Electronic Supplementary Material (ESI) for Chemical Communications

Palladium-Catalyzed Asymmetric Addition of Diarylphosphines to *α,β*-Unsaturated *N*-Acylpyrroles

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Supporting Information

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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.

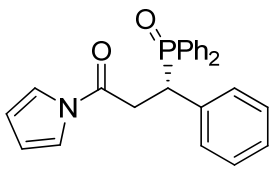
Toluene, Et_2O, THF, and hexane were distilled over sodium benzophenone ketyl under nitrogen. Dichloromethane was distilled over CaH_2 under nitrogen.

The catalysts **4**,[1] **5**,[2] diarylphosphines[3] and *α*,*β*-unsaturated *N*-acylpyrroles [4] were synthesized following the literature procedures. All other chemicals and solvents were purchased from commercial company and used as received.

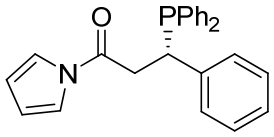
Experimental Details and Characterization Data

Experimental Procedures for Table 1:

Diphenylphosphine (44.7 mg, 0.24 mmol) was added to a solution of (*S*,*S*)-**4** (2.7 mg, 4 μmol Pd) in THF (3.0 mL) and the resulting solution was stirred for 2 min at room temperature, then *α*,*β*-unsaturated *N*-acylpyrrole **1a** (39.4 mg, 0.20 mmol) was added to it. The resulting solution was stirred for 2 h at room temperature, and then 30% H_2O_2 aqueous solution (0.1 mL) with EtOAc (2 mL) were added. After stirring for 1 h at room temperature, the mixture was concentrated under vacuum and the residue was purified by silica gel chromatography with CH_2Cl_2/MeOH = 100/1 to afford product as a white solid (75.9 mg, 0.190 mmol; 95% yield).



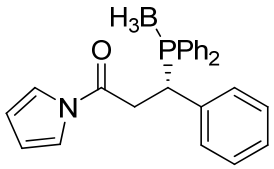
Entry 1. White solid. 95% yield. The ee was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 17.7 min [(*S*)-enantiomer], 23.9 min [(*R*)-enantiomer]. 99% ee. $[\alpha]^{20}_{D}$ = -144 (c 0.20, CH_2Cl_2), The absolute configuration was assigned by analogy with Table 2, entry 4. ^{1}H NMR ($CDCl_3$): δ 8.00-7.96 (m, 2H), 7.59-7.10 (m, 15H), 6.21 (t, J = 2.0 Hz, 2H), 4.36 (ddd, J_{HH} = 10.0 and 2.0 Hz, J_{HP} = 7.2 Hz, 1H), 3.75 (ddd, J_{HH} = 17.2 and 10.8 Hz, J_{HP} = 4.0 Hz, 1H), 3.31 (ddd, J_{HH} = 17.6 and 2.4 Hz, J_{HP} = 10.4 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 168.0 (d, J_{CP} = 15.6 Hz), 135.2 (d, J_{CP} = 6.0 Hz), 131.92 (d, J_{CP} = 66.9 Hz), 131.90 (d, J_{CP} = 67.0 Hz), 131.6 (d, J_{CP} = 21.6 Hz), 131.3 (d, J_{CP} = 8.9 Hz), 131.0 (d, J_{CP} = 8.9 Hz), 130.6 (d, J_{CP} = 14.8 Hz), 129.7 (d, J_{CP} = 5.2 Hz), 129.1 (d, J_{CP} = 11.2 Hz), 128.4 (d, J_{CP} = 1.5 Hz), 128.1 (d, J_{CP} = 11.9 Hz), 127.4 (d, J_{CP} = 3.0 Hz), 119.0, 113.4, 41.7 (d, J_{CP} = 68.4 Hz), 35.4. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 33.8 (s). HRMS (MALDI) calcd for $C_{25}H_{23}NO_2P$ ($M+H^+$) 400.1454, found 400.1461.



The reaction was carried out as described above in entry 1. After stirred 2 h at room temperature, the solution was concentrated under vacuum without addition of H_2O_2. The residue was purified by silica gel chromatography with hexane/CH_2Cl_2 = 2/1 to afford product as a white solid (69.8 mg, 0.182 mmol, 91% yield).

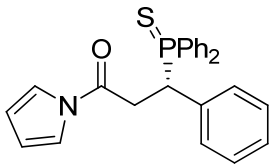
Entry 7. The absolute configuration was assigned by analogy with Table 2, entry 4. ^{1}H NMR ($CDCl_3$): δ 7.71-7.65 (m, 2H), 7.43-7.40 (m, 3H), 7.23-7.09 (m, 12H), 6.18 (t, J = 2.4 Hz, 2H), 4.27 (ddd, J_{HH} = 11.2 and 3.2 Hz, J_{HP} = 6.0 Hz, 1H), 3.43 (ddd, J_{HH} = 16.8 and 10.8 Hz, J_{HP} = 4.0 Hz, 1H), 3.06 (ddd, J_{HH} = 16.8 and 3.2 Hz, J_{HP} = 7.6 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 168.5 (d, J_{CP} = 15.5 Hz), 139.8 (d, J_{CP} = 8.5 Hz), 135.7 (d, J_{CP} = 16.2 Hz), 135.6 (d, J_{CP} = 18.6 Hz), 134.0 (d, J_{CP} = 20.5 Hz), 133.1 (d, J_{CP} = 18.2 Hz), 129.8 (d, J_{CP} = 0.8 Hz), 129.0 (d, J_{CP} = 7.3 Hz), 128.9 (d, J_{CP} = 7.3 Hz), 128.7, 128.4 (d, J_{CP} = 0.7 Hz), 128.0 (d, J_{CP} = 7.0 Hz), 126.7 (d, J_{CP} = 2.4 Hz),

118.9, 113.0, 40.2 (d, J_{CP} = 11.6 Hz), 38.6 (d, J_{CP} = 24.3 Hz). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ -0.1 (s). HRMS (EI) calcd for $C_{25}H_{22}NOP$ (M^+) 383.1439, found 383.1436.



Diphenylphosphine (44.7 mg, 0.24 mmol) was added to a solution of (*S*,*S*)-**4** (2.7 mg, 4 μmol Pd) in THF (3.0 mL) and the resulting solution was stirred for 2 min at room temperature, then *α*,*β*-unsaturated *N*-acylpyrrole **1a** (39.4 mg, 0.20 mmol) was added to it. The resulting solution was stirred for 2 h at room temperature, then 2 eq $Me_2S{\cdot}BH_3$ (2M solution in THF) was added. The mixture was stirred at room temperature for another 1 h and concentrated under vacuum. The residue was purified by silica gel chromatography with hexane/CH_2Cl_2 = 2/1 to afford product as a white solid (78.6 mg, 0.198 mmol, 99% yield).

Entry 8. 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: 7.2 min [(*S*)-enantiomer], 10.0 min [(*R*)-enantiomer]. 99% ee. $[\alpha]^{20}_{D}$ = -217 (c 1.00, CH_2Cl_2), The absolute configuration was assigned by analogy with Table 2, entry 4. ^{1}H NMR ($CDCl_3$): δ 7.99 (t, J_{HH} = 8.4 Hz, 2H), 7.60-7.13 (m, 15H), 6.22 (s, 2H), 4.59 (ddd, J_{HH} = 14.8 and 0.8 Hz, J_{HP} = 12.3 Hz, 1H), 3.79 (ddd, J_{HH} = 17.2 and 11.6 Hz, J_{HP} = 3.6 Hz, 1H), 3.20 (ddd, J_{HH} = 17.2 and 1.2 Hz, J_{HP} = 10.0 Hz, 1H), 1.0 (br, 3H). ^{13}C NMR ($CDCl_3$): δ 167.7 (d, J_{CP} = 16.2 Hz), 134.8 (d, J_{CP} = 1.2 Hz), 132.8 (d, J_{CP} = 8.4 Hz), 132.7 (d, J_{CP} = 8.8 Hz), 131.56 (d, J_{CP} = 67.0 Hz), 131.53 (d, J_{CP} = 67.4 Hz), 129.6 (d, J_{CP} = 4.4 Hz), 129.2 (d, J_{CP} = 9.3 Hz), 128.2 (d, J_{CP} = 10.1 Hz), 128.1 (d, J_{CP} = 2.0 Hz), 127.6 (d, J_{CP} = 2.4 Hz), 127.3, 127.0, 126.8, 118.9, 113.4, 37.9 (d, J_{CP} = 33.9 Hz), 35.8 (d, J_{CP} = 2.8 Hz). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 23.9 (brs). HRMS (MALDI) calcd for $C_{25}H_{24}BNOP$ ($M\text{-}H^+$) 396.1688, found 396.1683.

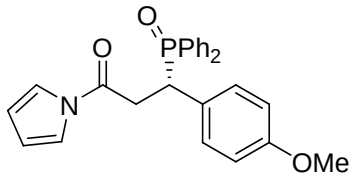


Diphenylphosphine (44.7 mg, 0.24 mmol) was added to a solution of (*S*,*S*)-**4** (2.7 mg, 4 μmol Pd) in THF (3.0 mL) and the resulting solution was stirred for 2 min at room temperature, then *α*,*β*-unsaturated *N*-acylpyrrole **1a** (39.4 mg, 0.20 mmol) was added to it. The resulting solution was stirred for 2 h at room temperature, and then 1 eq S_8 .was added. The mixture was stirred at room temperature for 1 h and concentrated under vacuum. The residue was purified by silica gel chromatography with hexane/CH_2Cl_2 = 2/1 to afford product as a pink solid (81.4 mg, 0.196 mmol, 98% yield).

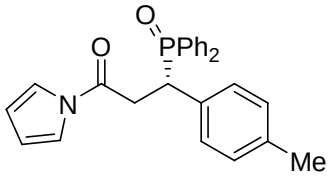
Entry 9. The ee was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 8.9 min [(*S*)-enantiomer], 10.6 min [(*R*)-enantiomer]. 98% ee. $[\alpha]^{20}_D$ = -209 (c 1.00, CH_2Cl_2), The absolute configuration was assigned by analogy with Table 2, entry 4.

^{1}H NMR ($CDCl_3$): δ 8.20-8.14 (m, 2H), 7.57-7.11 (m, 15H), 6.21 (t, J_{HH} = 2.0 Hz, 2H), 4.76 (td, J = 10.8 and 2.4 Hz, 1H), 3.83 (ddd, J_{HH} = 17.2 and 10.4 Hz, J_{HP} = 5.6 Hz, 1H), 3.27 (ddd, J_{HH} = 17.6 and 2.0 Hz, J_{HP} = 11.2 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 167.8 (d, J_{CP} = 18.1 Hz), 134.2 (d, J_{CP} = 4.4 Hz), 131.8 (d, J_{CP} = 9.3 Hz), 131.69 (d, J_{CP} = 71.0 Hz), 131.66 (d, J_{CP} = 71.4 Hz), 131.5 (d, J_{CP} = 9.7 Hz), 130.9 (d, J_{CP} = 40.3 Hz), 130.1 (d, J_{CP} = 34.7 Hz), 129.6 (d, J_{CP} = 5.3 Hz), 129.0 (d, J_{CP} = 11.7 Hz), 128.0 (d, J_{CP} = 3.7 Hz), 127.9 (d, J_{CP} = 5.6 Hz), 127.6 (d, J_{CP} = 3.2 Hz), 119.0, 113.4, 41.8 (d, J_{CP} = 52.9 Hz), 35.9 (d, J_{CP} = 5.2 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 50.8 (s). HRMS (MALDI) calcd for $C_{25}H_{22}NOPSNa$ ($M+Na^+$) 438.1063, found 438.1052.

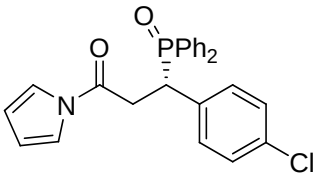
General procedure for Table 2: Diarylphosphine (0.24 mmol) was added to a solution of (*S*,*S*)-**4** (2.7 mg, 4 μmol Pd) in THF (3.0 mL) and the resulting solution was stirred for 2 min at room temperature, then *α*,*β*-unsaturated *N*-acylpyrrole **1** (0.20 mmol) was added to it. The resulting solution was stirred for 2 h at room temperature, and then 30% H_2O_2 aqueous solution (0.1 mL) with EtOAc (2 mL) were added. After stirring for 1 h at room temperature, the mixture was concentrated under vacuum and the residue was purified by silica gel chromatography to afford 1,4-adduct **3**.



Entry 2. 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: 27.9 min [(*S*)-enantiomer], 48.5 min [(*R*)-enantiomer]. 99% ee. $[\alpha]^{20}_{D}$ = -141 (c 1.00, 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 = 7.2 and 1.6 Hz, 2H), 7.59-7.26 (m, 10H), 7.20 (s, 2H), 6.71 (d, J = 8.8 Hz, 2H), 6.21 (t, J = 1.8 Hz, 2H), 4.31 (ddd, J_{HH} = 10.8 and 2.4 Hz, J_{HP} = 7.2 Hz, 1H), 3.70 (s, 3H), 3.69 (ddd, J_{HH} = 17.2 and 10.8 Hz, J_{HP} = 4.0 Hz, 1H), 3.27 (ddd, J_{HH} = 17.6 and 2.4 Hz, J_{HP} = 10.0 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 168.0 (d, J_{CP} = 16.2 Hz), 158.7 (d, J_{CP} = 2.4 Hz), 131.83 (d, J_{CP} = 62.4 Hz), 131.80 (d, J_{CP} = 62.4 Hz), 131.6 (d, J_{CP} = 20.1 Hz), 131.1 (d, J_{CP} = 8.3 Hz), 130.9 (d, J_{CP} = 8.7 Hz), 130.7 (d, J_{CP} = 5.6 Hz), 129.0 (d, J_{CP} = 11.1 Hz), 128.0 (d, J_{CP} = 11.9 Hz), 126.8 (d, J_{CP} = 5.5 Hz), 119.0, 113.9 (d, J_{CP} = 1.6 Hz), 113.3, 55.1, 40.7 (d, J_{CP} = 69.6 Hz), 35.4 (d, J_{CP} = 2.0 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 34.3 (s). MS (ESI): m/z (%) = 430 ($M+H^+$). Anal. Calcd for $C_{26}H_{24}NO_3P$: C, 72.72; H, 5.63; N, 3.26. Found: C, 72.68; H, 5.72; N, 3.13.



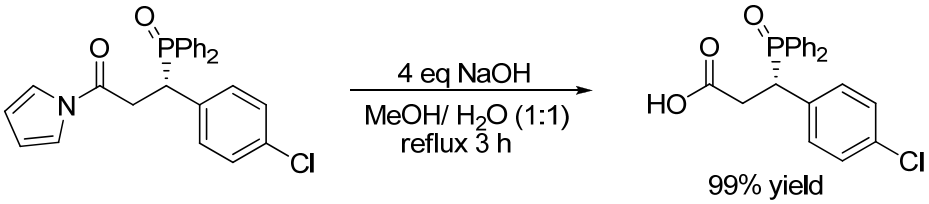
Entry 3. White solid. 99% yield. The ee was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 18.7 min [(*S*)-enantiomer], 32.8 min [(*R*)-enantiomer]. 99% ee. $[\alpha]^{20}_{D}$ = -145 (c 1.00, CH_2Cl_2), The absolute configuration was assigned by analogy with Table 2, entry 4. ^{1}H NMR ($CDCl_3$): δ 8.01-7.94 (m, 2H), 7.55-7.19 (m, 12H), 6.97 (d, J_{HH} = 8.1 Hz, 2H), 6.19 (t, J_{HH} = 2.4 Hz, 2H), 4.34 (ddd, J_{HH} = 10.2 and 2.4 Hz, J_{HP} = 7.5 Hz, 1H), 3.71 (ddd, J_{HH} = 17.7 and 10.8 Hz, J_{HP} = 4.5 Hz, 1H), 3.29 (ddd, J_{HH} = 17.7 and 2.4 Hz, J_{HP} = 10.2 Hz, 1H), 2.21 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 167.9 (d, J_{CP} = 16.2 Hz), 136.9 (d, J_{CP} = 2.3 Hz), 131.86 (d, J_{CP} = 5.8 Hz), 131.81 (d, J_{CP} = 62.3 Hz), 131.79 (d, J_{CP} = 62.3 Hz), 131.6 (d, J_{CP} = 11.2 Hz), 131.2 (d, J_{CP} = 8.5 Hz), 130.9 (d, J_{CP} = 8.9 Hz), 130.7 (d, J_{CP} = 4.3 Hz), 129.5 (d, J_{CP} = 5.4 Hz), 129.1 (d, J_{CP} = 1.9 Hz), 129.0 (d, J_{CP} = 11.2 Hz), 128.1 (d, J_{CP} = 11.6 Hz), 118.9, 113.3, 41.1 (d, J_{CP} = 68.9 Hz), 35.4 (d, J_{CP} = 1.6 Hz), 21.0 (d, J_{CP} = 0.8 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 34.9 (s). MS (ESI): m/z (%) = 414 ($M+H^+$). Anal. Calcd for $C_{26}H_{24}NO_2P$: C, 75.53; H, 5.74; N, 3.39. Found: C, 75.19; H, 5.74; N, 3.26.



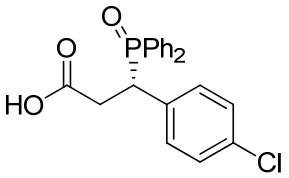
Entry 4. White solid. 98% yield. The ee was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 17.7 min [(*S*)-enantiomer], 36.9 min [(*R*)-enantiomer]. >99% ee. $[\alpha]^{20}_{D}$ = -165 (c 1.00, CH_2Cl_2), The absolute configurations of products were determined to be *S* by comparison of the specific optical rotation of the hydrolyzed product with the value reported in literature.

^{1}H NMR ($CDCl_3$): δ 7.99-7.95 (m, 2H), 7.62-7.19 (m, 12H), 7.14 (d, J_{HH} = 8.8 Hz, 2H), 6.22 (t, J_{HH} = 2.4 Hz, 2H), 4.33 (ddd, J_{HH} = 9.6 and 2.0 Hz, J_{HP} = 6.8 Hz, 1H), 3.68 (ddd, J_{HH} = 17.6 and 10.8 Hz, J_{HP} = 4.4 Hz, 1H), 3.29 (ddd, J_{HH} = 17.6 and 2.4 Hz, J_{HP} = 10.0 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 167.7 (d, J_{CP} = 16.2 Hz), 133.8 (d, J_{CP} = 15.4 Hz), 133.4 (d, J_{CP} = 3.1 Hz), 132.15 (d, J_{CP} = 57.7 Hz), 132.07 (d, J_{CP} = 57.7 Hz),

131.2 (d, J_{CP} = 21.7 Hz), 131.1 (d, J_{CP} = 8.5 Hz), 131.0 (d, J_{CP} = 5.4 Hz), 130.8 (d, J_{CP} = 8.9 Hz), 130.2 (d, J_{CP} = 15.5 Hz), 129.1 (d, J_{CP} = 11.2 Hz), 128.6 (d, J_{CP} = 1.9 Hz), 128.3 (d, J_{CP} = 12.0 Hz), 119.0, 113.5, 41.0 (d, J_{CP} = 58.2 Hz), 35.3 (d, J_{CP} = 1.5 Hz). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 33.3 (s). MS (ESI): m/z (%) = 434 ($M+H^+$). Anal. Calcd for $C_{25}H_{21}ClNO_2P$: C, 69.21; H, 4.88; N, 3.23. Found: C, 68.94; H, 4.94; N, 3.02.

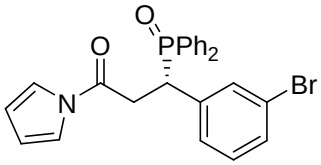


A solution of the obtained product (99.8 mg, 0.23 mmol) in entry 4 and NaOH (92 mg, 2.3 mmol) in MeOH (20 mL) and H_2O (20 mL) was stirred at 60 °C for 4 h. After cooling to room temperature, the solution was acidified to PH 1–2 with conc. hydrochloric acid and extracted with dichloromethane. The organic phase was concentrated under vacuum and the residue was purified by silica gel chromatography with CH_2Cl_2/MeOH = 50/1 to afford the hydrolyzed acid as a white solid (87.6 mg, 0.228 mmol; 99% yield).

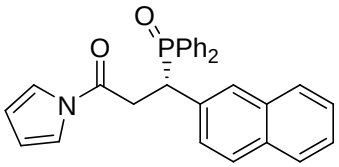


(CAS: 945743-40-8) 99% yield. >99% ee. $[\alpha]^{20}_D$ = -38 (c 0.040, $CHCl_3$).
^{1}H NMR ($CDCl_3$): δ 7.89-7.52 (m, 5H), 7.43-7.28 (m, 5H), 7.15-7.08 (m, 4H), 4.21 (td, J = 9.2 and 3.6 Hz, 1H), 3.24 (dt, J = 17.6 and 9.2 Hz, 1H), 2.98 (ddd, J_{HH} = 17.2 and 4.0 Hz, J_{HP} = 10.8 Hz, 1H).

The absolute configuration of the hydrolyzed product was determined to be *S* by comparison of the optical rotation with the literature value ($[\alpha]^{20}_D$ = -35.2 (c 1.00, $CHCl_3$) for *S*-product.[5] This assignment leads to the determination of the absolute configuration of the phosphination product (Table 2, entry 4) as *S*.

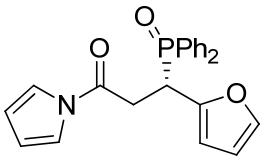


Entry 5. White solid. 97% yield. The ee was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 13.1 min [(*S*)-enantiomer], 20.0 min [(*R*)-enantiomer]. 99% ee. $[\alpha]^{20}_{D}$ = -135 (c 1.00, CH_2Cl_2), The absolute configuration was assigned by analogy with Table 2, entry 4. ^{1}H NMR ($CDCl_3$): δ 7.99-7.95 (m, 2H), 7.60-7.21 (m, 12H), 7.05 (d, J_{HH} = 8.4 Hz, 2H), 6.23 (t, J_{HH} = 2.0 Hz, 2H), 4.31 (ddd, J_{HH} = 10.0 and 2.0 Hz, J_{HP} = 6.8 Hz, 1H), 3.69 (ddd, J_{HH} = 18.0 and 10.8 Hz, J_{HP} = 3.6 Hz, 1H), 3.31 (ddd, J_{HH} = 17.6 and 2.4 Hz, J_{HP} = 9.6 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 167.6 (d, J_{CP} = 16.3 Hz), 137.5 (d, J_{CP} = 5.4 Hz), 132.7 (d, J_{CP} = 5.4 Hz), 132.13 (d, J_{CP} = 56.1 Hz), 132.11 (d, J_{CP} = 56.1 Hz), 131.2 (d, J_{CP} = 8.6 Hz), 131.1 (d, J_{CP} = 22.1 Hz), 130.8 (d, J_{CP} = 9.3 Hz), 130.5 (d, J_{CP} = 1.9 Hz), 130.1 (d, J_{CP} = 15.9 Hz), 129.9 (d, J_{CP} = 1.9 Hz), 129.1 (d, J_{CP} = 11.6 Hz), 128.3 (d, J_{CP} = 12.0 Hz), 128.1 (d, J_{CP} = 5.0 Hz), 122.3 (d, J_{CP} = 2.3 Hz), 119.0, 113.5, 41.4 (d, J_{CP} = 67.7 Hz), 35.1. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 38.3 (s). HRMS (MALDI) calcd for $C_{25}H_{22}BrNO_2P$ ($M+H^+$) 478.0555, found 478.0566.

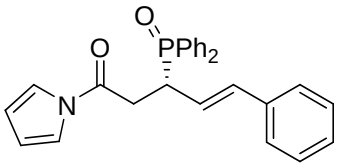


Entry 6. White solid. 95% yield. The ee was determined on a Daicel Chiralpak IC column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 9.2 min [(*S*)-enantiomer], 10.4 min [(*R*)-enantiomer]. 99% ee. $[\alpha]^{20}_{D}$ = -191 (c 1.00, CH_2Cl_2), The absolute configuration was assigned by analogy with Table 2, entry 4. ^{1}H NMR ($CDCl_3$): δ 8.04-7.99 (m, 2H), 7.88 (s, 1H), 7.77-7.70 (m, 2H), 7.65 (d, J_{HH} = 8.4 Hz, 1H), 7.58-7.16 (m, 9H), 7.21-7.15 (m, 4H), 6.18 (t, J_{HH} = 2.4 Hz, 2H), 4.54 (ddd, J_{HH} = 10.4 and 4.4 Hz, J_{HP} = 7.6 Hz, 1H), 3.85 (ddd, J_{HH} = 17.2 and 10.8 Hz, J_{HP} = 4.4 Hz, 1H), 3.40 (ddd, J_{HH} = 17.6 and 2.4 Hz, J_{HP} = 10.4 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 167.9 (d, J_{CP} = 16.3 Hz), 133.1 (d, J_{CP} = 1.9 Hz), 132.8 (d, J_{CP} = 5.8 Hz), 132.4 (d, J_{CP} = 1.9 Hz), 131.94 (d, J_{CP} = 64.6 Hz), 131.91 (d, J_{CP} = 64.7 Hz), 131.5,

131.2 (d, J_{CP} = 8.5 Hz), 130.9 (d, J_{CP} = 9.2 Hz), 130.5 (d, J_{CP} = 8.4 Hz), 129.1 (d, J_{CP} = 11.2 Hz), 128.8 (d, J_{CP} = 6.9 Hz), 128.1 (d, J_{CP} = 11.6 Hz), 128.07 (d, J_{CP} = 1.5 Hz), 127.9 (d, J_{CP} = 0.8 Hz), 127.6 (d, J_{CP} = 5.1 Hz), 127.5 (d, J_{CP} = 1.2 Hz), 126.0 (d, J_{CP} = 0.8 Hz), 125.9 (d, J_{CP} = 0.8 Hz), 119.0, 113.4, 41.7 (d, J_{CP} = 68.5 Hz), 35.6 (d, J_{CP} = 1.2 Hz). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 33.6 (s). HRMS (MALDI) calcd for $C_{29}H_{25}NO_2P$ ($M+H^+$) 450.1611, found 450.1617.

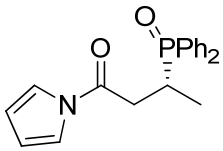


Entry 7. White solid. 94% yield. The ee was determined on a Daicel Chiralpak IC column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 14.0 min [(*S*)-enantiomer], 16.8 min [(*R*)-enantiomer]. 97% ee. $[\alpha]^{20}_{D}$ = -101 (c 1.00, CH_2Cl_2), The absolute configuration was assigned by analogy with Table 2, entry 4. ^{1}H NMR ($CDCl_3$): δ 7.92-7.87 (m, 2H), 7.59-7.19 (m, 11H), 6.25 (t, J_{HH} = 2.0 Hz, 2H), 6.19 (dd, J_{HH} = 4.8 and 2.0 Hz, 1H), 6.10 (t, J_{HH} = 3.2 Hz, 1H), 4.62 (ddd, J_{HH} = 10.8 and 2.8 Hz, J_{HP} = 10.8 Hz, 1H), 3.68 (ddd, J_{HH} = 17.6 and 10.8 Hz, J_{HP} = 4.4 Hz, 1H), 3.35 (ddd, J_{HH} = 17.6 and 2.8 Hz, J_{HP} = 9.2 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 167.8 (d, J_{CP} = 15.1 Hz), 148.1 (d, J_{CP} = 7.0 Hz), 142.1 (d, J_{CP} = 2.7 Hz), 132.20 (d, J_{CP} = 37.2 Hz), 132.17 (d, J_{CP} = 36.8 Hz), 131.23 (d, J_{CP} = 8.9 Hz), 131.18 (d, J_{CP} = 9.3 Hz), 130.9 (d, J_{CP} = 23.2 Hz), 129.9 (d, J_{CP} = 28.6 Hz), 129.0 (d, J_{CP} = 11.6 Hz), 128.3 (d, J_{CP} = 12.0 Hz), 119.0, 113.4, 110.8 (d, J_{CP} = 2.7 Hz), 109.1 (d, J_{CP} = 6.2 Hz), 36.5 (d, J_{CP} = 70.0 Hz), 32.8 (d, J_{CP} = 1.5 Hz). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 32.2 (s). HRMS (MALDI) calcd for $C_{23}H_{21}NO_3P$ ($M+H^+$) 390.1243, found 390.1254.

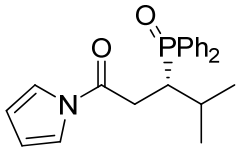


Entry 8. White solid. 83% yield. The ee was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 23.5

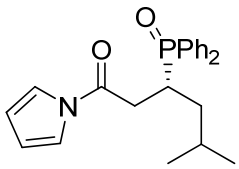
min [(*S*)-enantiomer], 31.5 min [(*R*)-enantiomer]. 98% ee. $[\alpha]^{20}_{D}$ = -113 (c 1.00, CH_2Cl_2), The absolute configuration was assigned by analogy with Table 2, entry 4. ^{1}H NMR ($CDCl_3$): δ 7.91 (t, J_{HH} = 8.8 Hz, 2H), 7.79 (dd, J = 10.0 and 8.0 Hz, 2H), 7.57-7.16 (m, 13H), 6.45 (dd, J = 15.6 and 3.6 Hz, 1H), 6.25 (s, 2H), 6.13 (ddd, J = 15.6, 8.8 and 2.4 Hz, 1H), 4.06 (q, J = 8.8 Hz, 1H), 3.41 (ddd, J_{HH} = 17.2 and 10.0 Hz, J_{HP} = 4.4 Hz, 1H), 3.21 (ddd, J_{HH} = 16.8 and 2.0 Hz, J_{HP} = 10.8 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 167.9 (d, J_{CP} = 15.6 Hz), 136.3 (d, J_{CP} = 2.6 Hz), 135.9 (d, J_{CP} = 11.2 Hz), 132.10 (d, J_{CP} = 26.3 Hz), 132.07 (d, J_{CP} = 26.7 Hz), 131.4 (d, J_{CP} = 1.3 Hz), 131.3 (d, J_{CP} = 8.6 Hz), 131.1 (d, J_{CP} = 9.1 Hz), 130.4 (d, J_{CP} = 3.4 Hz), 129.0 (d, J_{CP} = 11.6 Hz), 128.5 (d, J_{CP} = 11.6 Hz), 128.4, 127.7, 126.3 (d, J_{CP} = 1.3 Hz), 122.3 (d, J_{CP} = 7.3 Hz), 119.0, 113.4, 39.6 (d, J_{CP} = 69.8 Hz), 33.6. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 33.7 (s). HRMS (MALDI) calcd for $C_{27}H_{25}NO_2P$ ($M+H^+$) 426.1621, found 426.1617.



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: 12.5 min [(*S*)-enantiomer], 16.3 min [(*R*)-enantiomer]. 91% ee. $[\alpha]^{20}_{D}$ = +2.2 (c 1.70, CH_2Cl_2), The absolute configuration was assigned by analogy with Table 2, entry 4. ^{1}H NMR ($CDCl_3$): δ 7.87-7.45 (m, 10H), 7.25 (s, 2H), 6.26 (t, J_{HH} = 2.8 Hz, 1H), 3.24-3.22 (m, 1H), 3.12-2.98 (m, 2H), 1.25 (dd, J = 16.0 and 6.4 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 168.3 (d, J_{CP} = 16.4 Hz), 131.8 (d, J_{CP} = 3.0 Hz), 131.7 (d, J_{CP} = 3.0 Hz), 131.0 (d, J_{CP} = 95.2 Hz), 130.9 (d, J_{CP} = 97.4 Hz), 130.6 (d, J_{CP} = 8.9 Hz), 130.5 (d, J_{CP} = 8.9 Hz), 128.7 (d, J_{CP} = 11.2 Hz), 128.5 (d, J_{CP} = 11.8 Hz), 118.8, 113.2, 34.1, 28.1 (d, J_{CP} = 72.9 Hz), 12.7 (d, J_{CP} = 3.0 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 37.4 (s). HRMS (ESI) calcd for $C_{20}H_{20}NO_2P$ (M) 337.1232, found 337.1232.

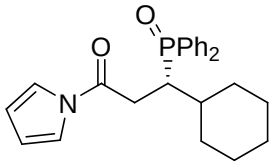


Entry 10. White solid. 92% yield. The ee was determined on a Daicel Chiralpak IC column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 8.1 min [(*S*)-enantiomer], 9.2 min [(*R*)-enantiomer]. 94% ee. $[\alpha]^{20}_{D}$ = -9.6 (c 0.80, CH_2Cl_2), The absolute configuration was assigned by analogy with Table 2, entry 4. ^{1}H NMR ($CDCl_3$): δ 7.93-7.80 (m, 4H), 7.53-7.22 (m, 8H), 6.23 (t, J_{HH} = 2.4 Hz, 1H), 3.42-3.36 (m, 1H), 3.13-3.09 (m, 2H), 2.25-2.14 (m, 1H), 1.09 (d, J_{HH} = 6.8 Hz, 3H), 0.93 (d, J_{HH} = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 169.2 (d, J_{CP} = 10.5 Hz), 132.2 (d, J_{CP} = 96.1 Hz), 132.1 (d, J_{CP} = 96.1 Hz), 131.64 (d, J_{CP} = 2.8 Hz), 131.61 (d, J_{CP} = 2.8 Hz), 130.8 (d, J_{CP} = 8.9 Hz), 130.7 (d, J_{CP} = 8.4 Hz), 128.7 (d, J_{CP} = 11.5 Hz), 128.6 (d, J_{CP} = 11.5 Hz), 118.9, 113.2, 37.6 (d, J_{CP} = 71.4 Hz), 28.0, 27.2 (d, J_{CP} = 1.2 Hz), 22.6 (d, J_{CP} = 13.7 Hz), 18.6 (d, J_{CP} = 2.0 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 38.5 (s). HRMS (MALDI) calcd for $C_{22}H_{25}NO_2P$ ($M+H^+$) 366.1613, found 366.1617.

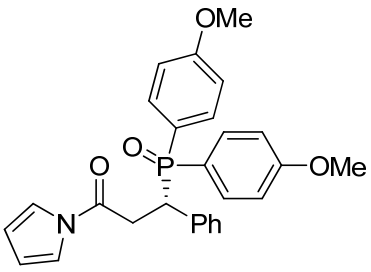


Entry 11. White solid. 93% yield. The ee was determined on a Daicel Chiralpak IC column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 7.6 min [(*R*)-enantiomer], 9.3 min [(*S*)-enantiomer]. 96% ee. $[\alpha]^{20}_{D}$ = -24.6 (c 1.00, CH_2Cl_2), The absolute configuration was assigned by analogy with Table 2, entry 4. ^{1}H NMR ($CDCl_3$): δ 7.90-7.80 (m, 4H), 7.53-7.38 (m, 6H), 7.19 (s, 2H), 6.95 (t, J_{HH} = 2.4 Hz, 2H), 3.46-3.39 (m, 1H), 3.23 (ddd, J_{HH} = 17.6 and 16.4 Hz, J_{HP} = 4.4 Hz, 1H), 2.95 (ddd, J_{HH} = 18.0 and 6.4 Hz, J_{HP} = 9.2 Hz, 1H), 1.68-1.42 (m, 3H), 0.83 (t, J_{HH} = 6.4 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 169.2 (d, J_{CP} = 10.5 Hz), 132.15 (d, J_{CP} = 2.7 Hz), 132.12 (d, J_{CP} = 2.7 Hz), 132.0 (d, J_{CP} = 96.8 Hz), 131.9 (d, J_{CP} = 94.8 Hz), 131.2 (d, J_{CP} = 8.9 Hz), 131.15 (d, J_{CP} = 8.9 Hz), 129.03 (d, J_{CP} = 11.8 Hz), 128.98 (d, J_{CP} = 11.3 Hz), 119.3, 113.6, 38.2 (d, J_{CP} = 2.3 Hz), 34.0, 30.8 (d, J_{CP} = 72.3 Hz), 26.0 (d,

J_{CP} = 11.2 Hz), 23.7, 21.5. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 36.8 (s). HRMS (MALDI) calcd for $C_{23}H_{27}NO_2P$ ($M+H^+$) 380.1778, found 380.1774.

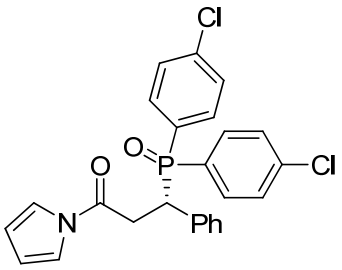


Entry 12. White solid. 99% yield. The ee was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 23.1 min [(*S*)-enantiomer], 29.0 min [(*R*)-enantiomer]. 96% ee. $[\alpha]^{20}_D$ = -26.9 (c 1.00, CH_2Cl_2), The absolute configuration was assigned by analogy with Table 2, entry 4. ^{1}H NMR ($CDCl_3$): δ 7.95-7.90 (m, 4H), 7.60-7.35 (m, 6H), 7. 23 (s, 2H), 6.24 (t, J_{HH} = 2.4 Hz, 2H), 3.38-3.30 (m, 1H), 3.26-3.00 (m, 2H), 2.20-2.12 (m, 1H), 1.85-1.45 (m, 5H), 1.18-0.94 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 169.3 (d, J_{CP} = 11.2 Hz), 132.3 (d, J_{CP} = 96.0 Hz), 132.2 (d, J_{CP} = 94.1 Hz), 131.68 (d, J_{CP} = 2.7 Hz), 131.66 (d, J_{CP} = 2.7 Hz), 130.80 (d, J_{CP} = 8.9 Hz), 130.79 (d, J_{CP} = 8.1 Hz), 128.7 (d, J_{CP} = 11.6 Hz), 128.6 (d, J_{CP} = 11.2 Hz), 119.0, 113.3, 37.8 (d, J_{CP} = 1.5 Hz), 37.6 (d, J_{CP} = 71.2 Hz), 32.8 (d, J_{CP} = 12.0 Hz), 29.4 (d, J_{CP} = 2.3 Hz), 29.2 (d, J_{CP} = 0.8 Hz), 26.6 (d, J_{CP} = 1.2 Hz), 26.3, 25.8. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 37.9 (s). HRMS (MALDI) calcd for $C_{25}H_{29}NO_2P$ ($M+H^+$) 406.1929, found 406.1930.



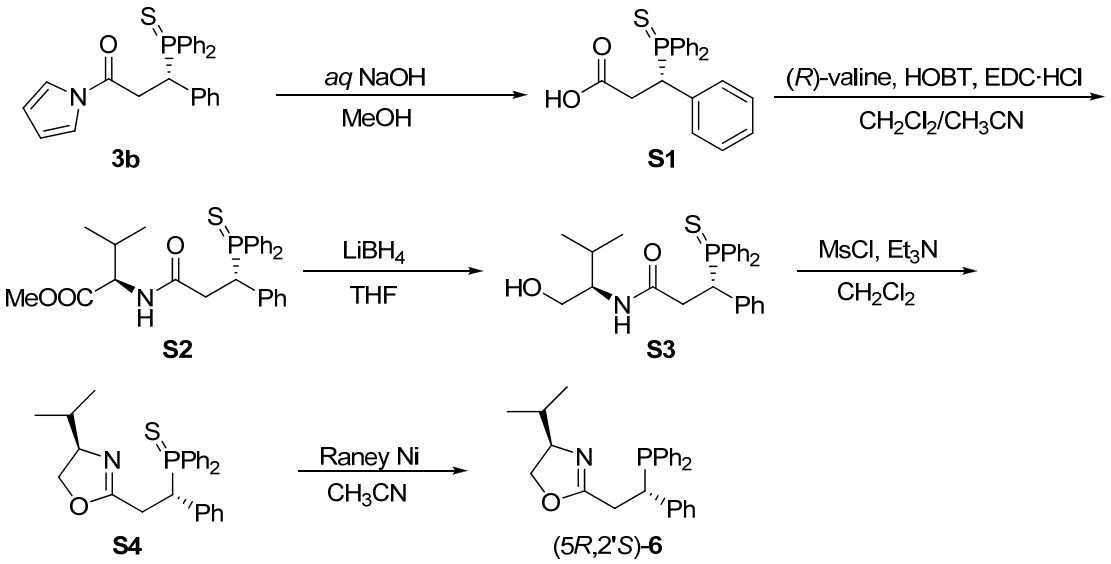
Entry 13. White solid. 98% yield. The ee was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 19.6 min [(*S*)-enantiomer], 40.5 min [(*R*)-enantiomer]. 97% ee. $[\alpha]^{20}_D$ = -139 (c 1.00, CH_2Cl_2), The absolute configuration was assigned by analogy with Table 2, entry 4. ^{1}H NMR ($CDCl_3$): δ 7.87 (dd, *J* = 10.0 and 8.8 Hz, 2H), 7.38-7.13 (m, 9H), 7.03 (dd, dd, *J* = 8.8 and 2.0 Hz, 2H), 6.73 (dd, dd, *J* = 9.2 and 2.4 Hz, 2H), 6.20 (t, *J* = 2.4 Hz,

2H), 4.26 (ddd, J_{HH} = 10.4 and 2.4 Hz, J_{HP} = 7.6 Hz, 1H), 3.84 (s, 3H), 3.73 (s, 3H), 3.70 (ddd, J_{HH} = 17.6 and 10.8 Hz, J_{HP} = 4.8 Hz, 1H), 3.32 (ddd, J_{HH} = 17.6 and 2.4 Hz, J_{HP} = 10.4 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 168.1 (d, J_{CP} = 15.9 Hz), 162.27 (d, J_{CP} = 57.7 Hz), 162.25 (d, J_{CP} = 58.1 Hz), 135.5 (d, J_{CP} = 5.4 Hz), 133.0 (d, J_{CP} = 10.1 Hz), 132.8 (d, J_{CP} = 10.1 Hz), 129.7 (d, J_{CP} = 5.4 Hz), 128.4 (d, J_{CP} = 1.9 Hz), 127.2 (d, J_{CP} = 2.7 Hz), 122.8 (d, J_{CP} = 70.5 Hz), 121.7 (d, J_{CP} = 63.9 Hz), 119.0, 114.6 (d, J_{CP} = 12.4 Hz), 113.6 (d, J_{CP} = 12.8 Hz), 113.2, 55.3, 55.1, 42.1 (d, J_{CP} = 68.9 Hz), 35.4. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 34.1 (s). HRMS (MALDI) calcd for $C_{27}H_{27}NO_4P$ ($M+H^+$) 460.1674, found 460.1672.



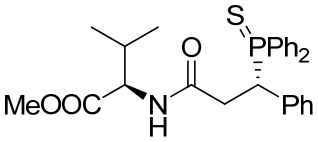
Entry 14. White solid. 97% yield. The ee was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 17.3 min [(*S*)-enantiomer], 21.3 min [(*R*)-enantiomer]. 98% ee. $[\alpha]^{20}_D$ = -137 (c 1.00, CH_2Cl_2), The absolute configuration was assigned by analogy with Table 2, entry 4. ^{1}H NMR ($CDCl_3$): δ 7.90 (dd, J = 10.0 and 8.0 Hz, 2H), 7.52 (d, J = 8.0 and 2.0 Hz, 2H), 7.40-7.34 (m, 4H), 7.25-7.14 (m, 7H), 6.20 (t, J = 2.4 Hz, 2H), 4.35 (ddd, J_{HH} = 10.0 and 2.8 Hz, J_{HP} = 7.2 Hz, 1H), 3.70 (ddd, J_{HH} = 17.6 and 10.0 Hz, J_{HP} = 5.2 Hz, 1H), 3.38 (ddd, J_{HH} = 16.8 and 1.6 Hz, J_{HP} = 11.2 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 167.6 (d, J_{CP} = 15.5 Hz), 138.76 (d, J_{CP} = 79.3 Hz), 138.72 (d, J_{CP} = 78.9 Hz), 134.6 (d, J_{CP} = 5.8 Hz), 132.5 (d, J_{CP} = 9.3 Hz), 132.2 (d, J_{CP} = 9.7 Hz), 129.7 (d, J_{CP} = 33.3 Hz), 129.6 (d, J_{CP} = 5.8 Hz), 129.5 (d, J_{CP} = 11.6 Hz), 128.7 (d, J_{CP} = 25.9 Hz), 128.6, 128.5 (d, J_{CP} = 10.4 Hz), 127.6 (d, J_{CP} = 2.4 Hz), 118.9, 113.5, 41.5 (d, J_{CP} = 69.7 Hz), 35.3. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 34.1 (s). HRMS (MALDI) calcd for $C_{25}H_{21}Cl_2NO_2P$ ($M+H^+$) 468.0682, found 468.0688.

Synthesis of Phosphine-Oxazoline Ligand 6 (Scheme 1)



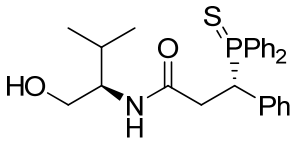
NaOH (480 mg, 12 mmol) was added to a solution of **3b** (1.246 g, 3 mmol; 98% ee) in MeOH/H_2O (20 mL/20 mL), and the resulting mixture was refluxed for 2 h. After cooled to room temperature, the solution was acidified to PH 1–2 with conc. hydrochloric acid and extracted with dichloromethane. The organic phase was concentrated under vacuum and the residue was purified by silica gel chromatography with CH_2Cl_2/MeOH = 50/1 to afford **S1** (CAS: 354816-38-9) as a white solid (1.090 g, 2.97 mmol; 99% yield). $[\alpha]^{20}_D$ = -167 (c 1.00, CH_2Cl_2).

^{1}H NMR ($CDCl_3$): δ 8.14-8.08 (m, 2H), 7.54-7.52 (m, 3H), 7.44 (dd, J_{HH} = 8.4 and 7.2 Hz, 2H), 7.36-7.11 (m, 8H), 4.38 (td, J = 11.2 and 3.2 Hz, 1H), 3.22 (ddd, J_{HH} = 17.6 and 11.2 Hz, J_{HP} = 6.8 Hz, 1H), 2.86 (ddd, J_{HH} = 17.2 and 3.2 Hz, J_{HP} = 10.4 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 176.9 (d, J_{CP} = 19.3 Hz), 133.8 (d, J_{CP} = 5.4 Hz), 131.94, 131.9 (d, J_{CP} = 12.7 Hz), 131.5 (d, J_{CP} = 9.7 Hz), 131.3 (d, J_{CP} = 3.0 Hz), 130.8 (d, J_{CP} = 45.3 Hz), 130.0 (d, J_{CP} = 39.4 Hz), 129.6 (d, J_{CP} = 5.2 Hz), 128.9 (d, J_{CP} = 11.2 Hz), 127.9 (d, J_{CP} = 14.1 Hz), 127.85, 127.7 (d, J_{CP} = 3.0 Hz), 42.7 (d, J_{CP} = 51.9 Hz), 35.2 (d, J_{CP} = 3.7 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 50.4 (s).



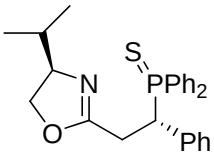
(*R*)-Valine (370 mg, 2.82 mmol) was added to a mixture of **S1** (860 mg, 2.35 mmol), HOBT (381 mg, 2.82 mmol) and EDC·HCl (540 mg, 2.82 mmol) in dichloromethane (20 mL) and acetonitrile (20 mL). The mixture was stirred at room temperature for 6 h until the starting materials disappeared (monitored by TLC). The solvent was removed under vacuum and the residue was purified by silica gel chromatography with CH_2Cl_2/MeOH = 100/1 to afford **S2** (CAS: 216862-91-8) as a white solid (1.014 g, 2.11 mmol; 90% yield). $[\alpha]^{20}_D$ = -94.7 (c 1.00, CH_2Cl_2).

^{1}H NMR ($CDCl_3$): δ 8.20-8.15 (m, 2H), 7.56-7.45 (m, 5H), 7.32-7.10 (m, 8H), 5.92 (d, J = 8.8 Hz, 1H), 4.54 (ddd, J_{HH} = 14.8 and 11.6 Hz, J_{HP} = 3.2 Hz, 1H), 4.33 (dd, J_{HH} = 9.2 and 4.8 Hz, 1H), 3.67 (s, 3H), 3.06 (ddd, J_{HH} = 18.8 and 11.6 Hz, J_{HP} = 7.2 Hz, 1H), 2.86 (ddd, J_{HH} = 14.4 and 3.2 Hz, J_{HP} = 8.8 Hz, 1H), 1.89-1.78 (m,1H), 0.49 (d, J_{HH} = 6.8 Hz, 3H), 0.41 (d, J_{HH} = 6.8 Hz, 3H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 45.4 (s).



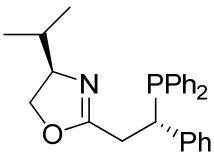
A mixture of **S2** (840 mg, 1.75 mmol) and $LiBH_4$ (76 mg, 3.50 mmol) in THF (40 mL) was stirred at room temperature for 6 h. The reaction was quenched by H_2O (1 mL) and the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography with CH_2Cl_2/MeOH = 100/1 to afford **S3** (CAS: 216863-12-6) as a white solid (771 mg, 1.71 mmol; 98% yield). $[\alpha]^{20}_D$ = -138 (c 1.00, CH_2Cl_2).

^{1}H NMR ($CDCl_3$): δ 8.21-8.15 (m, 2H), 7.56-7.42 (m, 5H), 7.32-7.08 (m, 8H), 5.66 (d, J = 7.6 Hz, 1H), 4.57 (td, J = 10.4 and 3.6 Hz, 1H), 3.50-3.38 (m, 3H), 3.00 (ddd, J_{HH} = 14.4 and 10.4 Hz, J_{HP} = 9.6 Hz, 1H), 2.82 (ddd, J_{HH} = 13.6 and 4.0 Hz, J_{HP} = 9.6 Hz, 1H), 2.32 (bs, 1H), 1.62-1.53 (m,1H), 0.61 (d, J_{HH} = 7.2 Hz, 3H), 0.47 (d, J_{HH} = 6.8 Hz, 3H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 45.4 (s).



MsCl (4.24 g, 37 mmol) was added to a solution of **S3** (667 mg, 1.48 mmol) in dichloromethane (30 mL) and Et_3N (10 ml) and the mixture was stirred at room temperature overnight. The mixture was filtered and washed with dichloromethane. The filtrate was concentrated under vacuum and the residue was purified by neutral alumina chromatography with dichloromethane to afford **S4** (CAS: 192371-97-4) as a white solid (457 mg, 1.05 mmol; 71% yield). $[\alpha]^{20}_D$ = -146 (c 1.00, CH_2Cl_2).

^{1}H NMR ($CDCl_3$): δ 8.19-8.14 (m, 2H), 7.57-7.43 (m, 5H), 7.33-7.07 (m, 8H), 5.66 (d, J = 7.6 Hz, 1H), 4.48 (ddd, J_{HH} = 13.2 and 3.2 Hz, J_{HP} = 10.0 Hz, 1H), 3.94 (dd, J_{HH} = 9.2 and 8.0 Hz, 1H), 3.76-3.67 (m, 2H), 3.21 (ddd, J_{HH} = 19.6 and 12.0 Hz, J_{HP} = 7.6 Hz, 1H), 2.75 (dddd, J_{HH} = 16.4, 8.4, 2.8 and 4.0 Hz, 1H), 1.45-1.37 (m, 1H), 0.59 (d, J_{HH} = 6.4 Hz, 3H), 0.47 (d, J_{HH} = 7.2 Hz, 3H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 50.3 (s).



Raney Ni (100 eq) in degassed H_2O (10 mL) was washed with degassed methanol (30 mL) for three times, then a solution of **S4** (320 mg, 0.74 mmol) in acetonitrile (30 mL) was added to it. The mixture was stirred at room temperature for two days. Raney nickel was filtered under nitrogen with dichloromethane. The solvent was removed under vacuum to afford **(5*R*,2'*S*)-6** (CAS: 192372-08-0) as a white solid (225 mg, 0.56 mmol; 76% yield). $[\alpha]^{20}_D$ = -97.2 (c 1.00, CH_2Cl_2).

^{1}H NMR ($CDCl_3$): δ 7.68-7.65 (m, 2H), 7.44-7.38 (m, 3H), 7.18-7.06 (m, 10H), 4.04-3.96 (m, 1H), 3.94 (dd, J_{HH} = 9.2 and 8.0 Hz, 1H), 3.72 (t, J_{HH} = 7.2 Hz, 1H), 3.70-3.62 (m, 1H), 2.80 (ddd, J_{HH} = 15.6 and 12.0 Hz, J_{HP} = 6.4 Hz, 1H), 2.64 (dt, J_{HH} = 16.8 and 5.2 Hz, 1H), 1.51-1.41 (m, 1H), 0.70 (d, J_{HH} = 6.8 Hz, 3H), 0.63 (d, J_{HH} = 6.8 Hz, 3H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 0.5 (s).

References:

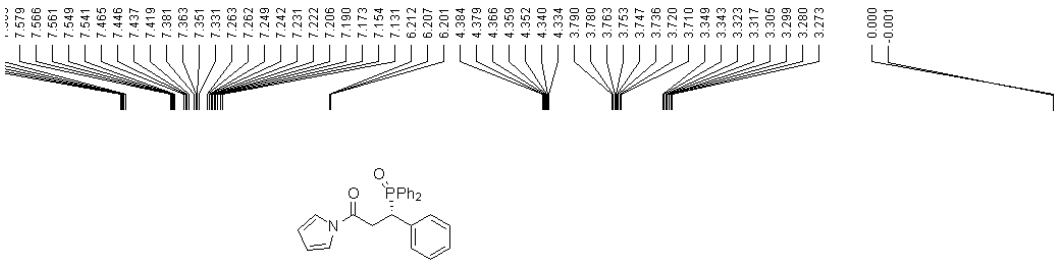
(1) J.-J. Feng, X.-F. Chen, M. Shi, W.-L. Duan, *J. Am. Chem. Soc*. **2010**, *132*, 5562.

(2) A. Bugarin, B. T. Connell, *Organometallics* **2008**, *27*, 4357.

(3) Z. Herseczki, I. Gergely, C. Hegedüs, A. Szöllősy, J. Bakos, *Tetrahedron*: *Asymmetry* **2004**, *15*, 1673.

(4) N. Yamagiwa, H. Qin, S. Matsunaga, M. Shibasaki, *J. Am. Chem. Soc. 2005*, **127**, 13419.

(5) a) I. Ibrahem, R. Rios, J. Vesely, P. Hammar, L. Eriksson, F. Himo, A. Córdova, *Angew. Chem.* **2007***, 119,* 4591; *Angew. Chem., Int. Ed*. **2007**, *46*, 4507; b) I. Ibrahem, P. Hammar, J. Vesely, R. Rios, L. Eriksson, A. Córdova, *Adv. Synth. Catal*. **2008**, *350*, 1875.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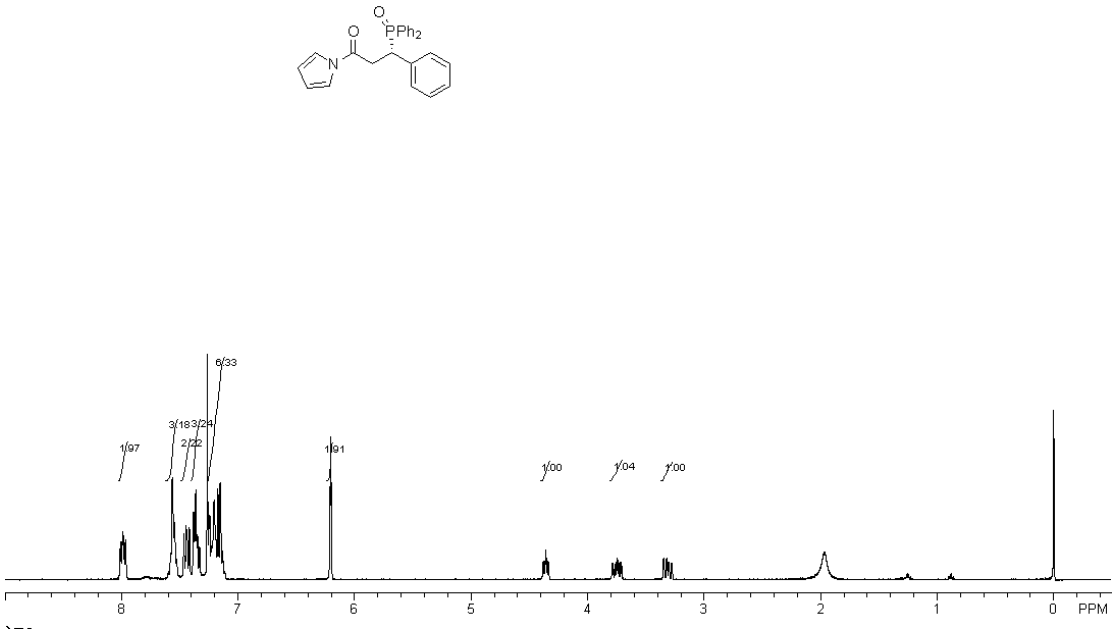
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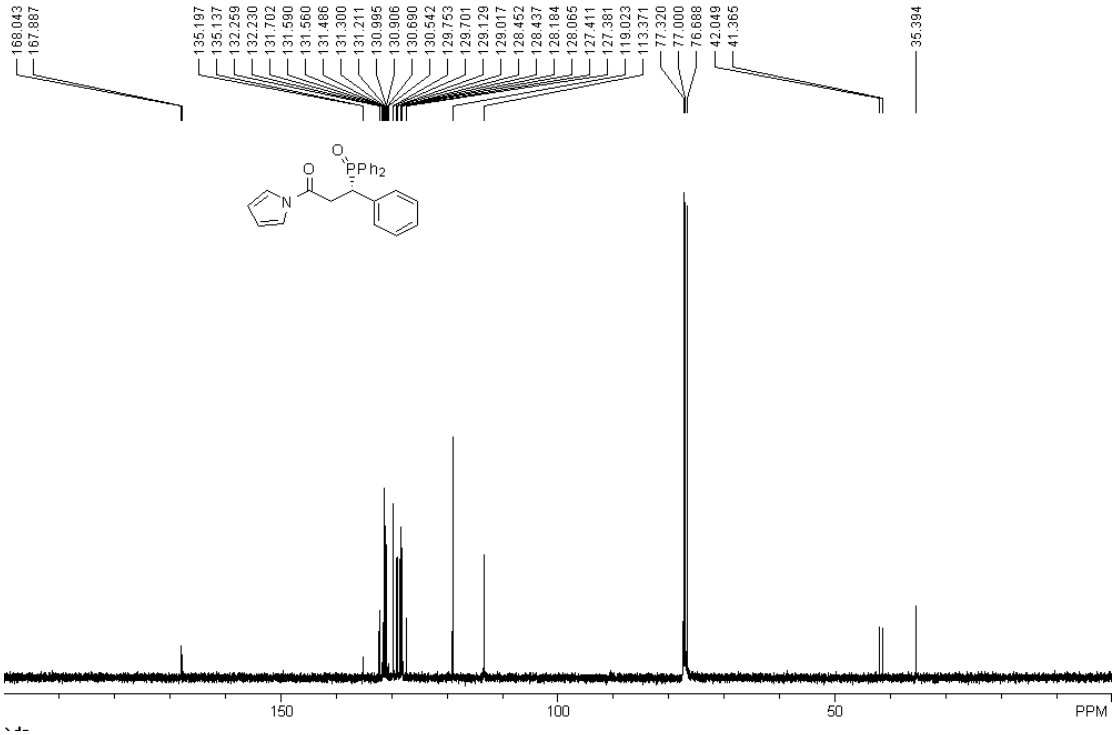
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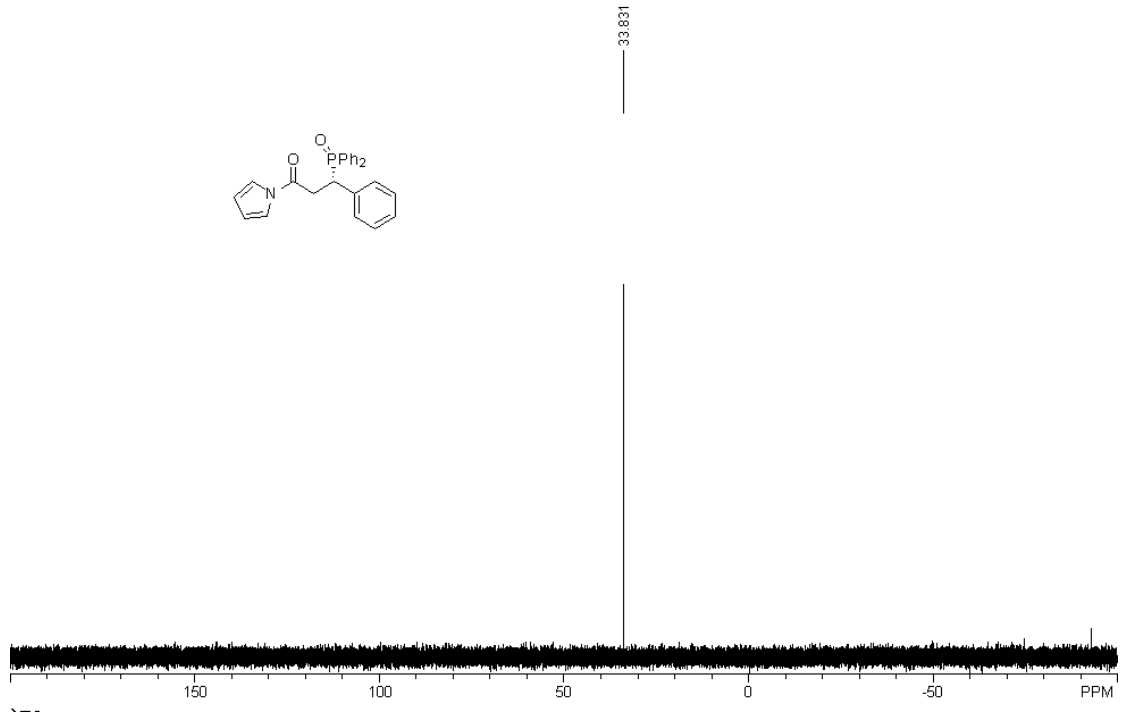
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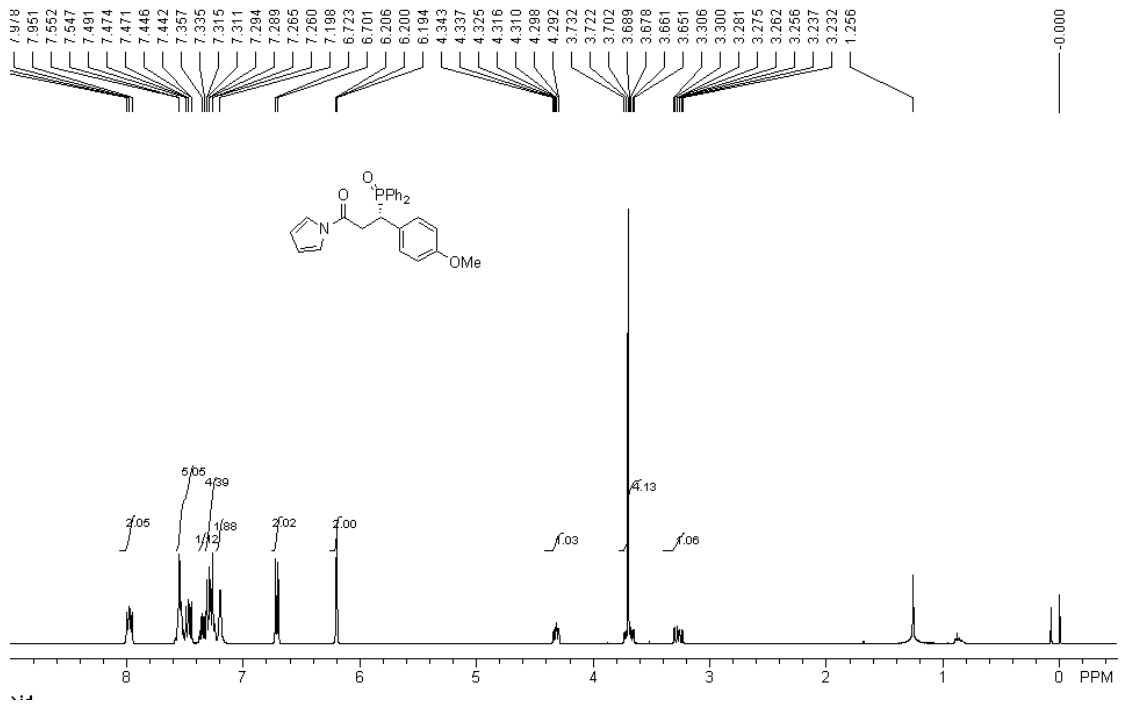
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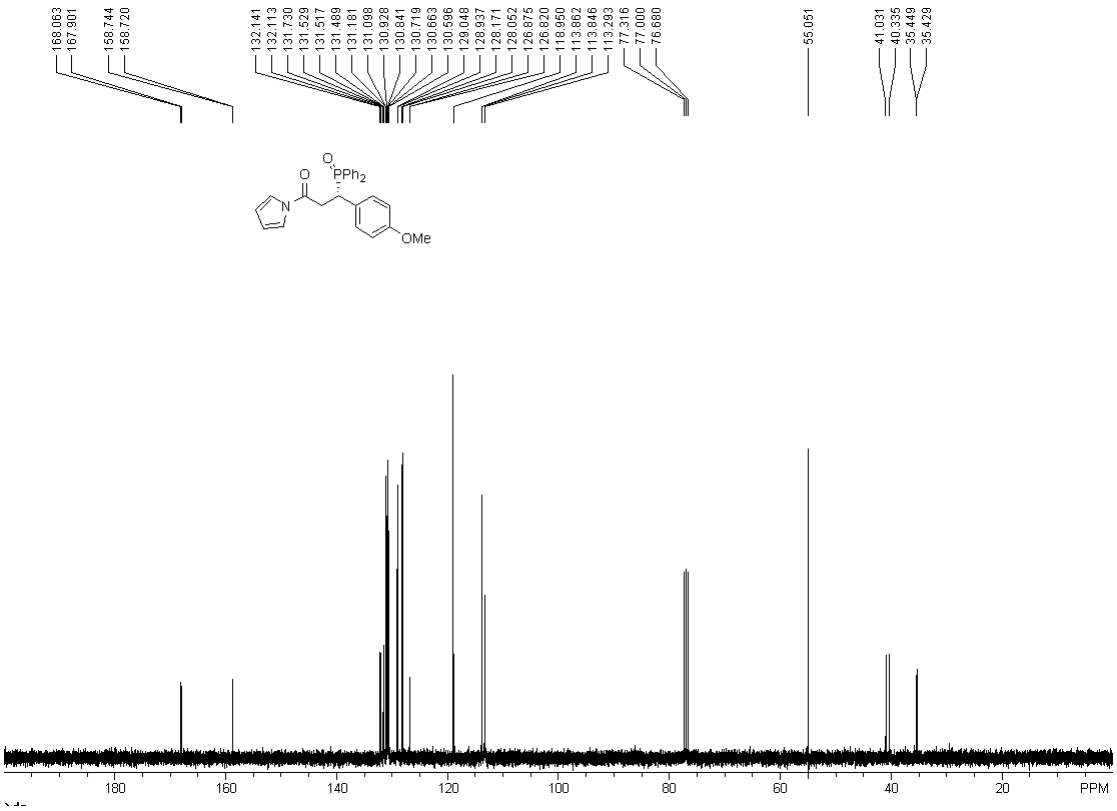
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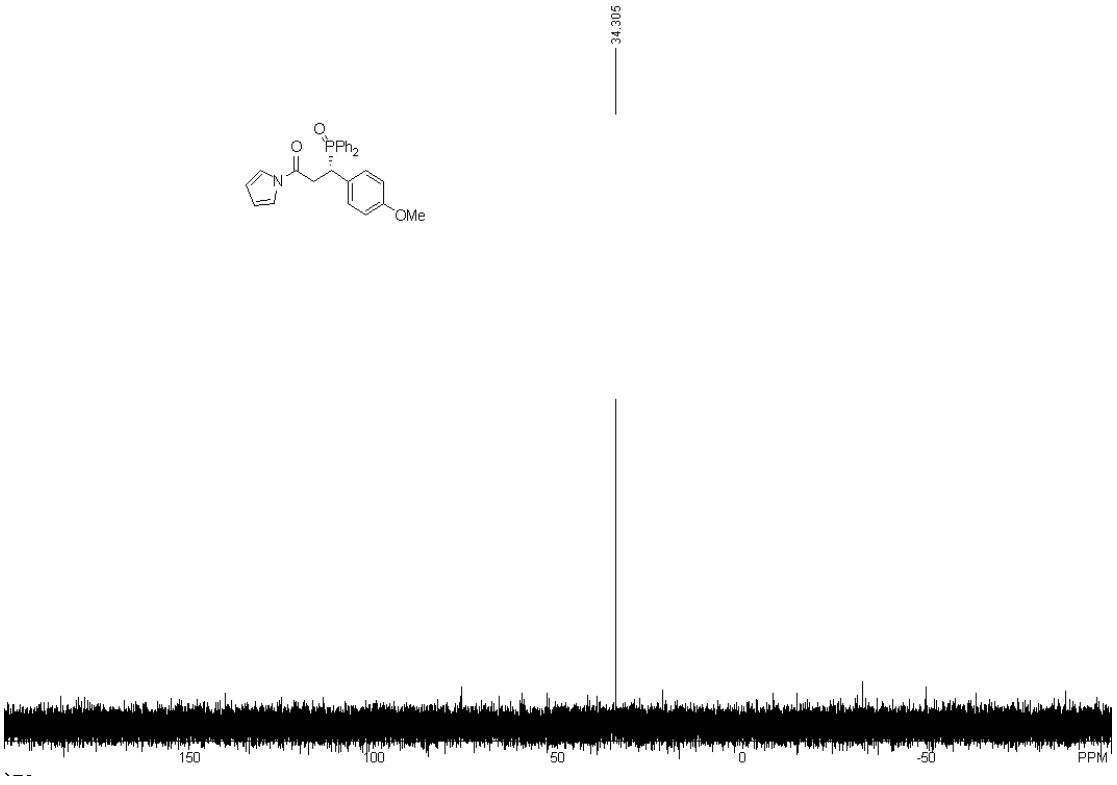
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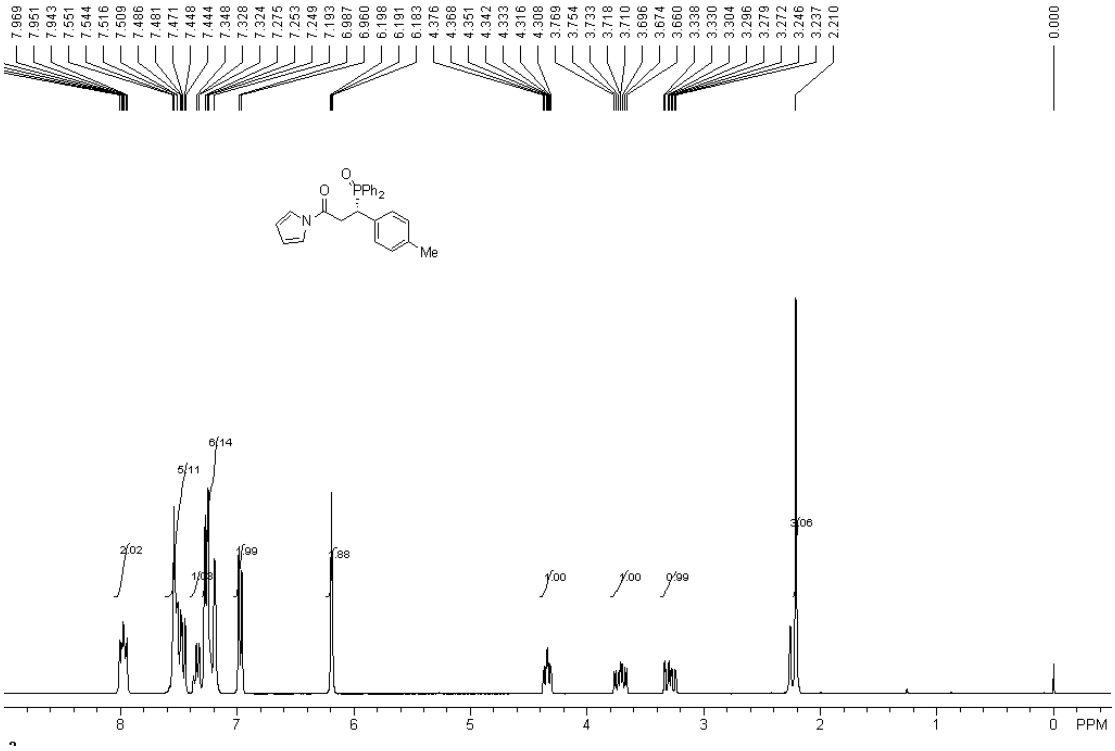
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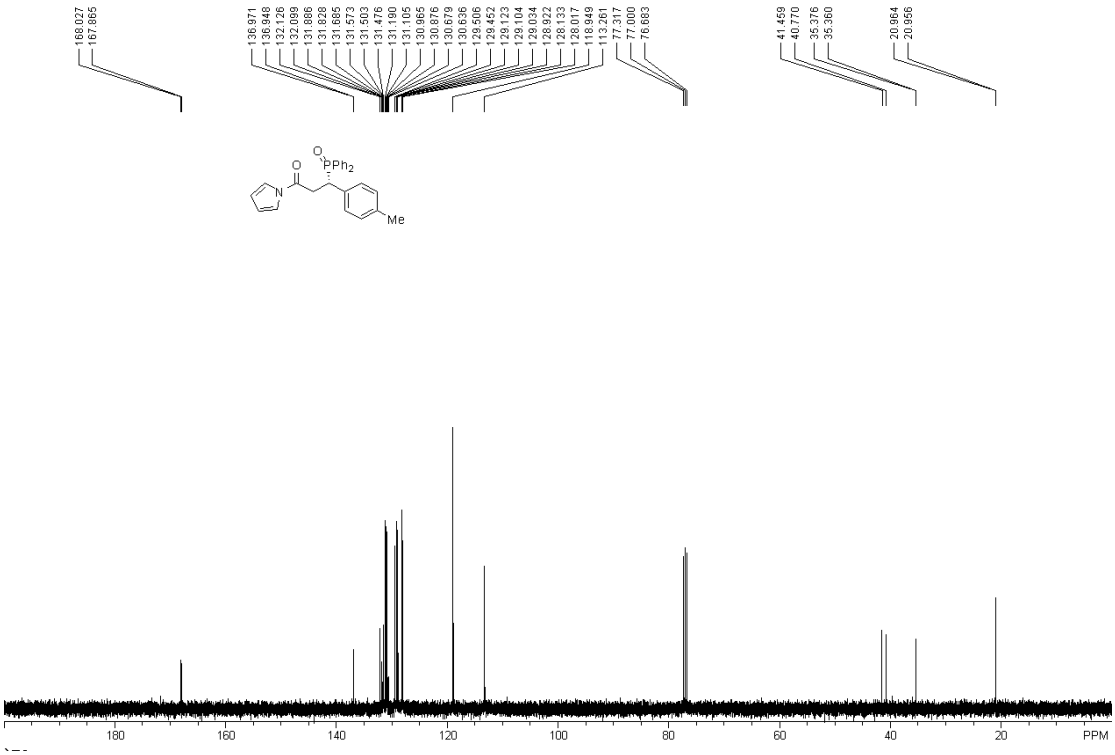
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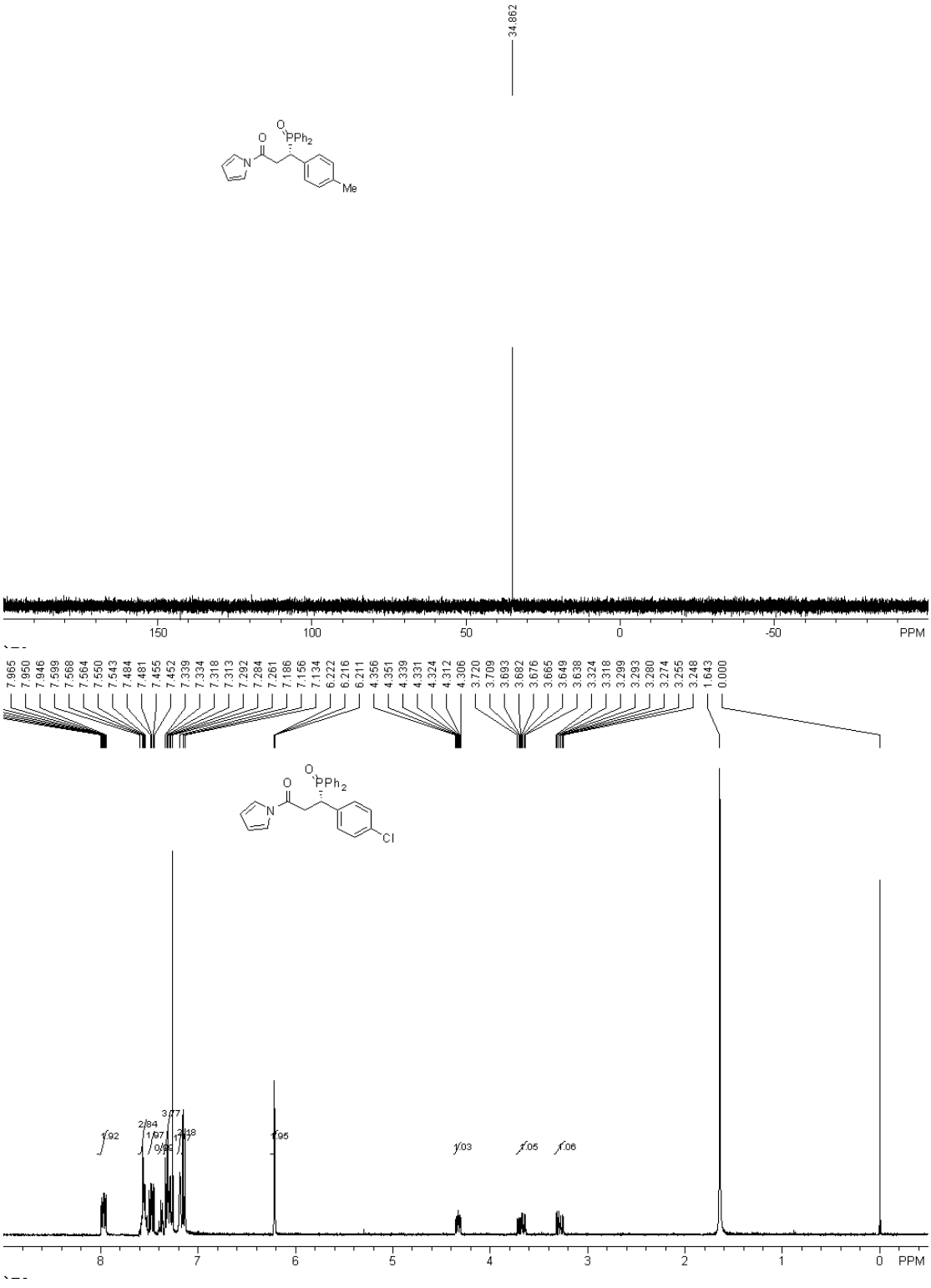
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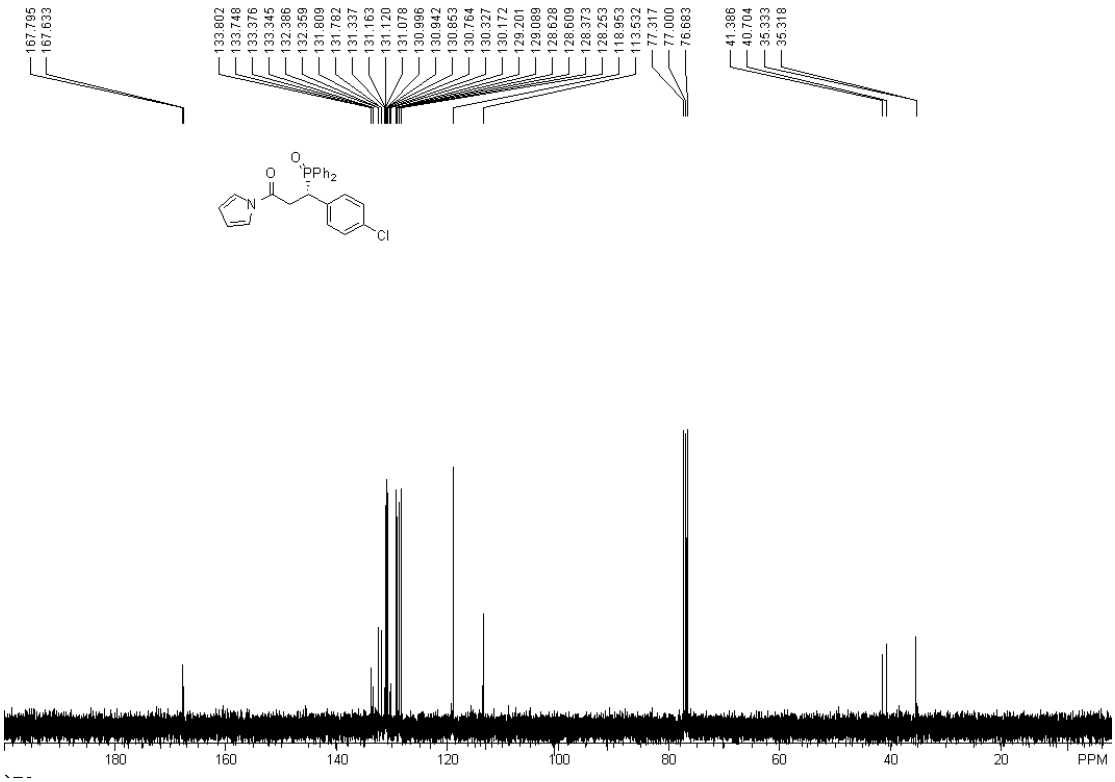
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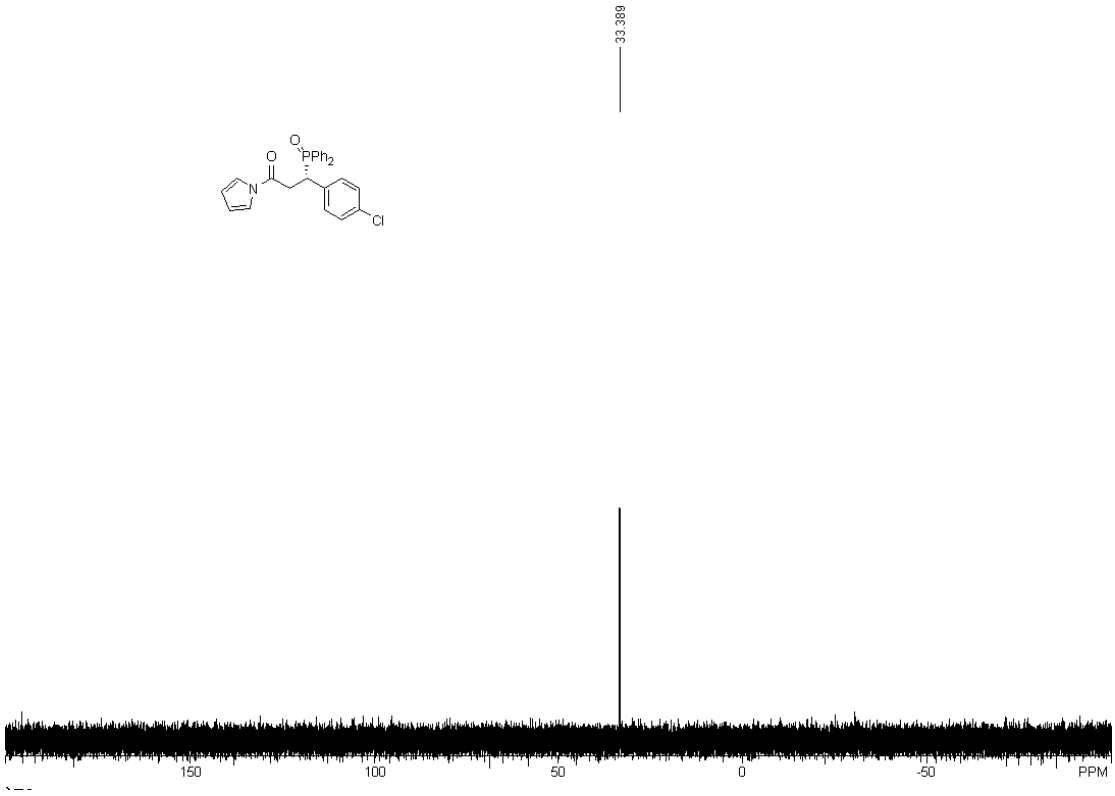
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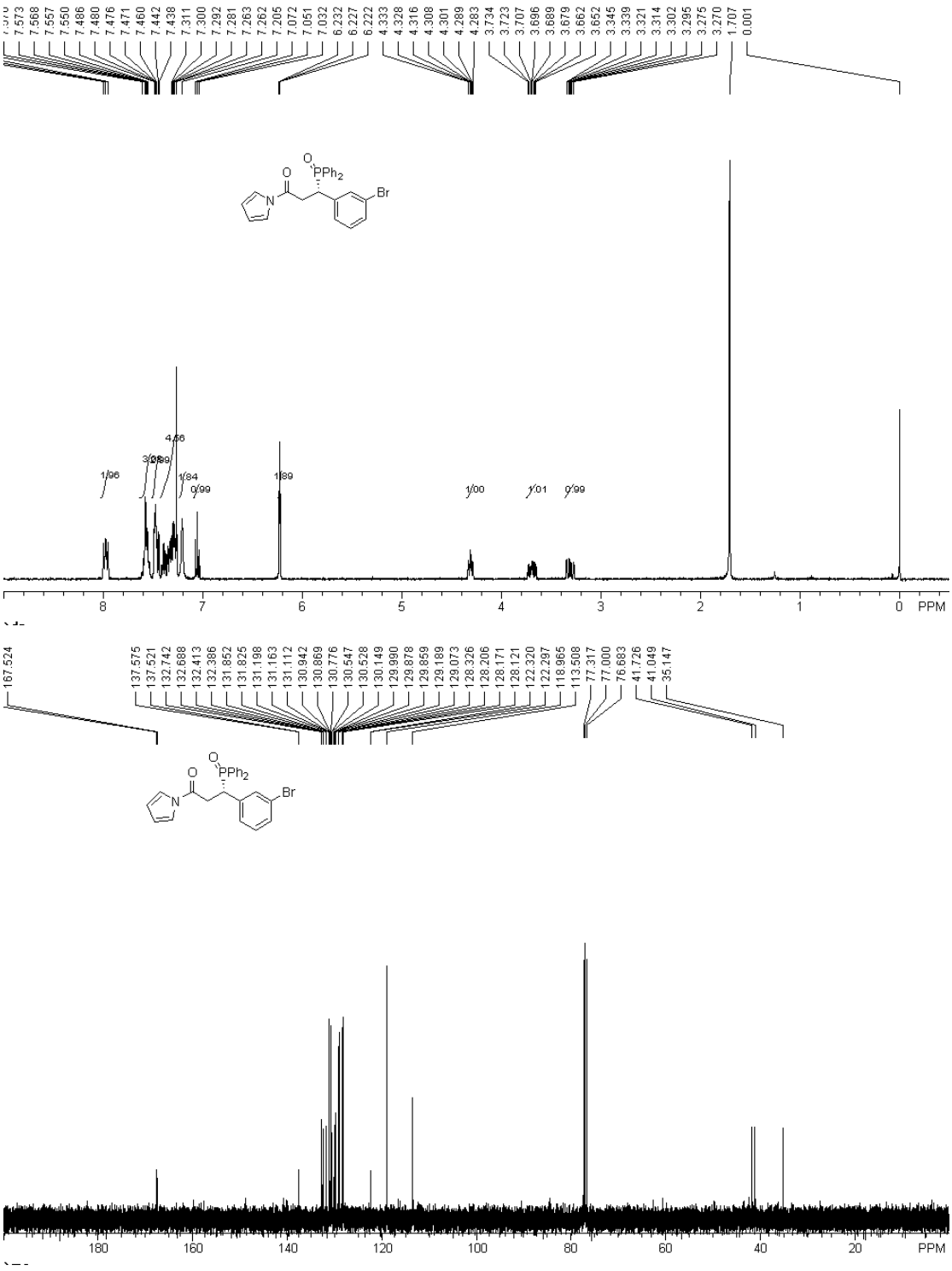
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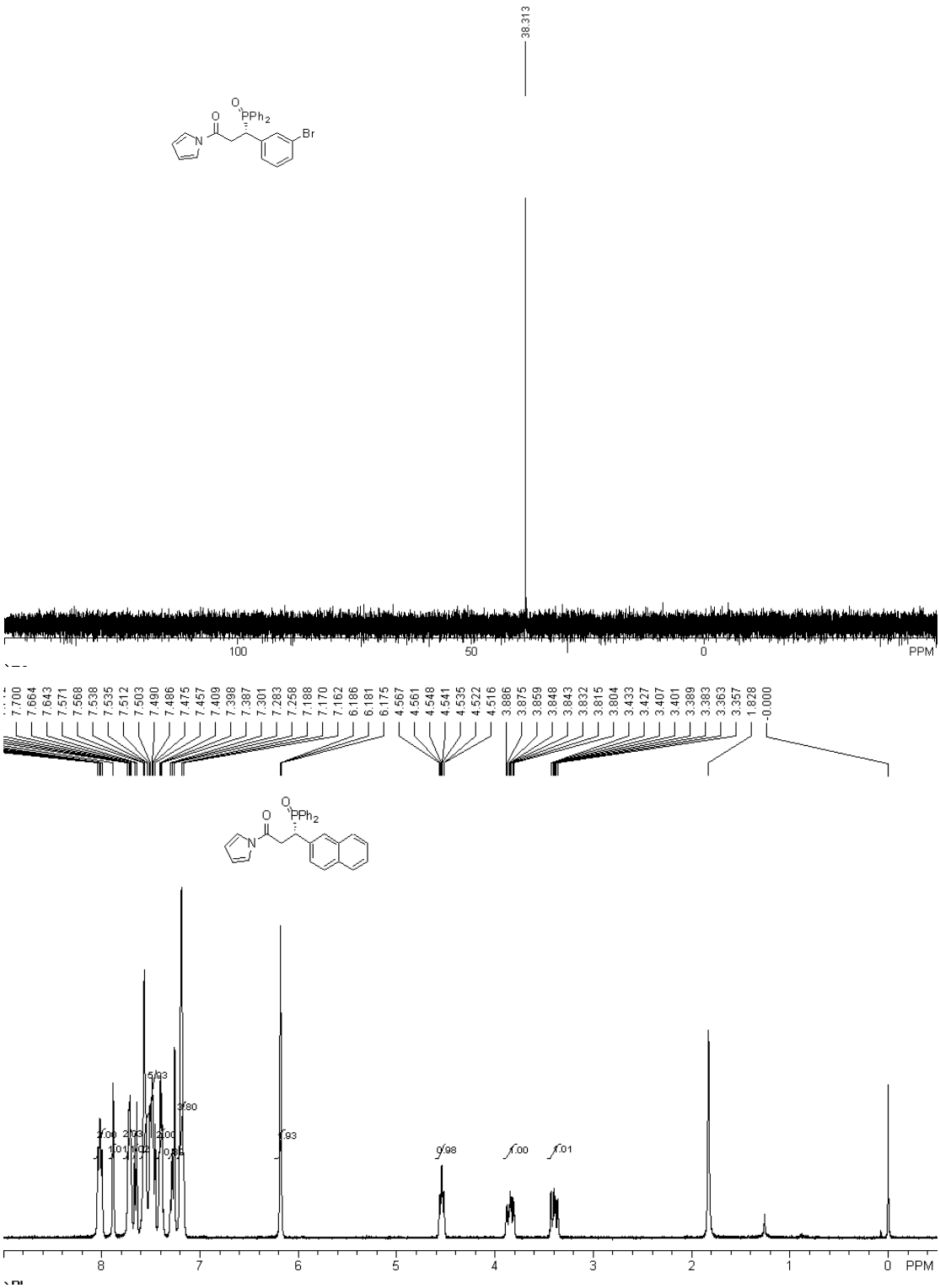
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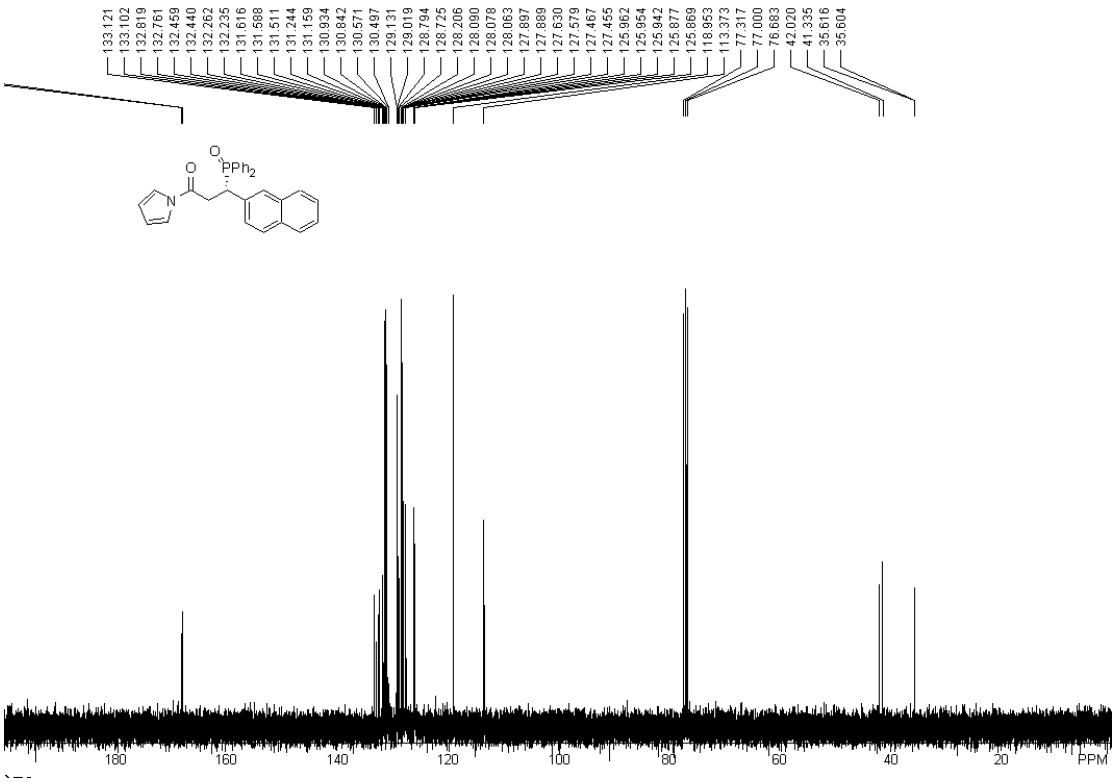
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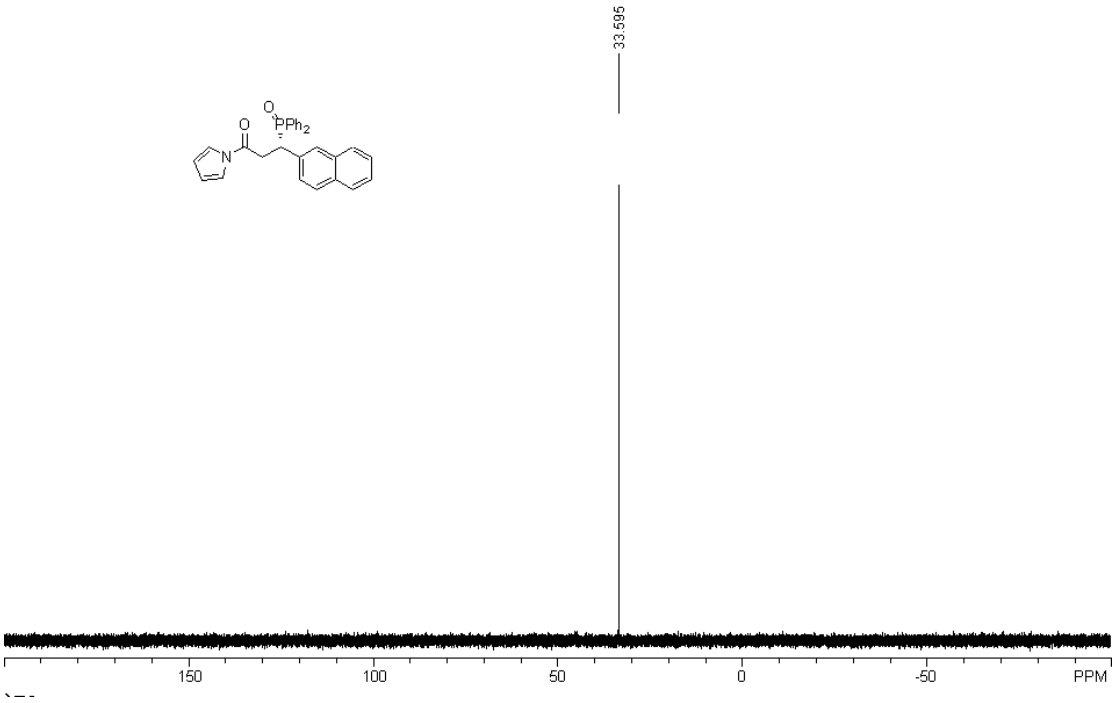
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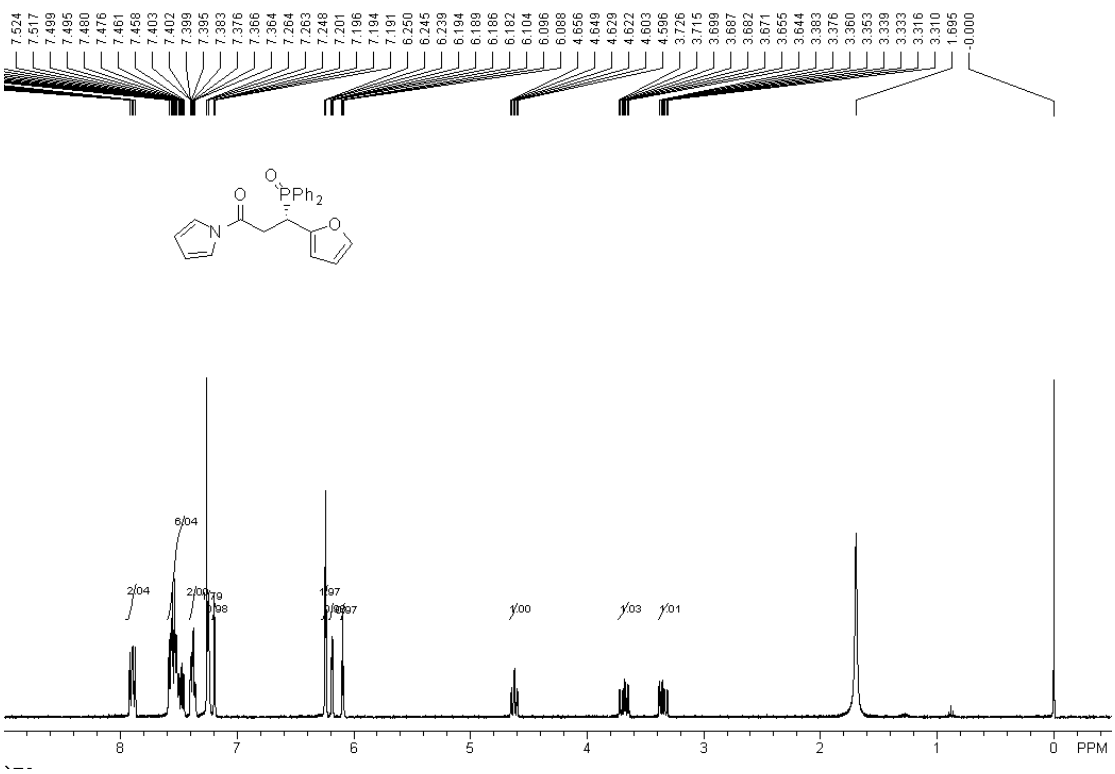
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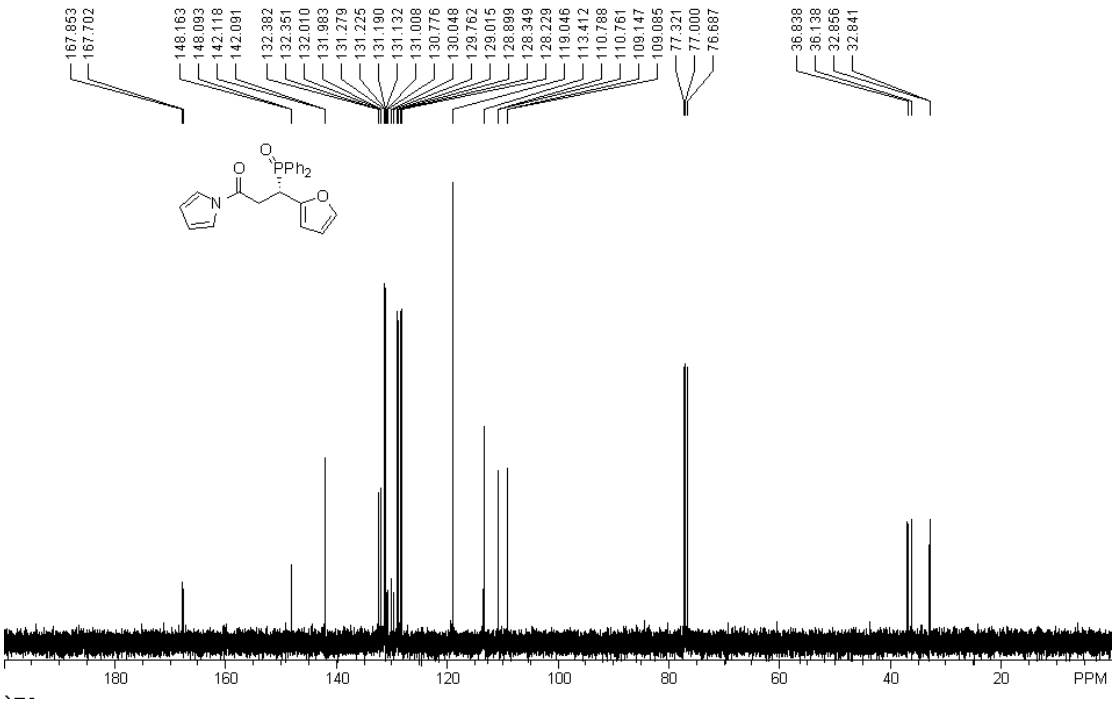
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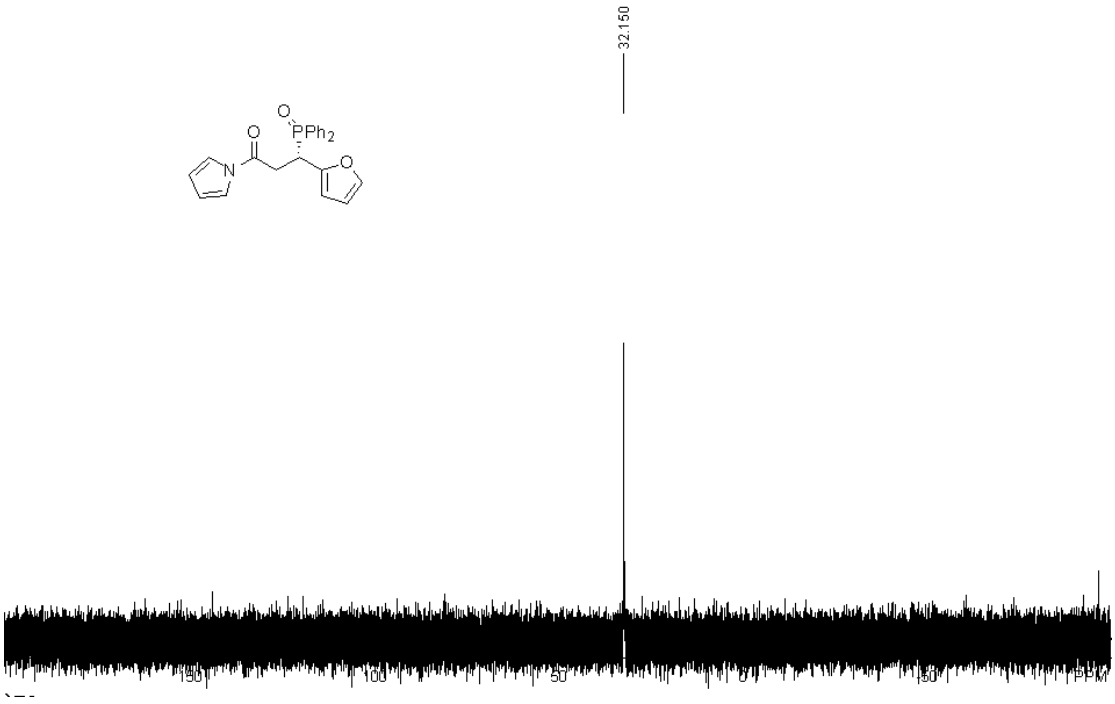
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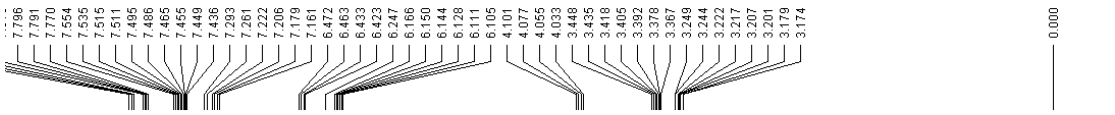
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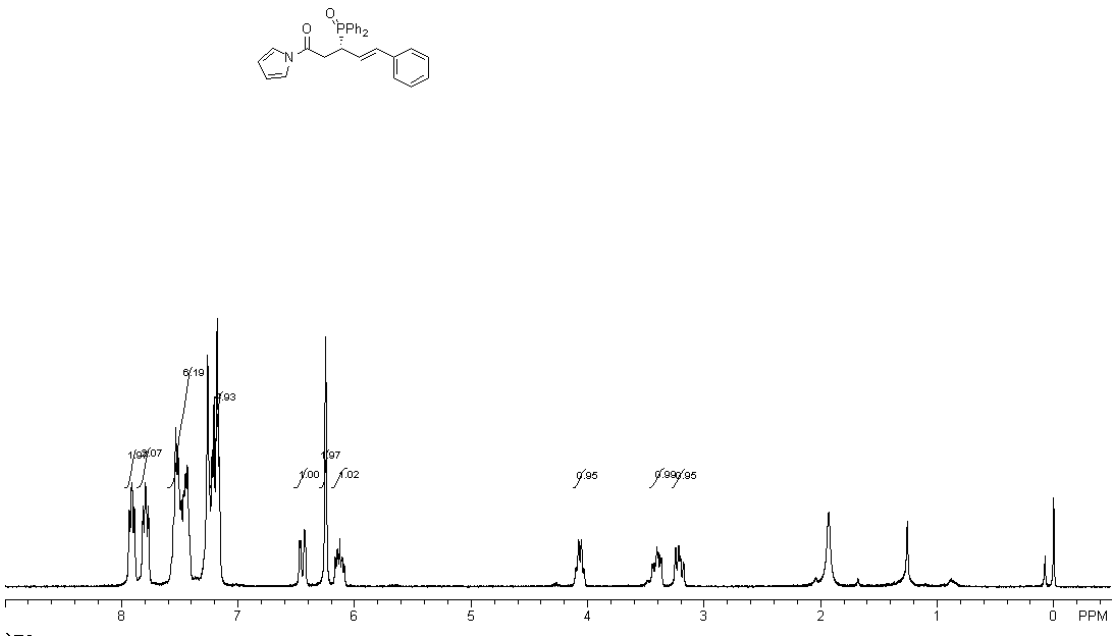
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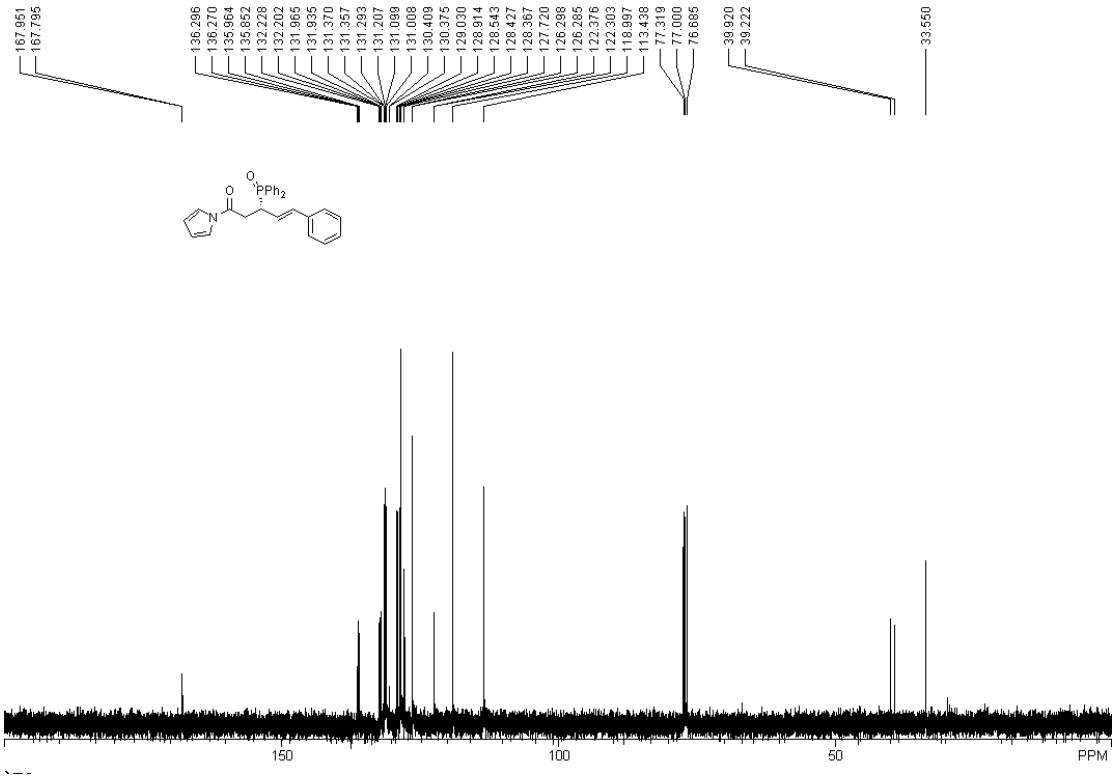
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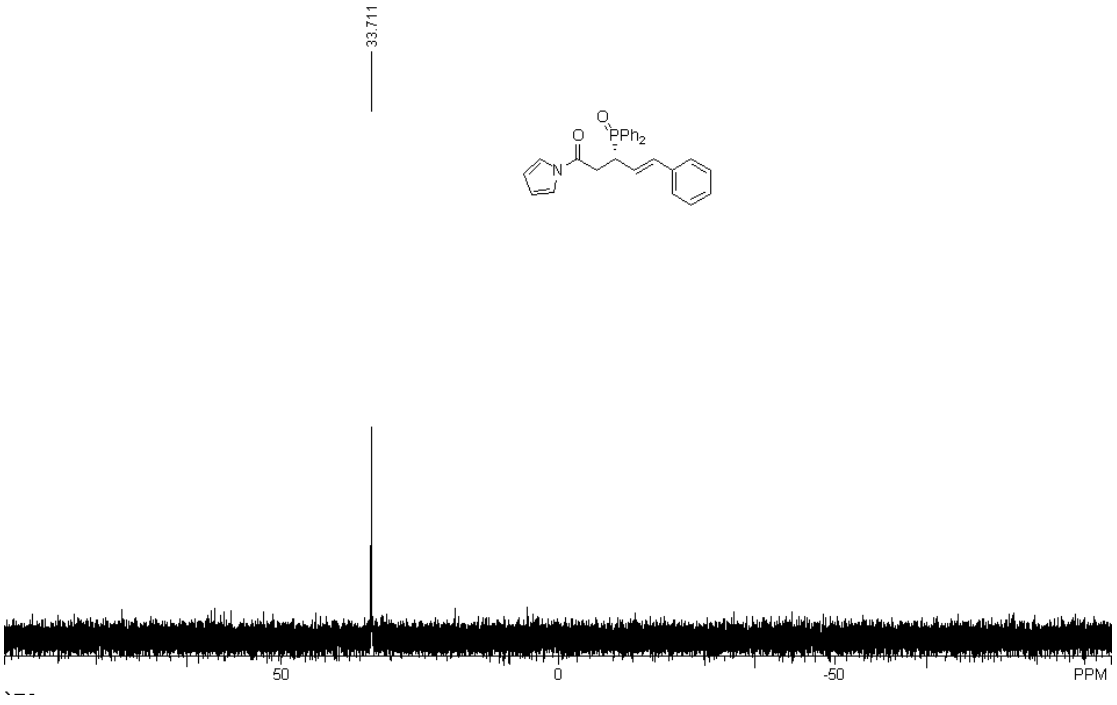
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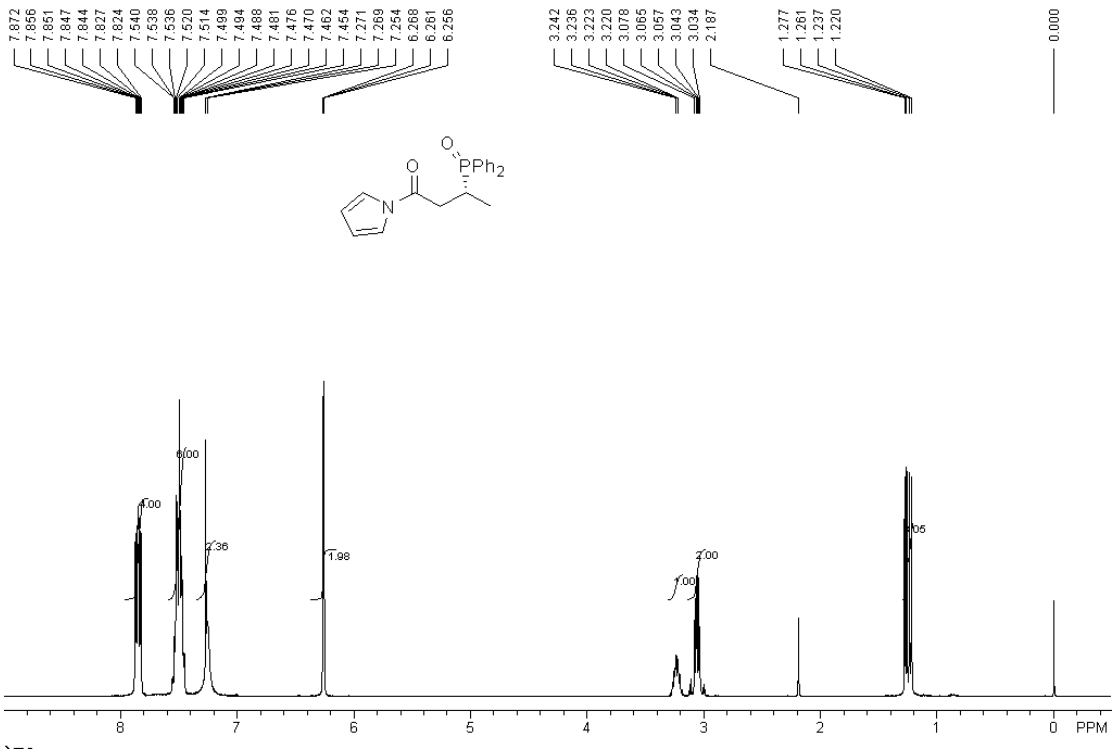
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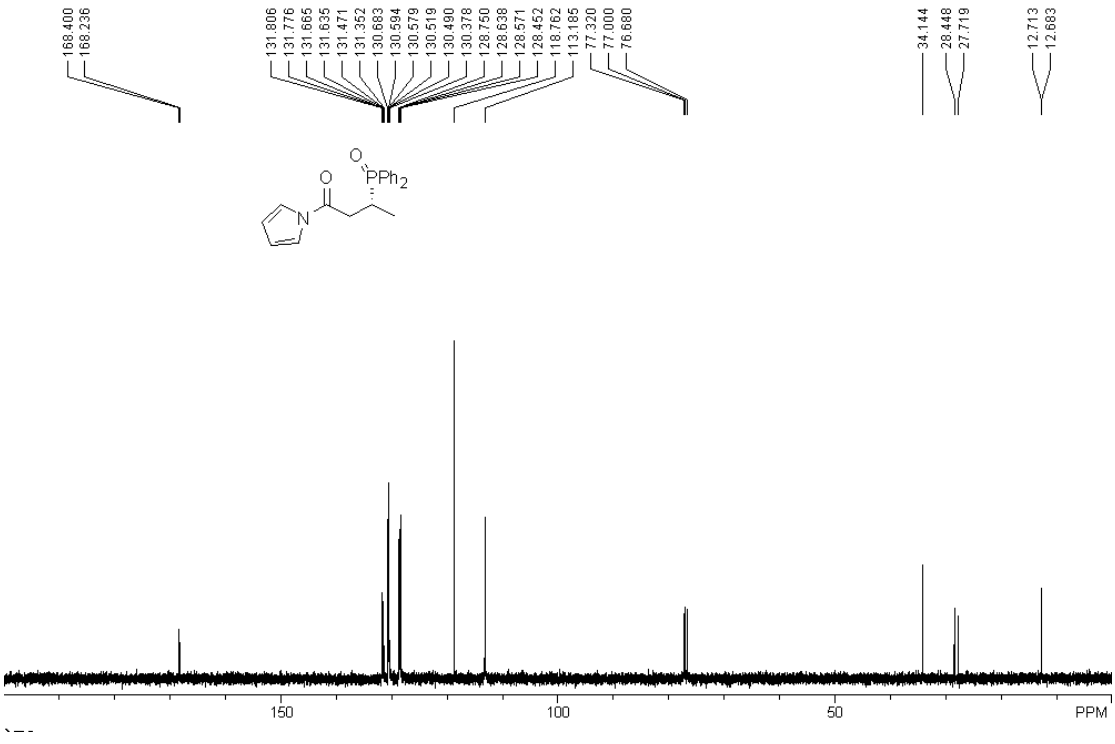
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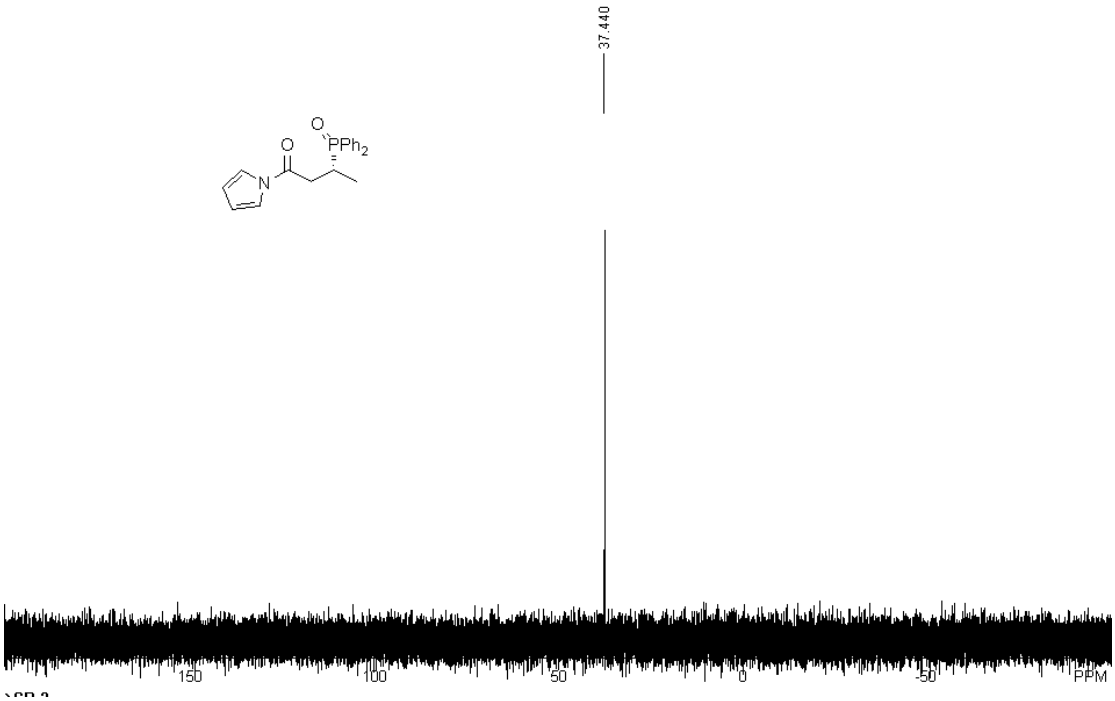
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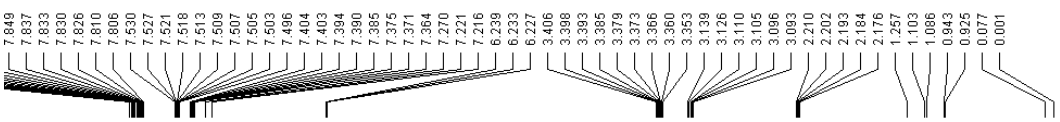
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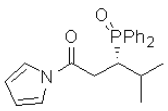
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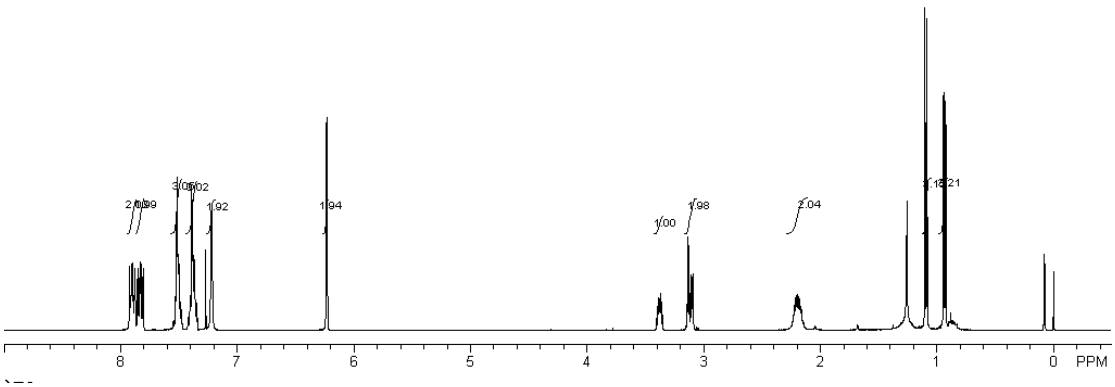
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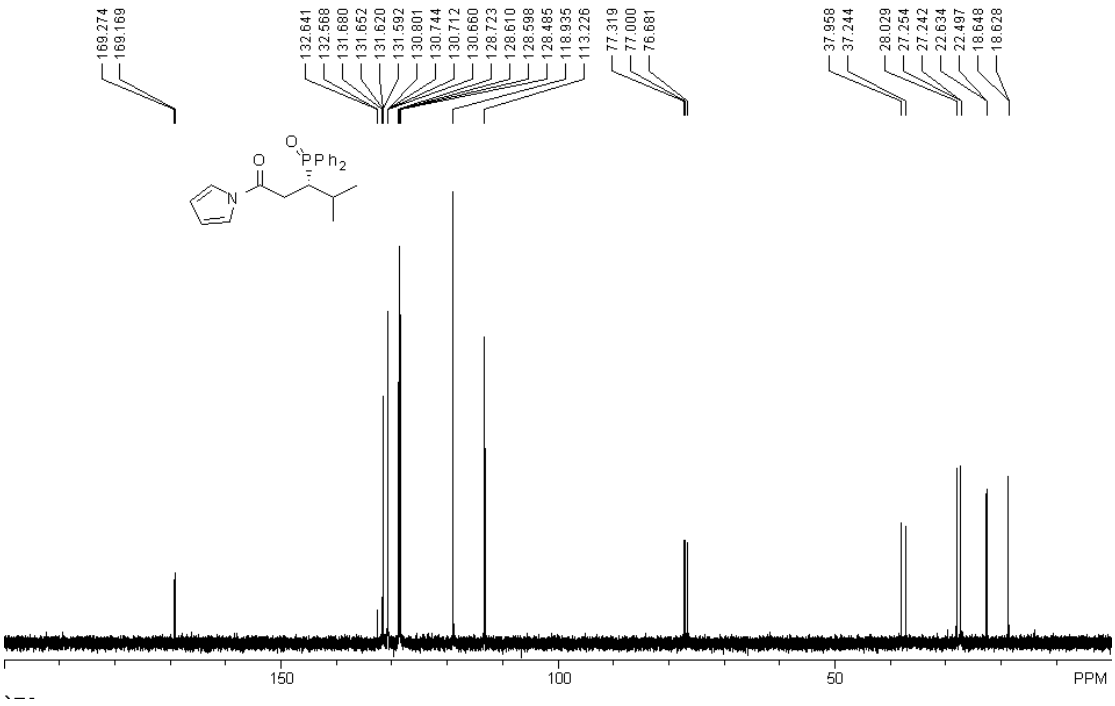
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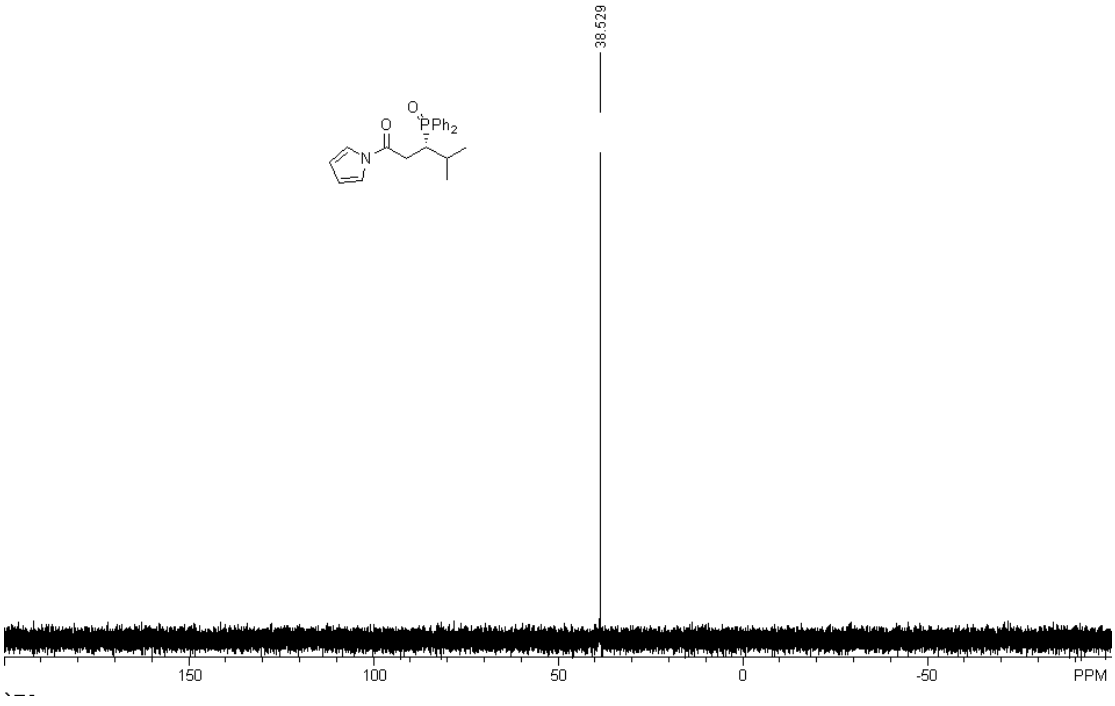
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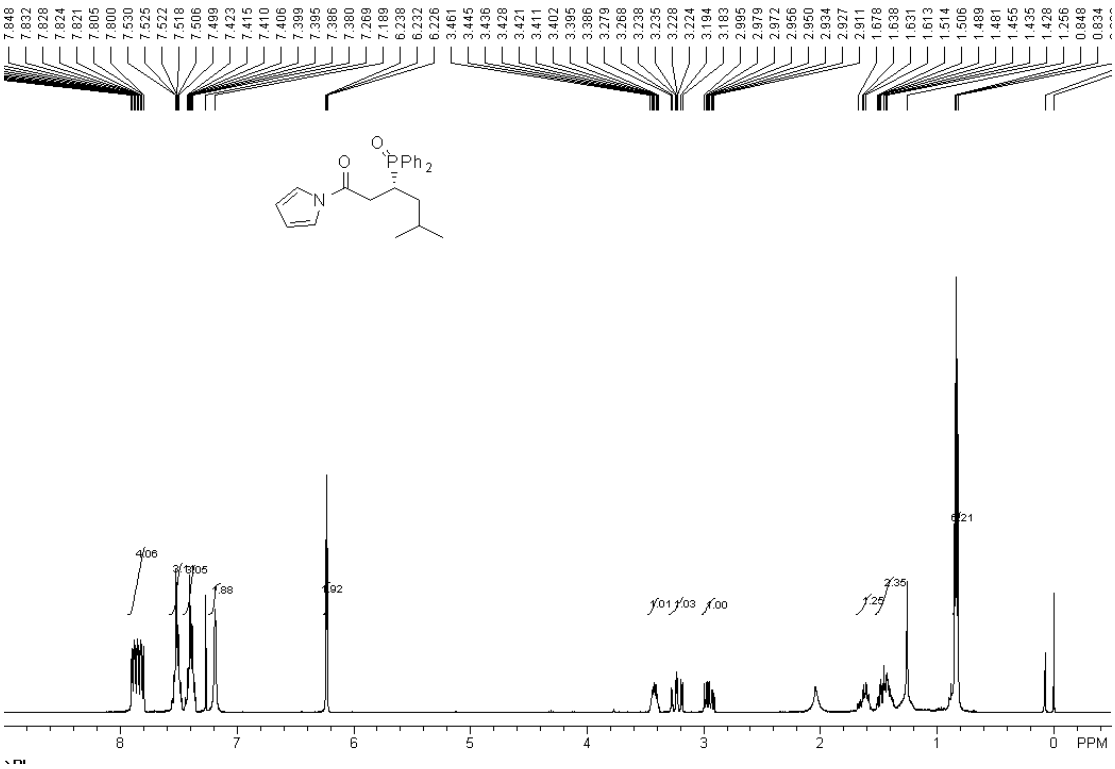
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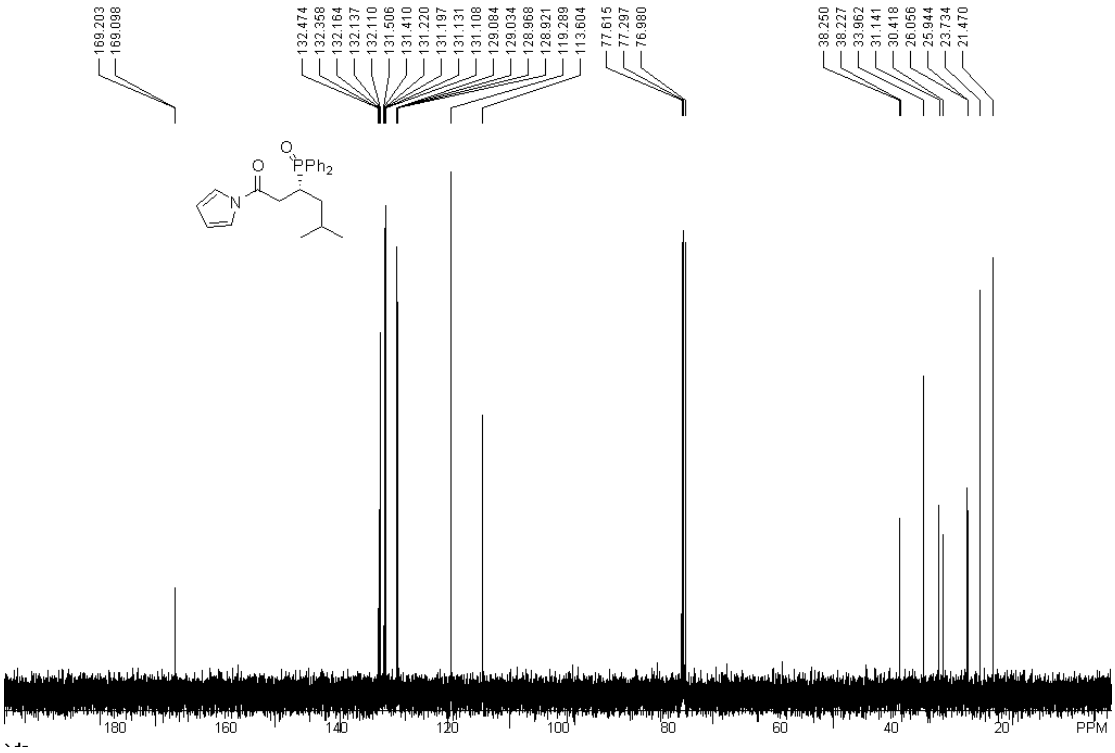
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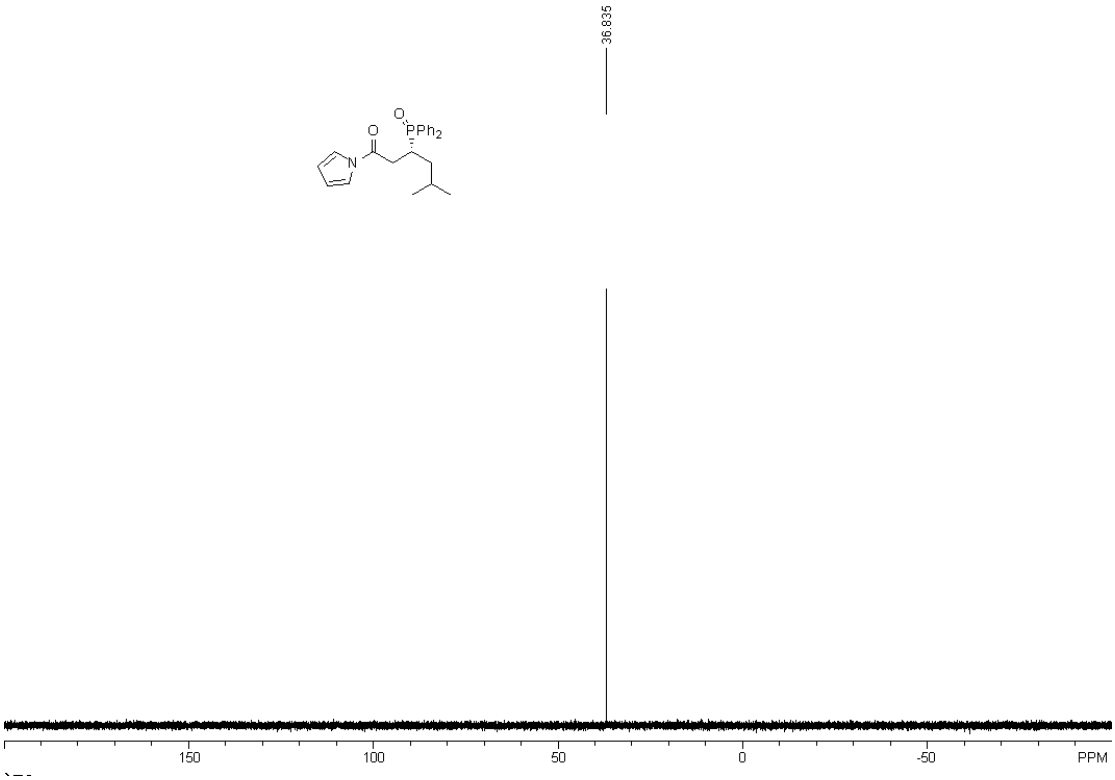
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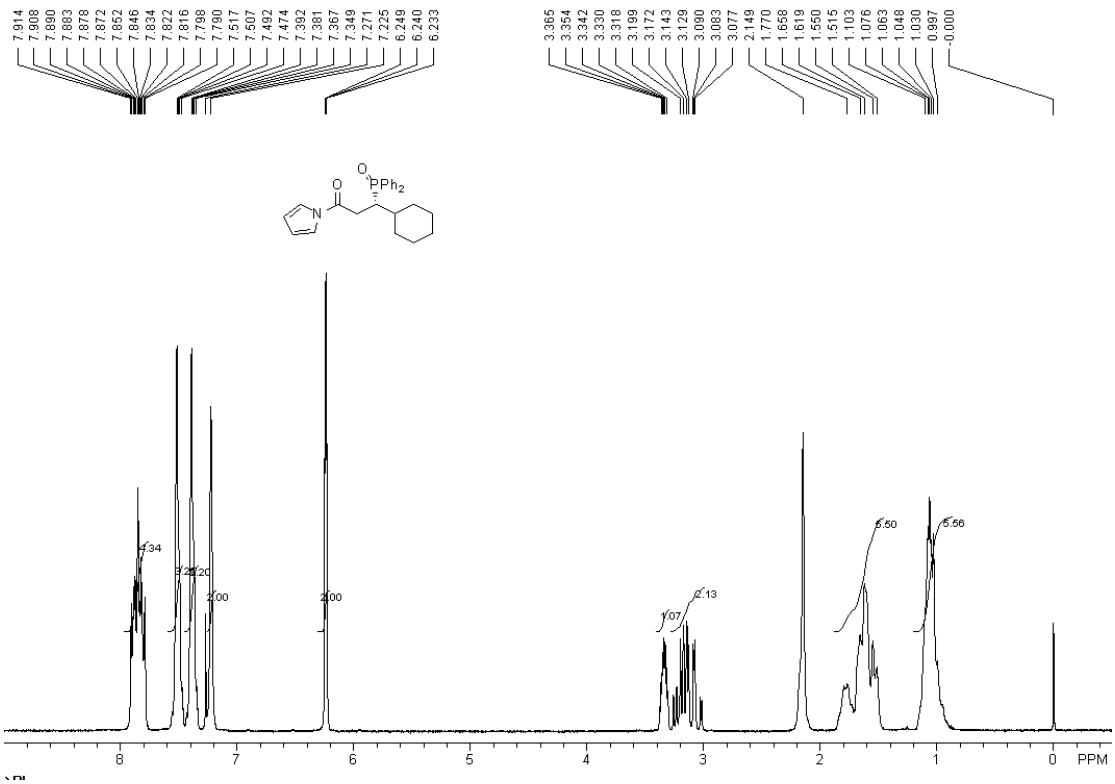
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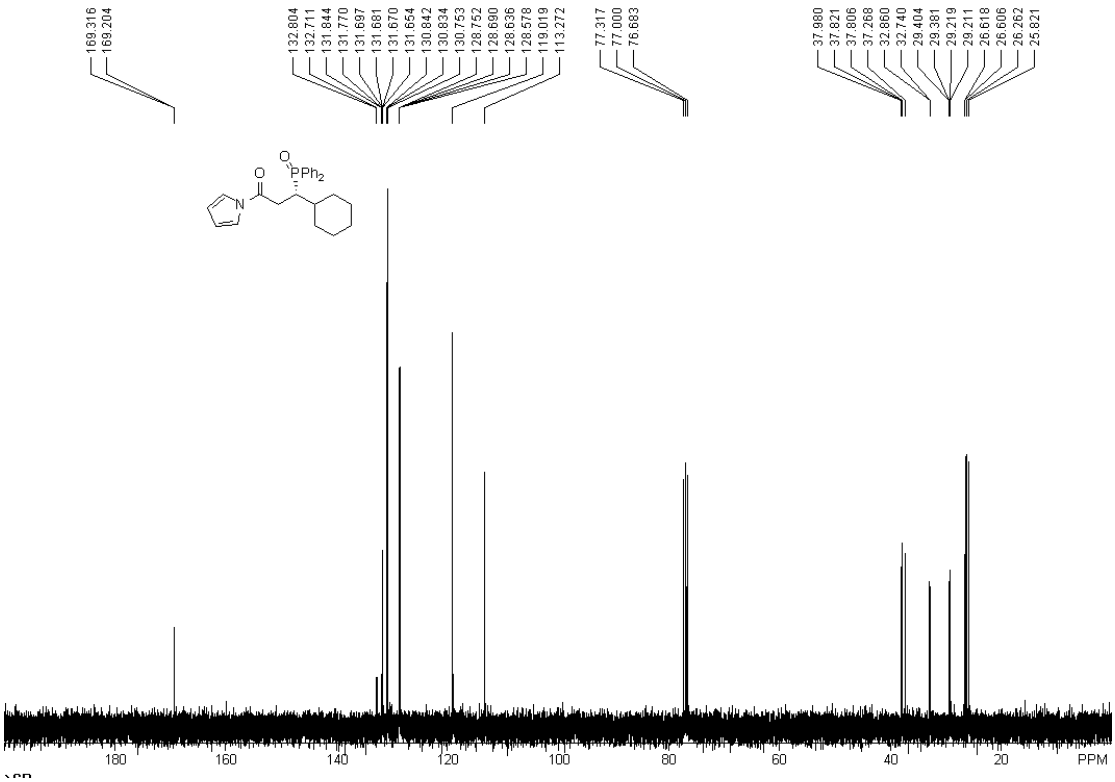
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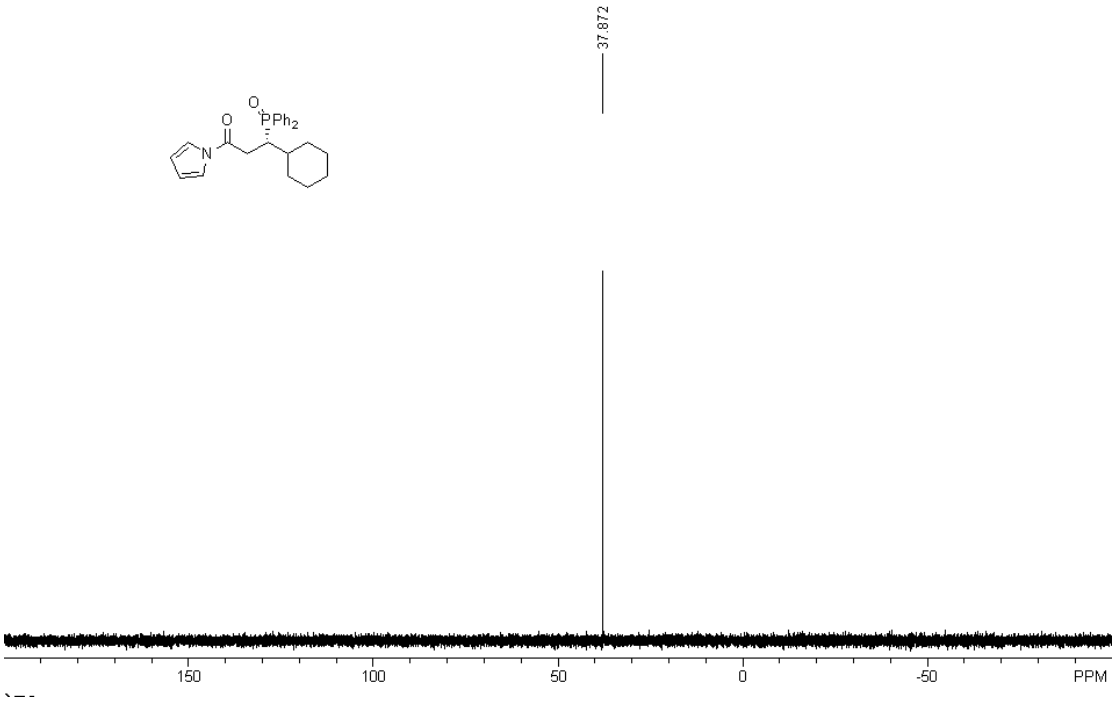
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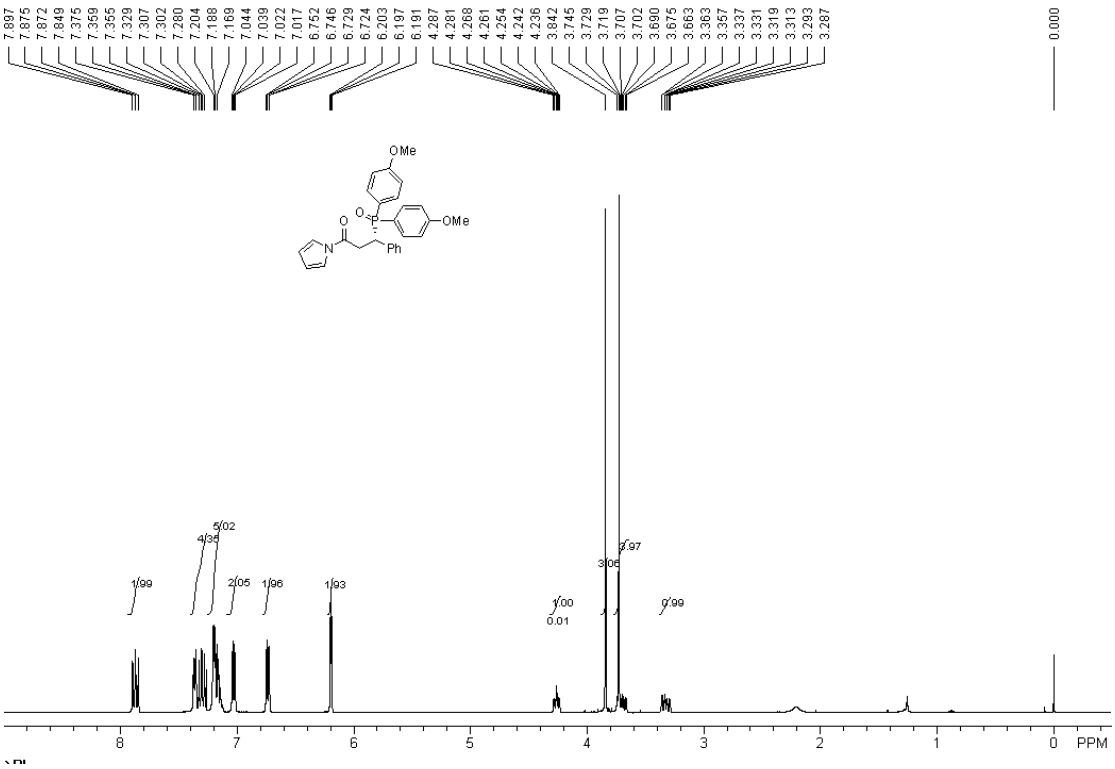
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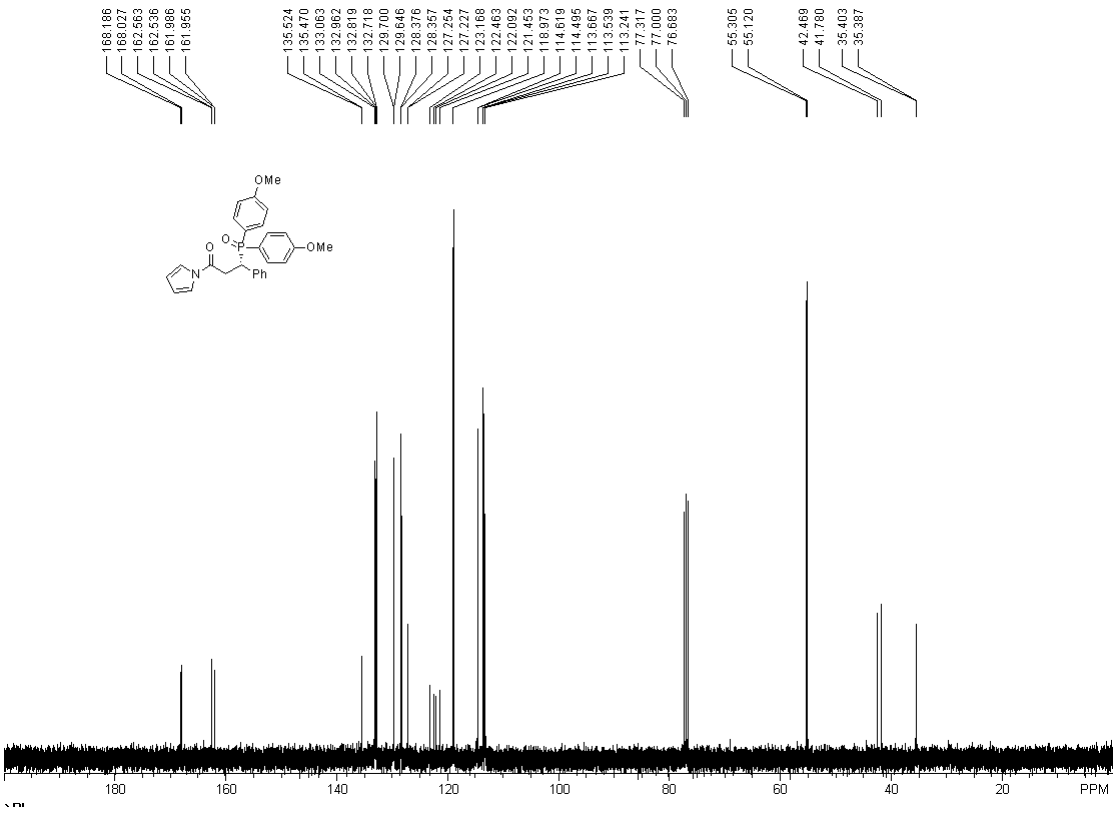
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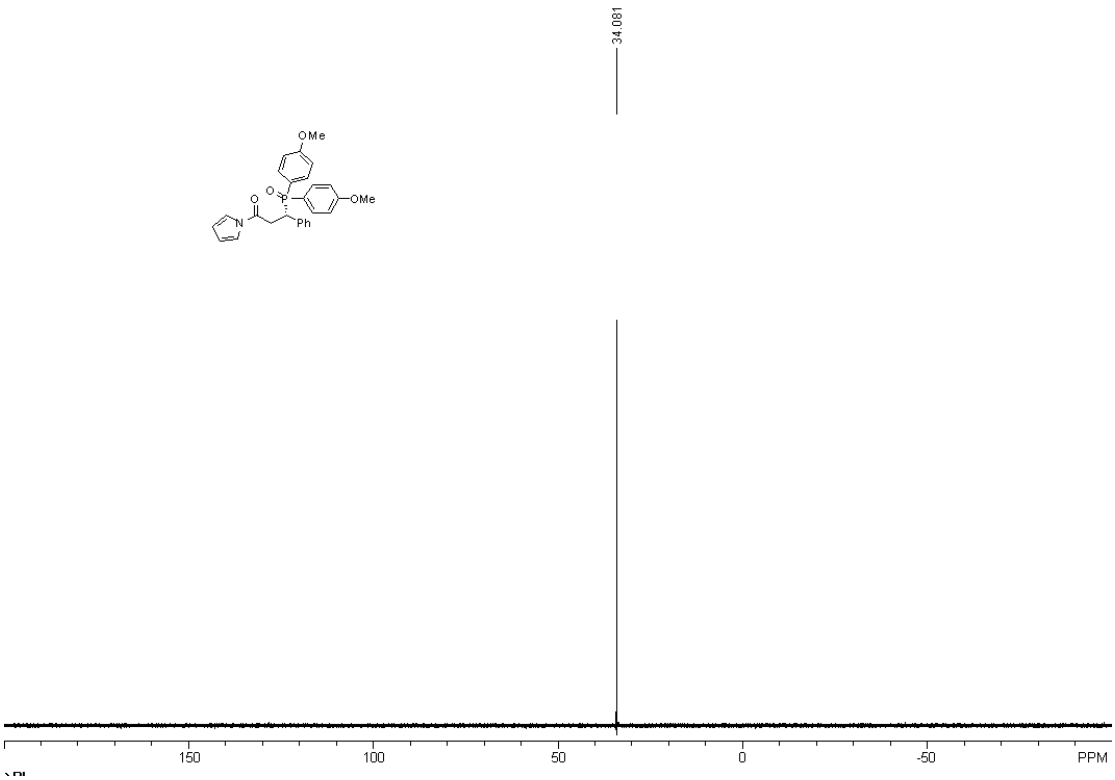
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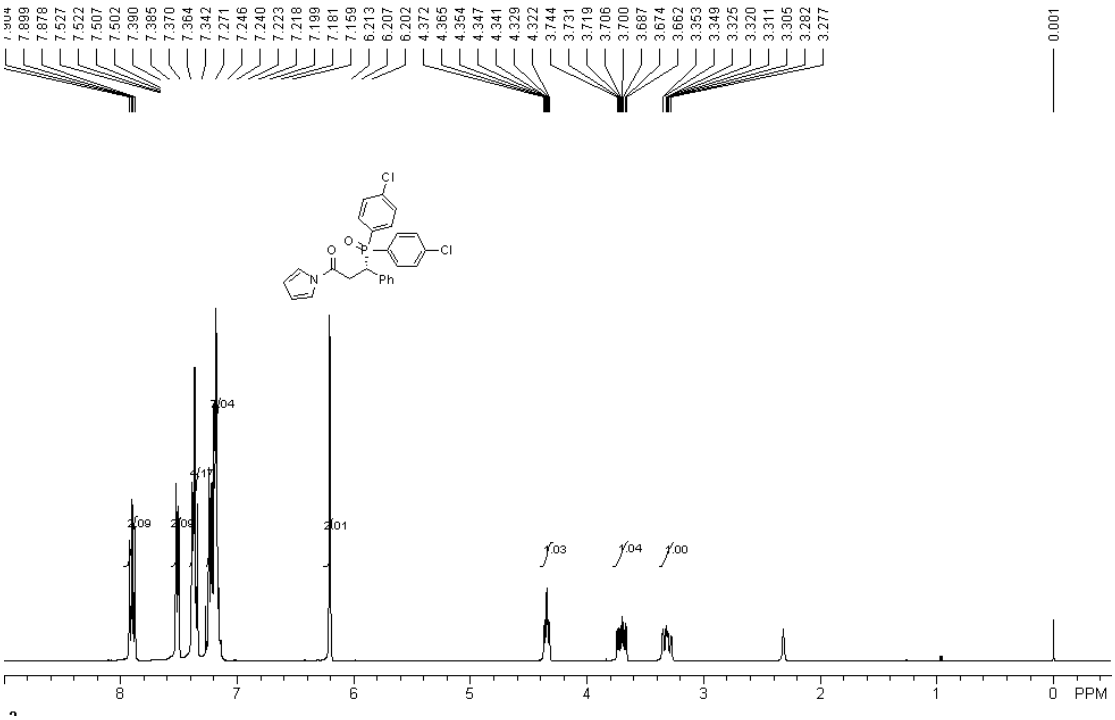
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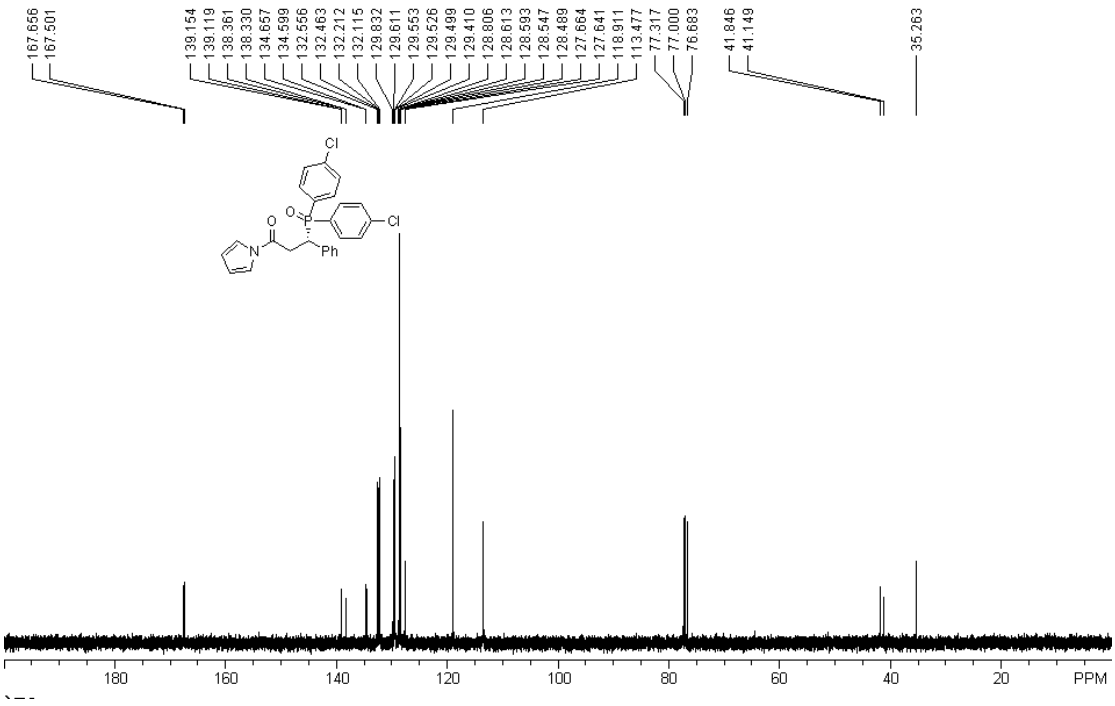
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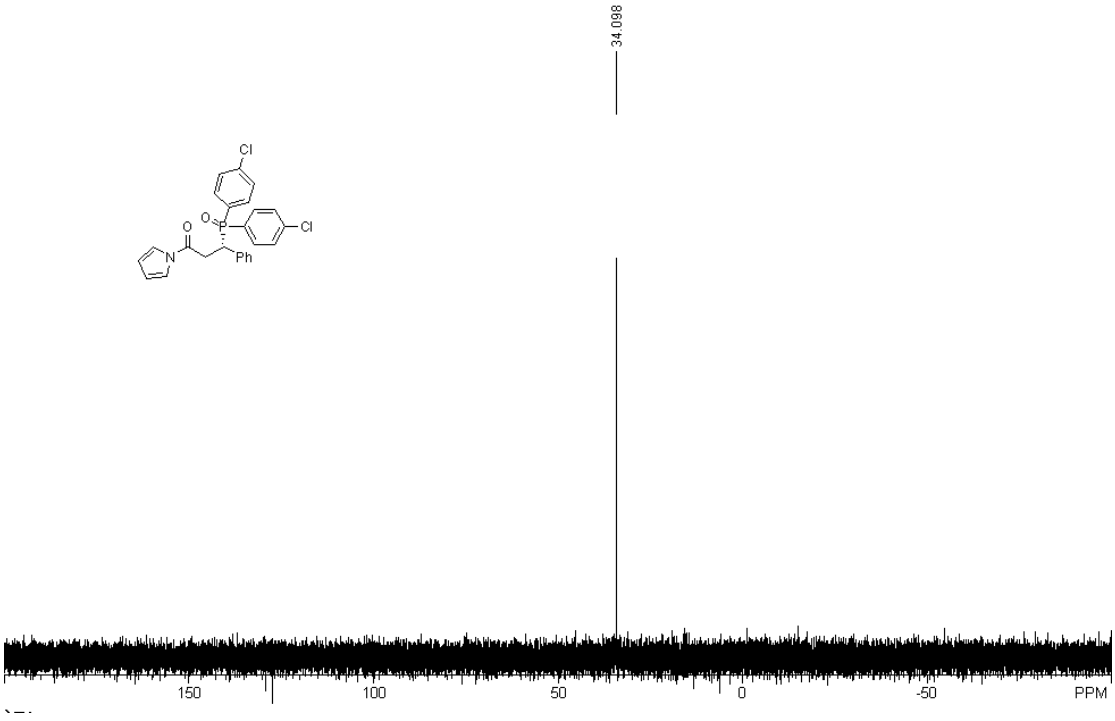
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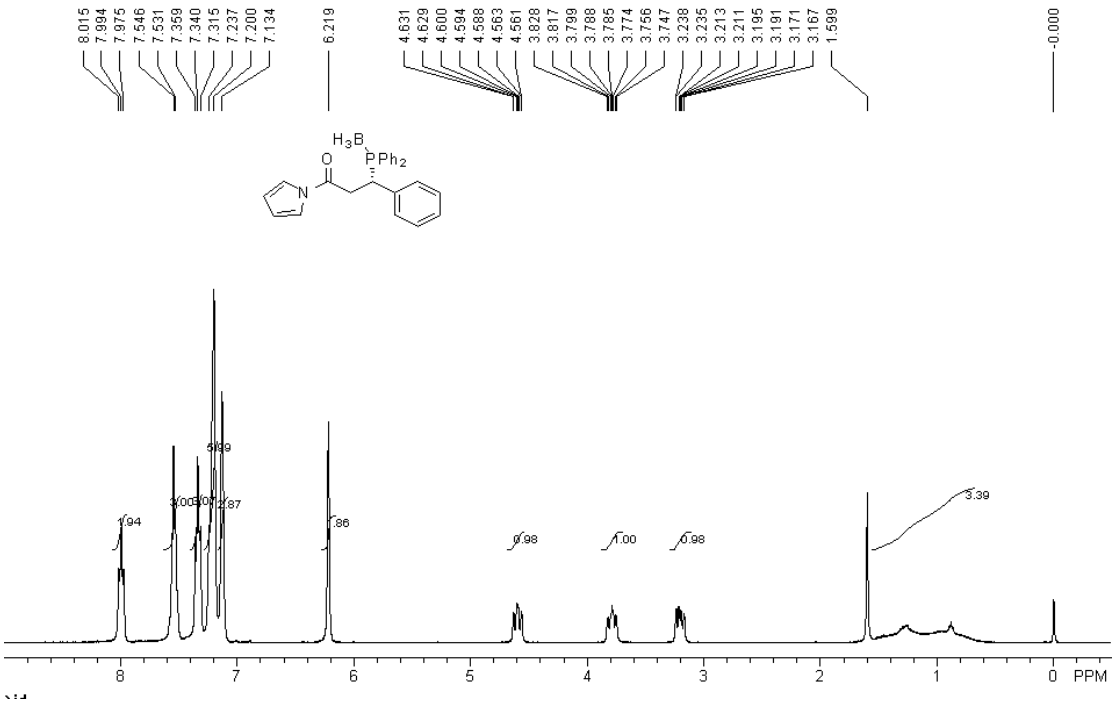
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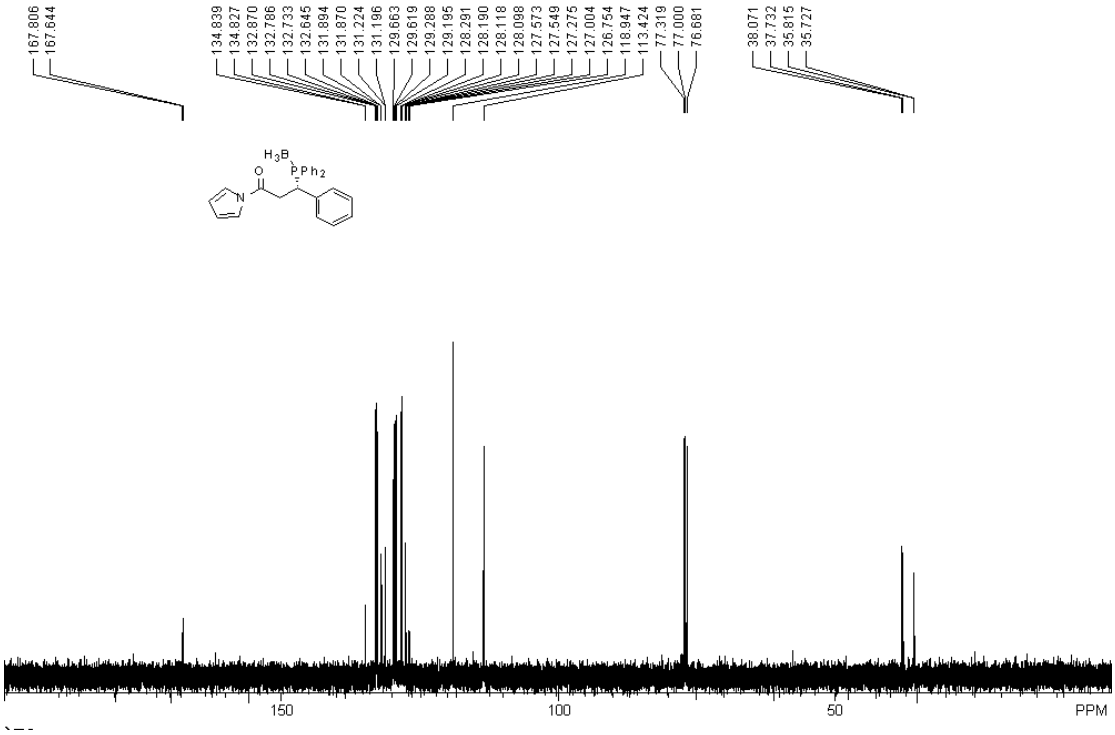
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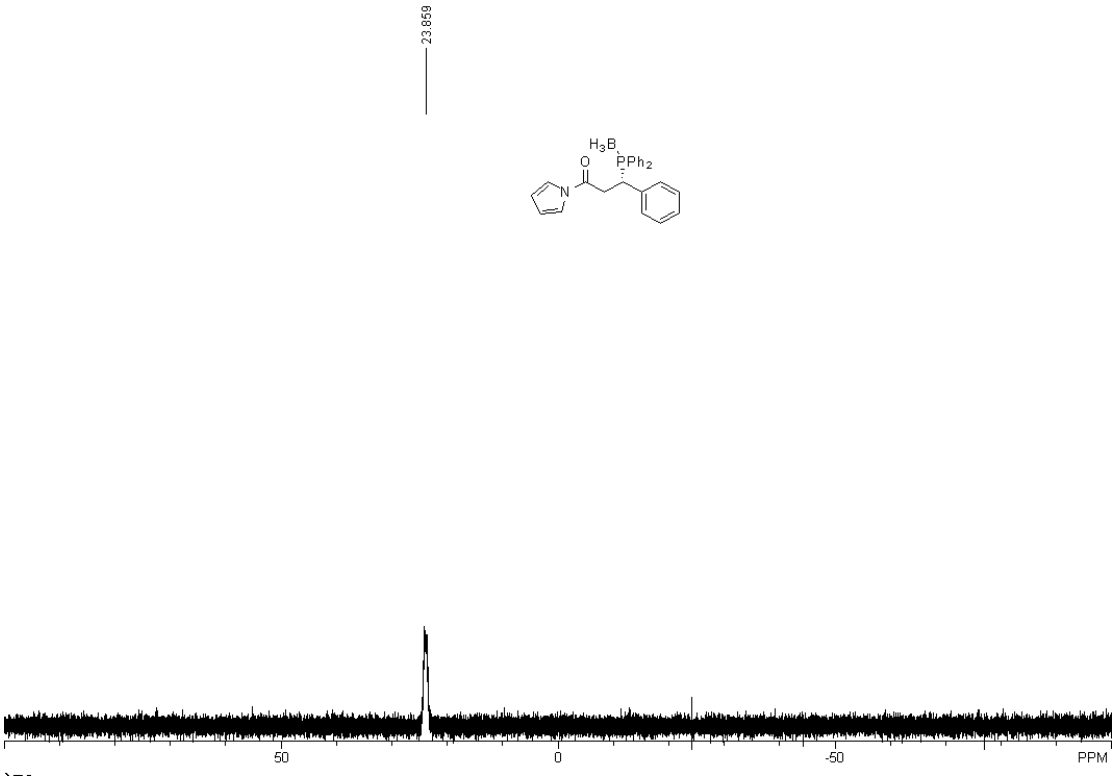
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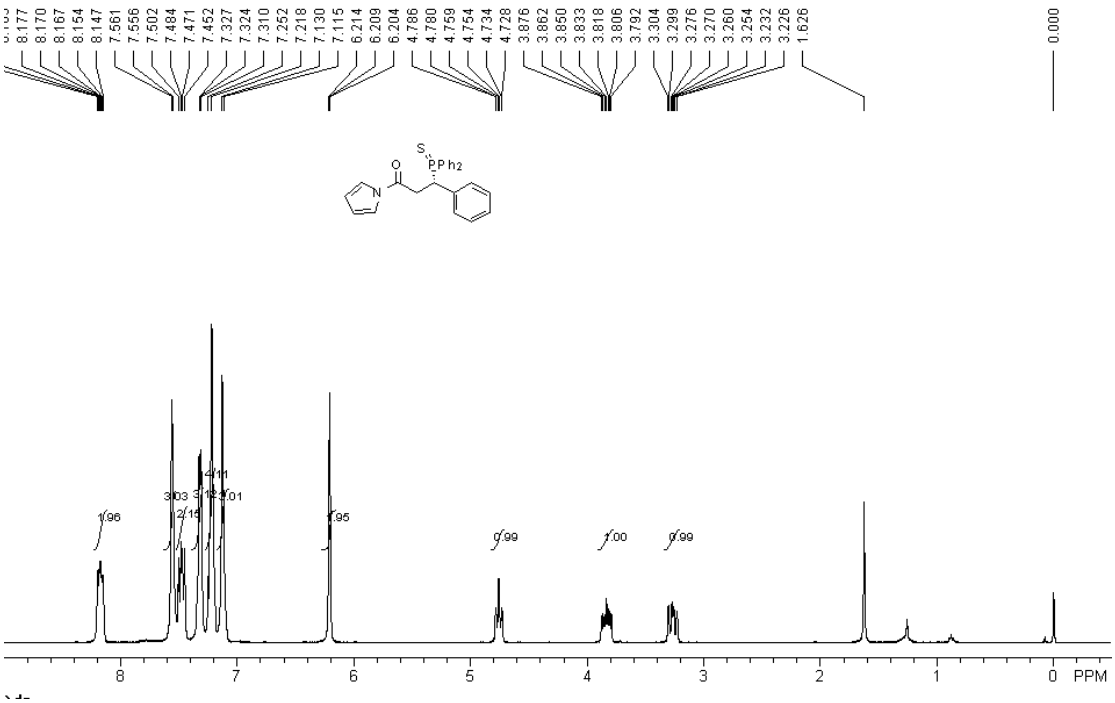
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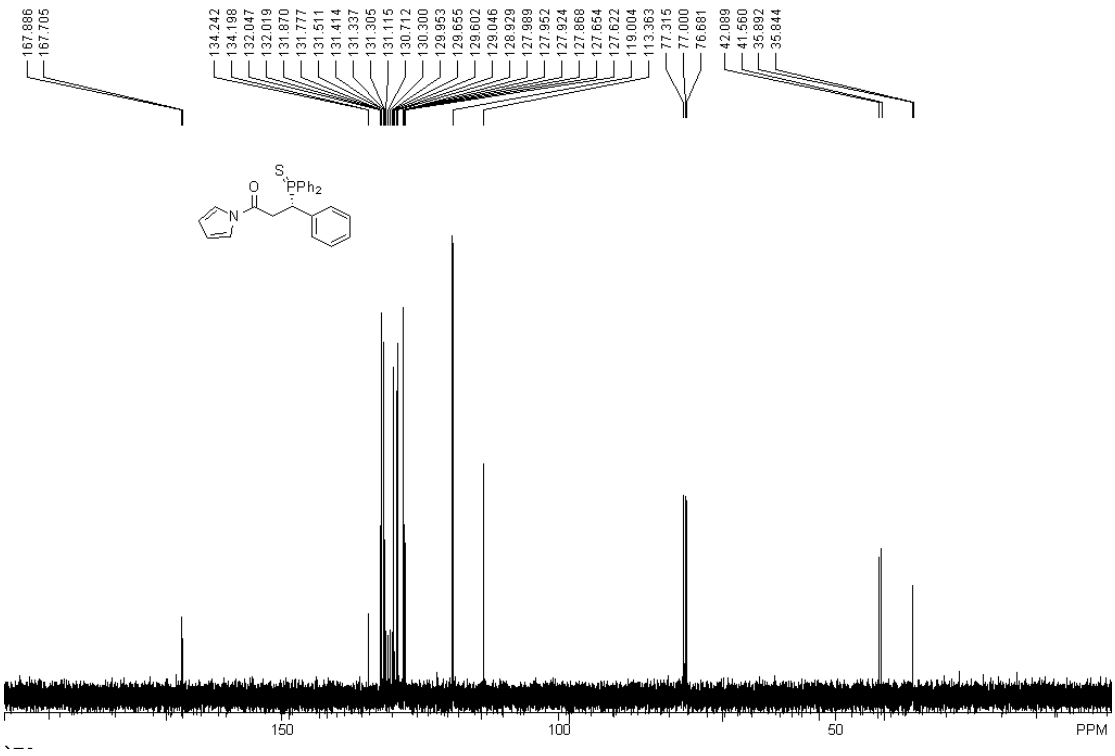
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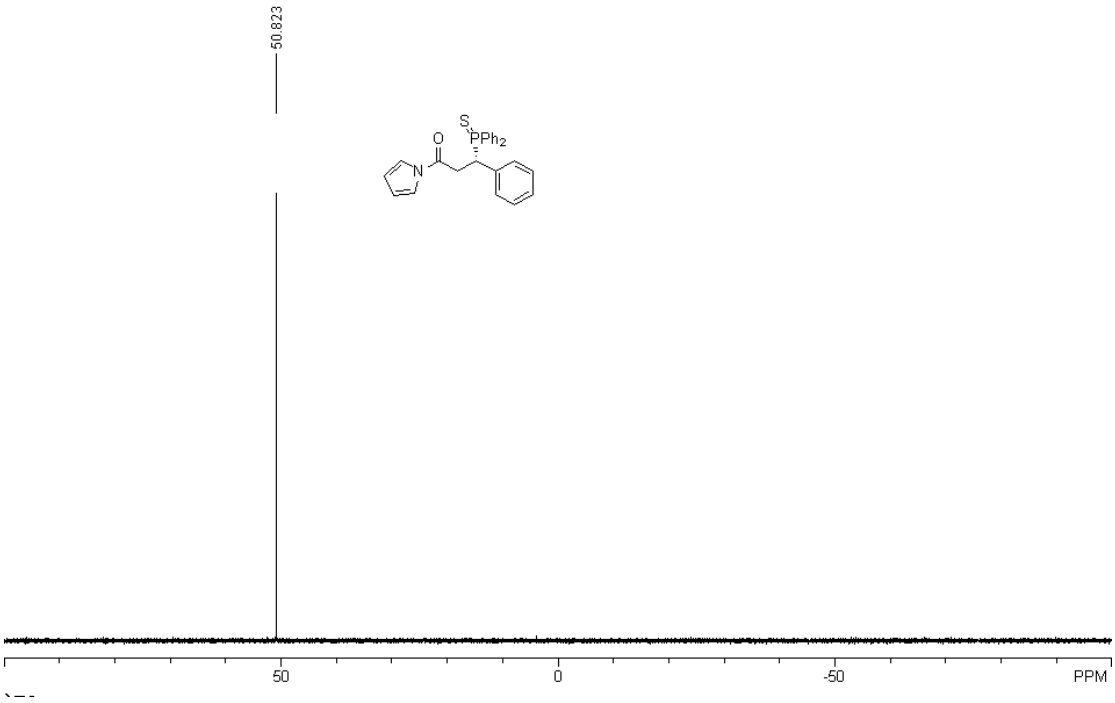
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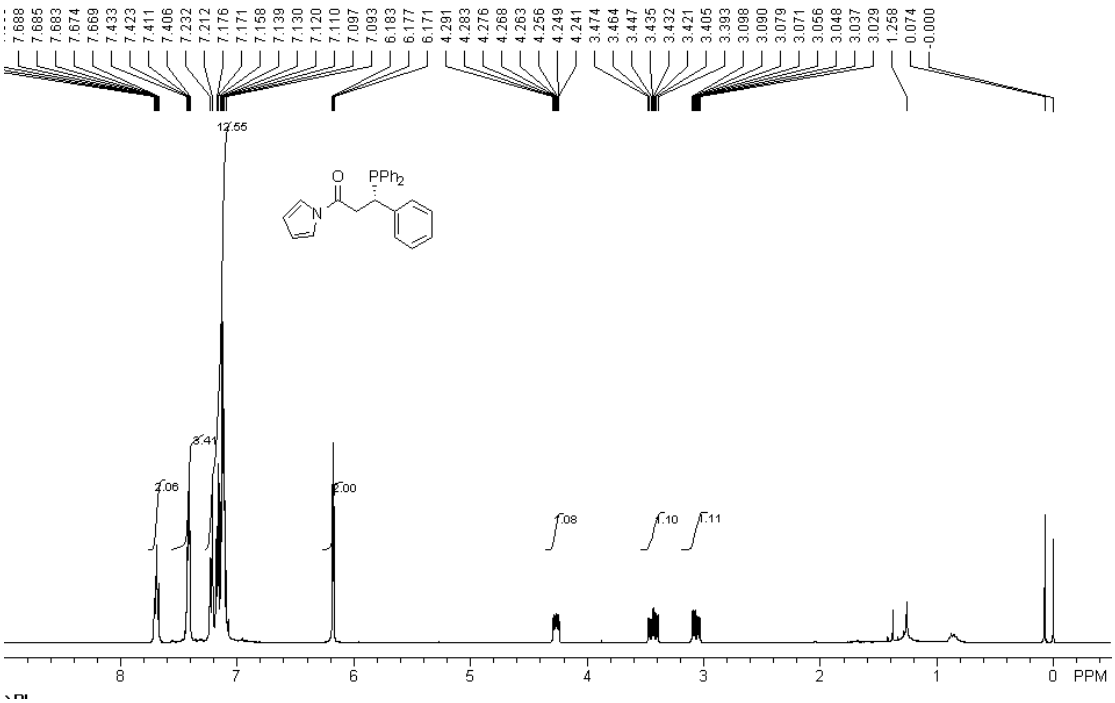
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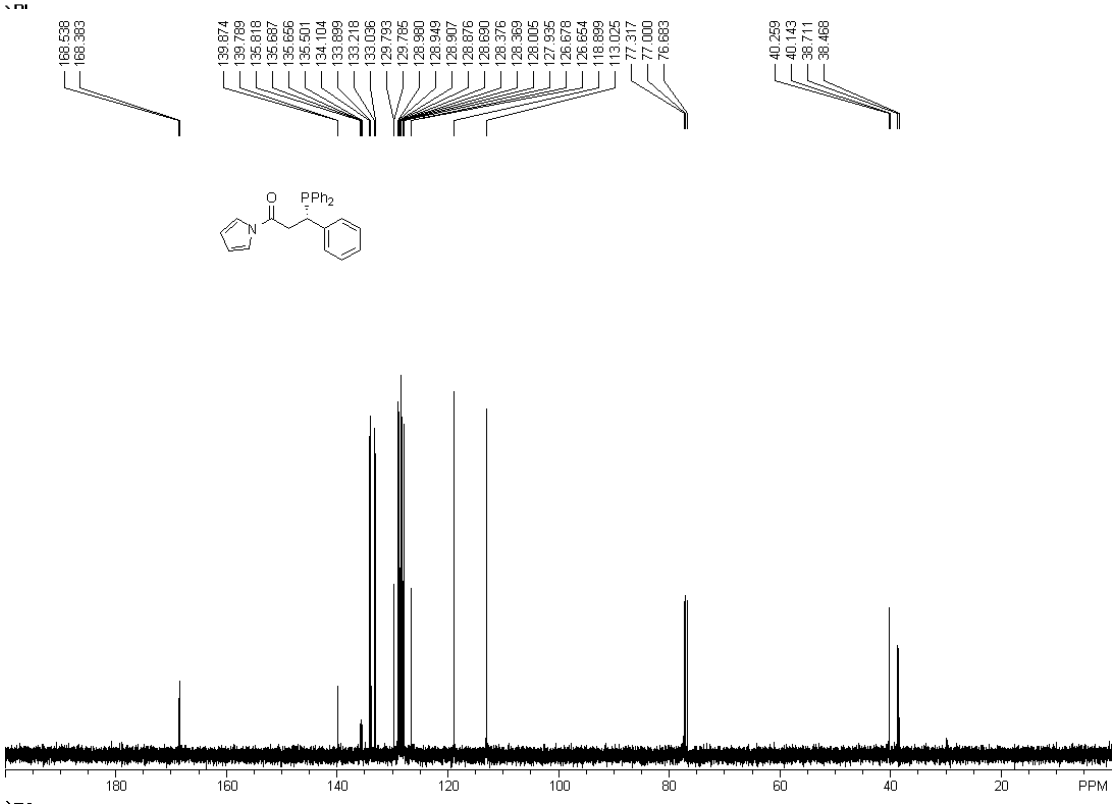
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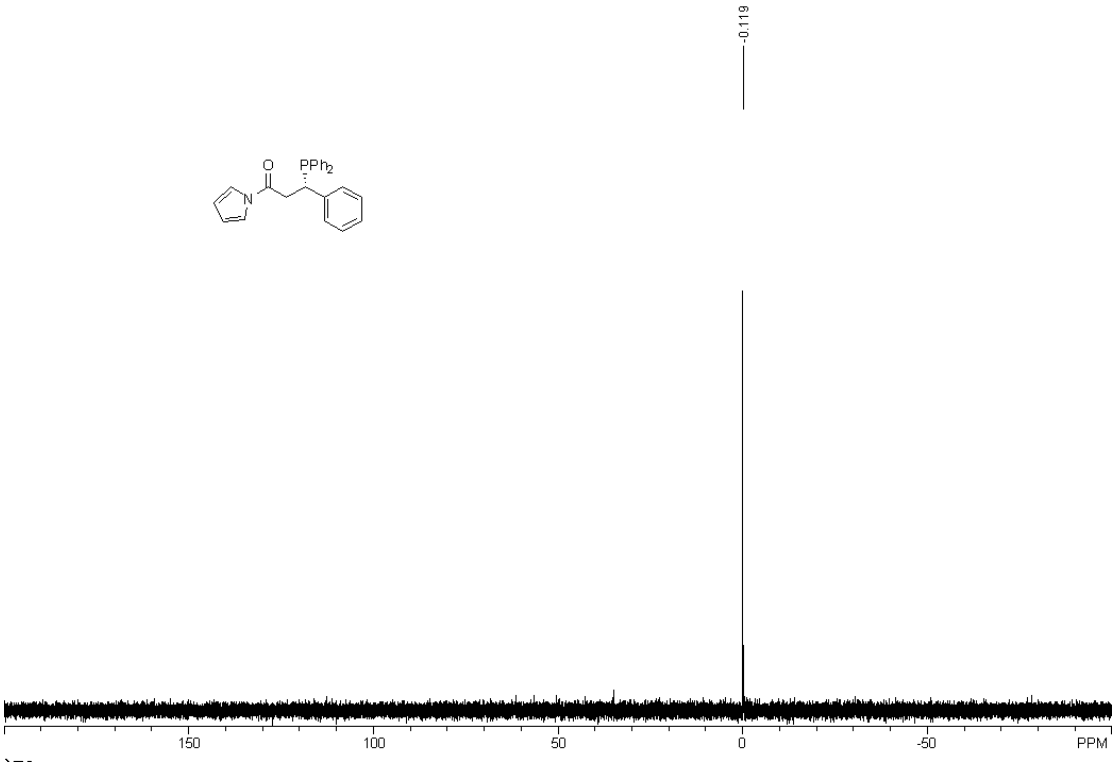
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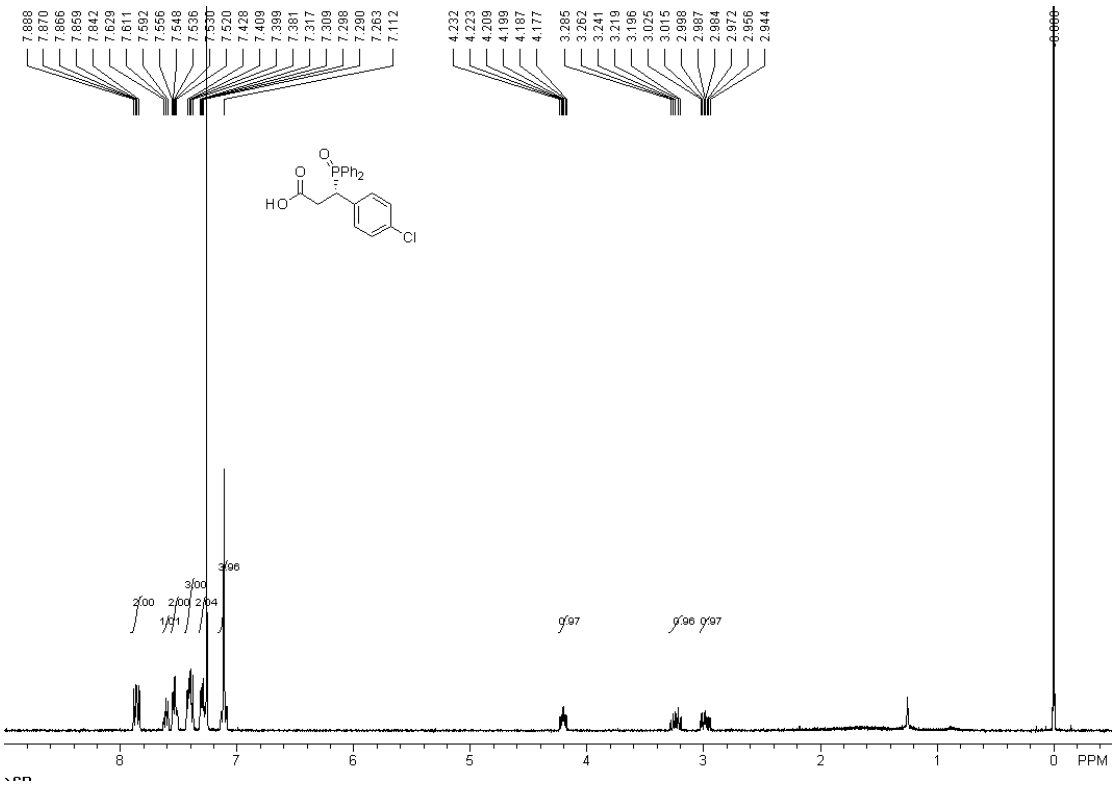
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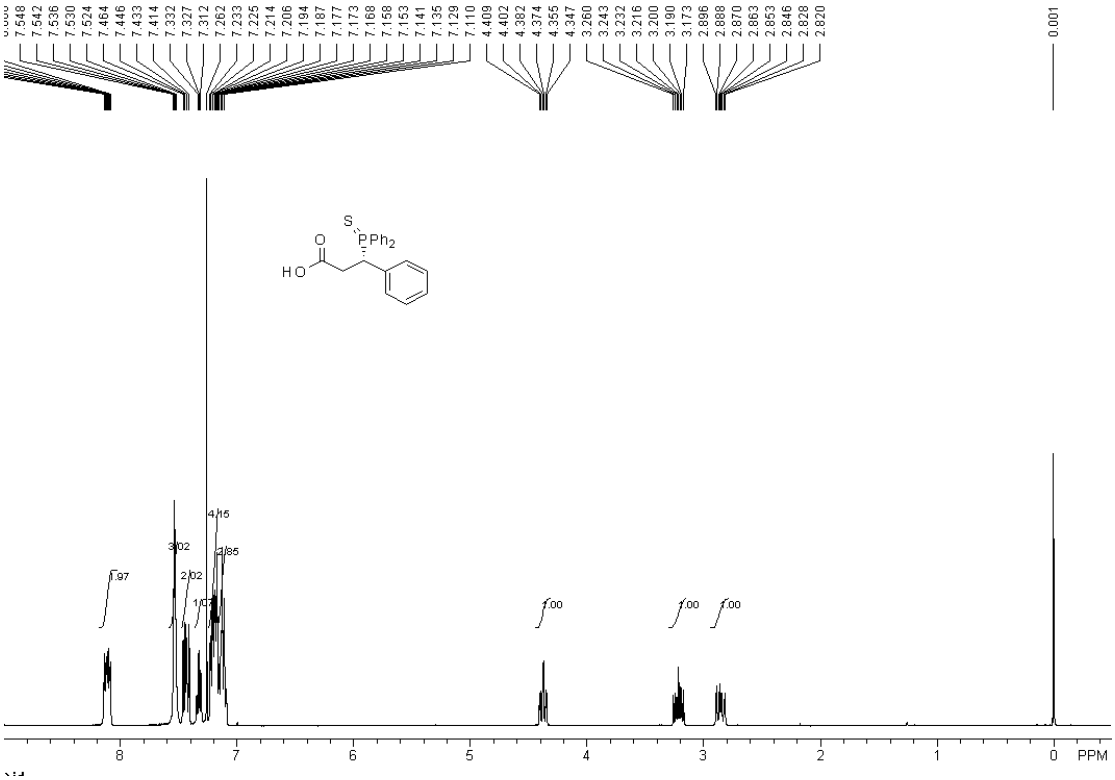
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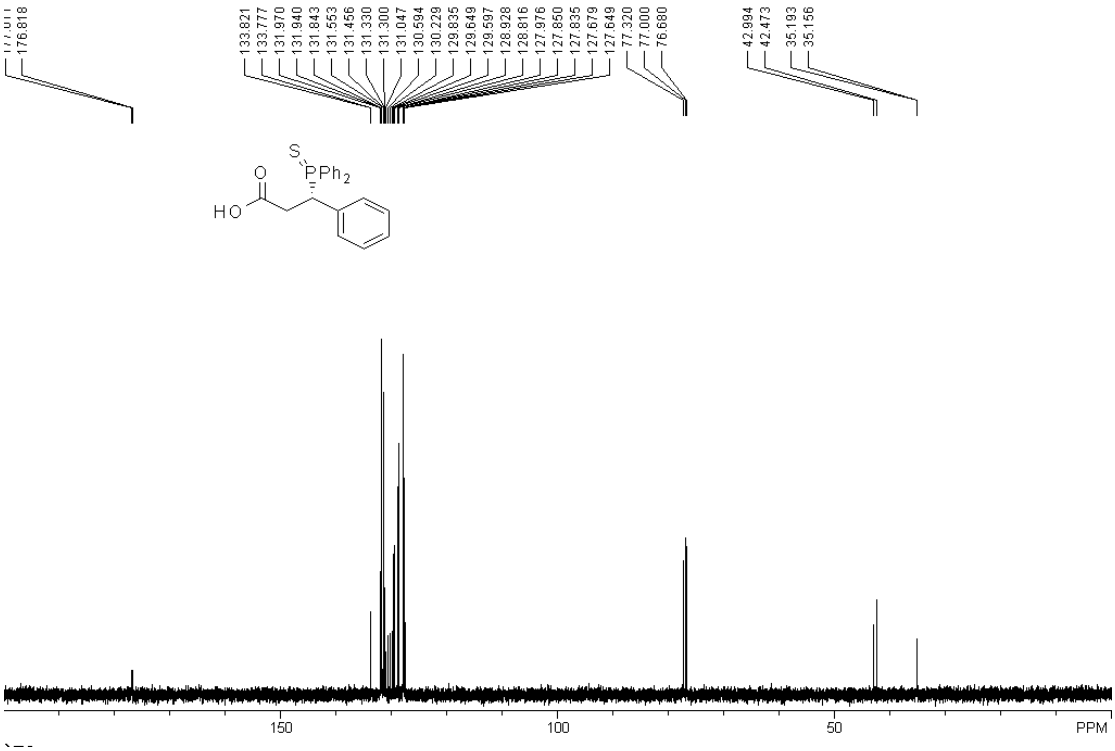
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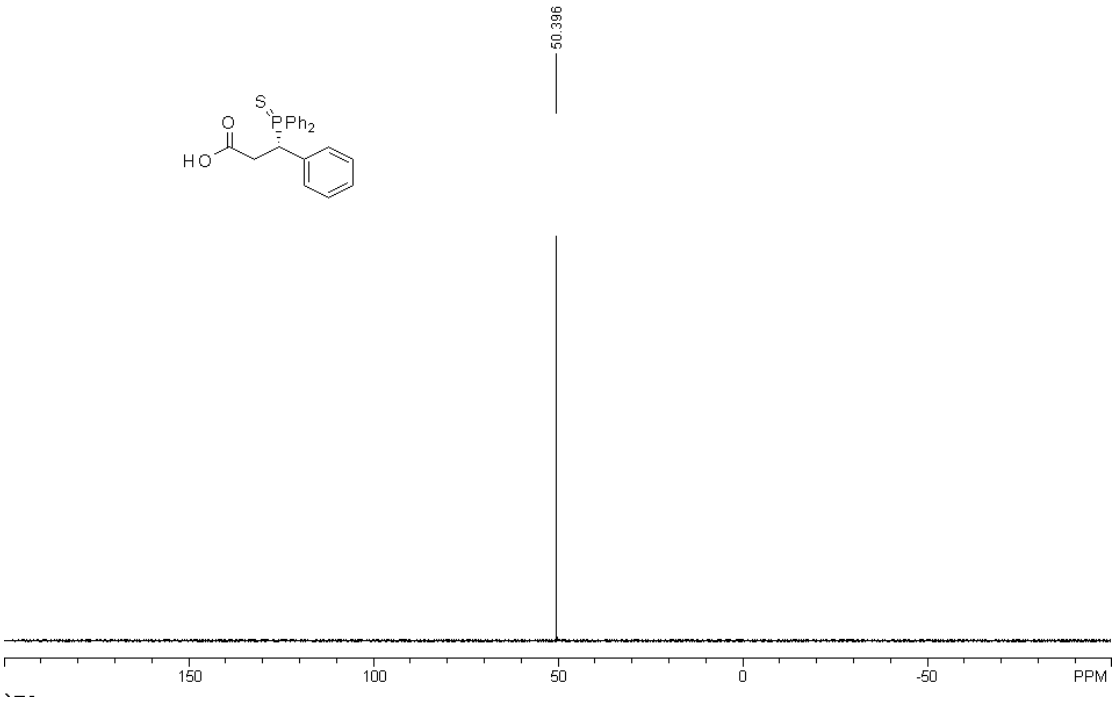
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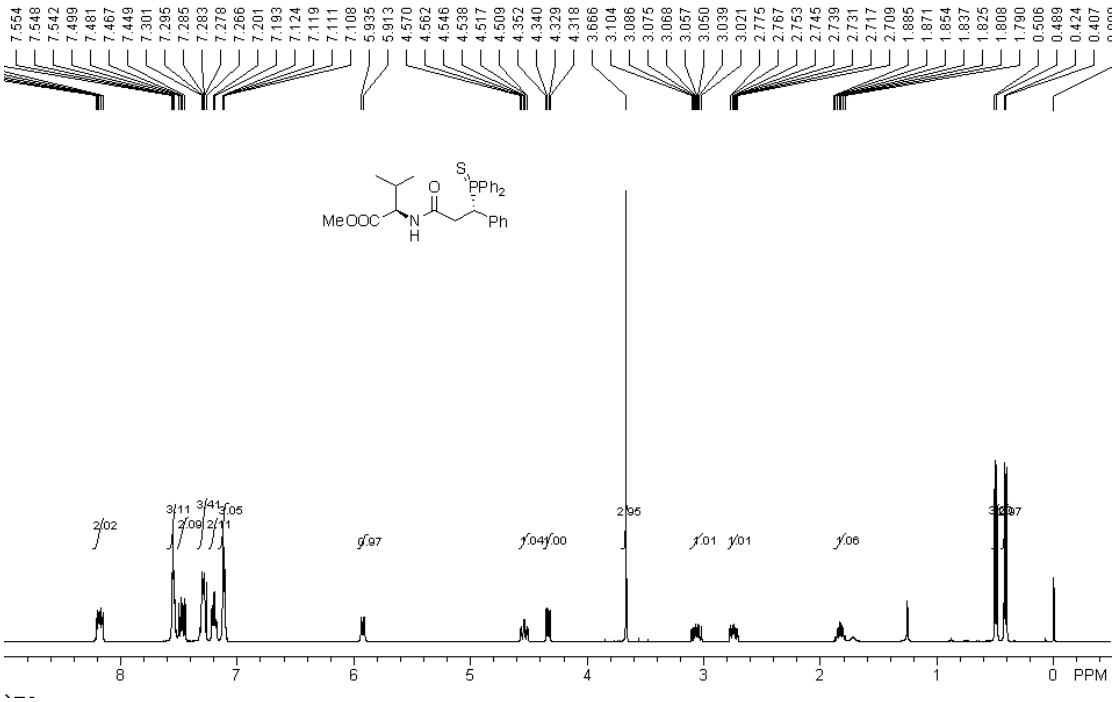
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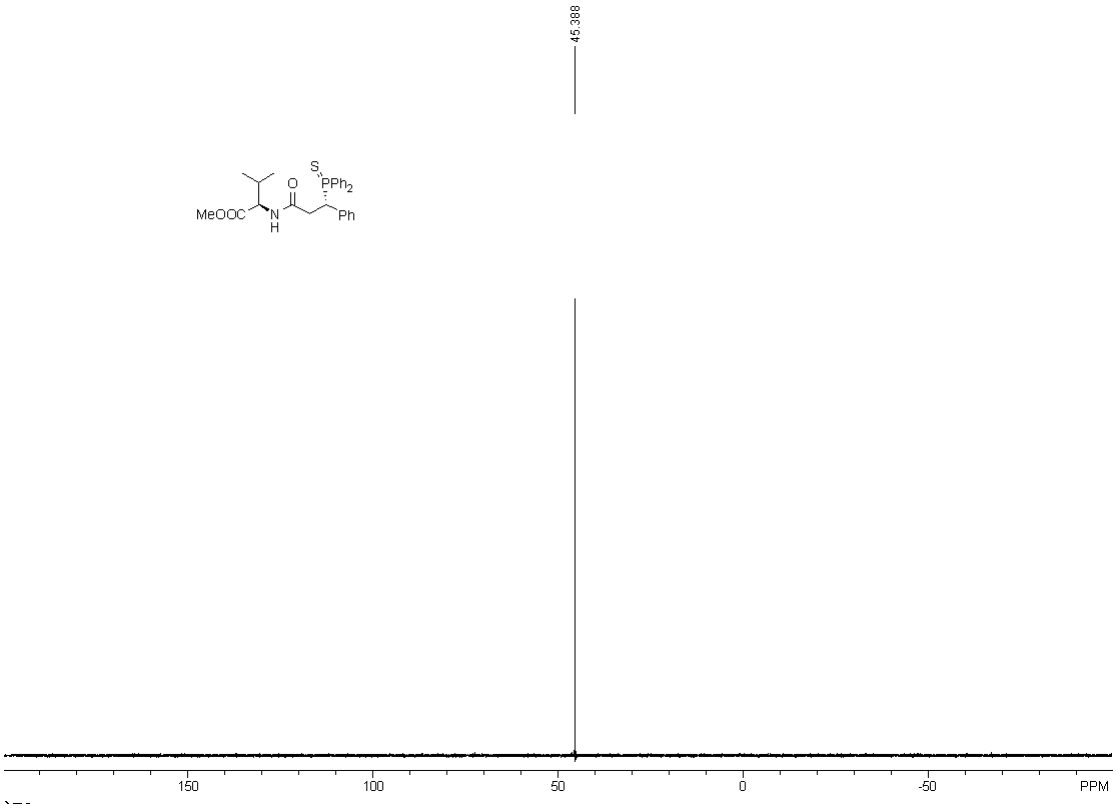
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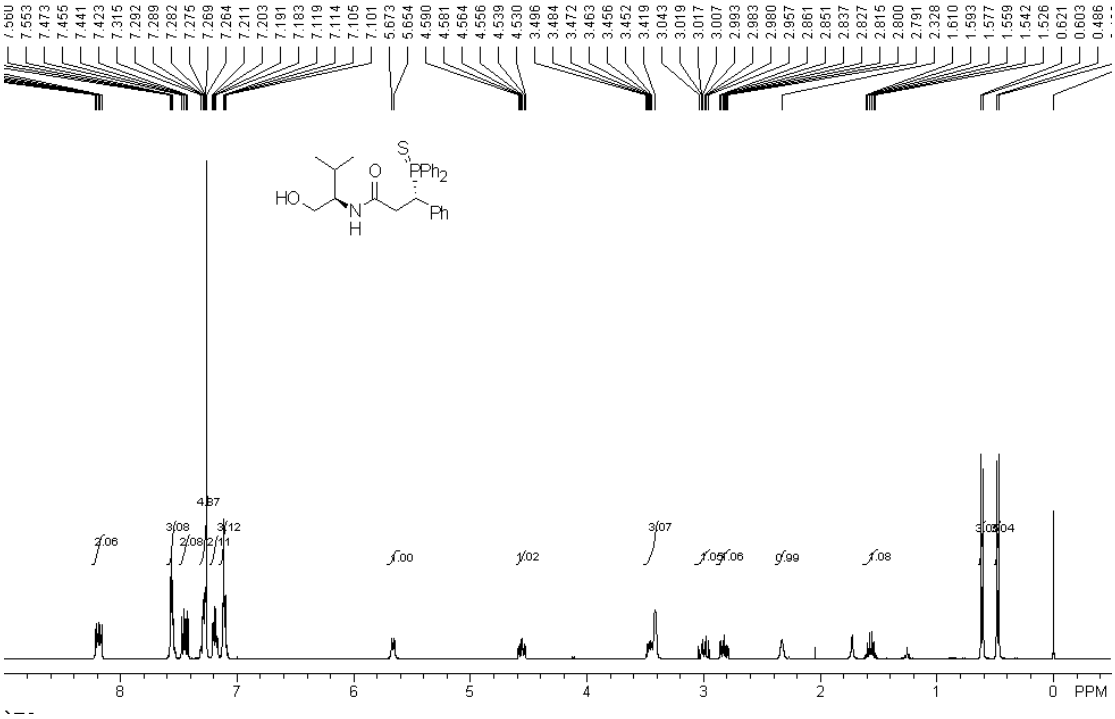
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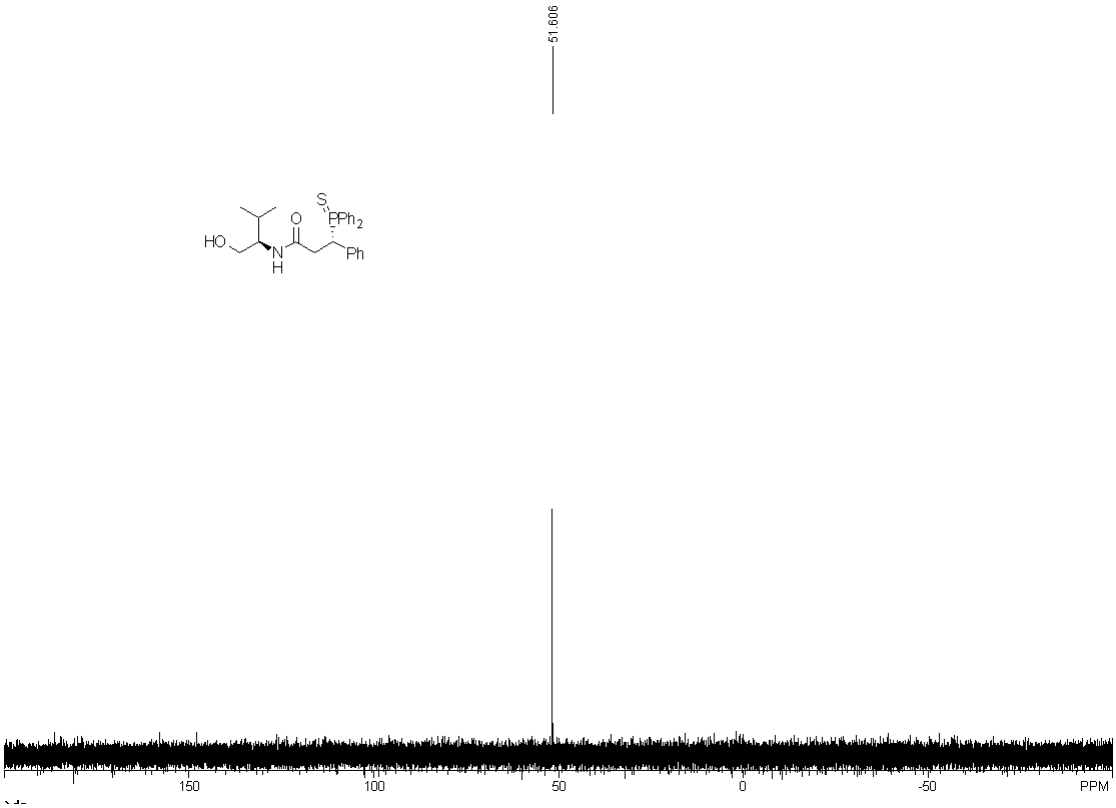
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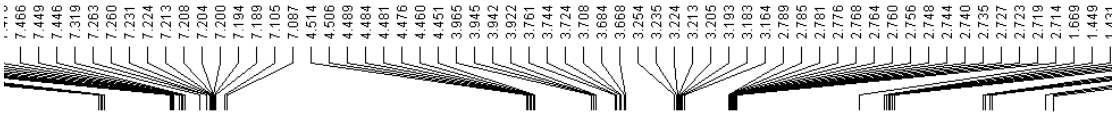
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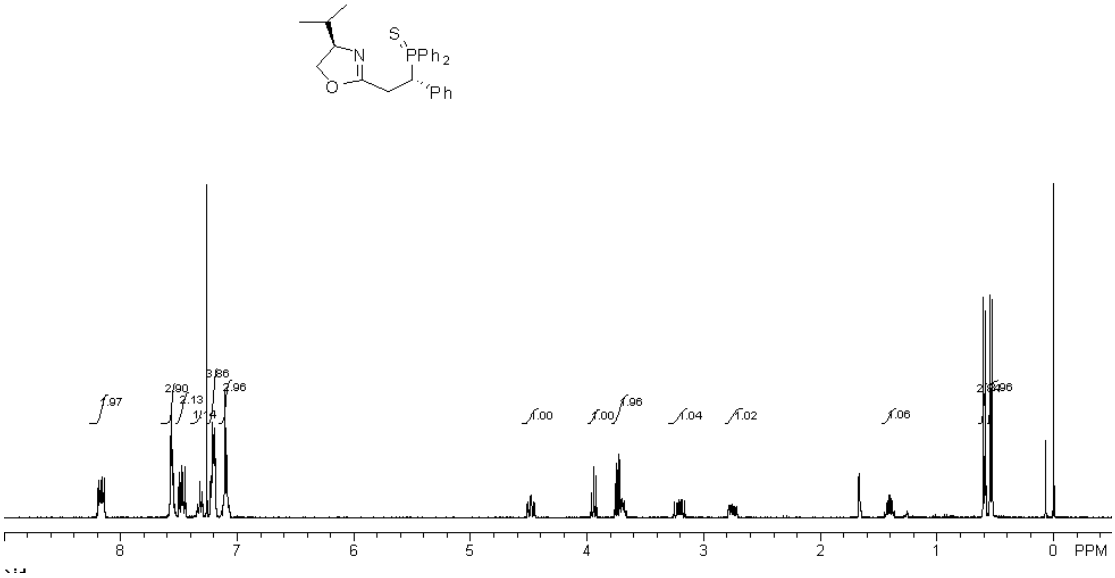
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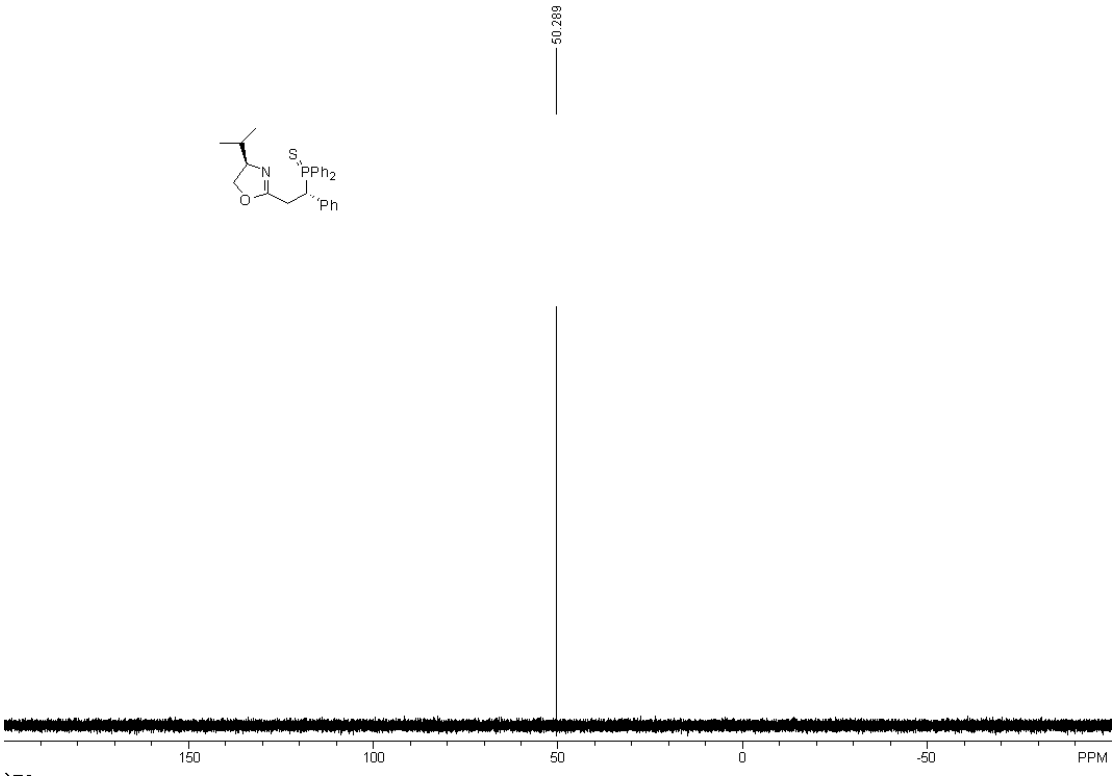
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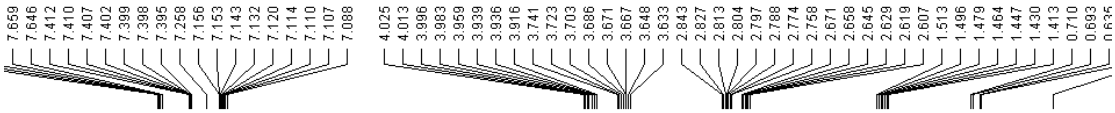
PPM


7.659
7.646
7.412
7.410
7.407
7.402
7.399
7.398
7.395
7.258
7.156
7.153
7.143
7.132
7.120
7.114
7.110
7.107
7.088
4.025
4.013
3.996
3.983
3.959
3.939
3.936
3.916
3.741
3.723
3.703
3.686
3.671
3.667
3.648
3.633
2.843
2.827
2.813
2.804
2.797
2.788
2.774
2.758
2.671
2.658
2.645
2.629
2.619
2.607
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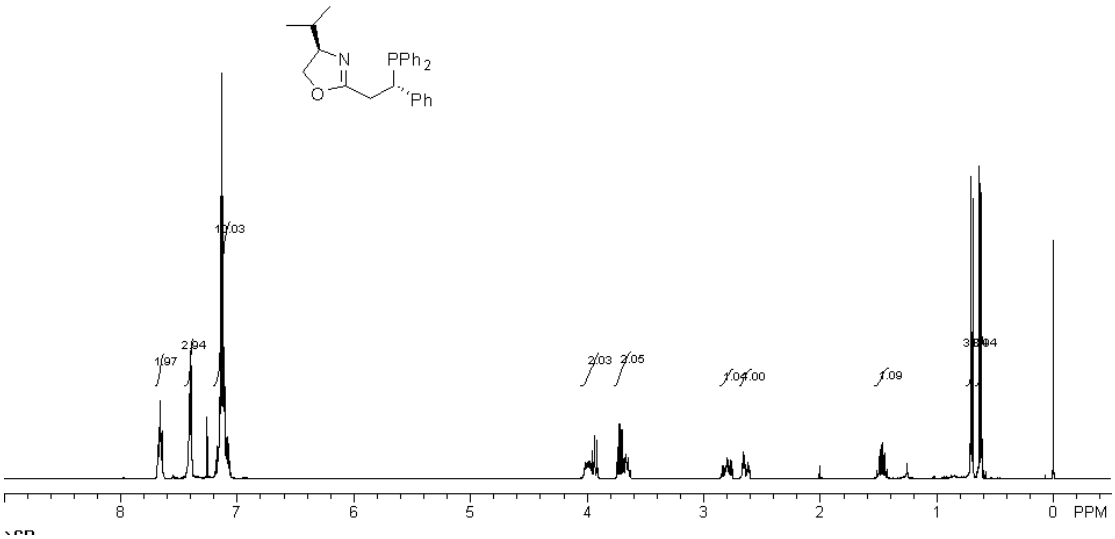
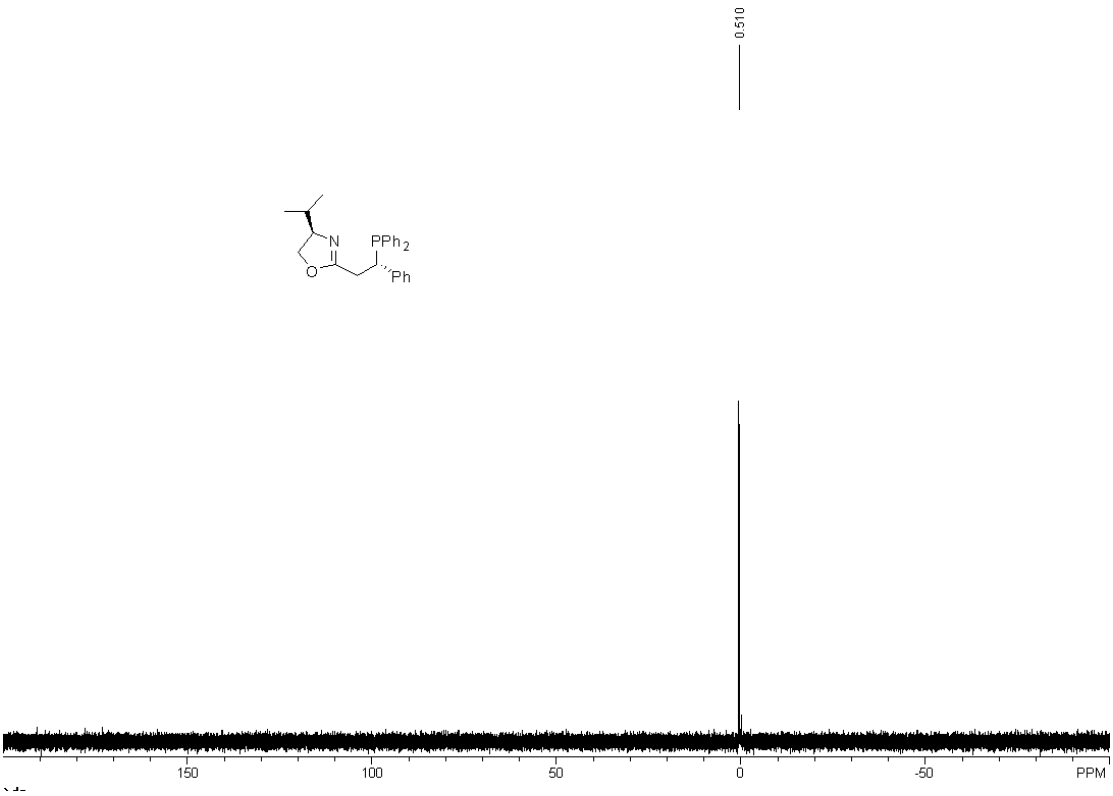
1.496
1.479
1.464
1.447
1.430
1.413
0.710
0.693


N
PPh2
O
Ph
1.03
1.97
2.04
2.03
2.05
1.04
1.00
1.09
8
7
6
5
4
3
2
1
0
PPM


0.510
N
PPh2
O
Ph
150
100
50
0
-50
PPM

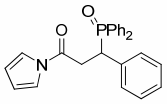
==== Shimadzu LCsolution Analysis Report ====

D:\dd\dd-1-16-r.lcd

Sample Name : dd-1-16-r Date:

Column: The mobile phase:

Velocity: The detection wavelength:



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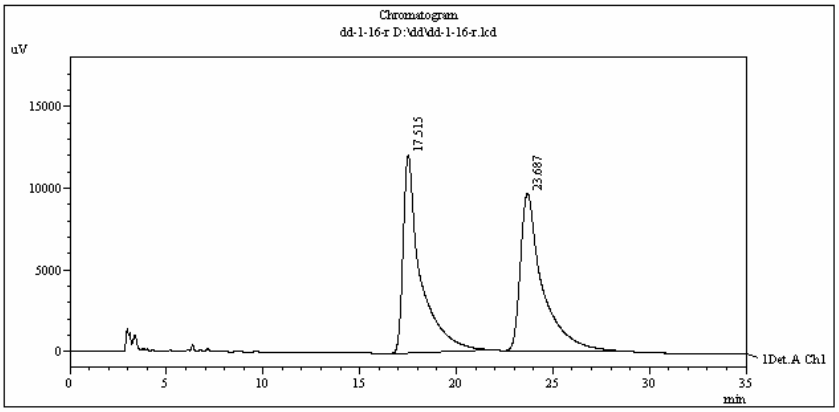


PeakTable

Detector A Ch1 230nm

Peak#	Ret. Time	Area	Height	Area %
1	17.515	754660	12133	49.982
2	23.687	755200	9662	50.018
Total		1509860	21795	100.000

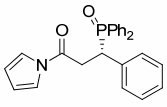
==== Shimadzu LCsolution Analysis Report ====

D:\dd\新建文件夹\1THF.lcd

Sample Name : dd-1-61 Date:

Column: The mobile phase:

Velocity: The detection wavelength:



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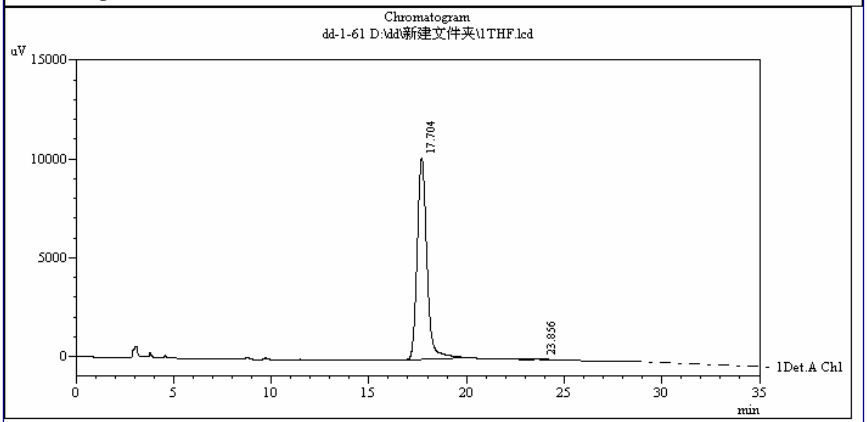


PeakTable

Detector A Ch1 245nm

Peak#	Ret. Time	Area	Height	Area %
1	17.704	352809	10173	99.412
2	23.856	2088	57	0.588
Total		354897	10230	100.000

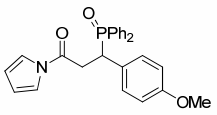
==== Shimadzu LCsolution Analysis Report ====

D:\新建文件夹\dd-1-75-o.lcd

Sample Name : dd-75-o Date:

Column: The mobile phase:

Velocity: The detection wavelength:



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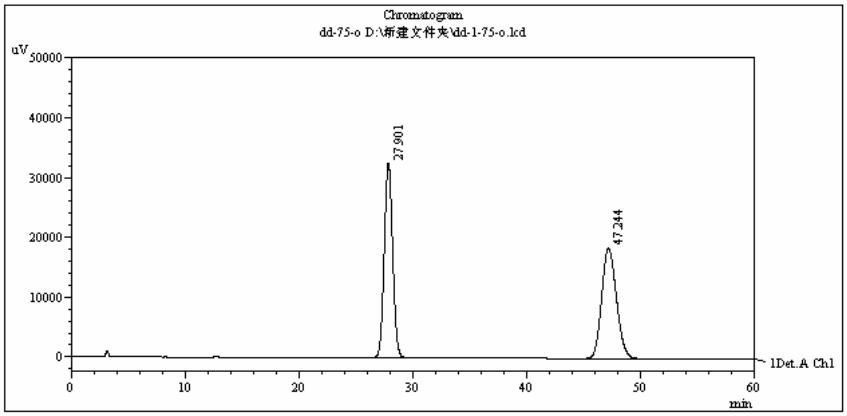


Peak Table

Detector A Ch1 245nm

Peak#	Ret. Time	Area	Height	Area %
1	27.901	1667155	32522	50.091
2	47.244	1661082	18439	49.909
Total		3328237	50961	100.000

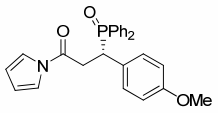
==== Shimadzu LCsolution Analysis Report ====

D:\新建文件夹\dd-1-75-2.lcd

Sample Name : dd-75-2 Date:

Column: The mobile phase:

Velocity: The detection wavelength:



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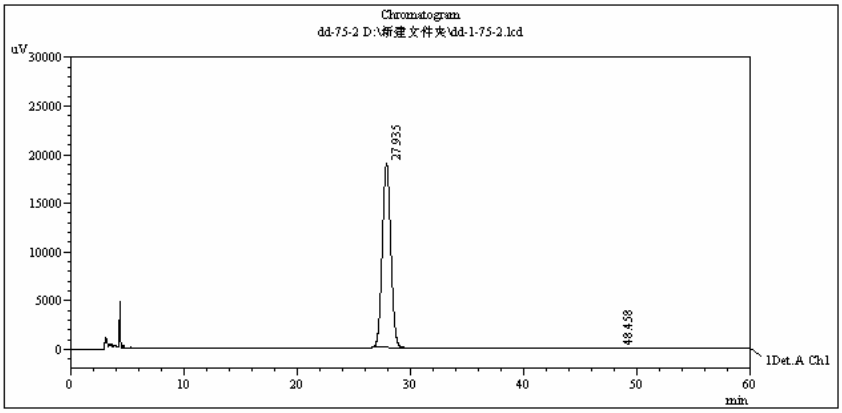


Peak Table

Detector A Ch1 245nm

Peak#	Ret. Time	Area	Height	Area %
1	27.935	988841	18917	99.725
2	48.458	2725	32	0.275
Total		991567	18949	100.000

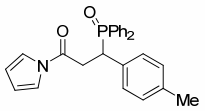
==== Shimadzu LCsolution Analysis Report ====

D:\新建文件夹\dd-1-74-o1.lcd

Sample Name : dd-74-o1 Date:

Column: The mobile phase:

Velocity: The detection wavelength:



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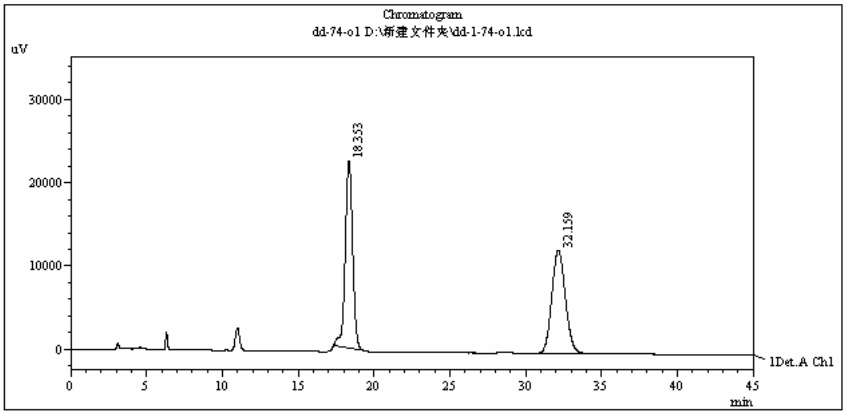


PeakTable

Detector A Ch1 245nm

Peak#	Ret. Time	Area	Height	Area %
1	18.353	772430	22488	50.120
2	32.159	768731	12362	49.880
Total		1541161	34850	100.000

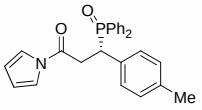
==== Shimadzu LCsolution Analysis Report ====

D:\新建文件夹\dd-1-74-1.lcd

Sample Name : dd-74-1 Date:

Column: The mobile phase:

Velocity: The detection wavelength:



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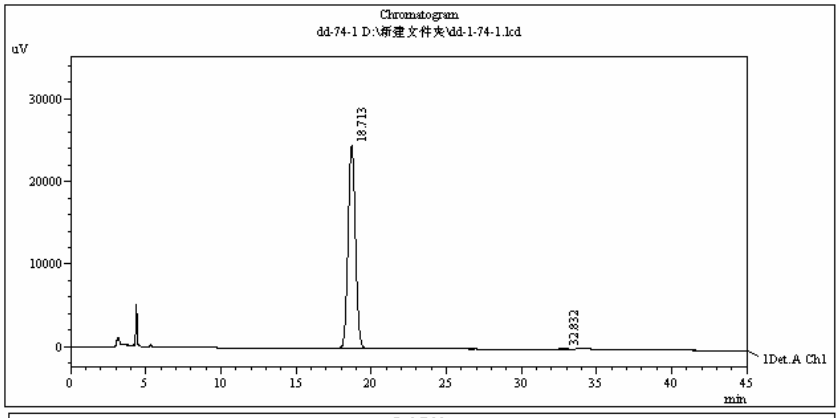


PeakTable

Detector A Ch1 245nm

Peak#	Ret. Time	Area	Height	Area %
1	18.713	834325	24483	99.865
2	32.832	1124	34	0.135
Total		835449	24518	100.000

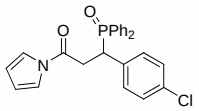
==== Shimadzu LCsolution Analysis Report ====

D:\新建文件夹\dd-1-95-o.lcd

Sample Name : dd-1-95-o Date:

Column: The mobile phase:

Velocity: The detection wavelength:



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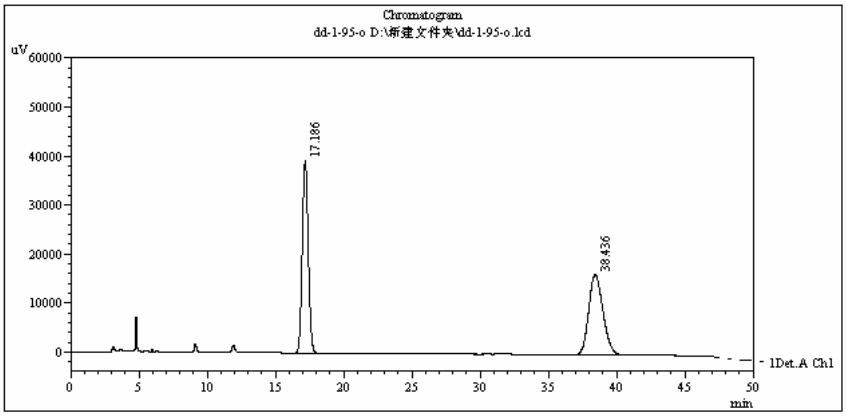


PeakTable

Detector A Ch1 245nm

Peak#	Ret. Time	Area	Height	Area %
1	17.186	1198007	39245	50.105
2	38.436	1192987	16368	49.895
Total		2390993	55613	100.000

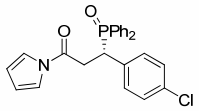
==== Shimadzu LCsolution Analysis Report ====

D:\dd\新建文件夹\dd-1-95.lcd

Sample Name : dd-1-95 Date:

Column: The mobile phase:

Velocity: The detection wavelength:



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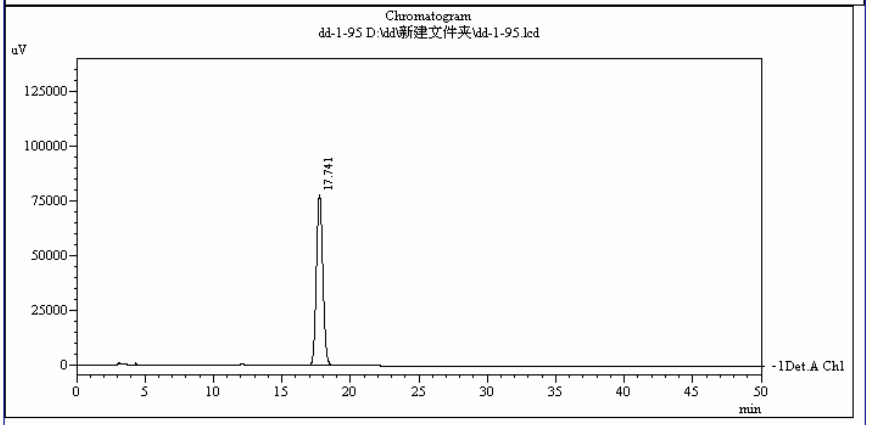


PeakTable

Detector A Ch1 245nm

Peak#	Ret. Time	Area	Height	Area %
1	17.741	2552838	78080	100.000
Total		2552838	78080	100.000

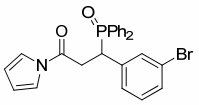
==== Shimadzu LCsolution Analysis Report ====

D:\dd\dd-1-99-o2.lcd

Sample Name : dd-1-70-o2 Date:

Column: The mobile phase:

Velocity: The detection wavelength:



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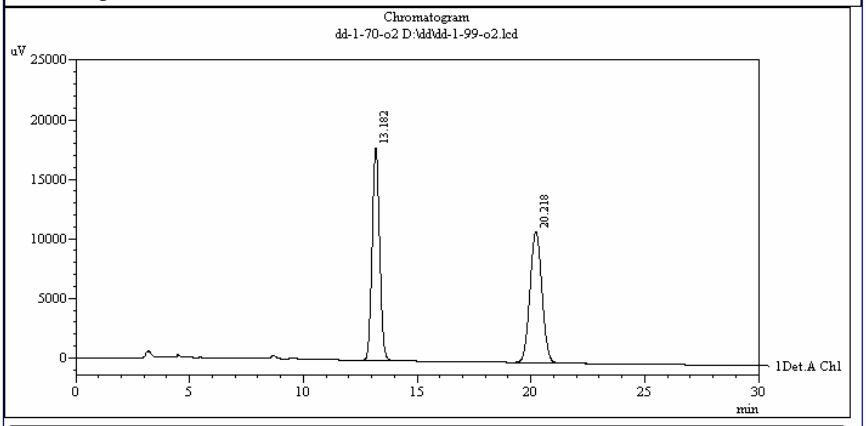


PeakTable

Detector A Ch1 245nm

Peak#	Ret. Time	Area	Height	Area %
1	13.182	409530	17830	50.538
2	20.218	400807	10984	49.462
Total		810337	28813	100.000

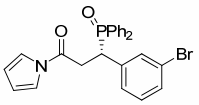
==== Shimadzu LCsolution Analysis Report ====

D:\dd\dd-1-99-1.lcd

Sample Name : dd-1-70-1 Date:

Column: The mobile phase:

Velocity: The detection wavelength:



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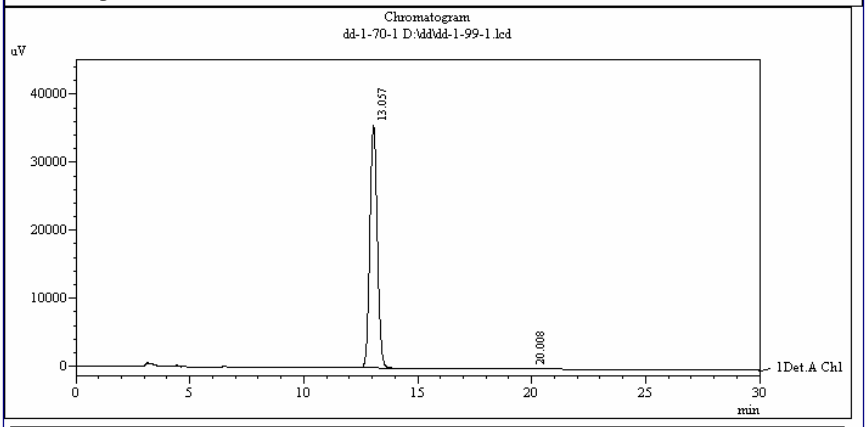


PeakTable

Detector A Ch1 245nm

Peak#	Ret. Time	Area	Height	Area %
1	13.057	813692	35681	99.629
2	20.008	3032	100	0.371
Total		816724	35782	100.000

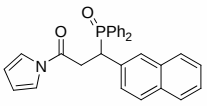
==== Shimadzu LCsolution Analysis Report ====

D:\dd\新建文件夹\8o.lcd

Sample Name : dd-1-78-o Date:

Column: The mobile phase:

Velocity: The detection wavelength:



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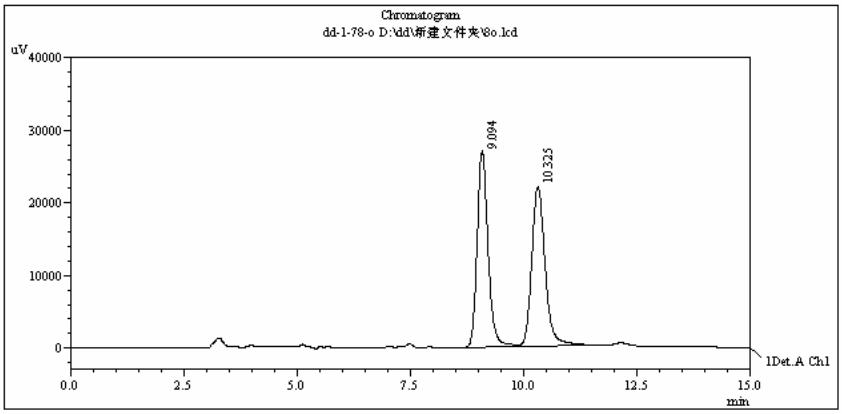


Peak Table

Detector A Ch1 245nm

Peak#	Ret. Time	Area	Height	Area %
1	9.094	456654	27026	50.152
2	10.325	453884	22005	49.848
Total		910538	49031	100.000

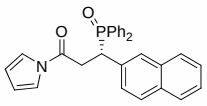
==== Shimadzu LCsolution Analysis Report ====

D:\dd\新建文件夹\8.lcd

Sample Name : dd-1-78 Date:

Column: The mobile phase:

Velocity: The detection wavelength:



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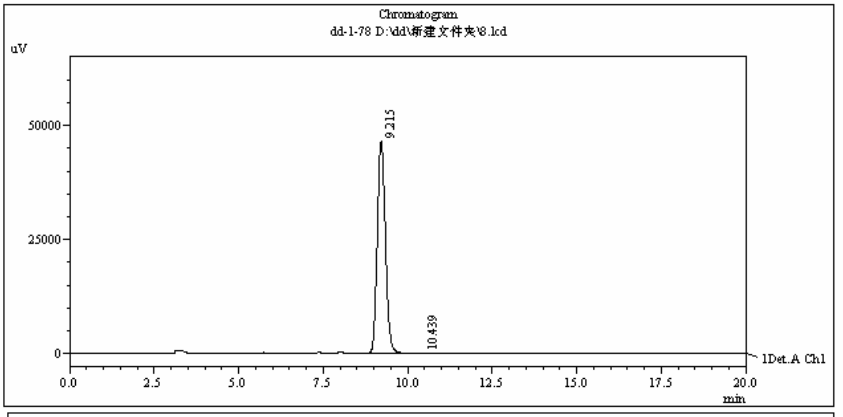


Peak Table

Detector A Ch1 245nm

Peak#	Ret. Time	Area	Height	Area %
1	9.215	776847	46557	99.685
2	10.439	2454	134	0.315
Total		779301	46692	100.000

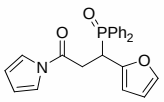
==== Shimadzu LCsolution Analysis Report ====

D:\dd\新建文件夹\7o.lcd

Sample Name : dd-1-77-o Date:

Column: The mobile phase:

Velocity: The detection wavelength:



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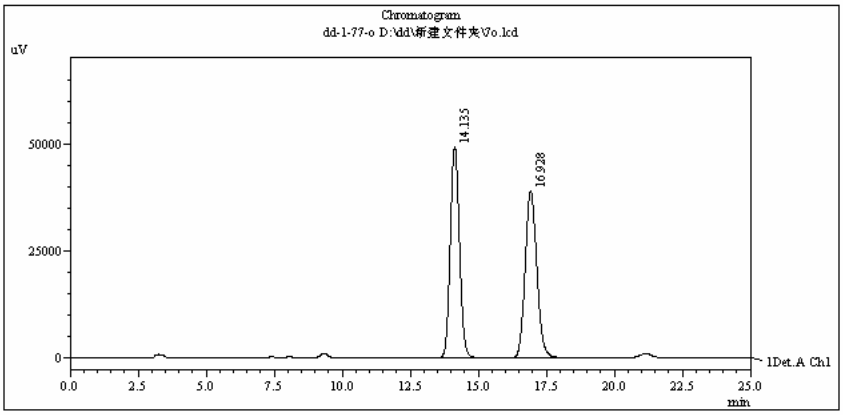


Peak Table

Detector A Ch1 245nm

Peak#	Ret. Time	Area	Height	Area %
1	14.135	1159206	49241	49.715
2	16.928	1172494	39064	50.285
Total		2331701	88305	100.000

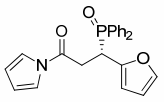
==== Shimadzu LCsolution Analysis Report ====

D:\dd\新建文件夹\7.lcd

Sample Name : dd-1-77 Date:

Column: The mobile phase:

Velocity: The detection wavelength:



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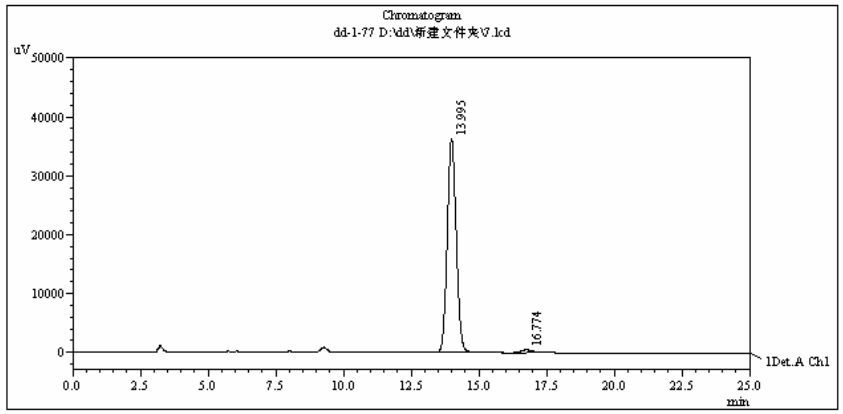


Peak Table

Detector A Ch1 245nm

Peak#	Ret. Time	Area	Height	Area %
1	13.995	836691	36339	98.671
2	16.774	11266	430	1.329
Total		847957	36769	100.000

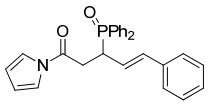
==== Shimadzu LCsolution Analysis Report ====

D:\dd\dd-1-82-o.lcd

Sample Name : dd-1-82-o Date:

Column: The mobile phase:

Velocity: The detection wavelength:



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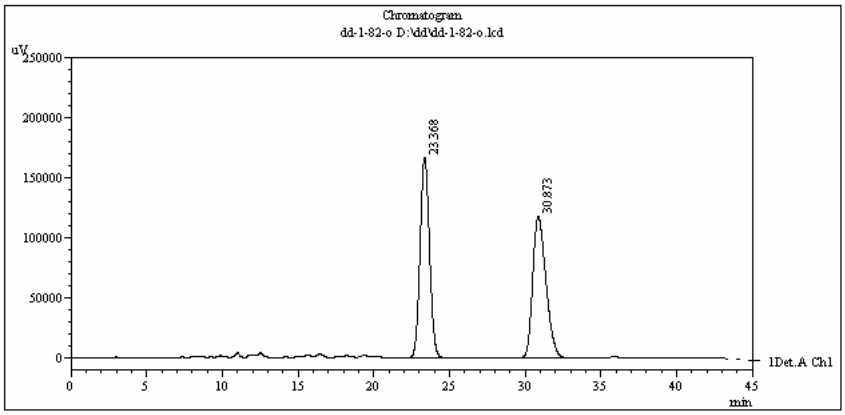


Peak Table

Detector A Ch1 245nm

Peak#	Ret. Time	Area	Height	Area %
1	23.368	7239253	167694	50.109
2	30.873	7207858	118112	49.891
Total		14447111	285806	100.000

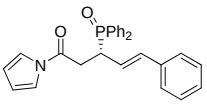
==== Shimadzu LCsolution Analysis Report ====

D:\dd\dd-1-82.lcd

Sample Name : dd-1-82 Date:

Column: The mobile phase:

Velocity: The detection wavelength:



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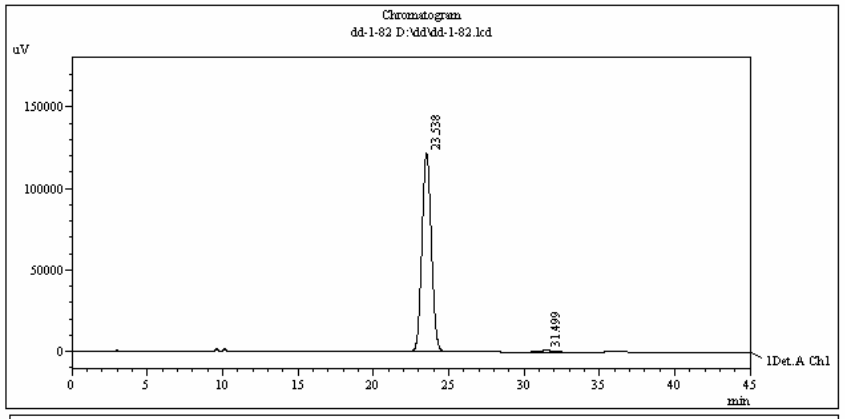


Peak Table

Detector A Ch1 245nm

Peak#	Ret. Time	Area	Height	Area %
1	23.538	5290752	121778	98.876
2	31.499	60139	983	1.124
Total		5350891	122760	100.000

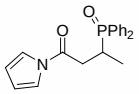
==== Shimadzu LCsolution Analysis Report ====

D:\dd\dd-2-71-o1.lcd

Sample Name : dd-2-73-o1 Date:

Column: The mobile phase:

Velocity: The detection wavelength:



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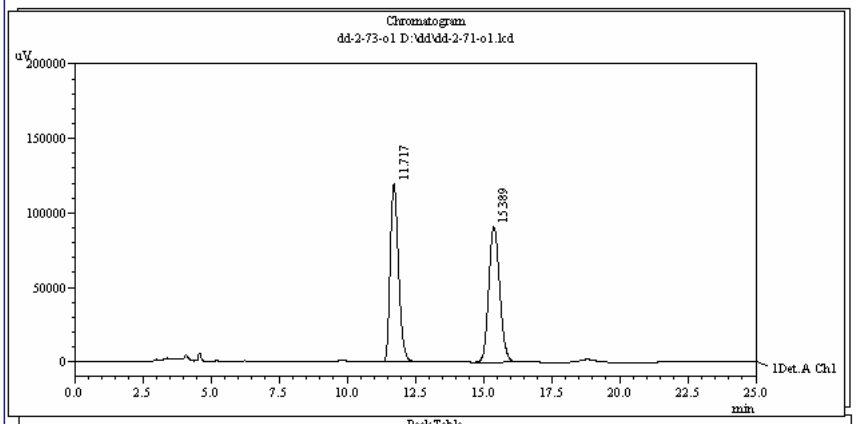


Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	11.717	2527392	119323	49.886
2	15.389	2538900	90693	50.114
Total		5066292	210016	100.000

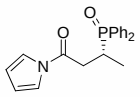
==== Shimadzu LCsolution Analysis Report ====

D:\dd\dd-2-71-2.lcd

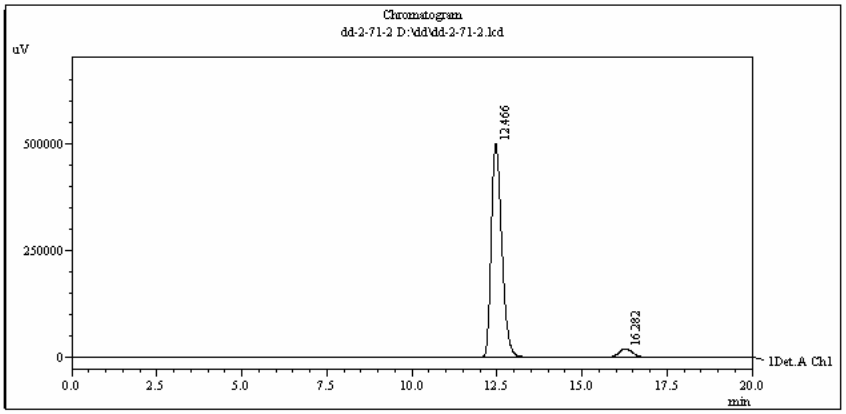
Sample Name : dd-2-71-2 Date:

Column: The mobile phase:

Velocity: The detection wavelength:



<Chromatogram>



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	12.466	10707049	497840	95.255
2	16.282	533400	19495	4.745
Total		11240448	517334	100.000

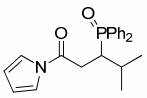
==== Shimadzu LCsolution Analysis Report ====

D:\dd\新建文件夹\12-o.lcd

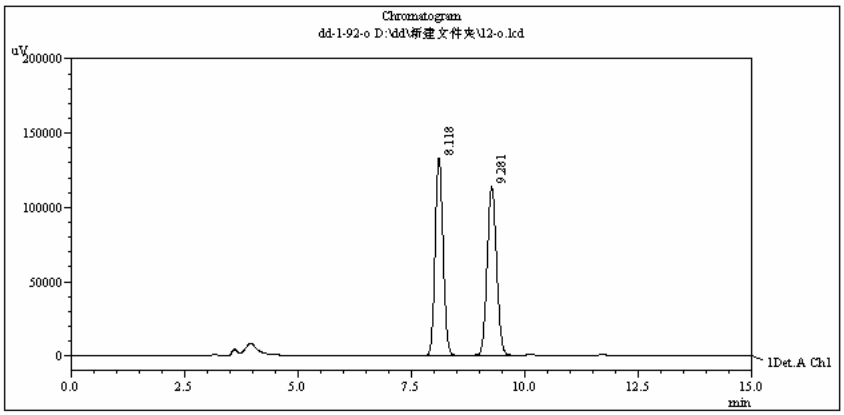
Sample Name : dd-1-92-o Date:

Column: The mobile phase:

Velocity: The detection wavelength:



<Chromatogram>



Peak Table

Detector A Ch1 245nm

Peak#	Ret. Time	Area	Height	Area %
1	8.118	1630504	133175	49.808
2	9.281	1643067	113585	50.192
Total		3273571	246760	100.000

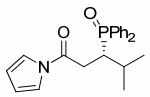
==== Shimadzu LCsolution Analysis Report ====

D:\dd\新建文件夹\12.lcd

Sample Name : dd-1-92 Date:

Column: The mobile phase:

Velocity: The detection wavelength:



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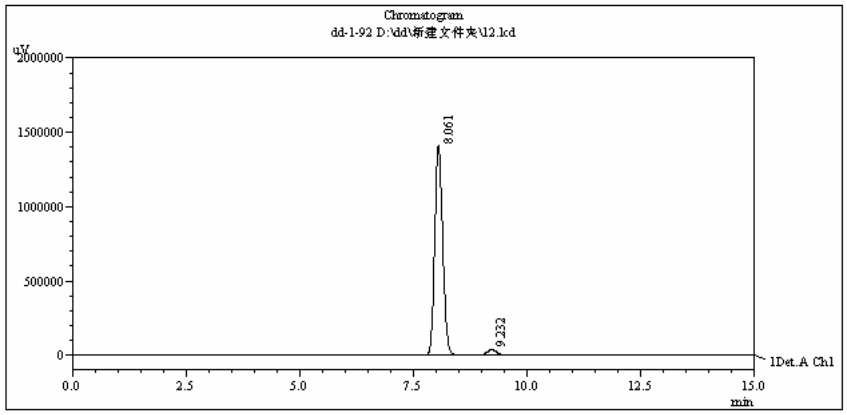


Peak Table

Detector A Ch1 245nm

Peak#	Ret. Time	Area	Height	Area %
1	8.061	17433605	1409367	96.930
2	9.232	552182	38549	3.070
Total		17985787	1447916	100.000

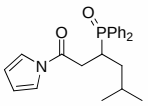
==== Shimadzu LCsolution Analysis Report ====

D:\dd\新建文件夹\11-o.lcd

Sample Name : dd-1-91-o Date:

Column: The mobile phase:

Velocity: The detection wavelength:



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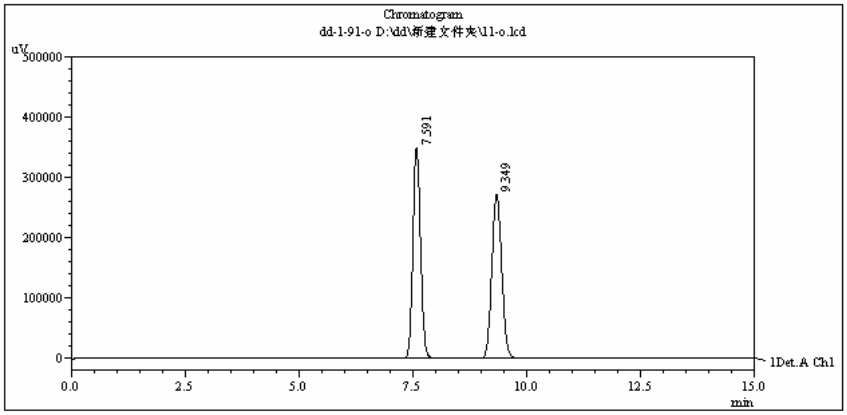


Peak Table

Detector A Ch1 245nm

Peak#	Ret. Time	Area	Height	Area %
1	7.591	4113685	349550	49.957
2	9.349	4120729	272412	50.043
Total		8234415	621962	100.000

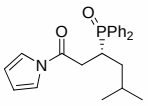
==== Shimadzu LCsolution Analysis Report ====

D:\dd\新建文件夹\11.lcd

Sample Name : dd-1-91 Date:

Column: The mobile phase:

Velocity: The detection wavelength:



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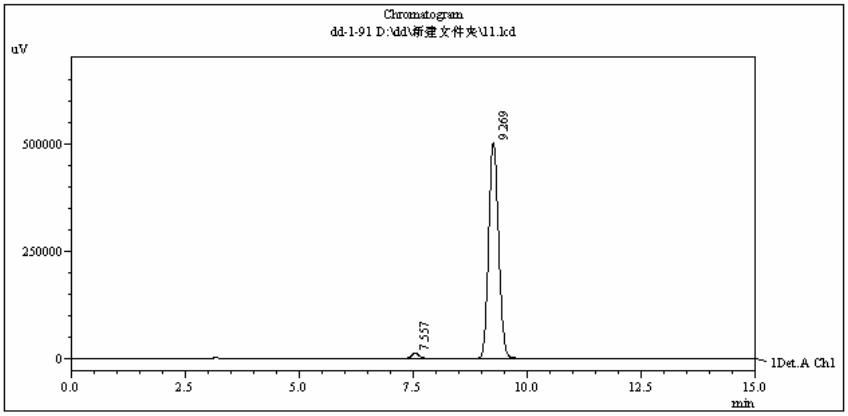


Peak Table

Detector A Ch1 245nm

Peak#	Ret. Time	Area	Height	Area %
1	7.557	141514	12174	1.840
2	9.269	7550988	503278	98.160
Total		7692502	515452	100.000

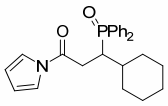
==== Shimadzu LCsolution Analysis Report ====

D:\dd\新建文件夹\9o.lcd

Sample Name : dd-1-80-o Date:

Column: The mobile phase:

Velocity: The detection wavelength:



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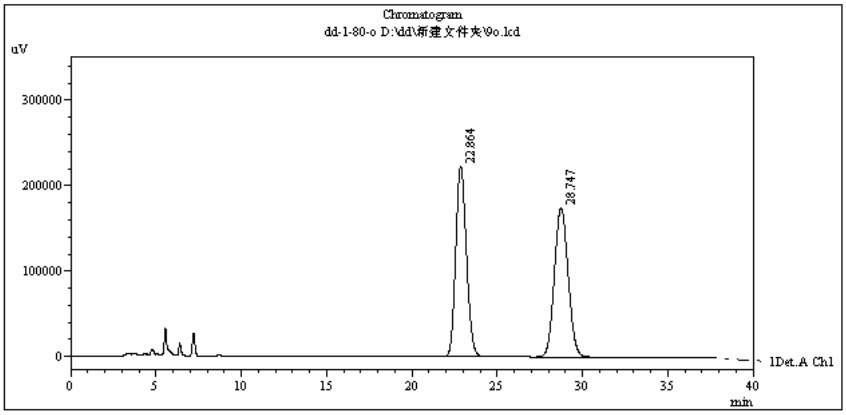


Peak Table

Detector A Ch1 245nm

Peak#	Ret. Time	Area	Height	Area %
1	22.864	9738082	223085	49.974
2	28.747	9748306	174448	50.026
Total		19486389	397533	100.000

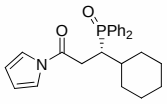
==== Shimadzu LCsolution Analysis Report ====

D:\dd\新建文件夹\9.lcd

Sample Name : dd-1-80 Date:

Column: The mobile phase:

Velocity: The detection wavelength:



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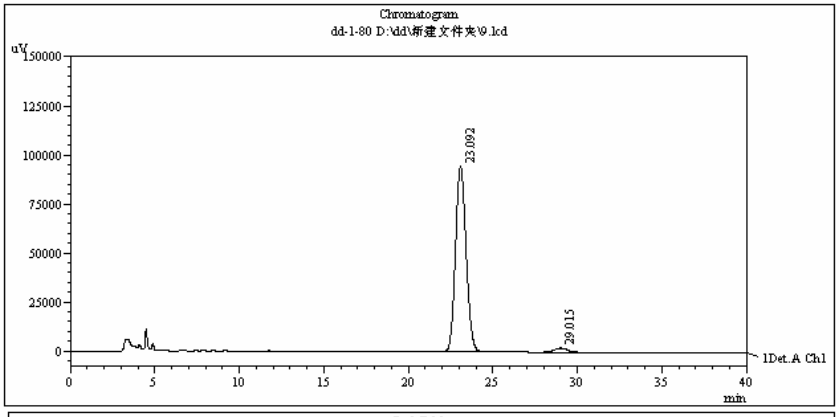


Peak Table

Detector A Ch1 245nm

Peak#	Ret. Time	Area	Height	Area %
1	23.092	4143734	94570	97.322
2	29.015	114004	2074	2.678
Total		4257738	96644	100.000

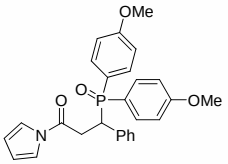
==== Shimadzu LCsolution Analysis Report ====

D:\dd\dd-2-17-oIC.lcd

Sample Name : dd-2-17-oIC Date:

Column: The mobile phase:

Velocity: The detection wavelength:



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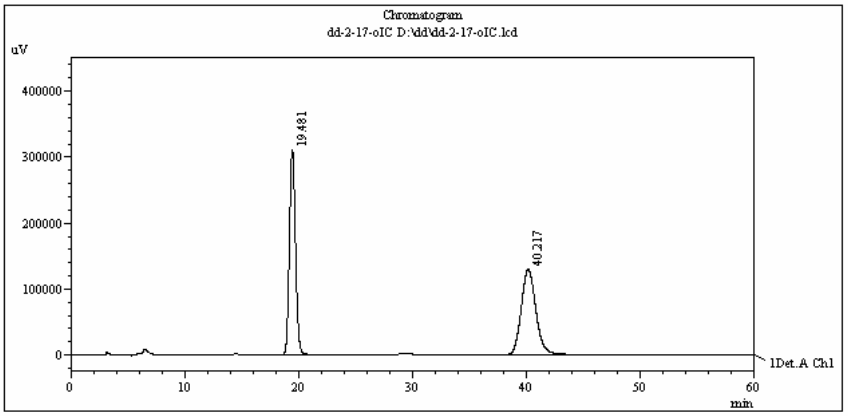


Peak Table

Detector A Ch1 245nm

Peak#	Ret. Time	Area	Height	Area %
1	19.481	11458057	311235	49.912
2	40.217	11498538	129460	50.088
Total		22956595	440696	100.000

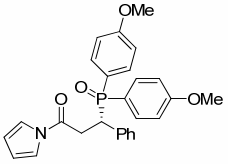
==== Shimadzu LCsolution Analysis Report ====

D:\dd\dd-2-17IC.lcd

Sample Name : dd-1-17IC Date:

Column: The mobile phase:

Velocity: The detection wavelength:



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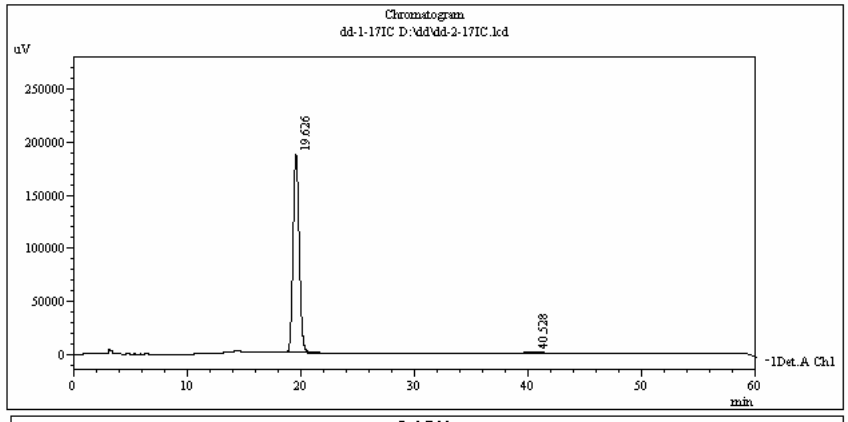


Peak Table

Detector A Ch1 245nm

Peak#	Ret. Time	Area	Height	Area %
1	19.626	7036840	187217	98.457
2	40.528	110281	1267	1.543
Total		7147121	188484	100.000

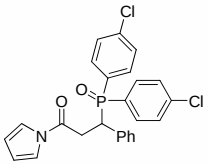
==== Shimadzu LCsolution Analysis Report ====

D:\dd\dd-2-42o.lcd

Sample Name : dd-1-97-o Date:

Column: The mobile phase:

Velocity: The detection wavelength:



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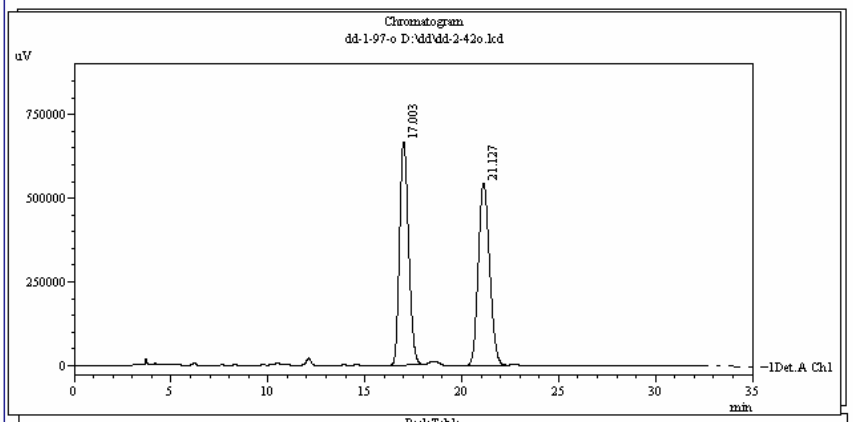


Peak Table

Detector A Ch1 245nm

Peak#	Ret. Time	Area	Height	Area %
1	17.003	21696733	667392	49.418
2	21.127	22208200	545054	50.582
Total		43904933	1212445	100.000

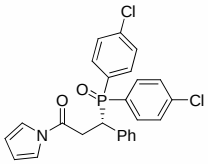
==== Shimadzu LCsolution Analysis Report ====

D:\dd\dd-2-42.lcd

Sample Name : dd-2-42 Date:

Column: The mobile phase:

Velocity: The detection wavelength:



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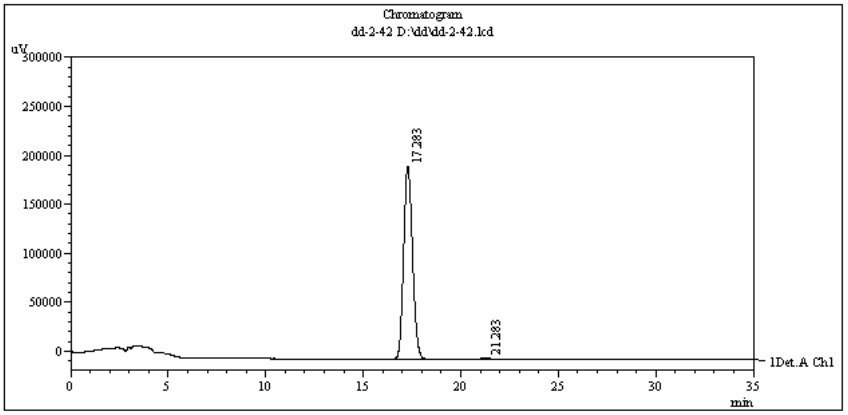


Peak Table

Detector A Ch1 245nm

Peak#	Ret. Time	Area	Height	Area %
1	17.283	6260501	197048	99.028
2	21.283	61426	1515	0.972
Total		6321927	198563	100.000

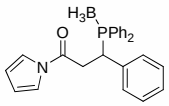
==== Shimadzu LCsolution Analysis Report ====

D:\dd\dd-2-26o1-AD.lcd

Sample Name : dd-2-26o1-AD Date:

Column: The mobile phase:

Velocity: The detection wavelength:



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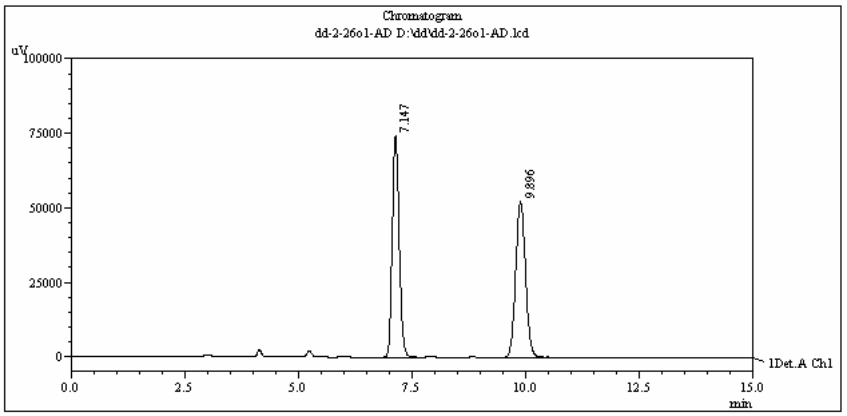


Peak Table

Detector A Ch1 245nm

Peak#	Ret. Time	Area	Height	Area %
1	7.147	785126	74172	49.941
2	9.896	786984	52223	50.059
Total		1572110	126395	100.000

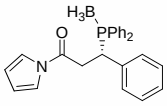
==== Shimadzu LCsolution Analysis Report ====

D:\dd\dd-2-26-AD.lcd

Sample Name : dd-2-26-AD Date:

Column: The mobile phase:

Velocity: The detection wavelength:



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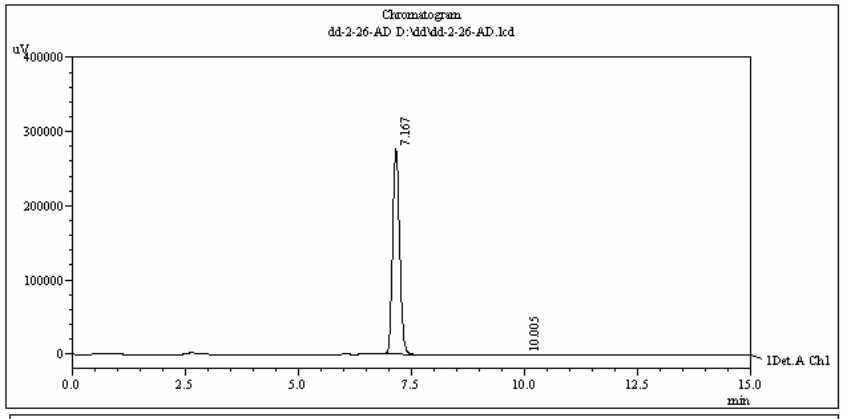


Peak Table

Detector A Ch1 245nm

Peak#	Ret. Time	Area	Height	Area %
1	7.167	2967374	277234	99.789
2	10.005	6276	426	0.211
Total		2973650	277660	100.000

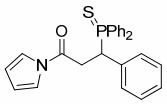
==== Shimadzu LCsolution Analysis Report ====

D:\dd\dd-2-27o1-AD.lcd

Sample Name : dd-2-27o1-AD Date:

Column: The mobile phase:

Velocity: The detection wavelength:



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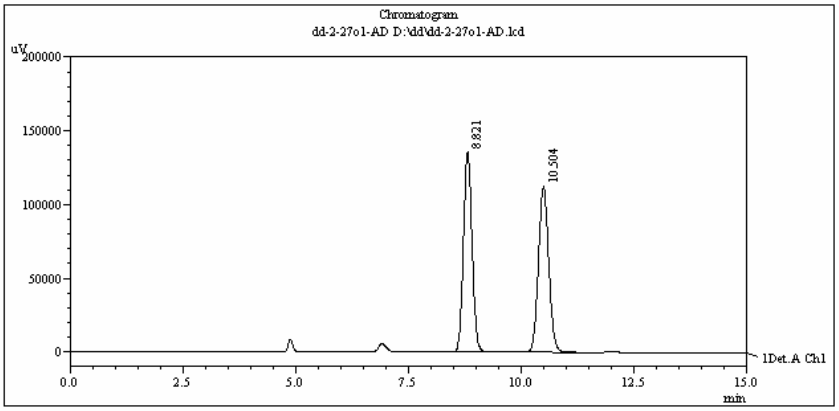


Peak Table

Detector A Ch1 245nm

Peak#	Ret. Time	Area	Height	Area %
1	8.821	1798673	135529	50.052
2	10.504	1794966	112298	49.948
Total		3593639	247827	100.000

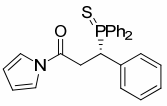
==== Shimadzu LCsolution Analysis Report ====

D:\dd\dd-2-27-AD.lcd

Sample Name : dd-2-27-AD Date:

Column: The mobile phase:

Velocity: The detection wavelength:



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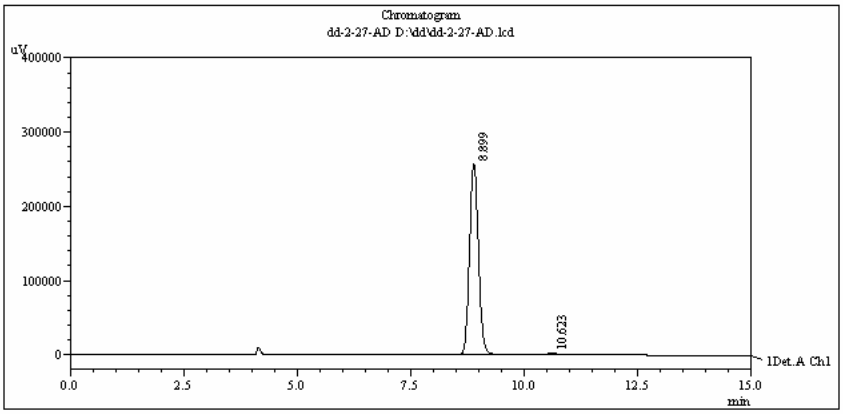

Peak Table

Detector A Ch1 245nm

Peak#	Ret. Time	Area	Height	Area %
1	8.899	3555412	258072	99.182
2	10.623	29312	1817	0.818
Total		3584724	259889	100.000