Supporting Information

Cycloaddition of Cyclobutenoneand Azomethine Imine Enabled by Chiral Isothiourea Organic Catalysts

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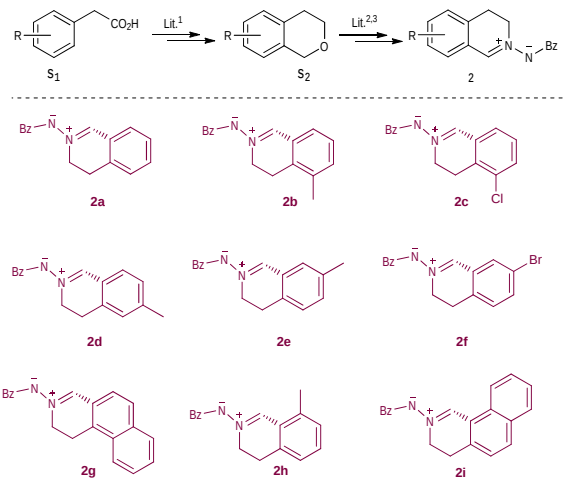
1. General Information

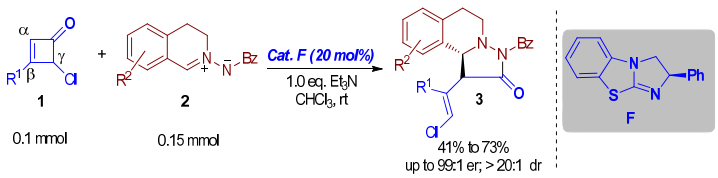
All reactions were carried out under standard conditions using N_2 as shielding gas with magnetic stirring. Analytical thin layer chromatography (TLC) was performed with TLC plates. All reactions and column chromatography were monitored by thin layer chromatography with UV light under a 254 nm and colorized with ethanol solution of phosphomolybdic acid, followed by heating using a heat gun. All products could be purified by column chromatography using ethyl acetate and hexane as eluent. Organic solutions were concentrated by rotary evaporation. All solvents were freshly distilled before use. ^{1}H and ^{13}C NMR chemical shifts are reported in $CDCl_3$ solution of compound by Bruker AV-300 MHz or Bruker AV-400 MHz instruments and marked in ppm relative to tetramethylsilane (TMS) (0) and $CDCl_3$ (77.0 ppm) as standard. The following abbreviations are used to describe peak patterns where appropriate: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants (*J*) are reported in Hertz (Hz). High resolution mass spectral analysis (HRMS) was performed on Waters Q-TOF Premier mass spectrometer. The determination of *ee* was performed *via* chiral phase HPLC analysis using Shimadzu LC-20AD HPLC workstation. Optical rotations were measured using a 1 mL cell with a 1 cm path length on a Jasco P1030 digital polarimeter and are reported as follows: $[\alpha]^D_{20}$. The dr values of the products were determined by the corresponding ^{1}H NMR spectra. The absolute and relative configuration of products could be assigned by the X-ray structures of **3a**.

2. General procedure for preparation of substrates 1 and 2

All cyclobutenones **1** were prepared in accordance with literature methods.[1] All azomethine imine **2a-2i** were synthesized according to the known literature process from arylacetic acid **S1**[2] (for syntheses of **2c**, **2g** and **2i**) or isochroman derivatives **S2**.[3,4]



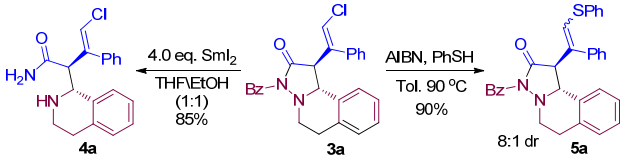
3. General procedure for syntheses of product 3



A mixture of the cyclobutenone **1** (0.1 mmol, 1.0 M), azomethine imine **2** (0.15 mmol) and the Et_3N (1.0 mmol, 14 μL) in CH_3Cl (1.0 mL) were stirred for 5 min at room temperature. Then the catalyst **F** (20 mol%, 5.4 mg), prepared *via* Birman's method[5], was added into the reaction system. After the reaction was stirred for 3 days, flash chromatography (SiO2, 10% EtOAc/hexanes) afforded the final product in 41%~73% yields with excellent er, which were determined using chiral HPLC.

Note: the racemate were prepared using catalyst **C** or **D** in table in text.

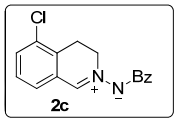
4. General procedure for the synthetic applicability



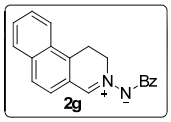
For synthesis of **4a**: under nitrogen atmosphere, the solution of SmI_2 in THF (4.0 mL, 0.1 M) was added into the solution of **3a** (0.1 mmol, 43 mg) in EtOH (2.0 mL) at room temperature. The reaction was stirred for 2 hours, the resulting solvent was removed by vaccum pump. The product **4a** could be obtained in 85% yield through isolation of silica gel column chromatography (SiO_2, 50% EtOAc/hexanes).

For synthesis of **5a**: under nitrogen atmosphere, the AIBN (20 mol%, 3.2 mg) was added into the mixture of **3a** (0.1 mmom, 43 mg) and PhSH (0.2 mmol, 22 mg) in toluene at room temperature. Then the reaction temperature was increased to 80 °C for overnight. Then the reaction system was cooled to room temperature and a direct isolation of silica gel column chromatography could offer the product **5a** in 90% yield (SiO_2, 10% EtOAc/hexanes).

5. Characterization of substrates (2c, 2g and 2i)

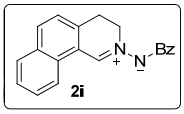


benzoyl(5-chloro-3,4-dihydroisoquinolin-2-ium-2-yl)amide. Following the literature[2] process, the corresponding acid (1.70 g, 10.0 mmol) gave the substrate **2c** (598 mg) in 21% yield as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.81 (brs, 1H), 8.12-8.06 (m, 2H), 7.50 (dd, *J* = 6.8, 2.3 Hz, 1H), 7.45-7.37 (m, 3H), 7.36-7.30 (m, 2H), 4.25 (t, *J* = 7.5 Hz, 2H), 3.30 (t, *J* = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ^{13}C NMR (100 MHz, DMSO-d_6): δ 168.6, 137.5, 132.8, 132.2, 131.7, 130.1, 129.2, 129.0, 128.6, 127.8, 127.6, 54.0, 23.8. HRMS (ESI) calcd. For $C_{16}H_{14}ClN_2O$ $[M+H]^+$: 285.0789, Found: 285.0785.



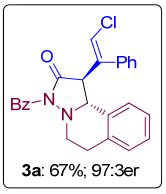
benzoyl(1,2-dihydrobenzo isoquinolin-3-ium-3-yl)amide. Following the literature[2] process, the corresponding acid (1.86 g, 10.0 mmol) gave the substrate **s5** (480 mg) in 16% yield as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.52 (s, 1H), 8.20 (d, *J* = 8.5 Hz, 1H), 8.17-8.13 (m, 2H), 7.98 (d, *J* = 8.3 Hz, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.68-7.63 (m, 1H),

7.60-7.54 (m, 1H), 7.46-7.39 (m, 4H), 4.34 (t, J = 7.8 Hz, 2H), 3.38 (t, J = 7.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 137.3, 134.0, 133.5, 132.8, 130.2, 130.1, 129.0, 128.6, 127.9, 127.9, 126.7, 125.3, 122.4, 121.8, 54.3, 27.7; HRMS (ESI) calcd. For $C_{20}H_{17}N_2O$ $[M+H]^+$: 301.1335, Found: 301.1336.

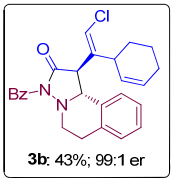


benzoyl(3,4-dihydrobenzo[h]isoquinolin-2-ium-2-yl)amide. Following the literature[2] process, the corresponding acid (1.86 g, 10.0 mmol) gave the substrate **s4** (390 mg) 13% yield as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.84 (s, 1H), 8.17-8.10 (m, 2H), 8.07-8.01 (m, 1H), 7.94-7.80 (m, 2H), 7.68-7.59 (m, 2H), 7.50-7.37 (m, 4H), 4.41 (t, J = 8.0 Hz, 2H), 3.64 (t, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 137.3, 135.5, 131.7, 130.2, 130.1, 129.0, 128.4, 127.9, 127.9, 127.6, 125.2, 124.3, 124.0, 54.3, 23.4; HRMS (ESI) calcd. For $C_{20}H_{17}N_2O$ $[M+H]^+$: 301.1335, Found: 301.1335.

6. Characterization of products 3, 4 and 5

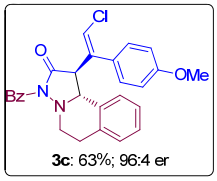


(1S,10bR)-3-benzoyl-1-((Z)-2-chloro-1-phenylvinyl)-1,5,6,10b-tetrahydropyrazolo[5,1-a]isoquinolin-2(3H)-one. White solid, m.p. 162-164 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.35 (m, 10H), 7.32-7.26 (m, 3H), 7.24-7.19 (m, 1H), 6.33 (s, 1H), 4.92 (d, J = 11.5 Hz, 1H), 3.95 (d, J = 11.5 Hz, 1H), 3.75 (ddd, J = 10.0 Hz, 4.8 Hz, 2.2 Hz, 1H), 3.25 (ddd, J = 16.8 Hz, 12.2 Hz, 4.9 Hz, 1H), 3.06 (ddd, J = 12.7 Hz, 10.2 Hz, 2.9 Hz, 1H), 2.84 (dt, J = 16.4 Hz, 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.9, 166.3, 136.6, 134.6, 133.3, 133.1, 132.8, 132.1, 129.7, 128.9, 128.7, 128.7, 128.6, 127.9, 127.6, 126.7, 126.5, 122.7, 59.6, 57.2, 48.9, 28.7; HRMS (ESI) calcd. For $C_{26}H_{21}ClN_2O_2$ $[M+H]^+$: 429.1370, Found: 429.1362. $[\alpha]^{20}_D$ = -13.0 (c = 2.0 mg/mL, $CHCl_3$). IR ν (cm^{-1}) 3067, 1751, 1690, 1275, 1160, 695. The er value was determined by HPLC (Chiralcel OD, hexane/isopropanol = 85:15, flow rate = 0.75 mL/min), retention time: t_1 = 17.3 min, t_2 = 38.1 min.



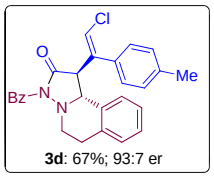
(1S,10bR)-3-benzoyl-1-((Z)-2-chloro-1-(cyclohex-1-en-1-yl)vinyl)-1,5,6,10b-tetrahydropyrazolo[5,1-a]isoquinolin-2(3H)-one. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64-7.60 (m, 2H), 7.53 (tt, J = 7.6 Hz, 2.0 Hz, 1H), 7.45-7.39 (m, 2H), 7.28-7.14 (m, 4H), 5.98 (s, 1H), 5.91 (pent, J = 2.0 Hz, 1H), 4.98 (d, J = 11.5 Hz, 1H), 3.74(ddd, J = 10.0 Hz, 4.8 Hz, 2.4 Hz, 1H), 3.68 (d, J = 11.4 Hz, 1H), 3.27 (ddd, J = 16.6 Hz, 12.1 Hz, 4.7 Hz, 1H), 3.03 (ddd, J =

12.8 Hz, 10.2 Hz, 2.9 Hz, 1H), 2.84 (dt, *J* = 16.4 Hz, 2.5 Hz, 1H), 2.28-2.18 (m, 4H), 1.80-1.64 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.1, 166.3, 138.2, 133.6, 133.1, 132.9, 132.1, 130.6, 128.7, 128.6, 127.9, 127.5, 126.9, 126.4, 120.6, 59.8, 56.6, 48.7, 28.9, 28.7, 25.4, 22.7, 21.8; HRMS (ESI) calcd. For $C_{26}H_{26}ClN_2O_2$ $[M+H]^+$: 433.1677, Found: 433.1675. $[\alpha]^{20}_D$ = -45.3 (*c* = 12.0 mg/mL, $CHCl_3$). The er value was determined by HPLC (Chiralcel OD, hexane/isopropanol = 85:15, flow rate = 0.75 mL/min), retention time: t_1 = 13.6 min, t_2 = 24.8 min.



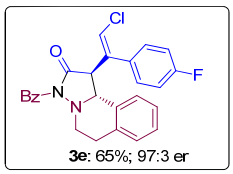
3c: 63%; 96:4 er

(1S,10bR)-3-benzoyl-1-((Z)-2-chloro-1-(4-methoxyphenyl)vinyl)-1,5,6,10b-tetrahydropyrazolo[5,1-a]isoquinolin-2(3H)-one. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (tt, *J* = 7.1 Hz, 1.8 Hz, 1H), 7.43-7.31 (m, 6H), 7.29-7.25 (m, 3H), 7.23-7.18 (m, 1H), 7.01 (dt, *J* = 9.6 Hz, 2.5 Hz, 1H), 6.30 (s, 1H), 4.90 (d, *J* = 11.4 Hz, 1H), 3.92 (d, *J* = 11.4 Hz, 1H), 3.86 (s, 3H), 3.72 (ddd, *J* = 10.0, 4.7, 2.2 Hz, 1H), 3.24 (ddd, *J* = 16.8, 12.2, 4.9 Hz, 1H), 3.06 (ddd, *J* = 12.7, 10.1, 2.9 Hz, 1H), 2.83 (dt, *J* = 16.4, 2.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.0, 166.3, 159.6, 136.2, 133.3, 133.1, 132.8, 132.1, 130.9, 128.8, 128.7, 127.9, 127.6, 126.7, 126.6, 126.4, 122.5, 114.1, 59.7, 57.4, 55.3, 49.0, 28.7; HRMS (ESI) calcd. For $C_{27}H_{24}ClN_2O_3$ $[M+H]^+$: 459.1470, Found: 459.1470. $[\alpha]^{20}_D$ = -64.2 (*c* = 7.0 mg/mL, $CHCl_3$). IR ν (cm^{-1}) 3071, 1756, 1696, 1510, 1293, 1179. The er value was determined by HPLC (Chiralcel OD, hexane/isopropanol = 85:15, flow rate = 0.75 mL/min), retention time: t_1 = 21.1 min, t_2 = 46.5 min.



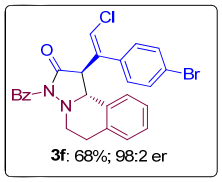
3d: 67%; 93:7 er

(1S,10bR)-3-benzoyl-1-((Z)-2-chloro-1-(p-tolyl)vinyl)-1,5,6,10b-tetrahydropyrazolo[5,1-a]isoquinolin-2(3H)-one. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.50 (m, 1H), 7.41-7.34 (m, 4H), 7.32-7.27 (m, 7H), 7.24-7.19 (m, 1H), 6.30 (s, 1H), 4.90 (d, *J* = 11.4 Hz, 1H), 3.92 (d, *J* = 11.4 Hz, 1H), 3.74(ddd, *J* = 9.9, 4.7, 2.1 Hz, 1H), 3.25 (ddd, *J* = 16.7, 12.2, 4.8 Hz, 1H), 3.05 (ddd, *J* = 12.7, 10.3, 2.9 Hz, 1H), 2.83 (dt, *J* = 16.4, 2.7 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.0, 166.3, 138.5, 136.5, 133.3, 133.1, 132.8, 132.1, 131.6, 129.5, 129.4, 128.8, 128.7, 127.9, 127.6, 126.8, 126.4, 122.4, 59.6, 57.3, 48.9, 28.7, 21.3; HRMS (ESI) calcd. For $C_{27}H_{24}ClN_2O_2$ $[M+H]^+$: 443.1521, Found: 443.1530. $[\alpha]^{20}_D$ = -53.4 (*c* = 7.0 mg/mL, $CHCl_3$). IR ν (cm^{-1}) 3076, 1763, 1294, 1185, 1122, 692. The er value was determined by HPLC (Chiralcel IA, hexane/isopropanol = 95:5, flow rate = 0.75 mL/min), retention time: t_1 = 20.0 min, t_2 = 22.5 min.



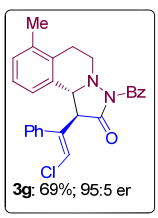
3e: 65%; 97:3 er

(1S,10bR)-3-benzoyl-1-((Z)-2-chloro-1-(4-fluorophenyl)vinyl)-1,5,6,10b-tetrahydropyrazolo[5,1-a]isoquinolin-2(3H)-one. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.49 (m, 1H), 7.41-7.35 (m, 6H), 7.31-7.27 (m, 2H), 7.26-7.15 (m, 4H), 6.34 (s, 1H), 4.87 (d, *J* = 11.5 Hz, 1H), 3.94 (d, *J* = 11.5 Hz, 1H), 3.72 (ddd, *J* = 9.9, 4.6, 2.1 Hz, 1H), 3.24 (ddd, *J* = 16.7, 12.3, 4.9 Hz, 1H), 3.07 (ddd, *J* = 12.6, 10.2, 2.8 Hz, 1H), 2.84 (dt, *J* = 16.4, 2.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.8, 166.2, 162.7 (*J* = 248.9 Hz), 135.8, 133.3, 133.2, 132.6, 132.3, 131.6 (*J* = 8.3 Hz), 130.6 (*J* = 3.7 Hz), 129.0, 128.7, 128.0, 127.7, 126.6, 126.5, 123.3, 115.9 (*J* = 21.5 Hz), 59.8, 57.2, 49.0, 28.7; HRMS (ESI) calcd. For $C_{26}H_{21}ClFN_2O_2$ $[M+H]^+$: 447.1270, Found: 447.1271. $[\alpha]^{20}_D$ = 27.7 (*c* = 9.0 mg/mL, $CHCl_3$). IR ν (cm^{-1}) 2920, 1688, 1279, 1221, 1012, 848. The er value was determined by HPLC (Chiralcel OD, hexane/isopropanol = 85:15, flow rate = 0.75 mL/min), retention time: t_1 = 25.9 min, t_2 = 39.8 min.



3f: 68%; 98:2 er

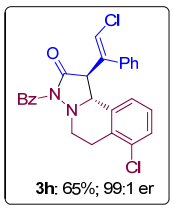
(1S,10bR)-3-benzoyl-1-((Z)-1-(4-bromophenyl)-2-chlorovinyl)-1,5,6,10b-tetrahydropyrazolo[5,1-a]isoquinolin-2(3H)-one. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65-7.60 (m, 2H), 7.57-7.50 (m, 1H), 7.41-7.36 (m, 4H), 7.31-7.27 (m, 4H), 7.25-7.20 (m, 2H), 6.34 (s, 1H), 4.86 (d, *J* = 11.5 Hz, 1H), 3.95 (d, *J* = 11.5 Hz, 1H), 3.71 (ddd, *J* = 9.9, 4.6, 2.1 Hz, 1H), 3.24 (ddd, *J* = 16.6, 12.1, 4.8 Hz, 1H), 3.03 (ddd, *J* = 12.6, 10.2, 2.7 Hz, 1H), 2.84 (dt, *J* = 16.4, 2.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.7, 166.2, 135.6, 133.6, 133.2, 133.2, 132.5, 132.3, 132.0, 131.4, 129.0, 128.7, 128.0, 127.7, 126.6, 126.5, 123.3, 123.0, 59.9, 57.0, 49.0, 28.7; HRMS (ESI) calcd. For $C_{26}H_{21}BrClN_2O_2$ $[M+H]^+$: 507.0469, Found: 507.0473. $[\alpha]^{20}_D$ = -25.7 (*c* = 5.0 mg/mL, $CHCl_3$). IR ν (cm^{-1}) 3073, 1760, 1296, 1183, 1010, 684. The er value was determined by HPLC (Chiralcel OD, hexane/isopropanol = 85:15, flow rate = 0.75 mL/min), retention time: t_1 = 23.7 min, t_2 = 38.7 min.



3g: 69%; 95:5 er

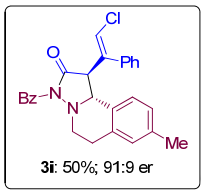
(1S,10bR)-3-benzoyl-1-((Z)-2-chloro-1-phenylvinyl)-7-methyl-1,5,6,10b-tetrahydropyrazolo[5,1-a]isoquinolin-2(3H)-one. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.48 (m, 3H), 7.47-7.45 (m, 1H), 7.44-7.40 (m, 2H), 7.38-7.35 (m, 4H), 7.24-7.12 (m, 3H), 6.33 (s,

1H), 4.89 (d, *J* = 11.4 Hz, 1H), 3.98 (d, *J* = 11.4 Hz, 1H), 3.83-3.74 (m, 1H), 3.10-2.95 (m, 2H), 2.89-2.79 (m, 1H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.1, 166.3, 136.7, 136.5, 134.7, 133.3, 132.6, 132.1, 131.7, 129.7, 129.0, 128.7, 128.7, 128.6, 127.9, 126.2, 124.6, 122.6, 59.9, 57.2, 48.8, 26.1, 19.4; HRMS (ESI) calcd. For $C_{27}H_{24}ClN_2O_2$ $[M+H]^+$: 443.1521, Found: 443.1519. $[\alpha]^{20}_D$ = -30.4 (*c* = 11.0 mg/mL, $CHCl_3$). IR ν (cm^{-1}) 3063, 1754, 1689, 1284, 1202, 700. The er value was determined by HPLC (Chiralcel OD, hexane/isopropanol = 85:15, flow rate = 0.75 mL/min), retention time: t_1 = 23.7 min, t_2 = 29.6 min.



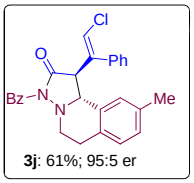
3h: 65%; 99:1 er

(1S,10bR)-3-benzoyl-7-chloro-1-((Z)-2-chloro-1-phenylvinyl)-1,5,6,10b-tetrahydropyrazolo[5,1-a]isoquinolin-2(3H)-one. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.44 (m, 4H), 7.41-7.33 (m, 7H), 7.27-7.19 (m, 2H), 6.33 (s, 1H), 4.88 (d, *J* = 11.4 Hz, 1H), 3.94 (d, *J* = 11.4 Hz, 1H), 3.84-3.75 (m, 1H), 3.17-2.98 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.6, 166.2, 136.4, 134.7, 134.5, 134.4, 133.1, 132.2, 131.5, 129.6, 128.8, 128.7, 128.4, 128.0, 127.5, 125.3, 123.0, 59.6, 57.1, 48.5, 26.7; HRMS (ESI) calcd. For $C_{19}H_{16}Cl_2N_2O$ $[M+H]^+$: 358.0634, Found: 358.0634. $[\alpha]^{20}_D$ = -25.6 (*c* = 14.0 mg/mL, $CHCl_3$). IR ν (cm^{-1}) 1748, 1689, 1650, 1279, 1015, 949. The er value was determined by HPLC (Chiralcel OD, hexane/isopropanol = 85:15, flow rate = 0.75 mL/min), retention time: t_1 = 24.2 min, t_2 = 37.1 min.



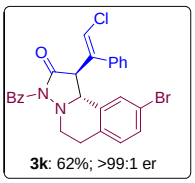
3i: 50%; 91:9 er

(1S,10bR)-3-benzoyl-1-((Z)-2-chloro-1-phenylvinyl)-8-methyl-1,5,6,10b-tetrahydropyrazolo[5,1-a]isoquinolin-2(3H)-one. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.44 (m, 4H), 7.43-7.38 (m, 2H), 7.37-7.33 (m, 4H), 7.20 (d, *J* = 7.9 Hz, 1H), 7.10 (d, *J* = 7.9 Hz, 1H), 7.04 (s, 1H), 6.32 (s, 1H), 4.89 (d, *J* = 11.4 Hz, 1H), 3.92 (d, *J* = 11.4 Hz, 1H), 3.73 (ddd, *J* = 9.9, 4.6, 2.2 Hz, 1H), 3.22 (ddd, *J* = 16.7, 12.2, 4.7 Hz, 1H), 3.04 (ddd, *J* = 12.7, 10.1, 2.8 Hz, 1H), 2.79 (dt, *J* = 16.4, 2.5 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.0, 166.3, 137.4, 136.6, 134.7, 133.3, 133.0, 132.1, 129.8, 129.7, 129.4, 128.7, 128.7, 128.6, 127.9, 127.3, 126.6, 122.6, 59.5, 57.4, 49.0, 28.7, 21.0; HRMS (ESI) calcd. For $C_{27}H_{24}ClN_2O_2$ $[M+H]^+$: 443.1521, Found: 443.1520. $[\alpha]^{20}_D$ = -81.9 (*c* = 7.0 mg/mL, $CHCl_3$). IR ν (cm^{-1}) 2920, 1757, 1691, 1290, 1197, 699. The er value was determined by HPLC (Chiralcel OD, hexane/isopropanol = 85:15, flow rate = 0.75 mL/min), retention time: t_1 = 12.7 min, t_2 = 33.3 min.



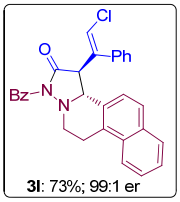
3j: 61%; 95:5 er

(1S,10bR)-3-benzoyl-1-((Z)-2-chloro-1-phenylvinyl)-9-methyl-1,5,6,10b-tetrahydropyrazolo[5,1-a]isoquinolin-2(3H)-one. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.48 (m, 3H), 7.47-7.44 (m, 1H), 7.43-7.39 (m, 2H), 7.38-7.34 (m, 4H), 7.12-7.06 (m, 3H), 6.34 (s, 1H), 4.88 (d, *J* = 11.4 Hz, 1H), 3.93 (d, *J* = 11.4 Hz, 1H), 3.73 (ddd, *J* = 9.9, 4.7, 2.2 Hz, 1H), 3.20 (ddd, *J* = 16.6, 12.3, 4.7 Hz, 1H), 3.04 (ddd, *J* = 12.6, 10.0, 2.8 Hz, 1H), 2.79 (dt, *J* = 16.2, 2.5 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.0, 166.3, 136.6, 135.9, 134.8, 133.3, 132.6, 132.1, 130.0, 129.6, 128.7, 128.7, 128.6, 128.5, 127.9, 127.2, 122.6, 59.8, 57.2, 49.1, 28.3, 21.2; HRMS (ESI) calcd. For $C_{27}H_{24}ClN_2O_2$ $[M+H]^+$: 443.1521, Found: 443.1526. $[\alpha]^{20}_D$ = -23.4 (*c* = 8.0 mg/mL, $CHCl_3$). IR ν (cm^{-1}) 3052, 1747, 1684, 1275, 1199, 699. The er value was determined by HPLC (Chiralcel OD, hexane/isopropanol = 85:15, flow rate = 0.75 mL/min), retention time: t_1 = 12.0 min, t_2 = 33.9 min.



3k: 62%; >99:1 er

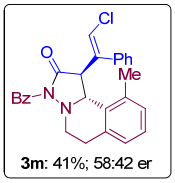
(1S,10bR)-3-benzoyl-9-bromo-1-((Z)-2-chloro-1-phenylvinyl)-1,5,6,10b-tetrahydropyrazolo[5,1-a]isoquinolin-2(3H)-one. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.48 (m, 3H), 7.48-7.44 (m, 1H), 7.42-7.35 (m, 8H), 7.08 (d, *J* = 8.2 Hz, 1H), 6.37 (s, 1H), 4.84 (d, *J* = 11.5 Hz, 1H), 3.92 (d, *J* = 11.5 Hz, 1H), 3.75 (ddd, *J* = 10.0, 4.7, 2.2 Hz, 1H), 3.17 (ddd, *J* = 16.7, 12.2, 4.7 Hz, 1H), 3.02 (ddd, *J* = 12.7, 10.1, 2.8 Hz, 1H), 2.79 (dt, *J* = 16.5, 2.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.5, 166.2, 136.1, 134.8, 134.5, 133.2 (2C), 132.1, 130.8, 130.5, 129.6, 129.5, 128.8, 128.7 (2C), 127.9, 123.1, 119.9, 59.4, 57.0, 48.6, 28.2; HRMS (ESI) calcd. For $C_{26}H_{21}BrClN_2O_2$ $[M+H]^+$: 507.0469, Found: 507.0466. $[\alpha]^{20}_D$ = 251.7 (*c* = 5.0 mg/mL, $CHCl_3$). IR ν (cm^{-1}) 1757, 1691, 1644, 1283, 1198, 1087. The er value was determined by HPLC (Chiralcel OD, hexane/isopropanol = 85:15, flow rate = 0.75 mL/min), retention time: t_1 = 16.4 min, t_2 = 51.5 min.



3l: 73%; 99:1 er

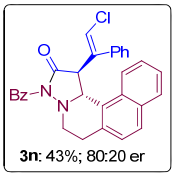
(3S)-1-benzoyl-3-((Z)-2-chloro-1-phenylvinyl)-3,3a,10,11-tetrahydrobenzo[f]pyrazolo[5,1-a]isoquinolin-2(1H)-one. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.3 Hz, 1H), 7.88 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.80 (d, *J* = 8.6 Hz, 1H), 7.62-7.50 (m, 5H), 7.49-7.44 (m, 3H), 7.42-7.35 (m, 5H), 6.37 (s, 1H), 5.04 (d, *J* = 11.4 Hz, 1H), 4.06 (d, *J* = 11.4 Hz, 1H), 3.96 (dt, *J* = 10.1, 3.7 Hz, 1H), 3.44-3.39 (m, 1H), 3.22-3.14 (m, 1H); ^{13}C NMR (100 MHz,

$CDCl_3$): δ 172.1, 166.4, 136.8, 134.8, 133.3, 132.5, 132.2, 131.4, 129.9, 129.7, 129.0, 128.8, 128.7, 128.7, 128.6, 127.9, 127.1, 126.8, 126.3, 124.2, 123.2, 122.7, 60.4, 57.2, 48.7, 25.2; HRMS (ESI) calcd. For $C_{27}H_{24}ClN_2O_2$ $[M+H]^+$: 479.1521, Found: 479.1522. $[\alpha]^{20}_D$ = -35.8 (*c* = 6.0 mg/mL, $CHCl_3$). IR ν (cm^{-1}) 3065, 1756, 1692, 1286, 1208, 700. The er value was determined by HPLC (Chiralcel OD, hexane/isopropanol = 85:15, flow rate = 0.75 mL/min), retention time: t_1 = 16.1 min, t_2 = 20.4 min.



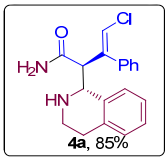
3m: 41%; 58:42 er

(1S,10bR)-3-benzoyl-1-((Z)-2-chloro-1-phenylvinyl)-10-methyl-1,5,6,10b-tetrahydropyrazolo[5,1-a]isoquinolin-2(3H)-one. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54-7.45 (m, 3H), 7.43-7.32 (m, 7H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.10 (d, *J* = 7.4 Hz, 1H), 7.06 (d, *J* = 7.4 Hz, 1H), 6.54 (s, 1H), 5.24 (d, *J* = 7.0 Hz, 1H), 3.78 (d, *J* = 7.0 Hz, 1H), 3.63 (ddd, *J* = 13.2, 9.8, 5.4 Hz, 1H), 3.33 (ddd, *J* = 13.2, 9.0, 4.2 Hz, 1H), 3.04 (ddd, *J* = 16.5, 9.0, 4.0 Hz, 1H), 2.84 (dt, *J* = 16.5, 4.8 Hz, 1H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.9, 166.4, 138.4, 136.1, 135.9, 134.4, 133.3, 132.6, 132.4, 129.6, 129.3, 128.7, 128.5, 128.3, 128.0, 127.5, 126.8, 120.7, 61.7, 57.9, 48.7, 26.0, 20.3; HRMS (ESI) calcd. For $C_{27}H_{24}ClN_2O_2$ $[M+H]^+$: 443.1521, Found: 443.1524. $[\alpha]^{20}_D$ = -68.5 (*c* = 10.0 mg/mL, $CHCl_3$). IR ν (cm^{-1}) 3056, 1748, 1684, 1289, 1207, 698. The er value was determined by HPLC (Chiralcel OD, hexane/isopropanol = 85:15, flow rate = 0.75 mL/min), retention time: t_1 = 12.7 min, t_2 = 16.1 min.

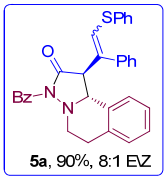


3n: 43%; 80:20 er

(1R)-3-benzoyl-1-((Z)-2-chloro-1-phenylvinyl)-1,5,6,12c-tetrahydrobenzo[h]pyrazolo[5,1-a]isoquinolin-2(3H)-one. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 7.8 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.61-7.57 (m, 2H), 7.53 (tt, *J* = 7.4, 1.3 Hz, 1H), 7.48 (td, *J* = 7.0, 0.5 Hz, 1H), 7.44-7.34 (m, 8H), 6.68 (s, 1H), 5.63 (d, *J* = 4.7 Hz, 1H), 3.91(d, *J* = 4.8 Hz, 1H), 3.87 (dt, *J* = 13.4, 4.5 Hz, 1H), 3.38 (ddd, *J* = 13.4, 9.3, 4.2 Hz, 1H), 3.16 (ddd, *J* = 16.9, 9.1, 3.9 Hz, 1H), 2.91 (dt, *J* = 17.1, 4.3 Hz, 1H); 171.4, 166.6, 138.9, 136.3, 133.3, 133.1, 132.9, 132.2, 130.4, 129.7, 129.2, 128.7, 128.5, 128.4, 128.2, 128.0, 127.1, 126.4, 125.6, 123.0, 120.6, 61.3, 57.9, 47.2, 25.2; HRMS (ESI) calcd. For $C_{27}H_{24}ClN_2O_2$ $[M+H]^+$: 479.1521, Found: 479.1518. $[\alpha]^{20}_D$ = -23.8 (*c* = 9.0 mg/mL, $CHCl_3$). IR ν (cm^{-1}) 2027, 1741, 1689, 1453, 1075, 1015. The er value was determined by HPLC (Chiralcel OD, hexane/isopropanol = 85:15, flow rate = 0.75 mL/min), retention time: t_1 = 12.4 min, t_2 = 15.8 min.

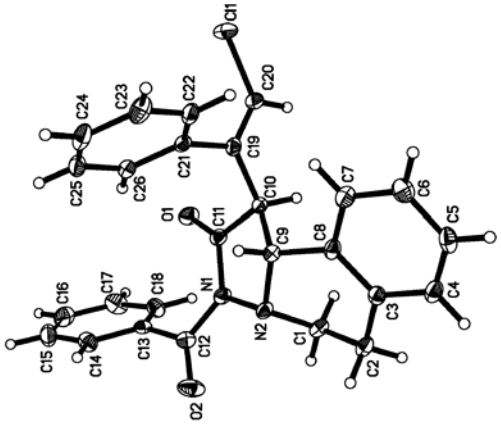


(S,Z)-4-chloro-3-phenyl-2-((R)-1,2,3,4-tetrahydroisoquinolin-1-yl)but-3-enamide: White solid, 174-176 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48-7.36 (m, 6H), 7.25-7.18 (m, 3H), 6.35 (s, 1H), 4.72 (d, *J* = 11.6 Hz, 1H), 3.79 (d, *J* = 11.6 Hz, 1H), 3.24-3.21 (m, 1H), 3.07-2.99 (m, 2H), 2.89-2.78 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.5, 137.4, 134.9, 133.8, 133.2, 129.5, 128.7, 128.6, 128.4, 127.3, 126.7, 126.6, 121.3, 62.3, 55.1, 52.2, 29.7, 28.8; HRMS (ESI) calcd. For $C_{19}H_{20}ClN_2O$ $[M+H]^+$: 327.1264, Found: 327.1266.



(1S,10bR)-3-benzoyl-1-(1-phenyl-2-(phenylthio)vinyl)-1,5,6,10b-tetrahydropyrazolo[5,1-a]isoquinolin-2(3H)-one. Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51-7.20 (m, 19H), 6.53 (s, 1H), 4.96 (d, *J* = 9.6 Hz, 1H), 4.01 (d, *J* = 9.6 Hz, 1H), 3.96-3.73 (d, *J* = 11.6 Hz, 1H), 3.31-3.23 (m, 1H), 3.10-3.04 (m, 1H), 2.83 (d, *J* = 11.6 Hz, 1H) ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.7, 166.4, 136.9, 135.5, 133.5, 133.1, 132.1, 131.9, 129.8, 129.6, 129.1, 128.8, 128.7, 128.5, 127.9, 127.6, 127.0, 127.0, 126.3, 60.6, 58.6, 48.9, 28.8; HRMS (ESI) calcd. For $C_{32}H_{27}N_2O_2S$ $[M+H]^+$: 503.1793, Found: 503.1794.

7. ORTEPS drawing of 3a from X-ray crystallographic analysis



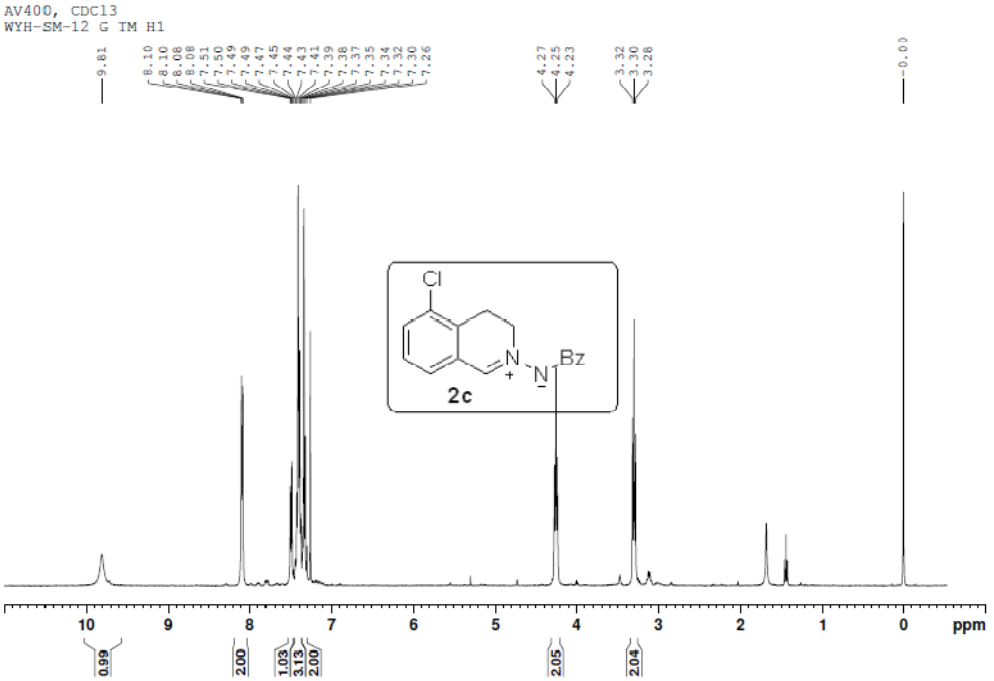
3a (CCDC 1041242)

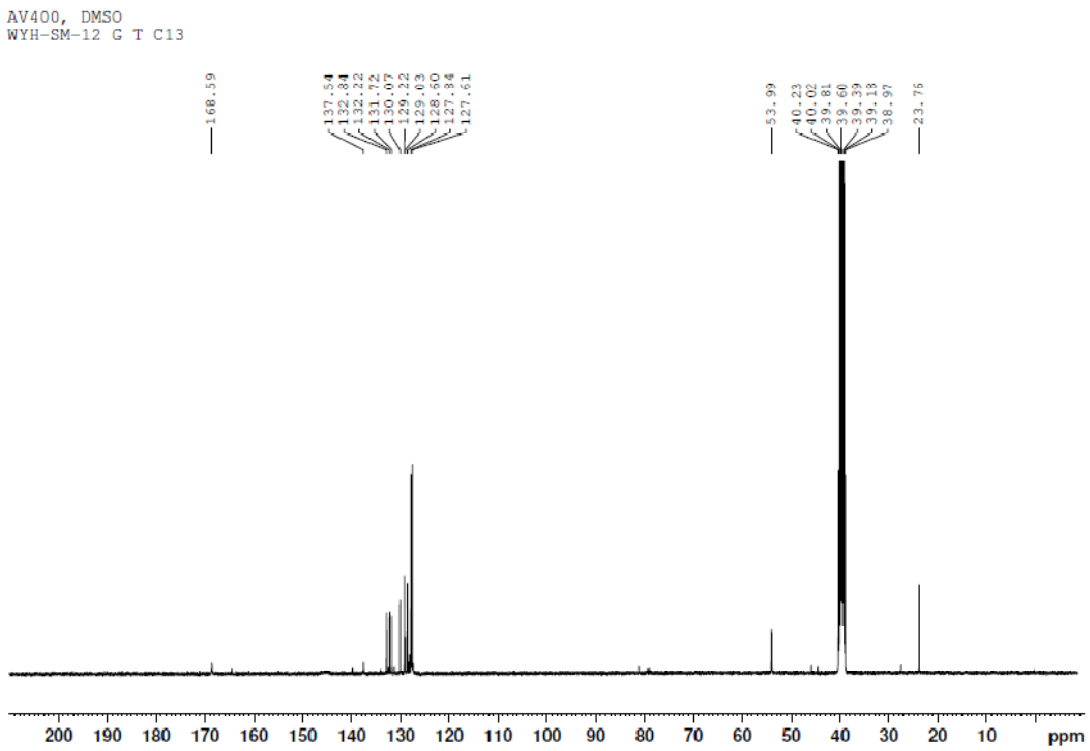
8. References

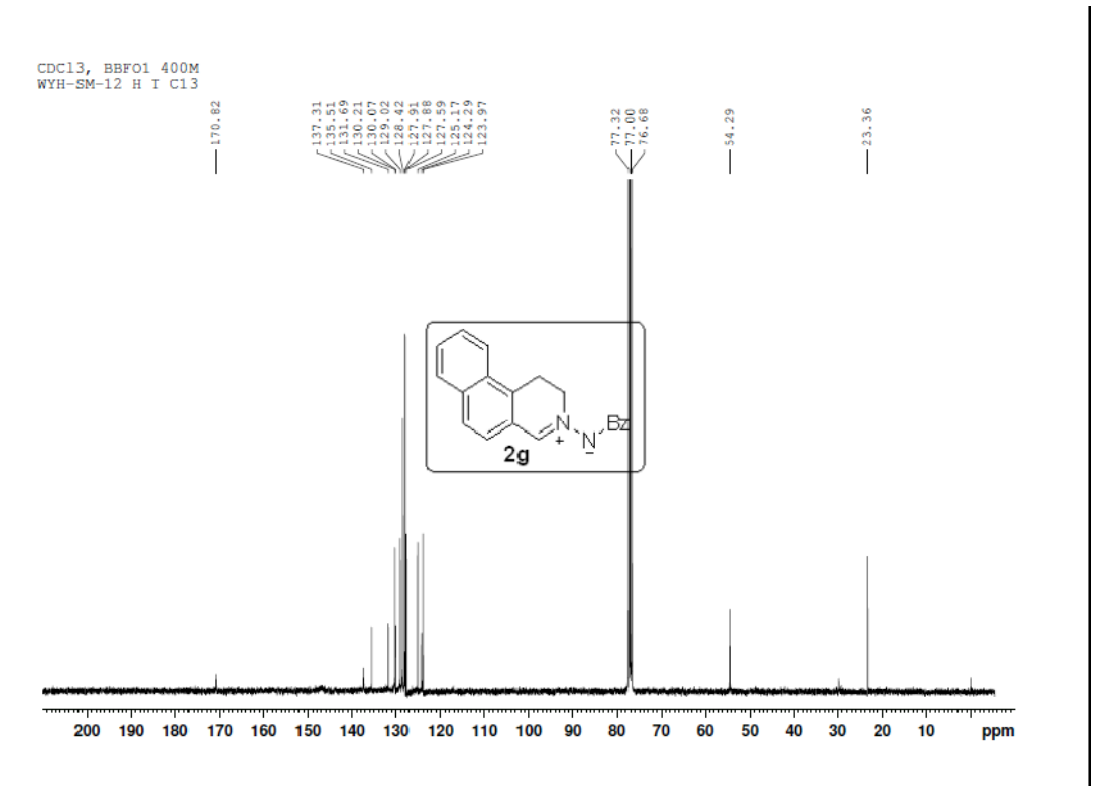
1. Bao-Sheng Li, Yuhuang Wang, Zhichao Jin, Pengcheng Zheng, Rakesh Ganguly, Yonggui Robin Chi, *Nat. Commun.* **2015**, *6*, 6207.
2. Takuya Hashimoto, Yuko Maeda, Masato Omote, Hiroki Nakatsu, and Keiji Maruoka *J. Am. Chem. Soc.*, **2010**, *132*, 4076.

3. W. Yan, D. Wang, J. Feng, P. Li, D. Zhao, R. Wang, **2012**, *14*, 2512.
4. K. Sugimoto, R. Hayashi, H. Nemoto, N. Toyooka, Y. Matsuya, *Org. Lett.* **2012**, *14*, 3510.
5. Birman, V. B.; Li, X.*Org. Lett*. **2006**, *8*, 1351.

9. ^{1}H and ^{13}C NMR spectra for substrates and products



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130.21
130.07
129.02
128.42
127.91
127.88
127.59
125.17
124.29
123.97
77.32
77.00
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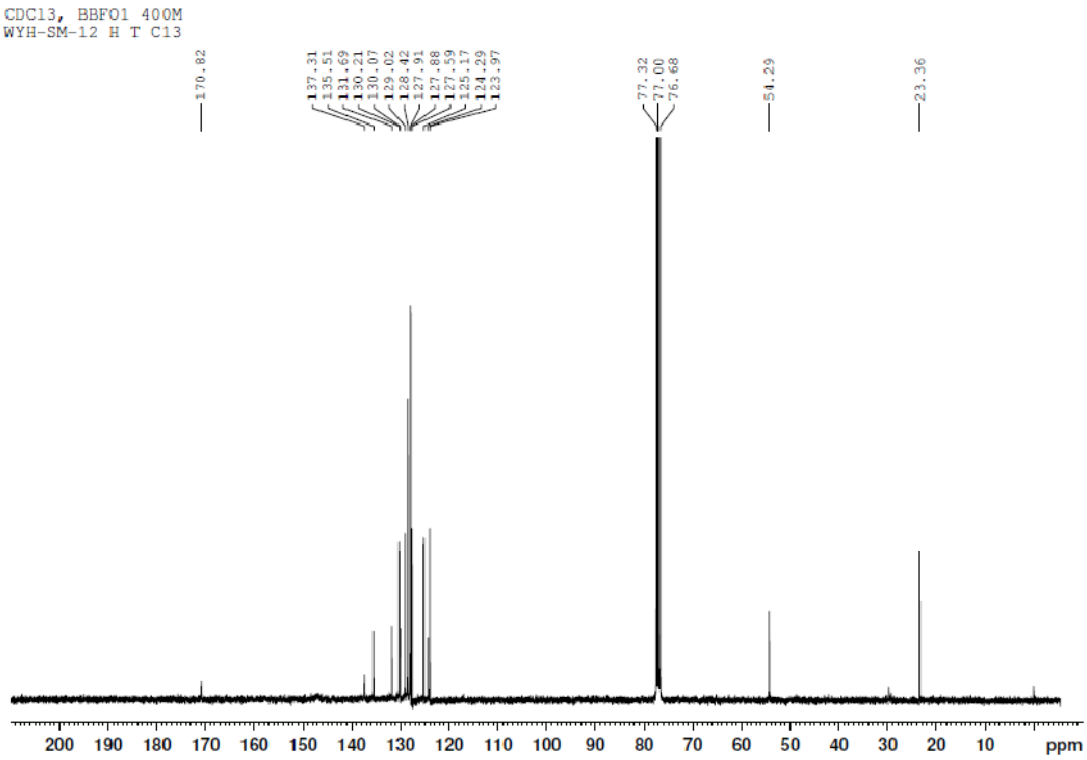
2g
Bz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


CDCl3, BBFO1 400M
WYH-SM-12 H T C13
170.82
137.31
135.51
131.69
130.21
130.07
129.02
128.42
127.91
127.88
127.59
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124.29
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77.32
77.00
76.68
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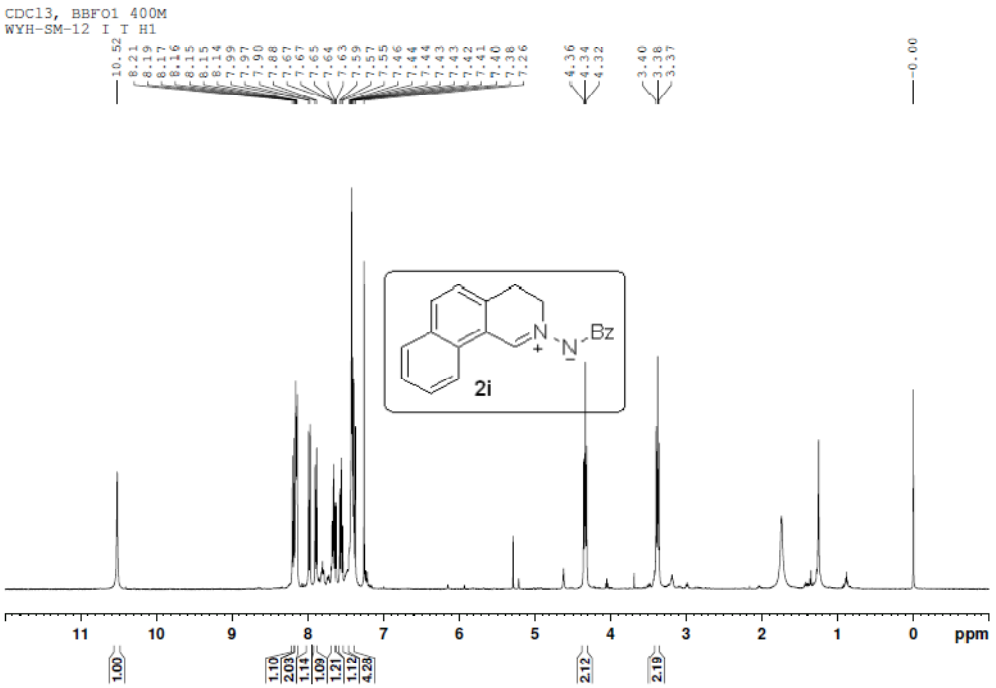
23.36
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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8.19
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8.16
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8.14
7.99
7.97
7.90
7.88
7.67
7.67
7.65
7.64
7.63
7.59
7.57
7.55
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3.38
3.37
0.00
N
N
Bz
2i
11
10
9
8
7
6
5
4
3
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1.09
1.21
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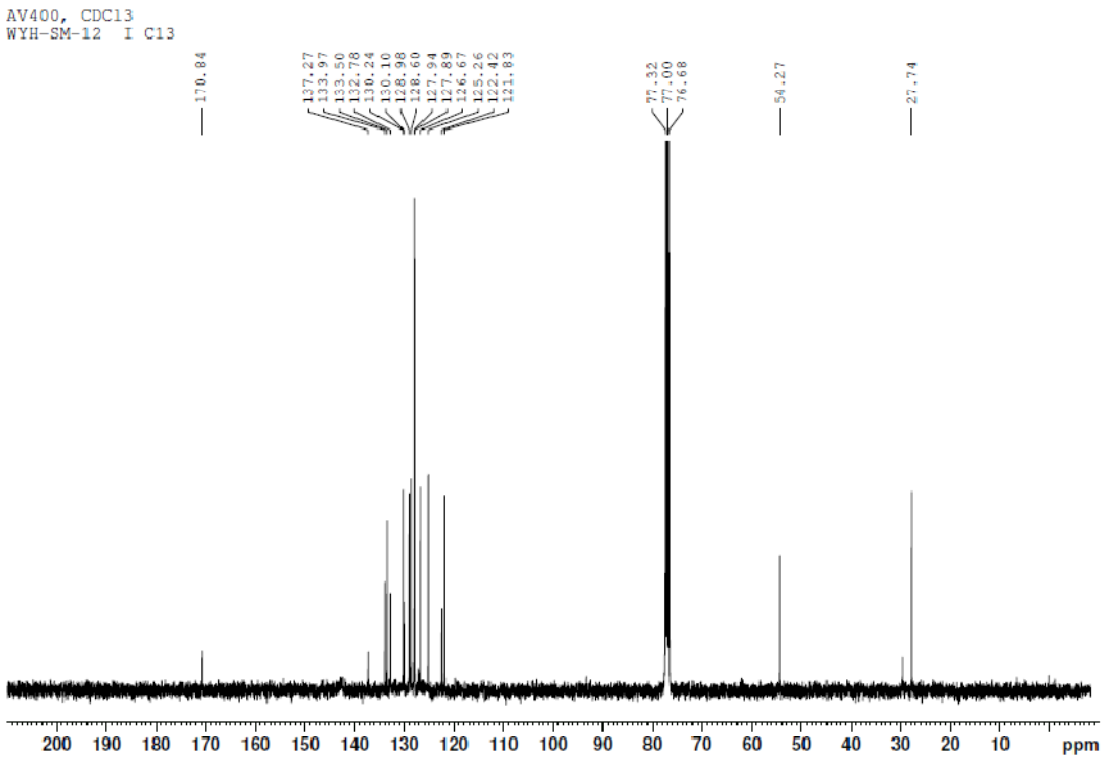
2.19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133.97
133.50
132.78
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130.10
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127.94
127.89
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40
30
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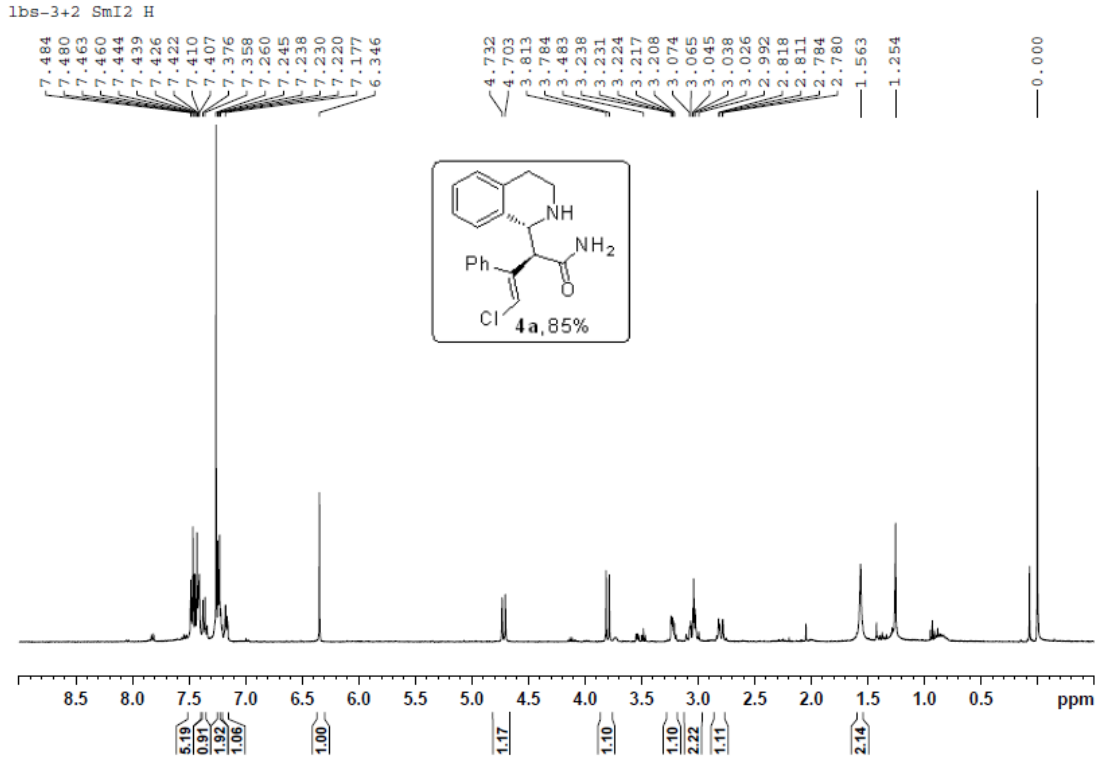
10
ppm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7.460
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7.422
7.410
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7.358
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3.074
3.065
3.045
3.038
3.026
2.992
2.818
2.811
2.784
2.780
1.563
1.254
0.000
NH
NH2
Ph
O
Cl
4a,85%
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
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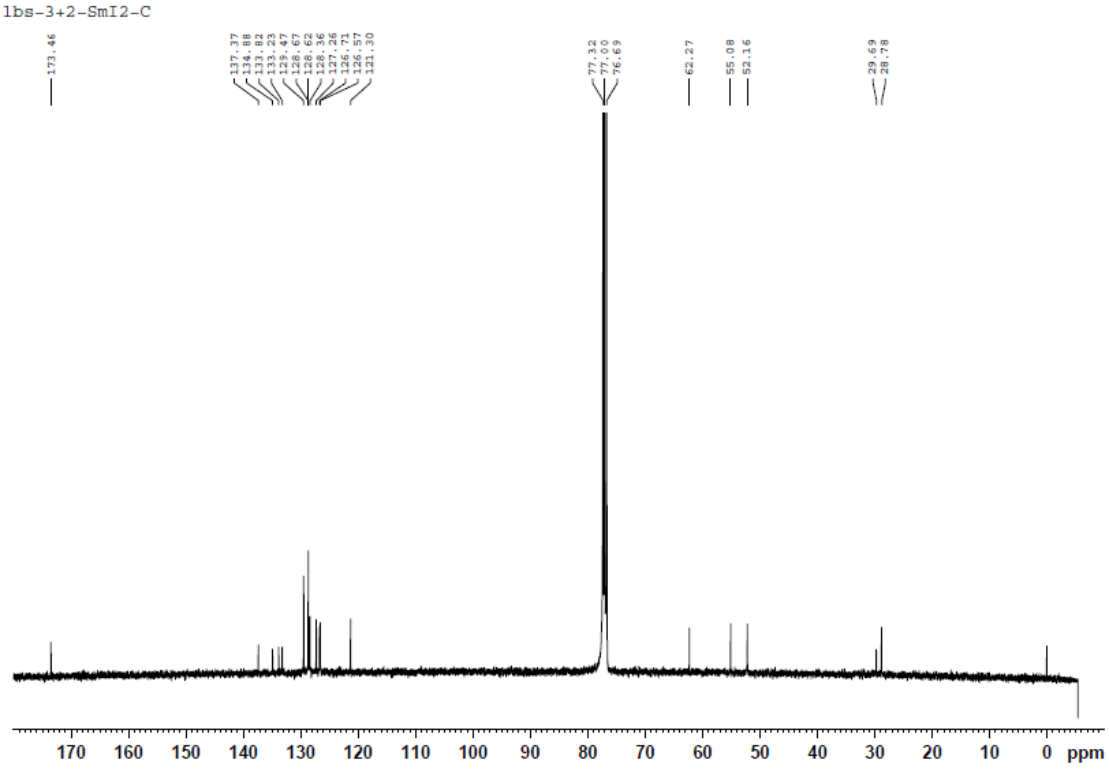
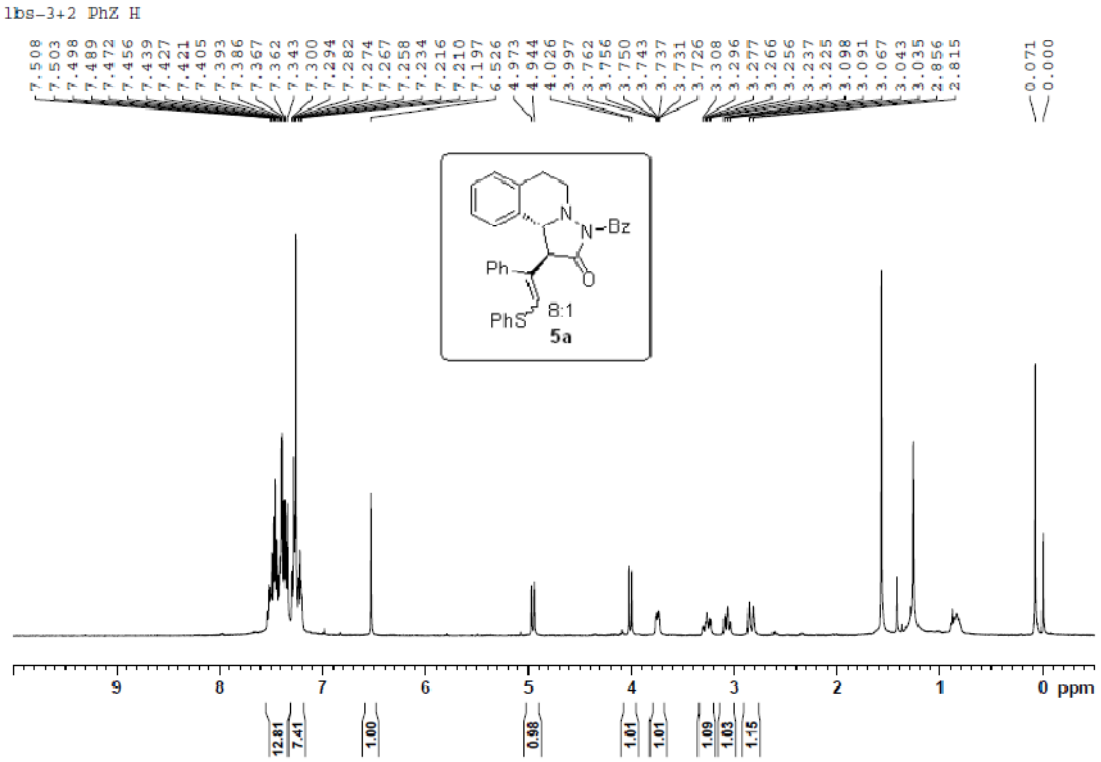
0.91
1.92
1.06
1.00
1.17
1.10
1.10
2.22
1.11
2.14


lbs-3+2-SmI2-C
173.46
137.37
134.88
133.83
133.23
129.47
128.67
128.62
128.36
127.26
126.71
126.57
121.30
77.32
77.00
76.69
62.27
55.08
52.16
29.69
28.78
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


lbs-3+2 PhZ H
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7.498
7.489
7.472
7.456
7.439
7.427
7.421
7.405
7.393
7.386
7.367
7.362
7.343
7.300
7.294
7.282
7.274
7.267
7.258
7.234
7.216
7.210
7.197
6.526
4.973
4.944
4.026
3.997
3.762
3.756
3.750
3.743
3.737
3.731
3.726
3.308
3.296
3.277
3.266
3.256
3.237
3.225
3.098
3.091
3.067
3.043
3.035
2.856
2.815
0.071
0.000
N
N-Bz
O
Ph
PhS
8:1
5a
9
8
7
6
5
4
3
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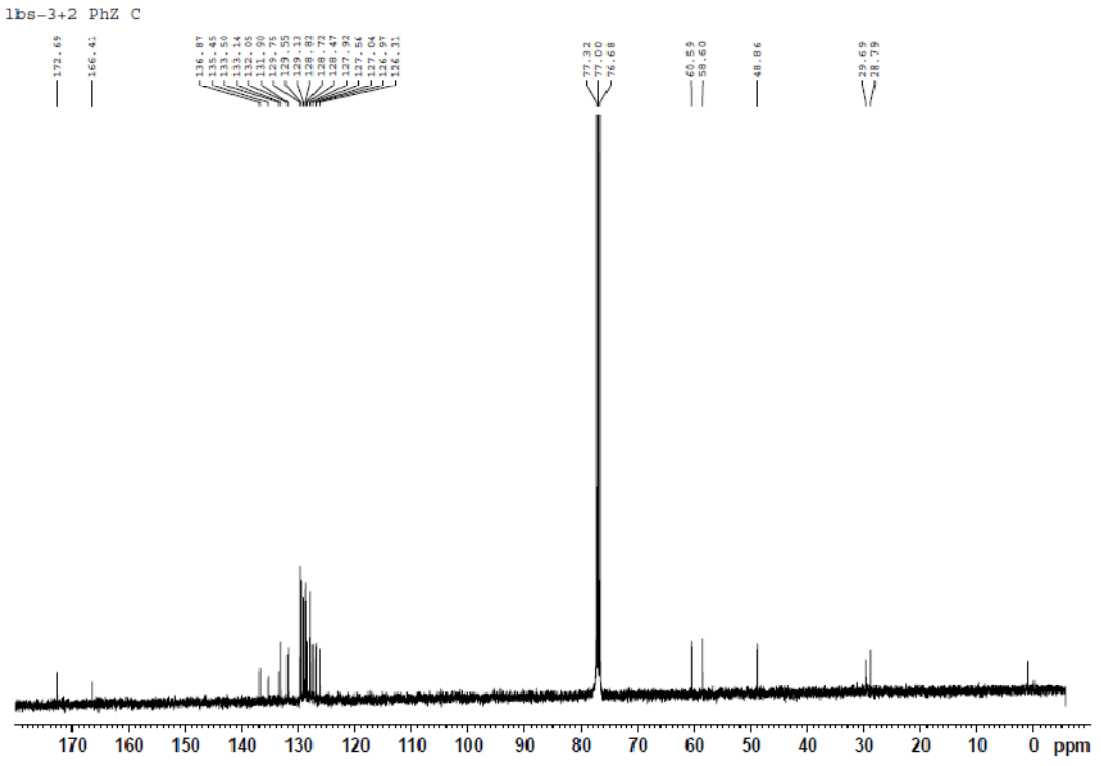
1.00
0.98
1.01
1.01
1.09
1.03
1.15


lbs-3+2 PhZ C
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136.87
135.46
133.59
133.14
132.05
131.90
129.75
129.55
129.33
128.88
128.72
128.47
127.92
127.56
127.04
126.97
126.31
77.32
77.00
76.68
60.53
58.60
48.86
29.69
28.79
170
160
150
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130
120
110
100
90
80
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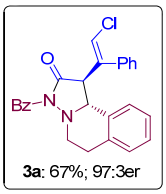
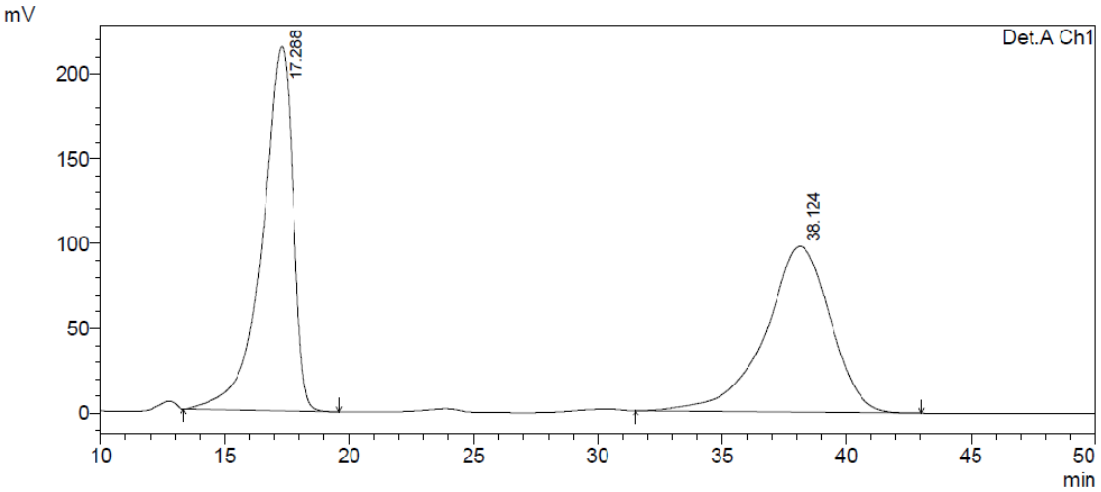
60
50
40
30
20
10
0 ppm

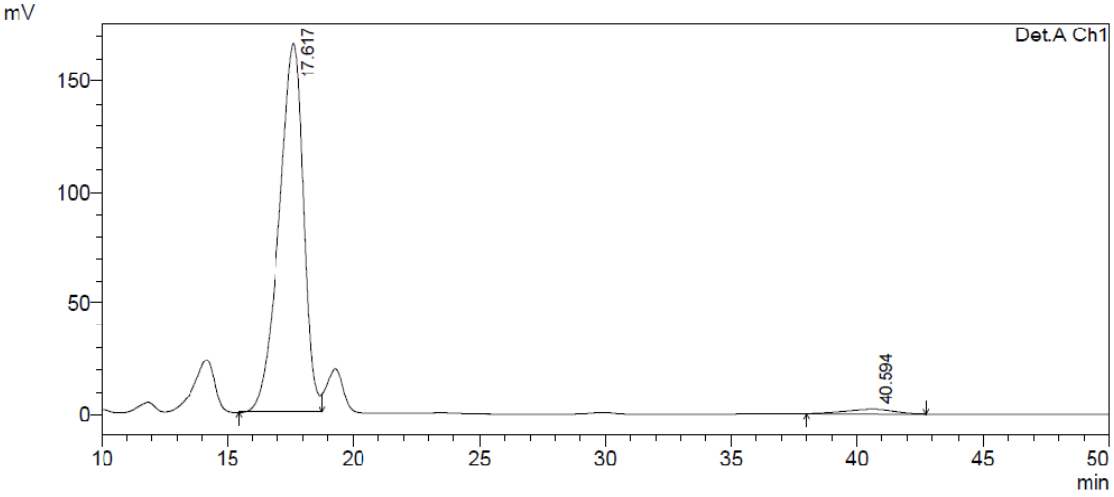
10. HPLC spectra for products



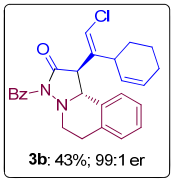
3a: 67%; 97:3er



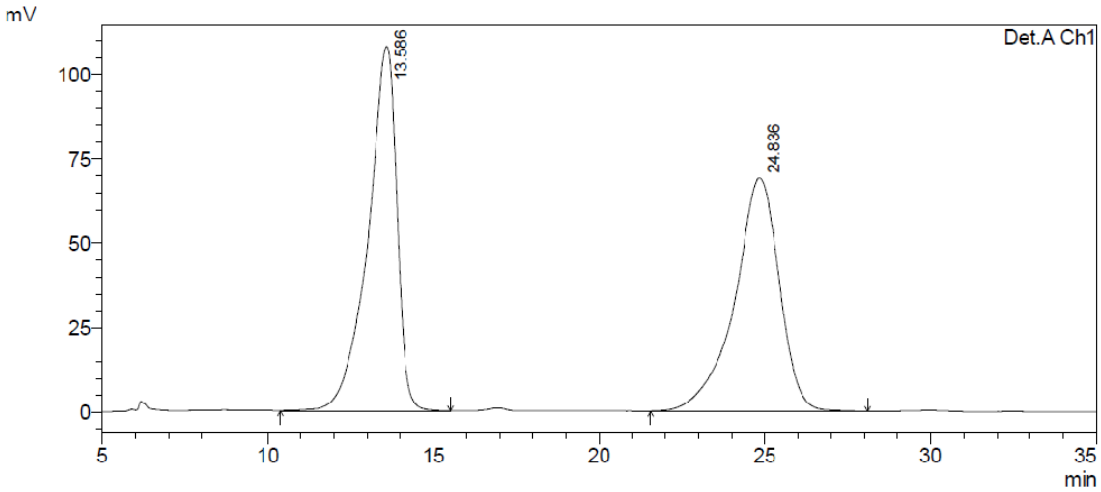
Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.288	18513968	214586	50.889	68.759
2	38.124	17866770	97498	49.111	31.241
Total		36380738	312084	100.000	100.000



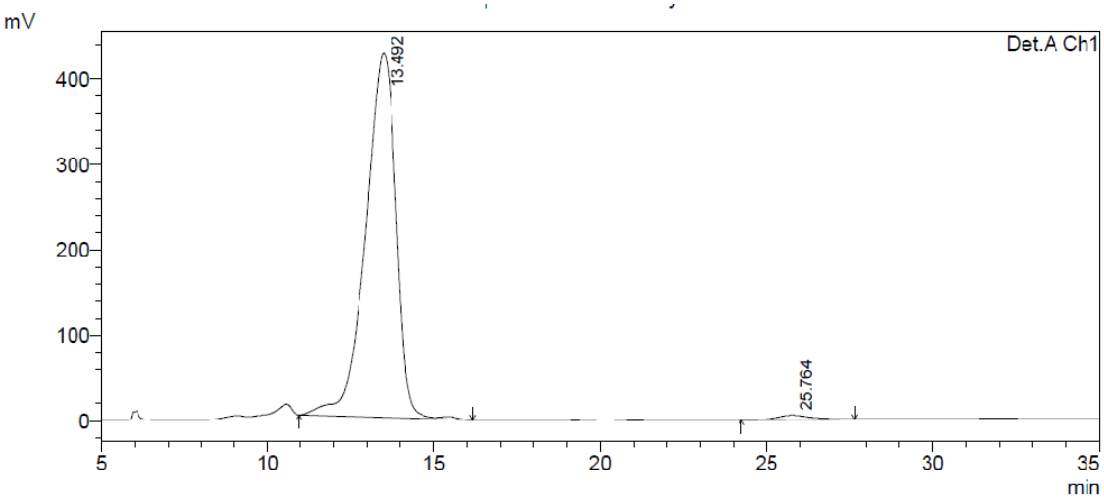
Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.617	11140413	165566	97.415	98.727
2	40.594	295603	2136	2.585	1.273
Total		11436016	167702	100.000	100.000



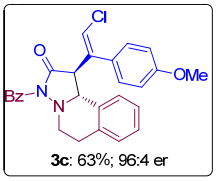
3b: 43%; 99:1 er



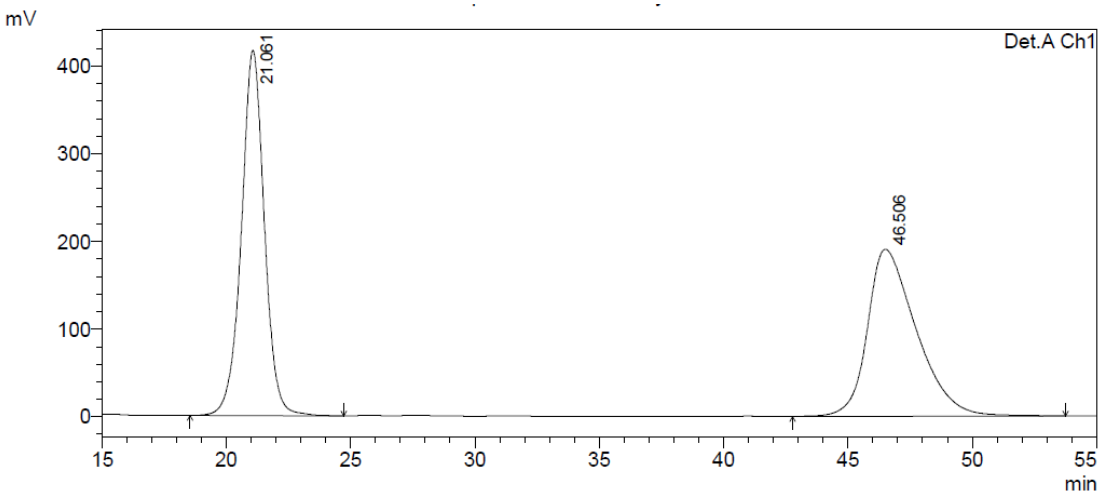
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.586	6543195	107823	50.159	60.959
2	24.836	6501679	69054	49.841	39.041
Total		13044873	176877	100.000	100.000



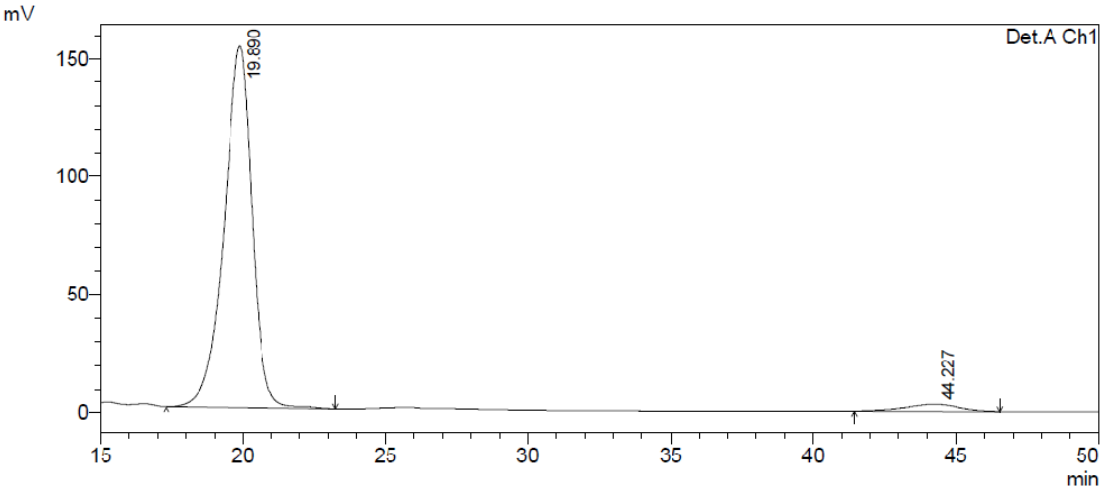
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.492	27006318	426479	98.587	98.756
2	25.764	387027	5373	1.413	1.244
Total		27393345	431852	100.000	100.000



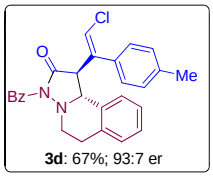
3c: 63%; 96:4 er



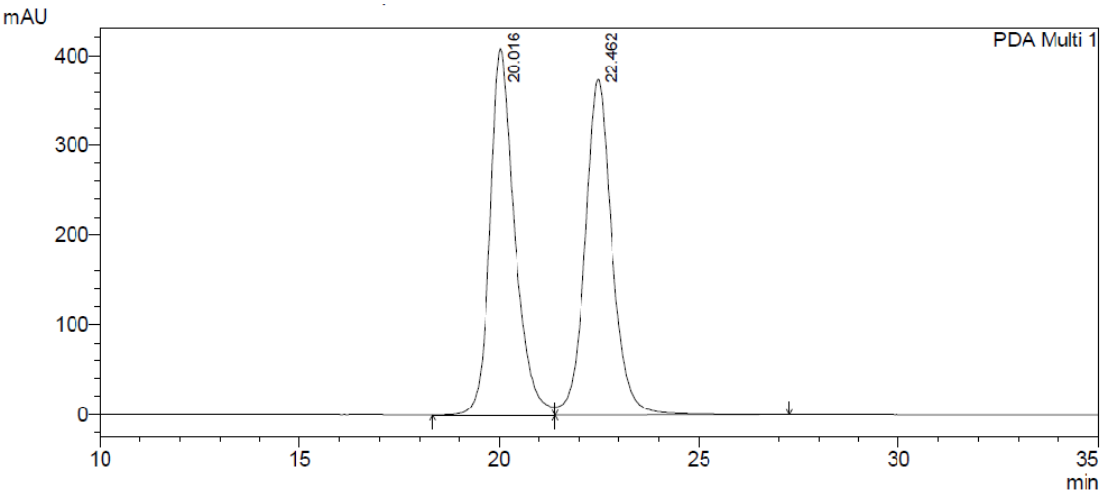
Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.061	26828661	416561	50.810	68.640
2	46.506	25972826	190318	49.190	31.360
Total		52801488	606879	100.000	100.000



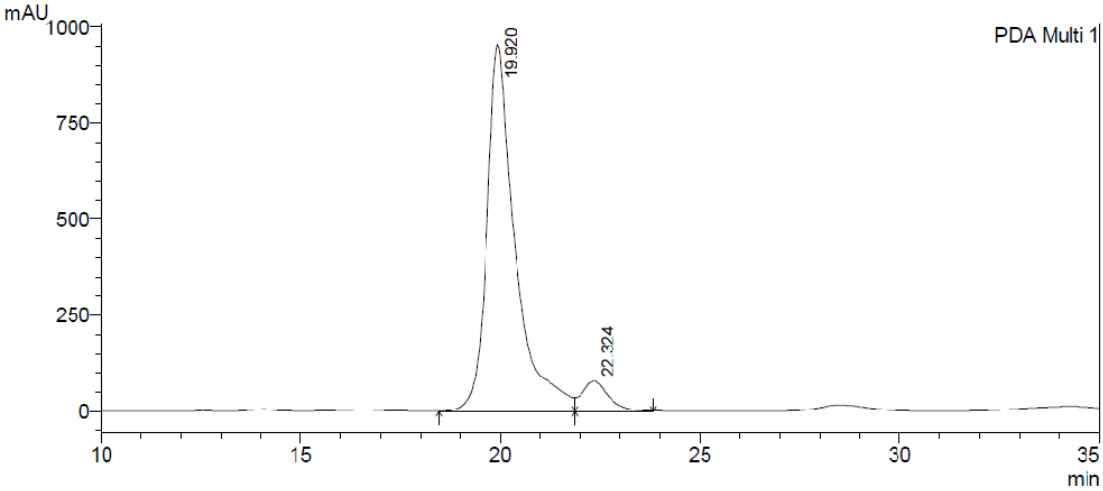
Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.890	10482960	153614	96.207	98.043
2	44.227	413295	3066	3.793	1.957
Total		10896255	156681	100.000	100.000



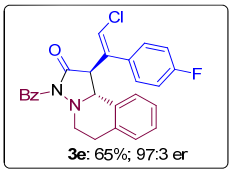
3d: 67%; 93:7 er



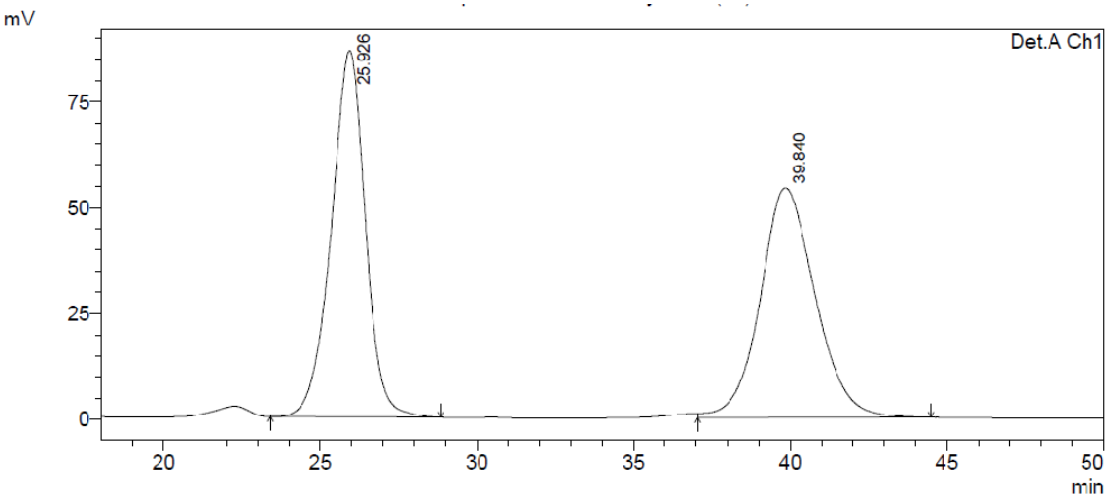
Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.016	17478011	408851	49.833	52.167
2	22.462	17595013	374890	50.167	47.833
Total		35073024	783741	100.000	100.000



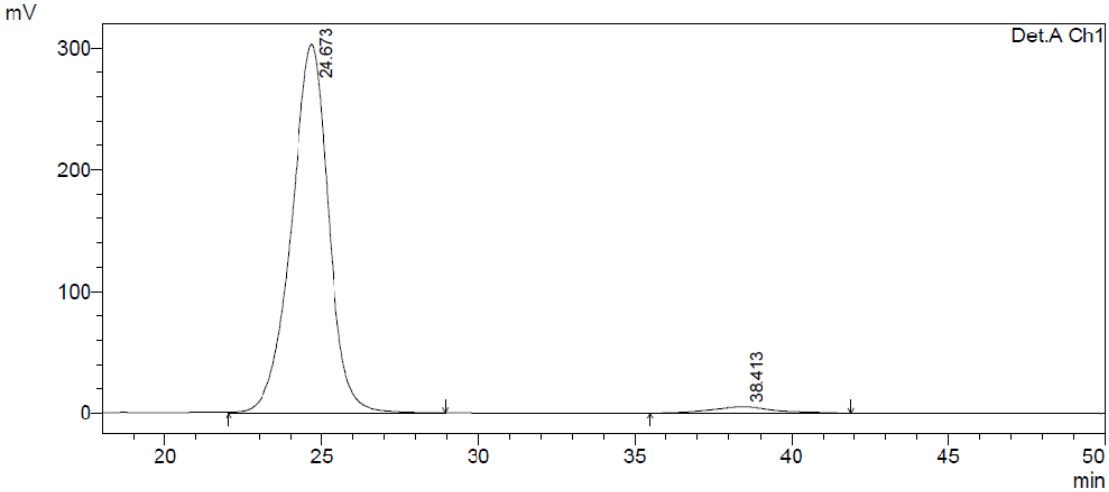
Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.920	46915121	954681	92.760	92.386
2	22.324	3661975	78680	7.240	7.614
Total		50577096	1033361	100.000	100.000



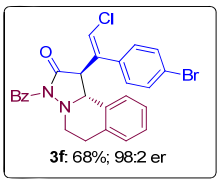
3e: 65%; 97:3 er



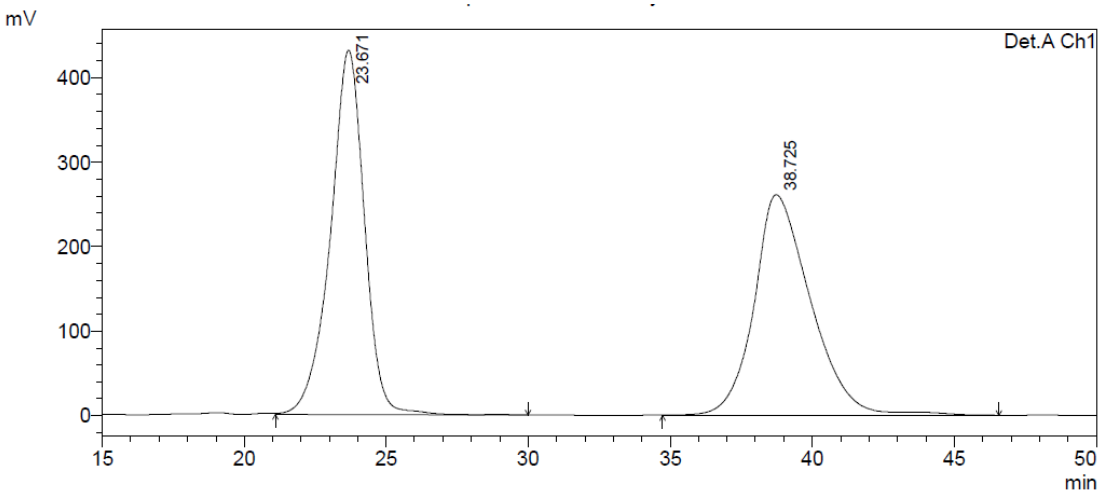
Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.926	6558446	86442	49.695	61.446
2	39.840	6638986	54237	50.305	38.554
Total		13197432	140679	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.673	24866028	302431	97.104	98.345
2	38.413	741467	5088	2.896	1.655
Total		25607496	307519	100.000	100.000

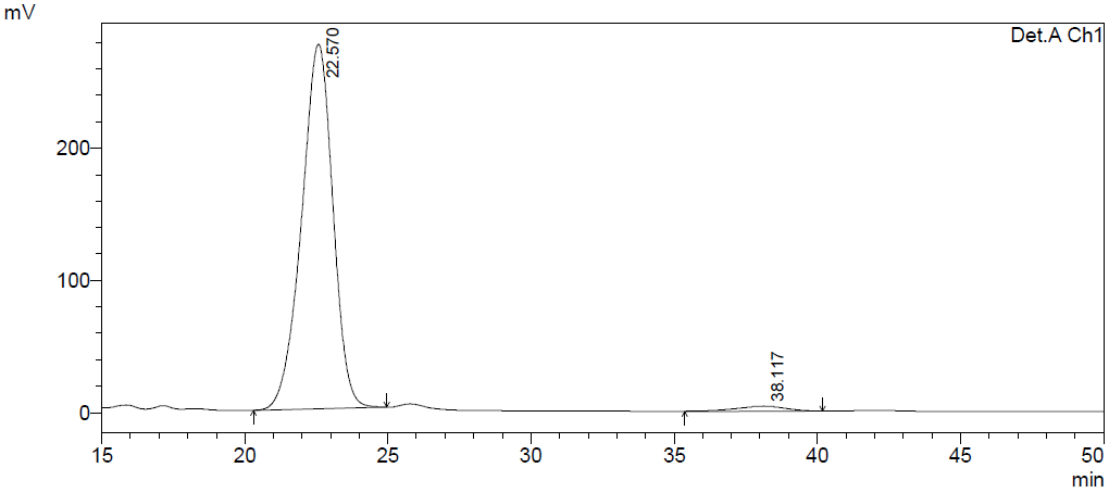


3f: 68%; 98:2 er

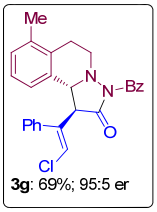


UV Detector Ch1 254nm

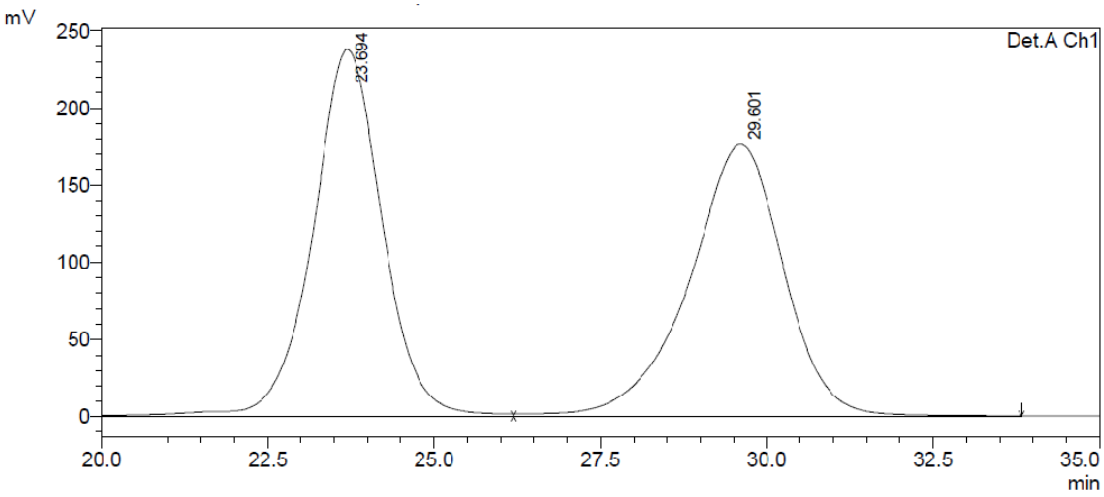
Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.671	36048215	431345	49.885	62.304
2	38.725	36214356	260978	50.115	37.696
Total		72262571	692323	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.570	21011295	275853	97.887	98.648
2	38.117	453538	3782	2.113	1.352
Total		21464833	279635	100.000	100.000

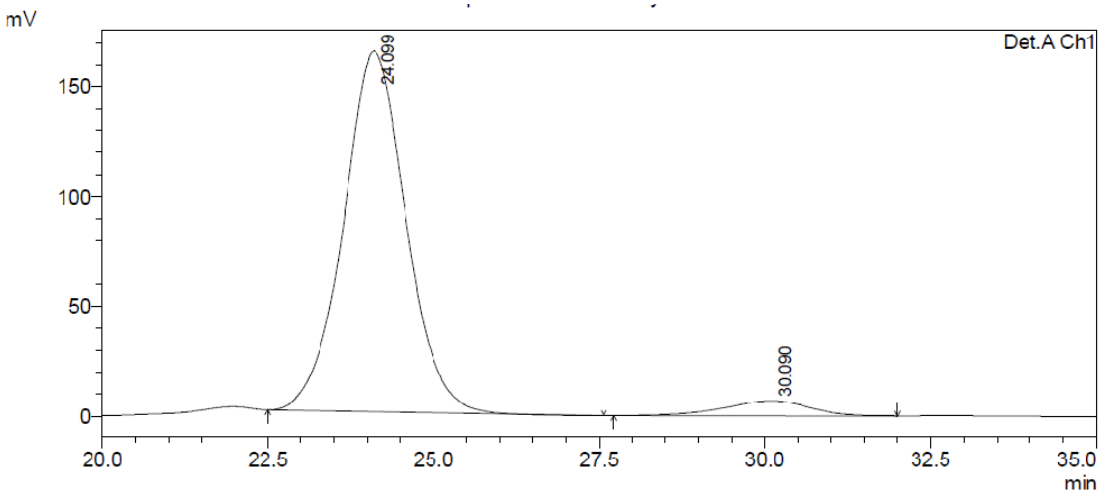


3g: 69%; 95:5 er



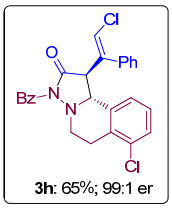
UV Detector Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.694	17232351	237447	49.827	57.459
2	29.601	17352278	175800	50.173	42.541
Total		34584629	413246	100.000	100.000

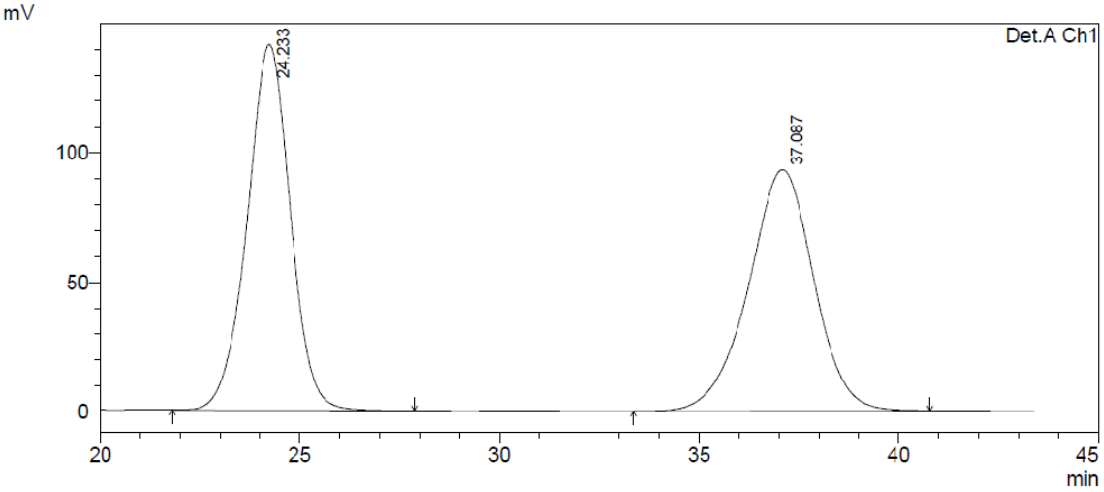


UV Detector Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.099	10757563	164154	94.676	96.044
2	30.090	604920	6761	5.324	3.956
Total		11362483	170915	100.000	100.000

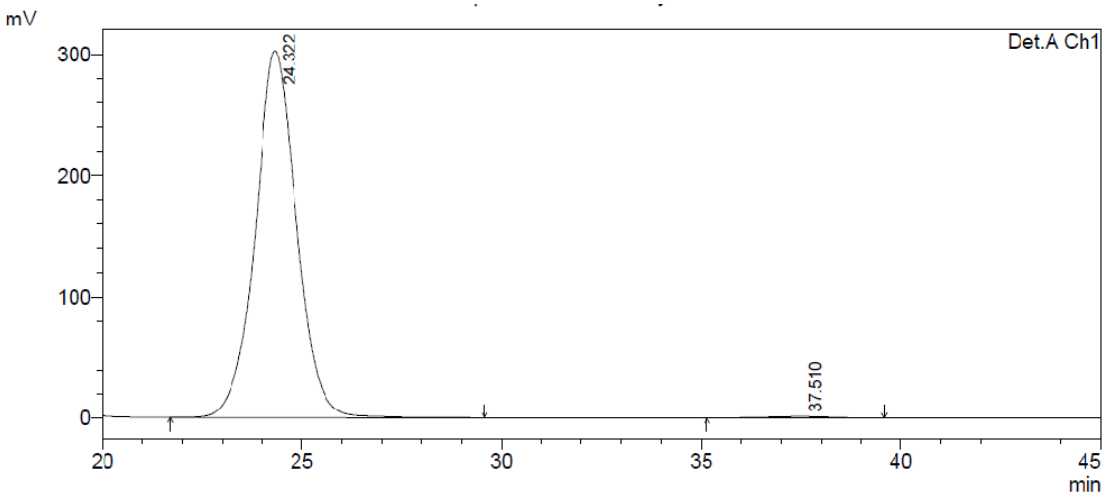


3h: 65%; 99:1 er



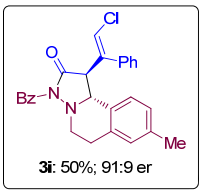
UV Detector Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.233	10655443	141335	50.038	60.249
2	37.087	10639468	93249	49.962	39.751
Total		21294911	234583	100.000	100.000

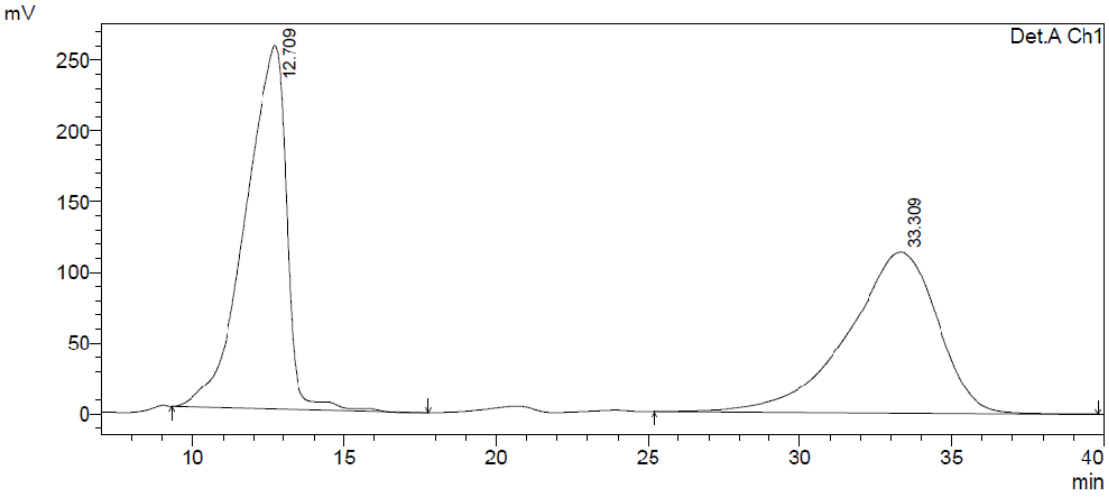


UV Detector Ch1 254nm

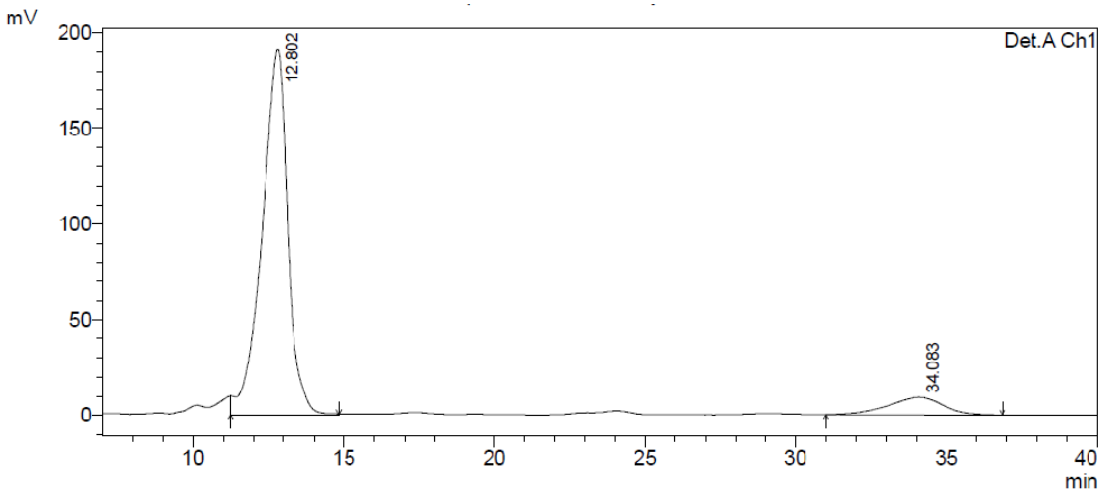
Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.322	21778806	302347	99.330	99.570
2	37.510	146976	1306	0.670	0.430
Total		21925782	303653	100.000	100.000



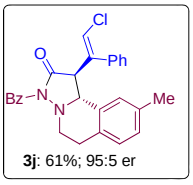
3i: 50%; 91:9 er



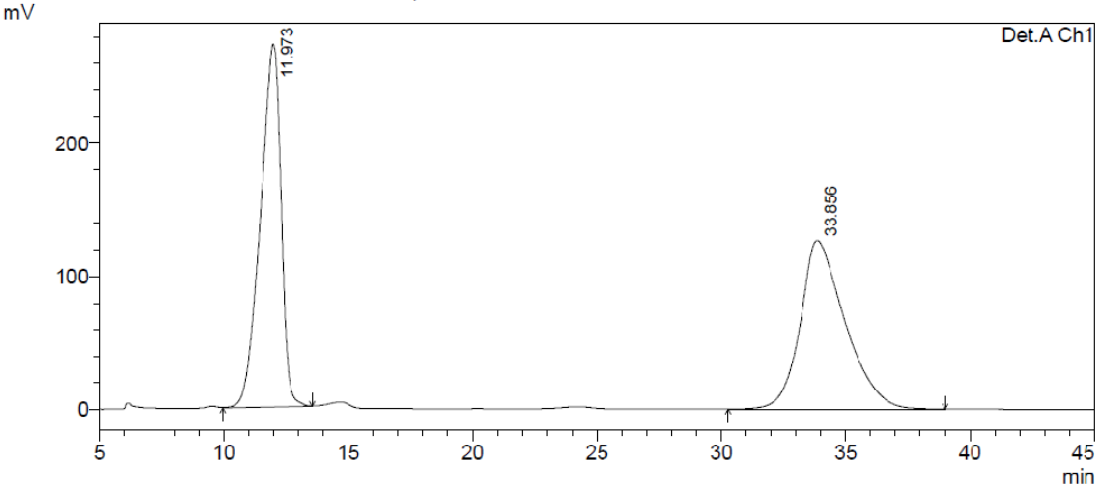
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.709	24037764	257032	50.734	69.369
2	33.309	23342300	113495	49.266	30.631
Total		47380064	370527	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.802	11297949	190935	90.552	95.404
2	34.083	1178831	9198	9.448	4.596
Total		12476780	200133	100.000	100.000

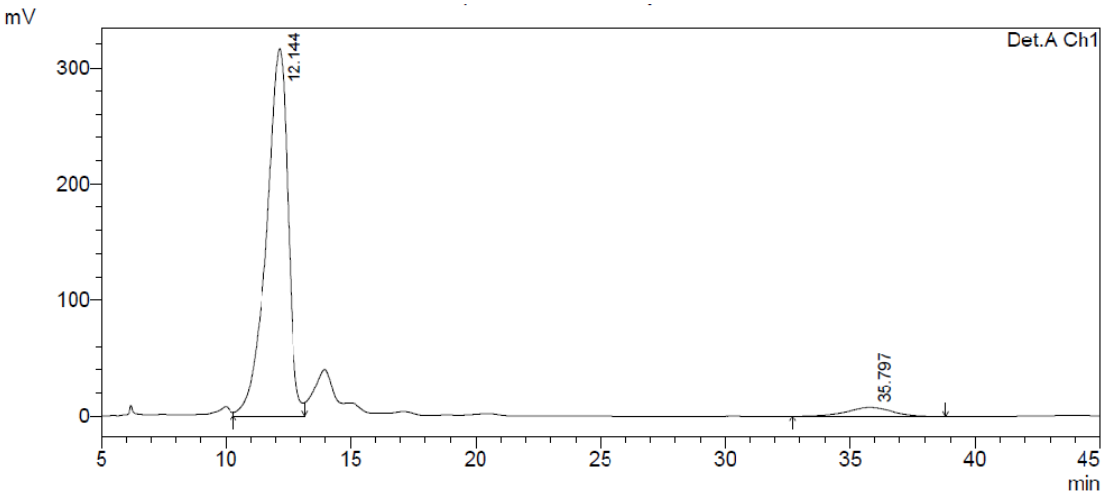


3j: 61%; 95:5 er



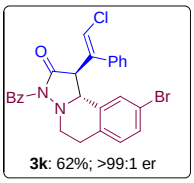
UV Detector Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.973	15748447	272877	49.701	68.255
2	33.856	15937825	126915	50.299	31.745
Total		31686273	399792	100.000	100.000

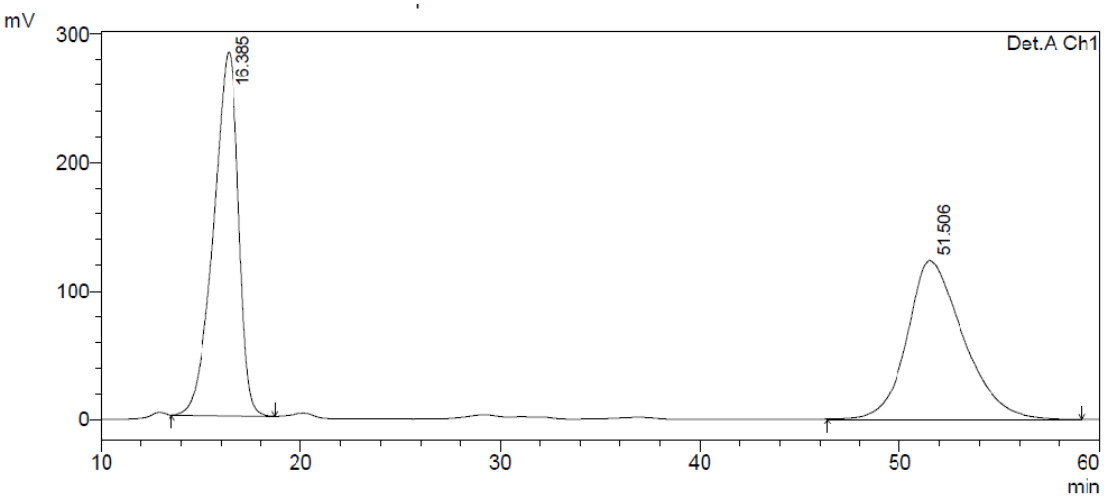


UV Detector Ch1 254nm

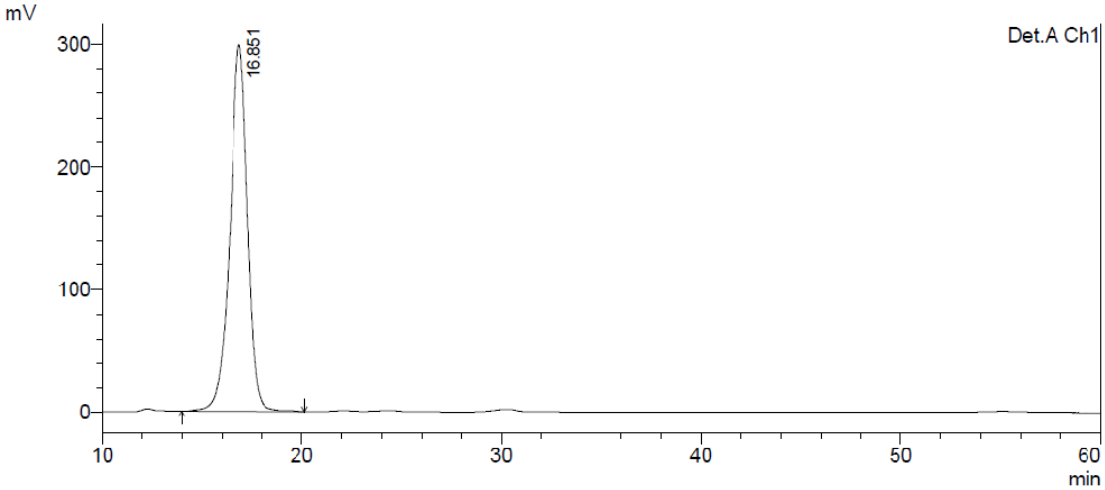
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.144	18835851	316337	95.051	97.639
2	35.797	980784	7650	4.949	2.361
Total		19816634	323987	100.000	100.000



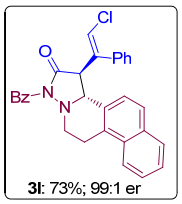
3k: 62%; >99:1 er



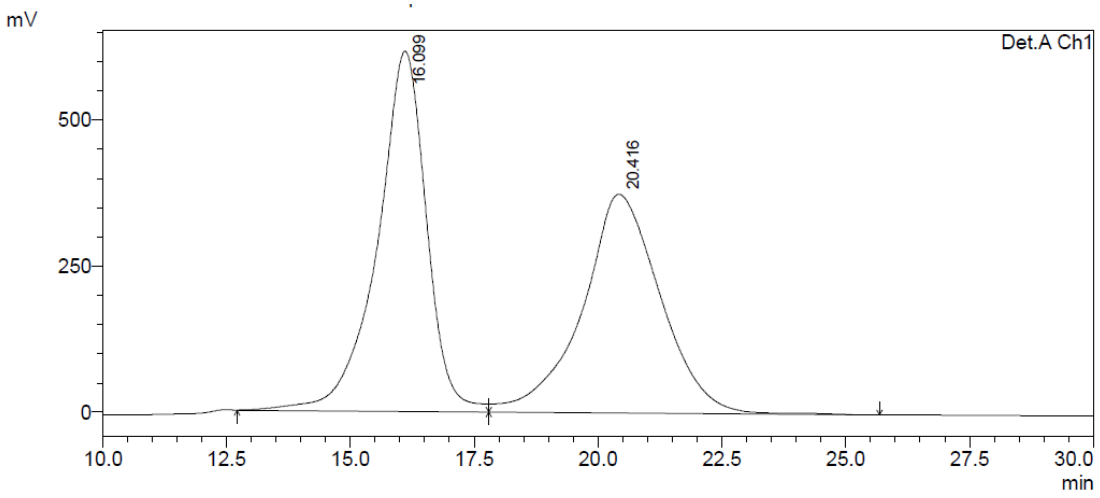
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.385	24510595	282264	50.400	69.539
2	51.506	24121105	123641	49.600	30.461
Total		48631700	405905	100.000	100.000



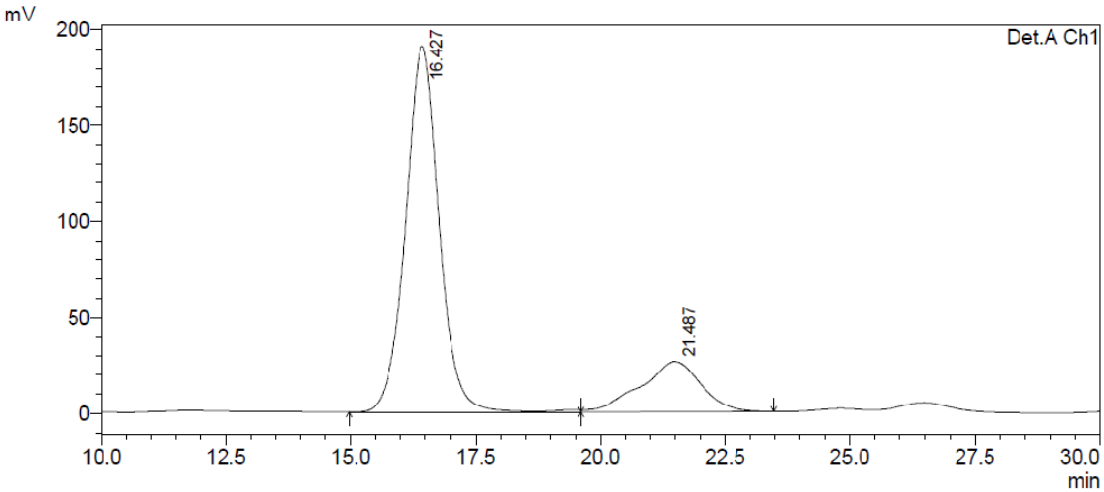
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.851	18170336	298775	100.000	100.000
Total		18170336	298775	100.000	100.000



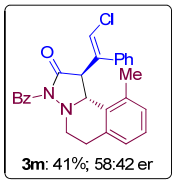
3l: 73%; 99:1 er



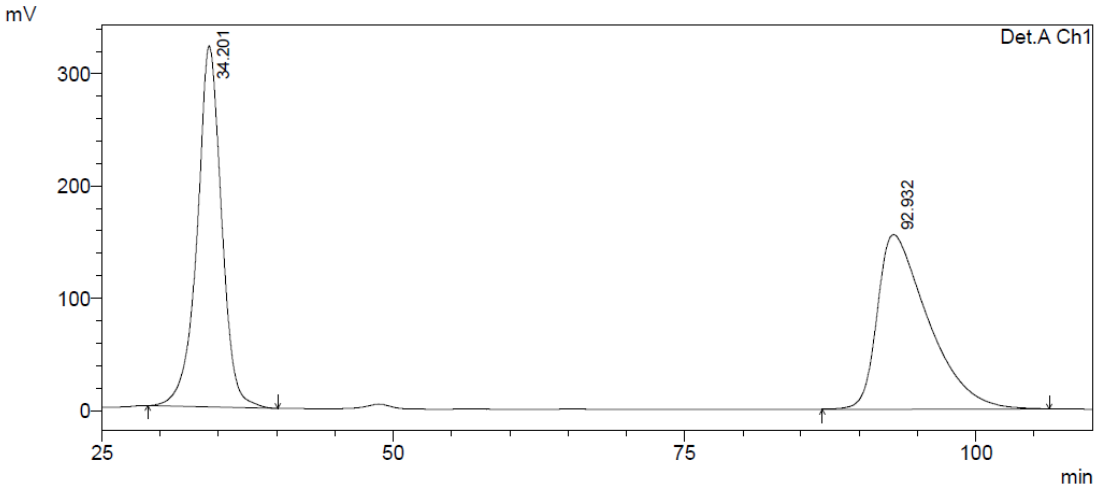
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.099	42628038	616344	50.731	62.204
2	20.416	41398983	374497	49.269	37.796
Total		84027021	990840	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.427	8947461	190519	80.286	87.938
2	21.487	2197062	26133	19.714	12.062
Total		11144523	216652	100.000	100.000

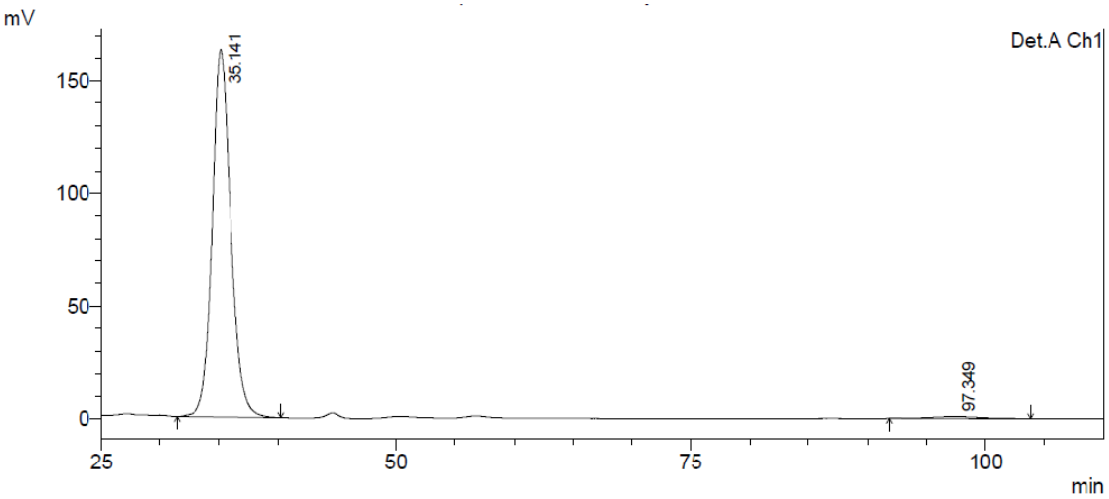


3m: 41%; 58:42 er

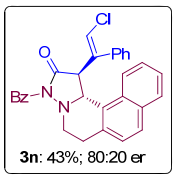


UV Detector Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	34.201	46914126	321968	49.770	67.401
2	92.932	47348105	155721	50.230	32.599
Total		94262231	477689	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	35.141	17718898	162902	98.643	99.453
2	97.349	243761	896	1.357	0.547
Total		17962658	163798	100.000	100.000



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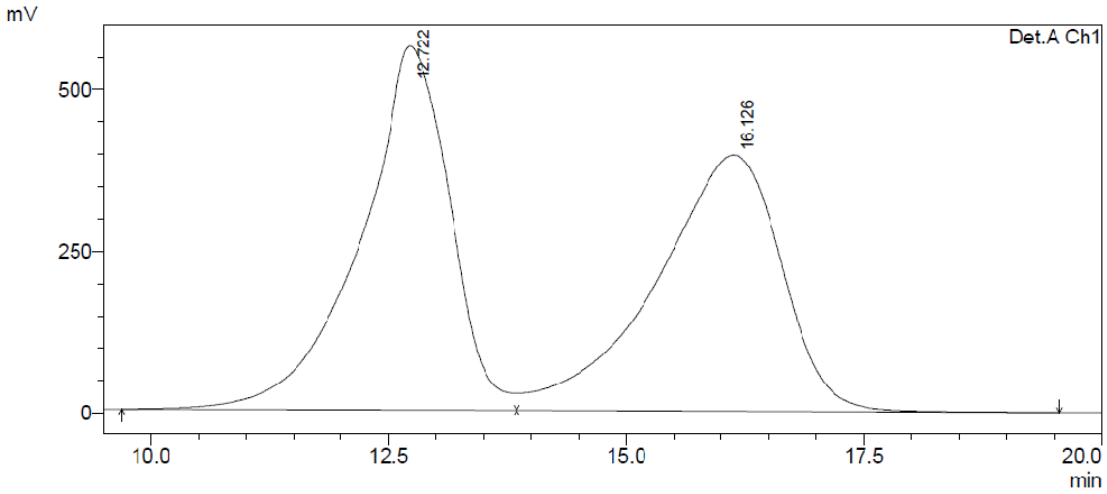
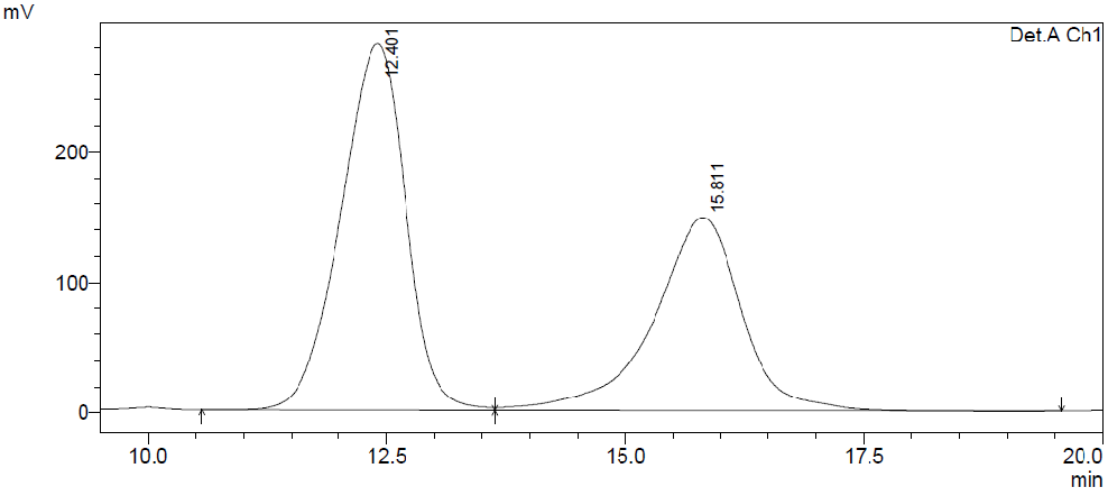


Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.722	36693324	562739	50.110	58.687
2	16.126	36532705	396147	49.890	41.313
Total		73226029	958886	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.401	13265436	280745	58.174	65.462
2	15.811	9537455	148122	41.826	34.538
Total		22802892	428867	100.000	100.000