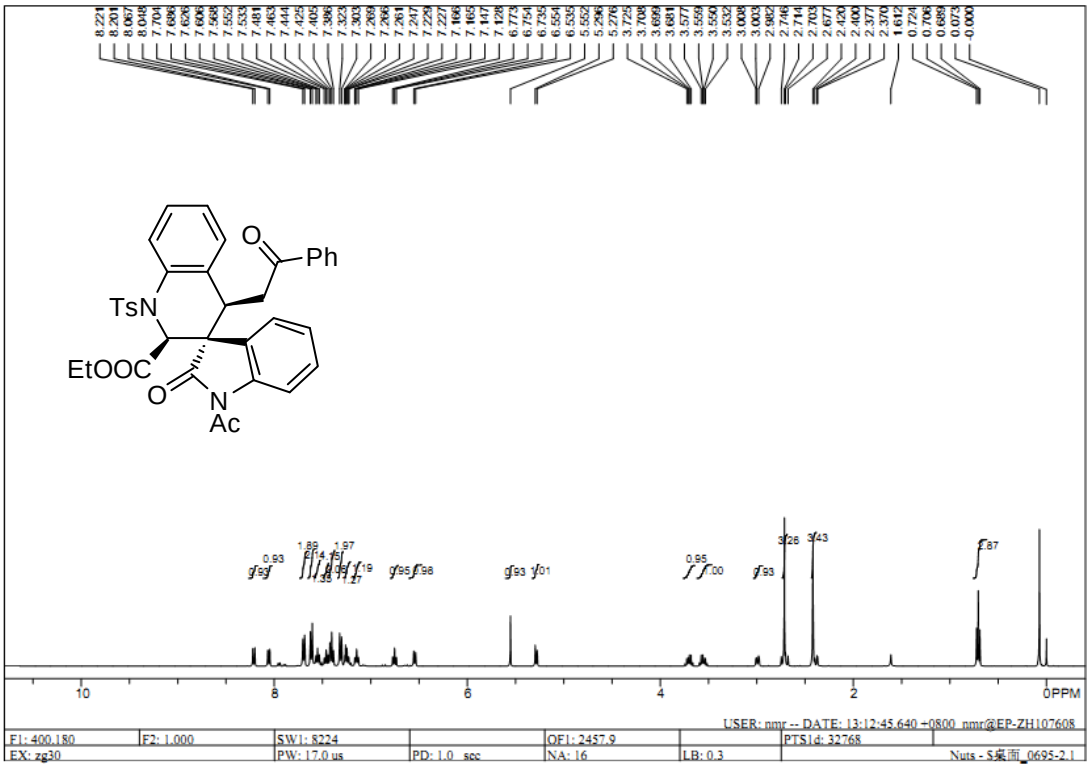

PPM
USER: nmr -- DATE: 00:05:39.281 +0800 nmr@EP-ZH107608
F1: 100.625 F2: 1.000 SW1: 26042 OF1: 10062.6 PTS1d: 32768
EX: zgpg30 PW: 8.1 us PD: 2.0 sec NA: 64 LB: 1.0
Nuts - $桌面 0918-c.1

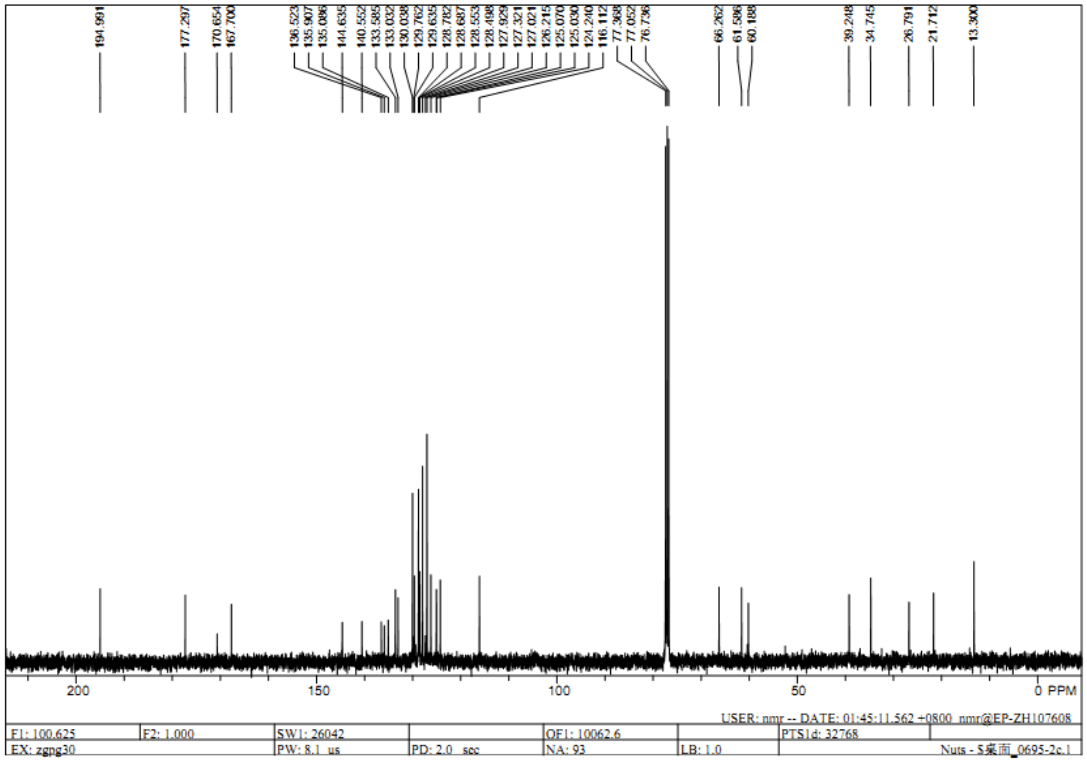
3s


O
Ph
TsN
EtOOC
O
N
Bn
10
8
6
4
2
PPM
USER: nmr -- DATE: 23:38:54.750 +0800 nmr@EP-ZH107608
F1: 400.180
F2: 1.000
SW1: 8224
OF1: 2425.1
PTS1d: 32768
EX: zg30
PW: 17.0 us
PD: 1.0 sec
NA: 8
LB: 0.3
Nuts - S20101690674-3_20.1

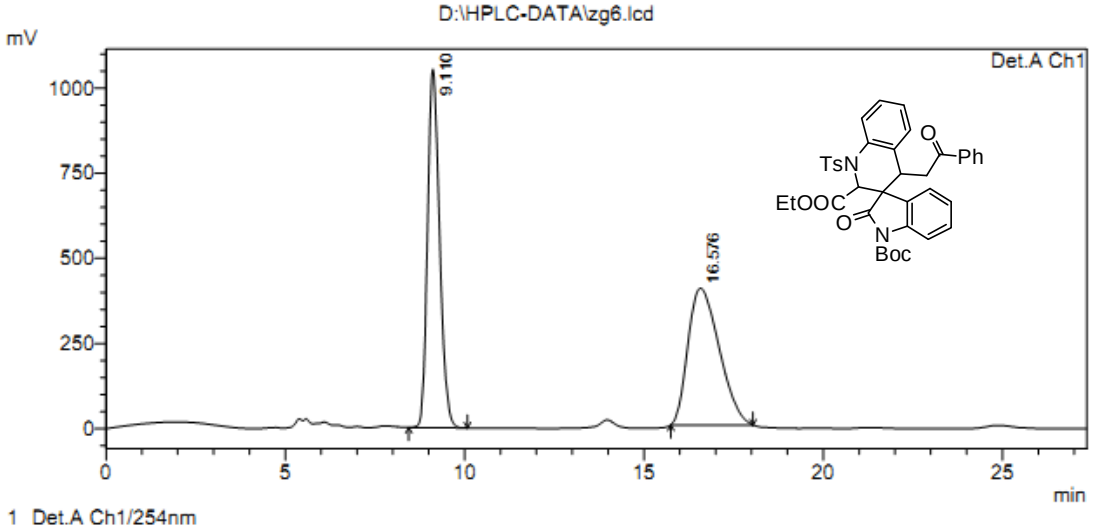

200
150
100
50
0 PPM
USER: nmr -- DATE: 00:07:57.968 +0800 nmr@EP-ZH107608
F1: 100.625
F2: 1.000
SW1: 26042
OF1: 10062.6
PTS1d: 32768
EX: zgpg30
PW: 8.1 us
PD: 2.0 sec
NA: 31
LB: 1.0
Nuts - S氢面_0674-3c.1

3t


O
Ph
TsN
EtOOC
O
N
Ac
10
8
6
4
2
0PPM
F1: 400.180
F2: 1.000
SW1: 8224
OF1: 2457.9
PTS1d: 32768
EX: zg30
PW: 17.0 us
PD: 1.0 scc
NA: 16
LB: 0.3
Nuts - S桌面_0695-2.1


200
150
100
50
0 PPM
F1: 100.625
F2: 1.000
SW1: 26042
OF1: 10062.6
PTS1d: 32768
EX: zgpg30
PW: 8.1 us
PD: 2.0 scc
NA: 93
LB: 1.0
Nuts - S桌面_0695-2c.1

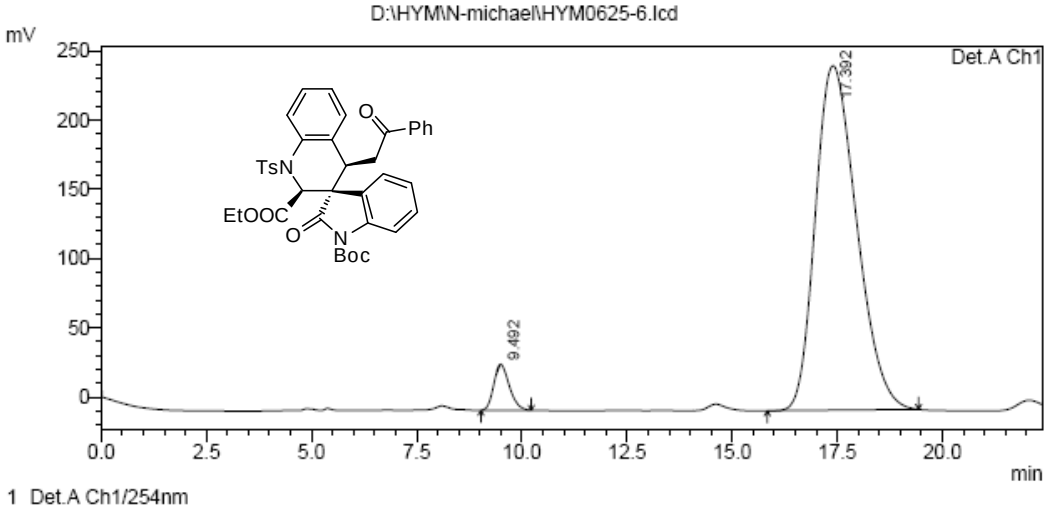
3a



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.110	24397017	1052428	50.036	72.392
2	16.576	24361813	401362	49.964	27.608
Total		48758829	1453790	100.000	100.000

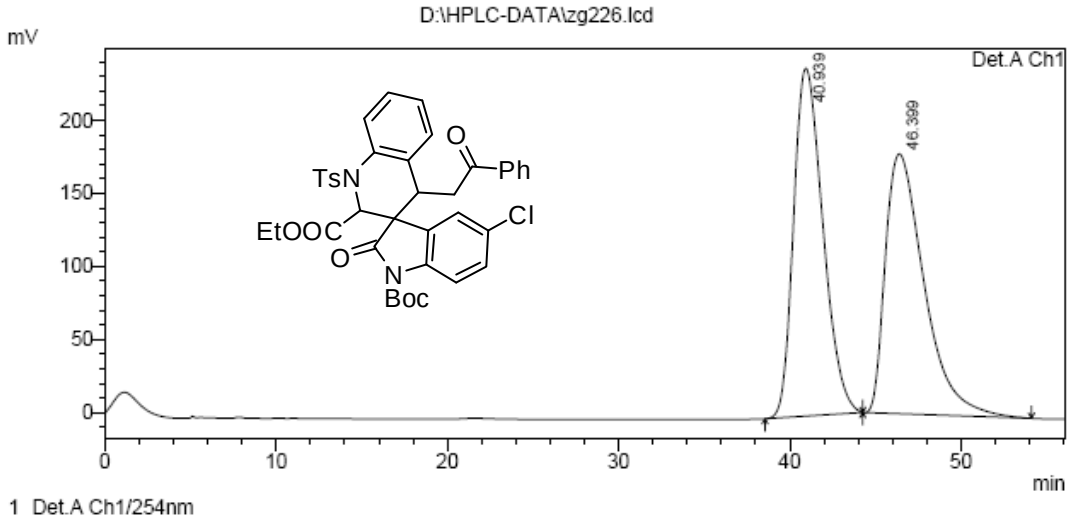


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.492	852436	33320	4.779	11.815
2	17.392	16985419	248682	95.221	88.185
Total		17837854	282001	100.000	100.000

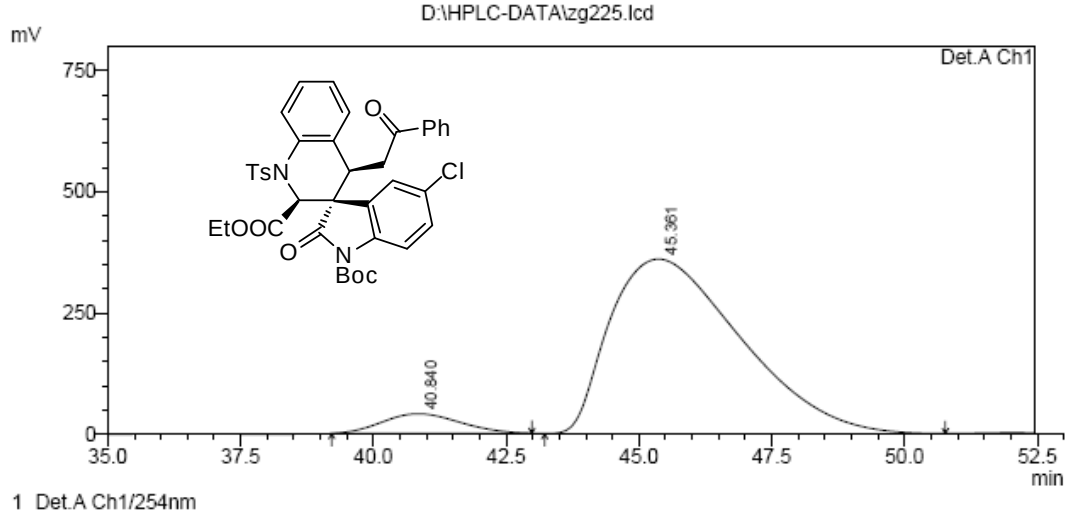
3b



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	40.939	28341458	237939	50.318	57.239
2	46.399	27982745	177752	49.682	42.761
Total		56324203	415691	100.000	100.000

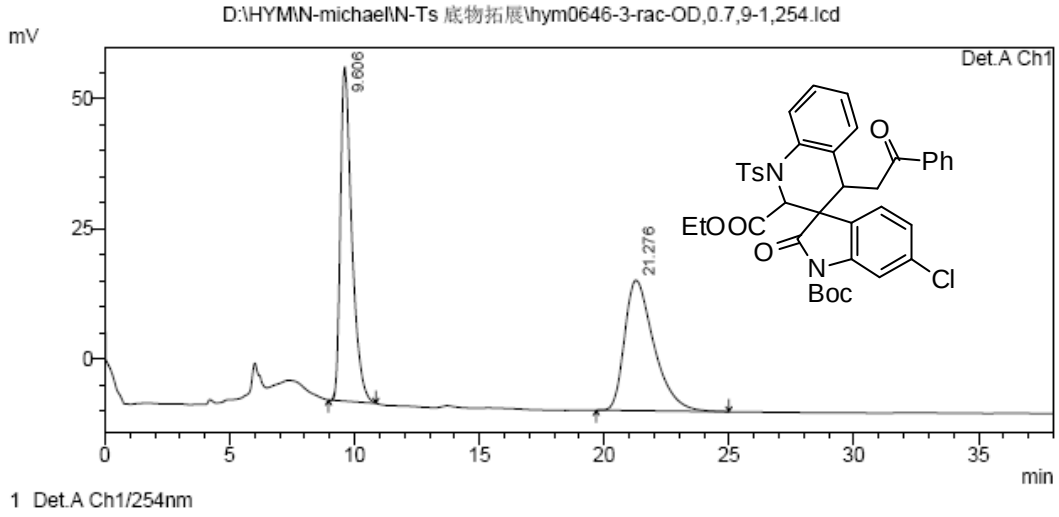


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	40.840	4146905	40554	6.289	10.126
2	45.361	61794514	359949	93.711	89.874
Total		65941419	400503	100.000	100.000

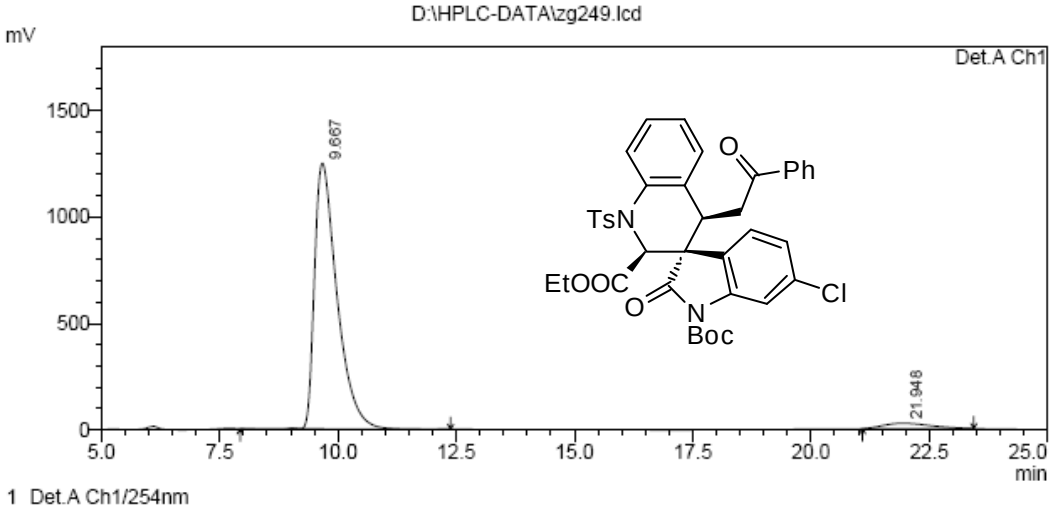
3c



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.606	2041564	64253	49.889	71.927
2	21.276	2050614	25078	50.111	28.073
Total		4092178	89331	100.000	100.000

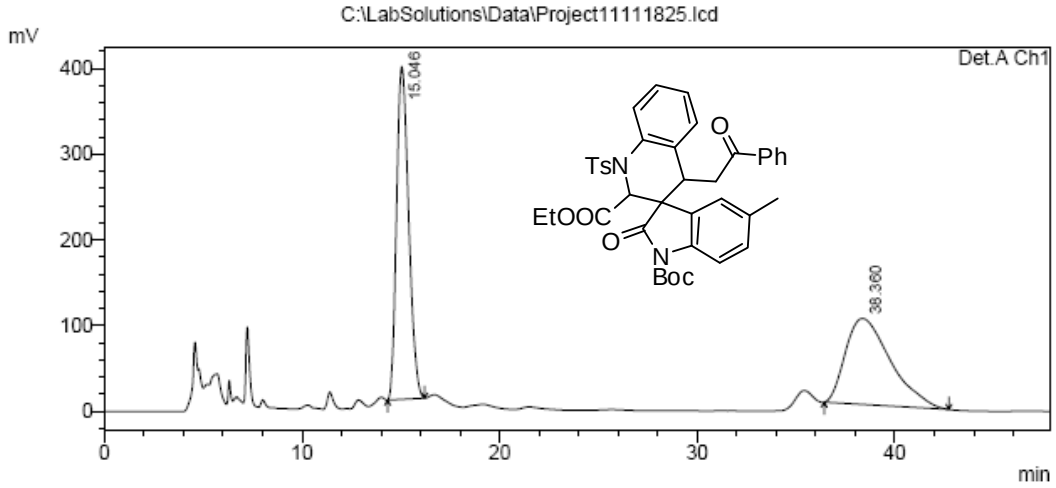


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.667	41077892	1248096	95.804	97.983
2	21.948	1799035	25697	4.196	2.017
Total		42876927	1273793	100.000	100.000

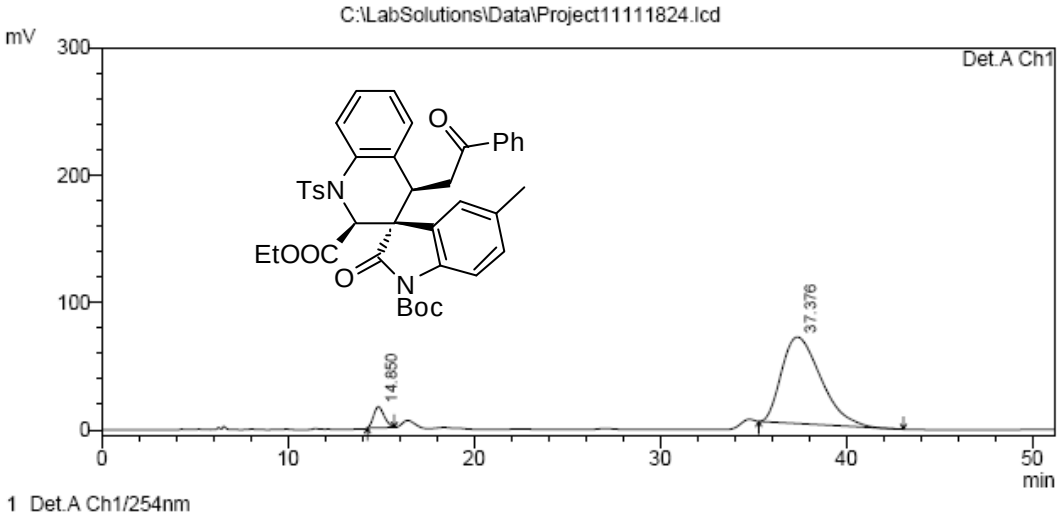
3d



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.046	16552854	388224	50.980	79.480
2	38.360	15916678	100233	49.020	20.520
Total		32469532	488457	100.000	100.000

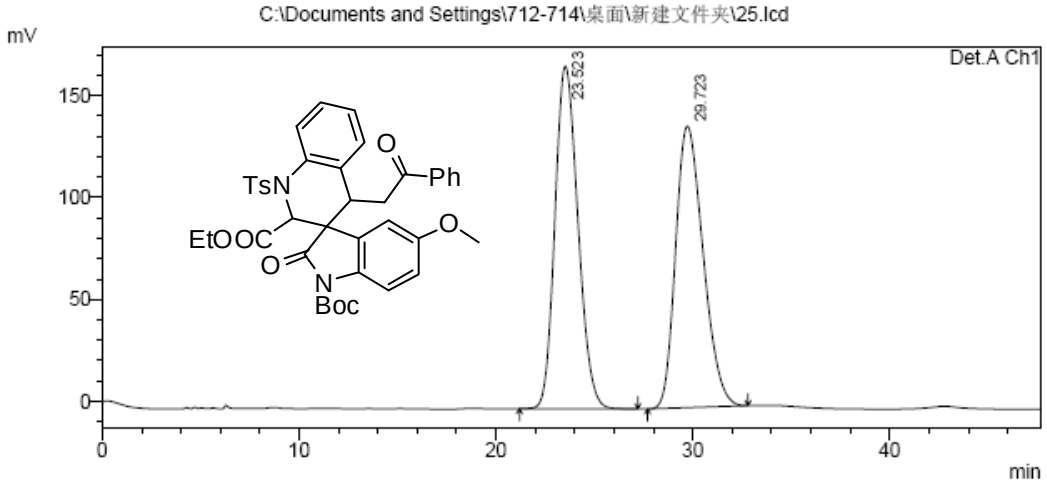


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.850	655455	16536	6.147	19.571
2	37.376	10007480	67956	93.853	80.429
Total		10662934	84492	100.000	100.000

3e

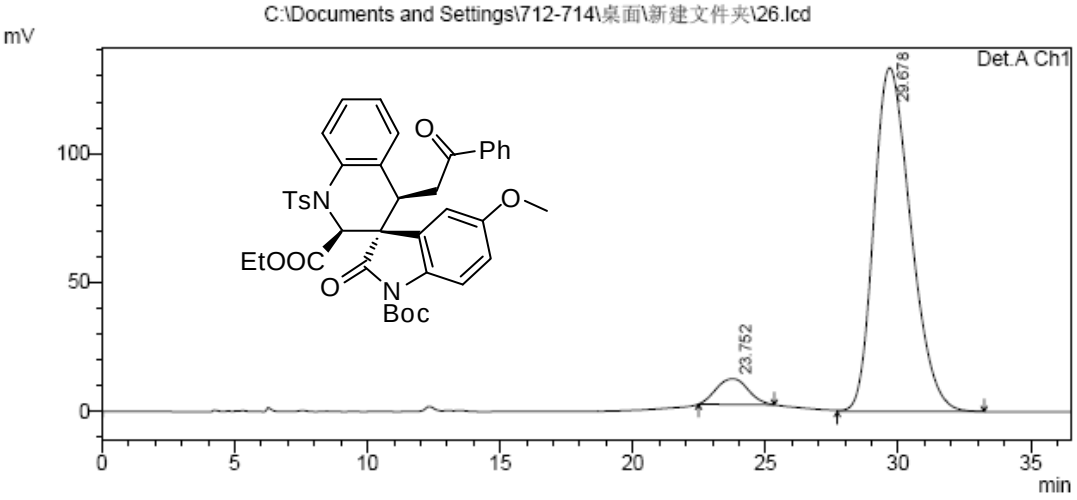


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.523	13658487	168068	50.469	54.914
2	29.723	13404463	137987	49.531	45.086
Total		27062950	306054	100.000	100.000



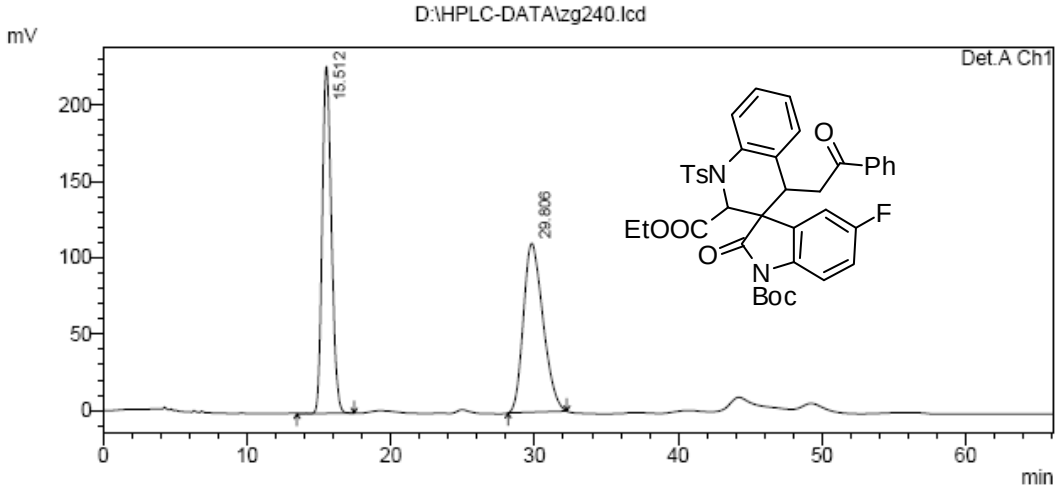
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.752	837304	9969	6.081	6.949
2	29.678	12932178	133493	93.919	93.051
Total		13769481	143462	100.000	100.000

3f

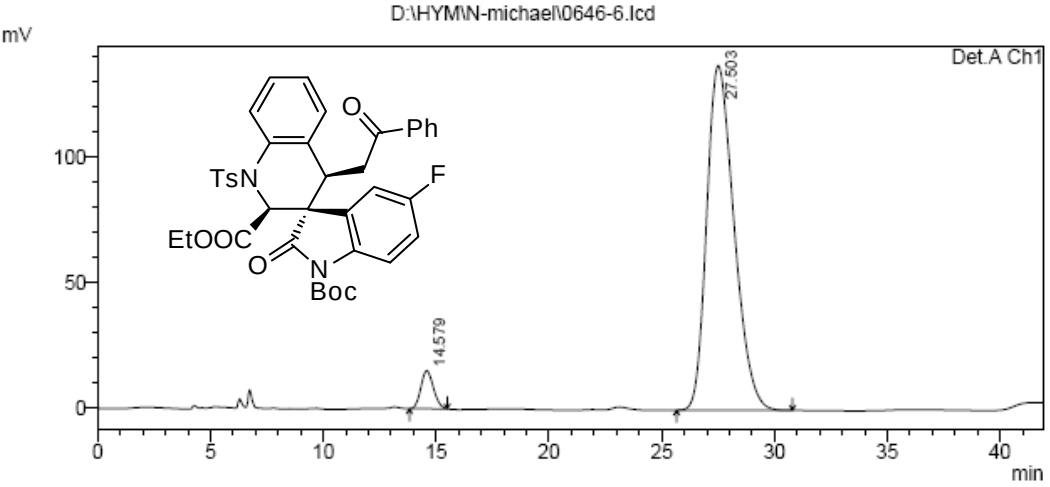


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.512	10127845	226913	49.023	67.258
2	29.806	10531732	110466	50.977	32.742
Total		20659577	337379	100.000	100.000



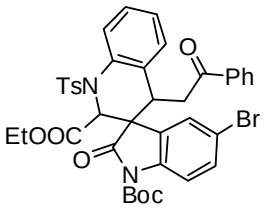
1 Det.A Ch1/254nm

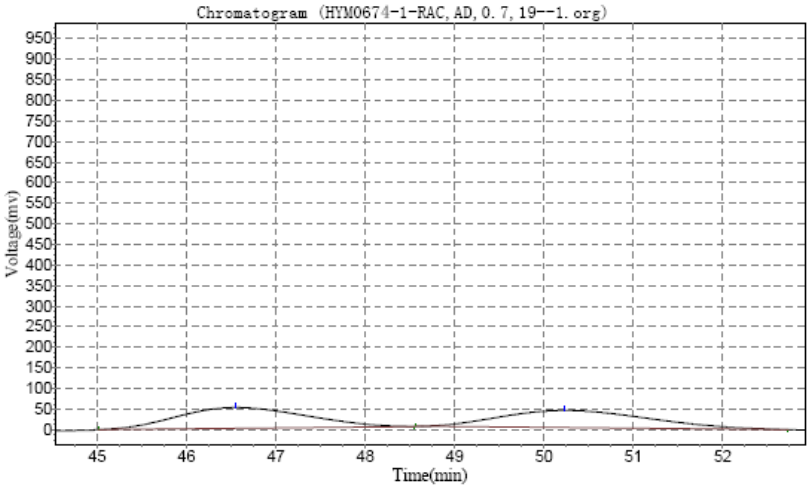
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.579	584971	15113	4.816	9.937
2	27.503	11562053	136980	95.184	90.063
Total		12147024	152093	100.000	100.000

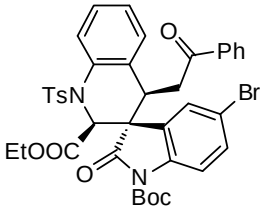
3g

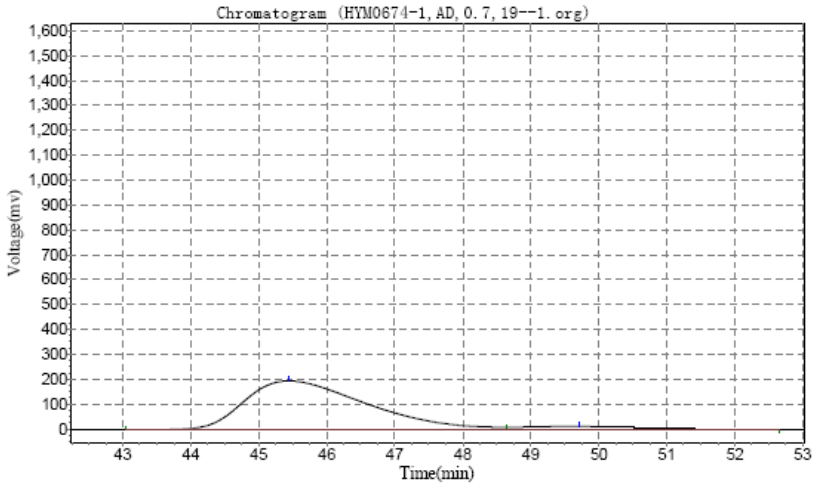




Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		46.545	50339.512	5014042.000	50.7491
2		50.232	41812.945	4866014.000	49.2509
Total			92152.457	9880056.000	100.0000

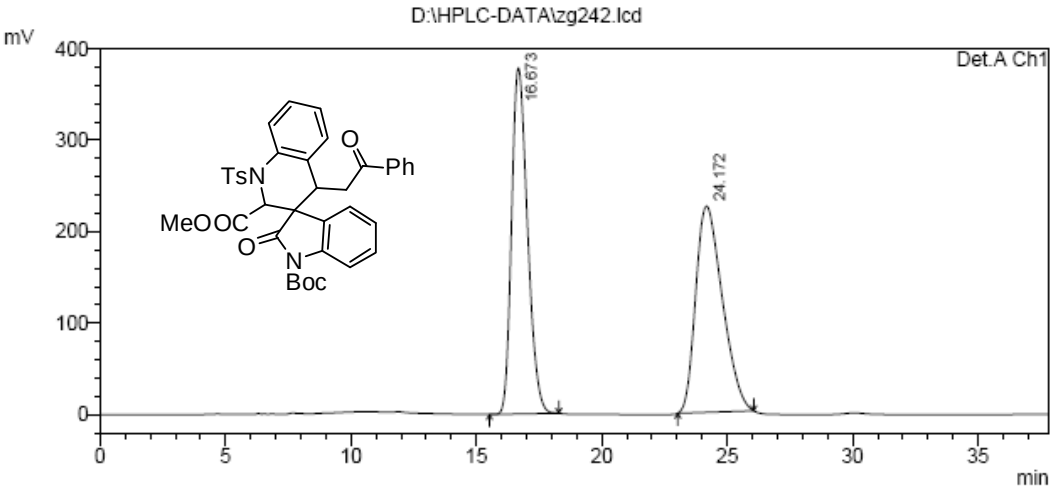




Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		45.448	195042.063	24406456.000	93.6752
2		49.715	13200.951	1647884.250	6.3248
Total			208243.014	26054340.250	100.0000

3h

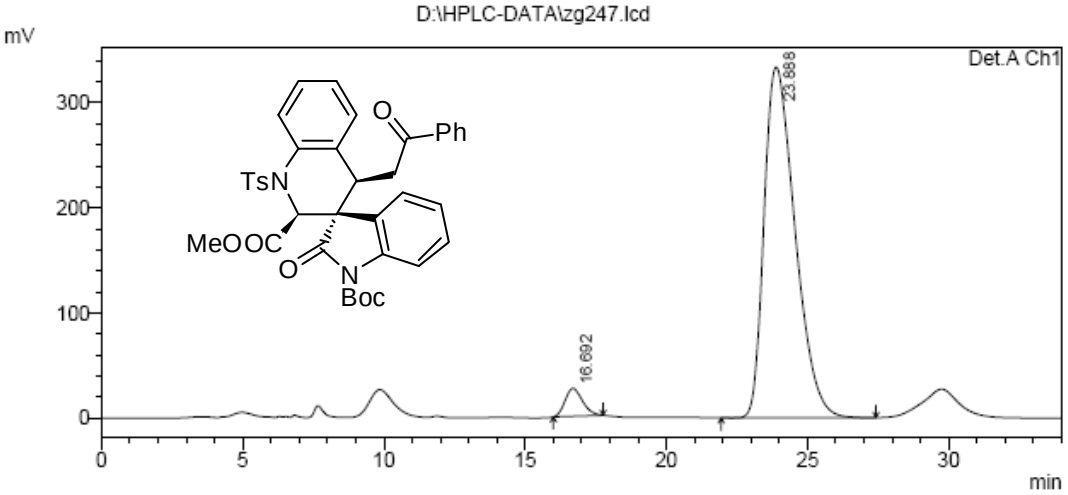


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.673	16675241	378360	49.942	62.647
2	24.172	16714249	225595	50.058	37.353
Total		33389489	603954	100.000	100.000



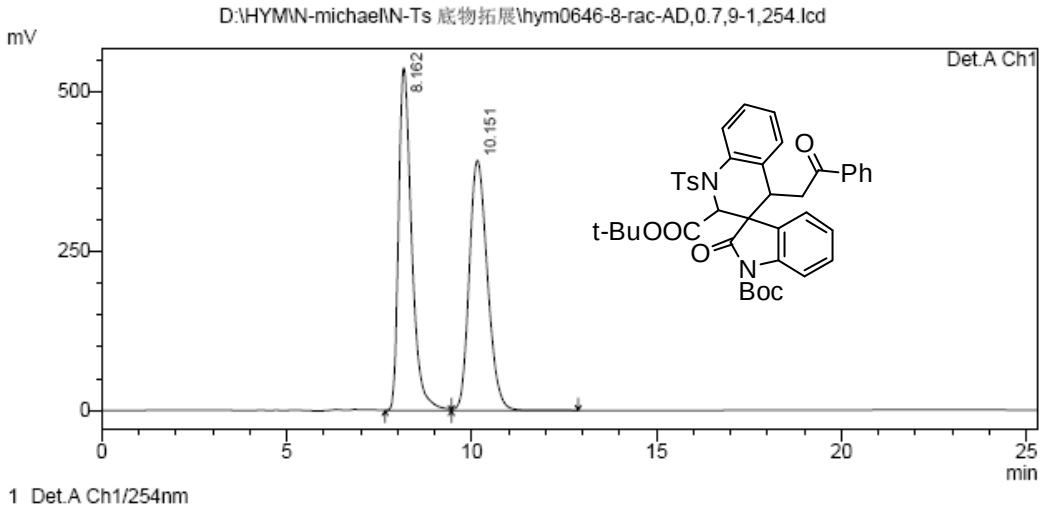
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.692	1140832	26498	4.298	7.353
2	23.888	25401500	333849	95.702	92.647
Total		26542332	360346	100.000	100.000

3i

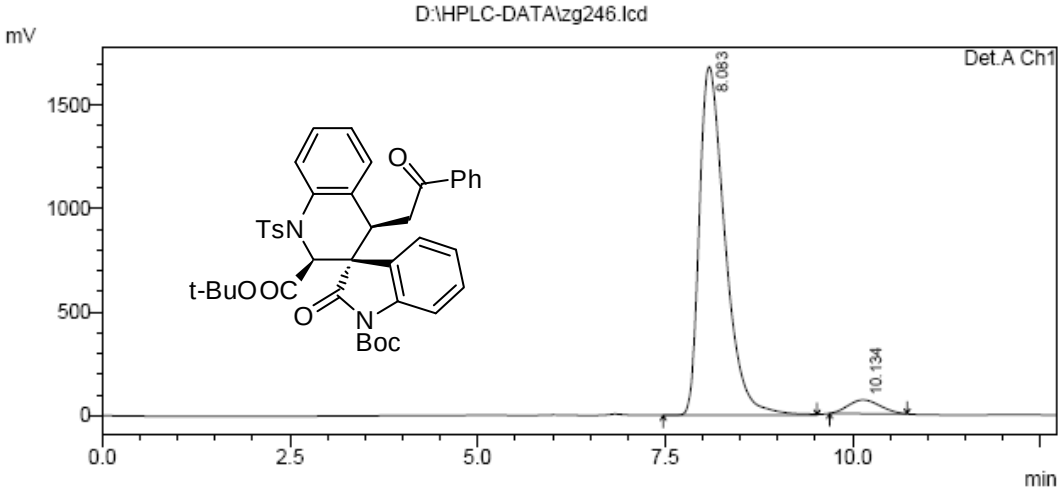


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.162	13222102	537707	49.657	57.824
2	10.151	13404660	392190	50.343	42.176
Total		26626762	929897	100.000	100.000



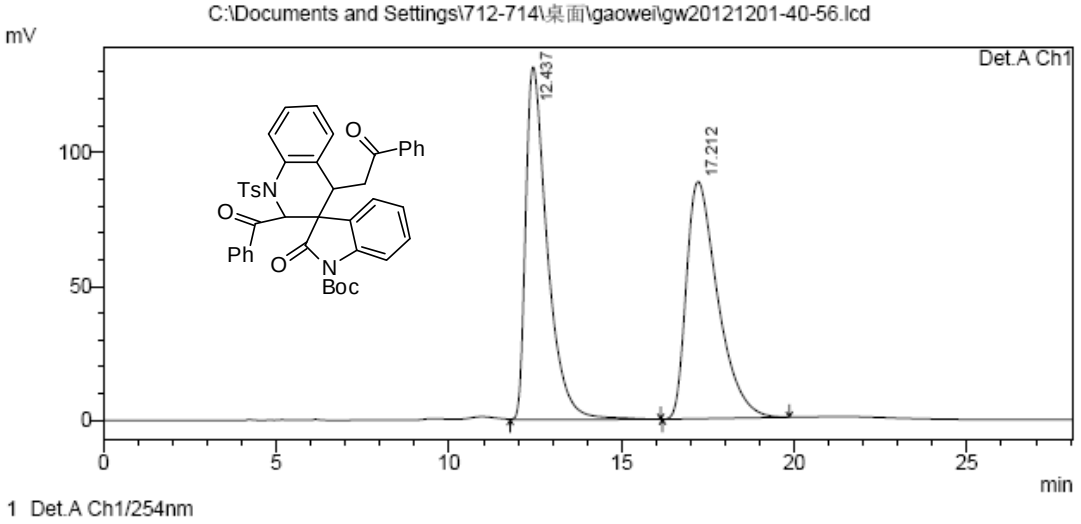
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.083	40174044	1684338	95.320	96.229
2	10.134	1972430	66006	4.680	3.771
Total		42146474	1750344	100.000	100.000

3j

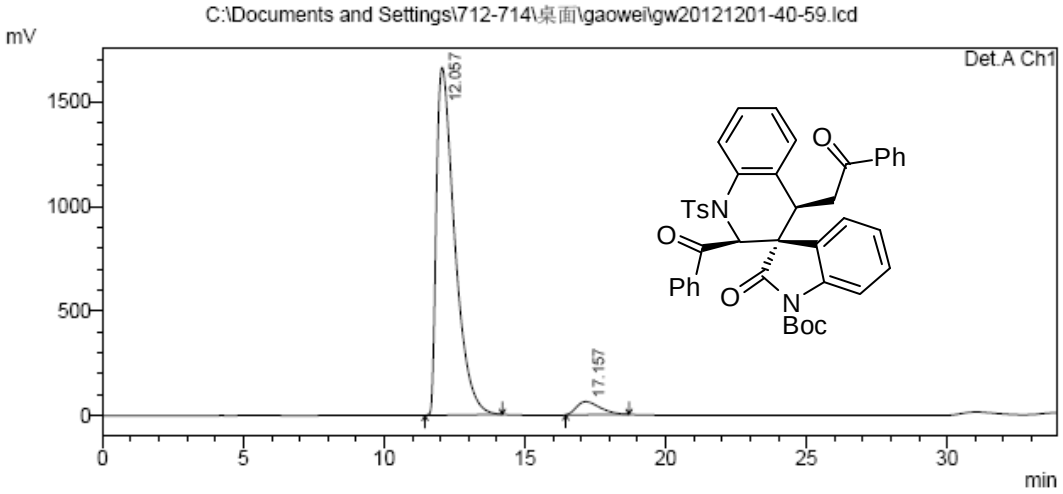


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.437	5736607	131524	50.648	59.782
2	17.212	5589775	88482	49.352	40.218
Total		11326382	220006	100.000	100.000



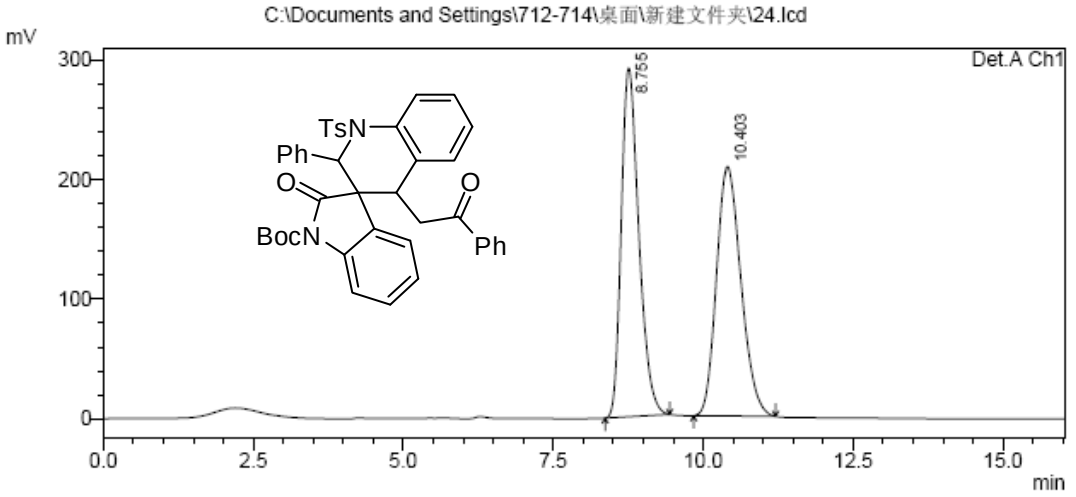
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.057	75104441	1664242	95.386	96.344
2	17.157	3633274	63157	4.614	3.656
Total		78737715	1727399	100.000	100.000

3k

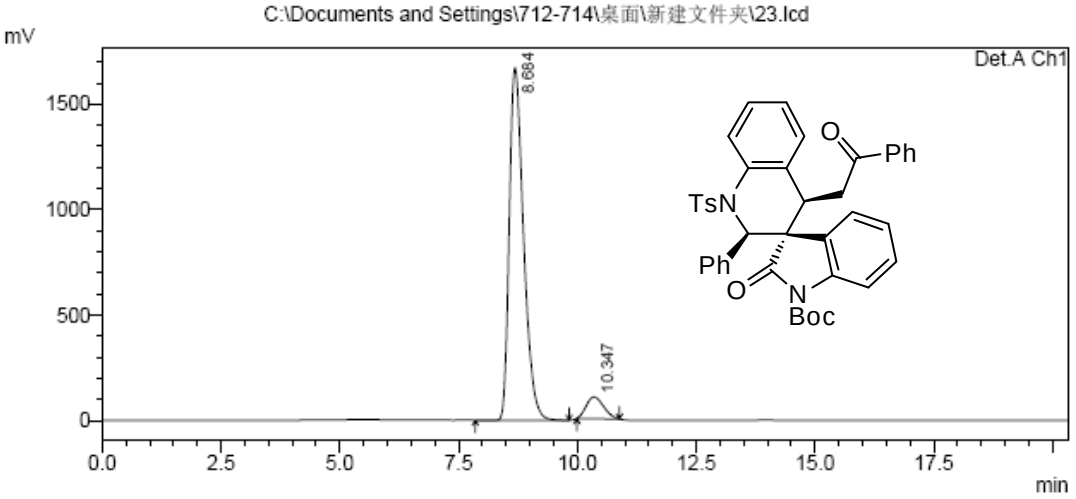


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.755	5952196	291907	50.054	58.301
2	10.403	5939326	208783	49.946	41.699
Total		11891522	500690	100.000	100.000



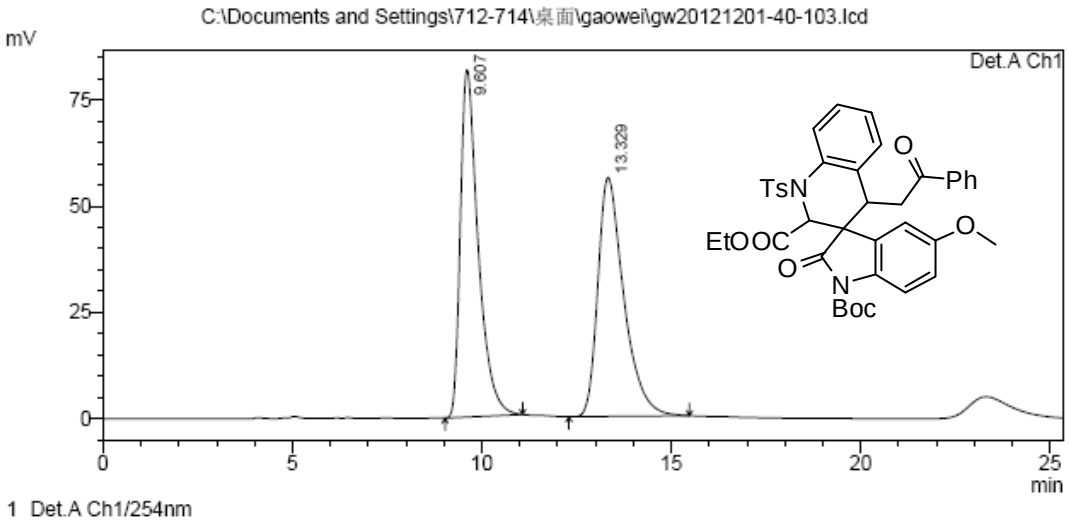
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.684	34863090	1671930	92.995	94.184
2	10.347	2626187	103246	7.005	5.816
Total		37489276	1775176	100.000	100.000

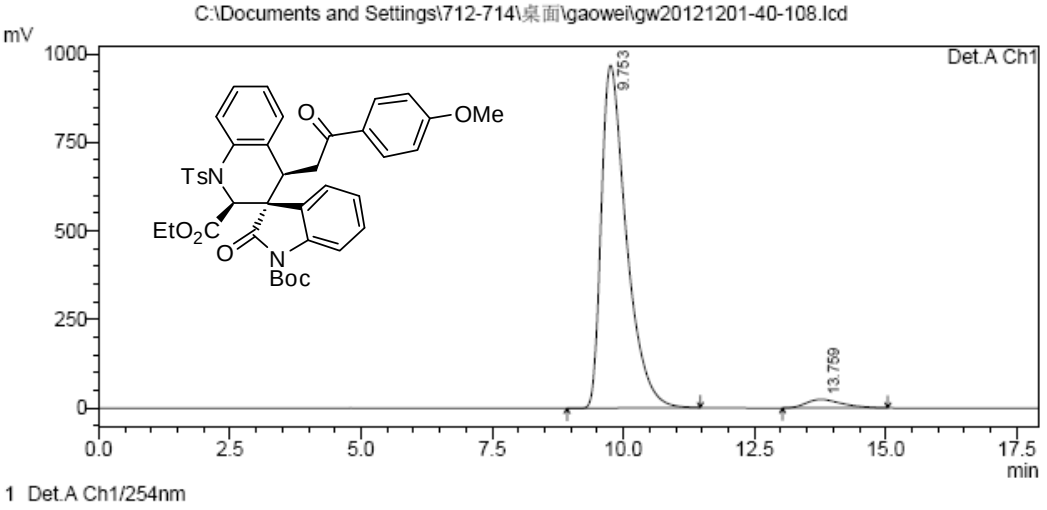
3l



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.607	2675236	81804	49.917	59.228
2	13.329	2684087	56314	50.083	40.772
Total		5359324	138118	100.000	100.000

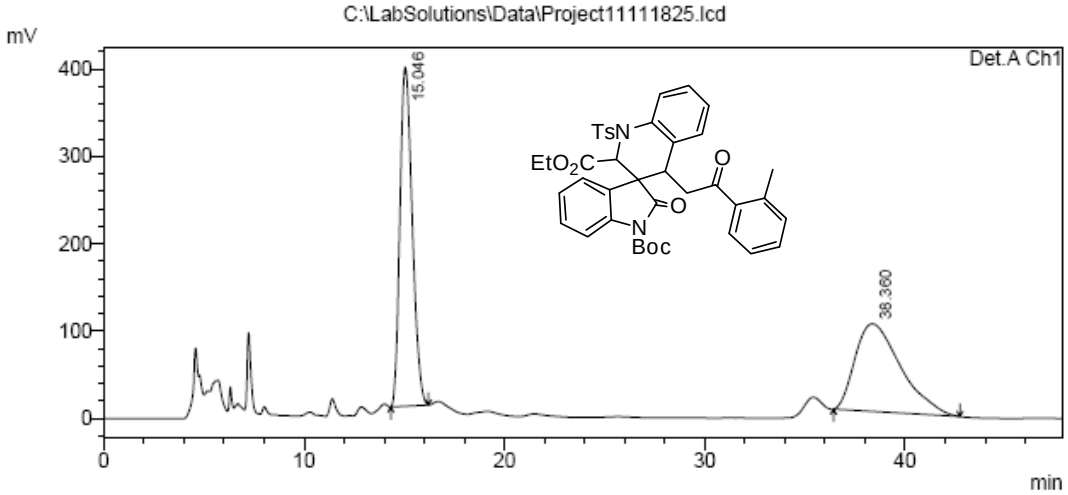


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.753	32143921	967171	96.541	97.554
2	13.759	1151714	24250	3.459	2.446
Total		33295635	991420	100.000	100.000

3m

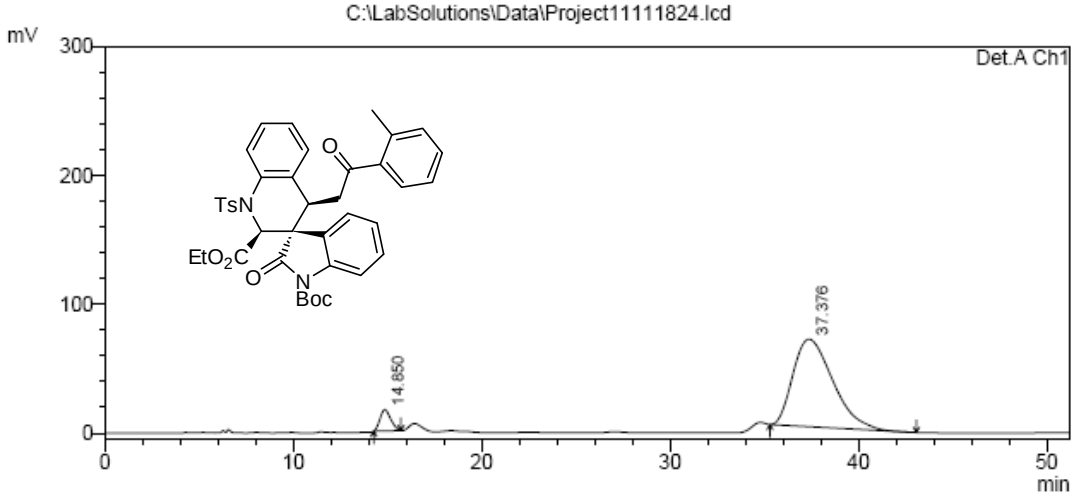


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.046	16552854	388224	50.980	79.480
2	38.360	15916678	100233	49.020	20.520
Total		32469532	488457	100.000	100.000



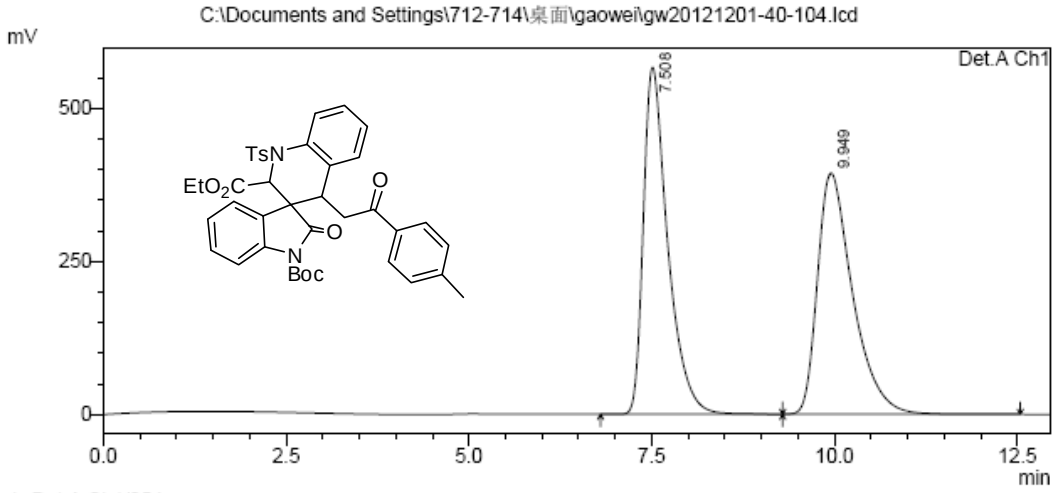
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.850	655455	16536	6.147	19.571
2	37.376	10007480	67956	93.853	80.429
Total		10662934	84492	100.000	100.000

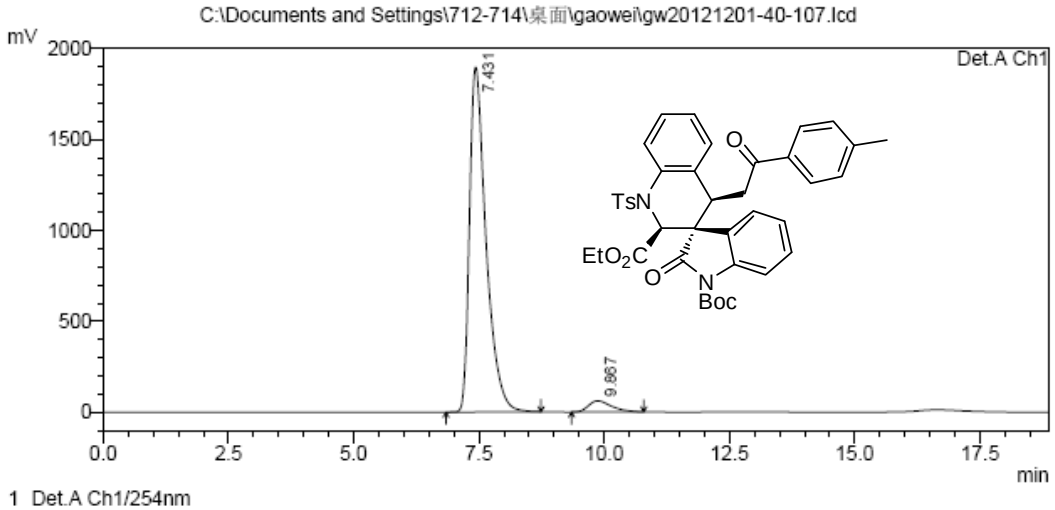
3n



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.508	13175102	566778	49.973	58.981
2	9.949	13189081	394178	50.027	41.019
Total		26364183	960956	100.000	100.000

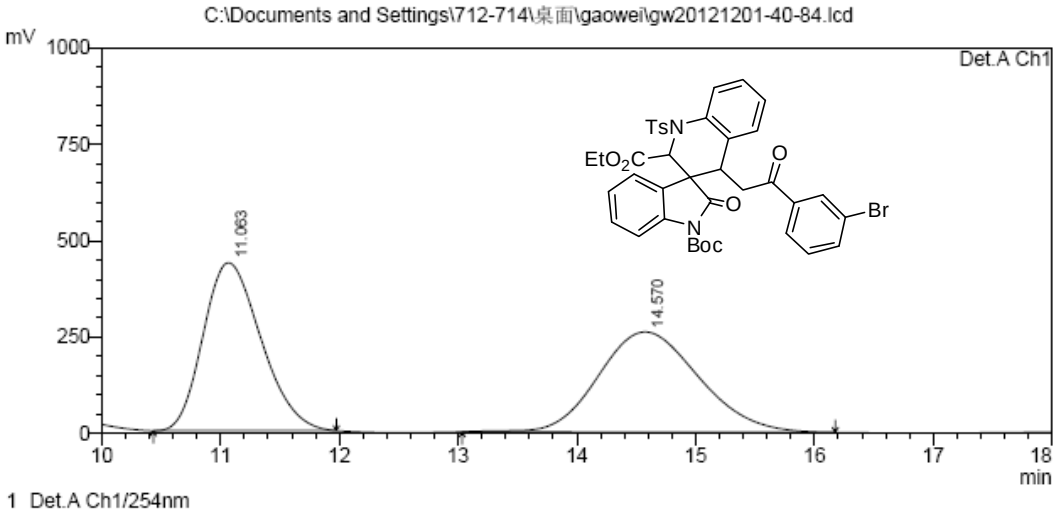


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.431	43557163	1897894	95.712	96.868
2	9.867	1951512	61354	4.288	3.132
Total		45508675	1959248	100.000	100.000

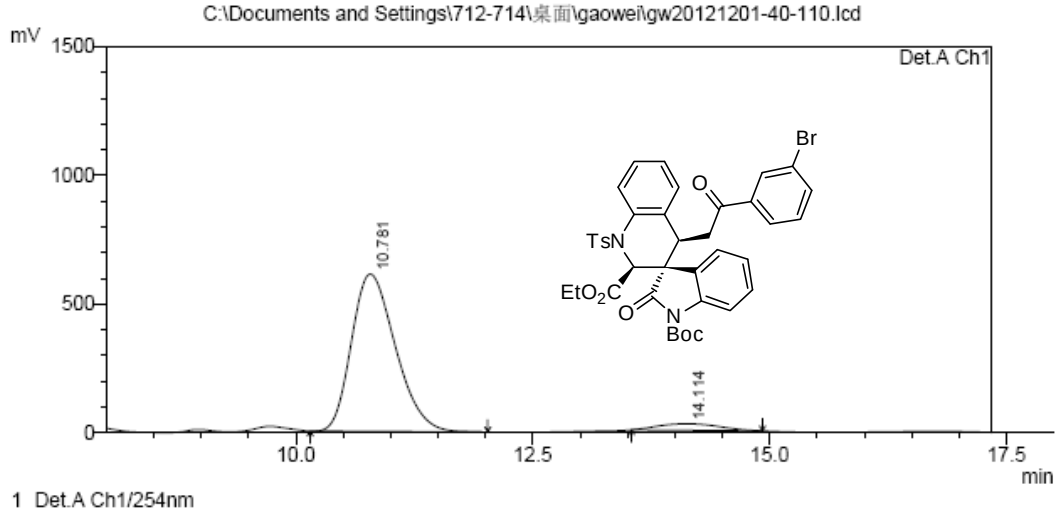
3o



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.063	14794060	436095	49.096	62.634
2	14.570	15339141	260161	50.904	37.366
Total		30133202	696256	100.000	100.000

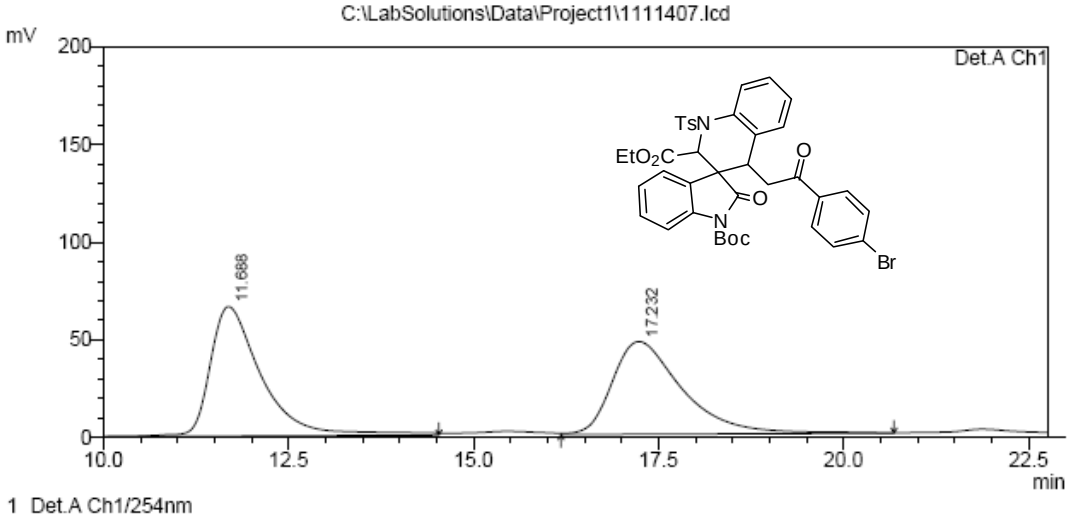


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.781	19739283	611732	94.512	95.956
2	14.114	1146263	25779	5.488	4.044
Total		20885546	637511	100.000	100.000

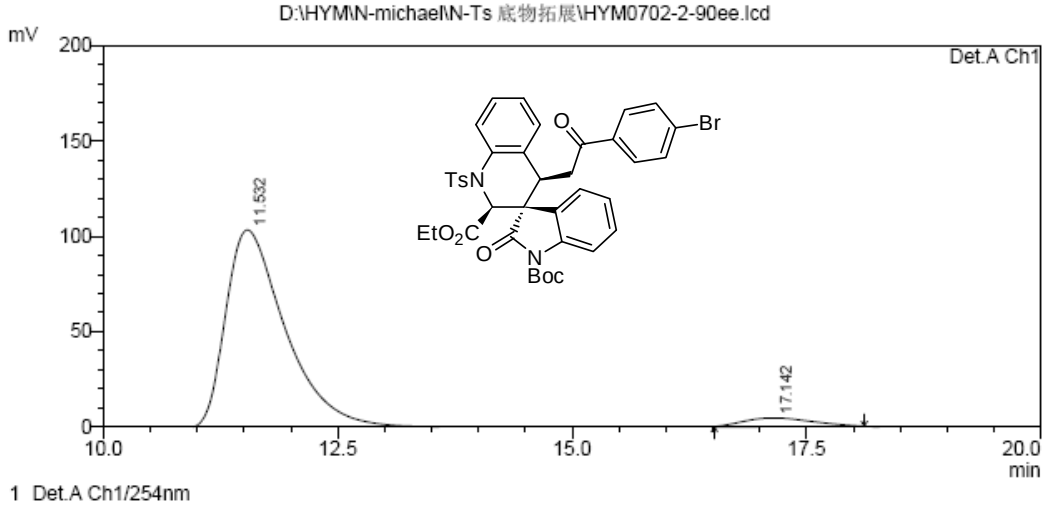
3p



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.688	3227666	66345	50.676	58.280
2	17.232	3141563	47494	49.324	41.720
Total		6369229	113839	100.000	100.000

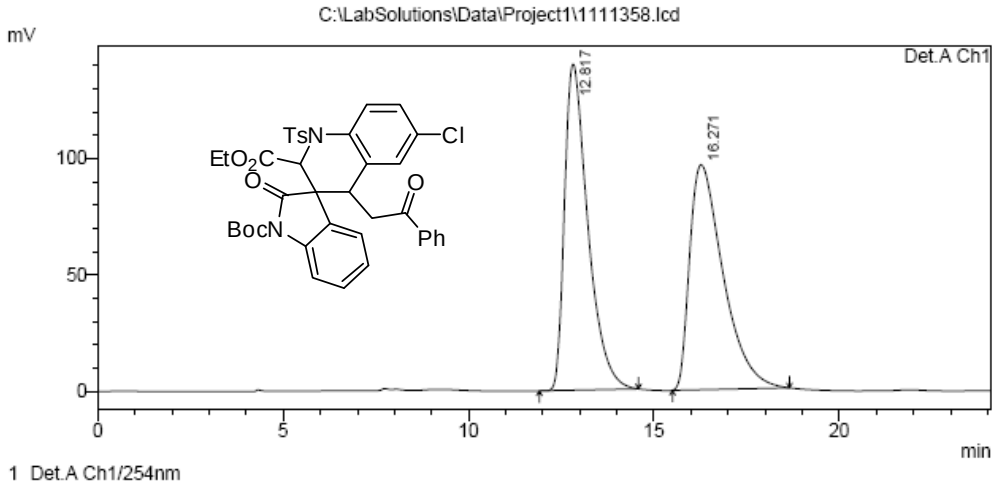


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.532	4619513	103908	95.262	95.817
2	17.142	229733	4536	4.738	4.183
Total		4849247	108444	100.000	100.000

3q

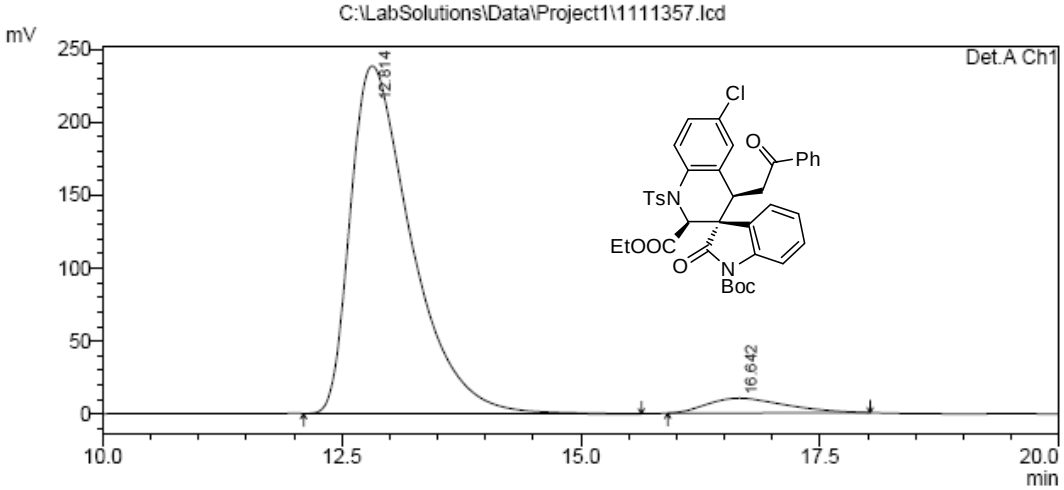


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.817	6131537	139936	50.271	59.160
2	16.271	6065409	96603	49.729	40.840
Total		12196946	236540	100.000	100.000



1 Det.A Ch1/254nm

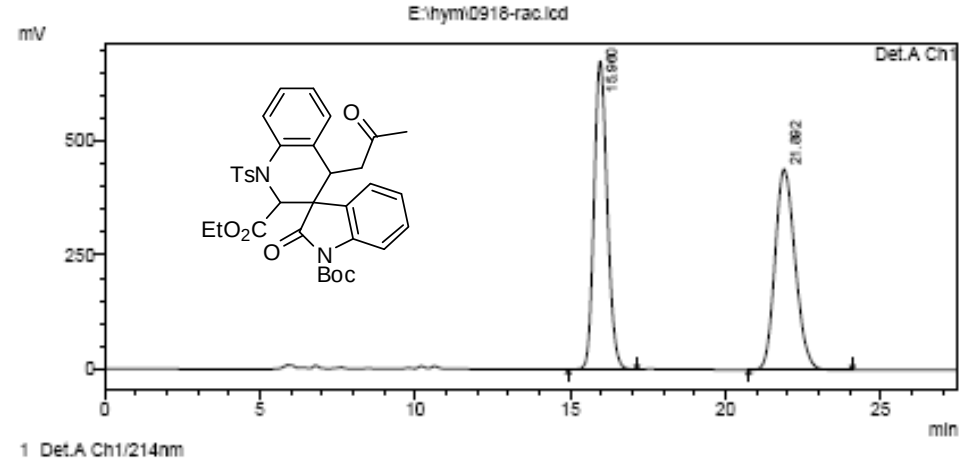
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.814	10590973	238533	94.836	95.949
2	16.642	576703	10071	5.164	4.051
Total		11167676	248604	100.000	100.000

3r

<Chromatogram>



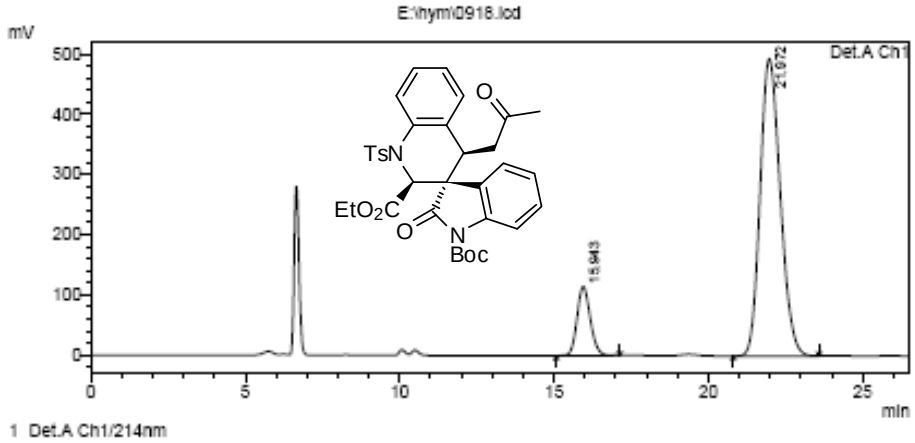
1 Det.A Ch1/214nm

PeakTable

Detector A Ch1 214nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.960	20016826	676551	50.184	60.573
2	21.892	19870311	440358	49.816	39.427
Total		39887136	1116909	100.000	100.000

<Chromatogram>



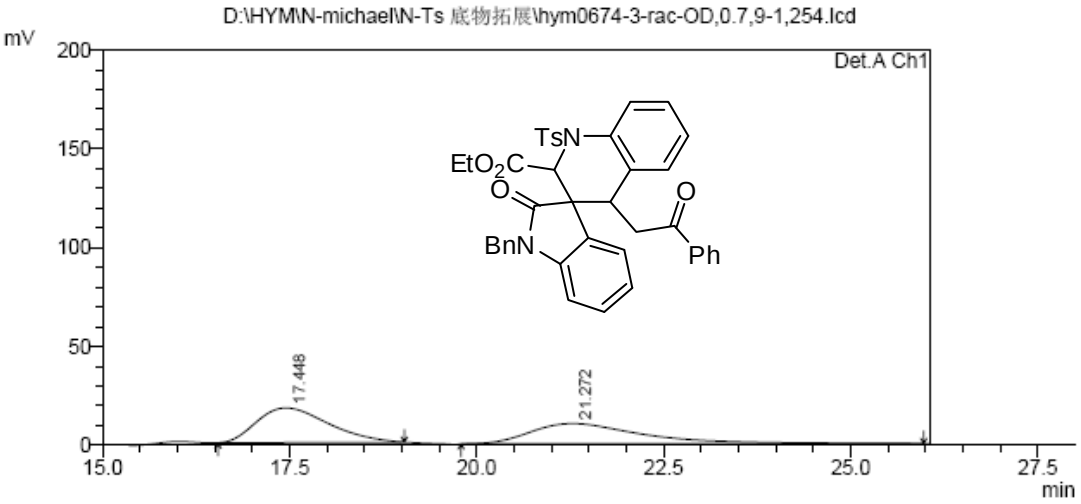
1 Det.A Ch1/214nm

PeakTable

Detector A Ch1 214nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.943	3404898	114535	13.187	18.839
2	21.972	22415002	493420	86.813	81.161
Total		25819900	607955	100.000	100.000

3s

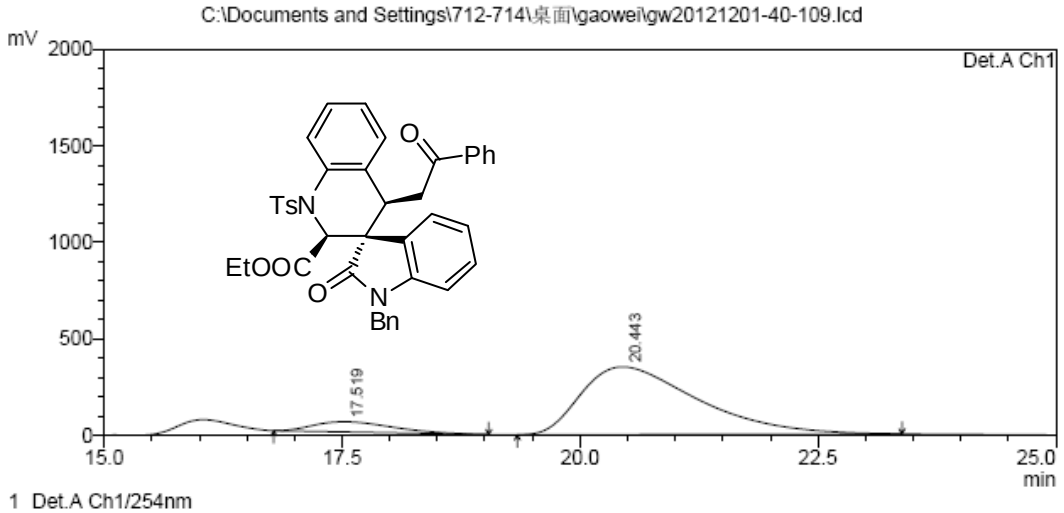


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.448	1177018	17581	52.070	63.096
2	21.272	1083425	10283	47.930	36.904
Total		2260443	27864	100.000	100.000



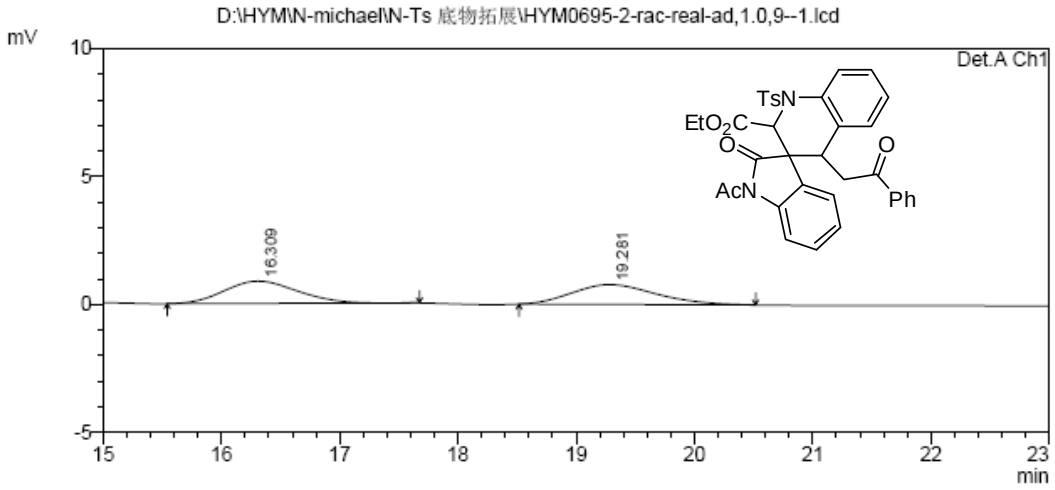
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.519	3044415	52859	9.208	13.087
2	20.443	30020018	351042	90.792	86.913
Total		33064433	403901	100.000	100.000

3t

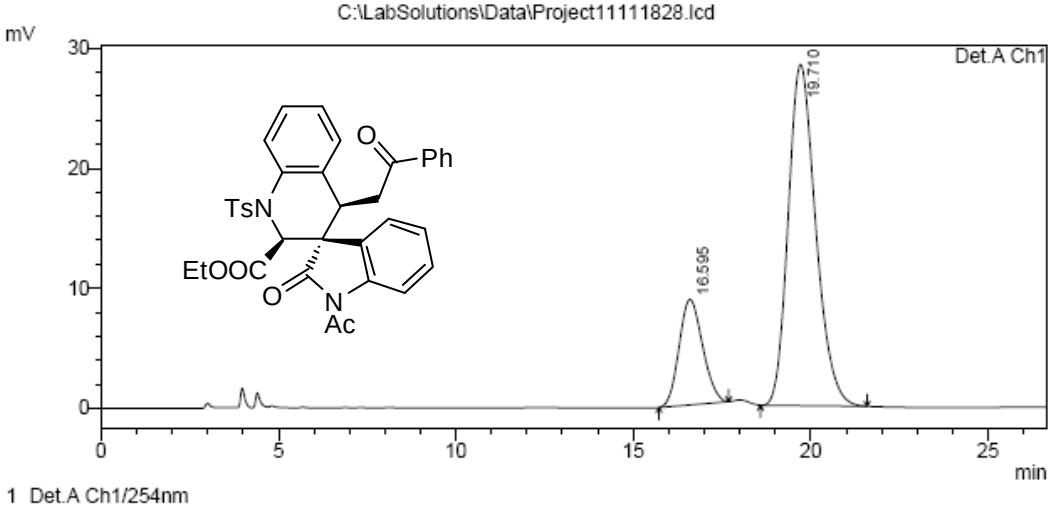


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.309	37632	870	49.375	52.850
2	19.281	38584	776	50.625	47.150
Total		76217	1646	100.000	100.000



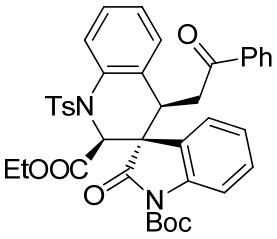
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.595	405382	8806	20.902	23.642
2	19.710	1534082	28442	79.098	76.358
Total		1939464	37248	100.000	100.000

6. X-Ray crystallographic analysis of 3a (CCDC 939070).



3a

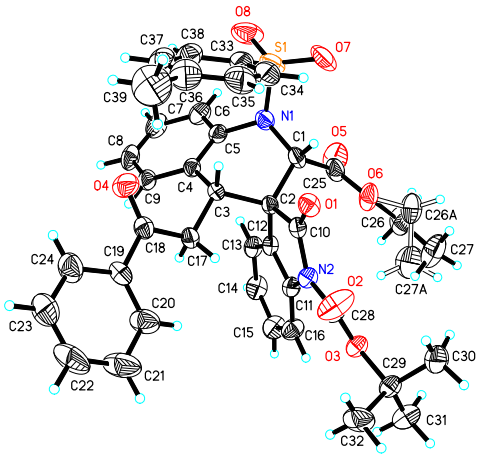


Table. Crystal data and structure refinement

Identification code	cd212663
Empirical formula	C39 H38 N2 O8 S
Formula weight	694.77
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)
Unit cell dimensions	a = 17.7927(14) A alpha = 90 deg.
	b = 11.1432(9) A beta = 102.033(2) deg.
	c = 18.4952(15) A gamma = 90 deg.
Volume	3586.4(5) A^3
Z, Calculated density	4, 1.287 Mg/m^3
Absorption coefficient	0.145 mm^-1
F(000)	1464
Crystal size	0.265 x 0.212 x 0.147 mm
Theta range for data collection	1.78 to 25.99 deg.
Limiting indices	-20<=h<=21, -13<=k<=13, -22<=l<=12
Reflections collected / unique	21908 / 13830 [R(int) = 0.0339]
Completeness to theta = 25.99	100.0 %

Absorption correction	Empirical
Max. and min. transmission	1.00000 and 0.46317
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	13830 / 179 / 979
Goodness-of-fit on F^2	1.019
Final R indices [I>2sigma(I)]	R1 = 0.0572, wR2 = 0.1375
R indices (all data)	R1 = 0.0760, wR2 = 0.1512
Absolute structure parameter	0.01(7)
Largest diff. peak and hole	0.387 and -0.236 e.A^-3