Supporting Information

Highly Stereoselective Synthesis of Functionalized Pyrrolo[3,2-*c*]-quinolines via *N*-Heterocyclic Carbene Catalyzed Cascade Sequence

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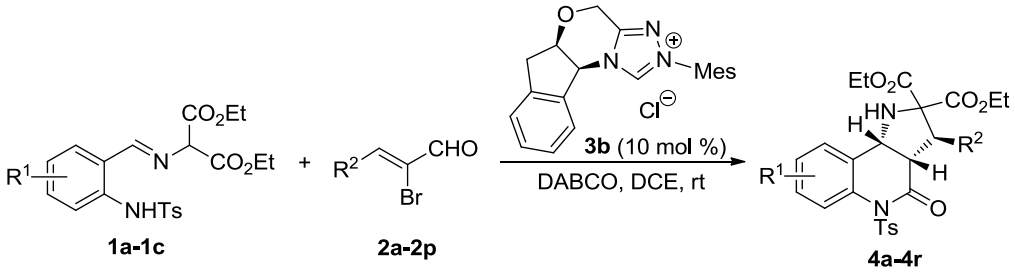
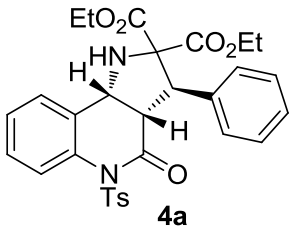
1. General information

Optical rotation was measured by the Perkin Elmer 341 polarimeter. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE III 400 spectrometer using tetramethylsilane as internal reference, and chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively. The HRMS analysis was obtained on a Bruker Apex II FT-ICR mass spectrometer with ESI ionization method. The *ee* value determination was carried out using chiral HPLC with Chirapak IC and AD column on Waters with a 2996 UV-detector. All syntheses and manipulations were carried out under a dry nitrogen atmosphere. Triazolium salt **3b** was commercially available from TCI. Dichloromethane and 1,2-dichloroethane were freshly distilled from phosphorous pentoxide. Toluene and THF were freshly distilled from a deep-blue solution of sodium-benzophenone under nitrogen. Triethylamine and acetonitrile were dried by calcium hydride and freshly distilled. Other chemicals were purchased from commercial suppliers and used directly. Flash column chromatography was carried out utilizing 200–300 mesh silica gel.

2. Procedure for *N*-heterocyclic carbene-catalyzed stereoselective synthesis of functionalized pyrrolo-[3,2-*c*]quinolines



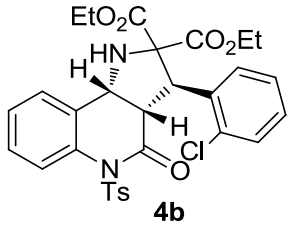


(3*R*,3a*S*,9b*R*)-diethyl-4-oxo-3-phenyl-5-tosyl-3,3a,4,5-tetrahydro-1H-pyrrolo[3,2-c]quinoline-2,2(9bH)-dicarboxylate (4a).

To a well-stirred solution of 2-bromoenals **2a** (21.1 mg, 0.10 mmol), *N*-heterocyclic carbene catalyst precursor **3b** (3.7 mg, 0.01 mmol) and DABCO (12.3 mg, 0.11 mmol) in DCE (0.5 mL) was added a solution of tosyl-protected *o*-amino aromatic aldimine **1a** (75.7 mg, 0.175 mmol) in DCE (1 mL) under the nitrogen atmosphere. The reaction mixture was stirred at room temperature for 1 h (monitored by TLC), and was quenched by water (2 mL). The aqueous layer was extracted with ethyl acetate (10 mL×3). The

combined organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the crude residue was purified by flash column chromatography on silica gel using petroleum ether/EtOAc (4:1) to afford the desired product **4a** (51.76 mg, 92% yield).

White solid, mp 76–78 ^oC, $[\alpha]_D^{20}$ –65 (c 1.00, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.89 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.60 (d, *J* = 7.2 Hz, 1H), 7.39 (t, 7.2 Hz, 1H), 7.29 – 7.26 (m, 4H), 7.24 – 7.18 (m, 4H), 4.84 (br s, 1H), 4.36 (d, *J* = 9.2 Hz, 1H), 4.14 – 4.08 (m, 2H), 3.75 – 3.70 (m, 1H), 3.60 (br s, 1H), 3.40 (dd, *J* = 9.2, 6.0 Hz, 1H), 3.28 – 3.24 (m, 1H), 2.43 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H), 0.66 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.1, 169.34, 169.29, 144.8, 136.3, 133.9, 129.4, 128.8, 128.7, 128.3, 128.21, 128.15, 127.6, 127.5, 126.1, 123.3, 62.2, 61.8, 57.7, 53.5, 52.0, 21.7, 13.9, 13.2. HRMS (ESI): Exact Mass Calcd. for $C_{30}H_{31}N_2O_7S$ $(M+H)^+$: 563.1846, Found: 563.1840. HPLC (Chiralpak IC column *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, retention time: t_{minor} = 59.000 min, t_{major} = 71.151 min, > 99% ee).



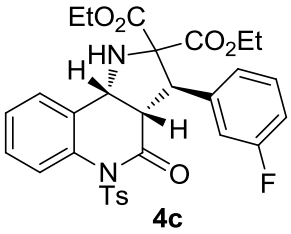
4b

(3*R*,3a*S*,9b*R*)-diethyl-3-(2-chlorophenyl)-4-oxo-5-tosyl-3,3a,4,5-tetrahydro-1H-pyrrolo[3,2-c]quinoline-2,2(9bH)-dicarboxylate (4b).

To a well-stirred solution of 2-bromoenals **2b** (24.6 mg, 0.10 mmol), *N*-heterocyclic carbene catalyst precursor **3b** (3.7 mg, 0.01 mmol) and DABCO (12.3 mg, 0.11 mmol) in DCE (0.5 mL) was added a solution of tosyl-protected *o*-amino aromatic aldimine **1a** (75.7 mg, 0.175 mmol) in DCE (1 mL) under the nitrogen atmosphere. The reaction mixture was stirred at room temperature for 1 h (monitored by TLC), and was quenched by water (2 mL). The aqueous layer was extracted with ethyl acetate (10 mL×3). The combined organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the crude residue was purified by flash column chromatography on silica gel using petroleum ether/EtOAc (4:1) to afford the desired product **4b** (43.59 mg, 73% yield).

White solid, mp 72–74 ^oC, $[\alpha]_D^{20}$ –11 (c 1.00, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.93 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 7.2 Hz, 1H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.33 – 7.23 (m, 4H), 7.16 – 7.14 (m, 3H), 5.27 (br s, 1H), 4.90 (br s, 1H), 4.04 (q, *J* = 7.2 Hz, 2H), 3.83 – 3.79 (m, 1H), 3.59 (br s, 1H), 3.42 – 3.38 (m, 1H), 3.26 (br s, 1H), 2.43 (s, 3H), 1.18 (t, *J* = 7.2 Hz, 3H), 0.76 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.2, 169.5, 168.2, 144.7, 136.6, 134.7, 129.9, 129.4, 128.8, 128.7, 126.8, 126.2, 125.9, 122.8, 62.0, 61.9, 58.5, 21.7, 13.9, 13.2. HRMS (ESI): Exact Mass Calcd. for $C_{30}H_{30}ClN_2O_7S$

$(M+H)^+$: 597.1457, Found: 597.1451. HPLC (Chiralpak AD column, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, retention time: t_{major} = 16.165 min, t_{minor} = 45.122 min, > 99% ee).

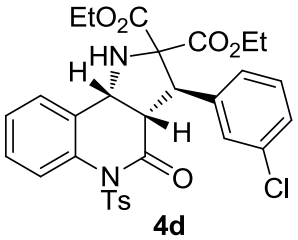


4c

(3*R*,3a*S*,9b*R*)-diethyl-3-(3-fluorophenyl)-4-oxo-5-tosyl-3,3a,4,5-tetrahydro-1H-pyrrolo[3,2-c]quinoline-2,2(9bH)-dicarboxylate (4c).

To a well-stirred solution of 2-bromoenals **2c** (22.9 mg, 0.10 mmol), *N*-heterocyclic carbene catalyst precursor **3b** (3.7 mg, 0.01 mmol) and DABCO (12.3 mg, 0.11 mmol) in DCE (0.5 mL) was added a solution of tosyl-protected *o*-amino aromatic aldimine **1a** (75.7 mg, 0.175 mmol) in DCE (1 mL) under the nitrogen atmosphere. The reaction mixture was stirred at room temperature for 1 h (monitored by TLC), and was quenched by water (2 mL). The aqueous layer was extracted with ethyl acetate (10 mL×3). The combined organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the crude residue was purified by flash column chromatography on silica gel using petroleum ether/EtOAc (4:1) to afford the desired product **4c** (47.03 mg, 81% yield).

White solid, mp 73–75 ^oC, $[\alpha]_D^{20}$ –64 (c 1.00, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.89 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.42 – 7.38 (m, 1H), 7.31 – 7.24 (m, 3H), 7.21 – 7.17 (m, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 6.97 – 6.88 (m, 2H), 4.83 (d, *J* = 5.6 Hz, 1H), 4.32 (d, *J* = 9.6 Hz, 1H), 4.15 – 4.09 (m, 2H), 3.80 – 3.71 (m, 1H), 3.62 (br s, 1H), 3.39 – 3.34 (m, 2H), 2.44 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H), 0.72 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.9, 169.2, 169.1, 163.7, 161.3, 144.9, 139.0, 138.9, 136.4, 133.9, 129.7, 129.6, 129.4, 128.8, 128.4, 128.2, 127.4, 127.3, 126.2, 124.3, 123.3, 116.2, 116.0, 114.7, 114.4, 62.2, 62.0, 57.7, 53.5, 51.7, 21.7, 13.9, 13.2. HRMS (ESI): Exact Mass Calcd. for $C_{30}H_{30}FN_2O_7S$ $(M+H)^+$: 581.1752, Found: 581.1744. HPLC (Chiralpak AD column, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, retention time: t_{major} = 13.292 min, t_{minor} = 54.256 min, > 99% ee).

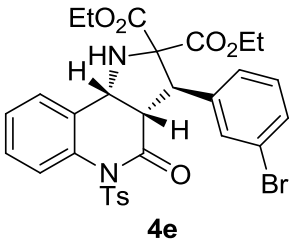


4d

(3*R*,3a*S*,9b*R*)-diethyl-3-(3-chlorophenyl)-4-oxo-5-tosyl-3,3a,4,5-tetrahydro-1H-pyrrolo[3,2-c]quinolin e-2,2(9bH)-dicarboxylate (4d).

To a well-stirred solution of 2-bromoenals **2d** (24.6 mg, 0.10 mmol), *N*-heterocyclic carbene catalyst precursor **3b** (3.7 mg, 0.01 mmol) and DABCO (12.3 mg, 0.11 mmol) in DCE (0.5 mL) was added a solution of tosyl-protected *o*-amino aromatic aldimine **1a** (75.7 mg, 0.175 mmol) in DCE (1 mL) under the nitrogen atmosphere. The reaction mixture was stirred at room temperature for 1 h (monitored by TLC), and was quenched by water (2 mL). The aqueous layer was extracted with ethyl acetate (10 mL×3). The combined organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the crude residue was purified by flash column chromatography on silica gel using petroleum ether/EtOAc (4:1) to afford the desired product **4d** (51.95 mg, 87% yield).

White solid, mp 75–77 ^{o}C, $[\alpha]_D^{20}$ –87 (c 1.00, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.31 – 7.23 (m, 4H), 7.18 – 7.11 (m, 3H), 4.84 (d, *J* = 6.0 Hz, 1H), 4.30 (d, *J* = 9.6 Hz, 1H), 4.14 – 4.09 (m, 2H), 3.82 – 3.74 (m, 1H), 3.61 (br s, 1H), 3.42 – 3.34 (m, 2H), 2.44 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H), 0.73 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.9, 169.12, 169.09, 144.9, 138.5, 136.4, 134.1, 133.9, 129.48, 129.46, 129.3, 128.8, 128.5, 128.2, 127.8, 127.3, 126.7, 126.2, 123.3, 62.3, 62.0, 57.7, 53.4, 51.7, 21.7, 13.9, 13.2. HRMS (ESI): Exact Mass Calcd. for $C_{30}H_{30}ClN_2O_7S$ $(M+H)^+$: 597.1457, Found: 597.1453. HPLC (Chiralpak AD column, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, retention time: t_{major} = 13.280 min, t_{minor} = 56.502 min, > 99% ee).



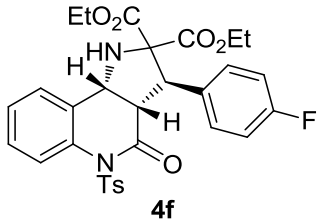
4e

(3*R*,3a*S*,9b*R*)-diethyl-3-(3-bromophenyl)-4-oxo-5-tosyl-3,3a,4,5-tetrahydro-1H-pyrrolo[3,2-c]quinolin e-2,2(9bH)-dicarboxylate (4e).

To a well-stirred solution of 2-bromoenals **2e** (29.0 mg, 0.10 mmol), *N*-heterocyclic carbene catalyst precursor **3b** (3.7 mg, 0.01 mmol) and DABCO (12.3 mg, 0.11 mmol) in DCE (0.5 mL) was added a solution of tosyl-protected *o*-amino aromatic aldimine **1a** (75.7 mg, 0.175 mmol) in DCE (1 mL) under the nitrogen atmosphere. The reaction mixture was stirred at room temperature for 1 h (monitored by TLC), and was quenched by water (2 mL). The aqueous layer was extracted with ethyl acetate (10 mL×3). The combined organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent under reduced

pressure, the crude residue was purified by flash column chromatography on silica gel using petroleum ether/EtOAc (4:1) to afford the desired product **4e** (53.25 mg, 83% yield).

White solid, mp 70–72 °C, $[\alpha]_D^{20}$ –69 (c 1.00, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.89 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.42 – 7.38 (m, 2H), 7.35 – 7.24 (m, 4H), 7.17 – 7.11 (m, 2H), 4.84 (br s, 1H), 4.29 (d, *J* = 9.6 Hz, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.80 – 3.76 (m, 1H), 3.61 (br s, 1H), 3.40 – 3.33 (m, 2H), 2.44 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H), 0.74 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.9, 169.10, 169.07, 145.0, 138.8, 136.3, 133.9, 132.2, 130.8, 129.8, 129.5, 128.8, 128.5, 128.2, 127.3, 127.1, 126.2, 123.2, 122.2, 76.9, 76.7, 62.4, 62.0, 57.7, 53.4, 51.7, 21.7, 13.9, 13.2. HRMS (ESI): Exact Mass Calcd. for $C_{30}H_{30}BrN_2O_7S$ $(M+H)^+$: 641.0952, Found: 641.0944. HPLC (Chiralpak AD column, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, retention time: t_{major} = 14.998 min, t_{minor} = 69.904 min, > 99% ee).



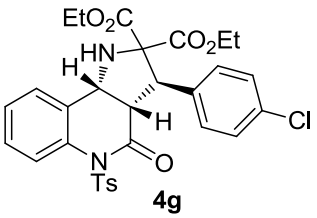
4f

(3*R*,3a*S*,9b*R*)-diethyl-3-(4-fluorophenyl)-4-oxo-5-tosyl-3,3a,4,5-tetrahydro-1H-pyrrolo[3,2-c]quinoline-2,2(9bH)-dicarboxylate (4f).

To a well-stirred solution of 2-bromoenals **2f** (22.9 mg, 0.10 mmol), *N*-heterocyclic carbene catalyst precursor **3b** (3.7 mg, 0.01 mmol) and DABCO (12.3 mg, 0.11 mmol) in DCE (0.5 mL) was added a solution of tosyl-protected *o*-amino aromatic aldimine **1a** (75.7 mg, 0.175 mmol) in DCE (1 mL) under the nitrogen atmosphere. The reaction mixture was stirred at room temperature for 1 h (monitored by TLC), and was quenched by water (2 mL). The aqueous layer was extracted with ethyl acetate (10 mL×3). The combined organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the crude residue was purified by flash column chromatography on silica gel using petroleum ether/EtOAc (4:1) to afford the desired product **4f** (51.09 mg, 88% yield).

White solid, mp 77–79 °C, $[\alpha]_D^{20}$ –59 (c 1.00, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.89 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.41 – 7.37 (m, 1H), 7.30 – 7.26 (m, 3H), 7.24 – 7.19 (m, 2H), 6.92 (t, *J* = 8.4 Hz, 2H), 4.83 (d, *J* = 5.2 Hz, 1H), 4.30 (d, *J* = 10.0 Hz, 1H), 4.14 – 4.09 (m, 2H), 3.80 – 3.76 (m, 1H), 3.61 (br s, 1H), 3.39 – 3.31 (m, 2H), 2.44 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H), 0.74 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.0, 169.4, 169.1, 163.5, 161.0, 144.9, 136.4, 133.8, 131.93, 131.90, 130.5, 130.4, 129.4, 128.8, 128.4, 128.1, 127.6, 126.2, 123.3, 115.2, 114.9, 62.3, 61.9, 57.5, 53.5, 51.3, 21.7, 13.9, 13.3. HRMS (ESI): Exact Mass Calcd. for $C_{30}H_{30}FN_2O_7S$ $(M+H)^+$: 581.1752, Found:

581.1758. HPLC (Chiralpak IC column, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, retention time: t_{minor} = 38.516 min, t_{major} = 50.212 min, > 99% ee).

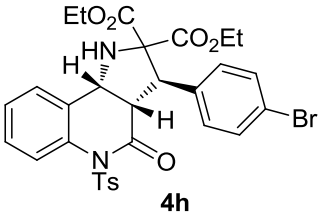


4g

(3*R*,3a*S*,9b*R*)-diethyl-3-(4-chlorophenyl)-4-oxo-5-tosyl-3,3a,4,5-tetrahydro-1H-pyrrolo[3,2-c]quinoline-2,2(9bH)-dicarboxylate (4g).

To a well-stirred solution of 2-bromoenals **2g** (24.6 mg, 0.10 mmol), *N*-heterocyclic carbene catalyst precursor **3b** (3.7 mg, 0.01 mmol) and DABCO (12.3 mg, 0.11 mmol) in DCE (0.5 mL) was added a solution of tosyl-protected *o*-amino aromatic aldimine **1a** (75.7 mg, 0.175 mmol) in DCE (1 mL) under the nitrogen atmosphere. The reaction mixture was stirred at room temperature for 1 h (monitored by TLC), and was quenched by water (2 mL). The aqueous layer was extracted with ethyl acetate (10 mL×3). The combined organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the crude residue was purified by flash column chromatography on silica gel using petroleum ether/EtOAc (4:1) to afford the desired product **4g** (54.93 mg, 92% yield).

White solid, mp 82–84 ^{o}C, $[\alpha]_D^{20}$ –78 (c 1.00, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 7.2 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.31 – 7.24 (m, 3H), 7.22 – 7.16 (m, 4H), 4.83 (d, *J* = 5.6 Hz, 1H), 4.28 (d, *J* = 10.0 Hz, 1H), 4.14 – 4.09 (m, 2H), 3.80 – 3.75 (m, 1H), 3.62 (br s, 1H), 3.39 – 3.35 (m, 2H), 2.44 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H), 0.73 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.0, 169.3, 169.1, 145.0, 136.4, 134.7, 133.8, 133.6, 130.2, 129.5, 128.8, 128.44, 128.36, 128.1, 127.6, 126.2, 123.3, 62.4, 62.0, 57.5, 53.4, 51.4, 21.7, 14.0, 13.2. HRMS (ESI): Exact Mass Calcd. for $C_{30}H_{30}ClN_2O_7S$ $(M+H)^+$: 597.1457, Found: 597.1455. HPLC (Chiralpak IC column, *n*-hexane/ *i*-PrOH = 80/20, flow rate = 1.0 mL/min, retention time: t_{minor} = 39.299 min, t_{major} = 56.364 min, > 99% ee).

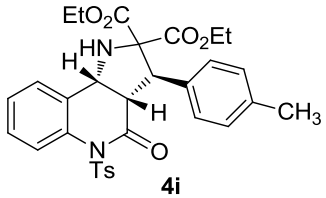


4h

(3*R*,3a*S*,9b*R*)-diethyl-3-(4-bromophenyl)-4-oxo-5-tosyl-3,3a,4,5-tetrahydro-1H-pyrrolo[3,2-c]quinoline-2,2(9bH)-dicarboxylate (4h).

To a well-stirred solution of 2-bromoenals **2h** (29.0 mg, 0.10 mmol), *N*-heterocyclic carbene catalyst precursor **3b** (3.7 mg, 0.01 mmol) and DABCO (12.3 mg, 0.11 mmol) in DCE (0.5 mL) was added a solution of tosyl-protected *o*-amino aromatic aldimine **1a** (75.7 mg, 0.175 mmol) in DCE (1 mL) under the nitrogen atmosphere. The reaction mixture was stirred at room temperature for 1 h (monitored by TLC), and was quenched by water (2 mL). The aqueous layer was extracted with ethyl acetate (10 mL×3). The combined organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the crude residue was purified by flash column chromatography on silica gel using petroleum ether/EtOAc (4:1) to afford the desired product **4h** (60.30 mg, 94% yield).

White solid, mp 76–78 ^{o}C, $[\alpha]_D^{20}$ –86 (c 1.00, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.40 – 7.34 (m, 3H), 7.30 – 7.24 (m, 3H), 7.11 (d, *J* = 8.4 Hz, 2H), 4.83 (br s, 1H), 4.26 (d, *J* = 10.0 Hz, 1H), 4.14 – 4.09 (m, 2H), 3.81 – 3.73 (m, 1H), 3.62 (br s, 1H), 3.41 – 3.33 (m, 2H), 2.43 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H), 0.73 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.9, 169.3, 169.0, 144.9, 136.4, 135.2, 133.8, 131.3, 130.5, 129.4, 128.8, 128.4, 128.1, 127.5, 126.2, 123.2, 121.7, 62.3, 62.0, 57.5, 53.3, 51.5, 21.7, 13.9, 13.2. HRMS (ESI): Exact Mass Calcd. for $C_{30}H_{30}BrN_2O_7S$ $(M+H)^+$: 641.0952, Found: 641.0945. HPLC (Chiralpak IC column, *n*-hexane/ *i*-PrOH = 80/20, flow rate = 1.0 mL/min, retention time: t_{minor} = 28.400 min, t_{major} = 39.767 min, 98.8% ee).

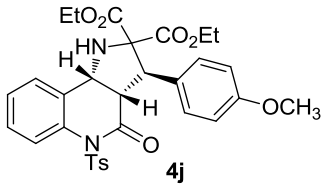


4i

(3*R*,3a*S*,9b*R*)-diethyl-4-oxo-3-(p-tolyl)-5-tosyl-3,3a,4,5-tetrahydro-1H-pyrrolo[3,2-c]quinoline-2,2(9bH)-dicarboxylate (4i).

To a well-stirred solution of 2-bromoenals **2i** (22.5 mg, 0.10 mmol), *N*-heterocyclic carbene catalyst precursor **3b** (3.7 mg, 0.01 mmol) and DABCO (12.3 mg, 0.11 mmol) in DCE (0.5 mL) was added a solution of tosyl-protected *o*-amino aromatic aldimine **1a** (75.7 mg, 0.175 mmol) in DCE (1 mL) under the nitrogen atmosphere. The reaction mixture was stirred at room temperature for 1 h (monitored by TLC), and was quenched by water (2 mL). The aqueous layer was extracted with ethyl acetate (10 mL×3). The combined organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the crude residue was purified by flash column chromatography on silica gel using petroleum ether/EtOAc (4:1) to afford the desired product **4i** (51.90 mg, 90% yield).

White solid, mp 79–81°C, $[\alpha]_D^{20}$ –75 (c 1.00, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.89 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.29 – 7.23 (m, 3H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 4.83 (d, *J* = 6.0 Hz, 1H), 4.31 (d, *J* = 9.6 Hz, 1H), 4.12 – 4.08 (m, 2H), 3.75 – 3.71 (m, 1H), 3.60 (br s, 1H), 3.40 – 3.29 (m, 2H), 2.43 (s, 3H), 2.25 (s, 3H), 1.21 (t, *J* = 7.2 Hz, 3H), 0.67 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.2, 169.4, 144.8, 137.2, 136.5, 134.0, 133.3, 129.4, 128.84, 128.78, 128.6, 128.3, 128.2, 127.7, 126.1, 123.2, 62.1, 61.8, 57.7, 53.6, 51.8, 21.7, 20.9, 13.9, 13.1. HRMS (ESI): Exact Mass Calcd. for $C_{31}H_{33}N_2O_7S$ $(M+H)^+$: 577.2003, Found: 577.2007. HPLC (Chiralpak AD column, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, retention time: t_{major} = 13.018 min, t_{minor} = 49.937 min, > 99% ee).

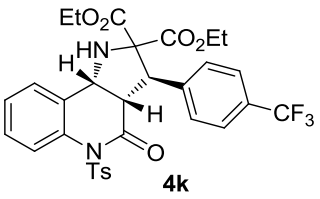


4j

(3*R*,3a*S*,9b*R*)-diethyl-3-(4-methoxyphenyl)-4-oxo-5-tosyl-3,3a,4,5-tetrahydro-1H-pyrrolo[3,2-c]quinoline-2,2(9bH)-dicarboxylate (4j).

To a well-stirred solution of 2-bromoenals **2j** (24.1 mg, 0.10 mmol), *N*-heterocyclic carbene catalyst precursor **3b** (3.7 mg, 0.01 mmol) and DABCO (12.3 mg, 0.11 mmol) in DCE (0.5 mL) was added a solution of tosyl-protected *o*-amino aromatic aldimine **1a** (75.7 mg, 0.175 mmol) in DCE (1 mL) under the nitrogen atmosphere. The reaction mixture was stirred at room temperature for 2 h (monitored by TLC), and was quenched by water (2 mL). The aqueous layer was extracted with ethyl acetate (10 mL×3). The combined organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the crude residue was purified by flash column chromatography on silica gel using petroleum ether/EtOAc (4:1) to afford the desired product **4j** (46.23 mg, 78% yield).

White solid, mp 75–77 °C, $[\alpha]_D^{20}$ –79 (c 1.00, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.89 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.30 – 7.23 (m, 3H), 7.14 (d, *J* = 8.8 Hz, 2H), 6.75 (d, *J* = 8.4 Hz, 2H), 4.82 (d, *J* = 6.0 Hz, 1H), 4.28 (d, *J* = 10.0 Hz, 1H), 4.13 – 4.08 (m, 2H), 3.83 – 3.77 (m, 1H), 3.76 (s, 3H), 3.60 (br s, 1H), 3.39 – 3.32 (m, 2H), 2.43 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H), 0.73 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.2, 169.5, 169.3, 159.1, 144.8, 136.5, 133.9, 129.8, 129.4, 128.8, 128.3, 128.14, 128.10, 127.8, 126.1, 123.3, 113.6, 76.9, 76.7, 62.2, 61.8, 57.5, 55.2, 53.7, 51.4, 21.7, 13.9, 13.3. HRMS (ESI): Exact Mass Calcd. for $C_{31}H_{33}N_2O_8S$ $(M+H)^+$: 593.1952, Found: 593.1960. HPLC (Chiralpak AD column, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, retention time: t_{major} = 19.488 min, t_{minor} = 74.565 min, > 99% ee).

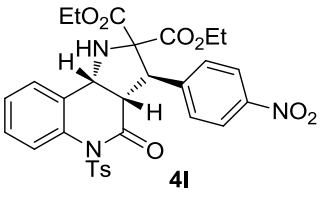


4k

(3*R*,3a*S*,9b*R*)-diethyl-4-oxo-5-tosyl-3-(4-(trifluoromethyl)phenyl)-3,3a,4,5-tetrahydro-1H-pyrrolo[3,2-c]quinoline-2,2(9bH)-dicarboxylate (4k).

To a well-stirred solution of 2-bromoenals **2k** (27.9 mg, 0.10 mmol), *N*-heterocyclic carbene catalyst precursor **3b** (3.7 mg, 0.01 mmol) and DABCO (12.3 mg, 0.11 mmol) in DCE (0.5 mL) was added a solution of tosyl-protected *o*-amino aromatic aldimine **1a** (75.7 mg, 0.175 mmol) in DCE (1 mL) under the nitrogen atmosphere. The reaction mixture was stirred at room temperature for 1 h (monitored by TLC), and was quenched by water (2 mL). The aqueous layer was extracted with ethyl acetate (10 mL×3). The combined organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the crude residue was purified by flash column chromatography on silica gel using petroleum ether/EtOAc (4:1) to afford the desired product **4k** (46.67 mg, 74% yield).

White solid, mp 78–80°C, $[\alpha]_D^{20}$ –73 (c 1.00, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.42 – 7.36 (m, 3H), 7.31 – 7.27 (m, 3H), 4.86 (d, *J* = 6.0 Hz, 1H), 4.36 (d, *J* = 10.0 Hz, 1H), 4.13 (q, *J* = 6.8 Hz, 2H), 3.77 – 3.69 (m, 1H), 3.65 (br s, 1H), 3.43 (dd, *J* = 10.4, *J* = 6.4 Hz, 1H), 3.35 – 3.27 (m, 1H), 2.44 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H), 0.65 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.8, 169.2, 169.0, 145.0, 140.4, 136.4, 133.8, 129.5, 129.3, 128.8, 128.5, 128.1, 127.5, 126.3, 125.14, 125.11, 123.3, 62.4, 62.1, 57.6, 53.3, 51.7, 21.7, 13.9, 13.0. HRMS (ESI): Exact Mass Calcd. for $C_{31}H_{30}F_3N_2O_7S$ $(M+H)^+$: 631.1720, Found: 631.1724. HPLC (Chiralpak AD column, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, retention time: t_{major} = 12.427 min, t_{minor} = 32.269 min, > 99% ee).



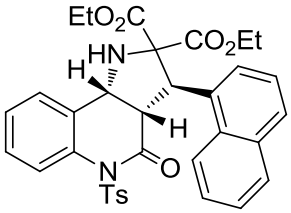
4l

(3*R*,3a*S*,9b*R*)-diethyl-3-(4-nitrophenyl)-4-oxo-5-tosyl-3,3a,4,5-tetrahydro-1H-pyrrolo[3,2-c]quinoline-2,2(9bH)-dicarboxylate (4l).

To a well-stirred solution of 2-bromoenals **2l** (25.6 mg, 0.10 mmol), *N*-heterocyclic carbene catalyst precursor **3b** (3.7 mg, 0.01 mmol) and DABCO (12.3 mg, 0.11 mmol) in DCE (0.5 mL) was added a solution of tosyl-protected *o*-amino aromatic aldimine **1a** (75.7 mg, 0.175 mmol) in DCE (1 mL) under the

nitrogen atmosphere. The reaction mixture was stirred at room temperature for 1 h (monitored by TLC), and was quenched by water (2 mL). The aqueous layer was extracted with ethyl acetate (10 mL×3). The combined organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the crude residue was purified by flash column chromatography on silica gel using petroleum ether/EtOAc (4:1) to afford the desired product **4l** (38.28 mg, 63% yield).

White solid, mp 88–90 ^oC, $[\alpha]_D^{20}$ –117 (c 1.00, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ: 8.10 (d, *J* = 8.8 Hz, 2H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.45 – 7.39 (m, 3H), 7.31 – 7.26 (m, 3H), 4.88 (d, *J* = 4.4 Hz, 1H), 4.38 (d, *J* = 10.4 Hz, 1H), 4.17 – 4.12 (m, 2H), 3.83 – 3.75 (m, 1H), 3.68 (br s, 1H), 3.45 (dd, *J* = 10.4, 6.4 Hz, 1H), 3.37 – 3.29 (m, 1H), 2.44 (s, 3H), 1.24 (t, *J* = 7.2 Hz, 3H), 0.70 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.6, 169.1, 168.7, 147.4, 145.1, 143.7, 136.2, 133.6, 130.0, 129.5, 128.8, 128.6, 128.0, 127.3, 126.3, 123.3, 123.2, 62.5, 62.3, 57.5, 53.3, 51.6, 21.7, 13.9, 13.3. HRMS (ESI): Exact Mass Calcd. for $C_{30}H_{30}N_3O_9S$ $(M+H)^+$: 608.1697, Found: 608.1690. HPLC (Chiralpak IC column, *n*-hexane/*i*-PrOH= 80/20, flow rate = 1.0 mL/min, retention time: t_{minor} = 67.598 min, t_{major} = 80.932 min, > 99% ee).



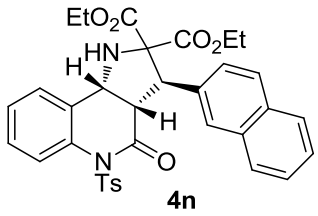
4m

(3*R*,3a*S*,9b*R*)-diethyl-3-(naphthalen-1-yl)-4-oxo-5-tosyl-3,3a,4,5-tetrahydro-1H-pyrrolo[3,2-c]quinoline-2,2(9bH)-dicarboxylate (4m).

To a well-stirred solution of 2-bromoenals **2m** (26.1 mg, 0.10 mmol), *N*-heterocyclic carbene catalyst precursor **3b** (3.7 mg, 0.01 mmol) and DABCO (12.3 mg, 0.11 mmol) in DCE (0.5 mL) was added a solution of tosyl-protected *o*-amino aromatic aldimine **1a** (75.7 mg, 0.175 mmol) in DCE (1 mL) under the nitrogen atmosphere. The reaction mixture was stirred at room temperature for 1 h (monitored by TLC), and was quenched by water (2 mL). The aqueous layer was extracted with ethyl acetate (10 mL×3). The combined organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the crude residue was purified by flash column chromatography on silica gel using petroleum ether/EtOAc (4:1) to afford the desired product **4m** (43.50 mg, 71% yield).

White solid, mp 91–93 ^oC, $[\alpha]_D^{20}$ –2.0 (c 1.00, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ: 8.51 (d, *J* =8.4 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 7.2 Hz, 1H), 7.52 – 7.42 (m, 3H), 7.36 – 7.26 (m, 5H), 5.71 (d, *J* = 3.6 Hz, 1H), 5.06 (d, *J* = 5.6 Hz, 1H), 4.11 – 4.05 (m,

2H), 3.49 – 3.43 (m, 2H), 3.41 – 3.38 (m, 1H), 2.89 – 2.81 (m, 1H), 2.44 (s, 3H), 1.18 (t, *J* = 7.2 Hz, 3H), 0.13 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.5, 170.2, 168.5, 144.5, 136.6, 135.9, 135.1, 133.6, 133.1, 129.3, 129.1, 128.8, 128.7, 128.21, 128.18, 126.3, 126.1, 125.9, 125.8, 124.8, 124.3, 123.1, 61.8, 61.4, 59.4, 55.5, 46.6, 21.7, 13.9, 12.5. HRMS (ESI): Exact Mass Calcd. for $C_{34}H_{33}N_2O_7S$ $(M+H)^+$: 613.2003, Found: 613.1995. HPLC (Chiralpak AD column, *n*-hexane/*i*-PrOH= 70/30, flow rate = 1.0 mL/min, retention time: t_{major} = 13.231 min, t_{minor} = 29.182 min, > 99% ee).

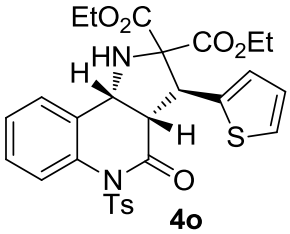


4n

(3*R*,3a*S*,9b*R*)-diethyl-3-(naphthalen-2-yl)-4-oxo-5-tosyl-3,3a,4,5-tetrahydro-1H-pyrrolo[3,2-c]quinoline-2,2(9bH)-dicarboxylate (4n).

To a well-stirred solution of 2-bromoenals **2n** (26.1 mg, 0.10 mmol), *N*-heterocyclic carbene catalyst precursor **3b** (3.7 mg, 0.01 mmol) and DABCO (12.3 mg, 0.11 mmol) in DCE (0.5 mL) was added a solution of tosyl-protected *o*-amino aromatic aldimine **1a** (75.7 mg, 0.175 mmol) in DCE (1 mL) under the nitrogen atmosphere. The reaction mixture was stirred at room temperature for 1 h (monitored by TLC), and was quenched by water (2 mL). The aqueous layer was extracted with ethyl acetate (10 mL×3). The combined organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the crude residue was purified by flash column chromatography on silica gel using petroleum ether/EtOAc (4:1) to afford the desired product **4n** (50.85 mg, 83% yield).

White solid, mp 93–95 ^{o}C, $[\alpha]_D^{20}$ –101 (c 1.00, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.90 (d, *J* = 8.0 Hz, 2H), 7.74 – 7.64 (m, 6H), 7.43 – 7.39 (m, 3H), 7.33 – 7.26 (m, 4H), 4.93 (d, *J* = 5.6 Hz, 1H), 4.53 (d. *J* = 9.6 Hz, 1H), 4.16 – 4.10 (m, 2H), 3.68 (br s, 1H), 3.62 – 3.52 (m, 2H), 3.10 – 3.06 (m, 1H), 2.43 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H), 0.38 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.1, 169.3, 144.8, 136.4, 134.0, 133.8, 133.1, 132.7, 129.4, 128.8, 128.4, 128.2, 128.0, 127.9, 127.7, 127.6, 127.3, 126.5, 126.1, 126.03, 125.97, 123.2, 62.1, 61.9, 57.8, 53.7, 52.3, 21.7, 13.9, 12.9. HRMS (ESI): Exact Mass Calcd. for $C_{34}H_{32}N_2O_7SNa$ $(M+Na)^+$: 635.1822, Found: 635.1831. HPLC (Chiralpak AD column, *n*-hexane/*i*-PrOH= 70/30, flow rate = 1.0 mL/min, retention time: t_{major} = 16.526 min, t_{minor} = 65.188 min, > 99% ee).

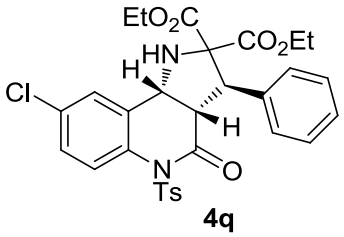


4o

(3*S*,3a*S*,9b*R*)-diethyl-4-oxo-3-(thiophen-2-yl)-5-tosyl-3,3a,4,5-tetrahydro-1H-pyrrolo[3,2-c]quinoline-2,2(9bH)-dicarboxylate (4o).

To a well-stirred solution of 2-bromoenals **2o** (21.7 mg, 0.10 mmol), *N*-heterocyclic carbene catalyst precursor **3b** (3.7 mg, 0.01 mmol) and DABCO (12.3 mg, 0.11 mmol) in DCE (0.5 mL) was added a solution of tosyl-protected *o*-amino aromatic aldimine **1a** (75.7 mg, 0.175 mmol) in DCE (1 mL) under the nitrogen atmosphere. The reaction mixture was stirred at room temperature for 1 h (monitored by TLC), and was quenched by water (2 mL). The aqueous layer was extracted with ethyl acetate (10 mL×3). The combined organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the crude residue was purified by flash column chromatography on silica gel using petroleum ether/EtOAc (4:1) to afford the desired product **4o** (38.67 mg, 68% yield).

White solid, mp 71–73 ^{o}C, $[\alpha]_D^{20}$ –67 (c 1.00, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.90 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.31 – 7.24 (m, 3H), 7.13 (d, *J* = 5.2 Hz, 1H), 6.93 (d, *J* = 3.2 Hz, 1H), 6.88 – 6.86 (m, 1H), 4.80 (br s, 1H), 4.63 (d, *J* = 8.8 Hz, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.88 – 3.80 (m, 1H), 3.61 (d, *J* = 2.8 Hz, 1H), 3.55 – 3.47 (m, 1H), 3.31 (dd, *J* = 8.8, 6.0 Hz, 1H), 2.44 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H), 0.82 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.0, 169.1, 168.7, 144.9, 139.1, 136.4, 134.0, 129.4, 128.8, 128.4, 128.3, 127.4, 126.8, 126.6, 126.2, 124.9, 123.4, 62.5, 61.9, 57.6, 55.1, 47.5, 21.7, 13.9, 13.4. HRMS (ESI): Exact Mass Calcd. for $C_{28}H_{29}N_2O_7S_2$ $(M+H)^+$: 569.1411, Found: 569.1417. HPLC (Chiralpak AD column, *n*-hexane/*i*-PrOH= 70/30, flow rate = 1.0 mL/min, retention time: t_{major} = 17.136 min, t_{minor} = 74.246 min, > 99% ee).



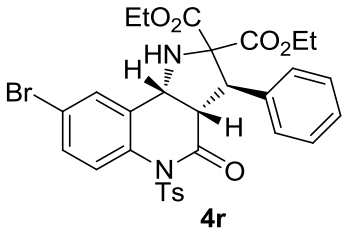
4q

(3*R*,3a*S*,9b*R*)-diethyl-8-chloro-4-oxo-3-phenyl-5-tosyl-3,3a,4,5-tetrahydro-1H-pyrrolo[3,2-c]quinoline-2,2(9bH)-dicarboxylate (4q).

To a well-stirred solution of 2-bromoenals **2a** (21.1 mg, 0.10 mmol), *N*-heterocyclic carbene catalyst precursor **3b** (3.7 mg, 0.01 mmol) and DABCO (12.3 mg, 0.11 mmol) in DCE (0.5 mL) was added a

solution of tosyl-protected *o*-amino aromatic aldimine **1b** (81.7 mg, 0.175 mmol) in DCE (1 mL) under the nitrogen atmosphere. The reaction mixture was stirred at room temperature for 1 h (monitored by TLC), and was quenched by water (2 mL). The aqueous layer was extracted with ethyl acetate (10 mL×3). The combined organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the crude residue was purified by flash column chromatography on silica gel using petroleum ether/EtOAc (4:1) to afford the desired product **4q** (45.98 mg, 77% yield).

White solid, mp 84–86 ^oC, $[\alpha]_D^{20}$ –73 (c 1.00, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.85 (d, *J*= 8.0 Hz, 2H), 7.79 (d, *J* = 1.2 Hz, 1H), 7.56 – 7.48 (m, 2H), 7.30 – 7.21 (m, 7H), 4.77 (d, *J* = 4.8 Hz, 1H), 4.28 (d, *J* = 10.8 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 3.78 – 3.71 (m, 2H), 3.43 (dd, *J* = 10.4, 6.4 Hz, 1H), 3.30 – 3.22 (m, 1H), 2.43 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H), 0.66 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.7, 169.5, 168.5, 145.2, 136.1, 135.6, 132.8, 131.3, 131.0, 130.2, 129.5, 128.8, 128.7, 128.3, 127.8, 125.0, 119.9, 62.3, 62.2, 57.2, 53.5, 52.0, 21.7, 14.0, 13.2. HRMS (ESI): Exact Mass Calcd. for $C_{30}H_{30}ClN_2O_7S$ $(M+H)^+$: 597.1457, Found: 597.1450. HPLC (Chiralpak IC column, *n*-hexane/DCM= 50/50, flow rate = 1.0 mL/min, retention time: t_{minor} = 40.501 min, t_{major} = 49.885 min, > 99% ee).



4r

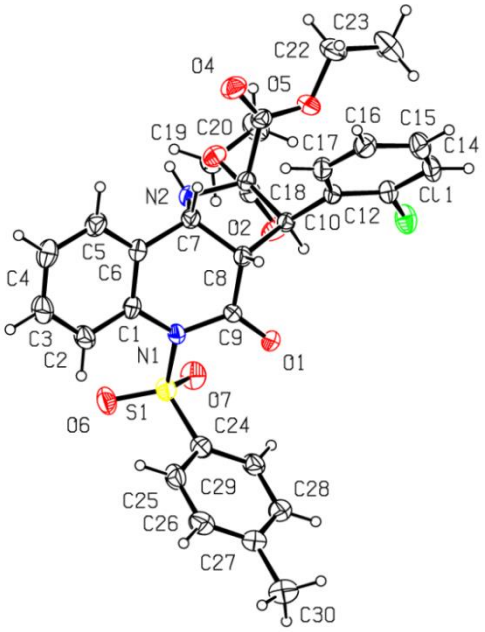
(3*R*,3a*S*,9b*R*)-diethyl-8-bromo-4-oxo-3-phenyl-5-tosyl-3,3a,4,5-tetrahydro-1H-pyrrolo[3,2-c]quinoline -2,2(9bH)-dicarboxylate (4r).

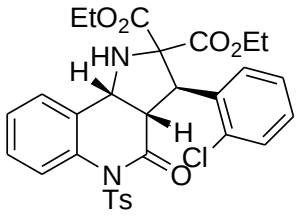
To a well-stirred solution of 2-bromoenals **2a** (21.1 mg, 0.10 mmol), *N*-heterocyclic carbene catalyst precursor **3b** (3.7 mg, 0.01 mmol) and DABCO (12.3 mg, 0.11 mmol) in DCE (0.5 mL) was added a solution of tosyl-protected *o*-amino aromatic aldimine **1c** (89.5 mg, 0.175 mmol) in DCE (1 mL) under the nitrogen atmosphere. The reaction mixture was stirred at room temperature for 1 h (monitored by TLC), and was quenched by water (2 mL). The aqueous layer was extracted with ethyl acetate (10 mL×3). The combined organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the crude residue was purified by flash column chromatography on silica gel using petroleum ether/EtOAc (4:1) to afford the desired product **4r** (48.76 mg, 76% yield).

White solid, mp 88–90^oC, $[\alpha]_D^{20}$ –145 (c 1.00, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.85 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 1.6 Hz, 1H), 7.56 – 7.48 (m, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.21 – 7.18 (m, 5H), 4.77 (d, *J* = 4.4 Hz, 1H), 4.28 (d, *J* = 10.8 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 3.78 – 3.71 (m, 2H), 3.43 (dd, *J* = 10.8, 6.4 Hz, 1H), 3.30 – 3.22 (m, 1H), 2.44 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H), 0.66 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR

(100 MHz, $CDCl_3$) δ: 169.8, 169.5, 168.5, 145.2, 136.1, 135.6, 132.8, 131.3, 131.0, 130.2, 129.5, 128.8, 128.7, 128.3, 127.8, 125.0, 119.9, 62.4, 62.2, 57.2, 53.5, 52.0, 21.7, 14.0, 13.2. HRMS (ESI): Exact Mass Calcd. for $C_{30}H_{30}BrN_2O_7S$ $(M+H)^+$: 641.0952, Found: 641.0943. HPLC (Chiralpak IC column, *n*-hexane/ DCM = 50/50, flow rate = 1.0 mL/min, retention time: t_{minor} = 47.766 min, t_{major} = 54.107 min, > 99% ee).

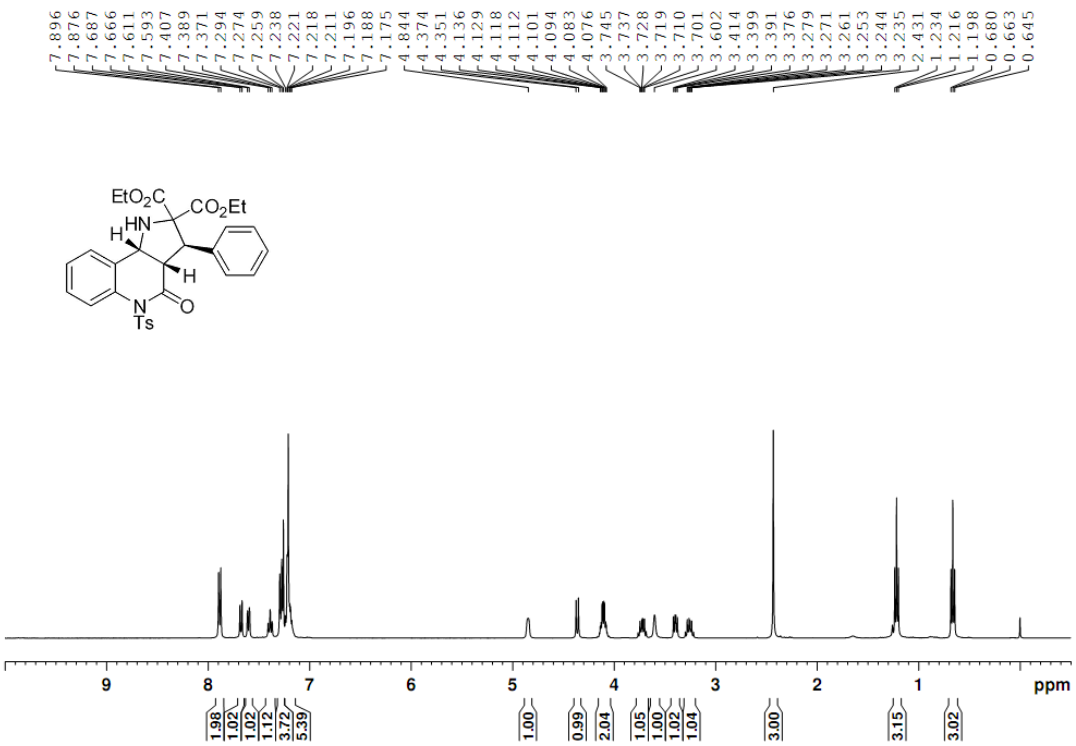
3. X-Ray crystal structure of compound 4b



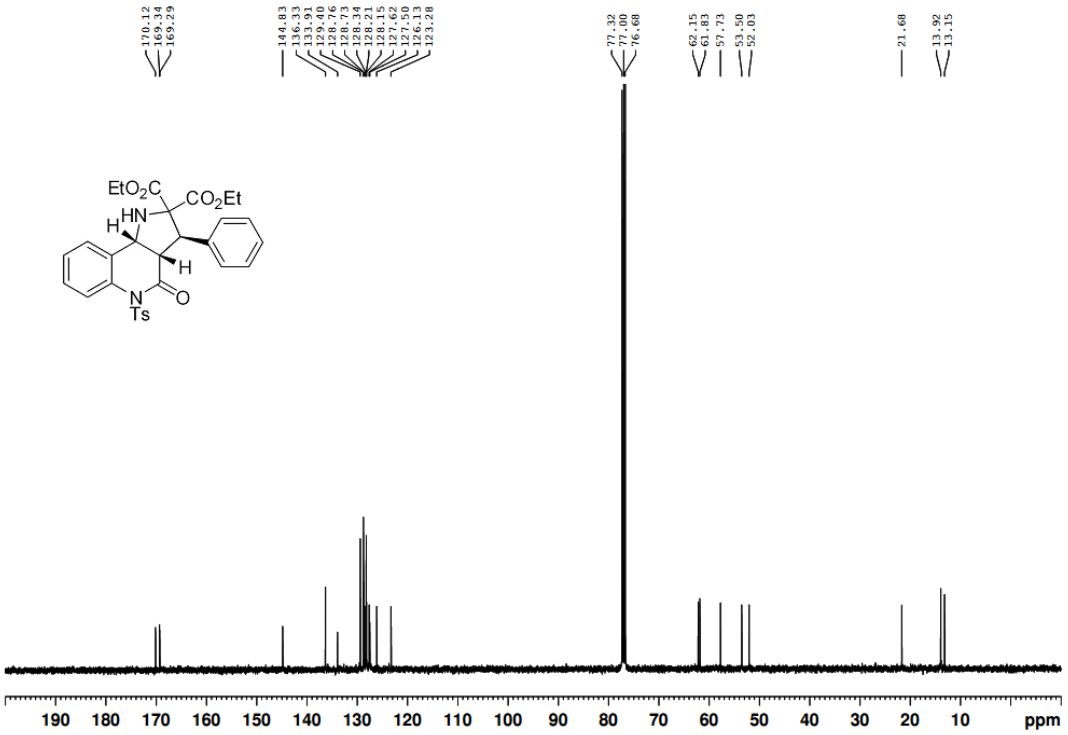


4. NMR spectra of compounds 4a–4r

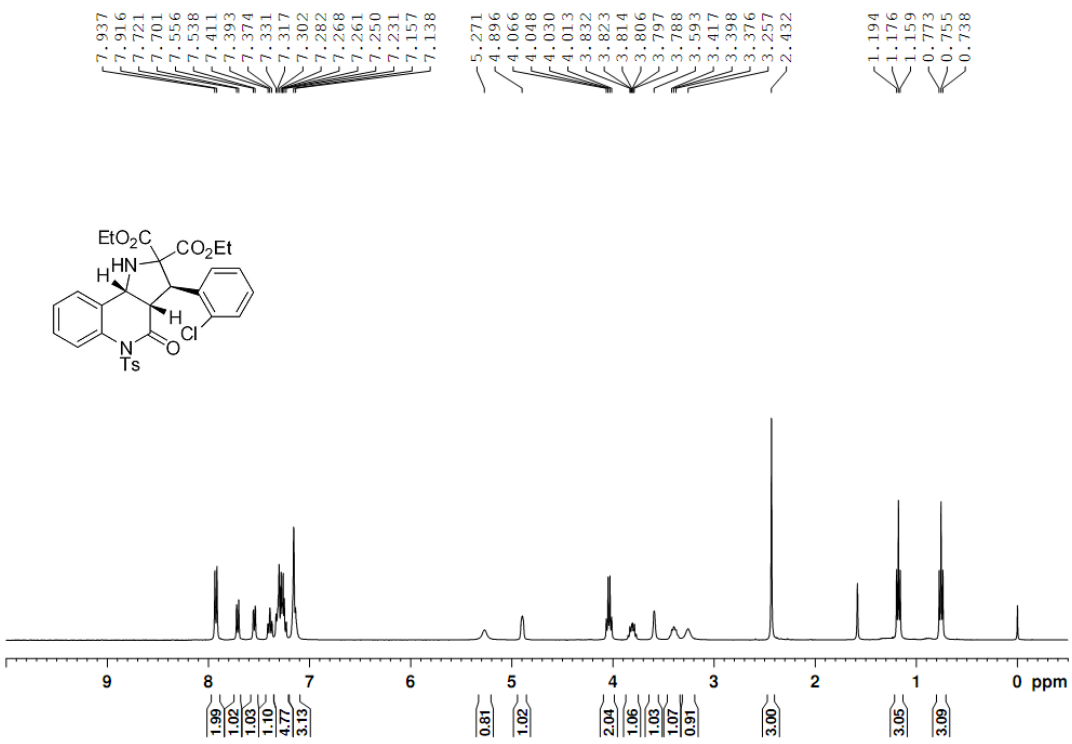
^{1}H NMR spectrum of compound **4a** ($CDCl_3$, 400 MHz)



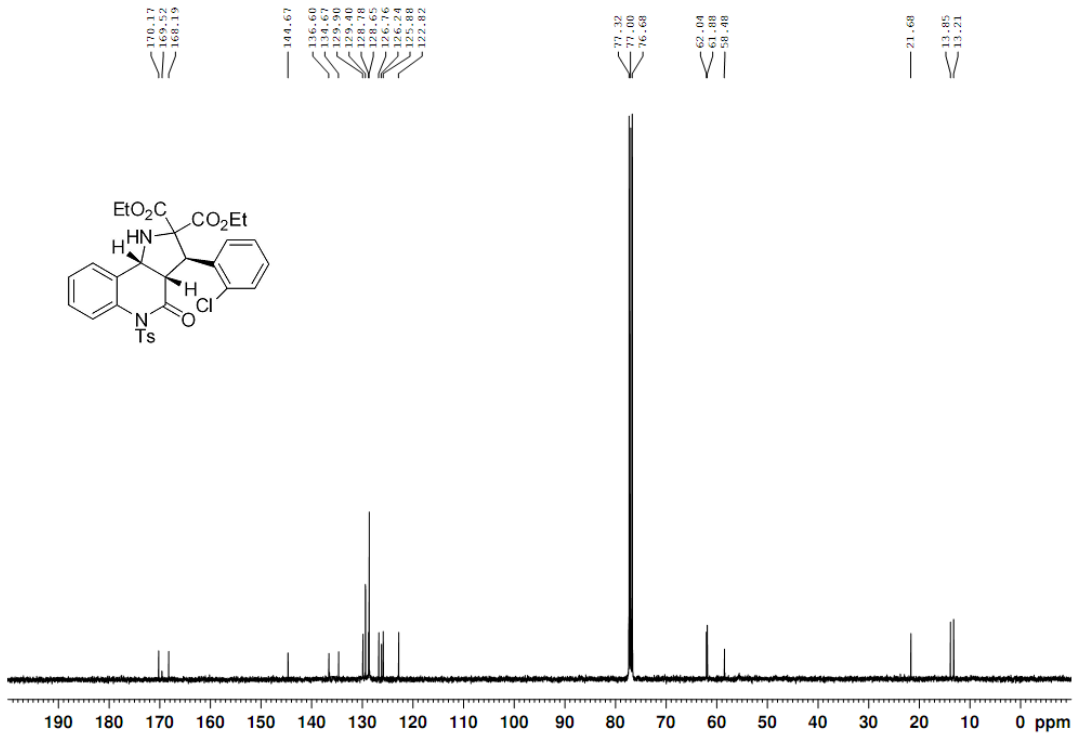
^{13}C NMR spectrum of compound **4a** ($CDCl_3$, 100 MHz)



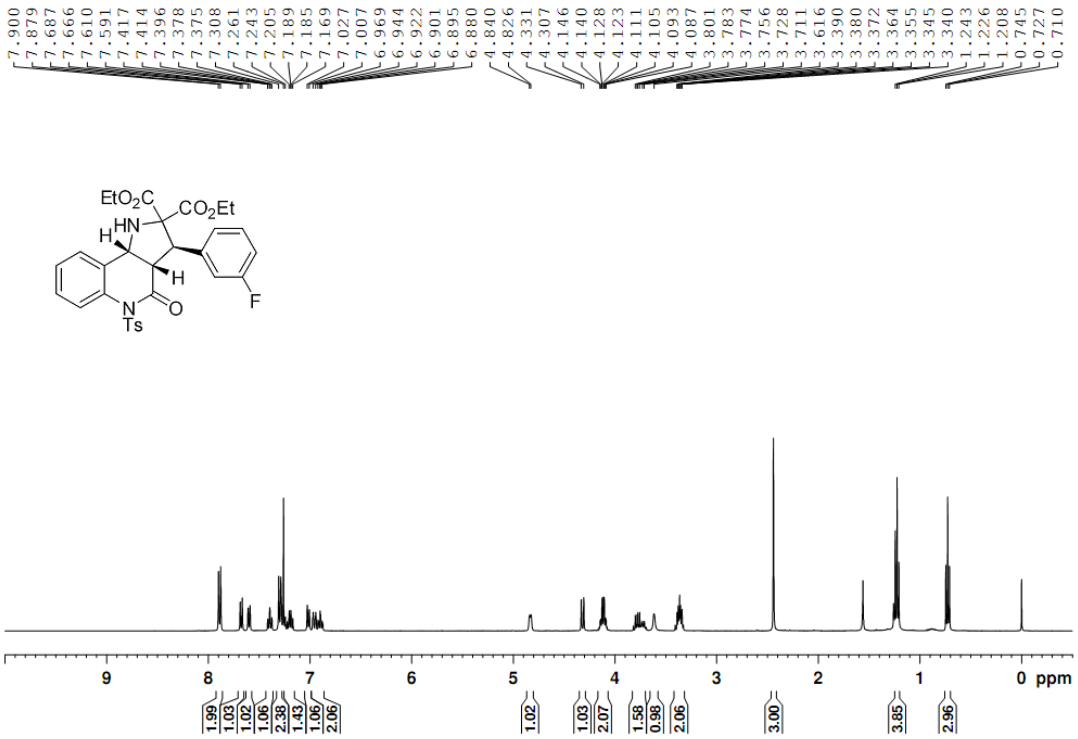
^{1}H NMR spectrum of compound **4b** ($CDCl_3$, 400 MHz)



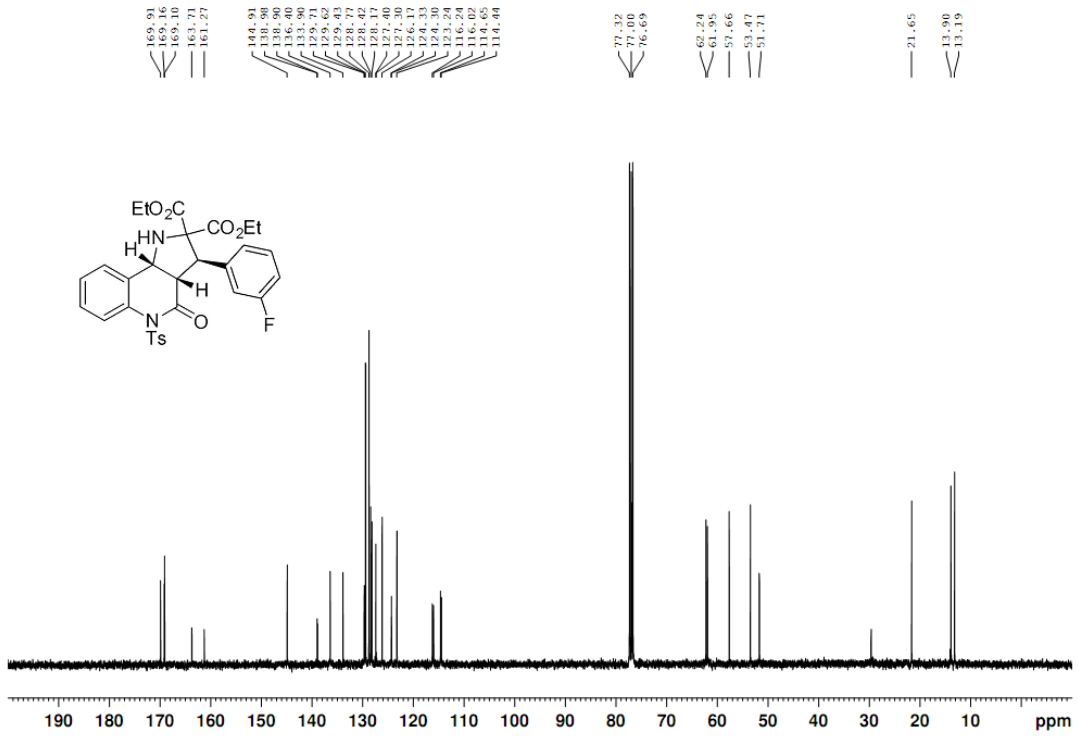
^{13}C NMR spectrum of compound **4b** ($CDCl_3$, 100 MHz)



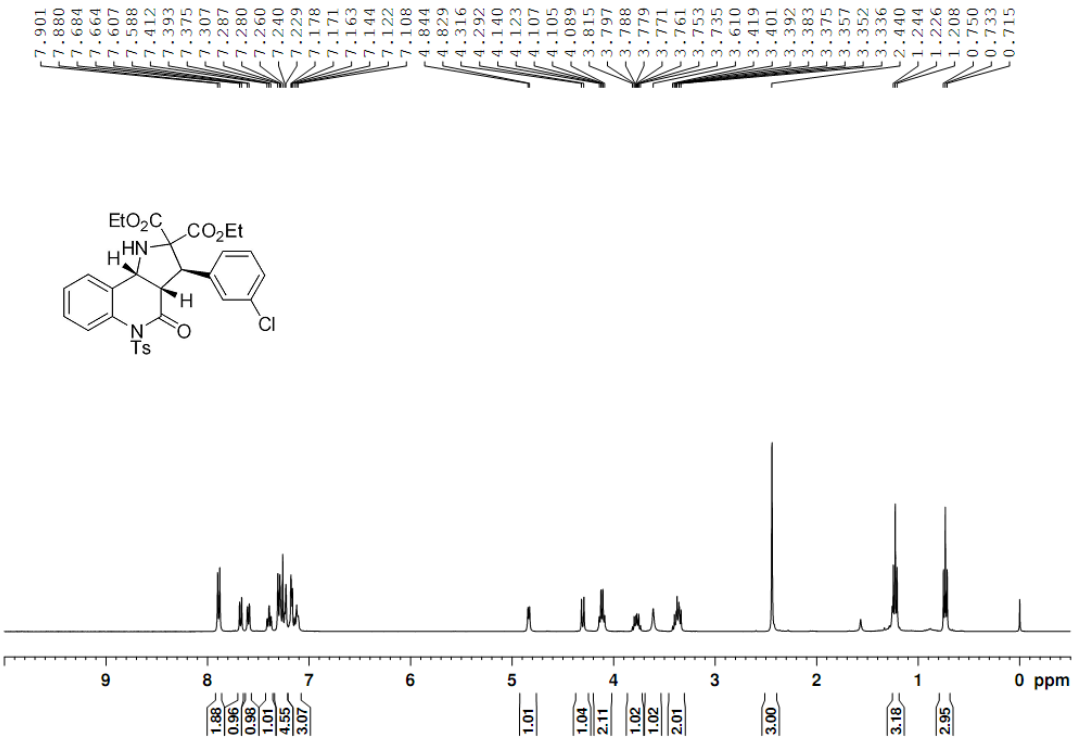
^{1}H NMR spectrum of compound **4c** ($CDCl_3$, 400 MHz)



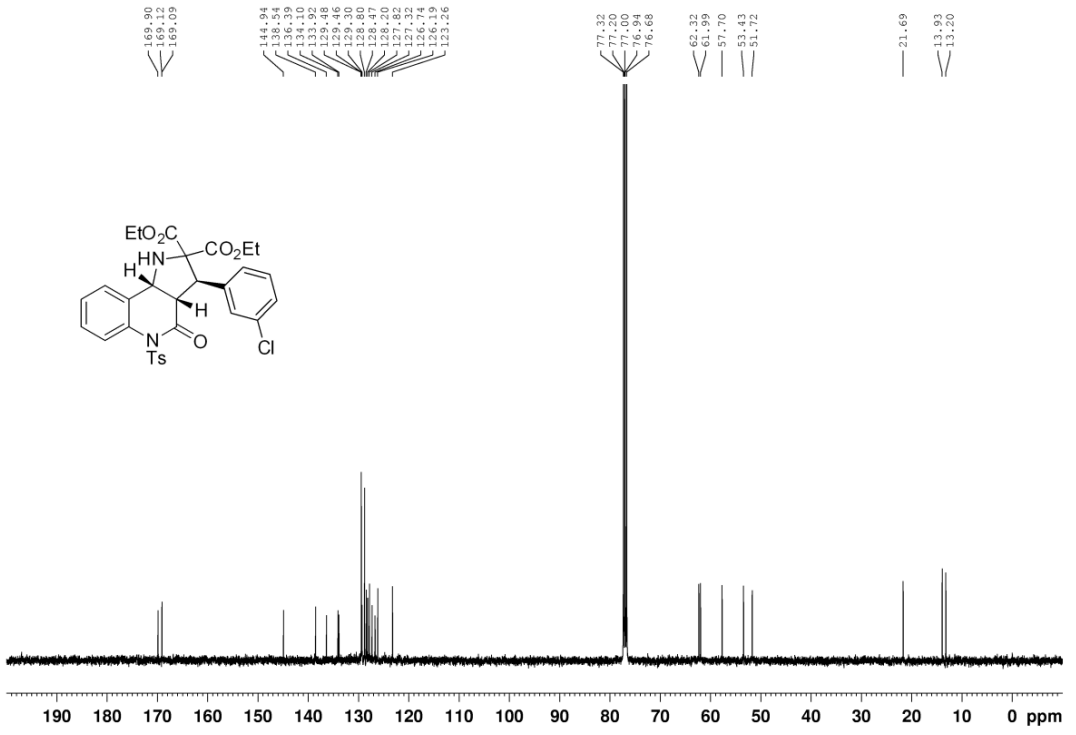
^{13}C NMR spectrum of compound **4c** ($CDCl_3$, 100 MHz)



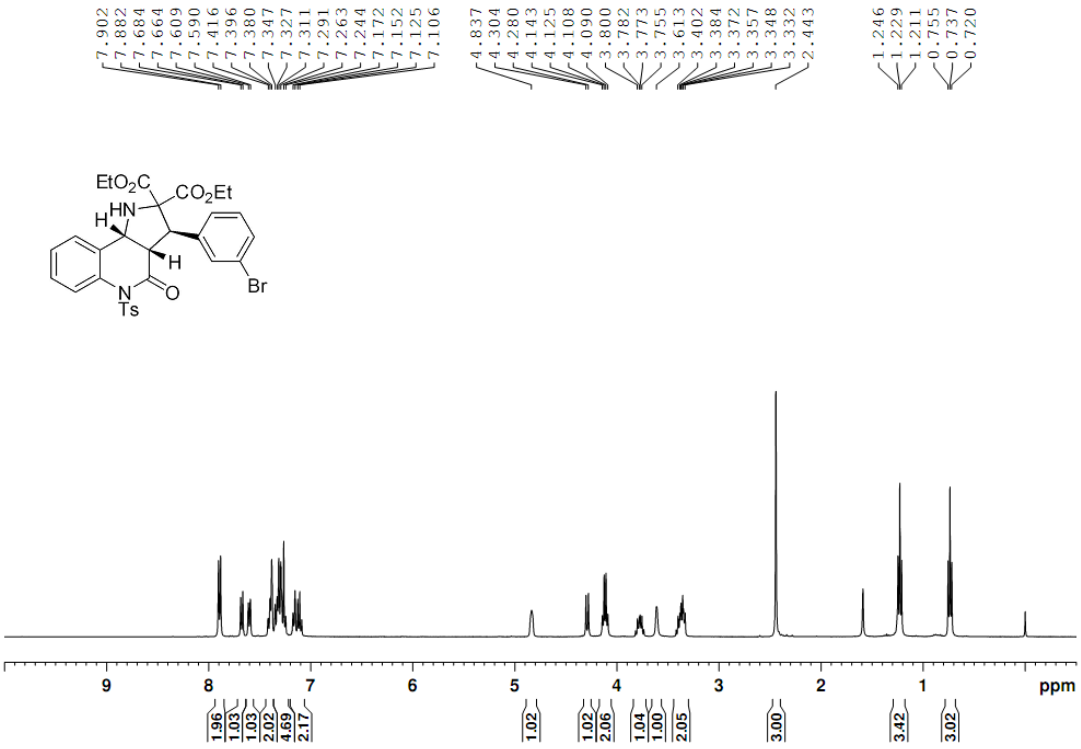
^{1}H NMR spectrum of compound **4d** ($CDCl_3$, 400 MHz)



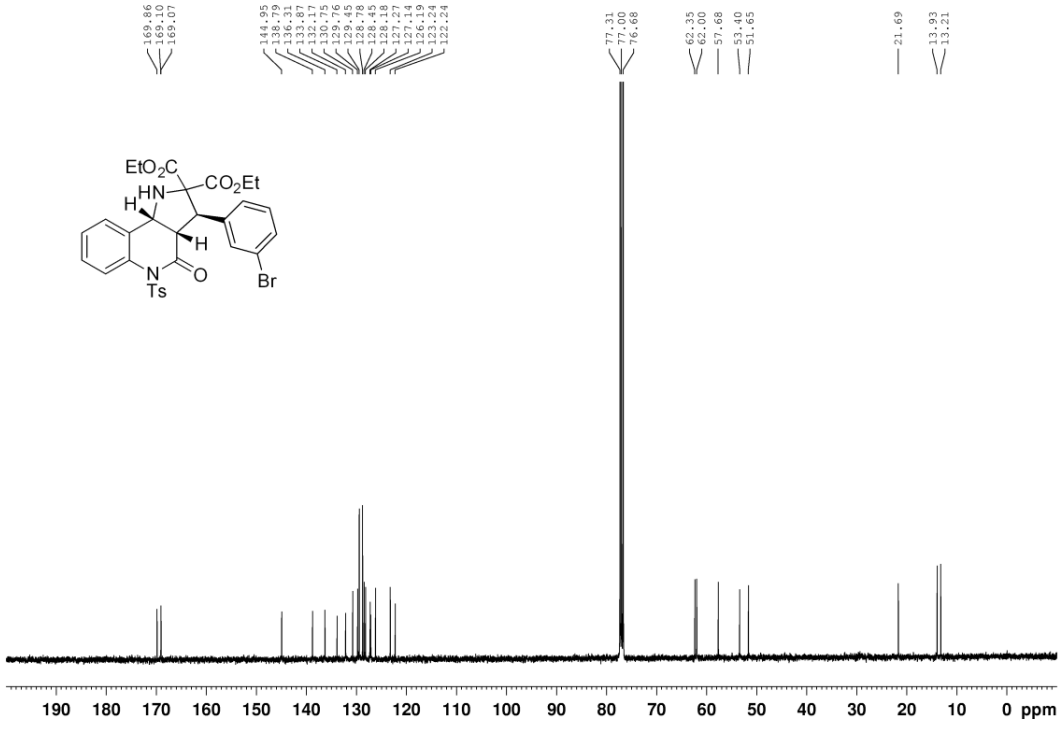
^{13}C NMR spectrum of compound **4d** ($CDCl_3$, 100 MHz)



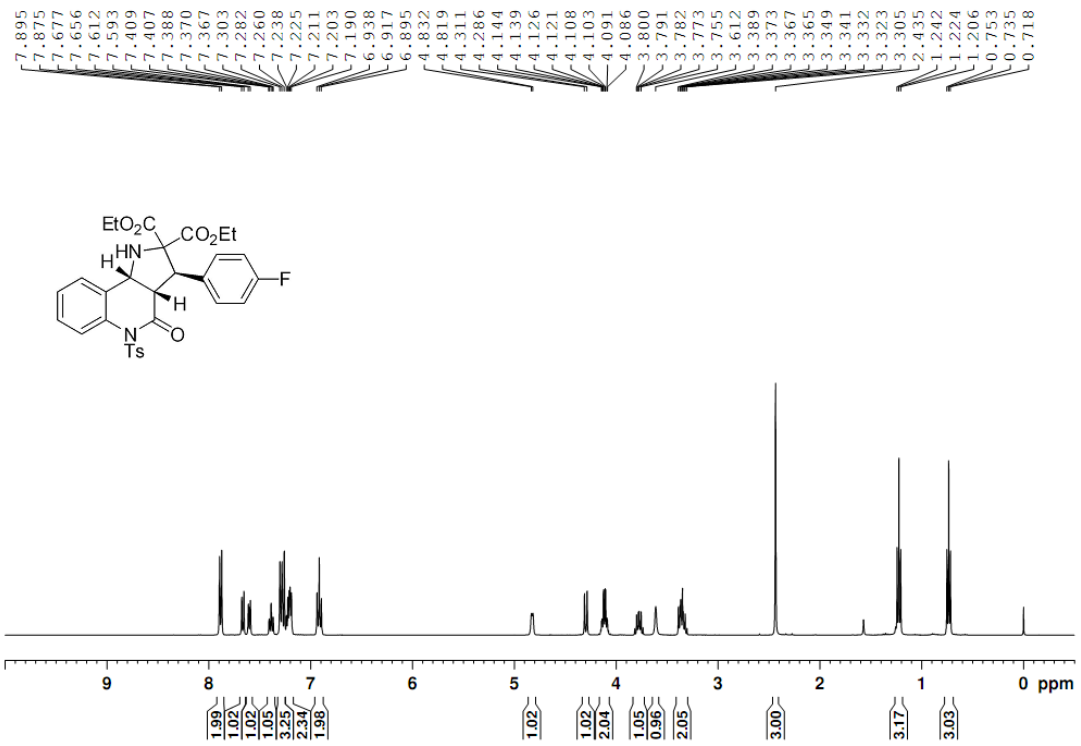
^{1}H NMR spectrum of compound **4e** ($CDCl_3$, 400 MHz)



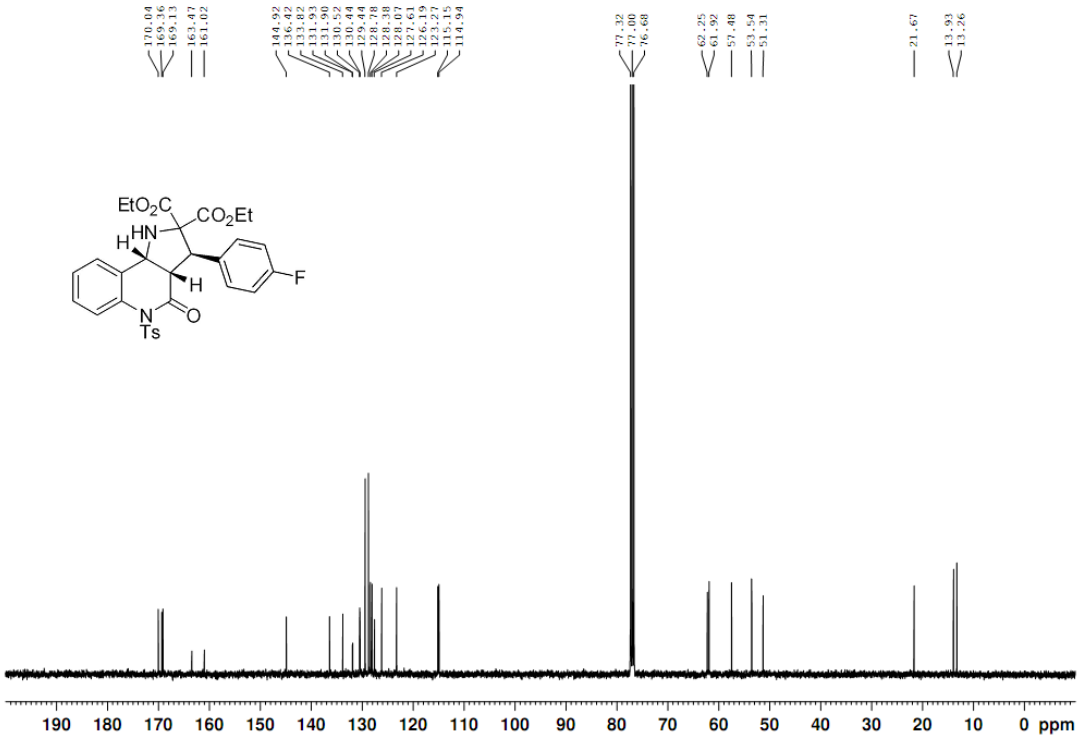
^{13}C NMR spectrum of compound **4e** ($CDCl_3$, 100 MHz)



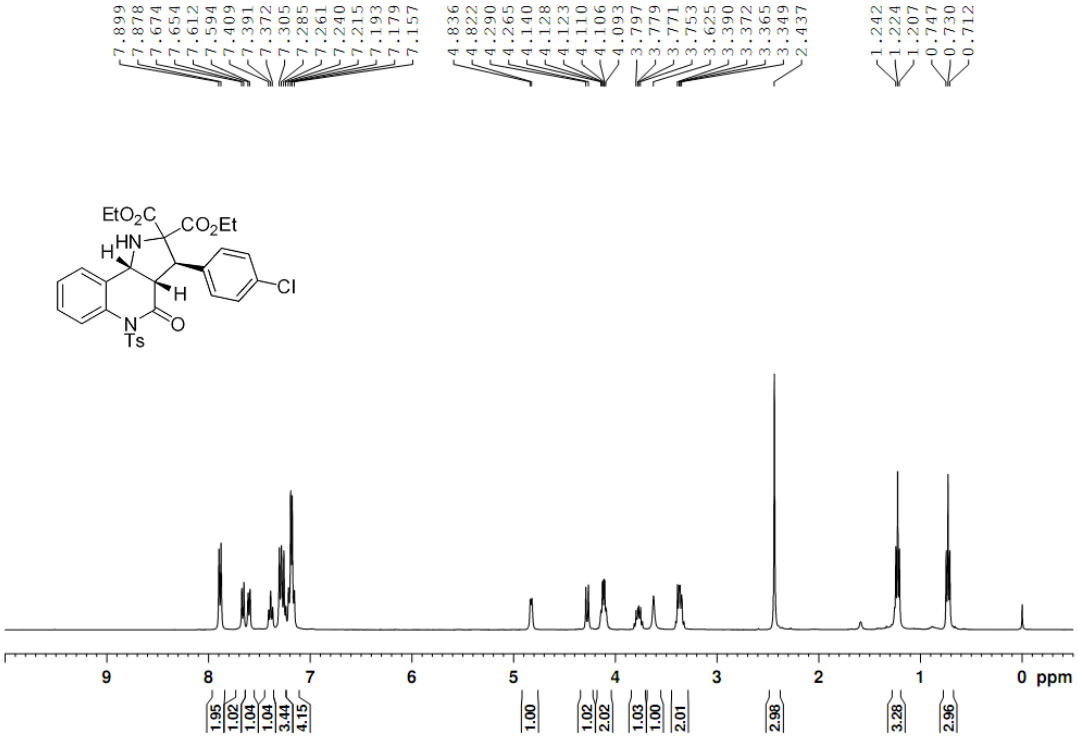
^{1}H NMR spectrum of compound **4f** ($CDCl_3$, 400 MHz)



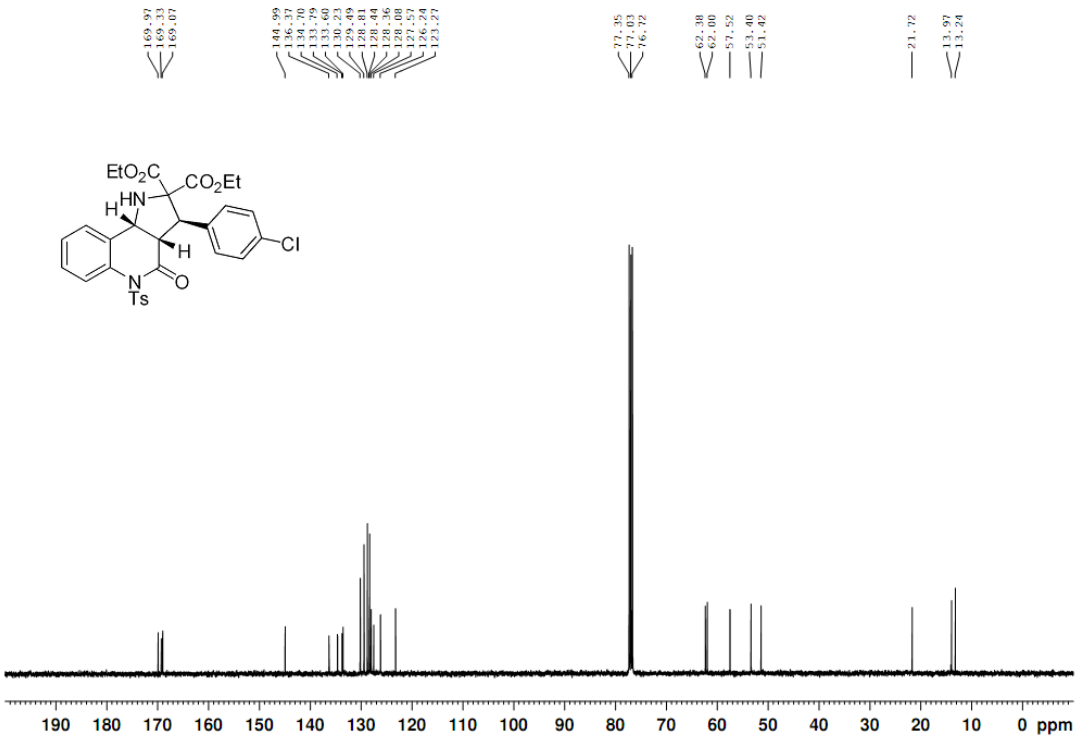
^{13}C NMR spectrum of compound **4f** ($CDCl_3$, 100 MHz)



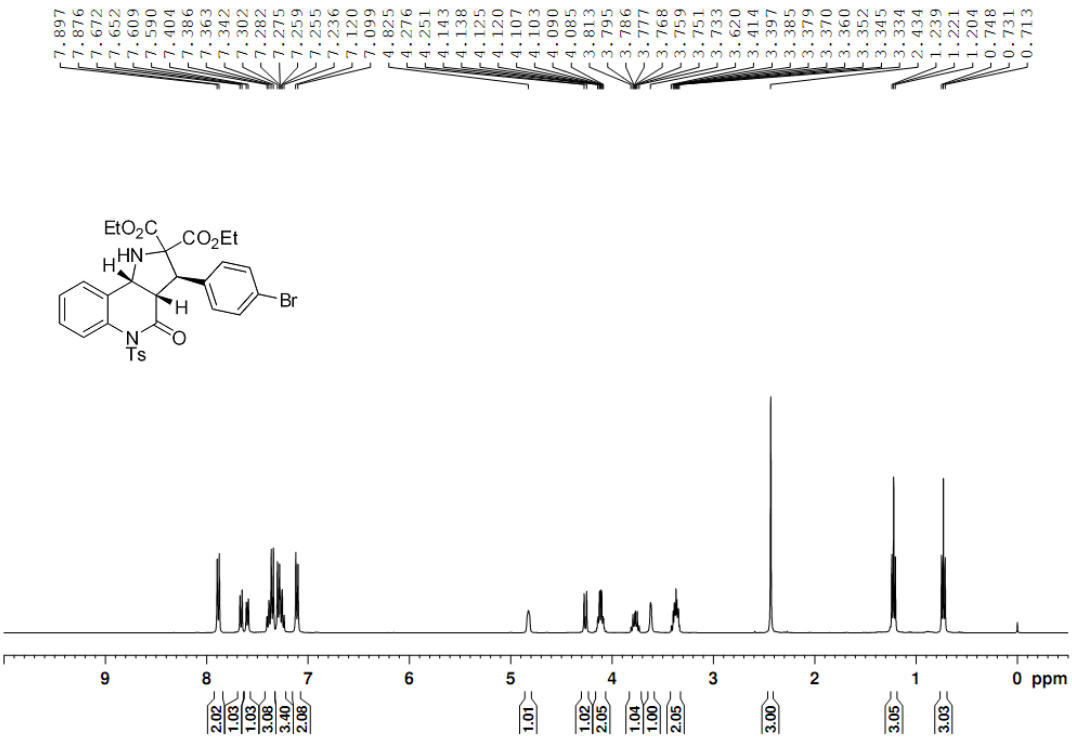
^{1}H NMR spectrum of compound **4g** ($CDCl_3$, 400 MHz)



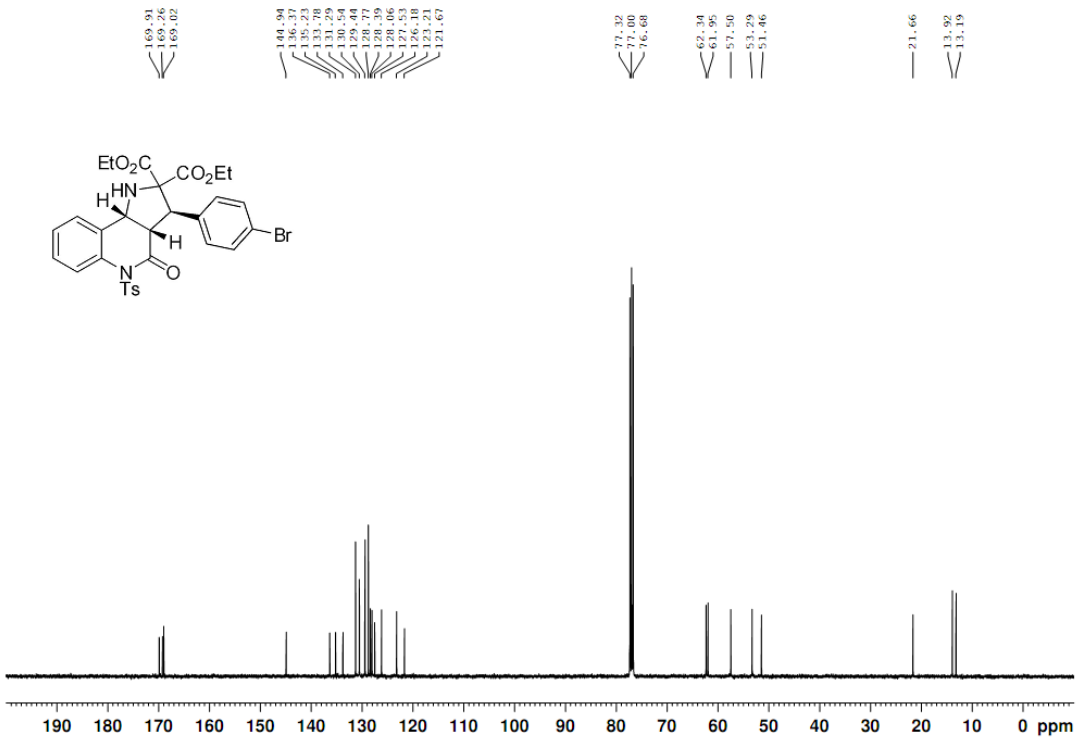
^{13}C NMR spectrum of compound **4g** ($CDCl_3$, 100 MHz)



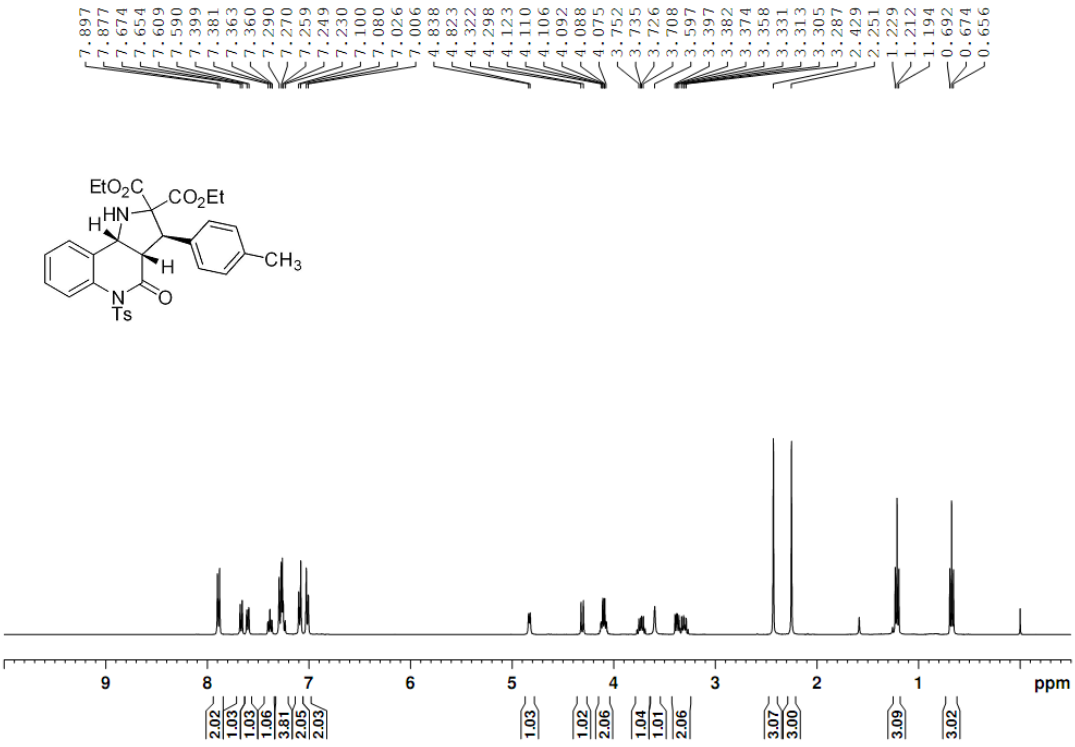
^{1}H NMR spectrum of compound **4h** ($CDCl_3$, 400 MHz)



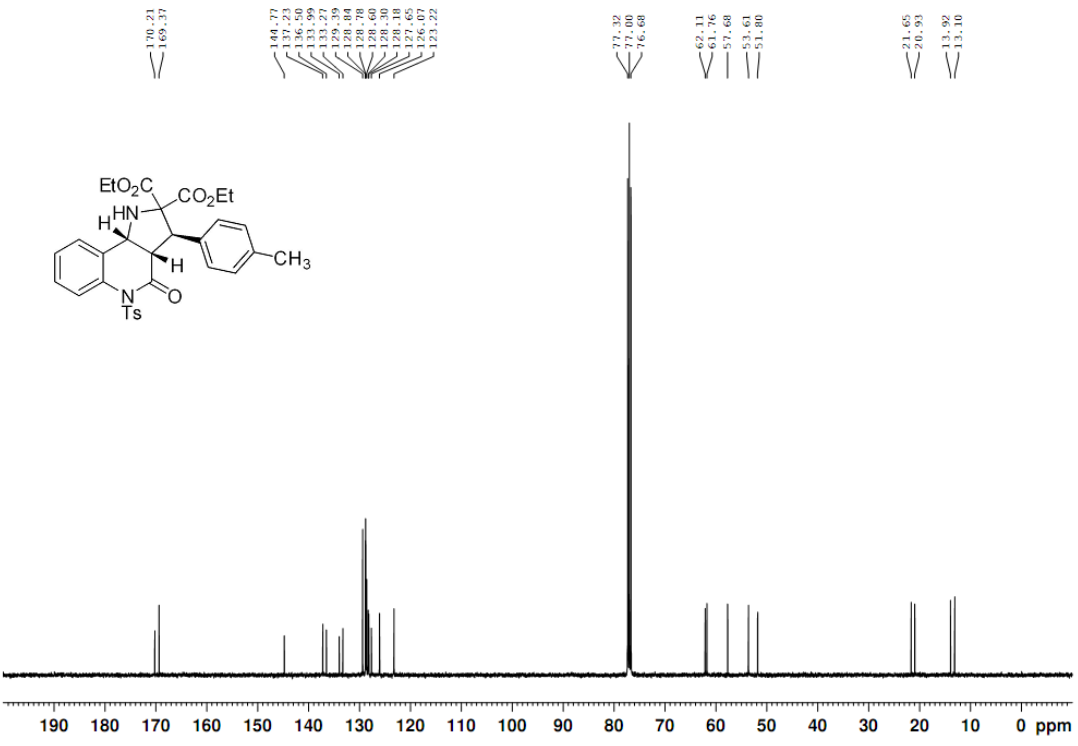
^{13}C NMR spectrum of compound **4h** ($CDCl_3$, 100 MHz)



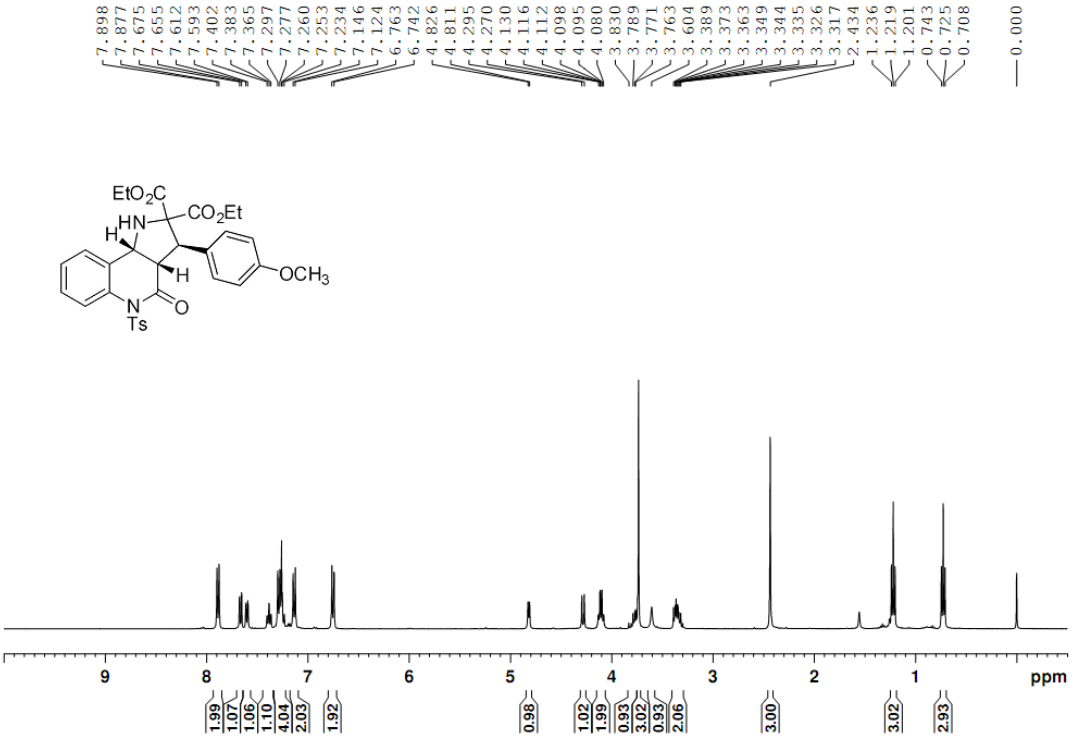
^{1}H NMR spectrum of compound **4i** ($CDCl_3$, 400 MHz)



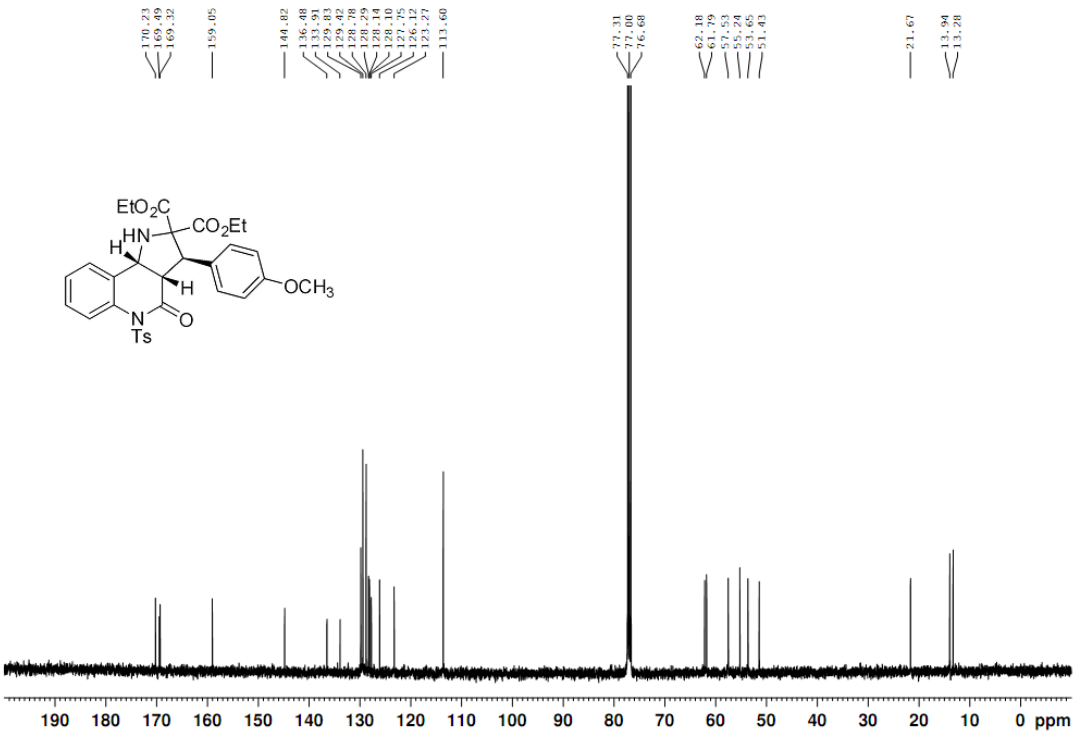
^{13}C NMR spectrum of compound **4i** ($CDCl_3$, 100 MHz)



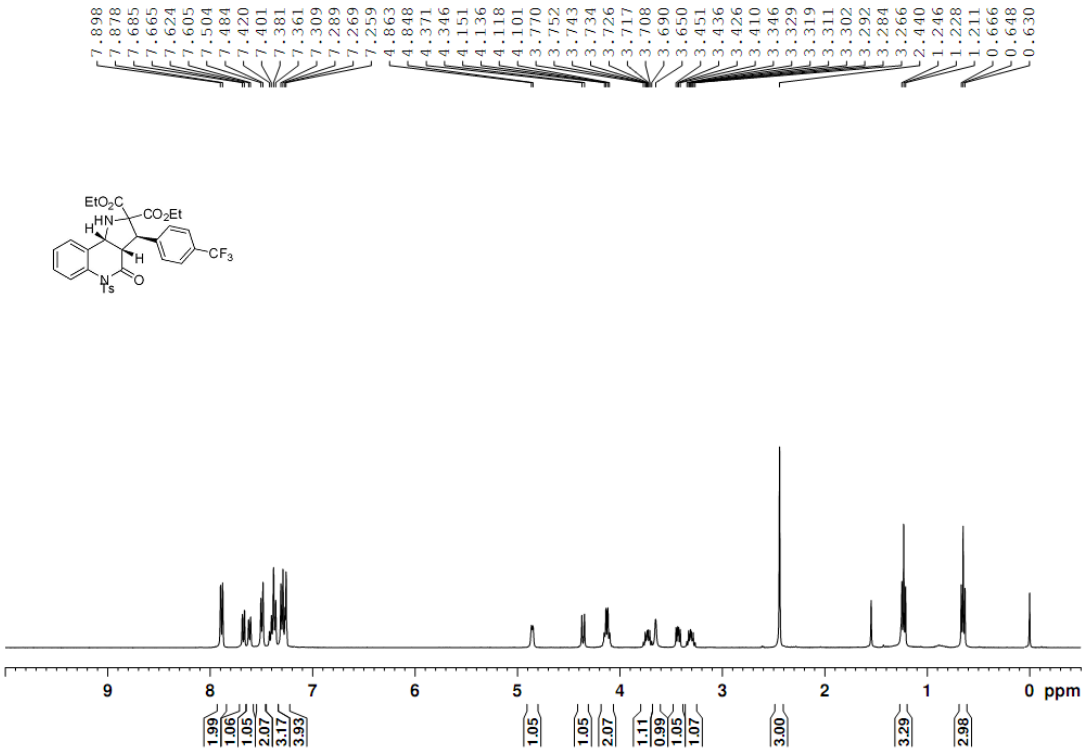
^{1}H NMR spectrum of compound **4j** ($CDCl_3$, 400 MHz)



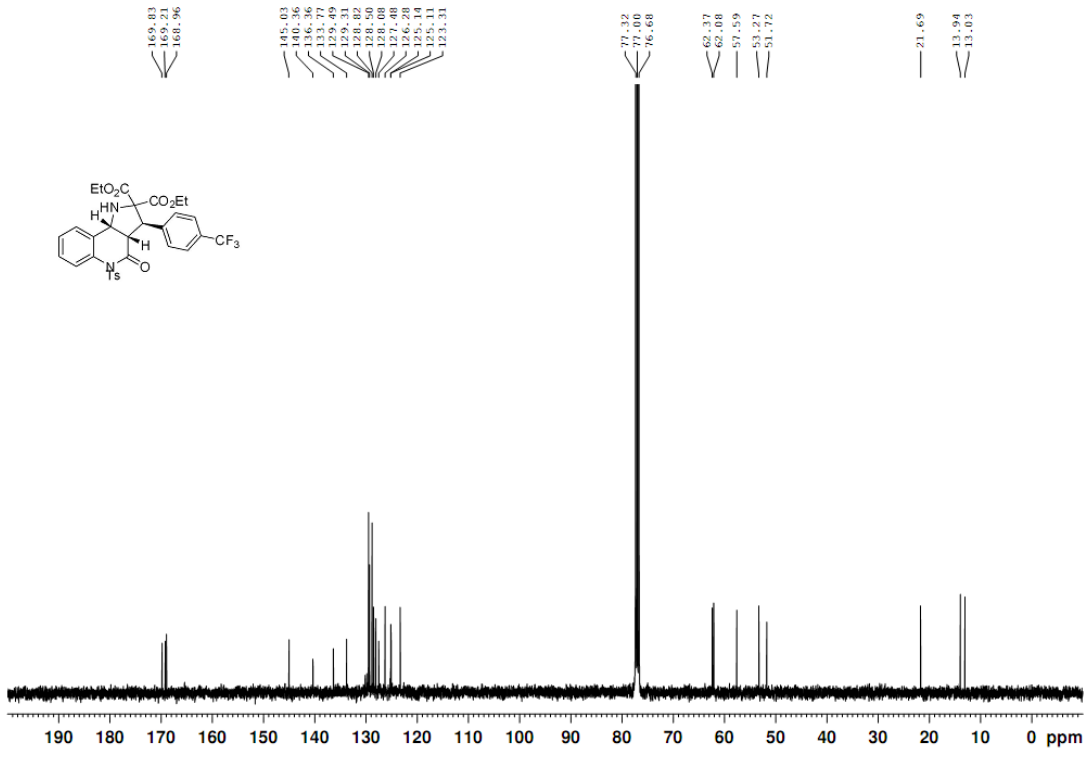
^{13}C NMR spectrum of compound **4j** ($CDCl_3$, 100 MHz)



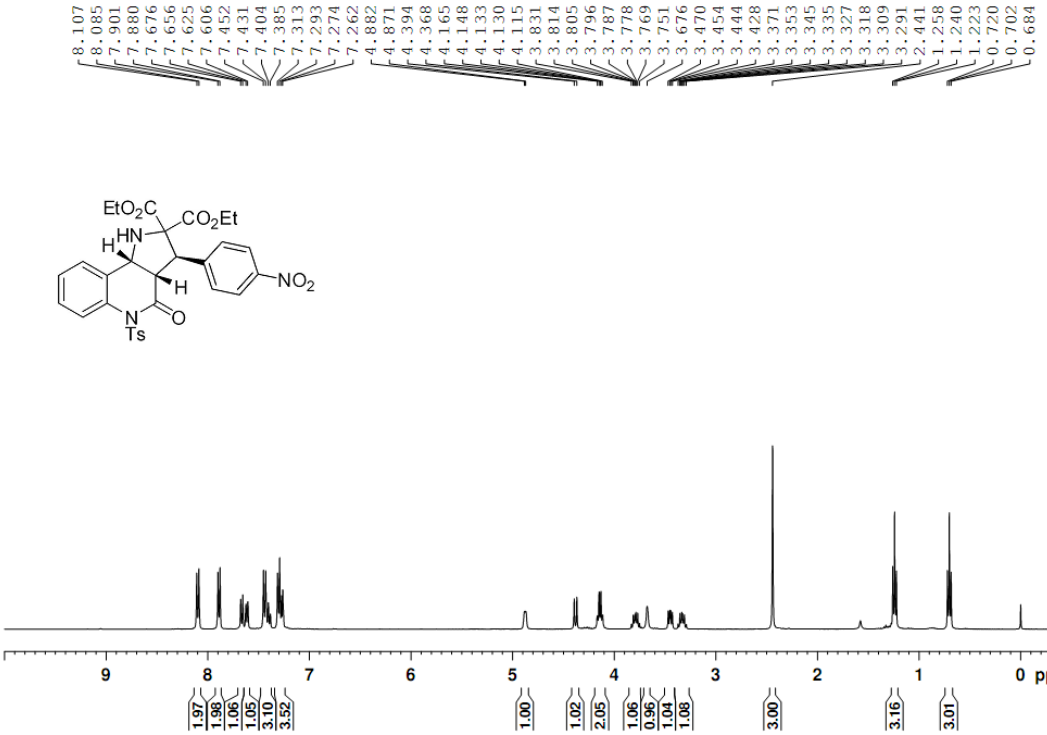
^{1}H NMR spectrum of compound **4k** ($CDCl_3$, 400 MHz)



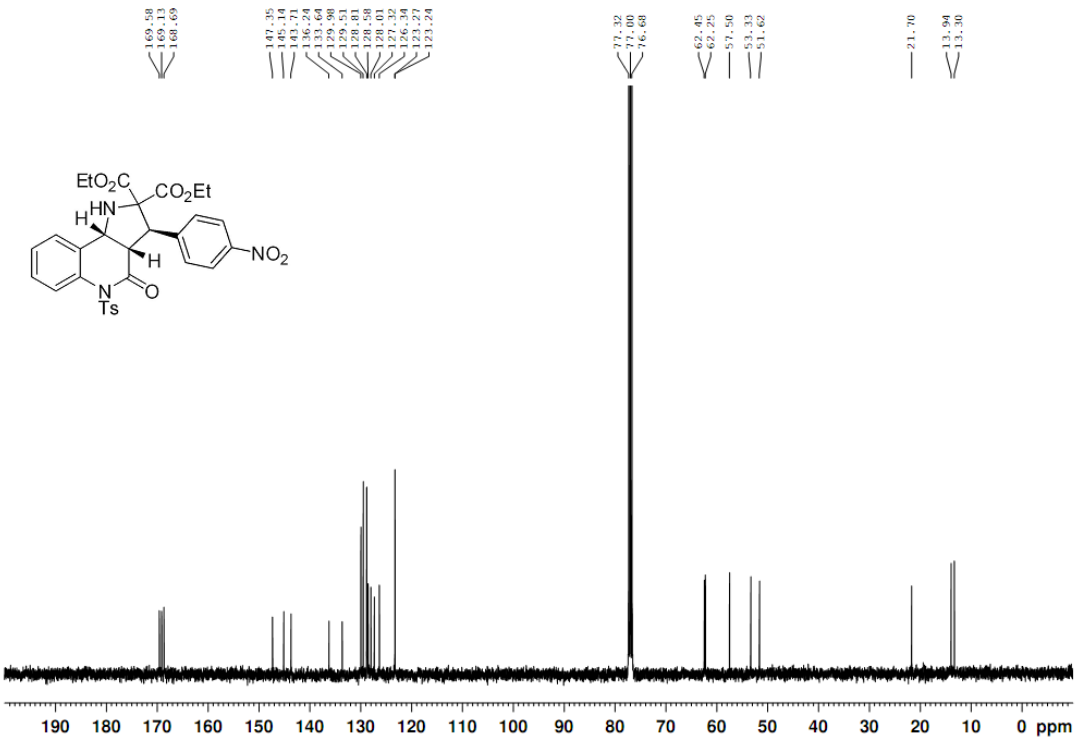
^{13}C NMR spectrum of compound **4k** ($CDCl_3$, 100 MHz)



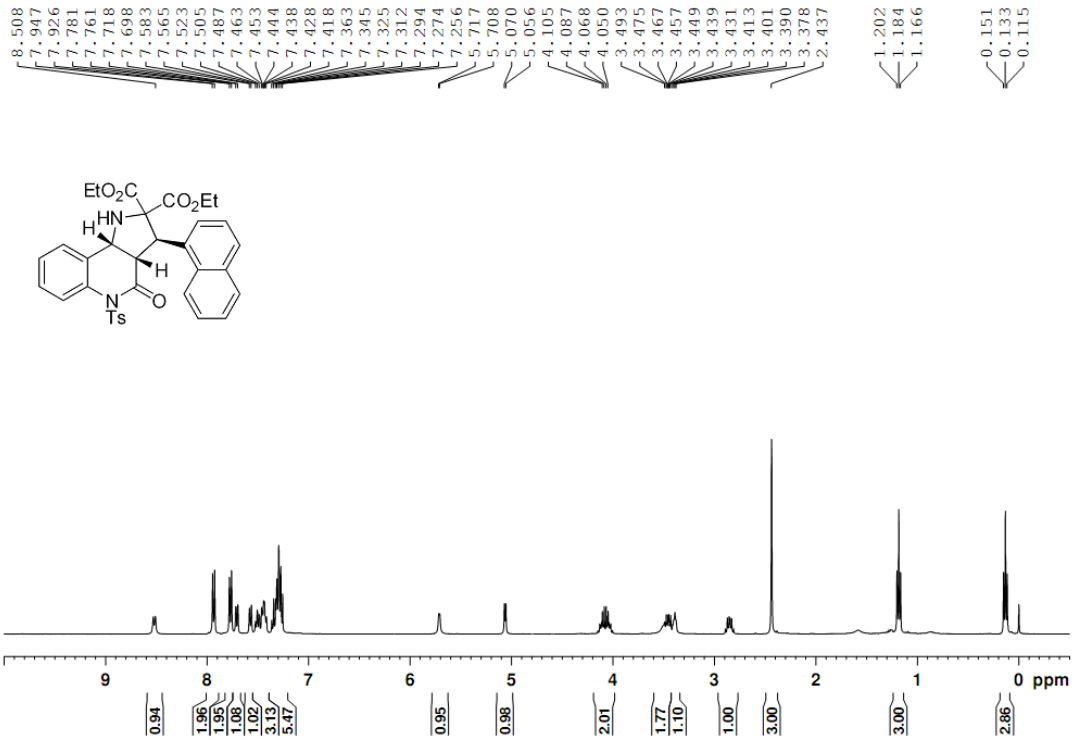
^{1}H NMR spectrum of compound **4l** ($CDCl_3$, 400 MHz)



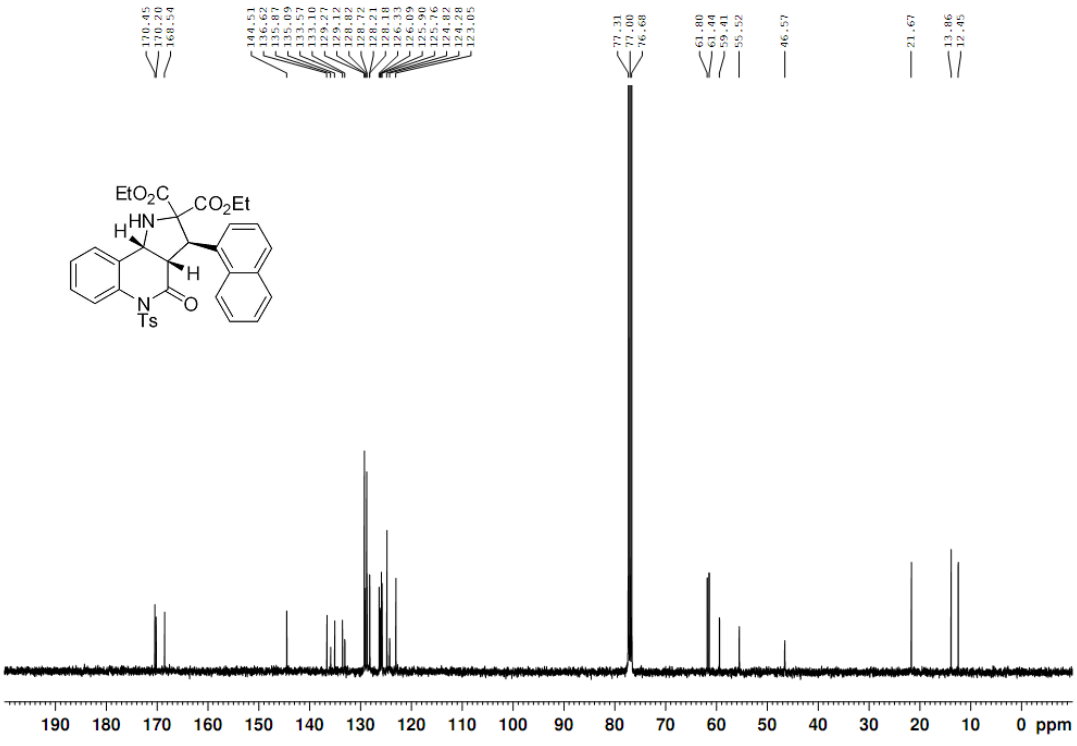
^{13}C NMR spectrum of compound **4l** ($CDCl_3$, 100 MHz)



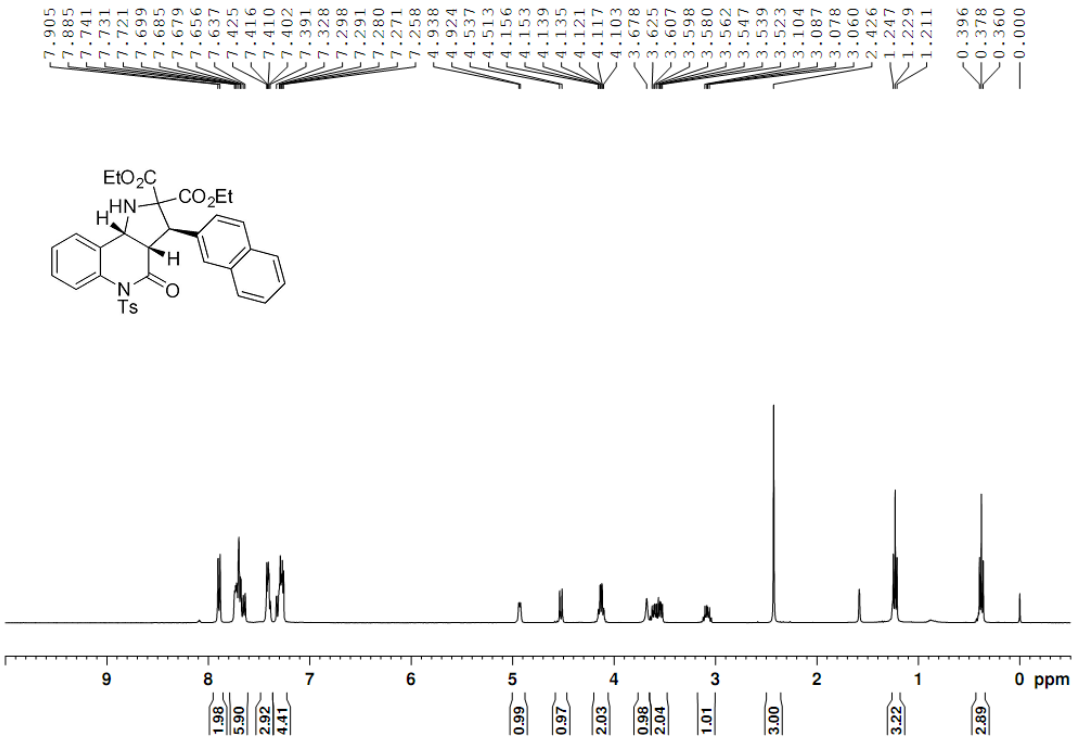
^{1}H NMR spectrum of compound **4m** ($CDCl_3$, 400 MHz)



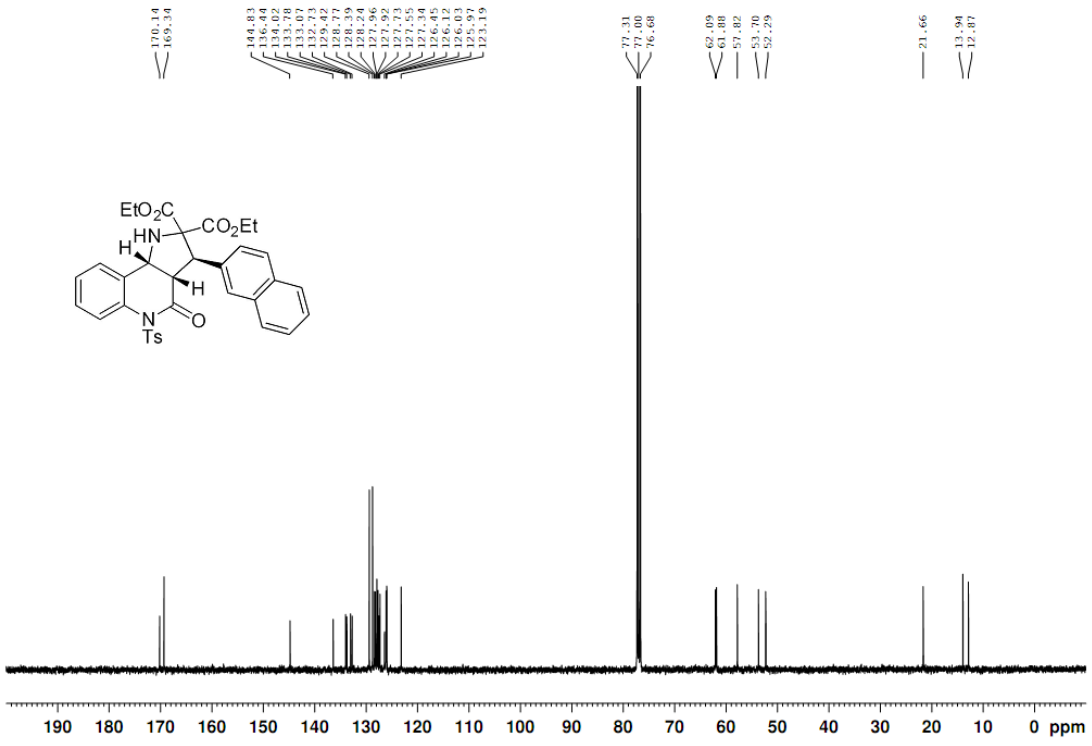
^{13}C NMR spectrum of compound **4m** ($CDCl_3$, 100 MHz)



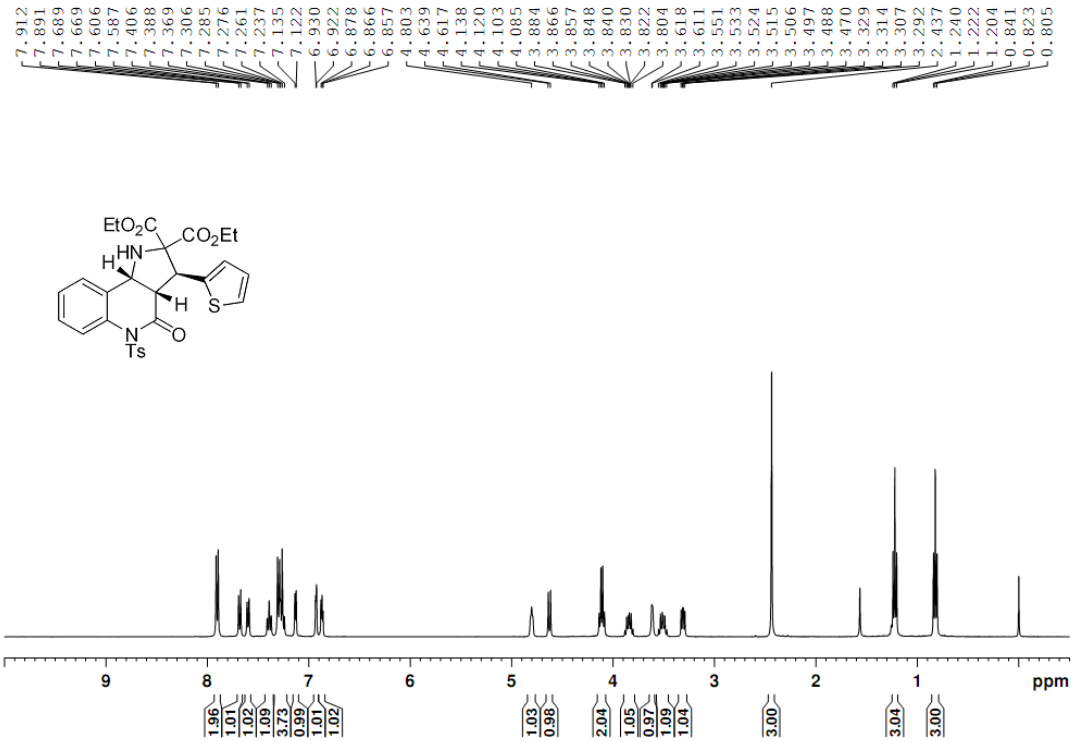
^{1}H NMR spectrum of compound **4n** ($CDCl_3$, 400 MHz)



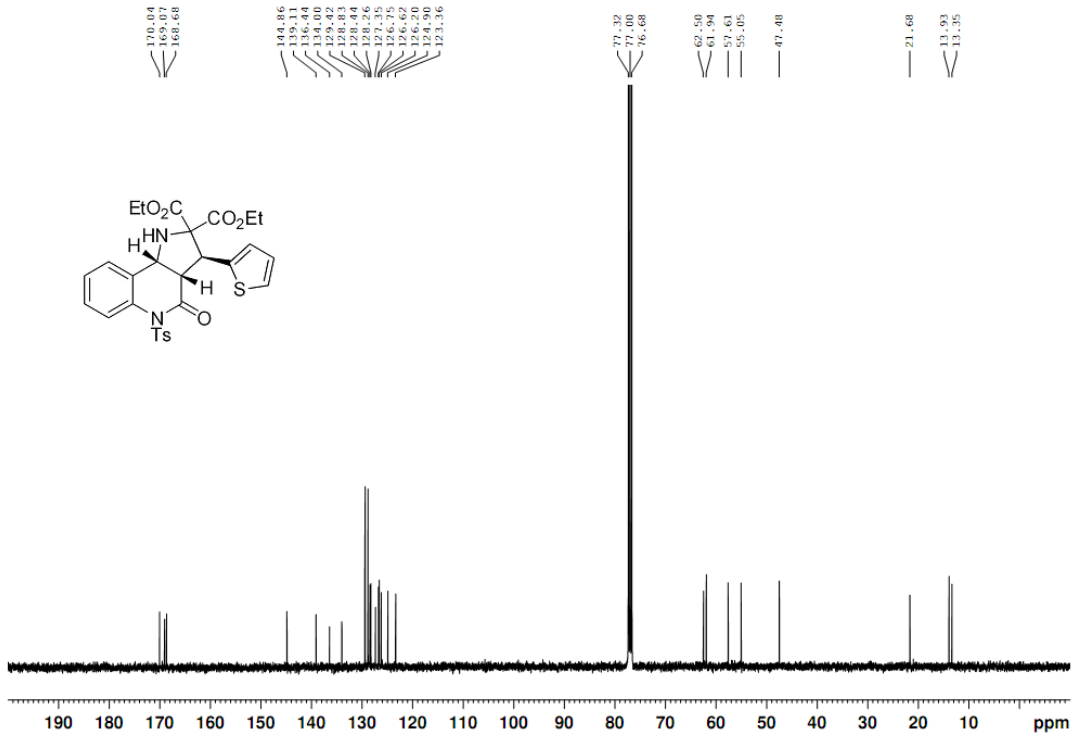
^{13}C NMR spectrum of compound **4n** ($CDCl_3$, 100 MHz)



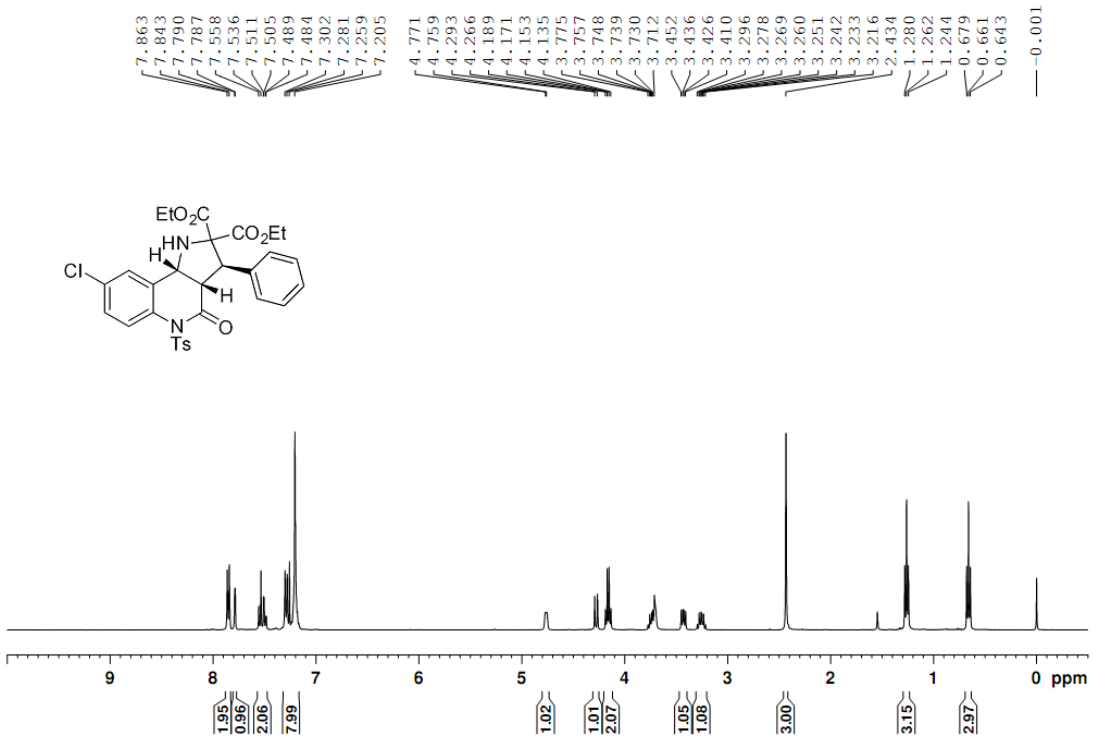
^{1}H NMR spectrum of compound **4o** ($CDCl_3$, 400 MHz)



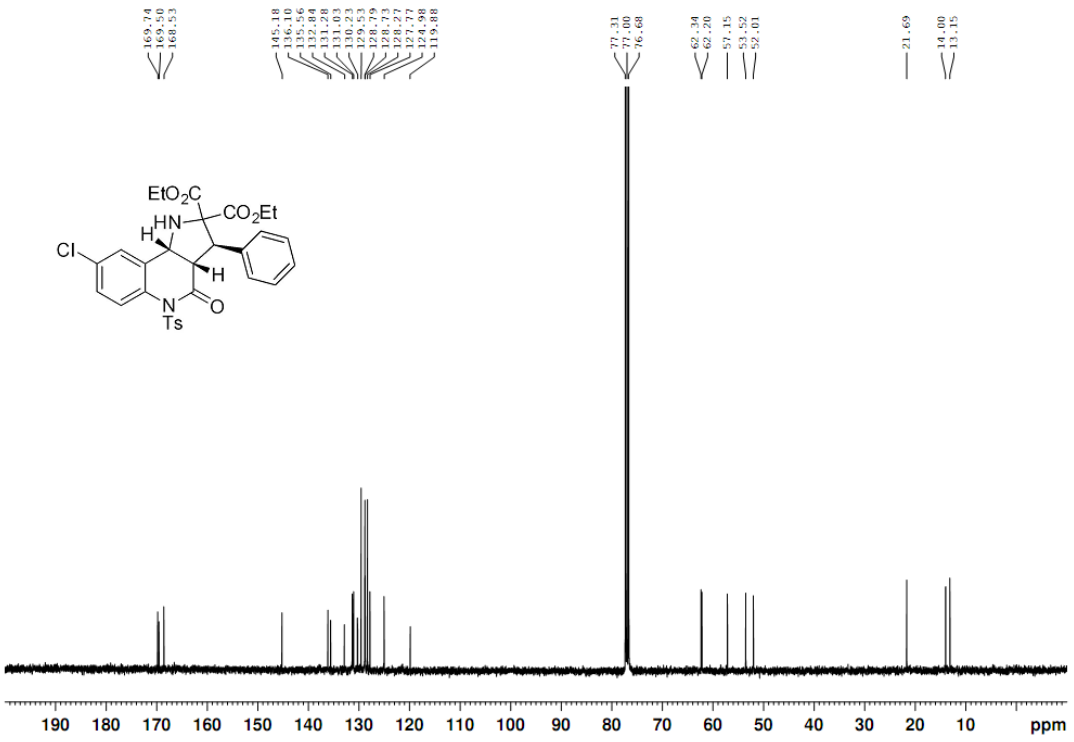
^{13}C NMR spectrum of compound **4o** ($CDCl_3$, 100 MHz)



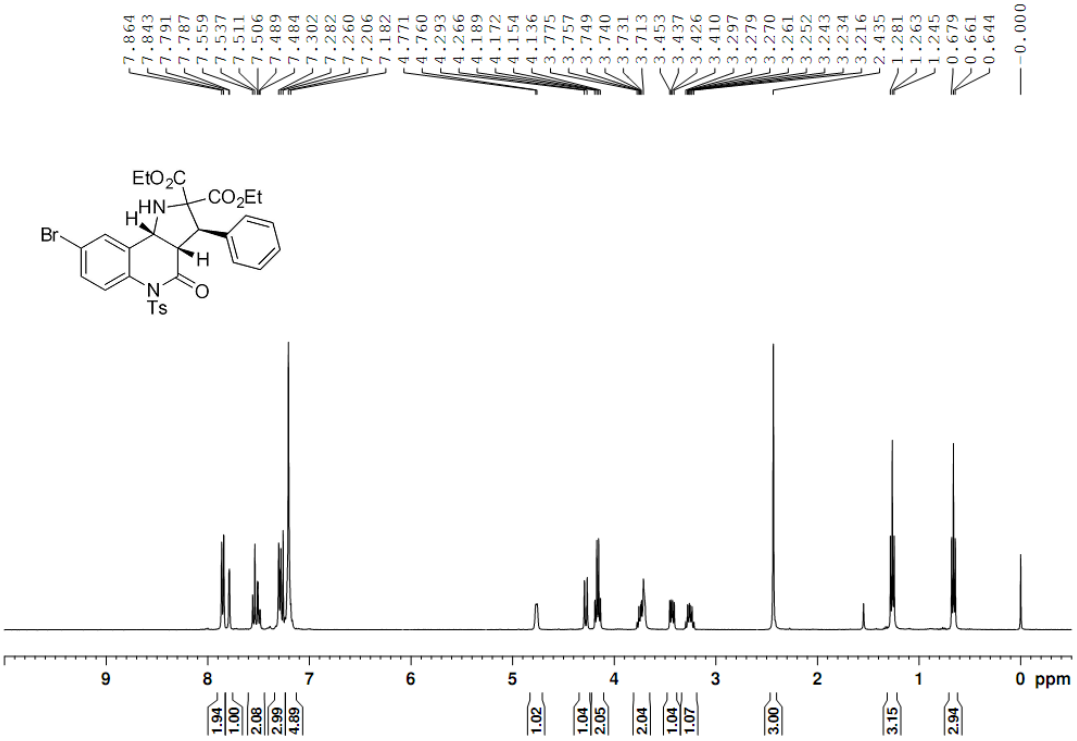
^{1}H NMR spectrum of compound **4q** ($CDCl_3$, 400 MHz)



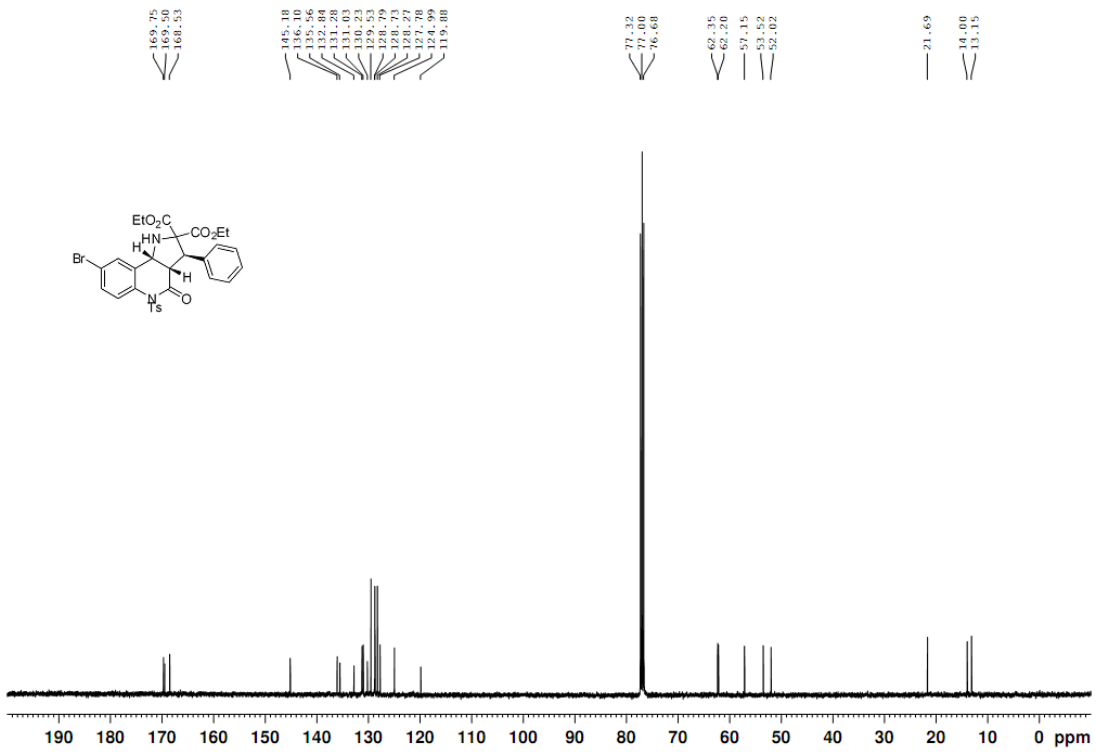
^{13}C NMR spectrum of compound **4q** ($CDCl_3$, 100 MHz)



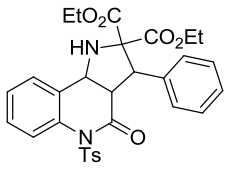
^{1}H NMR spectrum of compound **4r** ($CDCl_3$, 400 MHz)



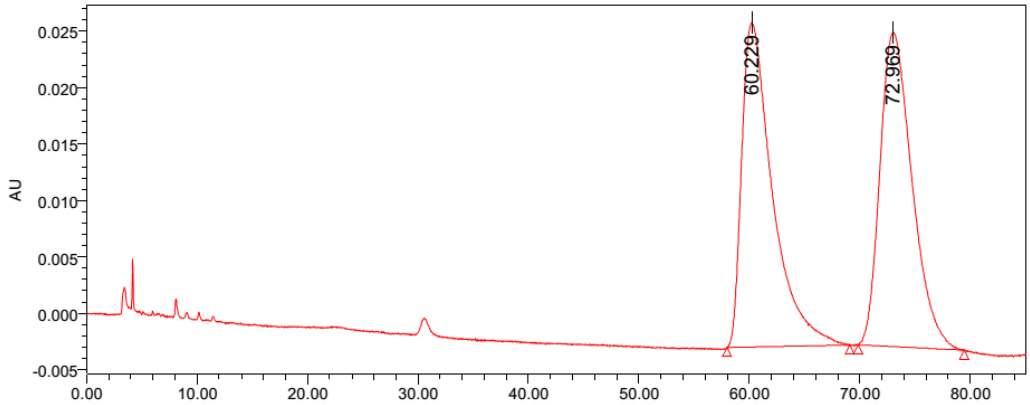
^{13}C NMR spectrum of compound **4r** ($CDCl_3$, 100 MHz)



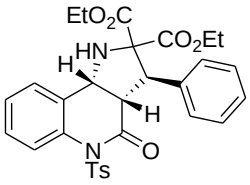
5. HPLC spectra of titled compounds 4a–4r



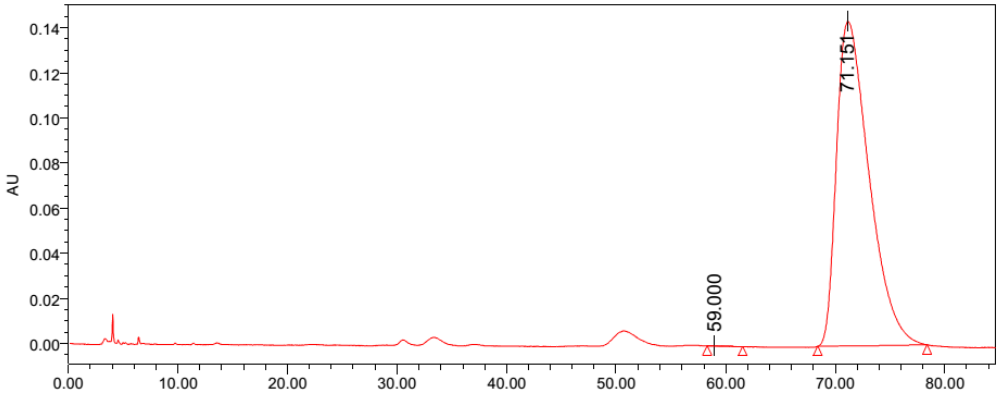
race-**4a**



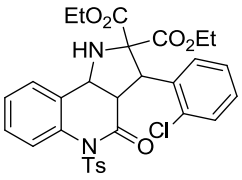
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 254.0 nm	60.229	5563096	28771	49.72
2	PDA 254.0 nm	72.969	5625489	27838	50.28



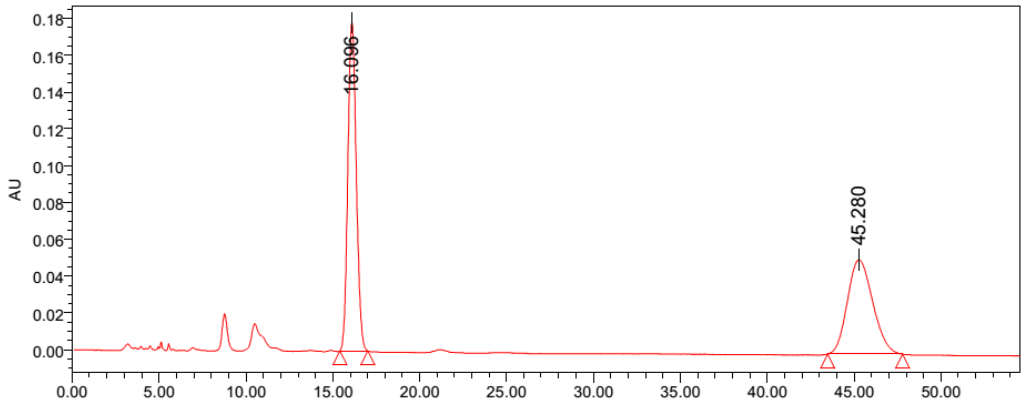
4a



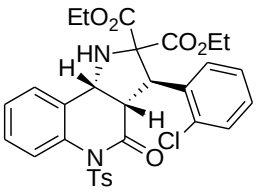
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 254.0 nm	59.000	6739	84	0.02
2	PDA 254.0 nm	71.151	29795161	143877	99.98



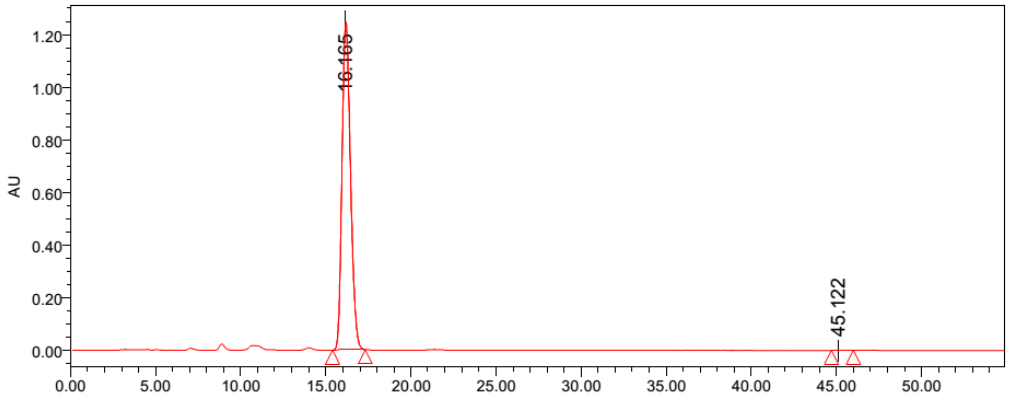
race-**4b**



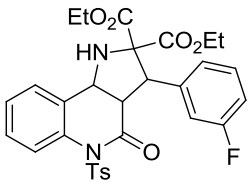
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 254.0 nm	16.096	5994064	178492	53.32
2	PDA 254.0 nm	45.280	5247134	51501	46.68



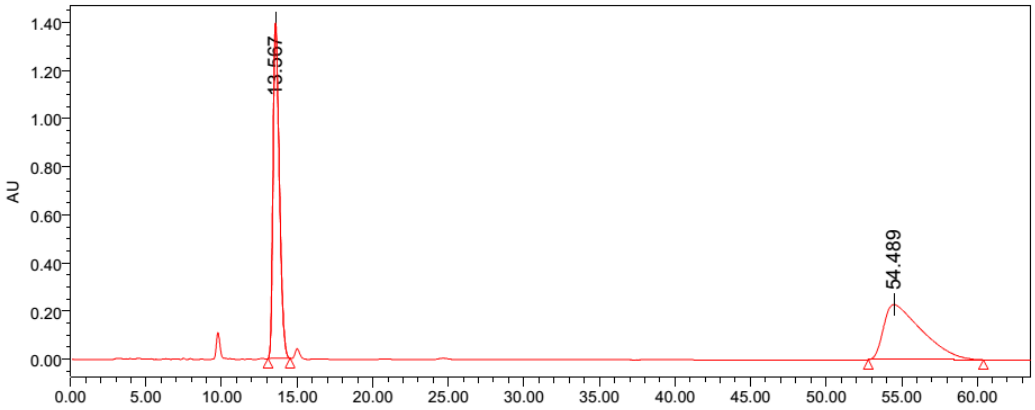
4b



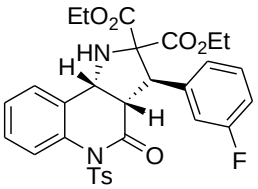
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 254.0 nm	16.165	43265221	1248815	99.99
2	PDA 254.0 nm	45.122	3304	-92	0.01



race-**4c**



Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 254.0 nm	13.567	40588771	1395063	50.32
2	PDA 254.0 nm	54.489	40068844	229003	49.68



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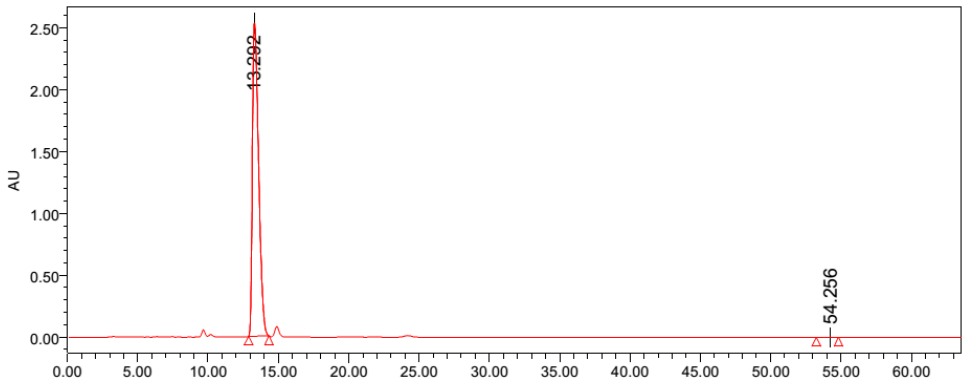
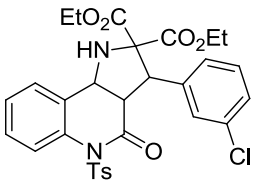
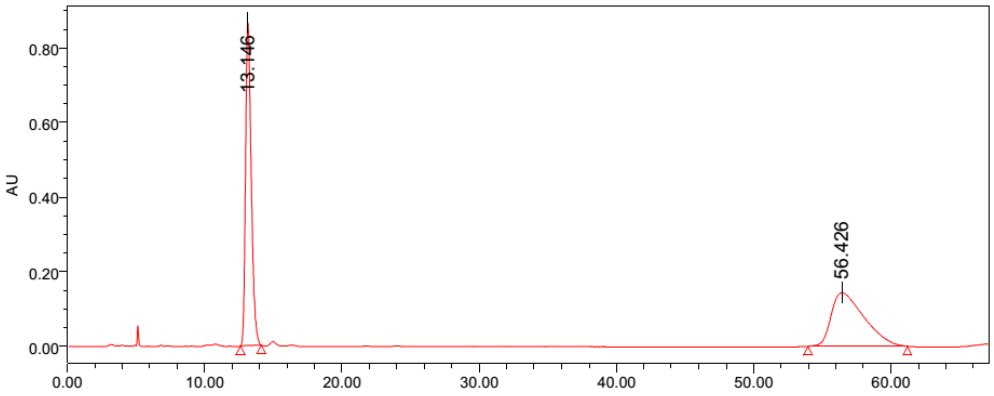


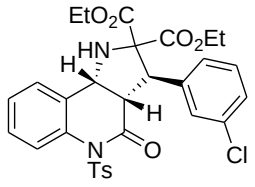
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 254.0 nm	13.292	78135750	2533418	99.99
2	PDA 254.0 nm	54.256	4584	-104	0.01



race-**4d**



Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 254.0 nm	13.146	24914576	866348	51.07
2	PDA 254.0 nm	56.426	23870010	143504	48.93



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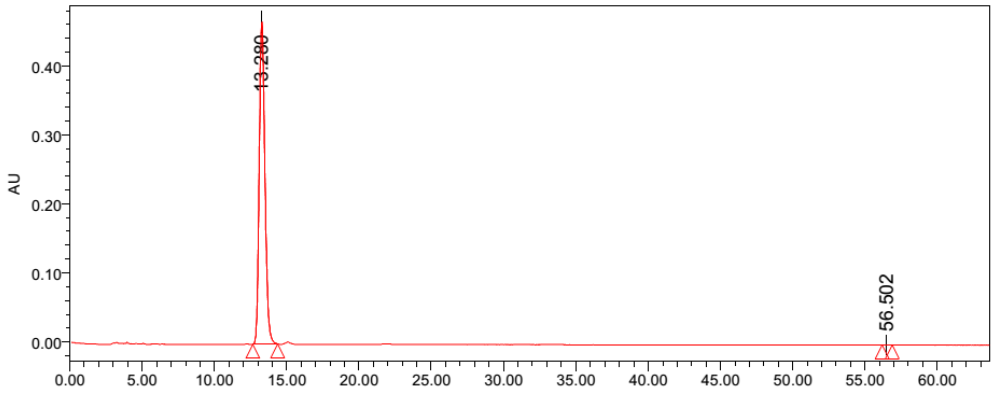
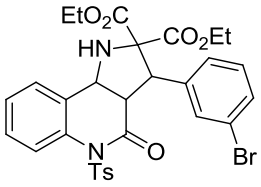
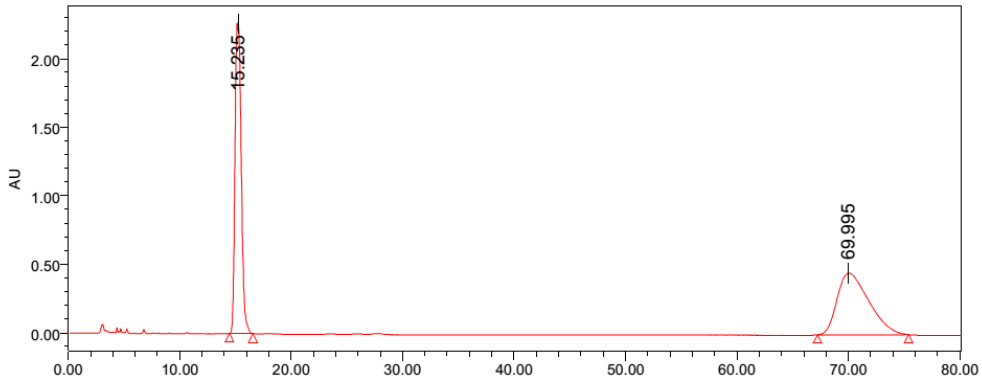


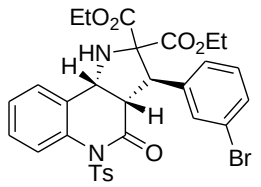
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 254.0 nm	13.280	12848333	466919	99.99
2	PDA 254.0 nm	56.502	1083	26	0.01



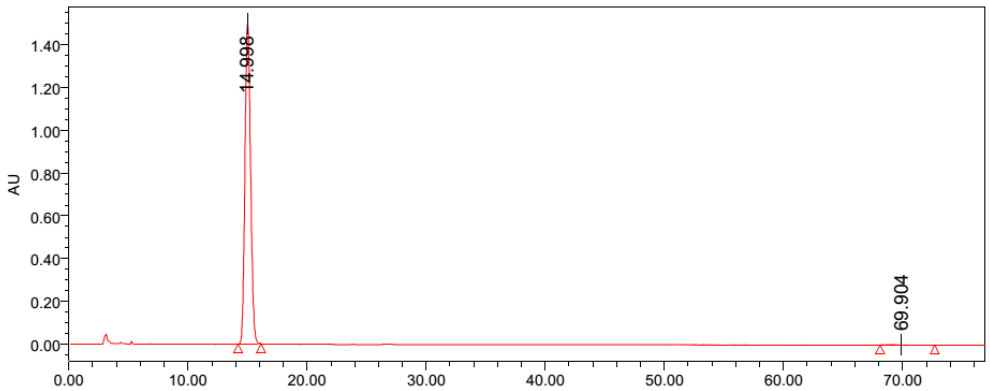
race-**4e**



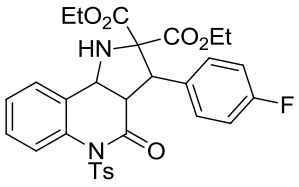
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 254.0 nm	15.235	87899866	2267256	49.74
2	PDA 254.0 nm	69.995	88813142	449343	50.26



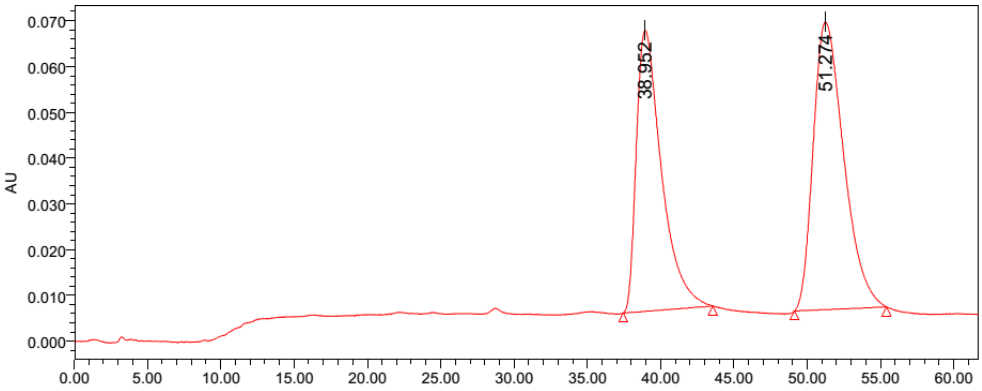
4e



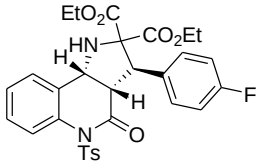
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 254.0 nm	14.998	48653263	1494032	99.92
2	PDA 254.0 nm	69.904	38260	307	0.08



race-**4f**



Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 254.0 nm	38.952	7333579	61449	44.61
2	PDA 254.0 nm	51.274	9107302	62841	55.39



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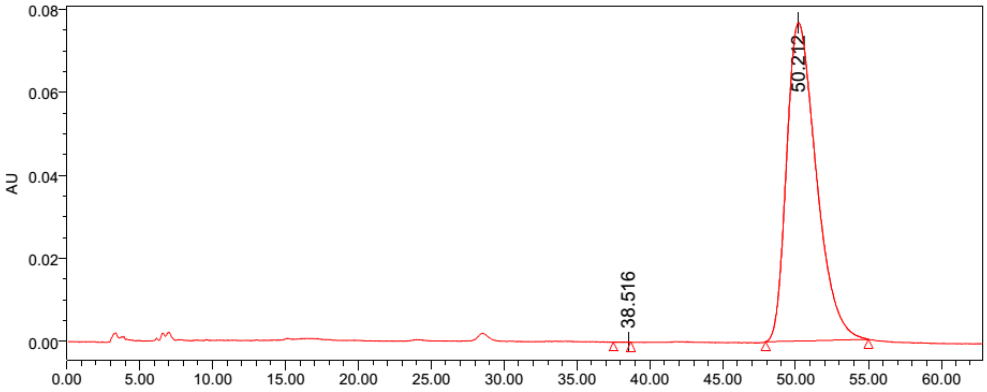
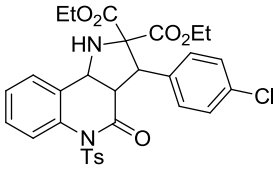
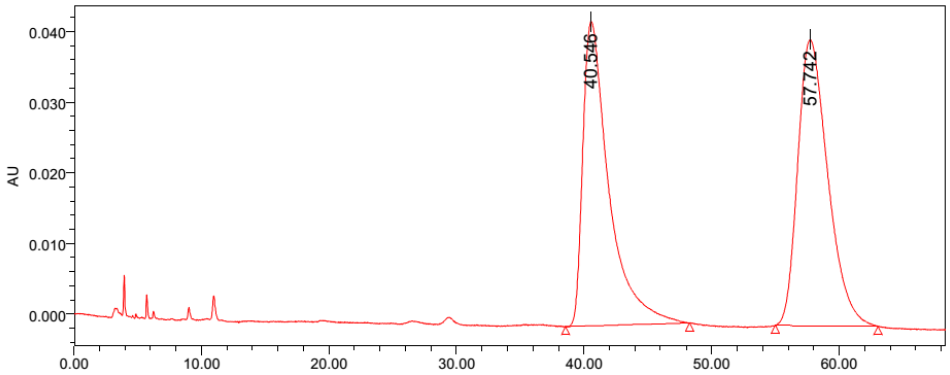


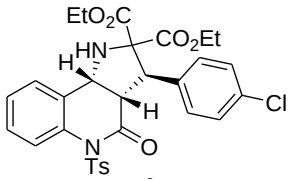
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 254.0 nm	38.516	1531	26	0.01
2	PDA 254.0 nm	50.212	10840348	76682	99.99



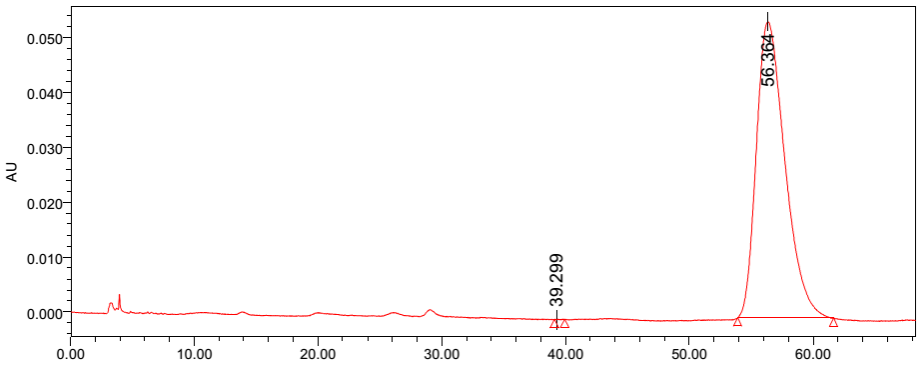
race-**4g**



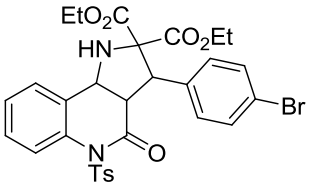
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 254.0 nm	40.546	6128815	43031	48.01
2	PDA 254.0 nm	57.742	6638130	40506	51.99



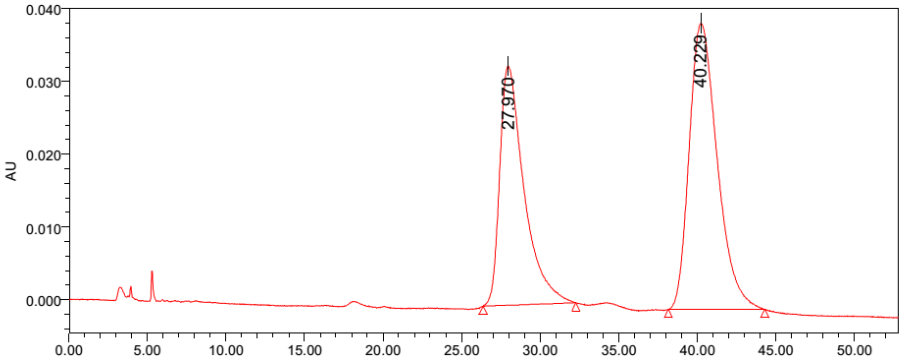
4g



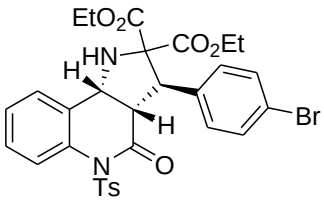
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 254.0 nm	39.299	1588	-77	0.02
2	PDA 254.0 nm	56.364	8675859	54000	99.98



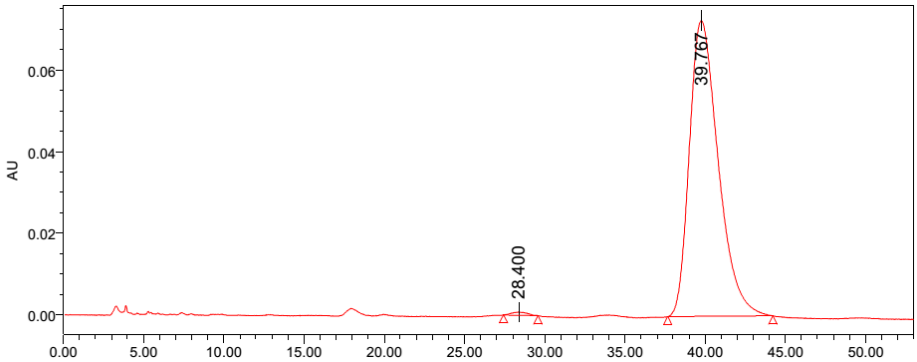
race-**4h**



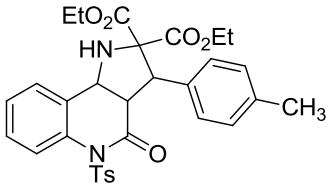
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 254.0 nm	27.970	3532608	32872	41.98
2	PDA 254.0 nm	40.229	4882143	39299	58.02



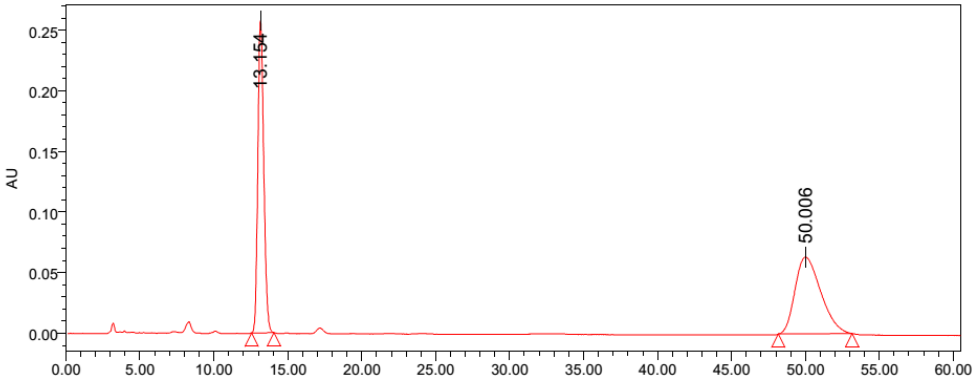
4h



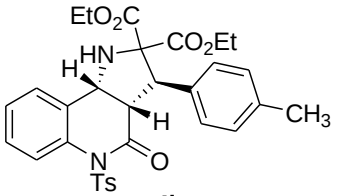
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 254.0 nm	28.400	52805	794	0.58
2	PDA 254.0 nm	39.767	9074184	72491	99.42



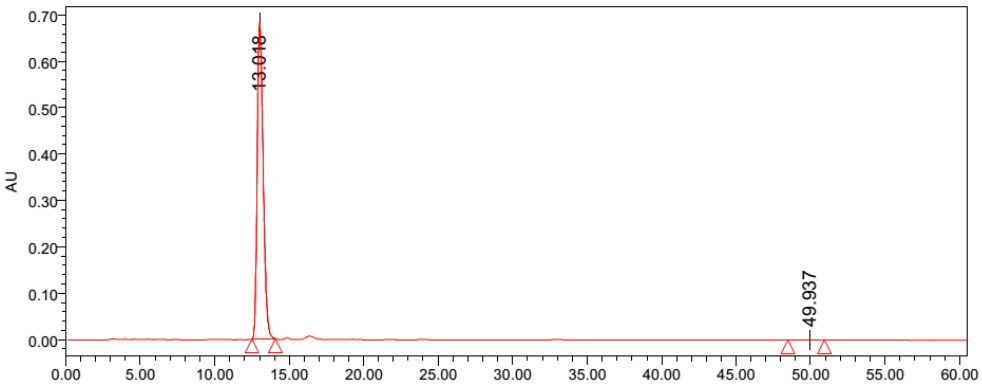
race-**4i**



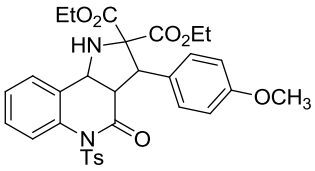
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 254.0 nm	13.154	7157208	257939	48.22
2	PDA 254.0 nm	50.006	7687032	63458	51.78



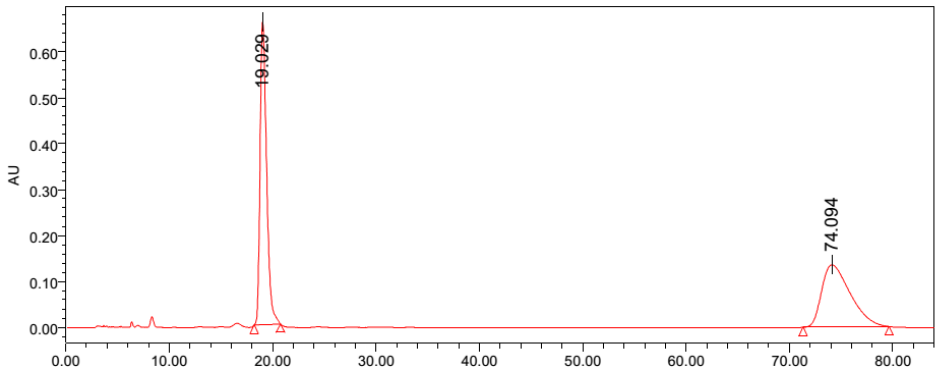
4i



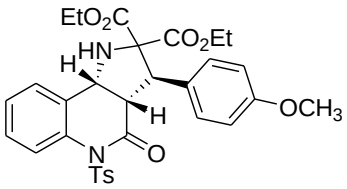
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 254.0 nm	13.018	18901176	682286	99.98
2	PDA 254.0 nm	49.937	3387	18	0.02



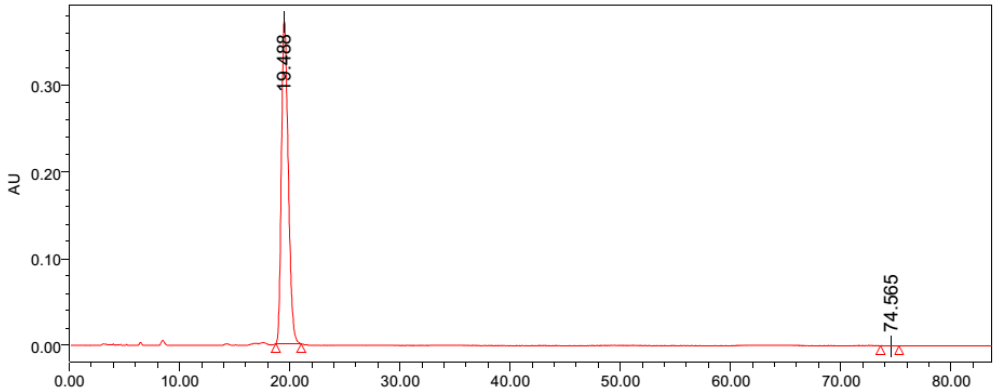
rac-**4j**



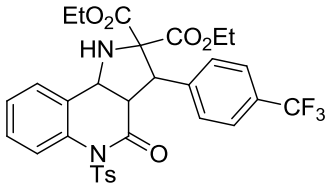
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 254.0 nm	19.029	28889358	658450	52.62
2	PDA 254.0 nm	74.094	26012995	135484	47.38



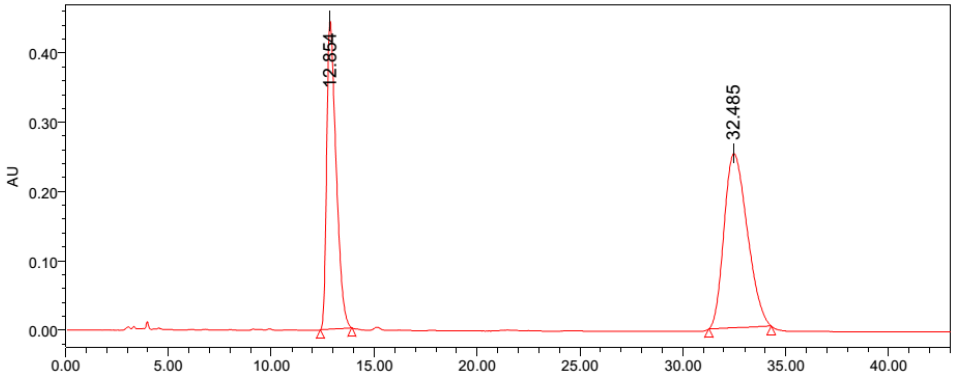
4j



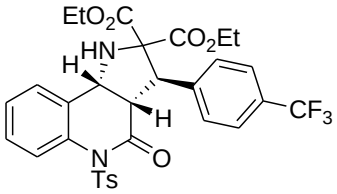
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 254.0 nm	19.488	16022491	371865	99.98
2	PDA 254.0 nm	74.565	2541	-36	0.02



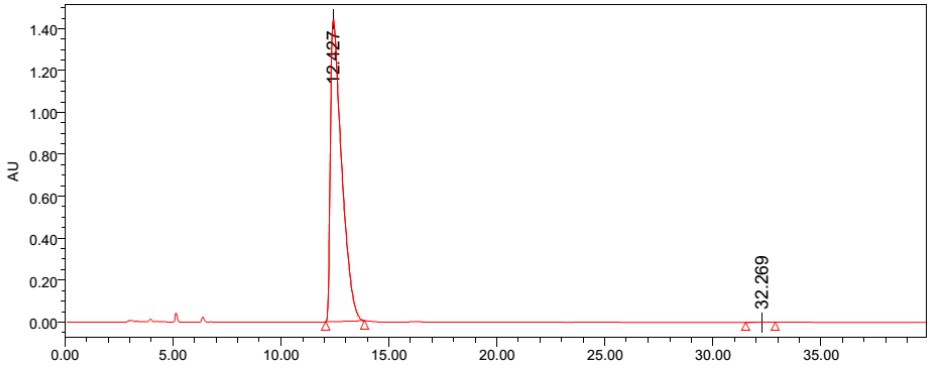
race-**4k**



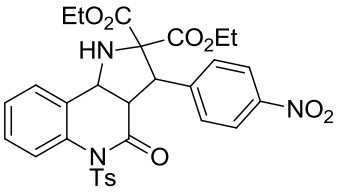
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 254.0 nm	12.854	14206813	445392	41.86
2	PDA 254.0 nm	32.485	19734067	251577	58.14



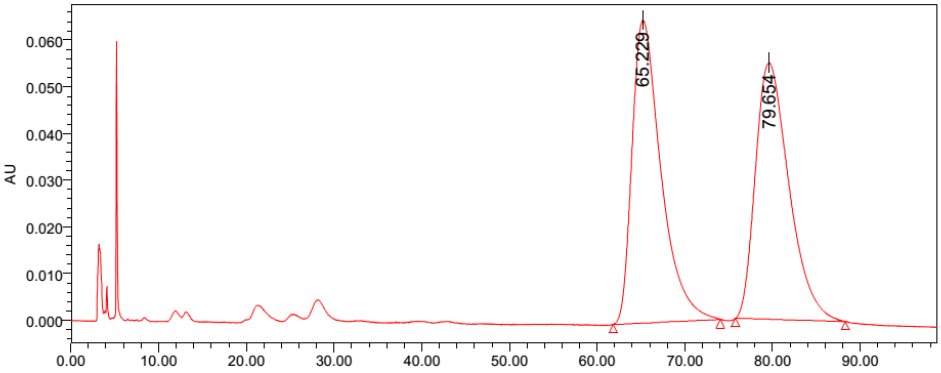
4k



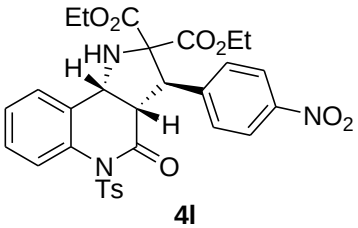
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 254.0 nm	12.427	52082297	1442106	99.98
2	PDA 254.0 nm	32.269	9555	-226	0.02



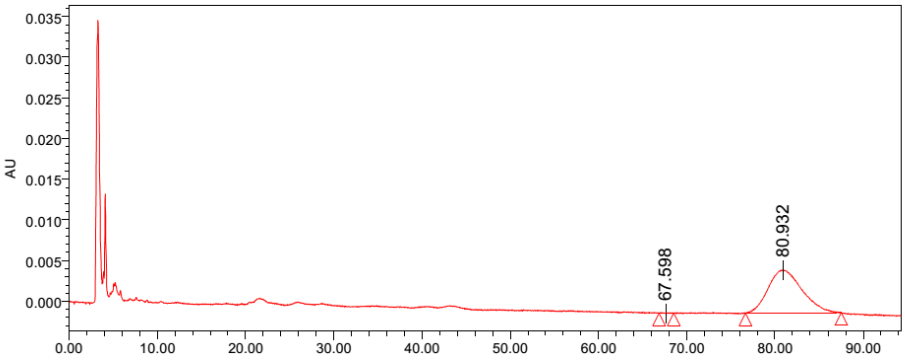
race-**4l**



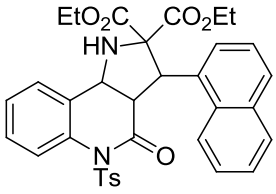
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 254.0 nm	65.229	14898834	64875	50.48
2	PDA 254.0 nm	79.654	14617710	54909	49.52



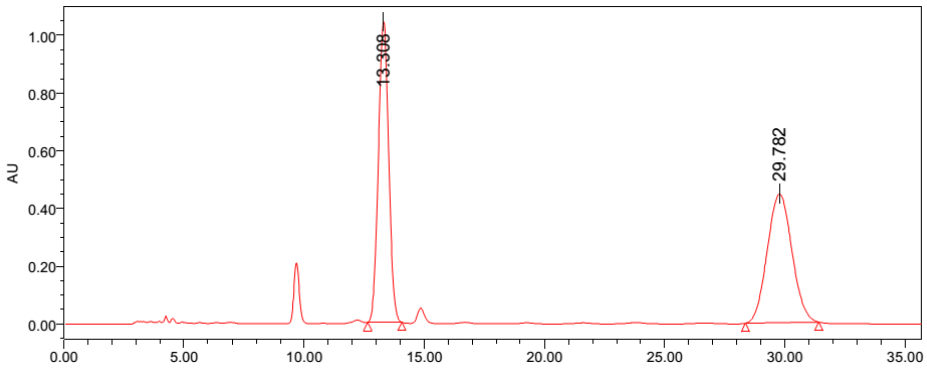
4l



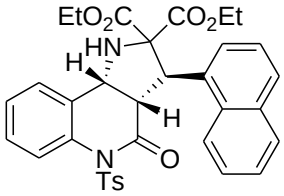
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 254.0 nm	67.598	2675	-26	0.19
2	PDA 254.0 nm	80.932	1401183	5280	99.81



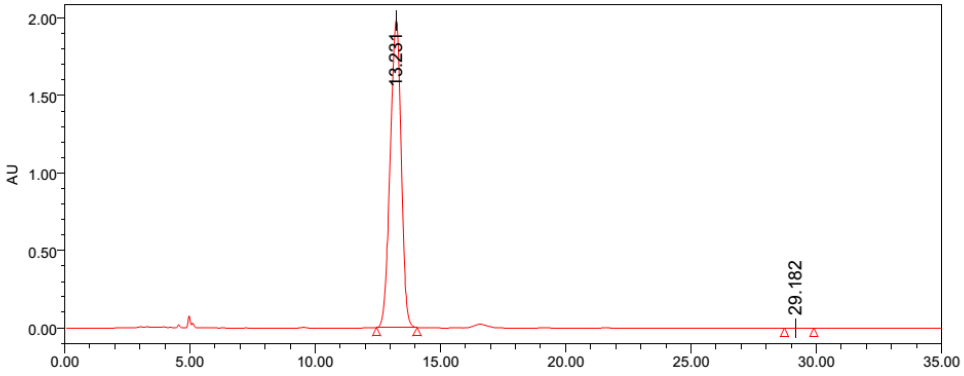
race-**4m**



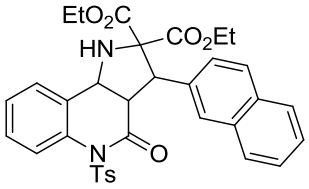
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 254.0 nm	13.308	31027171	1041954	49.34
2	PDA 254.0 nm	29.782	31852174	445886	50.66



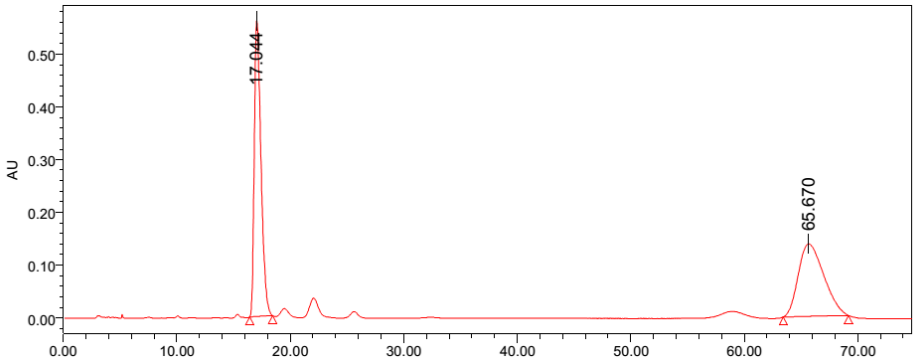
4m



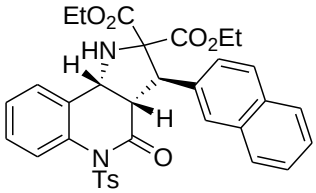
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 254.0 nm	13.231	60458744	1984348	99.99
2	PDA 254.0 nm	29.182	6117	-183	0.01



race-**4n**



Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 254.0 nm	17.044	23035411	560456	51.81
2	PDA 254.0 nm	65.670	21428949	137159	48.19



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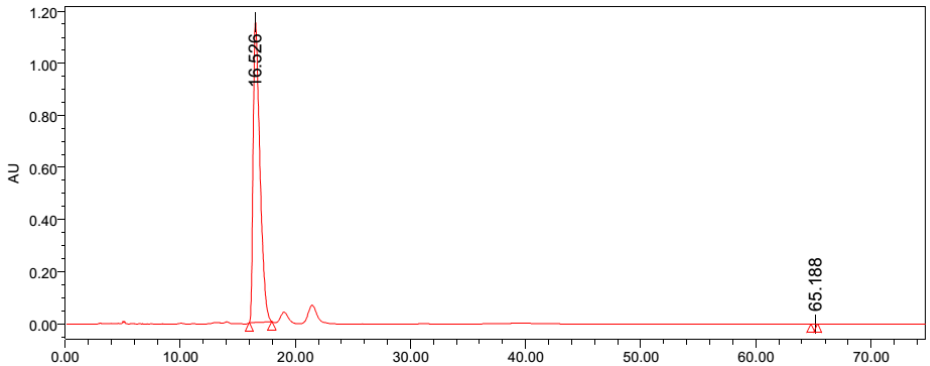
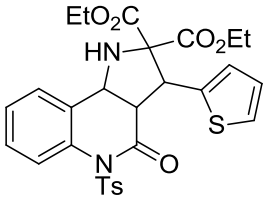
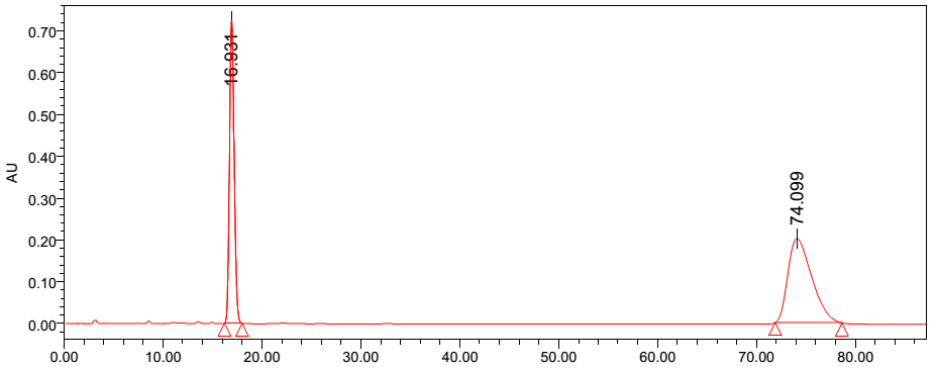


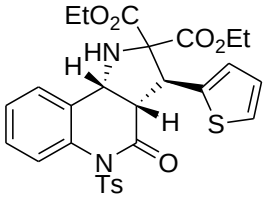
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 254.0 nm	16.526	47253216	1153851	100.00
2	PDA 254.0 nm	65.188	875	-42	0.00



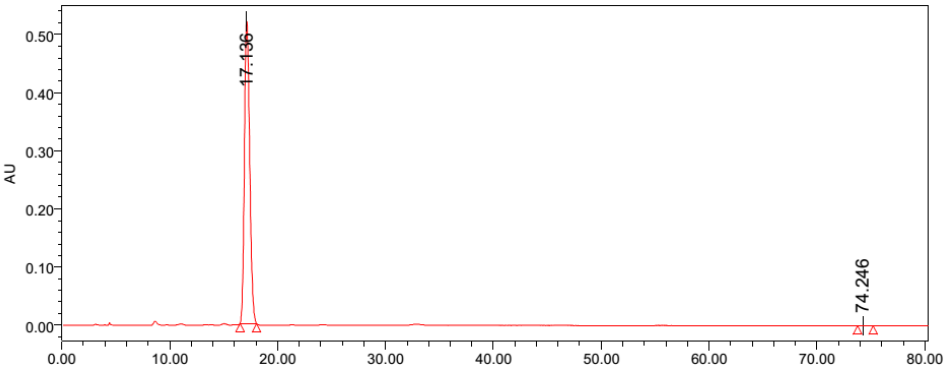
race-**4o**



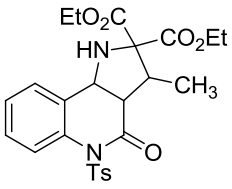
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 254.0 nm	16.931	24025349	723369	41.63
2	PDA 254.0 nm	74.099	33686806	201560	58.37



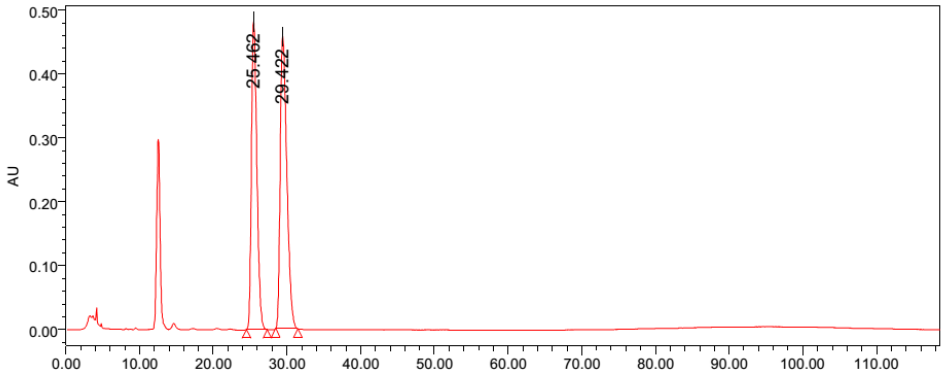
4o



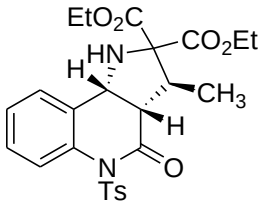
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 254.0 nm	17.136	17620331	520027	99.99
2	PDA 254.0 nm	74.246	1821	69	0.01



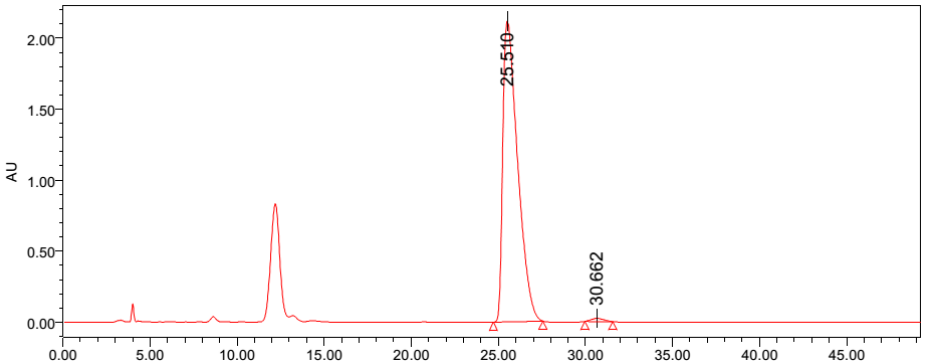
race-**4p**



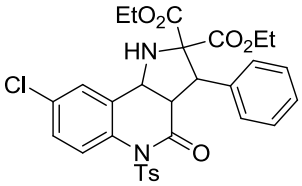
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 254.0 nm	25.462	24798219	482399	46.50
2	PDA 254.0 nm	29.422	28525967	457114	53.50



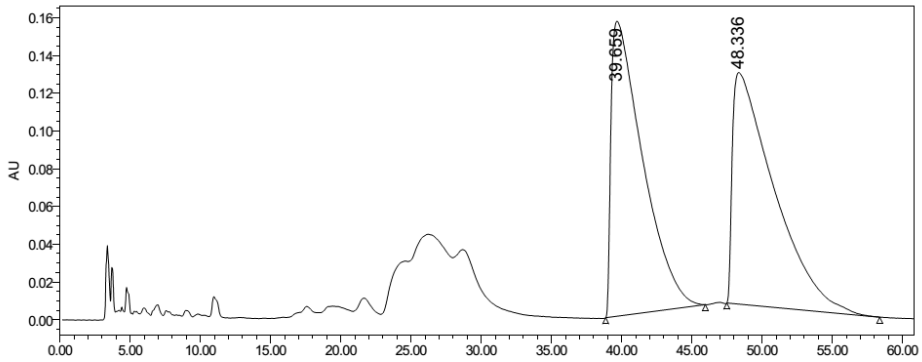
4p



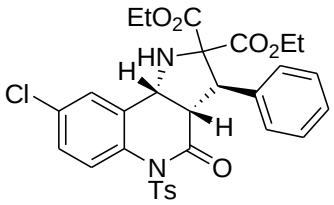
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	PDA 254.0 nm	25.510	125346353	2120504	99.10
2	PDA 254.0 nm	30.662	1133983	22087	0.90



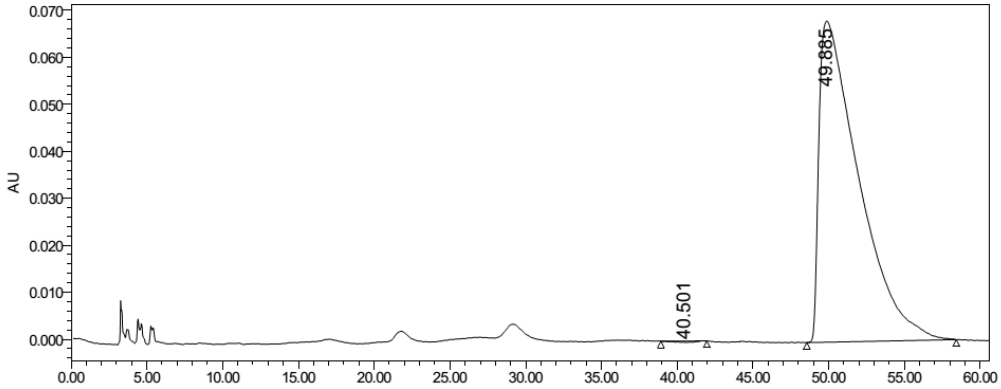
race-**4q**



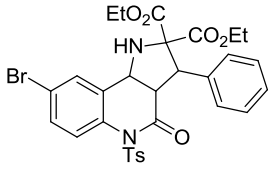
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	2998 (190- 400) nm	39.659	24430182	156211	49.14
2	2998 (190- 400) nm	48.336	25290282	122592	50.86



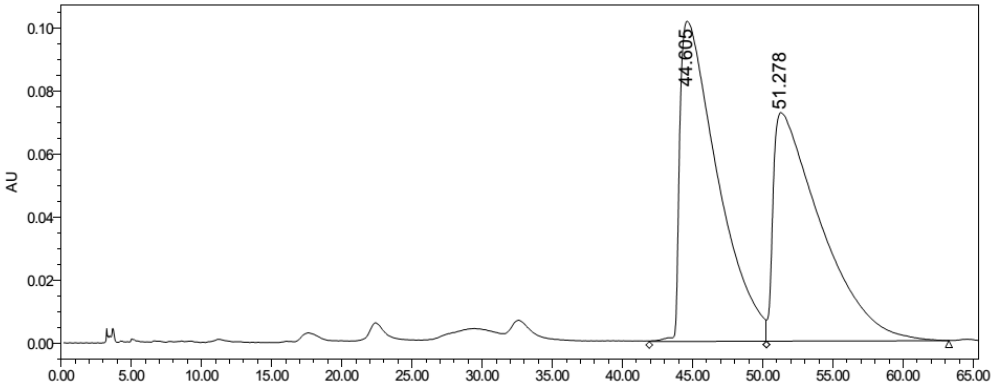
4q



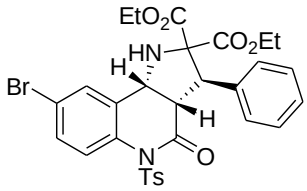
Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	2998 (190- 400) nm	40.501	29141	-313	0.23
2	2998 (190- 400) nm	49.885	12453630	68348	99.77



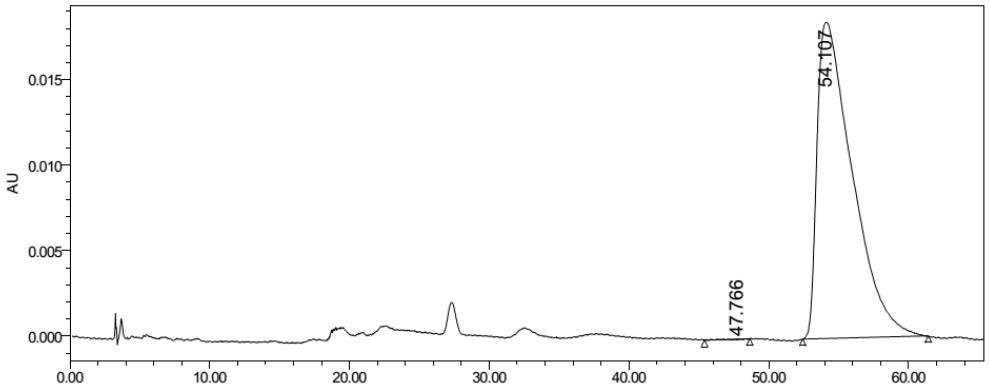
rac-**4r**



Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	2998 (190- 400) nm	44.605	18942891	101737	52.34
2	2998 (190- 400) nm	51.278	17249851	72643	47.66



4r



Peak	Processed channel	Ret. Time (min)	Area (mAu*s)	Height (mAu)	Area (%)
1	2998 (190- 400) nm	47.766	3818	-62	0.12
2	2998 (190- 400) nm	54.107	3234865	18496	99.88