Supporting Information

for

Organocatalytic asymmetric allylic amination of Morita–Baylis–Hillman carbonates of isatins

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General procedures and analytical data

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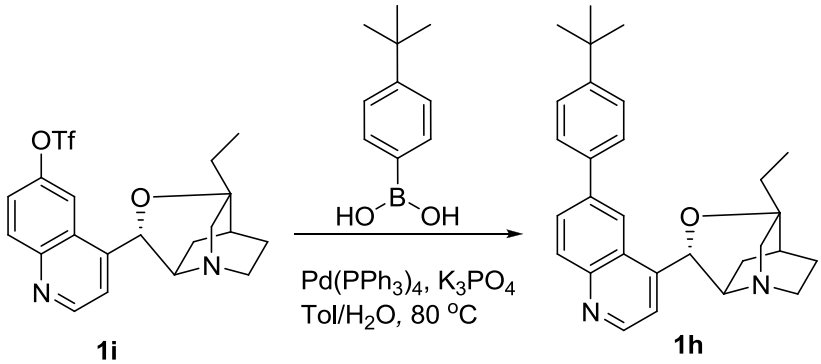
1. General Methods

NMR spectra were recorded with tetramethylsilane as the internal standard. TLC was performed on glass-backed silica plates. Column chromatography was performed using silica gel (200–300 mesh) eluting with ethyl acetate and petroleum ether (PE) (EtOAc/PE). ^{1}H NMR spectra were recorded at 400 MHz (Varian) and ^{13}C NMR spectra were recorded at 100 MHz (Varian). Chemical shifts are reported in ppm downfield from $CDCl_3$ (δ = 7.27 ppm) for ^{1}H NMR and relative to the central $CDCl_3$ resonance (δ = 77.0 ppm) for ^{13}C NMR spectroscopy. Coupling constants are given in hertz (Hz). Optical rotations were measured at 589 nm at 20 °C. Enantiomeric excess was determined by HPLC analysis on Chiralpak IC and Chiralcel OD columns. Et_2O was distilled from sodium (Na) under an argon (Ar) atmosphere. Mesitylene was distilled from CaH_2. Chlorobenzene was dried by 4 Å. All other chemicals were used as commercially available, without purification. Cinchona alkaloids catalysts **1a**, **1b**, **1d** and **1e**–**1h** were prepared according to the literature procedure [1]. Catalysts **1c** was prepared according to the literature procedure [2]. Morita−Baylis−Hillman carbonates of isatins [3] and N-silyloxycarbamates were prepared according to the literature procedure [4].

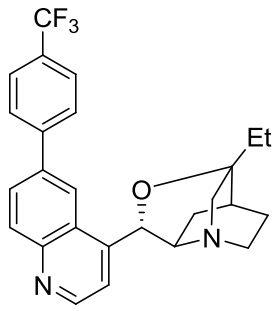
2. Preparation of modified β-ICD-type catalysts



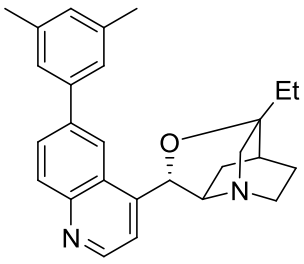
1i **1h**

To a tube charged with $Pd(PPh_3)_4$ (21.9 mg, 0.02 mmol), K_3PO_4 (201.7 mg, 0.95 mmol,), **1i** (168.0 mg, 0.38 mmol) [1] and 4-tert-butylphenylboronic acid (101.5 mg, 0.57 mmol) was added a solution of H_2O (0.4 mL) and toluene (1.2 mL) via syringe under a nitrogen atmosphere. The mixture was heated at 80 °C until **1i** had been consumed according to TLC analysis. The mixture was cooled to room temperature, diluted with ethyl acetate, filtered, and concentrated. The crude material was purified by flash chromatography on silica gel (DCM/MeOH = 20:1) to give **1h** as

white solid (100.3 mg, 62%). $[\alpha]_D^{20}$ = +46.1 (c = 0.8 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 8.92 (d, *J* = 4.8 Hz, 1H), 8.18 (d, *J* = 9.2 Hz, 1H), 8.12 (s, 1H), 7.96 (dd, *J* = 8.8 Hz, 1.6 Hz, 1H), 7.78 (d, *J* = 4.4 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 6.12 (s, 1H), 3.64–3.58 (m, 2H), 3.04–3.02 (m, 2H), 2.71 (d, *J* = 13.6 Hz, 1H), 2.18 (t, *J* = 4.8 Hz, 1H), 1.80 (qd, *J* = 6.8 Hz, 2.0 Hz, 1H), 1.73–1.67 (m, 3H), 1.65–1.53 (m, 1H), 1.37 (s, 9H), 1.32–1.26 (m, 1H), 1.05 (t, *J* = 7.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.9, 149.9, 147.2, 144.4, 139.6, 130.7, 128.9, 127.4, 126.0, 125.7, 119.9, 119.5, 110.7, 77.1, 73.0, 56.8, 54.8, 46.7, 34.6, 32.8, 31.3, 27.4, 24.0, 23.4, 7.3 ppm; ESI–HRMS: calcd. for $C_{29}H_{34}N_2O$ + H 427.2749, found 427.2749.



1f, 70% yield; $[\alpha]_D^{20}$ = +11.2 (*c* = 1.0 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 8.94 (d, *J* = 4.4 Hz, 1H), 8.24–8.20 (m, 2H), 7.91 (dd, *J* = 8.8 Hz, 2.0 Hz, 1H), 7.80–7.78 (m, 3H), 7.68 (d, *J* = 8.0 Hz, 2H), 6.18 (s, 1H), 3.60–3.57 (m, 2H), 3.10–3.00 (m, 2H), 2.66 (d, *J* = 13.6 Hz, 1H), 2.17 (s, 1H), 1.81–1.77 (m, 1H), 1.70–1.62 (m, 3H), 1.57–1.51 (m, 1H), 1.30–1.24 (m, 1H), 1.00 (t, *J* = 7.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.5, 147.6, 144.6, 143.7, 138.1, 133.9, 131.1, 128.6, 128.0, 125.8, 125.8, 125.7, 124.0, 120.9, 119.8, 77.0, 72.8, 56.9, 54.5, 46.6, 32.8, 27.3, 23.9, 23.3, 7.2 ppm; ESI–HRMS: calcd. for $C_{26}H_{25}F_3N_2O$ + H 439.1997, found 439.1996.

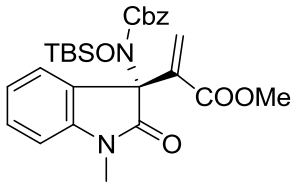


1g, 50% yield; $[\alpha]_D^{20}$ = +9.1 (*c* = 0.9 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 8.93 (d, *J* = 4.4 Hz, 1H), 8.19–8.17 (m, 2H), 7.95 (dd, *J* = 8.8 Hz, 1.6 Hz, 1H), 7.78 (d, *J* = 4.0 Hz, 1H), 7.38 (s, 2H), 7.04 (s, 1H), 6.18 (s, 1H), 3.79–3.75 (m, 2H), 3.11 (s, 2H), 2.79 (d, *J* = 13.6 Hz, 1H), 2.43 (s, 6H), 2.24 (s, 1H), 1.90–1.86 (m, 1H), 1.78–1.69 (m, 3H), 1.65–1.62 (m, 1H), 1.38–1.33 (m, 1H), 1.07 (t, *J* = 7.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.8, 147.3, 143.2, 140.5, 140.0, 138.5, 132.0, 130.7, 129.6, 129.5, 128.5, 125.9, 125.6, 119.9, 119.5, 77.2, 72.2, 57.1, 54.1, 46.1, 32.9, 27.3, 23.1, 22.7, 21.4, 7.3 ppm; ESI–HRMS: calcd. for $C_{27}H_{30}N_2O$ + H 399.2436, found 399.2437.

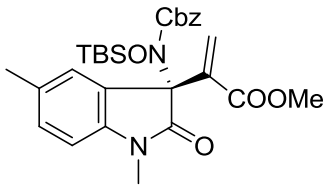
3. General procedure for assembly of MBH carbonates and *N*-silyloxycarbamates

To a solution of MBH carbonate **2a** (41.6 mg, 0.12 mmol), *N*-silyloxycarbamates **3d** (28.1 mg, 0.1

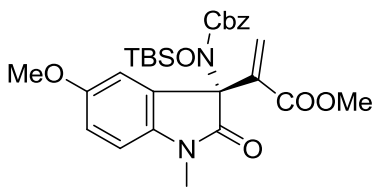
mmol) in chlorobenzene (0.5 mL) at 0 °C, catalyst **1h** (4.3 mg, 10 mol %) was added and the resulting mixture was kept at the temperature until the consumption of **3d**, as monitored by TLC analysis. Purification by flash chromatography on silica gel (AcOEt/petroleum ether = 1:15) gave **4d** as a reddish brown oil (47.0 mg, 92% yield).



4d, 92% yield; $[\alpha]_D^{20} = -100.8$ (c = 0.5 in $CHCl_3$); 91% ee, determined by HPLC analysis [Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, *t* (major) = 9.463 min, *t* (minor) = 13.188 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76（d, *J* = 6.8 Hz, 1H）, 7.32–7.27 (m, 6H), 7.01 (td, *J* = 7.6 Hz, 0.8 Hz, 1H), 6.78 (d, *J* = 7.6 Hz, 1H), 6.08 (s, 1H), 5.57 (s, 1H), 5.19 (d, *J* = 11.6 Hz, 1H), 5.11 (d, *J* = 12.0 Hz, 1H), 3.67 (s, 3H), 3.20 (s, 3H), 0.59 (s, 9H), 0.04 (s, 3H), −0.15 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.2, 165.1, 159.9, 143.8, 138.1, 135.1, 129.5, 128.8, 128.3, 128.2, 128.2, 126.9, 124.9, 122.6, 108.3, 68.5, 51.8, 26.4, 25.6, 17.9, −4.3, −4.6 ppm; ESI–HRMS: calcd. for $C_{27}H_{34}N_2O_6Si$ + Na 533.2084, found 533.2089.

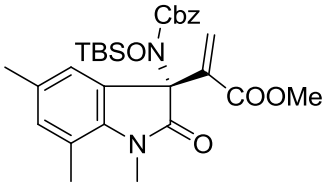


4f, 93% yield; $[\alpha]_D^{20} = -64.8$ (c = 1.1 in $CHCl_3$); 91% ee, determined by HPLC analysis [Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, *t* (major) = 10.204 min, *t* (minor) = 14.245 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (s, 1H), 7.34–7.31 (s, 5H), 7.07 (d, *J* = 7.6 Hz, 1H), 6.67 (d, *J* = 7.6 Hz, 1H), 6.06 (s, 1H), 5.55 (s, 1H), 5.20 (d, *J* = 12.0 Hz, 1H), 5.12 (d, *J* = 12.0 Hz, 1H), 3.67 (s, 3H), 3.19 (s, 3H), 2.29 (s, 3H), 0.59 (s, 9H), 0.03 (s, 3H), −0.15 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.2, 165.1, 159.9, 141.4, 138.3, 135.1, 132.1, 129.6, 128.8, 128.3, 128.2, 128.2, 127.8, 124.6, 108.0, 68.4, 51.8, 26.4, 25.6, 21.1, 17.9, −4.3, −4.7 ppm; ESI–HRMS: calcd. for $C_{28}H_{36}N_2O_6Si$ + Na 547.2240, found 547.2239.

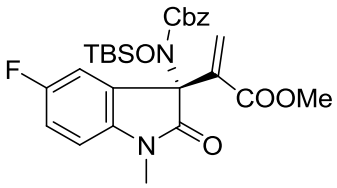


4g, 97% yield; $[\alpha]_D^{20} = -64.0$ (c = 1.0 in $CHCl_3$); 94% ee, determined by HPLC analysis [Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, *t* (major) = 13.032 min, *t* (minor) = 18.202 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 (d, *J* = 2.8 Hz, 1H), 7.31 (s, 5H), 6.81 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 6.68 (d, *J* = 8.4 Hz, 1H), 6.06 (s, 1H), 5.56 (s, 3H), 5.19 (d, *J* = 11.6 Hz, 1H), 5.11 (d, *J* = 11.6 Hz, 1H), 3.74 (s, 3H),

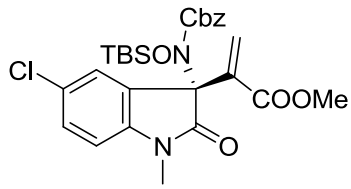
3.66 (s, 3H), 3.17 (s, 3H), 0.60 (s, 9H), 0.05 (s, 3H), −0.10 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.0, 165.0, 159.8, 155.8, 138.1, 137.2, 135.1, 129.4, 128.8, 128.2, 128.2, 124.9, 114.2, 114.0, 108.6, 75.6, 68.4, 55.7, 51.8, 26.4, 25.6, 17.9, −4.2, −4.5 ppm; ESI–HRMS: calcd. for $C_{28}H_{36}N_2O_7Si$ + Na 563.2189, found 563.2187.



4h, 93% yield; $[\alpha]_D^{20}$ = −60.0 (*c* = 0.8 in $CHCl_3$); 90% ee, determined by HPLC analysis [Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, *t* (major) = 12.702 min, *t* (minor) = 15.971 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (s, 1H), 7.33 (s, 5H), 6.81 (s, 1H), 6.06 (s, 1H), 5.54 (s, 1H), 5.18 (d, *J* = 12.0 Hz, 1H), 5.12 (d, *J* = 11.6 Hz, 1H), 3.66 (s, 3H), 3.44 (s, 3H), 2.46 (s, 3H), 2.23 (s, 3H), 0.62 (s, 9H), 0.04 (s, 3H), −0.14 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.1, 165.1, 160.0, 139.1, 138.5, 135.2, 133.6, 131.9, 129.1, 128.8, 128.2, 128.1, 125.5, 124.8, 119.4, 74.5, 68.4, 51.8, 29.9, 25.6, 20.8, 18.9, 17.9, −4.2, −4.7 ppm; ESI–HRMS: calcd. for $C_{29}H_{38}N_2O_6Si$ + Na 561.2397, found 561.2394.

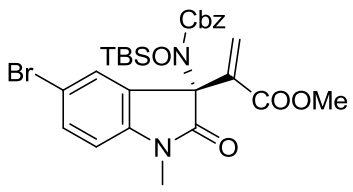


4i, 86% yield; $[\alpha]_D^{20}$ = −64.3 (*c* = 1.1 in $CHCl_3$); 90% ee, determined by HPLC analysis [Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, *t* (major) = 7.288 min, *t* (minor) = 8.890 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 7.32 (s, 5H), 6.99 (td, *J* = 8.4 Hz, 2.4 Hz, 1H), 6.70 (dd, *J* = 8.4 Hz, 4.0 Hz, 1H), 6.10 (s, 1H), 5.60 (s, 1H), 5.19 (d, *J* = 12.0 Hz, 1H), 5.11 (d, *J* = 12.0 Hz, 1H), 3.68 (s, 3H), 3.20 (s, 3H), 0.61 (s, 9H), 0.04 (s, 3H), -0.10 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.1, 164.9, 160.0 (d, $^1J_{C,F}$ = 239.1 Hz), 159.6, 139.8, 137.6, 134.9, 129.8, 128.9, 128.3, 128.3, 125.4, 115.6 (d, $^2J_{C,F}$ = 23.5 Hz), 115.4 (d, $^2J_{C,F}$ = 26.1 Hz), 108.6 (d, $^3J_{C,F}$ = 8.0 Hz), 68.6, 52.0, 26.6, 25.6, 17.9, -4.3, -4.6 ppm; ESI–HRMS: calcd. for $C_{27}H_{33}FN_2O_6Si$ + Na 551.1990, found 551.1993.

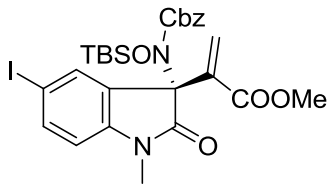


4j, 88% yield; $[\alpha]_D^{20}$ = −62.8 (*c* = 1.1 in $CHCl_3$); 89% ee, determined by HPLC analysis [Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, *t* (major) = 7.504 min, *t* (minor) = 9.269 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 2.0 Hz, 1H), 7.32 (s, 5H), 7.26 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 6.70 (d, *J* = 8.4 Hz, 1H), 6.10 (s, 1H), 5.59 (s, 1H), 5.19

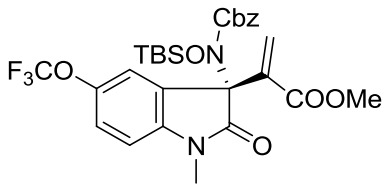
(d, J = 11.6 Hz, 1H), 5.11 (d, J = 11.6 Hz, 1H), 3.67 (s, 3H), 3.20 (s, 3H), 0.61 (s, 9H), 0.04 (s, 3H), −0.11 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.0, 164.8, 159.6, 142.4, 137.6, 134.9, 129.9, 129.3, 128.9, 128.3, 128.3, 128.0, 127.5, 125.3, 109.1, 68.6, 52.0, 26.5, 25.6, 17.9, −4.3, −4.6 ppm; ESI–HRMS: calcd. for $C_{27}H_{33}ClN_2O_6Si$ + Na 567.1694, found 567.1698.



4k, 81% yield; $[\alpha]_D^{20}$ = −54.6 (c = 0.9 in $CHCl_3$); 88% ee, determined by HPLC analysis [Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 7.186 min, t (minor) = 8.624 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (d, J = 2.0 Hz, 1H), 7.40 (dd, J = 8.0 Hz, 2.0 Hz, 1H), 7.32 (s, 5H), 6.65 (d, J = 8.4 Hz, 1H), 6.10 (s, 1H), 5.59 (s, 1H), 5.19 (d, J = 11.6 Hz, 1H), 5.10 (d, J = 11.6 Hz, 1H), 3.67 (s, 3H), 3.19 (s, 3H), 0.59 (s, 9H), 0.03 (s, 3H), −0.11 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.9, 164.8, 159.6, 142.9, 137.6, 134.9, 132.2, 130.2, 128.9, 128.3, 128.3, 125.3, 115.4, 109.7, 74.8, 68.6, 52.0, 26.5, 25.6, 17.9, −4.3, −4.6 ppm; ESI–HRMS: calcd. for $C_{27}H_{33}BrN_2O_6Si$ + Na 611.1189, found 611.1195.

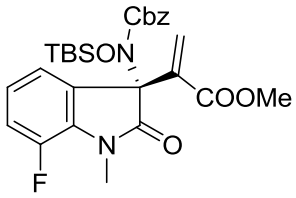


4l, 85% yield; $[\alpha]_D^{20}$ = −57.5 (c = 1.2 in $CHCl_3$); 86% ee, determined by HPLC analysis [Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 7.946 min, t (minor) = 9.788 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, J = 1.6 Hz, 1H), 7.60 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 7.32 (s, 5H), 6.56 (d, J = 8.4 Hz, 1H), 6.10 (s, 1H), 5.58 (s, 1H), 5.19 (d, J = 12.0 Hz, 1H), 5.11 (d, J = 11.6 Hz, 1H), 3.67 (s, 3H), 3.20 (s, 3H), 0.60 (s, 9H), 0.03 (s, 3H), −0.10 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.7, 164.8, 159.6, 143.6, 138.2, 137.6, 135.6, 134.9, 130.6, 128.9, 128.3, 128.3, 125.3, 110.3, 68.6, 52.0, 26.5, 25.6, 17.9, −4.3, −4.6 ppm; ESI–HRMS: calcd. for $C_{27}H_{33}IN_2O_6Si$ + Na 659.1050, found 659.1046.



4m, 71% yield; $[\alpha]_D^{20}$ = −59.4 (c = 0.6 in $CHCl_3$); 85% ee, determined by HPLC analysis [Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 5.957 min, t (minor) = 6.527 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 (s, 1H), 7.31 (s, 5H), 7.16 (d, J = 8.4 Hz, 1H), 6.75 (d, J = 8.4 Hz, 1H), 6.11 (s, 1H), 5.60 (s,

1H), 5.18 (d, J = 11.6 Hz, 1H), 5.09 (d, J = 11.6 Hz, 1H), 3.67 (s, 3H), 3.21 (s, 3H), 0.60 (s, 9H), 0.04 (s, 3H), −0.13 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.1, 164.9, 159.5, 144.6, 142.5, 137.5, 134.9, 129.7, 128.9, 128.3, 128.3, 125.6, 122.5, 121.1, 119.2, 108.6, 75.0, 68.7, 52.0, 26.6, 25.6, 17.9, −4.2, −4.9 ppm; ESI–HRMS: calcd. for $C_{28}H_{33}F_3N_2O_7Si$ + Na 617.1907, found 617.1912.



4n, 85% yield; $[\alpha]_D^{20}$ = −49.5 (c = 0.5 in $CHCl_3$); 90% ee, determined by HPLC analysis [Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 6.892 min, t (minor) = 8.365 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 (dd, J = 7.6 Hz, 0.8 Hz, 1H), 7.34-7.30 (m, 5H), 7.04–7.00 (m, 1H), 6.95–6.90 (m, 1H), 6.12 (s, 1H), 5.61 (s, 1H), 5.17 (d, J = 12.0 Hz, 1H), 5.11 (d, J = 12.0 Hz, 1H), 3.66 (s, 3H), 3.40 (d, J = 2.8 Hz, 3H), 0.64 (s, 9H), 0.05 (s, 3H), −0.13 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.0, 165.0, 159.6, 147.8 (d, $^1J_{C,F}$ = 241.7 Hz), 137.8, 135.0, 131.1, 130.6, 128.9, 128.3, 128.3, 125.7, 123.0 (d, $^3J_{C,F}$ = 6.3 Hz), 122.7 (d, $^4J_{C,F}$ = 3.5 Hz), 117.5 (d, $^2J_{C,F}$ = 19.0 Hz), 77.2, 68.6, 51.9, 29.0 (d, $^3J_{C,F}$ = 6.3 Hz), 25.7, 18.0, −4.2, −4.5 ppm; ESI–HRMS: calcd. for $C_{27}H_{33}FN_2O_6Si$ + Na 551.1990, found 551.1996.

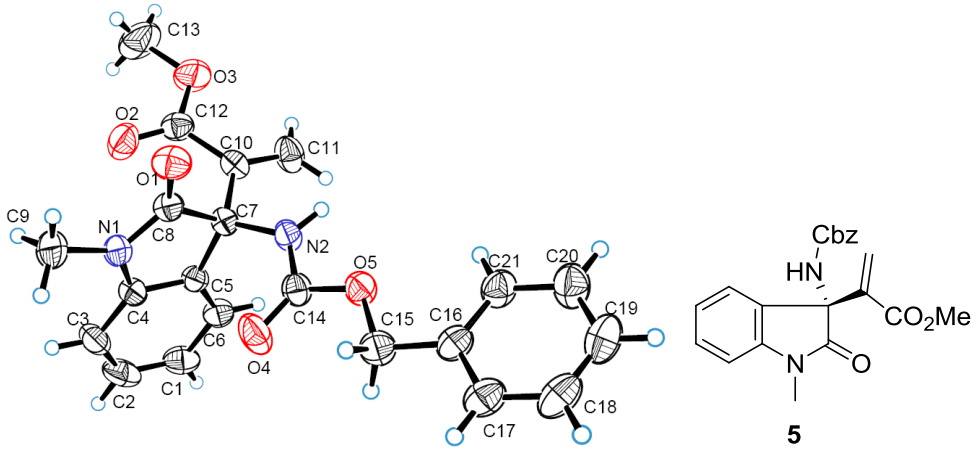
4. Synthetic transformations of multifunctional adduct 4d

Zinc powder (84.5 mg, 1.3 mmol) was added to a stirred solution of **4d** (25.5 mg, 0.05 mmol) in AcOH/H_2O/THF (3:1:1) (0.5 mL) under a nitrogen atmosphere. The mixture was stirred at room temperature for 0.5h, and then stirred at 60 °C until the consumption of **4d**. The mixture was diluted with water and filtered. The filtrate was extracted with Et_2O (3 × 5 mL), and the aqueous layer was washed with aq NaOH (6.0 M) until pH 7, and the aqueous layer was extracted with Et_2O (3 × 5 mL). The combined organic layers were dried with anhydrous Na_2SO_4 and concentrated. Flash chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) afforded pure product **5** as a white solid (6.7 mg, 35%). $[\alpha]_D^{20}$ = −64.7 (c = 0.9 in $CHCl_3$); 90% ee, determined by HPLC analysis [Daicel Chiralcel OD, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (minor) = 13.183 min, t (major) = 19.307 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 (d, J = 7.6 Hz, 1H), 7.34–7.29 (m, 4H), 7.25–7.22 (m, 2H), 7.05 (t, J = 7.6 Hz, 1H), 6.83 (d, J = 8.4 Hz, 1H), 6.57 (s, 1H), 6.32 (s, 1H), 5.87 (s, 1H), 4.97 (s, 2H), 3.73 (s, 3H), 3.23 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.2, 166.0, 154.6, 143.8, 136.3, 135.7, 129.6, 128.7, 128.4, 128.1, 128.1, 128.1,

124.6, 122.9 108.5, 67.2, 64.1, 52.5, 26.7 ppm; ESI–HRMS: calcd. for $C_{21}H_{20}N_2O_5$ + Na 403.1270, found 403.1271.

HF·pyridine (5.4 μL, 0.06 mmol) was added to a solution of **4d** (25.5 mg, 0.05 mmol) in THF (0.3 mL) at 0 °C. The mixture was stirred at room temperature until the consumption of **4d**. Then saturated $NaHCO_3$ was added until pH 7, and the aqueous layer was extracted with Et_2O (3 × 3.0 mL). The combined organic layers were dried with anhydrous Na_2SO_4 and concentrated. Flash chromatography on silica gel (petroleum ether/ethyl acetate = 3:1) afforded pure product **6** as a colorless oil (17.8 mg, 90%). K_2CO_3 (1.4 mg, 0.01 mmol) was added to a solution of **6** in THF (0.3 mL) at 0 °C. The mixture was stirred at room temperature until **6** was consumed. Then the reaction mixture was concentrated in vacuo at low temperature and purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) afforded pure product **7** as a white semisolid (9.5 mg, 53%). $[\alpha]_D^{20}$ = +8.8 (*c* = 0.5 in $CHCl_3$); 90% ee, determined by HPLC analysis [Daicel Chiralcel OD, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, *t* (minor) = 16.310 min, *t* (major) = 19.092 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (t, *J* = 7.2 Hz, 1H), 7.39–7.26 (m, 4H), 7.17–7.13 (m, 3H), 6.82 (d, *J* = 7.6 Hz, 1H), 6.43 (s, 1H), 5.40 (s, 1H), 5.18 (d, *J* = 12.0 Hz, 1H), 5.07 (d, *J* = 12.0 Hz, 1H), 3.02 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.0, 162.6, 153.6, 143.8, 135.0, 134.1, 130.9, 128.6, 128.5, 128.2, 126.7, 126.2, 124.1, 124.0, 109.1, 72.0, 69.1, 26.5 ppm; ESI–HRMS: calcd. for $C_{20}H_{16}N_2O_5$ + Na 387.0957, found 387.0959.

5. Crystal data and structure refinement for enantiopure 5

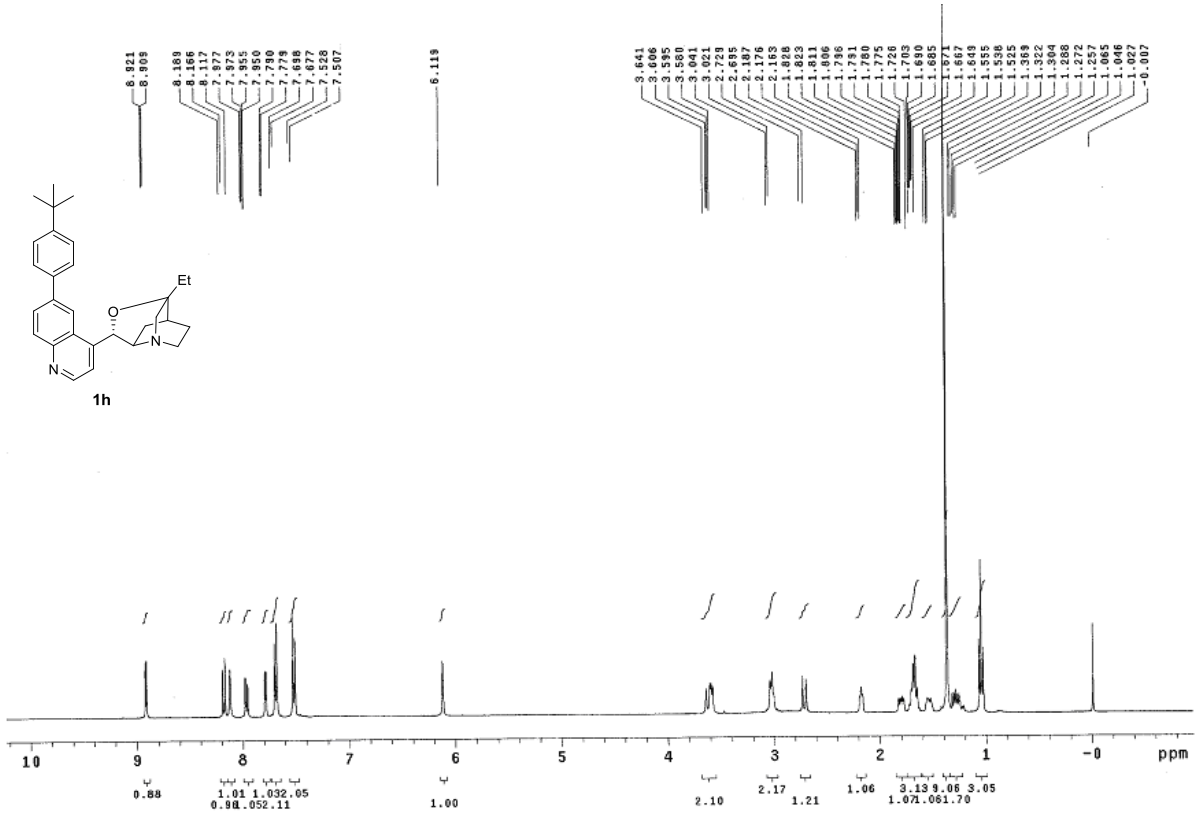


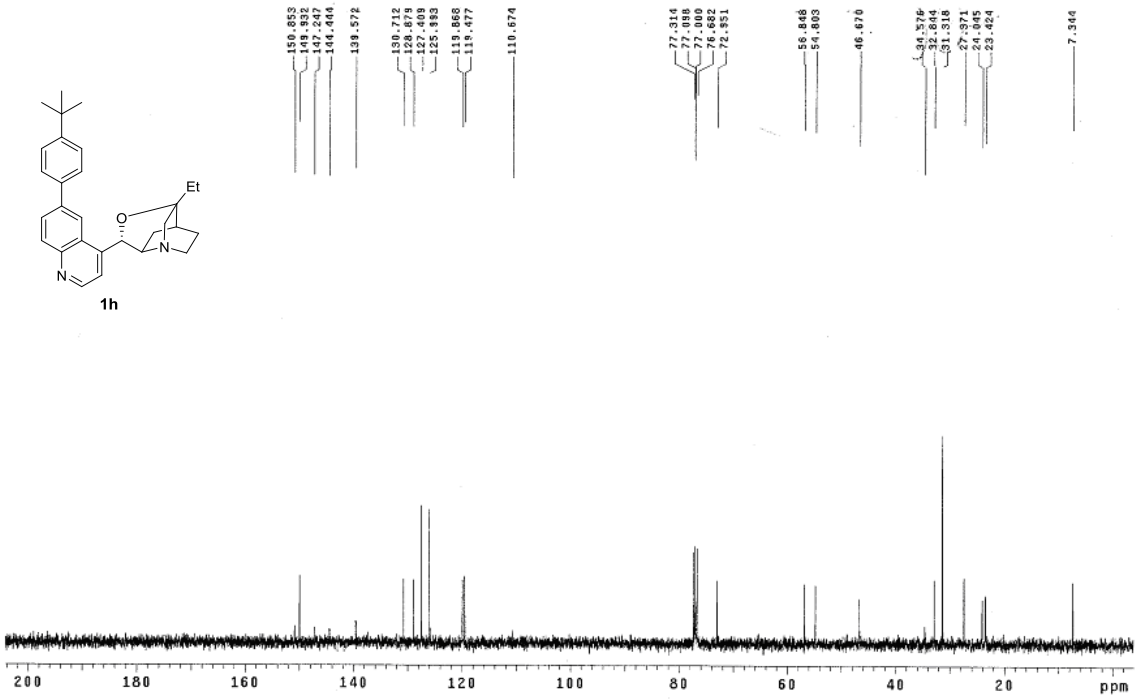
Identification code	5
Empirical formula	$C_{21}H_{20}O_5N_2$
Formula weight	380.39
Temperature	291(2)
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a/Å, b/Å, c/Å	8.6032(2), 9.40760(10), 23.8035(4)
α/°, β/°, γ/°,	90.00, 90.00, 90.00
Volume/$Å^3$	1926.55(6)

Z	4
ρ_{calc}mg/mm^3	1.311
m/mm^{-1}	0.782
F(000)	800
Crystal size	0.42 × 0.36 × 0.30
Theta range for data collection	5.06 to 69.79°
Index ranges	$-10 \leq h \leq 10$, $-11 \leq k \leq 11$, $-28 \leq l \leq 28$
Reflections collected	15142
Independent reflections	3601[R(int) = 0.0224]
Data/restraints/parameters	3601/0/256
Goodness-of-fit on F^2	1.041
Final R indexes [I>2σ (I)]	R_1 = 0.0279, wR_2 = 0.0782
Final R indexes [all data]	R_1 = 0.0289, wR_2 = 0.0793

Largest diff. peak/hole 0.141/-0.109

6. NMR spectra and HPLC chromatograms

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O
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N
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119.868
119.477
110.674
77.314
77.098
77.000
76.682
72.951
56.848
54.803
46.670
34.576
32.864
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200
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140
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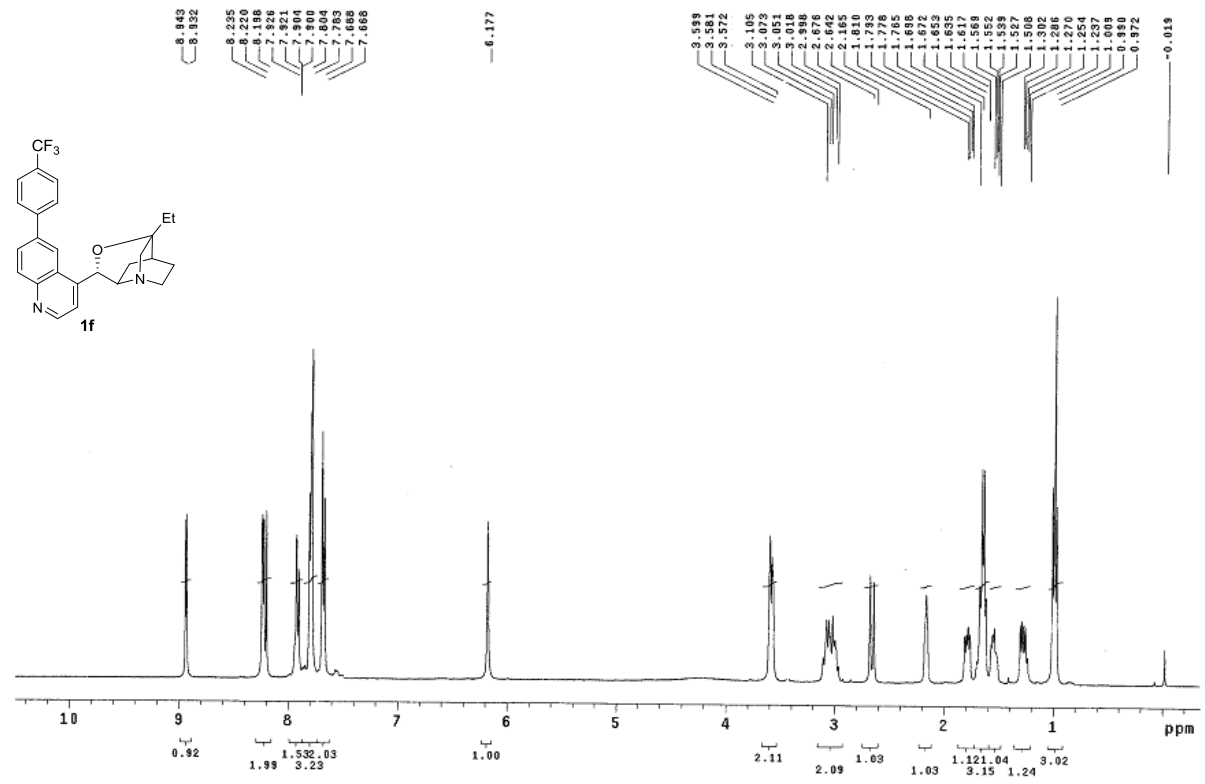
100
80
60
40
20
ppm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N
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8.220
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7.926
7.921
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7.900
7.804
7.783
7.668
7.668
6.177
3.599
3.581
3.572
3.105
3.073
3.051
3.018
2.998
2.676
2.642
2.165
1.810
1.733
1.778
1.765
1.698
1.672
1.653
1.635
1.617
1.569
1.552
1.539
1.527
1.508
1.302
1.286
1.270
1.254
1.237
1.009
0.980
0.972
-0.019
10
9
8
7
6
5
4
3
2
1
ppm
0.92
1.99
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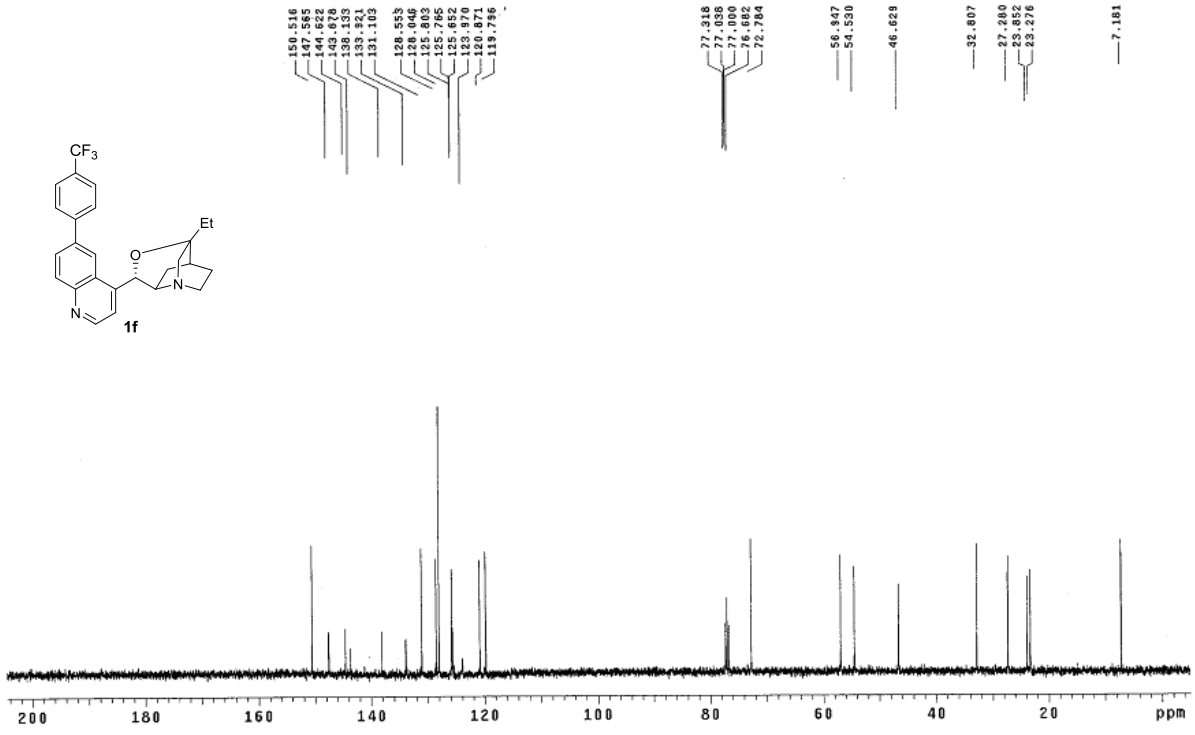
1.00
2.11
2.09
1.03
1.03
1.121.04
3.15
1.24
3.02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120.871
119.736
77.318
77.038
77.000
76.682
72.784
56.947
54.530
46.629
32.807
27.280
23.852
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7.181
CF3
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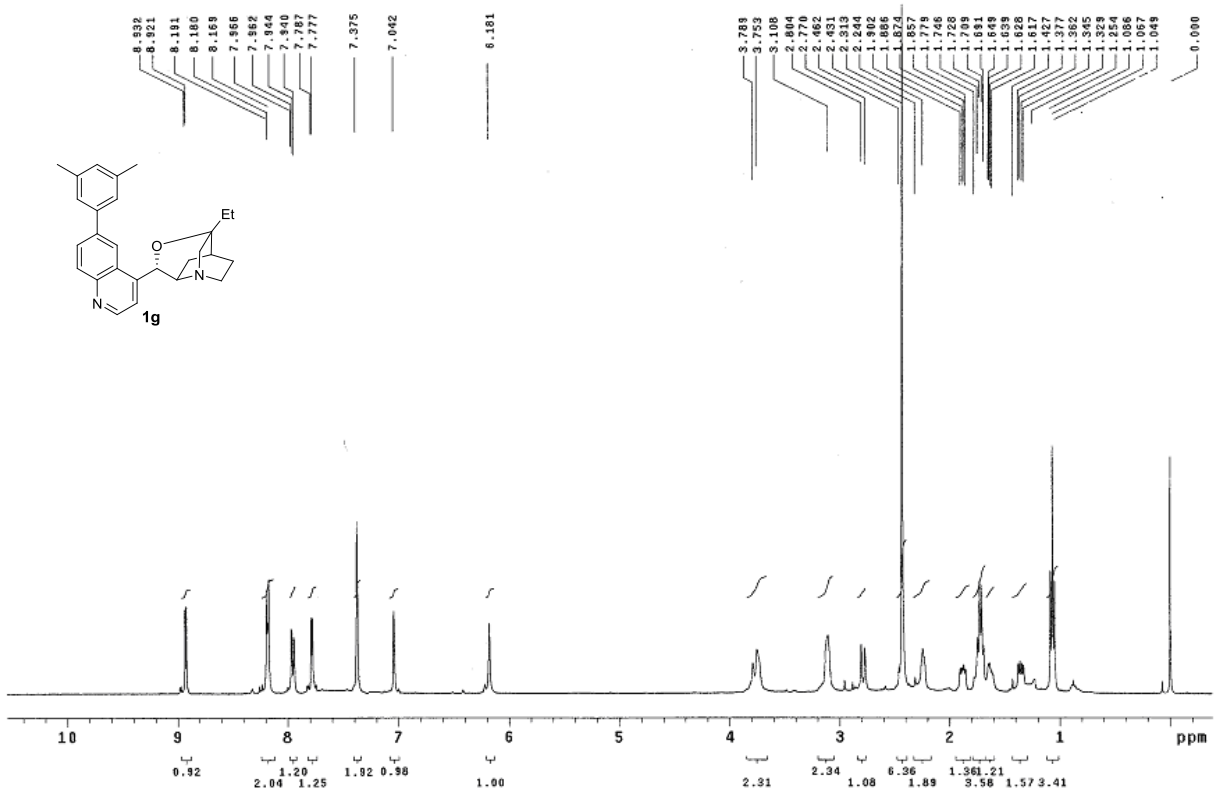
O
N
N
1f
200
180
160
140
120
100
80
60
40
20
ppm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7.940
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7.375
7.042
6.181
3.789
3.753
3.108
2.804
2.770
2.462
2.431
2.313
2.244
1.902
1.886
1.824
1.857
1.779
1.746
1.728
1.691
1.648
1.639
1.628
1.617
1.427
1.377
1.362
1.345
1.329
1.254
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1.049
0.000
Et
O
N
N
1g
10
9
8
7
6
5
4
3
2
1
ppm
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1.20
1.25
1.92
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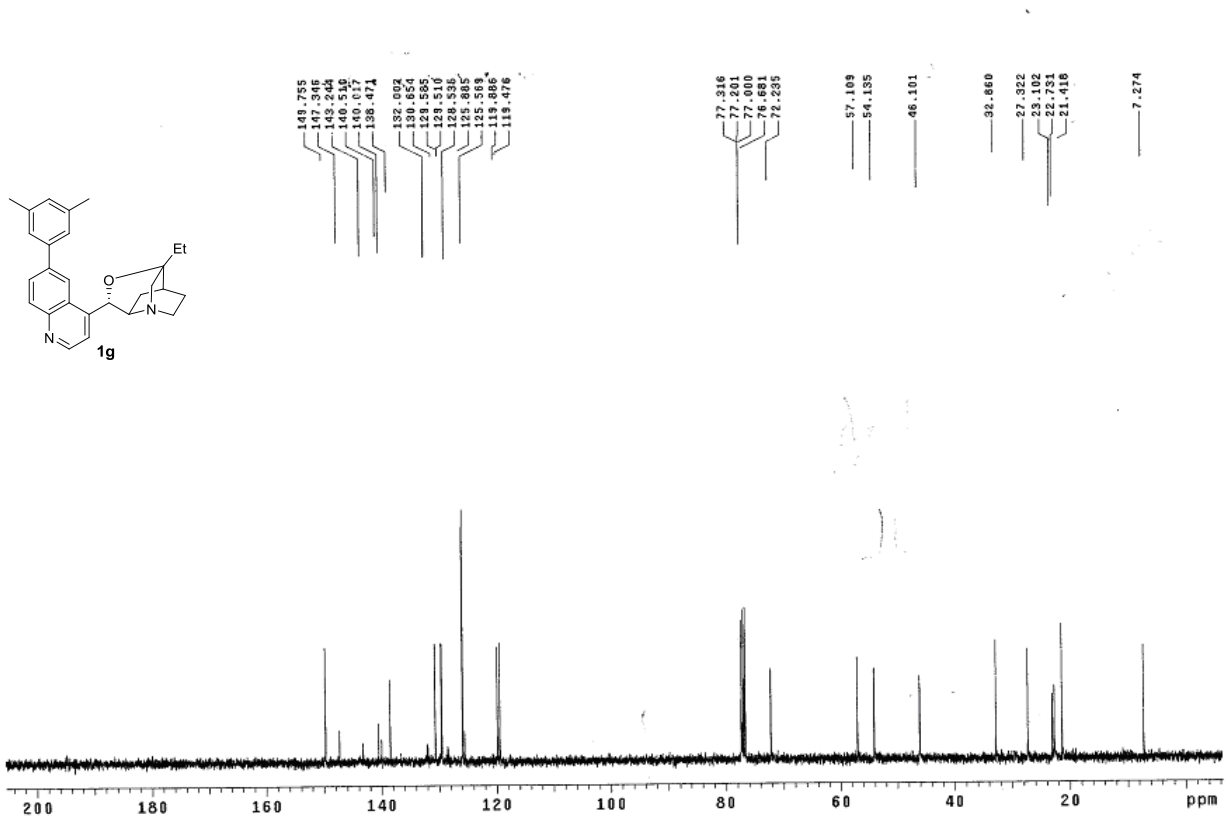
2.34
1.08
6.36
1.89
1.36
1.21
3.58
1.57
3.41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125.589
119.886
119.476
77.316
77.201
77.000
76.681
72.235
57.109
54.135
46.101
32.860
27.322
23.102
22.731
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N
1g
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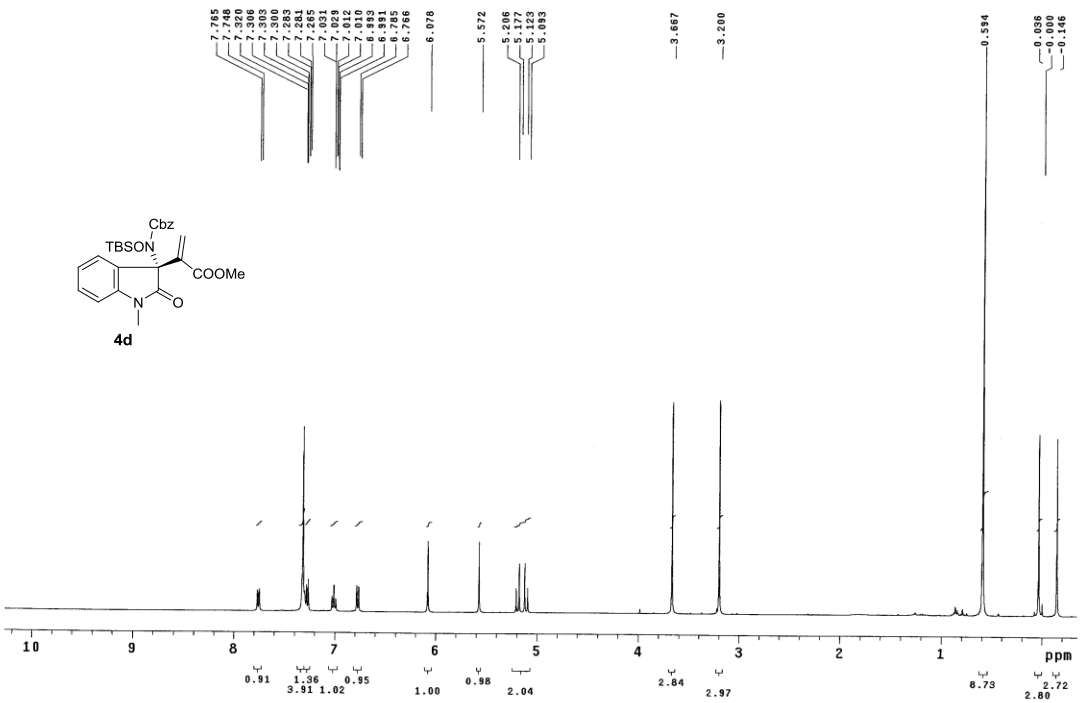
80
60
40
20
ppm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7.029
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6.993
6.981
6.785
6.766
6.078
5.572
5.206
5.177
5.123
5.093
3.667
3.200
0.594
0.036
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-0.146
Cbz
TBSON
COOMe
O
N
O
4d
10
9
8
7
6
5
4
3
2
1
ppm
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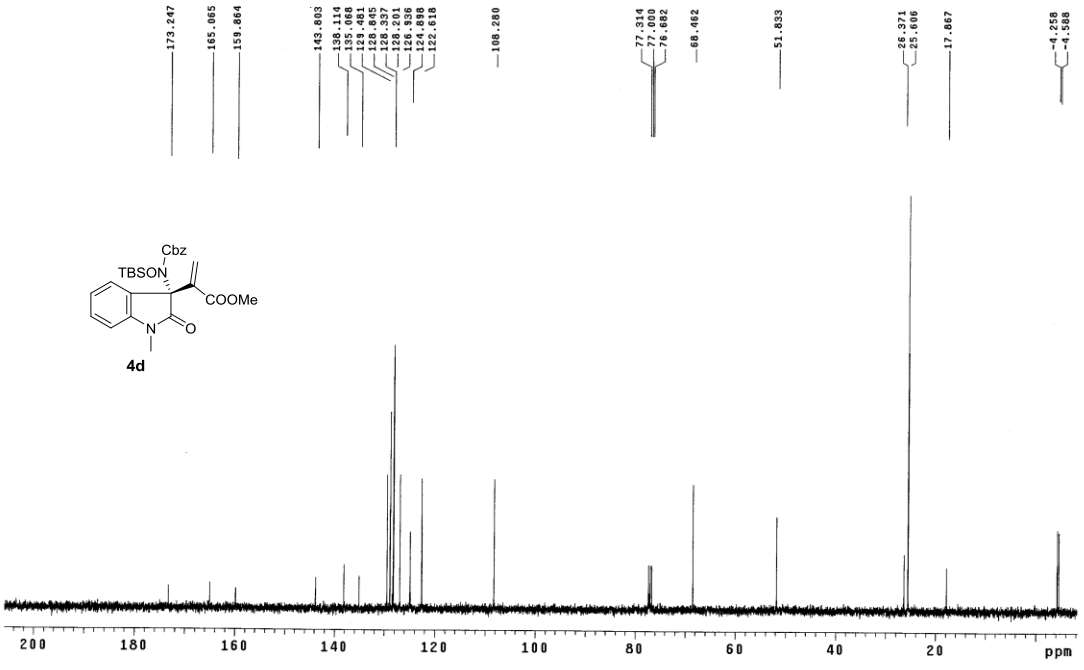
2.80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108.280
77.314
77.000
76.682
68.462
51.833
26.371
25.606
17.867
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O
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140
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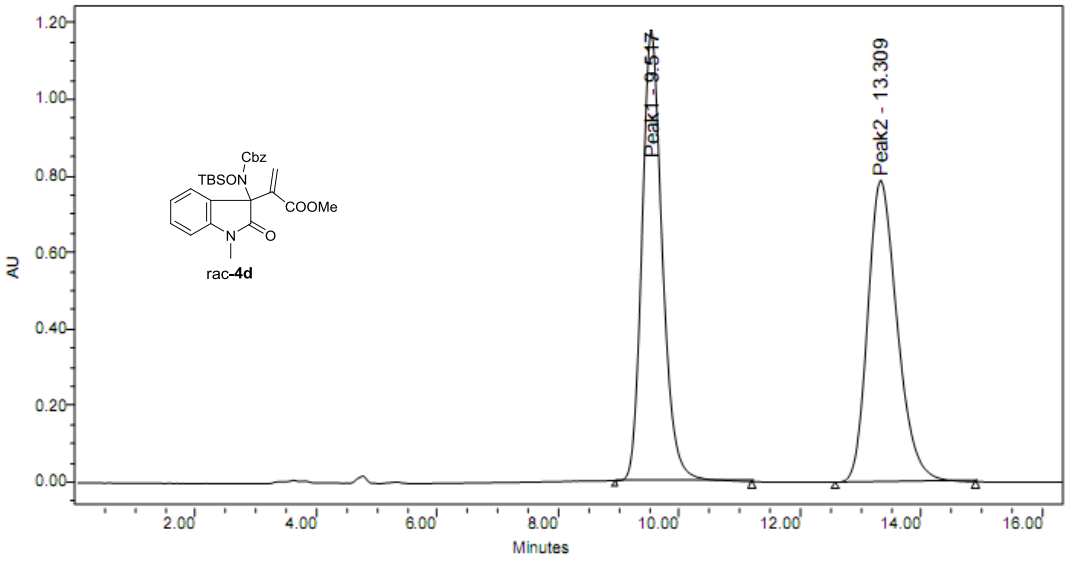
20
ppm



	Peak Name	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
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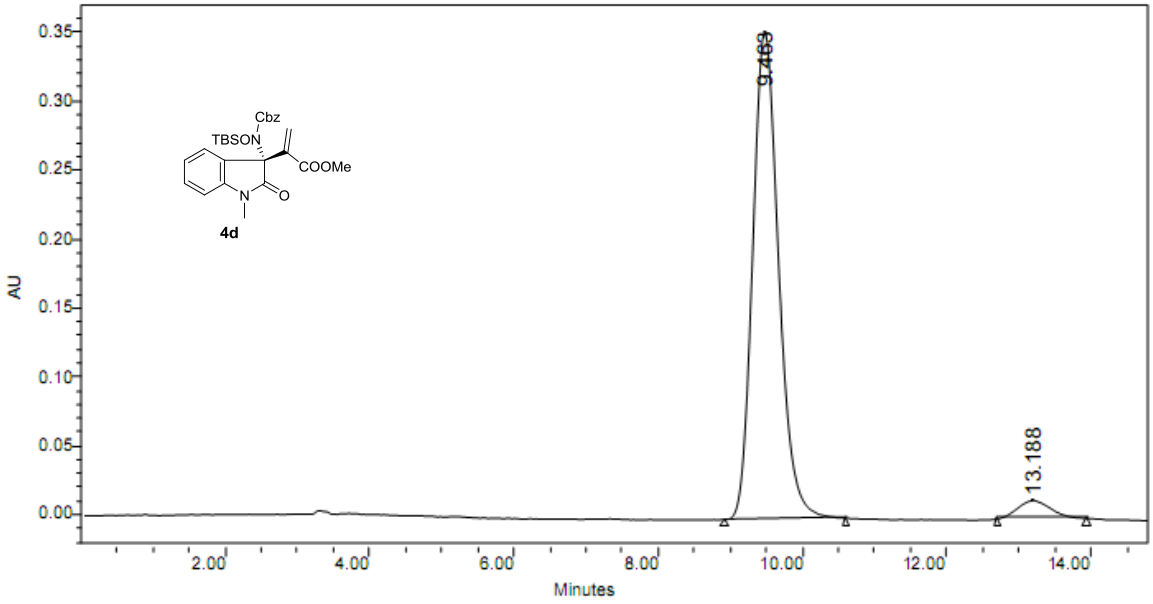
2	Peak2	13.309	26821039	49.39	787107	40.06



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
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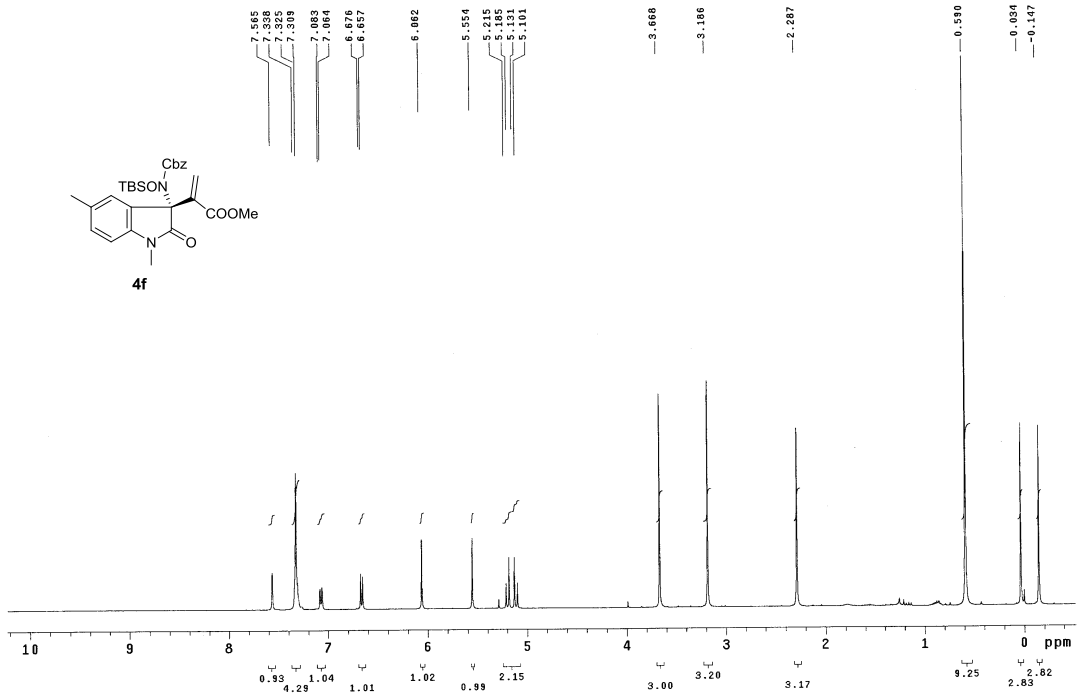
2	13.188	411939	4.46	12985	3.54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TBSON
COOMe
O
N
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7.325
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7.064
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6.062
5.554
5.215
5.185
5.131
5.101
3.668
3.186
2.287
0.590
0.034
-0.147
0.93
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1.04
1.01
1.02
0.99
2.15
3.00
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3.17
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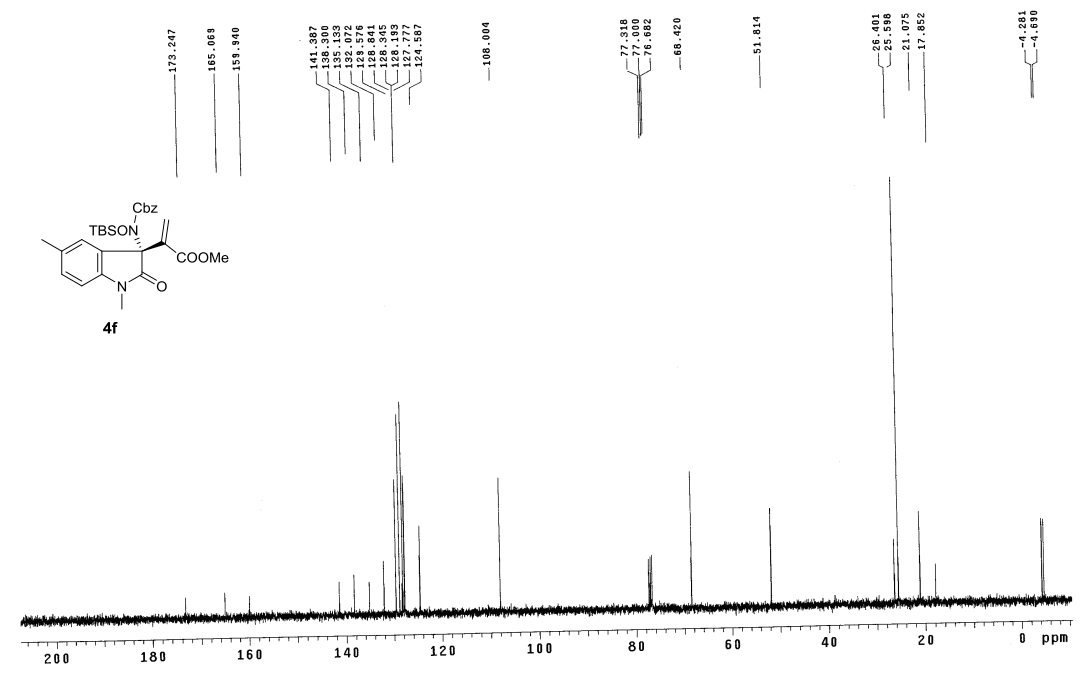
ppm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TBSON
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O
N
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128.193
127.777
124.567
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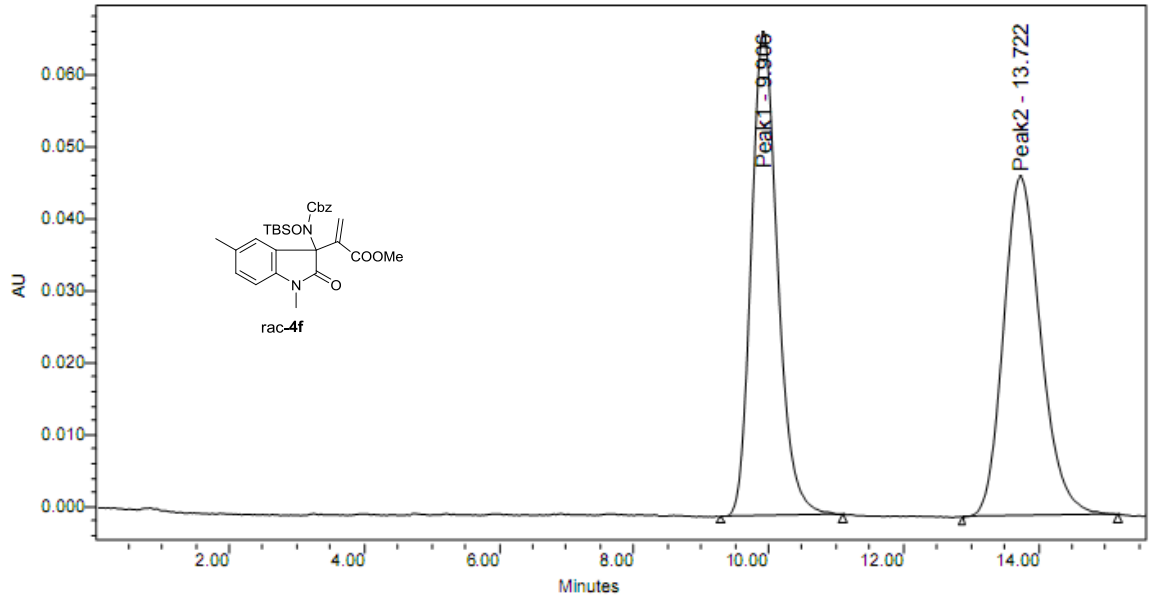
ppm



	Peak Name	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
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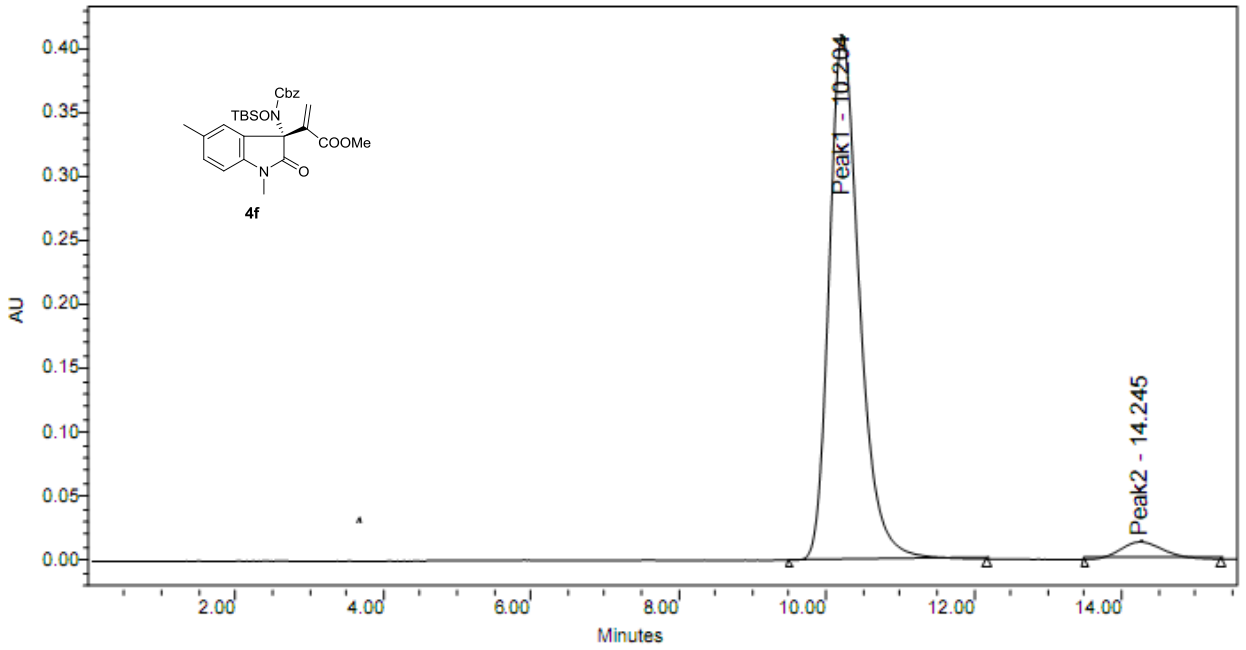

	Peak Name	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
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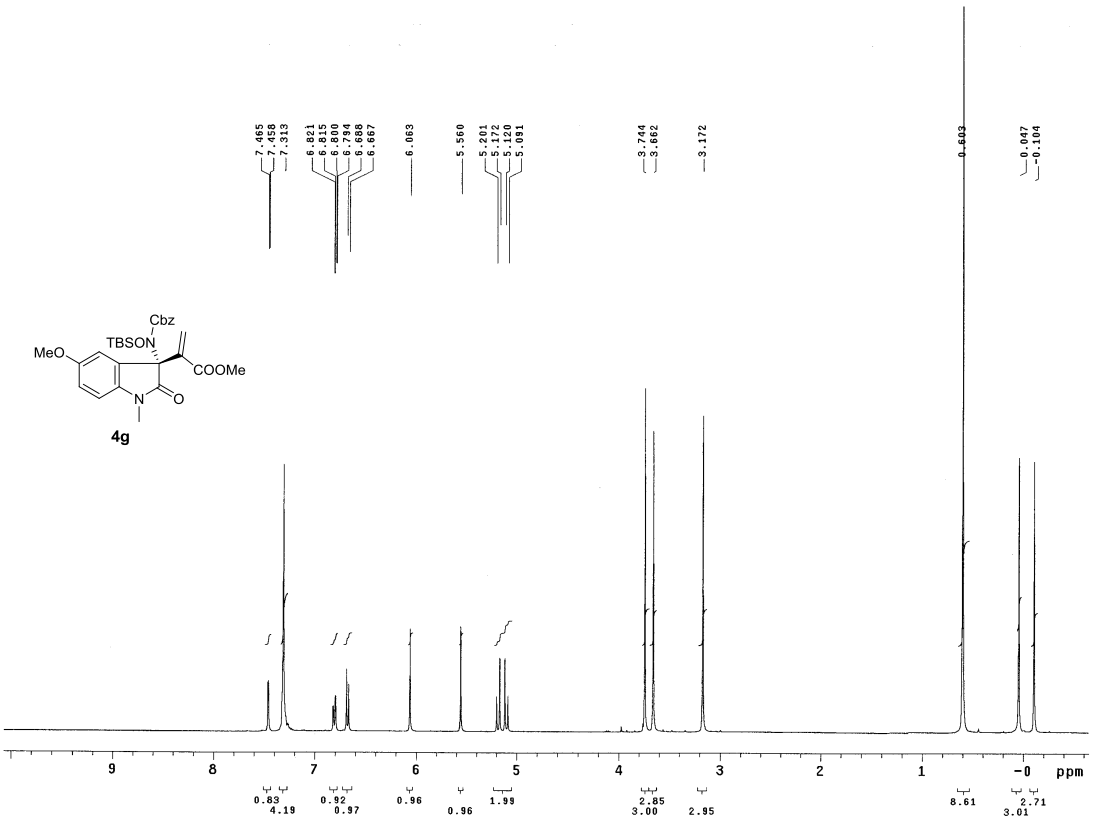
2	Peak2	14.245	561774	4.57	13595	3.20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5.172
5.120
5.091
3.744
3.662
3.172
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0.047
-0.104
Cbz
TBSON
MeO
COOMe
N
O
4g
9
8
7
6
5
4
3
2
1
-0
ppm
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0.97
0.96
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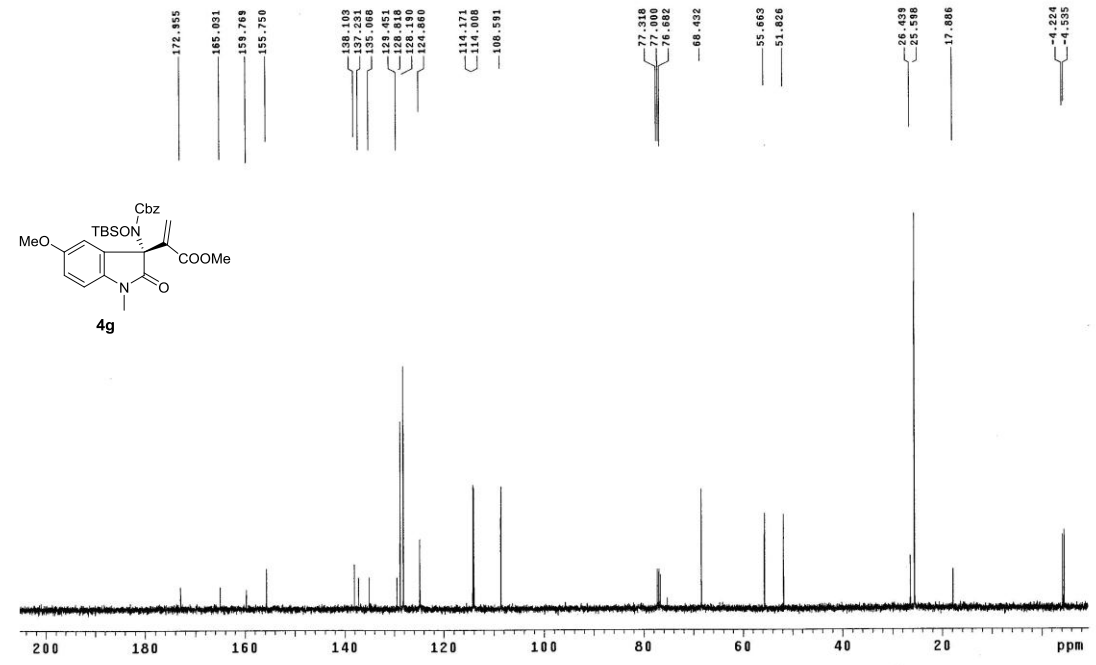
8.61
2.71
3.01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77.318
77.000
76.682
68.432
55.663
51.826
26.439
25.598
17.886
-4.224
-4.535
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COOMe
N
O
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140
120
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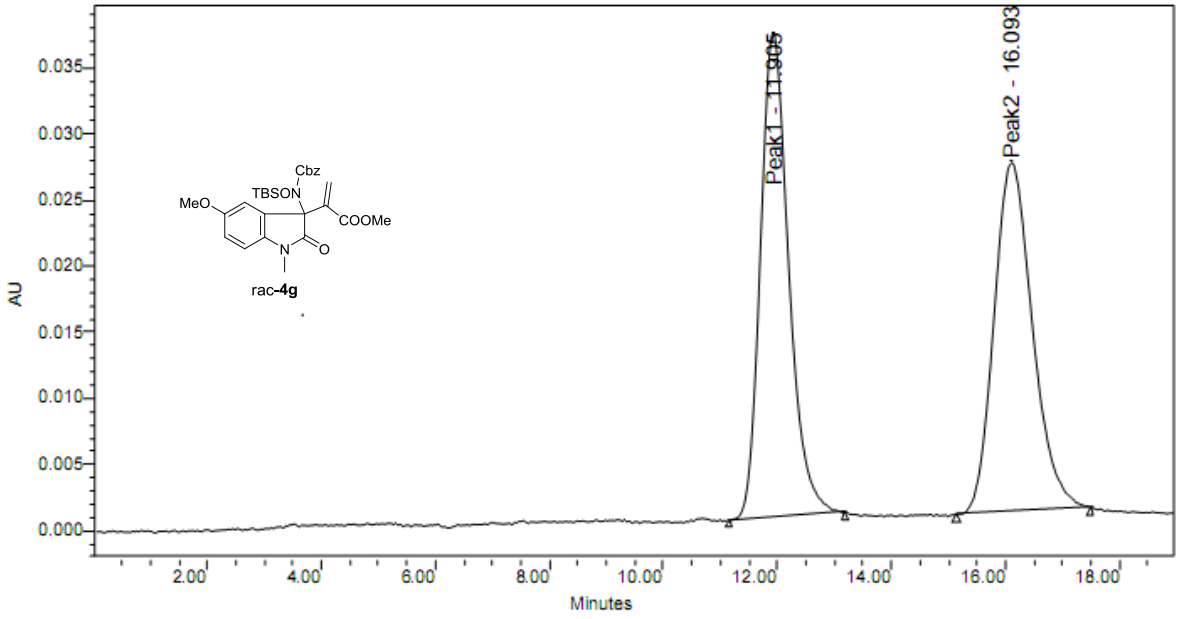
80
60
40
20
ppm



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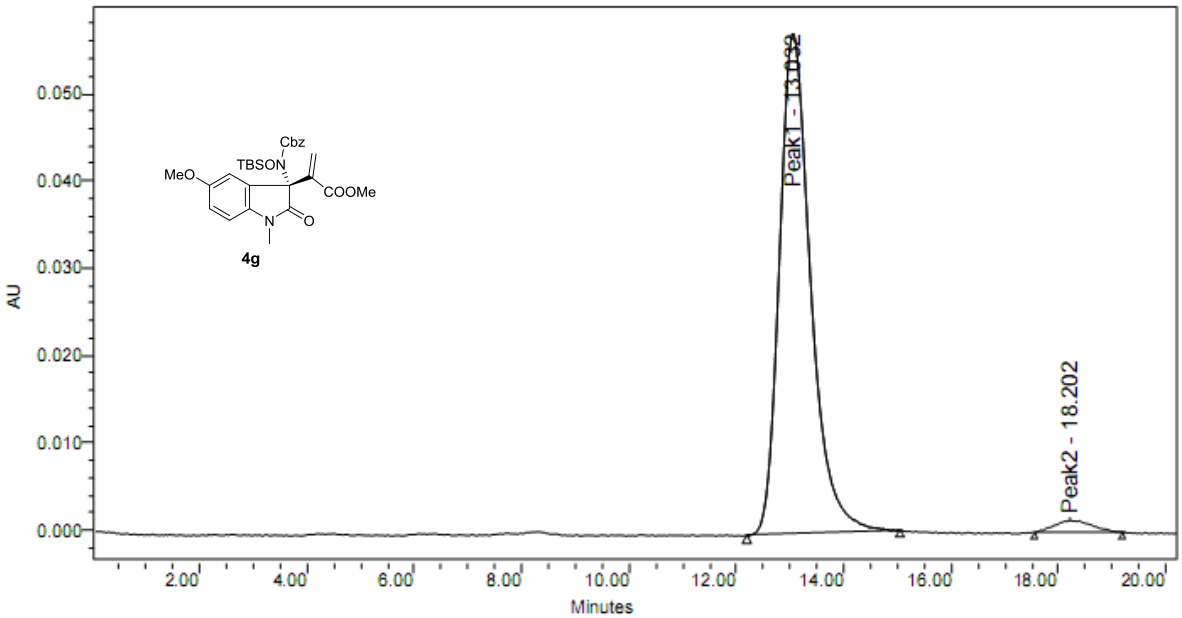

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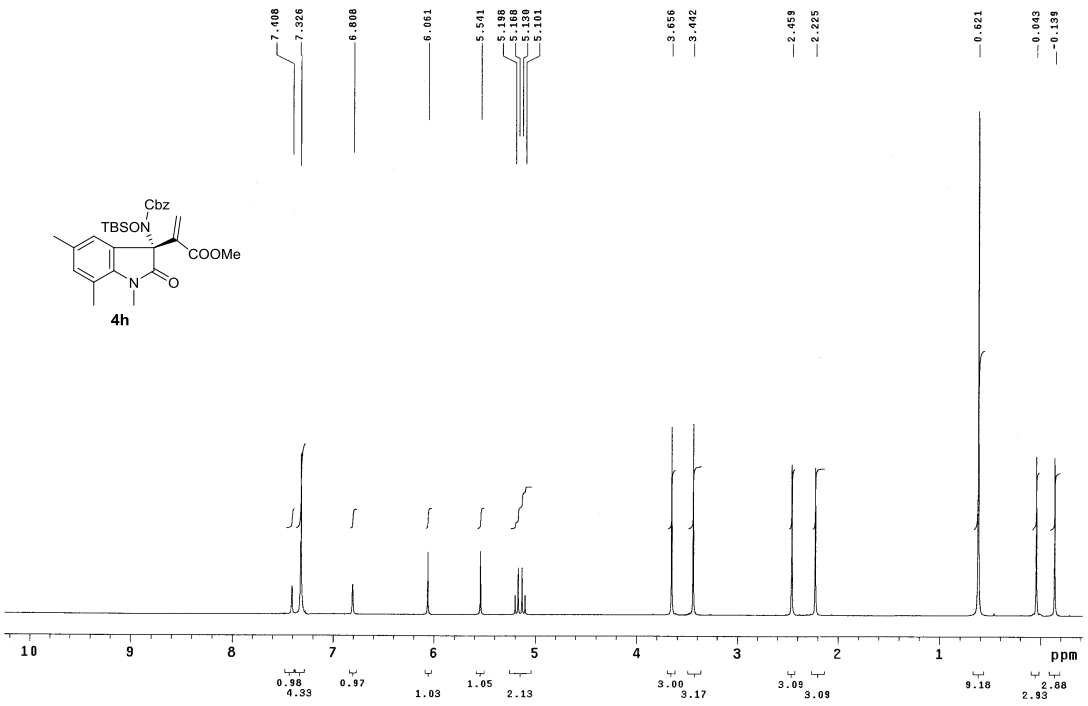
1	Peak1	13.032	2326947	97.15	57280	97.68
2	Peak2	18.202	68295	2.85	1362	2.32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2.225
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0.043
-0.139
Cbz
TBSON
COOMe
N
O
4h
10
9
8
7
6
5
4
3
2
1
ppm
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1.05
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3.09
3.09
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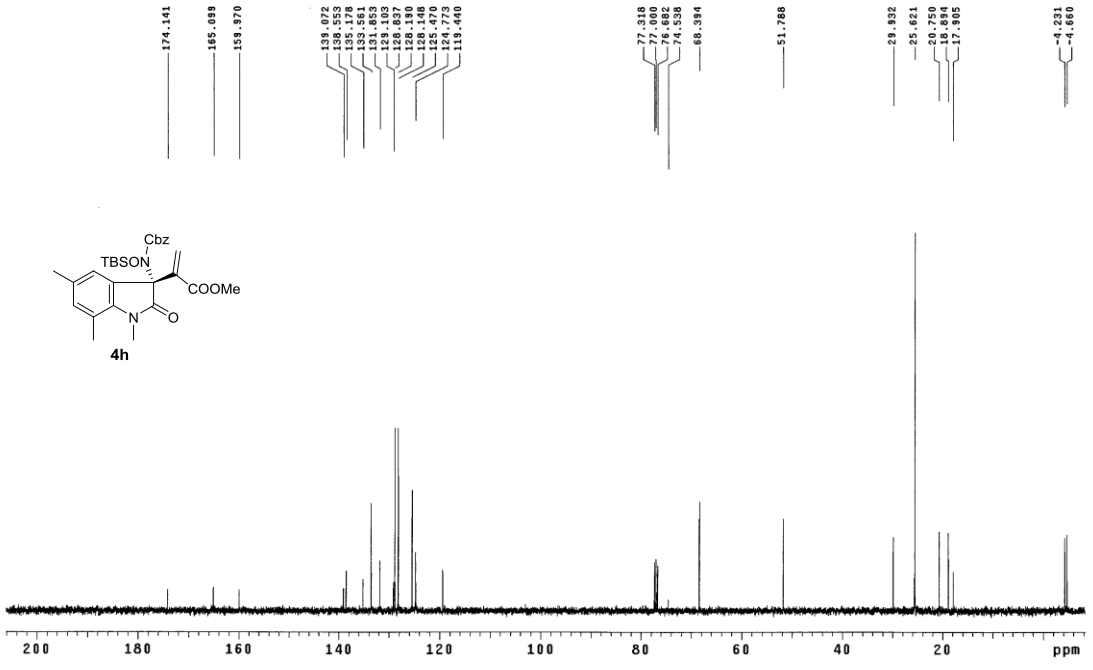
2.88
2.93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77.000
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17.905
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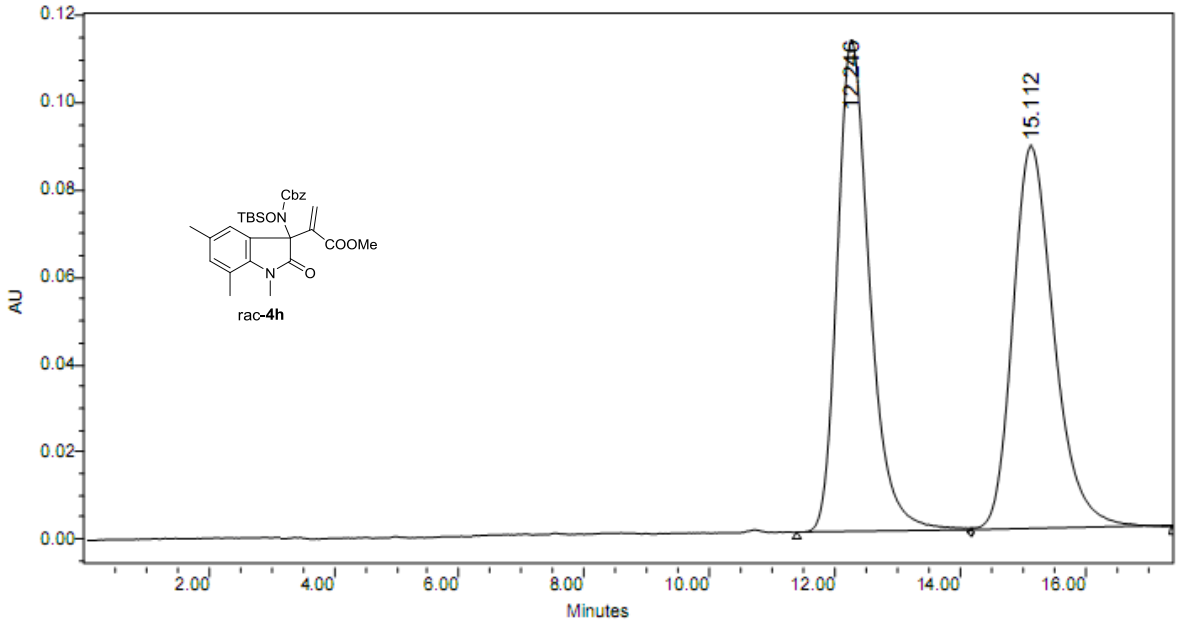
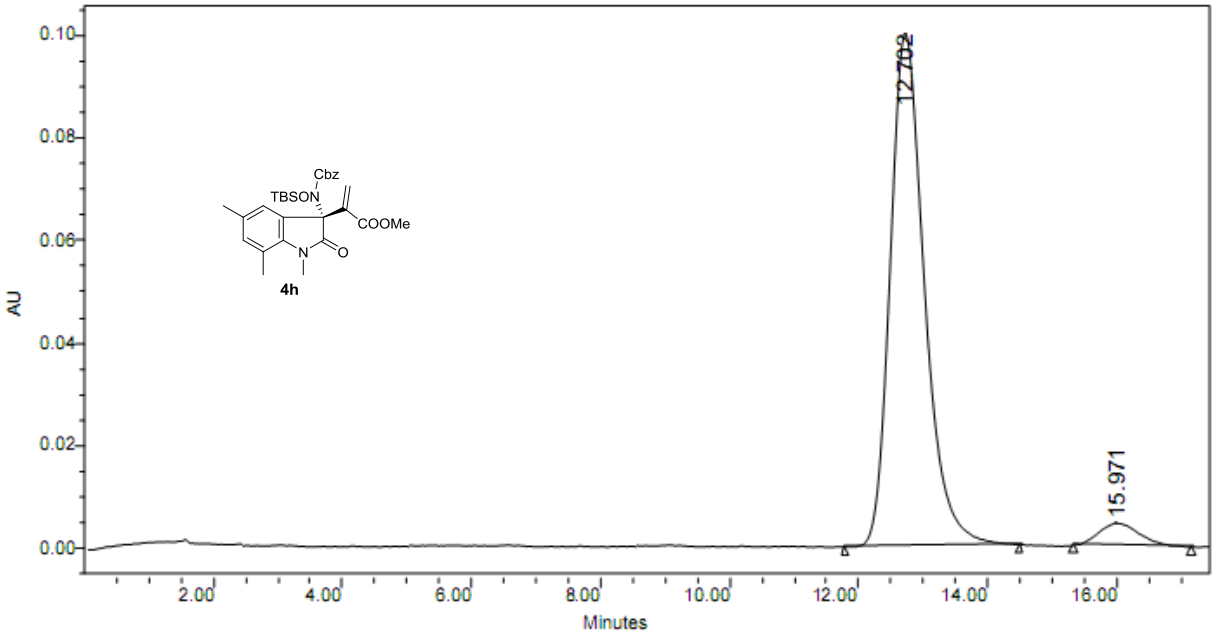
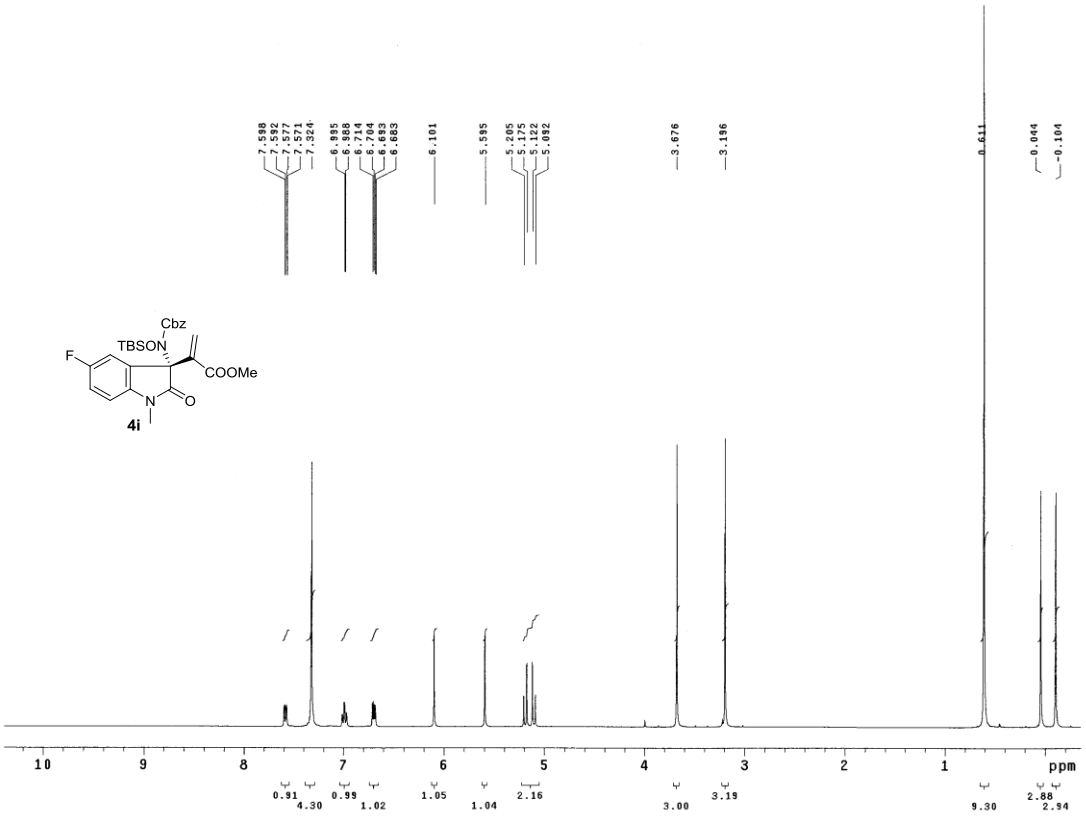
ppm



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	12.246	4049174	50.11	112615	56.24
2	15.112	4032010	49.89	87638	43.76



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	12.702	3669708	94.85	99767	95.74
2	15.971	199243	5.15	4443	4.26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Cbz
TBSON
F
COOMe
N
O
4i
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9
8
7
6
5
4
3
2
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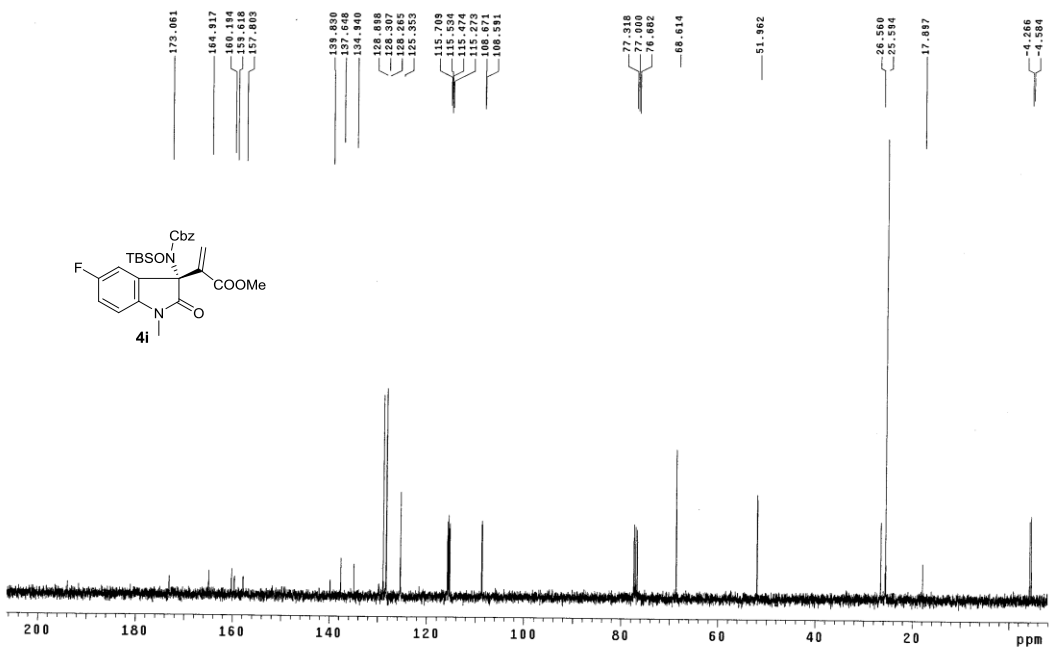
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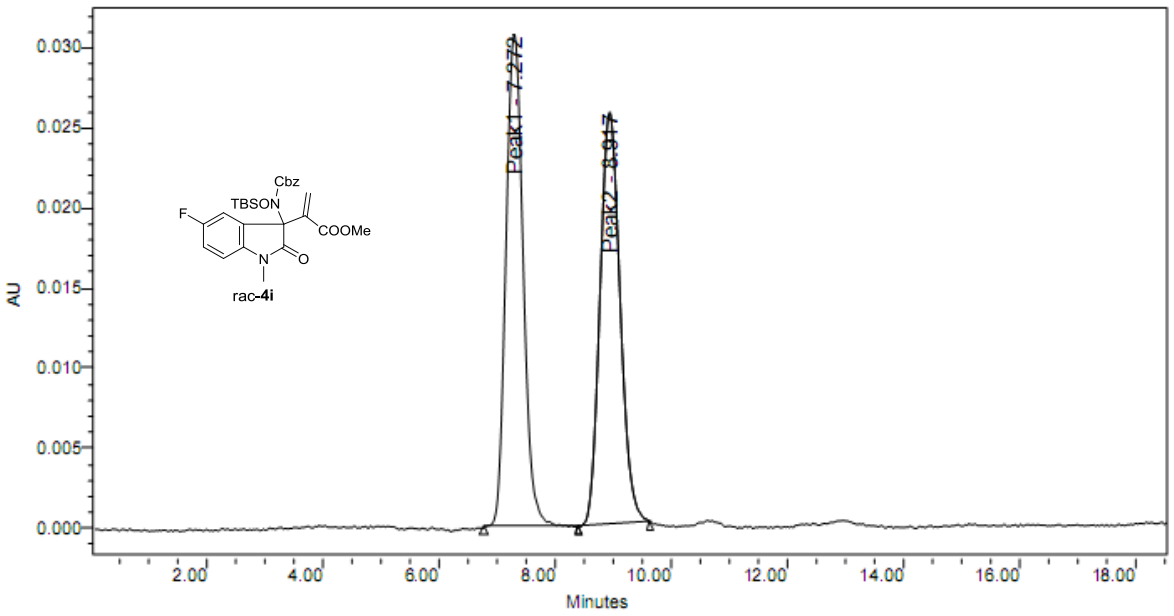
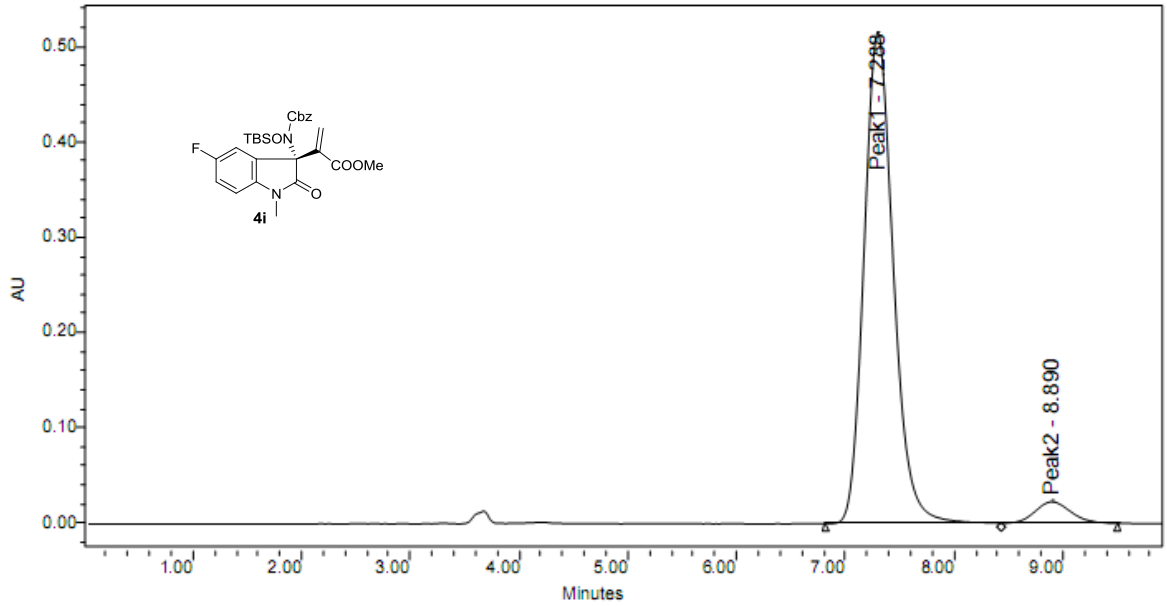
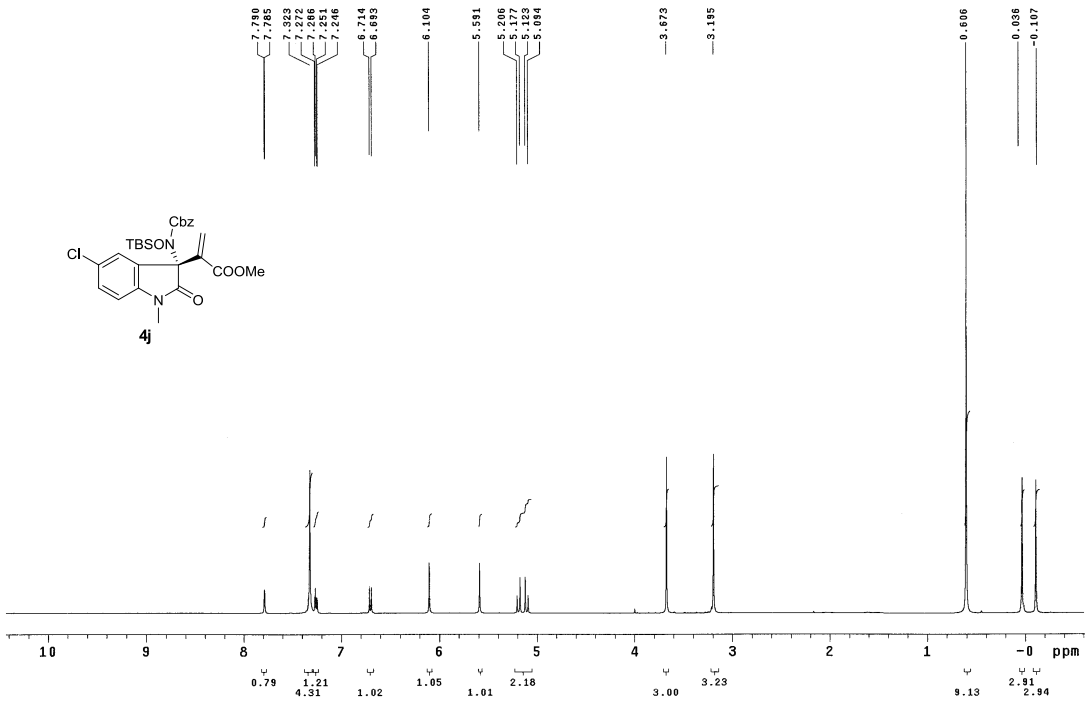
ppm



	Peak Name	RT (min)	Area (µV*sec)	% Area	Height (µV)	% Height
1	Peak1	7.272	641786	50.69	30809	54.47
2	Peak2	8.917	624374	49.31	25750	45.53



	Peak Name	RT (min)	Area (µV*sec)	% Area	Height (µV)	% Height
1	Peak1	7.288	9677512	94.90	516629	95.80
2	Peak2	8.890	519592	5.10	22676	4.20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7.251
7.246
6.714
6.693
6.104
5.591
5.206
5.177
5.123
5.094
3.673
3.185
0.606
0.036
-0.107
Cbz
TBSON
Cl
COOMe
N
O
4j
10
9
8
7
6
5
4
3
2
1
-0
ppm
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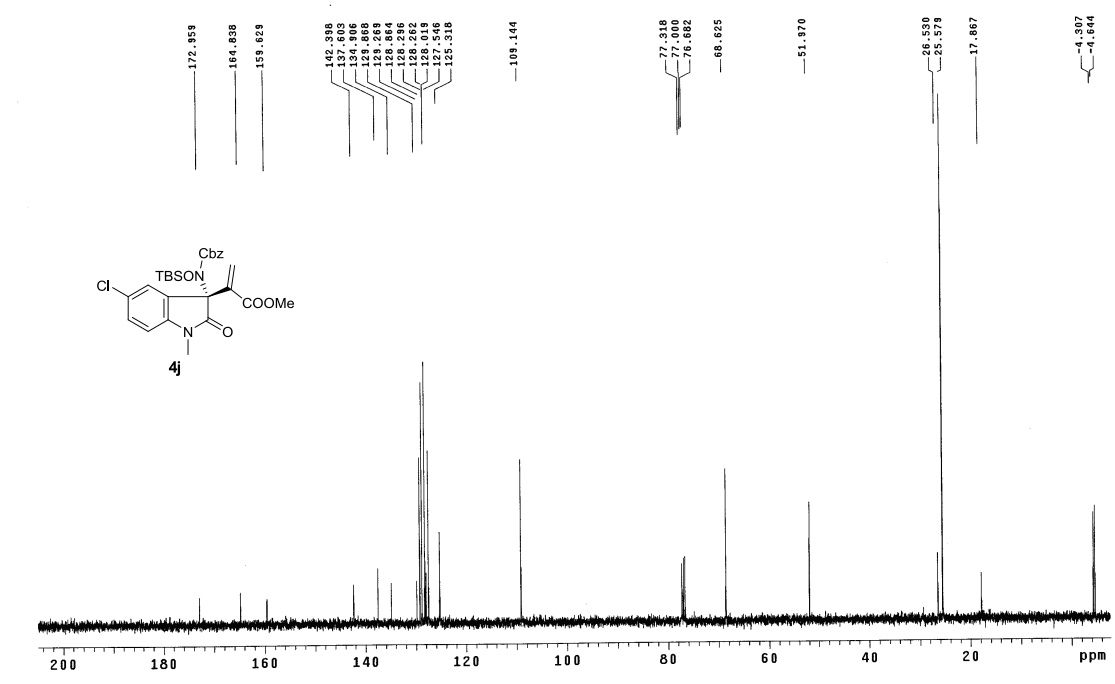
4.31
1.02
1.05
1.01
2.18
3.00
3.23
9.13
2.91
2.94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77.000
76.682
68.625
51.970
26.530
25.579
17.867
-4.307
-4.644
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TBSON
Cl
COOMe
N
O
4j
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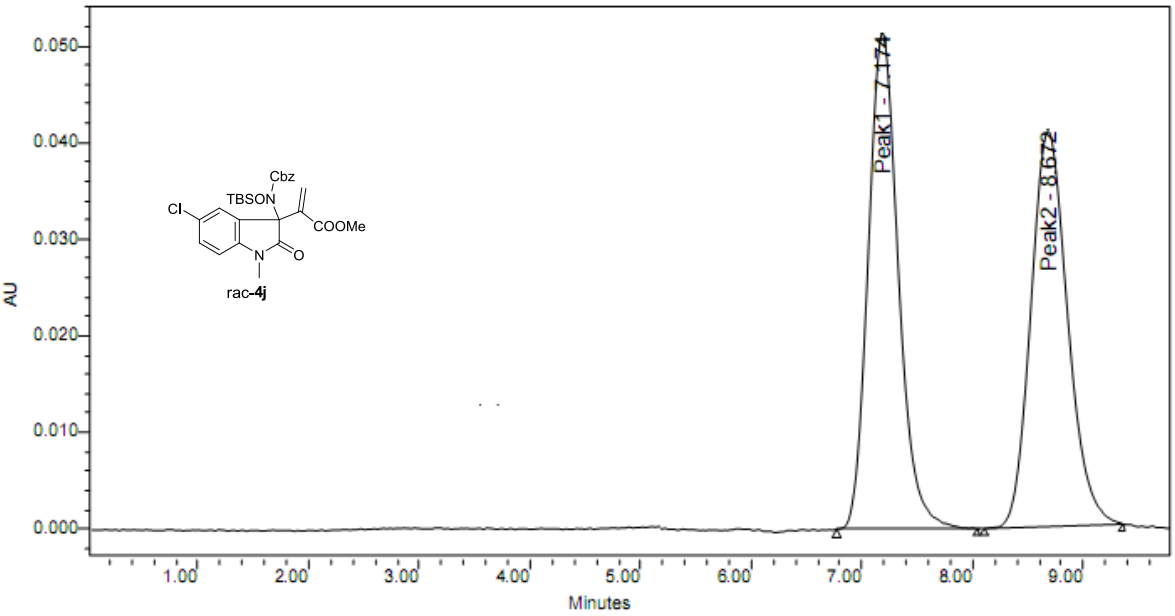
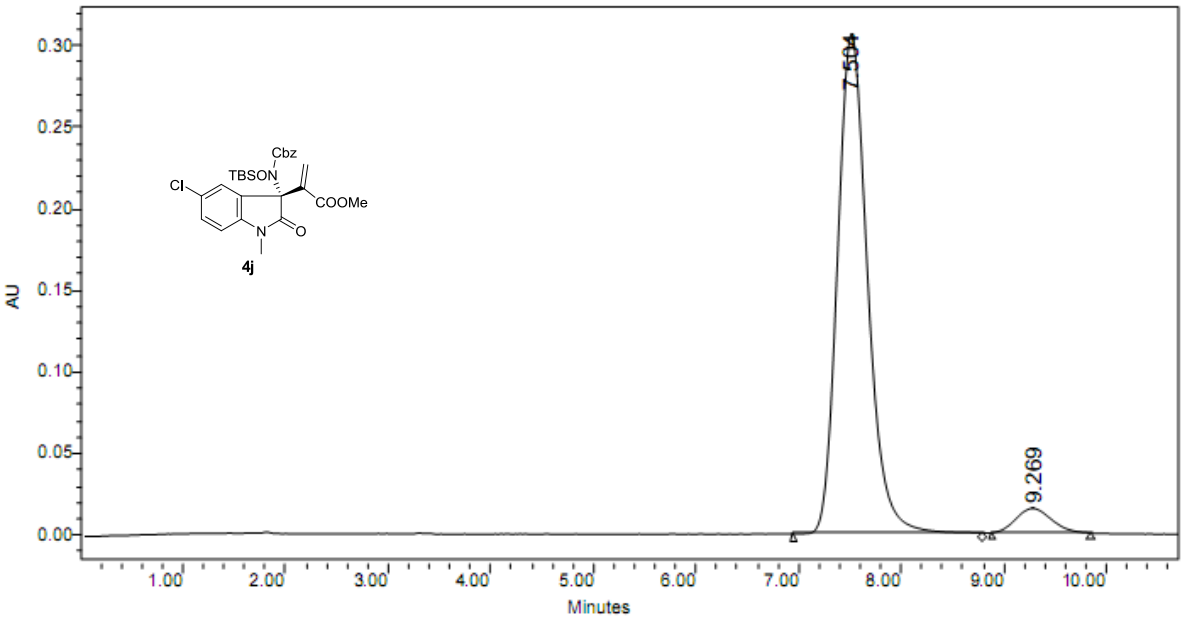
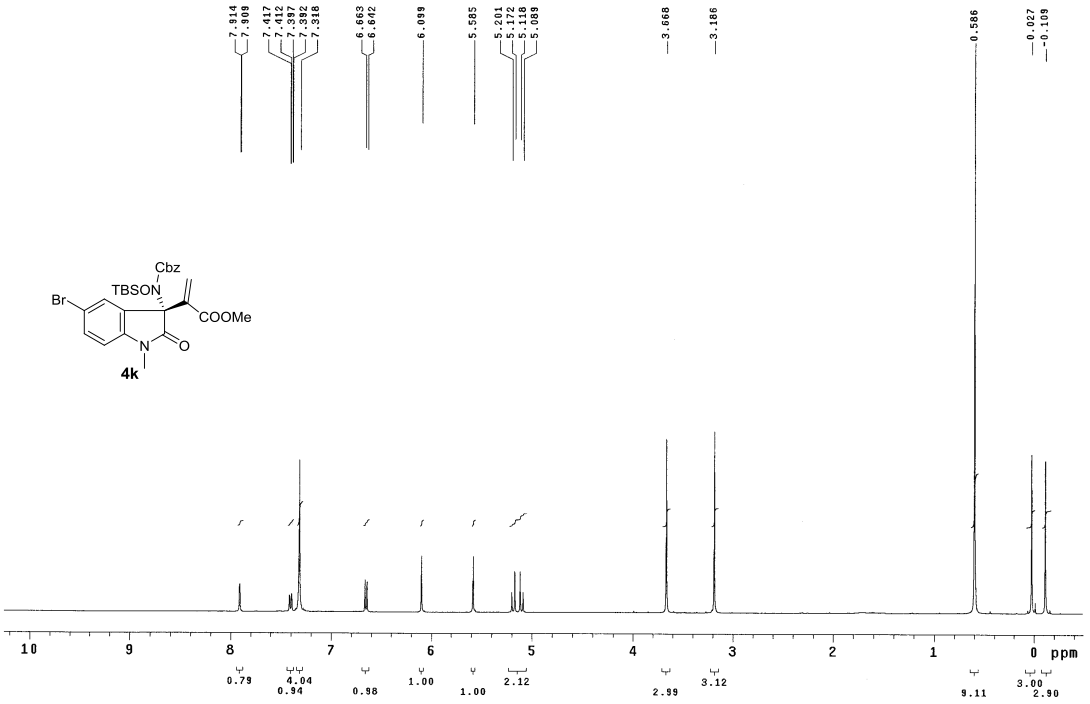
140
120
100
80
60
40
20
ppm



	Peak Name	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	Peak1	7.174	975497	50.76	51401	55.65
2	Peak2	8.672	946167	49.24	40970	44.35



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	7.504	6252754	94.53	306410	95.31
2	9.269	361884	5.47	15089	4.69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5.118
5.089
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0.027
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Br
COOMe
N
O
4k
10
9
8
7
6
5
4
3
2
1
0 ppm
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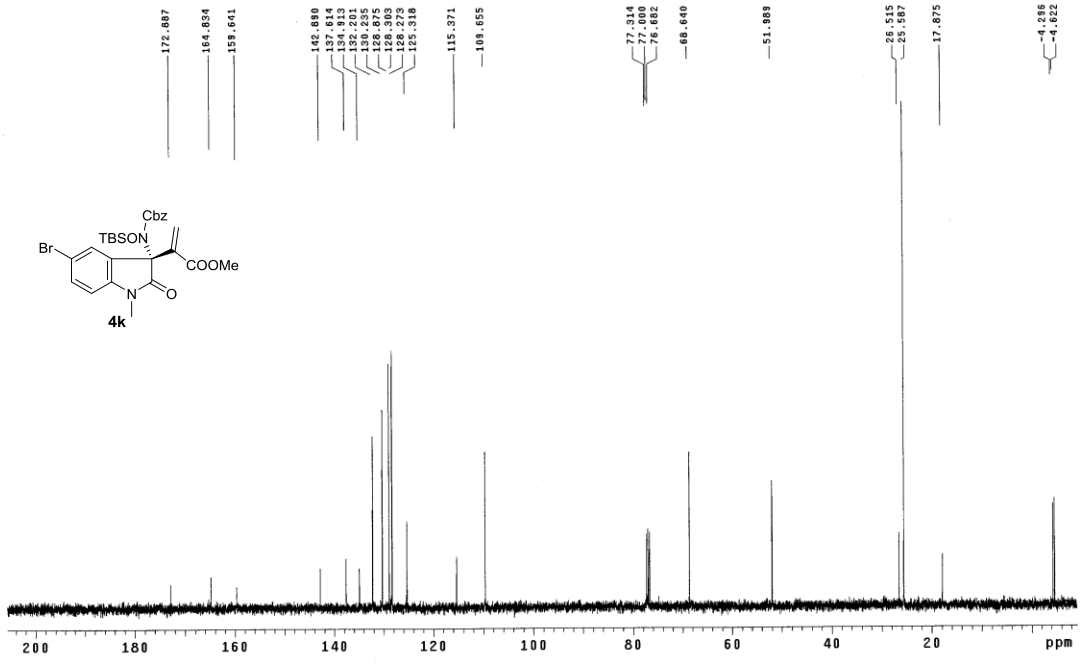
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26.515
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17.875
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COOMe
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20
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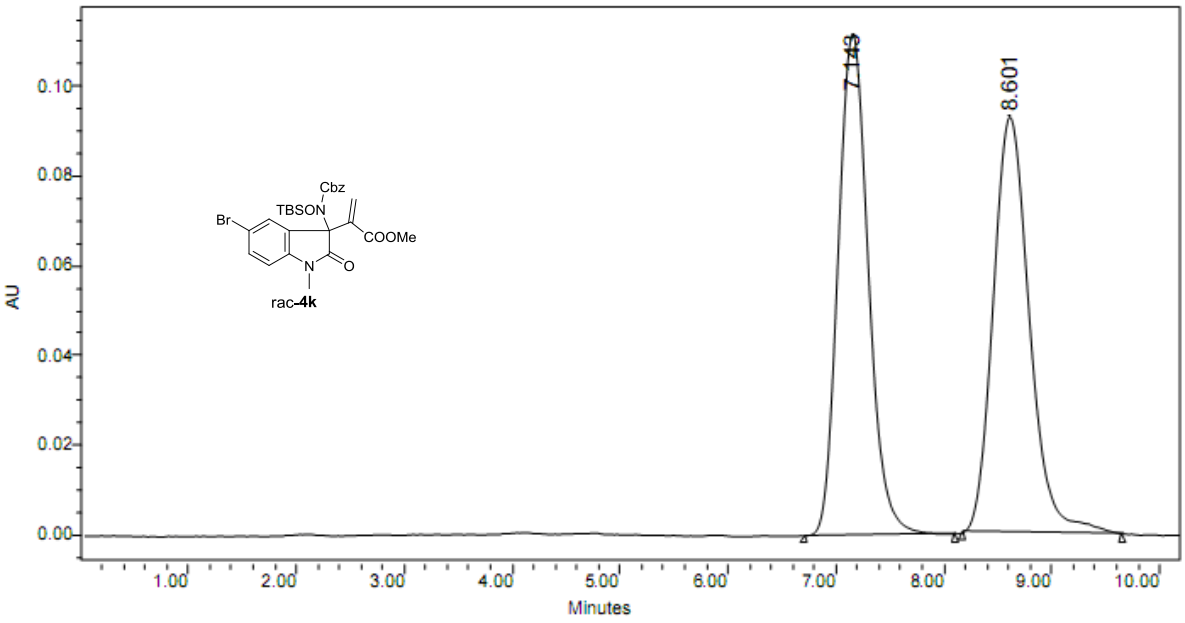
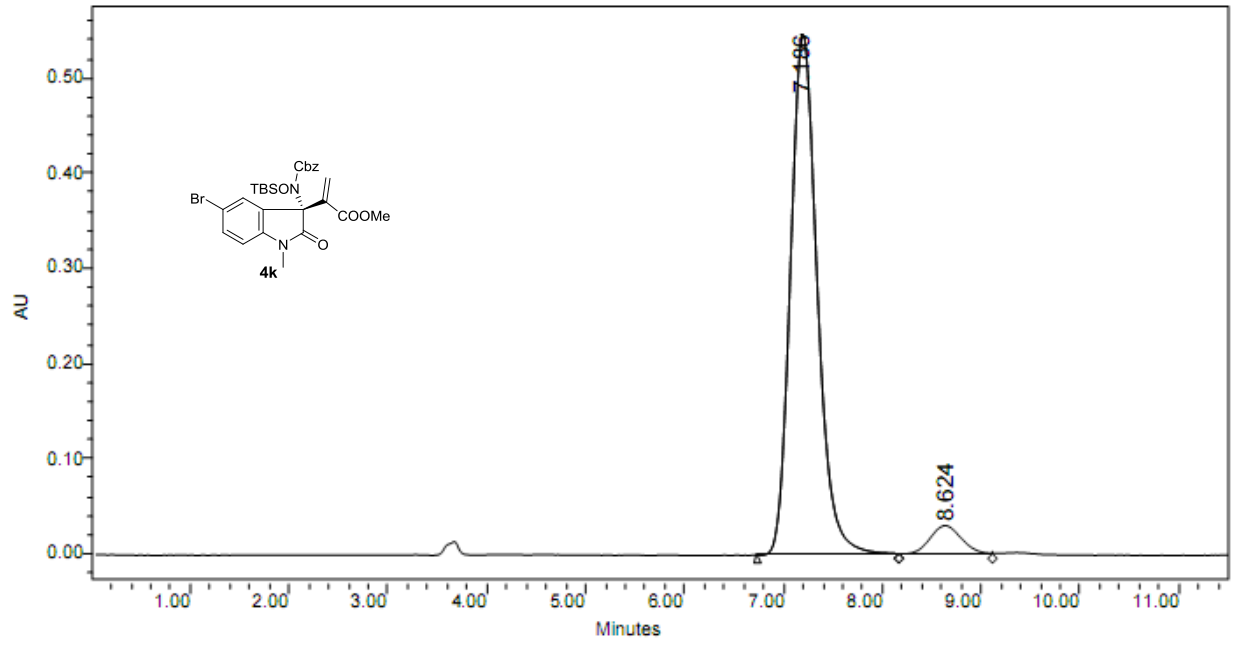
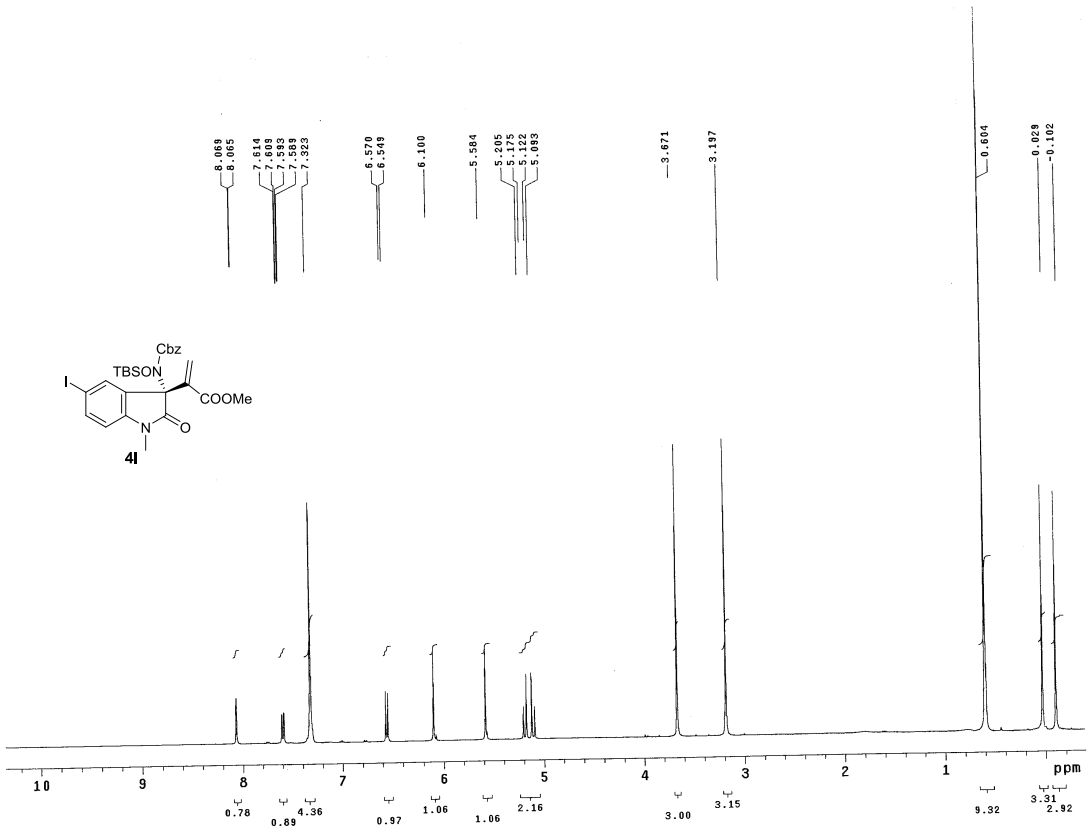


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	7.143	2177297	50.08	111955	54.68
2	8.601	2170090	49.92	92795	45.32



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	7.186	10347245	93.93	547314	94.62
2	8.624	727605	6.07	31110	5.38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5.175
5.122
5.093
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0.029
-0.102
Cbz
TBSON
COOMe
I
N
O
4l
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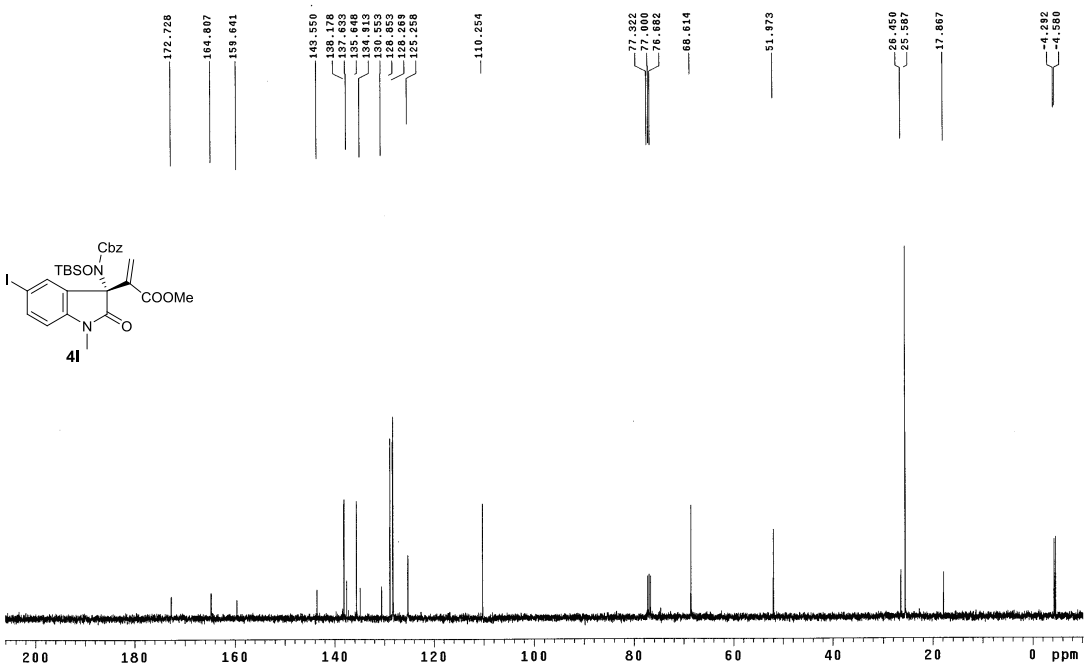
2.92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77.000
76.682
68.614
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26.450
25.587
17.867
-4.292
-4.580
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TBSON
COOMe
I
N
O
4l
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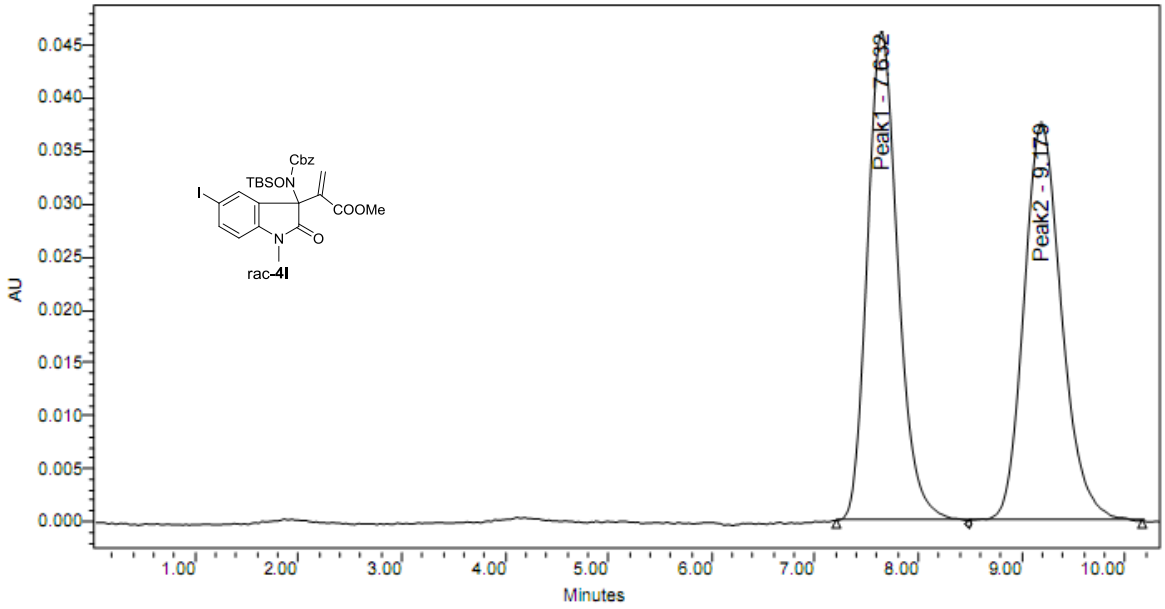
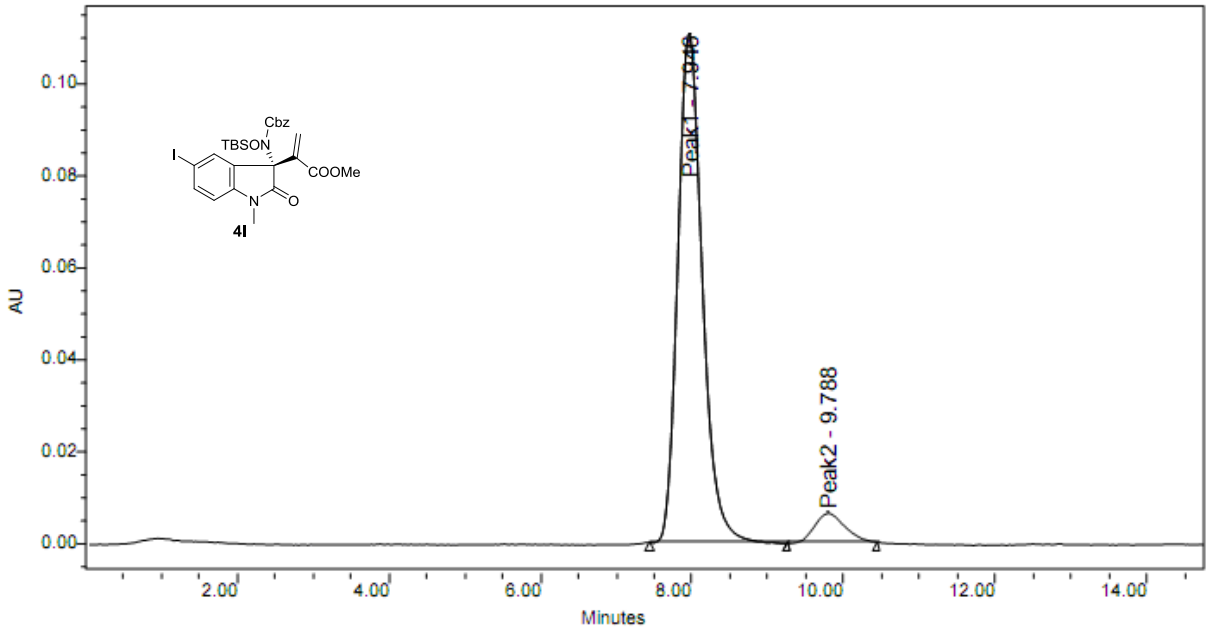
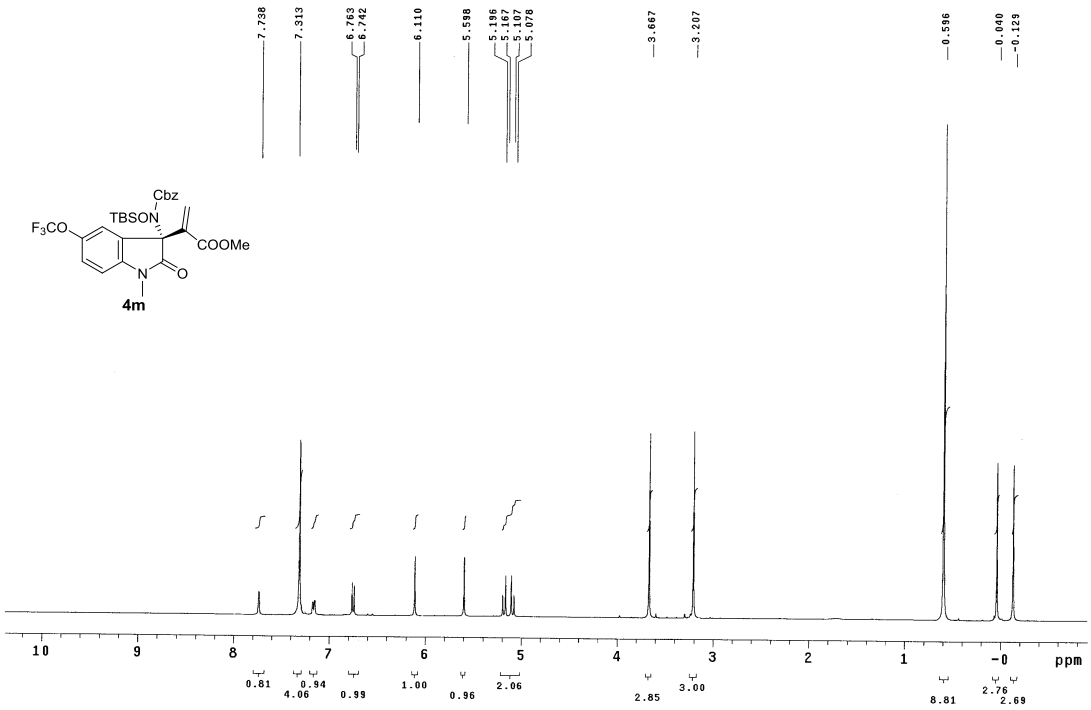
140
120
100
80
60
40
20
0 ppm



	Peak Name	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	Peak1	7.632	950992	49.85	46183	55.20
2	Peak2	9.179	956900	50.15	37476	44.80



	Peak Name	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	Peak1	7.946	2498444	93.10	110805	94.49
2	Peak2	9.788	185210	6.90	6460	5.51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0.596
0.040
-0.129
Cbz
TBSON
F3CO
COOMe
N
O
4m
10
9
8
7
6
5
4
3
2
1
-0
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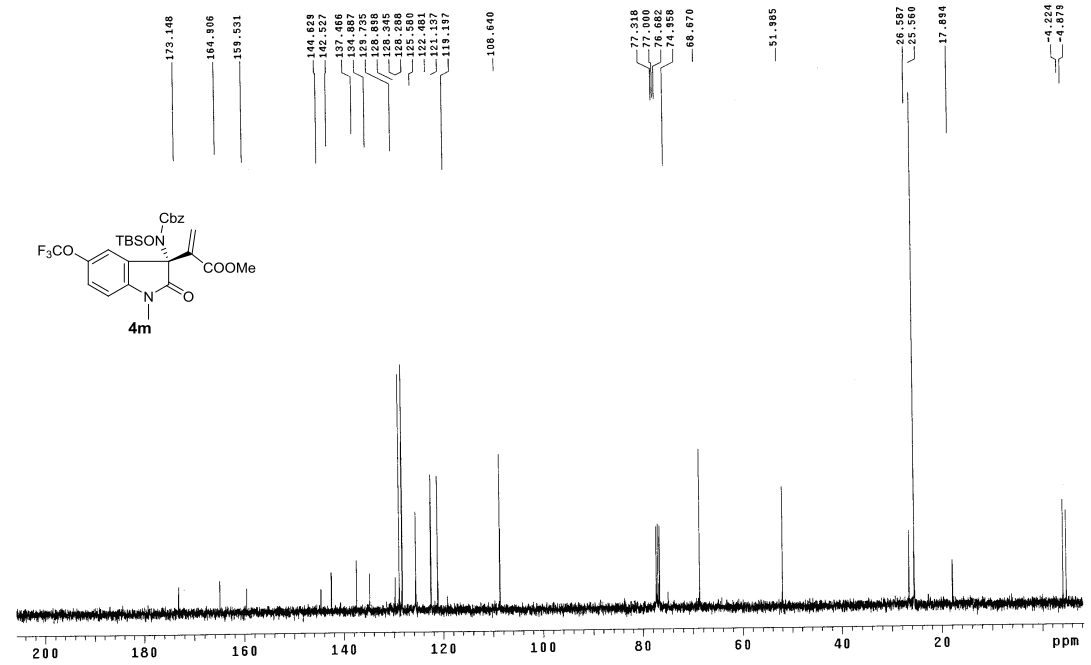
2.69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108.640
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77.000
76.682
74.958
68.670
51.985
26.587
25.560
17.894
-4.224
-4.878
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COOMe
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4m
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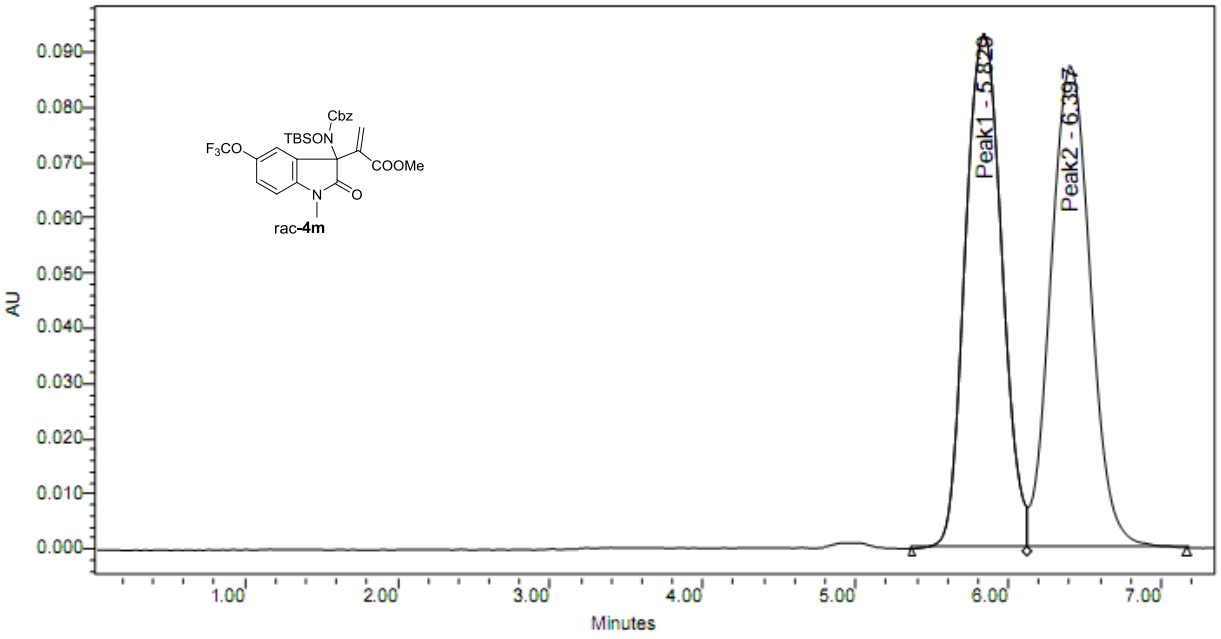
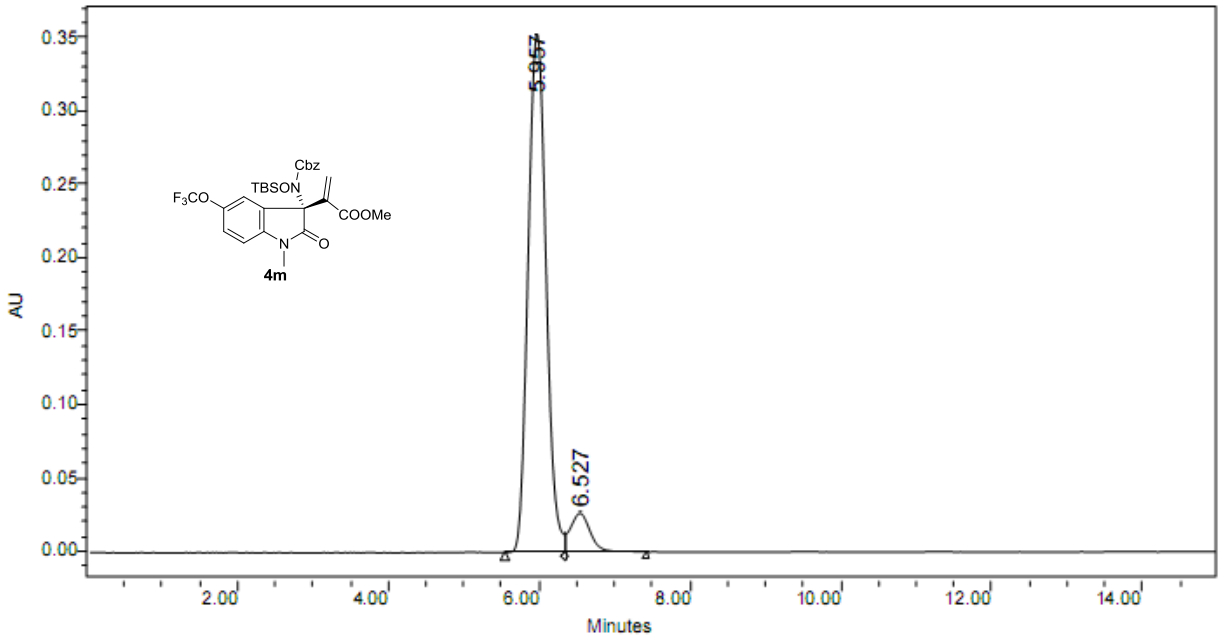
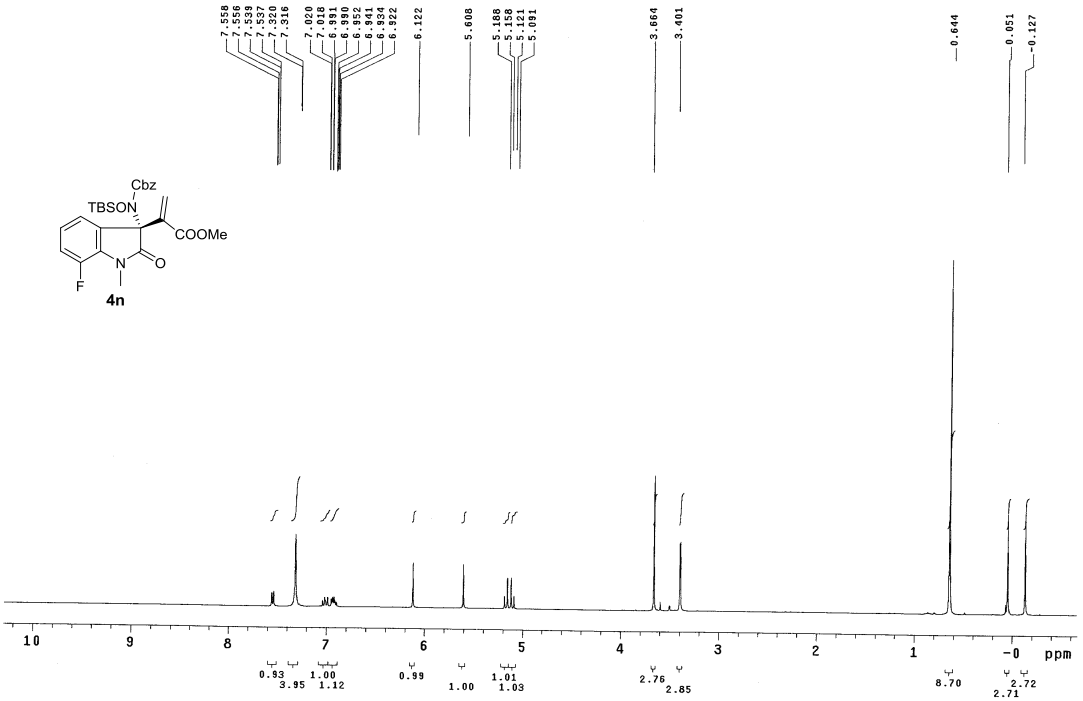
20
ppm



	Peak Name	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	Peak1	5.829	1562003	49.58	93275	51.65
2	Peak2	6.397	1588384	50.42	87309	48.35



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	5.957	5838881	92.30	353402	93.05
2	6.527	486900	7.70	26398	6.95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6.122
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5.188
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5.121
5.101
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Cbz
TBSON
COOMe
N
O
F
4n
10
9
8
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6
5
4
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2
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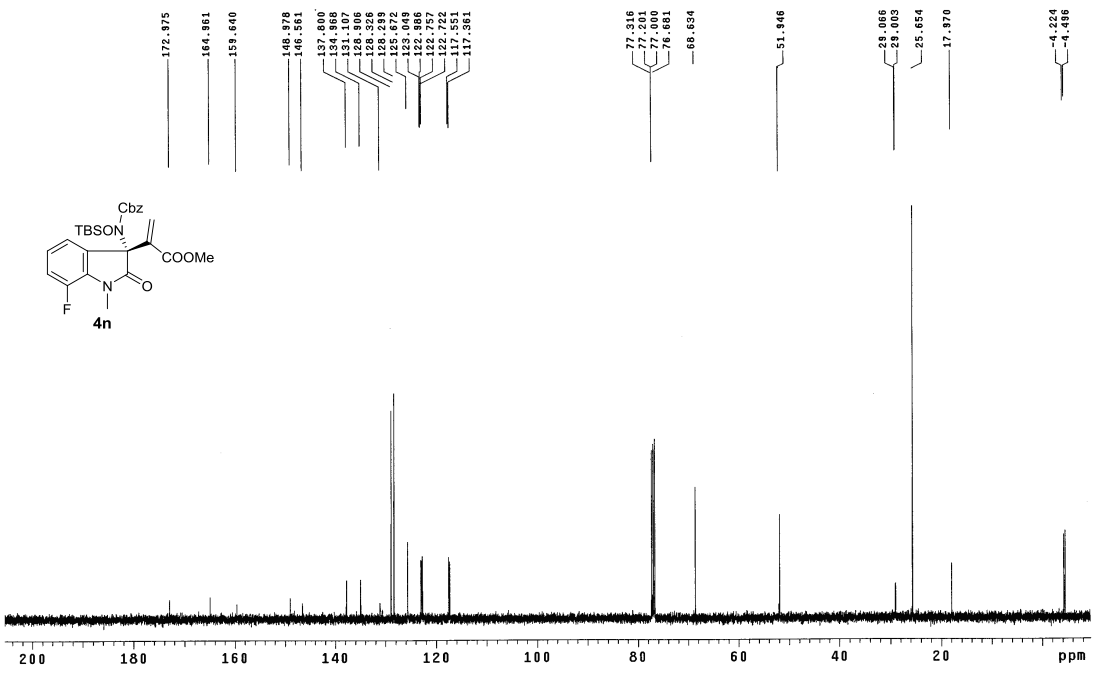
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28.066
28.003
25.654
17.970
-4.224
-4.496
Cbz
TBSON
COOMe
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O
F
4n
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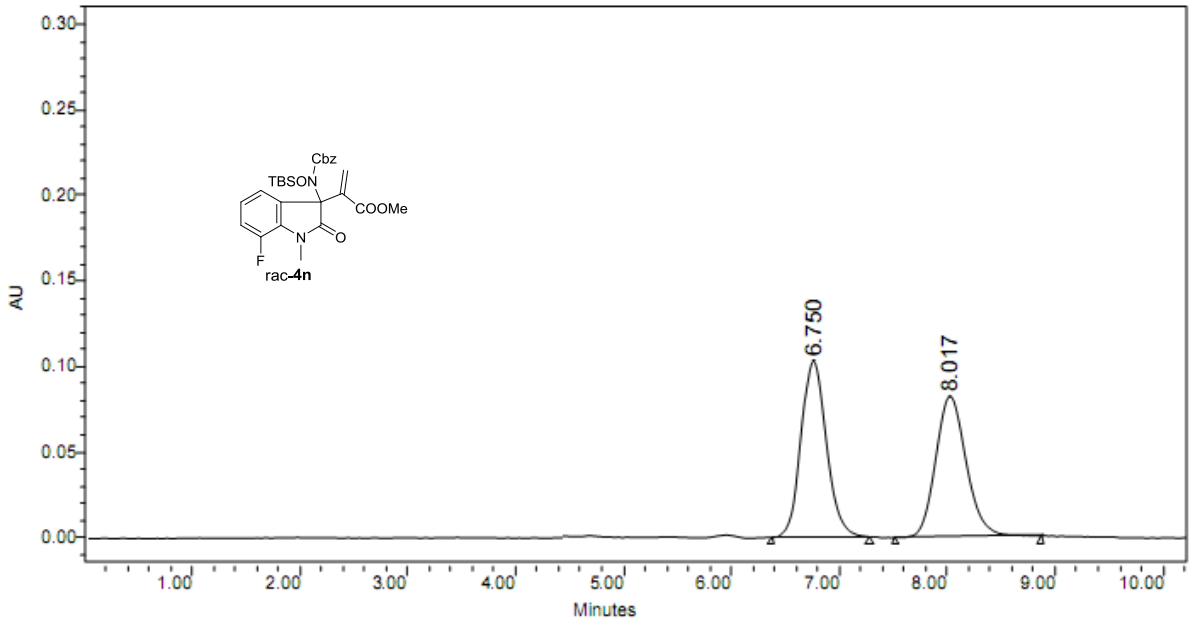
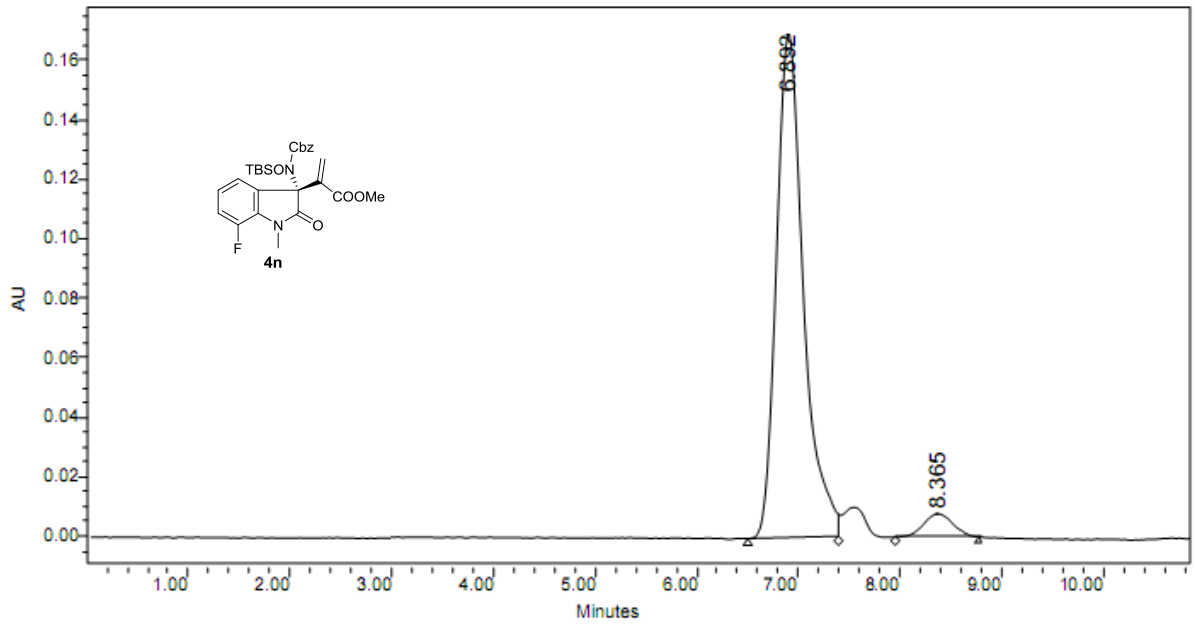
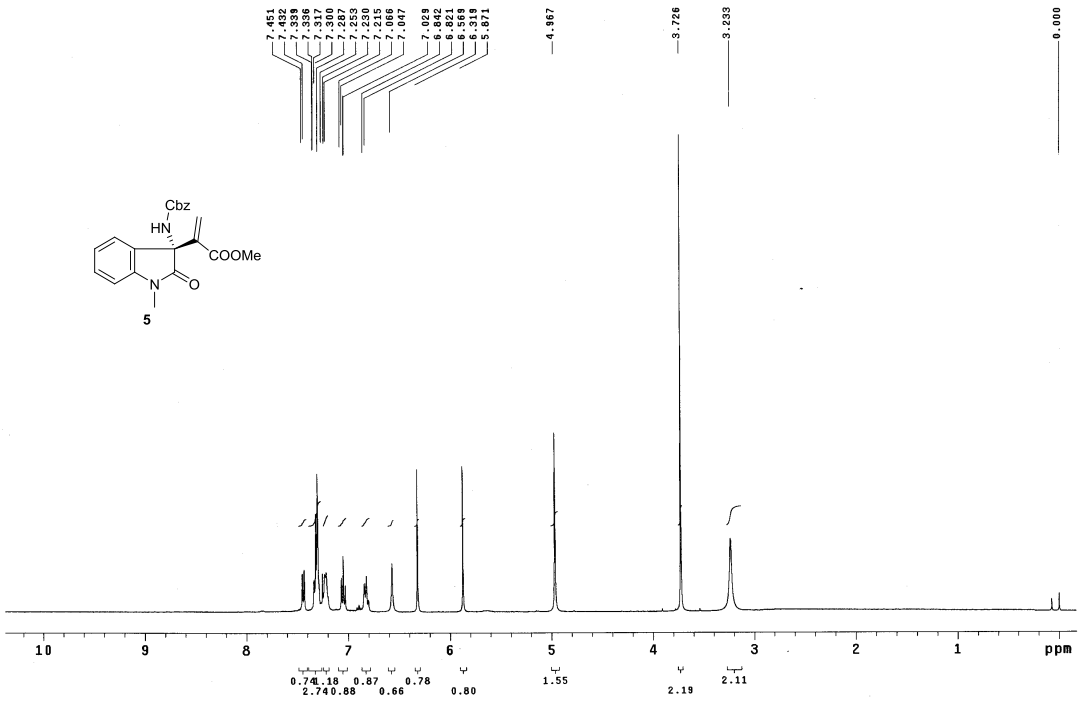
160
140
120
100
80
60
40
20
ppm



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	6.750	1708260	51.24	103140	55.66
2	8.017	1625556	48.76	82170	44.34



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	6.892	3143933	95.18	169780	95.60
2	8.365	159382	4.82	7811	4.40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7.047
7.029
6.842
6.821
6.558
6.318
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4.967
3.726
3.233
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Cbz
HN
COOMe
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10
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4
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2
1
ppm
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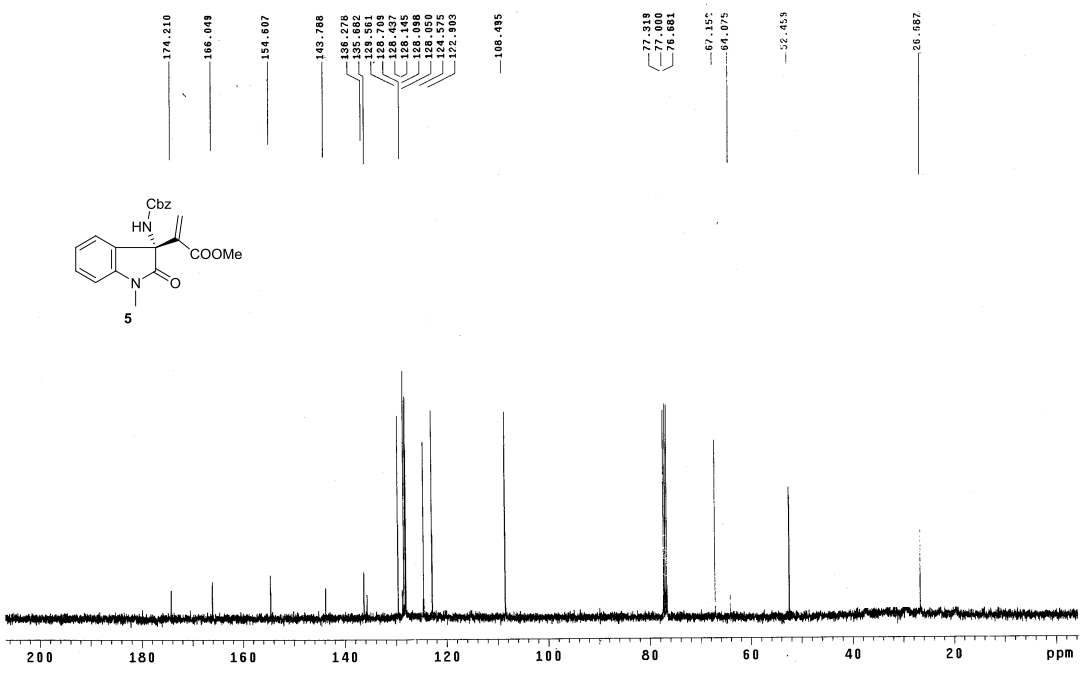
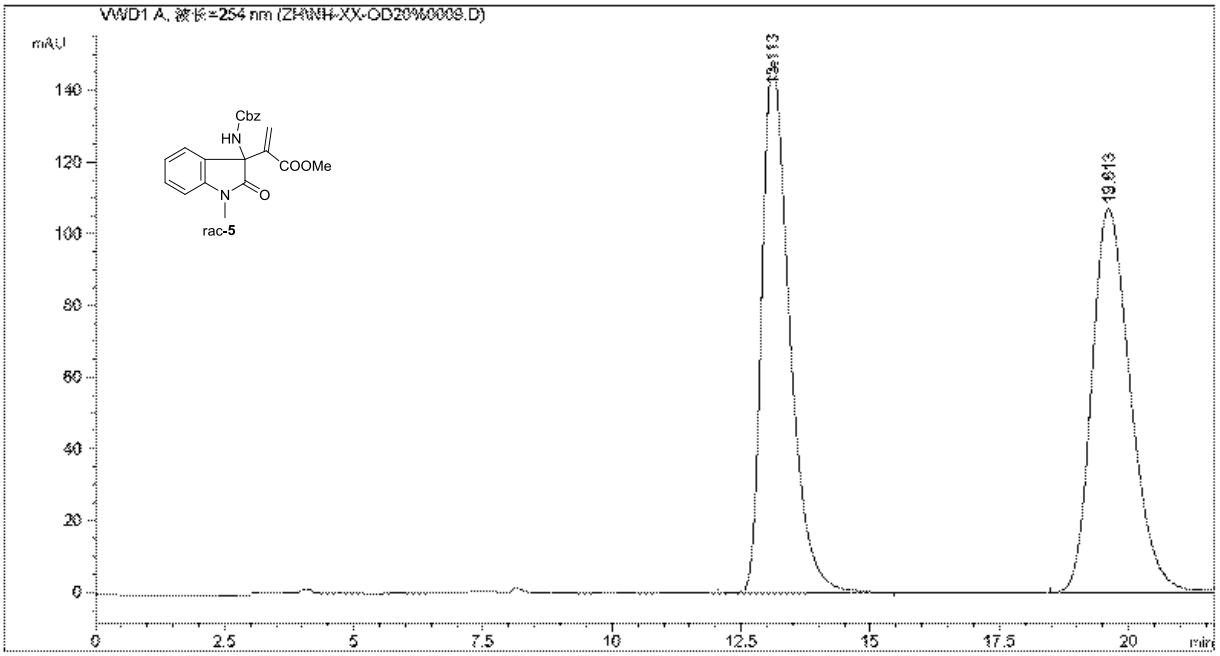
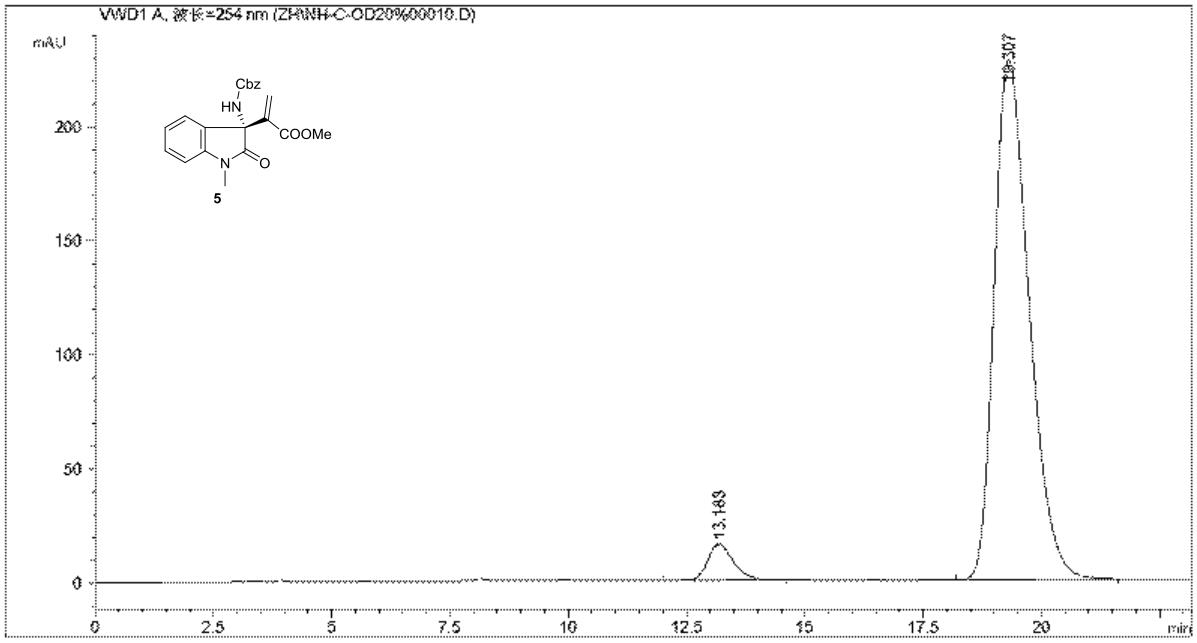
2.19
2.11

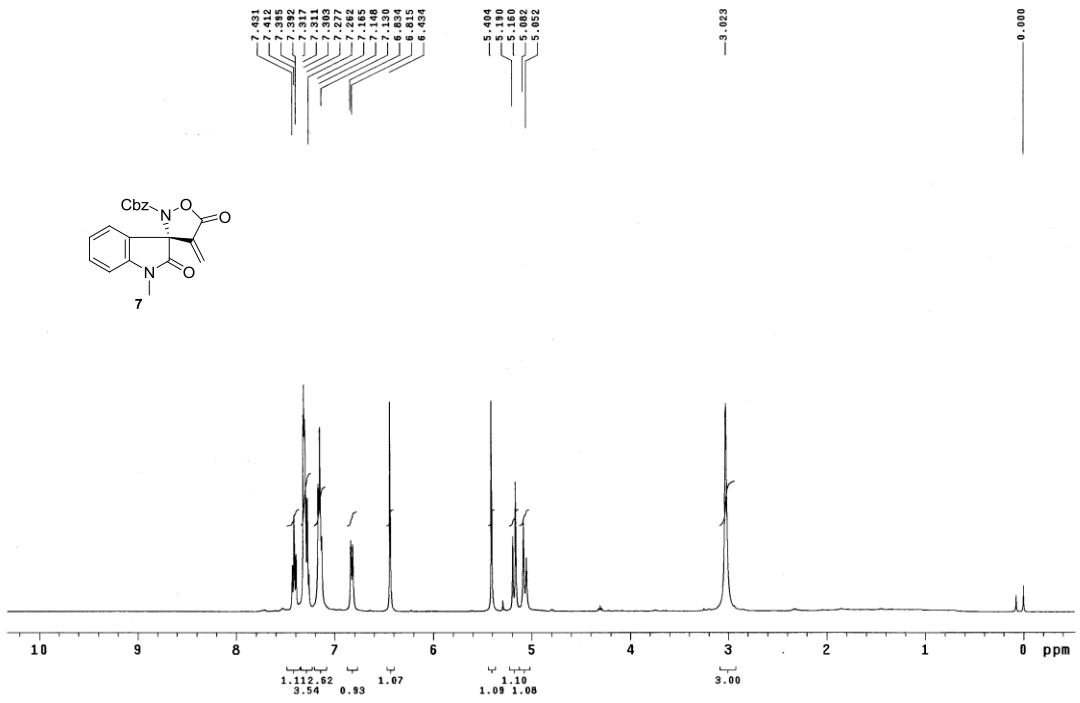

174.210
166.049
154.607
143.788
136.278
135.682
129.561
128.709
128.487
128.145
128.098
128.050
124.575
122.903
108.495
77.319
77.000
76.681
67.155
64.075
52.459
26.687
Cbz
HN
COOMe
N
O
5
200
180
160
140
120
100
80
60
40
20
ppm

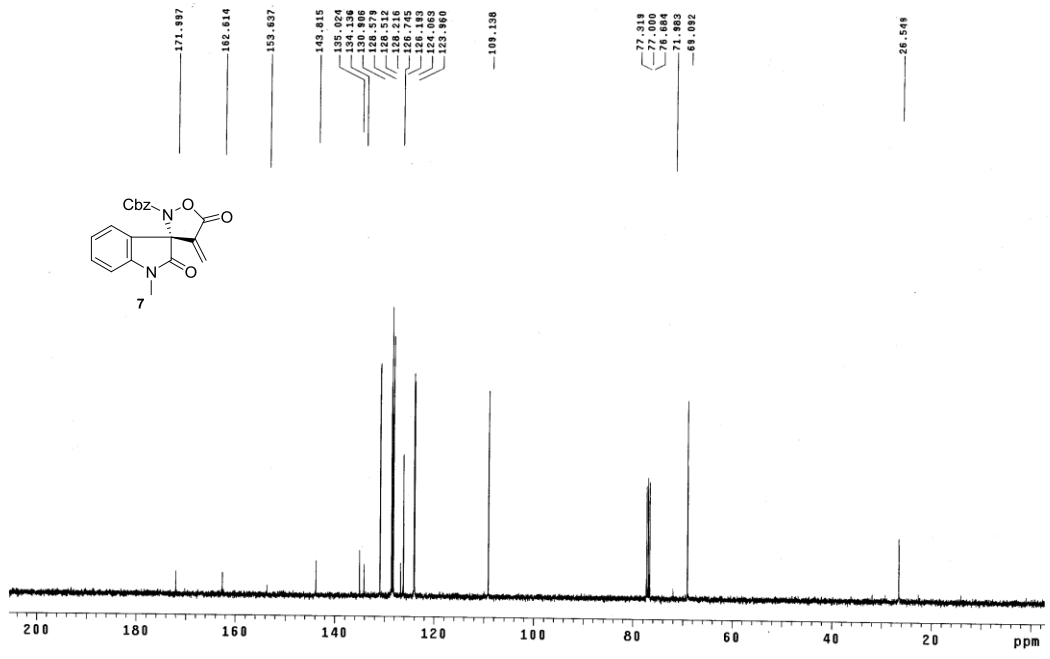


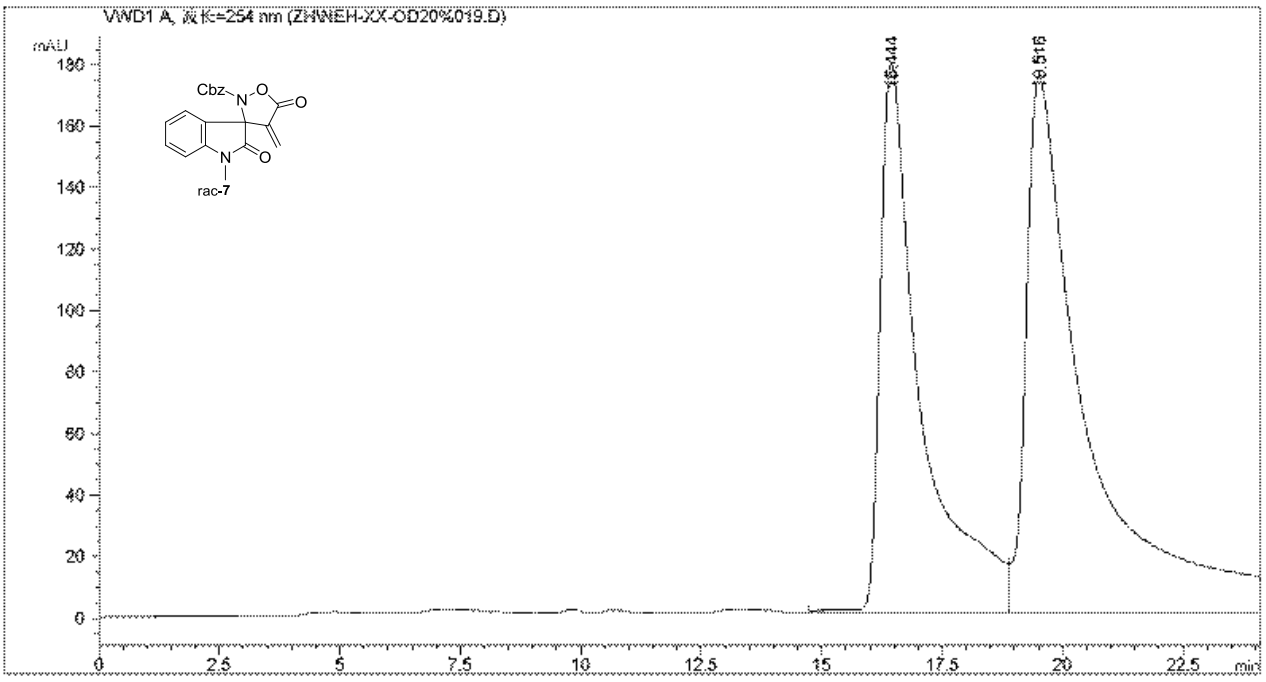
#	[min]		[min]	mAU	*s	[mAU]	%
1	13.113	VB	0.5677	5527.01123	148.65958	49.8333
2	19.613	BB	0.8043	5563.98584	107.06664	50.1667



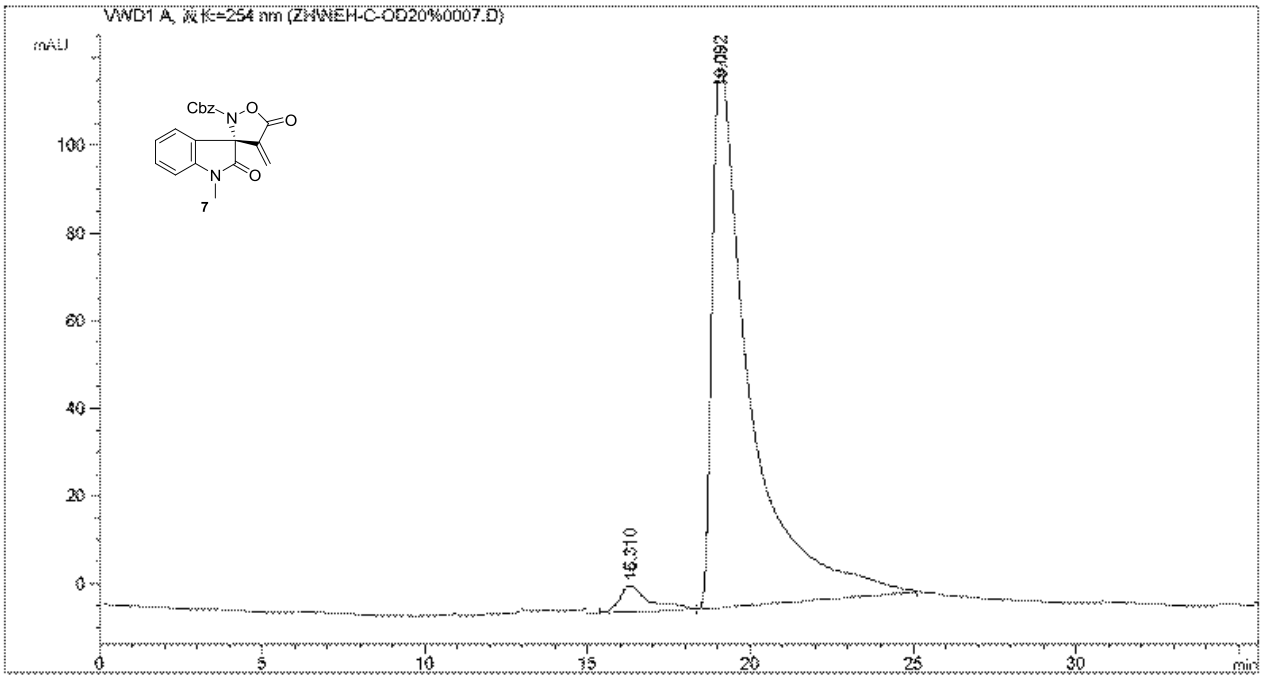
#	[min]		[min]	mAU	*s	[mAU]	%
1	13.183	VB	0.5804	604.95105	15.80855	4.9305
2	19.307	BB	0.7887	1.16646e4	228.14536	95.0695


7.431
7.412
7.395
7.392
7.317
7.311
7.303
7.277
7.262
7.155
7.148
7.130
6.834
6.815
6.434
5.404
5.130
5.160
5.082
5.052
3.023
0.000
Cbz
N
O
O
O
N
O
7
10
9
8
7
6
5
4
3
2
1
0
ppm
1.112.62
3.54
0.93
1.07
1.09
1.10
1.08
3.00


171.997
162.614
153.637
143.815
135.024
134.136
130.806
128.579
128.512
128.216
126.745
126.183
124.063
123.900
109.138
77.318
77.000
76.684
71.983
69.092
26.548
Cbz
N
O
O
O
N
O
7
200
180
160
140
120
100
80
60
40
20
ppm



#	[min]		[min]	mAU * s	[mAU]	%
1	16.444	BV	0.8291	1.04819e4	178.53511	46.4217
2	19.516	VBA	1.1734	1.46234e4	173.92662	53.5783



#	[min]		[min]	mAU * s	[mAU]	%
1	16.310	BB	0.8939	379.64362	5.96525	5.1383
2	19.092	BB	1.1322	1.00549e4	124.21668	94.8617

7. References

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2. Peng, J.; Huang, X.; Jiang, L.; Cui, H. L.; Chen, Y. C. *Org. Lett.* **2011,** *13,* 4584–4587.

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