

Highly Enantioselective Direct Mannich Reactions of Unfunctionalized Ketones Catalyzed by Bifunctional Organocatalysts

Qunsheng Guo and John Cong-Gui Zhao*

Department of Chemistry, University of Texas at San Antonio,

One UTSA Circle, San Antonio, TX 78249-0698

Supporting Information

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Experimental Procedures

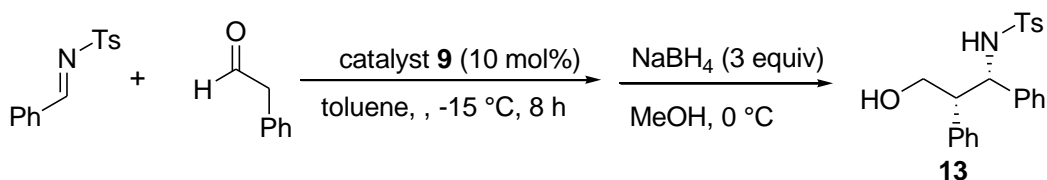
A. General information

The aldehydes used in this study were washed with aqueous NaHCO₃ solution, dried, and then distilled or recrystallized before use. All other reagents are commercial products and were used as received.

B. General Experimental Procedure for the Mannich Reaction

To a mixture of the ketone (0.40 mmol), 4 Å molecular sieves (50.0 mg), and *p*-toluenesulfonamide (68.4 mg, 0.40 mmol) in toluene (0.2 mL) at 0 °C were added catalyst **9** (13.5 mg, 0.02 mmol, 10 mol %) and the aldehyde (0.20 mmol). The mixture was further stirred at 0 °C for the indicated time. Upon completion, the reaction mixture was directly transferred to a silica gel column and purified by column chromatography (4:4:1 CH₂Cl₂/hexane/ethyl acetate) to afford the Mannich products.

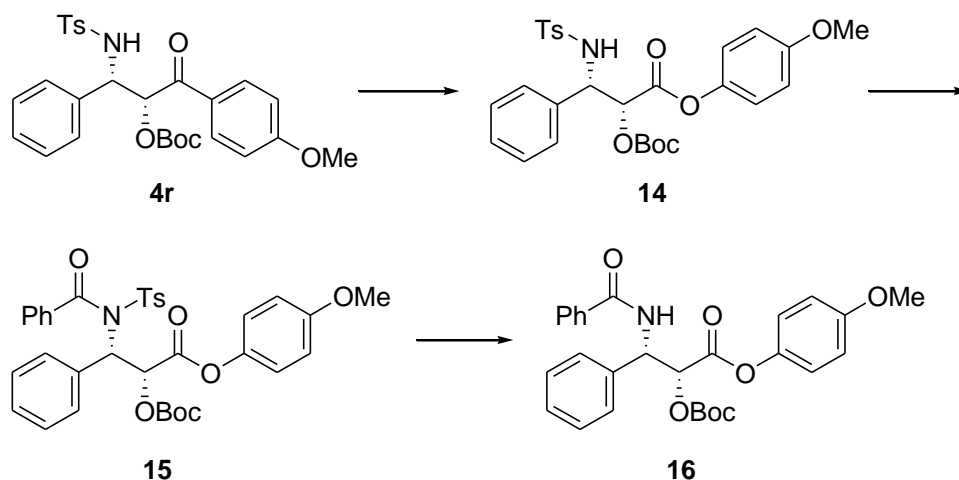
C. Procedure for the Mannich Reaction of 2-Phenylacetaldehyde



To a mixture of 2-phenylacetaldehyde (48.0 mg, 0.40 mmol) and (*E*)-*N*-benzylidene-4-methylbenzenesulfonamide (52.0 mg, 0.20 mmol) in toluene (2.0 mL) at -15 °C were added catalyst **9** (13.5 mg, 0.02 mmol, 10 mol %). After the reaction mixture had been stirred for 8 h at -15 °C, methanol (5.0 mL) and NaBH₄ (23.0 mg, 0.6 mmol) were added at 0 °C. The resulting reaction mixture was stirred for an additional 30 min at 0 °C before it was quenched with water (5 mL). The resulting mixture was extracted with ethyl acetate (10 mL × 3), and the combined organic phase was dried over Na₂SO₄. Purification by flash column chromatography on silica gel (ethyl acetate/hexane 1:2) gave the reduced Mannich product **13** (94 mg, 87% yield).

D. Synthesis of the Protected Paclitaxel Side-Chain **16** from the Mannich Reaction Product **4r**

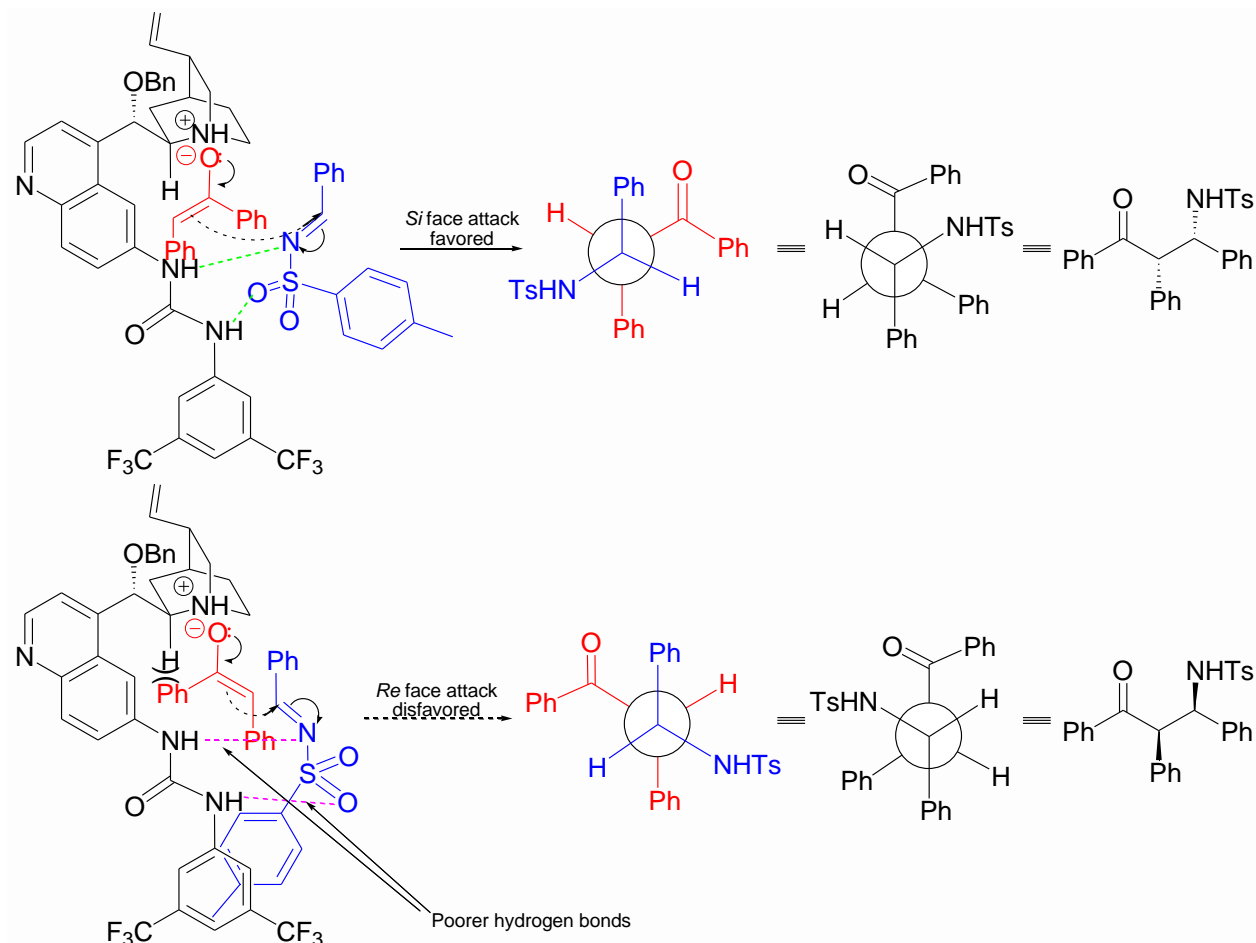
To a solution of **4r** (157.5 mg, 0.30 mmol) in CH₂Cl₂ (10.0 mL) at room temperature was added *m*-chloroperoxybenzoic acid (135 mg, 77%, 0.60 mmol) and NaHCO₃ (50.4 mg, 0.6 mmol). The mixture was further stirred for 12 h at the same temperature. Then the reaction mixture was washed by water (5 mL). The organic phase was dried over Na₂SO₄ and the solvent was removed under reduced pressure. The resulting crude mixture was purified by column chromatography (5:1 hexane/AcOEt) to afford product **14** (140 mg, 86% yield).



To a mixture of the compound **14** (108.0 mg, 0.20 mmol), 4-(dimethylamino)pyridine (4.5 mg, 0.04 mmol), benzoyl chloride (112.5 mg, 0.8 mmol) and Et₃N (81.0 mg, 0.8 mmol) in THF (4.0 mL) at rt was added 4-(dimethylamino)pyridine (3.7 mg, 0.03 mmol, 10 mol %) with stirring. The mixture was further stirred for 24 h at rt. Then the solvent was removed under reduced pressure and the residue was directly transferred to a silica gel column and purified by column chromatography (6:1 hexane/ethyl acetate) to afford the Boc-Ts-protected product **15** as colorless oil.

To a mixture of the Boc-Ts-protected compound and HMPA (0.4 mL) in THF (4.0 mL) under argon at -78 °C was added SmI₂ (8.0 mL, 0.1 M solution in THF, 0.8 mmol). The mixture was then stirred at -78 °C for 0.5 h. Then the reaction mixture was quenched by adding aq. NaHCO₃ solution (10 mL) and extracted with AcOEt (2×10 mL). The combined organic phase was dried over Na₂SO₄ and the solvent was then removed under reduced pressure. The resulting crude mixture was purified by column chromatography (5:1 hexane/AcOEt) to afford the Boc-protected product **16** (87 mg, 92%).

Proposed Transition State Models



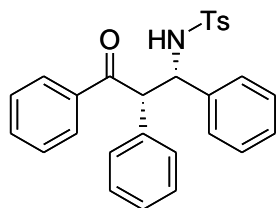
Scheme S-1. Proposed Transition State Models for the Three-Component Mannich Reaction

The formation of the (2*S*,3*S*)-product may be rationalized by using proposed transition state models shown in Scheme S-1. After its formation, the *E*-enolate of the ketone is closely associated with the ammonium ion through ionic interactions. The *Re* face orientation of this enolate is favored over the *Si* face orientation since there are less steric interactions between the enolate and the catalyst backbone. Simultaneously, the imine intermediate forms hydrogen bonds with the thiourea moiety of the catalyst. Not only do these hydrogen bonds help to fix the orientation of the imine, but they also activate the imine for the Mannich reaction (as is evident from the data in Table 1, improved yields and ee values were obtained with the thiourea catalysts). Again the *Re* face orientation of the imine is favored over the *Si* face orientation due to stronger hydrogen-bonding in the first scenario (the orientation of the lone-pairs on nitrogen

and oxygen atom in the *Re* face orientation is more desirable for the hydrogen bonds between the imine and the thiourea). Thus, in the favored transition state, the attack of the enolate from back onto the *Si* face of the imine leads to the formation of the observed (2*S*,3*S*)-product.

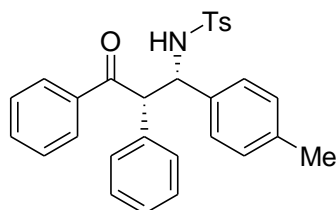
Compound Characterization Data

(2*S*,3*S*)-1,2,3-Triphenyl-3-(tosylamino)propan-1-one (4a)



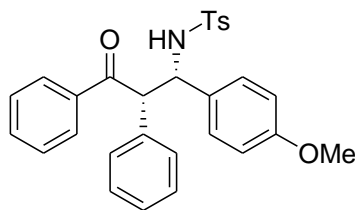
White solid, 88 mg, 96% yield, dr: > 99:1; m.p. 233-234 °C; ¹H NMR (300 MHz, *d*₆-DMSO): δ 2.24 (s, 3H), 5.02 (t, *J* = 9.9 Hz, 1H), 5.24 (d, *J* = 11.1 Hz, 1H), 6.95-7.05 (m, 5H), 7.12 (d, *J* = 8.1 Hz, 2H), 7.20-7.26 (m, 5H), 7.33-7.51 (m, 5H), 7.72 (d, *J* = 7.2 Hz, 2H), 8.18 (d, *J* = 9.9 Hz, 1H); ¹³C NMR (75 MHz, *d*₆-DMSO): δ 21.7, 58.4, 58.7, 60.4, 60.9, 126.6, 126.8, 128.0, 128.2, 128.7, 129.3, 129.5, 129.7, 134.2, 135.6, 136.3, 136.9, 139.2, 141.3, 142.2, 197.6. ν_{max} : 3331, 3058, 1667, 1595, 1492, 1445, 1327, 1275, 1153, 1070 cm⁻¹. Analytic calcd. for C₂₈H₂₅NO₃S: C, 73.82; H, 5.53; N, 3.07; found: C, 73.74; H, 5.53; N, 3.08. $[\alpha]_{\text{D}}^{25} = -169.6$ (*c* 0.25, CH₂Cl₂, 96% ee). Enantiomeric excess of the product was measured by chiral stationary phase HPLC analysis using a Chiracel AD-H column (80:20 hexanes/*i*-PrOH at 1.0 mL/min): major enantiomer: *t*_R = 18.8 min; minor enantiomer: *t*_R = 14.0 min.

(2*S*,3*S*)-3-(4-Methylphenyl)-1,2-diphenyl-3-(tosylamino)propan-1-one (4b)



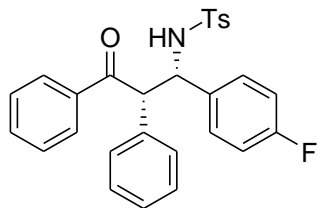
White solid, 89 mg, 95% yield, dr: > 99:1; m.p. 162-163 °C; ¹H NMR (300 MHz, *d*₆-DMSO): δ 2.10 (s, 3H), 2.25 (s, 3H), 4.97 (t, *J* = 7.5 Hz, 1H), 5.23 (d, *J* = 11.1 Hz, 1H), 6.80 (d, *J* = 7.8 Hz, 2H), 6.95 (d, *J* = 8.1 Hz, 2H), 7.07-7.23 (m, 7H), 7.33-7.51 (m, 5H), 7.72 (d, *J* = 8.1 Hz, 2H), 8.08 (d, *J* = 8.7 Hz, 1H); ¹³C NMR (75 MHz, *d*₆-DMSO): δ 20.6, 20.9, 57.7, 59.4, 125.9, 127.2, 127.3, 127.9, 128.1, 128.4, 128.6, 128.7, 128.9, 133.4, 135.4, 135.5, 135.8, 137.5, 138.3, 141.3, 196.7. ν_{max} : 3305, 1666, 1595, 1448, 1323, 1275, 1155, 1058 cm⁻¹. Analytic calcd. for C₂₉H₂₇NO₃S: C, 74.17; H, 5.80; N, 2.98; found: C, 74.31; H, 5.80; N, 2.98. $[\alpha]_{\text{D}}^{25} = -151.2$ (*c* 0.25, CH₂Cl₂, 96% ee). Enantiomeric excess of the product was measured by chiral stationary phase HPLC analysis using a Chiracel AD-H column (80:20 hexanes/*i*-PrOH at 1.0 mL/min): major enantiomer: *t*_R = 19.8 min; minor enantiomer: *t*_R = 15.2 min.

(2*S*,3*S*)-3-(4-Methoxyphenyl)-1,2-diphenyl-3-(tosylamino)propan-1-one (4c)



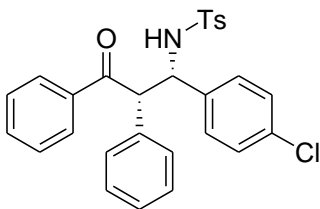
White solid, 86 mg, 88% yield, dr: > 99:1; m.p. 252-253 °C; ^1H NMR (300 MHz, d_6 -DMSO): δ 2.25 (s, 3H), 3.59 (s, 3H), 4.97 (t, J = 9.9 Hz, 1H), 5.21 (d, J = 11.1 Hz, 1H), 6.55 (d, J = 8.1 Hz, 2H), 6.97 (d, J = 8.1 Hz, 2H), 7.09-7.27 (m, 7H), 7.34-7.52 (m, 5H), 7.72 (d, J = 8.1 Hz, 2H), 8.04 (d, J = 8.1 Hz, 1H); ^{13}C NMR (75 MHz, d_6 -DMSO): δ 20.8, 54.8, 57.9, 59.1, 112.9, 125.9, 127.1, 127.9, 128.3, 128.5, 128.6, 128.7, 128.8, 132.4, 135.5, 135.6, 138.3, 141.2, 157.8, 196.8. ν_{max} : 3311, 1665, 1594, 1514, 1443, 1325, 1277, 1248, 1151, 1075 cm^{-1} . Analytic calcd. for $\text{C}_{29}\text{H}_{27}\text{NO}_4\text{S}$: C, 71.73; H, 5.60; N, 2.88; found: C, 71.92; H, 5.52; N, 2.90. $[\alpha]_{\text{D}}^{25}$ = -180.0 (c 0.3, CH_2Cl_2 , 96% ee). Enantiomeric excess of the product was measured by chiral stationary phase HPLC analysis using a Chiracel OD-H column (90:10 hexanes/*i*-PrOH at 1.0 mL/min): major enantiomer: t_{R} = 18.3 min; minor enantiomer: t_{R} = 12.2 min.

(2S,3S)-3-(4-Fluorophenyl)-1,2-diphenyl-3-(tosylamino)propan-1-one (4d)



White solid, 91 mg, 96% yield, dr: > 99:1; m.p. 227-228 °C; ^1H NMR (300 MHz, d_6 -DMSO): δ 2.24 (s, 3H), 5.01 (t, J = 10.8 Hz, 1H), 5.21 (d, J = 11.1 Hz, 1H), 6.83 (t, J = 8.7 Hz, 2H), 6.98 (d, J = 8.1 Hz, 2H), 7.13 (d, J = 8.1 Hz, 2H), 7.20-7.27 (m, 5H), 7.33-7.51 (m, 5H), 7.72 (d, J = 7.8 Hz, 2H), 8.17 (d, J = 9.9 Hz, 1H); ^{13}C NMR (75 MHz, d_6 -DMSO): δ 21.7, 58.8, 59.7, 115.0, 115.3, 126.7, 128.1, 128.7, 129.2, 129.5, 129.6, 130.2, 130.3, 134.2, 136.2, 137.4, 139.0, 142.3, 160.0, 163.2, 197.6. ν_{max} : 3314, 1662, 1595, 1510, 1447, 1325, 1277, 1227, 1152, 1095, 1076 cm^{-1} . Analytic calcd. for $\text{C}_{28}\text{H}_{24}\text{FNO}_3\text{S}$: C, 71.02; H, 5.11; N, 2.96; found: C, 70.50; H, 5.17; N, 2.88. $[\alpha]_{\text{D}}^{25}$ = -115.6 (c 0.3, CH_2Cl_2 , 95% ee). Enantiomeric excess of the product was measured by chiral stationary phase HPLC analysis using a Chiracel OD-H column (90:10 hexanes/*i*-PrOH at 0.8 mL/min): major enantiomer: t_{R} = 18.8 min; minor enantiomer: t_{R} = 27.7 min.

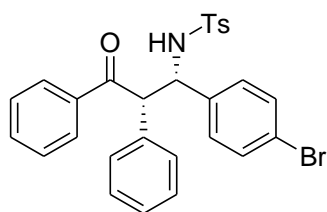
(2S,3S)-3-(4-Chlorophenyl)-1,2-diphenyl-3-(tosylamino)propan-1-one (4e)



White solid, 93 mg, 95% yield, dr: > 99:1; m.p. 235-237 °C; ^1H NMR (300 MHz, d_6 -DMSO): δ 2.26 (s, 3H), 4.99 (t, J = 10.5 Hz, 1H), 5.21 (d, J = 11.1 Hz, 1H), 6.98 (d, J = 8.1 Hz, 2H), 7.05 (d, J =

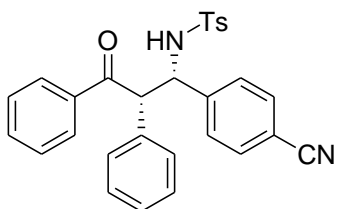
8.1 Hz, 2H), 7.12 (d, $J = 8.1$ Hz, 2H), 7.21-7.27 (m, 5H), 7.34-7.51(m, 5H), 7.12 (d, $J = 8.1$ Hz, 2H), 8.19 (d, $J = 9.9$ Hz, 1H); ^{13}C NMR (75 MHz, d_6 -DMSO): δ 20.9, 57.7, 59.0, 125.9, 127.3, 127.6, 127.9, 128.4, 128.7, 128.8, 129.3, 131.4, 133.5, 135.2, 135.3, 138.0, 139.2, 141.6, 196.6. ν_{max} : 3307, 1663, 1595, 1491, 1446, 1326, 1277, 1151, 1076 cm^{-1} . Analytic calcd. for $\text{C}_{28}\text{H}_{24}\text{ClNO}_3\text{S}$: C, 68.63; H, 4.94; N, 2.86; found: C, 68.71; H, 4.99; N, 2.85. $[\alpha]_{\text{D}}^{25} = -150.8$ (c 0.24, CH_2Cl_2 , 94% ee). Enantiomeric excess of the product was measured by chiral stationary phase HPLC analysis using a Chiracel AD-H column (90:10 hexanes/*i*-PrOH at 1.0 mL/min): major enantiomer: $t_{\text{R}} = 34.8$ min; minor enantiomer: $t_{\text{R}} = 41.7$ min.

(2*S*,3*S*)-3-(4-Bromophenyl)-1,2-diphenyl-3-(tosylamino)propan-1-one (4f)



White solid, 104 mg, 97% yield, dr: > 99:1; m.p. 255-256 °C; ^1H NMR (300 MHz, d_6 -DMSO): δ 2.28 (s, 3H), 4.97 (t, $J = 10.8$ Hz, 1H), 5.22 (d, $J = 11.1$ Hz, 1H), 6.98 (d, $J = 8.1$ Hz, 2H), 7.11-7.28 (m, 8H), 7.34-7.52(m, 5H), 7.74 (d, $J = 8.1$ Hz, 2H), 8.19 (d, $J = 9.9$ Hz, 1H); ^{13}C NMR (75 MHz, d_6 -DMSO): δ 20.9, 57.6, 59.1, 120.1, 125.9, 127.3, 127.9, 128.5, 128.7, 128.8, 129.7, 130.5, 133.5, 135.2, 135.3, 138.0, 139.6, 141.6, 196.6. ν_{max} : 3302, 1663, 1594, 1489, 1447, 1322, 1275, 1154, 1060, 1009 cm^{-1} . Analytic calcd. for $\text{C}_{28}\text{H}_{24}\text{BrNO}_3\text{S}$: C, 62.92; H, 4.53; N, 2.62; found: C, 63.17; H, 4.61; N, 2.62. $[\alpha]_{\text{D}}^{25} = -173.9$ (c 0.21, CH_2Cl_2 , 94% ee). Enantiomeric excess of the product was measured by chiral stationary phase HPLC analysis using a Chiracel AD-H column (90:10 hexanes/*i*-PrOH at 1.0 mL/min): major enantiomer: $t_{\text{R}} = 39.7$ min; minor enantiomer: $t_{\text{R}} = 46.6$ min.

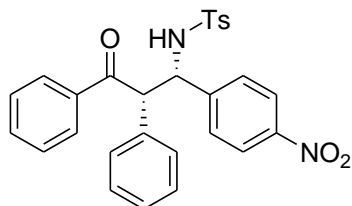
(2*S*,3*S*)-3-(4-Cyanophenyl)-1,2-diphenyl-3-(tosylamino)propan-1-one (4g)



White solid, 93 mg, 97% yield, dr: > 99:1; m.p. 235-237 °C; ^1H NMR (300 MHz, d_6 -DMSO): δ 2.26 (s, 3H), 5.04 (t, $J = 10.2$ Hz, 1H), 5.24 (d, $J = 10.8$ Hz, 1H), 6.98 (d, $J = 7.8$ Hz, 2H), 7.13 (d, $J = 8.1$ Hz, 2H), 7.25-7.51 (m, 12 H), 7.73 (d, $J = 8.1$ Hz, 2H), 8.32 (d, $J = 9.9$ Hz, 1H); ^{13}C NMR (75 MHz, d_6 -DMSO): δ 20.8, 57.6, 59.3, 109.5, 118.3, 126.0, 127.4, 128.0, 128.5, 128.6, 128.8, 131.6, 133.6, 134.9, 135.1, 137.8, 141.7, 145.6, 196.4. ν_{max} : 3299, 2228, 1658, 1595, 1446, 1325, 1277, 1154, 1079 cm^{-1} . Analytic calcd. for $\text{C}_{29}\text{H}_{24}\text{N}_2\text{O}_3\text{S}$: C, 72.48; H, 5.03; N, 5.83; found: C, 72.34; H, 5.07; N, 5.81. $[\alpha]_{\text{D}}^{25} = -209.2$ (c 0.25, CH_2Cl_2 , 97%

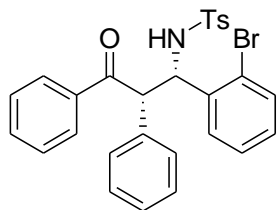
ee). Enantiomeric excess of the product was measured by chiral stationary phase HPLC analysis using a Chiracel AD-H column (80:20 hexanes/*i*-PrOH at 1.0 mL/min): major enantiomer: $t_R = 18.1$ min; minor enantiomer: $t_R = 30.8$ min.

(2*S*,3*S*)-3-(4-Nitrophenyl)-1,2-diphenyl-3-(tosylamino)propan-1-one (4h)



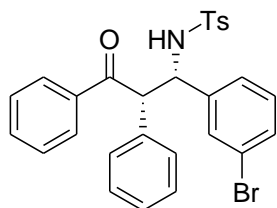
White solid, 93 mg, 93% yield, dr: > 99:1; m.p. 247-249 °C; ^1H NMR (300 MHz, d_6 -DMSO): δ 2.21 (s, 3H), 5.11 (t, $J = 9.9$ Hz, 1H), 5.30 (d, $J = 11.1$ Hz, 1H), 6.97 (d, $J = 8.1$ Hz, 2H), 7.15 (d, $J = 8.1$ Hz, 2H), 7.24-7.54 (m, 9H), 7.76 (d, $J = 8.1$ Hz, 2H), 7.90 (d, $J = 8.7$ Hz, 2H), 8.38 (d, $J = 9.9$ Hz, 1H); ^{13}C NMR (75 MHz, d_6 -DMSO): δ 20.7, 54.9, 57.6, 59.1, 122.8, 126.0, 127.5, 128.0, 128.6, 128.8, 129.0, 133.6, 134.9, 135.1, 137.8, 141.8, 146.0, 147.8, 196.4. ν_{max} : 3307, 1660, 1595, 1518, 1447, 1339, 1274, 1153, 1080 cm^{-1} . Analytic calcd. for $\text{C}_{28}\text{H}_{24}\text{N}_2\text{O}_5\text{S}$: C, 67.18; H, 4.83; N, 5.60; found: C, 67.10; H, 4.72; N, 5.59. $[\alpha]_{\text{D}}^{25} = -187.6$ (c 0.46, CH_2Cl_2 , 93% ee). Enantiomeric excess of the product was measured by chiral stationary phase HPLC analysis using a Chiracel AD-H column (70:30 hexanes/*i*-PrOH at 1.0 mL/min): major enantiomer: $t_R = 11.7$ min; minor enantiomer: $t_R = 18.8$ min.

(2*S*,3*S*)-3-(2-Bromophenyl)-1,2-diphenyl-3-(tosylamino)propan-1-one (4i)



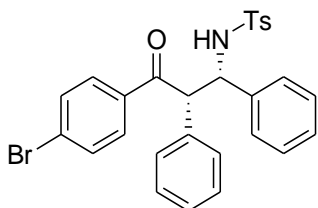
White solid, 103 mg, 96% yield, dr: > 99:1; m.p. 145-146 °C; ^1H NMR (300 MHz, d_6 -DMSO): δ 2.23 (s, 3H), 5.34 (d, $J = 10.5$ Hz, 1H), 5.46 (t, $J = 10.2$ Hz, 1H), 6.87 (t, $J = 7.5$ Hz, 1H), 6.96 (d, $J = 7.5$ Hz, 2H), 7.07 (t, $J = 7.5$ Hz, 1H), 7.17-7.29 (m, 6H), 7.33-7.58 (m, 6H), 7.71 (d, $J = 7.2$ Hz, 2H), 8.23 (d, $J = 9.3$ Hz, 1H); ^{13}C NMR (75 MHz, d_6 -DMSO): δ 20.9, 57.6, 57.8, 124.2, 125.9, 127.3, 127.5, 127.8, 128.1, 128.4, 128.5, 128.6, 128.7, 128.9, 132.1, 133.3, 135.4, 135.5, 137.6, 139.7, 141.5, 196.2. ν_{max} : 3325, 1677, 1597, 1446, 1301, 1267, 1157, 1096, 1021 cm^{-1} . Analytic calcd. for $\text{C}_{28}\text{H}_{24}\text{BrNO}_3\text{S}$: C, 62.92; H, 4.53; N, 2.62; found: C, 63.04; H, 4.61; N, 2.56. $[\alpha]_{\text{D}}^{25} = -181.0$ (c 0.29, CH_2Cl_2 , 95% ee). Enantiomeric excess of the product was measured by chiral stationary phase HPLC analysis using a Chiracel OD-H column (90:10 hexanes/*i*-PrOH at 0.8 mL/min): major enantiomer: $t_R = 21.0$ min; minor enantiomer: $t_R = 25.8$ min.

(2*S*,3*S*)-3-(3-Bromophenyl)-1,2-diphenyl-3-(tosylamino)propan-1-one (4j)



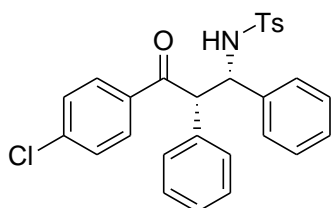
White solid, 96% yield, 103 mg, dr: > 99:1; m.p. 242-244 °C; ¹H NMR (300 MHz, *d*₆-DMSO): δ 2.25 (s, 3H), 4.94 (d, *J* = 10.8 Hz, 1H), 5.22 (d, *J* = 10.8 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 3H), 7.13 (d, *J* = 7.5 Hz, 3H), 7.19-7.27 (m, 5H), 7.33-7.51 (m, 5H), 7.74 (d, *J* = 7.5 Hz, 2H), 8.13 (brs, 1H); ¹³C NMR (75 MHz, *d*₆-DMSO): δ 20.9, 57.6, 59.1, 121.1, 125.8, 126.6, 127.3, 128.0, 128.5, 128.7, 128.8, 129.6, 129.8, 130.3, 133.5, 135.2, 135.3, 137.8, 141.7, 142.6, 196.6. *v*_{max}: 3303, 1661, 1594, 1447, 1326, 1277, 1153, 1073 cm⁻¹. Analytic calcd. for C₂₈H₂₄BrNO₃S: C, 62.92; H, 4.53; N, 2.62; found: C, 63.04; H, 4.39; N, 2.64. [α]_D²⁵ = -126.3 (*c* 0.15, CH₂Cl₂, 95% ee). Enantiomeric excess of the product was measured by chiral stationary phase HPLC analysis using a Chiracel AD-H column (80:20 hexanes/*i*-PrOH at 1.0 mL/min): major enantiomer: *t*_R = 14.9 min; minor enantiomer: *t*_R = 9.5 min.

(2*S*,3*S*)-1-(4-Bromophenyl)-2,3-diphenyl-3-(tosylamino)propan-1-one (4k)



White solid, 102 mg, 95% yield, dr: > 99:1; m.p. 223-224 °C; ¹H NMR (300 MHz, *d*₆-DMSO): δ 2.23 (s, 3H), 5.00 (t, *J* = 10.8 Hz, 1H), 5.19 (d, *J* = 10.8 Hz, 1H), 6.86-7.07 (m, 6H), 7.11 (d, *J* = 8.1 Hz, 2H), 7.21-7.39 (m, 6H), 7.36-7.73 (m, 4H), 8.16 (d, *J* = 8.1 Hz, 1H); ¹³C NMR (75 MHz, *d*₆-DMSO): δ 20.9, 57.9, 59.5, 125.8, 126.7, 127.3, 127.4, 127.6, 127.7, 128.4, 128.7, 128.9, 129.8, 131.8, 134.4, 135.1, 138.2, 140.3, 141.4, 196.1. *v*_{max}: 3344, 1671, 1584, 1493, 1453, 1398, 1329, 1274, 1181, 1069 cm⁻¹. Analytic calcd. for C₂₈H₂₄BrNO₃S: C, 62.92; H, 4.53; N, 2.62; found: C, 62.84; H, 4.39; N, 2.57. [α]_D²⁵ = -125.0 (*c* 0.3, CH₂Cl₂, 98% ee). Enantiomeric excess of the product was measured by chiral stationary phase HPLC analysis using a Chiracel AD-H column (80:20 hexanes/*i*-PrOH at 1.0 mL/min): major enantiomer: *t*_R = 26.5 min; minor enantiomer: *t*_R = 19.3 min.

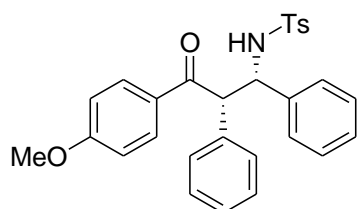
(2*S*,3*S*)-1-(4-Chlorophenyl)-2,3-diphenyl-3-(tosylamino)propan-1-one (4l)



White solid, 93 mg, 95% yield, dr: > 99:1; m.p. 211-212 °C; ¹H NMR (300 MHz, *d*₆-DMSO): δ 2.22 (s, 3H), 4.99 (t, *J* = 10.8 Hz, 1H), 5.20 (d, *J* = 10.8 Hz, 1H), 6.93-7.04 (m, 5H), 7.10 (d, *J* = 8.1

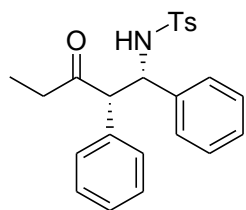
H₂, 2H), 7.16-7.21 (m, 5H), 7.23-7.26 (m, 4H), 7.71 (d, *J* = 8.1 Hz, 2H), 8.17 (d, *J* = 8.1 Hz, 1H); ¹³C NMR (75 MHz, *d*₆-DMSO): δ 20.9, 58.0, 59.5, 125.8, 126.7, 127.3, 127.4, 127.6, 128.4, 128.7, 128.9, 129.7, 134.1, 135.2, 138.2, 138.4, 140.4, 141.4, 195.9. *v*_{max}: 3348, 1673, 1587, 1492, 1400, 1330, 1275, 1155, 1089 cm⁻¹. Analytic calcd. for C₂₈H₂₄ClNO₃S: C, 68.63; H, 4.94; N, 2.86; found: C, 68.72; H, 4.83; N, 2.87. [α]_D²⁵ = -130.0 (*c* 0.29, CH₂Cl₂, 96% ee). Enantiomeric excess of the product was measured by chiral stationary phase HPLC analysis using a Chiracel AD-H column (80:20 hexanes/*i*-PrOH at 1.0 mL/min): major enantiomer: *t*_R = 23.7 min; minor enantiomer: *t*_R = 17.8 min.

(2*S*,3*S*)-1-(4-Methoxyphenyl)-2,3-diphenyl-3-(tosylamino)propan-1-one (4m)



White solid, 73 mg, 75% yield, dr: > 99:1; m.p. 242-244 °C; ¹H NMR (300 MHz, *d*₆-DMSO): δ 2.24 (s, 3H), 3.73 (s, 3H), 5.02 (t, *J* = 6.0 Hz, 1H), 5.19 (d, *J* = 6.6 Hz, 1H), 6.88 (d, *J* = 5.4 Hz, 2H), 6.96-7.04 (m, 5H), 7.12 (d, *J* = 4.8 Hz, 2H), 7.19-7.25 (m, 5H), 7.41 (d, *J* = 4.2 Hz, 2H), 7.72 (d, *J* = 5.4 Hz, 2H), 8.14 (d, *J* = 5.7 Hz, 1H); ¹³C NMR (75 MHz, *d*₆-DMSO): δ 21.5, 56.2, 58.2, 60.3, 114.8, 126.7, 127.5, 127.9, 128.3, 128.4, 129.1, 129.2, 129.5, 129.7, 131.2, 136.8, 139.2, 141.5, 142.2, 164.0, 196.0. *v*_{max}: 3329, 1659, 1599, 1326, 1264, 1154, 1090, 1070 cm⁻¹. Analytic calcd. for C₂₉H₂₇ClNO₄S: C, 71.73; H, 5.60; N, 2.88; found: C, 71.83; H, 5.73; N, 2.87. [α]_D²⁵ = -112.5 (*c* 0.21, CH₂Cl₂, 96% ee). Enantiomeric excess of the product was measured by chiral stationary phase HPLC analysis using a Chiracel AD-H column (80:20 hexanes/*i*-PrOH at 1.0 mL/min): major enantiomer: *t*_R = 35.1 min; minor enantiomer: *t*_R = 26.6 min.

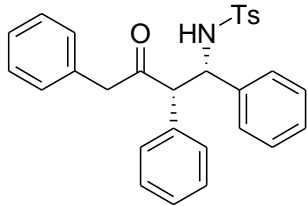
(1*S*,2*S*)-1,2-diphenyl-1-(tosylamino)pentan-3-one (4n)



White solid, 61 mg, 75% yield, dr: > 99:1; m.p. 195-196 °C; ¹H NMR (300 MHz, *d*₆-DMSO): δ 0.67 (t, *J* = 7.2 Hz, 3H), 1.85 (dd, *J* = 7.2, 18.0 Hz, 1H), 2.22 (dd, *J* = 7.2, 18.0 Hz, 1H), 2.39 (s, 3H), 4.00 (d, *J* = 10.2 Hz, 1H), 4.73 (d, *J* = 4.8 Hz, 1H), 4.82 (dd, *J* = 4.8, 10.2 Hz, 1H), 7.05-7.21 (m, 9H), 7.22-7.29 (m, 5H); ¹³C NMR (75 MHz, *d*₆-DMSO): δ 7.3, 21.6, 36.8, 59.4, 64.6, 127.1, 127.5, 127.8, 128.1, 128.3, 128.8, 129.1, 129.2, 133.7, 136.2, 138.9, 142.9, 207.6. *v*_{max}: 3291, 1704, 1599, 1493, 1447, 1332, 1156, 1090, 1071 cm⁻¹. Analytic calcd. for

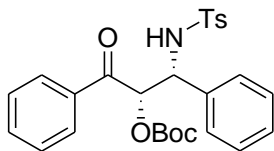
C₂₄H₂₅NO₃S: C, 70.73; H, 6.18; N, 3.44; found: C, 70.52; H, 5.98; N, 3.41. [α]_D²⁵ = -162.4 (*c* 0.32, CH₂Cl₂, >99% ee). Enantiomeric excess of the product was measured by chiral stationary phase HPLC analysis using a Chiracel AD-H column (80:20 hexanes/*i*-PrOH at 1.0 mL/min): major enantiomer: *t*_R = 7.5 min; minor enantiomer: *t*_R = 9.2 min.

(3*S*,4*S*)-1,3,4-Triphenyl-4-(tosylamino)butan-2-one (4o)



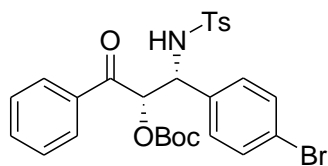
White solid, 89 mg, 95% yield, dr: > 99:1; m.p. 236-237 °C; ¹H NMR (300 MHz, *d*₆-DMSO): δ 2.22 (s, 3H), 3.19 (d, *J* = 16.8 Hz, 1H), 3.46 (d, *J* = 16.8 Hz, 1H), 4.37 (d, *J* = 11.1 Hz, 1H), 4.84 (t, *J* = 10.5 Hz, 1H), 6.49 (d, *J* = 6.0 Hz, 2H), 6.93 (d, *J* = 7.8 Hz, 2H), 7.01-7.21 (m, 9H), 7.23-7.41 (m, 5H), 8.12 (d, *J* = 9.6 Hz, 1H); ¹³C NMR (75 MHz, *d*₆-DMSO): δ 20.9, 49.3, 58.8, 62.8, 125.8, 126.3, 126.8, 127.3, 127.4, 127.6, 127.9, 128.3, 128.6, 128.9, 129.1, 133.1, 134.9, 138.2, 139.7, 141.3, 204.9. ν_{max} : 3297, 1705, 1599, 1493, 1453, 1327, 1154, 1064 cm⁻¹. Analytic calcd. for C₂₉H₂₇NO₃S: C, 74.17; H, 5.80; N, 2.98; found: C, 74.00; H, 5.68; N, 3.01. [α]_D²⁵ = -182.5 (*c* 0.32, CH₂Cl₂, 96% ee). Enantiomeric excess of the product was measured by chiral stationary phase HPLC analysis using a Chiracel IB column (95:5 hexanes/*i*-PrOH at 1.0 mL/min): major enantiomer: *t*_R = 30.8 min; minor enantiomer: *t*_R = 39.3 min.

(2*S*,3*R*)-2-*tert*-Butoxycarbonyloxy-1,3-diphenyl-3-(tosylamino)propan-1-one (4p)



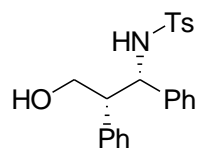
White solid, 95 mg, 96% yield, dr: 93:7; m.p. 144-145 °C; ¹H NMR (300 MHz, CDCl₃): δ 1.42 (s, 9H), 2.34 (s, 3H), 5.00 (dd, *J* = 4.2, 8.4 Hz, 1H), 5.83 (d, *J* = 8.4 Hz, 1H), 5.99 (d, *J* = 3.9 Hz, 1H), 6.96 (d, *J* = 7.2 Hz, 2H), 7.03-7.12 (m, 5H), 7.38 (t, *J* = 7.2 Hz, 2H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.58 (d, *J* = 8.1 Hz, 2H), 7.67 (d, *J* = 8.7 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 21.5, 27.6, 57.9, 78.4, 83.5, 126.9, 127.4, 128.1, 128.2, 129.3, 133.6, 134.6, 134.8, 137.0, 143.1, 152.1, 193.7. ν_{max} : 3273, 1740, 1700, 1450, 1367, 1331, 1282, 1242, 1158, 1091 cm⁻¹. Analytic calcd. for C₂₇H₂₉NO₆S: C, 65.44; H, 5.90; N, 2.83; found: C, 65.28; H, 5.80; N, 2.83. [α]_D²⁵ = -46.5 (*c* 0.32, CH₂Cl₂, >99% ee). Enantiomeric excess of the product was measured by chiral stationary phase HPLC analysis using a Chiracel ID column (80:20 hexanes/*i*-PrOH at 1.0 mL/min): major enantiomer: *t*_R = 38.0 min; minor enantiomer: *t*_R = 32.7 min.

(2*S*,3*R*)-3-(4-Bromophenyl)-2-*tert*-butoxycarbonyloxy-1-phenyl-3-(tosylamino)propan-1-one (4q)



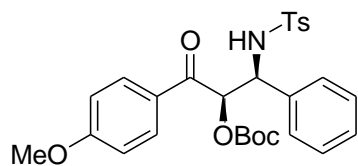
White solid, 110 mg, 96% yield, dr: 92:8; m.p. 166-167 °C; ¹H NMR (300 MHz, *d*₆-DMSO): δ 1.27 (s, 9H), 2.31 (s, 3H), 4.66 (dd, *J* = 6.3, 8.4 Hz, 1H), 5.89 (d, *J* = 6.0 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.54 (t, *J* = 7.8 Hz, 2H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.77 (d, *J* = 7.2 Hz, 2H), 8.69 (d, *J* = 8.7 Hz, 1H); ¹³C NMR (75 MHz, *d*₆-DMSO): δ 21.0, 27.1, 57.4, 77.3, 82.9, 121.0, 126.4, 128.1, 128.9, 129.1, 130.0, 130.6, 134.0, 134.5, 134.9, 137.4, 142.5, 151.4, 193.6. ν_{max} : 3300, 1735, 1674, 1596, 1444, 1396, 1284, 1250, 1152, 1071 cm⁻¹. Analytic calcd. for C₂₇H₂₈BrNO₆S: C, 56.45; H, 4.91; N, 2.44; found: C, 56.50; H, 5.01; N, 2.46. $[\alpha]_{\text{D}}^{25}$ = -68.0 (*c* 0.25, CH₂Cl₂, >99% ee). Enantiomeric excess of the product was measured by chiral stationary phase HPLC analysis using a Chiracel ID column (80:20 hexanes/*i*-PrOH at 1.0 mL/min): major enantiomer: *t*_R = 26.2 min; minor enantiomer: *t*_R = 24.2 min.

(2*S*,3*S*)-2,3-Diphenyl-3-(tosylamino)propan-1-ol (13)



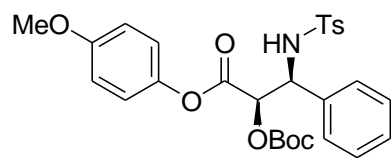
Colorless liquid, 94 mg, 87% yield. dr: 97:3; ¹H NMR (300 MHz, CDCl₃): δ 2.15 (t, *J* = 6.0 Hz, 1H), 2.32 (s, 3H), 3.05-3.11 (m, 1H), 3.64-3.72 (m, 1H), 3.91-4.00 (m, 1H), 4.77 (dd, *J*₁ = 6.0, *J*₂ = 7.8 Hz, 1H), 5.12 (d, *J* = 7.8 Hz, 1H), 6.78 (dd, *J* = 1.8, 8.1 Hz, 2H), 6.91 (dd, *J* = 2.1, 5.7 Hz, 2H), 7.02-7.14 (m, 4H), 7.13-7.26 (m, 3H), 7.40 (d, *J* = 8.4 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 21.5, 54.0, 58.2, 63.0, 126.9, 127.2, 127.6, 127.9, 128.6, 128.8, 129.1, 136.6, 138.5, 142.9. ν_{max} : 3552, 3320, 2939, 1597, 1428, 1316, 1147, 1086, 1066 cm⁻¹. HRMS calcd. for C₂₂H₂₃NO₃S: 381.1399; found: 381.1391. $[\alpha]_{\text{D}}^{25}$ = -26.3 (*c* 0.25, CH₂Cl₂, 96% ee). Enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis using a ChiraCel AD-H (80:20 hexanes/*i*-PrOH at 1.0 mL/min); major enantiomer: *t*_R = 10.57 min, minor enantiomer: *t*_R = 14.19 min.

(2*R*,3*S*)-2-*tert*-Butoxycarbonyloxy-1-(4-methoxyphenyl)-3-phenyl-3-(tosylamino)propan-1-one (4r)



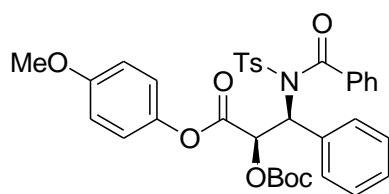
White solid, 101 mg, 96% yield, dr: 90:10; m.p. 131-132 °C; ^1H NMR (300 MHz, CDCl_3): δ 1.43 (s, 9H), 2.34 (s, 3H), 3.85 (s, 3H), 4.99 (dd, $J = 4.2, 8.4$ Hz, 1H), 5.89 (d, $J = 8.1$ Hz, 1H), 5.95 (d, $J = 3.9$ Hz, 1H), 6.84 (d, $J = 8.7$ Hz, 2H), 6.84 (d, $J = 9.3$ Hz, 2H), 6.99-7.12 (m, 5H), 7.58 (d, $J = 8.1$ Hz, 2H), 7.68 (d, $J = 8.7$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 21.5, 27.6, 55.5, 58.1, 77.7, 83.4, 113.9, 126.9, 127.4, 127.7, 128.0, 129.2, 130.7, 134.8, 137.1, 143.0, 152.1, 163.8, 191.8. ν_{max} : 3256, 1740, 1692, 1600, 1454, 1246, 1157, 1089 cm^{-1} . Analytic calcd. for $\text{C}_{28}\text{H}_{31}\text{NO}_7\text{S}$: C, 63.98; H, 5.94; N, 2.66; found: C, 63.82; H, 5.98; N, 2.68. $[\alpha]_{\text{D}}^{25} = -68.0$ (c 0.25, CH_2Cl_2 , >99% ee). Enantiomeric excess of the product was measured by chiral stationary phase HPLC analysis using a Chiracel IB column (85:15 hexanes/*i*-PrOH at 1.0 mL/min): major enantiomer: $t_{\text{R}} = 14.5$ min; minor enantiomer: $t_{\text{R}} = 11.9$ min.

(2R,3S)-4-Methoxyphenyl 2-(tert-butoxycarbonyloxy)-3-phenyl-3-(tosylamino)propanoate (14)



White solid, 140 mg, 86% yield; m.p. 95-96 °C; ^1H NMR (300 MHz, CDCl_3): δ 1.47 (s, 9H), 2.33 (s, 3H), 3.73 (s, 3H), 5.07 (dd, $J = 4.1, 8.2$ Hz, 1H), 5.35 (d, $J = 4.5$ Hz, 1H), 5.91 (d, $J = 9.0$ Hz, 1H), 6.61 (d, $J = 8.7$ Hz, 2H), 6.76 (d, $J = 8.7$ Hz, 2H), 7.09 (d, $J = 7.8$ Hz, 2H), 7.16-7.22 (m, 5H), 7.57 (d, $J = 8.1$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 21.5, 27.6, 55.5, 57.4, 76.4, 83.8, 114.2, 121.6, 126.8, 127.8, 128.3, 129.3, 133.3, 134.8, 136.9, 143.0, 143.1, 152.0, 157.2, 165.8. ν_{max} : 2932, 1746, 1503, 1457, 1280, 1245, 1156, 1113 cm^{-1} . Analytic calcd. for $\text{C}_{28}\text{H}_{31}\text{NO}_8\text{S}$: C, 62.09; H, 5.77; N, 2.59; found: C, 62.17; H, 5.68; N, 2.70. $[\alpha]_{\text{D}}^{25} = +49.2$ (c 0.25, CH_2Cl_2).

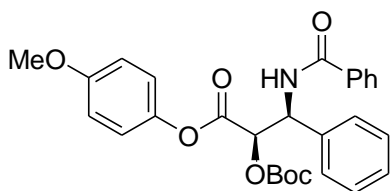
(2R,3S)-4-Methoxyphenyl 2-(tert-butoxycarbonyloxy)-3-phenyl-3-(N-tosylbenzamido)propanoate (15)



Colorless oil, ^1H NMR (300 MHz, CDCl_3): δ 1.46 (s, 9H), 2.36 (s, 3H), 3.79 (s, 3H), 6.07 (d, $J = 9.0$ Hz, 1H), 6.32 (d, $J = 9.3$ Hz, 1H), 6.87 (d, $J = 9.0$ Hz, 2H), 7.03-7.10 (m, 4H), 7.16-7.20 (m, 6H), 7.36-7.46 (m, 6H); ^{13}C NMR (75 MHz, CDCl_3): δ 21.6, 27.6,

55.5, 60.7, 73.5, 83.7, 114.3, 122.1, 127.6, 128.1, 128.3, 128.4, 128.5, 129.1, 129.3, 131.0, 134.6, 125.2, 135.6, 143.7, 144.6, 151.9, 157.2, 167.0, 171.7.

(2*R*,3*S*)-4-Methoxyphenyl 3-(benzamido)-2-(*tert*-butoxycarbonyloxy)-3-phenylpropanoate
(16)



White solid, 87 mg, 92% yield, m.p. 105-106 °C; ¹H NMR (300 MHz, CDCl₃): δ 1.51 (s, 9H), 3.76 (s, 3H), 5.58 (d, *J* = 4.8 Hz, 1H), 5.94 (dd, *J* = 4.1, 8.2 Hz, 1H), 6.68 (d, *J* = 9.3 Hz, 2H), 6.80 (d, *J* = 9.0 Hz, 2H), 7.08 (d, *J* = 8.1 Hz, 1H), 7.38-7.54 (m, 8H), 7.81 (dd, *J* = 1.5, 8.4 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 27.7, 53.8, 55.6, 75.7, 84.0, 114.3, 121.7, 127.0, 127.7, 128.5, 128.8, 131.7, 133.7, 136.1, 143.1, 152.4, 157.3, 166.5, 167.0. ν_{max} : 2980, 1741, 1644, 1528, 1503, 1288, 1241, 1151, 1102, 1028 cm⁻¹. Analytic calcd. for C₂₈H₂₉NO₇: C, 68.42; H, 5.95; N, 2.85; found: C, 68.20; H, 6.05; N, 2.81. $[\alpha]_{\text{D}}^{25} = +31.6$ (*c* 0.4, CH₂Cl₂).

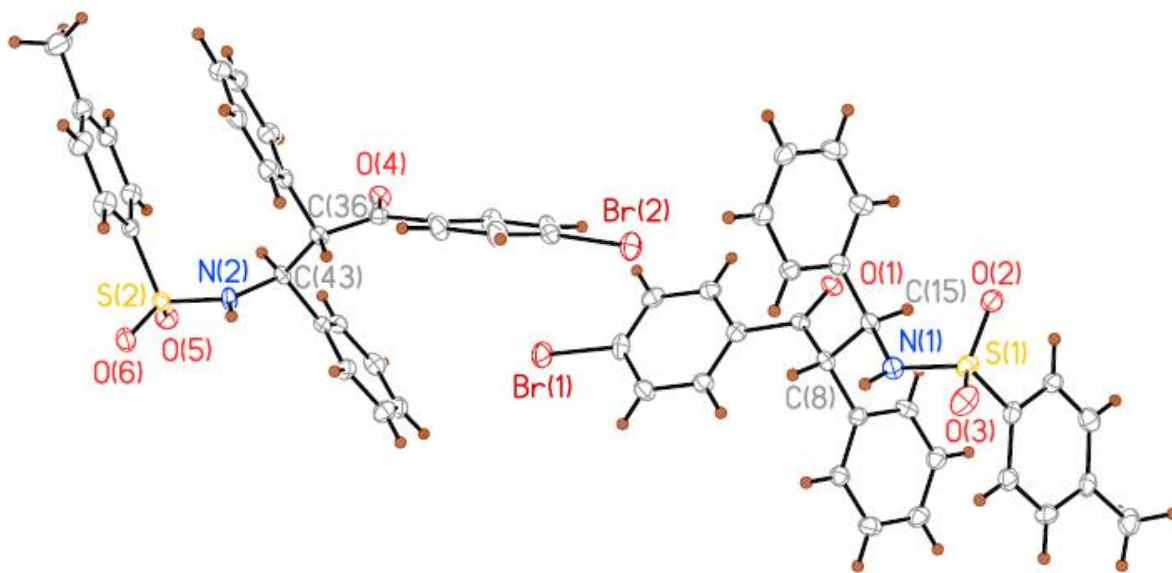
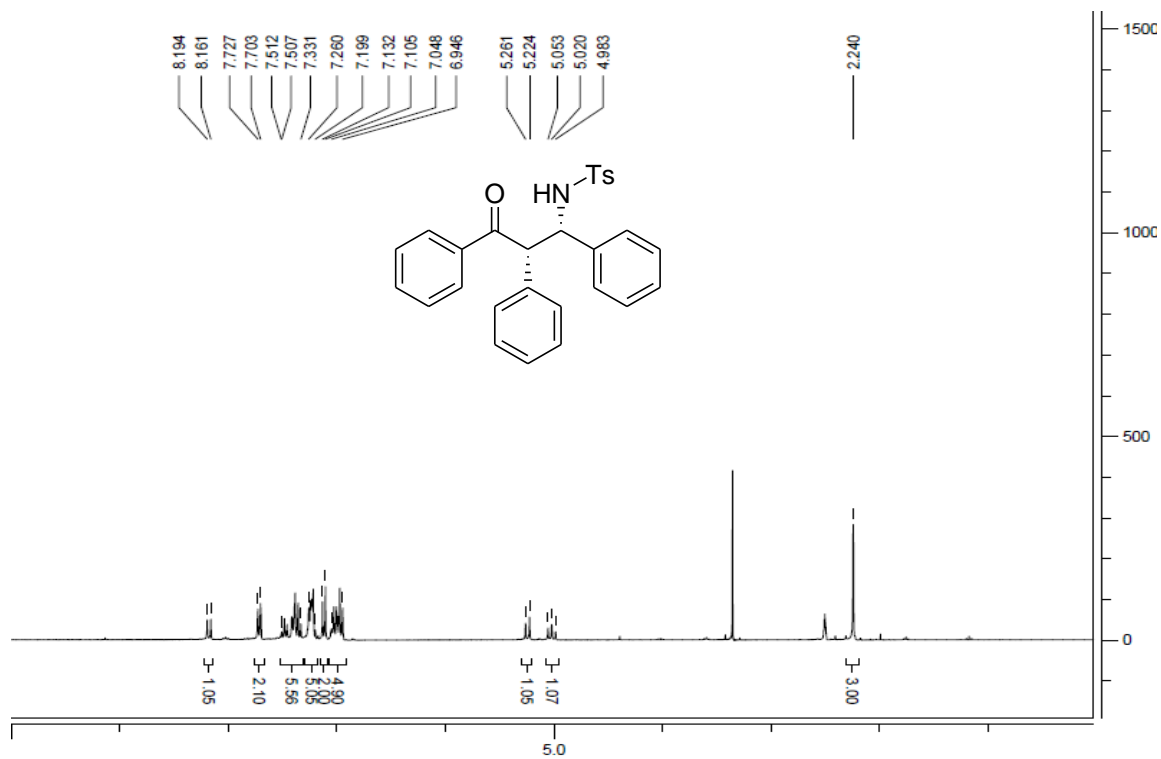
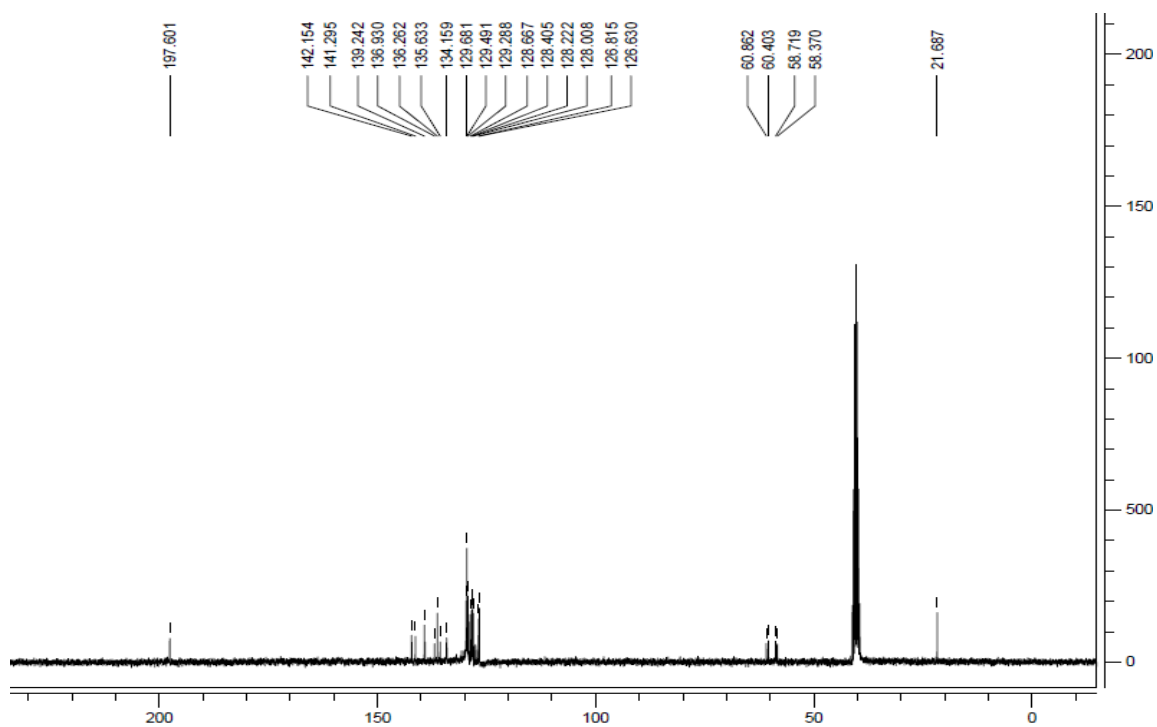


Figure S-1. ORTEP Drawing of Compound 4k

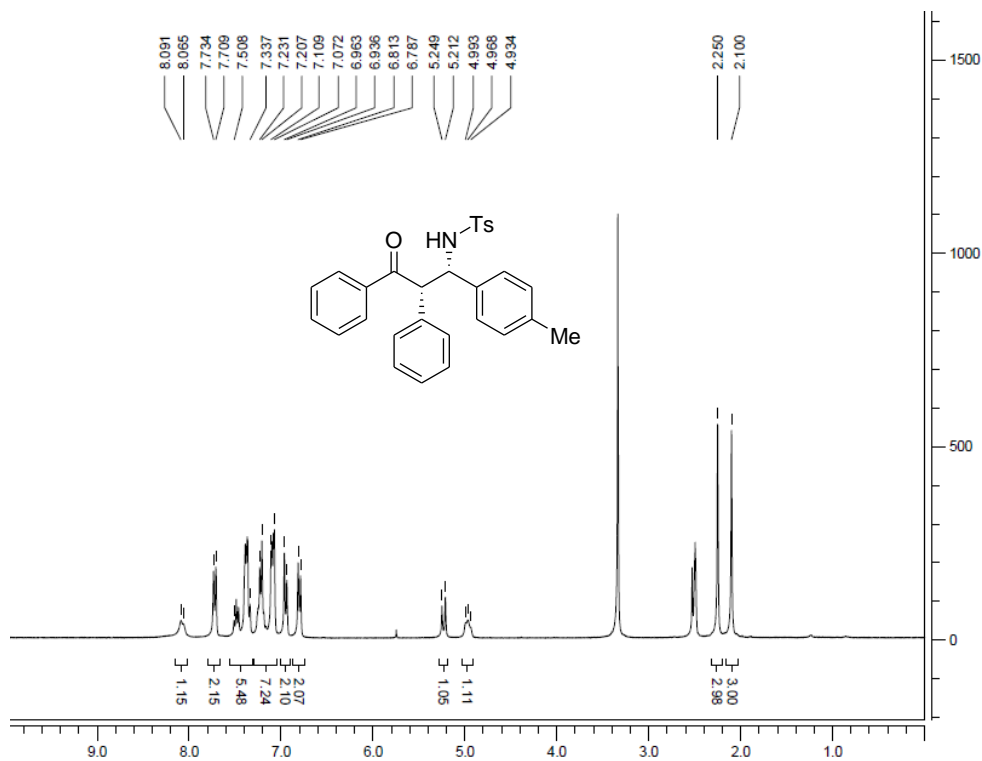
Note: There are two unique molecules in the asymmetric unit. The CSD deposition No. for this compound is 871462.



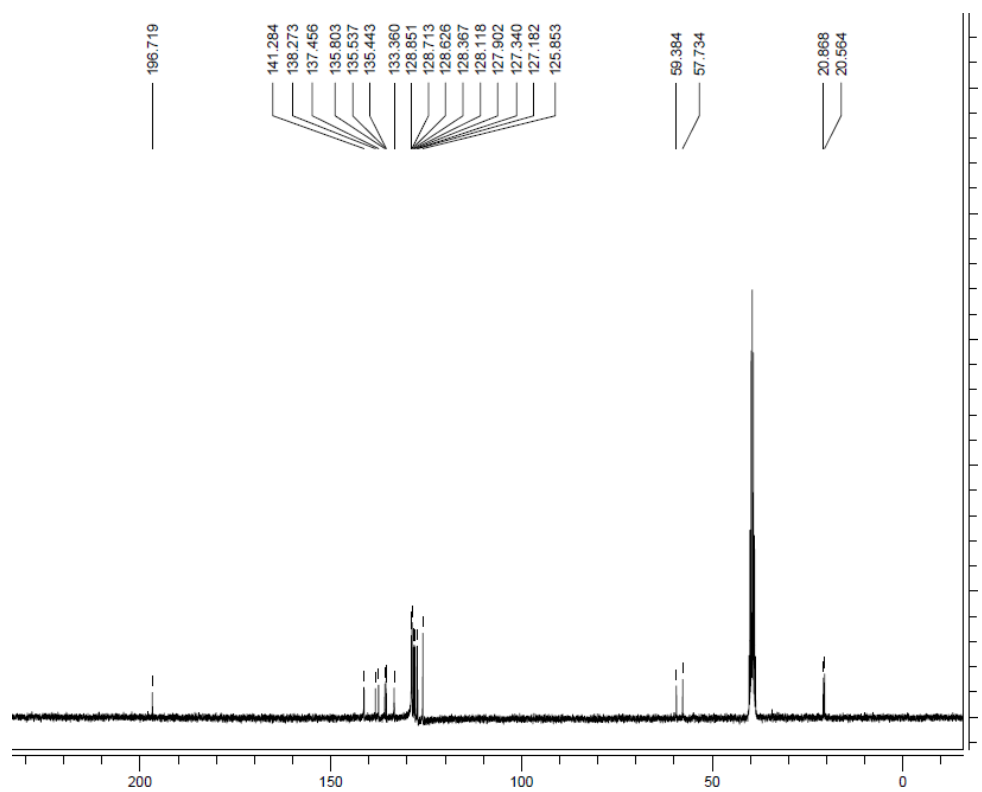
¹H NMR of 4a



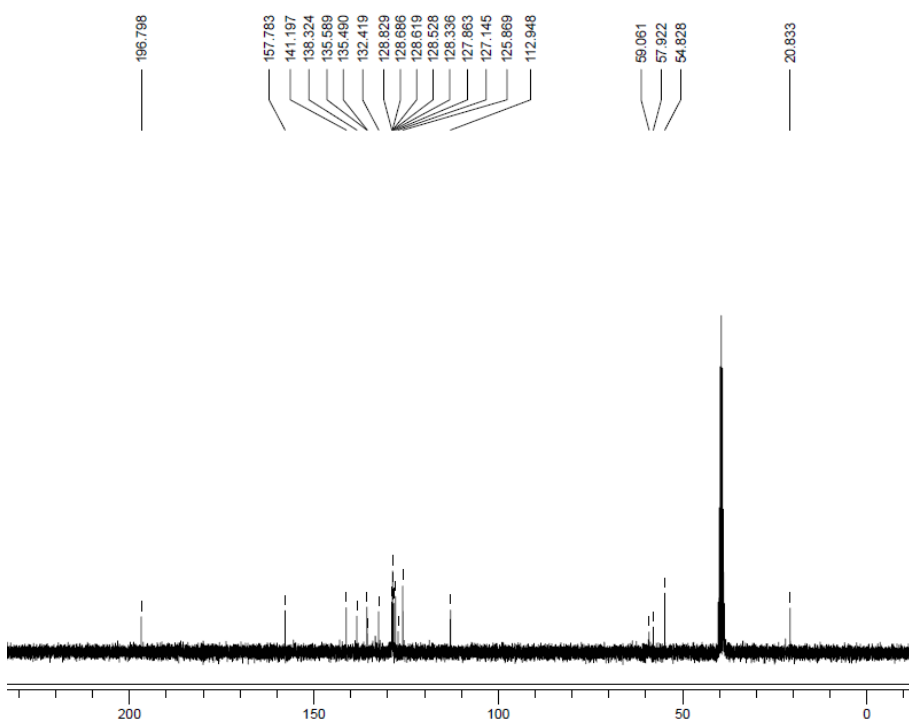
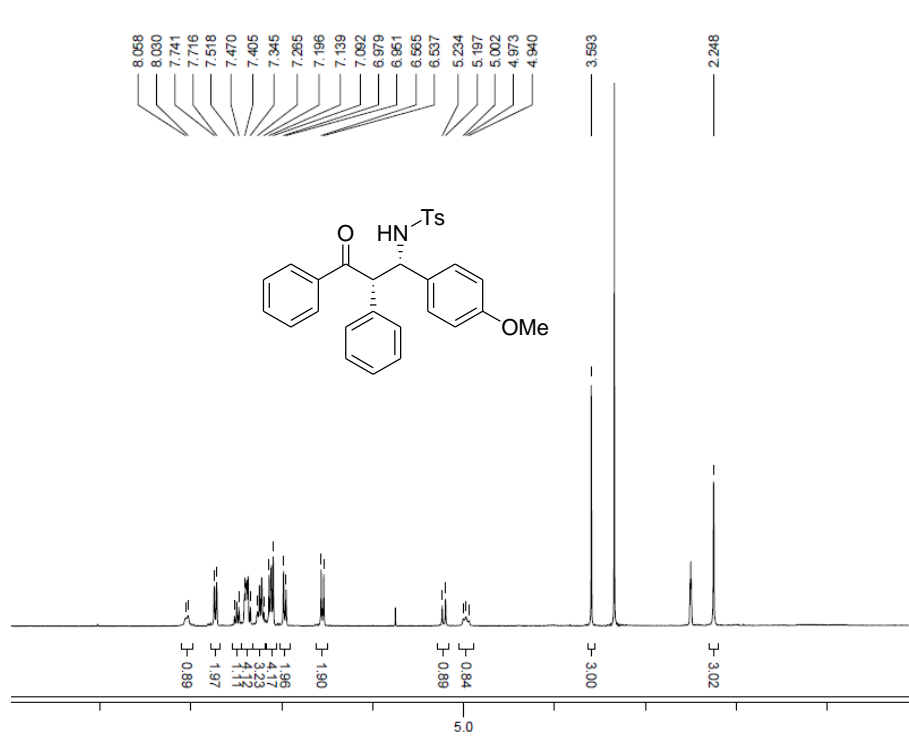
¹³C NMR of 4a

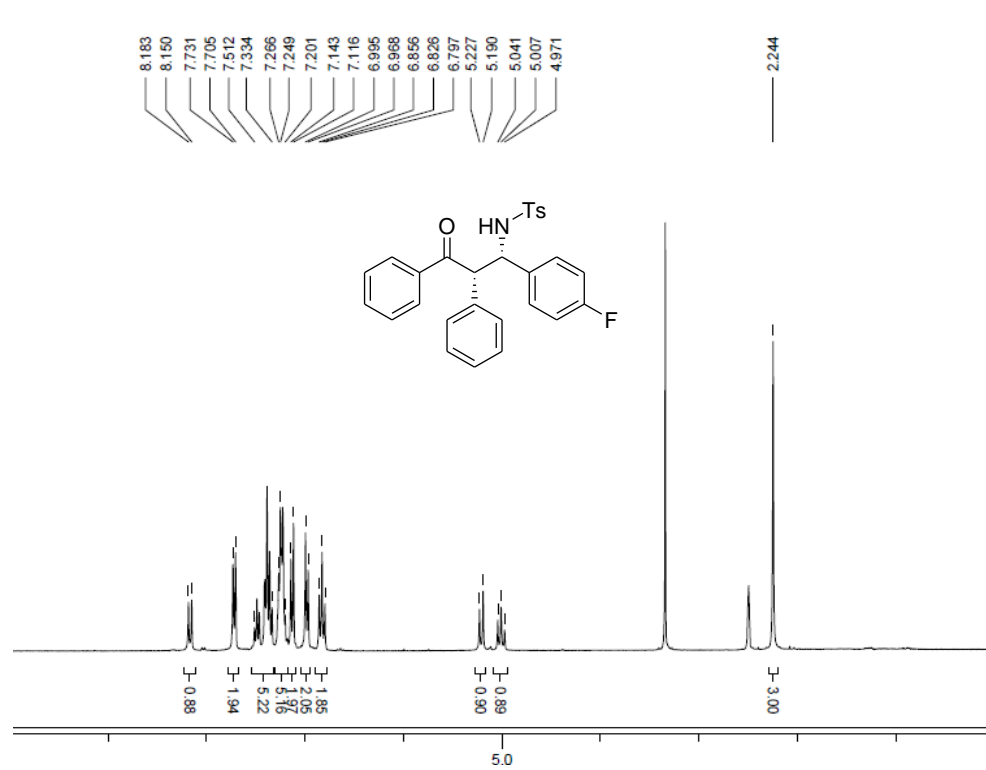


$^1\text{H NMR}$ of **4b**

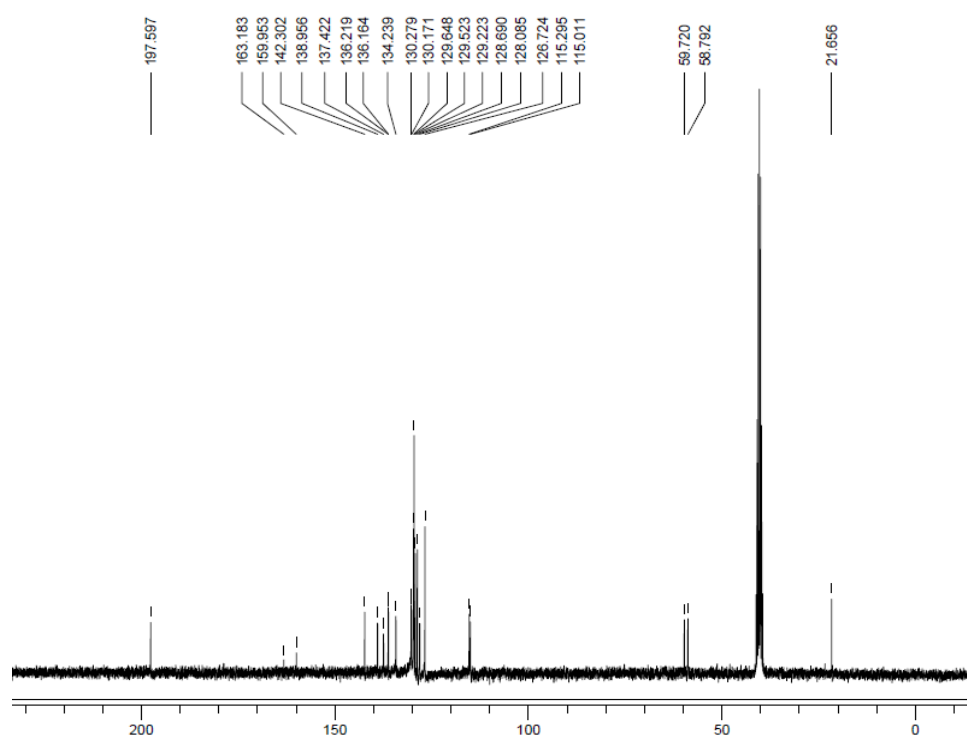


$^{13}\text{C NMR}$ of **4b**

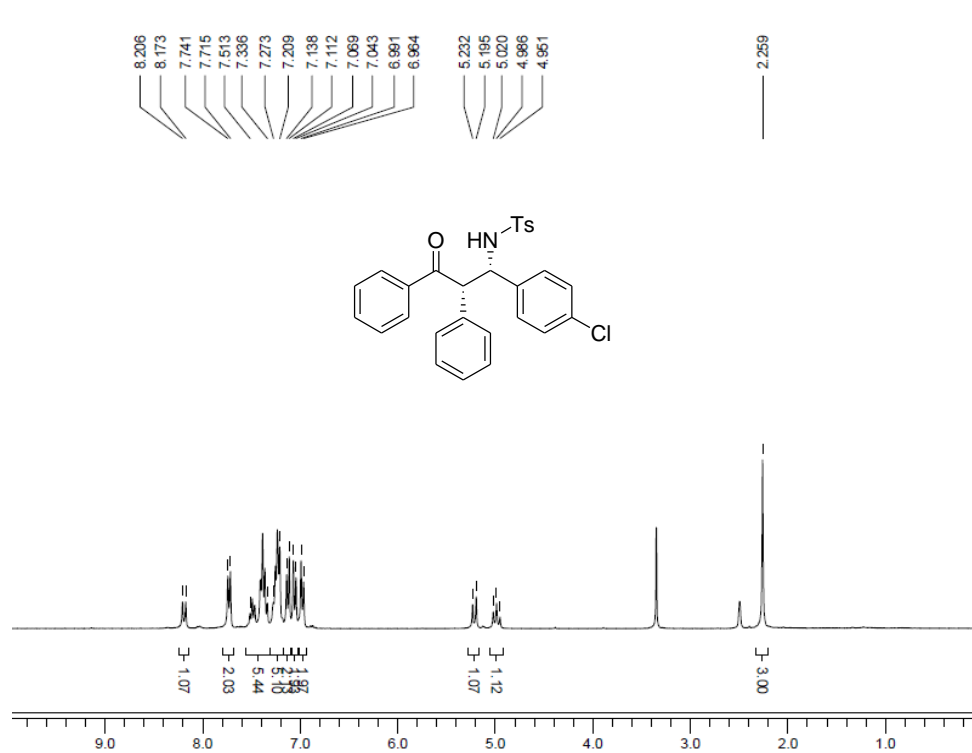




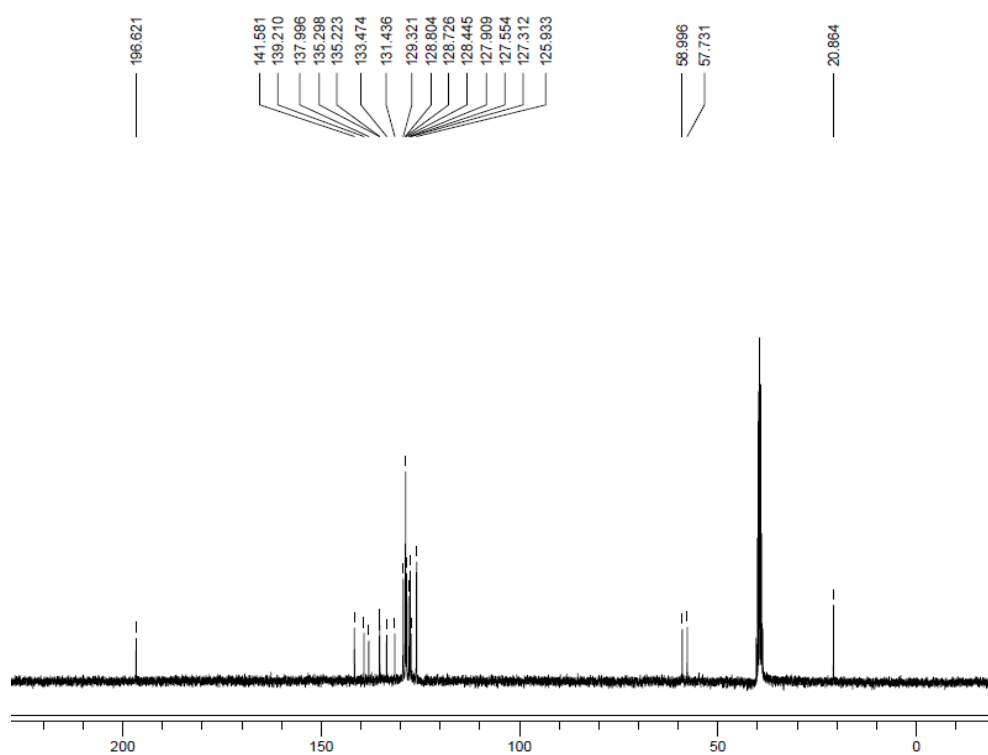
¹H NMR of 4d



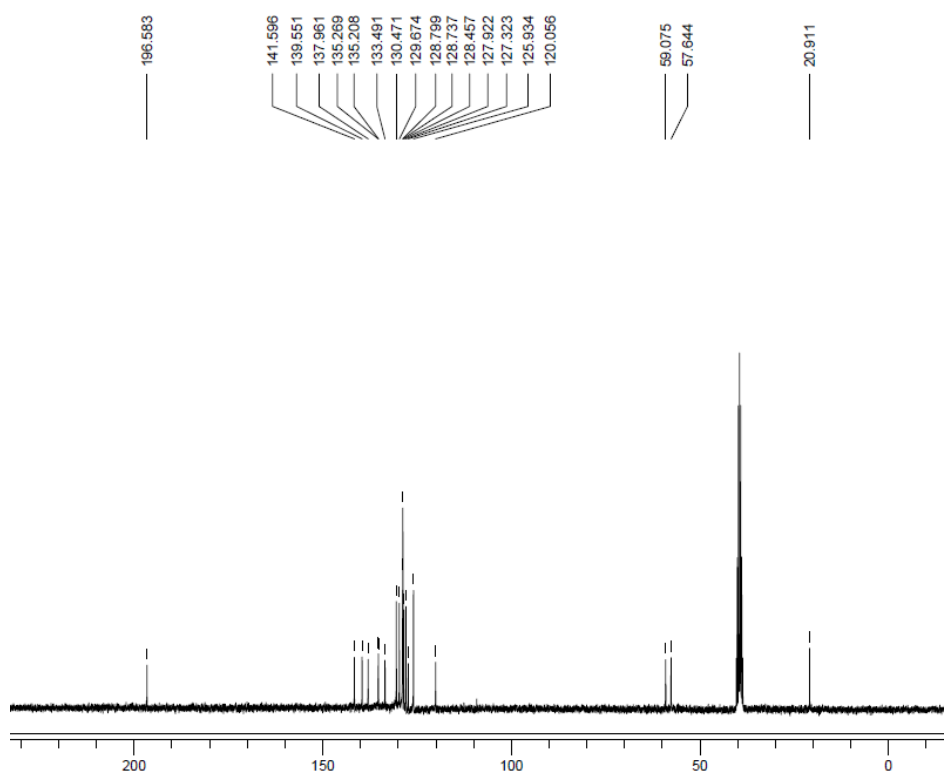
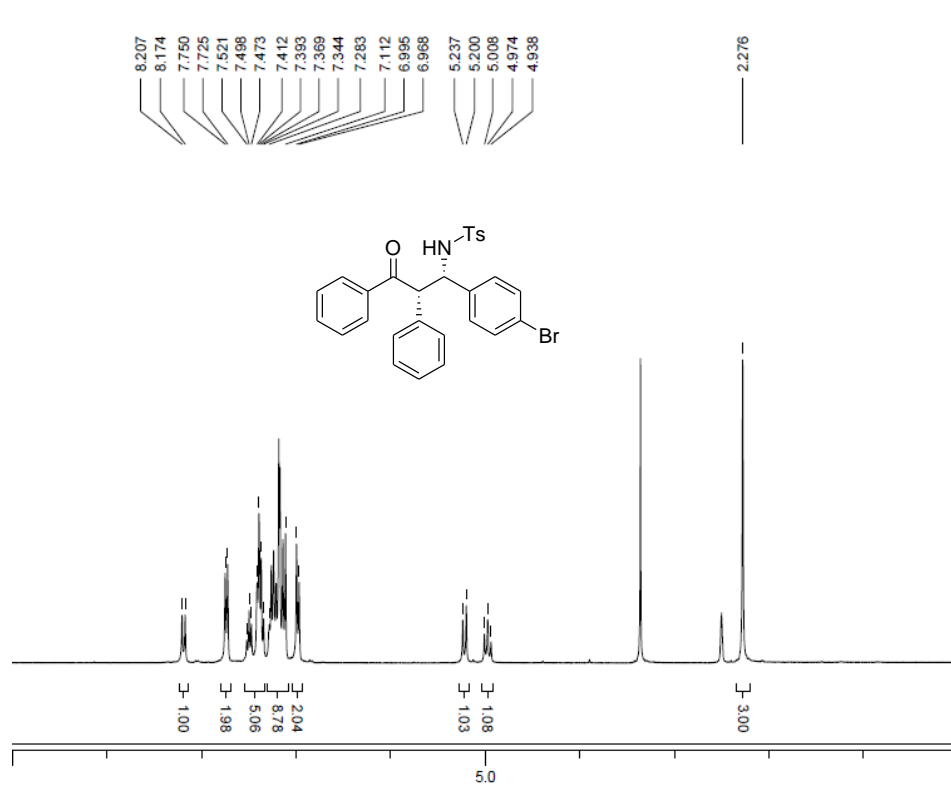
¹³C NMR of 4d

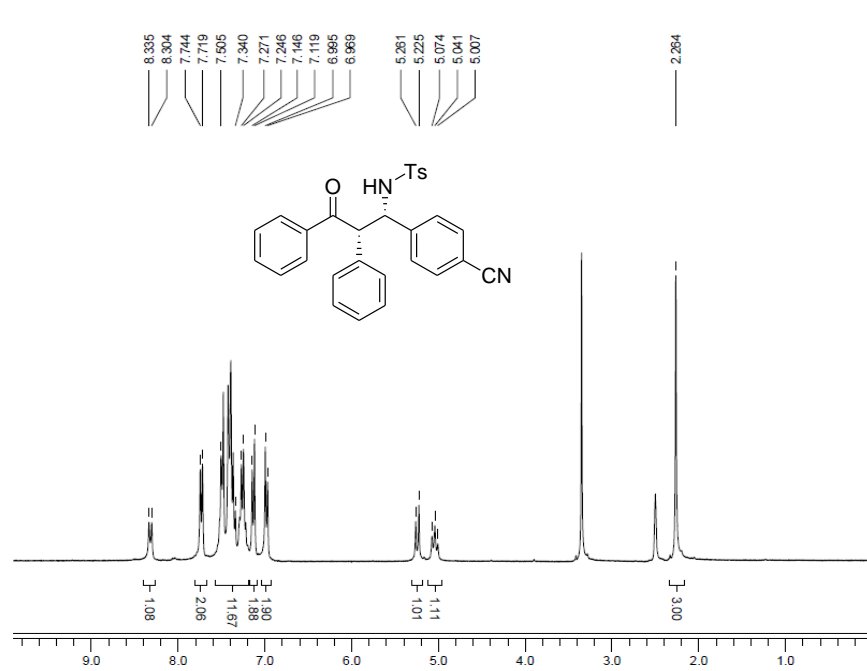


¹H NMR of **4e**

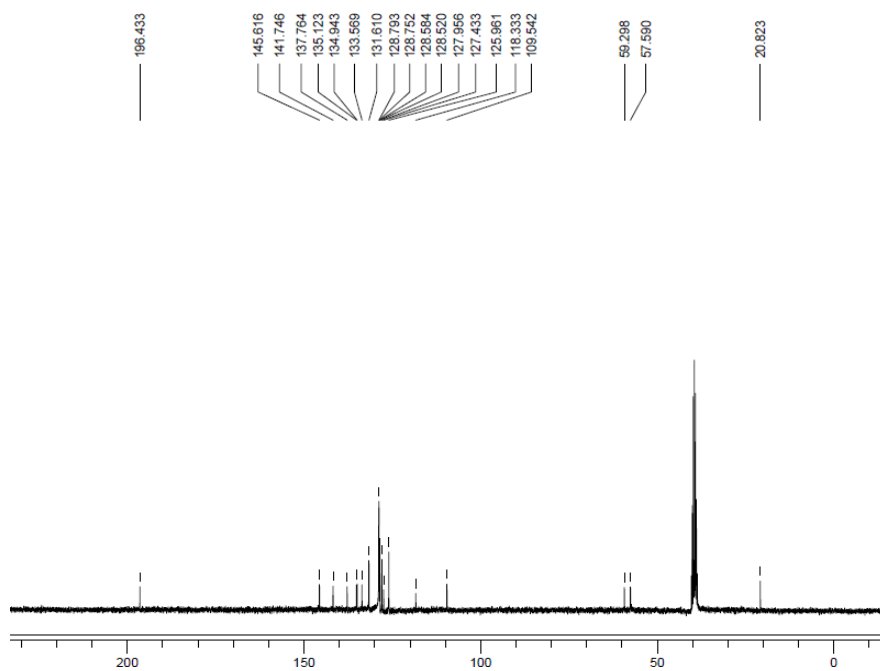


¹³C NMR of **4e**

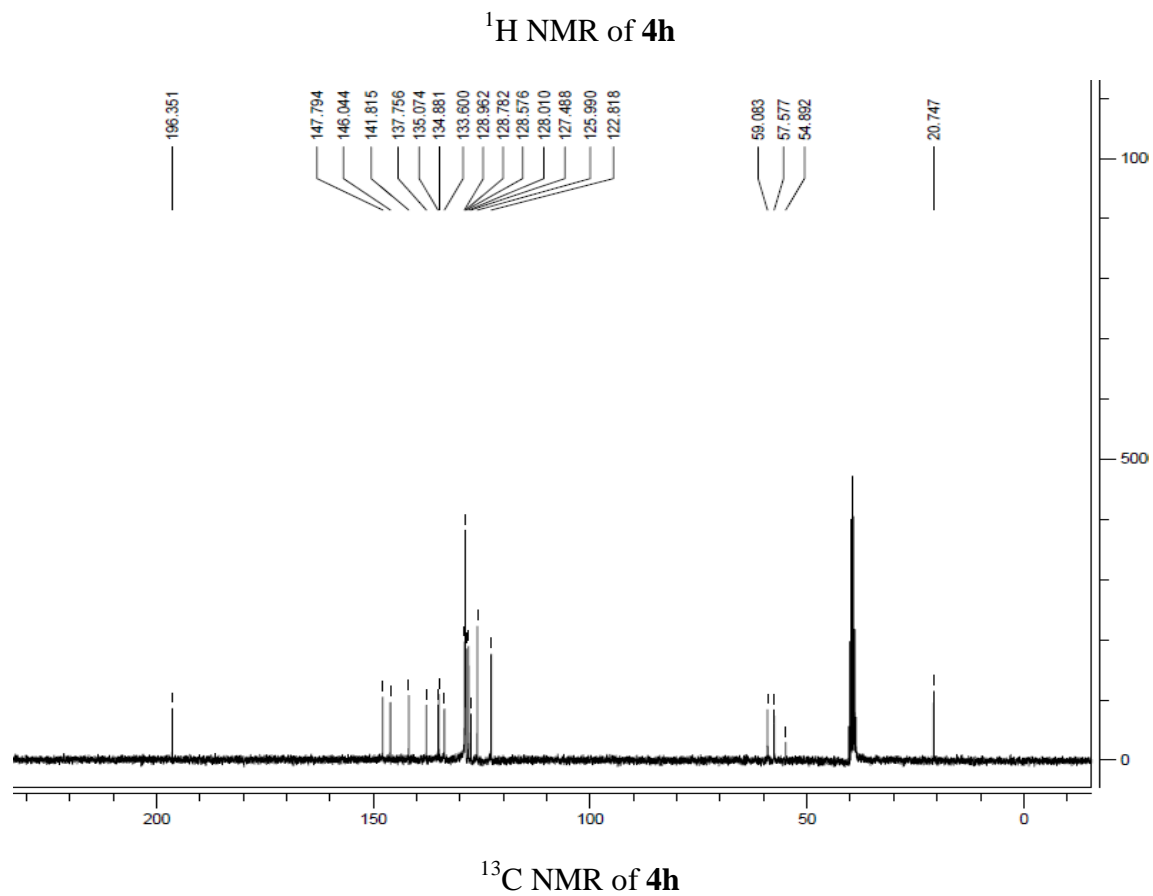
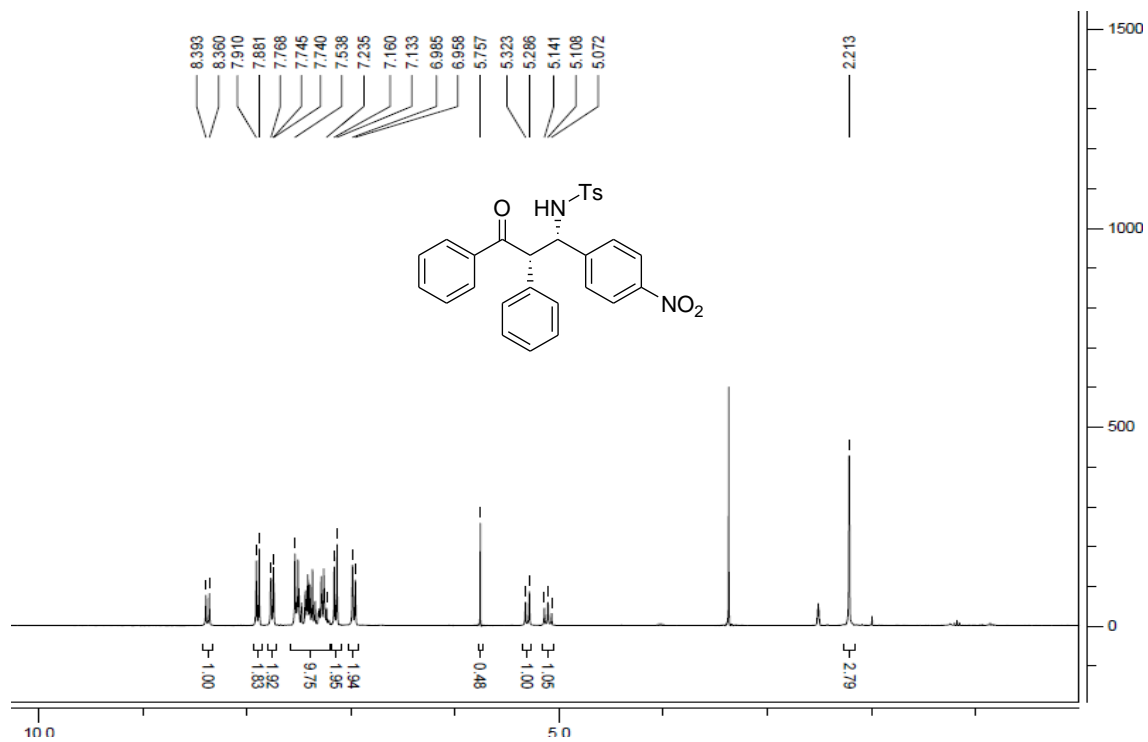


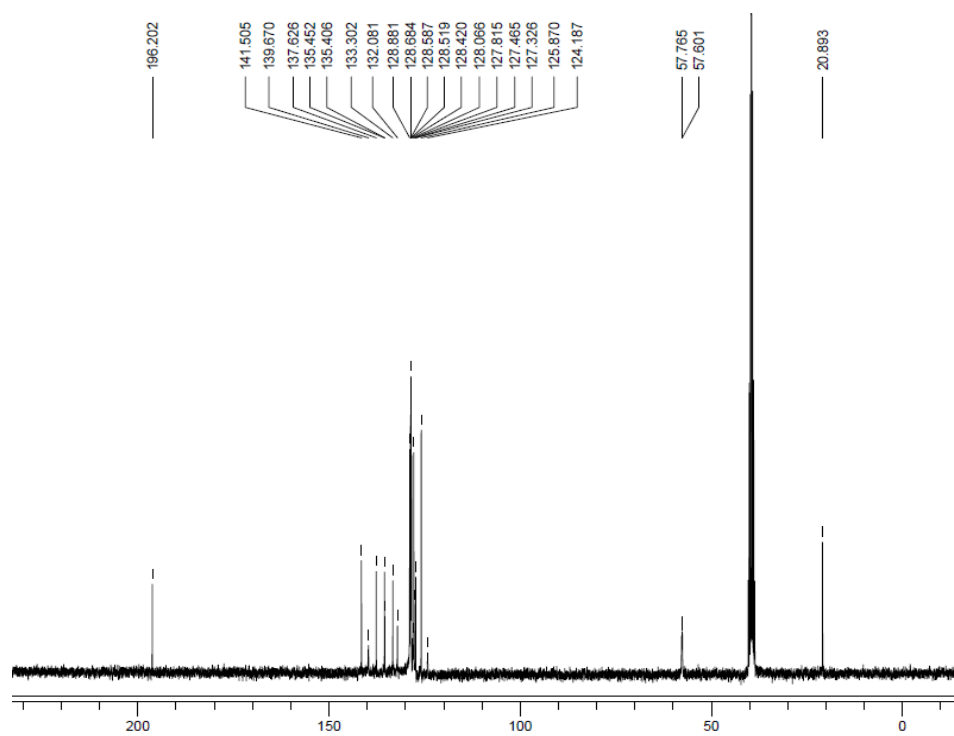
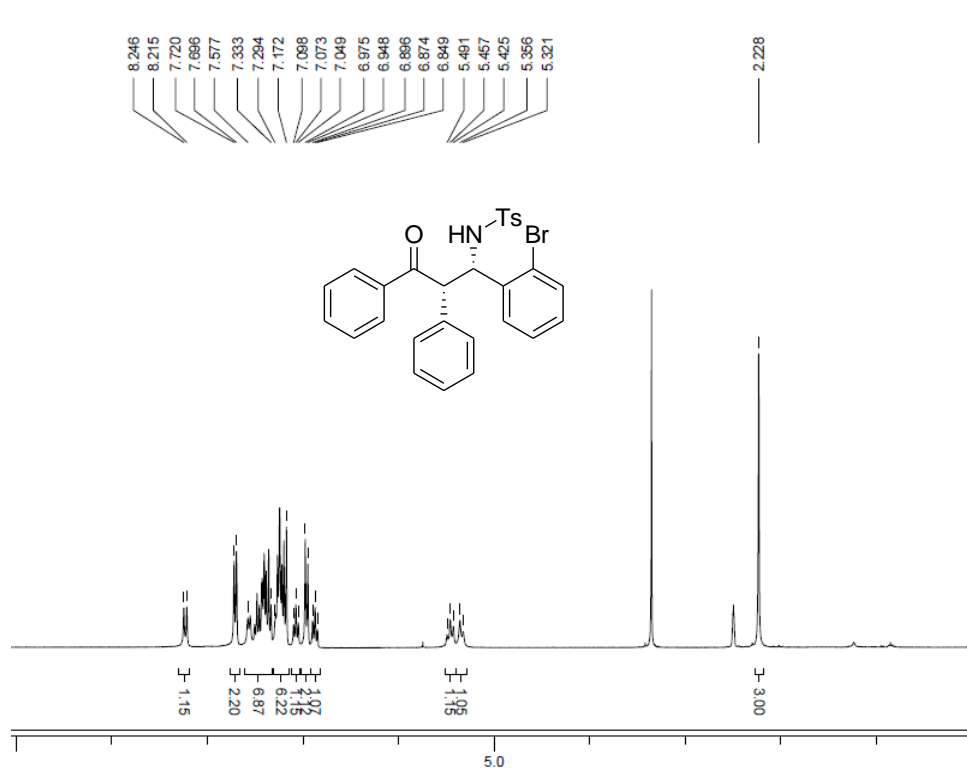


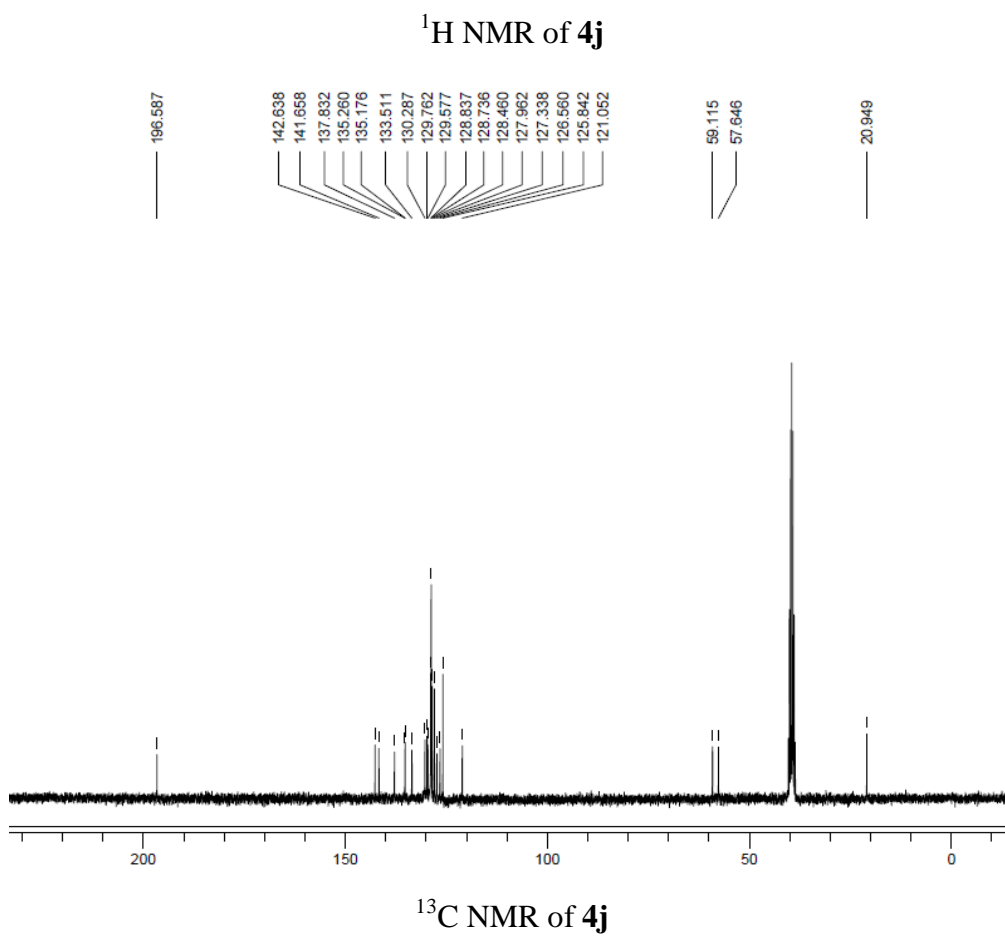
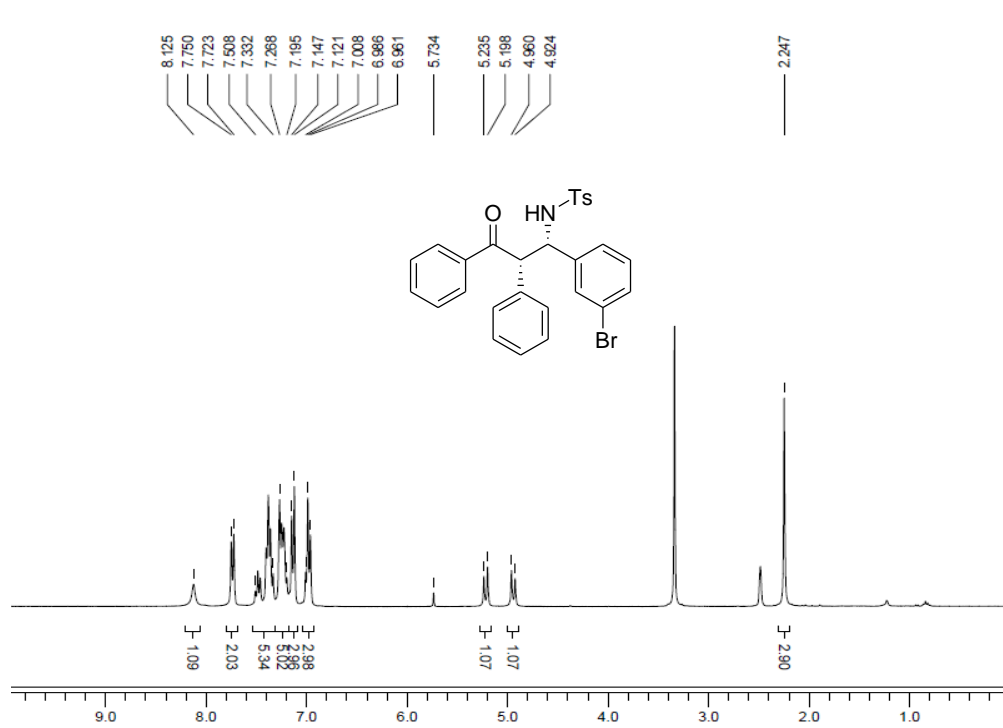
¹H NMR of **4g**

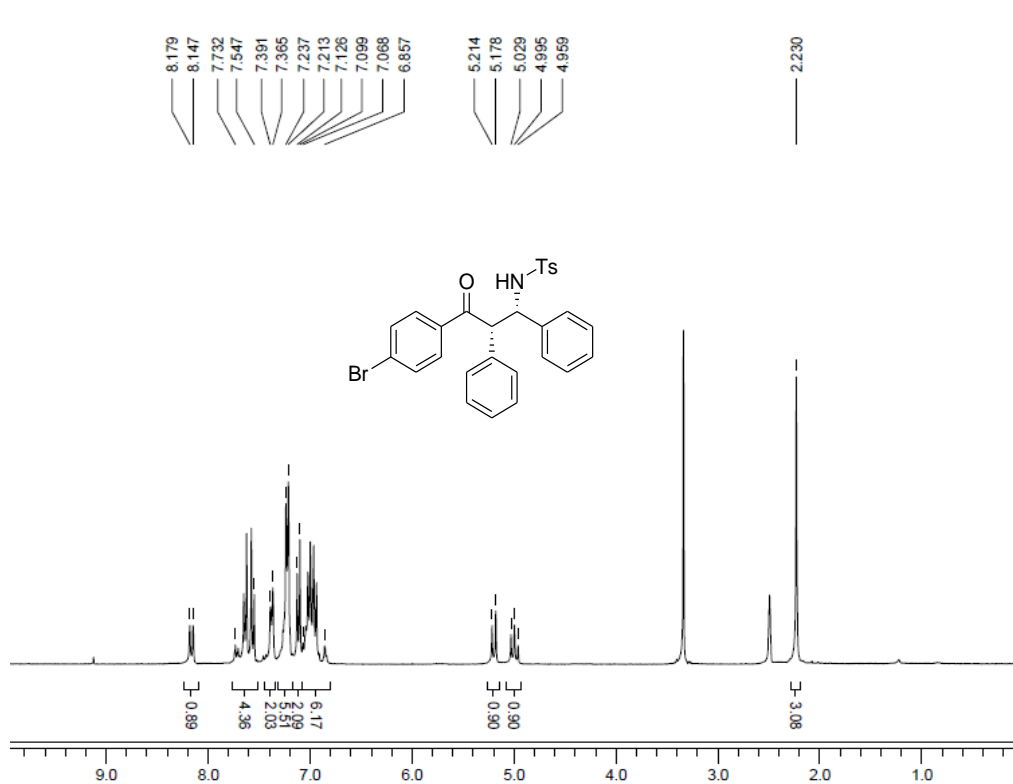


¹³C NMR of **4g**

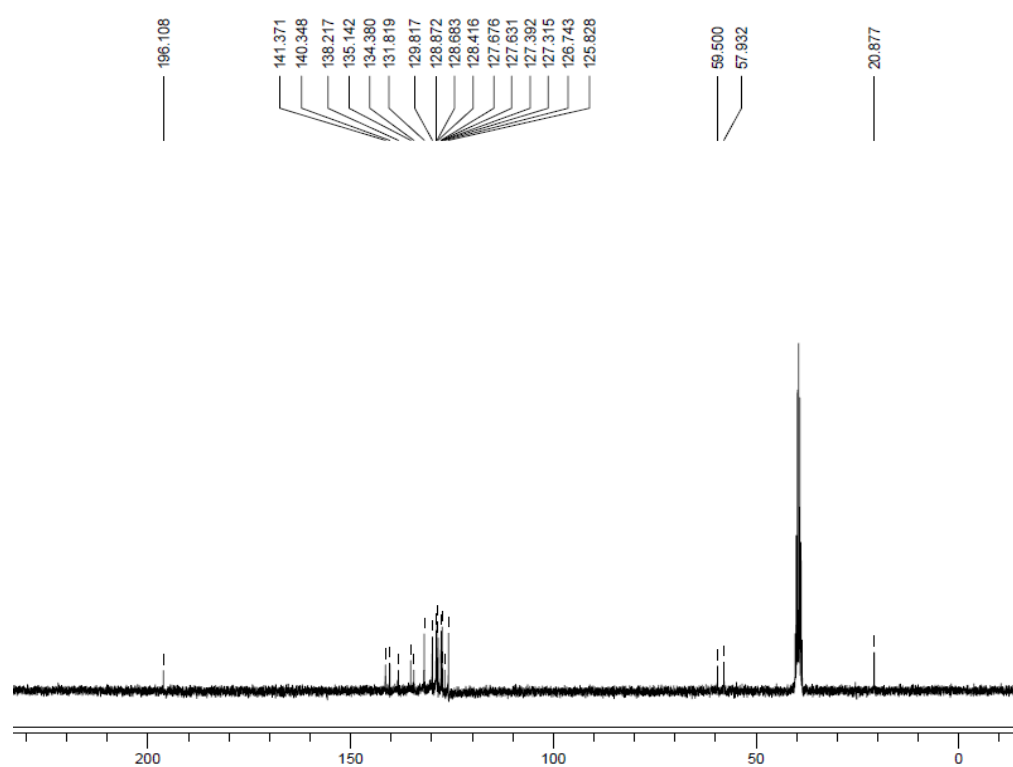




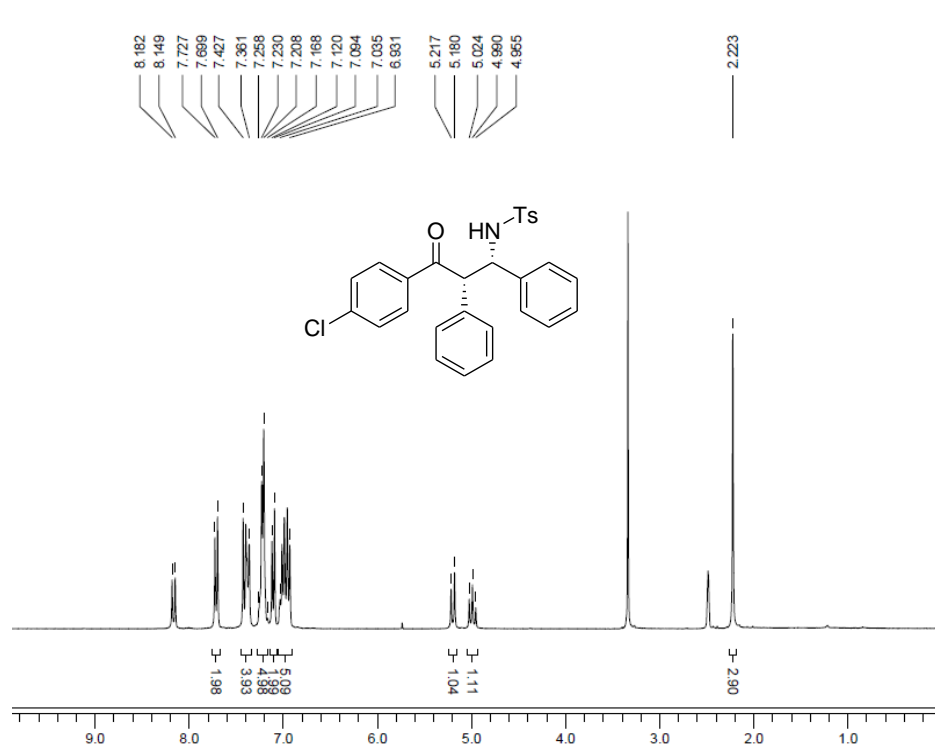




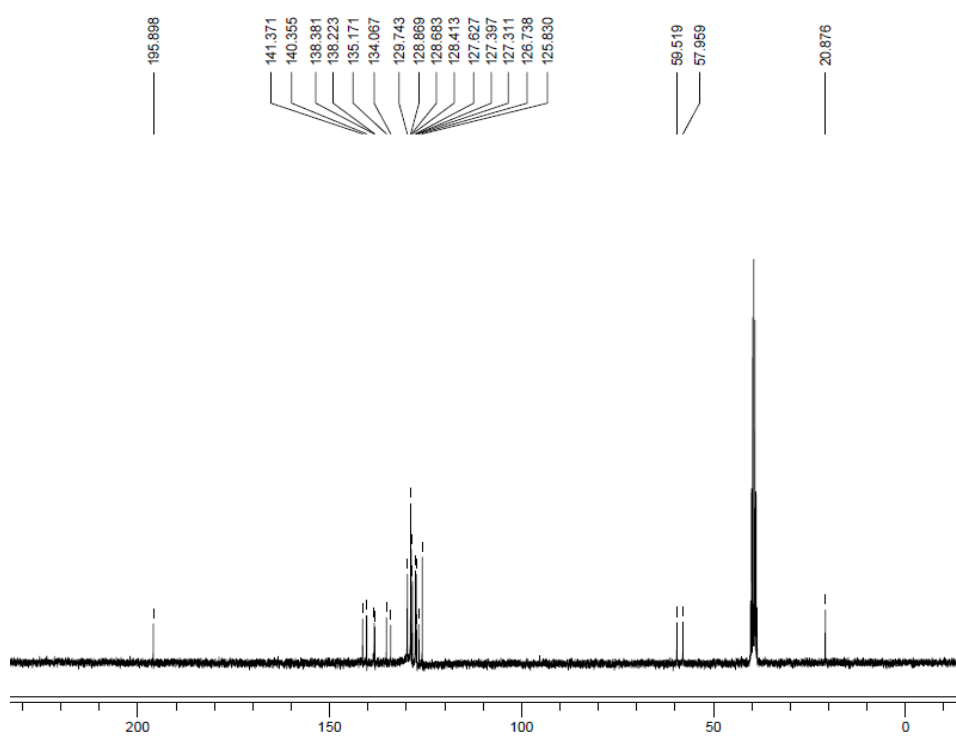
¹H NMR of **4k**



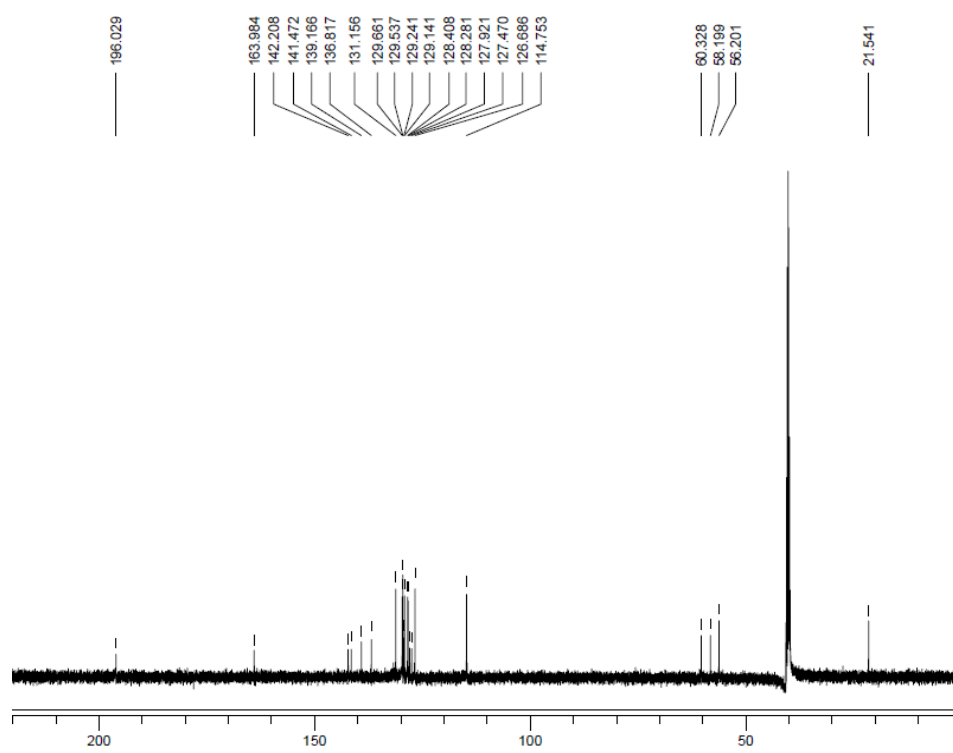
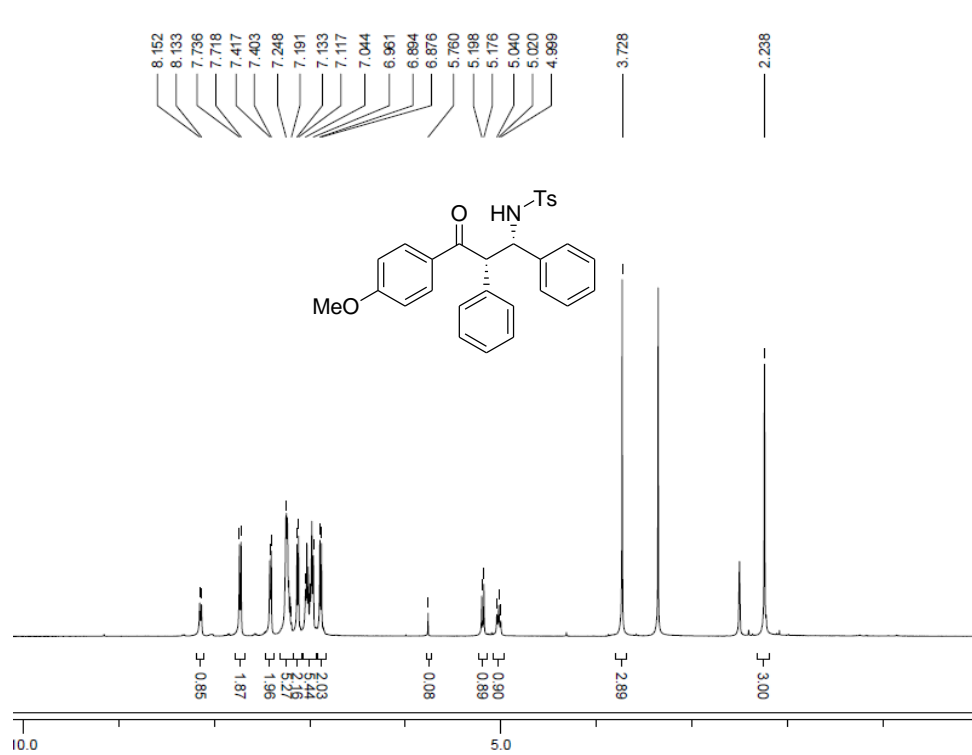
¹³C NMR of **4k**

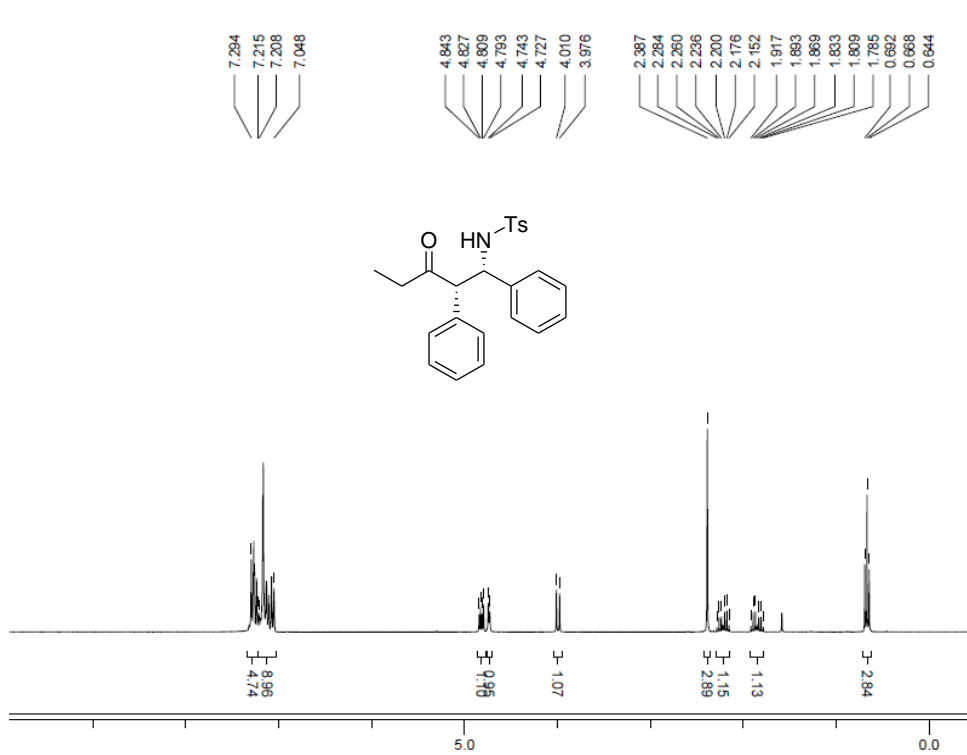


¹H NMR of **4I**

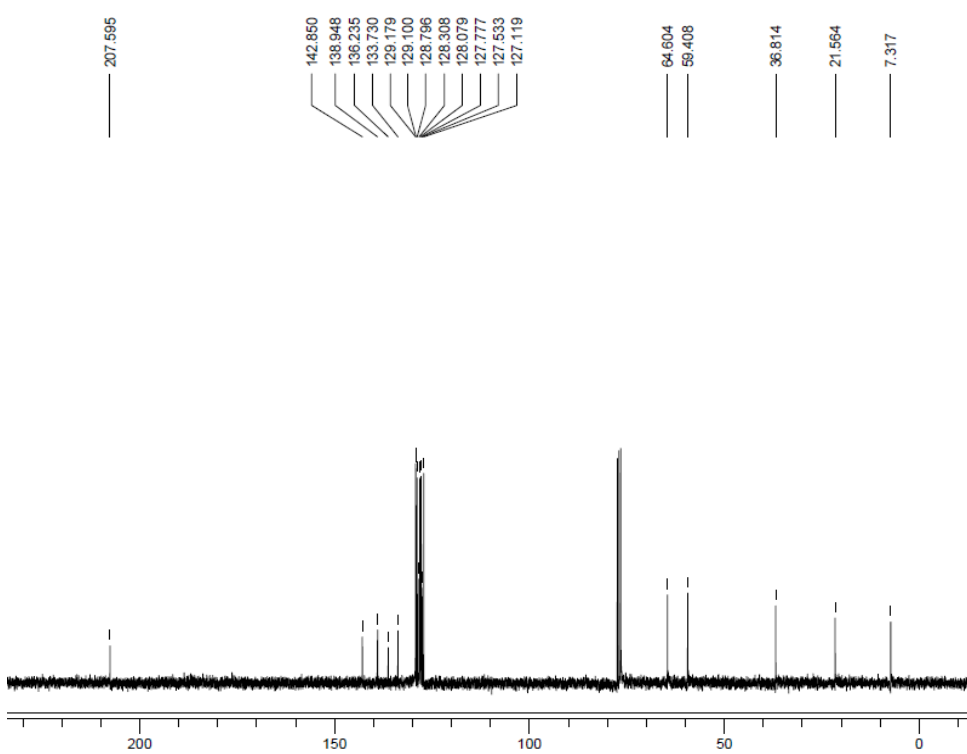


¹³C NMR of **4I**

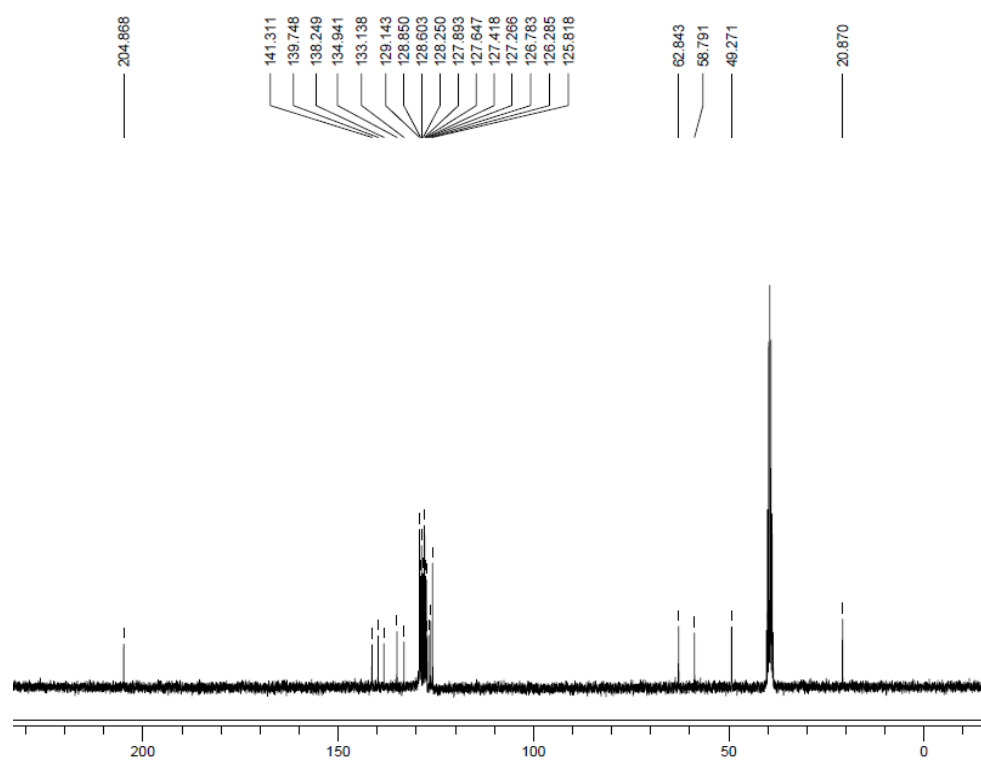
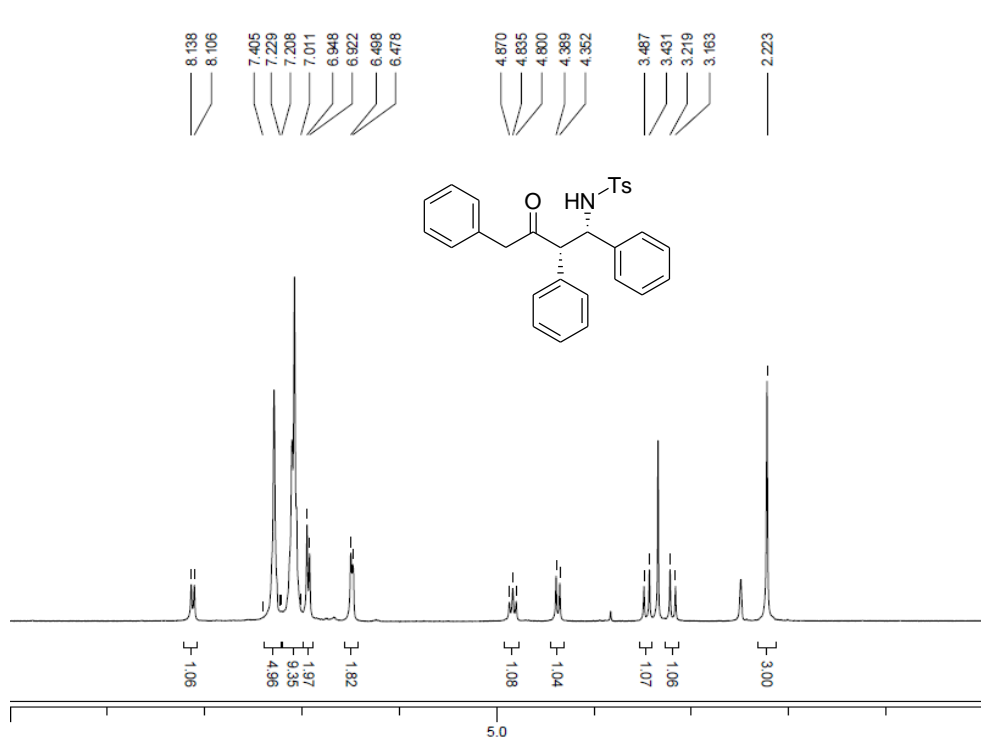


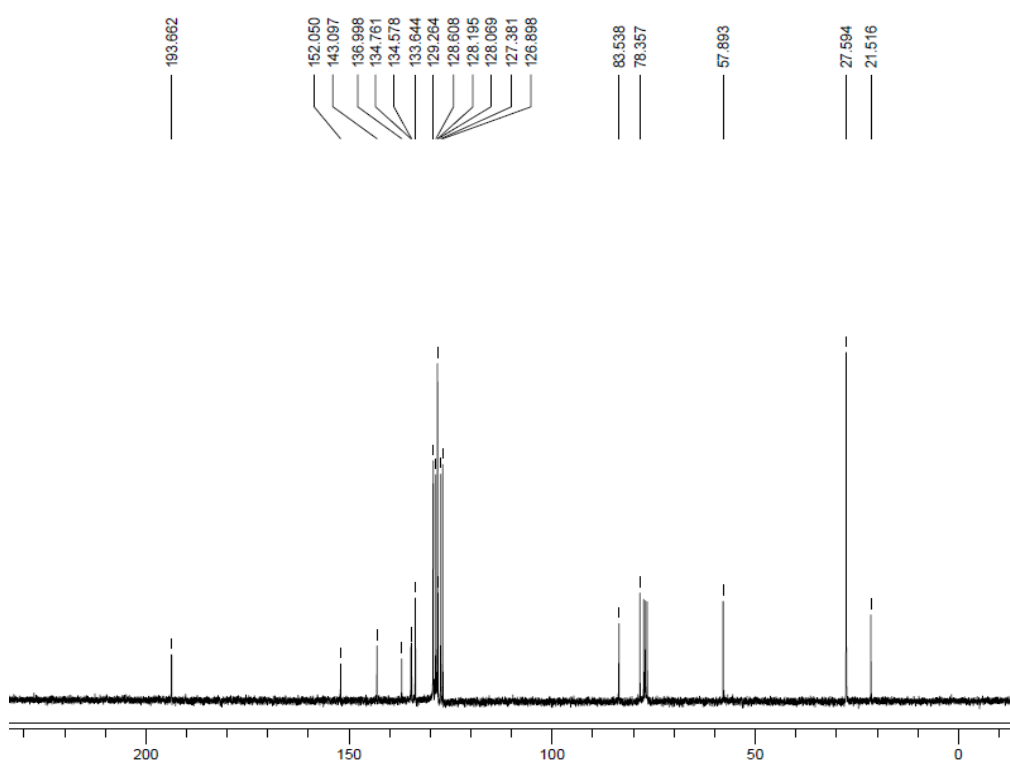
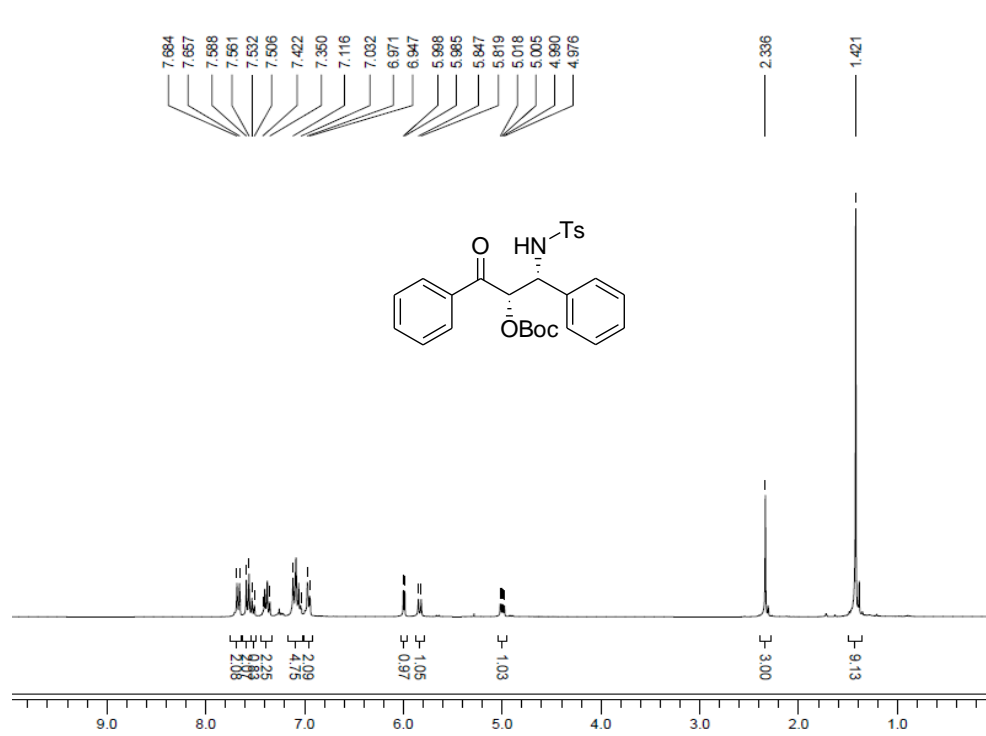


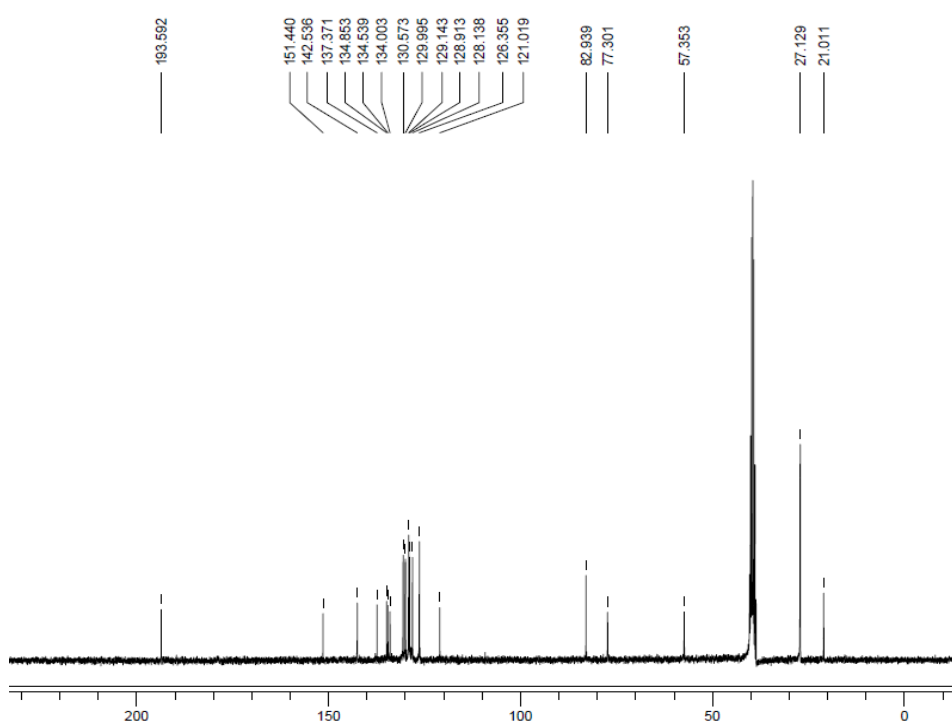
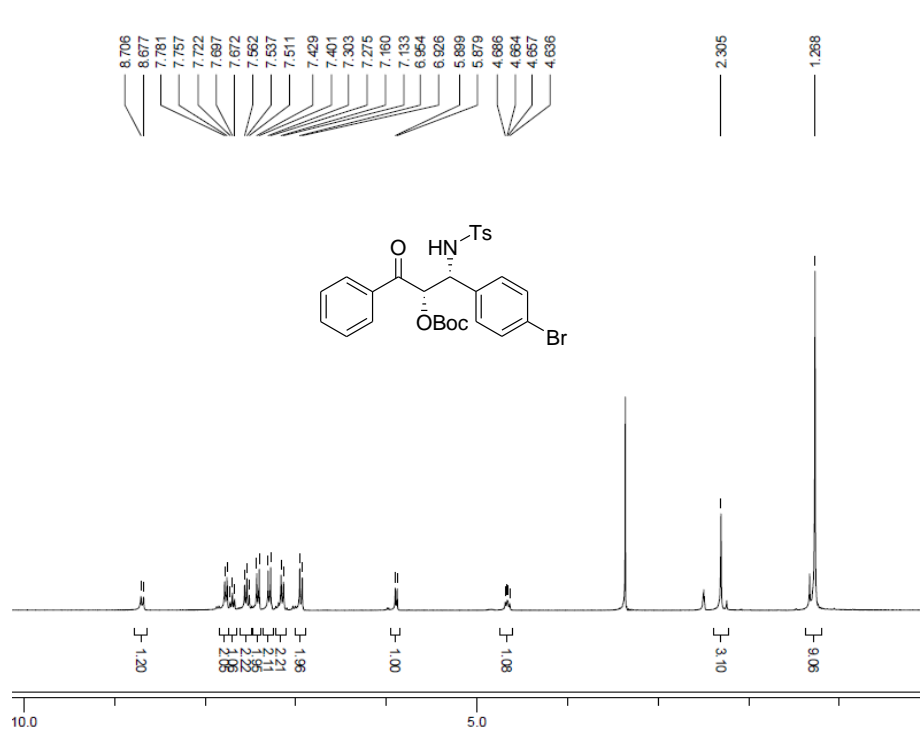
¹H NMR of **4n**

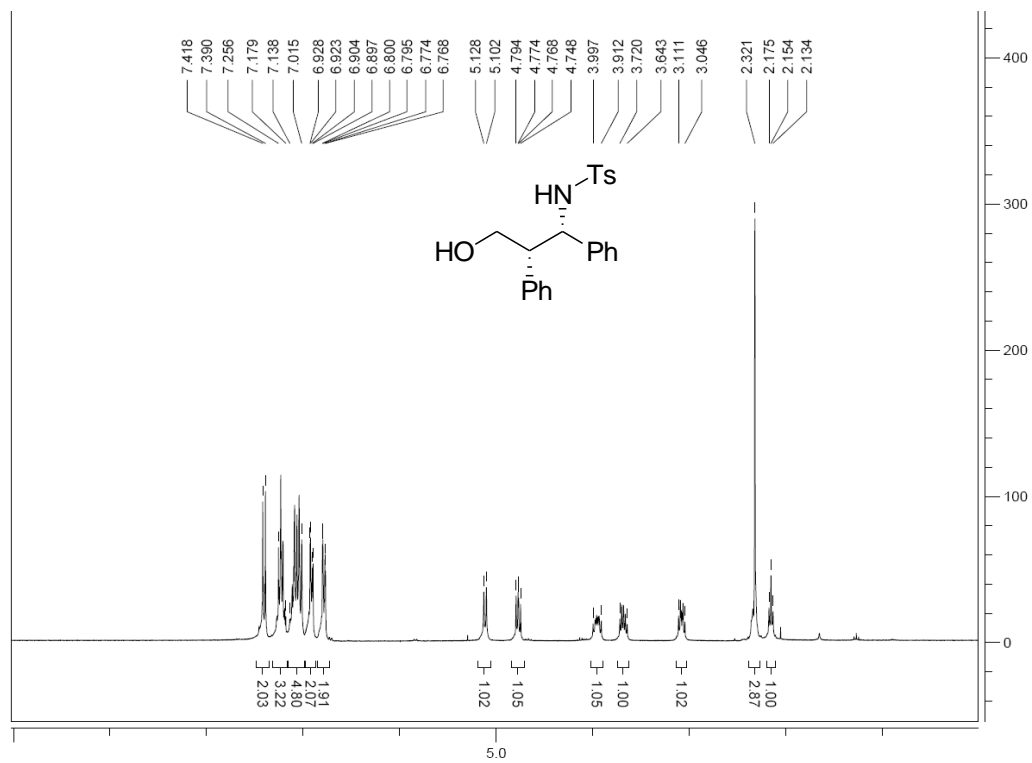


¹³C NMR of **4n**

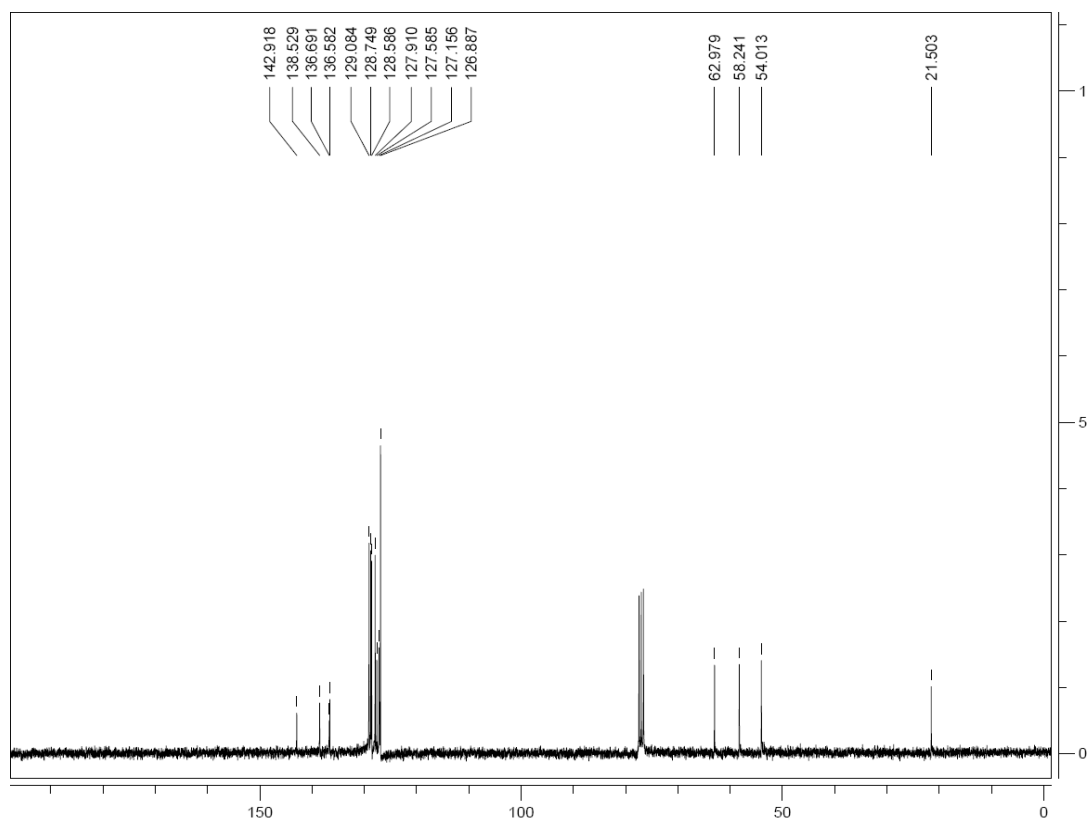




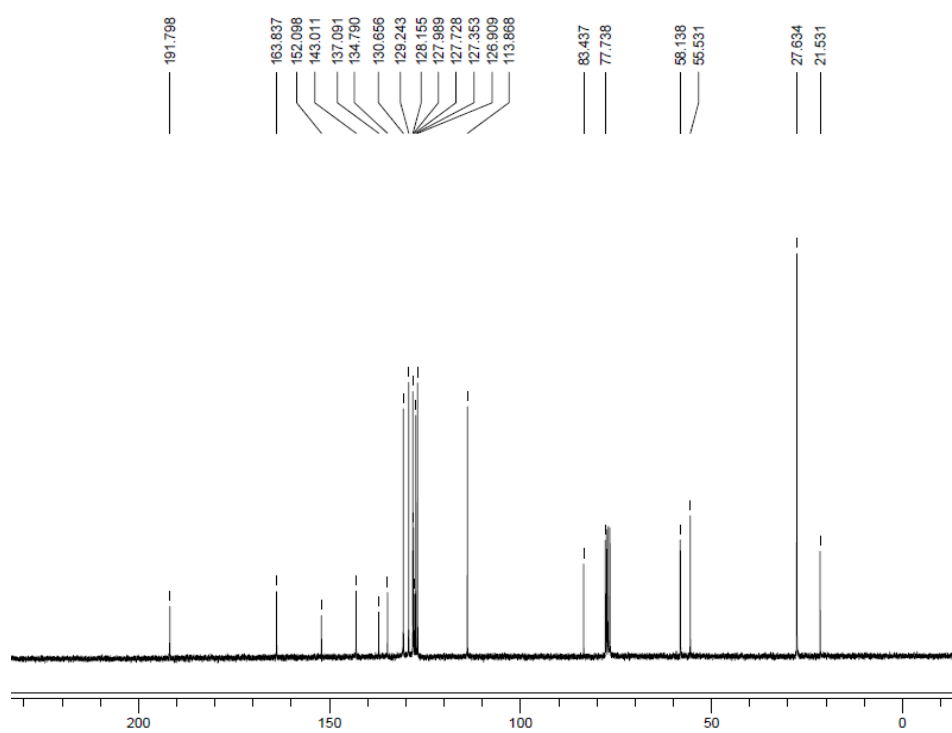
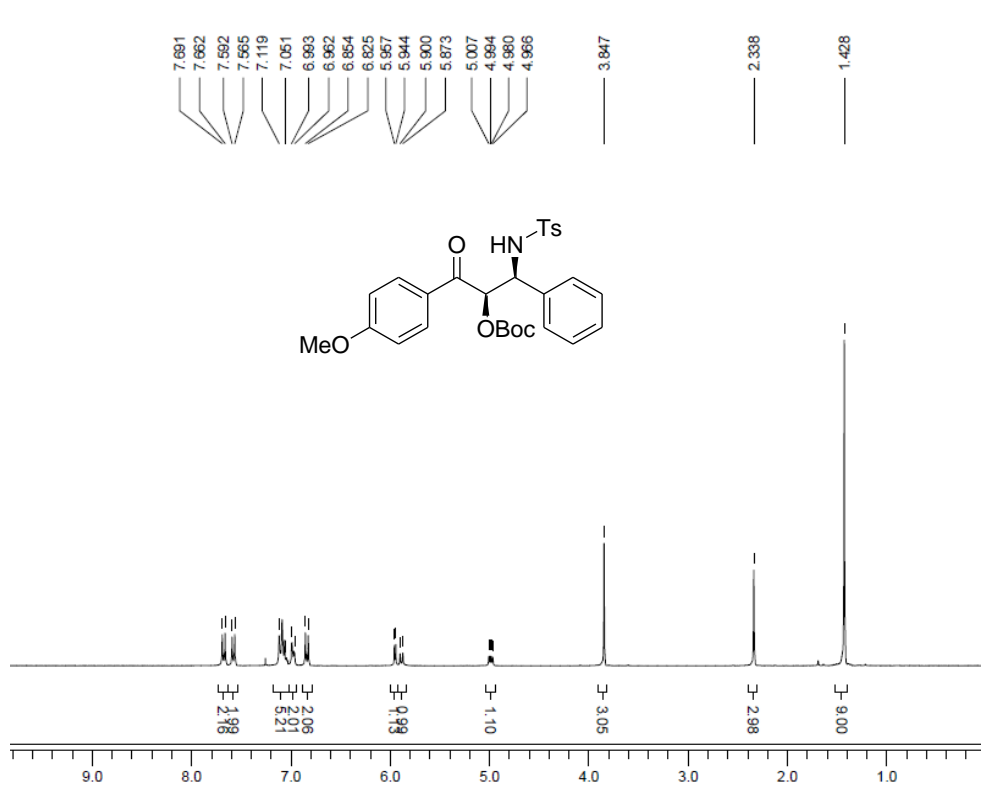


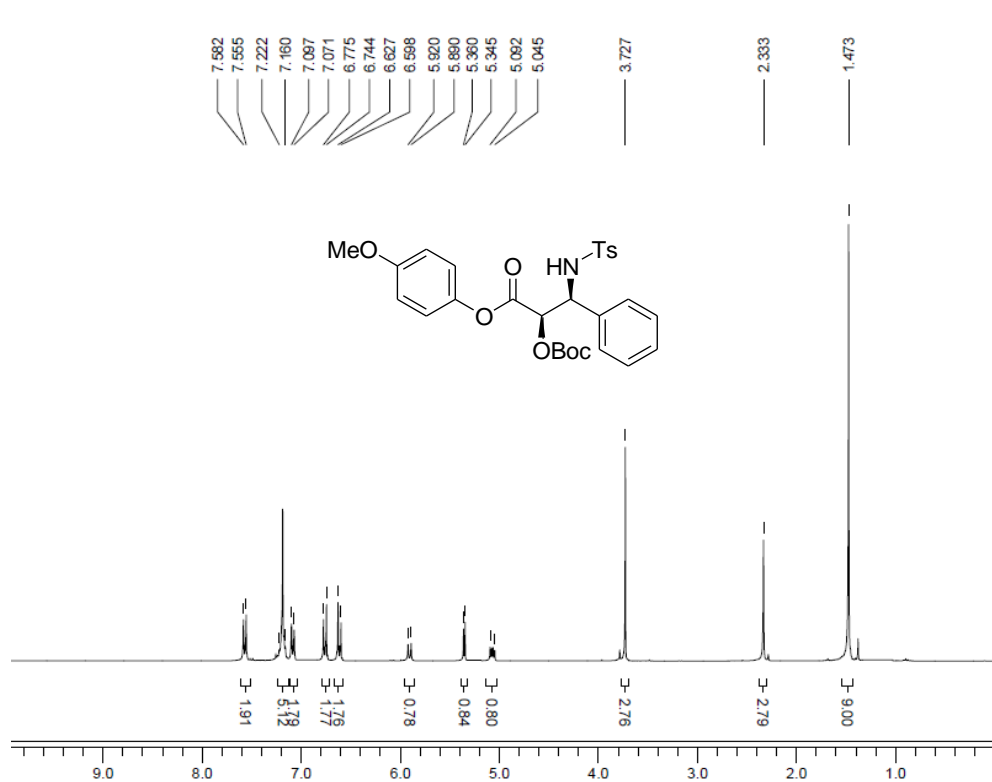


¹H NMR of 13

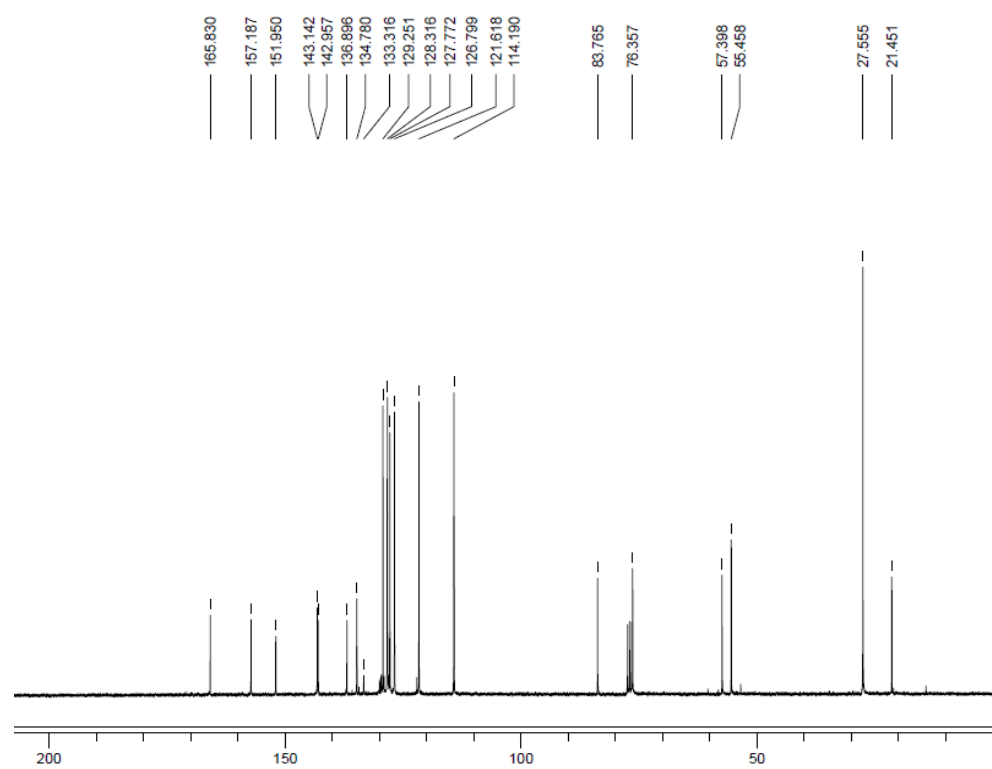


¹³C NMR of 13

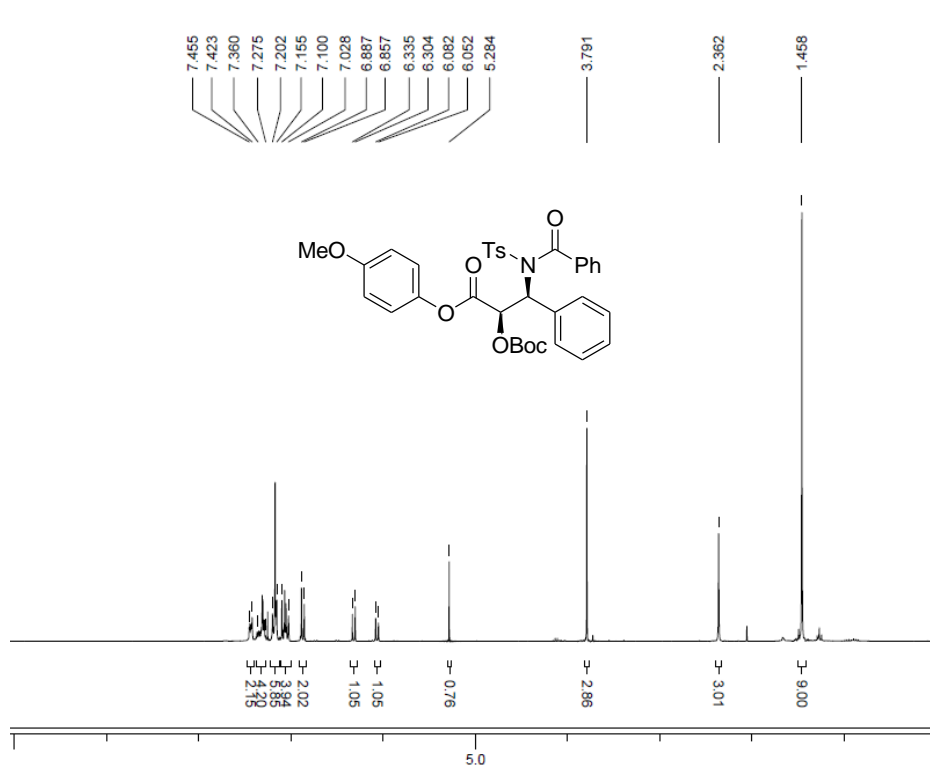




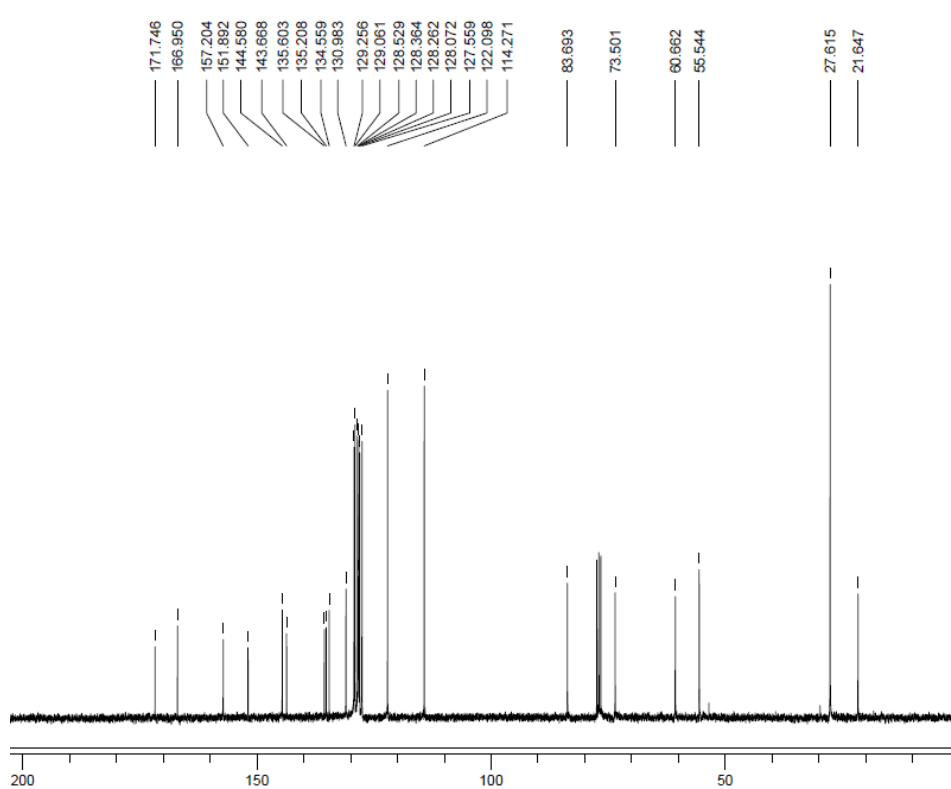
¹H NMR of 14



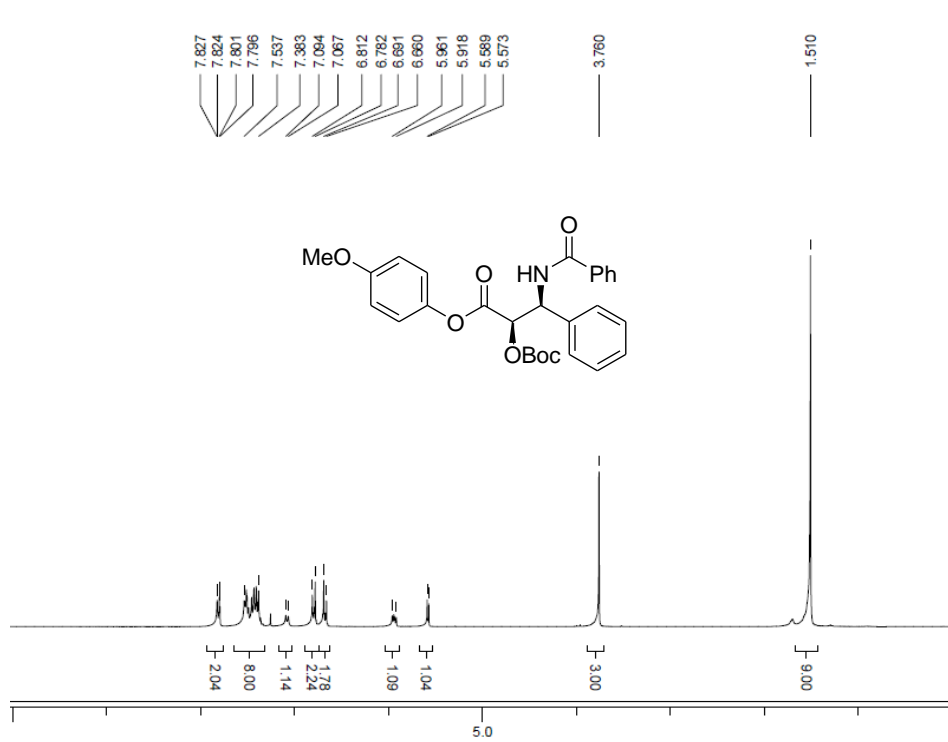
¹³C NMR of 14



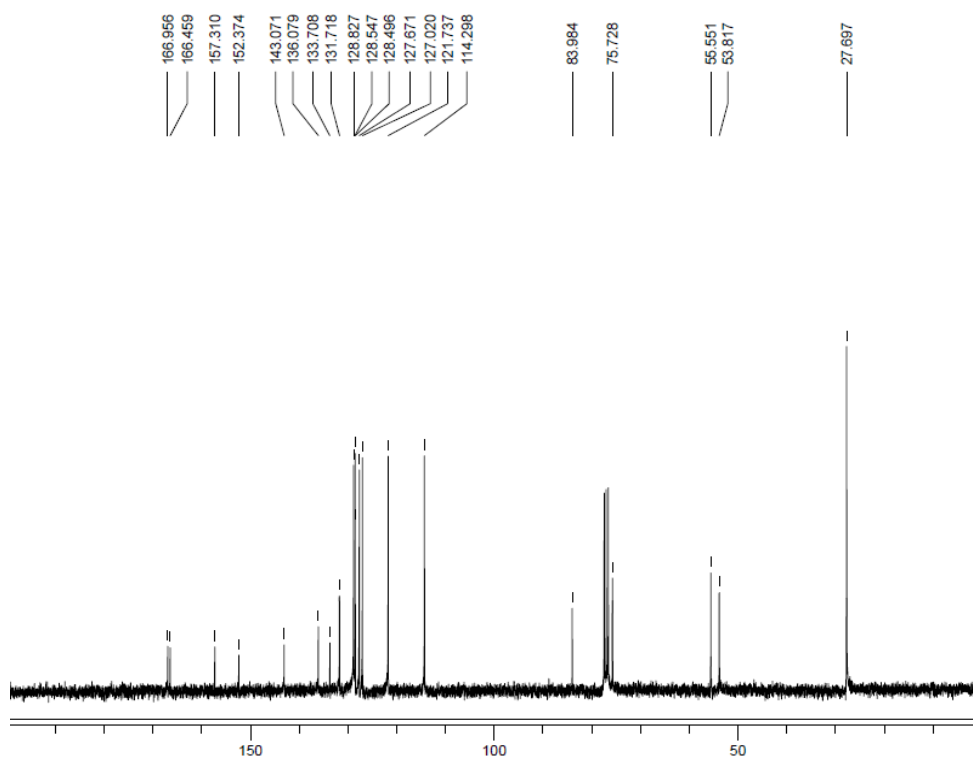
¹H NMR of 15



¹³C NMR of 15



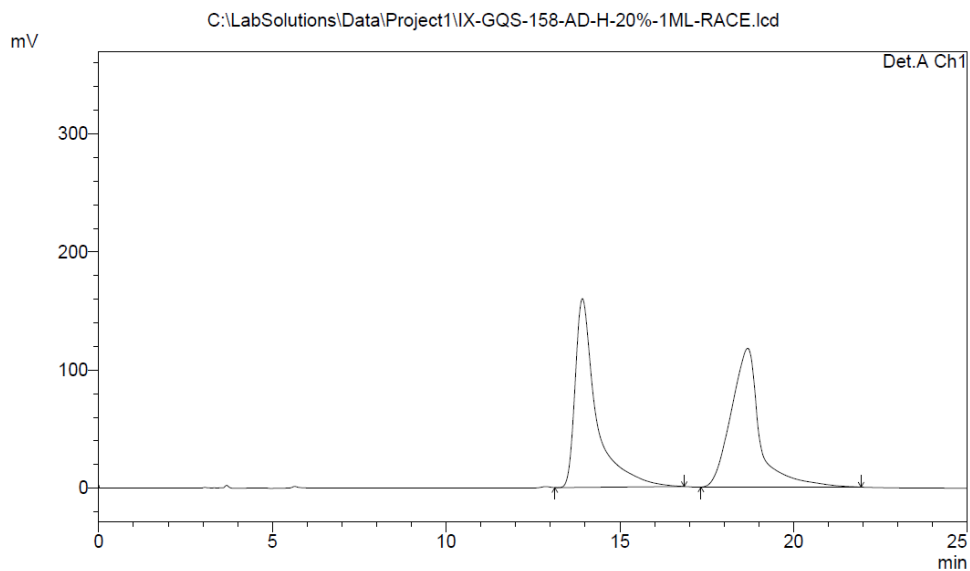
¹H NMR of 16



¹³C NMR of 16

==== Shimadzu LCsolution LC Data Image ====

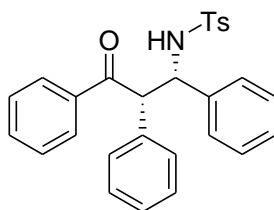
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PeakTable

Detector A Ch1 254nm

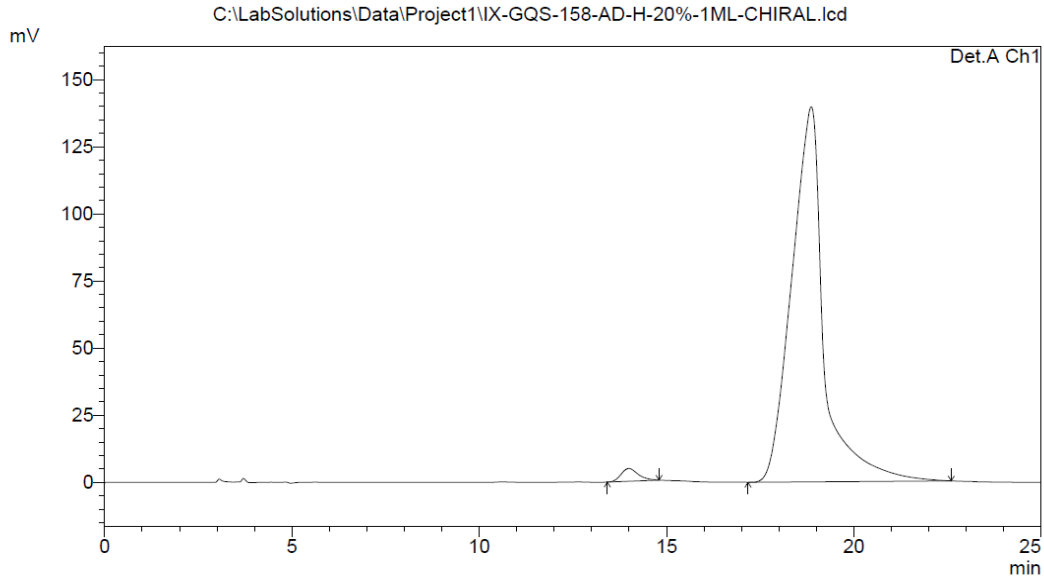
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.915	6768456	159869	50.013	57.633
2	18.673	6764830	117523	49.987	42.367
Total		13533286	277392	100.000	100.000



(2S*,3S*)-1,2,3-Triphenyl-3-(tosylamino)propan-1-one (**4a**)

==== Shimadzu LCsolution LC Data Image ====

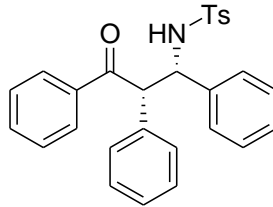
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Detector A Ch1 254nm

PeakTable

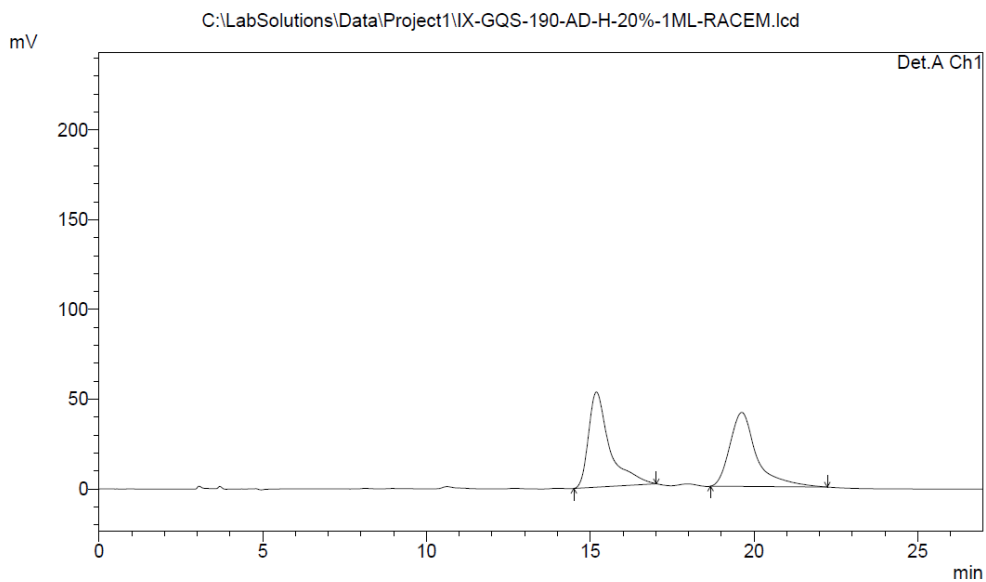
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.985	152761	4784	1.794	3.311
2	18.858	8360426	139698	98.206	96.689
Total		8513187	144482	100.000	100.000



(2S,3S)-1,2,3-Triphenyl-3-(tosylamino)propan-1-one (**4a**)

==== Shimadzu LCsolution LC Data Image ====

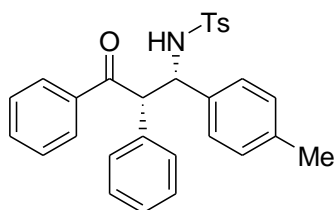
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PeakTable

Detector A Ch1 254nm

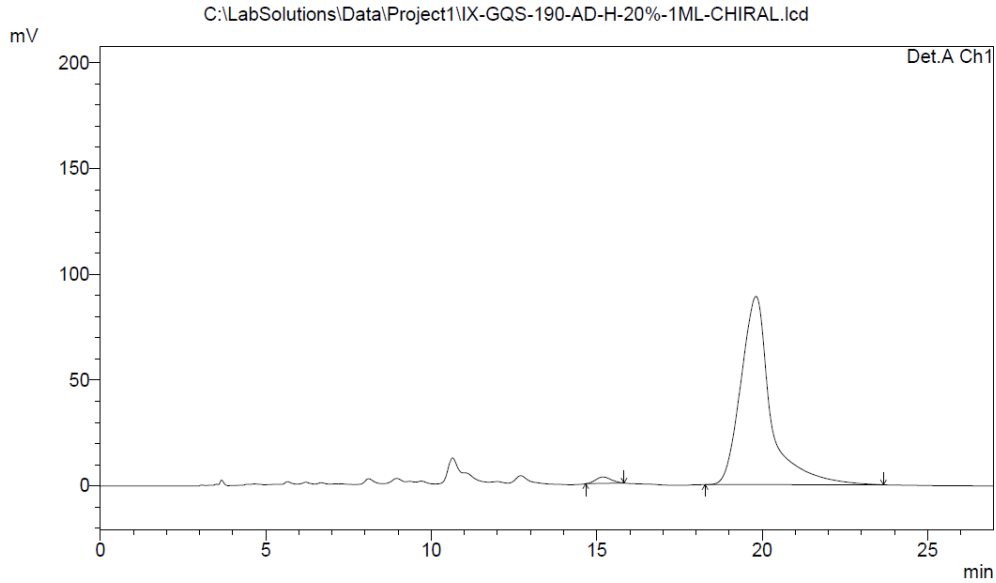
Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.184	2386690	53027	50.416	56.256
2	19.623	2347323	41233	49.584	43.744
Total		4734013	94260	100.000	100.000



(2S*,3S*)-3-(4-Methylphenyl)-1,2-diphenyl-3-(tosylamino)propan-1-one (**4b**)

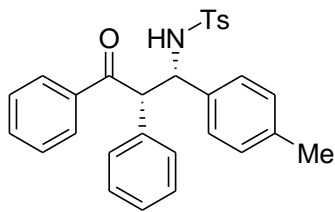
==== Shimadzu LCsolution LC Data Image ====

<Chromatogram>



PeakTable

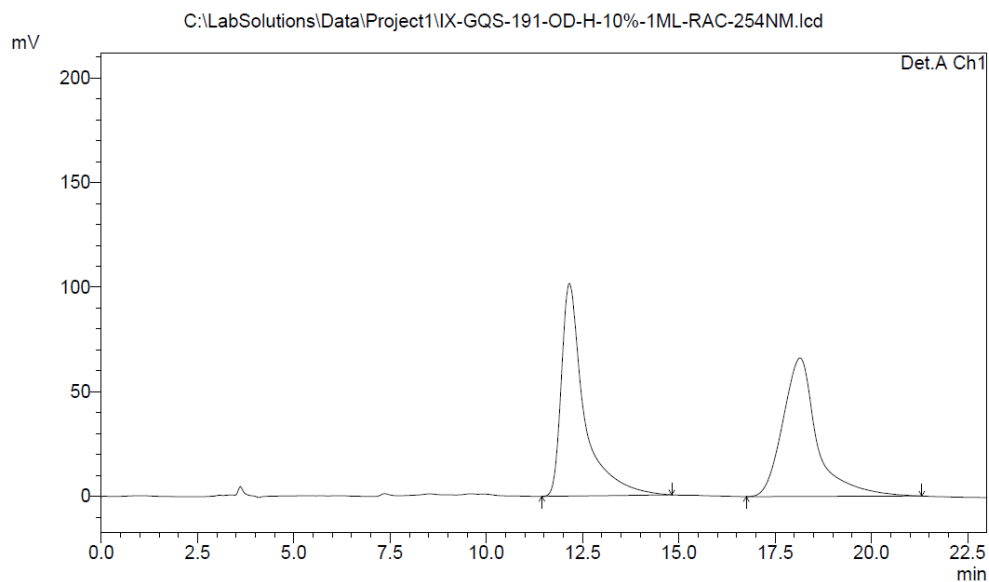
Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.183	100347	3058	1.768	3.323
2	19.809	5576878	88962	98.232	96.677
Total		5677224	92020	100.000	100.000



(2S,3S)-3-(4-Methylphenyl)-1,2-diphenyl-3-(tosylamino)propan-1-one (**4b**)

==== Shimadzu LCsolution LC Data Image ====

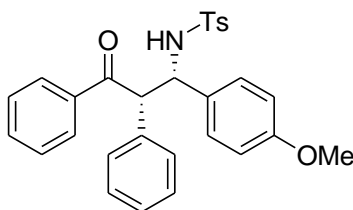
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PeakTable

Detector A Ch1 254nm

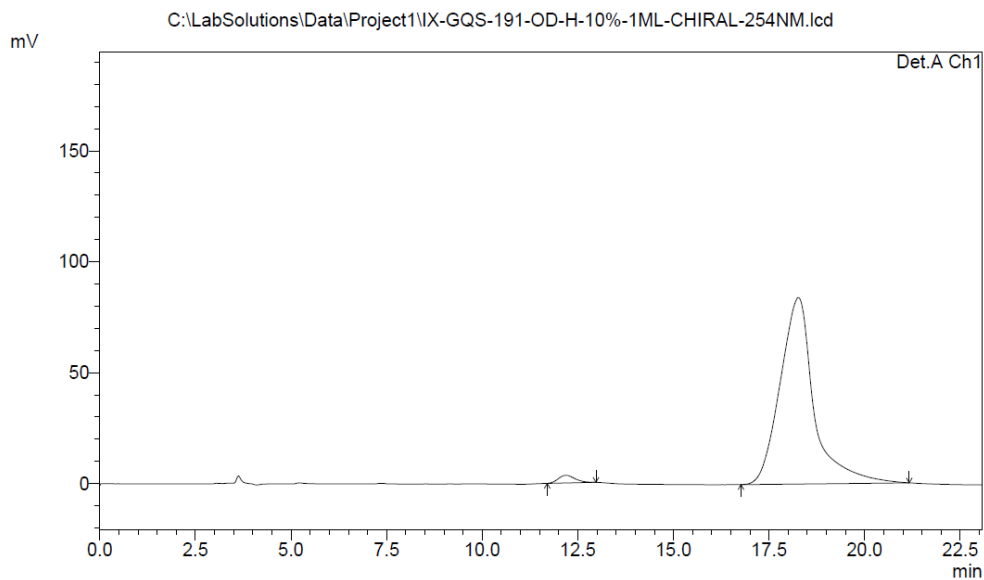
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.152	4176394	101713	50.481	60.570
2	18.140	4096736	66214	49.519	39.430
Total		8273130	167926	100.000	100.000



(2*S**,3*S**)-3-(4-Methoxyphenyl)-1,2-diphenyl-3-(tosylamino)propan-1-one (**4c**)

==== Shimadzu LCsolution LC Data Image ====

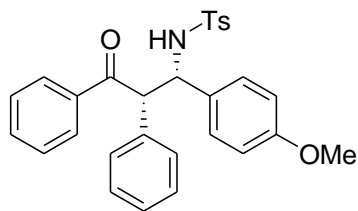
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PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.182	104037	3441	1.970	3.935
2	18.263	5177304	84021	98.030	96.065
Total		5281341	87463	100.000	100.000

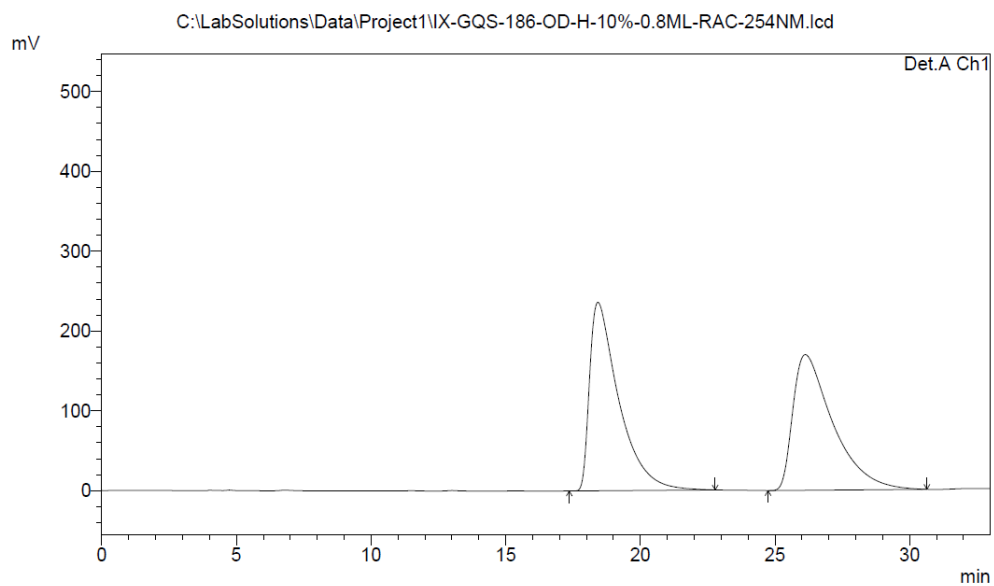
Detector A Ch1 254nm



(2S,3S)-3-(4-Methoxyphenyl)-1,2-diphenyl-3-(tosylamino)propan-1-one (**4c**)

==== Shimadzu LCsolution LC Data Image ====

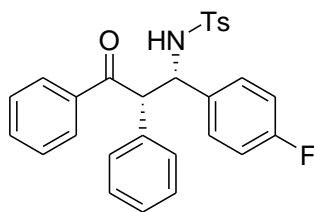
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PeakTable

Detector A Ch1 254nm

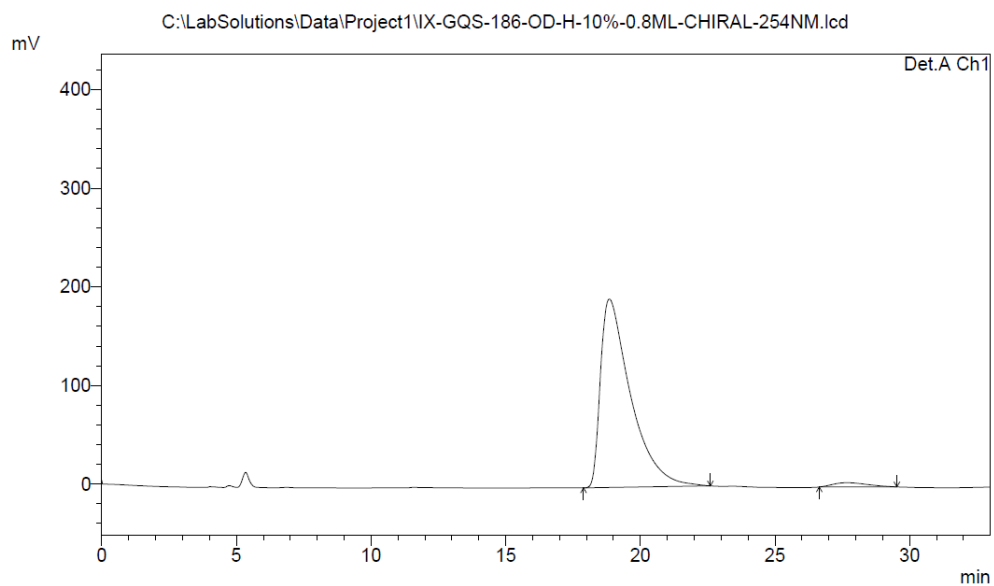
Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.420	17829446	236210	50.357	58.153
2	26.121	17576692	169980	49.643	41.847
Total		35406138	406190	100.000	100.000



(2S*,3S*)-3-(4-Fluorophenyl)-1,2-diphenyl-3-(tosylamino)propan-1-one (**4d**)

==== Shimadzu LCsolution LC Data Image ====

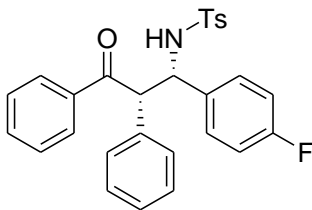
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PeakTable

Detector A Ch1 254nm

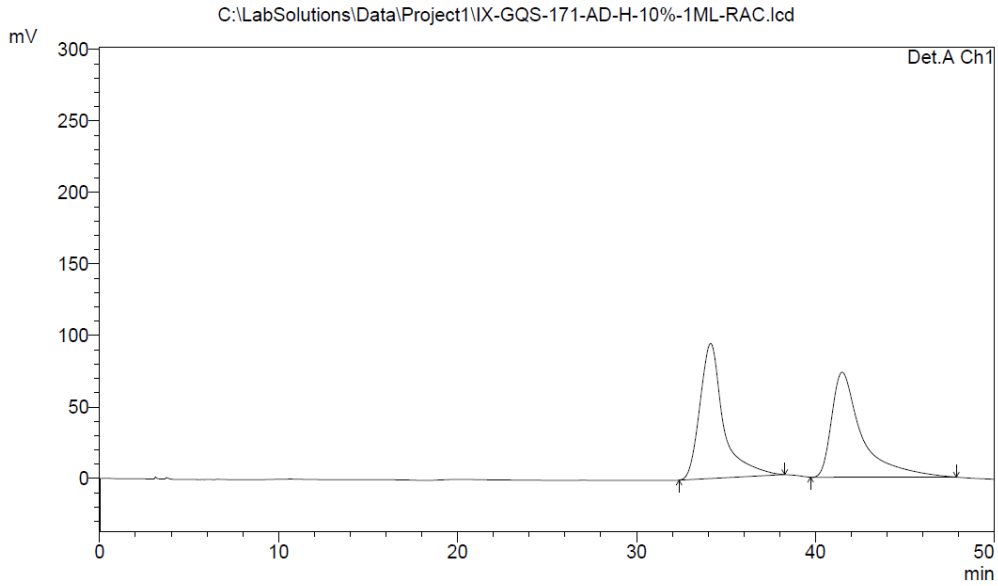
Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.845	14873115	191150	97.477	97.773
2	27.669	384885	4355	2.523	2.227
Total		15258000	195505	100.000	100.000



(2S,3S)-3-(4-Fluorophenyl)-1,2-diphenyl-3-(tosylamino)propan-1-one (**4d**)

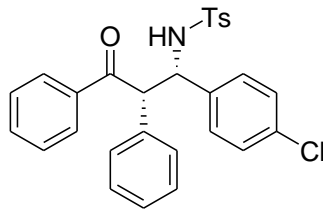
==== Shimadzu LCsolution LC Data Image ====

<Chromatogram>



PeakTable

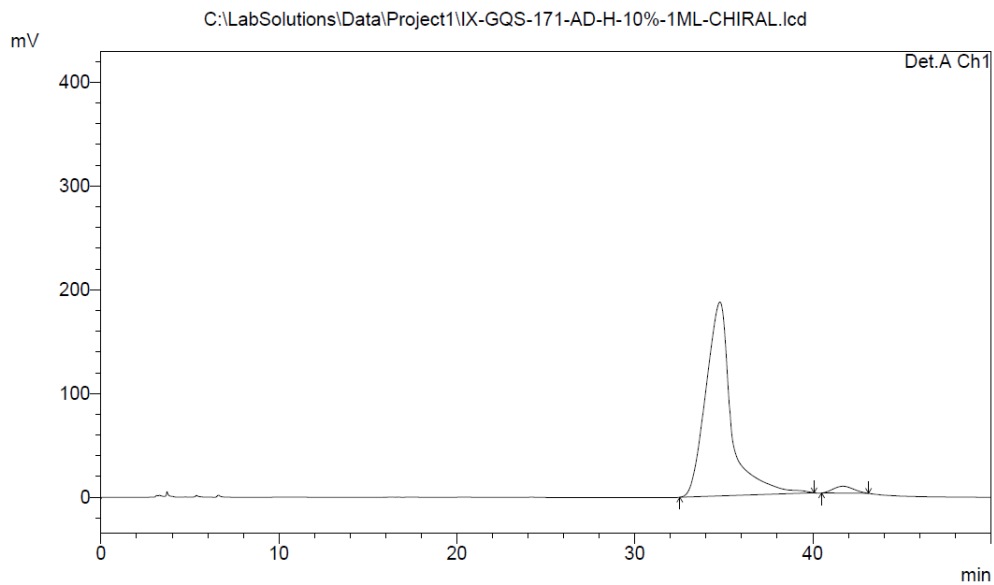
Peak#	Ret. Time	Area	Height	Area %	Height %
1	34.134	8635473	94359	50.009	56.216
2	41.484	8632408	73492	49.991	43.784
Total		17267881	167851	100.000	100.000



(2*S**,3*S**)-3-(4-Chlorophenyl)-1,2-diphenyl-3-(tosylamino)propan-1-one (**4e**)

==== Shimadzu LCsolution LC Data Image ====

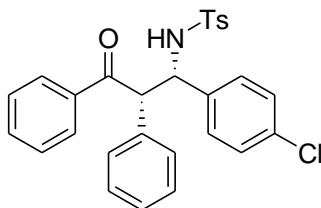
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PeakTable

Detector A Ch1 254nm

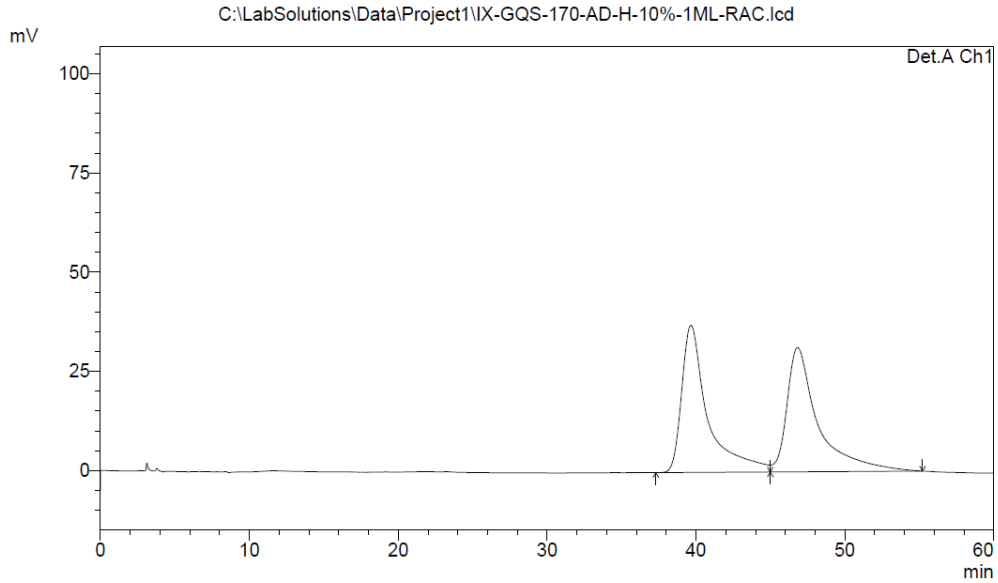
Peak#	Ret. Time	Area	Height	Area %	Height %
1	34.779	18748872	186859	97.241	96.566
2	41.698	531987	6644	2.759	3.434
Total		19280859	193503	100.000	100.000



(2S,3S)-3-(4-Chlorophenyl)-1,2-diphenyl-3-(tosylamino)propan-1-one (**4e**)

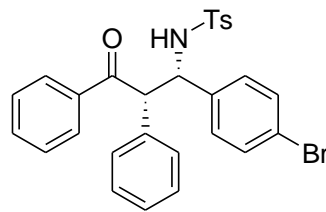
==== Shimadzu LCsolution LC Data Image ====

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PeakTable

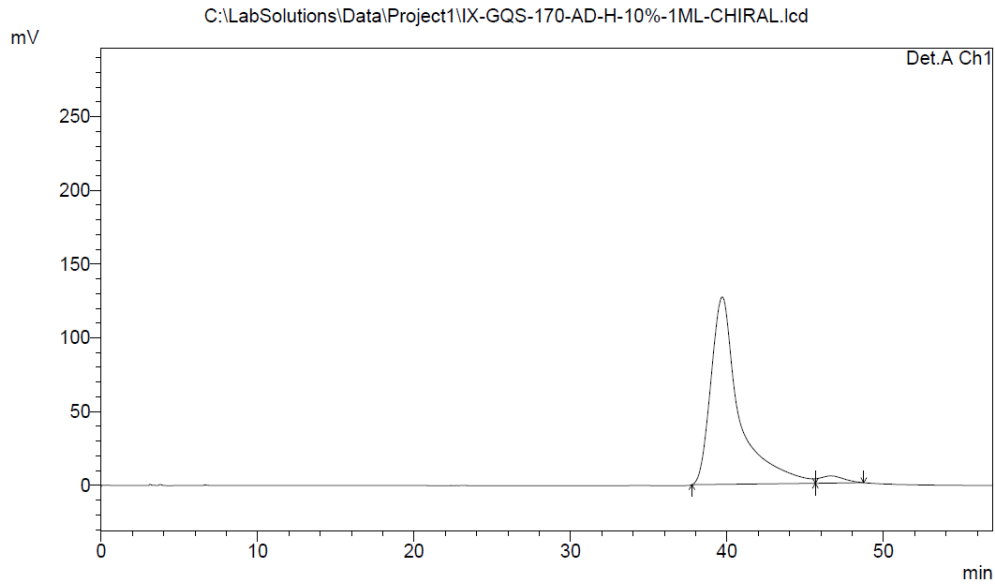
Peak#	Ret. Time	Area	Height	Area %	Height %
1	39.653	4506606	37086	49.774	54.221
2	46.816	4547519	31312	50.226	45.779
Total		9054126	68398	100.000	100.000



(2S*,3S*)-3-(4-Bromophenyl)-1,2-diphenyl-3-(tosylamino)propan-1-one (**4f**)

==== Shimadzu LCsolution LC Data Image ====

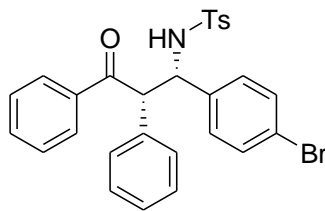
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PeakTable

Detector A Ch1 254nm

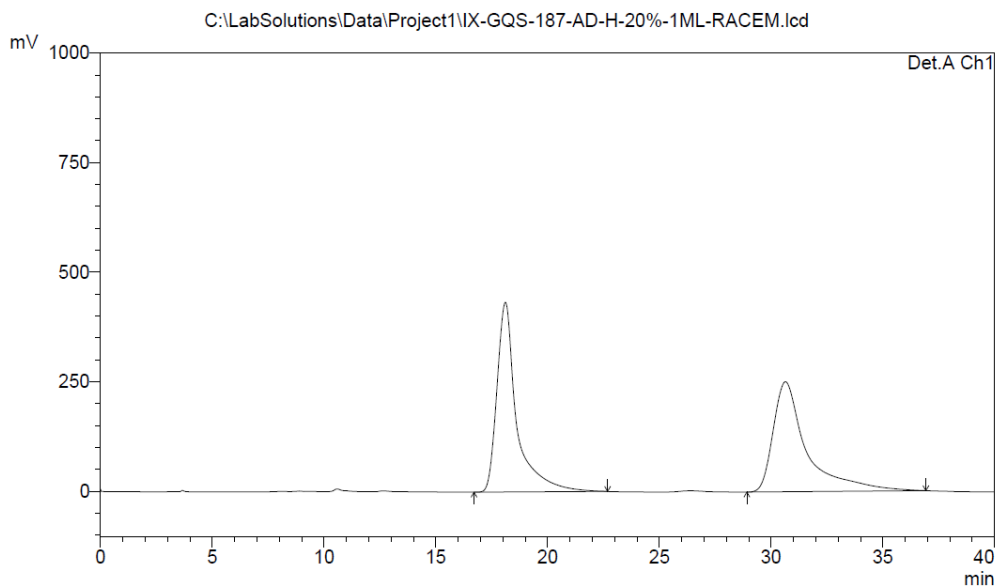
Peak#	Ret. Time	Area	Height	Area %	Height %
1	39.688	15960035	127157	96.827	96.336
2	46.635	523047	4837	3.173	3.664
Total		16483083	131994	100.000	100.000



(2S,3S)-3-(4-Bromophenyl)-1,2-diphenyl-3-(tosylamino)propan-1-one (**4f**)

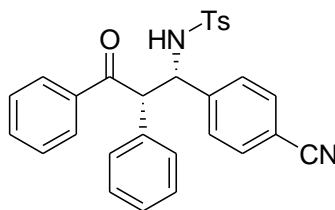
==== Shimadzu LCsolution LC Data Image ====

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PeakTable

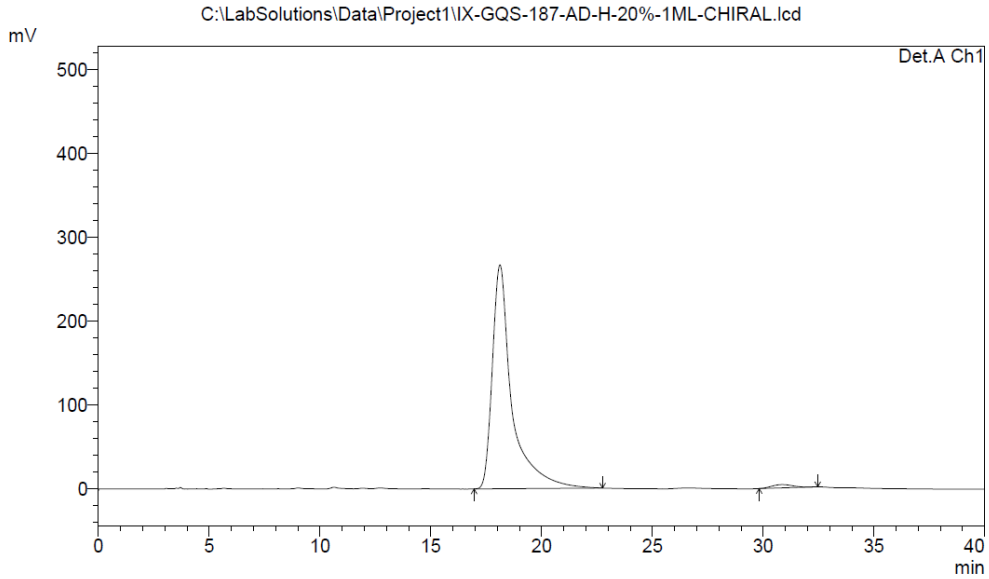
Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.108	26580241	432685	50.434	63.290
2	30.636	26122579	250971	49.566	36.710
Total		52702820	683656	100.000	100.000



(2S*,3S*)-3-(4-Cyanophenyl)-1,2-diphenyl-3-(tosylamino)propan-1-one (**4g**)

==== Shimadzu LCsolution LC Data Image ====

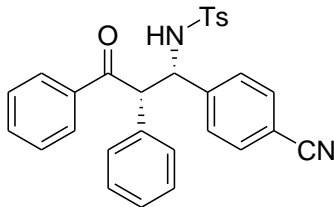
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PeakTable

Detector A Ch1 254nm

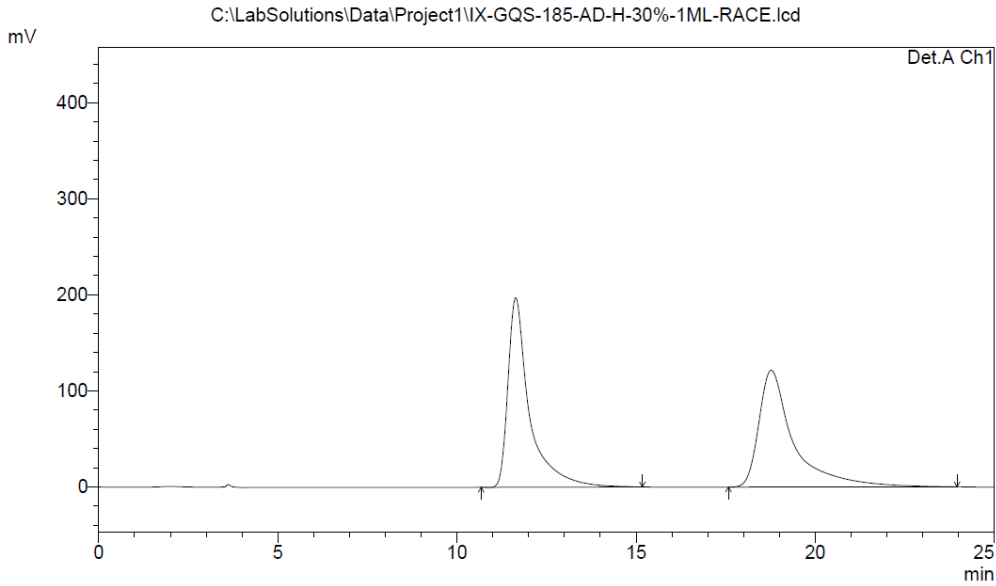
Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.115	16382736	267174	98.441	98.527
2	30.841	259514	3994	1.559	1.473
Total		16642250	271168	100.000	100.000



(2S,3S)-3-(4-Cyanophenyl)-1,2-diphenyl-3-(tosylamino)propan-1-one (**4g**)

==== Shimadzu LCsolution LC Data Image ====

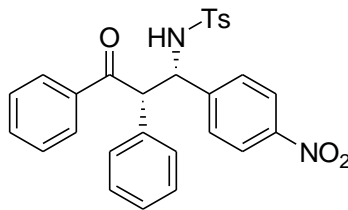
<Chromatogram>



PeakTable

Detector A Ch1 254nm

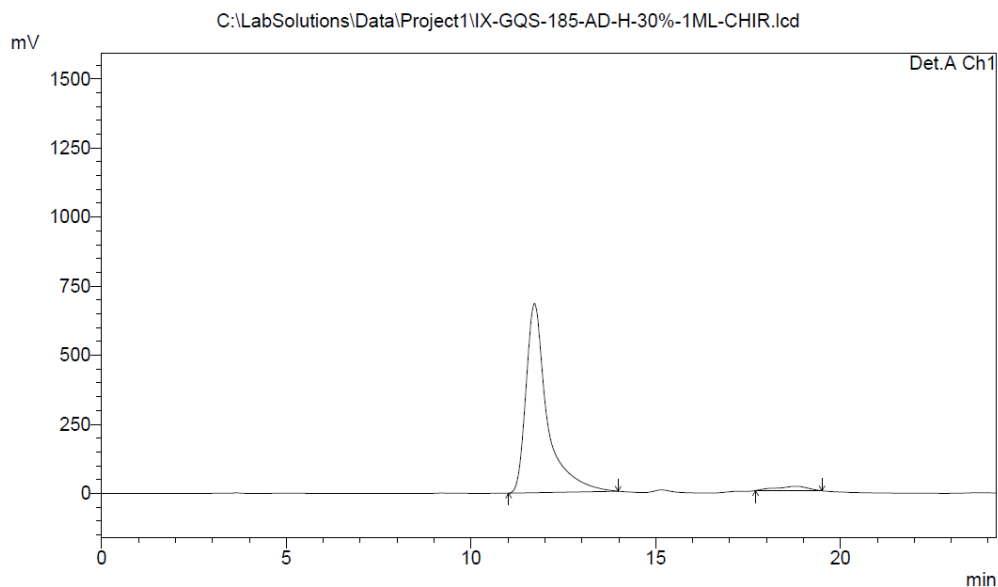
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.634	8247231	197295	50.139	61.866
2	18.765	8201376	121613	49.861	38.134
Total		16448607	318909	100.000	100.000



(2S*,3S*)-3-(4-Nitrophenyl)-1,2-diphenyl-3-(tosylamino)propan-1-one (**4h**)

==== Shimadzu LCsolution LC Data Image ====

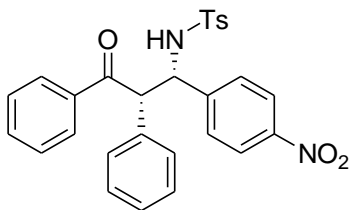
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PeakTable

Detector A Ch1 254nm

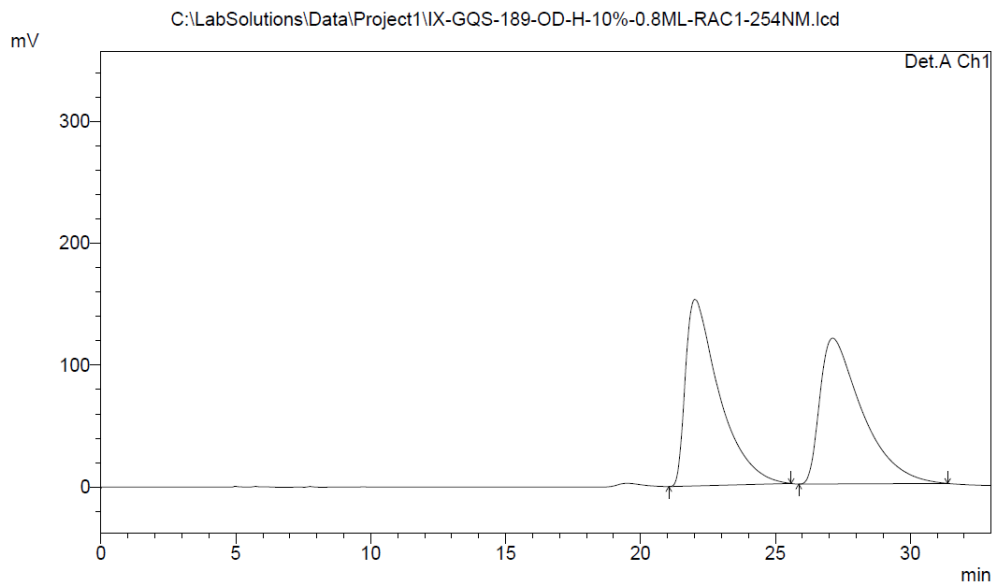
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.713	27291599	684751	96.620	97.725
2	18.778	954824	15942	3.380	2.275
Total		28246424	700692	100.000	100.000



(2S,3S)-3-(4-Nitrophenyl)-1,2-diphenyl-3-(tosylamino)propan-1-one (**4h**)

==== Shimadzu LCsolution LC Data Image ====

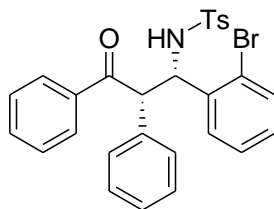
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PeakTable

Detector A Ch1 254nm

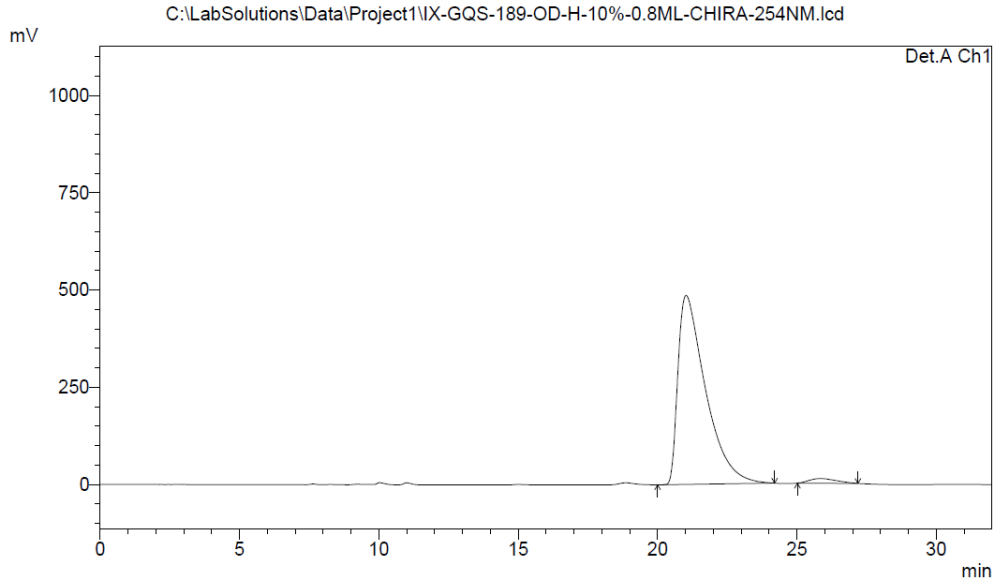
Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.016	13375907	153213	50.605	56.147
2	27.119	13056081	119664	49.395	43.853
Total		26431988	272877	100.000	100.000



(2*S**,3*S**)-3-(2-Bromophenyl)-1,2-diphenyl-3-(tosylamino)propan-1-one (**4i**)

==== Shimadzu LCsolution LC Data Image ====

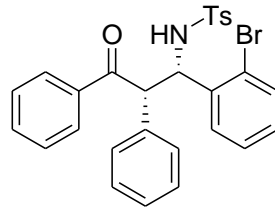
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PeakTable

Detector A Ch1 254nm

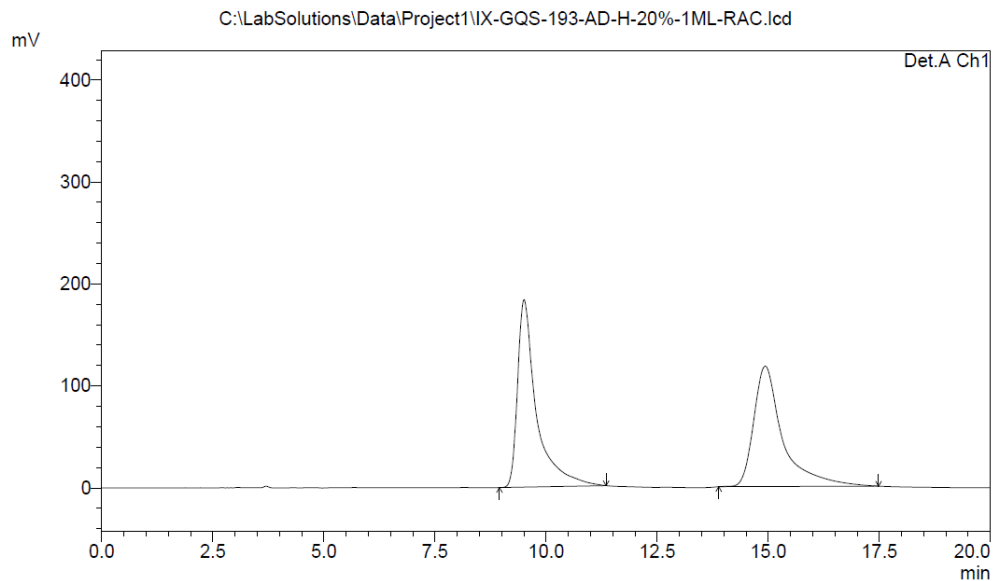
Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.020	33445334	485967	97.625	97.581
2	25.838	813606	12049	2.375	2.419
Total		34258941	498015	100.000	100.000



(2S,3S)-3-(2-Bromophenyl)-1,2-diphenyl-3-(tosylamino)propan-1-one (**4i**)

==== Shimadzu LCsolution LC Data Image ====

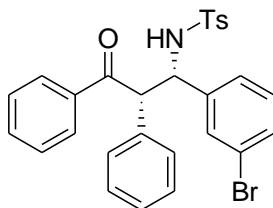
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PeakTable

Detector A Ch1 254nm

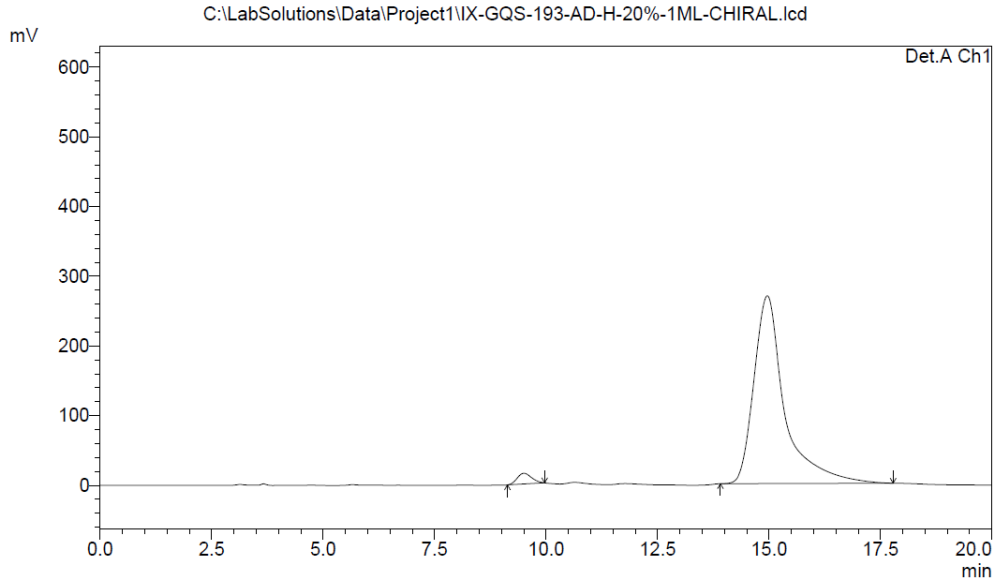
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.499	5446505	183957	50.392	60.899
2	14.926	5361820	118112	49.608	39.101
Total		10808326	302069	100.000	100.000



(2S*,3S*)-3-(3-Bromophenyl)-1,2-diphenyl-3-(tosylamino)propan-1-one (**4j**)

==== Shimadzu LCsolution LC Data Image ====

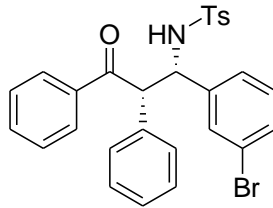
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PeakTable

Detector A Ch1 254nm

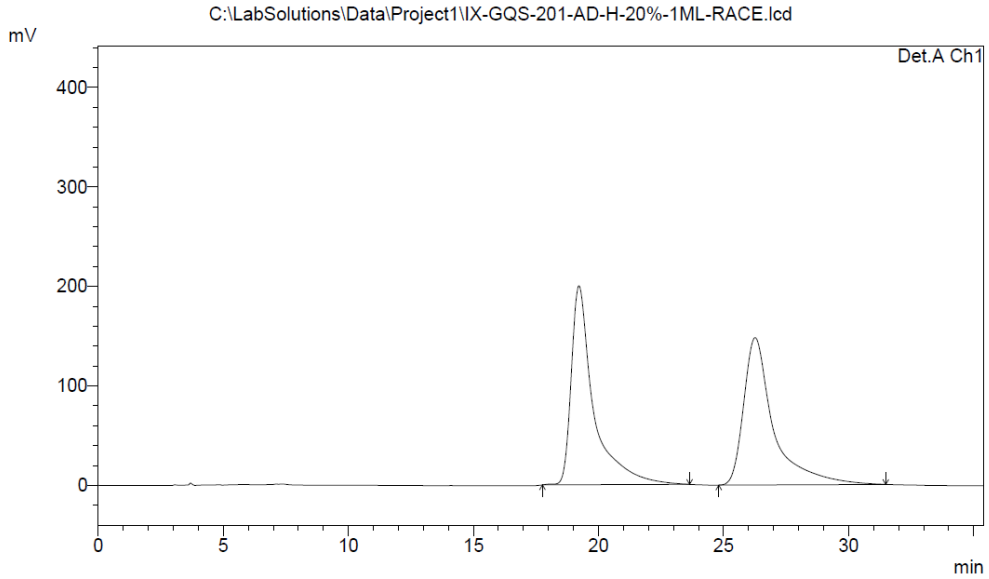
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.498	348207	15438	2.630	5.421
2	14.957	12893439	269348	97.370	94.579
Total		13241646	284786	100.000	100.000



(2S,3S)-3-(3-Bromophenyl)-1,2-diphenyl-3-(tosylamino)propan-1-one (4j)

==== Shimadzu LCsolution LC Data Image ====

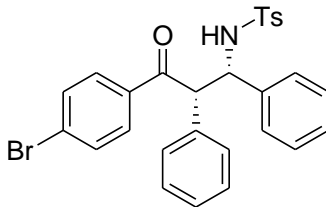
<Chromatogram>



PeakTable

Detector A Ch1 254nm

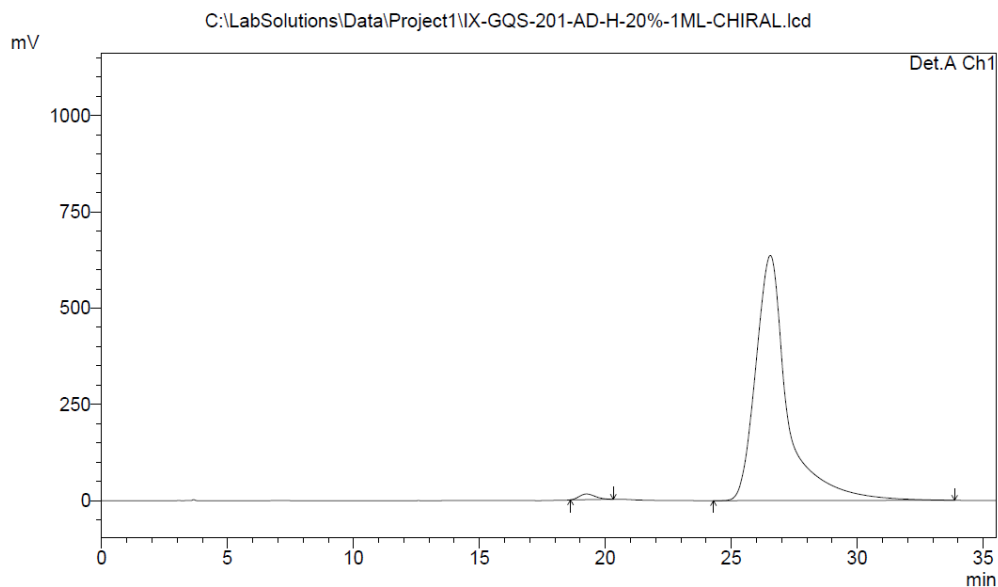
Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.212	12477502	200111	50.346	57.455
2	26.257	12305804	148181	49.654	42.545
Total		24783307	348292	100.000	100.000



(2S*,3S*)-1-(4-Bromophenyl)-2,3-diphenyl-3-(tosylamino)propan-1-one (**4k**)

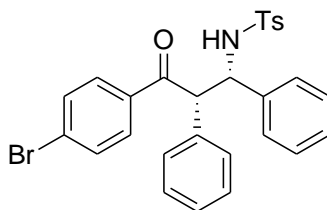
==== Shimadzu LCsolution LC Data Image ====

<Chromatogram>



PeakTable

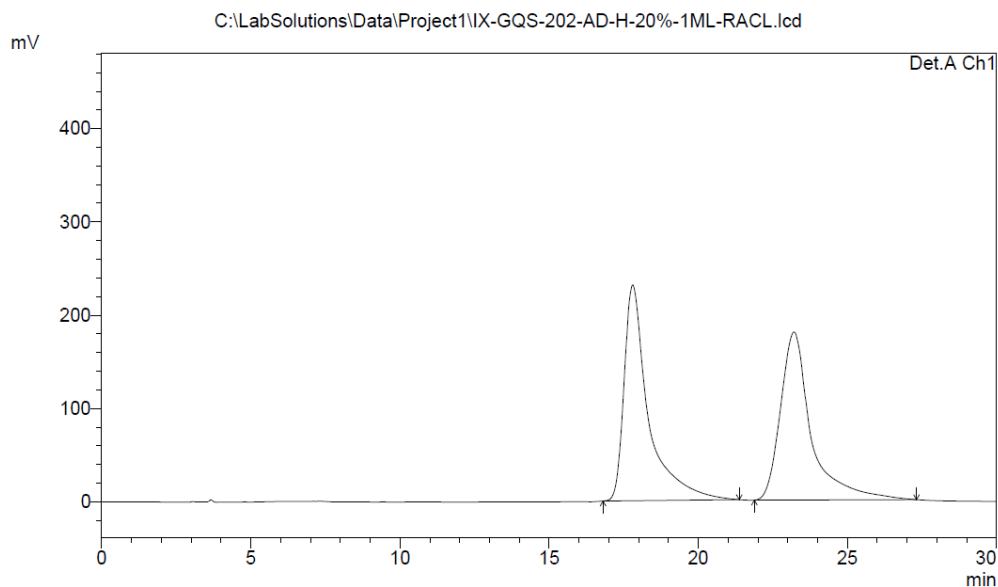
Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.251	652474	14801	1.158	2.271
2	26.544	55716684	636845	98.842	97.729
Total		56369158	651646	100.000	100.000



(2S,3S)-1-(4-Bromophenyl)-2,3-diphenyl-3-(tosylamino)propan-1-one (**4k**)

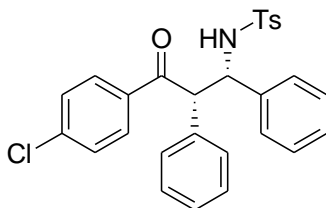
==== Shimadzu LCsolution LC Data Image ====

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PeakTable

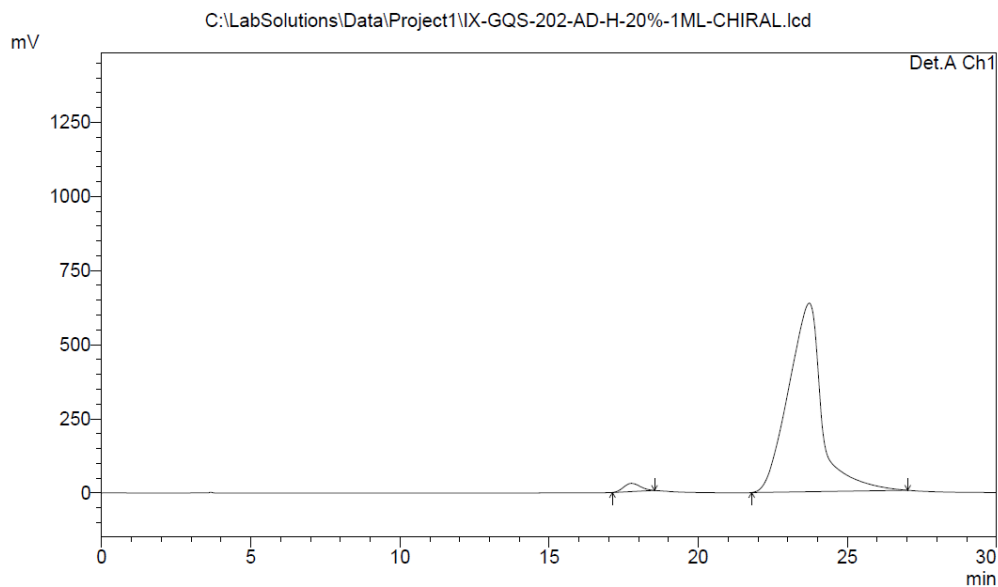
Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.798	13110430	231275	50.348	56.214
2	23.206	12929169	180144	49.652	43.786
Total		26039599	411419	100.000	100.000



(2S*,3S*)-1-(4-Chlorophenyl)-2,3-diphenyl-3-(tosylamino)propan-1-one (**41**)

==== Shimadzu LCsolution LC Data Image ====

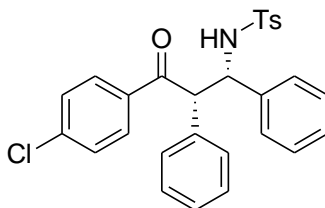
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PeakTable

Detector A Ch1 254nm

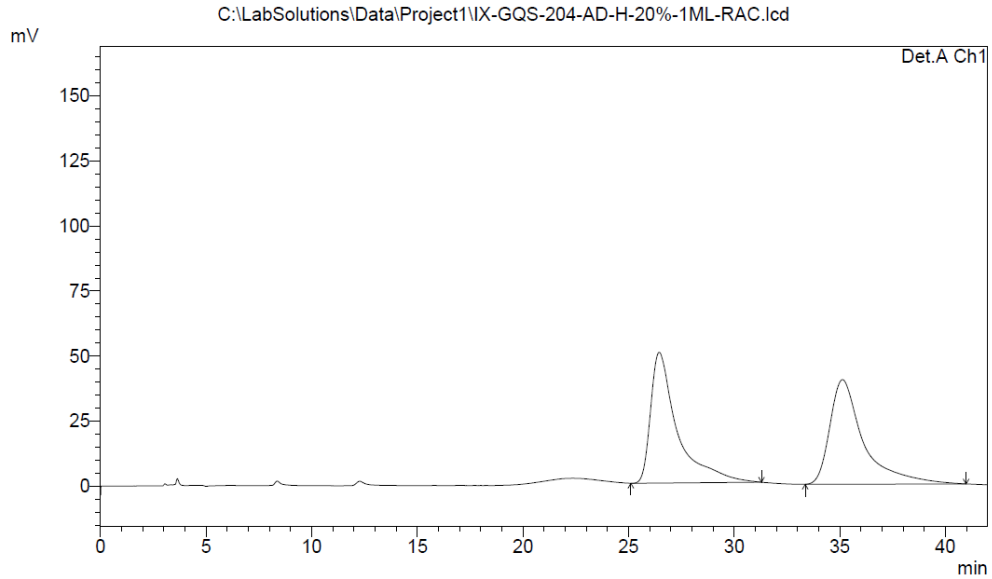
Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.765	1085225	27875	2.145	4.197
2	23.718	49509062	636240	97.855	95.803
Total		50594288	664115	100.000	100.000



(2S,3S)-1-(4-Chlorophenyl)-2,3-diphenyl-3-(tosylamino)propan-1-one (**4I**)

==== Shimadzu LCsolution LC Data Image ====

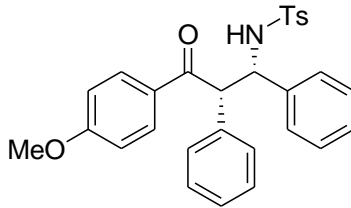
<Chromatogram>



PeakTable

Detector A Ch1 254nm

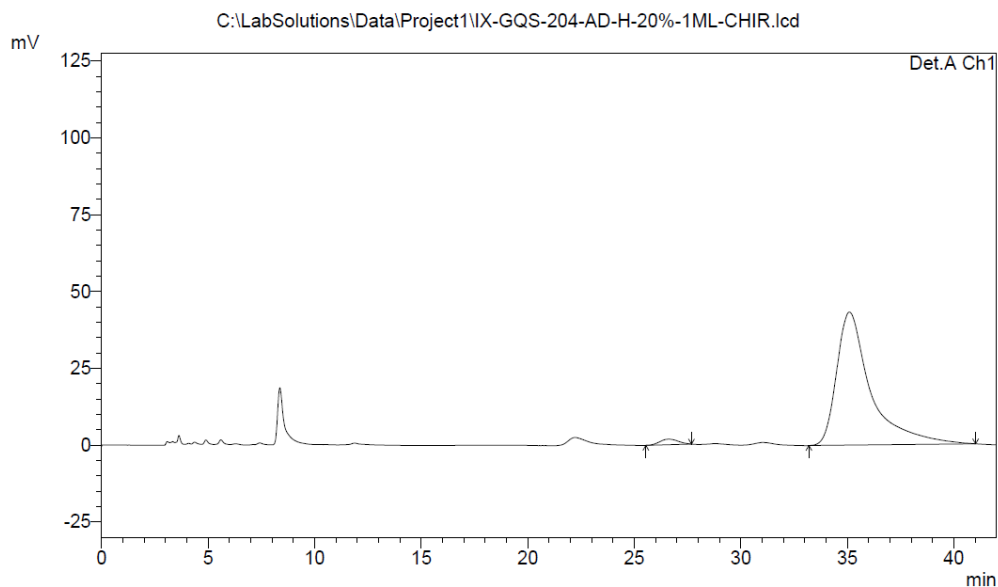
Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.445	4434461	50298	49.932	55.557
2	35.122	4446542	40236	50.068	44.443
Total		8881002	90533	100.000	100.000



(2S*,3S*)-1-(4-Methoxyphenyl)-2,3-diphenyl-3-(tosylamino)propan-1-one (4m)

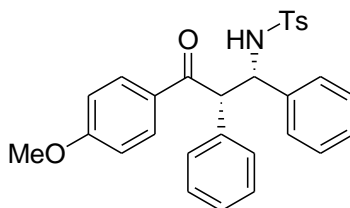
==== Shimadzu LCsolution LC Data Image ====

<Chromatogram>



PeakTable

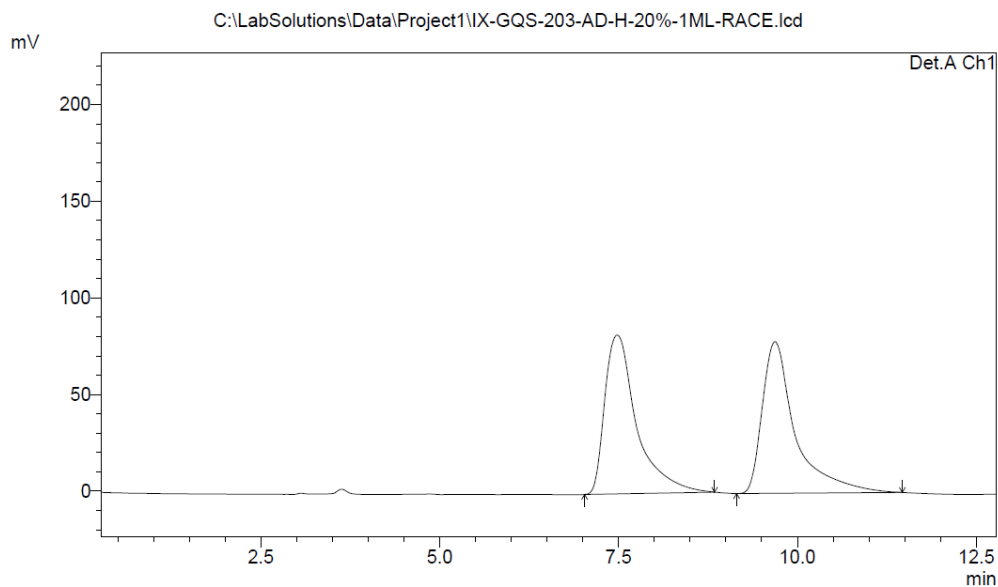
Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.628	109477	1825	2.219	4.046
2	35.092	4825087	43288	97.781	95.954
Total		4934564	45113	100.000	100.000



(2S,3S)-1-(4-Methoxyphenyl)-2,3-diphenyl-3-(tosylamino)propan-1-one (**4m**)

==== Shimadzu LCsolution LC Data Image ====

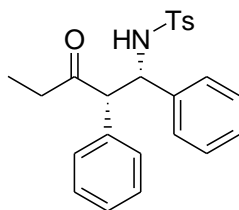
<Chromatogram>



PeakTable

Detector A Ch1 254nm

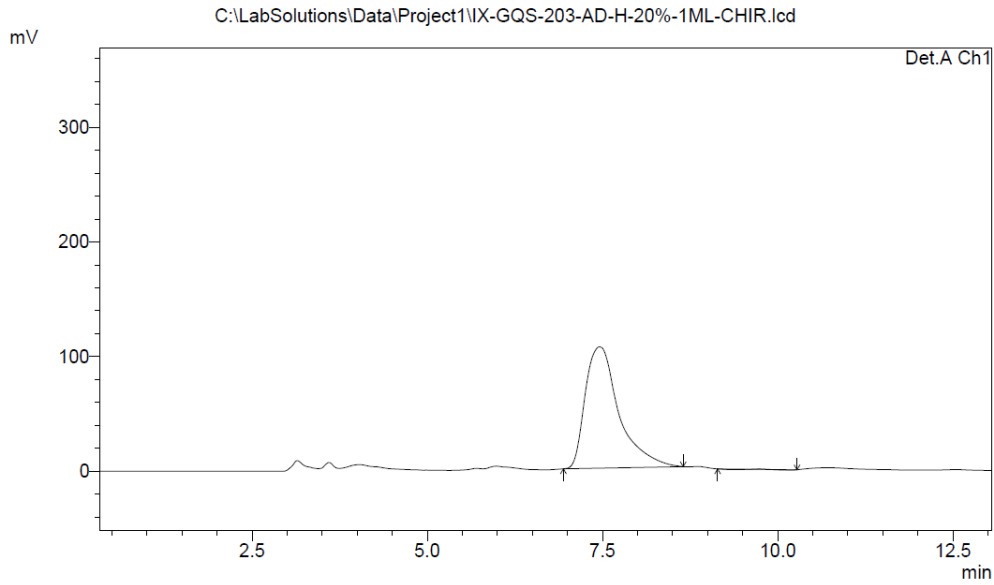
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.477	2537920	82171	50.192	51.146
2	9.683	2518499	78490	49.808	48.854
Total		5056419	160661	100.000	100.000



(1S*,2S*)-1,2-diphenyl-1-(tosylamino)pentan-3-one (**4n**)

==== Shimadzu LCsolution LC Data Image ====

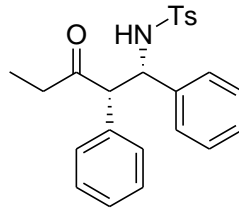
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PeakTable

Detector A Ch1 254nm

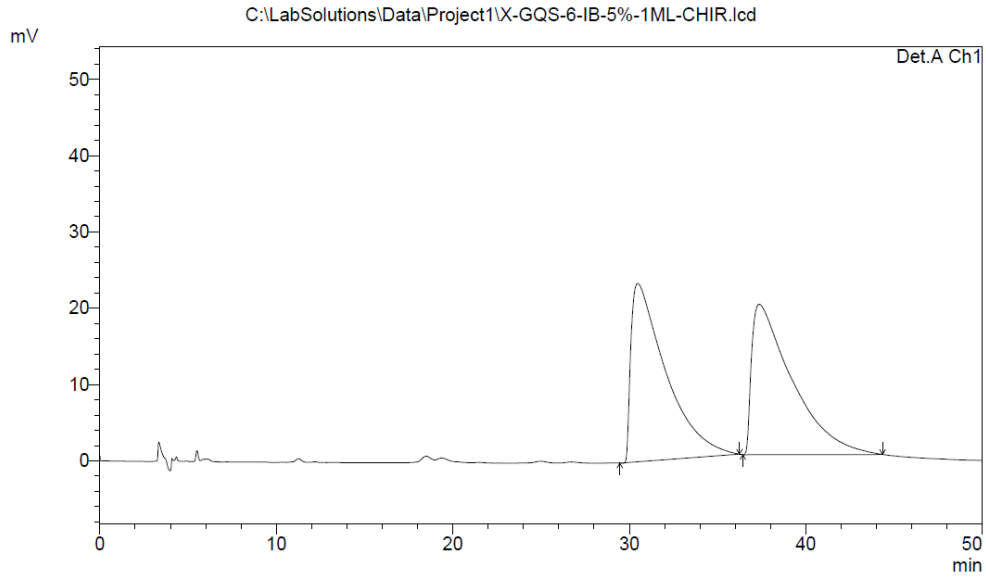
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.458	3543104	106018	100.311	100.035
2	9.150	-10999	-37	-0.311	-0.035
Total		3532105	105982	100.000	100.000



(1S,2S)-1,2-diphenyl-1-(tosylamino)pentan-3-one (**4n**)

==== Shimadzu LCsolution LC Data Image ====

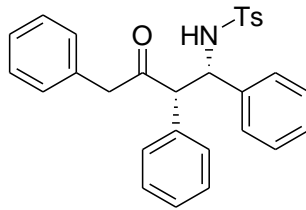
<Chromatogram>



PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	30.467	3203020	23371	50.450	54.237
2	37.353	3145888	19720	49.550	45.763
Total		6348908	43091	100.000	100.000

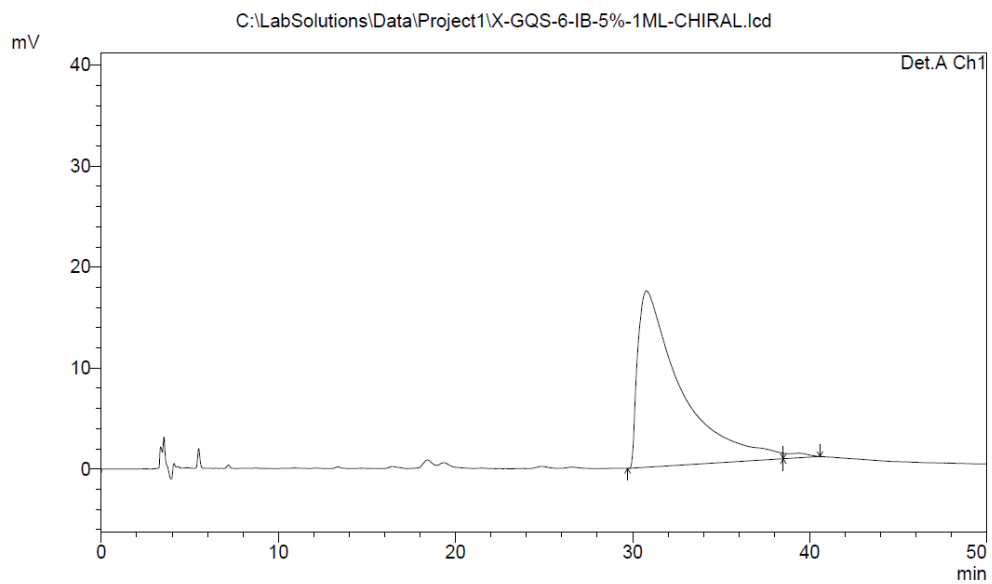
Detector A Ch1 254nm



(3*S**,4*S**)-1,3,4-Triphenyl-4-(tosylamino)butan-2-one (**4o**)

==== Shimadzu LCsolution LC Data Image ====

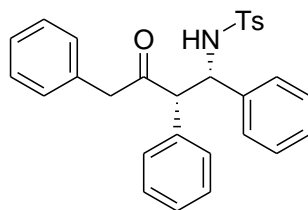
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PeakTable

Detector A Ch1 254nm

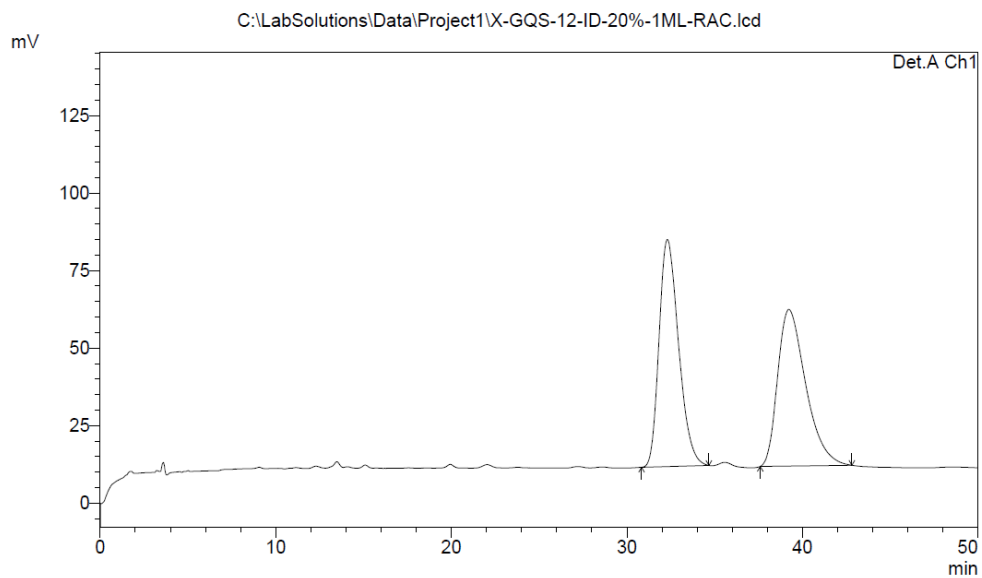
Peak#	Ret. Time	Area	Height	Area %	Height %
1	30.763	2969879	17485	98.643	97.411
2	39.346	40849	465	1.357	2.589
Total		3010728	17950	100.000	100.000



(3S,4S)-1,3,4-Triphenyl-4-(tosylamino)butan-2-one (**4o**)

==== Shimadzu LCsolution LC Data Image ====

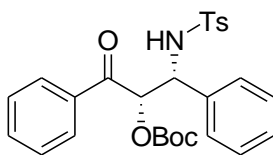
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PeakTable

Detector A Ch1 254nm

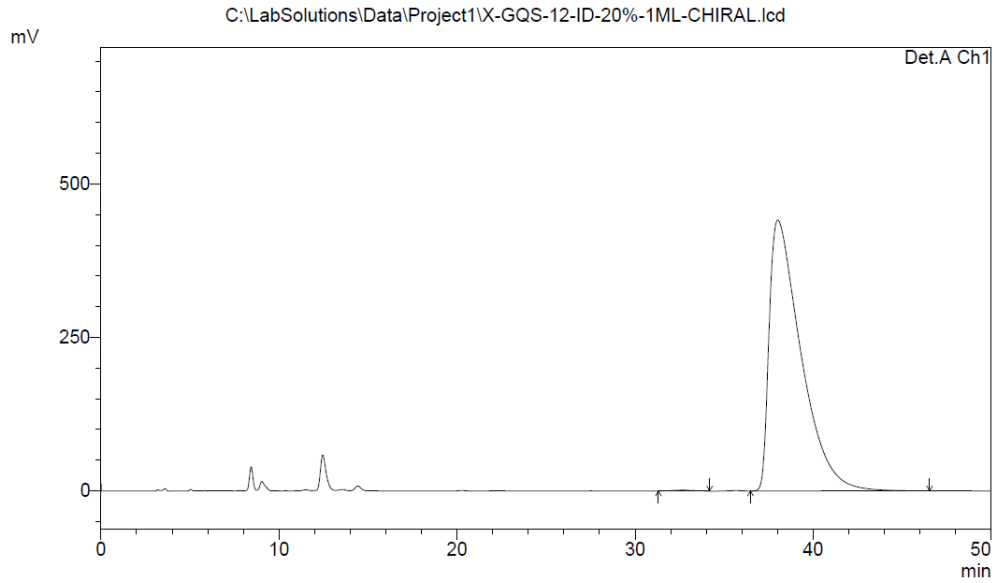
Peak#	Ret. Time	Area	Height	Area %	Height %
1	32.297	5671834	73220	50.329	59.173
2	39.218	5597617	50520	49.671	40.827
Total		11269451	123740	100.000	100.000



(2S*,3R*)-2-*tert*-Butoxycarbonyloxy-1,3-diphenyl-3-(tosylamino)propan-1-one (**4p**)

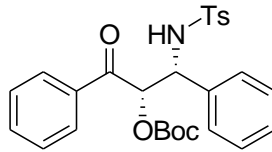
==== Shimadzu LCsolution LC Data Image ====

<Chromatogram>



PeakTable

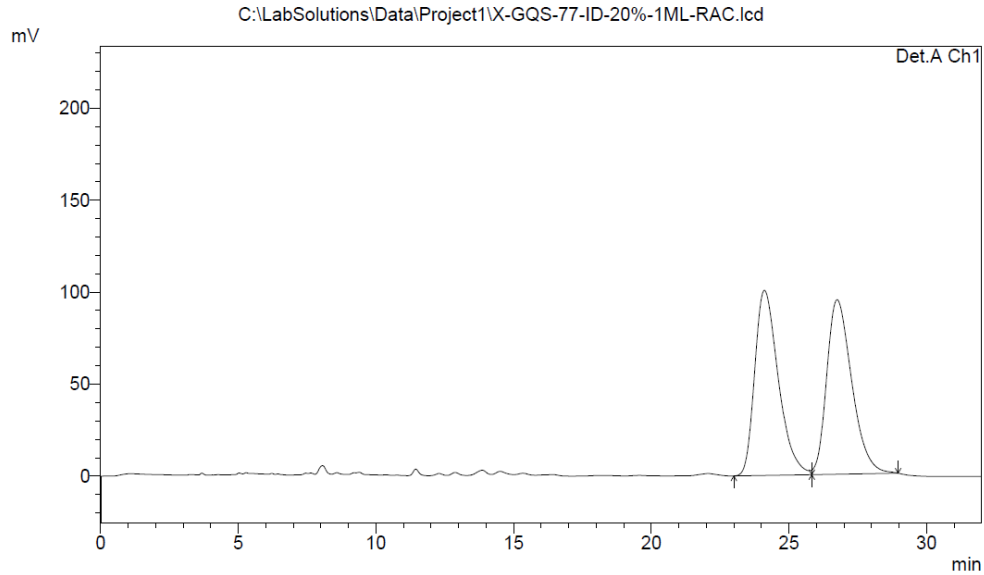
Peak#	Ret. Time	Area	Height	Area %	Height %
1	32.666	83352	1136	0.152	0.257
2	38.005	54671347	441221	99.848	99.743
Total		54754699	442357	100.000	100.000



(2*S*,3*R*)-2-*tert*-Butoxycarbonyloxy-1,3-diphenyl-3-(tosylamino)propan-1-one (**4p**)

==== Shimadzu LCsolution LC Data Image ====

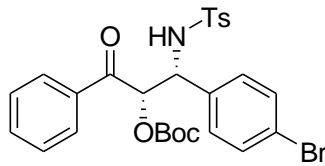
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PeakTable

Detector A Ch1 254nm

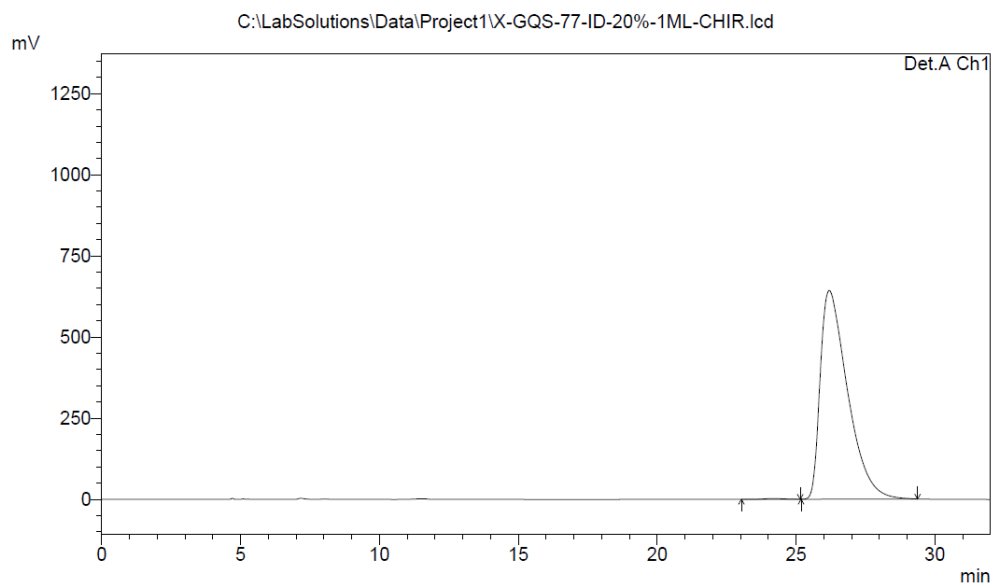
Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.106	6002035	100604	49.995	51.465
2	26.746	6003312	94876	50.005	48.535
Total		12005348	195480	100.000	100.000



(2S*,3R*)-3-(4-Bromophenyl)-2-tert-butoxycarbonyloxy-1-phenyl-3-(tosylamino)propan-1-one (**4q**)

==== Shimadzu LCsolution LC Data Image ====

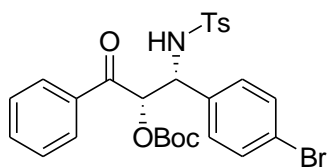
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PeakTable

Detector A Ch1 254nm

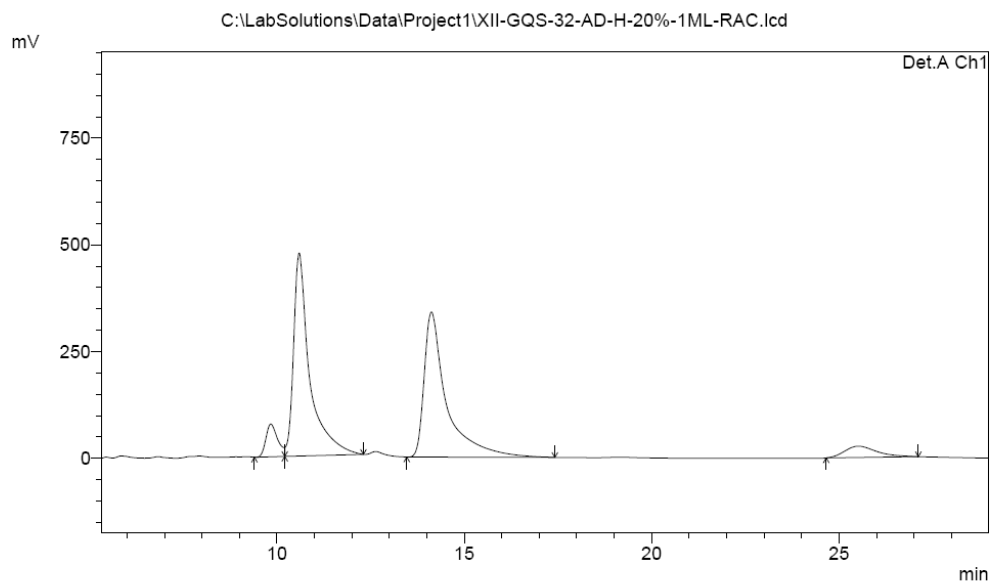
Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.187	119566	2452	0.271	0.380
2	26.191	43980714	643067	99.729	99.620
Total		44100280	645519	100.000	100.000



(2S,3R)-3-(4-Bromophenyl)-2-tert-butoxycarbonyloxy-1-phenyl-3-(tosylamino)propan-1-one (**4q**)

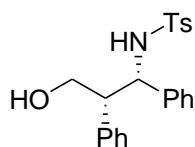
==== Shimadzu LCsolution LC Data Image ====

<Chromatogram>



PeakTable

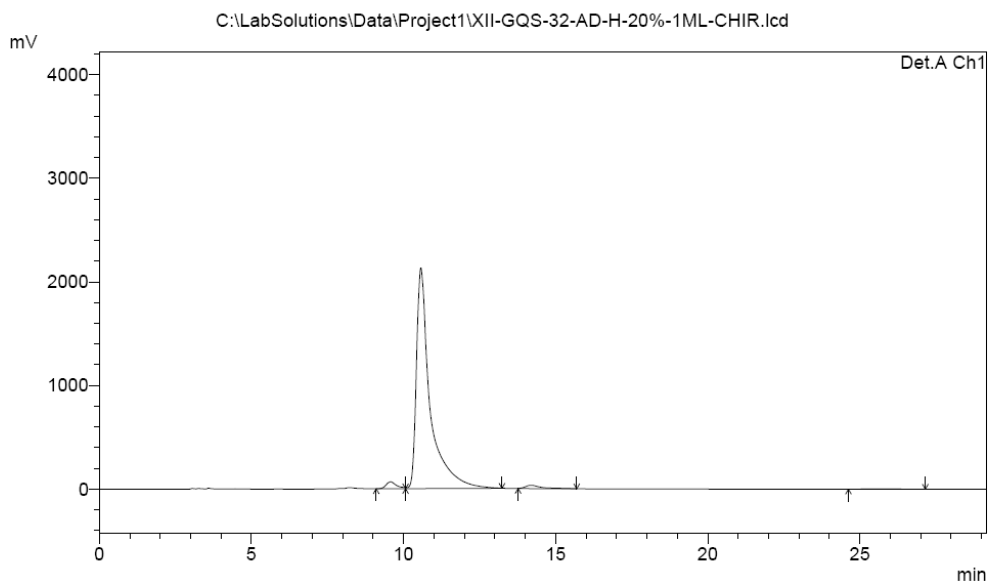
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.832	1683615	76906	5.332	8.370
2	10.589	14204273	475531	44.982	51.755
3	14.118	14110300	339922	44.684	36.996
4	25.514	1579808	26446	5.003	2.878
Total		31577995	918805	100.000	100.000



(2*S**,3*S**)-2,3-diphenyl-3-(tosylamino)propan-1-ol (**13**)

==== Shimadzu LCsolution LC Data Image ====

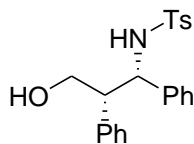
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PeakTable

Detector A Ch1 210nm

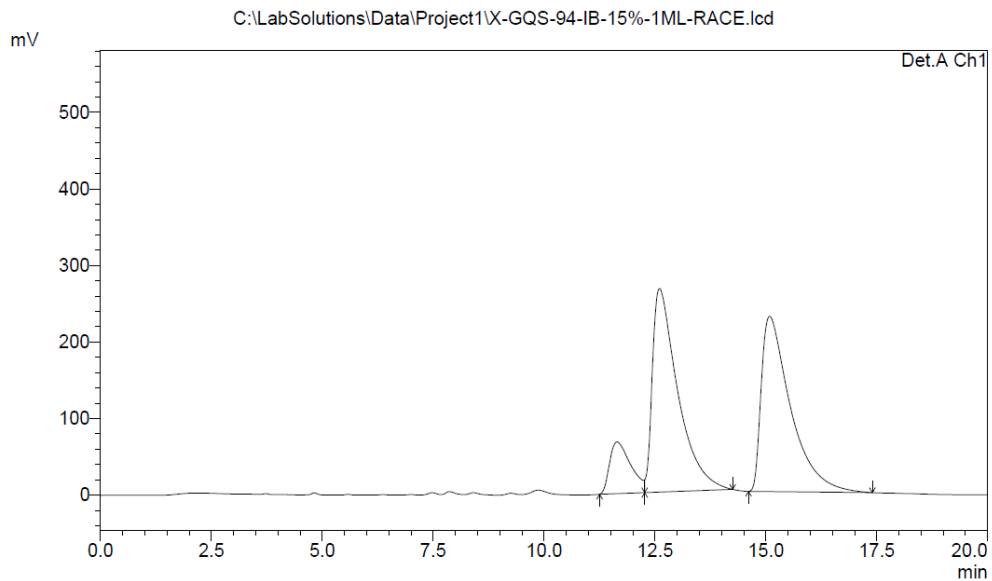
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.562	1597884	67575	2.295	3.030
2	10.566	66839718	2129399	95.979	95.495
3	14.189	1127268	31614	1.619	1.418
4	25.589	74885	1273	0.108	0.057
Total		69639755	2229860	100.000	100.000



(2S,3S)-2,3-diphenyl-3-(tosylamino)propan-1-ol (**13**)

==== Shimadzu LCsolution LC Data Image ====

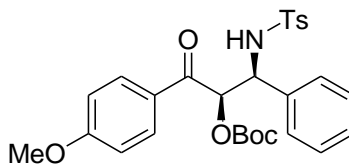
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PeakTable

Detector A Ch1 254nm

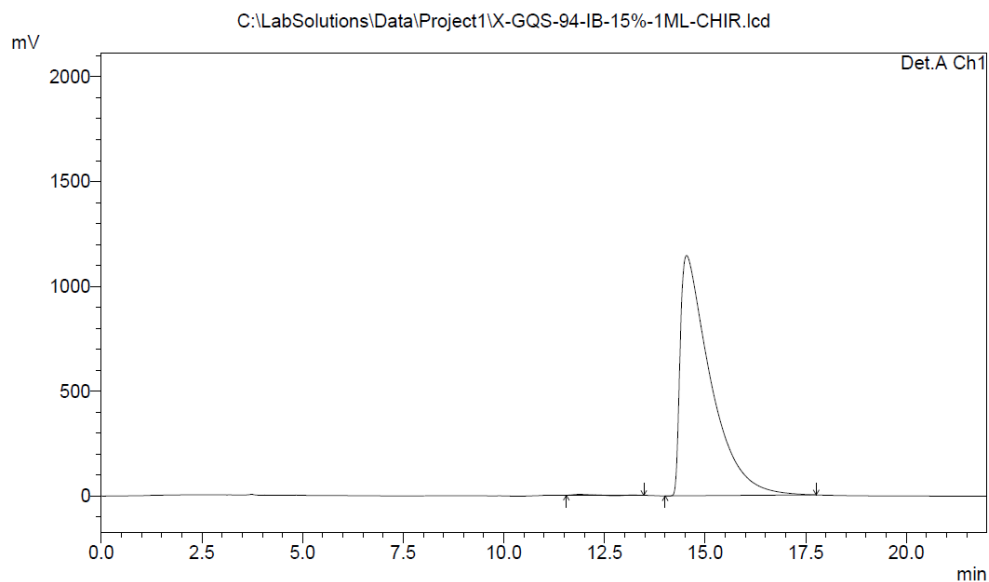
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.641	2231003	67492	9.564	12.001
2	12.598	10591854	265873	45.404	47.275
3	15.080	10505411	229029	45.033	40.724
Total		23328269	562394	100.000	100.000



(2R*,3S*)-2-tert-Butoxycarbonyloxy-1-(4-methoxyphenyl)-3-phenyl-3-(tosylamino)propan-1-one (4r)

==== Shimadzu LCsolution LC Data Image ====

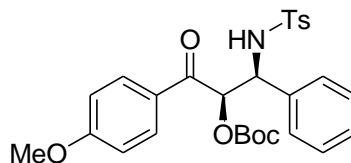
<Chromatogram>



PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.881	132035	4468	0.220	0.388
2	14.535	59814362	1146054	99.780	99.612
Total		59946397	1150523	100.000	100.000

Detector A Ch1 254nm



(2*R*,3*S*)-2-*tert*-Butoxycarbonyloxy-1-(4-methoxyphenyl)-3-phenyl-3-(tosylamino)propan-1-one (**4r**)