Electronic Supplementary Material (ESI) for Chemical Communications

Palladium-catalyzed asymmetric addition of diarylphosphines to *N*-tosylimines

Miao Huang,[b] Chun Li,[b] Jiang Huang,[b] Wei-Liang Duan*[a] and Sheng Xu [b]

[a] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China

[b] School of Chemistry & Molecular Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, China

E-mail: wlduan@mail.sioc.ac.cn

Supporting Information

Table of Contents

General Methods

All air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen or in a glove box under nitrogen. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Varian instrument (400 MHz, 100 MHz and 162 MHz, respectively). ^{1}H, ^{13}C NMR chemical shifts are reported vs tetramethylsilane signal or residual protio solvent signals.

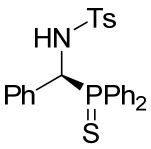
Toluene, Et_2O, THF, methyl *tert*-butyl ether (MTBE) and hexane were distilled over sodium benzophenone ketyl under nitrogen. Dichloromethane was distilled over CaH_2 under nitrogen.

The catalysts **4**,[1] diarylphosphines[2] and tosylimines[3] were synthesized following the literature procedures. All other chemicals and solvents were purchased from commercial company and used as received.

Experimental Details and Characterization Data

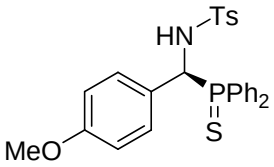
Expermential Procedures for Entry 9, Table 1.

N-tosylimine **1a** (51.9 mg, 0.20 mmol) was added to a solution of (*S*,*S*)-**4** (2.7 mg, 4 μmol Pd) in methyl *tert*-butyl ether (MTBE) (5.0 mL) and the resulting solution was stirred for 15 min at −30 °C, then Diphenylphosphine (39.1 mg, 0.21 mmol) was added to it. The resulting solution was stirred for 4 h at −30 °C, then 10 min at room temperature. The S_8 (51.9 mg, 0.20 mmol) and THF (2 mL)were added to it, and the resulting mixture was stirred for 6.5 h at room temperature. After evaporated solvent under vacumm, the residue was purified by silica gel chromatography with hexane/EtOAc = 5/1 to afford product as a white solid (86.1 mg, 0.180 mmol; 90% yield).



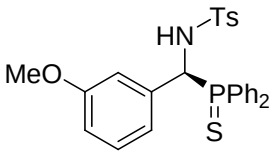
Entry 9. White solid. 90% yield. The ee was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 17.0 min [(*S*)-enantiomer], 29.7 min [(*R*)-enantiomer]. 93% ee. $[\alpha]^{20}_{D}$ = 162 (c 1.03, CH_2Cl_2), The absolute configuration was assigned by analogy with Table 2, entry 4. ^{1}H NMR ($CDCl_3$): δ 8.07 (dd, *J* = 12.1 and 6.8 Hz, 2H), 7.59-7.49 (m, 3H), 7.35-7.30 (m, 5H), 7.16 (td, *J* = 7.6 and 3.2 Hz, 2H), 6.96 (t, *J* = 8.4 Hz, 1H), 6.87-6.76 (m, 6H), 6.05 (dd, *J* = 10.0 and 6.4 Hz, 1H), 5.60 (dd, *J* = 11.6 and 10.4 Hz, 1H), 2.22 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 142.8, 137.3 (d, J_{CP} = 1.5 Hz), 132.0 (d, J_{CP} = 3.0 Hz), 131.9 (d, J_{CP} = 10.4 Hz), 131.75 (d, J_{CP} = 3.0 Hz), 131.74 (d, J_{CP} = 8.9 Hz), 129.9 (d, J_{CP} = 79.6 Hz), 128.94 (d, J_{CP} = 81.8 Hz), 128.90, 128.8, 128.3 (d, J_{CP} = 4.5 Hz), 128.0, 127.9, 127.6 (d, J_{CP} = 3.0 Hz), 127.2 (d, J_{CP} = 2.2 Hz), 126.8, 55.5 (d, J_{CP} = 57.3 Hz), 21.2. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 51.3 (s). HRMS (MALDI) calcd for $C_{26}H_{24}NO_2PS_2Na$ $[M+Na]^+$ 500.0878, found 500.0893.

Experimental Data for Table 2.

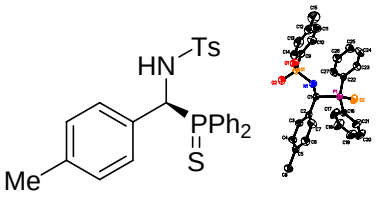


Entry 2. White solid. 98% yield. The ee was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 25.9 min [(*S*)-enantiomer], 48.7 min [(*R*)-enantiomer]. 96% ee. $[\alpha]^{20}_{D}$ = 181 (c 1.04, CH_2Cl_2), The absolute configuration was assigned by analogy with Table 2, entry 4. ^{1}H NMR ($CDCl_3$): δ 8.08-8.02 (m, 2H), 7.59-7.50 (m, 3H), 7.37-7.17 (m, 7H), 6.90 (d, *J* = 8.0 Hz, 2H), 6.70 (dd, *J* = 8.8 and 2.0 Hz, 2H), 6.35 (d, *J* = 8.8 Hz, 2H), 5.94 (dd, *J* = 9.6 and 6.4 Hz, 1H), 5.55 (dd, *J* = 11.2 and 9.6 Hz, 1H), 3.64 (s, 3H), 2.26 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 159.2 (d, J_{CP} = 3.0 Hz), 142.8, 137.5 (d, J_{CP} = 1.5 Hz), 132.00 (d, J_{CP} = 3.0 Hz), 131.9 (d, J_{CP} = 9.6 Hz), 131.78 (d, J_{CP} = 9.7 Hz), 131.77 (d, J_{CP} = 3.0

Hz), 130.14 (d, J_{CP} = 78.8 Hz), 129.6 (d, J_{CP} = 7.4 Hz), 129.15 (d, J_{CP} = 82.6 Hz), 128.94, 128.9 (d, J_{CP} = 12.6 Hz), 128.0 (d, J_{CP} = 11.9 Hz), 126.9, 123.9, 112.8 (d, J_{CP} = 2.2 Hz), 55.09, 55.05 (d, J_{CP} = 58.7 Hz), 21.3. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 48.9 (s). HRMS (MALDI) calcd for $C_{27}H_{26}NO_3PS_2Na$ $[M+Na]^+$ 530.0984, found 530.0973.



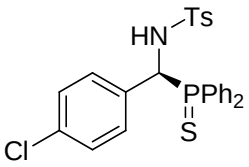
Entry 3. White solid. 84% yield. The ee was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 17.4 min [(*S*)-enantiomer], 30.7 min [(*R*)-enantiomer]. 95% ee. $[\alpha]^{20}_{D}$ = 172 (c 1.01, CH_2Cl_2), The absolute configuration was assigned by analogy with Table 2, entry 4. ^{1}H NMR ($CDCl_3$): δ 8.06 (dd, *J* = 12.0 and 6.8 Hz, 2H), 7.59-7.51 (m, 3H), 7.38-7.32 (m, 5H), 7.19-7.16 (m, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 6.72 (t, *J* = 8.4 Hz, 1H), 6.51 (d, *J* = 7.6 Hz, 1H), 6.33-6.30 (m, 2H), 6.04 (dd, *J* = 9.6 and 6.4 Hz, 1H), 5.58 (t, *J* = 10.8 Hz, 1H), 3.46 (s, 3H), 2.24 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 158.5 (d, J_{CP} = 2.2 Hz), 142.9, 137.3 (d, J_{CP} = 1.5 Hz), 133.1, 132.0 (d, J_{CP} = 3.8 Hz), 131.9 (d, J_{CP} = 9.6 Hz), 131.8 (d, J_{CP} = 3.0 Hz), 131.7 (d, J_{CP} = 8.9 Hz), 130.0 (d, J_{CP} = 79.6 Hz), 129.0 (d, J_{CP} = 81.8 Hz), 128.9, 128.85 (d, J_{CP} = 11.9 Hz), 128.2 (d, J_{CP} = 2.2 Hz), 127.9 (d, J_{CP} = 12.7 Hz), 126.8, 121.1 (d, J_{CP} = 5.2 Hz), 114.3 (d, J_{CP} = 2.9 Hz), 112.9 (d, J_{CP} = 3.7 Hz), 55.5 (d, J_{CP} = 57.2 Hz), 54.8, 21.2. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 51.2 (s). HRMS (MALDI) calcd for $C_{27}H_{26}NO_3PS_2Na$ $[M+Na]^+$ 530.0984, found 530.0971.



Entry 4. White solid. 93% yield. The ee was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 21.8 min [(*S*)-enantiomer], 37.8 min [(*R*)-enantiomer]. 94% ee. $[\alpha]^{20}_{D}$ = 165 (c 1.11,

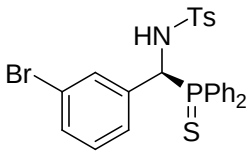
CH_2Cl_2), The absolute configuration was determined to be *S* by the X-ray crystal diffraction analysis of the product.

^{1}H NMR ($CDCl_3$): δ 8.05 (dd, *J* = 12.8 and 7.6 Hz, 2H), 7.58-7.50 (m, 3H), 7.39-7.16 (m, 7H), 6.87 (d, *J* = 8.0 Hz, 2H), 6.64 (q, *J* = 8.0 Hz, 4H), 5.95 (dd, *J* = 10.0 and 6.4 Hz, 1H), 5.57 (t, *J* = 10.4 Hz, 1H), 2.25 (s, 3H), 2.13 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 142.8, 137.5 (d, J_{CP} = 3.0 Hz), 137.4 (d, J_{CP} = 2.2 Hz), 132.0 (d, J_{CP} = 2.9 Hz), 131.9 (d, J_{CP} = 1.5 Hz), 131.8 (d, J_{CP} = 8.9 Hz), 131.7 (d, J_{CP} = 3.0 Hz), 130.1 (d, J_{CP} = 79.5 Hz), 129.1 (d, J_{CP} = 82.6 Hz), 128.9, 128.8 (d, J_{CP} = 11.9 Hz), 128.7, 128.3 (d, J_{CP} = 4.4 Hz), 128.0 (d, J_{CP} = 6.7 Hz), 127.9 (d, J_{CP} = 8.1 Hz), 126.8, 55.4 (d, J_{CP} = 58.1 Hz), 21.3, 20.9. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 50.9 (s). HRMS (MALDI) calcd for $C_{27}H_{26}NO_2PS_2Na$ $[M+Na]^+$ 514.1035, found 514.1054.

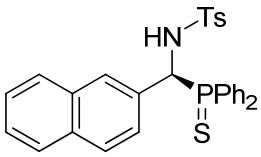


Entry 5. White solid. 99% yield. The ee was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 22.9 min [(*S*)-enantiomer], 58.0 min [(*R*)-enantiomer]. 86% ee. $[\alpha]^{20}_D$ = 179 (c 1.11, CH_2Cl_2), The absolute configuration was assigned by analogy with Table 2, entry 4.

^{1}H NMR ($CDCl_3$): δ 8.07-8.02 (m, 2H), 7.61-7.19 (m, 10H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.78 (d, *J* = 8.4 Hz, 2H), 6.69 (dd, *J* = 8.8 and 2.0 Hz, 2H), 5.97 (dd, *J* = 9.6 and 6.4 Hz, 1H), 5.56 (dd, *J* = 12.0 and 10.4 Hz, 1H), 2.29 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 143.4, 137.2 (d, J_{CP} = 1.5 Hz), 133.9 (d, J_{CP} = 3.0 Hz), 132.2 (d, J_{CP} = 3.0 Hz), 132.1 (d, J_{CP} = 3.0 Hz), 131.9 (d, J_{CP} = 10.4 Hz), 131.7 (d, J_{CP} = 9.7 Hz), 130.5, 129.8 (d, J_{CP} = 79.6 Hz), 129.6 (d, J_{CP} = 4.4 Hz), 129.1, 129.0 (d, J_{CP} = 11.9 Hz), 128.7 (d, J_{CP} = 82.6 Hz), 128.2 (d, J_{CP} = 12.6 Hz), 127.4 (d, J_{CP} = 2.2 Hz), 126.8, 54.9 (d, J_{CP} = 57.3 Hz), 21.3. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 50.9 (s). HRMS (MALDI) calcd for $C_{26}H_{23}NO_2PS_2ClNa$ $[M+Na]^+$ 534.0489, found 534.0490.

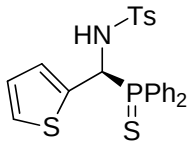


Entry 6. White solid. 89% yield. The ee was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 12.2 min [(*S*)-enantiomer], 22.1 min [(*R*)-enantiomer]. 78% ee. $[\alpha]^{20}_{D}$ = 128 (c 1.14, CH_2Cl_2), The absolute configuration was assigned by analogy with Table 2, entry 4. ^{1}H NMR ($CDCl_3$): δ 8.05 (dd, *J* = 12.4 and 7.2 Hz, 2H), 7.61-7.19 (m, 10H), 7.08 (d, *J* = 6.8 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 2H), 6.79, 6.68-6.63 (m, 2H), 5.98 (dd, *J* = 9.6 and 7.2 Hz, 1H), 5.52 (t, *J* = 10.8 Hz, 1H), 2.28 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 143.3, 137.0 (d, J_{CP} = 1.5 Hz), 133.9, 132.2 (d, J_{CP} = 3.0 Hz), 132.1 (d, J_{CP} = 3.0 Hz), 131.9 (d, J_{CP} = 9.7 Hz), 131.7 (d, J_{CP} = 9.7 Hz), 131.3 (d, J_{CP} = 3.8 Hz), 130.5 (d, J_{CP} = 3.0 Hz), 129.6 (d, J_{CP} = 81.1 Hz), 129.1, 129.0 (d, J_{CP} = 11.9 Hz), 128.6 (d, J_{CP} = 2.2 Hz), 128.5 (d, J_{CP} = 82.6 Hz), 128.1 (d, J_{CP} = 12.7 Hz), 126.9 (d, J_{CP} = 5.2 Hz), 126.7, 121.4 (d, J_{CP} = 3.0 Hz), 55.0 (d, J_{CP} = 55.6 Hz), 21.3. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 51.2 (s). HRMS (MALDI) calcd for $C_{26}H_{23}NO_2BrPS_2Na$ $[M+Na]^+$ 577.9983, found 577.9987.

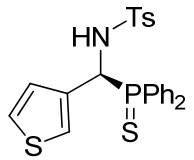


Entry 7. White solid. 86% yield. The ee was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 21.1 min [(*S*)-enantiomer], 38.9 min [(*R*)-enantiomer]. 85% ee. $[\alpha]^{20}_{D}$ = 155 (c 1.07, CH_2Cl_2), The absolute configuration was assigned by analogy with Table 2, entry 4. ^{1}H NMR ($CDCl_3$): δ 8.13-8.08 (m, 2H), 7.61-7.54 (m, 4H), 7.42-7.23 (m, 9H), 7.18 (s, 1H), 7.10 (td, *J* = 7.6 and 2.8 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.59 (d, *J* = 8.0 Hz, 2H), 6.10 (dd, *J* = 10.0 and 6.4 Hz, 1H), 5.75 (t, *J* = 11.6 and 10.4 Hz, 1H), 1.89 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 143.0, 137.3 (d, J_{CP} = 1.5 Hz), 132.5 (d, J_{CP} = 2.2 Hz), 132.2 (d, J_{CP} = 2.2 Hz), 132.1 (d, J_{CP} = 3.0 Hz), 132.0 (d, J_{CP} = 9.7 Hz), 131.9, 131.8

(d, J_{CP} = 9.7 Hz), 130.3 (d, J_{CP} = 79.6 Hz), 129.0, 128.90 (d, J_{CP} = 82.5 Hz), 128.86 (d, J_{CP} = 6.0 Hz), 128.7, 128.4 (d, J_{CP} = 5.9 Hz), 128.0 (d, J_{CP} = 11.9 Hz), 127.8 (d, J_{CP} = 1.5 Hz), 127.2 (d, J_{CP} = 1.4 Hz), 126.9 (d, J_{CP} = 1.5 Hz), 126.7, 126.1, 125.8, 125.7 (d, J_{CP} = 3.0 Hz), 55.8 (d, J_{CP} = 57.3 Hz), 20.9. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 50.7 (s). HRMS (MALDI) calcd for $C_{26}H_{23}NO_2BrPS_2Na$ $[M+Na]^+$ 577.9983, found 577.9987.

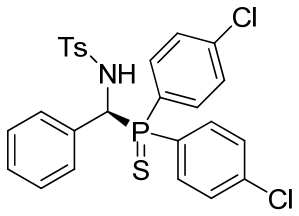


Entry 8. White solid. 90% yield. The ee was determined on a Daicel Chiralpak IC column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 21.8 min [(*S*)-enantiomer], 25.8 min [(*R*)-enantiomer]. 91% ee. $[\alpha]^{20}_D$ = 114 (c 1.00, CH_2Cl_2), the absolute configuration was assigned by analogy with Table 2, entry 4. ^1H NMR ($CDCl_3$): δ 8.08-8.01 (m, 2H), 7.60-7.47 (m, 5H), 7.39-7.23 (m, 5H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.91 (dt, *J* = 5.2 and 1.2 Hz, 1H), 6.56-6.54 (m, 1H), 6.51 (dd, *J* = 4.8 and 4.0 Hz, 1H), 5.91 (q, *J* = 10.4 Hz, 1H), 5.90-8.83 (m, 1H), 2.29 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 142.9, 137.3 (d, J_{CP} = 1.1 Hz), 134.9, 132.0 (d, J_{CP} = 2.9 Hz), 131.9 (d, J_{CP} = 3.5 Hz), 131.8 (d, J_{CP} = 7.0 Hz), 131.6 (d, J_{CP} = 7.0 Hz), 129.8 (d, J_{CP} = 72.2 Hz), 129.0, 128.8 (d, J_{CP} = 12.2 Hz), 128.6 (d, J_{CP} = 75.1 Hz), 128.07 (d, J_{CP} = 12.8 Hz), 128.06, 126.7, 126.3 (d, J_{CP} = 2.9 Hz), 125.85 (d, J_{CP} = 2.3 Hz), 52.2 (d, J_{CP} = 62.8 Hz), 21.3. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 51.7 (s). HRMS (ESI) calcd for $C_{24}H_{22}NO_2PS_3Na$ $[M+Na]^+$ 483.0550, found 483.0560.

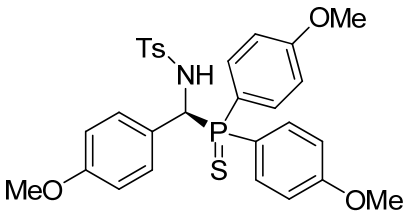


Entry 9. White solid. 95% yield. The ee was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 20.3 min [(*S*)-enantiomer], 26.5 min [(*R*)-enantiomer]. 86% ee. $[\alpha]^{20}_D$ = 122 (c 1.01, CH_2Cl_2), the absolute configuration was assigned by analogy with Table 2, entry 4.

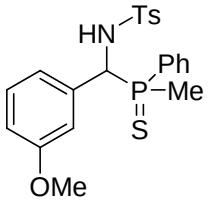
^{1}H NMR ($CDCl_3$): δ 8.01 (dd, J = 12.4 and 7.2 Hz, 2H), 7.58-7.51 (m, 3H), 7.43-7.34 (m, 5H), 7.24-7.18 (m, 2H), 6.91 (d, J = 8.0 Hz, 2H), 6.76 (dd, J = 4.8 and 3.2 Hz, 1H), 6.66 (s, 1H), 6.55 (d, J = 4.8 Hz, 1H), 6.93-5.88 (m, 1H), 5.77 (t, J = 10.4 Hz, 1H), 2.27 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 142.8, 137.3 (d, J_{CP} = 1.5 Hz), 132.8 (d, J_{CP} = 0.8 Hz), 131.9 (d, J_{CP} = 2.9 Hz), 131.8, 131.7 (d, J_{CP} = 9.7 Hz), 131.6 (d, J_{CP} = 10.1 Hz), 129.9 (d, J_{CP} = 79.1 Hz), 129.0 (d, J_{CP} = 83.6 Hz), 128.9, 128.7 (d, J_{CP} = 11.2 Hz), 128.0 (d, J_{CP} = 12.2 Hz), 126.8 (d, J_{CP} = 3.0 Hz), 126.6, 124.4 (d, J_{CP} = 1.4 Hz), 124.3 (d, J_{CP} = 7.0 Hz), 52.1 (d, J_{CP} = 60.6 Hz), 21.3. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 50.2 (s).



Entry 10. White solid. 97% yield. The ee was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 11.5 min [(*S*)-enantiomer], 32.7 min [(*R*)-enantiomer]. 86% ee. $[\alpha]^{20}_{D}$ = 158 (c 1.03, CH_2Cl_2), The absolute configuration was assigned by analogy with Table 2, entry 4. ^{1}H NMR ($CDCl_3$): δ 7.98 (dd, J = 12.0 and 8.4 Hz, 2H), 7.48 (dd, J = 8.4 and 2.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 7.24-7.21 (m, 2H), 7.18 (s, 1H), 7.16 (dd, J = 8.4 and 2.4 Hz, 2H), 7.02 (t, J = 6.8 Hz, 1H), 6.89-6.79 (m, 6H), 6.03-5.99 (m, 1H), 5.56 (t, J = 11.2 Hz, 1H), 2.25 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 143.2, 139.0 (d, J_{CP} = 3.0 Hz), 138.8 (d, J_{CP} = 3.7 Hz), 137.1 (d, J_{CP} = 1.5 Hz), 133.22 (d, J_{CP} = 10.5 Hz), 133.20 (d, J_{CP} = 10.4 Hz), 131.5, 129.3 (d, J_{CP} = 12.6 Hz), 129.0, 128.4 (d, J_{CP} = 6.4 Hz), 128.3, 128.2 (d, J_{CP} = 57.2 Hz), 128.0 (d, J_{CP} = 2.9 Hz), 127.5 (d, J_{CP} = 2.9 Hz), 127.4 (d, J_{CP} = 59.5 Hz), 126.8, 55.7 (d, J_{CP} = 58.7 Hz), 21.3. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 49.9 (s). HRMS (MALDI) calcd for $C_{26}H_{22}NO_2PS_2Cl_2Na$ $[M+Na]^+$ 568.0099, found 568.0093.



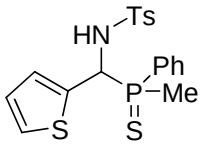
Entry 11. White solid. 89% yield. The ee was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol = 70/30, flow = 1.0 mL/min. Retention times: 19.5 min [(*S*)-enantiomer], 34.7 min [(*R*)-enantiomer]. 84% ee. $[\alpha]^{20}_{D}$ = 158 (c 1.04, CH_2Cl_2), The absolute configuration was assigned by analogy with Table 2, entry 4. ^{1}H NMR ($CDCl_3$): δ 7.94 (dd, *J* = 11.6 and 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.24 (dd, *J* = 12.4 and 8.4 Hz, 2H), 7.01 (dd, *J* = 8.8 and 2.4 Hz, 2H), 6.91 (d, *J* = 8.0 Hz, 2H), 6.73 (dd, *J* = 8.8 and 2.8 Hz, 2H), 6.69 (dd, *J* = 8.8 and 2.4 Hz, 2H), 6.39 (d, *J* = 8.4 Hz, 2H), 5.95-5.91 (m, 1H), 5.43 (dd, *J* = 11.2 and 10.4 Hz, 1H), 3.87 (s, 3H), 3.73 (s, 3H), 3.66 (s, 3H), 2.27 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 162.5 (d, J_{CP} = 3.1 Hz), 162.3 (d, J_{CP} = 3.1 Hz), 159.2 (d, J_{CP} = 2.7 Hz), 142.7, 137.6 (d, J_{CP} = 1.5 Hz), 133.9 (d, J_{CP} = 11.6 Hz), 133.6 (d, J_{CP} = 10.8 Hz), 129.6 (d, J_{CP} = 4.7 Hz), 128.9, 126.9, 124.3, 120.9 (d, J_{CP} = 12.6 Hz), 120.5 (d, J_{CP} = 89.4 Hz), 114.4 (d, J_{CP} = 13.2 Hz), 113.5 (d, J_{CP} = 13.6 Hz), 112.8 (d, J_{CP} = 2.3 Hz), 55.5 (d, J_{CP} = 58.8 Hz), 55.4, 55.3, 55.1, 21.3 (d, J_{CP} = 2.4 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 49.6 (s). HRMS (MALDI) calcd for $C_{29}H_{30}NO_5PS_2Na$ $[M+Na]^+$ 590.1195, found 590.1176.



Entry 12. White solid. 96% yield. dr = 1 : 0.9.

Major diastereomer: ^{1}H NMR ($CDCl_3$): δ 7.52 (dd, *J* = 12.6 and 7.8 Hz, 2H), 7.44-7.30 (m, 5H), 6.97 (d, *J* = 7.8 Hz, 2H), 6.73 (t, *J* = 7.8, 1H), 6.50 (d, *J* = 8.4 Hz, 1H), 6.22 (d, *J* = 7.5 Hz, 1H), 6.15-6.09 (m, 2H), 4.90 (t, *J* = 9.9 Hz, 1H), 3.44 (s, 3H), 2.26 (s, 3H), 2.22 (d, *J* = 6.9 Hz, 3H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 50.3 (s).

Minor diastereomer: ^{1}H NMR ($CDCl_3$): δ 7.82 (dd, *J* = 12.9 and 7.5 Hz, 2H), 7.57-7.43 (m, 3H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.10 (t, *J* = 8.1, 1H), 6.93 (d, *J* = 8.1 Hz, 2H), 6.76-6.71 (m, 1H), 6.67 (s, 1H), 5.96 (t, *J* = 8.1 Hz, 1H), 4.82 (t, *J* = 11.7 and 9.0 Hz, 1H), 3.66 (s, 3H), 2.29 (s, 3H), 1.64 (d, *J* = 12.9 Hz, 3H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 48.7 (s).



Entry 13. White solid. 87% yield. dr = 1.5:1. The ee of the minor diastereomer was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 12.1 min, 13.8 min. 16% ee.

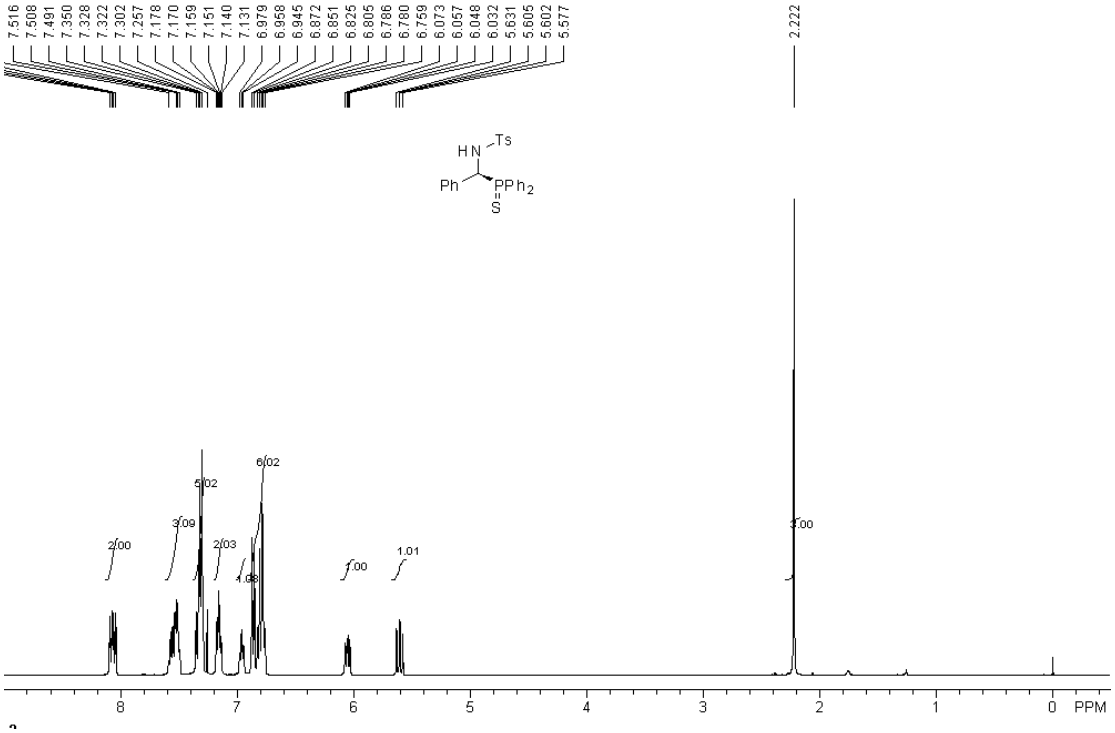
Major diastereomer: ^{1}H NMR ($CDCl_3$): δ 7.86 (dd, *J* = 12.6 and 8.1 Hz, 2H), 7.57-7.46 (m, 3H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.16 (t, *J* = 5.1, 1H), 6.98 (d, *J* = 7.8 Hz, 2H), 6.86-6.82 (m, 1H), 6.82 (t, *J* = 4.8 Hz, 1H), 5.76 (dd, *J* = 9.0 and 6.3 Hz, 1H), 5.21 (dd, *J* = 11.1 and 9.6 Hz, 1H), 2.31 (s, 3H), 1.75 (d, *J* = 12.9 Hz, 3H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 49.0 (s).

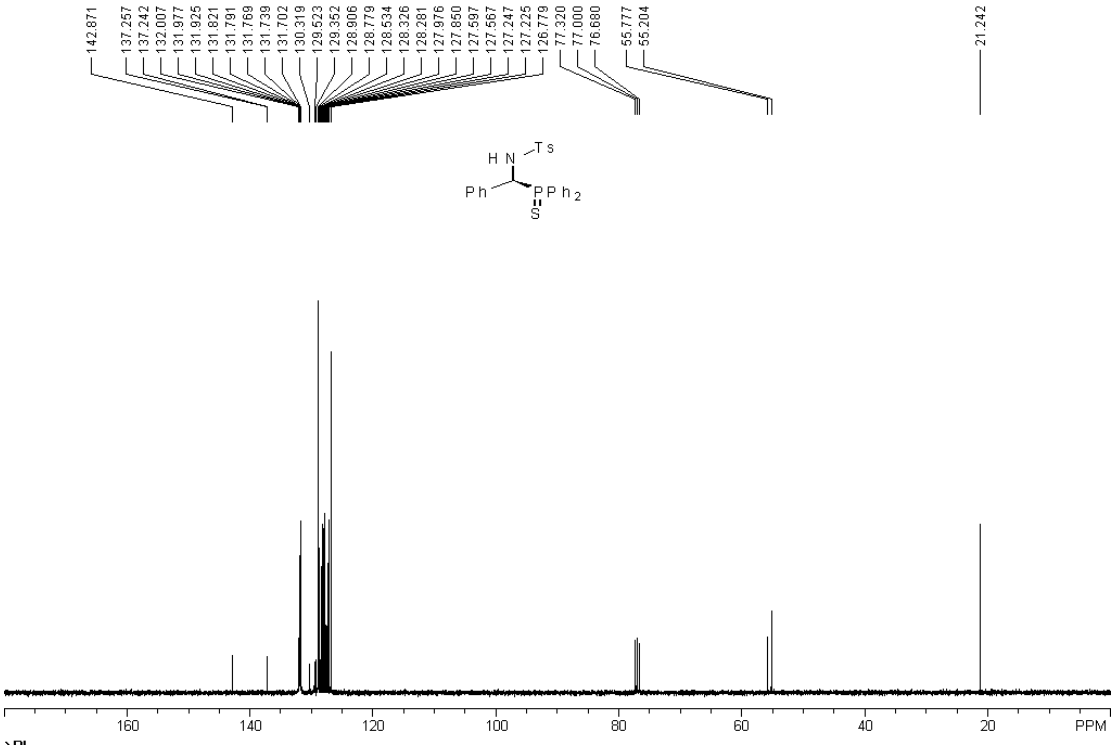
Minor diastereomer: ^{1}H NMR ($CDCl_3$): δ 7.64 (dd, *J* = 8.4 and 7.2 Hz, 2H), 7.60-7.33 (m, 5H), 7.04 (d, *J* = 8.1 Hz, 2H), 6.87 (t, *J* = 5.1, 1H), 6.49 (d, *J* = 3.9 Hz, 1H), 6.40-6.37 (m, 1H), 5.95 (dd, *J* = 9.9 and 4.5 Hz, 1H), 5.28 (t, *J* = 11.5 Hz, 1H), 2.29 (s, 3H), 2.24 (d, *J* = 12.6 Hz, 3H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 50.5 (s). HRMS (ESI) calcd for $C_{19}H_{20}NO_2PS_3Na$ $[M+Na]^+$ 421.0394, found 421.0406.

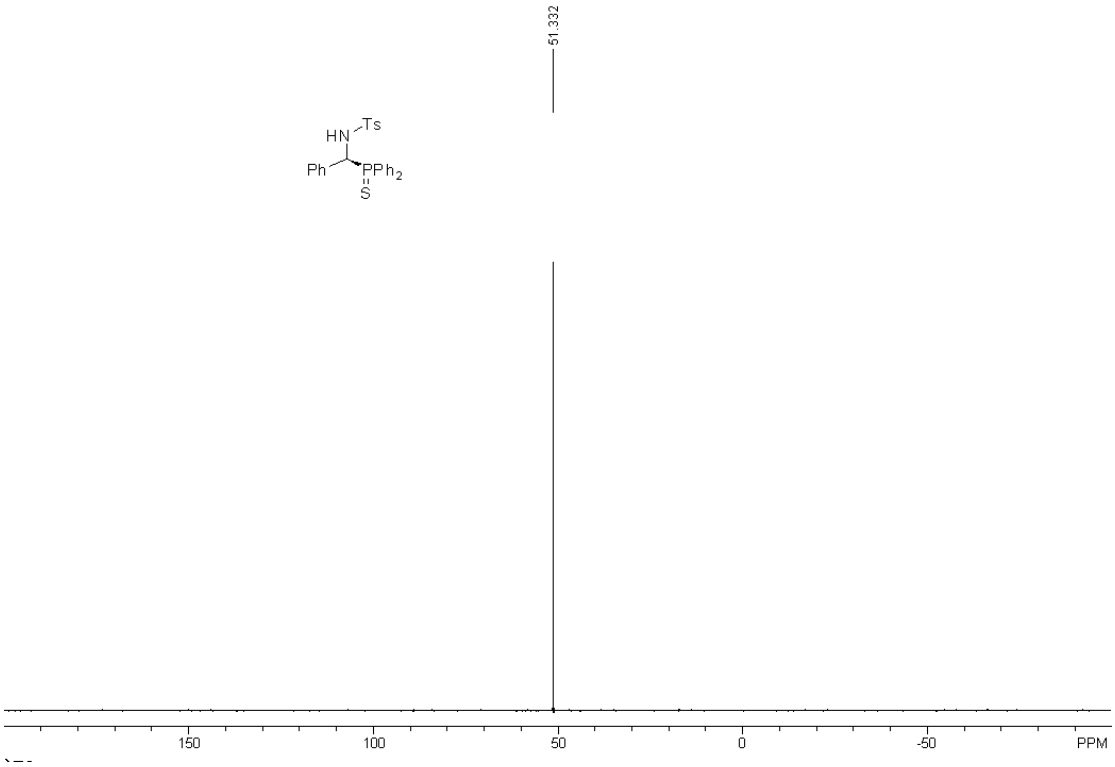
References:

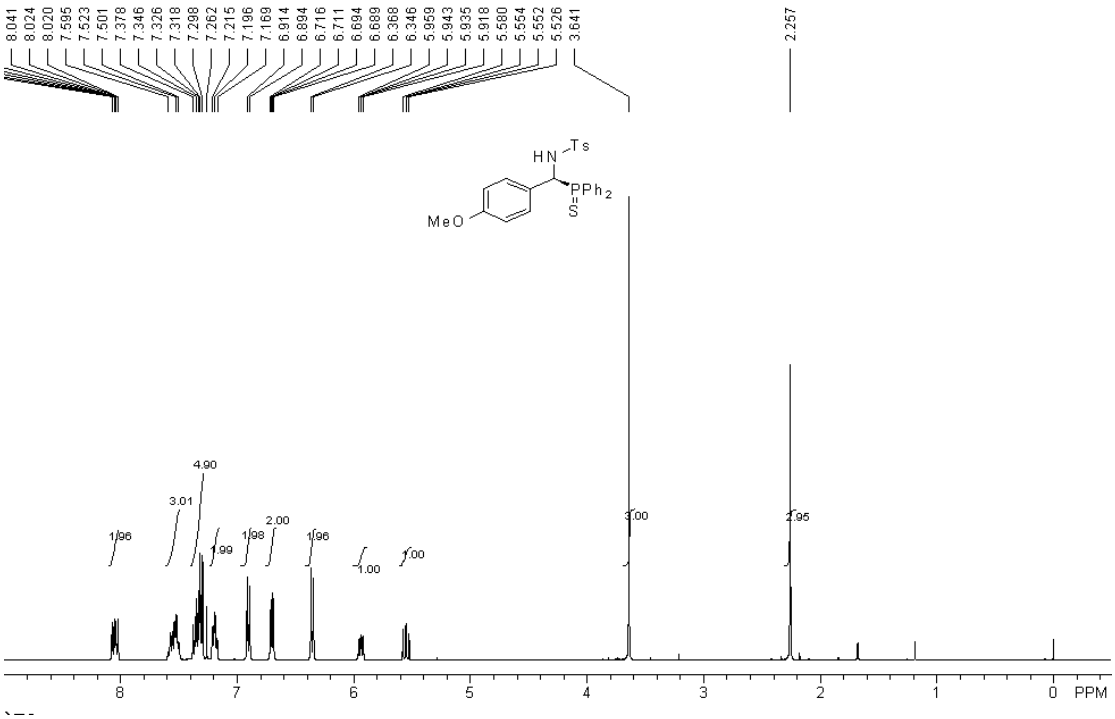
(1) Feng.; J.-J.; Chen, X.-F.; Shi, M.; Duan, W.-L. *J. Am. Chem. Soc*. **2010**, *132*, 5562.
(2) Herseczki, Z.; Gergely, I.; Hegedüs, C.; Szöllősy, A.; Bakos, J. *Tetrahedron*: *Asymmetry* **2004**, *15*, 1673.
(3) Fan, R.; Pu, Do., Qin, L., Wen, F., Yao, G., Wu, J. *J. Org. Chem*. **2007**, *72*, 3149.

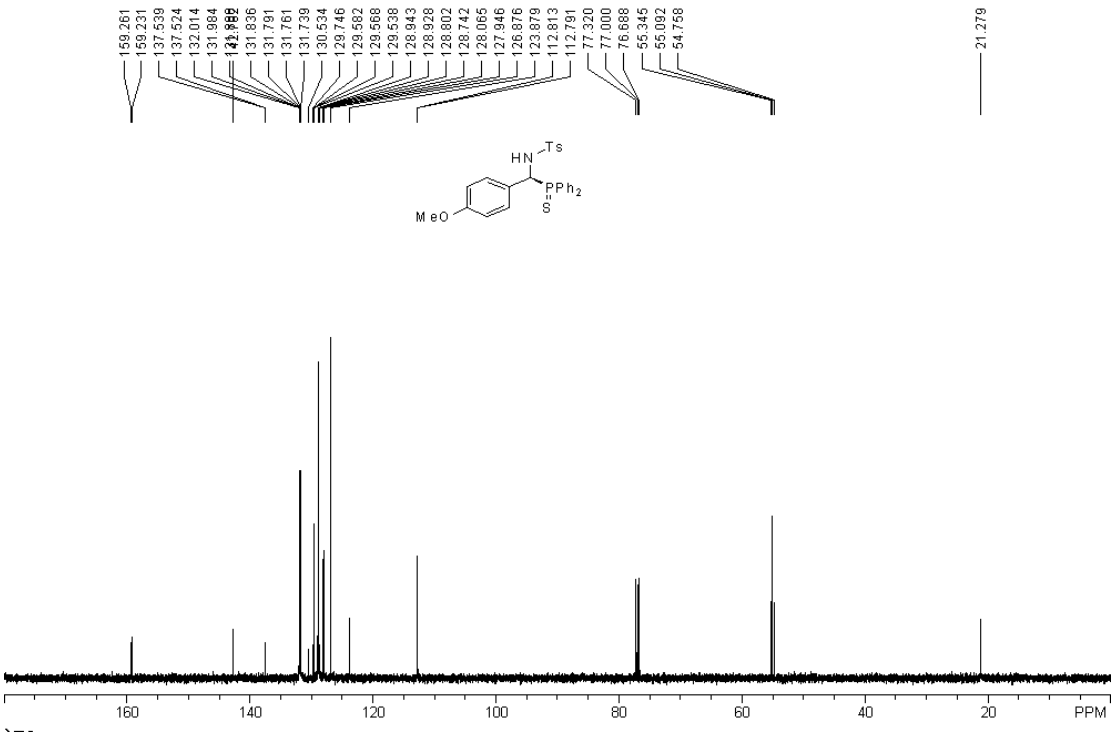
NMR Spectra

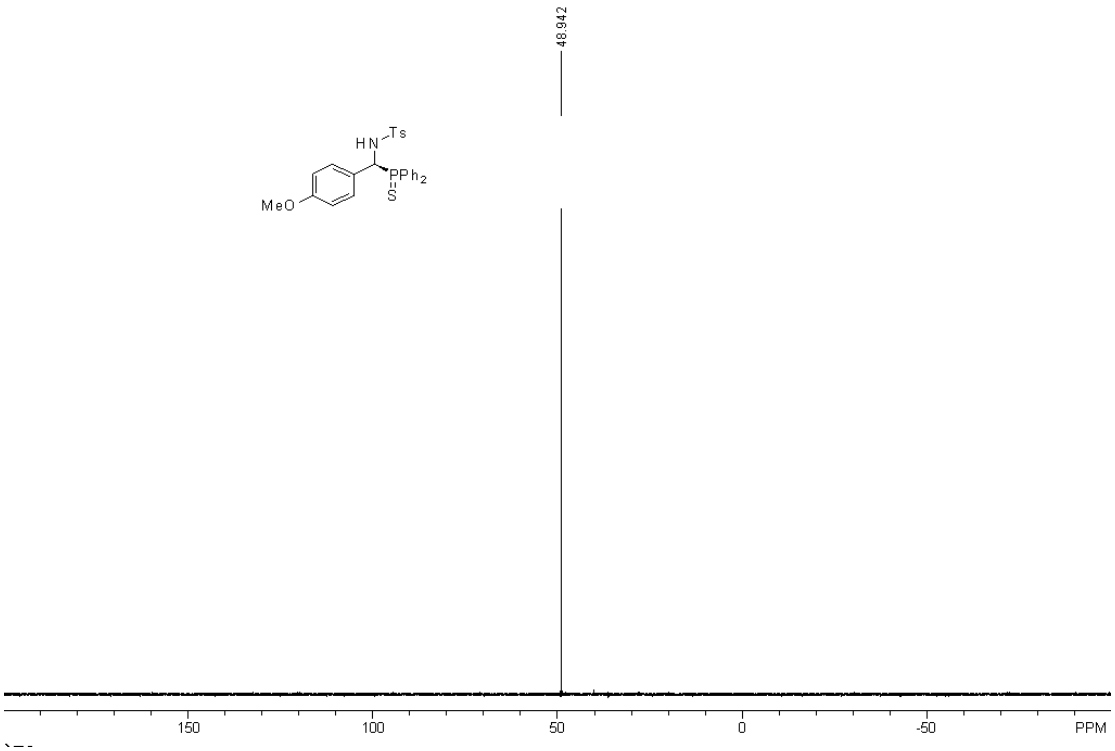

7.516
7.508
7.491
7.350
7.328
7.322
7.302
7.257
7.178
7.170
7.159
7.151
7.140
7.131
6.979
6.958
6.945
6.872
6.851
6.825
6.805
6.786
6.780
6.759
6.073
6.057
6.048
6.032
5.831
5.805
5.602
5.577
2.222
HN
Ts
Ph
PPh2
S
6.02
5.02
3.09
2.00
2.03
1.00
1.01
3.00
8
7
6
5
4
3
2
1
0
PPM

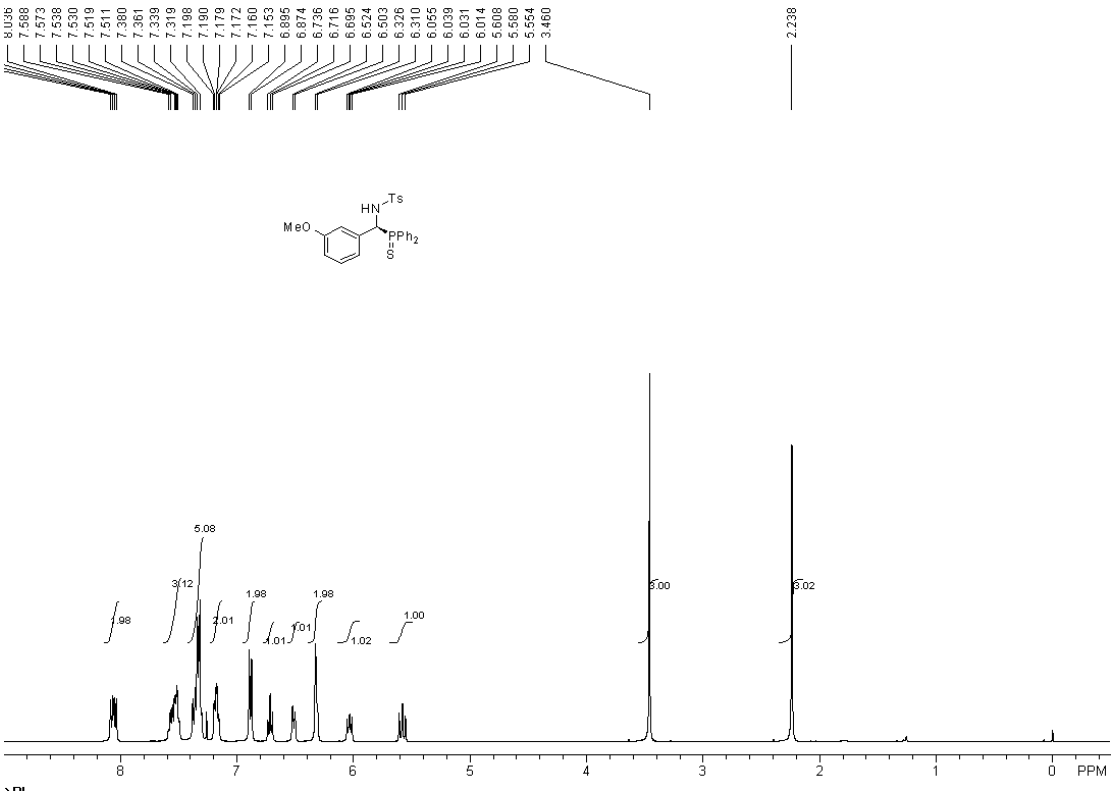

142.871
137.257
137.242
132.007
131.977
131.925
131.821
131.791
131.769
131.739
131.702
130.319
129.523
129.352
128.906
128.779
128.534
128.326
128.281
127.976
127.850
127.597
127.567
127.247
127.225
126.779
77.320
77.000
76.680
55.777
55.204
21.242
HN
Ts
Ph
PPh2
S
160
140
120
100
80
60
40
20
PPM

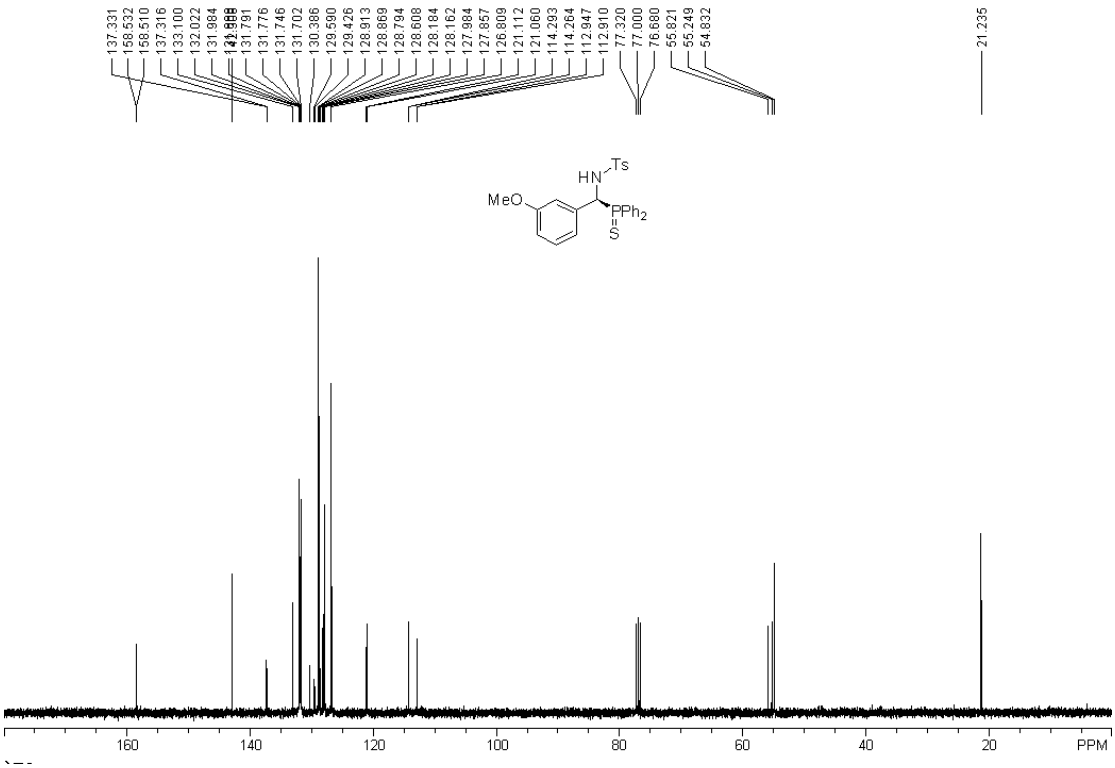

51.332
HN
Ts
Ph
PPh2
S
150
100
50
0
-50
PPM

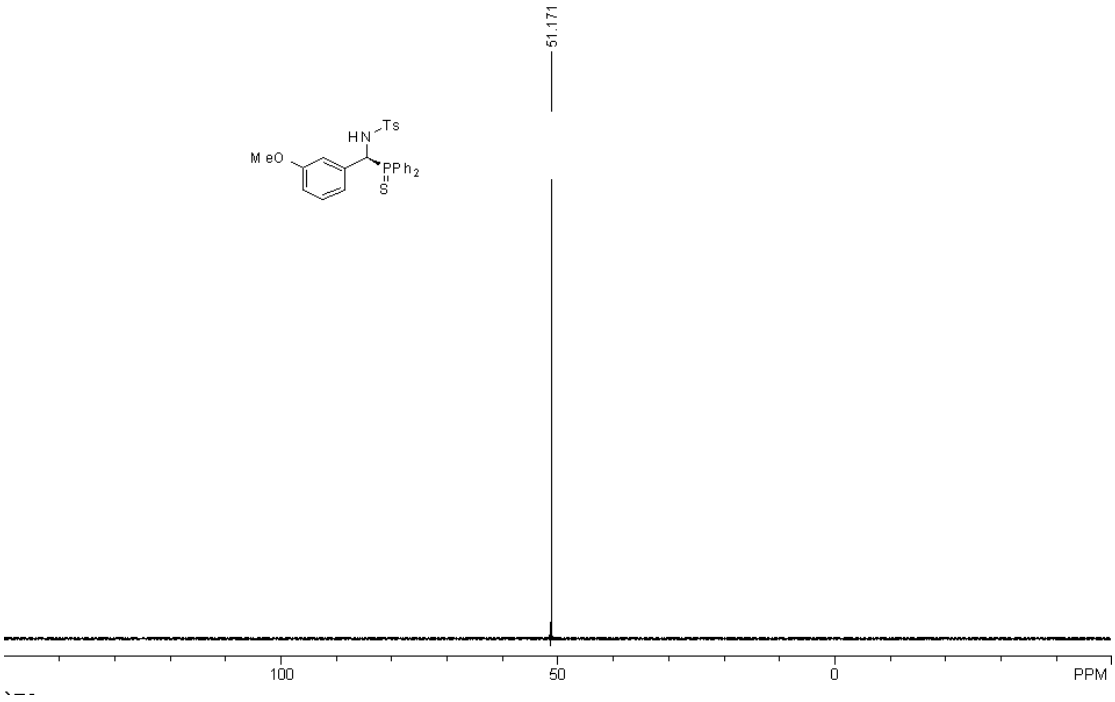

8.041
8.024
8.020
7.595
7.523
7.501
7.378
7.346
7.326
7.318
7.298
7.262
7.215
7.196
7.169
6.914
6.894
6.716
6.711
6.694
6.689
6.368
6.346
5.959
5.943
5.935
5.918
5.580
5.554
5.552
5.526
3.641
2.257
HN
Ts
PPh2
S
MeO
4.90
3.01
1.96
1.99
1.98
2.00
1.96
1.00
1.00
3.00
2.95
8
7
6
5
4
3
2
1
0
PPM

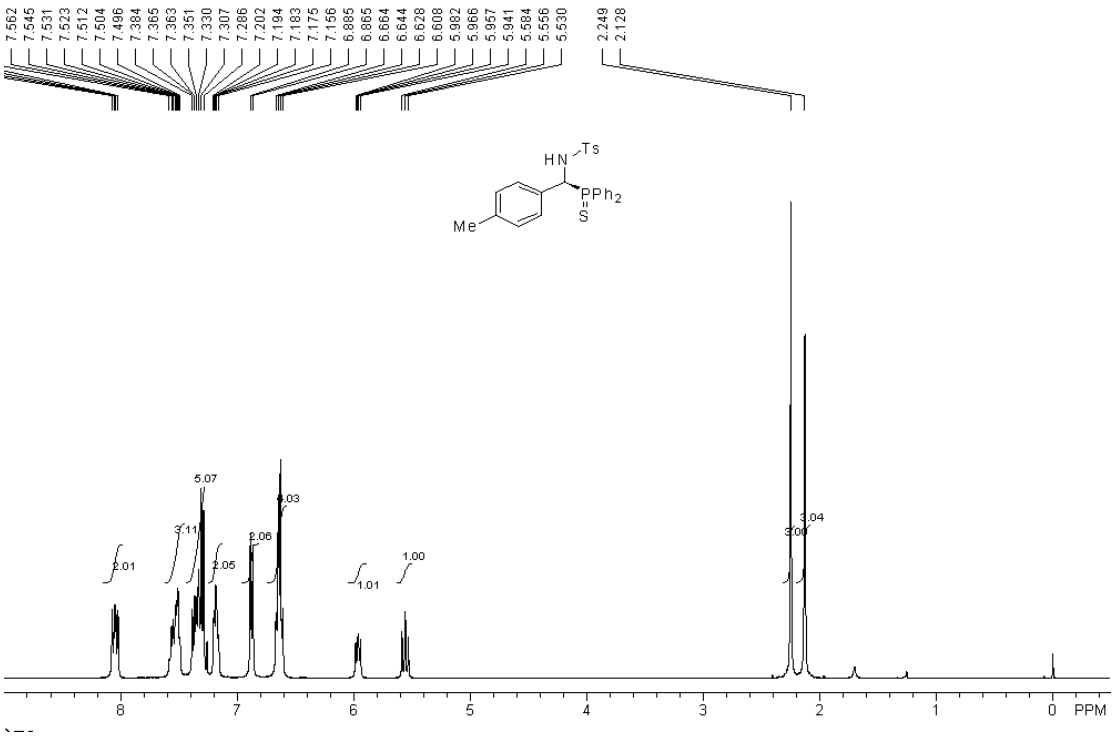

159.261
159.231
137.539
137.524
132.014
131.984
131.836
131.791
131.761
131.739
130.534
129.746
129.582
129.568
129.538
128.943
128.928
128.802
128.742
128.065
127.946
126.876
123.879
112.813
112.791
77.320
77.000
76.688
55.345
55.092
54.758
21.279
HN
Ts
PPh2
S
MeO
160
140
120
100
80
60
40
20
PPM

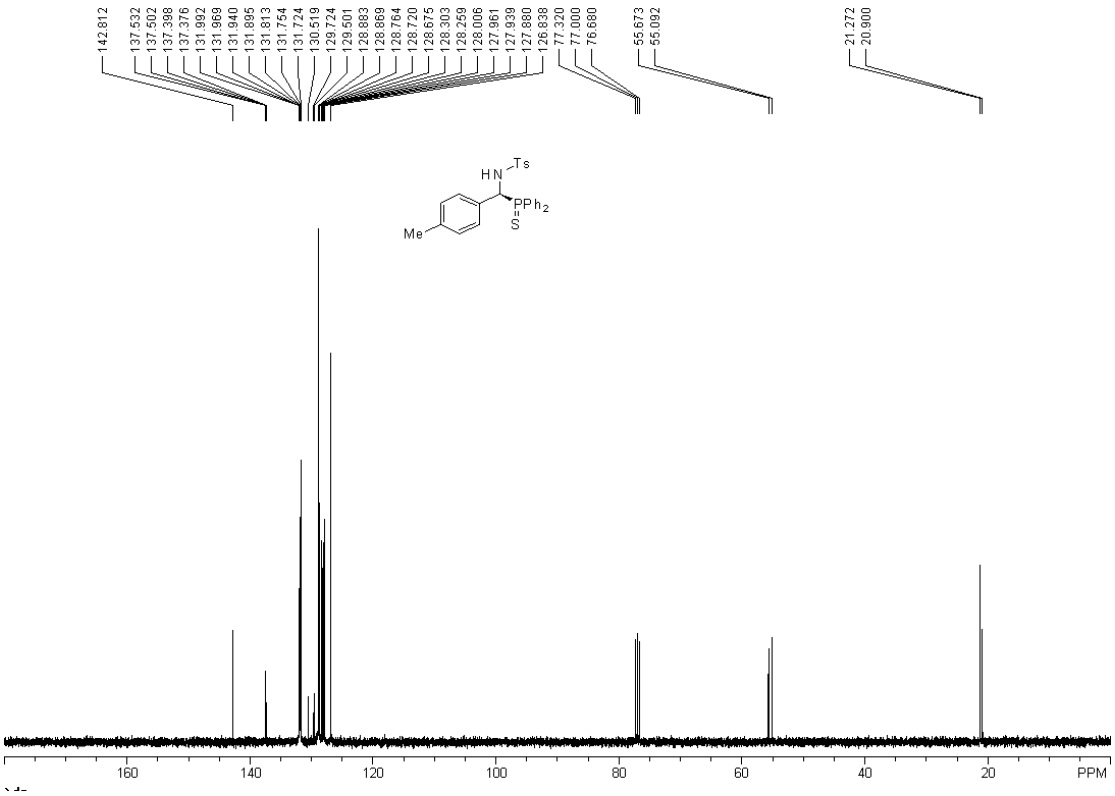

48.942
HN
Ts
PPh2
S
MeO
150
100
50
0
-50
PPM

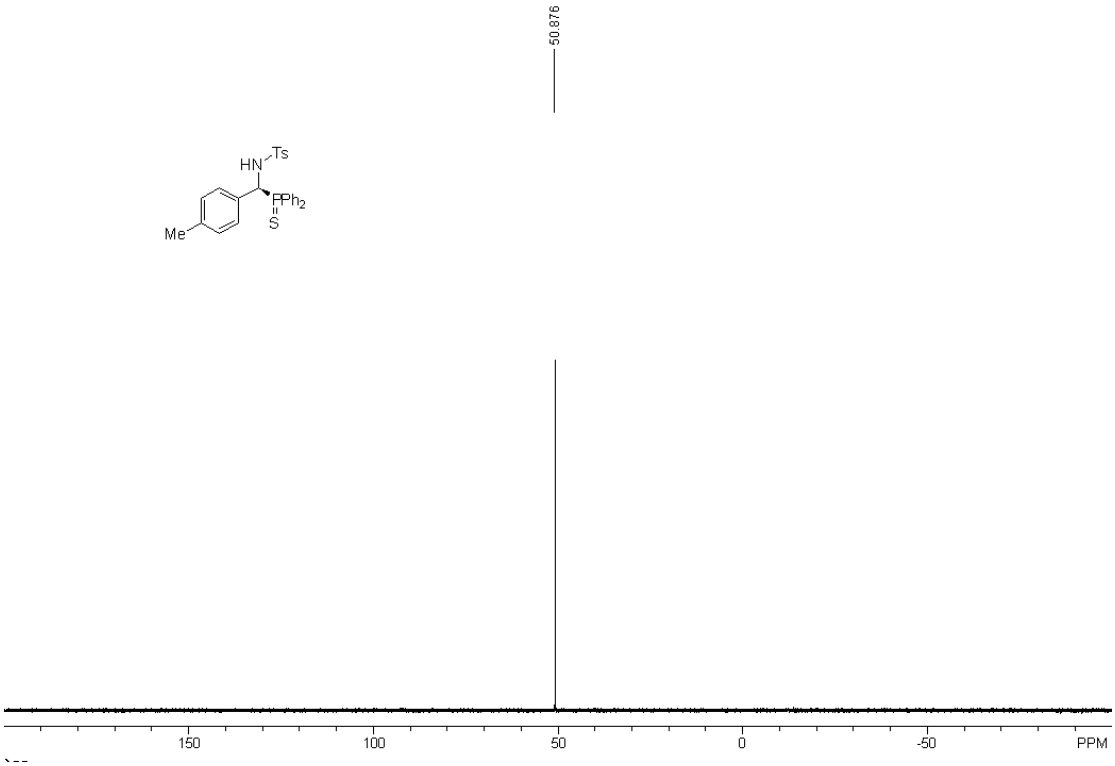

8.036
7.588
7.573
7.538
7.530
7.519
7.511
7.380
7.361
7.339
7.319
7.198
7.190
7.179
7.172
7.160
7.153
6.895
6.874
6.736
6.716
6.695
6.524
6.503
6.326
6.310
6.055
6.039
6.031
6.014
5.608
5.580
5.554
3.460
2.238
HN
Ts
MeO
PPh2
S
5.08
3.12
1.98
2.01
1.98
1.01
1.01
1.02
1.00
3.00
3.02
8
7
6
5
4
3
2
1
0
PPM

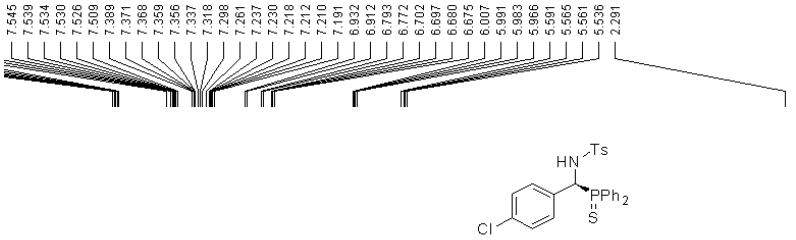

137.331
158.532
158.510
137.316
133.100
132.022
131.984
131.791
131.776
131.746
131.702
130.386
129.590
129.426
128.913
128.869
128.794
128.608
128.184
128.162
127.984
127.857
126.809
121.112
121.060
114.293
114.264
112.947
112.910
77.320
77.000
76.680
55.821
55.249
54.832
21.235
HN
Ts
MeO
PPh2
S
160
140
120
100
80
60
40
20
PPM


51.171
HN
Ts
MeO
PPh2
S
100
50
0
PPM

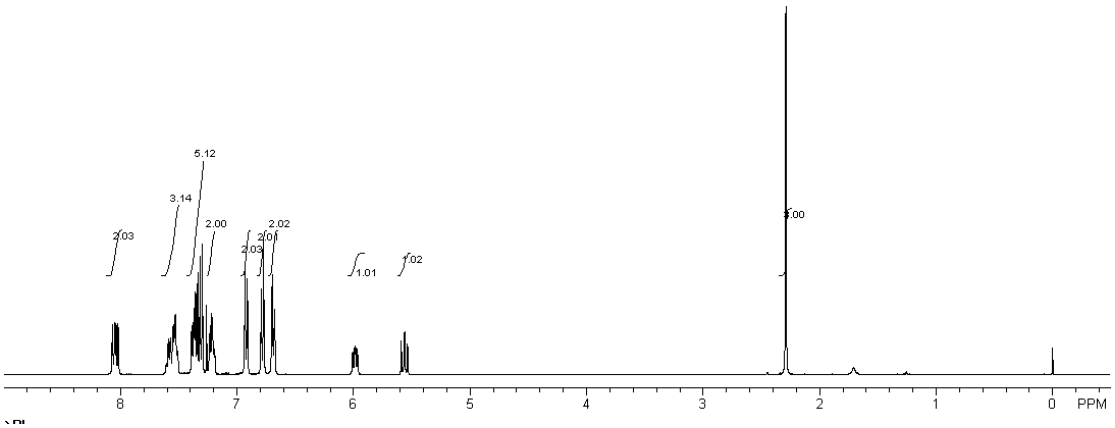

7.562
7.545
7.531
7.523
7.512
7.504
7.496
7.384
7.365
7.363
7.351
7.330
7.307
7.286
7.202
7.194
7.183
7.175
7.156
6.885
6.865
6.664
6.644
6.628
6.608
5.982
5.966
5.957
5.941
5.584
5.556
5.530
2.249
2.128
HN
Ts
PPh2
S
Me
2.01
3.11
5.07
2.05
2.06
4.03
1.01
1.00
3.00
3.04
8
7
6
5
4
3
2
1
0
PPM

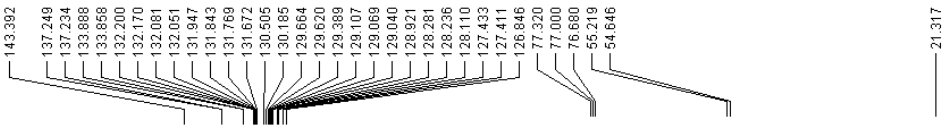

142.812
137.532
137.502
137.398
137.376
131.992
131.969
131.940
131.895
131.813
131.754
131.724
130.519
129.724
129.501
128.883
128.869
128.764
128.720
128.675
128.303
128.259
128.006
127.961
127.939
127.880
126.838
77.320
77.000
76.680
55.673
55.092
21.272
20.900
HN
Ts
PPh2
S
Me
160
140
120
100
80
60
40
20
PPM

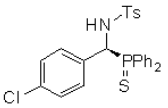

50.876
HN
Ts
PPh2
S
Me
150
100
50
0
-50
PPM

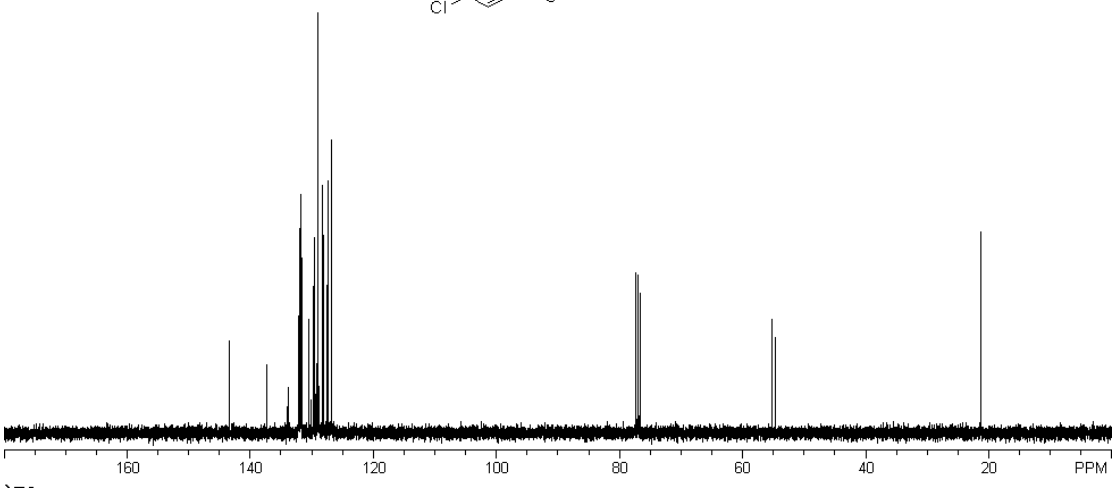

7.545
7.539
7.534
7.530
7.526
7.509
7.389
7.371
7.368
7.359
7.356
7.337
7.318
7.298
7.261
7.237
7.230
7.218
7.212
7.210
7.191
6.932
6.912
6.793
6.772
6.702
6.697
6.680
6.675
6.007
5.991
5.983
5.966
5.591
5.565
5.561
5.536
2.291

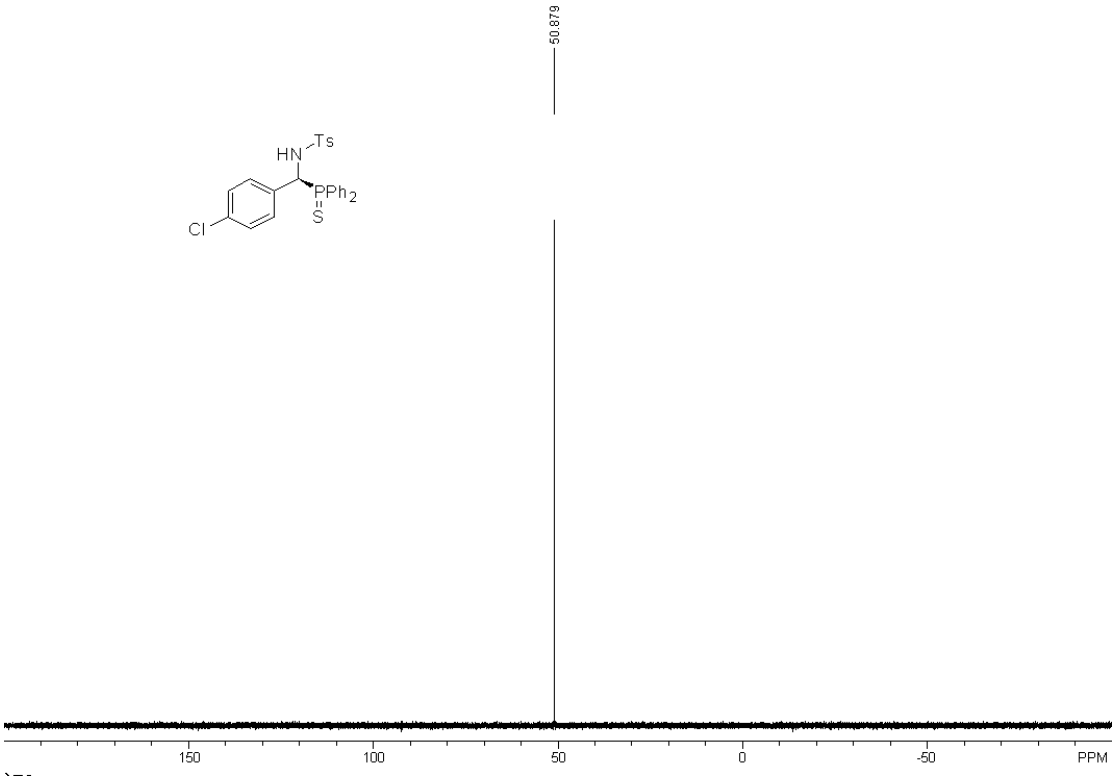
HN
Ts
PPh2
S
Cl

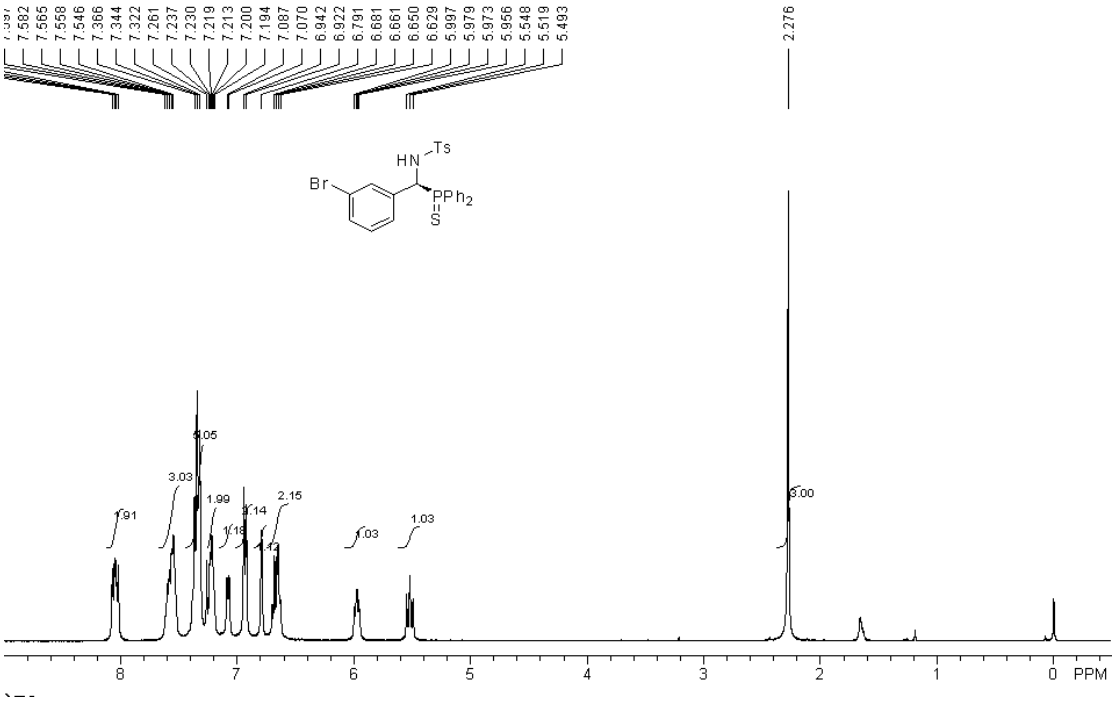

5.12
3.14
2.03
2.00
2.02
2.01
2.03
1.01
1.02
3.00
8
7
6
5
4
3
2
1
0
PPM

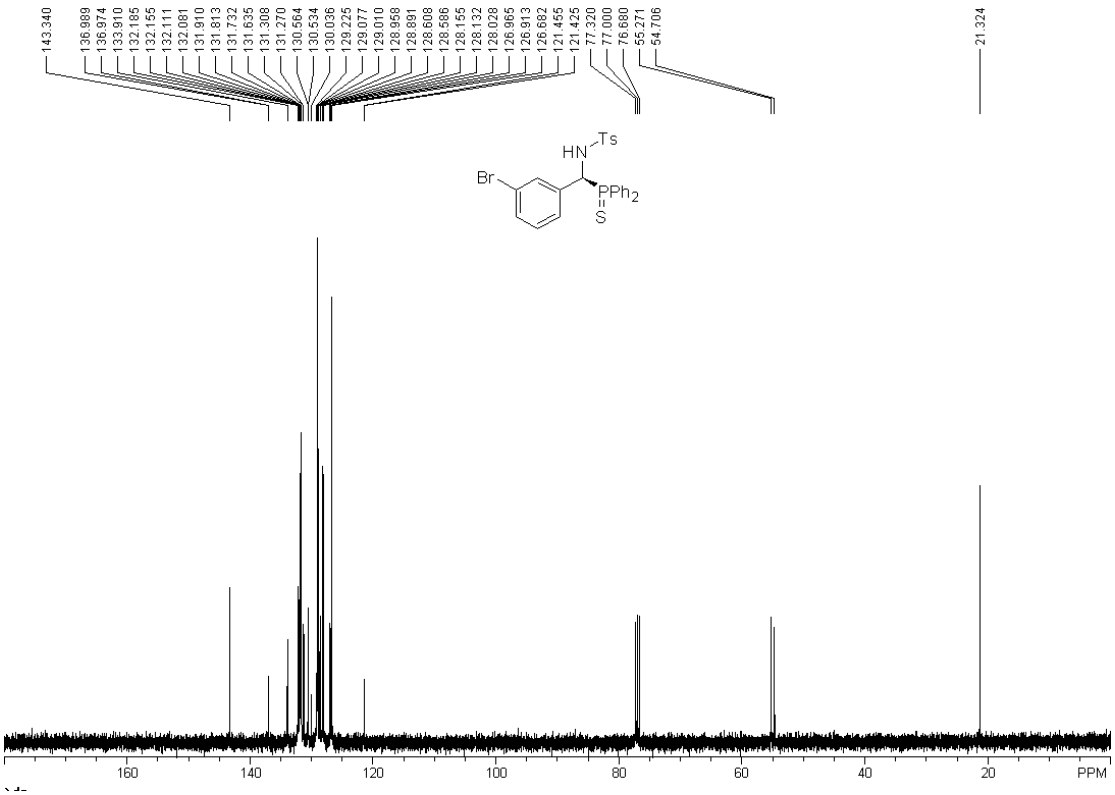

143.392
137.249
137.234
133.888
133.858
132.200
132.170
132.081
132.051
131.947
131.843
131.769
131.672
130.505
130.185
129.664
129.620
129.389
129.107
129.069
129.040
128.921
128.281
128.236
128.110
127.433
127.411
126.846
77.320
77.000
76.680
55.219
54.646
21.317

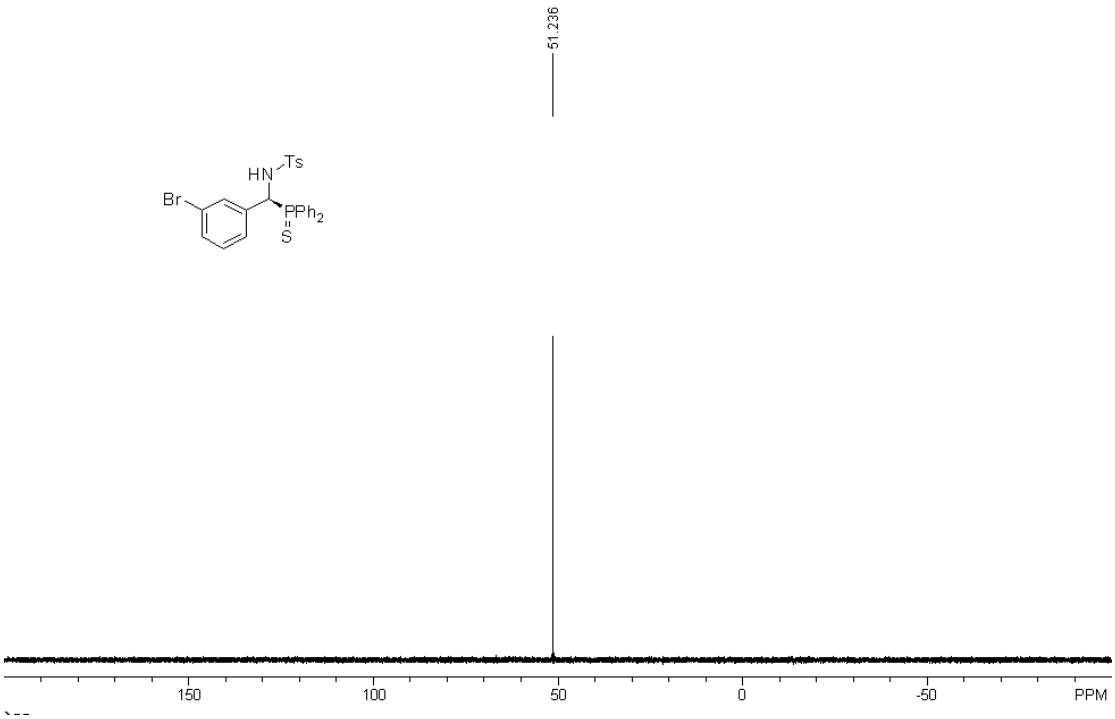

HN
Ts
PPh2
S
Cl

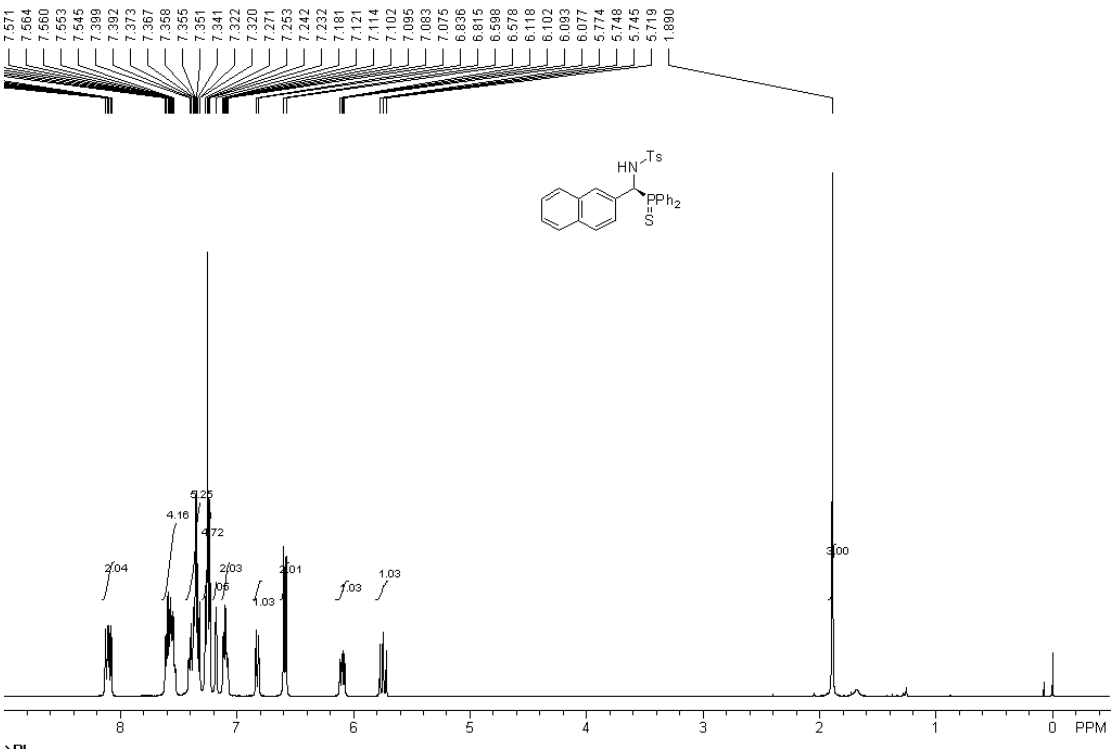

160
140
120
100
80
60
40
20
PPM

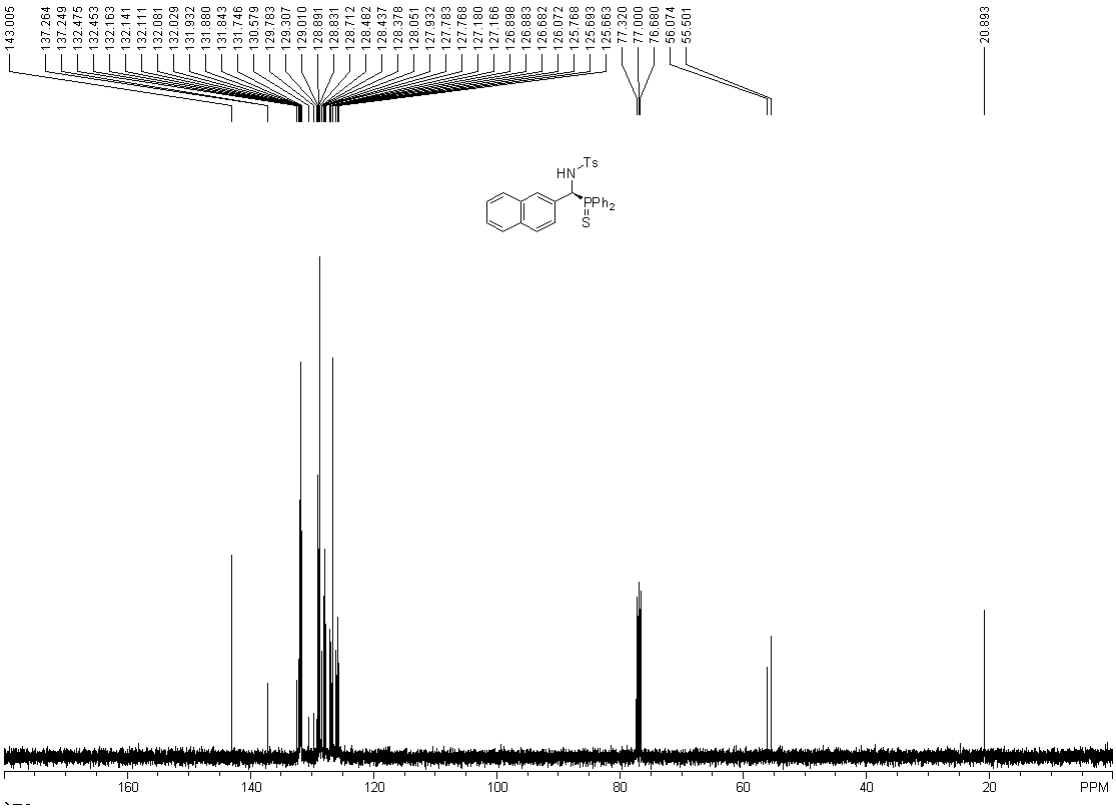

50.879
HN
Ts
PPh2
S
Cl
150
100
50
0
-50
PPM

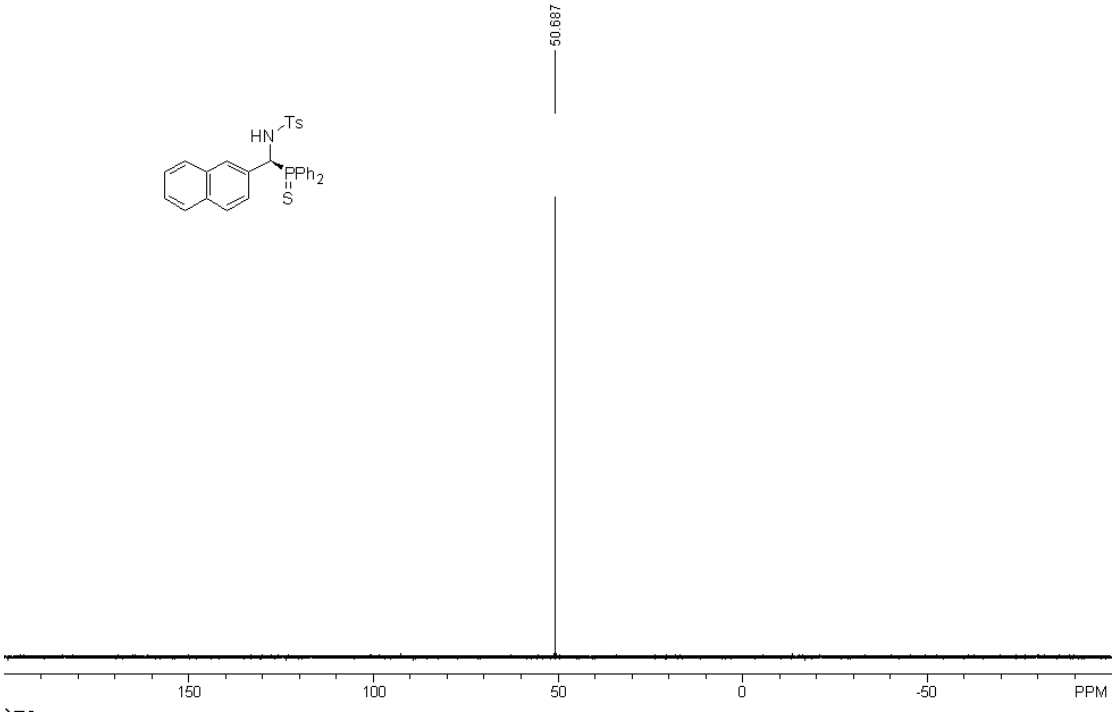

7.582
7.565
7.558
7.546
7.366
7.344
7.322
7.261
7.237
7.230
7.219
7.213
7.200
7.194
7.087
7.070
6.942
6.922
6.791
6.681
6.661
6.650
6.629
5.997
5.979
5.973
5.956
5.548
5.519
5.493
2.276
HN
Ts
Br
PPh2
S
3.05
3.03
1.99
2.15
1.91
1.03
1.03
6.00
8
7
6
5
4
3
2
1
0
PPM

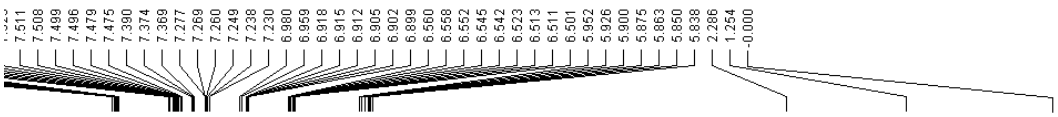

143.340
136.989
136.974
133.910
132.185
132.155
132.111
132.081
131.910
131.813
131.732
131.635
131.308
131.270
130.564
130.534
130.036
129.225
129.077
129.010
128.958
128.891
128.608
128.586
128.155
128.132
128.028
126.965
126.913
126.682
121.455
121.425
77.320
77.000
76.680
55.271
54.706
21.324
HN
Ts
Br
PPh2
S
160
140
120
100
80
60
40
20
PPM

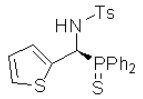

51.236
HN
Ts
Br
PPh2
S
150
100
50
0
-50
PPM

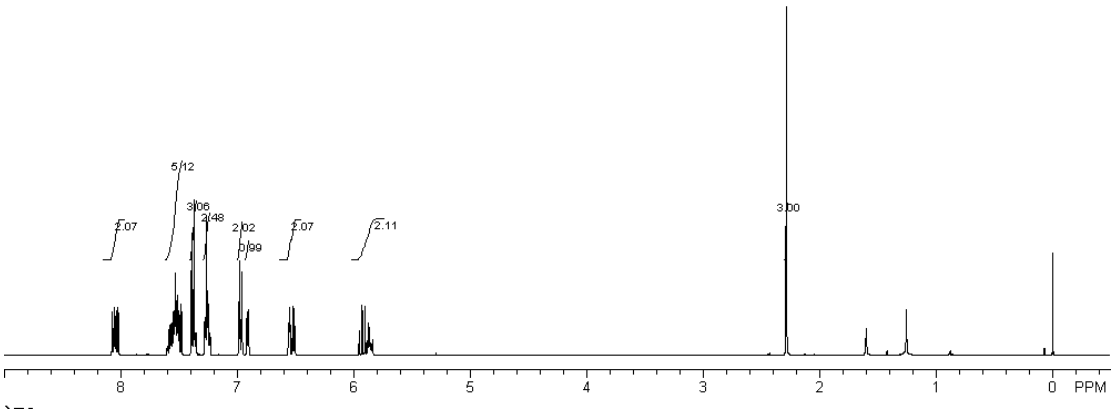

7.571
7.564
7.560
7.553
7.545
7.399
7.392
7.373
7.367
7.358
7.355
7.351
7.341
7.322
7.320
7.271
7.253
7.242
7.232
7.181
7.121
7.114
7.102
7.095
7.083
7.075
6.836
6.815
6.598
6.578
6.118
6.102
6.093
6.077
5.774
5.748
5.745
5.719
1.890
HN
Ts
PPh2
S
5.25
4.16
4.72
2.04
2.03
2.01
1.03
1.03
1.03
3.00
8
7
6
5
4
3
2
1
0
PPM

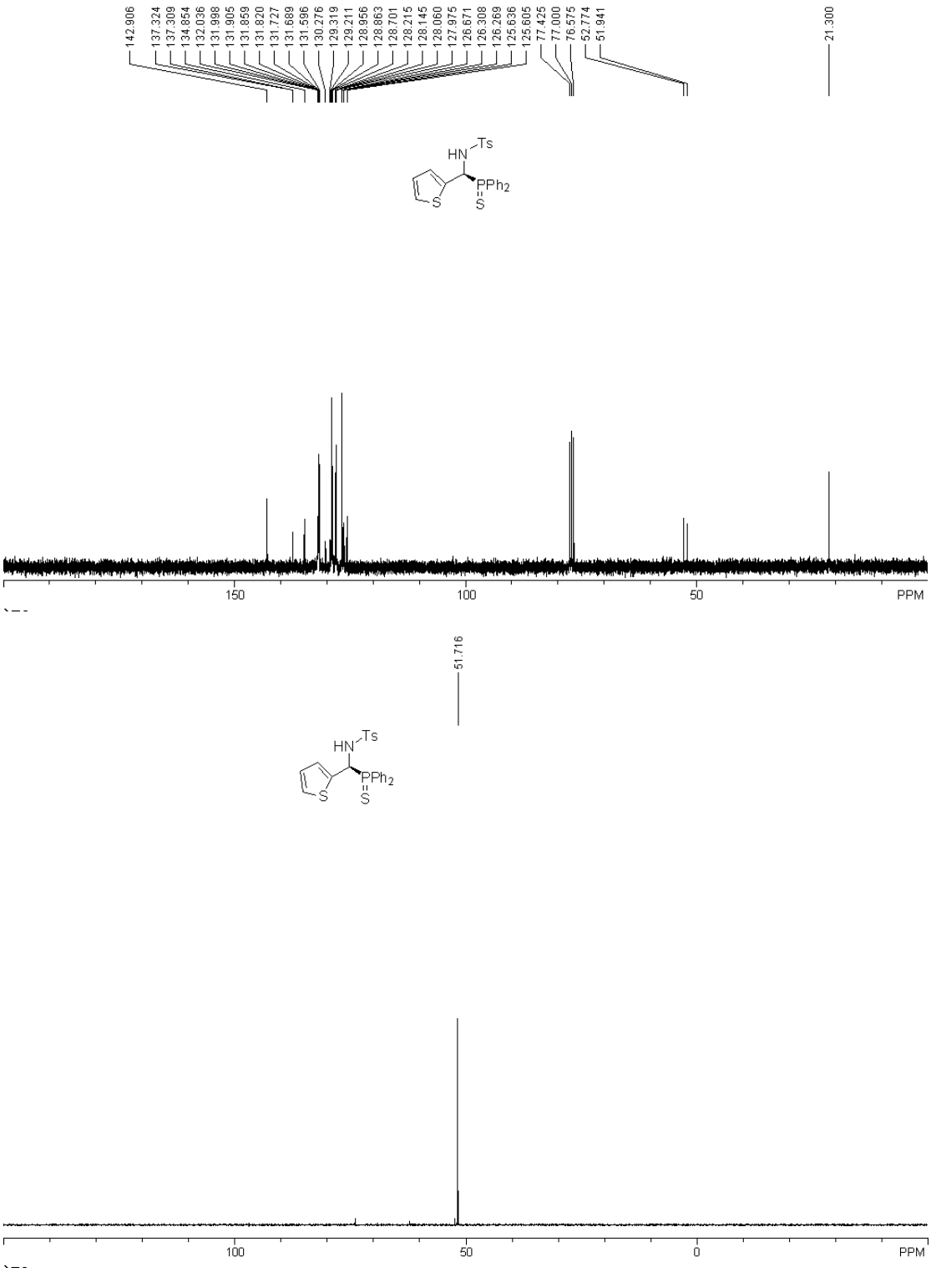

143.005
137.264
137.249
132.475
132.453
132.163
132.141
132.111
132.081
132.029
131.932
131.880
131.843
131.746
130.579
129.783
129.307
129.010
128.891
128.831
128.712
128.482
128.437
128.378
128.051
127.932
127.783
127.768
127.180
127.166
126.898
126.883
126.682
126.072
125.768
125.693
125.663
77.320
77.000
76.680
56.074
55.501
20.893
HN
Ts
PPh2
S
160
140
120
100
80
60
40
20
PPM

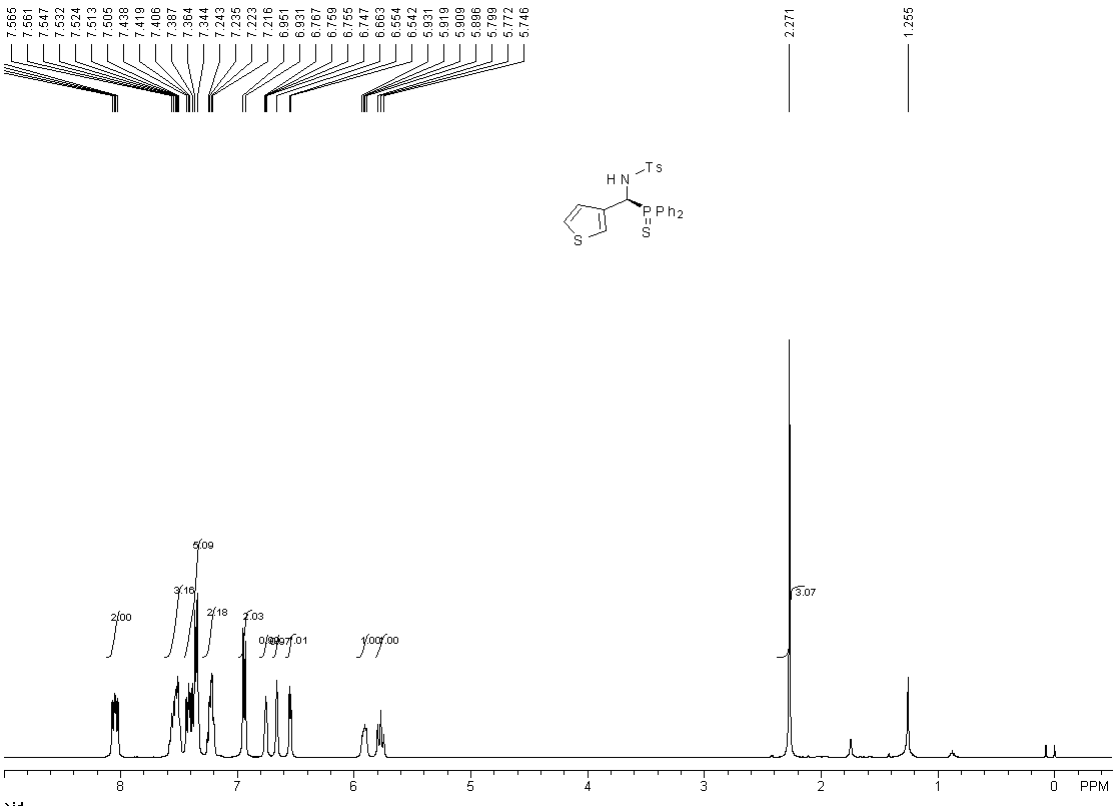

50.687
HN
Ts
PPh2
S
150
100
50
0
-50
PPM

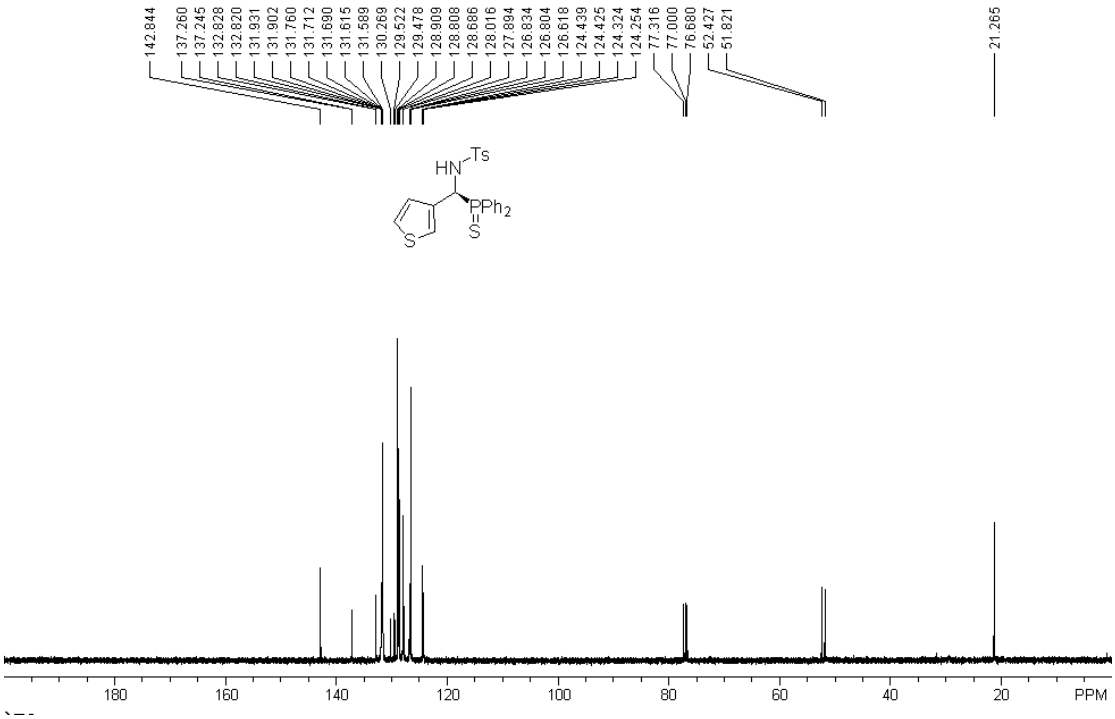

7.511
7.508
7.499
7.496
7.479
7.475
7.390
7.374
7.369
7.277
7.269
7.260
7.249
7.238
7.230
6.980
6.959
6.918
6.915
6.912
6.905
6.902
6.899
6.560
6.558
6.552
6.545
6.542
6.523
6.513
6.511
6.501
5.952
5.926
5.900
5.875
5.863
5.850
5.838
2.286
1.254
-0.000

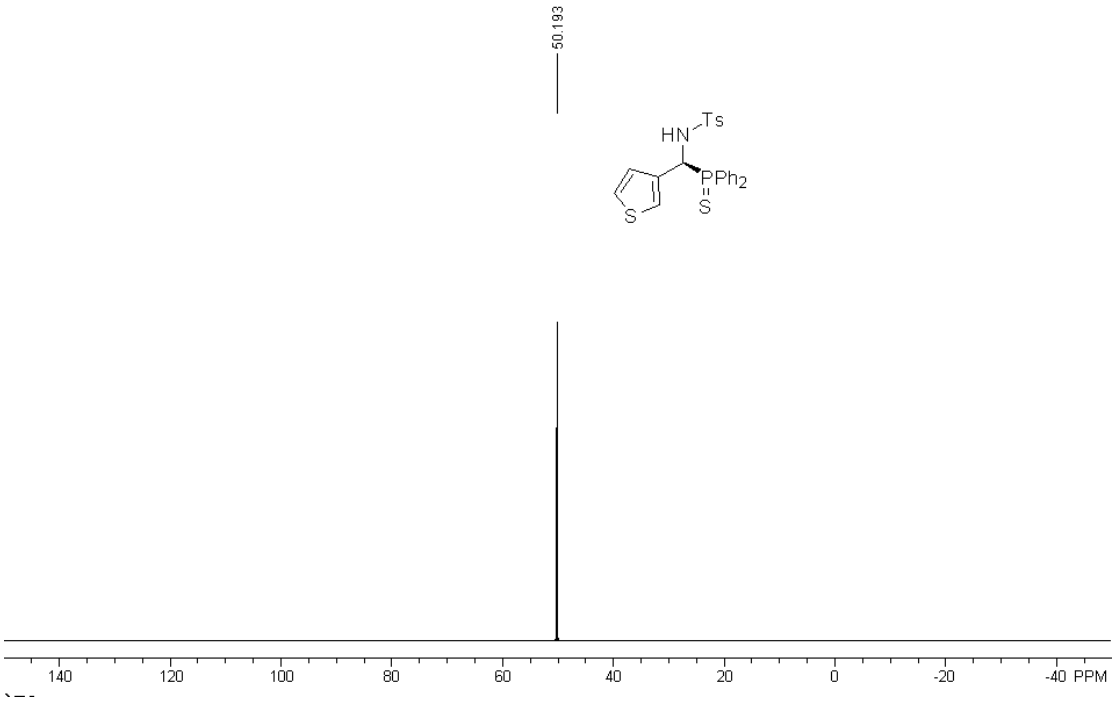

HN
Ts
PPh2
S
S

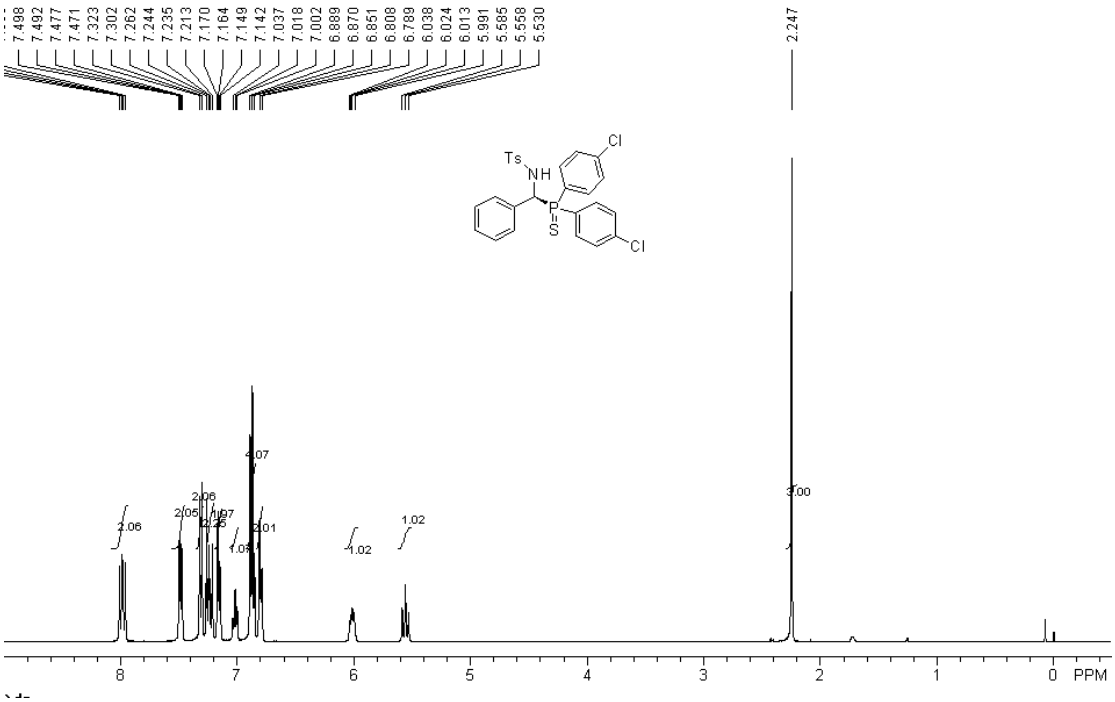

5.12
3.06
2.48
2.07
2.02
0.99
2.07
2.11
3.00
8
7
6
5
4
3
2
1
0
PPM

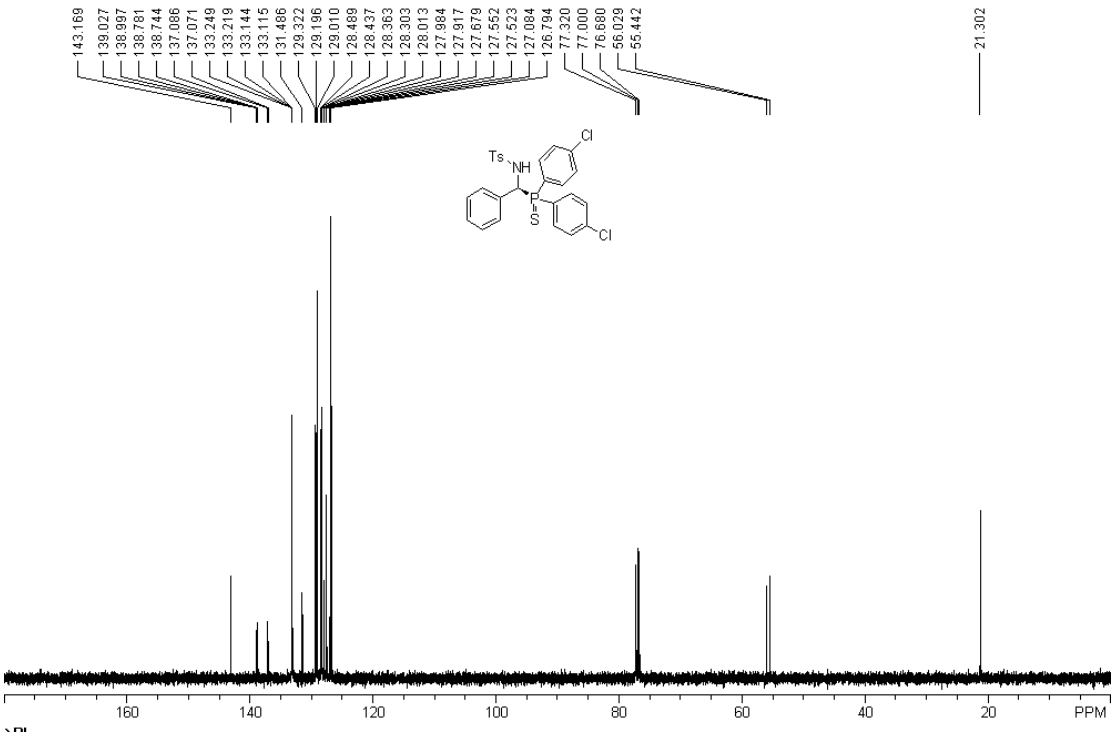

142.906
137.324
137.309
134.854
132.036
131.998
131.905
131.859
131.820
131.727
131.689
131.596
130.276
129.319
129.211
128.956
128.863
128.701
128.215
128.145
128.060
127.975
126.671
126.308
126.269
125.636
125.605
77.425
77.000
76.575
52.774
51.941
21.300
HN
Ts
PPh2
S
S
150
100
50
PPM
51.716
HN
Ts
PPh2
S
S
100
50
0
PPM

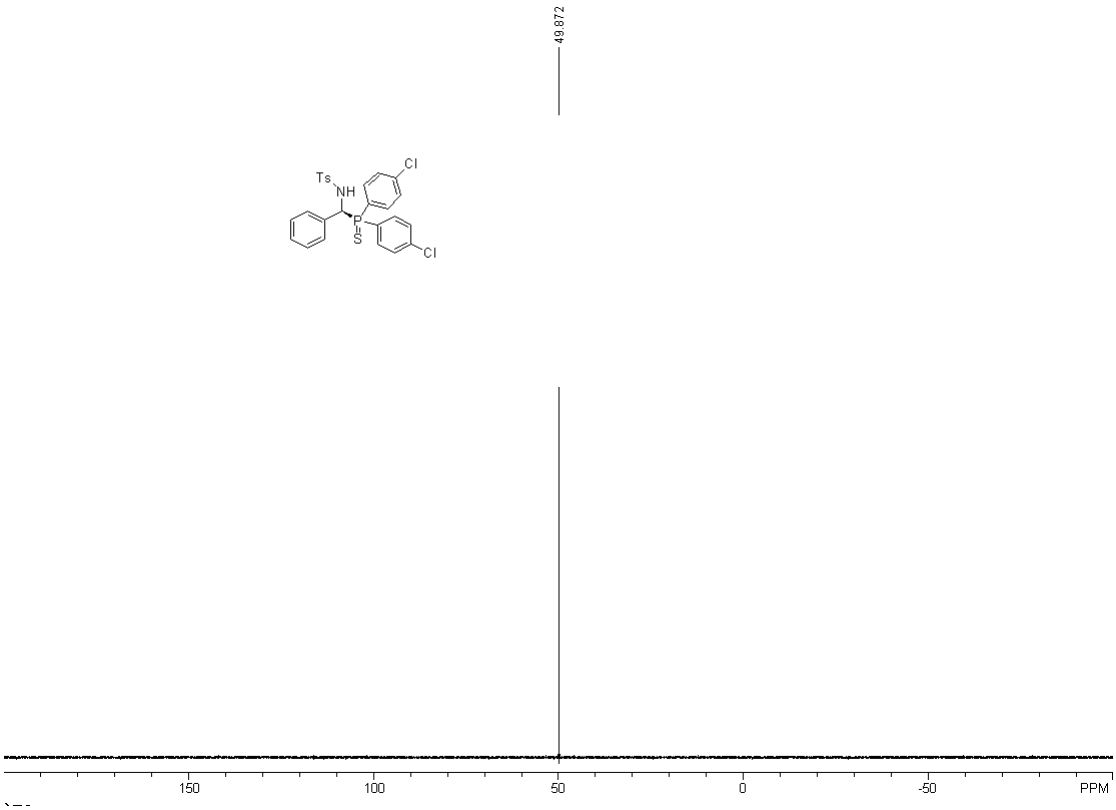

7.565
7.561
7.547
7.532
7.524
7.513
7.505
7.438
7.419
7.406
7.387
7.364
7.344
7.243
7.235
7.223
7.216
6.951
6.931
6.767
6.759
6.755
6.747
6.663
6.554
6.542
5.931
5.919
5.909
5.896
5.799
5.772
5.746
2.271
1.255
HN
Ts
PPh2
S
S
5.09
3.16
2.18
2.03
2.00
3.07
PPM

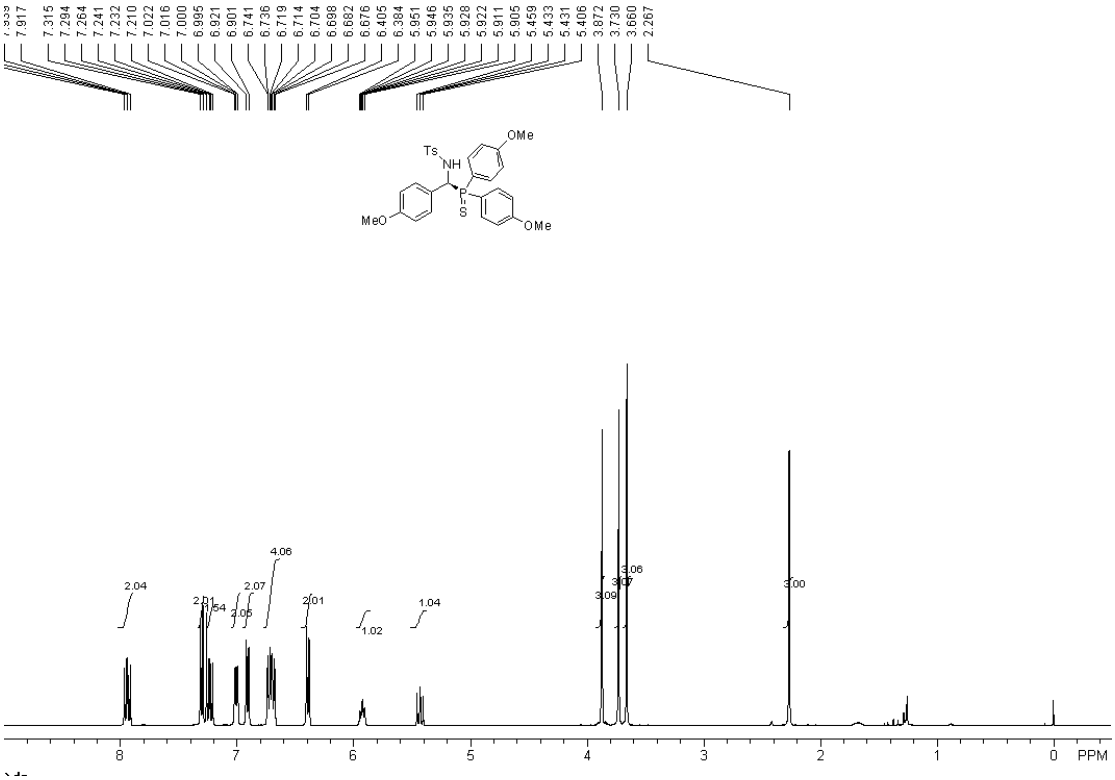

142.844
137.260
137.245
132.828
132.820
131.931
131.902
131.760
131.712
131.690
131.615
131.589
130.269
129.522
129.478
128.909
128.808
128.686
128.016
127.894
126.834
126.804
126.618
124.439
124.425
124.324
124.254
77.316
77.000
76.680
52.427
51.821
21.265
HN
Ts
PPh2
S
S
PPM

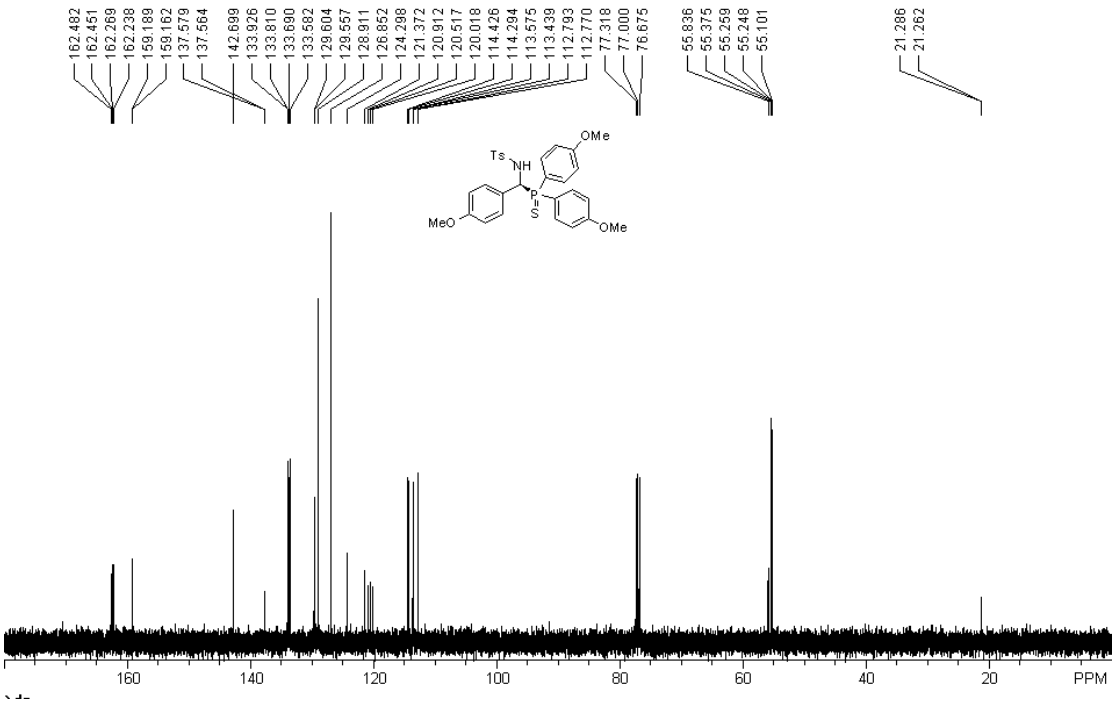

50.193
HN
Ts
PPh2
S
S
140
120
100
80
60
40
20
0
-20
-40 PPM

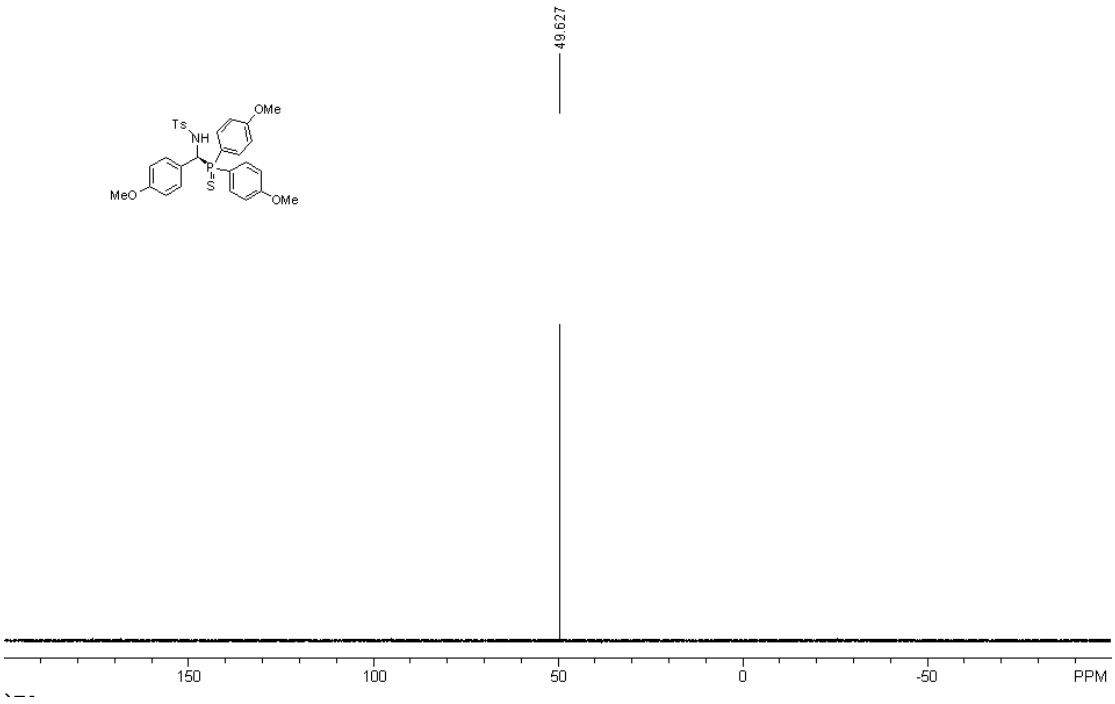

7.498
7.492
7.477
7.471
7.323
7.302
7.262
7.244
7.235
7.213
7.170
7.164
7.149
7.142
7.037
7.018
7.002
6.889
6.870
6.851
6.808
6.789
6.038
6.024
6.013
5.991
5.585
5.558
5.530
2.247
Ts
NH
Cl
P
S
Cl
4.07
2.06
2.05
2.06
2.01
1.02
1.02
3.00
8
7
6
5
4
3
2
1
0 PPM

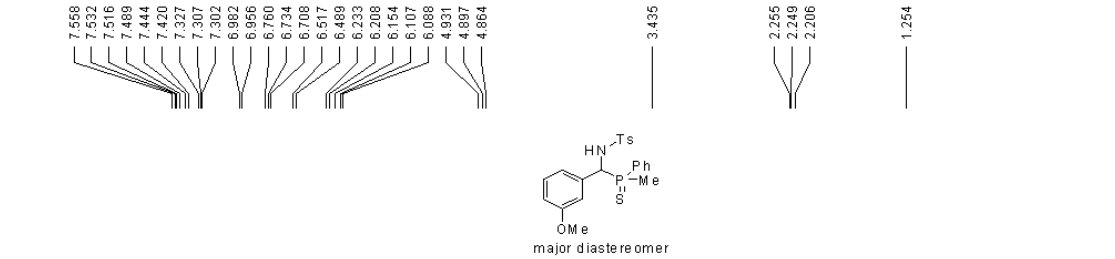

143.169
139.027
138.997
138.781
138.744
137.086
137.071
133.249
133.219
133.144
133.115
131.486
129.322
129.196
129.010
128.489
128.437
128.363
128.303
128.013
127.984
127.917
127.679
127.552
127.523
127.084
126.794
77.320
77.000
76.680
56.029
55.442
21.302
Ts
NH
P
S
Cl
Cl
160
140
120
100
80
60
40
20
PPM


49.872
Ts
NH
P
S
Cl
Cl
150
100
50
0
-50
PPM

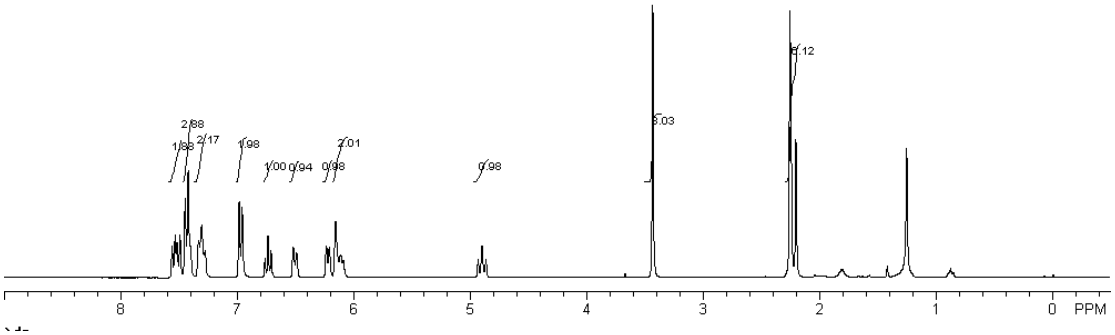

7.939
7.917
7.315
7.294
7.264
7.241
7.232
7.210
7.022
7.016
7.000
6.995
6.921
6.901
6.741
6.736
6.719
6.714
6.704
6.698
6.682
6.676
6.405
6.384
5.951
5.946
5.935
5.928
5.922
5.911
5.905
5.459
5.433
5.431
5.406
3.872
3.730
3.660
2.267
Ts
NH
P
S
OMe
MeO
OMe
2.04
2.01
2.54
2.05
2.07
4.06
2.01
1.02
1.04
3.09
3.07
3.06
3.00
8
7
6
5
4
3
2
1
0
PPM

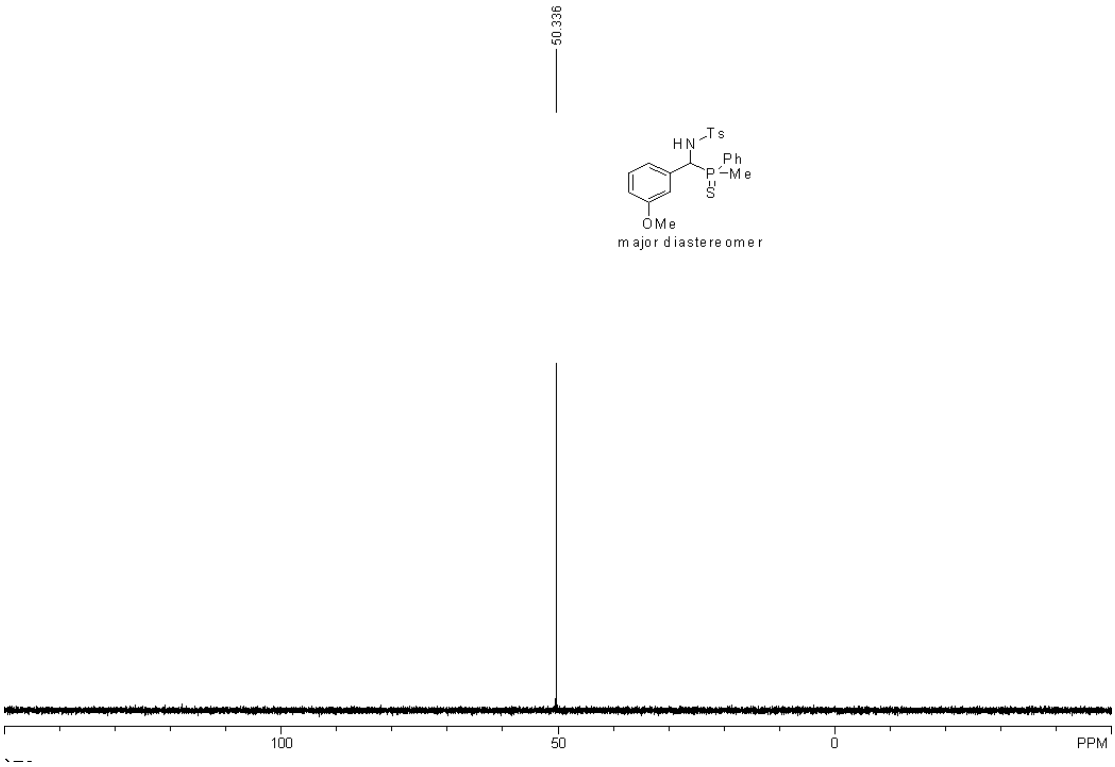

162.482
162.451
162.269
162.238
159.189
159.162
137.579
137.564
142.699
133.926
133.810
133.690
133.582
129.604
129.557
128.911
126.852
124.298
121.372
120.912
120.517
120.018
114.426
114.294
113.575
113.439
112.793
112.770
77.318
77.000
76.675
55.836
55.375
55.259
55.248
55.101
21.286
21.262
Ts
NH
P
S
OMe
MeO
OMe
160
140
120
100
80
60
40
20
PPM

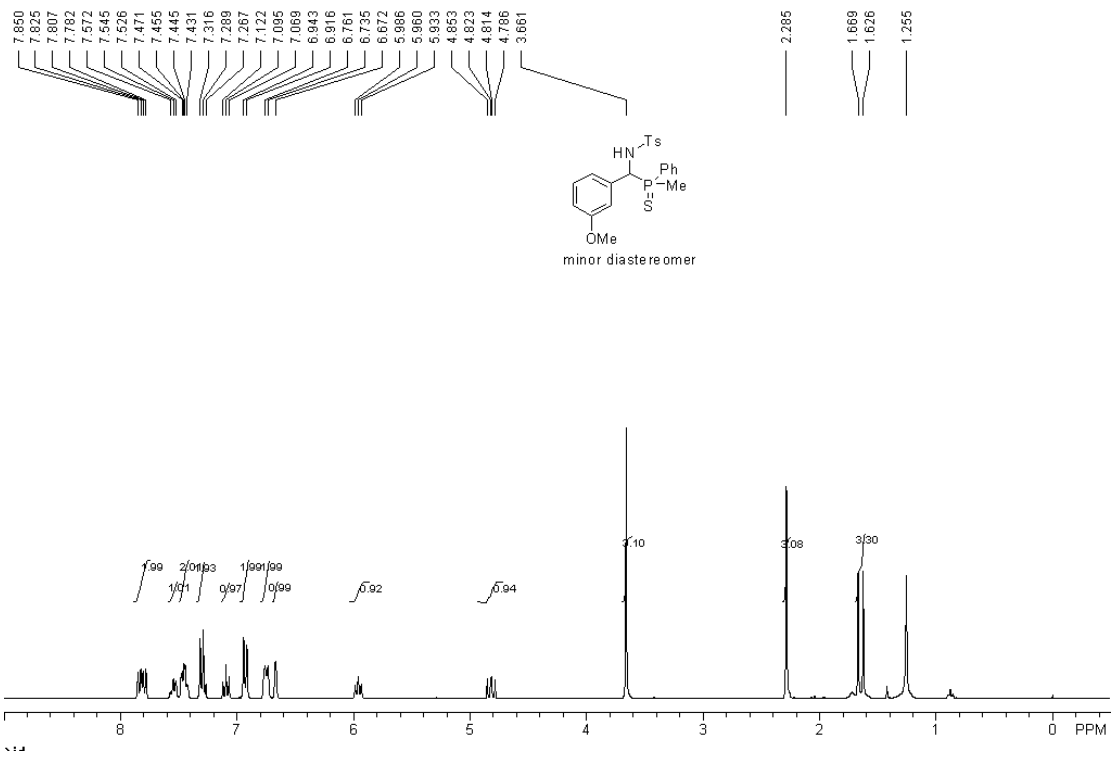


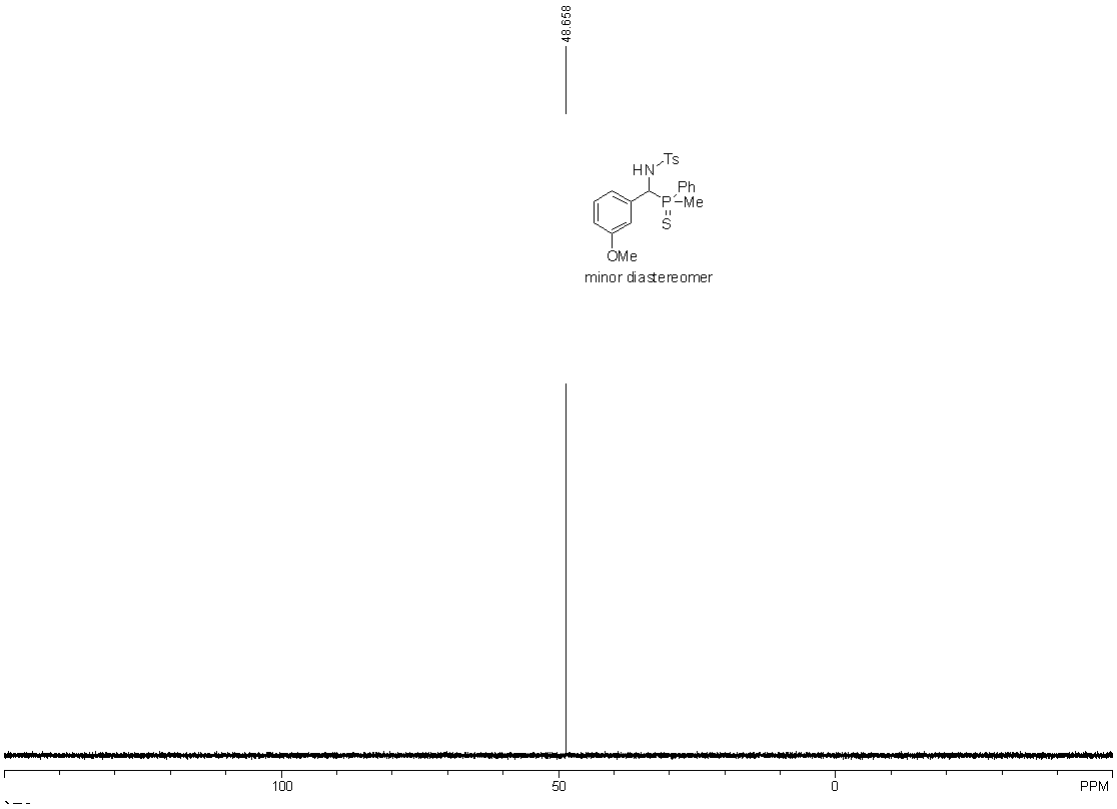


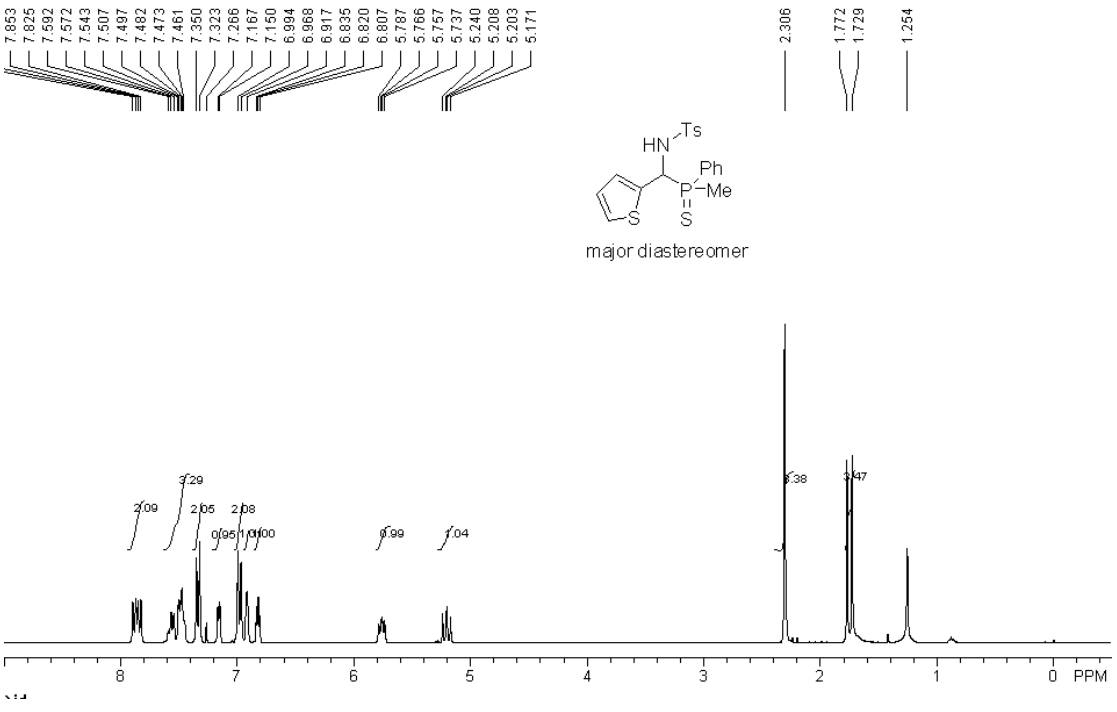
major diastereomer

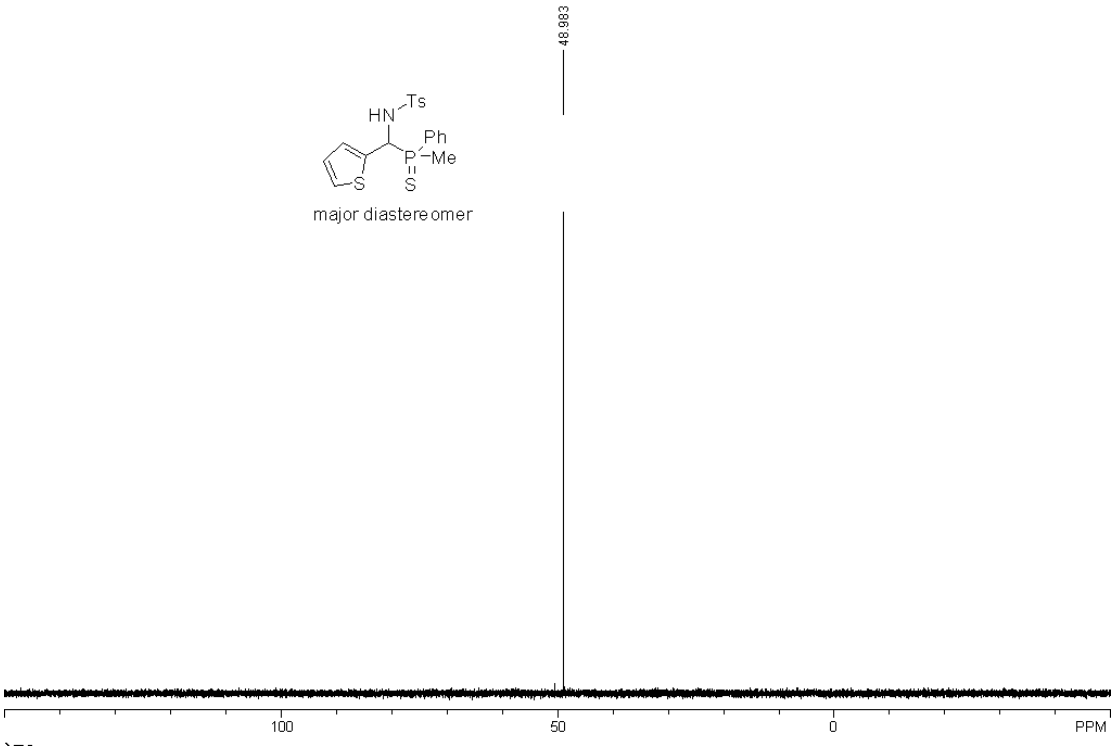


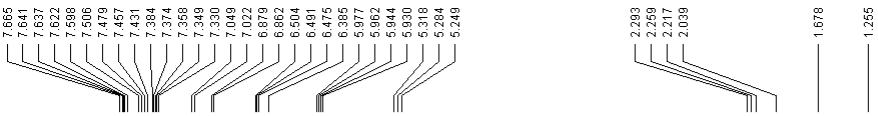

50.336
HN
Ts
Ph
P
Me
S
OMe
major diastereomer
100
50
0
PPM

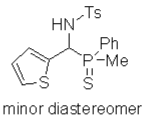

7.850
7.825
7.807
7.782
7.572
7.545
7.526
7.471
7.455
7.445
7.431
7.316
7.289
7.267
7.122
7.095
7.069
6.943
6.916
6.761
6.735
6.672
5.986
5.960
5.933
4.853
4.823
4.814
4.786
3.661
2.285
1.669
1.626
1.255
HN
Ts
Ph
P
Me
S
OMe
minor diastereomer
1.99
2.01
1.93
1.99
1.01
0.97
0.99
0.92
0.94
3.10
3.08
3.30
8
7
6
5
4
3
2
1
0
PPM

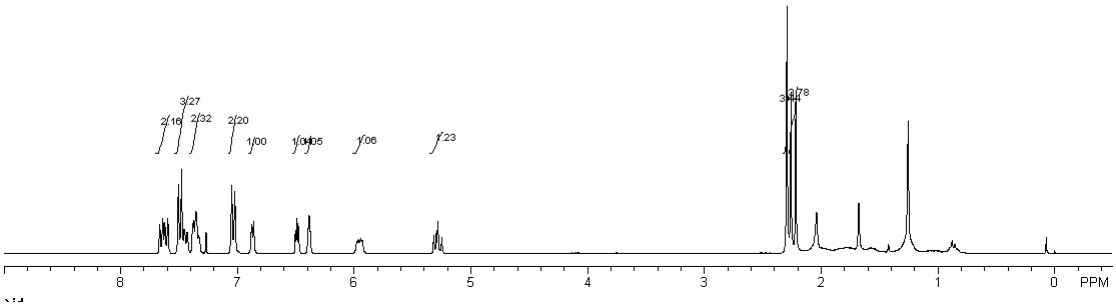

48.658
HN
Ts
Ph
P
Me
S
OMe
minor diastereomer
100
50
0
PPM

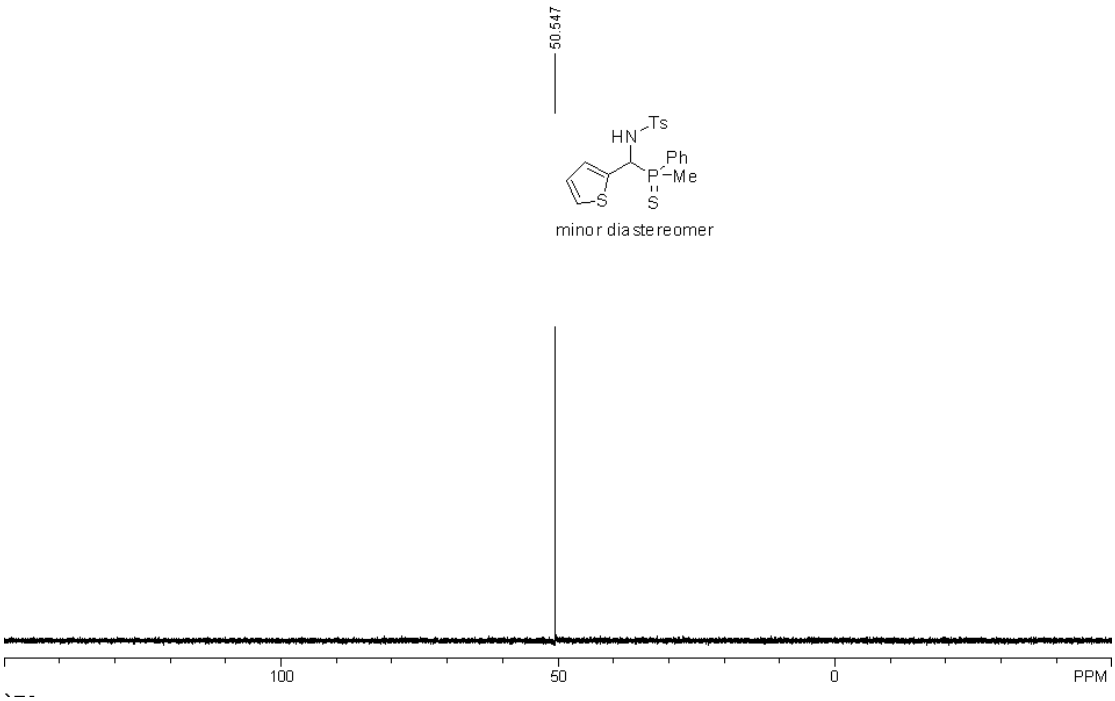

7.853
7.825
7.592
7.572
7.543
7.507
7.497
7.482
7.473
7.461
7.350
7.323
7.266
7.167
7.150
6.994
6.968
6.917
6.835
6.820
6.807
5.787
5.766
5.757
5.737
5.240
5.208
5.203
5.171
2.306
1.772
1.729
1.254
HN
Ts
Ph
P
Me
S
S
major diastereomer
3.29
2.09
2.05
2.08
0.95
1.00
0.99
1.04
3.38
3.47
8
7
6
5
4
3
2
1
0
PPM


48.983
HN
Ts
Ph
P
Me
S
S
major diastereomer
100
50
0
PPM


7.665
7.641
7.637
7.622
7.598
7.506
7.479
7.457
7.431
7.384
7.374
7.358
7.349
7.330
7.049
7.022
6.879
6.862
6.504
6.491
6.475
6.385
5.977
5.962
5.944
5.930
5.318
5.284
5.249
2.293
2.259
2.217
2.039
1.678
1.255


HN
Ts
Ph
P
Me
S
S
minor diastereomer


3.27
2.16
2.32
2.20
1.00
1.06
1.23
3.78
8
7
6
5
4
3
2
1
0
PPM


50.547
HN
Ts
Ph
P
Me
S
S
minor diastereomer
100
50
0
PPM

HLPC Charts

==== Shimadzu LCsolution Analysis Report ====

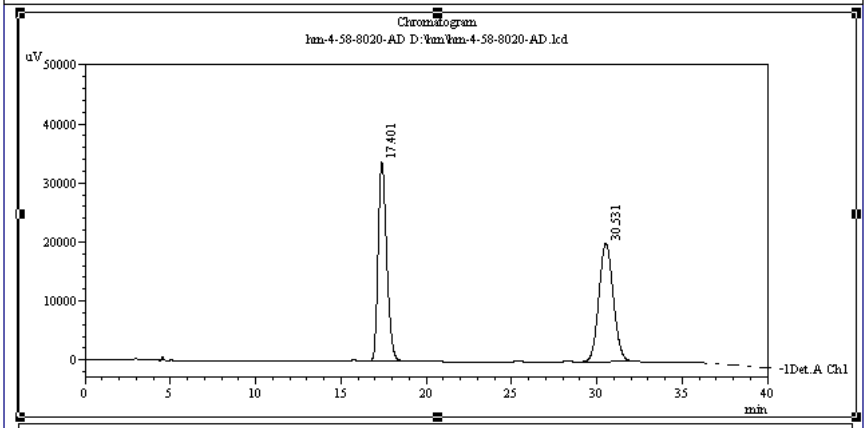
D:\hm\hm-4-58-8020-AD.lcd

Sample Name : hm-4-58-8020-AD Date:

Column: The mobile phase:

Velocity: The detection wavelength:

<Chromatogram>



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	17.401	1182406	33715	50.076
2	30.531	1178837	20023	49.924
Total		2361243	53738	100.000

==== Shimadzu LCsolution Analysis Report ====

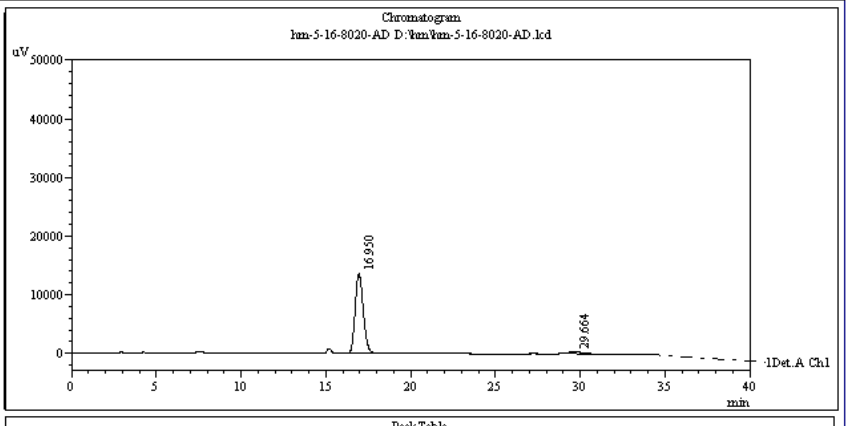
D:\hm\hm-5-16-8020-AD.lcd

Sample Name : hm-5-16-8020-AD Date:

Column: The mobile phase:

Velocity: The detection wavelength:

<Chromatogram>



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	16.950	452582	13598	96.225
2	29.664	17753	332	3.775
Total		470335	13930	100.000

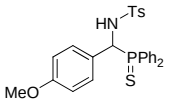
==== Shimadzu LCsolution Analysis Report ====

D:\hm\hm-5-28-8020-AD.lcd

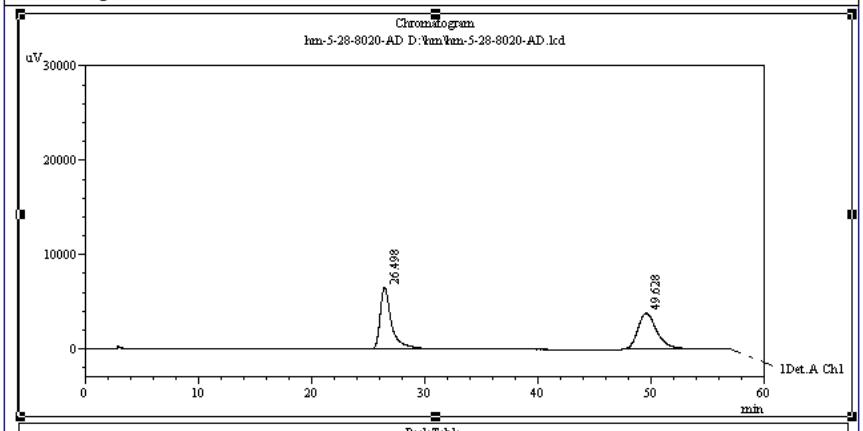
Sample Name : hm-5-28-8020-AD Date:

Column: The mobile phase:

Velocity: The detection wavelength:



<Chromatogram>



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	26.498	442630	6515	50.579
2	49.628	432492	3793	49.421
Total		875122	10307	100.000

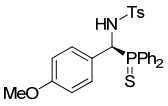
==== Shimadzu LCsolution Analysis Report ====

D:\hm\hm-5-29-8020-AD.lcd

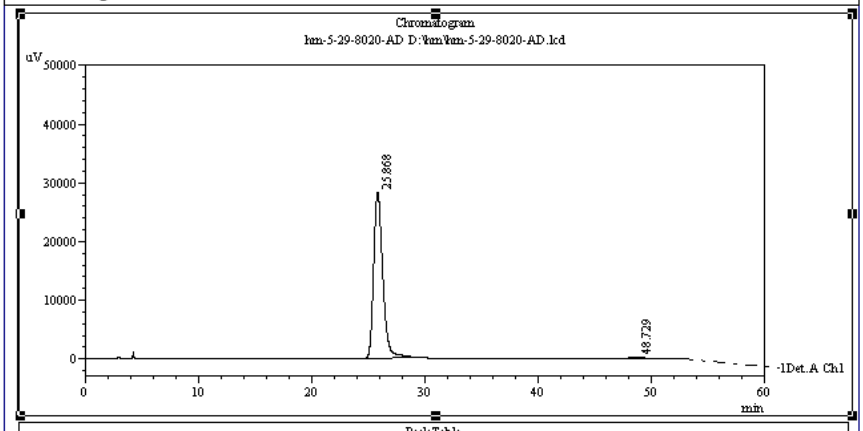
Sample Name : hm-5-29-8020-AD Date:

Column: The mobile phase:

Velocity: The detection wavelength:



<Chromatogram>



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	25.868	1610930	28366	97.801
2	48.729	36228	328	2.199
Total		1647157	28694	100.000

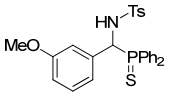
==== Shimadzu LCsolution Analysis Report ====

D:\hm\hm-5-25-8020-AD.lcd

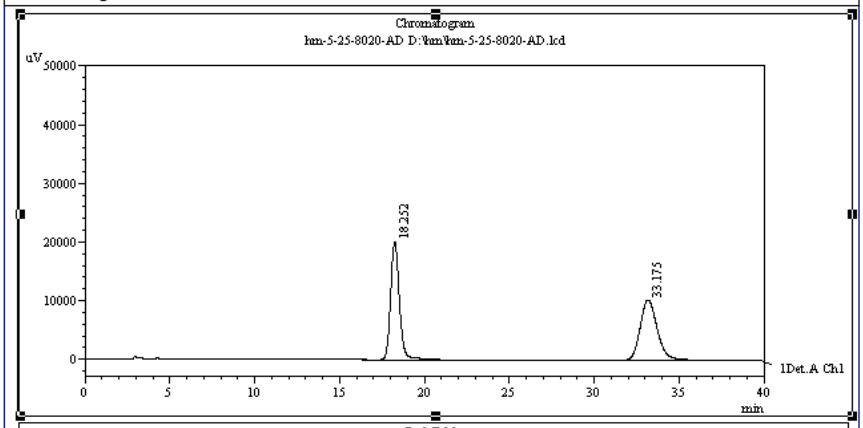
Sample Name : hm-5-25-8020-AD Date:

Column: The mobile phase:

Velocity: The detection wavelength:



<Chromatogram>



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	18.252	727630	20031	50.368
2	33.175	716992	10283	49.632
Total		1444621	30314	100.000

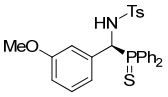
==== Shimadzu LCsolution Analysis Report ====

D:\hm\hm-5-27-8020-AD.lcd

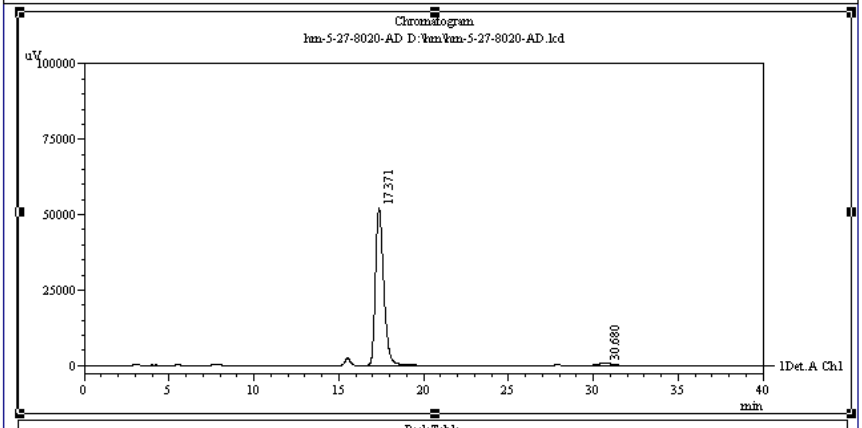
Sample Name : hm-5-27-8020-AD Date:

Column: The mobile phase:

Velocity: The detection wavelength:



<Chromatogram>



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	17.371	1783126	52107	97.671
2	30.680	42522	764	2.329
Total		1825648	52871	100.000

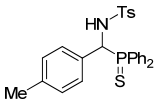
==== Shimadzu LCsolution Analysis Report ====

D:\hm\hm-5-14-8020-AD.lcd

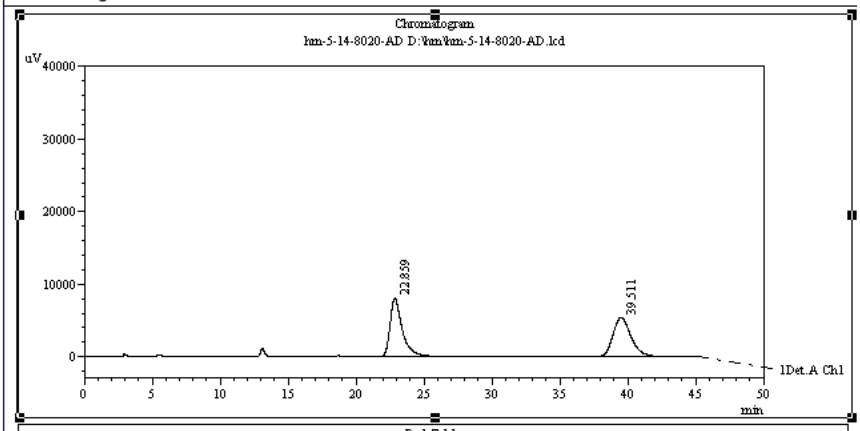
Sample Name : hm-5-14-8020-AD Date:

Column: The mobile phase:

Velocity: The detection wavelength:



<Chromatogram>



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	22.859	502644	8029	50.291
2	39.511	496824	5376	49.709
Total		999468	13405	100.000

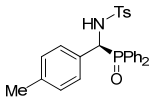
==== Shimadzu LCsolution Analysis Report ====

D:\hm\hm-5-22-8020-AD.lcd

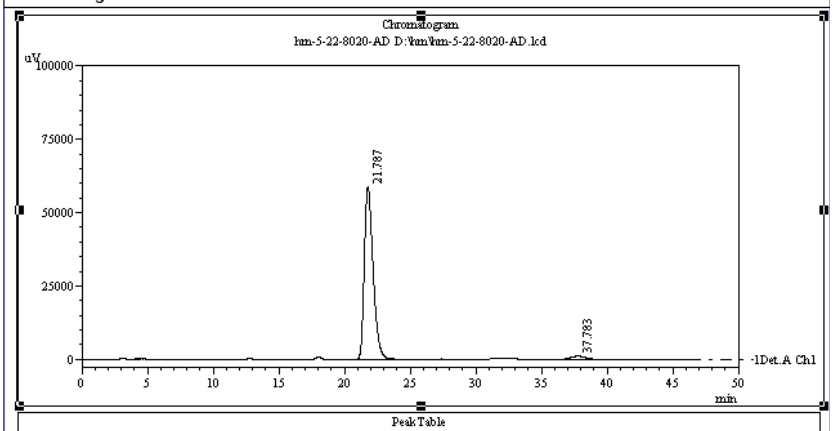
Sample Name : hm-5-22-8020-AD Date:

Column: The mobile phase:

Velocity: The detection wavelength:



<Chromatogram>



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	21.787	2746281	58942	97.062
2	37.783	83134	1125	2.938
Total		2829415	60067	100.000

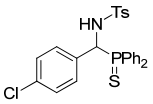
==== Shimadzu LCsolution Analysis Report ====

D:\hm\hm-5-13-8020-AD.lcd

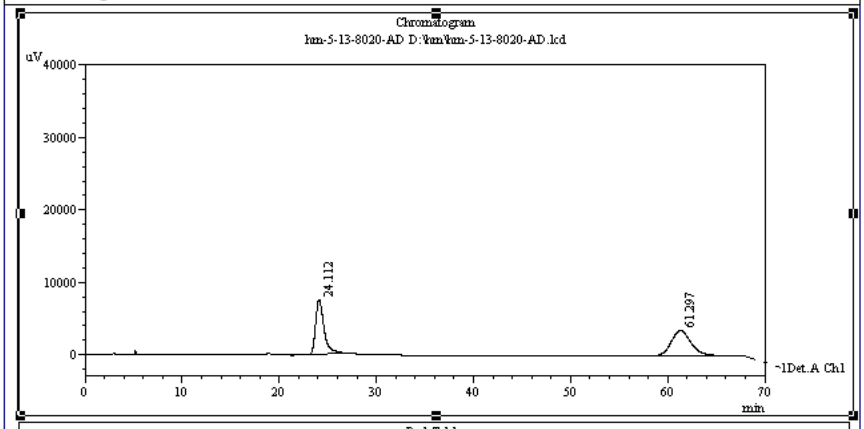
Sample Name : hm-5-13-8020-AD Date:

Column: The mobile phase:

Velocity: The detection wavelength:



<Chromatogram>



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	24.112	470630	7568	50.022
2	61.297	470220	3423	49.978
Total		940850	10991	100.000

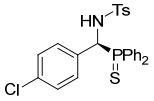
==== Shimadzu LCsolution Analysis Report ====

D:\hm\hm-5-21-8020-AD.lcd

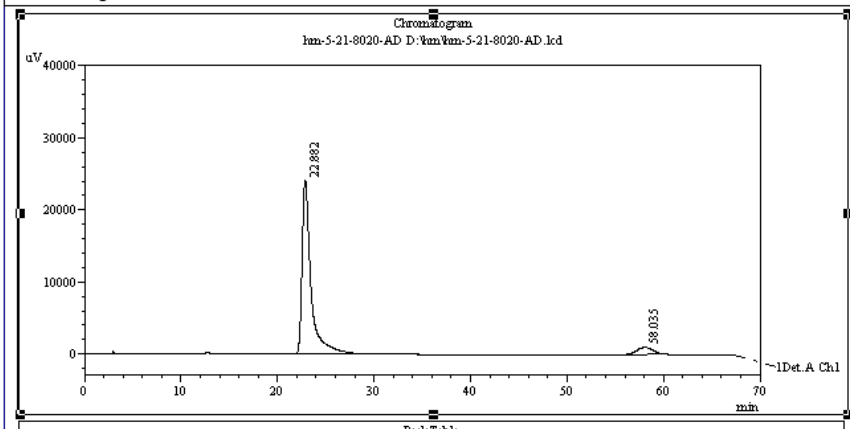
Sample Name : hm-5-21-8020-AD Date:

Column: The mobile phase:

Velocity: The detection wavelength:



<Chromatogram>



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	22.882	1548443	24165	93.052
2	58.035	115622	986	6.948
Total		1664065	25152	100.000

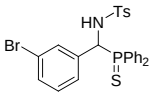
==== Shimadzu LCsolution Analysis Report ====

D:\hm\hm-5-17-8020-AD.lcd

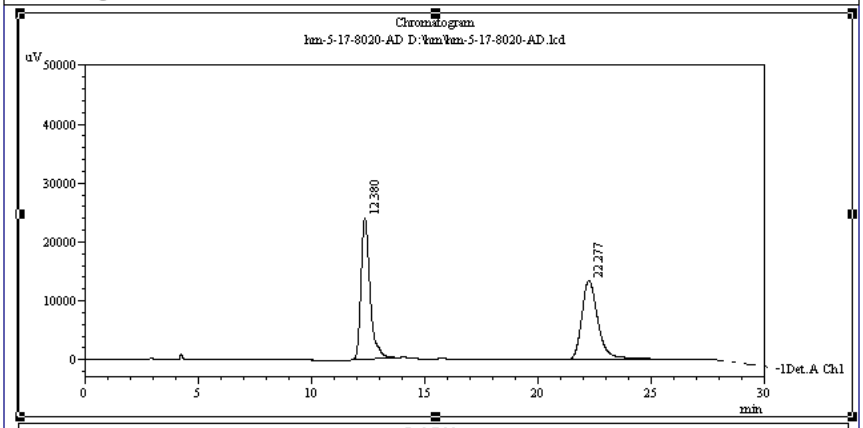
Sample Name : hm-5-17-8020-AD Date:

Column: The mobile phase:

Velocity: The detection wavelength:



<Chromatogram>



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	12.380	665452	24026	49.797
2	22.277	670871	13419	50.203
Total		1336322	37445	100.000

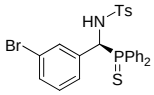
==== Shimadzu LCsolution Analysis Report ====

D:\hm\hm-5-24-8020-AD.lcd

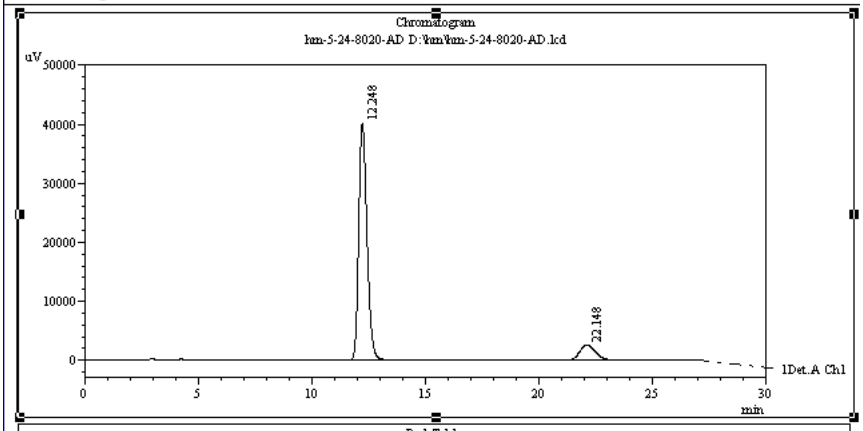
Sample Name : hm-5-24-8020-AD Date:

Column: The mobile phase:

Velocity: The detection wavelength:



<Chromatogram>



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	12.248	1013948	40231	89.149
2	22.148	123418	2635	10.851
Total		1137367	42866	100.000

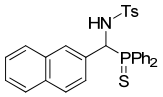
==== Shimadzu LCsolution Analysis Report ====

D:\hm\hm-5-12-8020-AD.lcd

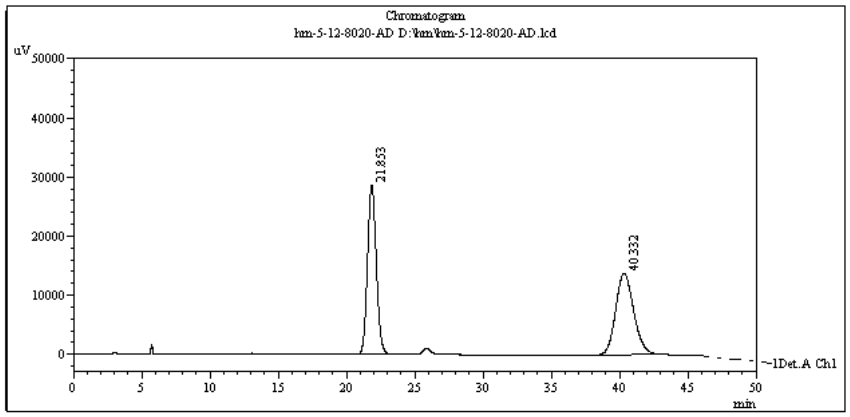
Sample Name : hm-5-12-8020-AD Date:

Column: The mobile phase:

Velocity: The detection wavelength:



<Chromatogram>



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	21.853	1283292	28607	50.267
2	40.332	1269645	13785	49.733
Total		2552937	42392	100.000

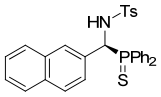
==== Shimadzu LCsolution Analysis Report ====

D:\hm\hm-5-20-8020-AD.lcd

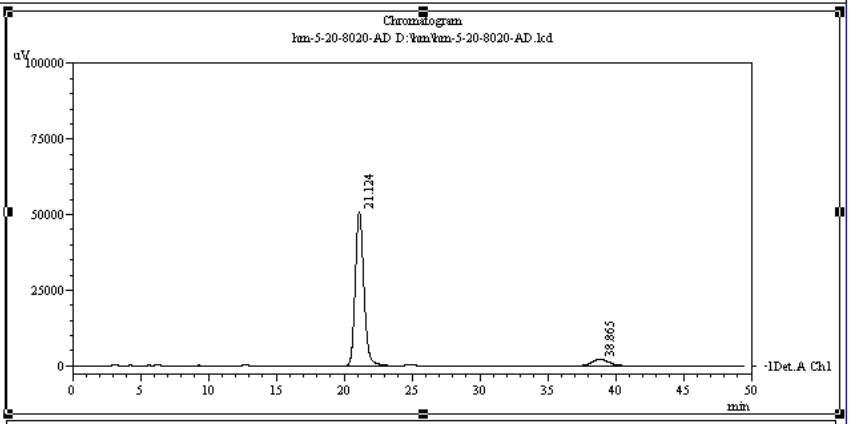
Sample Name : hm-5-20-8020-AD Date:

Column: The mobile phase:

Velocity: The detection wavelength:



<Chromatogram>



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	21.124	2240202	51119	92.290
2	38.865	187161	2203	7.710
Total		2427363	53322	100.000

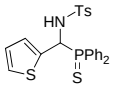
==== Shimadzu LCsolution Analysis Report ====

E:\lc\lc-4-82-ic-1ml-8020.lcd

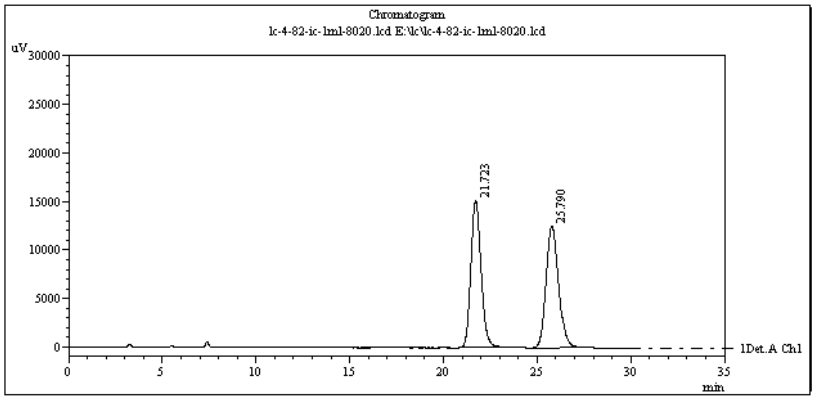
Sample Name : lc-4-82-ic-1ml-8020.lcd Date:

Column: The mobile phase:

Velocity: The detection wavelength:



<Chromatogram>



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	21.723	573500	15091	49.700
2	25.790	580426	12531	50.300
Total		1153926	27622	100.000

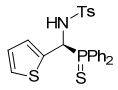
==== Shimadzu LCsolution Analysis Report ====

E:\lc\lc-4-81-ic-1ml-8020.lcd

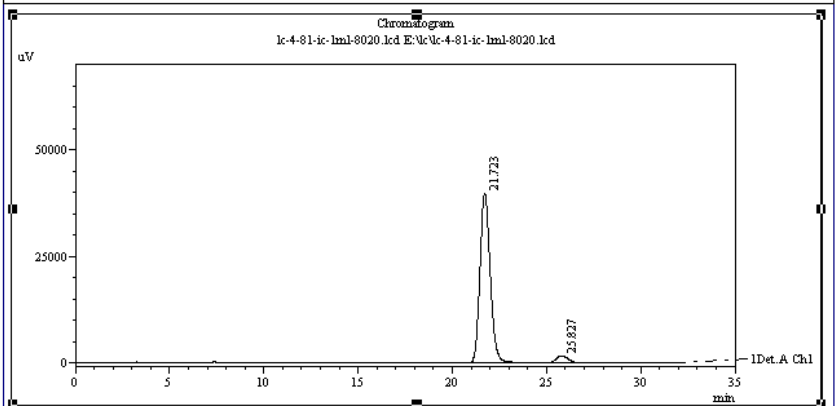
Sample Name : lc-4-81-ic-1ml-8020.lcd Date:

Column: The mobile phase:

Velocity: The detection wavelength:



<Chromatogram>



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	21.723	1514621	39911	95.355
2	25.827	73788	1677	4.645
Total		1588409	41588	100.000

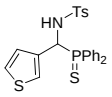
==== Shimadzu LCsolution Analysis Report ====

E:\lc\lc-4-92-IC-1ml-8020.lcd

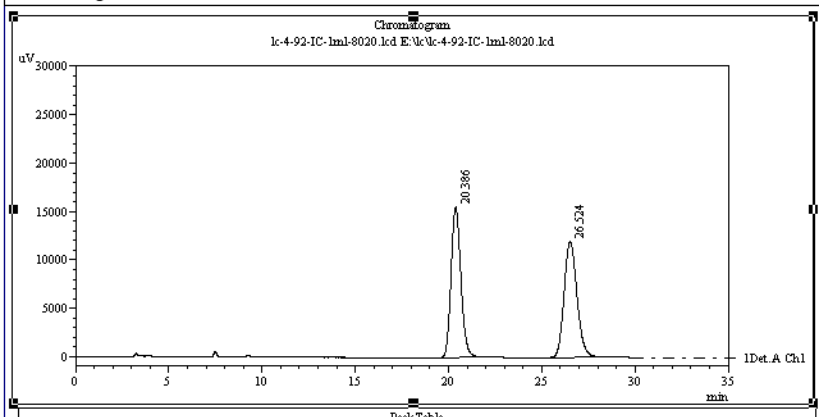
Sample Name : lc-4-92-IC-1ml-8020.lcd Date:

Column: The mobile phase:

Velocity: The detection wavelength:



<Chromatogram>



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	20.386	567364	15503	49.896
2	26.524	569721	11947	50.104
Total		1137085	27449	100.000

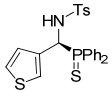
==== Shimadzu LCsolution Analysis Report ====

E:\lc\lc-4-91-IC-1ml-8020.lcd

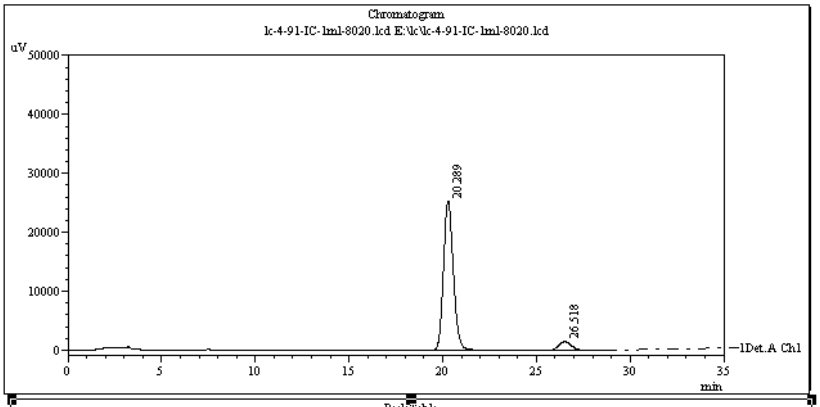
Sample Name : lc-4-91-IC-1ml-8020.lcd Date:

Column: The mobile phase:

Velocity: The detection wavelength:



<Chromatogram>



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	20.289	926172	25343	93.055
2	26.518	69123	1472	6.945
Total		995295	26814	100.000

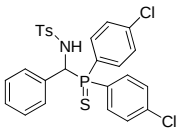
==== Shimadzu LCsolution Analysis Report ====

D:\hm\hm-5-39-AD.lcd

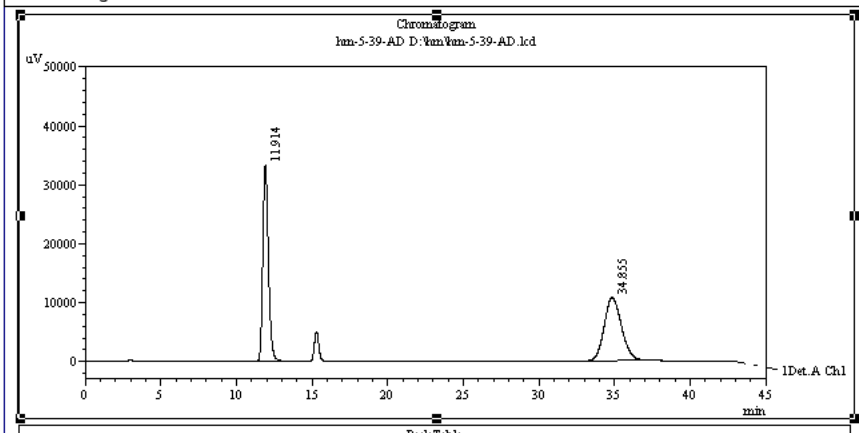
Sample Name : hm-5-39-AD Date:

Column: The mobile phase:

Velocity: The detection wavelength:



<Chromatogram>



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	11.914	858266	33205	50.303
2	34.855	847921	10661	49.697
Total		1706187	43866	100.000

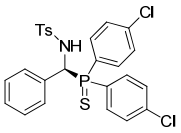
==== Shimadzu LCsolution Analysis Report ====

D:\hm\hm-5-46-AD.lcd

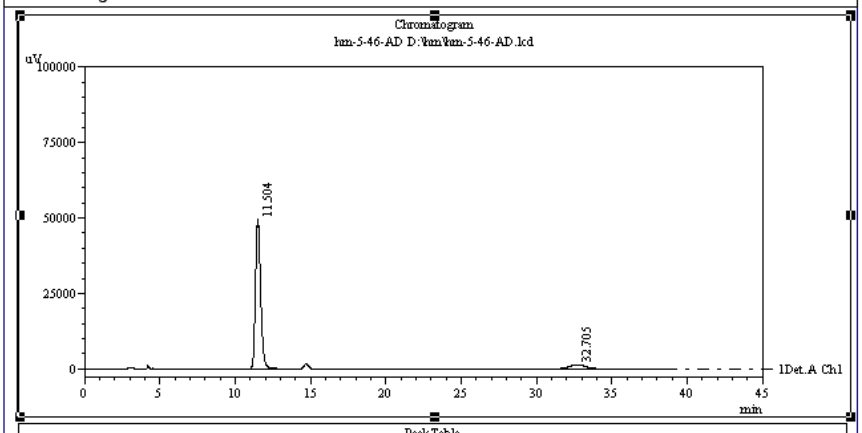
Sample Name : hm-5-46-AD Date:

Column: The mobile phase:

Velocity: The detection wavelength:



<Chromatogram>



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	11.504	1181096	49431	92.858
2	32.705	90845	1294	7.142
Total		1271941	50725	100.000

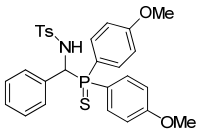
==== Shimadzu LCsolution Analysis Report ====

D:\hm\hm-5-54-7030-AD.lcd

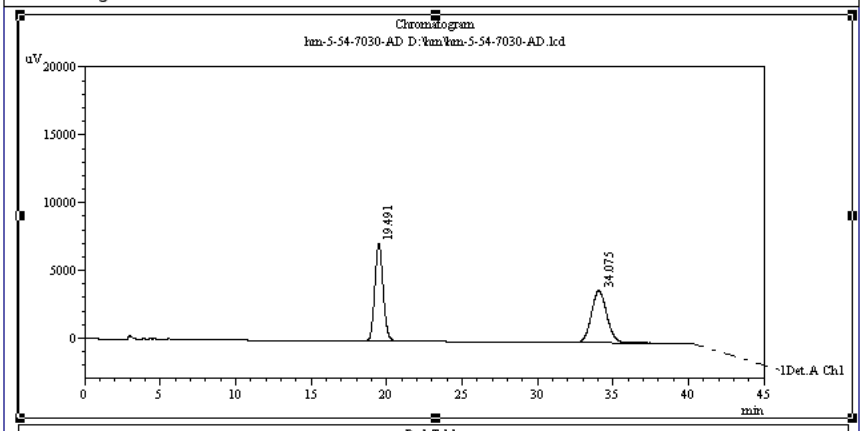
Sample Name : hm-5-54-7030-AD Date:

Column: The mobile phase:

Velocity: The detection wavelength:



<Chromatogram>



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	19.491	274509	7154	50.265
2	34.075	271618	3823	49.735
Total		546127	10977	100.000

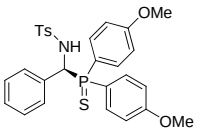
==== Shimadzu LCsolution Analysis Report ====

D:\hm\hm-5-58-7030-AD.lcd

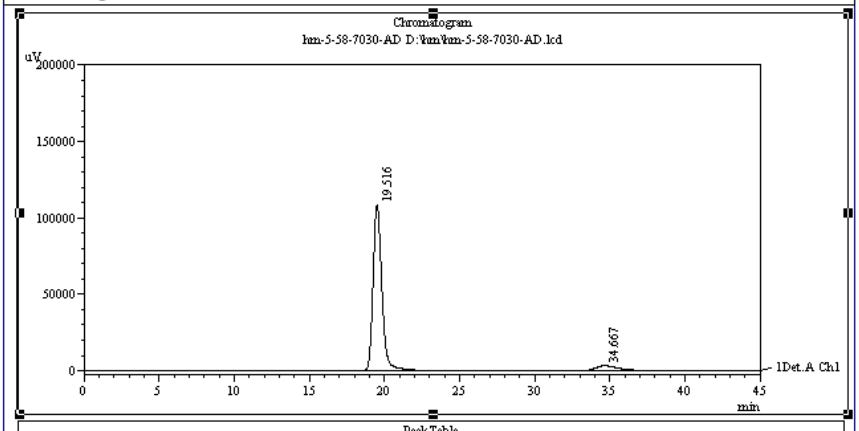
Sample Name : hm-5-58-7030-AD Date:

Column: The mobile phase:

Velocity: The detection wavelength:



<Chromatogram>



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	19.516	4477606	108541	91.779
2	34.667	401094	3387	8.221
Total		4878700	111928	100.000

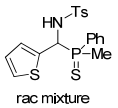
==== Shimadzu LCsolution Analysis Report ====

E:\lc\lc-4-80-zhengque-ad-1ml-8020.lcd

Sample Name : lc-4-80-zhengque-ad-1ml-8020.lcd Date:

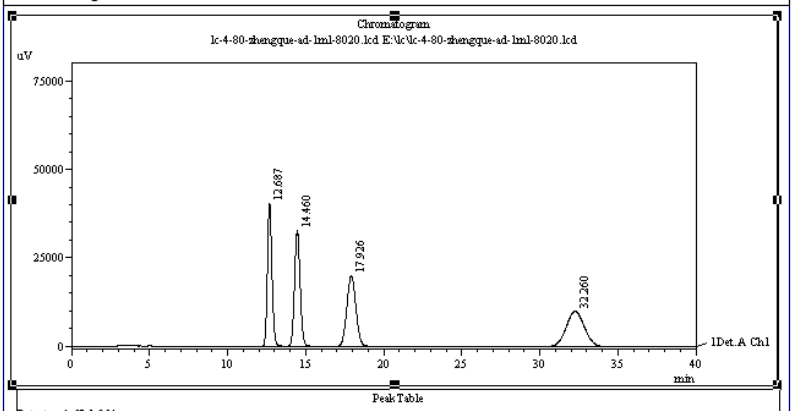
Column: The mobile phase:

Velocity: The detection wavelength:



rac mixture

<Chromatogram>



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	12.687	815674	40397	25.204
2	14.460	813349	32675	25.132
3	17.926	804827	19911	24.868
4	32.260	802489	9975	24.796
Total		3236338	102958	100.000

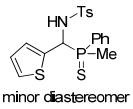
==== Shimadzu LCsolution Analysis Report ====

E:\lc\lc-4-79-1dian-ad-1ml-8020.lcd

Sample Name : lc-4-79-1dian-ad-1ml-8020.lcd Date:

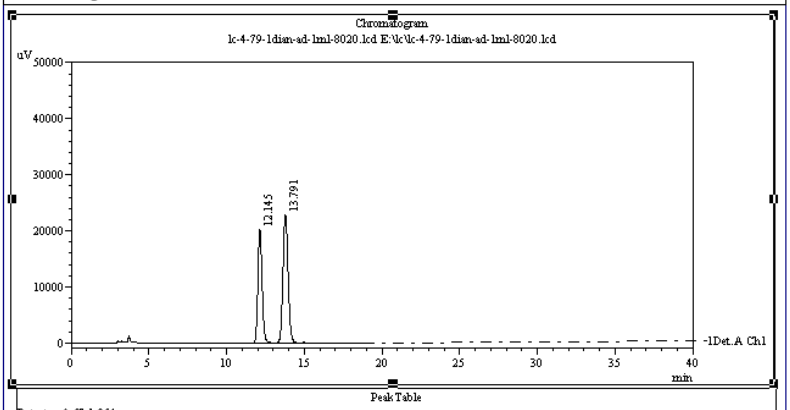
Column: The mobile phase:

Velocity: The detection wavelength:



minor diastereomer

<Chromatogram>



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	12.145	383283	20170	42.186
2	13.791	525264	22783	57.814
Total		908547	42953	100.000