Supporting Information

Phosphine-Catalyzed Enantioselective [4+3] Annulation of Allenoates with C,N-Cyclic Azomethine Imines: Synthesis of Quinazoline-Based Tricyclic Heterocycles

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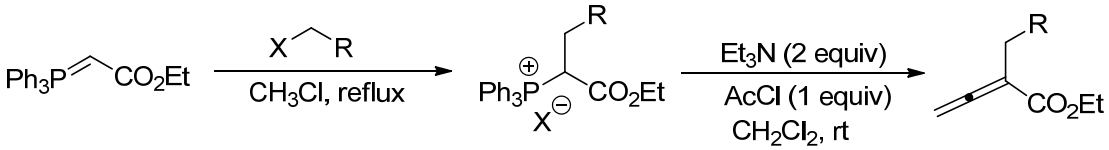
General Information

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. All solvents were purified and dried according to standard methods prior to use. 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 254 nm. 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. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 using a 300 MHz NMR instrument (referenced internally to Me_4Si). ^{1}H 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 VI automatic polarimeter. Accurate mass measurements were performed using an Agilent instrument with the ESI-MS technique. Melting points were determined on a Stuard SMP3 melting point apparatus. X-ray crystallographic data were collected using a MM007HF Saturn724+. HPLC analysis was performed on Agilent 1100 or 1200 series, UV detection monitored at 254 nm, using Chiralpak AD-H column, Chiralpak IA column, Lux cellulose 1 column and Lux cellulose 2 column with hexane and *i*-PrOH or alcohol as the eluent.

General procedure for preparation of N-iminoquinazolinium ylides[1]

N-iminoquinazolinium ylides were prepared by the reported procedure.

General procedure for preparation of Allenoates 2[2]



The alkyl halide (1.0 – 1.2 equiv) was added to a stirred solution of (carbethoxy-methylene)triphenylphosphorane in $CHCl_3$ (80 mL) at room temperature. The mixture was heated under reflux until all of the (carbethoxymethylene)triphenylphosphorane had disappeared (monitored using TLC or ^{1}H NMR). The solvent was evaporated under reduced pressure. DCM (100 mL) and triethylamine (8.4 mL, 2.2 equiv) were added to the resulting phosphonium salt. After stirring for 1 h, AcCl (1.96 mL, 1.0 equiv) was added dropwise over 30 min using a syringe pump. The mixture was

[1] (a) Wang, T.; Luo, J.; Gu, C.; Li, R.; Tang, X.; Yu, D.; Li, J. CN 103172575A.(b) Wang, T.; Shao, A.-L.; Feng, H.-Y.; Yang, S.-W.; Gao, M.; Tian, J.; Lei, A.-W. *Tetrahedron.* **2015**, *71,* 4473-4477.

[2] (a) Buono, G. *Tetrahedron Lett.* **1972**, *13*, 3257. (b) Zhu, X.-F.; Lan, J.; Kwon, O. *J. Am. Chem. Soc.* **2003**, *125*, 4716.

stirred overnight and then passed through a Buchner funnel packed with silica gel and washed several times with DCM. The combined filtrates were carefully concentrated and the residue subjected to a flash column chromatography (eluent: 10–15% EtOAc in hexanes) to afford the corresponding allenoates in 50–85% yield.

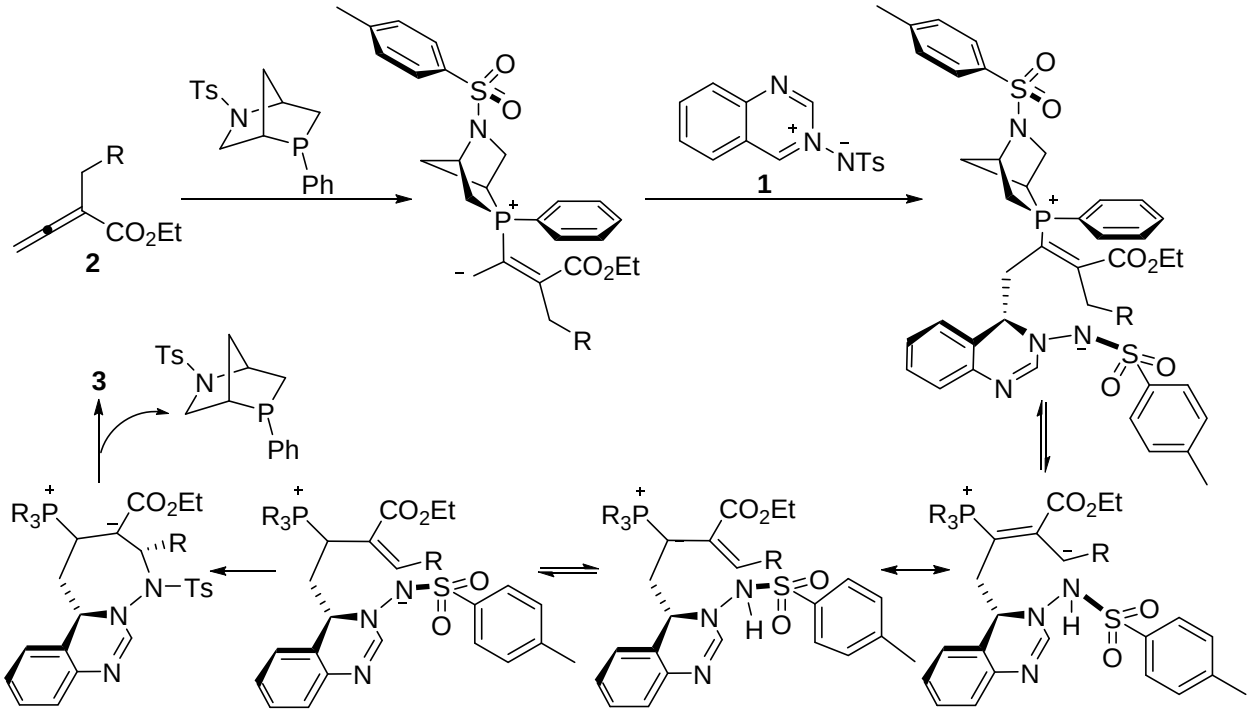
General Procedure for Achiral Phosphine-Catalyzed [4+3] Cycloaddition

Under a nitrogen atmosphere, to a stirred solution of N-iminoquinazolinium ylide **1** (0.1 mmol, 1.0 equiv) and the catalyst PMe_2Ph (0.02 mmol, 20 mol %) in DCM (1 mL) was added allenoate **2** (0.15 mmol, 1.5 equiv) via a syringe. Then the reaction solution was vigorously stirred at room temperature and monitored by TLC. After the reaction was complete, the mixture was directly purified by column chromatography on silica gel (petroleum ether/EtOAc as the eluent) to furnish the corresponding product.

General Procedure for Chiral Phosphine-Catalyzed Asymmetric [4+3] Cycloaddition

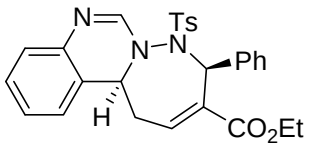
Under a nitrogen atmosphere, to a stirred solution of N-iminoquinazolinium ylides **1** (0.125 mmol, 1.0 equiv) and the catalyst **P2** (0.025 mmol, 20 mol %) in THF (2 mL) was added allenoate **2** (0.1875 mmol, 1.5 equiv) via a syringe. Then the reaction solution was vigorously stirred at 0 °C and monitored by TLC. After the reaction was complete, the mixture was directly purified by column chromatography on silica gel (petroleum ether/EtOAc as the eluent) to furnish the corresponding product.

A Proposed Mechanism of Chiral Phosphine-Catalyzed Asymmetric [4+3] Cycloaddition



Characterization Data for the [4+3] Cycloaddition Products 3

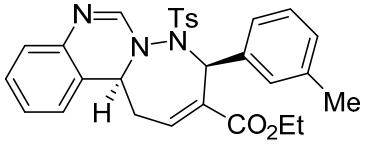
(4*S*,12b*S*)-ethyl 4-phenyl-5-tosyl-1,4,5,12b-tetrahydro-[1,2]diazepino[1,7-*c*]quinazoline-3-carboxylate (3aa)



3aa

Prepared according to the general procedure as described above in 97% yield (60.8 mg). It was purified by flash chromatography (25% EtOAc/PE) to afford a white solid. mp = 150 – 151 °C; $[\alpha]^{20}_{D}$ = + 19.5 (*c* 0.56, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85–7.72 (m, 2H), 7.43 (dd, *J* = 9.1, 3.4 Hz, 1H), 7.37–7.26 (m, 7H), 7.17 (td, *J* = 7.6, 1.5 Hz, 1H), 7.06 (td, *J* = 7.5, 1.4 Hz, 1H), 7.00 (dd, *J* = 7.8, 1.3 Hz, 1H), 6.89 (s, 1H), 6.80 (dd, *J* = 7.6, 1.5 Hz, 1H), 6.05 (d, *J* = 0.8 Hz, 1H), 4.92 (d, *J* = 10.3 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.03 (ddd, *J* = 14.5, 11.2, 2.8 Hz, 1H), 2.56–2.33 (m, 4H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 165.3, 149.1, 144.7, 141.7, 139.0, 135.8, 134.5, 134.4, 129.9, 128.9, 128.7, 128.6, 128.1, 127.7, 125.7, 125.4, 125.2, 124.7, 61.6, 61.4, 57.3, 38.5, 21.5, 13.9; IR (film) ν_{max} 547, 582, 661, 704, 736, 762, 816, 984, 1051, 1091, 1164 1247, 1356, 1453, 1483, 1595, 1617, 1706, 2981; HRMS (ESI) calcd for $C_{28}H_{28}N_3O_4S^+$ $[M+H]^+$ 502.1795, found 502.1800; HPLC analysis: 94% ee (Lux cellulose 1, isopropanol/hexane = 15:85, 1.0 ml/min, UV: 254 nm), t_R = 13.782 min (minor), 17.736 min (major).

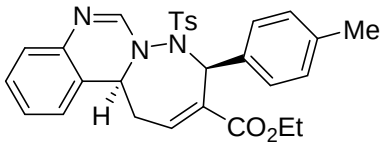
(4*S*,12b*S*)-ethyl 4-(m-tolyl)-5-tosyl-1,4,5,12b-tetrahydro-[1,2]diazepino[1,7-*c*]quinazoline-3-carboxylate (3ab)



3ab

Prepared according to the general procedure as described above in 97% yield (62.6 mg). It was purified by flash chromatography (25% EtOAc/PE) to afford a white solid. mp = 70 – 72 °C; $[\alpha]^{20}_{D}$ = + 9.8 (*c* 0.54, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 – 7.67 (m, 2H), 7.41 (dd, *J* = 9.1, 3.5 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.23 – 7.14 (m, 2H), 7.13 – 6.96 (m, 5H), 6.84 (s, 1H), 6.80 (dd, *J* = 7.8, 1.1 Hz, 1H), 6.06 (s, 1H), 4.90 (d, *J* = 10.5 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.02 (ddd, *J* = 16.3, 10.9, 3.0 Hz, 1H), 2.49 – 2.37 (m, 4H), 2.26 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 165.3, 149.1, 144.6, 141.6, 139.1, 138.7, 135.9, 134.5, 134.3, 129.8, 129.5, 128.8, 128.7, 128.6, 127.7, 125.7, 125.4, 125.2, 125.1, 124.8, 61.7, 61.4, 57.4, 38.3, 21.5, 21.3, 13.9; IR (film) ν_{max} 548, 586, 663, 736, 1053, 1091, 1164, 1252, 1356, 1484, 1596, 1618, 1706; HRMS (ESI) calcd for $C_{29}H_{30}N_3O_4S^+$ $[M+H]^+$ 516.1952, found 516.1951; HPLC analysis: 92% ee (Lux cellulose 1, isopropanol/hexane = 15:85, 1.0 ml/min, UV: 254 nm), t_R = 10.329 min (minor), 12.568 min (major).

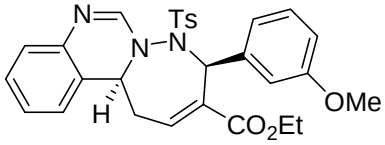
(4*S*,12b*S*)-ethyl 4-(p-tolyl)-5-tosyl-1,4,5,12b-tetrahydro-[1,2]diazepino[1,7-*c*]quinazoline-3-carboxylate (3ac)



3ac

Prepared according to the general procedure as described above in 95% yield (61.3 mg). It was purified by flash chromatography (25% EtOAc/PE) to afford a white solid. mp = 198 – 199 °C; $[\alpha]^{20}_D$ = + 3.4 (*c* 0.58, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.40 (dd, *J* = 9.1, 3.3 Hz, 1H), 7.27 (d, *J* = 9.6 Hz, 2H), 7.20 – 7.09 (m, 5H), 7.05 (td, *J* = 7.5, 1.3 Hz, 1H), 7.00 (dd, *J* = 7.8, 1.0 Hz, 1H), 6.86 (s, 1H), 6.80 (dd, *J* = 7.3, 0.8 Hz, 1H), 6.05 (s, 1H), 4.89 (d, *J* = 10.8 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.02 (ddd, *J* = 16.6, 11.3, 3.2 Hz, 1H), 2.51 – 2.33 (m, 4H), 2.29 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 165.3, 149.2, 144.6, 141.5, 139.0, 138.6, 135.9, 134.6, 131.3, 129.8, 129.7, 128.6, 128.1, 127.7, 125.7, 125.4, 125.2, 124.8, 61.4, 61.3, 57.3, 38.5, 21.5, 20.9, 13.9; IR (film) ν_{max} 547, 585, 658, 737, 814, 1052, 1092, 1164, 1247, 1356, 1595, 1617, 1707, 2981; HRMS (ESI) calcd for $C_{29}H_{30}N_3O_4S^+$ $[M+H]^+$ 516.1952, found 516.1949; HPLC analysis: 92% ee (CHIRALPAK IA, isopropanol/hexane = 10:90, 1.0 ml/min, UV: 254 nm), t_R = 24.541 min (minor), 34.367 min (major).

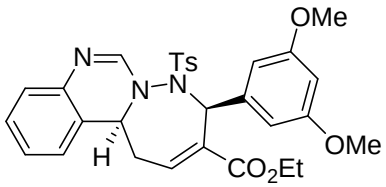
(4*S*,12b*S*)-ethyl 4-(3-methoxyphenyl)-5-tosyl-1,4,5,12b-tetrahydro-[1,2]diazepino[1,7-*c*] quinazoline-3-carboxylate (3ad)



3ad

Prepared according to the general procedure as described above in 96% yield (63.8 mg). It was purified by flash chromatography (25% EtOAc/PE) to afford a white solid. mp = 70 – 72 °C; $[\alpha]^{20}_D$ = + 2.0 (*c* 0.60, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 – 7.71 (m, 2H), 7.41 (dd, *J* = 9.1, 3.4 Hz, 1H), 7.30 – 7.26 (m, 2H), 7.25 – 7.12 (m, 2H), 7.05 (td, *J* = 7.5, 1.4 Hz, 1H), 7.00 (dd, *J* = 7.7, 1.2 Hz, 1H), 6.87 – 6.80 (m, 3H), 6.77 (m, 2H), 6.13 (d, *J* = 0.8 Hz, 1H), 4.91 (d, *J* = 10.2 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.69 (s, 3H), 3.02 (ddd, *J* = 16.4, 11.1, 3.4 Hz, 1H), 2.59 – 2.23 (m, 4H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 165.3, 159.9, 149.0, 144.7, 141.8, 139.0, 135.9, 135.8, 134.4, 129.9, 129.9, 128.6, 127.7, 125.7, 125.4, 125.2, 124.7, 120.3, 114.1, 113.9, 61.5, 61.4, 57.4, 55.0, 38.4, 21.4, 14.0; IR (film) ν_{max} 560, 664, 736, 766, 1050, 1091, 1165, 1260, 1356, 1456, 1489, 1596, 1707, 2925; HRMS (ESI) calcd for $C_{29}H_{30}N_3O_5S^+$ $[M+H]^+$ 532.1901, found 532.1901; HPLC analysis: 93% ee (CHIRALPAK IA, isopropanol/hexane = 10:90, 1.0 ml/min, UV: 254 nm), t_R = 36.519 min (minor), 38.557 min (major).

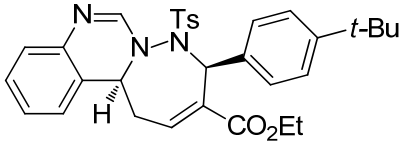
(4*S*,12b*S*)-ethyl 4-(3,5-dimethoxyphenyl)-5-tosyl-1,4,5,12b-tetrahydro-[1,2]diazepino[1,7-*c*] quinazoline-3-carboxylate (3ae)



3ae

Prepared according to the general procedure as described above in 95% yield (66.7 mg). It was purified by flash chromatography (25% EtOAc/PE) to afford a white solid. mp = 70 – 72 °C; $[\alpha]^{20}_{D}$ = – 12.2 (*c* 0.85, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 – 7.72 (m, 2H), 7.40 (dd, *J* = 9.1, 3.4 Hz, 1H), 7.27 (d, *J* = 8.1 Hz, 2H), 7.16 (td, *J* = 7.6, 1.4 Hz, 1H), 7.05 (td, *J* = 7.5, 1.4 Hz, 1H), 7.00 (dd, *J* = 7.7, 1.1 Hz, 1H), 6.84 – 6.73 (m, 2H), 6.36 – 6.30 (m, 3H), 6.22 (d, *J* = 0.6 Hz, 1H), 4.91 (d, *J* = 10.3 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.66 (s, 6H), 3.03 (ddd, *J* = 16.6, 11.1, 3.4 Hz, 1H), 2.51 – 2.31 (m, 4H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 165.2, 161.0, 149.0, 144.7, 141.8, 139.0, 136.6, 135.9, 134.4, 129.9, 128.6, 127.7, 125.7, 125.4, 125.2, 124.8, 106.4, 100.1, 61.5, 61.4, 57.5, 55.1, 38.3, 21.4, 14.0; IR (film) ν_{max} 554, 660, 707, 1056, 1091, 1164, 1205, 1259, 1354, 1457, 1596, 1707, 2931; HRMS (ESI) calcd for $C_{30}H_{32}N_3O_6S^+$ $[M+H]^+$ 562.2006, found 562.2012; HPLC analysis: 95% ee (CHIRALPAK IA, isopropanol/hexane = 15:85, 1.0 ml/min, UV: 254 nm), t_R = 15.060 min (minor), 25.453 min (major).

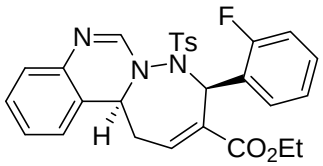
(4*S*,12b*S*)-ethyl 4-(4-(tert-butyl)phenyl)-5-tosyl-1,4,5,12b-tetrahydro-[1,2]diazepino[1,7-*c*] quinazoline-3-carboxylate (3af)



3af

Prepared according to the general procedure as described above in 96% yield (67.0 mg). It was purified by flash chromatography (25% EtOAc/PE) to afford a white solid. mp = 93 – 94 °C; $[\alpha]^{20}_{D}$ = – 3.1 (*c* 0.58, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 – 7.76 (m, 2H), 7.41 (dd, *J* = 9.2, 3.3 Hz, 1H), 7.35 – 7.25 (m, 4H), 7.19 – 7.13 (m, 3H), 7.05 (td, *J* = 7.5, 1.4 Hz, 1H), 7.00 (dd, *J* = 7.7, 1.1 Hz, 1H), 6.86 (s, 1H), 6.79 (dd, *J* = 7.8, 1.1 Hz, 1H), 6.15 (s, 1H), 4.90 (d, *J* = 10.6 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.03 (ddd, *J* = 16.2, 11.2, 3.2 Hz, 1H), 2.64 – 2.18 (m, 4H), 1.37 – 1.12 (m, 12H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 165.4, 151.6, 149.2, 144.6, 141.6, 139.0, 135.8, 134.6, 131.2, 129.9, 128.6, 127.8, 127.7, 125.8, 125.7, 125.5, 125.1, 124.8, 61.3, 61.2, 57.3, 38.6, 34.4, 31.1, 21.5, 14.0; IR (film) ν_{max} 586, 658, 765, 1052, 1092, 1164, 1246, 1361, 1595, 1708, 2963; HRMS (ESI) calcd for $C_{32}H_{36}N_3O_4S^+$ $[M+H]^+$ 558.2421, found 558.2431; HPLC analysis: 94% ee (CHIRALPAK IA, isopropanol/hexane = 10:90, 1.0 ml/min, UV: 254 nm), t_R = 14.008 min (minor), 15.762 min (major).

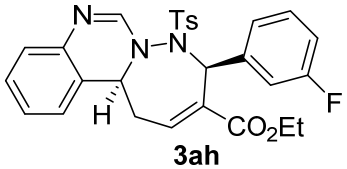
(4*R*,12b*S*)-ethyl 4-(2-fluorophenyl)-5-tosyl-1,4,5,12b-tetrahydro-[1,2]diazepino[1,7-*c*] quinazoline-3-carboxylate (3ag)



3ag

Prepared according to the general procedure as described above in 96% yield (62.4 mg). It was purified by flash chromatography (25% EtOAc/PE) to afford a white solid. mp = 162 – 164 °C; $[\alpha]^{20}_D$ = + 86.2 (*c* 0.50, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.50 (dd, *J* = 9.0, 3.5 Hz, 1H), 7.34 – 7.26 (m, 2H), 7.23 (s, 1H), 7.21 – 7.13 (m, 3H), 7.09 (td, *J* = 7.5, 1.4 Hz, 2H), 7.05 – 7.00 (m, 1H), 6.98 (dd, *J* = 7.7, 1.3 Hz, 1H), 6.92 (dd, *J* = 7.5, 1.4 Hz, 1H), 5.83 (s, 1H), 5.36 (d, *J* = 10.6 Hz, 1H), 4.17 (t, *J* = 7.2 Hz,2H), 3.11 (ddd, *J* = 16.9, 11.0, 3.6 Hz, 1H), 2.61 (ddd, *J* = 17.0, 9.0, 2.5 Hz, 1H), 2.39 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 165.0, 160.5 (d, *J* = 251.1 Hz), 148.7, 144.6, 142.0, 139.0, 134.9, 134.5, 131.0 (d, *J* = 8.4 Hz), 129.6, 129.4 (d, *J* = 2.7 Hz), 128.6, 128.0 (d, *J* = 2.7 Hz), 125.8, 125.6, 125.2, 124.8, 124.3 (d, *J* = 3.9 Hz), 121.9 (d, *J* = 13.4 Hz), 116.3, 116.0, 61.4, 57.5, 56.0 (d, *J* = 2.9 Hz), 38.2, 21.4, 13.9; IR (film) ν_{max} 541, 583, 658, 736, 765, 813, 984, 1053, 1092, 1164, 1252, 1353, 1456, 1488, 1595, 1617, 1707, 2982; HRMS (ESI) calcd for $C_{28}H_{27}FN_3O_4S^+$ $[M+H]^+$ 520.1701, found 520.1706; HPLC analysis: 96% ee (Lux cellulose 1, alcohol/hexane = 5:95, 1.0 ml/min, UV: 220 nm), t_R = 21.449 min (minor), 31.683 min (major).

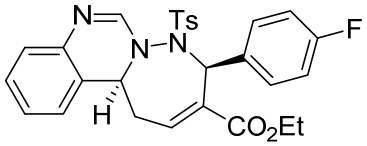
(4*S*,12b*S*)-ethyl 4-(3-fluorophenyl)-5-tosyl-1,4,5,12b-tetrahydro-[1,2]diazepino[1,7-*c*] quinazoline-3-carboxylate (3ah)



3ah

Prepared according to the general procedure as described above in 95% yield (61.8 mg). It was purified by flash chromatography (25% EtOAc/PE) to afford a white solid. mp = 109 – 110 °C; $[\alpha]^{20}_D$ = + 14.7 (*c* 0.53, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78–7.75 (m, 2H), 7.43 (dd, *J* = 9.1, 3.4 Hz, 1H), 7.34 – 7.24 (m, 3H), 7.17 (td, *J* = 7.6, 1.4 Hz, 1H), 7.07 (dd, *J* = 7.5, 1.2 Hz, 2H), 7.04 – 6.97 (m, 2H), 6.97 – 6.91 (m, 1H), 6.85 (d, *J* = 3.3 Hz, 1H), 6.82 – 6.76 (m, 1H), 6.13 (s, 1H), 4.91 (d, *J* = 10.3 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 2.99 (ddd, *J* = 16.9, 11.2, 3.3 Hz, 1H), 2.54 – 2.33 (m, 4H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 165.1, 162.9 (d, *J* = 247.8 Hz), 148.8, 144.9, 142.2, 138.9, 137.30 (d, *J* = 6.7 Hz), 135.6, 133.9, 130.6 (d, *J* = 8.2 Hz), 130.0, 128.7, 127.7, 125.9, 125.4 (d, *J* = 6.2 Hz), 124.5, 123.8 (d, *J* = 3.3 Hz), 115.9, 115.6, 115.3, 115.0, 61.5, 61.1 (d, *J* = 2.0 Hz), 57.3, 38.4, 21.5, 13.9; IR (film) ν_{max} 555, 592, 663, 685, 736, 766, 942, 1054, 1091, 1166, 1255, 1357, 1447, 1486, 1594, 1616, 1707, 2981; HRMS (ESI) calcd for $C_{28}H_{27}FN_3O_4S^+$ $[M+H]^+$ 520.1701, found 520.1704; HPLC analysis: 94% ee (CHIRALPAK IA, isopropanol/hexane = 10:90, 1.0 ml/min, UV: 254 nm), t_R = 22.936 min (minor), 37.750 min (major).

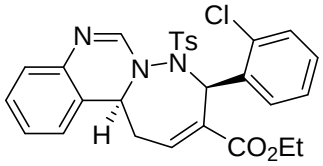
(4*S*,12b*S*)-ethyl 4-(4-fluorophenyl)-5-tosyl-1,4,5,12b-tetrahydro-[1,2]diazepino[1,7-*c*] quinazoline-3-carboxylate (3ai)



3ai

Prepared according to the general procedure as described above in 98% yield (63.7 mg). It was purified by flash chromatography (25% EtOAc/PE) to afford a white solid. mp = 166 – 168 °C; $[\alpha]^{20}_D$ = + 3.7 (*c* 0.57, CH_2Cl_2); ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.83 – 7.71 (m, 2H), 7.43 (dd, *J* = 9.1, 3.4 Hz, 1H), 7.34 – 7.25 (m, 4H), 7.21 (td, *J* = 7.6, 1.2 Hz, 1H), 7.10 (td, *J* = 7.5, 1.1 Hz, 1H), 7.07 – 7.00 (m, 3H), 6.89 (s, 1H), 6.83 (d, *J* = 7.2 Hz, 1H), 6.09 (s, 1H), 4.92 (d, *J* = 10.3 Hz, 1H), 4.22 (qd, *J* = 7.1, 2.0 Hz, 2H), 3.02 (ddd, *J* = 17.0, 11.0, 3.4 Hz, 1H), 2.62 – 2.31 (m, 4H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}CNMR (101 MHz, $CDCl_3$) δ 165.37, 162.81 (d, *J* = 249.0 Hz), 149.07, 145.03, 141.93, 139.09, 135.82, 134.46, 130.65 (d, *J* = 3.2 Hz), 130.18, 130.15, 130.10, 128.89, 127.83, 126.04, 125.54 (d, *J* = 8.5 Hz), 124.77, 116.19 (d, *J* = 21.8 Hz), 61.69, 61.16, 57.42, 38.58, 21.70, 14.14; IR (film) ν_{max} 548, 586, 661, 708, 736, 765, 985, 1054, 1091, 1164, 1247, 1357, 1478, 1574, 1595, 1618, 1707, 2981; HRMS (ESI) calcd for $C_{28}H_{27}FN_3O_4S^+$ $[M+H]^+$ 520.1701, found 520.1704; HPLC analysis: 94% ee (CHIRALPAK IA, isopropanol/hexane = 15:85, 1.0 ml/min, UV: 254 nm), t_R = 24.210 min (minor), 32.165 min (major).

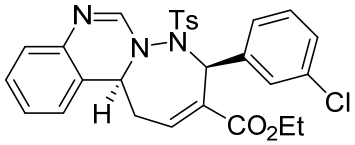
(4*R*,12b*S*)-ethyl 4-(2-chlorophenyl)-5-tosyl-1,4,5,12b-tetrahydro-[1,2]diazepino[1,7-*c*] quinazoline-3-carboxylate (3aj)



3aj

Prepared according to the general procedure as described above in 94% yield (63.0 mg) It was purified by flash chromatography (25% EtOAc/PE) to afford a white solid. mp = 136 – 138 °C; $[\alpha]^{20}_D$ = + 61.3 (*c* 0.82, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 – 7.71 (m, 2H), 7.48 (dd, *J* = 8.8, 3.6 Hz, 1H), 7.42 – 7.35 (m, 1H), 7.25 – 7.19 (m, 4H), 7.19 – 7.11 (m, 3H), 7.10 – 7.05 (m, 1H), 7.00 – 6.92 (m, 2H), 5.75 (s, 1H), 5.55 (dd, *J* = 10.6, 2.5 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.17 (ddd, *J* = 14.4, 11.0, 3.8 Hz, 1H), 2.72 (ddd, *J* = 17.2, 8.8, 2.7 Hz, 1H), 2.36 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 165.0, 149.1, 144.7, 141.5, 139.1, 135.4, 134.5, 134.4, 131.9, 130.7, 130.3, 129.9, 129.6, 128.6, 128.3, 126.9, 125.9, 125.5, 125.2, 124.7, 61.4, 59.3, 57.1, 37.9, 21.4, 13.8; IR (film) ν_{max} 582, 656, 706, 764, 1052, 1091, 1165, 1246, 1350, 1595, 1617, 1707; HRMS (ESI) calcd for $C_{28}H_{27}ClN_3O_4S^+$ $[M+H]^+$ 536.1405, found 536.1408; HPLC analysis: 90%ee (CHIRALPAK IA, isopropanol/hexane = 10:90, 1.0 ml/min, UV: 254 nm), t_R = 19.383 min (minor), 34.570 min (major), 90% ee, t_R = 23.727 min (major), 25.991 min (minor).

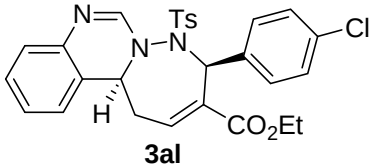
(4*S*,12b*S*)-ethyl 4-(3-chlorophenyl)-5-tosyl-1,4,5,12b-tetrahydro-[1,2]diazepino[1,7-*c*] quinazoline-3-carboxylate (3ak)



3ak

Prepared according to the general procedure as described above in 98% yield (65.7 mg). It was purified by flash chromatography (25% EtOAc/PE) to afford a white solid. mp = 166 – 168 °C; $[\alpha]^{20}_{D}$ = + 3.7 (*c* 0.57, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 – 7.70 (m, 2H), 7.44 (dd, *J* = 9.1, 3.5 Hz, 1H), 7.31 – 7.25 (m, 3H), 7.25 – 7.21 (m, 1H), 7.20 – 7.12 (m, 3H), 7.06 (td, *J* = 7.5, 1.4 Hz, 1H), 7.01 (dd, *J* = 7.7, 1.2 Hz, 1H), 6.86 – 6.71 (m, 2H), 6.11 (s, 1H), 4.91 (d, *J* = 10.2 Hz, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 2.98 (ddd, *J* = 16.5, 11.2, 3.4 Hz, 1H), 2.55 – 2.32 (m, 4H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 165.1, 148.7, 145.0, 142.2, 138.9, 136.8, 135.6, 134.9, 133.7, 130.2, 130.0, 128.9, 128.7, 128.2, 127.7, 126.2, 125.9, 125.4, 125.3, 124.5, 61.5, 61.1, 57.4, 38.4, 21.5, 13.9; IR (film) ν_{max} 548, 586, 661, 708, 736, 765, 985, 1054, 1091, 1164, 1246, 1357, 1478, 1574, 1595, 1618, 1707, 2981; HRMS (ESI) calcd for $C_{28}H_{27}ClN_3O_4S^+$ $[M+H]^+$ 536.1405, found 536.1410; HPLC analysis: 94% ee (Lux cellulose 1, isopropanol/hexane = 12:88, 1.0 ml/min, UV: 254 nm), t_R = 13.969 min (minor), 17.597 min (major).

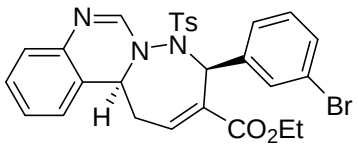
(4*S*,12b*S*)-ethyl 4-(4-chlorophenyl)-5-tosyl-1,4,5,12b-tetrahydro-[1,2]diazepino[1,7-*c*] quinazoline-3-carboxylate (3al)



3al

Prepared according to the general procedure as described above in 96% yield (64.3 mg). It was purified by flash chromatography (25% EtOAc/PE) to afford a white solid. mp = 203 – 204 °C; $[\alpha]^{20}_{D}$ = – 11.2 (*c* 0.57, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 – 7.73 (m, 2H), 7.41 (dd, *J* = 9.1, 3.4 Hz, 1H), 7.32 – 7.25 (m, 4H), 7.24 – 7.18 (m, 2H), 7.16 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.06 (td, *J* = 7.6, 1.4 Hz, 1H), 7.03 – 6.98 (m, 1H), 6.84 (s, 1H), 6.79 (d, *J* = 6.7 Hz, 1H), 6.08 (s, 1H), 4.88 (d, *J* = 10.0 Hz, 1H), 4.18 (q, *J* = 7.0 Hz, 2H), 2.97 (ddd, *J* = 16.8, 11.0, 3.2 Hz, 1H), 2.62 – 2.15 (m, 4H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 165.1, 148.8, 144.9, 141.9, 138.9, 135.6, 134.8, 134.0, 133.3, 130.0, 129.5, 129.2, 128.7, 127.7, 125.9, 125.6, 125.3, 124.6, 61.5, 61.1, 57.3, 38.4, 21.5, 13.9; IR (film) ν_{max} 582, 659, 706, 736, 817, 983, 1053, 1091, 1164, 1247, 1357, 1490, 1595, 1618, 1707, 2981; HRMS (ESI) calcd for $C_{28}H_{27}ClN_3O_4S^+$ $[M+H]^+$ 536.1405, found 536.1411; HPLC analysis: 93% ee (CHIRALPAK IA, isopropanol/hexane = 10:90, 1.0 ml/min, UV: 254 nm), t_R = 30.500 min (minor), 39.458 min (major).

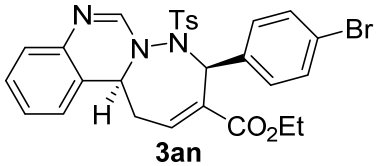
(4*S*,12b*S*)-ethyl 4-(3-bromophenyl)-5-tosyl-1,4,5,12b-tetrahydro-[1,2]diazepino[1,7-*c*] quinazoline-3-carboxylate (3am)



3am

Prepared according to the general procedure as described above in 93% yield (67.5 mg). It was purified by flash chromatography (25% EtOAc/PE) to afford a white solid. mp = 170 – 172 °C; $[\alpha]^{20}_D$ = – 1.9 (*c* 0.59, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 – 7.73 (m, 2H), 7.48 – 7.36 (m, 2H), 7.33 – 7.27 (m, 3H), 7.23 – 7.14 (m, 3H), 7.06 (td, *J* = 7.5, 1.4 Hz, 1H), 7.01 (dd, *J* = 7.8, 1.2 Hz, 1H), 6.84 – 6.77 (m, 2H), 6.10 (s, 1H), 4.92 (d, *J* = 9.9 Hz, 1H), 4.19 (qd, *J* = 7.1, 1.0 Hz, 2H), 2.98 (ddd, *J* = 16.9, 11.0, 3.3 Hz, 1H), 2.52 – 2.45 (m, 1H), 2.42 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 165.1, 148.7, 145.0, 142.3, 138.9, 137.1, 135.6, 133.7, 131.8, 131.1, 130.4, 130.0, 128.7, 127.7, 126.6, 125.9, 125.4, 125.3, 124.5, 123.0, 61.5, 61.1, 57.4, 38.3, 21.5, 13.9; IR (film) ν_{max} 548, 585, 660, 764, 1053, 1091, 1164, 1246, 1357, 1474, 1595, 1617, 1706, 2981; HRMS (ESI) calcd for $C_{28}H_{27}BrN_3O_4S^+$ $[M+H]^+$ 580.0900, found 580.0904; HPLC analysis: 94% ee (Lux cellulose 1, isopropanol/hexane = 10:90, 1.0 ml/min, UV: 254 nm), t_R = 16.659 min (minor), 21.459 min (major).

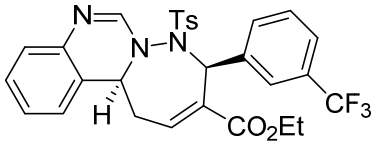
(4*S*,12b*S*)-ethyl 4-(4-bromophenyl)-5-tosyl-1,4,5,12b-tetrahydro-[1,2]diazepino[1,7-*c*] quinazoline-3-carboxylate (3an)



3an

Prepared according to the general procedure as described above in 96% yield (69.7 mg). It was purified by flash chromatography (25% EtOAc/PE) to afford a white solid. mp = 200 – 202 °C; $[\alpha]^{20}_D$ = – 18.5 (*c* 0.53, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 – 7.73 (m, 2H), 7.49 – 7.35 (m, 3H), 7.27 (d, *J* = 9.7 Hz, 2H), 7.20 – 7.13 (m, 3H), 7.10 – 6.97 (m, 2H), 6.82 (s, 1H), 6.79 (d, *J* = 6.7 Hz, 1H), 6.08 (s, 1H), 4.88 (d, *J* = 10.2 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 2.96 (ddd, *J* = 16.6, 11.0, 3.2 Hz, 1H), 2.53 – 2.35 (m, 4H), 1.24 (t, *J* = 7.1 Hz, 3H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 165.1, 148.8, 144.9, 141.9, 138.9, 135.6, 133.9, 133.9, 132.2, 130.0, 129.8, 128.7, 127.7, 125.9, 125.4, 124.6, 123.0, 61.5, 61.1, 57.3, 38.4, 21.5, 13.9; IR (film) ν_{max} 581, 736, 766, 816, 983, 1011, 1053, 1091, 1165, 1247, 1356, 1486, 1595, 1618, 1707, 2981; HRMS (ESI) calcd for $C_{28}H_{27}BrN_3O_4S^+$ $[M+H]^+$ 580.0900, found 580.0901; HPLC analysis: 96% ee (CHIRALPAK IA, isopropanol/hexane = 10:90, 1.0 ml/min, UV: 254 nm), t_R = 32.419 min (minor), 40.930 min (major).

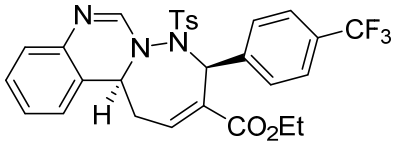
(4*S*,12b*S*)-ethyl 5-tosyl-4-(3-(trifluoromethyl)phenyl)-1,4,5,12b-tetrahydro-[1,2]diazepino[1,7-*c*] quinazoline-3-carboxylate (3ao)



3ao

Prepared according to the general procedure as described above in 95% yield (67.6 mg). It was purified by flash chromatography (25% EtOAc/PE) to afford a white solid. mp = 70 – 72 °C; $[\alpha]^{20}_{D}$ = + 25.3 (*c* 0.62, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 – 7.76 (m, 2H), 7.57 – 7.52 (m, 1H), 7.49 (dd, *J* = 9.0, 3.6 Hz, 1H), 7.44 (d, *J* = 5.2 Hz, 2H), 7.40 (s, 1H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.18 (td, *J* = 7.6, 1.4 Hz, 1H), 7.08 (td, *J* = 7.5, 1.4 Hz, 1H), 7.00 (dd, *J* = 7.7, 1.2 Hz, 1H), 6.87 (s, 1H), 6.86 – 6.81 (m, 1H), 5.97 (s, 1H), 5.02 (d, *J* = 9.5 Hz, 1H), 4.19 (qd, *J* = 7.1, 2.1 Hz, 2H), 2.97 (ddd, *J* = 16.8, 10.8, 3.5 Hz, 1H), 2.54 (ddd, *J* = 17.1, 9.0, 2.2 Hz, 1H), 2.42 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.1, 148.4, 145.1, 142.4, 138.9, 136.1, 135.5, 133.6, 131.2, 130.0, 129.5, 128.7, 127.6, 126.0, 125.5 (q, *J* = 3.7 Hz), 125.4, 125.0 (q, *J* = 4.0 Hz), 124.5, 123.5 (q, *J* = 270.8 Hz), 61.6, 61.2, 57.7, 38.2, 21.4, 13.9; IR (film) ν_{max} 576, 675, 706, 806, 1092, 1129, 1166, 1249, 1331, 1595, 1618, 1707, 2926; HRMS (ESI) calcd for $C_{29}H_{27}F_3N_3O_4S^+$ $[M+H]^+$ 570.1669, found 570.1673; HPLC analysis: 94% ee (CHIRALPAK IA, isopropanol/hexane = 5:95, 1.0 ml/min, UV: 254 nm), t_R = 40.282 min (minor), 46.183 min (major).

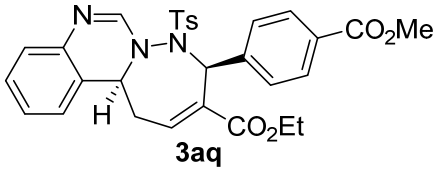
(4*S*,12b*S*)-ethyl 5-tosyl-4-(4-(trifluoromethyl)phenyl)-1,4,5,12b-tetrahydro-[1,2]diazepino[1,7-*c*] quinazoline-3-carboxylate (3ap)



3ap

Prepared according to the general procedure as described above in 98% yield (69.8 mg). It was purified by flash chromatography (25% EtOAc/PE) to afford a white solid. mp = 158 – 160 °C; $[\alpha]^{20}_{D}$ = + 9.7 (*c* 0.53, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.46 (dd, *J* = 9.1, 3.4 Hz, 1H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.24 – 7.13 (m, 1H), 7.07 (td, *J* = 7.4, 1.1 Hz, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.91 (s, 1H), 6.80 (d, *J* = 7.1 Hz, 1H), 6.09 (s, 1H), 4.92 (d, *J* = 10.3 Hz, 1H), 4.19 (q, *J* = 7.0 Hz, 2H), 2.98 (ddd, *J* = 16.5, 11.0, 3.2 Hz, 1H), 2.62 – 2.35 (m, 4H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 165.1, 148.6, 145.0, 142.3, 139.0, 138.8, 135.5, 133.7, 130.9 (q, *J* = 32.7 Hz), 130.0, 128.7, 128.5, 127.7, 126.0 (q, *J* = 3.4 Hz), 125.4 (q, *J* = 4.0 Hz), 124.8 (q, *J* = 469.7 Hz), 124.4, 61.6, 61.1, 57.4, 38.5, 21.5, 13.9; IR (film) ν_{max} 578, 669, 737, 835, 983, 1018, 1068, 1091, 1128, 1166, 1251, 1326, 1596, 1618, 1707, 2982; HRMS (ESI) calcd for $C_{29}H_{27}F_3N_3O_4S^+$ $[M+H]^+$ 570.1669, found 570.1677; HPLC analysis: 94% ee (CHIRALPAK IA, isopropanol/hexane = 10:90, 1.0 ml/min, UV: 254 nm), t_R = 22.713 min (minor), 23.939 min (major).

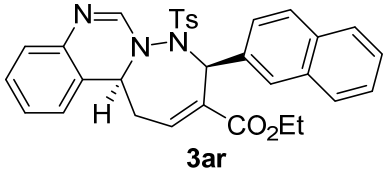
(4*S*,12b*S*)-ethyl 4-(4-(methoxycarbonyl)phenyl)-5-tosyl-1,4,5,12b-tetrahydro-[1,2]diazepino [1,7-*c*]quinazoline-3-carboxylate (3aq)



3aq

Prepared according to the general procedure as described above in 98% yield (68.6 mg). It was purified by flash chromatography (25% EtOAc/PE) to afford a white solid. mp = 165 – 166 °C; $[\alpha]^{20}_{D}$ = – 20.5 (*c* 0.57, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 – 7.92 (m, 2H), 7.80 – 7.69 (m, 2H), 7.45 (dd, *J* = 9.1, 3.4 Hz, 1H), 7.39 – 7.25 (m, 4H), 7.16 (td, *J* = 7.6, 1.4 Hz, 1H), 7.05 (td, *J* = 7.5, 1.4 Hz, 1H), 6.98 (dd, *J* = 7.7, 1.2 Hz, 1H), 6.89 (s, 1H), 6.79 (dd, *J* = 7.5, 1.4 Hz, 1H), 6.02 (s, 1H), 4.93 (d, *J* = 9.7 Hz, 1H), 4.17 (qd, *J* = 7.1, 1.0 Hz, 2H), 3.87 (s, 3H), 2.98 (ddd, *J* = 16.5, 11.0, 3.4 Hz, 1H), 2.59 – 2.18 (m, 4H), 1.23 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.3, 165.3, 148.813, 145.113, 142.4, 139.9, 139.0, 135.7, 134.0, 130.7, 130.4, 130.2, 128.9, 128.3, 127.9, 126.1, 125.5, 125.5, 124.7, 61.7, 61.5, 57.6, 52.2, 38.6, 21.7, 14.1; IR (film) ν_{max} 581, 716, 766, 816, 1054, 1092, 1165, 1284, 1354, 1594, 1615, 1722, 2954; HRMS (ESI) calcd for $C_{30}H_{29}N_3O_6S^+$ $[M+H]^+$ 560.1850, found 560.1854; HPLC analysis: 96% ee (CHIRALPAK IA, isopropanol/hexane = 10:90, 1.0 ml/min, UV: 254 nm), t_R = 39.287 min (minor), 65.950 min (major).

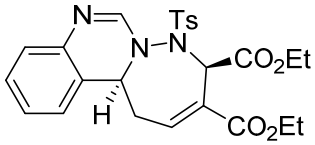
(4*S*,12b*S*)-ethyl 4-(naphthalen-2-yl)-5-tosyl-1,4,5,12b-tetrahydro-[1,2]diazepino[1,7-*c*] quinazoline-3-carboxylate (3ar)



3ar

Prepared according to the general procedure as described above in 82% yield (56.6 mg). It was purified by flash chromatography (25% EtOAc/PE) to afford a white solid. mp = 190 – 192 °C; $[\alpha]^{20}_{D}$ = – 12.2 (*c* 0.53, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 – 7.76 (m, 4H), 7.74 – 7.65 (m, 1H), 7.61 (d, *J* = 4.9 Hz, 1H), 7.54 (dd, *J* = 9.1, 3.4 Hz, 1H), 7.51 – 7.39 (m, 3H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.15 (td, *J* = 7.5, 1.4 Hz, 1H), 7.10 – 7.01 (m, 2H), 6.94 (dd, *J* = 7.7, 1.2 Hz, 1H), 6.82 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.09 (s, 1H), 4.95 (d, *J* = 10.4 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.10 (ddd, *J* = 16.8, 11.3, 3.6 Hz, 1H), 2.57 – 2.36 (m, 4H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 165.3, 148.9, 144.7, 142.1, 139.0, 135.8, 134.4, 133.1, 132.9, 131.4, 129.9, 129.2, 128.6, 128.0, 127.8, 127.5, 127.1, 126.6, 126.4, 125.8, 125.7, 125.4, 125.2, 124.7, 61.8, 61.5, 57.2, 38.5, 21.5, 14.0; IR (film) ν_{max} 479, 547, 582, 662, 735, 818, 1053, 1091, 1165, 1254, 1359, 1483, 1595, 1617, 1707, 2926; HRMS (ESI) calcd for $C_{32}H_{30}N_3O_4S^+$ $[M+H]^+$ 552.1952, found 552.1957; HPLC analysis: 94% ee (CHIRALPAK IA, isopropanol/hexane = 15:85, 1.0 ml/min, UV: 254 nm), t_R = 22.084 min (minor), 26.592 min (major).

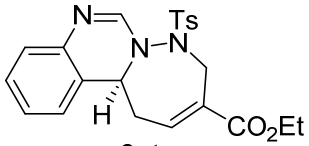
(4*R*,12b*S*)-diethyl 5-tosyl-1,4,5,12b-tetrahydro-[1,2]diazepino[1,7-*c*]quinazoline-3,4-dicarboxylate (3as)



3as

Prepared according to the general procedure as described above in 60% yield (37.3 mg). It was purified by flash chromatography (25% EtOAc/PE) to afford a white semi-solid.; $[\alpha]^{20}_{D}$ = + 7.4 (*c* 0.76, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 – 7.75 (m, 2H), 7.36 – 7.25 (m, 3H), 7.20 (td, *J* = 7.6, 1.4 Hz, 1H), 7.13 – 7.05 (m, 2H), 6.86 (d, *J* = 8.2 Hz, 2H), 6.49 (s, 1H), 5.09 (d, *J* = 10.7 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 2.97 (ddd, *J* = 16.7, 11.0, 3.8 Hz, 1H), 2.52 – 2.35 (m, 4H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.2 Hz, 3H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 166.9, 165.1, 148.7, 145.0, 142.6, 138.8, 134.9, 132.6, 129.8, 128.7, 128.0, 125.9, 125.7, 125.4, 124.6, 62.4, 61.5, 60.3, 57.9, 38.7, 21.5, 14.0, 13.8; IR (film) ν_{max} 557, 663, 759, 1024, 1092, 1166, 1260, 1455, 1598, 1619, 1740, 2927; HRMS (ESI) calcd for $C_{25}H_{28}N_3O_6S^+$ $[M+H]^+$ 498.1693, found 498.1694; HPLC analysis: 95% ee (CHIRALPAK AD-H, isopropanol/hexane = 20:80, 1.0 ml/min, UV: 254 nm), t_R = 13.631 min (minor), 26.352 min (major).

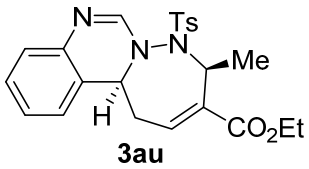
(*S*)-ethyl 5-tosyl-1,4,5,12b-tetrahydro-[1,2]diazepino[1,7-*c*]quinazoline-3-carboxylate (3at)



3at

Prepared according to the general procedure as described above in 70% yield (37.2 mg). It was purified by flash chromatography (27% EtOAc/PE) to afford a white solid. mp = 76 – 78 °C; $[\alpha]^{20}_{D}$ = + 2.7 (*c* 0.73, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 7.6 Hz, 2H), 7.25 – 7.15 (m, 2H), 7.14 – 7.04 (m, 2H), 6.83 (d, *J* = 7.5 Hz, 2H), 5.15 – 4.86 (m, 2H), 4.38 (d, *J* = 16.0 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.94 – 2.79 (m, 1H), 2.62 (ddd, *J* = 16.6, 6.9, 3.7 Hz, 1H), 2.43 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 165.1, 148.8, 144.8, 142.2, 139.3, 134.1, 131.2, 129.9, 128.7, 127.9, 126.0, 125.4, 125.3, 61.2, 57.1, 48.8, 37.3, 21.5, 14.0; IR (film) ν_{max} 557, 682, 760, 814, 1094, 1166, 1261, 1357, 1456, 1597, 1616, 1706, 2964; HRMS (ESI) calcd for $C_{22}H_{24}N_3O_4S^+$ $[M+H]^+$ 426.1482, found 426.1486; HPLC analysis: 90% ee (CHIRALPAK IA, isopropanol/hexane = 10:90, 1.0 ml/min, UV: 254 nm), t_R = 34.678 min (minor), 42.844 min (major).

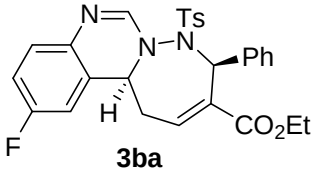
(4*S*,12b*S*)-ethyl 4-methyl-5-tosyl-1,4,5,12b-tetrahydro-[1,2]diazepino[1,7-*c*]quinazoline-3-carboxylate (3au)



3au

Prepared according to the general procedure as described above in 95% yield (52.3 mg). It was purified by flash chromatography (25% EtOAc/PE) to afford a white solid. mp = 146 – 148 °C; $[\alpha]^{20}_D$ = + 71.6 (*c* 0.57, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 – 7.65 (m, 2H), 7.28 – 7.22 (m, 1H), 7.22 – 7.15 (m, 2H), 7.15 – 6.96 (m, 3H), 6.86 – 6.80 (m, 1H), 6.78 (d, *J* = 0.9 Hz, 1H), 5.70 (q, *J* = 7.0 Hz, 1H), 4.97 (d, *J* = 11.0 Hz, 1H), 4.24 (qd, *J* = 7.1, 0.8 Hz, 2H), 3.02 (ddd, *J* = 16.6, 11.3, 3.4 Hz, 1H), 2.46 – 2.22 (m, 4H), 1.39 (d, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 165.4, 149.6, 144.6, 139.5, 139.0, 137.9, 135.9, 129.8, 128.7, 127.5, 125.9, 125.7, 125.3, 124.7, 61.2, 57.5, 54.2, 38.1, 21.4, 17.5, 14.0; IR (film) ν_{max} 577, 679, 740, 766, 815, 1053, 1113, 1167, 1257, 1358, 1455, 1575, 1597, 1618, 1704, 2980; HRMS (ESI) calcd for $C_{23}H_{26}N_3O_4S^+$ $[M+H]^+$ 440.1639, found 440.1643; HPLC analysis: 70% ee (Lux cellulose 2, ethanol/hexane = 30:70, 1.0 ml/min, UV: 210 nm), t_R = 9.249 min (major), 9.931 min (minor).

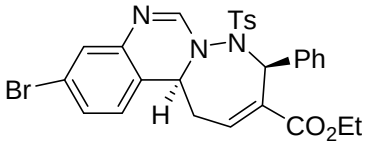
(4*S*,12b*S*)-ethyl 11-fluoro-4-phenyl-5-tosyl-1,4,5,12b-tetrahydro-[1,2]diazepino[1,7-*c*] quinazoline-3-carboxylate(3ba)



3ba

Prepared according to the general procedure as described above in 96% yield (62.4 mg). It was purified by flash chromatography (25% EtOAc/PE) to afford a white solid. mp = 198 – 200 °C; $[\alpha]^{20}_D$ = + 20.0 (*c* 0.50, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 – 7.72 (m, 2H), 7.41 (dd, *J* = 9.1, 3.4 Hz, 1H), 7.35 – 7.20 (m, 7H), 6.97 (dd, *J* = 8.7, 5.4 Hz, 1H), 6.91 – 6.80 (m, 2H), 6.52 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.01 (s, 1H), 4.88 (d, *J* = 10.5 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.02 (ddd, *J* = 17.4, 11.2, 3.6 Hz, 1H), 2.42 (s, 4H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 165.2, 160.3 (d, J = 245.4 Hz), 148.4, 148.4, 144.8, 141.2, 135.7, 135.5, 135.4, 134.5 (d, *J* = 7.5 Hz), 129.9, 129.0, 128.7, 128.1, 127.7, 126.9 (d, *J* = 8.3 Hz), 126.2 (d, *J* = 8.0 Hz), 115.4 (d, *J* = 22.1 Hz), 112.0 (d, *J* = 23.6 Hz), 61.7, 61.4, 57.2, 57.1, 38.1, 21.5, 13.9; IR (film) ν_{max} 547, 585, 662, 704, 737, 816, 990, 1051, 1092, 1165, 1247, 1358, 1492, 1619, 1707, 2982; HRMS (ESI) calcd for $C_{28}H_{27}FN_3O_4S^+$ $[M+H]^+$ 520.1701, found 520.1702; HPLC analysis: 94% ee (CHIRALPAK IA, isopropanol/hexane = 88:12, 1.0 ml/min, UV: 254 nm), t_R = 18.394 min (minor), 33.623 min (major).

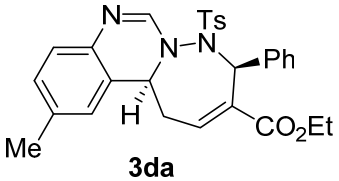
(4*S*,12b*S*)-ethyl 10-bromo-4-phenyl-5-tosyl-1,4,5,12b-tetrahydro-[1,2]diazepino[1,7-*c*] quinazoline-3-carboxylate (3ca)



3ca

Prepared according to the general procedure as described above in 85% yield (61.7 mg). It was purified by flash chromatography (16% EtOAc/PE) to afford a white solid. mp = 88 – 90 °C; $[\alpha]^{20}_{D}$ = – 4.8 (*c* 0.52, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 – 7.72 (m, 2H), 7.41 (dd, *J* = 9.1, 3.4 Hz, 1H), 7.37 – 7.25 (m, 7H), 7.27 – 7.16 (m, 1H), 7.18 – 7.13 (m, 1H), 6.88 (s, 1H), 6.68 (d, *J* = 8.1 Hz, 1H), 6.02 (d, *J* = 1.0 Hz, 1H), 4.89 (d, *J* = 10.8 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.10 – 2.91 (m, 1H), 2.54 – 2.20 (m, 4H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 165.2, 149.9, 144.9, 141.2, 140.7, 135.5, 134.5, 134.3, 129.9, 129.0, 128.8, 128.5, 128.1, 128.1, 127.7, 126.7, 123.6, 121.9, 61.7, 61.4, 57.1, 38.3, 21.5, 13.9; IR (film) ν_{max} 545, 668, 737, 812, 1086, 1168, 1362, 1492, 1594, 1682, 2926; HRMS (ESI) calcd for $C_{28}H_{27}BrN_3O_4S^+$ $[M+H]^+$ 580.0900, found 580.0897; HPLC analysis: 83% ee (CHIRALPAK IA, isopropanol/hexane = 15:85, 1.0 ml/min, UV: 254 nm), t_R = 13.442 min (minor), 31.547 min (major), 56% ee t_R = 16.056 min (major), 18.516 min (minor).

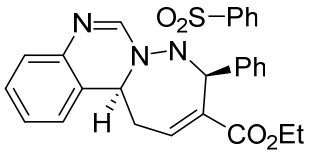
(4*S*,12b*S*)-ethyl 11-methyl-4-phenyl-5-tosyl-1,4,5,12b-tetrahydro-[1,2]diazepino[1,7-*c*] quinazoline-3-carboxylate (3da)



3da

Prepared according to the general procedure as described above in 97% yield (62.6 mg). It was purified by flash chromatography (25% EtOAc/PE) to afford a white solid. mp = 88 – 90 °C; $[\alpha]^{20}_{D}$ = + 56.0 (*c* 0.50, CH_2Cl_2);^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.3 Hz, 2H), 7.49 (dd, *J* = 9.1, 3.4 Hz, 1H), 7.39 – 7.34 (m, 6H), 7.04 – 6.93 (m, 3H), 6.68 – 6.68 (m, 1H), 6.05 (s, 1H), 4.98 (d, *J* = 10.3 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.06 (ddd, *J* = 16.6, 11.0, 3.4 Hz, 1H), 2.56 – 2.49 (m, 1H), 2.47 (s, 3H), 2.33 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.2, 148.2, 144.5, 141.6, 136.5, 135.7, 135.3, 134.4, 134.2, 129.7, 129.1, 128.8, 128.5, 128.0, 127.5, 125.8, 124.9, 124.4, 61.5, 61.2, 57.2, 38.3, 21.3, 20.7, 13.8; IR (film) ν_{max} 546, 585, 661, 703, 736, 815, 1050, 1091, 1164, 1244, 1357, 1495, 1599, 1624, 1705, 3406; HRMS (ESI) calcd for $C_{29}H_{30}N_3O_4S$+ $[M+H]^+$ 516.1952, found 516.1951; HPLC analysis: 90% ee (CHIRALPAK AD-H, isopropanol/hexane = 8:92, 1.0 ml/min, UV: 220 nm), t_R = 42.829 min (minor), 55.083 min (major).

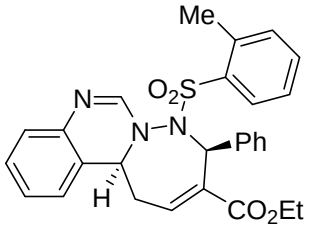
(4*S*,12b*S*)-ethyl 4-phenyl-5-(phenylsulfonyl)-1,4,5,12b-tetrahydro-[1,2]diazepino[1,7-*c*] quinazoline-3-carboxylate (3ea)



3ea

Prepared according to the general procedure as described above in 96% yield (58.6 mg). It was purified by flash chromatography (25% EtOAc/PE) to afford a white solid. mp = 132 – 134 °C; $[\alpha]^{20}_D$ = + 10.4 (*c* 0.54, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 – 7.81 (m, 2H), 7.65 – 7.55 (m, 1H), 7.54 – 7.46 (m, 2H), 7.42 (dd, J = 9.2, 3.4 Hz, 1H), 7.36 – 7.22 (m, 2H), 7.17 (td, J = 7.6, 1.5 Hz, 1H), 7.05 (td, J = 7.5, 1.4 Hz, 1H), 7.00 (dd, J = 7.8, 1.4 Hz, 1H), 6.91 (s, 1H), 6.83 – 6.73 (m, 1H), 6.06 (d, J = 1.1 Hz, 1H), 4.85 (d, J = 11.3 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 3.02 (ddd, J = 16.9, 11.2, 3.7 Hz, 1H), 2.43 (ddd, J = 17.0, 9.1, 2.2 Hz, 1H), 1.25 (t, J = 7.1 Hz, 3H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 165.3, 148.9, 141.7, 139.0, 138.8, 134.4, 134.3, 133.6, 129.3, 129.0, 128.8, 128.6, 128.1, 127.7, 125.8, 125.4, 125.3, 124.7, 61.7, 61.4, 57.4, 38.5, 13.9; IR (film) ν_{max} 592, 703, 737, 1051, 1091, 1167, 1248, 1359, 1449, 1595, 1617, 1706; HRMS (ESI) calcd for $C_{27}H_{26}N_3O_4S^+$ $[M+H]^+$ 488.1639, found 488.1640; HPLC analysis: 93% ee (CHIRALPAK IA, isopropanol/hexane = 15:85, 1.0 ml/min, UV: 254 nm), t_R = 15.193 min (minor), 22.075 min (major).

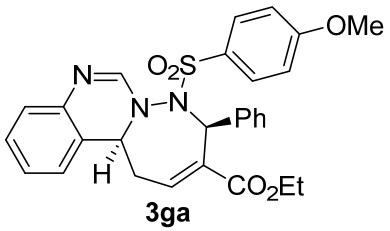
(4*S*,12b*S*)-ethyl 4-phenyl-5-(o-tolylsulfonyl)-1,4,5,12b-tetrahydro-[1,2]diazepino[1,7-*c*] quinazoline-3-carboxylate (3fa)



3fa

Prepared according to the general procedure as described above in 95% yield (59.6 mg). It was purified by flash chromatography (25% EtOAc/PE) to afford a white solid. mp = 78 – 80 °C; $[\alpha]^{20}_D$ = + 1.4 (*c* 0.56, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.53 – 7.39 (m, 2H), 7.40 – 7.26 (m, 6H), 7.26 – 7.09 (m, 2H), 7.07 – 6.95 (m, 2H), 6.91 (s, 1H), 6.72 – 6.62 (m, 1H), 6.13 (d, *J* = 1.1 Hz, 1H), 4.58 (d, *J* = 10.9 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.03 (ddd, *J* = 17.3, 11.4, 2.6 Hz, 1H), 2.59 (s, 3H), 2.39 (ddd, *J* = 17.2, 9.2, 2.2 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 165.3, 148.9, 141.5, 138.8, 138.0, 135.9, 134.8, 134.4, 133.7, 132.8, 131.0, 129.1, 128.8, 128.6, 128.3, 126.5, 125.7, 125.2, 125.1, 124.8, 61.7, 61.4, 57.6, 38.6, 20.5, 13.9; IR (film) ν_{max} 595, 705, 737, 760, 1067, 1133, 1167, 1247, 1347, 1454, 1594, 1615, 1706, 2926; HRMS (ESI) calcd for $C_{28}H_{28}N_3O_4S^+$ $[M+H]^+$ 502.1795, found 502.1795; HPLC analysis: 92% ee (Lux cellulose 2, alcohol/hexane = 20:80, 1.0 ml/min, UV: 254 nm), t_R = 11.112 min (minor), 12.842 min (major).

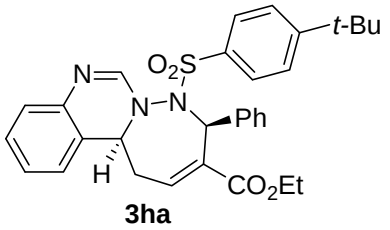
(4*S*,12b*S*)-ethyl 5-((4-methoxyphenyl)sulfonyl)-4-phenyl-1,4,5,12b-tetrahydro-[1,2]diazepino [1,7-*c*]quinazoline-3-carboxylate (3ga)



3ga

Prepared according to the general procedure as described above in 91% yield (58.9 mg). It was purified by flash chromatography (25% EtOAc/PE) to afford a white solid. mp = 140 – 141 °C; $[\alpha]^{20}_D$ = + 28.6 (*c* 0.56, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 – 7.74 (m, 2H), 7.43 (dd, *J* = 9.1, 3.4 Hz, 1H), 7.36 – 7.22 (m, 5H), 7.16 (td, *J* = 7.6, 1.5 Hz, 1H), 7.05 (td, *J* = 7.5, 1.4 Hz, 1H), 6.99 (dd, *J* = 7.7, 1.4 Hz, 1H), 6.98 – 6.87 (m, 2H), 6.88 (s, 1H), 6.85 – 6.76 (m, 1H), 6.06 (d, *J* = 1.0 Hz, 1H), 4.93 (d, *J* = 10.2 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 3.02 (ddd, *J* = 17.3, 11.3, 3.4 Hz, 1H), 2.44 (ddd, *J* = 17.0, 9.2, 2.2 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 165.3, 163.6, 149.1, 141.7, 139.0, 134.6, 134.4, 130.0, 129.9, 129.9, 128.9, 128.7, 128.6, 128.1, 128.4, 125.7, 125.4, 125.2, 124.7, 114.4, 61.5, 61.4, 57.3, 55.5, 38.5, 13.9; IR (film) ν_{max} 556, 584, 664, 737, 763, 837, 1051, 1092, 1159, 1264, 1497, 1595, 1705; HRMS (ESI) calcd for $C_{28}H_{28}N_3O_5S^+$ $[M+H]^+$ 518.1744, found 518.1748; HPLC analysis: 93% ee (CHIRALPAK IA, isopropanol/hexane = 15:85, 1.0 ml/min, UV: 254 nm), t_R = 17.889 min (minor), 30.783 min (major).

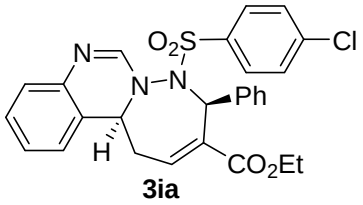
(4*S*,12b*S*)-ethyl 5-((4-(tert-butyl)phenyl)sulfonyl)-4-phenyl-1,4,5,12b-tetrahydro-[1,2]diazepino [1,7-*c*]quinazoline-3-carboxylate (3ha)



3ha

Prepared according to the general procedure as described above in 98% yield (66.6 mg). It was purified by flash chromatography (25% EtOAc/PE) to afford a white solid. mp = 98 – 99 °C; $[\alpha]^{20}_D$ = + 13.9 (*c* 0.54, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 – 7.77 (m, 2H), 7.53 – 7.46 (m, 2H), 7.42 (dd, *J* = 9.0, 3.4 Hz, 1H), 7.34 – 7.25 (m, 3H), 7.28 – 7.19 (m, 1H), 7.16 (td, *J* = 7.6, 1.4 Hz, 1H), 7.08 – 6.97 (m, 2H), 6.87 (s, 1H), 6.80 – 6.68 (m, 1H), 6.10 (d, *J* = 1.1 Hz, 1H), 4.83 (d, *J* = 10.4 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.02 (ddd, *J* = 16.4, 11.0, 3.3 Hz, 1H), 2.45 (ddd, *J* = 17.0, 9.1, 2.2 Hz, 1H), 1.33 (s, 9H), 1.24 (t, *J* = 7.2 Hz, 3H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 165.3, 157.7, 149.0, 141.6, 139.0, 135.6, 134.6, 134.4, 128.9, 128.7, 128.6, 128.1, 127.7, 126.2, 125.7, 125.3, 125.2, 124.8, 61.7, 61.4, 57.5, 38.4, 35.1, 30.9, 13.9; IR (film) ν_{max} 586, 646, 763, 1052, 1087, 1167, 1247, 1360, 1454, 1594, 1617, 1708, 2964; HRMS (ESI) calcd for $C_{31}H_{34}N_3O_4S^+$ $[M+H]^+$ 544.2265, found 544.2266; HPLC analysis: 93% ee (Lux cellulose 1, isopropanol/hexane = 10:90, 1.0 ml/min, UV: 254 nm), t_R = 12.336 min (minor), 18.998 min (major).

(4*S*,12b*S*)-ethyl 5-((4-chlorophenyl)sulfonyl)-4-phenyl-1,4,5,12b-tetrahydro-[1,2]diazepino [1,7-*c*]quinazoline-3-carboxylate (3ia)

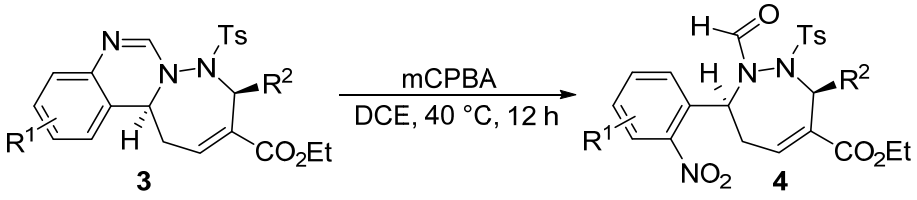


3ia

Prepared according to the general procedure as described above in 96% yield (62.7 mg). It was purified by flash chromatography (25% EtOAc/PE) to afford a white solid. mp = 82 – 83°C; $[\alpha]^{20}_{D}$ = + 12.6 (*c* 0.52, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 – 7.71 (m, 2H), 7.51 – 7.40 (m, 3H), 7.40 – 7.23 (m, 5H), 7.19 (td, *J* = 7.6, 1.5 Hz, 1H), 7.08 (td, *J* = 7.4, 1.4 Hz, 1H), 7.02 (dd, *J* = 7.7, 1.4 Hz, 1H), 6.91 (s, 1H), 6.81 (dd, *J* = 7.6, 1.5 Hz, 1H), 6.05 (s, 1H), 4.86 (d, *J* = 10.6 Hz, 1H), 4.19 (q, *J* = 6.9 Hz, 2H), 3.04 (ddd, *J* = 16.9, 11.1, 3.2 Hz, 1H), 2.44 (ddd, *J* = 17.1, 9.2, 2.2 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 165.2, 148.7, 141.7, 140.3, 138.9, 137.3, 134.3, 134.2, 129.6, 129.1, 128.9, 128.7, 128.1, 125.9, 125.4, 124.6, 61.9, 61.5, 57.4, 38.5, 13.9; IR (film) ν_{max} 576, 617, 704, 761, 1051, 1093, 1168, 1248, 1363, 1477, 1594, 1618, 1708, 2925; HRMS (ESI) calcd for $C_{27}H_{25}ClN_3O_4S^+$ $[M+H]^+$ 522.1249, found 522.1247; HPLC analysis: 92% ee (CHIRALPAK IA, isopropanol/hexane = 12:88, 1.0 ml/min, UV: 254 nm), t_R = 26.921 min (minor), 28.897 min (major).

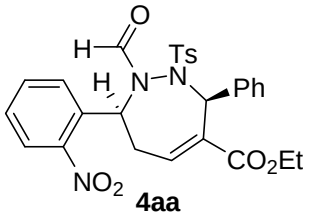
Transformations of the products 3

To the solution of the product **3** (0.1 mmol) in 2 mL of DCE, MCPBA (8.0 equiv, 0.8 mmol) was added. The resulting mixture was stirred at 40 °C for 12 h. Once starting material was consumed (monitored by TLC), the mixture was concentrated and the residue was purified through flash column chromatography (13% EtOAc/PE) to afford the corresponding derivative **4** as a white solid.



3 **4**

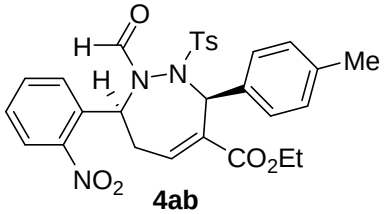
(3*S*,7*S*)-ethyl 1-formyl-7-(2-nitrophenyl)-3-phenyl-2-tosyl-2,3,6,7-tetrahydro-1*H*-1,2-diazepine-4-carboxylate (4aa)



4aa

Prepared according to the general procedure as described above in 73% yield (40.2 mg). It was purified by flash chromatography (13% EtOAc/PE) to afford a yellow solid. mp = 68– 70 °C; $[\alpha]^{20}_D$ = + 61.7 (*c* 0.54, CH_2Cl_2); ^{1}HNMR (400 MHz, $CDCl_3$) δ 8.03 – 7.90 (m, 3H), 7.54 – 7.48 (m, 2H), 7.47 – 7.34 (m, 7H), 7.27 – 7.19 (m, 2H), 6.99 (ddd, *J* = 9.8, 3.4, 1.8 Hz, 1H), 6.68 (t, *J* = 2.1 Hz, 1H), 5.84 (dt, *J* = 7.1, 1.3 Hz, 1H), 4.28 – 3.98 (m, 2H), 3.14 (ddt, *J* = 17.2, 6.8, 3.3 Hz, 1H), 2.83 – 2.69 (m, 1H), 2.57 (s, 3H), 1.11 (t, *J* = 7.1 Hz, 3H); ^{13}CNMR (101 MHz, $CDCl_3$) δ 165.9, 165.2, 147.6, 145.8, 138.4, 137.0, 136.0, 135.3, 133.0, 132.7, 130.7, 129.0, 128.9, 128.2, 128.0, 127.8, 127.2, 125.4, 64.6, 61.4, 60.4, 29.6, 21.9, 14.0; IR (film) ν_{max} 703, 736, 802, 1048, 1091, 1164, 1261, 1354, 1453, 1526, 1706, 2923, 2961; HRMS (ESI) calcd for $C_{28}H_{27}N_3O_7SNa^+$ $[M+Na]^+$ 572.1462, found 572.1462; HPLC analysis: 92% ee (Lux cellulose 1, isopropanol/hexane = 10:90, 1.0 ml/min, UV: 254 nm), t_R = 27.808 min (minor), 33.200 min (major).

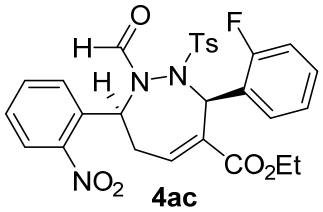
(3*S*,7*S*)-ethyl 1-formyl-7-(2-nitrophenyl)-3-(*p*-tolyl)-2-tosyl-2,3,6,7-tetrahydro-1*H*-1,2-diazepine-4-carboxylate (4ab)



4ab

Prepared according to the general procedure as described above in 85% yield (47.9 mg). It was purified by flash chromatography (16% EtOAc/PE) to afford a white solid. mp = 64 – 66 °C; $[\alpha]^{20}_D$ = + 138.4 (*c* 0.57, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 – 7.92 (m, 3H), 7.51 – 7.45 (m, 4H), 7.44 – 7.35 (m, 2H), 7.19 – 7.04 (m, 4H), 6.96 (ddd, *J* = 9.8, 3.4, 1.7 Hz, 1H), 6.64 (s, 1H), 5.84 (d, *J* = 6.8 Hz, 1H), 4.35 – 3.98 (m, 2H), 3.23 – 3.08 (m, 1H), 2.76 (ddt, *J* = 17.2, 9.8, 1.3 Hz, 1H), 2.56 (s, 3H), 2.36 (s, 3H), 1.13 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.5, 164.8, 147.2, 145.2, 138.3, 137.5, 135.7, 134.9, 133.5, 132.8, 132.2, 130.2, 129.2, 127.7, 127.5, 127.4, 126.9, 124.9, 64.0, 60.9, 59.9, 29.3, 21.4, 20.7, 13.6; IR (film) ν_{max} 543, 585, 666, 705, 735, 815, 987, 1050, 1091, 1163, 1249, 1354, 1526, 1597, 1706, 2926; HRMS (ESI) calcd for $C_{29}H_{30}N_3O_7S^+$ $[M+H]^+$ 564.1799, found 564.1809; HPLC analysis: 92% ee (CHIRALPAK IA, isopropanol/hexane = 10:90, 1.0 ml/min, UV: 254 nm), t_R = 30.445 min (minor), 36.296 min (major).

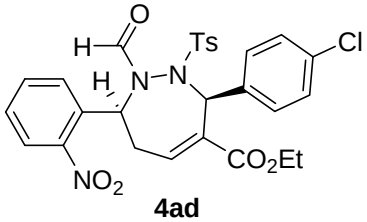
(3*R*,7*S*)-ethyl 3-(2-fluorophenyl)-1-formyl-7-(2-nitrophenyl)-2-tosyl-2,3,6,7-tetrahydro-1*H*-1,2-diazepine-4-carboxylate (4ac)



4ac

Prepared according to the general procedure as described above in 84% yield (47.7 mg). It was purified by flash chromatography (16% EtOAc/PE) to afford a white solid. mp = 76 – 78 °C; $[\alpha]^{20}_{D}$ = + 191.0 (*c* 0.44, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 – 7.96 (m, 1H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.54 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.50 – 7.41 (m, 4H), 7.40 – 7.34 (m, 3H), 7.20 – 7.04 (m, 3H), 6.87 – 6.86 (m, 1H), 5.97 (d, *J* = 7.1 Hz, 1H), 4.13 (ddq, *J* = 36.3, 10.8, 7.1 Hz, 2H), 3.69 – 3.56 (m, 1H), 2.86 (dd, *J* = 17.3, 9.8 Hz, 1H), 2.52 (s, 3H), 1.09 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.0, 164.5, 160.2 (d, *J* = 250.0 Hz), 147.6, 145.1, 138.3, 135.0, 134.7, 132.2 (d, *J* = 5.5 Hz), 130.6, 130.5, 129.9, 129.4 (d, *J* = 2.9 Hz), 127.8 (d, *J* = 2.2 Hz), 127.8, 127.8, 126.7 (d, *J* = 2.1 Hz), 124.9, 124.3, 124.1, 123.8 (d, *J* = 3.5 Hz), 116.2, 115.9, 60.9, 60.3, 59.5, 29.6, 21.4, 13.4; IR (film) ν_{max} 541, 578, 669, 739, 813, 986, 1052, 1091, 1165, 1254, 1354, 1490, 1527, 1706, 2923; HRMS (ESI) calcd for $C_{28}H_{27}FN_3O_7S^+$ $[M+H]^+$ 568.1548, found 568.1556; HPLC analysis: 92% ee (Lux cellulose 1, isopropanol/hexane = 10:90, 1.0 ml/min, UV: 220 nm), t_R = 26.681 min (minor), 43.874 min (major).

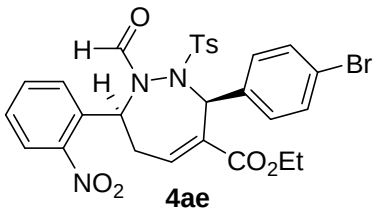
(3*S*,7*S*)-ethyl 3-(4-chlorophenyl)-1-formyl-7-(2-nitrophenyl)-2-tosyl-2,3,6,7-tetrahydro-1*H*-1,2-diazepine-4-carboxylate (4ad)



4ad

Prepared according to the general procedure as described above in 70% yield (40.9 mg). It was purified by flash chromatography (16% EtOAc/PE) to afford a white solid. mp = 80 – 82 °C; $[\alpha]^{20}_{D}$ = + 157.6 (*c* 0.43, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 – 7.91 (m, 3H), 7.52 – 7.47 (m, 3H), 7.44 – 7.35 (m, 5H), 7.20 – 7.16 (m, 2H), 7.00 (ddd, *J* = 9.7, 3.4, 1.8 Hz, 1H), 6.62 (s, 1H), 5.82 (d, *J* = 6.7 Hz, 1H), 4.26 – 4.05 (m, 2H), 3.07 (ddt, *J* = 17.2, 6.8, 3.2 Hz, 1H), 2.75 (ddt, *J* = 17.3, 9.9, 1.3 Hz, 1H), 2.57 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.2, 164.5, 147.3, 145.5, 138.4, 135.5, 135.4, 134.8, 134.4, 132.2, 132.1, 130.4, 128.9, 128.8, 127.8, 127.3, 126.4, 125.1, 63.6, 61.1, 59.8, 29.2, 21.4, 13.6; IR (film) ν_{max} 544, 578, 666, 738, 817, 1050, 1091, 1166, 1248, 1354, 1492, 1526, 1706, 2925; HRMS (ESI) calcd for $C_{28}H_{27}ClN_3O_7S^+$ $[M+H]^+$ 584.1253, found 584.1263; HPLC analysis: 93% ee (CHIRALPAK AD-H, isopropanol/hexane =10:90, 1.0 ml/min, UV: 220 nm), t_R = 41.268 min (minor), 56.306 min (major).

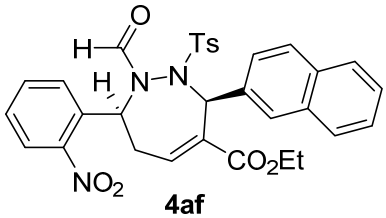
(3*S*,7*S*)-ethyl 3-(4-bromophenyl)-1-formyl-7-(2-nitrophenyl)-2-tosyl-2,3,6,7-tetrahydro-1*H*-1,2-diazepine-4-carboxylate (4ae)



4ae

Prepared according to the general procedure as described above in 78% yield (41.2 mg). It was purified by flash chromatography (16% EtOAc/PE) to afford a white solid. mp = 66 – 68 °C; $[\alpha]^{20}_{D}$ = + 135.7 (*c* 0.51, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 – 7.91 (m, 3H), 7.54 – 7.49 (m, 4H), 7.47 – 7.46 (m, 1H), 7.44 – 7.37 (m, 3H), 7.14 – 7.09 (m, 2H), 7.00 (ddd, *J* = 9.8, 3.4, 1.8 Hz, 1H), 6.60 (t, *J* = 2.2 Hz, 1H), 5.83 (d, *J* = 6.8 Hz, 1H), 4.26 – 4.05 (m, 2H), 3.08 (ddt, *J* = 17.1, 6.9, 3.0 Hz, 1H), 2.80 – 2.70 (m, 1H), 2.57 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.2, 164.5, 147.3, 145.5, 138.4, 136.0, 135.5, 134.8, 132.2, 132.1, 131.7, 130.4, 129.2, 127.8, 127.3, 126.4, 125.0, 122.5, 63.7, 61.1, 59.8, 29.2, 21.4, 13.6; IR (film) ν_{max} 544, 577, 667, 738, 816, 1012, 1090, 1165, 1262, 1355, 1488, 1526, 1706; HRMS (ESI) calcd for $C_{28}H_{27}BrN_3O_7S^+$ $[M+H]^+$ 628.0748, found 628.0759; HPLC analysis: 96% ee (CHIRALPAK AD-H, isopropanol/hexane = 15:85, 1.0 ml/min, UV: 220 nm), t_R = 30.171 min (minor), 37.569 min (major).

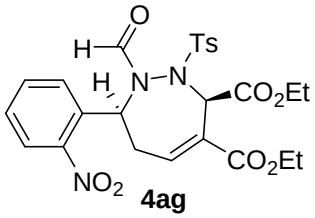
(3*S*,7*S*)-ethyl 1-formyl-3-(naphthalen-2-yl)-7-(2-nitrophenyl)-2-tosyl-2,3,6,7-tetrahydro-1*H*-1,2-diazepine-4-carboxylate (4af)



4af

Prepared according to the general procedure as described above in 72% yield (43.2 mg). It was purified by flash chromatography (16% EtOAc/PE) to afford a white solid. mp = 204 – 206 °C; $[\alpha]^{20}_{D}$ = + 218.7 (*c* 0.31, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 – 7.97 (m, 3H), 7.92 – 7.80 (m, 2H), 7.81 – 7.77 (m, 1H), 7.67 (d, *J* = 10.6 Hz, 1H), 7.64 – 7.52 (m, 3H), 7.50 (d, *J* = 17.0 Hz, 3H), 7.44 – 7.30 (m, 2H), 7.27 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.06 (ddd, *J* = 9.8, 3.4, 1.7 Hz, 1H), 6.82 (t, *J* = 2.1 Hz, 1H), 5.90 (d, *J* = 6.9 Hz, 1H), 4.25 – 4.07 (m, 2H), 3.22 (ddt, *J* = 17.3, 6.6, 3.1 Hz, 1H), 2.91 – 2.75 (m, 1H), 2.60 (s, 3H), 1.09 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.5, 164.5, 147.2, 145.4, 138.1, 135.7, 134.9, 133.9, 132.8, 132.6, 132.5, 132.3, 130.3, 128.8, 127.7, 127.5, 127.3, 127.0, 127.0, 126.6, 125.0, 125.0, 64.4, 61.0, 60.1, 29.3, 21.4, 13.6; IR (film) ν_{max} 543, 579, 664, 736, 1058, 1090, 1164, 1256, 1355, 1526, 1706; HRMS (ESI) calcd for $C_{32}H_{30}N_3O_7S^+$ $[M+H]^+$ 600.1799, found 600.1802; HPLC analysis: 93% ee (CHIRALPAK AD-H, isopropanol/hexane = 15:85, 1.0 ml/min, UV: 220 nm), t_R = 51.267 min (major), 74.499 min (minor).

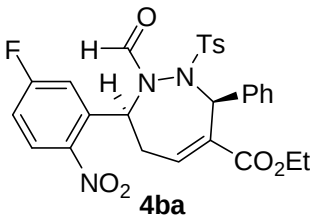
(3*R*,7*S*)-diethyl 1-formyl-7-(2-nitrophenyl)-2-tosyl-2,3,6,7-tetrahydro-1*H*-1,2-diazepine-3,4-dicarboxylate (4ag)



4ag

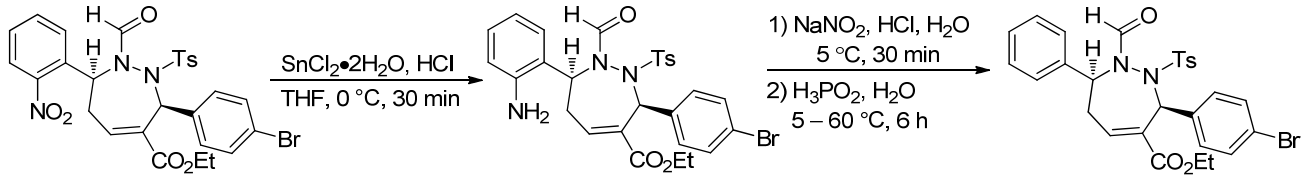
Prepared according to the general procedure as described above in 71% yield (38.8 mg). It was purified by flash chromatography (16% EtOAc/PE) to afford a white solid. mp = 52 – 54 °C; $[\alpha]^{20}_D$ = + 211.0 (*c* 1.03, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 – 7.89 (m, 3H), 7.82 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.57 – 7.49 (m, 2H), 7.45 – 7.38 (m, 3H), 7.02 (ddd, *J* = 9.9, 4.0, 1.9 Hz, 1H), 6.11 (t, *J* = 2.1 Hz, 1H), 5.85 (d, *J* = 6.1 Hz, 1H), 4.35 – 4.09 (m, 4H), 3.65 (dddd, *J* = 16.6, 6.4, 4.0, 2.5 Hz, 1H), 2.95 (ddt, *J* = 16.6, 9.8, 1.5 Hz, 1H), 2.51 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.17 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.5, 164.5, 162.7, 147.8, 145.3, 138.5, 135.1, 134.3, 132.6, 129.9, 129.1, 127.7, 127.7, 124.4, 64.2, 61.9, 61.1, 60.6, 28.4, 21.3, 13.7, 13.6; IR (film) ν_{max} 544, 566, 666, 742, 858, 1092, 1165, 1260, 1297, 1358, 1526, 1707, 1739; HRMS (ESI) calcd for $C_{25}H_{28}N_3O_9S^+$ $[M+H]^+$ 546.1541, found 546.1542; HPLC analysis: 95% ee (CHIRALPAK AD-H, isopropanol/hexane = 20:80, 1.0 ml/min, UV: 254 nm), t_R = 11.225 min (major), 25.390 min (minor).

(3*S*,7*S*)-ethyl 7-(5-fluoro-2-nitrophenyl)-1-formyl-3-phenyl-2-tosyl-2,3,6,7-tetrahydro-1*H*-1,2-diazepine-4-carboxylate (4ba)



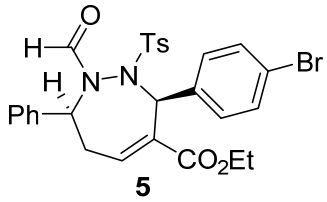
4ba

Prepared according to the general procedure as described above in 86% yield (48.8 mg). It was purified by flash chromatography (16% EtOAc/PE) to afford a white solid. mp = 78 – 80 °C; $[\alpha]^{20}_D$ = + 128.8 (*c* 0.48, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 9.1, 5.2 Hz, 1H), 7.97 – 7.93 (m, 2H), 7.53 – 7.50 (m, 3H), 7.39 – 7.35 (m, 3H), 7.21 – 7.14 (m, 3H), 7.05 (ddd, *J* = 9.5, 6.9, 2.8 Hz, 1H), 6.98 (ddd, *J* = 9.8, 3.3, 1.6 Hz, 1H), 6.66 (t, *J* = 2.1 Hz, 1H), 5.90 (d, *J* = 6.3 Hz, 1H), 4.28 – 4.06 (m, 2H), 3.24 – 3.13 (m, 1H), 2.78 (ddt, *J* = 17.3, 9.9, 1.3 Hz, 1H), 2.57 (s, 3H), 1.13 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.3, 164.3 (d, *J* = 256.6 Hz), 164.7, 145.4, δ143.0 (d, *J* = 3.3 Hz), 138.9 (d, *J* = 8.5 Hz), 137.4, 136.2, 135.5, 132.8, 130.3, 128.8, 128.6, 128.0 (d, *J* = 9.8 Hz), 127.5, 127.4, 114.8 (d, *J* = 23.0 Hz), 114.2 (d, *J* = 25.5 Hz), 64.2, 61.0, 60.0, 29.0, 21.4, 13.5; IR (film) ν_{max} 541, 575, 666, 704, 733, 1051, 1091, 1165, 1249, 1354, 1528, 1590, 1705; HRMS (ESI) calcd $C_{28}H_{27}FN_3O_7S^+$ $[M+H]^+$ 568.1548, found 568.1555; HPLC analysis: 94% ee (CHIRALPAK AD-H, isopropanol/hexane = 10:90, 1.0 ml/min, UV: 254 nm), t_R = 24.666 min (minor), 36.106 min (major).

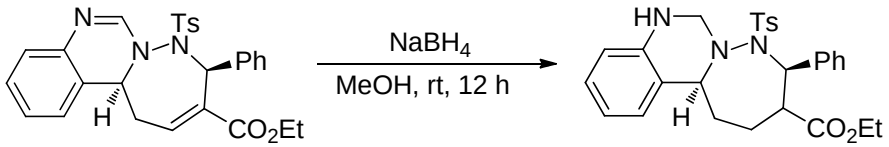


The $SnCl_2 \cdot 2H_2O$ (0.42 mmol) was dissolved in conc. HCl (0.74 M) and cooled to 0 °C, then **4ae** (0.1 mmol) in 1 ml of THF was added. After stirring for 30 min at rt, the reaction mixture was diluted with H_2O, cooled to 0 °C and basified with NaOH. The reaction mixture was extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4, and evaporated under reduced pressure. The crude product was dissolved in conc. HCl (0.03 mL) and H_2O (0.03 mL) and stirred below 5 °C, then 7.7 mg of $NaNO_2$ in 0.2 mL of H_2O was added dropwise at such a rate that the temperature of the reaction remained below 5 °C. After stirring for 30 min, H_3PO_2 (8 M in water, 2.2 mL) was added to the reaction mixture. After stirring at 60 °C for 6h, the reaction mixture was extracted with ethyl acetate and washed with saturated $NaHCO_3$ and dried using anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified through flash column chromatography (10% EtOAc/PE) to afford the corresponding product **5** as a white solid, 33% yield.

(3*S*,7*S*)-ethyl 3-(4-bromophenyl)-1-formyl-7-phenyl-2-tosyl-2,3,6,7-tetrahydro-1*H*-1,2-diazepine-4-carboxylate (5)

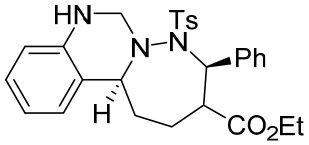


Prepared according to the general procedure as described above in 33% yield (19.2 mg). It was purified by flash chromatography (10% EtOAc/PE) to afford a white solid. mp = 54 – 56 °C; $[\alpha]^{20}_D$ = + 185.7 (*c* 0.11 CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 – 7.85 (m, 2H), 7.60 – 7.50 (m, 4H), 7.42 – 7.33 (m, 5H), 7.31 – 7.26 (m, 1H), 7.20 – 7.15 (m, 2H), 6.78 – 6.74 (m, 2H), 5.00 (dd, *J* = 12.7, 2.4 Hz, 1H), 4.23 – 4.05 (m, 2H), 3.23 (ddt, *J* = 18.0, 12.8, 2.7 Hz, 1H), 2.61 – 2.50 (m, 1H), 2.46 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.0, 164.5, 144.8, 140.2, 139.6, 135.3, 134.7, 132.2, 132.0, 129.9, 129.7, 128.2, 127.3, 127.2, 126.2, 123.4, 65.1, 64.0, 60.9, 32.1, 21.3, 13.6; IR (film) ν_{max} 579, 734, 817, 912, 1050, 1166, 1249, 1356, 1488, 1707, 2926; HRMS (ESI) calcd $C_{28}H_{28}BrN_2O_5S^+$ $[M+H]^+$ 583.0897, found 583.0909; HPLC analysis: 80% ee (CHIRALPAK AD-H, isopropanol/hexane = 5:95, 1.0 ml/min, UV: 220 nm), t_R = 29.717 min (minor), 44.538 min (major).



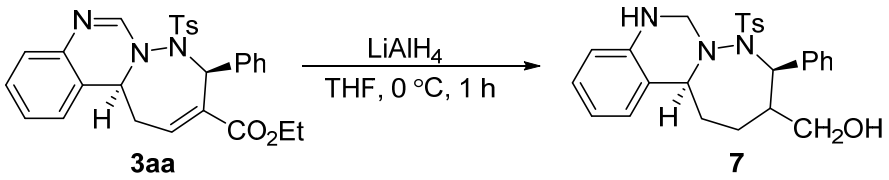
3aa **6**

The cycloaddition **3aa** (50.1 mg, 0.1 mmol) was dissolved in 2 mL MeOH, then $NaBH_4$ (11.3 mg, 0.3 mmol) was added, the mixture was stirred at room temperature for 12 hours. Once starting material was consumed (monitored by TLC), the mixture was concentrated to dryness. The residue was purified through flash column chromatography (EtOAc/PE) to afford the corresponding product **6** as a white solid, 36.2 mg, 72% yield.



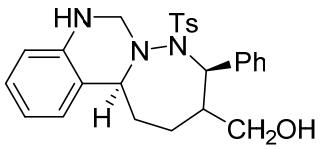
6

Prepared according to the general procedure as described above in 72% yield (36.4 mg). It was purified by flash chromatography (12% EtOAc/PE) to afford a white solid. mp = 64 – 66 °C; $[\alpha]^{20}_{D}$ = + 44.0 (*c* 0.52, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.64 (s, 1H), 7.42 – 7.30 (m, 6H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.07 – 7.02 (m, 1H), 6.93 – 6.89 (m, 1H), 6.77 – 6.72 (m, 1H), 6.64 – 6.56 (m, 2H), 4.26 (q, *J* = 7.1 Hz, 2H), 4.19 – 4.11 (m, 2H), 3.87 (d, *J* = 12.1 Hz, 1H), 3.62 (dd, *J* = 11.3, 3.9 Hz, 1H), 2.69 (td, *J* = 13.0, 4.3 Hz, 1H), 2.34 (s, 3H), 2.20 (td, *J* = 12.9, 4.3 Hz, 1H), 1.89 – 1.80 (m, 1H), 1.74 – 1.63 (m, 1H), 1.35 (t, *J* = 7.1 Hz, 3H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 168.0, 143.7, 141.3, 138.7, 135.5, 135.4, 132.7, 129.2, 129.1, 128.4, 128.3, 128.2, 127.5, 121.8, 118.9, 114.9, 65.4, 60.6, 58.3, 37.6, 31.7, 24.3, 21.3, 14.2; IR (film) ν_{max} 545, 702, 749, 1093, 1161, 1253, 1305, 1496, 1609, 1703, 2927, 3404; HRMS (ESI) calcd for $C_{28}H_{31}N_3O_4SNa^+$ $[M+Na]^+$ 528.1927, found 528.1926; HPLC analysis: 92% ee (CHIRALPAK IA, isopropanol/hexane = 10:90, 1.0 ml/min, UV: 254 nm), t_R = 25.656 min (major), 27.572 min (minor), 93% ee t_R = 28.848 min (major), 33.210 min (minor).



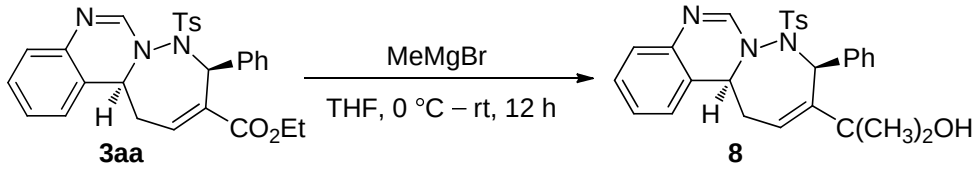
3aa **7**

The cycloaddition product **3aa** (50.1 mg, 0.1 mmol) was dissolved in 1 ml of THF, then added to $LiAlH_4$ (15.2 mg, 0.4 mmol) in 1ml of THF, the resulting mixture was stirred at 0 °C for 1 h. Once starting material was consumed (monitored by TLC), the mixture was concentrated to dryness. The residue was purified through flash column chromatography (25% EtOAc/PE) to afford the corresponding product **7** as a white solid, 33.4 mg, 72% yield.



7

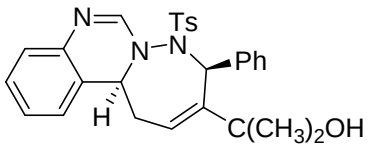
Prepared according to the general procedure as described above in 72% yield (33.4 mg). It was purified by flash chromatography (25% EtOAc/PE) to afford a white solid. mp = 70 – 72 °C; $[\alpha]^{20}_{D}$ = + 57.6 (*c* 0.51, CH_2Cl_2); ^{1}HNMR (300 MHz, DMSO-d_6) δ 8.49 (s, 1H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.28–7.15 (m, 7H), 7.94–6.89 (m, 1H), 6.80 (d, *J* = 7.2 Hz, 1H), 6.55–6.50 (m, 2H), 6.38 (s, 1H), 3.94 (s, 2H), 3.84 (d, *J* = 12.6 Hz, 1H), 3.50–3.45 (m, 2H), 2.42–2.35 (m, 1H), 2.29 (s, 3H), 1.88–1.78 (m, 1H), 1.67–1.42 (m, 2H); ^{13}CNMR (75 MHz, DMSO-d_6) δ 143.5, 143.4, 142.6, 137.8, 136.8, 129.6, 128.6, 128.4, 128.3, 127.2, 126.4, 123.4, 122.2, 117.3, 115.3, 79.5, 65.5, 65.1, 57.9, 36.9, 25.7, 21.4; IR (film) ν_{max} 545, 664, 670, 750, 814, 1093, 1161, 1318, 1496, 1643, 3444; HRMS (ESI) calcd for $C_{26}H_{29}N_3O_3SNa^+$ $[M+Na]^+$ 486.1822, found 486.1822; HPLC analysis: 93% ee (CHIRALPAK AD-H, isopropanol/hexane = 20:80, 1.0 ml/min, UV: 254 nm), t_R = 25.467 min (minor), 45.987 min (major).



3aa **8**

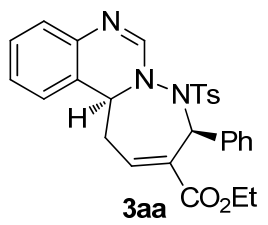
The cycloaddition product **3aa** (50.1 mg, 0.1 mmol) was dissolved in 1 ml of THF, then MeMgBr (0.5 mmol, 1.0 M in THF) was added at 0 °C, the resulting mixture was stirred at room temperature for 12 h. Once starting material was consumed (monitored by TLC), the mixture was concentrated to dryness. The residue was purified through flash column chromatography (50% EtOAc/PE) to afford the corresponding product **8** as a white solid, 34.0 mg, 70% yield.

2-((4*S*,12b*S*)-4-phenyl-5-tosyl-1,4,5,12b-tetrahydro-[1,2]diazepino[1,7-*c*]quinazolin-3-yl)propan-2-ol (8)

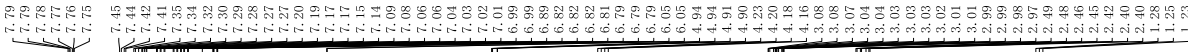


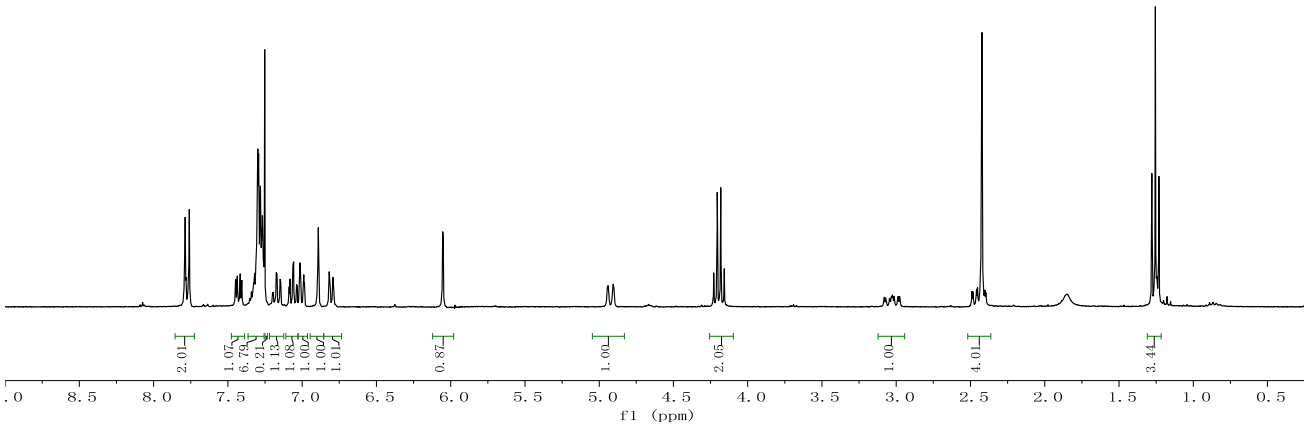
8

Prepared according to the general procedure as described above in 70% yield (34.0 mg). It was purified by flash chromatography (50% EtOAc/PE) to afford a white solid. mp = 178– 180 °C; $[\alpha]^{20}_{D}$ = + 34.8 (*c* 0.51, CH_2Cl_2); ^{1}HNMR (300 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.29–7.26 (m, 7H), 7.15–7.09 (m, 1H), 7.05–7.00 (m, 1H), 6.94–6.91 (m, 1H), 6.85–6.79 (m, 1H), 6.46 (s, 1H), 6.30 (dd, *J* = 9.5, 3.3 Hz, 1H), 5.90 (s, 1H), 4.89 (d, *J* = 11.4 Hz, 1H), 2.92 (ddd, *J* = 15.5, 11.6, 3.3 Hz, 1H), 2.40 (s, 3H), 2.25–2.16 (m, 2H), 1.40 (s, 3H), 1.31 (s, 3H); ^{13}CNMR (101 MHz, $CDCl_3$) δ 149.2, 148.7, 144.7, 139.0, 135.3, 135.1, 129.9, 129.0, 128.9, 128.6, 128.4, 128.0, 125.8, 125.6, 125.0, 73.3, 62.0, 58.0, 38.3, 29.8, 29.6, 21.6; IR (film) ν_{max} 601, 662, 671, 766, 1037, 1092, 1164, 1261, 1352, 1596, 2344, 2926; HRMS (ESI) calcd for $C_{28}H_{30}N_3O_3S^+$ $[M+H]^+$ 488.2002, found 488.2000; HPLC analysis: 93% ee (CHIRALPAK IA, isopropanol/hexane = 15:85, 1.0 ml/min, UV: 254 nm), t_R = 16.945 min (minor), 18.854 min (major).


N
N
NTs
H
Ph
CO2Et

3aa

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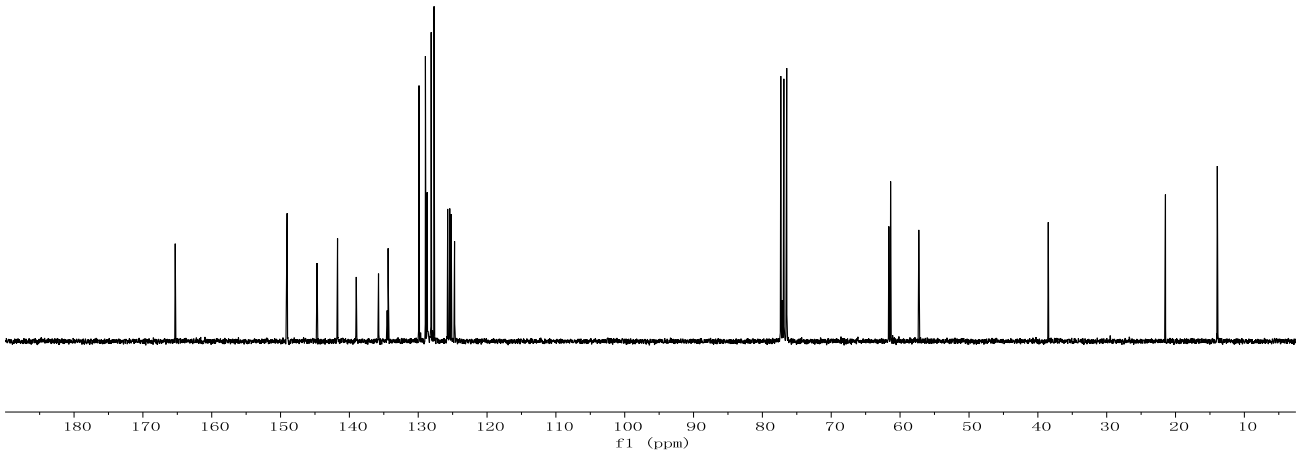
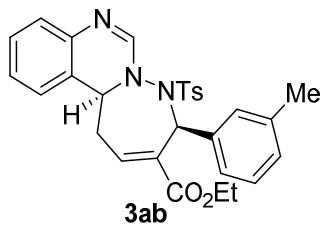
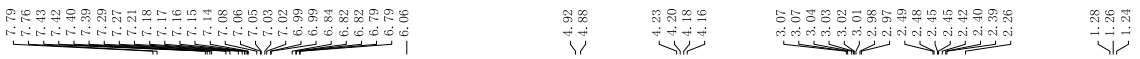
1.13
1.08
1.00
1.00
1.01
0.87
1.00
2.05
1.00
4.01
3.44
f1 (ppm)


f1 (ppm)


N
N
NTs
Me
H
CO2Et

3ab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7.08
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7.05
7.03
7.02
6.99
6.99
6.84
6.82
6.82
6.79
6.79
6.06
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4.88
4.23
4.20
4.18
4.16
3.07
3.07
3.04
3.03
3.02
3.01
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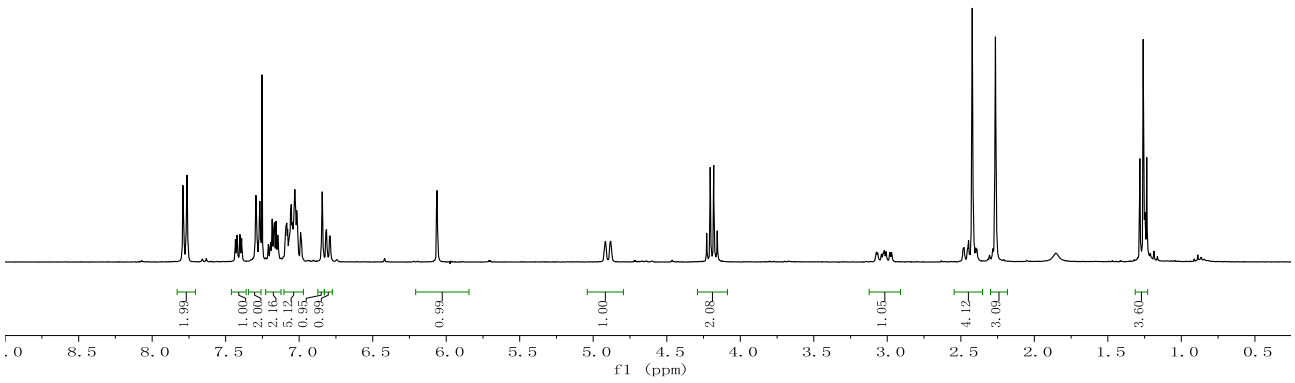
1.24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3.60
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


165.33
149.09
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139.07
138.65
135.93
134.45
134.28
129.84
129.48
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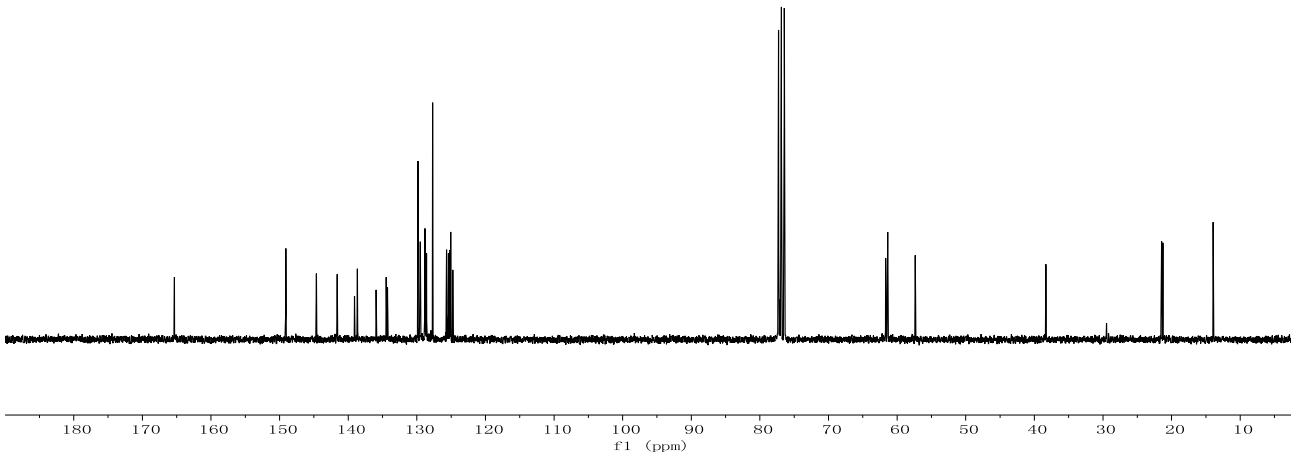
21.45
21.28
13.94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120
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100
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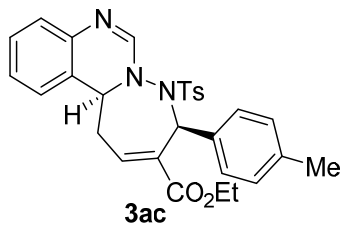
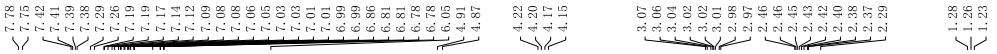
80
70
60
50
40
30
20
10
f1 (ppm)


N
N
NTs
H
Me
CO2Et

3ac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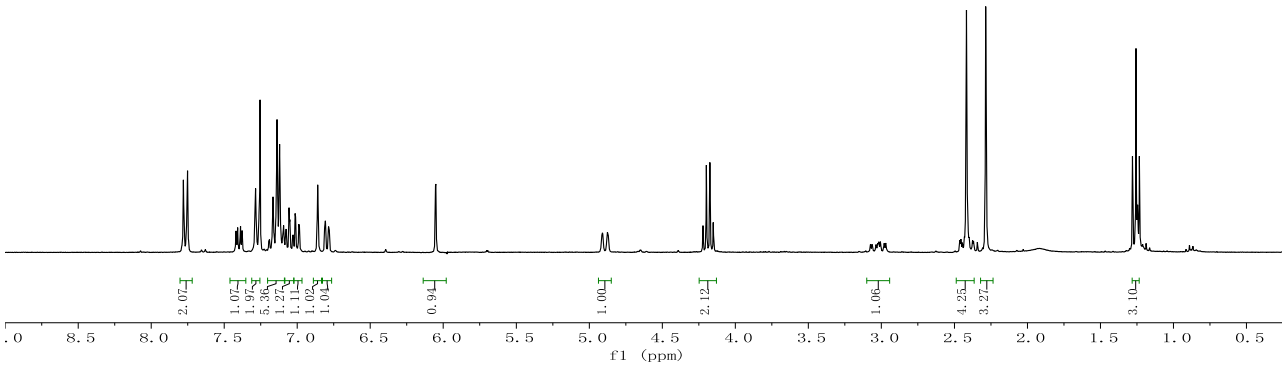
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2.12
1.06
4.25
3.27
3.10
f1 (ppm)


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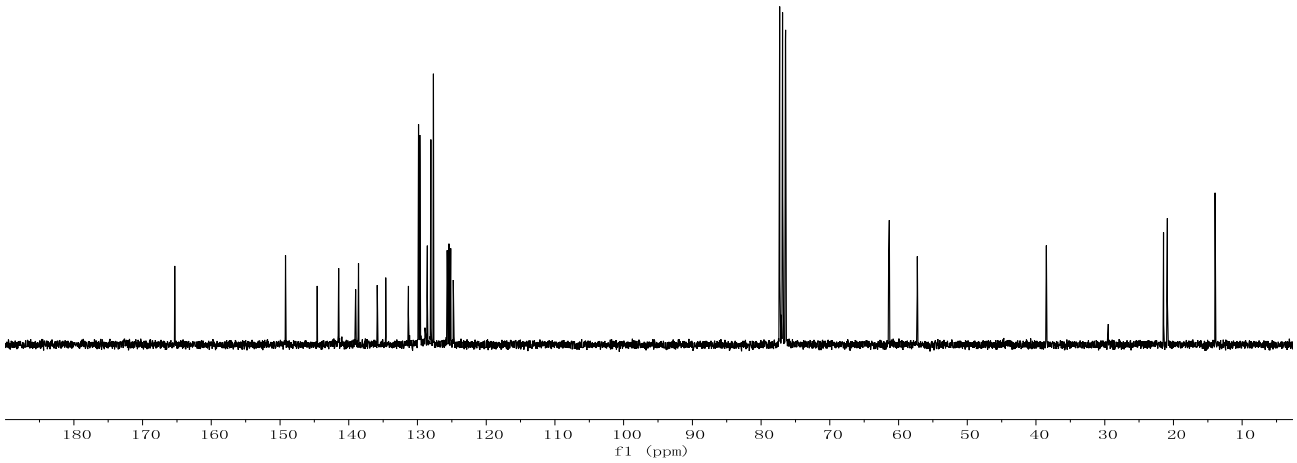
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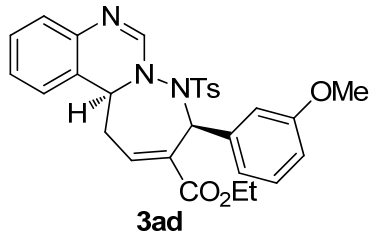
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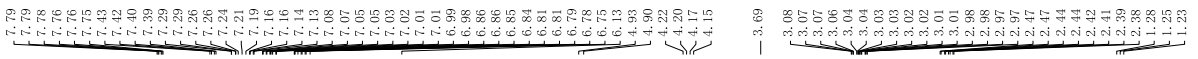
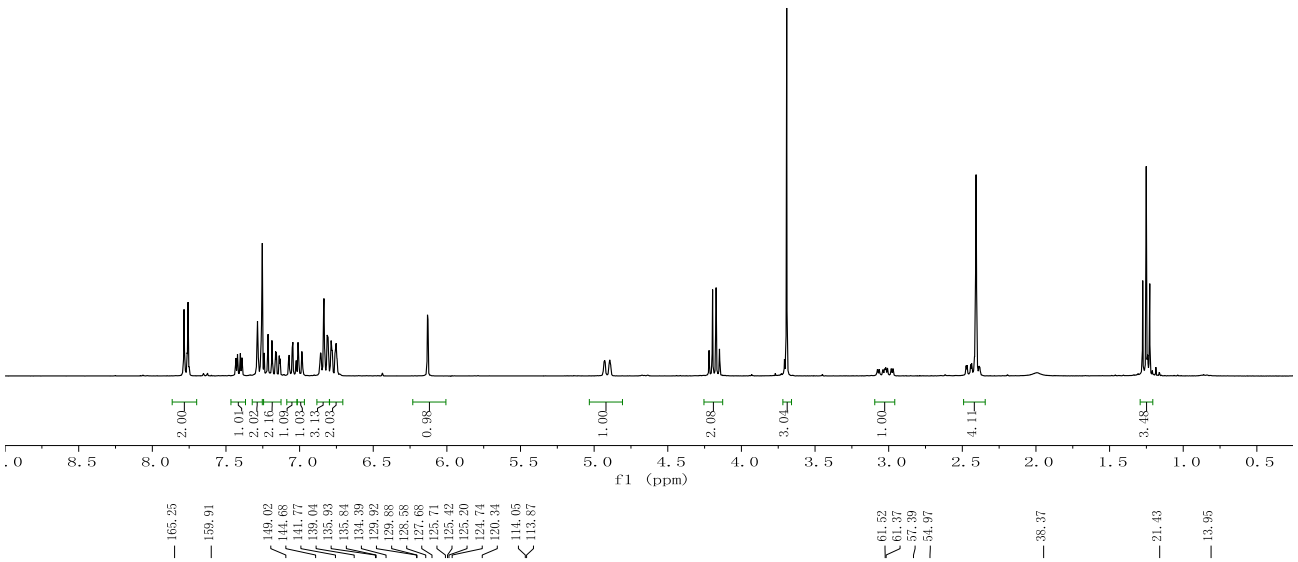
OMe
CO2Et

3ad

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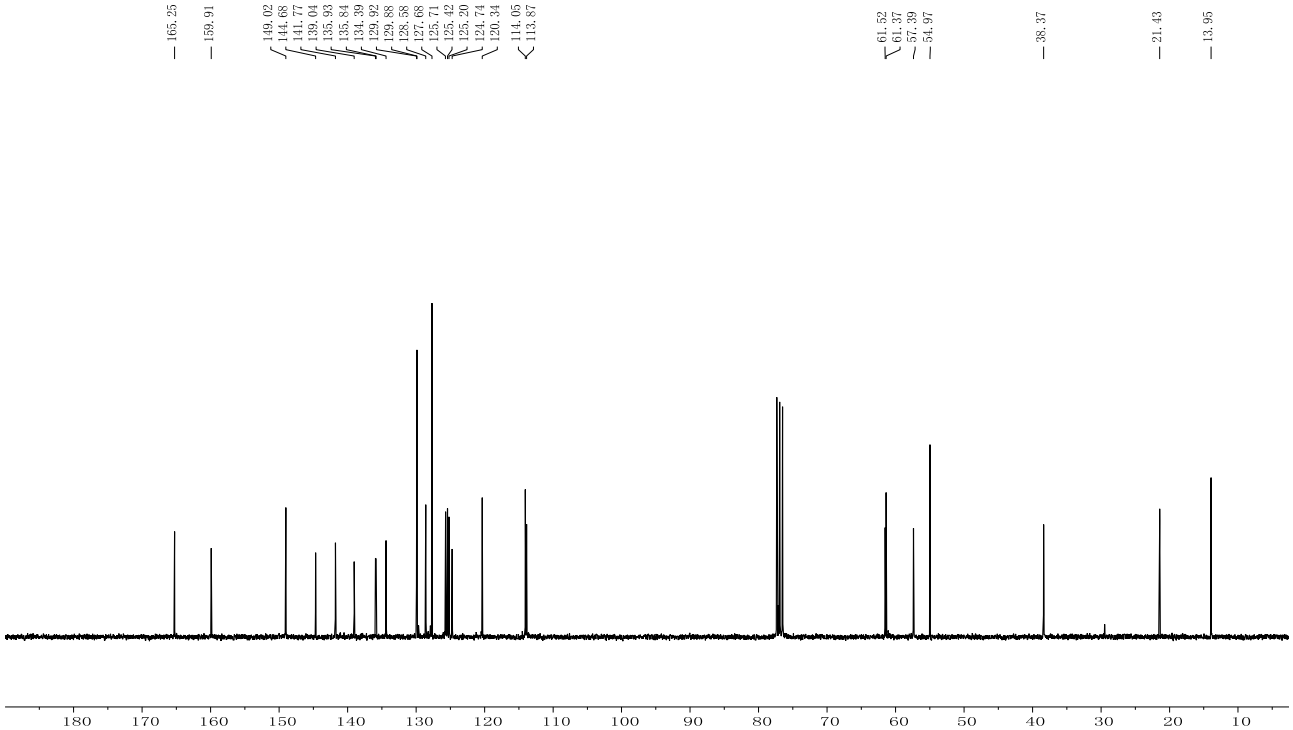
f1 (ppm)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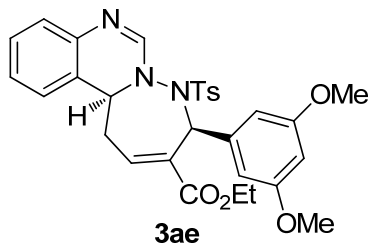
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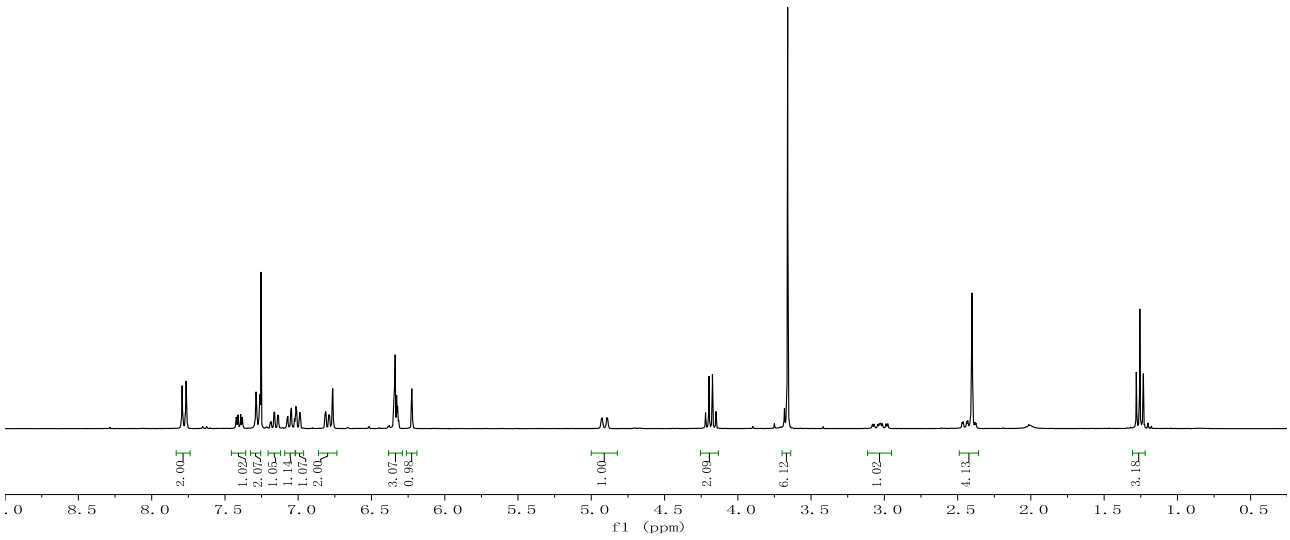
OMe
CO2Et
OMe

3ae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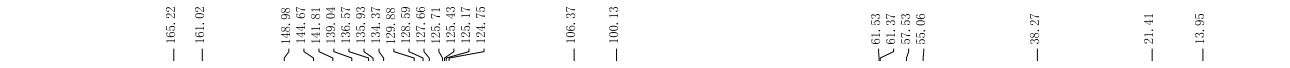
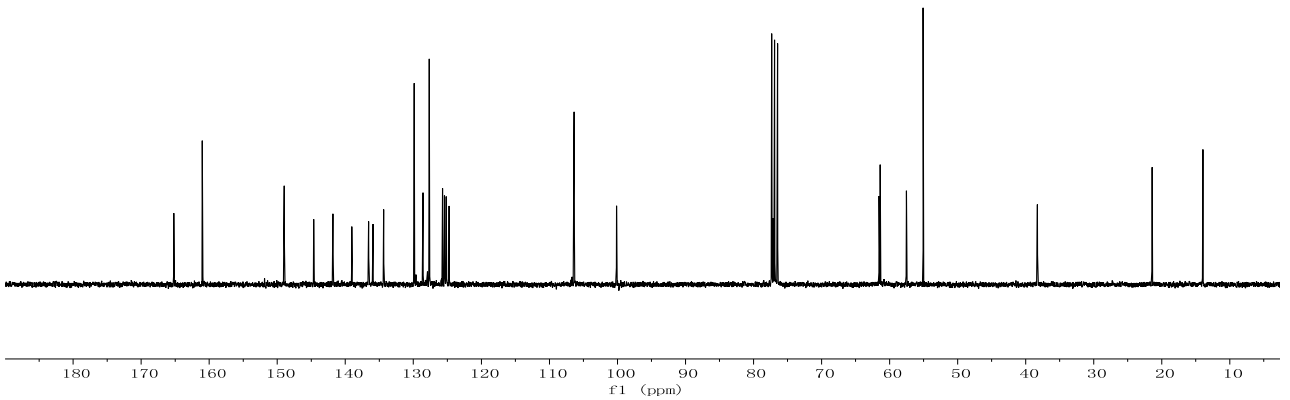
f1 (ppm)

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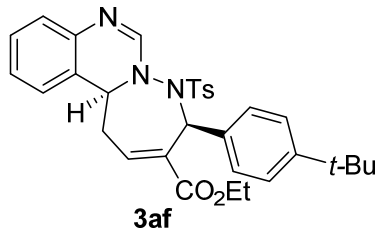

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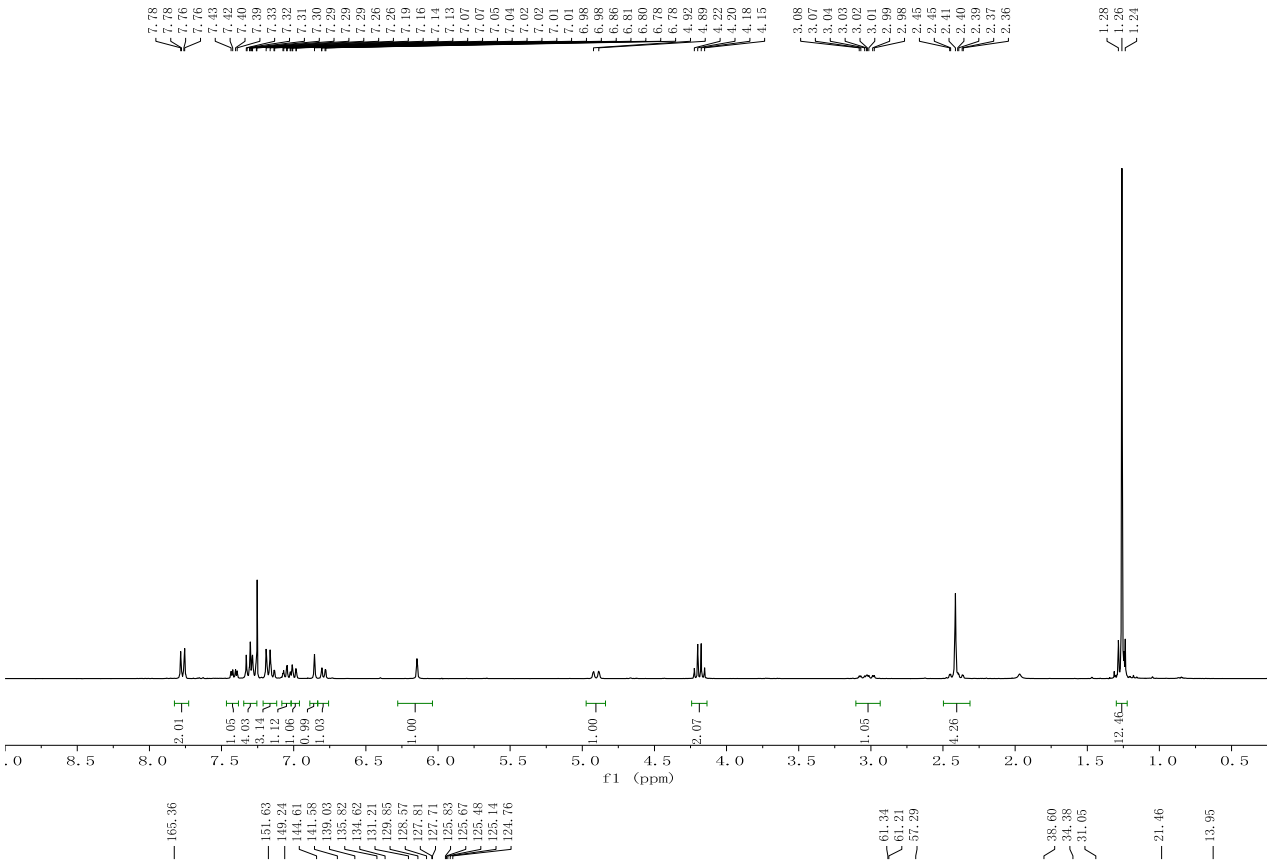

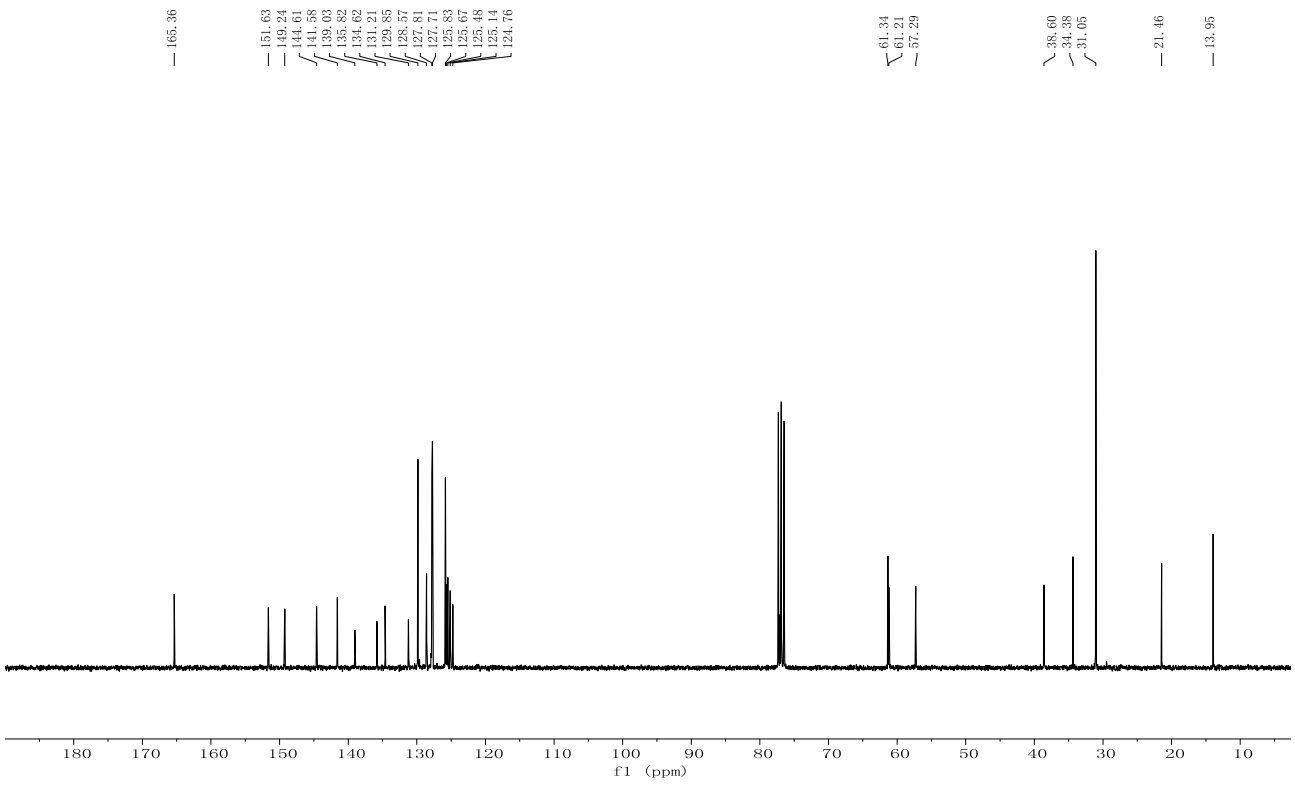

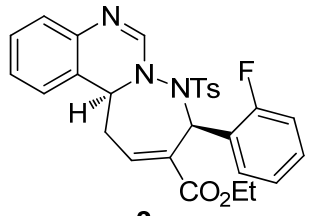

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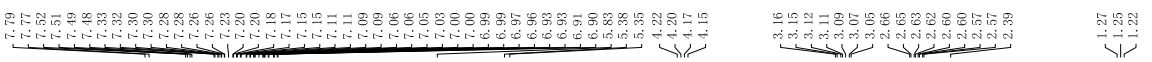

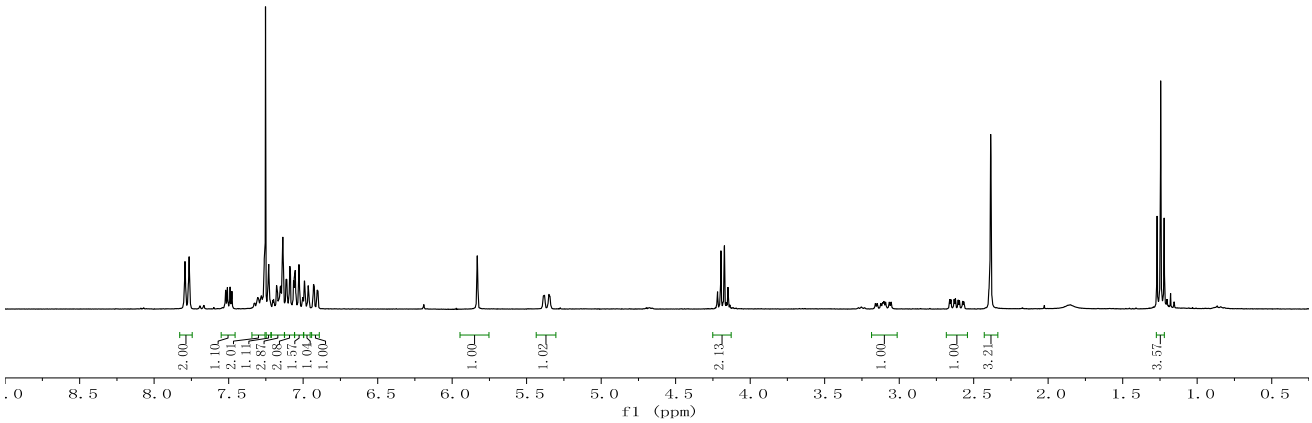

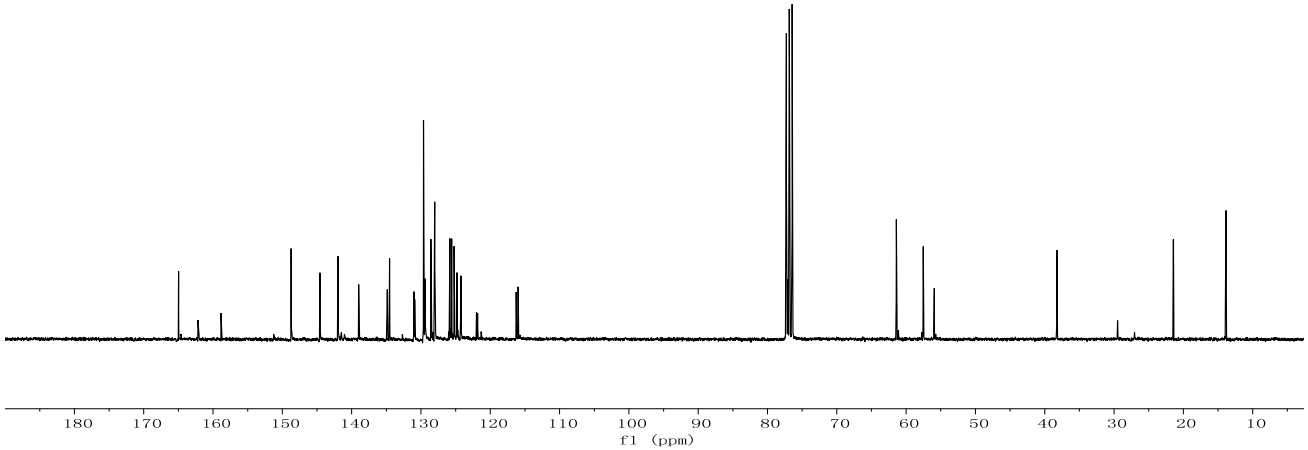

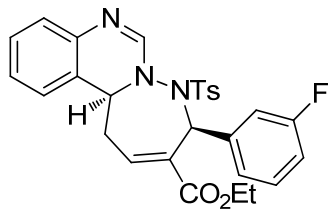

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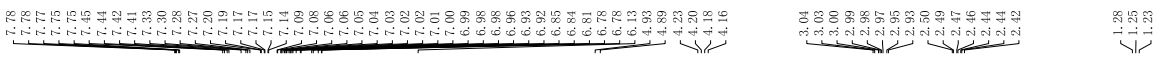

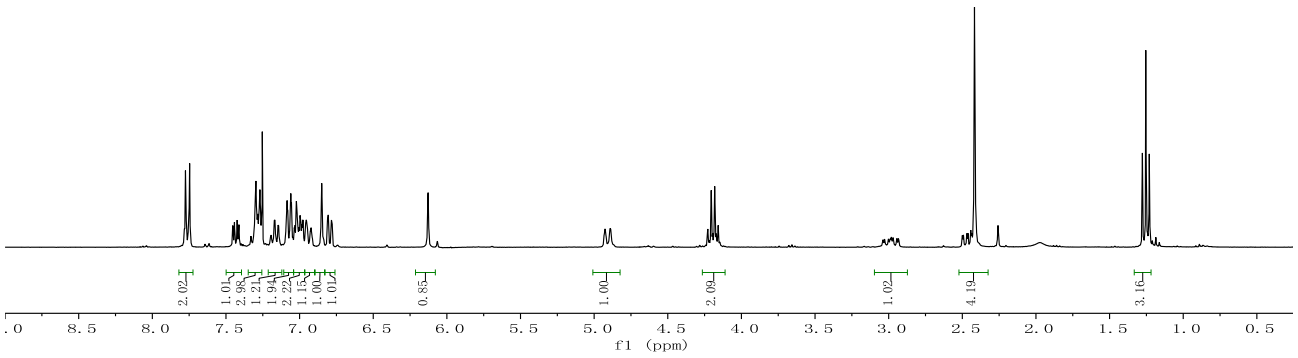

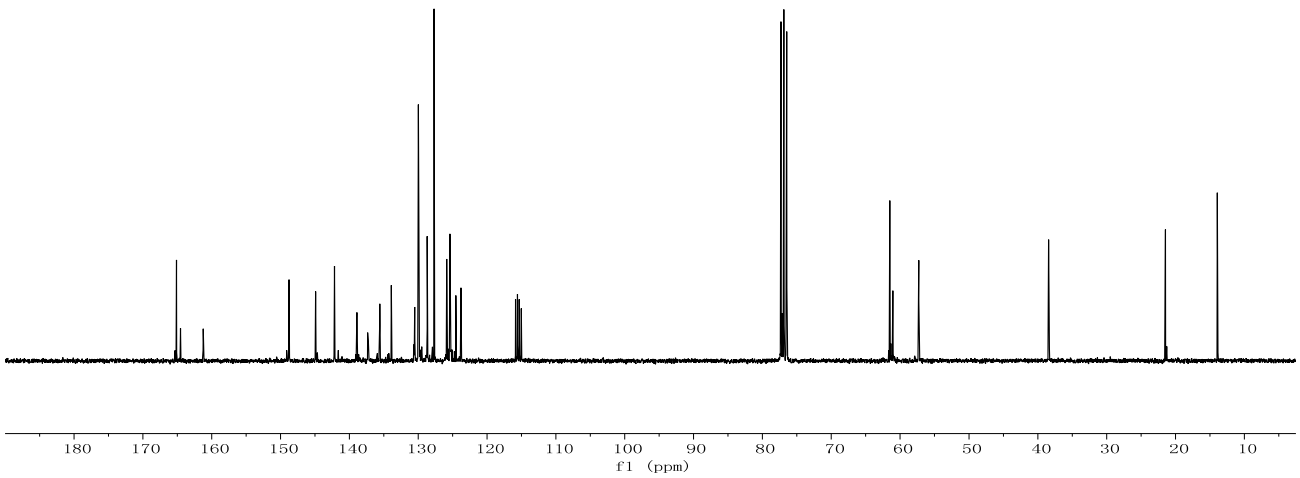

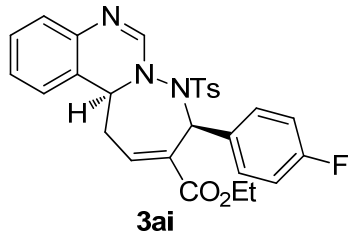
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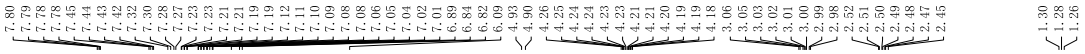
N
NTs
H
F
CO2Et

3ai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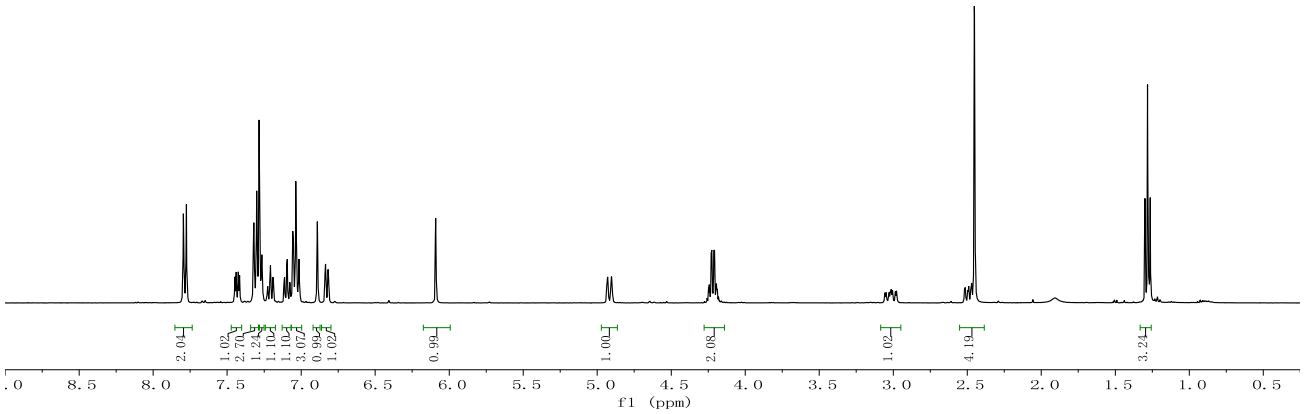
1.30 1.28 1.26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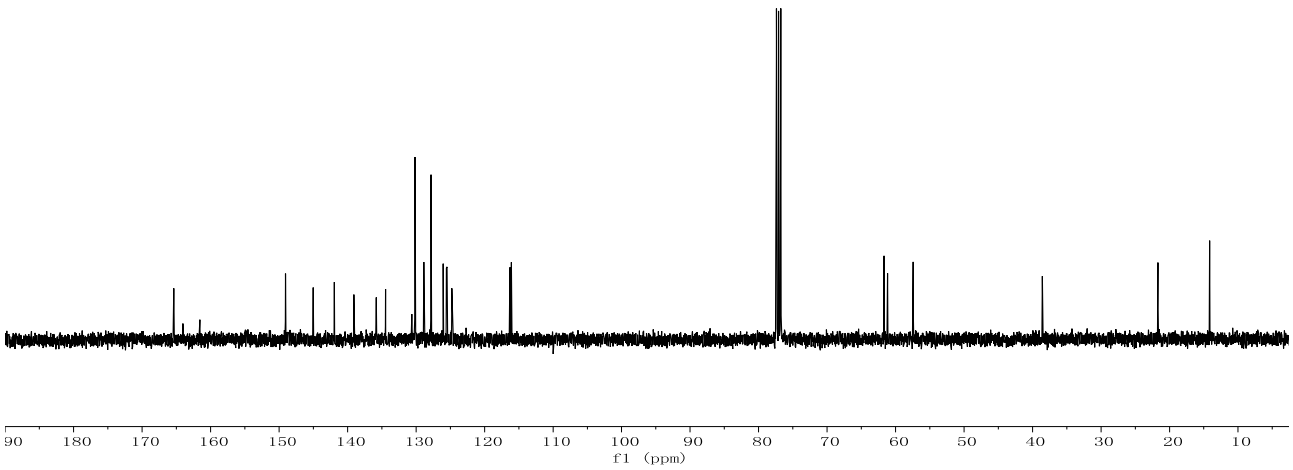
f1 (ppm)


165.37 164.65 161.57 149.07 145.03 141.93 139.09 135.82 134.46 130.63 130.18 130.15 130.10 128.89 127.83 126.04 125.38 125.49 124.77 116.30 116.09 61.69 61.16 57.42 38.58 21.70 14.14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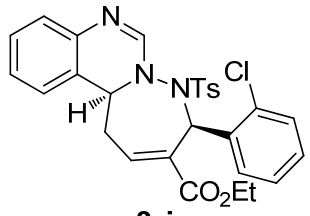

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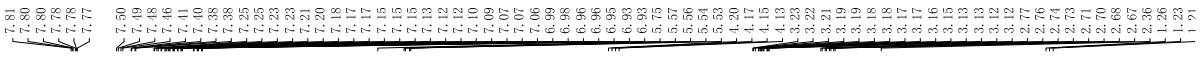

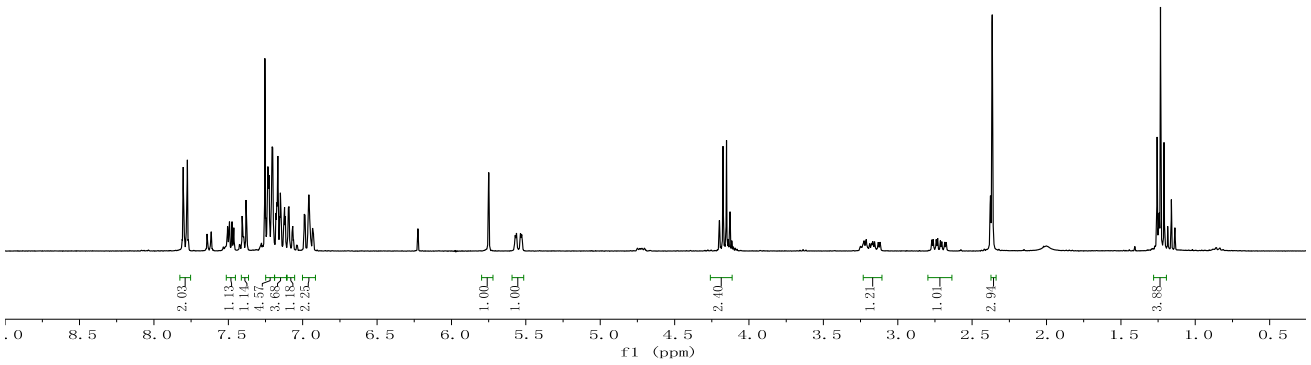

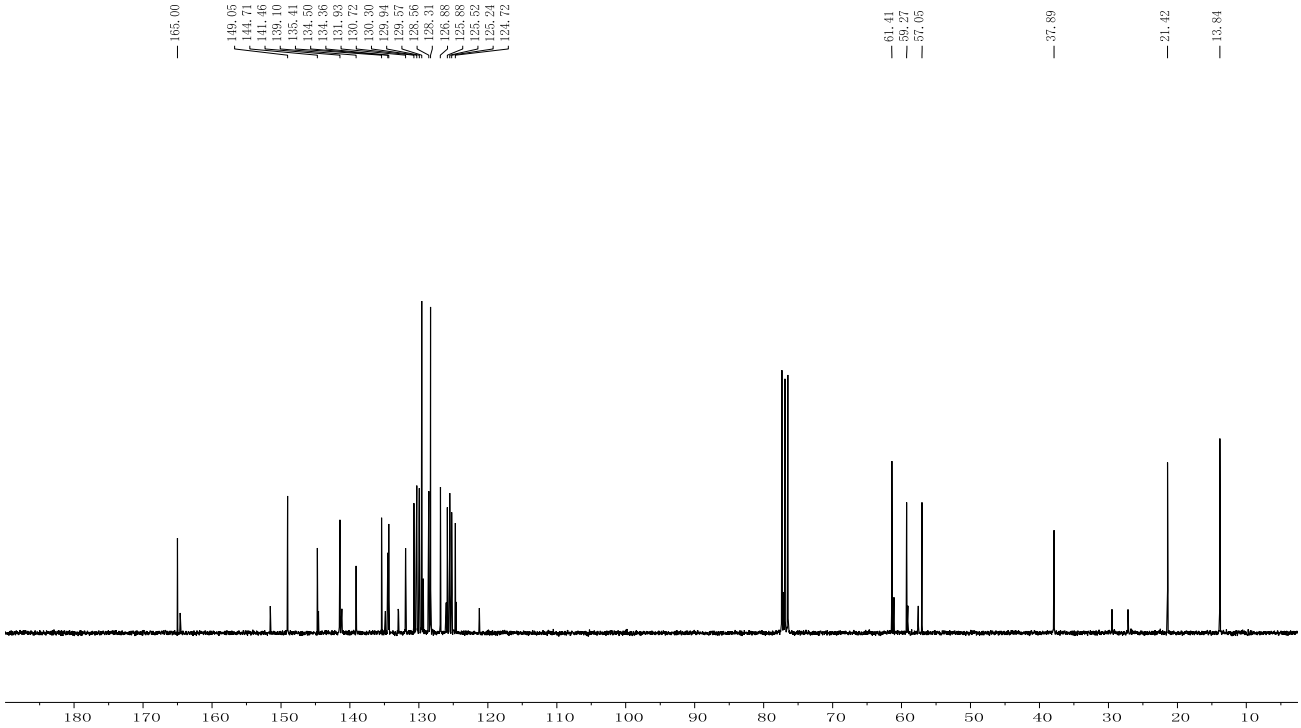

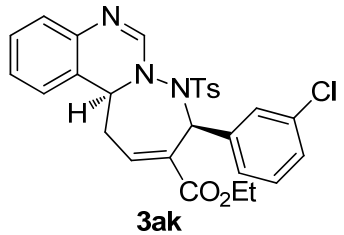

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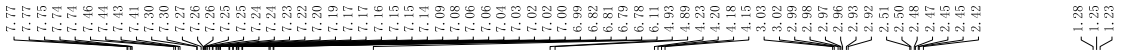

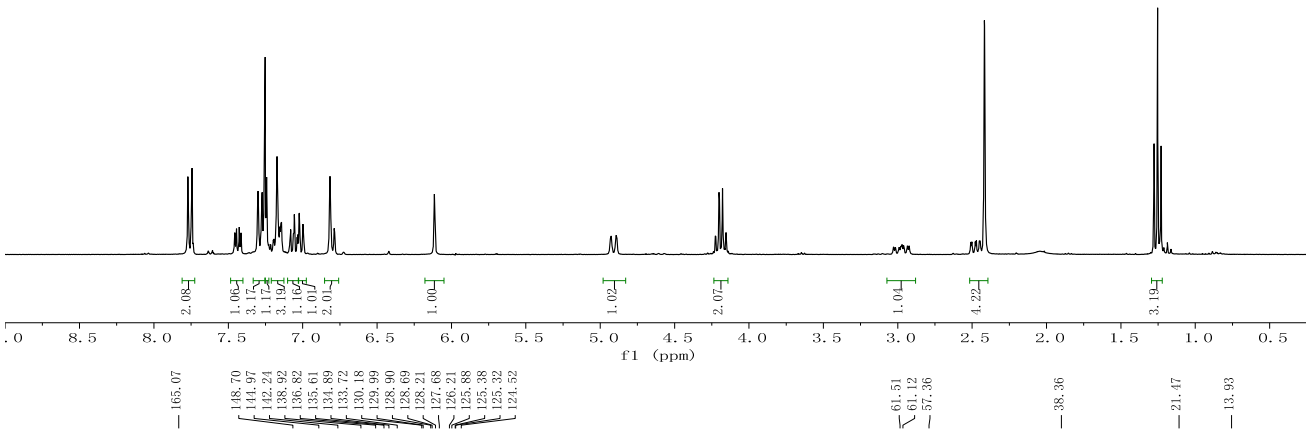

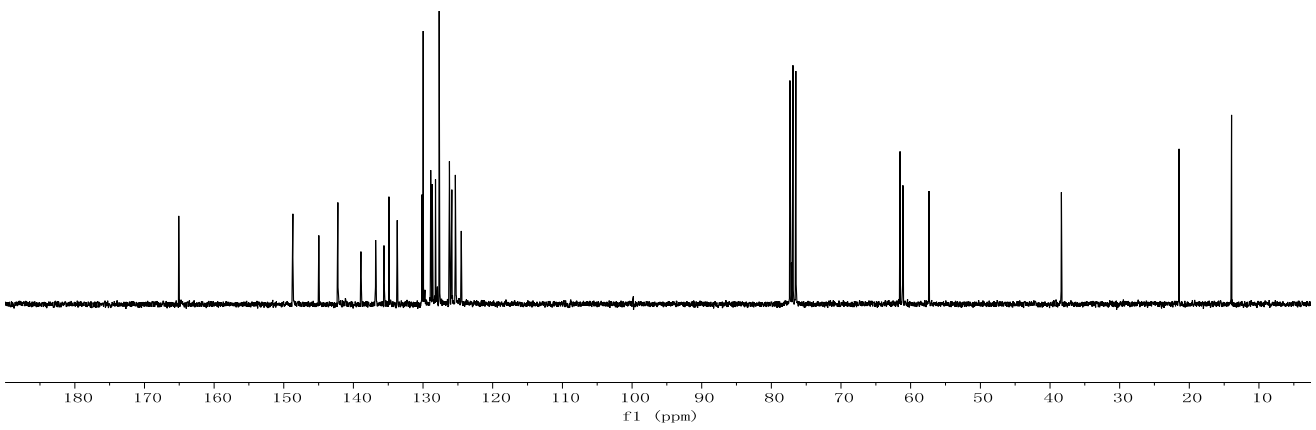

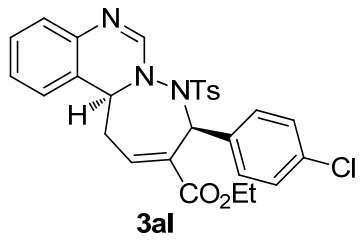
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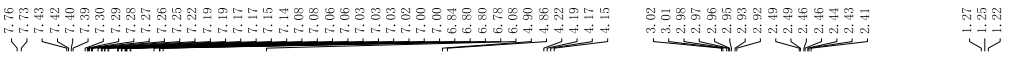

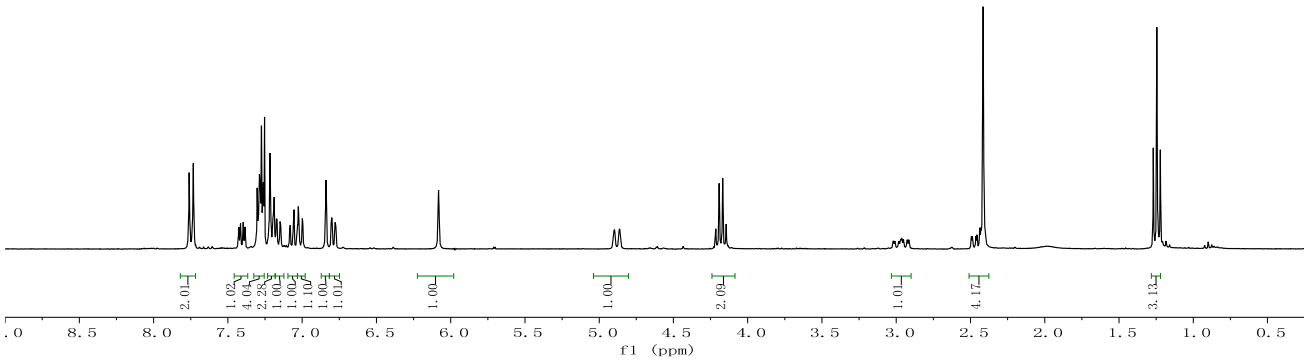
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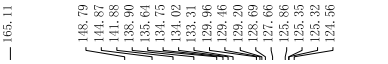
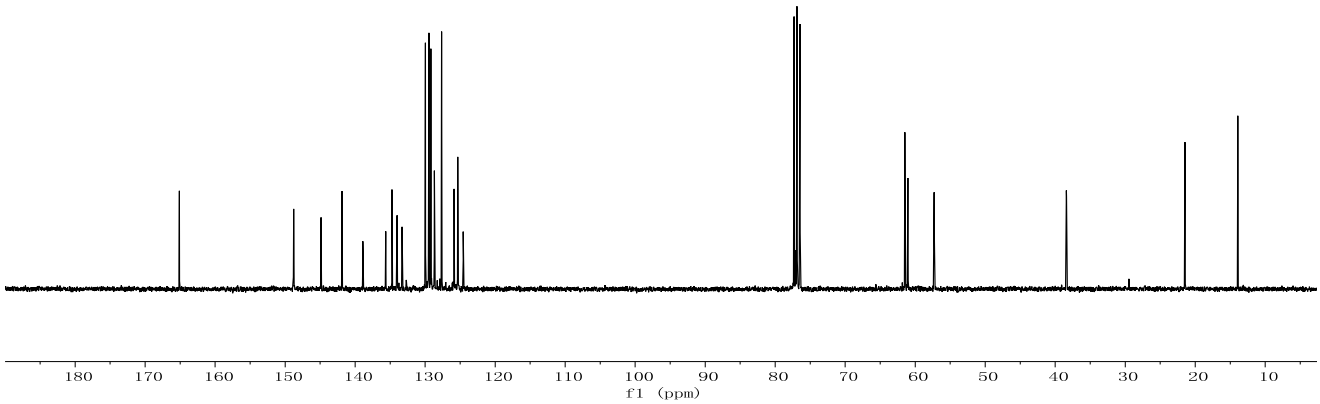
f1 (ppm)

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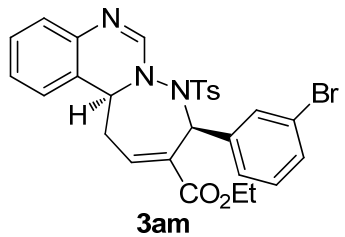

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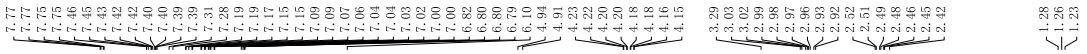

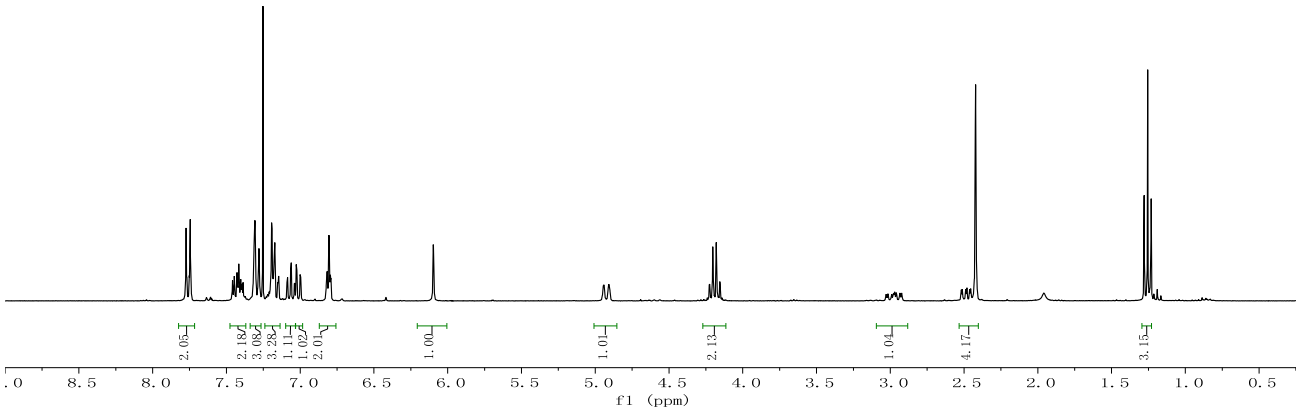

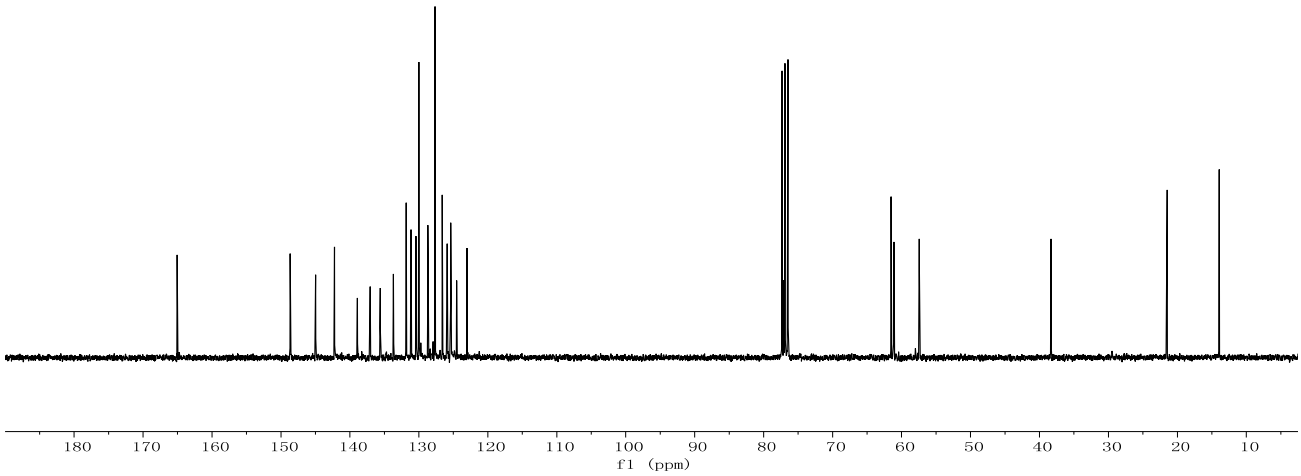

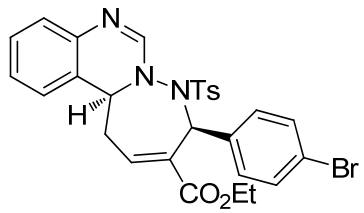
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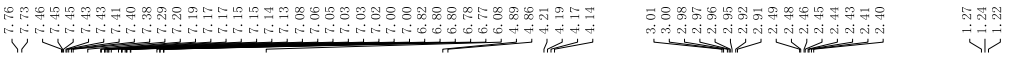
N
NTs
H
Br
CO2Et

3an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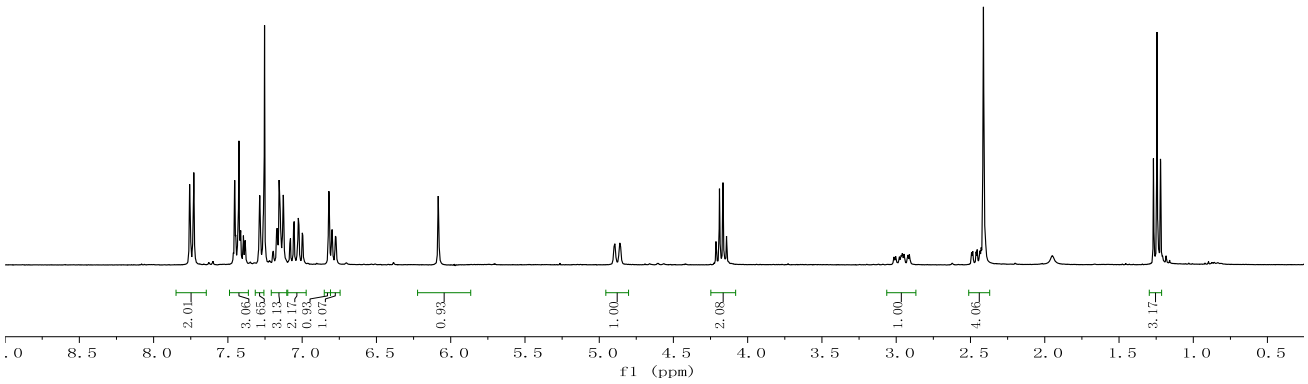
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4.06
3.17
f1 (ppm)


165.10
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144.88
141.93
138.90
135.62
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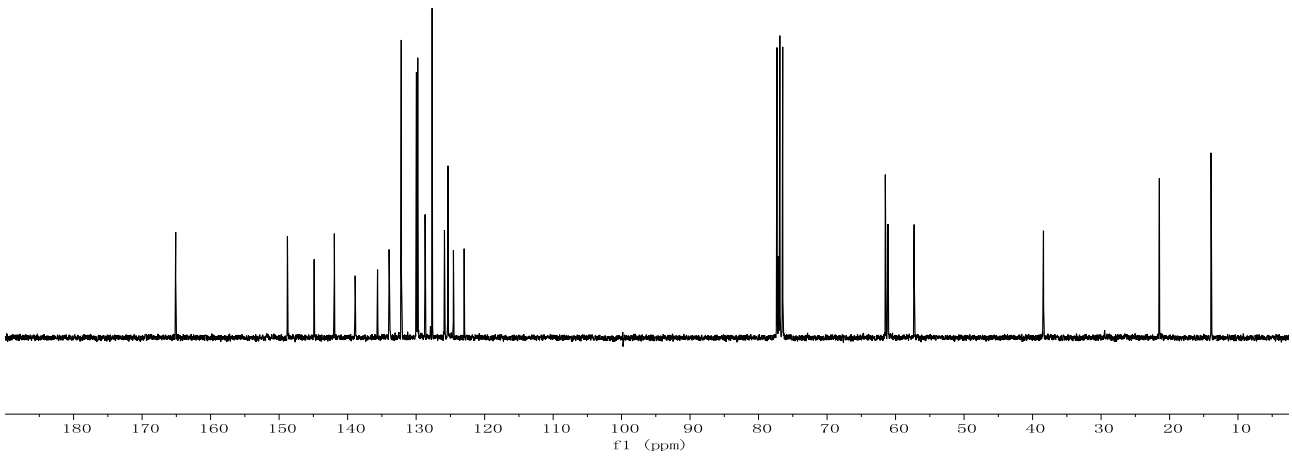
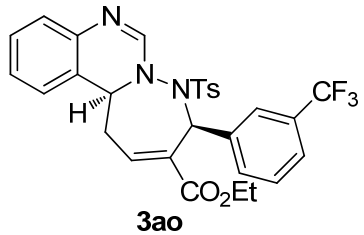
13.94


f1 (ppm)



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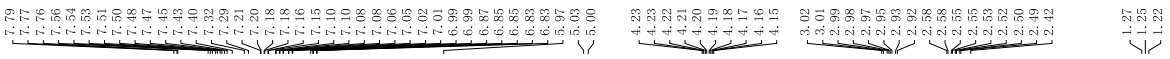
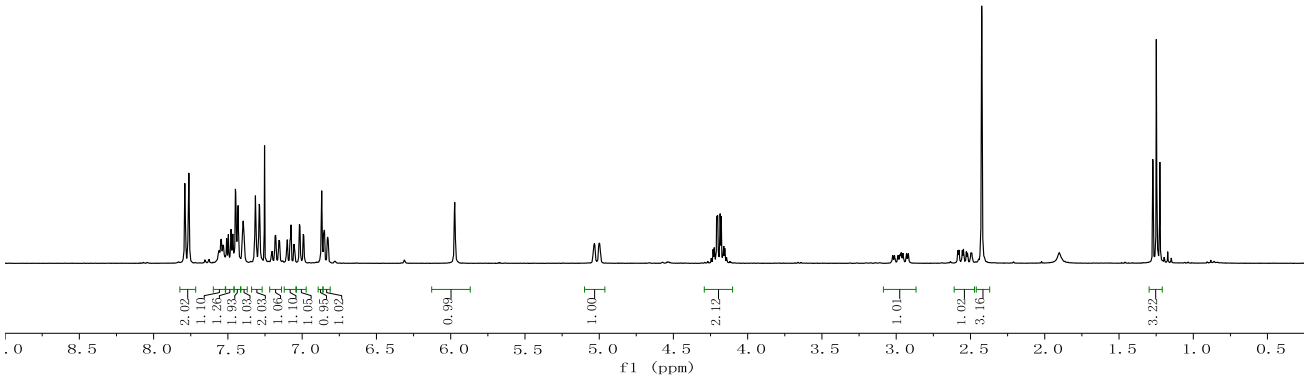
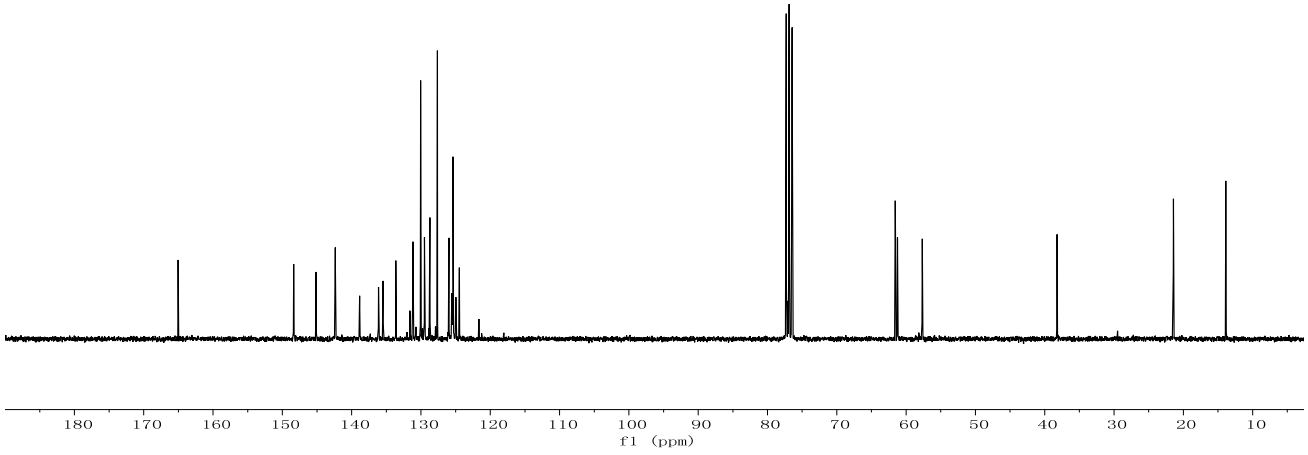
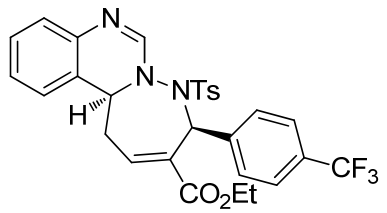
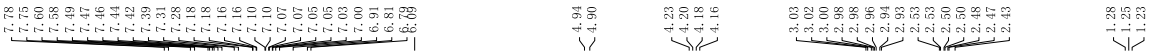


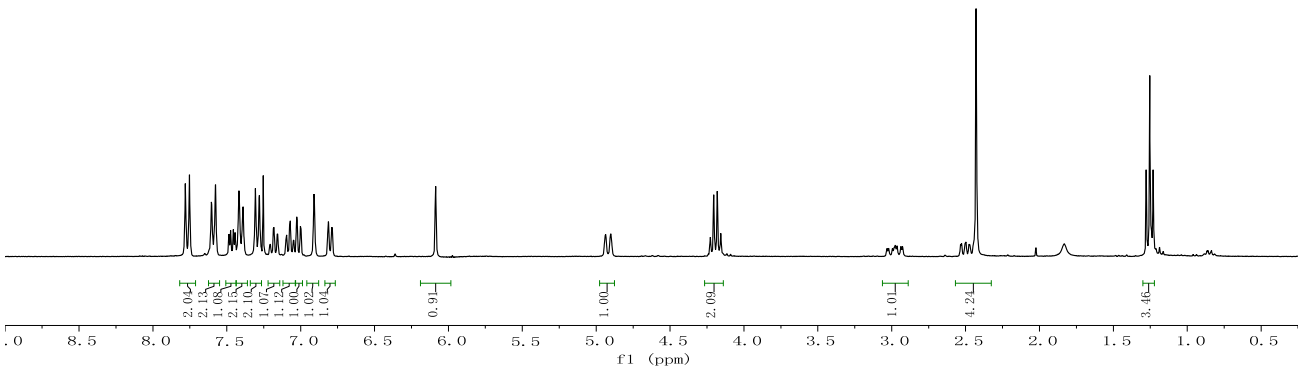


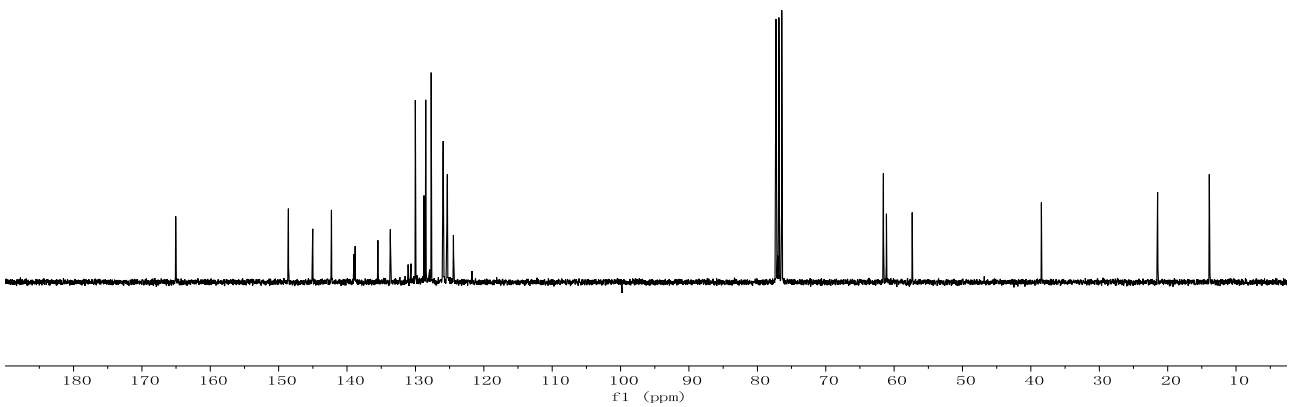


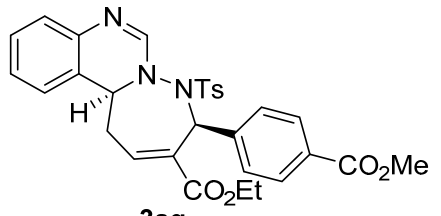


3ap

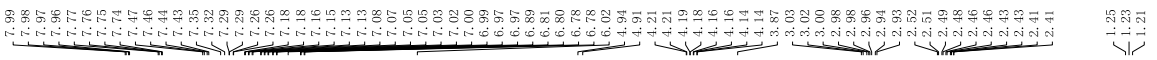


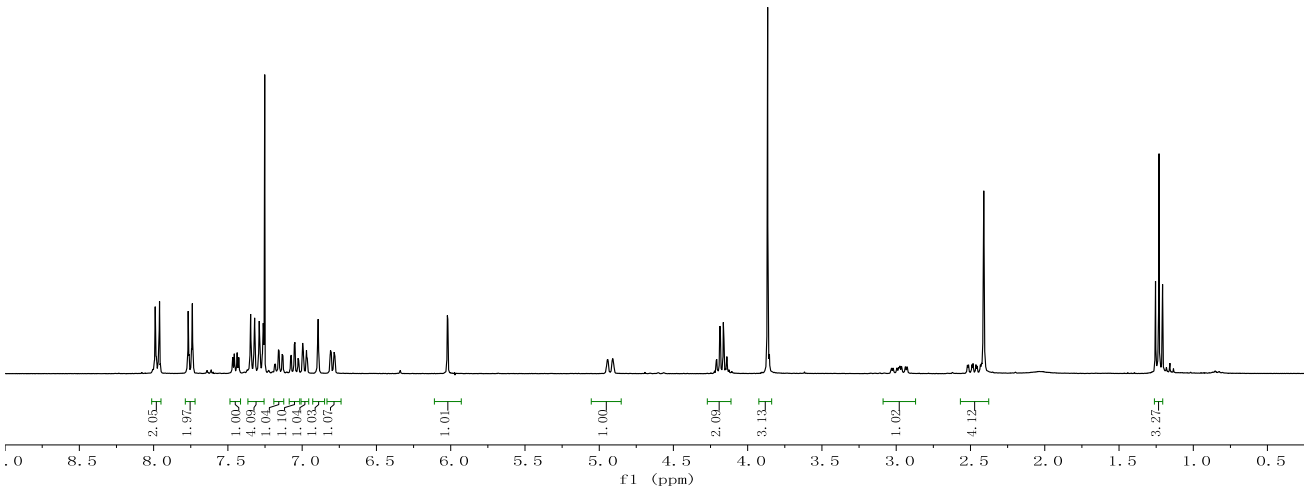


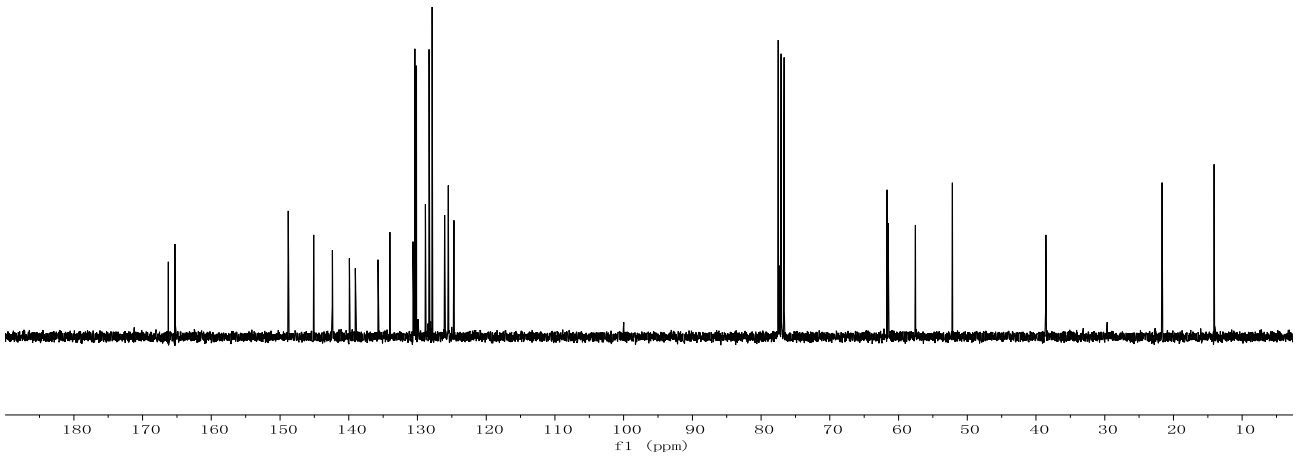


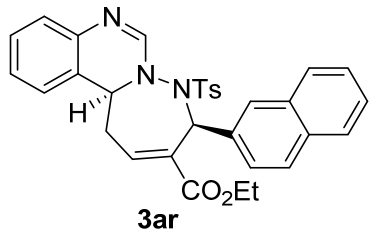


3aq

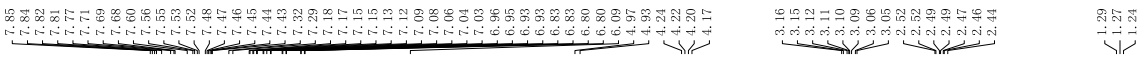


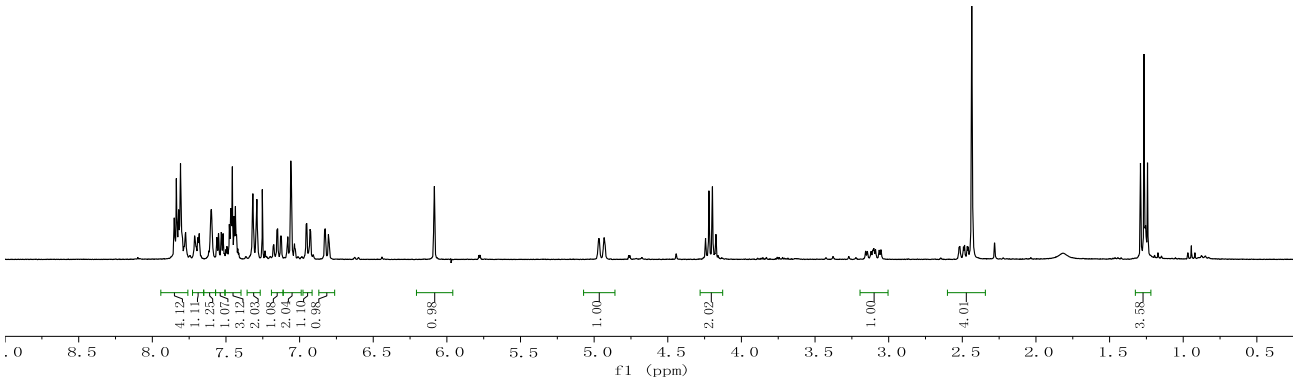


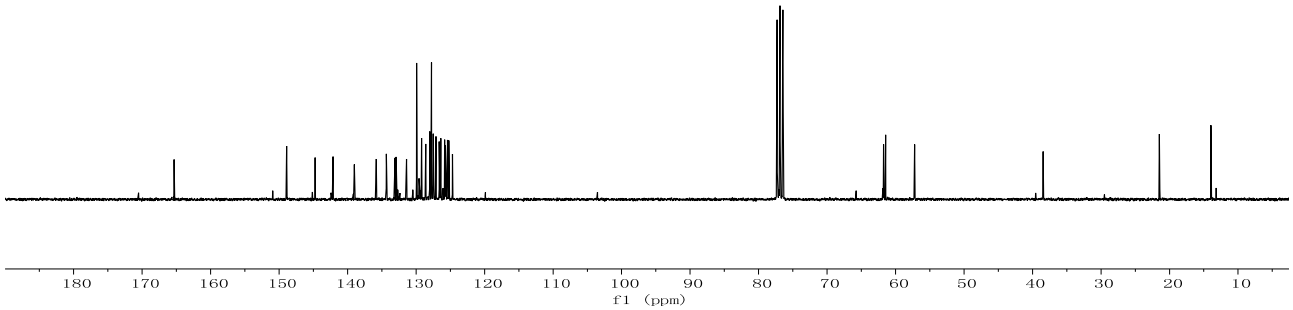


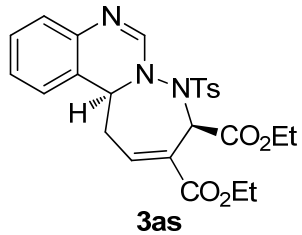

N
N
NTs
H
CO2Et

3ar

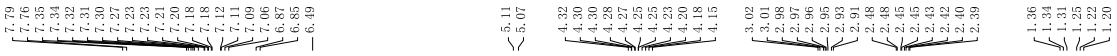


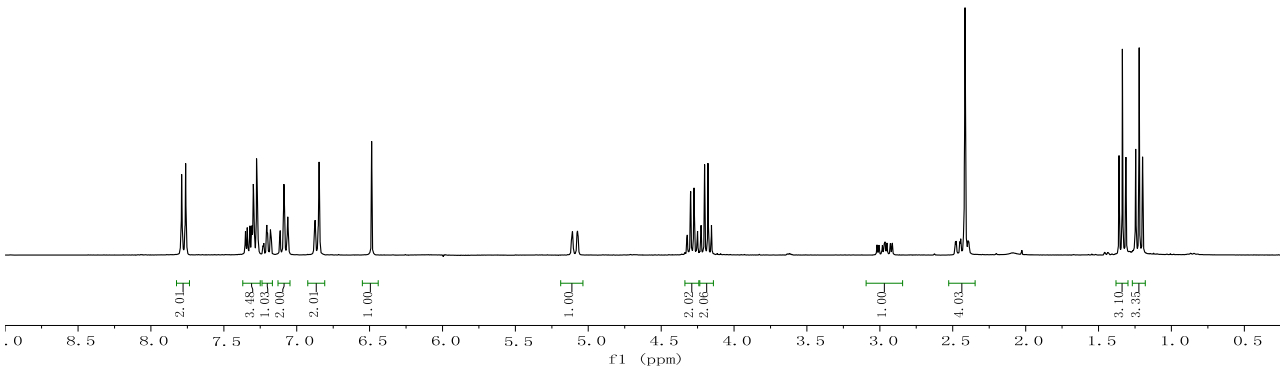

4.12
1.11
1.25
1.07
3.12
2.03
1.08
2.04
1.10
0.98
0.98
1.00
2.02
1.00
4.01
3.58
f1 (ppm)


f1 (ppm)

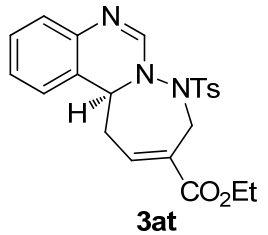

N
N
NTs
H
CO2Et
CO2Et

3as

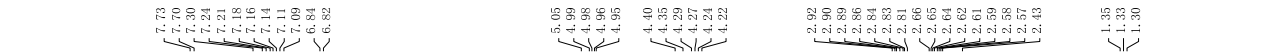

7.79 7.76 7.35 7.34 7.32 7.31 7.30 7.27 7.23 7.23 7.21 7.20 7.18 7.18 7.12 7.11 7.09 7.06 6.87 6.85 6.49
5.11 5.07
4.32 4.30 4.30 4.28 4.27 4.25 4.25 4.23 4.20 4.18 4.15
3.02 3.01 2.98 2.97 2.96 2.95 2.93 2.91 2.48 2.48 2.45 2.45 2.43 2.42 2.40 2.39
1.36 1.34 1.31 1.25 1.22 1.20


2.01 3.48 1.03 2.00 2.01 1.00 1.00 2.02 2.06 1.00 4.03 3.10 3.35
f1 (ppm)


166.92 165.05
148.66 144.99 142.55 138.83 134.92 132.59 129.81 128.68 128.03 125.94 125.66 125.35 124.63
62.42 61.51 60.28 57.87
38.72
21.46
14.00 13.81
f1 (ppm)


N
N
NTs
H
CO2Et

3at


7.73
7.70
7.30
7.24
7.21
7.18
7.16
7.14
7.11
7.09
6.84
6.82
5.05
4.99
4.98
4.96
4.95
4.40
4.35
4.29
4.27
4.24
4.22
2.92
2.90
2.89
2.86
2.84
2.83
2.81
2.66
2.65
2.64
2.62
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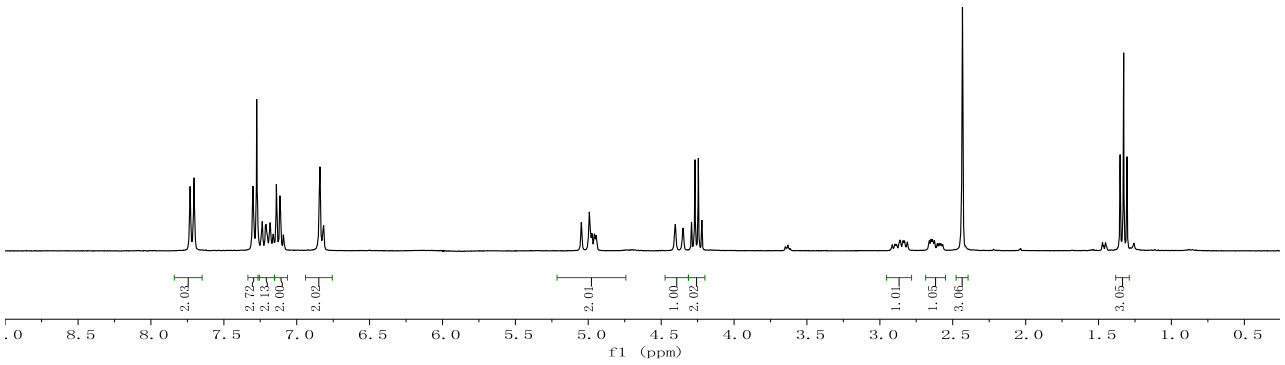
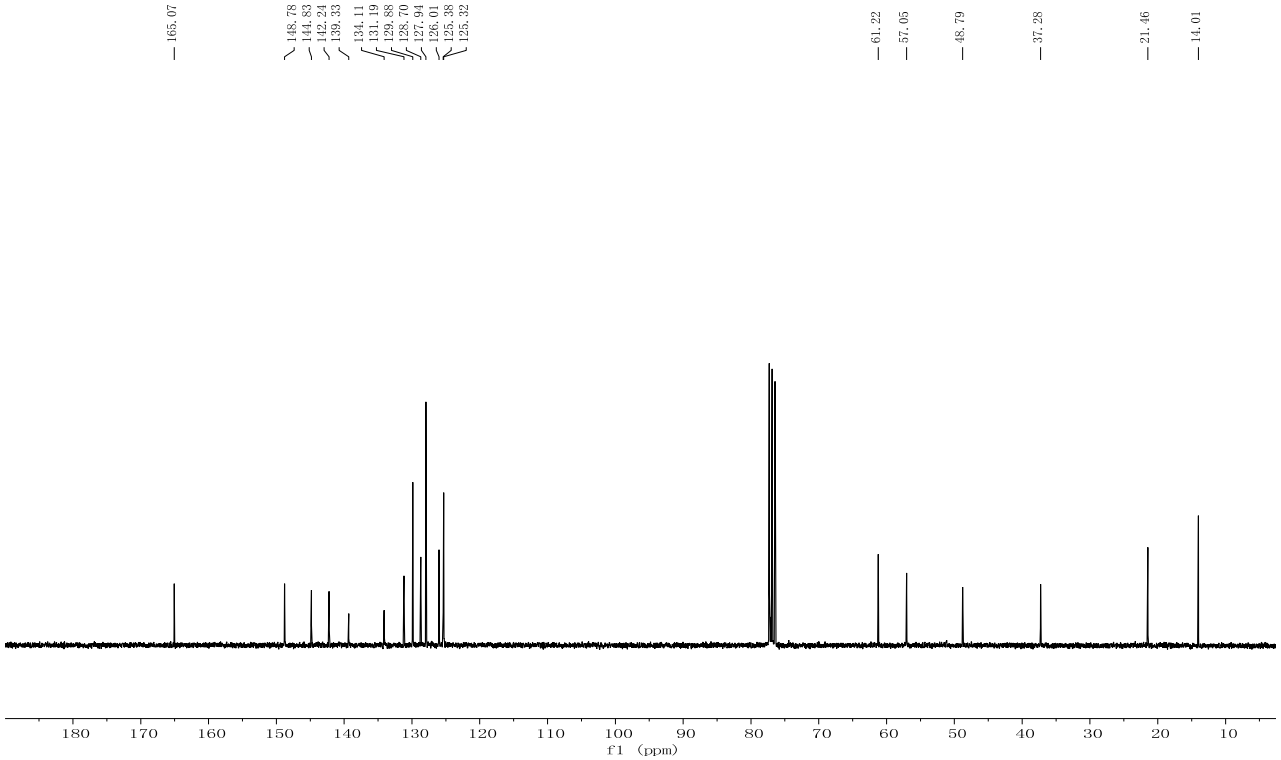
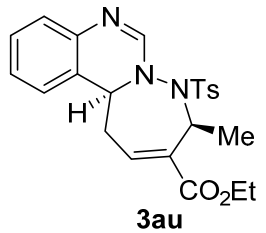
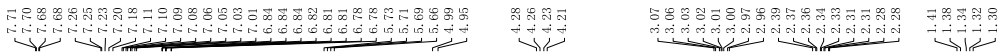
2.58
2.57
2.43
1.35
1.33
1.30

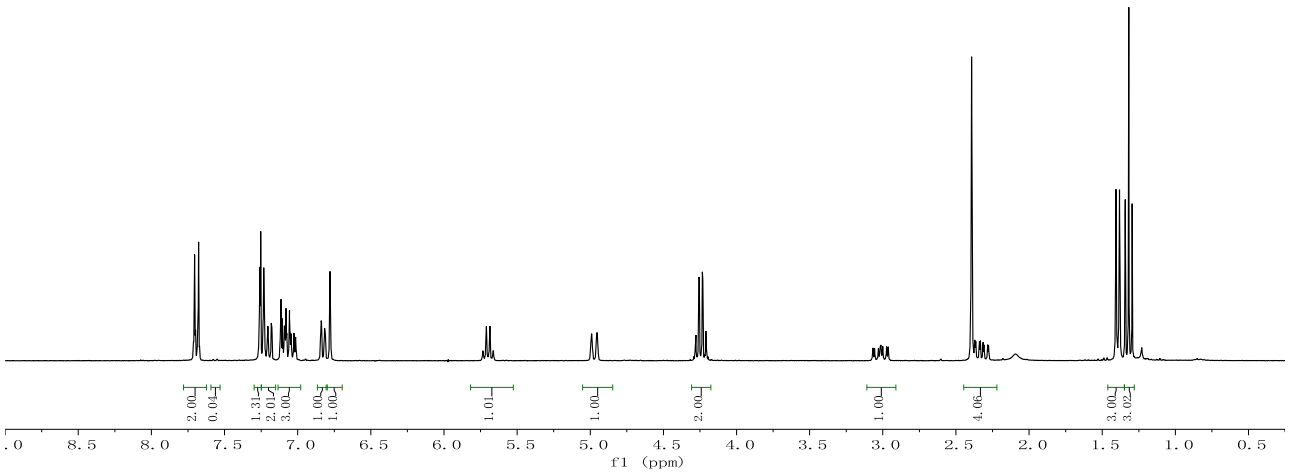

2.03
2.72
2.13
2.00
2.02
2.01
1.00
2.02
1.01
1.05
3.06
3.05
f1 (ppm)


165.07
148.78
144.83
142.24
139.33
134.11
131.19
129.88
128.70
127.94
126.01
125.38
125.32
61.22
57.05
48.79
37.28
21.46
14.01
f1 (ppm)

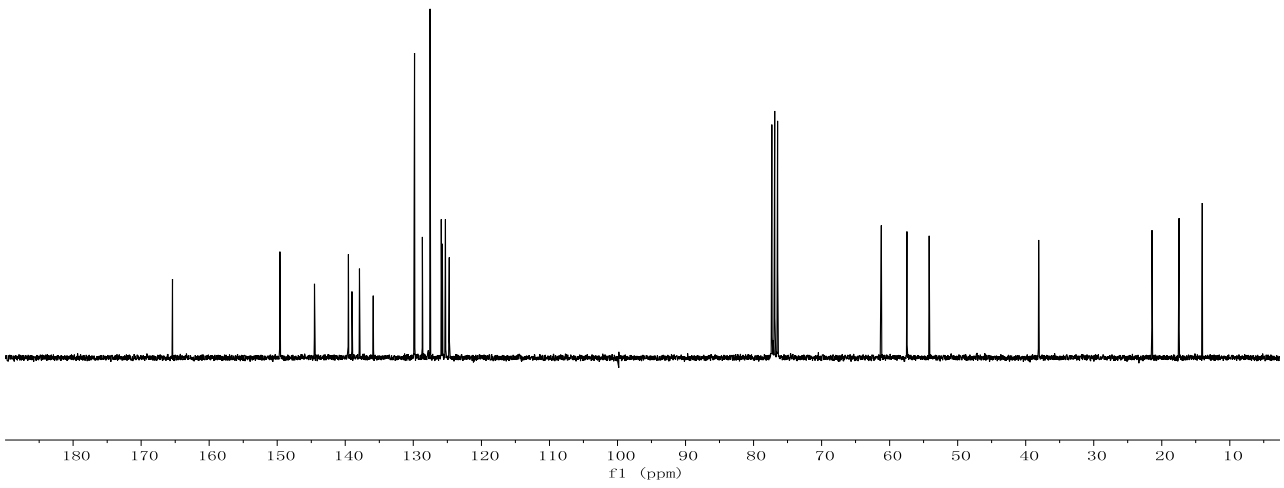

N
N
NTs
H
Me
CO2Et

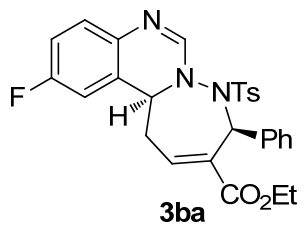
3au


7.71
7.70
7.68
7.68
7.26
7.25
7.23
7.20
7.18
7.11
7.10
7.09
7.08
7.06
7.05
7.03
7.01
6.84
6.84
6.84
6.82
6.81
6.81
6.78
6.78
5.73
5.71
5.69
5.66
4.99
4.95
4.28
4.26
4.23
4.21
3.07
3.06
3.03
3.02
3.01
3.00
2.97
2.96
2.39
2.37
2.36
2.34
2.33
2.31
2.31
2.28
2.28
1.41
1.38
1.34
1.32
1.30

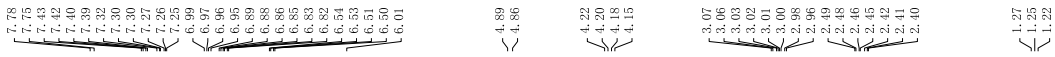

2.00
0.04
1.31
2.01
3.00
1.00
1.00
1.01
1.00
2.00
1.00
4.06
3.00
3.02
f1 (ppm)

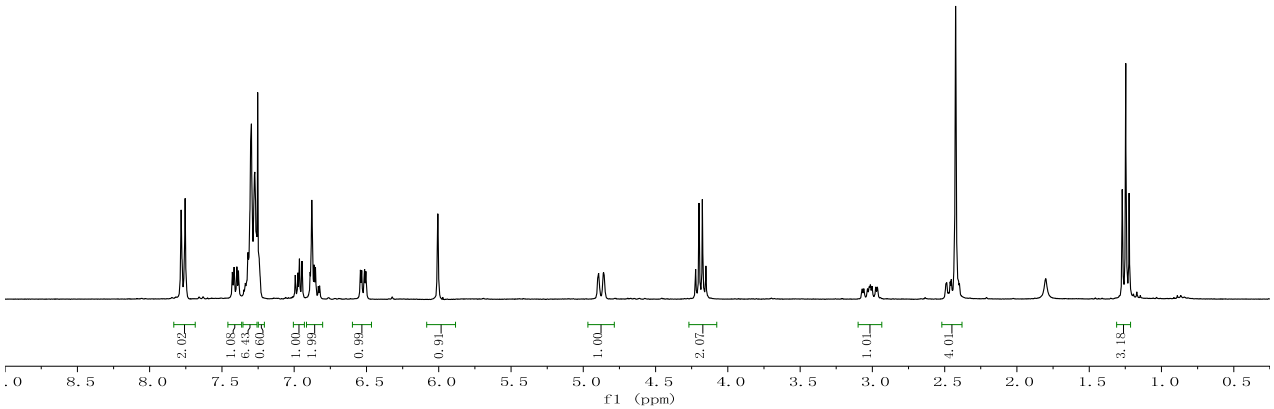

165.40
149.62
144.55
139.54
139.03
137.93
135.90
129.83
128.67
127.53
125.89
125.72
125.28
124.71
61.20
57.45
54.18
38.09
21.42
17.45
14.04

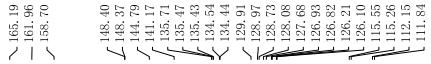

f1 (ppm)

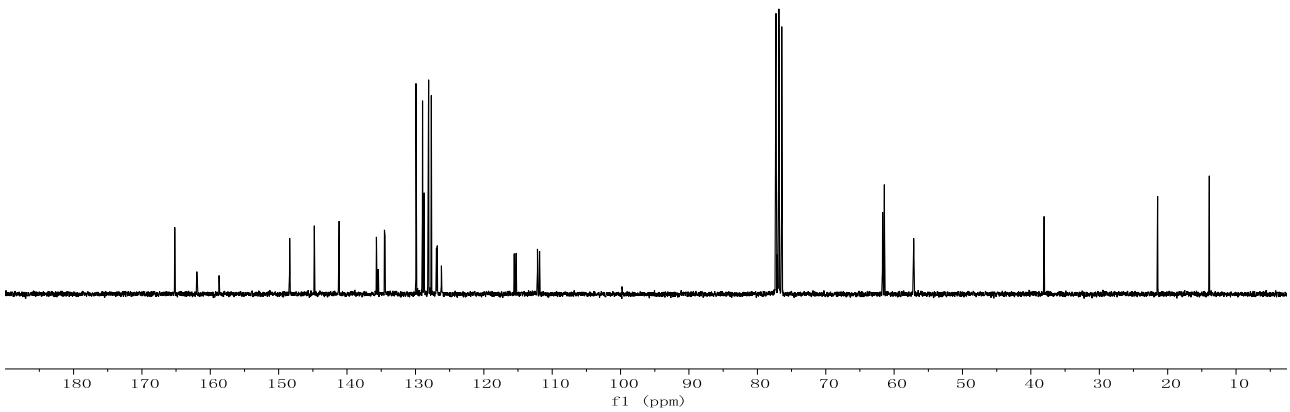

N
F
N
NTs
H
Ph
CO2Et

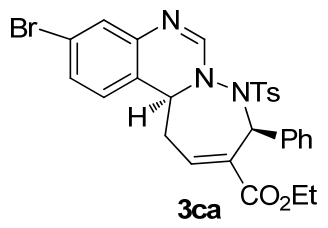
3ba


7.78 7.75 7.43 7.42 7.40 7.39 7.32 7.30 7.30 7.27 7.26 7.25 6.99 6.97 6.96 6.95 6.89 6.88 6.86 6.85 6.83 6.82 6.54 6.53 6.51 6.50 6.01
4.89 4.86
4.22 4.20 4.18 4.15
3.07 3.06 3.03 3.02 3.01 3.00 2.98 2.96
2.49 2.48 2.46 2.45 2.42 2.41 2.40
1.27 1.25 1.22

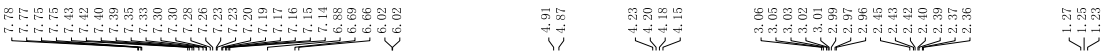

2.02 1.08 6.43 0.60 1.00 1.99 0.99 0.91 1.00 2.07 1.01 4.01 3.18
f1 (ppm)


165.19 161.96 158.70
148.40 148.37 144.79 141.17 135.71 135.47 135.43 134.54 134.44 129.91 128.97 128.73 128.08 127.68 126.93 126.82 126.21 126.10 115.55 115.26 112.15 111.84
61.68 61.42 57.16 57.13
38.06
21.46
13.91


f1 (ppm)


Br
N
N
NTs
H
Ph
CO2Et

3ca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7.42
7.40
7.39
7.35
7.33
7.30
7.30
7.28
7.26
7.23
7.23
7.20
7.19
7.17
7.16
7.15
7.14
6.88
6.69
6.66
6.02
6.02
4.91
4.87
4.23
4.20
4.18
4.15
3.06
3.05
3.03
3.02
3.01
2.99
2.97
2.96
2.45
2.43
2.42
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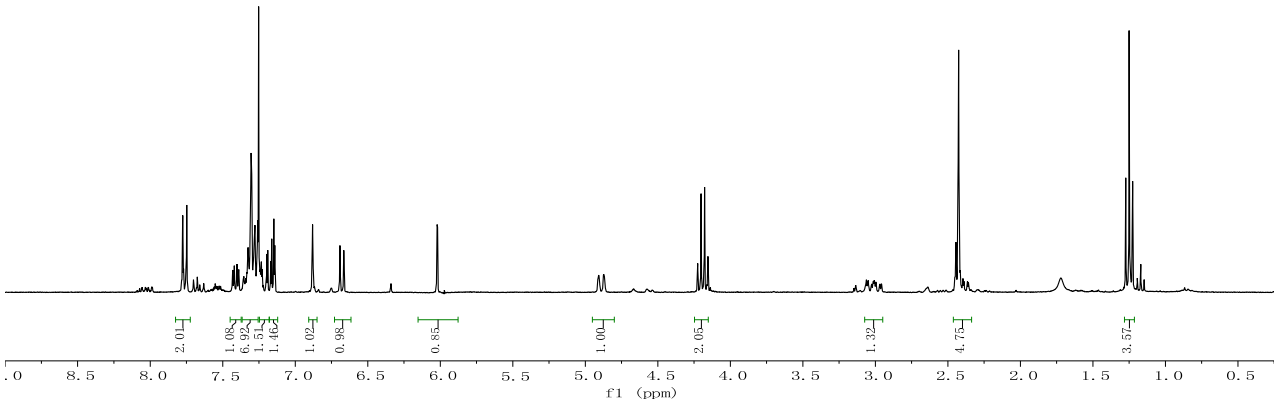
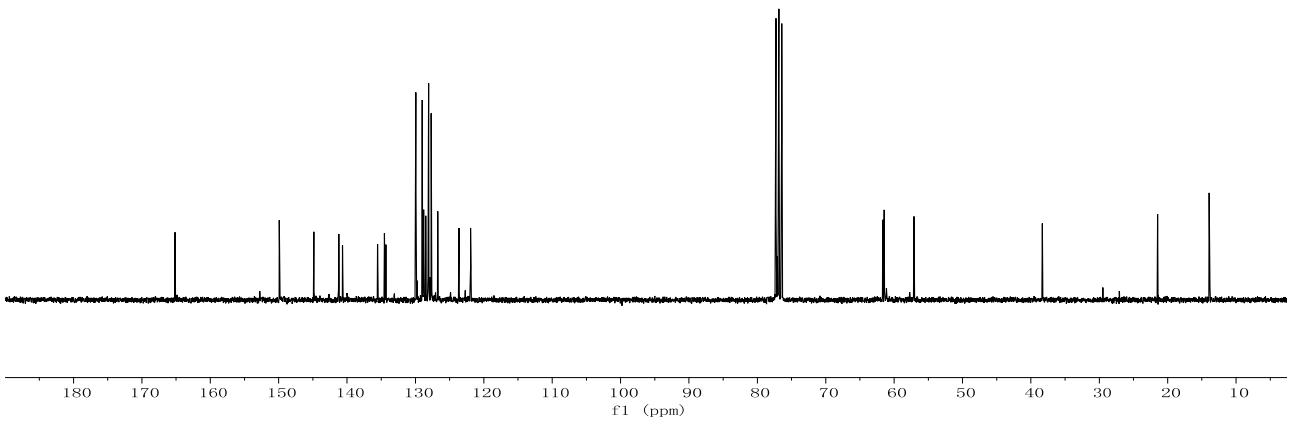
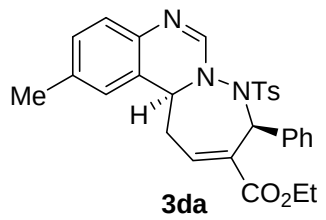
2.39
2.37
2.36
1.27
1.25
1.23

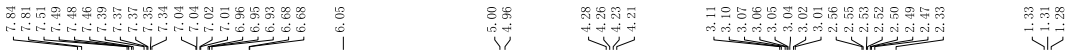

2.01
1.08
6.92
1.51
1.46
1.02
0.98
0.85
1.00
2.05
1.32
4.75
3.57
f1 (ppm)


165.16
149.90
144.85
141.21
140.67
135.53
134.54
134.33
129.94
129.01
128.79
128.48
128.11
128.06
127.69
126.73
123.61
121.94
61.65
61.44
57.10
38.32
21.48
13.92


f1 (ppm)


N
N
NTs
Me
H
Ph
CO2Et

3da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7.49
7.48
7.46
7.39
7.37
7.37
7.35
7.34
7.04
7.04
7.02
7.01
6.96
6.95
6.93
6.68
6.68
6.05
5.00
4.96
4.28
4.26
4.23
4.21
3.11
3.10
3.07
3.06
3.05
3.04
3.02
3.01
2.56
2.55
2.53
2.52
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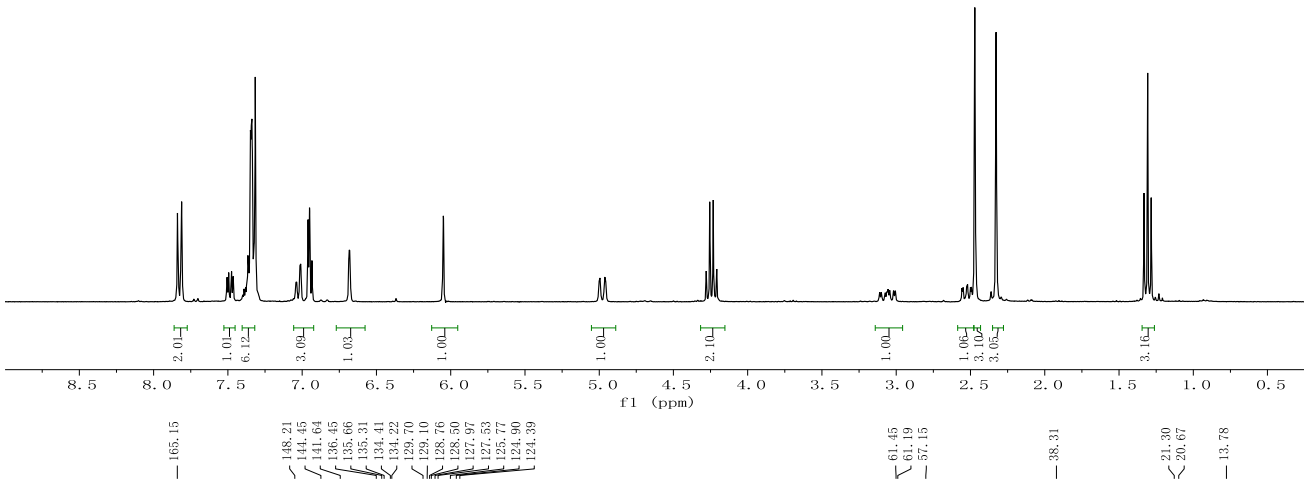
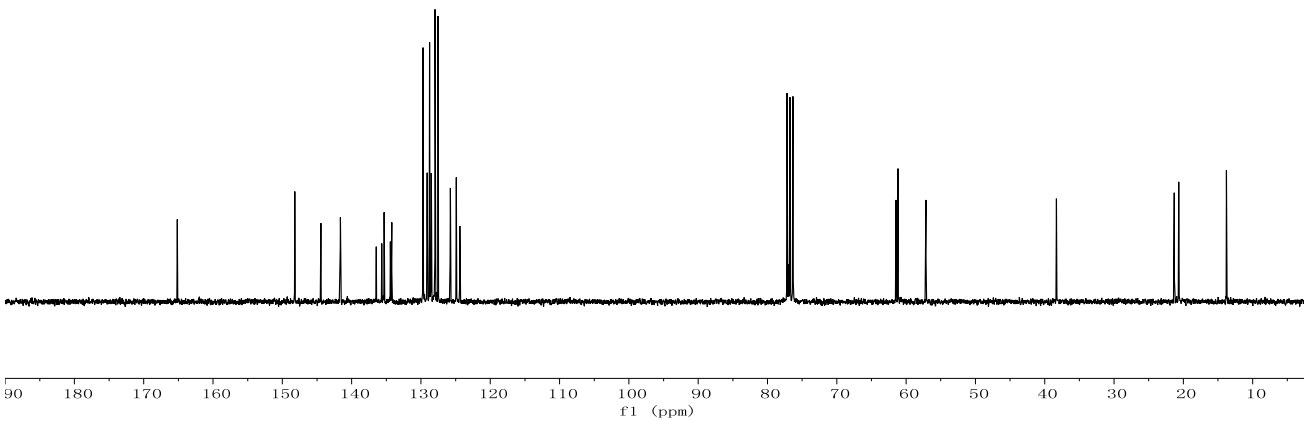
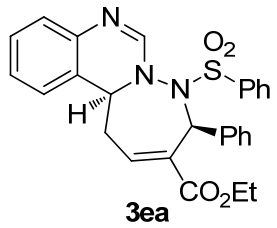
2.49
2.47
2.33
1.33
1.31
1.28

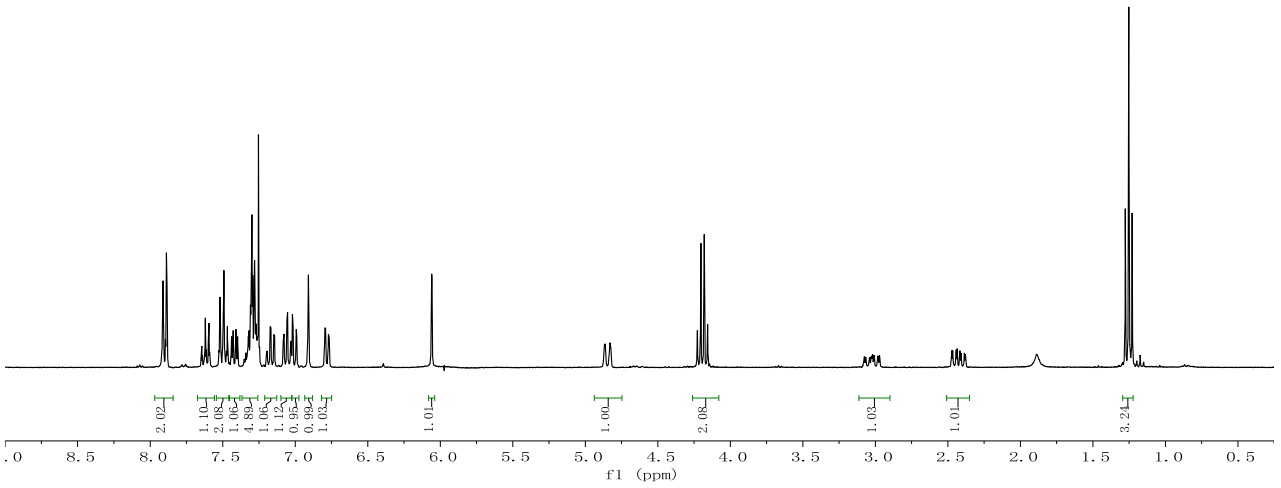

2.01
1.01
6.12
3.09
1.03
1.00
1.00
2.10
1.00
1.06
3.10
3.05
3.16
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

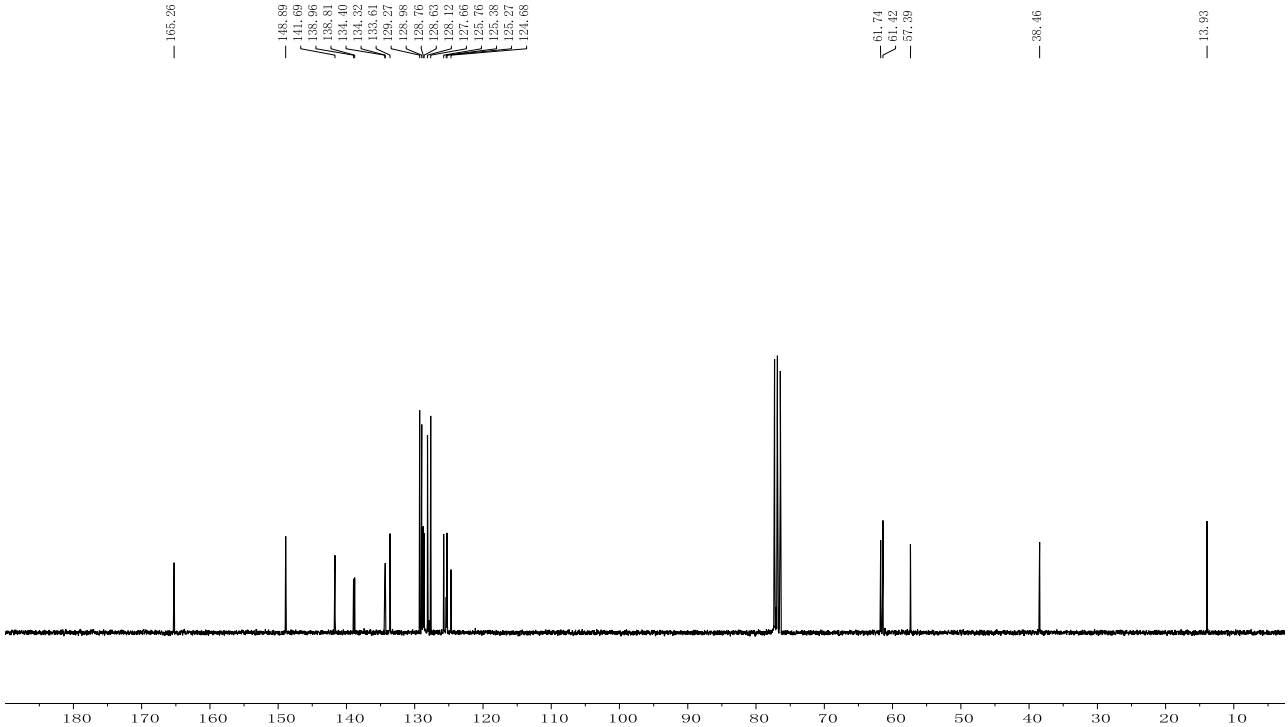
165.15
148.21
144.45
141.64
136.45
135.66
135.31
134.41
134.22
129.70
129.10
128.76
128.50
127.97
127.53
125.77
124.90
124.39
61.45
61.19
57.15
38.31
21.30
20.67
13.78


90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


N
O2
S
Ph
N
N
H
Ph
CO2Et

3ea


2.02
1.10
2.08
1.06
4.89
1.06
1.12
0.95
0.99
1.03
1.01
1.00
2.08
1.03
1.01
3.24
f1 (ppm)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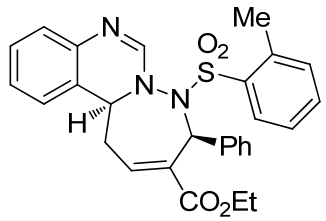
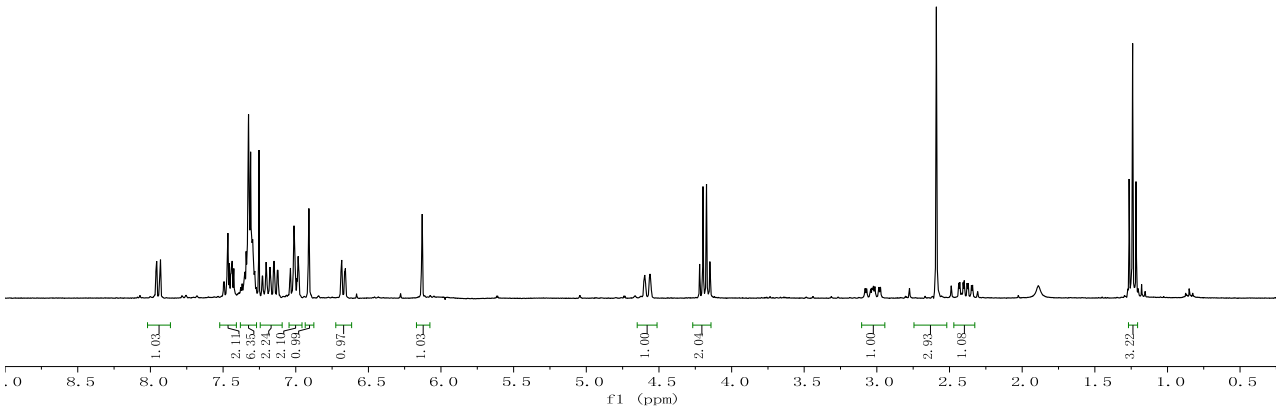
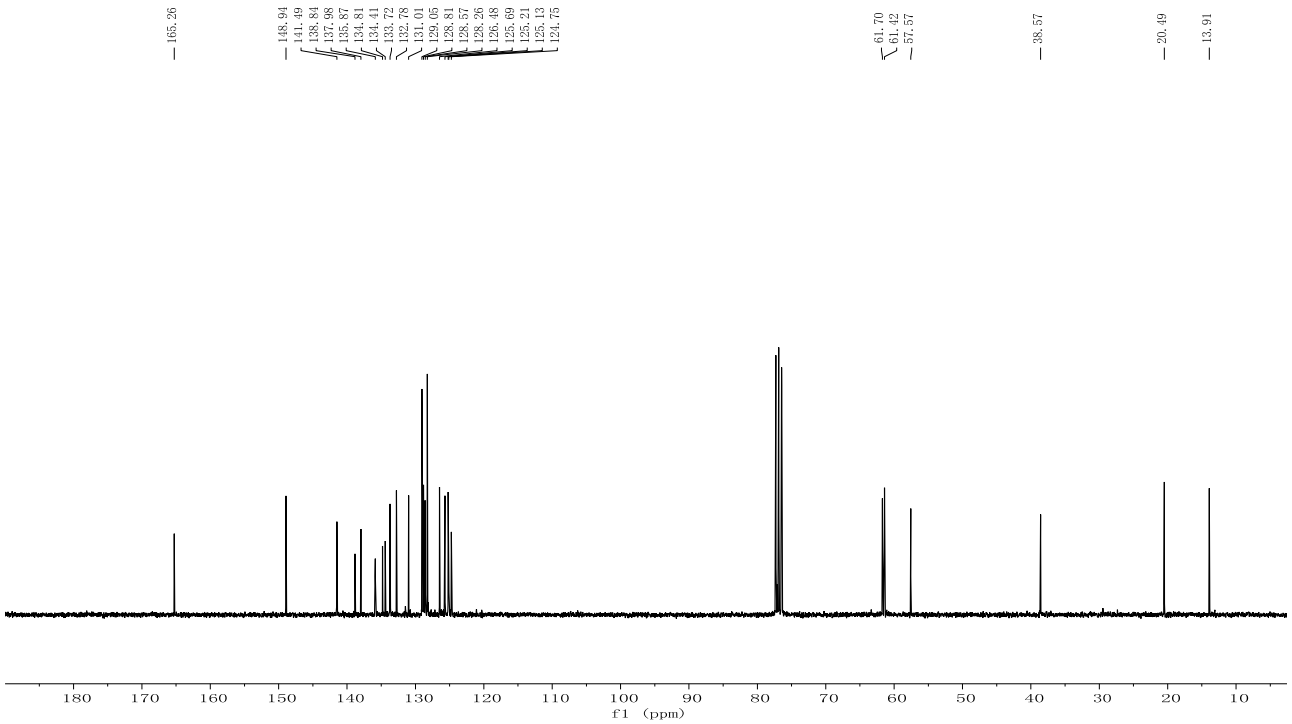
138.96
138.81
134.40
134.32
133.61
129.27
128.98
128.76
128.63
128.12
127.66
125.76
125.38
125.27
124.68
61.74
61.42
57.39
38.46
13.93
f1 (ppm)

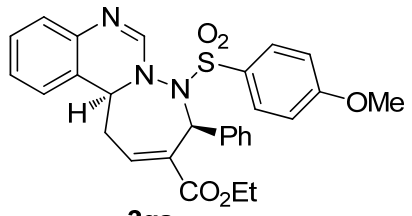

Me
O2
S
N
N
N
H
Ph
CO2Et

3fa

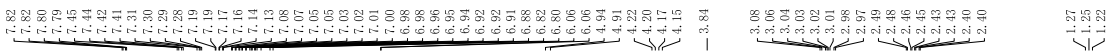

7.96
7.96
7.93
7.93
7.50
7.47
7.44
7.43
7.33
7.31
7.23
7.20
7.18
7.15
7.15
7.13
7.12
7.04
7.01
6.98
6.91
6.68
6.66
6.13
4.60
4.56
4.22
4.20
4.17
4.15
3.08
3.07
3.04
3.03
3.02
3.01
2.99
2.98
2.59
2.44
2.43
2.41
2.40
2.38
2.37
2.35
2.34
1.26
1.24
1.22

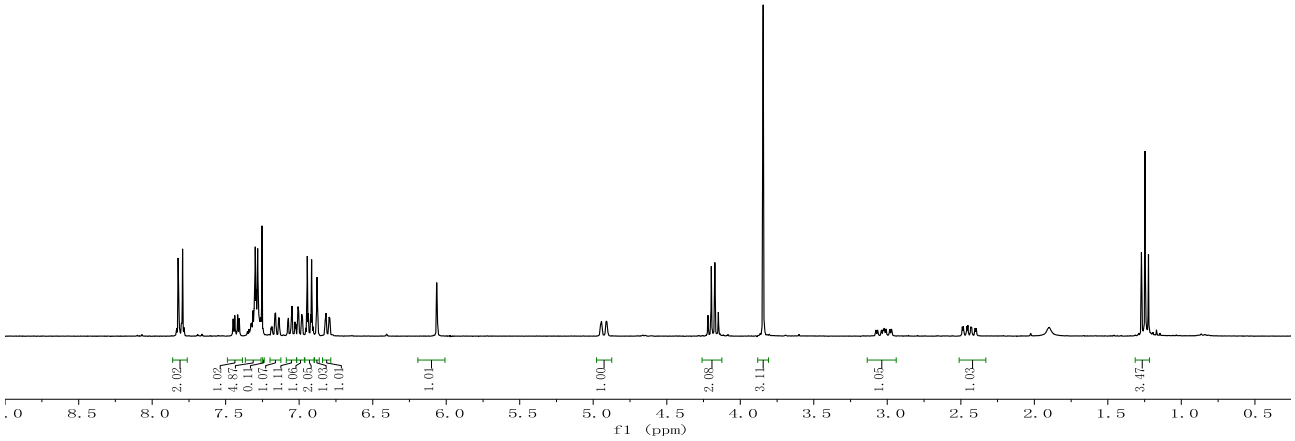

1.03
2.11
6.35
2.24
2.10
0.99
0.97
1.03
1.00
2.04
1.00
2.93
1.08
3.22
f1 (ppm)

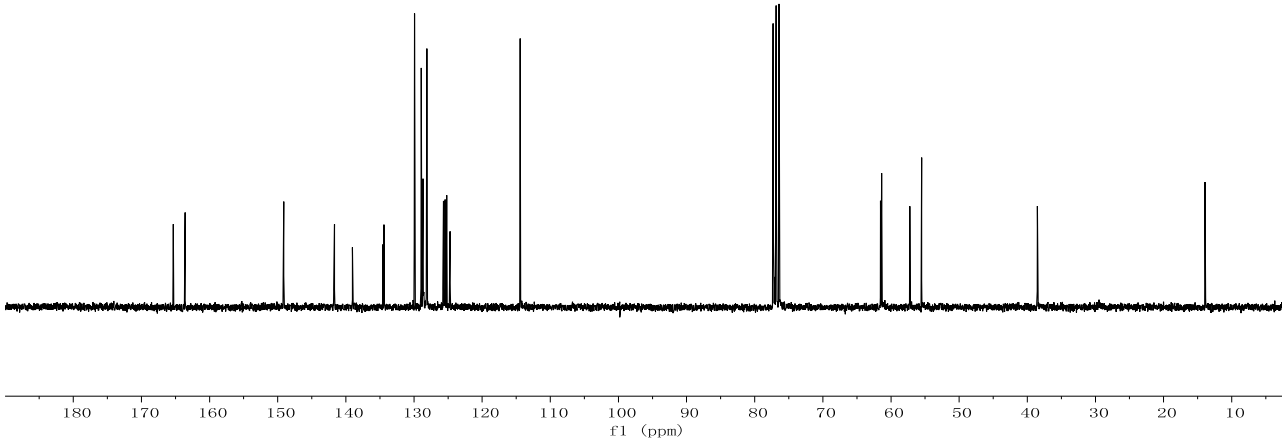

165.26
148.94
141.49
138.84
137.98
135.87
134.81
134.41
133.72
132.78
131.01
129.05
128.81
128.57
128.26
126.48
125.69
125.21
125.13
124.75
61.70
61.42
57.57
38.57
20.49
13.91
f1 (ppm)

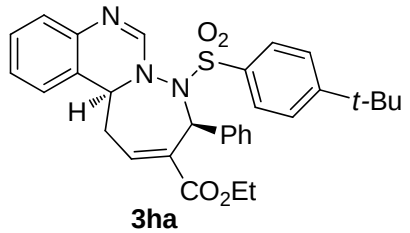


3ga

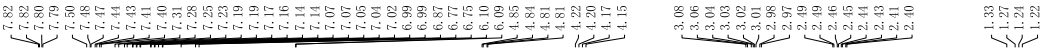


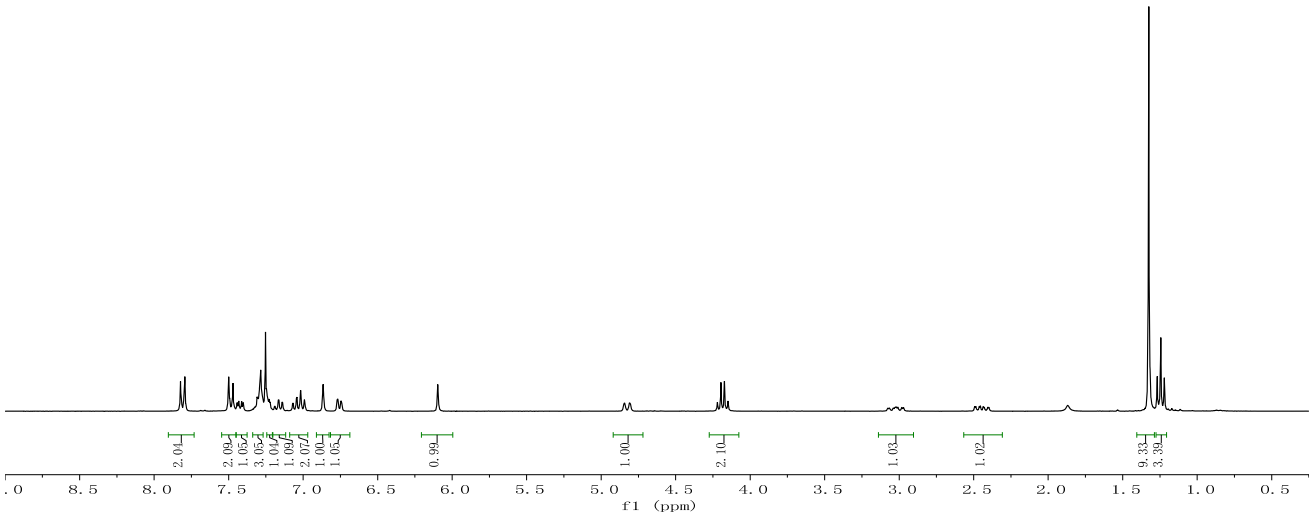


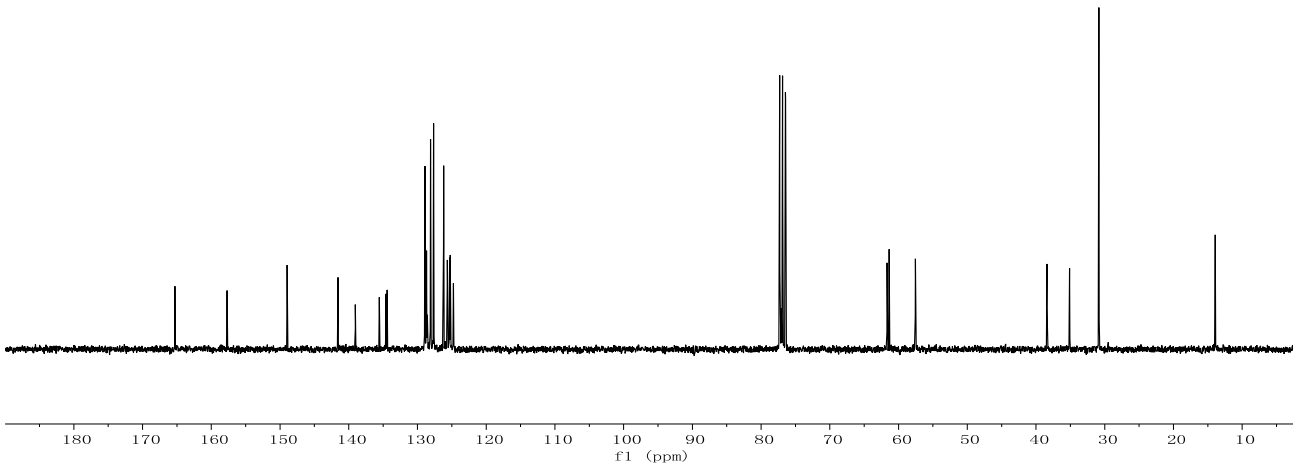


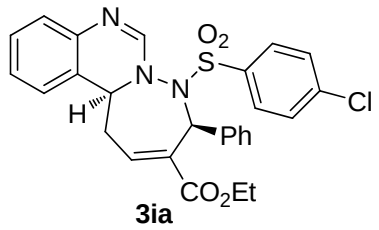

N
O2
S
N
N
H
t-Bu
Ph
CO2Et

3ha

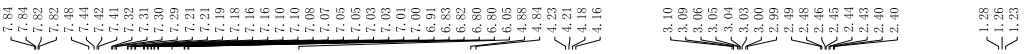


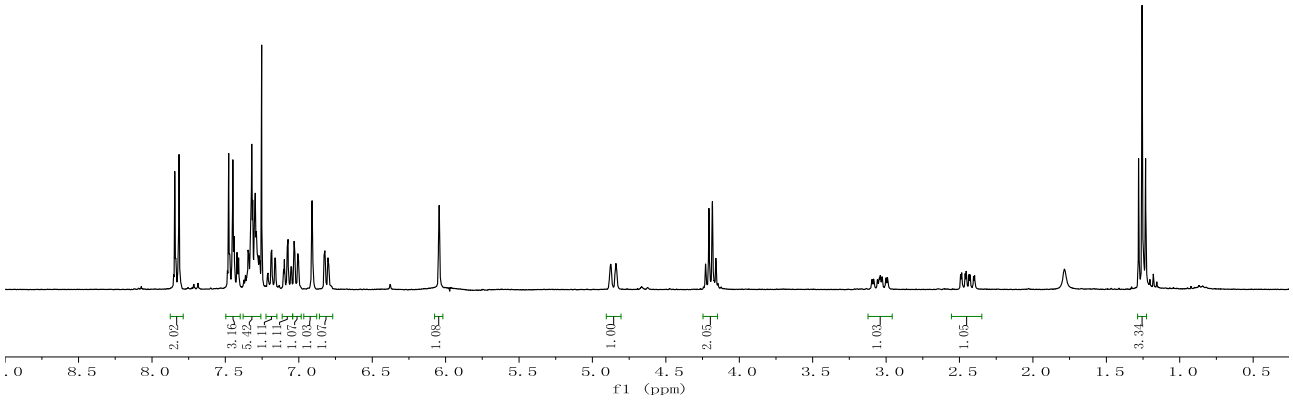

2.04
2.09
1.05
3.05
1.04
1.09
2.07
1.00
1.05
0.99
1.00
2.10
1.03
1.02
9.33
3.39
f1 (ppm)

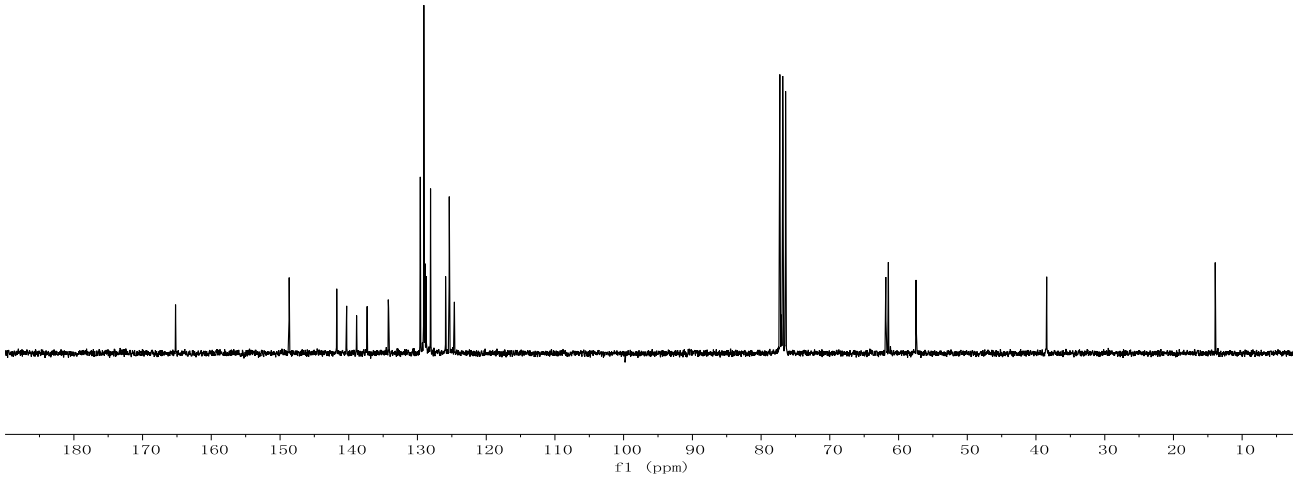

f1 (ppm)

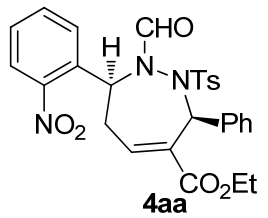


3ia

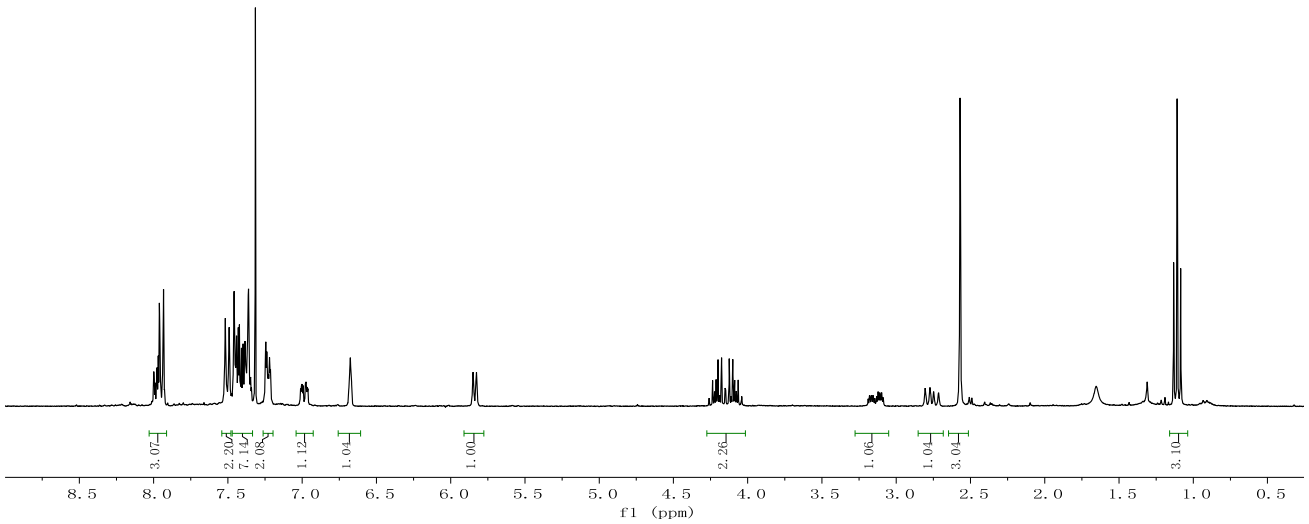


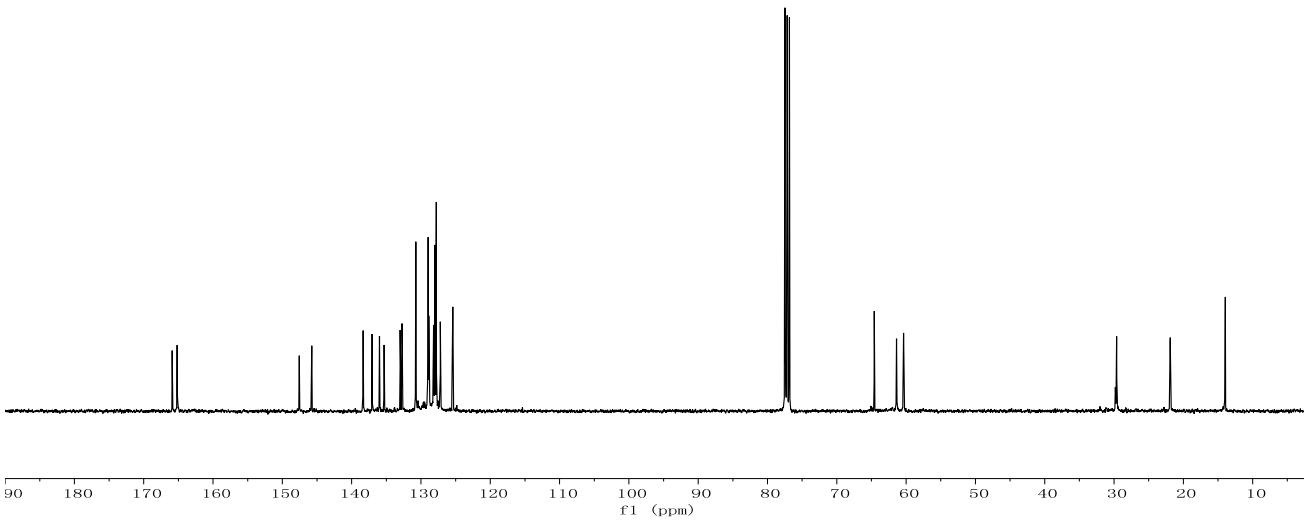


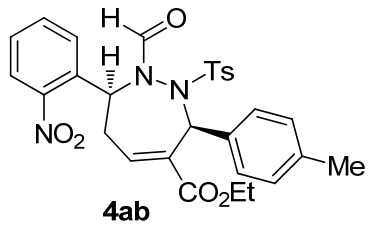



CHO
H
N
NTs
NO2
Ph
CO2Et

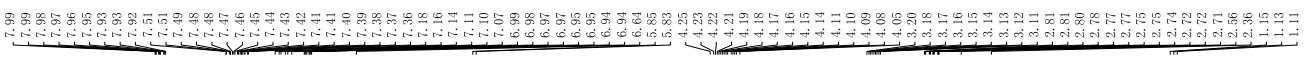
4aa

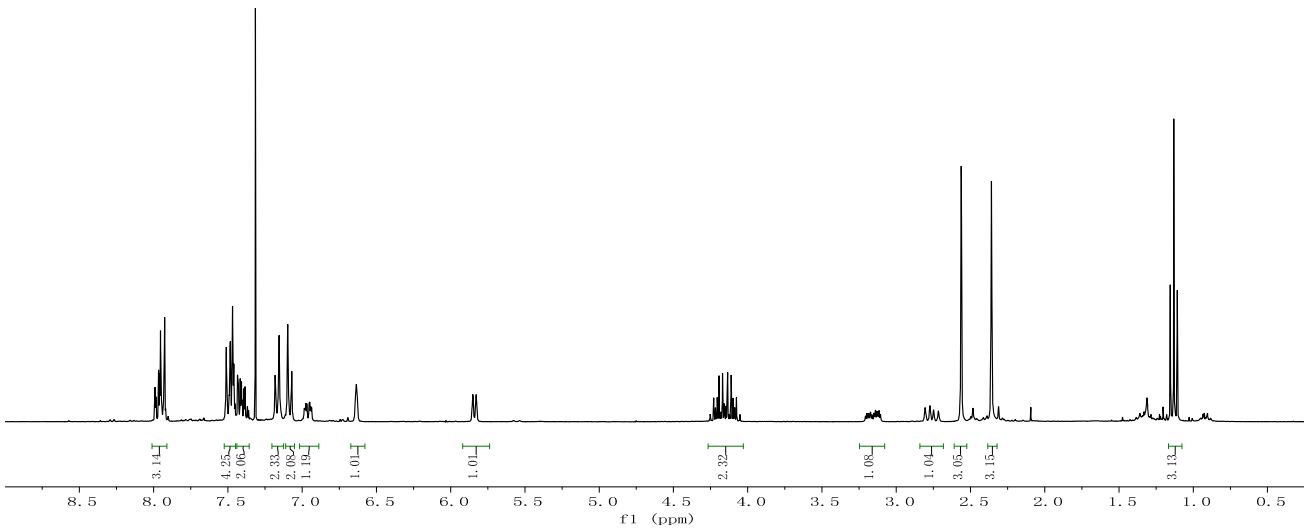

3.07
2.20
7.14
2.08
1.12
1.04
1.00
2.26
1.06
1.04
3.04
3.10
f1 (ppm)

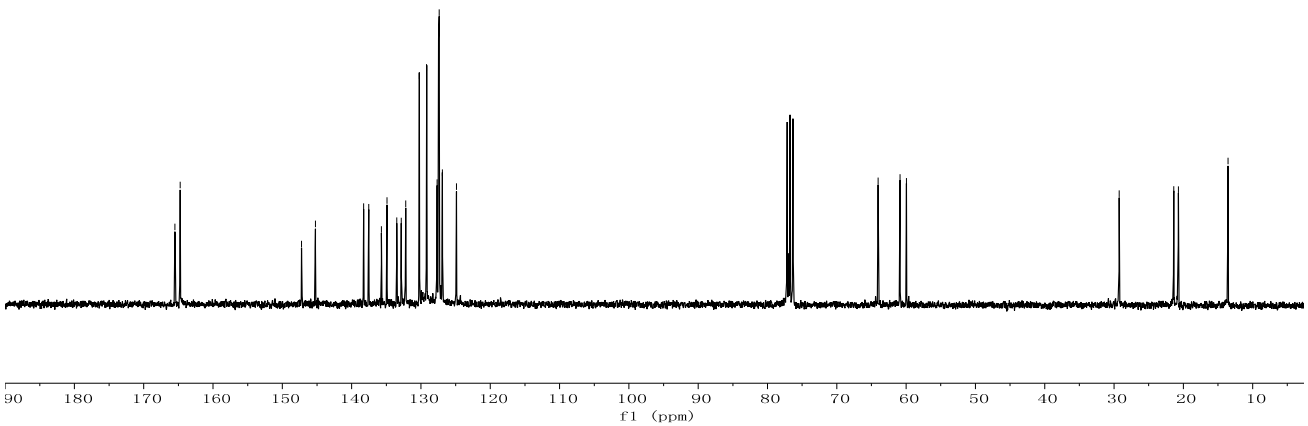

f1 (ppm)

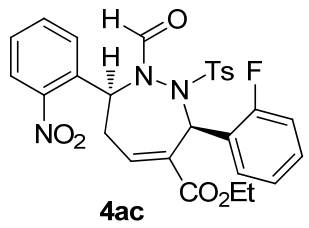

H
O
H
N
N
Ts
NO2
Me
CO2Et

4ab

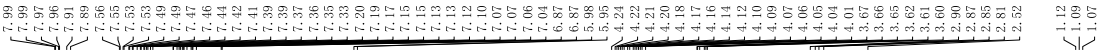


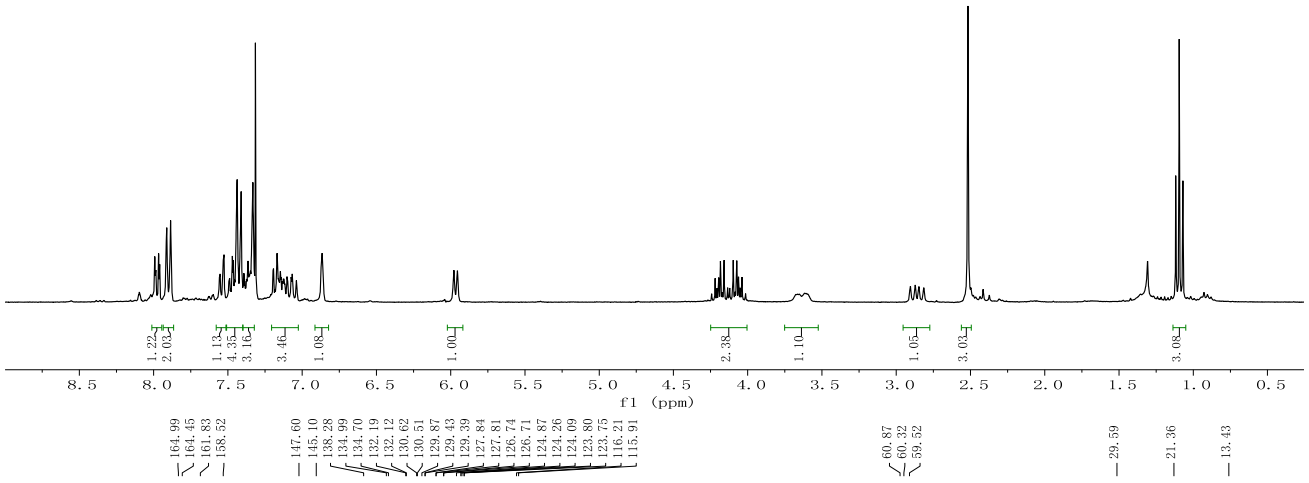

3.14
4.25
2.06
2.33
2.08
1.19
1.01
1.01
2.32
1.08
1.04
3.05
3.15
3.13
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

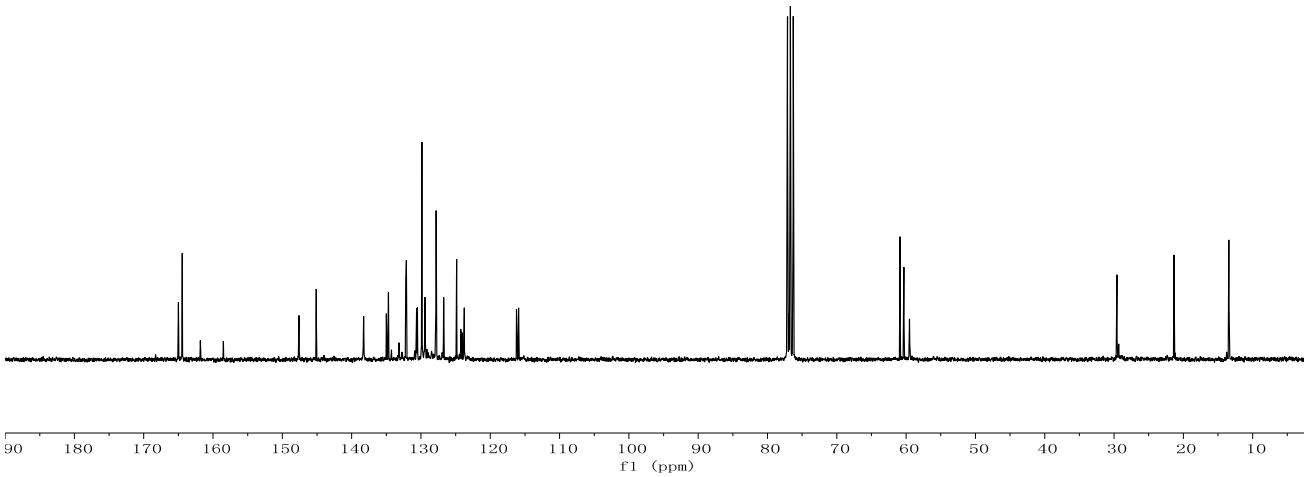

90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

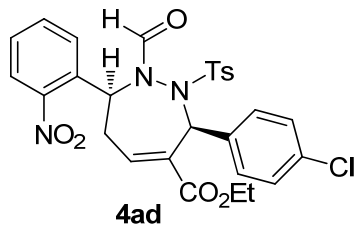


4ac

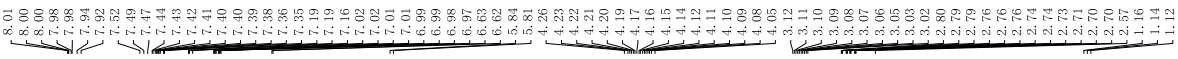


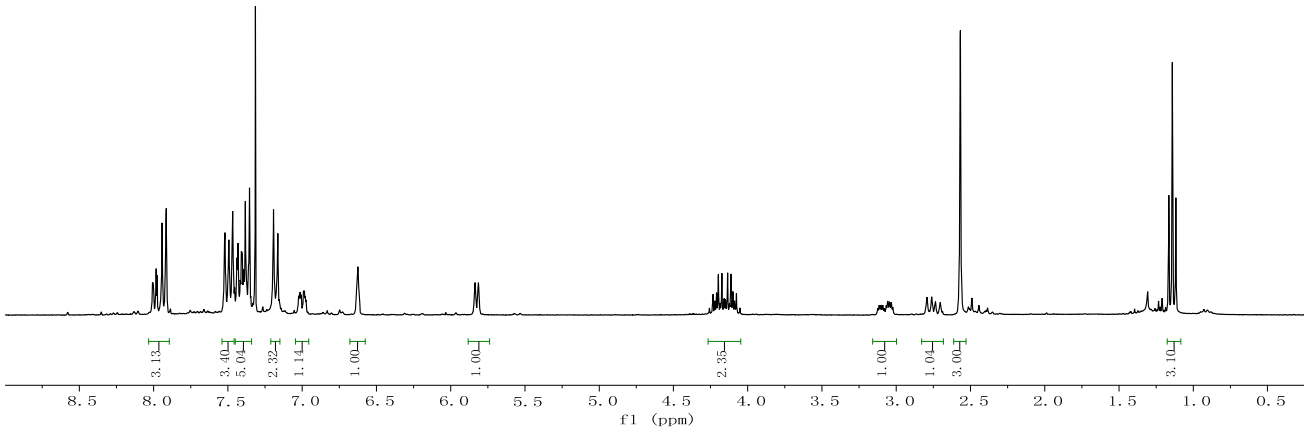


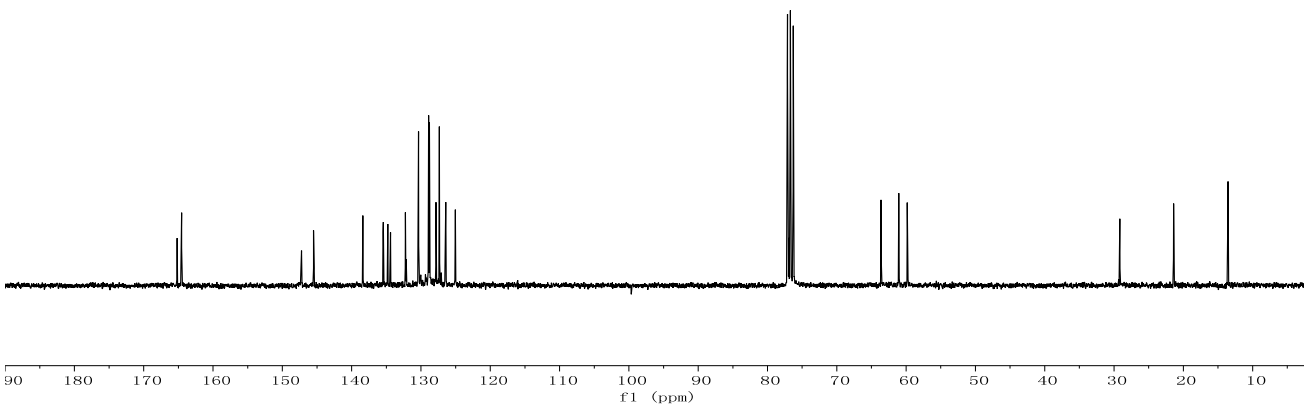


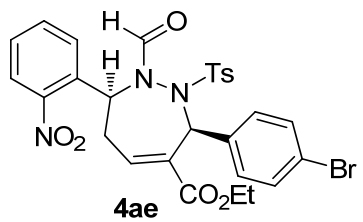

H
O
H
N
N
Ts
NO2
Cl
CO2Et

4ad

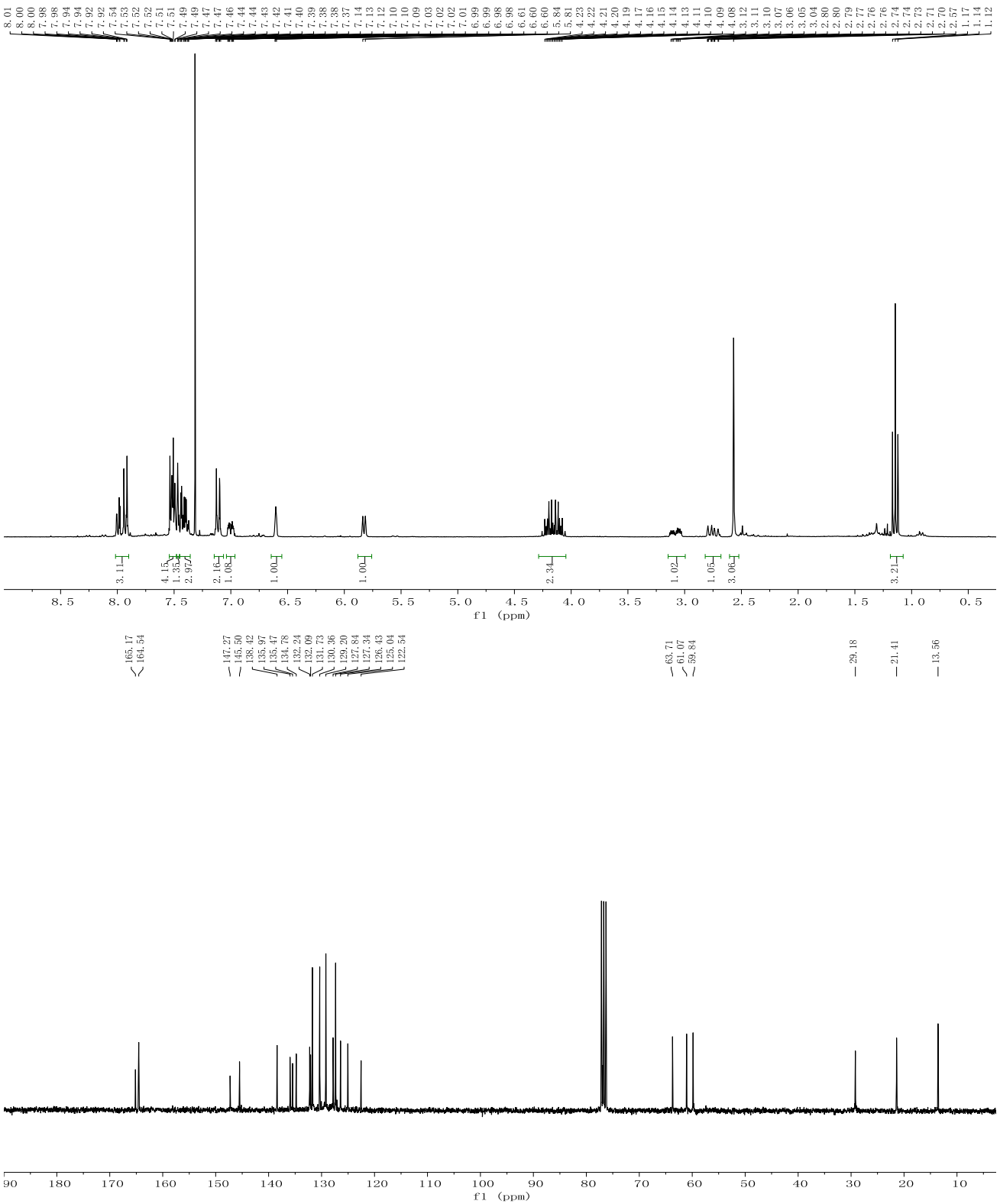


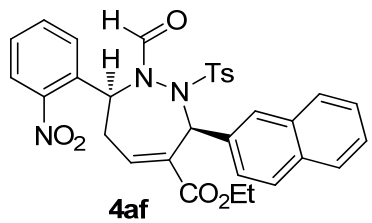

3.13
3.40
5.04
2.32
1.14
1.00
1.00
2.35
1.00
1.04
3.00
3.10
f1 (ppm)


f1 (ppm)

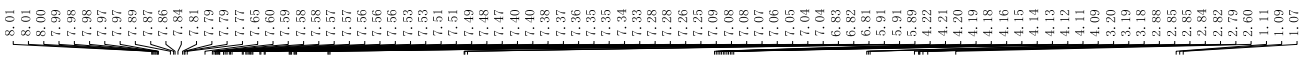


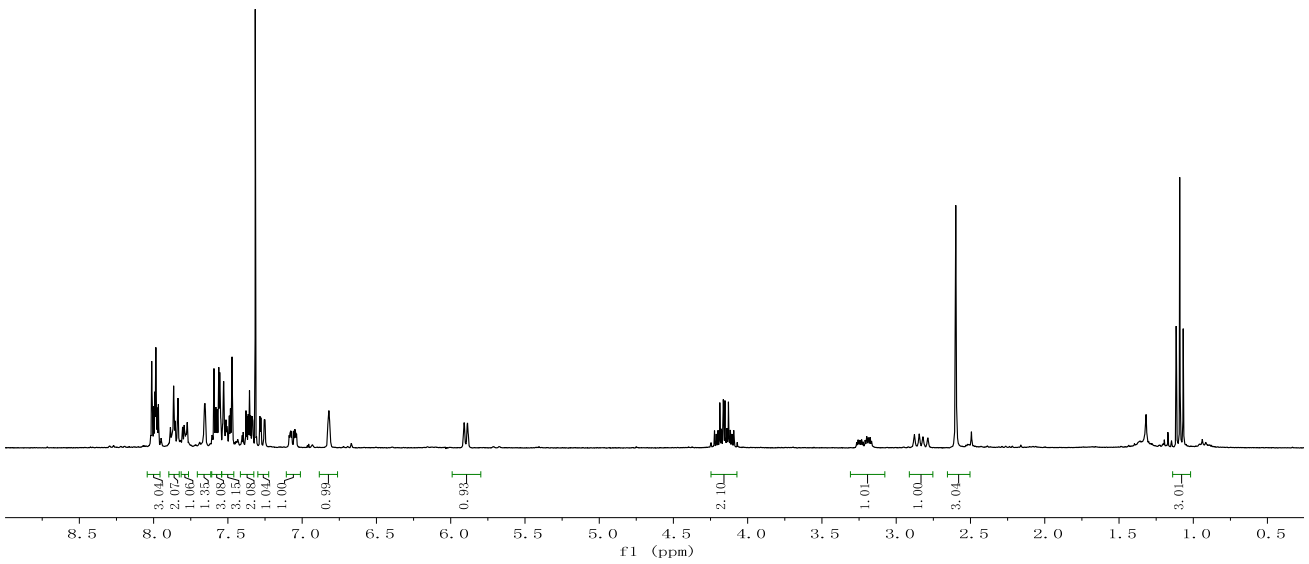
4ae

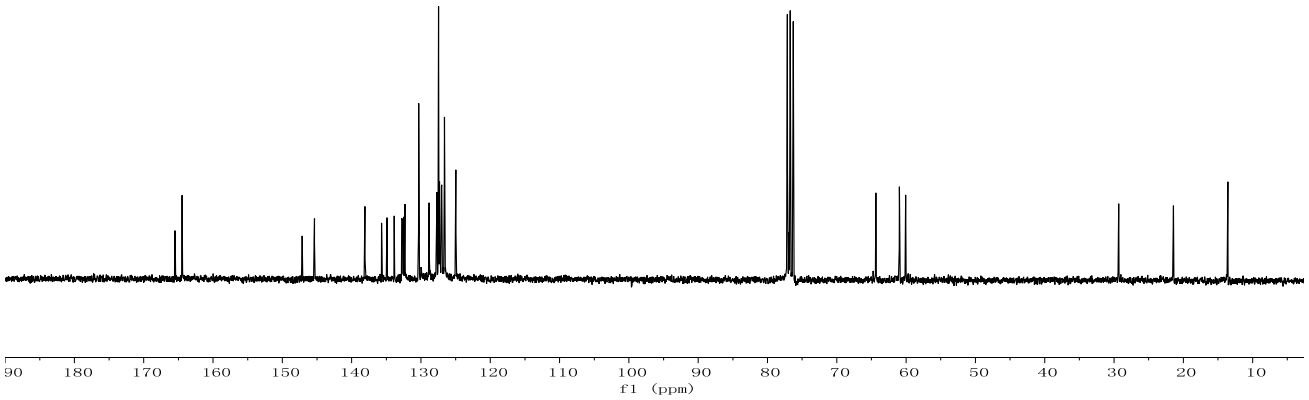


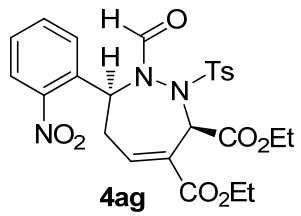


4af

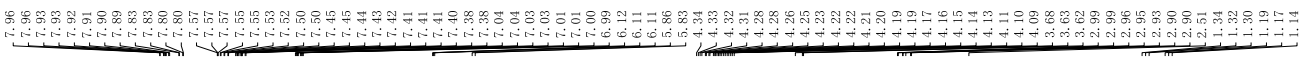


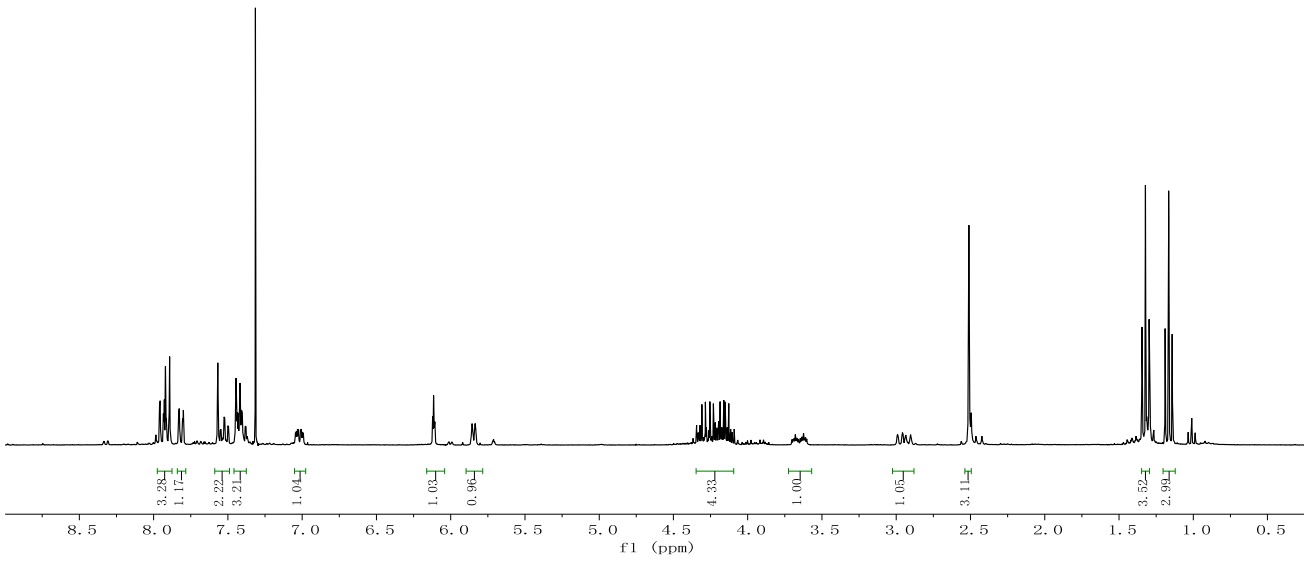


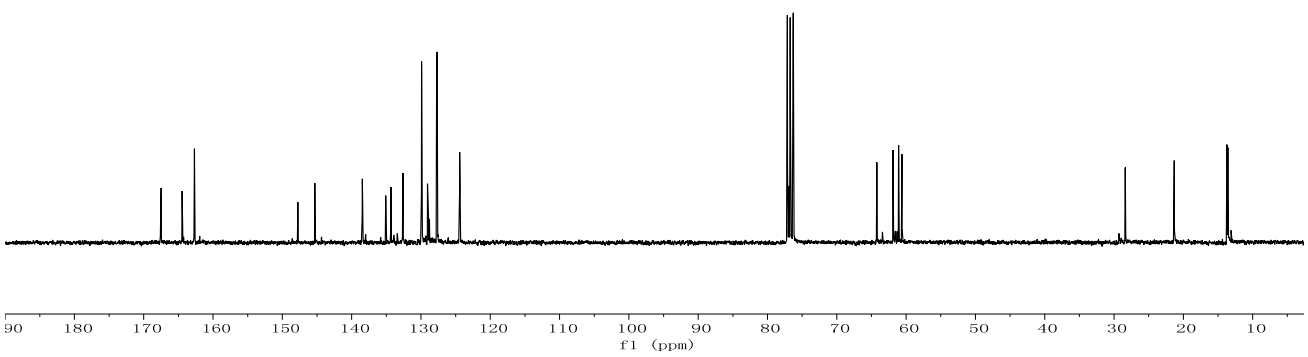


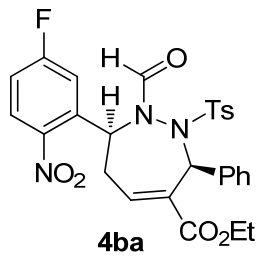

H
O
H
N
N
Ts
NO2
CO2Et
CO2Et

4ag

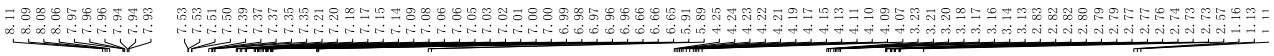


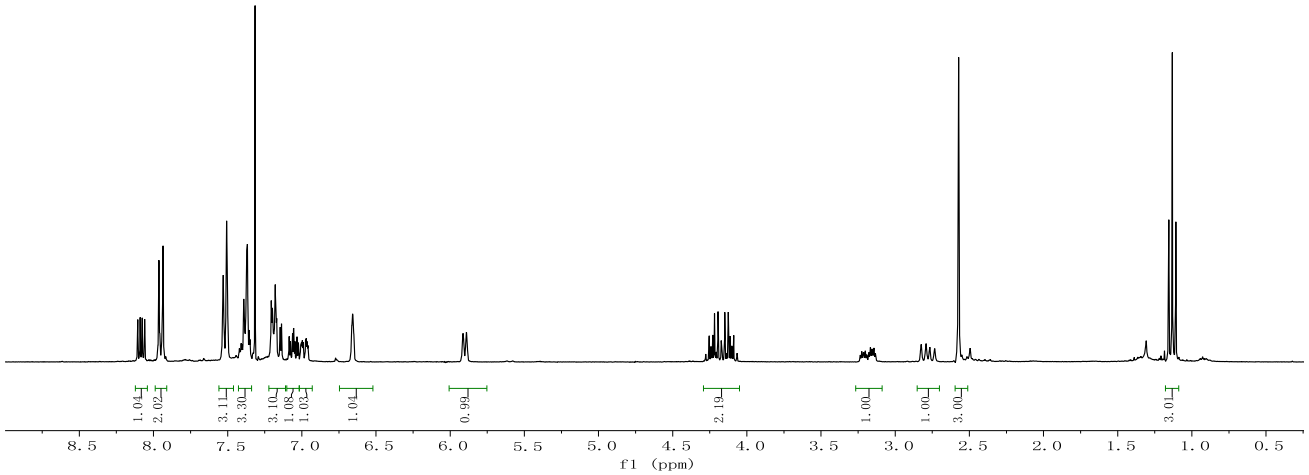

3.28
1.17
2.22
3.21
1.04
1.03
0.96
4.33
1.00
1.05
3.11
3.52
2.99
f1 (ppm)

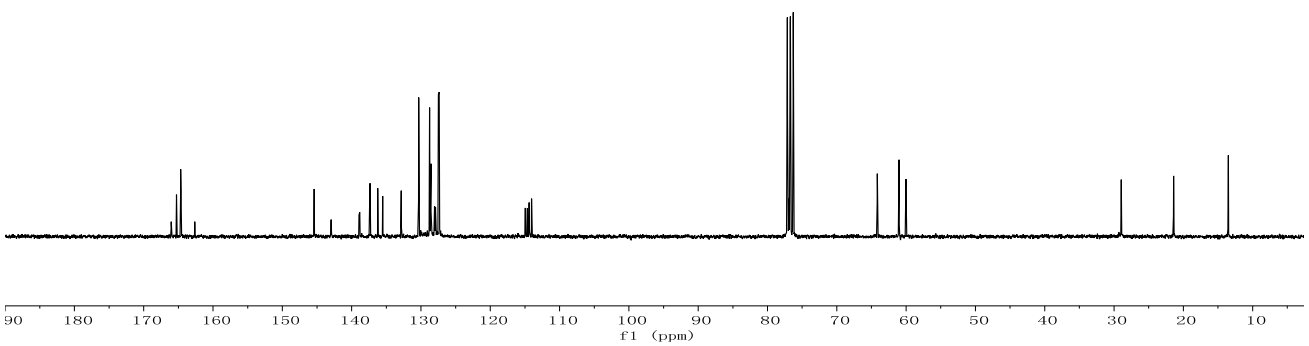

f1 (ppm)

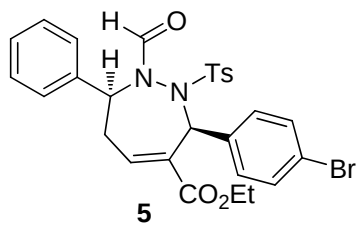

F
H
O
H
N
N
Ts
NO2
Ph
CO2Et

4ba




1.04
2.02
3.11
3.30
3.10
1.08
1.03
1.04
0.99
2.19
1.00
1.00
3.00
3.01
f1 (ppm)


f1 (ppm)


H
O
H
N
N
Ts
Br
CO2Et

5


7.88
7.88
7.86
7.85
7.60
7.60
7.57
7.53
7.53
7.51
7.51
7.42
7.39
7.39
7.37
7.34
7.33
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7.30
7.29
7.26
7.20
7.18
7.18
7.16
7.15
6.78
6.78
6.77
6.75
6.74
6.74
5.02
5.01
4.98
4.97
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3.22
3.21
3.19
3.18
3.17
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2.54
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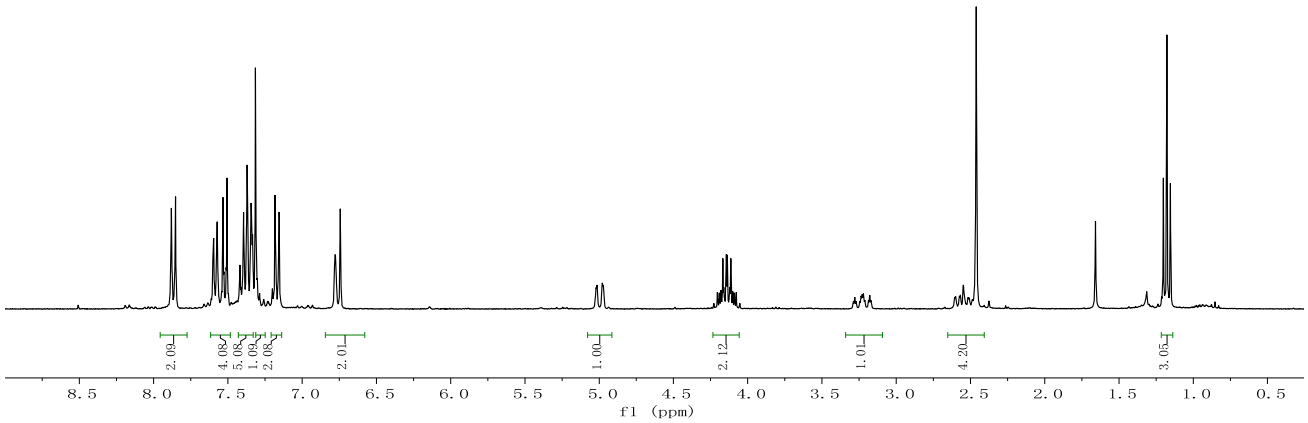
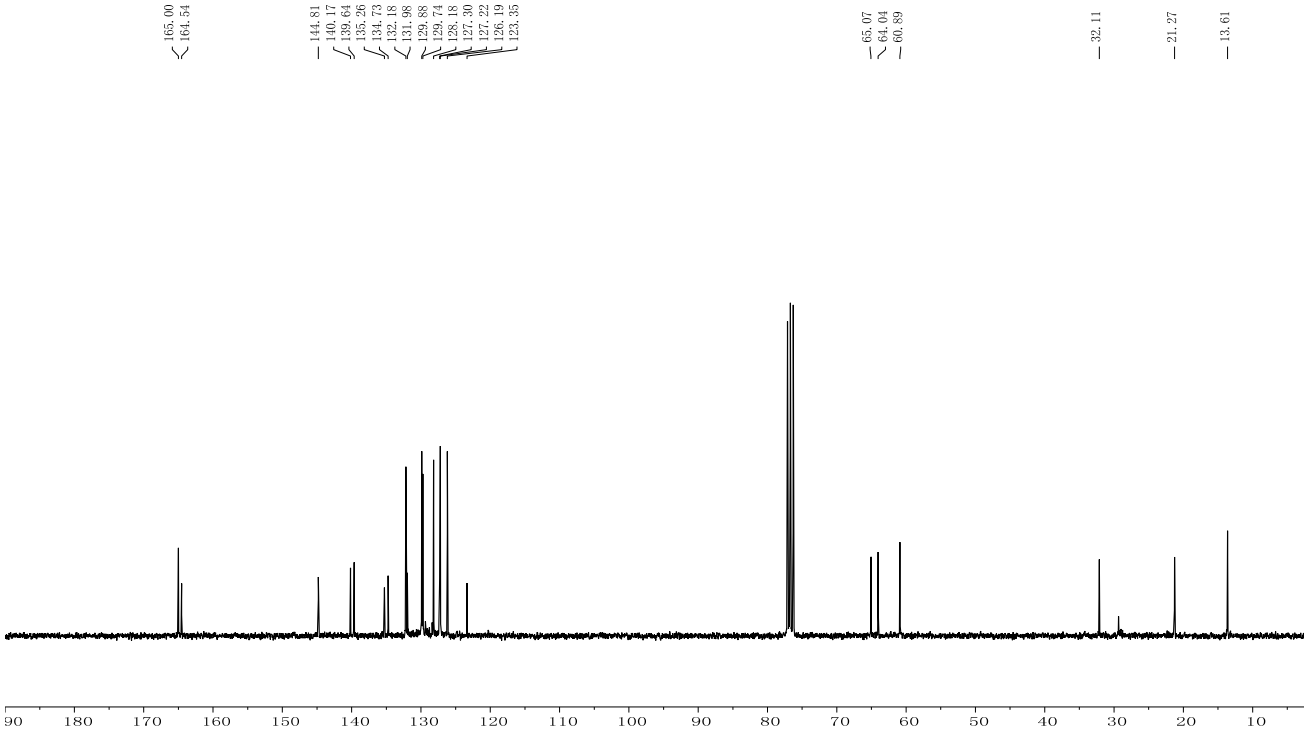
2.51
2.46
1.20
1.18
1.15


2.09
4.08
5.08
1.00
2.08
2.01
1.00
2.12
1.01
4.20
3.05
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
f1 (ppm)


165.00
164.54
144.81
140.17
139.64
135.26
134.73
132.18
131.98
129.88
129.74
128.18
127.30
127.22
126.19
123.35
65.07
64.04
60.89
32.11
21.27
13.61
90
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150
140
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120
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100
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80
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60
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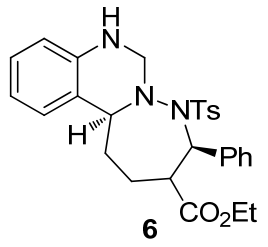
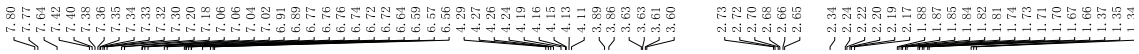
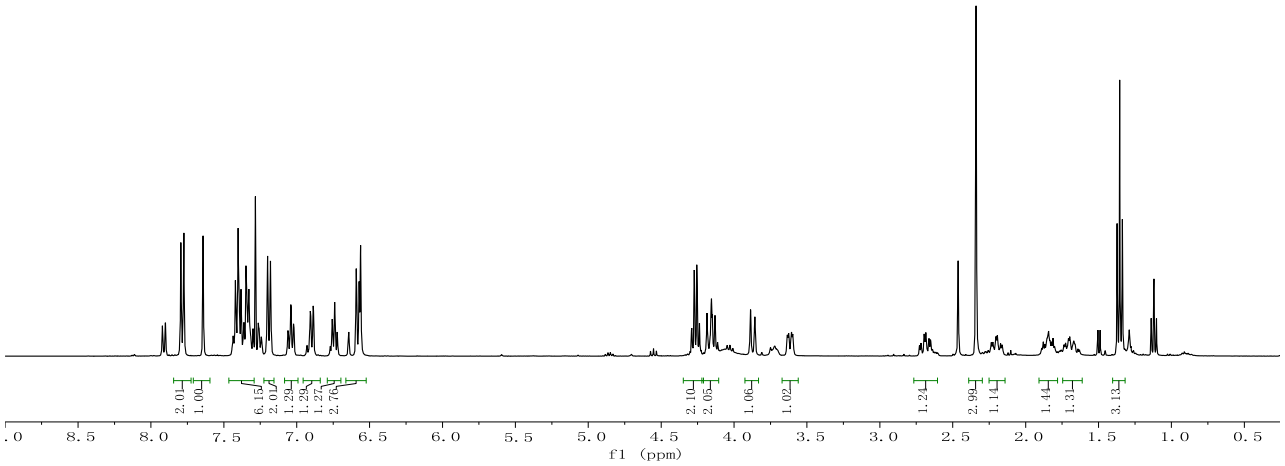
30
20
10
f1 (ppm)


H
N
N
NTs
H
Ph
CO2Et

6

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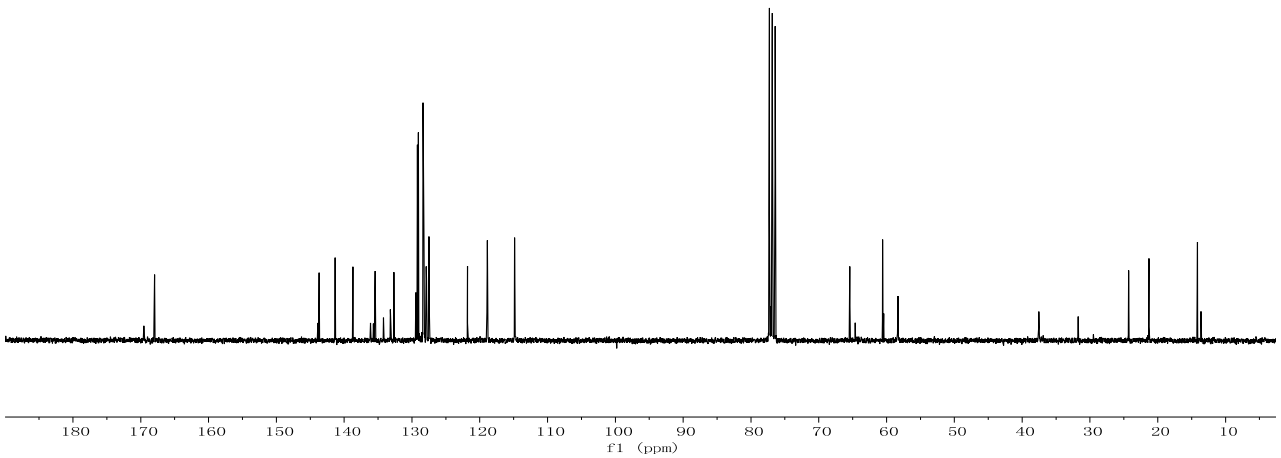
3.13
f1 (ppm)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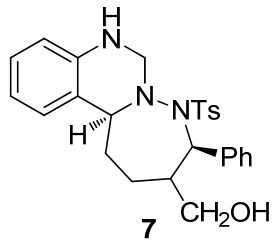
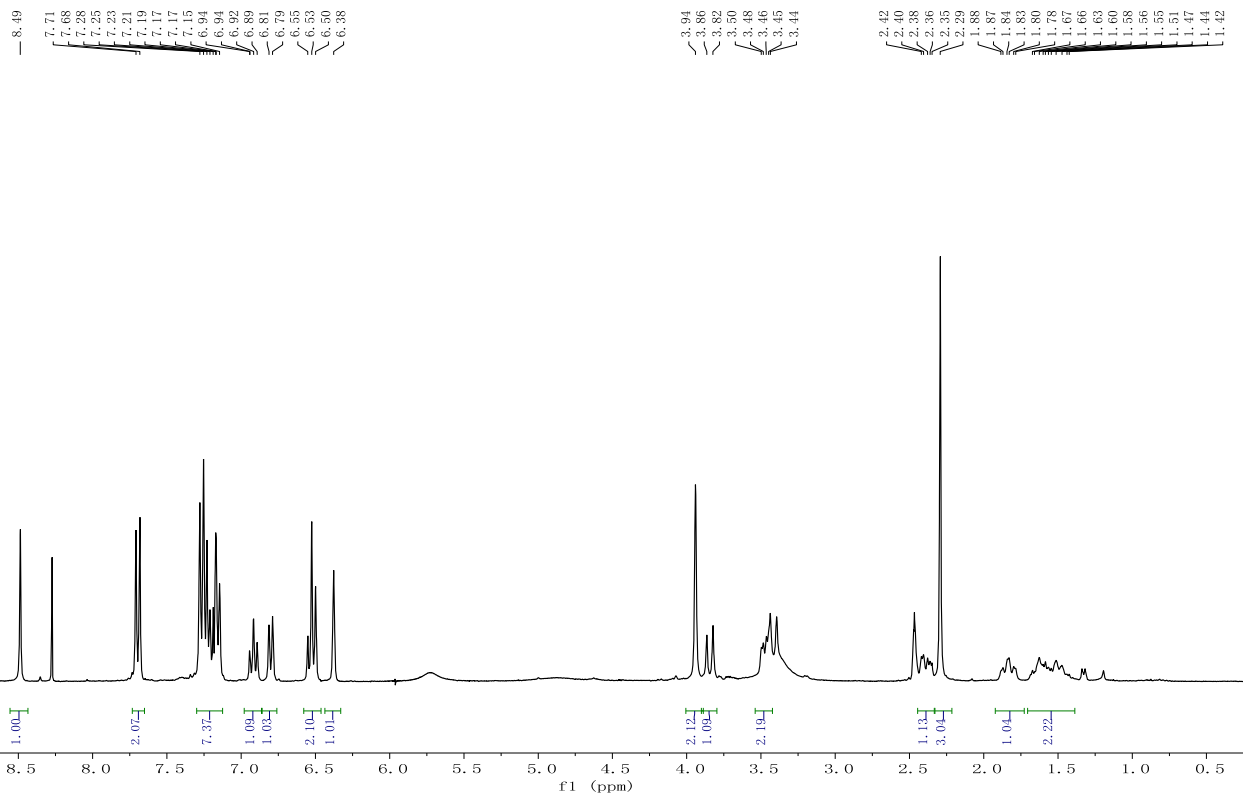

H
N
N
NTs
H
Ph
CH2OH

7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6.92
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6.79
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6.38
3.94
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3.82
3.50
3.48
3.46
3.45
3.44
2.42
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1.51
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1.13
3.04
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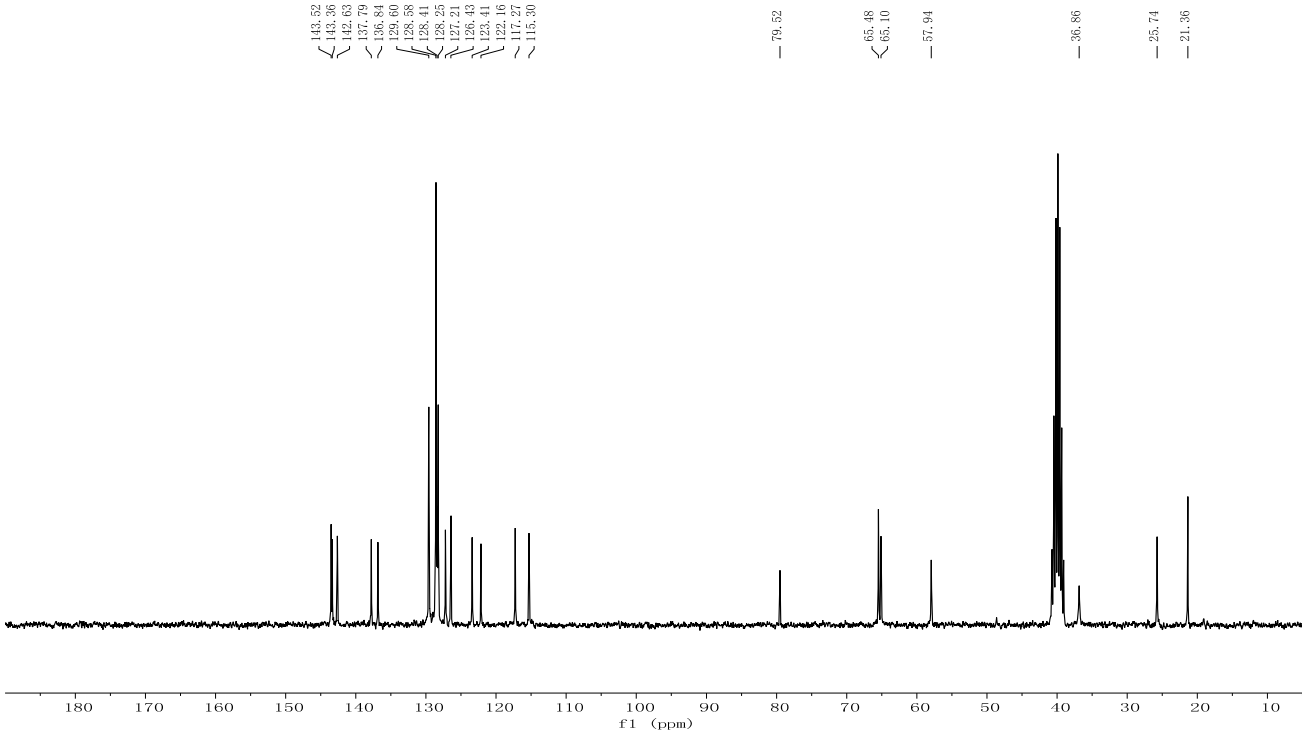
2.22
f1 (ppm)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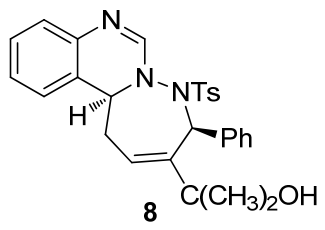
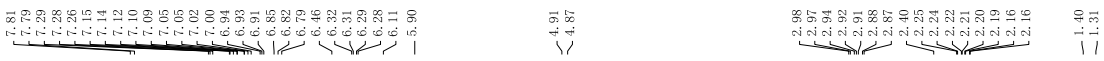
21.36
f1 (ppm)


N
N
NTs
H
Ph
C(CH3)2OH

8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6.82
6.79
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6.29
6.28
6.11
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4.87
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2.97
2.94
2.92
2.91
2.88
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2.24
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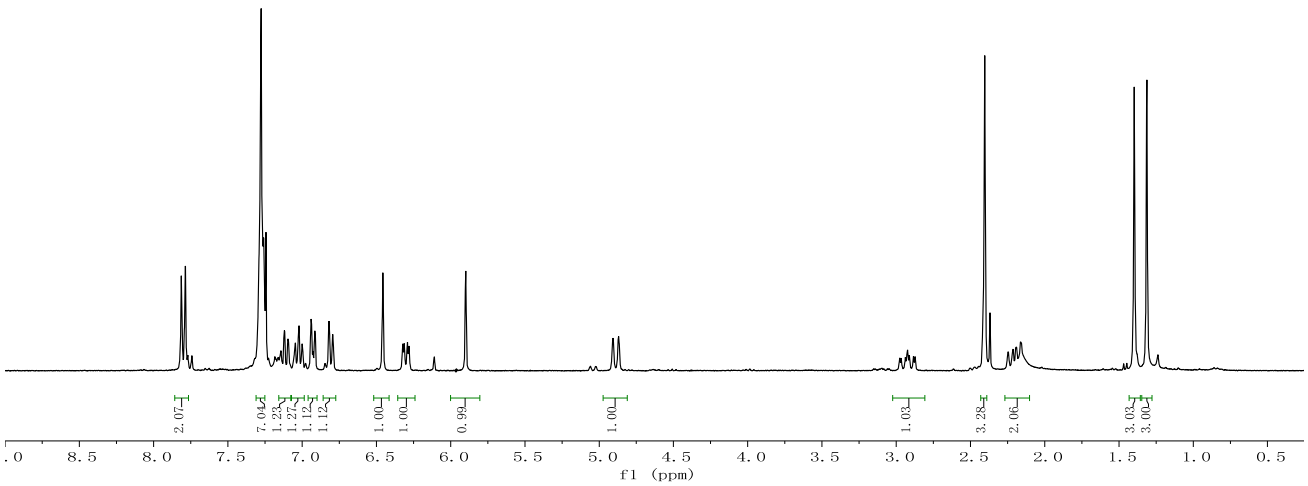
1.31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1.12
1.12
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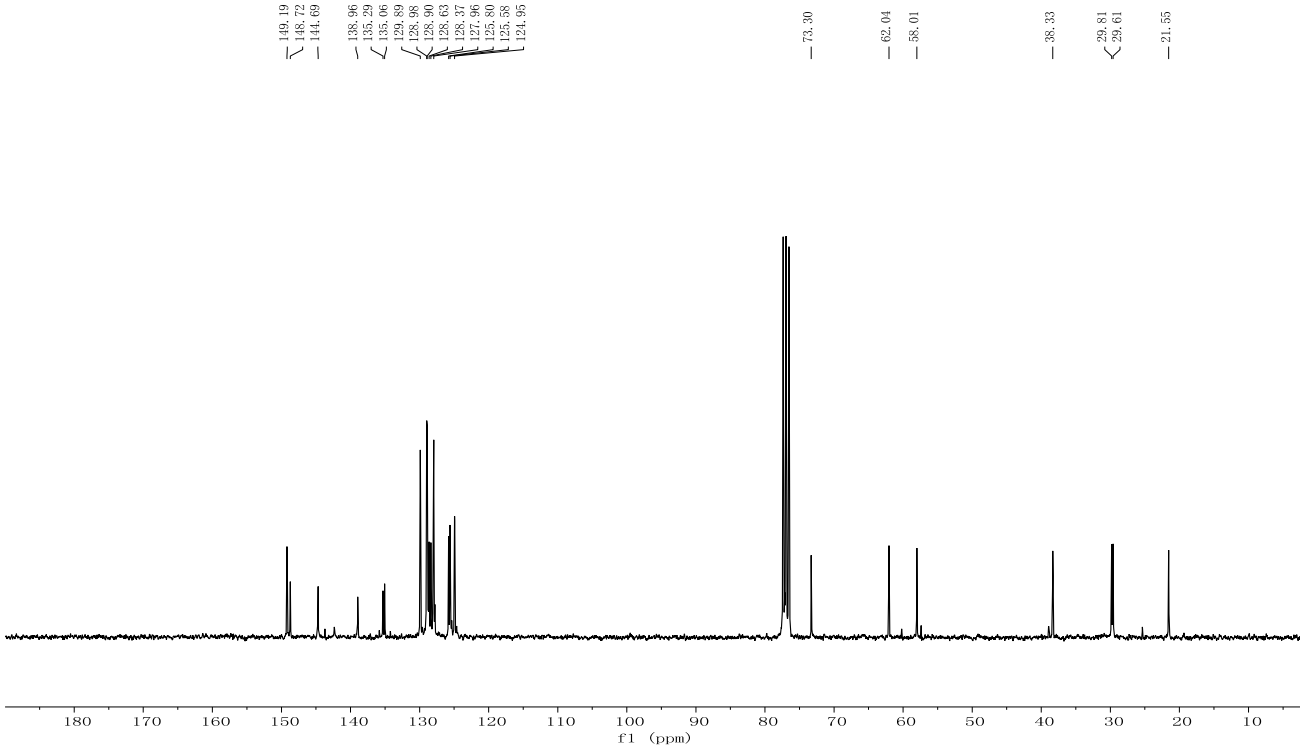
1.00
0.99
1.00
1.03
3.28
2.06
3.03
3.00
f1 (ppm)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62.04
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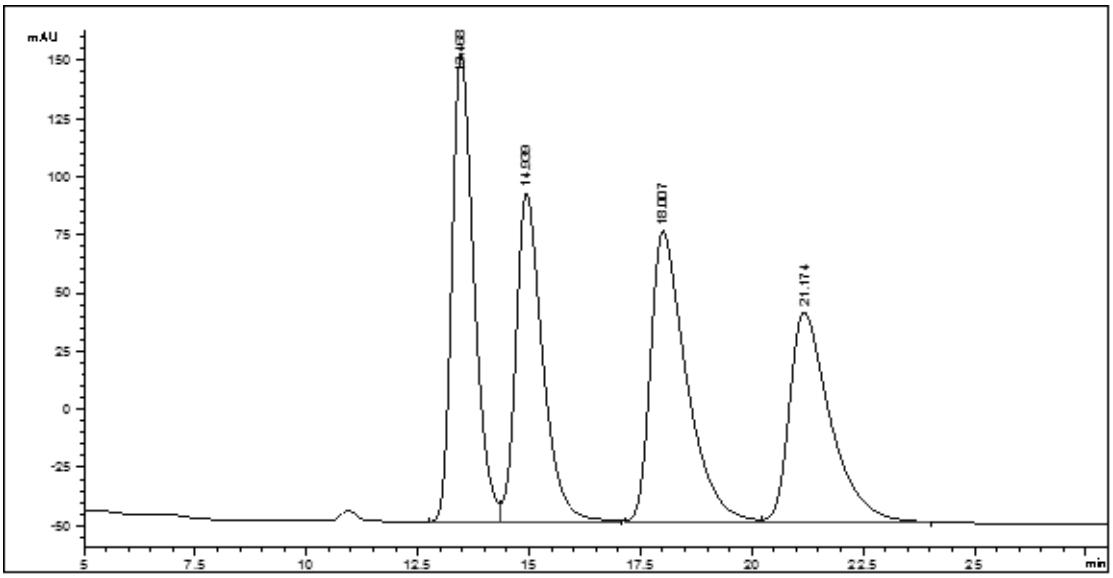
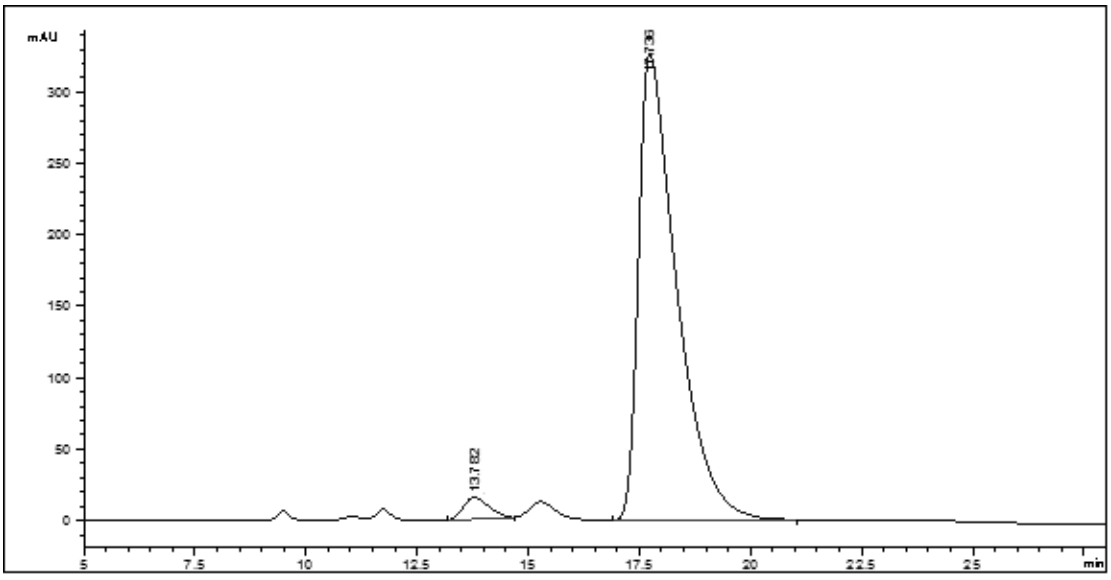
38.33
29.81
29.61
21.55
f1 (ppm)

HPLC chromatogram of racemic 3aa



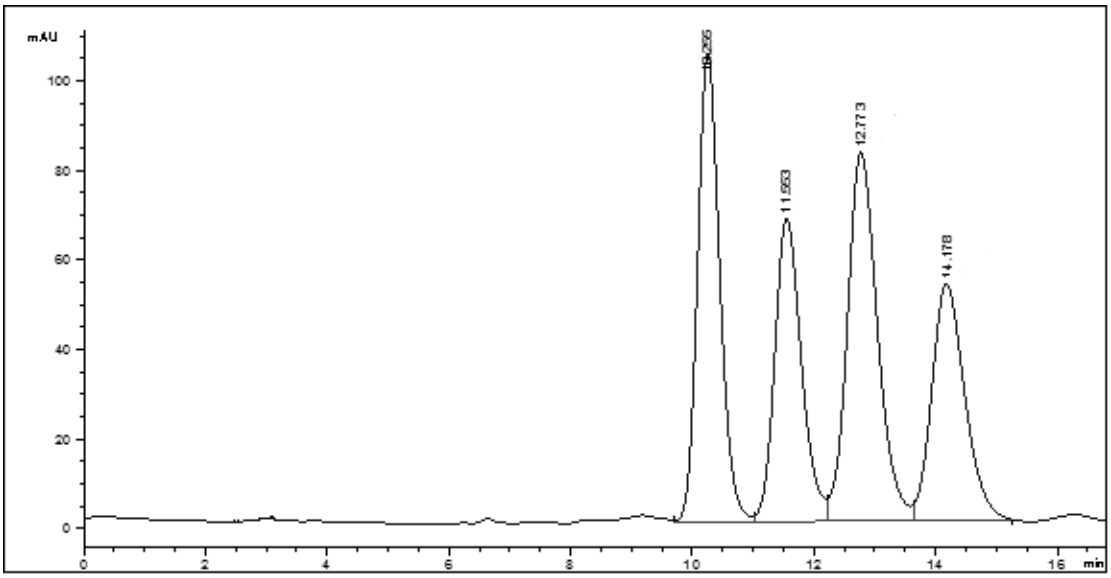
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.468	BV	0.5224	6900.17725	201.20909	27.0600
2	14.939	VB	0.6254	5879.29395	141.24168	23.0565
3	18.007	BB	0.8293	6989.32324	125.13176	27.4096
4	21.174	BB	0.9415	5730.76025	90.27921	22.4740

HPLC chromatogram of chiral 3aa



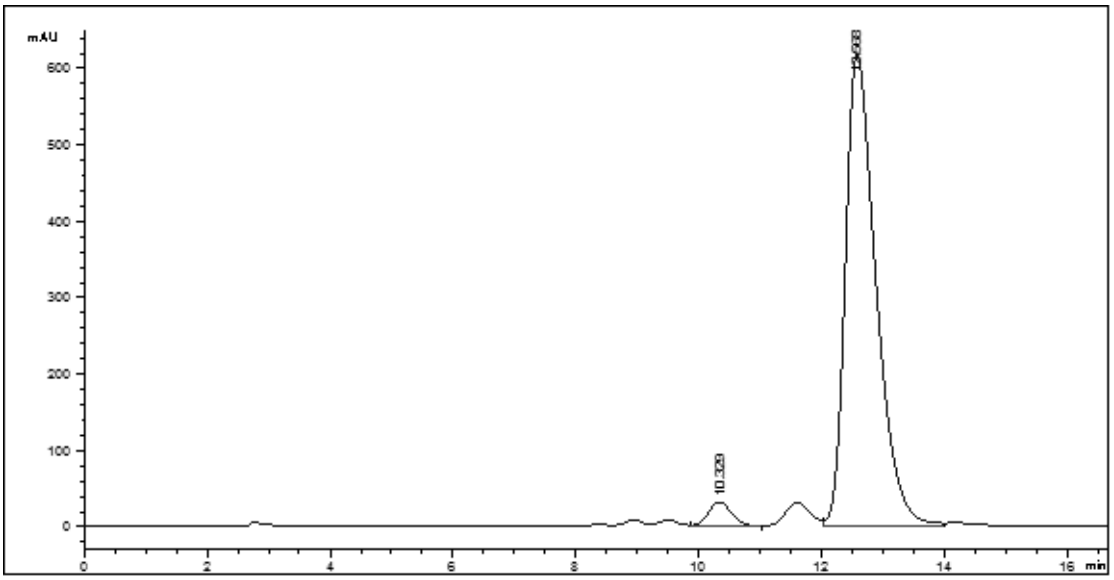
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.782	MM	0.6569	606.26654	15.38143	3.0186
2	17.736	BB	0.8735	1.94783e4	326.58994	96.9814

HPLC chromatogram of racemic 3ab



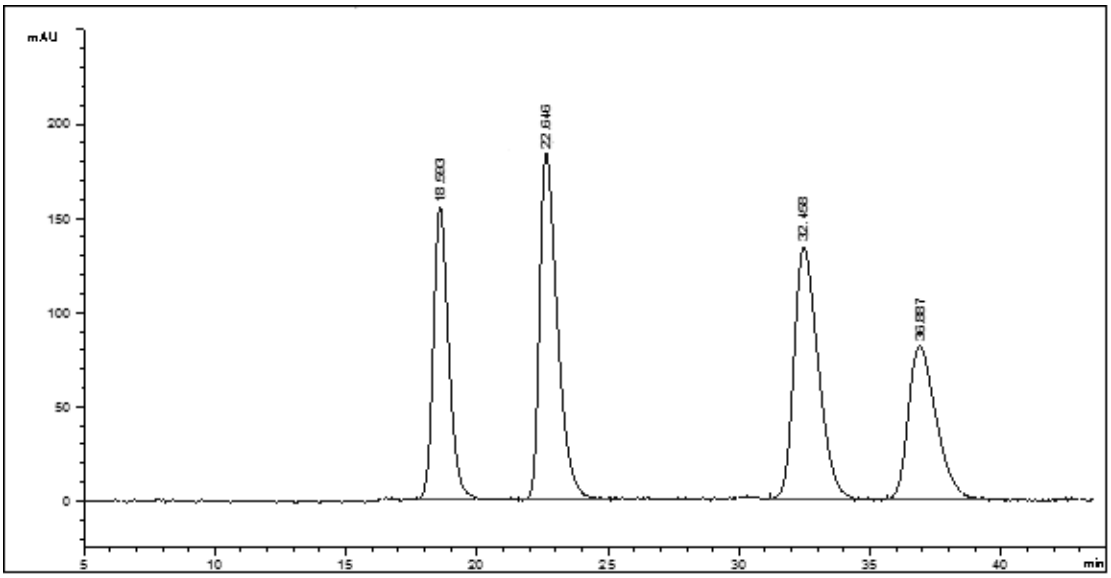
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.255	MF	0.4233	2659.86890	104.73468	27.9119
2	11.553	FM	0.5083	2065.43701	67.72909	21.6741
3	12.773	FM	0.5721	2826.32812	82.33399	29.6586
4	14.178	FM	0.6253	1977.89075	52.72002	20.7554

HPLC chromatogram of chiral 3ab



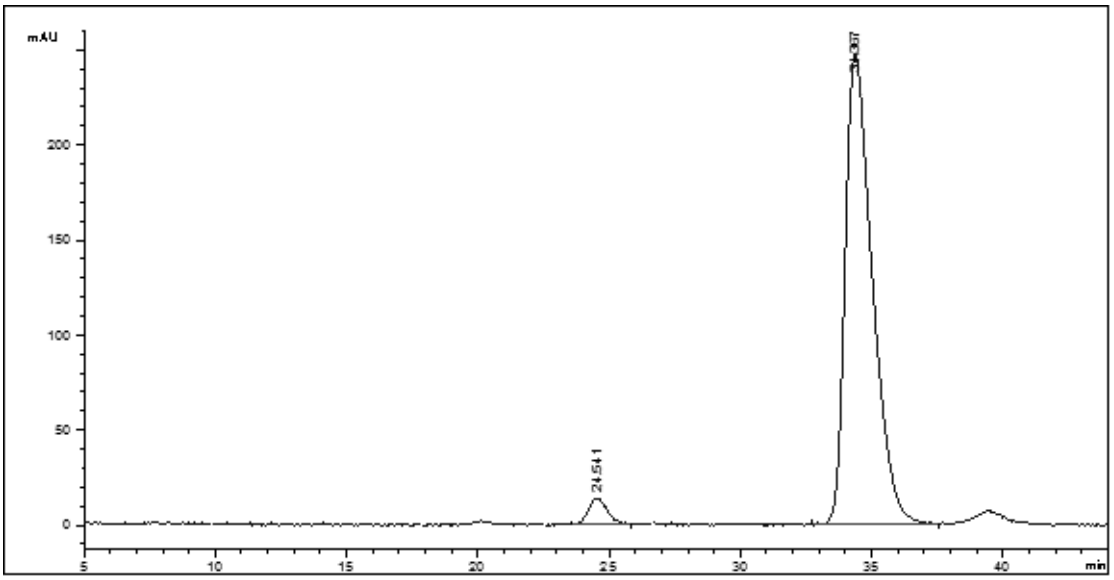
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.329	VV	0.4003	827.31799	31.72395	3.7290
2	12.568	VB	0.5254	2.13585e4	618.15289	96.2710

HPLC chromatogram of racemic 3ac



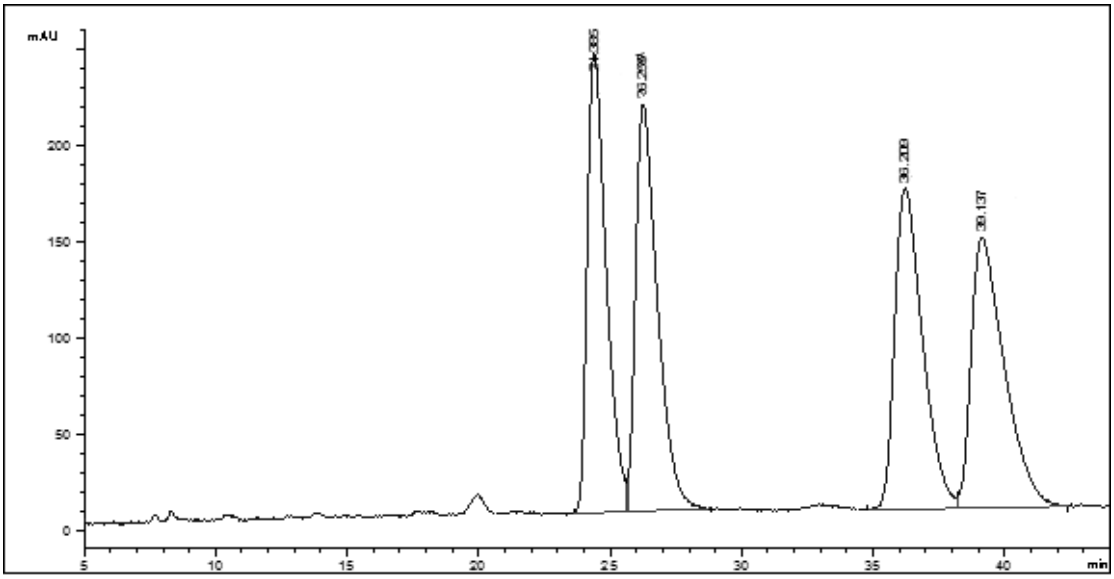
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.593	MM	0.6727	6255.10596	154.96571	21.2159
2	22.646	MM	0.7829	8627.96680	183.67267	29.2641
3	32.458	MM	1.0634	8574.00586	134.37621	29.0811
4	36.887	MM	1.2307	6026.00977	81.60905	20.4389

HPLC chromatogram of chiral 3ac



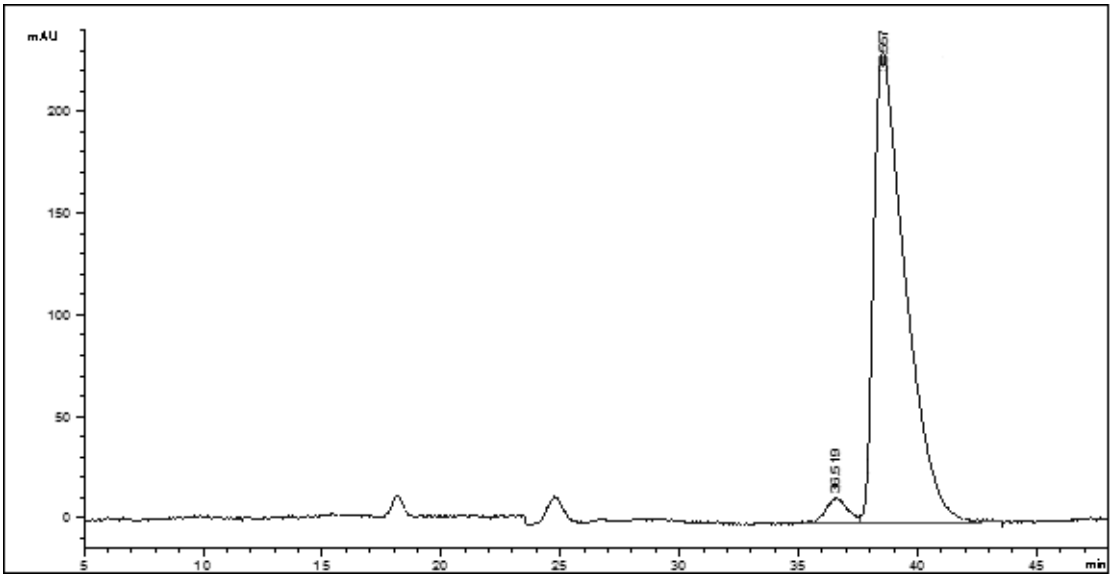
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	24.541	MM	0.8255	699.29242	14.11907	3.7908
2	34.367	MM	1.1946	1.77477e4	247.60641	96.2092

HPLC chromatogram of racemic 3ad



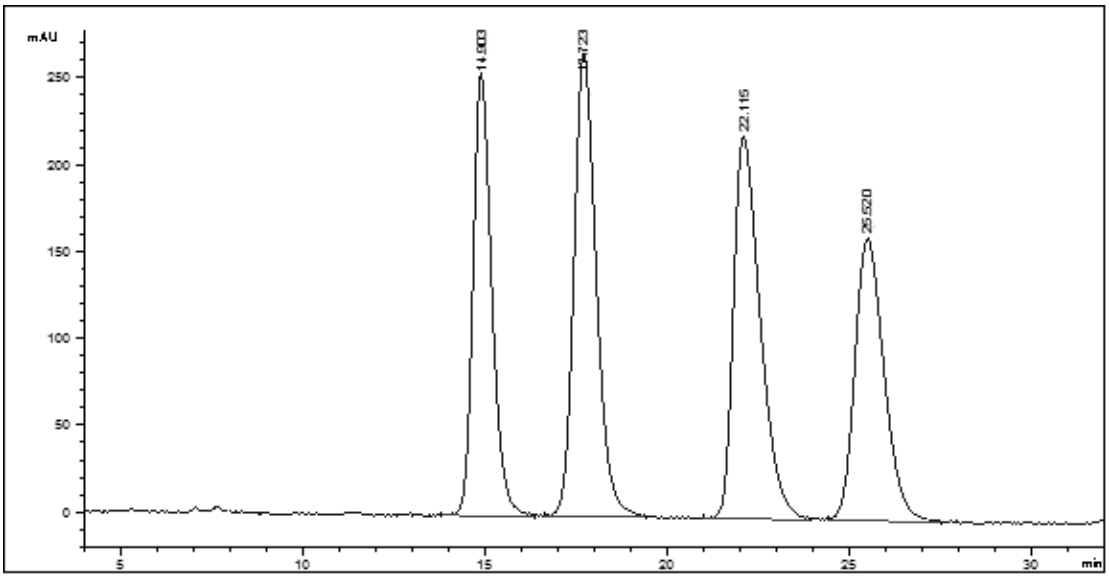
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	24.385	MF	0.8349	1.19745e4	239.03329	24.5467
2	26.255	FM	0.9605	1.21861e4	211.45656	24.9804
3	36.209	MF	1.2278	1.23038e4	167.01877	25.2216
4	39.137	FM	1.4582	1.23183e4	140.79289	25.2513

HPLC chromatogram of chiral 3ad



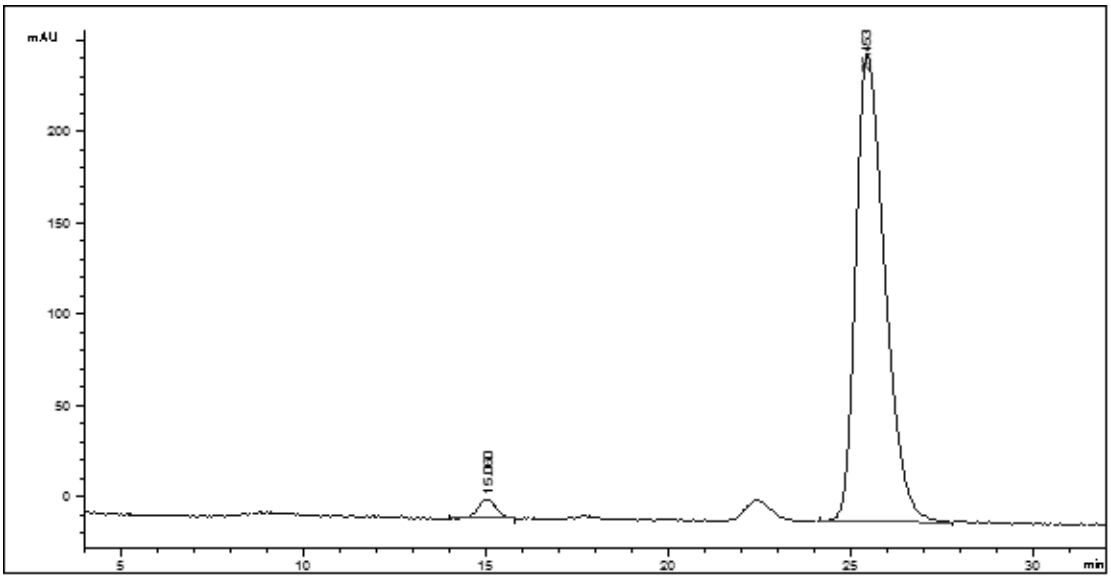
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	36.519	MF	1.0548	775.36456	12.25181	3.4947
2	38.557	FM	1.5425	2.14112e4	231.34729	96.5053

HPLC chromatogram of racemic 3ae



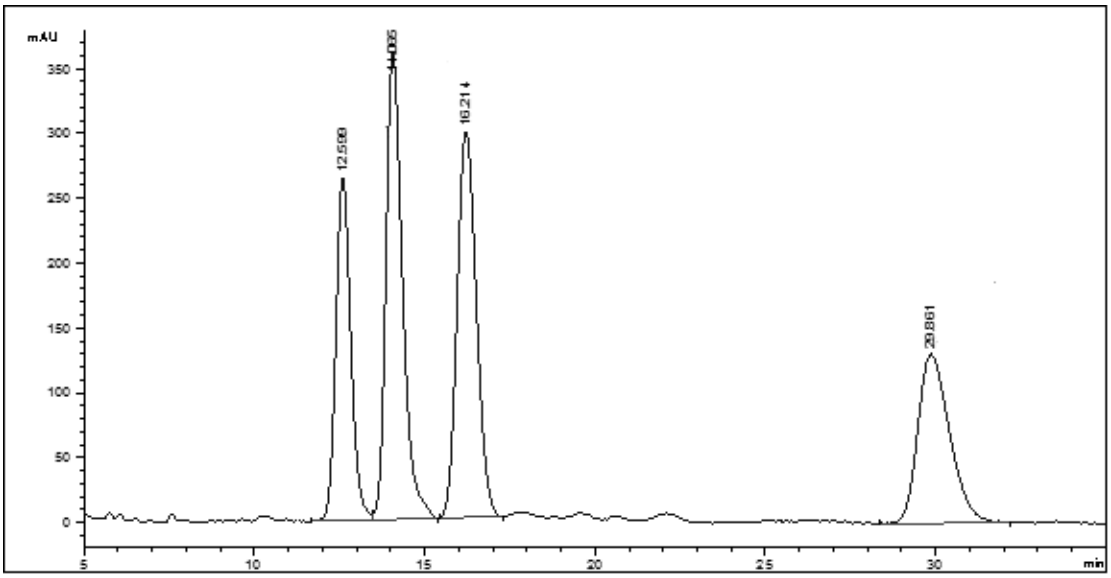
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.903	MM	0.5961	9107.36426	254.65642	22.3630
2	17.723	MM	0.7091	1.13507e4	266.79068	27.8716
3	22.115	MM	0.8503	1.12099e4	219.71497	27.5258
4	25.520	MM	0.9282	9057.08008	162.63362	22.2396

HPLC chromatogram of chiral 3ae



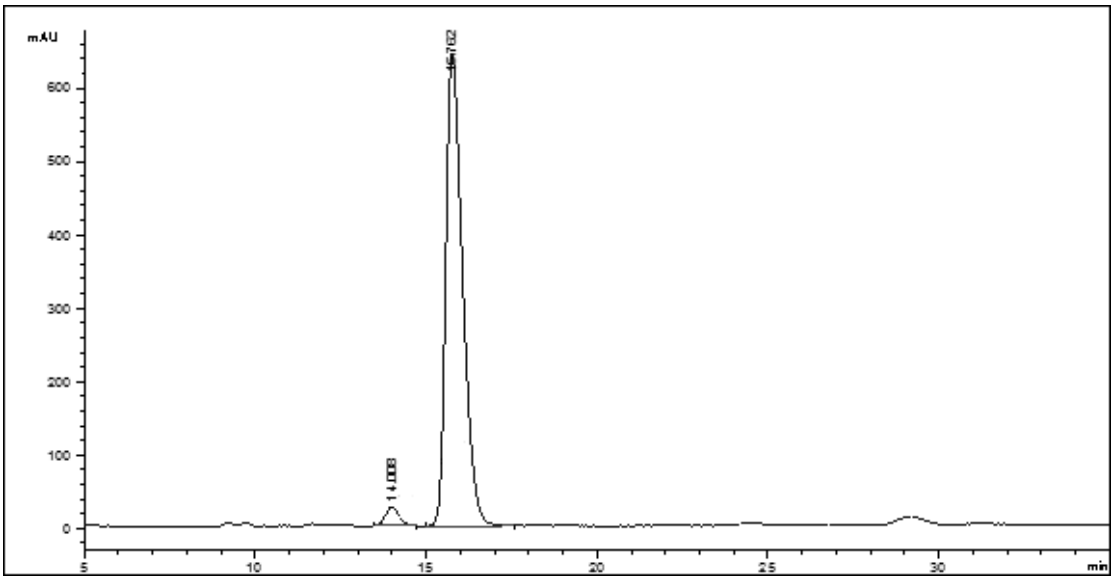
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.060	MM	0.5723	356.54700	10.38390	2.4487
2	25.453	MM	0.9224	1.42041e4	256.64432	97.5513

HPLC chromatogram of racemic 3af



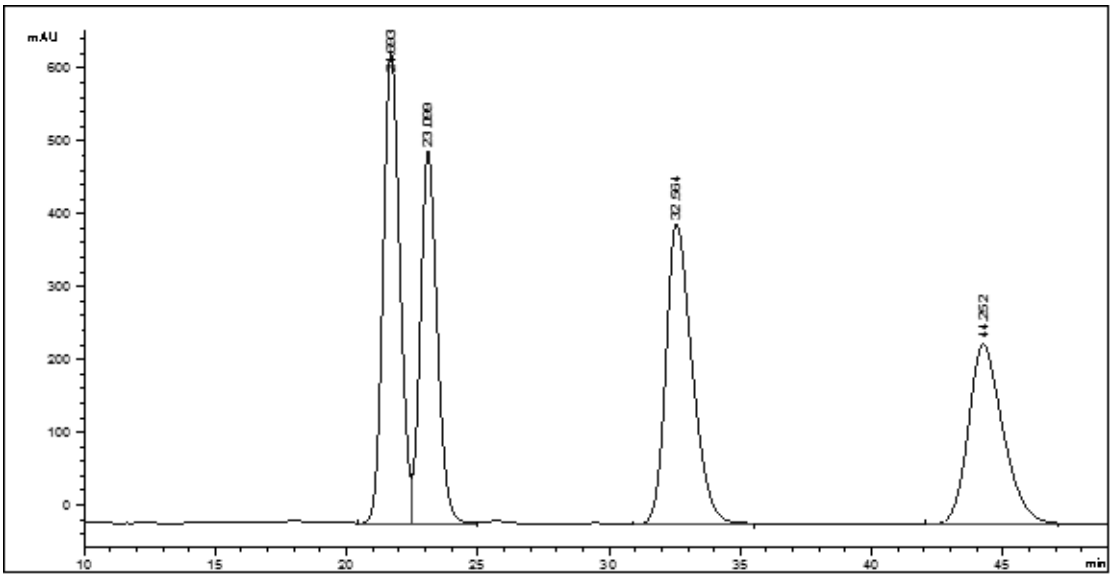
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.599	MF	0.5082	8081.84229	265.03131	20.0101
2	14.065	FM	0.5647	1.21802e4	359.50537	30.1572
3	16.214	MM	0.6515	1.16510e4	298.05423	28.8471
4	29.861	MM	1.0772	8475.84082	131.13400	20.9856

HPLC chromatogram of chiral 3af



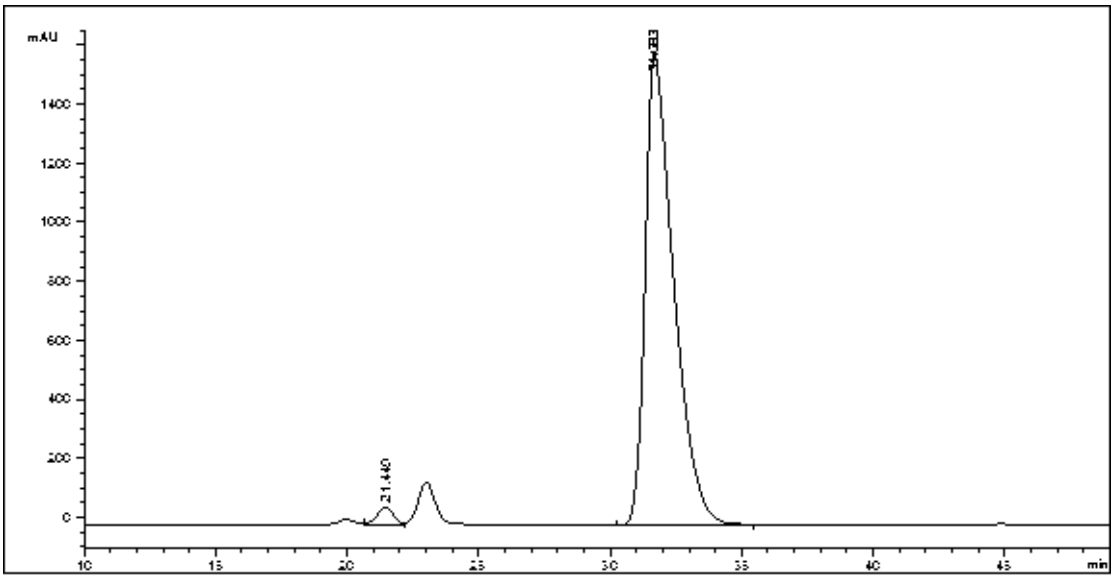
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.008	MM	0.4527	708.00354	26.06692	3.1136
2	15.762	MM	0.5702	2.20313e4	643.97821	96.8864

HPLC chromatogram of racemic 3ag



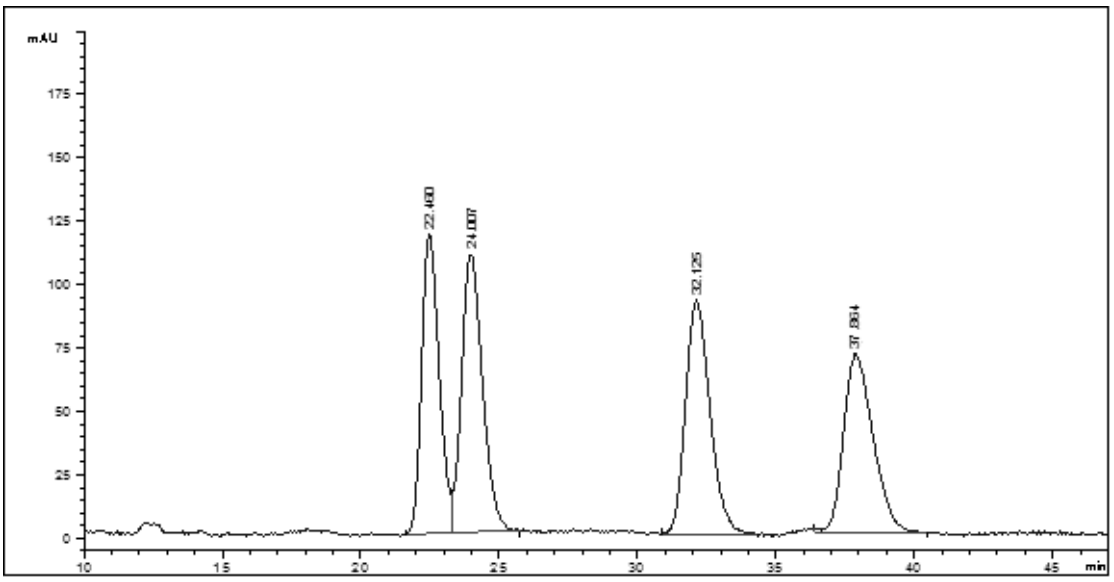
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	21.693	VV	0.6758	2.85303e4	645.50647	27.8608
2	23.099	VB	0.6820	2.27946e4	511.04572	22.2596
3	32.564	VB	1.0299	2.85774e4	411.56168	27.9068
4	44.252	BB	1.3900	2.25009e4	246.76456	21.9729

HPLC chromatogram of chiral 3ag



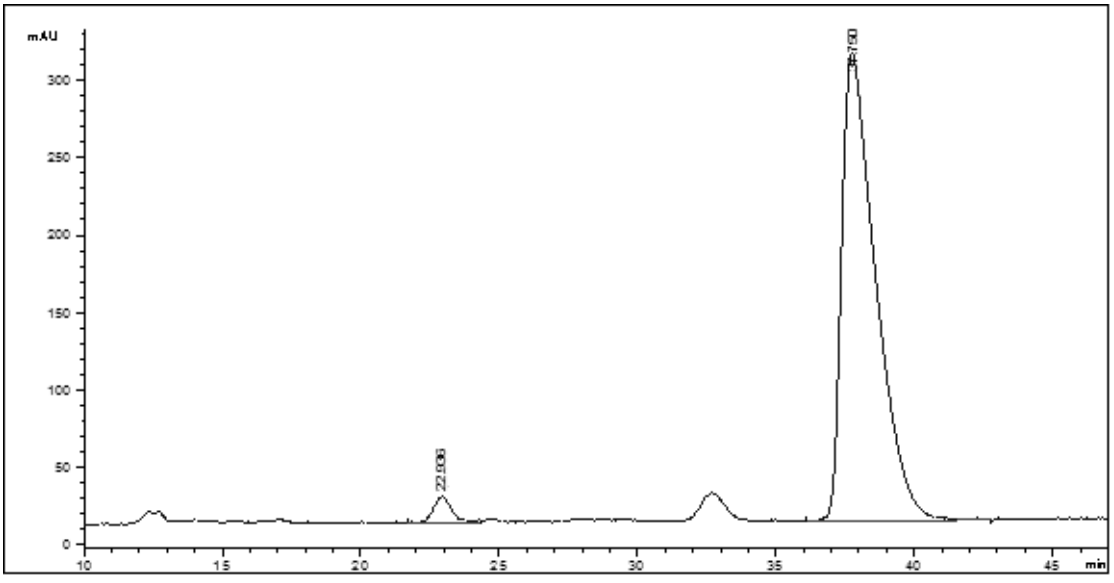
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	21.449	VV	0.6849	2719.67725	60.80878	2.2108
2	31.683	VB	1.1174	1.20301e5	1597.45300	97.7892

HPLC chromatogram of racemic 3ah



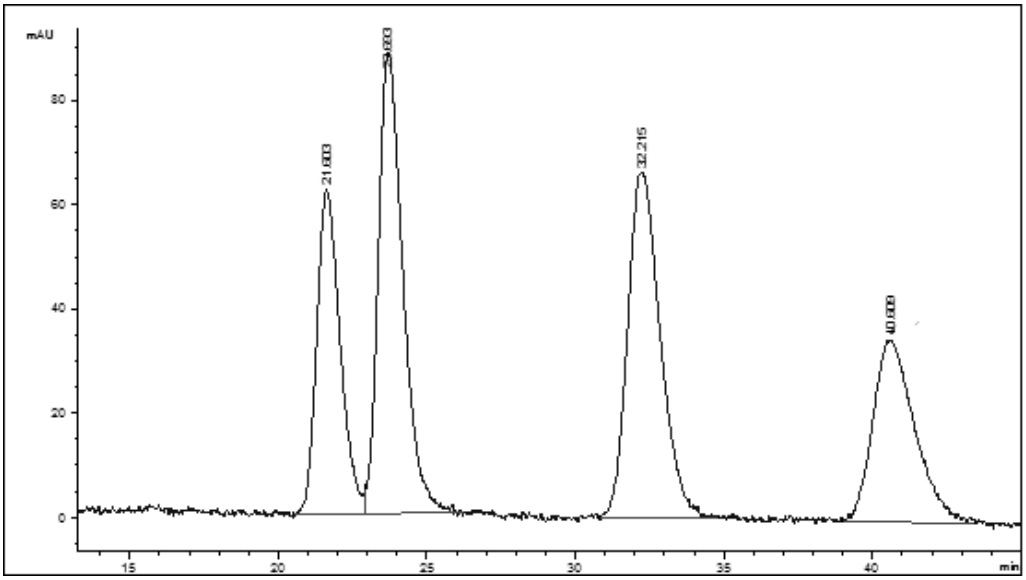
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	22.460	MF	0.7387	5221.25732	117.80003	23.8843
2	24.007	FM	0.8727	5731.53809	109.45585	26.2186
3	32.125	MM	1.0256	5669.16113	92.12329	25.9332
4	37.864	MM	1.2357	5238.65332	70.65952	23.9639

HPLC chromatogram of chiral 3ah



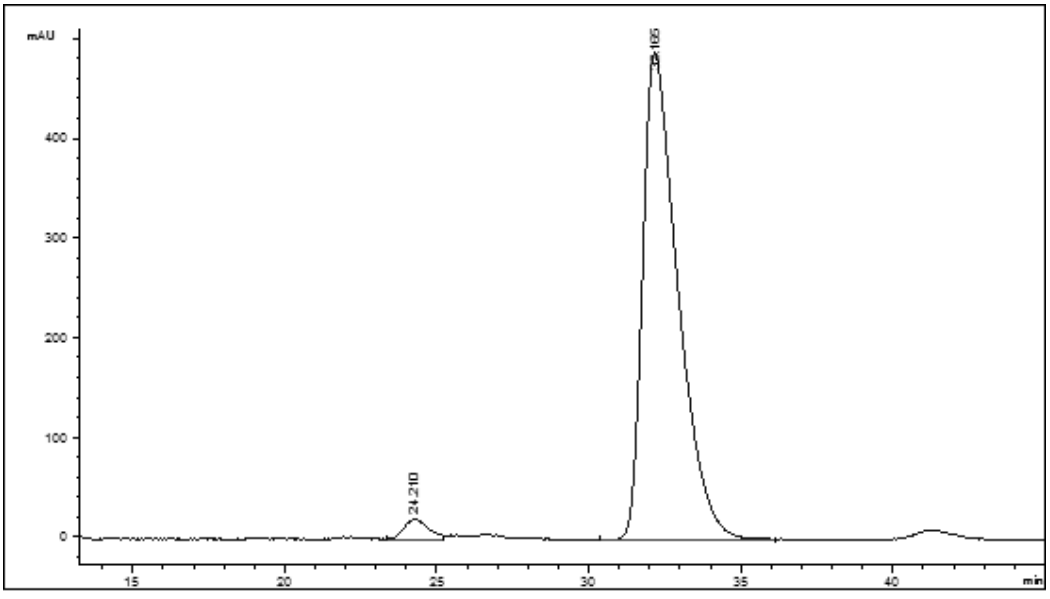
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	22.936	MM	0.7816	784.62830	16.73020	2.9468
2	37.750	MM	1.4243	2.58422e4	302.39554	97.0532

HPLC chromatogram of racemic 3ai



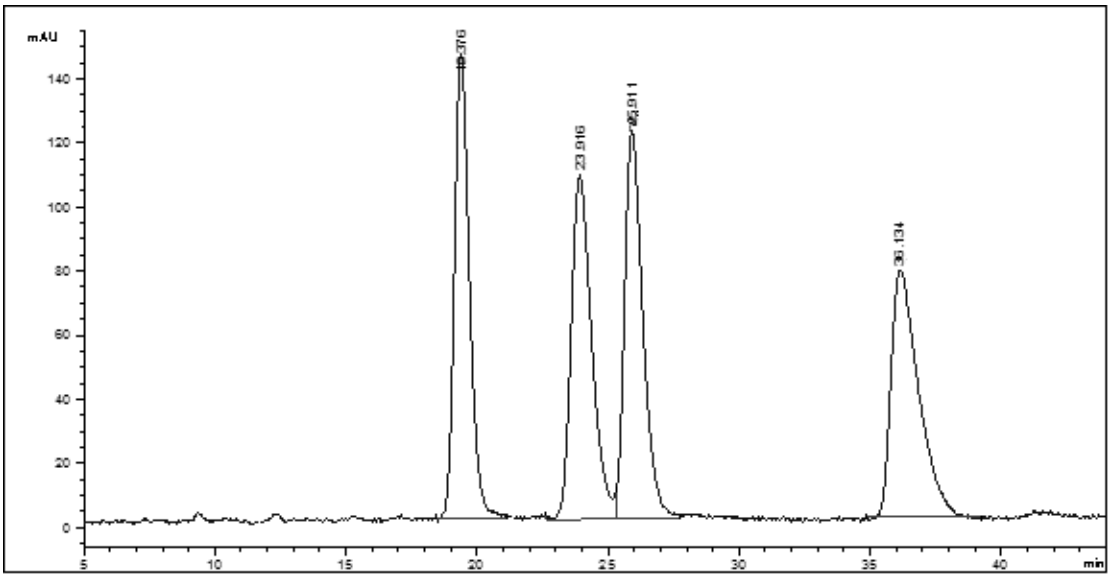
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	21.603	MF	0.9144	3425.03784	62.42932	20.1348
2	23.693	FM	0.9553	5073.34326	88.51180	29.8248
3	32.215	MM	1.2754	5084.93799	66.44942	29.8929
4	40.609	MM	1.6372	3427.18335	34.88947	20.1475

HPLC chromatogram of chiral 3ai



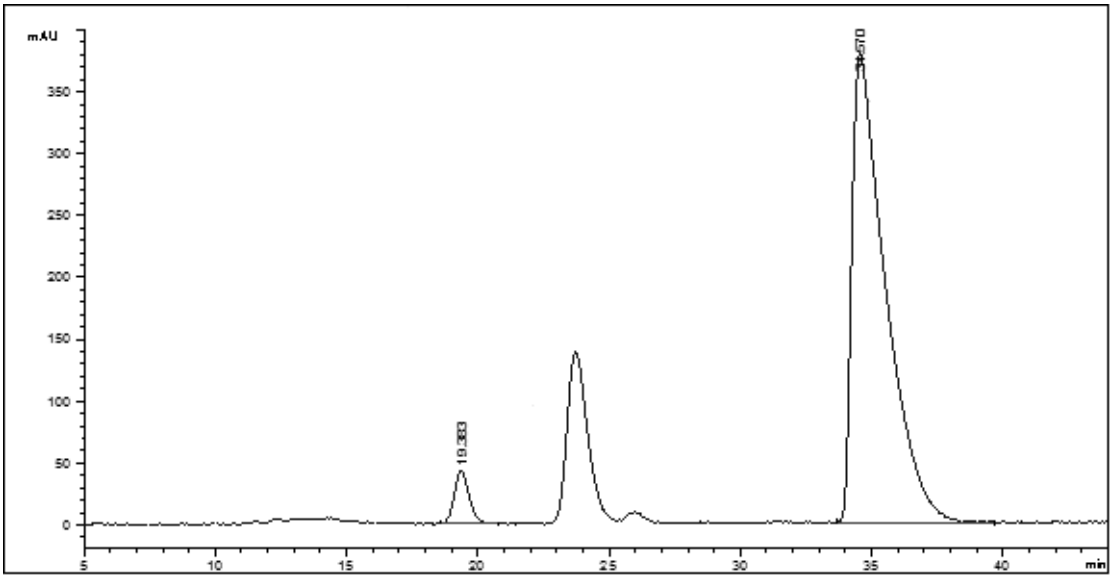
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	24.210	MM	0.9271	1134.19055	20.39011	2.7908
2	32.165	MM	1.3474	3.95067e4	488.67813	97.2092

HPLC chromatogram of racemic 3aj



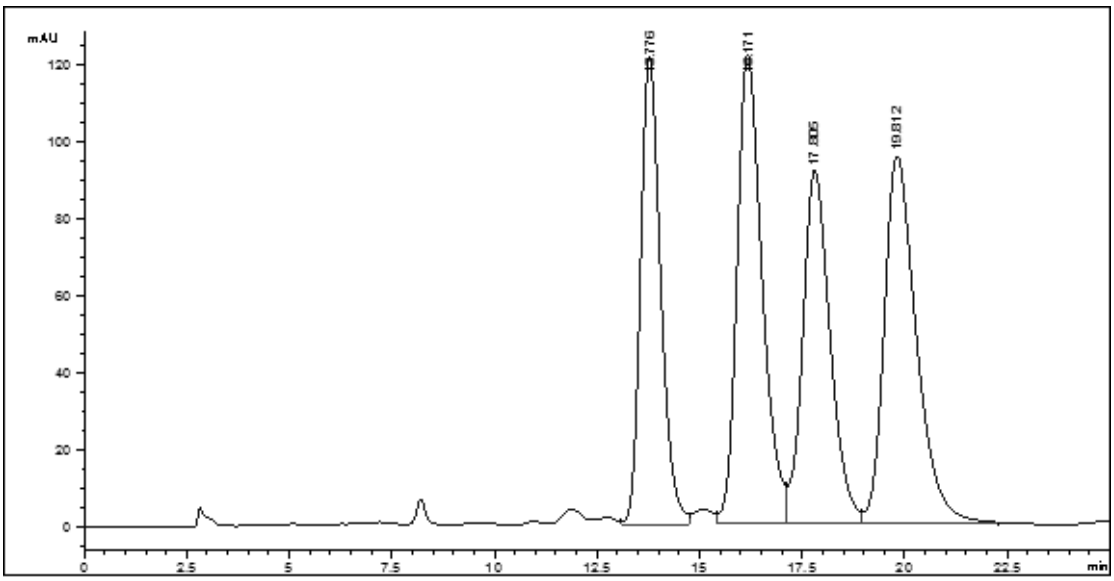
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.376	MM	0.6639	5774.26611	144.95042	24.9844
2	23.916	MF	0.9083	5859.89795	107.52573	25.3549
3	25.911	FM	0.8077	5851.65820	120.74954	25.3192
4	36.134	MM	1.2179	5625.69629	76.98445	24.3415

HPLC chromatogram of chiral 3aj



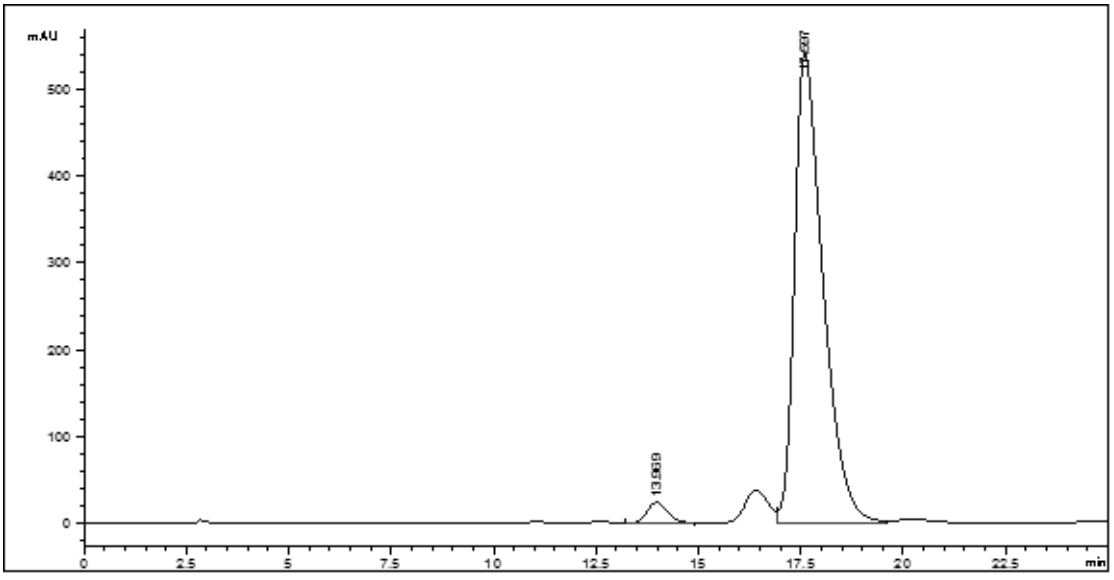
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.383	MM	0.6509	1685.04834	43.14407	4.7425
2	34.570	MM	1.4834	3.38458e4	380.27649	95.2575

HPLC chromatogram of racemic 3ak



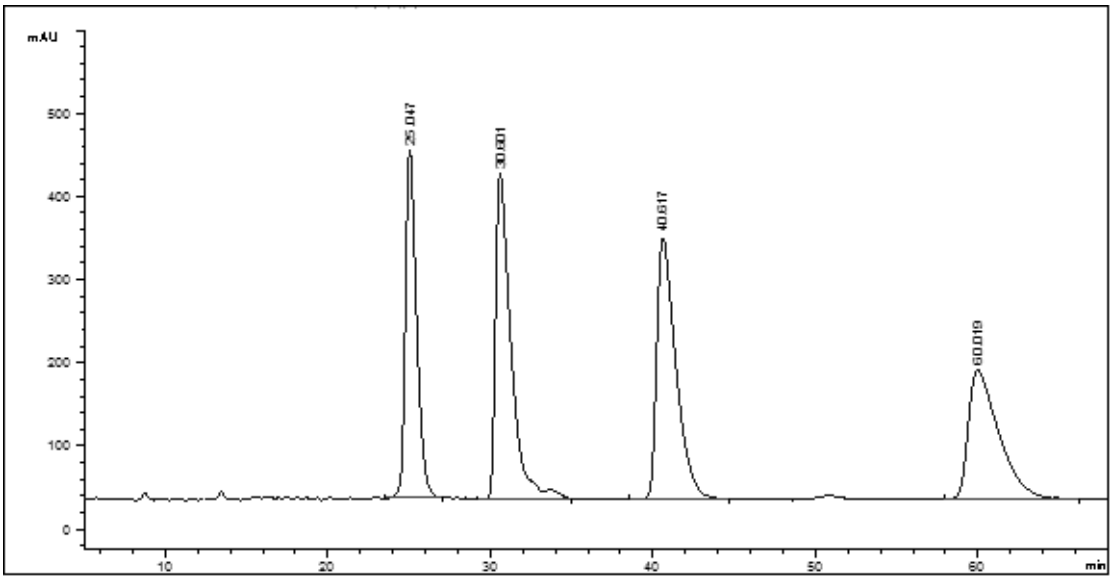
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.776	VV	0.5225	4129.13770	121.24339	22.0307
2	16.171	VV	0.6486	5179.86719	121.56141	27.6367
3	17.805	VV	0.7031	4259.90576	91.53841	22.7284
4	19.812	VB	0.8199	5173.78223	95.27236	27.6043

HPLC chromatogram of chiral 3ak



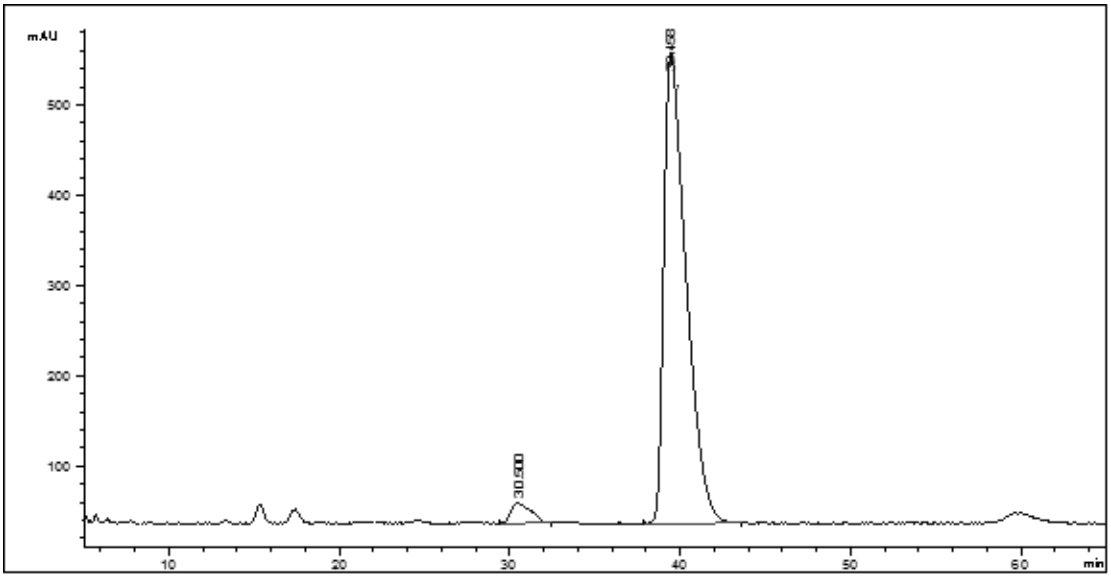
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.969	VB	0.5359	822.79156	23.70710	3.0458
2	17.597	VB	0.7220	2.61910e4	541.03162	96.9542

HPLC chromatogram of racemic 3al



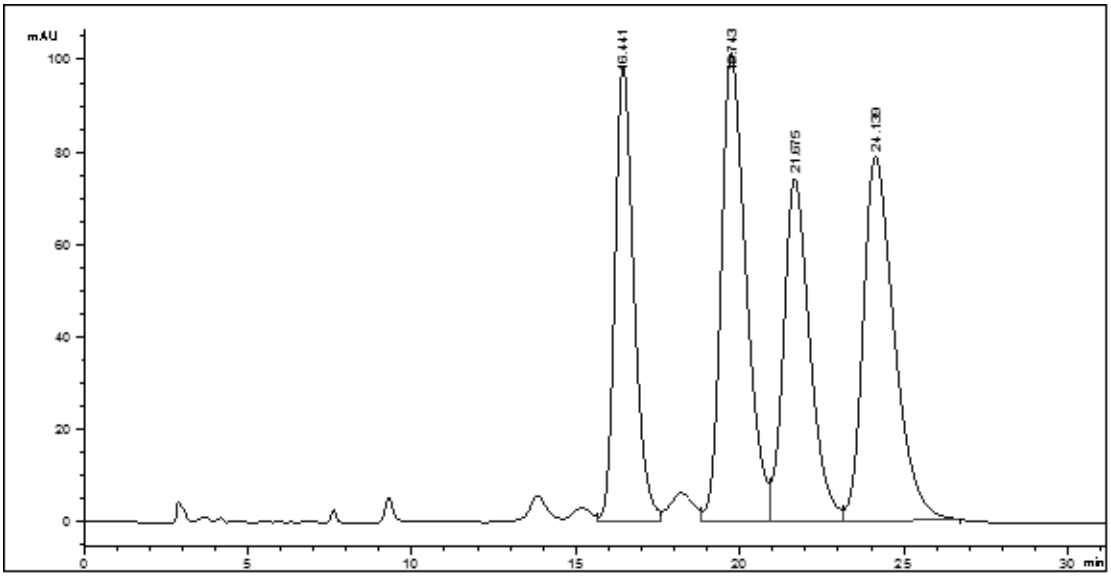
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	25.047	MM	0.7981	2.00390e4	418.46405	21.7812
2	30.601	MM	1.1038	2.58510e4	390.34036	28.0985
3	40.617	MM	1.3658	2.57442e4	314.14456	27.9825
4	60.019	MM	2.1735	2.03671e4	156.17754	22.1378

HPLC chromatogram of chiral 3al



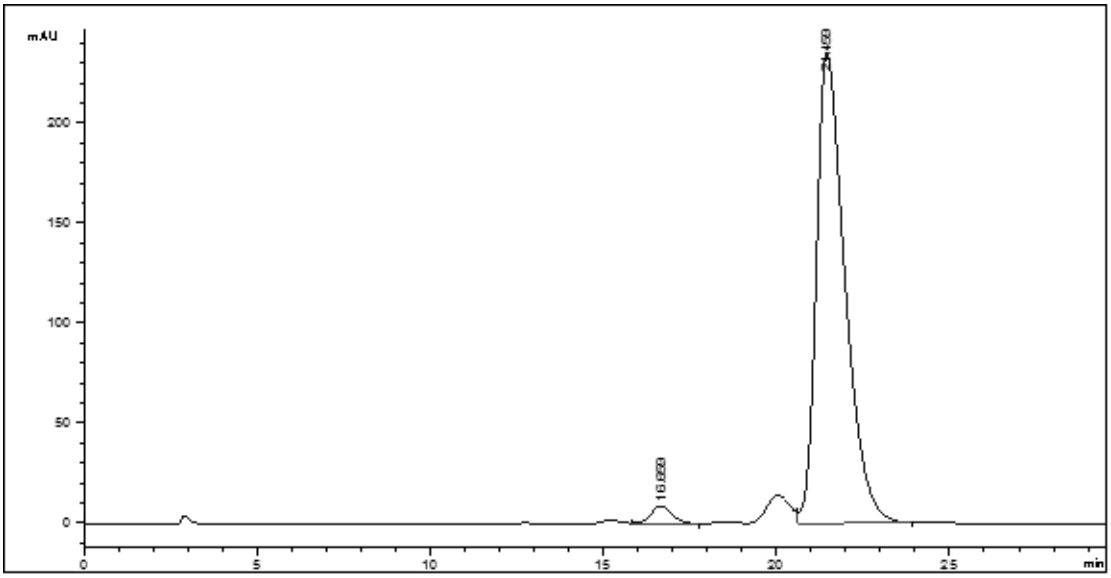
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	30.500	MM	1.3166	1821.06018	23.05290	3.7010
2	39.458	MM	1.5134	4.73840e4	521.83820	96.2990

HPLC chromatogram of racemic 3am



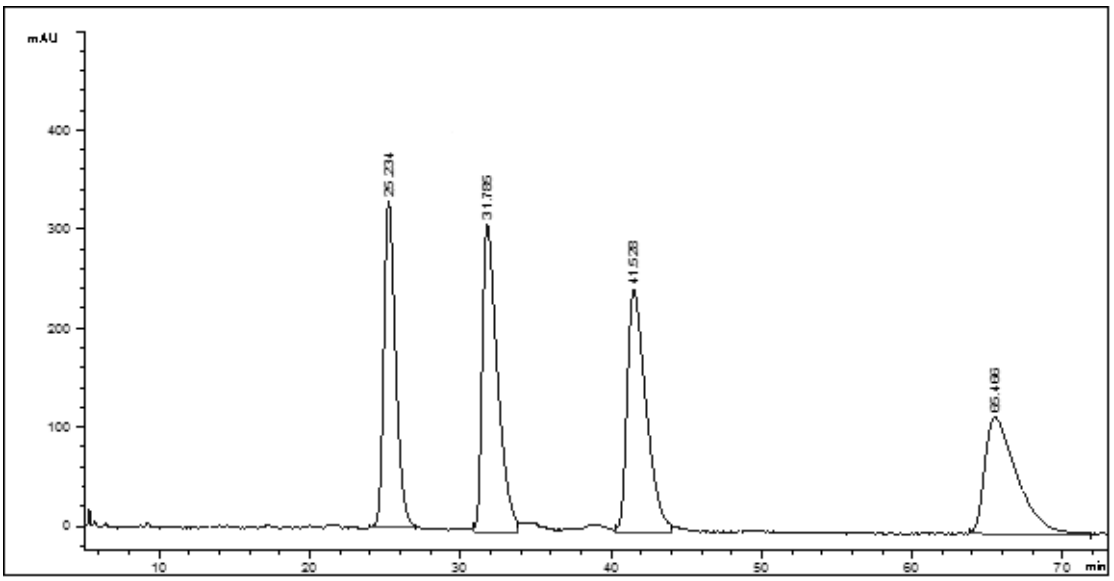
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.441	VV	0.6089	3972.87158	98.81164	21.3933
2	19.743	VV	0.7919	5313.20166	101.39877	28.6107
3	21.675	VV	0.8369	4109.74512	74.03786	22.1303
4	24.139	VB	0.9844	5174.83154	78.81339	27.8656

HPLC chromatogram of chiral 3am



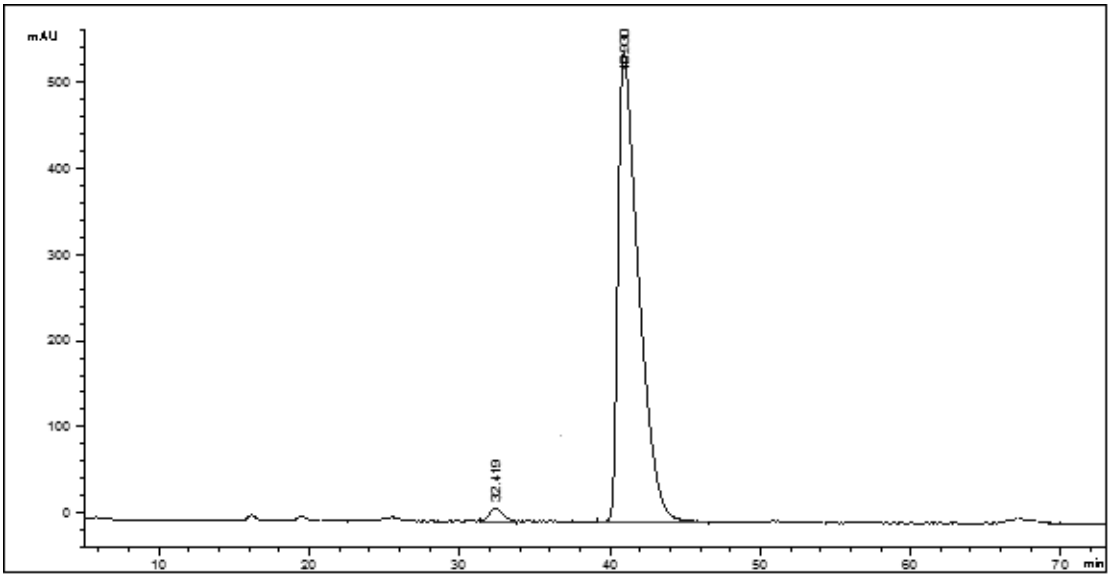
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.659	VB	0.6688	391.15677	8.92154	2.8206
2	21.459	VB	0.8662	1.34768e4	235.30028	97.1794

HPLC chromatogram of racemic 3an



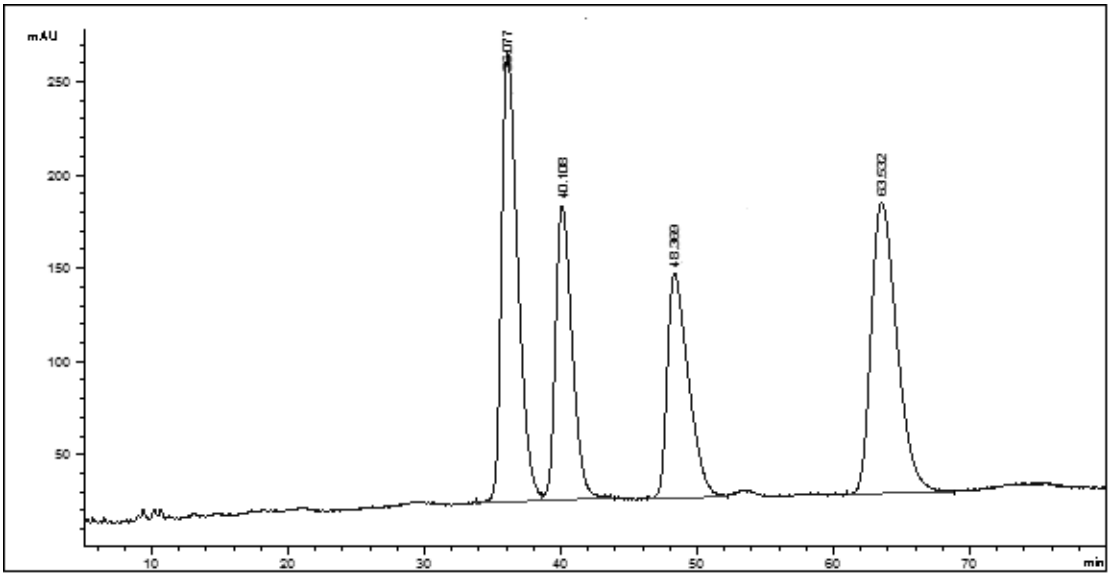
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	25.234	MM	0.9021	1.78271e4	329.35999	22.6243
2	31.785	VV	0.9050	2.18146e4	311.25320	27.6848
3	41.528	VV	1.0388	2.16278e4	245.30238	27.4477
4	65.466	MM	2.4823	1.75269e4	117.67701	22.2433

HPLC chromatogram of chiral 3an



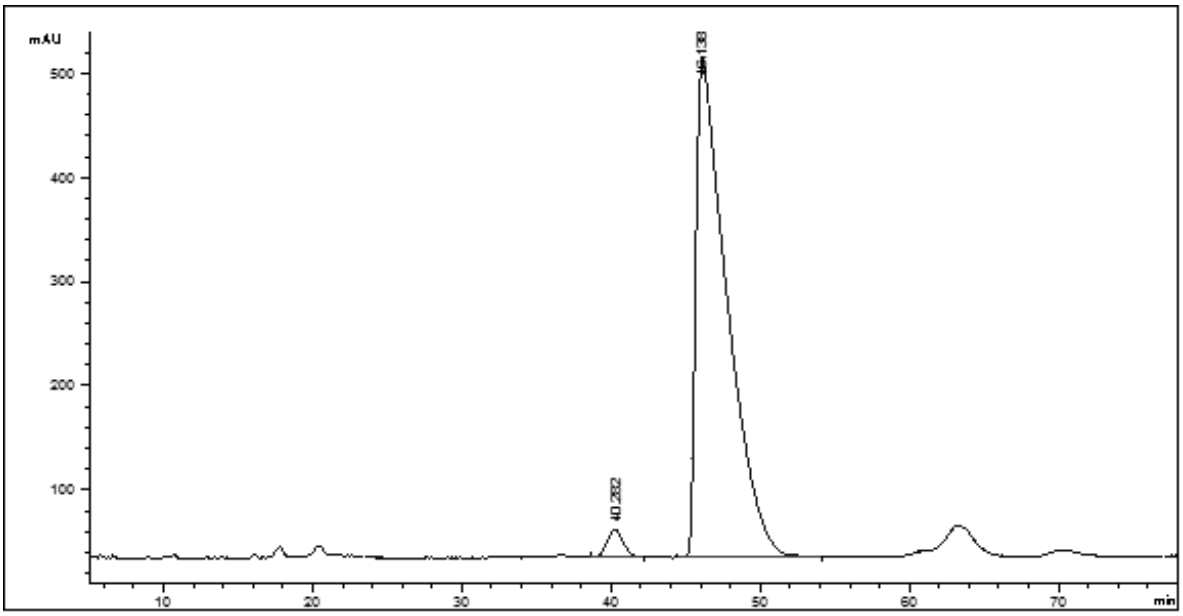
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	32.419	MM	1.0250	996.55426	16.20367	1.8795
2	40.930	MM	1.5912	5.20257e4	544.91559	98.1205

HPLC chromatogram of racemic 3ao



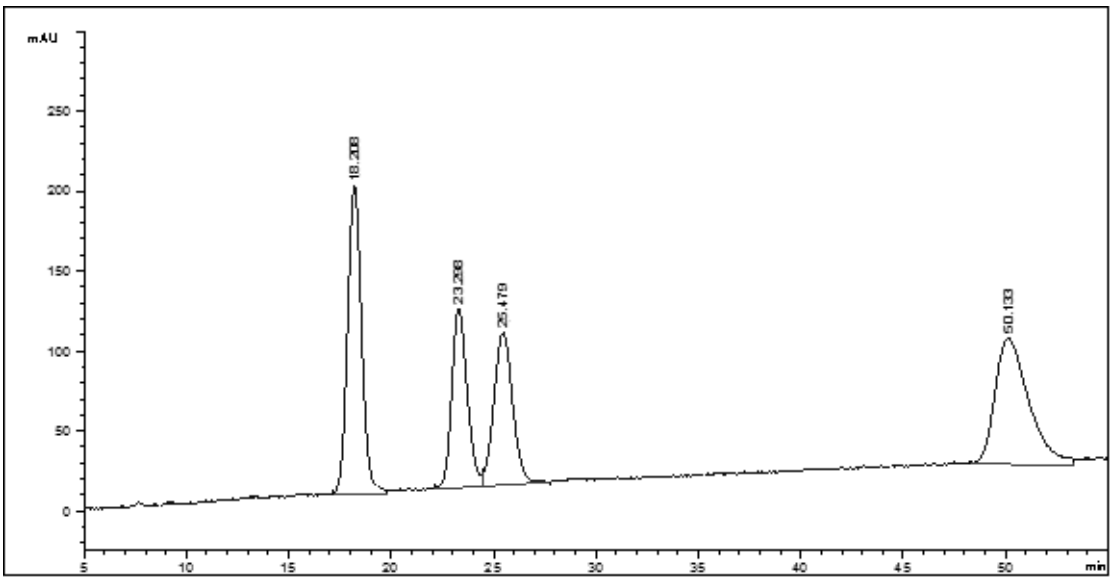
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	36.077	MF	1.3838	2.00237e4	241.17598	29.8676
2	40.108	FM	1.4120	1.33876e4	158.02104	19.9692
3	48.369	MM	1.7971	1.30276e4	120.82171	19.4322
4	63.532	MM	2.1929	2.06025e4	156.58789	30.7310

HPLC chromatogram of chiral 3ao



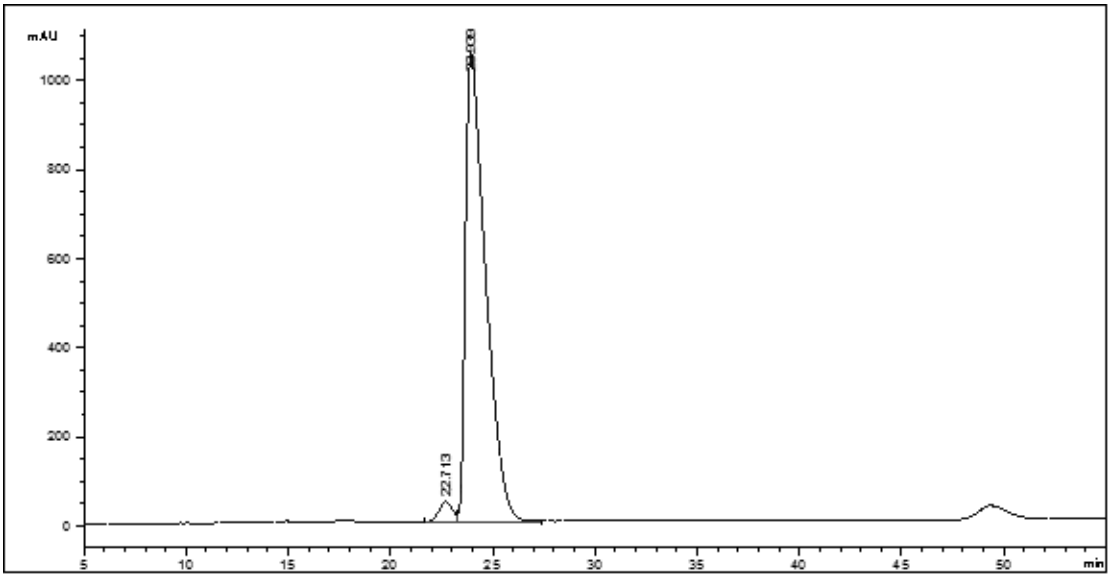
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	40.282	MM	1.2387	1991.11890	26.79025	2.7786
2	46.138	MM	2.4156	6.96674e4	480.66904	97.2214

HPLC chromatogram of racemic 3ap



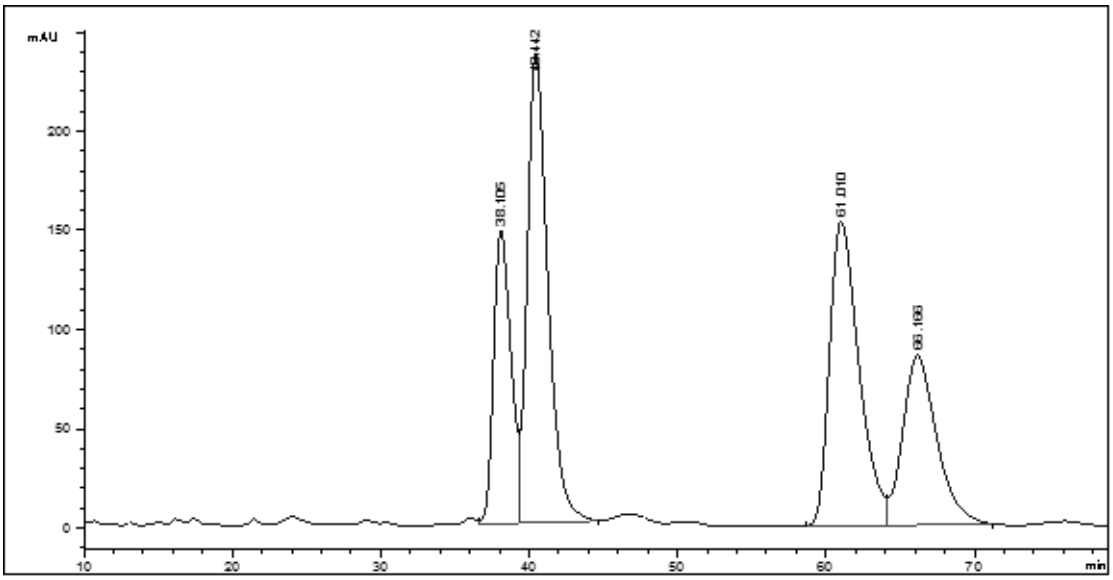
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.208	MM	0.7948	9178.61719	192.48132	30.3922
2	23.298	MF	0.8798	5909.13428	111.94302	19.5663
3	25.479	FM	1.0648	6094.77979	95.40112	20.1810
4	50.133	MM	1.8986	9018.01660	79.16340	29.8604

HPLC chromatogram of chiral 3ap



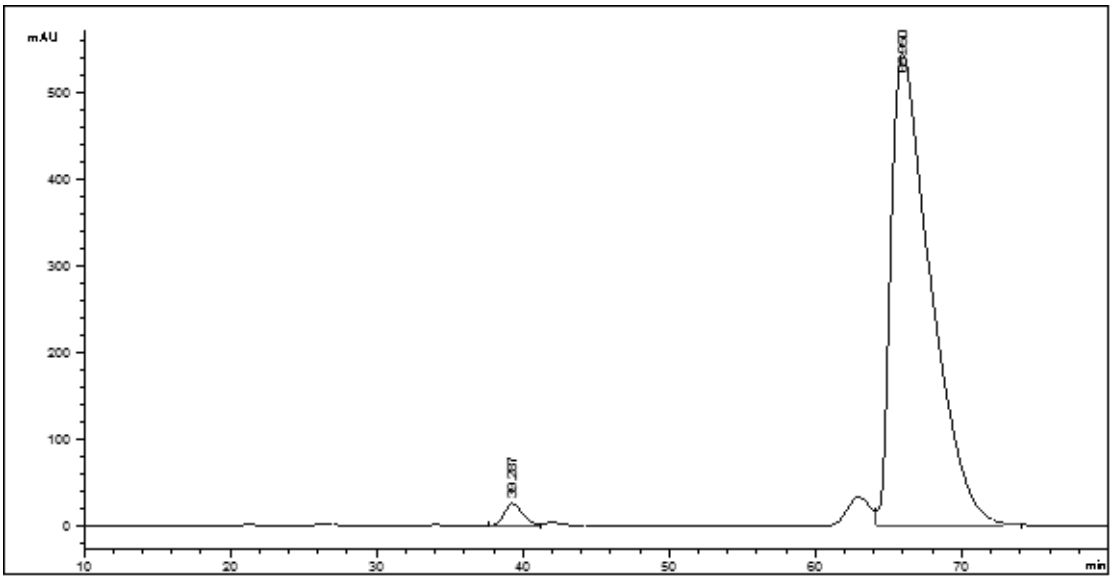
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	22.713	MF	0.7971	2225.48462	46.53009	2.9845
2	23.939	FM	1.1433	7.23420e4	1054.54138	97.0155

HPLC chromatogram of racemic 3aq



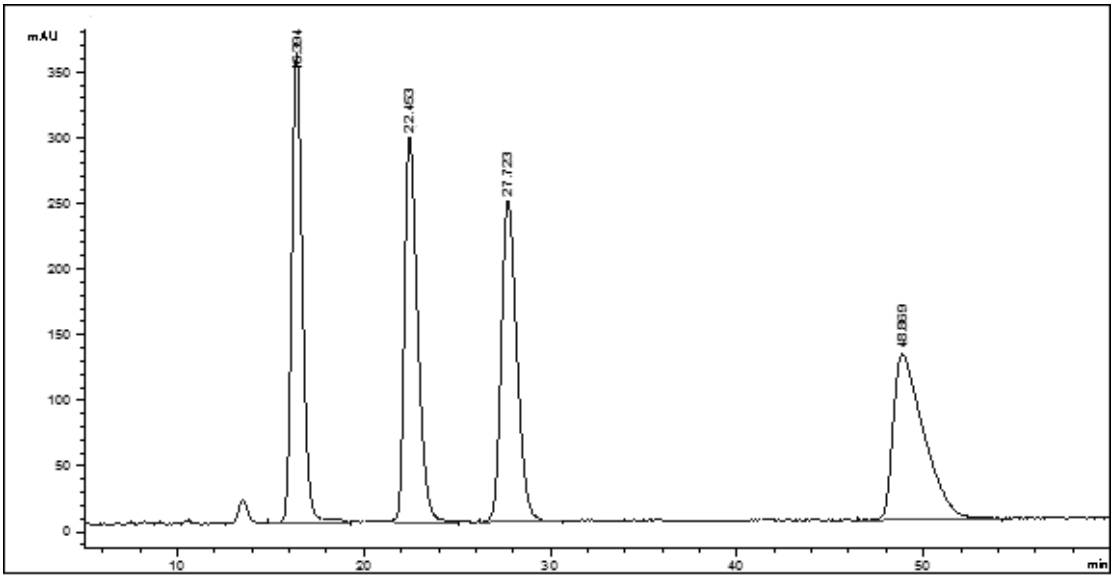
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	38.105	VV	1.2666	1.19782e4	147.68250	17.1764
2	40.442	VB	1.4709	2.29011e4	236.40271	32.8394
3	61.010	BV	2.0455	2.11816e4	153.33664	30.3738
4	66.166	VB	2.3288	1.36756e4	86.04829	19.6104

HPLC chromatogram of chiral 3aq



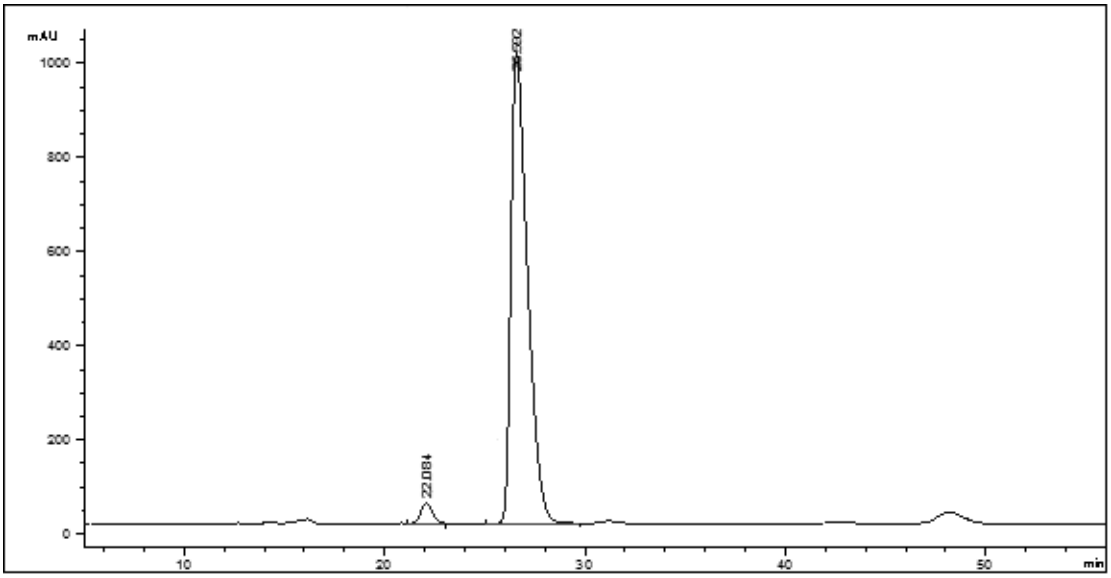
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	39.287	BV	1.3498	2311.09399	25.89854	2.2057
2	65.950	VB	2.6044	1.02467e5	544.92719	97.7943

HPLC chromatogram of racemic 3ar



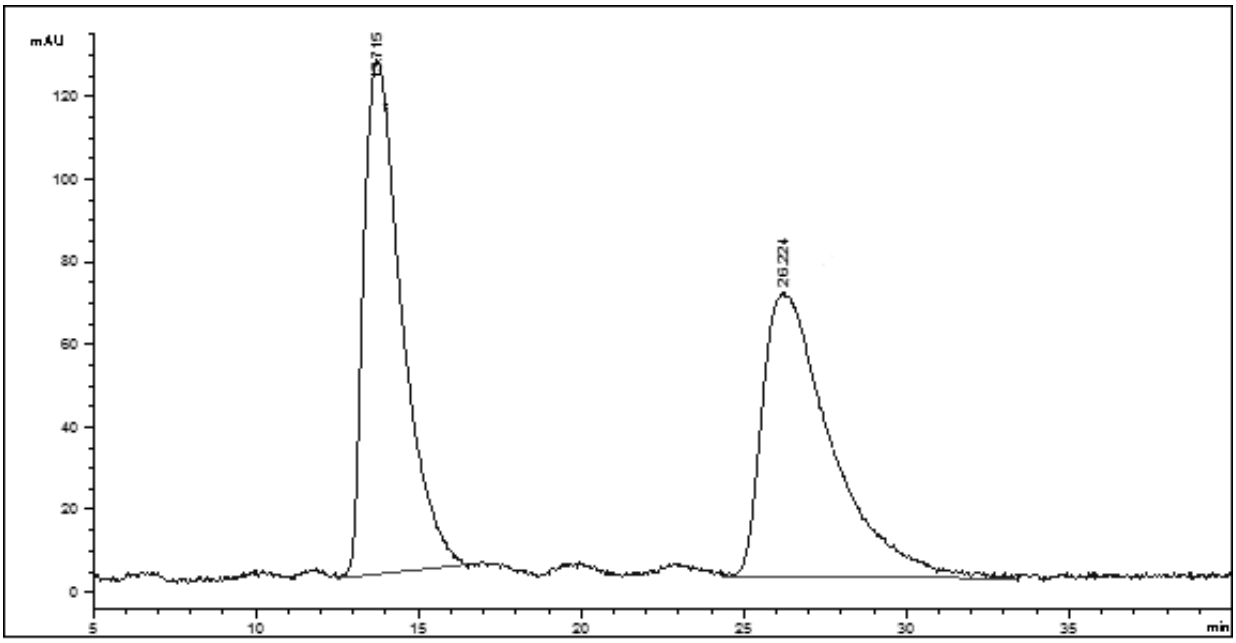
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.394	MM	0.6678	1.43258e4	357.53201	25.0294
2	22.453	MM	0.8111	1.42623e4	293.07620	24.9185
3	27.723	MM	0.9655	1.41609e4	244.43803	24.7412
4	48.869	MM	1.9101	1.44869e4	126.40580	25.3109

HPLC chromatogram of chiral 3ar



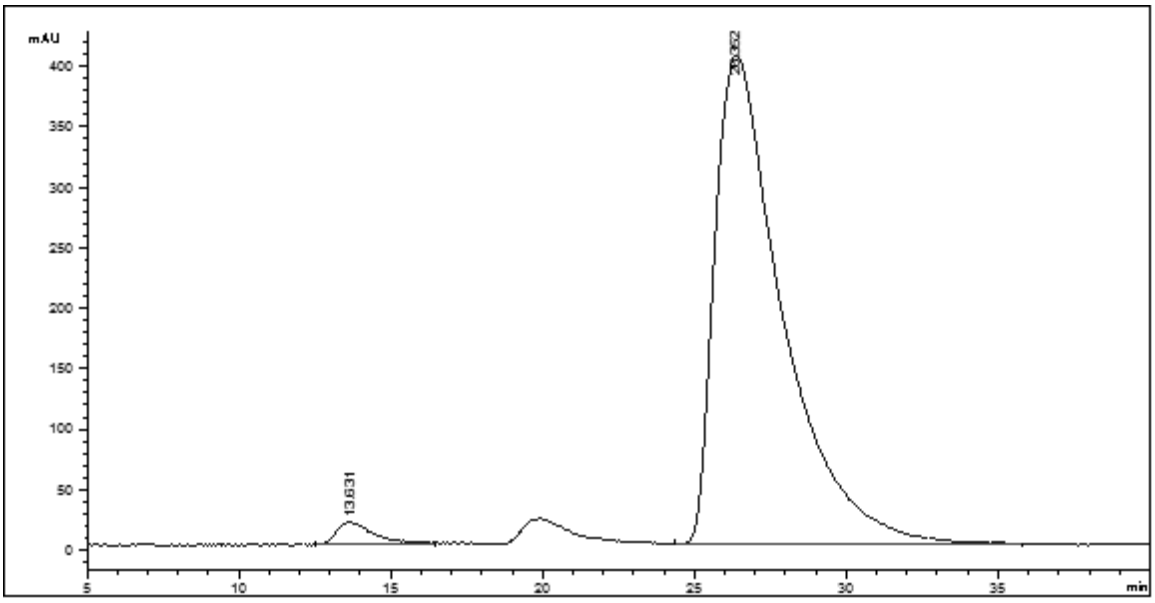
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	22.084	MM	0.6974	1838.33643	43.93312	3.0816
2	26.592	MM	0.9620	5.78166e4	1001.65808	96.9184

HPLC chromatogram of racemic 3as



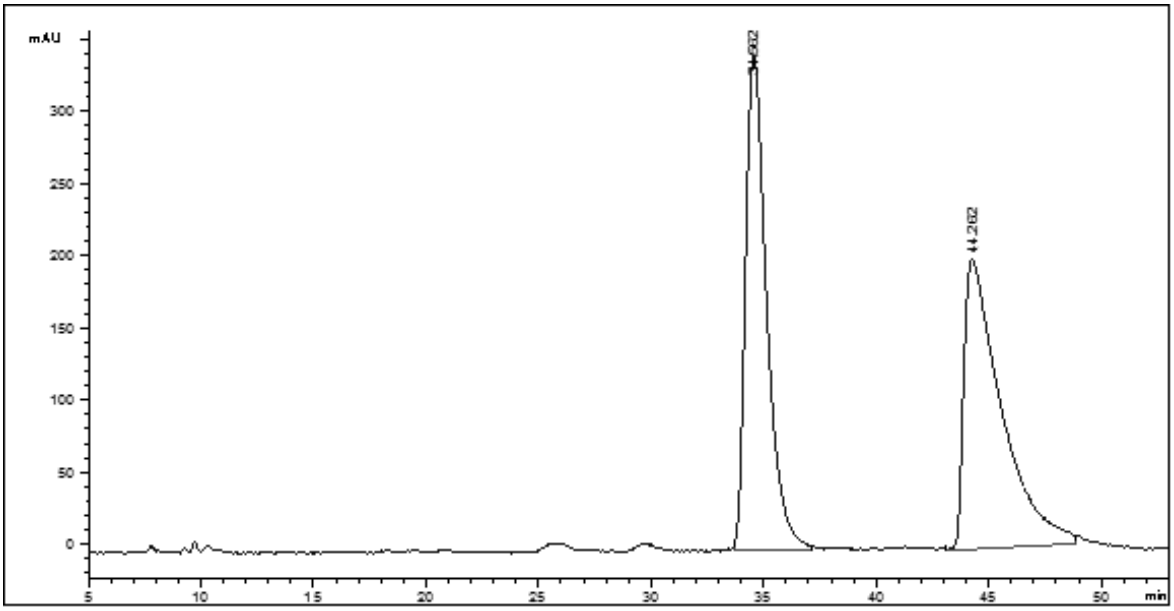
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.715	MM	1.3566	1.01478e4	124.67048	50.1509
2	26.224	MM	2.4402	1.00868e4	68.89429	49.8491

HPLC chromatogram of chiral 3as



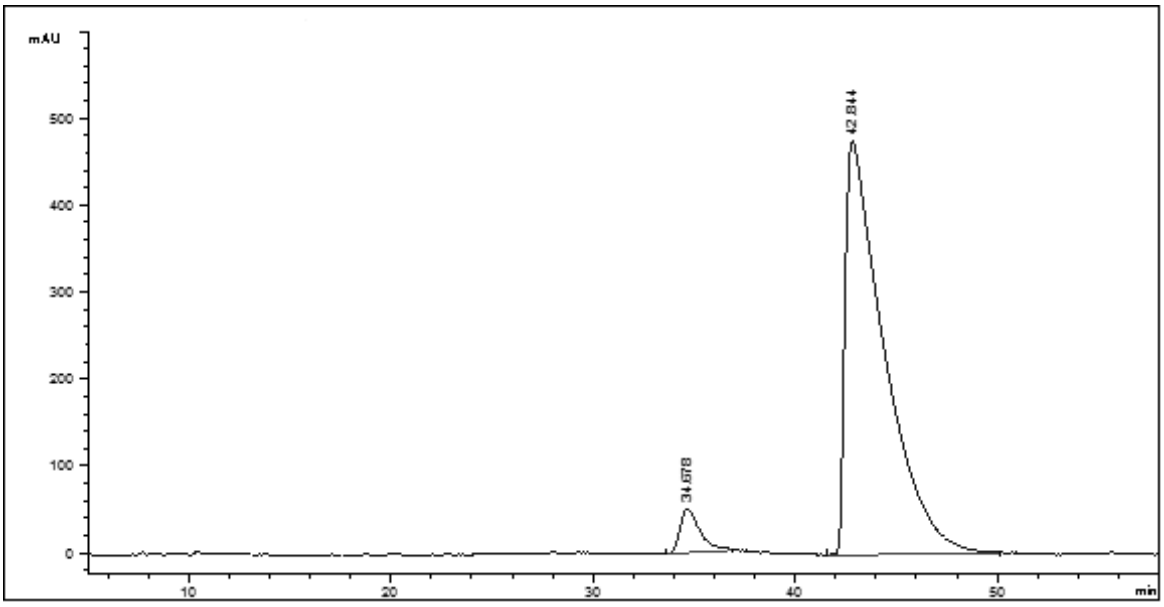
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.631	MM	1.4311	1587.41772	18.48737	2.4692
2	26.352	MM	2.5871	6.27009e4	403.93378	97.5308

HPLC chromatogram of racemic 3at



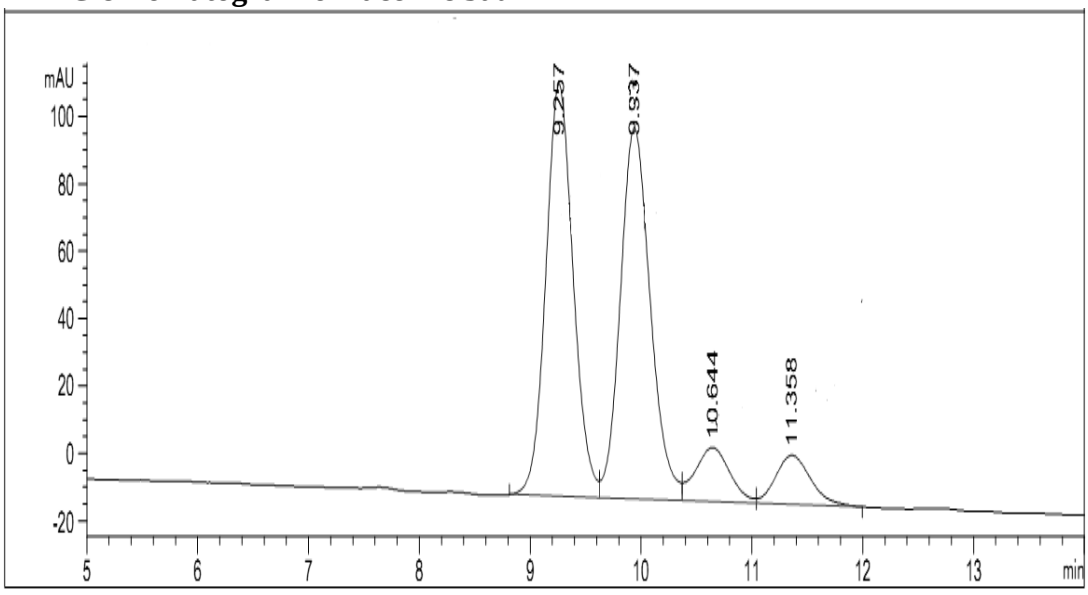
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	34.562	MM	1.0915	2.24462e4	342.75534	49.1457
2	44.262	MM	1.9294	2.32265e4	200.63618	50.8543

HPLC chromatogram of chiral 3at



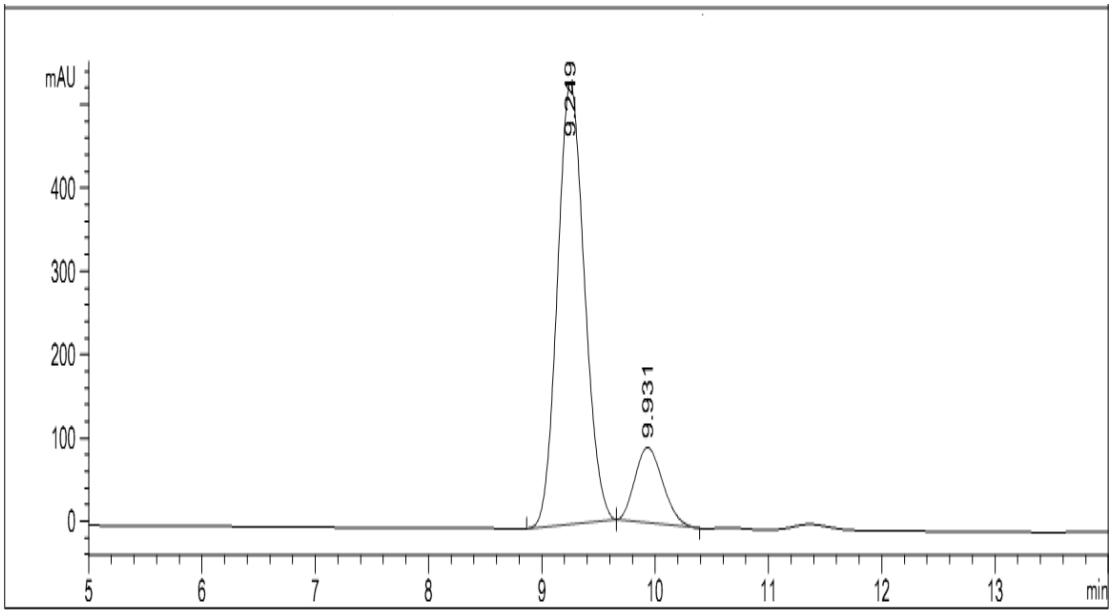
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	34.678	MM	1.1178	3435.07495	51.21899	5.0974
2	42.844	MM	2.2370	6.39535e4	476.48846	94.9026

HPLC chromatogram of racemic 3au



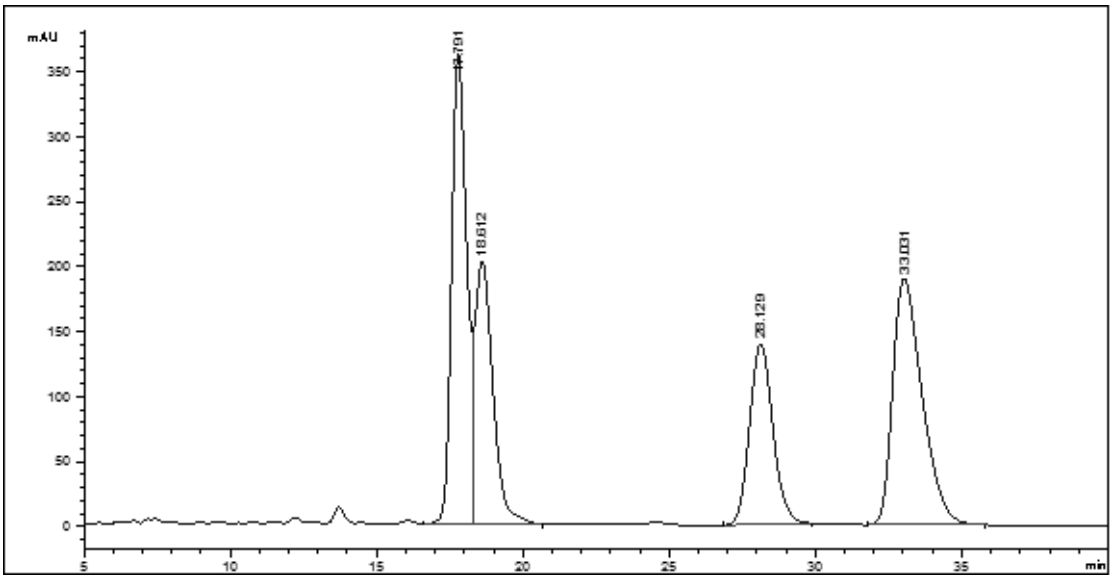
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.257	MF	0.2852	2089.88159	122.12829	43.3575
2	9.937	MF	0.3131	2065.78882	109.96769	42.8577
3	10.644	MF	0.3588	344.20093	15.98792	7.1409
4	11.358	FM	0.3664	320.24109	14.56599	6.6439

HPLC chromatogram of chiral 3au



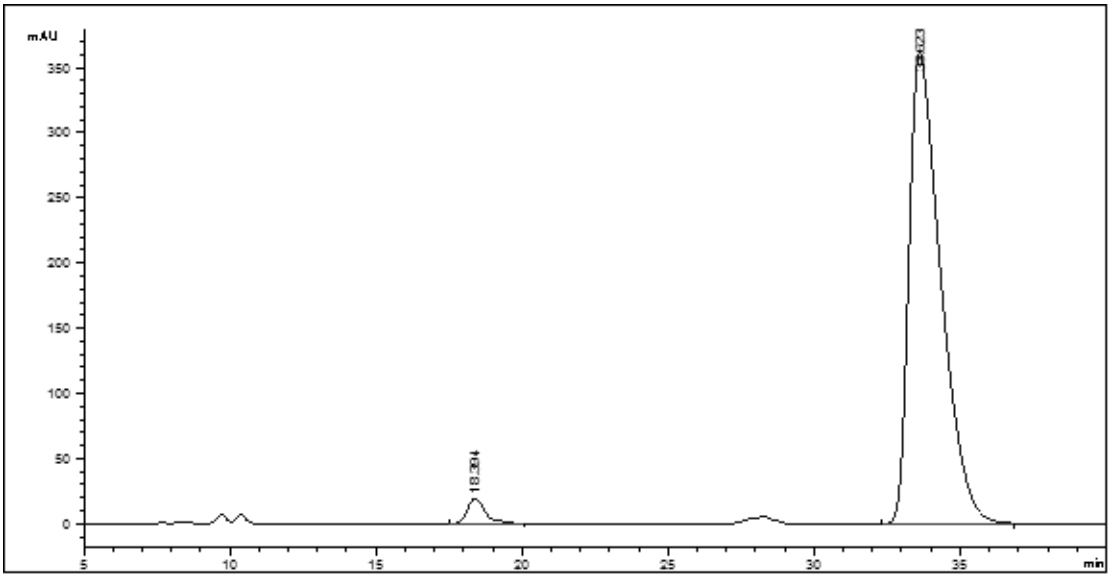
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.249	BB	0.2572	8766.00098	529.30994	84.9690
2	9.931	BB	0.2702	1550.69995	90.37865	15.0310

HPLC chromatogram of racemic 3ba



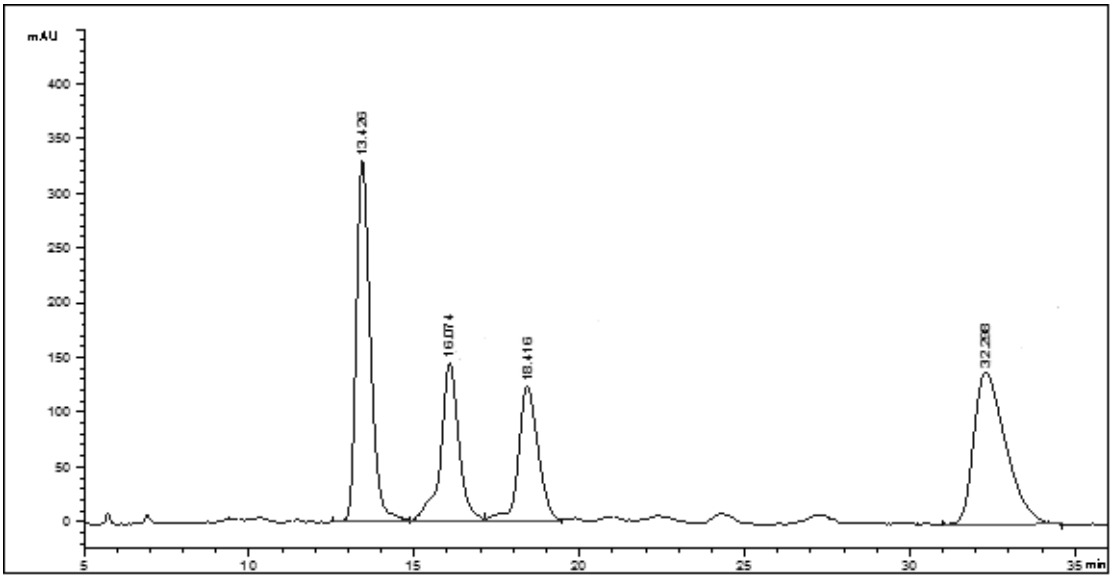
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.791	VV	0.5476	1.29314e4	362.16187	30.3222
2	18.612	VB	0.6477	8758.54785	202.33405	20.5374
3	28.129	BB	0.8609	7704.28809	139.26125	18.0654
4	33.031	BB	1.0452	1.32525e4	189.67358	31.0750

HPLC chromatogram of chiral 3ba



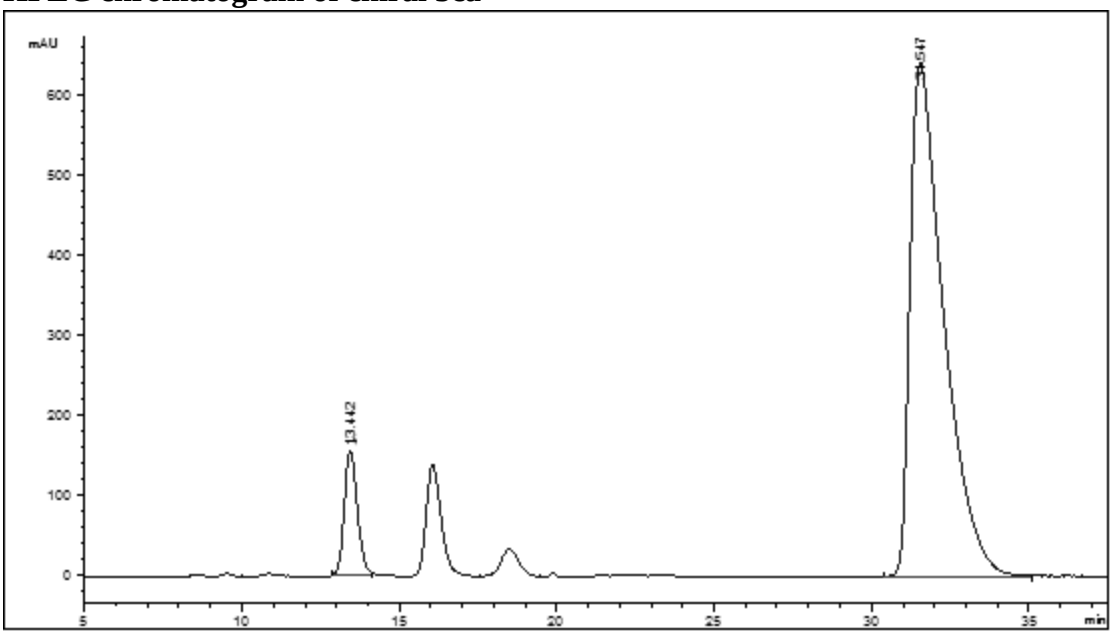
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.394	BB	0.6664	882.88641	19.77801	3.1275
2	33.623	BB	1.1351	2.73471e4	361.83572	96.8725

HPLC chromatogram of racemic 3ca



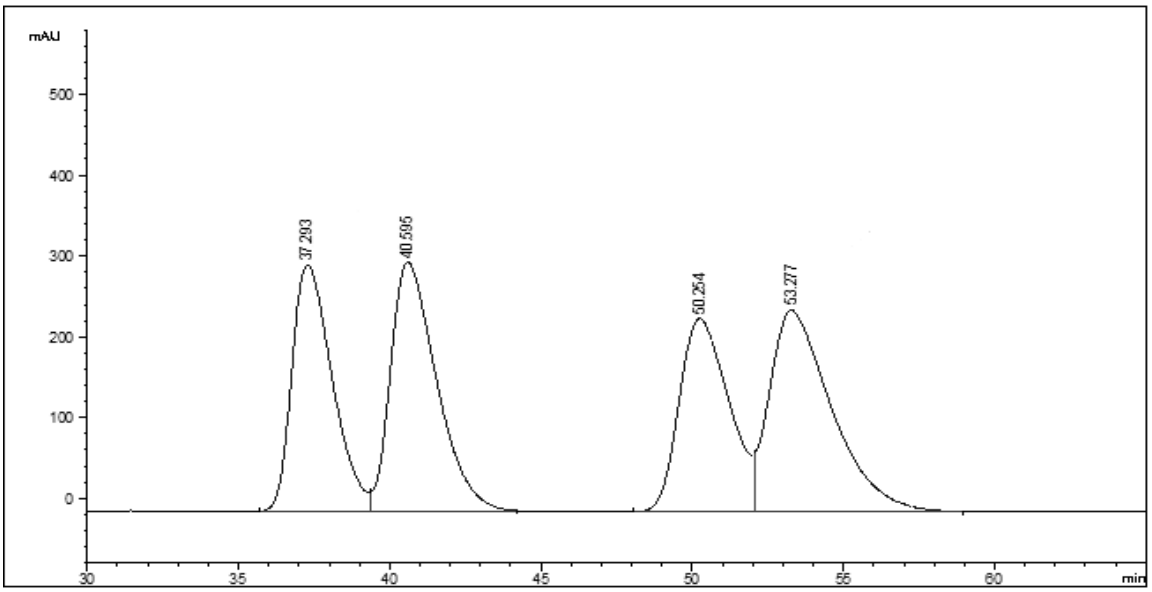
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.426	MF	0.4954	9792.64648	329.48154	32.8904
2	16.074	FM	0.6386	5564.72217	145.23325	18.6901
3	18.416	FM	0.6898	5081.88135	122.79475	17.0684
4	32.298	MM	1.1172	9334.36523	139.25082	31.3511

HPLC chromatogram of chiral 3ca



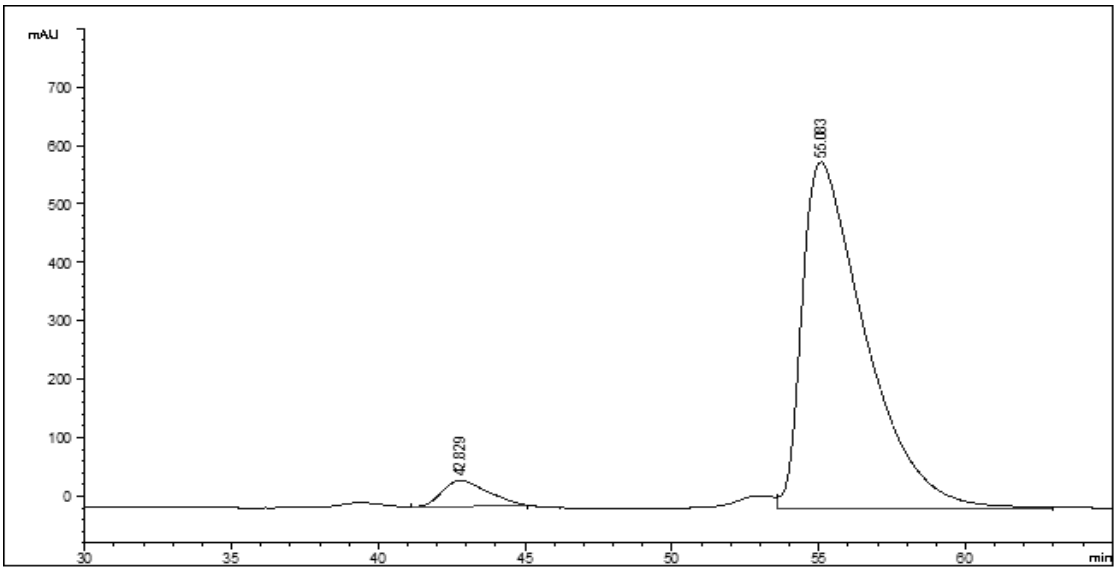
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.442	MM	0.4798	4511.71387	156.72169	8.5500
2	31.547	MM	1.2487	4.82568e4	644.07642	91.4500

HPLC chromatogram of racemic 3da



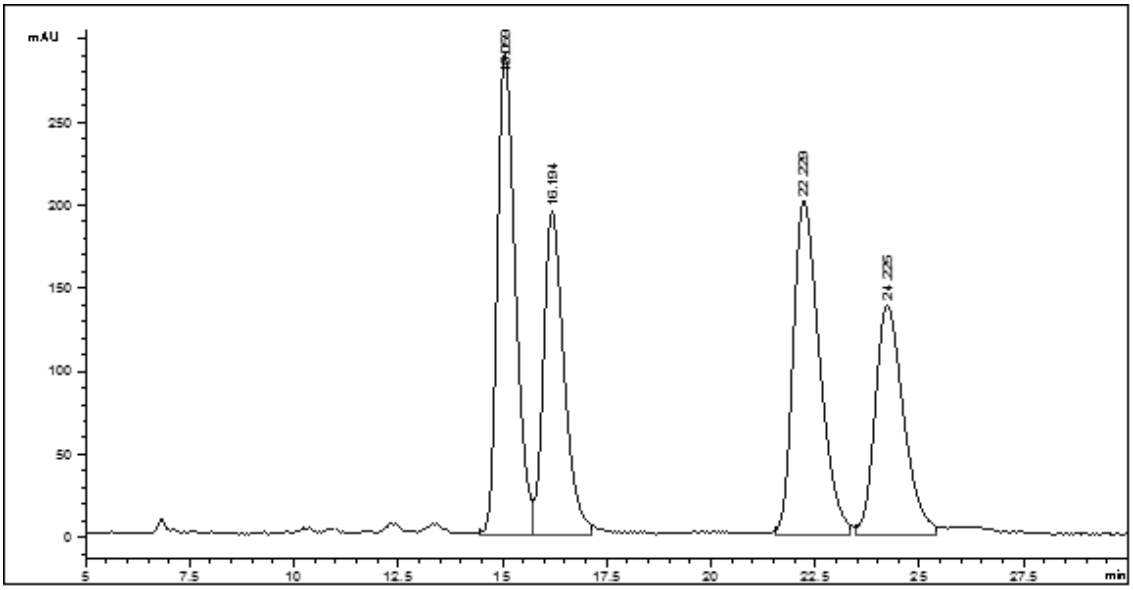
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	37.293	MF	1.5497	2.84532e4	306.00061	22.9534
2	40.595	FM	1.7584	3.25990e4	308.97647	26.2978
3	50.254	MF	1.9125	2.74707e4	239.39371	22.1608
4	53.277	FM	2.3570	3.54381e4	250.58421	28.5881

HPLC chromatogram of chiral 3da



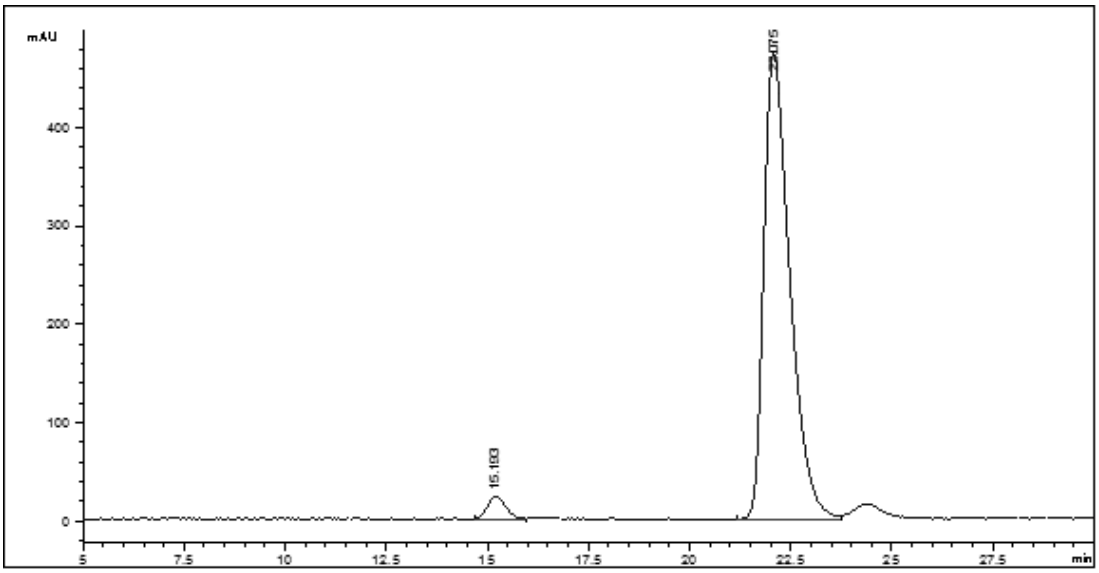
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	42.829	MM	1.7798	4767.58838	44.64569	5.0865
2	55.083	MM	2.4989	8.89632e4	593.35681	94.9135

HPLC chromatogram of racemic 3ea



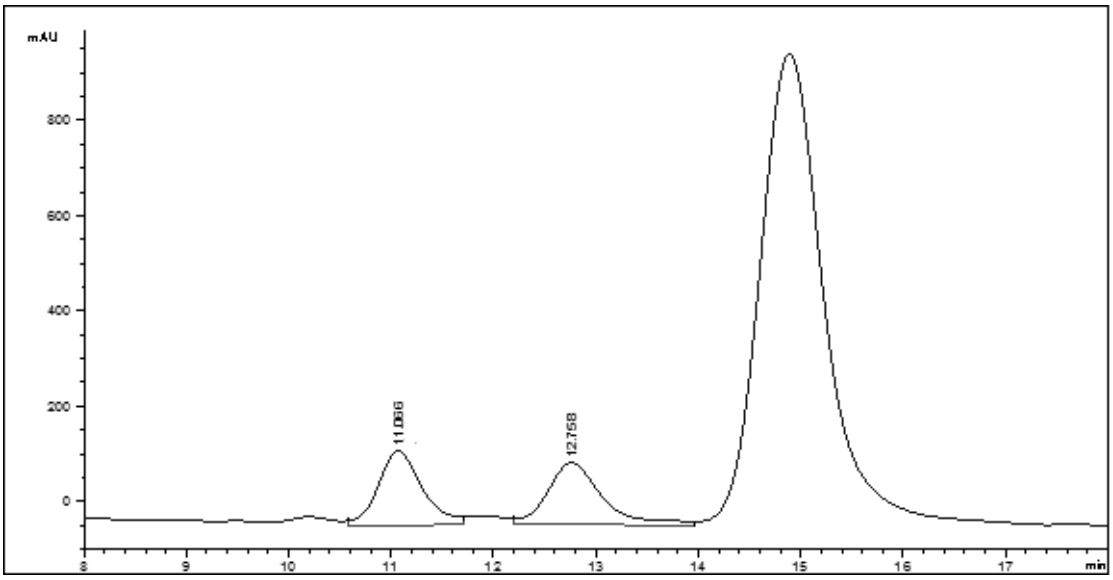
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.059	VV	0.4455	8758.44824	290.01736	28.3343
2	16.194	VV	0.4927	6691.60938	194.67509	21.6479
3	22.229	VV	0.6033	8853.84082	201.34688	28.6429
4	24.225	VV	0.6136	6607.22070	138.80832	21.3749

HPLC chromatogram of chiral 3ea



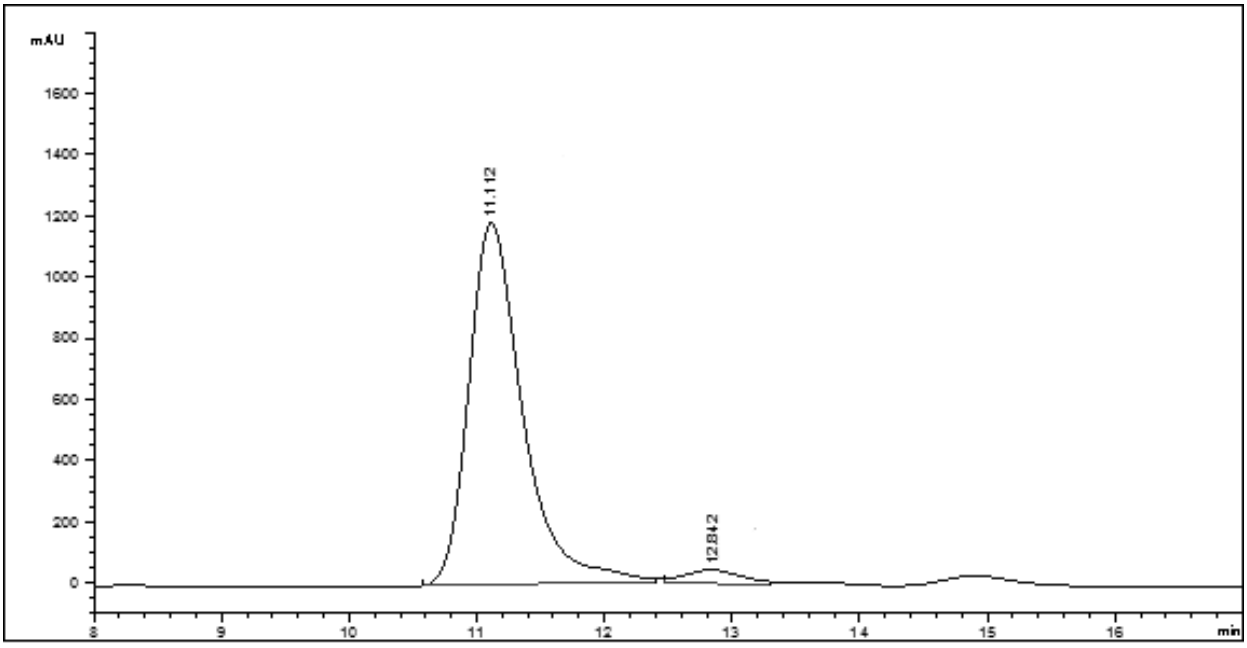
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.193	MM	0.5117	727.08862	23.68271	3.3172
2	22.075	MF	0.7455	2.11914e4	473.76532	96.6828

HPLC chromatogram of racemic 3fa



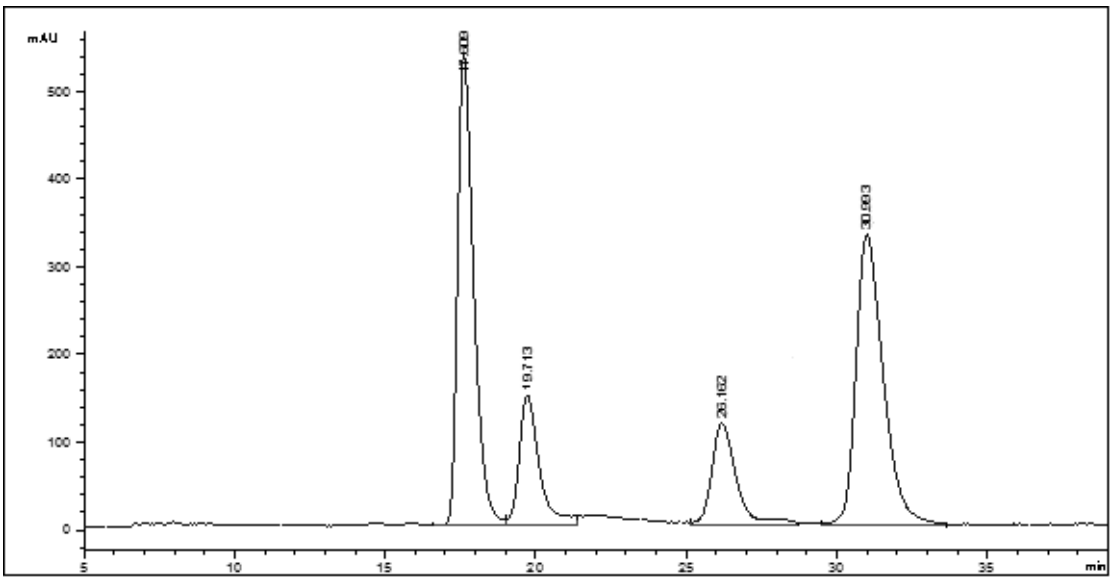
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.066	MM	0.5002	4696.83936	156.51373	49.4302
2	12.758	VV	0.5560	4805.11572	129.27487	50.5698

HPLC chromatogram of chiral 3fa



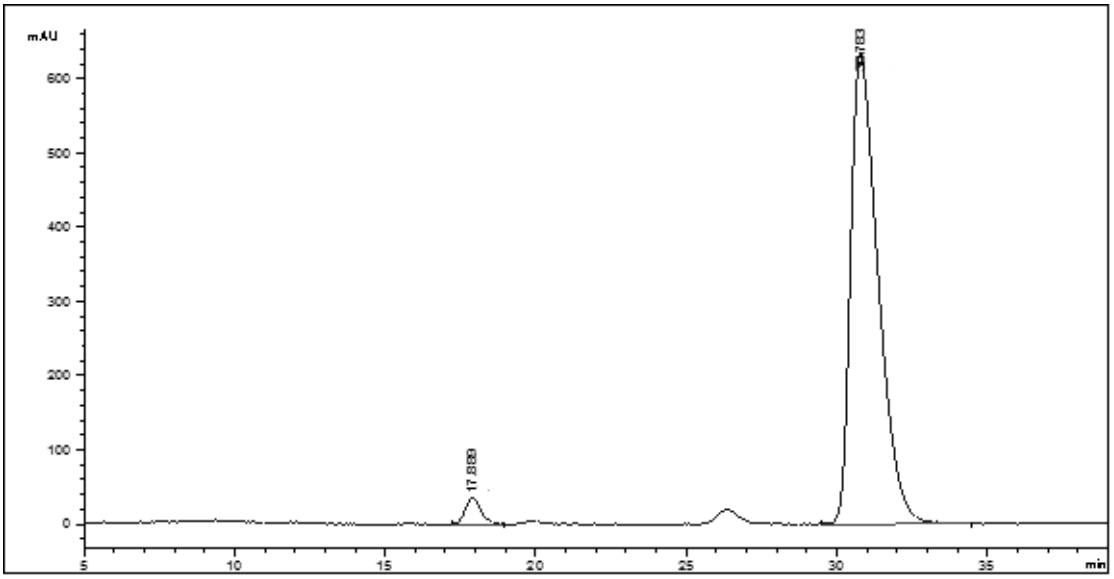
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.112	MM	0.4896	3.46876e4	1180.78882	96.1807
2	12.842	MM	0.5214	1377.43652	44.02686	3.8193

HPLC chromatogram of racemic 3ga



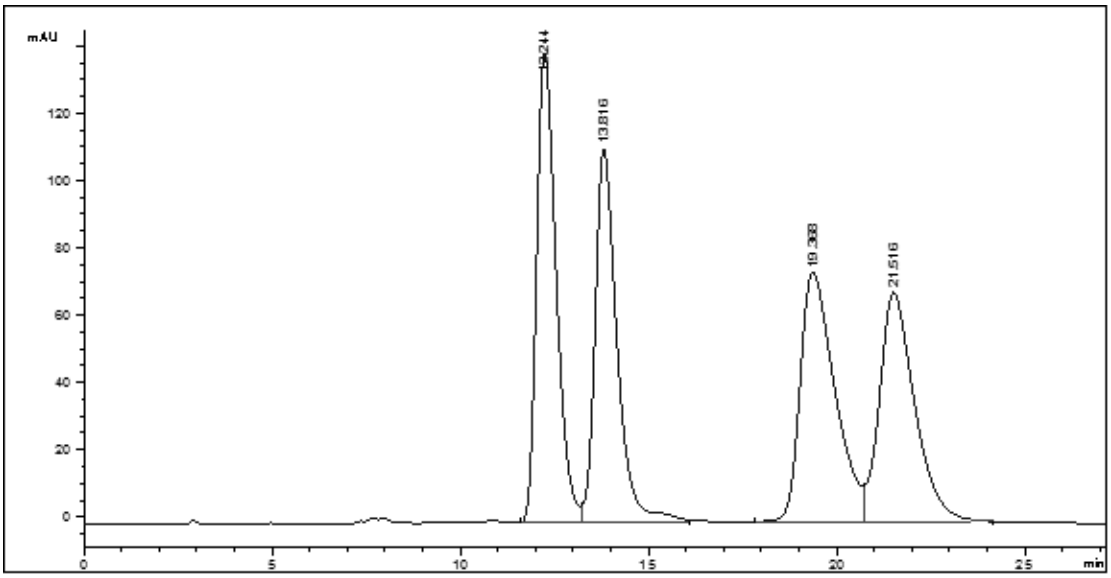
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.609	MF	0.6214	2.00090e4	536.69897	36.6240
2	19.713	MF	0.7780	6915.66406	148.14848	12.6583
3	26.162	MF	0.9747	6798.32861	116.24279	12.4435
4	30.993	MM	1.0513	2.09106e4	331.51184	38.2743

HPLC chromatogram of chiral 3ga



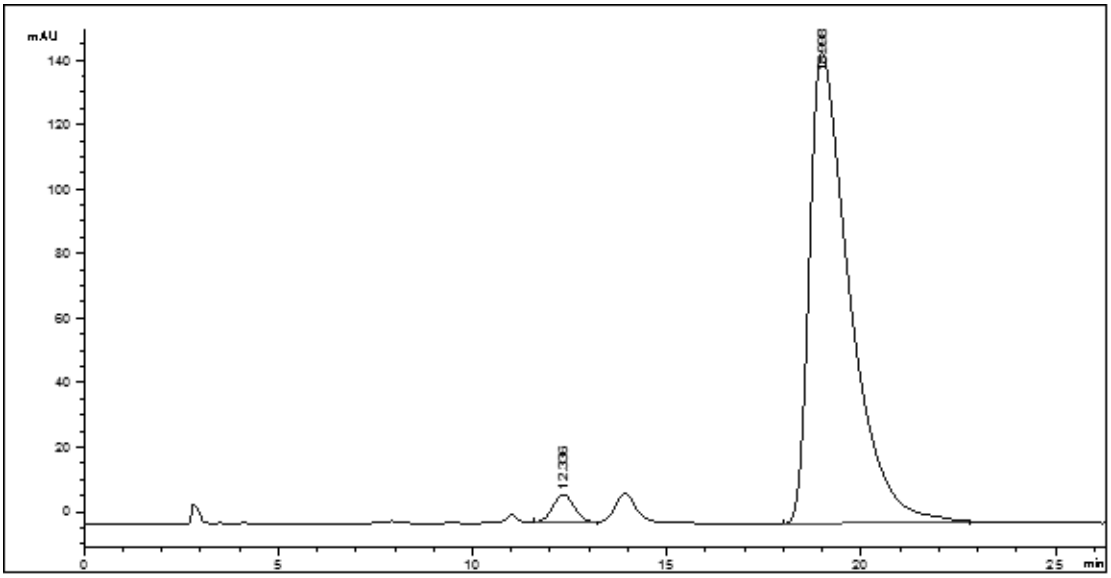
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.889	MM	0.6040	1282.14587	35.38114	3.0826
2	30.783	MM	1.0581	4.03108e4	634.96613	96.9174

HPLC chromatogram of racemic 3ha



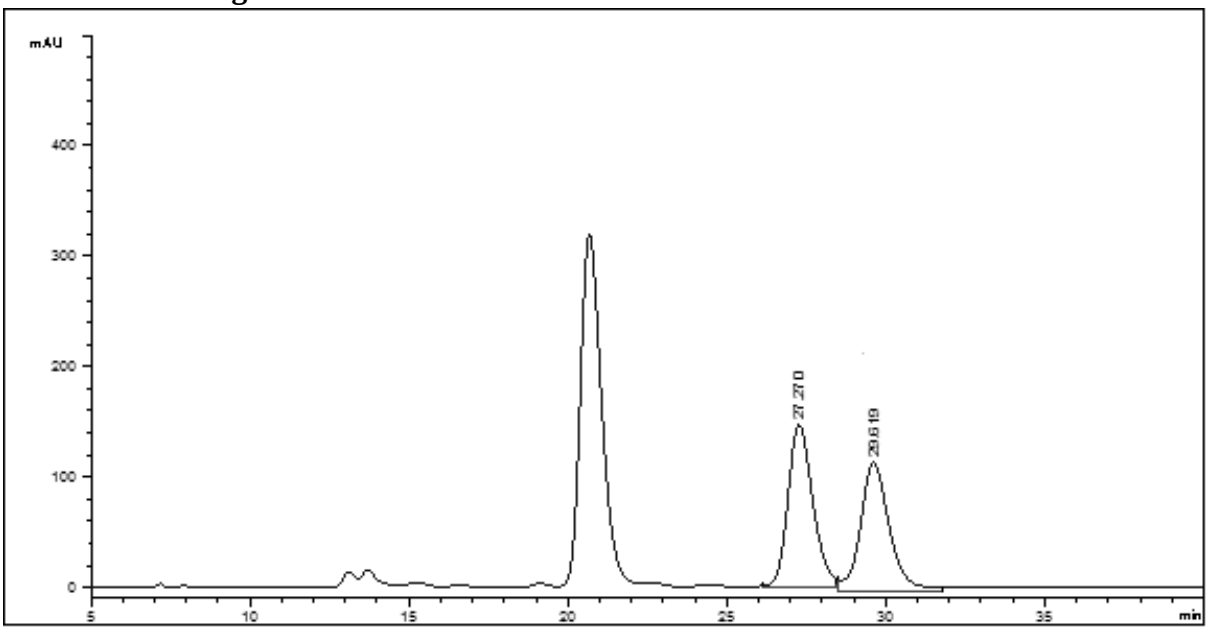
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.244	MF	0.6012	5026.62646	139.34380	26.8535
2	13.816	FM	0.6752	4500.91357	111.09346	24.0450
3	19.368	MF	1.0739	4781.72656	74.20834	25.5451
4	21.516	FM	1.0789	4409.46533	68.11363	23.5564

HPLC chromatogram of chiral 3ha



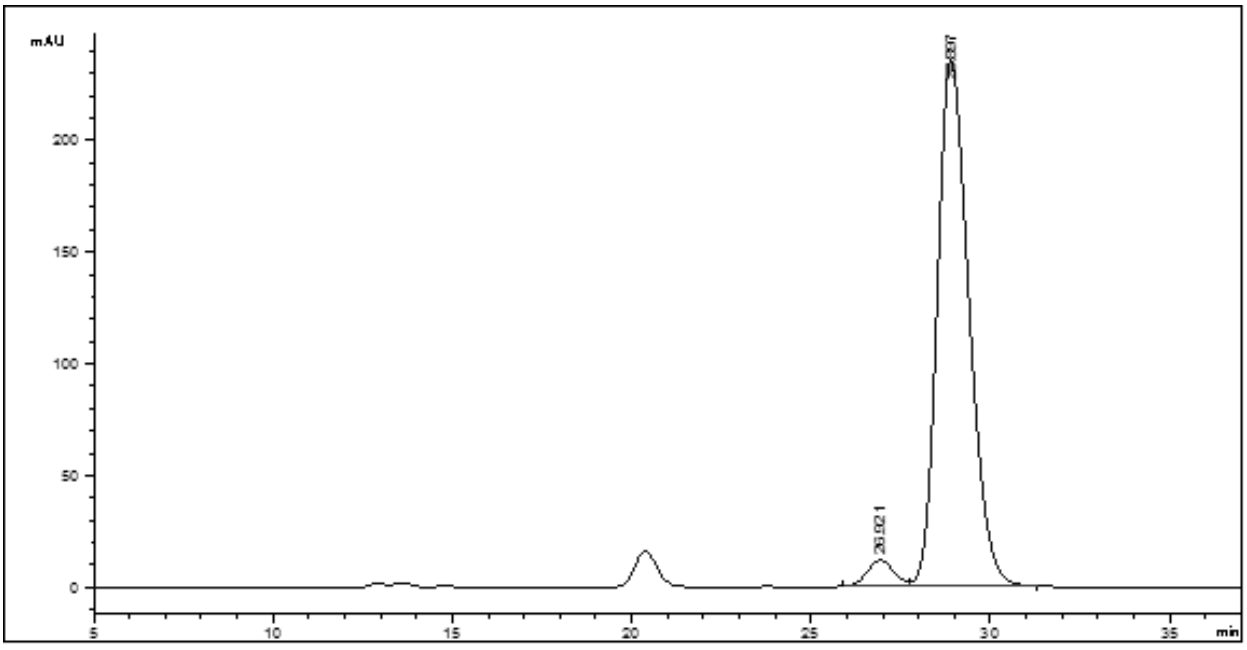
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.336	BV	0.6125	346.00888	8.75556	3.2074
2	18.998	BB	1.0535	1.04419e4	145.88475	96.7926

HPLC chromatogram of racemic 3ia



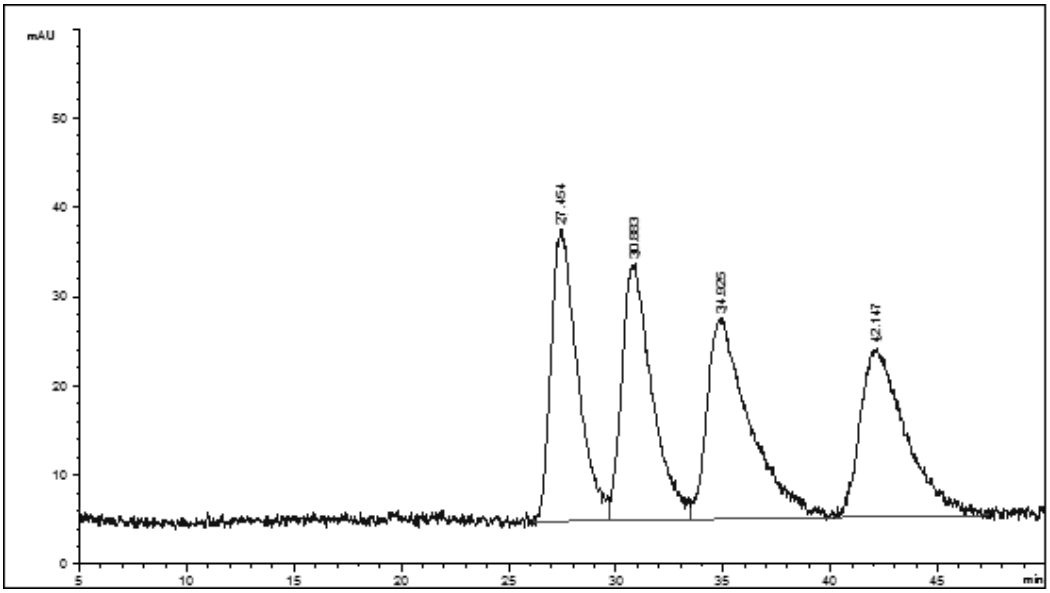
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	27.270	MM	0.9156	8128.26367	147.96188	51.9429
2	29.619	MM	1.0688	7520.20605	117.26537	48.0571

HPLC chromatogram of chiral 3ia



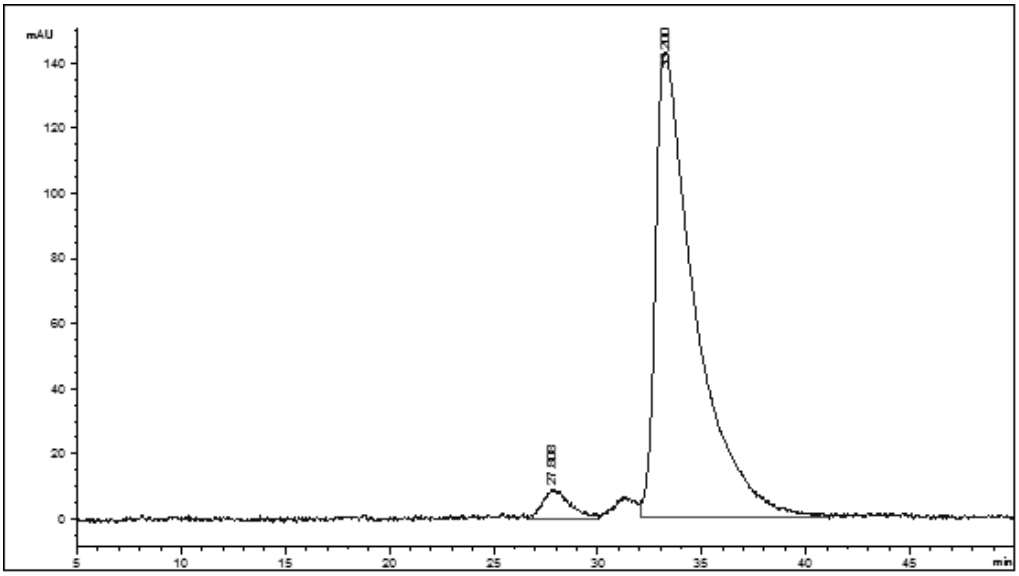
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	26.921	BV	0.8217	615.77533	11.73759	4.0846
2	28.897	VB	0.9481	1.44597e4	235.89873	95.9154

HPLC chromatogram of racemic 4aa



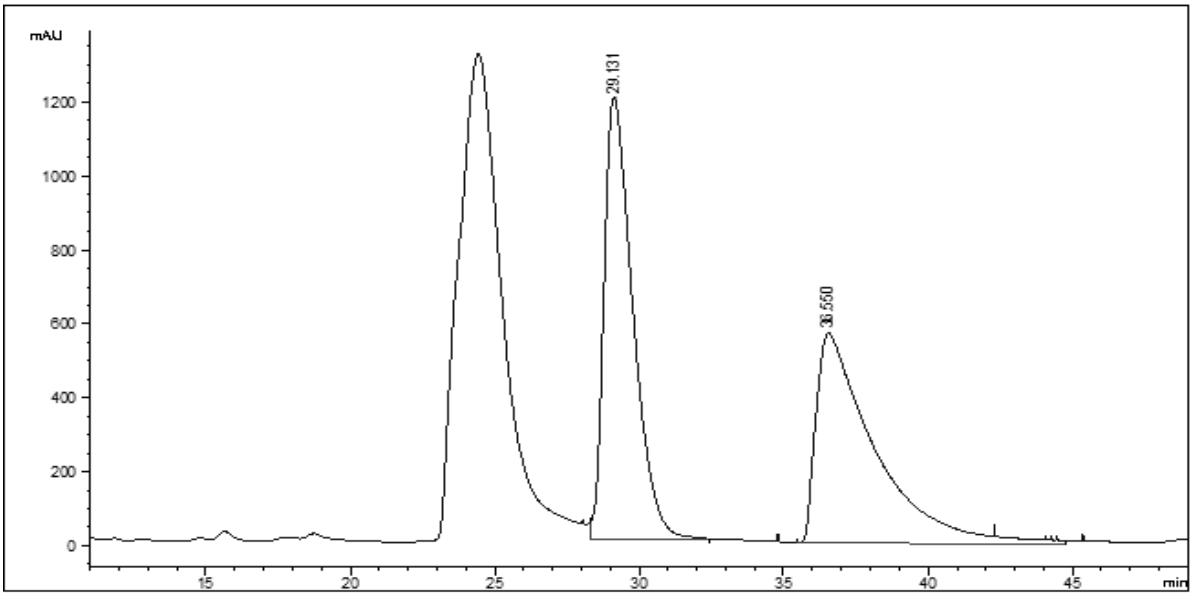
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	27.454	MF	1.4268	2799.78833	32.70589	24.3922
2	30.883	FM	1.6270	2804.55493	28.72905	24.4337
3	34.925	FM	2.2877	3093.16528	22.53477	26.9481
4	42.147	FM	2.4549	2780.71094	18.87848	24.2260

HPLC chromatogram of chiral 4aa



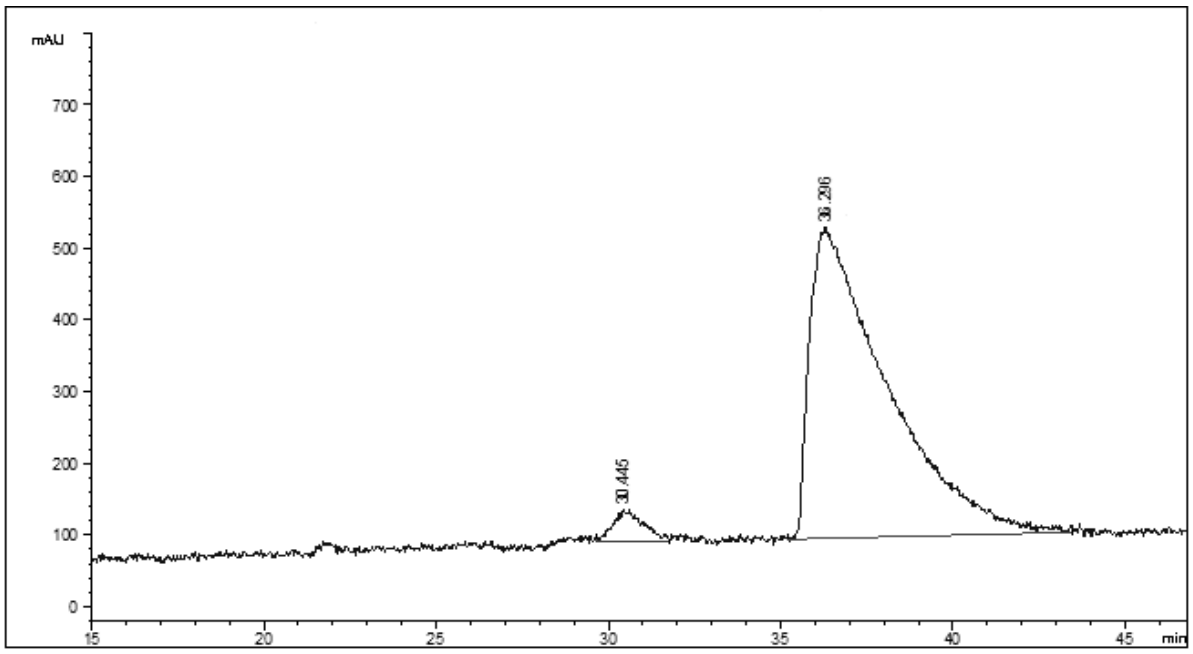
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	27.808	MM	1.4585	769.42145	8.79249	3.9612
2	33.200	FM	2.1765	1.86547e4	142.84915	96.0388

HPLC chromatogram of racemic 4ab



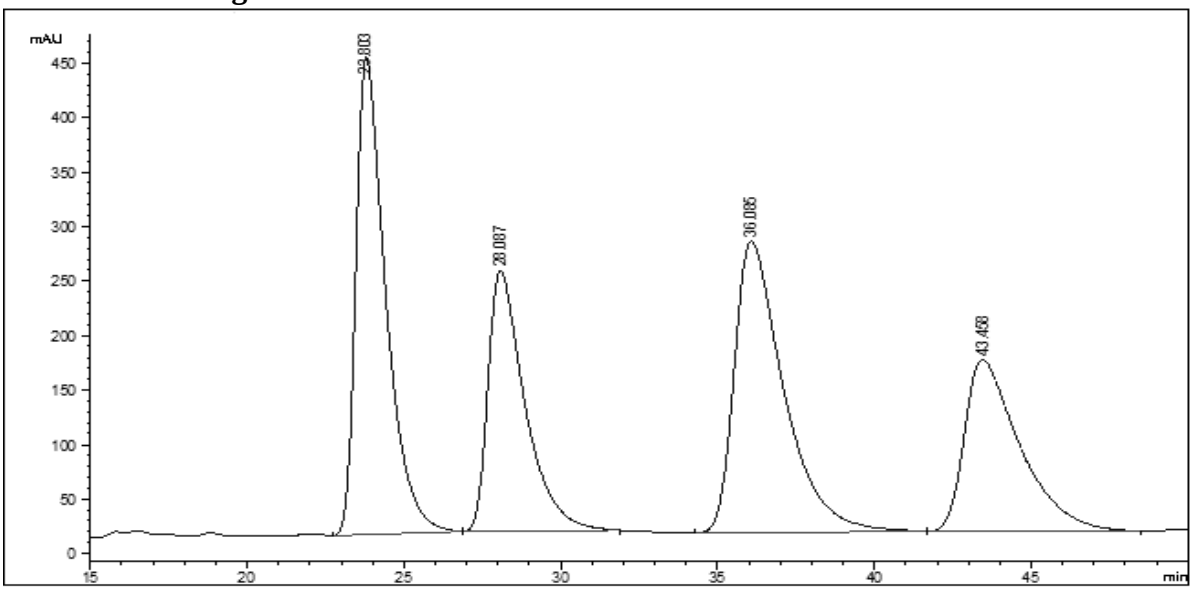
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	29.131	MM	1.1514	8.23126e4	1191.52502	50.6406
2	36.550	MM	2.3494	8.02301e4	569.15521	49.3594

HPLC chromatogram of chiral 4ab



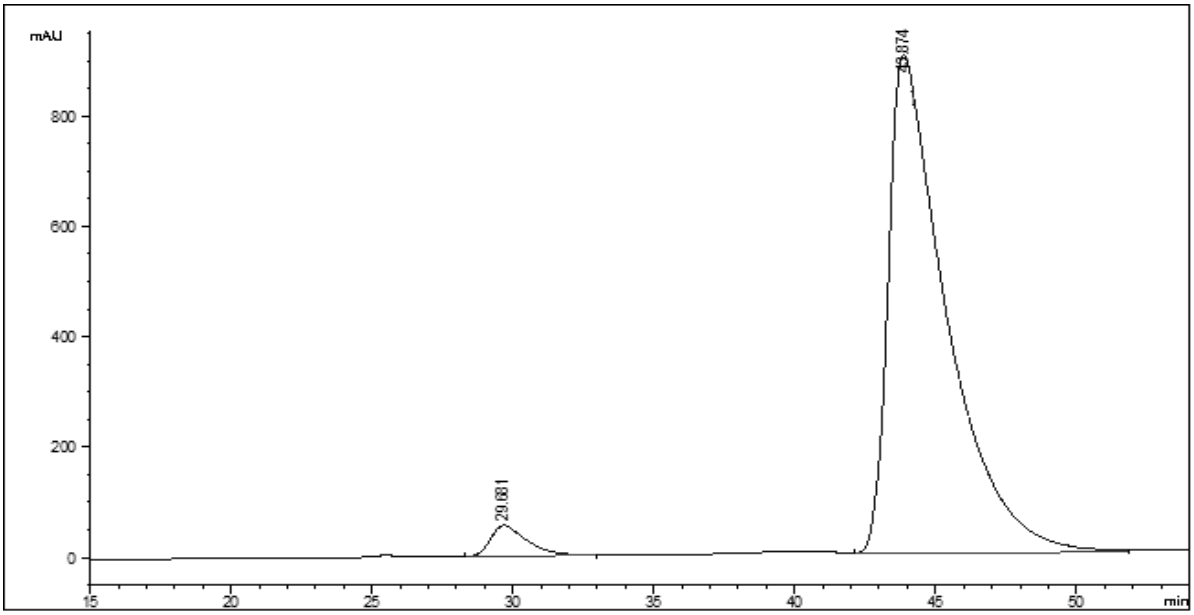
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	30.445	MM	1.0048	2705.02979	44.86776	3.8580
2	36.296	MM	2.5874	6.74105e4	434.21814	96.1420

HPLC chromatogram of racemic 4ac



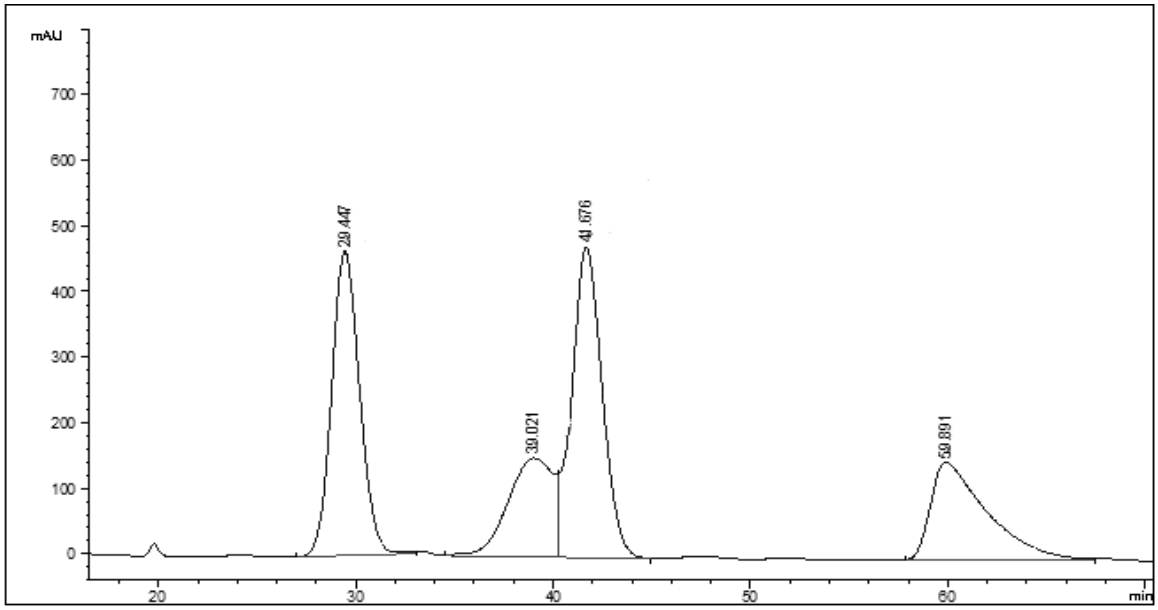
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	23.803	BB	1.0003	2.89821e4	438.14648	29.8258
2	28.087	BB	1.1980	1.95123e4	239.14029	20.0804
3	36.085	BB	1.5106	2.92736e4	267.60605	30.1258
4	43.458	BB	1.6881	1.94031e4	157.13933	19.9679

HPLC chromatogram of chiral 4ac



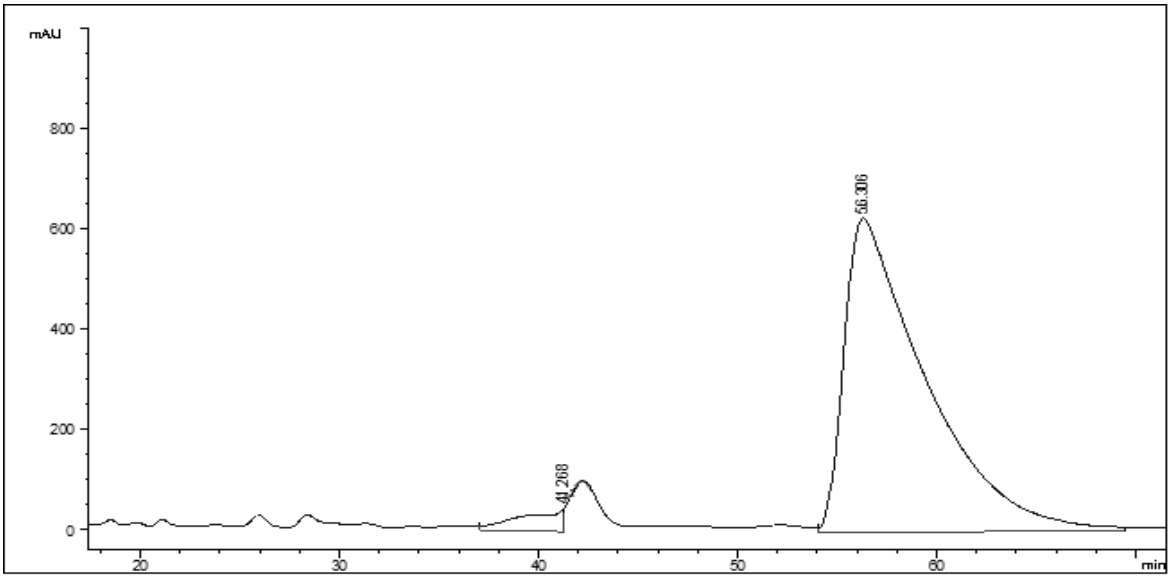
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	29.681	BB	1.2972	5056.89893	55.66518	3.7602
2	43.874	MM	2.3891	1.29429e5	902.93188	96.2398

HPLC chromatogram of racemic 4ad



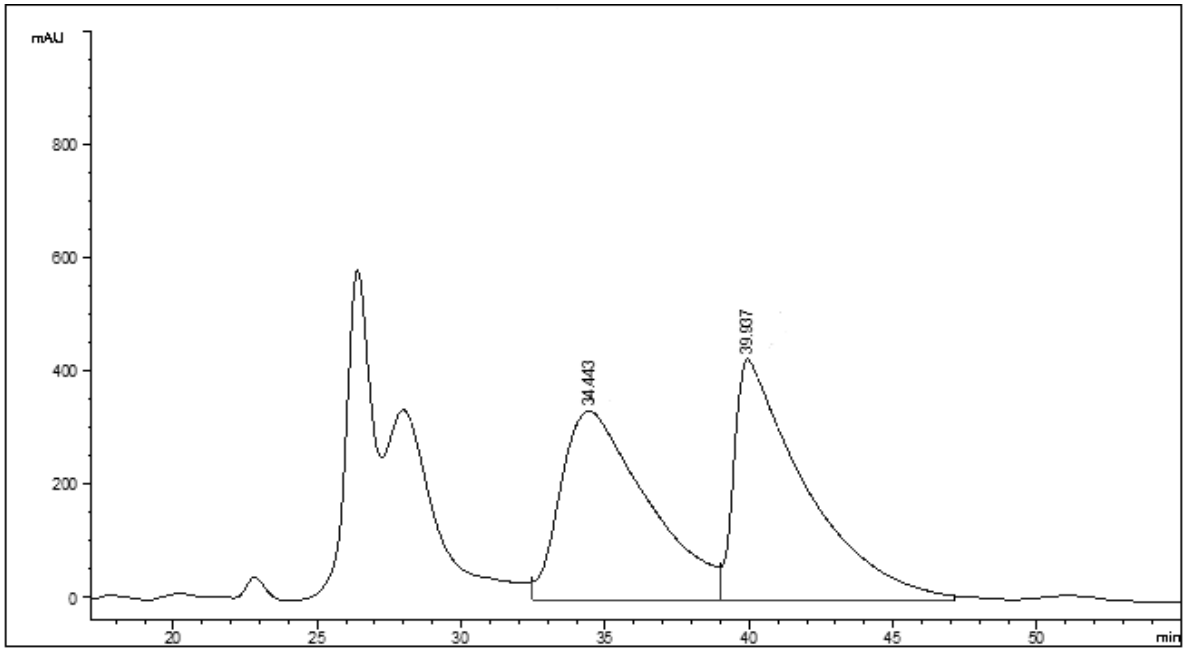
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	29.447	MM	1.6443	4.58116e4	464.34296	30.6234
2	39.021	MF	2.6721	2.41410e4	150.57529	16.1374
3	41.676	FM	1.7743	5.04468e4	473.87766	33.7219
4	59.891	MM	3.2565	2.91972e4	149.43120	19.5173

HPLC chromatogram of chiral 4ad



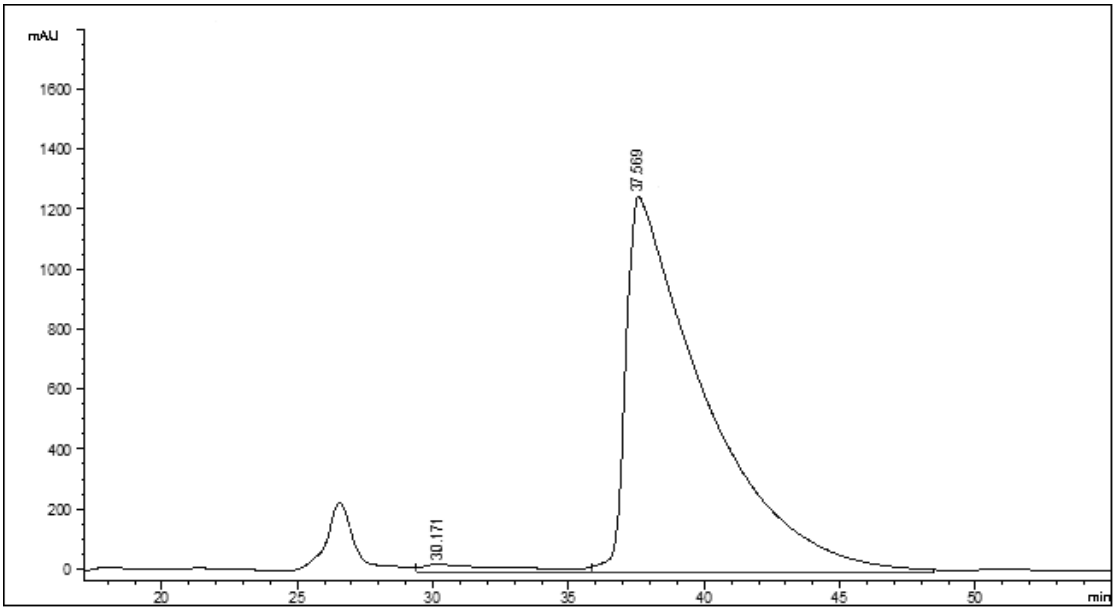
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	41.268	MF	2.3044	6494.14551	46.96972	3.5238
2	56.306	MM	4.7308	1.77797e5	626.38702	96.4762

HPLC chromatogram of racemic 4ae



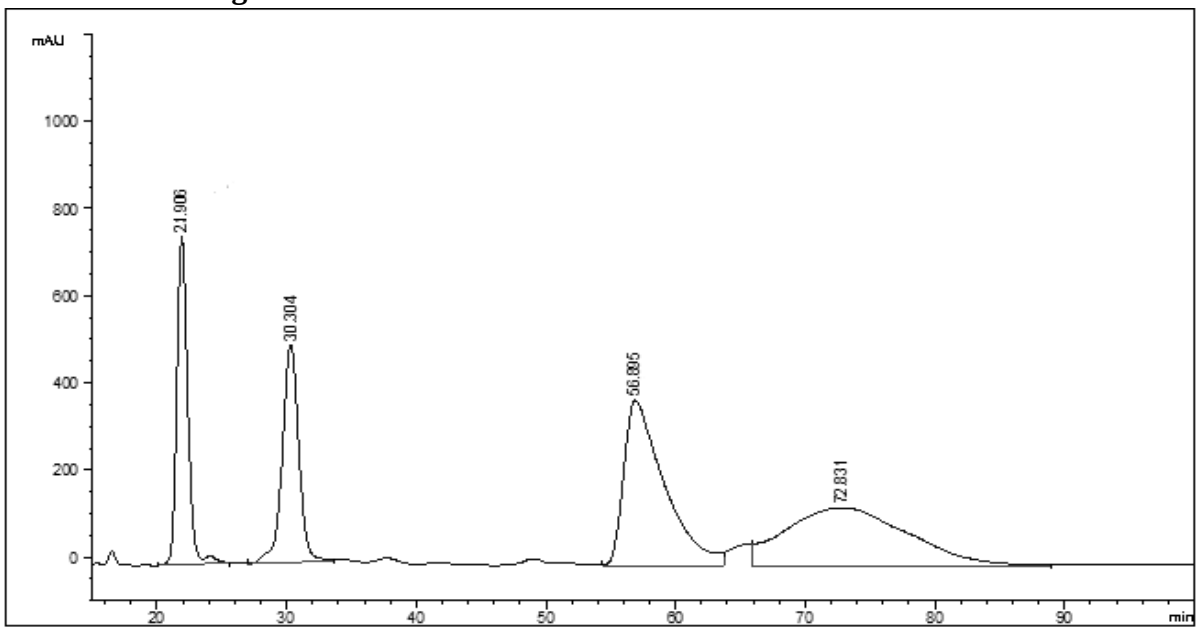
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	34.443	MF	3.4781	6.95617e4	333.32947	48.8703
2	39.937	MF	2.8538	7.27778e4	425.03479	51.1297

HPLC chromatogram of chiral 4ae



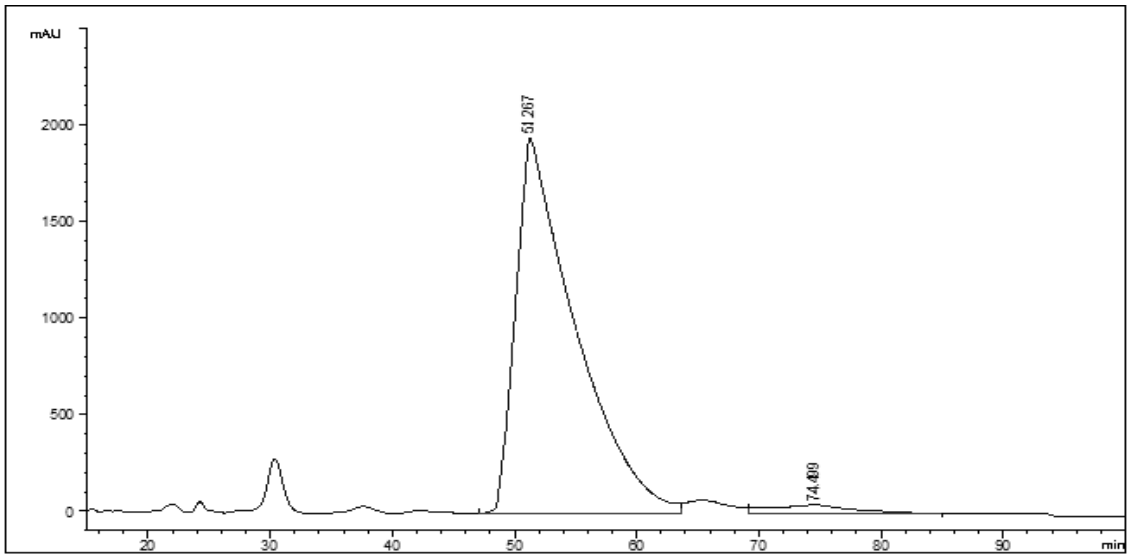
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	30.171	MF	3.5466	5278.03027	24.80306	2.0563
2	37.569	FM	3.3460	2.51396e5	1252.23206	97.9437

HPLC chromatogram of racemic 4af



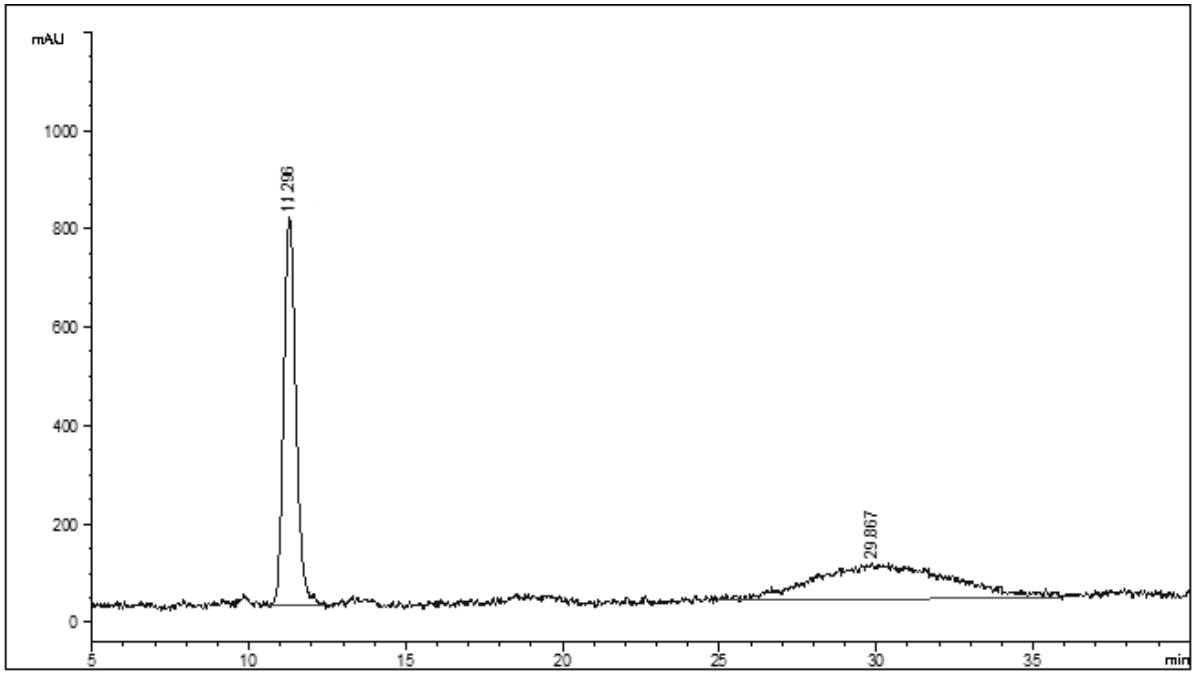
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	21.906	MM	0.9730	4.38363e4	750.86920	17.0465
2	30.304	MM	1.4852	4.44810e4	499.17282	17.2972
3	56.895	MF	3.6178	8.22357e4	378.85181	31.9788
4	72.831	FM	10.8776	8.66039e4	132.69406	33.6774

HPLC chromatogram of chiral 4af



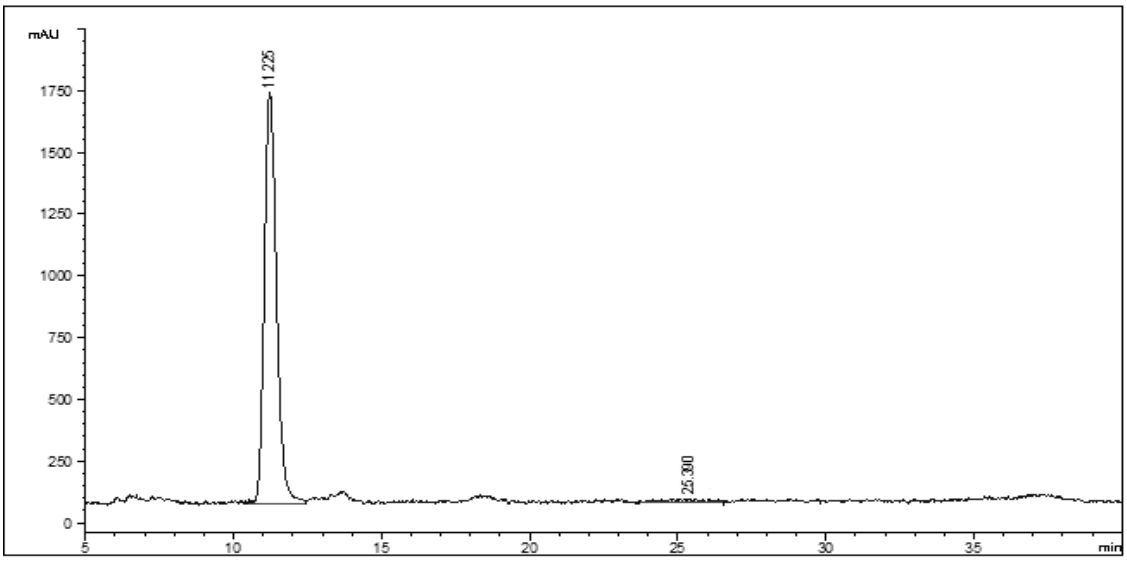
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	51.267	MF	5.6427	6.58130e5	1943.88647	96.6471
2	74.499	FM	8.2287	2.28320e4	46.24451	3.3529

HPLC chromatogram of racemic 4ag



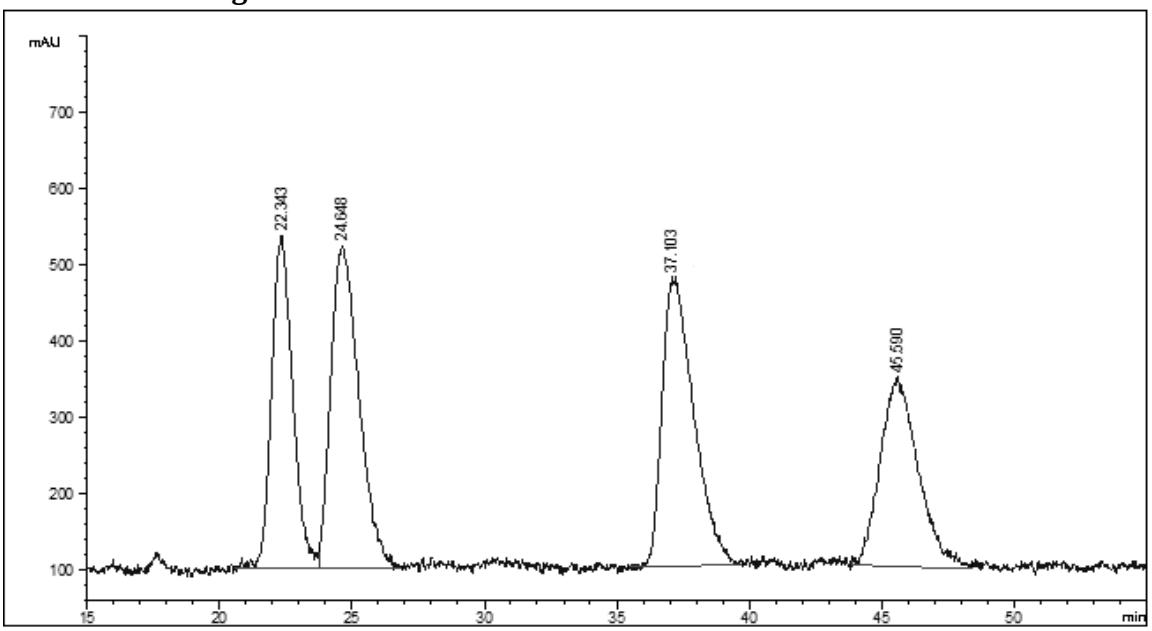
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.296	MM	0.4587	2.17205e4	789.13391	50.1590
2	29.867	MM	4.8975	2.15828e4	73.44823	49.8410

HPLC chromatogram of chiral 4ag



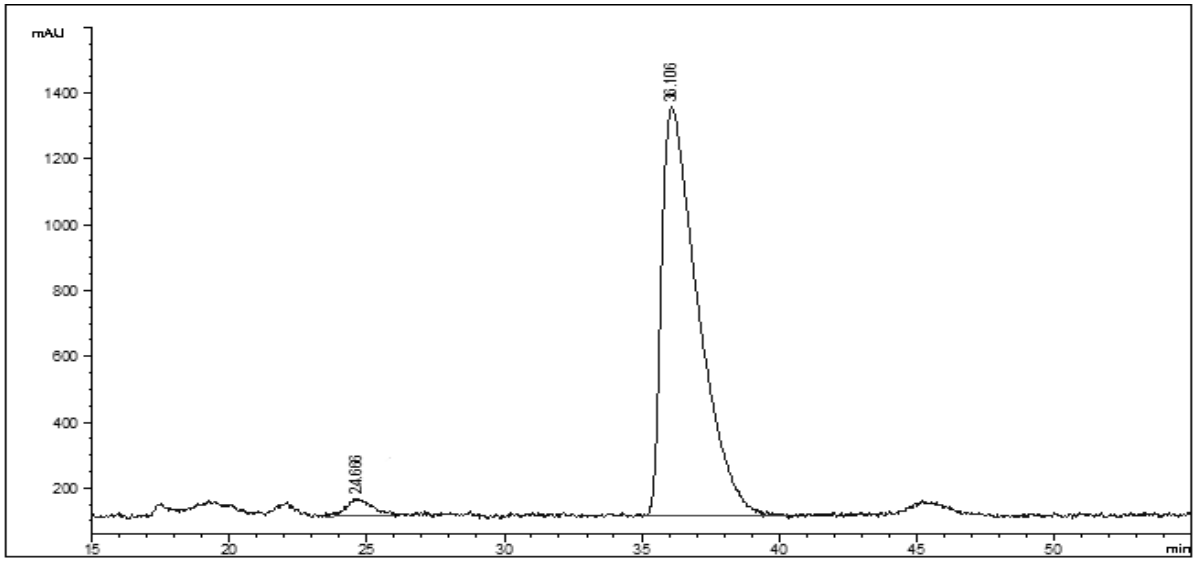
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.225	MM	0.4792	4.78413e4	1663.78418	97.4382
2	25.390	MM	1.2461	1257.84180	16.82425	2.5618

HPLC chromatogram of racemic 4ba



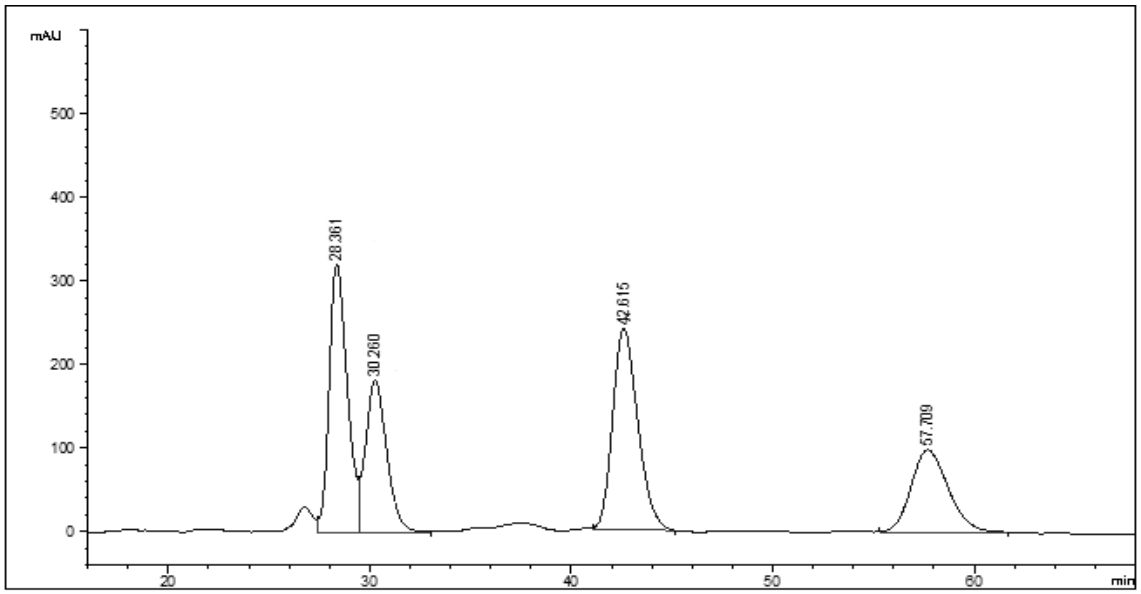
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	22.343	MF	0.9282	2.43534e4	437.28275	21.8048
2	24.648	FM	1.2320	3.13305e4	423.82977	28.0518
3	37.103	MM	1.3801	3.13393e4	378.47632	28.0597
4	45.590	MM	1.6512	2.46649e4	248.96072	22.0837

HPLC chromatogram of chiral 4ba



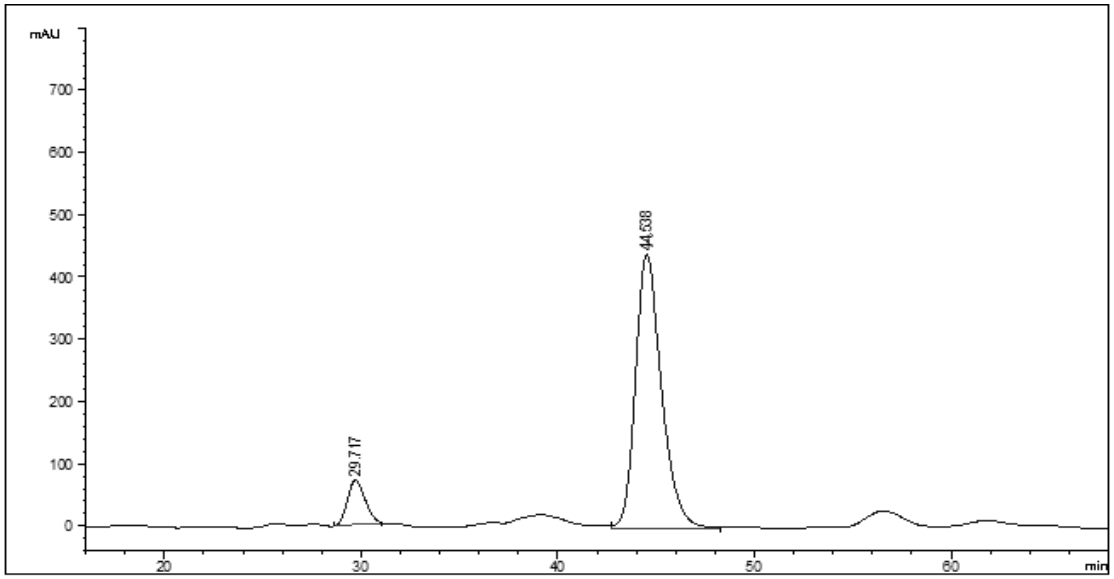
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	24.666	MM	1.0947	3632.74634	55.30640	3.0682
2	36.106	MM	1.5356	1.14768e5	1245.65051	96.9318

HPLC chromatogram of racemic 5



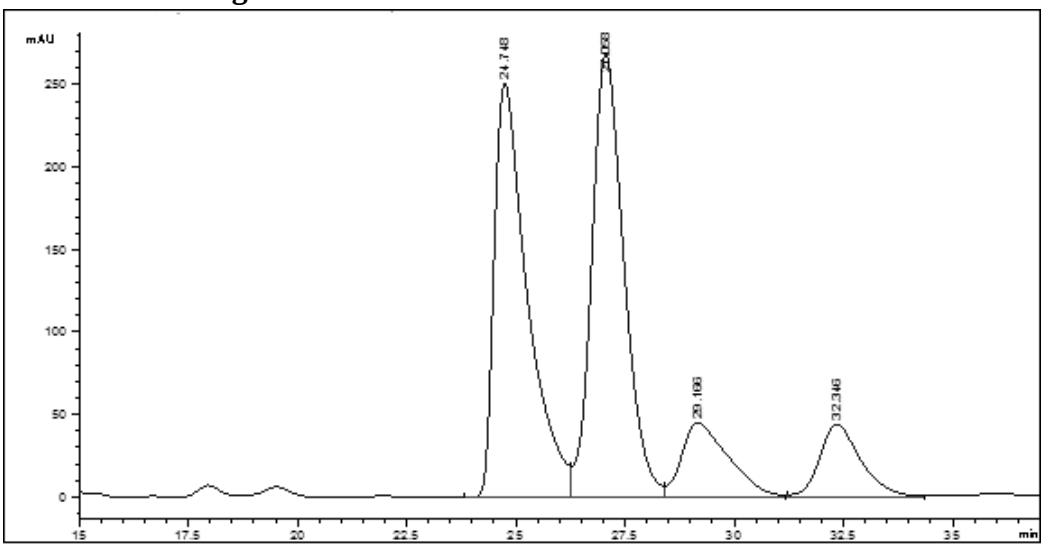
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	28.361	FM	1.0472	2.01112e4	320.08160	30.1013
2	30.260	FM	1.2097	1.32314e4	182.29094	19.8040
3	42.615	MM	1.4445	2.07802e4	239.76752	31.1026
4	57.709	MM	2.1448	1.26890e4	98.60047	18.9921

HPLC chromatogram of chiral 5



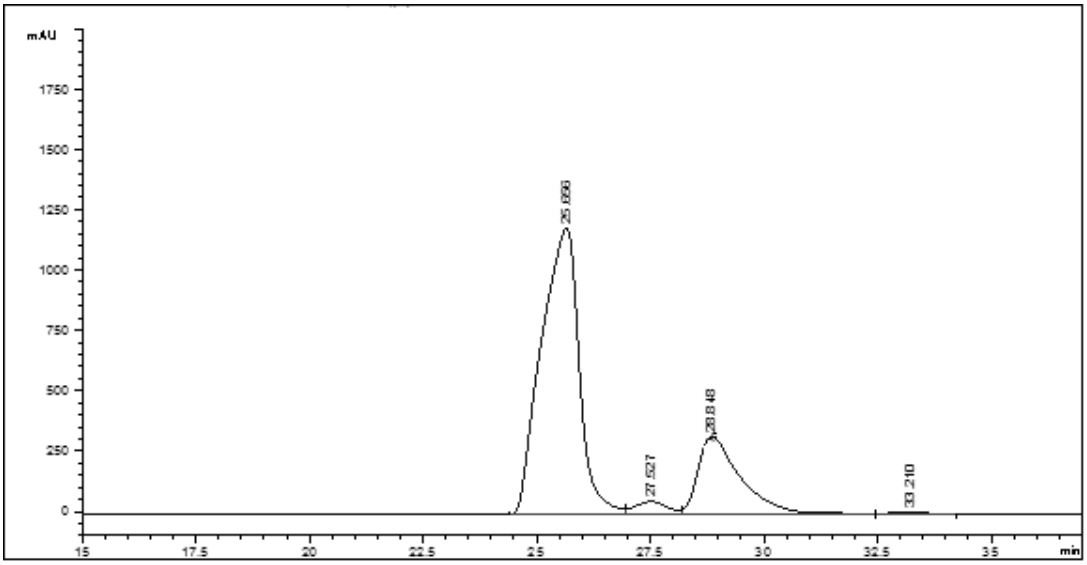
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	29.717	MM	1.0364	4436.66553	71.34398	9.9094
2	44.538	MM	1.5300	4.03358e4	439.38422	90.0906

HPLC chromatogram of racemic 6



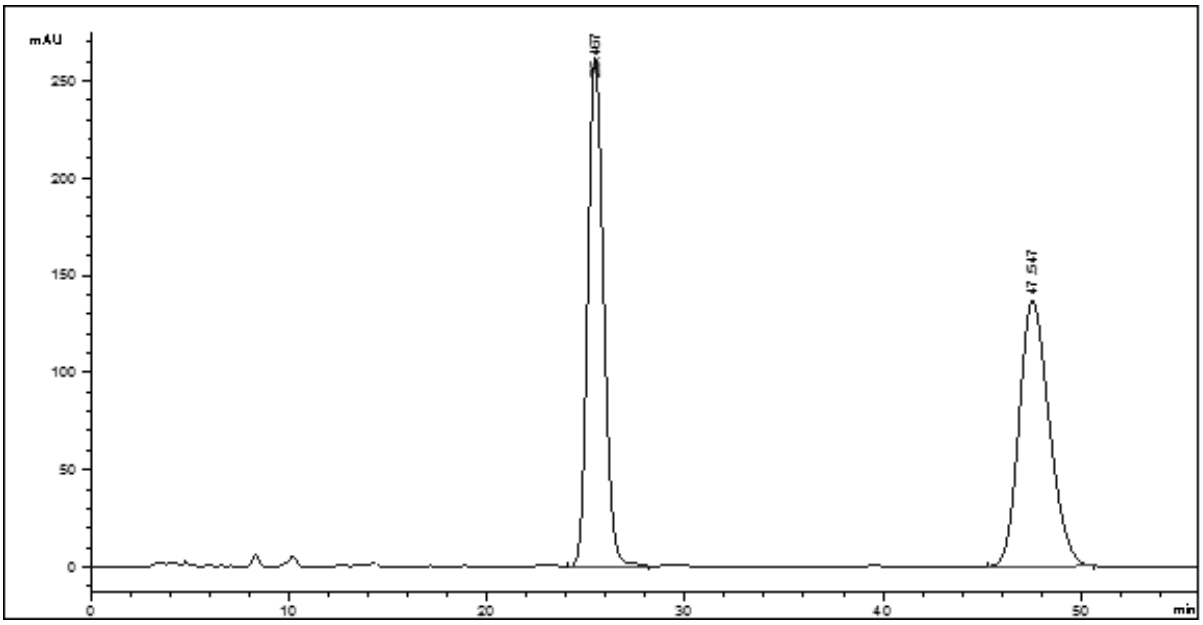
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	24.748	VV	0.7755	1.32264e4	250.77818	39.8968
2	27.058	VV	0.7828	1.37798e4	268.24139	41.5662
3	29.166	VB	1.0605	3312.60034	44.96305	9.9923
4	32.346	BB	0.9722	2832.70435	43.67537	8.5447

HPLC chromatogram of chiral 6



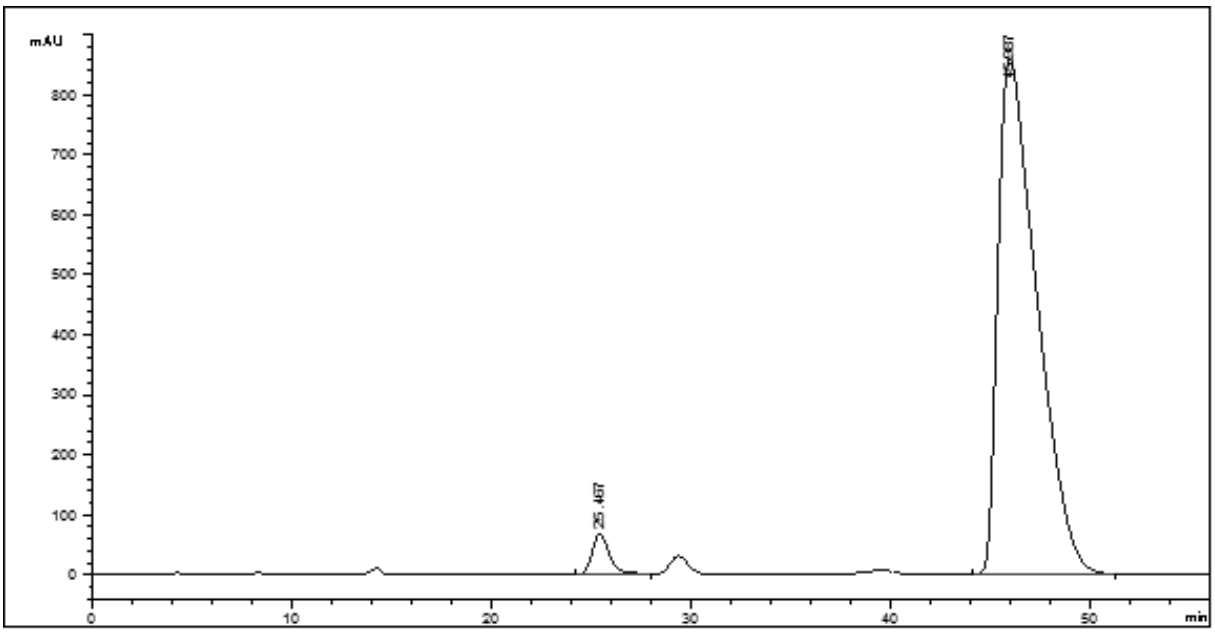
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	25.656	MF	0.9653	6.87808e4	1187.60706	73.5139
2	27.527	FM	0.8308	2754.09424	55.24966	2.9436
3	28.848	FM	1.1110	2.13892e4	320.85712	22.8611
4	33.210	FM	0.9439	637.59485	11.25761	0.6815

HPLC chromatogram of racemic 7



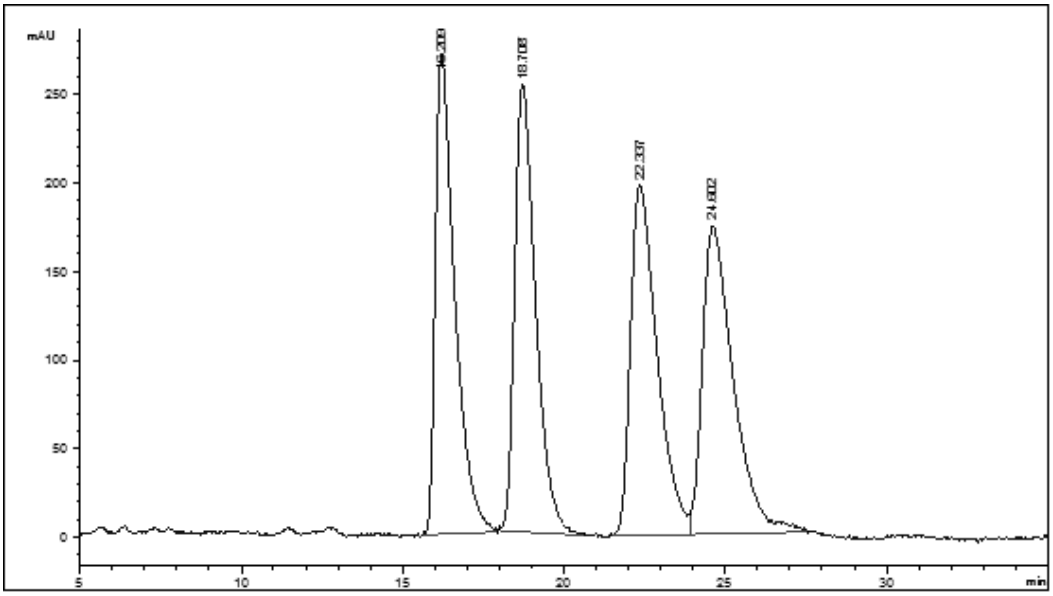
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	25.467	VB	0.8605	1.45269e4	261.58810	50.1936
2	47.547	BB	1.6190	1.44148e4	136.54135	49.8064

HPLC chromatogram of chiral 7



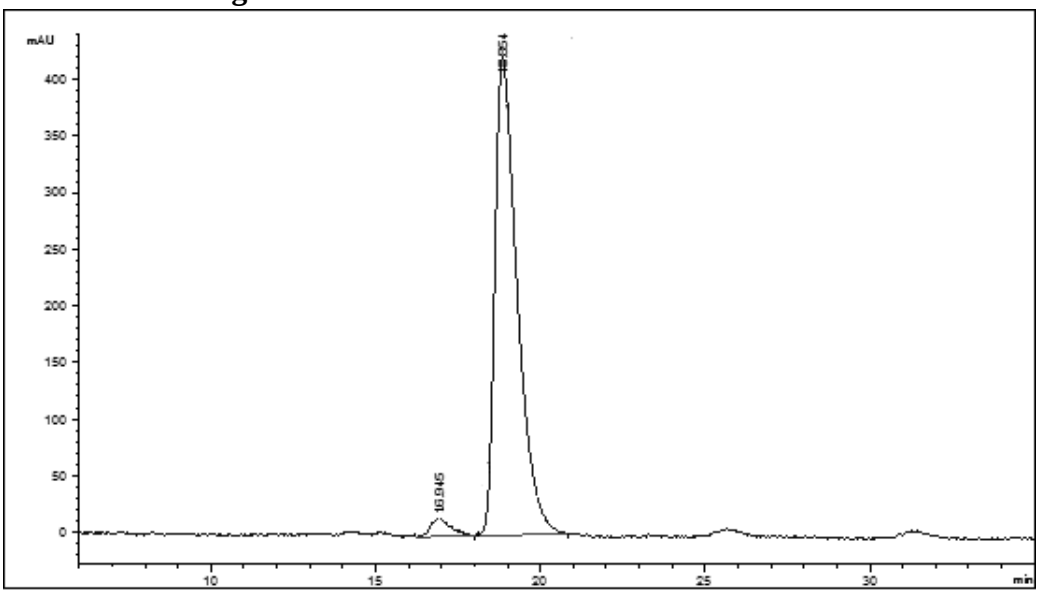
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	25.467	VB	0.9100	4017.05225	67.19777	3.3471
2	45.987	BB	1.9377	1.16000e5	858.38947	96.6529

HPLC chromatogram of racemic 8



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.209	MM	0.6992	1.13841e4	271.35934	24.8900
2	18.708	MM	0.7521	1.13947e4	252.52190	24.9131
3	22.337	MF	0.9559	1.13305e4	197.55472	24.7728
4	24.602	FM	1.1135	1.16284e4	174.04681	25.4241

HPLC chromatogram of chiral 8

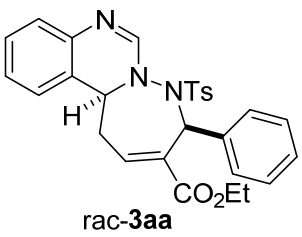


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.945	MM	0.7426	699.18005	15.69160	3.4113
2	18.854	MM	0.7824	1.97966e4	421.72415	96.5887

X-Ray Crystallography Data

Crystallographic data for rac-**3aa**, **3am** and rac-**4af** have been deposited with the Cambridge Crystallographic Data Centre as deposition number CCDC 995194 and 995195. 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.

X-Ray Crystallography Data of rac-**3aa**



rac-**3aa**

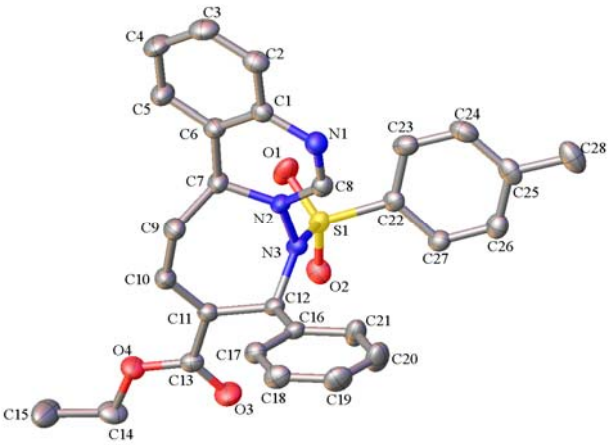


Table 1. Crystal data and structure refinement for rac-**3aa**.

Identification code	rac-**3aa**	
Empirical formula	$C_{28}H_{27}N_3O_4S$	
Formula weight	501.58	
Temperature	173.1500 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 12.294(3) Å	= 90°.
	b = 12.519(4) Å	= 100.996(3)°.
	c = 16.523(4) Å	= 90°.
Volume	2496.4(12) $Å^3$	
Z	4	
Density (calculated)	1.335 Mg/m^3	

Absorption coefficient	0.170 mm^{-1}
F(000)	1056
Crystal size	0.47 x 0.41 x 0.35 mm^3
Theta range for data collection	2.288 to 27.480°.
Index ranges	-15<=h<=15, -16<=k<=16, -21<=l<=18
Reflections collected	17292
Independent reflections	5683 [R(int) = 0.0297]
Completeness to theta = 26.000°	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.8384
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5683 / 0 / 327
Goodness-of-fit on F^2	1.176
Final R indices [I>2sigma(I)]	R1 = 0.0564, wR2 = 0.1422
R indices (all data)	R1 = 0.0590, wR2 = 0.1439
Extinction coefficient	n/a
Largest diff. peak and hole	0.756 and -0.378 e.$Å^{-3}$

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

	x	y	z	U(eq)
S1	5080(1)	6946(1)	3573(1)	26(1)
O1	4188(1)	6334(1)	3779(1)	41(1)
O2	5786(1)	6480(1)	3071(1)	32(1)
O3	8455(1)	5522(1)	4018(1)	42(1)
O4	8348(1)	4364(1)	5035(1)	34(1)
N1	4558(1)	8959(1)	5725(1)	30(1)
N2	5380(1)	7568(1)	5084(1)	24(1)
N3	5915(1)	7334(1)	4436(1)	24(1)
C1	4145(2)	8176(2)	6203(1)	26(1)
C2	3441(2)	8514(2)	6727(1)	33(1)

C3	3018(2)	7793(2)	7220(1)	38(1)
C4	3272(2)	6717(2)	7185(2)	42(1)
C5	3951(2)	6366(2)	6661(1)	37(1)
C6	4398(2)	7090(2)	6173(1)	28(1)
C7	5187(2)	6687(2)	5636(1)	29(1)
C8	5129(2)	8615(2)	5202(1)	27(1)
C9	6269(2)	6281(2)	6159(1)	31(1)
C10	6988(2)	5656(2)	5685(1)	31(1)
C11	7357(1)	5979(2)	5012(1)	24(1)
C12	7113(1)	7058(2)	4602(1)	23(1)
C13	8103(2)	5282(2)	4629(1)	28(1)
C14	9019(2)	3601(2)	4683(2)	40(1)
C15	9257(3)	2695(2)	5282(2)	60(1)
C16	7772(1)	7992(2)	5041(1)	24(1)
C17	8492(2)	7890(2)	5793(1)	28(1)
C18	9118(2)	8763(2)	6141(1)	35(1)
C19	9023(2)	9735(2)	5742(1)	39(1)
C20	8301(2)	9846(2)	4994(2)	44(1)
C21	7682(2)	8977(2)	4648(1)	36(1)
C22	4536(2)	8151(2)	3125(1)	26(1)
C23	3598(2)	8591(2)	3350(1)	34(1)
C24	3245(2)	9591(2)	3052(1)	38(1)
C25	3795(2)	10154(2)	2528(1)	33(1)
C26	4709(2)	9672(2)	2281(1)	32(1)
C27	5083(2)	8683(2)	2583(1)	28(1)
C28	3448(2)	11271(2)	2252(2)	46(1)

Table 3. Bond lengths [Å] and angles [°] for rac-**3aa**.

S1-O1	1.4307(15)
S1-O2	1.4333(15)
S1-N3	1.6625(15)
S1-C22	1.756(2)
O3-C13	1.210(2)
O4-C13	1.337(2)
O4-C14	1.455(2)

N1-C1	1.413(3)
N1-C8	1.287(3)
N2-N3	1.392(2)
N2-C7	1.479(2)
N2-C8	1.368(3)
N3-C12	1.486(2)
C1-C2	1.400(3)
C1-C6	1.399(3)
C2-H2	0.9300
C2-C3	1.381(3)
C3-H3	0.9300
C3-C4	1.386(3)
C4-H4	0.9300
C4-C5	1.385(3)
C5-H5	0.9300
C5-C6	1.394(3)
C6-C7	1.519(3)
C7-H7	0.9800
C7-C9	1.529(3)
C8-H8	0.9300
C9-H9A	0.9700
C9-H9B	0.9700
C9-C10	1.507(3)
C10-H10	0.9300
C10-C11	1.341(3)
C11-C12	1.516(3)
C11-C13	1.491(3)
C12-H12	0.9800
C12-C16	1.525(3)
C14-H14A	0.9700
C14-H14B	0.9700
C14-C15	1.496(4)
C15-H15A	0.9600
C15-H15B	0.9600
C15-H15C	0.9600
C16-C17	1.388(3)
C16-C21	1.388(3)
C17-H17	0.9300

C17-C18	1.395(3)
C18-H18	0.9300
C18-C19	1.378(3)
C19-H19	0.9300
C19-C20	1.385(3)
C20-H20	0.9300
C20-C21	1.386(3)
C21-H21	0.9300
C22-C23	1.391(3)
C22-C27	1.389(3)
C23-H23	0.9300
C23-C24	1.385(3)
C24-H24	0.9300
C24-C25	1.388(3)
C25-C26	1.402(3)
C25-C28	1.507(3)
C26-H26	0.9300
C26-C27	1.380(3)
C27-H27	0.9300
C28-H28A	0.9600
C28-H28B	0.9600
C28-H28C	0.9600

O1-S1-O2	119.70(10)
O1-S1-N3	109.15(9)
O1-S1-C22	108.23(9)
O2-S1-N3	105.78(8)
O2-S1-C22	109.30(9)
N3-S1-C22	103.48(9)
C13-O4-C14	117.02(16)
C8-N1-C1	116.31(17)
N3-N2-C7	118.22(15)
C8-N2-N3	117.65(15)
C8-N2-C7	123.98(16)
N2-N3-S1	114.64(12)
N2-N3-C12	120.28(14)
C12-N3-S1	121.21(12)
C2-C1-N1	117.84(18)

C6-C1-N1	123.23(17)
C6-C1-C2	118.93(18)
C1-C2-H2	119.5
C3-C2-C1	120.9(2)
C3-C2-H2	119.5
C2-C3-H3	120.1
C2-C3-C4	119.82(19)
C4-C3-H3	120.1
C3-C4-H4	120.0
C5-C4-C3	120.1(2)
C5-C4-H4	120.0
C4-C5-H5	119.7
C4-C5-C6	120.5(2)
C6-C5-H5	119.7
C1-C6-C7	121.00(17)
C5-C6-C1	119.71(18)
C5-C6-C7	119.26(18)
N2-C7-C6	107.95(16)
N2-C7-H7	108.5
N2-C7-C9	111.82(16)
C6-C7-H7	108.5
C6-C7-C9	111.39(16)
C9-C7-H7	108.5
N1-C8-N2	125.68(18)
N1-C8-H8	117.2
N2-C8-H8	117.2
C7-C9-H9A	108.7
C7-C9-H9B	108.7
H9A-C9-H9B	107.6
C10-C9-C7	114.41(17)
C10-C9-H9A	108.7
C10-C9-H9B	108.7
C9-C10-H10	116.6
C11-C10-C9	126.82(18)
C11-C10-H10	116.6
C10-C11-C12	124.74(17)
C10-C11-C13	120.59(17)
C13-C11-C12	114.62(16)

N3-C12-C11	113.21(15)
N3-C12-H12	106.1
N3-C12-C16	109.15(15)
C11-C12-H12	106.1
C11-C12-C16	115.38(15)
C16-C12-H12	106.1
O3-C13-O4	123.43(18)
O3-C13-C11	123.80(19)
O4-C13-C11	112.77(16)
O4-C14-H14A	110.4
O4-C14-H14B	110.4
O4-C14-C15	106.69(19)
H14A-C14-H14B	108.6
C15-C14-H14A	110.4
C15-C14-H14B	110.4
C14-C15-H15A	109.5
C14-C15-H15B	109.5
C14-C15-H15C	109.5
H15A-C15-H15B	109.5
H15A-C15-H15C	109.5
H15B-C15-H15C	109.5
C17-C16-C12	123.14(17)
C17-C16-C21	118.67(18)
C21-C16-C12	118.12(16)
C16-C17-H17	119.8
C16-C17-C18	120.33(19)
C18-C17-H17	119.8
C17-C18-H18	119.8
C19-C18-C17	120.33(19)
C19-C18-H18	119.8
C18-C19-H19	120.1
C18-C19-C20	119.8(2)
C20-C19-H19	120.1
C19-C20-H20	120.1
C19-C20-C21	119.8(2)
C21-C20-H20	120.1
C16-C21-H21	119.5
C20-C21-C16	121.10(19)

C20-C21-H21	119.5
C23-C22-S1	119.76(15)
C27-C22-S1	119.41(15)
C27-C22-C23	120.74(18)
C22-C23-H23	120.6
C24-C23-C22	118.81(19)
C24-C23-H23	120.6
C23-C24-H24	119.2
C23-C24-C25	121.61(19)
C25-C24-H24	119.2
C24-C25-C26	118.39(19)
C24-C25-C28	121.1(2)
C26-C25-C28	120.5(2)
C25-C26-H26	119.6
C27-C26-C25	120.76(19)
C27-C26-H26	119.6
C22-C27-H27	120.2
C26-C27-C22	119.58(18)
C26-C27-H27	120.2
C25-C28-H28A	109.5
C25-C28-H28B	109.5
C25-C28-H28C	109.5
H28A-C28-H28B	109.5
H28A-C28-H28C	109.5
H28B-C28-H28C	109.5

Symmetry transformations used to generate equivalent atoms:

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

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S1	26(1)	29(1)	21(1)	2(1)	0(1)	-5(1)
O1	34(1)	46(1)	37(1)	10(1)	-3(1)	-19(1)
O2	38(1)	33(1)	24(1)	-5(1)	1(1)	3(1)

O3	45(1)	47(1)	40(1)	4(1)	24(1)	9(1)
O4	38(1)	30(1)	38(1)	0(1)	18(1)	9(1)
N1	33(1)	29(1)	30(1)	0(1)	8(1)	3(1)
N2	24(1)	27(1)	23(1)	3(1)	9(1)	1(1)
N3	20(1)	32(1)	18(1)	1(1)	3(1)	0(1)
C1	24(1)	31(1)	24(1)	0(1)	4(1)	2(1)
C2	31(1)	37(1)	31(1)	-6(1)	7(1)	4(1)
C3	33(1)	51(1)	35(1)	-7(1)	16(1)	1(1)
C4	40(1)	49(1)	42(1)	6(1)	24(1)	1(1)
C5	39(1)	35(1)	41(1)	5(1)	19(1)	4(1)
C6	27(1)	33(1)	26(1)	3(1)	9(1)	4(1)
C7	32(1)	29(1)	28(1)	5(1)	12(1)	3(1)
C8	27(1)	27(1)	26(1)	1(1)	4(1)	-2(1)
C9	32(1)	36(1)	28(1)	6(1)	9(1)	4(1)
C10	30(1)	30(1)	35(1)	6(1)	10(1)	5(1)
C11	22(1)	26(1)	25(1)	0(1)	6(1)	1(1)
C12	20(1)	29(1)	21(1)	2(1)	6(1)	-1(1)
C13	24(1)	31(1)	28(1)	-3(1)	6(1)	-2(1)
C14	37(1)	38(1)	48(1)	-9(1)	18(1)	8(1)
C15	69(2)	32(1)	94(2)	8(1)	49(2)	13(1)
C16	20(1)	30(1)	24(1)	2(1)	6(1)	-2(1)
C17	27(1)	34(1)	25(1)	3(1)	4(1)	0(1)
C18	31(1)	45(1)	27(1)	-2(1)	2(1)	-6(1)
C19	34(1)	39(1)	42(1)	-6(1)	5(1)	-13(1)
C20	44(1)	35(1)	49(1)	10(1)	0(1)	-12(1)
C21	33(1)	36(1)	35(1)	10(1)	-3(1)	-9(1)
C22	24(1)	32(1)	20(1)	1(1)	0(1)	-1(1)
C23	25(1)	48(1)	29(1)	3(1)	6(1)	-1(1)
C24	26(1)	50(1)	36(1)	-3(1)	2(1)	9(1)
C25	34(1)	34(1)	26(1)	-3(1)	-7(1)	4(1)
C26	37(1)	35(1)	24(1)	3(1)	3(1)	-2(1)
C27	27(1)	34(1)	22(1)	1(1)	6(1)	0(1)
C28	48(1)	37(1)	45(1)	-2(1)	-10(1)	9(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for rac-**3aa**.

	x	y	z	U(eq)
H2	3256	9232	6743	39
H3	2564	8030	7573	46
H4	2985	6231	7515	50
H5	4111	5643	6635	44
H7	4830	6096	5297	34
H8	5394	9121	4876	32
H9A	6688	6888	6417	38
H9B	6094	5832	6595	38
H10	7199	4975	5880	37
H12	7327	7002	4061	28
H14A	9705	3931	4603	48
H14B	8621	3347	4154	48
H15A	9664	2151	5058	91
H15B	8572	2403	5380	91
H15C	9688	2950	5791	91
H17	8557	7238	6067	34
H18	9601	8688	6644	42
H19	9443	10314	5975	47
H20	8230	10501	4725	53
H21	7200	9056	4145	43
H23	3214	8220	3694	41
H24	2625	9894	3206	45
H26	5067	10023	1910	39
H27	5698	8375	2424	33
H28A	2803	11468	2466	68
H28B	3281	11298	1661	68
H28C	4041	11759	2455	68

Table 6. Torsion angles [°] for rac-**3aa**.

S1-N3-C12-C11	-86.76(17)
S1-N3-C12-C16	143.25(13)
S1-C22-C23-C24	173.79(16)
S1-C22-C27-C26	-174.83(15)
O1-S1-N3-N2	-34.99(16)
O1-S1-N3-C12	122.91(15)
O1-S1-C22-C23	29.30(18)

O1-S1-C22-C27	-154.08(15)
O2-S1-N3-N2	-165.02(12)
O2-S1-N3-C12	-7.12(16)
O2-S1-C22-C23	161.23(15)
O2-S1-C22-C27	-22.15(17)
N1-C1-C2-C3	-179.20(19)
N1-C1-C6-C5	-179.63(19)
N1-C1-C6-C7	2.5(3)
N2-N3-C12-C11	69.9(2)
N2-N3-C12-C16	-60.1(2)
N2-C7-C9-C10	-71.7(2)
N3-S1-C22-C23	-86.42(17)
N3-S1-C22-C27	90.20(16)
N3-N2-C7-C6	-168.62(15)
N3-N2-C7-C9	68.5(2)
N3-N2-C8-N1	173.87(17)
N3-C12-C16-C17	124.43(18)
N3-C12-C16-C21	-58.6(2)
C1-N1-C8-N2	-1.2(3)
C1-C2-C3-C4	-1.4(3)
C1-C6-C7-N2	-11.7(2)
C1-C6-C7-C9	111.4(2)
C2-C1-C6-C5	-0.2(3)
C2-C1-C6-C7	-177.98(17)
C2-C3-C4-C5	0.3(4)
C3-C4-C5-C6	0.9(4)
C4-C5-C6-C1	-0.9(3)
C4-C5-C6-C7	177.0(2)
C5-C6-C7-N2	170.44(18)
C5-C6-C7-C9	-66.4(2)
C6-C1-C2-C3	1.3(3)
C6-C7-C9-C10	167.46(17)
C7-N2-N3-S1	87.75(17)
C7-N2-N3-C12	-70.4(2)
C7-N2-C8-N1	-10.5(3)
C7-C9-C10-C11	54.7(3)
C8-N1-C1-C2	-174.59(18)
C8-N1-C1-C6	4.9(3)
C8-N2-N3-S1	-96.38(17)
C8-N2-N3-C12	105.49(19)
C8-N2-C7-C6	15.8(2)

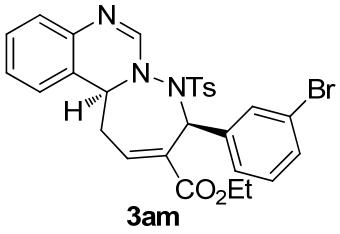
C8-N2-C7-C9	-107.1(2)
C9-C10-C11-C12	0.3(3)
C9-C10-C11-C13	177.54(18)
C10-C11-C12-N3	-50.4(2)
C10-C11-C12-C16	76.3(2)
C10-C11-C13-O3	179.3(2)
C10-C11-C13-O4	-1.0(3)
C11-C12-C16-C17	-4.4(2)
C11-C12-C16-C21	172.64(17)
C12-C11-C13-O3	-3.3(3)
C12-C11-C13-O4	176.48(15)
C12-C16-C17-C18	176.38(18)
C12-C16-C21-C20	-176.8(2)
C13-O4-C14-C15	175.2(2)
C13-C11-C12-N3	132.23(16)
C13-C11-C12-C16	-101.01(18)
C14-O4-C13-O3	-3.8(3)
C14-O4-C13-C11	176.50(17)
C16-C17-C18-C19	0.4(3)
C17-C16-C21-C20	0.4(3)
C17-C18-C19-C20	0.2(3)
C18-C19-C20-C21	-0.4(4)
C19-C20-C21-C16	0.1(4)
C21-C16-C17-C18	-0.6(3)
C22-S1-N3-N2	80.08(14)
C22-S1-N3-C12	-122.02(14)
C22-C23-C24-C25	0.9(3)
C23-C22-C27-C26	1.8(3)
C23-C24-C25-C26	1.9(3)
C23-C24-C25-C28	-175.93(19)
C24-C25-C26-C27	-2.9(3)
C25-C26-C27-C22	1.1(3)
C27-C22-C23-C24	-2.8(3)
C28-C25-C26-C27	174.89(18)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for rac-**3aa** [Å and °].

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

X-Ray Crystallography Data of **3am**



3am

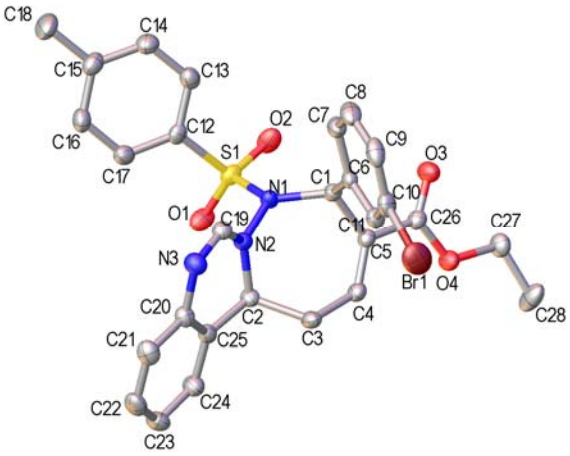


Table 1. Crystal data and structure refinement for **3am**.

Identification code	**3am**	
Empirical formula	$C_{28}H_{26}BrN_3O_4S$	
Formula weight	580.49	
Temperature	173.1500 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 11.331(2) Å	= 90°.
	b = 11.352(2) Å	= 90°.
	c = 20.576(4) Å	= 90°.
Volume	2646.7(8) $Å^3$	
Z	4	
Density (calculated)	1.457 Mg/m^3	
Absorption coefficient	1.671 mm^{-1}	
F(000)	1192	
Crystal size	0.26 x 0.22 x 0.15 mm^3	
Theta range for data collection	2.540 to 27.475°.	
Index ranges	-14<=h<=14, -14<=k<=14, -26<=l<=26	
Reflections collected	18077	
Independent reflections	6030 [R(int) = 0.0402]	
Completeness to theta = 26.000°	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.7756	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6030 / 0 / 336
Goodness-of-fit on F^2	1.106
Final R indices [I>2sigma(I)]	R1 = 0.0399, wR2 = 0.0812
R indices (all data)	R1 = 0.0444, wR2 = 0.0833
Absolute structure parameter	-0.010(5)
Extinction coefficient	n/a
Largest diff. peak and hole	0.458 and -0.467 e.$Å^{-3}$

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

	x	y	z	U(eq)
Br1	5183(1)	3631(1)	836(1)	53(1)
S1	1731(1)	4135(1)	4064(1)	25(1)
O1	2372(2)	3763(2)	4627(1)	33(1)
O2	626(2)	3592(2)	3907(1)	34(1)
O3	774(2)	1276(2)	2562(1)	34(1)
O4	2181(2)	-72(2)	2740(1)	30(1)
N1	2573(2)	3964(2)	3412(1)	21(1)
N2	3760(2)	4232(2)	3512(1)	21(1)
N3	5243(3)	5645(3)	3300(2)	28(1)
C1	2225(3)	3182(3)	2868(2)	22(1)
C2	4541(3)	3319(3)	3771(2)	22(1)
C3	4782(3)	2327(3)	3280(2)	27(1)
C4	3740(3)	1577(3)	3103(2)	25(1)
C5	2663(3)	1919(3)	2928(2)	22(1)
C6	2546(3)	3778(3)	2228(2)	22(1)
C7	1877(3)	4742(3)	2025(2)	29(1)
C8	2155(4)	5322(3)	1453(2)	35(1)
C9	3122(4)	4986(3)	1088(2)	36(1)
C10	3801(4)	4055(4)	1301(2)	31(1)
C11	3517(3)	3424(3)	1860(2)	26(1)

C12	1525(3)	5665(3)	4135(2)	24(1)
C13	579(3)	6175(3)	3809(2)	29(1)
C14	336(4)	7355(3)	3901(2)	33(1)
C15	1036(4)	8046(3)	4299(2)	33(1)
C16	2001(4)	7521(3)	4613(2)	33(1)
C17	2243(3)	6333(3)	4531(2)	29(1)
C18	772(5)	9335(4)	4399(2)	49(1)
C19	4192(3)	5250(3)	3241(2)	23(1)
C20	6003(3)	4986(3)	3707(2)	25(1)
C21	7106(3)	5470(4)	3867(2)	31(1)
C22	7863(3)	4874(4)	4272(2)	35(1)
C23	7547(3)	3791(4)	4537(2)	34(1)
C24	6454(3)	3317(3)	4387(2)	31(1)
C25	5686(3)	3897(3)	3972(2)	24(1)
C26	1768(3)	1034(3)	2726(2)	24(1)
C27	1376(3)	-989(3)	2529(2)	31(1)
C28	2070(4)	-2113(3)	2517(3)	44(1)

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

Br1-C10	1.897(4)
S1-O1	1.431(3)
S1-O2	1.432(3)
S1-N1	1.659(3)
S1-C12	1.759(3)
O3-C26	1.208(4)
O4-C26	1.339(4)
O4-C27	1.450(4)
N1-N2	1.394(4)
N1-C1	1.482(4)
N2-C2	1.463(4)
N2-C19	1.374(4)
N3-C19	1.278(4)
N3-C20	1.416(5)
C1-H1	0.9800
C1-C5	1.523(5)
C1-C6	1.523(5)

C2-H2	0.9800
C2-C3	1.536(5)
C2-C25	1.512(4)
C3-H3A	0.9700
C3-H3B	0.9700
C3-C4	1.501(5)
C4-H4	0.9300
C4-C5	1.329(5)
C5-C26	1.487(5)
C6-C7	1.395(5)
C6-C11	1.396(5)
C7-H7	0.9300
C7-C8	1.384(5)
C8-H8	0.9300
C8-C9	1.381(6)
C9-H9	0.9300
C9-C10	1.379(6)
C10-C11	1.392(5)
C11-H11	0.9300
C12-C13	1.390(5)
C12-C17	1.379(5)
C13-H13	0.9300
C13-C14	1.380(5)
C14-H14	0.9300
C14-C15	1.384(5)
C15-C16	1.403(5)
C15-C18	1.507(5)
C16-H16	0.9300
C16-C17	1.387(5)
C17-H17	0.9300
C18-H18A	0.9600
C18-H18B	0.9600
C18-H18C	0.9600
C19-H19	0.9300
C20-C21	1.405(5)
C20-C25	1.397(5)
C21-H21	0.9300
C21-C22	1.375(5)

C22-H22	0.9300
C22-C23	1.391(6)
C23-H23	0.9300
C23-C24	1.386(5)
C24-H24	0.9300
C24-C25	1.386(5)
C27-H27A	0.9700
C27-H27B	0.9700
C27-C28	1.499(5)
C28-H28A	0.9600
C28-H28B	0.9600
C28-H28C	0.9600

O1-S1-O2	120.01(17)
O1-S1-N1	109.18(14)
O1-S1-C12	106.95(17)
O2-S1-N1	105.62(14)
O2-S1-C12	109.14(16)
N1-S1-C12	105.00(15)
C26-O4-C27	116.5(3)
N2-N1-S1	114.2(2)
N2-N1-C1	120.0(3)
C1-N1-S1	121.9(2)
N1-N2-C2	118.9(3)
C19-N2-N1	117.9(3)
C19-N2-C2	121.9(3)
C19-N3-C20	115.9(3)
N1-C1-H1	106.2
N1-C1-C5	114.5(3)
N1-C1-C6	108.8(3)
C5-C1-H1	106.2
C5-C1-C6	114.3(3)
C6-C1-H1	106.2
N2-C2-H2	108.5
N2-C2-C3	112.8(3)
N2-C2-C25	108.1(3)
C3-C2-H2	108.5
C25-C2-H2	108.5

C25-C2-C3	110.2(3)
C2-C3-H3A	108.3
C2-C3-H3B	108.3
H3A-C3-H3B	107.4
C4-C3-C2	115.9(3)
C4-C3-H3A	108.3
C4-C3-H3B	108.3
C3-C4-H4	115.8
C5-C4-C3	128.5(3)
C5-C4-H4	115.8
C4-C5-C1	126.6(3)
C4-C5-C26	120.3(3)
C26-C5-C1	113.0(3)
C7-C6-C1	118.5(3)
C7-C6-C11	119.4(3)
C11-C6-C1	122.0(3)
C6-C7-H7	119.9
C8-C7-C6	120.3(4)
C8-C7-H7	119.9
C7-C8-H8	119.6
C9-C8-C7	120.7(4)
C9-C8-H8	119.6
C8-C9-H9	120.6
C10-C9-C8	118.8(4)
C10-C9-H9	120.6
C9-C10-Br1	119.7(3)
C9-C10-C11	121.9(4)
C11-C10-Br1	118.4(3)
C6-C11-H11	120.6
C10-C11-C6	118.8(3)
C10-C11-H11	120.6
C13-C12-S1	118.3(3)
C17-C12-S1	120.9(3)
C17-C12-C13	120.7(3)
C12-C13-H13	120.3
C14-C13-C12	119.5(3)
C14-C13-H13	120.3
C13-C14-H14	119.5

C13-C14-C15	121.1(4)
C15-C14-H14	119.5
C14-C15-C16	118.6(3)
C14-C15-C18	121.2(4)
C16-C15-C18	120.3(4)
C15-C16-H16	119.6
C17-C16-C15	120.8(4)
C17-C16-H16	119.6
C12-C17-C16	119.3(3)
C12-C17-H17	120.3
C16-C17-H17	120.3
C15-C18-H18A	109.5
C15-C18-H18B	109.5
C15-C18-H18C	109.5
H18A-C18-H18B	109.5
H18A-C18-H18C	109.5
H18B-C18-H18C	109.5
N2-C19-H19	117.0
N3-C19-N2	126.1(3)
N3-C19-H19	117.0
C21-C20-N3	118.2(3)
C25-C20-N3	122.8(3)
C25-C20-C21	118.9(3)
C20-C21-H21	119.9
C22-C21-C20	120.3(4)
C22-C21-H21	119.9
C21-C22-H22	119.6
C21-C22-C23	120.8(3)
C23-C22-H22	119.6
C22-C23-H23	120.5
C24-C23-C22	119.0(4)
C24-C23-H23	120.5
C23-C24-H24	119.5
C23-C24-C25	121.0(4)
C25-C24-H24	119.5
C20-C25-C2	119.9(3)
C24-C25-C2	120.1(3)
C24-C25-C20	119.9(3)

O3-C26-O4	123.0(3)
O3-C26-C5	124.1(3)
O4-C26-C5	112.9(3)
O4-C27-H27A	110.4
O4-C27-H27B	110.4
O4-C27-C28	106.7(3)
H27A-C27-H27B	108.6
C28-C27-H27A	110.4
C28-C27-H27B	110.4
C27-C28-H28A	109.5
C27-C28-H28B	109.5
C27-C28-H28C	109.5
H28A-C28-H28B	109.5
H28A-C28-H28C	109.5
H28B-C28-H28C	109.5

Symmetry transformations used to generate equivalent atoms:

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

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br1	50(1)	74(1)	35(1)	-3(1)	16(1)	-8(1)
S1	28(1)	22(1)	25(1)	1(1)	7(1)	0(1)
O1	45(2)	30(1)	24(1)	6(1)	7(1)	8(1)
O2	27(1)	31(1)	45(2)	-4(1)	13(1)	-6(1)
O3	30(1)	26(1)	48(2)	-3(1)	-9(1)	-2(1)
O4	30(1)	18(1)	43(2)	-2(1)	-7(1)	-2(1)
N1	18(1)	22(2)	23(2)	-2(1)	2(1)	-2(1)
N2	22(1)	19(1)	23(2)	1(1)	-1(1)	-1(1)
N3	30(2)	26(2)	29(2)	6(1)	-1(1)	-6(1)
C1	21(2)	19(2)	27(2)	-1(1)	-1(1)	-1(1)
C2	25(2)	18(2)	23(2)	3(1)	-2(1)	-1(1)
C3	23(2)	21(2)	36(2)	-2(2)	-6(2)	2(2)
C4	29(2)	18(2)	27(2)	-1(1)	-2(1)	2(1)

C5	26(2)	17(2)	21(2)	1(1)	0(1)	0(1)
C6	26(2)	18(2)	21(2)	-2(1)	-5(1)	-1(1)
C7	36(2)	22(2)	30(2)	-2(2)	-8(2)	0(2)
C8	52(2)	24(2)	30(2)	3(2)	-16(2)	3(2)
C9	58(3)	28(2)	22(2)	2(2)	-5(2)	-15(2)
C10	40(2)	33(2)	20(2)	-4(2)	1(2)	-6(2)
C11	29(2)	27(2)	22(2)	-3(1)	-1(1)	-2(2)
C12	28(2)	24(2)	20(2)	-2(1)	6(1)	0(1)
C13	28(2)	34(2)	25(2)	-4(2)	0(1)	-2(2)
C14	37(2)	30(2)	33(2)	1(2)	-5(2)	7(2)
C15	43(2)	27(2)	29(2)	-2(2)	2(2)	5(2)
C16	39(2)	29(2)	31(2)	-8(2)	-4(2)	-2(2)
C17	28(2)	34(2)	26(2)	-3(2)	-2(1)	5(2)
C18	67(3)	28(2)	52(3)	-10(2)	-13(2)	10(2)
C19	27(2)	21(2)	22(2)	3(1)	-1(1)	0(1)
C20	27(2)	26(2)	21(2)	1(1)	0(1)	-4(2)
C21	28(2)	33(2)	31(2)	2(2)	3(2)	-10(2)
C22	23(2)	44(2)	38(2)	-7(2)	-2(2)	-7(2)
C23	27(2)	38(2)	38(2)	-2(2)	-8(2)	3(2)
C24	34(2)	25(2)	35(2)	1(2)	-7(2)	0(2)
C25	23(2)	27(2)	22(2)	-3(1)	-1(1)	0(1)
C26	29(2)	19(2)	24(2)	1(1)	1(1)	-1(1)
C27	34(2)	22(2)	36(2)	0(2)	-1(2)	-9(2)
C28	39(2)	23(2)	71(3)	-12(2)	13(2)	-6(2)

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

	x	y	z	U(eq)
H1	1361	3141	2878	27
H2	4171	2976	4157	27
H3A	5093	2677	2886	32
H3B	5390	1820	3458	32
H4	3863	768	3116	30
H7	1241	4995	2274	35

H8	1686	5944	1313	42
H9	3312	5382	707	43
H11	3967	2777	1985	31
H13	114	5725	3532	35
H14	-309	7691	3691	40
H16	2484	7975	4879	40
H17	2883	5990	4741	35
H18A	135	9567	4120	74
H18B	1461	9792	4299	74
H18C	552	9466	4844	74
H19	3672	5694	2992	28
H21	7325	6198	3698	37
H22	8596	5198	4371	42
H23	8063	3391	4811	41
H24	6232	2600	4567	38
H27A	1070	-812	2100	37
H27B	718	-1055	2829	37
H28A	2675	-2061	2192	67
H28B	1553	-2758	2417	67
H28C	2426	-2240	2935	67

Table 6. Torsion angles [°] for **3am**.

Br1-C10-C11-C6	175.8(3)
S1-N1-N2-C2	85.6(3)
S1-N1-N2-C19	-107.6(3)
S1-N1-C1-C5	-90.9(3)
S1-N1-C1-C6	139.9(2)
S1-C12-C13-C14	174.5(3)
S1-C12-C17-C16	-175.2(3)
O1-S1-N1-N2	-37.9(3)
O1-S1-N1-C1	119.6(3)
O1-S1-C12-C13	-155.5(3)
O1-S1-C12-C17	21.1(3)
O2-S1-N1-N2	-168.2(2)
O2-S1-N1-C1	-10.7(3)
O2-S1-C12-C13	-24.3(3)

O2-S1-C12-C17	152.3(3)
N1-S1-C12-C13	88.6(3)
N1-S1-C12-C17	-94.9(3)
N1-N2-C2-C3	70.2(4)
N1-N2-C2-C25	-167.7(3)
N1-N2-C19-N3	177.9(3)
N1-C1-C5-C4	-44.5(5)
N1-C1-C5-C26	139.4(3)
N1-C1-C6-C7	-72.4(4)
N1-C1-C6-C11	104.6(3)
N2-N1-C1-C5	65.3(4)
N2-N1-C1-C6	-63.9(4)
N2-C2-C3-C4	-66.4(4)
N2-C2-C25-C20	-21.4(4)
N2-C2-C25-C24	162.5(3)
N3-C20-C21-C22	178.6(3)
N3-C20-C25-C2	6.4(5)
N3-C20-C25-C24	-177.5(3)
C1-N1-N2-C2	-72.3(4)
C1-N1-N2-C19	94.4(4)
C1-C5-C26-O3	-3.8(5)
C1-C5-C26-O4	176.0(3)
C1-C6-C7-C8	178.8(3)
C1-C6-C11-C10	-176.1(3)
C2-N2-C19-N3	-15.8(5)
C2-C3-C4-C5	48.0(5)
C3-C2-C25-C20	102.4(4)
C3-C2-C25-C24	-73.7(4)
C3-C4-C5-C1	0.0(6)
C3-C4-C5-C26	175.8(3)
C4-C5-C26-O3	179.9(4)
C4-C5-C26-O4	-0.3(5)
C5-C1-C6-C7	158.2(3)
C5-C1-C6-C11	-24.8(4)
C6-C1-C5-C4	81.9(4)
C6-C1-C5-C26	-94.1(3)
C6-C7-C8-C9	-2.4(6)
C7-C6-C11-C10	0.9(5)

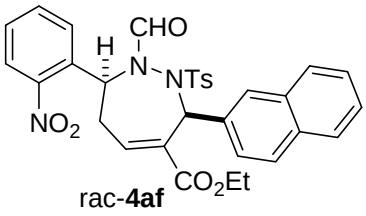
C7-C8-C9-C10	0.6(6)
C8-C9-C10-Br1	-176.5(3)
C8-C9-C10-C11	2.0(6)
C9-C10-C11-C6	-2.7(5)
C11-C6-C7-C8	1.6(5)
C12-S1-N1-N2	76.5(3)
C12-S1-N1-C1	-126.0(3)
C12-C13-C14-C15	1.6(6)
C13-C12-C17-C16	1.2(5)
C13-C14-C15-C16	-0.3(6)
C13-C14-C15-C18	-180.0(4)
C14-C15-C16-C17	-0.6(6)
C15-C16-C17-C12	0.1(6)
C17-C12-C13-C14	-2.1(5)
C18-C15-C16-C17	179.1(4)
C19-N2-C2-C3	-96.0(4)
C19-N2-C2-C25	26.1(4)
C19-N3-C20-C21	-170.6(3)
C19-N3-C20-C25	7.3(5)
C20-N3-C19-N2	-3.0(5)
C20-C21-C22-C23	-0.8(6)
C21-C20-C25-C2	-175.8(3)
C21-C20-C25-C24	0.3(5)
C21-C22-C23-C24	0.0(6)
C22-C23-C24-C25	0.9(6)
C23-C24-C25-C2	175.0(3)
C23-C24-C25-C20	-1.1(6)
C25-C2-C3-C4	172.6(3)
C25-C20-C21-C22	0.7(6)
C26-O4-C27-C28	173.8(3)
C27-O4-C26-O3	1.7(5)
C27-O4-C26-C5	-178.1(3)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for **3am** [Å and °].

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

X-Ray Crystallography Data of rac-**4af**



rac-**4af**

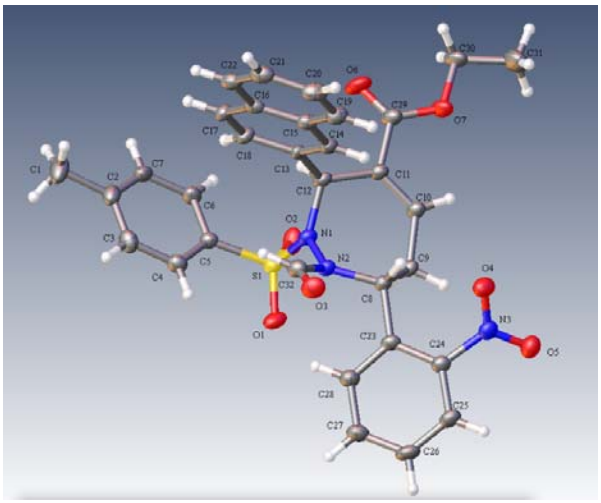


Table 1. Crystal data and structure refinement for rac-**4af**.

Identification code	rac-**4af**	
Empirical formula	$C_{32}H_{29}N_3O_7S$	
Formula weight	599.64	
Temperature	173.1500 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 10.840(2) Å	= 113.98(3)°.
	b = 12.665(3) Å	= 112.44(3)°.
	c = 12.992(3) Å	= 91.38(3)°.
Volume	1472.0(7) $Å^3$	
Z	2	
Density (calculated)	1.353 Mg/m^3	
Absorption coefficient	0.164 mm^{-1}	
F(000)	628	
Crystal size	0.47 x 0.16 x 0.06 mm^3	
Theta range for data collection	1.801 to 27.509°.	
Index ranges	-14<=h<=14, -16<=k<=16, -14<=l<=16	
Reflections collected	17685	
Independent reflections	6679 [R(int) = 0.0704]	
Completeness to theta = 26.000°	99.7 %	
Absorption correction	Semi-empirical from equivalents	

Max. and min. transmission	1.0000 and 0.6161
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6679 / 492 / 511
Goodness-of-fit on F^2	1.133
Final R indices [I>2sigma(I)]	R1 = 0.0751, wR2 = 0.1748
R indices (all data)	R1 = 0.0842, wR2 = 0.1817
Extinction coefficient	n/a
Largest diff. peak and hole	0.312 and -0.404 e.$Å^{-3}$

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

	x	y	z	U(eq)
S1	5063(1)	7134(1)	3195(1)	41(1)
O1	6309(2)	7154(2)	4147(2)	55(1)
O2	4950(2)	8062(2)	2828(2)	57(1)
O3	3786(2)	5661(2)	5443(2)	55(1)
O4	3741(2)	9226(2)	7986(2)	57(1)
O5	5435(2)	10681(2)	9393(2)	61(1)
O6	650(2)	8415(2)	1838(2)	69(1)
N1	3867(2)	7109(2)	3686(2)	38(1)
N2	4141(2)	6966(2)	4755(2)	36(1)
N3	4970(2)	9663(2)	8562(2)	45(1)
C1	2829(4)	2452(3)	-1424(3)	79(1)
C2	3455(3)	3628(3)	-276(3)	54(1)
C3	4258(3)	3691(2)	891(3)	53(1)
C4	4797(3)	4765(2)	1953(3)	44(1)
C5	4543(3)	5790(2)	1848(2)	38(1)
C6	3791(3)	5757(3)	687(2)	47(1)
C7	3263(3)	4670(3)	-356(3)	54(1)
C8	4365(2)	8017(2)	5924(2)	34(1)
C9	4469(2)	9133(2)	5763(2)	36(1)
C10	3178(3)	9302(2)	4896(2)	40(1)

C11	2337(2)	8526(2)	3726(2)	38(1)
C12	2496(2)	7301(2)	3021(2)	38(1)
C23	5655(2)	8129(2)	7036(2)	37(1)
C24	5945(3)	8942(2)	8265(2)	40(1)
C25	7163(3)	9129(3)	9283(2)	49(1)
C26	8126(3)	8481(3)	9085(3)	55(1)
C27	7877(3)	7674(3)	7886(3)	53(1)
C28	6657(3)	7507(2)	6876(2)	44(1)
C29	1200(3)	8908(2)	2959(3)	52(1)
C32	3773(3)	5855(2)	4602(3)	44(1)
O7	965(5)	9929(4)	3594(4)	56(1)
C13	1434(7)	6226(6)	2534(5)	30(1)
C14	779(5)	6212(5)	3248(5)	36(1)
C15	-195(6)	5185(5)	2844(5)	38(1)
C16	-453(7)	4197(6)	1730(7)	36(1)
C17	235(5)	4237(4)	999(4)	42(1)
C18	1158(5)	5234(4)	1412(5)	39(1)
C19	-878(5)	5137(5)	3552(5)	48(1)
C20	-1812(6)	4139(6)	3127(6)	57(2)
C21	-2109(7)	3148(7)	1986(7)	51(2)
C22	-1435(5)	3162(5)	1294(5)	48(1)
C30	7(6)	10421(4)	2882(5)	56(2)
C31	-74(12)	11528(8)	3890(9)	96(3)
C30A	-427(13)	10258(10)	3326(15)	72(4)
C15A	-126(6)	5845(5)	3694(6)	45(1)
C19A	-1590(8)	3837(8)	2480(9)	59(2)
C17A	-113(9)	4456(7)	1706(8)	36(2)
C21A	-1578(7)	2506(6)	541(7)	59(2)
C16A	-605(7)	4712(6)	2672(7)	43(2)
C18A	870(6)	5334(5)	1906(6)	38(1)
C20A	-2036(10)	2747(9)	1451(8)	62(2)
C22A	-627(6)	3329(5)	666(5)	45(2)
C31A	160(20)	11420(20)	3470(20)	86(6)
O7A	646(11)	9639(10)	3754(10)	71(3)
C13A	1340(9)	6427(7)	2925(7)	32(2)
C14A	830(6)	6680(6)	3826(7)	43(2)

Table 3. Bond lengths [Å] and angles [°] for rac-**4af**.

S1-O1	1.432(2)
S1-O2	1.429(2)
S1-N1	1.654(2)
S1-C5	1.749(3)
O3-C32	1.209(3)
O4-N3	1.228(3)
O5-N3	1.226(3)
O6-C29	1.203(3)
N1-N2	1.393(3)
N1-C12	1.490(3)
N2-C8	1.483(3)
N2-C32	1.366(3)
N3-C24	1.474(4)
C1-H1A	0.9600
C1-H1B	0.9600
C1-H1C	0.9600
C1-C2	1.509(4)
C2-C3	1.398(4)
C2-C7	1.379(4)
C3-H3	0.9300
C3-C4	1.384(4)
C4-H4	0.9300
C4-C5	1.384(3)
C5-C6	1.396(3)
C6-H6	0.9300
C6-C7	1.383(4)
C7-H7	0.9300
C8-H8	0.9800
C8-C9	1.518(3)
C8-C23	1.531(3)
C9-H9A	0.9700
C9-H9B	0.9700
C9-C10	1.510(3)
C10-H10	0.9300
C10-C11	1.338(3)
C11-C12	1.502(4)

C11-C29	1.493(3)
C12-H12	0.9800
C12-H12A	0.9800
C12-C13	1.500(7)
C12-C13A	1.586(9)
C23-C24	1.405(3)
C23-C28	1.388(4)
C24-C25	1.395(3)
C25-H25	0.9300
C25-C26	1.380(4)
C26-H26	0.9300
C26-C27	1.384(4)
C27-H27	0.9300
C27-C28	1.397(4)
C28-H28	0.9300
C29-O7	1.314(5)
C29-O7A	1.417(9)
C32-H32	0.9300
O7-C30	1.446(5)
C13-C14	1.371(6)
C13-C18	1.398(6)
C14-H14	0.9300
C14-C15	1.428(8)
C15-C16	1.392(8)
C15-C19	1.401(7)
C16-C17	1.428(8)
C16-C22	1.429(8)
C17-H17	0.9300
C17-C18	1.364(6)
C18-H18	0.9300
C19-H19	0.9300
C19-C20	1.368(6)
C20-H20	0.9300
C20-C21	1.407(9)
C21-H21	0.9300
C21-C22	1.363(7)
C22-H22	0.9300
C30-H30A	0.9700

C30-H30B	0.9700
C30-C31	1.513(7)
C31-H31A	0.9600
C31-H31B	0.9600
C31-H31C	0.9600
C30A-H30C	0.9700
C30A-H30D	0.9700
C30A-C31A	1.502(10)
C30A-O7A	1.477(9)
C15A-H15A	0.9300
C15A-C16A	1.407(9)
C15A-C14A	1.373(7)
C19A-H19A	0.9300
C19A-C16A	1.394(8)
C19A-C20A	1.379(12)
C17A-C16A	1.468(11)
C17A-C18A	1.392(7)
C17A-C22A	1.411(10)
C21A-H21A	0.9300
C21A-C20A	1.378(8)
C21A-C22A	1.363(9)
C18A-H18A	0.9300
C18A-C13A	1.375(9)
C20A-H20A	0.9300
C22A-H22A	0.9300
C31A-H31D	0.9600
C31A-H31E	0.9600
C31A-H31F	0.9600
C13A-C14A	1.406(7)
C14A-H14A	0.9300

O1-S1-N1	106.36(11)
O1-S1-C5	110.35(13)
O2-S1-O1	120.73(14)
O2-S1-N1	106.30(12)
O2-S1-C5	107.85(12)
N1-S1-C5	103.89(12)
N2-N1-S1	120.82(16)

N2-N1-C12	119.09(19)
C12-N1-S1	120.02(16)
N1-N2-C8	118.75(18)
C32-N2-N1	117.6(2)
C32-N2-C8	120.3(2)
O4-N3-C24	119.4(2)
O5-N3-O4	122.9(2)
O5-N3-C24	117.8(2)
H1A-C1-H1B	109.5
H1A-C1-H1C	109.5
H1B-C1-H1C	109.5
C2-C1-H1A	109.5
C2-C1-H1B	109.5
C2-C1-H1C	109.5
C3-C2-C1	120.9(3)
C7-C2-C1	120.8(3)
C7-C2-C3	118.4(3)
C2-C3-H3	119.4
C4-C3-C2	121.1(3)
C4-C3-H3	119.4
C3-C4-H4	120.5
C5-C4-C3	119.0(2)
C5-C4-H4	120.5
C4-C5-S1	119.57(19)
C4-C5-C6	121.0(2)
C6-C5-S1	119.29(19)
C5-C6-H6	120.7
C7-C6-C5	118.6(3)
C7-C6-H6	120.7
C2-C7-C6	121.8(3)
C2-C7-H7	119.1
C6-C7-H7	119.1
N2-C8-H8	108.4
N2-C8-C9	110.04(18)
N2-C8-C23	112.4(2)
C9-C8-H8	108.4
C9-C8-C23	109.06(19)
C23-C8-H8	108.4

C8-C9-H9A	108.1
C8-C9-H9B	108.1
H9A-C9-H9B	107.3
C10-C9-C8	116.7(2)
C10-C9-H9A	108.1
C10-C9-H9B	108.1
C9-C10-H10	116.3
C11-C10-C9	127.4(2)
C11-C10-H10	116.3
C10-C11-C12	126.2(2)
C10-C11-C29	119.5(2)
C29-C11-C12	114.0(2)
N1-C12-C11	111.38(19)
N1-C12-H12	104.2
N1-C12-H12A	109.9
N1-C12-C13	109.1(3)
N1-C12-C13A	110.0(4)
C11-C12-H12	104.2
C11-C12-H12A	109.9
C11-C12-C13A	105.8(4)
C13-C12-C11	121.8(3)
C13-C12-H12	104.2
C13A-C12-H12A	109.9
C24-C23-C8	121.8(2)
C28-C23-C8	121.7(2)
C28-C23-C24	116.2(2)
C23-C24-N3	121.7(2)
C25-C24-N3	115.4(2)
C25-C24-C23	122.9(3)
C24-C25-H25	120.5
C26-C25-C24	119.0(3)
C26-C25-H25	120.5
C25-C26-H26	120.2
C25-C26-C27	119.6(2)
C27-C26-H26	120.2
C26-C27-H27	119.7
C26-C27-C28	120.6(3)
C28-C27-H27	119.7

C23-C28-C27	121.6(3)
C23-C28-H28	119.2
C27-C28-H28	119.2
O6-C29-C11	123.6(3)
O6-C29-O7	121.3(3)
O6-C29-O7A	126.3(5)
O7-C29-C11	114.4(3)
O7A-C29-C11	107.1(5)
O3-C32-N2	122.8(3)
O3-C32-H32	118.6
N2-C32-H32	118.6
C29-O7-C30	116.8(4)
C14-C13-C12	118.4(4)
C14-C13-C18	120.2(5)
C18-C13-C12	121.4(5)
C13-C14-H14	120.0
C13-C14-C15	120.1(5)
C15-C14-H14	120.0
C16-C15-C14	119.3(5)
C16-C15-C19	119.1(6)
C19-C15-C14	121.6(5)
C15-C16-C17	119.6(5)
C15-C16-C22	120.5(6)
C17-C16-C22	119.8(6)
C16-C17-H17	120.2
C18-C17-C16	119.6(5)
C18-C17-H17	120.2
C13-C18-H18	119.4
C17-C18-C13	121.3(5)
C17-C18-H18	119.4
C15-C19-H19	120.1
C20-C19-C15	119.8(6)
C20-C19-H19	120.1
C19-C20-H20	119.3
C19-C20-C21	121.5(6)
C21-C20-H20	119.3
C20-C21-H21	120.1
C22-C21-C20	119.8(7)

C22-C21-H21	120.1
C16-C22-H22	120.4
C21-C22-C16	119.2(6)
C21-C22-H22	120.4
O7-C30-H30A	111.3
O7-C30-H30B	111.3
O7-C30-C31	102.5(6)
H30A-C30-H30B	109.2
C31-C30-H30A	111.3
C31-C30-H30B	111.3
C30-C31-H31A	109.5
C30-C31-H31B	109.5
C30-C31-H31C	109.5
H31A-C31-H31B	109.5
H31A-C31-H31C	109.5
H31B-C31-H31C	109.5
H30C-C30A-H30D	107.9
C31A-C30A-H30C	109.2
C31A-C30A-H30D	109.2
O7A-C30A-H30C	109.2
O7A-C30A-H30D	109.2
O7A-C30A-C31A	111.9(14)
C16A-C15A-H15A	119.3
C14A-C15A-H15A	119.3
C14A-C15A-C16A	121.4(6)
C16A-C19A-H19A	119.4
C20A-C19A-H19A	119.4
C20A-C19A-C16A	121.2(9)
C18A-C17A-C16A	117.2(7)
C18A-C17A-C22A	124.5(8)
C22A-C17A-C16A	118.2(6)
C20A-C21A-H21A	119.8
C22A-C21A-H21A	119.8
C22A-C21A-C20A	120.4(7)
C15A-C16A-C17A	118.4(6)
C19A-C16A-C15A	123.8(8)
C19A-C16A-C17A	117.6(8)
C17A-C18A-H18A	118.5

C13A-C18A-C17A	123.1(7)
C13A-C18A-H18A	118.5
C19A-C20A-H20A	119.4
C21A-C20A-C19A	121.1(8)
C21A-C20A-H20A	119.4
C17A-C22A-H22A	119.4
C21A-C22A-C17A	121.3(7)
C21A-C22A-H22A	119.4
C30A-C31A-H31D	109.5
C30A-C31A-H31E	109.5
C30A-C31A-H31F	109.5
H31D-C31A-H31E	109.5
H31D-C31A-H31F	109.5
H31E-C31A-H31F	109.5
C29-O7A-C30A	121.7(9)
C18A-C13A-C12	116.1(6)
C18A-C13A-C14A	119.3(7)
C14A-C13A-C12	124.6(6)
C15A-C14A-C13A	120.5(7)
C15A-C14A-H14A	119.8
C13A-C14A-H14A	119.8

Symmetry transformations used to generate equivalent atoms:

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

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S1	43(1)	39(1)	35(1)	14(1)	13(1)	2(1)
O1	33(1)	77(1)	38(1)	17(1)	7(1)	1(1)
O2	84(2)	35(1)	58(1)	20(1)	40(1)	7(1)
O3	64(1)	50(1)	56(1)	35(1)	18(1)	11(1)
O4	46(1)	73(1)	44(1)	20(1)	18(1)	12(1)
O5	71(2)	50(1)	46(1)	14(1)	18(1)	15(1)

O6	67(1)	63(1)	44(1)	27(1)	-12(1)	8(1)
N1	38(1)	42(1)	29(1)	17(1)	7(1)	7(1)
N2	37(1)	36(1)	32(1)	18(1)	8(1)	8(1)
N3	53(1)	48(1)	32(1)	19(1)	14(1)	12(1)
C1	67(2)	60(2)	73(2)	-7(2)	34(2)	-7(2)
C2	43(2)	49(2)	52(2)	6(1)	20(1)	6(1)
C3	62(2)	38(1)	64(2)	24(1)	32(2)	16(1)
C4	47(2)	48(2)	44(1)	28(1)	18(1)	17(1)
C5	38(1)	40(1)	34(1)	20(1)	11(1)	10(1)
C6	55(2)	50(2)	37(1)	24(1)	14(1)	24(1)
C7	43(2)	66(2)	34(1)	15(1)	8(1)	21(1)
C8	35(1)	35(1)	29(1)	15(1)	8(1)	8(1)
C9	38(1)	32(1)	30(1)	14(1)	6(1)	4(1)
C10	42(1)	35(1)	34(1)	18(1)	8(1)	8(1)
C11	36(1)	38(1)	34(1)	20(1)	5(1)	6(1)
C12	35(1)	38(1)	30(1)	16(1)	2(1)	2(1)
C23	37(1)	41(1)	33(1)	22(1)	8(1)	8(1)
C24	42(1)	42(1)	34(1)	21(1)	11(1)	10(1)
C25	51(2)	50(2)	32(1)	19(1)	4(1)	6(1)
C26	43(2)	63(2)	41(2)	28(1)	-3(1)	7(1)
C27	43(2)	63(2)	51(2)	32(1)	11(1)	20(1)
C28	42(1)	49(2)	38(1)	22(1)	11(1)	13(1)
C29	48(2)	40(1)	49(2)	21(1)	1(1)	9(1)
C32	42(1)	37(1)	46(1)	21(1)	10(1)	9(1)
O7	54(2)	42(2)	53(2)	24(2)	1(2)	18(2)
C13	31(2)	34(3)	19(3)	10(3)	7(2)	10(2)
C14	34(2)	42(3)	27(2)	15(2)	8(2)	7(2)
C15	35(3)	45(3)	36(3)	24(2)	12(2)	11(2)
C16	29(3)	41(3)	44(3)	29(2)	11(2)	9(2)
C17	40(2)	37(2)	33(2)	10(2)	8(2)	5(2)
C18	33(2)	40(2)	31(2)	12(2)	6(2)	0(2)
C19	41(2)	59(3)	43(3)	25(2)	15(2)	7(2)
C20	41(3)	74(4)	63(3)	43(3)	16(3)	7(2)
C21	43(3)	54(4)	62(4)	38(3)	14(3)	9(3)
C22	39(3)	47(3)	52(3)	28(2)	6(2)	9(2)

C30	47(3)	46(2)	60(3)	31(2)	0(2)	17(2)
C31	89(6)	76(4)	89(6)	30(4)	12(4)	47(4)
C30A	62(6)	61(5)	75(6)	30(4)	12(4)	31(4)
C15A	45(3)	45(3)	45(3)	22(3)	19(2)	6(2)
C19A	51(4)	54(4)	65(4)	35(3)	8(3)	2(3)
C17A	32(4)	33(3)	36(3)	20(3)	3(3)	3(3)
C21A	49(3)	31(3)	60(4)	18(3)	-9(3)	0(3)
C16A	39(3)	40(3)	47(3)	28(3)	6(3)	4(3)
C18A	37(3)	36(3)	29(3)	14(2)	4(2)	9(2)
C20A	50(4)	56(5)	67(5)	35(4)	4(4)	-7(3)
C22A	41(3)	32(3)	41(3)	14(2)	-2(2)	8(2)
C31A	69(9)	93(11)	98(12)	68(9)	11(8)	21(8)
O7A	60(5)	40(4)	84(6)	34(4)	-4(4)	15(4)
C13A	35(4)	26(3)	21(4)	4(3)	5(3)	5(3)
C14A	38(3)	44(3)	36(3)	14(3)	10(3)	3(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for rac-**4af**.

	x	y	z	U(eq)
H1A	1973	2128	-1497	119
H1B	3436	1919	-1356	119
H1C	2681	2560	-2149	119
H3	4432	3000	955	63
H4	5322	4796	2727	53
H6	3649	6450	617	57
H7	2763	4640	-1133	64
H8	3578	7943	6106	41
H9A	4790	9807	6578	44
H9B	5159	9140	5461	44
H10	2940	10028	5210	47
H12	2514	7296	2270	46

H12A	2360	7168	2183	46
H25	7324	9683	10083	58
H26	8938	8585	9755	65
H27	8527	7240	7752	64
H28	6514	6966	6077	53
H32	3500	5221	3817	53
H14	969	6873	3996	43
H17	55	3587	246	50
H18	1611	5253	938	47
H19	-697	5782	4309	57
H20	-2261	4115	3603	68
H21	-2763	2486	1705	62
H22	-1612	2505	546	58
H30A	-877	9882	2352	68
H30B	343	10610	2370	68
H31A	-706	11924	3512	143
H31B	812	12044	4399	143
H31C	-380	11318	4397	143
H30C	-962	10392	3802	86
H30D	-1034	9762	2455	86
H15A	-464	6032	4291	54
H19A	-1953	3991	3057	71
H21A	-1919	1777	-163	71
H18A	1225	5174	1324	45
H20A	-2655	2164	1369	74
H22A	-311	3145	54	54
H31D	749	11301	3054	129
H31E	683	11948	4342	129
H31F	-562	11763	3114	129
H14A	1142	7418	4517	51

Table 6. Torsion angles [°] for rac-**4af**.

S1-N1-N2-C8	103.1(2)
S1-N1-N2-C32	-97.3(2)
S1-N1-C12-C11	-103.3(2)
S1-N1-C12-C13	119.4(3)
S1-N1-C12-C13A	139.7(3)
S1-C5-C6-C7	-173.1(2)
O1-S1-N1-N2	-7.8(2)
O1-S1-N1-C12	169.08(18)
O1-S1-C5-C4	33.9(3)
O1-S1-C5-C6	-150.7(2)
O2-S1-N1-N2	-137.64(18)
O2-S1-N1-C12	39.2(2)
O2-S1-C5-C4	167.7(2)
O2-S1-C5-C6	-16.9(3)
O4-N3-C24-C23	37.3(3)
O4-N3-C24-C25	-143.0(2)
O5-N3-C24-C23	-143.3(2)
O5-N3-C24-C25	36.4(3)
O6-C29-O7-C30	0.6(7)
O6-C29-O7A-C30A	-24.4(13)
N1-S1-C5-C4	-79.8(2)
N1-S1-C5-C6	95.6(2)
N1-N2-C8-C9	-9.1(3)
N1-N2-C8-C23	-130.8(2)
N1-N2-C32-O3	-169.3(2)
N1-C12-C13-C14	94.3(6)
N1-C12-C13-C18	-82.4(6)
N1-C12-C13A-C18A	-87.9(7)
N1-C12-C13A-C14A	89.1(9)
N2-N1-C12-C11	73.6(3)
N2-N1-C12-C13	-63.6(3)
N2-N1-C12-C13A	-43.4(4)
N2-C8-C9-C10	69.0(3)
N2-C8-C23-C24	-169.5(2)

N2-C8-C23-C28	16.1(3)
N3-C24-C25-C26	179.4(2)
C1-C2-C3-C4	-177.8(3)
C1-C2-C7-C6	178.0(3)
C2-C3-C4-C5	-0.6(4)
C3-C2-C7-C6	-2.7(5)
C3-C4-C5-S1	173.4(2)
C3-C4-C5-C6	-2.0(4)
C4-C5-C6-C7	2.2(4)
C5-S1-N1-N2	108.70(19)
C5-S1-N1-C12	-74.4(2)
C5-C6-C7-C2	0.2(4)
C7-C2-C3-C4	2.9(4)
C8-N2-C32-O3	-10.0(4)
C8-C9-C10-C11	-50.8(4)
C8-C23-C24-N3	5.0(4)
C8-C23-C24-C25	-174.7(2)
C8-C23-C28-C27	175.4(2)
C9-C8-C23-C24	68.2(3)
C9-C8-C23-C28	-106.2(3)
C9-C10-C11-C12	0.4(4)
C9-C10-C11-C29	-172.4(2)
C10-C11-C12-N1	-11.1(4)
C10-C11-C12-C13	119.9(4)
C10-C11-C12-C13A	108.4(4)
C10-C11-C29-O6	158.2(3)
C10-C11-C29-O7	-12.7(5)
C10-C11-C29-O7A	-40.2(7)
C11-C12-C13-C14	-37.6(8)
C11-C12-C13-C18	145.6(5)
C11-C12-C13A-C18A	151.7(6)
C11-C12-C13A-C14A	-31.4(9)
C11-C29-O7-C30	171.8(4)
C11-C29-O7A-C30A	174.7(9)
C12-N1-N2-C8	-73.8(3)
C12-N1-N2-C32	85.8(3)

C12-C11-C29-O6	-15.5(4)
C12-C11-C29-O7	173.6(4)
C12-C11-C29-O7A	146.1(6)
C12-C13-C14-C15	-177.2(5)
C12-C13-C18-C17	177.0(5)
C12-C13A-C14A-C15A	-176.7(6)
C23-C8-C9-C10	-167.3(2)
C23-C24-C25-C26	-0.9(4)
C24-C23-C28-C27	0.7(4)
C24-C25-C26-C27	1.0(4)
C25-C26-C27-C28	-0.3(5)
C26-C27-C28-C23	-0.6(4)
C28-C23-C24-N3	179.7(2)
C28-C23-C24-C25	0.0(4)
C29-C11-C12-N1	162.1(2)
C29-C11-C12-C13	-66.9(4)
C29-C11-C12-C13A	-78.4(4)
C29-O7-C30-C31	176.8(9)
C32-N2-C8-C9	-168.2(2)
C32-N2-C8-C23	70.1(3)
O7-C29-O7A-C30A	64.2(12)
C13-C12-C13A-C18A	2.8(13)
C13-C12-C13A-C14A	180(3)
C13-C14-C15-C16	1.0(9)
C13-C14-C15-C19	179.7(6)
C14-C13-C18-C17	0.3(10)
C14-C15-C16-C17	-1.4(9)
C14-C15-C16-C22	-179.2(5)
C14-C15-C19-C20	179.5(5)
C15-C16-C17-C18	1.3(9)
C15-C16-C22-C21	-0.6(10)
C15-C19-C20-C21	0.0(9)
C16-C15-C19-C20	-1.8(8)
C16-C17-C18-C13	-0.7(9)
C17-C16-C22-C21	-178.3(6)
C18-C13-C14-C15	-0.4(10)

C19-C15-C16-C17	179.8(5)
C19-C15-C16-C22	2.1(10)
C19-C20-C21-C22	1.5(9)
C20-C21-C22-C16	-1.2(9)
C22-C16-C17-C18	179.1(5)
C17A-C18A-C13A-C12	178.1(7)
C17A-C18A-C13A-C14A	1.0(13)
C16A-C15A-C14A-C13A	1.1(11)
C16A-C19A-C20A-C21A	-3.6(13)
C16A-C17A-C18A-C13A	-3.0(12)
C16A-C17A-C22A-C21A	1.5(11)
C18A-C17A-C16A-C15A	4.0(11)
C18A-C17A-C16A-C19A	-180.0(7)
C18A-C17A-C22A-C21A	179.0(7)
C18A-C13A-C14A-C15A	0.1(12)
C20A-C19A-C16A-C15A	179.0(8)
C20A-C19A-C16A-C17A	3.3(12)
C20A-C21A-C22A-C17A	-1.7(10)
C22A-C17A-C16A-C15A	-178.2(7)
C22A-C17A-C16A-C19A	-2.2(12)
C22A-C17A-C18A-C13A	179.4(8)
C22A-C21A-C20A-C19A	2.7(12)
C31A-C30A-O7A-C29	-86(2)
O7A-C29-O7-C30	-108.8(14)
C13A-C12-C13-C14	-1.8(14)
C13A-C12-C13-C18	-179(2)
C14A-C15A-C16A-C19A	-178.9(7)
C14A-C15A-C16A-C17A	-3.2(10)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for rac-**4af** [Å and °].

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