

Supporting Information

Efficient Palladium-catalyzed Asymmetric Allylic Alkylation of Ketones and Aldehydes

Xiaohu Zhao,^a Delong Liu,^b Fang Xie,^a Yangang Liu^b and Wanbin Zhang*^{a,b}

^a School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, P. R. China

^b School of Pharmacy, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, P. R. China

wanbin@sjtu.edu.cn

Contents

General Methods.....	S2
Synthesis and Characterization Data.....	S2
Copies of NMR Spectra.....	S4
Copies of HPLC Spectra.....	S19

1. General Methods.

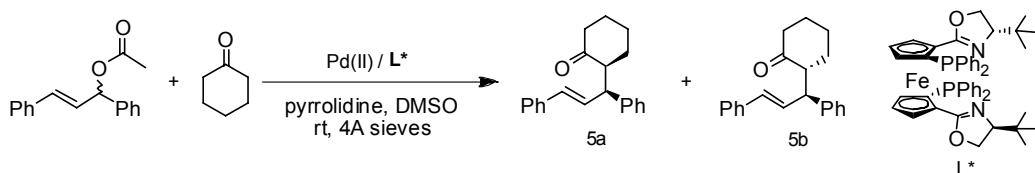
All reactions were performed under a nitrogen atmosphere, and the workup was carried out in air. The reaction solvents were distilled prior to use (Tetrahydrofuran was distilled from sodium-benzophenone ketyl. Dichloromethane, *N,N*-dimethylformamide and toluene were distilled from CaH₂). The commercially available reagents were used without further purification. The substrate of asymmetric allylic alkylation was prepared according to literature procedure.¹ TLC was run on 2 cm × 5 cm silica plate. Column chromatography was run on silica gel (100-200 mesh). ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were recorded on a Varian MERCURY plus-400 spectrometer. The ee values were determined by HPLC using Daicel Chiralcel AD-H, OD-H, OJ-H column.

2. Synthesis and Characterization Data.

General procedure for palladium-catalyzed asymmetric allylic alkylation.

A mixture of ligand (for **1** and **2** 7.5 μmol; for **3** and **4** 15 μmol) and [Pd(*η*³-C₃H₅)Cl]₂ (2.3 mg, 6.3 μmol) in dry DMSO (1 mL) was stirred at room temperature under N₂ atmosphere for 1 h and 1,3-diphenyl-2-propenyl acetate (126 mg, 0.500 mmol) was added for another 10 min followed by the addition of pyrrolidine (0.50 mmol) and ketone or aldehyde (1.50 mmol). The reaction was monitored by TLC for the disappearance of 1,3-diphenyl-2-propenyl acetate. The reaction mixture was quenched by iced saturated NH₄Cl solution (10 mL) for 2 h and the aqueous layer was extracted with ethyl ether (5 mL×3). The combined organic extracts were washed with water, brine, dried over Na₂SO₄ and concentrated under reduced pressure after filtration. The ratio of *anti* and *syn*-configuration was determined by ¹H NMR of the mixture and the residue was purified on silica gel column chromatography with petrol ether-ethyl acetate (10:1) to afford pure product of *anti*-configuration and *syn*-configuration, respectively. For the determination of ee value by HPLC, a mixture of the products of *anti* and *syn*-configuration was used.

Table 1. Allylic Alkylation of 1,3-Diphenyl-2-Propenyl Acetate of Cyclohexane^a



Entry	Time / h	Yield / % ^b	Anti / Syn ^{c,d}	Ee / % ^e
1	16	95	63 / 37	98 / 97

^a Molecular ratio: [Pd(*η*³-C₃H₅)Cl]₂/ligand/substrate/pyrrolidine/ketone = 5.0/6.0/200/200/600; Reactions were conducted under nitrogen; The catalysts were prepared by treating [Pd(*η*³-C₃H₅)Cl]₂ with ligands in a suitable solvent at 20 °C for 1 h before use. ^b Isolated yield. ^c Determined by ¹H NMR. ^d The absolute configuration of *syn* / *anti*-products was determined according to ref. 2. ^e Determined by the HPLC using chiral AD-H column.

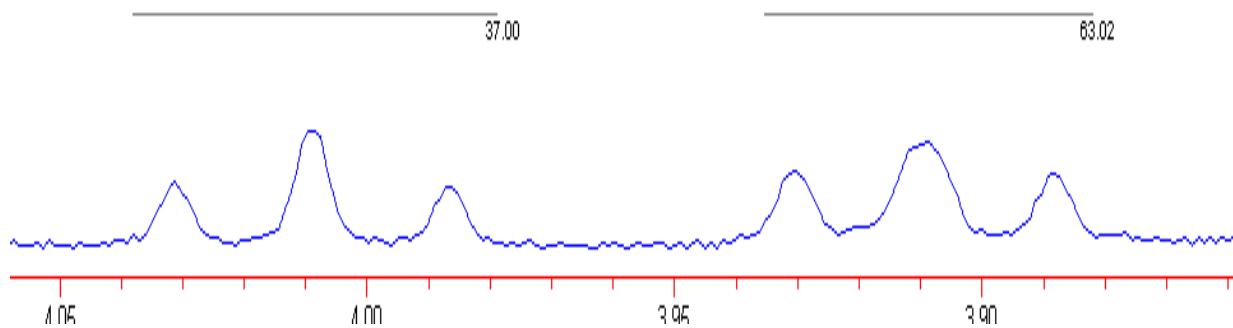
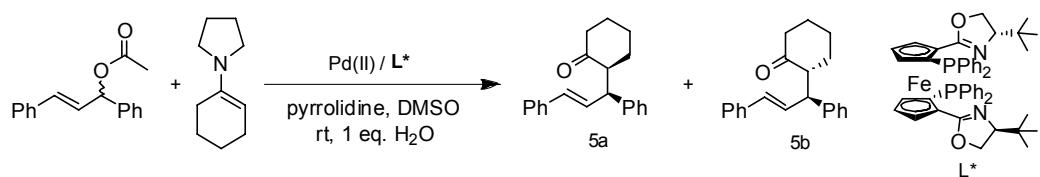


Table 2. Allylic Alkylation of 1,3-Diphenyl-2-Propenyl Acetate of Enamine^a



Entry	Time / h	Yield / % ^b	Anti / Syn ^{c,d}	Ee / % ^e
1	12	80	75 / 25	98 / 97

^a Molecular ratio: [Pd($\eta^3\text{-C}_3\text{H}_5$)Cl]₂/ligand/substrate/enamine=2.5/6.0/200/600; Reactions were conducted under nitrogen; The catalysts were prepared by treating [Pd($\eta^3\text{-C}_3\text{H}_5$)Cl]₂ with ligands in a suitable solvent at 20 °C for 1 h before use. ^b Isolated yield. ^c Determined by ¹H NMR. ^d The absolute configuration of syn / anti-products was determined according to ref. 2. ^e Determined by the HPLC using chiral AD-H column.

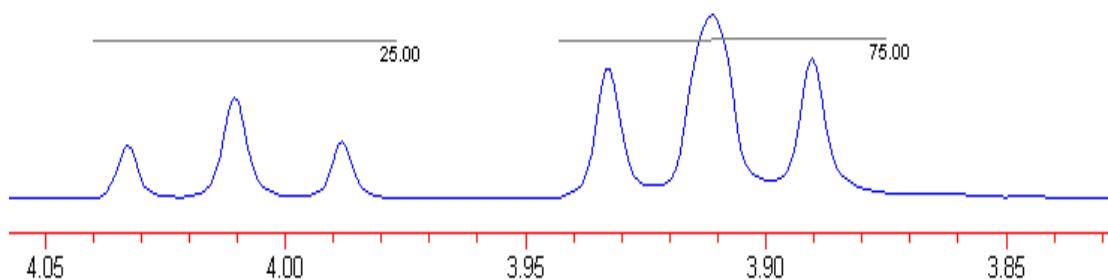


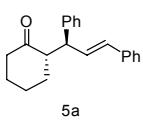
Table 3 ^1H NMR Spectra of Pyrrolidine, Cyclohexanone and Enamine Generated in situ in d_6 -DMSO

¹H NMR spectra

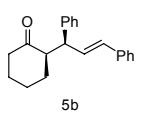
<i>d</i> ₆ -DMSO	
<i>d</i> ₆ -DMSO	
<i>d</i> ₆ -DMSO	
(in situ) ^a	 <img alt="1H NMR spectrum of a mixture of piperazine and cyclohexanone in d6-DMSO, recorded 'in situ'. Peaks are labeled at 1.00, 2.73, 4.19, 4.26, 4.35, 4.32, 4.56, 4.61, 4.64, 4.70, 4.73, 4.76, 4.80, 4.83, 4.86, 4.90, 4.93, 4.96, 5.00, 5.03, 5.06, 5.09, 5.12, 5.15, 5.18, 5.21, 5.24, 5.27, 5.30, 5.33, 5.36, 5.39, 5.42, 5.45, 5.48, 5.51, 5.54, 5.57, 5.60, 5.63, 5.66, 5.69, 5.72, 5.75, 5.78, 5.81, 5.84, 5.87, 5.90, 5.93, 5.96, 5.99, 6.02, 6.05, 6.08, 6.11, 6.14, 6.17, 6.20, 6.23, 6.26, 6.29, 6.32, 6.35, 6.38, 6.41, 6.44, 6.47, 6.50, 6.53, 6.56, 6.59, 6.62, 6.65, 6.68, 6.71, 6.74, 6.77, 6.80, 6.83, 6.86, 6.89, 6.92, 6.95, 6.98, 7.01, 7.04, 7.07, 7.10, 7.13, 7.16, 7.19, 7.22, 7.25, 7.28, 7.31, 7.34, 7.37, 7.40, 7.43, 7.46, 7.49, 7.52, 7.55, 7.58, 7.61, 7.64, 7.67, 7.70, 7.73, 7.76, 7.79, 7.82, 7.85, 7.88, 7.91, 7.94, 7.97, 8.00, 8.03, 8.06, 8.09, 8.12, 8.15, 8.18, 8.21, 8.24, 8.27, 8.30, 8.33, 8.36, 8.39, 8.42, 8.45, 8.48, 8.51, 8.54, 8.57, 8.60, 8.63, 8.66, 8.69, 8.72, 8.75, 8.78, 8.81, 8.84, 8.87, 8.90, 8.93, 8.96, 8.99, 9.02, 9.05, 9.08, 9.11, 9.14, 9.17, 9.20, 9.23, 9.26, 9.29, 9.32, 9.35, 9.38, 9.41, 9.44, 9.47, 9.50, 9.53, 9.56, 9.59, 9.62, 9.65, 9.68, 9.71, 9.74, 9.77, 9.80, 9.83, 9.86, 9.89, 9.92, 9.95, 9.98, 10.01, 10.04, 10.07, 10.10, 10.13, 10.16, 10.19, 10.22, 10.25, 10.28, 10.31, 10.34, 10.37, 10.40, 10.43, 10.46, 10.49, 10.52, 10.55, 10.58, 10.61, 10.64, 10.67, 10.70, 10.73, 10.76, 10.79, 10.82, 10.85, 10.88, 10.91, 10.94, 10.97, 11.00, 11.03, 11.06, 11.09, 11.12, 11.15, 11.18, 11.21, 11.24, 11.27, 11.30, 11.33, 11.36, 11.39, 11.42, 11.45, 11.48, 11.51, 11.54, 11.57, 11.60, 11.63, 11.66, 11.69, 11.72, 11.75, 11.78, 11.81, 11.84, 11.87, 11.90, 11.93, 11.96, 11.99, 12.02, 12.05, 12.08, 12.11, 12.14, 12.17, 12.20, 12.23, 12.26, 12.29, 12.32, 12.35, 12.38, 12.41, 12.44, 12.47, 12.50, 12.53, 12.56, 12.59, 12.62, 12.65, 12.68, 12.71, 12.74, 12.77, 12.80, 12.83, 12.86, 12.89, 12.92, 12.95, 12.98, 13.01, 13.04, 13.07, 13.10, 13.13, 13.16, 13.19, 13.22, 13.25, 13.28, 13.31, 13.34, 13.37, 13.40, 13.43, 13.46, 13.49, 13.52, 13.55, 13.58, 13.61, 13.64, 13.67, 13.70, 13.73, 13.76, 13.79, 13.82, 13.85, 13.88, 13.91, 13.94, 13.97, 14.00, 14.03, 14.06, 14.09, 14.12, 14.15, 14.18, 14.21, 14.24, 14.27, 14.30, 14.33, 14.36, 14.39, 14.42, 14.45, 14.48, 14.51, 14.54, 14.57, 14.60, 14.63, 14.66, 14.69, 14.72, 14.75, 14.78, 14.81, 14.84, 14.87, 14.90, 14.93, 14.96, 14.99, 15.02, 15.05, 15.08, 15.11, 15.14, 15.17, 15.20, 15.23, 15.26, 15.29, 15.32, 15.35, 15.38, 15.41, 15.44, 15.47, 15.50, 15.53, 15.56, 15.59, 15.62, 15.65, 15.68, 15.71, 15.74, 15.77, 15.80, 15.83, 15.86, 15.89, 15.92, 15.95, 15.98, 16.01, 16.04, 16.07, 16.10, 16.13, 16.16, 16.19, 16.22, 16.25, 16.28, 16.31, 16.34, 16.37, 16.40, 16.43, 16.46, 16.49, 16.52, 16.55, 16.58, 16.61, 16.64, 16.67, 16.70, 16.73, 16.76, 16.79, 16.82, 16.85, 16.88, 16.91, 16.94, 16.97, 17.00, 17.03, 17.06, 17.09, 17.12, 17.15, 17.18, 17.21, 17.24, 17.27, 17.30, 17.33, 17.36, 17.39, 17.42, 17.45, 17.48, 17.51, 17.54, 17.57, 17.60, 17.63, 17.66, 17.69, 17.72, 17.75, 17.78, 17.81, 17.84, 17.87, 17.90, 17.93, 17.96, 17.99, 18.02, 18.05, 18.08, 18.11, 18.14, 18.17, 18.20, 18.23, 18.26, 18.29, 18.32, 18.35, 18.38, 18.41, 18.44, 18.47, 18.50, 18.53, 18.56, 18.59, 18.62, 18.65, 18.68, 18.71, 18.74, 18.77, 18.80, 18.83, 18.86, 18.89, 18.92, 18.95, 18.98, 19.01, 19.04, 19.07, 19.10, 19.13, 19.16, 19.19, 19.22, 19.25, 19.28, 19.31, 19.34, 19.37, 19.40, 19.43, 19.46, 19.49, 19.52, 19.55, 19.58, 19.61, 19.64, 19.67, 19.70, 19.73, 19.76, 19.79, 19.82, 19.85, 19.88, 19.91, 19.94, 19.97, 20.00, 20.03, 20.06, 20.09, 20.12, 20.15, 20.18, 20.21, 20.24, 20.27, 20.30, 20.33, 20.36, 20.39, 20.42, 20.45, 20.48, 20.51, 20.54, 20.57, 20.60, 20.63, 20.66, 20.69, 20.72, 20.75, 20.78, 20.81, 20.84, 20.87, 20.90, 20.93, 20.96, 20.99, 21.02, 21.05, 21.08, 21.11, 21.14, 21.17, 21.20, 21.23, 21.26, 21.29, 21.32, 21.35, 21.38, 21.41, 21.44, 21.47, 21.50, 21.53, 21.56, 21.59, 21.62, 21.65, 21.68, 21.71, 21.74, 21.77, 21.80, 21.83, 21.86, 21.89, 21.92, 21.95, 21.98, 22.01, 22.04, 22.07, 22.10, 22.13, 22.16, 22.19, 22.22, 22.25, 22.28, 22.31, 22.34, 22.37, 22.40, 22.43, 22.46, 22.49, 22.52, 22.55, 22.58, 22.61, 22.64, 22.67, 22.70, 22.73, 22.76, 22.79, 22.82, 22.85, 22.88, 22.91, 22.94, 22.97, 23.00, 23.03, 23.06, 23.09, 23.12, 23.15, 23.18, 23.21, 23.24, 23.27, 23.30, 23.33, 23.36, 23.39, 23.42, 23.45, 23.48, 23.51, 23.54, 23.57, 23.60, 23.63, 23.66, 23.69, 23.72, 23.75, 23.78, 23.81, 23.84, 23.87, 23.90, 23.93, 23.96, 23.99, 24.02, 24.05, 24.08, 24.11, 24.14, 24.17, 24.20, 24.23, 24.26, 24.29, 24.32, 24.35, 24.38, 24.41, 24.44, 24.47, 24.50, 24.53, 24.56, 24.59, 24.62, 24.65, 24.68, 24.71, 24.74, 24.77, 24.80, 24.83, 24.86, 24.89, 24.92, 24.95, 24.98, 25.01, 25.04, 25.07, 25.10, 25.13, 25.16, 25.19, 25.22, 25.25, 25.28, 25.31, 25.34, 25.37, 25.40, 25.43, 25.46, 25.49, 25.52, 25.55, 25.58, 25.61, 25.64, 25.67, 25.70, 25.73, 25.76, 25.79, 25.82, 25.85, 25.88, 25.91, 25.94, 25.97, 26.00, 26.03, 26.06, 26.09, 26.12, 26.15, 26.18, 26.21, 26.24, 26.27, 26.30, 26.33, 26.36, 26.39, 26.42, 26.45, 26.48, 26.51, 26.54, 26.57, 26.60, 26.63, 26.66, 26.69, 26.72, 26.75, 26.78, 26.81, 26.84, 26.87, 26.90, 26.93, 26.96, 26.99, 27.02, 27.05, 27.08, 27.11, 27.14, 27.17, 27.20, 27.23, 27.26, 27.29, 27.32, 27.35, 27.38, 27.41, 27.44, 27.47, 27.50, 27.53, 27.56, 27.59, 27.62, 27.65, 27.68, 27.71, 27.74, 27.77, 27.80, 27.83, 27.86, 27.89, 27.92, 27.95, 27.98, 28.01, 28.04, 28.07, 28.10, 28.13, 28.16, 28.19, 28.22, 28.25, 28.28, 28.31, 28.34, 28.37, 28.40, 28.43, 28.46, 28.49, 28.52, 28.55, 28.58, 28.61, 28.64, 28.67, 28.70, 28.73, 28.76, 28.79, 28.82, 28.85, 28.88, 28.91, 28.94, 28.97, 29.00, 29.03, 29.06, 29.09, 29.12, 29.15, 29.18, 29.21, 29.24, 29.27, 29.30, 29.33, 29.36, 29.39, 29.42, 29.45, 29.48, 29.51, 29.54, 29.57, 29.60, 29.63, 29.66, 29.69, 29.72, 29.75, 29.78, 29.81, 29.84, 29.87, 29.90, 29.93, 29.96, 29.99, 30.02, 30.05, 30.08, 30.11, 30.14, 30.17, 30.20, 30.23, 30.26, 30.29, 30.32, 30.35, 30.38, 30.41, 30.44, 30.47, 30.50, 30.53, 30.56, 30.59, 30.62, 30.65, 30.68, 30.71, 30.74, 30.77, 30.80, 30.83, 30.86, 30.89, 30.92, 30.95, 30.98, 31.01, 31.04, 31.07, 31.10, 31.13, 31.16, 31.19, 31.22, 31.25, 31.28, 31.31, 31.34, 31.37, 31.40, 31.43, 31.46, 31.49, 31.52, 31.55, 31.58, 31.61, 31.64, 31.67, 31.70, 31.73, 31.76, 31.79, 31.82, 31.85, 31.88, 31.91, 31.94, 31.97, 32.00, 32.03, 32.06, 32.09, 32.12, 32.15, 32.18, 32.21, 32.24, 32.27, 32.30, 32.33, 32.36, 32.39, 32.42, 32.45, 32.48, 32.51, 32.54, 32.57, 32.60, 32.63, 32.66, 32.69, 32.72, 32.75, 32.78, 32.81, 32.84, 32.87, 32.90, 32.93, 32.96, 32.99, 33.02, 33.05, 33.08, 33.11, 33.14, 33.17, 33.20, 33.23, 33.26, 33.29, 33.32, 33.35, 33.38, 33.41, 33.44, 33.47, 33.50, 33.53, 33.56, 33.59, 33.62, 33.65, 33.68, 33.71, 33.74, 33.77, 33.80, 33.83, 33.86, 33.89, 33.92, 33.95, 33.98, 34.01, 34.04, 34.07, 34.10, 34.13, 34.16, 34.19, 34.22, 34.25, 34.28, 34.31, 34.34, 34.37, 34.40, 34.43, 34.46, 34.49, 34.52, 34.55, 34.58, 34.61, 34.64, 34.67, 34.70, 34.73, 34.76, 34.79, 34.82, 34.85, 34.88, 34.91, 34.94, 34.97, 35.00, 35.03, 35.06, 35.09, 35.12, 35.15, 35.18, 35.21, 35.24, 35.27, 35.30, 35.33, 35.36, 35.39, 35.42, 35.45, 35.48, 35.51, 35.54, 35.57, 35.60, 35.63, 35.66, 35.69, 35.72, 35.75, 35.78, 35.81, 35.84, 35.87, 35.90, 35.93, 35.96, 35.99, 36.02, 36.05, 36.08, 36.11, 36.14, 36.17, 36.20, 36.23, 36.26, 36.29, 36.32, 36.35, 36.38, 36.41, 36.44, 36.47, 36.50, 36.53, 36.56, 36.59, 36.62, 36.65, 36.68, 36.71, 36.74, 36.77, 36.80, 36.83, 36.86, 36.89, 36.92, 36.95, 36.98, 37.01, 37.04, 37.07, 37.10, 37.13, 37.16, 37.19, 37.22, 37.25, 37.28, 37.31, 37.34, 37.37, 37.40, 37.43, 37.46, 37.49, 37.52, 37.55, 37.58, 37.61, 37.64, 37.67, 37.70, 37.73, 37.76, 37.79, 37.82, 37.85, 37.88, 37.91, 37.94, 37.97, 38.00, 38.03, 38.06, 38.09, 38.12, 38.15, 38.18, 38.21, 38.24, 38.27, 38.30, 38.33, 38.36, 38.39, 38.42, 38.45, 38.48, 38.51, 38.54, 38.57, 38.60, 38.63, 38.66, 38.69, 38.72, 38.75, 38.78, 38.81, 38.84, 38.87, 38.90, 38.93, 38.96, 38.99, 39.02, 39.05, 39.08, 39.11, 39.14, 39.17, 39.20, 39.23, 39.26, 39.29, 39.32, 39.35, 39.38, 39.41, 39.44, 39.47, 39.50, 39.53, 39.56, 39.59, 39.62, 39.65, 39.68, 39.71, 39.74, 39.77, 39.80, 39.83, 39.86, 39.89, 39.92, 39.95, 39.98, 40.01, 40.04, 40.07, 40.10, 40.13, 40.16, 40.19, 40.22, 40.25, 40.28, 40.31, 40.34, 40.37, 40.40, 40.43, 40.46, 40.49, 40.52, 40.55, 40.58, 40.61, 40.64, 40.67, 40.70, 40.73, 40.76, 40.79, 40.82, 40.85, 40.88, 40.91, 40.94, 40.97, 41.00, 41.03, 41.06, 41.09, 41.12, 41.15, 41.18, 41.21, 41.24, 41.27, 41.30, 41.33, 41.36, 41.39, 41.42, 41.45, 41.48, 41.51, 41.54, 41.57, 41.60, 41.63, 41.66, 41.69, 41.72, 41.75, 41.78, 41.81, 41.84, 41.87, 41.90, 41.93, 41.96, 41.99, 42.02, 42.05, 42.08, 42.11, 42.14, 42.17, 42.20, 42.23, 42.26, 42.29, 42.32, 42.35, 42.38, 42.41, 42.44, 42.47, 42.50, 42.53, 42.56, 42.59, 42.62, 42.65, 42.68, 42.71, 42.74, 42.77, 42.80, 42.83, 42.86, 42.89, 42.92, 42.95, 42.98, 43.01, 43.04, 43.07, 43.10, 43.13, 43.16, 43.19, 43.22, 43.25, 43.28, 43.31, 43.34, 43.37, 43.40, 43.43, 43.46, 43.49, 43.52, 43.55, 43.58, 43.61, 43.64, 43.67, 43.70, 43.73, 43.76, 43.79, 43.82, 43.85, 43.88, 43.91, 43.94, 43.97, 44.00, 44.03, 44.06, 44.09, 44.12, 44.15, 44.18, 44.21, 44.24, 44.27, 44.30, 44.33, 44.36, 44.39, 44.42, 44.45, 44.48, 44.51, 44.54, 44.57, 44.60, 44.63, 44.66, 44.69, 44.72, 44.75, 44.78, 44.81, 44.84, 44.87, 44.90, 44.93, 44.96, 44.99, 45.02, 45.05, 45.08, 45.11, 45.14, 45.17, 45.20, 45.23, 45.26, 45.29, 45.32, 45.35, 45.38, 45.41, 45.44, 45.47, 45.50, 45.53, 45.56, 45.59, 45.62, 45.65, 45.68, 45.71, 45.74, 45.77, 45.80, 45.83, 45.86, 45.89, 45.92, 45.95, 45.98, 46.01, 46.04, 46.07, 46.10, 46.13, 46.16, 46.19, 46.22, 46.25, 46.28, 46.31, 46.34, 46.37, 46.40, 46.43, 46.46, 46.49, 46.52, 46.55, 46.58, 46.61, 46.64, 46.67, 46.70, 46.73, 46.76, 46.79, 46.82, 46.85, 46.88, 46.91, 46.94, 46.97, 47.00, 47.03, 47.06, 47.09, 47.12, 47.15, 47.18, 47.21, 47.24, 47.27, 47.30, 47.33, 47.36, 47.39, 47.42, 47.45, 47.48, 47.51, 47.54, 47.57, 47.60, 47.63, 47.66, 47.69, 47.72, 47.75, 47.78, 47.81, 47.84, 47.87, 47.90, 47.93, 47.96, 47.99, 48.02, 48.05, 48.08, 48.11, 48.14, 48.17, 48.20, 48.23, 48.26, 48.29, 48.32, 48.35, 48.38, 48.41, 48.44, 48.47, 48.50, 48.53, 48.56, 48.59, 48.62, 48.65, 48.68, 48.71, 48.74, 48.77, 48.80, 48.83, 48.86, 48.89, 48.92, 48.95, 48.98, 49.01, 49.04, 49.07, 49.10, 49.13, 49.16, 49.19, 49.22, 49.25, 49.28, 49.31, 49.34, 49.37, 49.40, 49.43, 49.46, 49.49, 49.52, 49.55, 49.58, 49.61, 49.64, 49.67, 49.70, 49.73, 49.76, 49.79, 49.82, 49.85, 49.88, 49.91, 49.94, 49.97, 50.00, 50.03, 50.06, 50.09, 50.12, 50.15, 50.18, 50.21, 50.24, 50.27, 50.30, 50.33, 50.36, 50.39, 50.42, 50.45, 50.48, 50.51, 50.54, 50.57, 50.60, 50.63, 50.66, 50.69, 50.72, 50.75, 50.78, 50.81, 50.84, 50.87, 50.90, 50.93, 50.96, 50.99, 51.02, 51.05, 51.08, 51.11, 51.14, 51.17, 51.20, 51.23, 51.26, 51.29, 51.32, 51.35, 51.38, 51.41, 51.44, 51.47, 51.50, 51.53, 51.56, 51.59, 51.62, 51.65, 51.68, 51.71, 51.74, 51.77, 51.80, 51.83, 51.86, 51.89, 51.92, 51.95, 51.98, 52.01, 52.04, 52.07, 52.10, 52.13, 52.16, 52.19, 52.22, 52.25, 52.28, 52.31, 52.34, 52.37, 52.40, 52.43, 52.46, 52.49, 52.52, 52.55, 52.58, 52.61, 52.64, 52.67, 52.70, 52.73, 52.76, 52.79, 52.82, 52.85, 52.88, 52.91, 52.94, 52.97, 53.00, 53.03, 53.06, 53.09, 53.12, 53.15, 53.18, 53.21, 53.24, 53.27, 53.30, 53.33, 53.36, 53.39, 53.42, 53.45, 53.48, 53.51, 53.54, 53.57, 53.60, 53.63, 53.66, 53.69, 53.72, 53.75, 53.78, 53.81, 53.84, 53.87, 53.90, 53.93, 53.96, 53.99, 54.02, 54.05, 54.08, 54.11, 54.14, 54.17, 54.20, 54.23, 54.26, 54.29, 54.32, 54.35, 54.38, 54.41, 54.44, 54.47, 54.50, 54.53, 54.56, 54.59, 54.62, 54.65, 54.68, 54.71, 54.74, 54.77, 54.80, 54.83, 54.86, 54.89, 54.92, 54.95, 54.98, 55.01, 55.04, 55.07, 55.10, 55.13, 55.16, 55.19, 55.22, 55.25, 55.28, 55.31, 55.34, 55.37, 55.40, 55.43, 55.46, 55.49, 55.52, 55.55, 55.58, 55.61, 55.64, 55.67, 55.70, 55.73, 55.76, 55.79, 55.82, 55.85, 55.88, 55.91, 55.94, 55.97, 55.10, 55.13, 55.16, 55.19, 55.22, 55.25, 55.28, 55.31, 55.34, 55.37, 55.40, 55.43, 55.46, 55.49, 55.52, 55.55, 55.58, 55.61, 55.64, 55.67, 55.70, 5

^a Pyrrolidine (0.020 ml, 1 equiv.) and cyclohexanone (0.026 ml, 1 equiv.) were added to NMR tube in d^6 -DMSO, a set of new peaks appeared after 10 minutes, which attributed to the formation of enamine. 1H NMR (d^6 -DMSO, 400 Hz): δ 1.70-1.78 (m, 4H), 1.94-2.11 (m, 4H), 2.61-2.69 (m, 1H), 2.84-2.95 (m, 4H), 3.17-3.35 (m, 3H), 4.05-4.11 (m, 1H).

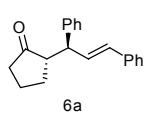
(S)-2-((S,E)-1,3-diphenylallyl)cyclohexanone (5a**)**


5a Colorless oil. ^1H NMR (CDCl_3 , 400 Hz): δ 1.33-1.41 (m, 1H), 1.56-1.63 (m, 1H), 1.70-1.81 (m, 3H), 1.90-1.95 (m, 1H), 2.31-2.46 (m, 2H), 2.83-2.89 (m, 1H), 3.87 (t, $J=8.4$ Hz, 1H), 6.32 (d, $J=16$ Hz, 1H), 6.44 (dd, $J=8.0, 16$ Hz, 1H), 7.12-7.32 (m, 10H). ^{13}C NMR (CDCl_3 , 100 Hz): δ 24.2, 28.8, 32.4, 42.5, 48.6, 56.1, 126.5, 126.8, 127.4, 128.6, 128.7, 128.9, 130.7, 132.2, 137.6, 140.1, 212.7.

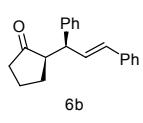
(R)-2-((S,E)-1,3-diphenylallyl)cyclohexanone (5b**)**


5b Colorless oil. ^1H NMR (CDCl_3 , 400 Hz): δ 1.57-1.77 (m, 3H), 1.86-2.10 (m, 2H), 2.15-2.37 (m, 3H), 2.85-2.91 (m, 1H), 3.97 (t, $J=8.4$ Hz, 1H), 6.25 (dd, $J=9.6, 15.6$ Hz, 1H), 6.45 (d, $J=15.6$ Hz, 1H), 7.14-7.33 (m, 10H). ^{13}C NMR (CDCl_3 , 100 Hz): δ 24.8, 28.6, 32.1, 42.6, 48.7, 55.9, 126.5, 126.6, 127.5, 128.1, 128.7, 128.8, 131.3, 131.6, 137.5, 143.5, 211.8.

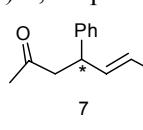
(S)-2-((R,E)-1,3-diphenylallyl)cyclopentanone (6a**)**


6a Colorless oil. ^1H NMR (CDCl_3 , 400 Hz): δ 1.70-1.78 (m, 1H), 1.93-2.03 (m, 3H), 2.16-2.23 (m, 1H), 2.27-2.34 (m, 1H), 2.55-2.61 (m, 1H), 4.09-4.12 (m, 1H), 6.40 (d, $J=4.4$ Hz, 1H), 6.41 (s, 1H), 7.17-7.35 (m, 10H). ^{13}C NMR (CDCl_3 , 100 Hz): δ 20.9, 26.1, 39.1, 48.0, 55.1, 126.5, 126.7, 127.6, 128.1, 128.7, 128.8, 129.3, 132.6, 137.4, 143.0, 219.3.

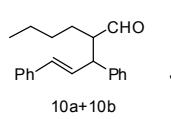
(R)-2-((R,E)-1,3-diphenylallyl)cyclopentanone (6b**)**


6b Colorless oil. ^1H NMR (CDCl_3 , 400 Hz): δ 1.70-1.86 (m, 1H), 1.94-2.11 (m, 3H), 2.18-2.28 (m, 1H), 2.29-2.38 (m, 1H), 2.58-2.64 (m, 1H), 4.05-4.10 (m, 1H), 6.44 (d, $J=3.2$ Hz, 1H), 6.45 (s, 1H), 7.20-7.41 (m, 10H). ^{13}C NMR (CDCl_3 , 100 Hz): δ 21.0, 26.1, 39.1, 48.0, 55.1, 126.4, 126.6, 128.7, 129.2, 129.3, 132.5, 132.6, 132.7, 137.4, 143.1, 219.3.

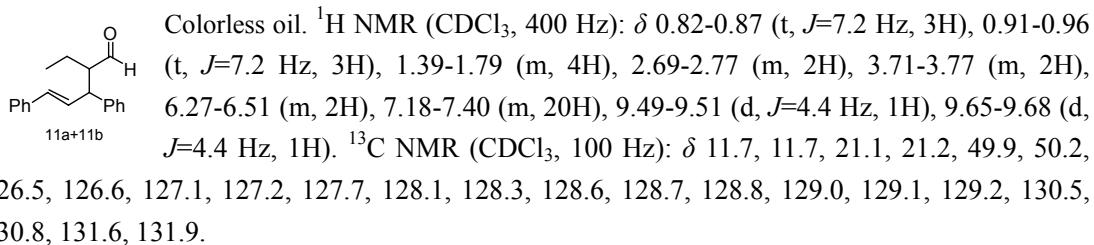
(E)-4,6-diphenylhex-5-en-2-one (7**)**


7 Colorless oil. ^1H NMR (CDCl_3 , 400 Hz): δ 2.11 (s, 3H), 2.93-2.97 (m, 2H), 4.05-4.12 (dd, $J=6.8, 7.2$ Hz, 1H), 6.28-6.41 (m, 2H), 7.17-7.36 (m, 10H). ^{13}C NMR (CDCl_3 , 100 Hz): δ 21.0, 26.1, 39.1, 48.0, 55.1, 126.4, 126.6, 128.7, 129.2, 129.3, 132.5, 132.6, 132.7, 137.4, 143.1, 219.3.

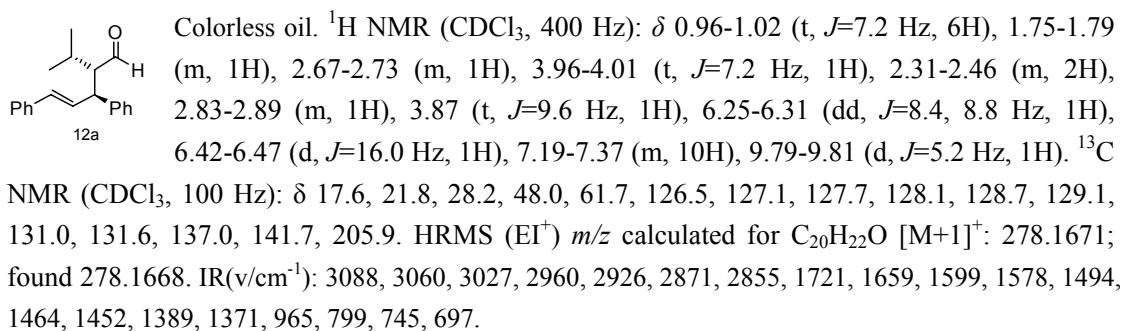
(E)-2-(1,3-diphenylallyl)hexanal (10a** and **10b**)**


10a+10b Colorless oil. ^1H NMR (CDCl_3 , 400 Hz): δ 0.77-0.81 (t, $J=9.6$ Hz, 3H), 0.83-0.88 (t, $J=9.6$ Hz, 3H), 1.11-1.38 (m, 8H), 1.47-1.72 (m, 4H), 2.72-2.82 (m, 2H), 3.67-3.77 (m, 2H), 6.25-6.52 (m, 4H), 7.16-7.38 (m, 20H), 9.47-9.50 (d, $J=4.0$ Hz, 1H), 9.62-9.66 (d, $J=4.0$ Hz, 1H). ^{13}C NMR (CDCl_3 , 100 Hz): δ 14.0, 14.1, 22.8, 22.9, 27.6, 27.7, 29.3, 29.5, 50.2, 50.4, 56.6, 56.8, 126.5, 126.6, 127.1, 127.2, 127.7, 128.1, 128.2, 128.7, 128.8, 129.0, 129.1, 130.4, 130.8, 131.6, 131.9, 137.0, 137.1, 141.5, 141.6, 204.6, 204.9. HRMS (EI^+) m/z calculated for $\text{C}_{21}\text{H}_{24}\text{O}$ [$\text{M}+1$] $^+$: 293.1905; found 293.1911. IR(ν/cm^{-1}): 3086, 3063, 3030, 2957, 2929, 2871, 2860, 1724, 1693, 1638, 1603, 1566, 1493, 1455, 1416, 1379, 966, 749, 699.

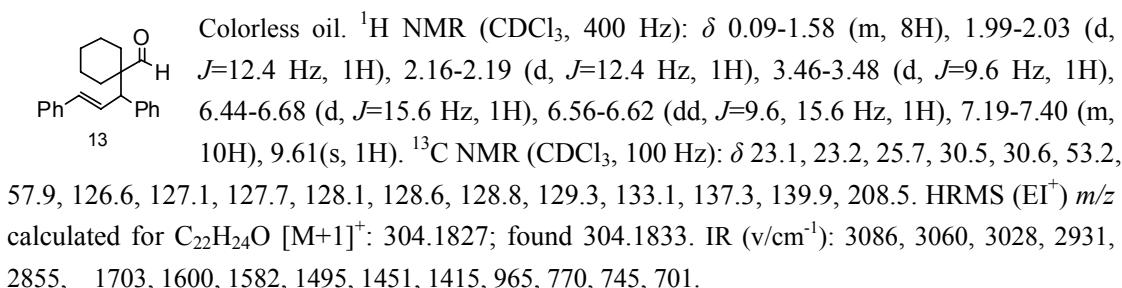
(E)-2-ethyl-3,5-diphenylpent-4-enal (**11a** and **11b**)



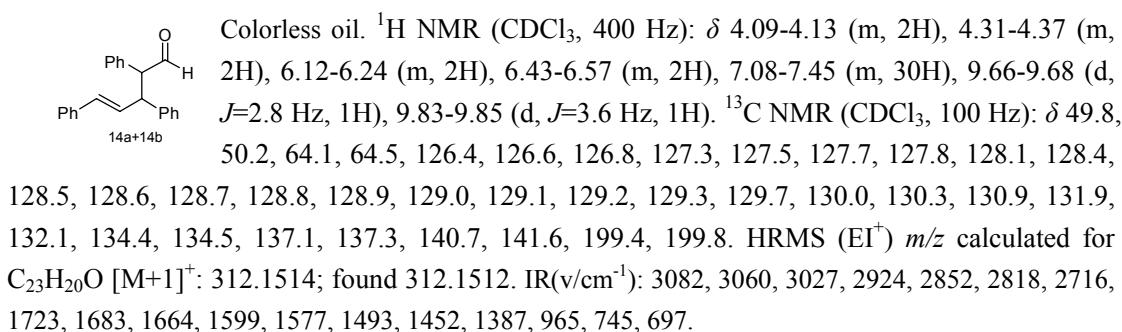
(S)-2-((S,E)-1,3-diphenylallyl)cyclohexanone (**12a**)



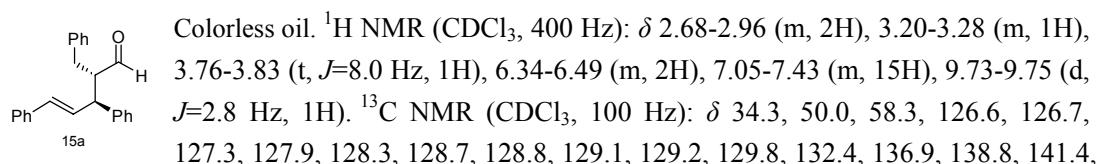
(E)-1-(1,3-diphenylallyl)cyclohexanecarbaldehyde (**13**)



(E)-2,3,5-triphenylpent-4-enal (**14a** and **14b**)



(2*S*,3*R*,*E*)-2-benzyl-3,5-diphenylpent-4-enal (**15a**)

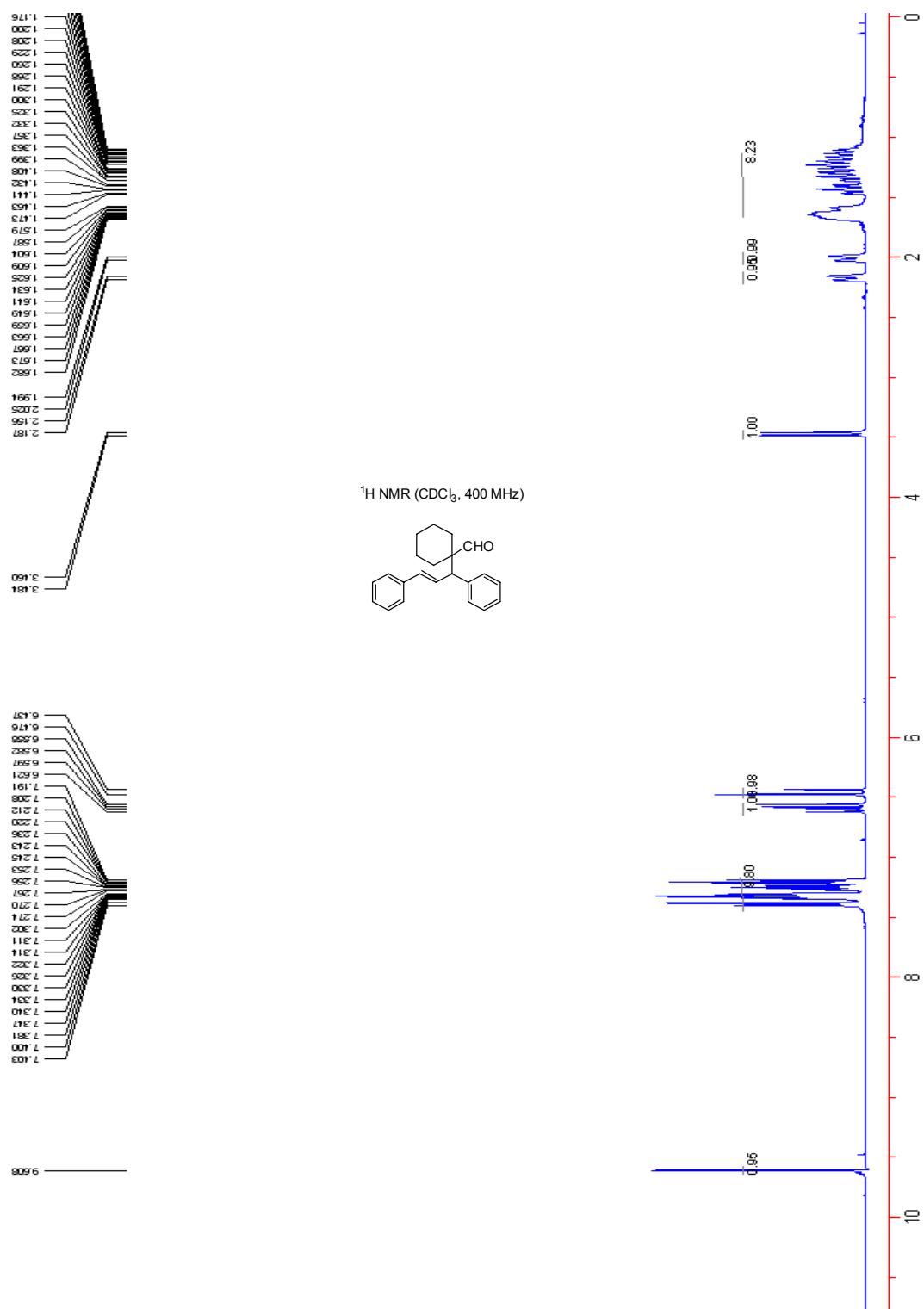


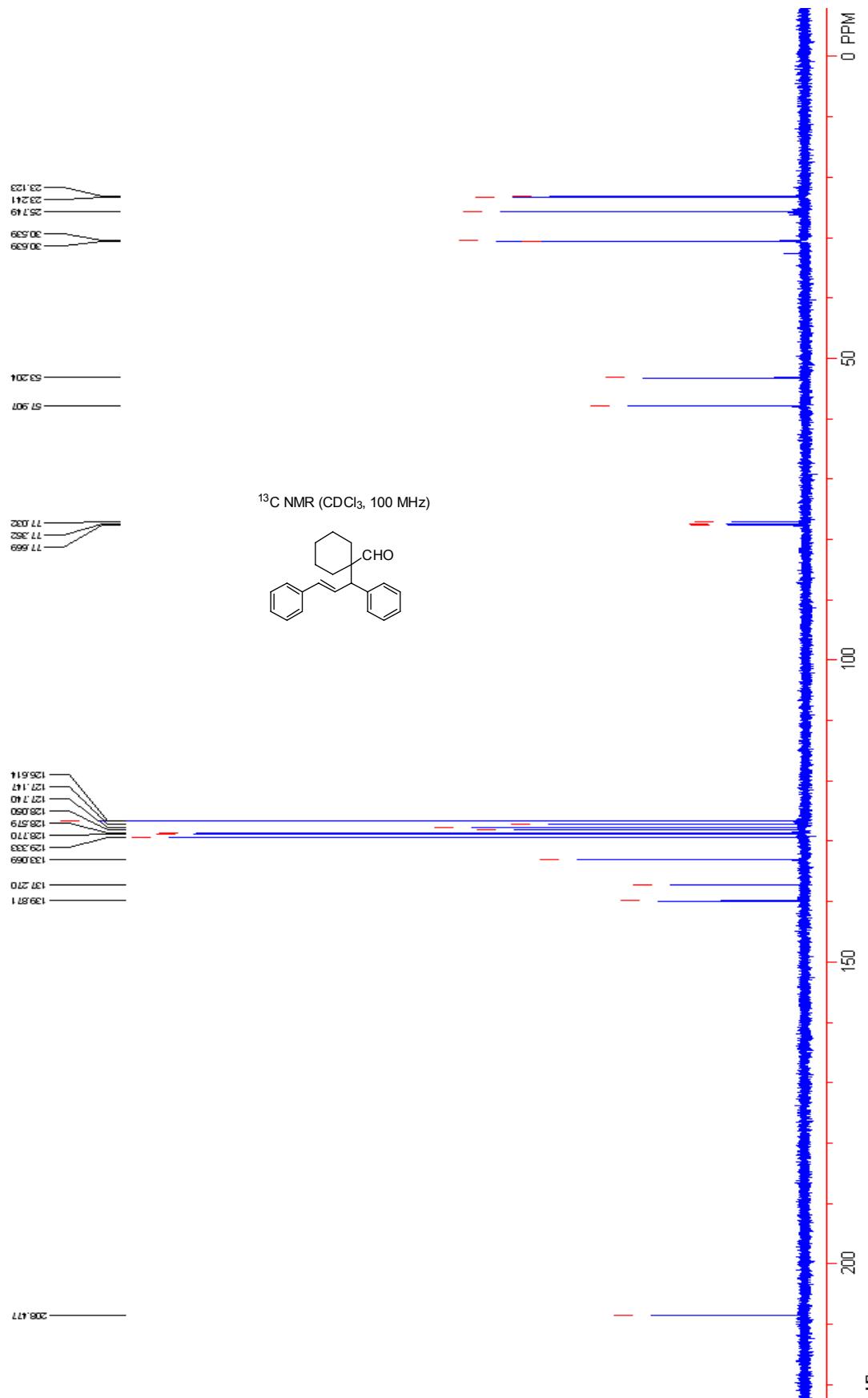
204.4. HRMS (EI⁺) *m/z* calculated for C₂₄H₂₂O [M+1]⁺: 326.1701; found 326.1671. IR(v/cm⁻¹): 3083, 3060, 3027, 2924, 2851, 2724, 1724, 1681, 1600, 1583, 1494, 1453, 1393, 966, 745, 698.

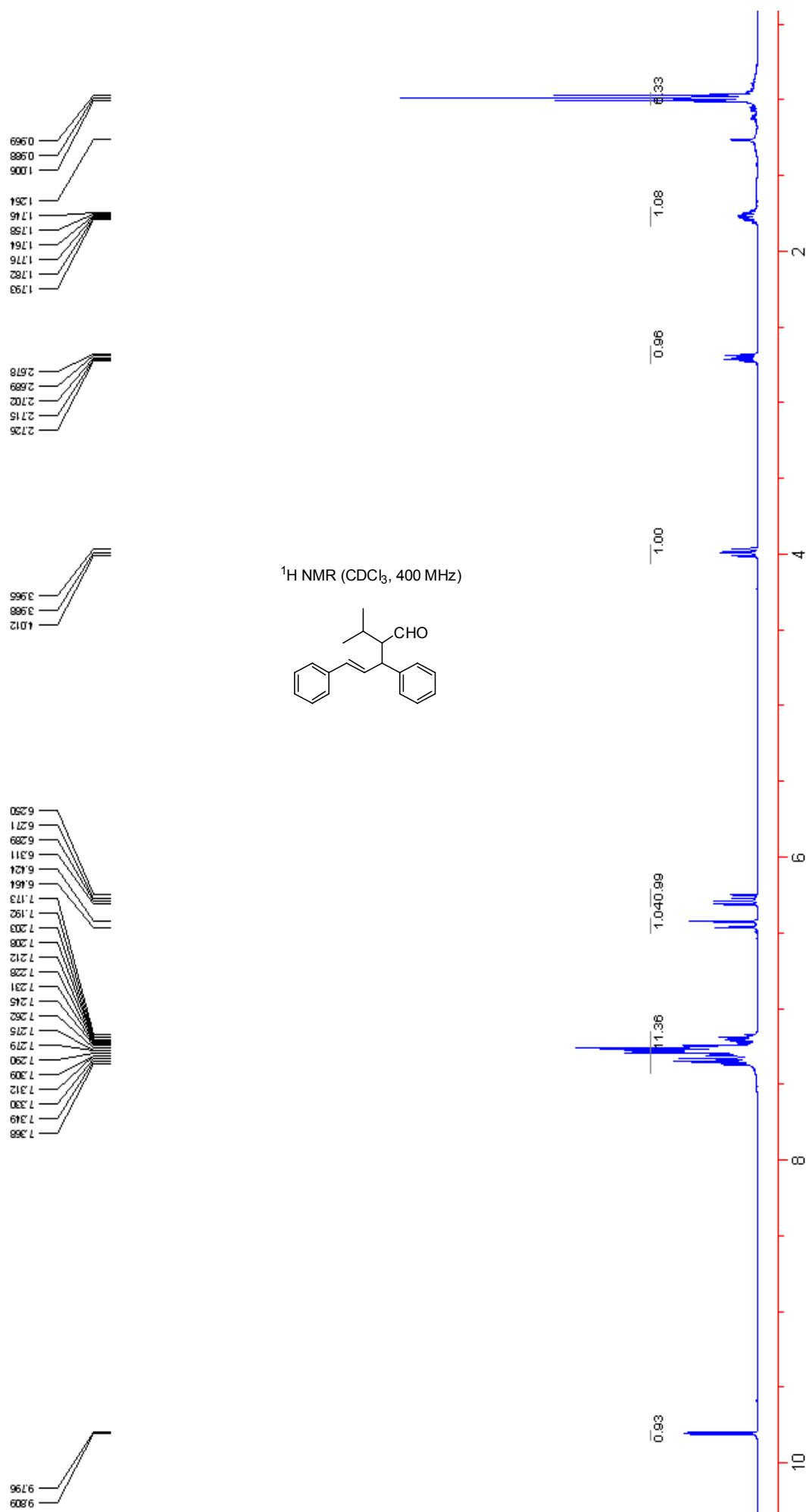
References

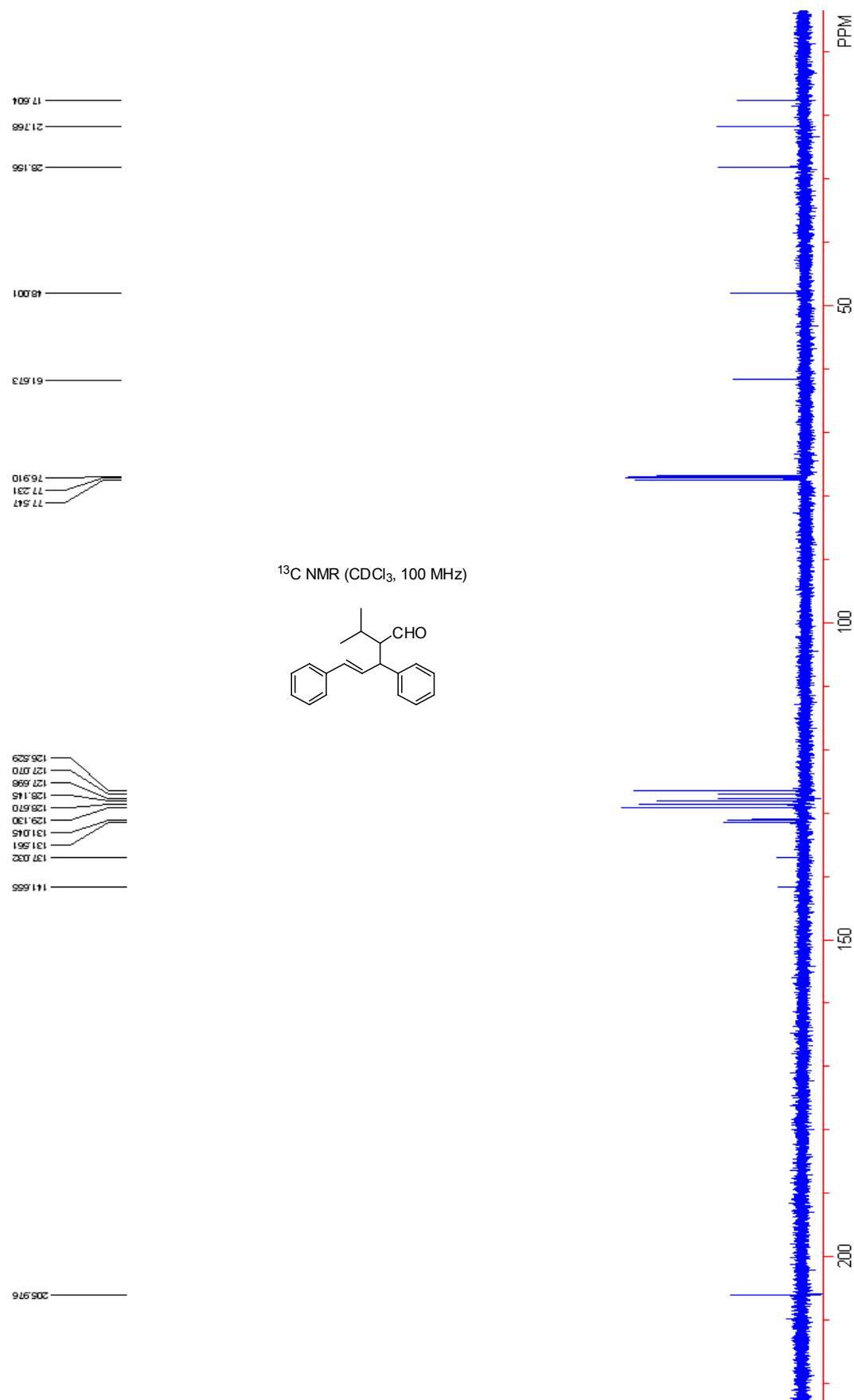
- 1 Watson, L. D. G.; Styler, S. A.; Yudin, A. K. *J. Am. Chem. Soc.* **2004**, *126*, 5086-5087.
- 2 Braun, M.; Laicher, F.; Meier, T. *Angew. Chem., Int. Ed.* **2000**, *39*, 3494-3497.

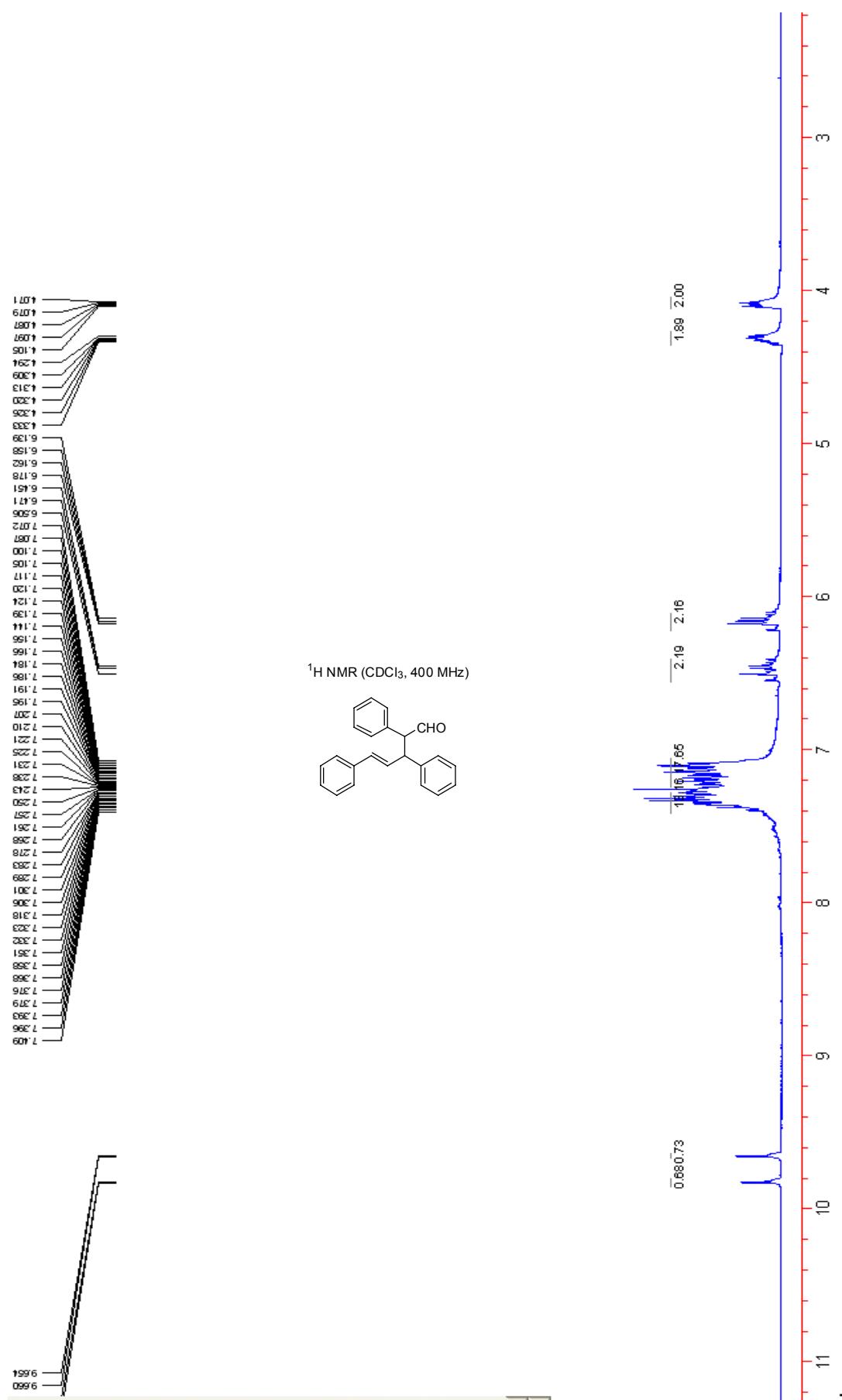
3. Copies of NMR Spectra

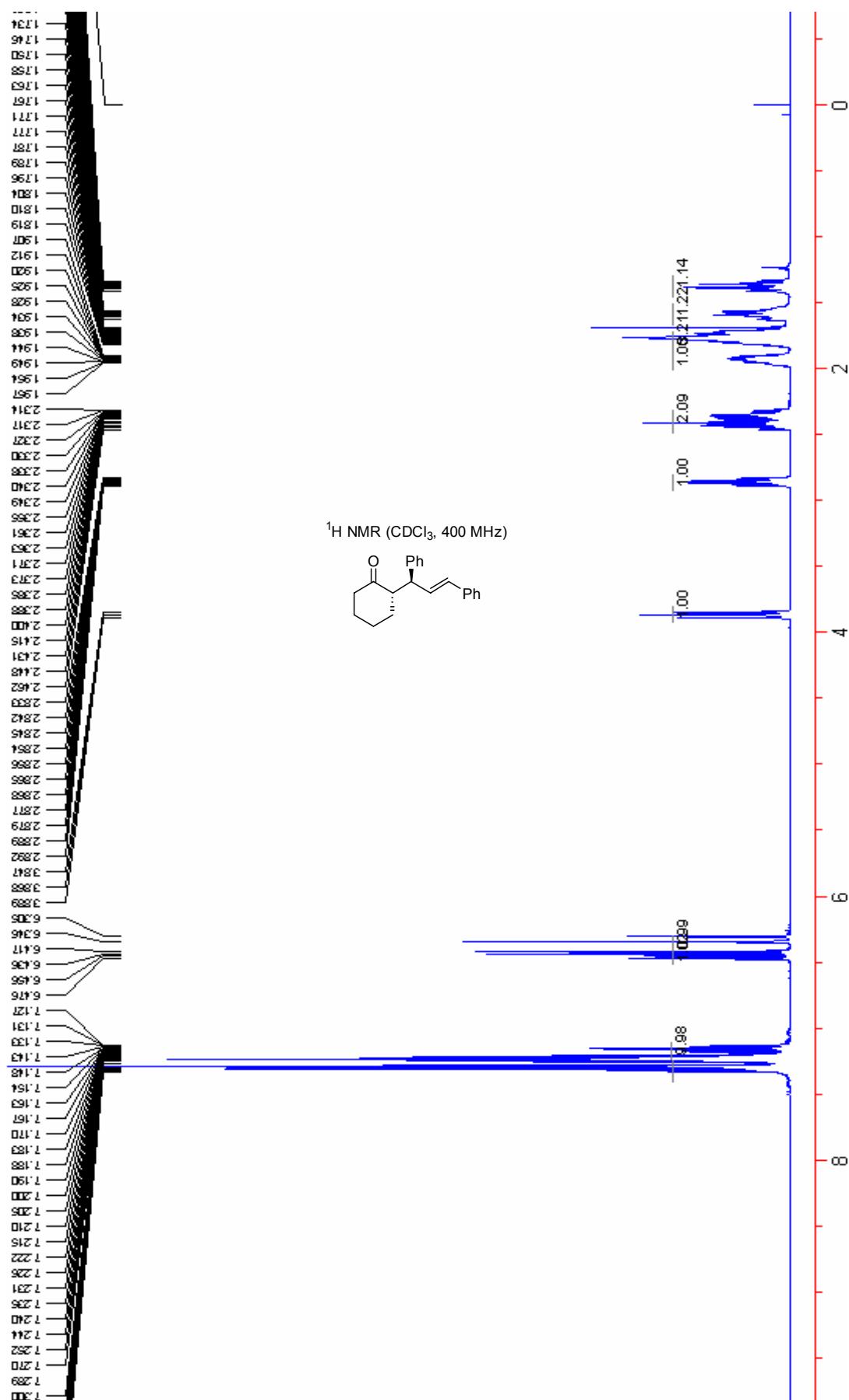


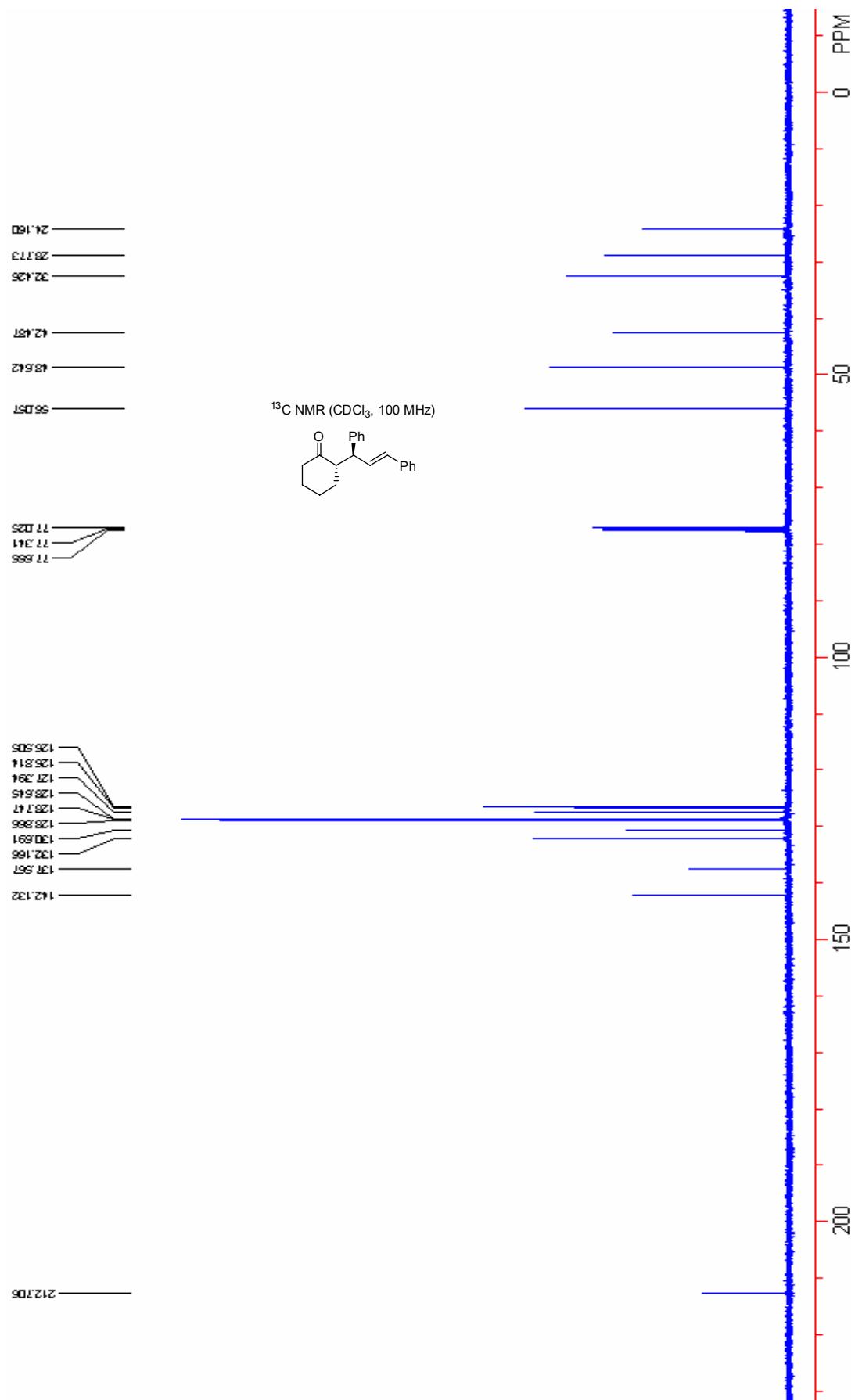


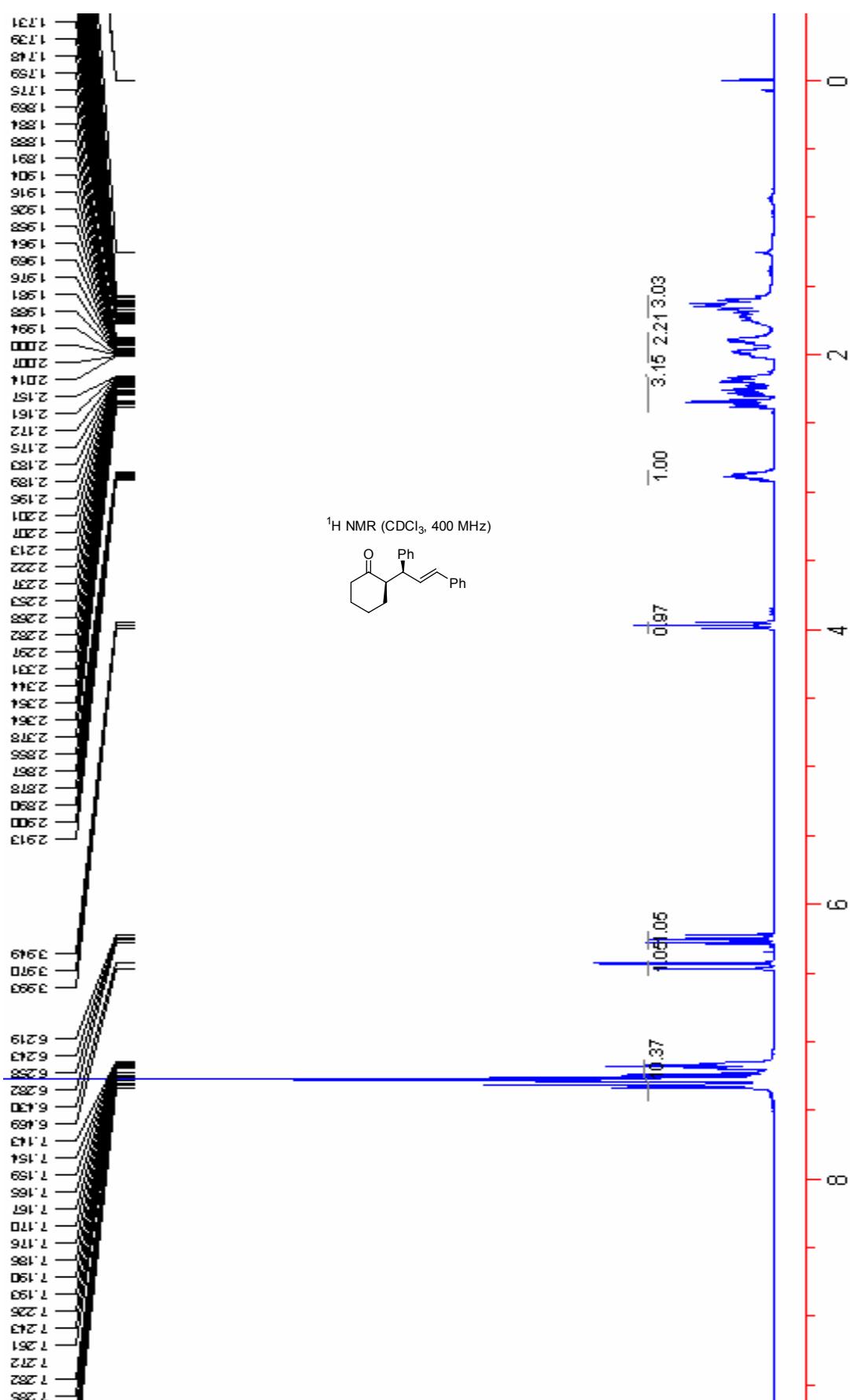


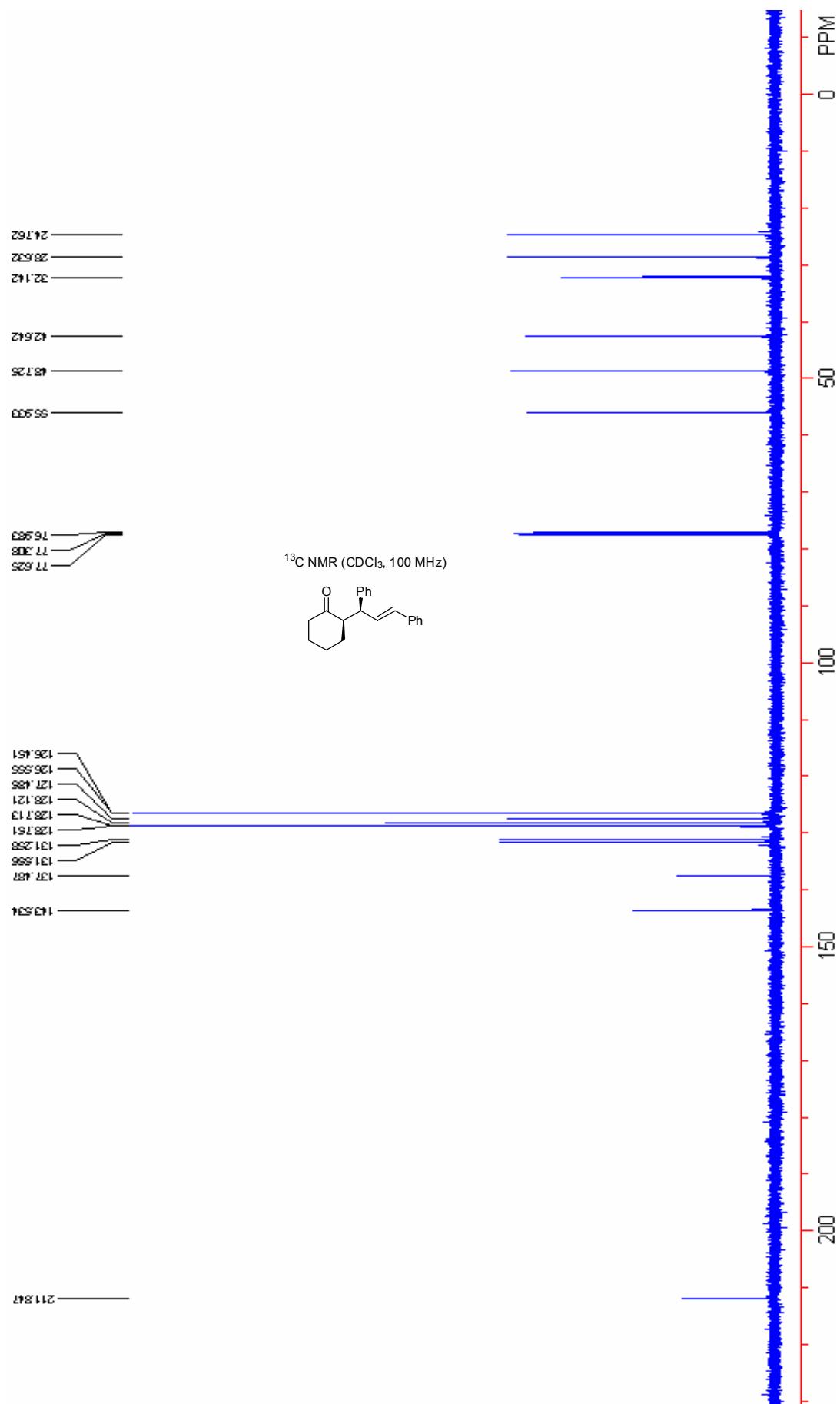


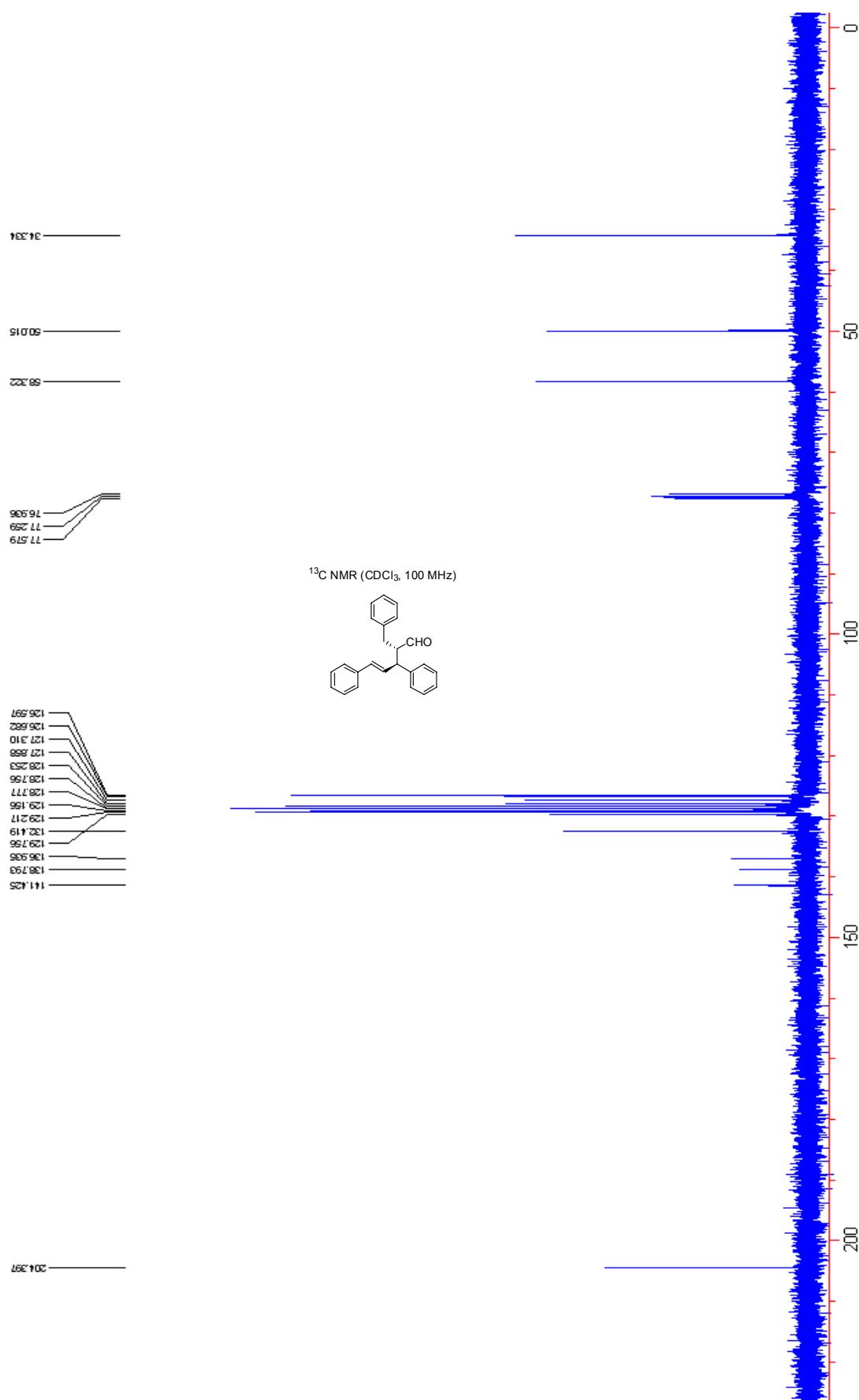


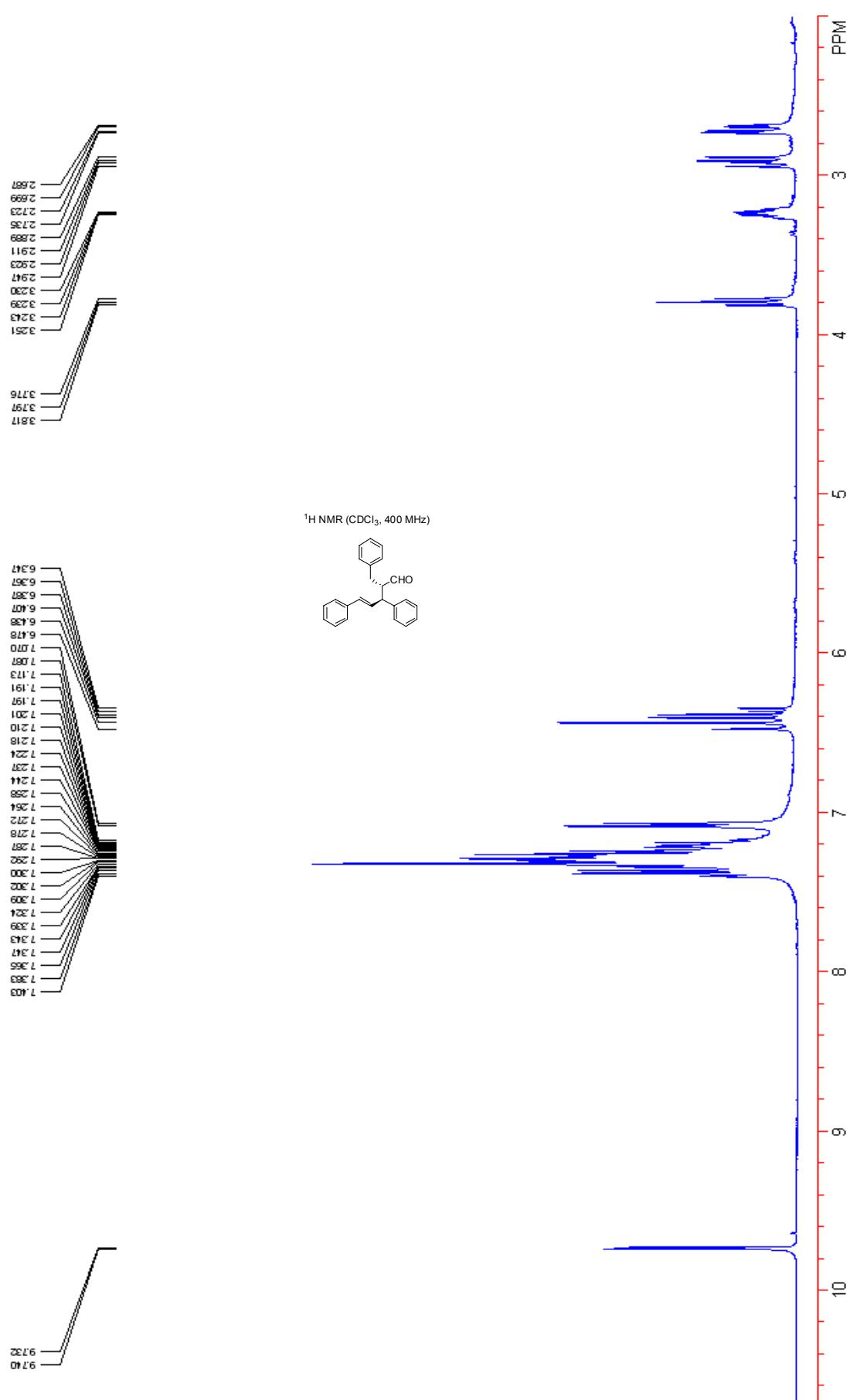


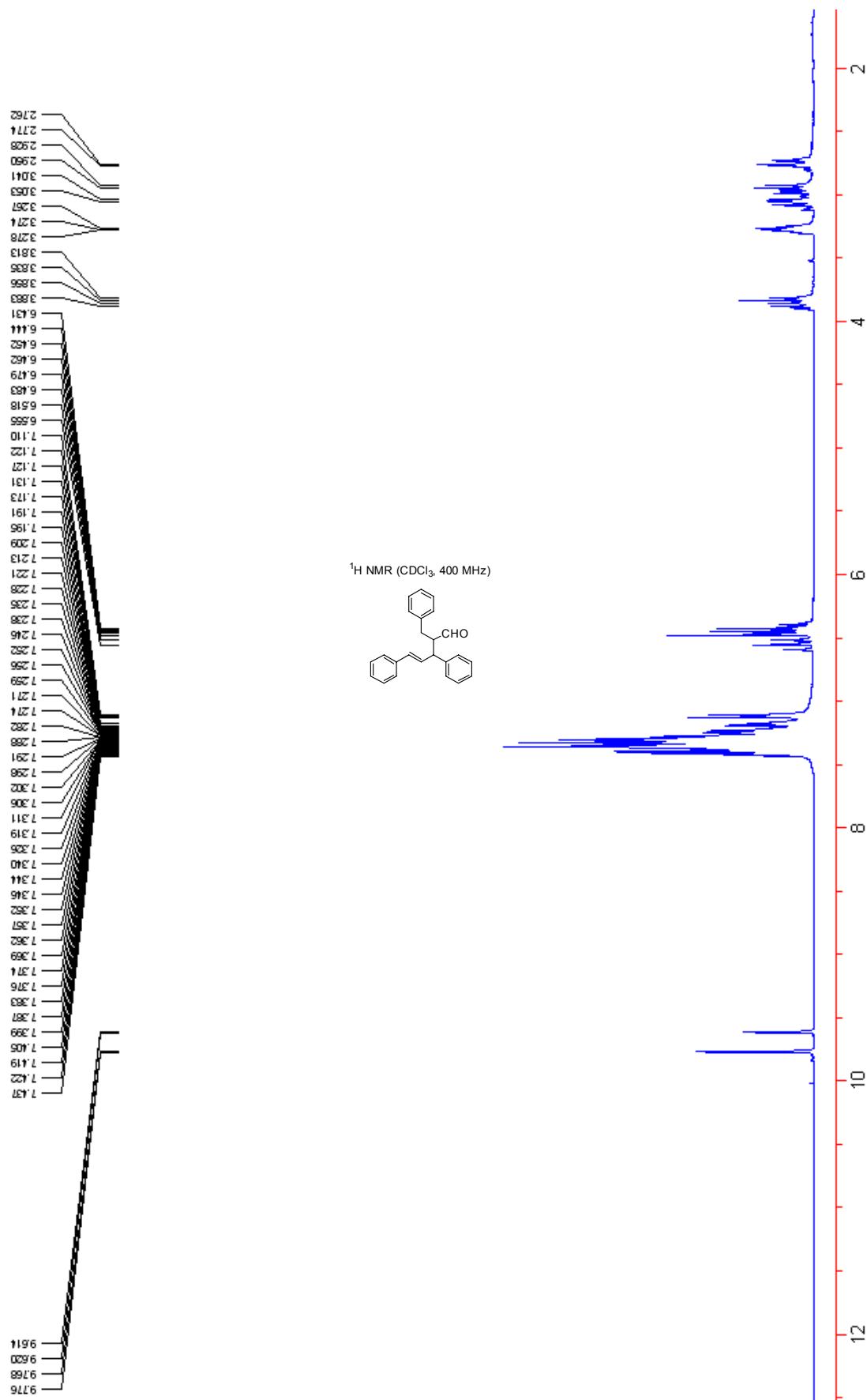


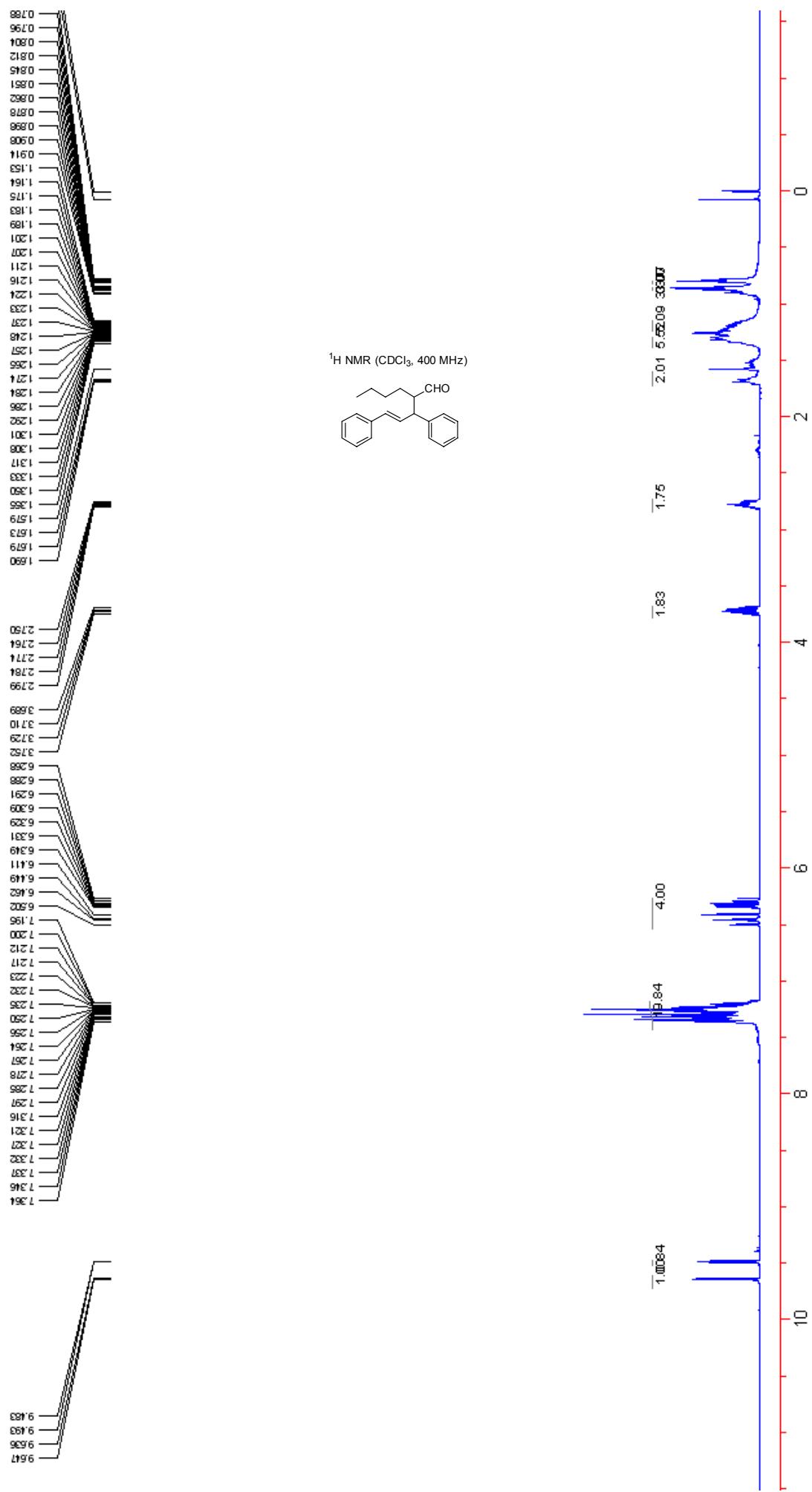


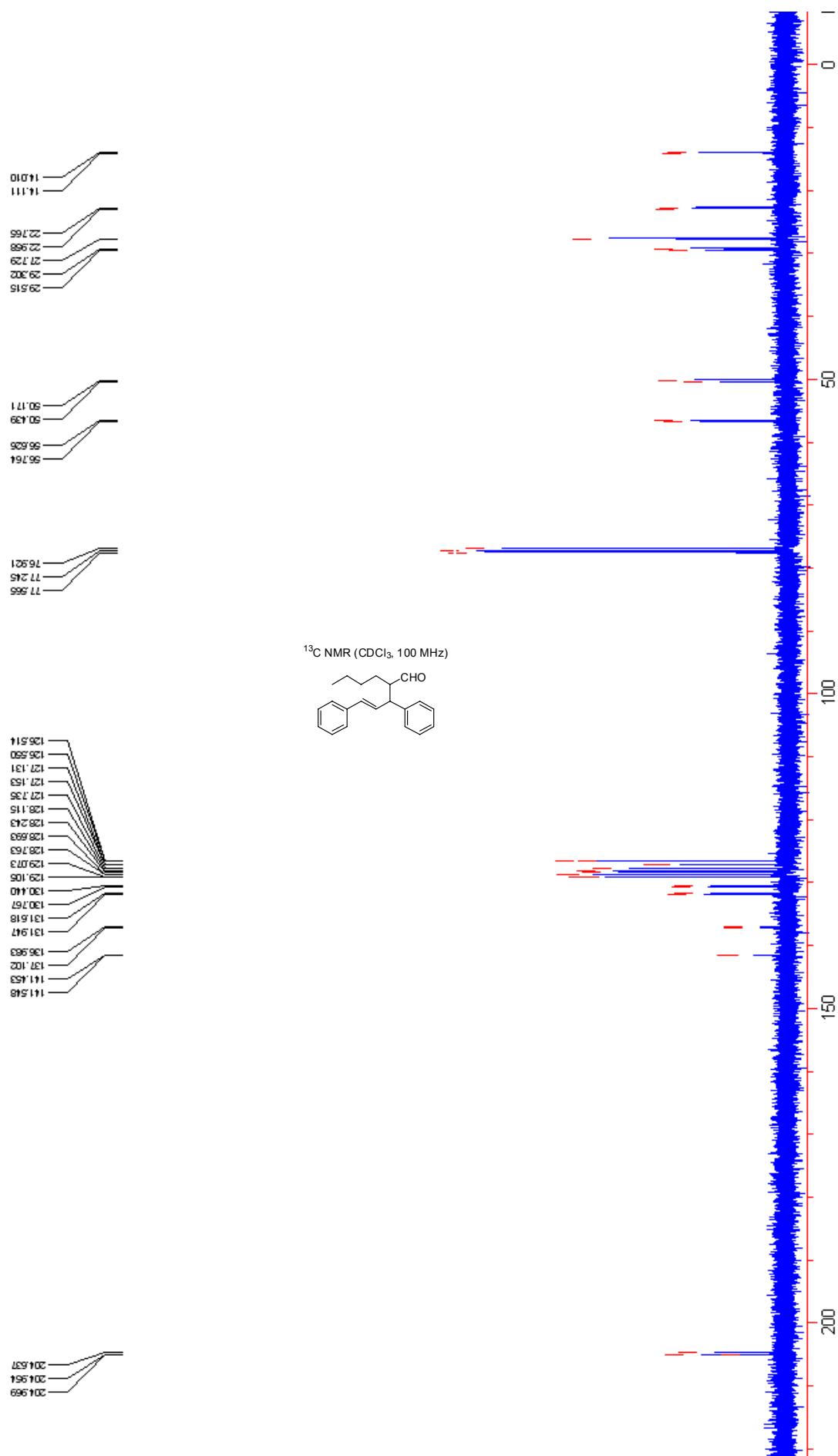












4. Copies of HPLC Spectra

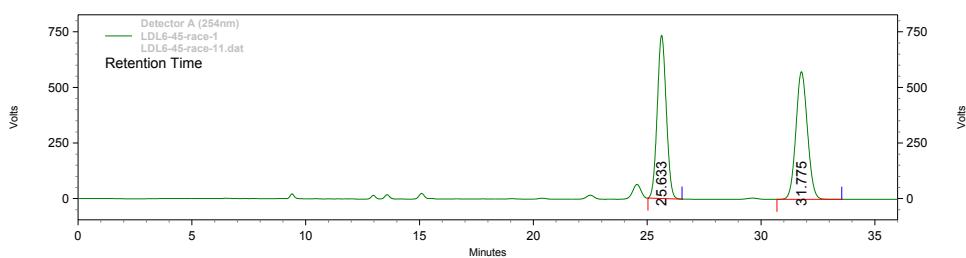


Figure 1. HPLC chromatogram showing the separation product using a Daicel Chiralcel AD-H column (hexane: 2-propanol = 96: 4, flow = 0.5 mL/min). *Anti*-product (**5a**) from asymmetric allylic alkylation using PPh₃ in DMSO at room temperature, racemic isomers.

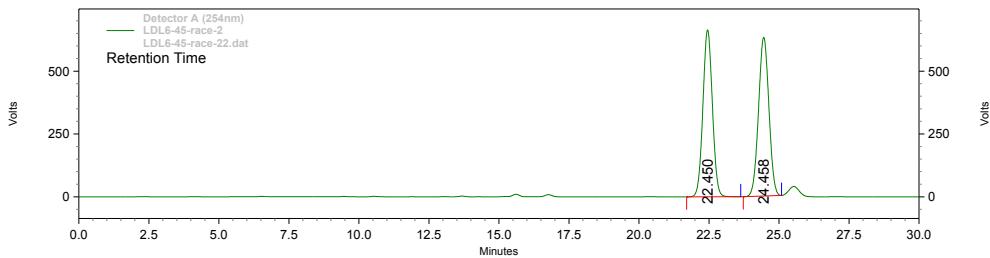


Figure 2. HPLC chromatogram showing the separation product using a Daicel Chiralcel AD-H column (hexane: 2-propanol = 96: 4, flow = 0.5 mL/min). *Syn*-product (**5b**) from asymmetric allylic alkylation using PPh₃ in DMSO at room temperature, racemic isomers.

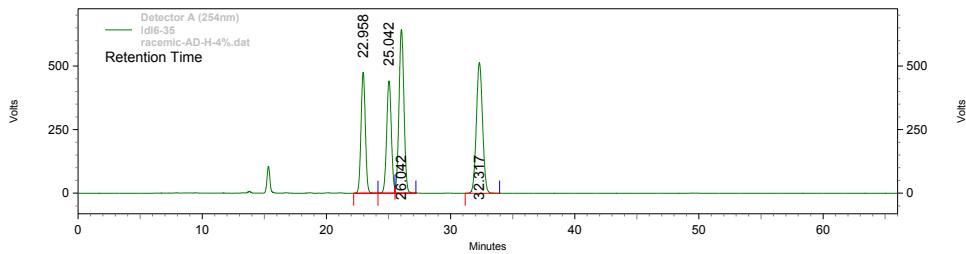


Figure 3. HPLC chromatogram showing the separation racemic mixture of *anti*- and *syn*-product (**5a** and **5b**) using a Daicel Chiralcel AD-H column (hexane: 2-propanol = 96: 4, flow = 0.5 mL/min).

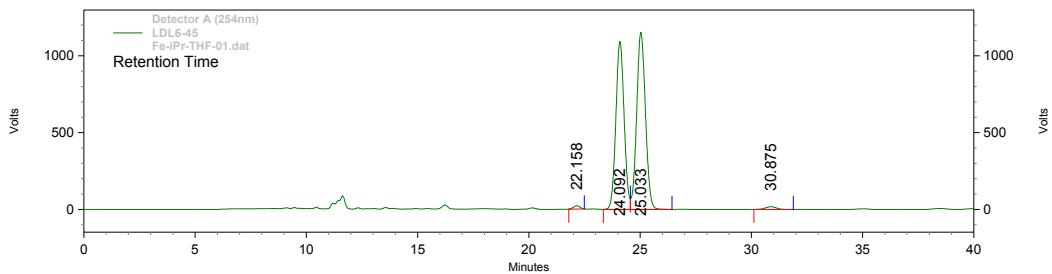


Figure 4. HPLC chromatogram using a Daicel Chiralcel AD-H column (hexane: 2-propanol = 96: 4, flow = 0.5 mL/min). Enantioselective mixture of *anti*- and *syn*-product (**5a** and **5b**) from asymmetric allylic alkylation using **1a** as a ligand in DMSO at room temperature (Table 1, entry 7), 94% ee (*anti*-) and 94% ee (*syn*-).

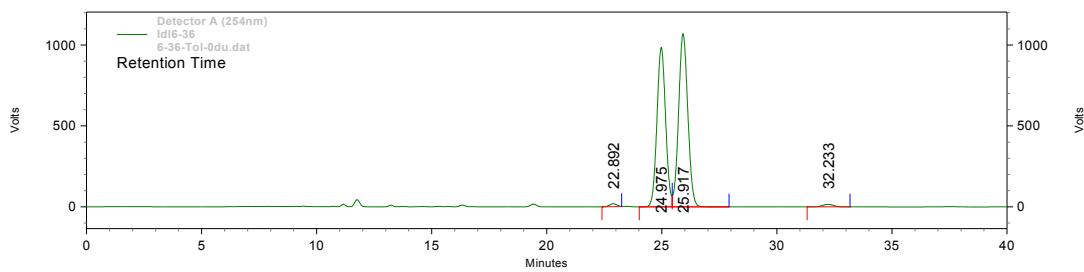


Figure 5. HPLC chromatogram using a Daicel Chiralcel AD-H column (hexane: 2-propanol = 96: 4, flow = 0.5 mL/min). Enantioselective mixture of *anti*- and *syn*-product (**5a** and **5b**) from asymmetric allylic alkylation using **1b** as aligand at room temperature in DMSO (Table 1, entry 15), 98% ee (*anti*-) and 97% ee (*syn*-).

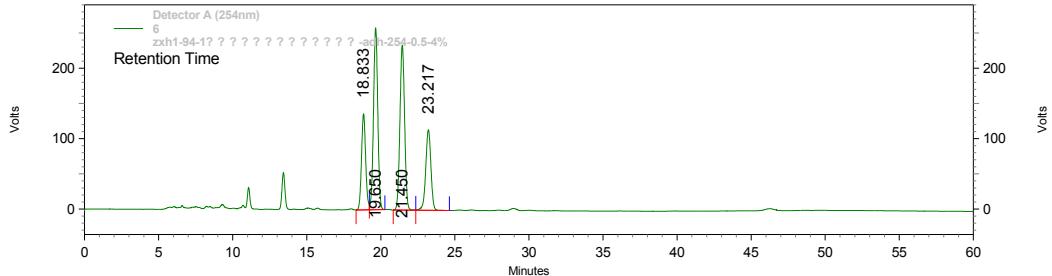


Figure 6. HPLC chromatogram showing the racemic mixture of *anti*- and *syn*-product (**6a** and **6b**) using a Daicel Chiralcel AD-H column (hexane: 2-propanol = 96: 4, flow = 0.5 mL/min).

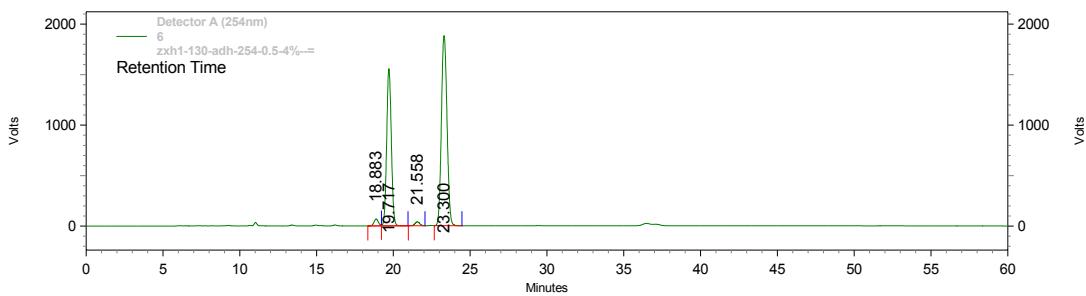


Figure 7. HPLC chromatogram using a Daicel Chiralcel AD-H column (hexane: 2-propanol = 96: 4, flow = 0.5 mL/min). Enantioselective mixture of *anti*- and *syn*-product (**6a** and **6b**) from asymmetric allylic alkylation using **1b** as a ligand at room in DMSO temperature (Scheme 1), 97% ee (*anti*-) and 96 % ee (*syn*-).

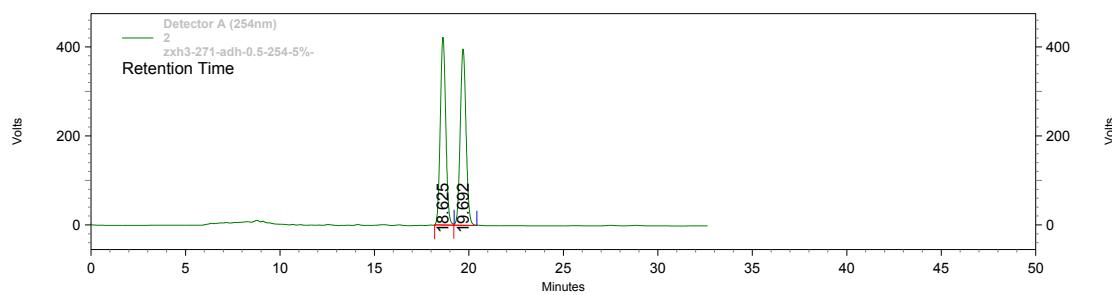


Figure 8. HPLC chromatogram showing the racemic product (**7**) using a Daicel Chiralcel AD-H column (hexane: 2-propanol = 95: 5, flow=0.5mL/min).

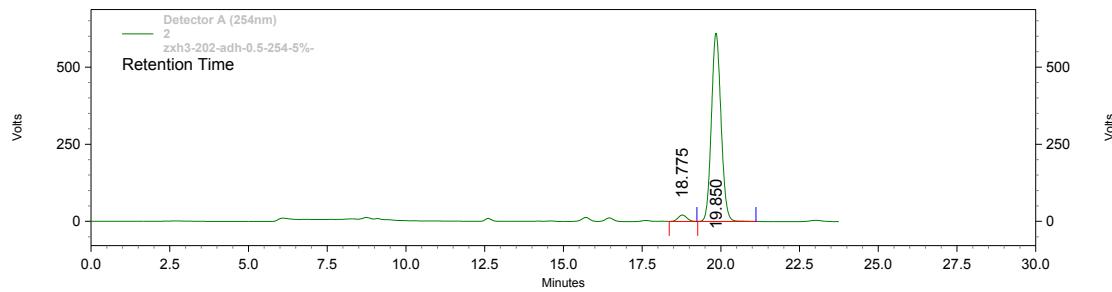


Figure 9. HPLC chromatogram using a Daicel Chiralcel AD-H column (hexane: 2-propanol = 95: 5, flow = 0.5 mL/min). Enantioselective product (**7**) from asymmetric allylic alkylation using **1b** as a ligand in DMSO at room temperature (Scheme 2), 90% ee .

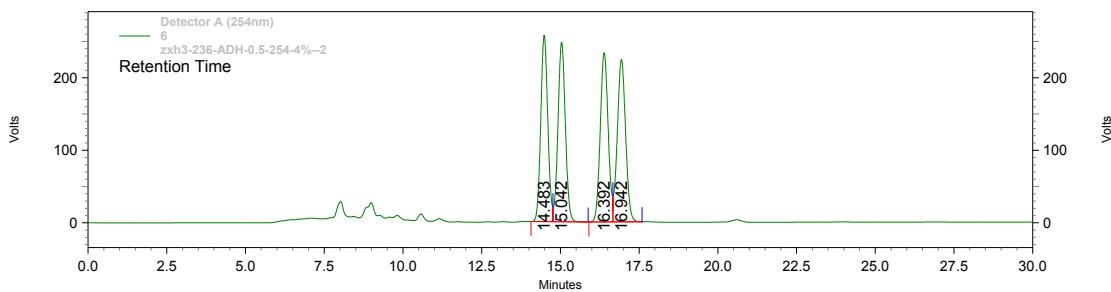


Figure 10. HPLC chromatogram showing the racemic mixture of *anti*- and *syn*-product (**10a** and **10b**) using a Daicel Chiralcel AD-H column (hexane: 2-propanol = 96: 4, flow = 0.5 mL/min).

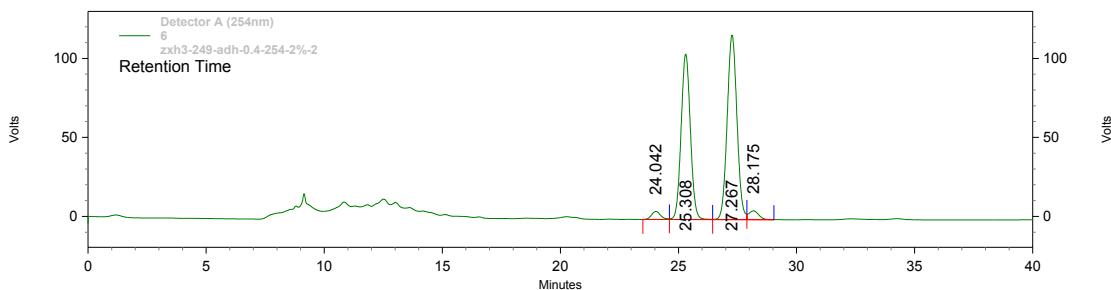


Figure 11. HPLC chromatogram using a Daicel Chiralcel AD-H column (hexane: 2-propanol = 98: 2, flow = 0.4 mL/min). Enantioselective mixture of *anti*- and *syn*-product (**10a** and **10b**) from asymmetric allylic alkylation using **4b** as a ligand in DMSO at room temperature (Table 2, entry 8), 91% ee (*anti*) and 91% ee (*syn*).

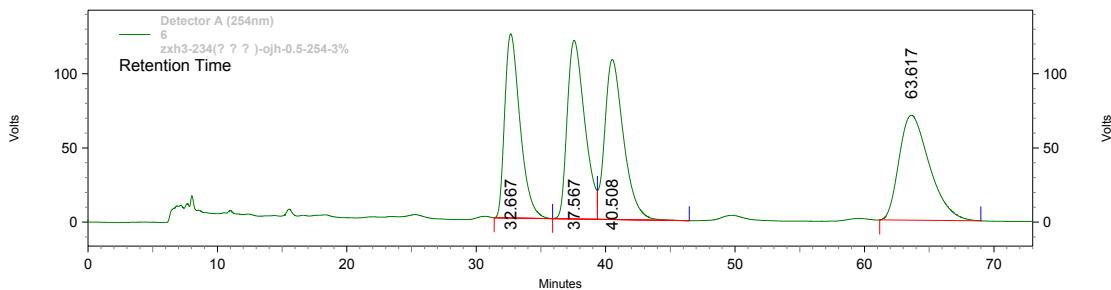


Figure 12. HPLC chromatogram showing the racemic mixture of *anti*-product and *syn*-product (**11a** and **11b**) using a Daicel Chiralcel OJ-H column (hexane: 2-propanol = 97: 3, flow = 0.5 mL/min).

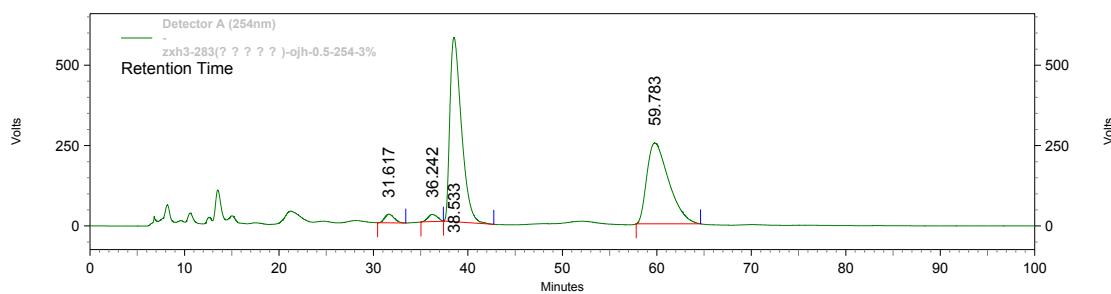


Figure 13. HPLC chromatogram using a Daicel Chiralcel OJ-H column (hexane: 2-propanol = 97: 3, flow = 0.5 mL/min). Enantioselective mixture of *anti*- and *syn*-product (**11a** and **11b**) from asymmetric allylic alkylation using **4b** as a ligand in DMSO at room temperature (Table 3, entry 1), 92% ee (*anti*-) and 93 % ee (*syn*-).

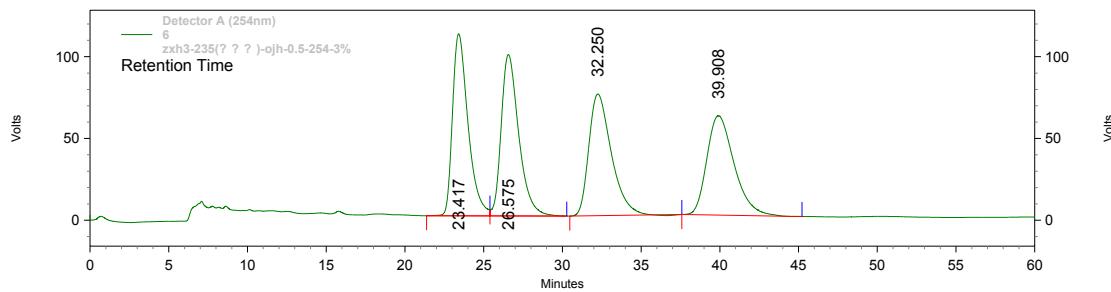


Figure 14. HPLC chromatogram showing the racemic mixture of *anti*- and *syn*-product (**12a** and **12b**) using a Daicel Chiralcel OJ-H column (hexane: 2-propanol = 97: 3, flow=0.5mL/min).

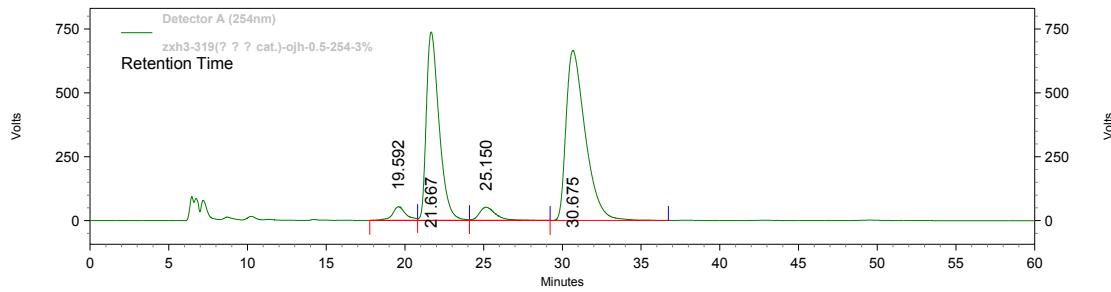


Figure 15. HPLC chromatogram using a Daicel Chiralcel OJ-H column (hexane: 2-propanol = 97: 3, flow = 0.5 mL/min). Enantioselective mixture of *anti*- and *syn*-product (**12a** and **12b**) from asymmetric allylic alkylation using **4b** as a ligand in DMSO at room temperature (Table 3, entry 2), 89% ee (*anti*-) and 89 % ee (*syn*-)

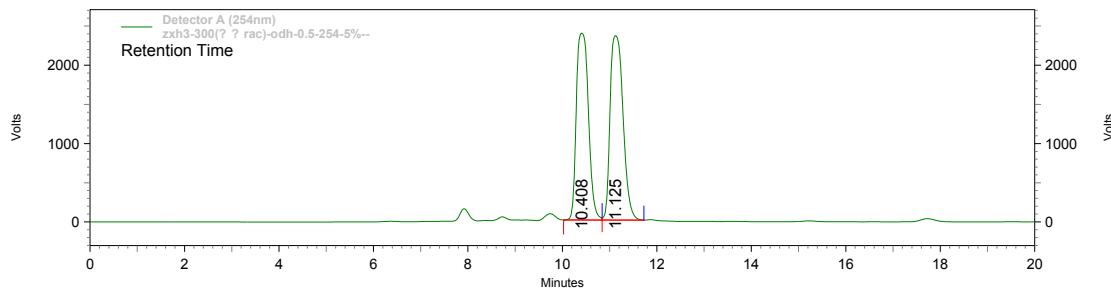


Figure 16. HPLC chromatogram showing the racemic product (**13**) using a Daicel Chiralcel OD-H column (hexane: 2-propanol = 95: 5, flow=0.5mL/min).

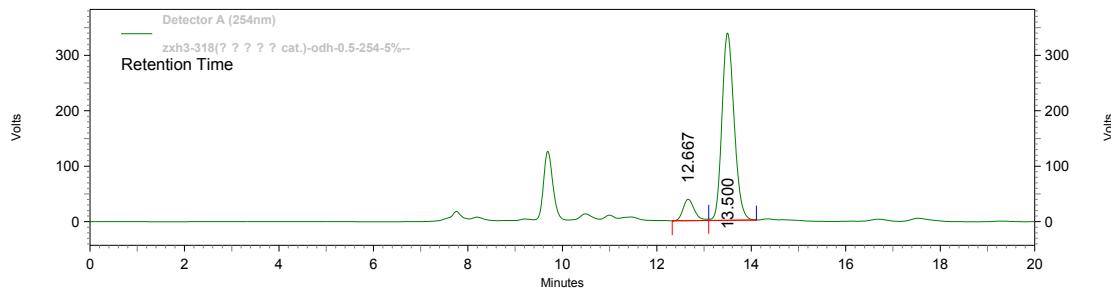


Figure 17. HPLC chromatogram using a Daicel Chiralcel OD-H column (hexane: 2-propanol = 95: 5, flow = 0.5 mL/min). Enantioselective product (**13**) from asymmetric allylic alkylation using **4b** as a ligand in DMSO at room temperature (Table 3, entry 3), 79 % ee .

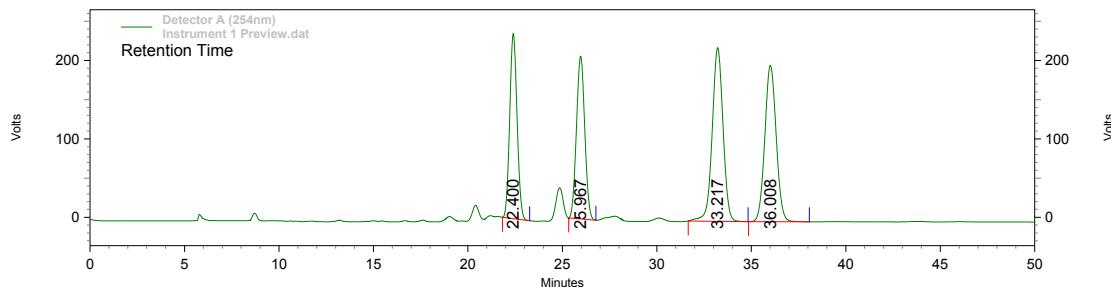


Figure 18. HPLC chromatogram showing the racemic mixture of *anti*- and *syn*-product (**14a** and **14b**) using a Daicel Chiralcel AD-H column (hexane: 2-propanol = 95: 5, flow = 0.5 mL/min).

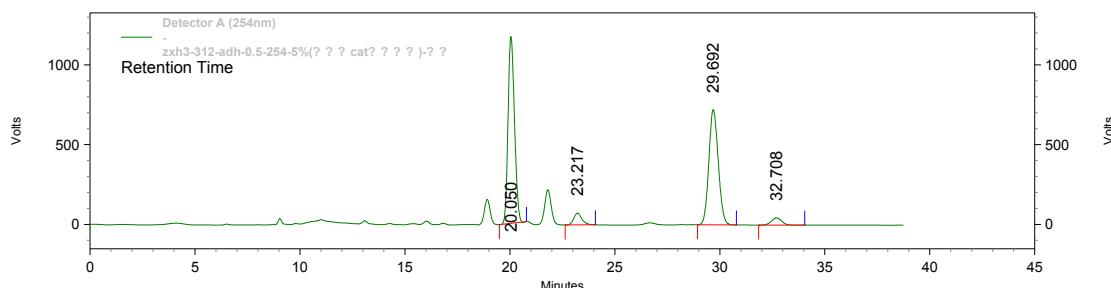


Figure 19. HPLC chromatogram using a Daicel Chiralcel AD-H column (hexane: 2-propanol = 95: 5, flow = 0.5 mL/min). Enantioselective mixture of *anti*- and *syn*-product (**14a** and **14b**) from asymmetric allylic alkylation using **4b** in DMSO at room temperature (Table 3, entry 4), 87% ee

(*anti*-) and 87 % *ee* (*syn*-).

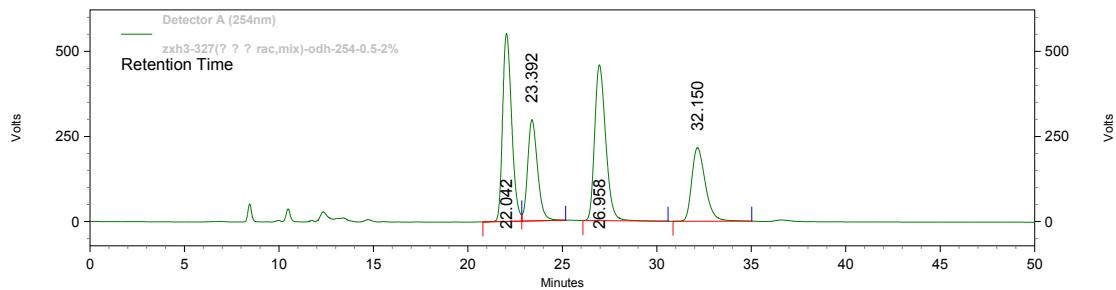


Figure 20. HPLC chromatogram showing the racemic mixture of *anti*- and *syn*-product (**15a** and **15b**) using a Daicel Chiralcel OD-H column (hexane: 2-propanol = 98: 2, flow = 0.5 mL/min).

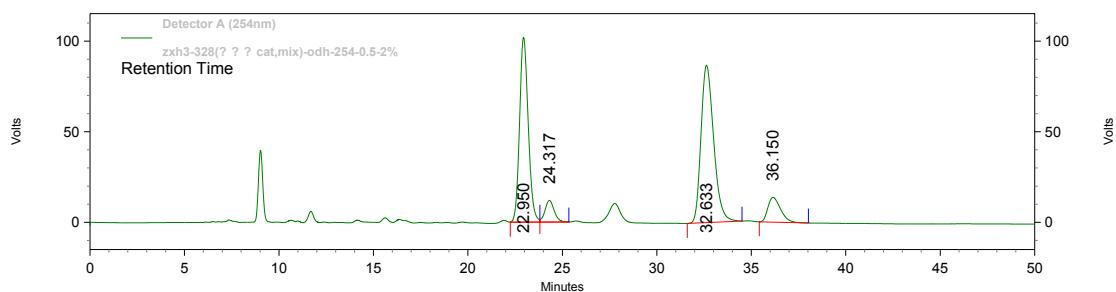


Figure 21. HPLC chromatogram using a Daicel Chiralcel OD-H column (hexane: 2-propanol = 98: 2, flow = 0.5 mL/min). Enantioselective mixture of *anti*- and *syn*-product (**15a** and **15b**) from asymmetric allylic alkylation using **4b** as a ligand in DMSO at room temperature (Table 3, entry 5), 90% *ee* (*anti*-) and 90 % *ee* (*syn*-).