Supporting Information

Phosphine-Catalyzed Highly Enantioselective [3 + 3] Cycloaddition of Morita–Baylis–Hillman Carbonates with C,N-Cyclic Azomethine Imines

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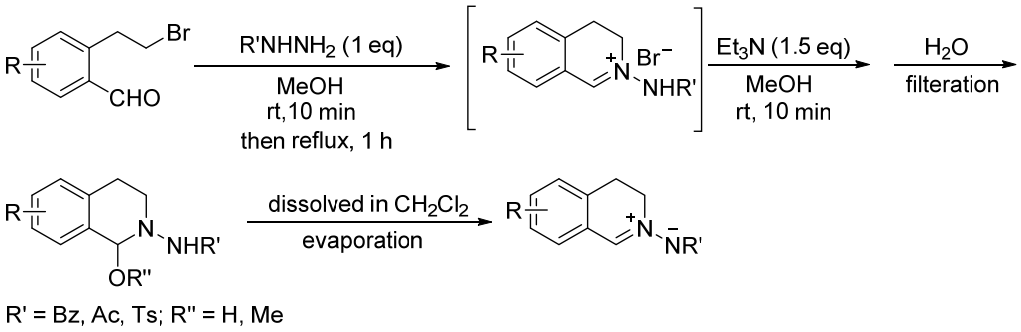
General Information

All reactions were performed under N_2 atmospheres in oven-dried glassware with magnetic stirring. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. Dichloromethane employed in the reactions was freshly distilled from CaH_2. Organic solutions were concentrated under reduced pressure on a rotary evaporator or an oil pump. Reactions were monitored through thin layer chromatography (TLC) on silica gel–precoated glass plates. Chromatograms were visualized by fluorescence quenching with UV-light at 254nm. Flash column chromatography was performed using Qingdao Haiyang flash silica gel (200–300 mesh). Infrared spectra were recorded using a Bruker Optics TENSOR 27 instrument. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 using a 300MHz NMR instrument (referenced internally to Me_4Si). Chemical shifts (δ, ppm) are relative to tetramethylsilane (TMS) with the resonance of the non-deuterated solvent or TMS as the internal standard. ^1H NMR data are reported as follows: chemical shift, multiplicity (s = singlet; d = doublet; q = quartet; m = multiplet; br = broad), coupling constant (Hz), and integral. Data for ^{13}C NMR spectra are reported in terms of chemical shift. Optical rotation was obtained on an Autopol V Plus polarimeter. Accurate mass measurements were performed using an Agilent instrument with the ESI-MS technique. Melting points were determined by a X-4 digital micro melting point apparatus. X-ray crystallographic data were collected using a MM007HF Saturn 724+. HPLC analysis was performed on Agilent 1100 series, UV detection monitored at 254 nm, using a Chiralcel OD-H column with hexane and *i*-PrOH as the eluent.

Preparation of C,N-Cyclic Azomethine Imines (2, 3, 4)[1, 2]



C,N-cyclic azomethine imines were prepared following the literature procedures. Known substituted 2-(2-bromoethyl)benzaldehyde [1] and 1-(2-bromoethyl)-2-naphthaldehyde [2] were prepared via routes adapted from those described in the literature (see general procedure below).

To a 0.5 M solution of the corresponding 2-(2-bromoethyl)benzaldhyde or 1-(2-bromoethyl)-2-naphthaldehyde (1.2 equiv) in MeOH was added substituted benzoylhydrazine, acetylhydrazine or sulfonylhydrazine (1.0 equiv) at rt. After the immediate formation of the insoluble material, this white suspension was heated to reflux and stirred for additional 1 h to give a clear solution. Once cooling to room temperature, the reaction solution was treated with Et_3N (1.5 equiv) for 10 minutes, poured into water and stirred for 30 min to give a white precipitate. This solid material was washed with cold ether and then dissolved in CH_2Cl_2 to give a yellow solution. According to the properties of azomethine imines (**2**, **3**, **4**), this colored solution was treated using different way. For azomethine imine **2**, this solution was dried over Na_2SO_4 and evaporated in vacuo to give **2** as a yellow solid. For azomethine imines **3** and **4**, this solution was dried over Na_2SO_4 and evaporated *in vacuo*. The residue was purified through flash column chromatography to afford the corresponding C,N-cyclic azomethine imine **3** or **4**.

Preparation of Morita-Baylis-Hillman Carbonates

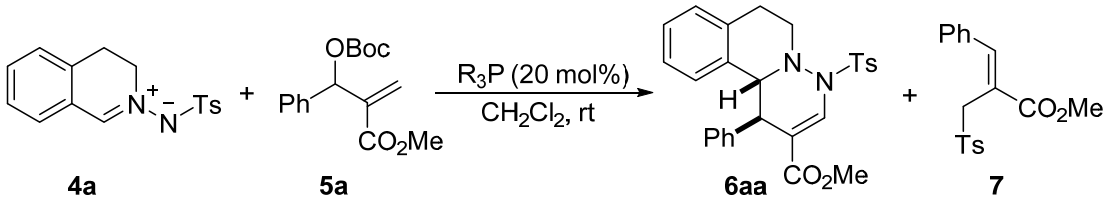
The Morita-Baylis-Hillman carbonates **5** were prepared according to the literature.[3]

[1] Hashimoto, T.; Maeda, Y.; Omote, M.; Nakatsu, H.; Maruoka, K. *J. Am. Chem. Soc*. **2010**, *132*, 4076–4077.
[2] Maity, P.; Srinivas, H. D.; Watson, M. P. *J. Am. Chem. Soc*. **2011**, *133*, 17142–17145.
[3] Feng, J.; Lu, X.; Kong, A.; Han, X. *Tetrahedron* **2007**, *63*, 6035–6041.

General Procedure for Achiral Phosphine-Catalyzed [3 + 3] Cycloaddition

An oven-dried 10 mL of Schlenk tube was charged with azomethine imine **4a** (0.1 mmol), 2 mL of CH_2Cl_2 and MBH carbonate **5a** (0.12 mmol) under nitrogen atmosphere at rt. Then, phosphine (0.02 mmol) was added to the above solution and the mixture was stirred at rt. Once the starting material was completely consumed (monitored by TLC), the mixture was concentrated to dryness. The residue was purified by flash column chromatography (ethyl acetate/petroleum ether) to afford the corresponding cycloaddition product **6aa**.

Screening of Reaction Conditions for Phosphine-Catalyzed [3 + 3] Cycloaddition



4a **5a** **6aa** **7**

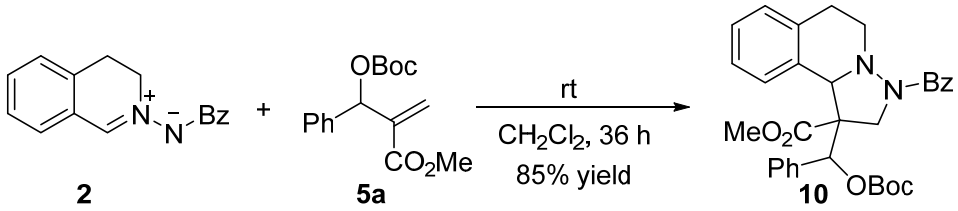
entry[a]	R_3P	*t*/h	**6aa**/**7** yield (%)[b]
1	Ph_3P	15	--/56
2	$MePPh_2$	13	40/32
3	Me_2PPh	13	84/trace

[a]Unless otherwise stated, the reaction of **4a** (0.1 mmol), **5a** (0.12 mmol) and phosphine (0.02 mmol) were carried out in 2 mL of CH_2Cl_2 at rt. [b]Isolated yield. dr is > 20:1, determined by ^{1}H NMR analysis of the crude product.

General Procedure for Chiral Phosphine-Catalyzed Asymmetric [3 + 3] Cycloaddition

Under nitrogen atmosphere, azomethine imine **4** (0.1 mmol), MBH carbonate **5** (0.2 mmol), K_2CO_3 (20.7 mg, 0.15 mmol), 4Å MS (100 mg) and chiral phosphine **P5** (7.3 mg, 0.02 mmol) were dissolved in 2 mL of CH_2Cl_2. The resulting mixture was stirred at −10 °C. Upon the completion of the reaction as monitored by TLC, the mixture was concentrated *in vacuo*. The residue was purified through flash column chromatography (7% EtOAc/PE) to afford the corresponding cycloaddition product.

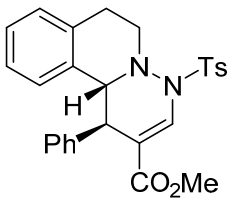
General Procedure for the Thermal [3 + 2] Cycloaddition of 2 with 5a



A mixture of azomethine imine **2** (0.2 mmol) and MBH carbonate **5a** (0.24 mmol) in 2 mL of CH_2Cl_2 was stirred at rt for 36 h. After removal of the solvent, the residue was subjected to flash column chromatography to give the corresponding thermal [3 + 2] cycloaddition product **10** in 85% yield (dr: 8:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, *J* = 6.6 Hz, 2H), 7.59 – 6.95 (m, 12H), 6.51 (s, 1H), 5.05 (d, *J* = 12.7 Hz, 1H), 4.69 (s, 1H), 4.33 (d, *J* = 12.7 Hz, 1H), 3.56 – 3.34 (m, 1H), 3.10 (s, 3H), 3.04 – 2.59 (m, 3H), 1.46 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.5, 169.0, 152.7, 136.9, 135.1, 133.1, 130.8, 130.0, 128.8, 128.6, 128.5, 128.4, 128.1, 127.9, 127.4, 127.3, 126.4, 125.4, 82.9, 67.4, 65.7, 51.4, 47.2, 46.7, 28.5, 27.6, 27.4.

Analytic and Characterization Data for Chiral [3 + 3] Cycloadducts 6

(1*R*,11b*R*)-Methyl 1-phenyl-4-tosyl-4,6,7,11b-tetrahydro-1*H*-pyridazino[6,1-*a*]iso-quinoline-2-carboxylate (6aa)

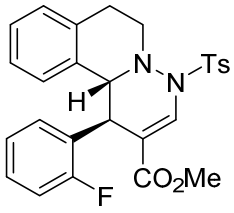


6aa

Prepared according to the general procedure as described above in 87% yield. Purified by flash chromatography (7% EtOAc/PE). White solid, mp = 145.6 – 147.2 °C; $[\alpha]^{20}_D$ = + 17.4 (*c* 1.15, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.30 (d, *J* = 1.3 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.23 – 7.11 (m, 3H), 7.08 (d, *J* = 3.9 Hz, 2H), 6.71 – 6.60 (m, 3H), 5.33 (d, *J* = 7.7 Hz, 1H), 3.50 (s, 3H), 3.48 – 3.45 (m, 1H), 3.42 – 3.09 (m, 3H), 3.06 (d, *J* = 9.9 Hz, 1H), 2.96 – 2.77 (m, 1H), 2.41 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.6, 144.9, 140.1, 134.3, 133.5, 132.9, 132.3, 129.6,

128.5, 128.4, 128.1, 127.8, 127.2, 126.7, 124.1, 112.5, 62.8, 51.2, 47.2, 41.4, 29.0, 21.6; IR (film) ν_{max} 2950, 2859, 1715, 1626, 1598, 1492, 1454, 1435, 1400, 1367, 1319, 1290, 1263, 1240, 1207, 1185, 1171, 1135, 1103, 1032, 1014, 903, 858, 815, 764, 736, 726, 702, 667, 655, 631, 618, 576, 553, 517 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{26}N_2NaO_4S^+$ $[M+Na]^+$ 497.1505, found 497.1502; HPLC analysis: >99% ee (CHIRALCEL OD-H, isopropanol/hexane=5/95, 1.0 mL/min, UV: 254 nm), t_R = 9.69 min (major), 18.32 min (minor).

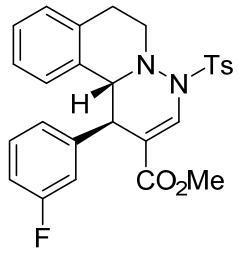
(1*S*,11b*R*)-Methyl 1-(2-fluorophenyl)-4-tosyl-4,6,7,11b-tetrahydro-1*H*-pyridazino [6,1-*a*]isoquinoline-2-carboxylate (6ab)



6ab

Prepared according to the general procedure as described above in 68% yield. Purified by flash chromatography (7% EtOAc/PE). White solid, mp = 128.2 – 129.2 °C; $[\alpha]^{20}_D$ = + 76.7 (*c* 1.32, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.36 (d, *J* = 1.3 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 2H), 7.35 – 7.24 (m, 2H), 7.24 – 6.95 (m, 4H), 6.96 – 6.80 (m, 1H), 6.79 – 6.60 (m, 2H), 5.47 (d, *J* = 7.7 Hz, 1H), 4.01 (d, *J* = 9.9 Hz, 1H), 3.53 (s, 3H), 3.47 – 2.99 (m, 4H), 2.95 – 2.80 (m, 1H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.3,161.6 (d, *J* = 246.7 Hz) , 145.0, 134.1, 133.8, 133.4, 132.2, 129.7, 128.6 (d, *J* = 19.8 Hz), 128.2 (d, *J* = 8.1 Hz), 127.8 (d, *J* = 14.7 Hz), 127.3 (d, *J* = 15.1 Hz), 126.4, 124.6, 124.1 (d, *J* = 3.2 Hz), 115.1 (d, *J* = 23.0 Hz), 111.6, 62.4, 51.3, 47.2, 44.3, 32.4, 29.7, 29.0, 22.7, 21.6; IR (film) ν_{max} 2922, 2851, 1714, 1628, 1597, 1493, 1454, 1436, 1368, 1320, 1292, 1262, 1233, 1208, 1185, 1172, 1107, 1092, 1035, 1014, 903, 863, 812, 759, 723, 667, 646, 618, 581, 567, 554 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{26}FN_2O_4S^+$ $[M+H]^+$ 493.1592, found 493.1588; HPLC analysis: >99% ee (CHIRALCEL OD-H, isopropanol/hexane=5/95, 1.0 mL/min, UV: 254 nm), t_R = 10.51 min (major), 18.91 min (minor).

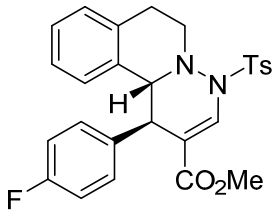
(1*R*,11b*R*)-Methyl 1-(3-fluorophenyl)-4-tosyl-4,6,7,11b-tetrahydro-1*H*-pyridazino [6,1-*a*]isoquinoline-2-carboxylate (6ac)



6ac

Prepared according to the general procedure as described above in 87% yield. Purified by flash chromatography (7% EtOAc/PE). White solid, mp = 136.2 – 137.4 °C; $[\alpha]^{20}_{D}$ = +71.1 (*c* 1.53, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.32 (d, *J* = 1.3 Hz, 1H), 7.88 – 7.77 (m, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.18 – 7.05 (m, 3H), 6.95 – 6.82 (m, 1H), 6.75 – 6.62 (m, 1H), 6.50 (d, *J* = 7.7 Hz, 1H), 6.36 (d, *J* = 9.9 Hz, 1H), 5.37 (d, *J* = 7.7 Hz, 1H), 3.53 (s, 3H), 3.47 (d, *J* = 9.9 Hz, 1H), 3.38 – 3.10 (m, 3H), 3.05 – 2.82 (m, 2H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.4, 162.7 (d, *J* = 245.8 Hz),145.1, 143.0 (d, *J* = 7.0 Hz), 133.9, 133.4, 132.3, 129.8, 129.5 (d, *J* = 8.2 Hz), 128.6, 128.3, 127.5 (d, *J* = 14.9 Hz), 124.3, 113.7 (d, *J* = 21.1 Hz), 111.9, 62.7, 51.3, 47.2, 41.3, 28.9, 21.6; IR (film) ν_{max} 2921, 2851, 1716, 1626, 1593, 1489, 1436, 1369, 1290, 1261, 1241, 1207, 1185, 1172, 1138, 1103, 1017, 900, 855, 795, 764, 754, 722, 697, 667, 620, 578, 554, 522 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{26}FN_2O_4S^+$ $[M+H]^+$ 493.1592, found 493.1586; HPLC analysis: >99% ee (CHIRALCEL OD-H, isopropanol/hexane=5/95, 1.0 mL/min, UV: 254 nm), t_R = 9.16 min (major), 18.42 min (minor).

(1*R*,11b*R*)-Methyl 1-(4-fluorophenyl)-4-tosyl-4,6,7,11b-tetrahydro-1*H*-pyridazino [6,1-*a*]isoquinoline-2-carboxylate (6ad)

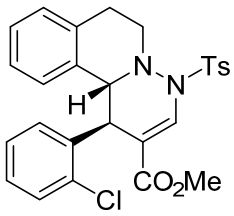


6ad

Prepared according to the general procedure as described above in 80% yield. Purified

by flash chromatography (7% EtOAc/PE). White solid, mp = 157.2 – 157.7 °C; $[\alpha]^{20}_{D}$ = +87.7 (*c* 1.55, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.30 (d, *J* = 1.3 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.14 – 7.06 (m, 2H), 6.94 – 6.81 (m, 2H), 6.73 – 6.60 (m, 3H), 5.38 (d, *J* = 7.7 Hz, 1H), 3.52 (s, 3H), 3.46 (d, *J* = 9.9 Hz, 1H), 3.38 – 3.06 (m, 3H), 3.02 (d, *J* = 9.9 Hz, 1H), 2.94 – 2.80 (m, 1H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.5, 161.7 (d, *J* = 245.2 Hz), 145.0, 136.0 (d, *J* = 3.2 Hz), 134.1, 133.5, 133.1, 132.3, 129.7, 128.6, 128.4, 127.7, 127.4, 124.2, 115.0 (d, *J* = 21.4 Hz), 112.1, 62.8, 51.3, 47.1, 40.8, 29.0, 21.7; IR (film) ν_{max} 2922, 2852, 1716, 1625, 1599, 1508, 1435, 1368, 1290, 1223, 1207, 1185, 1171, 1104, 1015, 903, 858, 828, 815, 757, 668, 641, 606, 583, 560, 531 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{26}FN_2O_4S^+$ $[M+H]^+$ 493.1592, found 493.1590; HPLC analysis: >99% ee (CHIRALCEL OD-H, isopropanol/hexane=5/95, 1.0 mL/min, UV: 254 nm), t_R = 8.80 min (major), 14.59 min (minor).

(1*S*,11b*R*)-Methyl 1-(2-chlorophenyl)-4-tosyl-4,6,7,11b-tetrahydro-1*H*-pyridazino [6,1-*a*]isoquinoline-2-carboxylate (6ae)

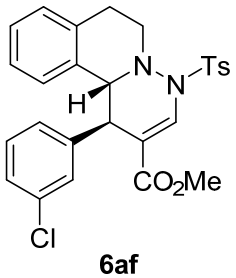


6ae

Prepared according to the general procedure as described above in 71% yield. Purified by flash chromatography (7% EtOAc/PE). White solid, mp = 144.5 – 145.7 °C; $[\alpha]^{20}_{D}$ = +99.5 (*c* 1.01, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.35 (d, *J* = 1.3 Hz, 1H), 7.87 – 7.81 (m, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.24 – 7.03 (m, 5H), 6.78 – 6.57 (m, 2H), 5.39 (d, *J* = 7.7 Hz, 1H), 4.22 (dd, *J* = 1.3，9.9 Hz, 1H), 3.51 (s, 3H), 3.45 – 3.05 (m, 3H), 3.00 (d, *J* = 9.9 Hz, 1H), 2.95 – 2.85 (m, 1H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.3, 145.0, 138.2, 136.3, 133.6, 133.6, 133.4, 132.2, 129.7, 129.6, 129.2, 128.6, 128.4, 127.7, 127.4, 127.4, 126.8, 126.5, 124.7, 111.9, 62.7, 51.4,

47.4, 36.4, 28.9, 21.7; IR (film) ν_{max} 2920, 2850, 1715, 1628, 1597, 1492, 1472, 1436, 1369, 1291, 1208, 1185, 1172, 1121, 1102, 1036, 1014, 904, 859, 815, 762, 726, 704, 667, 644, 579, 565, 554 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{26}ClN_2O_4S^+$ $[M+H]^+$ 509.1296, found 509.1294; HPLC analysis: >99% ee (CHIRALCEL OD-H, isopropanol/hexane=5/95, 1.0 mL/min, UV: 254 nm), t_R = 11.19 min (major), 22.48 min (minor).

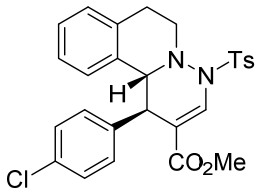
(1*R*,11b*R*)-Methyl 1-(3-chlorophenyl)-4-tosyl-4,6,7,11b-tetrahydro-1*H*-pyridazino [6,1-*a*]isoquinoline-2-carboxylate (6af)



6af

Prepared according to the general procedure as described above in 85% yield. Purified by flash chromatography (7% EtOAc/PE). White solid, mp = 152.5 – 152.9 °C; $[\alpha]^{20}_D$ = –94.1 (*c* 1.05, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.32 (d, *J* = 1.3 Hz, 1H), 8.00 – 7.68 (m, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.21 – 7.03 (m, 4H), 6.75 – 6.64 (m, 1H), 6.64 – 6.55 (m, 2H), 5.34 (d, *J* = 7.7 Hz, 1H), 3.53 (s, 3H), 3.43 (dd, *J* = 1.3，9.9 Hz, 1H), 3.37 – 3.10 (m, 3H), 3.00 – 2.77 (m, 2H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.3, 145.2, 142.5, 134.0, 133.9, 133.6, 133.3, 132.3, 129.8, 129.3, 128.7, 128.3, 127.6, 127.5, 127.0, 124.3, 112.0, 62.7, 51.4, 47.2, 41.2, 28.9, 21.7; IR (film) ν_{max} 2921, 2851, 1715, 1626, 1596, 1434, 1369, 1290, 1240, 1207, 1185, 1172, 1104, 1015, 855, 787, 765, 731, 696, 667, 578, 554 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{26}ClN_2O_4S^+$ $[M+H]^+$ 509.1296, found 509.1292; HPLC analysis: >99% ee (CHIRALCEL OD-H, isopropanol/hexane=5/95, 1.0 mL/min, UV: 254 nm), t_R = 8.55 min (major), 13.99 min (minor).

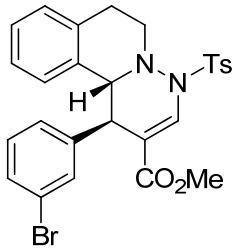
(1*R*,11b*R*)-Methyl 1-(4-chlorophenyl)-4-tosyl-4,6,7,11b-tetrahydro-1*H*-pyridazino [6,1-*a*]isoquinoline-2-carboxylate (6ag)



6ag

Prepared according to the general procedure as described above in 80% yield. Purified by flash chromatography (7% EtOAc/PE). White solid, mp = 173.4 – 174.9 °C; $[\alpha]^{20}_{D}$ = –110.6 (*c* 1.12, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.31 (d, *J* = 1.3 Hz, 1H), 7.87 – 7.77 (m, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.20 – 7.02 (m, 4H), 6.74 – 6.66 (m, 1H), 6.63 (d, *J* = 8.1 Hz, 2H), 5.40 (d, *J* = 7.7 Hz, 1H), 3.52 (s, 3H), 3.49 – 3.40 (m, 1H), 3.37 – 3.07 (m, 3H), 3.01 (d, *J* = 9.9 Hz, 1H), 2.95 – 2.77 (m, 1H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.4, 145.0, 138.9, 134.0, 133.4, 133.3, 132.5, 132.3, 129.7, 128.7, 128.4, 127.7, 127.4, 124.3, 111.9, 62.8, 51.3, 47.1, 41.0, 28.9, 21.7; IR (film) ν_{max} 2918, 2850, 1714, 1625, 1597, 1491, 1436, 1410, 1368, 1316, 1292, 1266, 1240, 1208, 1186, 1171, 1137, 1099, 1034, 1015, 904, 859, 817, 764, 731, 703, 668, 590, 553 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{26}ClN_2O_4S^+$ $[M+H]^+$ 509.1296, found 509.1300; HPLC analysis: >99% ee (CHIRALCEL OD-H, isopropanol/hexane= 5/95, 1.0 mL/min, UV: 254 nm), t_R = 8.43 min (major), 13.66 min (minor).

(1*R*,11b*R*)-Methyl 1-(3-bromophenyl)-4-tosyl-4,6,7,11b-tetrahydro-1*H*-pyridazino[6,1-*a*]isoquinoline-2-carboxylate (6ah)

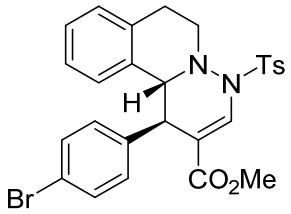


6ah

Prepared according to the general procedure as described above in 85% yield. Purified by flash chromatography (7% EtOAc/PE).White solid, mp = 158.2 – 159.9 °C; $[\alpha]^{20}_{D}$

= –20.78 (*c* 1.16, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.82 (d, *J* = 8.1 Hz, 2H), 7.43 – 7.27 (m, 3H), 7.17 – 6.95 (m, 3H), 6.80 – 6.55 (m, 3H), 5.31 (d, *J* = 7.7 Hz, 1H), 3.53 (s, 3H), 3.45 – 3.08 (m, 4H), 2.98 – 2.72 (m, 2H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ165.0, 145.1, 143.0, 133.9, 133.4, 133.3, 132.3, 129.8, 129.5, 128.7, 128.3, 127.6, 127.4, 124.2, 122.1, 112.3, 62.6, 60.2, 47.1, 41.2, 28.9, 21.7; IR (film) ν_{max} 2920, 2850, 1715, 1625, 1595, 1492, 1472, 1434, 1369, 1289, 1240, 1207, 1185, 1172, 1104, 1014, 855, 815, 784, 764, 729, 697, 667, 647, 577, 554 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{26}BrN_2O_4S^+$ $[M+H]^+$ 553.0791, found 553.0787; HPLC analysis: >99% ee (CHIRALCEL OD-H, isopropanol/hexane=5/95, 1.0 mL/min, UV: 254 nm), t_R = 8.90 min (major), 14.50 min (minor).

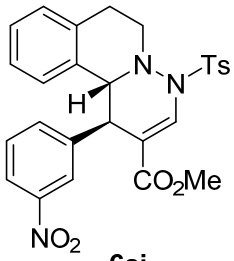
(1*R*,11b*R*)-Methyl 1-(4-bromophenyl)-4-tosyl-4,6,7,11b-tetrahydro-1*H*-pyridazino[6,1-*a*]isoquinoline-2-carboxylate (6ai)



6ai

Prepared according to the general procedure as described above in 90% yield. Purified by flash chromatography (7% EtOAc/PE). White solid, mp = 179.3 – 180.1 °C; $[\alpha]^{20}_D$ = –29.4 (*c* 0.81, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.81 (d, *J* = 8.1 Hz, 2H), 7.34 – 7.25 (m, 4H), 7.14 – 7.03 (m, 2H), 6.77 – 6.63 (m, 1H), 6.56 (d, *J* = 8.1 Hz, 2H), 5.39 (d, *J* = 7.7 Hz, 1H), 3.51 (s, 3H), 3.43 (d, *J* = 10.0 Hz, 1H), 3.36 – 3.05 (m, 3H), 3.00 (d, *J* = 9.9 Hz, 1H), 2.85 (d, *J* = 9.9 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.4, 145.0, 139.5, 134.0, 133.4, 133.3, 132.3, 131.3, 129.7, 128.7, 128.4, 127.7, 127.4, 124.3, 120.6, 111.8, 62.7, 51.3, 47.1, 41.1, 28.9, 21.7; IR (film) ν_{max} 2920, 2851, 1715, 1626, 1487, 1435, 1369, 1291, 1207, 1185, 1171, 1099, 1073, 1011, 858, 815, 763, 727, 668, 585, 553 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{26}BrN_2O_4S^+$ $[M+H]^+$ 553.0791, found 553.0785; HPLC analysis: >99% ee (CHIRALCEL OD-H, isopropanol/hexane=5/95, 1.0 mL/min, UV: 254 nm), t_R = 10.53 min (major), 18.39 min (minor).

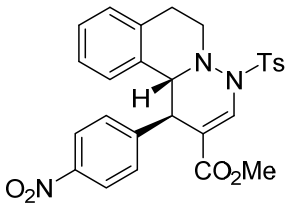
(1*R*,11b*R*)-Methyl 1-(3-nitrophenyl)-4-tosyl-4,6,7,11b-tetrahydro-1*H*-pyridazino [6,1-*a*]isoquinoline-2-carboxylate (6aj)



6aj

Prepared according to the general procedure as described above in 86% yield. Purified by flash chromatography (7% EtOAc/PE). White solid, mp = 168.3 – 169.7 °C; $[\alpha]^{20}_{D}$ = –13.8 (*c* 0.78, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.40 (d, *J* = 1.3 Hz, 1H), 8.14 – 8.00 (m, 1H), 7.84 (d, *J* = 8.1 Hz, 2H), 7.49 (s, 1H), 7.40 – 7.28 (m, 3H), 7.16 – 7.02(m, 3H), 6.71 – 6.56 (m, 1H), 5.23 (d, *J* = 7.7 Hz, 1H), 3.70 – 3.45 (m, 4H), 3.40 – 3.12 (m, 3H), 3.05 – 2.75 (m, 2H), 2.41 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.2, 145.4, 143.0, 134.4, 133.4, 133.1, 132.4, 129.9, 129.0, 128.2, 127.7, 127.2, 124.4, 122.0, 110.9, 62.7, 51.4, 47.3, 41.3, 28.8, 21.7; IR (film) ν_{max} 2922, 2852, 2353, 1713, 1624, 1530, 1436, 1369, 1351, 1291, 1209, 1186, 1172, 1104, 1015, 898, 856, 813, 764, 728, 689, 667, 578 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{26}N_3O_6S^+$ $[M+H]^+$ 520.1537, found 520.1536; HPLC analysis: >99% ee (CHIRALCEL OD-H, isopropanol/hexane=5/95, 1.0 mL/min, UV: 254 nm), t_R = 14.07 min (major), 22.98 min (minor).

(1*R*,11b*R*)-Methyl 1-(4-nitrophenyl)-4-tosyl-4,6,7,11b-tetrahydro-1*H*-pyridazino [6,1-*a*]isoquinoline-2-carboxylate (6ak)

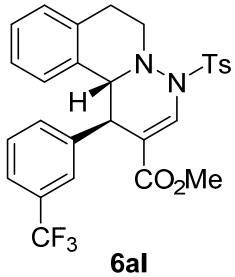


6ak

Prepared according to the general procedure as described above in 77% yield. Purified by flash chromatography (7% EtOAc/PE). White solid, mp = 159.0 – 160.4 °C; $[\alpha]^{20}_{D}$ = –73.6 (*c* 1.47, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.39 (s, 1H), 8.05 (d, *J* = 8.1 Hz, 2H), 7.84 (d, *J* = 8.1 Hz, 2H), 7.40 – 7.27 (m, 2H), 7.18 – 7.06 (m, 2H), 6.92 –

6.84 (m, 2H), 6.73 – 6.62 (m, 1H), 5.31 (d, *J* = 7.7 Hz, 1H), 3.62 (d, *J* = 9.9 Hz, 1H), 3.53 (s, 3H), 3.41 – 2.99 (m, 4H), 2.97 – 2.84 (m, 1H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.2, 148.6, 146.8, 145.3, 134.1, 133.4, 133.3, 132.3, 129.8, 128.9, 128.4, 127.8, 127.4, 124.4, 123.4, 110.6, 62.8, 51.4, 47.2, 41.6, 28.8, 21.7; IR (film) ν_{max} 2923, 2852, 1713, 1625, 1598, 1520, 1493, 1436, 1369, 1346, 1292, 1263, 1241, 1208, 1186, 1171, 1137, 1101, 1034, 1015, 906, 861, 846, 815, 764, 728, 701, 668, 588, 553 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{26}N_3O_6S^+$ $[M+H]^+$ 520.1537, found 520.1533; HPLC analysis: >99% ee (CHIRALCEL OD-H, isopropanol/hexane=5/95, 1.0 mL/min, UV: 254 nm), t_R = 37.21 min (minor), 45.15 min (major).

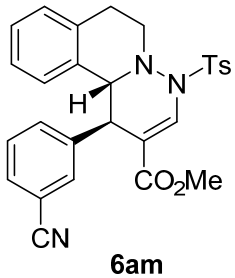
(1*R*,11b*R*)-Methyl 4-tosyl-1-(3-(trifluoromethyl)phenyl)-4,6,7,11b-tetrahydro-1*H*-pyridazino[6,1-*a*]isoquinoline-2-carboxylate (6al)



6al

Prepared according to the general procedure as described above in 84% yield. Purified by flash chromatography (7% EtOAc/PE). White solid, mp = 173.7 – 174.6 °C; $[\alpha]^{20}_D$ = +62.5 (*c* 1.89, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.34 (d, *J* = 1.3 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 2H), 7.49 – 7.39 (m, 1H), 7.35 – 7.25 (m, 3H), 7.13-7.04 (m, 2H), 6.89 (d, *J* = 7.7 Hz, 1H), 6.82 (s, 1H), 6.69 – 6.57 (m, 1H), 5.16 (d, *J* = 7.7 Hz, 1H), 3.62 – 3.42 (m, 4H), 3.34 – 3.16 (m, 3H), 2.98 – 2.65 (m, 2H), 2.39 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.3, 145.2, 141.6, 134.0, 133.6, 133.2, 132.3, 129.8, 128.8, 128.3, 127.6, 127.4, 124.3, 124.0 (q, *J* = 272.4 Hz), 123.6 (q, *J* = 3.8 Hz), 62.7, 51.3, 47.2, 41.4, 28.9, 21.5; IR (film) ν_{max} 2920, 2850, 1716, 1626, 1597, 1492, 1437, 1370, 1331, 1291, 1261, 1186, 1172, 1124, 1106, 1094, 1073, 1015, 894, 856, 803, 763, 754, 725, 705, 669, 648, 575, 554 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{26}F_3N_2O_4S^+$ $[M+H]^+$ 543.1560, found 543.1555; HPLC analysis: >99% ee (CHIRALCEL OD-H, isopropanol/hexane=5/95, 1.0 mL/min, UV: 254 nm), t_R = 8.13 min (major), 11.43 min (minor).

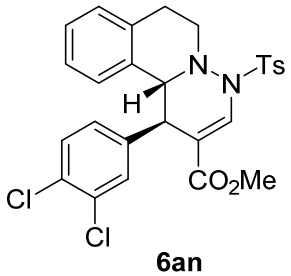
(1*R*,11b*R*)-Methyl 1-(3-cyanophenyl)-4-tosyl-4,6,7,11b-tetrahydro-1*H*-pyridazino [6,1-*a*]isoquinoline-2-carboxylate (6am)



6am

Prepared according to the general procedure as described above in 93% yield. Purified by flash chromatography (7% EtOAc/PE). White solid, mp = 167.3 – 168.6 °C; $[\alpha]^{20}_{D}$ = –8.5 (*c* 1.89, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.35 (d, *J* = 1.3 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 2H), 7.54 – 7.43 (m, 1H), 7.40 – 7.20 (m, 3H), 7.15 – 7.05 (m, 2H), 7.02 – 6.83 (m, 2H), 6.75 – 6.57 (m, 1H), 5.23 (d, *J* = 7.7 Hz, 1H), 3.60 – 3.42 (m, 4H), 3.37 – 3.09 (m, 3H), 3.06 – 2.73 (m, 2H), 2.44 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.1, 145.5, 142.3, 134.2, 133.5, 133.3, 132.4, 130.5, 129.9, 128.9, 128.3, 127.7, 127.3, 124.4, 118.7, 112.3, 111.1, 62.8, 51.4, 47.2, 41.3, 28.8, 21.7; IR (film) ν_{max} 2921, 2851, 2230, 1714, 1625, 1597, 1493, 1483, 1455, 1435, 1369, 1291, 1262, 1239, 1207, 1185, 1172, 1136, 1105, 1017, 896, 856, 799, 764, 745, 695, 668, 623, 580, 519 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{26}N_3O_4S^+$ $[M+H]^+$ 500.1639, found 500.1634; HPLC analysis: >99% ee (CHIRALCEL OD-H, isopropanol/hexane=5/95, 1.0 mL/min, UV: 254 nm), t_R = 16.63 min (major), 23.96 min (minor).

(1*R*,11b*R*)-Methyl 1-(3,4-dichlorophenyl)-4-tosyl-4,6,7,11b-tetrahydro-1*H*-pyridazino[6,1-*a*]isoquinoline-2-carboxylate (6an)

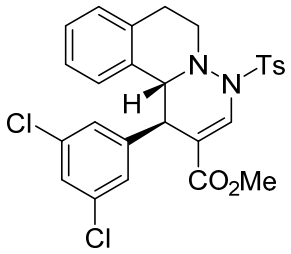


6an

Prepared according to the general procedure as described above in 93% yield. Purified by flash chromatography (7% EtOAc/PE). White solid, mp = 166.0 – 167.3 °C; $[\alpha]^{20}_{D}$ = –77.3 (*c* 1.50, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.31 (d, *J* = 1.3 Hz, 1H),

7.81 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 7.25 – 7.18 (m, 1H), 7.15 – 7.05 (m, 2H), 6.77 – 6.64 (m, 2H), 6.59 – 6.52 (m, 1H), 5.38 (d, J = 7.7 Hz, 1H), 3.54 (s, 3H), 3.44 – 3.36 (m, 1H), 3.33 – 3.09 (m, 3H), 2.94 – 2.77 (m, 2H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.2, 145.3, 140.9, 133.9, 133.7, 133.3, 132.3, 130.7, 130.0, 129.9, 128.8, 128.3, 127.6, 127.5, 124.4, 111.5, 62.7, 51.4, 47.1, 40.8, 28.9, 21.7; IR (film) ν_{max} 2923, 2852, 1715, 1625, 1597, 1493, 1469, 1436, 1400, 1370, 1290, 1264, 1240, 1208, 1186, 1172, 1133, 1103, 1031, 901, 856, 816, 764, 739, 705, 667, 592, 554 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{25}Cl_2N_2O_4S^+$ $[M+H]^+$ 543.0907, found 543.0905; HPLC analysis: 98% ee (CHIRALCEL OD-H, isopropanol/ hexane=5/95, 1.0 mL/min, UV: 254 nm), t_R = 6.82 min (major), 9.60 min (minor).

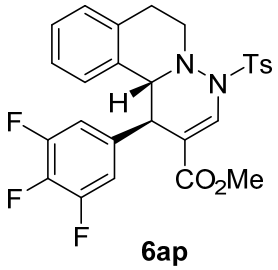
(1*R*,11b*R*)-Methyl 1-(3,5-dichlorophenyl)-4-tosyl-4,6,7,11b-tetrahydro-1*H*-pyridazino[6,1-*a*]isoquinoline-2-carboxylate (6ao)



6ao

Prepared according to the general procedure as described above in 95% yield. Purified by flash chromatography (7% EtOAc/PE). White solid, mp = 168.5 – 168.8 °C; $[\alpha]^{20}_D$ = –36.1 (*c* 0.89, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.82 (d, J = 8.1 Hz, 2H), 7.41 – 7.06 (m, 5H), 6.85 – 6.65 (m, 1H), 6.61 – 6.40(m, 2H), 5.36 (d, J = 7.7 Hz, 1H), 3.57 (s, 3H), 3.45 – 3.10 (m, 4H), 2.97 – 2.72 (m, 2H), 2.44 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.1, 145.4, 144.1, 134.5, 134.2, 133.4, 133.2, 132.2, 129.9, 128.8, 128.3, 127.7, 127.4, 127.0, 124.4, 111.4, 62.6, 51.5, 47.2, 41.1, 28.8, 21.7; IR (film) ν_{max} 2924, 1714, 1625, 1588, 1568, 1493, 1434, 1370, 1290, 1238, 1208, 1185, 1173, 1105, 1017, 901, 856, 815, 796, 764, 730, 693, 666, 621, 580, 569, 555 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{25}Cl_2N_2O_4S^+$ $[M+H]^+$ 543.0907, found 543.0903; HPLC analysis: >99% ee (CHIRALCEL OD-H, isopropanol/hexane=5/95, 1.0 mL/min, UV: 254 nm), t_R = 8.36 min (major), 13.26 min (minor).

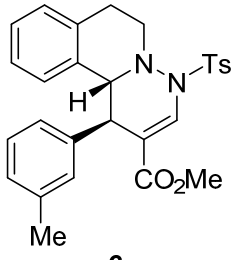
(1*R*,11b*R*)-Methyl 4-tosyl-1-(3,4,5-trifluorophenyl)-4,6,7,11b-tetrahydro-1*H*-pyridazino[6,1-*a*]isoquinoline-2-carboxylate (6ap)



6ap

Prepared according to the general procedure as described above in 63% yield. Purified by flash chromatography (7% EtOAc/PE). White solid, mp = 179.2 – 180.5 °C; $[\alpha]^{20}_{D}$ = +66.0 (*c* 1.33, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.82 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.21 – 7.05 (m, 2H), 6.83 – 6.70(m, 1H), 6.40 – 6.22 (m, 2H), 5.44 (d, *J* = 7.7 Hz, 1H), 3.58 (s, 3H), 3.44 – 3.35 (m, 1H), 3.34 – 3.08 (m, 3H), 3.02 – 2.76 (m, 2H), 2.44 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.1, 150.9 (d, *J* = 250.8 Hz), 145.4, 140.2 (t, *J* = 15.2 Hz), 137.0(m), 134.1, 133.4 (d, *J* = 12.3 Hz), 132.3, 129.8, 128.9, 128.3, 127.8, 127.3, 124.5, 110.9, 62.6, 51.5, 47.2, 41.1, 28.8, 21.6; IR (film) ν_{max} 2920, 2851, 1715, 1625, 1530, 1493, 1449, 1370, 1351, 1291, 1237, 1208, 1186, 1173, 1104, 1045, 905, 861, 815, 764, 730, 705, 670, 621, 583, 554 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{24}F_3N_2O_4S^+$ $[M+H]^+$ 529.1403, found 529.1405; HPLC analysis: >99% ee (CHIRALCEL OD-H, isopropanol/hexane=5/95, 1.0 mL/min, UV: 254 nm), t_R = 8.36 min (major), 14.22 min (minor).

(1*R*,11b*R*)-Methyl 1-(*m*-tolyl)-4-tosyl-4,6,7,11b-tetrahydro-1*H*-pyridazino[6,1-*a*] isoquinoline-2-carboxylate (6aq)

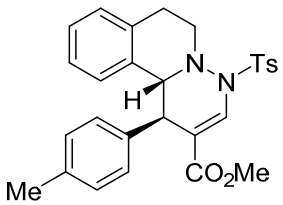


6aq

Prepared according to the general procedure as described above in 88% yield. Purified

by flash chromatography (7% EtOAc/PE). White solid, mp = 148.5 – 150.3 °C; $[\alpha]^{20}_{D}$ = +44.6 (*c* 1.83, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.27 (d, *J* = 1.3 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.13 – 6.91 (m, 4H), 6.70 – 6.58 (m, 1H), 6.53 – 6.38 (m, 2H), 5.31 (d, *J* = 7.7 Hz, 1H), 3.50 (s, 3H), 3.45 – 3.36 (m, 1H), 3.36 – 3.06 (m, 3H), 3.00 (d, *J* = 9.9 Hz, 1H), 2.93 – 2.77 (m, 1H), 2.40 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.6, 144.8, 139.9, 137.5, 134.4, 133.6, 132.9, 132.3, 129.7, 128.4, 128.4, 127.9, 127.5, 127.2, 124.0, 112.9, 62.8, 51.2, 47.2, 41.3, 29.1, 21.6, 21.3; IR (film) ν_{max} 2920, 2850, 1717, 1627, 1491, 1435, 1368, 1289, 1261, 1237, 1206, 1185, 1172, 1103, 1020, 897, 856, 815, 794, 763, 751, 721, 705, 667, 579, 554 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{29}N_2O_4S^+$ $[M+H]^+$ 489.1843, found 489.1841; HPLC analysis: >99% ee (CHIRALCEL OD-H, isopropanol/hexane=5/95, 1.0 mL/min, UV: 254 nm), t_R = 8.69 min (major), 17.81 min (minor).

(1*R*,11b*R*)-Methyl 1-(*p*-tolyl)-4-tosyl-4,6,7,11b-tetrahydro-1*H*-pyridazino[6,1-*a*] isoquinoline-2-carboxylate (6ar)

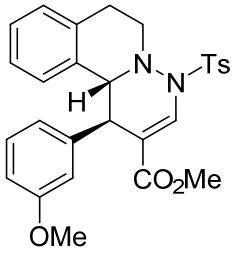


6ar

Prepared according to the general procedure as described above in 80% yield. Purified by flash chromatography (7% EtOAc/PE). White solid, mp = 157.3 – 158.3 °C; $[\alpha]^{20}_{D}$ = +35.8 (*c* 1.44, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 (d, *J* = 1.3 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.14 – 7.04 (m, 2H), 6.97 (d, *J* = 7.7 Hz, 2H), 6.73 – 6.62 (m, 1H), 6.58 (d, *J* = 8.1 Hz, 2H), 5.40 (d, *J* = 7.7 Hz, 1H), 3.51 (s, 3H), 3.47 – 3.40 (m, 1H), 3.39 – 3.01 (m, 4H), 2.95 – 2.78 (m, 1H), 2.42 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.6, 144.8, 136.9, 136.2, 134.5,

133.6, 132.7, 132.3, 129.6, 128.9, 128.5, 128.4, 128.0, 127.2, 124.1, 112.8, 62.8, 51.2, 47.1, 41.0, 29.1, 21.7, 21.1; IR (film) ν_{max} 2921, 2851, 1716, 1627, 1597, 1512, 1493, 1435, 1368, 1289, 1239, 1206, 1185, 1171, 1101, 1014, 902, 859, 813, 755, 668, 639, 607, 560, 514 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{29}N_2O_4S^+$ $[M+H]^+$ 489.1843, found 489.1845; HPLC analysis: >99% ee (CHIRALCEL OD-H, isopropanol /hexane=5/95, 1.0 mL/min, UV: 254 nm), t_R = 9.00 min (major), 16.26 min (minor).

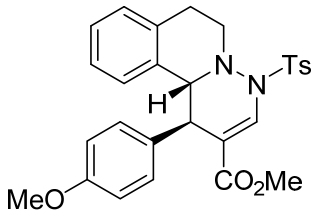
(1*R*,11b*R*)-Methyl 1-(3-methoxyphenyl)-4-tosyl-4,6,7,11b-tetrahydro-1*H*-pyridazino[6,1-*a*]isoquinoline-2-carboxylate (6as)



6as

Prepared according to the general procedure as described above in 72% yield. Purified by flash chromatography (7% EtOAc/PE). White solid, mp = 80.9 – 82.1 °C; $[\alpha]^{20}_D$ = +43.7 (*c* 0.52, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.29 (d, *J* = 1.3 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.14 – 7.02 (m, 3H), 6.76 – 6.62 (m, 2H), 6.39 – 6.15 (m, 2H), 5.41 (d, *J* = 7.7 Hz, 1H), 3.67 (s, 3H), 3.52 (s, 3H), 3.48 – 3.39 (m, 1H), 3.38 – 3.09 (m, 3H), 3.08 – 2.98 (m, 1H), 2.95 – 2.78 (m, 1H), 2.41 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.6, 159.4, 144.9, 141.7, 134.2, 133.5, 133.0, 132.3, 129.7, 129.0, 128.5, 128.3, 128.0, 127.3, 124.1, 112.5, 112.3, 62.7, 55.1, 51.3, 47.2, 41.5, 29.0, 21.6; IR (film) ν_{max} 2920, 2850, 1716, 1627, 1598, 1490, 1454, 1435, 1367, 1290, 1264, 1206, 1185, 1171, 1102, 1042, 897, 856, 790, 764, 751, 722, 701, 667, 580, 553 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{29}N_2O_5S^+$ $[M+H]^+$ 505.1792, found 505.1790; HPLC analysis: >99% ee (CHIRALCEL OD-H, isopropanol/hexane=5/95, 1.0 mL/min, UV: 254 nm), t_R = 12.79 min (major), 22.65 min (minor).

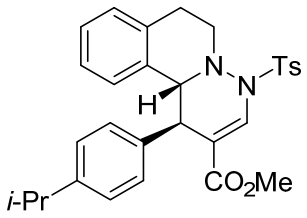
(1*R*,11b*R*)-Methyl 1-(4-methoxyphenyl)-4-tosyl-4,6,7,11b-tetrahydro-1*H*-pyridazino[6,1-*a*]isoquinoline-2-carboxylate (6at)



6at

Prepared according to the general procedure as described above in 70% yield. Purified by flash chromatography (7% EtOAc/PE). White solid, mp = 155.0 – 155.7 °C; $[\alpha]^{20}_{D}$ = +14.9 (*c* 1.24, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.27 (d, *J* = 1.3 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.14 – 7.03 (m, 2H), 6.78 – 6.54 (m, 5H), 5.42 (d, *J* = 7.7 Hz, 1H), 3.77 (s, 3H), 3.52 (s, 3H), 3.42 (d, *J* = 9.9 Hz, 1H), 3.38 – 2.98 (m, 4H), 2.92 – 2.79 (m, 1H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.7, 158.3, 144.9, 134.5, 133.6, 132.7, 132.3, 132.0, 129.6, 128.5, 128.4, 127.9, 127.2, 124.2, 113.6, 112.8, 62.8, 55.1, 51.2, 47.1, 40.6, 29.0, 21.7; IR (film) ν_{max} 2921, 2850, 1716, 1626, 1511, 1493, 1435, 1367, 1290, 1259, 1242, 1207, 1170, 1100, 1034, 901, 859, 824, 754, 668, 641, 608, 566 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{29}N_2O_5S^+$ $[M+H]^+$ 505.1792, found 505.1789; HPLC analysis: >99% ee (CHIRALCEL OD-H, isopropanol/hexane=5/95, 1.0 mL/min, UV: 254 nm), t_R = 14.24 min (major), 23.58 min (minor).

(1*R*,11b*R*)-Methyl 1-(4-isopropylphenyl)-4-tosyl-4,6,7,11b-tetrahydro-1*H*-pyridazino[6,1-*a*]isoquinoline-2-carboxylate (6au)

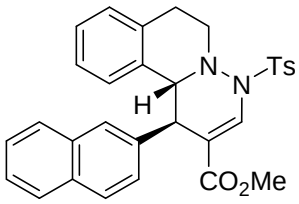


6au

Prepared according to the general procedure as described above in 75% yield. Purified by flash chromatography (7% EtOAc/PE). White solid, mp = 161.9 – 162.4 °C; $[\alpha]^{20}_{D}$

= +21.0 (*c* 1.52, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 (d, *J* = 1.3 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.13 – 6.96 (m, 4H), 6.70 – 6.54 (m, 3H), 5.34 (d, *J* = 7.7 Hz, 1H), 3.50 (s, 3H), 3.44 (dd, *J* = 1.3，9.9 Hz, 1H), 3.37 – 3.05 (m, 4H), 2.97 – 2.75 (m, 2H), 2.42 (s, 3H), 1.22 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.7, 147.3, 144.8, 137.2, 134.5, 133.6, 132.6, 132.3, 129.6, 128.4, 128.4, 127.9, 127.1, 126.1, 124.1, 112.8, 62.8, 51.2, 47.2, 41.0, 33.6, 29.1, 24.0, 23.9, 21.6; IR (film) ν_{max} 2958, 2923, 2852, 1717, 1627, 1597, 1511, 1493, 1435, 1368, 1290, 1261, 1240, 1207, 1185, 1171, 1101, 1019, 902, 859, 822, 764, 738, 668, 607, 588, 567, 553 cm^{-1}; HRMS (ESI) calcd for $C_{30}H_{33}N_2O_4S^+$ $[M+H]^+$ 517.2156, found 517.2152; HPLC analysis: >99% ee (CHIRALCEL OD-H, isopropanol/hexane=5/95, 1.0 mL/min, UV: 254 nm), t_R = 6.73 min (major), 11.31 min (minor).

(1*R*,11b*R*)-Methyl 1-(naphthalen-2-yl)-4-tosyl-4,6,7,11b-tetrahydro-1*H*-pyridazino[6,1-*a*]isoquinoline-2-carboxylate (6av)

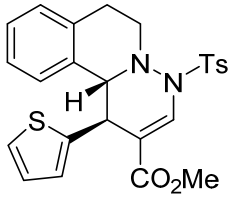


6av

Prepared according to the general procedure as described above in 89% yield. Purified by flash chromatography (7% EtOAc/PE). White solid, mp = 175.3 – 176.8 °C; $[\alpha]^{20}_D$ = –162.4 (*c* 1.57, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.37 (d, *J* = 1.3 Hz, 1H), 7.89 (d, *J* = 8.1 Hz, 2H), 7.84 – 7.73 (m, 1H), 7.72 – 7.58 (m, 2H), 7.51 – 7.39 (m, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.19 – 7.01 (m, 3H), 6.89 – 6.82 (m,1H), 6.59 – 6.46 (m, 1H), 5.27 (d, *J* = 7.7 Hz, 1H), 3.66 (d, *J* = 9.9 Hz, 1H), 3.46 (s, 3H), 3.44 – 3.25 (m, 2H), 3.25 – 3.12 (m, 2H), 2.97 – 2.84 (m, 1H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.6, 145.0, 134.4, 133.6, 133.3, 133.0, 132.5, 132.3, 129.7, 128.6, 128.4,

127.8, 127.7, 127.6, 127.3, 125.9, 125.5, 124.2, 112.8, 62.9, 51.3, 47.2, 41.6, 29.1, 21.7; IR (film) ν_{max} 2922, 2852, 1715, 1626, 1598, 1493, 1435, 1368, 1290, 1239, 1207, 1185, 1172, 1102, 1015, 885, 858, 817, 763, 749, 704, 670, 641, 600, 561, 478 cm^{-1}; HRMS (ESI) calcd for $C_{31}H_{29}N_2O_4S^+$ $[M+H]^+$ 525.1843, found 525.1839; HPLC analysis: >99% ee (CHIRALCEL OD-H, isopropanol/hexane=5/95, 1.0 mL/min, UV: 254 nm), t_R = 11.24 min (major), 23.04 min (minor).

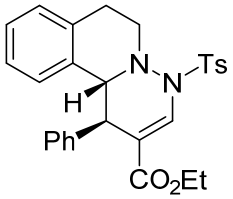
(1*R*,11b*R*)-Methyl 1-(thiophen-2-yl)-4-tosyl-4,6,7,11b-tetrahydro-1*H*-pyridazino [6,1-*a*]isoquinoline-2-carboxylate (6aw)



6aw

Prepared according to the general procedure as described above in 61% yield. Purified by flash chromatography (7% EtOAc/PE). White solid, mp = 147.7 – 148.5 °C; $[\alpha]^{20}_D$ = +109.8 (*c* 1.23, CH_2Cl_2); ^1H NMR (300 MHz, $CDCl_3$) δ 8.25 (d, *J* = 1.3 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.18 – 7.03 (m, 3H), 6.86 – 6.81 (m, 1H), 6.79 – 6.70 (m, 1H), 6.45 (d, *J* = 3.5 Hz, 1H), 5.58 (d, *J* = 7.7 Hz, 1H), 3.83 – 3.75 (m, 1H), 3.57 (s, 3H), 3.39 – 3.01 (m, 4H), 2.96 – 2.77 (m, 1H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.4, 144.9, 143.5, 134.2, 133.4, 132.6, 132.2, 129.7, 128.5, 128.3, 127.6, 127.4, 126.6, 126.4, 124.4, 123.9, 112.1, 63.0, 51.3, 47.1, 36.8, 29.0, 21.7; IR (film) ν_{max} 2920, 2850, 1717, 1625, 1597, 1455, 1435, 1367, 1290, 1262, 1240, 1206, 1185, 1171, 1137, 1119, 1101, 1035, 1013, 856, 815, 784, 764, 751, 735, 703, 669, 579, 552 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{25}N_2O_4S_2^+$ $[M+H]^+$ 481.1250, found 481.1253; HPLC analysis: >99% ee (CHIRALCEL OD-H, isopropanol/hexane=5/95, 1.0 mL/min, UV: 254 nm), t_R = 11.72 min (major), 21.50 min (minor).

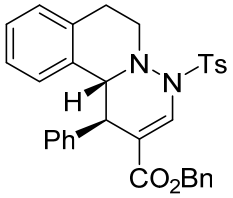
(1*R*,11b*R*)-Ethyl 1-phenyl-4-tosyl-4,6,7,11b-tetrahydro-1*H*-pyridazino[6,1-*a*]isoquinoline-2-carboxylate (6ay)



6ay

Prepared according to the general procedure as described above in 81% yield. Purified by flash chromatography (7% EtOAc/PE). White solid, mp = 122.0 – 123.5 °C; $[\alpha]^{20}_{D}$ = +18.3 (*c* 1.21, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.83 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H),7.17 – 7.13 (m, 3H), 7.10 – 7.07 (m, 2H), 6.72 – 6.58 (m, 3H), 5.35 (d, *J* = 7.7 Hz, 1H), 4.05 – 3.78 (m, 2H), 3.46 (d, *J* = 9.9Hz, 1H), 3.38 – 3.11 (m, 3H), 3.05 (d, *J* = 9.9 Hz, 1H), 2.93 – 2.80 (m, 1H), 2.41 (s, 3H), 0.95 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.3, 144.8, 140.3, 134.3, 133.6, 132.7, 132.3, 129.6, 128.5, 128.4, 128.0, 127.9, 127.2, 126.6, 124.1, 112.8, 62.7, 60.1, 47.2, 41.5, 29.0, 21.6, 13.8; IR (film) ν_{max} 2981, 2901, 2838, 1711, 1627, 1598, 1493, 1455, 1369, 1288, 1262, 1206, 1185, 1171, 1137, 1121, 1101, 1015, 811, 764, 725, 702, 668, 655, 577, 553 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{29}N_2O_4S^+$ $[M+H]^+$ 489.1843, found 489.1846; HPLC analysis: >99% ee (CHIRALCEL OD-H, isopropanol/hexane=5/95, 1.0 mL/min, UV: 254 nm), t_R = 8.74 min (major), 19.42 min (minor).

(1*R*,11b*R*)-Benzyl 1-phenyl-4-tosyl-4,6,7,11b-tetrahydro-1*H*-pyridazino[6,1-*a*]isoquinoline-2-carboxylate (6az)

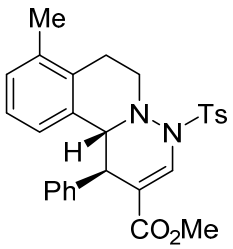


6az

Prepared according to the general procedure as described above in 72% yield. Purified

by flash chromatography (7% EtOAc/PE). White solid, mp = 125.7 – 126.3 °C; $[\alpha]^{20}_{D}$ = +20.1 (*c* 1.32, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.35 (d, *J* = 1.4 Hz, 1H), 7.89 – 7.74 (m, 2H), 7.31–7.20(m, 5H) , 7.17 – 7.12 (m, 3H), 7.09 – 7.03 (m, 2H), 7.03 – 6.95 (m, 2H), 6.71 – 6.59 (m, 3H), 5.32 (d, *J* = 7.7 Hz, 1H), 4.91 (dd, *J* = 31.7, 12.4 Hz, 2H), 3.47 (dd, *J* = 1.3，9.9 Hz, 1H), 3.34 – 3.09 (m, 3H), 3.05 (d, *J* = 9.9 Hz, 1H), 2.90 – 2.81 (m, 1H), 2.40 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.2, 144.8, 140.1, 135.8, 134.2, 133.5, 133.2, 132.3, 129.6, 128.4, 128.4, 128.3, 128.1, 127.9, 127.2, 126.7, 124.1, 112.4, 66.0, 62.8, 47.1, 41.5, 29.0, 21.6; IR (film) ν_{max} 2945, 2893, 1711, 1624, 1597, 1493, 1454, 1368, 1318, 1285, 1239, 1206, 1185, 1171, 1136, 1120, 1097, 1030, 1013, 904, 848, 815, 763, 737, 724, 700, 668, 655, 631, 575, 553, 512 cm^{-1}; HRMS (ESI) calcd for $C_{33}H_{31}N_2O_4S^+$ $[M+H]^+$ 551.1999, found 551.1998; HPLC analysis: >99% ee (CHIRALCEL OD-H, isopropanol/hexane=5/95, 1.0 mL/min, UV: 254 nm), t_R = 11.17 min (major), 21.15 min (minor).

(1*R*,11b*R*)-Methyl 8-methyl-1-phenyl-4-tosyl-4,6,7,11b-tetrahydro-1*H*-pyridazino [6,1-*a*]isoquinoline-2-carboxylate (6ba)

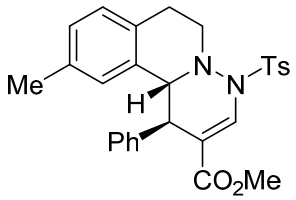


6ba

Prepared according to the general procedure as described above in 84% yield. Purified by flash chromatography (7% EtOAc/PE). White solid, mp = 169.3 – 171.1 °C; $[\alpha]^{20}_{D}$ = +90.5 (*c* 1.52, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.30 (d, *J* = 1.3 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.20 – 7.10 (m, 3H), 6.95 (d, *J* = 7.7 Hz, 1H), 6.75 – 6.64 (m, 2H), 6.63 – 6.52 (m, 1H), 5.19 (d, *J* = 7.7 Hz, 1H), 3.53 – 3.43 (m, 4H), 3.42 – 3.14 (m, 2H), 3.13 – 2.91 (m, 2H), 2.85 – 2.71 (m, 1H), 2.41

(s, 3H), 2.20 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.6, 144.8, 140.3, 136.0, 134.2, 133.6, 132.8, 130.8, 129.7, 128.6, 128.3, 128.0, 126.7, 125.8, 124.1, 112.6, 63.1, 51.2, 47.0, 41.3, 27.0, 21.6, 19.3; IR (film) ν_{max} 2980, 2905, 1713, 1626, 1597, 1474, 1369, 1286, 1265, 1224, 1198, 1185, 1173, 1105, 1072, 1015, 895, 816, 766, 737, 706, 669, 648, 574, 554, 542 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{29}N_2O_4S^+$ $[M+H]^+$ 489.1843, found 489.1840; HPLC analysis: >99% ee (CHIRALCEL OD-H, isopropanol/ hexane=5/95, 1.0 mL/min, UV: 254 nm), t_R = 9.01 min (major), 11.91 min (minor).

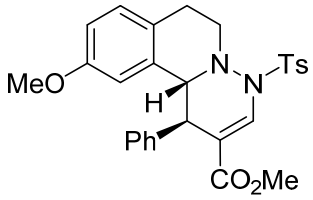
(1*R*,11b*R*)-Methyl 10-methyl-1-phenyl-4-tosyl-4,6,7,11b-tetrahydro-1*H*-pyridazino[6,1-*a*]isoquinoline-2-carboxylate (6ca)



6ca

Prepared according to the general procedure as described above in 75% yield. Purified by flash chromatography (7% EtOAc/PE). White solid, mp = 167.9 – 168.4 °C; $[\alpha]^{20}_D$ = +102.2 (*c* 1.63, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.32 (d, *J* = 1.3 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.23 – 7.12 (m, 3H), 6.99 – 6.86 (m, 2H), 6.74 – 6.64 (m, 2H), 5.05 (s, 1H), 3.50 (s, 3H), 3.44 (dd, *J* =1.3， 9.9Hz, 1H), 3.38 – 2.98 (m, 4H), 2.86 – 2.73 (m, 1H), 2.42 (s, 3H), 1.88 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.7, 144.8, 140.4, 134.0, 133.6, 133.4, 133.0, 129.7, 129.1, 128.6, 128.4, 128.2, 127.9, 126.7, 112.3, 62.9, 51.2, 47.5, 41.5, 28.7, 21.7, 20.6; IR (film) ν_{max} 2980, 2868, 2837, 1716, 1626, 1598, 1508, 1493, 1454, 1369, 1288, 1239, 1203, 1185, 1171, 1135, 1102, 895, 807, 759, 719, 702, 667, 577, 554 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{29}N_2O_4S^+$ $[M+H]^+$ 489.1843, found 489.1841; HPLC analysis: >99% ee (CHIRALCEL OD-H, isopropanol/hexane=2/98, 1.0 mL/min, UV: 254 nm), t_R = 13.15 min (major), 25.04 min (minor).

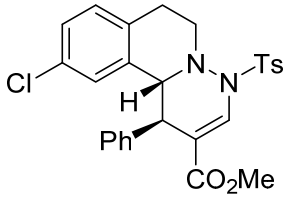
(1*R*,11b*R*)-Methyl 10-methoxy-1-phenyl-4-tosyl-4,6,7,11b-tetrahydro-1*H*-pyridazino[6,1-*a*]isoquinoline-2-carboxylate (6da)



6da

Prepared according to the general procedure as described above in 76% yield. Purified by flash chromatography (7% EtOAc/PE). White solid, mp = 169.1 – 170.8 °C; $[\alpha]^{20}_{D}$ = +90.6 (*c* 1.72, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.31 (d, *J* = 1.3 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.24 – 7.10 (m, 3H), 7.02 – 6.90 (m, 1H), 6.83 – 6.70 (m, 2H), 6.67 – 6.60 (m, 1H), 4.95 – 6.85 (m, 1H), 3.49 (d, *J* = 7.7 Hz, 4H), 3.37 – 3.02 (m, 7H), 2.85 – 2.71 (m, 1H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.6, 155.9, 144.9, 140.5, 135.2, 133.5, 132.9, 129.7, 129.4, 128.4, 128.2, 126.7, 124.2, 114.8, 112.4, 111.7, 62.9, 54.6, 51.2, 47.4, 41.4, 28.3, 21.6; IR (film) ν_{max} 2980, 2869, 2837, 1716, 1626, 1599, 1508, 1494, 1454, 1369, 1288, 1241, 1203, 1185, 1173, 1135, 1102, 896, 807, 759, 718, 703, 667, 578, 554 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{29}N_2O_5S^+$ $[M+H]^+$ 505.1792, found 505.1795; HPLC analysis: >99% ee (CHIRALCEL OD-H, isopropanol/hexane=5/95, 1.0 mL/min, UV: 254 nm), t_R = 12.25 min (major), 25.16 min (minor).

(1*R*,11b*R*)-Methyl 10-chloro-1-phenyl-4-tosyl-4,6,7,11b-tetrahydro-1*H*-pyridazino[6,1-*a*]isoquinoline-2-carboxylate (6ea)

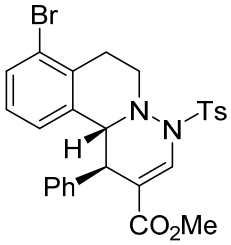


6ea

Prepared according to the general procedure as described above in 72% yield. Purified

by flash chromatography (7% EtOAc/PE). White solid, mp = 158.3 – 159.0 °C; $[\alpha]^{20}_{D}$ = +79.2 (*c* 0.95, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.32 (d, *J* = 1.3 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.25 – 7.16 (m, 3H), 7.11 – 6.96 (m, 2H), 6.74 – 6.62 (m, 2H), 5.24 (d, *J* = 1.8 Hz, 1H), 3.51 (s, 3H), 3.44 (d, *J* = 9.9 Hz, 1H), 3.35 – 3.11 (m, 3H), 2.96 (d, *J* = 9.9 Hz, 1H), 2.89 – 2.76 (m, 1H), 2.44 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.5, 145.1, 139.6, 135.8, 133.4, 133.0, 130.8, 129.83, 129.75, 128.3, 127.8, 127.4, 127.1, 112.1, 62.5, 51.3, 47.1, 41.3, 28.6, 21.7; IR (film) ν_{max} 2917, 2849, 1716, 1626, 1598, 1490, 1463, 1435, 1368, 1290, 1186, 1171, 1104, 1033, 858, 796, 752, 703, 680, 663, 576, 557 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{26}ClN_2O_4S^+$ $[M+H]^+$ 509.1296, found 509.1296; HPLC analysis: >99% ee (CHIRALCEL OD-H, isopropanol/hexane=5/95, 1.0 mL/min, UV: 254 nm), t_R = 8.03 min (major), 14.29 min (minor).

(1*R*,11b*R*)-Methyl 8-bromo-1-phenyl-4-tosyl-4,6,7,11b-tetrahydro-1*H*-pyridazino [6,1-*a*]isoquinoline-2-carboxylate (6fa)

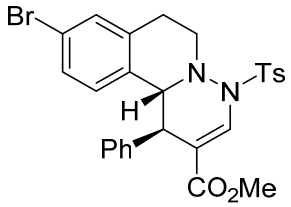


6fa

Prepared according to the general procedure as described above in 72% yield. Purified by flash chromatography (7% EtOAc/PE). White solid, mp = 173.0 – 173.8 °C; $[\alpha]^{20}_{D}$ = +81.2 (*c* 1.28, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.30 (d, *J* = 1.3 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 2H), 7.41 – 7.27 (m, 3H), 7.24 – 7.09 (m, 3H), 6.75 – 6.65 (m, 2H), 6.60 – 6.47(m, 1H), 5.29 (d, *J* = 7.7 Hz, 1H), 3.57 – 3.39 (m, 4H), 3.38 – 3.24 (m, 1H), 3.24 – 2.87 (m, 4H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ165.5, 145.0, 139.8, 136.4, 133.4, 132.8, 132.2, 131.4, 129.7, 128.4, 128.2, 127.1, 126.9,

125.7, 124.8, 112.3, 62.8, 51.3, 46.8, 41.2, 30.4, 21.7; IR (film) ν_{max} 2949, 1716, 1625, 1597, 1566, 1492, 1437, 1369, 1290, 1224, 1200, 1185, 1171, 1135, 1104, 1015, 903, 858, 814, 780, 764, 732, 703, 667, 639, 572, 554 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{26}BrN_2O_4S^+$ $[M+H]^+$ 553.0791, found 553.0794; HPLC analysis: >99% ee (CHIRALCEL OD-H, isopropanol/hexane=5/95, 1.0 mL/min, UV: 254 nm), t_R = 9.99 min (major), 12.71 min (minor).

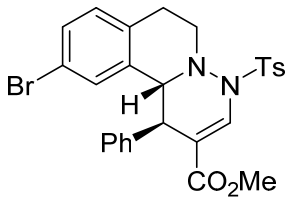
(1*R*,11b*R*)-Methyl 9-bromo-1-phenyl-4-tosyl-4,6,7,11b-tetrahydro-1*H*-pyridazino [6,1-*a*]isoquinoline-2-carboxylate (6ga)



6ga

Prepared according to the general procedure as described above in 66% yield. Purified by flash chromatography (7% EtOAc/PE). White solid, mp = 165.8 – 167.3 °C; $[\alpha]^{20}_D$ = +106.7 (*c* 1.59, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.29 (d, *J* = 1.3 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.26 – 7.22 (m, 1H), 7.21 – 7.11 (m, 3H), 6.80 – 6.74 (m, 1H), 6.72 – 6.65 (m, 2H), 5.17 (d, *J* = 8.3 Hz, 1H), 3.50 (s, 3H), 3.46 – 3.39 (m, 1H), 3.35 – 3.08 (m, 3H), 2.98 (d, *J* = 9.9 Hz, 1H), 2.91 – 2.77 (m, 1H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.0, 145.1, 142.9, 133.9, 133.4, 133.3, 132.3, 129.8, 129.5, 128.6, 128.3, 127.6, 127.4, 124.2, 122.1, 112.3, 62.5, 60.2, 47.1, 41.2, 28.9, 21.7; IR (film) ν_{max} 2980, 1716, 1626, 1597, 1568, 1492, 1437, 1369, 1293, 1224, 1185, 1171, 1138, 1104, 1015, 903, 858, 814, 783, 764, 732, 667, 639, 578, 554 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{26}BrN_2O_4S^+$ $[M+H]^+$ 553.0791, found 553.0795. HPLC analysis: >99% ee (CHIRALCEL OD-H, isopropanol/hexane=5/95, 1.0 mL/min, UV: 254 nm), t_R = 11.28 min (major), 23.44 min (minor).

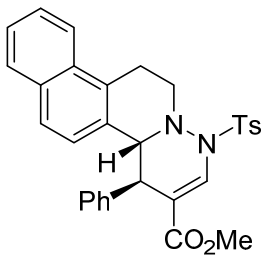
(1*R*,11b*R*)-Methyl 10-bromo-1-phenyl-4-tosyl-4,6,7,11b-tetrahydro-1*H*-pyridazino[6,1-*a*]isoquinoline-2-carboxylate (6ha)



6ha

Prepared according to the general procedure as described above in 71% yield. Purified by flash chromatography (7% EtOAc/PE). White solid, mp = 162.9 – 163.9 °C; $[\alpha]^{20}_{D}$ = +145.9 (*c* 1.01, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.82 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.25 – 7.13 (m, 4H),7.01 – 6.91 (m, 1H), 6.74 – 6.62 (m, 2H), 5.34 (s, 1H), 3.51 (s, 3H), 3.43 (d, *J* = 9.9 Hz, 1H), 3.34 – 3.08 (m, 3H), 2.96 (d, *J* = 9.9 Hz, 1H), 2.88 – 2.73 (m, 1H), 2.44 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.5, 145.1, 139.6, 136.1, 133.4, 133.1, 131.3, 130.7, 130.2, 130.1, 129.8, 128.3, 127.1, 117.8, 112.0, 62.5, 51.3, 47.1, 41.3, 28.7, 21.7; IR (film) ν_{max} 2920, 2850, 1716, 1627, 1597, 1486, 1454, 1435, 1368, 1313, 1291, 1238, 1205, 1185, 1171, 1131, 1104, 1034, 1014, 905, 858, 815, 795, 760, 723, 703, 673, 660, 623, 575, 555, 530 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{26}BrN_2O_4S^+$ $[M+H]^+$ 553.0791, found 553.0789; HPLC analysis: >99% ee (CHIRALCEL OD-H, isopropanol/hexane=5/95, 1.0 mL/min, UV: 254 nm), t_R = 11.47 min (major), 24.00 min (minor).

(4*R*,4a*R*)-Methyl 4-phenyl-1-tosyl-4,4a,11,12-tetrahydro-1*H*-benzo[f]pyridazino[6,1-*a*]isoquinoline-3-carboxylate (6ia)

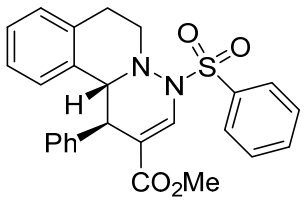


6ia

Prepared according to the general procedure as described above in 86% yield. Purified

by flash chromatography (7% EtOAc/PE). White solid, mp = 123.3 – 125.2 °C; $[\alpha]^{20}_D$ = +85.7 (*c* 1.03, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.37 (d, *J* = 1.3 Hz, 1H), 7.82 – 7.76 (m, 3H), 7.72 (d, *J* = 7.7 Hz, 1H), 7.60 – 7.40 (m, 2H), 7.36 – 7.12 (m, 6H), 6.82 – 6.68 (m, 2H), 5.52 – 5.38 (m, 1H), 3.60 (d, *J* = 9.9 Hz, 1H), 3.56 – 3.33 (m, 7H), 3.16 (d, *J* = 9.9 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.6, 144.9, 140.2, 133.5, 133.0, 132.6, 132.5, 131.6, 129.7, 128.4, 128.2, 127.9, 126.9, 126.2, 126.1, 125.7, 124.5, 123.0, 112.6, 63.0, 51.3, 46.9, 41.7, 26.3, 21.7; IR (film) ν_{max} 2920, 2854, 1725, 1626, 1598, 1497, 1437, 1368, 1293, 1235, 1218, 1186, 1015, 886, 859, 817, 765,705, 670, 643, 554, 479 cm^{-1}; HRMS (ESI) calcd for $C_{31}H_{29}N_2O_4S^+$ $[M+H]^+$ 525.1843, found 525.1841; HPLC analysis: 98% ee (CHIRALCEL OD-H, isopropanol/hexane=5/95, 1.0 mL/min, UV: 254 nm), t_R = 9.94 min (major), 14.61 min (minor).

(1*R*,11b*R*)-Methyl 1-phenyl-4-(phenylsulfonyl)-4,6,7,11b-tetrahydro-1*H*-pyridazino[6,1-*a*]isoquinoline-2-carboxylate (6ja)

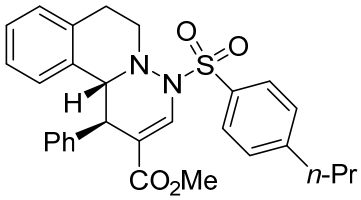


6ja

Prepared according to the general procedure as described above in 70% yield. Purified by flash chromatography (7% EtOAc/PE). White solid, mp = 163.6 – 164.4 °C; $[\alpha]^{20}_D$ = –18.7 (*c* 1.17, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.31 (d, *J* = 1.3 Hz, 1H), 8.07 – 7.89 (m, 2H), 7.71 – 7.57 (m, 1H), 7.57 – 7.45 (m, 2H), 7.22 – 7.11 (m, 3H), 7.11 – 7.03 (m, 2H), 6.74 – 6.58 (m, 3H), 5.31 (d, *J* = 8.1 Hz, 1H), 3.55 – 3.42 (m, 4H), 3.40 – 3.12 (m, 3H), 2.98 (d, *J* = 9.9 Hz, 1H), 2.93 – 2.79 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.5, 140.0, 136.4, 134.2, 133.8, 132.8, 132.2, 129.0, 128.5, 128.3,

128.1, 127.9, 127.3, 126.8, 124.2, 112.9, 62.7, 51.3, 47.2, 41.4, 29.0; IR (film) ν_{max} 2920, 2850, 1713, 1626, 1448, 1437, 1370, 1267, 1208, 1173, 1105, 1093, 1034, 896, 859, 740, 707, 655, 640, 589, 554 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{25}N_2O_4S^+$ $[M+H]^+$ 461.1530, found 461.1525; HPLC analysis: >99% ee (CHIRALCEL OD-H, isopropanol/hexane=5/95, 1.0 mL/min, UV: 254 nm), t_R = 10.22 min (major), 19.66 min (minor).

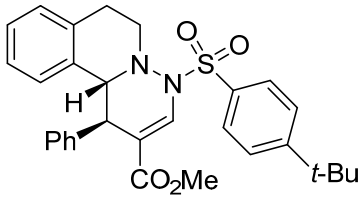
(1*R*,11b*R*)-Methyl 1-phenyl-4-((4-propylphenyl)sulfonyl)-4,6,7,11b-tetrahydro-1H-pyridazino[6,1-*a*]isoquinoline-2-carboxylate (6ka)



6ka

Prepared according to the general procedure as described above in 67% yield. Purified by flash chromatography (7% EtOAc/PE). White solid, mp = 119.5 – 121.3 °C; $[\alpha]^{20}_D$ = –50.7 (*c* 1.02, CH_2Cl_2); ^1H NMR (300 MHz, $CDCl_3$) δ 8.30 (d, *J* = 1.3 Hz, 1H), 7.93 – 7.78 (m, 2H), 7.34 – 7.26 (m, 2H), 7.22 – 7.11 (m, 3H), 7.10 – 7.03 (m, 2H), 6.77 – 6.52 (m, 3H), 5.27 (d, *J* = 7.7 Hz, 1H), 3.50 (s, 3H), 3.48 – 3.41 (m, 1H), 3.39 – 3.13 (m, 3H), 2.97 – 2.80 (m, 2H), 2.71 – 2.57 (m, 2H), 1.69 – 1.53 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.6, 149.5, 140.1, 134.2, 133.5, 133.1, 132.3, 129.1, 128.5, 128.4, 128.1, 127.8, 127.2, 126.7, 124.1, 112.8, 62.6, 51.2, 47.2, 41.4, 37.8, 29.0, 24.2, 13.5; IR (film) ν_{max} 2956, 2919, 2850, 1716, 1626, 1598, 1492, 1455, 1436, 1409, 1369, 1318, 1290, 1265, 1241, 1207, 1186, 1172, 1137, 1104, 1032, 1015, 899, 858, 764, 740, 707, 683, 655, 638, 621, 554, 512 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{31}N_2O_4S^+$ $[M+H]^+$ 503.1999, found 503.1999; HPLC analysis: >99% ee (CHIRALCEL OD-H, isopropanol/hexane=5/95, 1.0 mL/min, UV: 254 nm), t_R = 7.78 min (major), 13.94 min (minor).

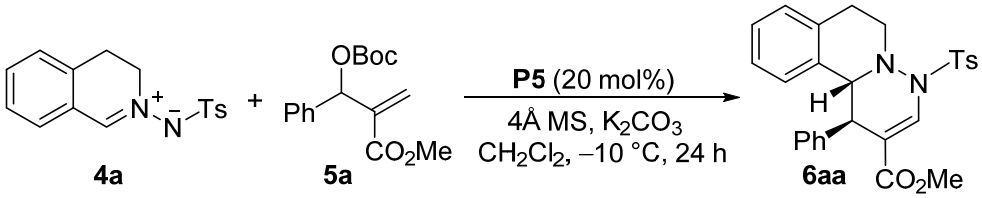
(1*R*,11b*R*)-Methyl 4-((4-(*tert*-butyl)phenyl)sulfonyl)-1-phenyl-4,6,7,11b-tetrahydro-1*H*-pyridazino[6,1-*a*]isoquinoline-2-carboxylate (6la)



6la

Prepared according to the general procedure as described above in 74% yield. Purified by flash chromatography (7% EtOAc/PE). White solid, mp = 122.1 – 122.7 °C; $[\alpha]^{20}_{D}$ = –54.3 (*c* 1.15, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 (d, *J* = 1.3 Hz, 1H), 7.92 – 7.81 (m, 2H), 7.56 – 7.46 (m, 2H), 7.21 – 7.02 (m, 5H), 6.70 – 6.56(m, 3H), 5.19 (d, *J* = 7.7 Hz, 1H), 3.50 (s, 3H), 3.46 – 3.38 (m, 1H), 3.38 – 3.12 (m, 3H), 2.96 – 2.81 (m, 1H), 2.69 (d, *J* = 9.9 Hz, 1H), 1.30 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.6, 158.0, 140.1, 134.2, 133.3, 133.0, 132.4, 128.5, 128.2, 128.0, 127.7, 127.2, 126.8, 126.0, 124.1, 113.2, 62.4, 51.2, 47.2, 41.3, 35.3, 31.0, 29.0; IR (film) ν_{max} 2918, 2850, 1716, 1626, 1594, 1438, 1371, 1267, 1197, 1176, 1104, 1086, 1043, 897, 857, 743, 707, 647, 623, 582, 554 cm^{-1}; HRMS (ESI) calcd for $C_{30}H_{33}N_2O_4S^+$ $[M+H]^+$ 517.2156, found 517.2154; HPLC analysis: >99% ee (CHIRALCEL OD-H, isopropanol/hexane=5/95, 1.0 mL/min, UV: 254 nm), t_R = 7.31 min (major), 12.88 min (minor).

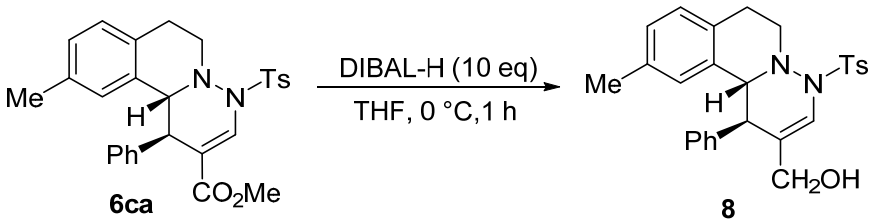
Asymmetric [3 + 3] Cycloaddition of Morita–Baylis–Hillman Carbonate with C,N-Cyclic Azomethine Imine on a Large Scale



Under nitrogen atmosphere, azomethine imine **4a** (0.3 g, 1.0 mmol), MBH carbonate **5a** (584 mg, 2.0 mmol), K_2CO_3 (200 mg), 4Å MS (100 mg) and chiral phosphine **P5** (73 mg, 0.2 mmol) were dissolved in 40 mL of CH_2Cl_2. The resulting mixture was stirred at −10 °C for about 24 h, and then was concentrated in vacuo. The residue was purified through flash column chromatography (7% EtOAc/PE) to afford the

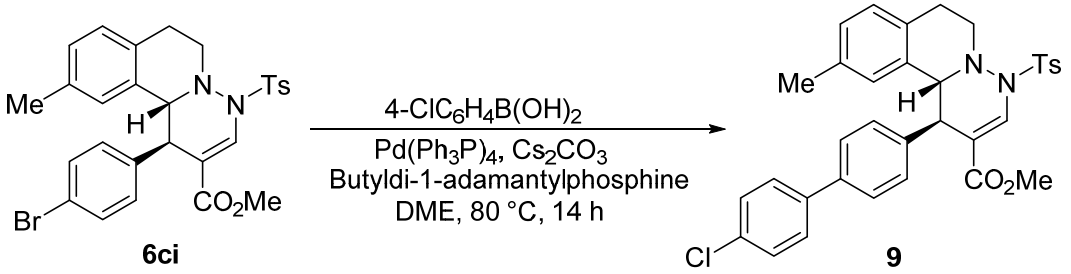
corresponding product **6aa** in 76% yield (0.36 g). White solid, mp = 145.6 – 147.2 °C; $[\alpha]^{20}_D$ = + 17.4 (*c* 1.15, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.30 (d, *J* = 1.3 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.23 – 7.11 (m, 3H), 7.08 (d, *J* = 3.9 Hz, 2H), 6.71 – 6.60 (m, 3H), 5.33 (d, *J* = 7.7 Hz, 1H), 3.50 (s, 3H), 3.48 – 3.45 (m, 1H), 3.42 – 3.09 (m, 3H), 3.06 (d, *J* = 9.9 Hz, 1H), 2.96 – 2.77 (m, 1H), 2.41 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.6, 144.9, 140.1, 134.3, 133.5, 132.9, 132.3, 129.6, 128.5, 128.4, 128.1, 127.8, 127.2, 126.7, 124.1, 112.5, 62.8, 51.2, 47.2, 41.4, 29.0, 21.6; IR (film) ν_{max} 2950, 2859, 1715, 1626, 1598, 1492, 1454, 1435, 1400, 1367, 1319, 1290, 1263, 1240, 1207, 1185, 1171, 1135, 1103, 1032, 1014, 903, 858, 815, 764, 736, 726, 702, 667, 655, 631, 618, 576, 553, 517 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{26}N_2NaO_4S^+$ $[M+Na]^+$ 497.1505, found 497.1502; HPLC analysis: 98% ee (CHIRALCEL OD-H, isopropanol/hexane=5/95, 1.0 mL/min, UV: 254 nm), t_R = 9.28 min (major), 17.87 min (minor).

Further Transformations of the Products

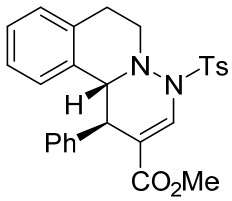


Under nitrogen atmosphere, a solution of **6ca** (50.2 mg, 0.1 mmol, >99% ee) in 1.0 mL of dry THF was added dropwise to a solution of DIBAL (1.1 M in cyclohexane, 10.0 equiv) in 0.2 mL of dry THF at 0 °C within 20 minutes, and then the resulting solution continued to be stirred at 0 °C for 40 minutes. The reaction was quenced with saturated aqueous NH_4Cl solution followed by 2 N of HCl solution. The mixture was extracted four times with Et_2O and the combined organic phase was washed with brine and was dried with anhydrous Na_2SO_4. Removal of the solvent yielded the crude product, which was purified by flash chromatography on silica gel (25% EtOAc/PE containing) to afford the product **8** in 76 % yield (35.0 mg). Brownish yellow solid, mp = 98.7 – 99.6 °C; $[\alpha]^{20}_D$ = +51.35 (*c* 1.04, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 – 7.73 (m, 2H), 7.34 – 7.13 (m, 6H), 6.94 – 6.83 (m, 2H), 6.69 – 6.66 (m, 2H), 5.07 (s, 1H), 3.89 – 3.77 (m, 2H), 3.39 – 3.22 (m, 2H), 3.22 – 3.00 (m, 3H), 2.82 – 2.68 (m, 1H), 2.43 (s, 3H), 1.85 (s, 3H), 1.67 – 1.49 (m, 1H); ^{13}C NMR (75 MHz,

$CDCl_3$) δ 144.1, 138.8, 134.6, 133.9, 133.3, 129.4, 129.3, 128.4, 128.3, 128.2, 127.6, 127.1, 122.1, 120.6, 63.1, 61.3, 47.4, 42.2, 28.8, 21.6, 20.6; IR (film) ν_{max} 3385, 2924, 2855, 1599, 1492, 1454, 1359, 1305, 1262, 1236, 1167, 1093, 1021, 879, 814, 794, 756, 737, 703, 674, 639, 612, 582, 554, 523, 507, 488, 470 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{27}N_2O_3S^-$ $[M-H]^-$ 459.1748, found 459.1750; HPLC analysis: >99% ee (CHIRALCEL OD-H, isopropanol/hexane=20/80, 1.0 mL/min, UV: 254 nm), t_R = 8.80 min (major), 15.37 min (minor).



Under argon atmosphere, the compound **6ci** (56.6 mg, 0.1 mmol, >99% ee), 4-chlorophenylboronic acid (0.15 mmol), Cs_2CO_3 (0.2 mmol), $Pd(Ph_3P)_4$ (0.005 mmol) and butyldi-1-adamantylphosphine (0.006 mmol) were added sequentially to a dry tube. After adding DME (1.0 mL) to the reaction system, the reaction mixture was stirred at 80 °C for 14 h. Then, the reaction mixture was subjected to flash column chromatography (petroleum ether/ethyl acetate = 15/1) to afford the product **9** in 66% yield (39.5 mg). White solid, mp = 173.7 – 175.4 °C; $[\alpha]^{20}_D$ = –130.14 (*c* 1.05, CH_2Cl_2); ^1H NMR (300 MHz, $CDCl_3$) δ 8.35 (d, *J* = 1.3 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 2H), 7.54 – 7.44 (m, 2H), 7.45 – 7.26 (m, 6H), 7.03 – 6.84 (m, 2H), 6.85 – 6.66 (m, 2H), 5.12 (s, 1H), 3.54 (s, 3H), 3.51 – 3.44 (m, 1H), 3.34 – 3.04 (m, 4H), 2.89 – 2.74 (m, 1H), 2.42 (s, 3H), 1.86 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.6, 144.9, 140.0, 139.3, 138.3, 133.9, 133.6, 133.4, 133.3, 129.7, 129.1, 128.9, 128.6, 128.4, 128.3, 128.2, 128.0, 126.5, 111.8, 62.9, 51.3, 47.5, 41.3, 28.7, 21.7; IR (film) ν_{max} 2922, 2853, 1716, 1623, 1485, 1435, 1368, 1290, 1262, 1185, 1170, 1134, 1099, 1005, 861, 815, 797, 752, 667, 584, 554, 512 cm^{-1}; HRMS (ESI) calcd for $C_{34}H_{32}ClN_2O_4S^+$ $[M+H]^+$ 599.1766, found 599.1764; HPLC analysis: >99% ee (CHIRALCEL OD-H, isopropanol/hexane=4/96, 1.0 mL/min, UV: 254 nm), t_R =13.3 min (major), 30.87 min (minor).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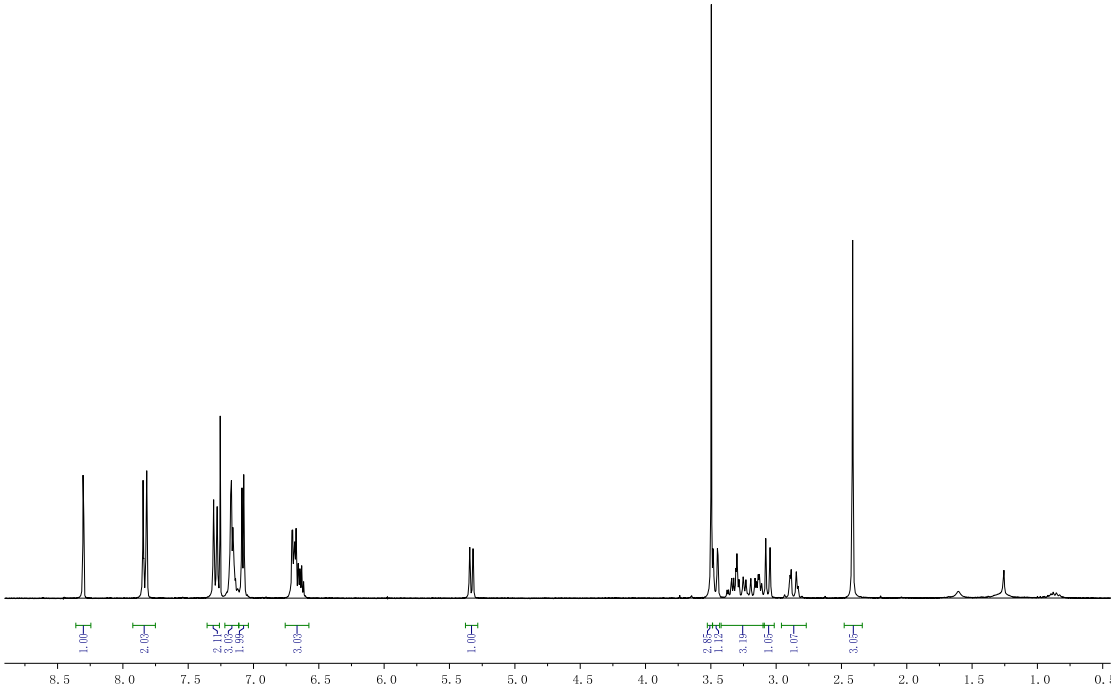
6aa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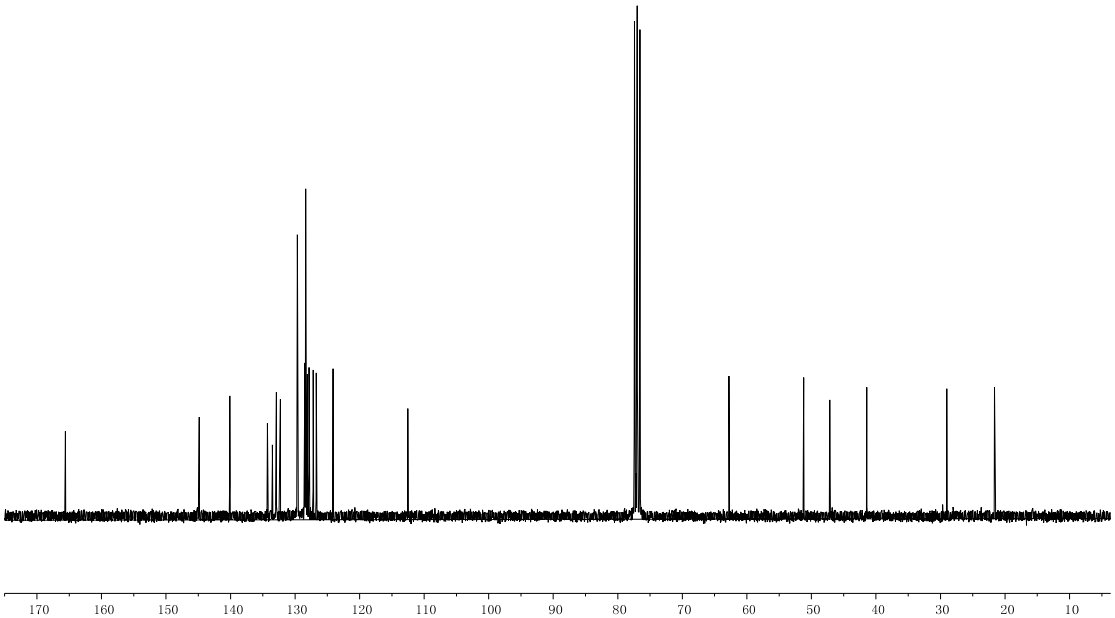
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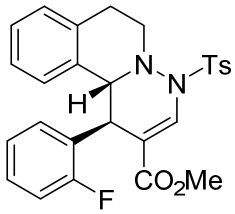
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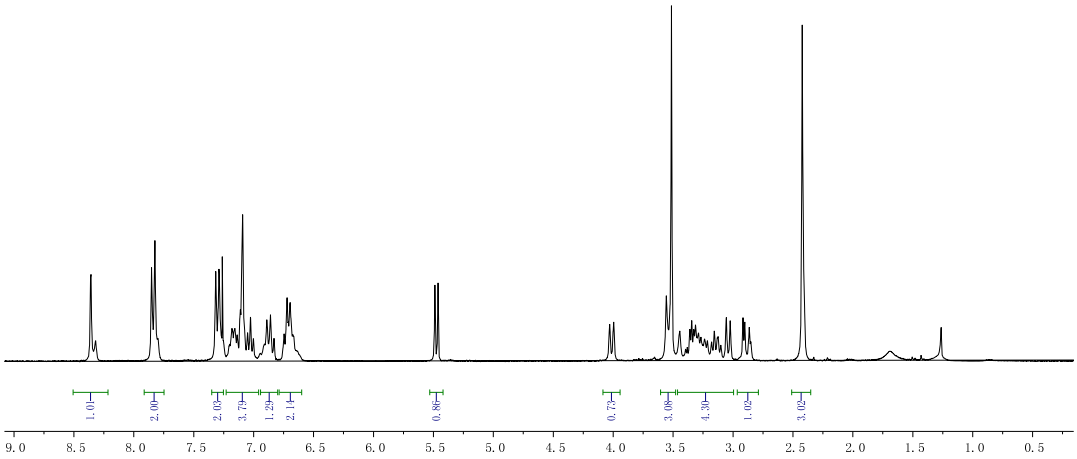
6ab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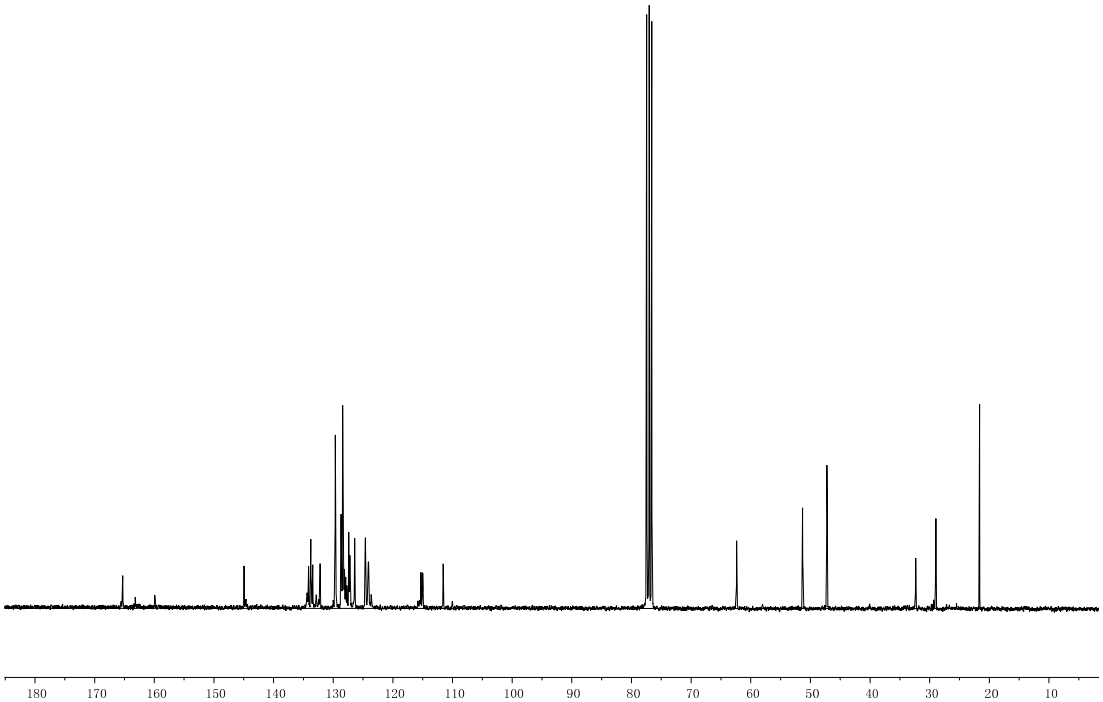
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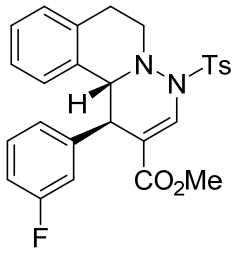
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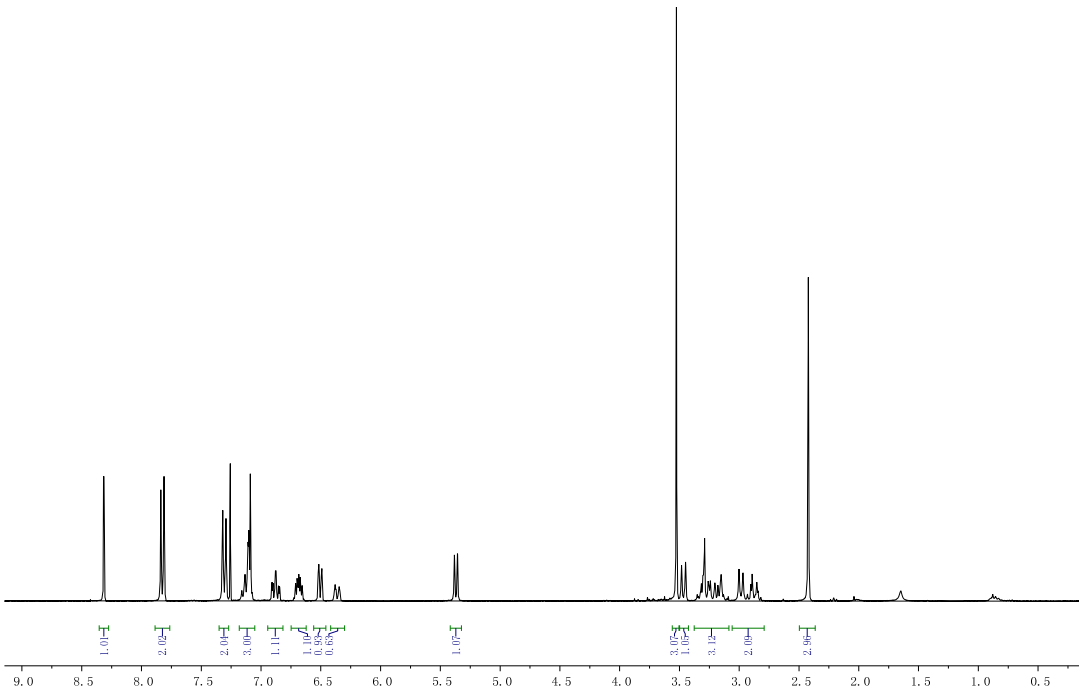
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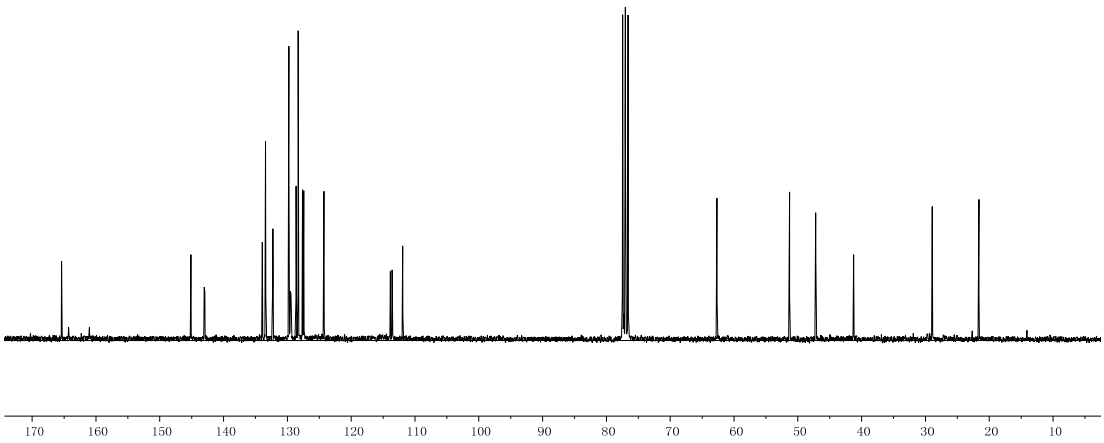
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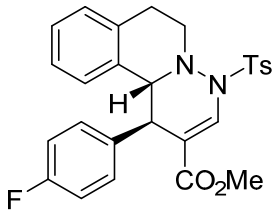
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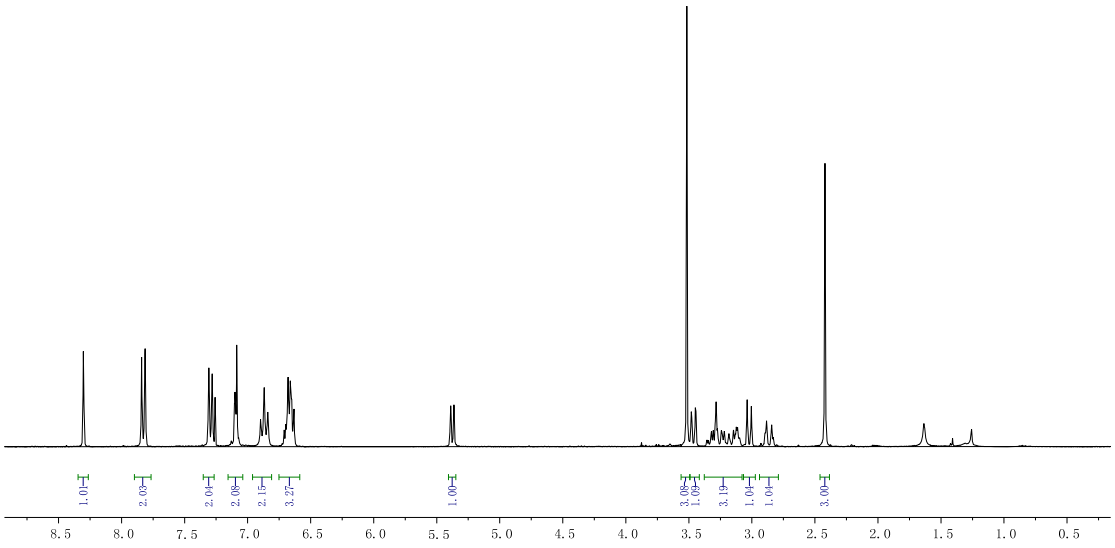
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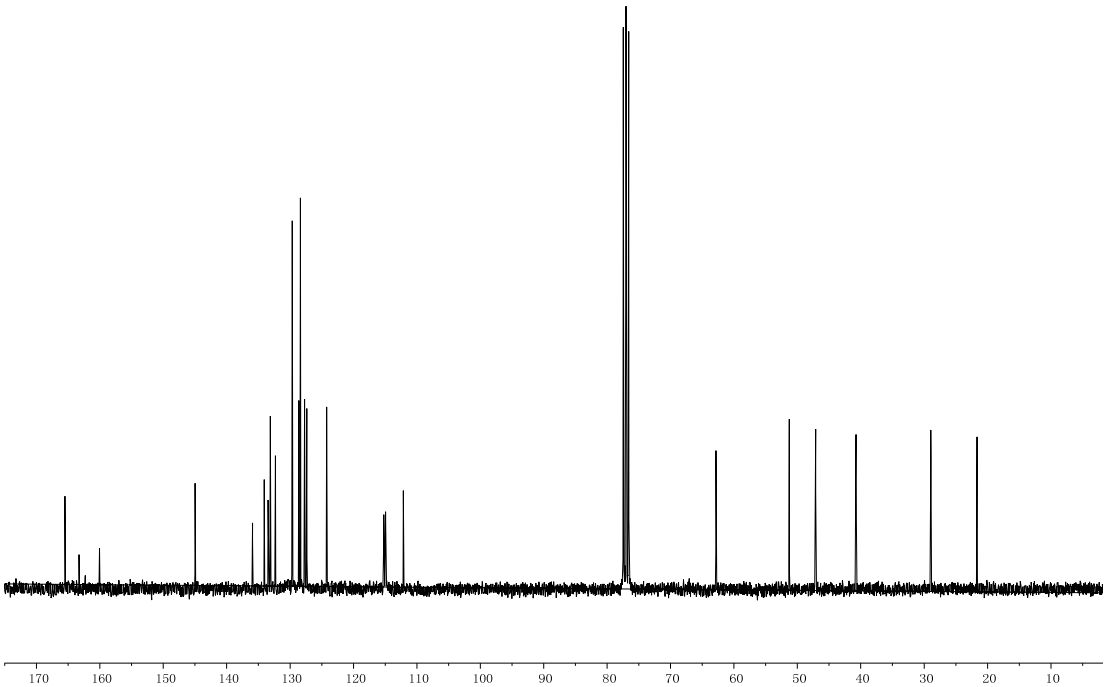
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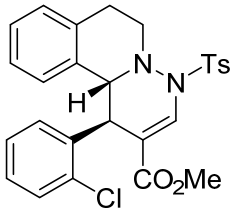
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CO2Me
Cl

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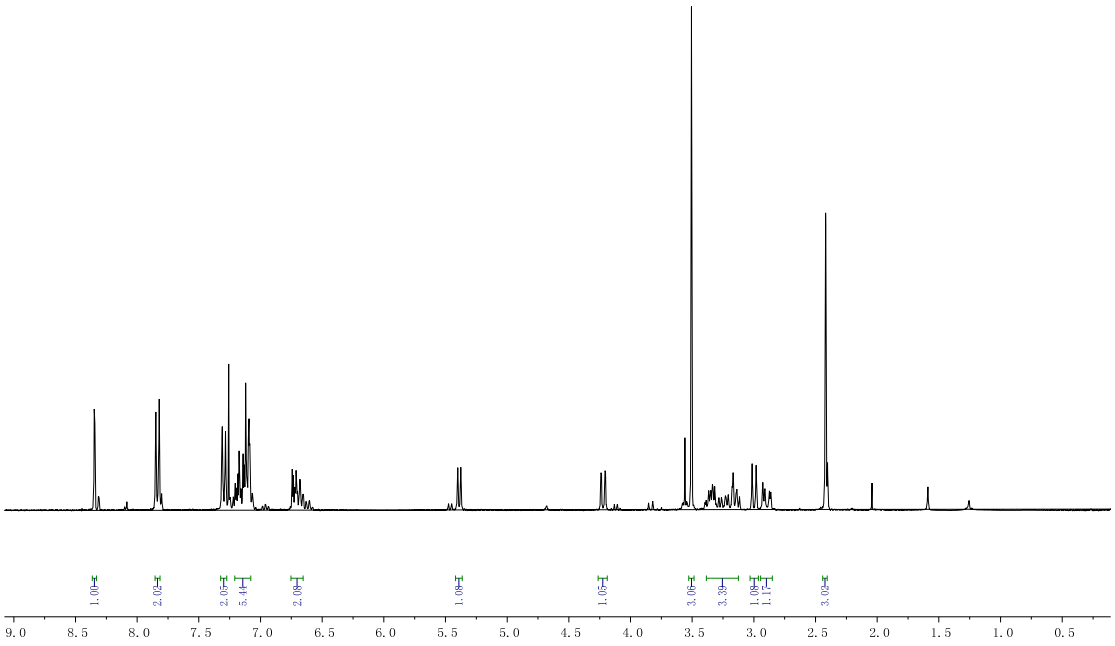
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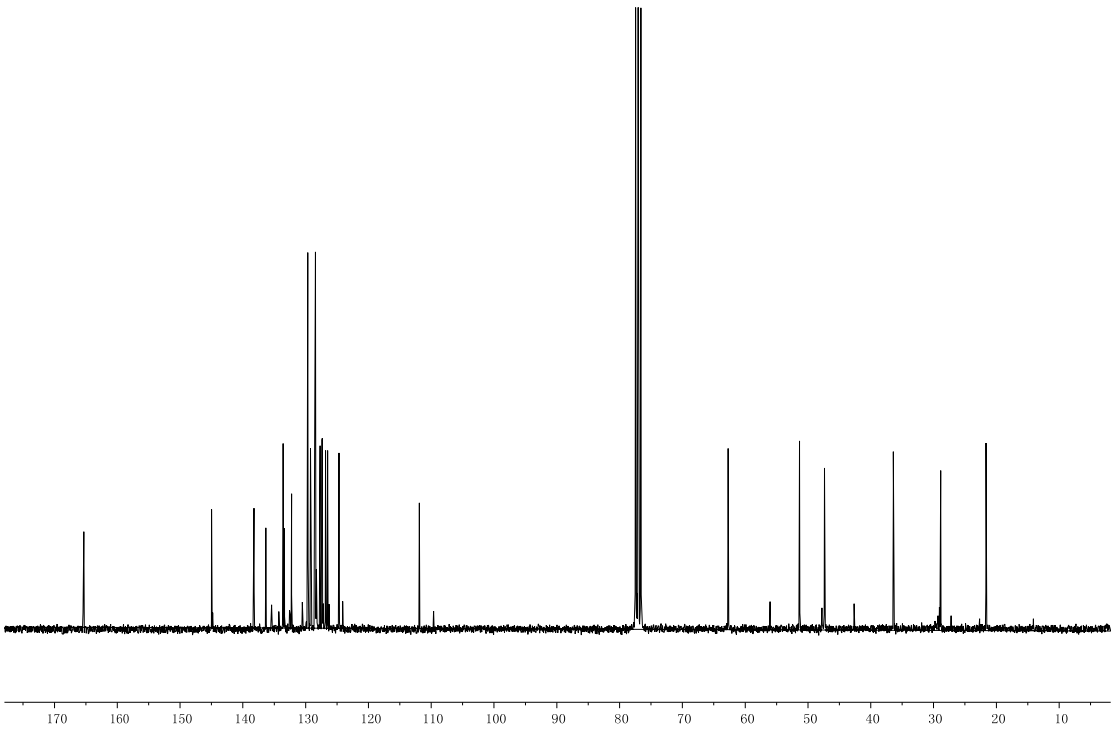
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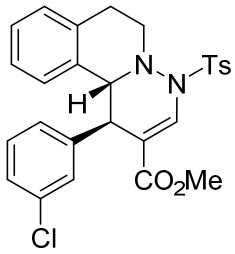
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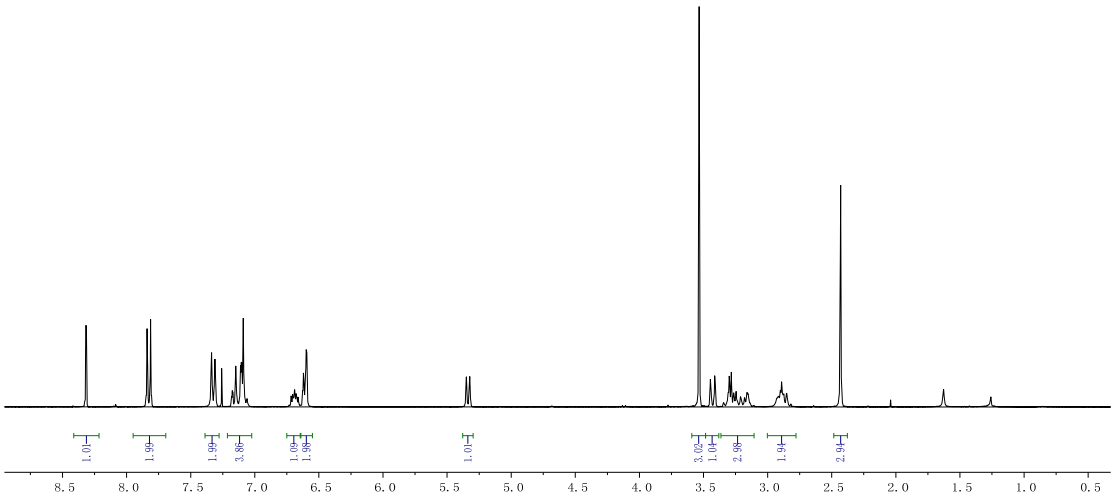
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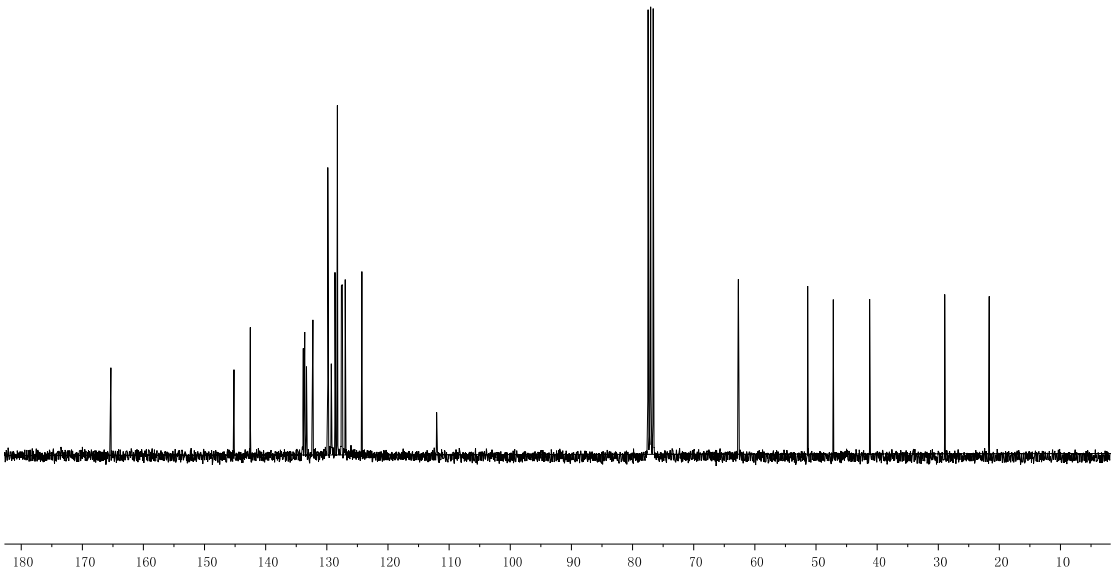
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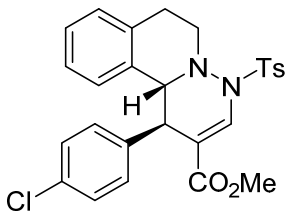

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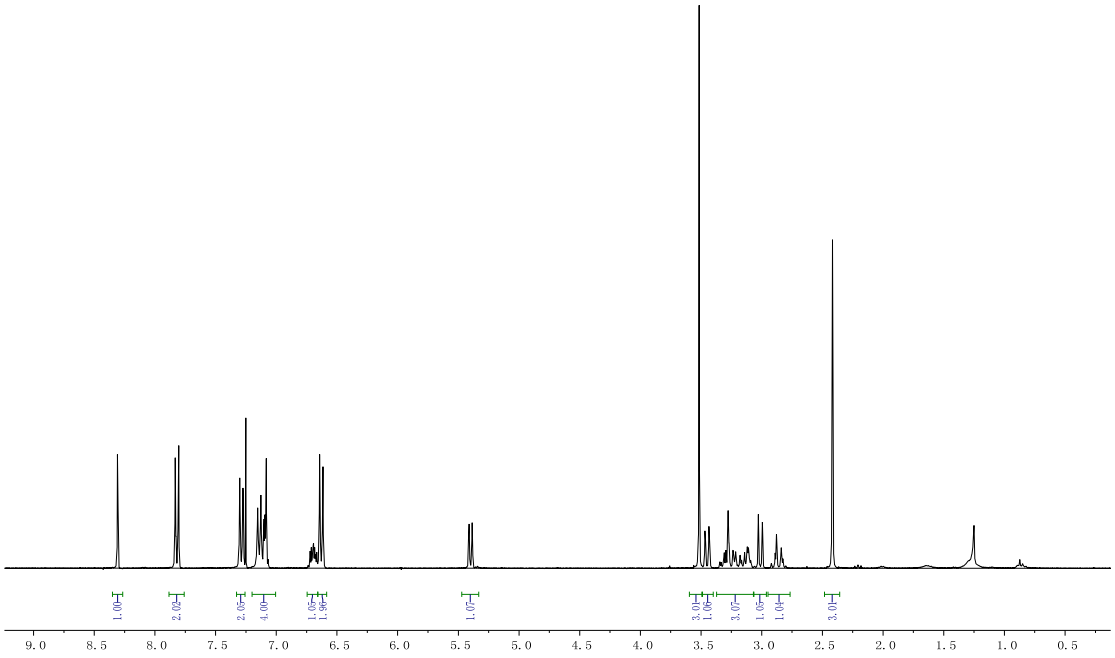

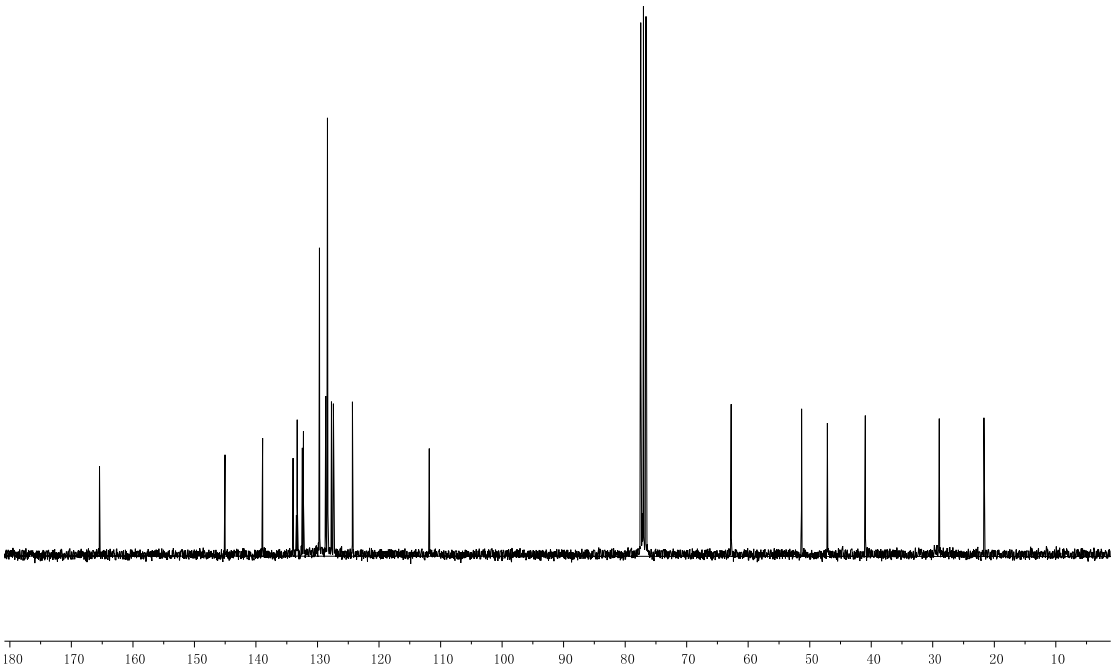

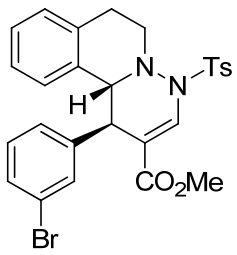
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Ts
H
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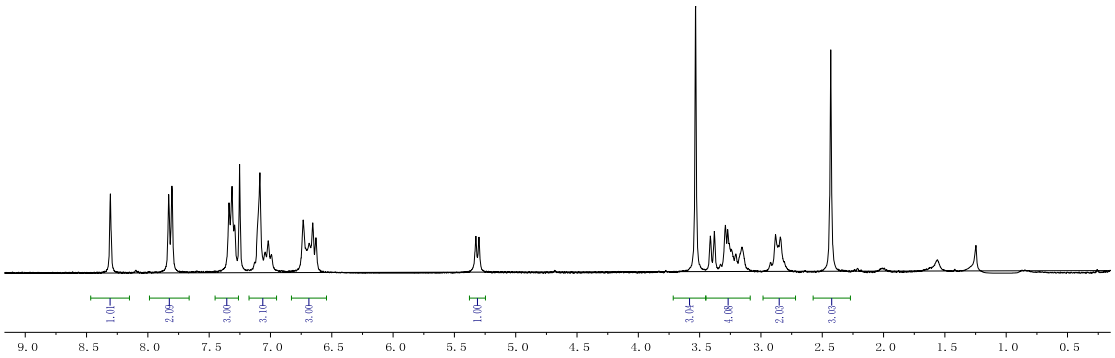
Br

6ah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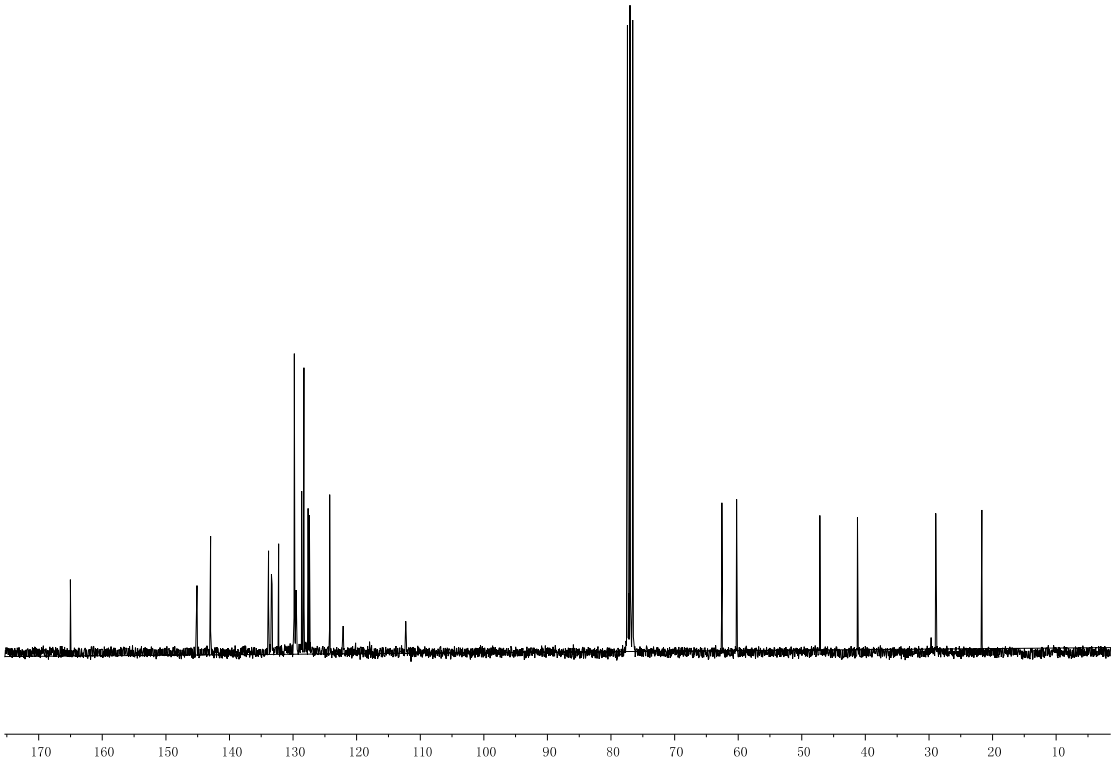
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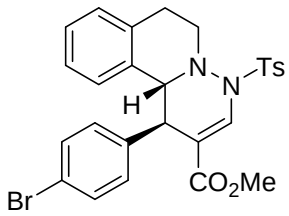
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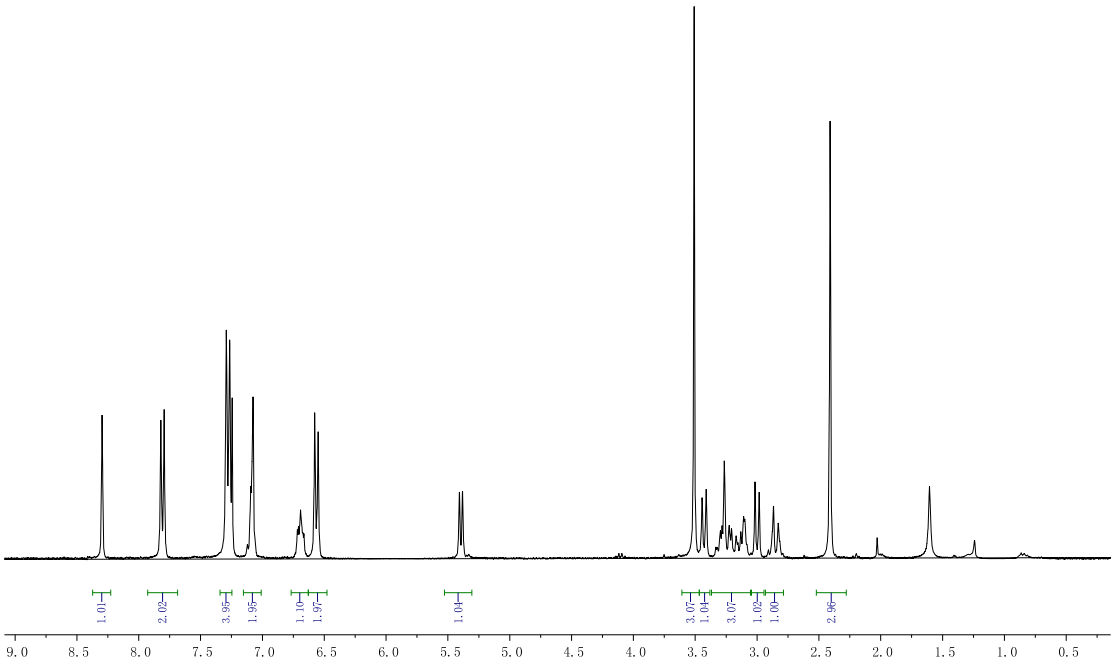
6ai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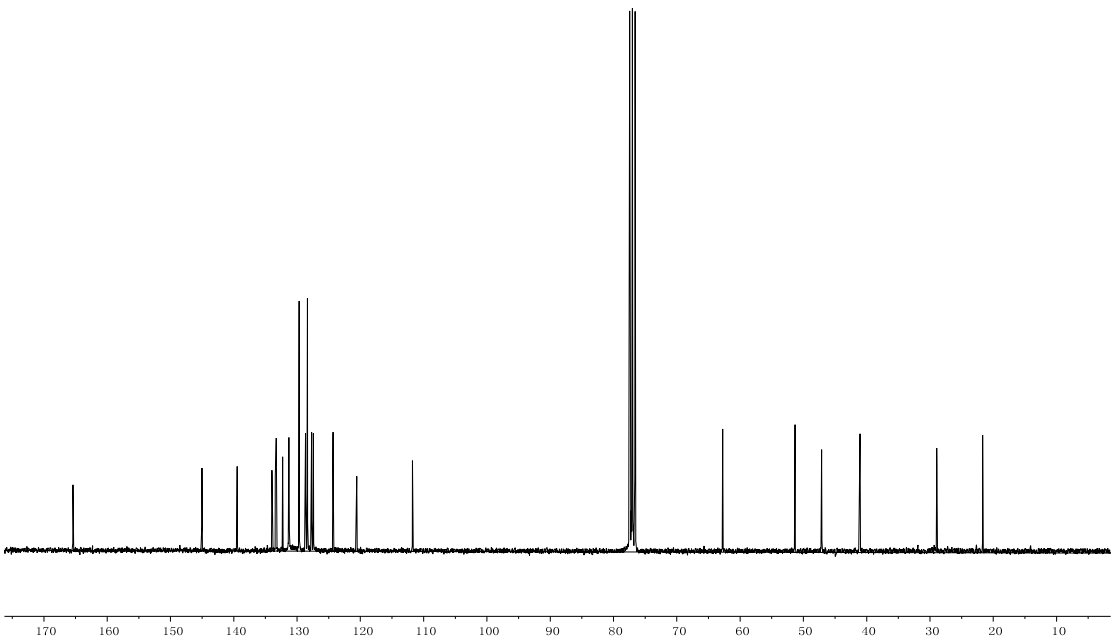
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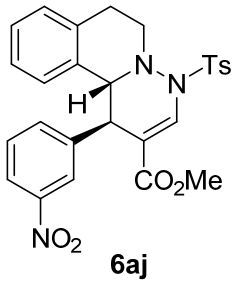
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CO2Me
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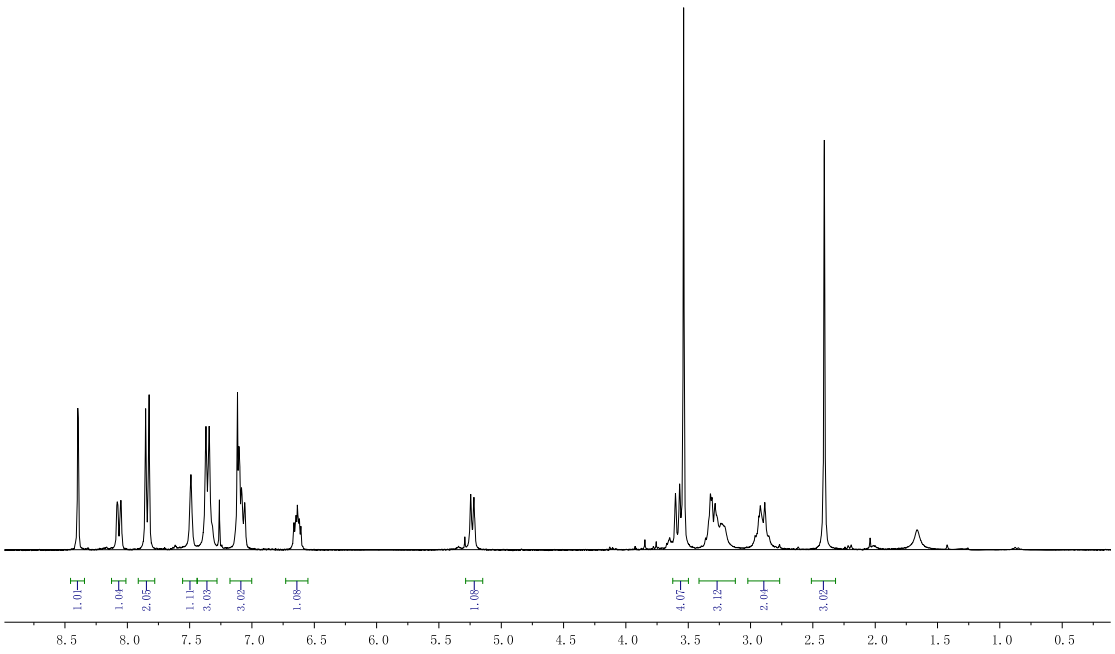
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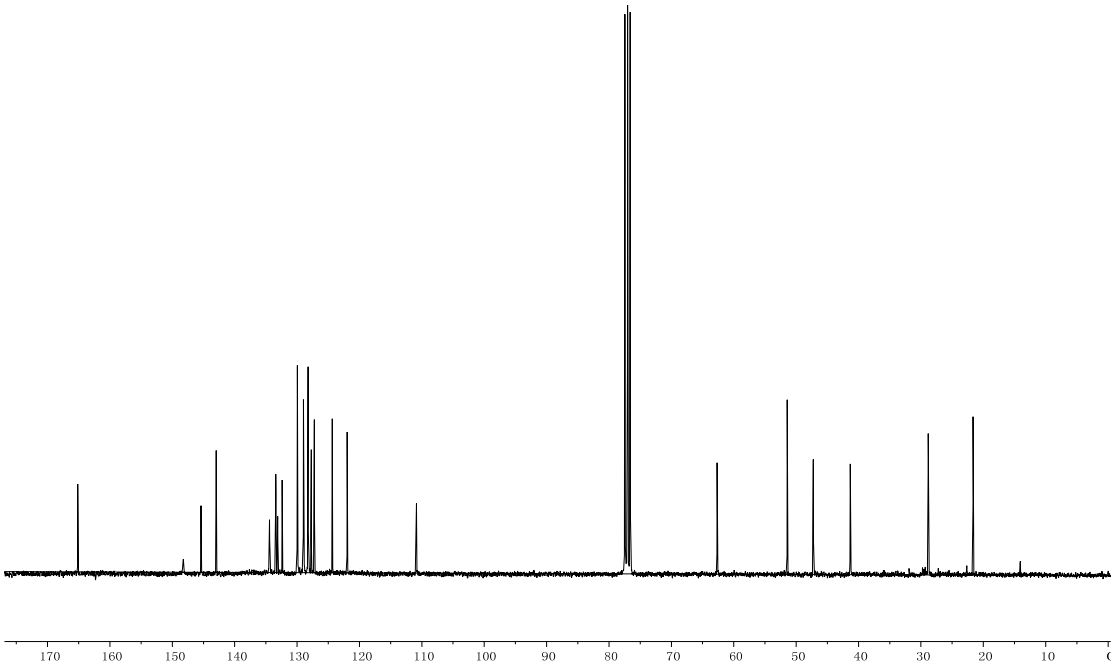
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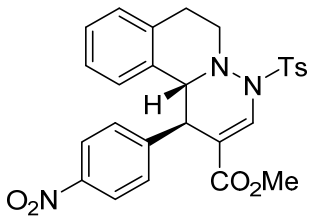
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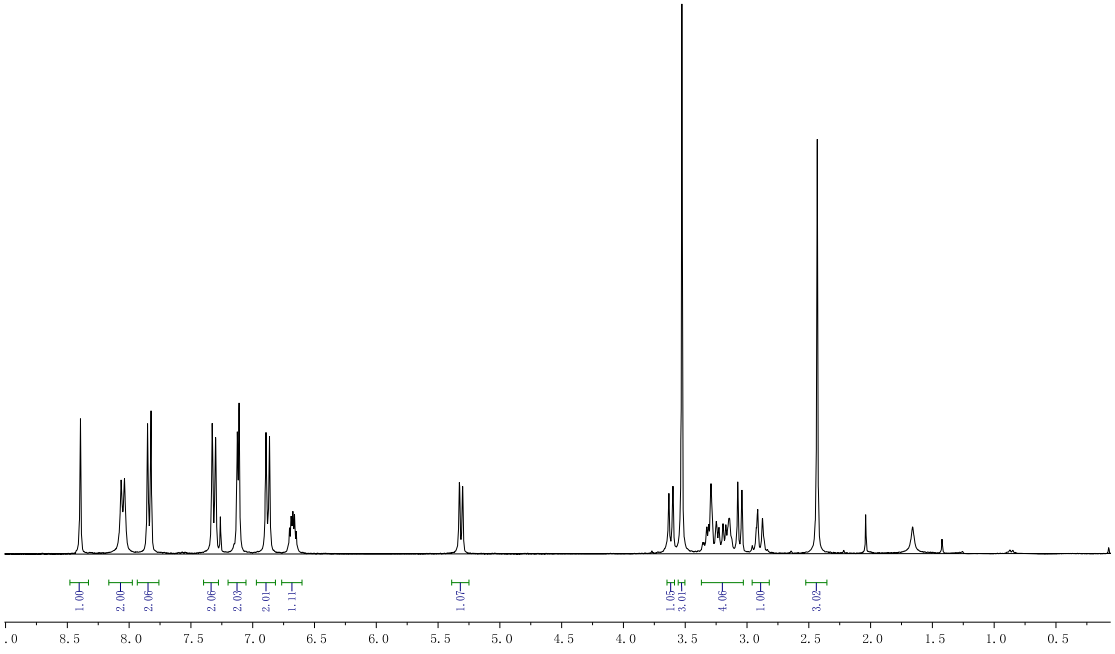
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3.02
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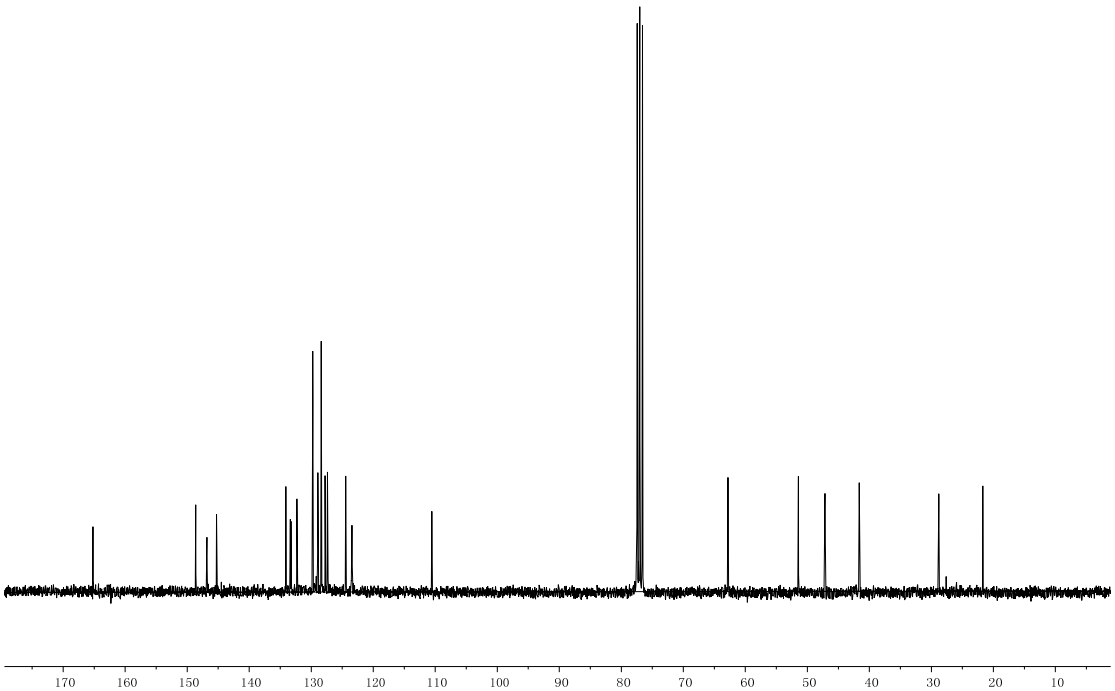
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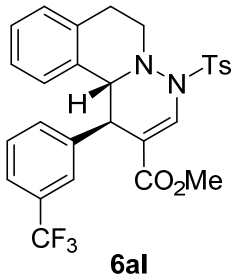
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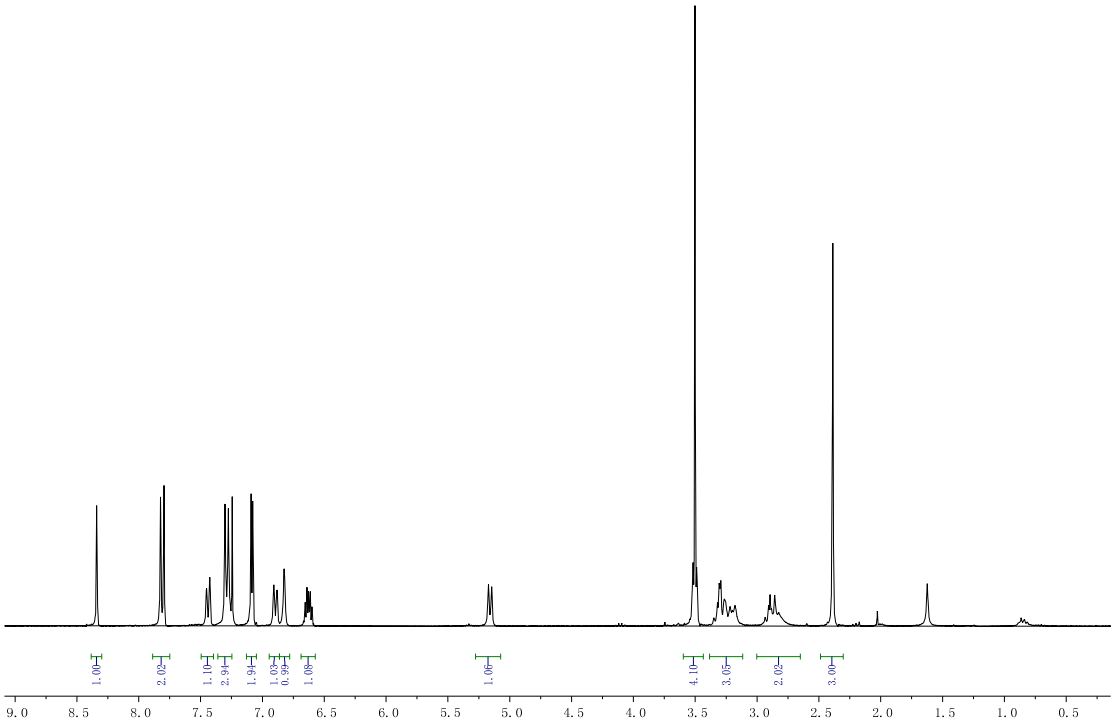
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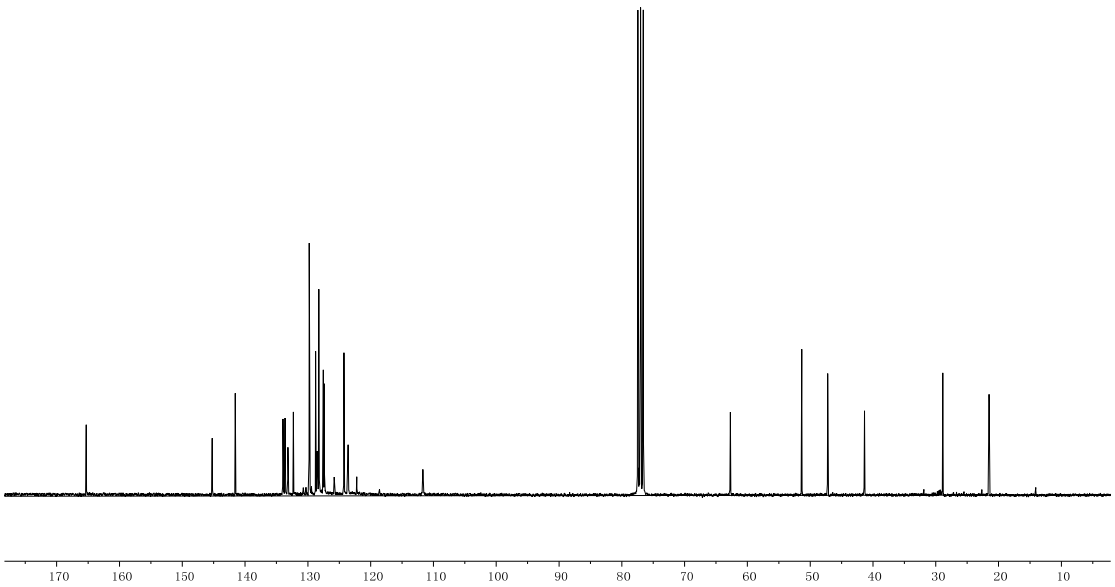
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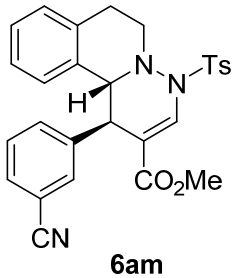
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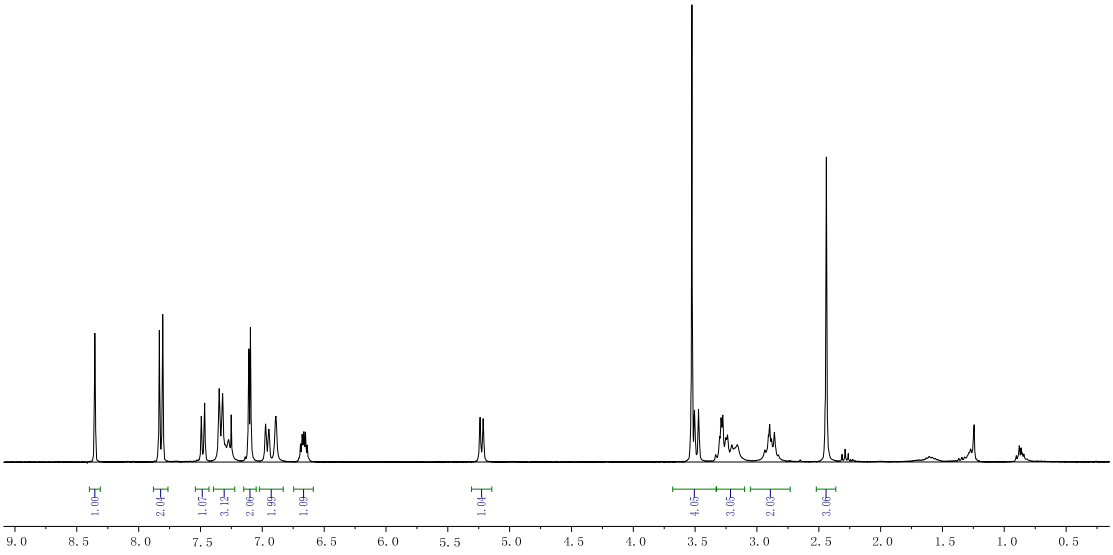
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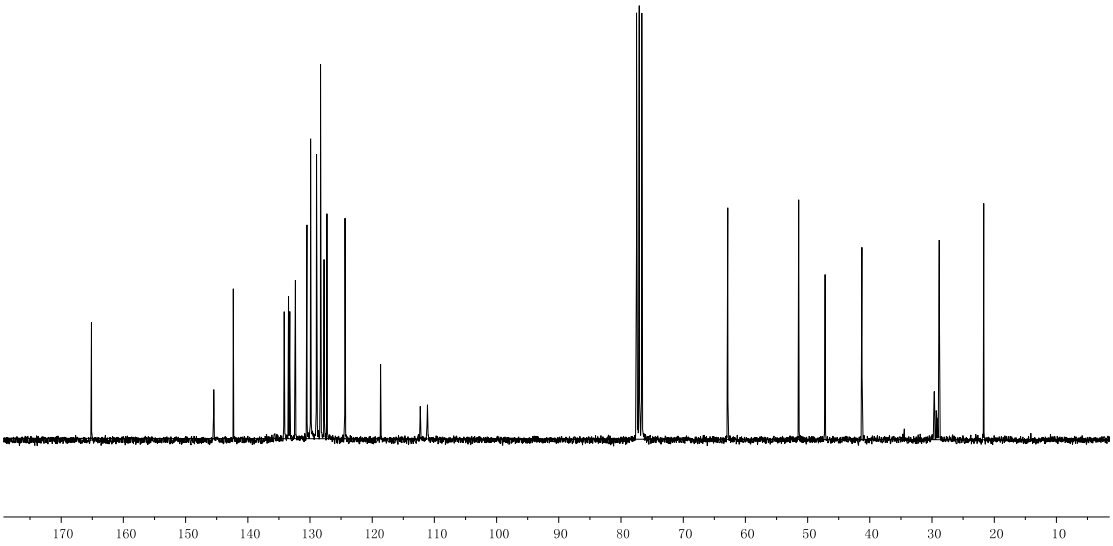
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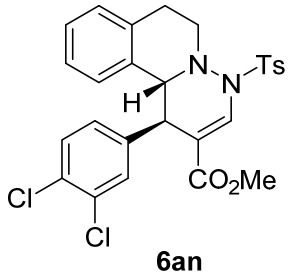
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Cl

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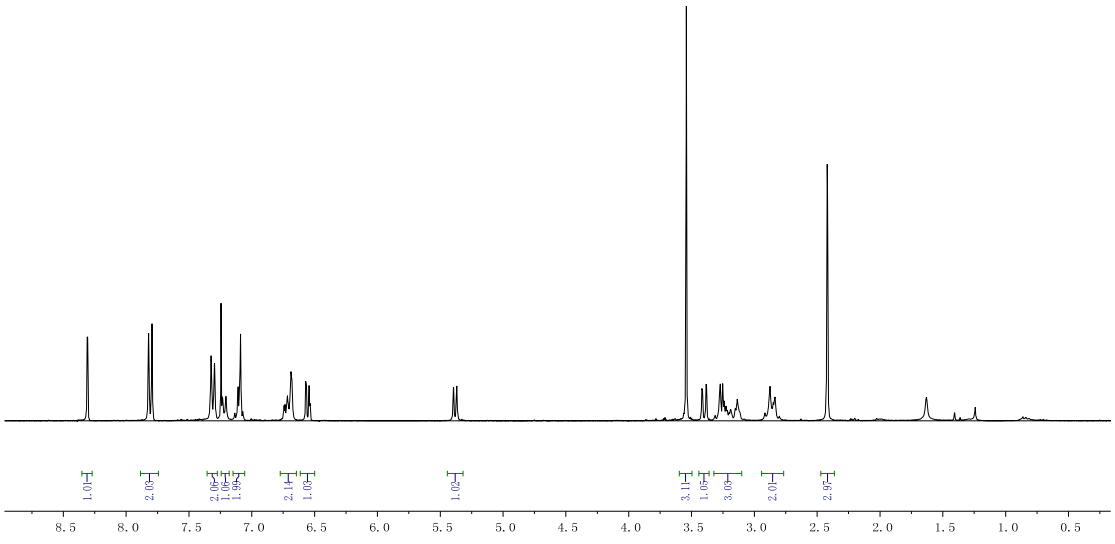
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2.01
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7.0
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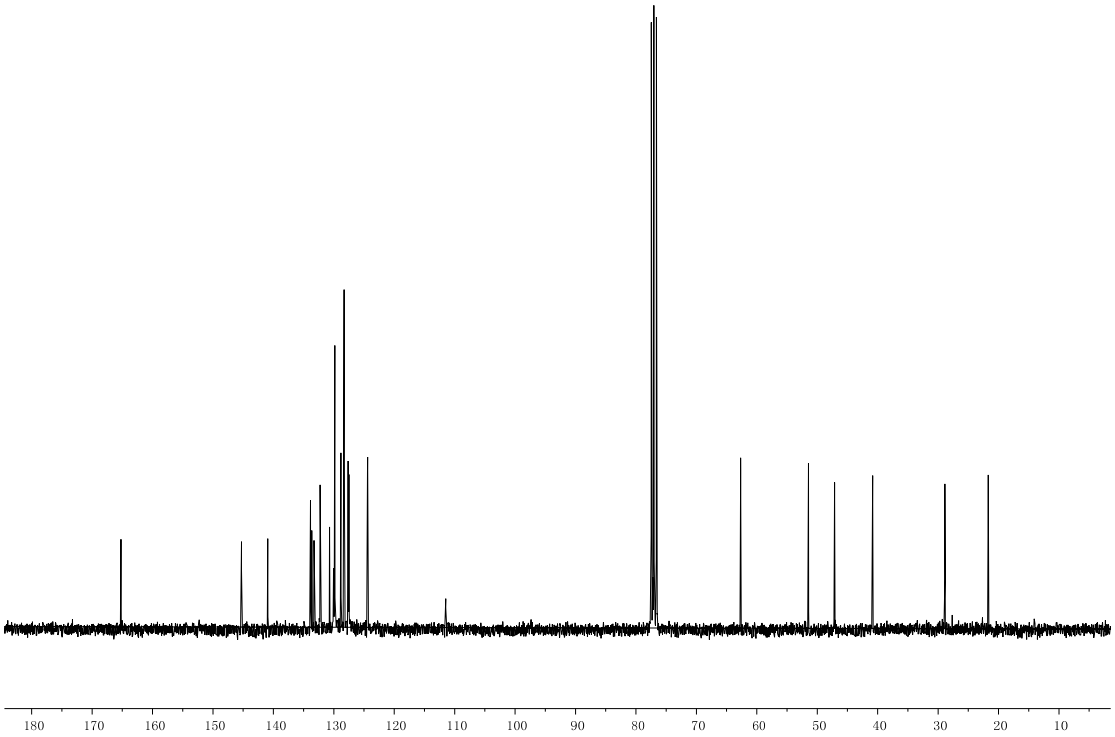
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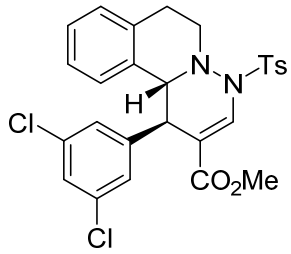
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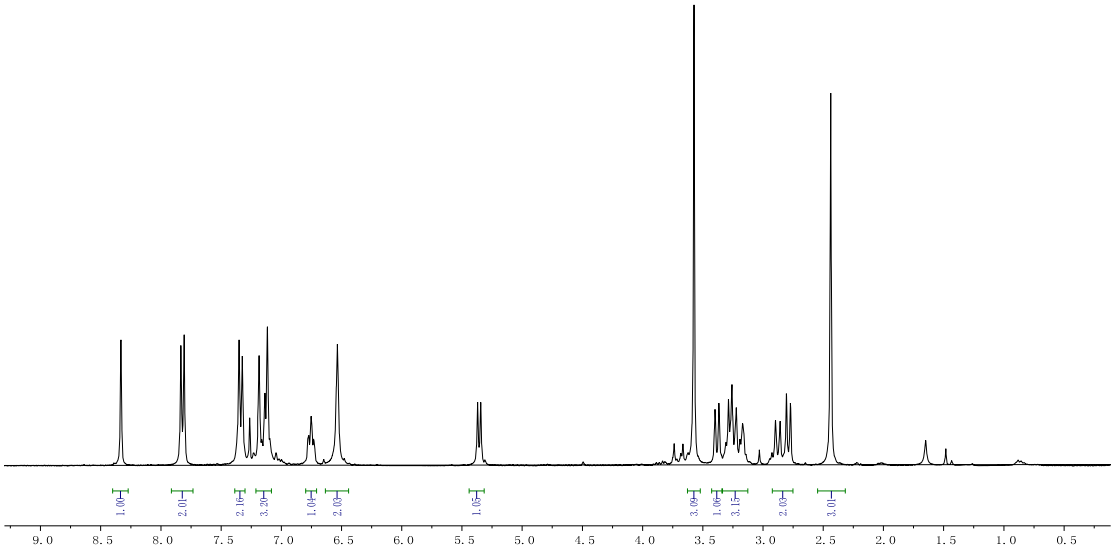
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7.5
7.0
6.5
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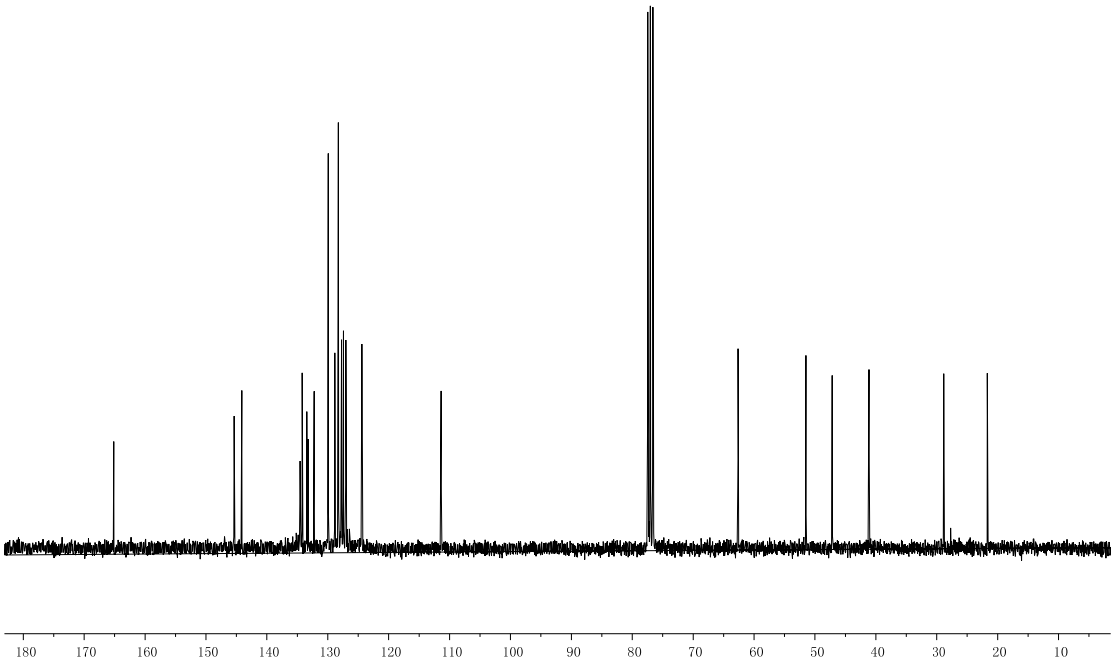
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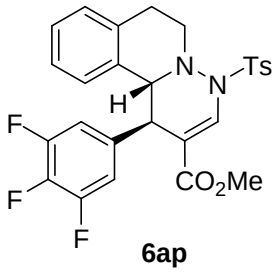
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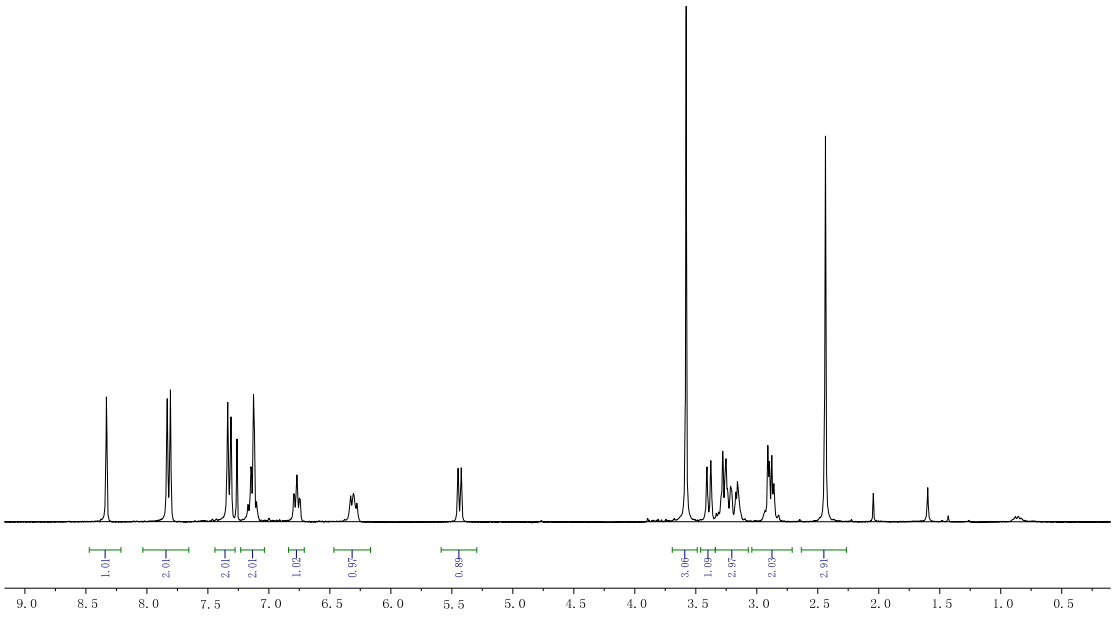
CO2Me

6ap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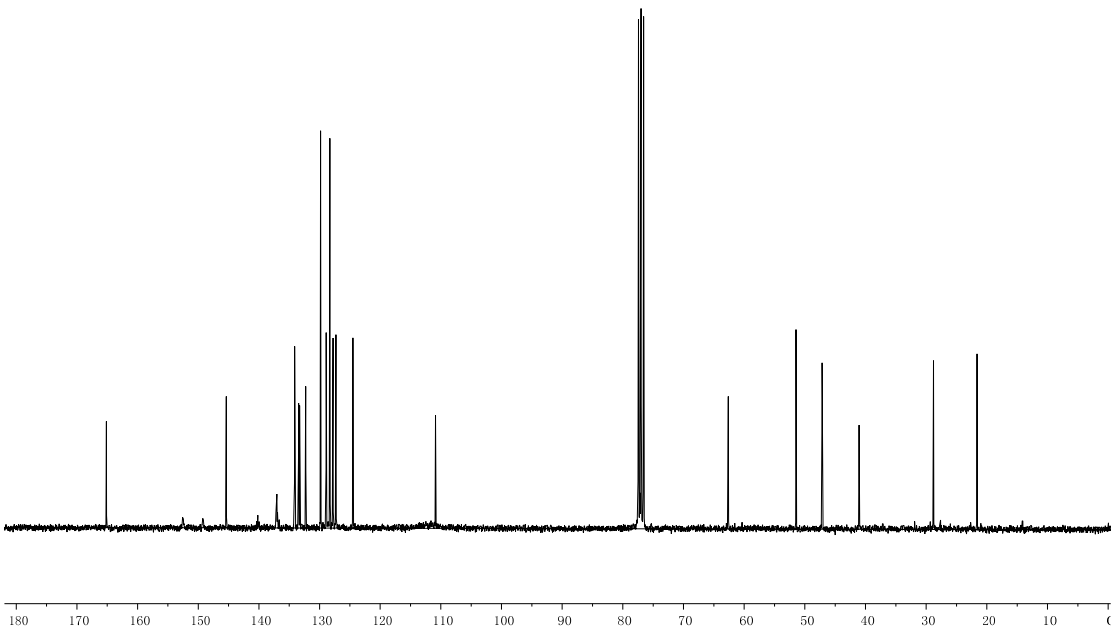
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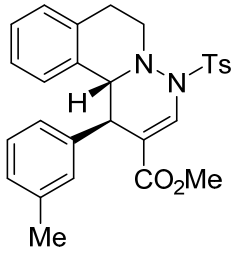
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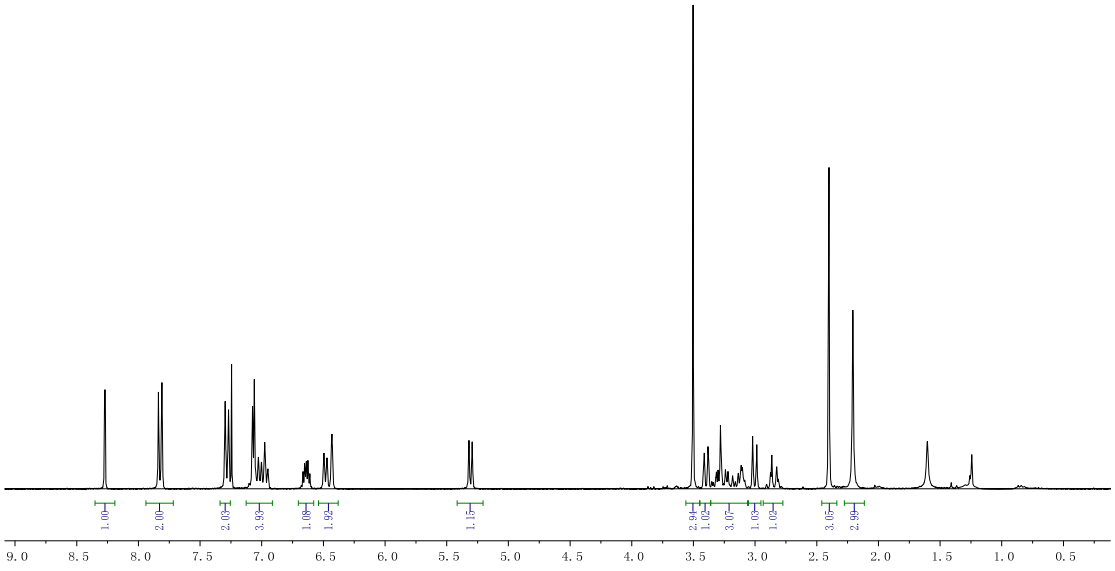
Ts
H
CO2Me
Me

6aq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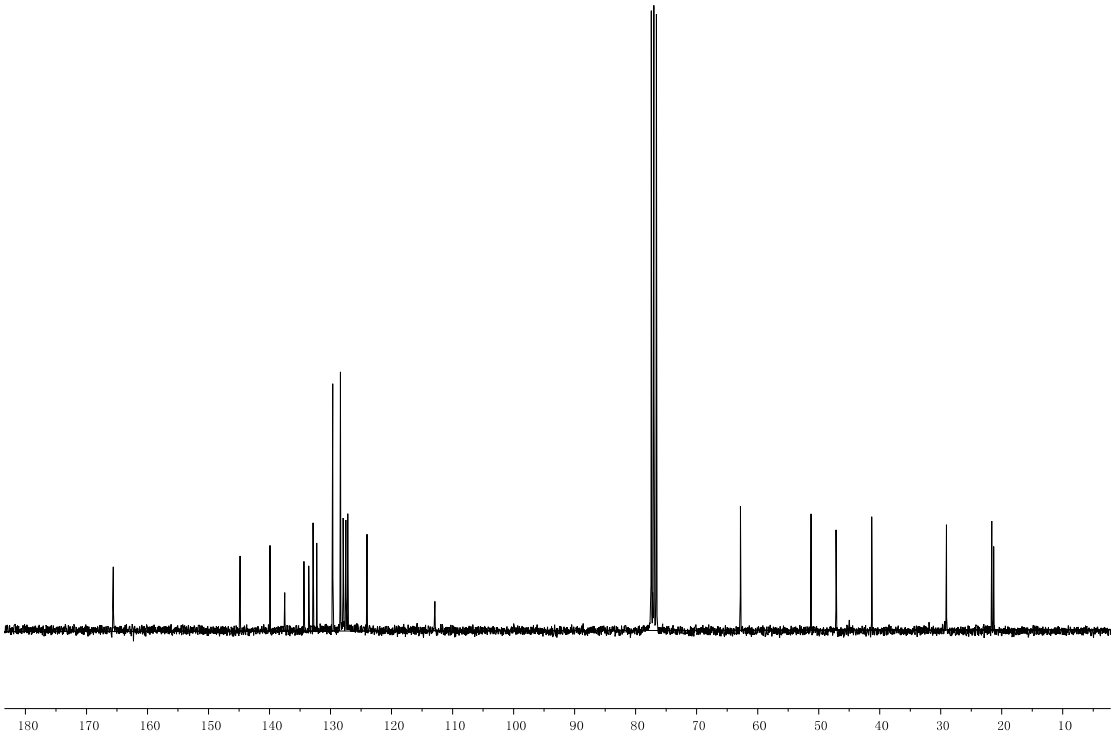
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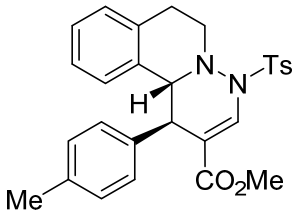
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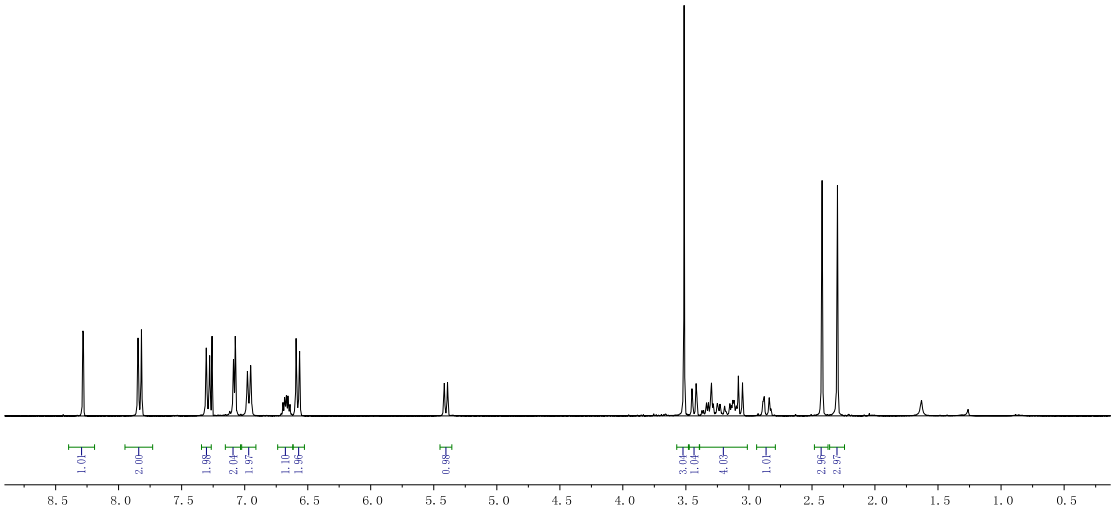
H
CO2Me
Me

6ar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1.04
4.03
1.01
2.96
2.97
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7.5
7.0
6.5
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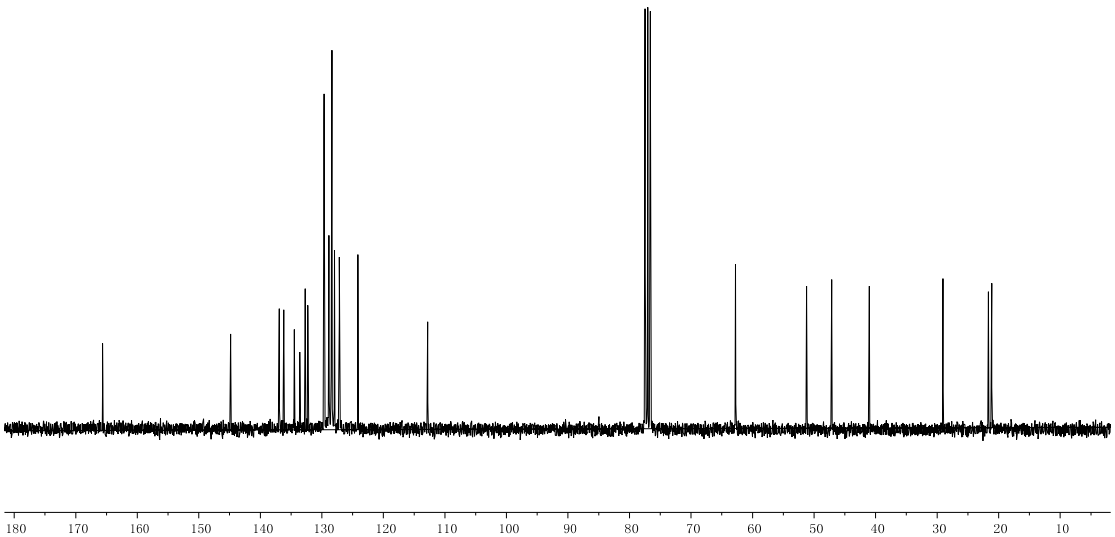
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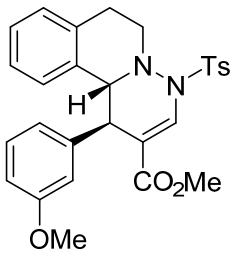

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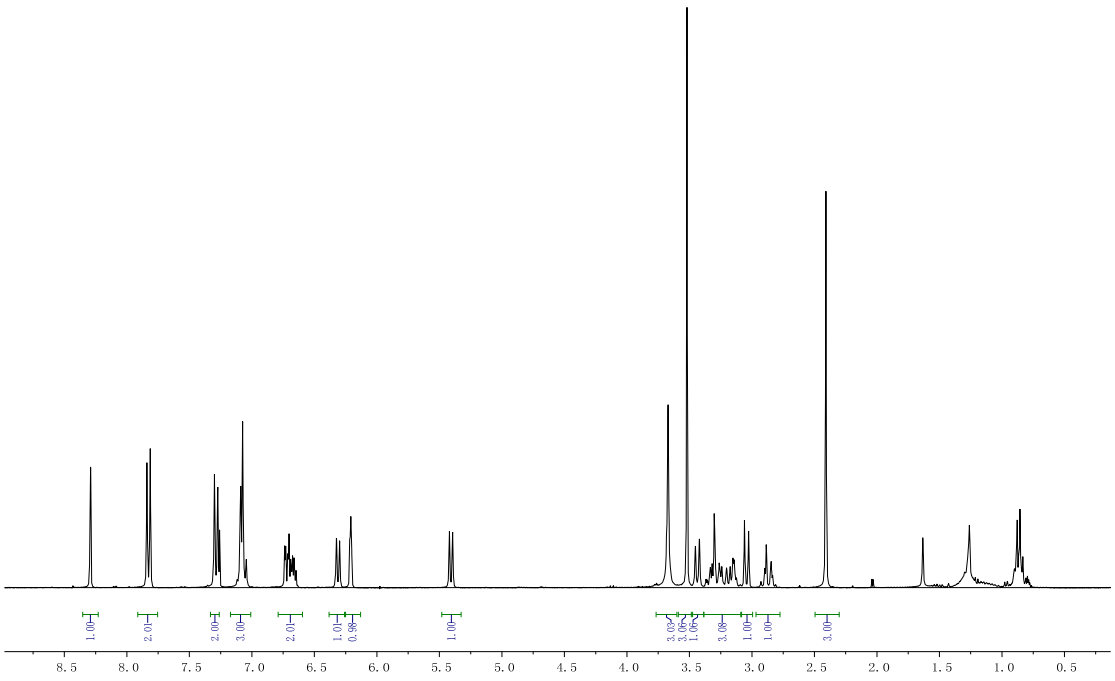

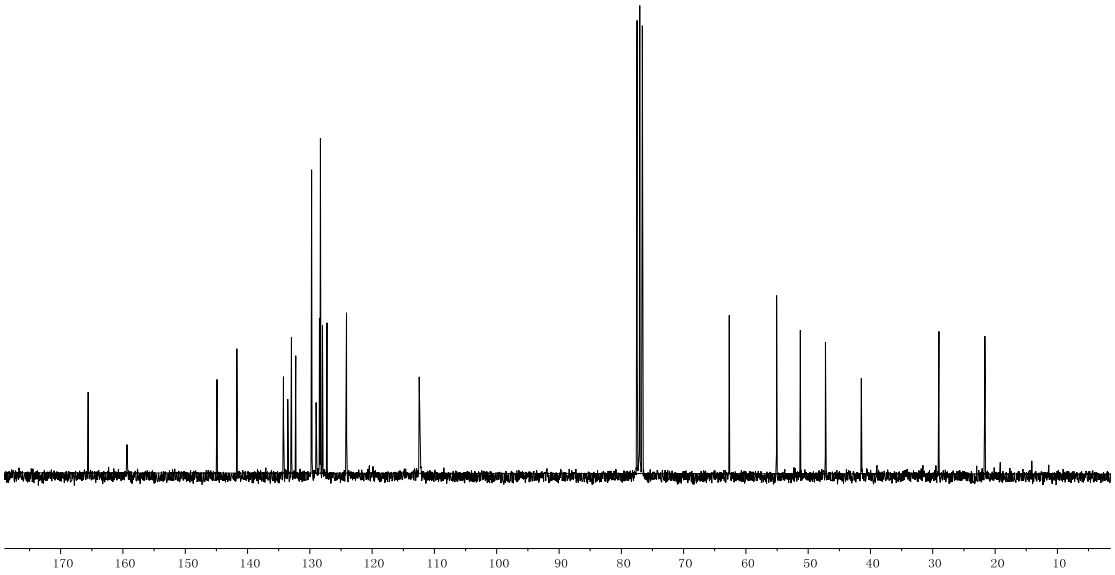

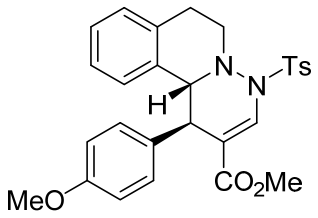
N
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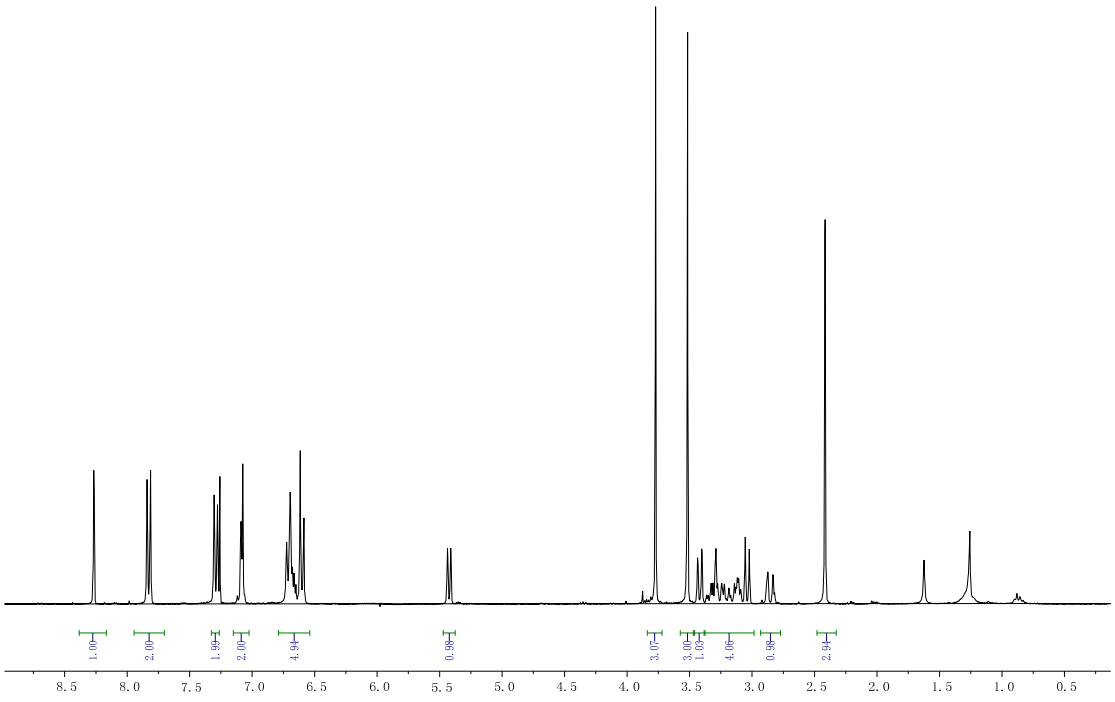
Ts
H
MeO
CO2Me

6at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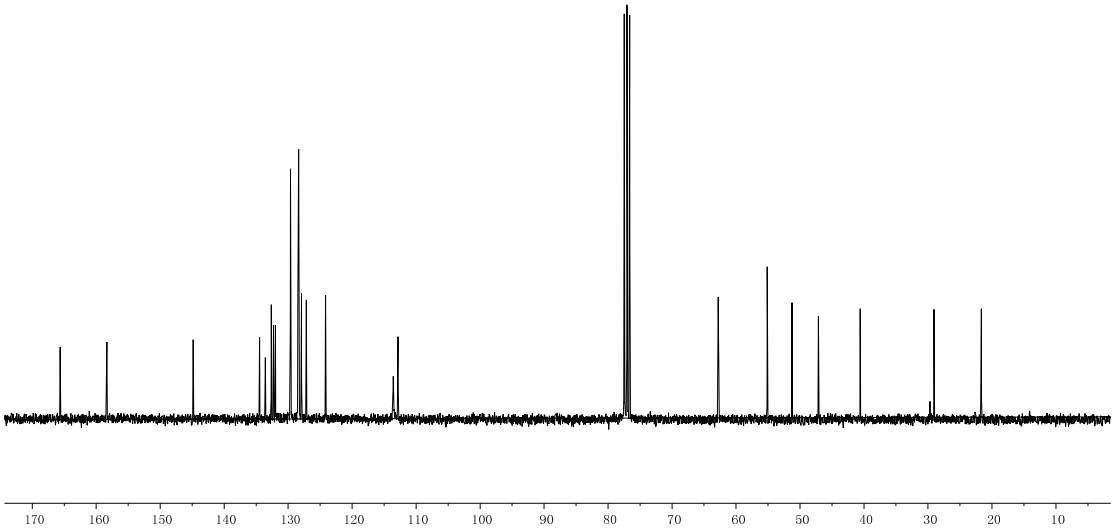
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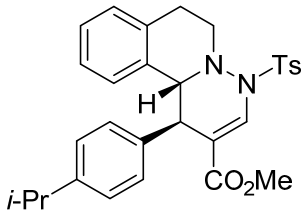
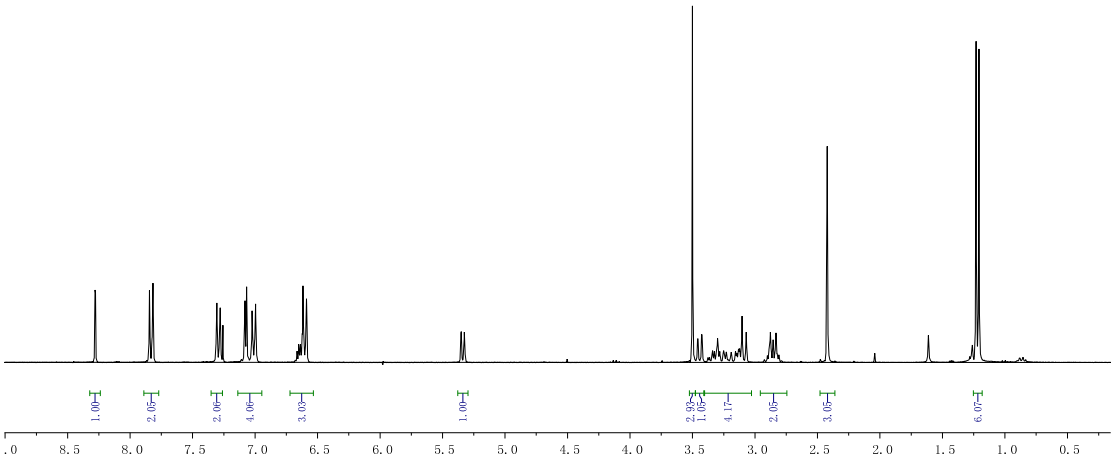

N
N
Ts
H
CO2Me
i-Pr

6au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3.05
6.07
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7.0
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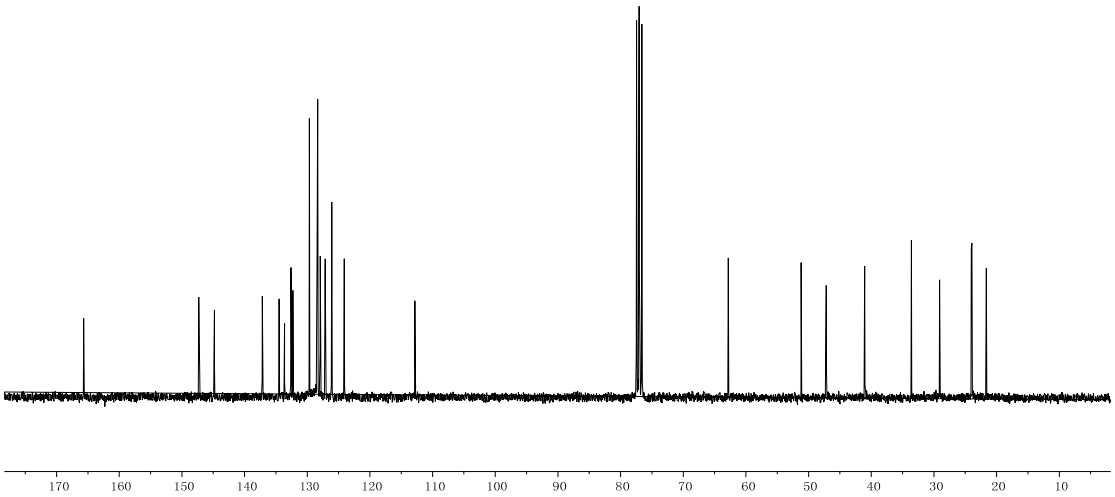
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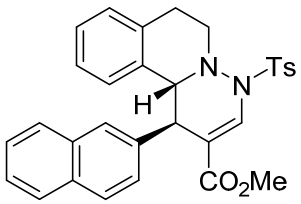
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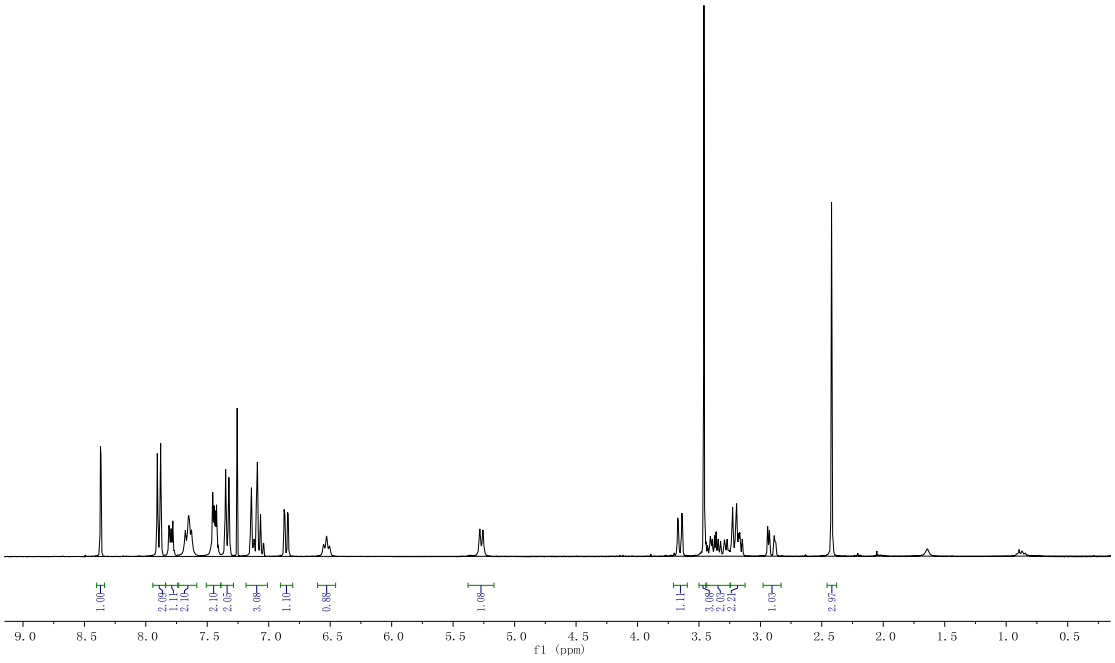
Ts
H
CO2Me

6av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2.05
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1.03
2.95
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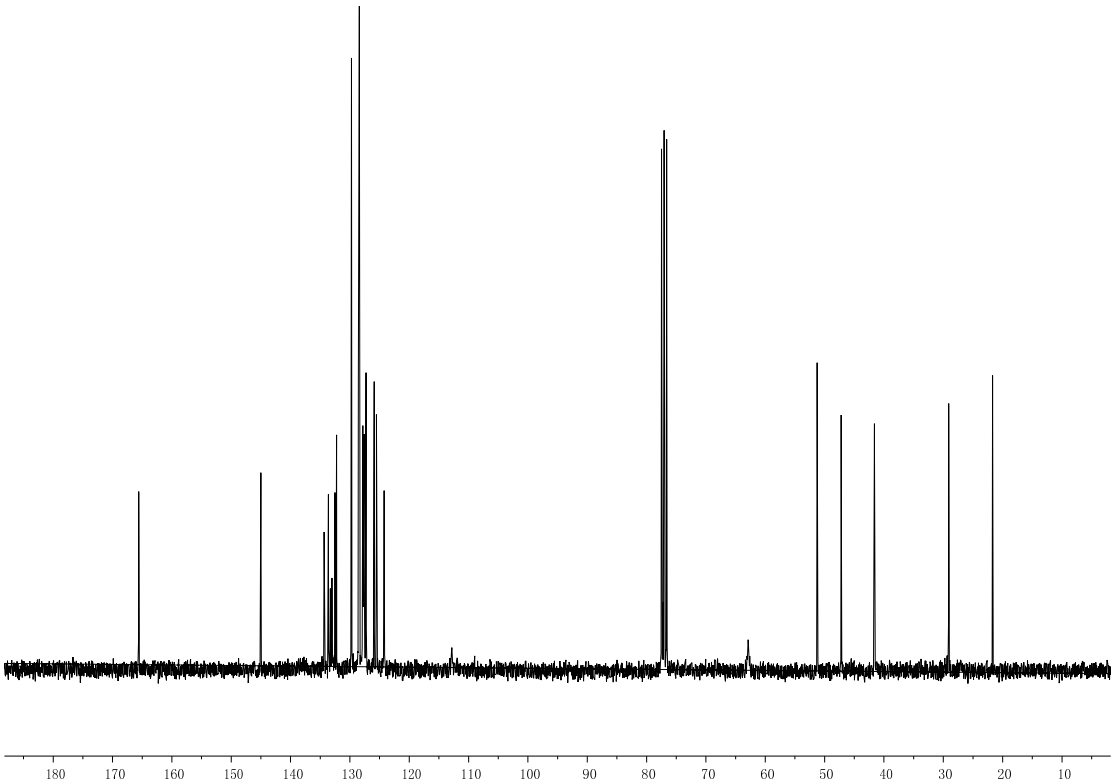
f1 (ppm)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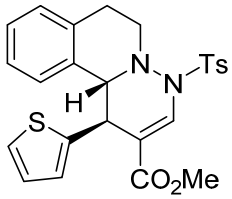
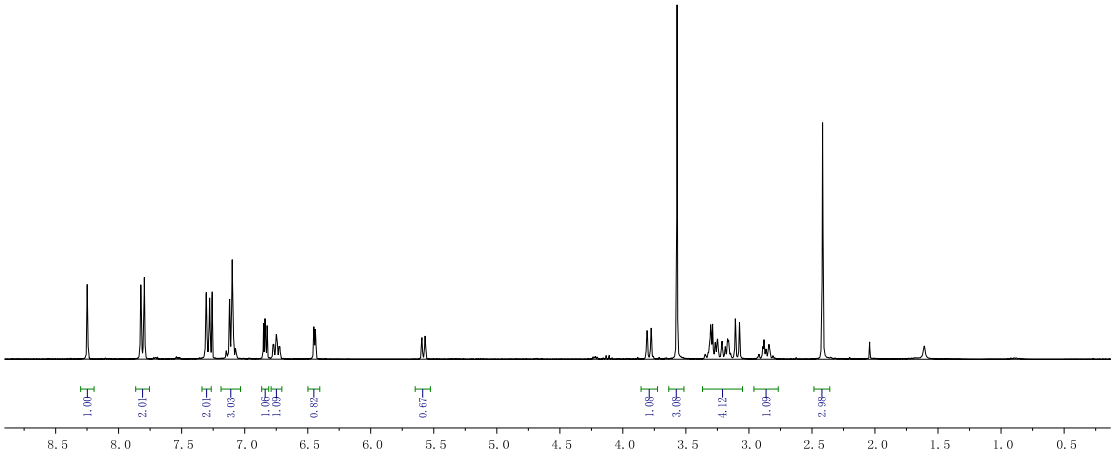

N
N
Ts
H
S
CO2Me

6aw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1.09
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1.5
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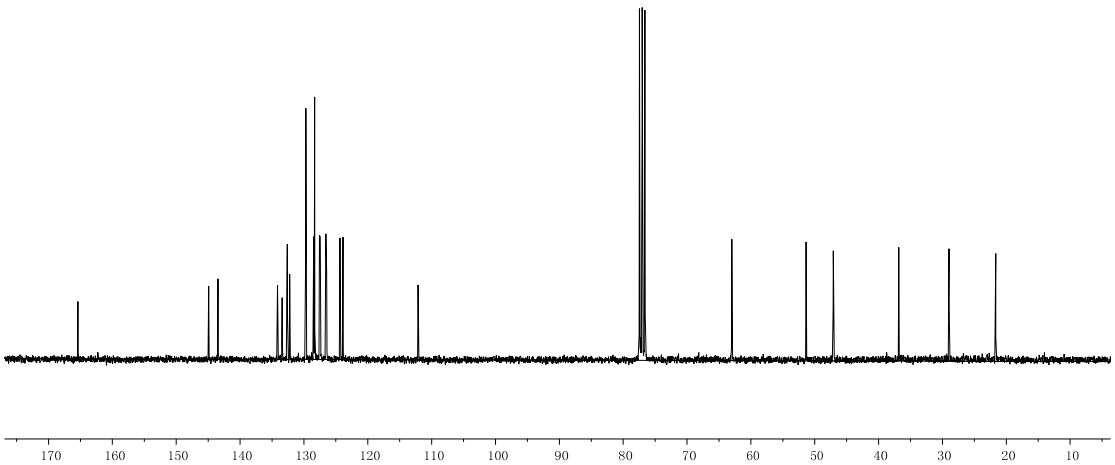
0.5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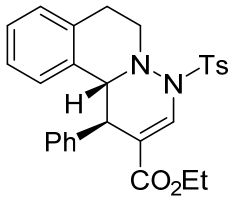
N
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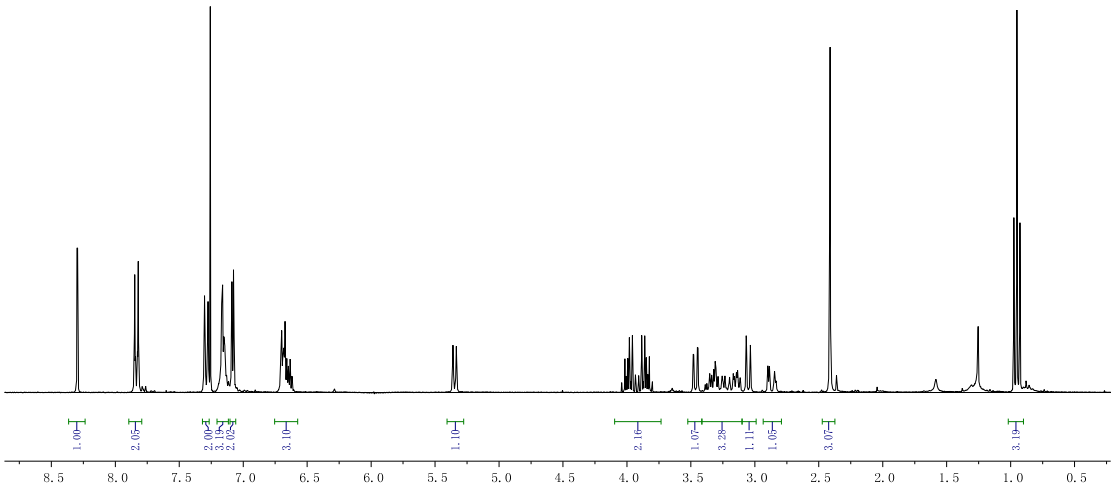
Ts
H
Ph
CO2Et

6ay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2.00
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1.10
2.10
1.07
3.28
1.11
1.05
3.07
3.19
8.5
8.0
7.5
7.0
6.5
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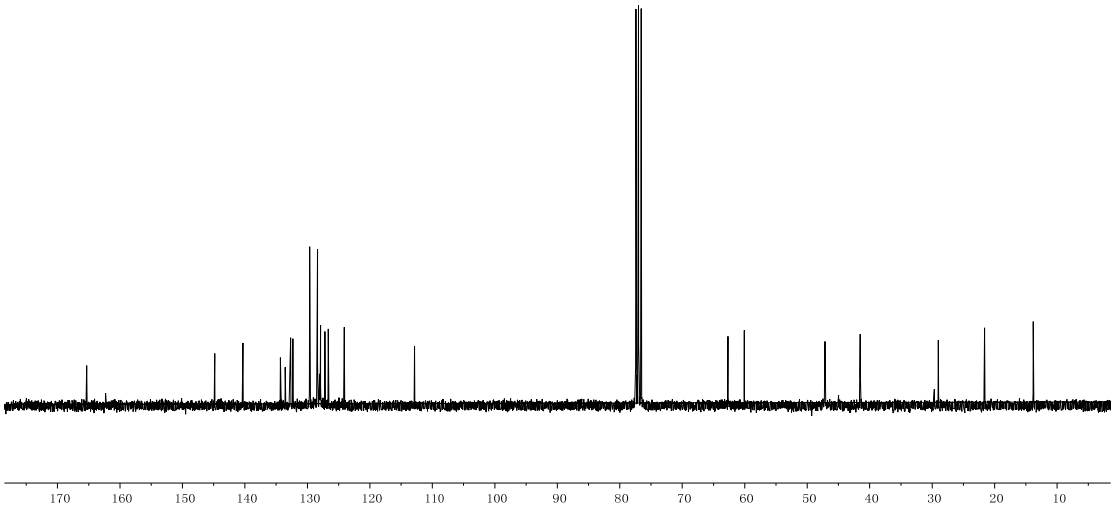
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5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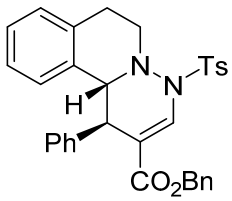
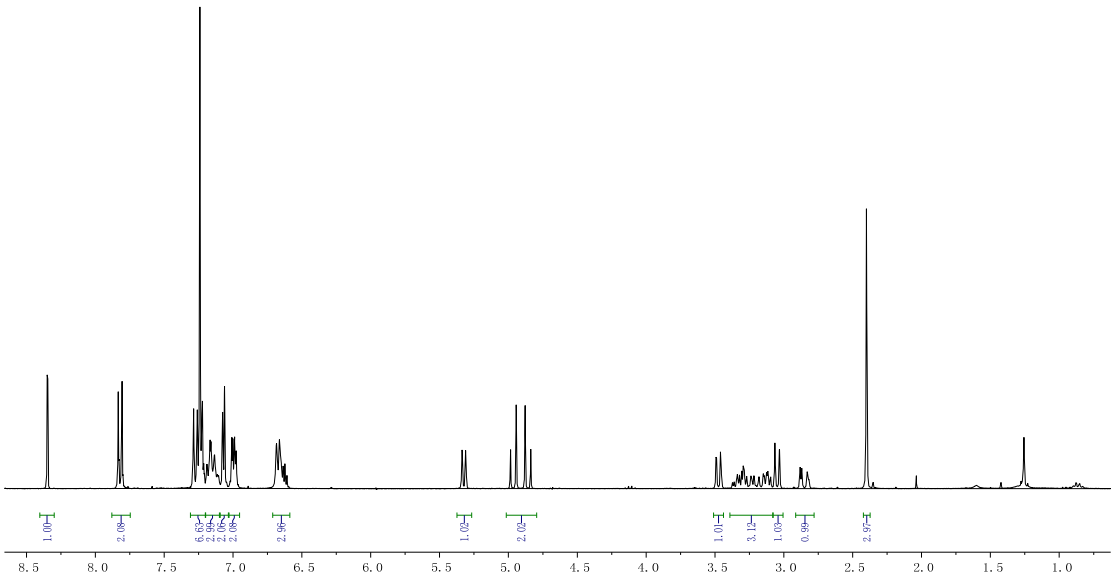

N
N
Ts
H
Ph
CO2Bn

6az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2.08
2.96
1.02
2.02
1.01
3.12
1.03
0.99
2.97
8.5
8.0
7.5
7.0
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5.0
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4.0
3.5
3.0
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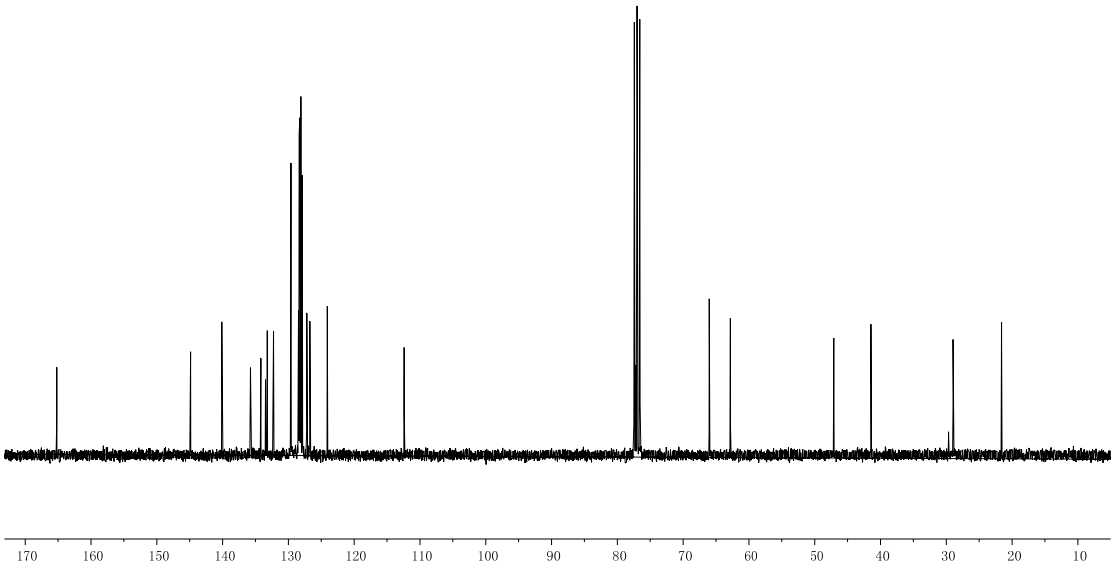
1.0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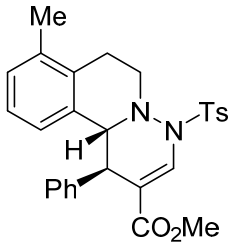
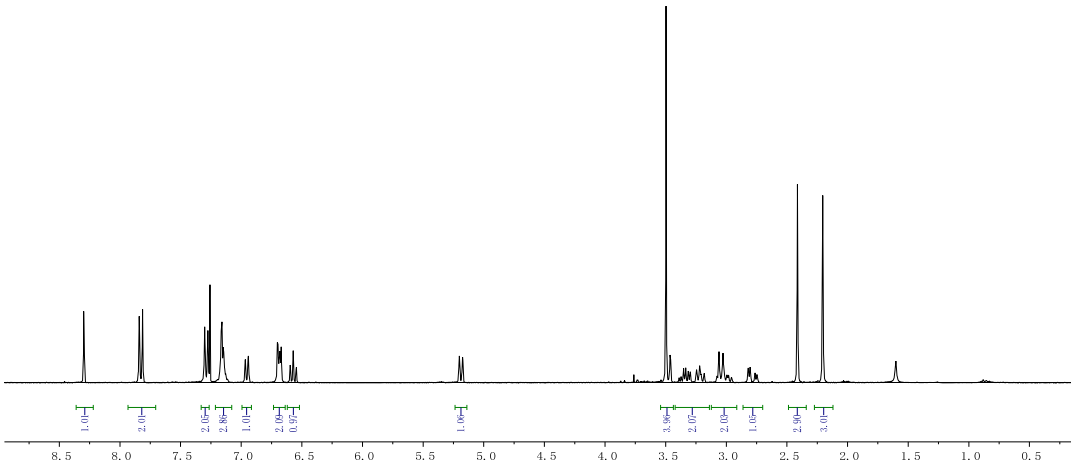

Me
N
N
Ts
H
Ph
CO2Me

6ba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0.97
1.06
3.96
2.07
2.03
1.05
2.99
3.01
8.5
8.0
7.5
7.0
6.5
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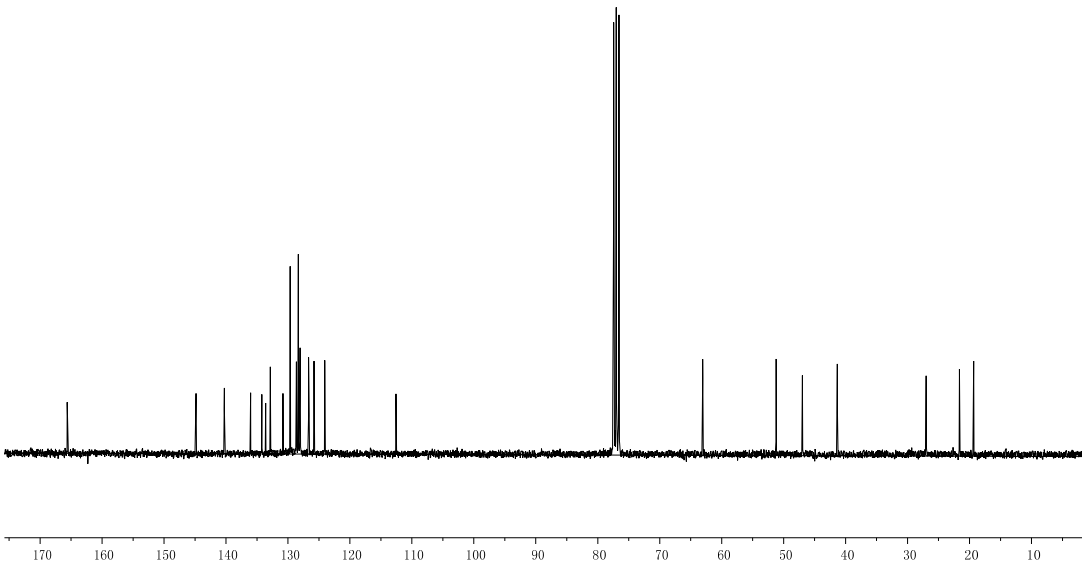
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5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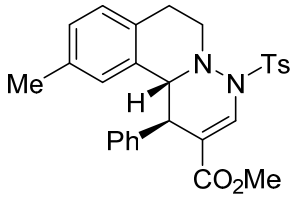
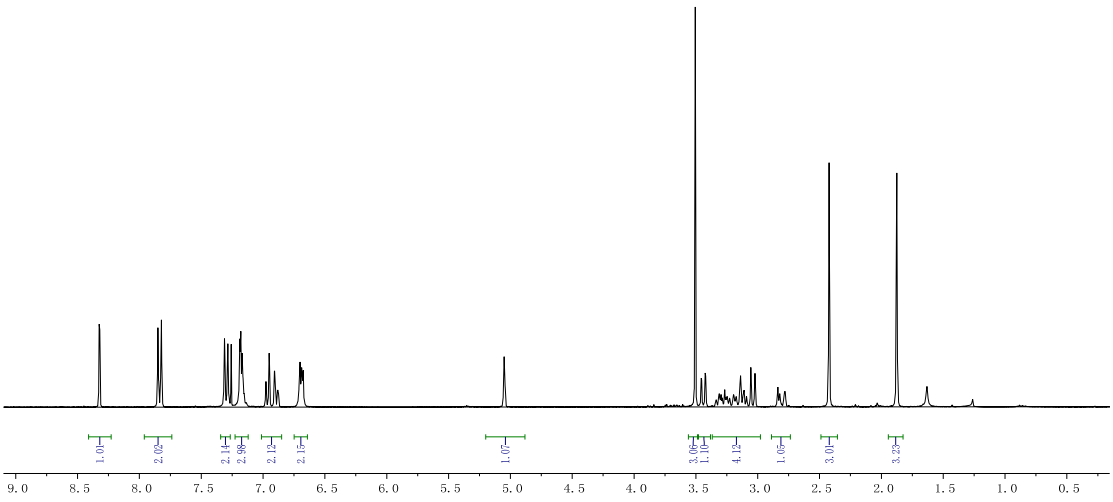

Me
N
N
Ts
H
Ph
CO2Me

6ca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2.02
2.14
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2.15
1.07
3.06
1.10
4.12
1.05
3.01
3.23
9.0
8.5
8.0
7.5
7.0
6.5
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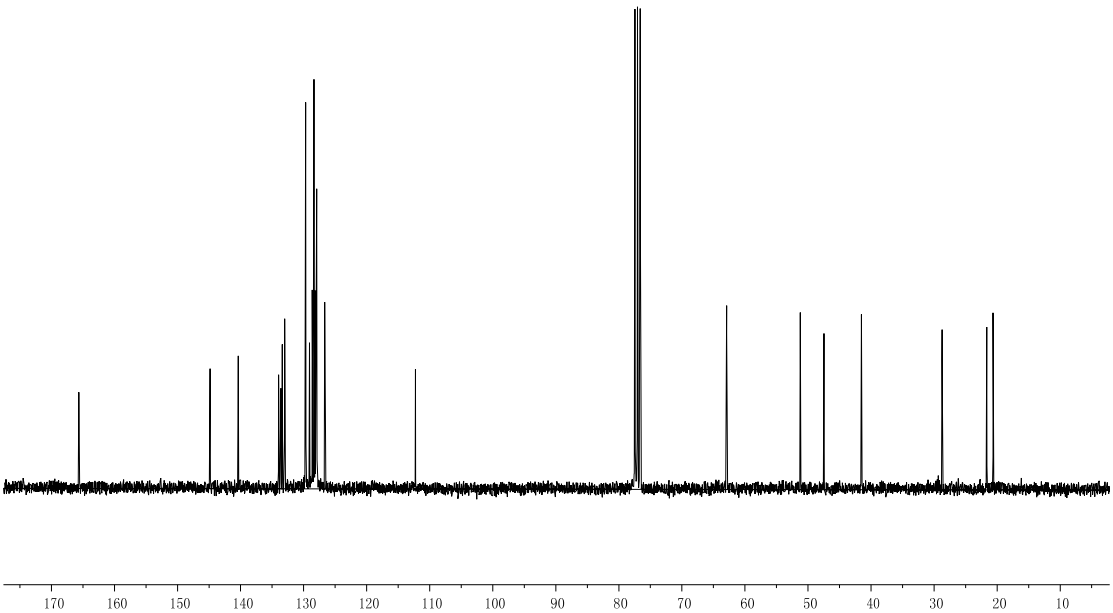
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5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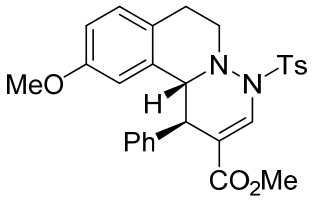
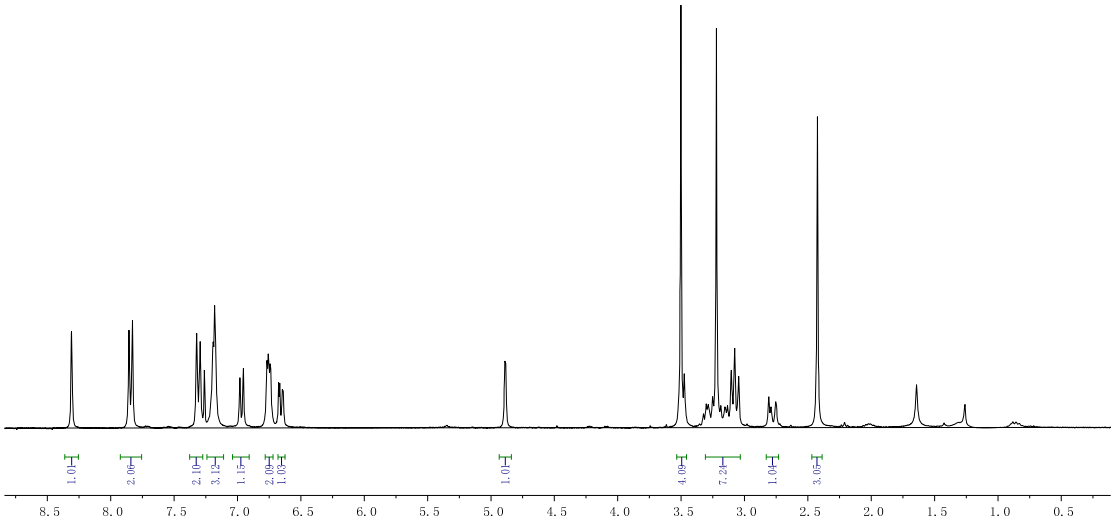

MeO
N
N
Ts
H
Ph
CO2Me

6da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2.08
1.03
1.01
4.09
7.24
1.04
3.05
8.5
8.0
7.5
7.0
6.5
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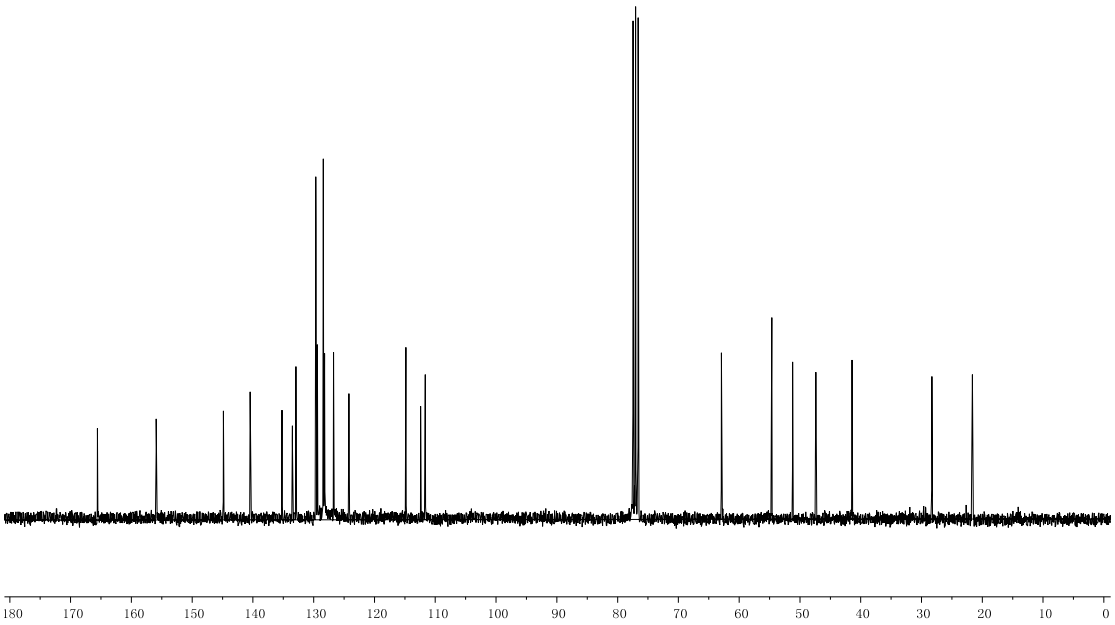
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5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100
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60
50
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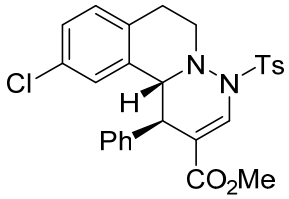
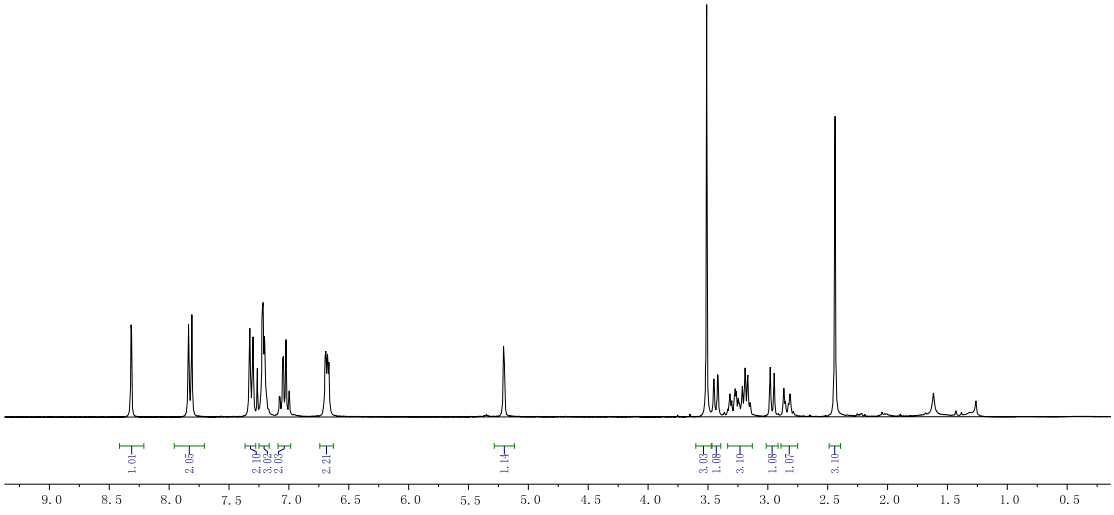
30
20
10
0


Cl
N
N
Ts
H
Ph
CO2Me

6ea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2.02
2.05
2.21
1.14
3.08
1.06
3.10
1.08
1.07
3.10
9.0
8.5
8.0
7.5
7.0
6.5
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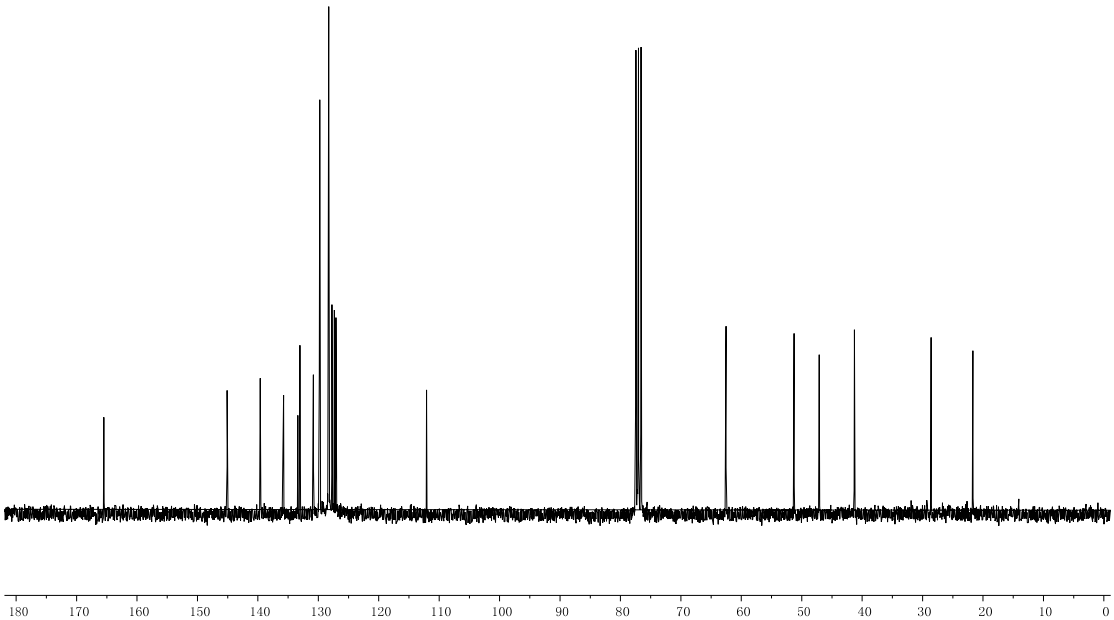
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5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140
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100
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80
70
60
50
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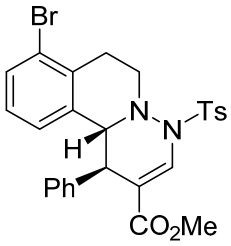
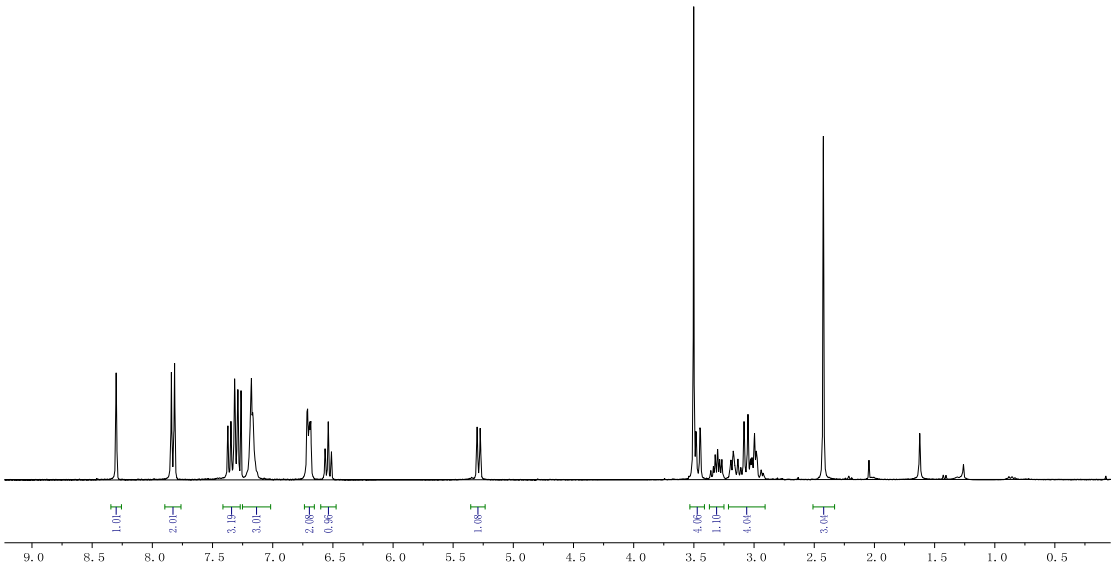
30
20
10
0


Br
N
N
Ts
H
Ph
CO2Me

6fa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1.08
4.06
1.10
4.04
3.04
9.0
8.5
8.0
7.5
7.0
6.5
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5.0
4.5
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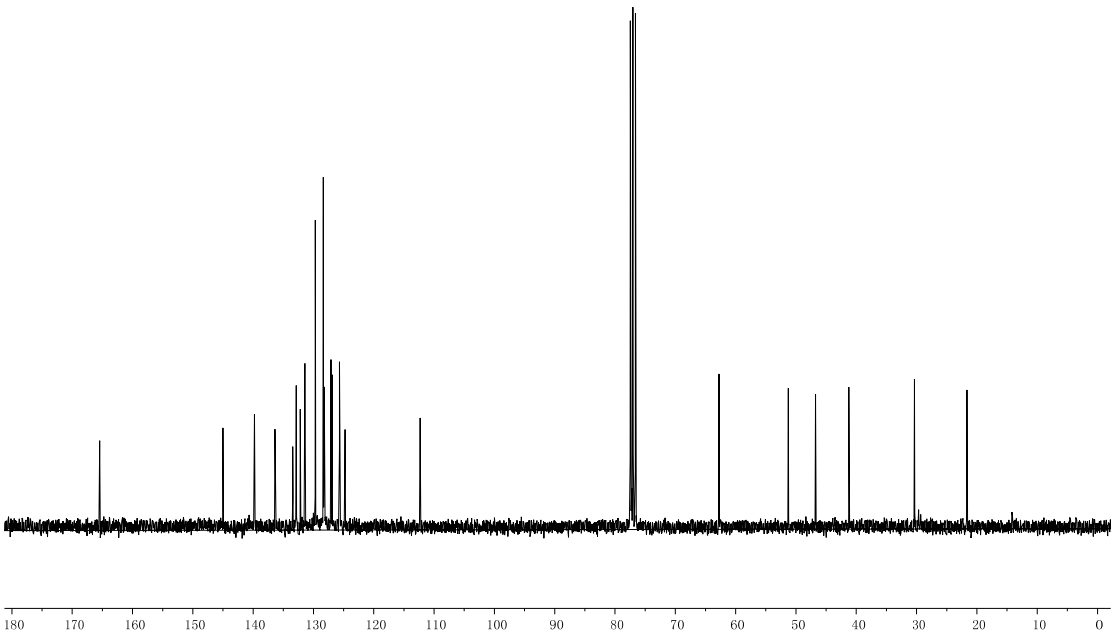
3.5
3.0
2.5
2.0
1.5
1.0
0.5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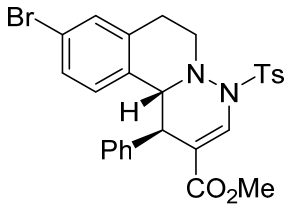
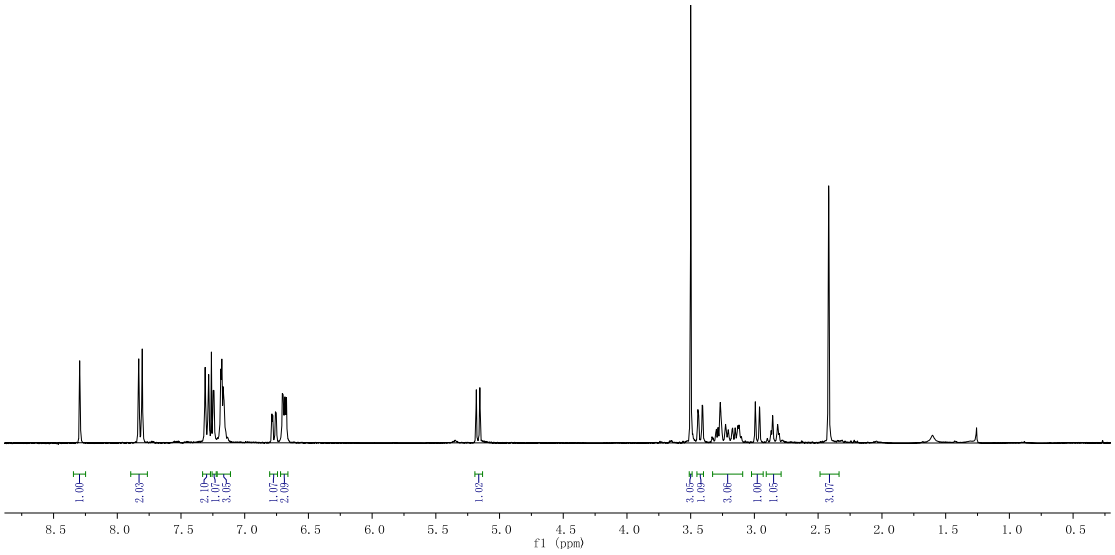
0


Br
N
N
Ts
H
Ph
CO2Me

6ga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2.03
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1.07
3.05
1.07
2.09
1.02
3.05
1.09
3.06
1.00
1.05
3.07
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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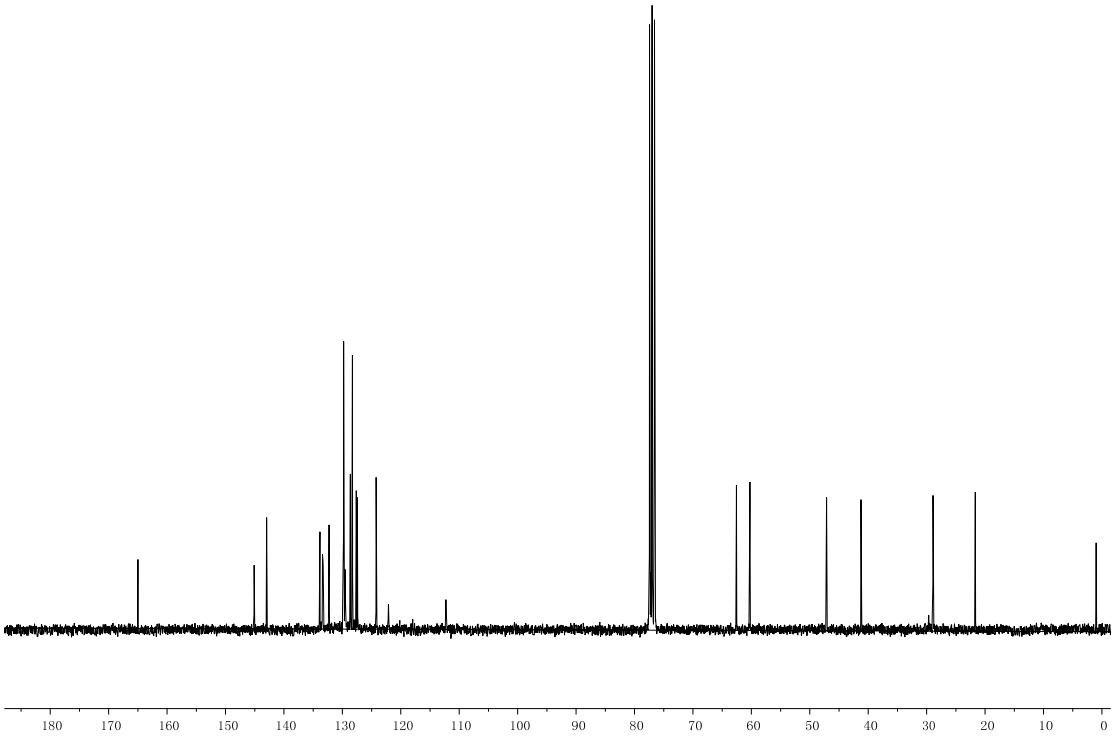
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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110
100
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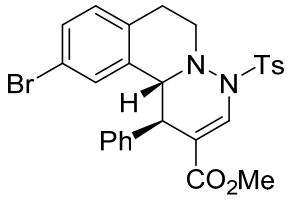
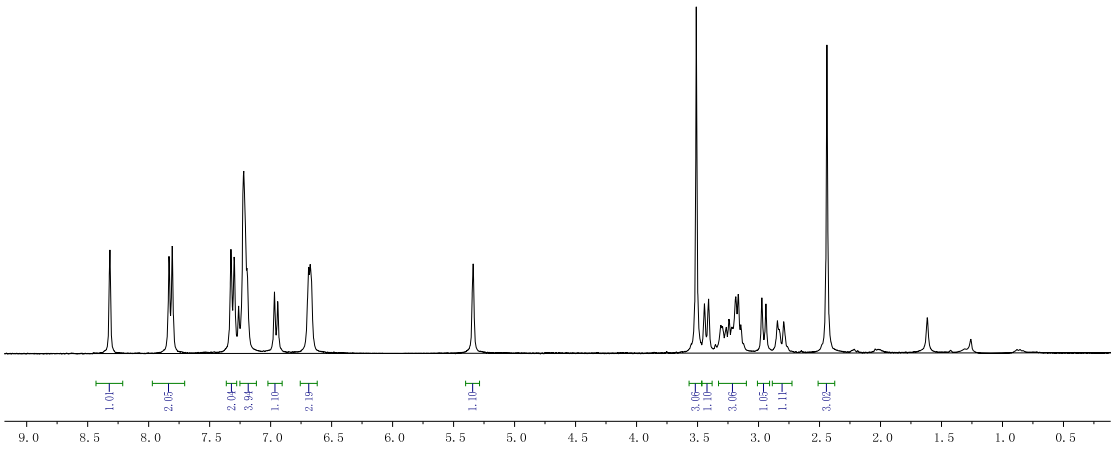
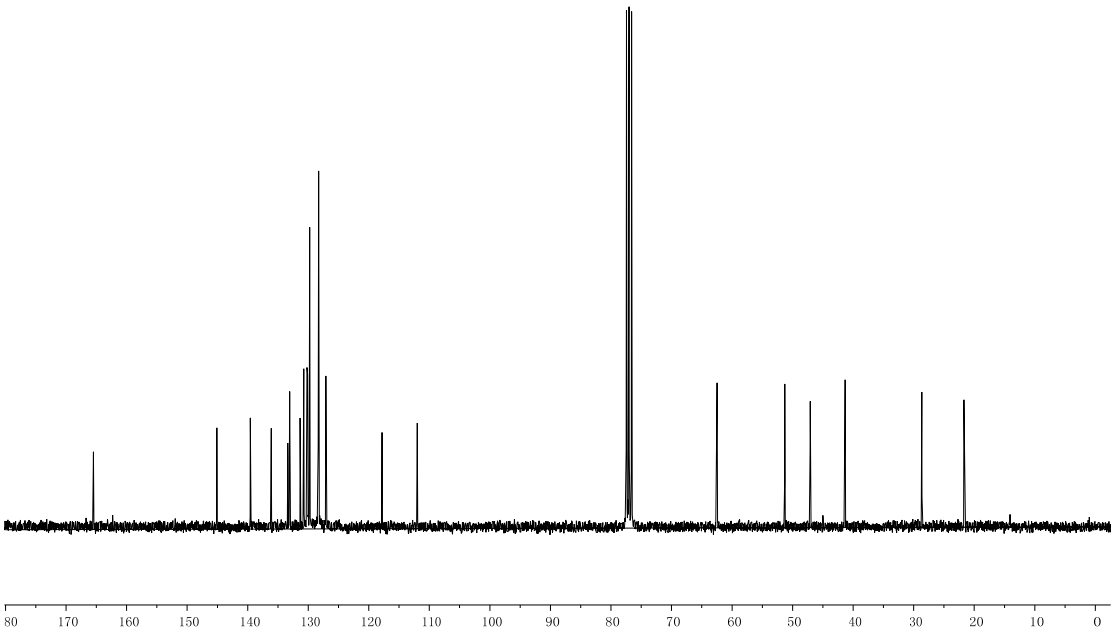
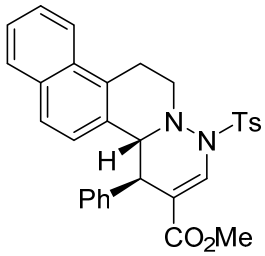
60
50
40
30
20
10
0



6ha







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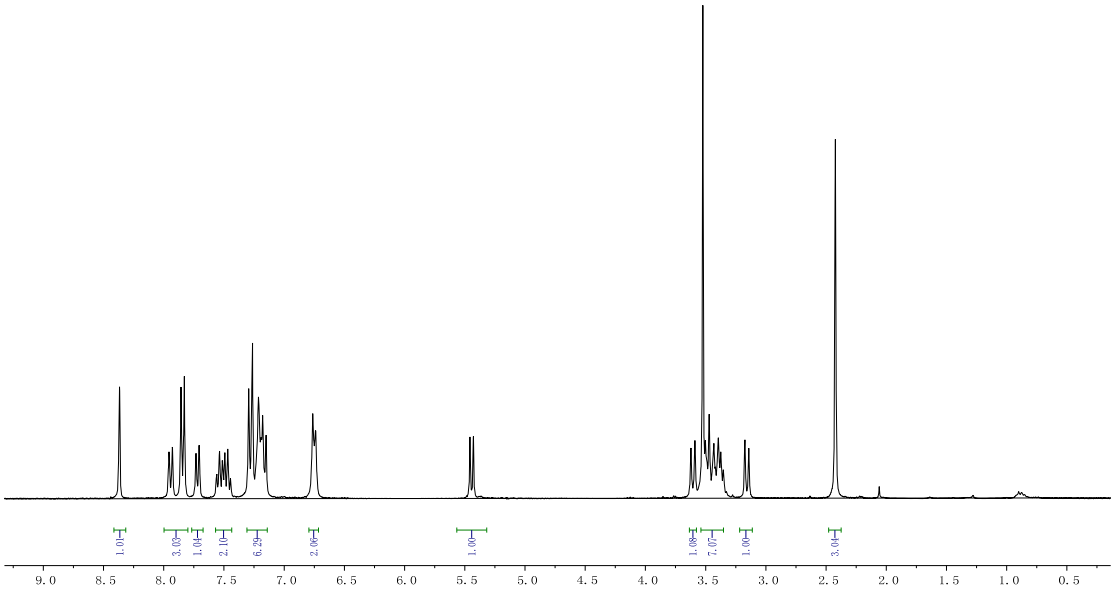
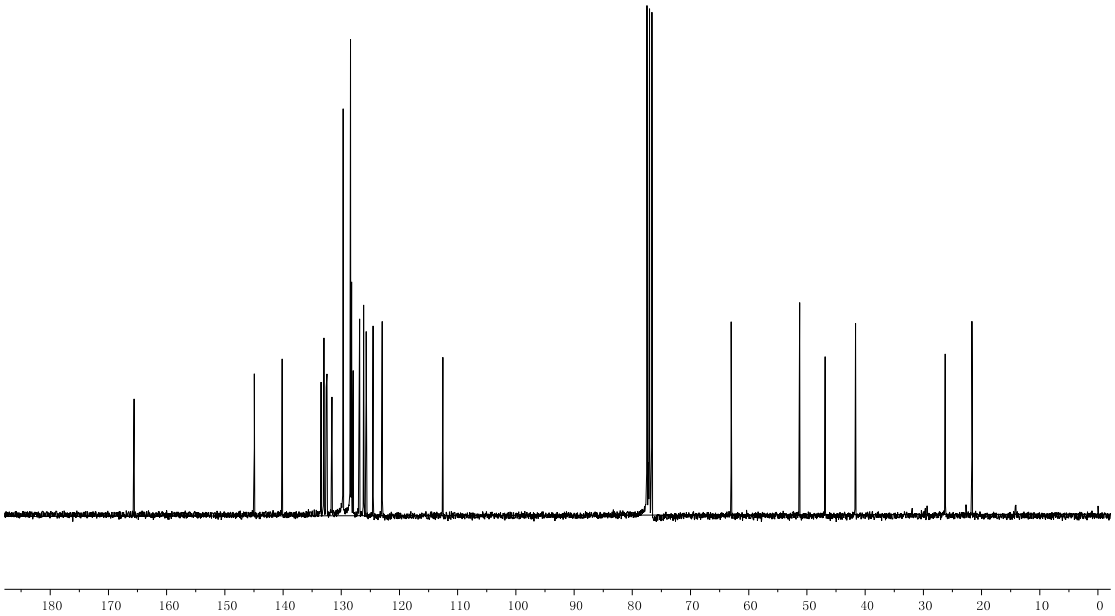
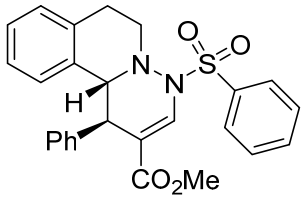
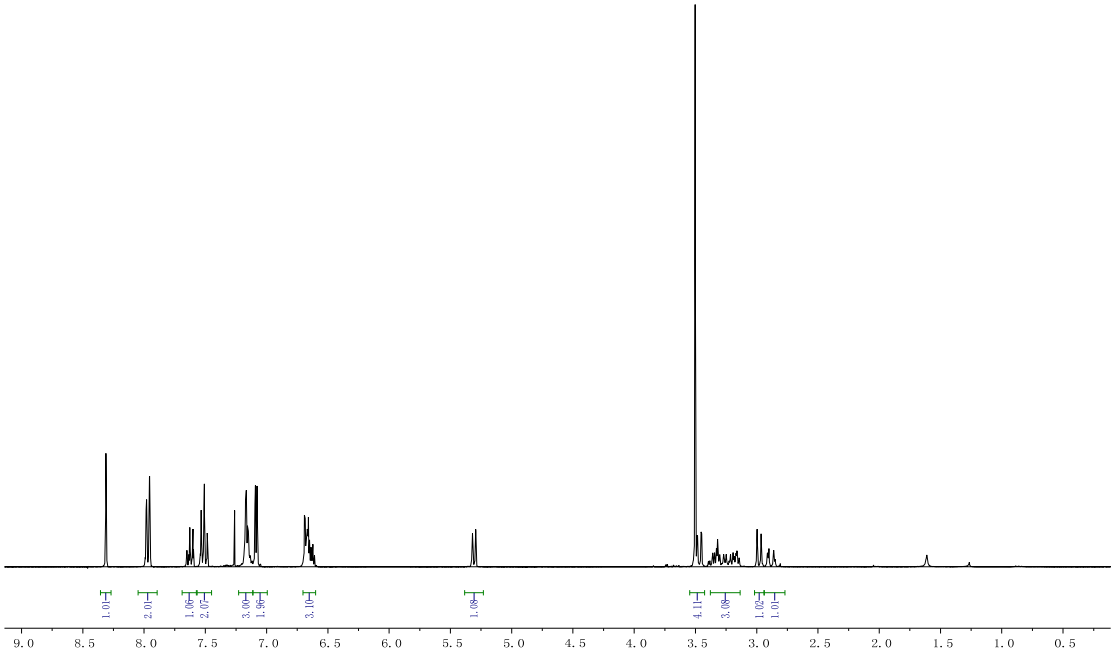





O
O
S
N
N
H
Ph
CO2Me

6ja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1.08
4.11
3.08
1.02
1.01
9.0
8.5
8.0
7.5
7.0
6.5
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5.0
4.5
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3.5
3.0
2.5
2.0
1.5
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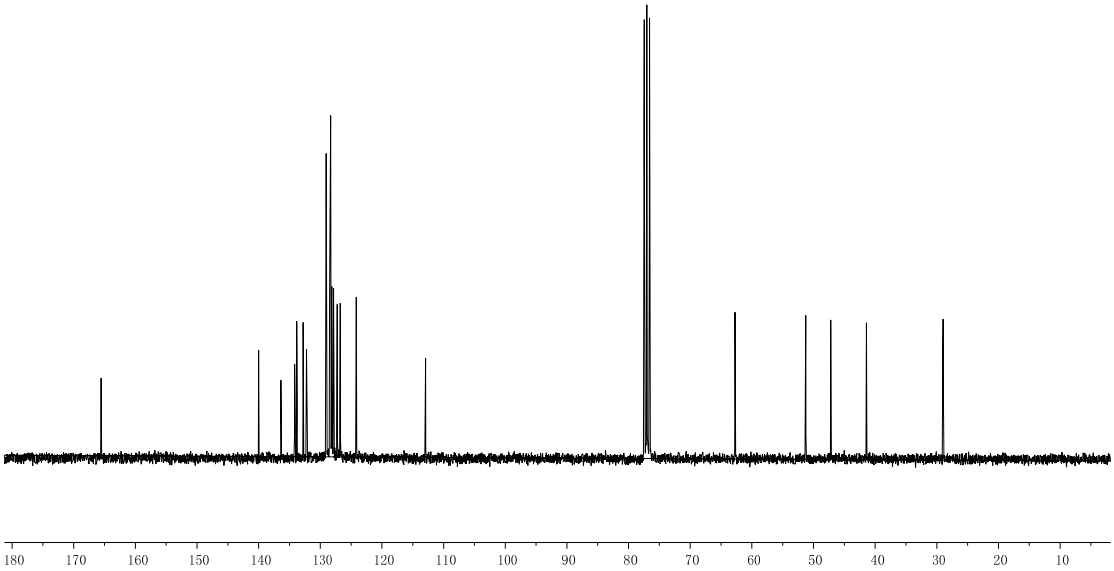
0.5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20
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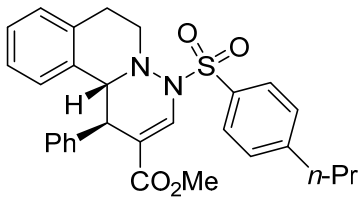
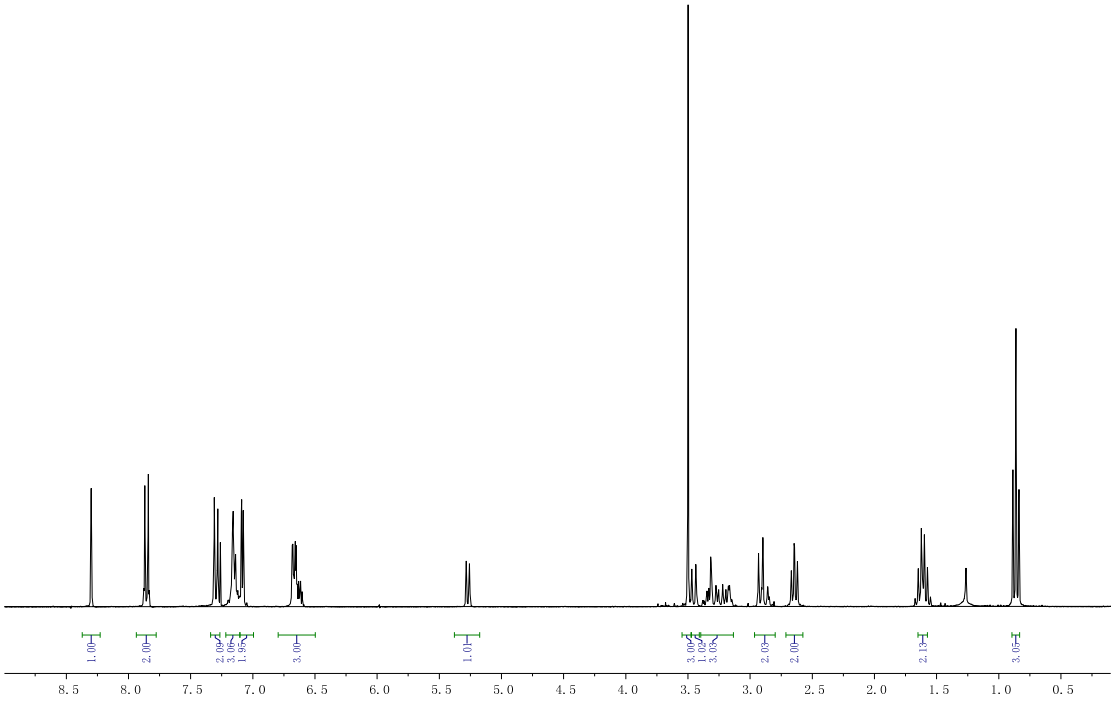

O
O
S
N
N
H
Ph
CO2Me
n-Pr

6ka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2.00
2.09
3.06
1.99
3.00
1.01
3.00
1.08
2.05
2.03
2.00
2.13
3.05
8.5
8.0
7.5
7.0
6.5
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3.0
2.5
2.0
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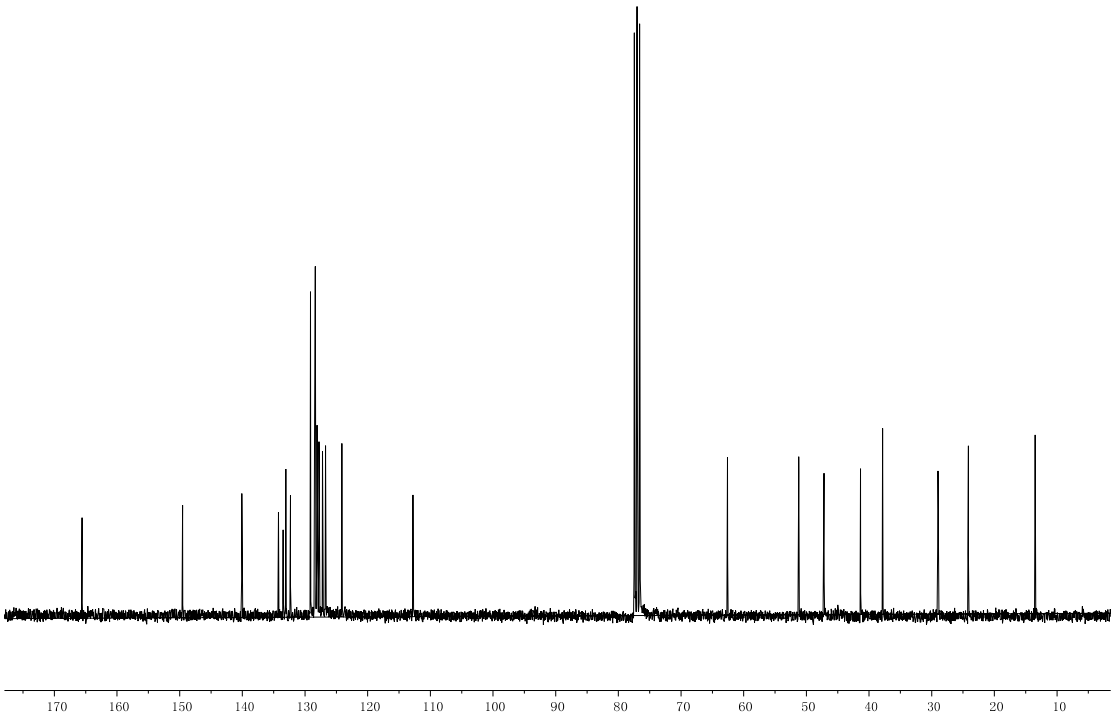
1.0
0.5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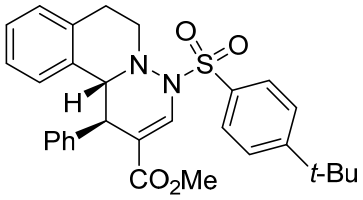
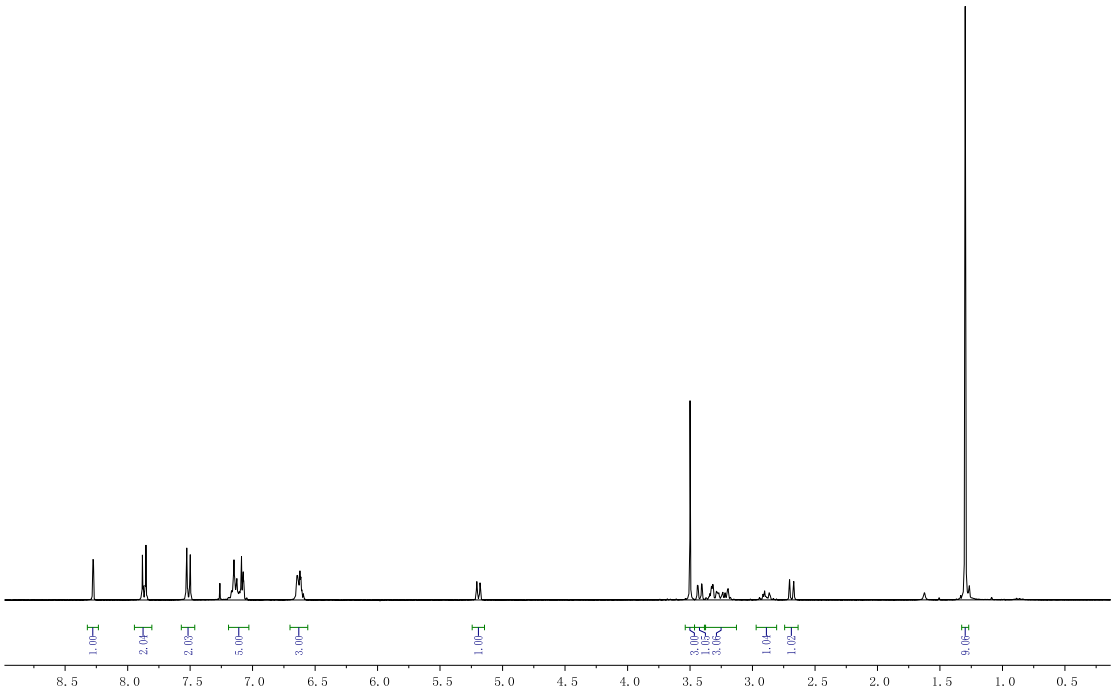
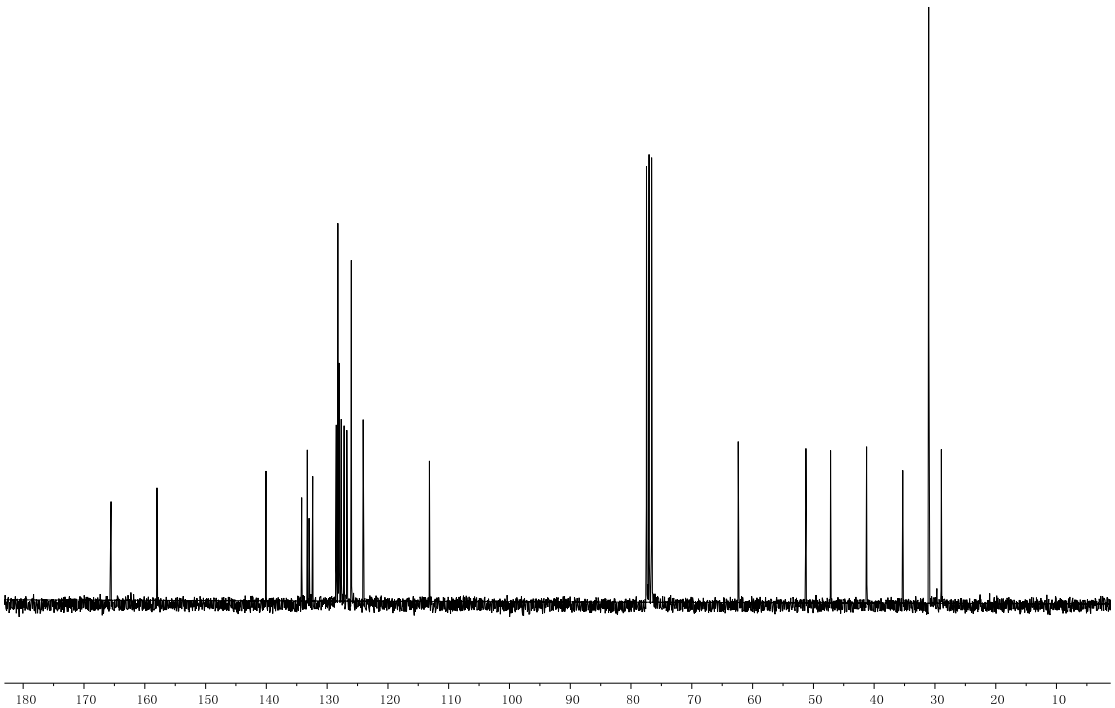

O
O
S
N
N
H
Ph
CO2Me
t-Bu

6la


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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100
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60
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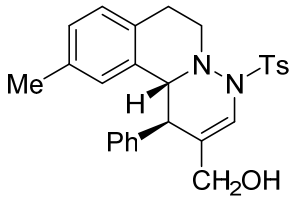
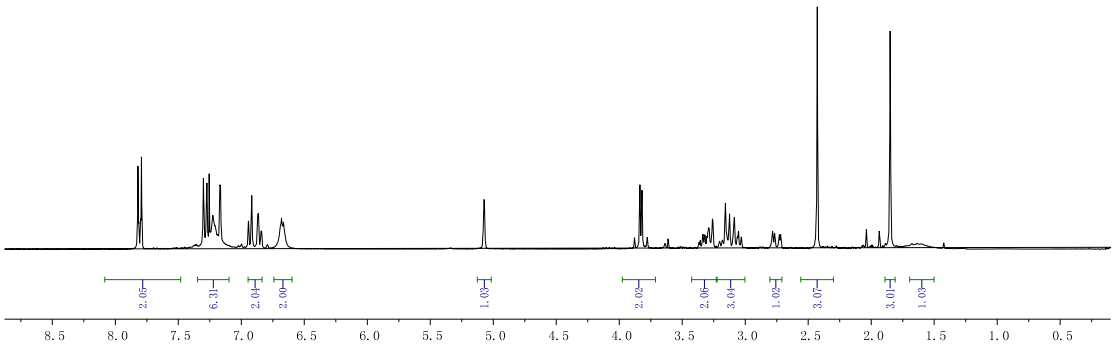
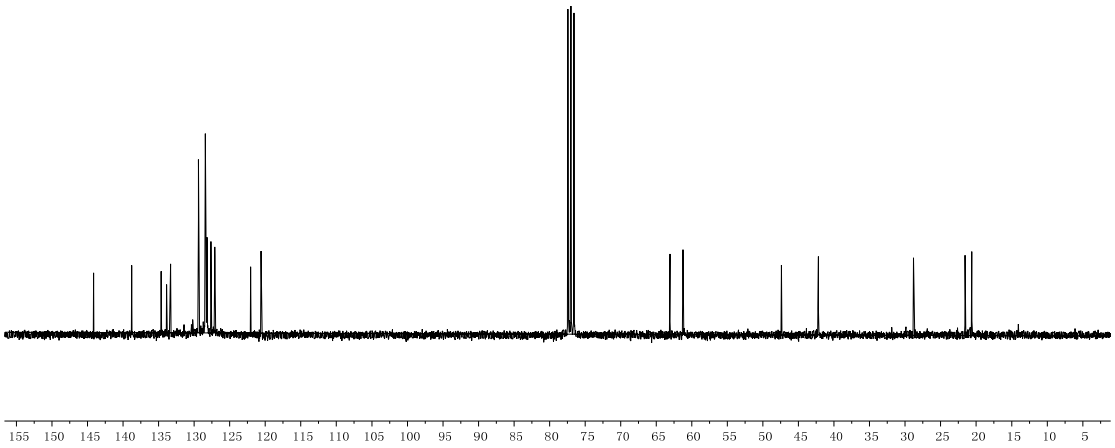
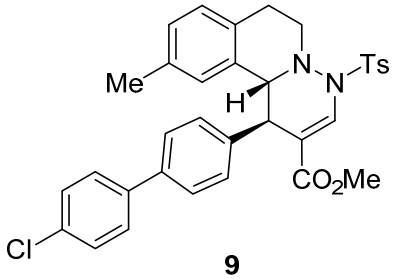
20
10


Me
N
N
Ts
H
Ph
CH2OH

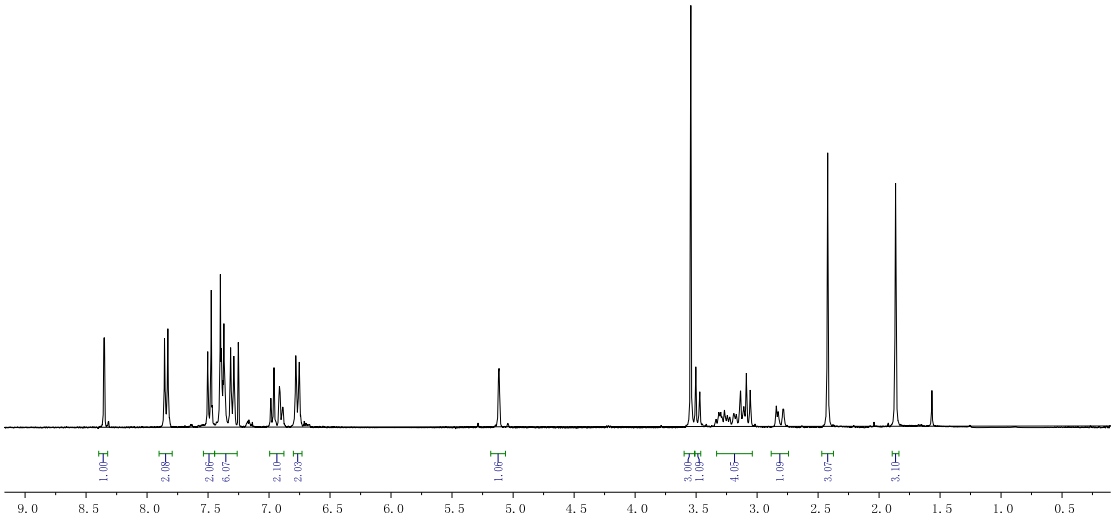
8


2.05
6.31
2.04
2.00
1.00
2.02
2.06
3.04
1.02
3.07
3.01
1.03
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


155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5


Me
H
N
N
Ts
CO2Me
Cl

9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9.0
8.5
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7.0
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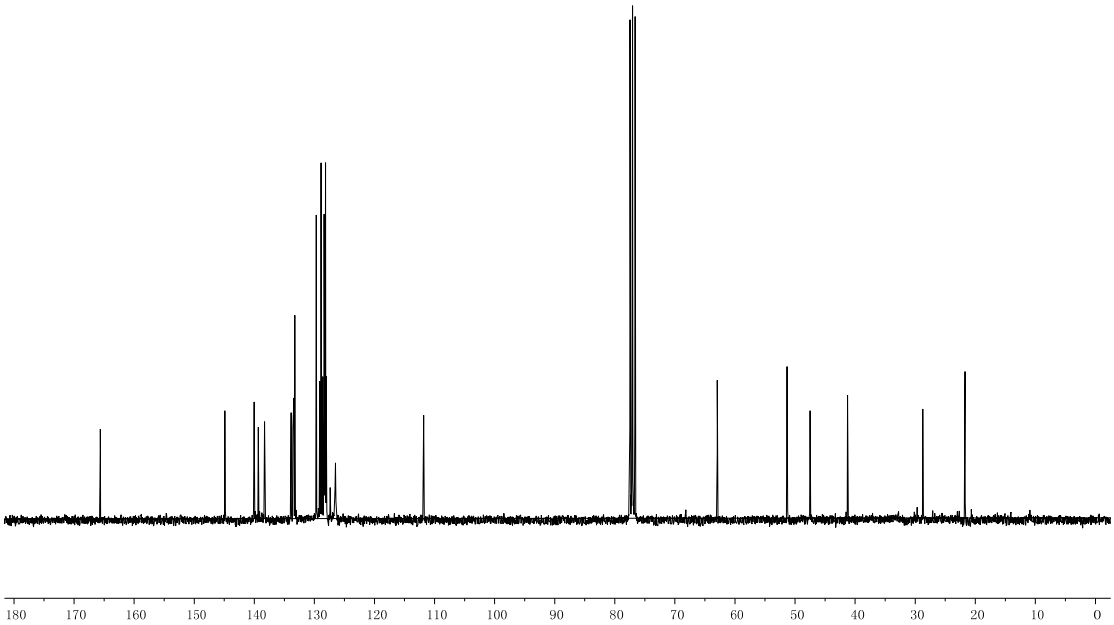
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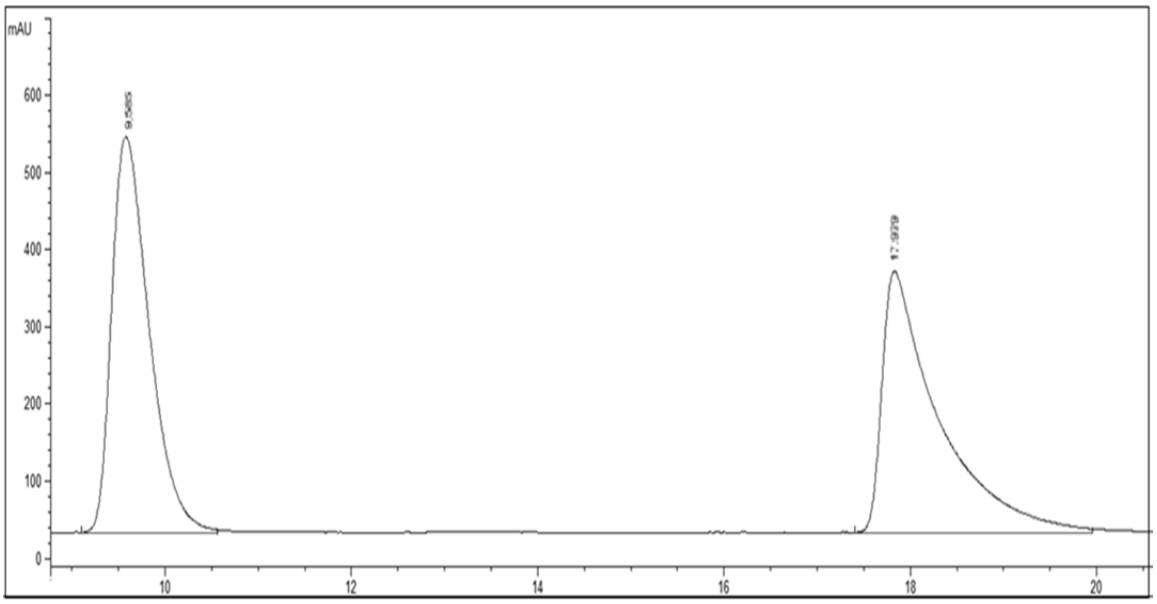
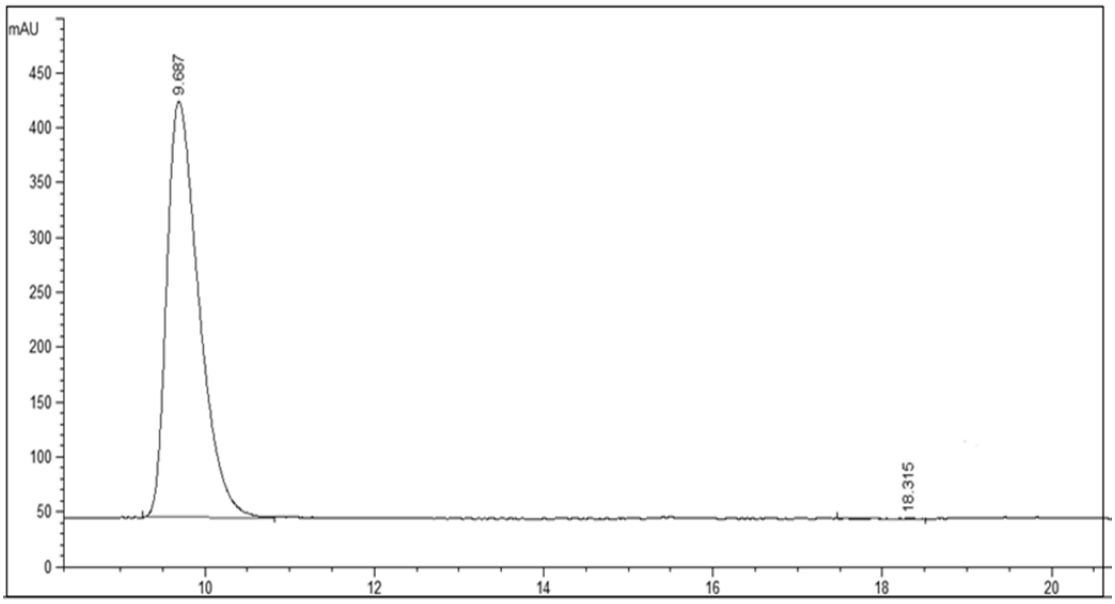
HPLC chromatogram of racemic product 6aa



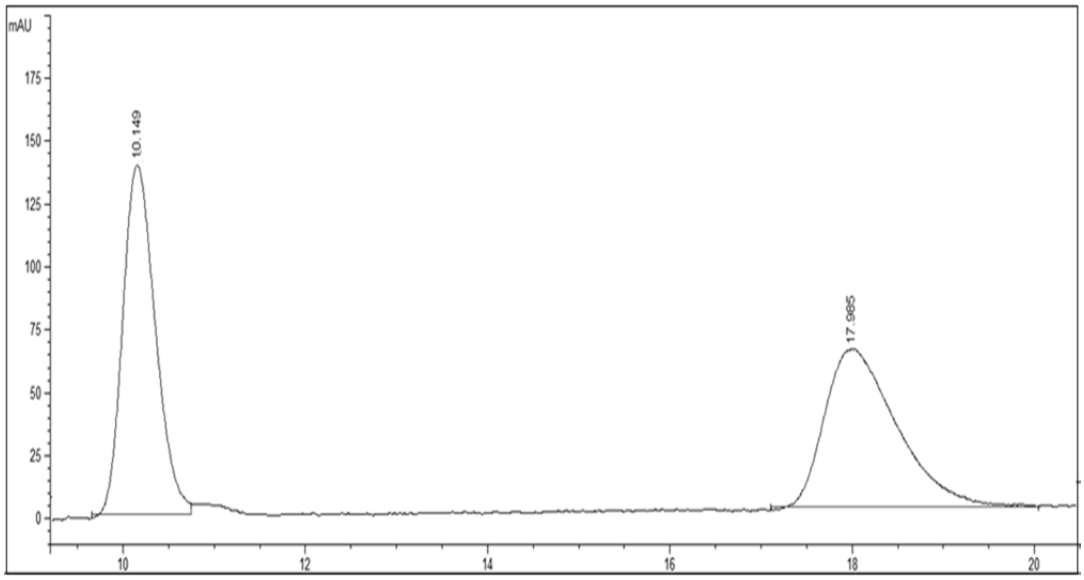
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.585	MM	0.4447	2.08345e4	780.88208	50.0751
2	17.979	MM	1.1970	2.07719e4	289.23416	49.9249

HPLC chromatogram of chiral product 6aa



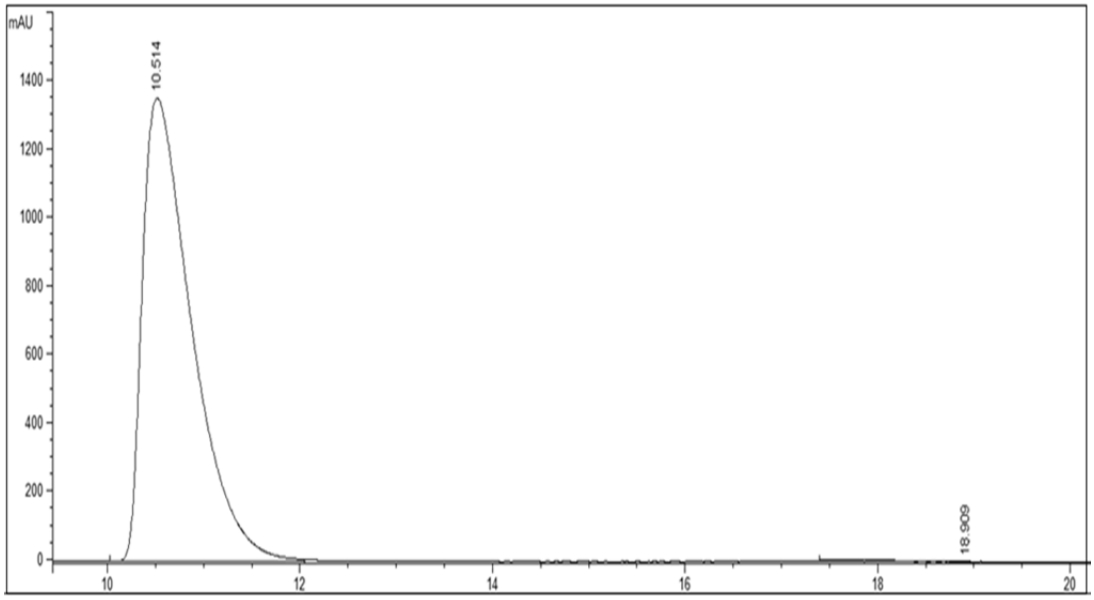
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.687	MM	0.4397	1.00123e4	379.48767	99.8239
2	18.315	MM	0.3375	17.66166	8.72215e-1	0.1761

HPLC chromatogram of racemic product 6ab



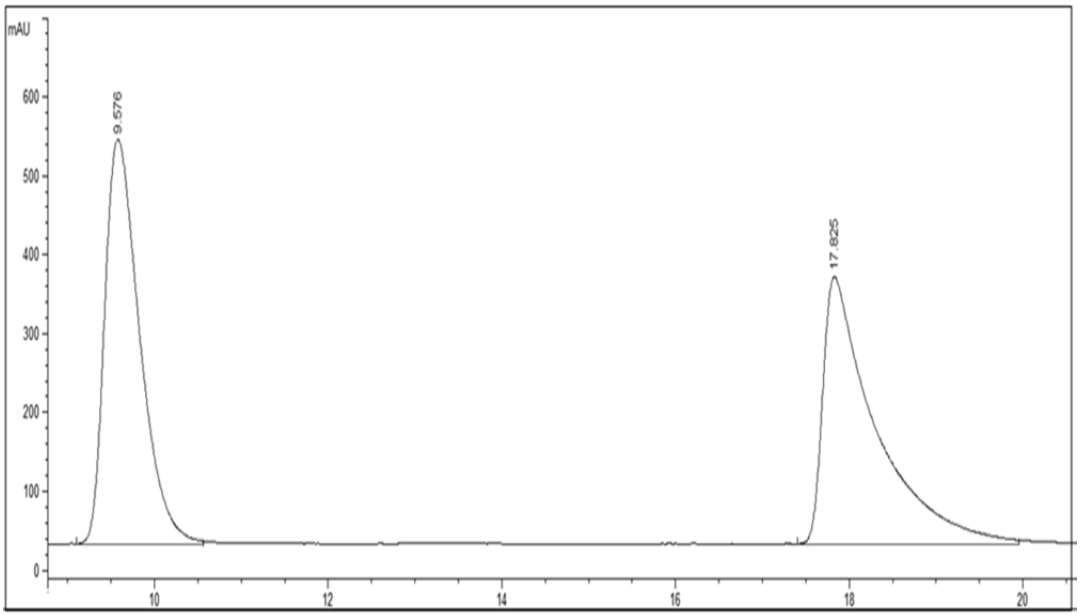
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.149	MF	0.4150	3458.14990	138.88312	49.9184
2	17.985	MM	0.9218	3469.45166	62.72758	50.0816

HPLC chromatogram of chiral product 6ab



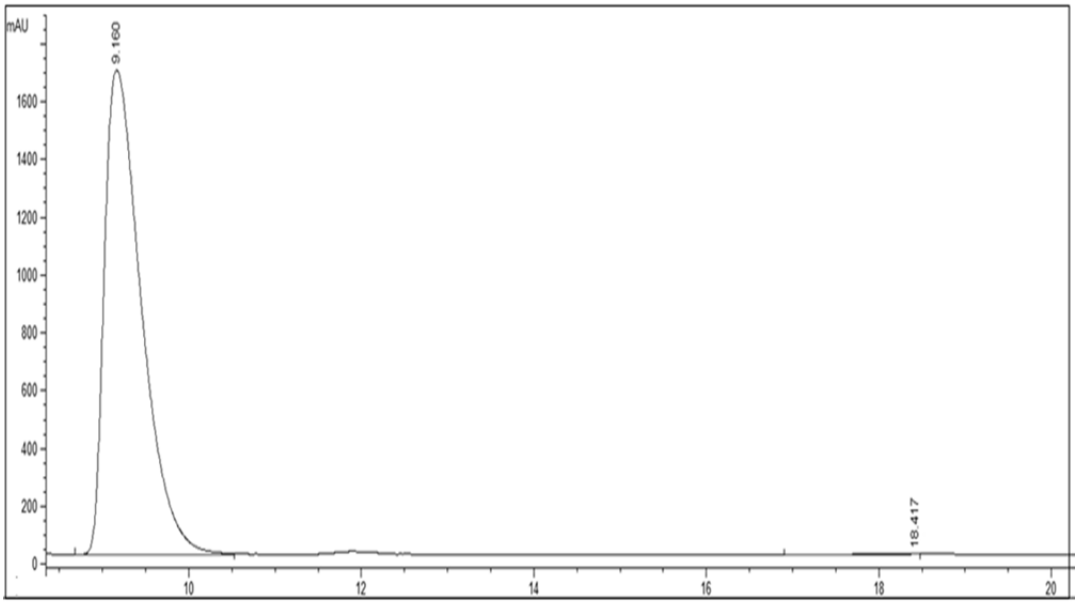
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.514	VV	0.5385	4.81248e4	1353.70813	99.9886
2	18.909	MM	0.1540	5.47514	5.92633e-1	0.0114

HPLC chromatogram of racemic product 6ac



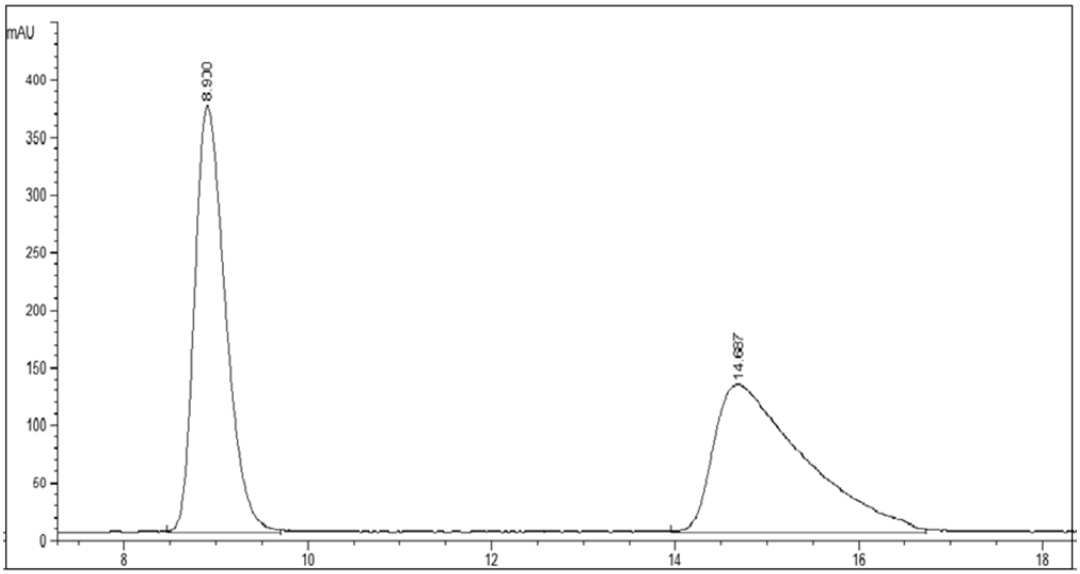
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.576	VV	0.4359	1.44474e4	513.64093	50.1619
2	17.825	VV	0.5675	1.43541e4	339.53351	49.8381

HPLC chromatogram of chiral product 6ac



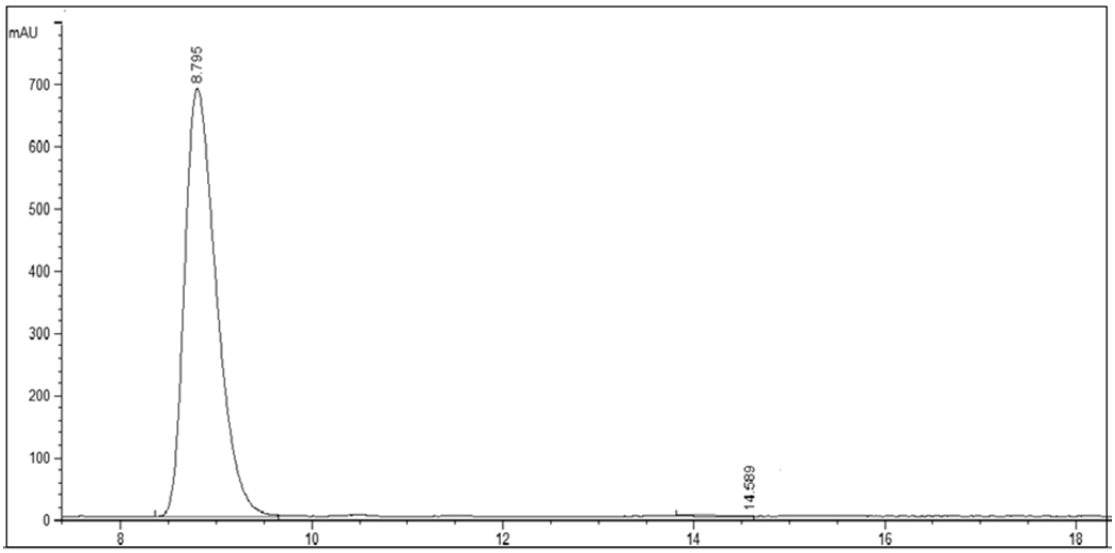
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.160	VV	0.4589	5.00574e4	1677.13086	99.9577
2	18.417	MM	0.2031	21.20158	1.73966	0.0423

HPLC chromatogram of racemic product 6ad



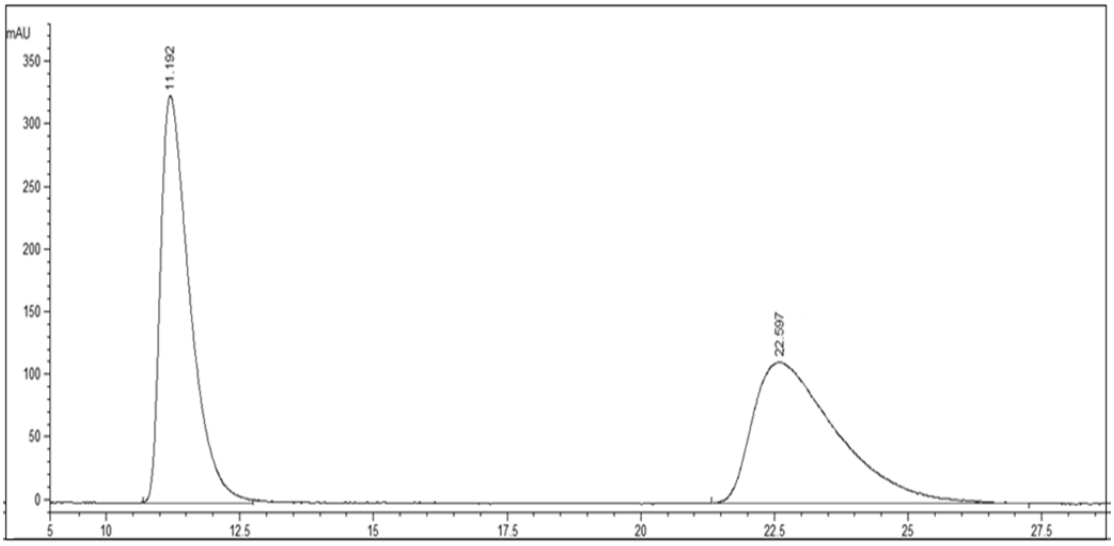
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.900	VV	0.3615	8660.41211	370.58380	49.6806
2	14.687	VV	0.9191	8771.78125	127.96967	50.3194

HPLC chromatogram of chiral product 6ad



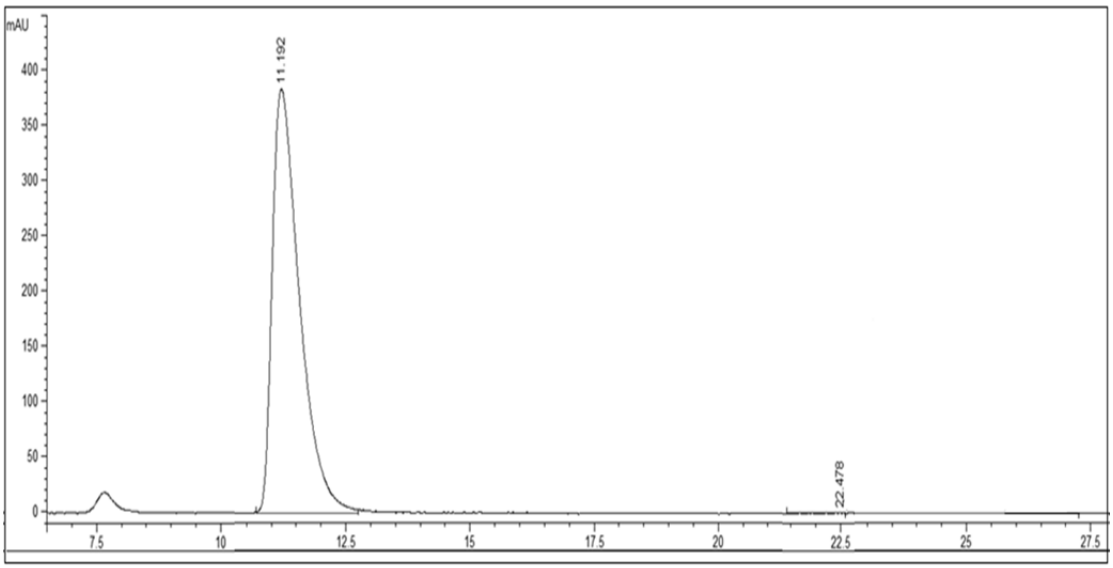
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.795	VV	0.3573	1.60694e4	690.79352	99.9927
2	14.589	MM	0.0671	1.17285	2.91319e-1	7.298e-3

HPLC chromatogram of racemic product 6ae



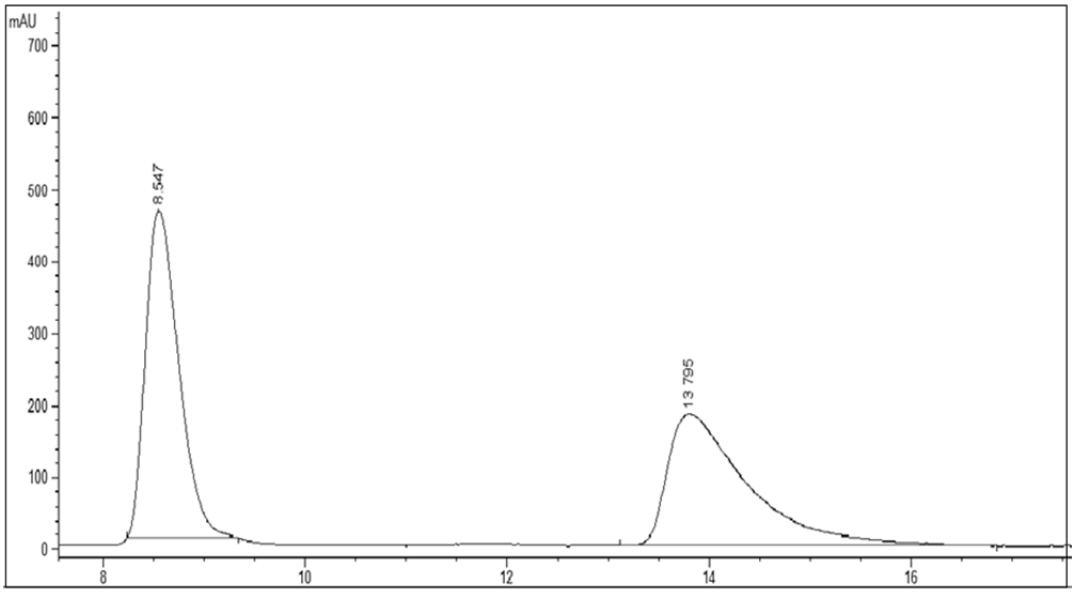
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.192	VV	0.5625	1.24960e4	325.79202	49.9482
2	22.597	MM	1.8418	1.25220e4	113.30974	50.0518

HPLC chromatogram of chiral product 6ae



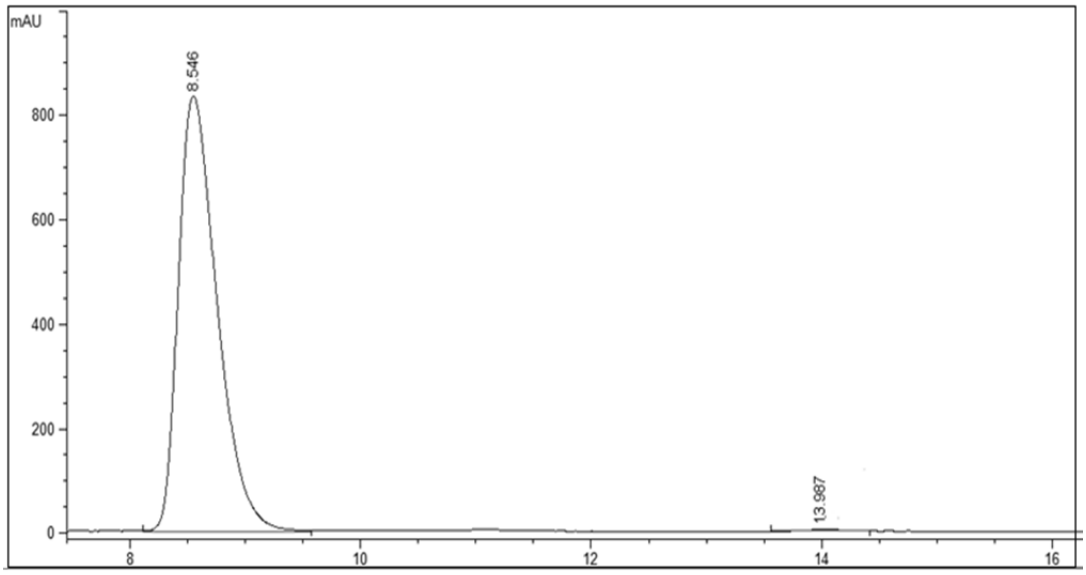
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.192	MF	0.6584	1.24027e4	313.96936	99.8972
2	22.478	MM	0.4012	12.75985	5.30107e-1	0.1028

HPLC chromatogram of racemic product 6af



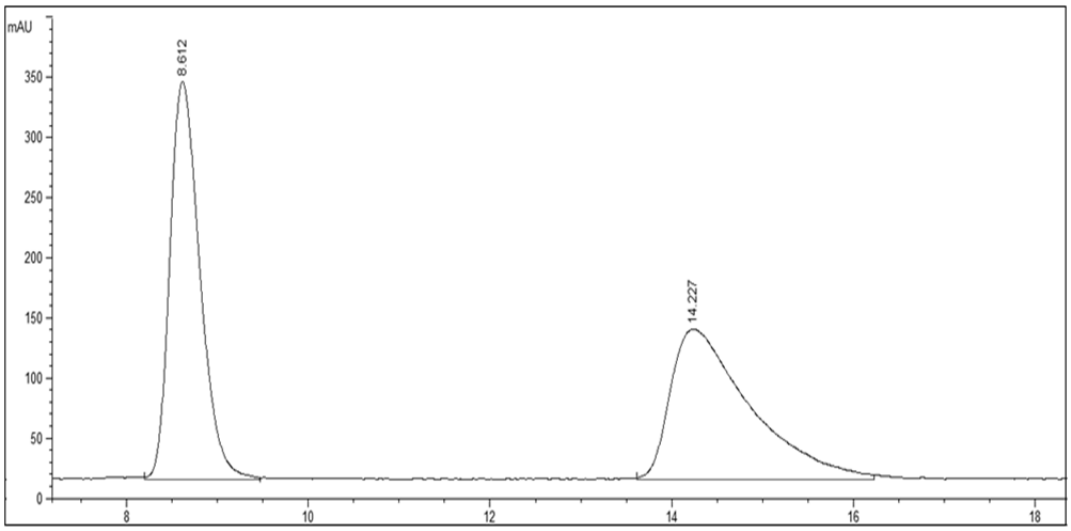
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.547	MM	0.3812	1.04429e4	456.61319	50.6449
2	13.795	MM	0.9218	1.01770e4	183.99834	49.3551

HPLC chromatogram of chiral product 6af



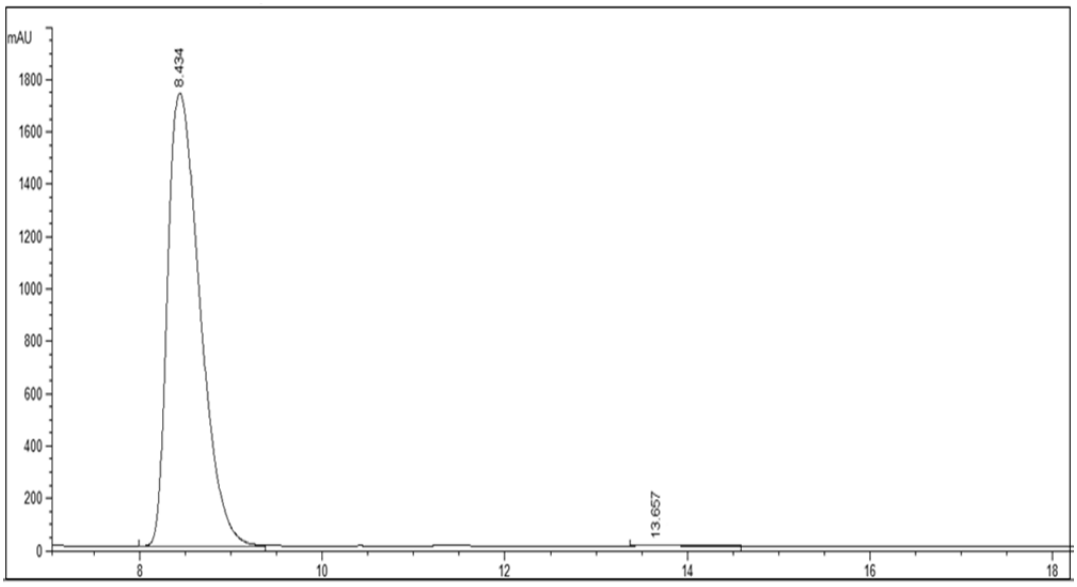
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.546	VV	0.3627	1.95596e4	833.17670	99.5234
2	13.987	MM	0.4583	93.66019	3.40638	0.4766

HPLC chromatogram of racemic product 6ag



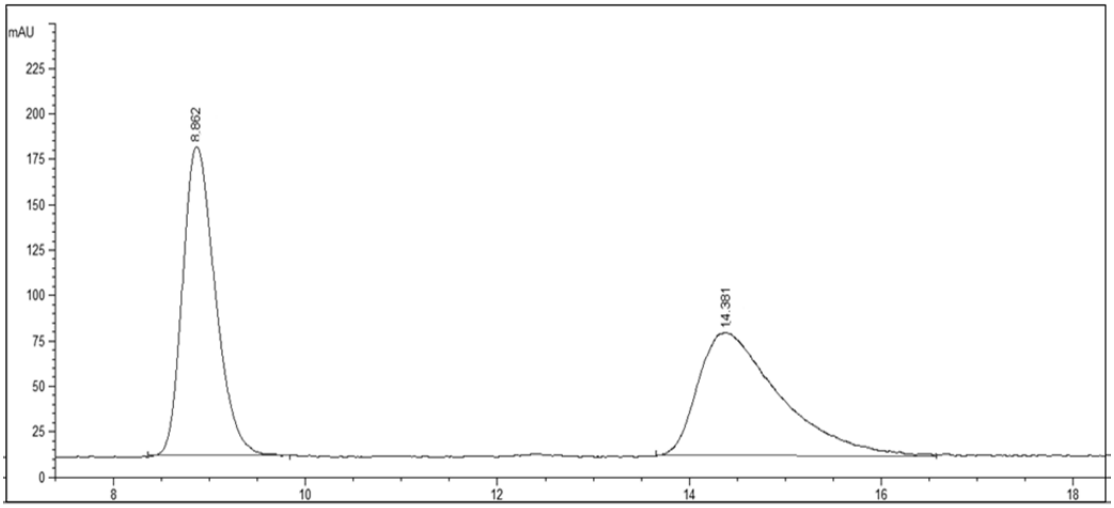
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.612	VV	0.3564	7647.78613	331.58701	49.9335
2	14.227	VV	0.8002	7668.14502	125.24094	50.0665

HPLC chromatogram of chiral product 6ag



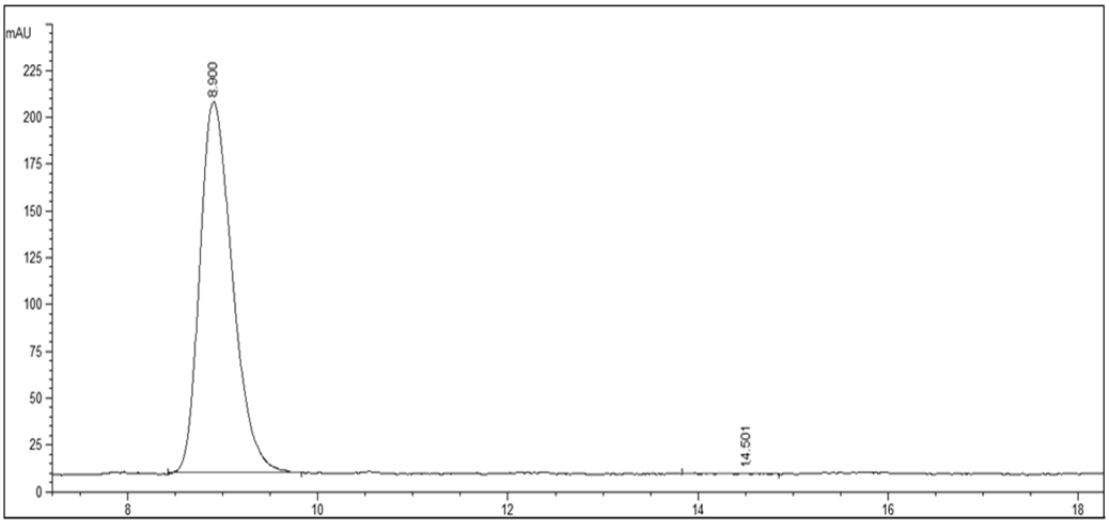
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.434	VV	0.3857	4.28269e4	1733.83289	99.7009
2	13.657	MM	0.3754	128.47194	5.70451	0.2991

HPLC chromatogram of racemic product 6ah



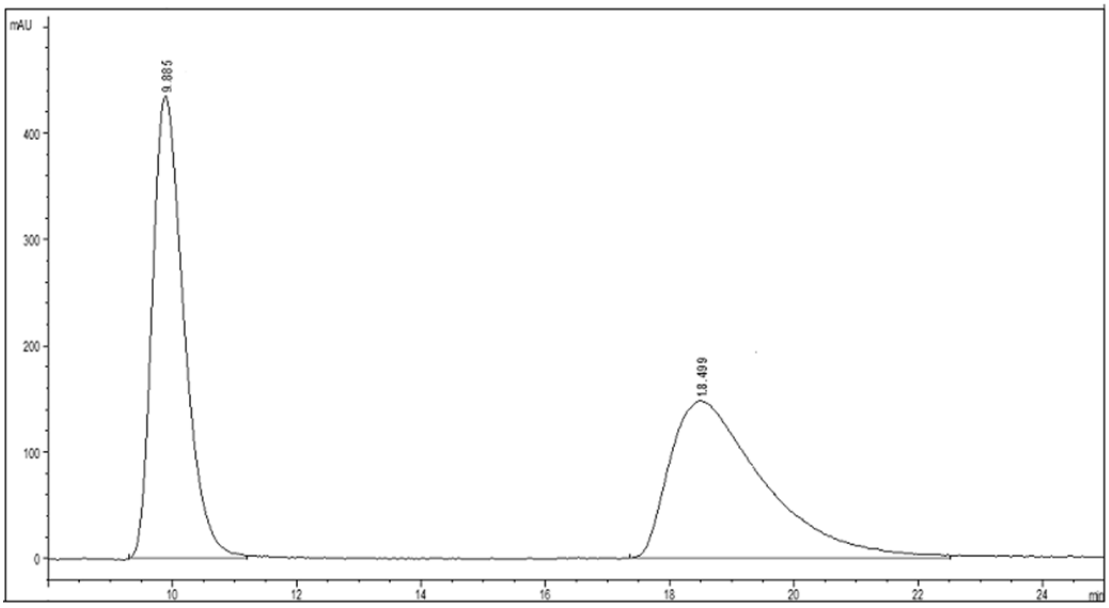
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.862	MM	0.3940	4022.40112	170.14165	50.0065
2	14.381	MM	0.9904	4021.35449	67.67087	49.9935

HPLC chromatogram of chiral product 6ah



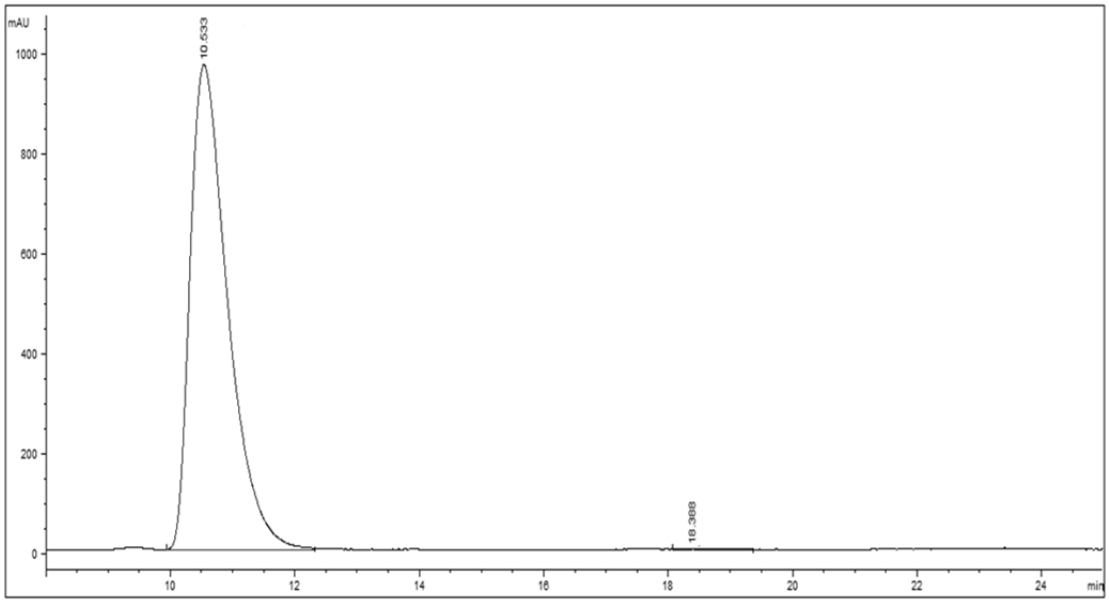
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.900	MM	0.3983	4739.91211	198.35173	99.7596
2	14.501	MM	0.3237	11.42220	5.88051e-1	0.2404

HPLC chromatogram of racemic product 6ai



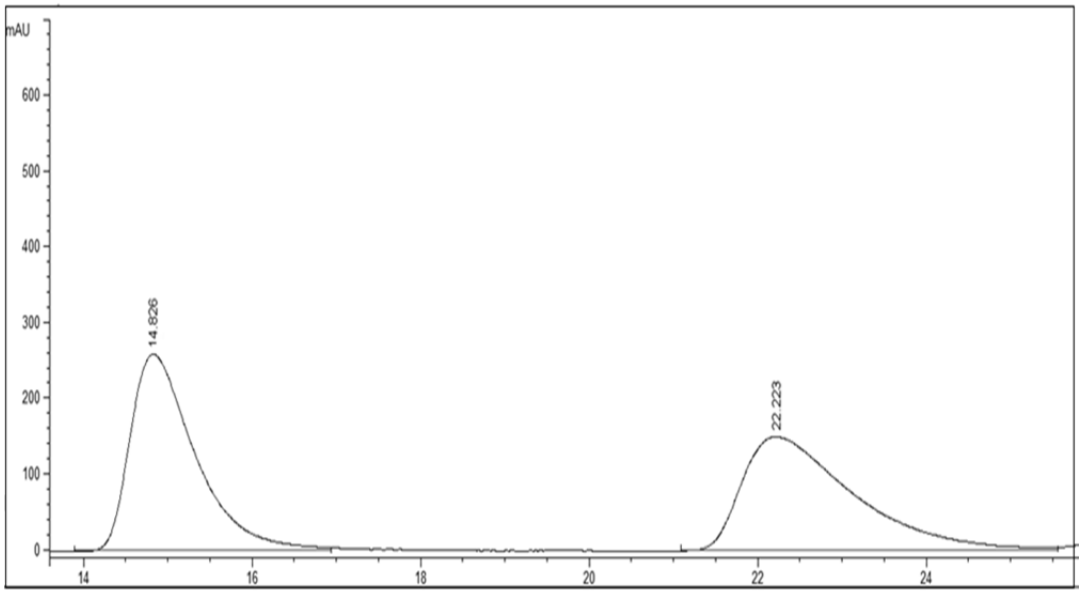
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.885	MM	0.5891	1.54248e4	436.41086	50.0119
2	18.499	MM	1.7376	1.54175e4	147.88333	49.9881

HPLC chromatogram of chiral product 6ai



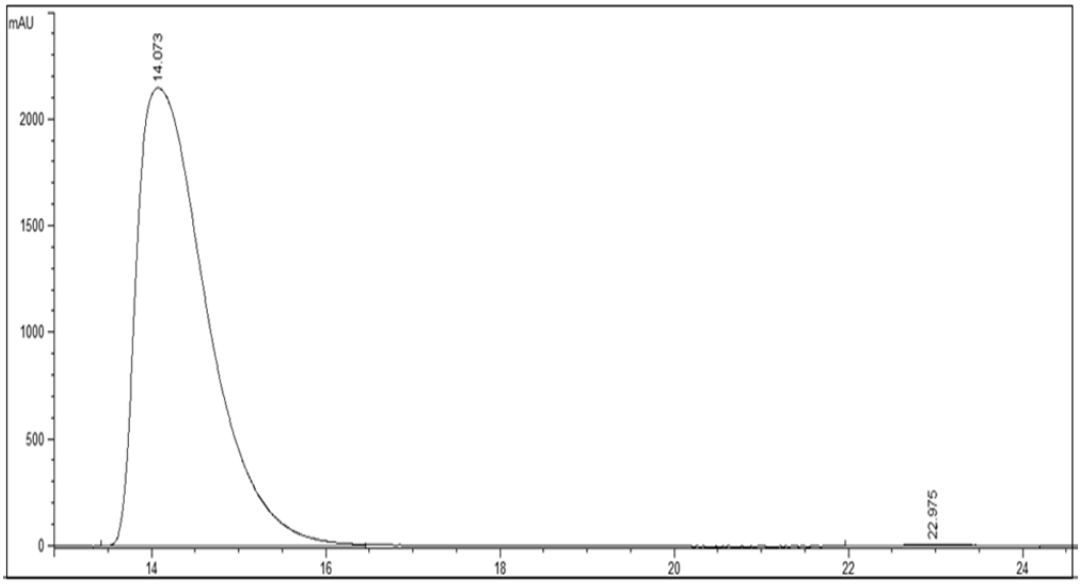
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.533	MM	0.7027	4.09640e4	971.55347	99.8962
2	18.388	MM	0.5531	42.56326	1.28255	0.1038

HPLC chromatogram of racemic product 6aj



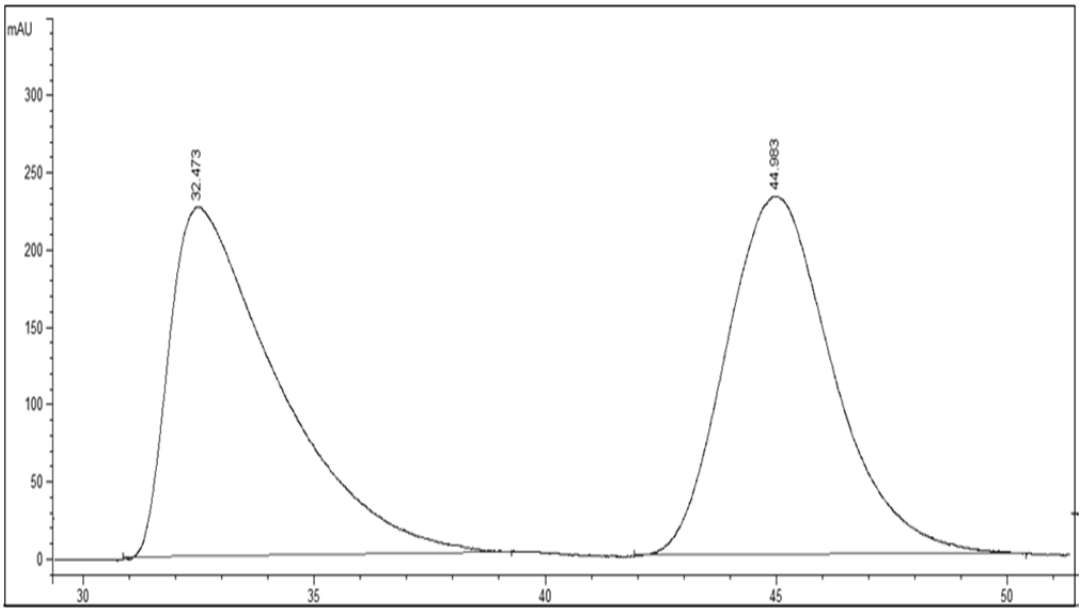
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.826	MF	0.8939	1.39317e4	259.76071	50.1909
2	22.223	MF	1.5357	1.38257e4	150.04497	49.8091

HPLC chromatogram of chiral product 6aj



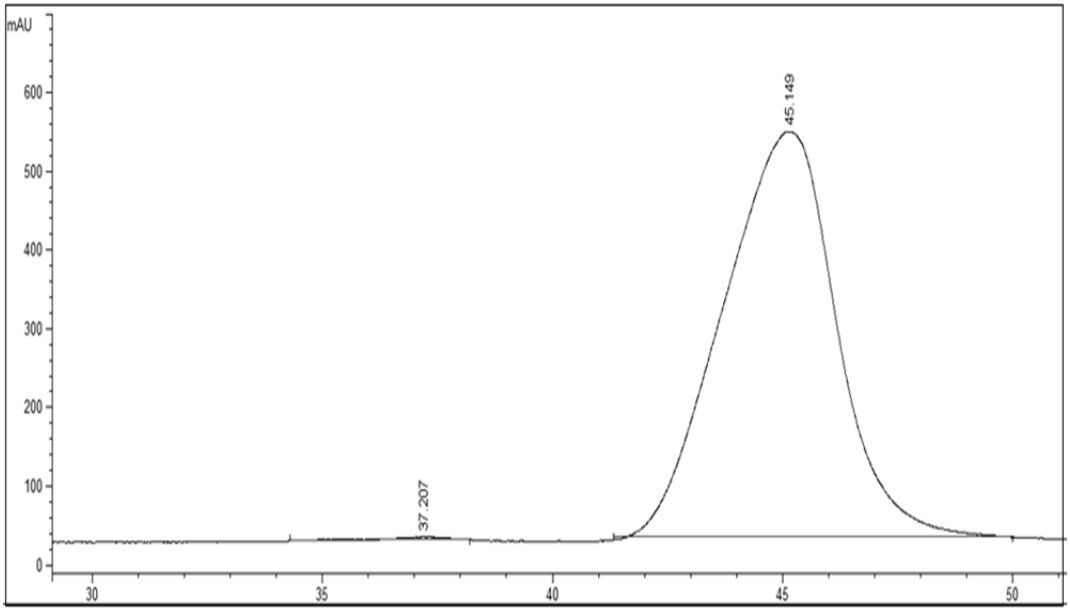
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.073	VV	0.8650	1.20575e5	2151.19458	99.7128
2	22.975	MM	1.1045	347.28311	5.24029	0.2872

HPLC chromatogram of racemic product 6ak



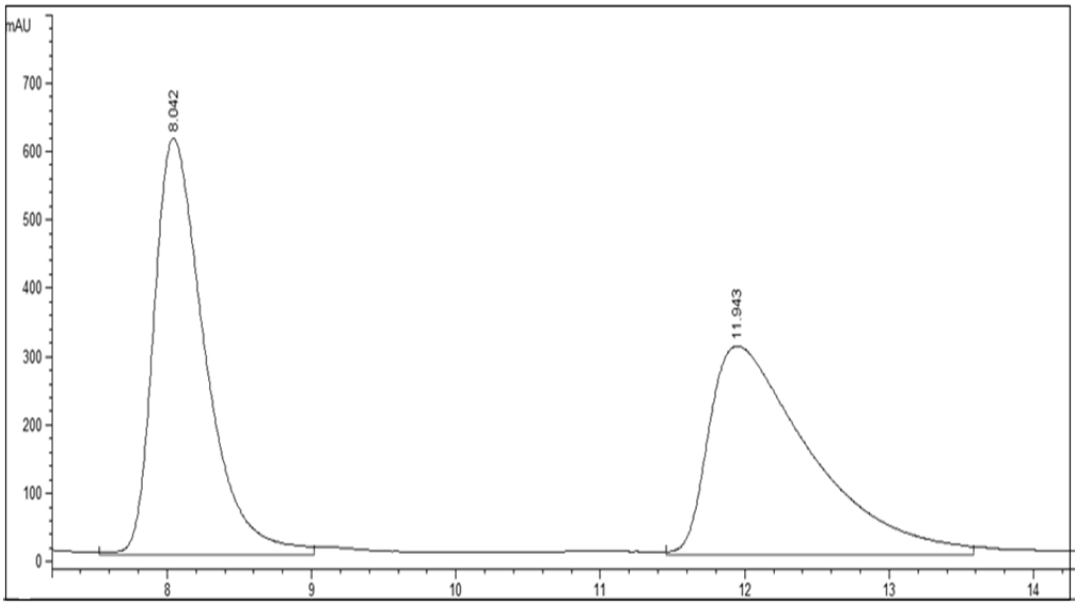
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	32.473	MM	2.7385	3.72548e4	226.73643	49.9294
2	44.983	MM	2.6832	3.73602e4	232.06348	50.0706

HPLC chromatogram of chiral product 6ak



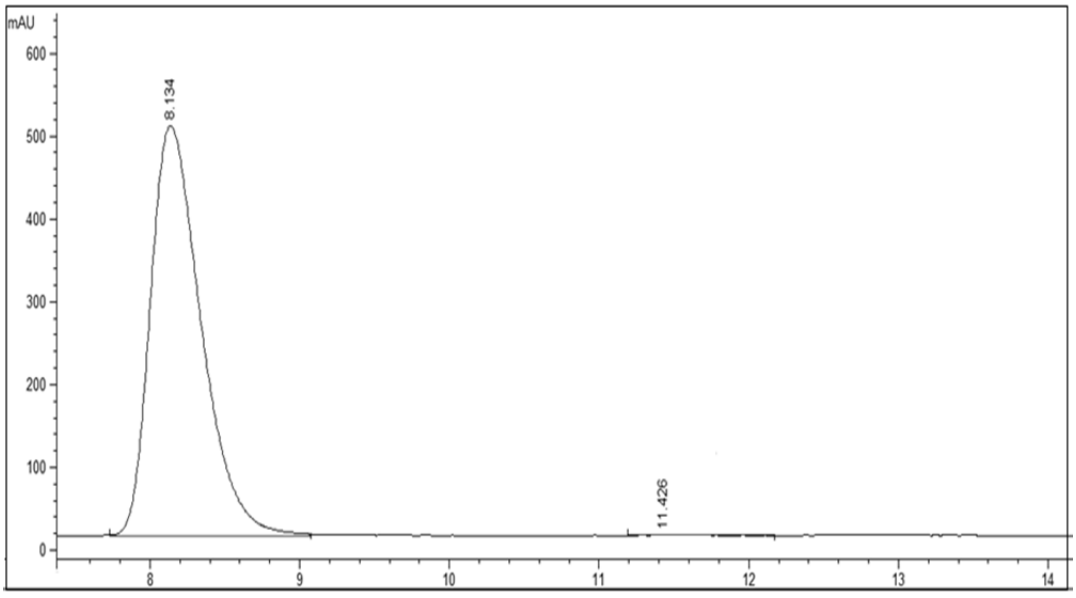
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	37.207	MM	1.5897	403.90829	4.23463	0.4568
2	45.149	MM	2.8476	8.80234e4	515.19775	99.5432

HPLC chromatogram of racemic product 6al



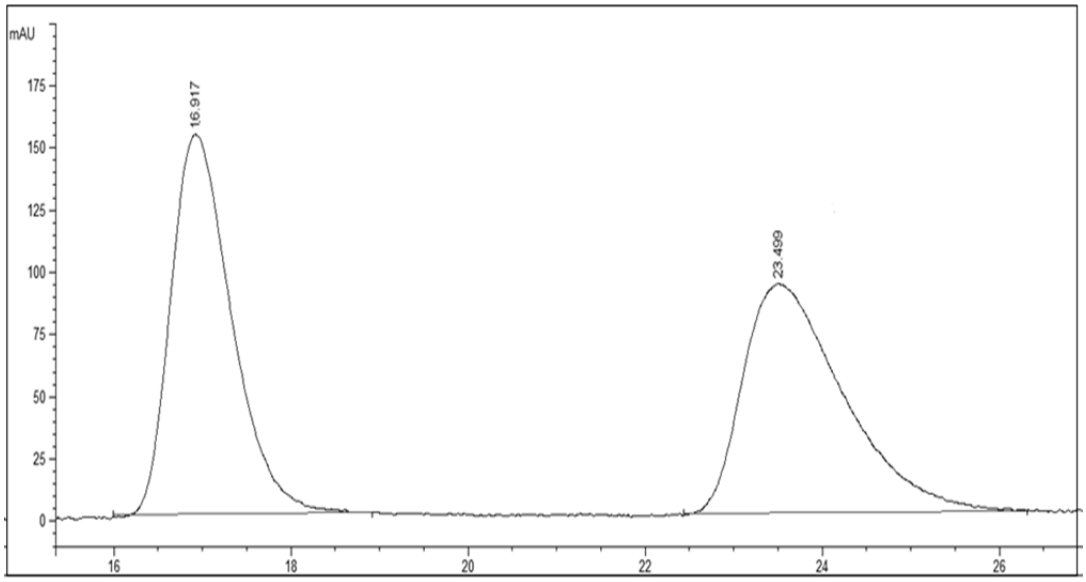
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.042	VV	0.3709	1.49644e4	609.41931	50.0028
2	11.943	VV	0.6835	1.49628e4	305.51321	49.9972

HPLC chromatogram of chiral product 6al



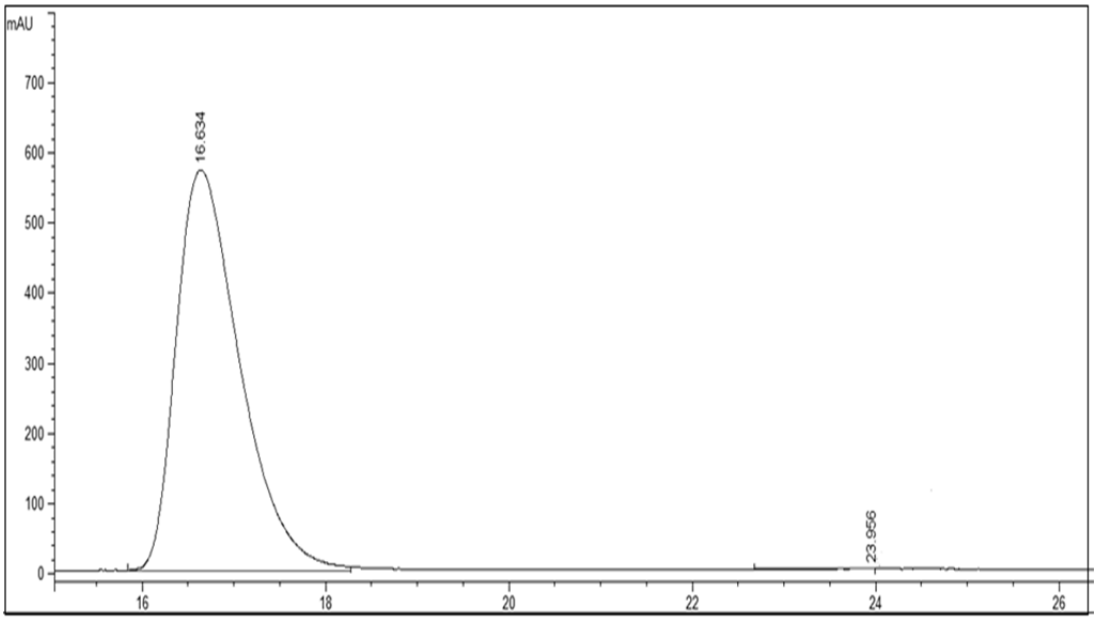
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.134	VV	0.3682	1.17535e4	495.97723	99.7213
2	11.426	MM	0.4015	32.85394	1.36366	0.2787

HPLC chromatogram of racemic product 6am



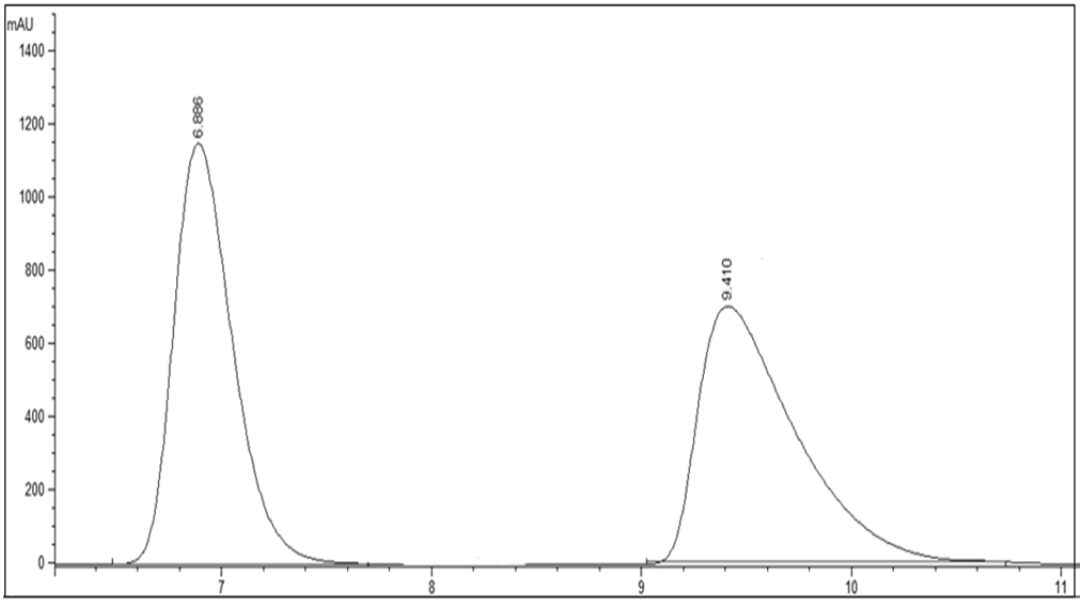
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.917	MM	0.7964	7298.99902	152.75783	49.9782
2	23.499	MM	1.3195	7305.36816	92.27367	50.0218

HPLC chromatogram of chiral product 6am



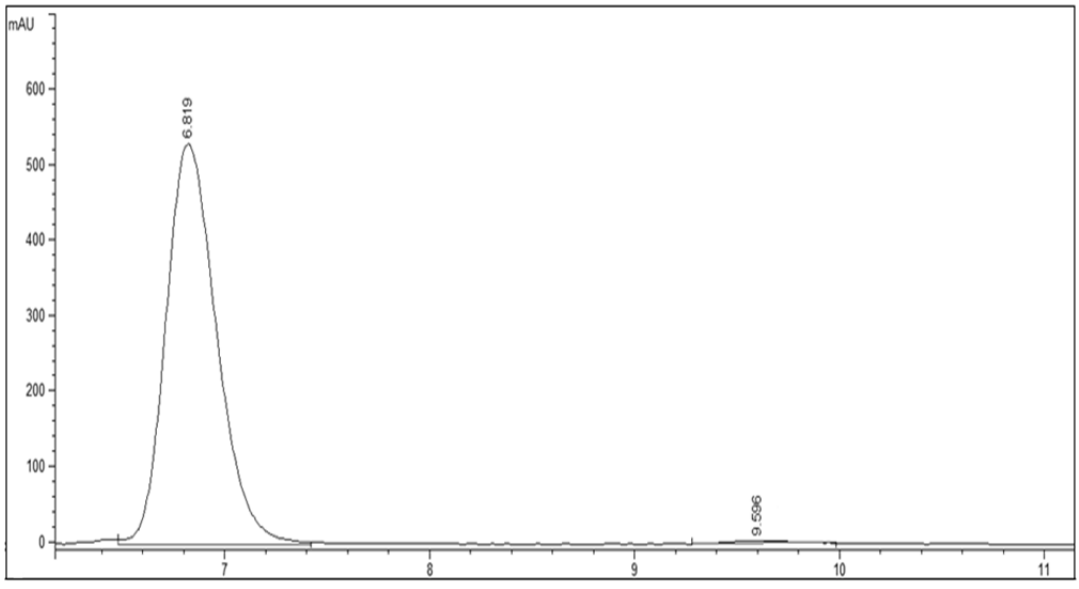
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.634	VV	0.7214	2.77403e4	572.21881	99.9235
2	23.956	MM	0.3395	21.23580	1.04237	0.0765

HPLC chromatogram of racemic product 6an



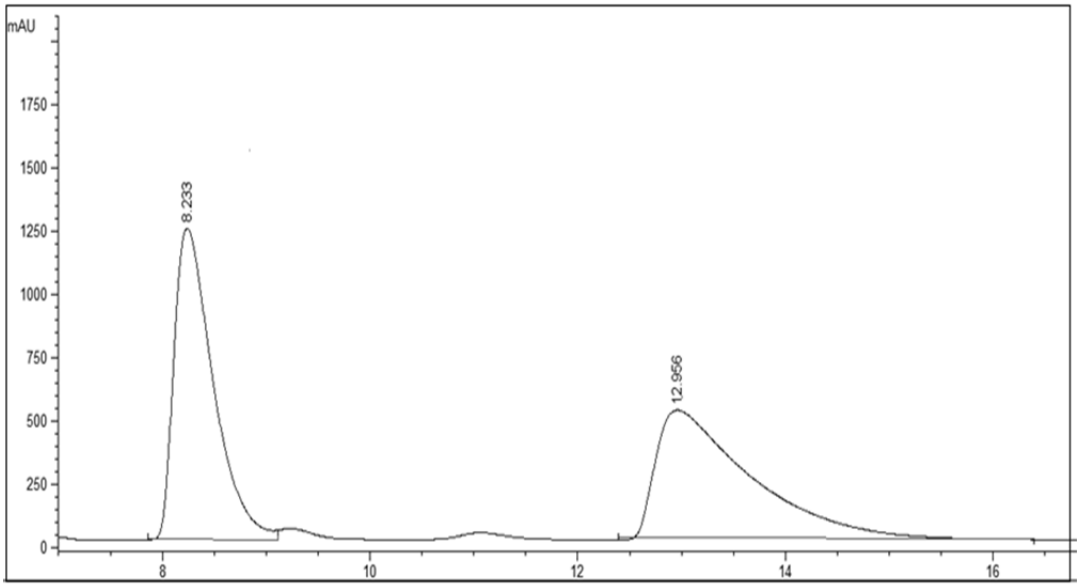
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.886	VV	0.3029	2.25488e4	1150.57288	49.9725
2	9.410	MM	0.5370	2.25737e4	700.55298	50.0275

HPLC chromatogram of chiral product 6an



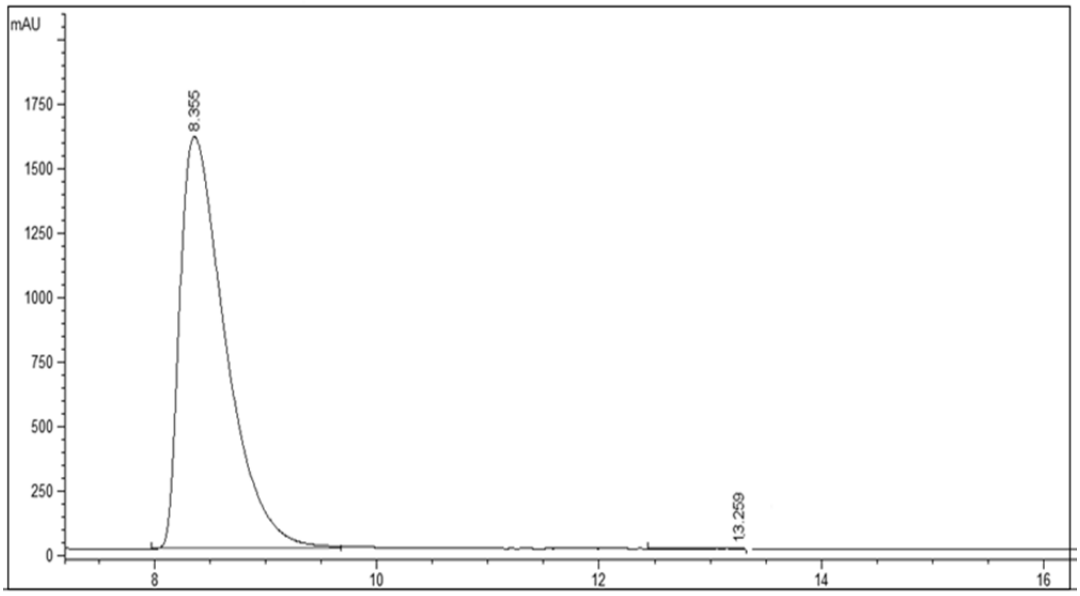
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.819	VV	0.2686	9188.49023	531.64844	99.0729
2	9.596	MM	0.3986	85.98297	3.59478	0.9271

HPLC chromatogram of racemic product 6ao



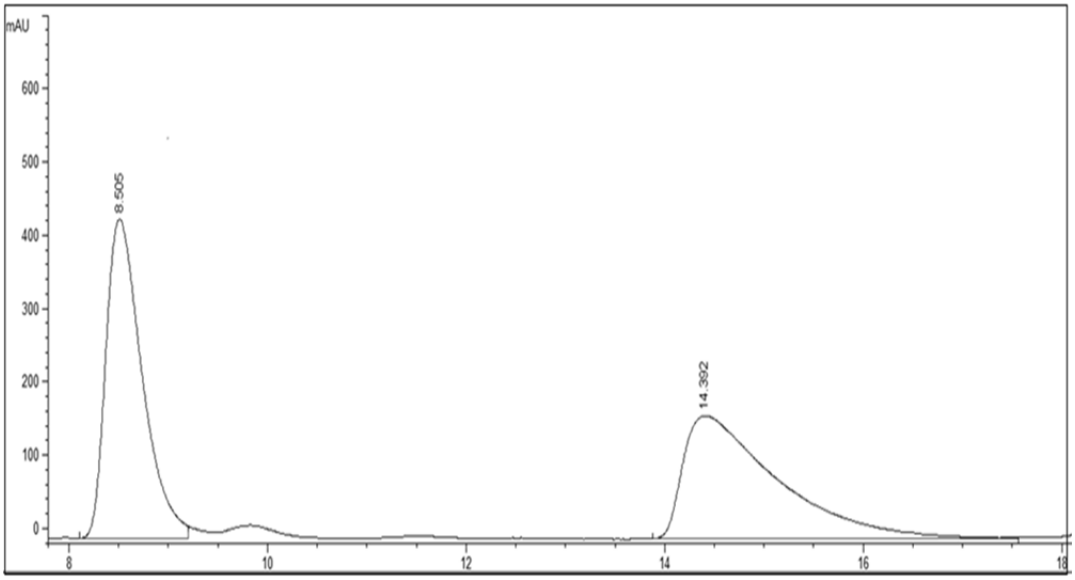
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.233	MF	0.4385	3.22613e4	1226.16150	49.9624
2	12.956	MM	1.0617	3.23099e4	507.22614	50.0376

HPLC chromatogram of chiral product 6ao



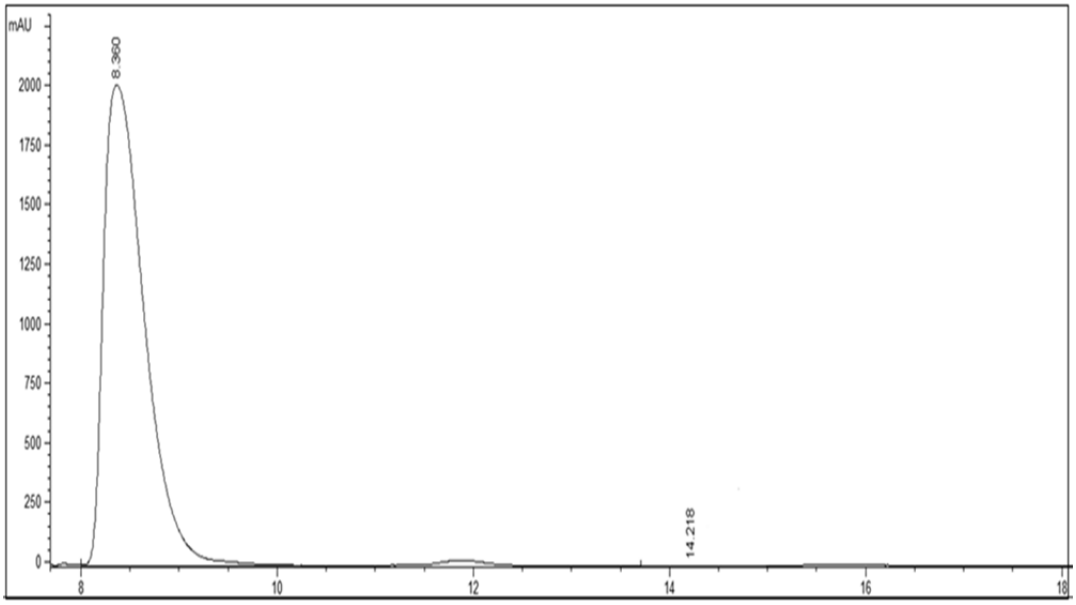
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.355	VV	0.4353	4.56034e4	1595.84143	99.9734
2	13.259	MM	0.2204	12.15605	9.19256e-1	0.0266

HPLC chromatogram of racemic product 6ap



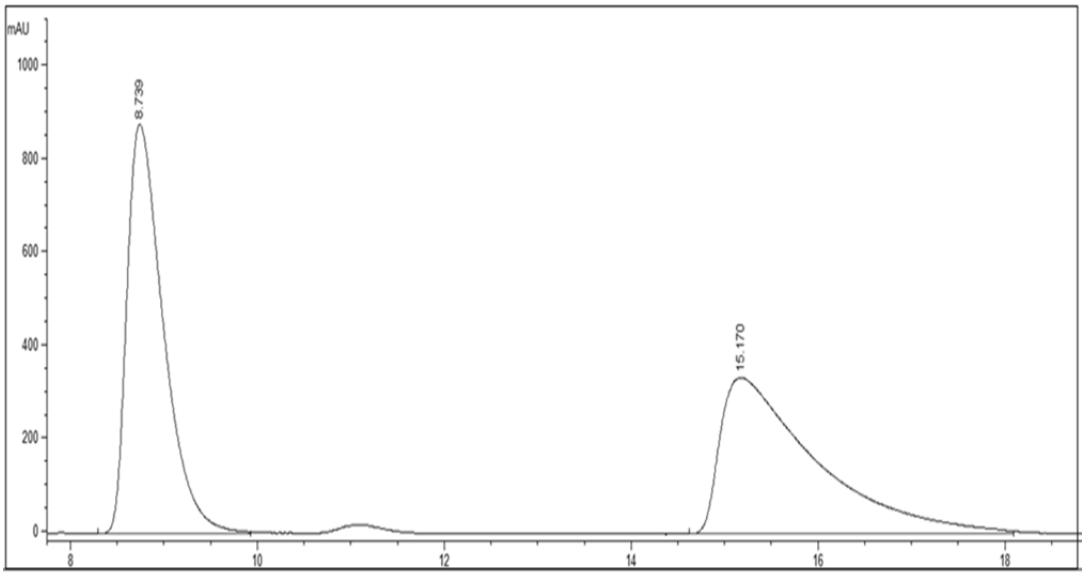
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.505	MF	0.4230	1.10704e4	436.15265	50.2443
2	14.392	MM	1.0903	1.09627e4	167.57391	49.7557

HPLC chromatogram of chiral product 6ap



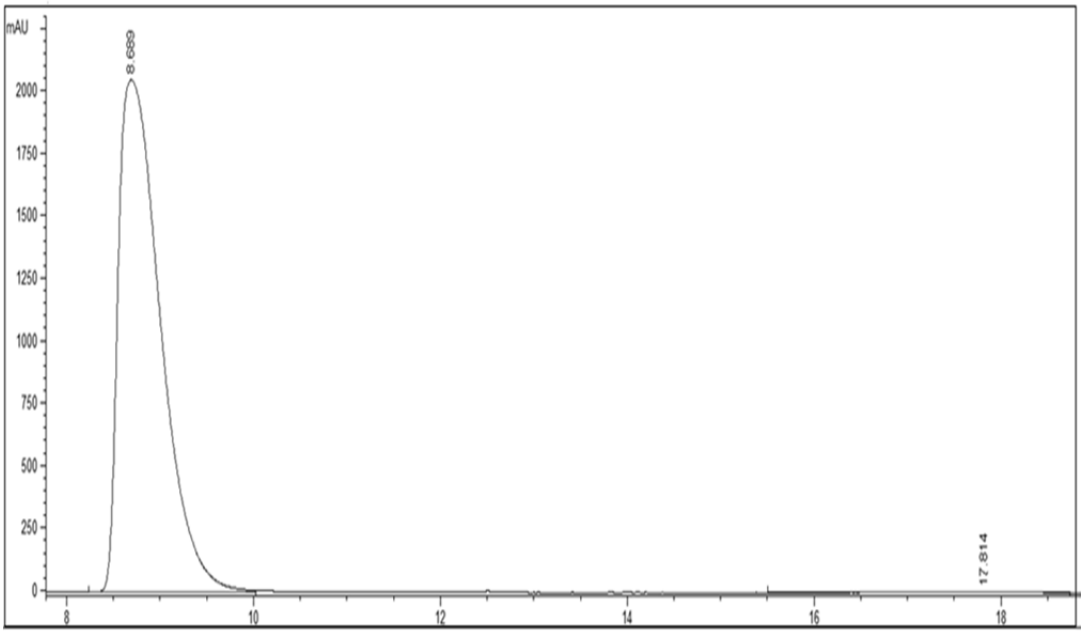
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.360	VV	0.4497	5.84643e4	2020.16724	99.7558
2	14.218	MM	0.9100	143.10991	2.62116	0.2442

HPLC chromatogram of racemic product 6aq



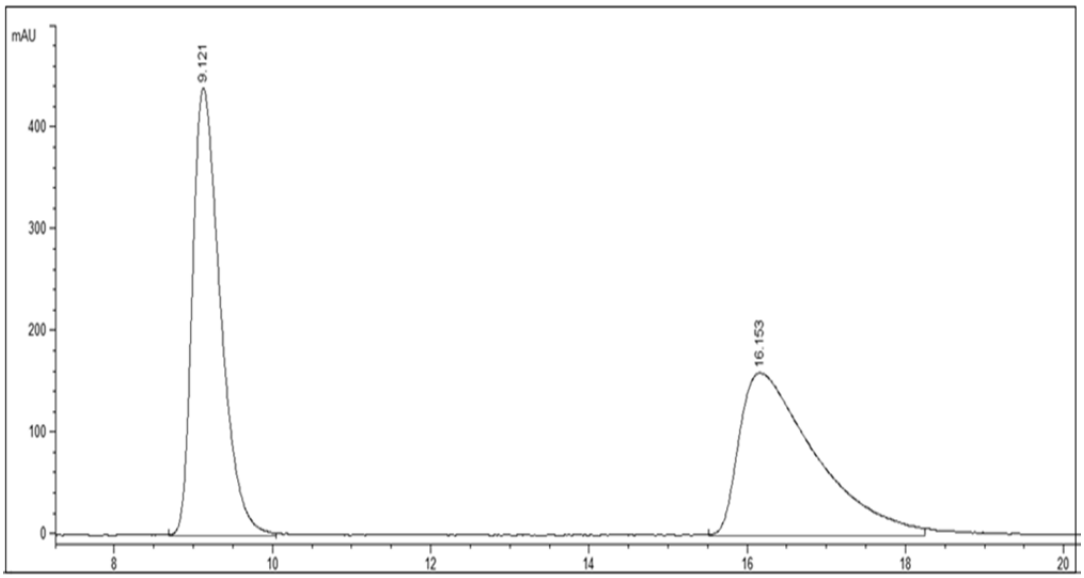
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.739	VV	0.4175	2.39073e4	879.80402	49.8640
2	15.170	VV	0.9670	2.40377e4	336.03723	50.1360

HPLC chromatogram of chiral product 6aq



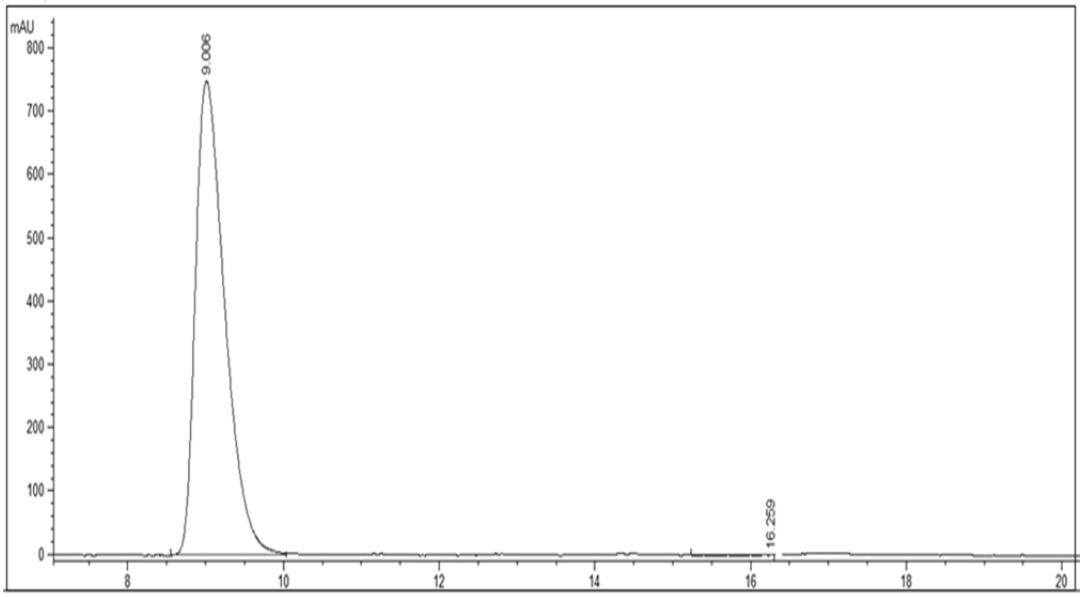
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.689	VV	0.4894	6.45944e4	2052.67725	99.6248
2	17.814	MM	1.3244	243.29512	3.06179	0.3752

HPLC chromatogram of racemic product 6ar



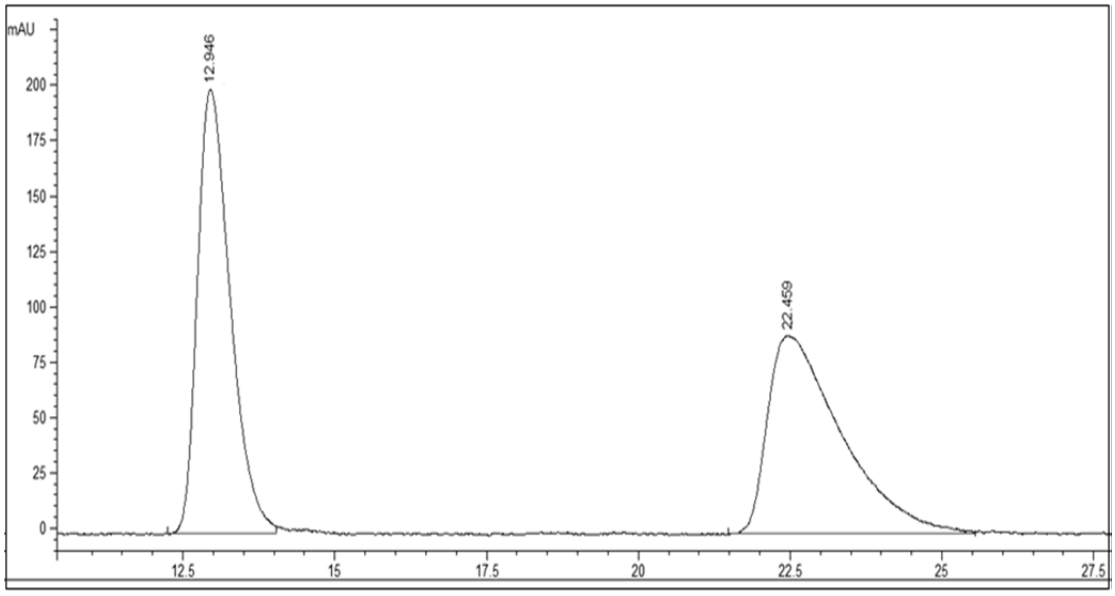
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.121	VV	0.3695	1.08280e4	440.97556	50.1211
2	16.153	VV	0.8710	1.07757e4	160.42058	49.8789

HPLC chromatogram of chiral product 6ar



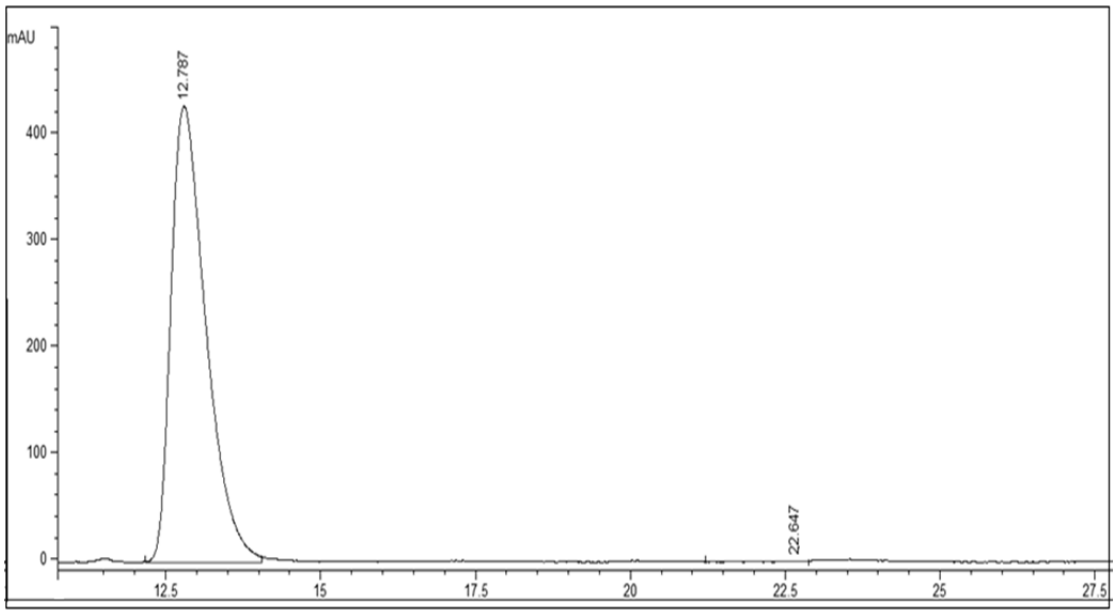
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.006	VV	0.4042	1.97315e4	750.62579	99.9762
2	16.259	MM	1.3511	4.70042	5.79830e-2	0.0238

HPLC chromatogram of racemic product 6as



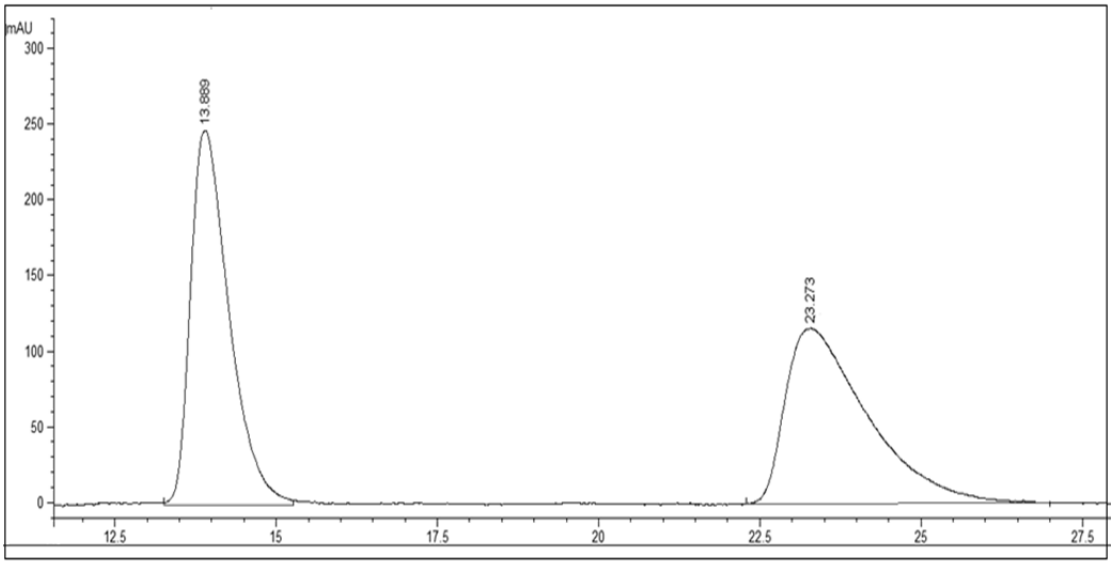
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.946	MF	0.6255	7528.44092	200.58514	50.0258
2	22.459	MM	1.4023	7520.66504	89.38356	49.9742

HPLC chromatogram of chiral product 6as



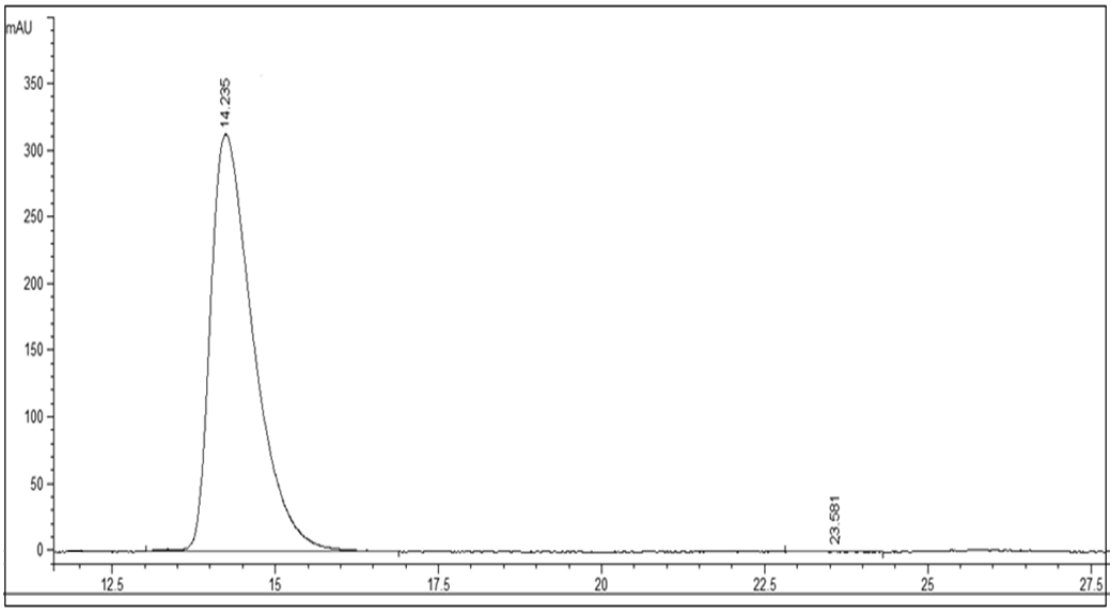
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.787	VV	0.5858	1.68846e4	429.08414	99.9375
2	22.647	MM	0.4590	10.55107	3.83097e-1	0.0625

HPLC chromatogram of racemic product 6at



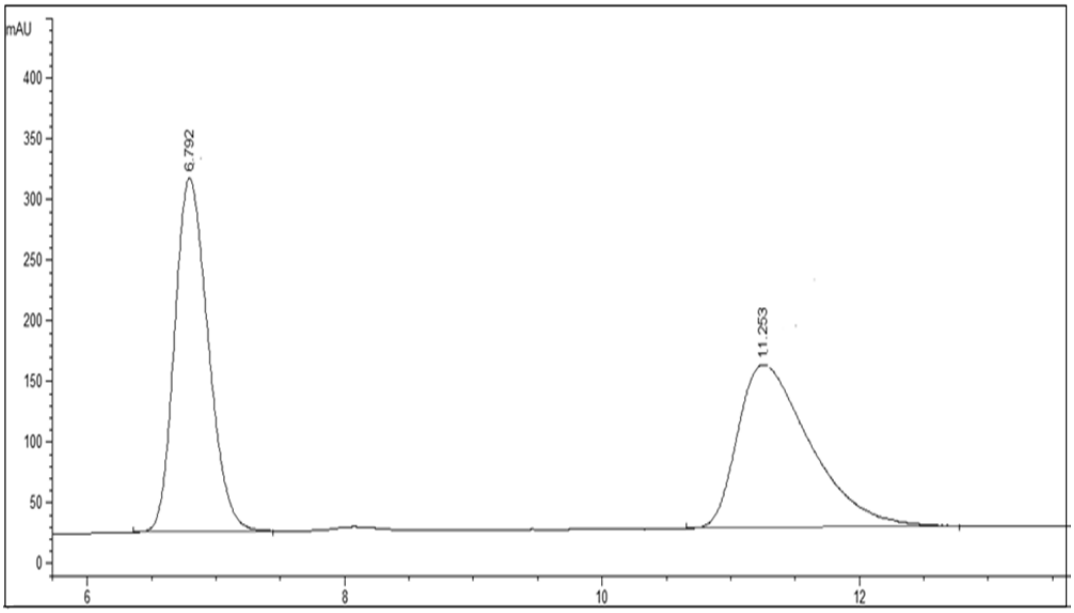
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.889	VV	0.6229	1.03704e4	248.19749	49.8929
2	23.273	MM	1.4919	1.04150e4	116.35132	50.1071

HPLC chromatogram of chiral product 6at



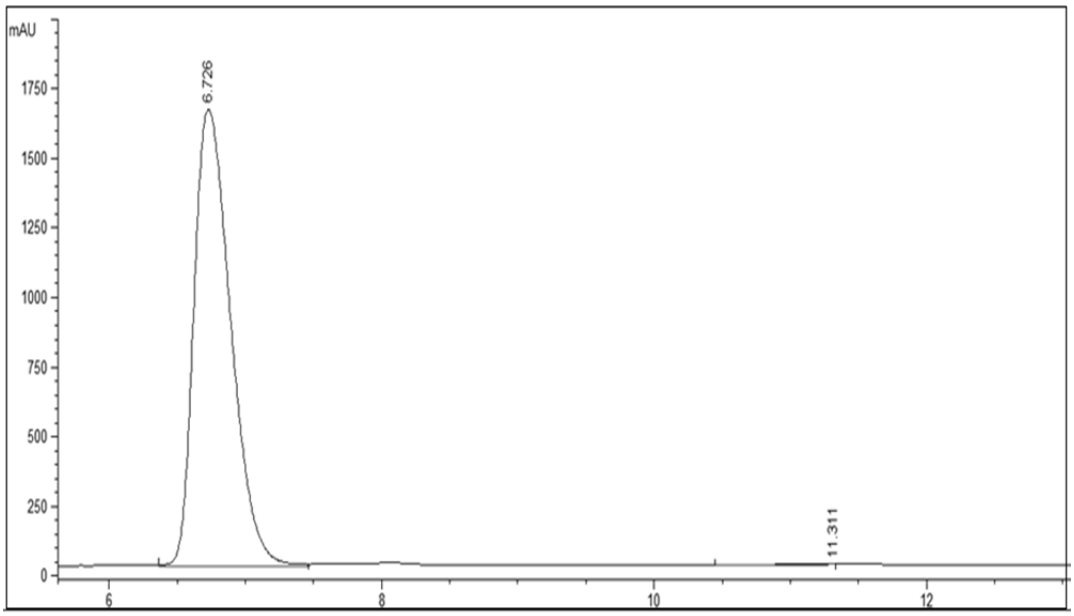
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.235	MM	0.7619	1.43046e4	312.91602	99.9111
2	23.581	MM	0.3482	12.73144	6.09383e-1	0.0889

HPLC chromatogram of racemic product 6au



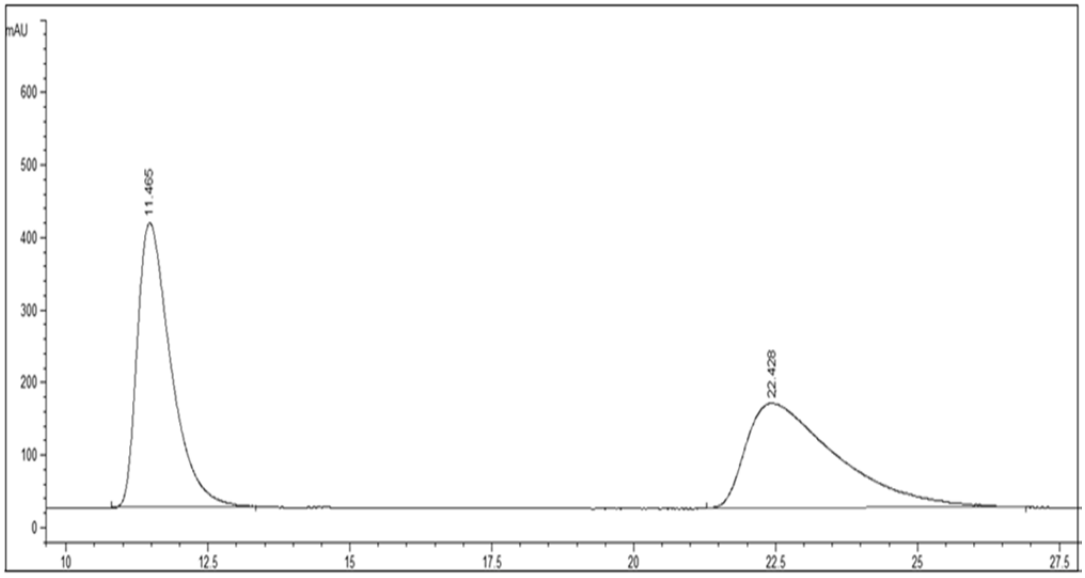
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.792	MM	0.3034	5322.87012	292.40213	50.0191
2	11.253	MM	0.6593	5318.80811	134.45193	49.9809

HPLC chromatogram of chiral product 6au



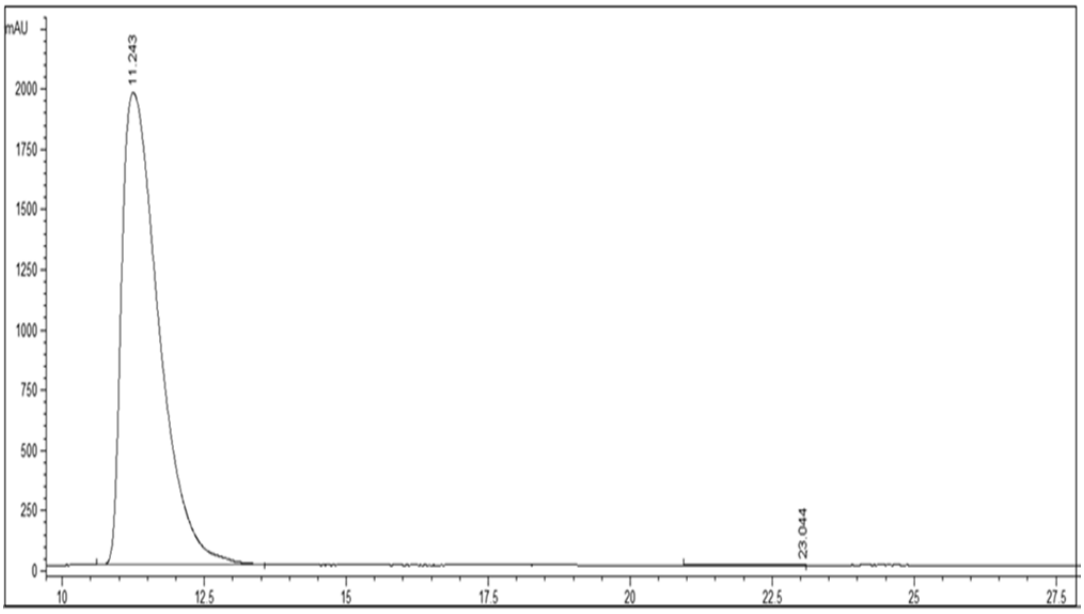
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.726	VV	0.2937	3.08889e4	1642.54199	99.9781
2	11.311	MM	0.0828	6.76571	1.36171	0.0219

HPLC chromatogram of racemic product 6av



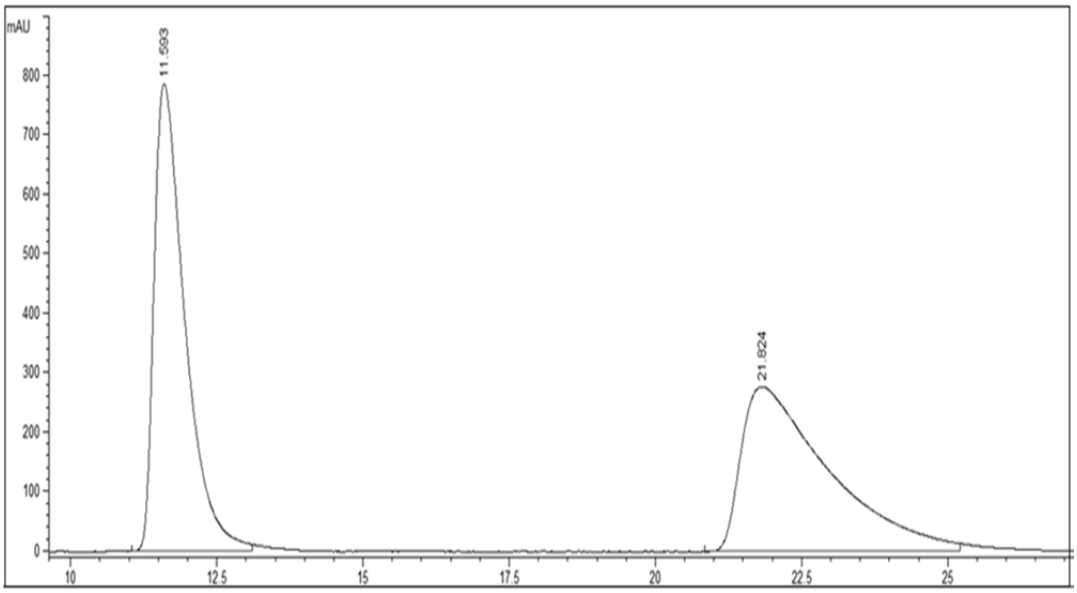
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.465	MM	0.6854	1.61054e4	391.62161	49.9556
2	22.428	MM	1.8572	1.61341e4	144.78705	50.0444

HPLC chromatogram of chiral product 6av



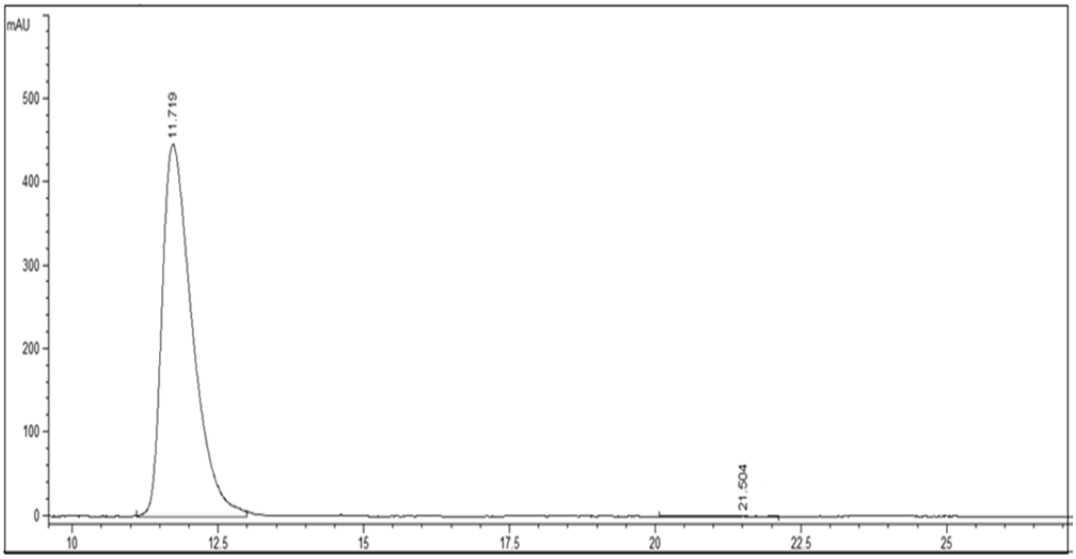
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.243	VV	0.6899	8.94424e4	1964.33081	99.9830
2	23.044	MM	0.2567	15.23431	9.88967e-1	0.0170

HPLC chromatogram of racemic product 6aw



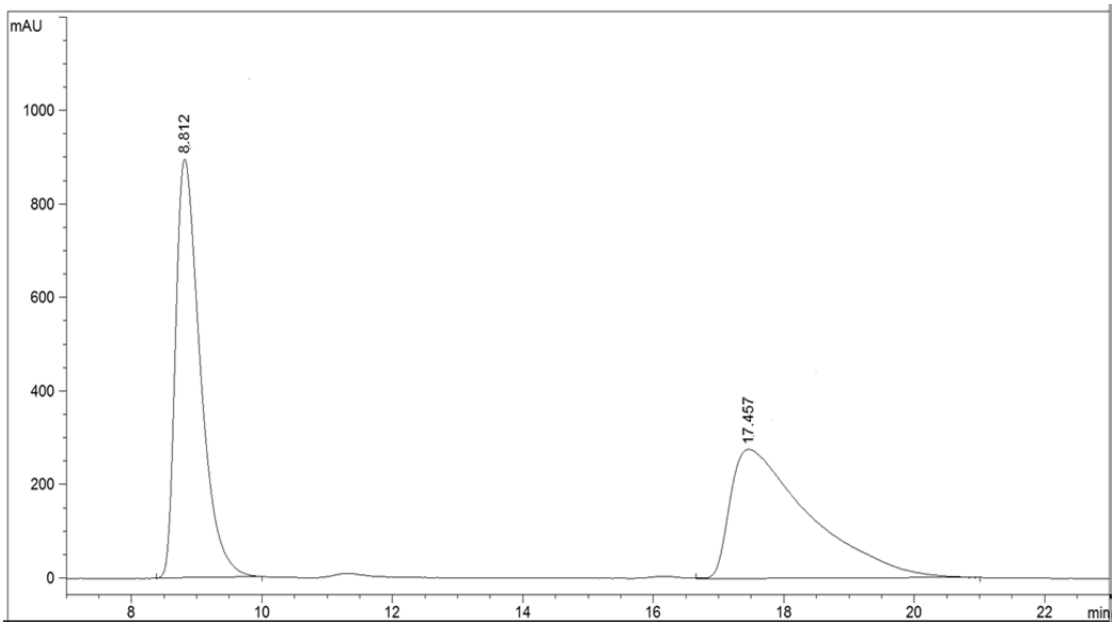
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.593	VV	0.5529	2.89957e4	788.27393	49.8990
2	21.824	VV	1.2871	2.91130e4	278.38080	50.1010

HPLC chromatogram of chiral product 6aw



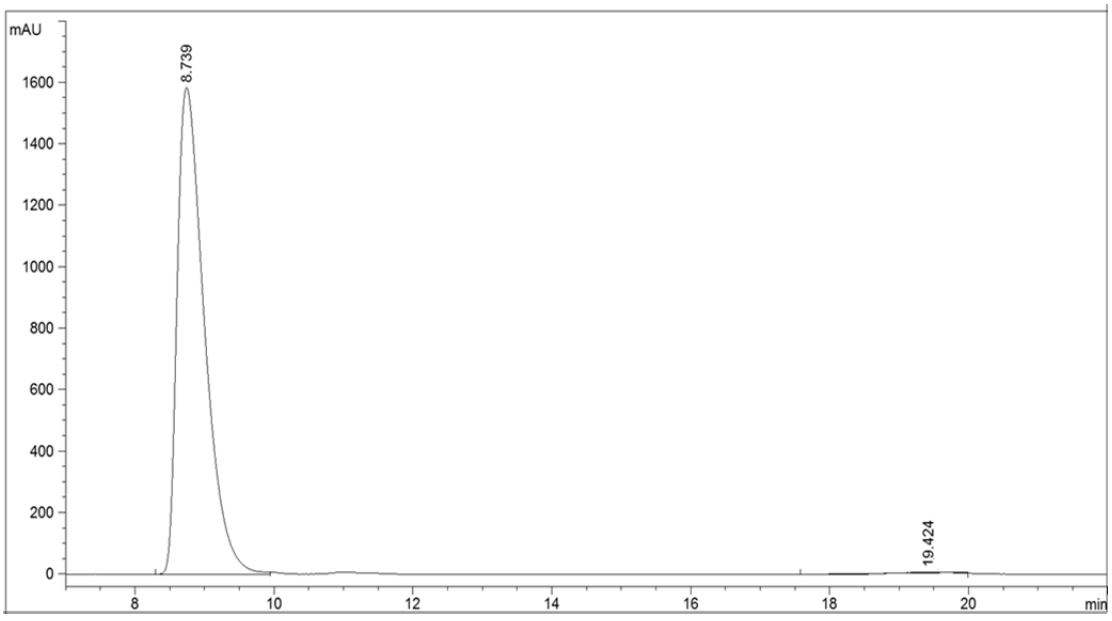
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.719	VV	0.5389	1.61958e4	447.29132	99.8794
2	21.504	MM	0.4046	19.55289	8.05410e-1	0.1206

HPLC chromatogram of racemic product 6ay



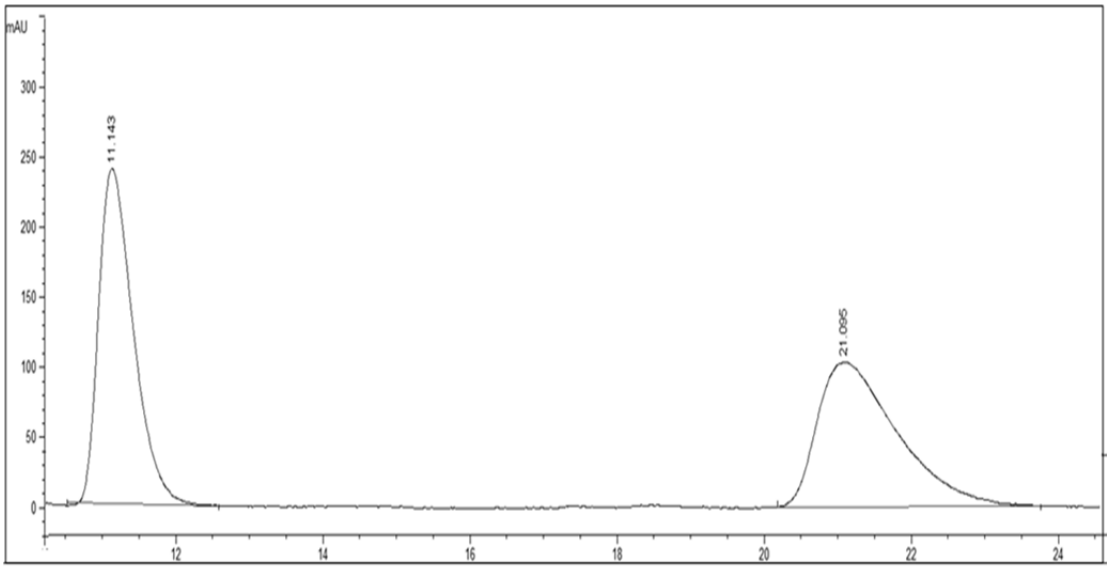
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.812	MM	0.4373	2.35174e4	896.31732	50.1020
2	17.457	MM	1.4085	2.34217e4	277.14072	49.8980

HPLC chromatogram of chiral product 6ay



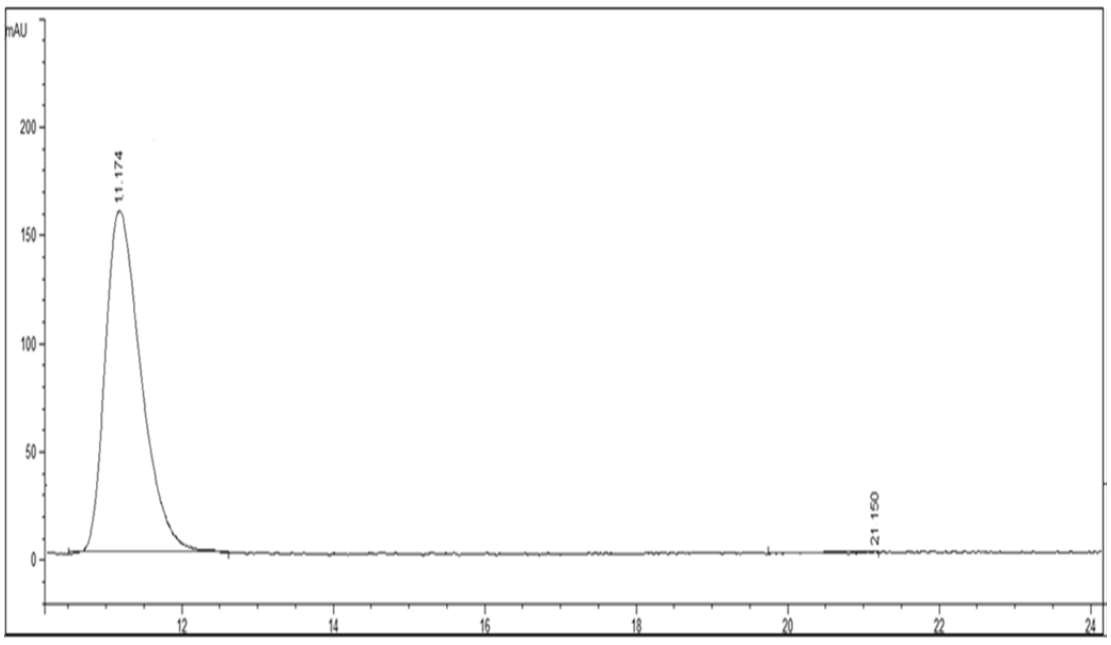
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.739	VV	0.4201	4.32537e4	1586.17322	99.7866
2	19.424	MM	0.6734	92.50896	2.28971	0.2134

HPLC chromatogram of racemic product 6az



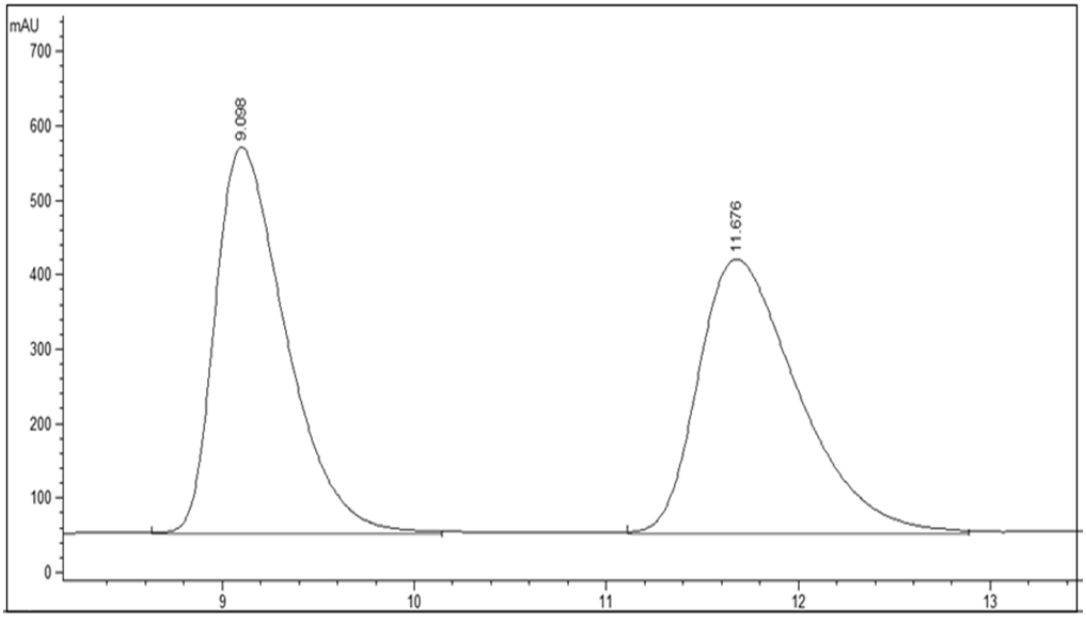
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.143	MM	0.5483	7871.69971	239.25969	50.1783
2	21.095	MM	1.2599	7815.75391	103.39093	49.8217

HPLCchromatogram of chiral product 6az



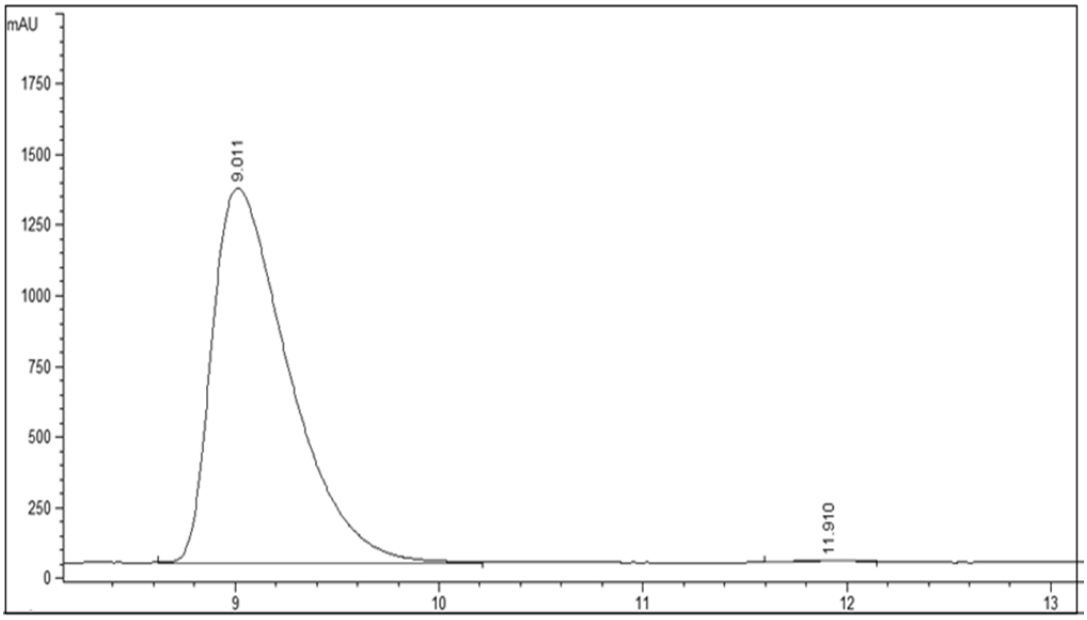
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.174	MM	0.5492	5195.19287	157.65662	99.8968
2	21.150	MM	0.5383	5.36843	1.66206e-1	0.1032

HPLC chromatogram of racemic product 6ba



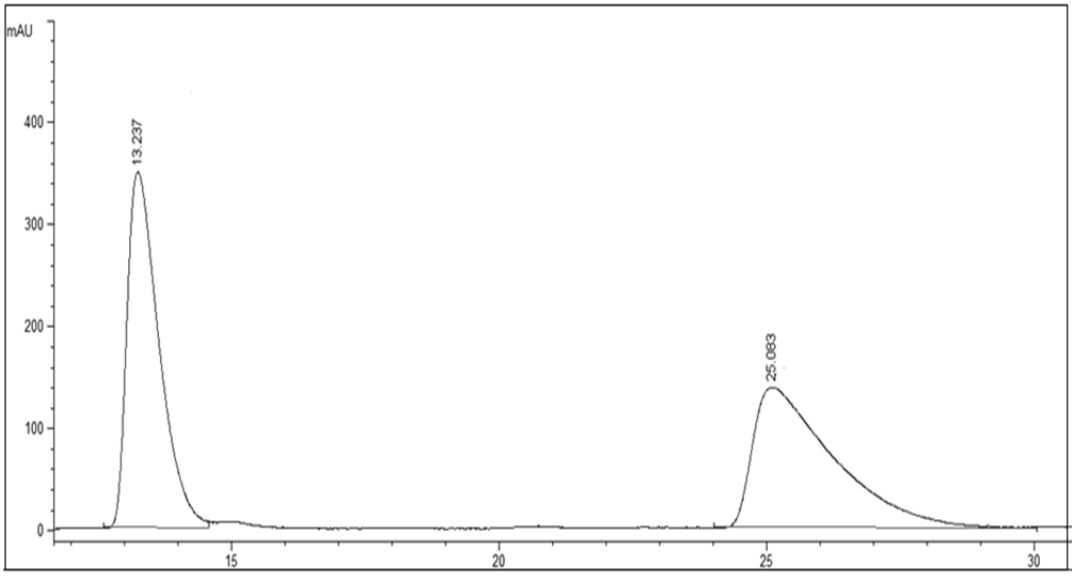
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.098	VV	0.3916	1.34501e4	520.70441	49.9056
2	11.676	VV	0.5567	1.35010e4	370.04495	50.0944

HPLC chromatogram of chiral product 6ba



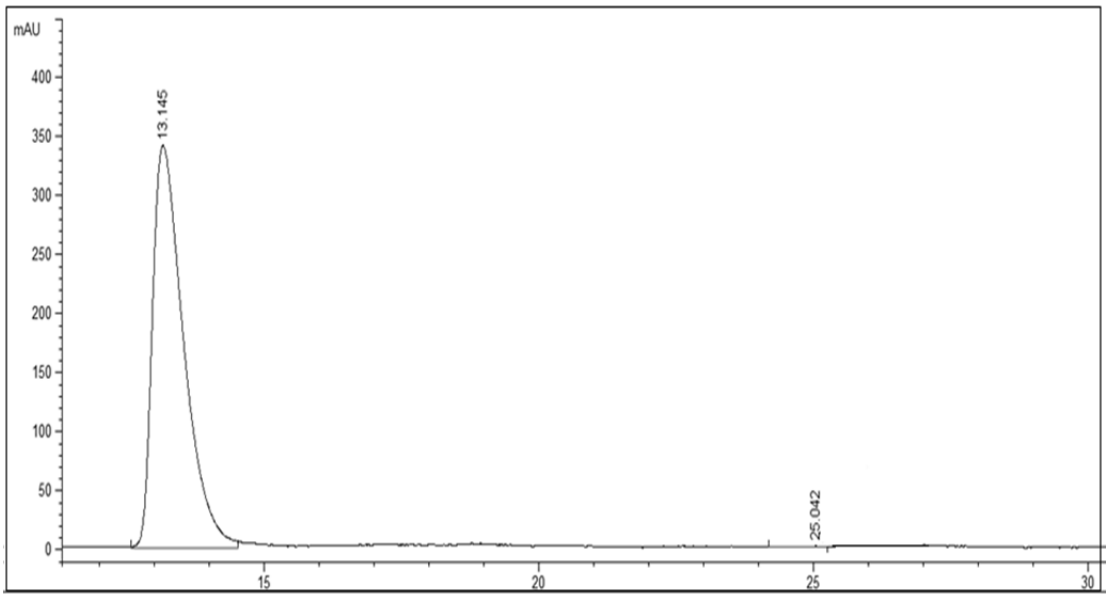
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.011	VV	0.3971	3.49290e4	1327.92896	99.7073
2	11.910	MM	0.3437	102.55258	4.97316	0.2927

HPLC chromatogram of racemic product 6ca



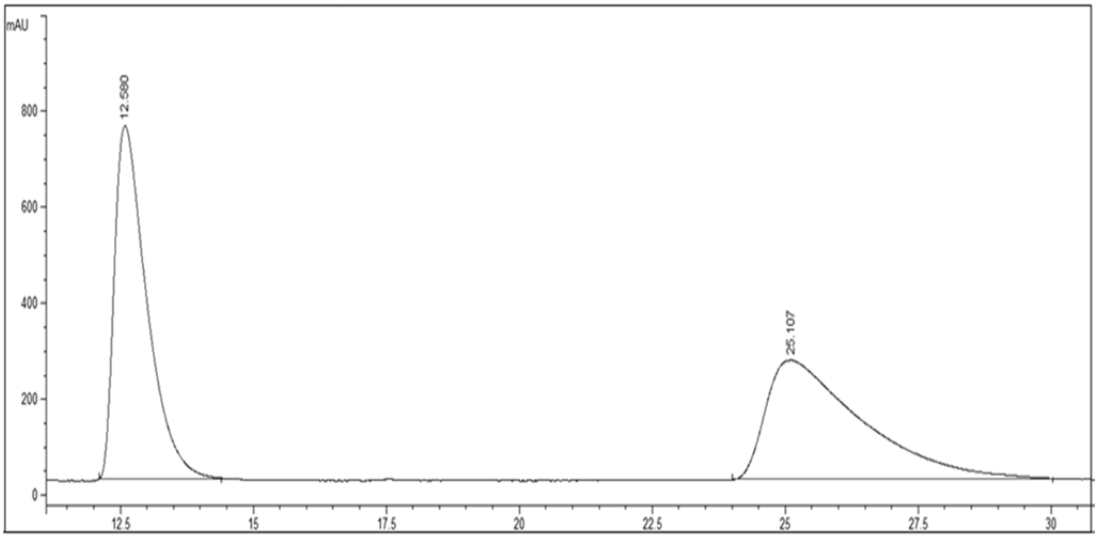
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.237	MF	0.6946	1.45474e4	349.07040	49.9314
2	25.083	MM	1.7660	1.45873e4	137.67146	50.0686

HPLC chromatogram of chiral product 6ca



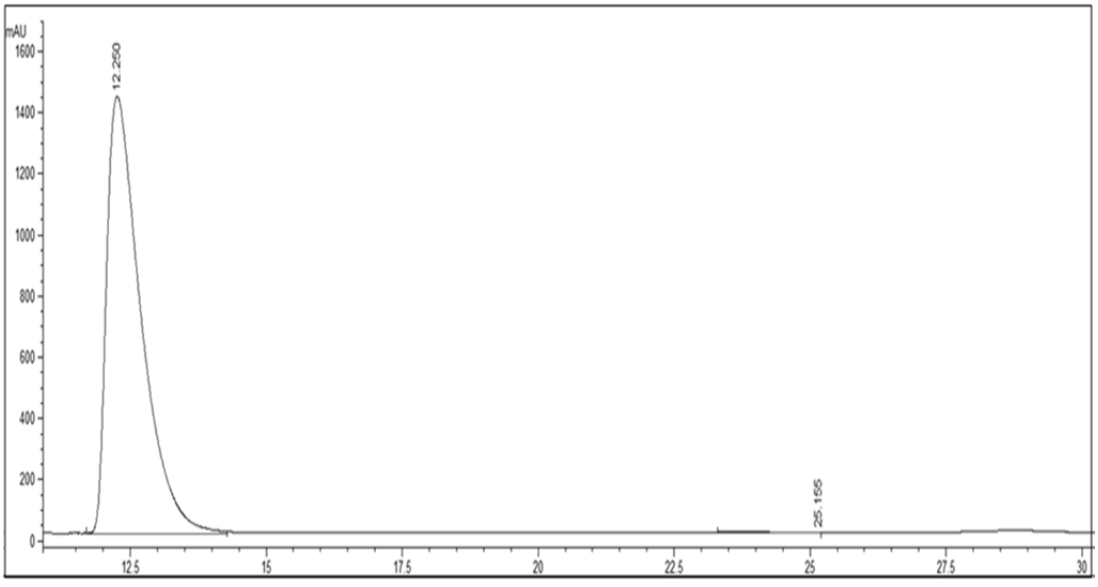
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.145	VV	0.5870	1.35090e4	341.31085	99.8760
2	25.042	MM	0.3874	16.76526	7.21264e-1	0.1240

HPLC chromatogram of racemic product 6da



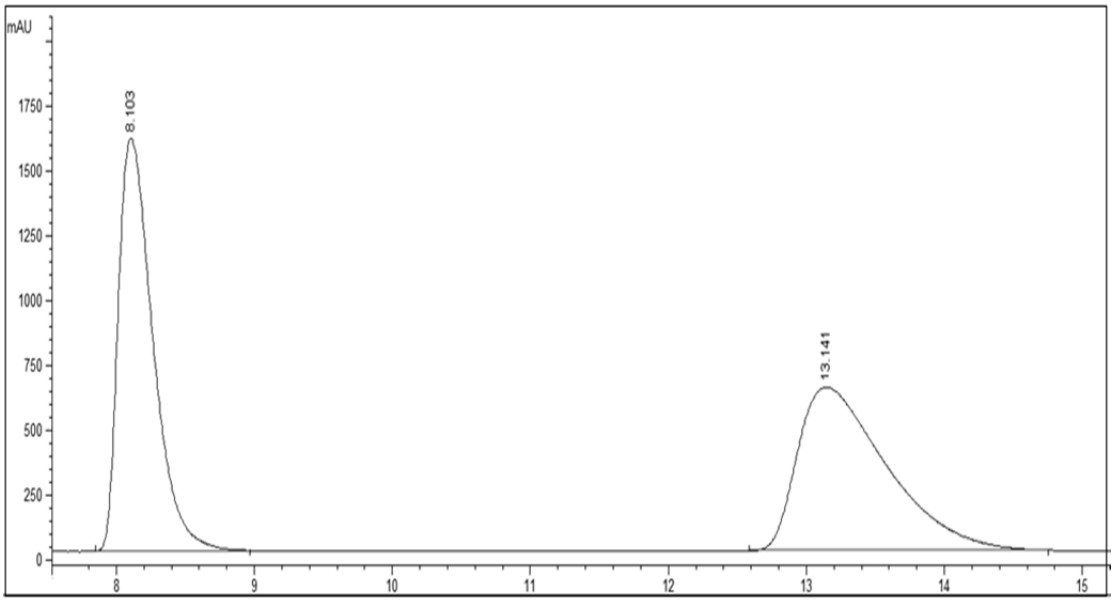
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.580	MM	0.7108	3.14885e4	738.33990	49.9829
2	25.107	MM	2.1041	3.15100e4	249.58806	50.0171

HPLC chromatogram of chiral product 6da



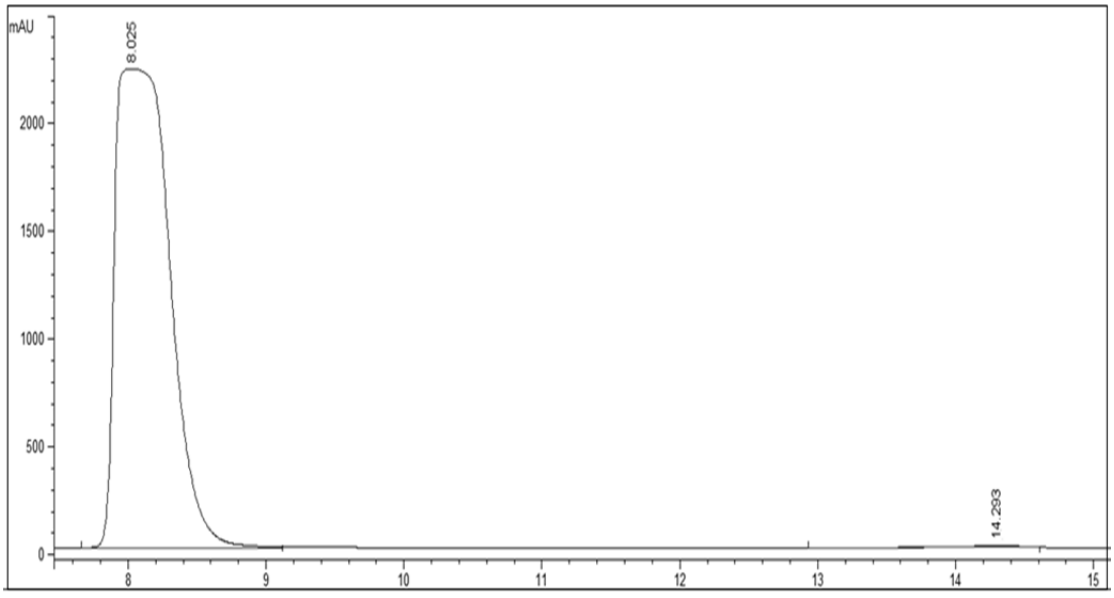
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.250	VV	0.6690	6.31951e4	1432.65759	99.9961
2	25.155	MM	0.1051	2.44718	3.87894e-1	3.872e-3

HPLC chromatogram of racemic product 6ea



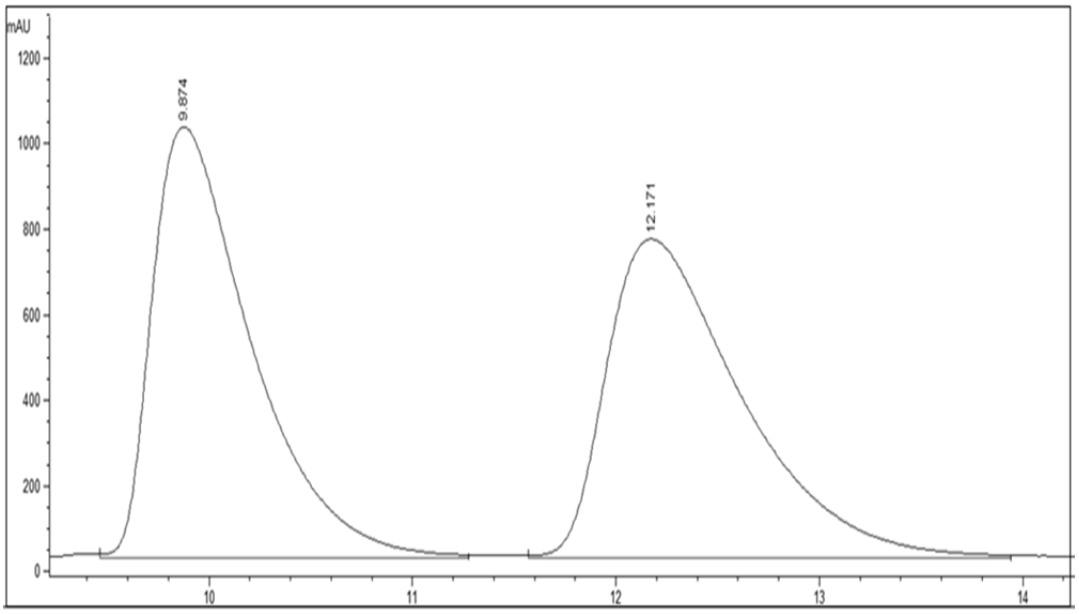
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.103	MM	0.2915	2.79923e4	1600.36145	50.0439
2	13.141	MM	0.7403	2.79432e4	629.13397	49.9561

HPLC chromatogram of chiral product 6ea



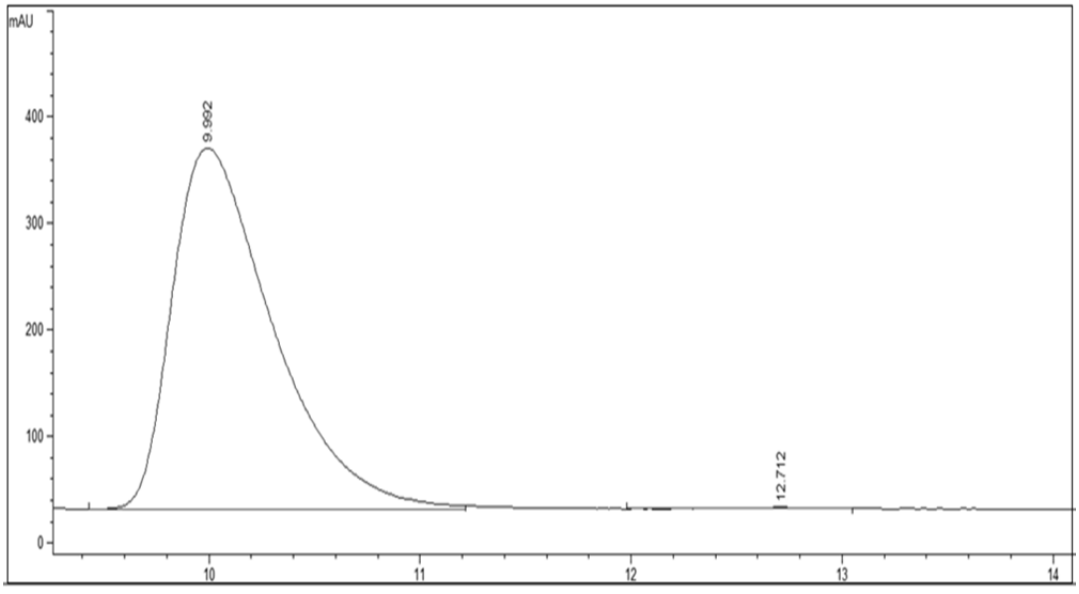
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.025	VV	0.3810	6.13080e4	2226.21167	99.6023
2	14.293	MM	0.4432	244.78391	9.20551	0.3977

HPLC chromatogram of racemic product 6fa



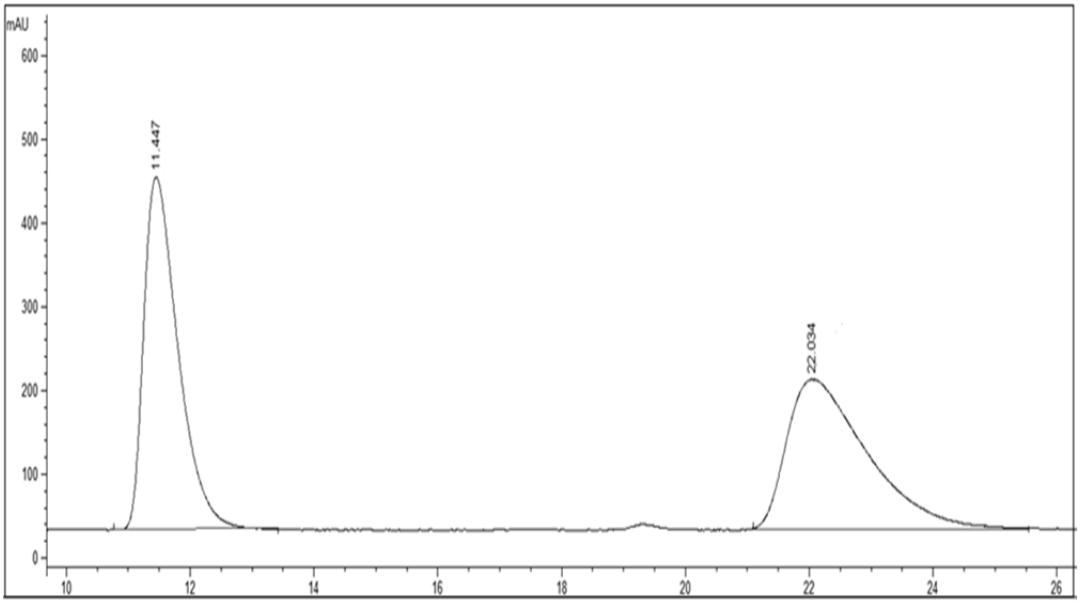
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.874	VV	0.5155	3.44172e4	1009.86578	49.7456
2	12.171	VV	0.6850	3.47692e4	747.94714	50.2544

HPLC chromatogram of chiral product 6fa



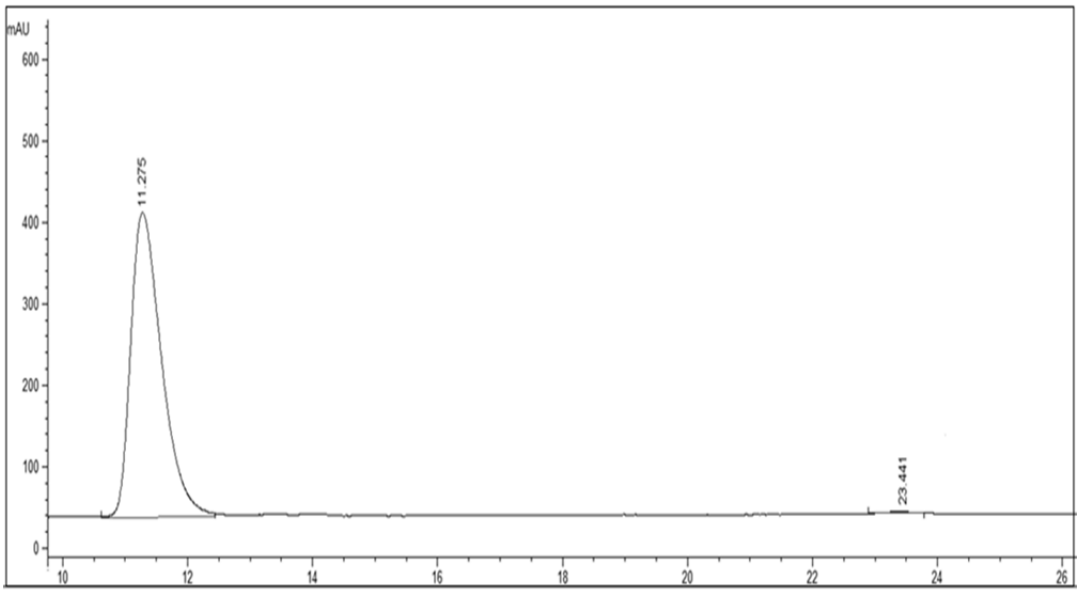
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.992	VV	0.4950	1.13662e4	339.83041	99.5663
2	12.712	MM	0.5409	49.51328	1.52569	0.4337

HPLC chromatogram of racemic product 6ga



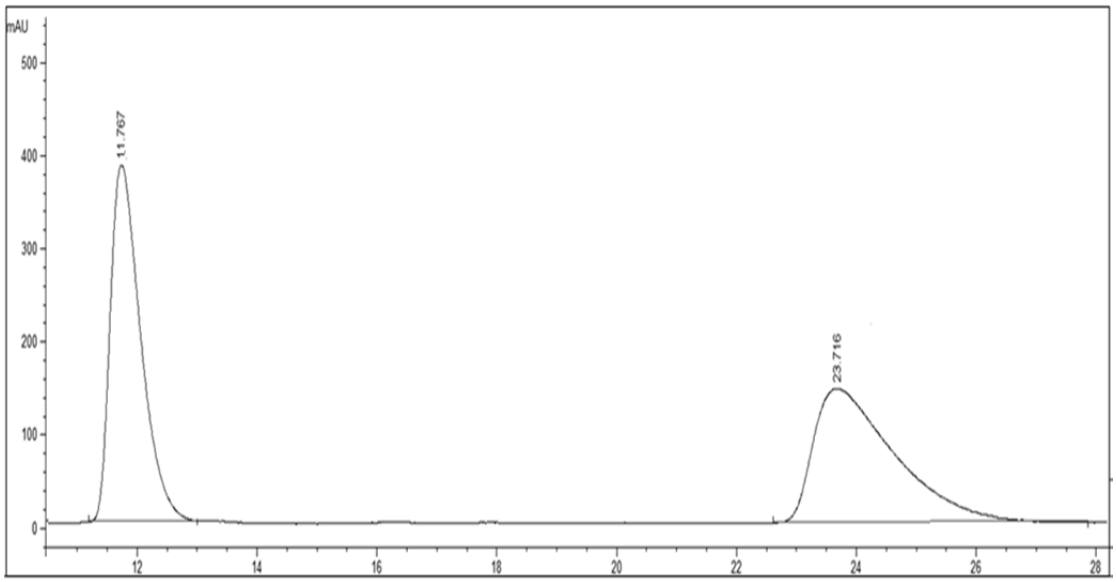
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.447	MM	0.6421	1.62133e4	420.84860	49.7541
2	22.034	MM	1.5187	1.63736e4	179.68340	50.2459

HPLC chromatogram of chiral product 6ga



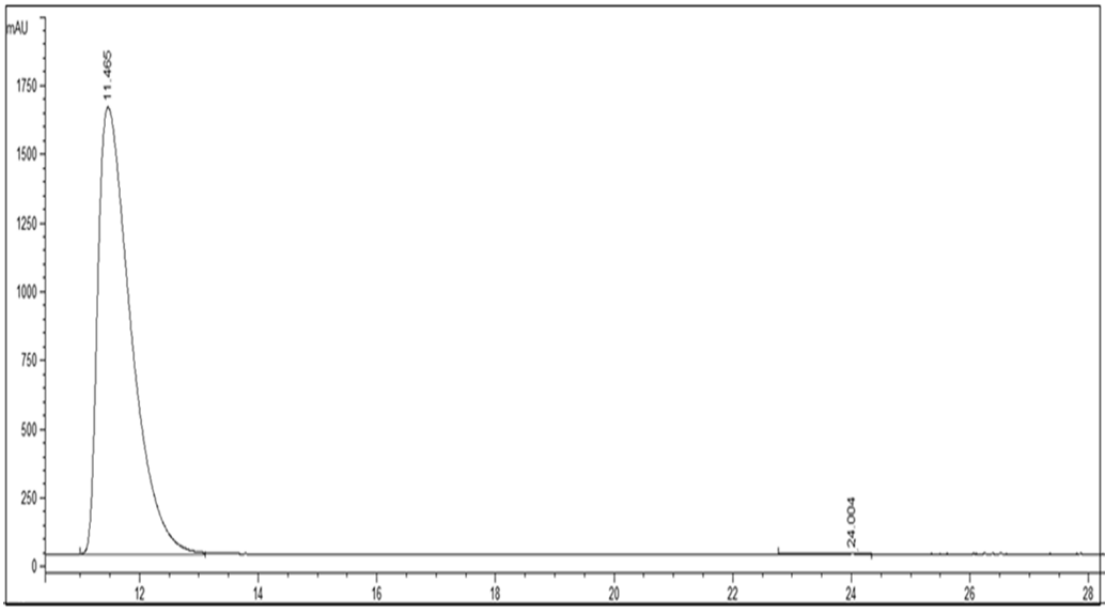
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.275	VV	0.5199	1.29503e4	374.48962	99.5144
2	23.441	MM	0.4623	63.19398	2.27841	0.4856

HPLC chromatogram of racemic product 6ha



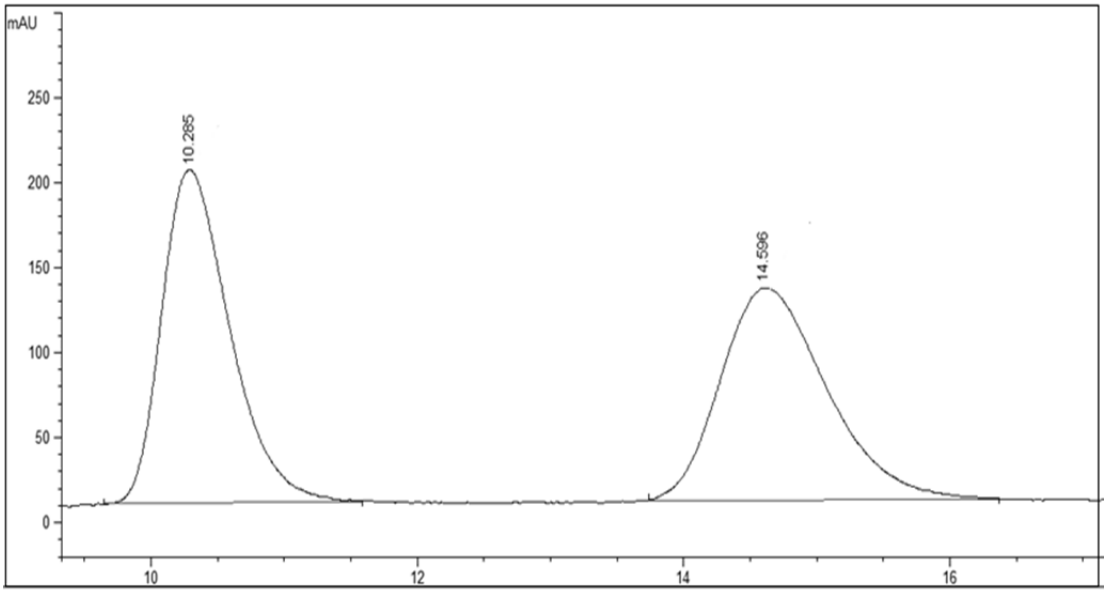
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.767	MM	0.5890	1.35401e4	383.11029	50.0432
2	23.716	MM	1.5644	1.35167e4	144.00511	49.9568

HPLC chromatogram of chiral product 6ha



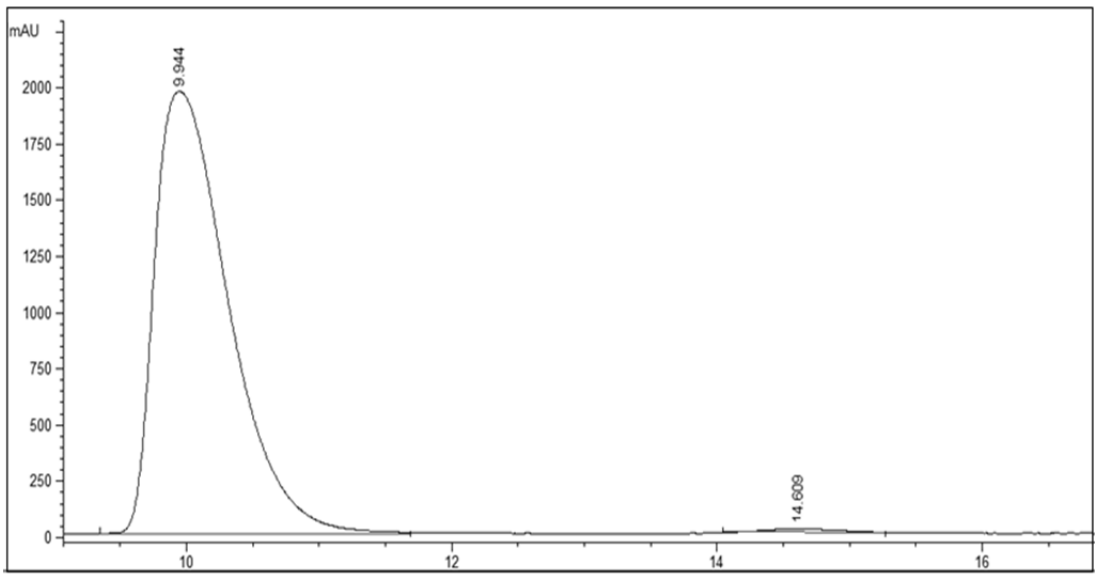
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.465	VV	0.5914	6.30640e4	1629.27551	99.9796
2	24.004	MM	0.2564	12.87504	8.36920e-1	0.0204

HPLC chromatogram of racemic product 6ia



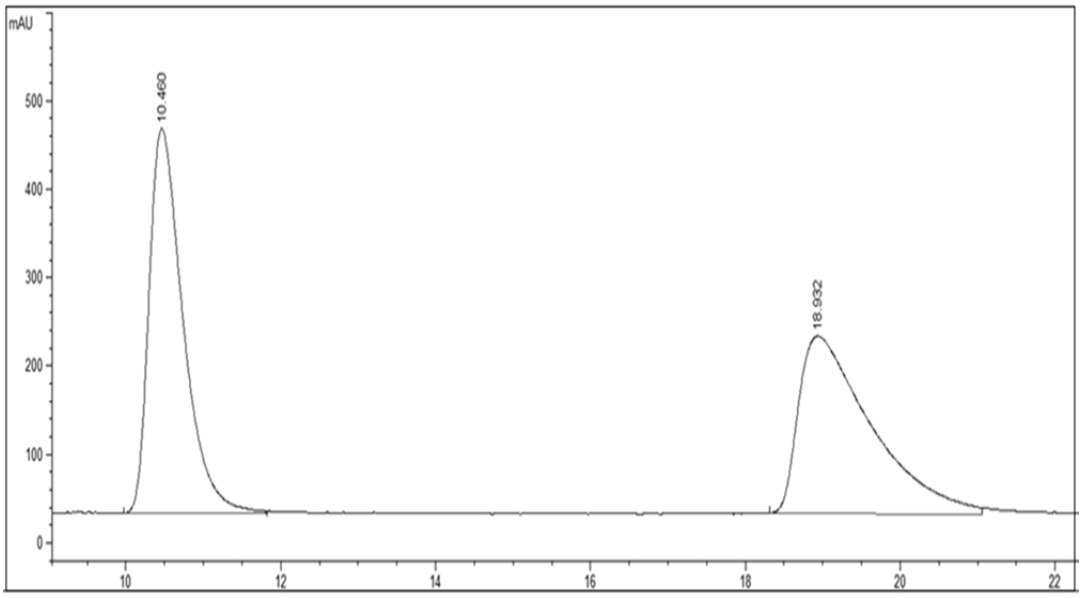
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.285	MM	0.5952	7001.55664	196.06467	50.0713
2	14.596	MM	0.9292	6981.62842	125.22440	49.9287

HPLC chromatogram of chiral product 6ia



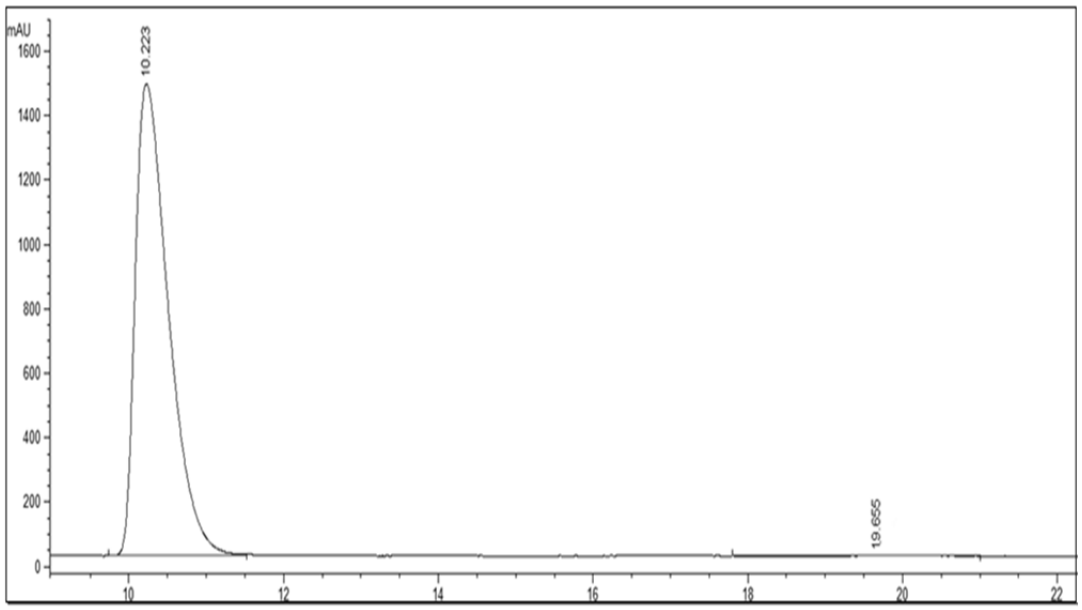
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.944	VV	0.5999	7.67707e4	1971.54138	99.1533
2	14.609	MM	0.6534	655.58728	16.72319	0.8467

HPLC chromatogram of racemic product 6ja



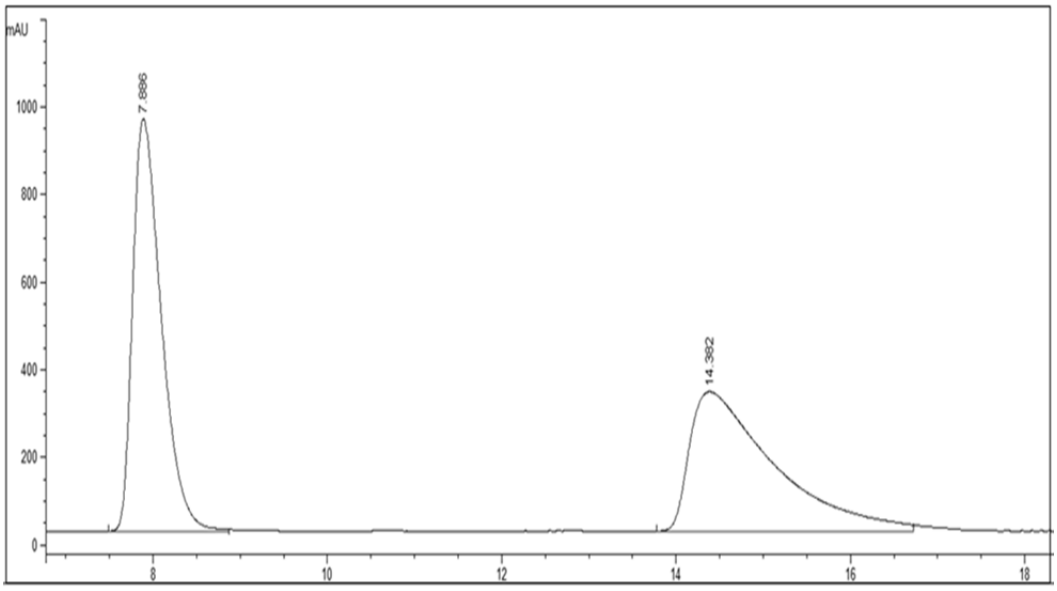
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.460	VV	0.4653	1.33698e4	436.20001	50.3422
2	18.932	VV	0.8747	1.31880e4	201.76753	49.6578

HPLC chromatogram of chiral product 6ja



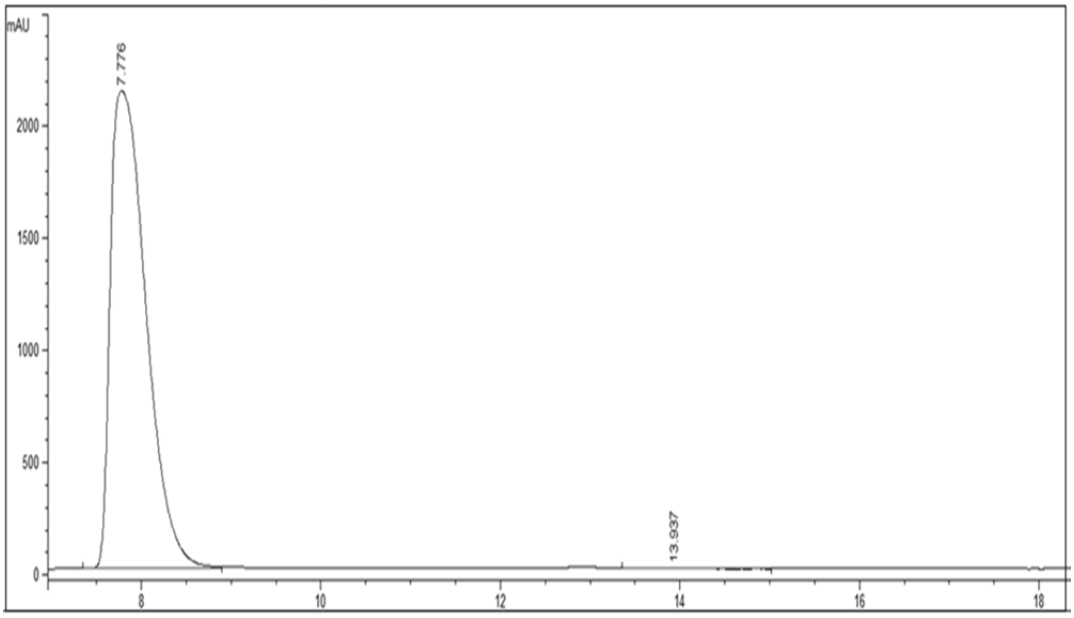
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.223	VV	0.4596	4.39043e4	1467.74451	99.9933
2	19.655	MM	0.1298	2.96310	3.80615e-1	6.749e-3

HPLC chromatogram of racemic product 6ka



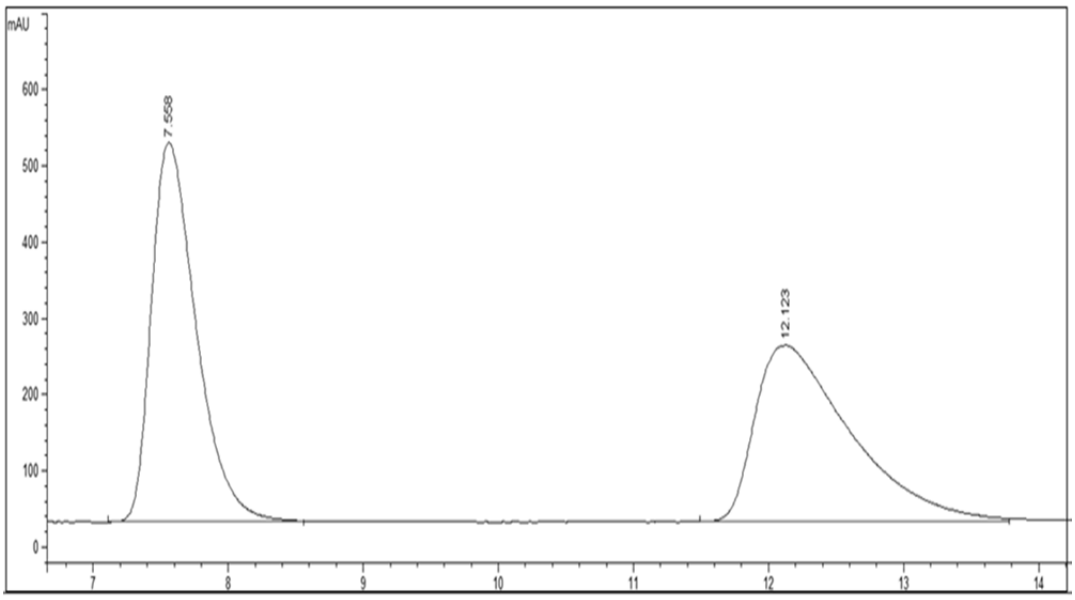
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.886	VV	0.3550	2.16290e4	942.78784	50.0032
2	14.382	VV	0.8827	2.16262e4	320.14926	49.9968

HPLC chromatogram of chiral product 6ka



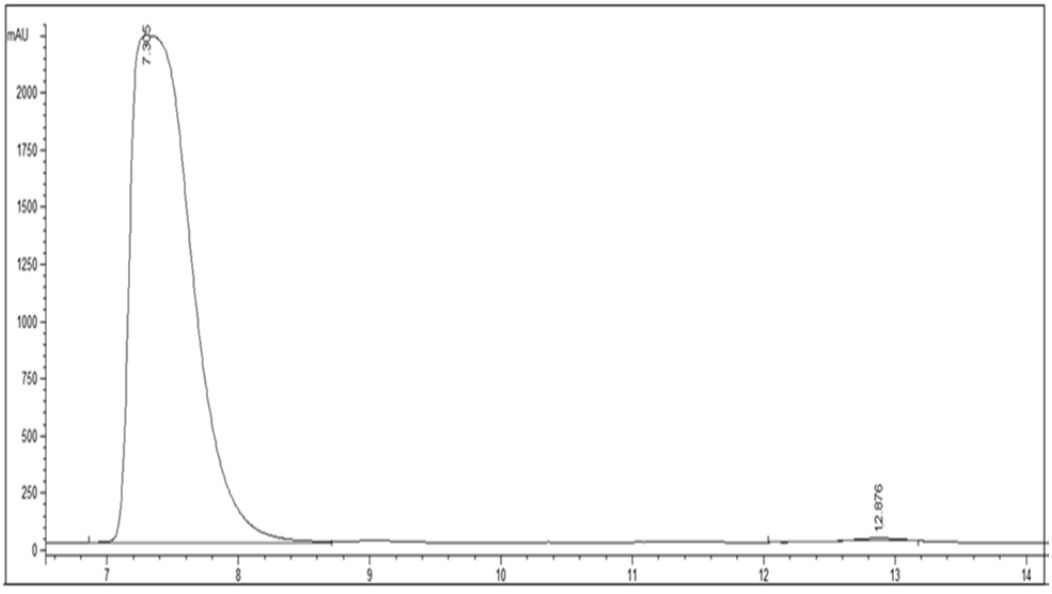
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.776	VV	0.4356	5.90927e4	2131.06738	99.9961
2	13.937	MM	0.1102	2.29265	3.46861e-1	3.880e-3

HPLC chromatogram of racemic product 6la



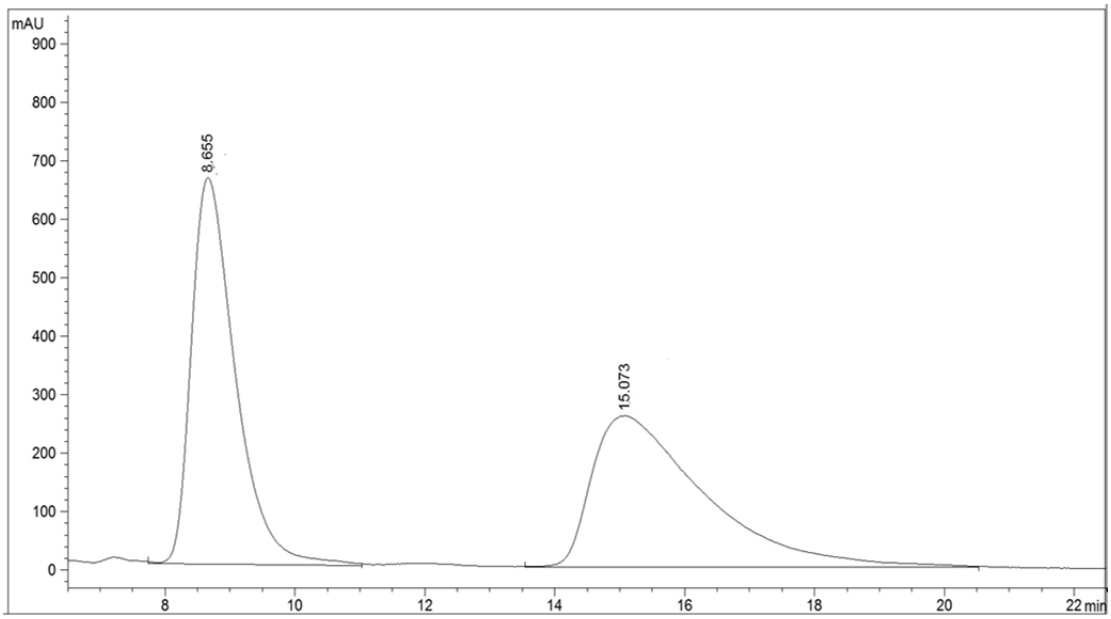
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.558	VV	0.3517	1.15403e4	498.39215	50.0958
2	12.123	VV	0.6857	1.14962e4	232.07610	49.9042

HPLC chromatogram of chiral product 6la



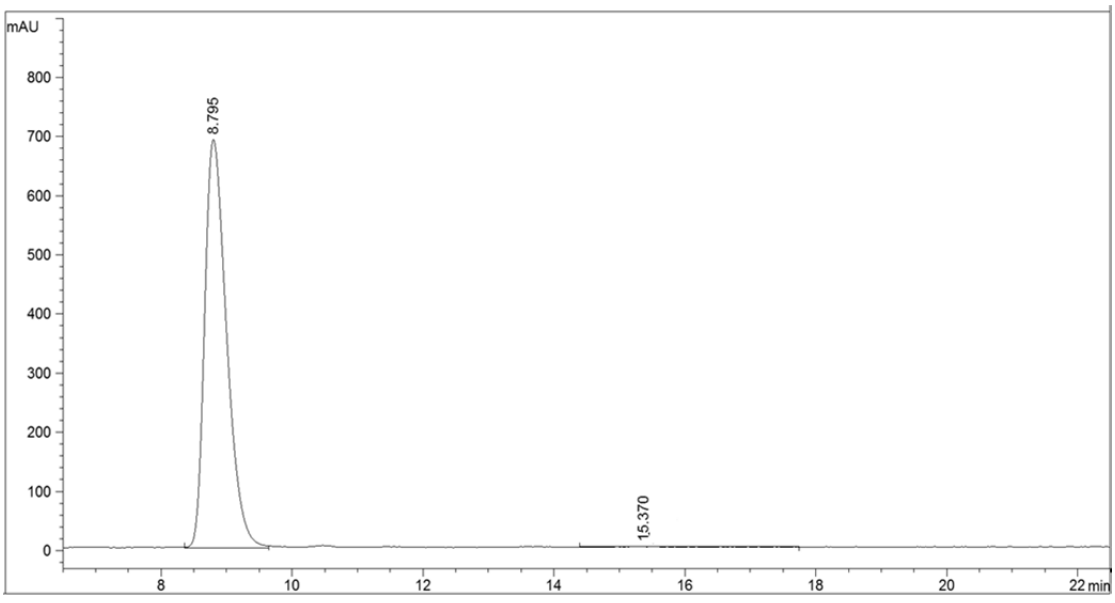
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.305	VV	0.4249	7.17438e4	2220.81909	99.5992
2	12.876	MM	0.3950	288.71228	12.18198	0.4008

HPLC chromatogram of racemic compound 8



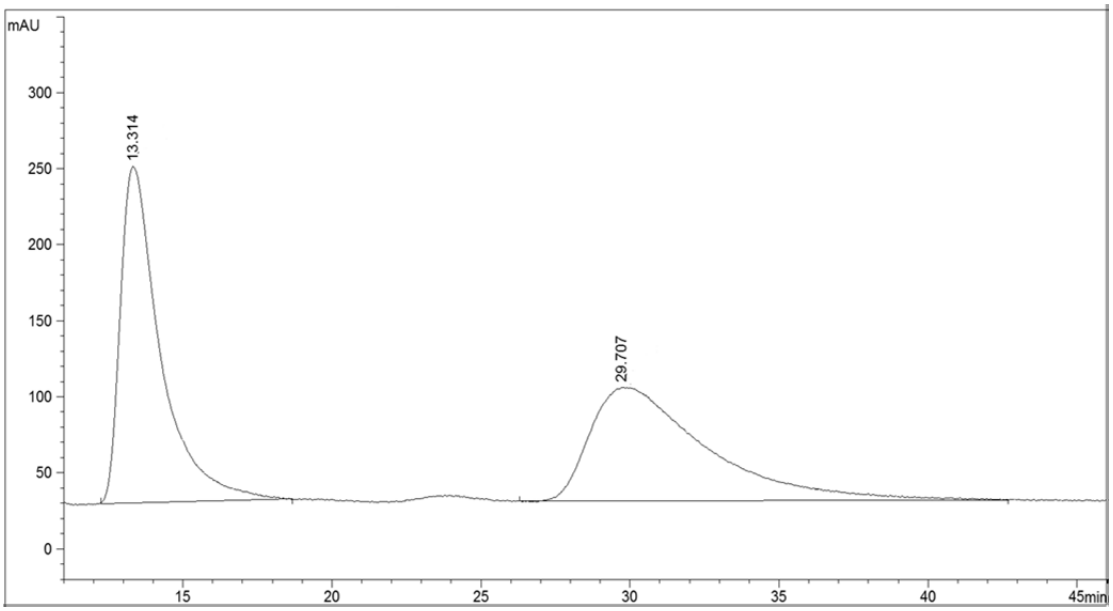
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.655	MM	0.7840	3.11240e4	661.65668	49.8664
2	15.073	MM	2.0106	3.12908e4	259.38251	50.1336

HPLC chromatogram of chiral compound 8



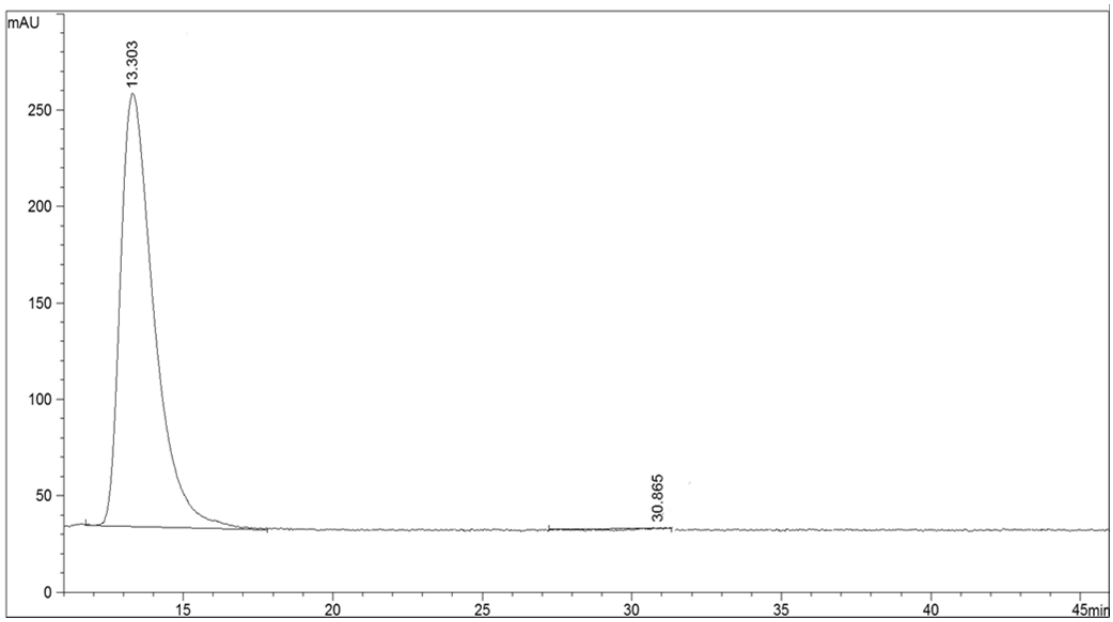
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.795	VV	0.3573	1.60694e4	690.79352	99.6856
2	15.370	MM	0.7774	50.68940	1.08674	0.3144

HPLCchromatogram of racemic compound 9



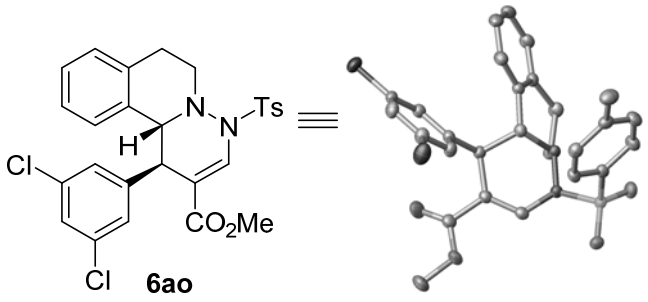
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.314	MM	1.5599	2.07294e4	221.48836	50.3694
2	29.707	MM	4.5445	2.04253e4	74.90872	49.6306

HPLC chromatogram of chiral compound 9



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.303	MM	1.3030	1.75789e4	224.84500	99.8804
2	30.865	MM	0.4772	21.05367	7.35312e-1	0.1196

Crystallographic data for **6ao** has been deposited with the Cambridge Crystallographic Data Centre as deposition number CCDC 1041720. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.



6ao

Table 1. Crystal data and structure refinement for **6ao**.

Identification code	**6ao**	
Empirical formula	$C_{27}H_{24}Cl_2N_2O_4S$	
Formula weight	543.44	
Temperature	173.1500 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 12.181(3) Å	= 90°.
	b = 11.497(3) Å	= 108.349(3)°.
	c = 19.231(5) Å	= 90°.
Volume	2556.4(11) $Å^3$	
Z	4	
Density (calculated)	1.412 Mg/m^3	
Absorption coefficient	0.373 mm^{-1}	
F(000)	1128	
Crystal size	0.37 x 0.25 x 0.23 mm^3	
Theta range for data collection	1.116 to 27.505°.	
Index ranges	-15<=h<=15, -14<=k<=14, -24<=l<=24	
Reflections collected	28034	
Independent reflections	10918 [R(int) = 0.0298]	
Completeness to theta = 26.000°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.8636	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10918 / 143 / 690	
Goodness-of-fit on F^2	1.070	

Final R indices [I>2sigma(I)]	R1 = 0.0326, wR2 = 0.0723
R indices (all data)	R1 = 0.0334, wR2 = 0.0729
Absolute structure parameter	-0.019(17)
Extinction coefficient	n/a
Largest diff. peak and hole	0.239 and -0.282 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **6ao**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cl1A	6606(1)	7059(1)	5320(1)	32(1)
Cl2A	3667(1)	4163(1)	6032(1)	45(1)
S1A	8007(1)	792(1)	8609(1)	35(1)
O1A	6964(2)	1053(2)	5744(1)	36(1)
O2A	8014(2)	2606(2)	5625(1)	28(1)
O3A	8767(2)	945(2)	9332(1)	46(1)
O4A	7778(3)	-334(2)	8284(1)	52(1)
N1A	8560(2)	1532(2)	8044(1)	27(1)
N2A	8921(2)	2676(2)	8298(1)	24(1)
C1A	8195(2)	3580(2)	7833(1)	21(1)
C2A	8116(2)	3459(2)	7011(1)	20(1)
C3A	7961(2)	2188(2)	6800(1)	22(1)
C4A	8100(2)	1336(2)	7288(2)	25(1)
C5A	10162(2)	2820(3)	8388(2)	30(1)
C6A	10575(2)	3909(3)	8830(2)	32(1)
C7A	9769(2)	4929(2)	8588(1)	25(1)
C8A	10133(3)	6042(3)	8848(2)	31(1)
C9A	9382(3)	6977(3)	8675(2)	33(1)
C10A	8249(3)	6817(3)	8239(2)	33(1)
C11A	7876(2)	5714(2)	7984(2)	28(1)
C12A	8626(2)	4763(2)	8141(1)	22(1)
C13A	7110(2)	4169(2)	6536(1)	21(1)
C14A	7301(2)	5162(2)	6175(1)	22(1)
C15A	6364(2)	5817(2)	5769(1)	25(1)
C16A	5236(2)	5523(3)	5708(2)	28(1)
C17A	5073(2)	4540(3)	6077(2)	29(1)
C18A	5983(2)	3853(2)	6484(2)	25(1)

C19A	7581(2)	1864(2)	6013(1)	23(1)
C20A	7601(3)	2449(3)	4839(2)	36(1)
C21A	6711(3)	1509(3)	8527(2)	33(1)
C22A	6644(3)	2334(3)	9036(2)	42(1)
C23A	5592(9)	2842(12)	8975(8)	46(3)
C24A	4658(10)	2606(12)	8353(7)	47(2)
C25A	4729(10)	1831(12)	7822(9)	37(2)
C26A	5761(3)	1306(3)	7907(2)	38(1)
C27A	3530(10)	3183(17)	8280(8)	81(4)
Cl1	2871(1)	3085(1)	399(1)	33(1)
Cl2	6492(1)	427(1)	409(1)	40(1)
S1	10574(1)	3559(1)	3567(1)	21(1)
O1	7027(2)	5030(3)	607(1)	53(1)
O2	8877(2)	4593(2)	799(1)	38(1)
O3	10812(2)	4090(2)	4269(1)	29(1)
O4	11399(2)	3584(2)	3179(1)	27(1)
N1	9406(2)	4218(2)	3009(1)	21(1)
N2	8467(2)	4271(2)	3295(1)	21(1)
C1	7430(2)	3693(2)	2802(1)	21(1)
C2	7067(2)	4188(2)	2005(1)	21(1)
C3	8136(2)	4393(2)	1782(1)	22(1)
C4	9207(2)	4317(2)	2255(1)	22(1)
C5	8252(2)	5502(2)	3432(2)	25(1)
C6	7412(2)	5539(3)	3874(2)	28(1)
C7	6403(2)	4715(2)	3586(1)	23(1)
C8	5431(2)	4829(3)	3822(2)	30(1)
C9	4536(2)	4036(3)	3619(2)	33(1)
C10	4611(2)	3089(3)	3187(2)	33(1)
C11	5559(2)	2970(3)	2942(2)	28(1)
C12	6448(2)	3787(2)	3127(1)	23(1)
C13	6251(2)	3356(2)	1474(1)	22(1)
C14	5067(2)	3581(2)	1211(1)	24(1)
C15	4349(2)	2803(2)	727(2)	24(1)
C16	4758(2)	1820(3)	479(2)	29(1)
C17	5939(2)	1623(3)	742(2)	29(1)
C18	6682(2)	2361(2)	1239(2)	26(1)
C19	7939(2)	4709(3)	1008(2)	27(1)
C20	8742(3)	4901(4)	46(2)	48(1)

C21	10112(2)	2117(2)	3627(1)	22(1)
C22	10127(3)	1674(3)	4300(2)	30(1)
C23	9775(3)	532(3)	4340(2)	33(1)
C24	9401(2)	-157(3)	3719(2)	28(1)
C25	9378(2)	320(2)	3049(2)	27(1)
C26	9745(2)	1453(2)	2997(2)	24(1)
C27	9070(3)	-1412(3)	3776(2)	39(1)
C25B	4835(16)	2100(16)	7782(13)	42(4)
C24B	4728(17)	2980(20)	8256(10)	51(4)
C23B	5715(14)	3120(17)	8864(11)	48(4)
C27B	3646(18)	3790(30)	8049(13)	86(7)

Table 3. Bond lengths [Å] and angles [°] for **6ao**.

Cl1A-C15A	1.741(3)
Cl2A-C17A	1.741(3)
S1A-O3A	1.418(2)
S1A-O4A	1.427(2)
S1A-N1A	1.679(2)
S1A-C21A	1.744(3)
O1A-C19A	1.208(3)
O2A-C19A	1.346(3)
O2A-C20A	1.446(3)
N1A-N2A	1.423(3)
N1A-C4A	1.402(4)
N2A-C1A	1.472(3)
N2A-C5A	1.476(3)
C1A-C2A	1.560(3)
C1A-C12A	1.510(4)
C2A-C3A	1.512(4)
C2A-C13A	1.516(3)
C3A-C4A	1.331(4)
C3A-C19A	1.483(4)
C5A-C6A	1.509(4)
C6A-C7A	1.506(4)
C7A-C8A	1.394(4)
C7A-C12A	1.399(4)

C8A-C9A	1.383(4)
C9A-C10A	1.383(4)
C10A-C11A	1.384(4)
C11A-C12A	1.396(4)
C13A-C14A	1.394(4)
C13A-C18A	1.393(3)
C14A-C15A	1.385(4)
C15A-C16A	1.384(4)
C16A-C17A	1.381(4)
C17A-C18A	1.386(4)
C21A-C22A	1.384(4)
C21A-C26A	1.395(4)
C22A-C23A	1.380(11)
C22A-C23B	1.404(13)
C23A-C24A	1.393(12)
C24A-C25A	1.379(13)
C24A-C27A	1.493(16)
C25A-C26A	1.358(11)
C26A-C25B	1.411(13)
Cl1-C15	1.740(3)
Cl2-C17	1.739(3)
S1-O3	1.425(2)
S1-O4	1.4284(18)
S1-N1	1.671(2)
S1-C21	1.766(3)
O1-C19	1.194(3)
O2-C19	1.333(3)
O2-C20	1.448(3)
N1-N2	1.419(3)
N1-C4	1.397(3)
N2-C1	1.478(3)
N2-C5	1.478(3)
C1-C2	1.563(3)
C1-C12	1.518(3)
C2-C3	1.513(3)
C2-C13	1.519(4)
C3-C4	1.338(4)
C3-C19	1.475(4)

C5-C6	1.522(4)
C6-C7	1.512(4)
C7-C8	1.401(4)
C7-C12	1.397(4)
C8-C9	1.380(4)
C9-C10	1.390(5)
C10-C11	1.384(4)
C11-C12	1.393(4)
C13-C14	1.395(4)
C13-C18	1.392(4)
C14-C15	1.385(4)
C15-C16	1.380(4)
C16-C17	1.385(4)
C17-C18	1.381(4)
C21-C22	1.386(4)
C21-C26	1.381(4)
C22-C23	1.391(4)
C23-C24	1.386(4)
C24-C25	1.393(4)
C24-C27	1.511(4)
C25-C26	1.390(4)
C25B-C24B	1.397(13)
C24B-C23B	1.399(13)
C24B-C27B	1.56(3)

O3A-S1A-O4A	121.29(16)
O3A-S1A-N1A	107.52(14)
O3A-S1A-C21A	108.87(15)
O4A-S1A-N1A	103.87(13)
O4A-S1A-C21A	110.04(16)
N1A-S1A-C21A	103.73(13)
C19A-O2A-C20A	115.7(2)
N2A-N1A-S1A	112.91(18)
C4A-N1A-S1A	118.6(2)
C4A-N1A-N2A	119.0(2)
N1A-N2A-C1A	112.5(2)
N1A-N2A-C5A	109.8(2)
C1A-N2A-C5A	112.9(2)

N2A-C1A-C2A	112.7(2)
N2A-C1A-C12A	109.2(2)
C12A-C1A-C2A	112.4(2)
C3A-C2A-C1A	108.7(2)
C3A-C2A-C13A	110.5(2)
C13A-C2A-C1A	110.0(2)
C4A-C3A-C2A	123.0(2)
C4A-C3A-C19A	117.6(2)
C19A-C3A-C2A	119.3(2)
C3A-C4A-N1A	122.2(3)
N2A-C5A-C6A	107.9(2)
C7A-C6A-C5A	113.7(2)
C8A-C7A-C6A	120.0(3)
C8A-C7A-C12A	119.2(3)
C12A-C7A-C6A	120.6(2)
C9A-C8A-C7A	121.1(3)
C8A-C9A-C10A	120.0(3)
C9A-C10A-C11A	119.4(3)
C10A-C11A-C12A	121.4(3)
C7A-C12A-C1A	121.3(2)
C11A-C12A-C1A	119.8(2)
C11A-C12A-C7A	118.9(3)
C14A-C13A-C2A	120.7(2)
C18A-C13A-C2A	119.7(2)
C18A-C13A-C14A	119.6(2)
C15A-C14A-C13A	119.3(2)
C14A-C15A-Cl1A	119.2(2)
C16A-C15A-Cl1A	118.5(2)
C16A-C15A-C14A	122.3(3)
C17A-C16A-C15A	117.2(2)
C16A-C17A-Cl2A	118.5(2)
C16A-C17A-C18A	122.5(2)
C18A-C17A-Cl2A	119.0(2)
C17A-C18A-C13A	119.1(2)
O1A-C19A-O2A	123.5(2)
O1A-C19A-C3A	125.7(2)
O2A-C19A-C3A	110.9(2)
C22A-C21A-S1A	120.8(3)
C22A-C21A-C26A	120.1(3)

C26A-C21A-S1A	118.8(2)
C21A-C22A-C23B	119.8(9)
C23A-C22A-C21A	119.3(6)
C22A-C23A-C24A	118.4(11)
C23A-C24A-C27A	118.2(10)
C25A-C24A-C23A	122.6(12)
C25A-C24A-C27A	119.2(10)
C26A-C25A-C24A	118.0(12)
C21A-C26A-C25B	116.1(10)
C25A-C26A-C21A	121.1(7)
O3-S1-O4	121.30(12)
O3-S1-N1	107.00(12)
O3-S1-C21	108.37(12)
O4-S1-N1	104.56(11)
O4-S1-C21	110.10(12)
N1-S1-C21	104.07(12)
C19-O2-C20	116.0(2)
N2-N1-S1	113.41(16)
C4-N1-S1	122.60(17)
C4-N1-N2	120.1(2)
N1-N2-C1	111.19(18)
N1-N2-C5	108.71(19)
C1-N2-C5	112.4(2)
N2-C1-C2	112.8(2)
N2-C1-C12	109.2(2)
C12-C1-C2	111.2(2)
C3-C2-C1	109.4(2)
C3-C2-C13	110.3(2)
C13-C2-C1	110.7(2)
C4-C3-C2	122.6(2)
C4-C3-C19	121.1(2)
C19-C3-C2	116.3(2)
C3-C4-N1	121.7(2)
N2-C5-C6	108.3(2)
C7-C6-C5	113.0(2)
C8-C7-C6	119.7(2)
C12-C7-C6	121.4(2)
C12-C7-C8	118.8(3)

C9-C8-C7	121.3(3)
C8-C9-C10	119.5(2)
C11-C10-C9	120.0(3)
C10-C11-C12	120.7(3)
C7-C12-C1	120.5(2)
C11-C12-C1	119.8(2)
C11-C12-C7	119.6(2)
C14-C13-C2	120.7(2)
C18-C13-C2	120.1(2)
C18-C13-C14	119.2(2)
C15-C14-C13	119.1(2)
C14-C15-Cl1	119.1(2)
C16-C15-Cl1	118.2(2)
C16-C15-C14	122.7(2)
C15-C16-C17	117.1(3)
C16-C17-Cl2	118.2(2)
C18-C17-Cl2	119.7(2)
C18-C17-C16	122.1(3)
C17-C18-C13	119.9(2)
O1-C19-O2	123.2(3)
O1-C19-C3	123.5(3)
O2-C19-C3	113.4(2)
C22-C21-S1	119.6(2)
C26-C21-S1	119.0(2)
C26-C21-C22	121.4(3)
C21-C22-C23	119.0(3)
C24-C23-C22	121.0(3)
C23-C24-C25	118.6(3)
C23-C24-C27	120.4(3)
C25-C24-C27	121.0(3)
C26-C25-C24	121.5(3)
C21-C26-C25	118.5(3)
C24B-C25B-C26A	126.3(18)
C25B-C24B-C23B	113.3(19)
C25B-C24B-C27B	120.8(15)
C23B-C24B-C27B	125.6(15)
C24B-C23B-C22A	122.8(17)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$ x 10^3) for **6ao**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl1A	43(1)	24(1)	29(1)	7(1)	11(1)	6(1)
Cl2A	20(1)	49(1)	64(1)	0(1)	10(1)	-1(1)
S1A	57(1)	24(1)	27(1)	7(1)	16(1)	1(1)
O1A	44(1)	33(1)	27(1)	-4(1)	6(1)	-12(1)
O2A	32(1)	32(1)	20(1)	1(1)	10(1)	-4(1)
O3A	62(2)	47(1)	25(1)	11(1)	9(1)	7(1)
O4A	98(2)	20(1)	45(1)	5(1)	31(1)	-4(1)
N1A	37(1)	21(1)	21(1)	3(1)	8(1)	2(1)
N2A	27(1)	20(1)	23(1)	3(1)	5(1)	3(1)
C1A	20(1)	22(1)	21(1)	2(1)	4(1)	2(1)
C2A	18(1)	21(1)	22(1)	3(1)	6(1)	0(1)
C3A	22(1)	22(1)	21(1)	2(1)	7(1)	2(1)
C4A	29(1)	22(1)	26(1)	-1(1)	10(1)	2(1)
C5A	25(1)	34(2)	28(1)	4(1)	4(1)	6(1)
C6A	22(1)	42(2)	28(2)	0(1)	1(1)	3(1)
C7A	27(1)	30(1)	18(1)	1(1)	7(1)	-2(1)
C8A	33(2)	39(2)	19(1)	-2(1)	7(1)	-10(1)
C9A	50(2)	29(2)	24(1)	-6(1)	17(1)	-9(1)
C10A	46(2)	26(2)	27(2)	-1(1)	12(1)	3(1)
C11A	31(1)	26(1)	26(1)	0(1)	8(1)	2(1)
C12A	26(1)	23(1)	18(1)	1(1)	8(1)	-1(1)
C13A	20(1)	22(1)	19(1)	-1(1)	3(1)	0(1)
C14A	20(1)	24(1)	20(1)	0(1)	5(1)	0(1)
C15A	32(1)	23(1)	19(1)	1(1)	6(1)	3(1)
C16A	24(1)	31(2)	26(1)	-1(1)	2(1)	8(1)
C17A	20(1)	32(2)	32(2)	-4(1)	5(1)	1(1)
C18A	24(1)	23(1)	26(1)	1(1)	5(1)	-3(1)
C19A	22(1)	22(1)	24(1)	1(1)	6(1)	2(1)
C20A	45(2)	44(2)	22(1)	0(1)	13(1)	-5(1)
C21A	44(2)	29(2)	27(1)	1(1)	14(1)	-11(1)
C22A	43(2)	52(2)	31(2)	-12(2)	11(1)	-8(2)
C23A	43(4)	59(6)	40(5)	-13(4)	21(3)	-4(4)
C24A	38(4)	52(5)	50(4)	-11(4)	14(3)	-3(4)

C25A	29(3)	42(5)	43(4)	-9(4)	14(3)	-18(4)
C26A	46(2)	37(2)	33(2)	-8(1)	16(1)	-19(1)
C27A	50(5)	109(10)	72(7)	-23(7)	6(4)	22(6)
Cl1	20(1)	40(1)	37(1)	3(1)	5(1)	0(1)
Cl2	40(1)	32(1)	44(1)	-15(1)	5(1)	7(1)
S1	20(1)	24(1)	20(1)	0(1)	5(1)	0(1)
O1	34(1)	83(2)	40(1)	35(1)	10(1)	17(1)
O2	32(1)	60(2)	23(1)	12(1)	12(1)	6(1)
O3	29(1)	33(1)	21(1)	-4(1)	3(1)	-1(1)
O4	20(1)	32(1)	28(1)	4(1)	8(1)	2(1)
N1	19(1)	25(1)	19(1)	1(1)	6(1)	2(1)
N2	20(1)	23(1)	21(1)	-3(1)	7(1)	0(1)
C1	23(1)	18(1)	20(1)	-2(1)	6(1)	0(1)
C2	20(1)	21(1)	21(1)	1(1)	6(1)	1(1)
C3	24(1)	20(1)	21(1)	2(1)	8(1)	1(1)
C4	25(1)	19(1)	23(1)	2(1)	10(1)	1(1)
C5	24(1)	21(1)	29(1)	-5(1)	8(1)	-3(1)
C6	29(1)	28(1)	27(1)	-7(1)	9(1)	0(1)
C7	22(1)	28(1)	19(1)	1(1)	5(1)	1(1)
C8	30(1)	35(2)	25(1)	0(1)	12(1)	4(1)
C9	26(1)	46(2)	29(2)	11(1)	14(1)	5(1)
C10	27(1)	42(2)	30(2)	9(1)	8(1)	-8(1)
C11	31(1)	30(2)	23(1)	1(1)	8(1)	-5(1)
C12	22(1)	25(1)	21(1)	4(1)	6(1)	0(1)
C13	24(1)	22(1)	18(1)	1(1)	6(1)	1(1)
C14	25(1)	25(1)	22(1)	1(1)	8(1)	2(1)
C15	20(1)	29(1)	21(1)	5(1)	4(1)	1(1)
C16	29(1)	28(2)	26(1)	-3(1)	2(1)	-2(1)
C17	30(1)	26(1)	28(1)	-4(1)	6(1)	3(1)
C18	23(1)	28(1)	24(1)	-1(1)	4(1)	4(1)
C19	28(1)	27(1)	28(1)	6(1)	9(1)	0(1)
C20	47(2)	75(3)	25(2)	13(2)	15(1)	-4(2)
C21	22(1)	24(1)	22(1)	2(1)	8(1)	4(1)
C22	36(2)	34(2)	21(1)	-1(1)	11(1)	-1(1)
C23	37(2)	37(2)	27(1)	10(1)	12(1)	-1(1)
C24	22(1)	28(1)	35(2)	5(1)	9(1)	1(1)
C25	26(1)	25(1)	28(1)	-2(1)	8(1)	2(1)
C26	28(1)	24(1)	21(1)	5(1)	7(1)	4(1)

C27	33(2)	31(2)	54(2)	10(2)	15(1)	-1(1)
C25B	36(6)	62(9)	30(5)	-10(6)	13(4)	-37(6)
C24B	43(5)	67(8)	46(6)	-12(6)	18(5)	-3(6)
C23B	49(6)	64(8)	36(6)	-14(6)	21(5)	-12(6)
C27B	65(8)	121(16)	75(11)	-18(10)	24(7)	40(10)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **6ao**.

	x	y	z	U(eq)
H1A	7411	3489	7862	25
H2A	8835	3743	6945	24
H4A	7885	584	7122	30
H5AA	10276	2886	7913	36
H5AB	10594	2152	8640	36
H6AA	10671	3746	9341	38
H6AB	11327	4120	8795	38
H8A	10893	6157	9142	37
H9A	9639	7715	8851	40
H10A	7742	7444	8119	40
H11A	7109	5604	7701	33
H14A	8050	5383	6207	26
H16A	4615	5968	5432	34
H18A	5843	3190	6720	30
H20A	7649	1642	4725	55
H20B	8068	2900	4620	55
H20C	6811	2703	4651	55
H22A	7302	2544	9416	51
H22B	7213	2368	9491	51
H23A	5507	3331	9340	55
H25A	4088	1672	7417	45
H26A	5836	803	7546	46
H26B	5739	684	7594	46
H27A	3257	2940	8674	121
H27B	2975	2968	7821	121
H27C	3631	4011	8298	121
H1	7612	2867	2779	25

H2	6670	4932	1995	25
H4	9835	4329	2078	26
H5A	7925	5908	2971	30
H5B	8972	5880	3702	30
H6A	7825	5341	4379	33
H6B	7120	6325	3866	33
H8	5389	5450	4122	36
H9	3887	4136	3769	39
H10	4025	2535	3063	40
H11	5602	2338	2650	33
H14	4763	4244	1358	28
H16	4263	1311	151	35
H18	7468	2194	1416	31
H20D	8160	4417	-277	72
H20E	9464	4789	-48	72
H20F	8514	5702	-35	72
H22	10369	2134	4719	36
H23	9790	226	4791	40
H25	9112	-129	2627	32
H26	9743	1756	2548	29
H27G	9736	-1899	3844	59
H27H	8477	-1634	3334	59
H27I	8787	-1500	4186	59
H25B	4239	2029	7341	51
H23B	5758	3759	9168	58
H27D	3538	4130	7576	130
H27E	3758	4397	8408	130
H27F	2975	3344	8037	130

Table 6. Torsion angles [°] for **6ao**.

Cl1A-C15A-C16A-C17A	-179.3(2)
Cl2A-C17A-C18A-C13A	-178.4(2)
S1A-N1A-N2A-C1A	-111.8(2)
S1A-N1A-N2A-C5A	121.6(2)
S1A-N1A-C4A-C3A	142.2(2)
S1A-C21A-C22A-C23A	-176.7(8)

S1A-C21A-C22A-C23B	162.6(11)
S1A-C21A-C26A-C25A	179.1(8)
S1A-C21A-C26A-C25B	-165.4(11)
O3A-S1A-N1A-N2A	-46.5(2)
O3A-S1A-N1A-C4A	167.4(2)
O3A-S1A-C21A-C22A	16.4(3)
O3A-S1A-C21A-C26A	-168.6(2)
O4A-S1A-N1A-N2A	-176.2(2)
O4A-S1A-N1A-C4A	37.7(2)
O4A-S1A-C21A-C22A	151.5(3)
O4A-S1A-C21A-C26A	-33.4(3)
N1A-S1A-C21A-C22A	-97.9(3)
N1A-S1A-C21A-C26A	77.2(3)
N1A-N2A-C1A-C2A	-54.7(3)
N1A-N2A-C1A-C12A	179.6(2)
N1A-N2A-C5A-C6A	-166.0(2)
N2A-N1A-C4A-C3A	-1.8(4)
N2A-C1A-C2A-C3A	42.6(3)
N2A-C1A-C2A-C13A	163.7(2)
N2A-C1A-C12A-C7A	23.6(3)
N2A-C1A-C12A-C11A	-156.0(2)
N2A-C5A-C6A-C7A	-44.9(3)
C1A-N2A-C5A-C6A	67.6(3)
C1A-C2A-C3A-C4A	-11.7(3)
C1A-C2A-C3A-C19A	165.3(2)
C1A-C2A-C13A-C14A	111.1(3)
C1A-C2A-C13A-C18A	-66.3(3)
C2A-C1A-C12A-C7A	-102.3(3)
C2A-C1A-C12A-C11A	78.1(3)
C2A-C3A-C4A-N1A	-9.2(4)
C2A-C3A-C19A-O1A	-145.6(3)
C2A-C3A-C19A-O2A	34.1(3)
C2A-C13A-C14A-C15A	-177.6(2)
C2A-C13A-C18A-C17A	177.0(2)
C3A-C2A-C13A-C14A	-128.9(2)
C3A-C2A-C13A-C18A	53.7(3)
C4A-N1A-N2A-C1A	34.1(3)
C4A-N1A-N2A-C5A	-92.5(3)

C4A-C3A-C19A-O1A	31.5(4)
C4A-C3A-C19A-O2A	-148.8(2)
C5A-N2A-C1A-C2A	70.2(3)
C5A-N2A-C1A-C12A	-55.5(3)
C5A-C6A-C7A-C8A	-167.8(3)
C5A-C6A-C7A-C12A	16.5(4)
C6A-C7A-C8A-C9A	-175.4(3)
C6A-C7A-C12A-C1A	-5.4(4)
C6A-C7A-C12A-C11A	174.1(2)
C7A-C8A-C9A-C10A	0.2(4)
C8A-C7A-C12A-C1A	178.8(2)
C8A-C7A-C12A-C11A	-1.6(4)
C8A-C9A-C10A-C11A	0.3(4)
C9A-C10A-C11A-C12A	-1.6(4)
C10A-C11A-C12A-C1A	-178.2(2)
C10A-C11A-C12A-C7A	2.2(4)
C12A-C1A-C2A-C3A	166.6(2)
C12A-C1A-C2A-C13A	-72.3(3)
C12A-C7A-C8A-C9A	0.5(4)
C13A-C2A-C3A-C4A	-132.4(2)
C13A-C2A-C3A-C19A	44.5(3)
C13A-C14A-C15A-Cl1A	179.9(2)
C13A-C14A-C15A-C16A	0.2(4)
C14A-C13A-C18A-C17A	-0.4(4)
C14A-C15A-C16A-C17A	0.3(4)
C15A-C16A-C17A-Cl2A	178.4(2)
C15A-C16A-C17A-C18A	-0.9(4)
C16A-C17A-C18A-C13A	1.0(4)
C18A-C13A-C14A-C15A	-0.2(4)
C19A-C3A-C4A-N1A	173.8(2)
C20A-O2A-C19A-O1A	6.1(4)
C20A-O2A-C19A-C3A	-173.6(2)
C21A-S1A-N1A-N2A	68.7(2)
C21A-S1A-N1A-C4A	-77.4(2)
C21A-C22A-C23A-C24A	-7.4(13)
C21A-C22A-C23B-C24B	12(2)
C21A-C26A-C25B-C24B	-7(2)

C22A-C21A-C26A-C25A	-5.9(9)
C22A-C21A-C26A-C25B	9.7(12)
C22A-C23A-C24A-C25A	4.2(16)
C22A-C23A-C24A-C27A	-178.4(9)
C23A-C22A-C23B-C24B	-81(4)
C23A-C24A-C25A-C26A	-1.7(16)
C24A-C25A-C26A-C21A	2.5(13)
C24A-C25A-C26A-C25B	-72(6)
C25A-C26A-C25B-C24B	106(7)
C26A-C21A-C22A-C23A	8.3(9)
C26A-C21A-C22A-C23B	-12.4(12)
C26A-C25B-C24B-C23B	7(3)
C26A-C25B-C24B-C27B	-179.3(17)
C27A-C24A-C25A-C26A	-179.1(10)
Cl1-C15-C16-C17	179.3(2)
Cl2-C17-C18-C13	176.2(2)
S1-N1-N2-C1	-121.60(19)
S1-N1-N2-C5	114.1(2)
S1-N1-C4-C3	152.4(2)
S1-C21-C22-C23	-179.2(2)
S1-C21-C26-C25	-179.7(2)
O3-S1-N1-N2	-50.8(2)
O3-S1-N1-C4	151.3(2)
O3-S1-C21-C22	-5.1(2)
O3-S1-C21-C26	175.0(2)
O4-S1-N1-N2	179.34(17)
O4-S1-N1-C4	21.5(2)
O4-S1-C21-C22	129.7(2)
O4-S1-C21-C26	-50.2(2)
N1-S1-C21-C22	-118.7(2)
N1-S1-C21-C26	61.4(2)
N1-N2-C1-C2	-55.1(3)
N1-N2-C1-C12	-179.3(2)
N1-N2-C5-C6	-169.1(2)
N2-N1-C4-C3	-4.0(4)
N2-C1-C2-C3	41.2(3)
N2-C1-C2-C13	162.93(19)
N2-C1-C12-C7	27.7(3)

N2-C1-C12-C11	-155.1(2)
N2-C5-C6-C7	-45.0(3)
C1-N2-C5-C6	67.4(3)
C1-C2-C3-C4	-9.2(3)
C1-C2-C3-C19	171.9(2)
C1-C2-C13-C14	103.2(3)
C1-C2-C13-C18	-77.4(3)
C2-C1-C12-C7	-97.3(3)
C2-C1-C12-C11	79.9(3)
C2-C3-C4-N1	-10.0(4)
C2-C3-C19-O1	15.5(4)
C2-C3-C19-O2	-164.1(2)
C2-C13-C14-C15	179.9(2)
C2-C13-C18-C17	-178.4(2)
C3-C2-C13-C14	-135.5(2)
C3-C2-C13-C18	43.9(3)
C4-N1-N2-C1	36.9(3)
C4-N1-N2-C5	-87.4(3)
C4-C3-C19-O1	-163.4(3)
C4-C3-C19-O2	17.1(4)
C5-N2-C1-C2	67.0(3)
C5-N2-C1-C12	-57.1(3)
C5-C6-C7-C8	-165.7(3)
C5-C6-C7-C12	18.9(4)
C6-C7-C8-C9	-174.6(3)
C6-C7-C12-C1	-10.2(4)
C6-C7-C12-C11	172.6(3)
C7-C8-C9-C10	1.8(4)
C8-C7-C12-C1	174.4(2)
C8-C7-C12-C11	-2.9(4)
C8-C9-C10-C11	-2.5(4)
C9-C10-C11-C12	0.5(4)
C10-C11-C12-C1	-175.0(3)
C10-C11-C12-C7	2.2(4)
C12-C1-C2-C3	164.2(2)

C12-C1-C2-C13	-74.0(3)
C12-C7-C8-C9	0.9(4)
C13-C2-C3-C4	-131.2(3)
C13-C2-C3-C19	50.0(3)
C13-C14-C15-Cl1	179.9(2)
C13-C14-C15-C16	-1.4(4)
C14-C13-C18-C17	1.0(4)
C14-C15-C16-C17	0.6(4)
C15-C16-C17-Cl2	-177.1(2)
C15-C16-C17-C18	1.0(4)
C16-C17-C18-C13	-1.8(4)
C18-C13-C14-C15	0.5(4)
C19-C3-C4-N1	168.8(2)
C20-O2-C19-O1	1.1(5)
C20-O2-C19-C3	-179.4(3)
C21-S1-N1-N2	63.80(19)
C21-S1-N1-C4	-94.0(2)
C21-C22-C23-C24	-0.7(4)
C22-C21-C26-C25	0.4(4)
C22-C23-C24-C25	-0.4(4)
C22-C23-C24-C27	177.3(3)
C23-C24-C25-C26	1.5(4)
C24-C25-C26-C21	-1.5(4)
C26-C21-C22-C23	0.7(4)
C27-C24-C25-C26	-176.2(3)
C25B-C24B-C23B-C22A	-9(2)
C23B-C22A-C23A-C24A	89(5)
C27B-C24B-C23B-C22A	177.4(15)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for **6ao** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

Crystallographic data for **6ea** has been deposited with the Cambridge Crystallographic Data Centre as deposition number CCDC 1041719. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

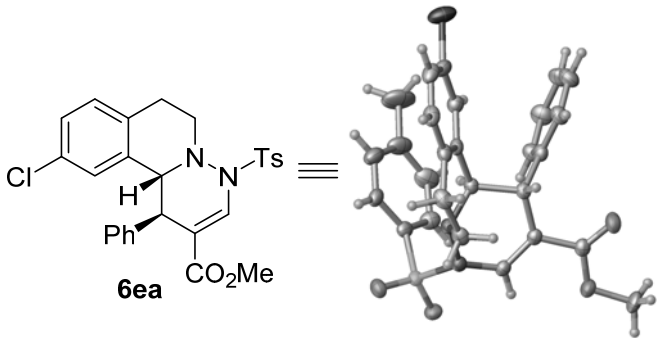


Table 1. Crystal data and structure refinement for **6ea**.

Identification code	**6ea**	
Empirical formula	$C_{27}H_{25}ClN_2O_4S$	
Formula weight	509.00	
Temperature	173.1500 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 8.8234(19) Å	α = 90°.
	b = 9.577(2) Å	β = 90°.
	c = 29.407(7) Å	γ = 90°.
Volume	2484.8(9) $Å^3$	
Z	4	
Density (calculated)	1.361 Mg/m^3	
Absorption coefficient	0.275 mm^{-1}	
F(000)	1064	
Crystal size	0.216 x 0.207 x 0.203 mm^3	
Theta range for data collection	2.410 to 27.459°.	
Index ranges	-10<=h<=11, -12<=k<=9, -38<=l<=38	
Reflections collected	15306	
Independent reflections	5633 [R(int) = 0.0348]	
Completeness to theta = 26.000°	99.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.75209	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	5633 / 0 / 318
Goodness-of-fit on F^2	1.075
Final R indices [I>2sigma(I)]	R1 = 0.0389, wR2 = 0.0831
R indices (all data)	R1 = 0.0420, wR2 = 0.0846
Absolute structure parameter	-0.01(3)
Extinction coefficient	n/a
Largest diff. peak and hole	0.244 and -0.223 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **6ea**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cl1	6614(1)	4533(1)	3216(1)	55(1)
S1	318(1)	10665(1)	3414(1)	24(1)
O1	339(2)	11144(2)	2955(1)	33(1)
O2	-746(2)	11231(2)	3731(1)	31(1)
O3	4739(2)	10641(2)	5035(1)	39(1)
O4	2581(2)	11872(2)	4979(1)	34(1)
N1	2041(2)	11006(2)	3641(1)	24(1)
N2	3236(2)	10344(2)	3392(1)	23(1)
C1	3825(3)	9139(3)	3648(1)	23(1)
C2	4429(3)	9526(3)	4130(1)	24(1)
C3	3352(3)	10569(3)	4344(1)	24(1)
C4	2205(3)	11143(3)	4111(1)	25(1)
C5	4999(3)	8415(3)	3359(1)	24(1)
C6	5222(3)	6977(3)	3407(1)	30(1)
C7	6328(3)	6327(3)	3148(1)	34(1)
C8	7192(3)	7052(3)	2838(1)	37(1)
C9	6945(3)	8467(3)	2789(1)	34(1)
C10	5857(3)	9179(3)	3048(1)	28(1)
C11	5580(3)	10712(3)	2967(1)	34(1)
C12	4440(3)	11372(3)	3290(1)	30(1)
C13	4577(3)	8171(3)	4394(1)	26(1)
C14	5985(3)	7544(3)	4448(1)	33(1)
C15	6111(4)	6215(3)	4626(1)	41(1)
C16	4828(4)	5481(3)	4755(1)	44(1)
C17	3425(4)	6099(3)	4712(1)	42(1)

C18	3299(3)	7436(3)	4532(1)	33(1)
C19	3653(3)	11005(3)	4818(1)	28(1)
C20	2814(4)	12394(4)	5436(1)	42(1)
C21	236(3)	8841(3)	3423(1)	27(1)
C22	836(3)	8093(3)	3057(1)	33(1)
C23	999(4)	6670(3)	3104(1)	44(1)
C24	596(4)	5982(3)	3501(1)	48(1)
C25	-41(3)	6748(3)	3852(1)	45(1)
C26	-211(3)	8181(3)	3819(1)	34(1)
C27	862(5)	4430(4)	3551(2)	78(1)

Table 3. Bond lengths [Å] and angles [°] for **6ea**.

Cl1-C7	1.748(3)
S1-O1	1.4268(19)
S1-O2	1.4301(19)
S1-N1	1.692(2)
S1-C21	1.749(3)
O3-C19	1.204(3)
O4-C19	1.345(3)
O4-C20	1.449(3)
N1-N2	1.431(3)
N1-C4	1.398(3)
N2-C1	1.473(3)
N2-C12	1.479(3)
C1-C2	1.557(3)
C1-C5	1.509(3)
C2-C3	1.515(3)
C2-C13	1.518(3)
C3-C4	1.340(4)
C3-C19	1.478(3)
C5-C6	1.399(4)
C5-C10	1.394(4)
C6-C7	1.386(4)
C7-C8	1.377(4)
C8-C9	1.379(4)
C9-C10	1.402(4)

C10-C11	1.507(4)
C11-C12	1.520(4)
C13-C14	1.389(4)
C13-C18	1.390(4)
C14-C15	1.381(4)
C15-C16	1.384(5)
C16-C17	1.378(5)
C17-C18	1.390(4)
C21-C22	1.398(4)
C21-C26	1.383(4)
C22-C23	1.377(4)
C23-C24	1.387(5)
C24-C25	1.385(5)
C24-C27	1.512(5)
C25-C26	1.383(4)

O1-S1-O2	120.28(12)
O1-S1-N1	107.40(11)
O1-S1-C21	109.65(13)
O2-S1-N1	105.05(11)
O2-S1-C21	110.00(13)
N1-S1-C21	102.92(11)
C19-O4-C20	116.1(2)
N2-N1-S1	112.04(15)
C4-N1-S1	120.07(17)
C4-N1-N2	118.1(2)
N1-N2-C1	110.25(18)
N1-N2-C12	109.76(19)
C1-N2-C12	111.85(19)
N2-C1-C2	113.5(2)
N2-C1-C5	108.3(2)
C5-C1-C2	112.8(2)
C3-C2-C1	108.7(2)
C3-C2-C13	113.9(2)
C13-C2-C1	107.0(2)
C4-C3-C2	122.1(2)
C4-C3-C19	120.0(2)
C19-C3-C2	117.7(2)
C3-C4-N1	123.0(2)

C6-C5-C1	119.4(2)
C10-C5-C1	120.1(2)
C10-C5-C6	120.4(2)
C7-C6-C5	119.0(3)
C6-C7-Cl1	118.7(2)
C8-C7-Cl1	119.5(2)
C8-C7-C6	121.8(3)
C7-C8-C9	118.5(3)
C8-C9-C10	122.0(3)
C5-C10-C9	118.2(3)
C5-C10-C11	121.7(2)
C9-C10-C11	120.0(2)
C10-C11-C12	114.5(2)
N2-C12-C11	109.0(2)
C14-C13-C2	120.4(2)
C14-C13-C18	118.2(2)
C18-C13-C2	120.8(2)
C15-C14-C13	120.9(3)
C14-C15-C16	120.4(3)
C17-C16-C15	119.5(3)
C16-C17-C18	120.2(3)
C17-C18-C13	120.8(3)
O3-C19-O4	123.4(2)
O3-C19-C3	124.2(2)
O4-C19-C3	112.3(2)
C22-C21-S1	119.0(2)
C26-C21-S1	118.8(2)
C26-C21-C22	121.5(3)
C23-C22-C21	118.0(3)
C22-C23-C24	121.8(3)
C23-C24-C27	120.5(4)
C25-C24-C23	118.7(3)
C25-C24-C27	120.8(4)
C26-C25-C24	121.2(3)
C21-C26-C25	118.8(3)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **6ea**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl1	53(1)	33(1)	80(1)	-13(1)	14(1)	6(1)
S1	23(1)	27(1)	23(1)	-1(1)	-1(1)	2(1)
O1	31(1)	42(1)	26(1)	3(1)	-3(1)	4(1)
O2	27(1)	34(1)	32(1)	-6(1)	2(1)	5(1)
O3	36(1)	52(1)	30(1)	-4(1)	-8(1)	3(1)
O4	36(1)	38(1)	27(1)	-9(1)	-3(1)	4(1)
N1	23(1)	25(1)	24(1)	-1(1)	0(1)	0(1)
N2	21(1)	26(1)	23(1)	2(1)	2(1)	1(1)
C1	23(1)	26(1)	22(1)	1(1)	0(1)	-2(1)
C2	22(1)	28(1)	22(1)	2(1)	1(1)	-1(1)
C3	27(1)	23(1)	23(1)	1(1)	0(1)	-3(1)
C4	28(1)	23(1)	25(1)	-3(1)	1(1)	-2(1)
C5	20(1)	33(1)	20(1)	-2(1)	-2(1)	0(1)
C6	28(1)	33(1)	28(1)	-2(1)	1(1)	-1(1)
C7	32(1)	33(2)	38(2)	-12(1)	-3(1)	2(1)
C8	25(1)	52(2)	33(2)	-15(1)	3(1)	1(1)
C9	24(1)	51(2)	27(1)	-2(1)	4(1)	-2(1)
C10	22(1)	39(2)	24(1)	-1(1)	-1(1)	-1(1)
C11	26(1)	43(2)	34(1)	11(1)	4(1)	-2(1)
C12	31(1)	28(1)	31(1)	8(1)	-2(1)	-5(1)
C13	29(1)	30(1)	21(1)	1(1)	0(1)	0(1)
C14	28(1)	40(2)	32(2)	4(1)	-2(1)	3(1)
C15	38(2)	44(2)	41(2)	8(1)	-5(1)	10(1)
C16	53(2)	35(2)	43(2)	14(1)	1(1)	8(2)
C17	44(2)	39(2)	42(2)	12(1)	6(1)	-2(1)
C18	29(1)	36(2)	35(2)	6(1)	2(1)	2(1)
C19	29(1)	28(1)	26(1)	1(1)	-1(1)	-4(1)
C20	53(2)	49(2)	26(1)	-14(1)	-4(1)	2(2)
C21	20(1)	28(1)	33(1)	-5(1)	-4(1)	-1(1)
C22	30(1)	38(2)	30(1)	-12(1)	-5(1)	2(1)
C23	40(2)	38(2)	54(2)	-18(2)	-6(2)	7(1)
C24	37(2)	27(2)	80(3)	-8(2)	-8(2)	-3(1)
C25	36(2)	34(2)	64(2)	10(2)	1(2)	-10(1)
C26	28(1)	33(1)	42(2)	-1(1)	6(1)	-3(1)
C27	80(3)	26(2)	128(4)	-6(2)	-4(3)	1(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **6ea**.

	x	y	z	U(eq)
H1	2982	8484	3690	28
H2	5432	9955	4100	29
H4	1484	11656	4271	30
H6	4638	6465	3611	36
H8	7925	6599	2665	44
H9	7517	8963	2578	41
H11A	5224	10836	2658	41
H11B	6536	11205	2995	41
H12A	4942	11653	3569	36
H12B	4000	12197	3151	36
H14	6856	8026	4364	40
H15	7062	5810	4660	49
H16	4913	4579	4869	52
H17	2560	5620	4803	50
H18	2347	7844	4503	40
H20A	3791	12831	5455	64
H20B	2764	11633	5648	64
H20C	2040	13064	5507	64
H22	1115	8542	2789	39
H23	1391	6156	2863	53
H25	-359	6292	4114	54
H26	-619	8691	4059	41
H27A	575	3965	3275	117
H27B	264	4077	3798	117
H27C	1916	4261	3611	117

Table 6. Torsion angles [°] for **6ea**.

Cl1-C7-C8-C9	179.9(2)
S1-N1-N2-C1	-105.85(18)
S1-N1-N2-C12	130.50(17)
S1-N1-C4-C3	136.7(2)
S1-C21-C22-C23	169.0(2)

S1-C21-C26-C25	-169.6(2)
O1-S1-N1-N2	-58.42(18)
O1-S1-N1-C4	156.29(19)
O1-S1-C21-C22	27.1(2)
O1-S1-C21-C26	-162.3(2)
O2-S1-N1-N2	172.42(16)
O2-S1-N1-C4	27.1(2)
O2-S1-C21-C22	161.5(2)
O2-S1-C21-C26	-27.9(3)
N1-S1-C21-C22	-86.9(2)
N1-S1-C21-C26	83.6(2)
N1-N2-C1-C2	-58.0(2)
N1-N2-C1-C5	175.96(19)
N1-N2-C12-C11	-171.6(2)
N2-N1-C4-C3	-6.6(4)
N2-C1-C2-C3	41.3(3)
N2-C1-C2-C13	164.6(2)
N2-C1-C5-C6	-150.5(2)
N2-C1-C5-C10	29.9(3)
C1-N2-C12-C11	65.6(3)
C1-C2-C3-C4	-7.5(3)
C1-C2-C3-C19	175.8(2)
C1-C2-C13-C14	101.2(3)
C1-C2-C13-C18	-69.9(3)
C1-C5-C6-C7	-178.5(2)
C1-C5-C10-C9	179.4(2)
C1-C5-C10-C11	-4.0(4)
C2-C1-C5-C6	83.1(3)
C2-C1-C5-C10	-96.6(3)
C2-C3-C4-N1	-10.3(4)
C2-C3-C19-O3	3.9(4)
C2-C3-C19-O4	-176.7(2)
C2-C13-C14-C15	-170.1(3)
C2-C13-C18-C17	170.2(3)
C3-C2-C13-C14	-138.7(3)
C3-C2-C13-C18	50.2(3)
C4-N1-N2-C1	40.2(3)
C4-N1-N2-C12	-83.5(3)
C4-C3-C19-O3	-172.8(3)
C4-C3-C19-O4	6.6(3)
C5-C1-C2-C3	164.9(2)
C5-C1-C2-C13	-71.8(2)
C5-C6-C7-Cl1	179.2(2)

C5-C6-C7-C8	-1.2(4)
C5-C10-C11-C12	7.0(4)
C6-C5-C10-C9	-0.3(4)
C6-C5-C10-C11	176.3(2)
C6-C7-C8-C9	0.4(4)
C7-C8-C9-C10	0.6(4)
C8-C9-C10-C5	-0.6(4)
C8-C9-C10-C11	-177.2(3)
C9-C10-C11-C12	-176.5(3)
C10-C5-C6-C7	1.2(4)
C10-C11-C12-N2	-35.7(3)
C12-N2-C1-C2	64.4(3)
C12-N2-C1-C5	-61.6(3)
C13-C2-C3-C4	-126.6(3)
C13-C2-C3-C19	56.7(3)
C13-C14-C15-C16	-0.1(5)
C14-C13-C18-C17	-1.1(4)
C14-C15-C16-C17	-1.2(5)
C15-C16-C17-C18	1.3(5)
C16-C17-C18-C13	-0.1(5)
C18-C13-C14-C15	1.3(4)
C19-C3-C4-N1	166.3(2)
C20-O4-C19-O3	1.6(4)
C20-O4-C19-C3	-177.8(2)
C21-S1-N1-N2	57.27(18)
C21-S1-N1-C4	-88.0(2)
C21-C22-C23-C24	-0.4(4)
C22-C21-C26-C25	0.7(4)
C22-C23-C24-C25	2.5(5)
C22-C23-C24-C27	-177.0(3)
C23-C24-C25-C26	-3.0(5)
C24-C25-C26-C21	1.5(5)
C26-C21-C22-C23	-1.3(4)
C27-C24-C25-C26	176.4(3)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for **6ea** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)